Supporting Information

Enantioselective Difunctionalization of Alkenes by a Palladium-Catalyzed Heck/Borylation Sequence

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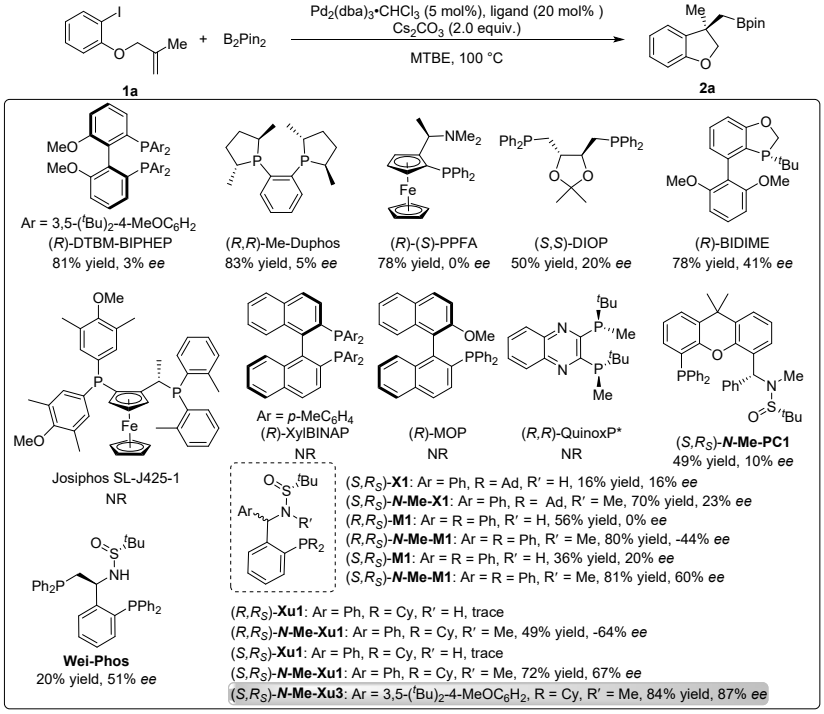
1. General Information

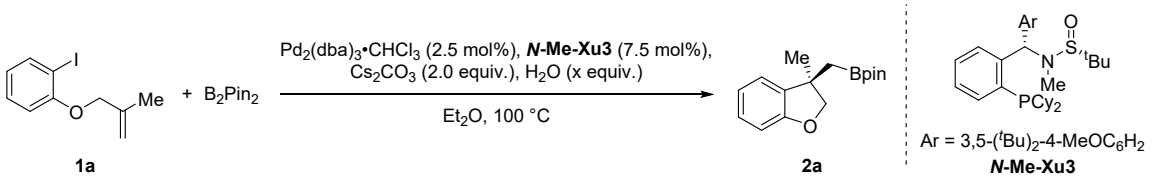
All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. ^{1}H NMR spectra, ^{19}F NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 300, 400 and 500 MHz spectrometer in $CDCl_3$ or acetone-*d6*. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quarte, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). The ligands (*R*, *Rs*)-***N*-Me-PC1**,[1] **Wei-Phos**,[2] (*S*, *Rs*)-**X1**, (*S*, *Rs*)-***N*-Me-X1**,[3] (*R*, *Rs*)-**M1**, (*R*, *Rs*)-***N*-Me-M1**, (*S*, *Rs*)-**M1**, (*S*, *Rs*)-***N*-Me-M1**,[4] (*R*, *Rs*)-**Xu1**, (*R*, *Rs*)-***N*-Me-Xu1**, (*S*, *Rs*)-**Xu1**, (*S*, *Rs*)-***N*-Me-Xu1**, (*S*, *Rs*)-***N*-Me- Xu3**[5] and substrates **1a**-**1aa**, **3a**-**3g**, **3i**, **3j**[6] ,**3h**[7], **3k**[8], were synthesized according to published procedures. The spectral data of the substrates were consisted with that reported in the literature. The enantionmeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralpak AD-3, IC, AD-H, OJH.

2. Table S1. Screening of the ligands



[a]Reaction conditions: **1a** (0.1 mmol), B_2Pin_2 (1.1 equiv.), $Pd_2(dba)_3$•$CHCl_3$ (5 mol%), Ligand (20 mol%), Cs_2CO_3 (2.0 equiv.), 1 mL of solvent under N_2 atmosphere at 100 °C for 12 h. [b]Determined by ^{1}H NMR analysis with CH_2Br_2 as an internal standard. [c]The *ee* value of **2a** was determined by HPLC analysis.

3. Table S2. Screening of the Amount of H_2O for Heck/Borylation Sequence



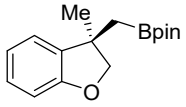
Entry	H_2O (x)	Yield (%)[b]	*ee* (%)[c]
1	1.0	97	88
2	2.0	98	89
3	3.0	97	90
4	4.0	97	91
5	5.0	95	91
6	6.0	96	90

[a]Reaction conditions: **1a** (0.1 mmol), B_2Pin_2 (1.1 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (10 mol%), Cs_2CO_3 (2.0 equiv), 1 mL of Et_2O under N_2 atmosphere at 100 °C for 12h. [b]Determined by ^1H NMR analysis with CH_2Br_2 as the internal standard. [c]Determined by HPLC analysis.

4. Typical procedure for Palladium-Catalyzed Enantioselective Heck/Borylation Sequence.

To a sealed tube was added $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%), B_2Pin_2 (0.33 mmol) and Cs_2CO_3 (0.6 mmol). The flask was evacuated and refilled with argon. Then *o*-iodophenol-derived allyl ether **1** (0.3 mmol), Et_2O (3 mL) and H_2O (22 μL) was added to the tube, and stirred at 80 °C. Following complete consumption of the allyl ether **1** (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to afford the desired product.

4.1 Synthesis of (*R*)-4,4,5,5-tetramethyl-2-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2a**).

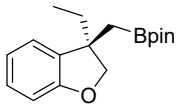


2a

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1a** (82.2 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol),

Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2a** as a colorless ropy liquid (81 mg, 98% yield) with 91% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.08 (td, *J* = 7.7, 1.5 Hz, 1H), 6.84 (td, *J* = 7.4, 1.0 Hz, 1H), 6.79-6.72 (m, 1H), 4.41 (d, *J* = 8.6 Hz, 1H), 4.25 (d, *J* = 8.6 Hz, 1H), 1.37 (s, 3H), 1.30 (d, *J* = 15.5 Hz, 1H), 1.24 (d, *J* = 13.7 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 137.29, 127.64, 122.54, 120.31, 109.40, 84.04, 83.13, 43.11, 28.04, 24.75, 24.69. MS (EI): m/z (%) = 275 ($M+H^+$, 2.75), 133 (100); HRMS calculated for $[C_{16}H_{24}BO_3]^+$: 275.1803 found: 275.1807. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.8 min, major enantiomer tr = 10.3 min. $[\alpha]_D^{25}$ = 20.6 (c = 0.4, $CHCl_3$).

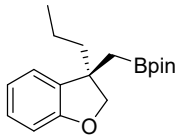
4.2 Synthesis of (*S*)-2-((3-ethyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**).



2b

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1b** (86.5 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2b** as a colorless ropy liquid (60.5 mg, 70% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-6.96 (m, 2H), 6.79-6.73 (m, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.38-4.25 (m, 2H), 1.70-1.53 (m, 2H), 1.24 (d, *J* = 15.4 Hz, 1H), 1.13 (d, *J* = 15.4 Hz, 1H), 1.08 (s, 6H), 1.05 (s, 6H), 0.72 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.70, 135.07, 127.70, 123.33, 120.04, 109.17, 83.08, 81.81, 46.90, 34.09, 24.69, 24.63, 8.89. MS (EI): m/z (%) = 289 ($M+H^+$, 7.85), 147 (100); HRMS calculated for $[C_{17}H_{26}BO_3]^+$: 289.1970 found: 289.1964. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.5 min, major enantiomer tr = 13.0 min. $[\alpha]_D^{25}$ = 25.4 (c = 0.4, $CHCl_3$).

4.3 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-propyl-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2c**).

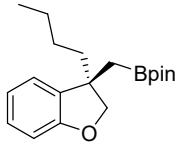


2c

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1c** (90.6 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2c** as a colorless ropy liquid (73 mg, 81% yield) with 91% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-6.95 (m, 2H), 6.79-6.71 (m, 1H), 6.69-6.62 (m, 1H), 4.35-4.26 (m, 2H), 1.64-1.45 (m, 2H), 1.35-1.22 (m, 2H), 1.22-1.10 (m, 2H), 1.08 (s, 6H), 1.06 (s, 6H), 0.77 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.59, 135.50, 127.67, 123.30, 120.05, 109.19, 83.07, 82.26, 46.60, 44.10, 24.68, 24.63, 17.79, 14.49. MS (EI): m/z (%) = 303 ($M+H^+$, 7.22), 83 (100); HRMS calculated for $[C_{18}H_{28}BO_3]^+$: 303.2126 found: 303.2120.

Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.1 min, major enantiomer tr = 12.7 min. $[\alpha]_D^{25}$ = 27.7 (c = 0.4, $CHCl_3$).

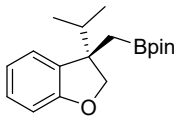
4.4 Synthesis of (*S*)-2-((3-butyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**).



2d

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1d** (94.9 mg, 0.3 mmol), B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2d** as a colorless ropy liquid (76.6 mg, 81% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-6.96 (m, 2H), 6.80-6.72 (m, 1H), 6.69-6.63 (m, 1H), 4.35 -4.27 (m, 2H), 1.67-1.47 (m, 2H), 1.25 (d, *J* = 15.5 Hz, 2H), 1.20-1.10 (m, 4H), 1.09 (s, 6H), 1.06 (s, 6H), 0.77 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.60, 135.58, 127.68, 123.33, 120.08, 109.23, 83.10, 82.28, 46.54, 41.38, 26.70, 24.70, 24.67, 23.13, 13.96. MS (EI): m/z (%) = 317 ($M+H^+$, 4.40), 83 (100); HRMS calculated for $[C_{19}H_{30}BO_3]^+$: 317.2283 found: 317.2275. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 8.9 min, major enantiomer tr = 12.3 min. $[\alpha]_D^{25}$ = 21.8 (c = 0.4, $CHCl_3$).

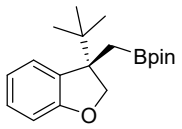
4.5 Synthesis of (*S*)-2-((3-isopropyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**).



2e

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1e** (90.7 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2e** as a colorless ropy liquid (77.7 mg, 90% yield) with 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.95 (m, 2H), 6.77-6.70 (m, 1H), 6.66-6.60 (m, 1H), 4.42-4.30 (m, 2H), 1.91-1.78 (m, 1H), 1.26 (d, *J* = 15.2 Hz, 1H), 1.14 (d, *J* = 15.2 Hz, 1H), 1.02 (s, 6H), 0.97 (s, 6H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.08, 133.84, 127.73, 124.05, 119.73, 108.96, 82.94, 79.73, 49.96, 37.15, 24.65, 24.43, 17.74, 17.57. MS (EI): m/z (%) = 303 ($M+H^+$, 3.19), 259 (100); HRMS calculated for $[C_{18}H_{27}BO_3]^+$: 303.2126 found: 303.2119. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.4 min, major enantiomer tr = 10.1 min. $[\alpha]_D^{25}$ = 32.8 (c = 0.4, $CHCl_3$).

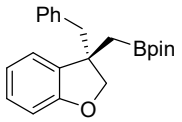
4.6 Synthesis of (*S*)-2-((3-(tert-butyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**).



2f

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1f** (94.9 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2f** as a colorless ropy liquid (80.4 mg, 85% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.02 (m, 1H), 7.02-6.95 (m, 1H), 6.75-6.67 (m, 1H), 6.64 -6.58(m, 1H), 4.55-4.45 (m, 2H), 1.39 (d, *J* = 14.9 Hz, 1H), 1.02 (d, *J* = 14.7 Hz, 1H), 0.93 (s, 6H), 0.82 (s, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.56, 132.61, 127.78, 125.75, 119.19, 108.83, 82.80, 78.75, 52.43, 37.02, 25.22, 24.64, 24.17. MS (EI): m/z (%) = 317 ($M+H^+$, 0.97), 83 (100); HRMS calculated for $[C_{19}H_{30}BO_3]^+$: 317.2283 found: 317.2276. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 10.5 min, major enantiomer tr = 8.5 min. $[\alpha]_D^{25}$ = 41.5 (c = 0.4, $CHCl_3$).

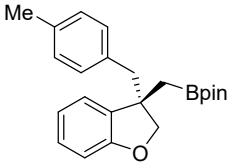
4.7 Synthesis of (*S*)-2-((3-benzyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2g**).



2g

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1g** (105.1 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2g** as a colorless ropy liquid (81.8 mg, 78% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.07 (m, 3H), 7.05-6.95 (m, 1H), 6.88-6.76 (m, 3H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 4.44 (d, *J* = 8.8 Hz, 1H), 4.26 (d, *J* = 8.8 Hz, 1H), 2.86 (s, 2H), 1.26 (d, *J* = 15.6 Hz, 1H), 1.15 (d, *J* = 15.6 Hz, 1H), 1.09 (s, 6H), 1.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.58, 137.65, 134.64, 130.50, 127.94, 127.68, 126.24, 124.05, 119.80, 109.32, 83.17, 81.72, 47.51, 46.96, 24.72, 24.64. MS (EI): m/z (%) = 350 (M^+, 1.84), 259 (100); HRMS calculated for $[C_{22}H_{27}BO_3Na]^+$: 373.1945 found: 373.1938. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 12.1 min, major enantiomer tr = 16.1 min. $[\alpha]_D^{25}$ = 27.5 (c = 0.4, $CHCl_3$).

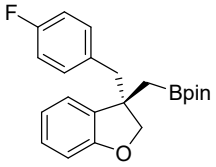
4.8 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-(4-methylbenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2h**).



2h

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1h** (109.2 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2h** as a colorless ropy liquid (91.8 mg, 84% yield) with 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.03 (m, 1H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.93-6.87 (m, 1H), 6.85-6.74 (m, 3H), 6.69 (d, *J* = 7.9 Hz, 1H), 4.51 (d, *J* = 8.8 Hz, 1H), 4.33 (d, *J* = 8.8 Hz, 1H), 2.90 (s, 2H), 2.28 (s, 3H), 1.32 (d, *J* = 15.7 Hz, 1H), 1.22 (d, *J* = 15.6 Hz, 1H), 1.15 (s, 6H), 1.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.60, 135.65, 134.79, 134.54, 130.36, 128.41, 127.87, 124.05, 119.78, 109.28, 83.12, 81.69, 47.49, 46.56, 24.71, 24.62, 20.96. MS (EI): m/z (%) = 365 ($M+H^+$, 0.33), 259 (100); HRMS calculated for $[C_{23}H_{30}BO_3]^+$: 365.2283 found: 365.2275. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 13.1 min, major enantiomer tr = 16.7 min. $[\alpha]_D^{25}$ = 32.6 (c = 0.4, $CHCl_3$).

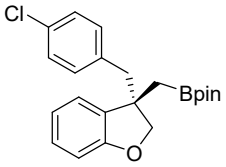
4.9 Synthesis of (*S*)-2-((3-(4-fluorobenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2i**).



2i

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1i** (110.5 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2i** as a colorless ropy liquid (101.2 mg, 92% yield) with 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.04 (m, 1H), 6.92-6.76 (m, 6H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.48 (d, *J* = 8.9 Hz, 1H), 4.33 (d, *J* = 8.9 Hz, 1H), 2.90 (s, 2H), 1.34 (d, *J* = 15.6 Hz, 1H), 1.22 (d, *J* = 15.6 Hz, 1H), 1.18 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.65 (d, *J* = 244.3 Hz), 159.60, 134.31, 133.33 (d, *J* = 3.3 Hz), 131.81 (d, *J* = 7.8 Hz), 128.07, 123.99, 119.86, 114.45 (d, *J* = 21.0 Hz), 109.40, 83.27, 81.66, 47.51, 46.11, 24.74, 24.67. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.91. MS (EI): m/z (%) = 369 ($M+H^+$, 0.28), 259 (100); HRMS calculated for $[C_{22}H_{27}BFO_3]^+$: 369.2032 found: 369.2015. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 11.0 min, major enantiomer tr = 17.6 min. $[\alpha]_D^{25}$ = 27.4 (c = 0.4, $CHCl_3$).

4.10 Synthesis of (*S*)-2-((3-(4-chlorobenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2j**).

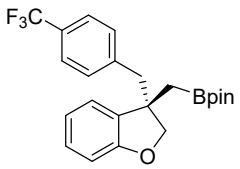


2j

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1j** (115.4 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol),

Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2j** as a colorless ropy liquid (110.2 mg, 95% yield) with 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.11 (m, 2H), 7.10-7.05 (m, 1H), 6.88-6.75 (m, 4H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 8.9 Hz, 1H), 4.33 (d, *J* = 8.9 Hz, 1H), 2.89 (s, 2H), 1.30 (d, *J* = 9.7 Hz, 1H), 1.24 (d, *J* = 7.8 Hz, 1H), 1.17 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.55, 136.09, 134.17, 132.18, 131.72, 128.10, 127.77, 123.94, 119.87, 109.43, 83.25, 81.61, 47.44, 46.23, 24.72, 24.63. MS (EI): m/z (%) = 384 (M^+, 0.56), 259 (100); HRMS calculated for $[C_{22}H_{27}BClO_3]^+$: 385.1736 found: 385.1725. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 11.0 min, major enantiomer tr = 17.8 min. $[\alpha]_D^{25}$ = 38.7 (c = 0.4, $CHCl_3$).

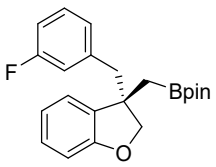
4.11 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-(4-(trifluoromethyl)benzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2k**).



2k

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1k** (125.5 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2k** as a colorless ropy liquid (103.4 mg, 82% yield) with 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.14-7.05 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.88-6.77 (m, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 9.0 Hz, 1H), 4.35 (d, *J* = 8.9 Hz, 1H), 2.99 (s, 2H), 1.35 (d, *J* = 15.7 Hz, 1H), 1.27 (d, *J* = 15.3 Hz, 1H), 1.19 (s, 6H), 1.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.51, 141.76, 133.99, 130.73, 128.53 (d, *J* = 32.2 Hz), 128.25, 124.55 (q, *J* = 3.7 Hz), 124.29 (q, *J* = 272.9 Hz), 123.94, 119.98, 109.55, 83.34, 81.66, 47.48, 46.65, 24.74, 24.65. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.25. MS (EI): m/z (%) = 418 (M^+, 1.40), 259 (100); HRMS calculated for $[C_{23}H_{26}BF_3O_3]^+$: 418.1972 found: 418.1930. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.3 min, major enantiomer tr = 16.0 min. $[\alpha]_D^{25}$ = 24.7 (c = 0.4, $CHCl_3$).

4.12 Synthesis of (*S*)-2-((3-(3-fluorobenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**).

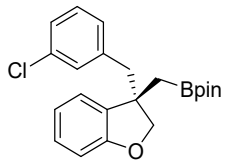


2l

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1l** (110.5 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2l** as a colorless ropy liquid (99.5 mg, 90% yield)

with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-6.95 (m, 2H), 6.83-6.75 (m, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.60 (t, *J* = 7.4 Hz, 2H), 6.52 (d, *J* = 10.1 Hz, 1H), 4.41 (d, *J* = 8.9 Hz, 1H), 4.24 (d, *J* = 9.0 Hz, 1H), 2.85 (s, 2H), 1.26 (d, *J* = 15.7 Hz, 1H), 1.18 (d, *J* = 16.4 Hz, 1H), 1.09 (s, 6H), 1.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.25 (d, *J* = 245.0 Hz), 159.54, 140.20 (d, *J* = 7.3 Hz), 134.26, 128.98 (d, *J* = 8.4 Hz), 128.13, 126.11 (d, *J* = 2.9 Hz), 123.88, 119.92, 117.23 (d, *J* = 21.0 Hz), 113.12 (d, *J* = 20.9 Hz), 109.43, 83.25, 81.65, 47.46, 46.54 (d, *J* = 2.0 Hz), 24.71, 24.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.10. MS (EI): m/z (%) = 369 ($M+H^+$, 0.32), 259 (100); HRMS calculated for $[C_{22}H_{27}BFO_3]^+$: 369.2032 found: 369.2022. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 10.7 min, major enantiomer tr = 15.4 min. $[\alpha]_D^{25}$ = 28.9 (c = 0.4, $CHCl_3$).

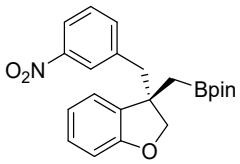
4.13 Synthesis of (*S*)-2-((3-(3-chlorobenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2m**).



2m

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1m** (115.4 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2m** as a colorless ropy liquid (102.9 mg, 89% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.1 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 9.3 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 4.40 (d, *J* = 8.9 Hz, 1H), 4.24 (d, *J* = 9.1 Hz, 1H), 2.82 (s, 2H), 1.24 (d, *J* = 15.4 Hz, 1H), 1.13 (d, *J* = 16.0 Hz, 1H), 1.10 (s, 6H), 1.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.51, 139.70, 134.19, 133.41, 130.50, 128.85, 128.55, 128.17, 126.41, 123.89, 119.91, 109.45, 83.26, 81.65, 47.43, 46.45, 24.74, 24.63. MS (EI): m/z (%) = 385 ($M+H^+$, 0.33), 259 (100); HRMS calculated for $[C_{22}H_{27}BClO_3]^+$: 385.1736 found: 385.1726. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 10.6 min, major enantiomer tr = 15.3 min. $[\alpha]_D^{25}$ = 30.0 (c = 0.4, $CHCl_3$).

4.14 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-(3-nitrobenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2n**).

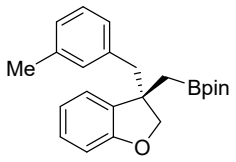


2n

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1n** (118.6 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2n** as a white soild (73.6 mg, 62% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.86 (m, 1H), 7.71 (t, *J* = 2.0 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H),

7.09-6.97 (m, 2H), 6.83-6.71 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.42 (d, *J* = 9.0 Hz, 1H), 4.25 (d, *J* = 9.0 Hz, 1H), 3.10-2.77 (m, 2H), 1.29 (d, *J* = 15.8 Hz, 1H), 1.19 (d, *J* = 11.3 Hz, 1H), 1.15 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.50, 147.68, 139.67, 136.44, 133.58, 128.50, 128.40, 125.13, 123.70, 121.45, 120.16, 109.64, 83.48, 81.58, 47.52, 46.37, 24.76, 24.68. MS (EI): m/z (%) = 395 ($M+H^+$, 1.63), 259 (100); HRMS calculated for $[C_{22}H_{27}BNO_5]^+$: 395.1904 found: 395.1908. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 95:5, 0.5 mL/min, 220 nm); minor enantiomer tr = 14.9 min, major enantiomer tr = 19.3 min. $[\alpha]_D^{20}$ = 24.6 (c = 0.4, acetone).

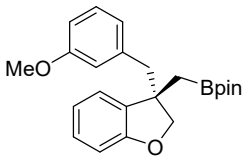
4.15 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-(3-methylbenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2o**).



2o

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1o** (109.2 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2o** as a colorless ropy liquid (92.3 mg, 85% yield) with 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.03 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93-6.88 (m, 1H), 6.83-6.77 (m, 1H), 6.76-6.68 (m, 3H), 4.52 (d, *J* = 8.8 Hz, 1H), 4.33 (d, *J* = 8.8 Hz, 1H), 2.90 (s, 2H), 2.24 (s, 3H), 1.32 (d, *J* = 15.7 Hz, 1H), 1.23 (d, *J* = 15.6 Hz, 1H), 1.16 (s, 6H), 1.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61, 137.56, 137.08, 134.82, 131.41, 127.91, 127.57, 127.50, 126.95, 124.07, 119.75, 109.29, 83.14, 81.72, 47.47, 46.92, 24.73, 24.63, 21.29. MS (EI): m/z (%) = 365 ($M+H^+$, 0.50), 259 (100); HRMS calculated for $[C_{23}H_{30}BO_3]^+$: 365.2283 found: 365.2274. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 11.5 min, major enantiomer tr = 14.9 min. $[\alpha]_D^{25}$ = 28.8 (c = 0.4, $CHCl_3$).

4.16 Synthesis of (*S*)-2-((3-(3-methoxybenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2p**).

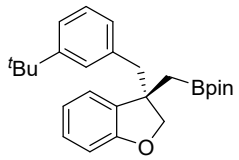


2p

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1p** (114.1 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2p** as a colorless ropy liquid (70.2 mg, 62% yield) with 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-6.97 (m, 2H), 6.88-6.80 (m, 1H), 6.78-6.69 (m, 1H), 6.68-6.59 (m, 2H), 6.48 (d, *J* = 7.6 Hz, 1H), 6.35-6.28 (m, 1H), 4.44 (d, *J* = 8.9 Hz, 1H), 4.25 (d, *J* = 8.8 Hz, 1H), 3.57 (s, 3H), 2.84 (s, 2H), 1.32-1.25 (m, 1H), 1.18 (s, 1H), 1.09 (s, 6H), 1.07

(s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.63, 158.93, 139.19, 134.69, 128.58, 127.97, 124.06, 122.94, 119.80, 115.71, 112.23, 109.37, 83.19, 81.70, 54.95, 47.52, 46.99, 24.72, 24.67. MS (EI): m/z (%) = 380 (M^+, 1.94), 259 (100); HRMS calculated for $[C_{23}H_{29}BO_4]^+$: 381.2232 found: 381.2221. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.4 min, major enantiomer tr = 12.1 min. $[\alpha]_D^{25}$ = 21.4 (c = 0.4, $CHCl_3$).

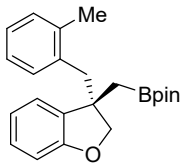
4.17 Synthesis of (*S*)-2-((3-(3-(tert-butyl)benzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2q**).



2q

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1q** (121.9 mg, 0.3 mmol), B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2q** as a colorless ropy liquid (114.6 mg, 94% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.11 (m, 2H), 7.10-7.03 (m, 1H), 6.89-6.74 (m, 4H), 6.72-6.66 (m, 1H), 4.52 (d, *J* = 8.8 Hz, 1H), 4.34 (d, *J* = 8.8 Hz, 1H), 3.12-2.83 (m, 2H), 1.32 (d, *J* = 7.2 Hz, 1H), 1.25-1.22 (m, 1H), 1.20 (s, 9H), 1.18 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.60, 150.22, 137.08, 134.62, 127.88, 127.82, 127.60, 127.32, 124.23, 123.08, 119.77, 109.30, 83.16, 81.92, 47.54, 47.12, 34.36, 31.22, 24.72. MS (EI): m/z (%) = 407 ($M+H^+$, 0.33), 259 (100); HRMS calculated for $[C_{26}H_{36}BO_3]^+$: 407.2752 found: 404.2744. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.3 min, major enantiomer tr = 12.6 min. $[\alpha]_D^{25}$ = 24.6 (c = 0.4, $CHCl_3$).

4.18 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-(2-methylbenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2r**).

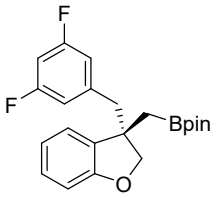


2r

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1r** (109.2 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2r** as a white soild (77.7 mg, 71% yield) with 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.00 (m, 4H), 6.96-6.92 (m, 1H), 6.74-6.69 (m, 2H), 6.65-6.54 (m, 1H), 4.48 (d, *J* = 8.8 Hz, 1H), 4.39 (d, *J* = 8.9 Hz, 1H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.88 (d, *J* = 13.5 Hz, 1H), 1.81 (s, 3H), 1.47 (d, *J* = 15.8 Hz, 1H), 1.27 (d, *J* = 12.7 Hz, 1H), 1.18 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.57, 137.65, 135.99, 134.64, 131.06, 130.14, 127.91, 126.30, 125.13, 124.00, 119.93, 109.23, 83.23, 82.38, 47.84, 42.35, 24.76, 24.62, 19.47. MS (EI):

m/z (%) = 365 ($M+H^+$, 0.34), 259 (100); HRMS calculated for $[C_{23}H_{30}BO_3]^+$: 365.2283 found: 365.2277. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 10.6 min, major enantiomer tr = 15.8 min. $[\alpha]_D^{25}$ = 34.2 (c = 0.4, $CHCl_3$).

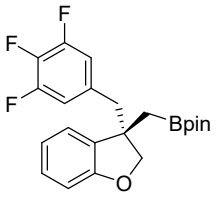
4.19 Synthesis of (*S*)-2-((3-(3,5-difluorobenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2s**).



2s

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1s** (115.9 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2s** as a colorless ropy liquid (101.7 mg, 88% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.72 (s, 1H), 6.63 (t, *J* = 9.0 Hz, 1H), 6.41 (d, *J* = 6.5 Hz, 2H), 4.47 (d, *J* = 9.0 Hz, 1H), 4.32 (d, *J* = 8.9 Hz, 1H), 2.92 (d, *J* = 1.7 Hz, 2H), 1.36 (d, *J* = 16.2 Hz, 1H), 1.27 (d, *J* = 15.9 Hz, 1H), 1.20 (s, 6H), 1.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.28 (dd, *J* = 247.4, 12.9 Hz), 159.48, 141.53 (t, *J* = 9.1 Hz), 133.88, 128.38, 123.74, 120.11, 113.15 (dd, *J* = 24.6, 11.9 Hz), 109.58, 101.80 (t, *J* = 25.3 Hz), 83.38, 81.59, 47.46, 46.47, 24.76, 24.66. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.05. MS (EI): m/z (%) = 386 (M^+, 2.08), 259 (100); HRMS calculated for $[C_{22}H_{25}BF_2O_3]^+$: 386.1865 found: 386.1867. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.6 min, major enantiomer tr = 15.3 min. $[\alpha]_D^{25}$ = 21.8 (c = 0.4, $CHCl_3$).

4.20 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-(3,4,5-trifluorobenzyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2t**).

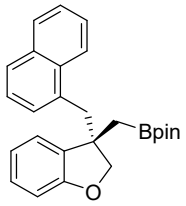


2t

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1t** (121.3 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2t** as a colorless ropy liquid (86 mg, 71% yield) with 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.6 Hz, 1H), 6.95-6.79 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.52-6.40 (m, 2H), 4.44 (d, *J* = 9.0 Hz, 1H), 4.31 (d, *J* = 9.0 Hz, 1H), 2.86 (s, 2H), 1.36 (d, *J* = 15.6 Hz, 1H), 1.25 (s, 1H), 1.21 (s, 6H), 1.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.50, 150.34 (ddd, *J* = 248.8, 9.8, 4.0 Hz), 138.47 (dt, *J* = 249.8, 15.3 Hz), 133.93 (td, *J* = 7.3, 4.8 Hz), 133.57, 128.51, 123.63, 120.18, 114.14 (dd, *J* = 15.5, 5.3 Hz), 109.65, 83.45, 81.42, 47.44, 46.13, 24.75, 24.66. ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.68 (d, *J* = 20.6 Hz), -163.79 (t, *J* =

20.7 Hz). MS (EI): m/z (%) = 404 (M^+, 1.58), 259 (100); HRMS calculated for $[C_{22}H_{24}BF_3O_3]^+$: 404.1771 found: 404.1766. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.8 min, major enantiomer tr = 18.1 min. $[\alpha]_D^{25}$ = 19.2 (c = 0.4, $CHCl_3$).

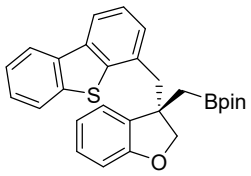
4.21 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-(naphthalen-1-ylmethyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2u**).



2u

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1u** (120.0 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2u** as a white soild (107.8 mg, 90% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.34-7.25 (m, 1H), 7.25-7.19 (m, 1H), 7.19-7.13 (m, 1H), 7.00-6.92 (m, 1H), 6.88 (d, *J* = 6.6 Hz, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.59 (t, *J* = 8.6 Hz, 2H), 4.46 (d, *J* = 8.9 Hz, 1H), 4.22 (d, *J* = 8.9 Hz, 1H), 3.52 (d, *J* = 13.8 Hz, 1H), 3.20 (d, *J* = 13.7 Hz, 1H), 1.39 (d, *J* = 15.9 Hz, 1H), 1.25 (d, *J* = 15.8 Hz, 1H), 1.10 (s, 6H), 1.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.44, 135.01, 134.07, 133.65, 133.29, 128.66, 128.46, 127.92, 127.03, 125.27, 124.99, 124.83, 124.34, 123.96, 119.96, 109.34, 83.26, 81.60, 48.28, 41.82, 24.83, 24.60. MS (EI): m/z (%) = 401 ($M+H^+$, 0.21), 259 (100); HRMS calculated for $[C_{26}H_{30}BO_3]^+$: 401.2283 found: 401.2273. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 14.4 min, major enantiomer tr = 24.9 min. $[\alpha]_D^{25}$ = -34.7 (c = 0.4, $CHCl_3$).

4.22 Synthesis of (*S*)-2-((3-(dibenzo[b,d]thiophen-4-ylmethyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2v**).

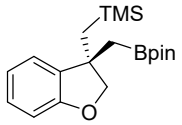


2v

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1v** (136.9 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2v** as a colorless ropy liquid (112.2 mg, 82% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.01 (m, 1H), 7.95 (s, 1H), 7.83-7.70 (m, 1H), 7.47-7.32 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.86-6.73 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.65 (d, *J* = 9.0 Hz, 1H), 4.38 (d, *J* = 9.0 Hz, 1H), 3.32-3.17 (m, 2H), 1.54-1.38 (m, 2H), 1.17 (s, 6H), 1.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.68, 141.40, 138.99, 136.07, 135.51, 134.56, 132.57, 128.38, 128.16, 126.46, 124.19, 123.83,

122.50, 121.55, 120.10, 119.74, 109.49, 83.27, 81.62, 48.39, 46.10, 24.81, 24.60. MS (EI): m/z (%) = 456 (M^+, 1.11), 259 (100); HRMS calculated for $[C_{28}H_{30}BO_3S]^+$: 457.2003 found: 457.1996. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 20.6 min, major enantiomer tr = 30.2 min. $[\alpha]_D^{25}$ = -46.1 (c = 0.4, $CHCl_3$).

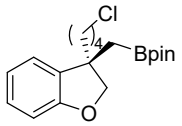
4.23 Synthesis of (*S*)-trimethyl((3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2,3-dihydrobenzofuran-3-yl)methyl)silane (**2w**).



2w

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1w** (103.8 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2w** as a colorless ropy liquid (93.3 mg, 90% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.15 (m, 2H), 7.00-6.81 (m, 2H), 4.54 (d, *J* = 8.7 Hz, 1H), 4.45 (d, *J* = 8.7 Hz, 1H), 1.52 (d, *J* = 15.2 Hz, 1H), 1.45-1.36 (m, 2H), 1.28 (s, 6H), 1.25 (s, 6H), 1.19 (d, *J* = 14.7 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.97, 137.32, 127.62, 123.23, 120.16, 109.35, 83.71, 83.04, 45.56, 32.05, 24.70. MS (EI): m/z (%) = 346 (M^+, 5.71), 259 (100); HRMS calculated for $[C_{19}H_{31}BO_3Si]^+$: 346.2136 found: 346.2139. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.0 min, major enantiomer tr = 11.8 min. $[\alpha]_D^{25}$ = 6.1 (c = 0.4, $CHCl_3$).

4.24 Synthesis of (*S*)-2-((3-(4-chlorobutyl)-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2x**).

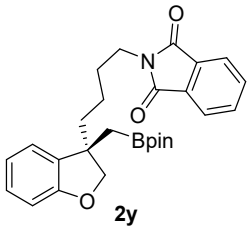


2x

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1x** (105.2 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2x** as a colorless ropy liquid (87.9 mg, 84% yield) with 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 12.2, 7.5 Hz, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 4.38 (s, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 1.77-1.56 (m, 4H), 1.47 (q, *J* = 14.8, 13.5 Hz, 1H), 1.38-1.20 (m, 3H), 1.16 (s, 6H), 1.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.53, 135.06, 127.86, 123.21, 120.17, 109.33, 83.14, 82.09, 46.42, 44.63, 40.70, 32.93, 24.68, 24.64, 21.91. MS (EI): m/z (%) = 350 (M^+, 16.07), 259 (100); HRMS calculated for $[C_{19}H_{28}BClO_3]^+$: 350.1820 found: 350.1816. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 11.6 min, major enantiomer tr = 19.0 min. $[\alpha]_D^{25}$ = 20.9 (c = 0.4, $CHCl_3$).

4.25 Synthesis of (*S*)-2-(4-(3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2,3-

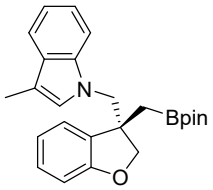
dihydrobenzofuran-3-yl)butyl)isoindoline-1,3-dione (**2y**).



2y

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1y** (138.3 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2y** as a colorless ropy liquid (101.6 mg, 74% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.77 (m, 2H), 7.73-7.65 (m, 2H), 7.15-7.00 (m, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 4.38 (s, 2H), 3.60 (t, *J* = 7.5 Hz, 2H), 1.82-1.53 (m, 4H), 1.44-1.18 (m, 4H), 1.15 (s, 6H), 1.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.19, 159.47, 134.96, 133.73, 132.02, 127.74, 123.20, 123.03, 120.09, 109.19, 83.06, 81.97, 46.37, 40.95, 37.65, 28.85, 24.63, 24.57, 21.75. MS (EI): m/z (%) = 461 ($M+H^+$, 13.22), 259 (100); HRMS calculated for $[C_{27}H_{32}BNO_5]^+$: 461.2374 found: 461.2376. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 18.0 min, major enantiomer tr = 21.8 min. $[\alpha]_D^{25}$ = 24.4 (c = 0.4, $CHCl_3$).

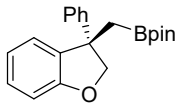
4.26 Synthesis of (*R*)-3-methyl-1-((3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1H-indole (**2z**).



2z

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1z** (121.0 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **2z** as a colorless ropy liquid (66.0 mg, 55% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 1H), 7.17-7.01 (m, 4H), 6.99-6.92 (m, 1H), 6.88-6.71 (m, 2H), 6.53 (s, 1H), 4.53 (d, *J* = 9.2 Hz, 1H), 4.27 (ddd, *J* = 29.2, 16.0, 9.6 Hz, 3H), 2.27-2.23 (m, 3H), 1.44 (d, *J* = 16.0 Hz, 1H), 1.35 (d, *J* = 15.9 Hz, 1H), 1.19 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.76, 137.71, 133.05, 128.68, 128.24, 126.62, 124.03, 121.34, 120.42, 118.71, 118.49, 110.47, 109.70, 109.39, 83.51, 80.20, 53.92, 49.24, 24.85, 24.59, 9.51. MS (EI): m/z (%) = 404 ($M+H^+$, 6.92), 145 (100); HRMS calculated for $[C_{25}H_{31}BNO_3]^+$: 404.2392 found: 404.2382. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 13.5 min, major enantiomer tr = 19.5 min. $[\alpha]_D^{25}$ = -14.2 (c = 0.4, $CHCl_3$).

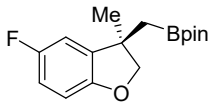
4.27 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((3-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**2aa**).



2aa

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **1aa** (100.9 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), H_2O (22 μL, 1.2 mmol) and EA (3 mL), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **1aa** as a colorless ropy liquid (51.8 mg, 52% yield) with 82% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 4H), 7.19-7.09 (m, 3H), 6.92-6.77 (m, 2H), 4.77-4.68 (m, 2H), 1.84 (d, *J* = 15.4 Hz, 1H), 1.61 (d, *J* = 15.4 Hz, 1H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.60, 147.65, 135.70, 128.21, 128.13, 126.17, 126.07, 124.71, 120.60, 109.69, 85.44, 83.20, 50.94, 24.60, 24.48. ESI-MS calculated for $C_{21}H_{25}BNaO_3$: m/z (%): 359.1789 ($M+Na^+$), found: 359.1791. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes : 2-propanol = 90:10, 0.5 mL/min, 220 nm); minor enantiomer tr = 16.5 min, major enantiomer tr = 22.0 min. $[\alpha]_D^{20}$ = -3.1 (c = 0.3, CHCl3).

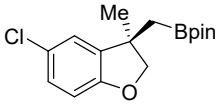
4.28 Synthesis of (*R*)-2-((5-fluoro-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4a**).



4a

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3a** (87.6 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **4a** as a colorless ropy liquid (80.2 mg, 92% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.75 (td, *J* = 8.8, 2.8 Hz, 1H), 6.64 (dd, *J* = 8.6, 4.1 Hz, 1H), 4.41 (d, *J* = 8.6 Hz, 1H), 4.25 (d, *J* = 8.6 Hz, 1H), 1.36 (s, 3H), 1.33-1.25 (m, 2H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.55 (d, *J* = 236.6 Hz), 154.84 (d, *J* = 1.5 Hz), 138.78 (d, *J* = 7.8 Hz), 113.67 (d, *J* = 24.2 Hz), 109.89 (d, *J* = 24.6 Hz), 109.49 (d, *J* = 8.4 Hz), 84.72, 83.25, 43.58, 27.61, 24.74, 24.70. ^{19}F NMR (282 MHz, $CDCl_3$) δ -124.34. MS (EI): m/z (%) = 292 (M^+, 20.62), 151 (100); HRMS calculated for $[C_{16}H_{22}BFO_3]^+$: 292.1646 found: 292.1642. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 8.9 min, major enantiomer tr = 9.7 min. $[\alpha]_D^{20}$ = 14.3 (c = 0.4, acetone).

4.29 Synthesis of (*R*)-2-((5-chloro-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4b**).

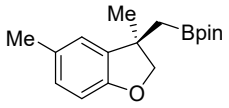


4b

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3b** (92.6 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **4b** as a colorless ropy liquid (79.7 mg, 86% yield)

with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 2.3 Hz, 1H), 6.97-6.91 (m, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 4.33 (d, *J* = 8.7 Hz, 1H), 4.18 (d, *J* = 8.6 Hz, 1H), 1.29 (s, 3H), 1.20 (d, *J* = 15.5 Hz, 2H), 1.13 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 139.20, 127.49, 124.92, 123.08, 110.41, 84.77, 83.27, 43.43, 27.70, 24.77, 24.69. MS (EI): m/z (%) = 309 ($M+H^+$, 6.67), 167 (100); HRMS calculated for $[C_{16}H_{23}BClO_3]^+$: 309.1423 found: 309.1427. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 10.3 min, major enantiomer tr = 11.1 min. $[\alpha]_D^{25}$ = 34.2 (c = 0.4, $CHCl_3$).

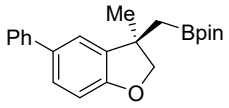
4.30 Synthesis of (*R*)-2-((3,5-dimethyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4c**).



4c

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3c** (86.5 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **4c** as a colorless ropy liquid (77.3 mg, 89% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 1.9 Hz, 1H), 6.82-6.76 (m, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 4.31 (d, *J* = 8.6 Hz, 1H), 4.14 (d, *J* = 8.6 Hz, 1H), 2.19 (s, 3H), 1.28 (s, 3H), 1.21 (d, *J* = 15.5 Hz, 2H), 1.12 (s, 6H), 1.11 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.86, 137.27, 129.44, 127.99, 123.14, 108.93, 84.21, 83.10, 43.14, 27.83, 24.76, 24.67, 20.82. MS (EI): m/z (%) = 289 ($M+H^+$, 3.42), 147 (100); HRMS calculated for $[C_{17}H_{26}BO_3]^+$: 289.1970 found: 289.1965. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 11.2 min, major enantiomer tr = 15.5 min. $[\alpha]_D^{25}$ = 32.8 (c = 0.4, $CHCl_3$).

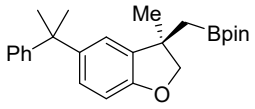
4.31 Synthesis of (*R*)-4,4,5,5-tetramethyl-2-((3-methyl-5-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**4d**).



4d

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3d** (105.1 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **4d** as a white soild (97.7 mg, 93% yield) with 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 2H), 7.35-7.27 (m, 3H), 7.26-7.21 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.39 (d, *J* = 8.6 Hz, 1H), 4.22 (d, *J* = 8.6 Hz, 1H), 1.33 (s, 3H), 1.26 (d, *J* = 15.5 Hz, 1H), 1.18 (d, *J* = 15.2 Hz, 1H), 1.09 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.80, 141.56, 137.88, 133.88, 128.57, 126.77, 126.70, 126.31, 121.64, 109.54, 84.61, 83.16, 43.19, 28.22, 24.73. MS (EI): m/z (%) = 350 (M^+, 58.53), 209 (100); HRMS calculated for $[C_{22}H_{27}BO_3Na]^+$: 373.1945 found: 373.1938. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 11.2 min, major enantiomer tr = 12.9 min. $[\alpha]_D^{25}$ = -65.5 (c = 0.4, $CHCl_3$).

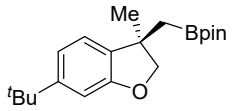
4.32 Synthesis of (*R*)-4,4,5,5-tetramethyl-2-((3-methyl-5-(2-phenylpropan-2-yl)-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (**4e**).



4e

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3e** (117.6 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **4e** as a colorless ropy liquid (113.1 mg, 96% yield) with 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.11 (m, 4H), 7.10-7.01 (m, 1H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.88-6.80 (m, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 4.31 (d, *J* = 8.6 Hz, 1H), 4.15 (d, *J* = 8.5 Hz, 1H), 1.57 (s, 6H), 1.25 (s, 3H), 1.15 (t, *J* = 16.1 Hz, 2H), 1.09 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.90, 151.19, 142.80, 136.75, 127.81, 126.66, 126.27, 125.36, 120.94, 108.48, 84.47, 83.06, 43.22, 42.57, 31.14, 27.95, 24.76, 24.70. MS (EI): m/z (%) = 392 (M^+, 58.25), 377 (100); HRMS calculated for $[C_{25}H_{33}BO_3]^+$: 392.2523 found: 392.2518. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 10.9 min, major enantiomer tr = 9.5 min. $[\alpha]_D^{20}$ = 23.5 (c = 0.4, acetone).

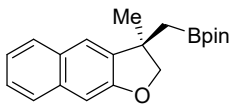
4.33 Synthesis of (*R*)-2-((5-(tert-butyl)-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4f**).



4f

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3f** (99.1 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **4f** as a colorless ropy liquid (90.2 mg, 91% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 2.1 Hz, 1H), 7.06-7.00 (m, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 4.32 (d, *J* = 8.5 Hz, 1H), 4.16 (d, *J* = 8.5 Hz, 1H), 1.29 (s, 3H), 1.26 (d, *J* = 2.8 Hz, 1H), 1.21 (s, 9H), 1.16 (s, 1H), 1.12 (s, 6H), 1.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.79, 143.25, 136.72, 124.40, 119.55, 108.49, 84.48, 83.08, 43.27, 34.33, 31.75, 28.07, 24.78, 24.72. MS (EI): m/z (%) = 331 ($M+H^+$, 9.23), 315 (100); HRMS calculated for $[C_{20}H_{32}BO_3]^+$: 331.2439 found: 331.2431. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 8.8 min, major enantiomer tr = 9.2 min. $[\alpha]_D^{25}$ = 31.8 (c = 0.4, $CHCl_3$).

4.34 Synthesis of (*R*)-4,4,5,5-tetramethyl-2-((3-methyl-2,3-dihydronaphtho[2,3-*b*]furan-3-yl)methyl)-1,3,2-dioxaborolane (**4g**).

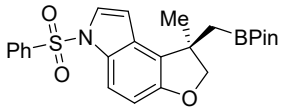


4g

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%),

***N*-Me-Xu3** (7.5 mol%) from allyl ether **3g** (97.3 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 100:1) afforded the product **4g** as a white soild (76.1 mg, 78% yield) with 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.54 (m, 2H), 7.48 (s, 1H), 7.26 (d, J = 6.9 Hz, 1H), 7.20-7.14 (m, 1H), 6.98 (s, 1H), 4.40 (d, J = 8.5 Hz, 1H), 4.24 (d, J = 8.5 Hz, 1H), 1.37 (d, J = 1.4 Hz, 3H), 1.35-1.19 (m, 2H), 1.10 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.14, 140.29, 134.34, 129.63, 127.68, 126.66, 125.46, 122.94, 121.27, 103.71, 84.35, 83.23, 42.77, 27.98, 24.78, 24.69. MS (EI): m/z (%) = 325 ($M+H^+$, 11.31), 183 (100); HRMS calculated for $[C_{20}H_{26}BO_3]^+$: 325.1970 found: 325.1963. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 99:1, 0.5 mL/min, 220 nm); minor enantiomer tr = 12.0 min, major enantiomer tr = 14.5 min. $[\alpha]_D^{25}$ = 46.8 (c = 0.4, $CHCl_3$).

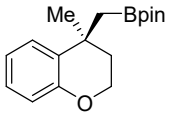
4.35 Synthesis of (*R*)-1-methyl-6-(phenylsulfonyl)-1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,6-dihydro-2*H*-furo[3,2-e]indole (**4h**).



4h

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3h** (136 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 6:1) afforded the product **4h** as a white soild (98.3 mg, 73% yield) with 80% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.56-7.47 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 4.49 (d, *J* = 8.6 Hz, 1H), 4.27 (d, *J* = 8.6 Hz, 1H), 1.45 (s, 3H), 1.39 (d, *J* = 12.8 Hz, 1H), 1.32 (d, *J* = 15.6 Hz, 1H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.43, 138.29, 133.58, 130.46, 129.13, 127.30, 127.13, 126.78, 126.57, 112.60, 107.37, 106.17, 83.88, 83.11, 44.21, 27.64, 24.59. ESI-MS calculated for $C_{24}H_{28}BNNaO_5S$: m/z (%): 476.1673 ($M+Na^+$), found: 476.1680. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes : 2-propanol = 80:20, 0.5 mL/min, 250 nm); major enantiomer tr = 16.7 min, minor enantiomer tr = 20.1 min. $[\alpha]_D^{20}$ = 34.1 (c = 0.3, $CHCl_3$).

4.36 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((4-methylchroman-4-yl)methyl)-1,3,2-dioxaborolane (**4i**).

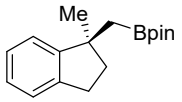


4i

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3i** (86.4 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 20:1) afforded the product **4i** as a colorless oil (63.2 mg, 73% yield) with 85% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.03 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1 H), 6.85 (td, *J* = 7.7, 1.3 Hz, 1 H), 6.75 (dd, *J* = 8.1, 1.2 Hz, 1 H), 4.20 (dddd, *J* = 20.1, 13.9, 7.6, 3.2 Hz, 2 H), 2.25 (ddd, *J* = 13.6, 9.0, 3.6 Hz, 1 H), 1.80 (ddd, *J* = 13.9, 6.1, 2.9 Hz, 1 H), 1.40 (s, 3

H), 1.30 (s, 2 H), 1.16 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.52, 132.53, 127.19, 126.79, 120.18, 116.63, 82.88, 63.05, 36.37, 32.06, 31.58, 24.72, 24.59. MS (EI): m/z (%) = 288 ($M+H^+$, 18.61), 147 (100); HRMS calculated for $[C_{17}H_{26}BO_3]^+$: 288.1897 found: 288.1902. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (hexanes : 2-propanol = 99.5:0.5, 0.3 mL/min, 254 nm); minor enantiomer tr = 18.2 min, major enantiomer tr = 19.4 min. $[\alpha]_D^{20}$ = 14.8 (c = 0.4, acetone).

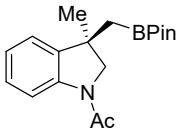
4.37 Synthesis of (*S*)-4,4,5,5-tetramethyl-2-((1-methyl-2,3-dihydro-1H-inden-1-yl)methyl)-1,3,2-dioxaborolane (**4j**).



4j

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3j** (81.6 mg, 0.3 mmol) , B_2Pin_2 (83.8 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 20:1) afforded the product **4j** as a colorless oil (62.1 mg, 77% yield) with 89% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.02 (m, 4 H), 2.88 (td, *J* = 7.2, 3.2 Hz, 2 H), 2.21-2.06 (m, 1 H), 1.94 (ddd, *J* = 12.5, 7.6, 6.2 Hz, 1 H), 1.31 (s, 3 H), 1.26 (d, *J* = 14.9 Hz, 1 H), 1.19 (s, 6H), 1.18 (s, 6H), 1.11 (d, *J* = 14.9 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.36, 142.44, 126.12, 125.96, 124.26, 122.29, 82.80, 45.32, 40.76, 30.08, 28.68, 24.81, 24.74. MS (EI): m/z (%) = 272 ($M+H^+$, 4.49), 131 (100); HRMS calculated for $[C_{17}H_{26}BO_2]^+$: 272.1948 found: 272.1950. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (hexanes : 2-propanol = 99.5:0.5, 0.3 mL/min, 254 nm); minor enantiomer tr = 12.3 min, major enantiomer tr = 13.9 min. $[\alpha]_D^{20}$ = 23.0 (c = 0.4, acetone).

4.38 Synthesis of (*R*)-1-(3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-1-yl)ethan-1-one (**4k**).

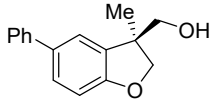


4k

Prepared according to typical procedure at 80 °C for 12 h by using $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%), ***N*-Me-Xu3** (7.5 mol%) from allyl ether **3k** (94.5 mg, 0.3 mmol) , B_2Pin_2 (99 mg, 0.39 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) and H_2O (22 μL, 1.2 mmol), after a flash column chromatography (hexanes: EA = 5:1) afforded the product **4k** as a yellow solid (87.1 mg, 92% yield) with 53% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.9 Hz, 1H), 7.21-7.11 (m, 2H), 7.02 (t, *J* = 7.0 Hz, 1H), 4.06 (d, *J* = 10.2 Hz, 1H), 3.76 (d, *J* = 10.2 Hz, 1H), 2.22 (s, 3H), 1.39 (s, 3H), 1.26 (s, 1H), 1.24 (s, 1H), 1.11 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.59, 141.52, 140.85, 127.47, 123.63, 122.04, 116.82, 83.14, 62.86, 41.48, 29.78, 24.70, 24.60, 24.18. ESI-MS calculated for $C_{18}H_{26}BNNaO_3$: m/z (%): 338.1898 ($M+Na^+$), found: 338.1905. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes : 2-propanol = 96:4, 0.5 mL/min, 220 nm); major enantiomer tr = 29.9 min, minor enantiomer tr = 33.6 min. $[\alpha]_D^{20}$ = -1.1 (c = 0.3, $CHCl_3$).

5. Synthetic Transformations

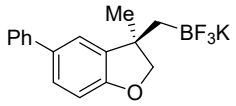
5.1 Synthesis of (*S*)-(3-methyl-5-phenyl-2,3-dihydrobenzofuran-3-yl)methanol (**5**).



5

The synthesis was conducted according to a modified literature procedure.[9] An aqueous hydrogen peroxide solution (0.4 mL, 30% w/w) was added dropwise to a solution of **4d** (105 mg, 0.3 mmol) in THF and aqueous sodium phosphate monobasic (1.5 mL, 0.75 mmol, 0.5 M) at 0 °C. The mixture was stirred at 0 °C for 30 min and at room temperature for 1.5 h. Upon the completion of the reaction as determined by TLC, the mixture was cooled to 0 °C and quenched with water. The aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The crude product was purified by column chromatography on silica gel (hexanes: EA = 5:1) to provide **5** as a colorless oil (45.4 mg, 99%) with 94% *ee.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.36-7.26 (m, 3H), 7.25-7.16 (m, 2H), 6.77 (d, *J* = 8.3 Hz, 1H), 4.51 (d, *J* = 8.9 Hz, 1H), 4.12 (d, *J* = 8.8 Hz, 1H), 3.58 (d, *J* = 10.8 Hz, 1H), 3.49 (d, *J* = 10.9 Hz, 1H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.86, 141.08, 134.18, 132.53, 128.68, 127.81, 126.73, 126.59, 121.88, 109.93, 80.51, 68.91, 47.62, 21.82. ESI-MS calculated for $C_{16}H_{16}NaO_2$: m/z (%): 263.1042 ($M+Na^+$), found: 263.1043. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 95:5, 0.5 mL/min, 220 nm); minor enantiomer tr = 16.3 min, major enantiomer tr = 17.8 min. $[\alpha]_D^{20}$ = 29.2 (c = 0.4, acetone).

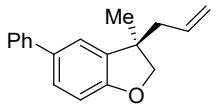
5.2 Synthesis of (*R*)-trifluoro((3-methyl-5-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)-λ^4-borane, potassium salt (**6**).



6

The synthesis was conducted according to a modified literature procedure.[10] The boronic ester **4d** (140 mg, 0.4 mmol) was dissolved in acetonitrile (2.5 mL) and saturated aqueous KHF_2 (4.5 M, 0.45 mL, 5.1 equiv) was added. The reaction mixture was stirred at room temperature for 3 h, concentrated, azeotroped with methanol, and placed on the vacuum for 3 h. The crude product was dissolved in hot acetone, filtered, and Then the solvent was removed under vacuum and the crude product was recrystallized from acetone to give the desired product **6** as a white solid (130.4 mg, 98%). ^{1}H NMR (400 MHz, Acetone-*d6*) δ 7.61-7.51 (m, 2H), 7.41-7.35 (m, 3H), 7.31-7.19 (m, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 4.48 (d, *J* = 8.6 Hz, 1H), 4.23 (d, *J* = 8.6 Hz, 1H), 1.33 (s, 3H), 0.89 (dq, *J* = 13.8, 6.8 Hz, 1H), 0.63 (dq, *J* = 13.7, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-*d6*) δ 159.87, 143.44, 142.75, 133.96, 129.47, 127.26, 126.91, 126.26, 122.11, 109.74, 109.65, 86.01, 44.91 (d, *J* = 1.9 Hz), 28.30. ^{19}F NMR (376 MHz, Acetone-*d6*) δ -135.50. ESI-MS calculated for $C_{16}H_{15}BF_3KNaO$: m/z (%):353.0700 ($M+Na^+$), found: 353.0691. $[\alpha]_D^{20}$ = 33.2 (c = 0.4, acetone).

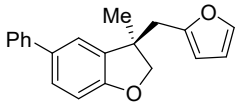
5.3 Synthesis of (*R*)-3-allyl-3-methyl-5-phenyl-2,3-dihydrobenzofuran (**7**).



7

The synthesis was conducted according to a modified literature procedure.[11] The boronic ester **4d** (140 mg, 0.4 mmol) was dissolved in THF (2.0 mL) under argon. The mixture was cooled to -78 °C, vinyl magnesium bromide (1.0 M in THF, 1.2 mL, 1.2 mmol) was added dropwise and the solution was stirred at room temperature for 2 h. Then a solution of I_2 (152 mg, 1.2 mmol) in MeOH (3.0 mL) was added dropwise at -78 °C. After 2 h, a solution of MeONa (108 mg, 2.0 mmol) in MeOH (3.0 mL) was dropwised at room temperature for 2 h. The reaction was quenched by the addition of saturated aqueous $Na_2S_2O_3$ (10 mL). The organic layer was separated and the aqueous phase extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel (hexanes: EA = 50:1) to give **7** as a colorless oil (50 mg, 99%) with 92% *ee*.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.36-7.26 (m, 3H), 7.24-7.18 (m, 2H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.75-5.54 (m, 1H), 5.03 (s, 1H), 4.99 (d, *J* = 6.7 Hz, 1H), 4.36 (d, *J* = 8.6 Hz, 1H), 4.10 (d, *J* = 8.6 Hz, 1H), 2.33 (d, *J* = 7.3 Hz, 2H), 1.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.25, 141.43, 135.53, 134.08, 133.89, 128.66, 127.23, 126.81, 126.50, 121.74, 118.45, 109.75, 82.32, 45.18, 45.10, 25.17. MS (ESI): m/z (%) = 250 ($M+H^+$, 17.78); HRMS calculated for $[C_{20}H_{25}BO_3]^+$: 250.1358 found: 250.1356. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 95:5, 0.5 mL/min, 220 nm); minor enantiomer tr = 11.5 min, major enantiomer tr = 10.6 min. $[\alpha]_D^{20}$ = 85.0 (c = 0.2, acetone).

