Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Pd(II)-catalyzed enantioconvergent twofold C-H annulation to access atropisomeric aldehydes: A platform for diversity-oriented-synthesis

Jitan Zhang,* Qiaoqiao Xu, Jian Fan, Lan Zhou, Nannan Liu, Li Zhu, Jiaping Wu,* and Meihua Xie*

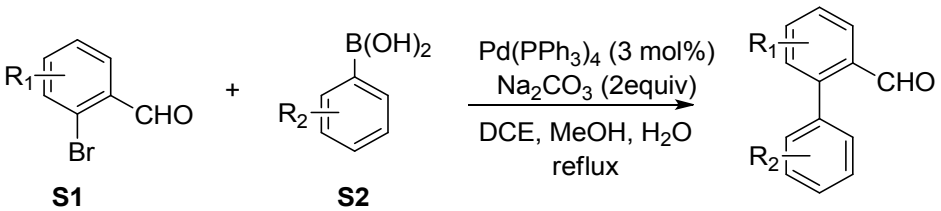
*Key Laboratory of Functional Molecular Solids (Ministry of Education), Anhui Key Laboratory of Molecular Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China*; **E-mail**: *zhangjt@ahnu.edu.cn; wujiaping@ahnu.edu.cn; xiemh@mail.ahnu.edu.cn*

# General Information and Procedure

## 1. General information

$Pd(OAc)_2$ (Energy Chemical), AgTFA (Energy Chemical) were purchased from above mentioned company and used without additional purification. Other chemical reagents were commercially available and directly used without any further purification. $^1H$ NMR spectra were recorded at 400 MHz and 500 MHz NMR spectrometers using TMS as an internal standard, $^{13}C$ NMR spectra were recorded at 100 MHz and 125 MHz NMR spectrometers using TMS as an internal standard, and were fully decoupled by broad band proton decoupling.$^{19}F$ NMR spectra were recorded at a 376 MHz NMR spectrometer using TMS as an internal standard and were fully decoupled by broad band proton decoupling.$^{31}P$ NMR spectra were recorded at a 162 MHz NMR spectrometer using TMS as an internal standard and were fully decoupled by broad band proton decoupling. Data for $^1H$ NMR are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. High resolution mass spectra (HRMS) were obtained on an APEXM Fourier transform mass spectrometry. High performance liquid chromatography (HPLC) was performed on DIONEX UltiMate 3000 LC systems or Agilent 1200 instrument using Daicel Chiralcel® columns as noted.

## 2. General Procedure for the Preparation of Substrates[1]

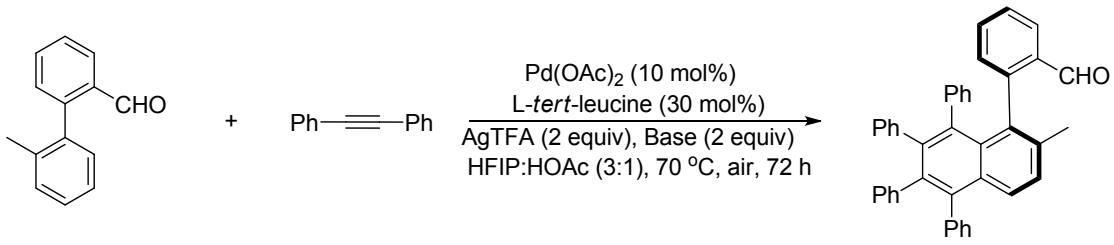



A Schlenk tube was charged with a solution of 2-bromobenzaldehyde **S1** (10.5 mmol) and $Pd(PPh_3)_4$ in DME (25 mL). A solution of $Na_2CO_3$ (2.2 g, 21 mmol) in $H_2O$ (10 mL) and a solution of the corresponding boronic acid **S2** (11.5 mmol) in MeOH (8 mL) were sequentially added. The reaction mixture was stirred at 80 °C overnight. After cooling to room temperature, the reaction mixture was quenched with $H_2O$ (20

mL) and extracted with $CH_2Cl_2$ (3×20 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, concentrated, and the residue was purified by silica gel column chromatography.

## 2. Optimization of reaction conditions

**Screening of Base**

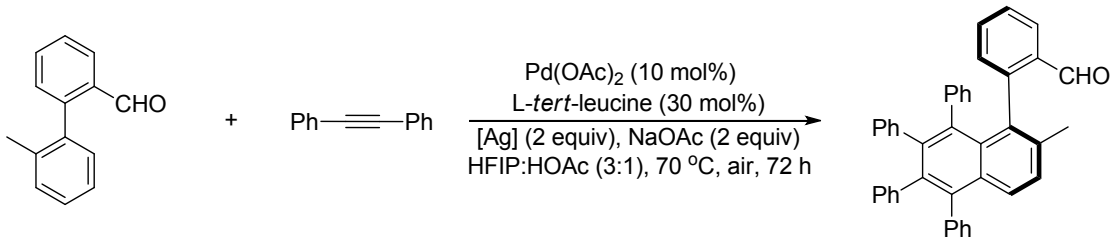



*rac*-**1a** **2a** **3a**

| Entry[a] | Base | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|
| 1 | LiOAc | 80 | 99 |
| 2 | NaOAc | 84 | 99 |
| 3 | KOAc | 75 | 99 |
| 4 | $NaHCO_3$ | 80 | 99 |
| 5 | NaTFA | 52 | 99 |
| 6 | $NaH_2PO_4$ | 63 | 99 |
| 7 | - | 68 | 99 |
| 8[d] | NaOAc | 88 | 99 |

[a] Reactions conditons: *rac*-**1a** (0.1 mmol), **2a** (0.30 mmol), $Pd(OAc)_2$ (0.01 mmol), L-*tert*-leucine (0.03 mmol), Base (0.2 mmol), AgTFA (0.20 mmol), HFIP:HOAc (3:1, 1 mL), 70 °C, 72 h. [b] Isolated yield by flash column chromatography. [c]The ee values were determined by HPLC using chiral columns after the aldehyde was reduced to the corresponding alcohol by $NaBH_4$. [d]3.0 equiv of NaOAc was used.

## Screening of [Ag]



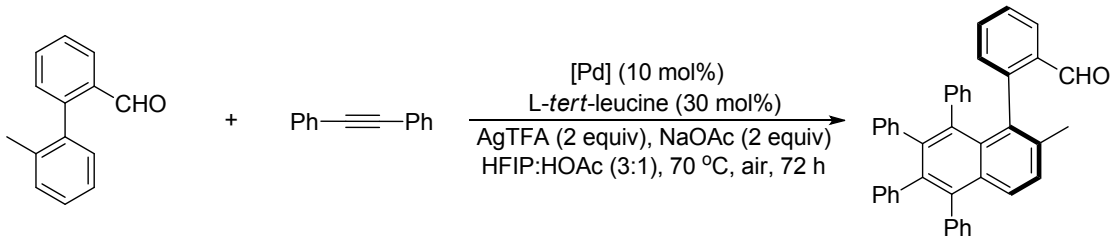

*rac*-**1a** **2a** **3a**

| Entry[a] | [Ag] | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|
| 1 | AgTFA | 84 | 99 |
| 2 | AgOAc | 62 | 98 |
| 3 | $Ag_2CO_3$ | 80 | 98 |

| | | | |
|---|---|---|---|
| 4 | $Ag_2O$ | 82 | 98 |
| 5 | - | 14 | 99 |

[a] Reactions conditons: *rac*-**1a** (0.1 mmol), **2a** (0.30 mmol), $Pd(OAc)_2$ (0.01 mmol), L-*tert*-leucine (0.03 mmol), NaOAc (0.2 mmol), [Ag] (0.20 mmol), HFIP:HOAc (3:1, 1 mL), 70 °C, 72 h. [b] Isolated yield by flash column chromatography. [c]The ee values were determined by HPLC using chiral columns after the aldehyde was reduced to the corresponding alcohol by $NaBH_4$.

## Screening of [Pd]

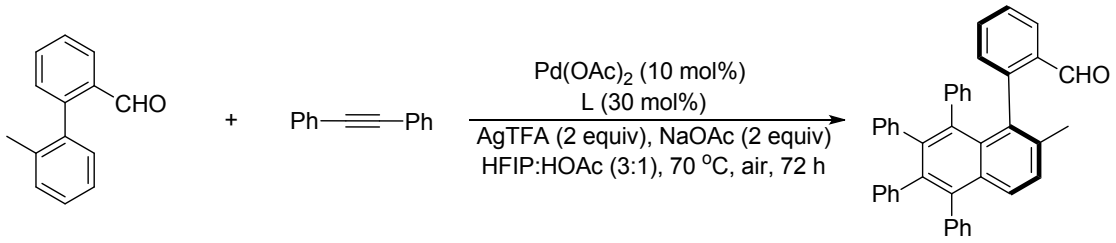



*rac*-**1a** **2a** **3a**

| Entry[a] | [Pd] | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|
| 1 | $Pd(OAc)_2$ | 84 | 99 |
| 2 | $Pd(TFA)_2$ | 66 | 99 |
| 3 | $PdCl_2$ | 69 | 98 |
| 4 | $Pd(acac)_2$ | 76 | 99 |

[a] Reactions conditons: *rac*-**1a** (0.1 mmol), **2a** (0.30 mmol), [Pd] (0.01 mmol), L-*tert*-leucine (0.03 mmol), NaOAc (0.2 mmol), AgTFA (0.20 mmol), HFIP:HOAc (3:1, 1 mL), 70 °C, 72 h. [b] Isolated yield by flash column chromatography. [c]The ee values were determined by HPLC using chiral columns after the aldehyde was reduced to the corresponding alcohol by $NaBH_4$.

## Screening of Ligands

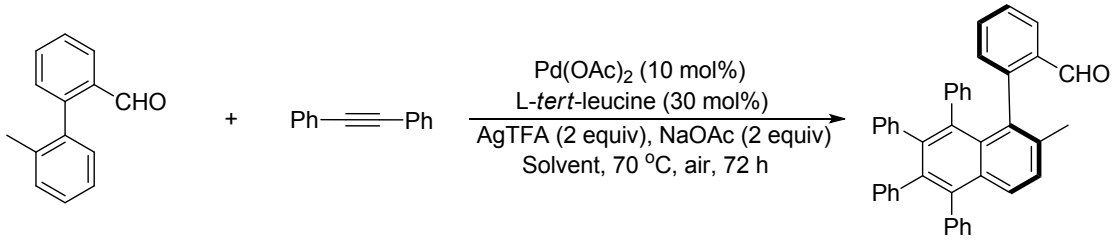



*rac*-**1a** **2a** **3a**

| Entry[a] | L | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|
| 1 | L-*tert*-leucine | 84 | 99 |
| 2 | L-valine | 76 | 70 |
| 3 | L-Alanine | 55 | 11 |
| 4 | L-Phenylglycine | 34 | 17 |
| 5 | L-Cyclohexylglycine | 69 | 65 |
| 6 | L-Phenylalanine | 16 | 64 |
| 7 | - | 0 | - |

[a] Reactions conditons: *rac*-**1a** (0.1 mmol), **2a** (0.30 mmol), $Pd(OAc)_2$ (0.01 mmol), L (0.03 mmol), NaOAc (0.2 mmol), AgTFA (0.20 mmol), HFIP:HOAc (3:1, 1 mL), 70 °C, 72 h. [b] Isolated yield by flash column chromatography. [c]The ee values were determined by HPLC using chiral columns after the aldehyde was reduced to the corresponding alcohol by $NaBH_4$.

## Screening of Solvent

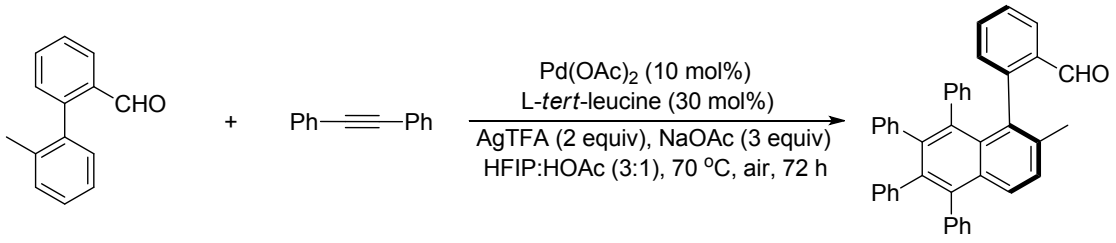



*rac*-**1a** **2a** **3a**

| Entry[a] | Solvent | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|
| 1 | Toluene | Trace | - |
| 2 | DCE | Trace | - |
| 3 | THF | 0 | - |
| 4 | HFIP | 25 | 99 |
| 5 | HOAc | 18 | 99 |
| 6 | HFIP:HOAc (1/1) | 74 | 97 |
| 7 | HFIP:HOAc (3/1) | 88 | 99 |

[a] Reactions conditons: *rac*-**1a** (0.1 mmol), **2a** (0.30 mmol), $Pd(OAc)_2$ (0.01 mmol), L-tert-leucine (0.03 mmol), NaOAc (0.3 mmol), AgTFA (0.20 mmol), Solvent (1 mL), 70 °C, 72 h. [b] Isolated yield by flash column chromatography. [c]The ee values were determined by HPLC using chiral columns after the aldehyde was reduced to the corresponding alcohol by $NaBH_4$.

## 4. General procedure for the Asymmetric Catalysis



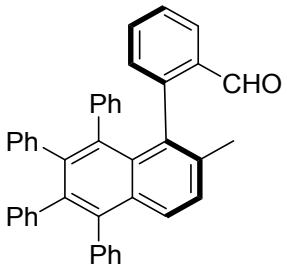

*rac*-**1a** **2a** **3a**

To an oven-dried 25 mL Schlenk tube was added substrate *rac*-**1a** (0.10 mmol), diphenylacetylene **2a** (0.3 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), L-*tert*-leucine (3.9 mg, 0.03 mmol), AgTFA (44.2 mg, 0.2 mmol), NaOAc (24.6 mg, 0.30 mmol), HFIP (0.75 mL) and HOAc (0.25 mL). The mixture was stirred for 72 h at 70 °C followed by cooling. The resulting mixture was quenched by filtered through a celite

pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent to afford the product **3a**.

# Analytic Data of Products

**2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3a)**




Pale yellow solid. Isolated yield: 48.4 mg, 88%. Melting point: 87-91 °C (petroleum ether/EtOAc = 20/1).

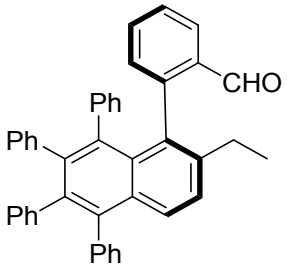
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.24-7.32 (m, 6H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.83-6.93 (m, 6H), 6.61-6.78 (m, 8H), 6.49-6.56 (m, 2H), 1.94 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.67, 146.51, 141.82, 141.33, 140.45, 139.82, 138.56, 138.43, 138.24, 136.48, 134.38, 133.53, 132.97, 132.42, 131.97, 131.75, 131.57, 131.39, 131.36, 131.22, 131.18, 131.08, 131.01, 128.38, 127.69, 127.66, 127.54, 126.89, 126.71, 126.67, 126.56, 126.53, 126.49, 126.20, 126.10, 125.31, 125.20, 125.01, 21.61.

**HRMS** (APCI) Calcd for $C_{42}H_{31}O$ $(M+H)^+$: 551.2369 Found: 551.2363.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 12.24 min, t (major) = 13.89 min, 99% ee; $[\alpha]_D^{20}$ = -137.2 (*c* = 1.00, $CHCl_3$).

**2-(2-Ethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3b)**




Pale yellow solid. Isolated yield: 47.8 mg, 85%. Melting point: 85-88 °C (petroleum ether/EtOAc = 20/1).

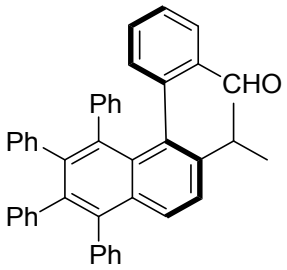
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.47-7.49 (m, 1H), 7.37 (d, *J* = 9.2 Hz, 1H), 7.26-7.29 (m, 4H), 7.18-7.24 (m, 2H), 7.07-7.12 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.77-6.84 (m, 5H), 6.62-6.74 (m, 6H), 6.49-6.58 (m, 3H), 6.44-6.47 (m, 1H), 2.09-2.26 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.71, 145.77, 142.36, 141.89, 141.42, 140.45, 140.43, 139.82, 138.51, 138.49, 133.91, 133.32, 132.54, 132.24, 131.56, 131.53, 131.36, 131.16, 131.06, 131.02, 128.08, 127.52, 126.91, 126.73, 126.69, 126.66, 126.53, 126.50, 126.45, 126.35, 126.16, 126.05, 125.28, 125.09, 124.96, 27.02, 15.14.

**HRMS** (APCI) Calcd for $C_{43}H_{33}O$ $(M+H)^+$: 565.2526 Found: 565.2533.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 0.5 mL/min, UV 254 nm, t (minor) = 23.60 min, t (major) = 27.88 min, 99% ee; $[\alpha]_D^{20}$ = -106.9 (*c* = 0.67, $CHCl_3$).

**2-(2-Isopropyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3c)**




White solid. Isolated yield: 49.2 mg, 85%. Melting point: 235-237 °C (petroleum ether/EtOAc = 20/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.44-7.47 (m, 2H), 7.23-7.29 (m, 4H), 7.17-7.23 (m, 2H), 7.07-7.11 (m, 1H), 6.89-6.91 (m, 1H),

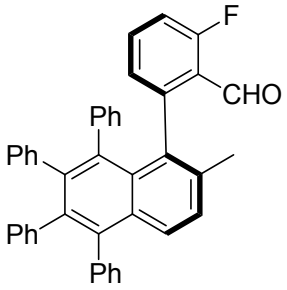
6.76-6.84 (m, 5H), 6.61-6.74 (m, 6H), 6.48-6.56 (m, 3H), 6.42 (d, *J* = 8.0 Hz, 1H), 2.31-2.38 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.54, 146.67, 145.77, 141.95, 141.54, 140.47, 140.42, 139.82, 138.71, 138.56, 138.48, 134.14, 132.51, 132.42, 132.36, 132.14, 131.46, 131.36, 131.33, 131.14, 131.08, 131.04, 131.01, 128.36, 127.61, 127.51, 126.92, 126.71, 126.68, 126.52, 126.50, 126.44, 126.33, 126.14, 126.02, 125.27, 125.02, 124.95, 123.44, 30.00, 24.03, 22.80.

**HRMS** (APCI) Calcd for $C_{44}H_{35}O$ $(M+H)^+$: 579.2682 Found: 579.26879.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 9.60 min, t (major) = 11.83 min, 98% ee; $[\alpha]_D^{20}$ = -17.1 (*c* = 1.00 , $CHCl_3$).

**2-Fluoro-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3d)**




Yellow solid. Isolated yield: 44.0 mg, 77%. Melting point: 92-94 °C (petroleum ether/EtOAc = 20/1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.17-7.30 (m, 8H), 6.72-6.84 (m, 10H), 6.65-6.72 (m, 4H), 6.53-6.56 (m, 1H), 6.48-6.52 (m, 1H), 6.42-6.45 (m, 1H), 1.90 (s, 3H).

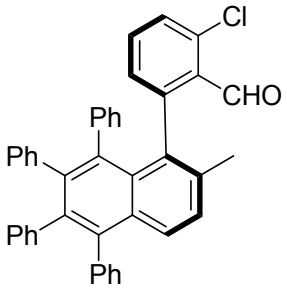
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 189.10 (d, *J* = 3.3 Hz), 163.47 (d, *J* = 260.5 Hz), 147.35, 141.70, 141.11, 140.44 (d, *J* = 5.3 Hz), 139.80, 138.65,138.35, 137.88, 135.90, 134.28, 134.26, 133.96 (d, *J* = 10.3 Hz), 132.58, 131.73, 131.51, 131.35, 131.19, 131.06, 131.03, 131.00, 130.97, 128.37, 127.99 (d, *J* = 3.3 Hz), 127.70, 127.64, 127.49, 126.56, 126.50, 126.09, 126.23, 126.21, 126.09, 125.46, 125.29, 125.02, 122.07 (d, *J* = 6.4 Hz), 115.26 (d, *J* = 21.3 Hz), 21.34.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -118.44

**HRMS** (APCI) Calcd for $C_{42}H_{30}FO$ $(M+H)^+$: 569.2275 Found: 569.2280.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 18.78 min, t (major) = 24.85 min, 98% ee; $[\alpha]_D^{20}$ = -164.3 (*c* = 1.00, $CHCl_3$).

**2-Chloro-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3e)**




Pale yellow oil. Isolated yield: 38.9 mg, 66%. (petroleum ether/EtOAc = 20/1).

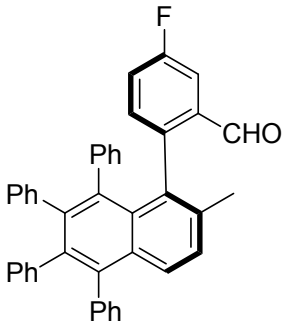
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.16-7.29 (m, 7H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.06-7.08 (m, 1H), 6.73-6.86 (m, 9H), 6.65-6.69 (m, 3H), 6.54-6.55 (m, 1H), 6.40-6.46 (m, 2H), 1.86 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 190.46, 147.05, 141.57, 140.80, 140.56, 140.47, 139.88, 138.67, 138.22, 137.81, 135.95, 135.69, 135.13, 132.52, 131.71, 131.54, 131.38, 131.33, 131.21, 131.08, 131.03, 130.93, 130.54, 130.41, 129.66, 128.37, 127.59, 127.53, 127.45, 126.51, 126.45, 126.42, 126.36, 126.19, 126.04, 125.71, 125.61, 125.24. 124.97, 21.38.

**HRMS** (APCI) Calcd for $C_{42}H_{30}ClO$ $(M+H)^+$: 585.1980 Found: 585.1979.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IB column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 8.55 min, t (major) = 9.58 min, 98% ee; $[\alpha]_D^{20}$ = -95.7 (*c* = 0.66, $CHCl_3$).

**5-Fluoro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3f)**




White solid. Isolated yield: 54.0 mg, 95%. Melting point: 209-212 °C (petroleum ether/EtOAc = 20/1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.21-7.26 (m, 4H), 7.18-7.20 (m, 1H), 7.12-7.15 (m, 1H), 6.89-6.94 (m, 1H), 6.75-6.86 (m, 6H), 6.54-6.61 (m, 3H), 6.45-6.48 (m, 1H), 1.90 (s, 3H).

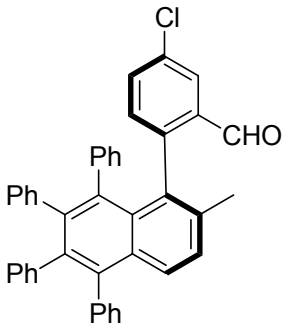
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.37 (d, *J* = 1.9 Hz), 161.41 (d, *J* = 246.1 Hz), 142.35 (d, *J* = 3.4 Hz), 142.04, 141.52, 140.33, 140.31, 139.70, 138.67, 138.57, 137.99, 136.75, 135.16 (d, *J* = 6.2 Hz), 133.70 (d, *J* = 7.0 Hz), 133.17, 132.30, 131.78, 131.34, 131.20, 131.04, 131.01, 130.96, 128.34, 128.02, 127.67, 127.56, 126.88, 126.78, 126.58, 126.51, 126.24, 126.14, 125.35, 125.29, 125.09, 120.15 (d, *J* = 21.8 Hz), 112.57 (d, *J* = 22.2 Hz), 21.63.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.78

**HRMS** (APCI) Calcd for $C_{42}H_{30}FO$ $(M+H)^+$: 569.2275 Found: 569.2280.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 12.76 min, t (major) = 15.75 min, 99% ee; $[\alpha]_D^{20}$ = -43.9 (*c* = 1.00, $CHCl_3$).

**5-Chloro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3g)**




Yellow solid. Isolated yield: 54.9 mg, 94%. Melting point: 89-92 °C (petroleum

ether/EtOAc = 20/1).

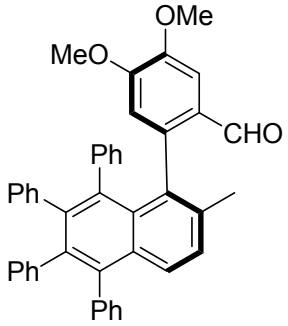
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.21-7.26 (m, 4H), 7.14-7.19 (m, 2H), 6.64-6.84 (m, 12H), 6.54-6.60 (m, 3H), 6.44-6.46 (m, 1H), 1.90 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 191.56, 145.02, 142.46, 141.84, 140.70, 140.68, 139.11, 139.03, 138.35, 136.84, 135.06, 133.77, 133.55, 133.42, 133.15, 132.82, 132.18, 132.09, 131.74, 131.71, 131.64, 131.52, 131.43, 131.41, 131.35, 128.74, 128.50, 128.09, 127.98, 127.29, 127.20, 127.00, 126.93, 126.78, 126.67, 126.58, 125.78, 125.65, 125.54, 22.04.

**HRMS** (APCI) Calcd for $C_{42}H_{30}ClO$ $(M+H)^+$: 585.1980 Found: 585.1979.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 0.5 mL/min, UV 254 nm, t (minor) = 26.23min, t (major) = 30.67 min, 99% ee; $[\alpha]_D^{20}$ = -98.1 (*c* = 1.40, $CHCl_3$).

**4,5-Dimethoxy-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3h)**




Yellow solid. Isolated yield: 40.7 mg, 67%. Melting point: 100-104 °C (petroleum ether/EtOAc = 5/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 1.2 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.17-7.26 (m, 5H), 7.05 (s, 1H), 6.75-6.82 (m, 5H), 6.60-6.70 (m, 9H), 6.51-6.53 (m, 1H), 6.27 (s, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 1.98 (s, 3H).

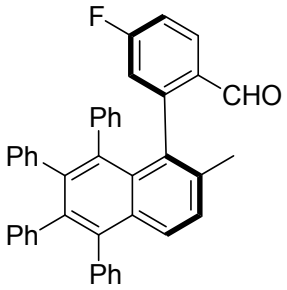
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.35, 152.70, 147.80, 142.07, 141.70, 141.47, 140.48, 140.40, 139.81, 138.71, 138.49, 138.15, 136.79, 133.72, 132.02, 131.92, 131.85, 131.63, 131.39, 131.28, 131.12, 131.08, 130.94, 128.30, 127.85, 127.74, 127.70, 127.53, 126.60, 126.55, 126.49, 126.46, 126.23, 126.10, 125.98, 125.32,

125.08, 125.03, 114.10, 108.00, 77.47, 77.15, 76.83, 55.98, 55.87, 21.65.

**HRMS** (APCI) Calcd for $C_{44}H_{35}O_3$ $(M+H)^+$: 611.2581 Found: 611.2583.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel AD-H column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 8.35 min, t (major) = 11.27 min, 99% ee; $[\alpha]_D^{20}$ = -7.3 (*c* = 1.40, $CHCl_3$).

**4-Fluoro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3i)**




Yellow solid. Isolated yield: 39.8 mg, 70%. Melting point: 188-190 °C (petroleum ether/EtOAc = 20/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.51-7.55 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.17-7.26 (m, 5H), 6.71-6.84 (m, 8H), 6.63-6.70 (m, 5H), 6.55-6.60 (m, 4H), 1.92 (s, 3H).

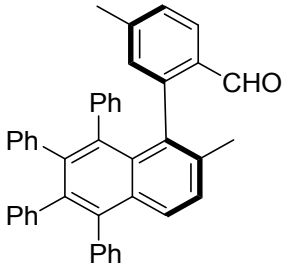
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 190.99, 166.51, 163.97, 149.36, 149.27, 142.08, 141.17, 140.31, 139.67, 138.72, 138.65, 137.90, 136.92, 132.88, 132.43, 131.73, 131.40, 131.35, 131.32, 131.11, 131.05, 131.03, 130.95, 130.52, 130.50, 129.50, 129.40, 128.35, 128.16, 127.68, 127.57, 126.85, 126.62, 126.59, 126.53, 126.24, 126.18, 125.53, 125.37, 125.10, 118.97, 118.75, 114.56, 114.34, 21.52.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -105.65.

**HRMS** (APCI) Calcd for $C_{42}H_{30}FO$ $(M+H)^+$: 569.2275 Found: 569.2280.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 16.01 min, t (major) = 19.80 min, 99% ee; $[\alpha]_D^{20}$ = -133.5 (*c* = 0.80, $CHCl_3$).

**4-Methyl-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3j)**




White solid. Isolated yield: 42.0 mg, 74%. Melting point: 210-213 °C (petroleum ether/EtOAc = 20/1).

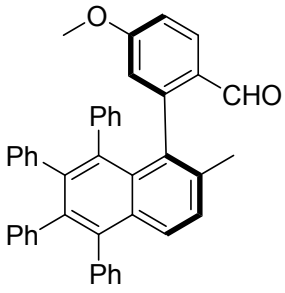
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.42, (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.24-7.27 (m, 4H), 7.18-7.22 (m, 1H), 6.77-6.87 (m, 6H), 6.66-6.73 (m, 4H), 6.57-6.64 (m, 5H), 6.50-6.56 (m, 2H), 2.20 (s, 3H), 1.91 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.44, 146.42, 143.57, 141.76, 141.24, 140.50, 140.46, 139.85, 138.56, 138.36, 138.22, 136.37, 134.38, 132.82, 132.34, 131.66, 131.60, 131.56, 131.38, 131.35, 131.32, 131.16, 131.09, 131.01, 128.33, 127.80, 127.64, 127.59, 127.49, 126.82, 126.64, 126.54, 126.49, 126.44, 126.18, 126.05, 125.93, 125.27, 125.18, 124.96, 21.61, 21.54.

**HRMS** (APCI) Calcd for $C_{43}H_{33}O$ $(M+H)^+$: 565.2526 Found: 565.2533.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 99/1, v = 1.0 mL/min, UV 254 nm, t (minor) = 8.09 min, t (major) = 9.18 min, 98% ee; $[\alpha]_D^{20}$ = -24.7 (*c* = 0.70, $CHCl_3$).

**4-Methoxy-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3k)**




Yellow solid. Isolated yield: 34.2 mg, 59%. Melting point: 98-103 °C (petroleum ether/EtOAc = 12/1)

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.23-7.28 (m, 4H)， 7.18-7.21 (m, 1H), 6.77-6.83

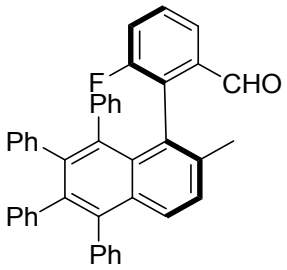
(m, 5H), 6.55-6.73 (m, 10H), 6.32 (d, $J$ = 2.4 Hz, 1H), 3.73 (s, 3H), 1.95 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.29, 162.99, 148.69, 141.89, 141.22, 140.49, 140.42, 139.81, 138.62, 138.44, 138.14, 136.24, 134.08, 132.32, 131.64, 131.41, 131.38, 131.32, 131.14, 131.08, 131.00, 129.02, 128.33, 127.95, 127.74, 127.65, 127.50, 126.58, 126.55, 126.51, 126.44, 126.18, 126.05, 125.28, 125.18, 124.98, 116.87, 113.22, 55.35, 21.52.

**HRMS** (APCI) Calcd for $C_{43}H_{33}O_2$ $(M+H)^+$: 581.2475 Found: 581.2471.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 90/10, v = 1.0 mL/min, UV 254 nm, t (minor) = 6.62 min, t (major) = 8.51 min, 99% ee; $[\alpha]_D^{20}$ = +106.6 ($c$ = 0.80, $CHCl_3$).

**3-Fluoro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3l)**




Pale yellow solid. Isolated yield: 35.0 mg, 62%. Melting point: 102-106 °C (petroleum ether/EtOAc = 20/1).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.71 (d, $J$ = 9.0 Hz, 1H), 7.39-7.41 (m, 1H), 7.33 (d, $J$ = 9.0 Hz, 1H), 7.16-7.29 (m, 5H), 7.02-7.06 (m, 1H), 6.90-6.93 (m, 1H), 6.75-6.87 (m, 6H), 6.59-6.72 (m, 7H), 6.53-6.56 (m, 1H), 6.45-6.47 (m, 1H), 1.93 (m, 3H).

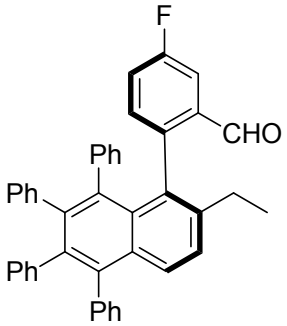
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 191.80 (d, $J$ = 4.1 Hz), 159.19 (d, $J$ = 243.1 Hz), 142.47, 140.99, 140.88, 140.79, 140.19, 139.29, 139.01, 135.97 (d, $J$ = 2.9 Hz), 134.22 (d, $J$ = 18.3 Hz), 132.08, 131.97, 131.81, 131.71, 131.55, 131.49, 131.31, 129.32 (d, $J$ = 8.0 Hz), 129.00, 128.79, 128.02, 127.97, 127.37, 127.17, 127.03, 126.95, 126.91, 126.58, 126.55, 126.17, 125.72, 125.41, 123.51 (d, $J$ = 3.1 Hz), 121.06 (d, $J$ = 22.9 Hz), 21.69.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -110.39

**HRMS** (APCI) Calcd for $C_{42}H_{30}FO$ $(M+H)^+$: 569.2275 Found: 569.2280.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 17.37 min, t (major) = 24.59 min, 99% ee; $[\alpha]_D^{20}$ = -28.42 (*c* = 0.70 , $CHCl_3$).

**2-(2-Ethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-fluorobenzaldehyde (3m)**




Pale yellow oil. Isolated yield: 50.3 mg, 86%. (petroleum ether/EtOAc = 20/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.12-7.28 (m, 6H), 6.87-6.89 (m, 2H), 6.75-6.83 (m, 5H), 6.64-6.74 (m, 6H), 6.55-6.62 (m, 2H), 6.46-6.53 (m, 2H), 2.11-2.25 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

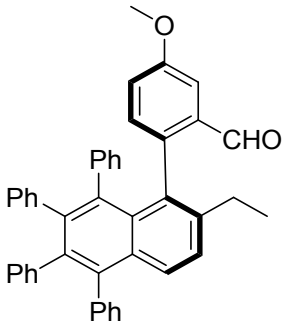
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.43 (d, *J* = 2.0 Hz), 161.46 (d, *J* = 246.4 Hz), 142.70, 142.15, 141.67, 141.66, 141.62, 140.35, 139.73, 138.69 (d, *J* = 1.6 Hz), 138.29, 135.54 (d, *J* = 6.4 Hz), 134.23 (d, *J* = 7.0 Hz), 132.17, 131.78, 131.65, 131.35, 131.17, 131.13, 131.05, 131.00, 128.47, 127.70, 127.60, 126.94, 126.78, 126.61, 126.53, 126.26, 126.16, 125.38, 125.25, 125.10, 119.79 (d, *J* = 21.9 Hz), 112.36 (d, *J* = 22.1 Hz), 27.11, 15.20.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.61.

**HRMS** (APCI) Calcd for $C_{43}H_{32}FO$ $(M+H)^+$: 583.2432 Found: 583.2435.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 99/1, v = 1.0 mL/min, UV 254 nm, t (minor) = 7.61 min, t (major) = 8.88 min, 99% ee; $[\alpha]_D^{20}$ = -83.1 (*c* = 1.0, $CHCl_3$).

**2-(2-Ethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-methoxybenzaldehyde (3n)**




White solid. Isolated yield: 48.6 mg, 82%. Melting point: 184-187 °C (petroleum ether/EtOAc = 12/1).

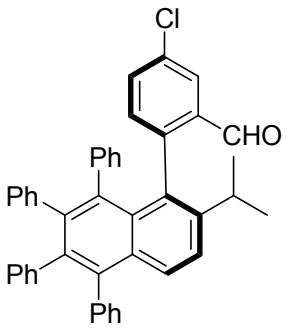
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.23-7.27 (m, 4H), 7.16-7.20 (m, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.73-6.82 (m, 7H), 6.64-6.70 (m, 6H), 6.56-6.58 (m, 2H), 6.48-6.51 (m, 2H), 3.76 (s, 3H), 2.15-2.27 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.56, 158.25, 142.84, 141.96, 141.80, 140.51, 140.46, 139.86, 138.69, 138.55, 138.51, 138.48, 134.82, 133.63, 133.00, 132.09, 131.59, 131.38, 131.35, 131.16, 131.12, 131.08, 131.06, 131.04, 128.08, 127.62, 127.54 126.74, 126.69, 126.58, 126.54 126.51, 126.46, 126.16, 126.07, 125.28, 124.96, 124.94, 120.63, 108.91, 55.47, 27.11, 15.23.

**HRMS** (APCI) Calcd for $C_{44}H_{35}O_2$ $(M+H)^+$: 595.2632 Found: 595.2635.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IE column, n-hexane/2-propanol = 98/2, v = 0.8 mL/min, UV 254 nm, t (minor) = 19.69 min, t (major) = 20.07 min, 99% ee; $[\alpha]_D^{20}$ = +108.1 (*c* = 0.60, $CHCl_3$).

**5-Chloro-2-(2-isopropyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3o)**




Yellow solid. Isolated yield: 57.6 mg, 94%. Melting point: 238-240 °C (petroleum ether/EtOAc = 20/1).

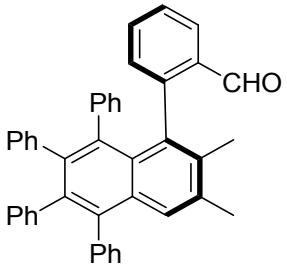
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.23-7.26 (m, 4H), 7.18-7.21 (m, 1H), 7.11-7.14 (m, 1H), 6.65-6.85 (m, 12H), 6.50-6.62 (m, 3H), 6.42-6.45 (m, 1H), 2.35-2.41 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.05, 146.73, 143.94, 142.22, 141.69, 140.31, 139.69, 138.79, 138.66, 138.45, 135.25, 133.74, 133.23, 132.33, 132.18, 131.54, 131.50, 131.33, 131.30, 131.13, 131.11, 131.03, 131.00, 130.97, 128.79, 127.67, 127.57, 126.93, 126.78, 126.59, 126.51, 126.24, 126.14, 125.37, 125.10, 123.42, 30.15, 24.04, 22.81.

**HRMS** (APCI) Calcd for $C_{44}H_{34}ClO$ $(M+H)^+$: 613.2293 Found: 613.2291.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 99/1, v = 0.5 mL/min, UV 254 nm, t (minor) = 11.05 min, t (major) = 14.52 min, 98% ee; $[\alpha]_D^{20}$ = +55.8 (*c* = 0.66, $CHCl_3$).

**2-(2,3-Dimethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3p)**




Pale yellow oil. Isolated yield: 49.1 mg, 87%. (petroleum ether/EtOAc = 20/1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.53 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.18-7.26 (m, 6H), 7.06-7.09 (m, 1H), 6.75-6.86 (m, 6H), 6.70-6.72 (m, 2H), 6.60-6.68 (m, 4H), 6.53-6.56 (m, 2H), 6.39-6.42 (m, 2H), 2.33 (s, 3H), 1.79 (s, 3H).

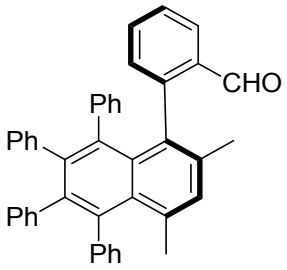
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.77, 147.01, 141.57, 140.94, 140.63, 140.60, 139.94, 138.46, 138.15, 137.80, 136.36, 134.94, 134.34, 133.91, 132.89, 132.30, 132.24, 131.53, 131.47, 131.43, 131.22, 131.16, 131.11, 130.45, 127.65, 127.53, 126.87, 126.72, 126.66, 126.53, 126.47, 126.18, 126.07, 125.24, 125.04, 124.93, 21.55, 17.72.

**HRMS** (APCI) Calcd for $C_{43}H_{33}O$ $(M+H)^+$: 565.2526 Found: 565.2533.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee

was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 10.73 min, t (major) = 12.94 min, 98% ee; $[\alpha]_D^{20}$ = -57.6 (*c* = 1.00, $CHCl_3$).

**2-(2,4-Dimethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3q)**




Yellow oil. Isolated yield: 45.2 mg, 80%. (petroleum ether/EtOAc = 20/1).

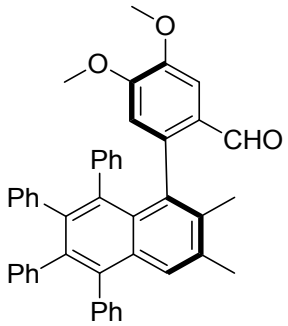
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.45-7.48 (m, 1H), 7.14-7.22 (m, 4H), 7.04-7.14 (m, 4H), 6.81-6.83 (m, 1H), 6.74-6.79 (m, 3H), 6.61-6.73 (m, 8H), 6.53-6.56 (m, 1H), 6.47-6.50 (m, 1H), 6.41-6.45 (m, 1H), 6.25-6.28 (m, 1H), 1.94 (m, 3H), 1.87 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.93, 146.71, 142.83, 142.13, 140.59, 140.57, 140.39, 139.30, 138.55, 137.66, 135.84, 135.65, 133.95, 133.12, 132.78, 132.70, 132.64, 132.32, 132.14, 131.86, 131.75, 131.50, 131.49, 131.14, 131.04, 130.97, 130.88, 127.05, 127.01, 126.74, 126.66, 126.38, 126.30, 126.27, 126.19, 126.14, 125.02, 124.99, 124.91, 25.05, 20.85.

**HRMS** (APCI) Calcd for $C_{43}H_{33}O$ $(M+H)^+$: 565.2526 Found: 565.2533.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 9.63 min, t (major) = 12.51 min, 98% ee; $[\alpha]_D^{20}$ = -279.4 (*c* = 0.70, $CHCl_3$).

**2-(2,3-Dimethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-4,5-dimethoxybenzaldehyde (3r)**




Yellow solid. Isolated yield: 38.1 mg, 61%. Melting point: 103-105 °C (petroleum ether/EtOAc = 5/1).

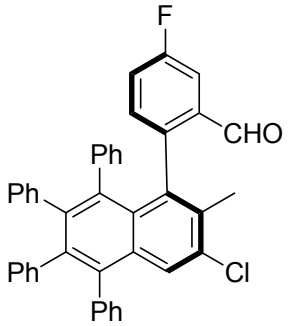
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.52 (s, 1H), 7.16-7.24 (m, 6H), 7.02 (s, 1H), 6.73-6.79 (m, 5H), 6.56-6.68 (m, 9H), 6.45-6.47 (m, 1H), 6.25 (s, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.32 (s, 3H), 1.87 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.48, 152.60, 147.78, 142.22, 141.64, 141.19, 140.61, 140.57, 139.91, 138.49, 138.02, 137.94, 136.65, 134.90, 133.65, 131.92, 131.79, 131.45, 131.37, 131.33, 131.21, 131.14, 131.12, 131.01, 130.72, 128.10, 127.79, 127.65, 127.48, 126.53, 126.45, 126.42, 126.39, 126.16, 126.03, 125.91, 125.22, 124.91, 114.39, 107.89, 77.44, 77.32, 77.12, 76.80, 55.96, 55.83, 21.50, 17.85.

**HRMS** (APCI) Calcd for $C_{45}H_{37}O_3$ $(M+H)^+$: 625.2737 Found: 625.2735.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IE column, n-hexane/2-propanol = 95/5, v = 1.0 mL/min, UV 254 nm, t (minor) = 15.10 min, t (major) = 16.97 min, 99% ee; $[\alpha]_D^{20}$ = +90.5 (*c* = 0.65, $CHCl_3$).

**2-(3-Chloro-2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-fluorobenzaldehyde (3s)**




Yellow solid. Isolated yield: 42.2 mg, 70%. Melting point: 100-104 °C (petroleum ether/EtOAc = 20/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.80 (s, 1H), 7.21-7.27 (m, 5H), 7.11-

7.14 (m, 1H), 6.90-6.95 (m, 1H), 6.76-6.85 (m, 6H), 6.65-6.75 (m, 6H), 6.57-6.61 (m, 1H), 6.51-6.54 (m, 2H), 6.38-6.41 (m, 1H), 1.96 (s, 3H).

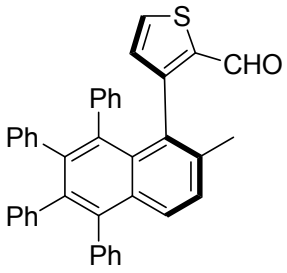
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 190.73 (d, *J* = 1.9 Hz), 161.60 (d, *J* = 247.0 Hz), 142.34, 141.62 (d, *J* = 3.6 Hz), 141.19, 140.00, 139.95, 139.60, 138.92, 138.11, 137.91, 135.41, 135.32 (d, *J* = 6.2 Hz), 134.96, 133.66, 133.59, 133.25, 132.21, 132.04, 131.28, 131.24, 131.01, 130.97, 130.89, 130.85, 130.69, 127.87, 127.74, 127.53, 126.94, 126.90, 126.86, 126.63, 126.57, 126.29, 126.20, 125.51, 125.39, 125.21, 120.19 (d, *J* = 21.9 Hz), 113.02 (d, *J* =22.3 Hz), 18.72.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -113.93.

**HRMS** (APCI) Calcd for $C_{42}H_{29}ClFO$ $(M+H)^+$: 603.1885 Found: 603.1881.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 11.93 min, t (major) = 18.92 min, 98% ee; $[\alpha]_D^{20}$ = -81.4 (*c* = 0.88, $CHCl_3$).

**3-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)thiophene-2-carbaldehyde (3t)**




Yellow solid. Isolated yield: 27.8 mg, 50%. Melting point: 85-89 °C (petroleum ether/EtOAc = 12/1).

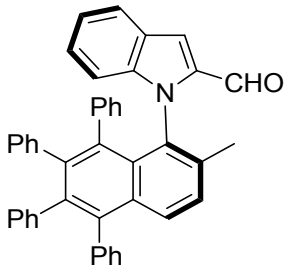
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.66 (d, *J* = 8.8 Hz), 7.31 (d, *J* = 8.8 Hz), 7.17-7.26 (m, 6H), 6.65-6.84 (m, 13H), 6.55-6.61 (m, 2H), 6.48 (d, *J* = 5.2 Hz), 2.00 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 184.27, 152.85, 142.01, 141.24, 140.34, 140.32, 139.66, 138.58, 138.23, 137.85, 136.96, 132.91, 132.36, 132.09, 131.67, 131.59, 131.56, 131.41, 131.26, 131.14, 131.12, 131.07, 130.85, 130.02, 128.31, 128.15, 127.64, 127.57, 127.20, 126.59, 126.57, 126.48, 126.27, 126.14, 125.45, 125.34, 125.07, 21.25.

**HRMS** (APCI) Calcd for $C_{40}H_{29}OS$ $(M+H)^+$: 557.1934 Found: 557.1934.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 22.64 min, t (major) = 26.70 min, 76% ee; $[\alpha]_D^{20}$ = +32.5 (*c* = 0.60, $CHCl_3$).

**1-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-1H-indole-2-carbaldehyde (3u)**




Yellow oil. Isolated yield: 14.7 mg, 25%. (petroleum ether/EtOAc = 8/1).

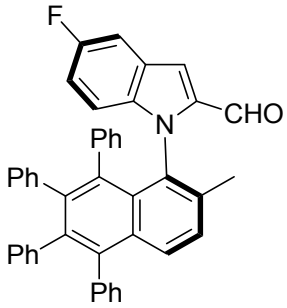
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.27-7.32 (m, 4H), 7.20-7.24 (m, 2H), 7.07-7.10 (m, 1H) 6.47-6.83 (m, 15H), 6.02-6.06 (m, 2H), 1.71 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 182.22, 142.57, 140.95, 140.40, 139.78, 139.12, 138.95, 138.75, 137.06, 136.71, 135.95, 132.58, 131.81, 131.41, 131.24, 131.16, 130.96, 130.32, 129.32, 128.83, 128.80, 128.63, 127.64, 127.52, 126.66, 126.55, 126.52, 126.49, 126.41, 126.06, 125.90, 125.57, 125.26, 124.93, 124.83, 122.78, 121.04, 115.68, 112.24, 17.63.

**HRMS** (APCI) Calcd for $C_{44}H_{32}NO$ $(M+H)^+$: 590.2478 Found: 590.2475.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 0.8 mL/min, UV 254 nm, t (minor) = 12.04 min, t (major) = 13.41 min, 96% ee; $[\alpha]_D^{20}$ = +134.4 (*c* = 0.30, $CHCl_3$).

**5-Fluoro-1-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-1H-indole-2-carbaldehyde (3v)**




Yellow solid. Isolated yield: 24.2 mg, 40%. Melting point: 189-192 °C (petroleum ether/EtOAc = 8/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.28-7.30 (m, 1H), 7.23-7.27 (m, 3H), 7.17-7.22 (m, 1H), 7.10-7.13 (m, 1H), 6.99-7.04 (m, 1H), 6.73-6.83 (m, 6H), 6.67-6.72 (m, 3H), 6.57-6.66 (m, 4H), 6.49-6.53 (m, 2H), 6.12-6.16 (m, 1H), 6.04-6.07 (m, 1H), 1.70 (s, 3H).

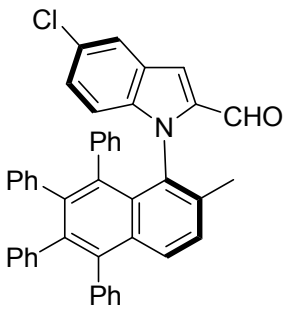
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 182.18, 158.46 (d, *J* = 236.0 Hz), 142.77, 140.30, 139.69, 139.76 (d, *J* = 4.1 Hz), 138.92, 137.85, 137.56, 137.10, 135.82, 132.63, 131.48, 131.39, 131.21, 131.13, 130.95, 130.92, 130.31, 129.25, 129.03, 128.87, 128.61, 127.68, 127.55, 126.67, 126.62, 126.56, 126.45, 126.12, 125.99, 125.69, 125.33, 125.10, 125.04, 124.93, 115.55 (d, *J* = 26.8 Hz), 114.72 (d, *J* = 5.5 Hz), 113.27 (d, *J* = 9.4 Hz), 106.82 (d, *J* = 23.2 Hz), 17.57.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -122.45.

**HRMS** (APCI) Calcd for $C_{44}H_{31}FNO$ $(M+H)^+$: 608.2384 Found: 608.2375.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IF column, n-hexane/2-propanol = 99/1, v = 0.8 mL/min, UV 254 nm, t (minor) = 13.08 min, t (major) = 14.68 min, 95% ee; $[\alpha]_D^{20}$ = +97.6 (*c* = 0.45, $CHCl_3$).

**5-Chloro-1-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-1H-indole-2-carbaldehyde (3w)**



Yellow solid. Isolated yield: 20.6 mg, 33%. Melting point: 107-110 °C (petroleum ether/EtOAc = 8/1).

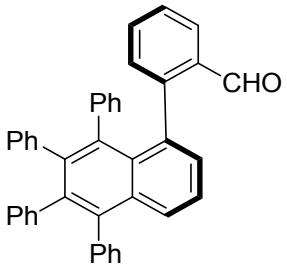
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.28-7.31 (m, 2H), 7.17-7.26 (m, 4H), 6.73-6.82 (m, 6H), 6.57-6.72 (m, 7H), 6.50-6.55 (m, 2H), 6.13-6.17 (m, 1H), 6.04-6.07 (m, 1H), 1.69 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 182.16, 142.81, 140.27, 139.66, 139.17, 139.14, 139.08, 138.95, 137.60, 137.03, 135.77, 132.63, 131.38, 131.30, 131.21, 131.13, 130.95, 130.92, 130.90, 130.35, 129.14, 129.10, 128.89, 128.61, 127.68, 127.56, 127.40, 126.88, 126.73, 126.63, 126.56, 126.46, 126.12, 126.01, 125.73, 125.35, 125.27, 125.18, 124.95, 121.86, 114.28, 113.42, 17.58.

**HRMS** (APCI) Calcd for $C_{44}H_{31}ClNO$ $(M+H)^+$: 624.2089 Found: 624.2085.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IE column, n-hexane/2-propanol = 98/2, v = 0.5 mL/min, UV 254 nm, t (minor) = 15.45 min, t (major) = 17.14 min, 96% ee; $[\alpha]_D^{20}$ = +148.2 (*c* = 0.34, $CHCl_3$).

**2-(5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3aa)**




White solid. Isolated yield: 33.7 mg, 63%. Melting point: 95-96 °C (petroleum ether/EtOAc = 30/1)

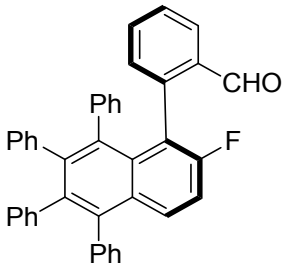
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.46-7.74 (m, 1H), 7.51-7.49 (m, 1H), 7.41-7.38 (m 1H), 7.28-7.25 (m, 4H), 7.23-7.15 (m, 3H), 7.08-7.03 (m, 2H), 6.85-6.80 (m, 5H), 6.77-6.74 (m, 1H), 6.72-6.70 (m, 3H), 6.65-6.61 (m, 5H), 6.56-6.53 (m, 1H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 193.1, 148.4, 142.0, 140.9, 140.7, 140.65, 140.2, 139.8, 139.3, 138.7, 136.7, 133.7, 133.5, 133.0, 132.6, 132.5, 131.9, 131.7, 131.69, 131.5, 131.4, 128.5, 128.1, 128.0, 127.14, 127.1, 127.03, 127.0, 126.9, 126.8, 126.7, 126.6, 126.1, 125.8, 125.5, 124.9.

**HRMS** (APCI) Calcd for $C_{41}H_{29}O$ $(M+H)^+$: 537.2212 Found: 537.2219.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 95/5, v = 1.0 mL/min, UV 254 nm, t (minor) = 11.77 min, t (major) = 14.00 min, 0% ee.

**2-(2-fluoro-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3bb)**




Yellow solid. Isolated yield: 34.2 mg, 43%. Melting point: 86-87 °C (petroleum ether/EtOAc = 30/1)

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.79-7.76 (m, 1H), 7.52-7.51 (m, 1H), 7.28-7.20 (m, 7H), 7.13 (t, J = 7.5 Hz, 1H), 7.01-6.99 (m 1H), 6.86-6.85 (m, 2H), 6.82-6.73 (m, 5H), 6.71-6.68 (m, 3H), 6.66-6.62 (m, 2H), 6.55-6.48 (m, 3H).

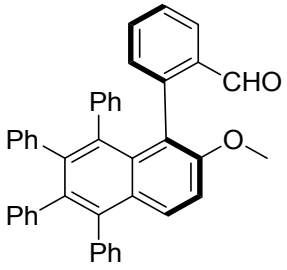
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 192.5, 159.0 (*J* = 242.3 Hz), 143.1, 140.5 (*J* = 2.9 Hz), 140.4, 139.8, 139.78, 139.4, 139.1 (*J* = 1.9 Hz), 138.6 (*J* = 5.8 Hz), 134.2, 133.0 (*J* = 3.4 Hz), 132.3 (*J* = 2.6 Hz), 131.7, 131.6, 131.5, 131.4, 131.2, 131.0, 130.95, 130.7, 128.2, 128.0, 127.9, 127.6, 127.2, 127.4, 127.1, 127.0, 126.95, 126.7, 126.6, 126.1, 125.8, 125.6, 121.1 (*J* = 16.0 Hz), 115.6 (*J* = 27.1 Hz).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -110.1.

**HRMS** (APCI) Calcd for $C_{41}H_{28}FO$ $(M+H)^+$: 555.2118 Found: 555.2114.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 95/15, v = 1.0 mL/min, UV 254 nm, t (major) = 11.70 min, t (minor) = 14.78 min, 26% ee; $[\alpha]_D^{20}$ = +56.2 (*c* = 0.50, $CHCl_3$).

**2-(2-methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3cc)**




White solid. Isolated yield: 53.8 mg, 95%. Melting point: 107-108 °C (petroleum ether/EtOAc = 10/1)

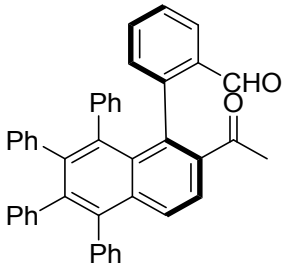
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.48-7.46 (m, 1H), 7.32-7.27 (m, 2H), 7.23-7.19 (m 5H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.92-6.85 (m, 3H), 6.82-6.78 (m, 4H), 6.78-6.70 (m, 3H), 6.69-6.66 (m, 2H), 6.65-6.60 (m, 1H), 3.66 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 193.8, 155.8, 143.4, 142.5, 141.5, 140.8, 140.75, 140.1, 138.8, 137.9, 137.6, 134.3, 133.1, 133.06, 132.94, 132.9, 131.8, 131.64, 131.62, 131.6, 131.4, 131.2, 130.2, 129.2, 128.1, 127.9, 127.2, 126.9, 126.88, 126.6, 126.5, 126.4, 125.7, 125.6, 125.4, 121.7, 112.6, 56.7.

**HRMS** (APCI) Calcd for $C_{42}H_{31}O_2$ $(M+H)^+$: 567.2318 Found: 567.2313.

Enantiomeric excess was determined by HPLC analysis using a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 95/5, v = 1.0 mL/min, UV 254 nm, t (minor) = 7.81 min, t (major) = 10.42 min, 35% ee; $[\alpha]_D^{20}$ = +74 (*c* = 1.2, $CHCl_3$).

**2-(2-acetyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3dd)**




White solid. Isolated yield: 20.2 mg, 35%. Melting point: 89-90 °C (petroleum ether/EtOAc = 5/1)

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.80-7.78 (m, 2H), 7.46-7.44 (m, 1H), 7.41-7.39 (m, 1H), 7.29-7.27 (m, 2H), 7.25-7.23 (m 2H), 7.21-7.18 (m, 1H), 7.01-6.99 (m, 1H), 6.85-6.80 (m, 5H), 6.75-6.70 (m, 3H), 6.68-6.63 (m, 3H), 6.57-6.55 (m, 2H),

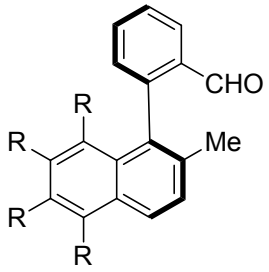
6.53-6.50 (m, 1H), 6.46-6.44 (m, 1H), 1.83 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 205.5, 192.1, 143.7, 143.2, 142.4, 141.0, 140.8, 140.4, 140.2, 139.7, 139.6, 139.2, 134.8, 134.0, 133.3, 133.0, 132.64, 132.6, 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 128.8, 128.2, 128.1, 128.06, 127.6, 127.2, 127.1, 127.0, 126.96, 126.7, 126.6, 125.9, 125.6, 123.0, 31.0

**HRMS** (APCI) Calcd for $C_{43}H_{31}O_2$ $(M+H)^+$: 579.2318 Found: 579.2315.

Enantiomeric excess was determined by HPLC analysis using a Daicel Chiralcel AD-H column, n-hexane/2-propanol = 95/5, v = 1.0 mL/min, UV 254 nm, t (minor) = 5.43 min, t (major) = 7.13 min, 52% ee; $[\alpha]_D^{20}$ = +86.4 (*c* = 0.35, $CHCl_3$).

**2-(2-Methyl-5,6,7,8-tetra-*p*-tolylnaphthalen-1-yl)benzaldehyde (4a)**




R = *p*-Me-$C_6H_4$

Pale yellow solid. Isolated yield: 41.3 mg, 68%. Melting point: 246-250 °C (petroleum ether/EtOAc = 20/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.46-7.49 (m, 1H), 7.23-7.25 (m, 1H), 7.17-7.21 (m, 1H), 7.09-7.13 (m, 3H), 7.05-7.07 (m, 2H), 6.81-6.83 (m, 1H), 6.58-6.71 (m, 5H), 6.42-6.55 (m, 5H), 6.28-6.30 (m, 1H), 6.21-6.24 (m, 1H), 2.32 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.84, (s, 3H).

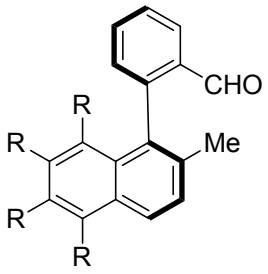
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.81, 146.92, 141.96, 138.62, 138.40, 138.18, 137.64, 137.61, 137.03, 136.12, 135.69, 134.22, 134.16, 133.97, 133.30, 132.73, 132.36, 131.98, 131.90, 131.24, 131.20, 131.03, 130.96, 130.87, 130.79, 128.31, 128.19, 127.97, 127.41, 127.36, 127.21, 127.15, 126.89, 126.74, 126.22, 126.13, 21.59, 21.27, 21.06, 20.98, 20.91.

**HRMS** (APCI) Calcd for $C_{46}H_{39}O$ $(M+H)^+$: 607.2995 Found: 607.2991.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-

propanol = 98/2, v = 0.5 mL/min, UV 254 nm, t (minor) = 22.33 min, t (major) = 25.57 min, 98% ee; $[\alpha]_D^{20}$ = -202.1 (*c* = 0.40, $CHCl_3$).

**2-(5,6,7,8-Tetrakis(4-fluorophenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4b)**




R = *p*-F-$C_6H_4$

Yellow solid. Isolated yield: 56.0 mg, 90%. Melting point: 94-96 °C (petroleum ether/EtOAc = 15/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.56-7.58 (m, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.25-7.29 (m, 1H), 7.16-7.22 (m, 3H), 6.96-7.01 (m, 2H), 6.85-6.87 (m, 1H), 6.71-6.77 (m, 2H), 6.55-6.62 (m, 3H), 6.41-6.52 (m, 5H), 6.33-6.38 (m, 1H), 6.22-6.27 (m, 1H), 1.90 (s, 3H).

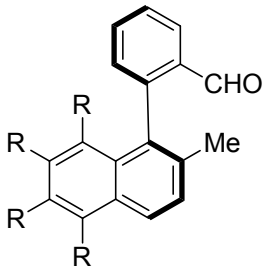
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.32, 161.6 (d, *J* = 244.8 Hz), 160.69 (d, *J* = 243.9 Hz), 160.48 (d, *J* = 243.7 Hz), 160.40 (d, *J* = 244.3 Hz), 146.09, 141.08, 138.20, 137.68, 136.99, 136.14, 130.10, 136.05, 135.35, 135.32, 134.37, 133.73, 133.65, 133.63, 133.15, 132.74, 132.70, 132.66, 132.63, 132.50, 132.44, 132.42, 132.36, 132.28, 132.25, 132.20, 132.17, 131.99, 131.75, 128.88, 127.50, 127.11, 115.01, 114.92, 114.80, 114.71, 114.07, 113.99, 113.86, 113.80, 113.78, 113.73, 113.69, 113.63, 113.59, 113.52, 113.41, 21.62.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -115.27, -116.41, -116.66, -116.72.

**HRMS** (APCI) Calcd for $C_{42}H_{27}F_4O$ $(M+H)^+$: 623.1993 Found: 623.1995.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-propanol = 95/5, v = 1.0 mL/min, UV 254 nm, t (minor) = 8.08 min, t (major) = 9.41 min, 96% ee; $[\alpha]_D^{20}$ = -142.1 (*c* = 0.48, $CHCl_3$).

**2-(5,6,7,8-Tetrakis(4-chlorophenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4c)**




*p*-Cl-$C_6H_4$

Yellow solid. Isolated yield: 27.5 mg, 40%. Melting point: 261-263 °C (petroleum ether/EtOAc = 20/1).

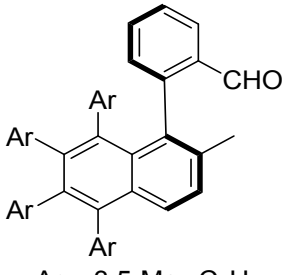
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.56-7.59 (m, 2H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.26-7.29 (m, 2H), 7.23-7.25 (m, 2H), 7.12-7.17 (m, 2H), 6.86-6.89 (m, 2H), 6.82-6.84 (m, 1H), 6.70-6.79 (m, 4H), 6.57-6.64 (m, 2H), 6.47-6.53 (m, 2H), 6.37-6.43 (m, 2H), 1.90 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 192.57, 146.11, 140.63, 139.56, 138.67, 138.61, 138.38, 138.06, 137.80, 137.60, 137.60, 137.34, 134.77, 134.04, 133.67, 133.56, 133.35, 132.80, 132.76, 132.59, 132.50, 132.41, 132.38, 132.36, 132.25, 132.09, 132.02, 131.98, 129.47, 128.61, 128.52, 127.80, 127.72, 127.66, 127.45, 127.40, 127.37, 127.28, 22.01.

**HRMS** (APCI) Calcd for $C_{42}H_{27}Cl_4O$ $(M+H)^+$: 687.0811 Found: 687.0815.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel AD-H column, n-hexane/2-propanol = 95/5, v = 1.0 mL/min, UV 254 nm, t (minor) = 8.41 min, t (major) = 14.86 min, 94% ee; $[\alpha]_D^{20}$ = -165.78 (*c* = 0.56, $CHCl_3$).

**2-(5,6,7,8-Tetrakis(3,5-dimethylphenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4d)**




Ar = 3,5-$Me_2$-$C_6H_3$

White solid. Isolated yield: 55.0 mg, 83%. Melting point: 190-194 °C (petroleum

ether/EtOAc = 15/1).

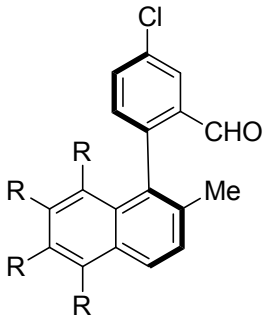
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 0.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.48-7.50 (m, 1H), 7.28-7.34 (m, 2H), 7.09-7.14 (m, 1H), 6.85-6.95 (m, 4H), 6.50 (s, 2H), 6.42 (s, 2H), 6.30 (s, 1H), 6.21-6.22 (m, 3H), 6.01 (s, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.99-2.01 (m, 6H), 1.96 (s, 3H), 1.93 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H), 1.80 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.92, 146.75, 142.00, 140.98, 140.12, 139.80, 138.60, 138.18, 137.90, 136.50, 136.46, 135.80, 135.38, 135.22, 134.98, 134.68, 134.48, 134.32, 133.30, 131.99, 131.70, 131.53, 131.23, 131.11, 129.22, 129.19, 129.16, 129.09, 129.05, 127.79, 127.75, 126.75, 126.41, 126.06, 125.64, 21.59, 21.25, 21.24, 20.95, 20.88, 20.79, 20.68, 20.63.

**HRMS** (APCI) Calcd for $C_{50}H_{47}O$ $(M+H)^+$: 663.3621 Found: 663.3625.

Transform the aldehyde group to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis using a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 0.8 mL/min, UV 254 nm, t (minor) = 9.17 min, t (major) = 12.26 min, 98% ee; $[\alpha]_D^{20}$ = -58.6 (*c* = 0.50, $CHCl_3$).

**5-Chloro-2-(5,6,7,8-tetrakis(4-fluorophenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4f)**




R = *p*-F-$C_6H_4$

Pale yellow oil. Isolated yield: 49.9 mg, 76%. (petroleum ether/EtOAc = 15/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.22-7.25 (m, 1H), 7.15-7.21 (m, 2H), 6.96-6.01 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.71-6.77 (m, 2H), 6.55-6.64 (m, 3H), 6.34-6.53 (m, 7H), 1.94 (s, 3H).

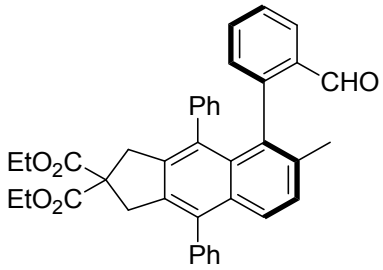
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 190.89, 161.67 (d, *J* = 244.8 Hz), 160.71 (d, *J* = 244.0 Hz), 160.68 (d, *J* = 245.4 Hz), 160.53 (d, *J* = 244.0 Hz), 144.31, 141.32, 138.32, 137.88, 137.39, 137.15, 137.11, 137.00, 135.96, 135.92, 135.19, 135.16, 134.70, 133.66, 133.58, 133.52, 133.36, 132.97, 132.94, 132.70, 132.69, 132.62, 132.61, 132.44, 132.36, 132.33, 132.23, 132.21, 132.14, 131.90, 131.86, 128.87, 127.91, 126.63, 115.07, 114.98, 114.85, 114.77, 114.13, 114.05, 114.02, 113.98, 113.91, 113.84, 113.81, 113.76, 113.73, 113.61, 113.51, 21.65.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -115.10, -115.70, -116.25, -116.47.

**HRMS** (APCI) Calcd for $C_{42}H_{26}ClF_4O$ $(M+H)^+$: 657.1603 Found: 657.1605.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 6.59 min, t (major) = 9.15 min, 97% ee, $[\alpha]_D^{20}$ = -39.6 (*c* = 0.60, $CHCl_3$).

**Diethyl-(*S*)-5-(2-formylphenyl)-6-methyl-4,9-diphenyl-1,3-dihydro-2*H*-cyclopent a[*b*]naphthalene-2,2-dicarboxylate (4g)**




Yellow oil. Isolated yield: 12.2 mg, 21%. (petroleum ether/EtOAc = 8/1).

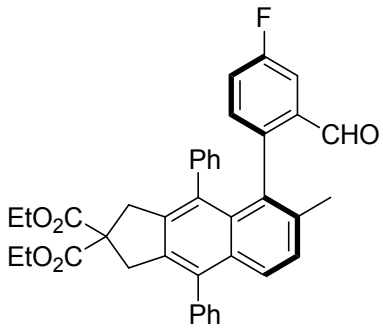
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.41-7.58 (m, 6H), 7.22-7.27 (m, 2H), 7.10-7.14 (m, 1H), 7.85-7.98 (m, 4H), 6.72-6.75 (m, 1H), 6.64-6.67 (m, 1H), 4.05-4.13 (m, 4H), 3.44-3.54 (m, 2H), 3.03-3.22 (m, 2H), 1.84 (s, 3H), 1.11-1.17 (m, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.52, 171.49, 171.32, 146.13, 141.32, 140.29, 139.09, 136.07, 135.48, 135.03, 134.94, 134.08, 133.84, 133.13, 132.21, 131.91, 131.36, 130.21, 130.03, 130.00, 129.31, 128.68, 128.60, 128.03, 127.98, 127.89, 127.69, 127.43, 127.19, 126.73, 126.62, 125.91, 61.62, 60.00, 41.02. 40.34, 21.41, 14.00.

**HRMS** (APCI) Calcd for $C_{39}H_{35}O_5$ $(M+H)^+$: 583.2479 Found: 583.2475.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IE column, n-hexane/2-propanol = 90/10, v = 1.0 mL/min, UV 254 nm, t (minor) = 11.73 min, t (major) = 15.34 min, 94% ee, $[\alpha]_D^{20}$ = +50.4 (*c* = 0.24, $CHCl_3$).

**Diethyl-(*S*)-5-(4-fluoro-2-formylphenyl)-6-methyl-4,9-diphenyl-1,3-dihydro-2*H*-cyclopenta[*b*]naphthalene-2,2-dicarboxylate (4h)**




Yellow oil. Isolated yield: 11.3 mg, 19%. (petroleum ether/EtOAc = 8/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.53-7.59 (m, 2H), 7.40-7.50 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.14-7.17 (m, 1H), 6.92-7.05 (m, 4H), 6.82-6.86 (m, 1H), 6.72-6.75 (m, 1H), 6.62-6.65 (m, 1H), 4.06-4.13 (m, 4H), 3.43-3.53 (m, 2H), 3.03-3.20 (m, 2H), 1.86 (m, 3H), 1.12-1.17 (m, 6H).

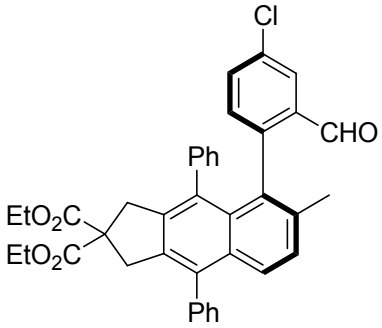
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.25, 171.46, 171.28, 323.07 (d, *J* = 246.5 Hz), 141.99 (d, *J* = 3.4 Hz), 141.42, 140.50, 138.95, 136.21, 135.76, 135.69, 135.14, 134.66, 134.48 (d, *J* = 6.9 Hz), 132.59, 131.94, 131.61, 130.11, 129.96 (d, *J* = 2.8 Hz), 129.29, 128.69, 128.62, 128.10, 128.06, 127.64, 127.47, 127.05, 125.97, 120.28 (d, *J* = 21.8 Hz), 112.52 (d, *J* = 22.2 Hz), 61.64, 59.95, 41.00, 40.31, 21.45, 13.98.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.50.

**HRMS** (APCI) Calcd for $C_{39}H_{34}FO_5$ $(M+H)^+$: 601.2385 Found: 601.2381.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IE column, n-hexane/2-propanol = 90/10, v = 1.0 mL/min, UV 254 nm, t (minor) = 9.77 min, t (major) = 11.31 min, 98% ee; $[\alpha]_D^{20}$ = +61.2 (*c* = 0.22, $CHCl_3$).

**Diethyl-(*S*)-5-(4-chloro-2-formylphenyl)-6-methyl-4,9-diphenyl-1,3-dihydro-2*H*-cyclopenta[*b*]naphthalene-2,2-dicarboxylate (4i)**




Pale yellow oil. Isolated yield: 17.3 mg, 28%, (petroleum ether/EtOAc = 8/1).

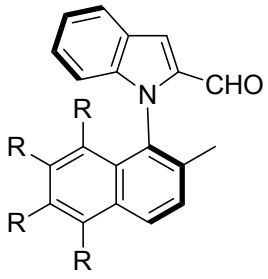
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.53-7.59 (m, 2H), 7.41-7.50 (m, 4H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.18-7.20 (m, 1H), 7.05-7.09 (m, 1H), 6.97-7.01 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.70-6.73 (m, 1H), 6.62-6.65 (m, 1H), 4.06-4.13 (m, 4H), 3.44-3.53 (m, 2H), 3.04-3.21 (m, 2H), 1.87 (s, 3H), 1.12-1.17 (m, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.07, 171.45, 171.27, 144.27, 141.30, 140.50, 138.92, 136.26, 135.43, 135.18, 135.16, 134.59, 133.62, 133.43, 132.88, 132.43, 131.93, 131.51, 130.20, 129.98, 129.94, 129.33, 128.70, 128.62, 128.10, 127.63, 127.48, 127.11, 126.32, 125.88, 61.64, 59.95, 41.00, 40.31, 21.44, 13.98.

**HRMS** (APCI) Calcd for $C_{39}H_{34}ClO_5$ $(M+H)^+$: 617.2089 Found: 617.2085.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IE column, n-hexane/2-propanol = 90/10, v = 1.0 mL/min, UV 254 nm, t (minor) = 9.83 min, t (major) = 11.17 min, 99% ee; $[\alpha]_D^{20}$ = +76.8 (*c* = 0.28, $CHCl_3$).

**1-(5,6,7,8-Tetrakis(4-fluorophenyl)-2-methylnaphthalen-1-yl)-1*H*-indole-2-carbaldehyde (4j)**




R = *p*-F-$C_6H_4$

Pale yellow solid. Isolated yield: 23.8 mg, 36%, Melting point: 118-120 °C (petroleum ether/EtOAc = 8/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.56-7.59 (m, 2H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.21-7.30 (m, 5H), 7.12-7.17 (m, 2H), 6.82-6.89 (m, 3H), 6.69-6.79 (m, 4H), 6.57-6.64 (m, 2H), 6.47-6.53 (m, 2H), 6.37-6.43 (m, 2H), 1.90 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 182.07, 161.67 (d, *J* = 245.0 Hz), 160.66 (d, *J* = 244.0 Hz), 160.44 (d, *J* = 243.0 Hz), 160.34 (d, *J* = 244.0 Hz), 141.83, 140.94, 138.58, 138.02, 137.51, 136.65, 136.12, 136.08, 136.04, 135.50, 135.33, 135.30, 134.84, 134.81, 132.80, 132.71, 132.60, 132.52, 132.46, 132.38, 132.26, 132.23, 132.17, 132.09, 132.03, 131.38, 130.10, 130.02, 129.47, 129.19, 128.56, 126.87, 126.69, 123.03, 121.38, 116.64, 115.06, 114.93, 114.84, 114.72, 114.08, 113.97, 113.84, 113.76, 113.65, 113.48, 113.43, 113.27, 112.77, 112.56, 112.01, 111.83, 111.61, 17.63.

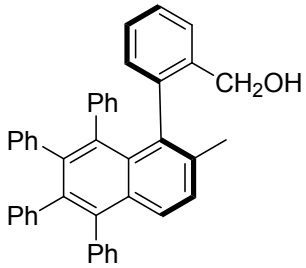
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -115.19, -116.38, -116.84, -117.32.

**HRMS** (APCI) Calcd for $C_{44}H_{28}F_4NO$ $(M+H)^+$: 662.2102 Found: 662.2105.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IE column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 10.07 min, t (major) = 12.42 min, 98% ee; $[\alpha]_D^{20}$ = +143.7 (*c* = 0.48, $CHCl_3$).

## Derivatization of product 3a

**(2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)phenyl)methanol (5)**




To a solution of **3a** (0.1 mmol) in 5 mL of MeOH at 0°C was added $NaBH_4$ (0.15 mmol). After addition, the mixture was stirred at room temperature for 1 hour, quenched with water (5 mL). After stirring for 30 minutes, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. Solvent was removed in vacuo to give the desired product.

White solid. Isolated yield: 55.2 mg, 100%, Melting point: 120-125 °C. (petroleum

ether/EtOAc = 8/1).

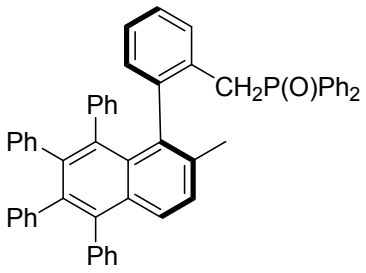
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.8 Hz, 1H), 7.16-7.31 (m, 6H), 6.90-7.05 (m, 3H), 6.74-6.84 (m, 6H), 6.58-6.70 (m, 8H), 6.54-6.57 (m, 2H), 4.19 (s, 2H), 1.90 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 141.70, 141.13, 140.74, 140.58, 140.15, 140.03, 138.65, 138.33, 138.18, 138.15, 136.63, 136.19, 132.76, 131.77, 131.43, 131.37, 131.24, 131.20, 131.15, 131.13, 131.11, 130.86, 130.42, 128.69, 127.62, 127.55, 127.14, 126.94, 126.72, 126.51, 126.47, 126.27, 126.19, 126.12, 125.26, 125.18, 125.10, 124.92, 63.35, 21.27.

**HRMS** (APCI) Calcd for $C_{42}H_{33}O$ $(M+H)^+$: 553.2526 Found: 553.2528.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IF column, n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 12.24 min, t (major) = 13.89 min, 99% ee; $[\alpha]_D^{20}$ = -7.8 (*c* = 1.00, $CHCl_3$).

**(2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzyl)diphenylphosphine oxide (6)**




To a stirred mixture of $Ph_2PCl$ (0.6 mmol), NaI (0.6 mmol) and anhydrous $CH_3CN$ (0.5 mL) was added **5** (0.1 mmol) at room temperature under argon atmosphere. The reaction mixture was stirred at 80 $^oC$ in oil bath for 12 h. When the reaction temperature was cooled to room temperature, 30% $H_2O_2$ aqueous (50 μL) was slowly added, and stirred for another 10 minutes. The organic layer was extracted with dichloromethane, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to obtain the corresponding phosphine oxide.

Pale yellow solid. Isolated yield: 44.0 mg, 60%. Melting point: 98-102 °C (petroleum ether/EtOAc = 2/1).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 1H), 7.50-7.54 (m, 3H), 7.42-7.46 (m, 2H), 737-7.38 (m, 1H), 7.19-7.33 (m, 11H), 6.87-6.89 (m, 2H), 6.61-6.83 (m, 13H), 6.43-6.47 (m, 3H), 3.20 (t, *J* = 16.5 Hz, 1H), 2.97-3.02 (m, 1H), 1.52 (s, 3H).

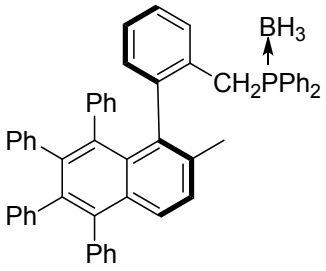
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 141.20, 140.94, 140.40, 138.97, 138.54, 138.47, 137.93, 137.00, 132.62, 132.22, 132.05, 132.02, 131.96, 131.84, 131.80, 131.70, 131.58, 131.50, 131.47, 131.42, 131.16, 131.09, 130.51, 130.29, 130.26, 129.75, 129.04, 128.95, 128.78, 128.68, 128.19, 127.81, 127.15, 126.95, 126.90, 126.86, 126.75, 126.58, 126.50, 126.41, 126.36, 125.66, 125.34, 34.24 (d, *J* = 68.8 Hz), 21.71.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.81

**HRMS** (APCI) Calcd for $C_{54}H_{42}OP$ $(M+H)^+$: 737.2968 Found: 737.2963.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IF column, n-hexane/2-propanol = 2/1, v = 1.0 mL/min, UV 254 nm, t (minor) = 9.07 min, t (major) = 12.74 min, 99% ee; $[\alpha]_D^{20}$ = +73.2 (*c* = 0.50, $CHCl_3$).

**(2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzyl)diphenylphosphane borane (7)**




To a stirred solution of **6** (0.1 mmol) in DME (1 mL) was added methyl trifluoromethanesulfonate (14 μL, 0.12 mmol) at room temperature under a nitrogen atmosphere. After being stirred at room temperature for 2 hours, the reaction vessel was cooled to −70 °C and a solution of lithium aluminum hydride (0.11 mL of a 2.0 M solution in THF, 0.22 mmol) was added dropwise. The mixture was stirred at -70 °C for 4 hours. The reaction solution was quenched by addition of $BH_3$·THF complex (1.0 M, 0.2 mL, 0.2 mmol). Water (5.0 mL) was then added and the aqueous layer was extracted three times with ethyl acetate. The combined organic extracts were dried over $MgSO_4$ and removed in vacuo and the residue was purified by flash column chromatography on silica gel to provide the title enantioenriched **7** adducts.

White solid. Isolated yield: 47.0 mg, 64%, Melting point: 108-111 °C (petroleum ether/EtOAc = 8/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 1H), 7.34-7.49 (m, 6H), 7.18-7.31 (m, 9H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.01-7.04 (m, 1H), 6.87-6.89 (m, 2H), 6.61-6.79 (m, 13H), 6.45-6.52 (m, 3H), 3.07-3.20 (m, 2H), 1.56 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 141.63, 140.82, 140.65, 140.61, 140.03, 138.67, 138.17, 138.04, 136.92, 136.45, 132.61, 132.51, 132.37, 132.19, 132.10, 132.00, 131.52, 131.47, 131.31, 131.23, 131.14, 131.11, 131.09, 130.99, 130.96, 130.94, 130.84, 130.33, 130.28, 130.28, 130.22, 130.20, 129.45, 128.86, 128.76, 128.71, 128.61, 127.81, 127.46, 126.86, 126.61, 126.54, 126.23, 126.17, 126.12, 126.03, 125.32, 125.26, 124.98. 30.05 (d, *J* = 34.0 Hz), 21.59.

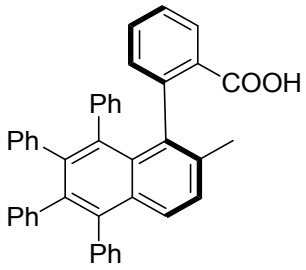
**$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 16.21.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ -38.08.

**HRMS** (APCI) Calcd for $C_{54}H_{45}BP$ $(M+H)^+$: 735.3346 Found: 735.3342.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IF column, n-hexane/2-propanol = 95/5, v = 0.8 mL/min, UV 254 nm, t (minor) = 8.26 min, t (major) = 8.92 min, 98% ee; $[\alpha]_D^{20}$ = -89.6 (*c* = 0.50, $CHCl_3$).

**2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzoic acid (8)**




To a stirred solution of compound **3a** (0.10 mmol) and 2-methylbut-2-ene (1.30 mmol) in $^t$BuOH (1.5 mL) were added a saturated solution of $NaClO_2$ (0.37 mmol) and $NaH_2PO_4$ (0.50 mmol). The mixture was stirred at room temperature for 18 hours. The mixture was quenched with saturated $NH_4Cl$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, concentrated, and purified by flash column chromatography (hexane : EtOAc =2:1) to give compound **8** (49.8 mg, 88%) as a white solid.

White solid. Isolated yield: 49.8 mg, 88%, Melting point: 94-98 °C. (petroleum ether/EtOAc = 2/1).

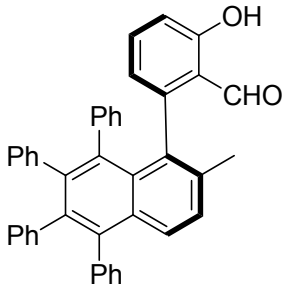
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.16-7.33 (m, 7H), 7.00-7.04 (m, 1H), 7.80-7.88 (m, 4H), 6.68-6.79 (m, 6H), 6.60-6.67 (m, 3H), 6.52-6.54 (m, 1H), 6.34-6.42 (m, 1H), 1.88 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 171.72, 145.36, 141.17, 141.09, 140.95, 140.81, 140.25, 138.73, 138.41, 138.18, 137.85, 134.65, 132.57, 132.44, 132.30, 131.79, 131.51, 131.41, 131.32, 131.23, 131.21, 131.17, 131.11, 130.43, 128.49, 127.59, 127.44, 126.54, 126.42, 126.37, 126.27, 126.19, 126.13, 126.08, 126.02, 125.15, 124.90, 124.81, 21.25.

**HRMS** (APCI) Calcd for $C_{42}H_{31}O_2$ $(M+H)^+$: 567.2319 Found: 567.2315.

The carboxyl group was converted to the corresponding methyl ester under reflux conditions in the presence of thionyl chloride and methanol, and then the ee was determined by HPLC analysis using a Daicel Chiralcel OD-H column. n-hexane/2-propanol = 98/2, v = 1.0 mL/min, UV 254 nm, t (minor) = 6.03 min, t (major) = 7.42 min, 98% ee; $[\alpha]_D^{20}$ = -74.7 (*c* = 0.50, $CHCl_3$).

**2-Hydroxy-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (9)**




To an oven-dried 100 mL Schlenk tube were added substrate **3a** (0.1 mmol), 2-amino-4-chlorobenzoic acid (0.05 mmol), $Pd(OAc)_2$ (0.01 mmol), *p*-toluenesulfonic acid (0.20 mmol), 1-fluoro-2,4,6-trimethylpyridnium triflate (0.15 mmol), HOAc (1 mL). The mixture was stirred for 24 h at 90 °C followed by cooling. The resulting mixture was diluted with EtOAc and filtered through a celite pad and concentrated in vacuo. The residue was purified by silica gel column chromatography.

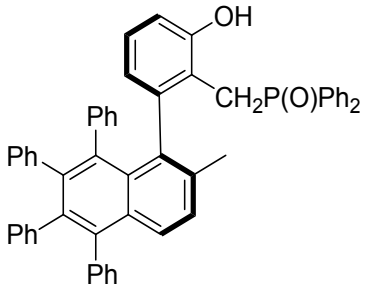
Pale yellow solid. Isolated yield: 18.1 mg, 32%, Melting point: 125-129 °C. (petroleum ether/EtOAc = 30/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 9.51 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.25-7.31 (m,3H), 7.23-7.24 (m, 2H), 7.17-7.23 (m, 1H), 7.13-7.17 (m 1H), 6.66-6.85 (m, 11H), 6.60-6.65 (m, 2H), 6.47-6.57 (m, 3H), 6.40-6.43 (m, 1H), 1.96 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.17, 161.77, 147.74, 141.75, 141.03, 140.39, 140.35, 139.74, 138.55, 138.46, 138.18, 136.34, 135.84, 133.62, 132.44, 131.76, 131.70, 131.38, 131.30, 131.16, 131.09, 131.05, 128.29, 127.84, 127.64, 127.58, 126.58, 126.55, 126.52, 126.24, 126.22, 126.15, 125.33, 125.08, 122.94, 118.16, 116.66, 21.57.

**HRMS** (APCI) Calcd for $C_{42}H_{31}O_2$ $(M+H)^+$: 567.2319 Found: 567.2315.

**(2-Hydroxy-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzyl)diphenylphosphine oxide (10)**




White solid. Isolated yield: 21.3 mg, 31%, Melting point: 170-173 °C. (petroleum ether/EtOAc = 5/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.56-7.60 (m, 1H), 7.43-7.51 (m, 5H), 7.19-7.35 (m, 8H), 7.09-7.15 (m, 3H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.89-6.90 (m, 2H), 6.60-6.83 (m, 11H), 6.41-6.45 (m, 2H), 6.05 (d, *J* = 8.0 Hz, 1H), 3.40-3.49 (m, 1H), 3.08 (q, *J* = 7.6 Hz, 1H), 1.15 (s, 3H).

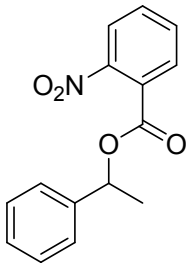
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.51 (d, *J* = 3.6 Hz), 143.06 (d, *J* = 6.7 Hz), 142.00, 140.40, 140.35, 140.12, 139.88, 138.70, 138.44, 137.92, 137.34 (d, *J* = 2.5 Hz), 133.22, 136.99, 135.58, 133.22, 132.44, 132.41, 132.30, 132.27, 132.24, 131.86, 131.42, 131.36, 131.32, 131.28, 131.25, 131.16, 131.13, 130.95, 130.72, 130.35, 130.26, 129.70, 129.48, 129.46, 128.94, 128.83, 128.73, 128.61, 128.46, 127.91, 127.51, 126.89, 126.66, 126.62, 126.49, 126.39, 126.27, 126.14, 126.08, 125.96, 125.37, 125.25, 125.09, 118.35 (d, *J* = 8.0 Hz), 87.42 (d, *J* = 3.0 Hz), 32.33 (d, *J* = 67.2 Hz), 20.82.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 37.43.

HRMS (APCI) Calcd for $C_{54}H_{42}O_2P$ $(M+H)^+$: 753.2917 Found: 753.2913.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel AD-H column, n-hexane/2-propanol = 9/1, v = 1.0 mL/min, UV 254 nm, t (minor) = 5.46 min, t (major) = 6.98 min, 98% ee; $[\alpha]_D^{20}$ = -59.4 (*c* = 0.40, $CHCl_3$).

**1-Phenylethyl 2-nitrobenzoate (14)** [2]



A suspension of 1-phenylethanol (0.2 mmol), 2-nitrobenzoic acid (0.2 mmol) and catalyst **10** (10 mol%) in toluene was heated to reflux in a Dean-Stark apparatus and stirred for 24 hours. The reaction mixture was then cooled to room temperature, diluted with EtOAc and washed with 1 M NaOH (aq) solution twice then brine. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by flash column chromatography to afford the corresponding ester product **14**.

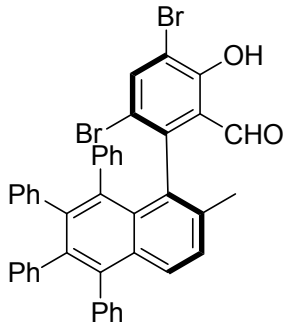
Yellow oil. Isolated yield: 44 mg, 82%. (petroleum ether/EtOAc = 5/1).

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.90-7.88 (m, 1H), 7.74-7.72 (m, 1H), 7.67-7.59 (m, 2H), 7.40-7.35 (m, 4H), 7.33-7.30 (m, 1H), 6.13 (q, *J* = 6.6 Hz, 1H), 1.67 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ 164.9, 148.7, 140.9, 133.1, 132.1, 130.4, 129.0, 128.7, 128.1, 126.7, 124.2, 75.4, 21.9.

**HRMS** (APCI) *m/z* calculated for $C_{15}H_{14}NO_4$ $[M+H]^+$: 272.0915, found 272.0912.

**3,5-Dibromo-2-hydroxy-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (11)**




To an oven-dried 15 mL Schlenk tube were added **9** (0.10 mmol), NBS (0.50 mmol), The mixture was dissolved in DCM (1.0 mL). After stirring overnight, the reaction was quenched by filtered through a celite pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent to afford the product **11**.

Pale yellow solid. Isolated yield: 44.2 mg, 61%, Melting point: 124-128 °C. (petroleum ether/EtOAc = 30/1).

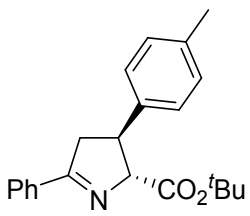
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 12.04 (s, 1H), 9.36 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.60 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.19-7.30 (m, 5H), 6.98-7.01 (m, 1H), 6.73-6.84 (m, 9H), 6.58-6.72 (m, 4H), 6.53-6.56 (m, 1H), 1.96 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 196.77, 157.65, 146.29, 142.36, 142.06, 140.45, 140.39, 140.23, 139.65, 139.12, 138.78, 137.11, 136.37, 131.58, 131.37, 131.33, 131.27, 131.07, 131.01, 130.96, 130.86, 130.62, 129.15, 128.43, 127.65, 127.54, 127.02, 126.61, 126.53, 126.21, 125.93, 125.73, 125.37, 124.14, 120.19, 116.06, 111.12, 21.36.

HRMS (APCI) Calcd for $C_{42}H_{29}Br_2O_2$ $(M+H)^+$: 723.0529 Found: 723.0525.

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel OD-H column, n-hexane/2-propanol = 99/1, v = 1.0 mL/min, UV 254 nm, t (minor) = 7.70 min, t (major) = 10.79 min, 98% ee; $[\alpha]_D^{20}$ = +13.8 (*c* = 0.90, $CHCl_3$).

***tert*-Butyl-5-phenyl-3-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (17)[3]**



A dry Schlenk tube was charged with Michael acceptors **16** (0.1 mmol), catalyst **11** (0.01mmol), 2,6-Pyridinedicarboxylic acid (0.025 mmol), TBD (0.1mmol) and glycine derivatives **15** (0.2 mmol). After addition of dry toluene (0.33 mL), the reaction mixture was effectively stirred at 50 ºC and monitored by TLC. After the complete consumption of acceptors **16**, the mixture was concentrated in vacuo and purified by flash chromatography on silica gel to afford products **17**.

white semi-solid. Isolated yield: 20.5 mg, 61%. (petroleum ether/EtOAc = 10/1).

Enantiomeric excess was determined by HPLC with a Daicel Chiralcel IC column, n-hexane/2-propanol = 9/1, v = 1.0 mL/min, UV 254 nm, t (minor) = 9.87 min, t (major) = 13.66 min, 86% ee; $[\alpha]_D^{20}$ = -17.5 (*c* = 0.60, $CHCl_3$). The absolute configuration of compound **17** (2R, 3S) was determined by comparison of the specific rotation with literature.

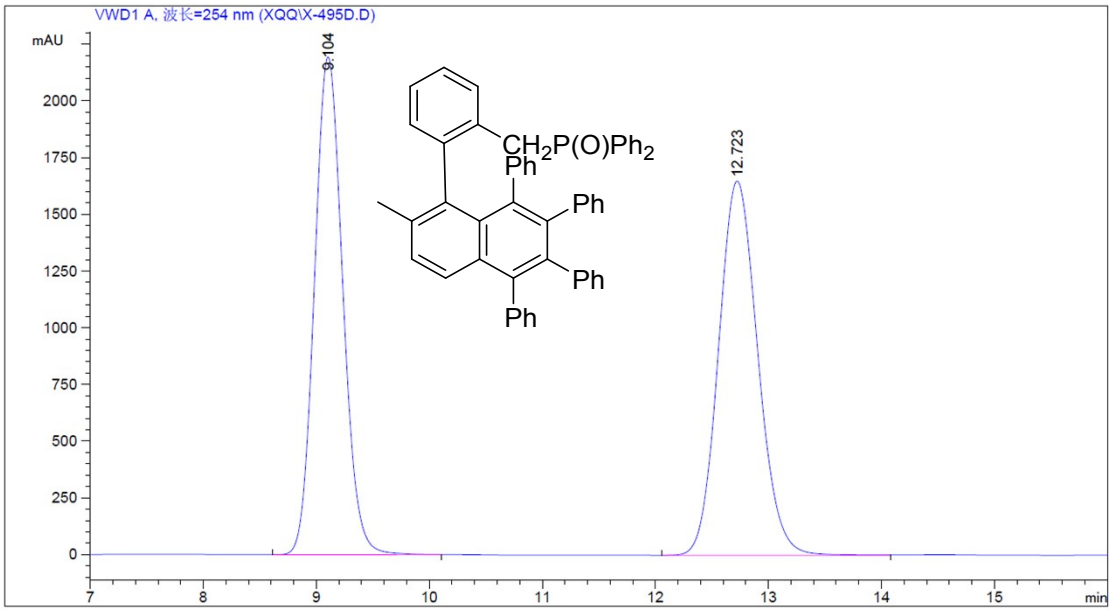
## Enantiomerisation Barrier Investigation for 6

About 1 mg of enantio-enriched **6** was refluxed in 1 mL of *i*-PrOH. Samples of 20 μL of this solution were injected on Daicel Chiralpak IF (*i*-PrOH/hexane = 1/2, flow rate 1.0 mL/min, λ = 254 nm) to monitor the percentage decrease of the second eluted enantiomer over time.

Solvent: *i*-PrOH, Temperature = 120 °C

| Time (min) | 0 | 90 | 360 | 1020 | 1440 | 2880 |
|---|---|---|---|---|---|---|
| % second eluted enantiomer (%t) | 98.79 | 98.76 | 98.77 | 98.77 | 98.75 | 98.69 |

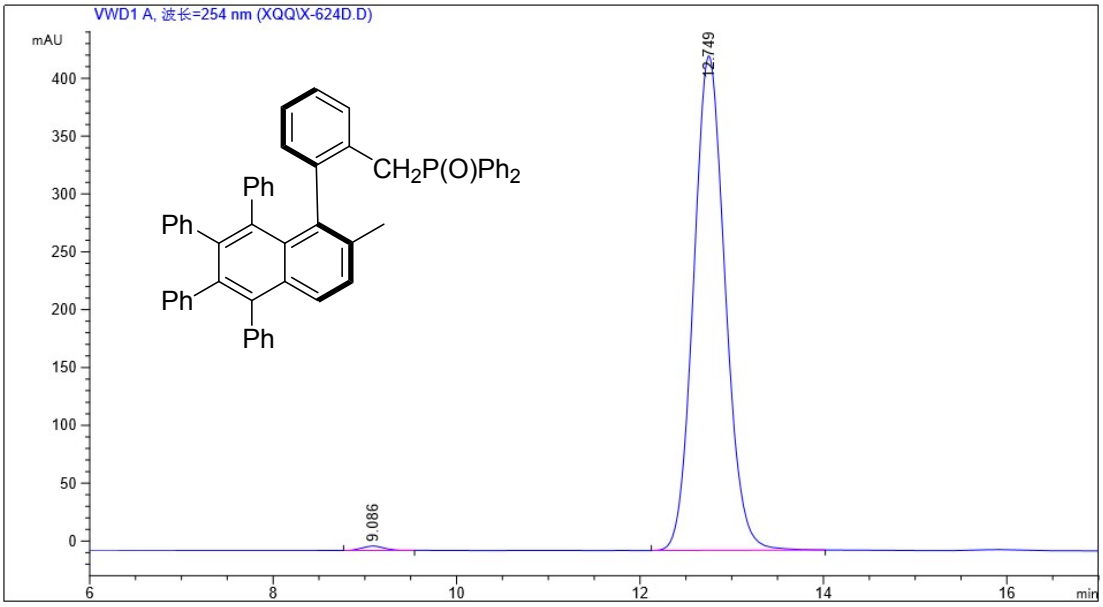
## Relatively Stable!




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.104 | VB | 0.2708 | 3.80679e4 | 2194.46899 | 48.9376 |
| 2 | 12.723 | VB | 0.3742 | 3.97208e4 | 1649.14380 | 51.0624 |

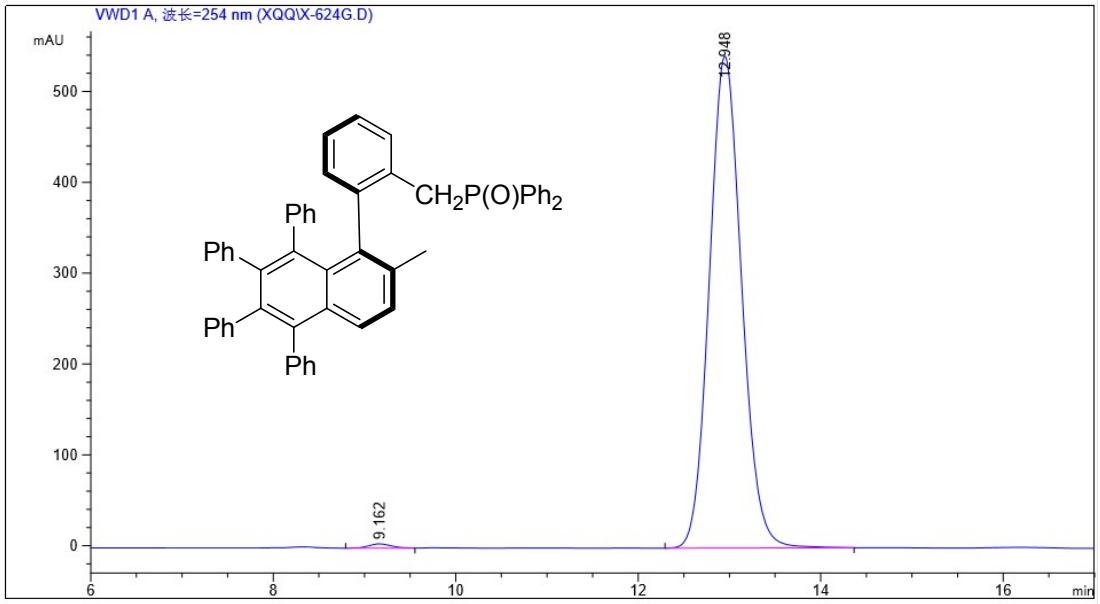
# 1.5 h




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.086 | BB | 0.2579 | 63.60486 | 3.82776 | 0.6200 |
| 2 | 12.749 | BB | 0.3700 | 1.01953e4 | 427.38693 | 99.3800 |

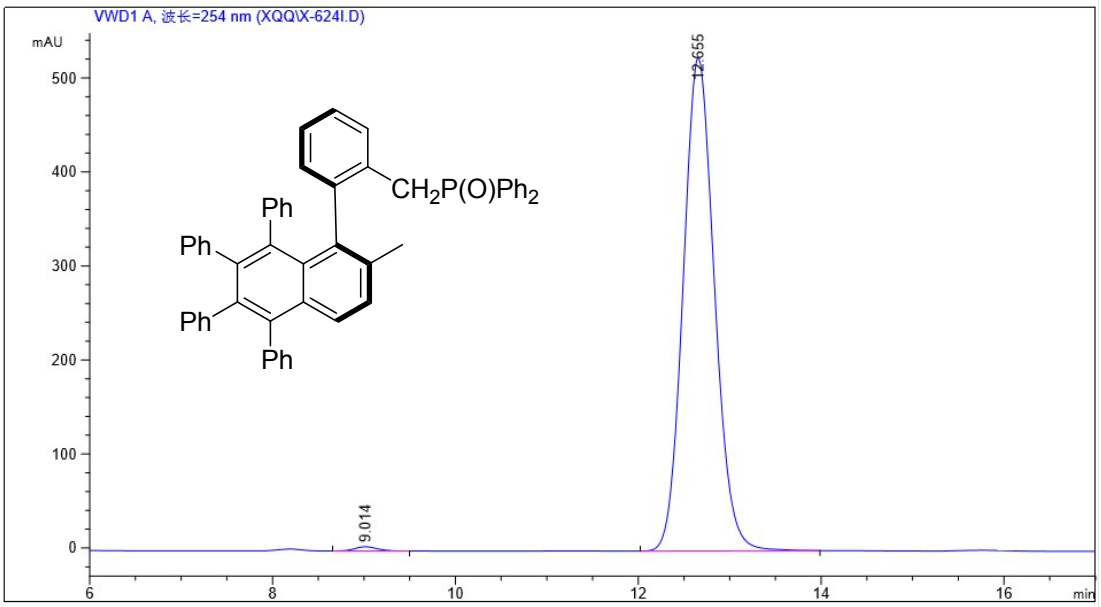
# 6 h




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.162 | VV | 0.2682 | 82.37383 | 4.77566 | 0.6148 |
| 2 | 12.948 | BB | 0.3815 | 1.33167e4 | 541.54779 | 99.3852 |

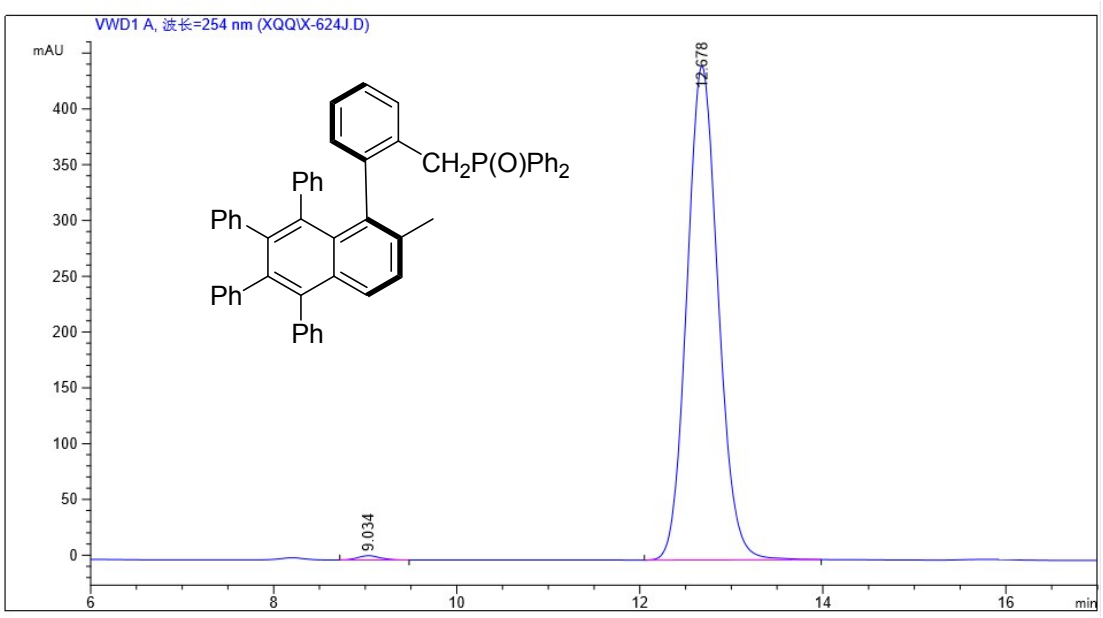
# 17 h




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.014 | VB | 0.2603 | 76.55989 | 4.58461 | 0.6128 |
| 2 | 12.655 | BB | 0.3665 | 1.24177e4 | 524.37775 | 99.3872 |

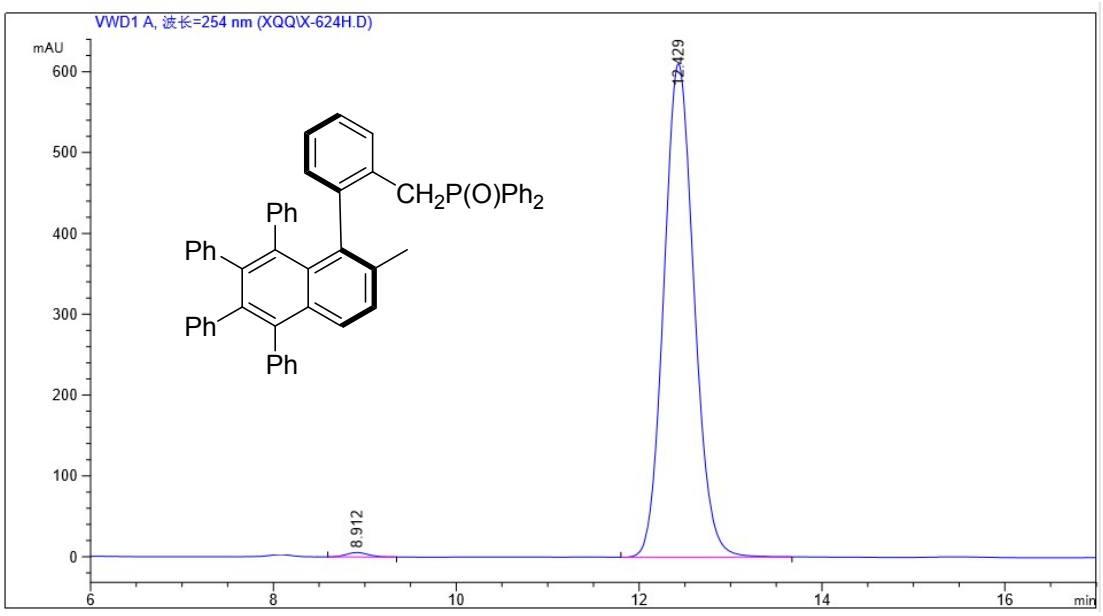
# 24 h




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.034 | BB | 0.2615 | 66.05228 | 3.90294 | 0.6254 |
| 2 | 12.678 | BB | 0.3684 | 1.04949e4 | 442.52170 | 99.3746 |

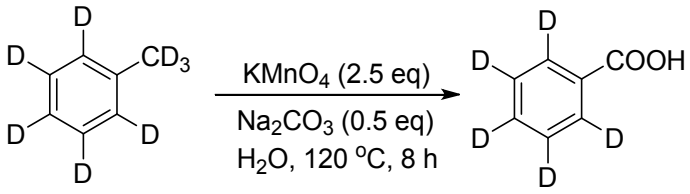
## 48 h



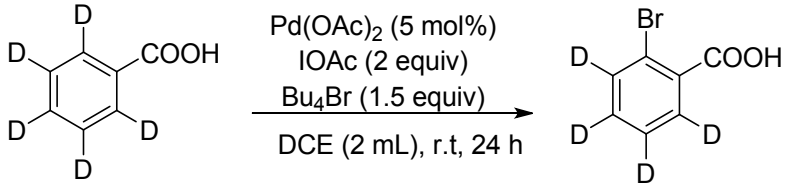

Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.912 | BB | 0.2551 | 92.27637 | 5.59386 | 0.6540 |
| 2 | 12.429 | VB | 0.3567 | 1.40167e4 | 610.43567 | 99.3460 |

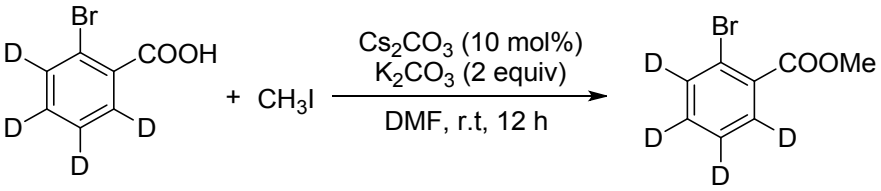
# Mechanistic Studies



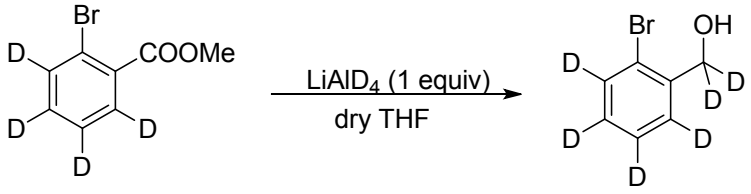

A round-bottom flask equipped with a stir bar and a condenser was charged with $d_8$-tolune (99.9 atom % D) (1 g, 10 mmol), $KMnO_4$ (4 g, 25 mmol), $Na_2CO_3$ (0.52 g, 5 mmol), and $H_2O$ (30 mL). The reaction mixture was refluxed for 8 h and then cooled to room temperature. The mixture was filtered through a pad of celite, and the filtrate was acidified with 12 M HCl and extracted with DCM (3 × 30 mL). The organic layer was washed with water and concentrated in vacuo. The crude product was recrystallized from water to give $C_6D_5CO_2H$ as white needle solid (0.64 g, 50% yield). Synthesis of $C_6D_5CO_2H$ was prepared using a similar procedure.



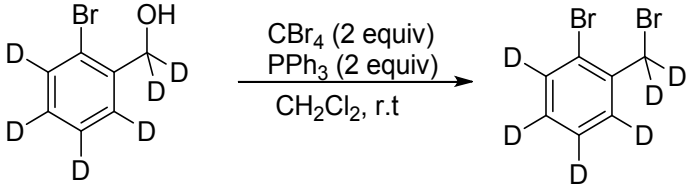

In a 20 mL glass tube, iodobenzene diacetate (128.8 mg, 0.4 mmol) and $I_2$ (101.6 mg, 0.4 mmol) were dissolved in dichloroethane (2 mL) under atmospheric air. The tube was sealed with a cap, and the reaction mixture was stirred at room temperature for 1 hour to generate iodoacetate in-situ. Substrate (0.2 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and tetrabutylammonium bromide (99.6 mg, 0.3 mmol) were added under atmospheric air. The tube was sealed with a cap, and the reaction mixture was stirred at 100 °C for 24 hours. The reaction mixture was cooled to room temperature and 10% aqueous $Na_2CO_3$ (5 mL) was added. The organic layer was separated and the aqueous layer was washed with diethyl ether (5 mL × 2). The aqueous layer was acidified with 2N HCl, extracted with ethyl acetate (10 mL × 3) and dried over $Na_2SO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane: ether/8:1) to give the [$^2H_4$]-2-bromobenzoic acid (16.3 mg, 40% yield).



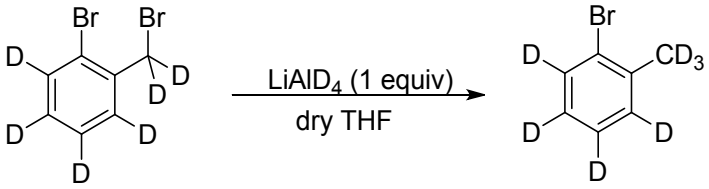

[$^2H_4$]-2-bromobenzoic acid (2.04 g, 10 mmol) was dissolved in DMF. Two equivalents (2.76 g, 20 mmol) of $K_2CO_3$ and 2.82 g (20 mmol, 2.0 equiv) of methyl iodide were added to the solution, as well as a catalytic amount of $Cs_2CO_3$. The reaction mixture was stirred overnight at room temperature and quenched with acidic water until all the base dissolved. The aqueous solution was extracted with ether. Afterward the organic layer was washed with water, dried over $MgSO_4$, and concentrated to a colourless oil[2].



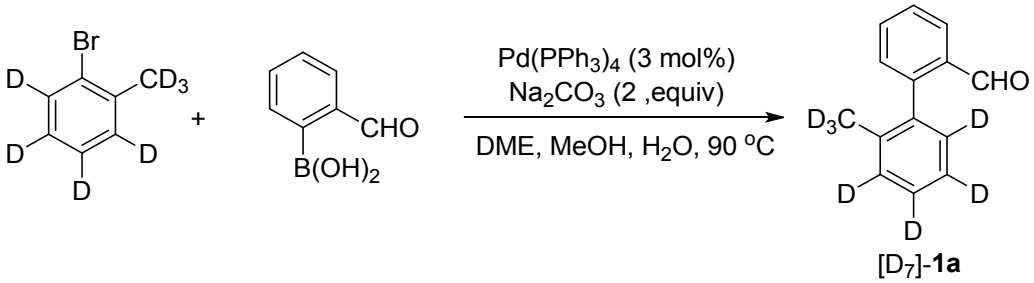

In a flame-dried round-bottom flask immersed in an ice bath, 0.336 g (8 mmol, 2.0 equiv) of lithium aluminum deuteride was suspended in 10 mL of dry THF. [$^2H_4$]-methyl 2-bromobenzoate (1.74 g, 8 mmol) diluted in 5 mL of dry THF was added dropwise at 0 °C. After the addition was complete, the slurry was stirred for 20 min. The reaction mixture was quenched and worked up following the standard procedure[2], to yield 1.3 g (85%) of a colourless oil.

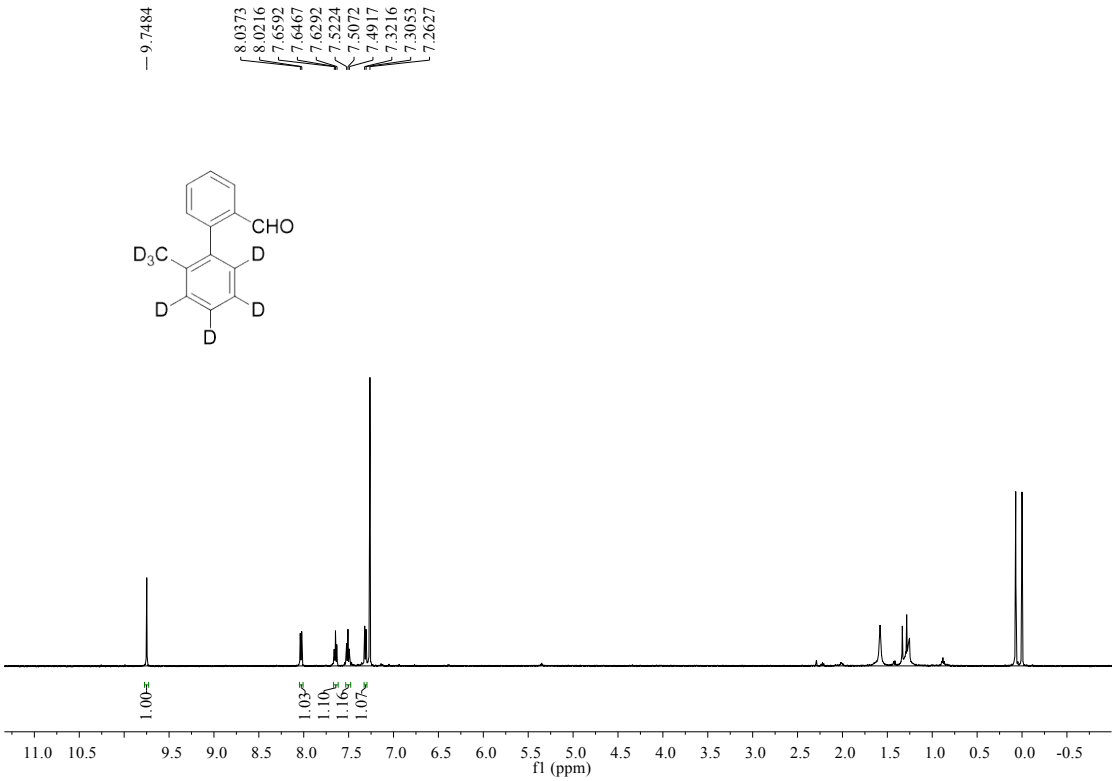



[$^2H_6$]-2-bromobenzyl alcohol (1.15 mg, 6 mmol) was suspended in a solution of $CBr_4$ (0.664 g, 12 mmol, 2 equiv) in dichloromethane. Triphenylphosphine (3.15 g, 12 mmol, 2 equiv) was added portionwise at room temperature to avoid overheating. After the addition was complete, the clear solution was precipitated in ether and filtered. As the solvent was evaporated, any remaining triphenylphosphine was further filtered. The crude product was purified via column chromatography using 5:1 hexanes- ethyl acetate to yield 1.14 g (75%) of a colourless oil.



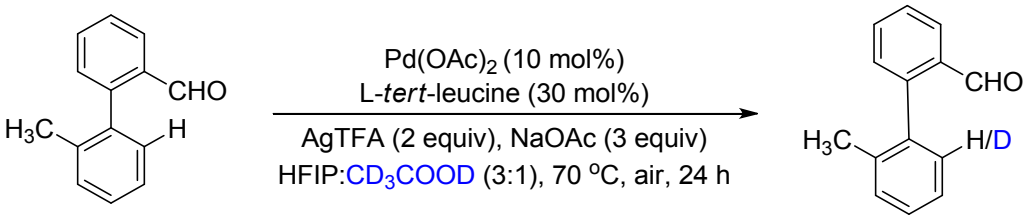

In a flame-dried flask, [$^2H_6$]-2-bromo-benzyl bromide (1.14 g, 4.5 mmol) in THF was added dropwise to a slurry of lithium aluminum deuteride (0.189 g, 4.5 mmol) in dry THF at room temperature. Then, the reaction mixture was quenched and worked up following the standard procedure[2].



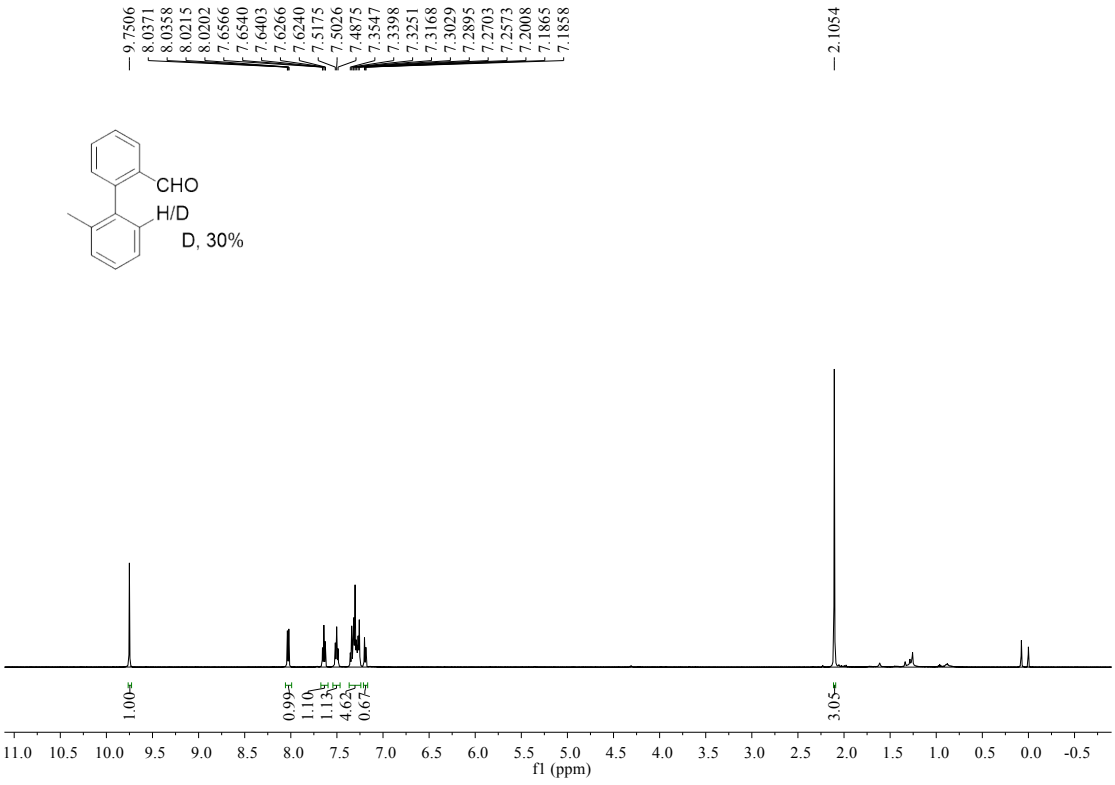

A round-bottom flask equipped with a condenser was charged with [$^2H_7$]-2-bromine toluene (99.9 atom % D) (0.177 g, 1 mmol), 2-formylphenylboric acid (0.18 g, 1.2 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol), $Na_2CO_3$ (0.212 g, 2 mmol), DME (5 mL), MeOH(2 mL), $H_2O$ (0.5 mL), and the reaction mixture was refluxed for 12 h. Then the reaction mixture was cooled to room temperature and aqueous $NH_4Cl$ was added.

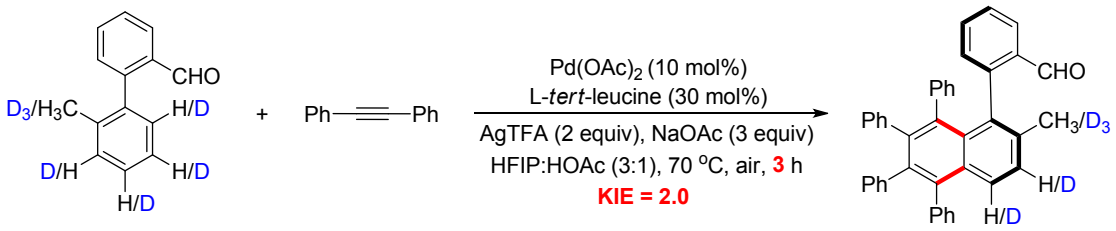
The aqueous layer was extracted with ethyl acetate (10 mL × 3) and dried over $Na_2SO_4$ and concentrated under vacuum. The crude product was purified via column chromatography (hexane: ethyl acetate /30:1) to give the [$D_7$]-**1a**.




**1a** [D]-**1a**, 92%, 30% **D**

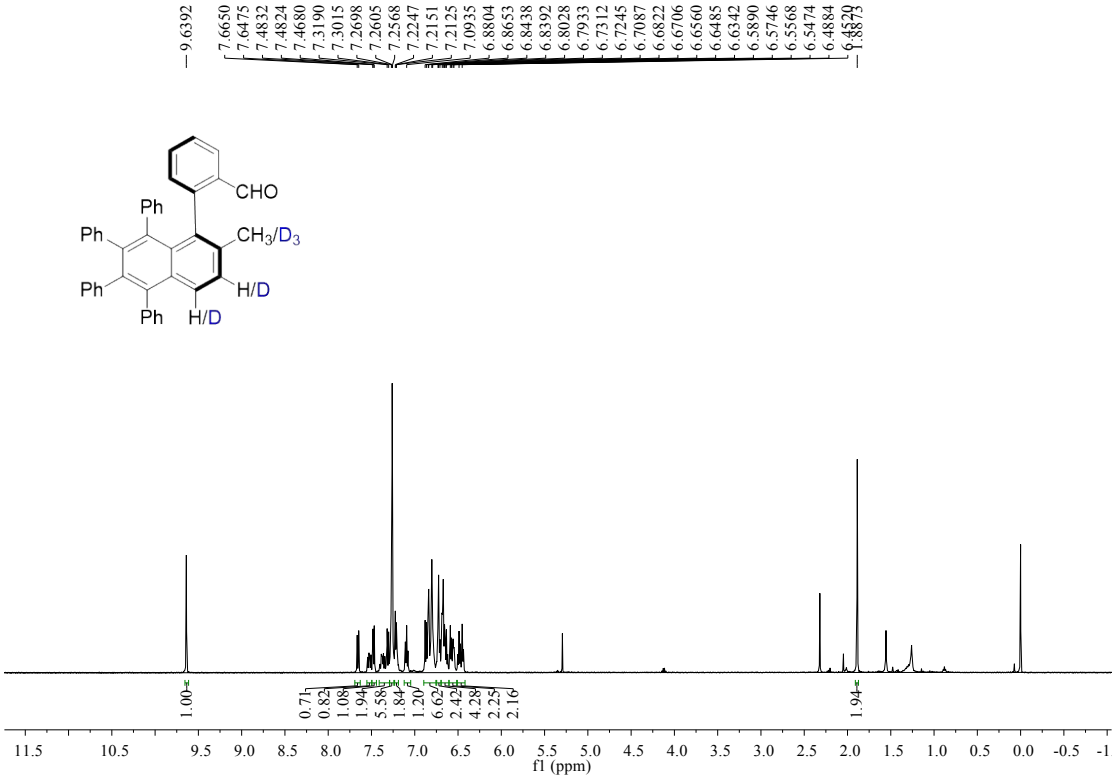
To an oven-dried 25 mL Schlenk tube was added substrate *rac*-**1a** (0.10 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), L-*tert*-leucine (3.9 mg, 0.03 mmol), AgTFA (44.2 mg, 0.2 mmol), NaOAc (24.6 mg, 0.30 mmol), HFIP (0.75 mL) and HOAc (0.25 mL). The mixture was stirred for 24 h at 70 °C followed by cooling. The resulting mixture was quenched by filtered through a celite pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent to afford the product [**D**]-**1a**.

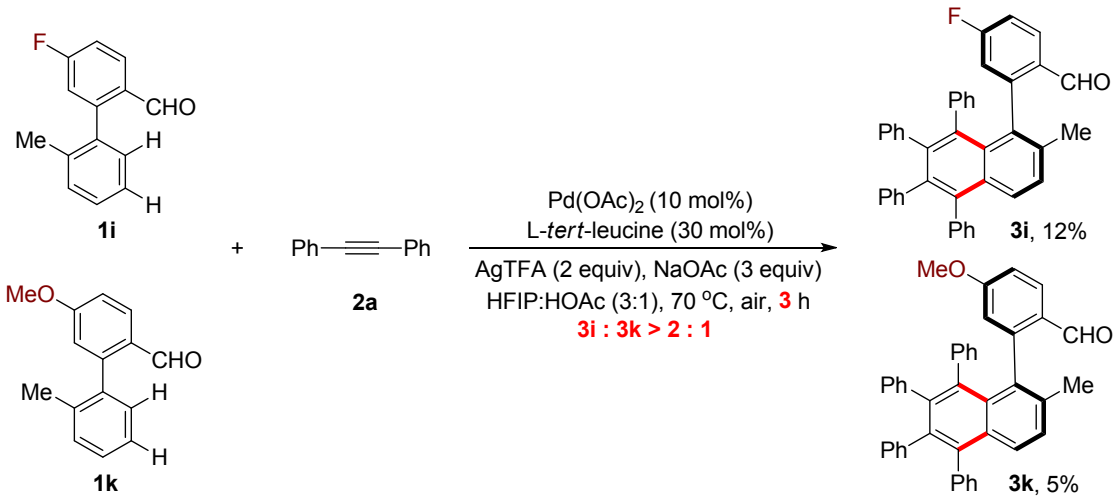





**1a**/[$D_7$]-**1a** **2a** **3a**/[$D_5$]-**3a**

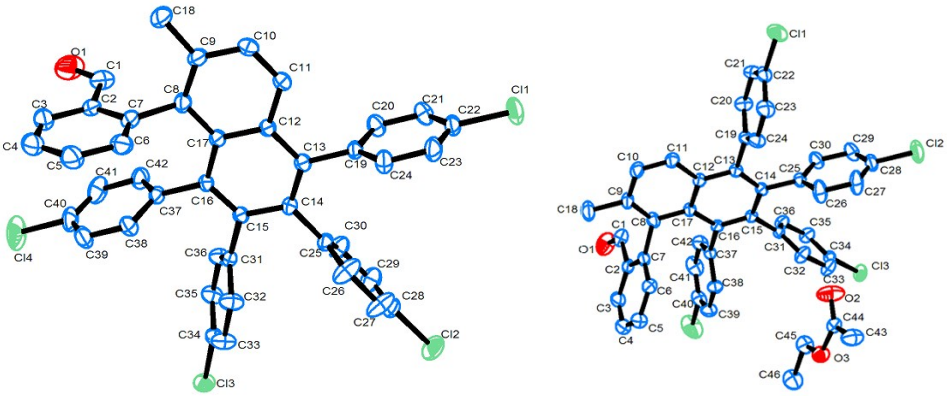
To an oven-dried 25 mL Schlenk tube was added substrate *rac*-**1a** (0.10 mmol), *rac*-[$D_7$]-**1a** (0.10 mmol), diphenylacetylene **2a** (0.3 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), L-*tert*-leucine (3.9 mg, 0.03 mmol), AgTFA (44.2 mg, 0.2 mmol), NaOAc (24.6 mg, 0.30 mmol), HFIP (0.75 mL) and HOAc (0.25 mL). The mixture was stirred for 3 h at 70 °C followed by cooling. The resulting mixture was quenched by filtered through a celite pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent to afford the products **3a** and [$D_5$]-**3a**.






To an oven-dried 25 mL Schlenk tube was added substrate *rac*-**1i** (0.10 mmol), *rac*-**1k** (0.10 mmol), diphenylacetylene **2a** (0.3 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), L-*tert*-leucine (3.9 mg, 0.03 mmol), AgTFA (44.2 mg, 0.2 mmol), NaOAc (24.6 mg, 0.30 mmol), HFIP (0.75 mL) and HOAc (0.25 mL). The mixture was stirred for 3 h at 70 °C followed by cooling. The resulting mixture was quenched by filtered through a celite pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent to afford the products **3i** and **3k** in 12% and 5% yield, respectively.

## X-ray Crystallographic Data of 4c (CCDC 2012651)



| | |
|---|---|
| Identification code | 200627a |
| Empirical formula | C44 H29.50 Cl4 O2 |
| Formula weight | 731.97 |
| Temperature | 293(2) K |

| | | |
|---|---|---|
| Wavelength | 1.54178 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 12.8068(4) Å | α= 86.978(2)°. |
| | b = 12.8153(4) Å | β= 69.822(2)°. |
| | c = 13.3549(4) Å | γ = 63.1370(10)°. |
| Volume | 1821.34(10) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.335 $Mg/m^3$ | |
| Absorption coefficient | 3.244 $mm^{-1}$ | |
| F(000) | 755 | |
| Crystal size | ? x ? x ? $mm^3$ | |
| Theta range for data collection | 3.553 to 68.557°. | |
| Index ranges | -15<=h<=14, -15<=k<=15, -16<=l<=16 | |
| Reflections collected | 56474 | |
| Independent reflections | 6690 [R(int) = 0.0578] | |
| Completeness to theta = 67.679° | 99.8 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 6690 / 6 / 531 | |
| Goodness-of-fit on $F^2$ | 0.994 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0835, wR2 = 0.2314 | |
| R indices (all data) | R1 = 0.0936, wR2 = 0.2379 | |
| Extinction coefficient | 0.0091(8) | |
| Largest diff. peak and hole | 0.451 and -0.467 e.$Å^{-3}$ | |

# References

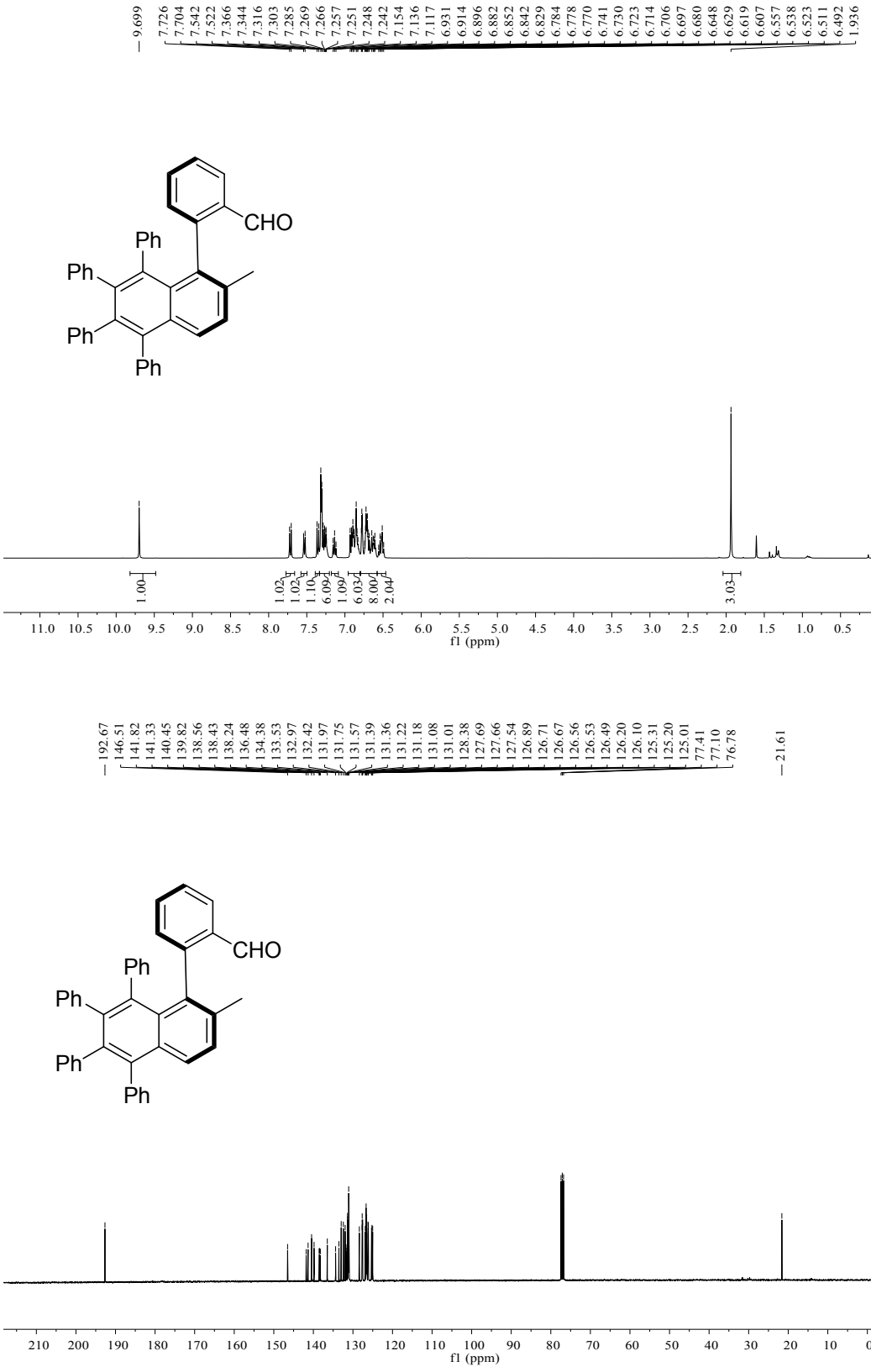

[1] (a) Mamane, V.; Louërat, F.; Iehl, J.; Abboud, M.; Fort, Y. *Tetrahedron* **2008**, *64*, 10699; (b) Yao, Q.-J.; Zhang, S.; Zhan, B.-B.; Shi, B.-F. *Angew. Chem. Int. Ed.* **2017**, *56*, 6617.

[2] Beddoe, R. H.; Andrews, K. G.; Magné, V.; Cuthbertson, J. D.; Saska, J.; Shannon-Little, A. L.; Shanahan, S. E.; Sneddon, H. F.; Denton, R. M. *Science* **2019**, *365*, 910.

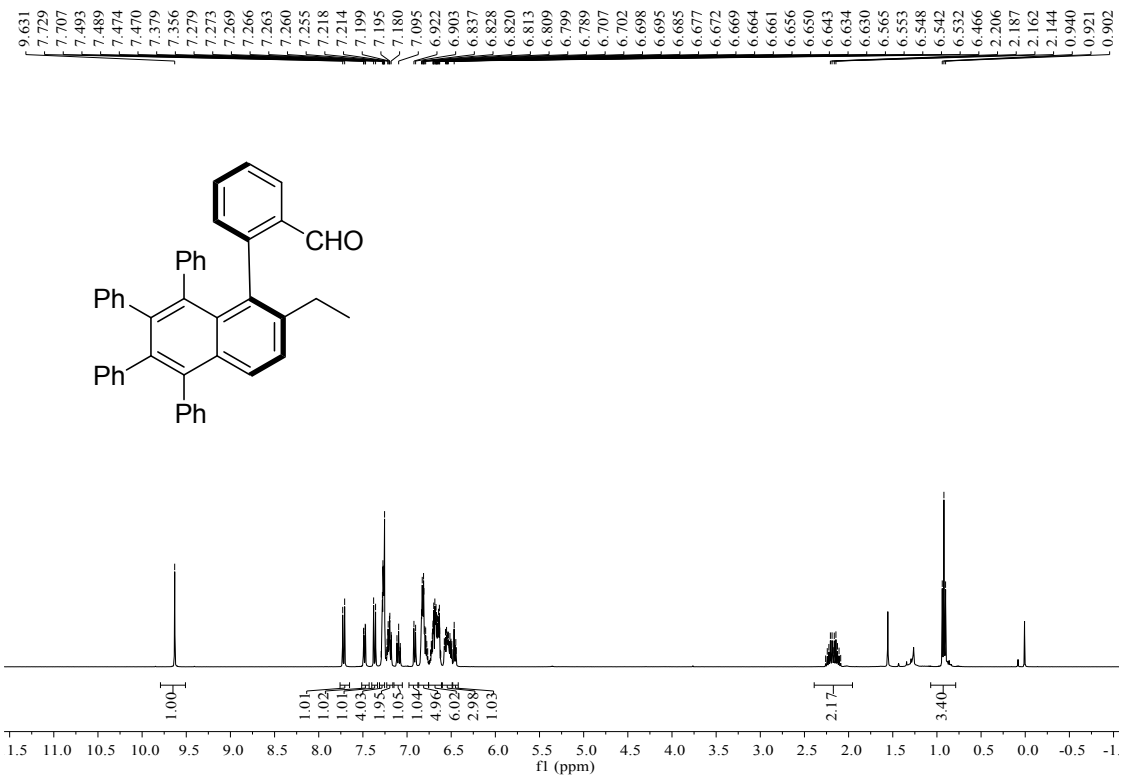
[3] Wen, W.; Chen, L.; Luo, M.-J.; Zhang, Y.; Chen, Y.-C.; Ouyang, Q.; Guo, Q.-X. *J. Am. Chem. Soc.* **2018**, *140*, 9774.

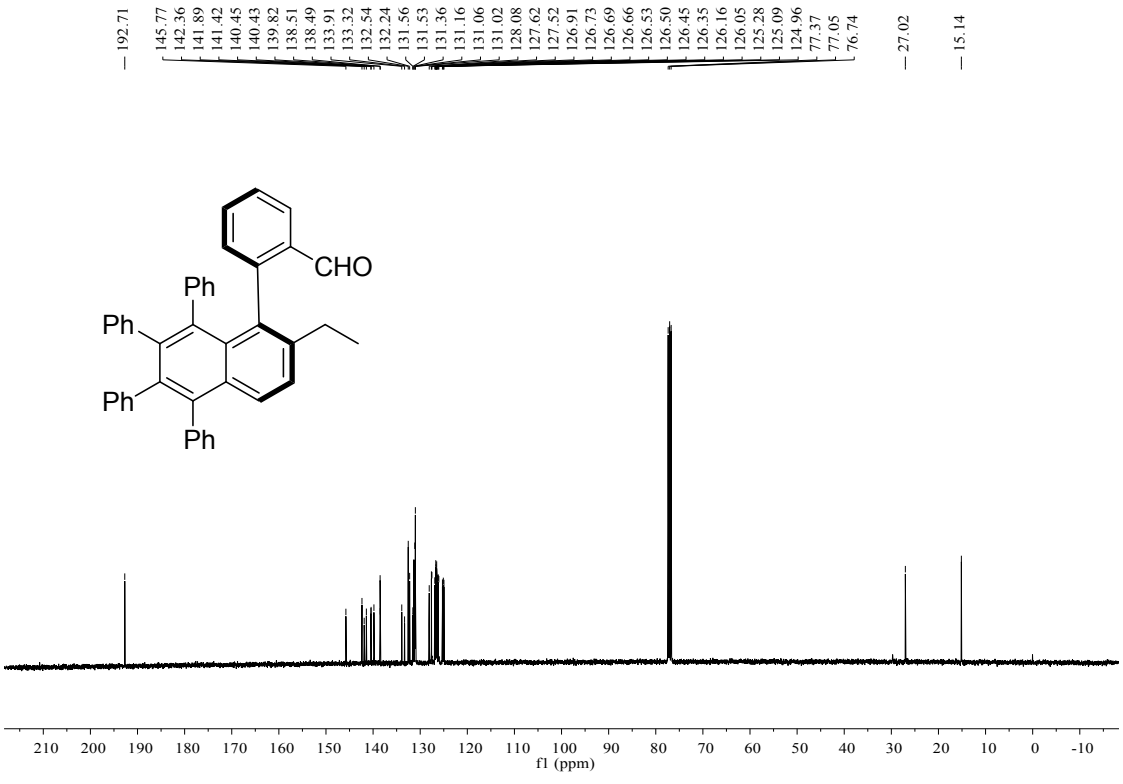

# NMR Spectra

## 2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3a)

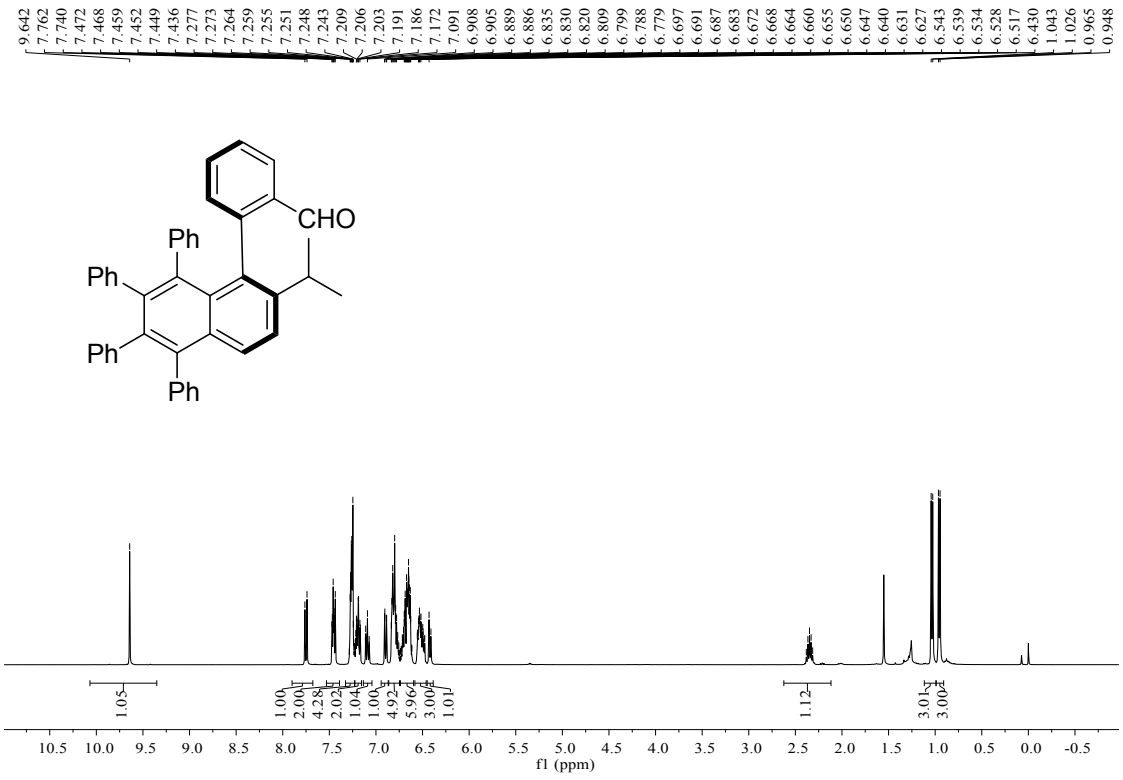


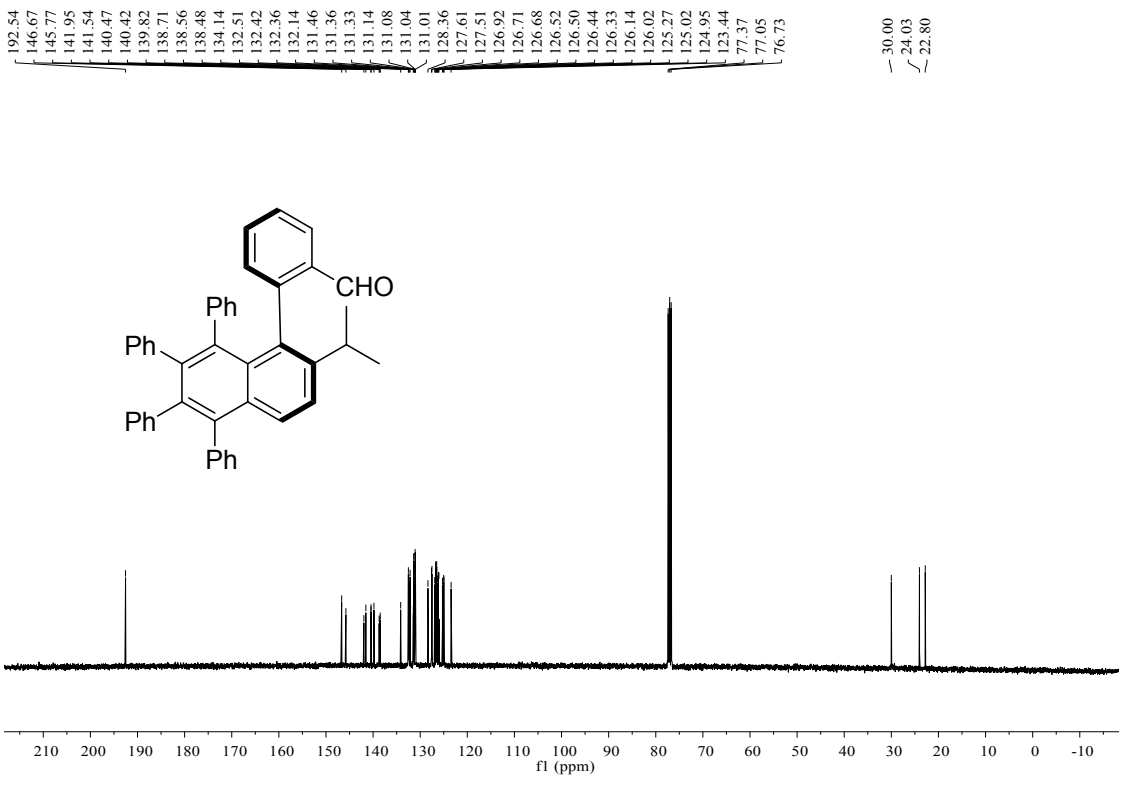

## 2-(2-Ethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3b)



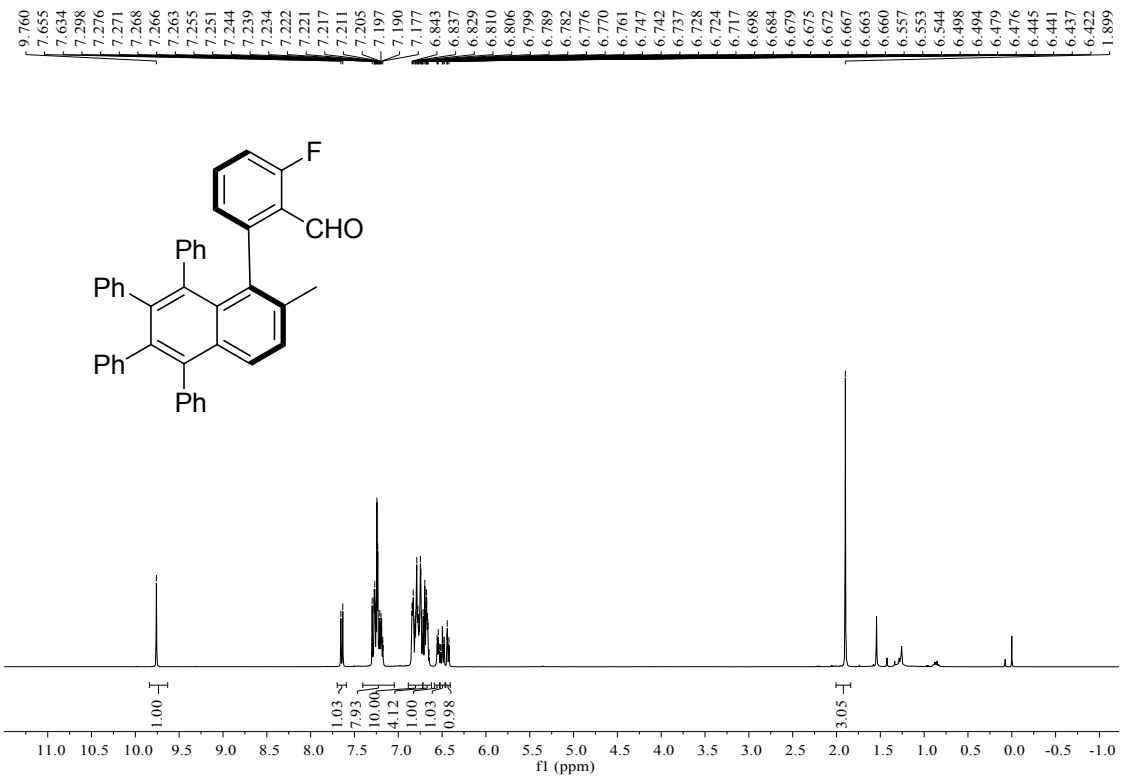



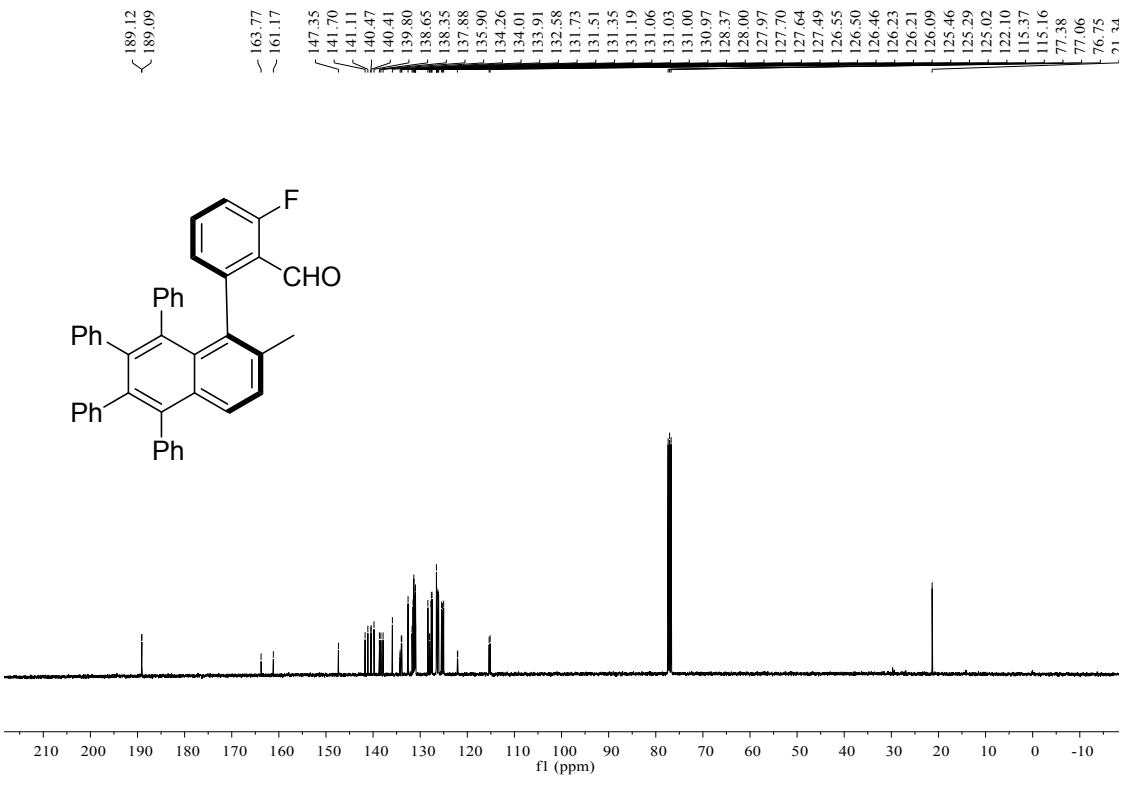

## 2-(2-Isopropyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3c)

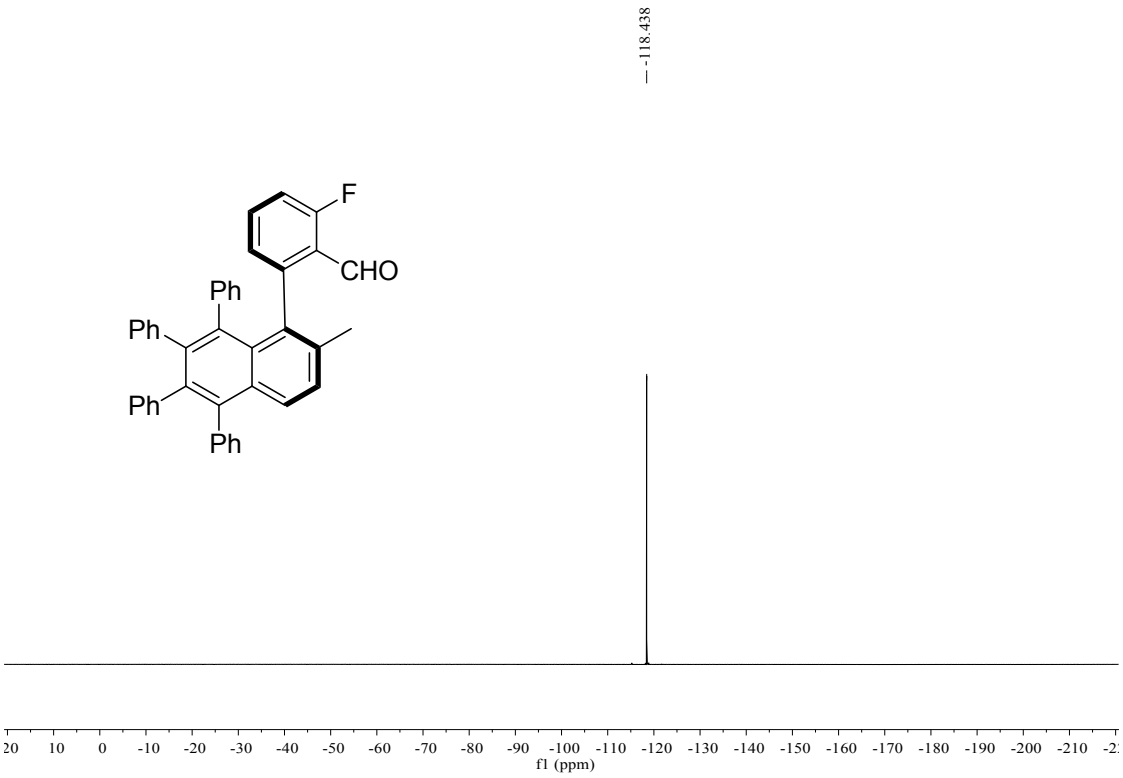


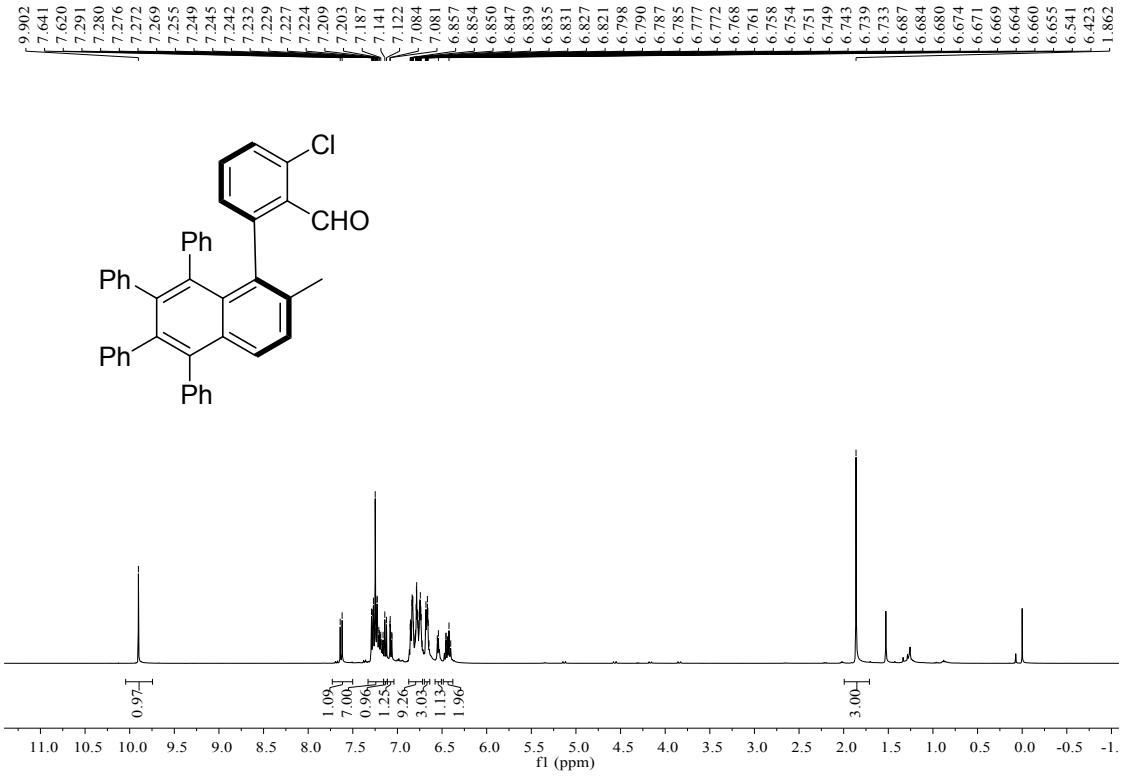

**2-Fluoro-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3d)**

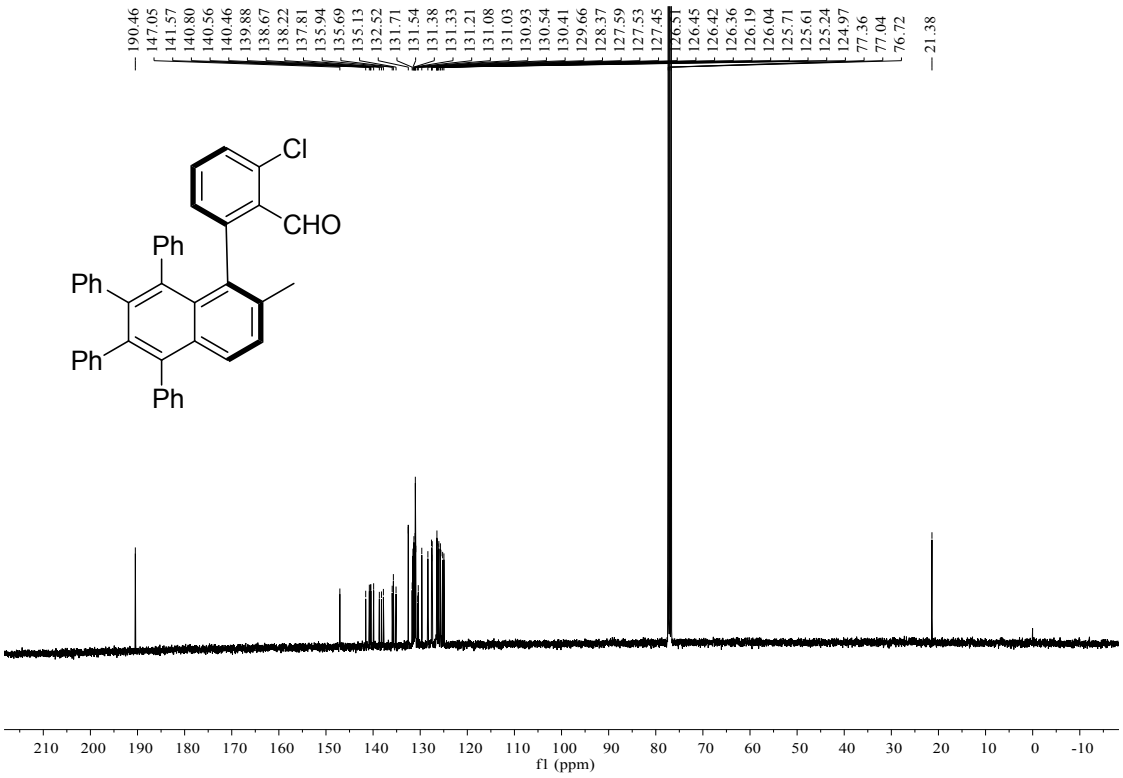

9.760
7.655
7.634
7.298
7.276
7.271
7.268
7.266
7.263
7.255
7.251
7.244
7.239
7.234
7.222
7.221
7.217
7.211
7.205
7.197
7.190
7.177
6.843
6.837
6.829
6.810
6.806
6.799
6.789
6.782
6.776
6.770
6.761
6.747
6.742
6.737
6.728
6.724
6.717
6.698
6.684
6.679
6.675
6.672
6.667
6.663
6.660
6.557
6.553
6.544
6.498
6.494
6.479
6.476
6.445
6.441
6.437
6.422
1.899
F
CHO
Ph
Ph
Ph
Ph
1.00
1.03
7.93
10.00
4.12
1.00
1.03
0.98
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