5.4 Synthesis of (*R*)-3-(furan-2-ylmethyl)-3-methyl-5-phenyl-2,3-dihydrobenzofuran (**8**).

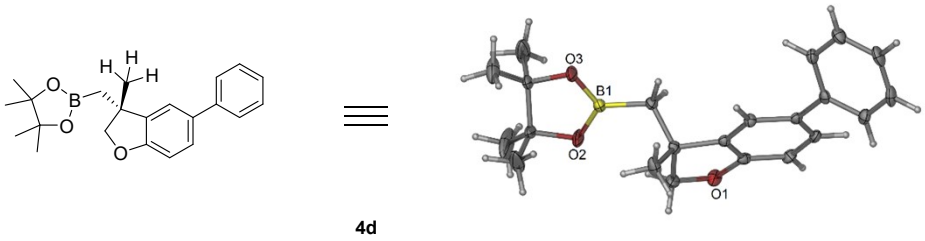


8

The synthesis was conducted according to a modified literature procedure.[11] *n*-BuLi (2.4 M in hexanes, 0.1 mL, 0.24 mmol) was added dropwise at -78 °C to a solution of furan (16.3 mg, 0.24 mmol) in THF (1.0 mL). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to -78 °C and boronic ester **4d** (70 mg, 0.2 mmol) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred for 1 h at -78 °C and a solution of *N*-bromosuccinimide (42.7 mg, 0.24 mmol) in THF (1.0 mL) was added dropwise. After 1 h at -78 °C, a saturated aqueous solution of $Na_2S_2O_3$ was added and the reaction mixture was allowed to warm to room temperature. After addition of Et_2O and water, the layers were separated and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexanes: EA = 50:1) to give **8** as a colorless oil (44 mg, 76%) with 95% *ee.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.47 (m, 2H), 7.43-7.35 (m, 3H), 7.34-7.32 (m, 1H), 7.31-7.25 (m, 1H), 7.23-7.19 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.29 (t, *J* = 2.5 Hz, 1H), 5.97 (d, *J* = 3.1 Hz, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.19 (d, *J* = 8.8 Hz, 1H), 2.96 (s, 2H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.12, 152.50, 141.53, 141.35, 135.35, 134.06, 128.65, 127.38, 126.77, 126.51, 121.77, 110.21, 109.81, 107.88, 82.72, 45.84, 38.73, 24.82. MS (EI): m/z (%) =

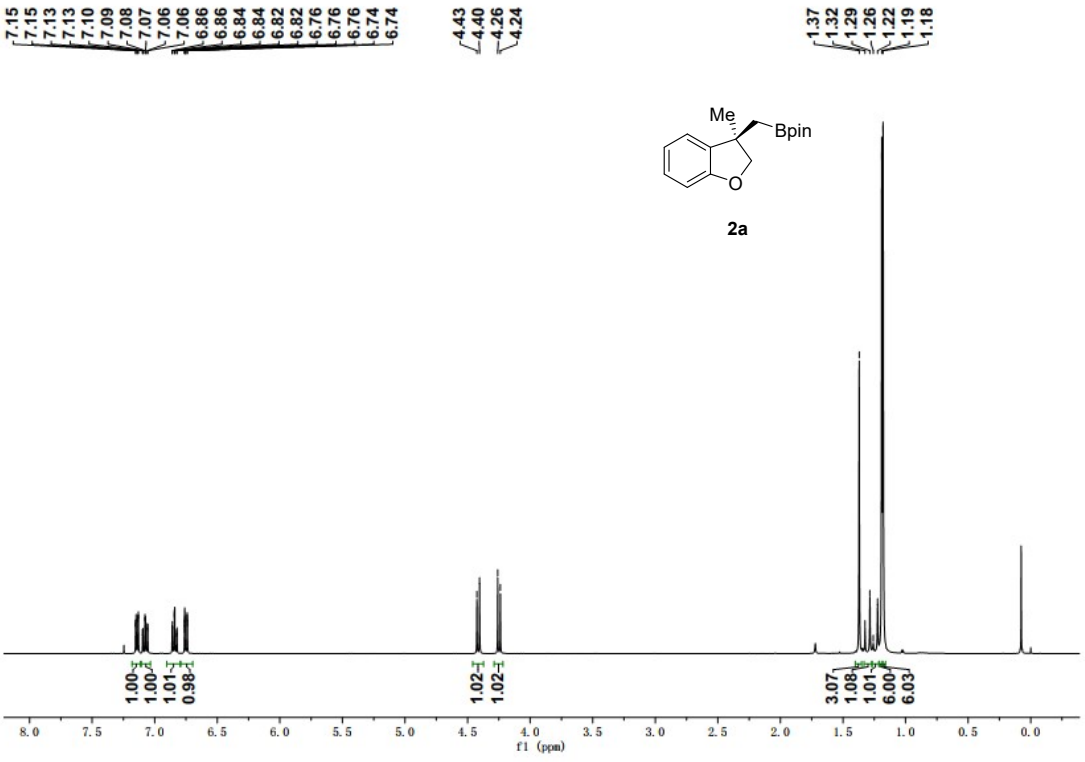
290 (M^+, 9.31), 209 (100); HRMS calculated for $[C_{20}H_{25}BO_3]^+$: 290.1307 found: 290.1311. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes : 2-propanol = 95:5, 0.5 mL/min, 220 nm); minor enantiomer tr = 9.5 min, major enantiomer tr = 8.1 min. $[\alpha]_D^{20}$ = 76.6 (c = 0.4, acetone).

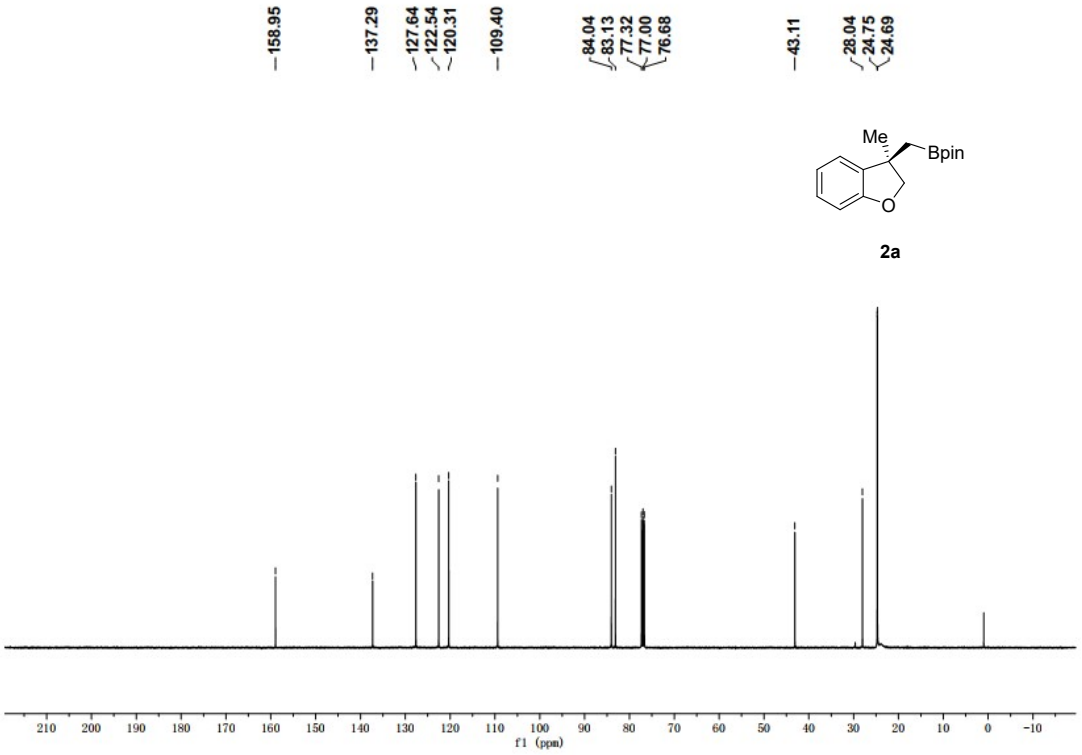
6. X-ray structure of 4d.



4d

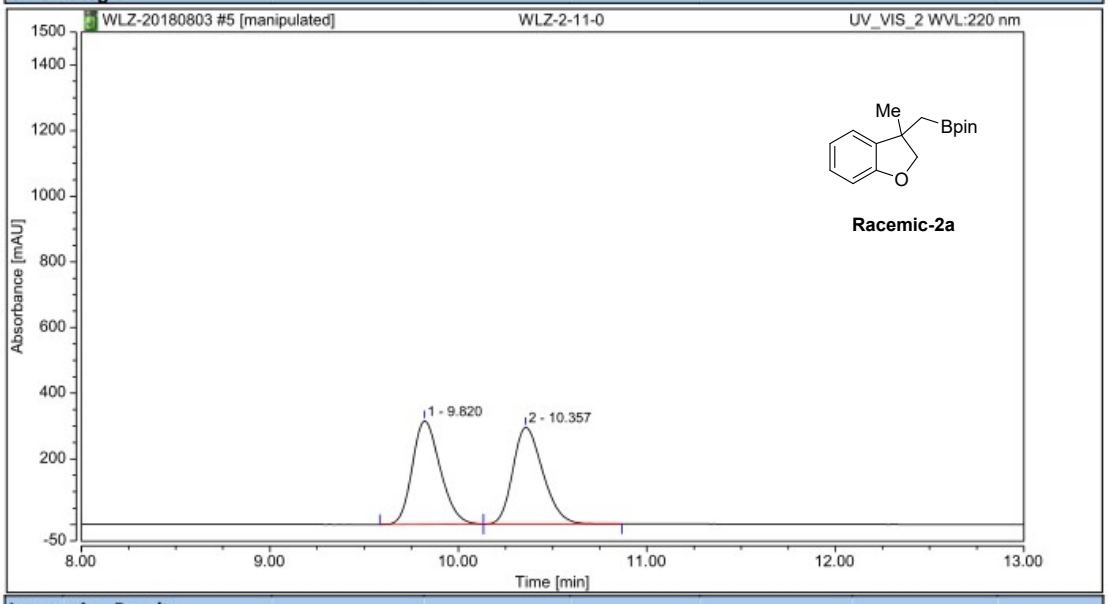
7. ^{1}H , ^{19}F, ^{13}C NMR and HPLC Spectra





2a

Chromatogram

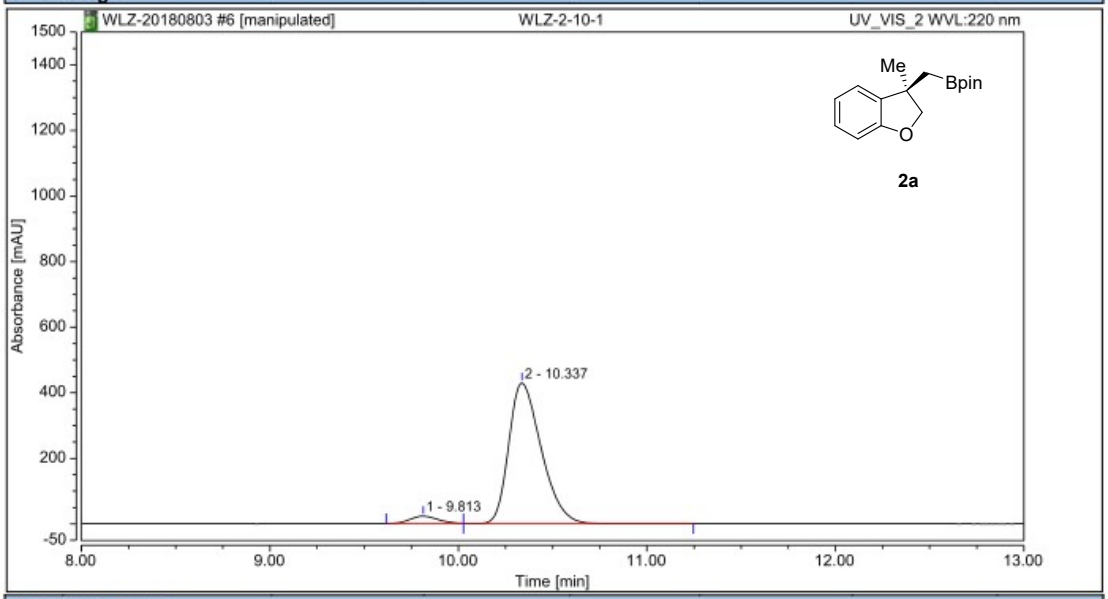


Racemic-2a

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.820	54.440	315.543	50.01	51.70	n.a.
2		10.357	54.412	294.762	49.99	48.30	n.a.
Total:			**108.852**	**610.305**	**100.00**	**100.00**	

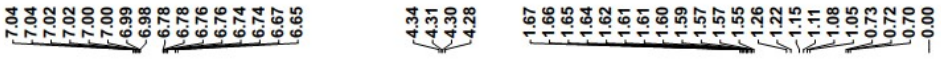
Chromatogram

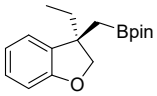


2a

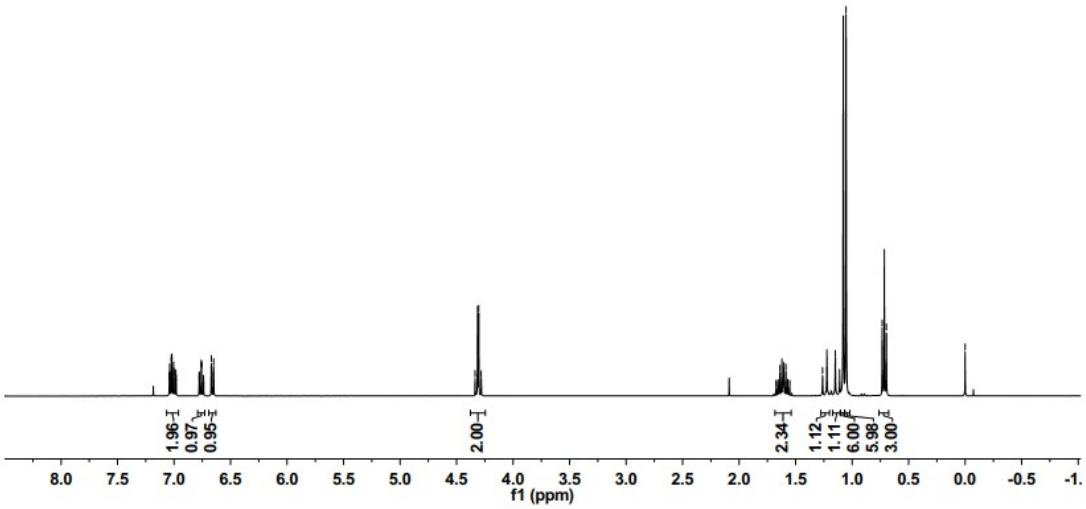
Integration Results

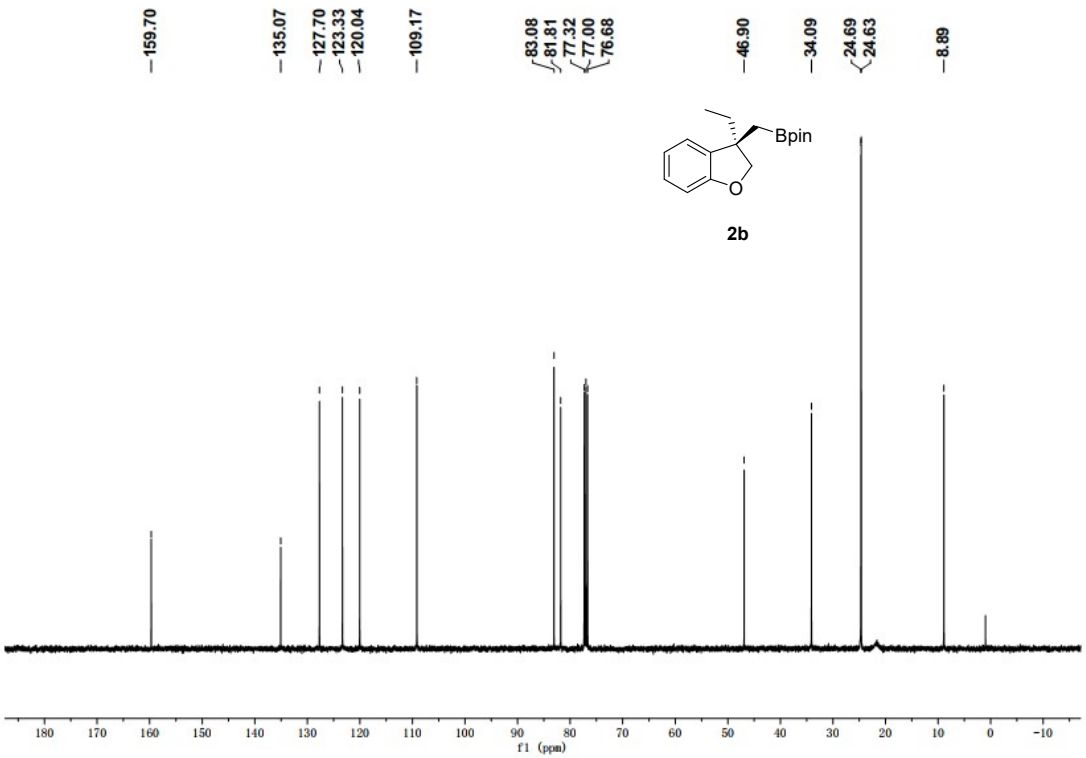
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.813	4.003	22.949	4.45	5.07	n.a.
2		10.337	85.900	429.489	95.55	94.93	n.a.
Total:			**89.903**	**452.437**	**100.00**	**100.00**	



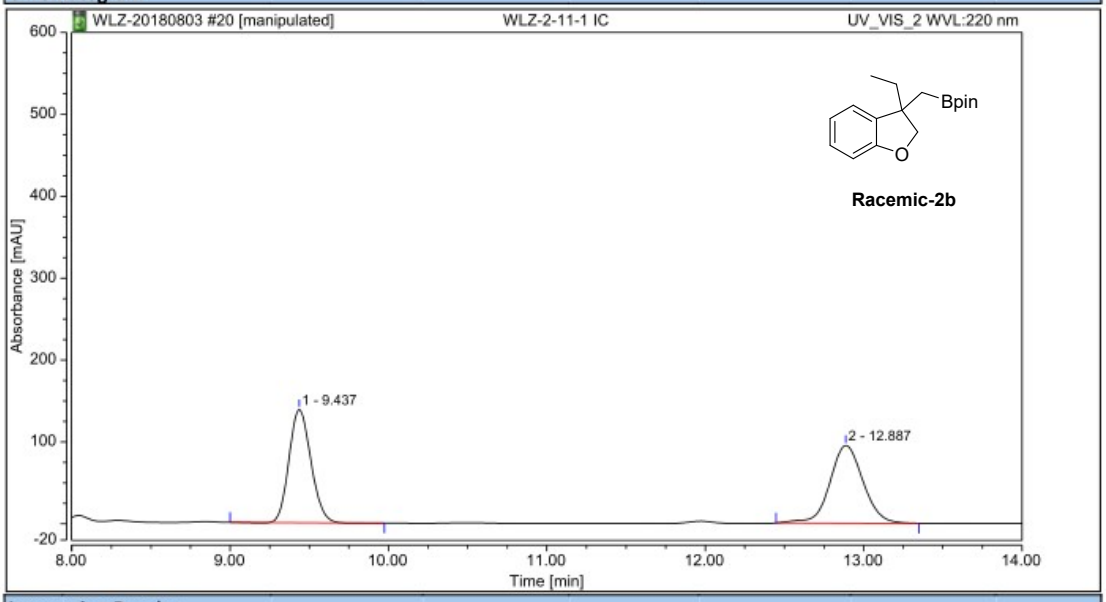


2b





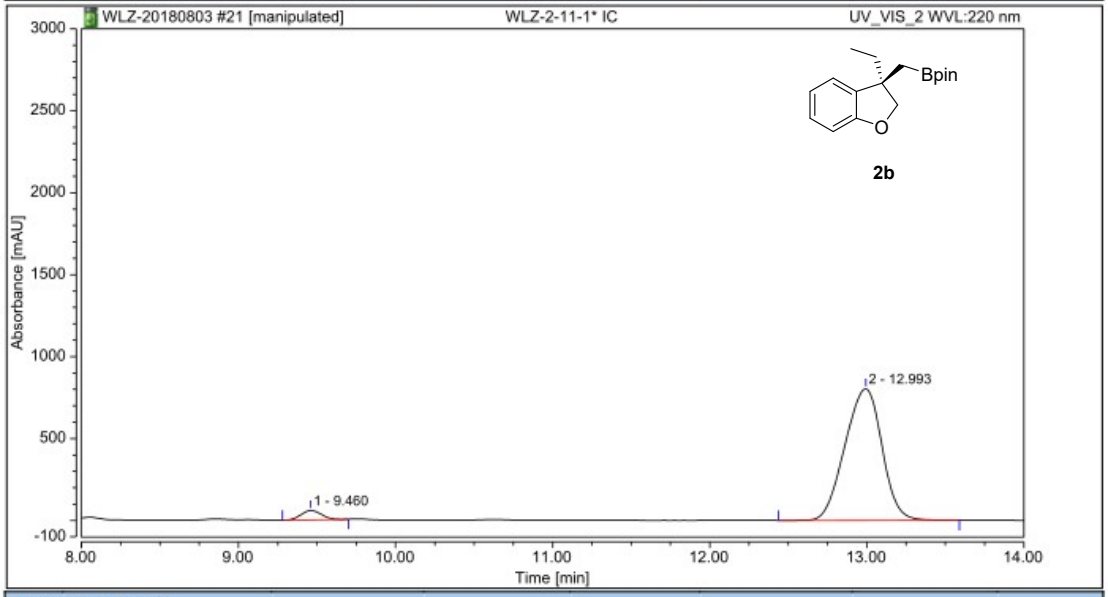
Chromatogram



Integration Results

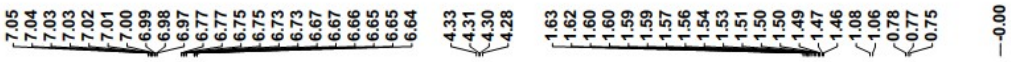
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.437	22.185	138.314	49.06	59.31	n.a.
2		12.887	23.031	94.886	50.94	40.69	n.a.
Total:			**45.217**	**233.200**	**100.00**	**100.00**	

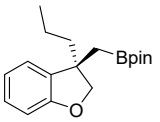
Chromatogram



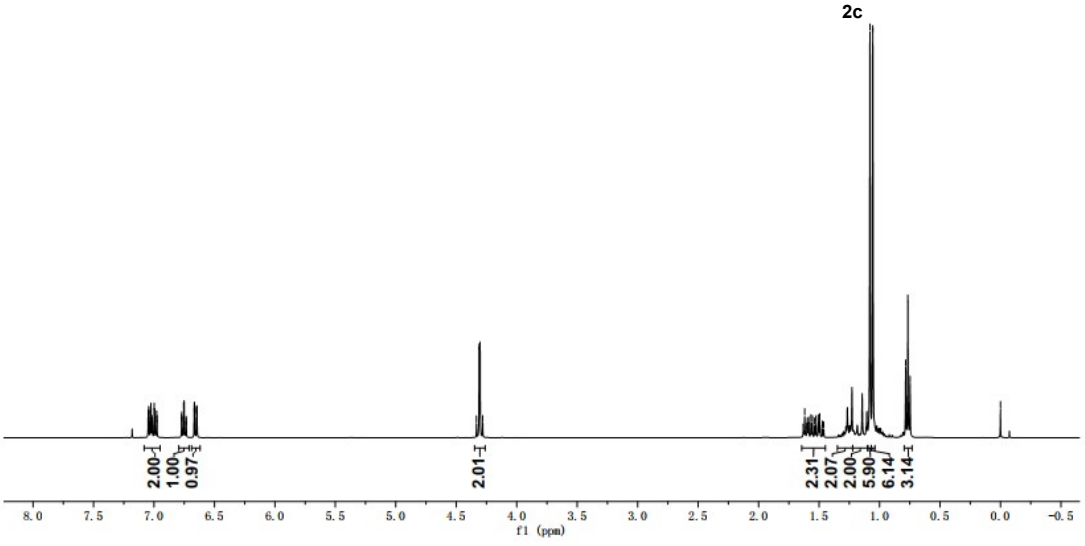
Integration Results

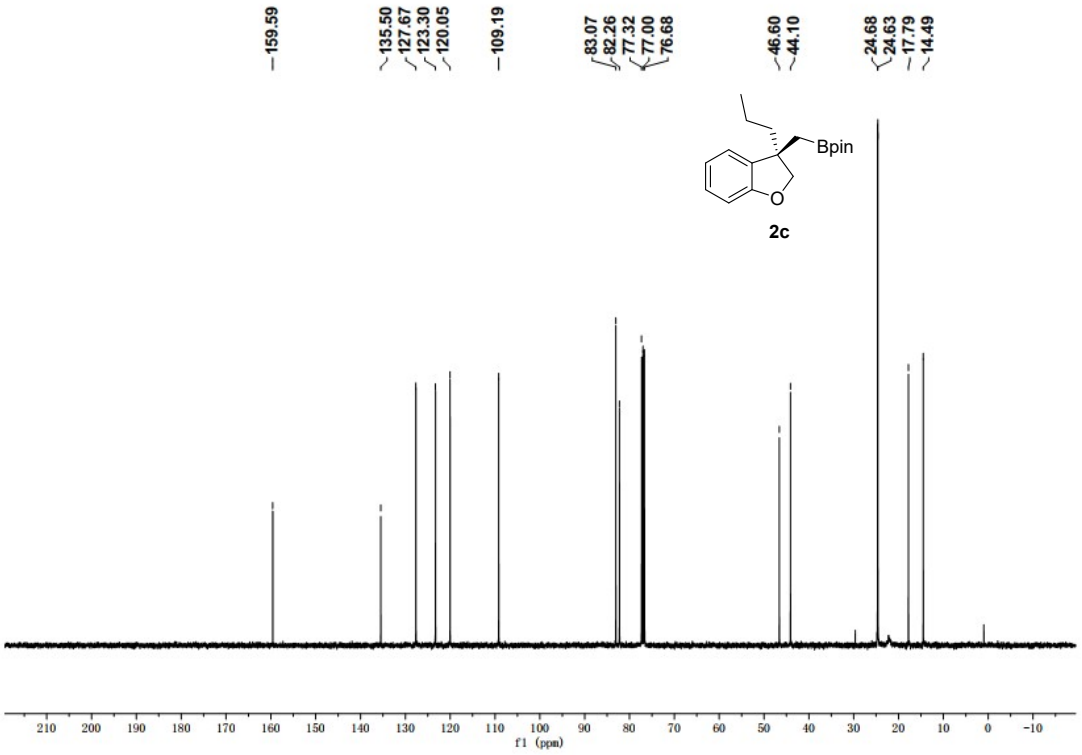
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.460	8.476	56.926	3.71	6.62	n.a.
2		12.993	220.189	802.861	96.29	93.38	n.a.
Total:			**228.665**	**859.787**	**100.00**	**100.00**	



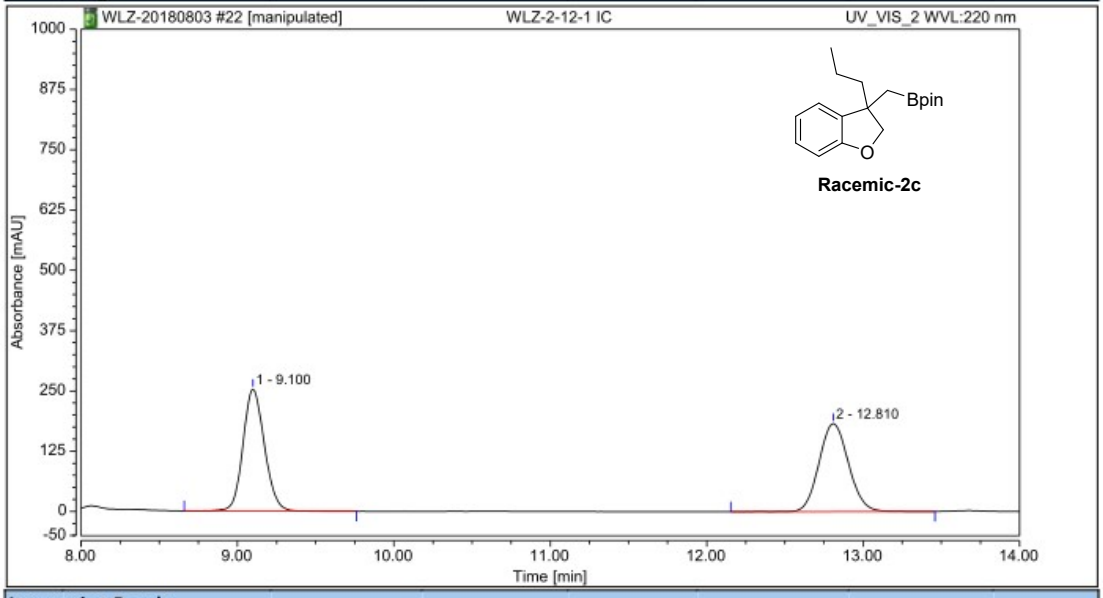


2c





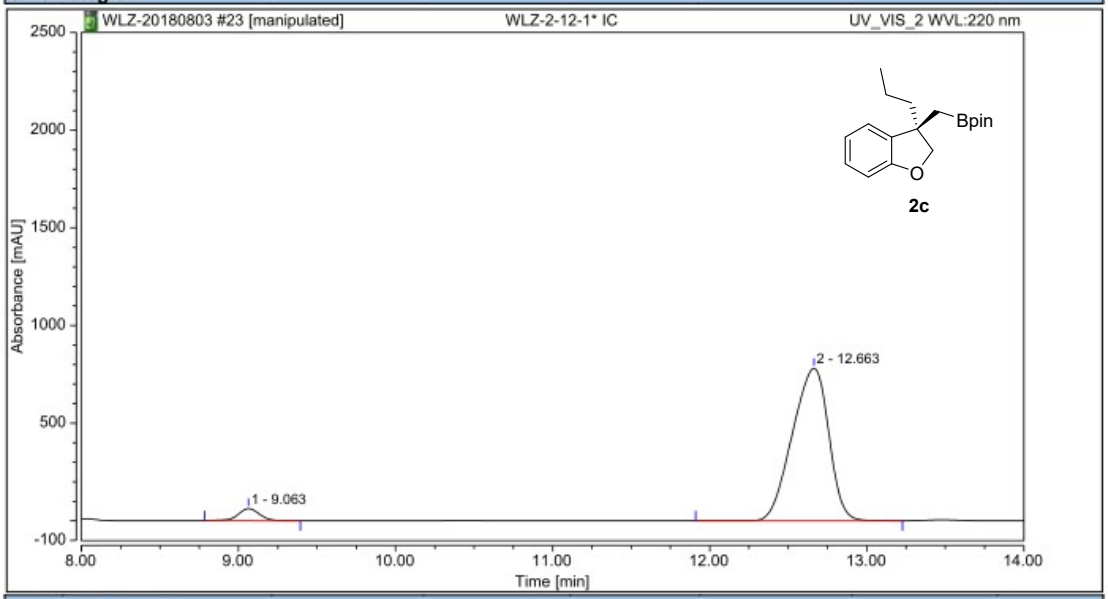
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.100	40.288	252.554	50.25	58.02	n.a.
2		12.810	39.890	182.713	49.75	41.98	n.a.
Total:			**80.178**	**435.267**	**100.00**	**100.00**	

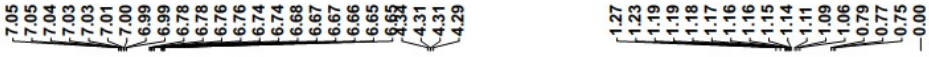
Chromatogram

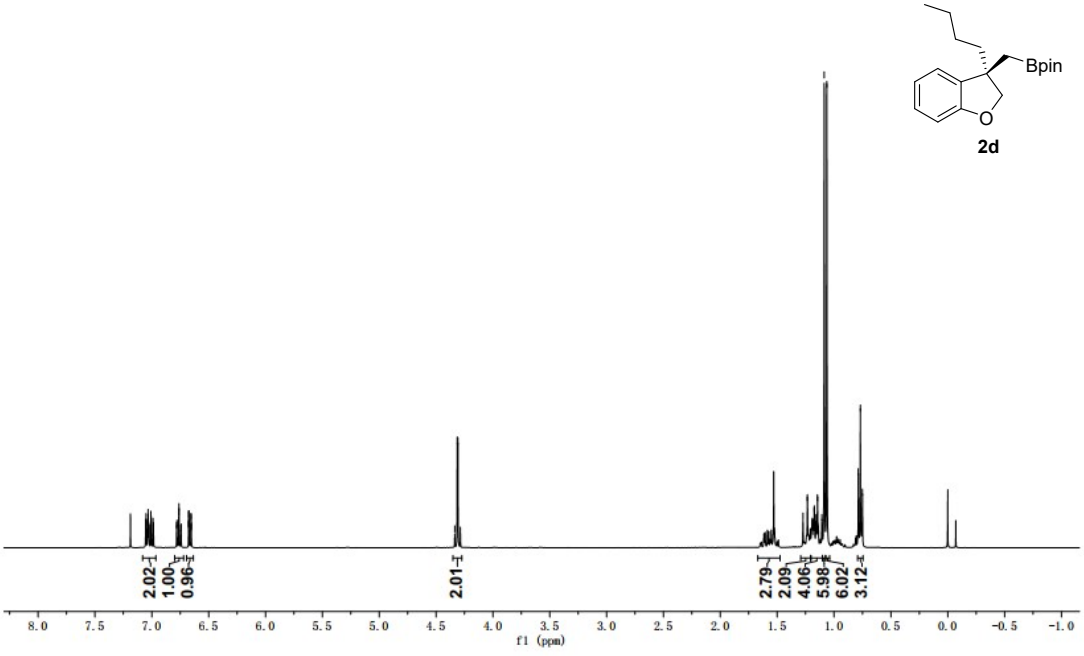


2c

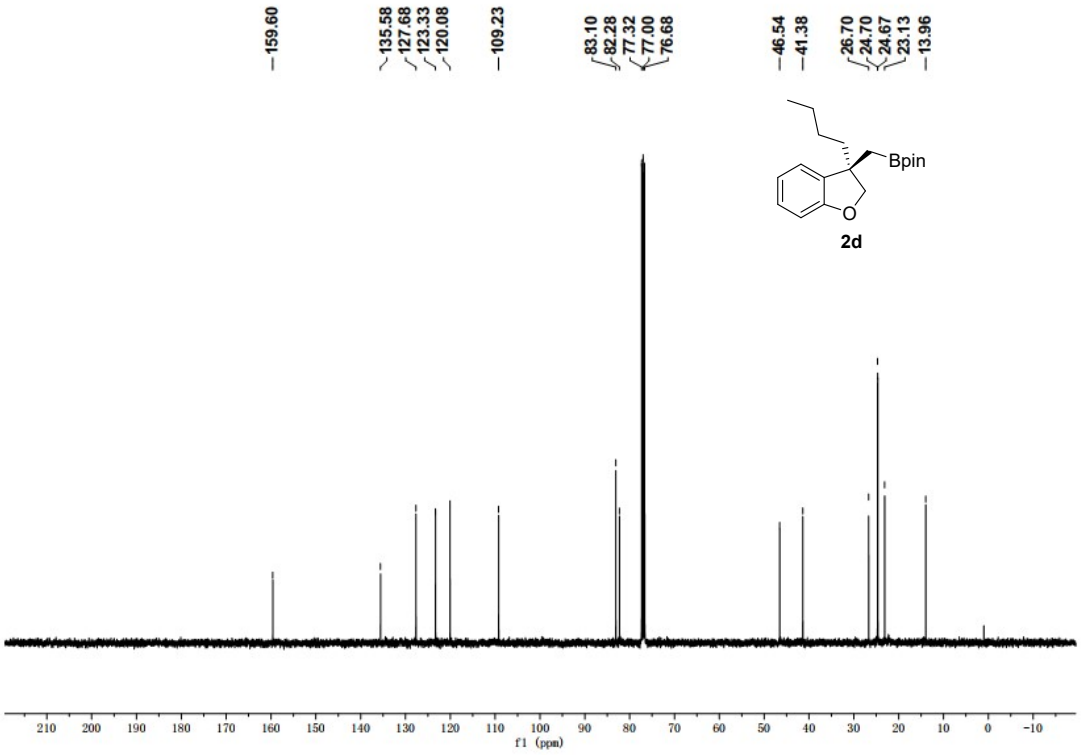
Integration Results

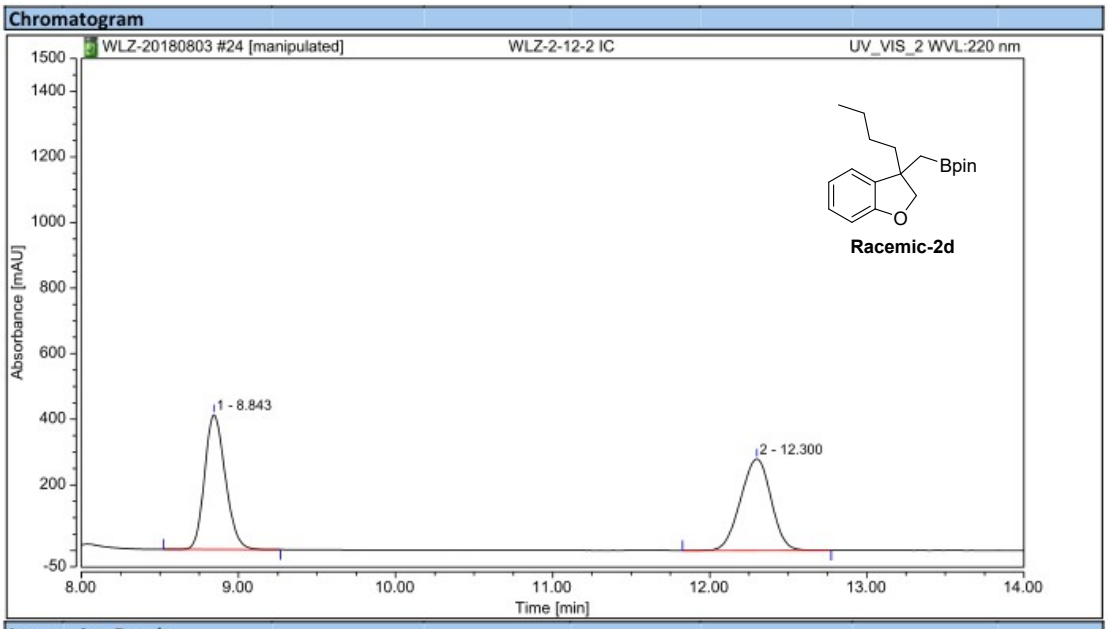
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.063	9.922	62.510	4.51	7.41	n.a.
2		12.663	209.903	780.820	95.49	92.59	n.a.
Total:			**219.824**	**843.330**	**100.00**	**100.00**	





2d

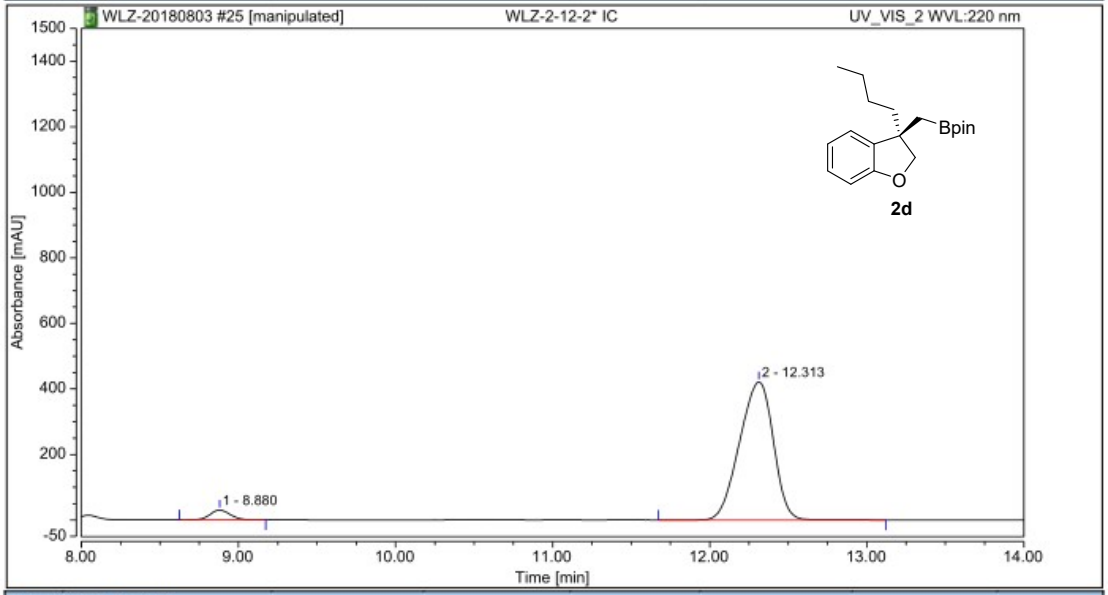




Integration Results

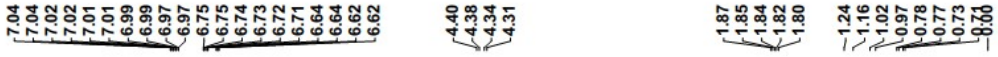
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.843	63.033	410.712	50.08	59.56	n.a.
2		12.300	62.840	278.828	49.92	40.44	n.a.
Total:			**125.873**	**689.540**	**100.00**	**100.00**	

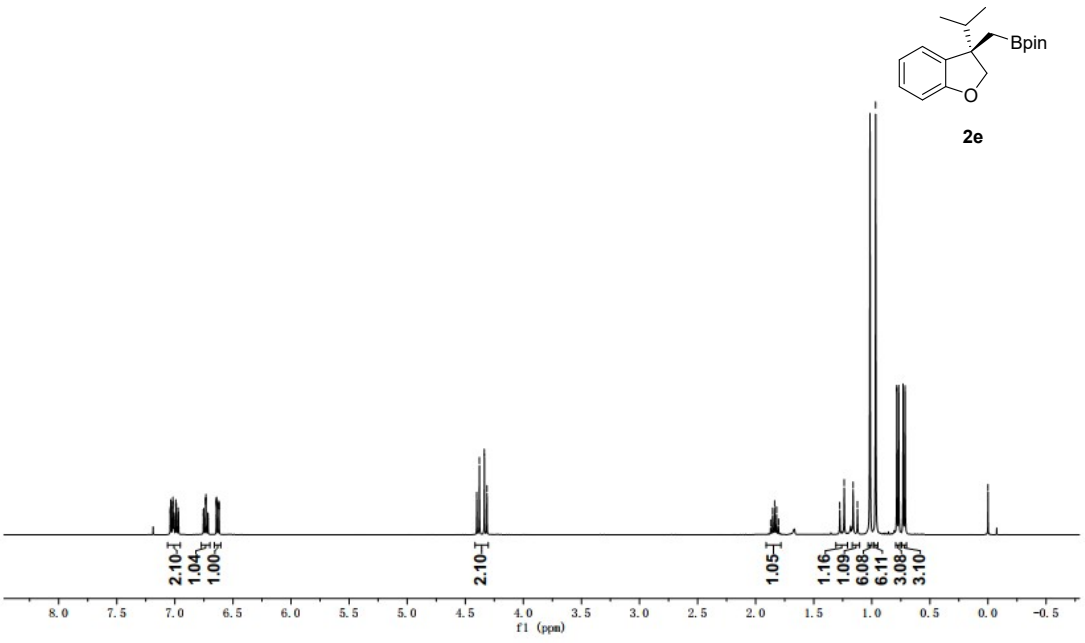
Chromatogram

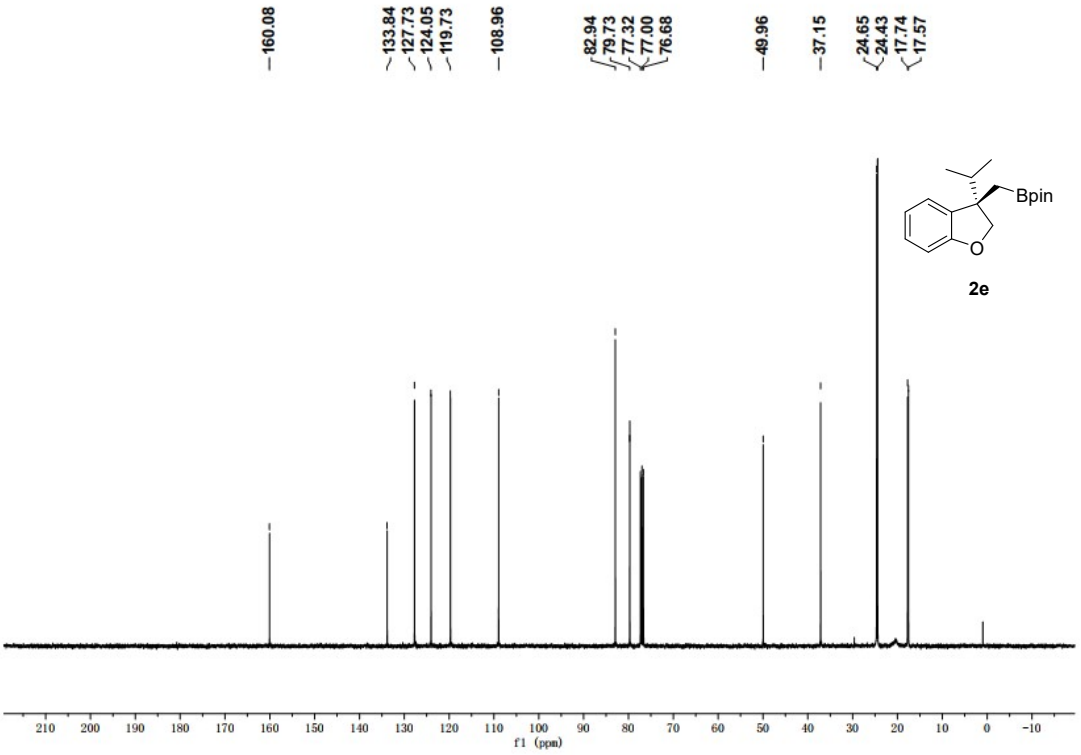


Integration Results

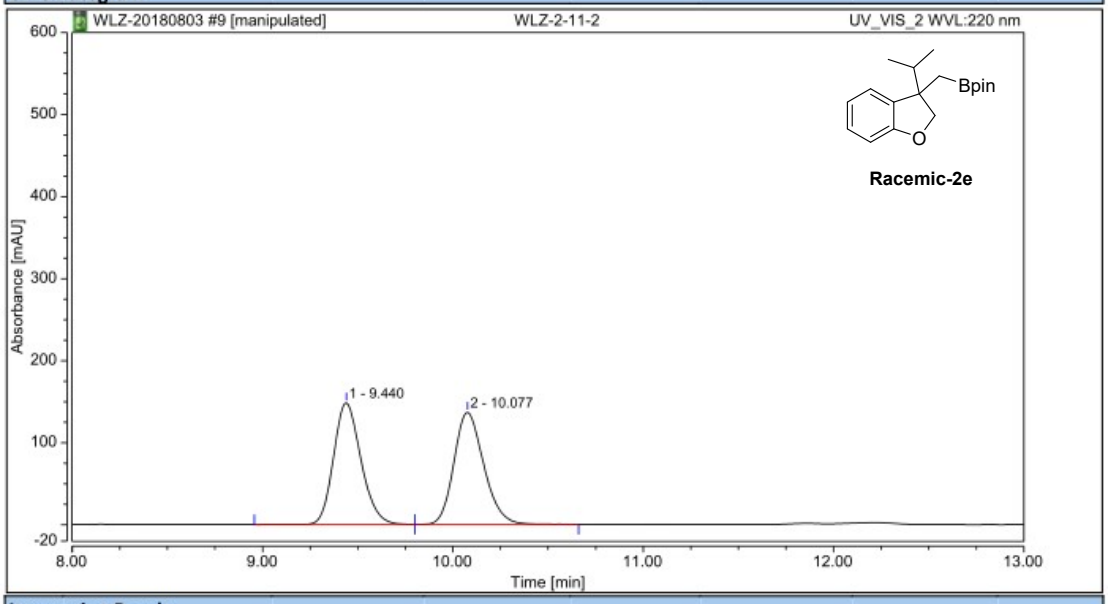
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.880	4.549	30.149	4.14	6.67	n.a.
2		12.313	105.303	421.690	95.86	93.33	n.a.
Total:			**109.852**	**451.839**	**100.00**	**100.00**	





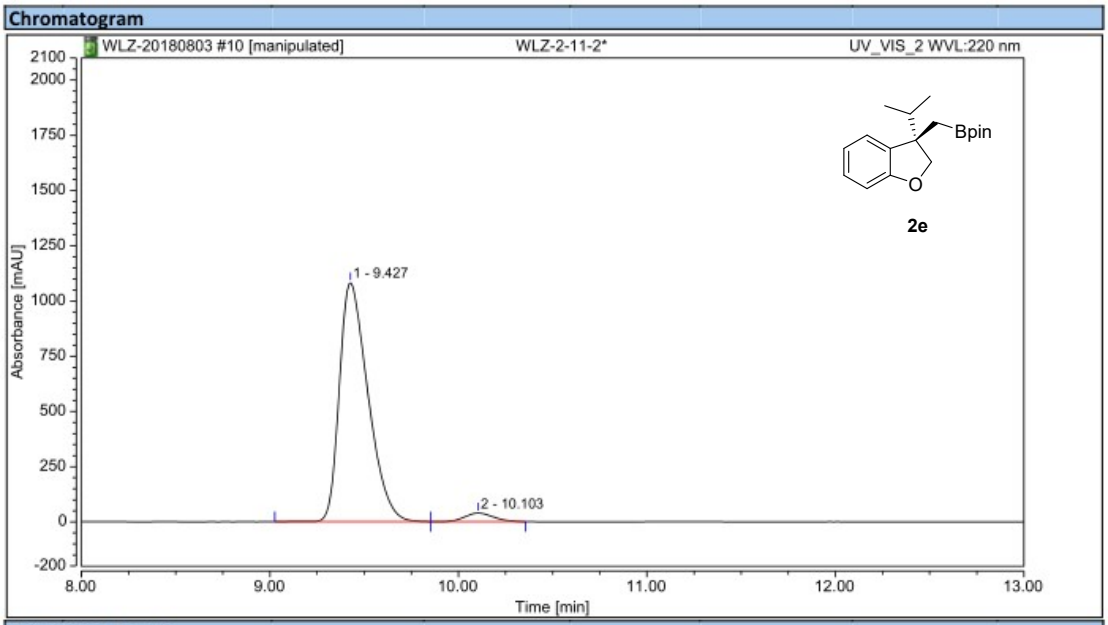


Chromatogram



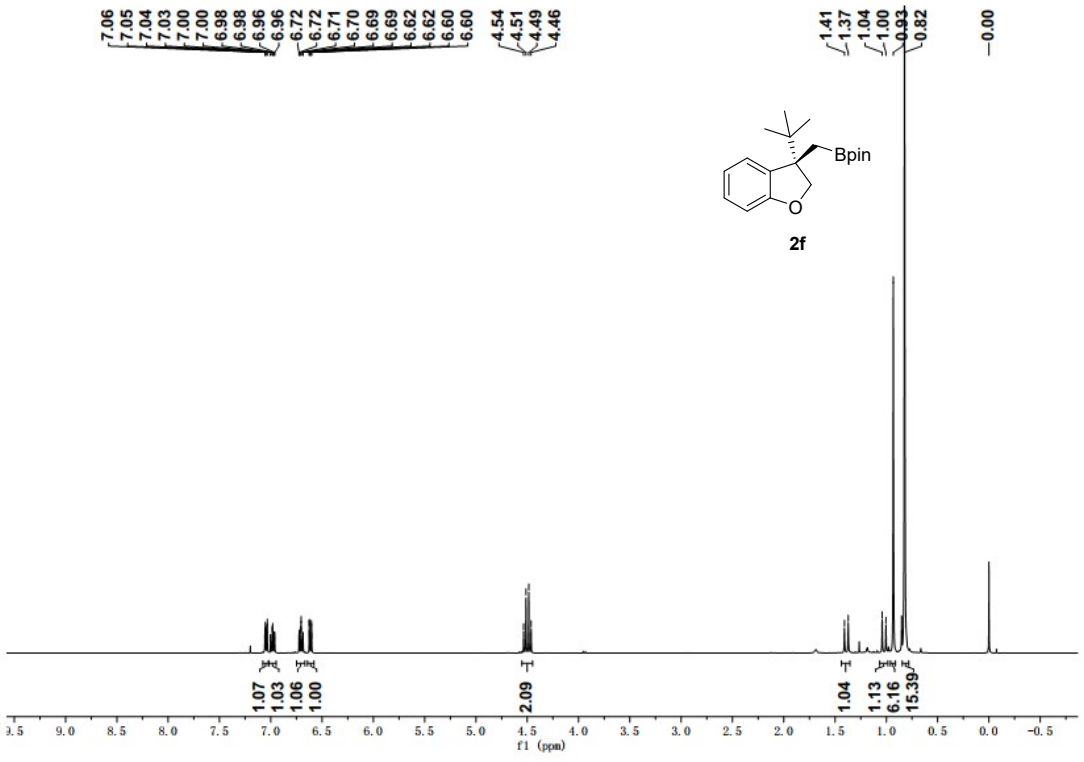
Integration Results

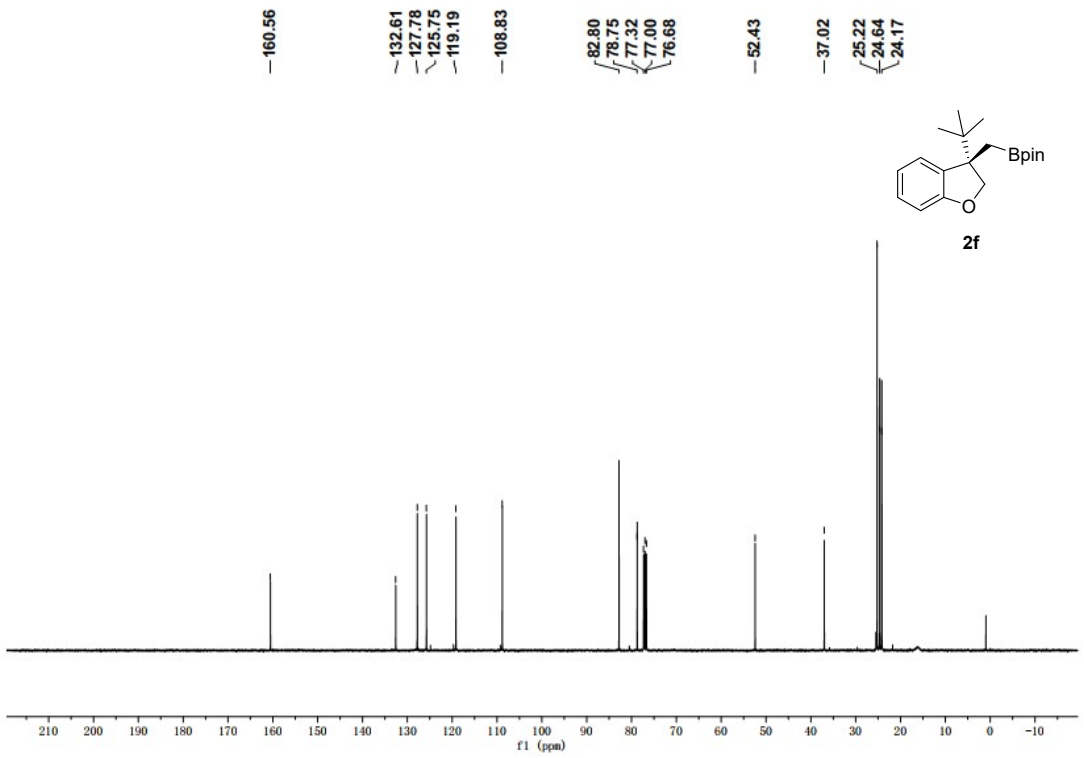
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.440	24.883	148.453	49.96	52.05	n.a.
2		10.077	24.925	136.739	50.04	47.95	n.a.
Total:			**49.808**	**285.193**	**100.00**	**100.00**	

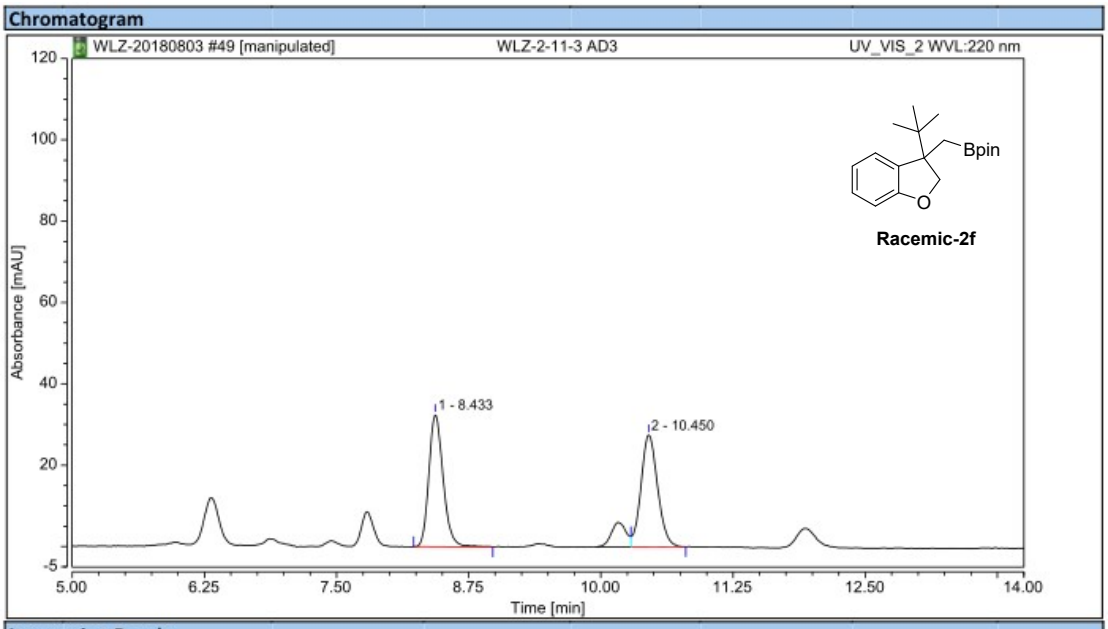


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.427	190.378	1082.549	96.50	96.56	n.a.
2		10.103	6.911	38.555	3.50	3.44	n.a.
Total:			**197.289**	**1121.104**	**100.00**	**100.00**	



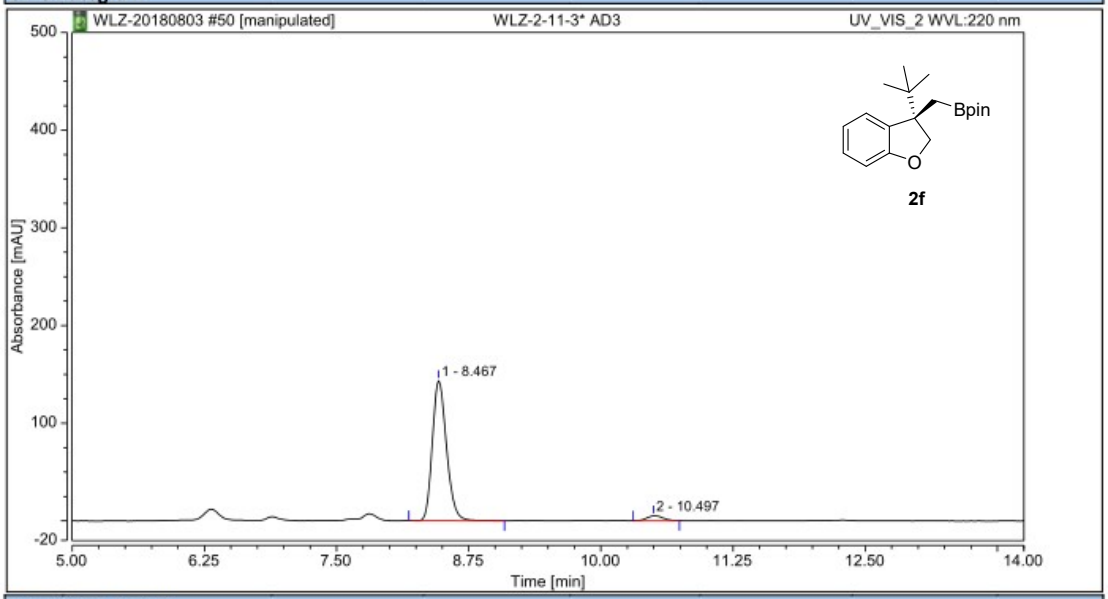




Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.433	5.064	32.535	50.17	54.12	n.a.
2		10.450	5.030	27.583	49.83	45.88	n.a.
Total:			**10.094**	**60.118**	**100.00**	**100.00**	