189.12
189.09
163.77
161.17
147.35
141.70
141.11
140.47
140.41
139.80
138.65
138.35
137.88
135.90
134.26
134.01
133.91
132.58
131.73
131.51
131.35
131.19
131.06
131.03
131.00
130.97
128.37
128.00
127.97
127.70
127.64
127.49
126.55
126.50
126.46
126.23
126.21
126.09
125.46
125.29
125.02
122.10
115.37
115.16
77.38
77.06
76.75
F
CHO
Ph
Ph
Ph
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

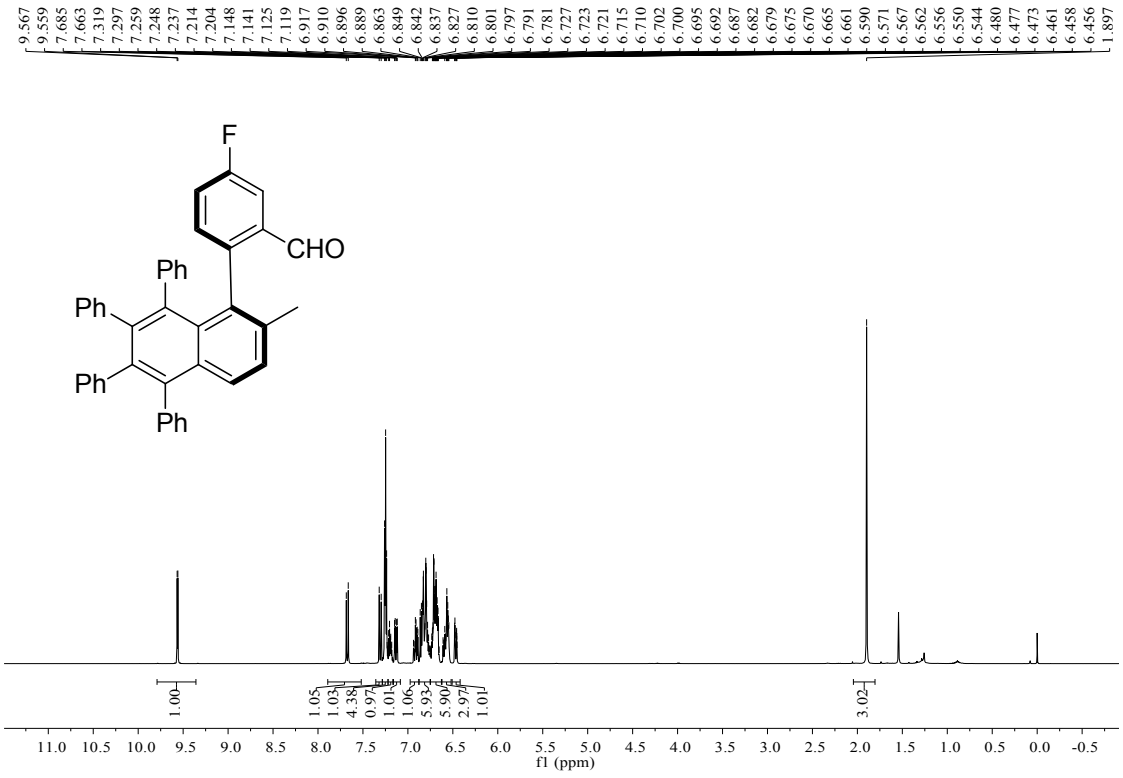


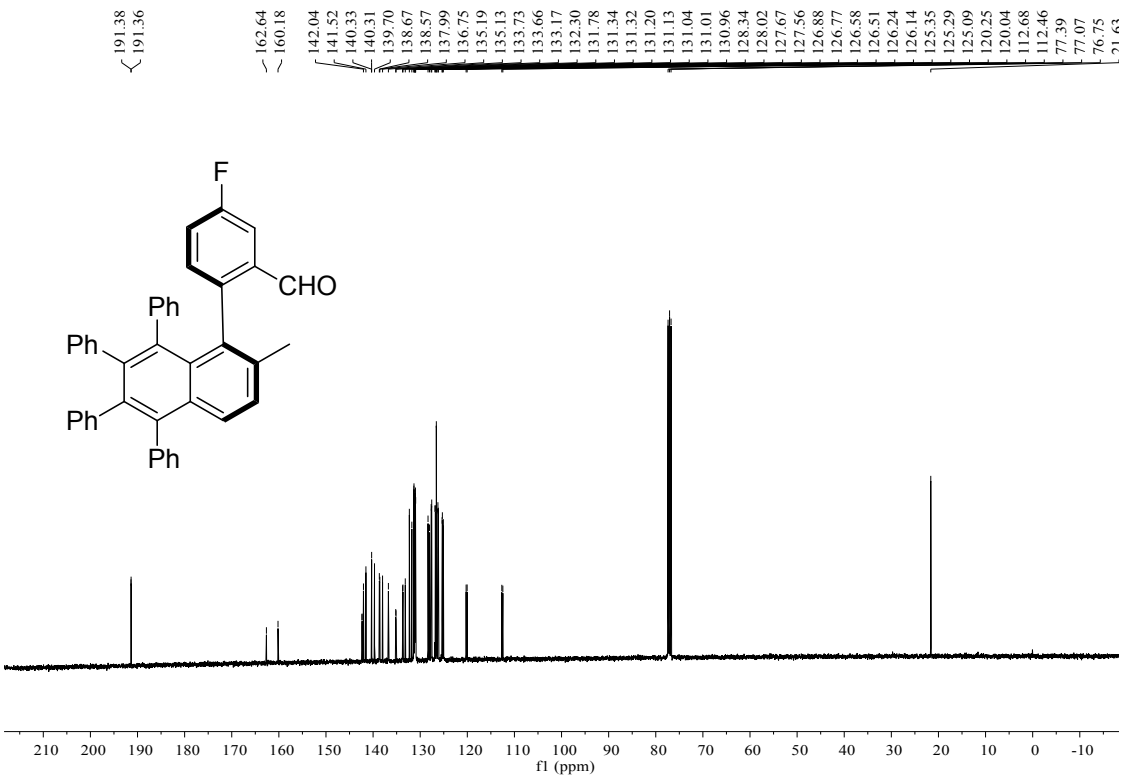

## 2-Chloro-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3e)

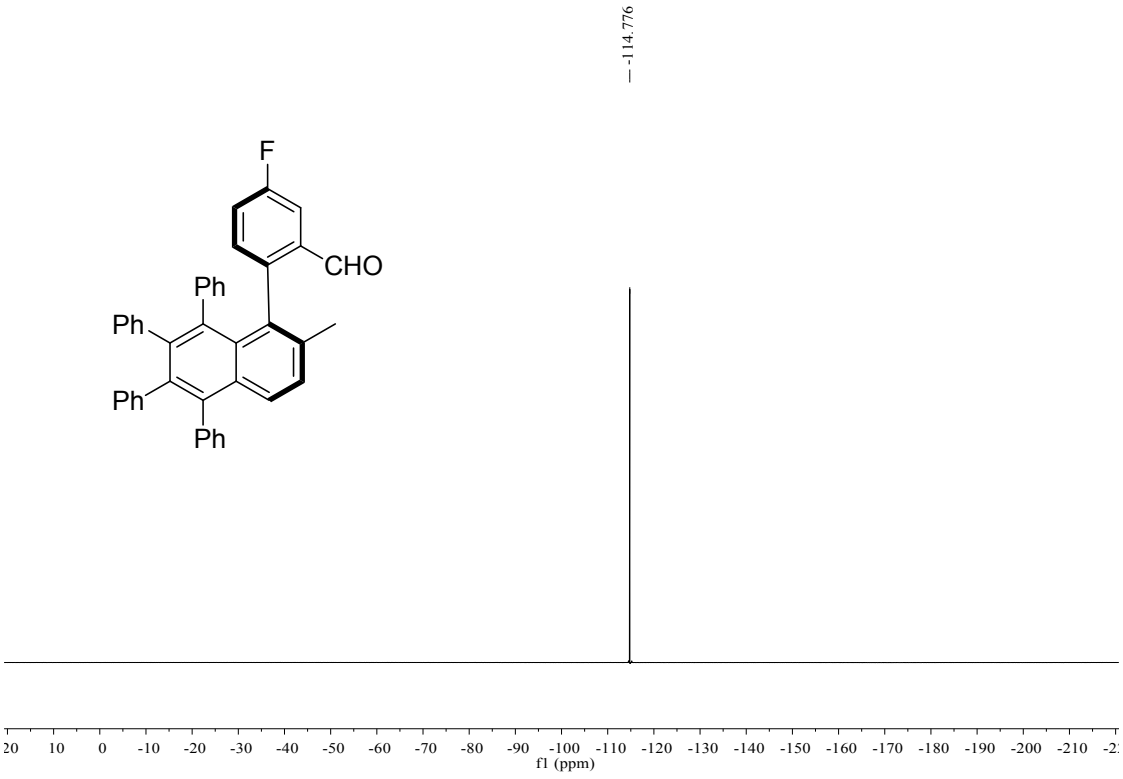




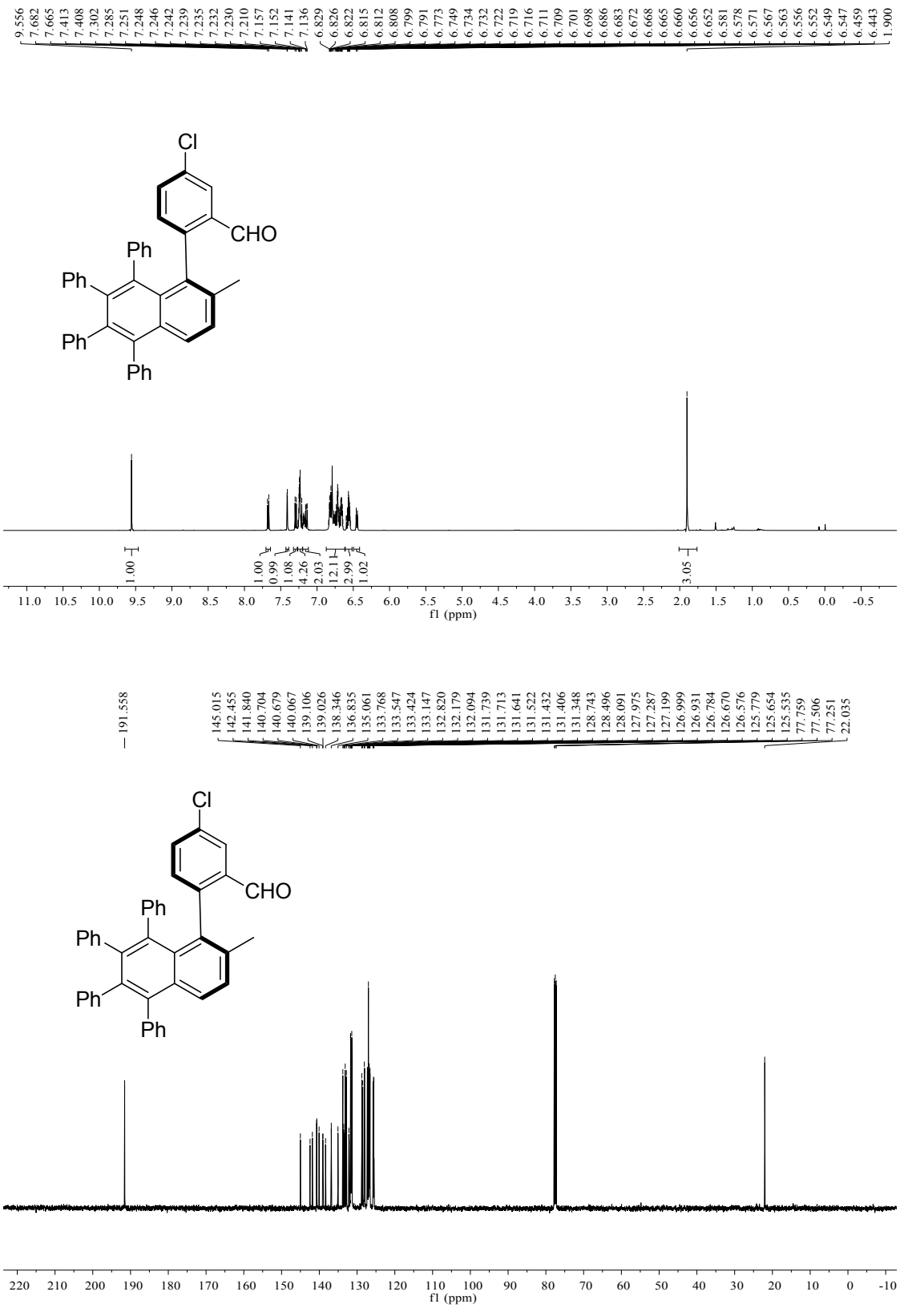

## 5-Fluoro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3f)



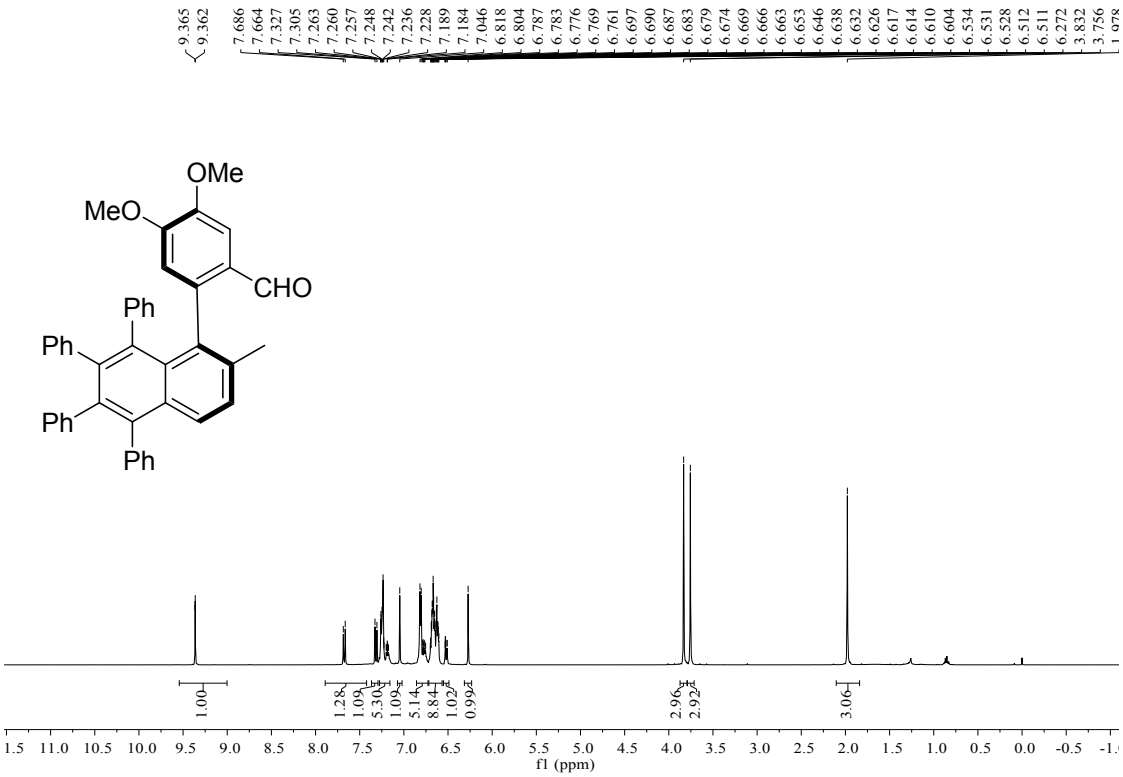


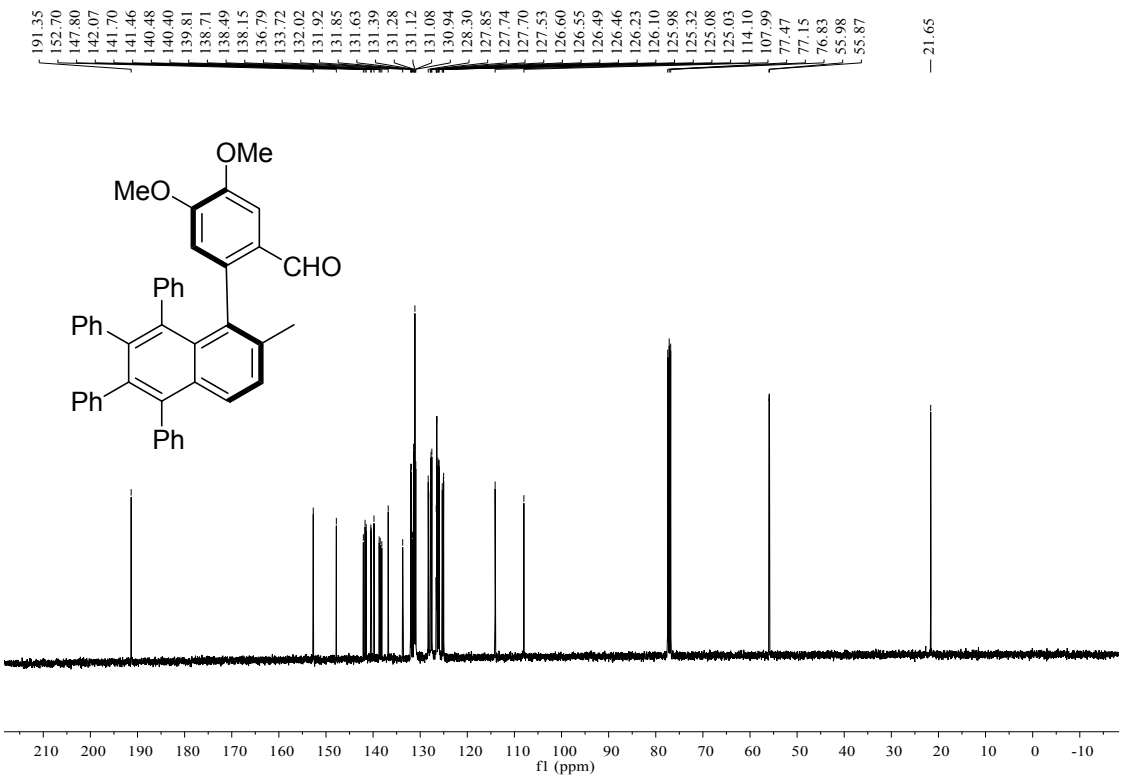




**5-Chloro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3g)**

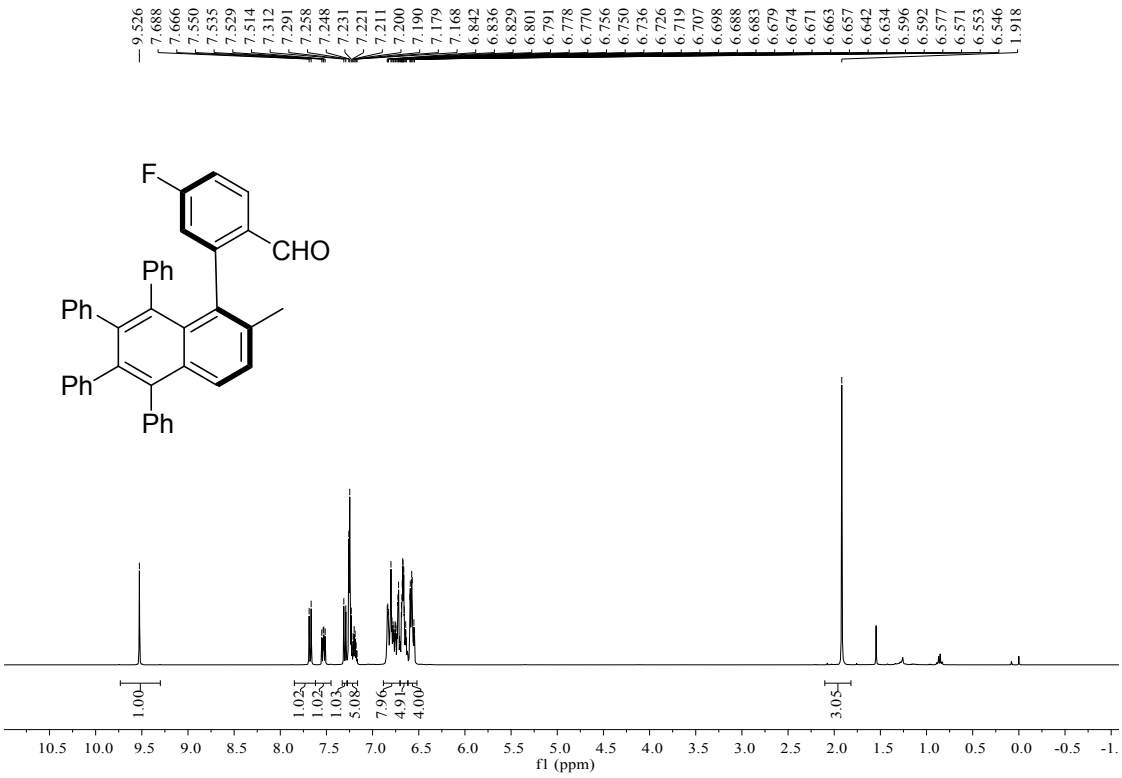


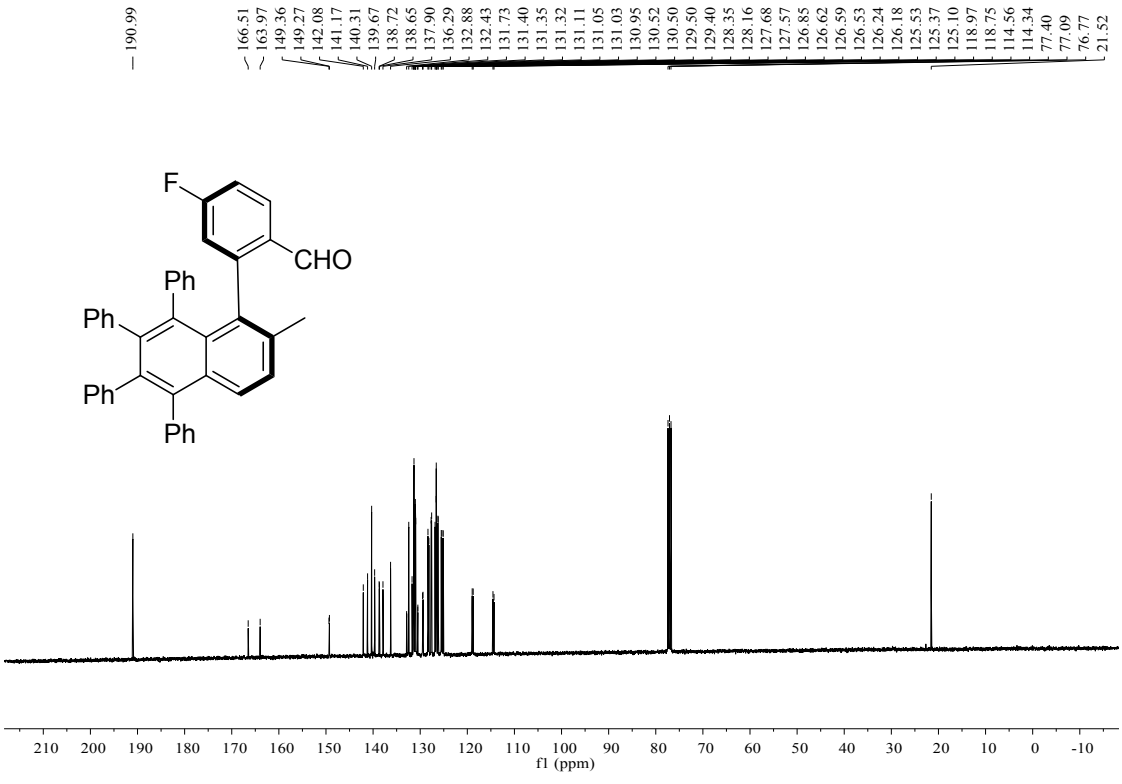

**4,5-Dimethoxy-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3 h)**

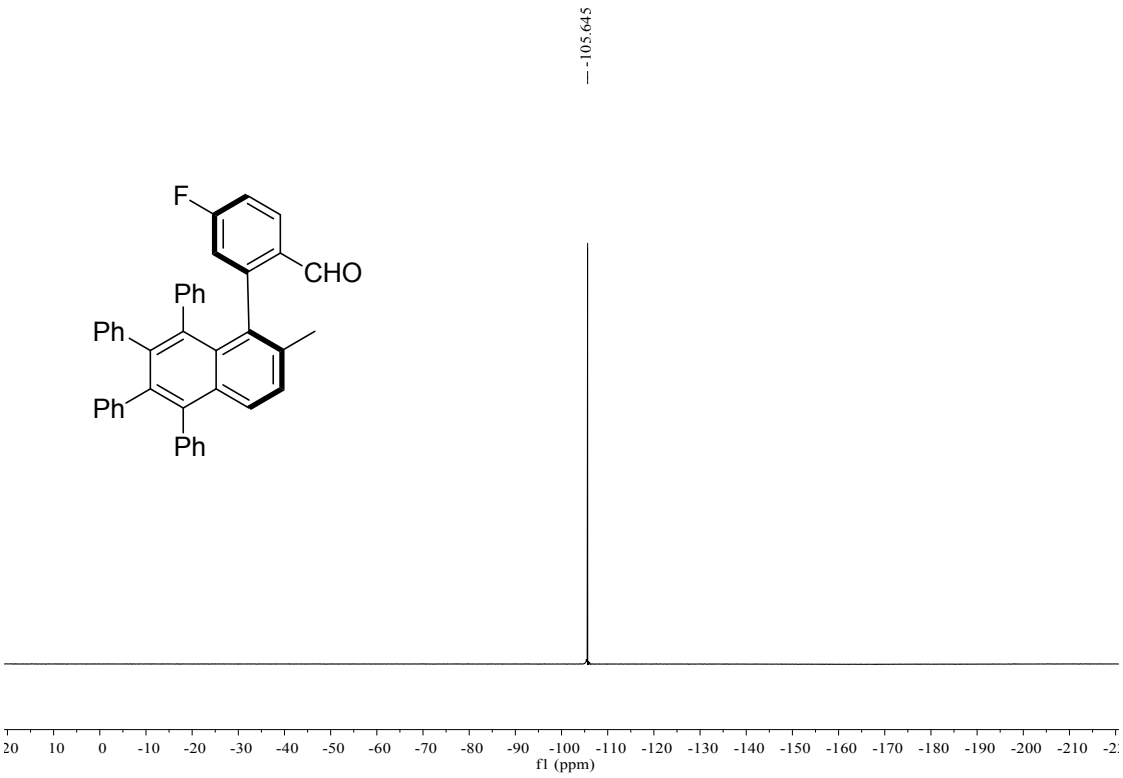


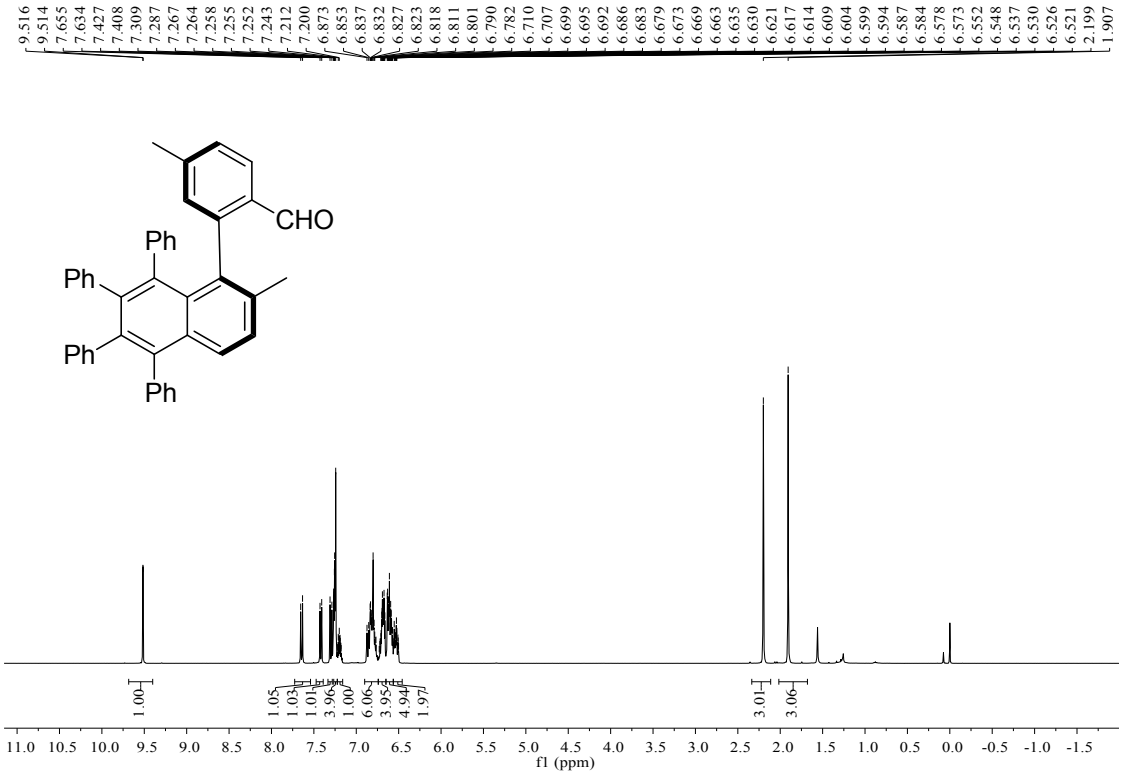

**4-Fluoro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3i)**

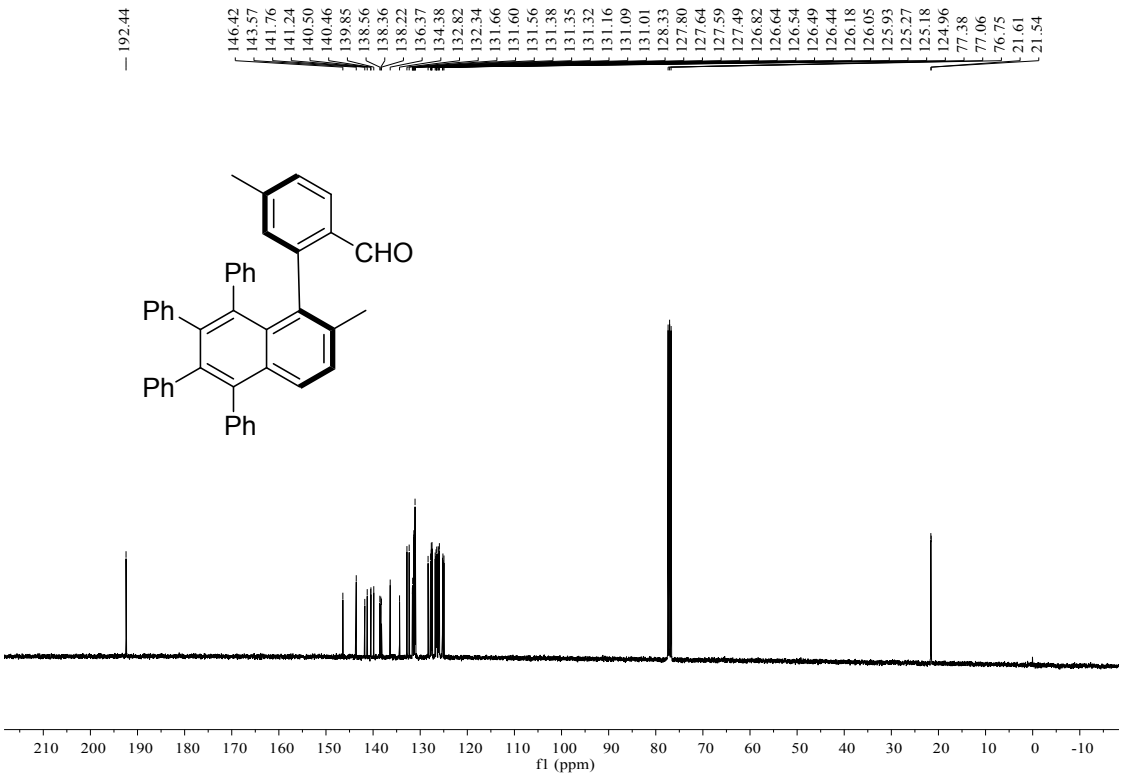

9.526
7.688
7.666
7.550
7.535
7.529
7.514
7.312
7.291
7.258
7.248
7.231
7.221
7.211
7.200
7.190
7.179
7.168
6.842
6.836
6.829
6.801
6.791
6.778
6.770
6.756
6.750
6.736
6.726
6.719
6.707
6.698
6.688
6.683
6.679
6.674
6.671
6.663
6.657
6.642
6.634
6.596
6.592
6.577
6.571
6.553
6.546
1.918
F
CHO
Ph
Ph
Ph
Ph
1.00
1.02
1.02
1.03
5.08
7.96
4.91
4.00
3.05
f1 (ppm)


190.99
166.51
163.97
149.36
149.27
142.08
141.17
140.31
139.67
138.72
138.65
137.90
136.29
132.88
132.43
131.73
131.40
131.35
131.32
131.11
131.05
131.03
130.95
130.52
130.50
129.50
129.40
128.35
128.16
127.68
127.57
126.85
126.62
126.59
126.53
126.24
126.18
125.53
125.37
125.10
118.97
118.75
114.56
114.34
77.40
77.09
76.77
21.52
F
CHO
Ph
Ph
Ph
Ph
f1 (ppm)

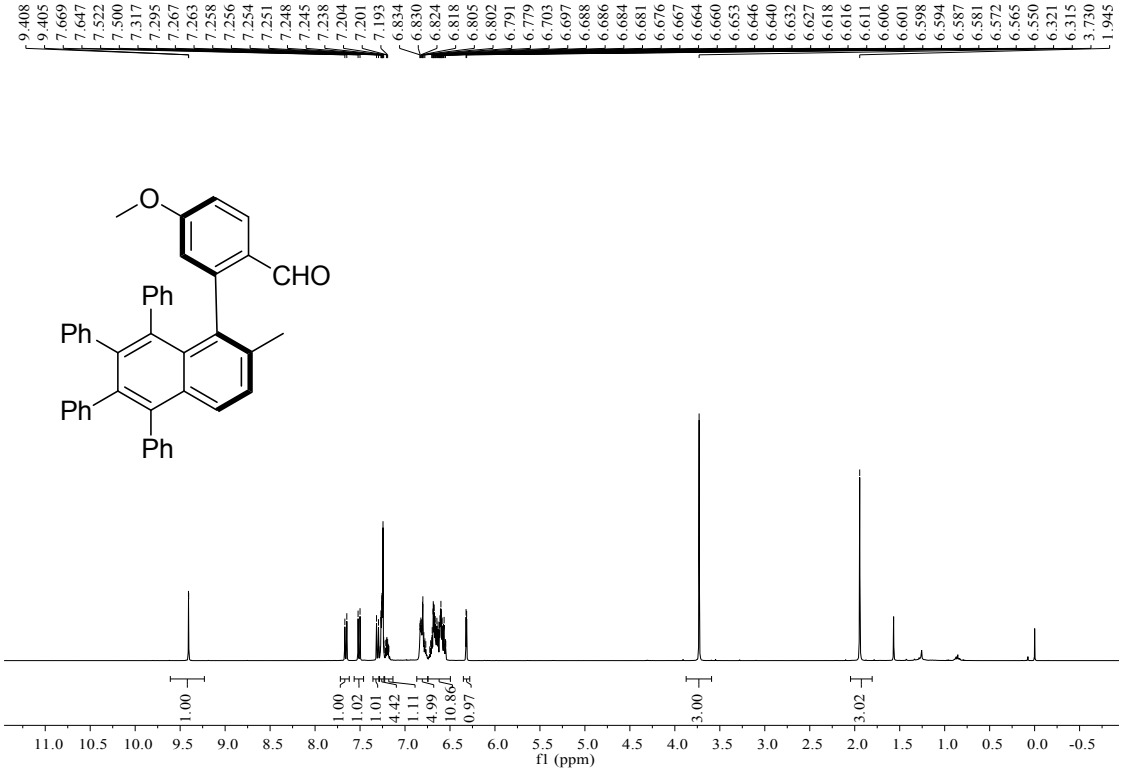


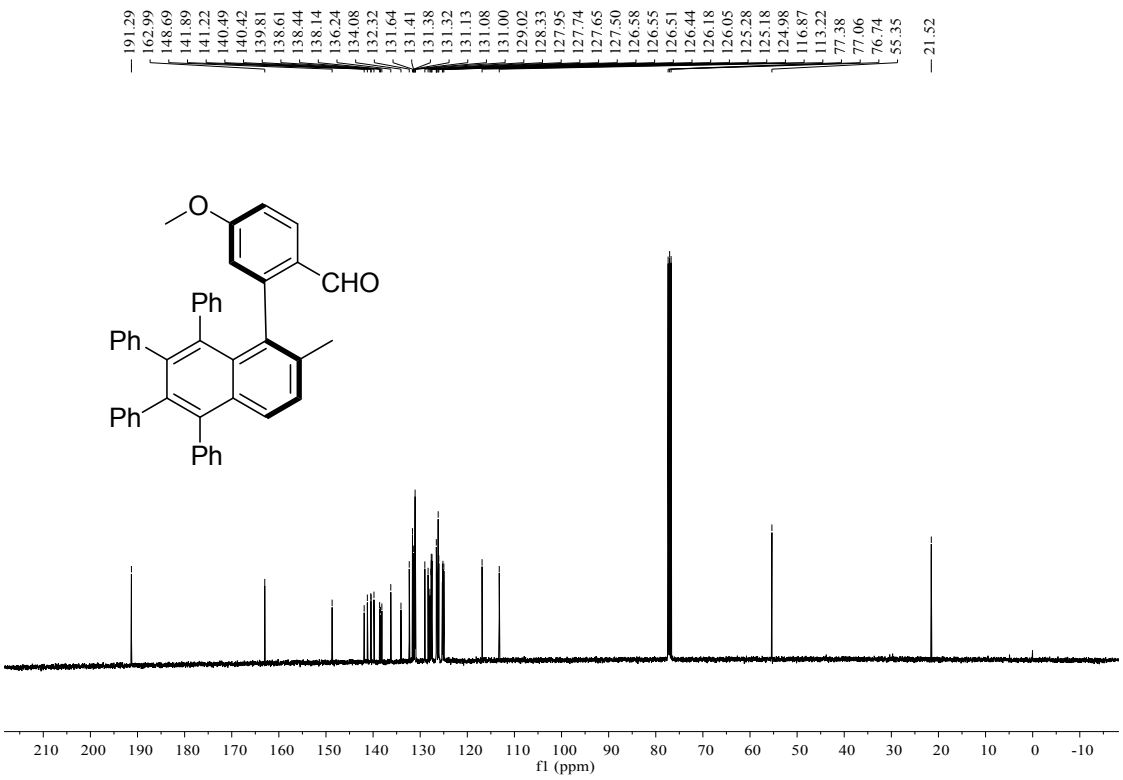

## 4-Methyl-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3j)



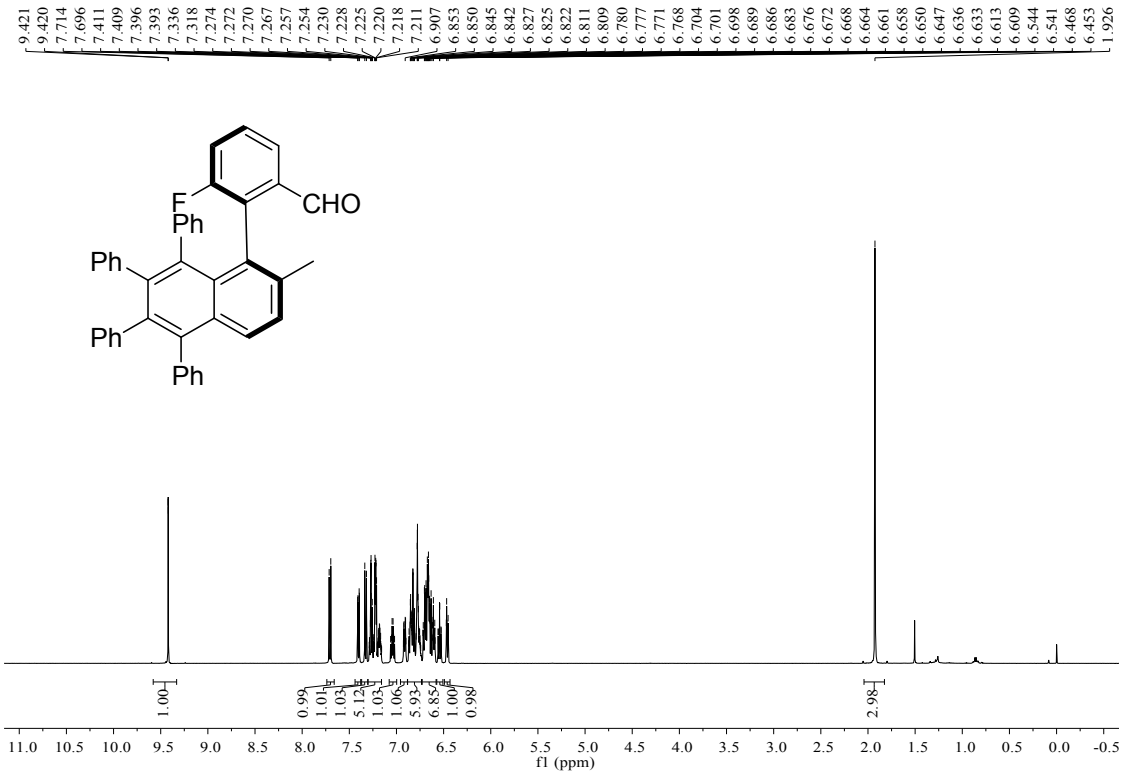


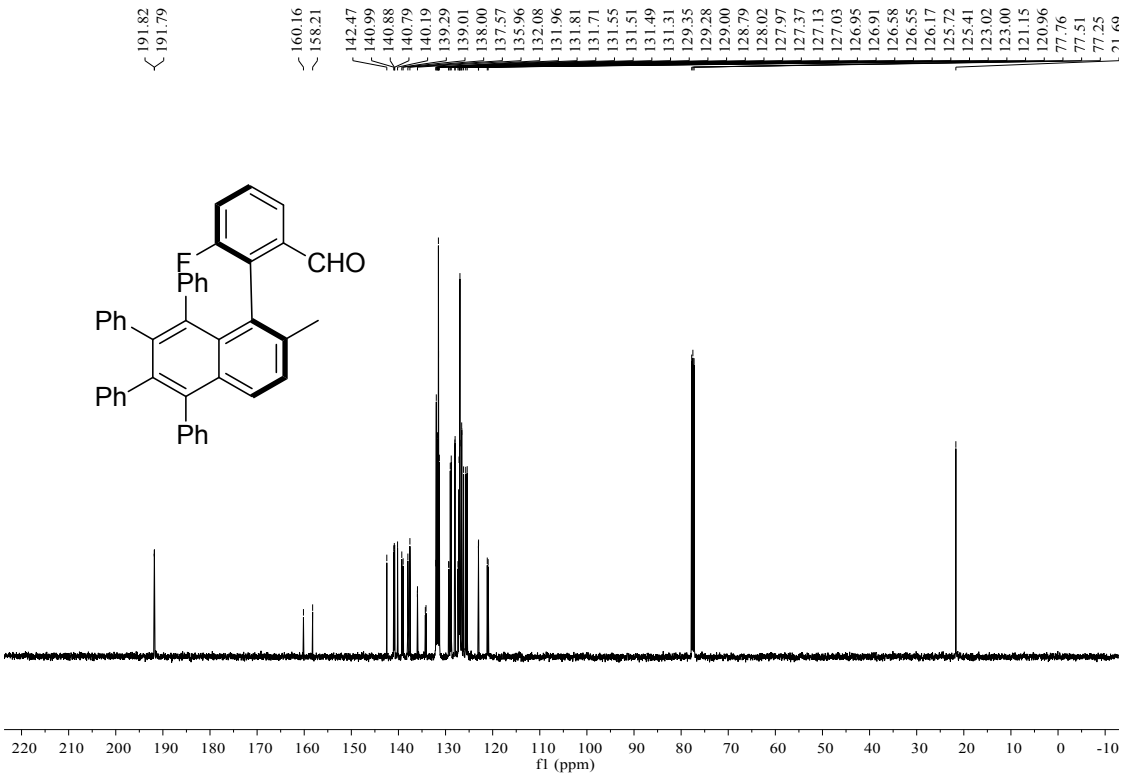

## 4-Methoxy-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3k)

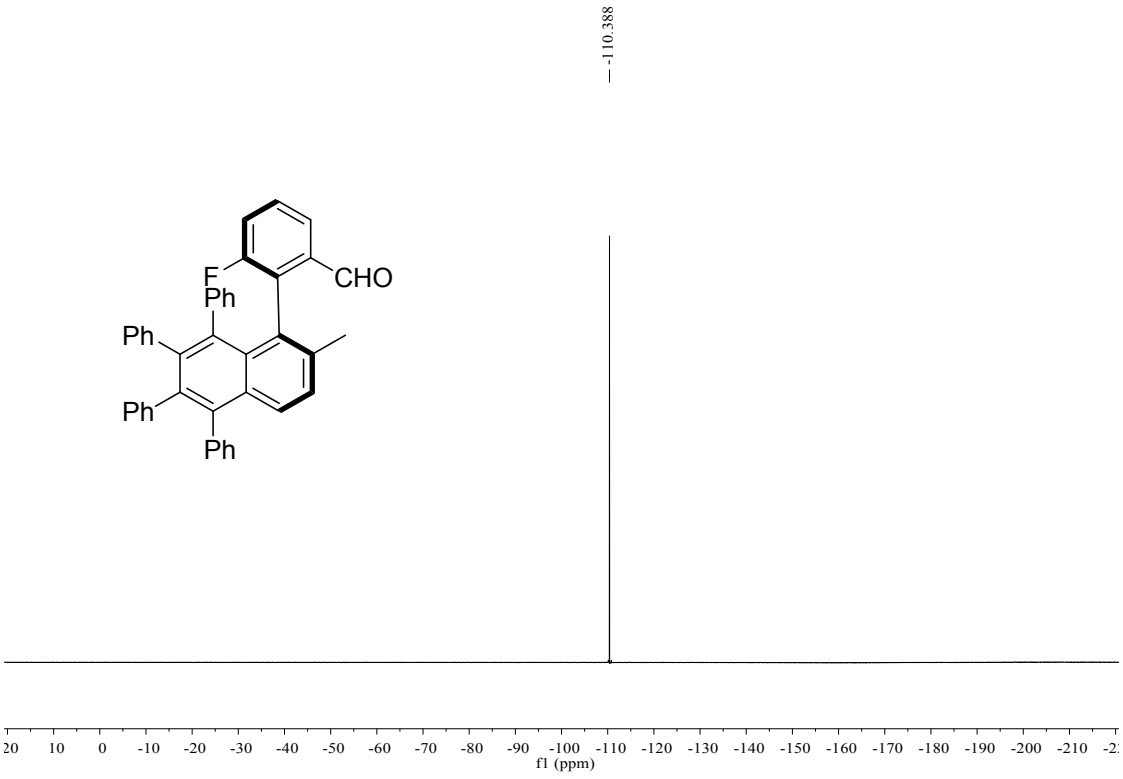




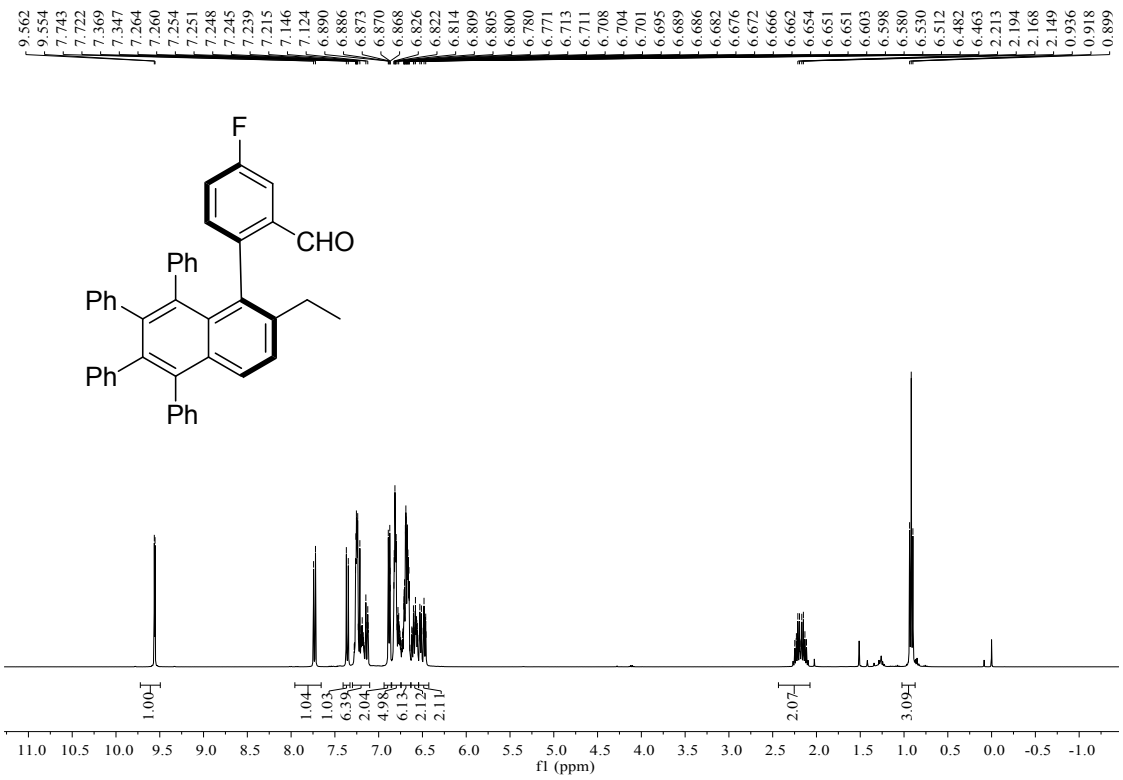

## 3-Fluoro-2-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3l)

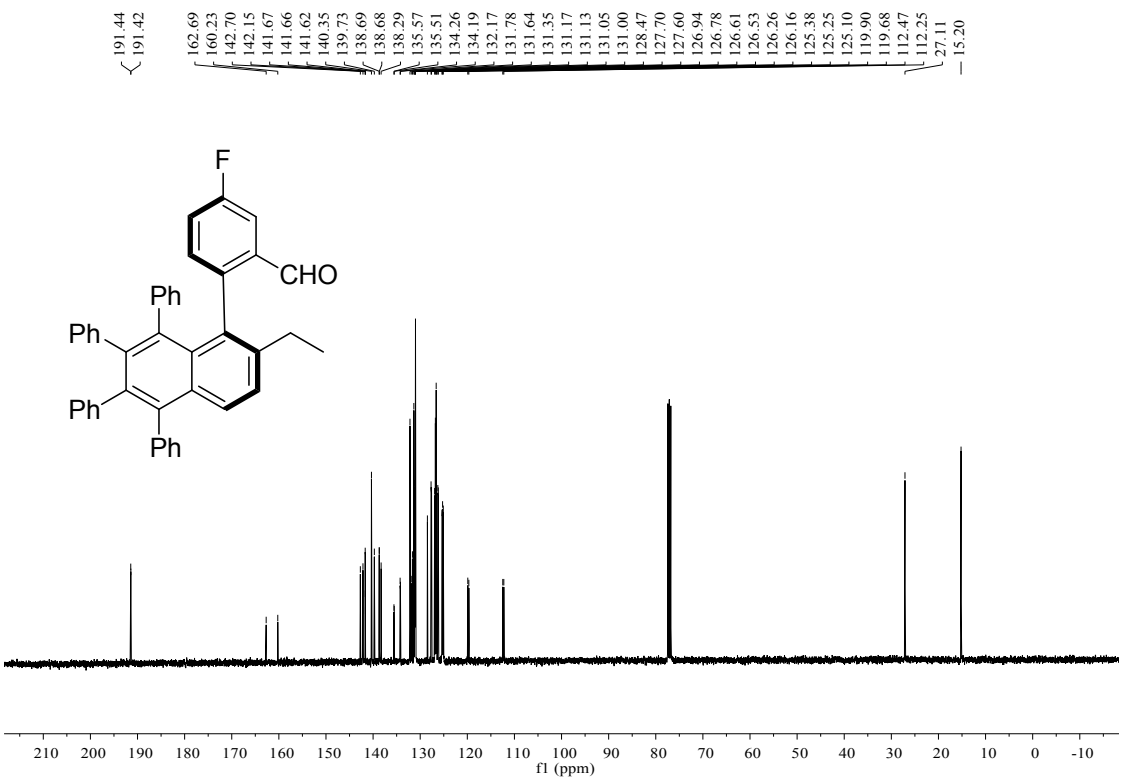


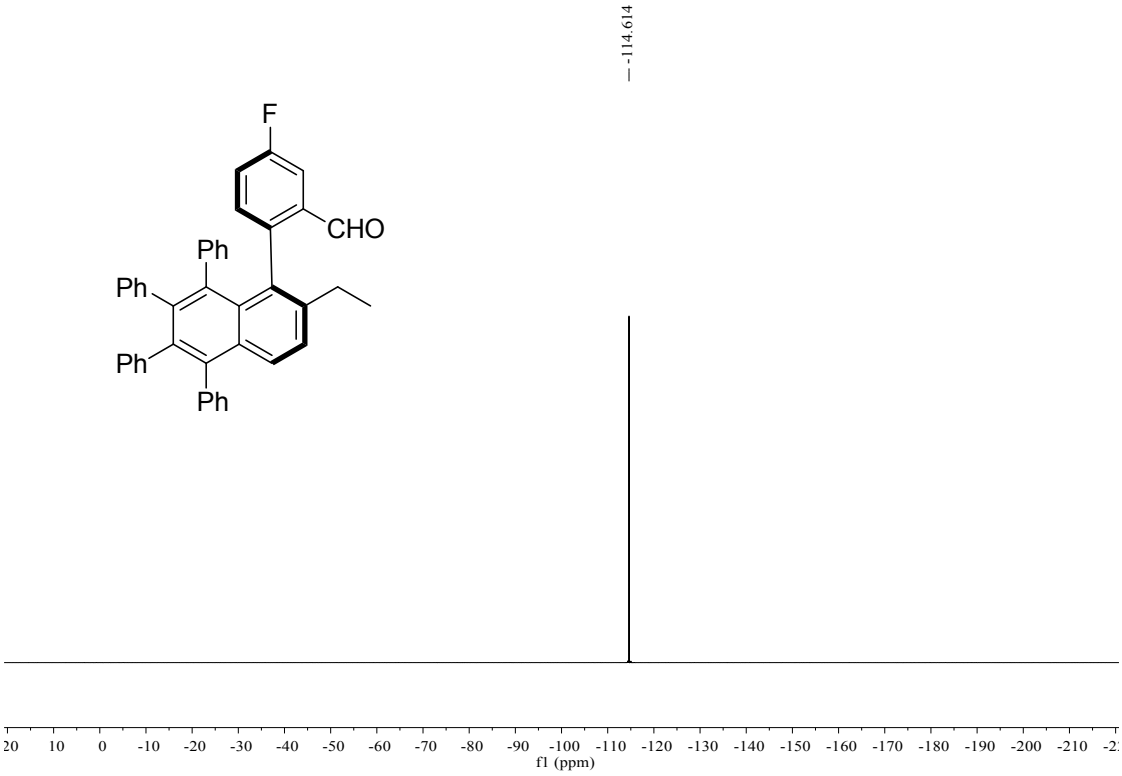


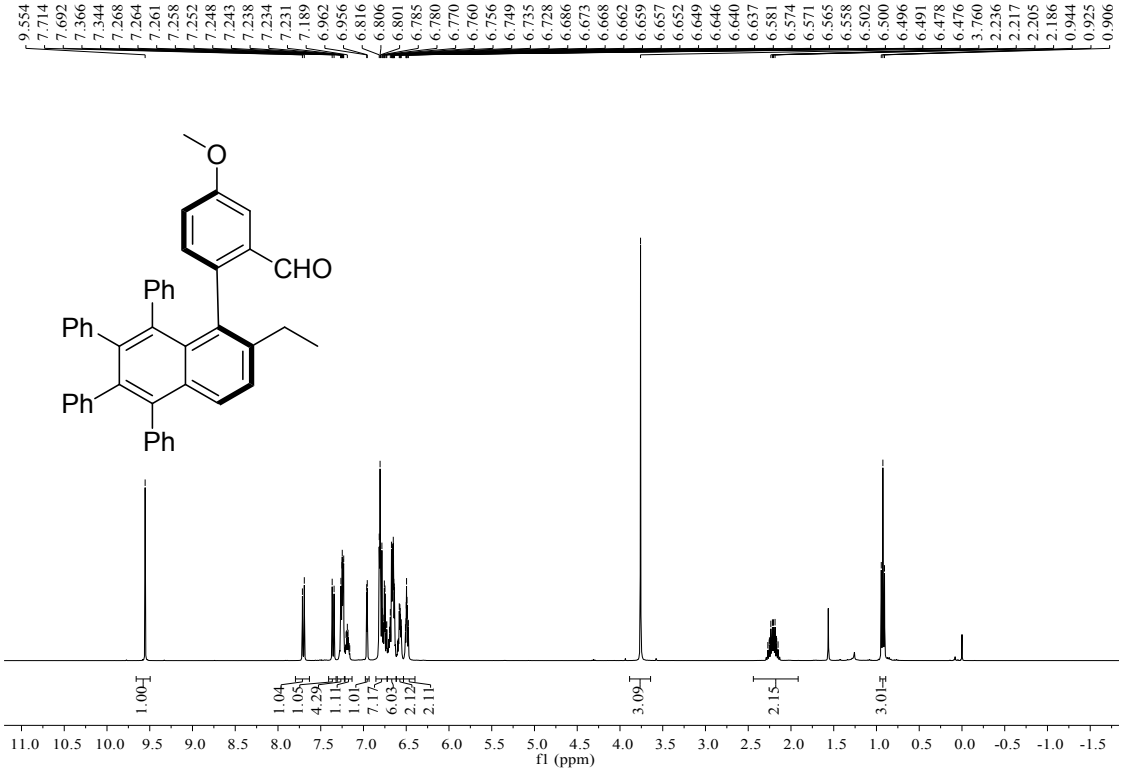

**2-(2-Ethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-fluorobenzaldehyde (3m)**

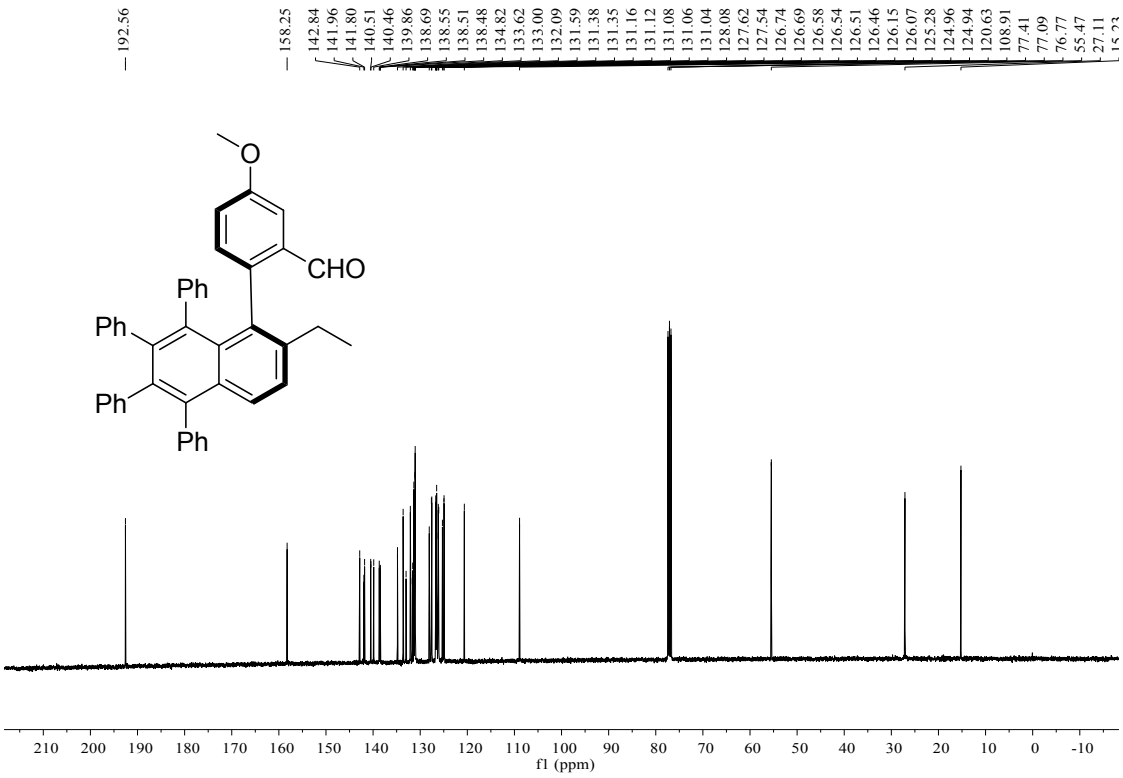

9.562
9.554
7.743
7.722
7.369
7.347
7.264
7.260
7.254
7.251
7.248
7.245
7.239
7.215
7.146
7.124
6.890
6.886
6.873
6.870
6.868
6.826
6.822
6.814
6.809
6.805
6.800
6.780
6.771
6.713
6.711
6.708
6.704
6.701
6.695
6.689
6.686
6.682
6.676
6.672
6.666
6.662
6.654
6.651
6.651
6.603
6.598
6.580
6.530
6.512
6.482
6.463
2.213
2.194
2.168
2.149
0.936
0.918
0.899
F
CHO
Ph
Ph
Ph
Ph
1.00
1.04
1.03
6.39
2.04
4.98
6.13
2.12
2.11
2.07
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


191.44
191.42
162.69
160.23
142.70
142.15
141.67
141.66
141.62
140.35
139.73
138.69
138.68
138.29
135.57
135.51
134.26
134.19
132.17
131.78
131.64
131.35
131.17
131.13
131.05
131.00
128.47
127.70
127.60
126.94
126.78
126.61
126.53
126.26
126.16
125.38
125.25
125.10
119.90
119.68
112.47
112.25
27.11
15.20
F
CHO
Ph
Ph
Ph
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