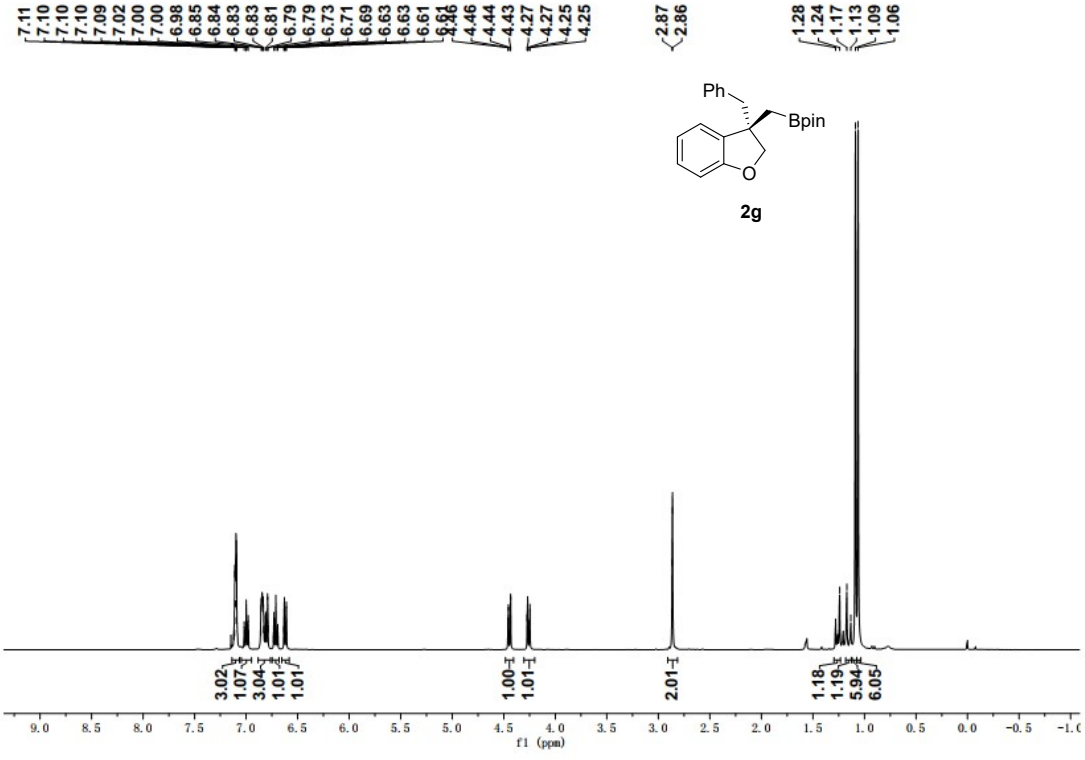
Chromatogram



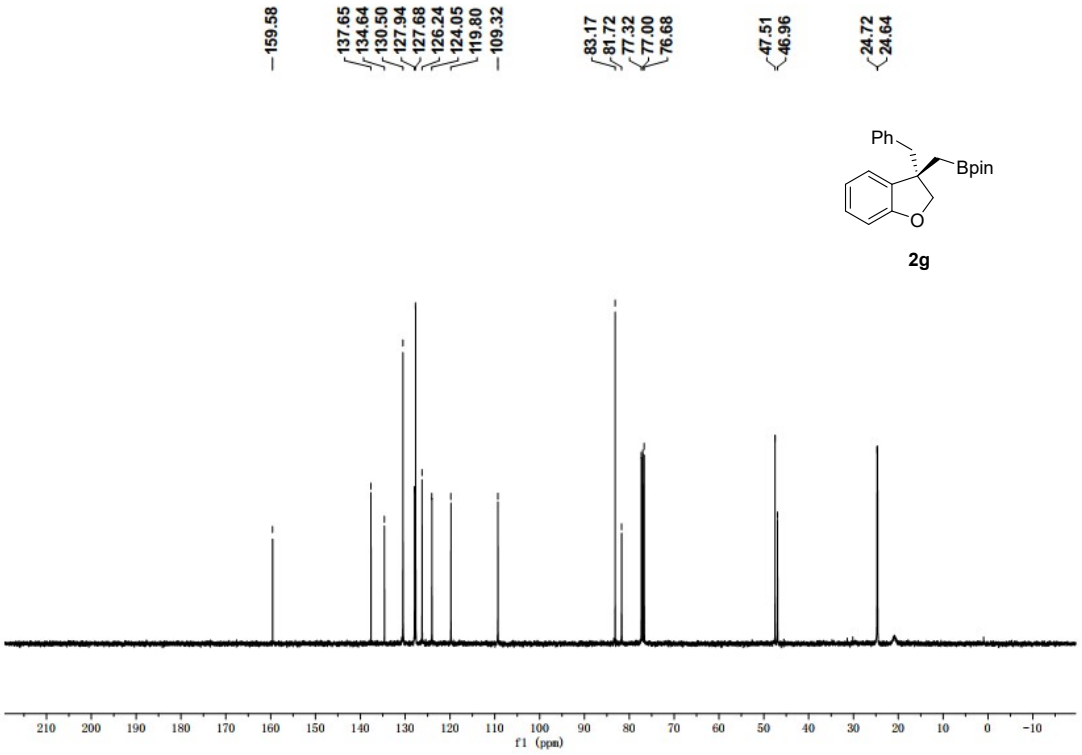
2f

Integration Results

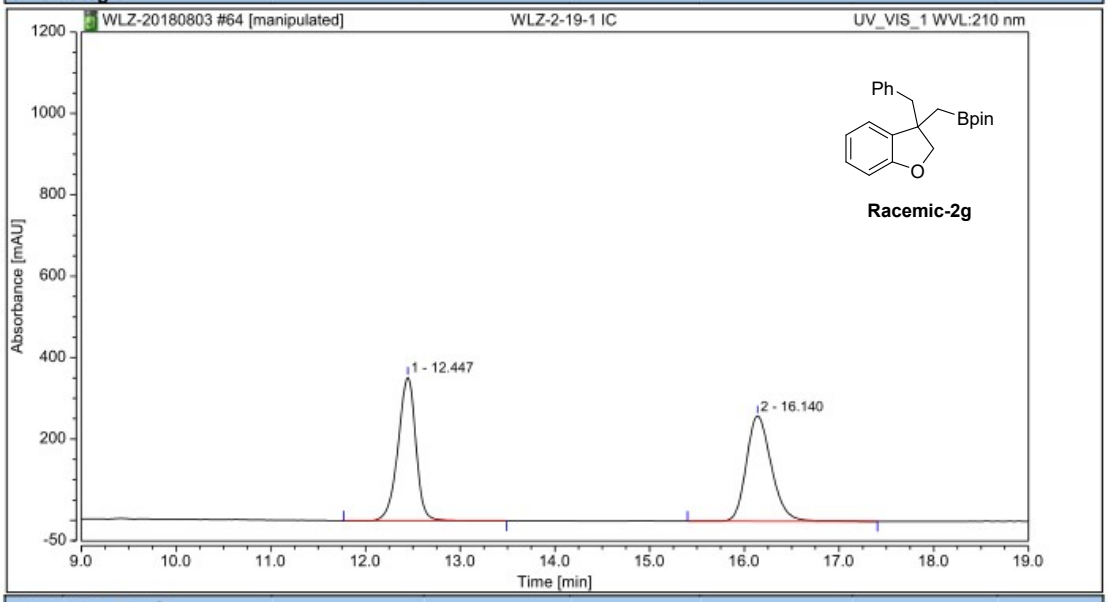
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.467	22.320	143.481	96.01	96.52	n.a.
2		10.497	0.928	5.167	3.99	3.48	n.a.
Total:			**23.248**	**148.648**	**100.00**	**100.00**	



2g



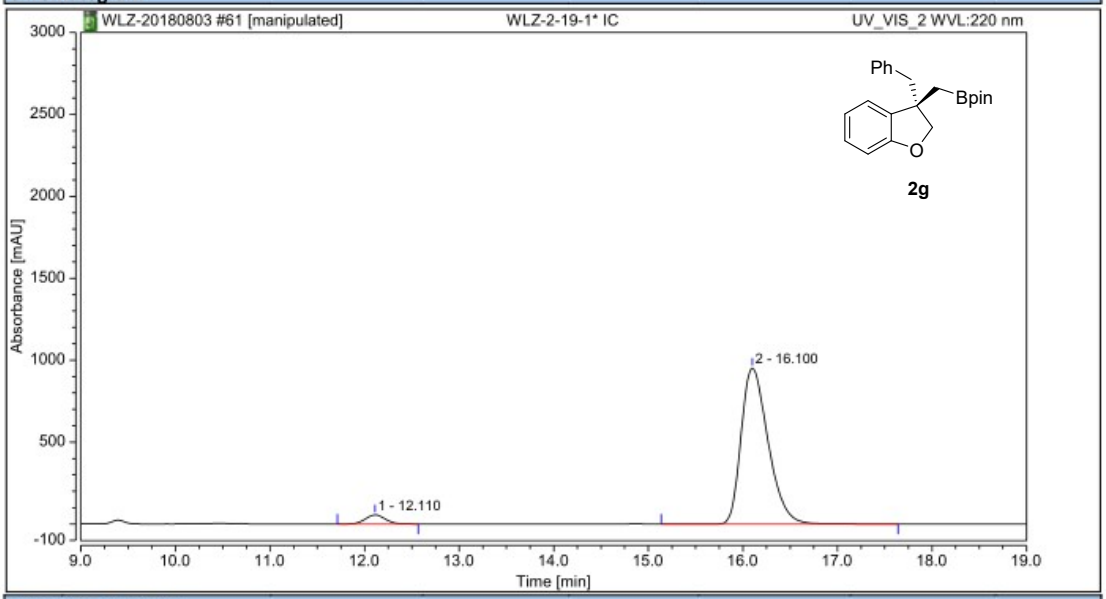
Chromatogram



Integration Results

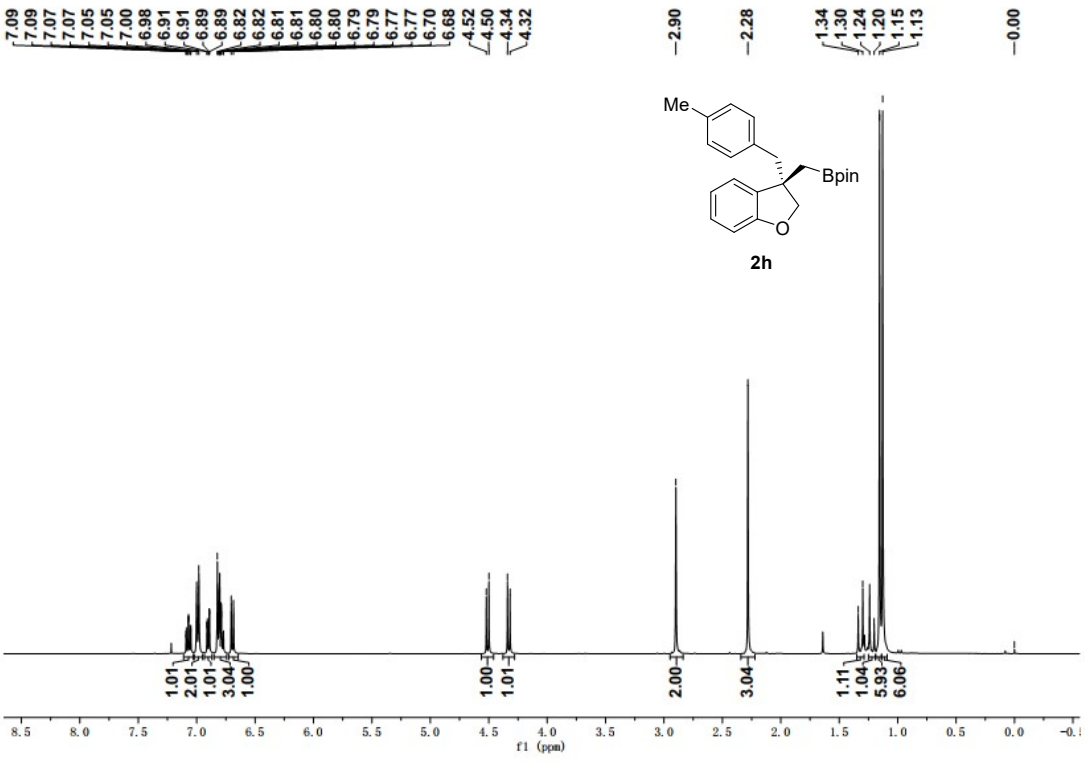
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.447	77.316	353.226	49.32	57.71	n.a.
2		16.140	79.453	258.850	50.68	42.29	n.a.
Total:			**156.768**	**612.075**	**100.00**	**100.00**	

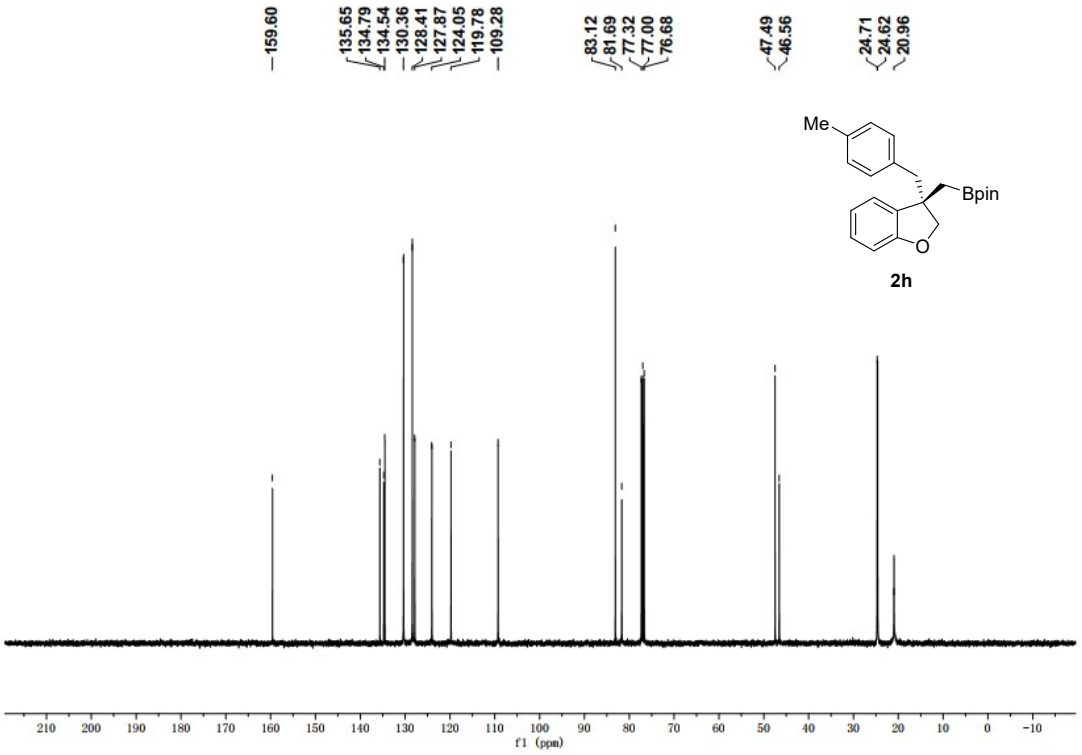
Chromatogram



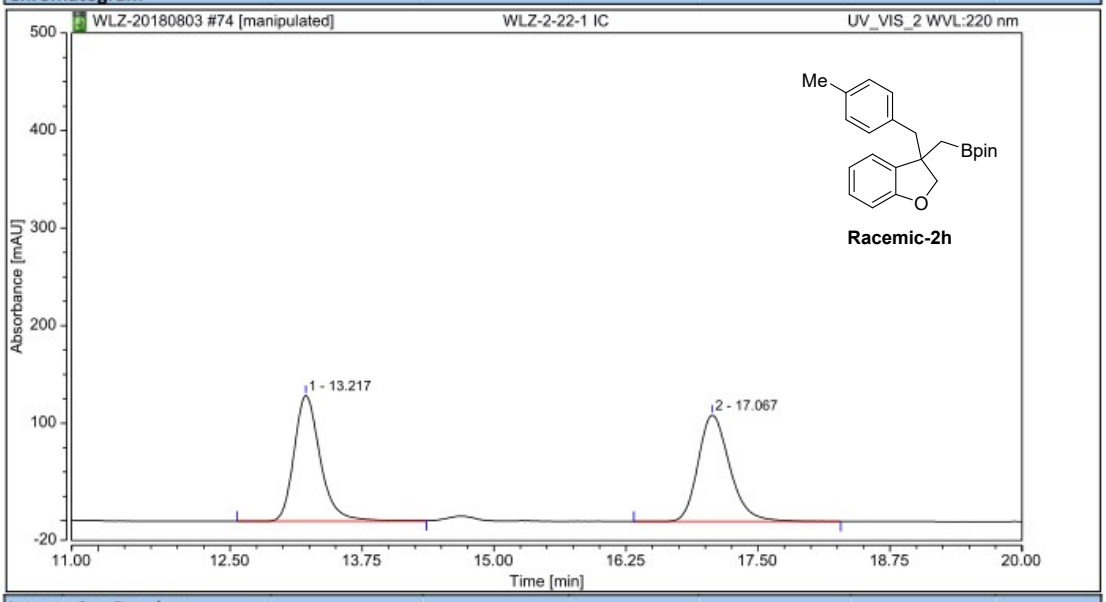
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.110	13.801	56.139	4.18	5.56	n.a.
2		16.100	316.038	952.972	95.82	94.44	n.a.
Total:			**329.839**	**1009.111**	**100.00**	**100.00**	





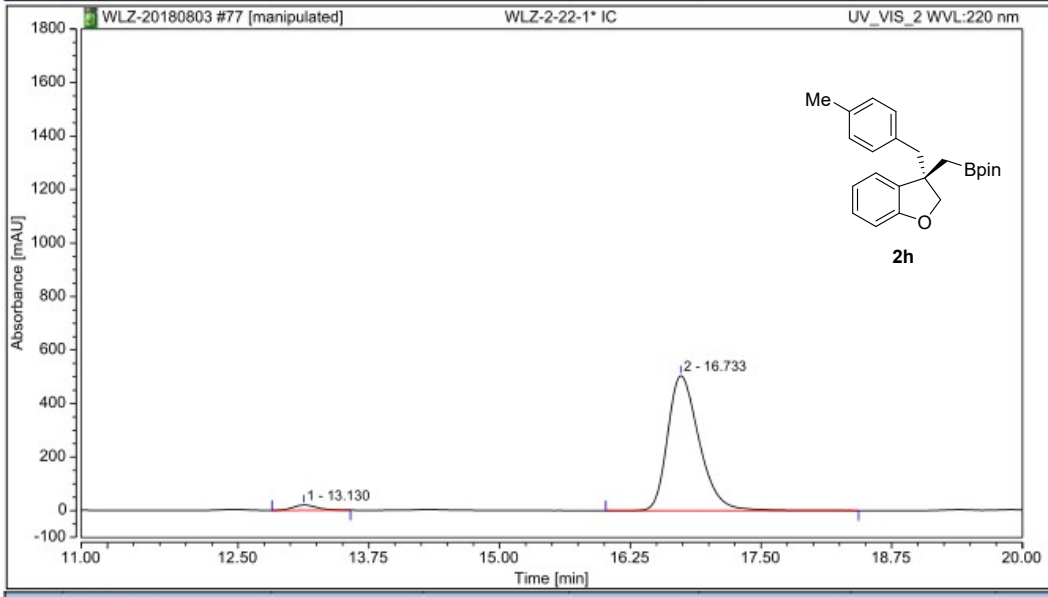
Chromatogram



Integration Results

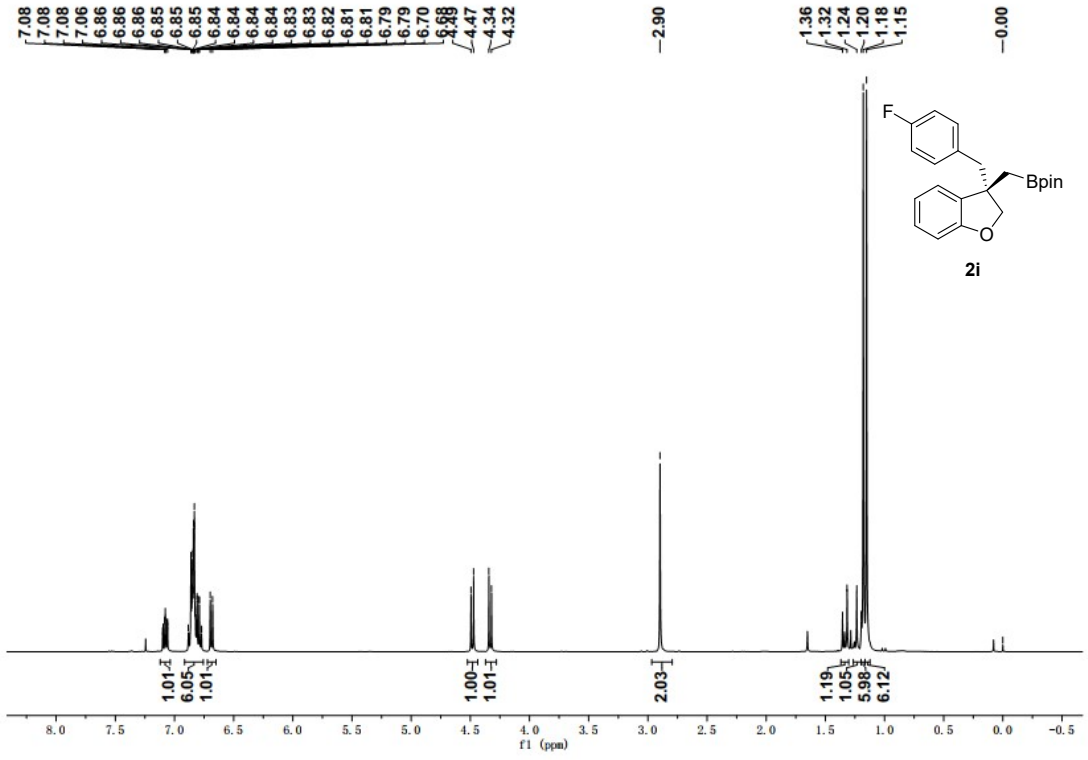
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.217	37.349	128.937	49.54	54.19	n.a.
2		17.067	38.036	108.979	50.46	45.81	n.a.
Total:			**75.386**	**237.916**	**100.00**	**100.00**	

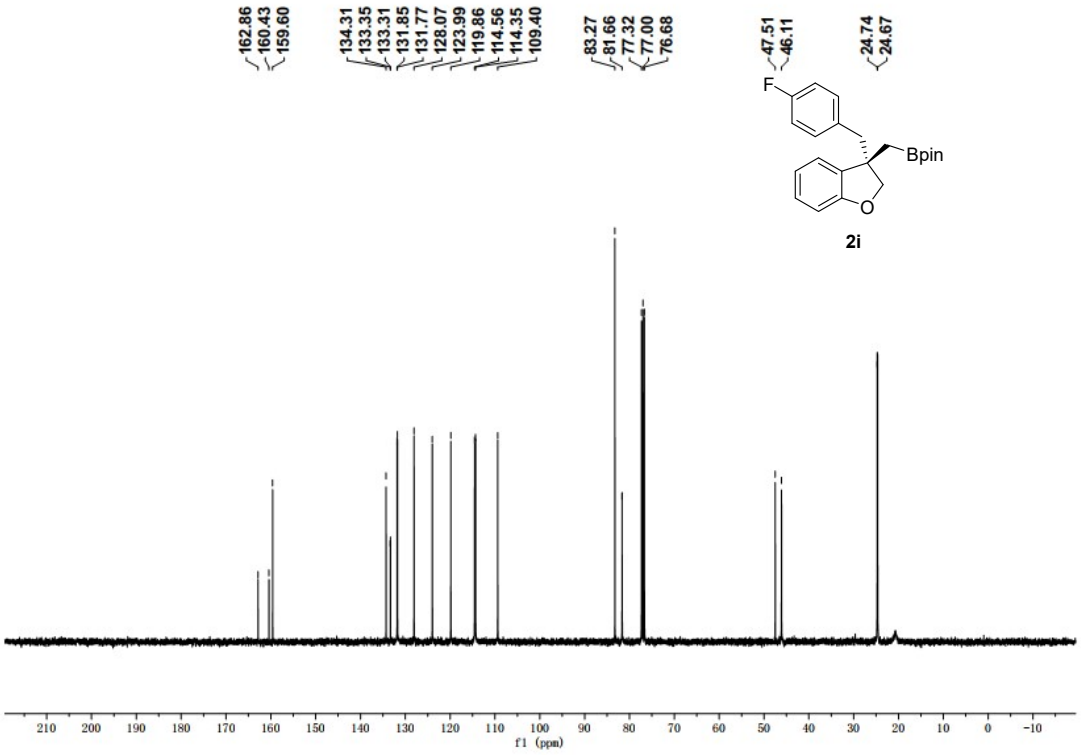
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.130	5.316	19.704	2.92	3.76	n.a.
2		16.733	176.673	504.250	97.08	96.24	n.a.
Total:			**181.989**	**523.954**	**100.00**	**100.00**	

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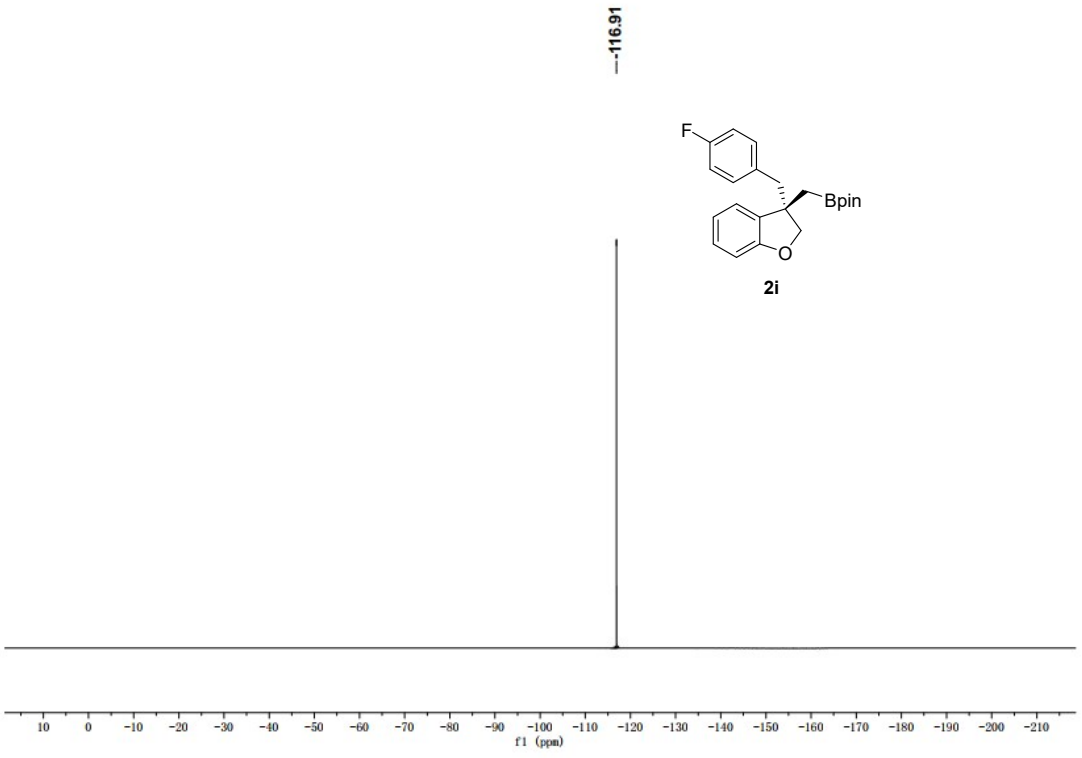
123.99
119.86
114.56
114.35
109.40
83.27
81.66
77.32
77.00
76.68
47.51
46.11
24.74
24.67
F
Bpin
O
2i
f1 (ppm)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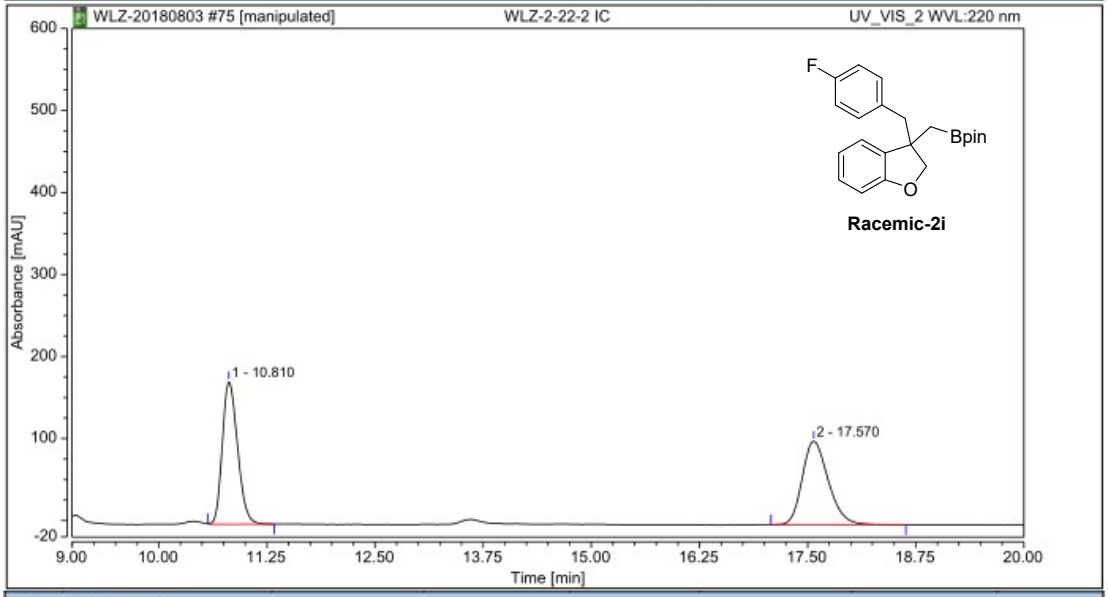
F
Bpin
O
2i
f1 (ppm)

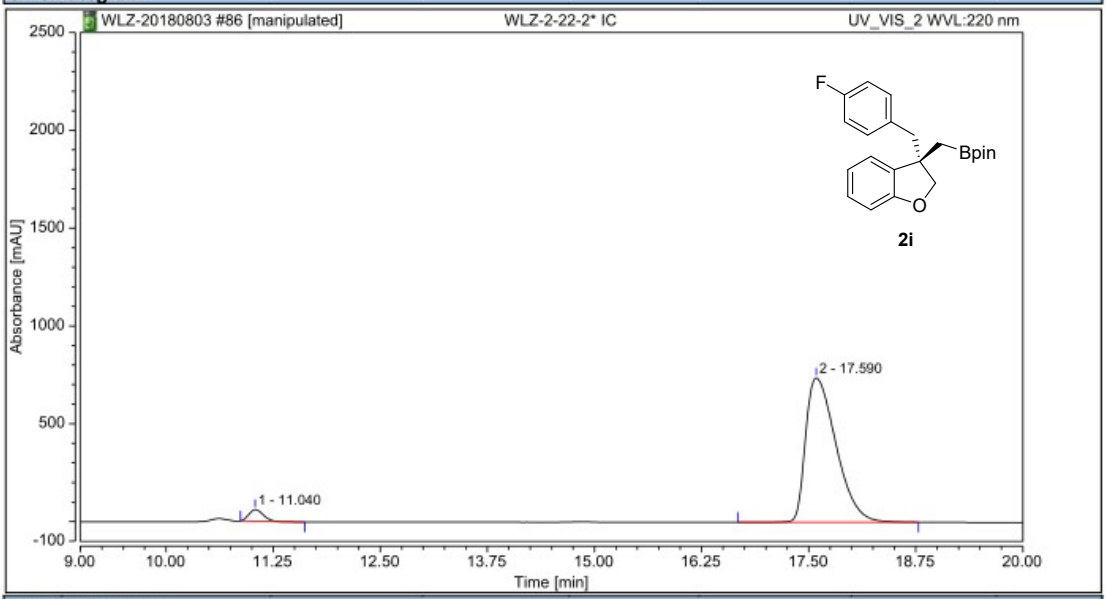
Chromatogram



Integration Results

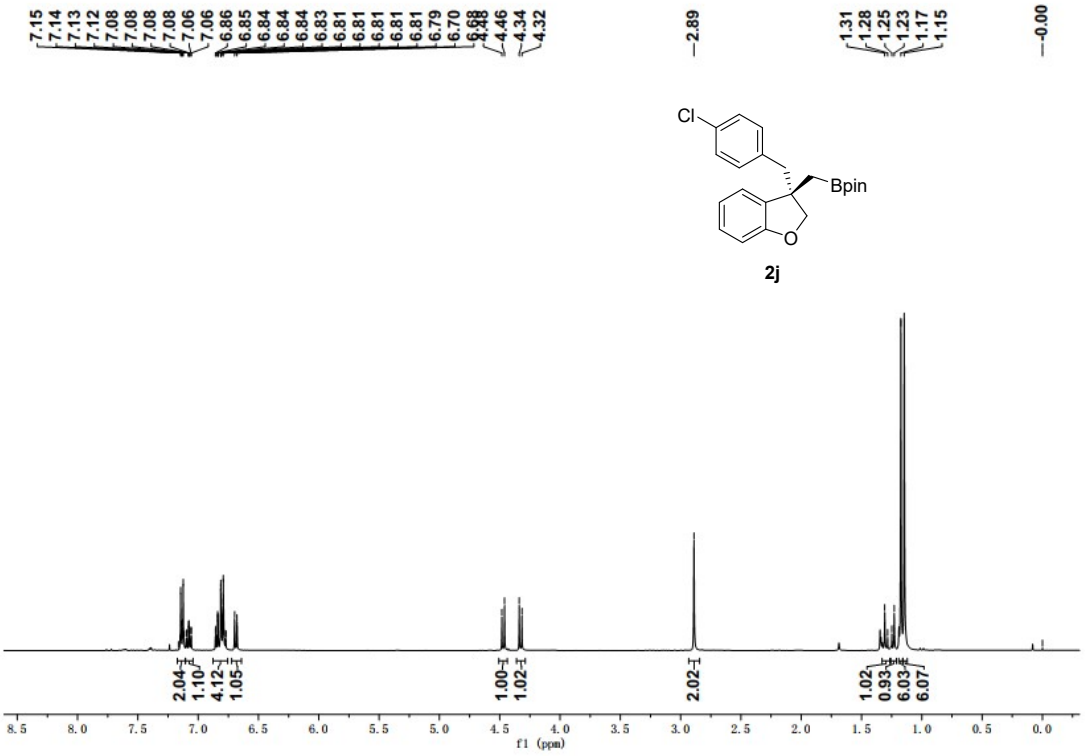
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.810	35.587	173.878	49.83	63.07	n.a.
2		17.570	35.834	101.804	50.17	36.93	n.a.
Total:			**71.421**	**275.683**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.040	11.124	58.471	3.52	7.34	n.a.
2		17.590	304.467	738.325	96.48	92.66	n.a.
Total:			**315.591**	**796.795**	**100.00**	**100.00**	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6.81
6.79
6.70
4.46
4.34
4.32
2.89
1.31
1.28
1.25
1.23
1.17
1.15
0.00
Cl
Bpin
O
2j
2.04
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1.05
1.00
1.02
2.02
1.02
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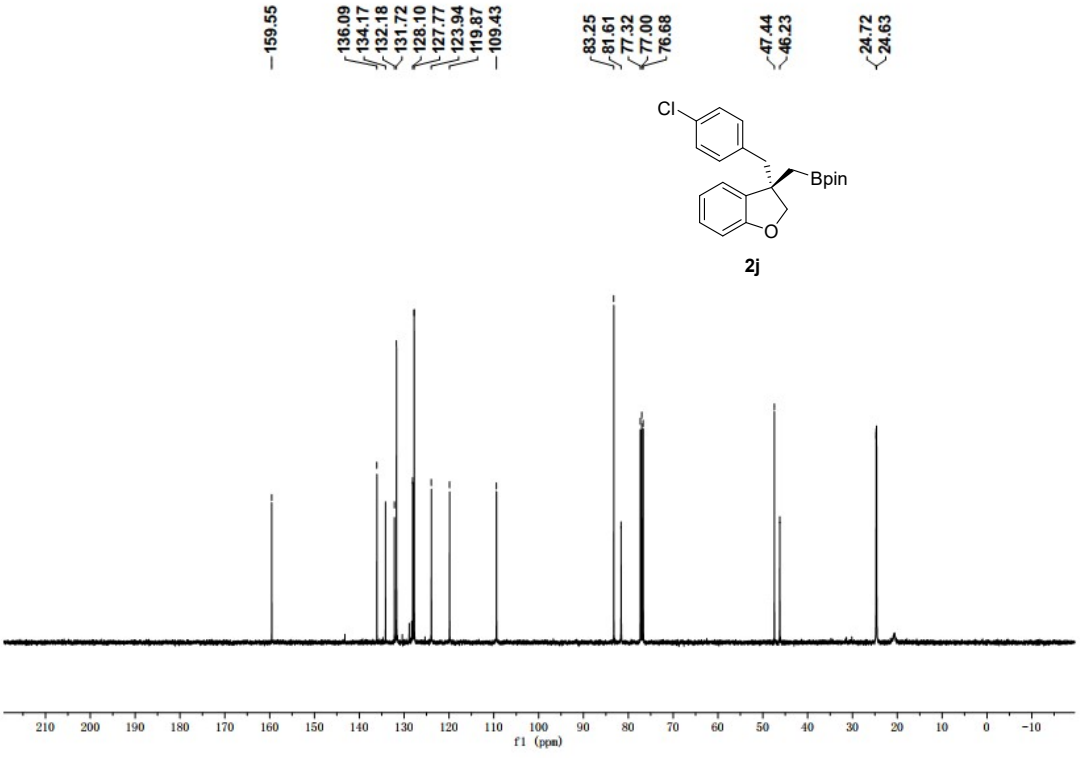
6.07
f1 (ppm)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81.61
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77.00
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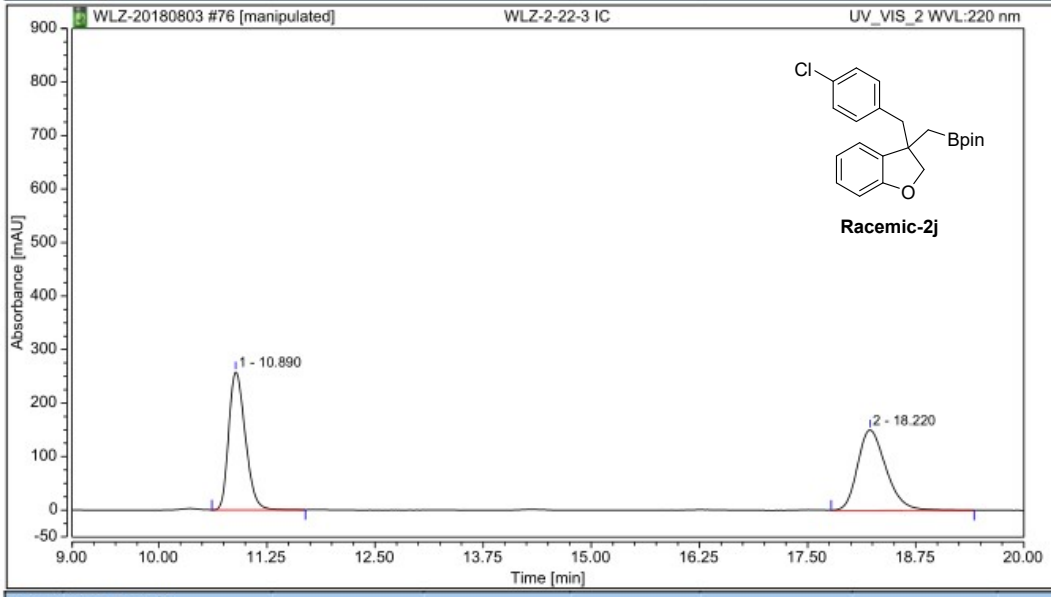
47.44
46.23
24.72
24.63
Cl
Bpin
O
2j
f1 (ppm)

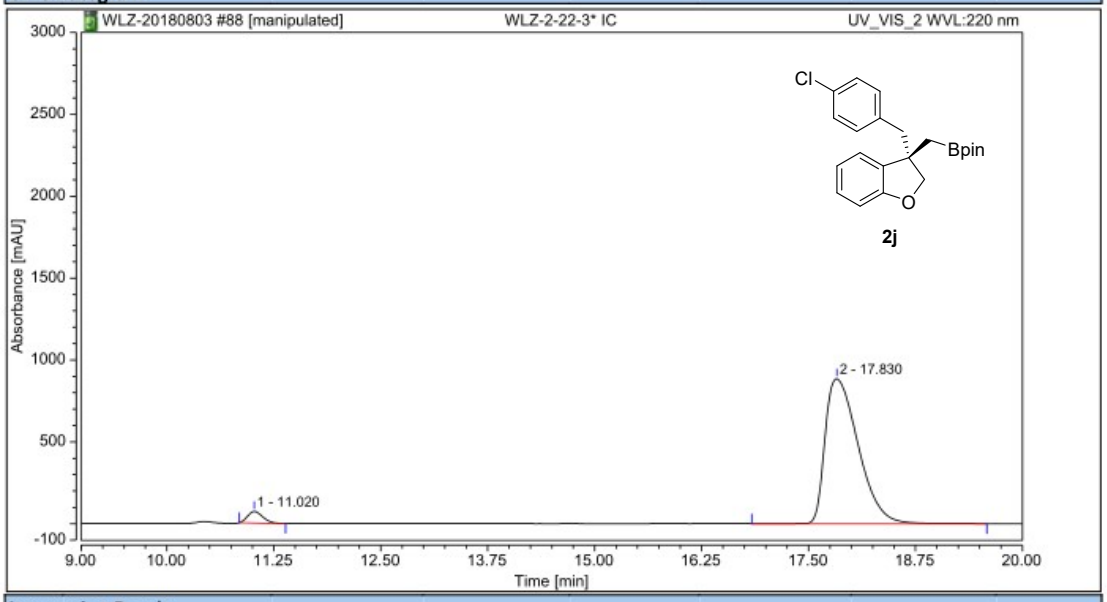
Chromatogram



Integration Results

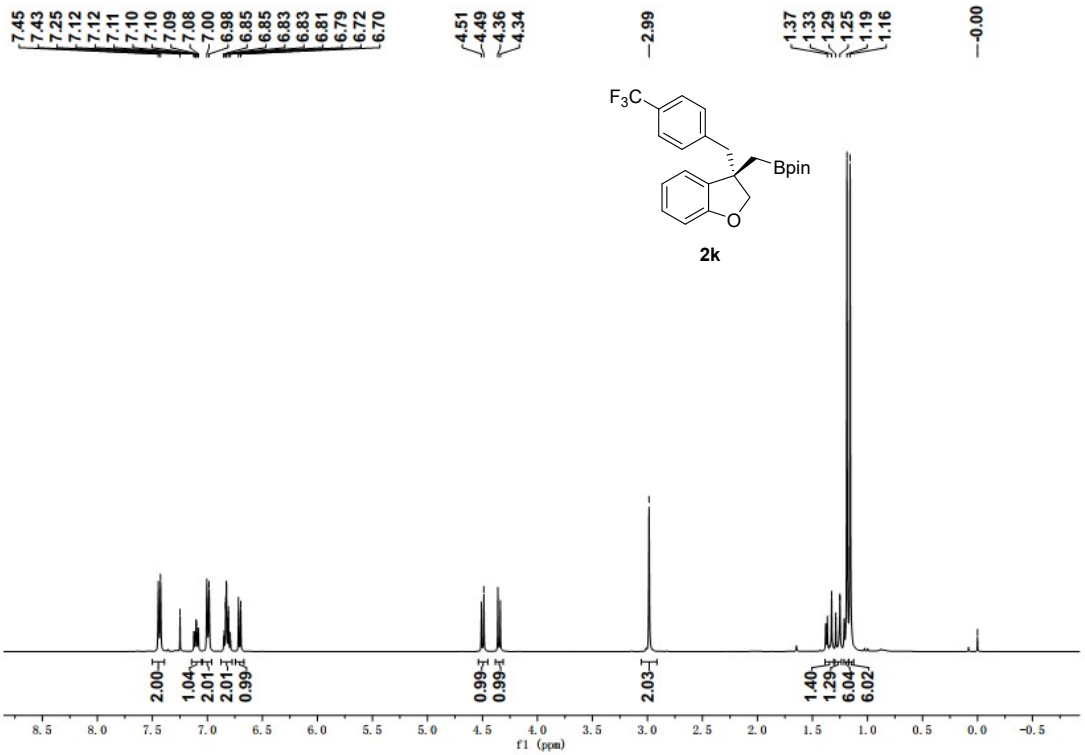
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.890	57.501	258.380	50.05	63.24	n.a.
2		18.220	57.379	150.217	49.95	36.76	n.a.
Total:			**114.880**	**408.598**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.020	14.407	70.398	3.50	7.37	n.a.
2		17.830	397.459	885.091	96.50	92.63	n.a.
Total:			**411.866**	**955.489**	**100.00**	**100.00**	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7.10
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7.08
7.00
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6.85
6.83
6.83
6.81
6.79
6.72
6.70
4.51
4.49
4.36
4.34
2.99
1.37
1.33
1.29
1.25
1.19
1.16
0.00
F3C
Bpin
O
2k
2.00
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0.99
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1.29
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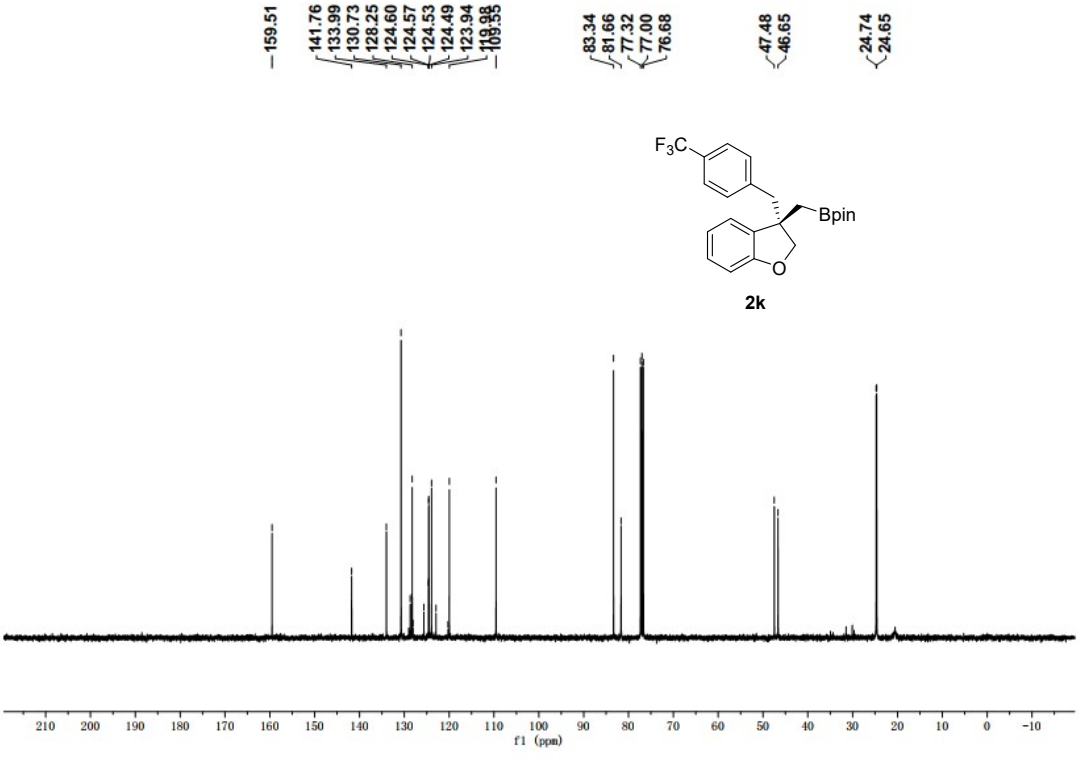
6.02
f1 (ppm)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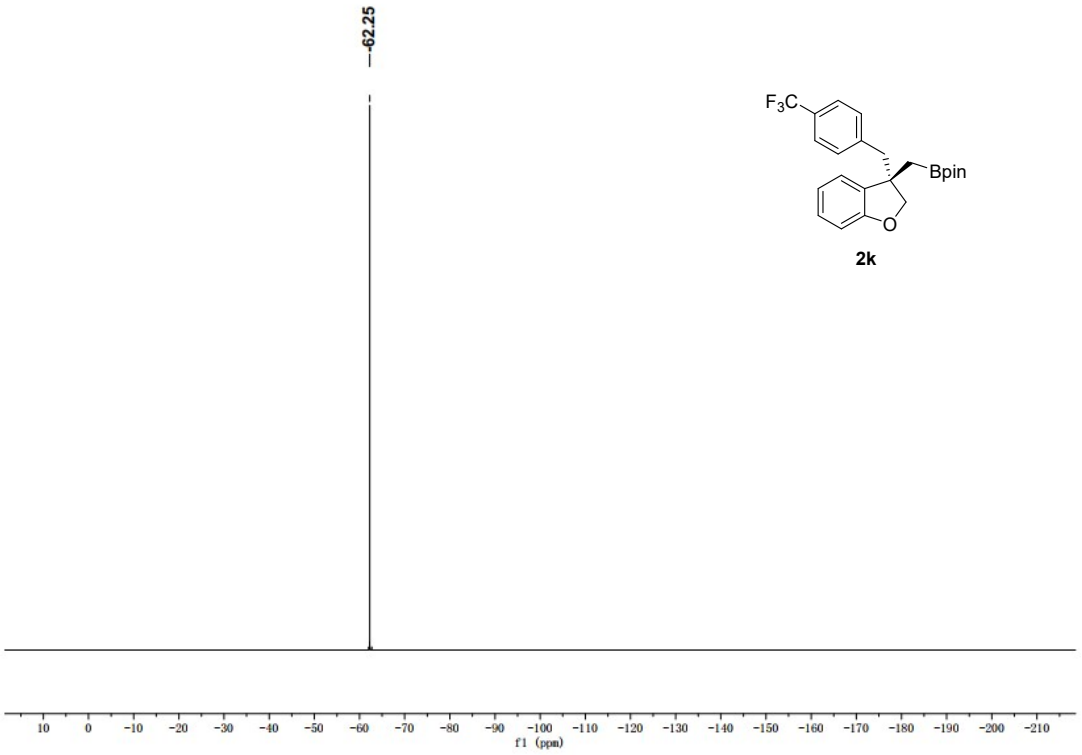
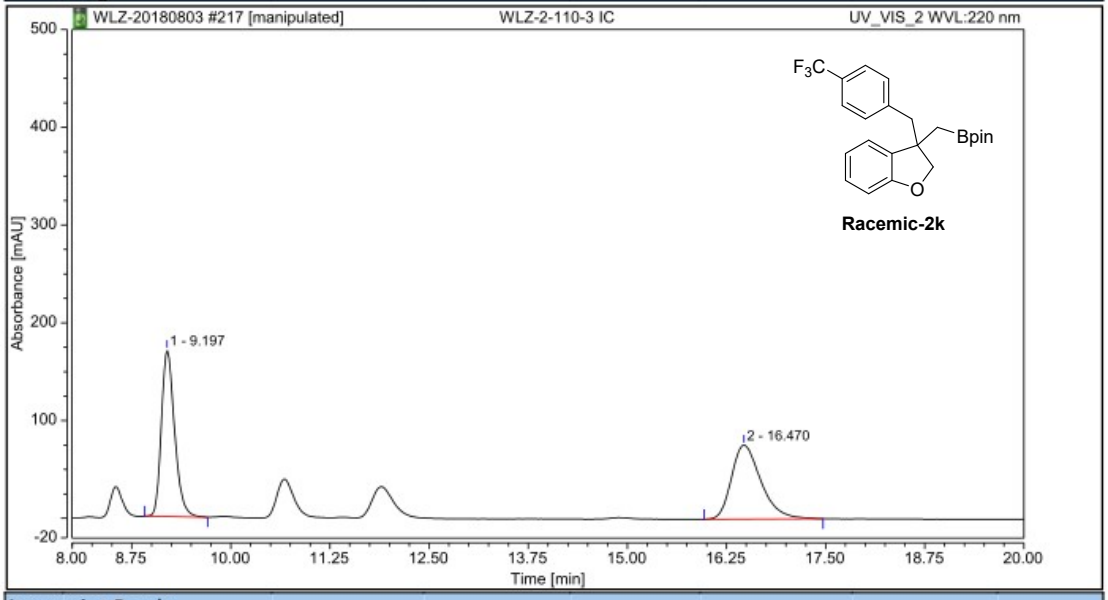
76.68
47.48
46.65
24.74
24.65
F3C
Bpin
O
2k
f1 (ppm)



2k

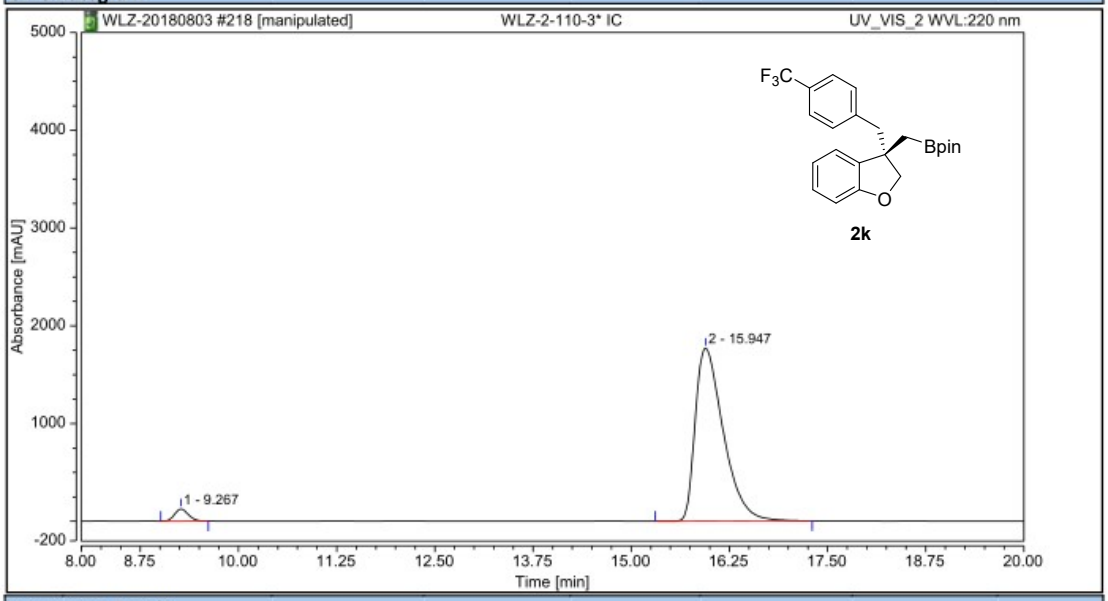
Chromatogram



Integration Results

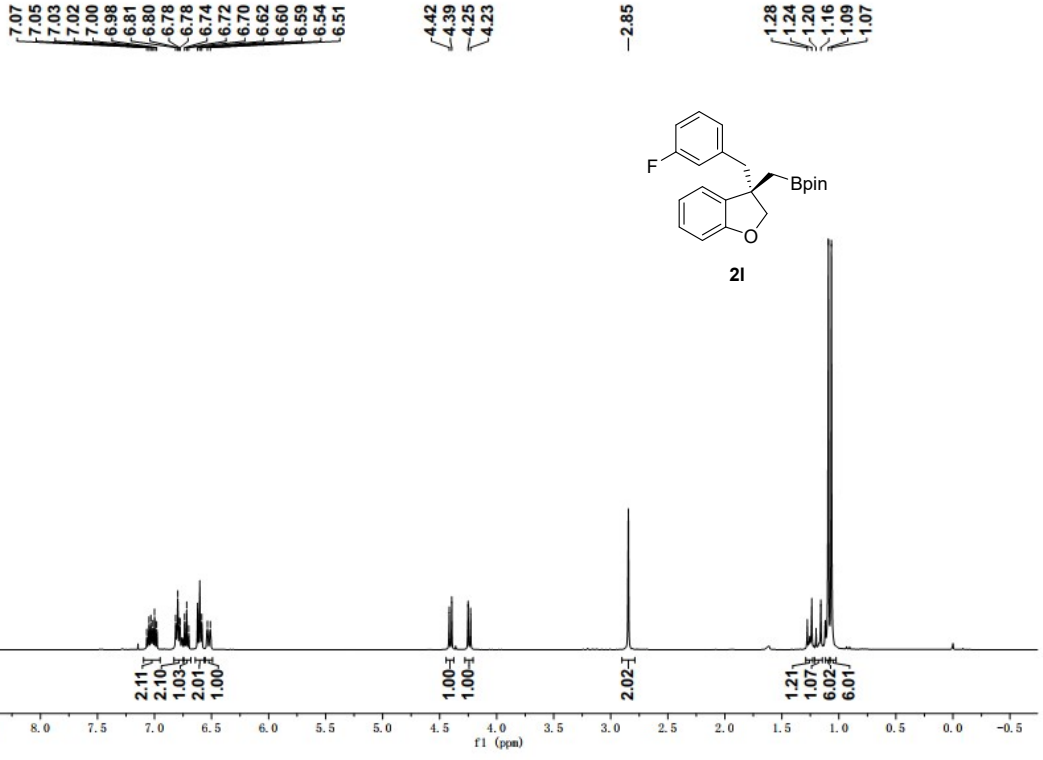
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.197	32.857	170.105	50.24	69.22	n.a.
2		16.470	32.547	75.637	49.76	30.78	n.a.
Total:			**65.404**	**245.742**	**100.00**	**100.00**	

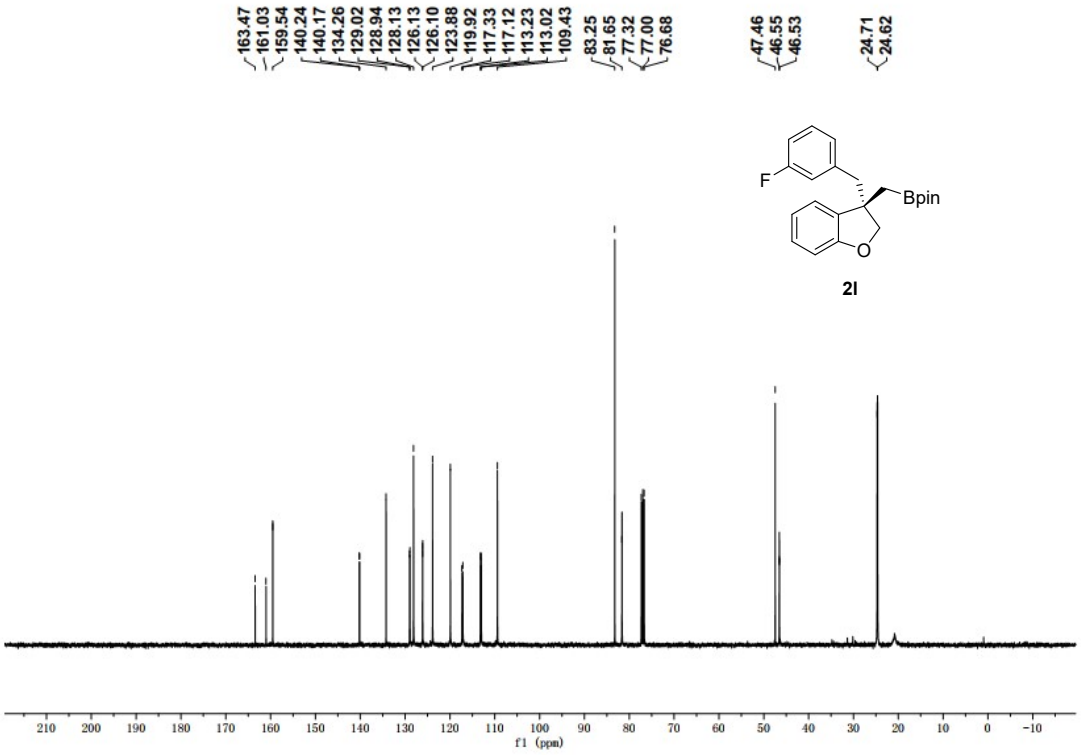
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.267	25.500	124.434	3.35	6.57	n.a.
2		15.947	735.375	1769.338	96.65	93.43	n.a.
Total:			**760.876**	**1893.772**	**100.00**	**100.00**	

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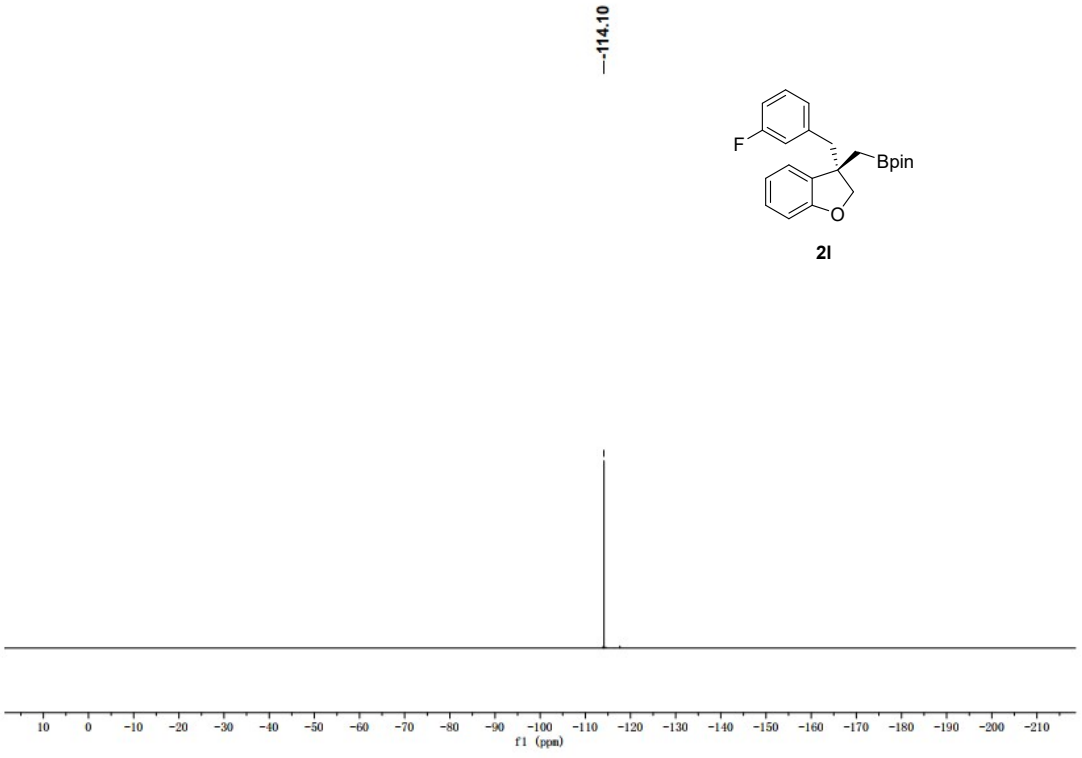
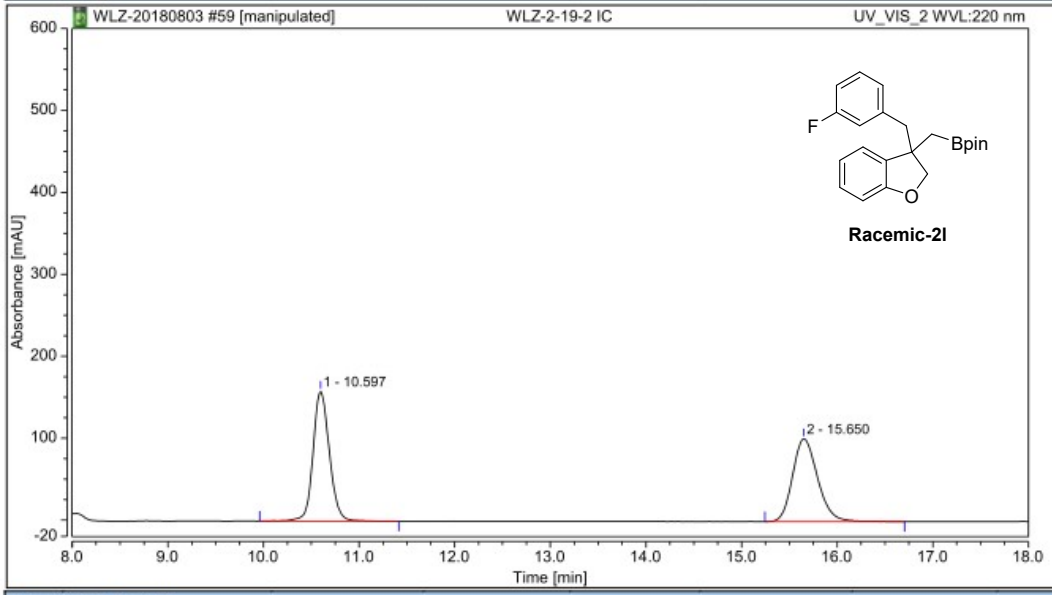
119.92
117.33
117.12
113.23
113.02
109.43
83.25
81.65
77.32
77.00
76.68
47.46
46.55
46.53
24.71
24.62
F
Bpin
O
f1 (ppm)

2l


-114.10
F
Bpin
O
f1 (ppm)

2l

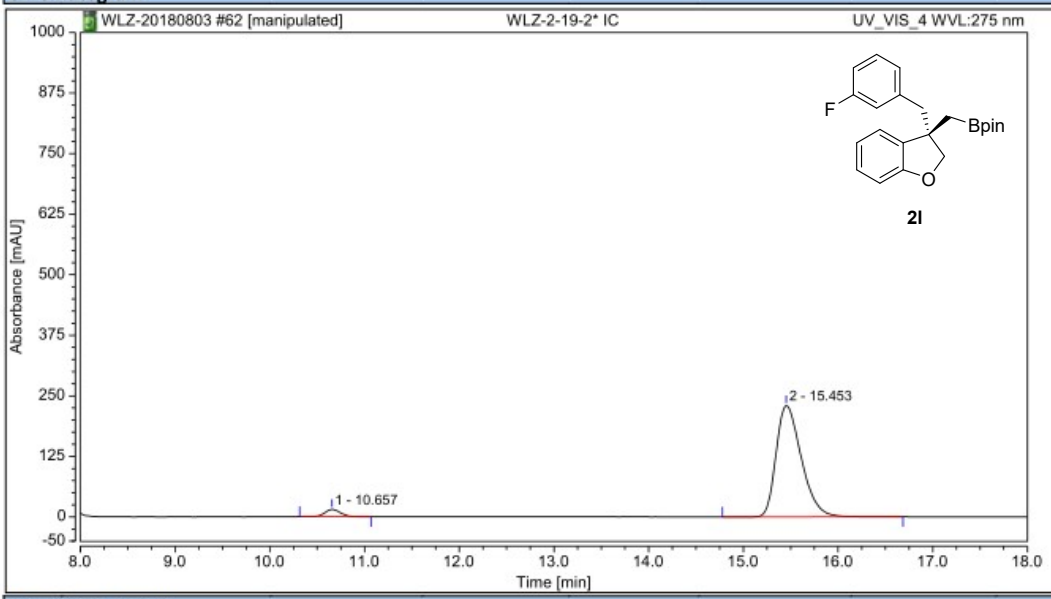
Chromatogram



Integration Results

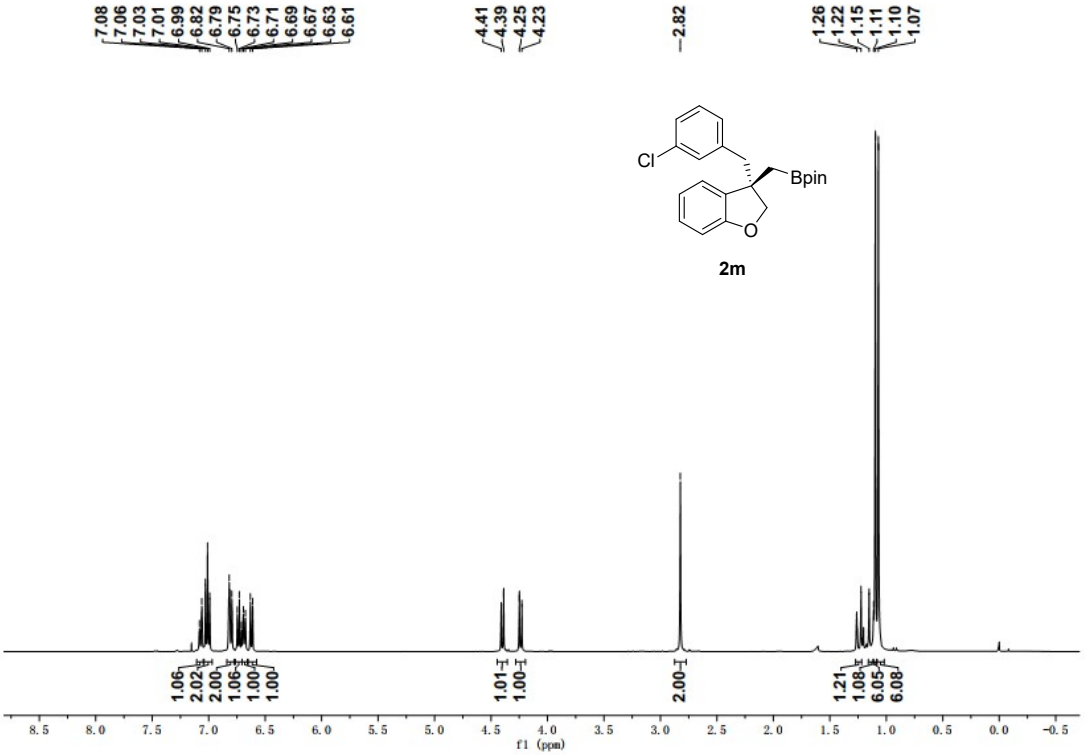
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.597	31.581	158.566	50.59	61.00	n.a.
2		15.650	30.847	101.377	49.41	39.00	n.a.
Total:			**62.428**	**259.943**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.657	2.891	14.905	3.90	6.09	n.a.
2		15.453	71.218	229.963	96.10	93.91	n.a.
Total:			**74.109**	**244.868**	**100.00**	**100.00**	


7.08
7.06
7.03
7.01
6.99
6.82
6.79
6.75
6.73
6.71
6.69
6.67
6.63
6.61
4.41
4.39
4.25
4.23
2.82
1.26
1.22
1.15
1.11
1.10
1.07
Cl
Bpin
O
2m
1.06
2.02
2.00
1.06
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1.01
1.00
2.00
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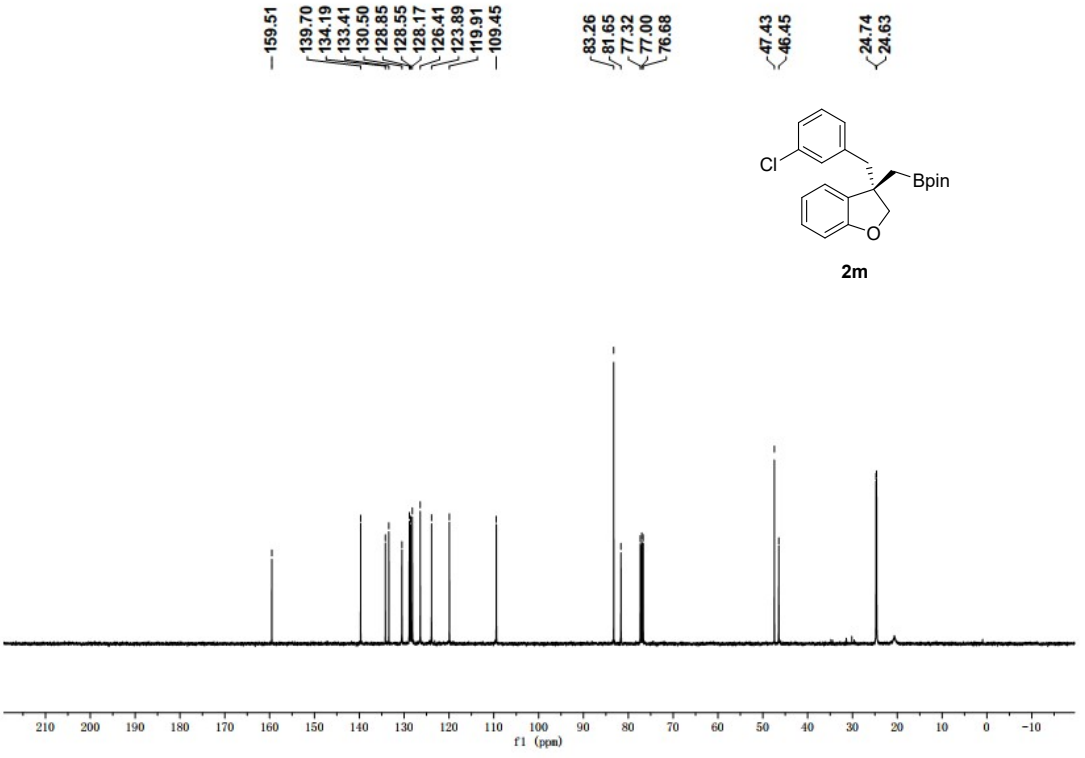
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81.65
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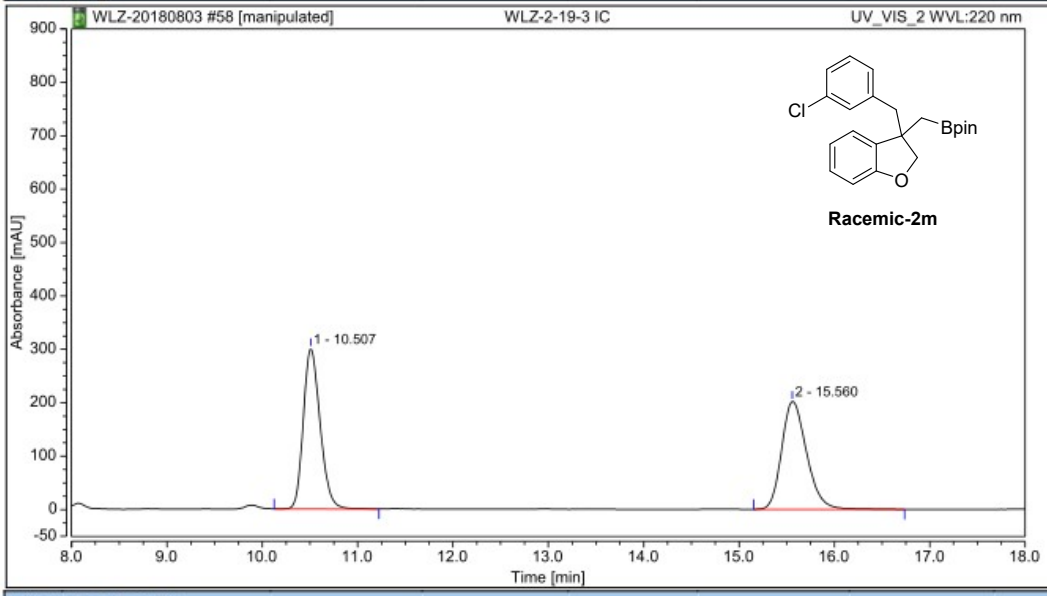
24.74
24.63
Cl
Bpin
O
2m
f1 (ppm)

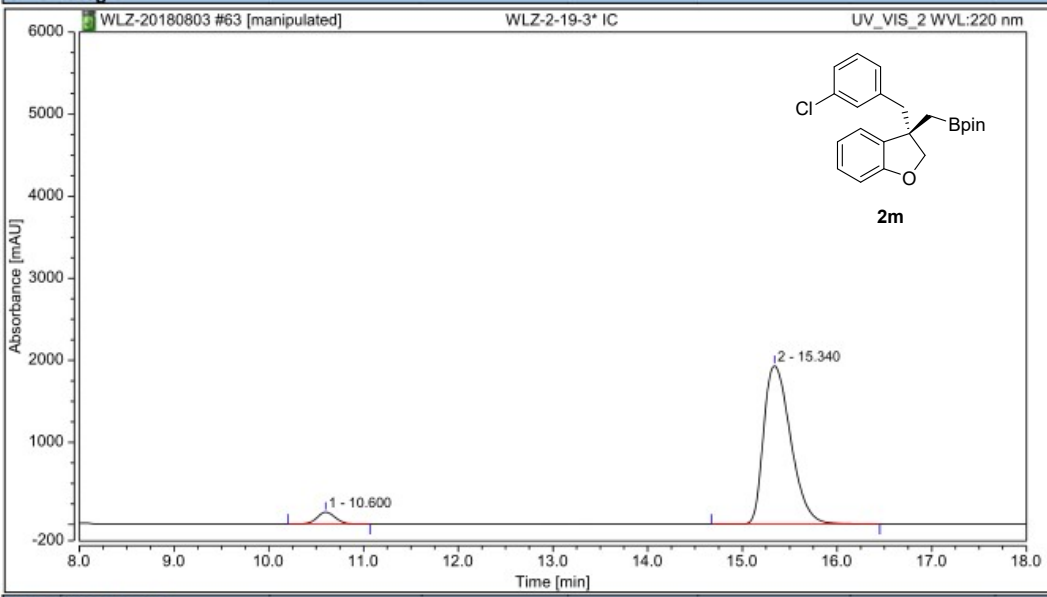
Chromatogram



Integration Results

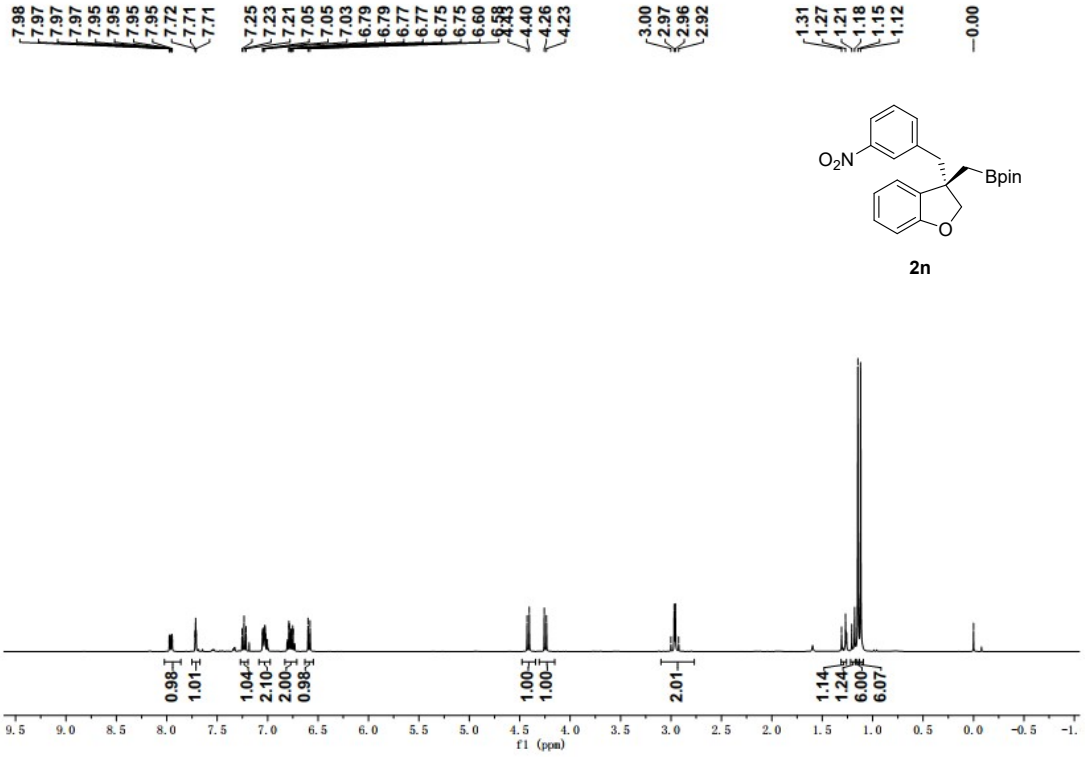
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.507	61.621	300.274	50.00	59.73	n.a.
2		15.560	61.625	202.444	50.00	40.27	n.a.
Total:			**123.245**	**502.718**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.600	33.649	146.344	4.99	7.04	n.a.
2		15.340	640.787	1931.901	95.01	92.96	n.a.
Total:			**674.436**	**2078.244**	**100.00**	**100.00**	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7.23
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7.05
7.05
7.03
6.79
6.79
6.77
6.77
6.75
6.75
6.60
6.58
4.43
4.40
4.26
4.23
3.00
2.97
2.96
2.92
1.31
1.27
1.21
1.18
1.15
1.12
0.00
O2N
Bpin
O
2n
0.98
1.01
1.04
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1.00
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1.24
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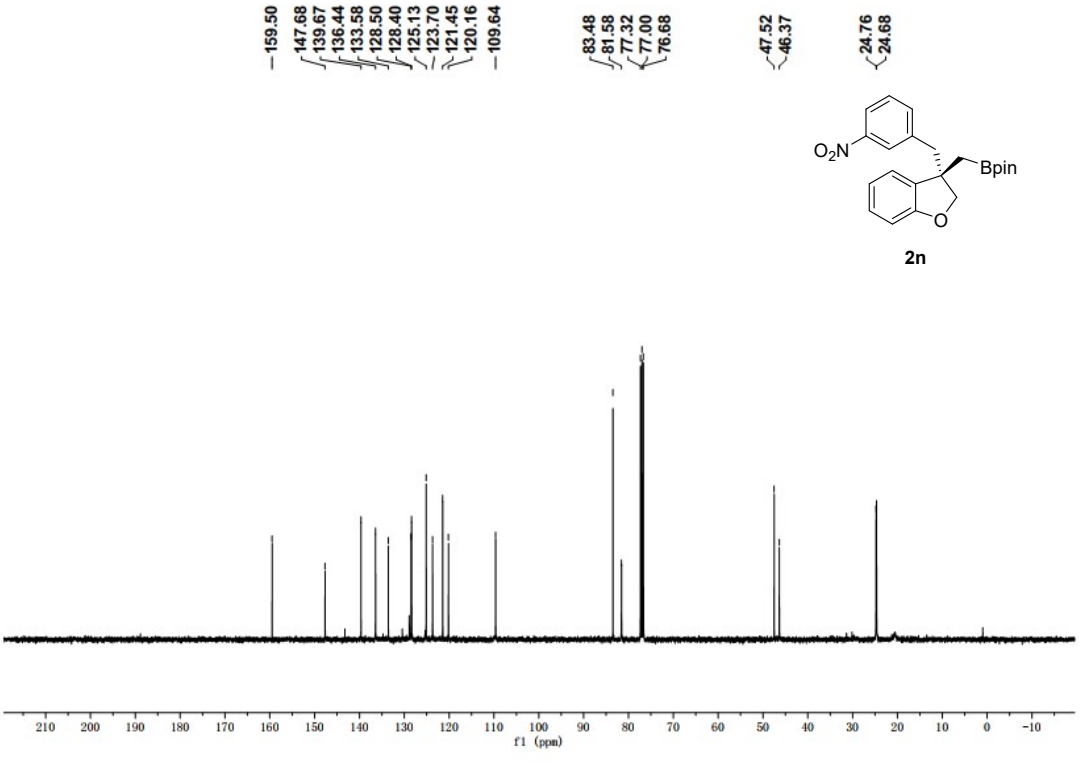
6.07
f1 (ppm)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125.13
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121.45
120.16
109.64
83.48
81.58
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77.00
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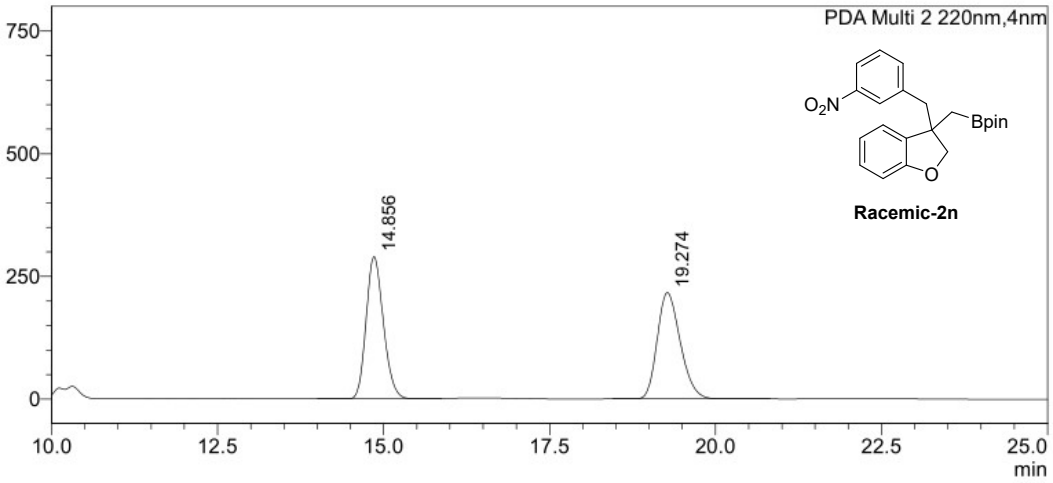
46.37
24.76
24.68
O2N
Bpin
O
2n
f1 (ppm)

<Chromatogram>

mAU



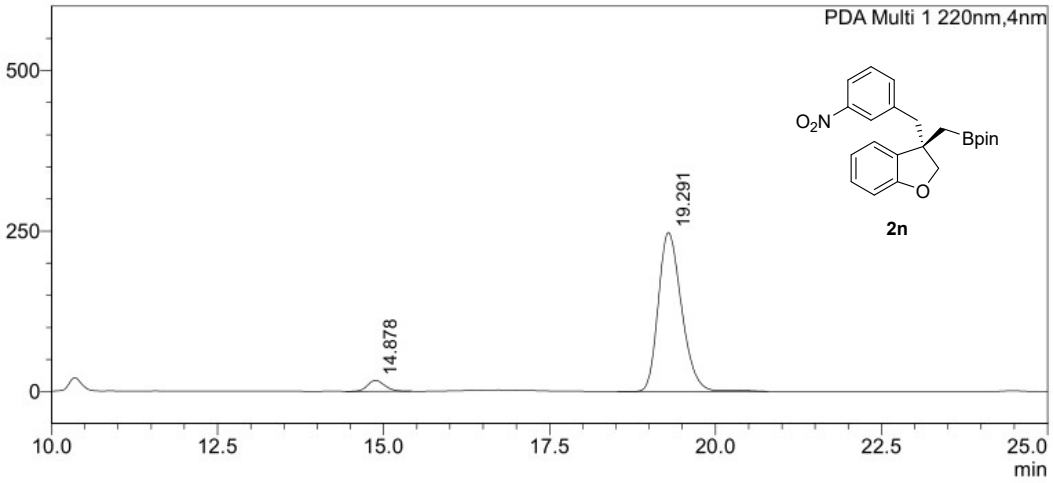
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.856	5208712	50.096	289354	57.252
2	19.274	5188806	49.904	216049	42.748
Total		10397517	100.000	505403	100.000

<Chromatogram>

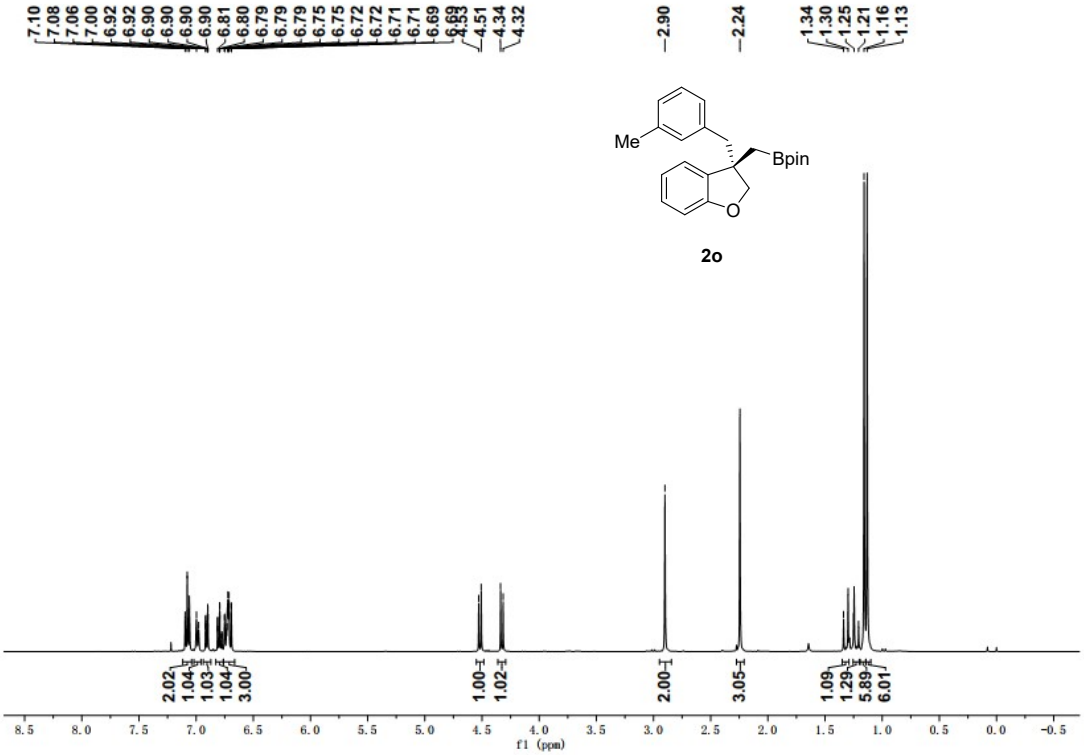
mAU



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.878	306521	4.815	17077	6.459
2	19.291	6060051	95.185	247306	93.541
Total		6366573	100.000	264383	100.000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6.90
6.90
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6.90
6.81
6.80
6.79
6.79
6.79
6.75
6.75
6.72
6.72
6.71
6.71
6.69
6.69
4.53
4.51
4.34
4.32
2.90
2.24
1.34
1.30
1.25
1.21
1.16
1.13
Me
Bpin
O
2o
2.02
1.04
1.03
1.04
3.00
1.00
1.02
2.00
3.05
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1.29
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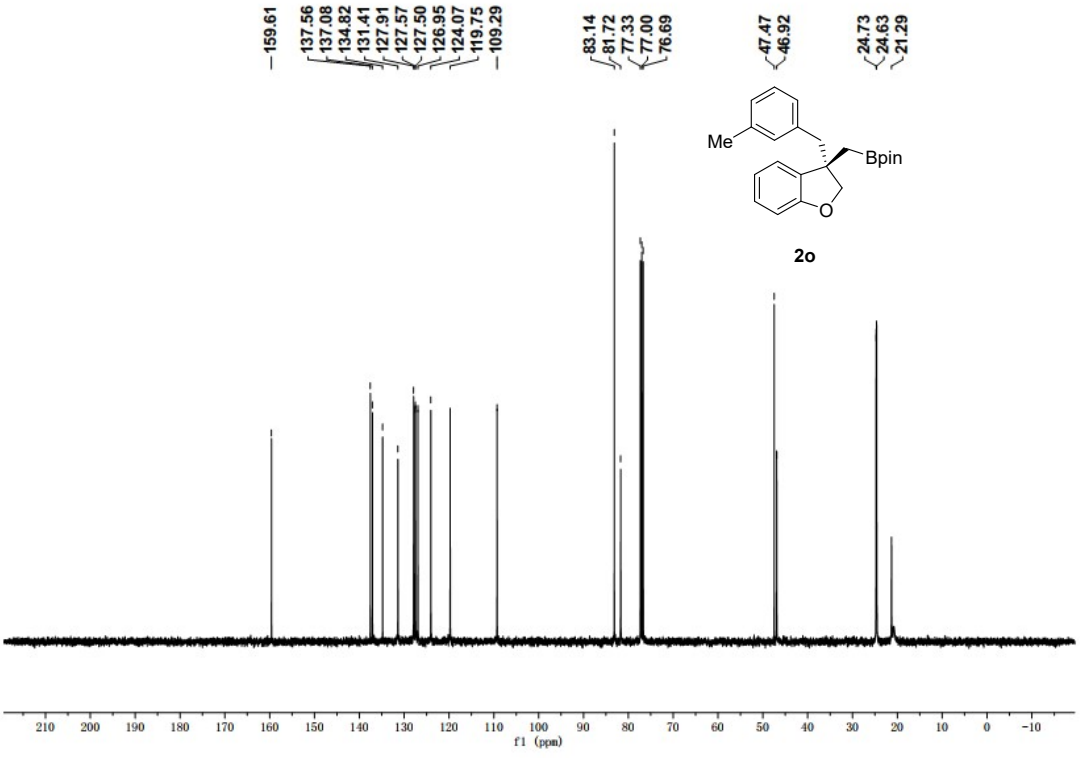
6.01
f1 (ppm)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134.82
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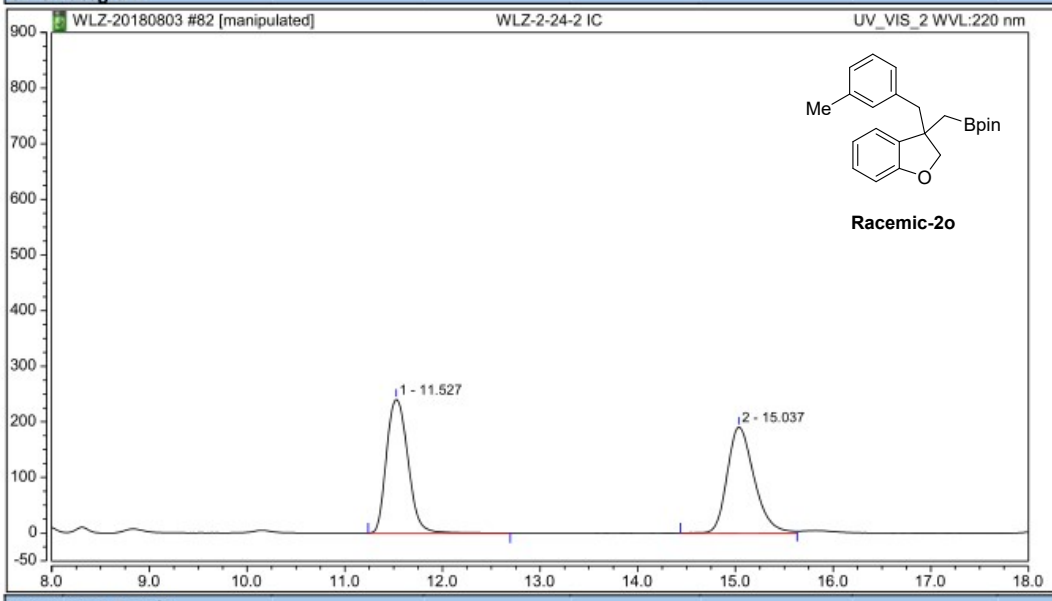
127.57
127.50
126.95
124.07
119.75
109.29
83.14
81.72
77.33
77.00
76.69
47.47
46.92
24.73
24.63
21.29
Me
Bpin
O
2o
f1 (ppm)

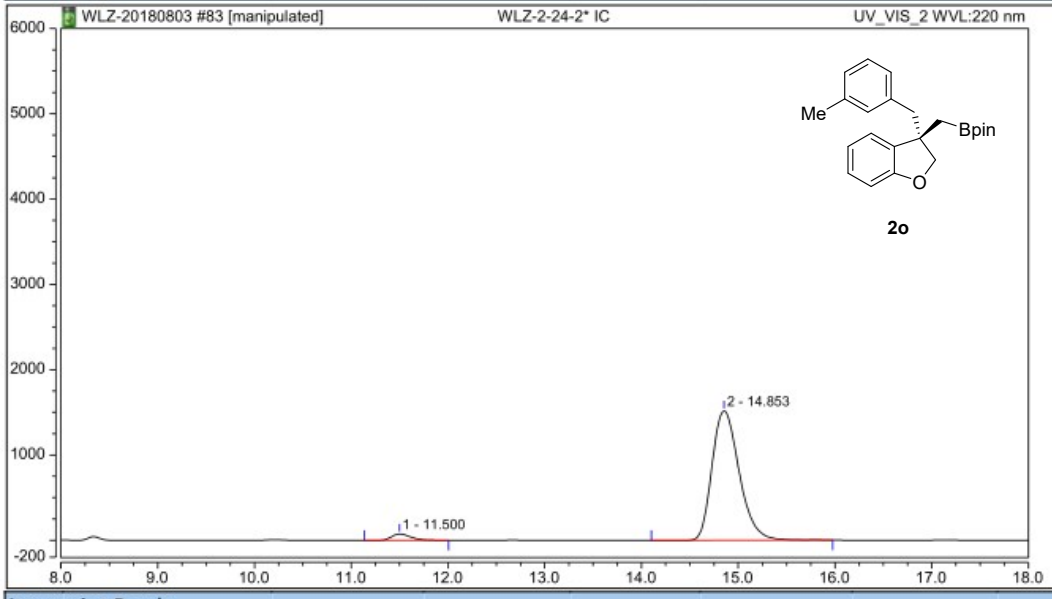
Chromatogram



Integration Results

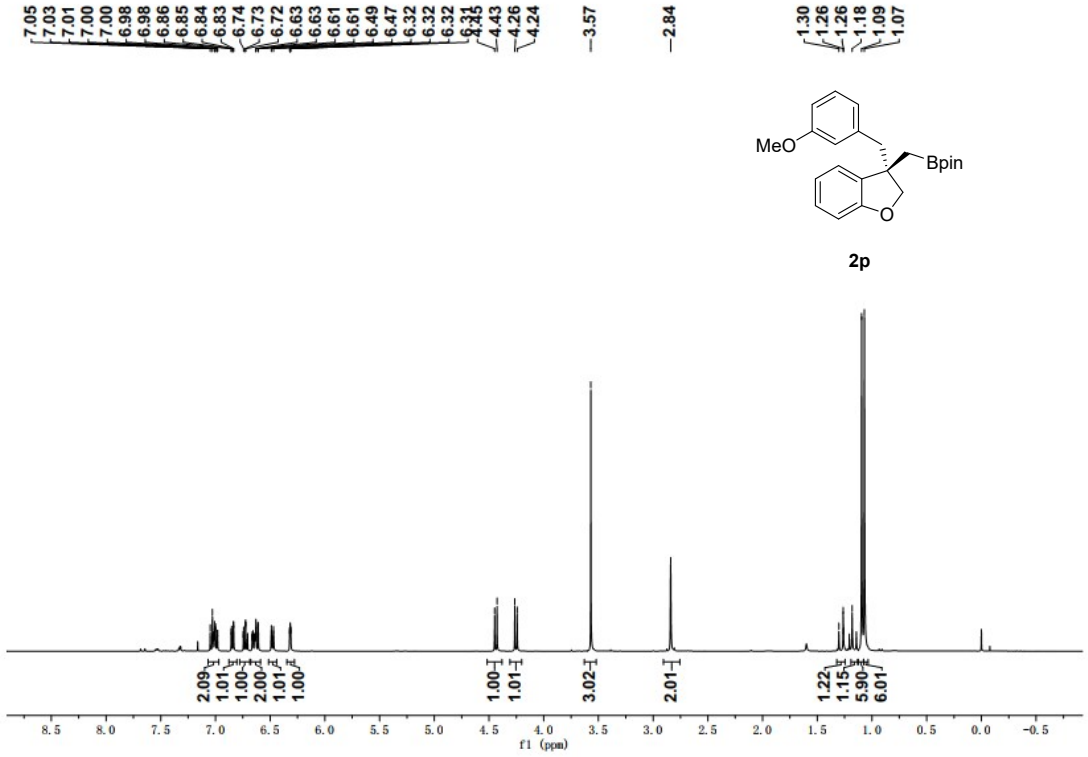
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.527	61.189	240.428	49.99	55.76	n.a.
2		15.037	61.221	190.718	50.01	44.24	n.a.
Total:			**122.410**	**431.145**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.500	17.135	75.749	3.35	4.76	n.a.
2		14.853	494.869	1516.961	96.65	95.24	n.a.
Total:			**512.004**	**1592.710**	**100.00**	**100.00**	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6.84
6.83
6.74
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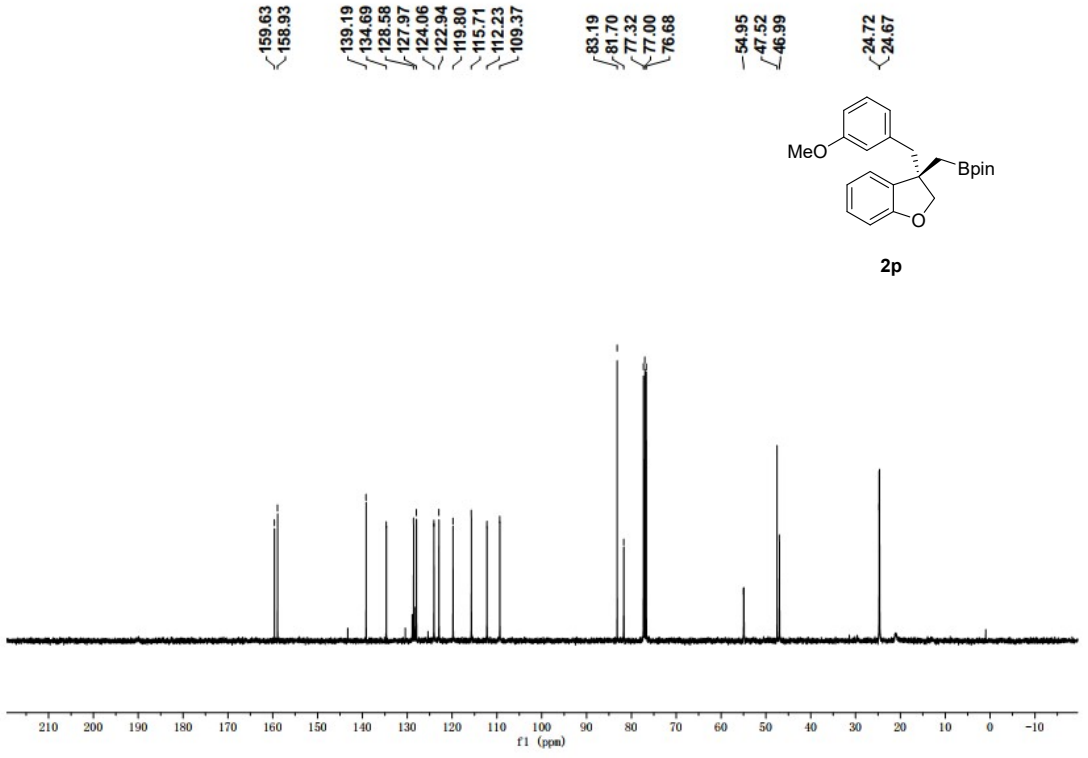
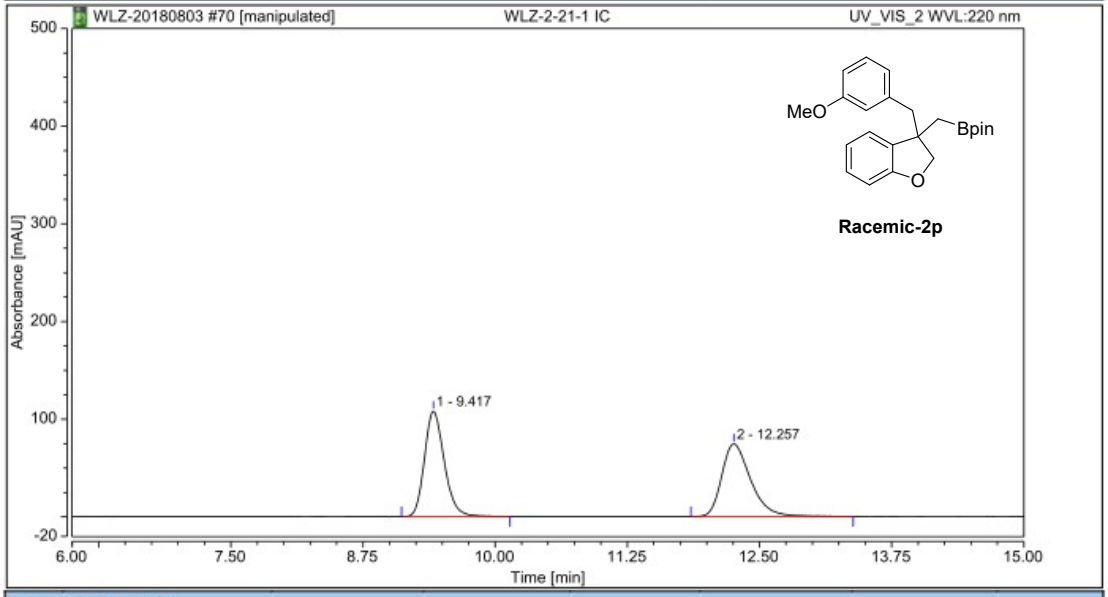
6.32
4.45
4.43
4.26
4.24
3.57
2.84
1.30
1.26
1.26
1.18
1.09
1.07
MeO
Bpin
O
2p
2.09
1.01
1.00
2.00
1.01
1.00
1.00
1.01
3.02
2.01
1.22
1.15
5.90
6.01
f1 (ppm)


159.63
158.93
139.19
134.69
128.58
127.97
124.06
122.94
119.80
115.71
112.23
109.37
83.19
81.70
77.32
77.00
76.68
54.95
47.52
46.99
24.72
24.67
MeO
Bpin
O
2p
f1 (ppm)

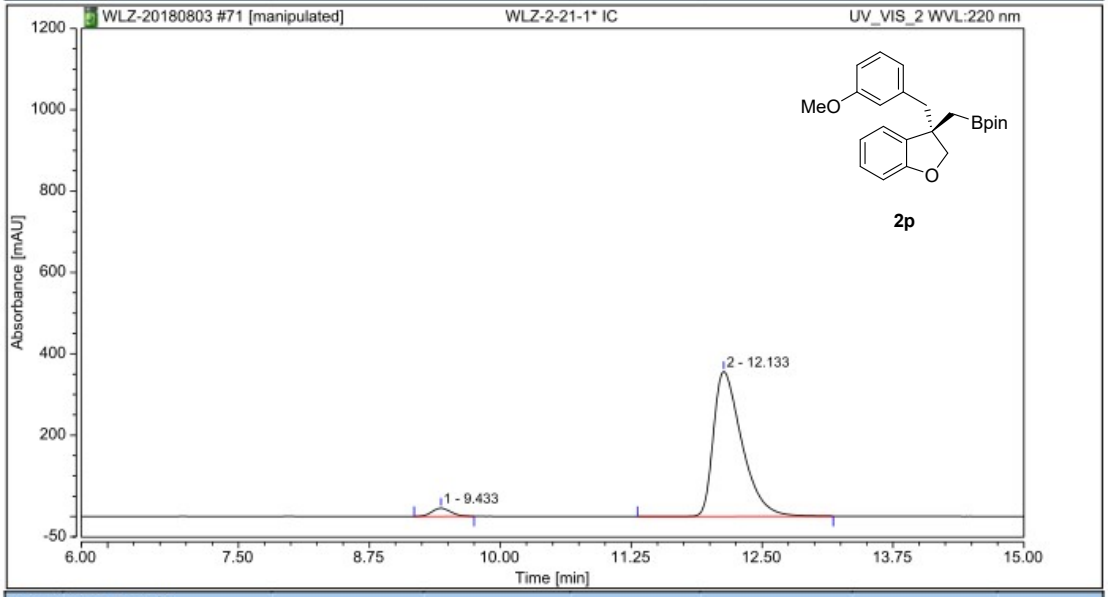
Chromatogram



Integration Results

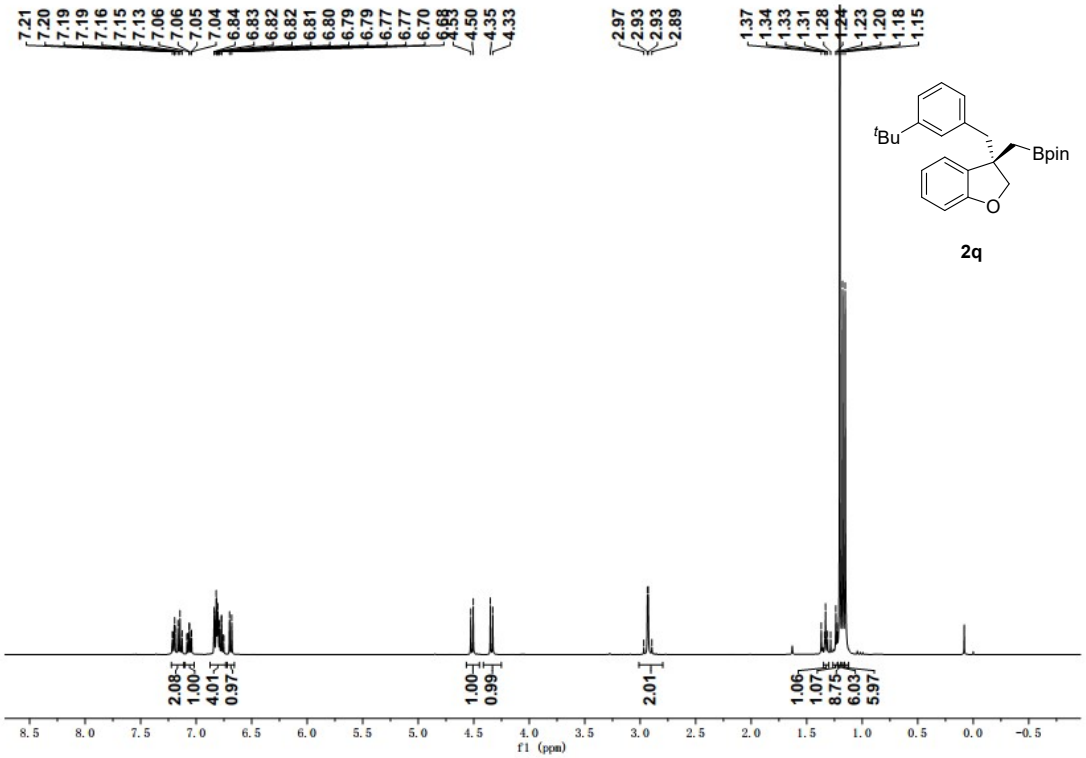
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.417	23.532	107.978	49.83	59.21	n.a.
2		12.257	23.696	74.381	50.17	40.79	n.a.
Total:			**47.229**	**182.359**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.433	4.260	20.257	3.65	5.38	n.a.
2		12.133	112.354	355.933	96.35	94.62	n.a.
Total:			**116.614**	**376.190**	**100.00**	**100.00**	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7.19
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7.15
7.13
7.06
7.06
7.05
7.04
6.84
6.83
6.82
6.82
6.81
6.80
6.79
6.79
6.77
6.77
6.70
6.68
4.53
4.50
4.35
4.33
2.97
2.93
2.93
2.89
1.37
1.34
1.33
1.31
1.28
1.24
1.23
1.20
1.18
1.15
tBu
Bpin
O
2q
2.08
1.00
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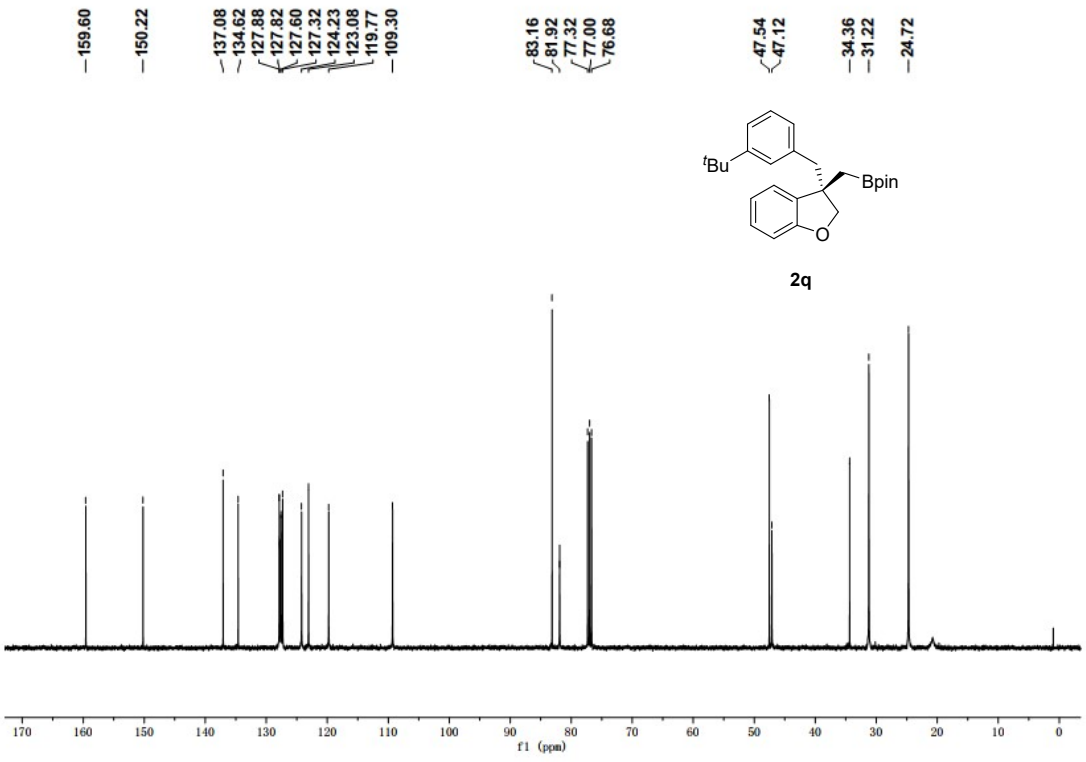
1.00
0.99
2.01
1.06
1.07
8.75
6.03
5.97
f1 (ppm)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127.60
127.32
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123.08
119.77
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83.16
81.92
77.32
77.00
76.68
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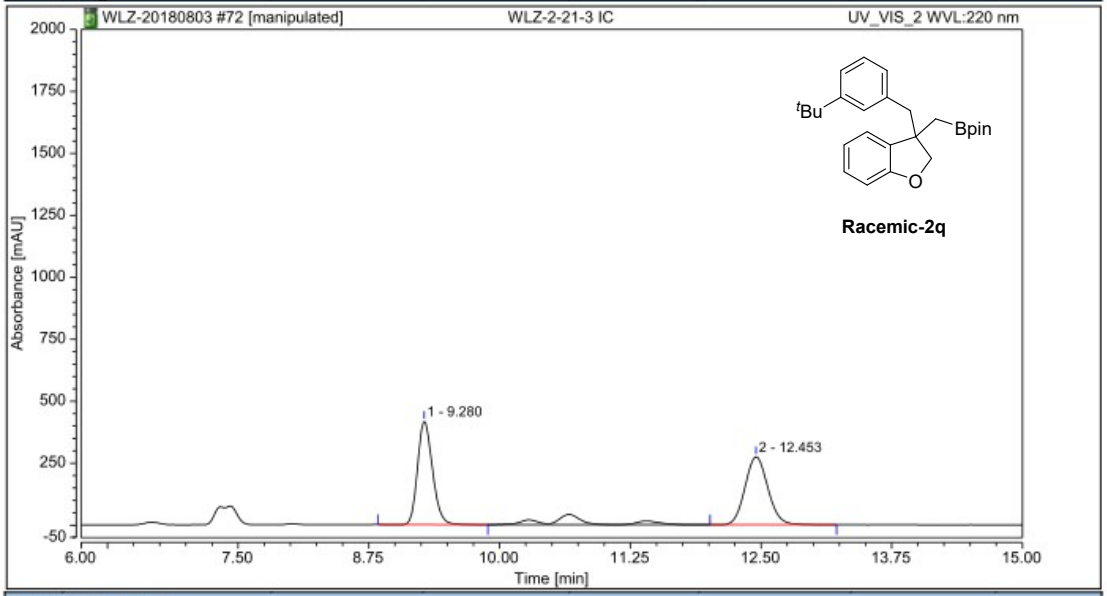
47.12
34.36
31.22
24.72
tBu
Bpin
O
2q
f1 (ppm)

Chromatogram

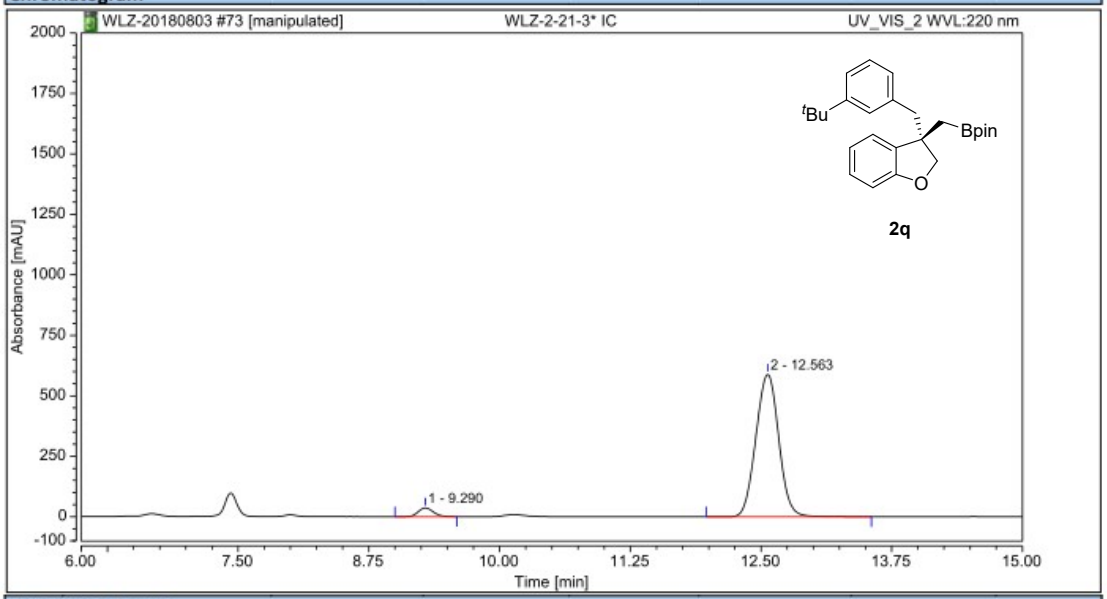


Racemic-2q

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.280	68.817	417.182	49.77	60.34	n.a.
2		12.453	69.448	274.232	50.23	39.66	n.a.
Total:			**138.266**	**691.414**	**100.00**	**100.00**	