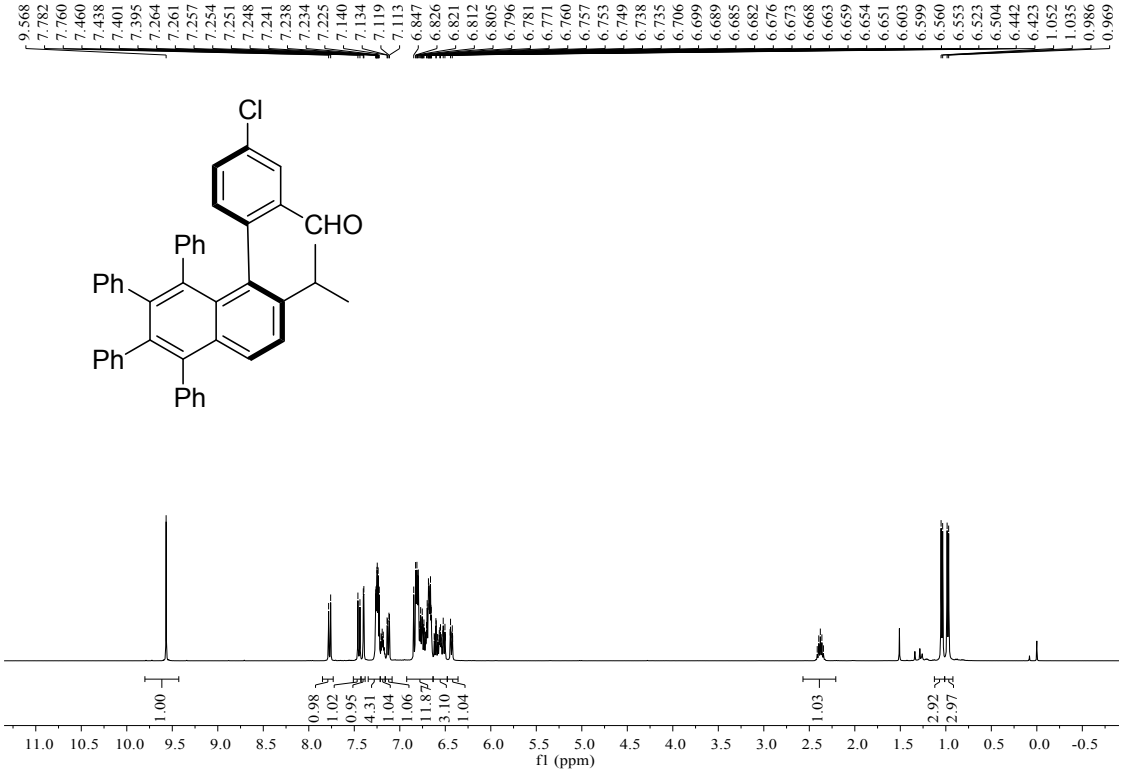


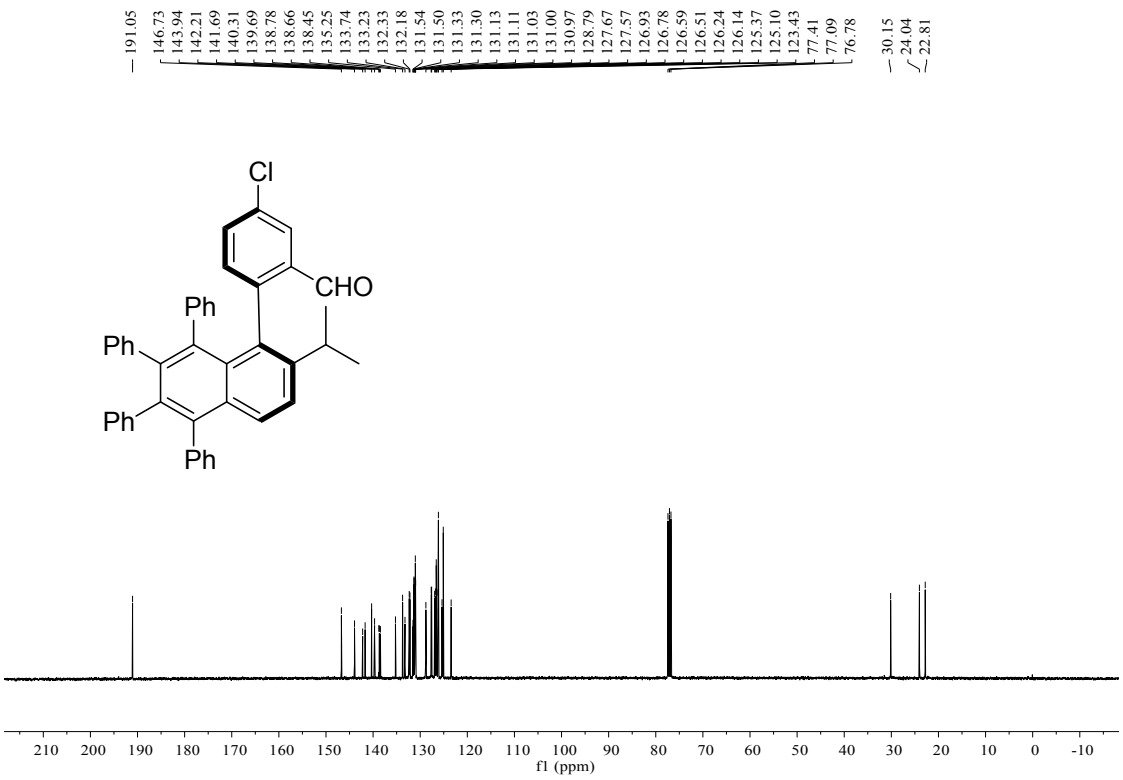

## 2-(2-Ethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-methoxybenzaldehyde (3n)



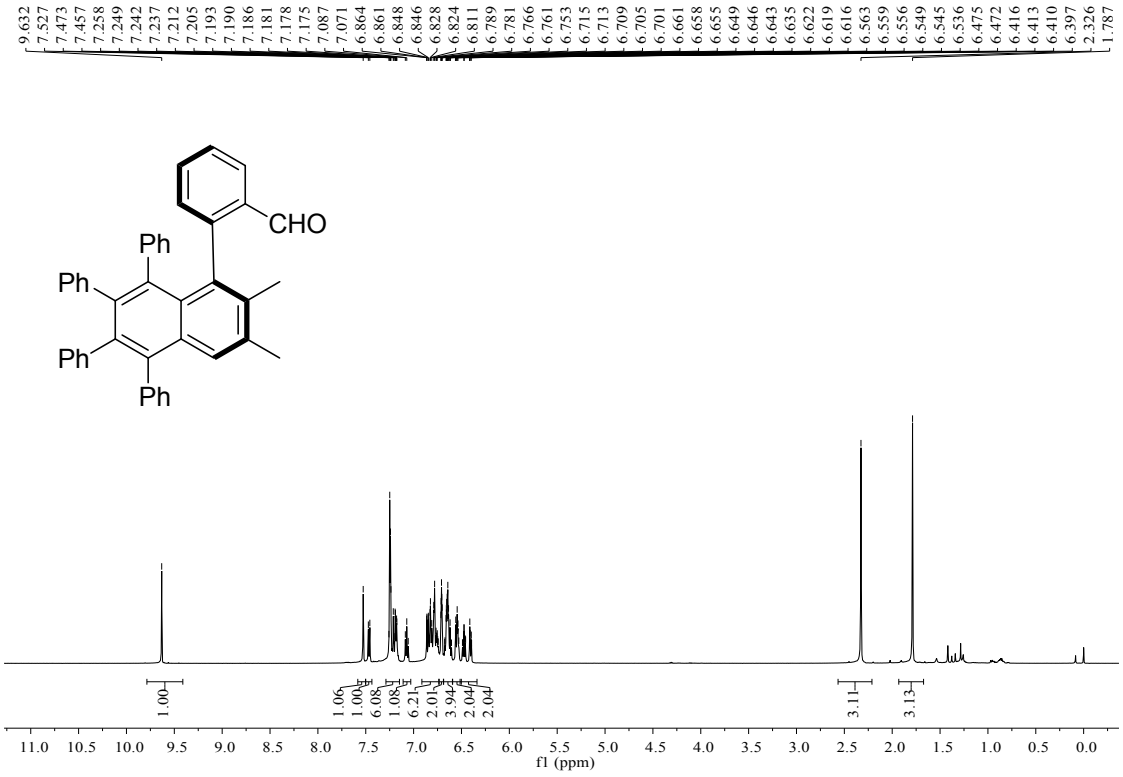


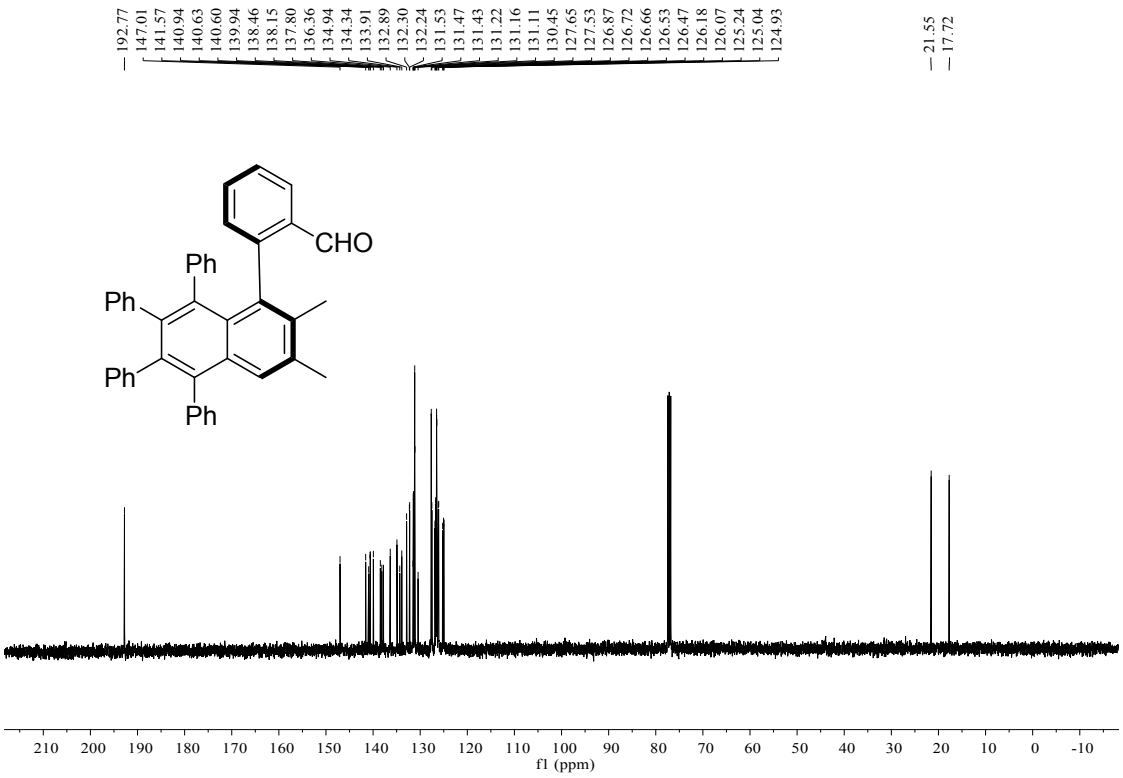

## 5-Chloro-2-(2-isopropyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3o)



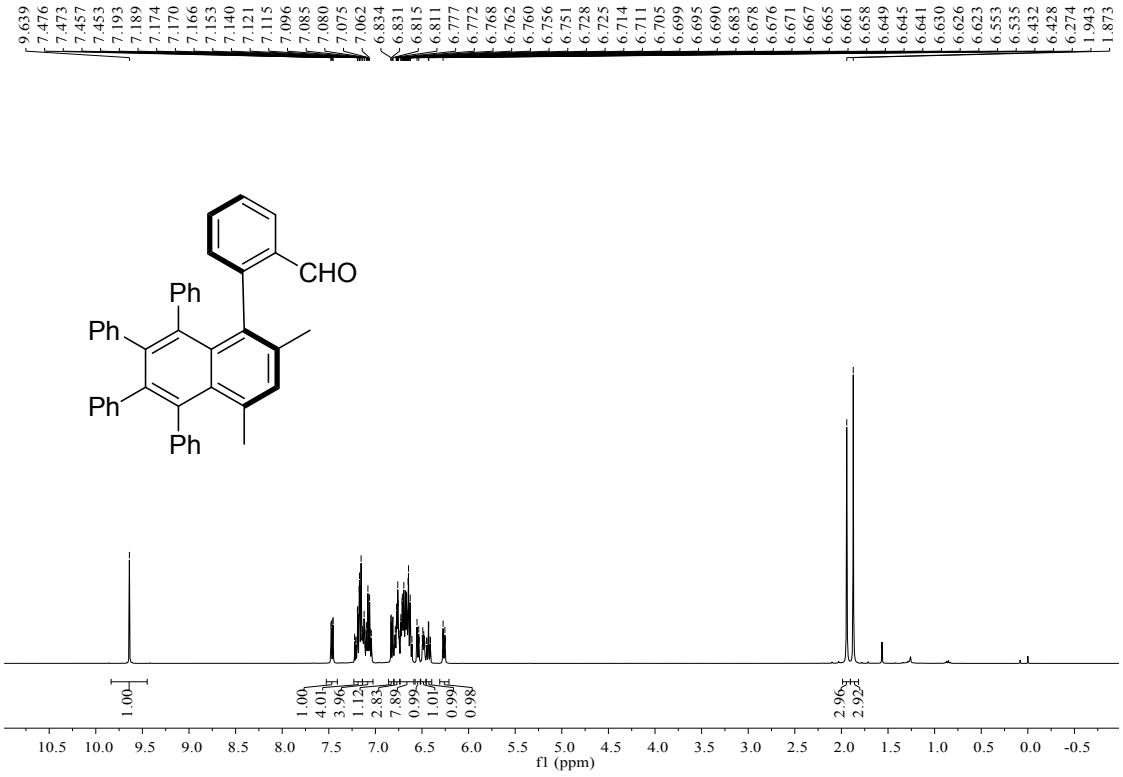


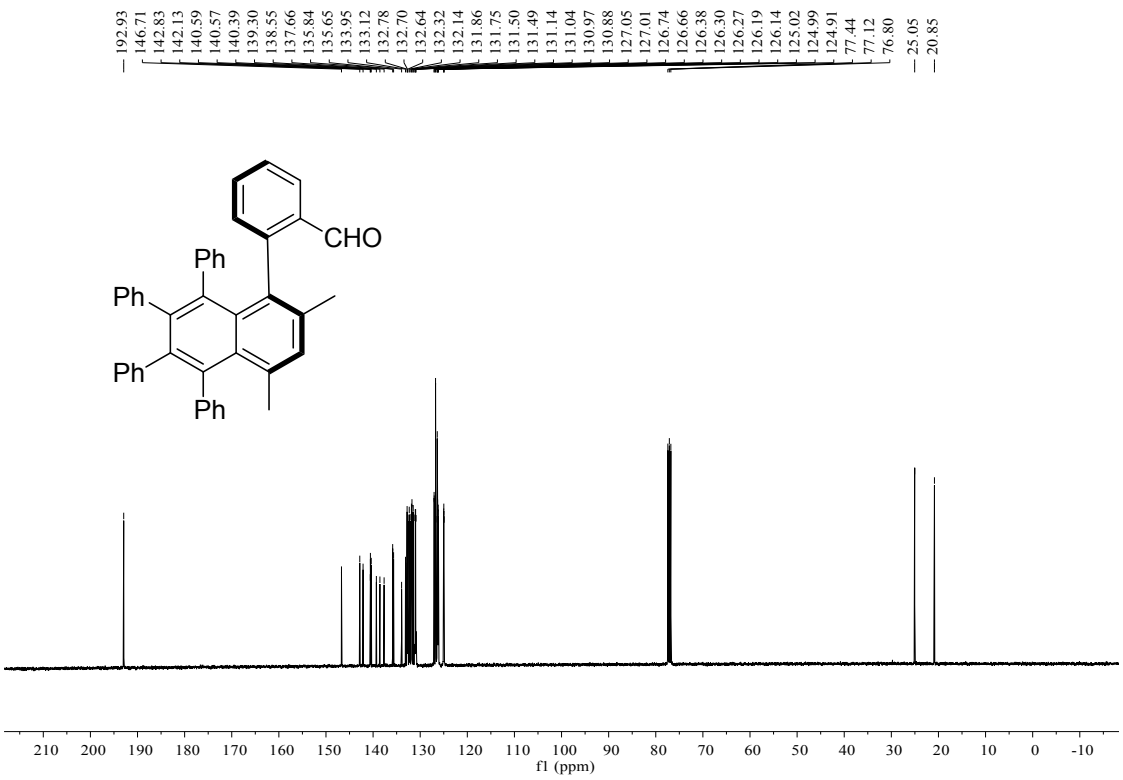

## 2-(2,3-Dimethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3p)



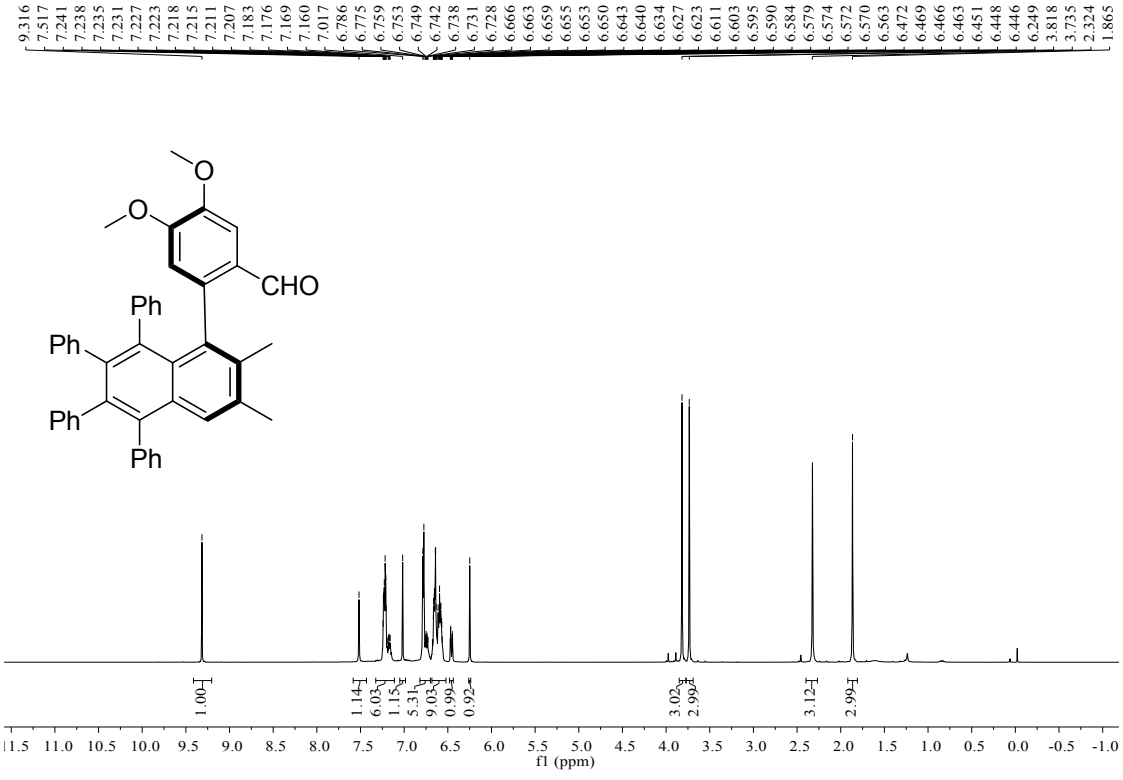


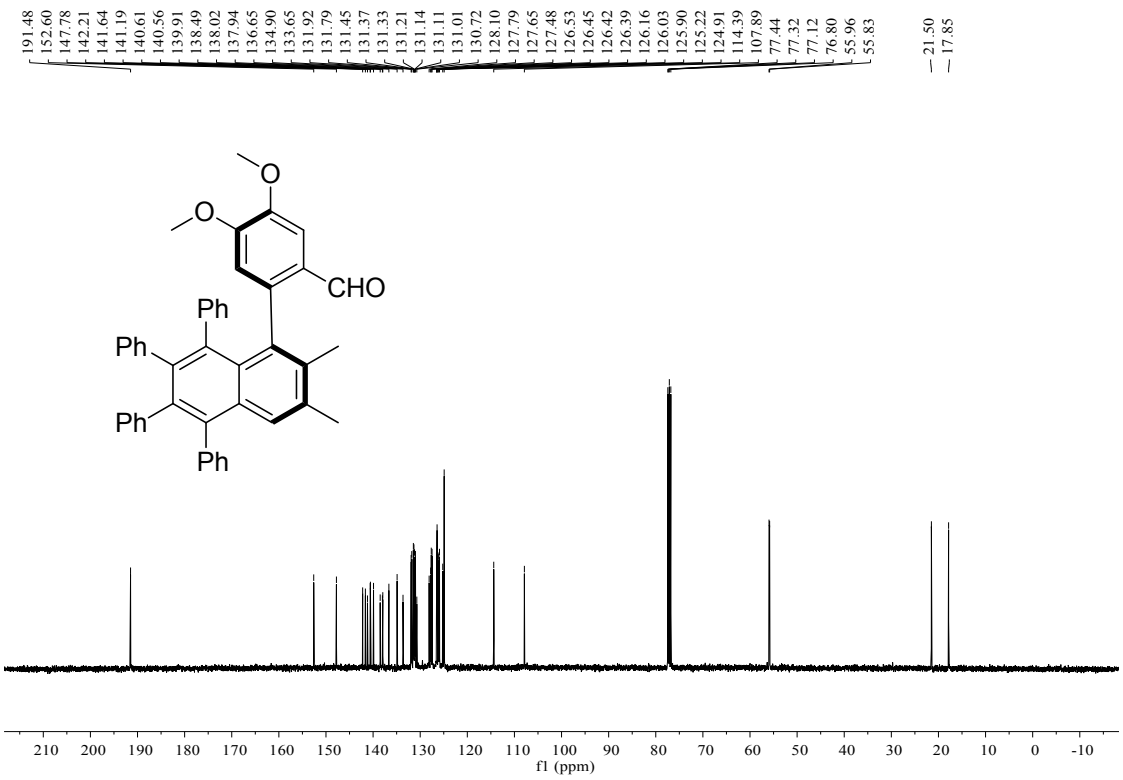

## 2-(2,4-Dimethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3q)



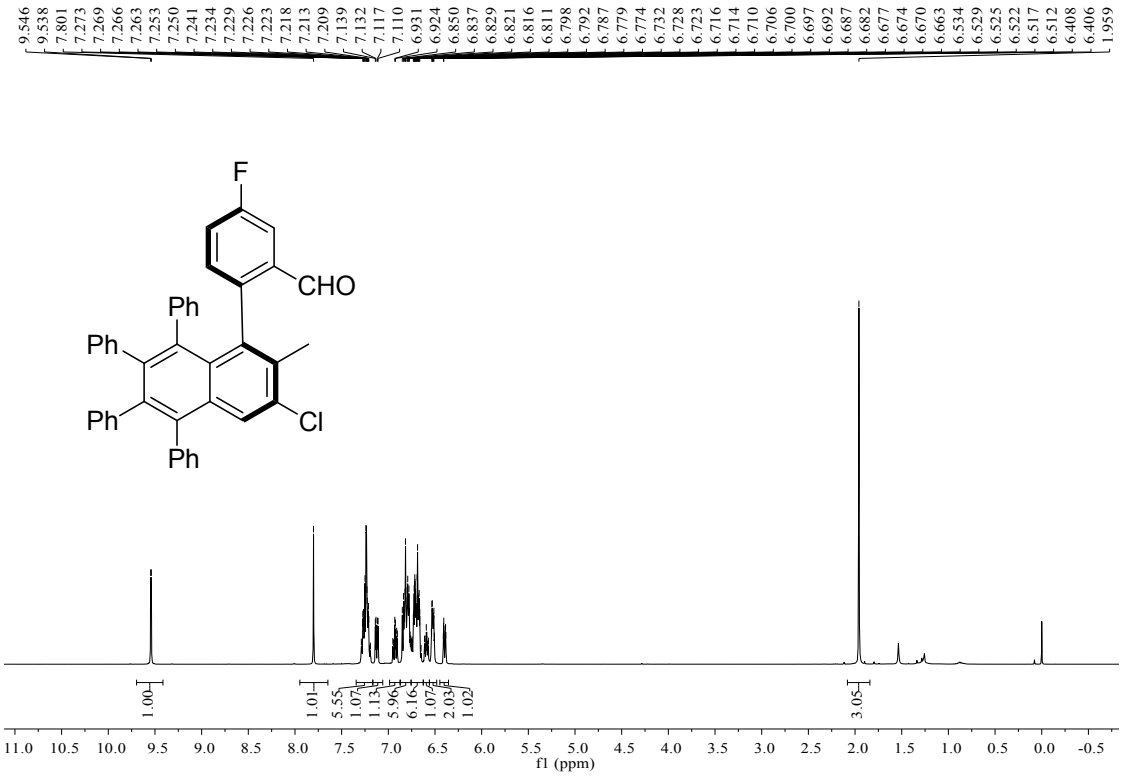


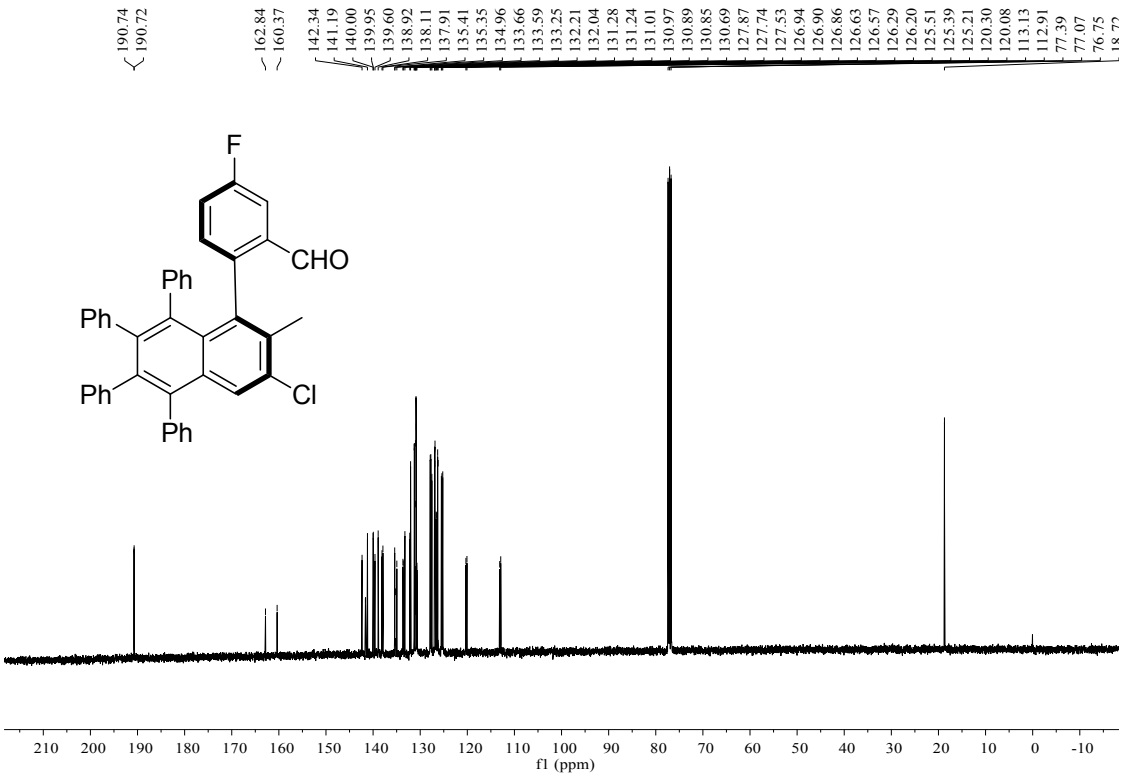

## 2-(2,3-Dimethyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-4,5-dimethoxybenzaldehyde (3r)

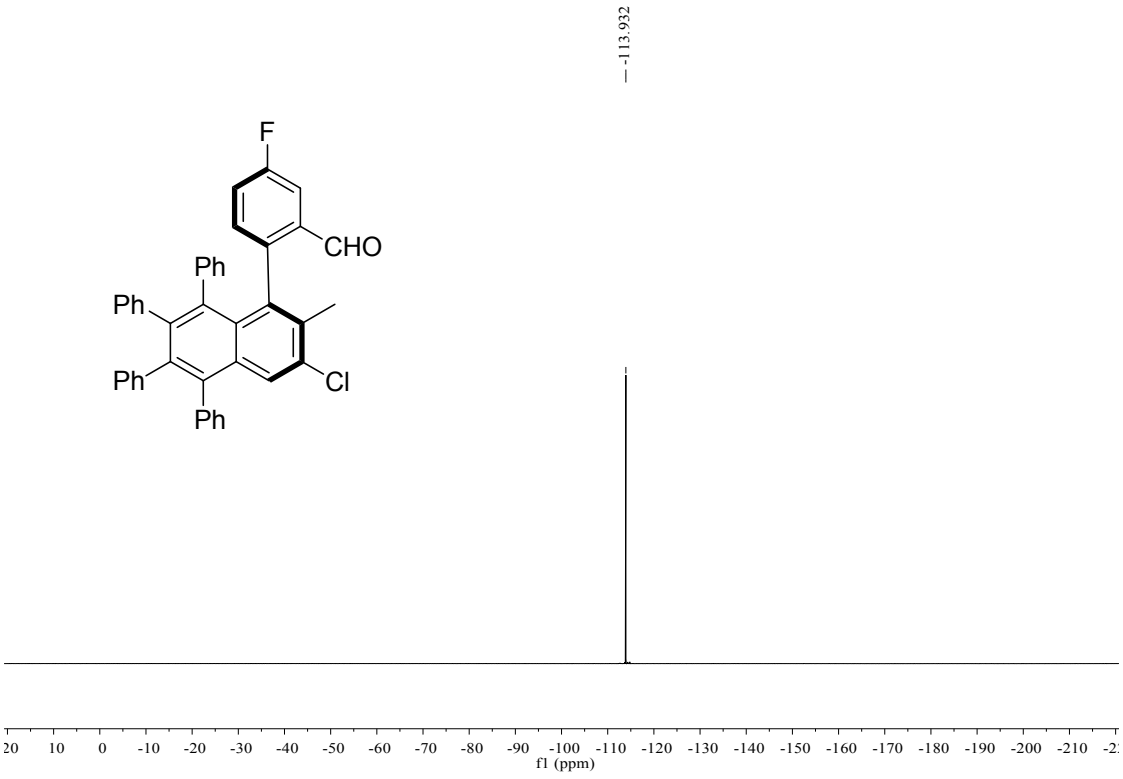




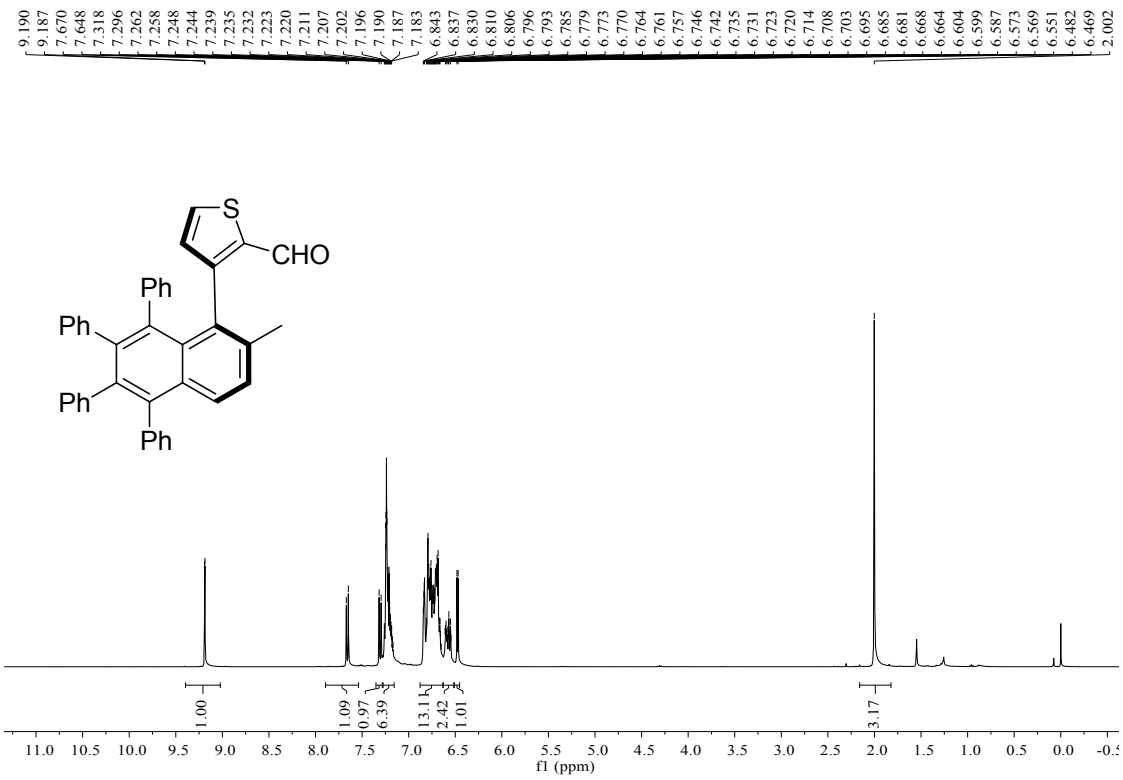

## 2-(3-Chloro-2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-fluorobenzaldehyde (3s)

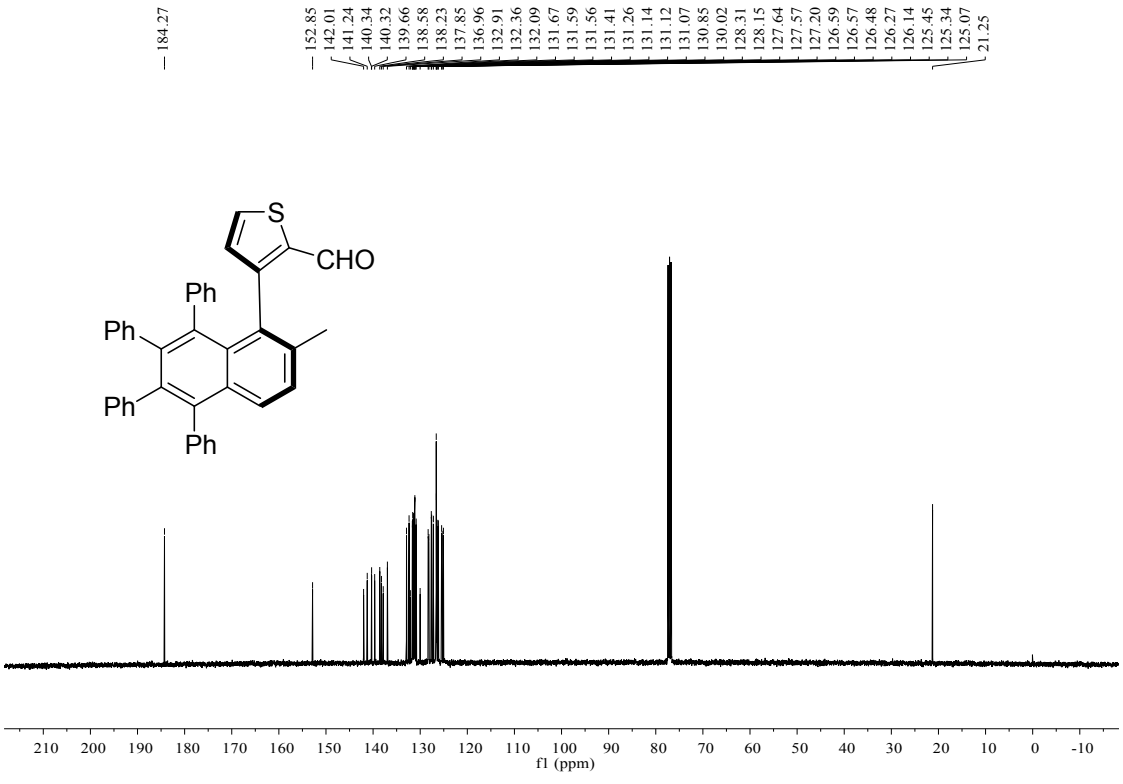




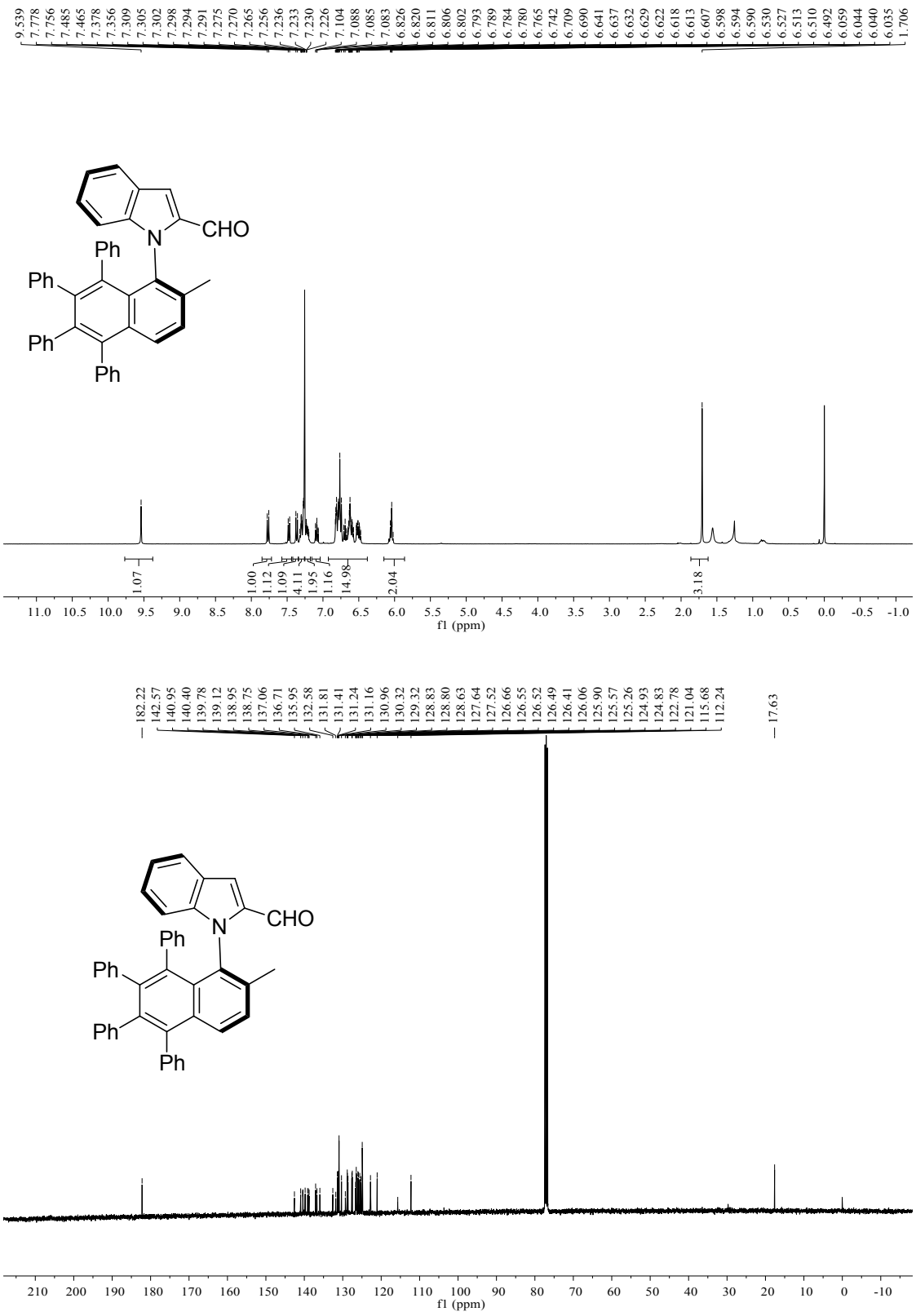




**3-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)thiophene-2-carbaldehyde (3t)**

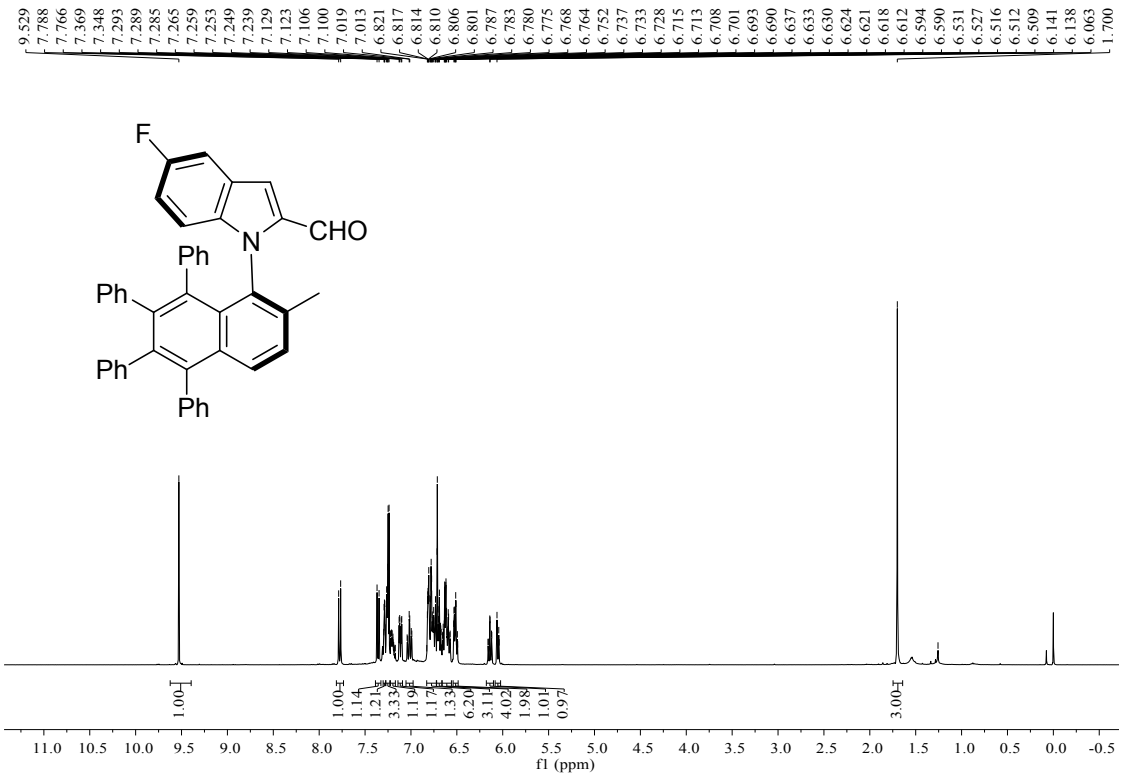


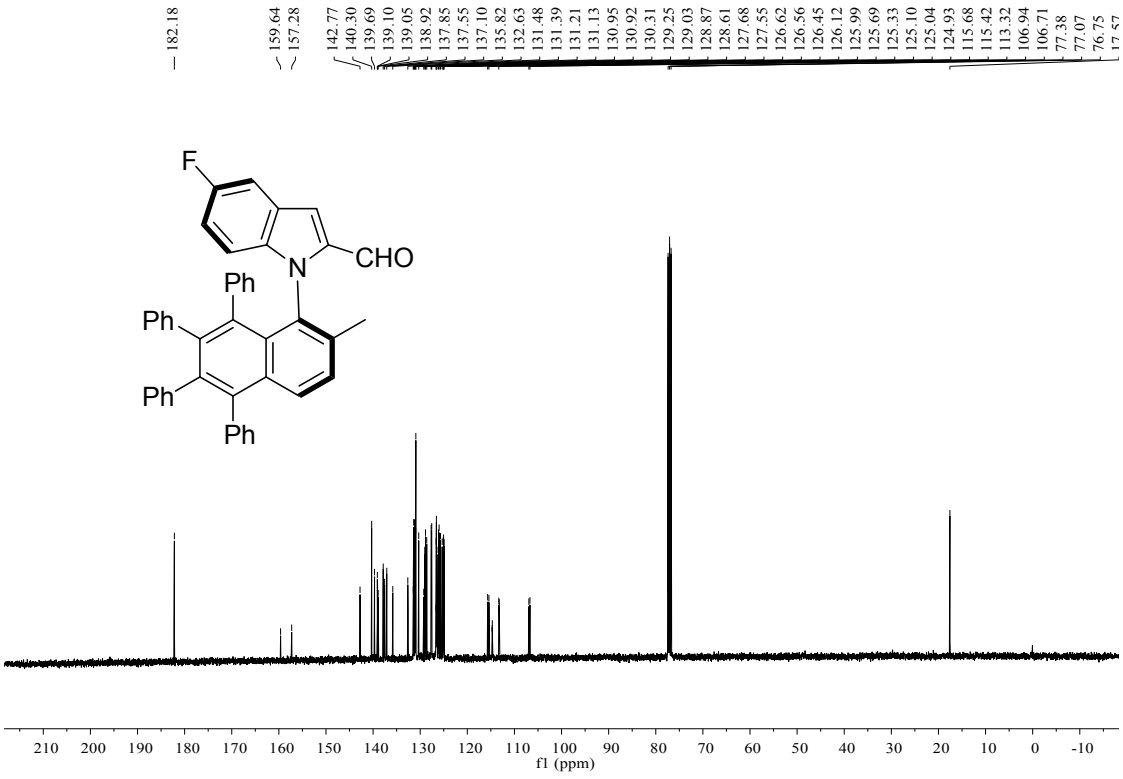



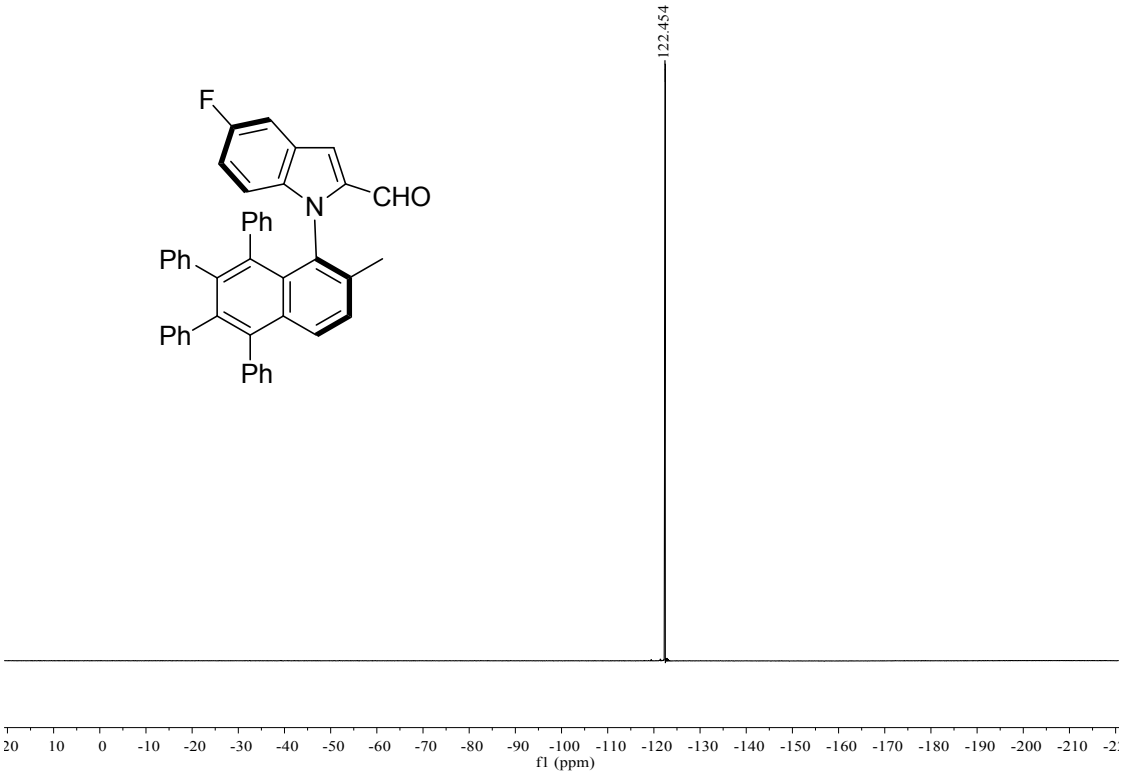

**1-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-indole-2-carbaldehyde (3u)**



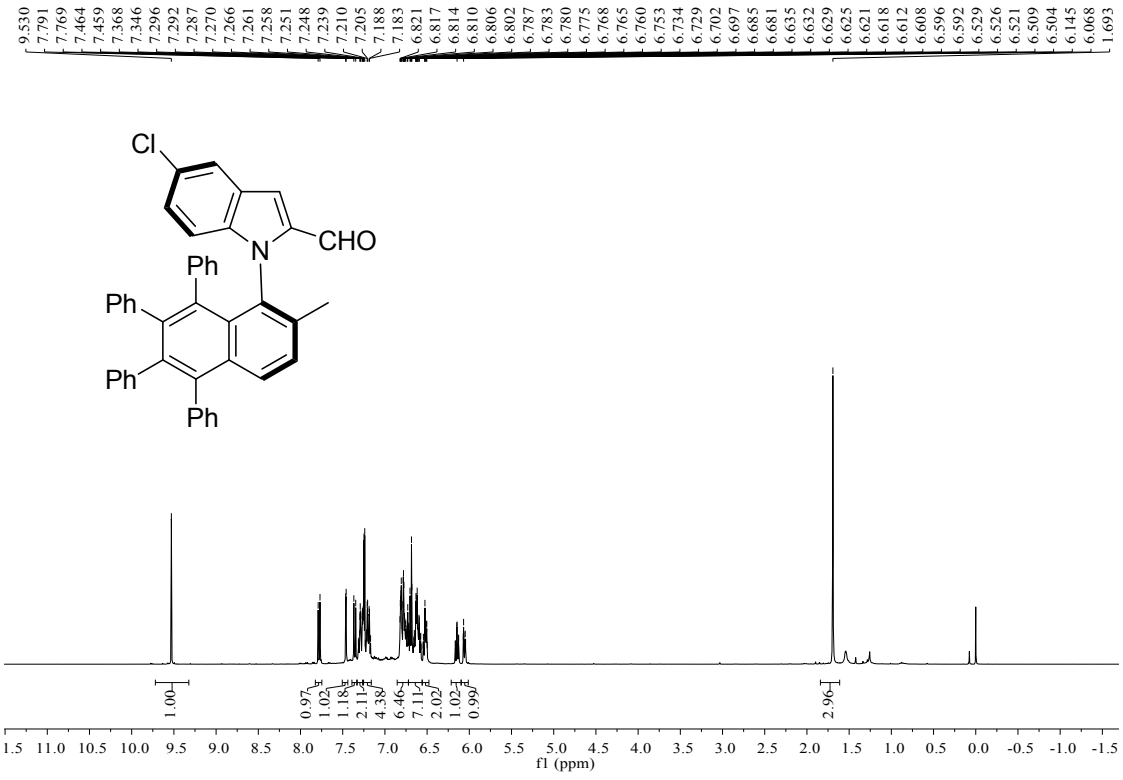

**5-Fluoro-1-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-indole-2-carbaldehyde (3v)**

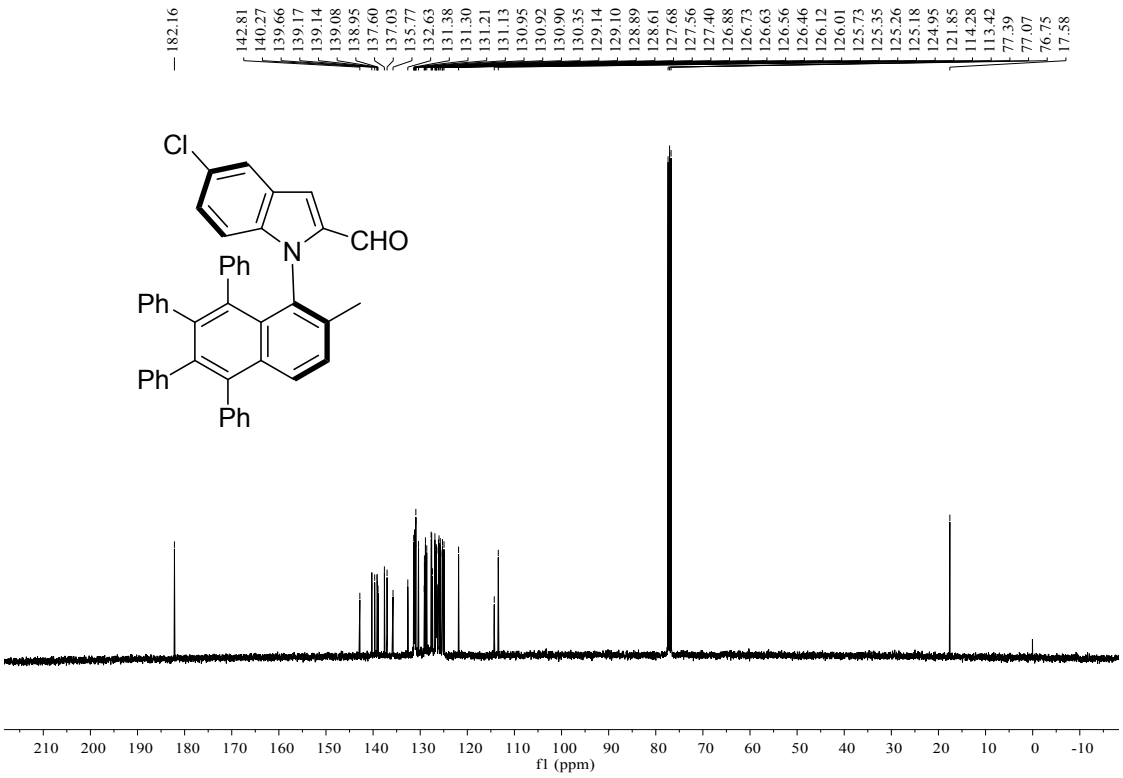

F
N
CHO
Ph
Ph
Ph
Ph
f1 (ppm)


F
N
CHO
Ph
Ph
Ph
Ph
f1 (ppm)

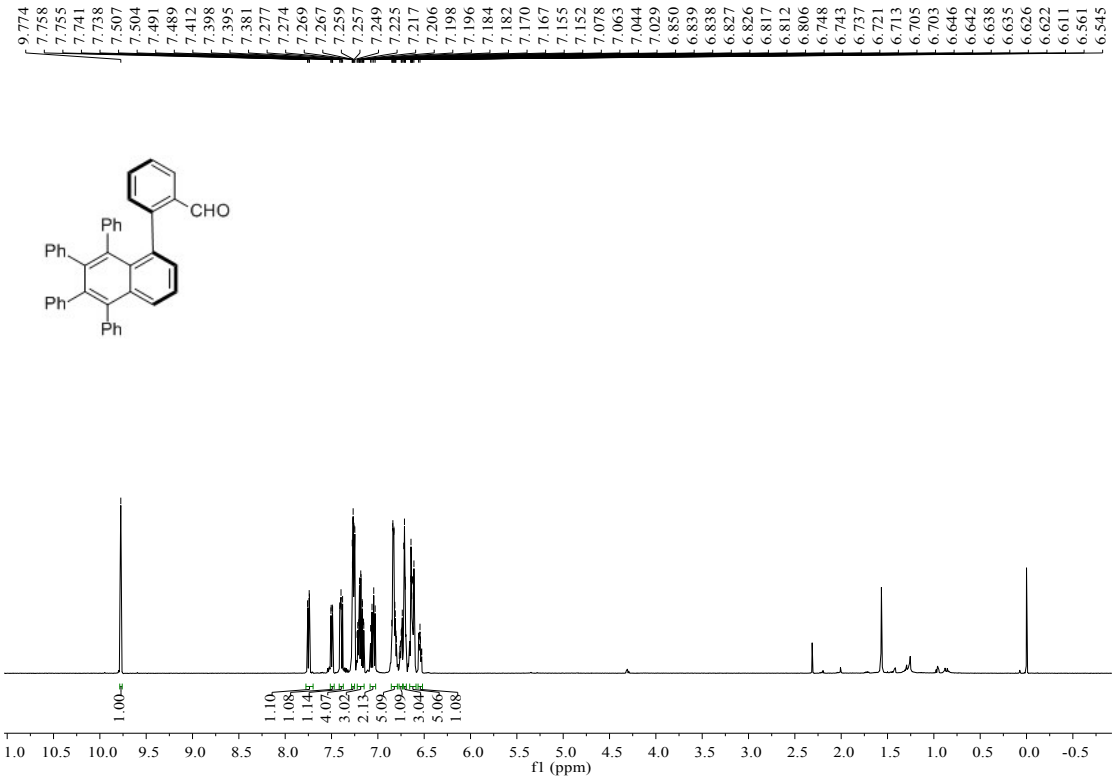


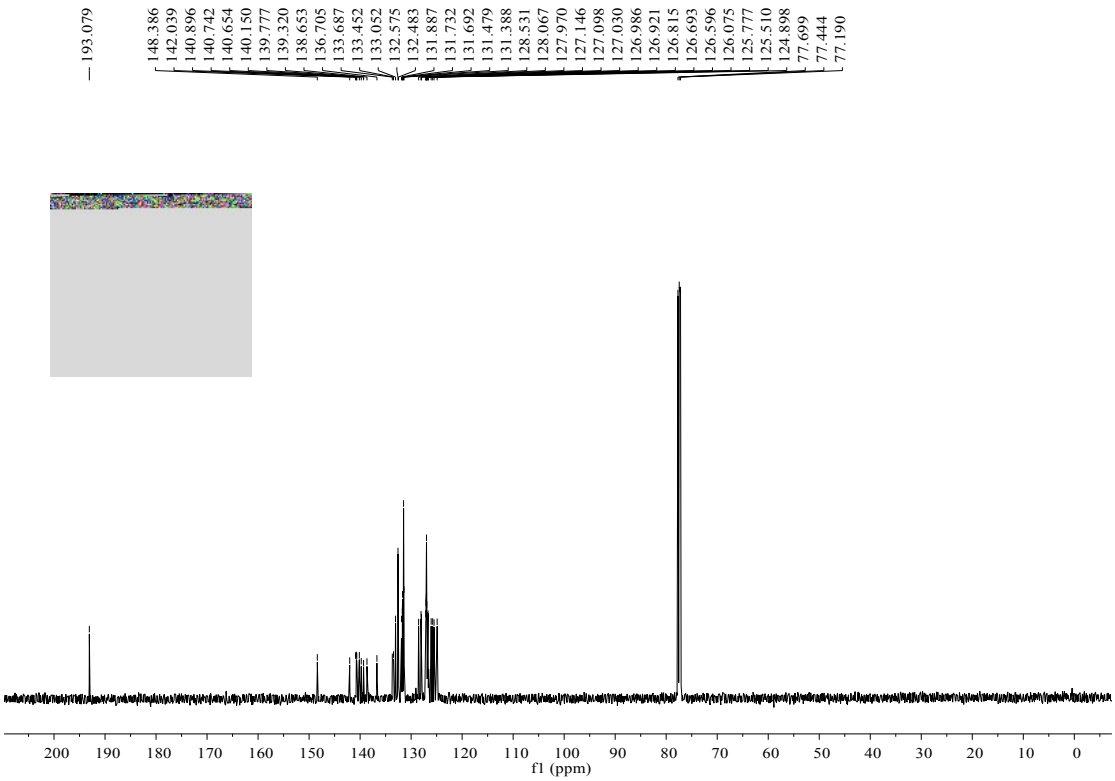

**5-Chloro-1-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-1H-indole-2-carbaldehyde (3w)**



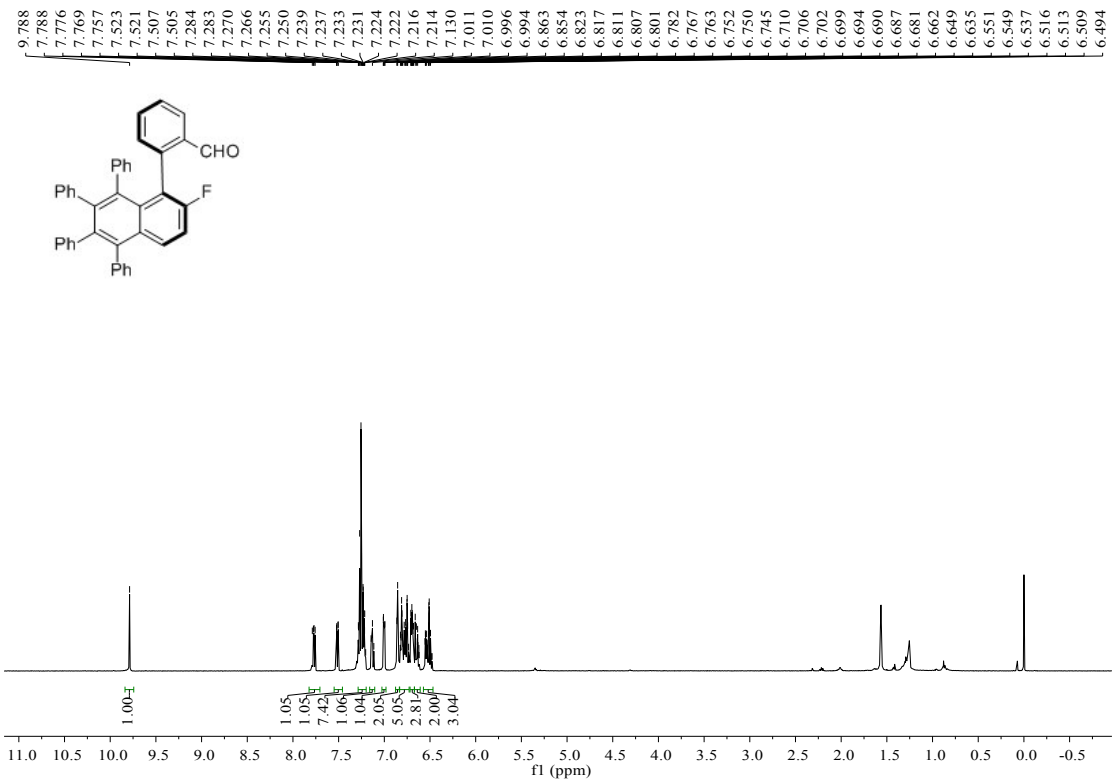


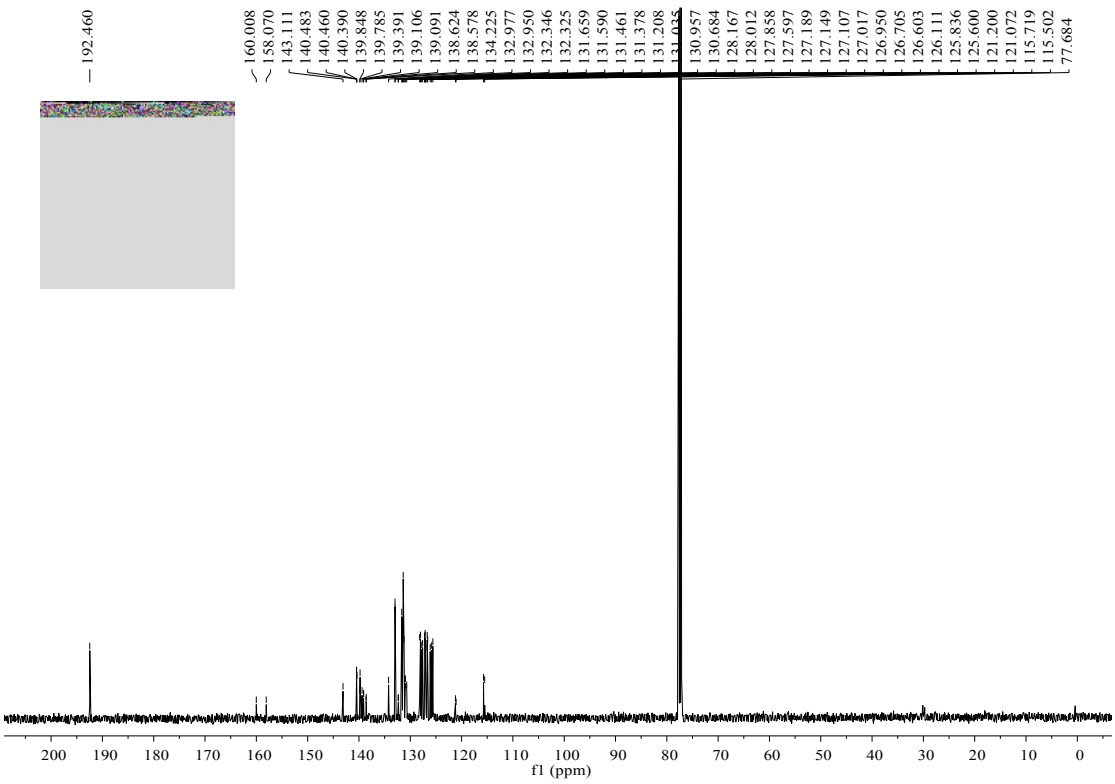

## 2-(5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3aa)

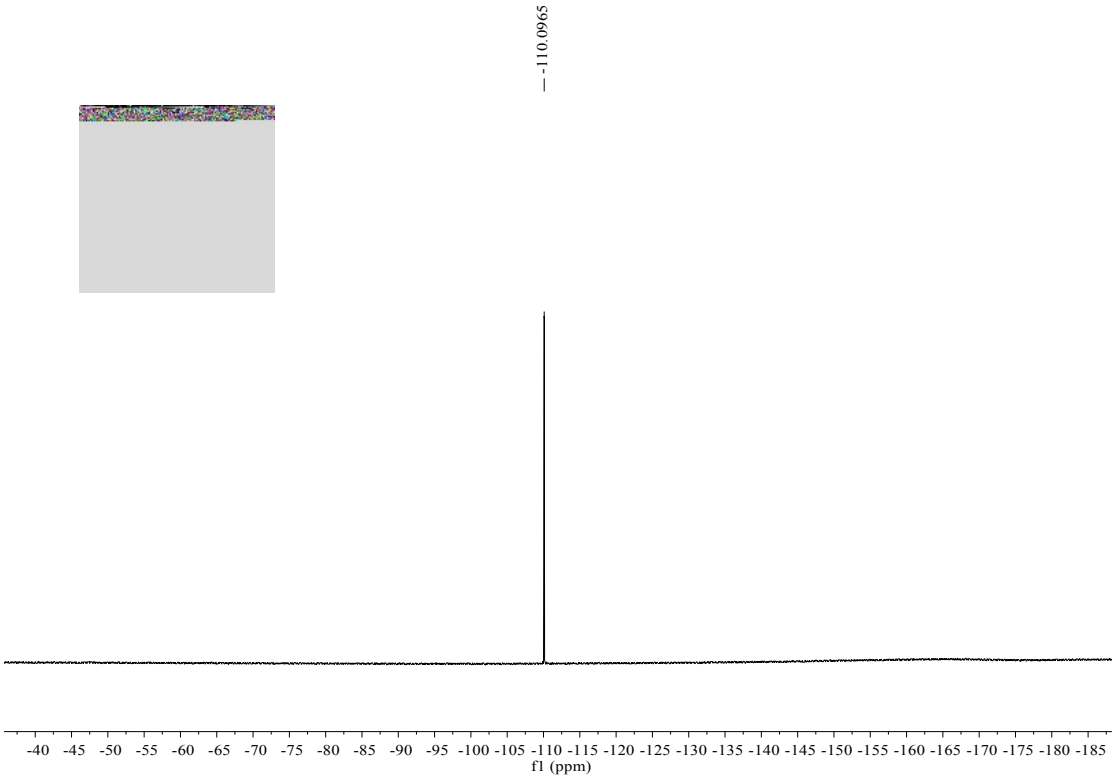




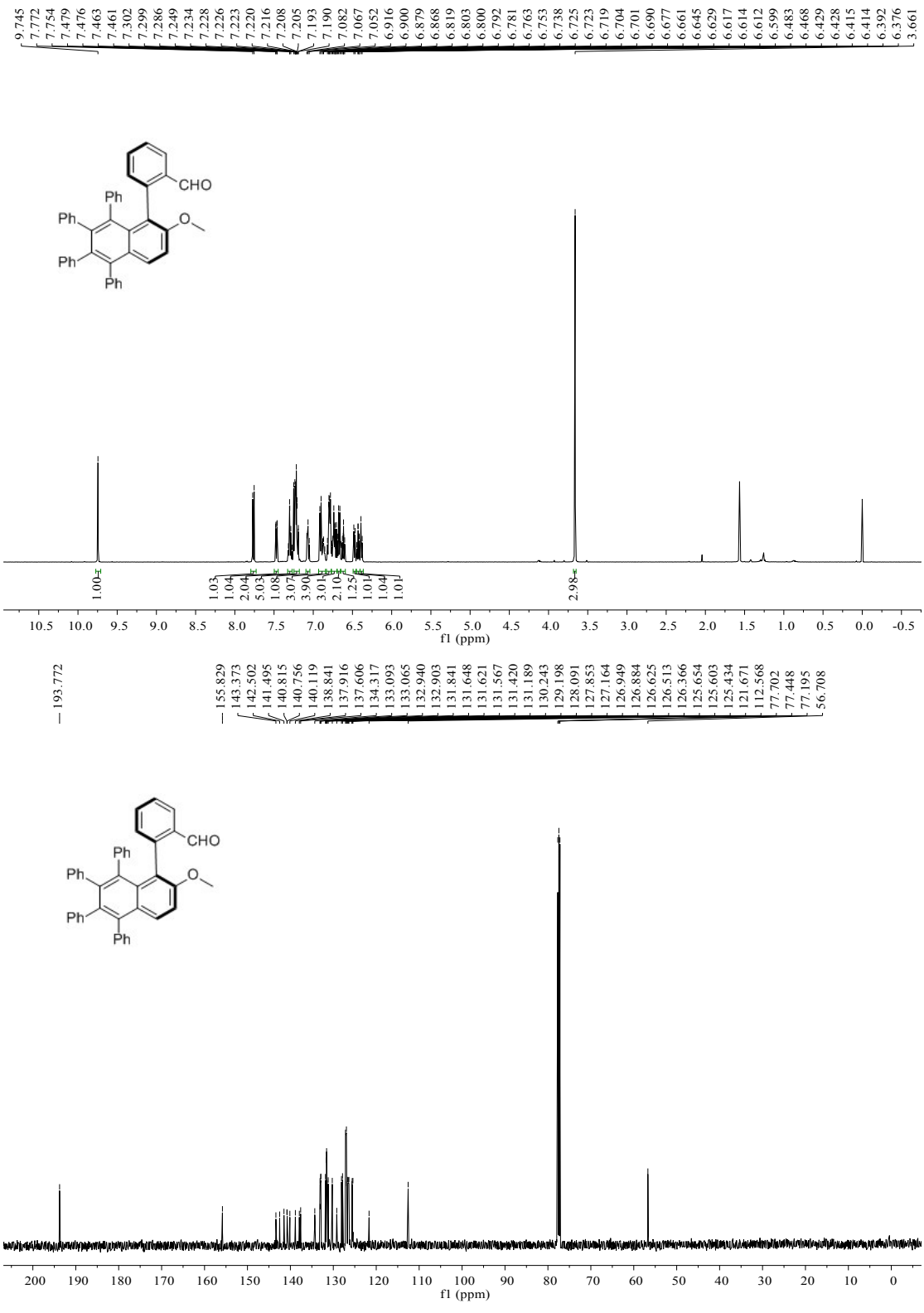

## 2-(2-fluoro-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3bb)



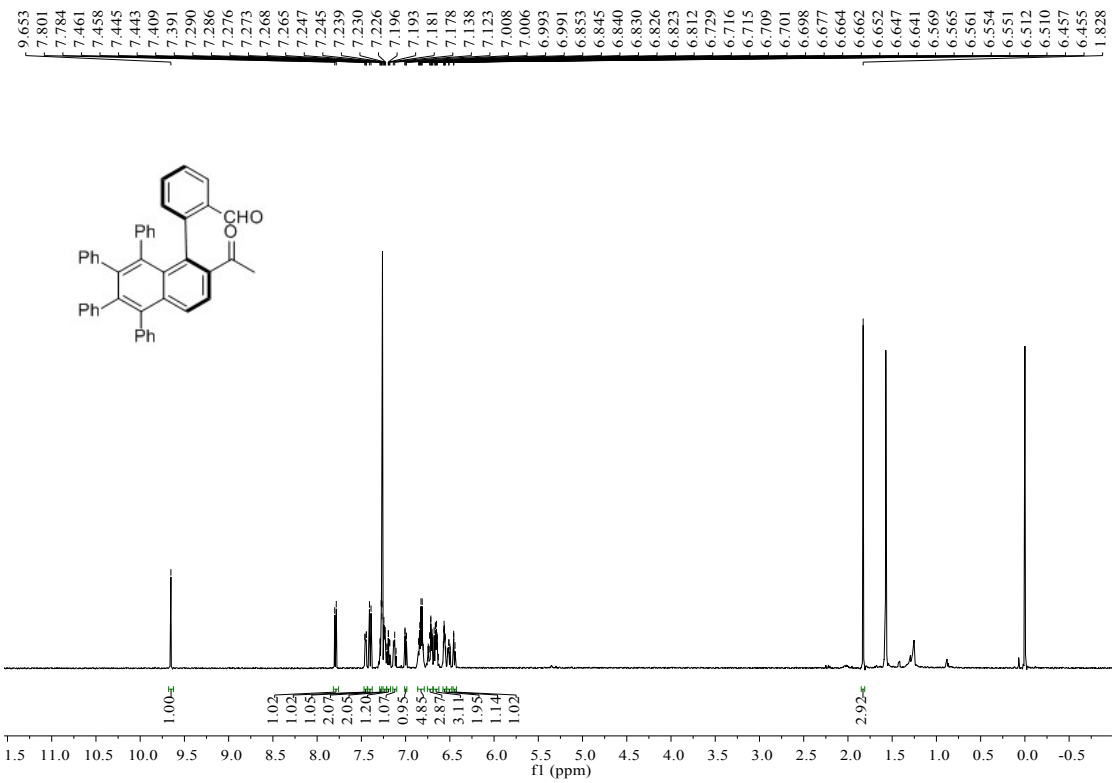


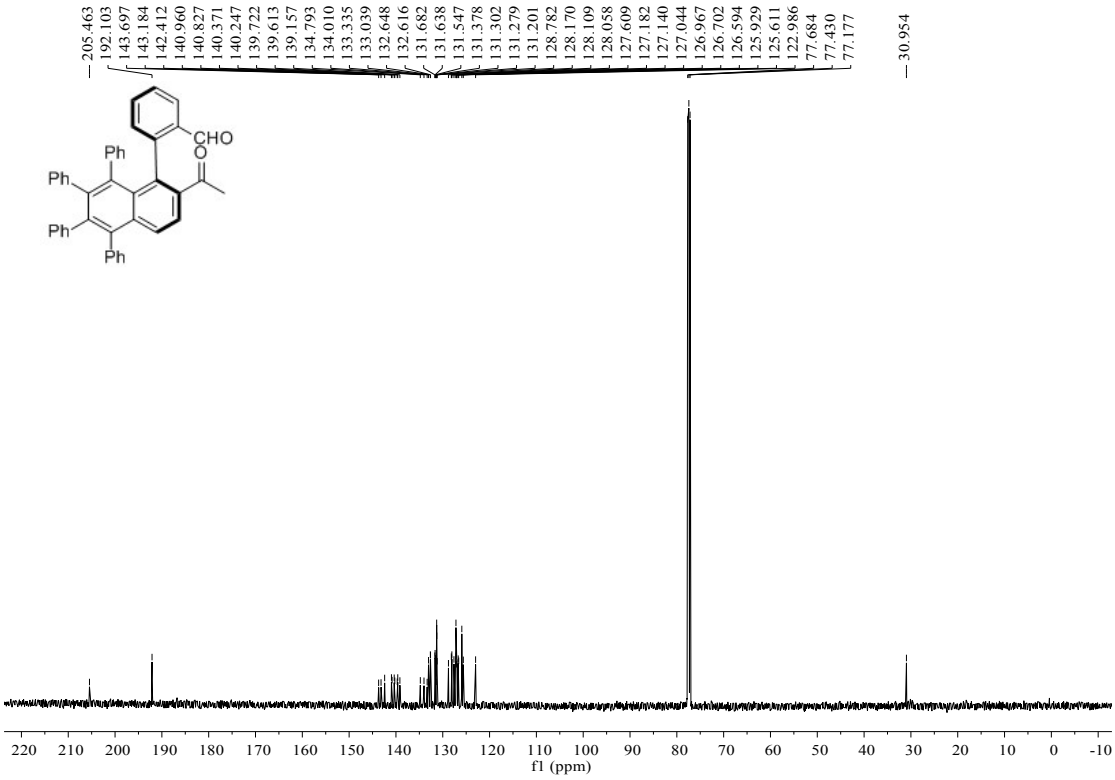




## 2-(2-methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3cc)

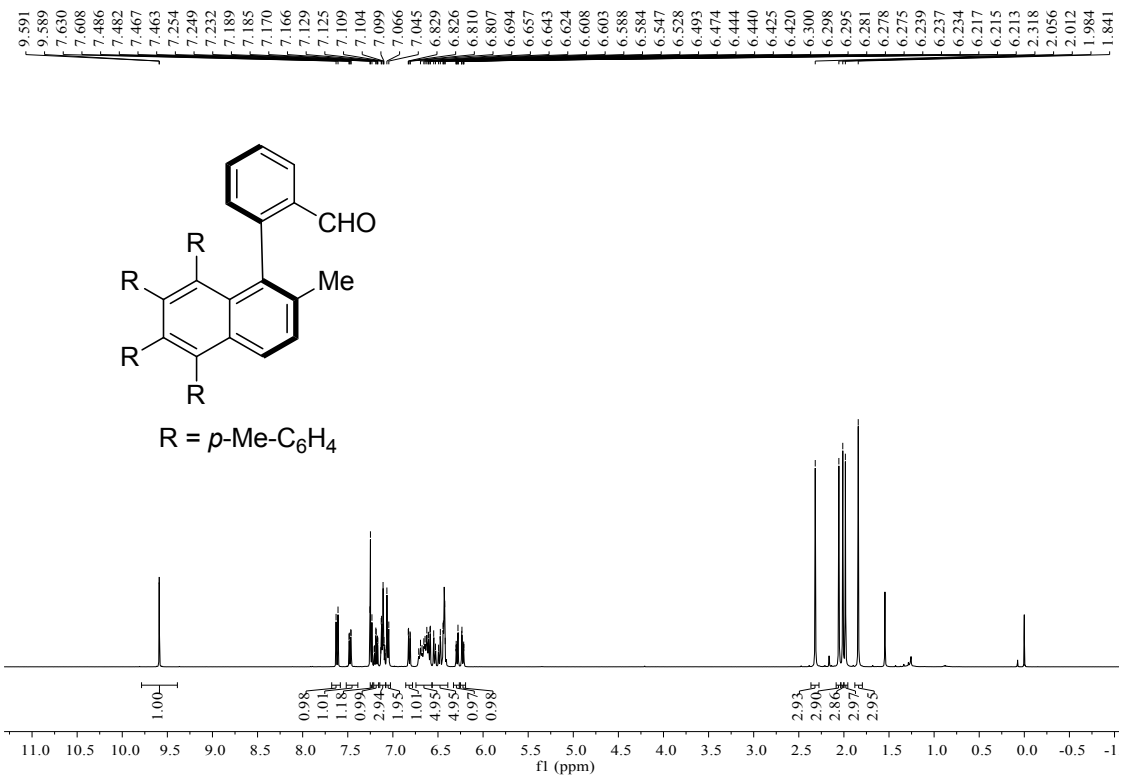


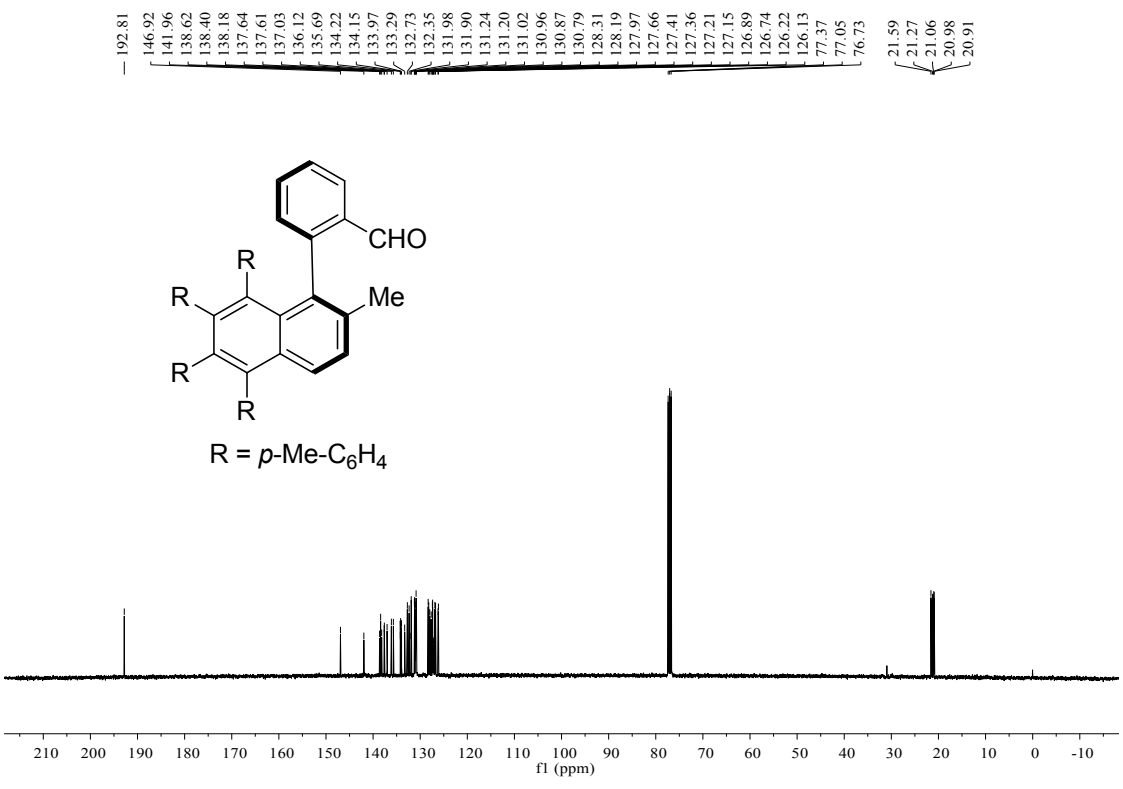

## 2-(2-acetyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (3dd)



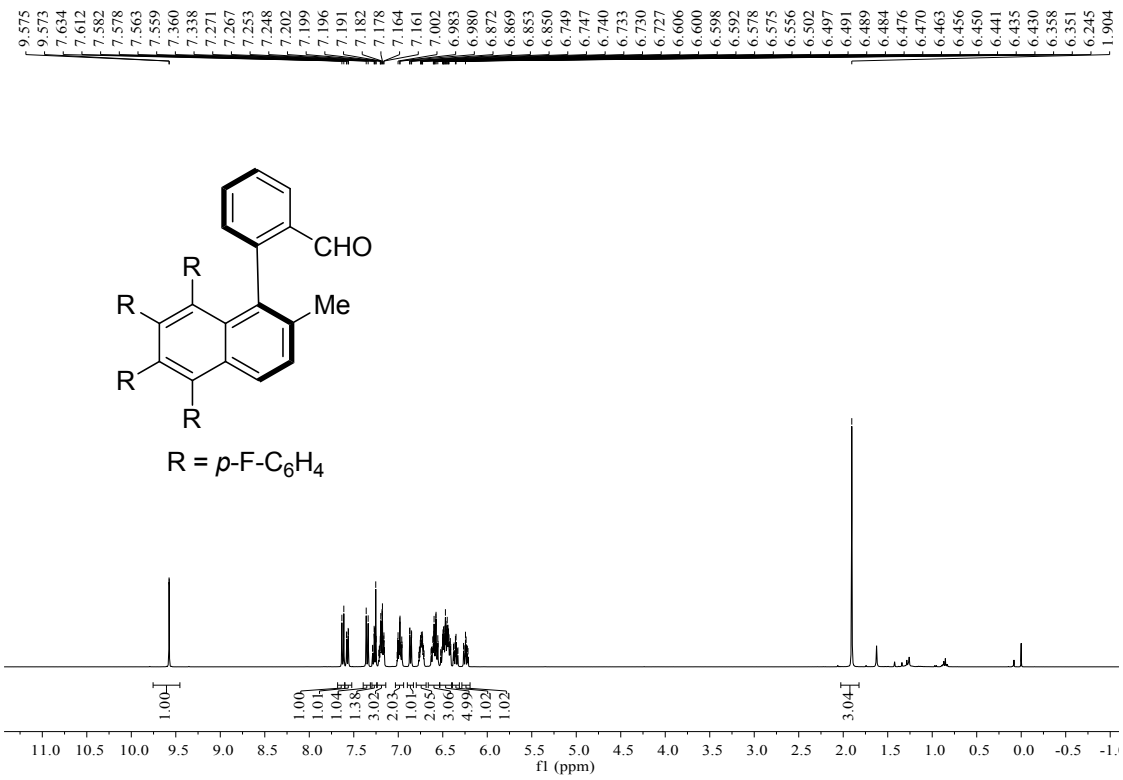



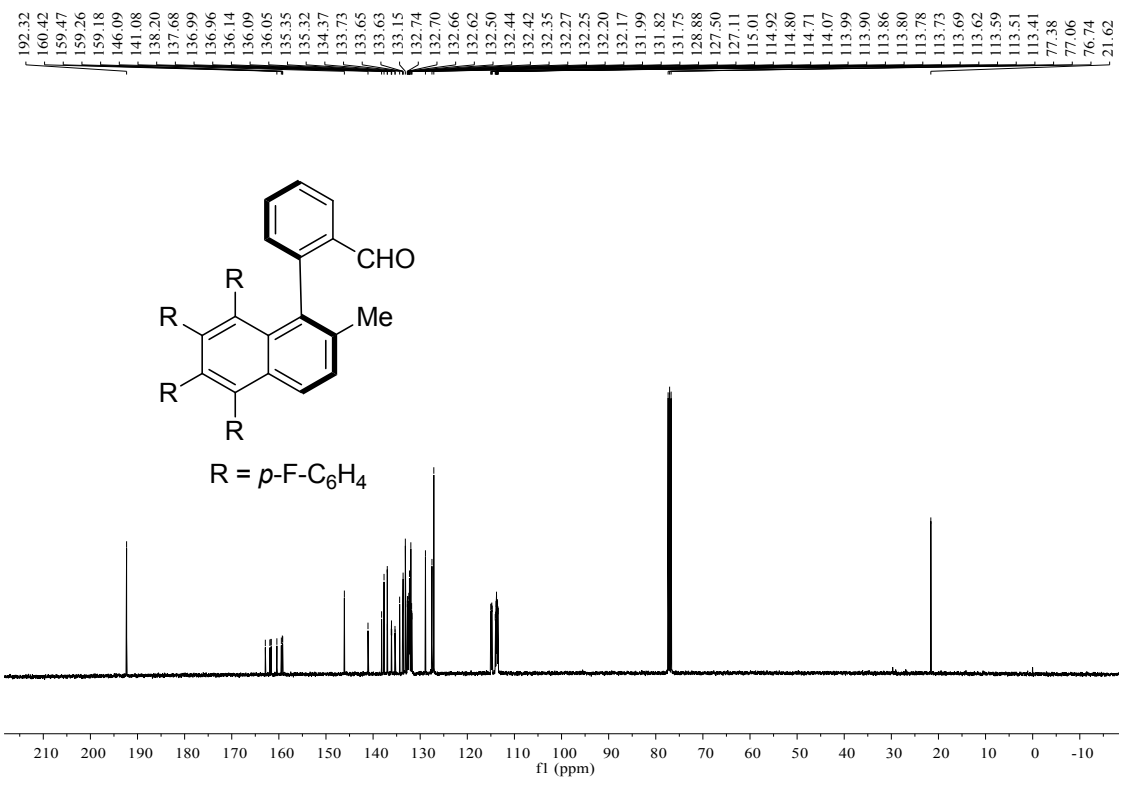

## 2-(2-Methyl-5,6,7,8-tetra-p-tolylnaphthalen-1-yl)benzaldehyde (4a)

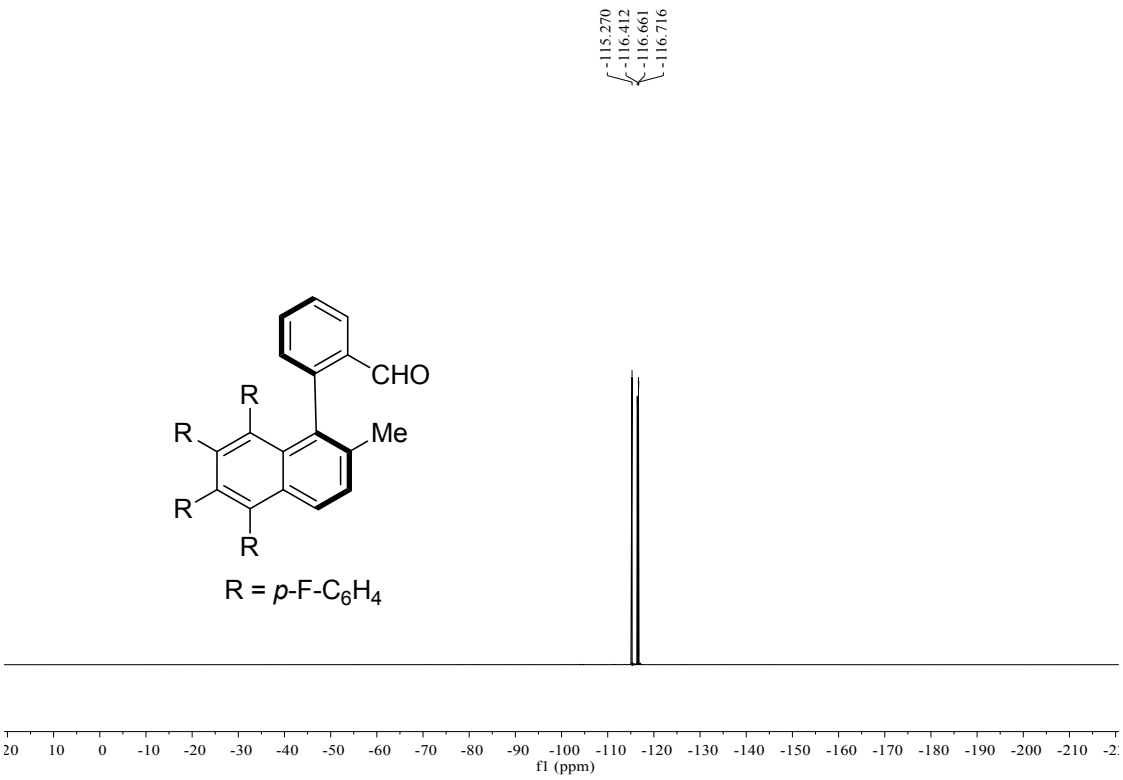


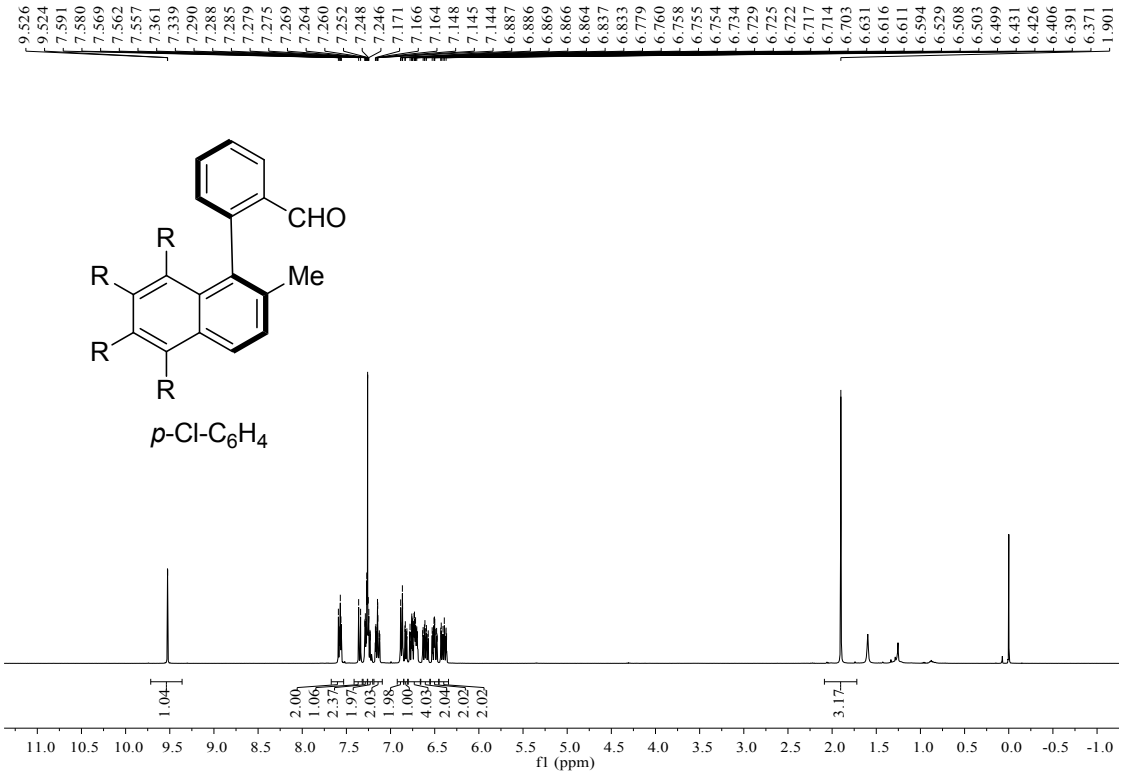

**2-(5,6,7,8-Tetrakis(4-fluorophenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4b)**

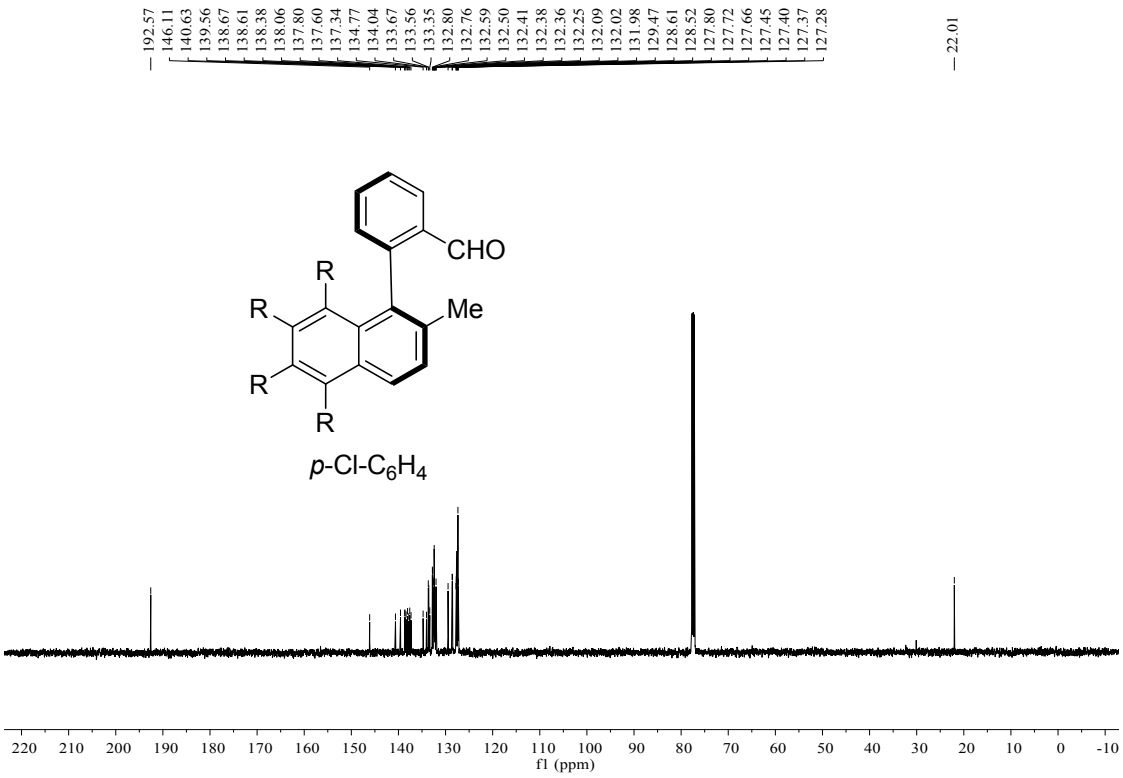

9.575
9.573
7.634
7.612
7.582
7.578
7.563
7.559
7.360
7.338
7.271
7.267
7.253
7.248
7.202
7.199
7.196
7.191
7.182
7.178
7.164
7.161
7.002
6.983
6.980
6.872
6.869
6.853
6.850
6.749
6.747
6.740
6.733
6.730
6.727
6.606
6.600
6.598
6.592
6.578
6.575
6.556
6.502
6.497
6.491
6.489
6.484
6.476
6.470
6.463
6.456
6.450
6.441
6.435
6.430
6.358
6.351
6.245
1.904
CHO
R
R
R
R
Me
R = p-F-C6H4
1.00
1.00
1.01
1.04
1.38
3.02
2.03
1.01
2.05
3.06
4.99
1.02
1.02
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


192.32
160.42
159.47
159.26
159.18
146.09
141.08
138.20
137.68
136.99
136.96
136.14
136.09
136.05
135.35
135.32
134.37
133.73
133.65
133.63
133.15
132.74
132.70
132.66
132.62
132.50
132.44
132.42
132.35
132.27
132.25
132.20
132.17
131.99
131.82
131.75
128.88
127.50
127.11
115.01
114.92
114.80
114.71
114.07
113.99
113.90
113.86
113.80
113.78
113.73
113.69
113.62
113.59
113.51
113.41
77.38
77.06
76.74
21.62
CHO
R
R
R
R
Me
R = p-F-C6H4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

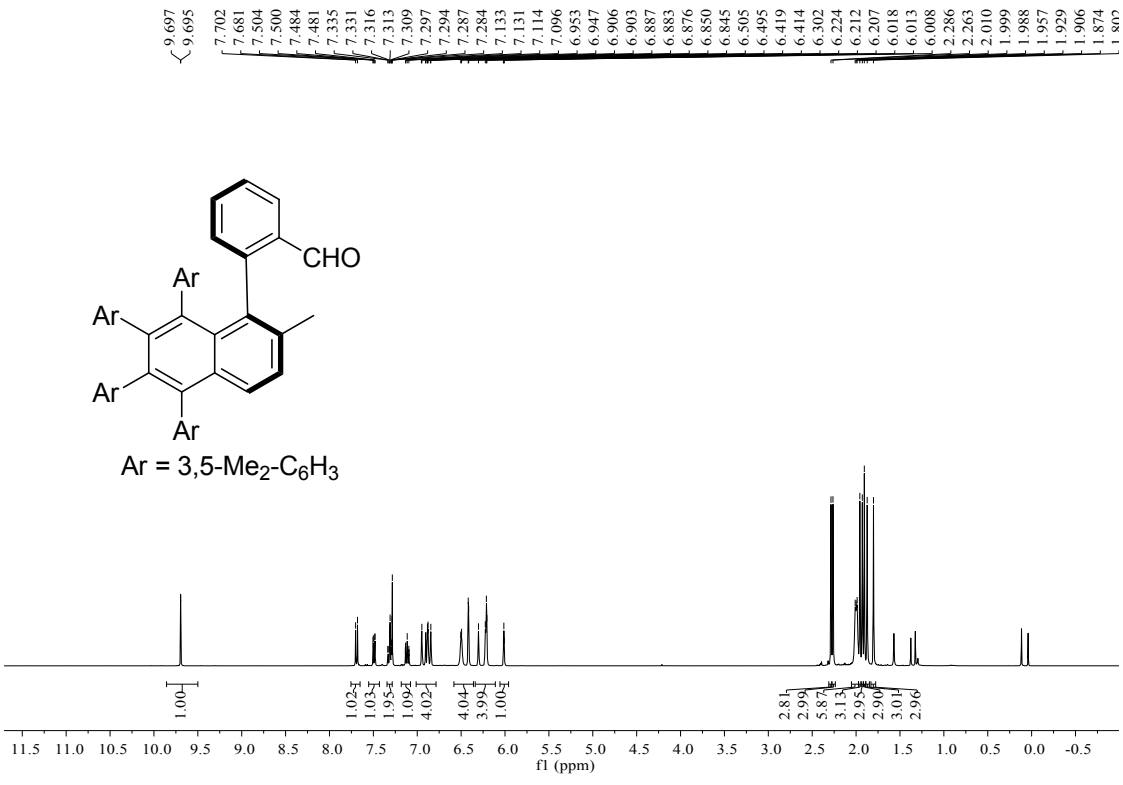


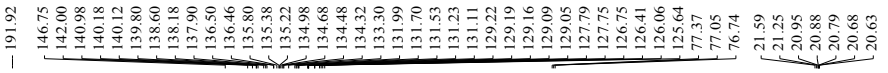

## 2-(5,6,7,8-Tetrakis(4-chlorophenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4c)

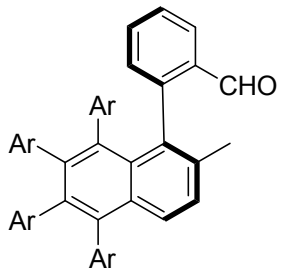




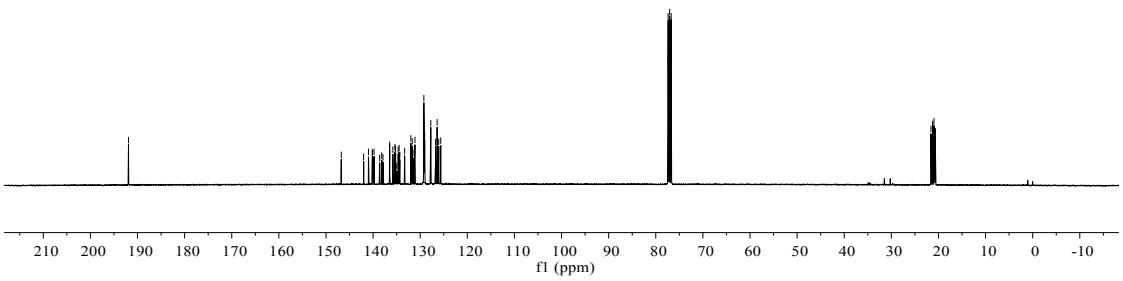

## 2-(5,6,7,8-Tetrakis(3,5-dimethylphenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4d)



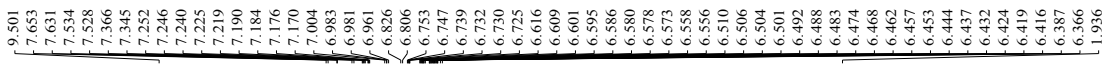


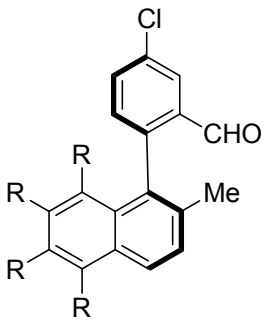




Ar = 3,5-$Me_2$-$C_6H_3$

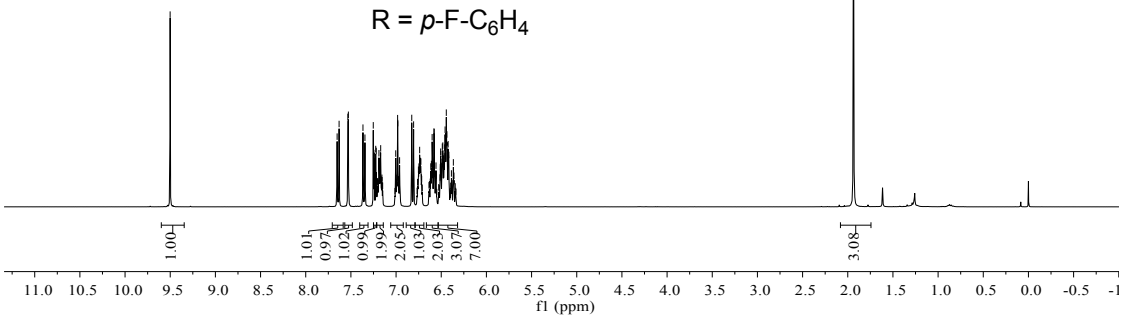


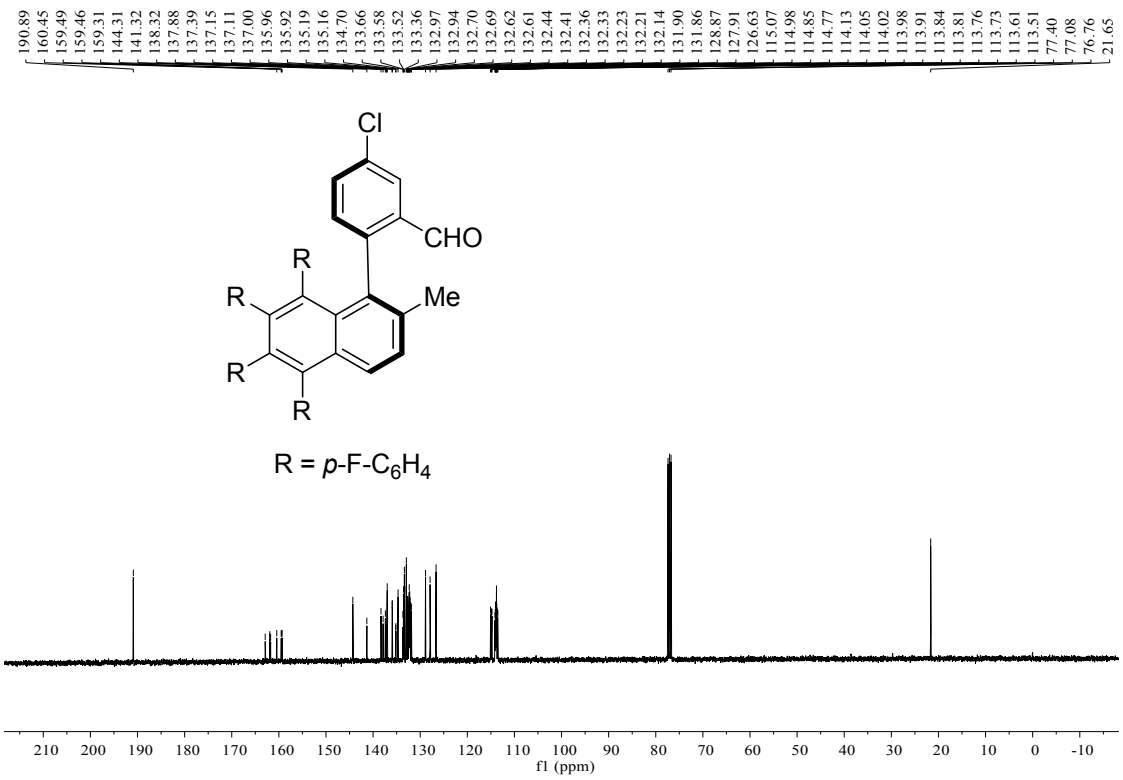

## 5-Chloro-2-(5,6,7,8-tetrakis(4-fluorophenyl)-2-methylnaphthalen-1-yl)benzaldehyde (4f)

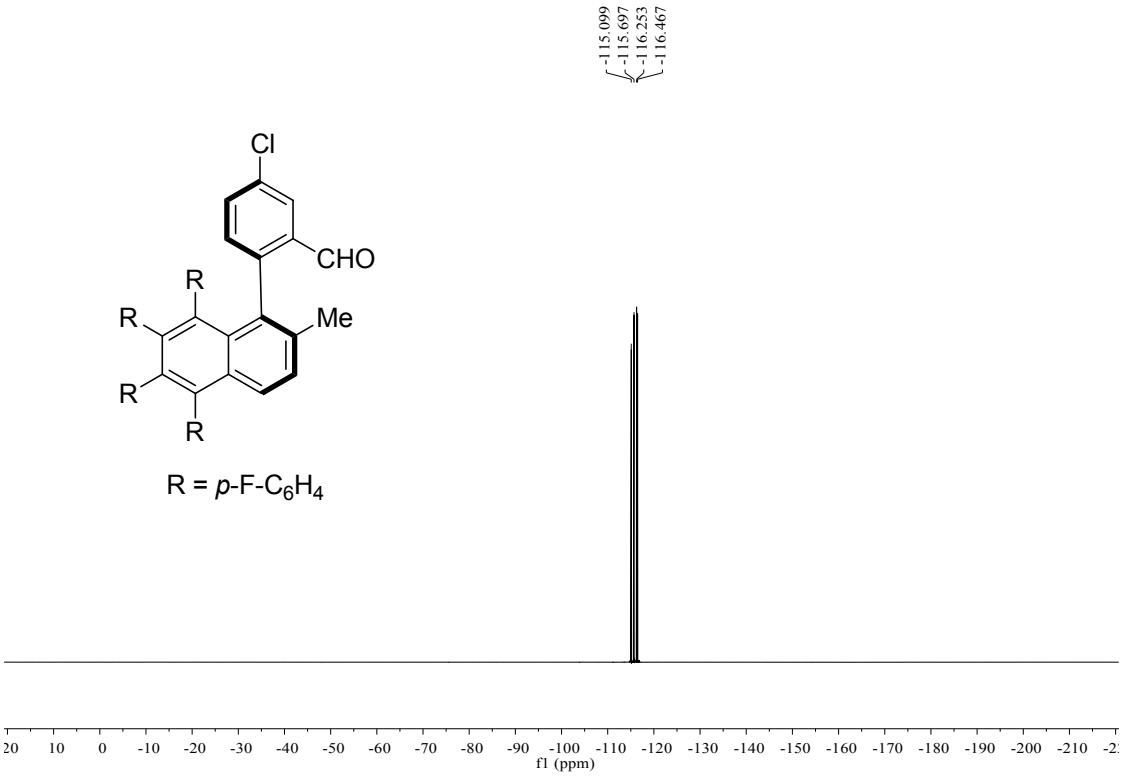


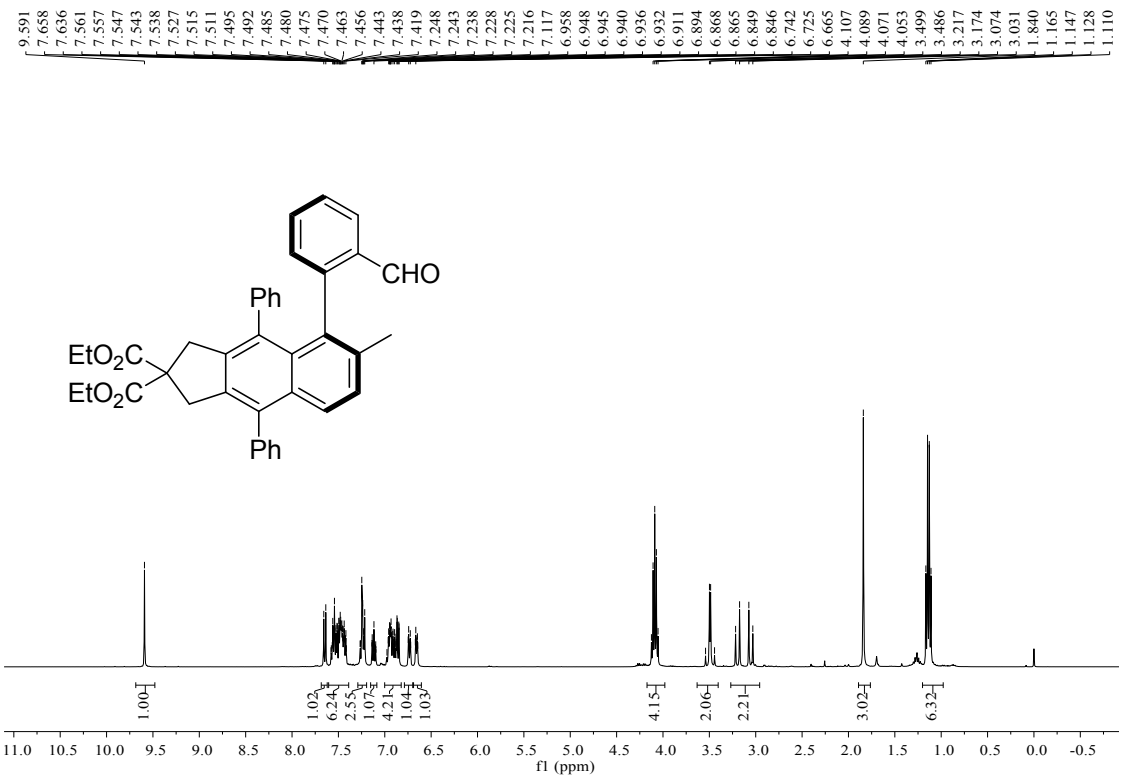

R = *p*-F-$C_6H_4$

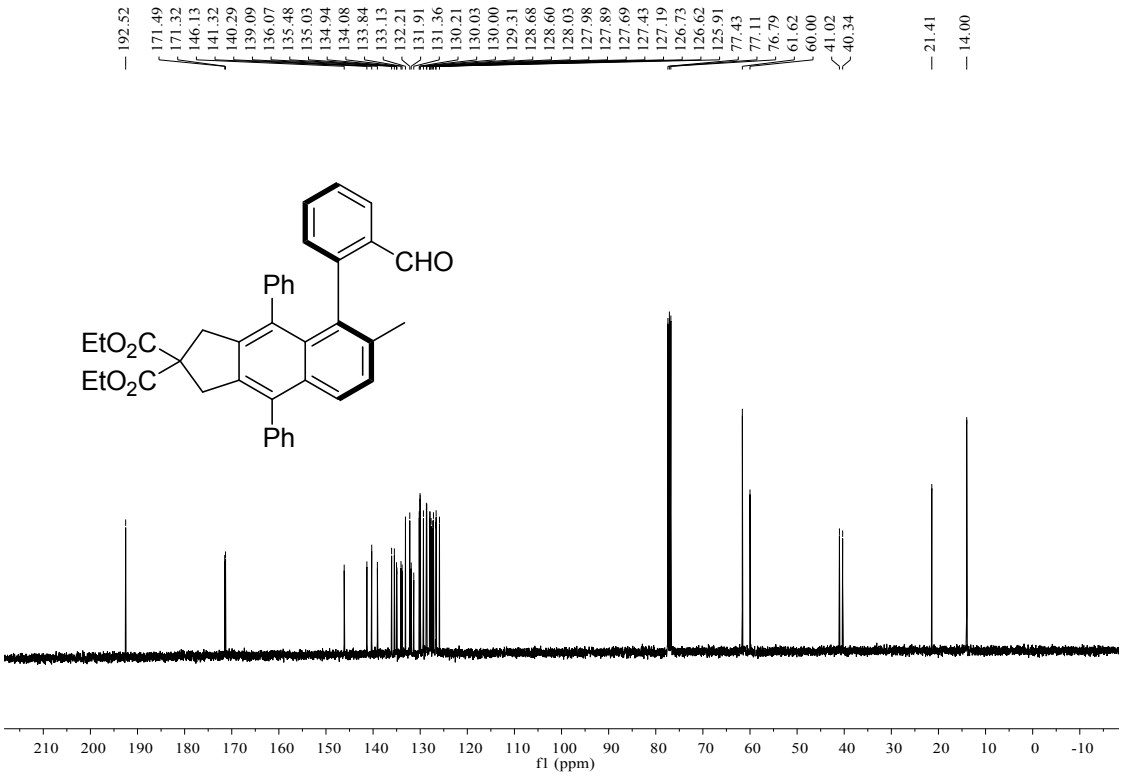




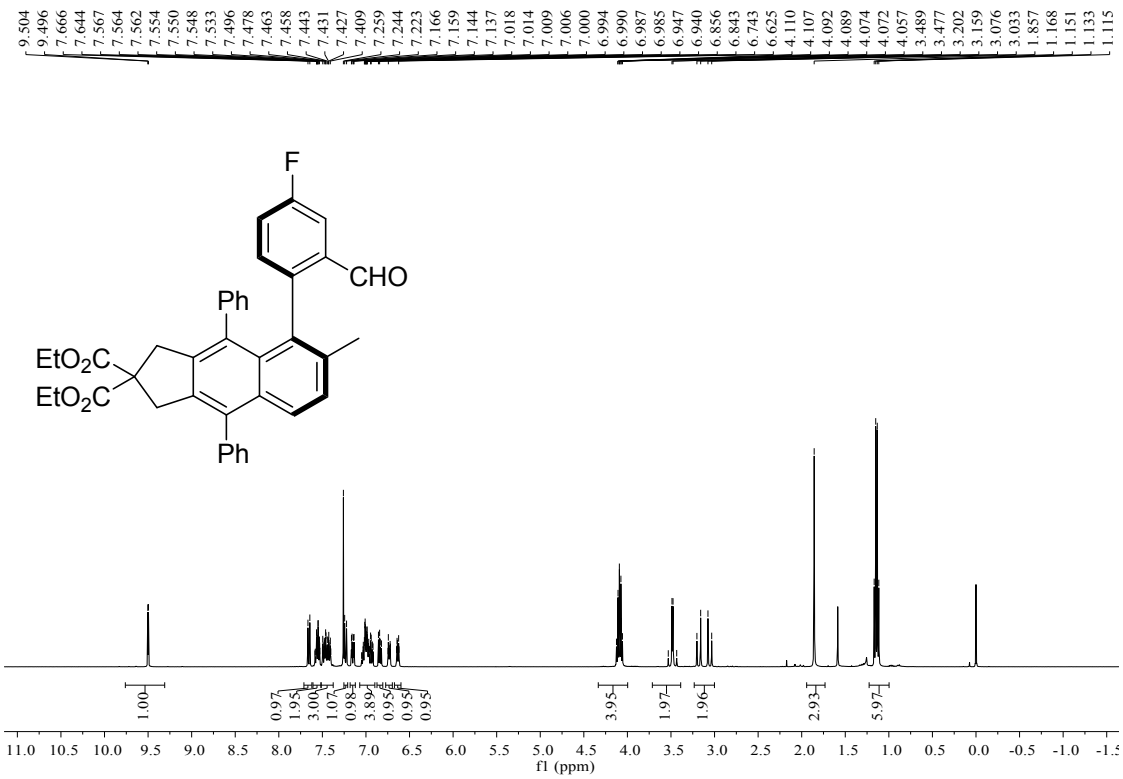



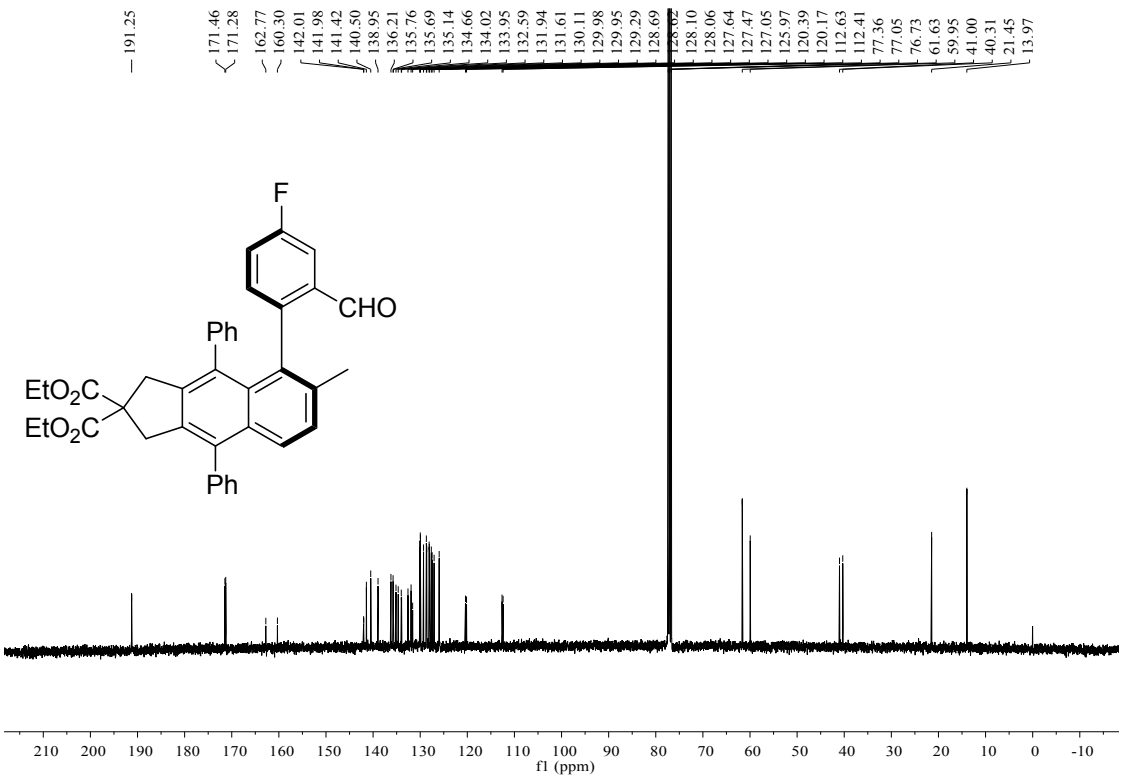

**Diethyl-5-(2-formylphenyl)-6-methyl-4,9-diphenyl-1,3-dihydro-2H-cyclopenta[*b*] naphthalene-2,2-dicarboxylate (4g)**

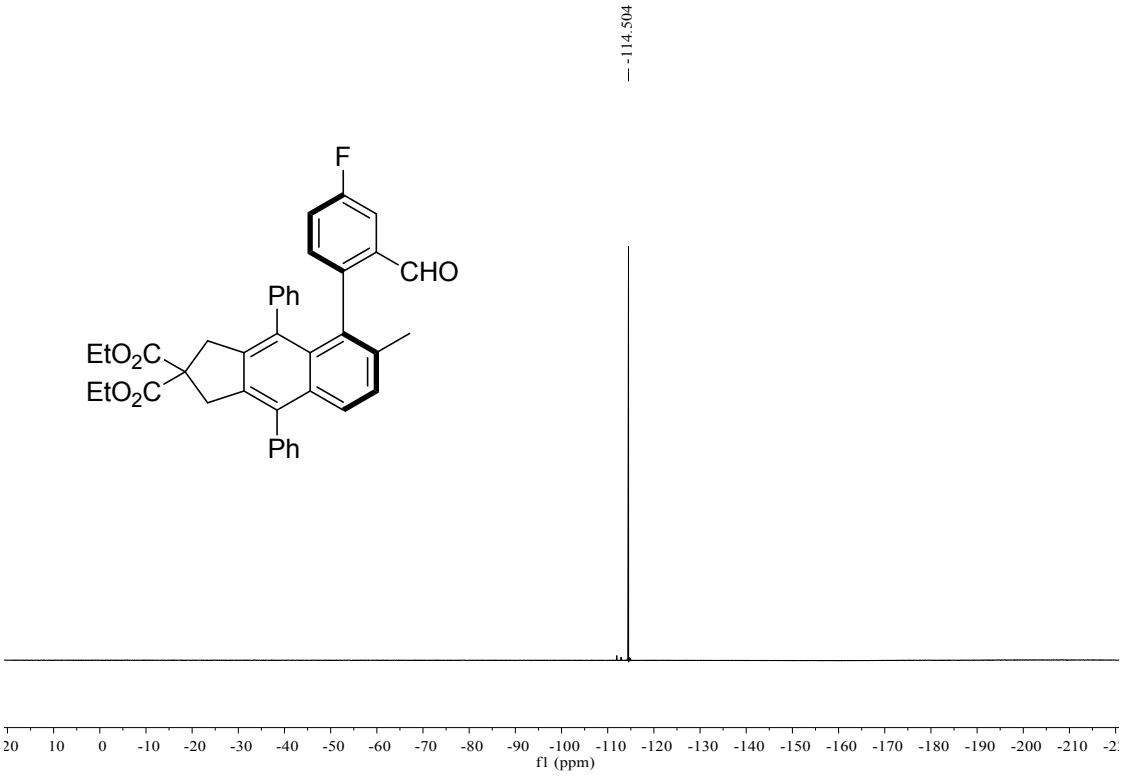


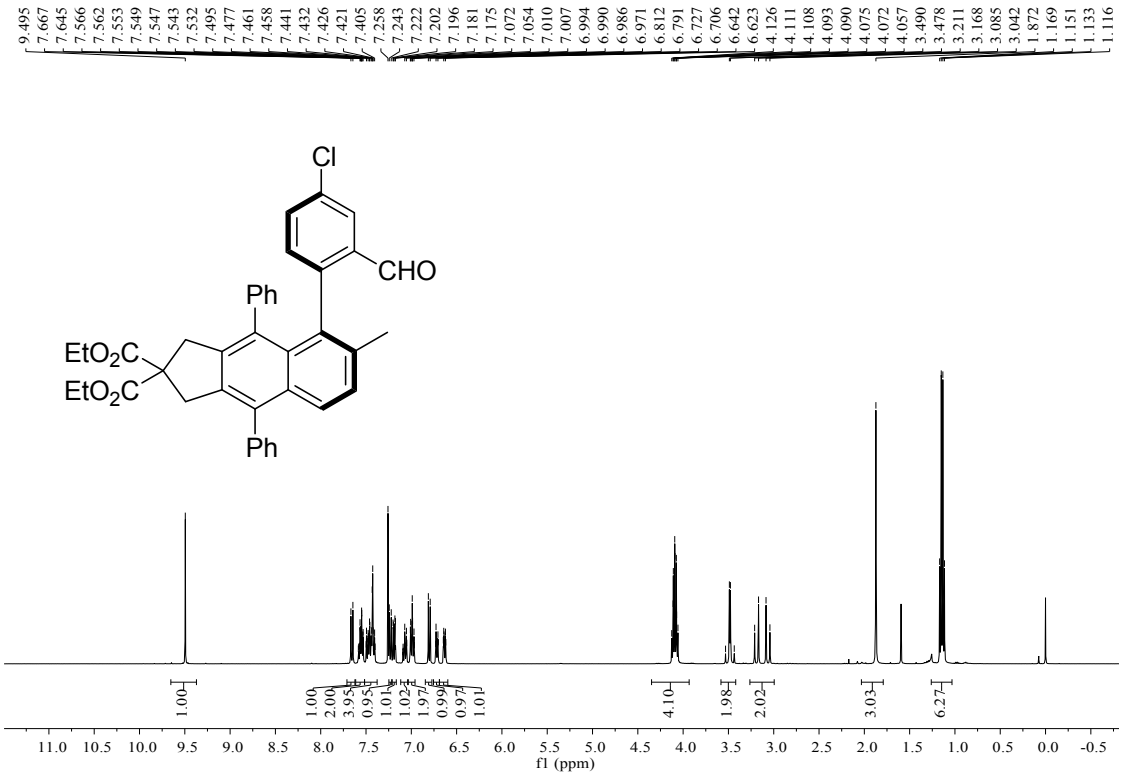

**Diethyl-5-(4-fluoro-2-formylphenyl)-6-methyl-4,9-diphenyl-1,3-dihydro-2*H*-cyclopenta[*b*]naphthalene-2,2-dicarboxylate （4h）**

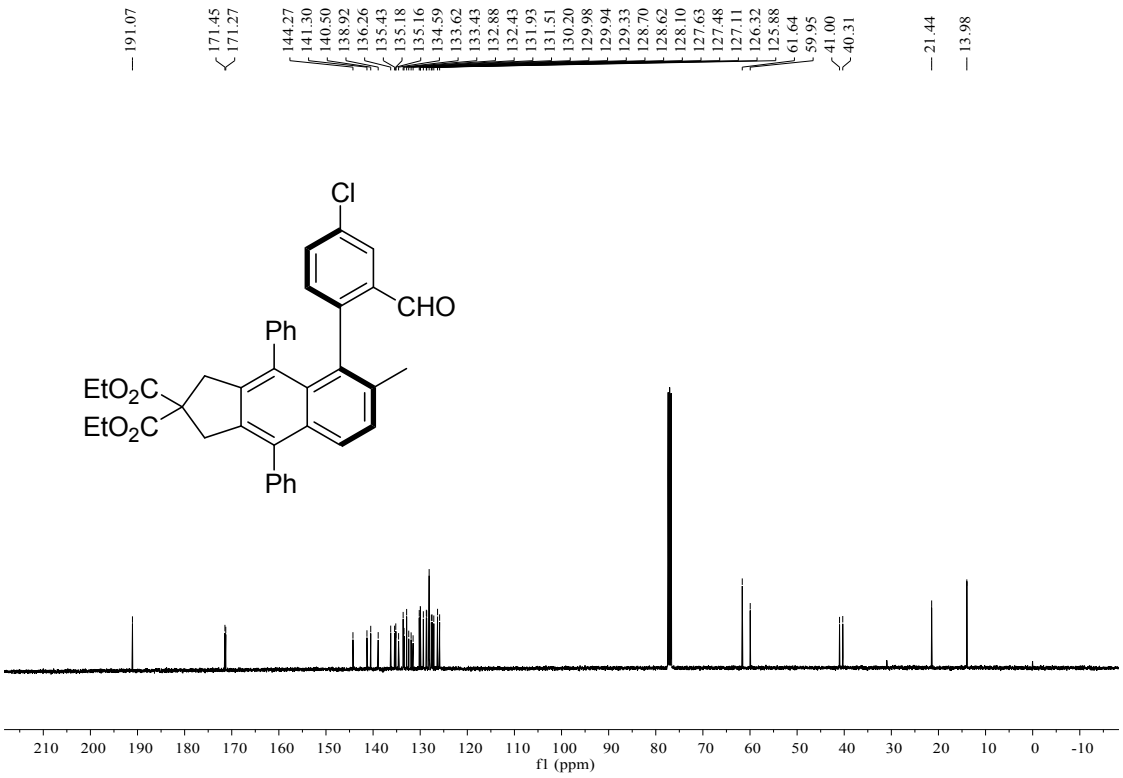

9.504
9.496
7.666
7.644
7.567
7.564
7.562
7.554
7.550
7.548
7.533
7.496
7.478
7.463
7.458
7.443
7.431
7.427
7.409
7.259
7.244
7.223
7.166
7.159
7.144
7.137
7.018
7.014
7.009
7.006
7.000
6.994
6.990
6.987
6.985
6.947
6.940
6.856
6.843
6.743
6.625
4.110
4.107
4.092
4.089
4.074
4.072
4.057
3.489
3.477
3.202
3.159
3.076
3.033
1.857
1.168
1.151
1.133
1.115
F
CHO
Ph
EtO2C
EtO2C
Ph
1.00
0.97
1.95
3.00
1.07
0.98
3.89
0.95
0.95
0.95
3.95
1.97
1.96
2.93
5.97
f1 (ppm)


191.25
171.46
171.28
162.77
160.30
142.01
141.98
141.42
140.50
138.95
136.21
135.76
135.69
135.14
134.66
134.02
133.95
132.59
131.94
131.61
130.11
129.98
129.95
129.29
128.69
128.10
128.06
127.64
127.47
127.05
125.97
120.39
120.17
112.63
112.41
77.36
77.05
76.73
61.63
59.95
41.00
40.31
21.45
13.97
F
CHO
Ph
EtO2C
EtO2C
Ph
f1 (ppm)

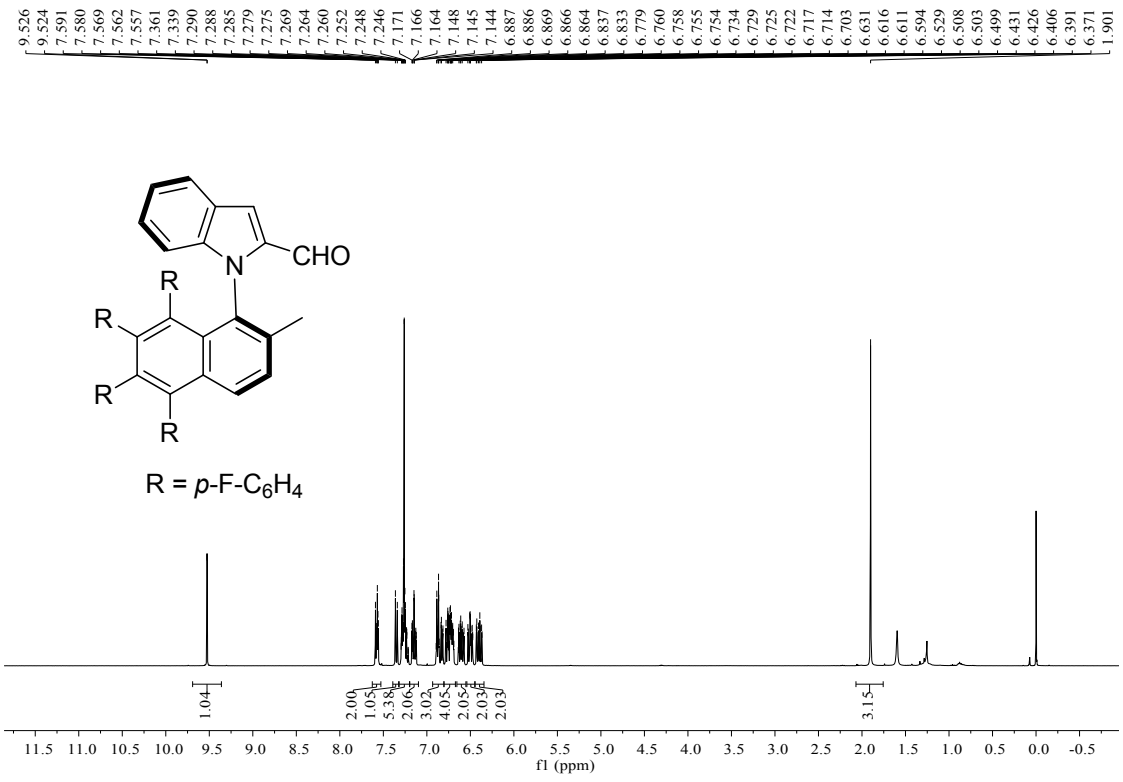


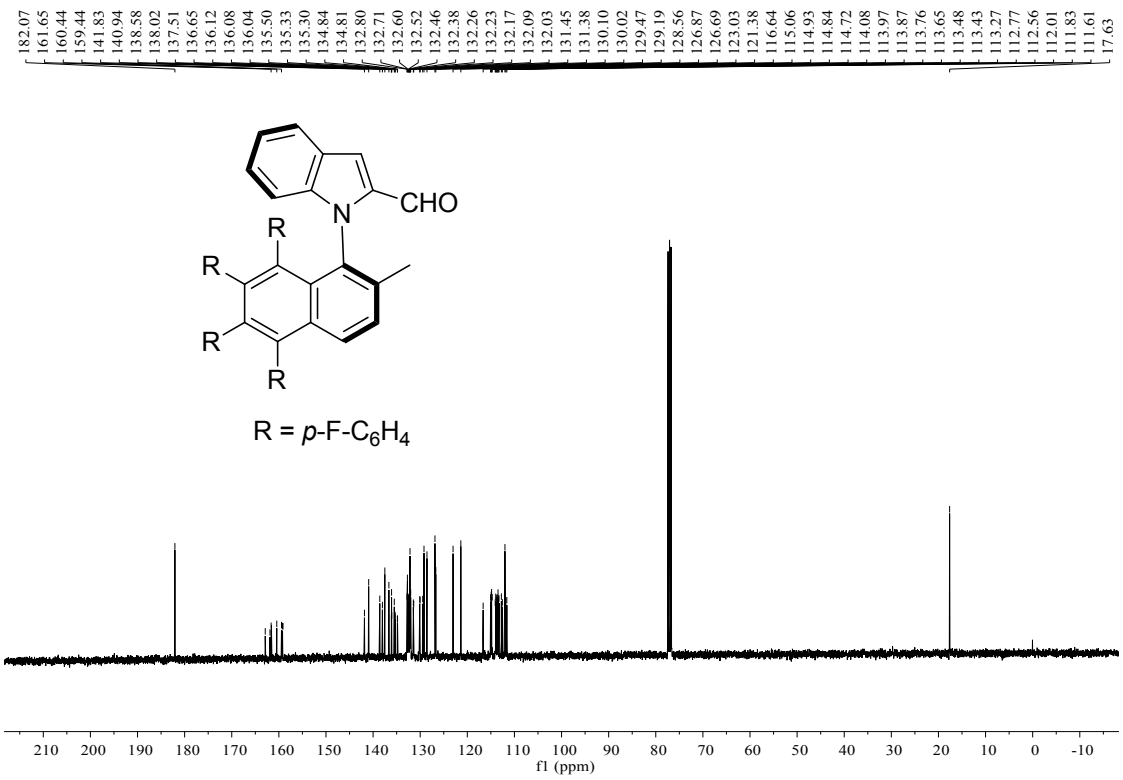

**Diethyl-5-(4-chloro-2-formylphenyl)-6-methyl-4,9-diphenyl-1,3-dihydro-2H-cyclopenta[*b*]naphthalene-2,2-dicarboxylate (4i)**

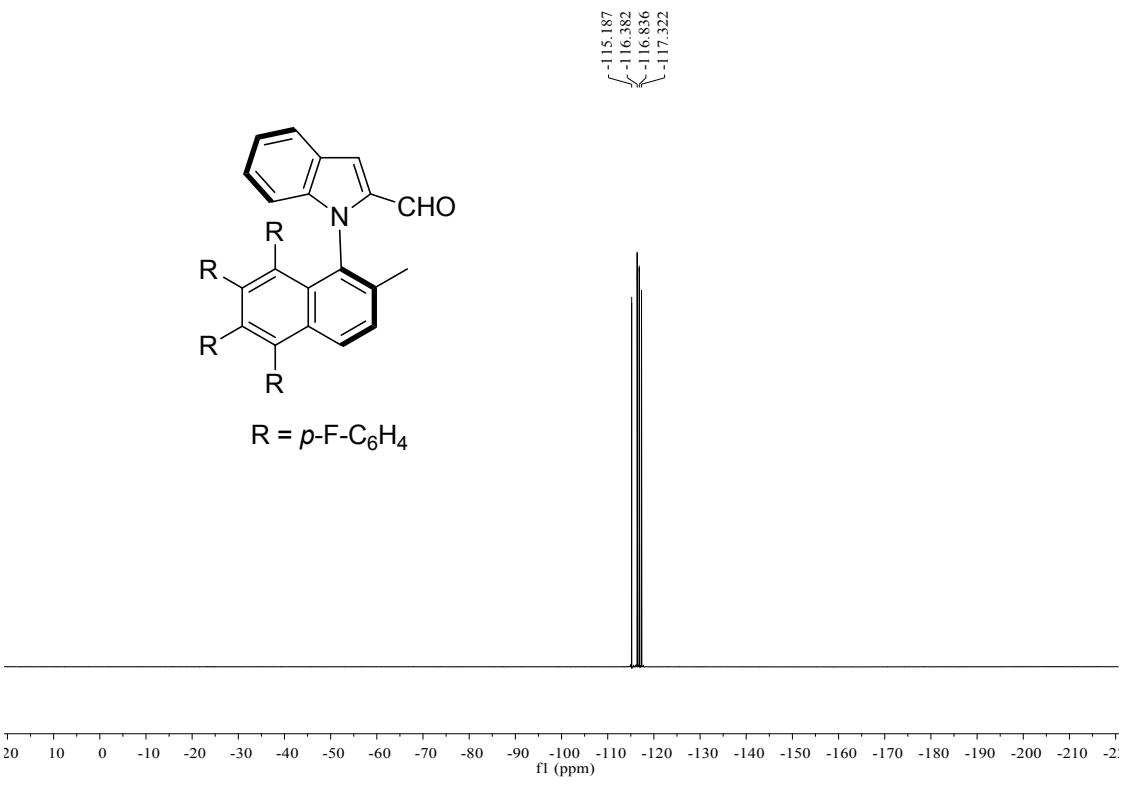




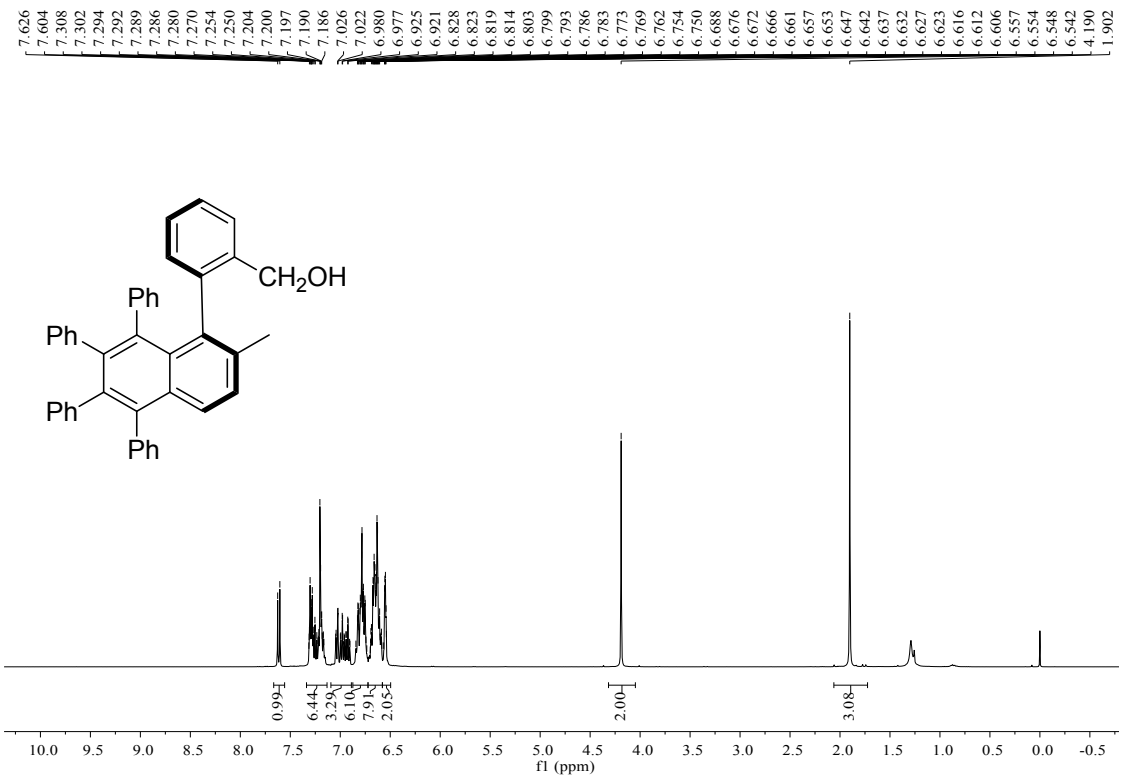

## 1-(5,6,7,8-Tetrakis(4-fluorophenyl)-2-methylnaphthalen-1-yl)-1H-indole-2-carbaldehyde (4j)

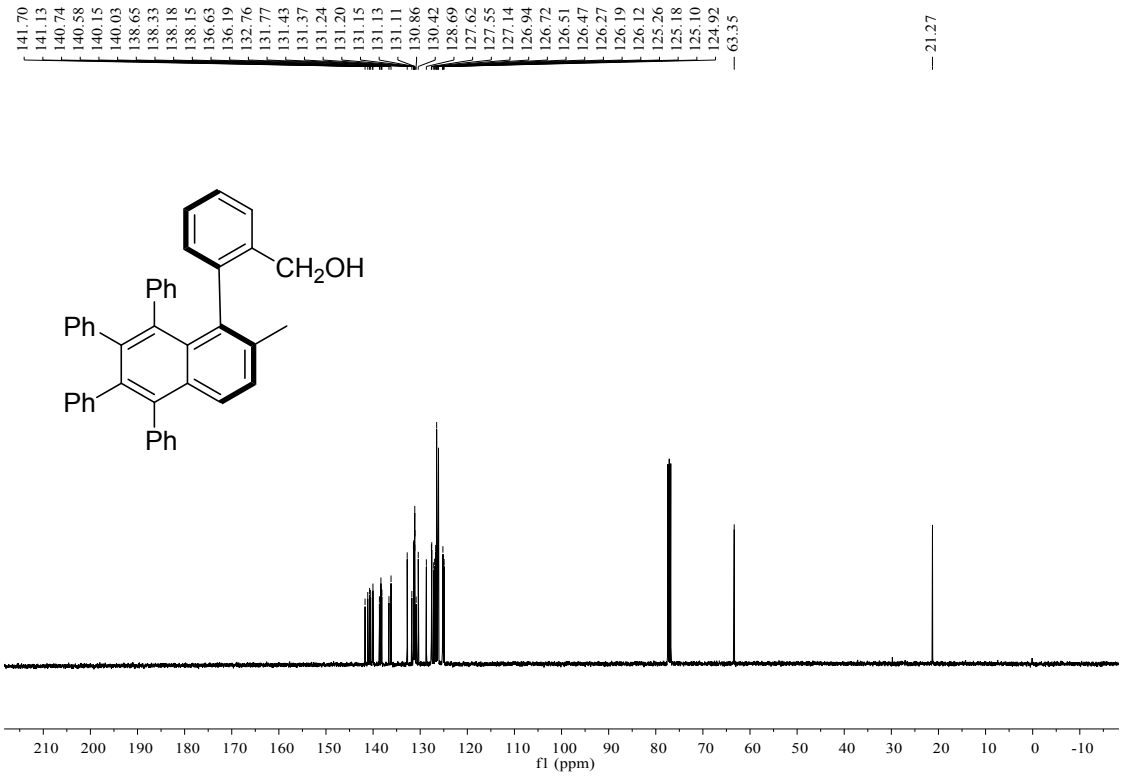




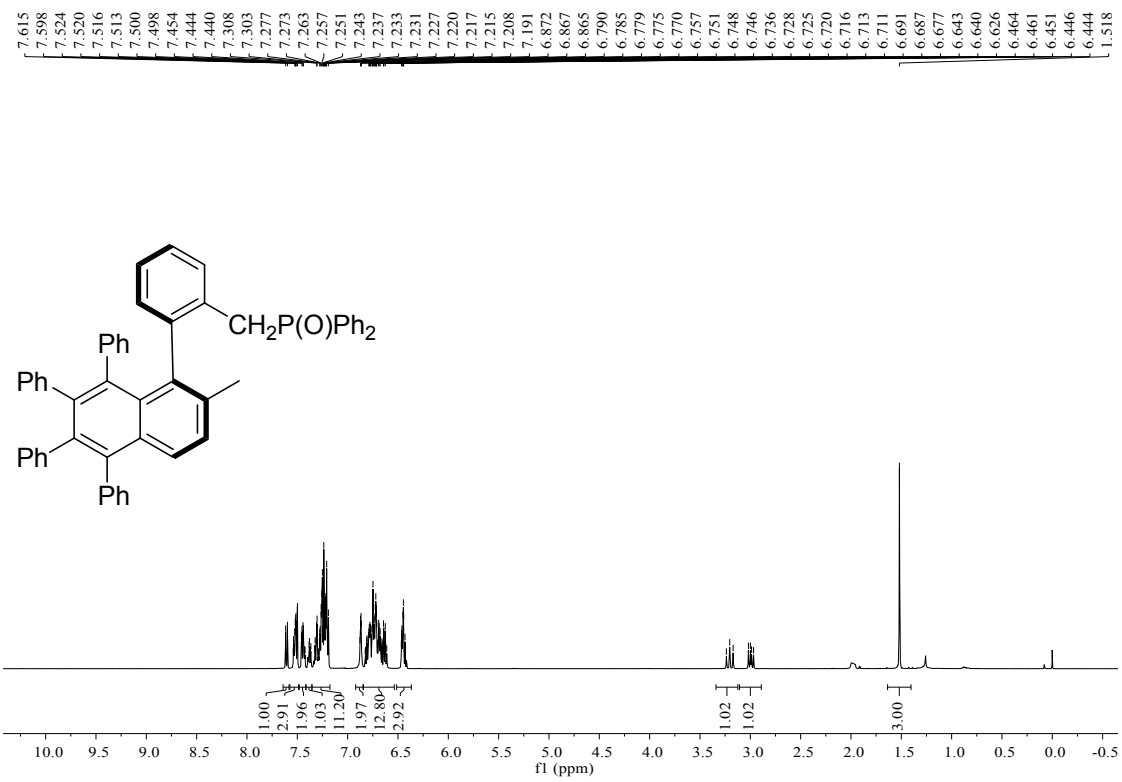



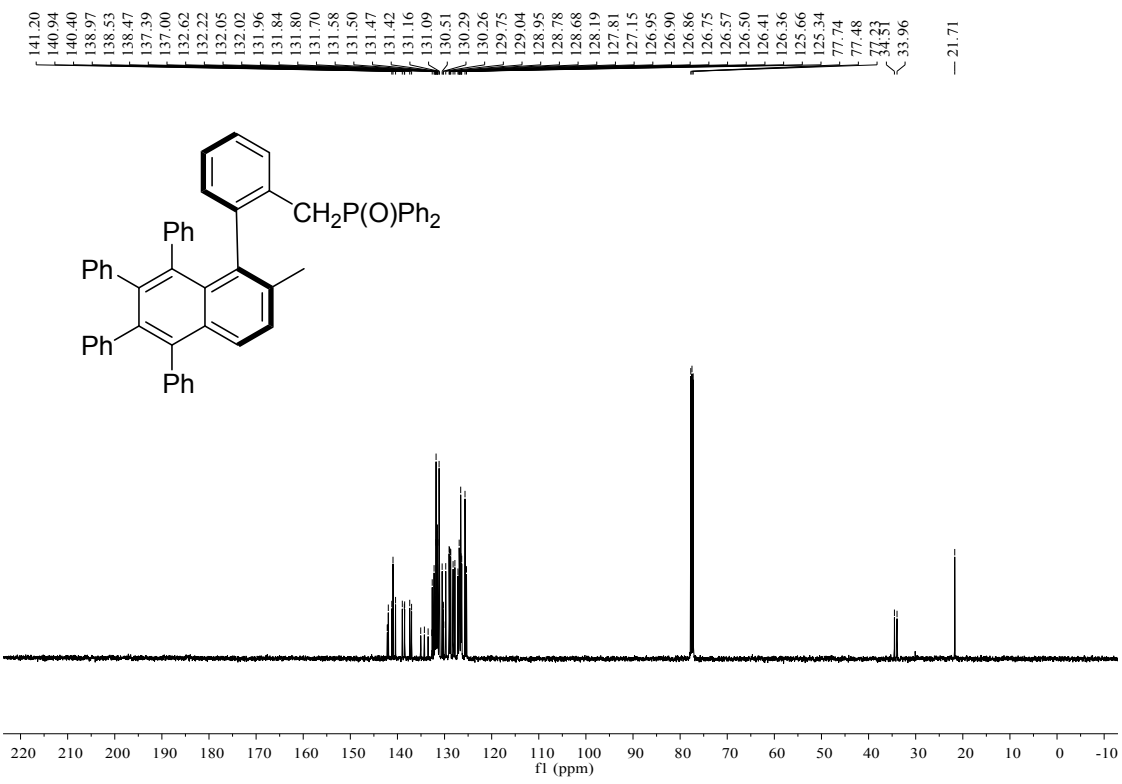

**(2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)phenyl)methanol (5)**

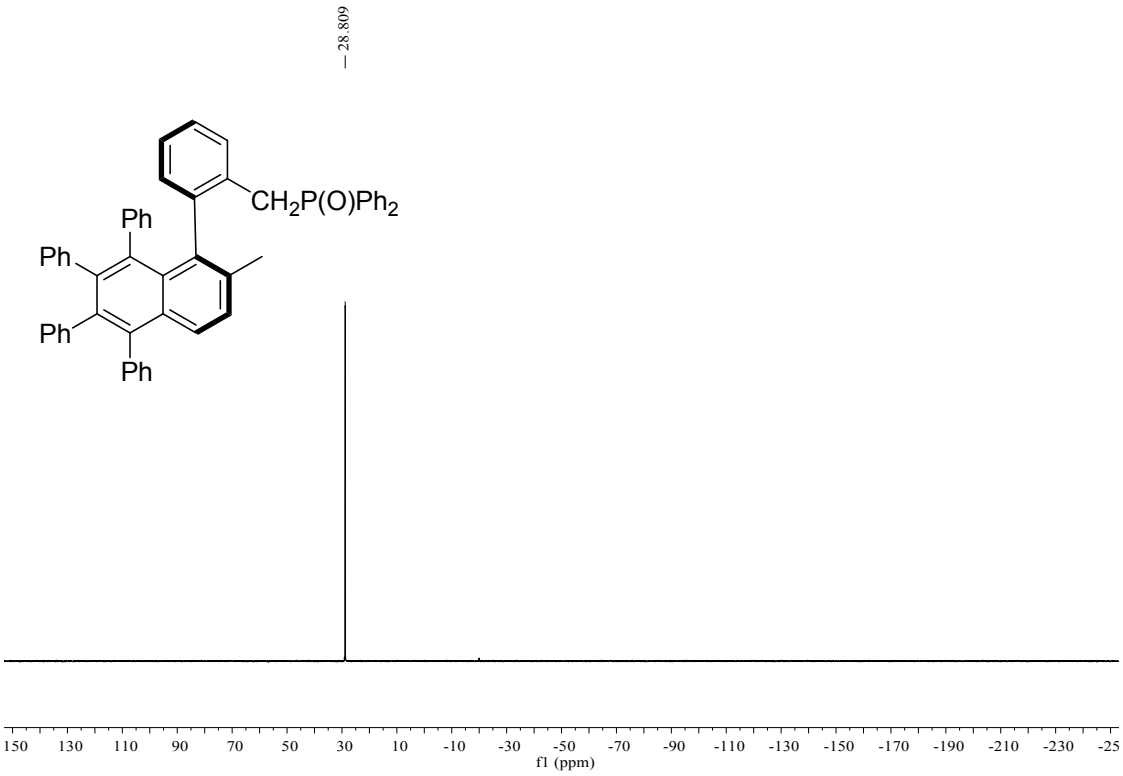


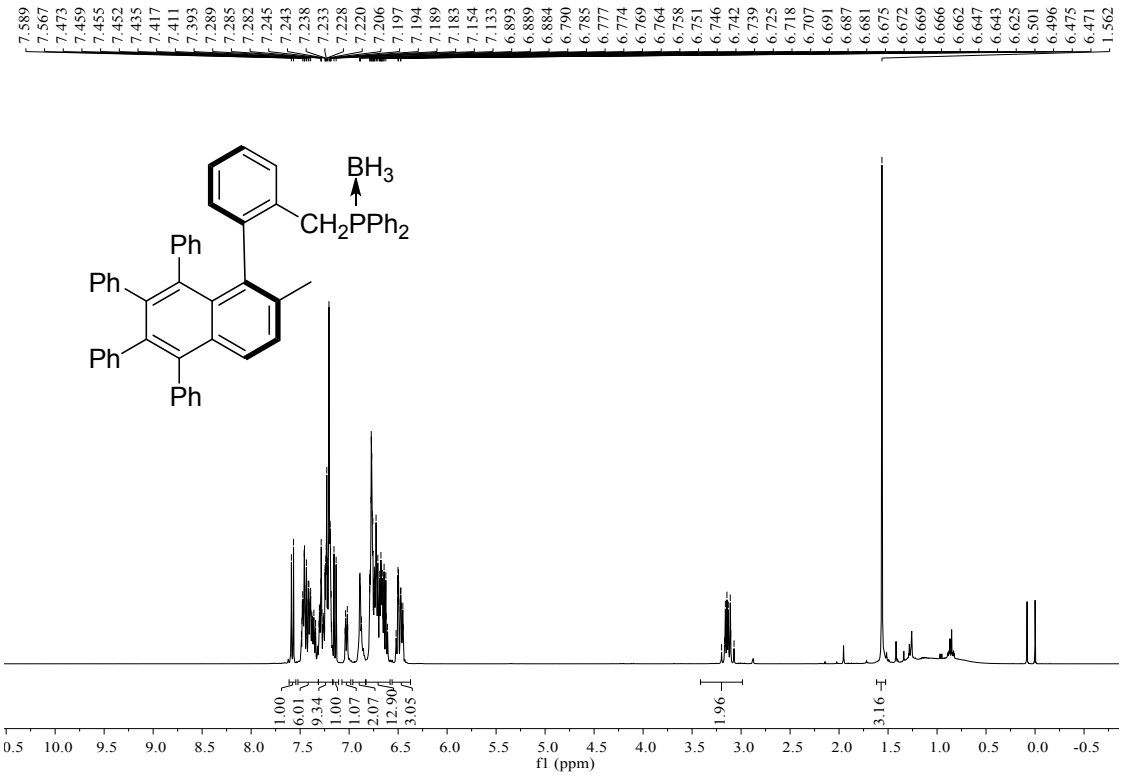

**(2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzyl)diphenylphosphine oxide (6)**

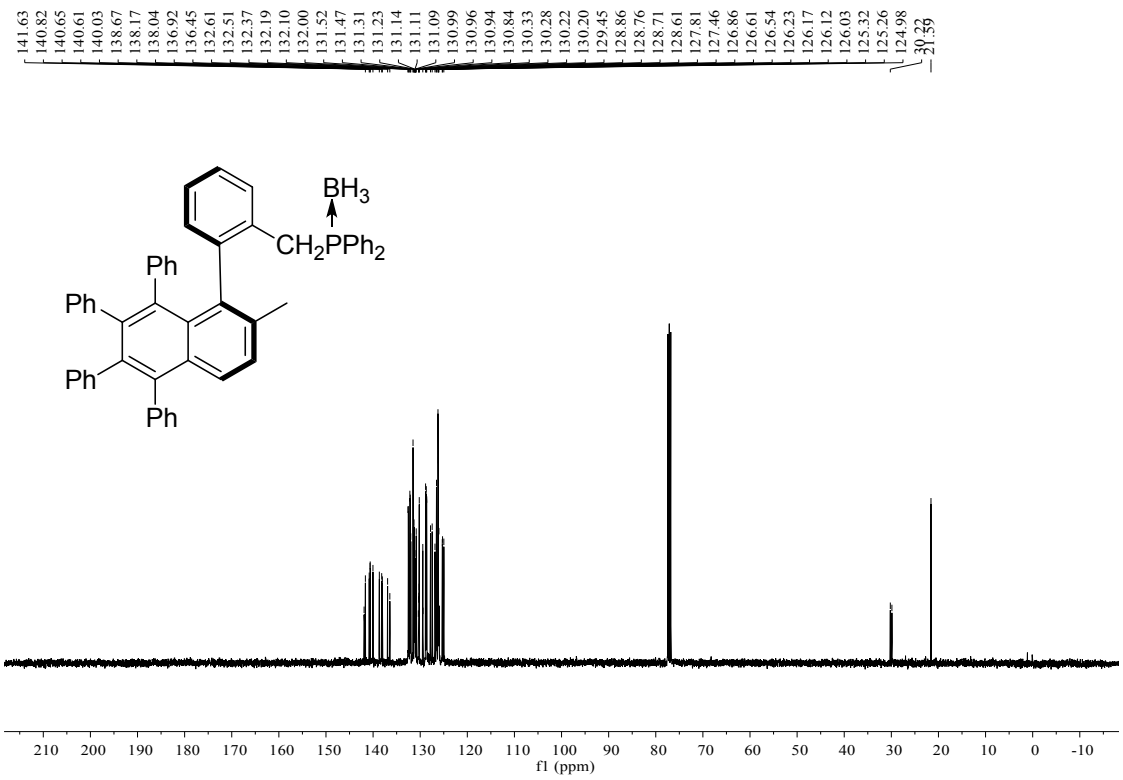

7.615
7.598
7.524
7.520
7.516
7.513
7.500
7.498
7.454
7.444
7.440
7.308
7.303
7.277
7.273
7.263
7.257
7.251
7.243
7.237
7.233
7.231
7.227
7.220
7.217
7.215
7.208
7.191
6.872
6.867
6.865
6.790
6.785
6.779
6.775
6.770
6.757
6.751
6.748
6.746
6.736
6.728
6.725
6.720
6.716
6.713
6.711
6.691
6.687
6.677
6.643
6.640
6.626
6.464
6.461
6.451
6.446
6.444
1.518
CH2P(O)Ph2
Ph
Ph
Ph
Ph
1.00
2.91
1.96
1.03
11.20
1.97
12.80
2.92
1.02
1.02
3.00
f1 (ppm)