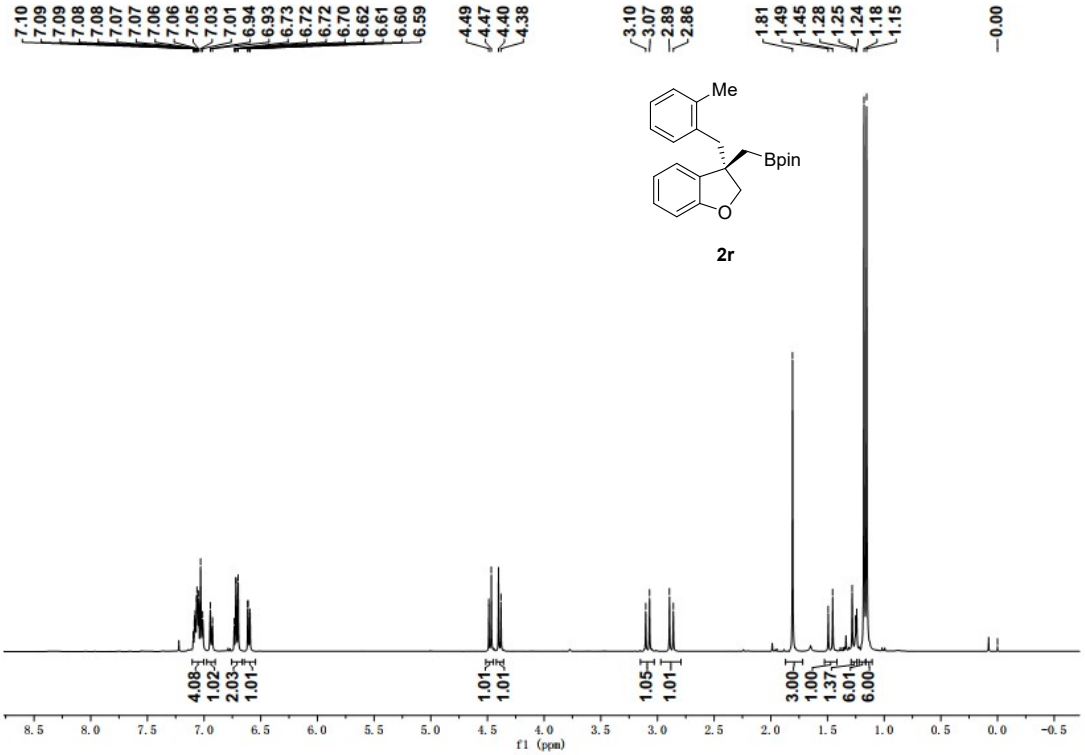
Chromatogram



2q

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.290	6.145	36.716	3.94	5.86	n.a.
2		12.563	149.734	589.390	96.06	94.14	n.a.
Total:			**155.879**	**626.106**	**100.00**	**100.00**	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7.08
7.07
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7.05
7.03
7.01
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6.72
6.72
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3.10
3.07
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1.28
1.25
1.24
1.18
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Bpin
O
2r
4.08
1.02
2.03
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1.05
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3.00
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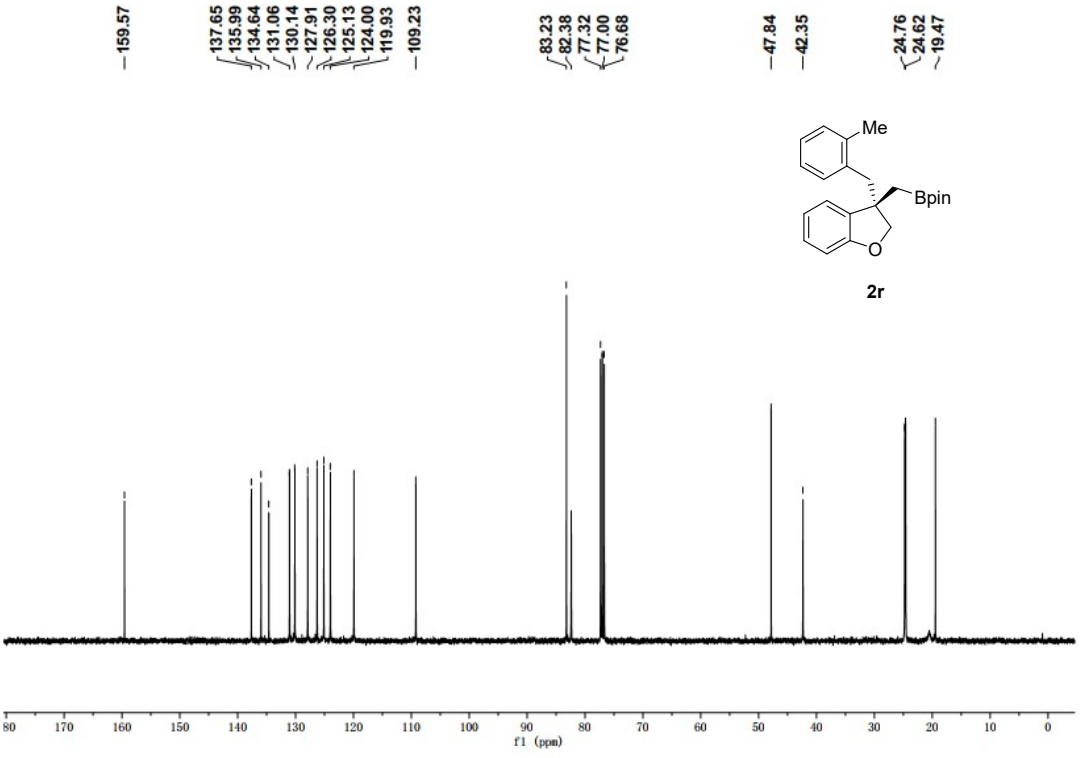
6.00
f1 (ppm)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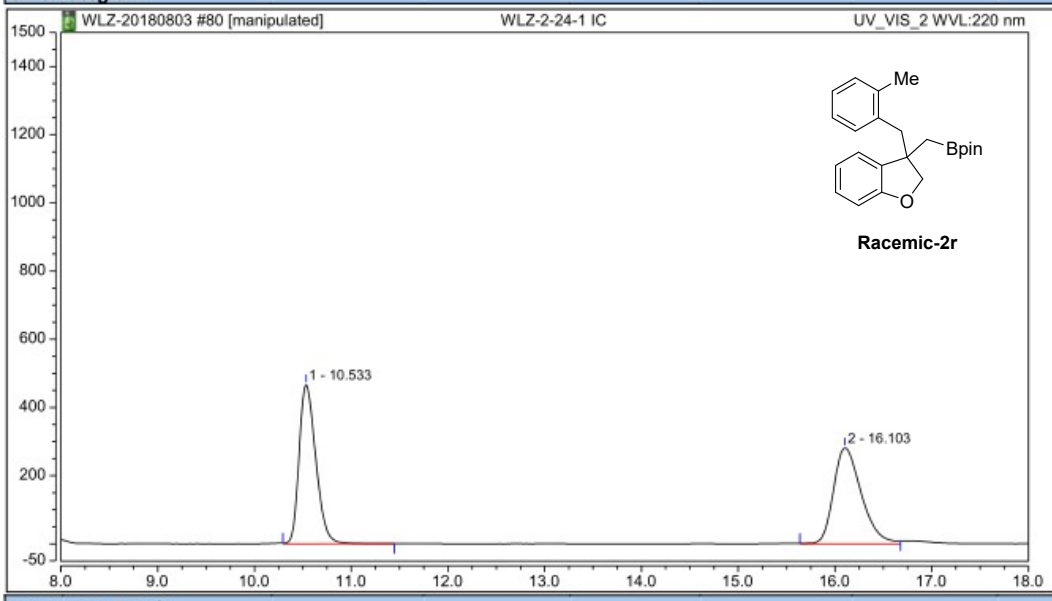
Me
Bpin
O
2r
f1 (ppm)

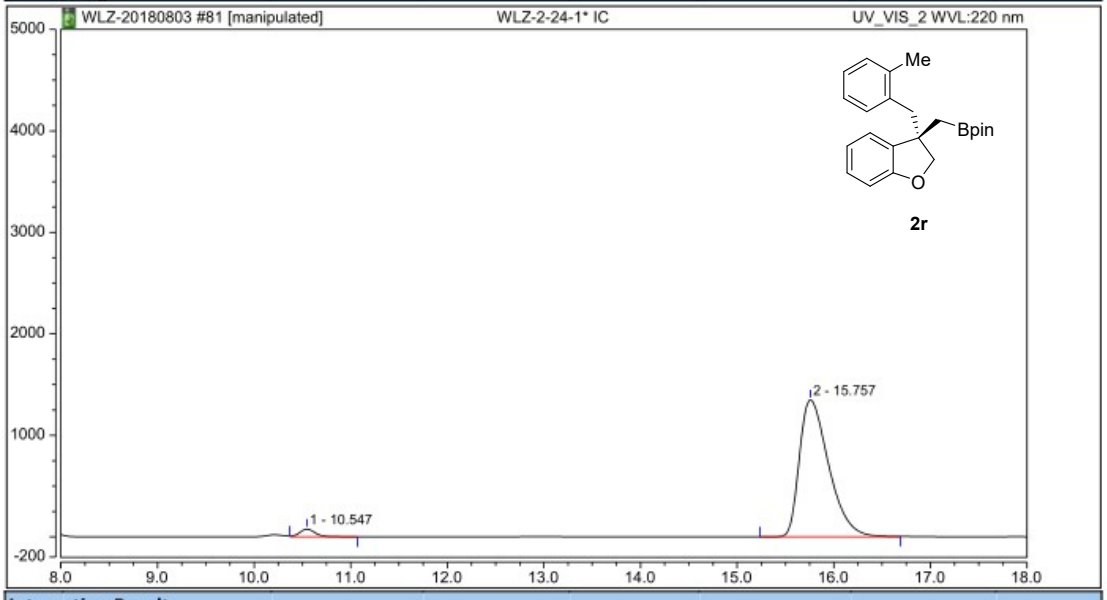
Chromatogram



Integration Results

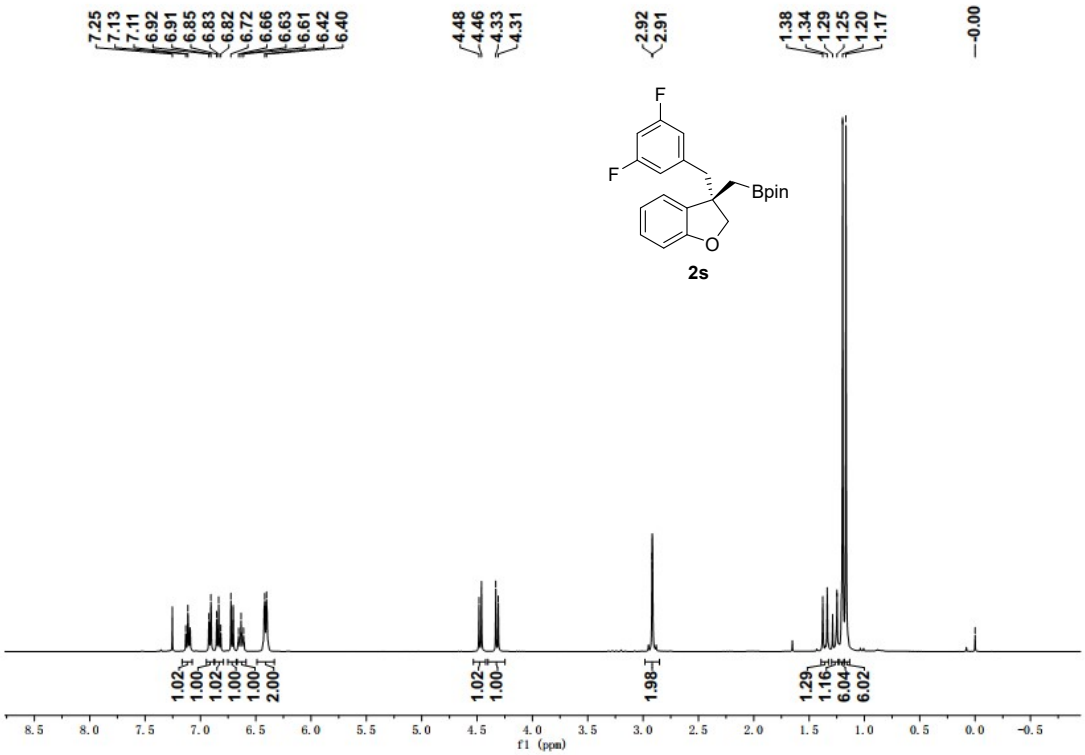
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.533	93.492	467.356	49.83	62.42	n.a.
2		16.103	94.118	281.350	50.17	37.58	n.a.
Total:			**187.610**	**748.706**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.547	14.236	75.911	2.91	5.33	n.a.
2		15.757	475.017	1349.233	97.09	94.67	n.a.
Total:			**489.253**	**1425.143**	**100.00**	**100.00**	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6.91
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6.82
6.72
6.66
6.63
6.61
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6.40
4.48
4.46
4.33
4.31
2.92
2.91
1.38
1.34
1.29
1.25
1.20
1.17
0.00
F
F
Bpin
O
2s
1.02
1.00
1.02
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1.02
1.00
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1.16
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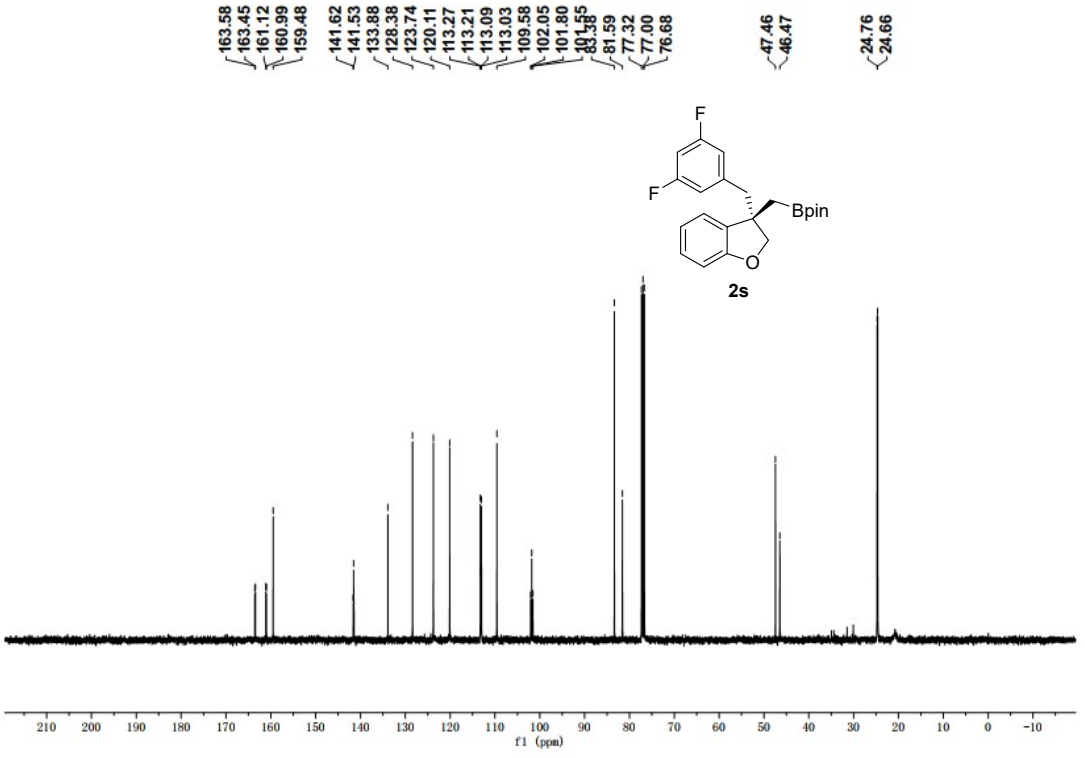
6.02
f1 (ppm)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113.09
113.03
109.58
102.05
101.80
101.55
83.38
81.59
77.32
77.00
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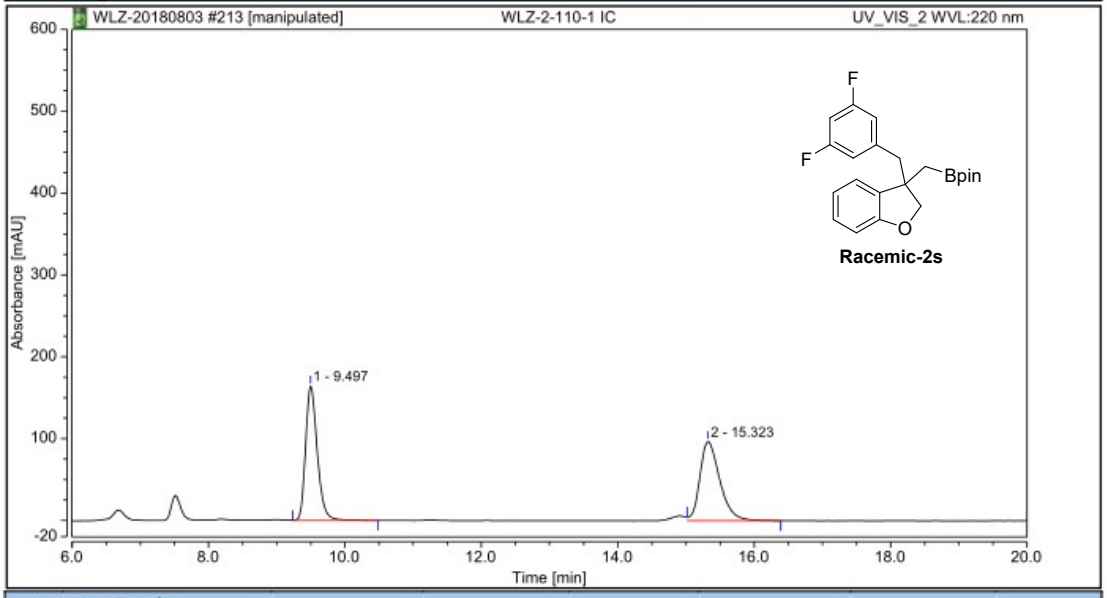
47.46
46.47
24.76
24.66
F
F
Bpin
O
2s
f1 (ppm)

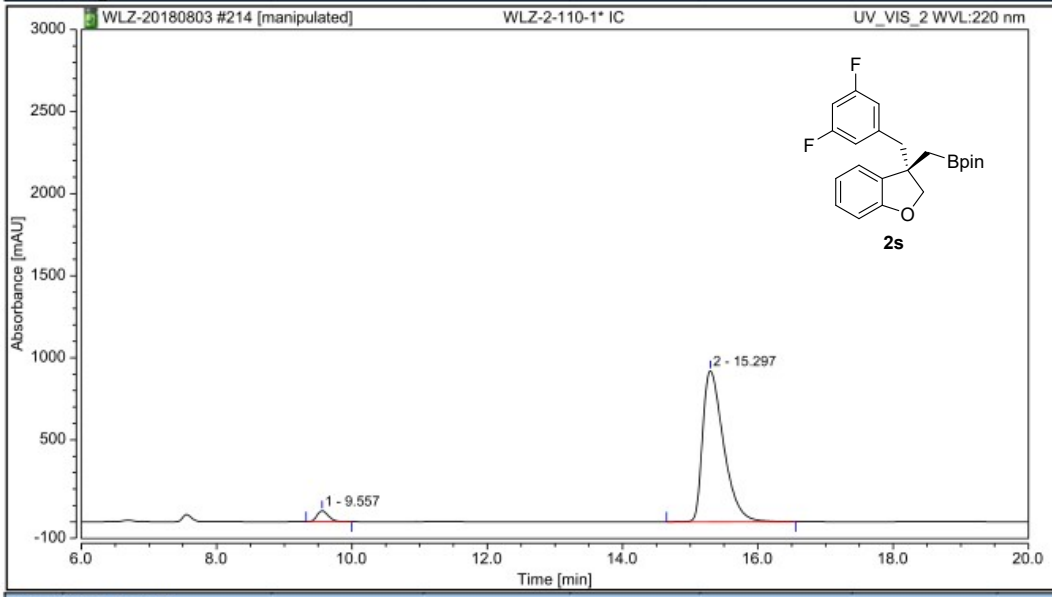
Chromatogram



Integration Results

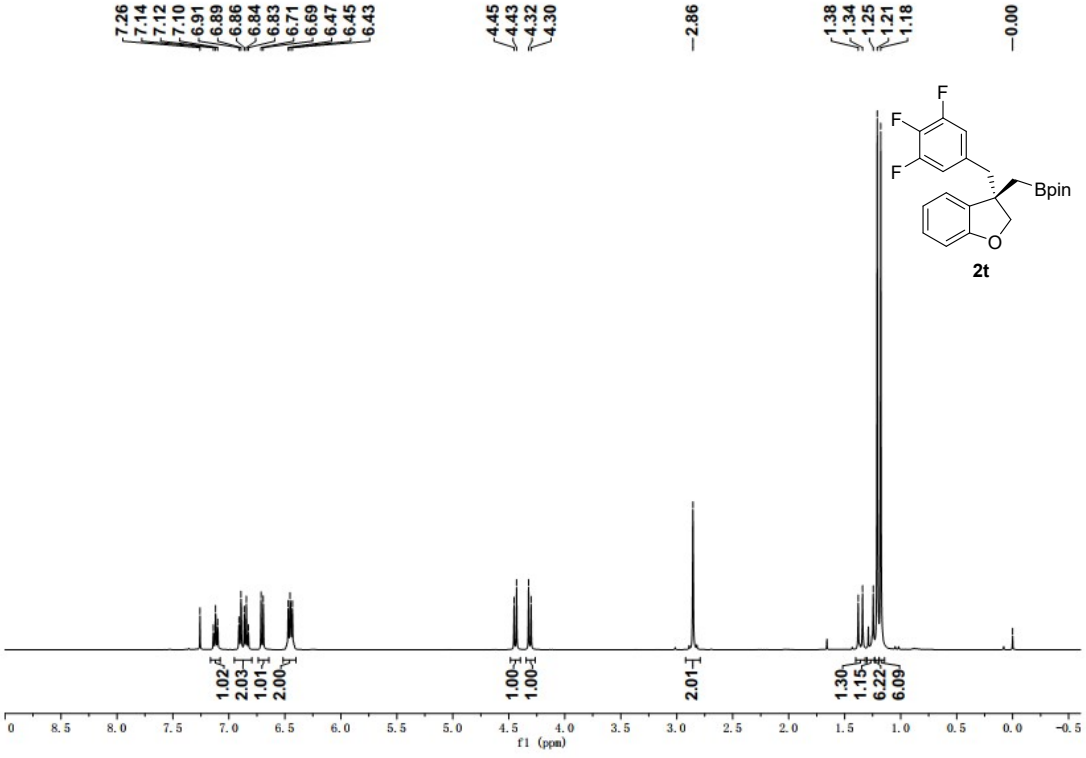
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.497	32.681	164.554	49.82	62.94	n.a.
2		15.323	32.923	96.911	50.18	37.06	n.a.
Total:			**65.605**	**261.465**	**100.00**	**100.00**	

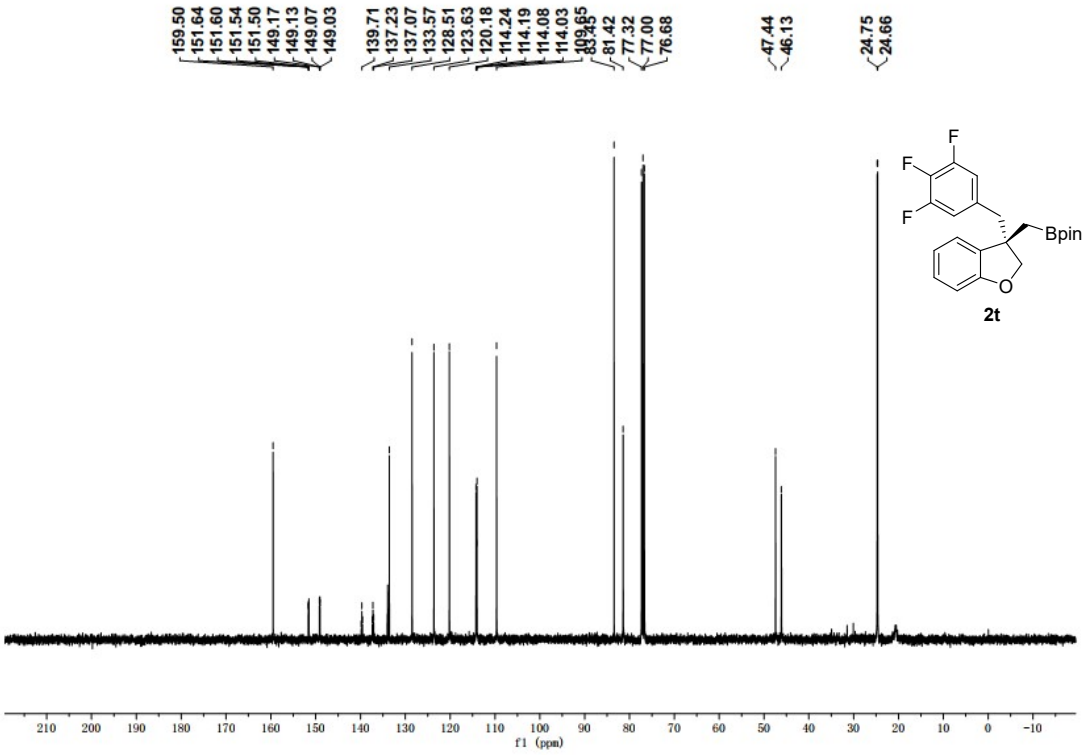
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.557	13.353	67.181	3.88	6.80	n.a.
2		15.297	331.060	920.485	96.12	93.20	n.a.
Total:			**344.413**	**987.666**	**100.00**	**100.00**	

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114.03
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81.42
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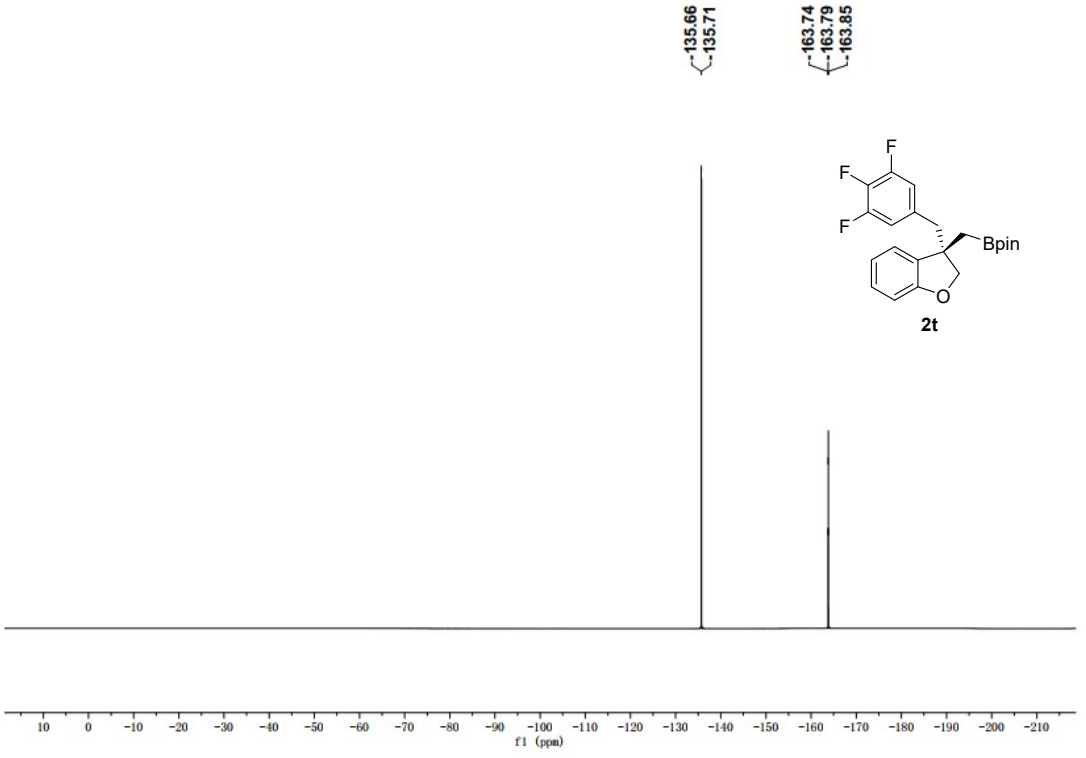
46.13
24.75
24.66
F
F
F
Bpin
O
2t
f1 (ppm)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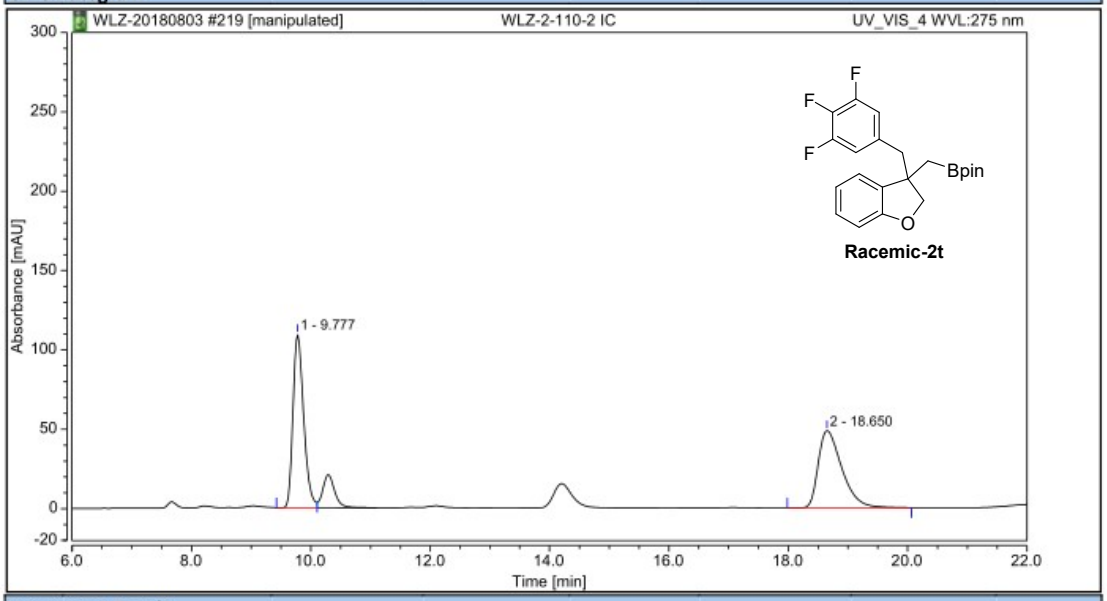
F
F
F
Bpin
O
2t
f1 (ppm)

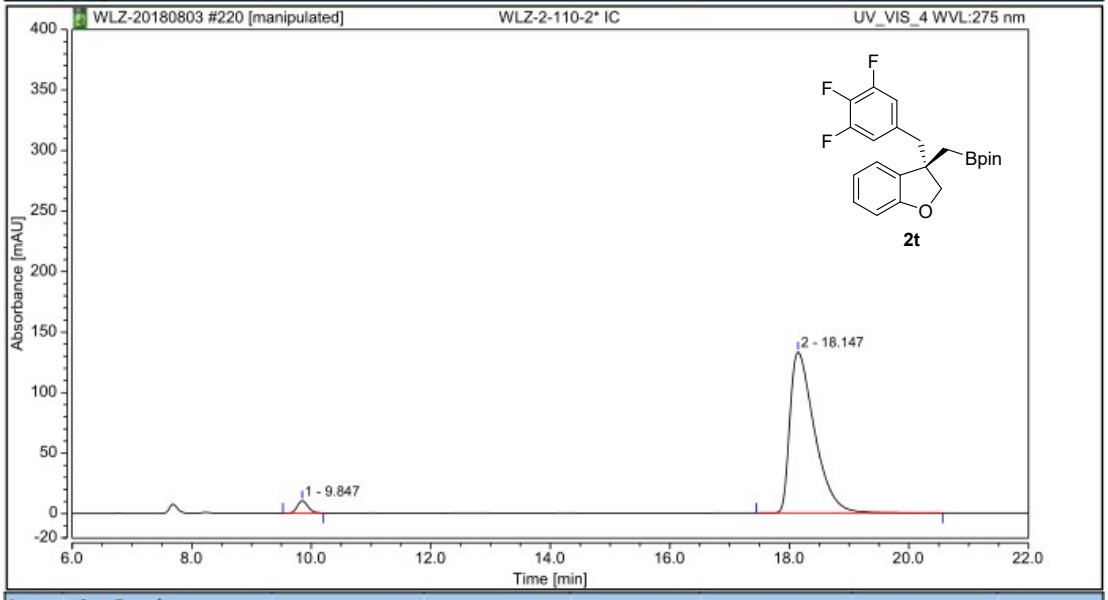
Chromatogram



Integration Results

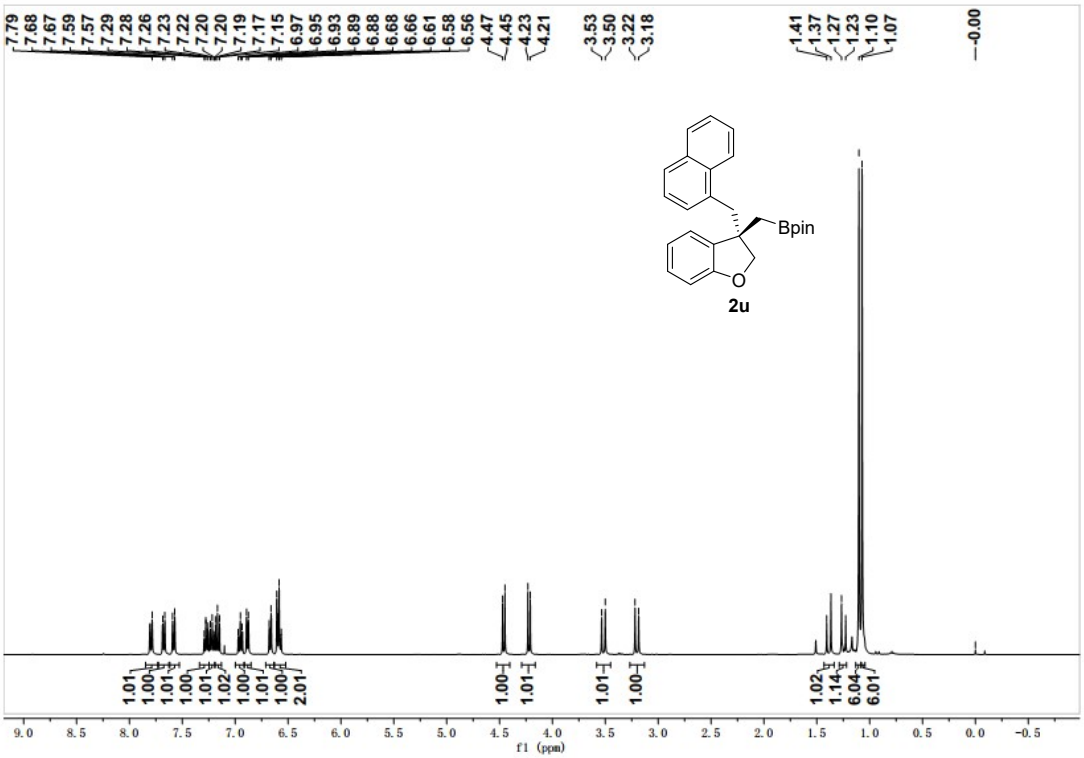
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.777	22.689	109.131	50.53	69.18	n.a.
2		18.650	22.215	48.607	49.47	30.82	n.a.
Total:			**44.904**	**157.739**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.847	2.137	10.206	3.25	7.12	n.a.
2		18.147	63.585	133.045	96.75	92.88	n.a.
Total:			**65.722**	**143.251**	**100.00**	**100.00**	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6.93
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6.61
6.58
6.56
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4.45
4.23
4.21
3.53
3.50
3.22
3.18
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1.27
1.23
1.10
1.07
0.00
Bpin
O
2u
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1.00
1.01
1.00
1.01
1.02
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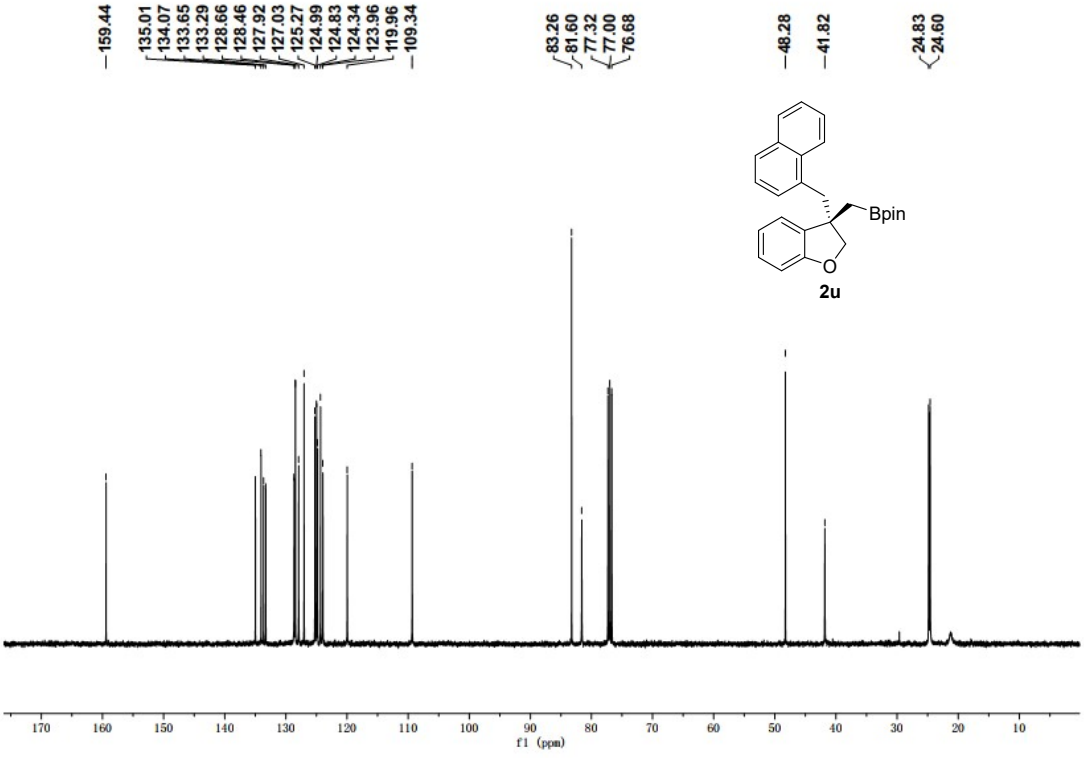
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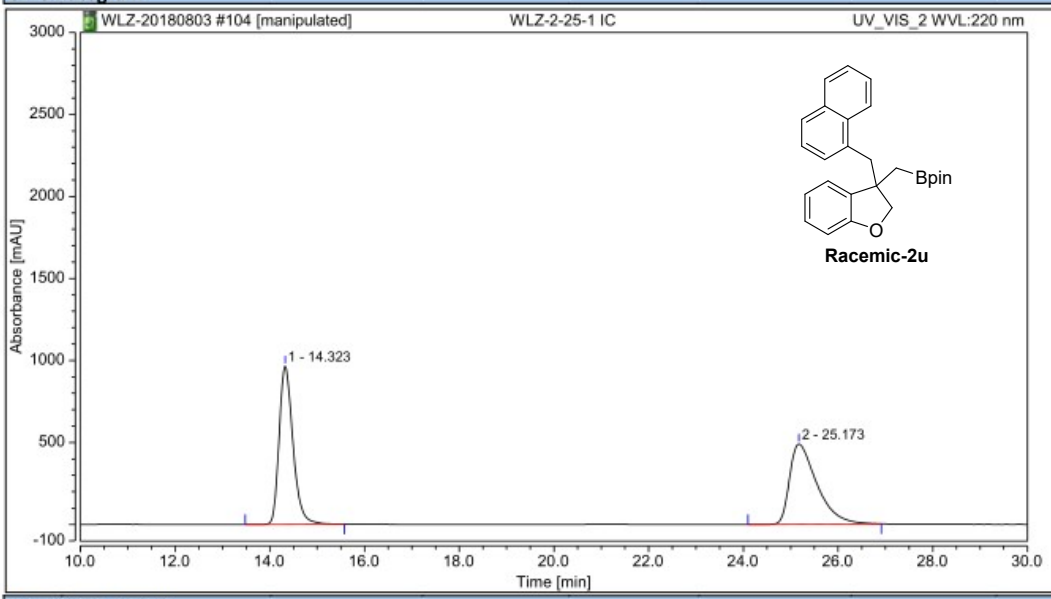
Bpin
O
2u
f1 (ppm)

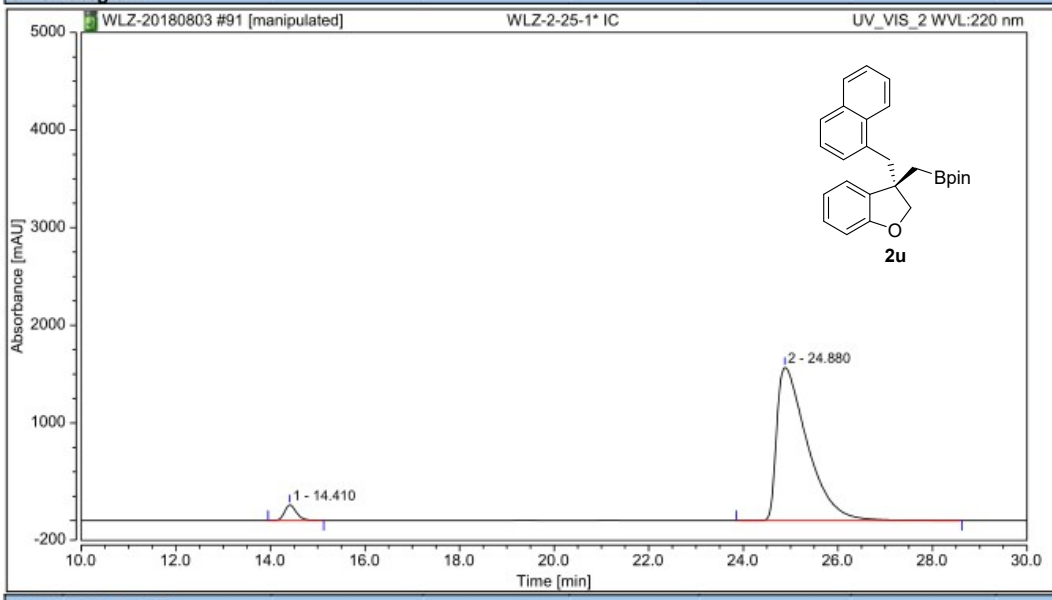
Chromatogram



Integration Results

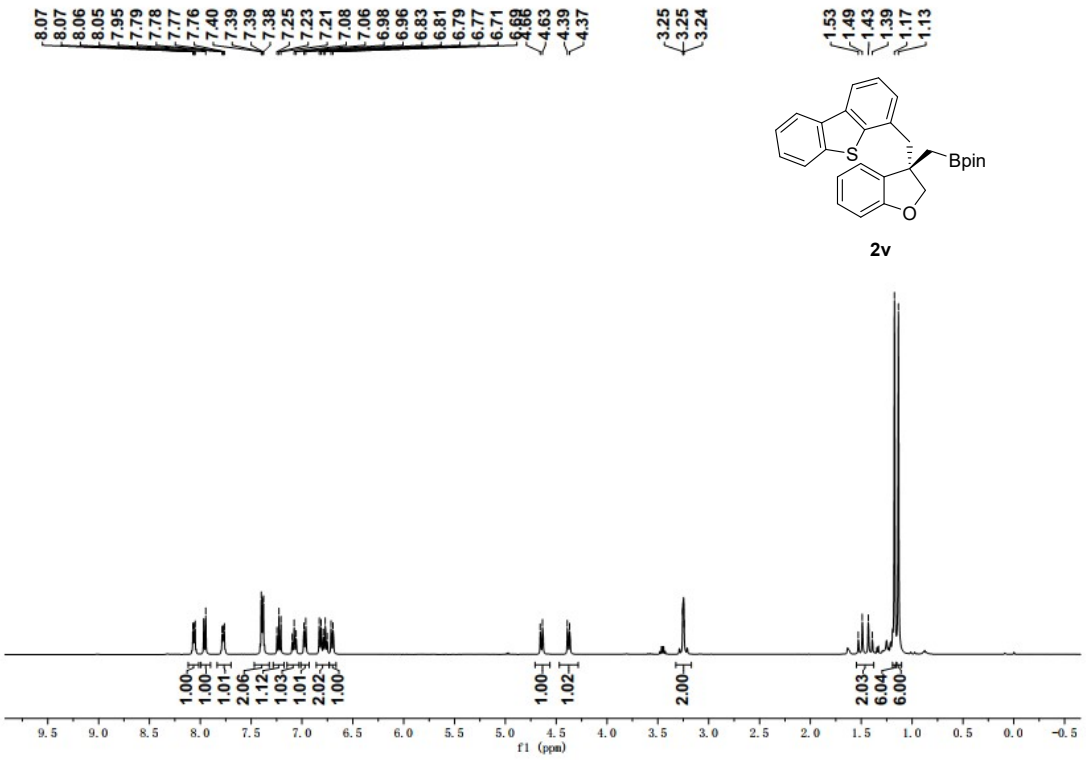
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.323	326.097	965.894	49.99	66.38	n.a.
2		25.173	326.220	489.300	50.01	33.62	n.a.
Total:			**652.317**	**1455.193**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.410	47.754	159.764	3.89	9.24	n.a.
2		24.880	1179.456	1568.631	96.11	90.76	n.a.
Total:			**1227.210**	**1728.395**	**100.00**	**100.00**	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7.23
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7.08
7.06
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6.81
6.79
6.77
6.71
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4.39
4.37
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S
Bpin
O
2v
1.00
1.00
1.01
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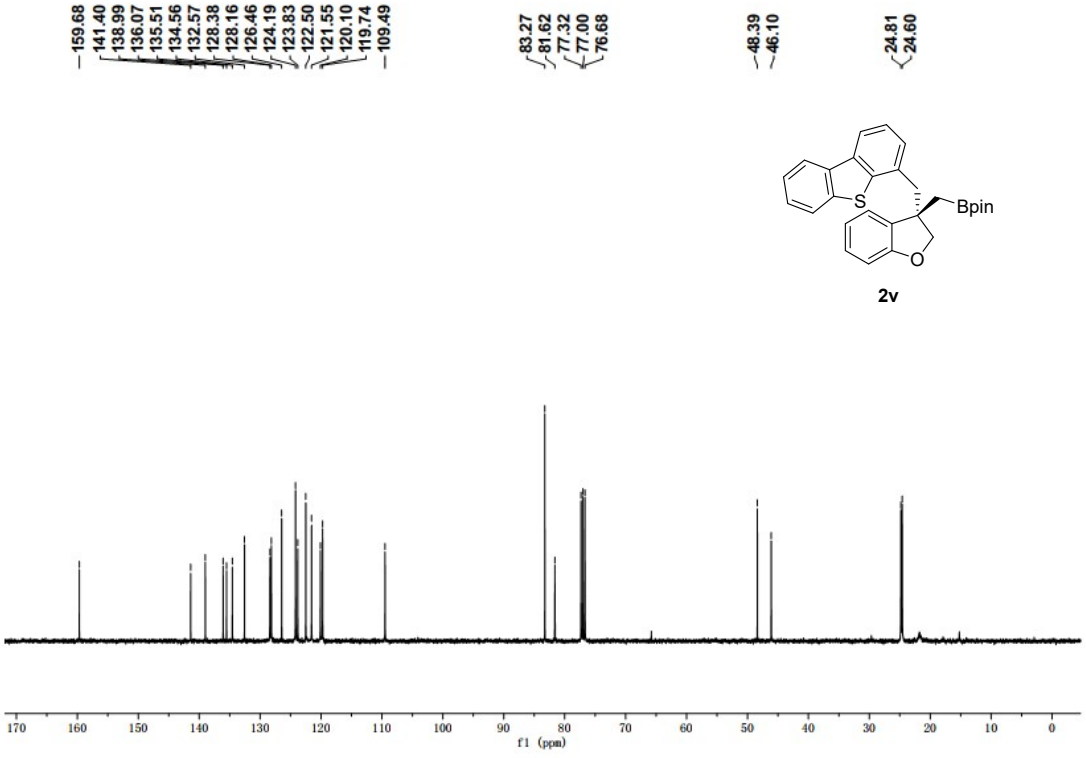
f1 (ppm)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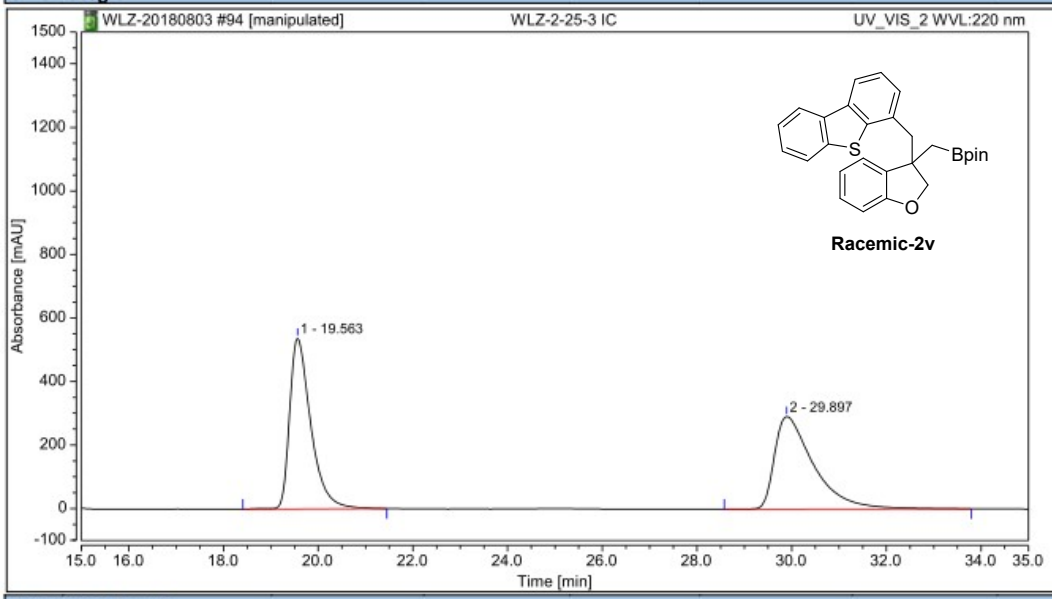
S
Bpin
O
2v
f1 (ppm)

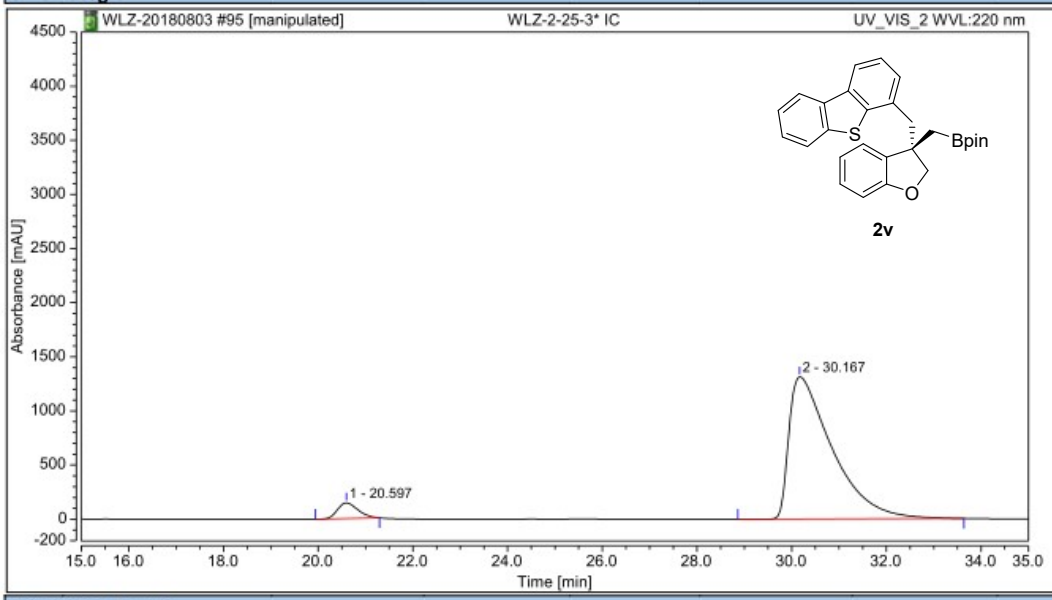
Chromatogram



Integration Results

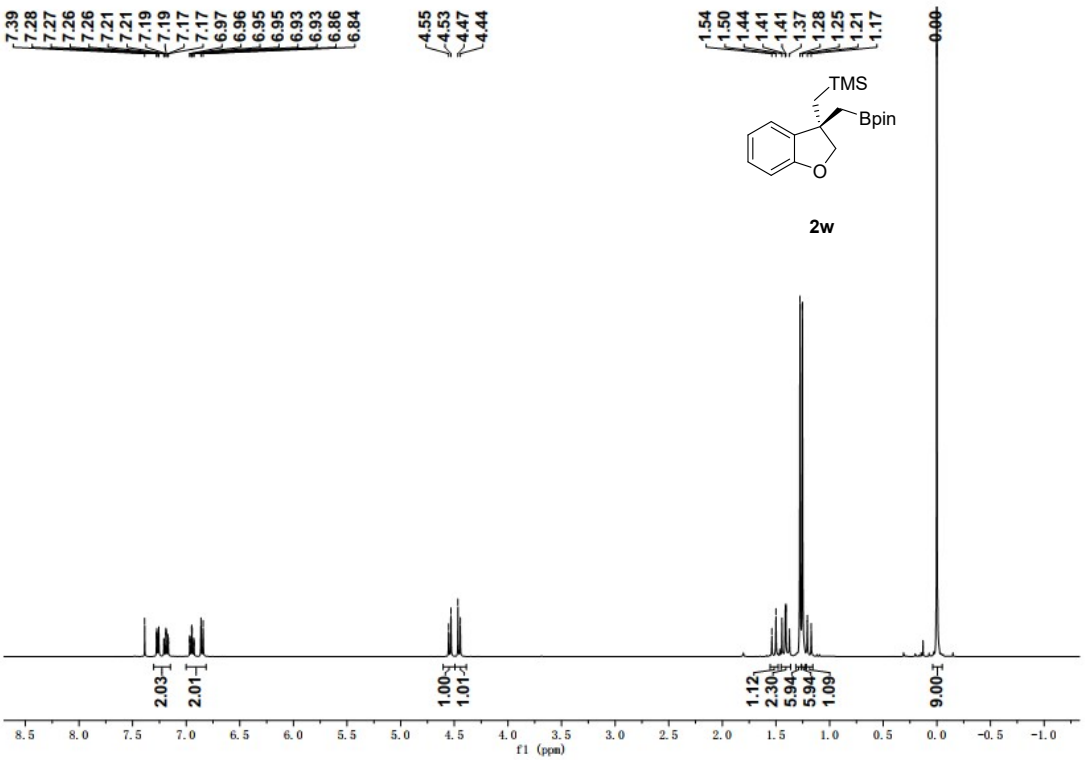
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.563	278.566	537.468	50.04	64.88	n.a.
2		29.897	278.174	290.943	49.96	35.12	n.a.
Total:			**556.740**	**828.411**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.597	72.611	144.611	4.97	9.92	n.a.
2		30.167	1388.033	1313.528	95.03	90.08	n.a.
Total:			**1460.644**	**1458.138**	**100.00**	**100.00**	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4.47
4.44
1.54
1.50
1.44
1.41
1.41
1.37
1.28
1.25
1.21
1.17
0.00
TMS
Bpin
O
2w
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1.00
1.01
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5.94
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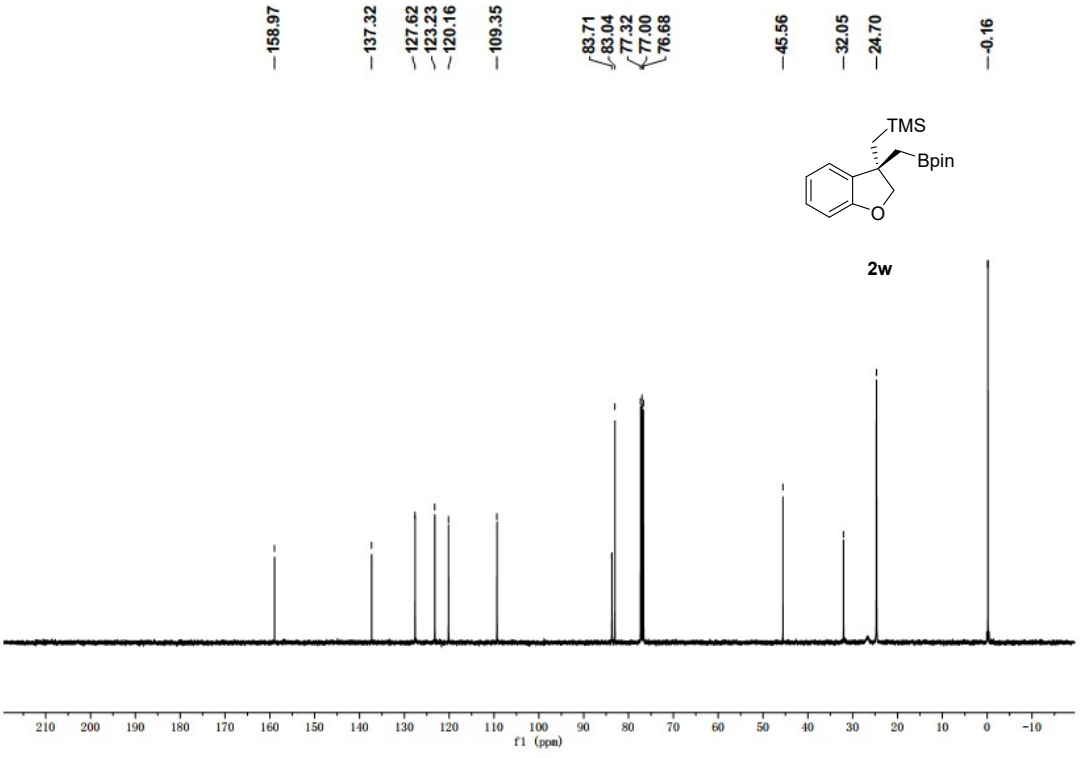
9.00
f1 (ppm)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83.04
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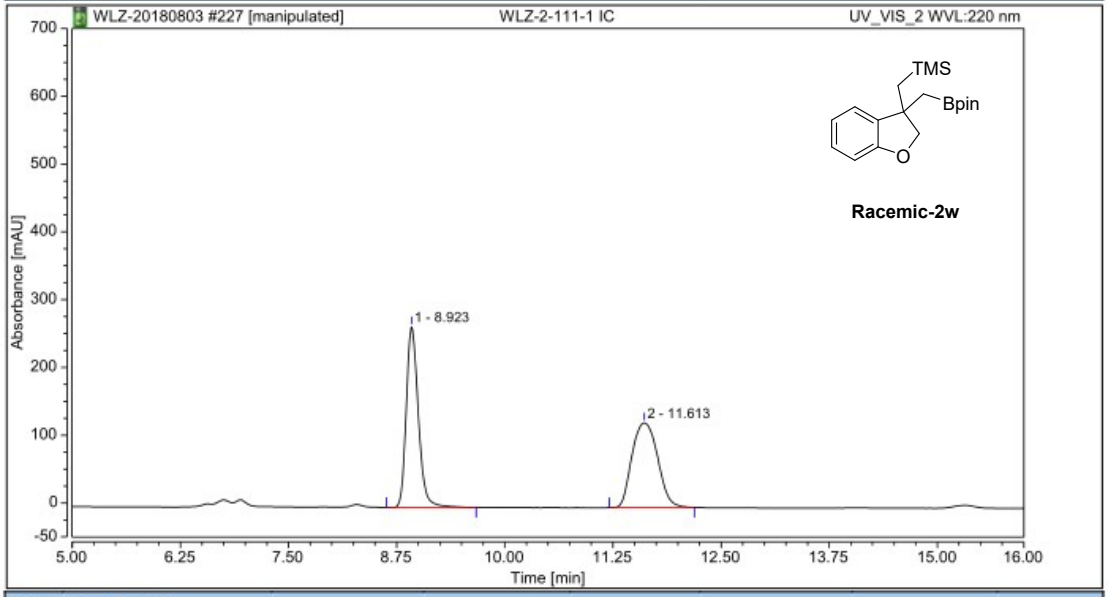
45.56
32.05
24.70
-0.16
TMS
Bpin
O
2w
f1 (ppm)