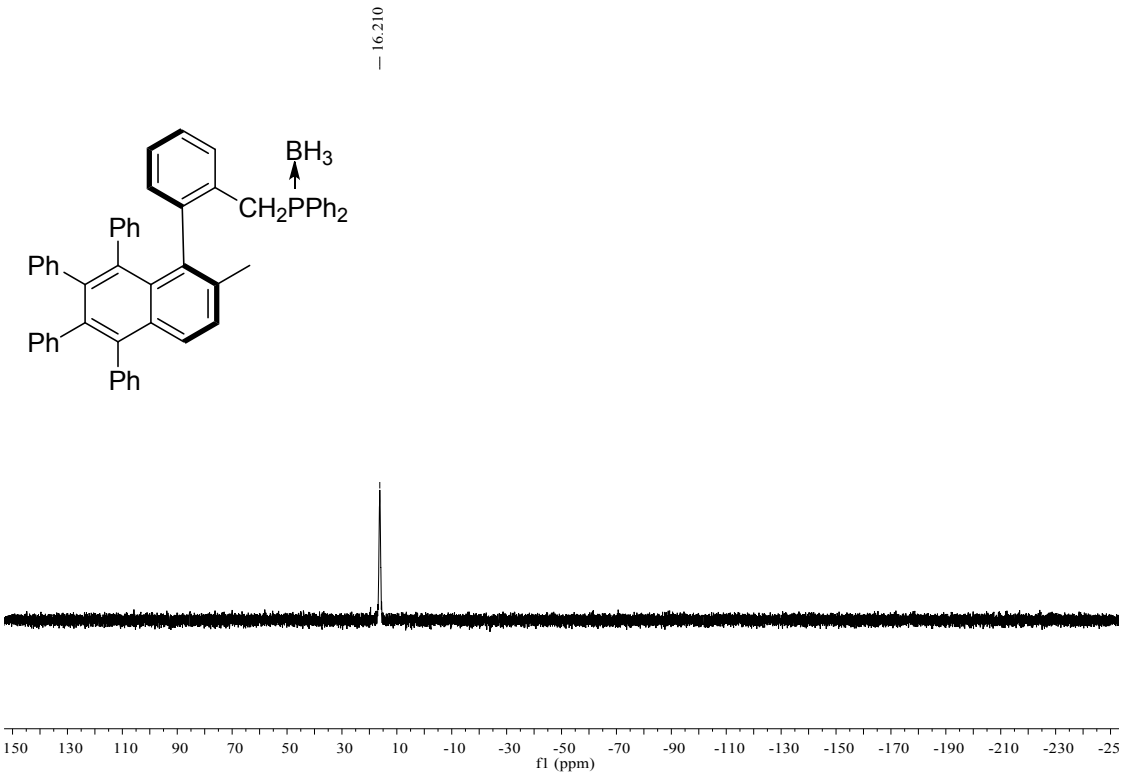

141.20
140.94
140.40
138.97
138.53
138.47
137.39
137.00
132.62
132.22
132.05
132.02
131.96
131.84
131.80
131.70
131.58
131.50
131.47
131.42
131.16
131.09
130.51
130.29
130.26
129.75
129.04
128.95
128.78
128.68
128.19
127.81
127.15
126.95
126.90
126.86
126.75
126.57
126.50
126.41
126.36
125.66
125.34
77.74
77.48
34.31
33.96
21.71
CH2P(O)Ph2
Ph
Ph
Ph
Ph
f1 (ppm)

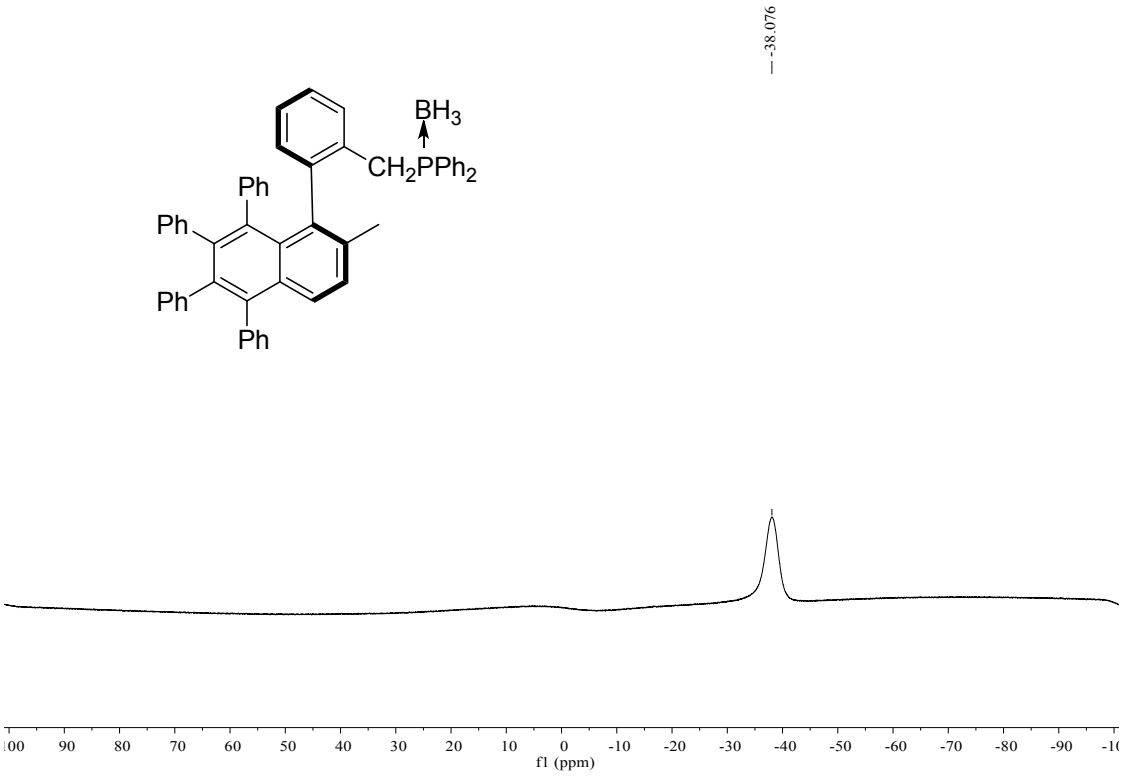



**(2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzyl)diphenylphosphane borane (7)**

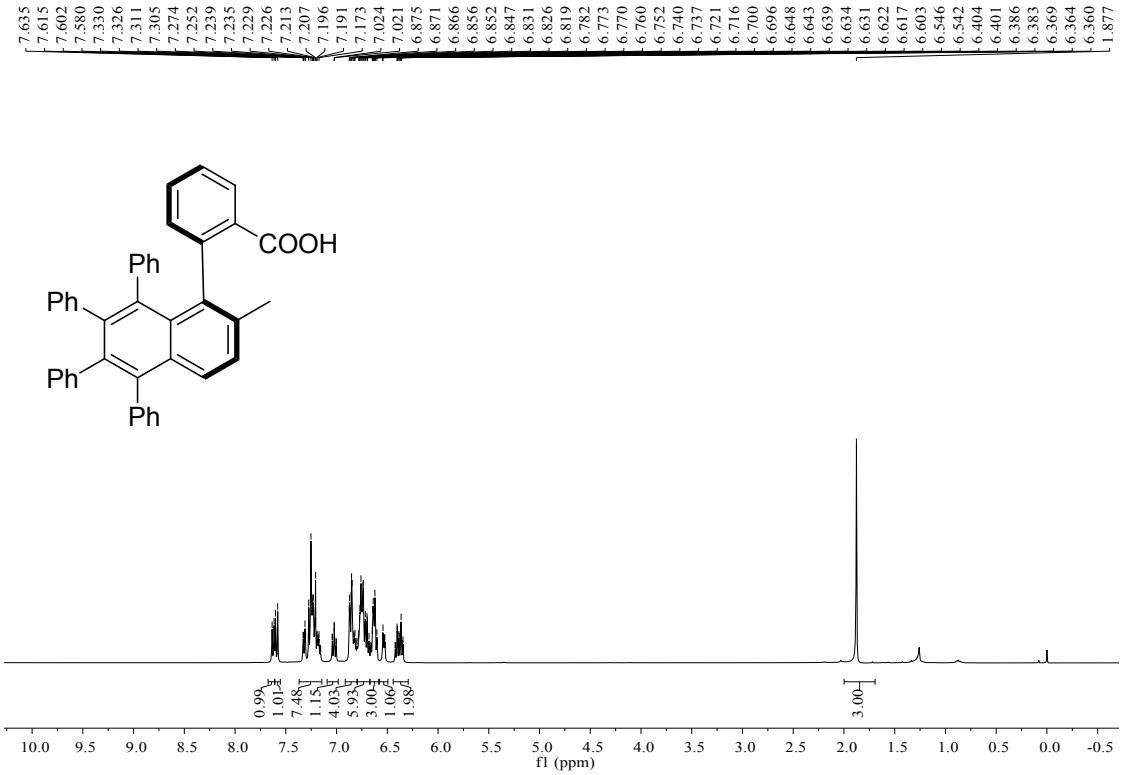


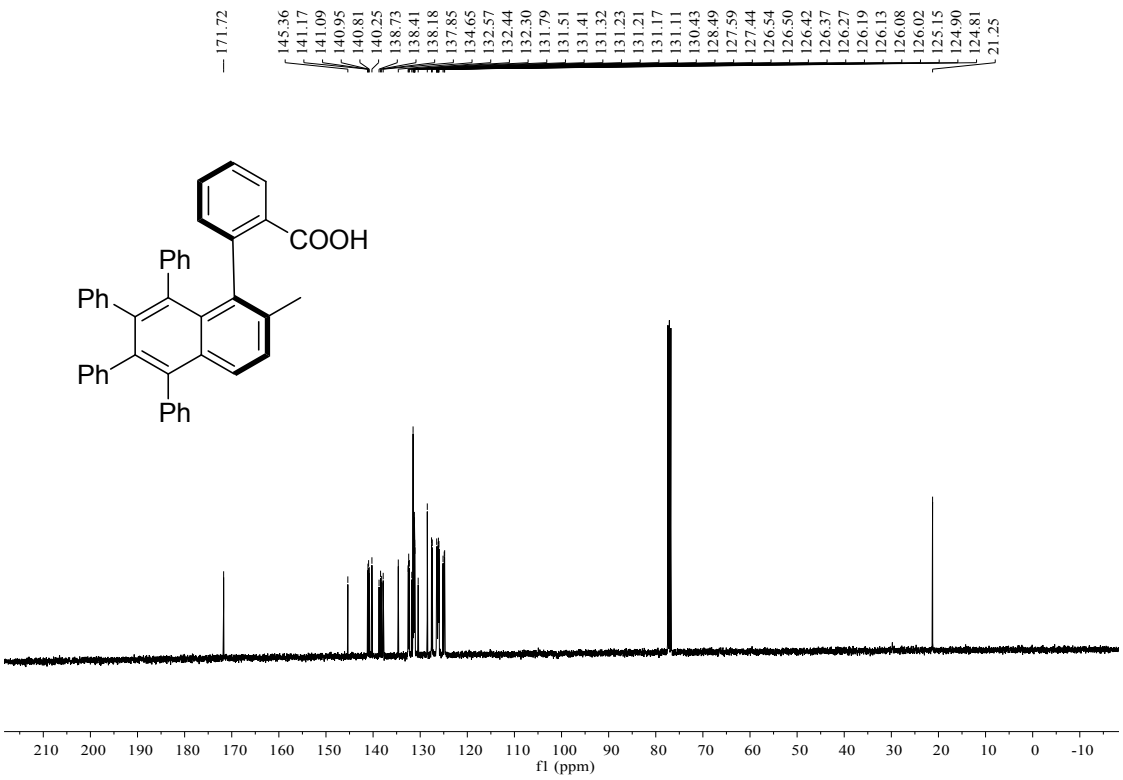

141.63
140.82
140.65
140.61
140.03
138.67
138.17
138.04
136.92
136.45
132.61
132.51
132.37
132.19
132.10
132.00
131.52
131.47
131.31
131.23
131.14
131.11
131.09
130.99
130.96
130.94
130.84
130.33
130.28
130.22
130.20
129.45
128.86
128.76
128.71
128.61
127.81
127.46
126.86
126.61
126.54
126.23
126.17
126.12
126.03
125.32
125.26
124.98
30.22
21.39
BH3
CH2PPh2
Ph
Ph
Ph
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


16.210
BH3
CH2PPh2
Ph
Ph
Ph
Ph
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

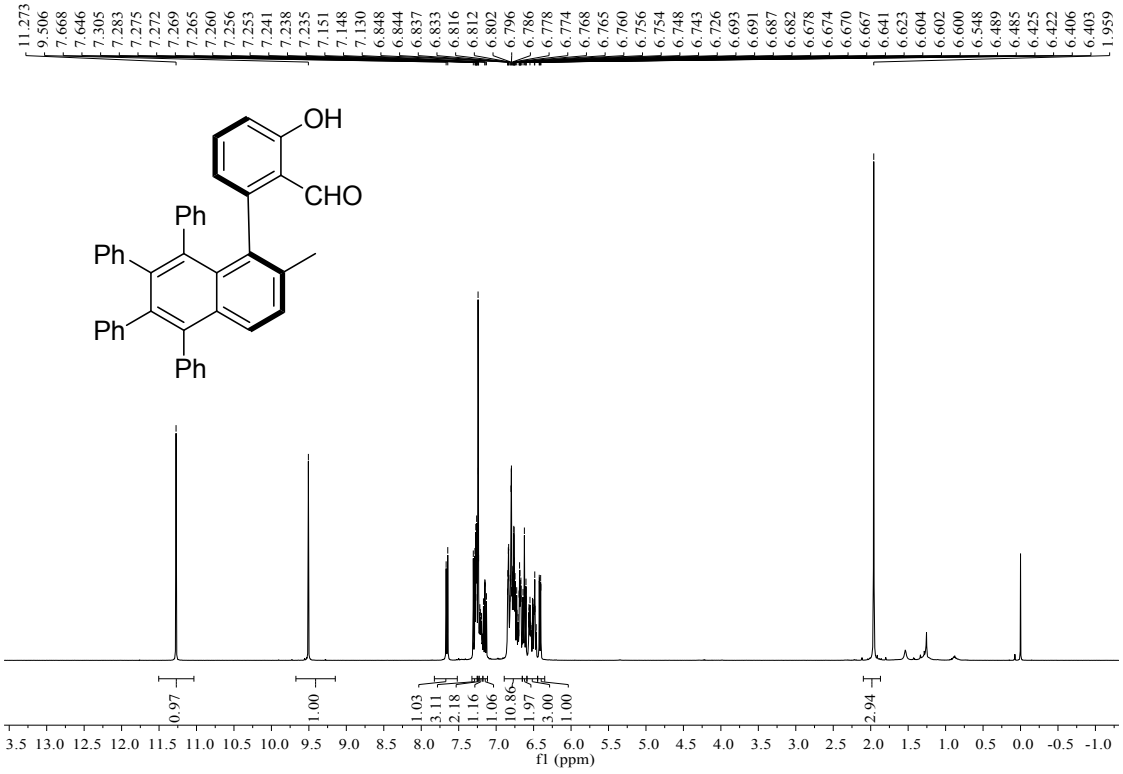


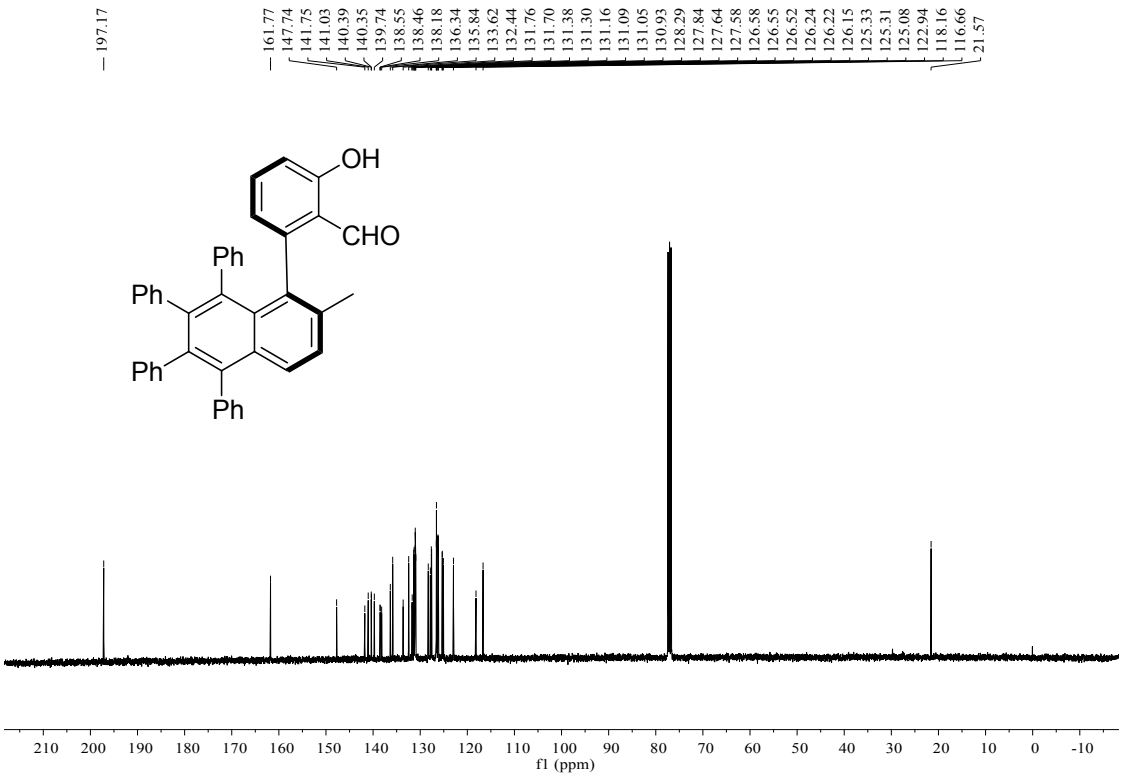

## 2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzoic acid (8)



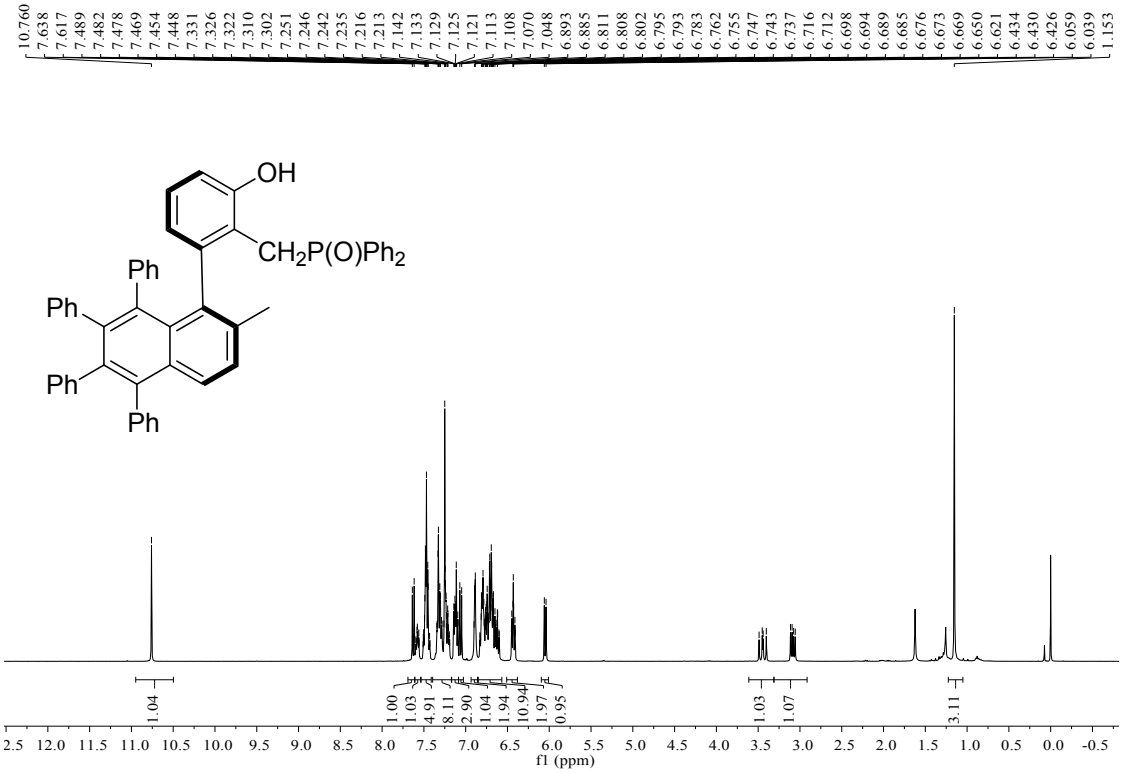


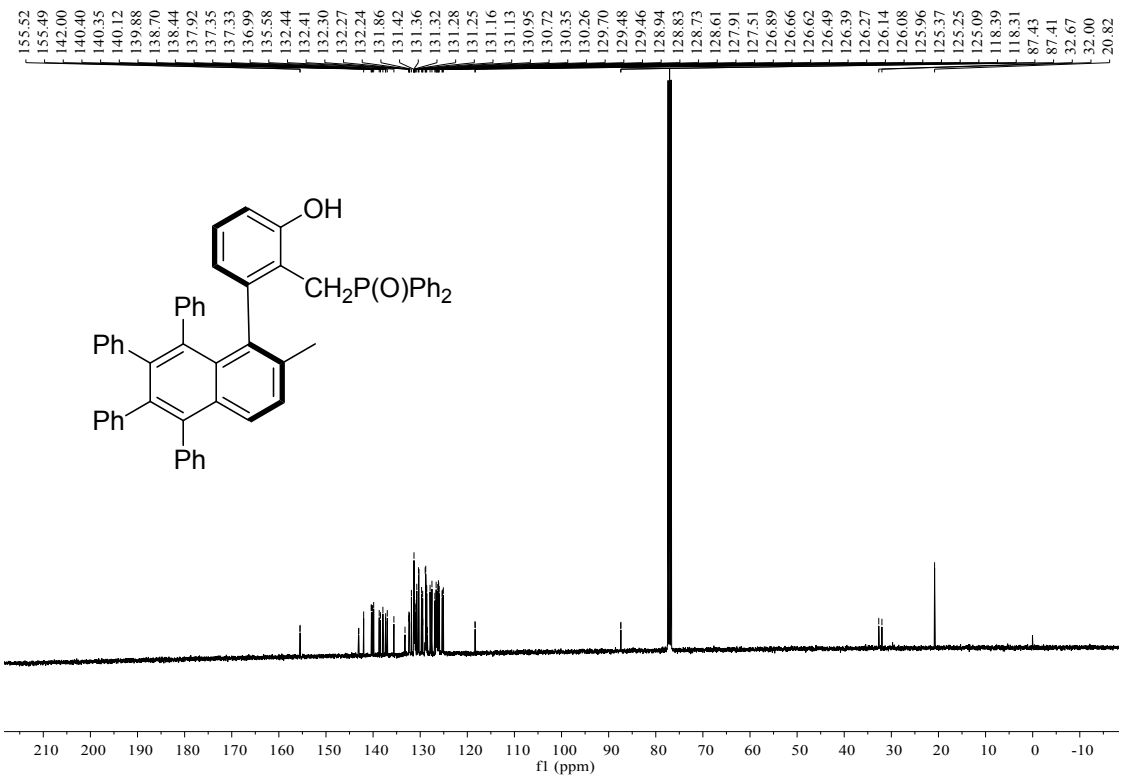

## 2-Hydroxy-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzaldehyde (9)

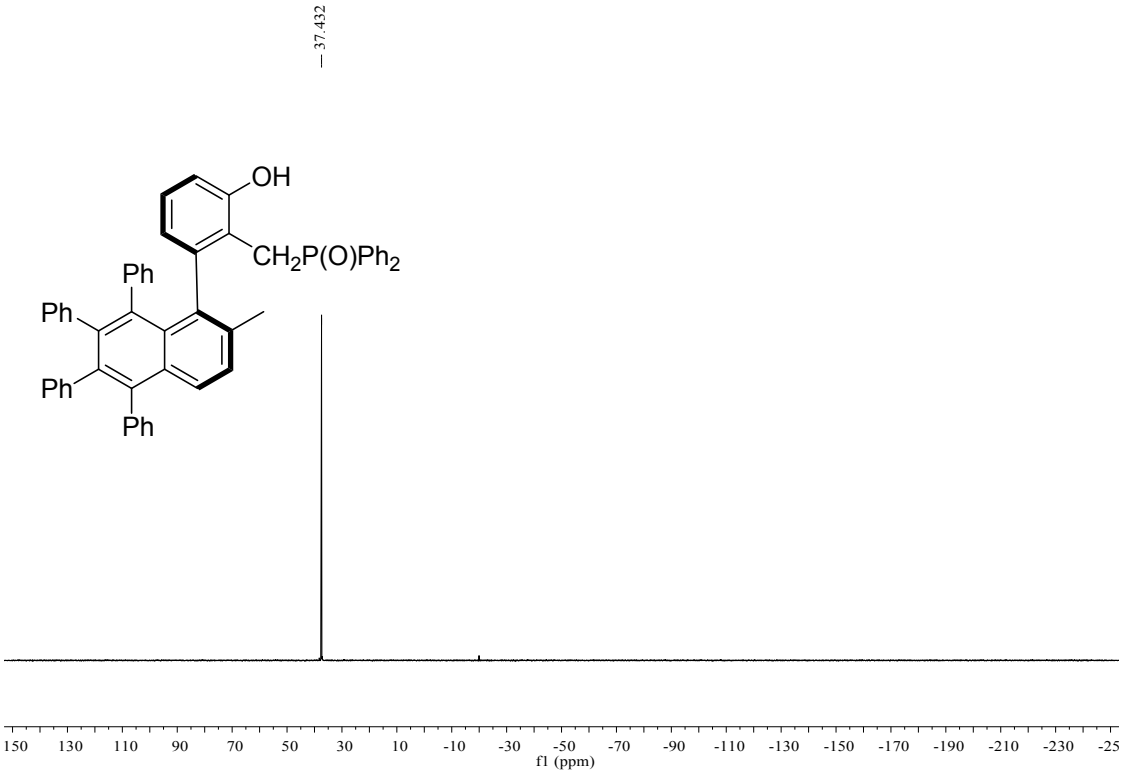




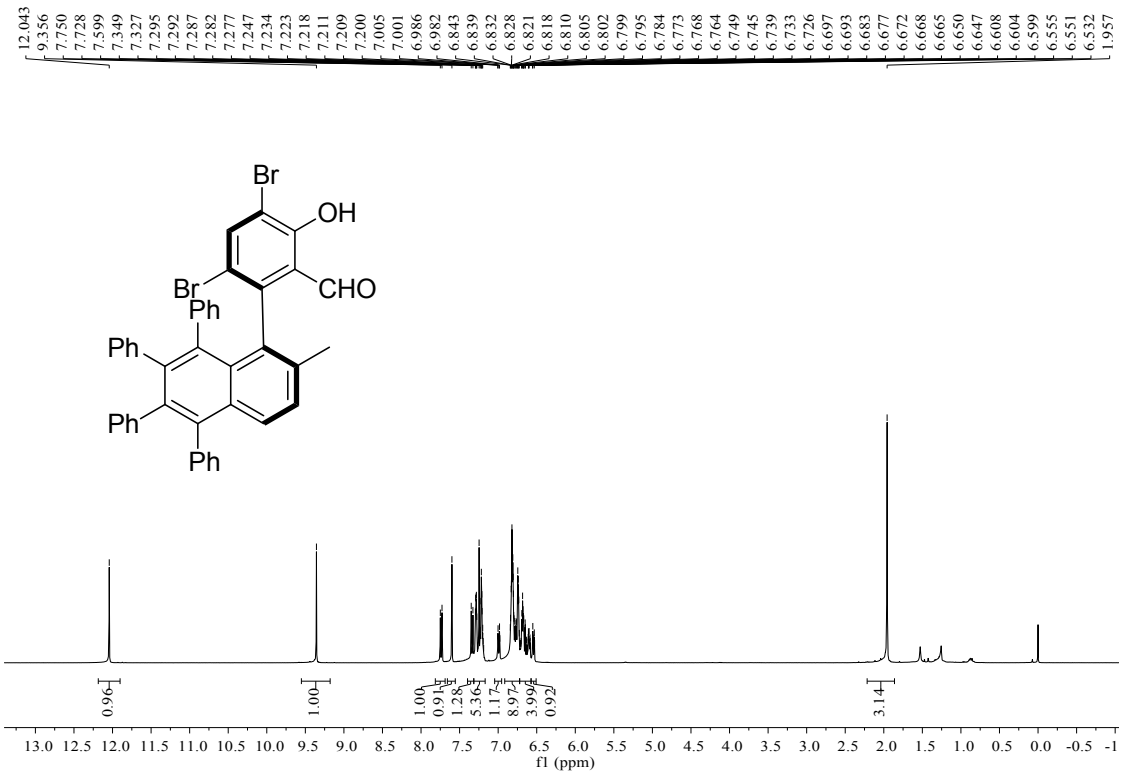

**(2-(2-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzyl)diphenylphosphine oxide (10)**

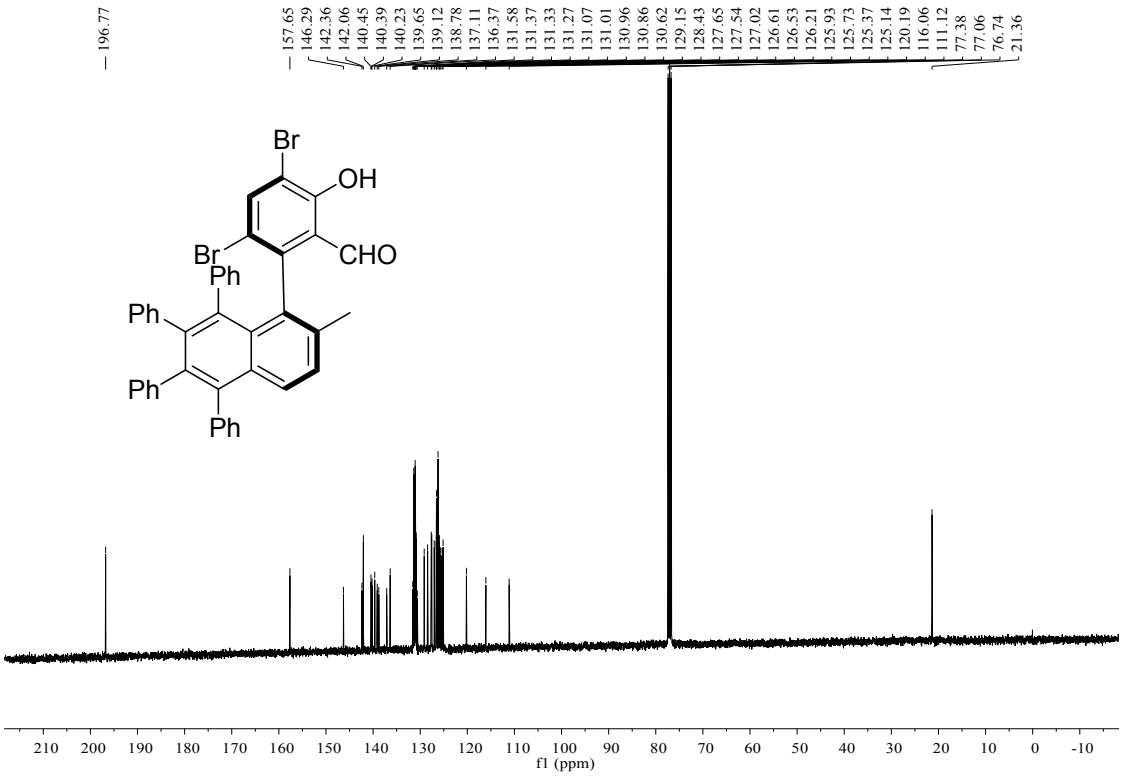




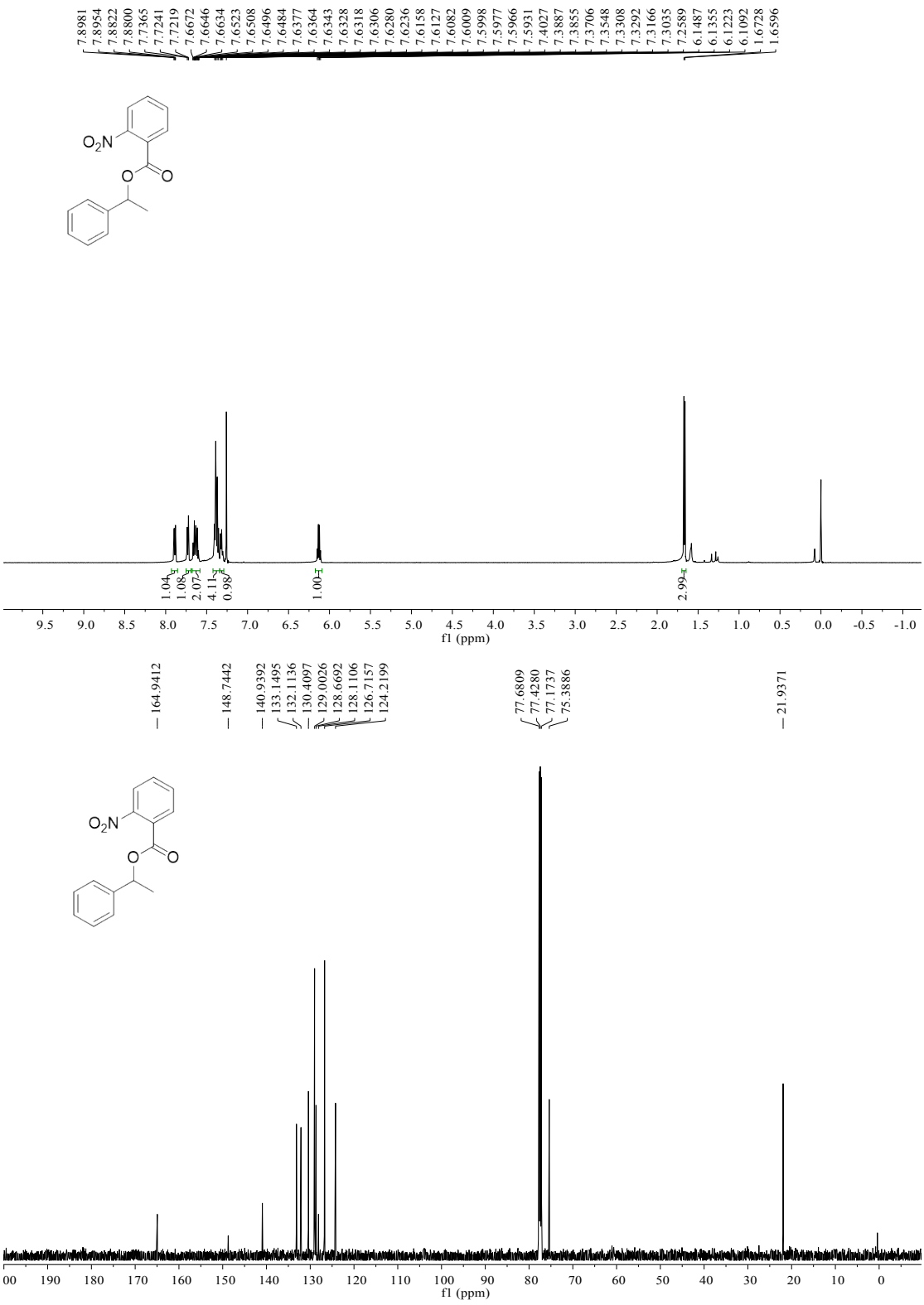




**3,5-Dibromo-2-hydroxy-6-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)benzald ehyde (11)**



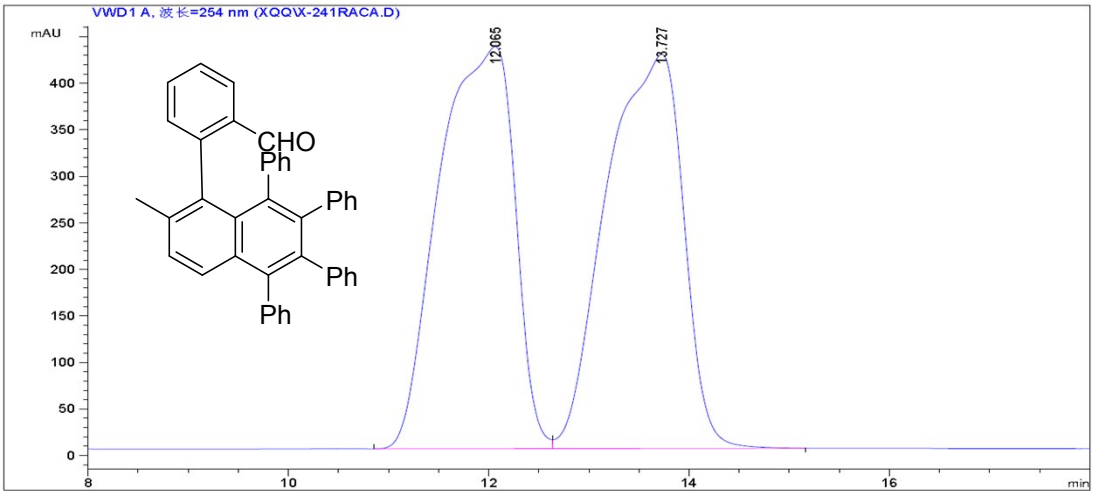

## 1-Phenylethyl 2-nitrobenzoate (14)




# Copies of HPLC Analysis

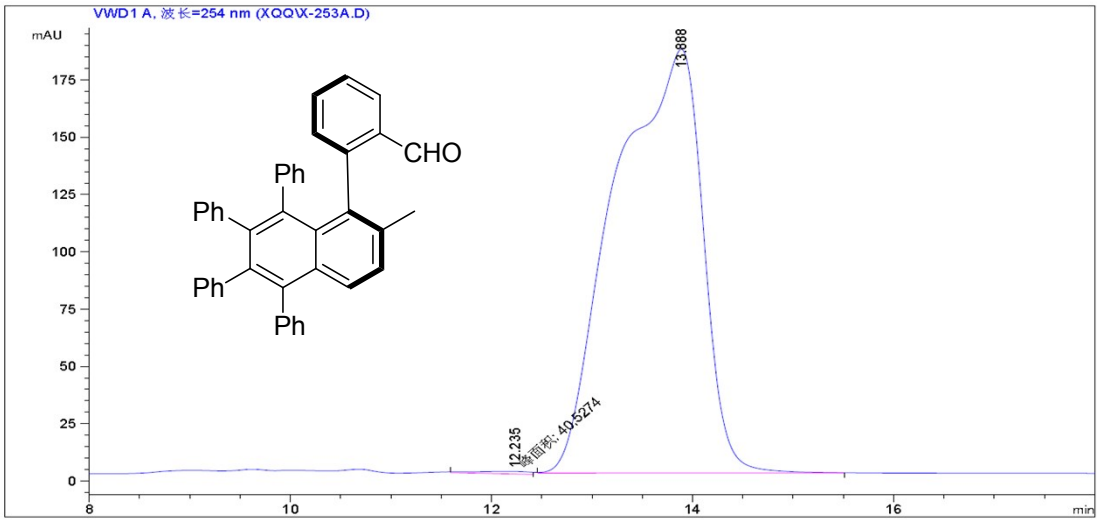
## 3a: IF, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.065 | BV | 0.7034 | 2.27142e4 | 432.19760 | 50.0311 |
| 2 | 13.727 | VB | 0.7159 | 2.26860e4 | 424.02032 | 49.9689 |

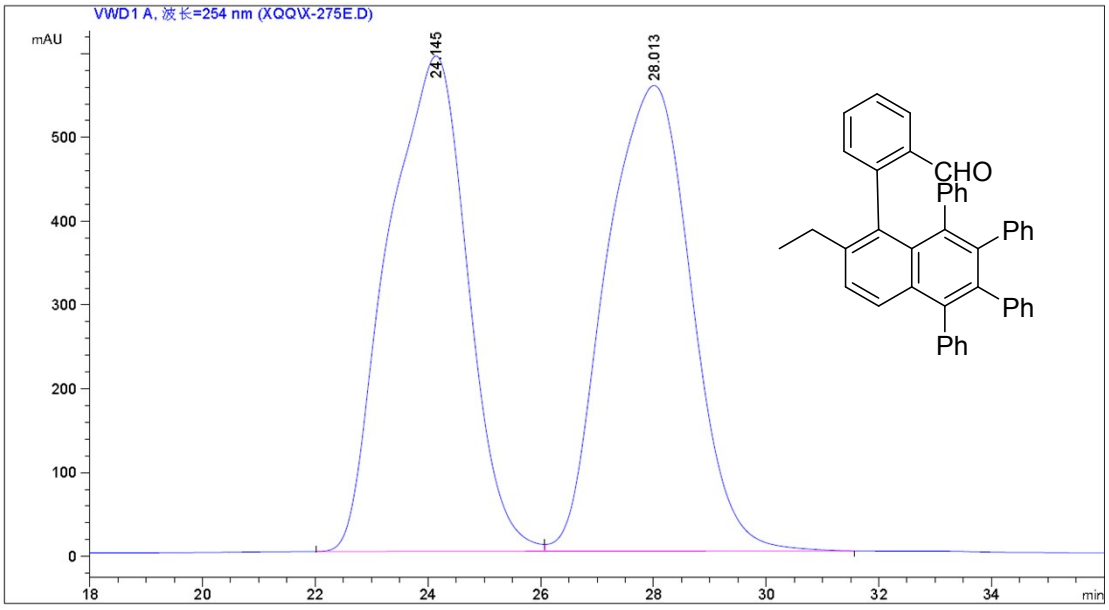



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.235 | MM | 0.5941 | 40.52739 | 1.13693 | 0.3602 |
| 2 | 13.888 | VB | 0.8068 | 1.12100e4 | 184.77913 | 99.6398 |

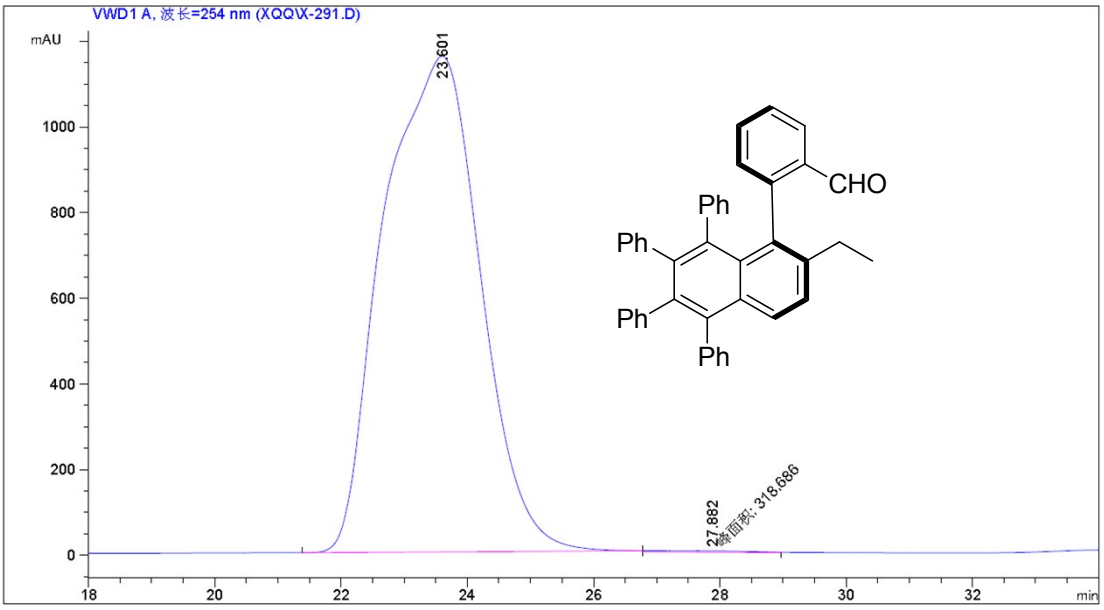
## 3b: OD-H, Hexane:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 24.145 | BV | 1.3818 | 5.80830e4 | 591.32349 | 49.8059 |
| 2 | 28.013 | VB | 1.7165 | 5.85358e4 | 555.80273 | 50.1941 |

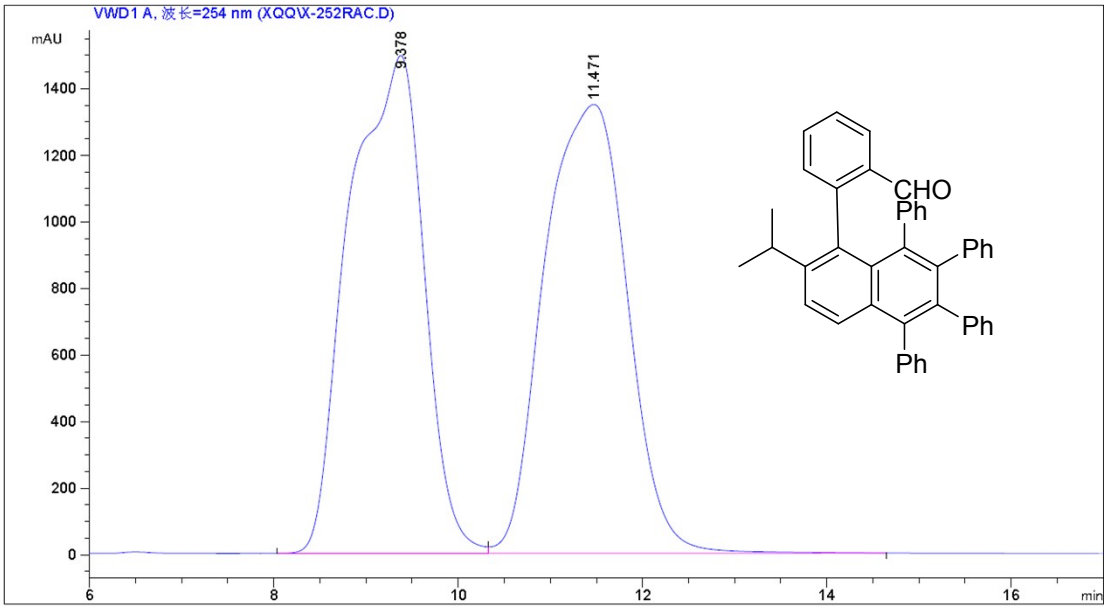



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 23.601 | BB | 1.4780 | 1.23489e5 | 1157.11926 | 99.7426 |
| 2 | 27.882 | MM | 1.8080 | 318.68585 | 2.93770 | 0.2574 |

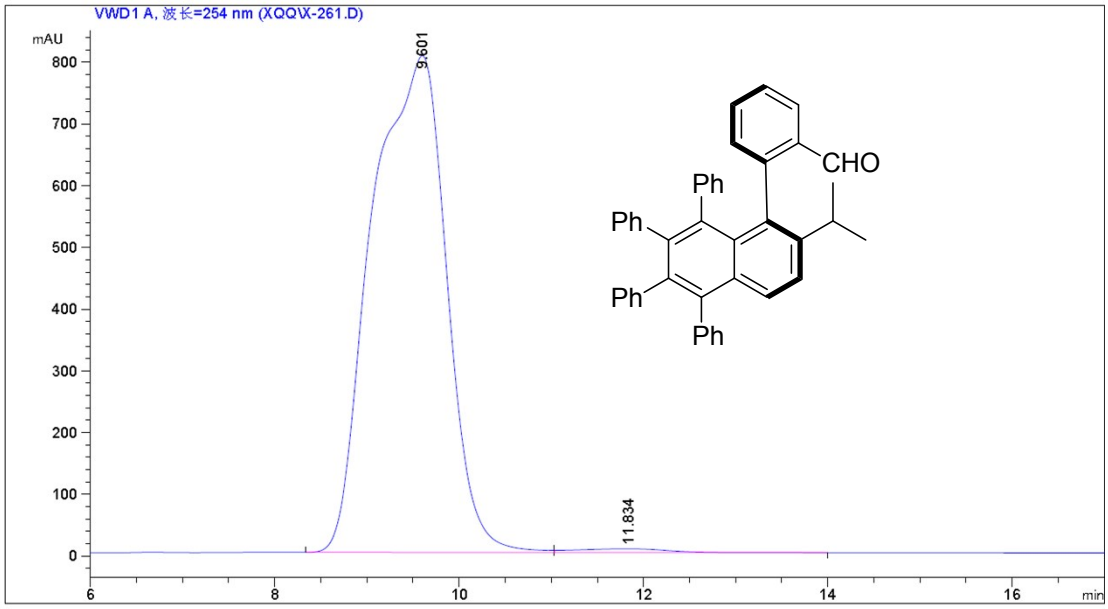
## 3c: OD-H, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.378 | BV | 0.7596 | 8.40555e4 | 1494.30103 | 49.9213 |
| 2 | 11.471 | VB | 1.0271 | 8.43206e4 | 1347.38940 | 50.0787 |

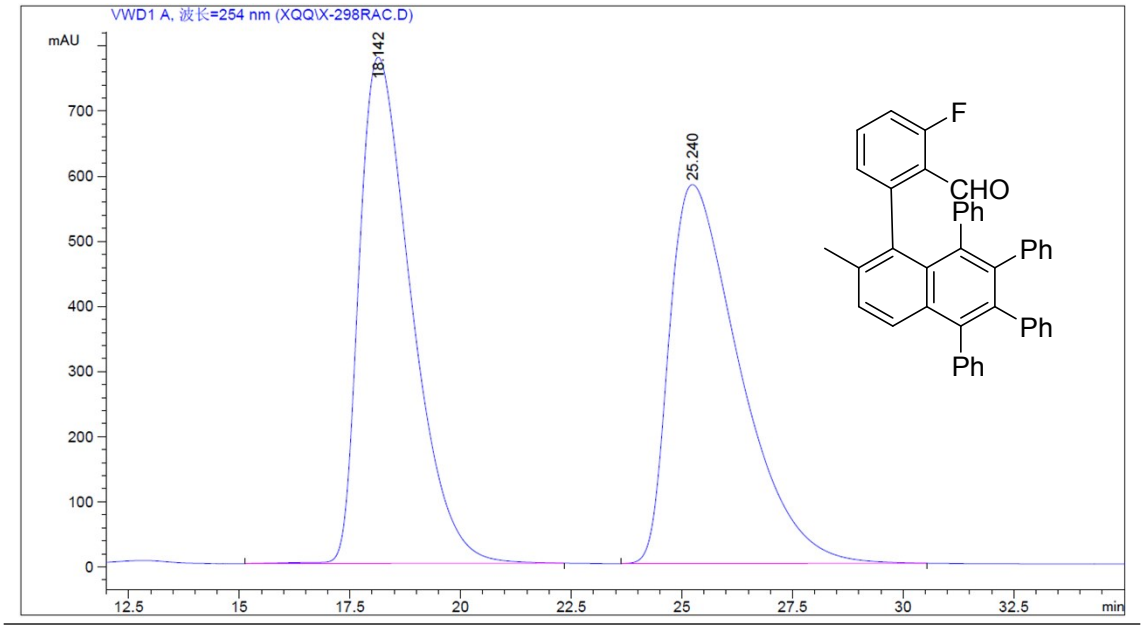



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.601 | BV | 0.7598 | 4.50912e4 | 804.94147 | 99.1169 |
| 2 | 11.834 | VB | 0.8271 | 401.75183 | 5.84172 | 0.8831 |

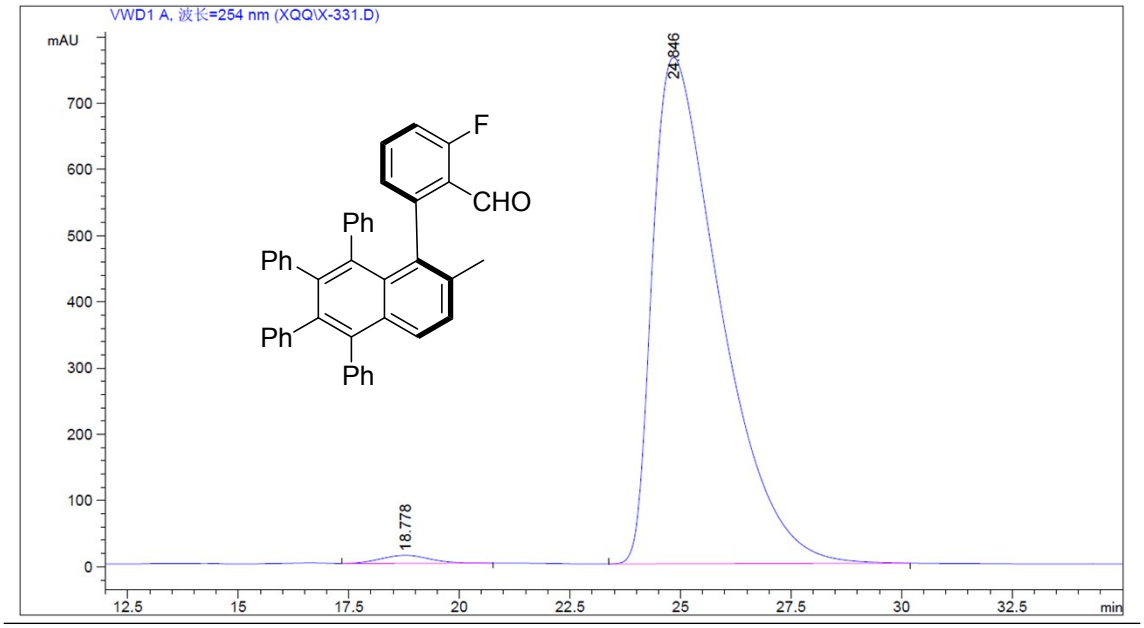
## 3d: OD-H, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.142 | BB | 1.2612 | 6.34687e4 | 777.40942 | 49.5350 |
| 2 | 25.240 | BB | 1.6834 | 6.46602e4 | 582.01898 | 50.4650 |

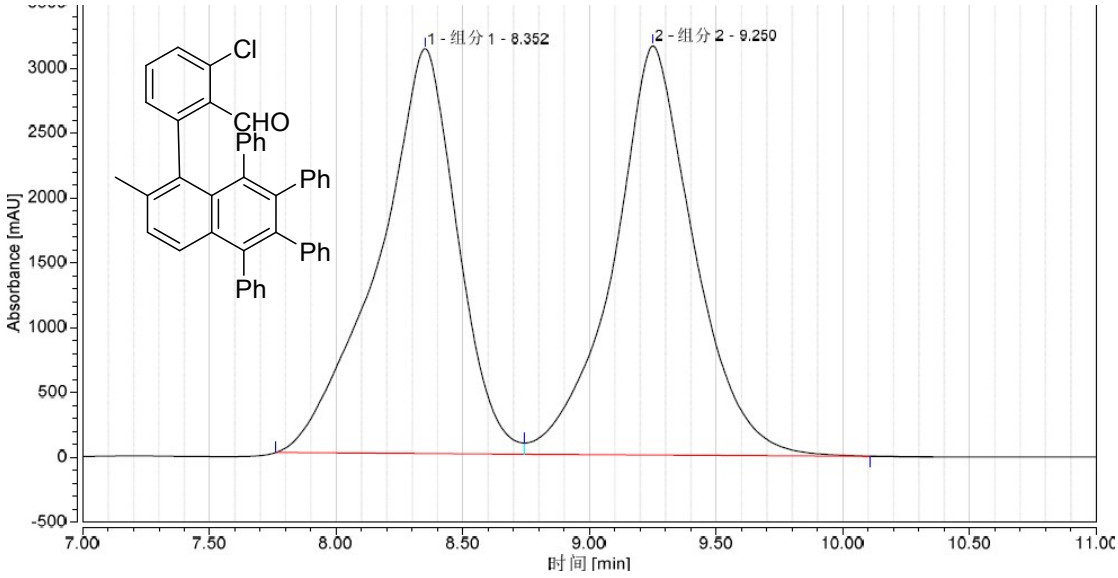



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.778 | VB | 1.1484 | 933.52057 | 12.14779 | 1.1370 |
| 2 | 24.846 | BB | 1.5984 | 8.11739e4 | 764.50098 | 98.8630 |

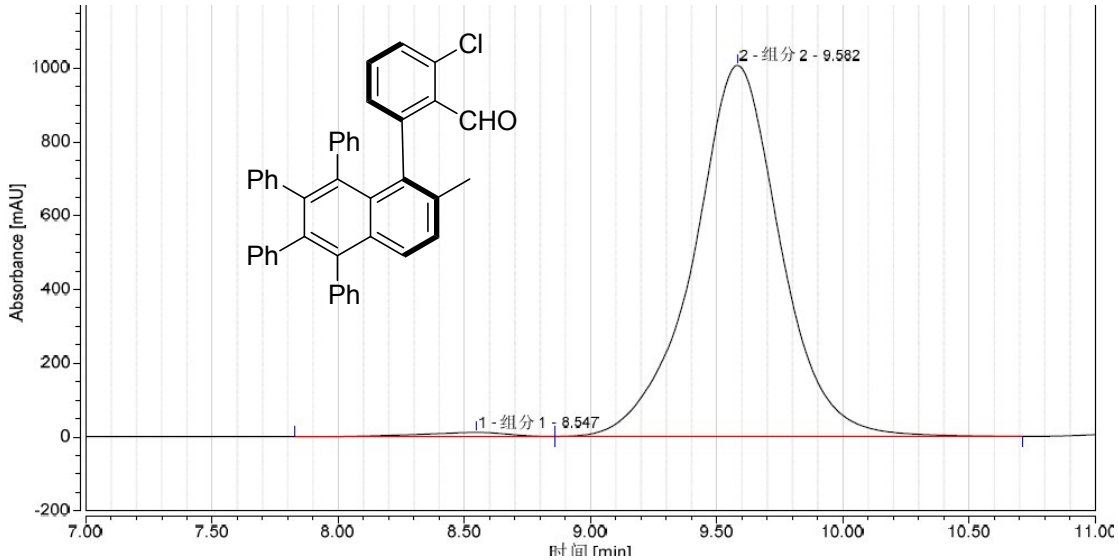
## 3e: IB, Hexane:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Height [mAU] | Area [mAU *min] | Height % | Area % |
|---|---|---|---|---|---|
| 1 | 8.352 | 3119.660 | 1132.497 | 49.71 | 49.34 |
| 2 | 9.250 | 3155.578 | 1162.576 | 50.29 | 50.66 |

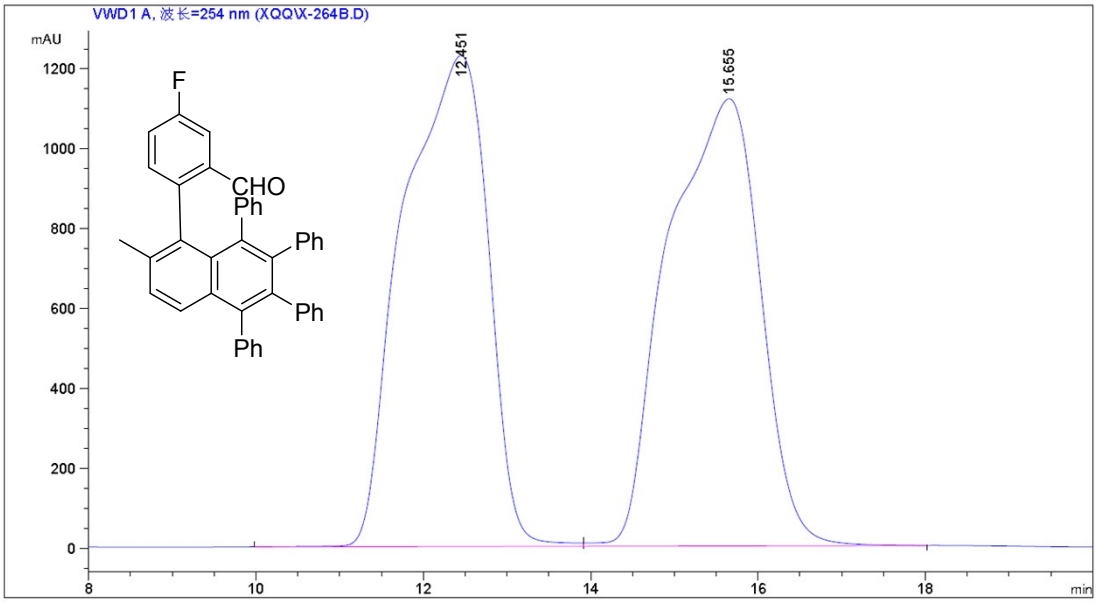



Area Percent Report

| Peak # | RetTime [min] | Height [mAU] | Area [mAU *min] | Height % | Area % |
|---|---|---|---|---|---|
| 1 | 8.547 | 11.457 | 4.657 | 1.13 | 1.15 |
| 2 | 9.582 | 1005.923 | 401.104 | 98.87 | 98.85 |

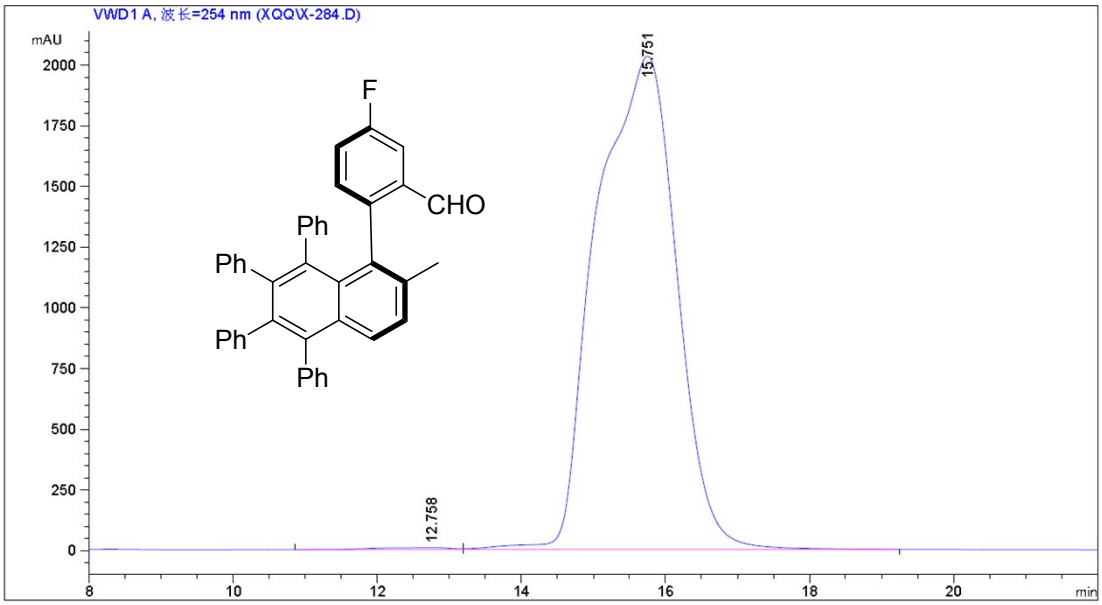
## 3f: IF, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.451 | BV | 0.9965 | 8.65786e4 | 1229.21179 | 50.1797 |
| 2 | 15.655 | VB | 1.0749 | 8.59584e4 | 1119.46985 | 49.8203 |

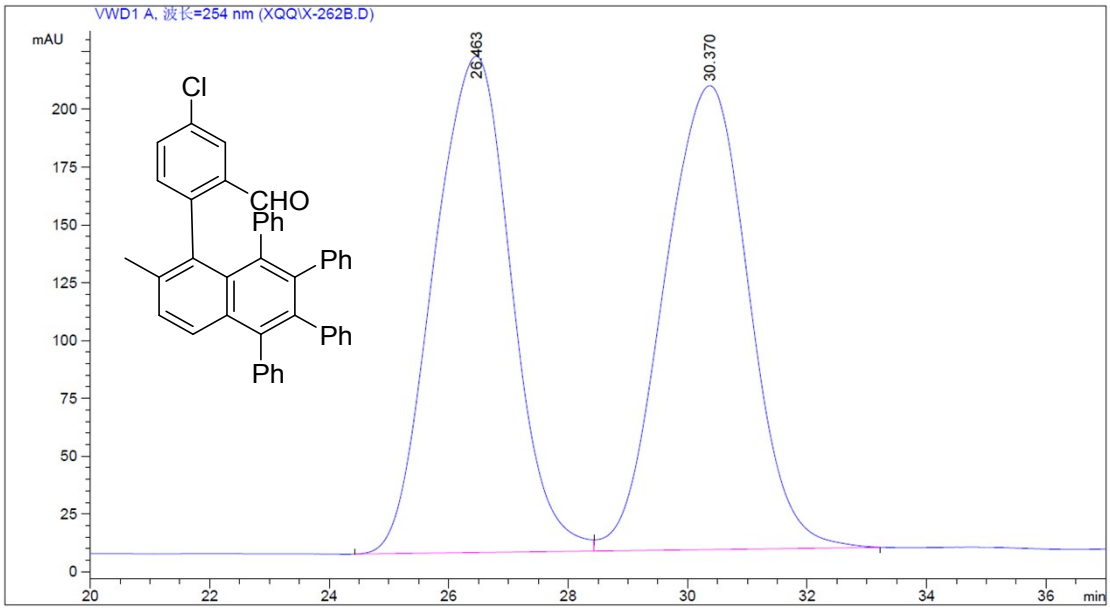



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.758 | BV | 0.9247 | 574.16833 | 8.14180 | 0.3646 |
| 2 | 15.751 | VB | 1.0639 | 1.56910e5 | 2032.10791 | 99.6354 |

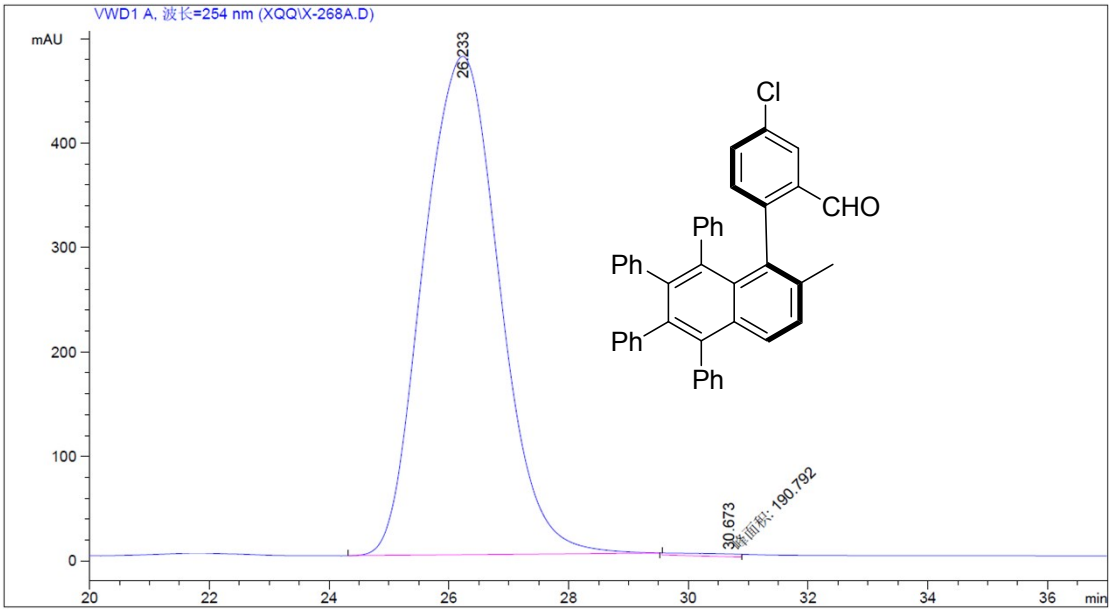
## 3g: OD-H, Hexane:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

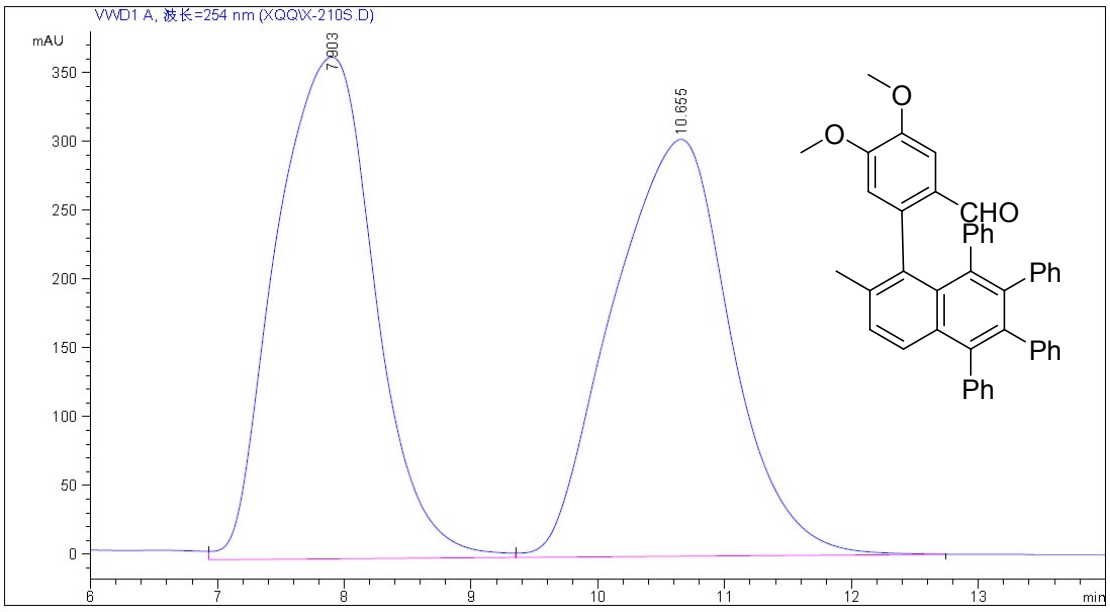
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 26.463 | BV | 1.4425 | 1.93575e4 | 214.60863 | 49.4710 |
| 2 | 30.370 | VB | 1.4890 | 1.97716e4 | 200.62175 | 50.5290 |




Area Percent Report

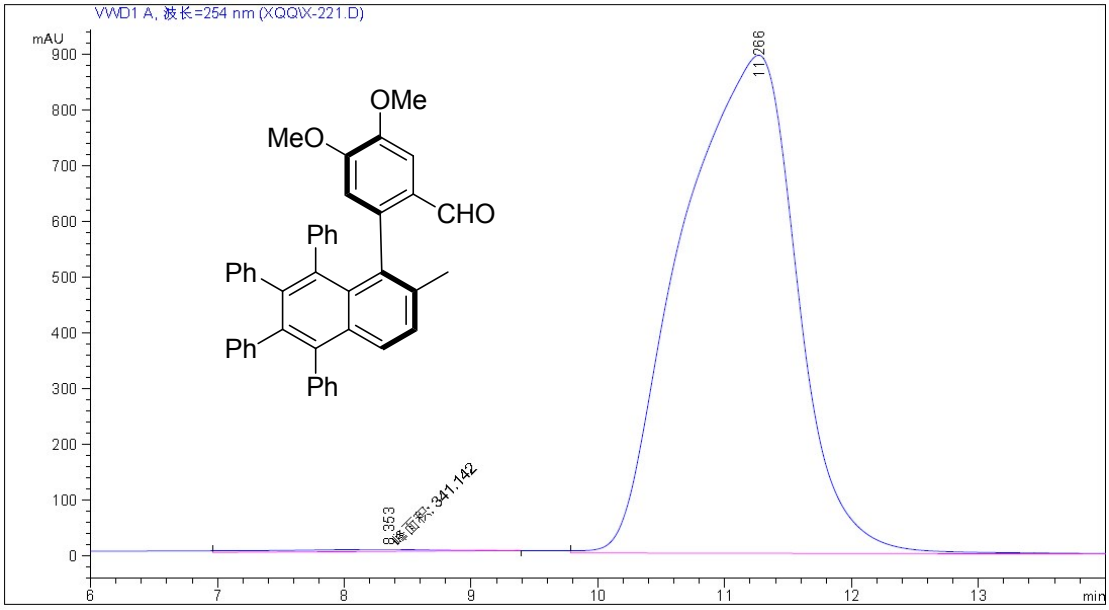
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 26.233 | BB | 1.3994 | 4.21086e4 | 477.17404 | 99.5489 |
| 2 | 30.673 | MM | 1.1955 | 190.79202 | 2.65983 | 0.4511 |

## 3h: AD-H, Hexane:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.903 | VV | 0.8922 | 1.97895e4 | 364.73416 | 50.1061 |
| 2 | 10.655 | VB | 1.0717 | 1.97057e4 | 303.04559 | 49.8939 |