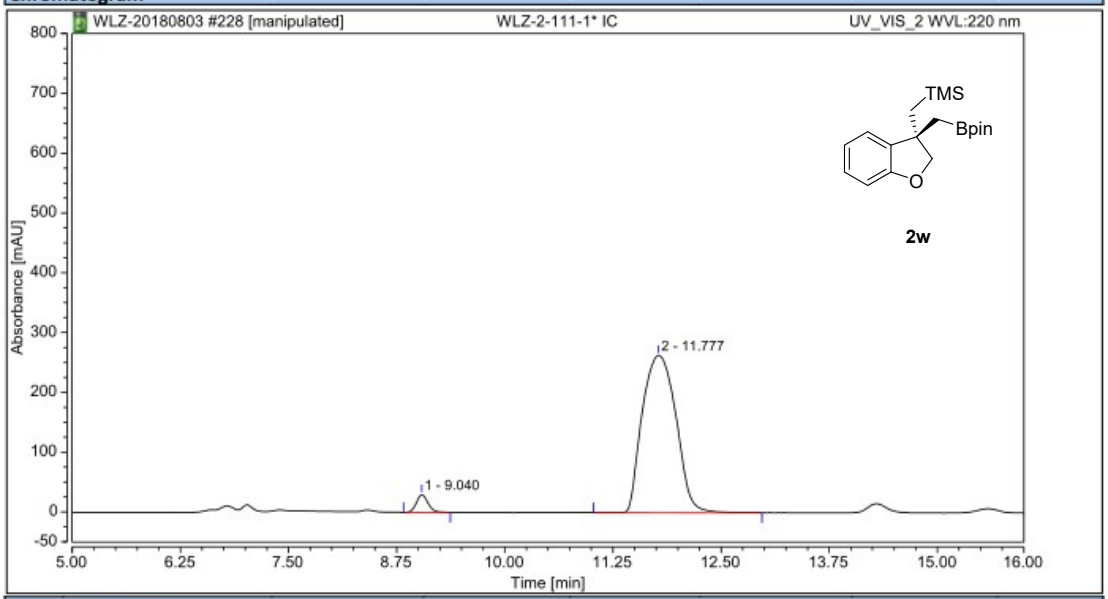
Chromatogram



Integration Results

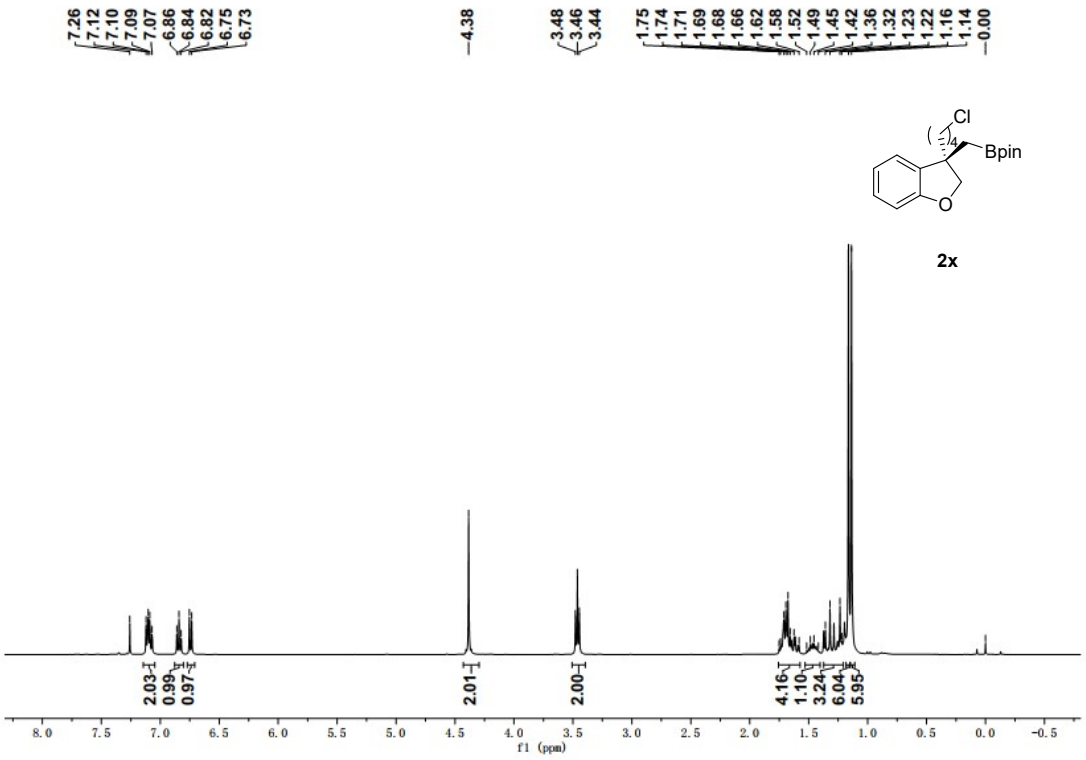
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.923	43.235	266.514	50.05	68.07	n.a.
2		11.613	43.141	124.993	49.95	31.93	n.a.
Total:			**86.375**	**391.507**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.040	4.603	29.431	3.72	10.06	n.a.
2		11.777	119.180	263.050	96.28	89.94	n.a.
Total:			**123.783**	**292.481**	**100.00**	**100.00**	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3.44
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1.74
1.71
1.69
1.68
1.66
1.62
1.58
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1.49
1.45
1.42
1.36
1.32
1.23
1.22
1.16
1.14
0.00
Cl
Bpin
O
2x
2.03
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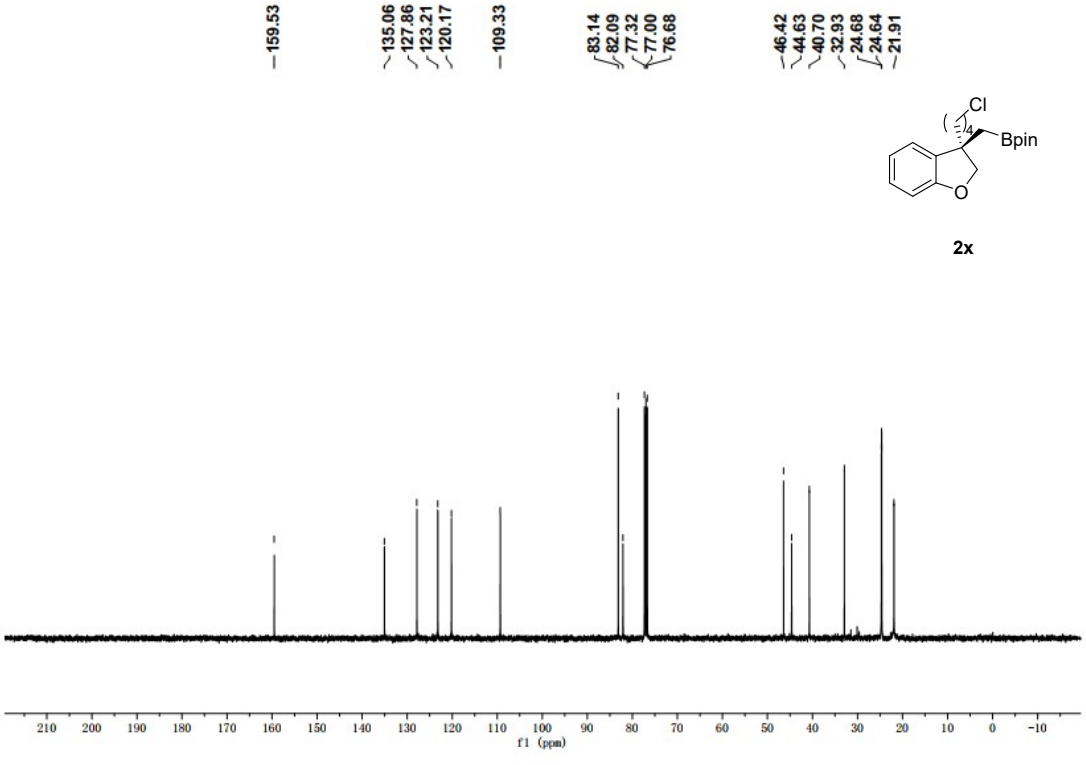
0.97
2.01
2.00
4.16
1.10
3.24
6.04
5.95
f1 (ppm)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82.09
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77.00
76.68
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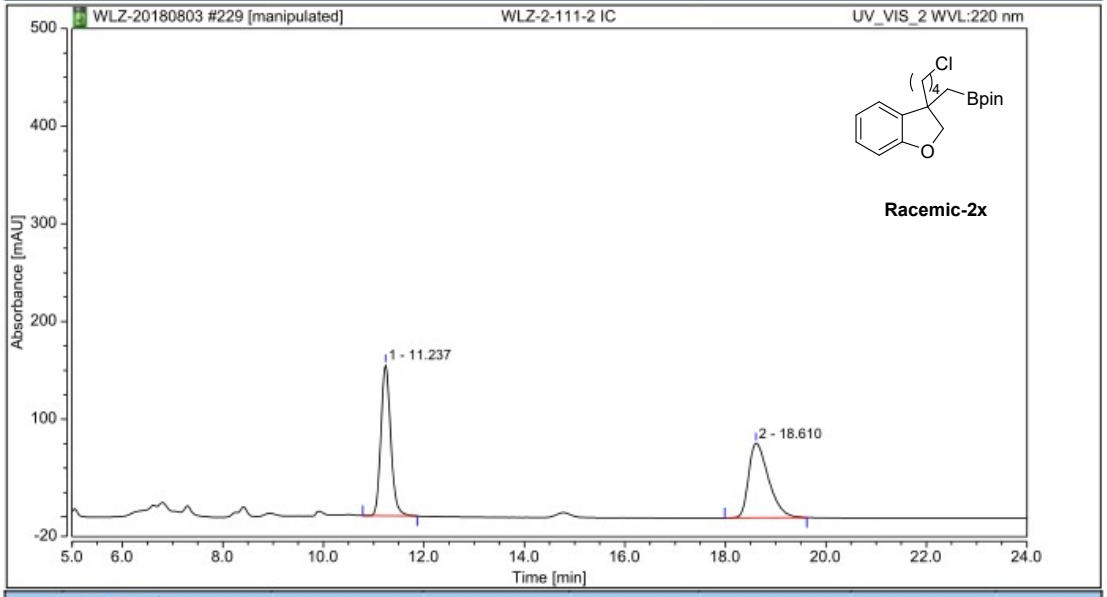
32.93
24.68
24.64
21.91
Cl
Bpin
O
2x
f1 (ppm)

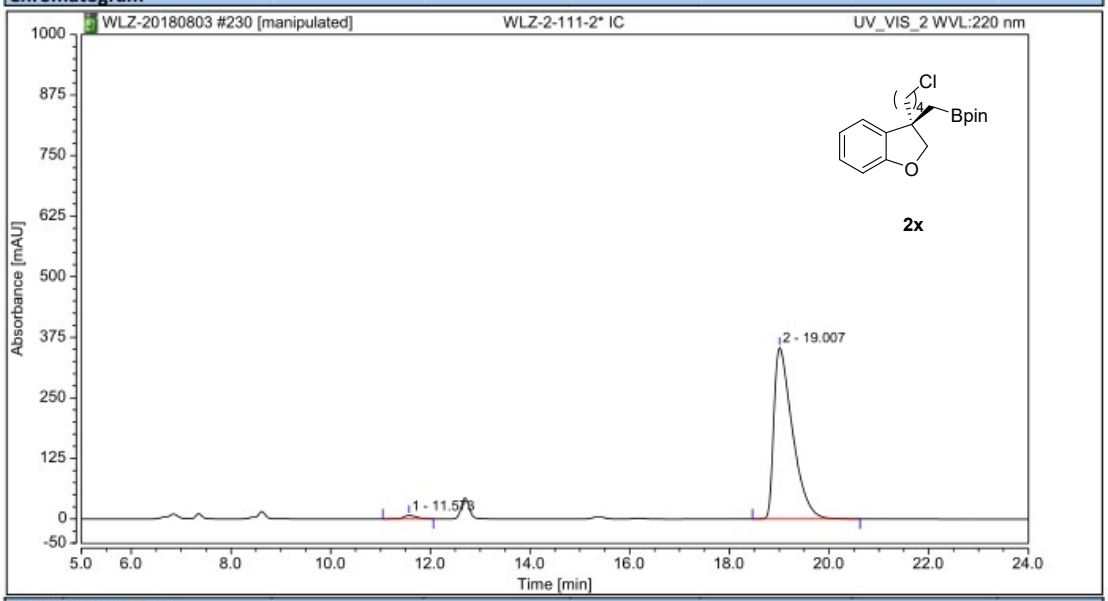
Chromatogram



Integration Results

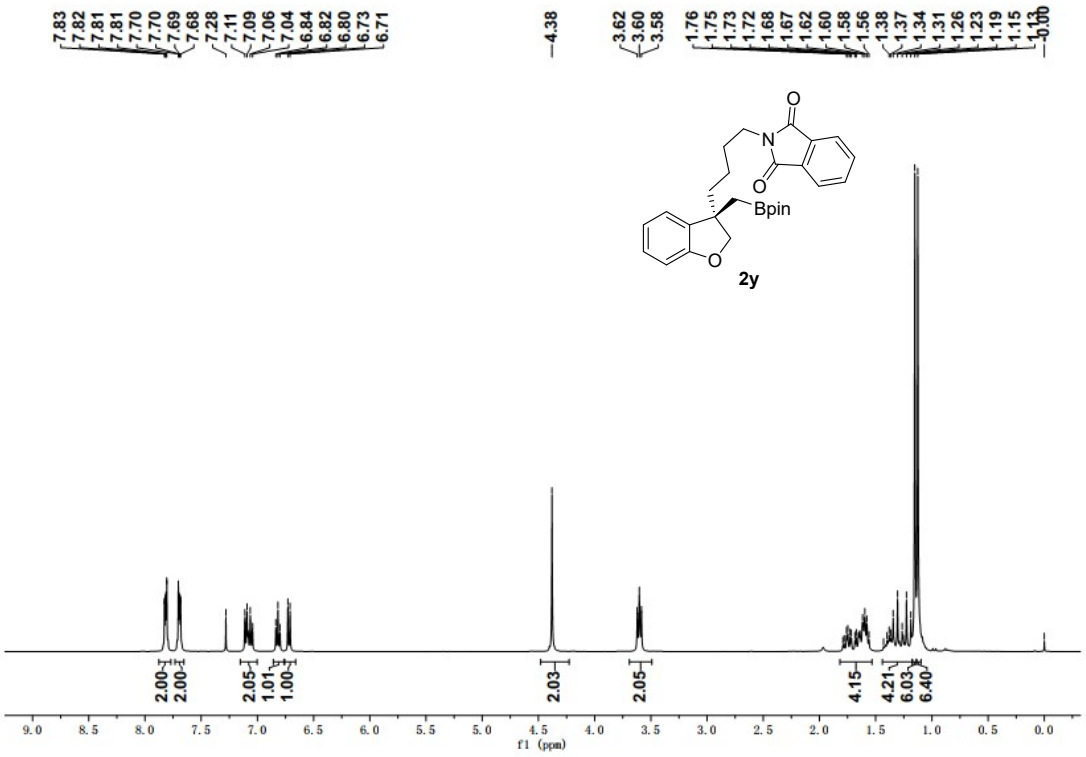
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.237	34.953	154.683	49.90	66.92	n.a.
2		18.610	35.090	76.477	50.10	33.08	n.a.
Total:			**70.043**	**231.159**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.573	2.207	7.141	1.42	1.98	n.a.
2		19.007	153.517	354.423	98.58	98.02	n.a.
Total:			**155.725**	**361.564**	**100.00**	**100.00**	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7.11
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1.38
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1.34
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1.26
1.23
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O
N
O
Bpin
O
2y
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2.00
2.05
1.01
1.00
2.03
2.05
4.15
4.21
6.03
6.40
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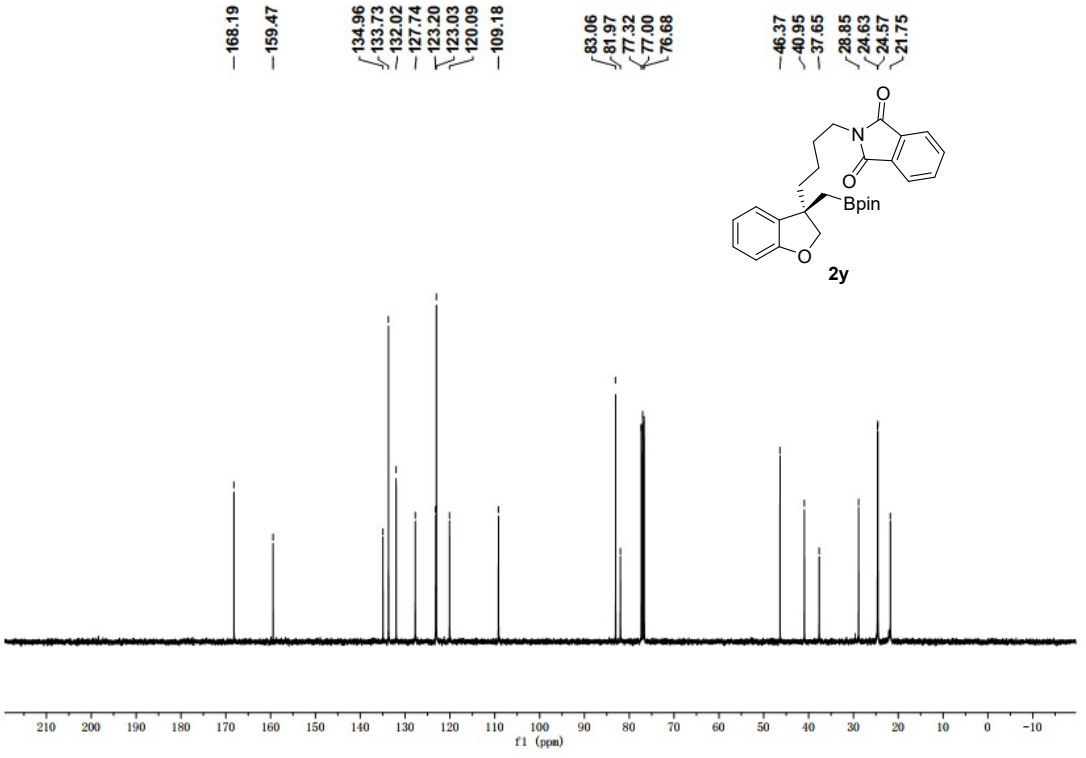
f1 (ppm)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40.95
37.65
28.85
24.63
24.57
21.75
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Bpin
O
2y
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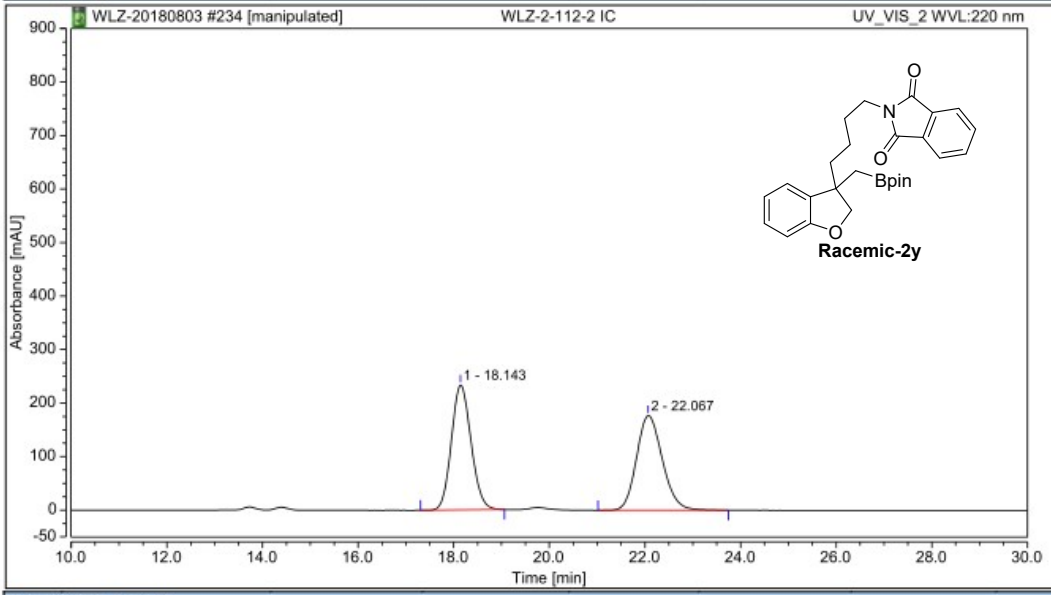
f1 (ppm)

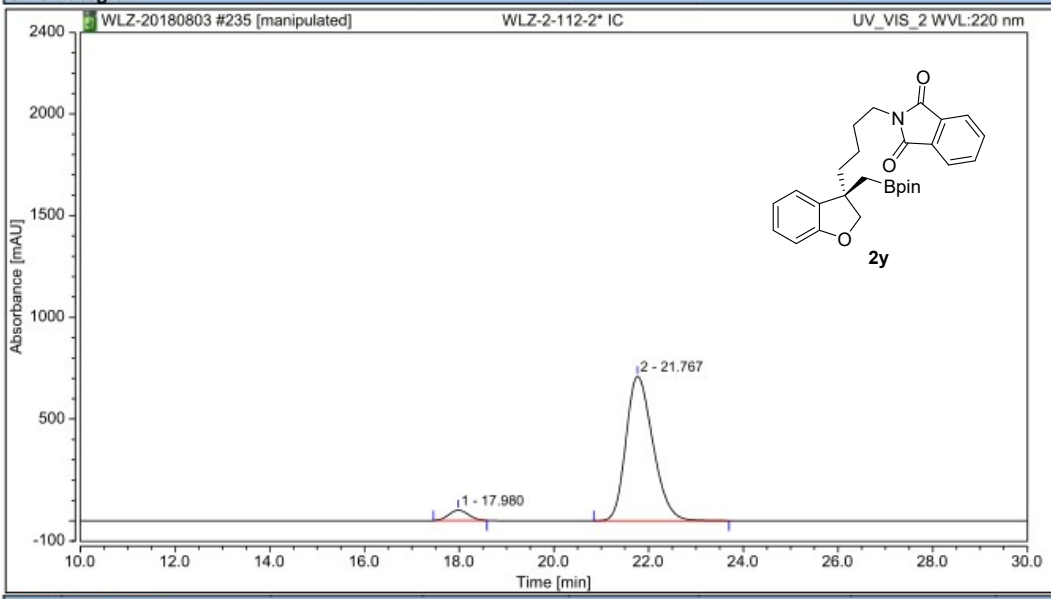
Chromatogram



Integration Results

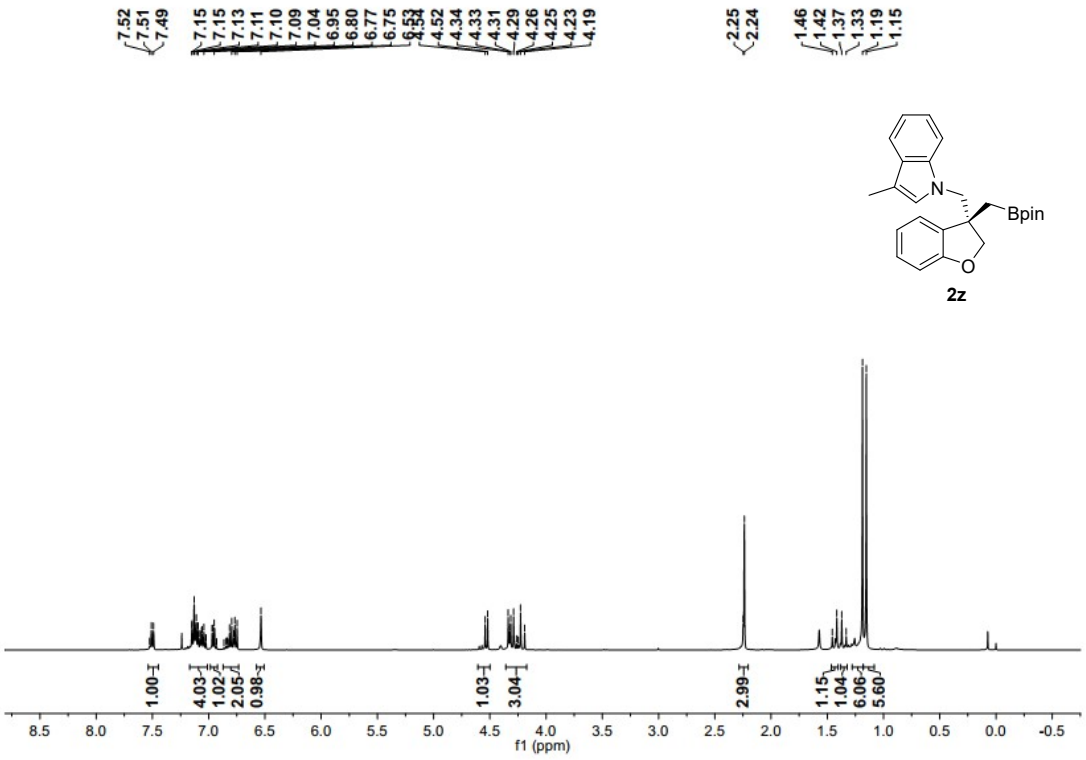
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.143	111.572	233.710	50.10	56.89	n.a.
2		22.067	111.112	177.068	49.90	43.11	n.a.
Total:			**222.684**	**410.778**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.980	24.634	51.034	4.98	6.70	n.a.
2		21.767	470.062	711.156	95.02	93.30	n.a.
Total:			**494.696**	**762.190**	**100.00**	**100.00**	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1.04
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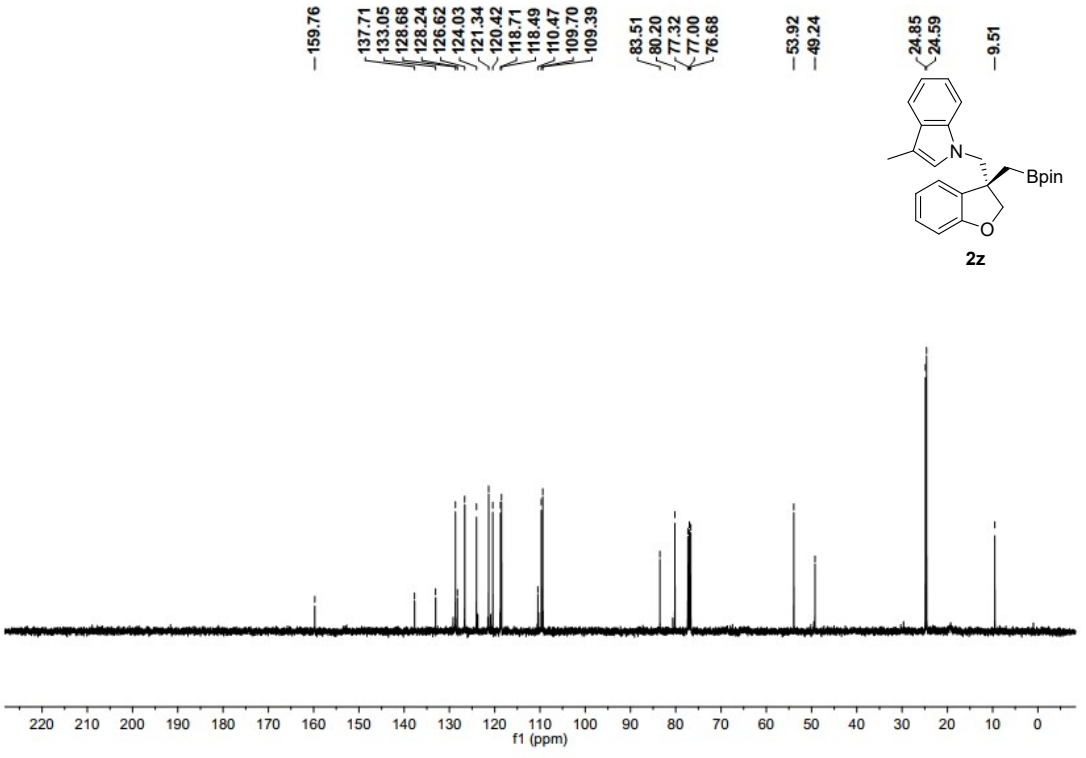
f1 (ppm)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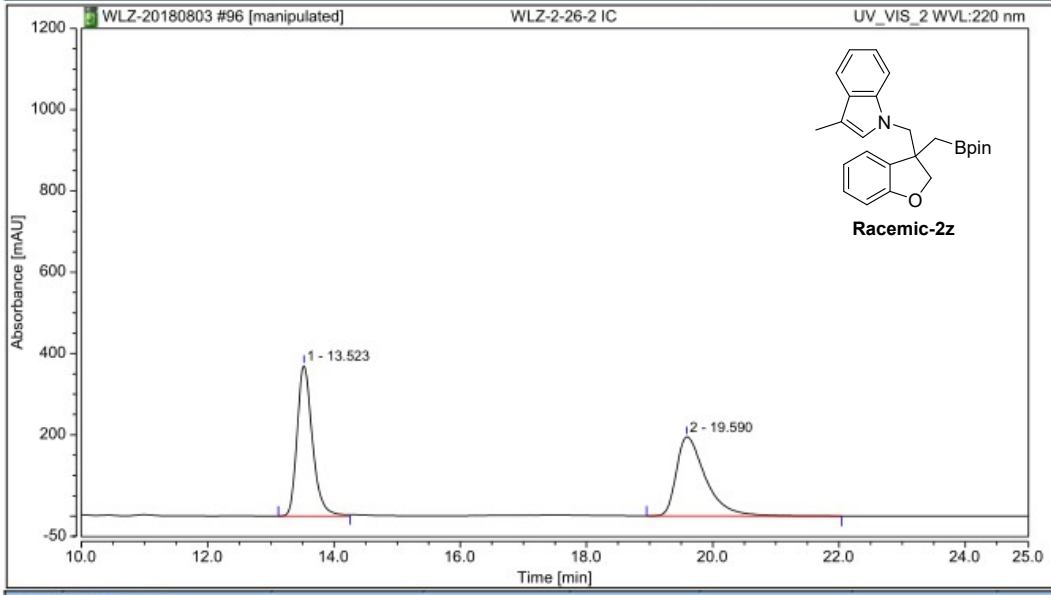
24.59
9.51
Bpin
2z
f1 (ppm)

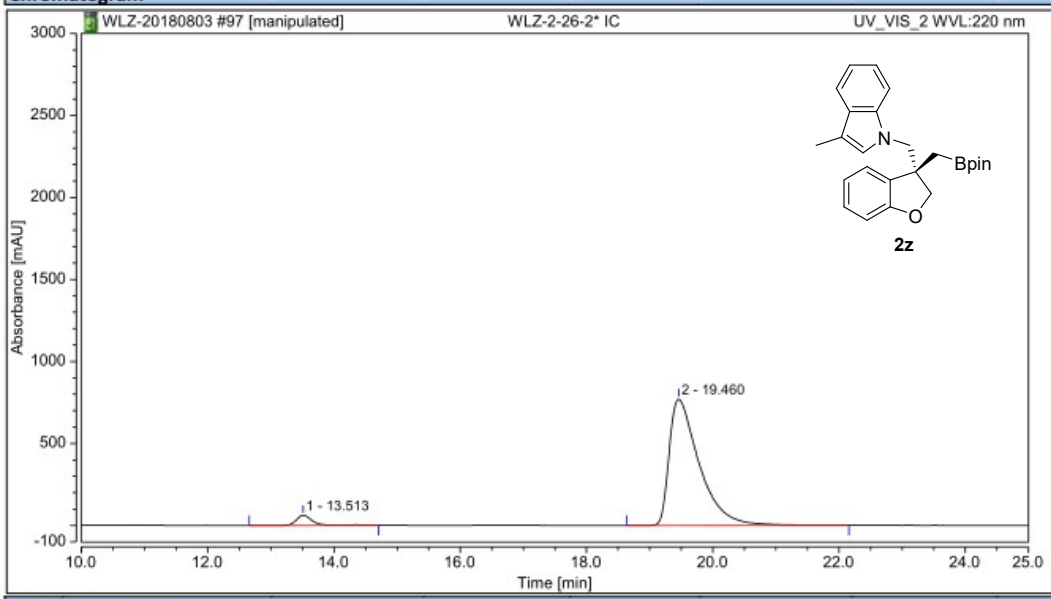
Chromatogram



Integration Results

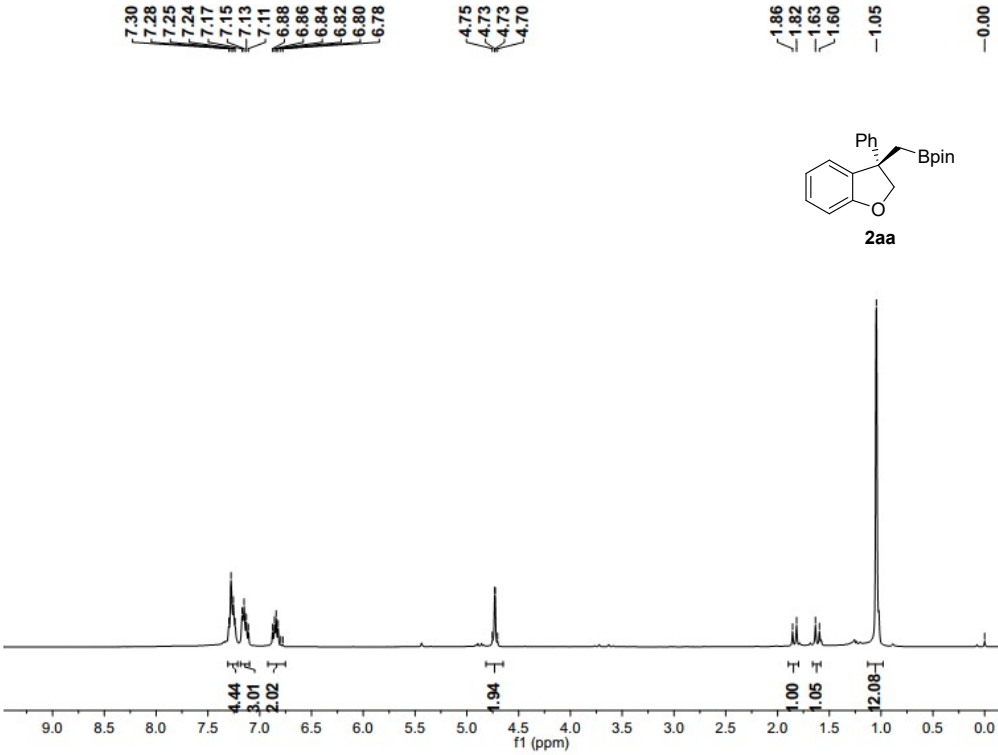
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.523	104.281	370.472	49.93	65.53	n.a.
2		19.590	104.587	194.884	50.07	34.47	n.a.
Total:			**208.869**	**565.356**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.513	18.398	61.422	4.16	7.38	n.a.
2		19.460	424.263	770.632	95.84	92.62	n.a.
Total:			**442.660**	**832.054**	**100.00**	**100.00**	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7.24
7.17
7.15
7.13
7.11
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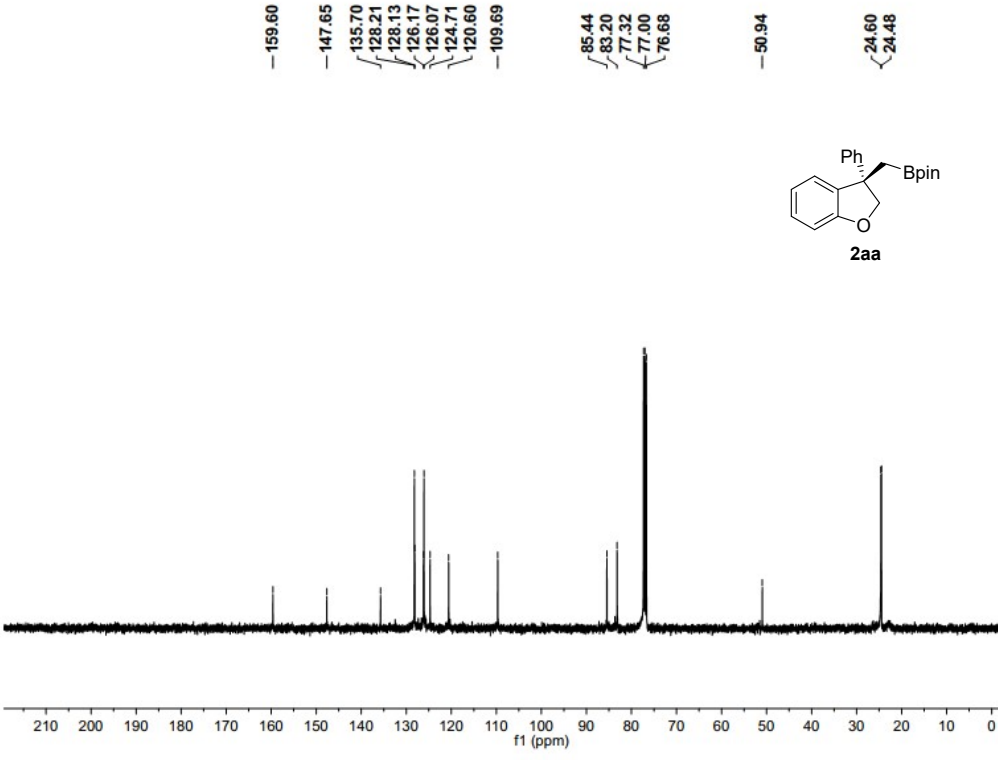
6.86
6.84
6.82
6.80
6.78
4.75
4.73
4.73
4.70
1.86
1.82
1.63
1.60
1.05
0.00
Ph
Bpin
O
2aa
4.44
3.01
2.02
1.94
1.00
1.05
12.08
f1 (ppm)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135.70
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128.13
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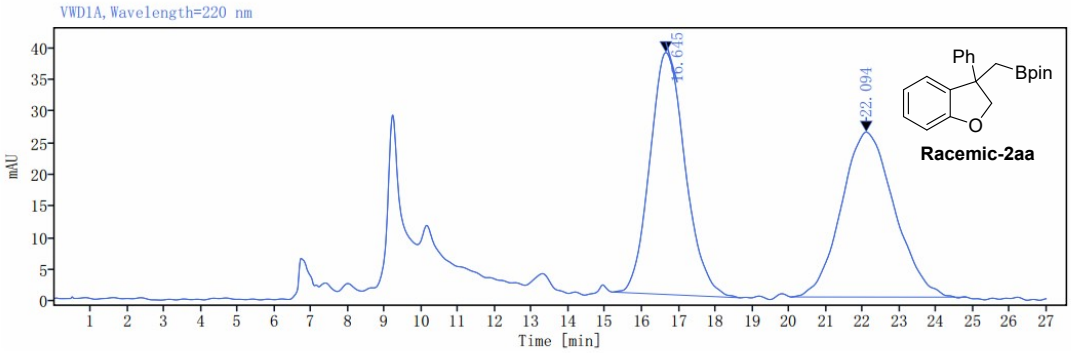
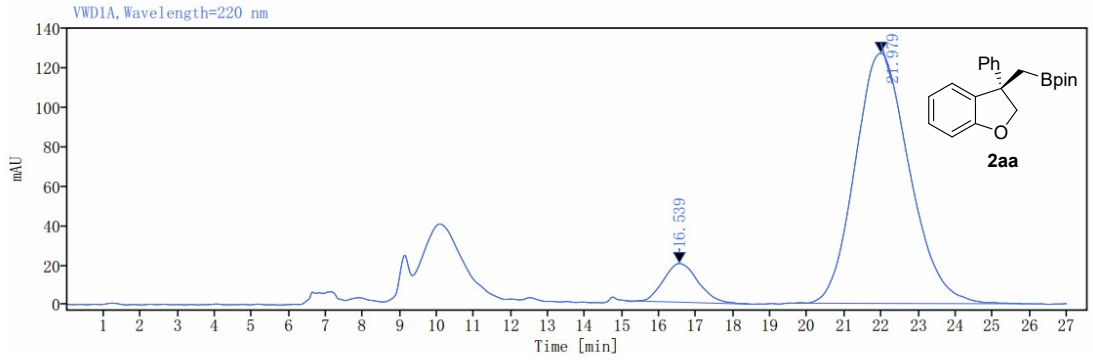
126.07
124.71
120.60
109.69
85.44
83.20
77.32
77.00
76.68
50.94
24.60
24.48
Ph
Bpin
O
2aa
f1 (ppm)



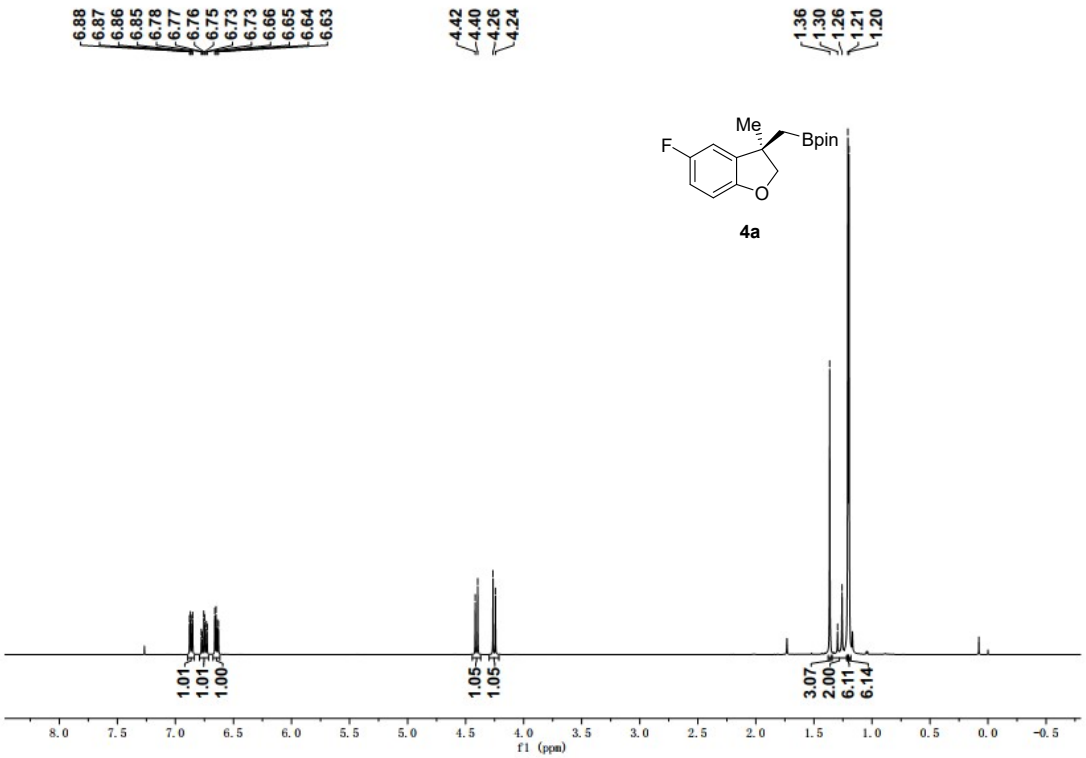
VWD1A, Wavelength=220 nm

Ret. Time [min]	Area	Height	Height%	Area%
16.645	2557.69	38.15	59.46	49.51
22.094	2608.13	26.01	40.54	50.49
Total.	5165.81	64.16	100.00	100.00



VWD1A, Wavelength=220 nm

Ret. Time [min]	Area	Height	Height%	Area%
16.539	1271.31	19.56	13.39	8.97
21.979	12897.34	126.53	86.61	91.03
Total.	14168.65	146.09	100.00	100.00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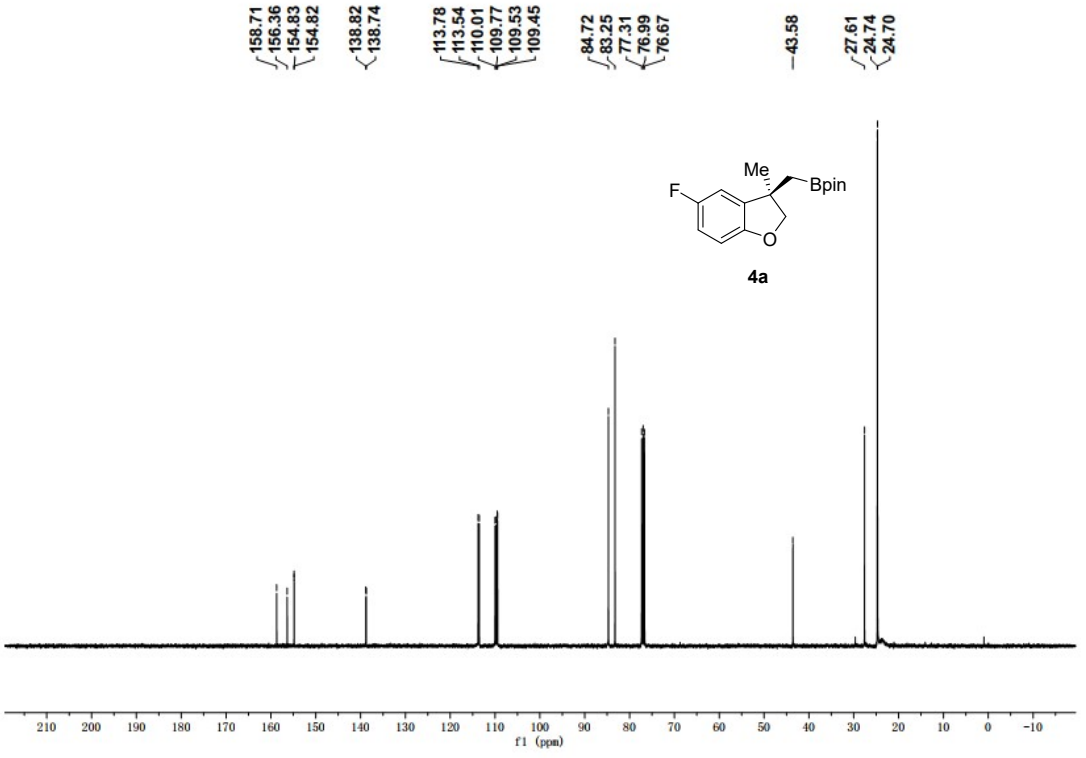
6.86
6.85
6.78
6.77
6.76
6.75
6.73
6.73
6.66
6.65
6.64
6.63
4.42
4.40
4.26
4.24
1.36
1.30
1.26
1.21
1.20
Me
Bpin
F
O
4a
1.01
1.01
1.00
1.05
1.05
3.07
2.00
6.11
6.14
f1 (ppm)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154.82
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138.74
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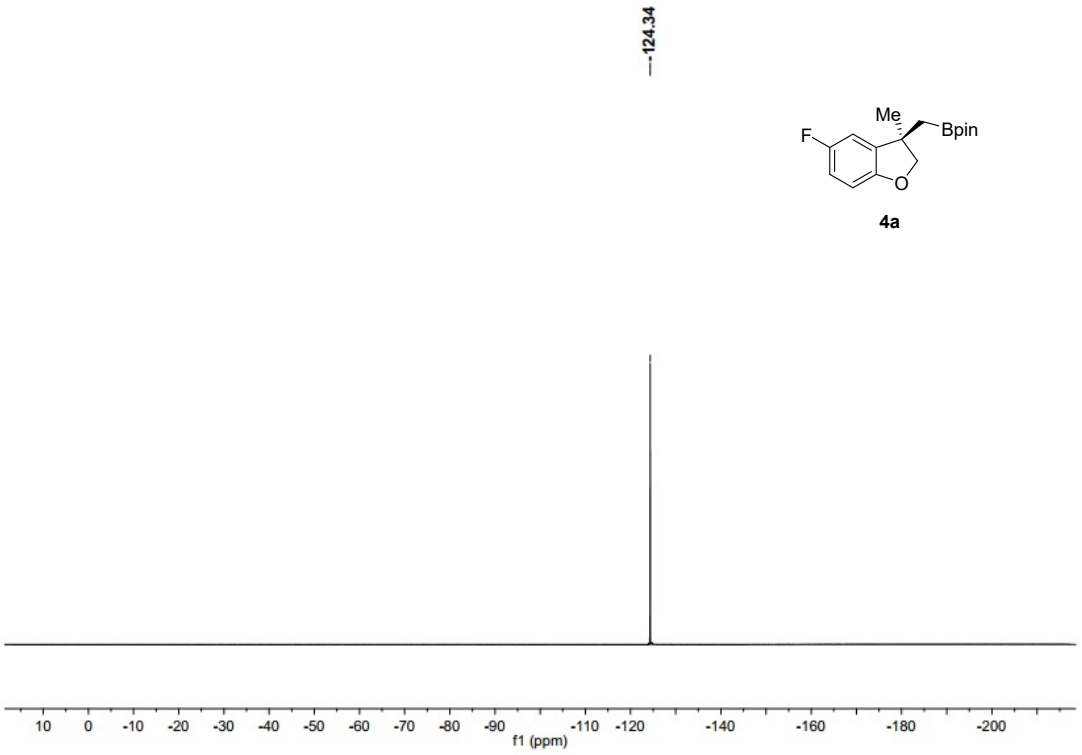
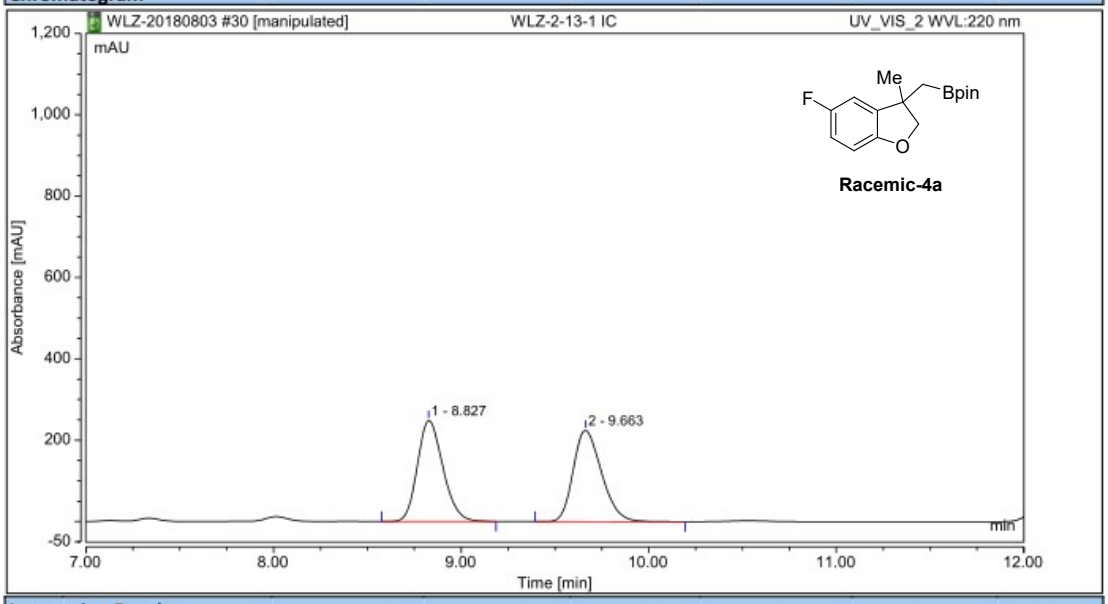
113.54
110.01
109.77
109.53
109.45
84.72
83.25
77.31
76.99
76.67
43.58
27.61
24.74
24.70
Me
Bpin
F
O
4a
f1 (ppm)



4a

Chromatogram

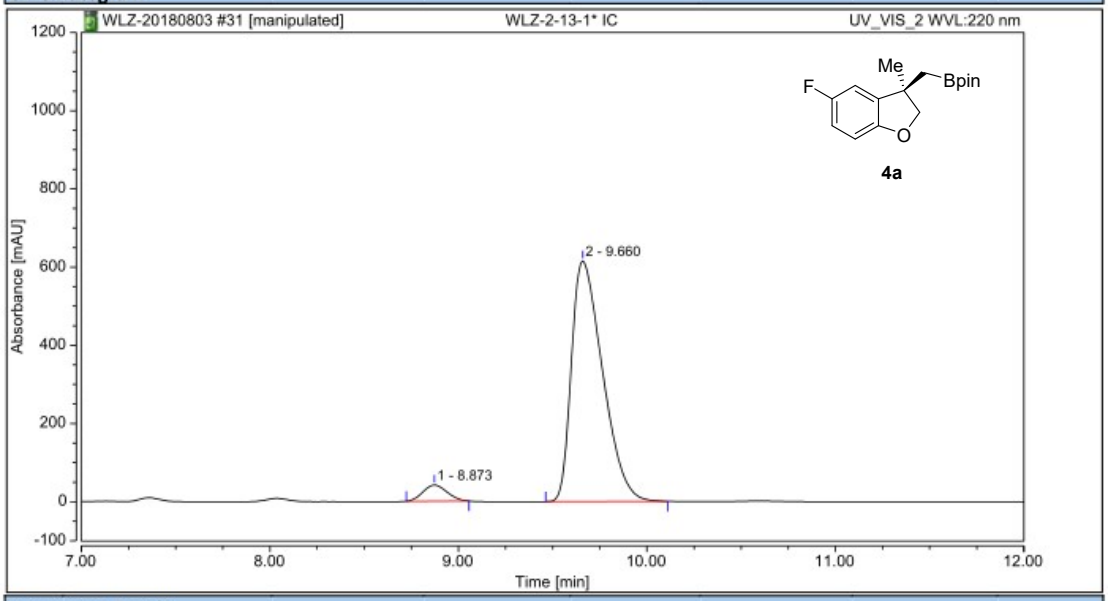


Racemic-4a

Integration Results

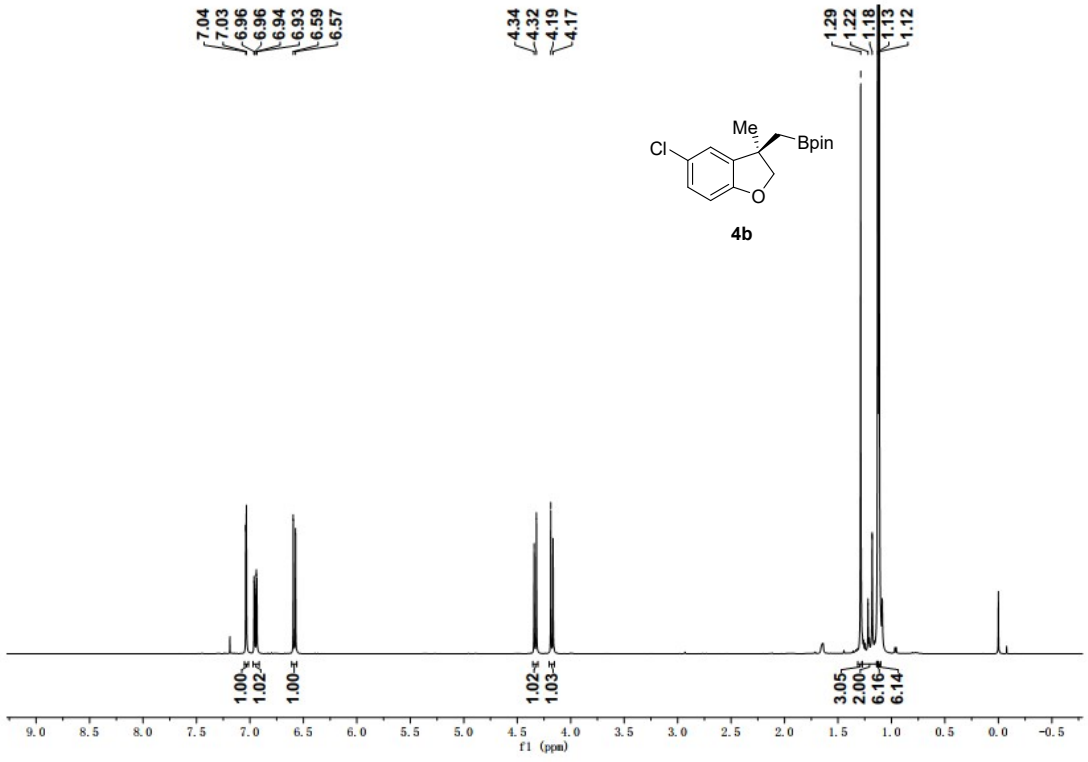
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.827	39.297	248.570	49.99	52.55	n.a.
2		9.663	39.305	224.470	50.01	47.45	n.a.
Total:			**78.602**	**473.039**	**100.00**	**100.00**	

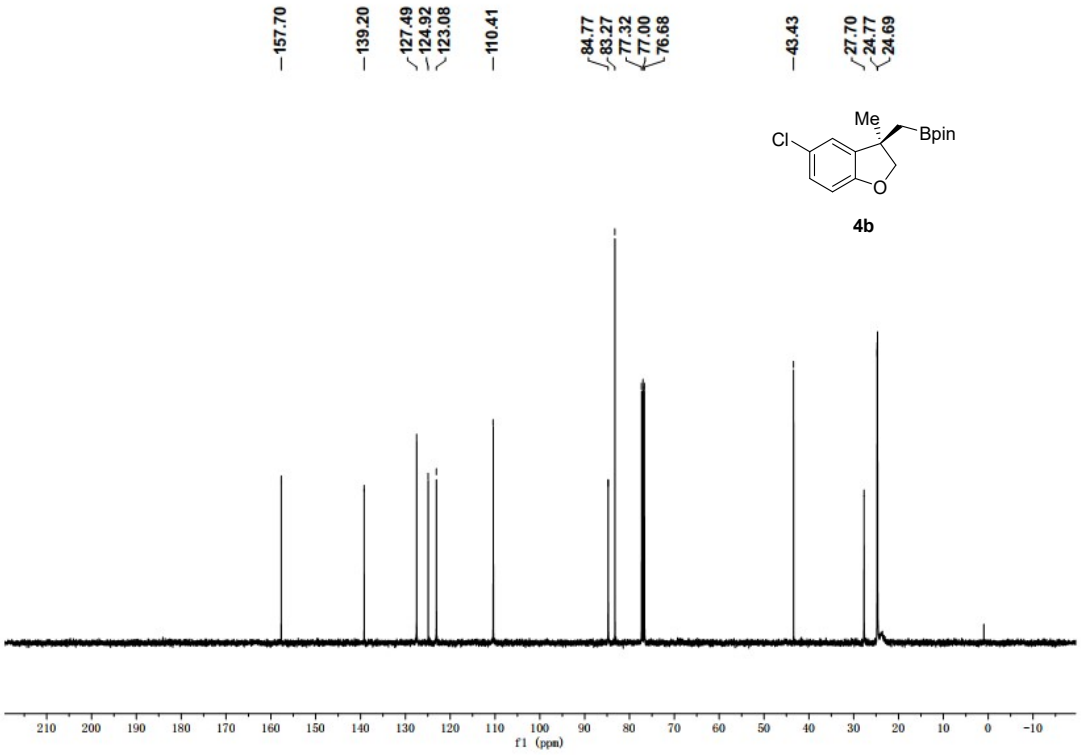
Chromatogram



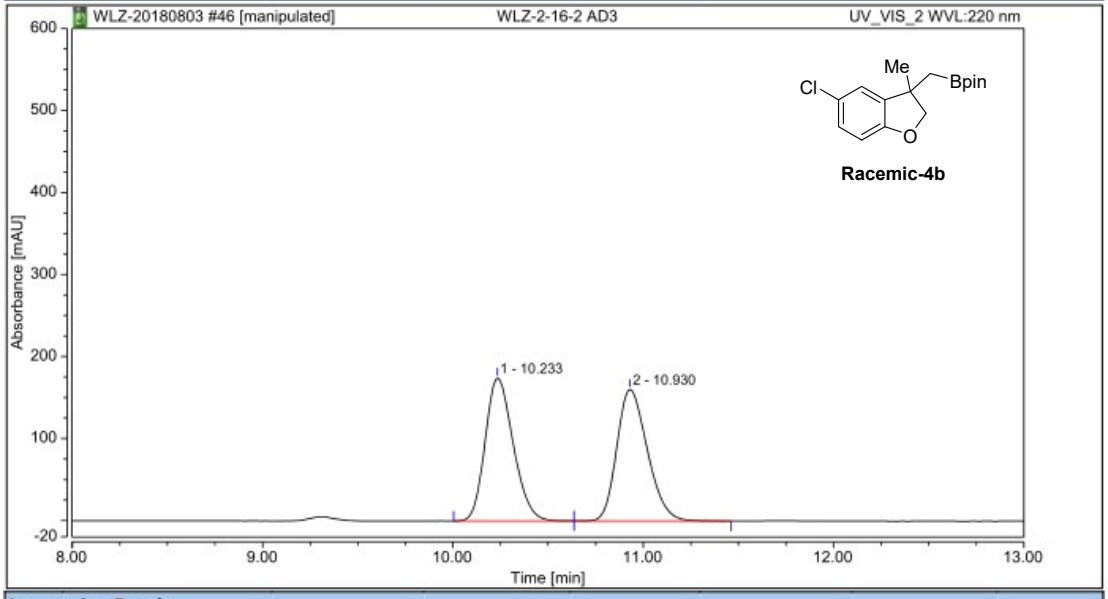
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.873	6.121	41.304	4.94	6.29	n.a.
2		9.660	117.877	615.363	95.06	93.71	n.a.
Total:			**123.998**	**656.667**	**100.00**	**100.00**	