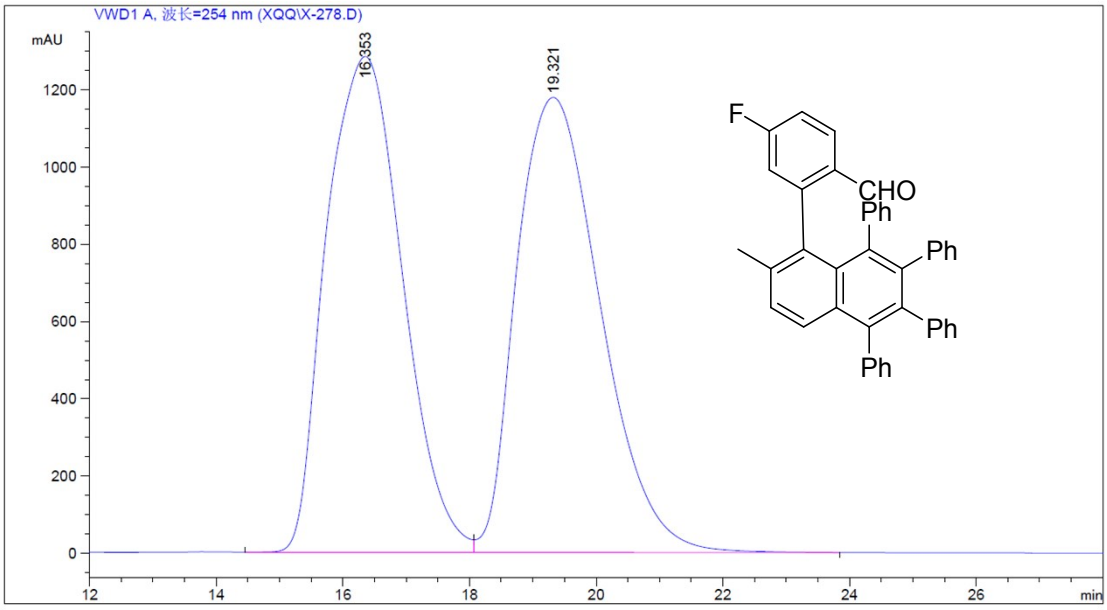



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.353 | MM | 1.2294 | 341.14221 | 3.28536 | 0.5973 |
| 2 | 11.266 | VB | 1.0761 | 5.67758e4 | 893.66174 | 99.40272 |

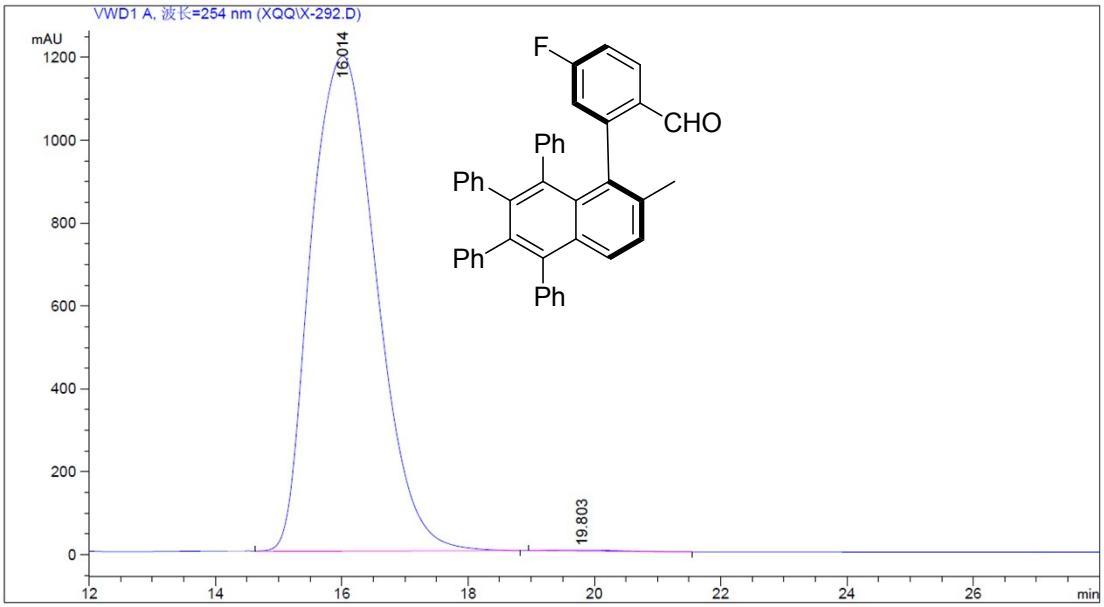
## 3i: OD-H, Hexane:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

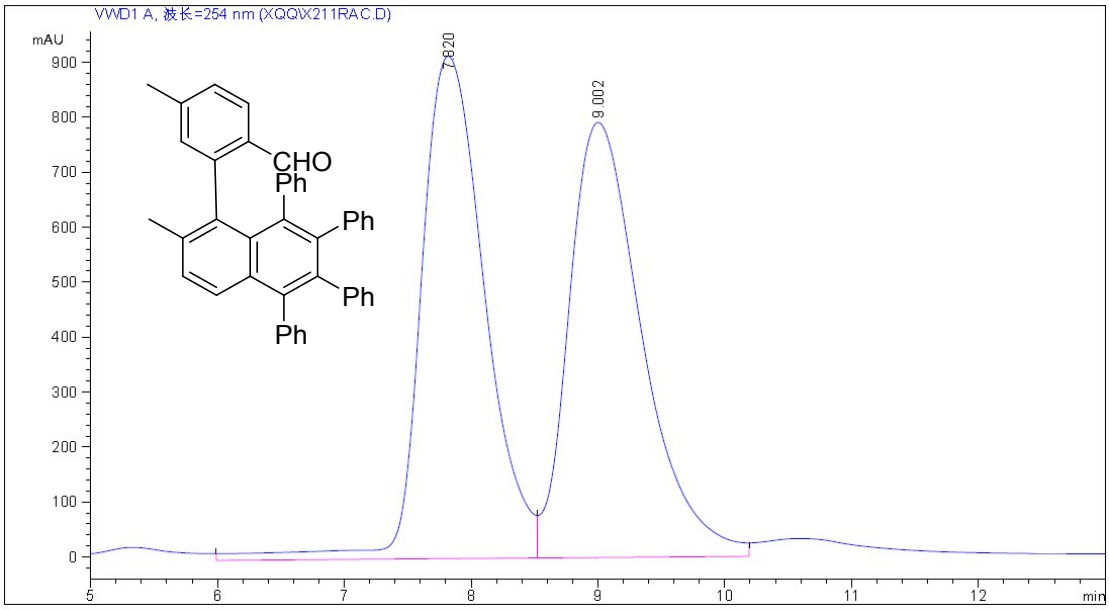
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.353 | VV | 1.3665 | 1.07417e5 | 1283.58044 | 49.7823 |
| 2 | 19.321 | VB | 1.4708 | 1.08357e5 | 1177.76404 | 50.2177 |




Area Percent Report

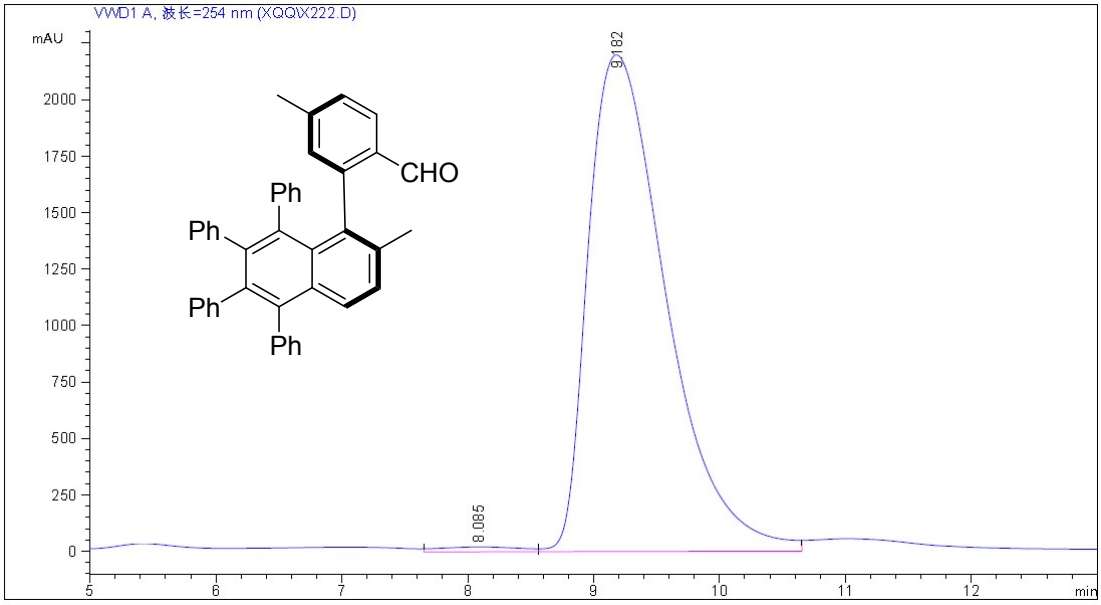
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.014 | VB | 1.1705 | 8.63688e4 | 1195.49597 | 99.8426 |
| 2 | 19.803 | BB | 0.7470 | 136.20114 | 2.19135 | 0.1574 |

## 3j:OD-H, Hexane:*i*-PrOH = 99:1, 1 mL/min, 254 nm




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.820 | VV | 0.5480 | 3.19758e4 | 913.80743 | 50.2236 |
| 2 | 9.002 | VV | 0.6200 | 3.16911e4 | 791.52496 | 49.7764 |

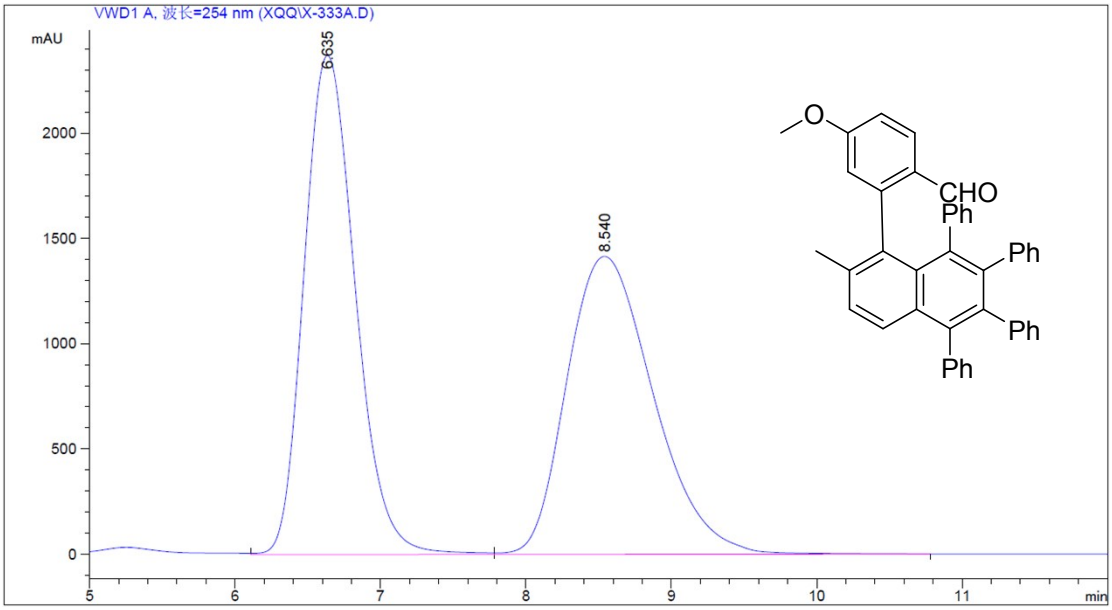



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.085 | VV | 0.6758 | 988.14191 | 22.04514 | 1.0331 |
| 2 | 9.182 | VV | 0.6739 | 9.46572e4 | 2199.49316 | 98.9669 |

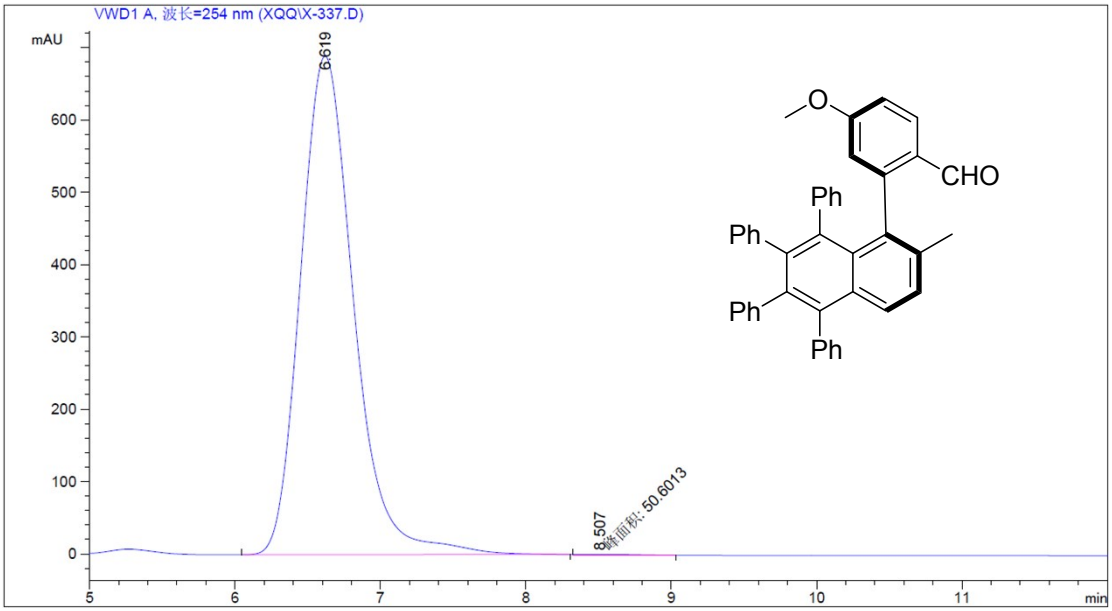
## 3k: OD-H, Hexane:*i*-PrOH = 90:10, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.635 | VV | 0.3833 | 5.80959e4 | 2371.92017 | 49.8509 |
| 2 | 8.540 | VB | 0.6505 | 5.84434e4 | 1415.87903 | 50.1491 |

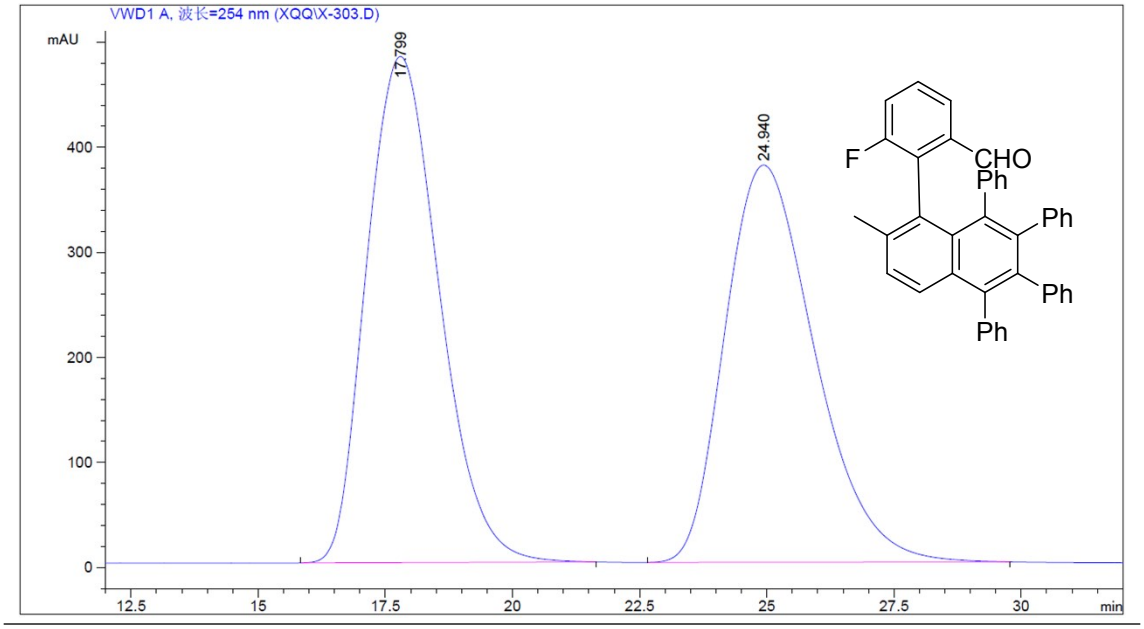



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.619 | BB | 0.3929 | 1.75339e4 | 689.31757 | 99.7122 |
| 2 | 8.507 | MM | 0.5380 | 50.60127 | 1.56761 | 0.2878 |

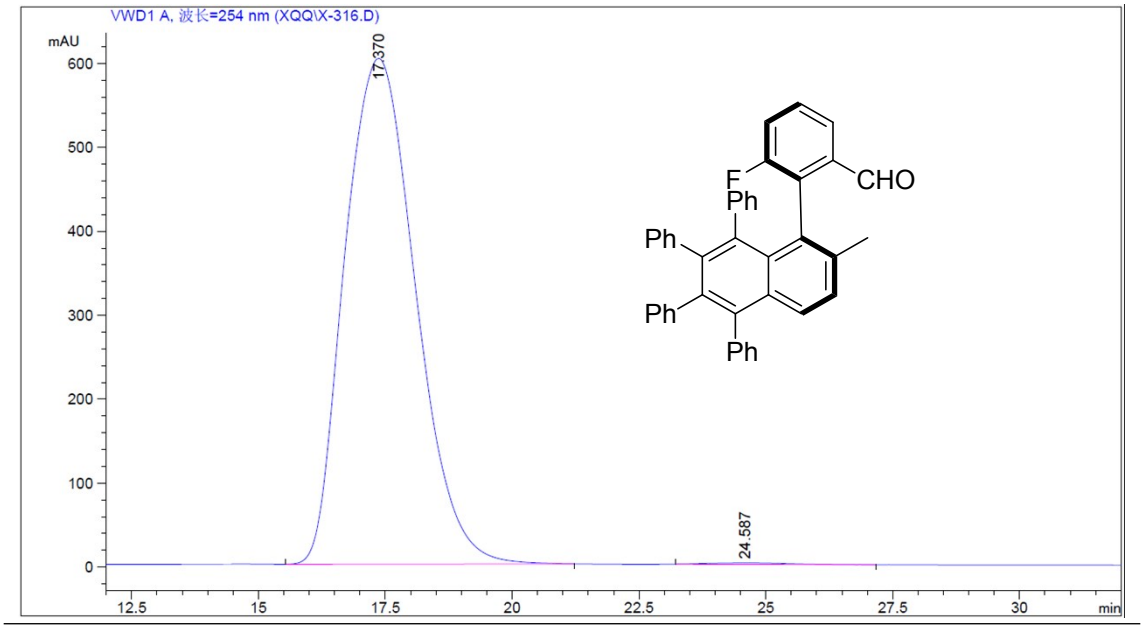
## 3l: OD-H, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

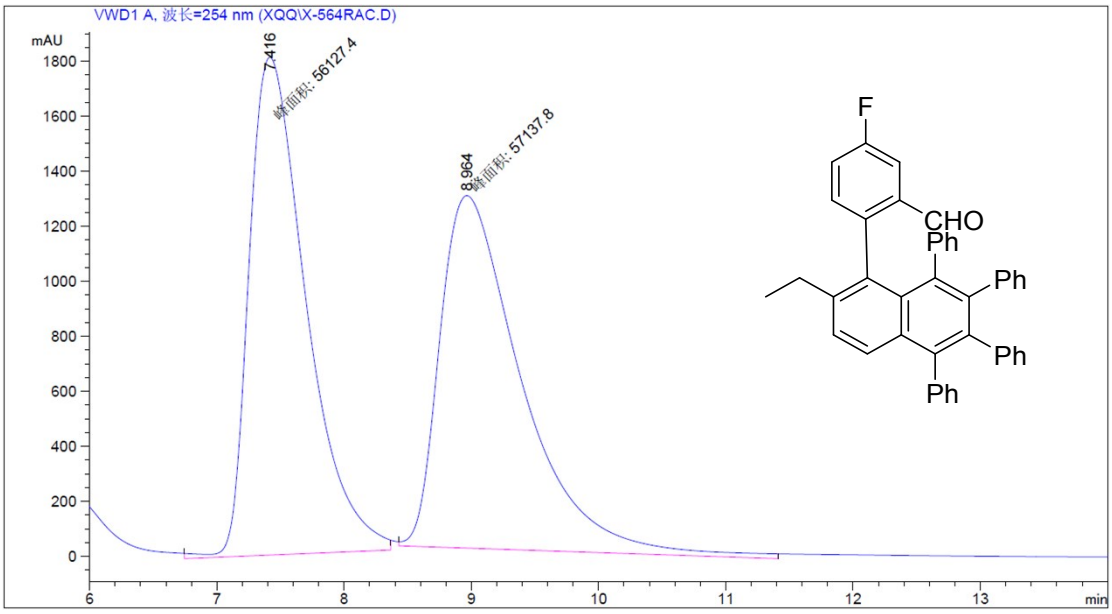
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.799 | BB | 1.5981 | 4.77744e4 | 481.77084 | 50.6592 |
| 2 | 24.940 | BB | 1.9221 | 4.65310e4 | 378.09964 | 49.3408 |




Area Percent Report

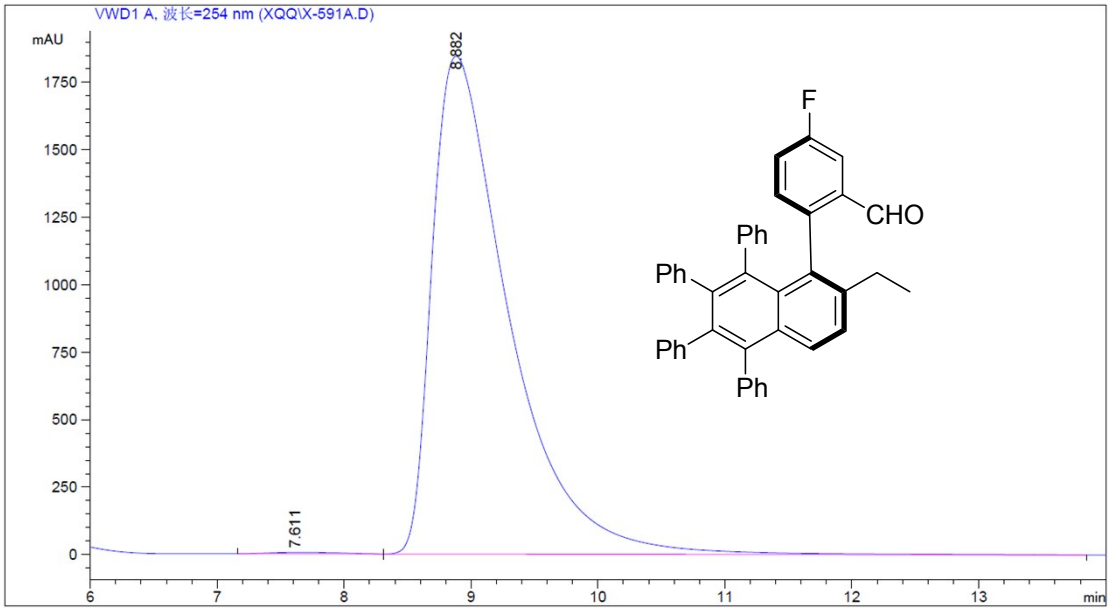
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.370 | BB | 1.5685 | 5.84411e4 | 602.45514 | 99.6627 |
| 2 | 24.587 | BB | 1.3008 | 197.76111 | 1.78978 | 0.3373 |

## 3m: OD-H, Hexane:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.416 | MM | 0.5170 | 5.61274e4 | 1809.28369 | 49.5540 |
| 2 | 8.964 | MM | 0.7434 | 5.71378e4 | 1280.99634 | 50.4460 |

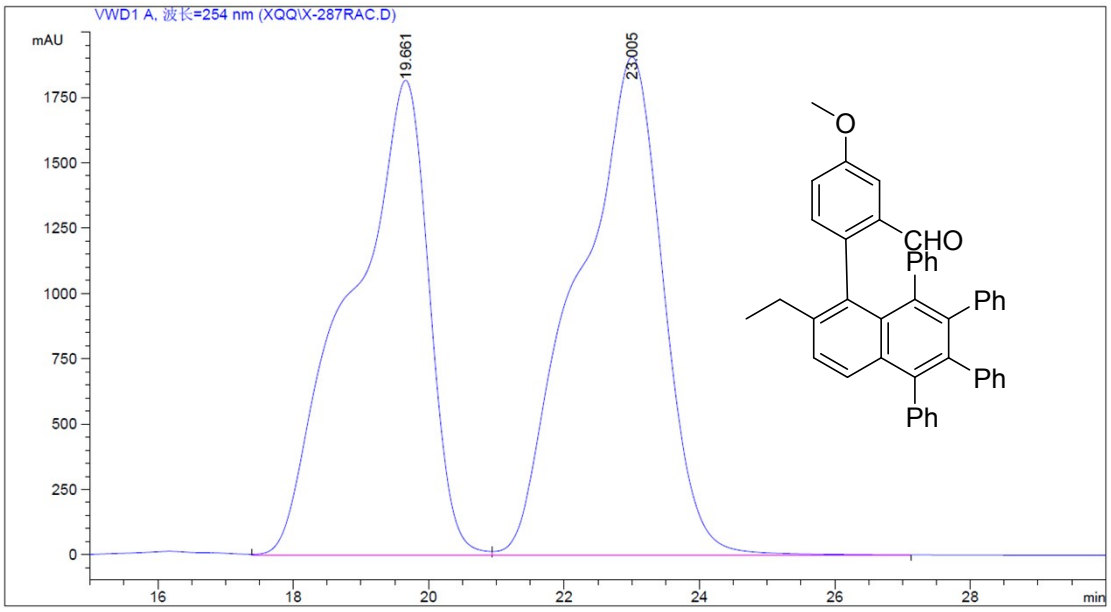



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.611 | BV | 0.5217 | 204.70100 | 5.61149 | 0.2627 |
| 2 | 8.882 | VB | 0.6297 | 7.77196e4 | 1845.17944 | 99.7373 |

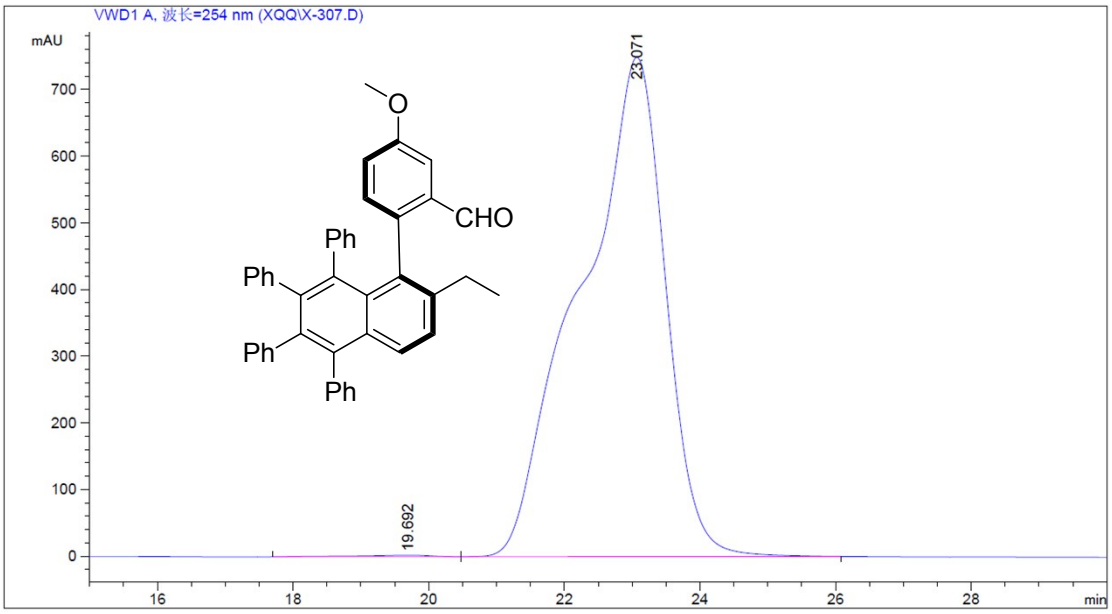
## 3n: IE, Hexane:*i*-PrOH = 98:2, 0.8 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

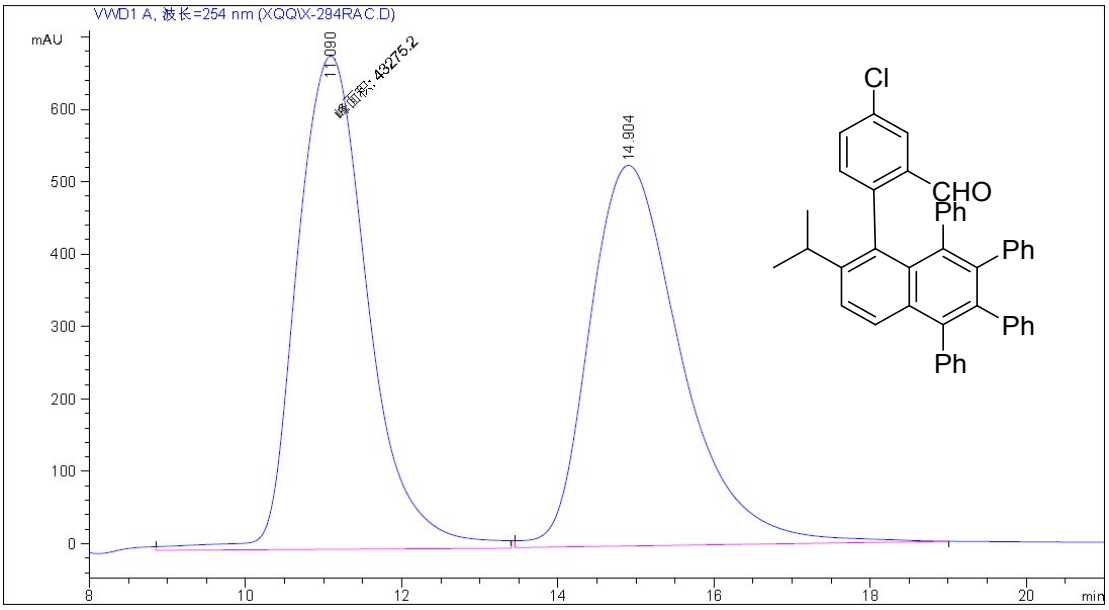
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.661 | VV | 1.1144 | 1.47183e5 | 1816.11108 | 46.9926 |
| 2 | 23.005 | VB | 1.2232 | 1.66021e5 | 1905.49634 | 53.0074 |




Area Percent Report

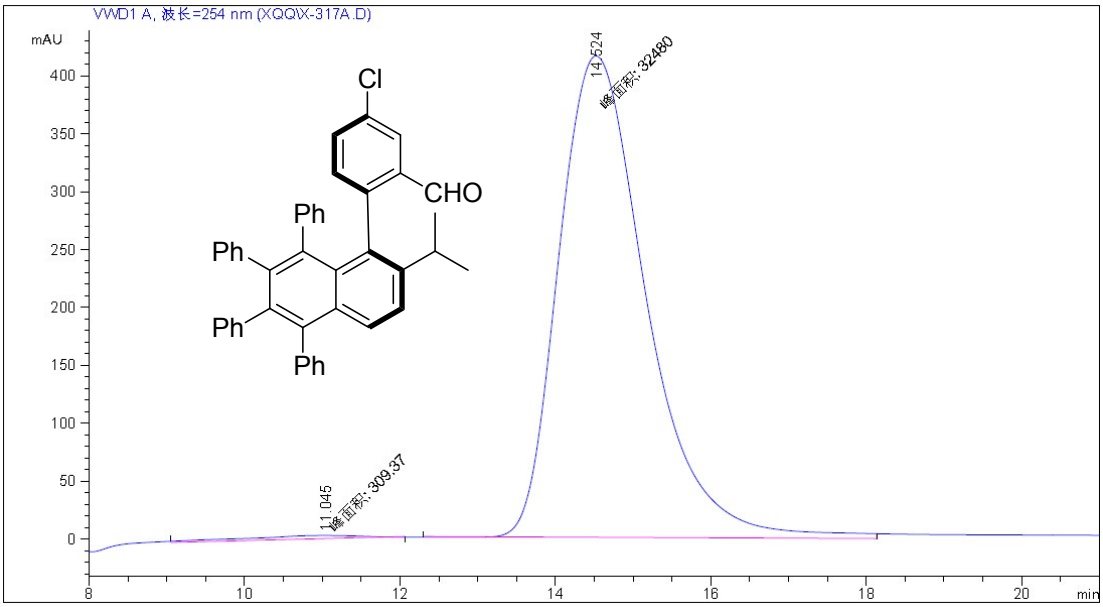
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.692 | BV | 0.9843 | 191.92633 | 2.45645 | 0.2946 |
| 2 | 23.071 | VB | 1.2012 | 6.49605e4 | 748.96716 | 99.7054 |

## 3o: OD-H, Hexane:*i*-PrOH = 99:1, 0.5 mL/min, 254 nm




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.090 | MM | 1.0589 | 4.32752e4 | 681.11542 | 50.1728 |
| 2 | 14.904 | BB | 1.2701 | 4.29771e4 | 525.51501 | 49.82722 |

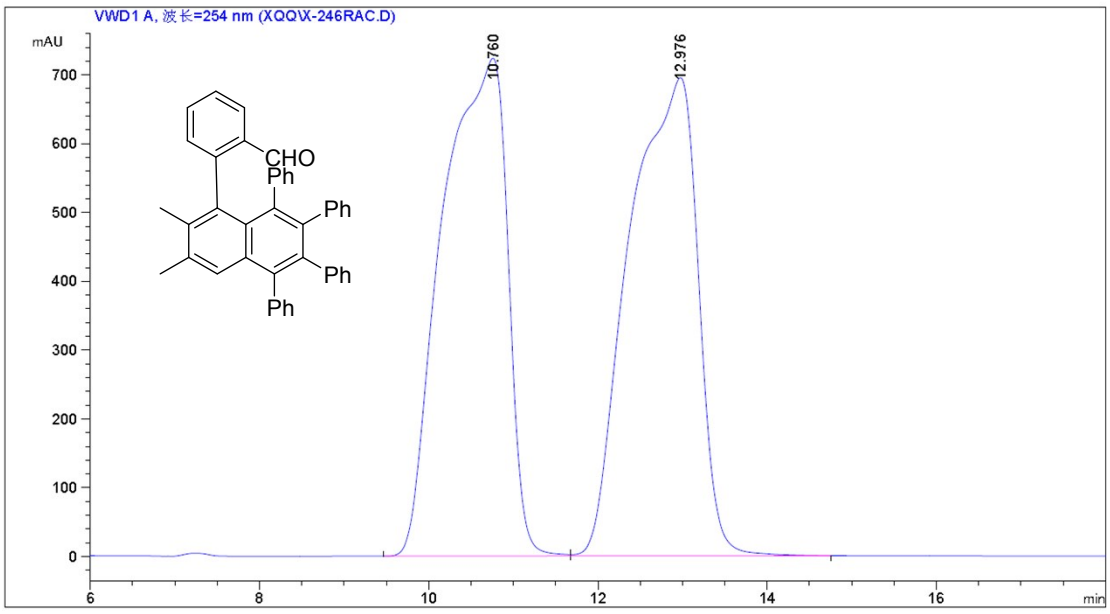



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.045 | MM | 1.3400 | 309.37045 | 2.75358 | 0.9435 |
| 2 | 14.524 | MM | 1.3021 | 3.24800e4 | 415.74069 | 99.0565 |

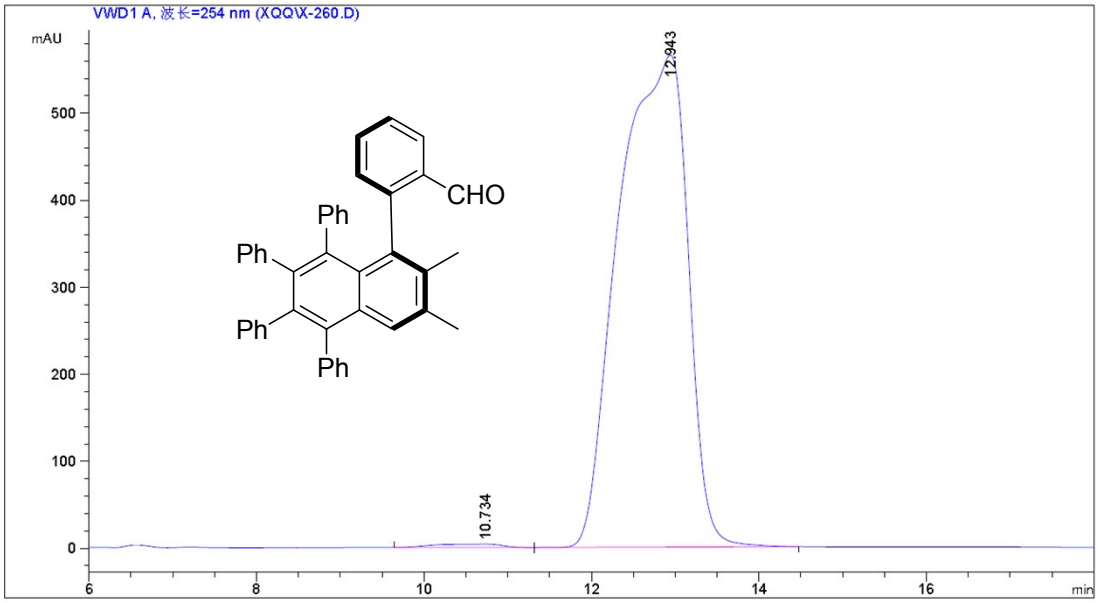
## 3p: IF, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.760 | BV | 0.7059 | 3.87175e4 | 723.42407 | 49.7485 |
| 2 | 12.976 | VB | 0.7498 | 3.91090e4 | 694.91608 | 50.2515 |

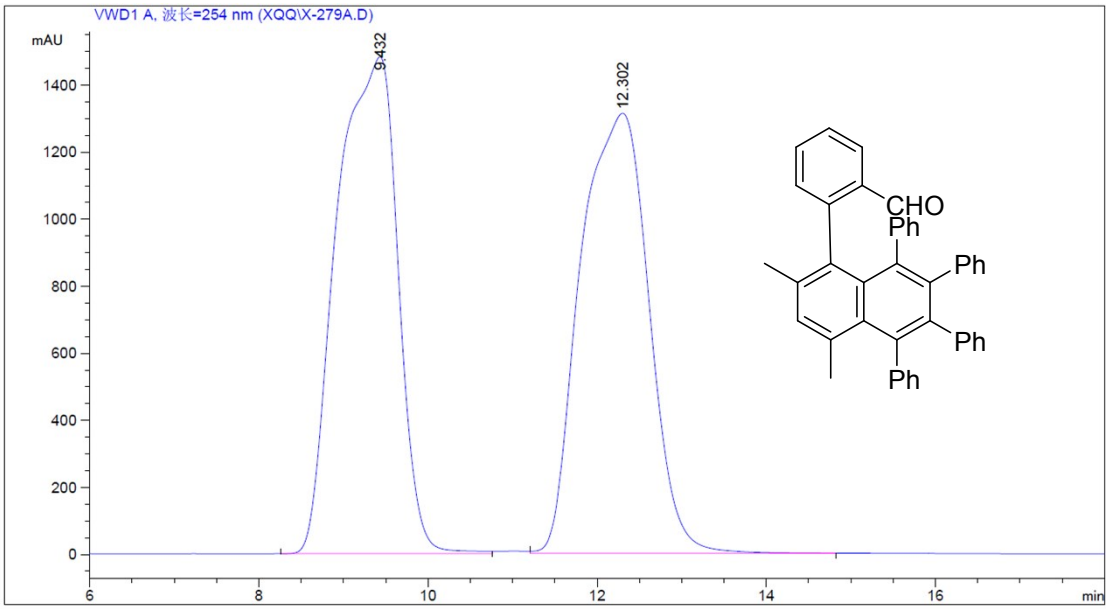



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.734 | BV | 0.7213 | 211.39554 | 3.81998 | 0.6506 |
| 2 | 12.943 | VB | 0.7579 | 3.22810e4 | 565.33911 | 99.3494 |

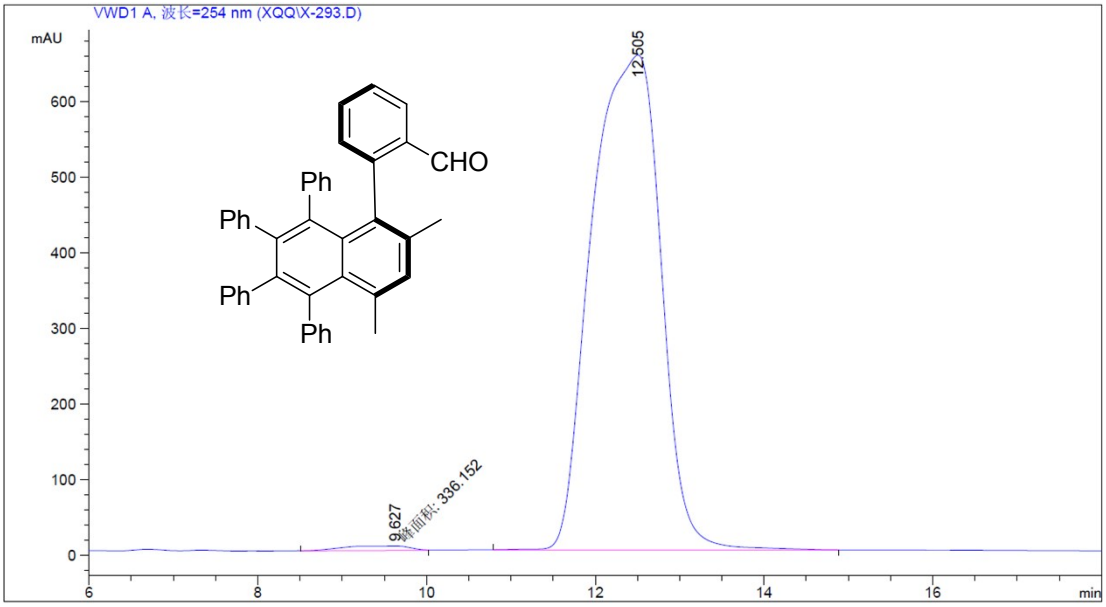
## 3q: IF, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

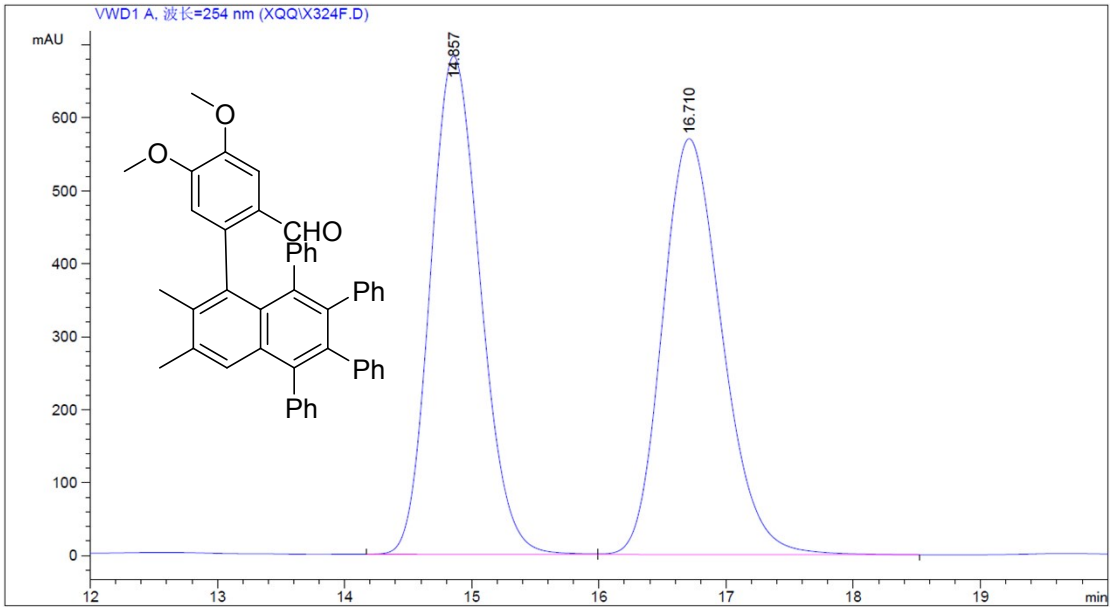
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.432 | BB | 0.6708 | 7.43068e4 | 1482.07251 | 50.2023 |
| 2 | 12.302 | VB | 0.7844 | 7.37080e4 | 1313.13452 | 49.7977 |




Area Percent Report

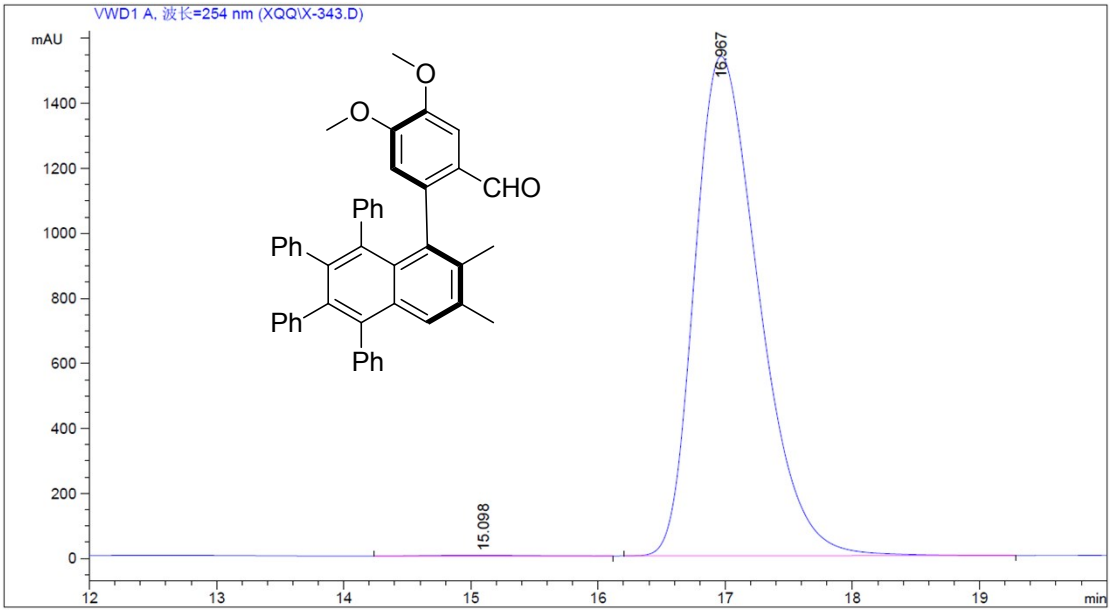
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.627 | MM | 0.9355 | 336.15219 | 5.98873 | 0.8951 |
| 2 | 12.505 | BB | 0.7759 | 3.72171e4 | 654.15155 | 99.1049 |

## 3r: IE, Hexane:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.857 | BV | 0.4267 | 1.85788e4 | 682.61273 | 49.9683 |
| 2 | 16.710 | VB | 0.5090 | 1.86023e4 | 569.88086 | 50.0317 |

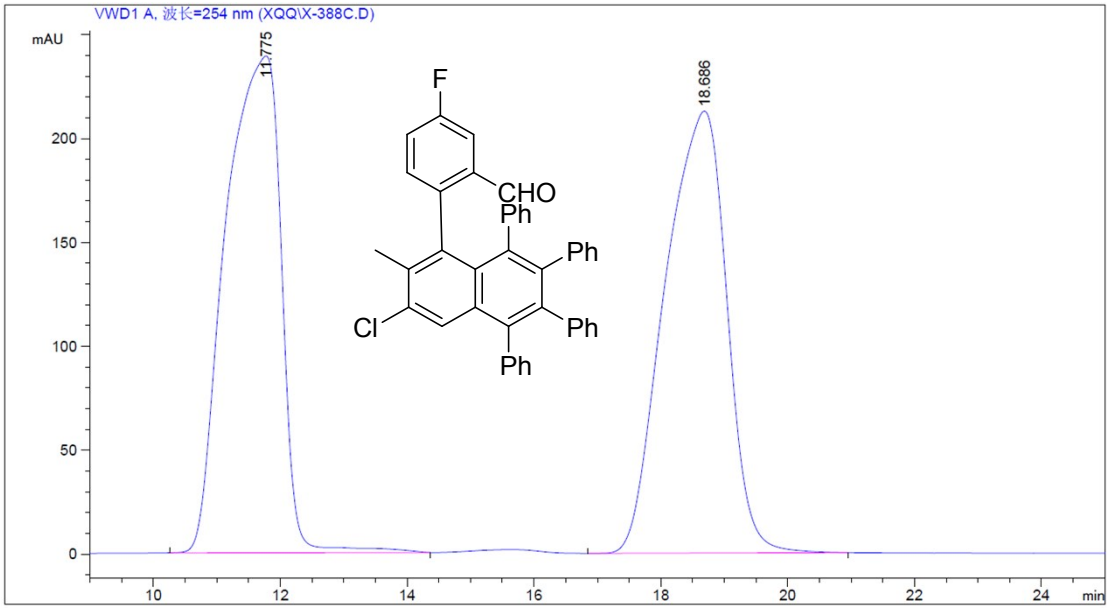



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.098 | BB | 0.5626 | 92.60342 | 2.33778 | 0.1714 |
| 2 | 16.967 | BB | 0.5434 | 5.39486e4 | 1537.21826 | 99.8286 |

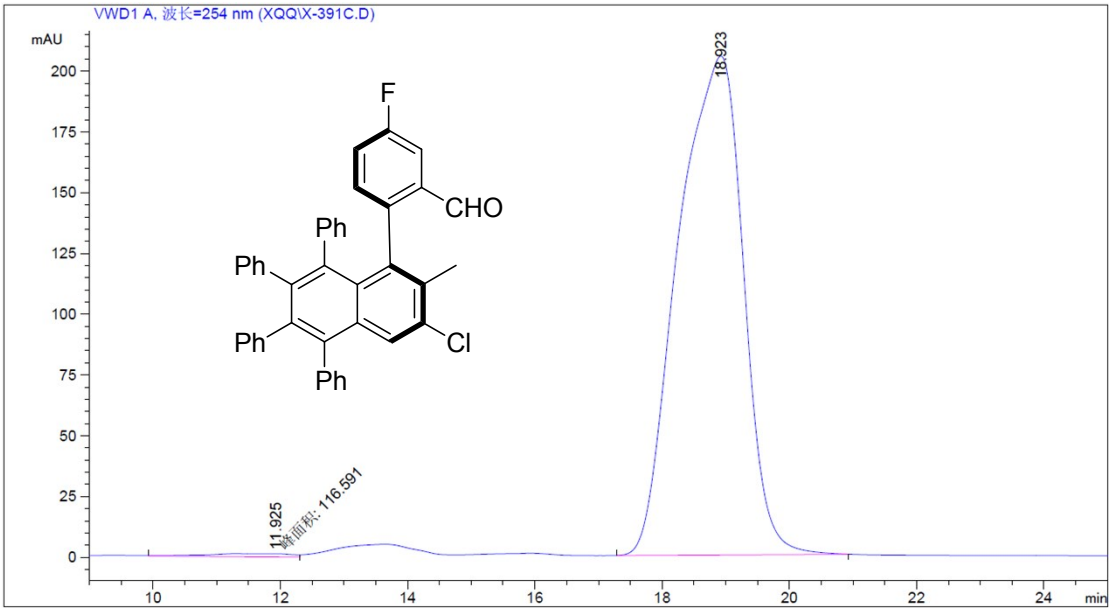
## 3s: IF, Hexane:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.775 | BB | 1.0345 | 1.45742e4 | 239.06995 | 50.3073 |
| 2 | 18.686 | VB | 1.1290 | 1.43961e4 | 212.67229 | 49.6927 |

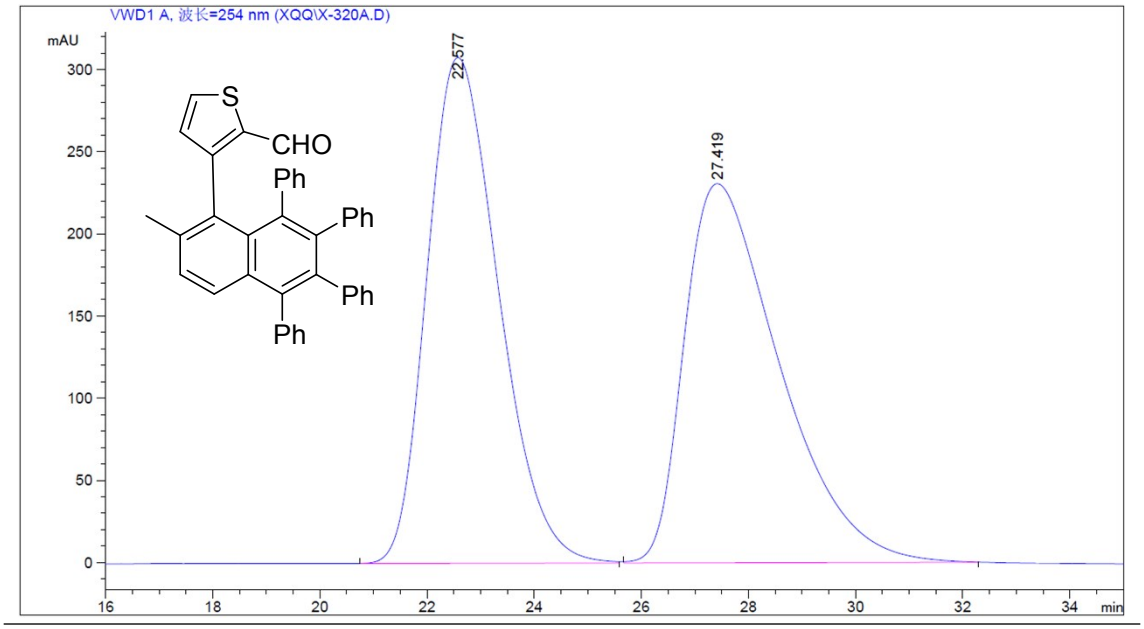



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.925 | MM | 1.5354 | 116.59081 | 1.26558 | 0.7921 |
| 2 | 18.923 | BB | 0.9944 | 1.46021e4 | 205.27820 | 99.2079 |

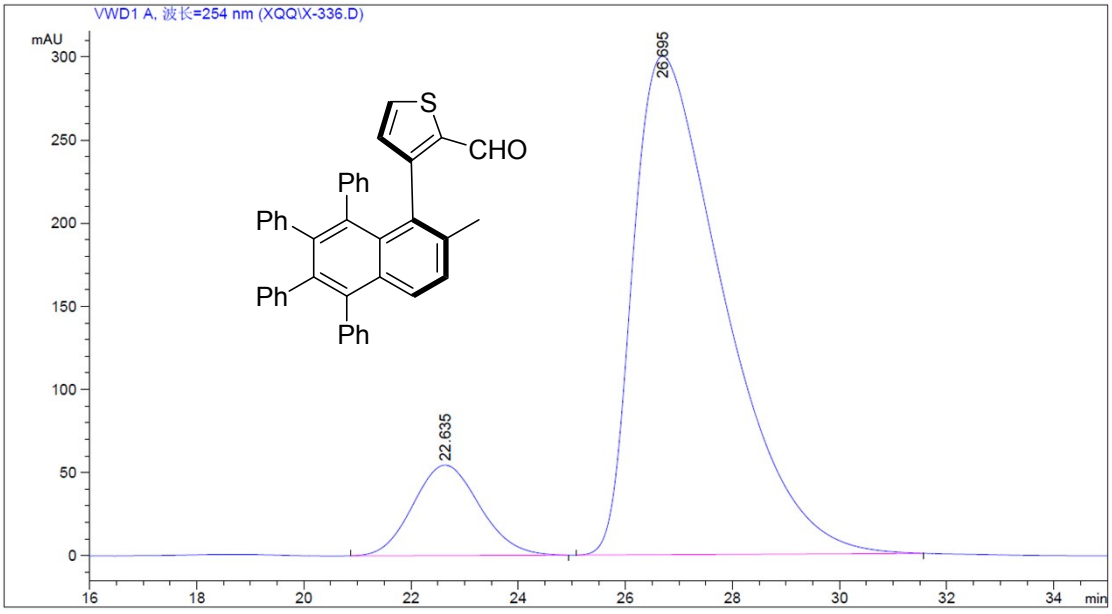
## 3t: OD-H, Hexane:*i*-PrOH = 98:2, 1 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

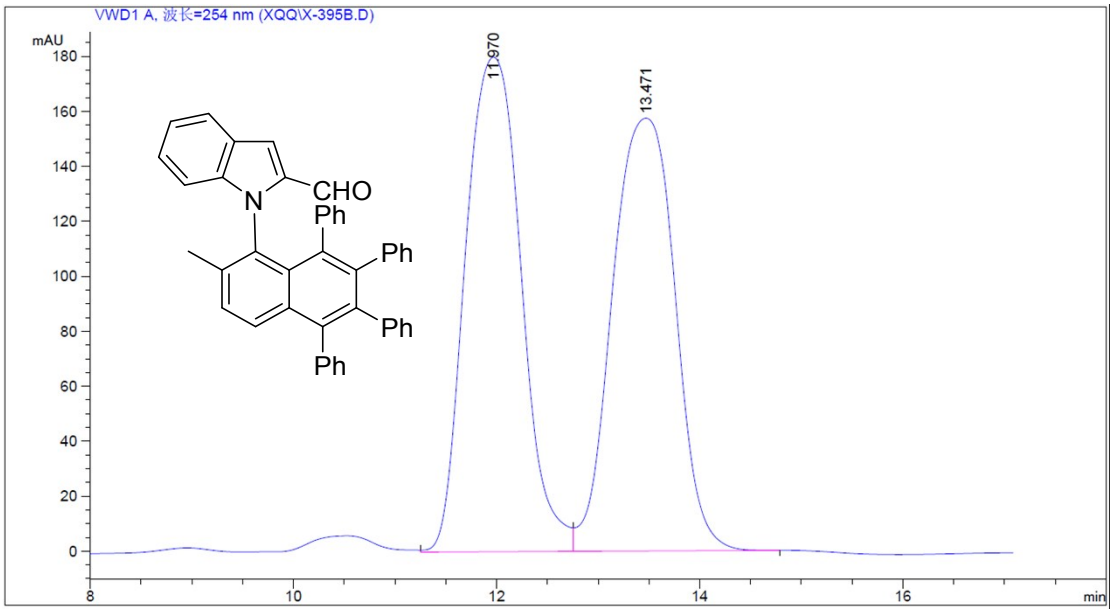
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.577 | BB | 1.4523 | 2.85215e4 | 307.79858 | 50.0081 |
| 2 | 27.419 | BB | 1.8804 | 2.85122e4 | 230.66533 | 49.9919 |




Area Percent Report

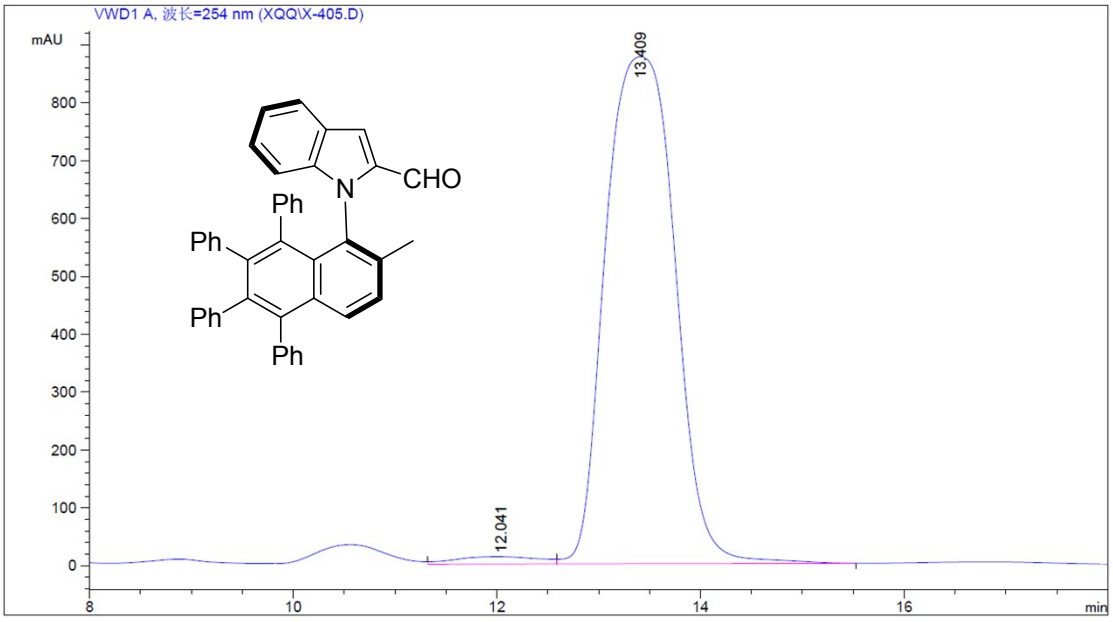
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.635 | BB | 1.3278 | 4719.09521 | 54.40889 | 11.8059 |
| 2 | 26.695 | BB | 1.7780 | 3.52534e4 | 299.81866 | 88.1941 |

## 3u: IE, Hexane:*i*-PrOH = 98:2, 0.8 mL/min, 254 nm




Area Percent Report

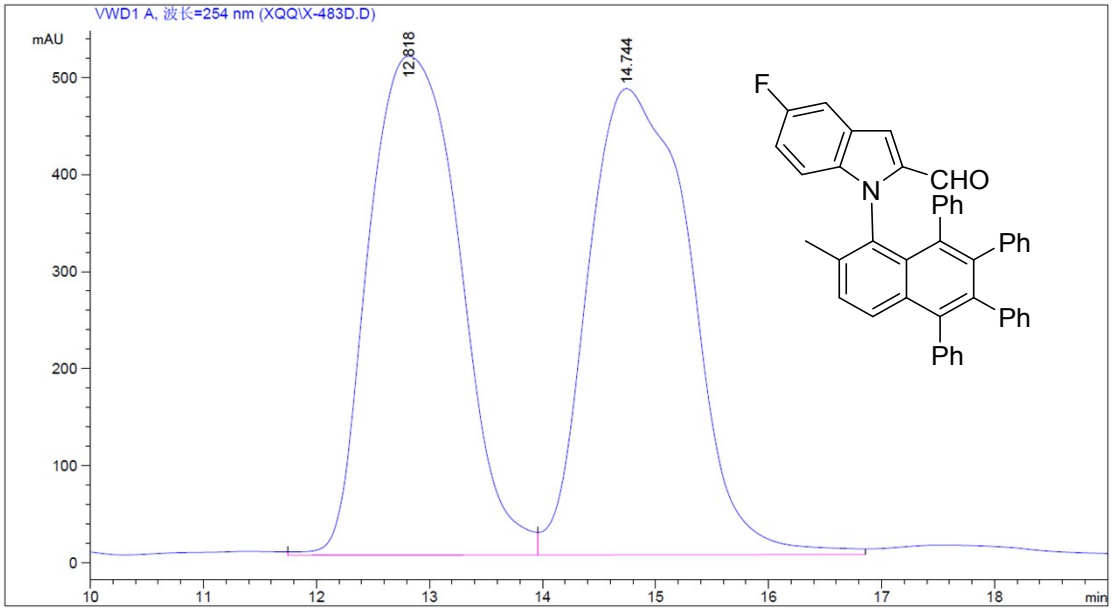
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.970 | VV | 0.6193 | 6855.26270 | 179.90010 | 50.3468 |
| 2 | 13.471 | VB | 0.6990 | 6760.81104 | 157.43958 | 49.6532 |




Area Percent Report

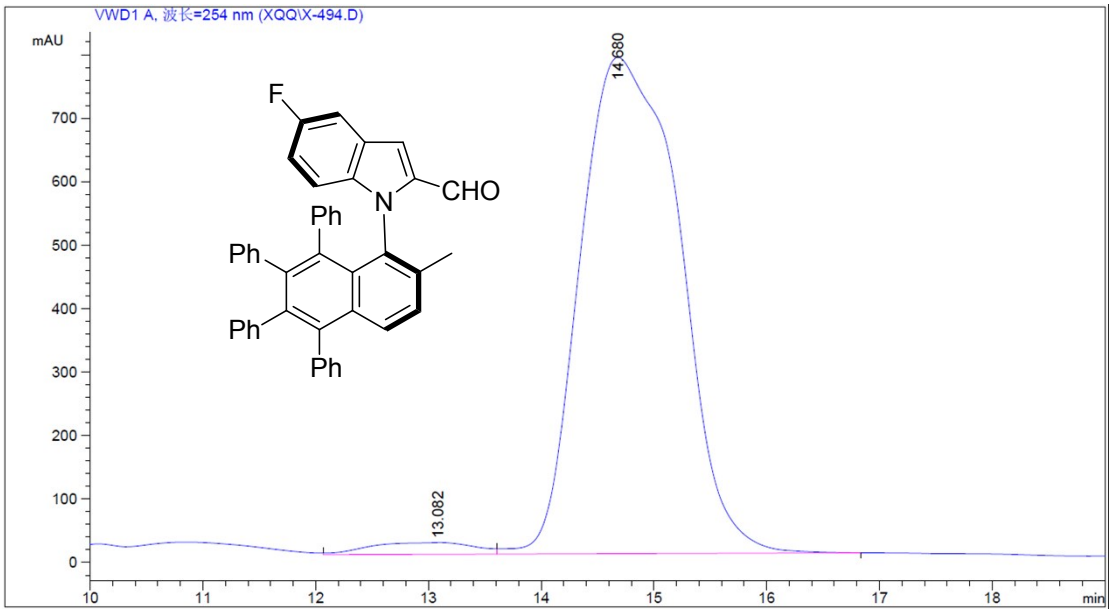
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.041 | VV | 0.7701 | 737.07098 | 12.62151 | 1.7440 |
| 2 | 13.409 | VB | 0.7784 | 4.15260e4 | 876.51514 | 98.2560 |

## 3v:IE, Hexane:*i*-PrOH = 99:1, 0.8 mL/min, 254 nm




Area Percent Report

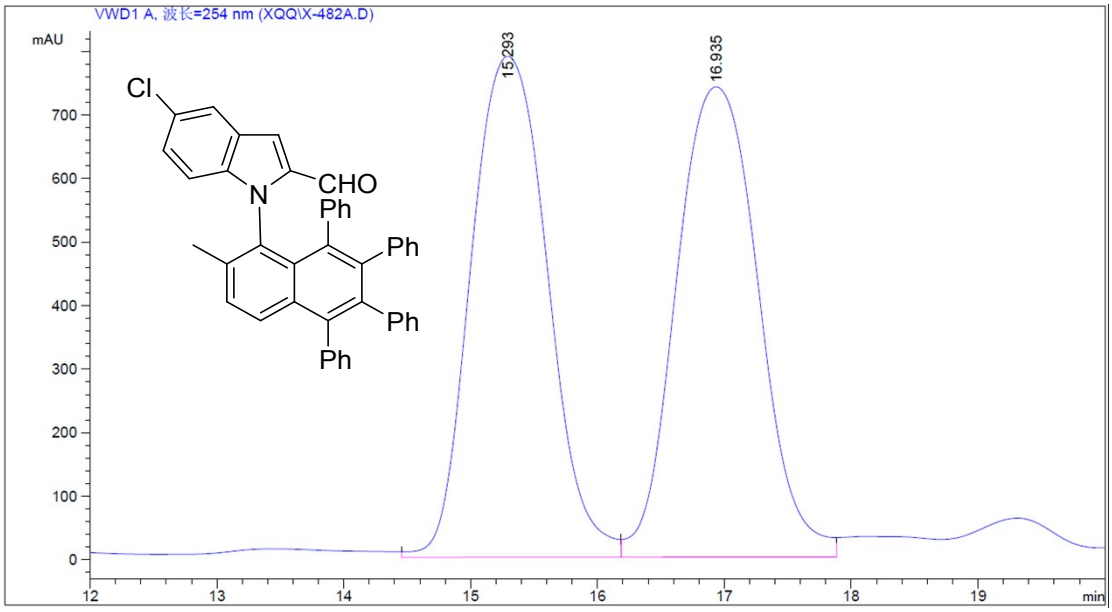
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.818 | VV | 0.9335 | 2.88951e4 | 514.35602 | 48.8020 |
| 2 | 14.744 | VB | 0.9006 | 3.03138e4 | 480.47192 | 51.1980 |




Area Percent Report

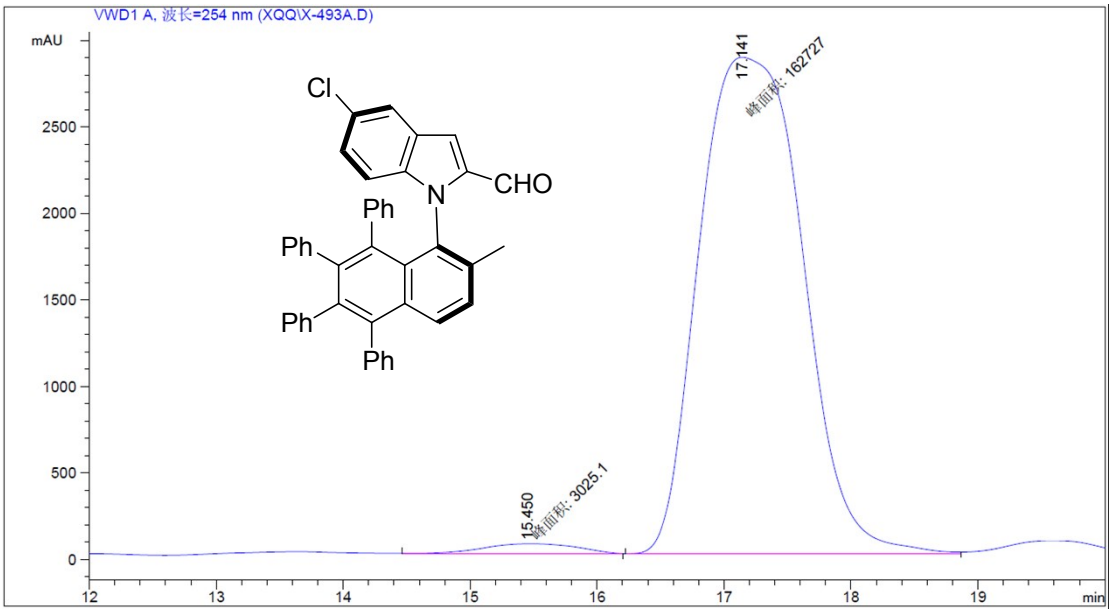
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.082 | VV | 0.8797 | 1202.29089 | 18.59020 | 2.4486 |
| 2 | 14.680 | VB | 0.8763 | 4.78981e4 | 781.91364 | 97.5514 |

## 3w: IE, Hexane:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm




Area Percent Report

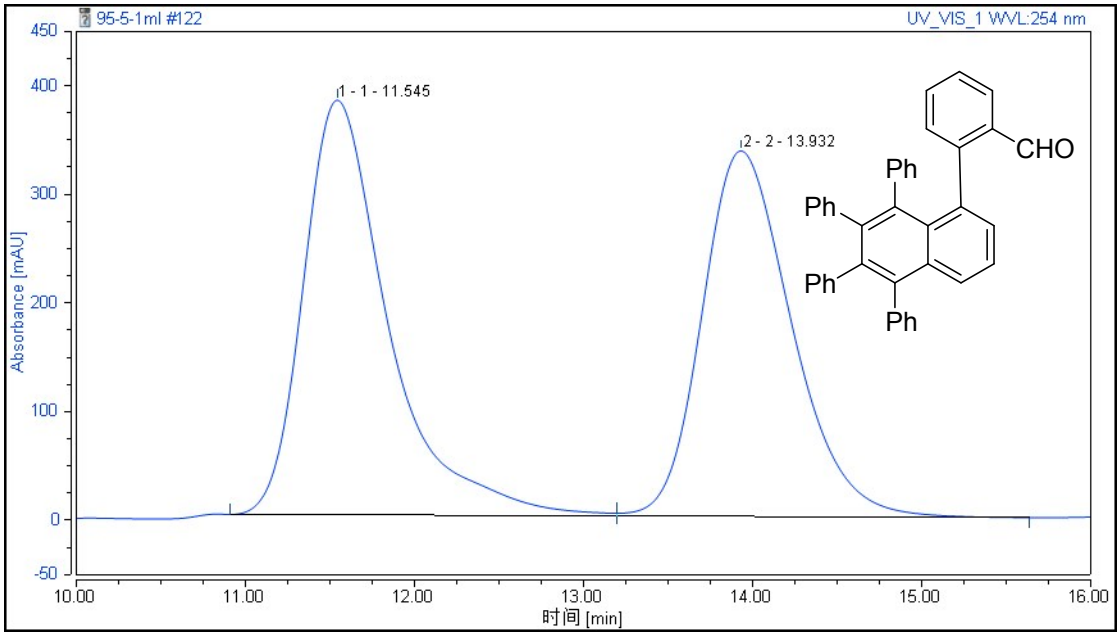
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.293 | VV | 0.6730 | 3.29785e4 | 788.23993 | 49.7497 |
| 2 | 16.935 | VV | 0.7261 | 3.33104e4 | 739.96698 | 50.2503 |




Area Percent Report

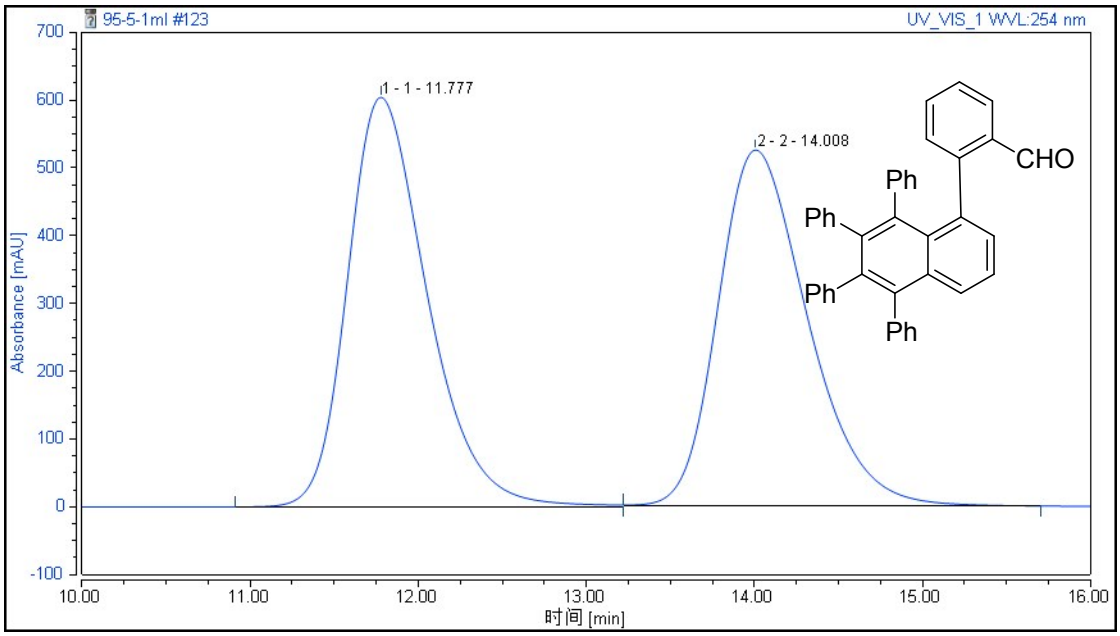
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.450 | MM | 0.8636 | 3025.10278 | 58.38102 | 1.8251 |
| 2 | 17.141 | MM | 0.9451 | 1.62727e5 | 2869.56323 | 98.1749 |