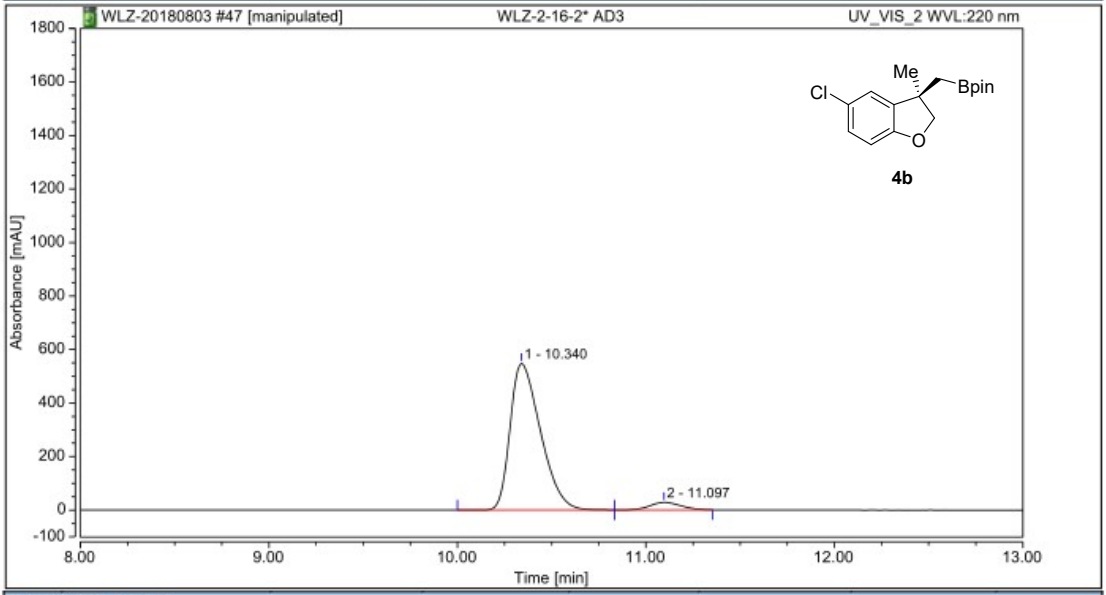
Chromatogram



Integration Results

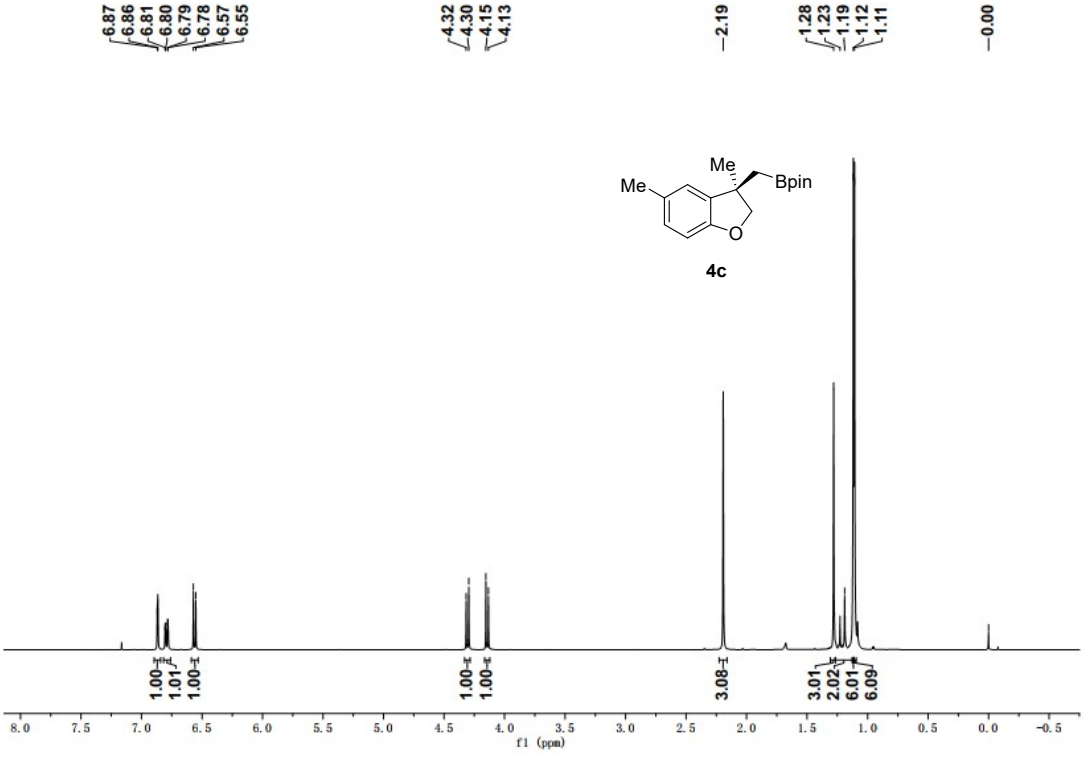
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.233	29.855	174.430	49.96	52.07	n.a.
2		10.930	29.904	160.567	50.04	47.93	n.a.
Total:			**59.760**	**334.997**	**100.00**	**100.00**	

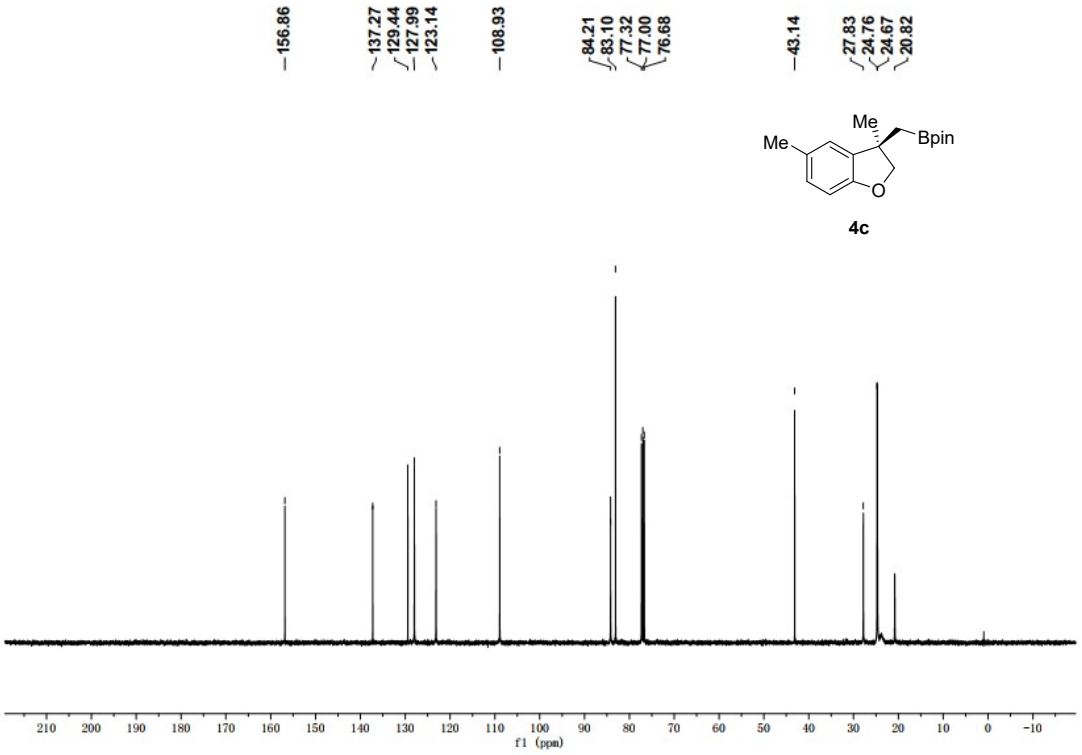
Chromatogram



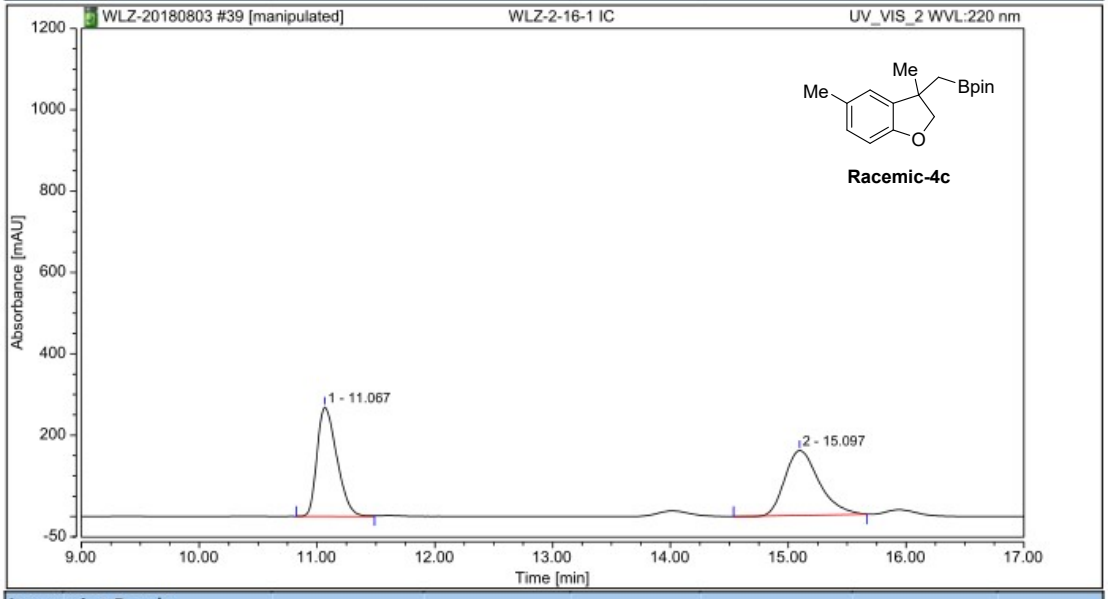
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.340	102.165	547.571	95.07	95.14	n.a.
2		11.097	5.293	27.999	4.93	4.86	n.a.
Total:			**107.458**	**575.570**	**100.00**	**100.00**	



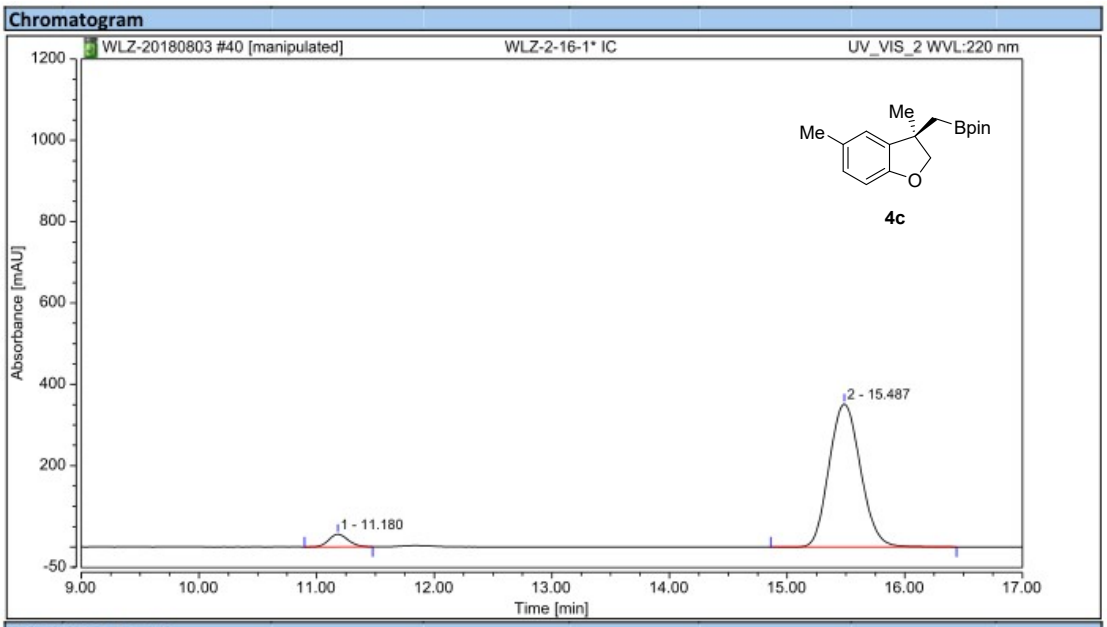


Chromatogram



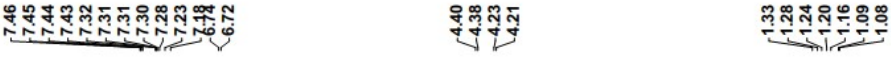
Integration Results

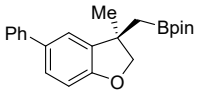
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.067	52.393	268.443	49.32	62.72	n.a.
2		15.097	53.832	159.555	50.68	37.28	n.a.
Total:			**106.225**	**427.998**	**100.00**	**100.00**	



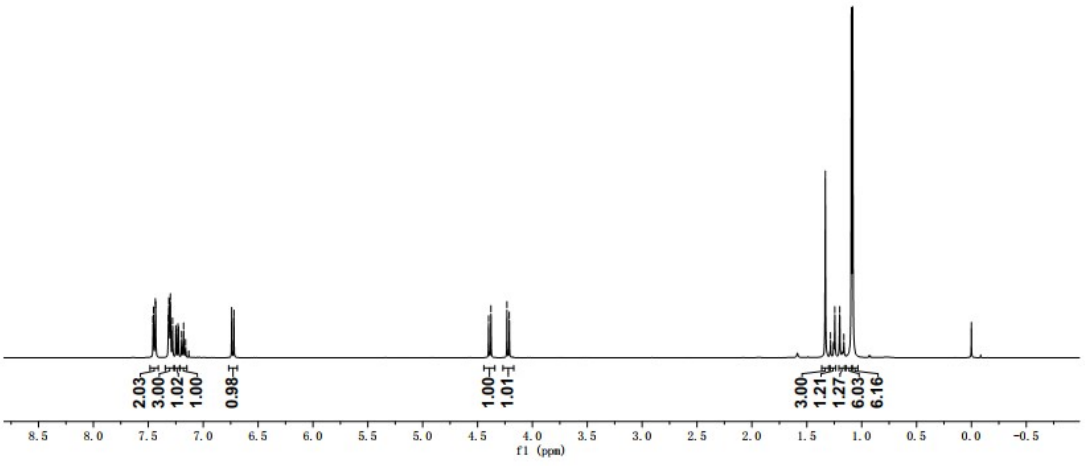
Integration Results

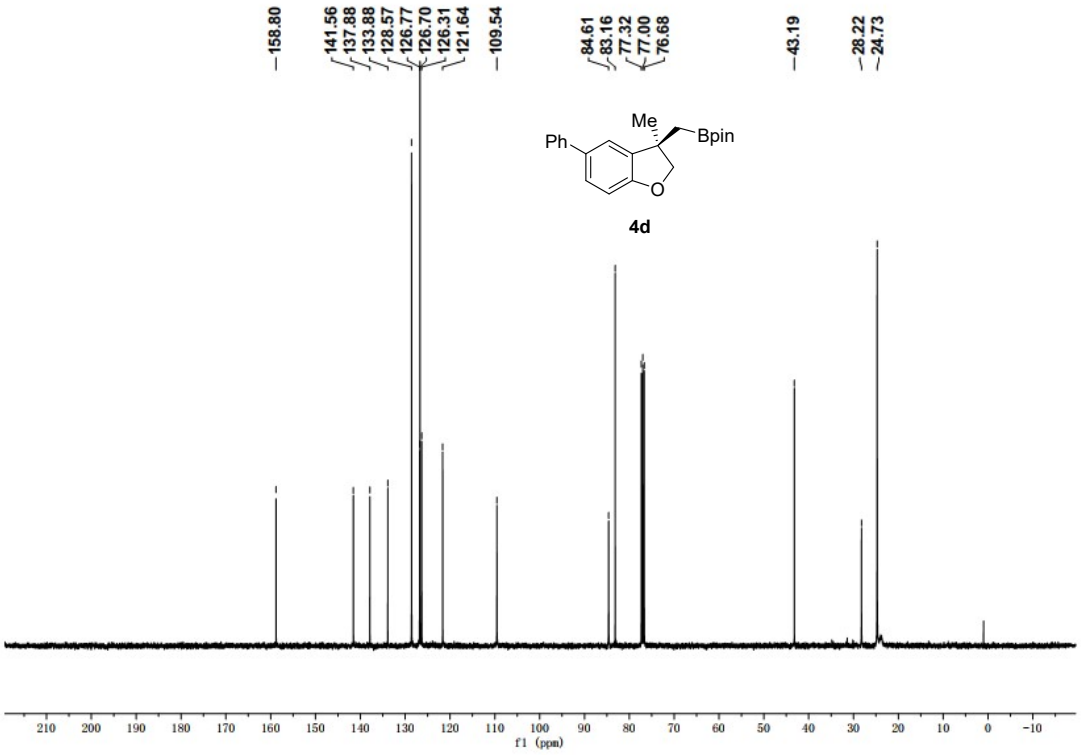
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.180	5.858	30.785	5.09	8.05	n.a.
2		15.487	109.162	351.748	94.91	91.95	n.a.
Total:			**115.019**	**382.533**	**100.00**	**100.00**	

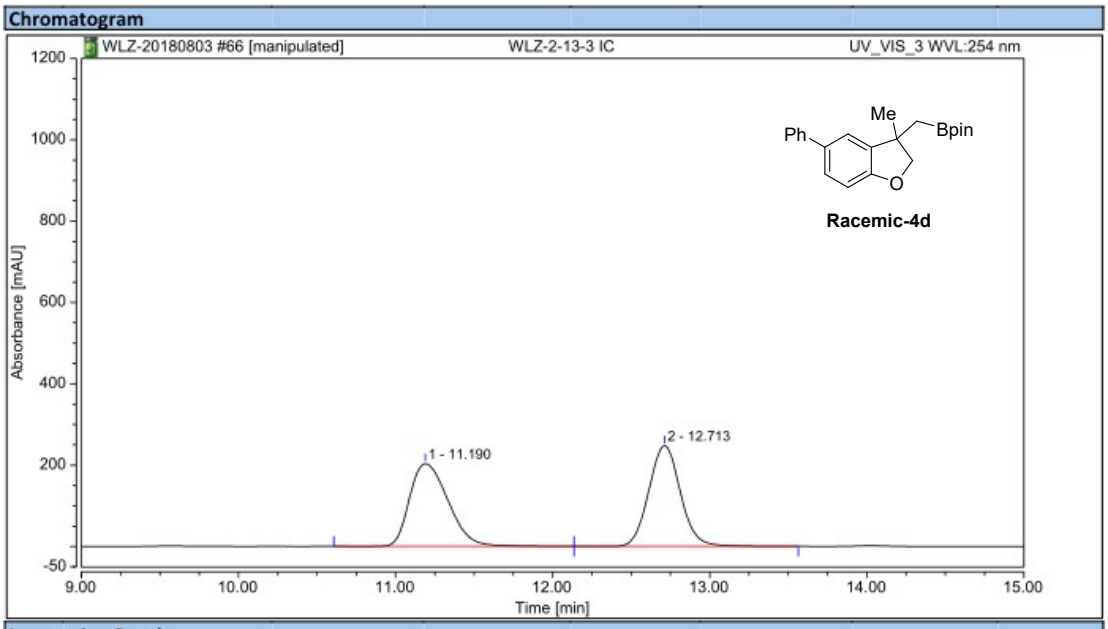




4d



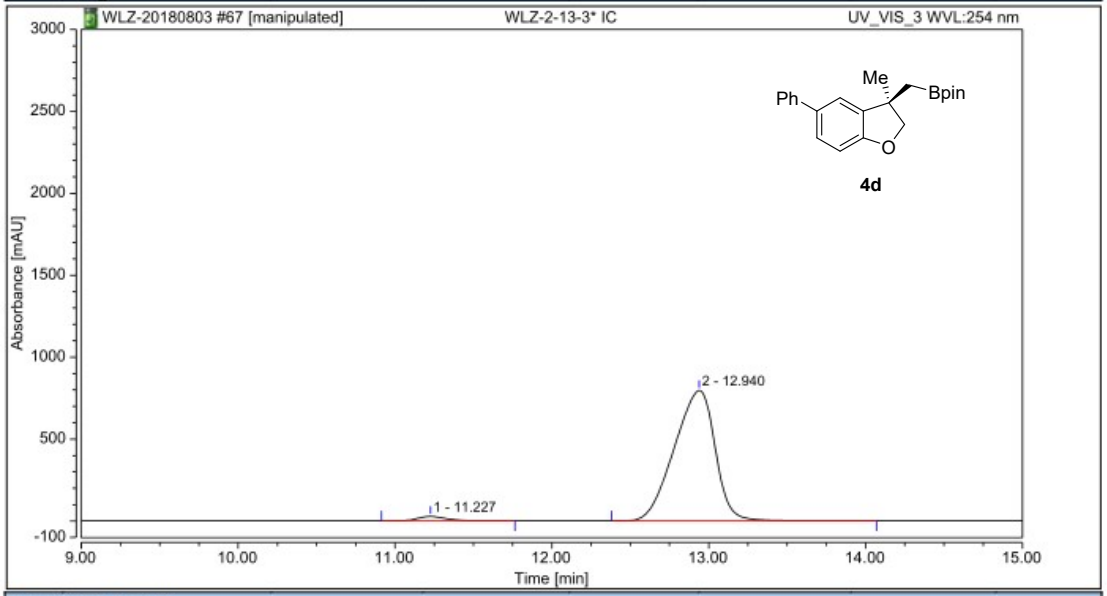




Integration Results

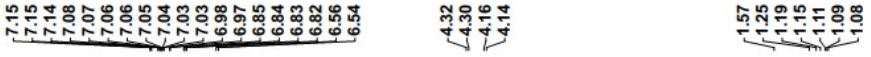
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.190	57.844	203.283	49.97	45.09	n.a.
2		12.713	57.908	247.557	50.03	54.91	n.a.
Total:			**115.752**	**450.840**	**100.00**	**100.00**	

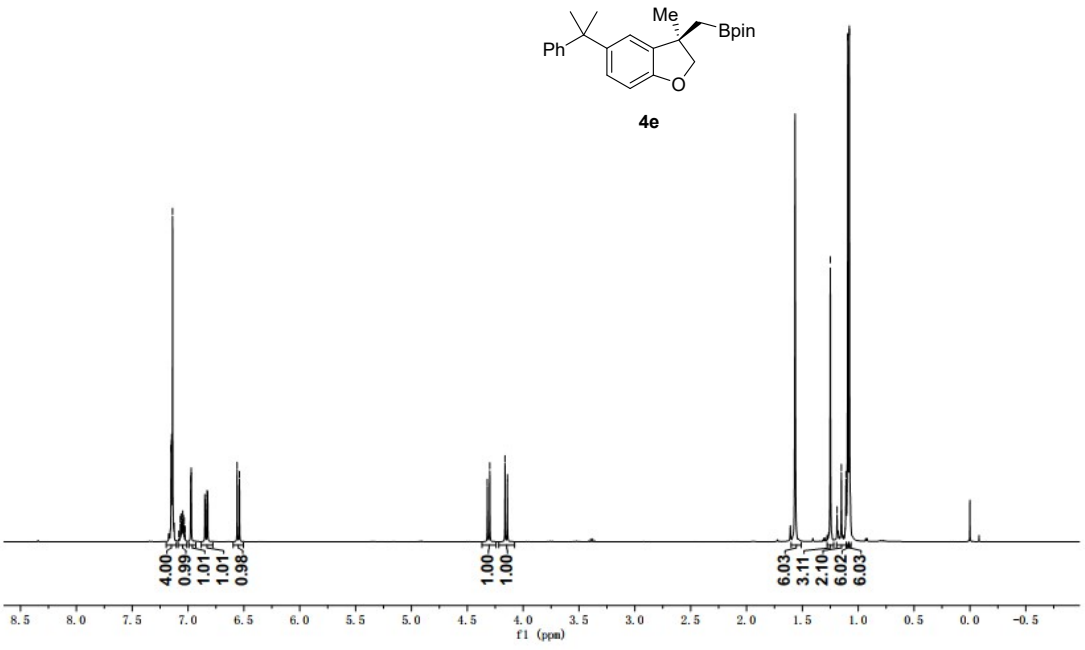
Chromatogram

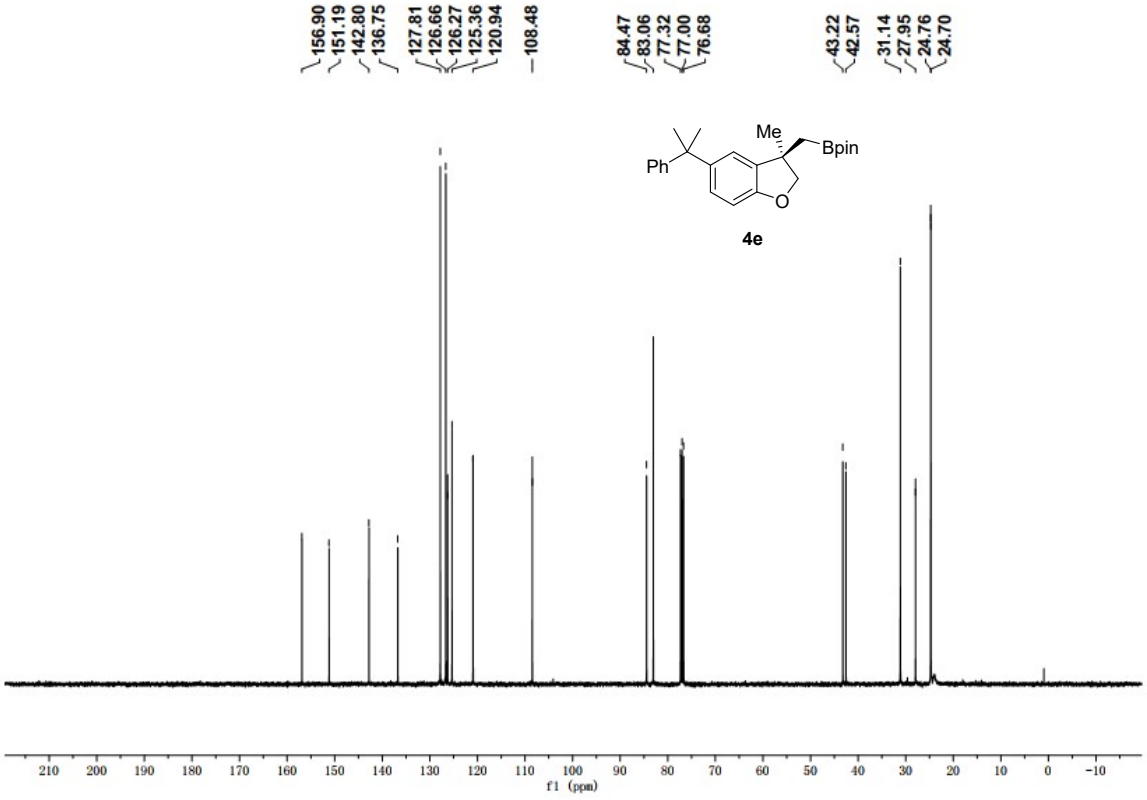


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.227	6.188	27.572	2.49	3.35	n.a.
2		12.940	242.190	796.496	97.51	96.65	n.a.
Total:			**248.378**	**824.068**	**100.00**	**100.00**	







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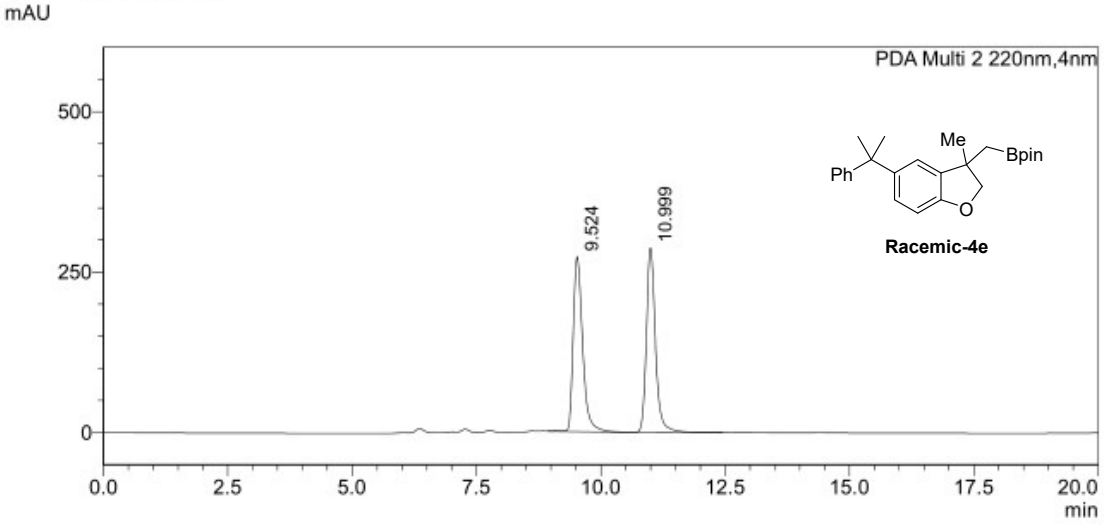
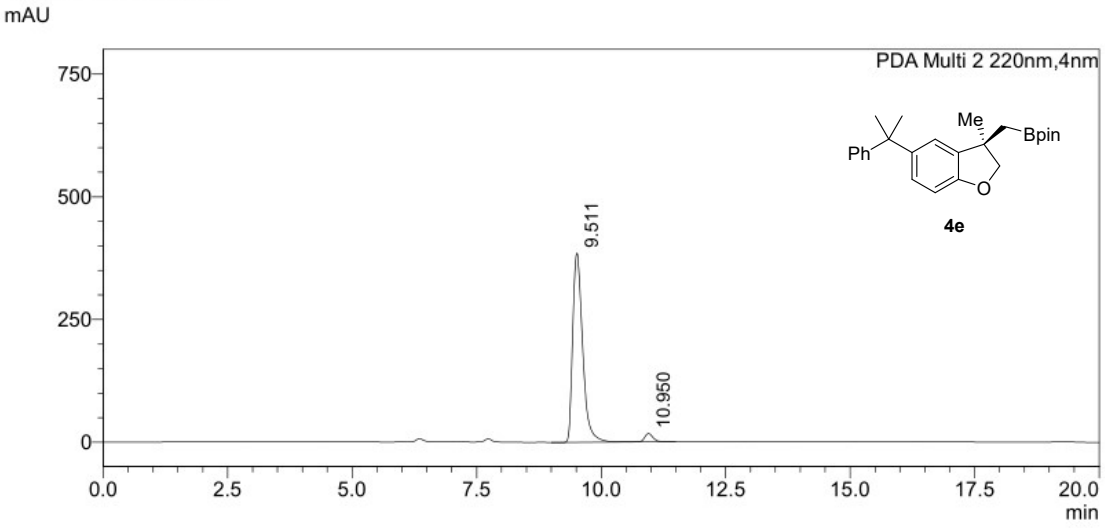


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.524	3591441	49.845	272658	48.687
2	10.999	3613770	50.155	287364	51.313
Total		7205211	100.000	560023	100.000

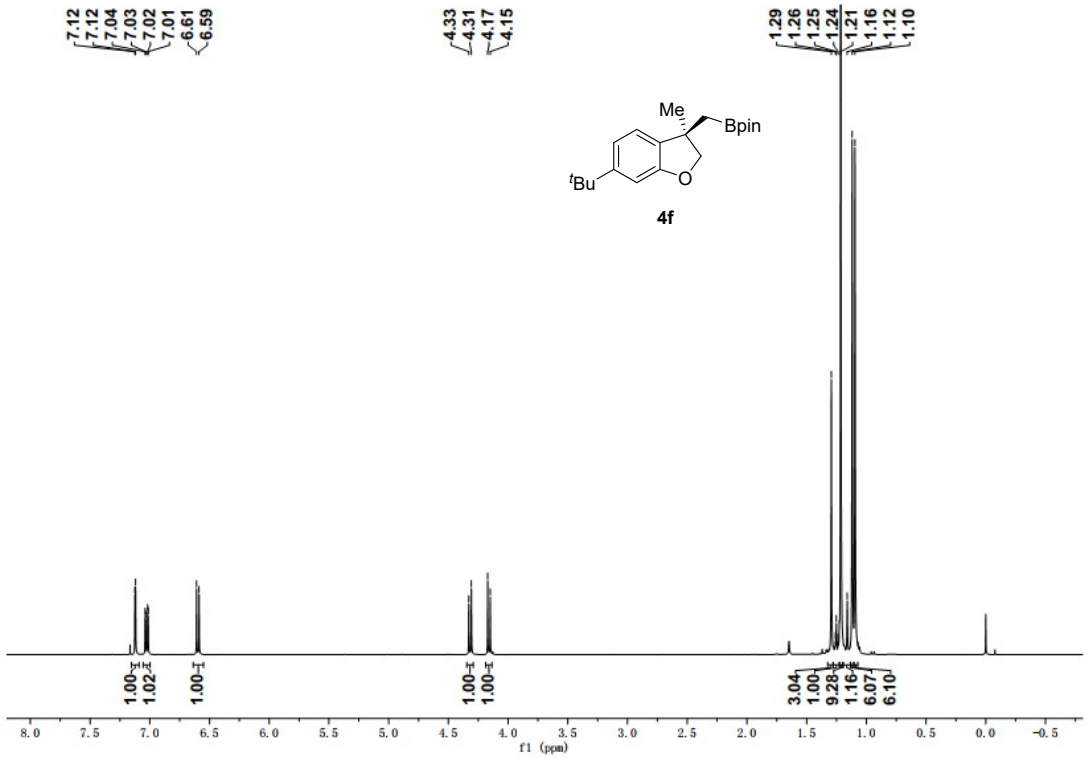
<Chromatogram>

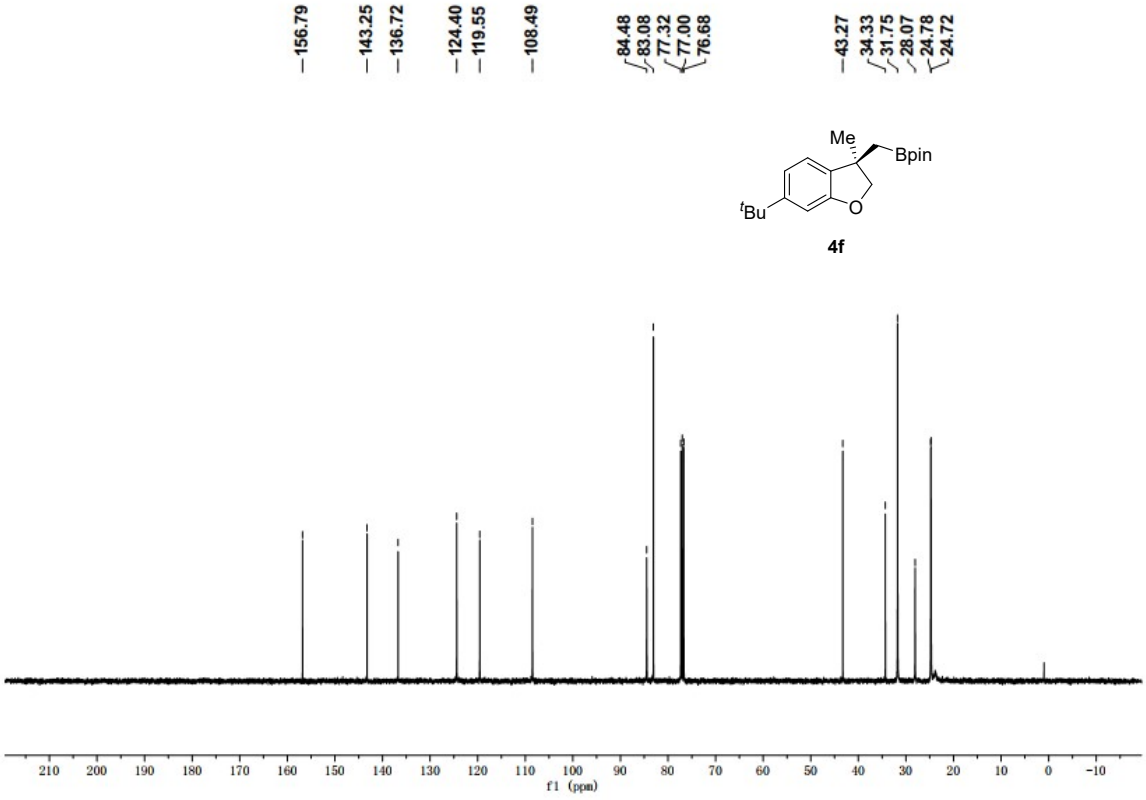


<Peak Table>

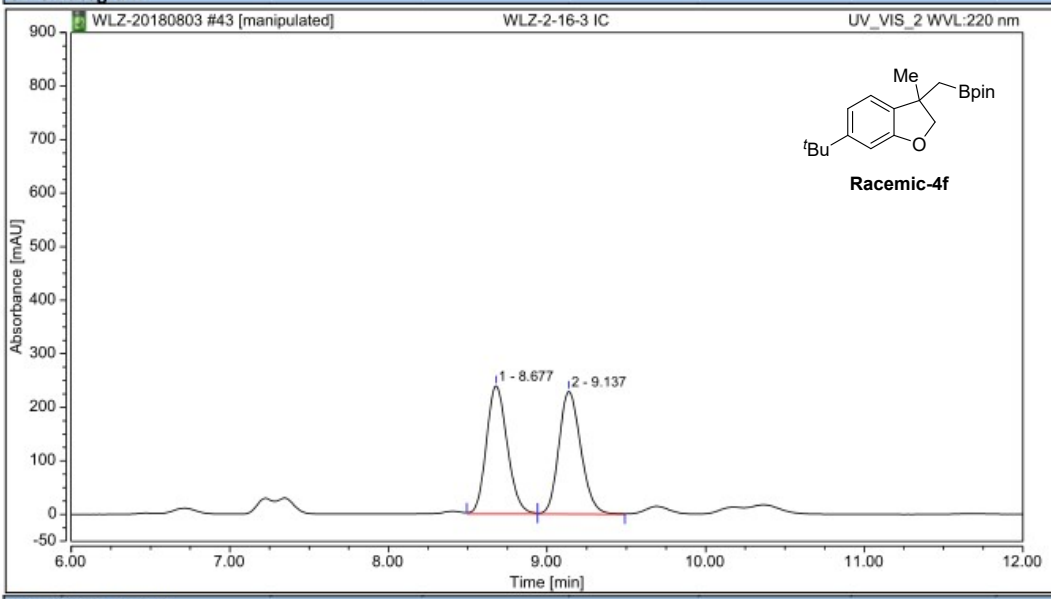
PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.511	5360592	96.165	385696	95.688
2	10.950	213761	3.835	17382	4.312
Total		5574353	100.000	403078	100.000





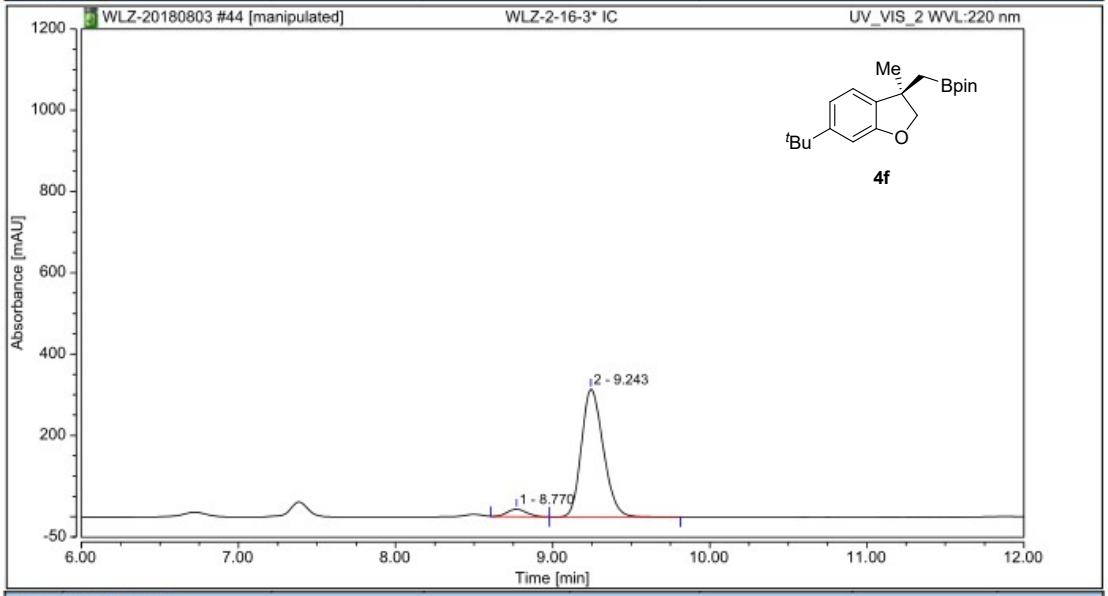
Chromatogram



Integration Results

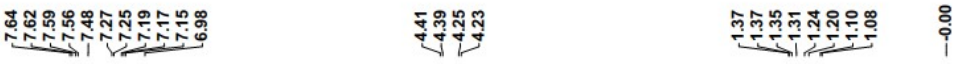
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.677	36.770	239.580	49.88	51.09	n.a.
2		9.137	36.945	229.392	50.12	48.91	n.a.
Total:			**73.715**	**468.972**	**100.00**	**100.00**	

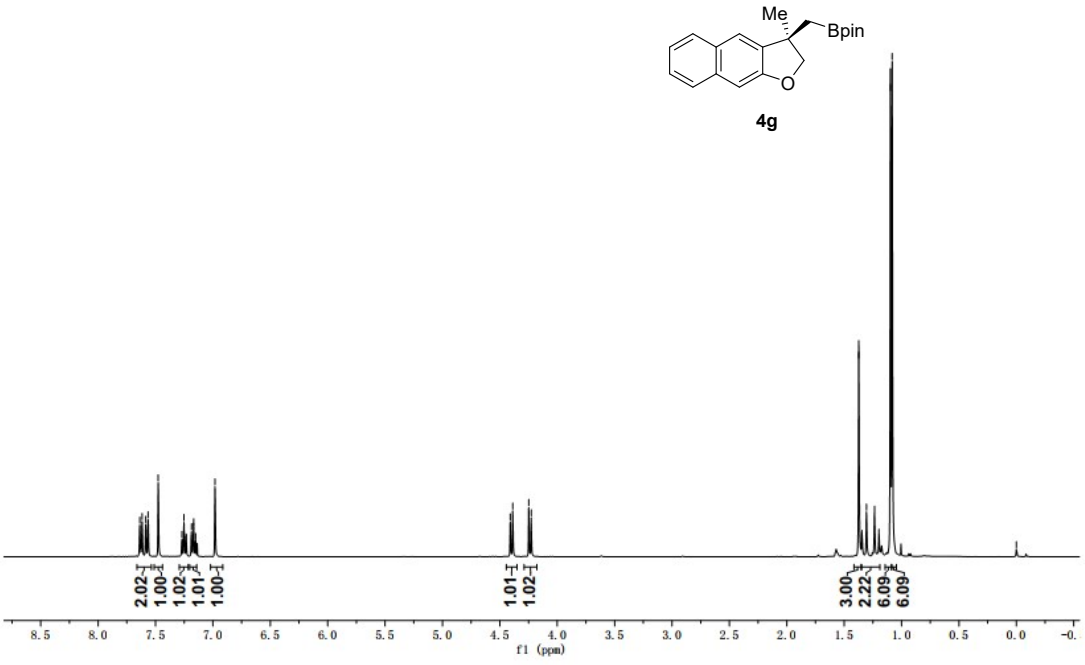
Chromatogram

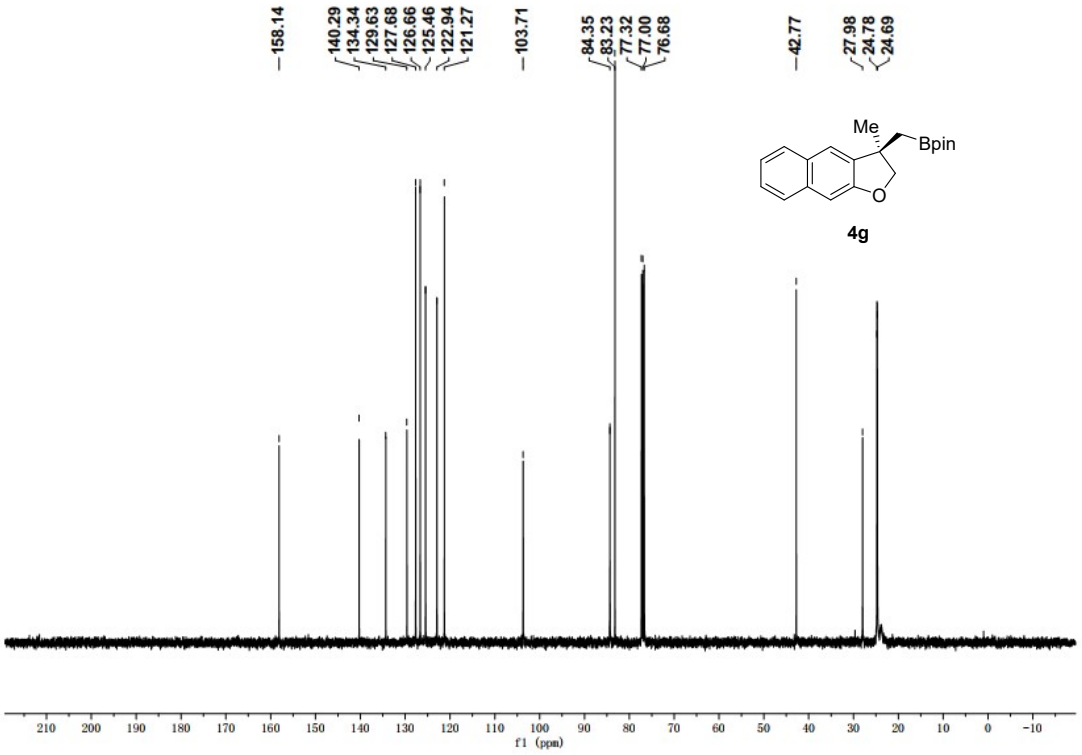


Integration Results

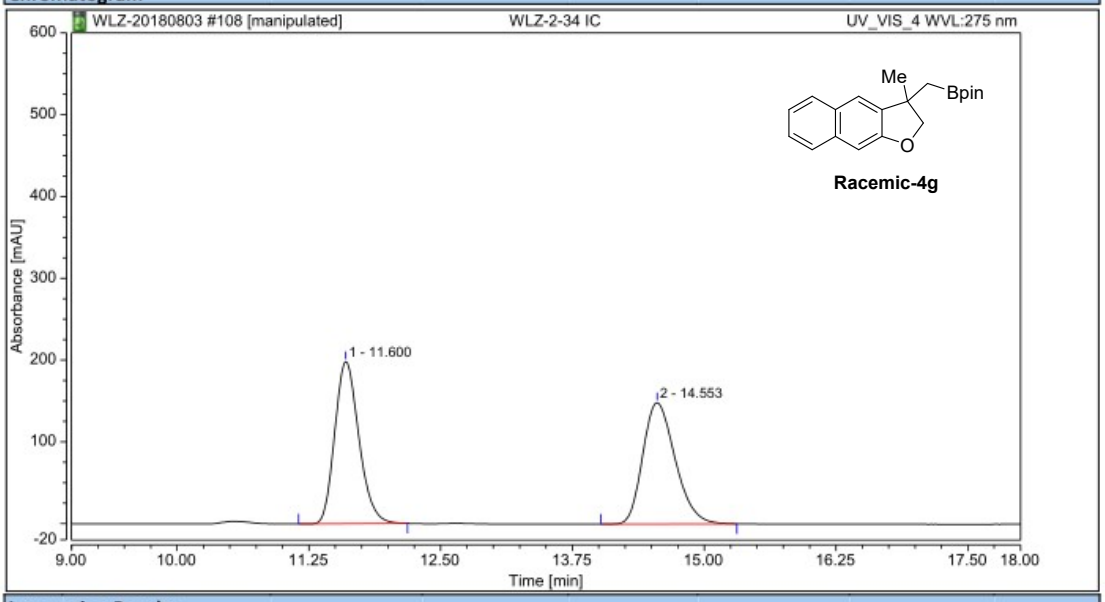
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.770	2.646	18.442	4.94	5.54	n.a.
2		9.243	50.952	314.707	95.06	94.46	n.a.
Total:			**53.598**	**333.149**	**100.00**	**100.00**	







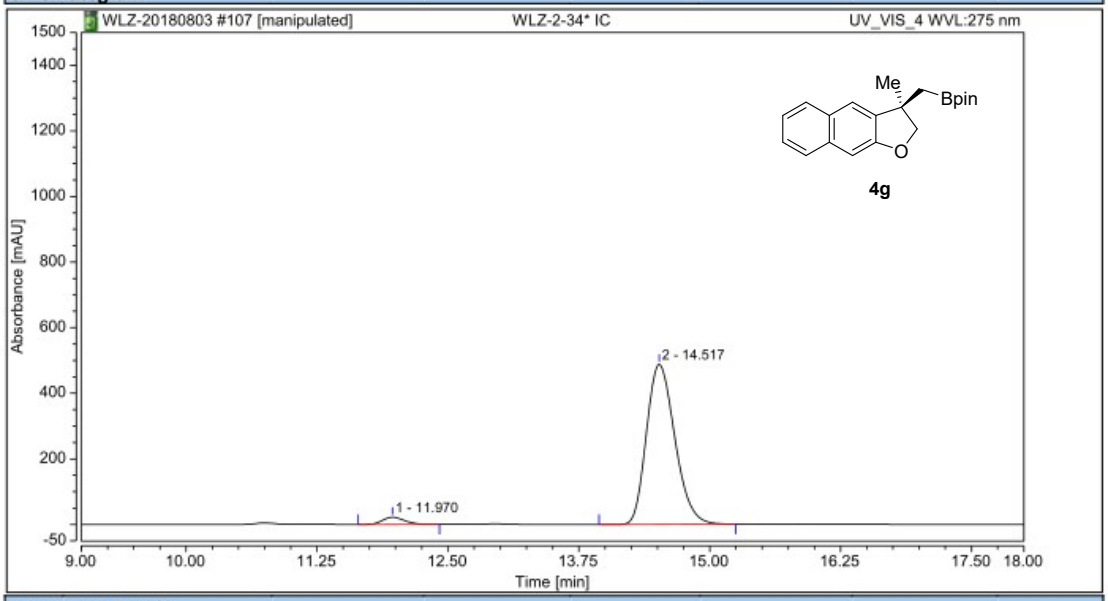
Chromatogram



Integration Results

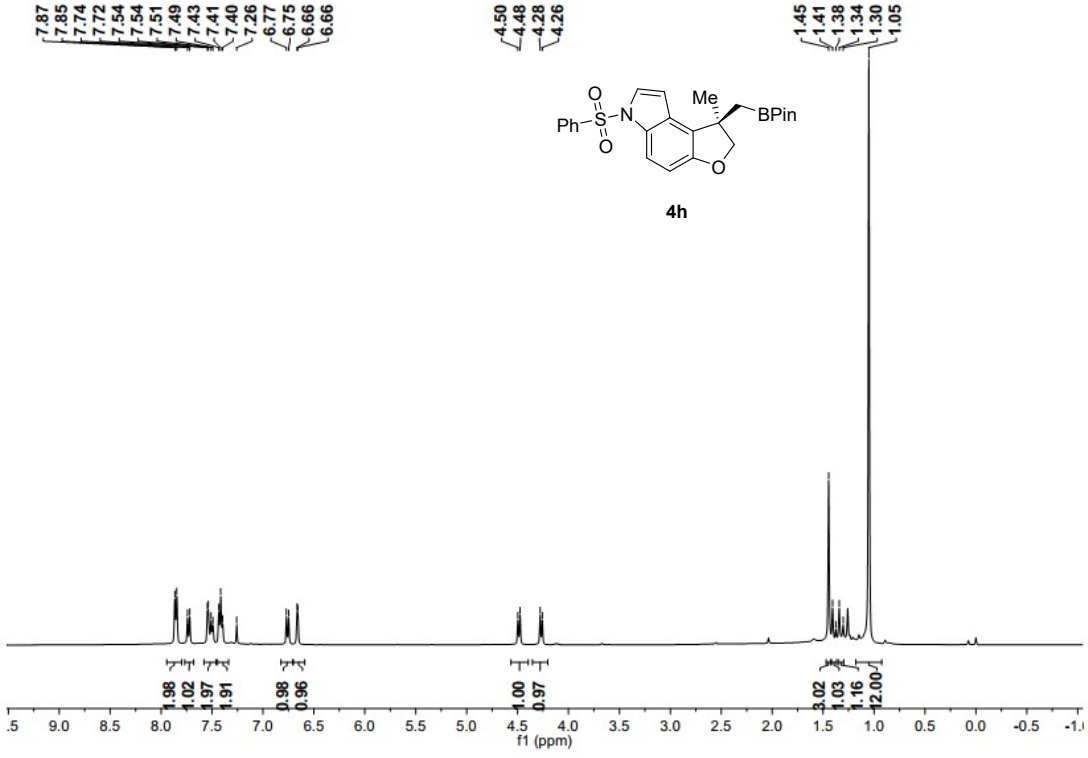
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.600	52.713	198.166	49.91	57.18	n.a.
2		14.553	52.908	148.375	50.09	42.82	n.a.
Total:			**105.621**	**346.541**	**100.00**	**100.00**	

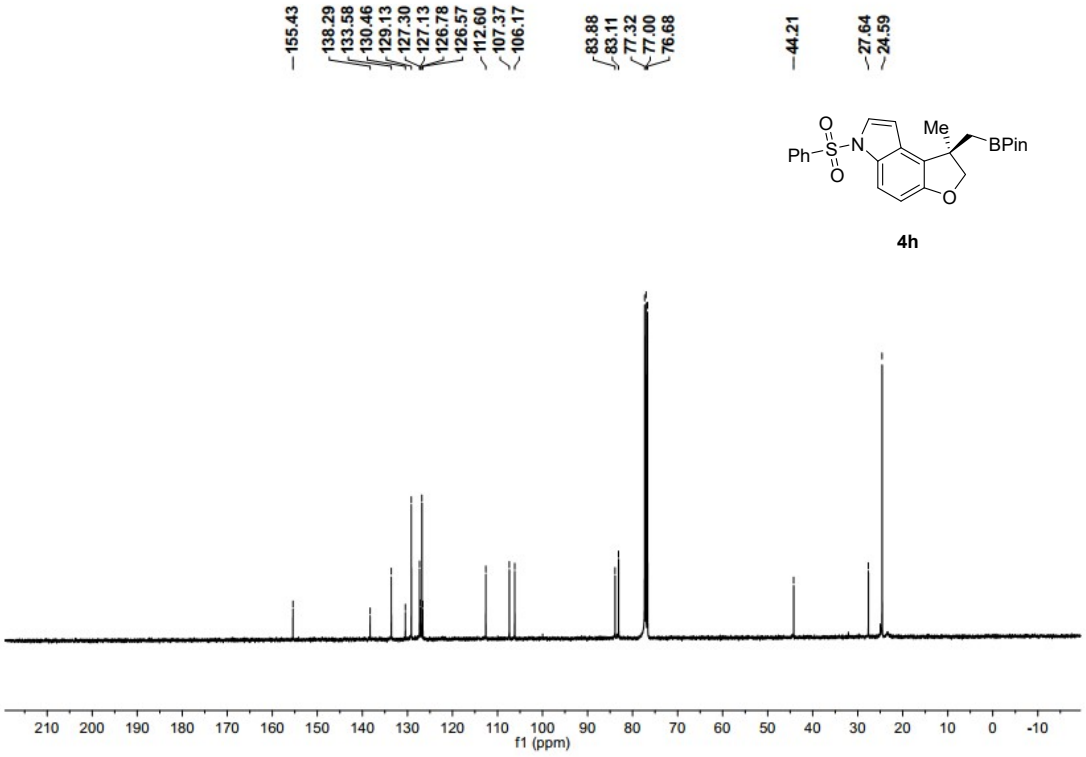
Chromatogram

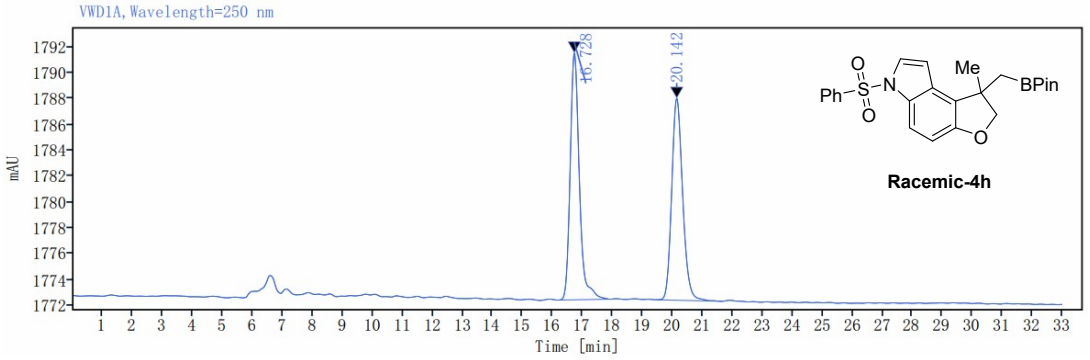


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.970	5.427	22.232	3.41	4.36	n.a.
2		14.517	153.737	487.964	96.59	95.64	n.a.
Total:			**159.164**	**510.196**	**100.00**	**100.00**	

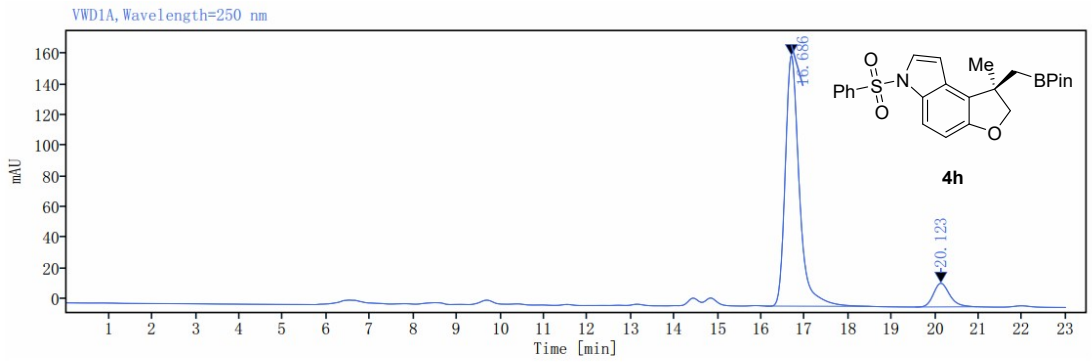






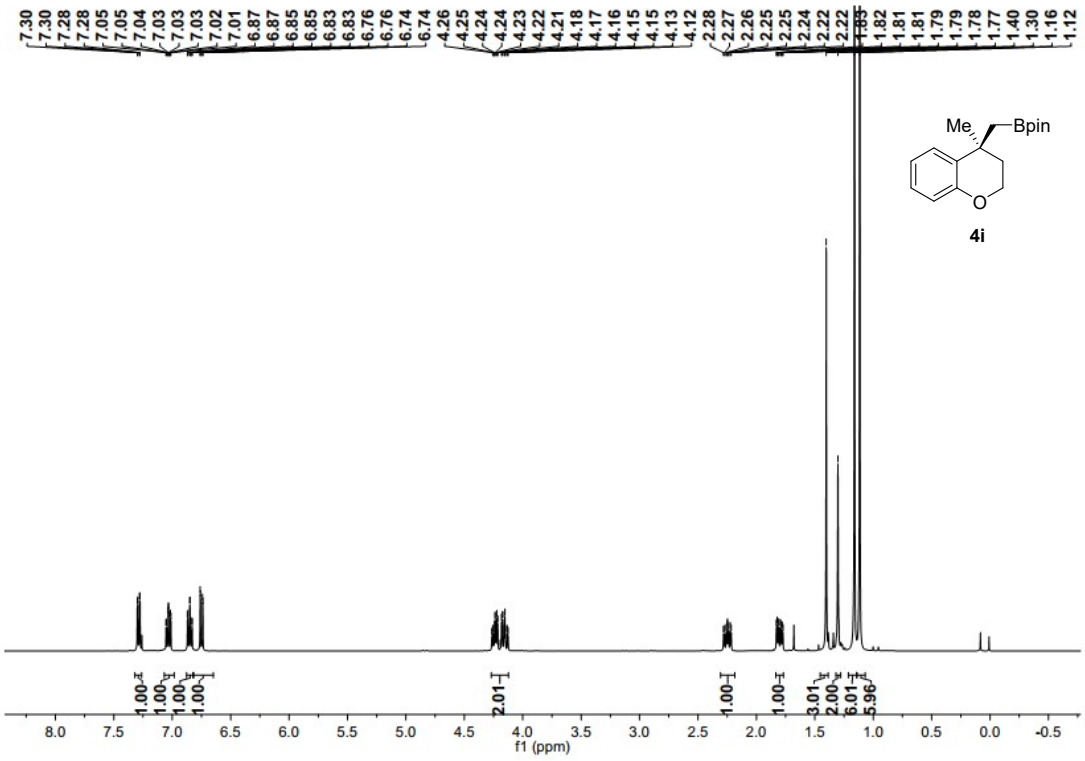
VWD1A,Wavelength=250 nm

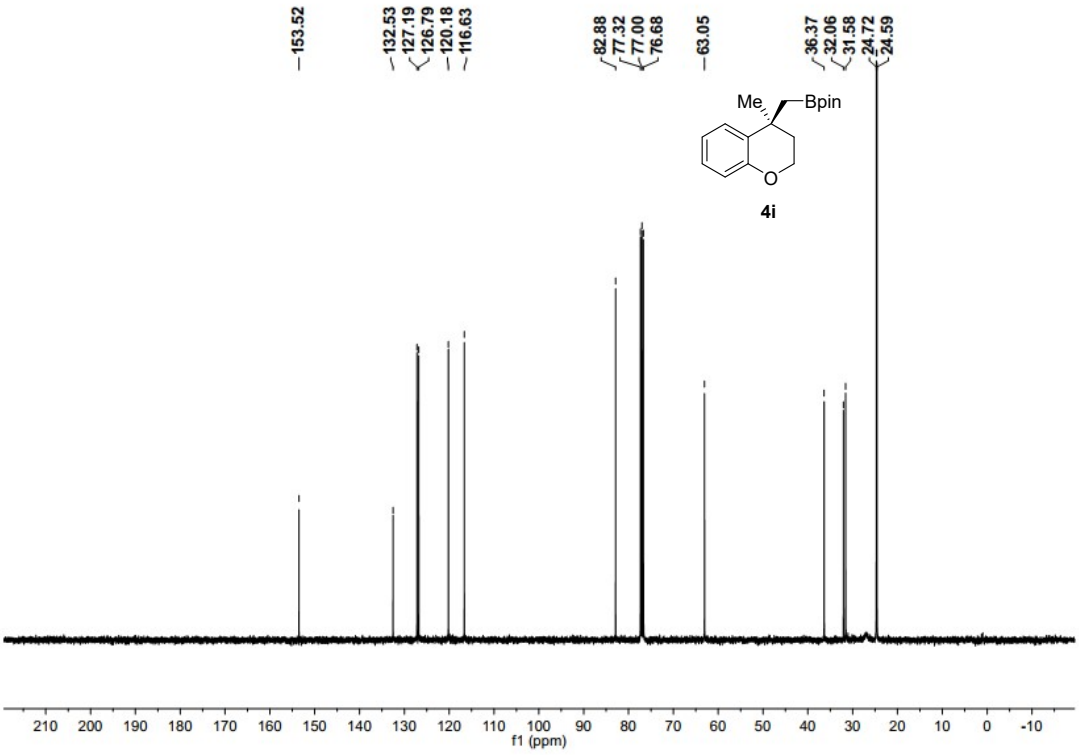
Ret.Time [min]	Area	Height	Height%	Area%
16.728	407.03	19.09	55.00	50.67
20.142	396.21	15.62	45.00	49.33
Total.	803.24	34.71	100.00	100.00



VWD1A, Wavelength=250 nm

Ret. Time [min]	Area	Height	Height%	Area%
16.686	3669.47	163.65	91.38	90.17
20.123	400.01	15.43	8.62	9.83
Total.	4069.48	179.08	100.00	100.00





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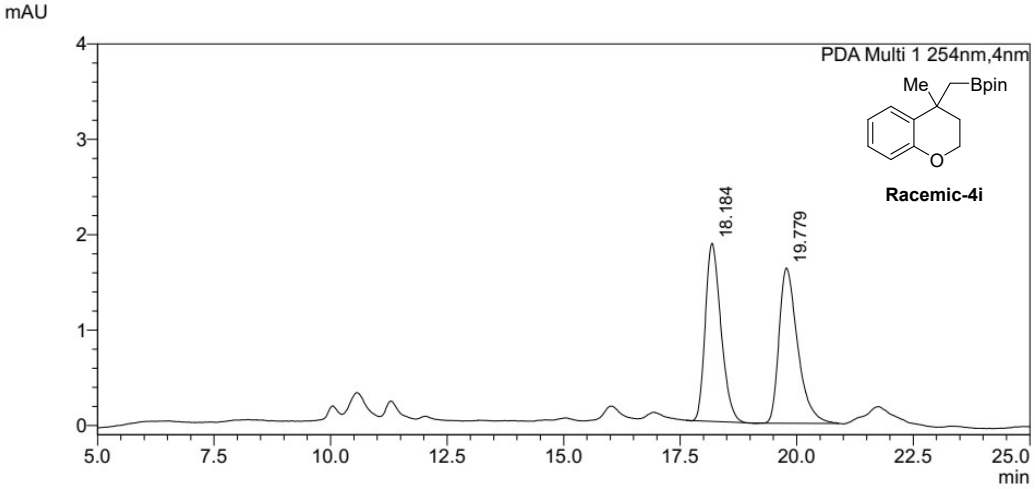
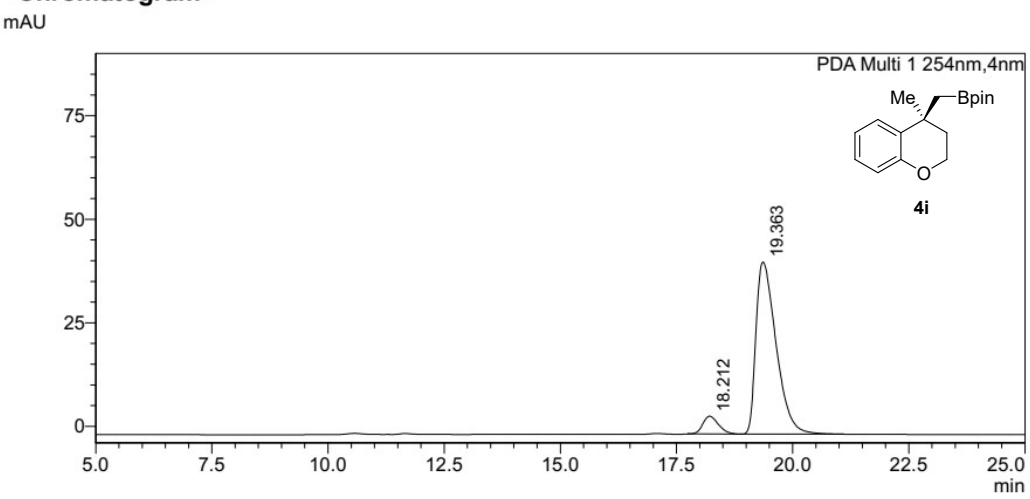


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	18.184	43596	49.008	1868	53.413
2	19.779	45362	50.992	1629	46.587
Total		88958	100.000	3497	100.000

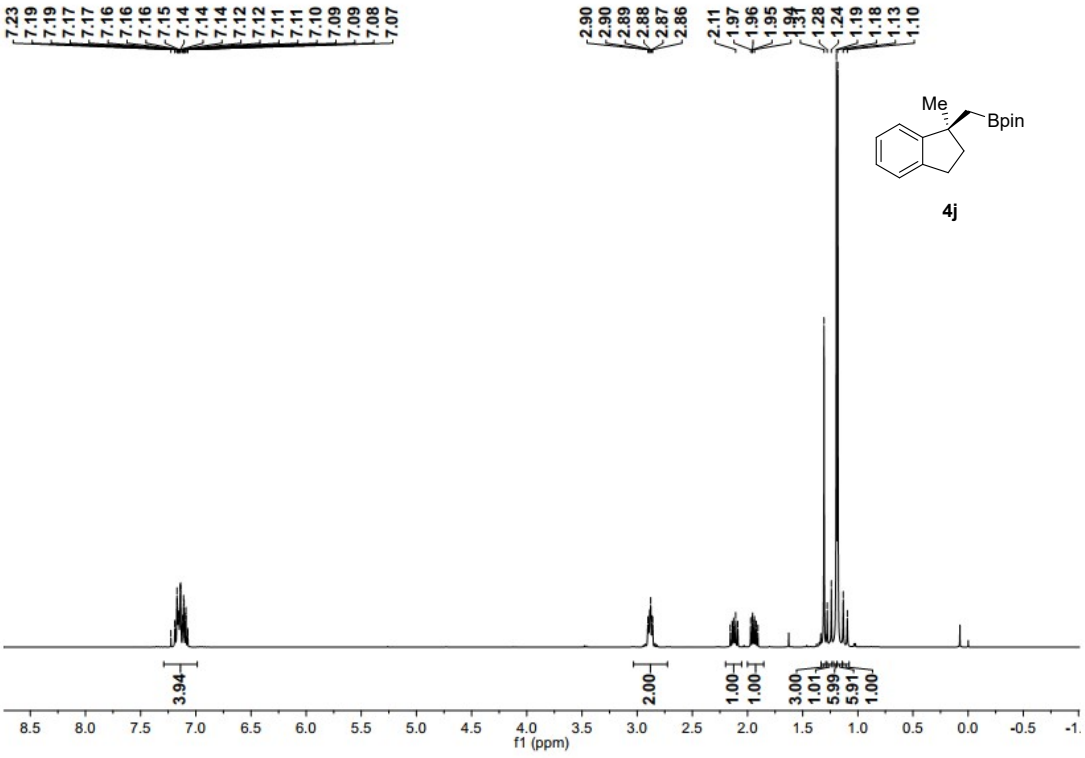
<Chromatogram>

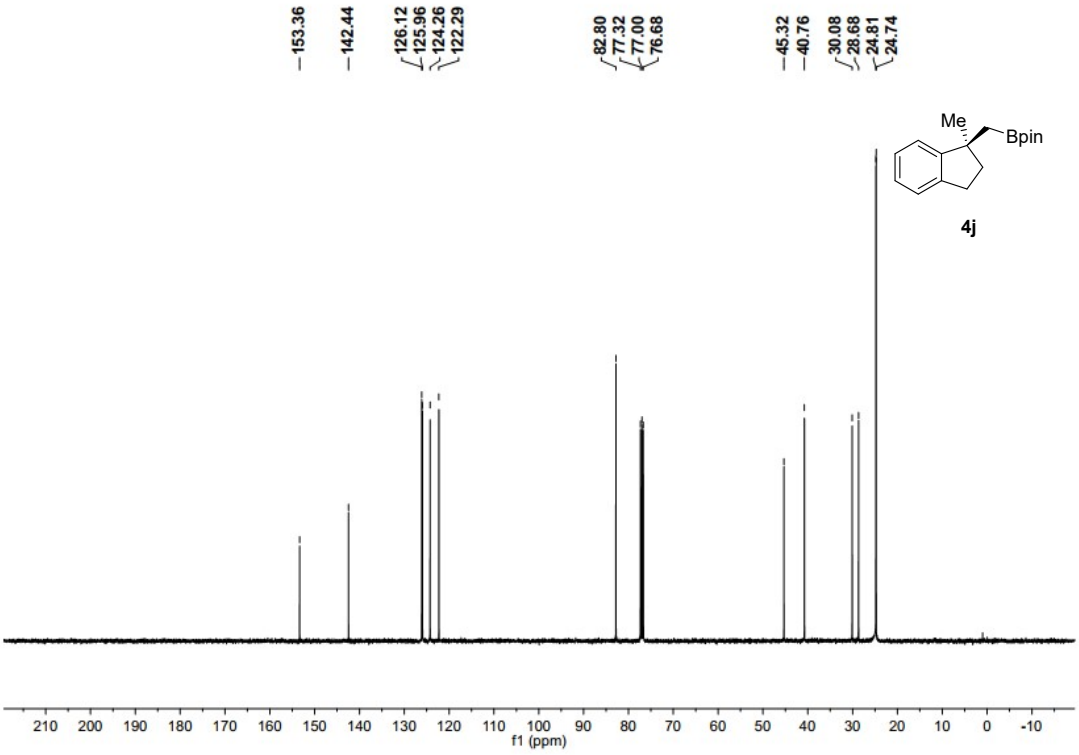


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	18.212	101465	7.464	4314	9.405
2	19.363	1257906	92.536	41560	90.595
Total		1359371	100.000	45874	100.000





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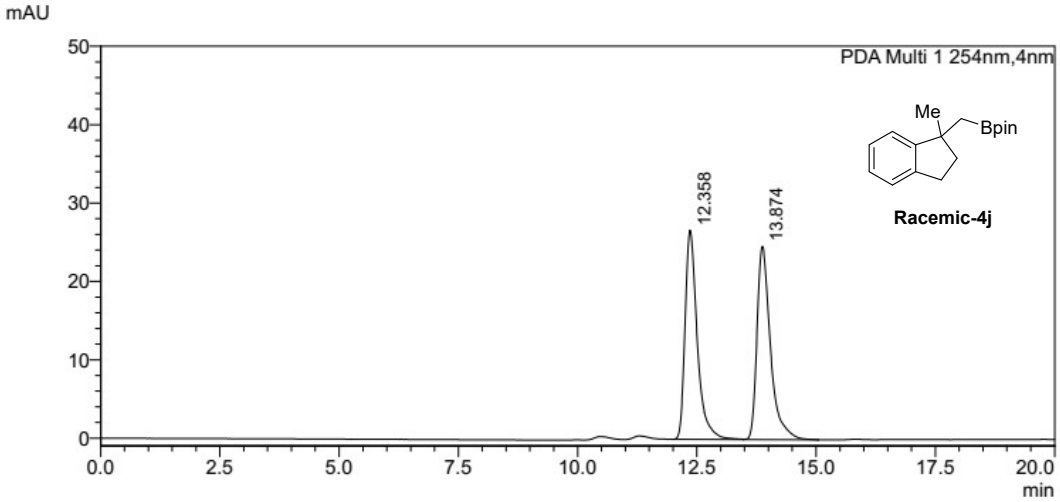
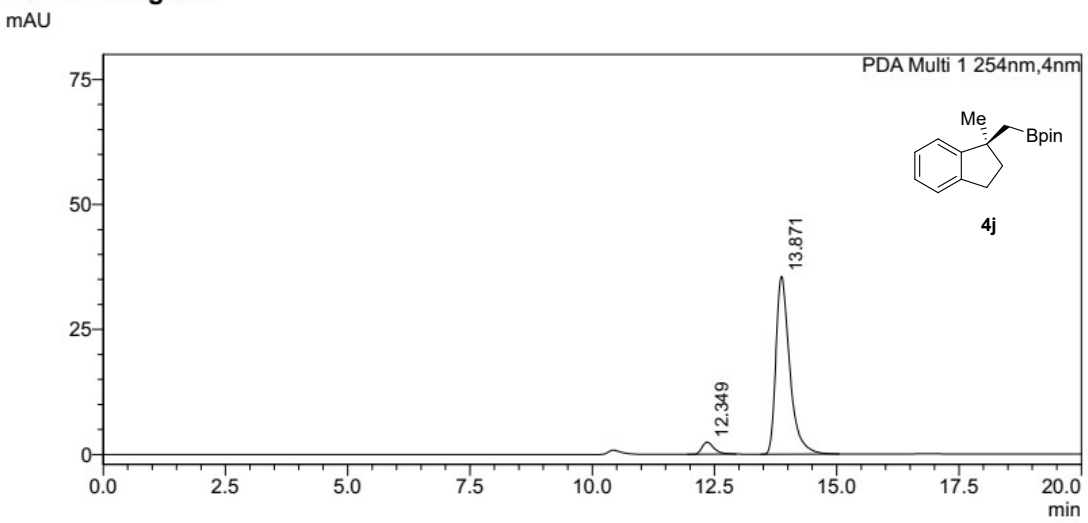


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.358	474361	49.449	26692	51.991
2	13.874	484928	50.551	24648	48.009
Total		959289	100.000	51340	100.000

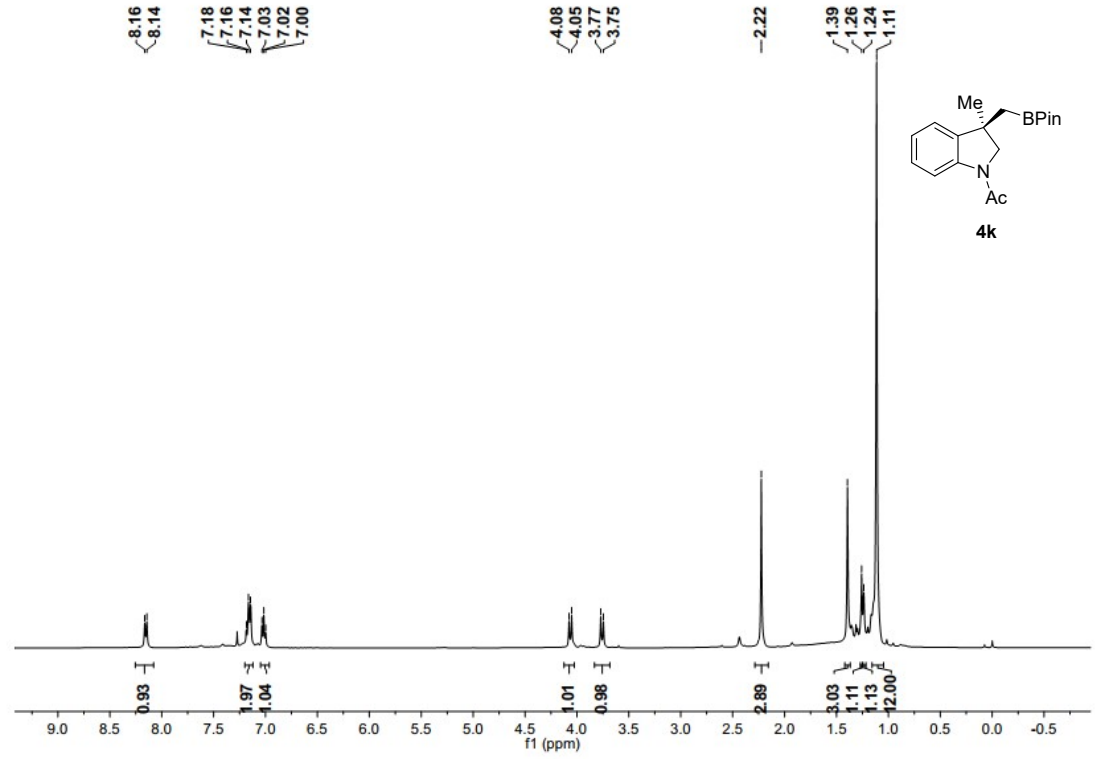
<Chromatogram>

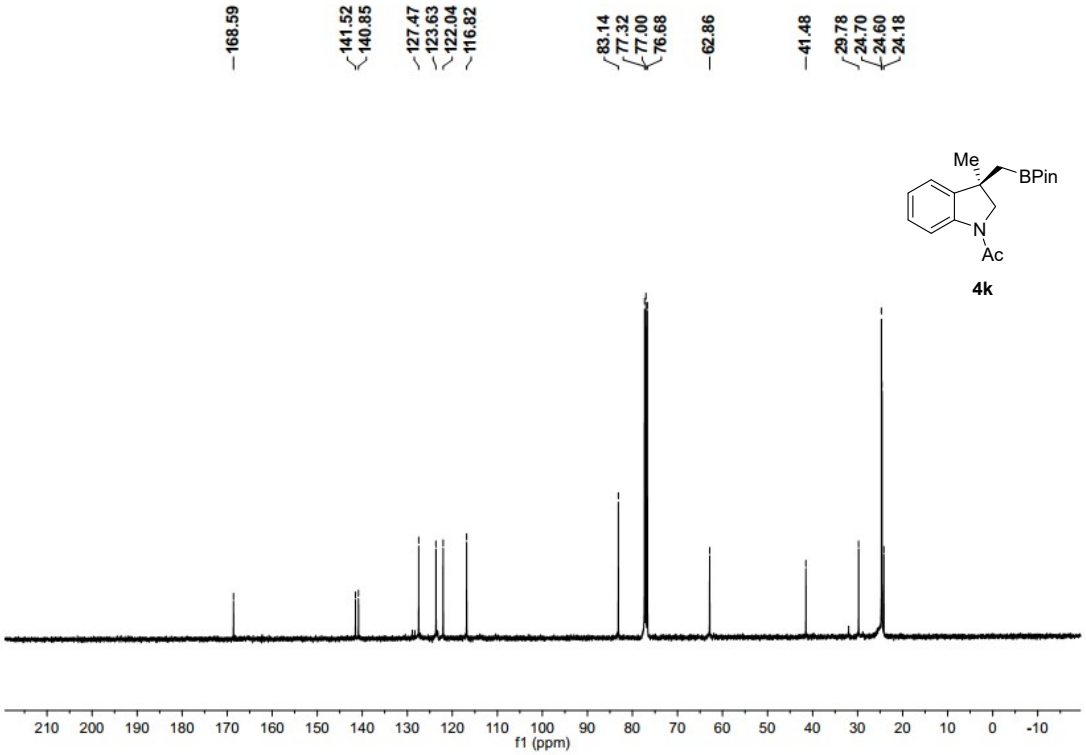


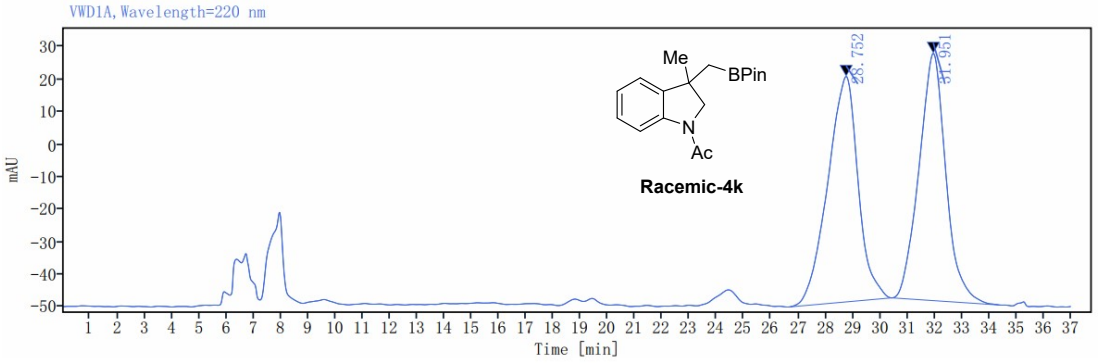
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.349	41346	5.577	2420	6.369
2	13.871	700075	94.423	35572	93.631
Total		741421	100.000	37992	100.000

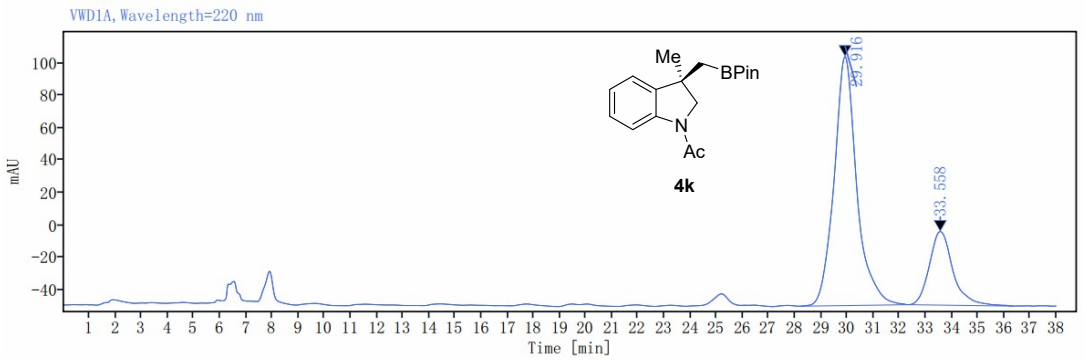






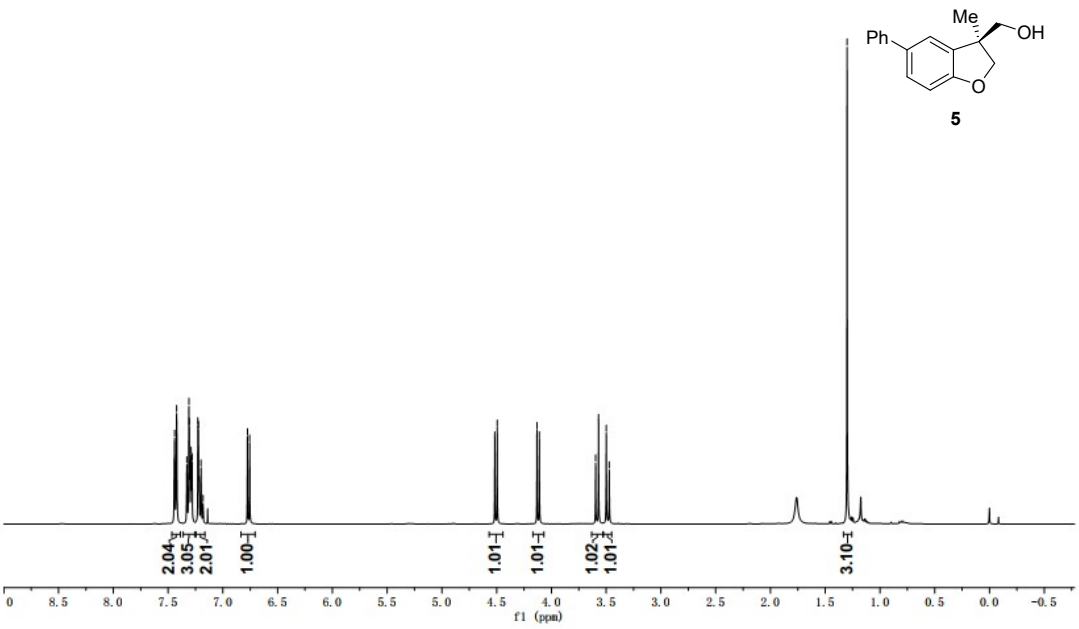
VWD1A, Wavelength=220 nm

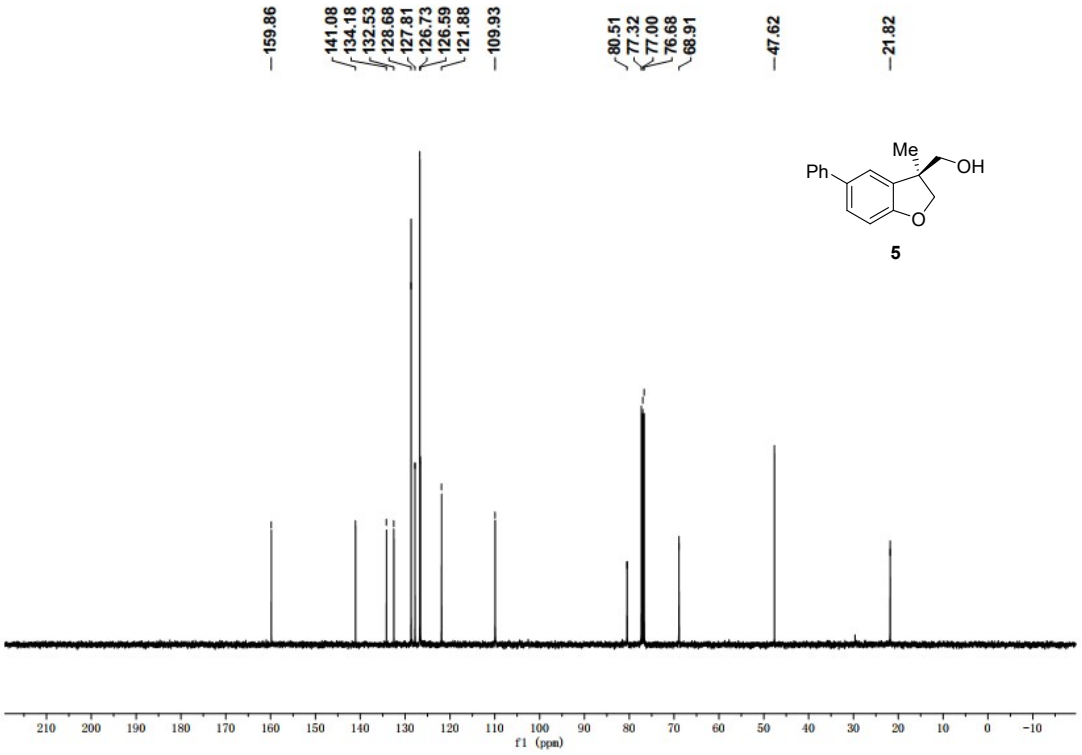
Ret. Time [min]	Area	Height	Height%	Area%
28.752	5373.05	69.33	47.69	50.75
31.951	5213.97	76.04	52.31	49.25
Total.	10587.02	145.38	100.00	100.00



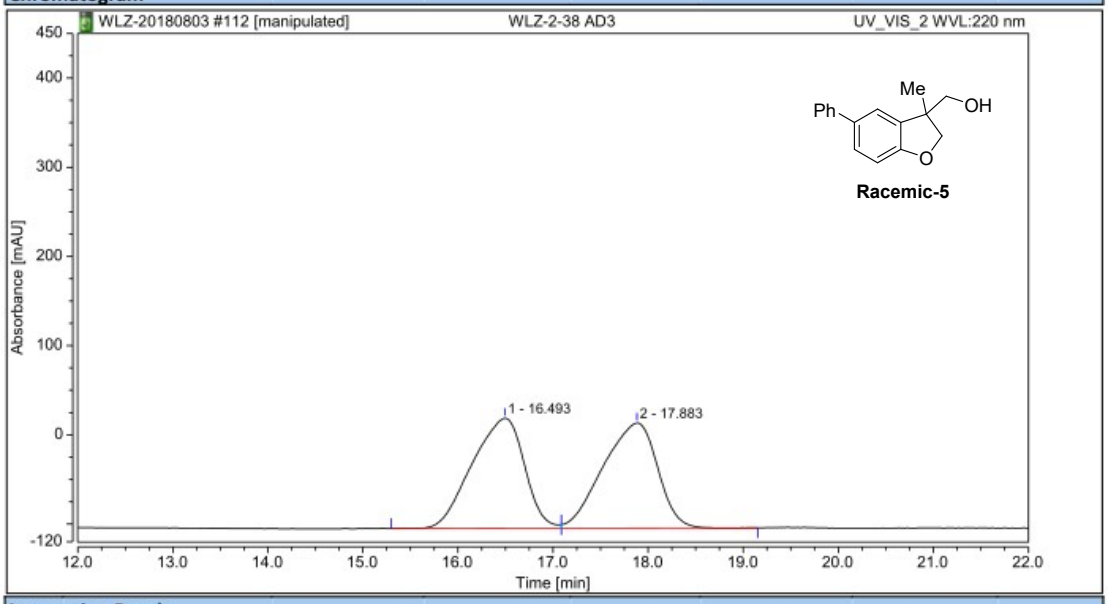
VWD1A,Wavelength=220 nm

Ret.Time [min]	Area	Height	Height%	Area%
29.916	9252.23	153.44	77.21	76.49
33.558	2844.20	45.30	22.79	23.51
Total.	12096.42	198.74	100.00	100.00





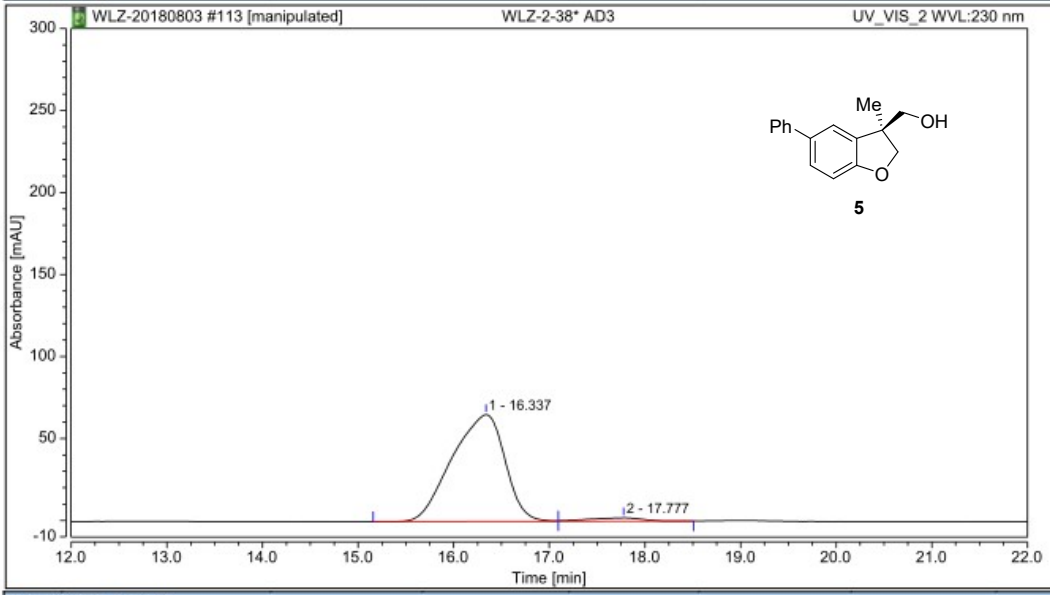
Chromatogram



Integration Results

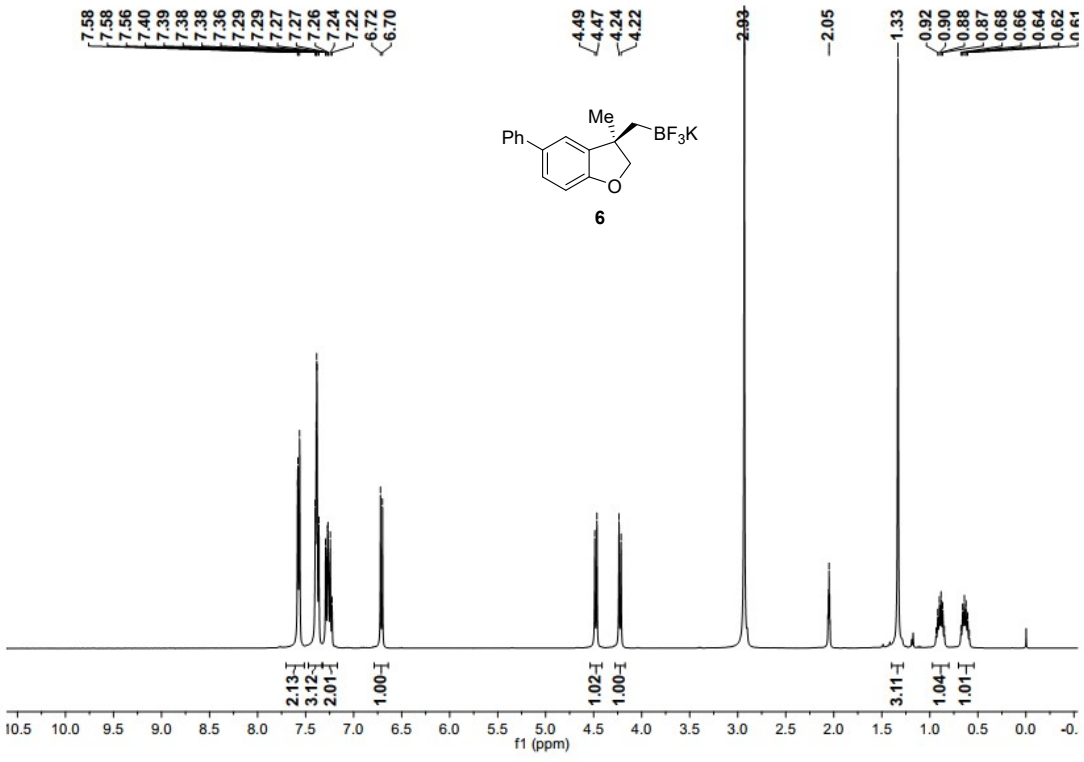
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.493	78.578	123.332	50.22	51.17	n.a.
2		17.883	77.904	117.714	49.78	48.83	n.a.
Total:			**156.482**	**241.046**	**100.00**	**100.00**	

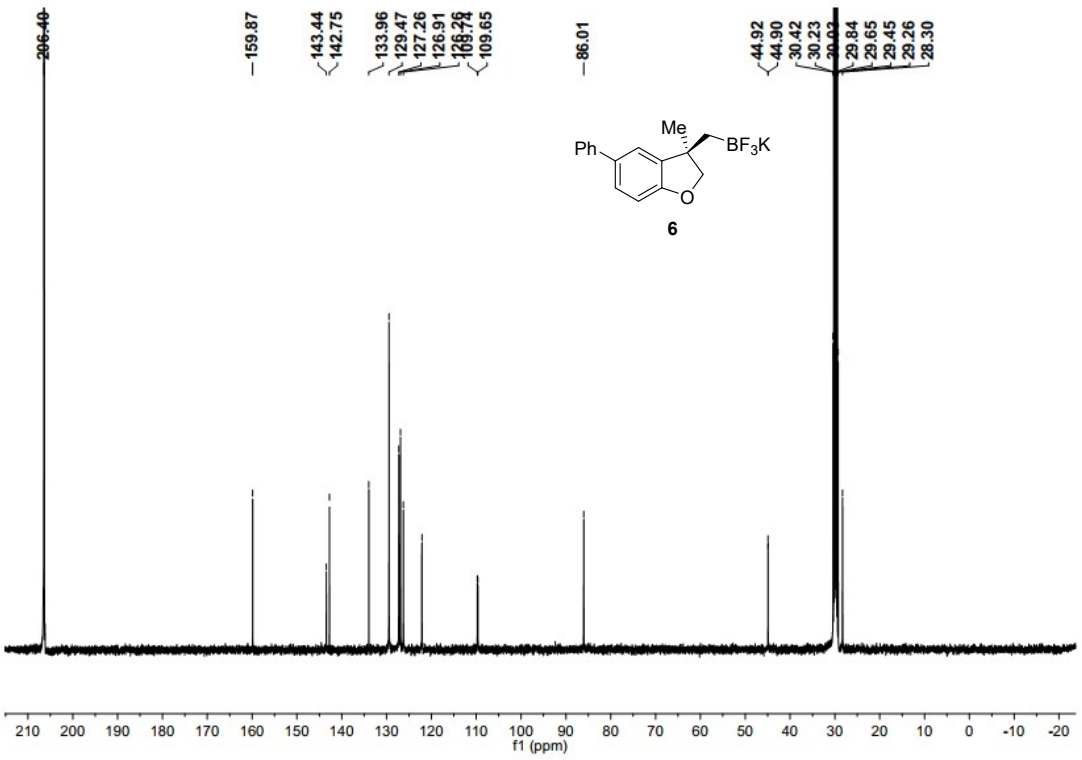
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.337	41.741	65.114	97.08	97.03	n.a.
2		17.777	1.254	1.994	2.92	2.97	n.a.
Total:			**42.995**	**67.109**	**100.00**	**100.00**	

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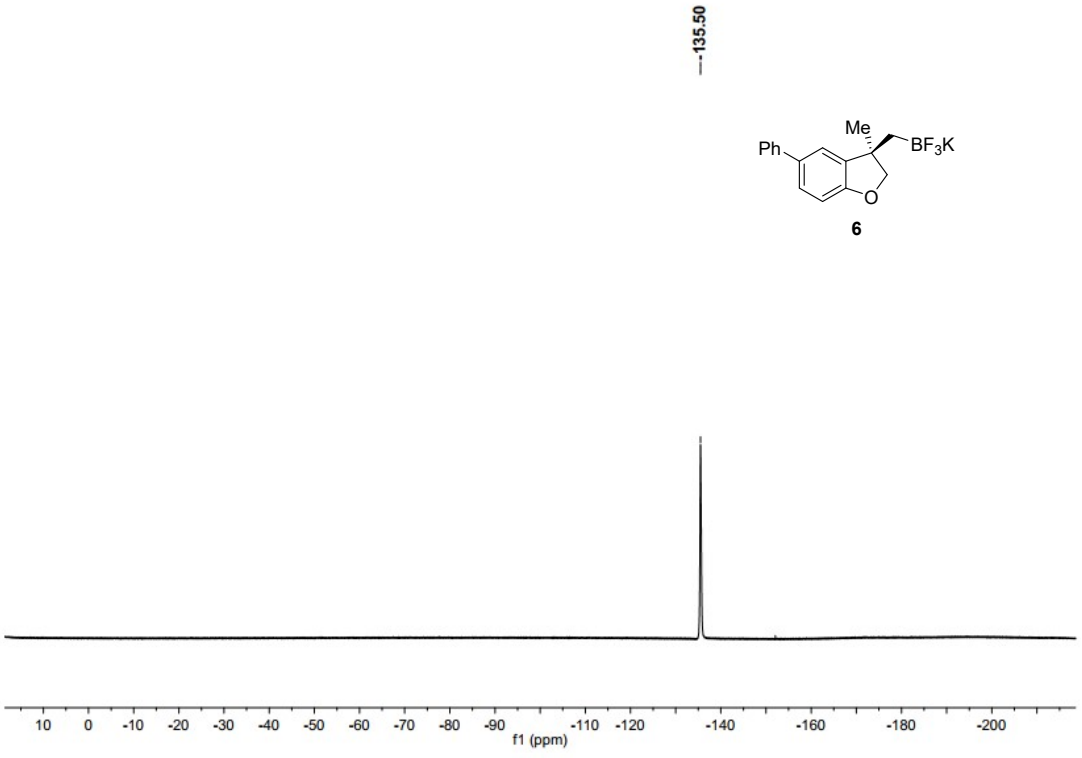
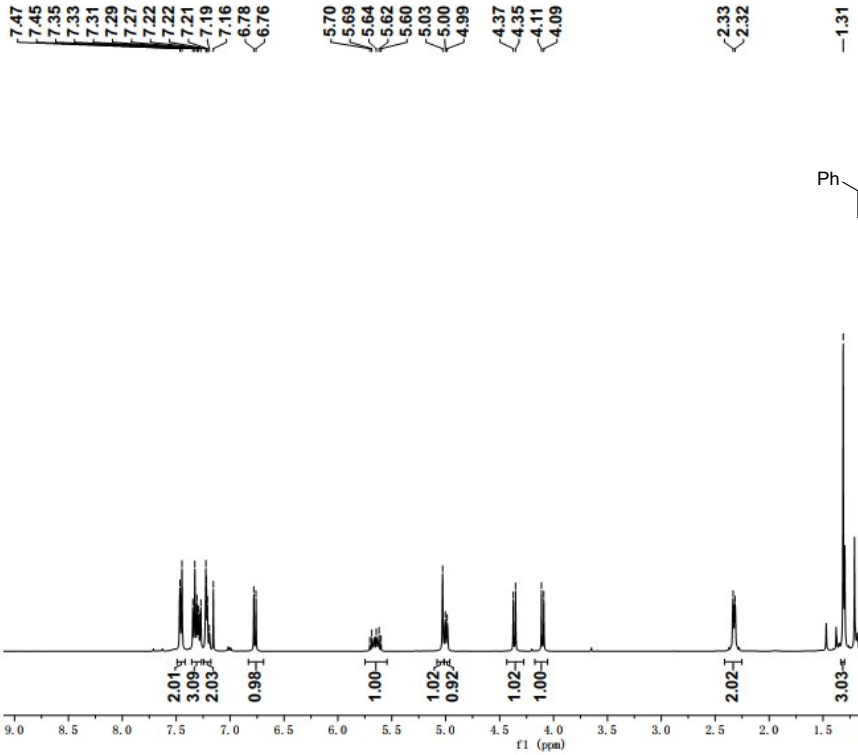
159.87
143.44
142.75
133.96
129.47
127.26
126.91
126.26
109.74
109.65
86.01
44.92
44.90
30.42
30.23
30.03
29.84
29.65
29.45
29.26
28.30
Me
BF3K
Ph
O
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


135.50
Me
BF3K
Ph
O
6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -140 -160 -180 -200
f1 (ppm)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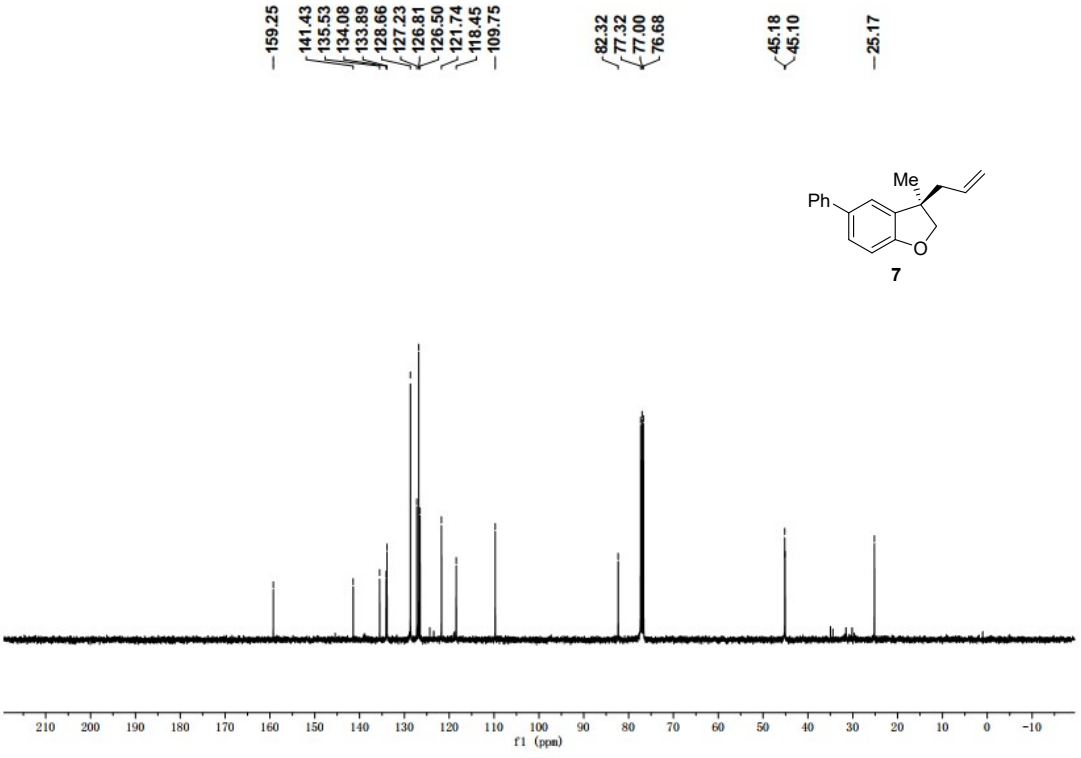
7.35
7.33
7.31
7.29
7.27
7.22
7.22
7.21
7.19
7.16
6.78
6.76
5.70
5.69
5.64
5.62
5.60
5.03
5.00
4.99
4.37
4.35
4.11
4.09
2.33
2.32
1.31
Me
Ph
O
7
2.01
3.09
2.03
0.98
1.00
1.02
0.92
1.02
1.00
2.02
3.03
f1 (ppm)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141.43
135.53
134.08
133.89
128.66
127.23
126.81
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121.74
118.45
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77.32
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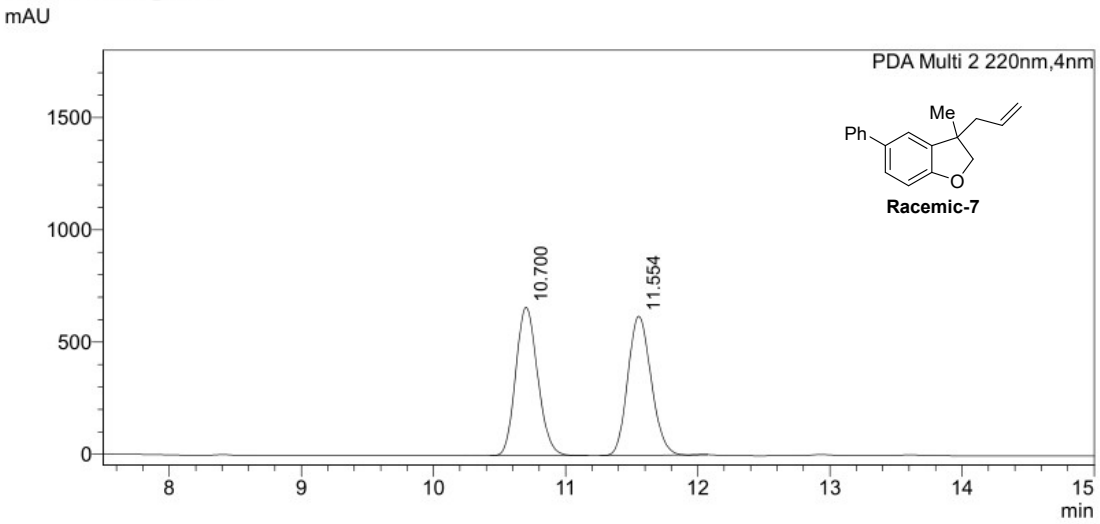
45.18
45.10
25.17
Me
Ph
O
7
f1 (ppm)

<Chromatogram>

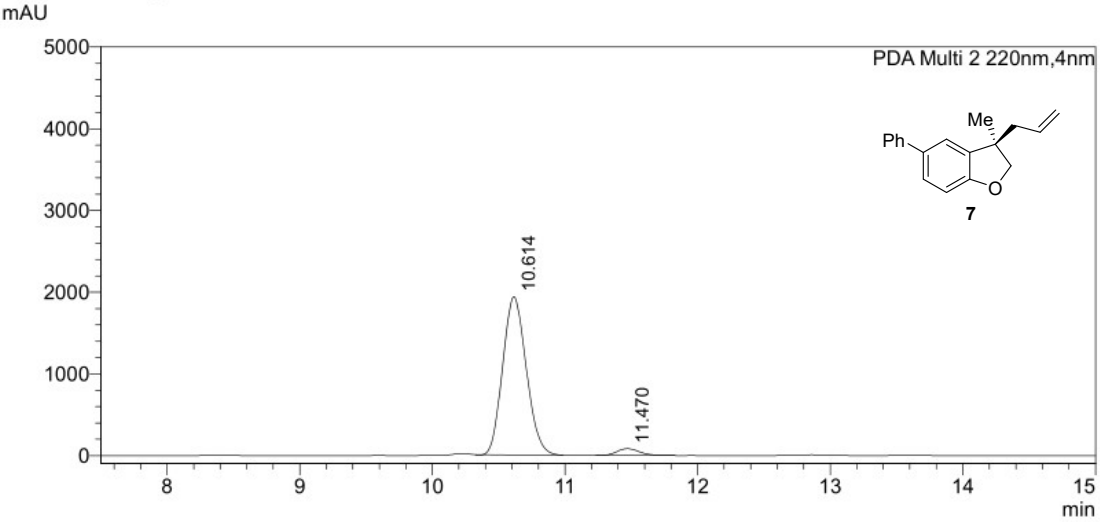


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	10.700	7654150	50.047	661981	51.596
2	11.554	7639885	49.953	621037	48.404
Total		15294036	100.000	1283018	100.000

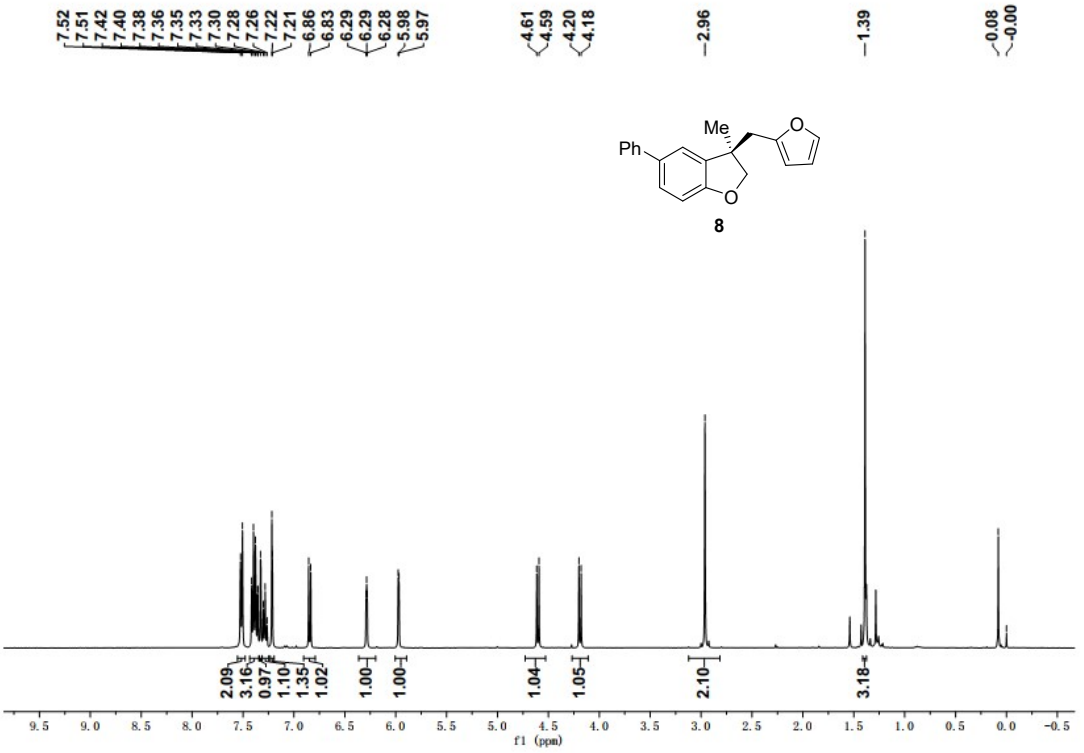
<Chromatogram>



<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	10.614	23993482	95.883	1939038	95.804
2	11.470	1030228	4.117	84917	4.196
Total		25023710	100.000	2023954	100.000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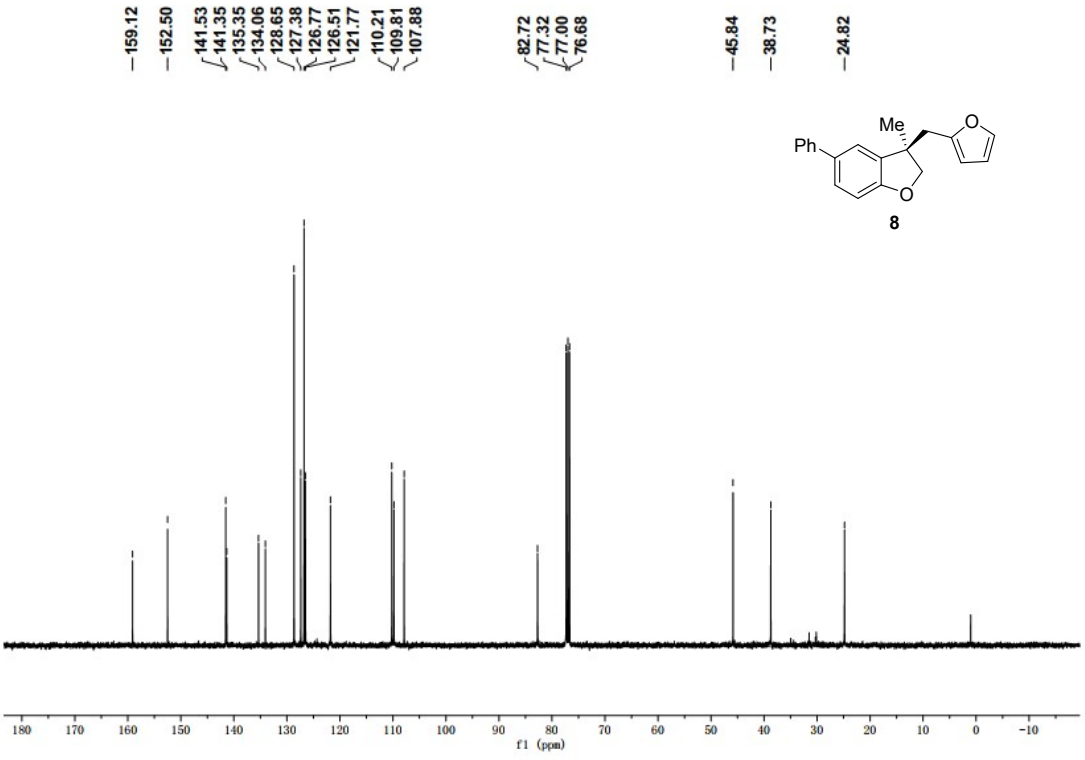
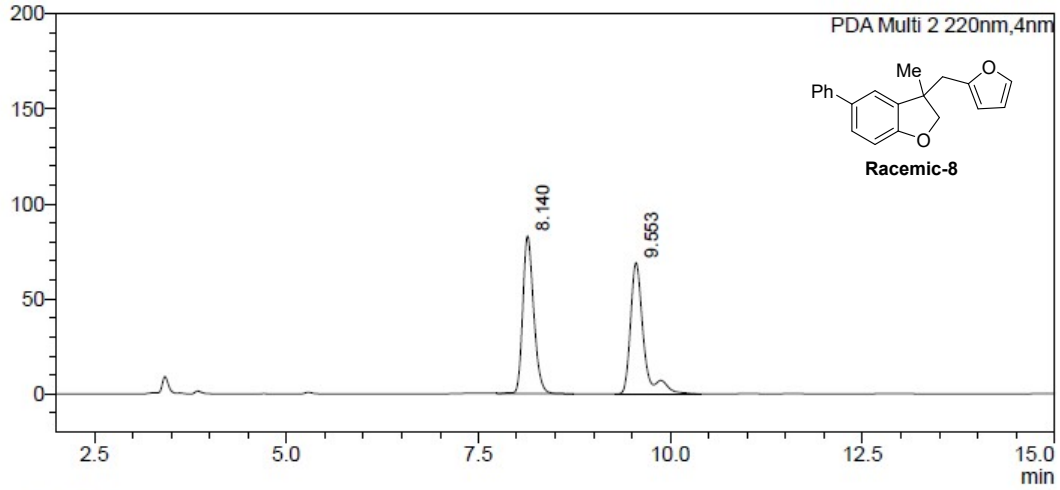
7.51
7.42
7.40
7.38
7.36
7.35
7.33
7.30
7.28
7.26
7.22
7.21
6.86
6.83
6.29
6.29
6.28
5.98
5.97
4.61
4.59
4.20
4.18
2.96
1.39
0.08
-0.00
Me
O
Ph
O
8
2.09
3.16
0.97
1.10
1.35
1.02
1.00
1.00
1.04
1.05
2.10
3.18
f1 (ppm)


159.12
152.50
141.53
141.35
135.35
134.06
128.65
127.38
126.77
126.51
121.77
110.21
109.81
107.88
82.72
77.32
77.00
76.68
45.84
38.73
24.82
Me
O
Ph
O
8
f1 (ppm)

<Chromatogram>

mAU



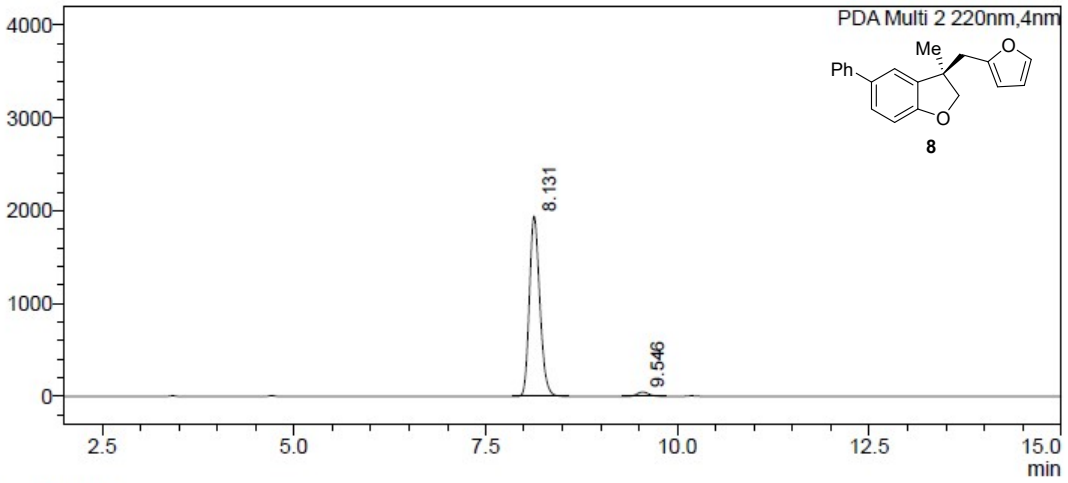
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	8.140	815402	49.977	83032	54.629
2	9.553	816138	50.023	68961	45.371
Total		1631540	100.000	151994	100.000

<Chromatogram>

mAU



<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	8.131	18254957	97.318	1942884	97.611
2	9.546	503172	2.682	47555	2.389
Total		18758129	100.000	1990439	100.000

8. References

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