**3aa: OD-H, Hexane:*i*-PrOH = 95:5, 1 mL/min, 254 nm**




Area Percent Report

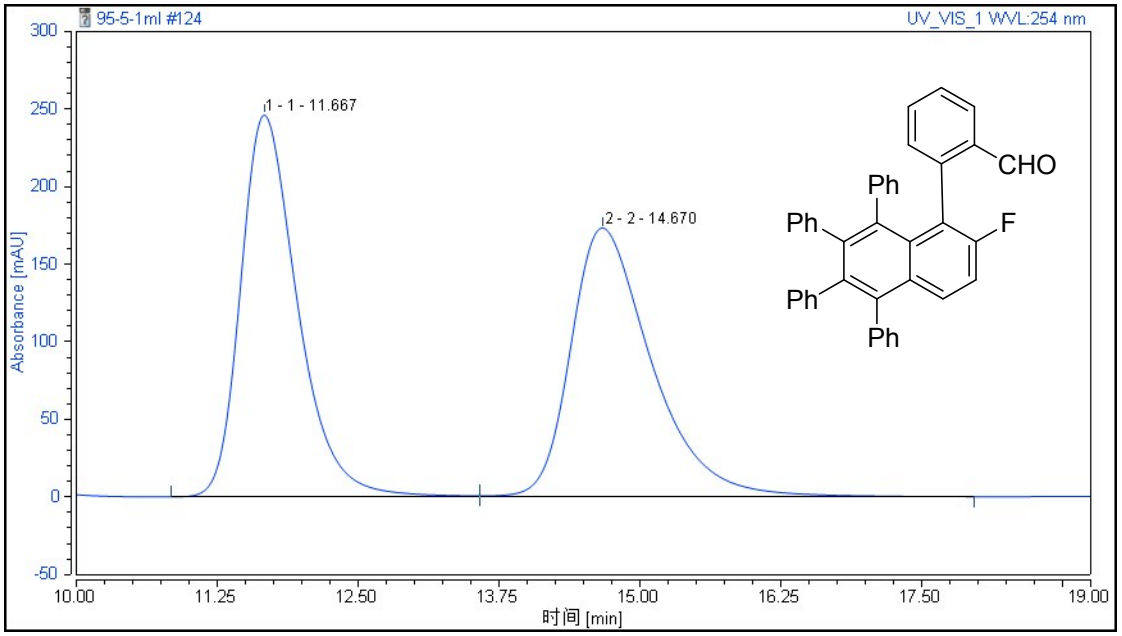
| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.545 | 222.604 | 381.728 | 51.85 | 53.14 |
| 2 | 13.932 | 206.680 | 336.556 | 48.15 | 46.86 |




Area Percent Report

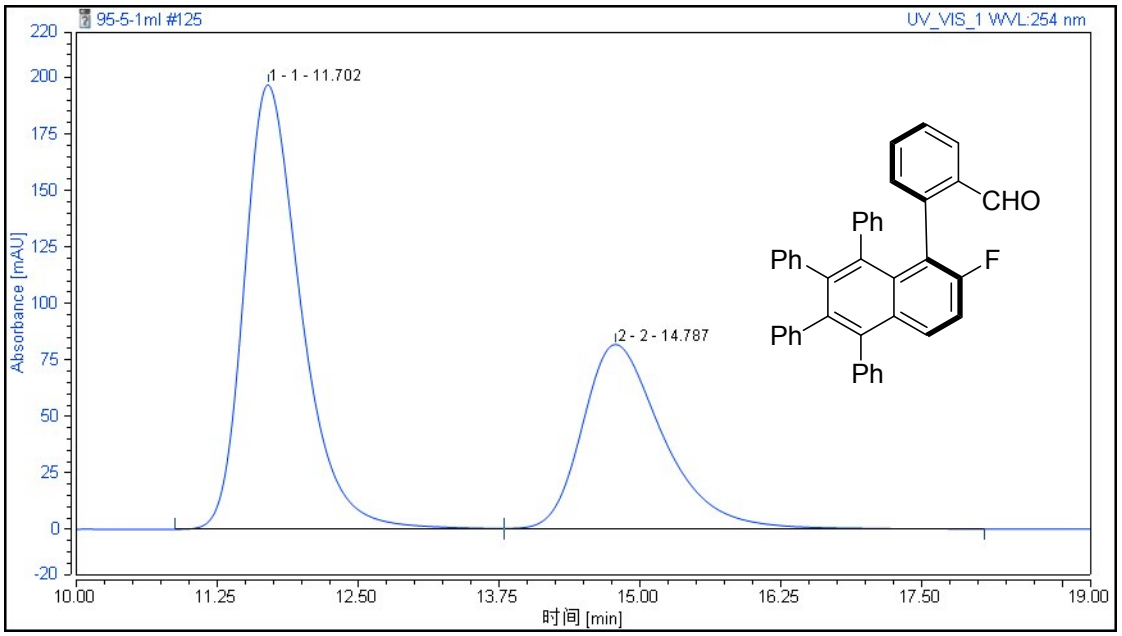
| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.777 | 332.012 | 604.051 | 50.42 | 53.47 |
| 2 | 14.008 | 326.541 | 525.636 | 49.58 | 46.53 |

## 3bb: OD-H, Hexane:*i*-PrOH = 95:5, 1 mL/min, 254 nm




Area Percent Report

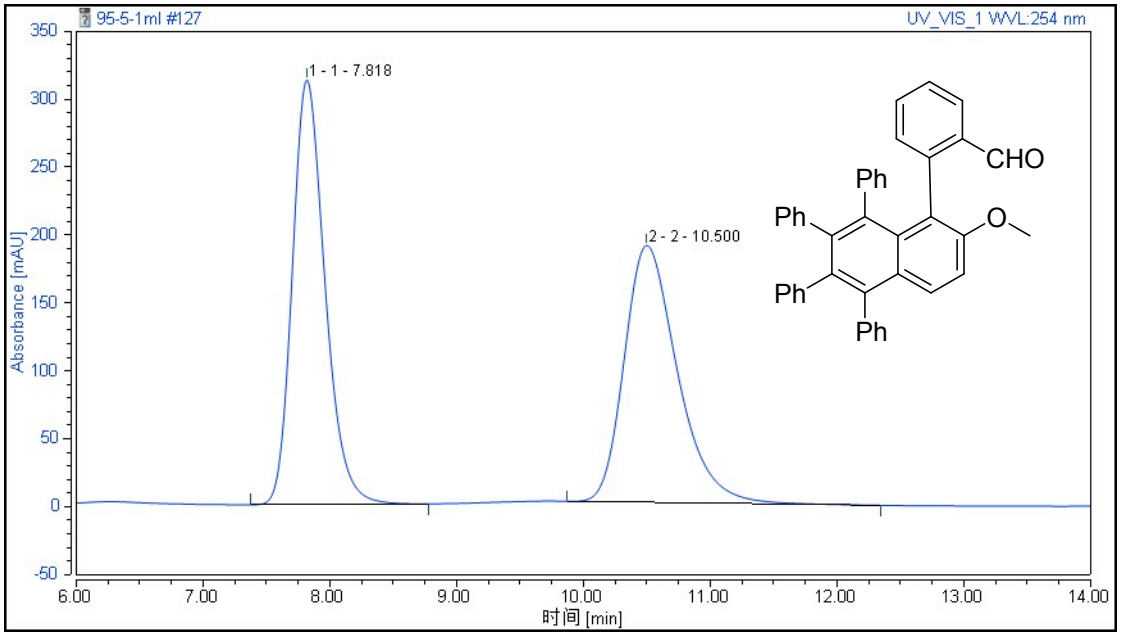
| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.667 | 144.052 | 246.049 | 49.96 | 58.68 |
| 2 | 14.670 | 144.282 | 173.231 | 50.04 | 41.32 |




Area Percent Report

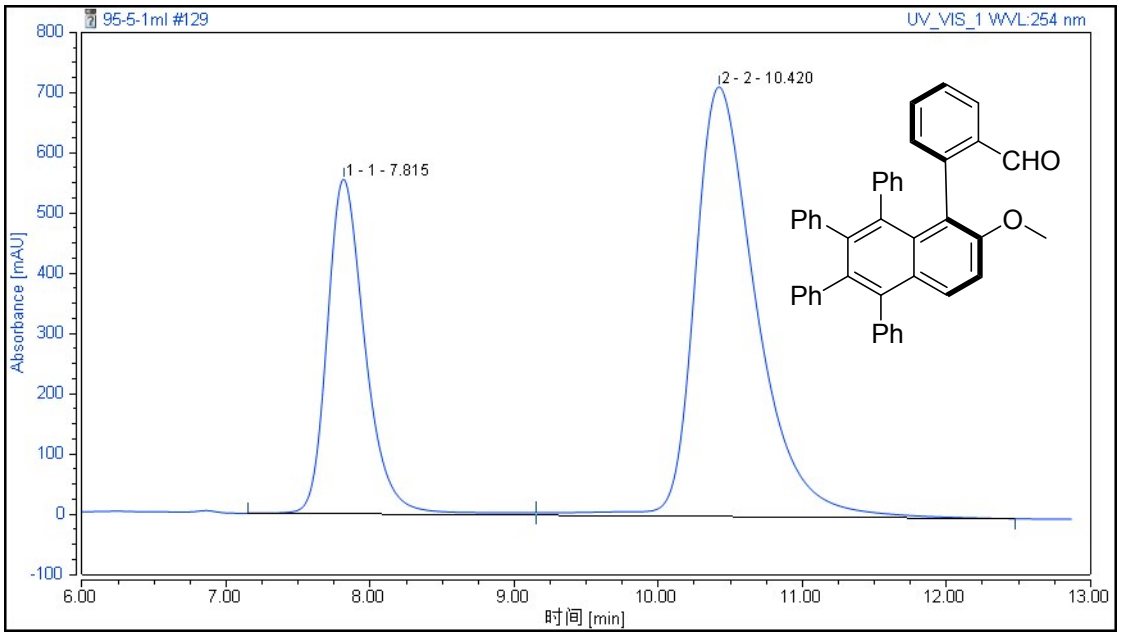
| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.702 | 114.728 | 196.673 | 62.68 | 70.64 |
| 2 | 14.787 | 68.312 | 81.740 | 37.32 | 29.36 |

## 3cc: OD-H, Hexane:*i*-PrOH = 95:5, 1 mL/min, 254 nm




Area Percent Report

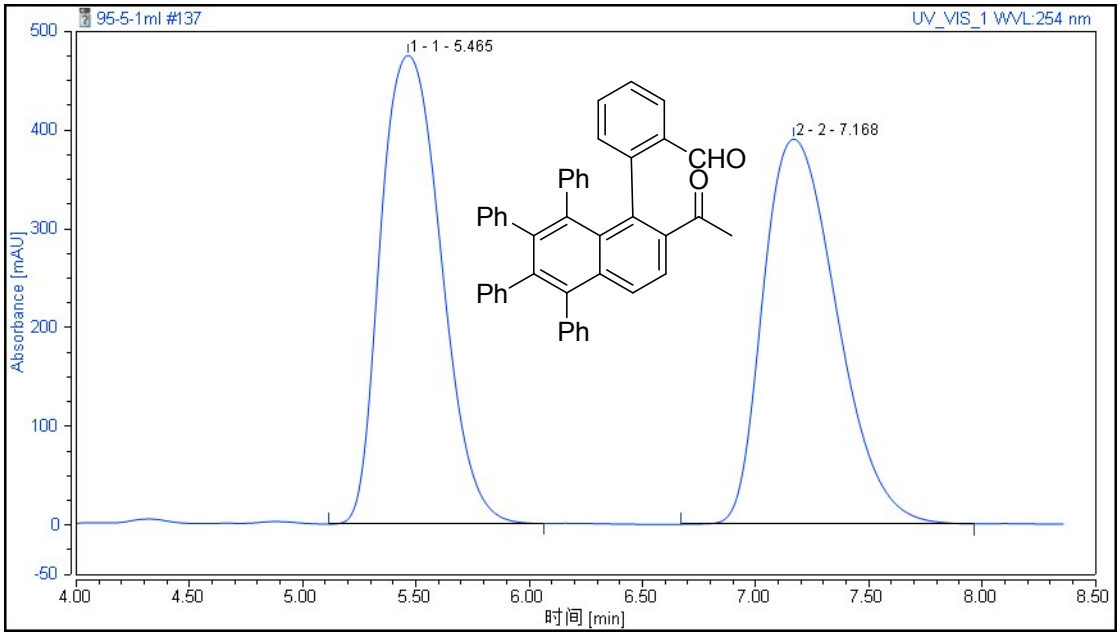
| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.818 | 93.195 | 312.793 | 50.38 | 62.31 |
| 2 | 10.500 | 91.793 | 189.199 | 49.62 | 37.69 |




Area Percent Report

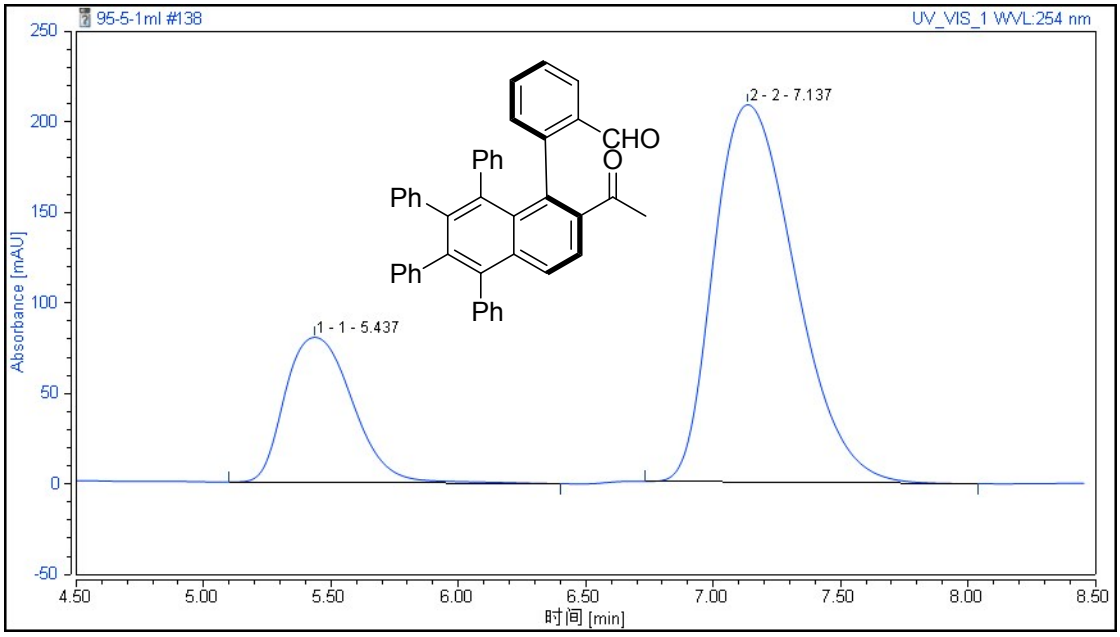
| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.815 | 170.348 | 555.560 | 32.49 | 43.79 |
| 2 | 10.420 | 353.952 | 713.266 | 67.51 | 56.21 |

## 3dd: AD-H, Hexane:*i*-PrOH = 95:5, 1 mL/min, 254 nm




Area Percent Report

| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.465 | 147.303 | 474.437 | 50.00 | 54.90 |
| 2 | 7.168 | 147.297 | 389.807 | 50.00 | 45.10 |

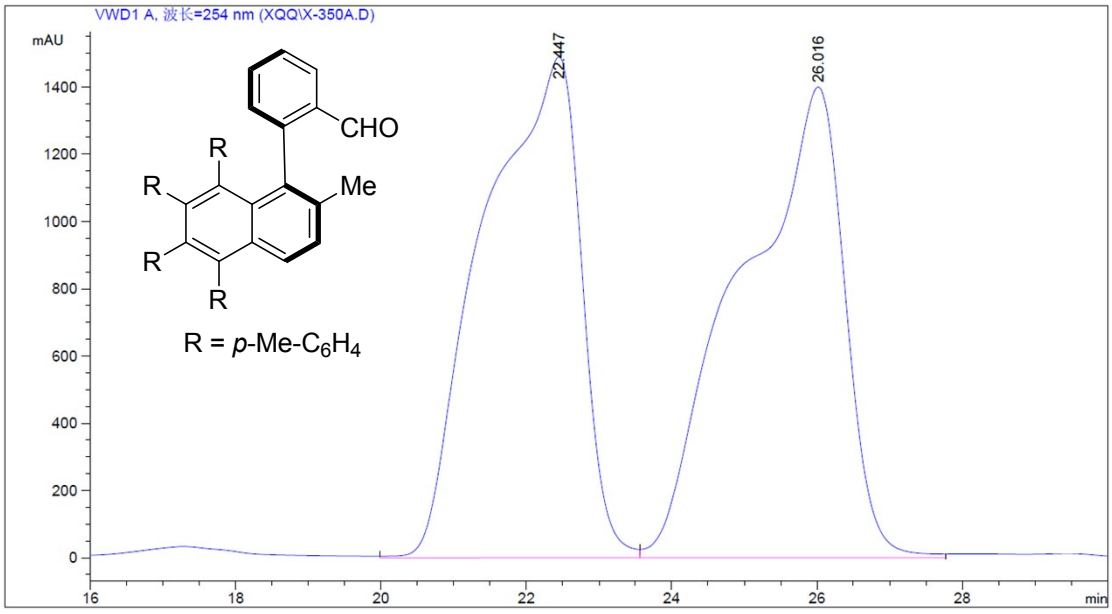



Area Percent Report

| Peack # | RetTime [min] | Area [mAU*min] | Height [mAU] | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.437 | 24.759 | 80.170 | 24.24 | 27.78 |
| 2 | 7.137 | 77.370 | 208.464 | 75.76 | 72.22 |

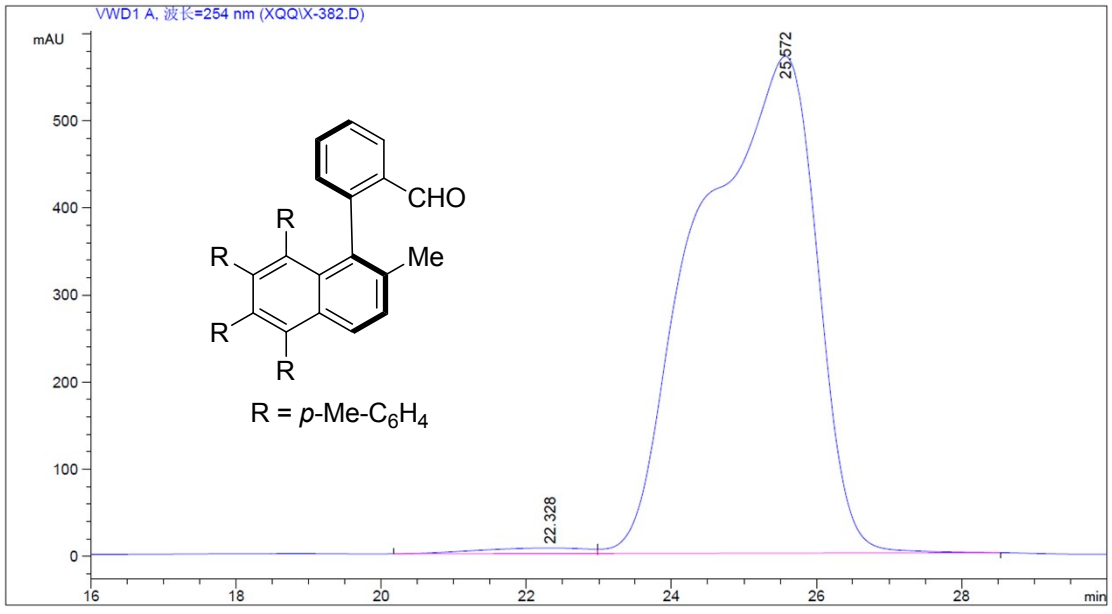
## 4a: IF, Hexane:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.447 | BV | 1.2293 | 1.39244e5 | 1489.07483 | 50.0212 |
| 2 | 26.016 | VV | 1.3390 | 1.39126e5 | 1399.31702 | 49.9788 |

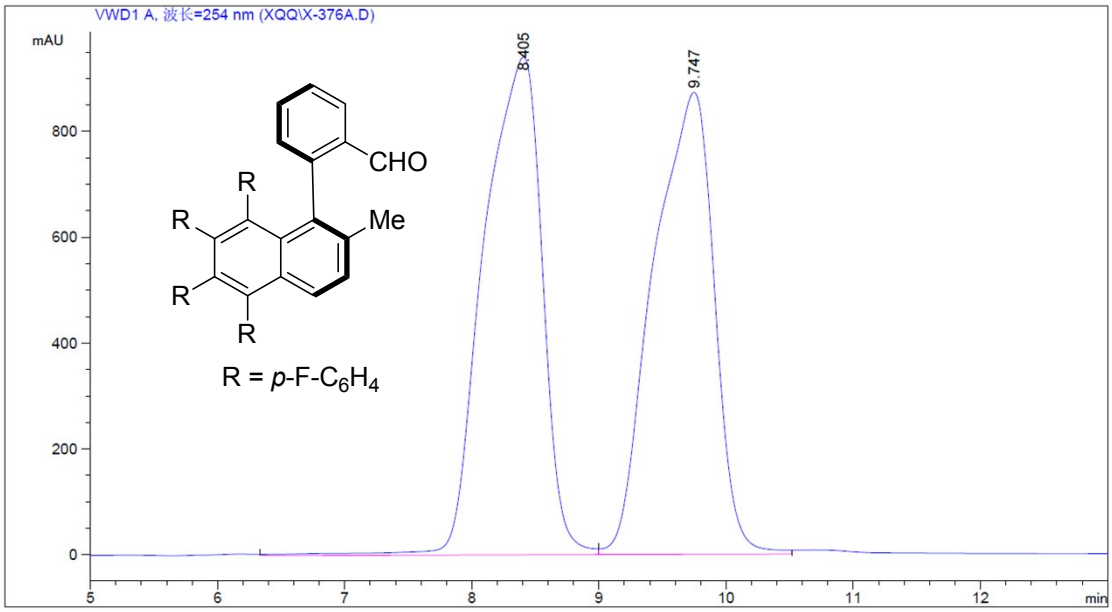



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.328 | BV | 1.2225 | 656.18213 | 6.38363 | 1.0149 |
| 2 | 25.572 | VB | 1.5084 | 6.39994e4 | 570.43384 | 98.9851 |

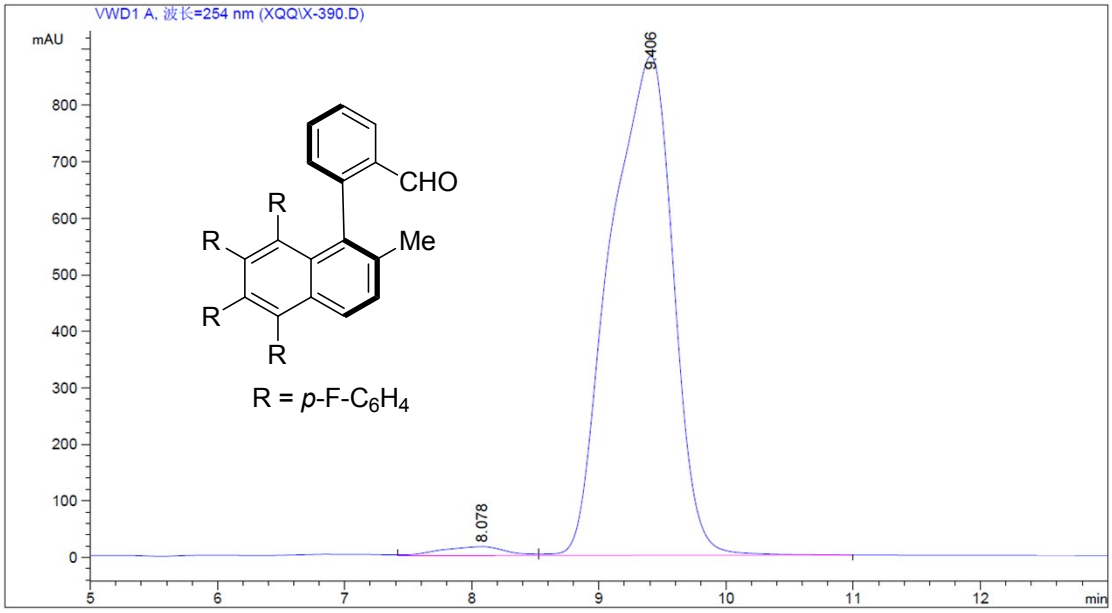
## 4b: IF, Hexane:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.405 | VV | 0.5399 | 3.00346e4 | 940.76556 | 50.8109 |
| 2 | 9.747 | VV | 0.4642 | 2.90759e4 | 873.20990 | 49.1891 |

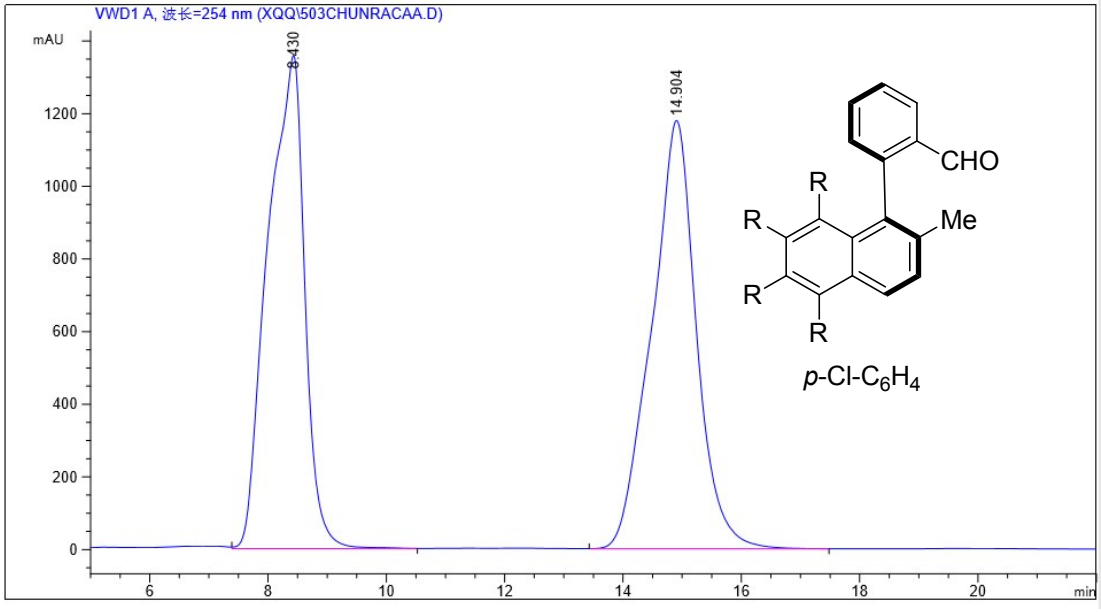



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.078 | VV | 0.4930 | 564.74939 | 15.95645 | 1.8298 |
| 2 | 9.406 | VB | 0.4859 | 3.02998e4 | 883.72321 | 98.1702 |

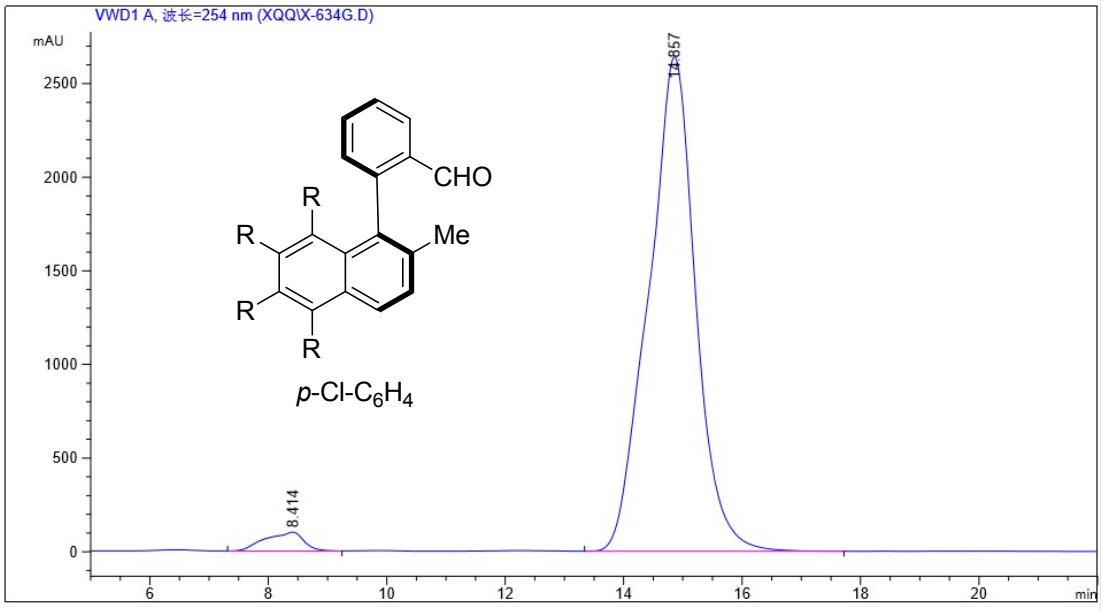
## 4c: AD-H, Hexane:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.430 | VB | 0.5758 | 5.87046e4 | 1357.64685 | 48.7507 |
| 2 | 14.904 | BB | 0.7447 | 6.17134e4 | 1178.87463 | 51.2493 |

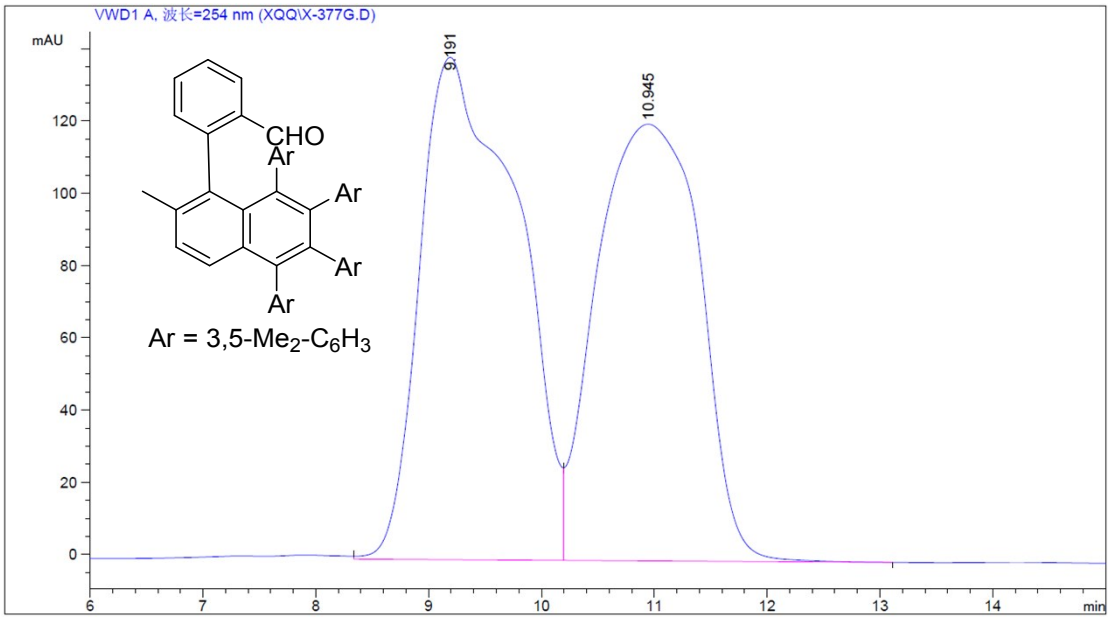



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.414 | VV | 0.5985 | 4589.33691 | 101.28914 | 3.0657 |
| 2 | 14.857 | VB | 0.7868 | 1.45110e5 | 2640.30298 | 96.9343 |

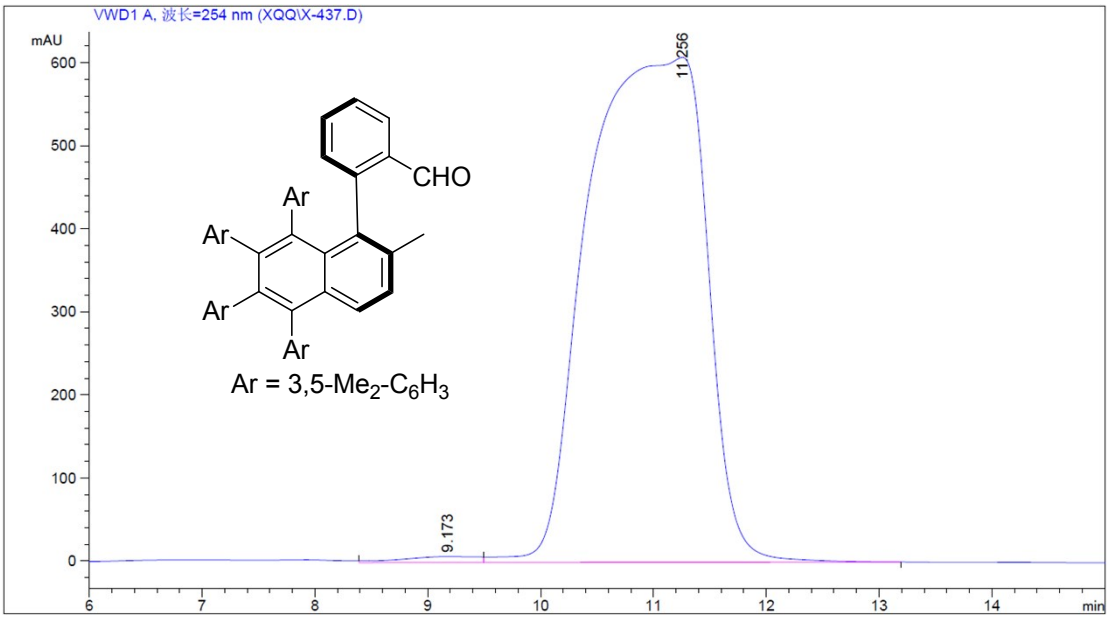
## 4d: IF, Hexane:*i*-PrOH = 98:2, 0.8 mL/min, 254 nm

Transform the aldehyde to the corresponding alcohol by $NaBH_4$ and then the ee was determined by HPLC analysis.




Area Percent Report

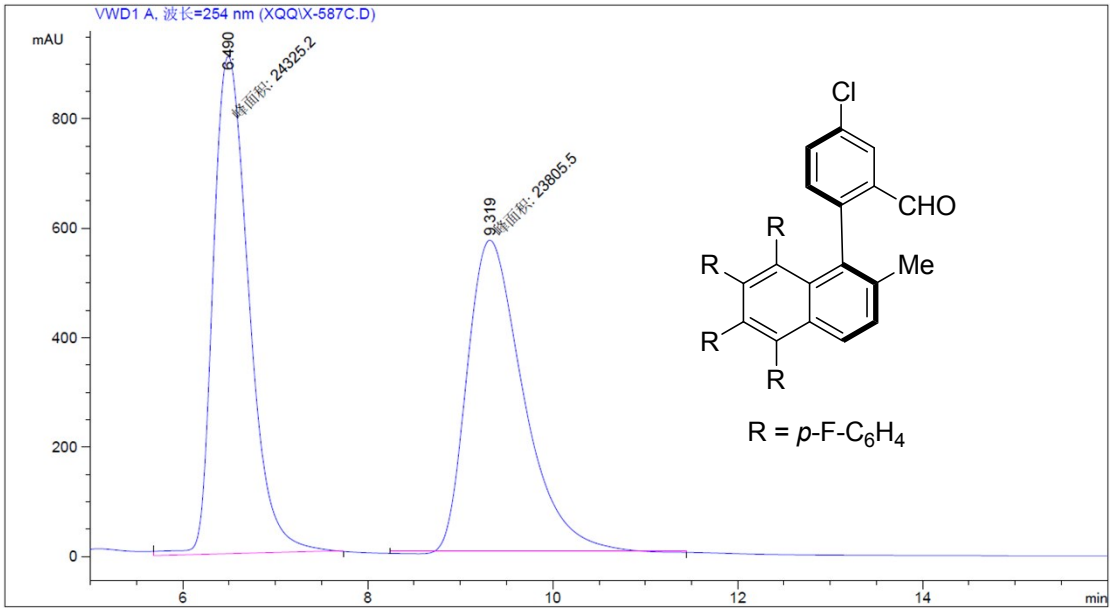
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.191 | VV | 0.8130 | 8333.54102 | 139.00182 | 51.9120 |
| 2 | 10.945 | VB | 1.0699 | 7719.67236 | 120.85593 | 48.0880 |




Area Percent Report

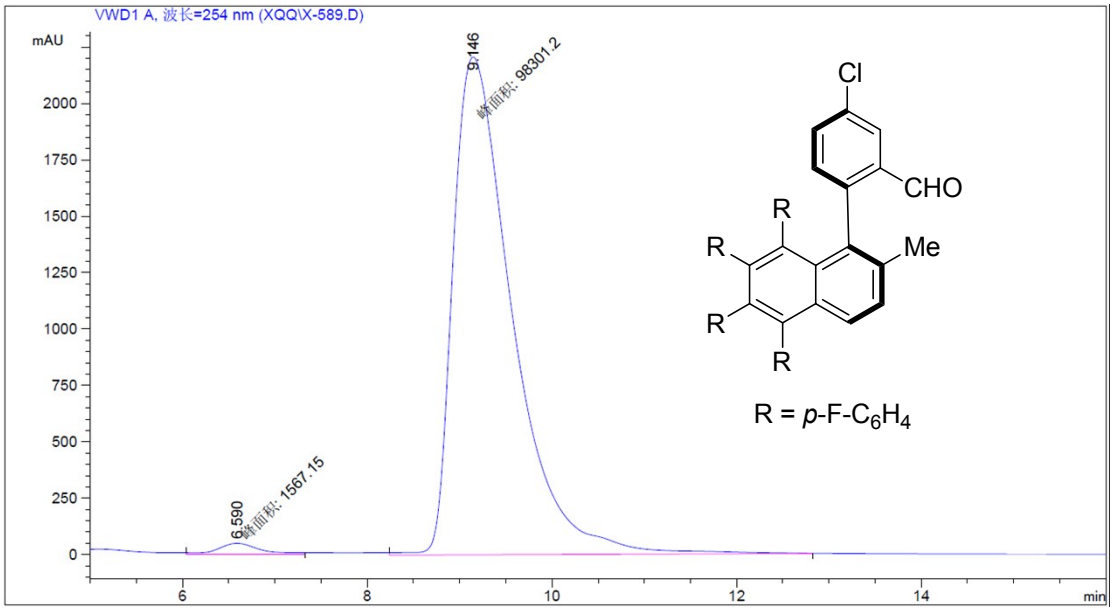
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.173 | VV | 0.6303 | 340.67642 | 7.18587 | 0.7651 |
| 2 | 11.256 | VB | 0.9338 | 4.41870e4 | 607.99768 | 99.2349 |

## 4f: OD-H, Hexane:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm




Area Percent Report

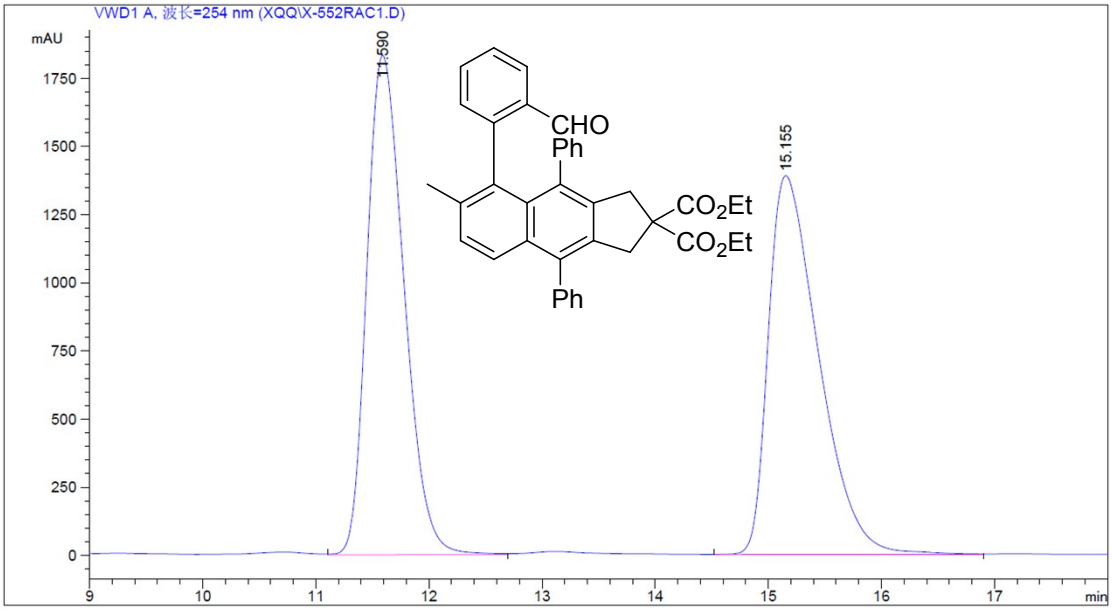
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.490 | MM | 0.4458 | 2.43252e4 | 909.51648 | 50.5400 |
| 2 | 9.319 | MM | 0.6987 | 2.38055e4 | 567.84180 | 49.4600 |




Area Percent Report

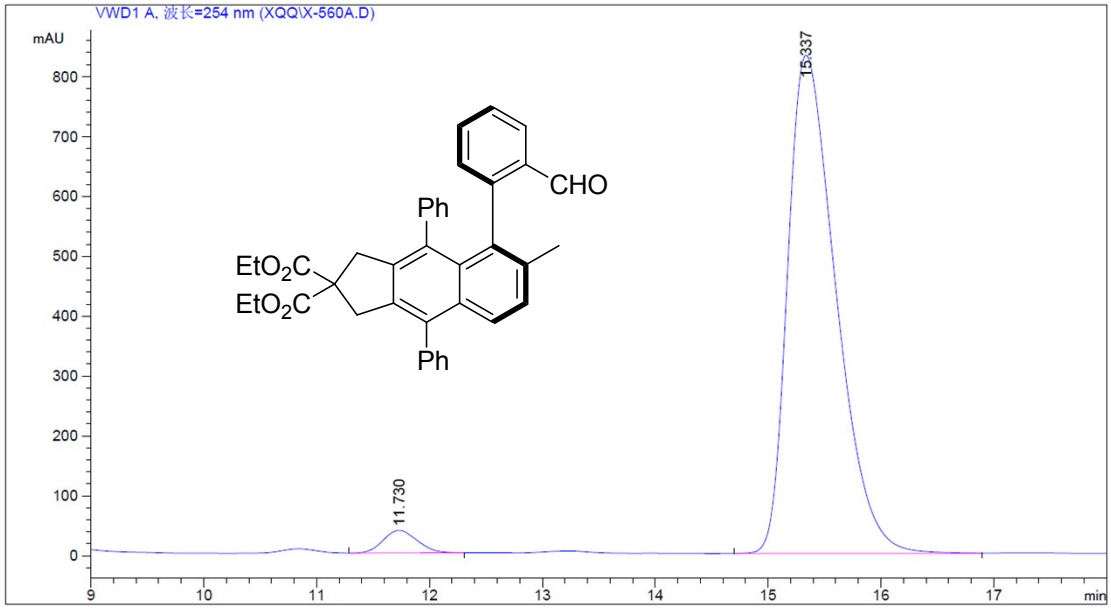
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.590 | MM | 0.5373 | 1567.15442 | 48.61612 | 1.5692 |
| 2 | 9.146 | MM | 0.7423 | 9.83012e4 | 2207.03760 | 98.4308 |

## 4g: IE, Hexane:*i*-PrOH = 9:1, 1.0 mL/min, 254 nm




Area Percent Report

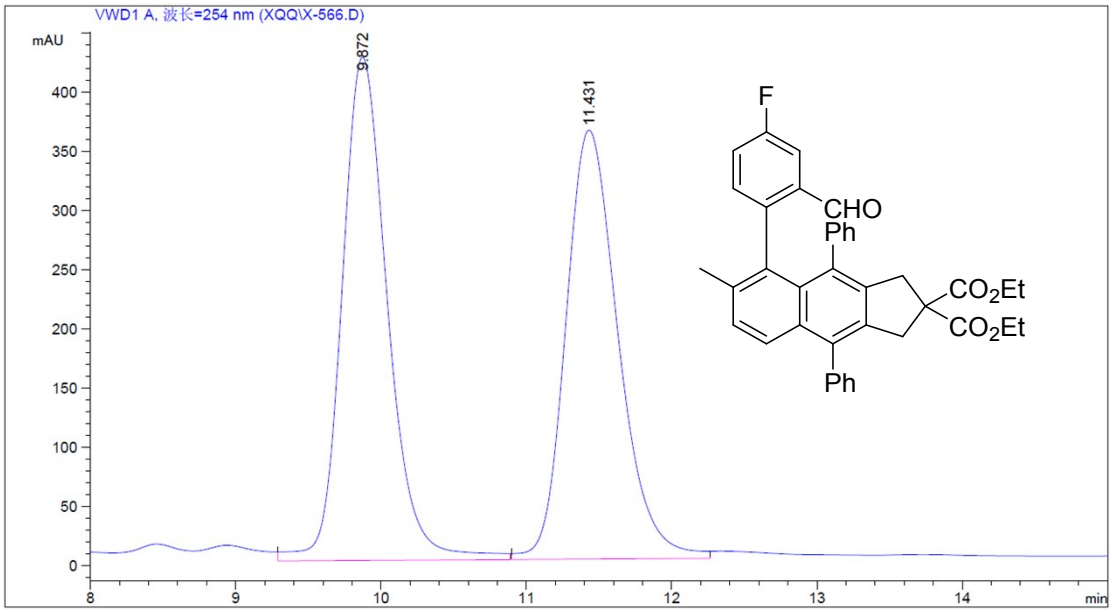
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.590 | VV | 0.3585 | 4.18932e4 | 1831.93298 | 49.3791 |
| 2 | 15.155 | BB | 0.4756 | 4.29467e4 | 1389.45398 | 50.6209 |




Area Percent Report

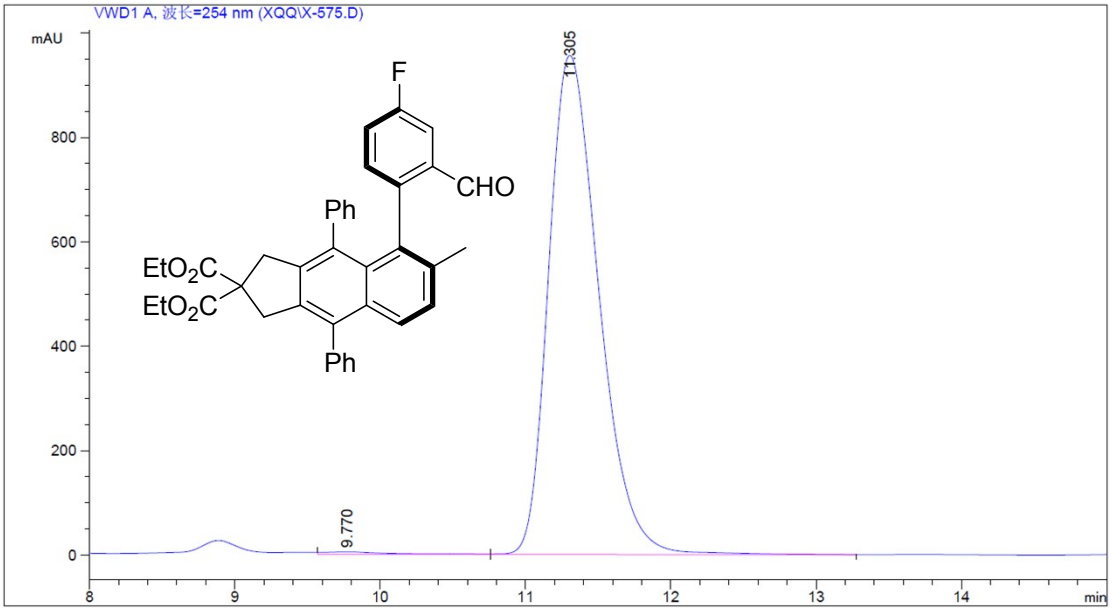
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.730 | VB | 0.3272 | 789.65918 | 37.72771 | 3.1077 |
| 2 | 15.337 | BB | 0.4575 | 2.46202e4 | 831.58112 | 96.8923 |

## 4h: IE, Hexane:*i*-PrOH = 9:1, 1.0 mL/min, 254 nm




Area Percent Report

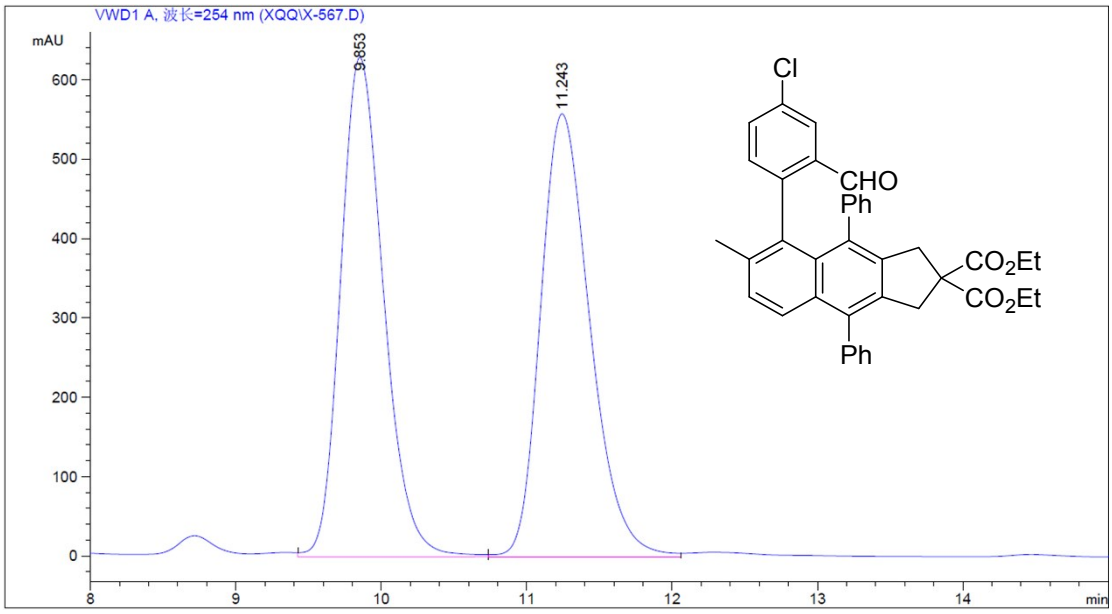
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.872 | VB | 0.3347 | 9278.74512 | 425.11365 | 50.5507 |
| 2 | 11.431 | BB | 0.3855 | 9076.59375 | 362.27454 | 49.4493 |




Area Percent Report

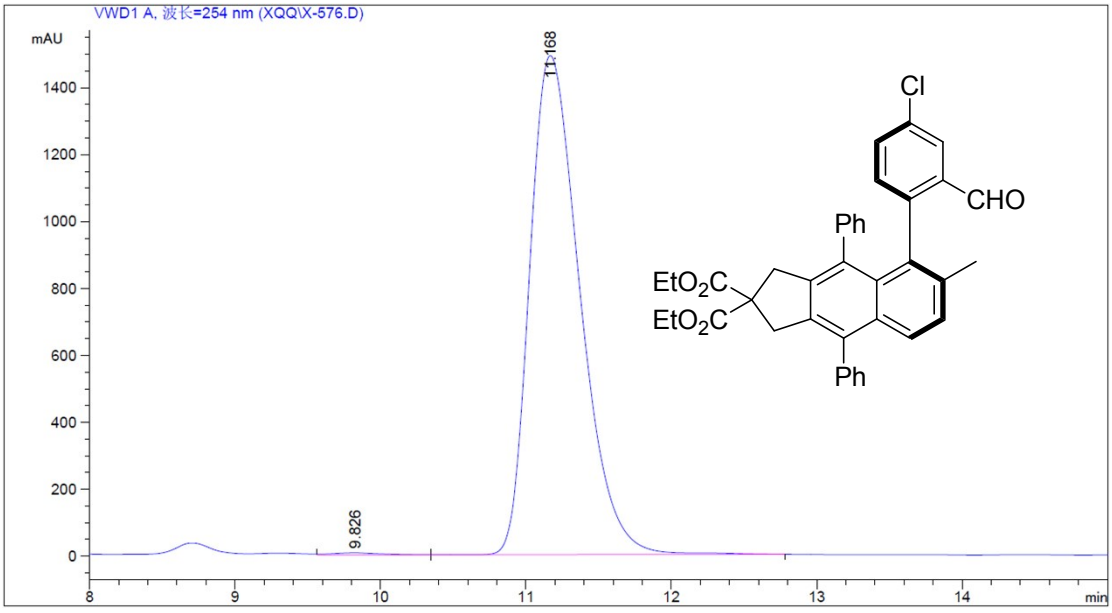
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.770 | VV | 0.4677 | 173.04166 | 5.00151 | 0.7484 |
| 2 | 11.305 | VB | 0.3731 | 2.29478e4 | 956.38550 | 99.2516 |

## 4i: IE, Hexane:*i*-PrOH = 9:1, 1.0 mL/min, 254 nm




Area Percent Report

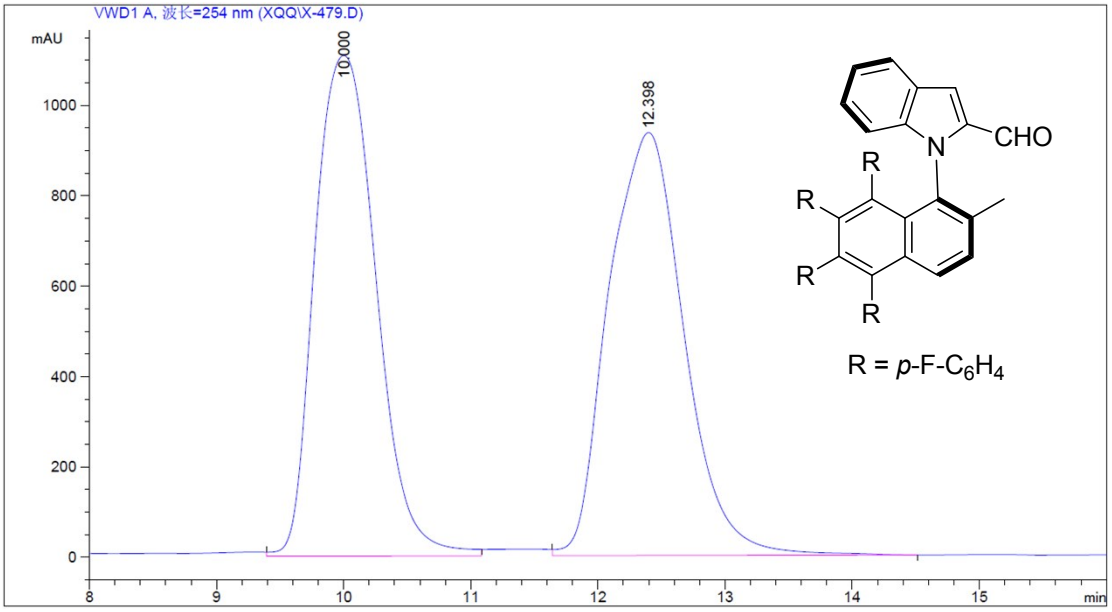
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.853 | VV | 0.3186 | 1.29416e4 | 629.25543 | 49.5472 |
| 2 | 11.243 | VV | 0.3643 | 1.31782e4 | 558.01477 | 50.4528 |




Area Percent Report

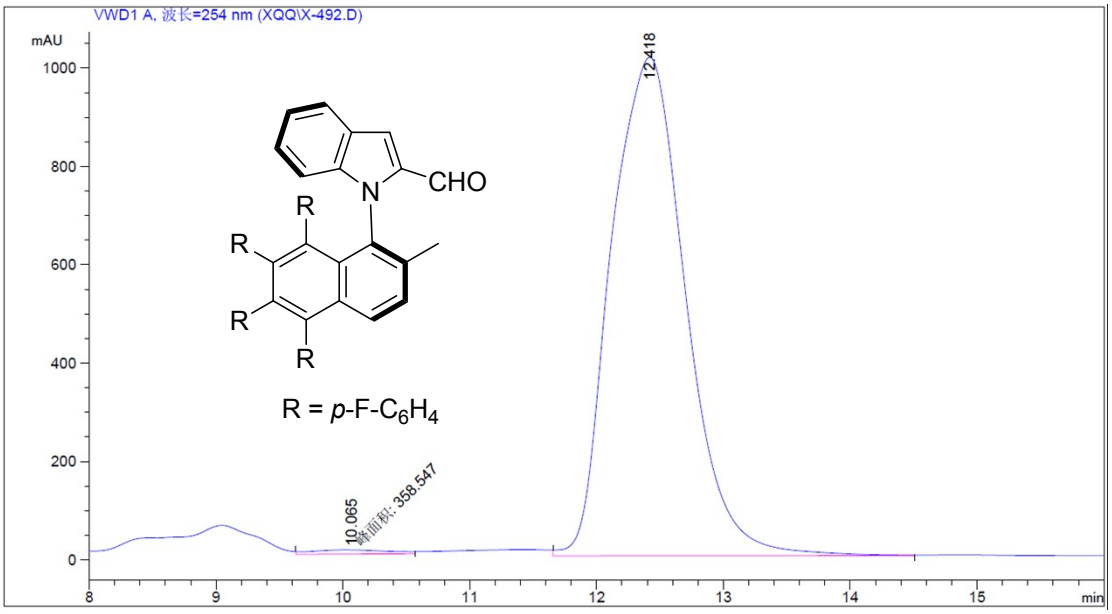
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.826 | VV | 0.3447 | 143.72667 | 6.19924 | 0.4003 |
| 2 | 11.168 | VB | 0.3728 | 3.57572e4 | 1491.77087 | 99.5997 |

## 4j: IE, Hexane:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm




Area Percent Report

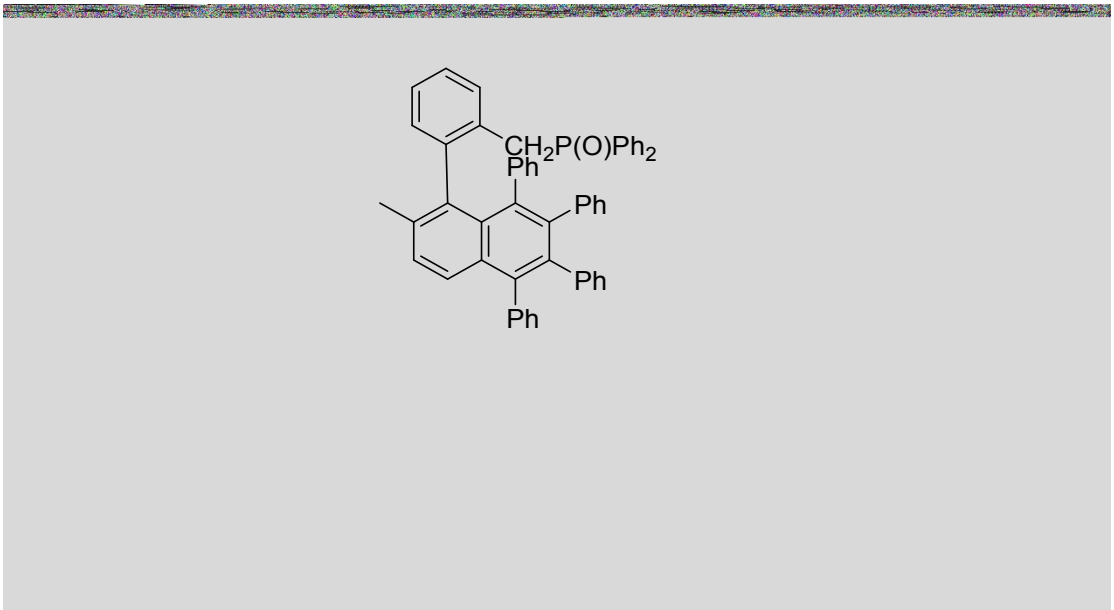
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.000 | VV | 0.5392 | 3.71037e4 | 1107.98828 | 49.0154 |
| 2 | 12.398 | VB | 0.6688 | 3.85943e4 | 936.08612 | 50.9846 |




Area Percent Report

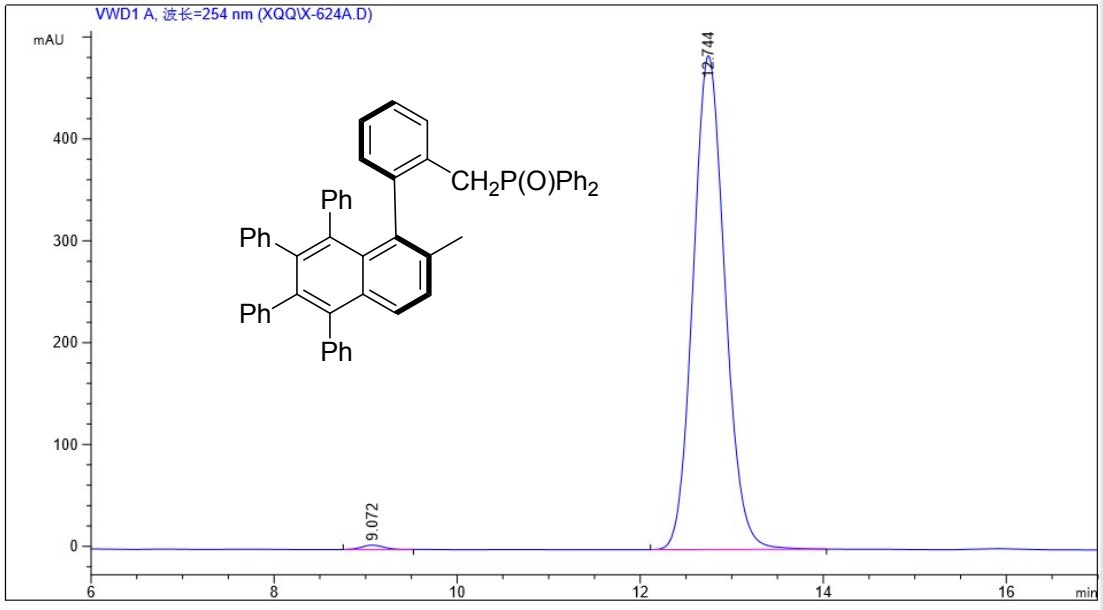
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.065 | MM | 0.7297 | 358.54733 | 8.18951 | 0.8599 |
| 2 | 12.418 | VB | 0.6578 | 4.13391e4 | 1013.67187 | 99.1401 |

## 6: IF, Hexane:*i*-PrOH = 2:1, 1.0 mL/min, 254 nm




Area Percent Report

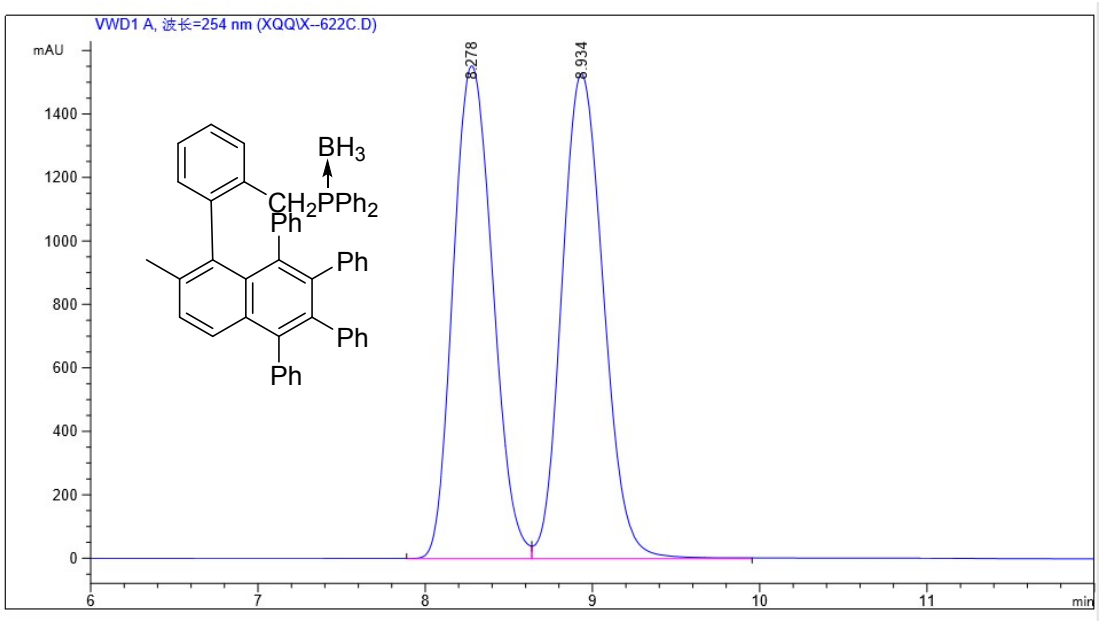
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.104 | VB | 0.2708 | 3.80679e4 | 2194.46899 | 48.9376 |
| 2 | 12.723 | VB | 0.3742 | 3.97208e4 | 1649.14380 | 51.0624 |




Area Percent Report

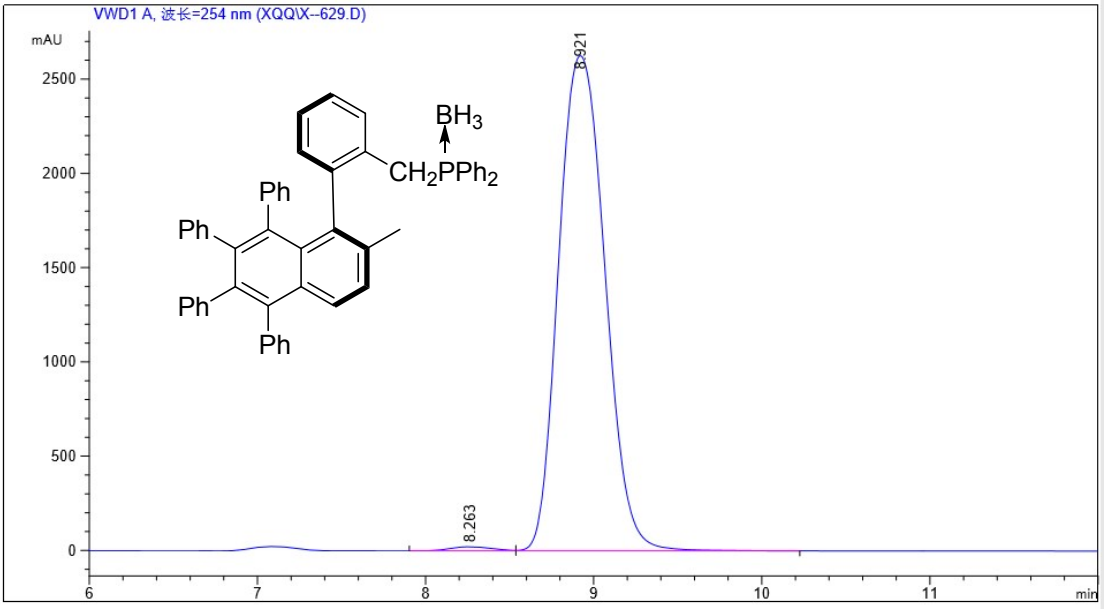
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.072 | BB | 0.2558 | 71.31815 | 4.33882 | 0.6069 |
| 2 | 12.744 | BB | 0.3729 | 1.16803e4 | 484.73236 | 99.3931 |

## 7: IF, Hexane:*i*-PrOH = 95:5, 0.8 mL/min, 254 nm




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.278 | VV | 0.2629 | 2.54964e4 | 1552.80371 | 49.1675 |
| 2 | 8.934 | VB | 0.2727 | 2.63597e4 | 1527.54041 | 50.8325 |

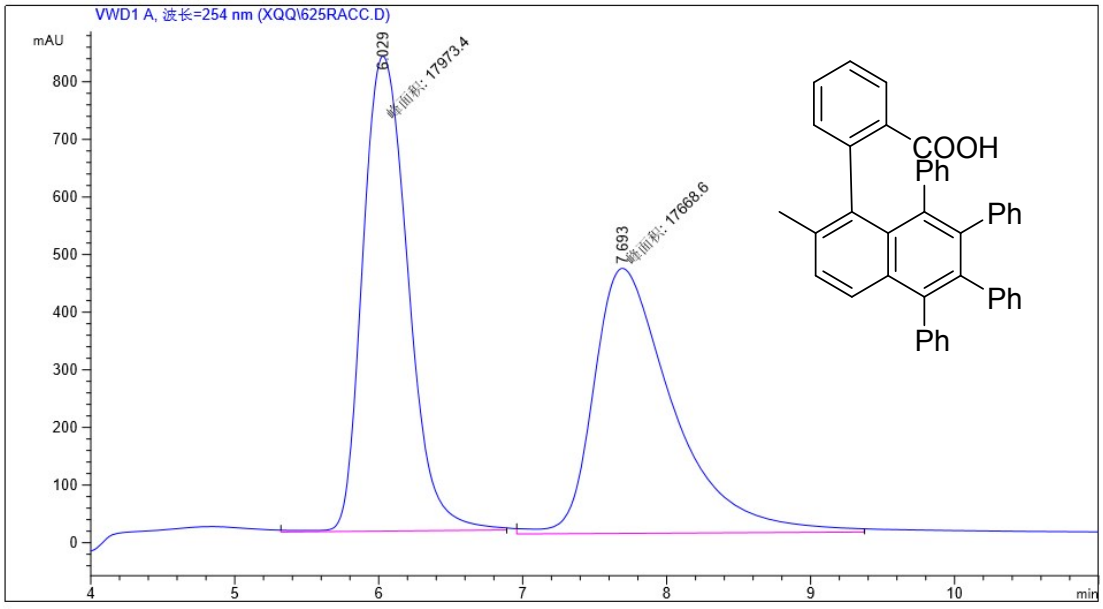



Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.263 | BV | 0.2789 | 378.17578 | 22.03197 | 0.7468 |
| 2 | 8.921 | VB | 0.3077 | 5.02640e4 | 2626.19580 | 99.2532 |

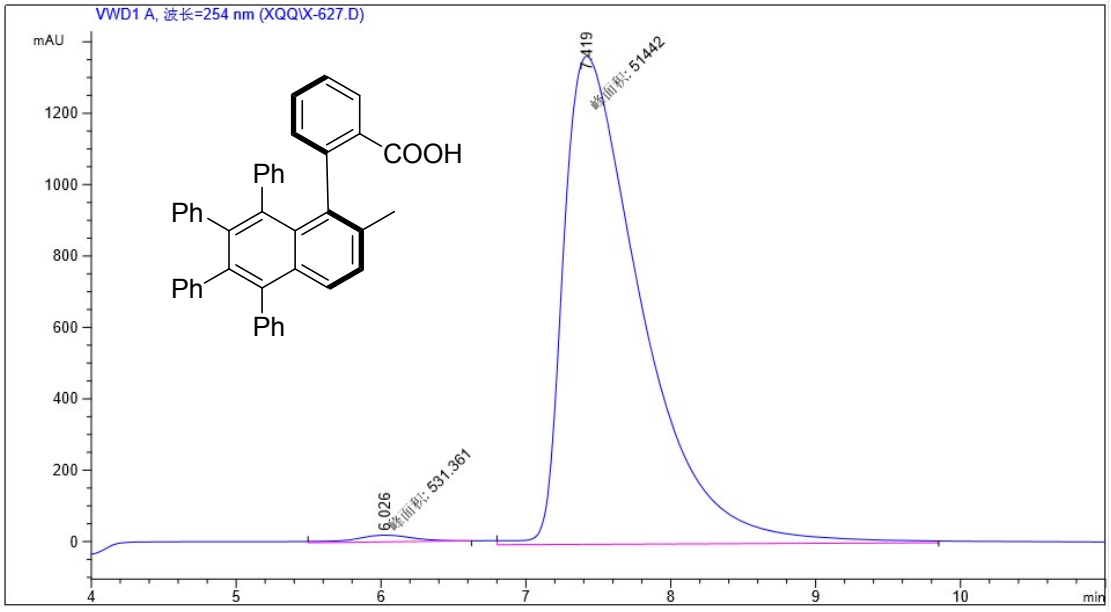
## 8: OD-H, Hexane:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm

Transform the carboxylic acid to the corresponding methyl ester then determined by HPLC analysis.




Area Percent Report

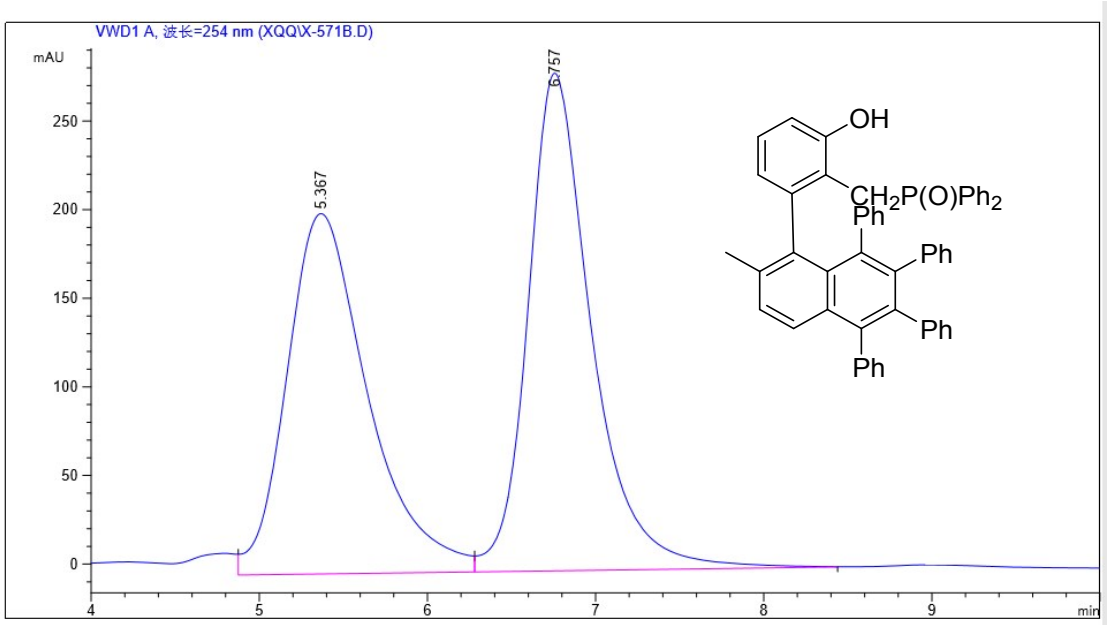
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.029 | MM | 0.3635 | 1.79734e4 | 823.99023 | 50.4276 |
| 2 | 7.693 | MM | 0.6401 | 1.76686e4 | 460.01428 | 49.5724 |




Area Percent Report

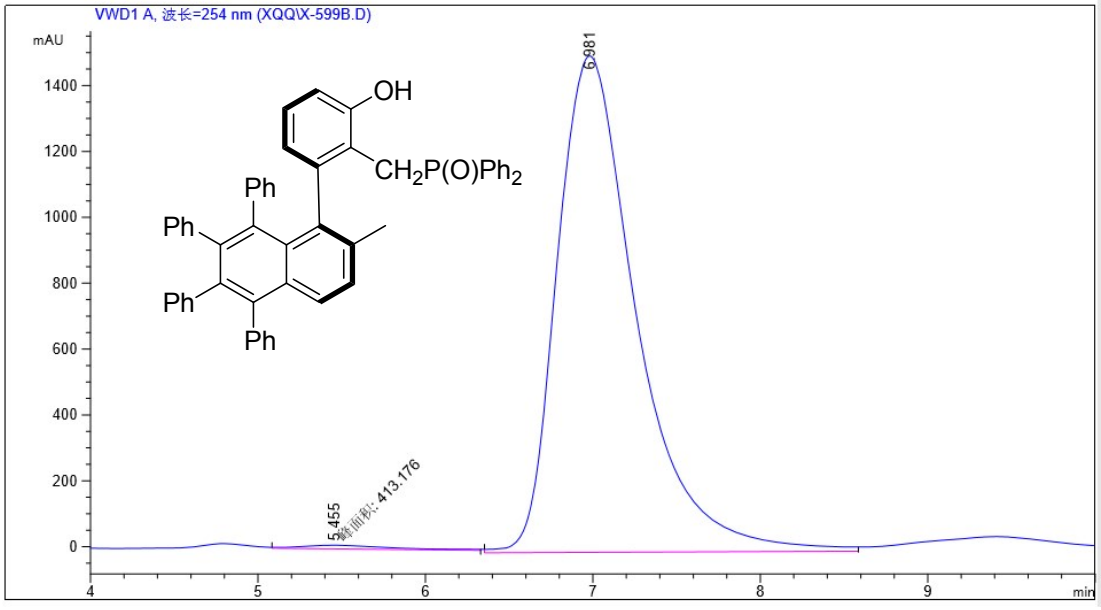
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.026 | MM | 0.4664 | 531.36096 | 18.98667 | 1.0224 |
| 2 | 7.419 | MM | 0.6269 | 5.14420e4 | 1367.58679 | 98.9776 |

## 10: AD-H, Hexane:*i*-PrOH = 9:1, 1.0 mL/min, 254 nm




Area Percent Report

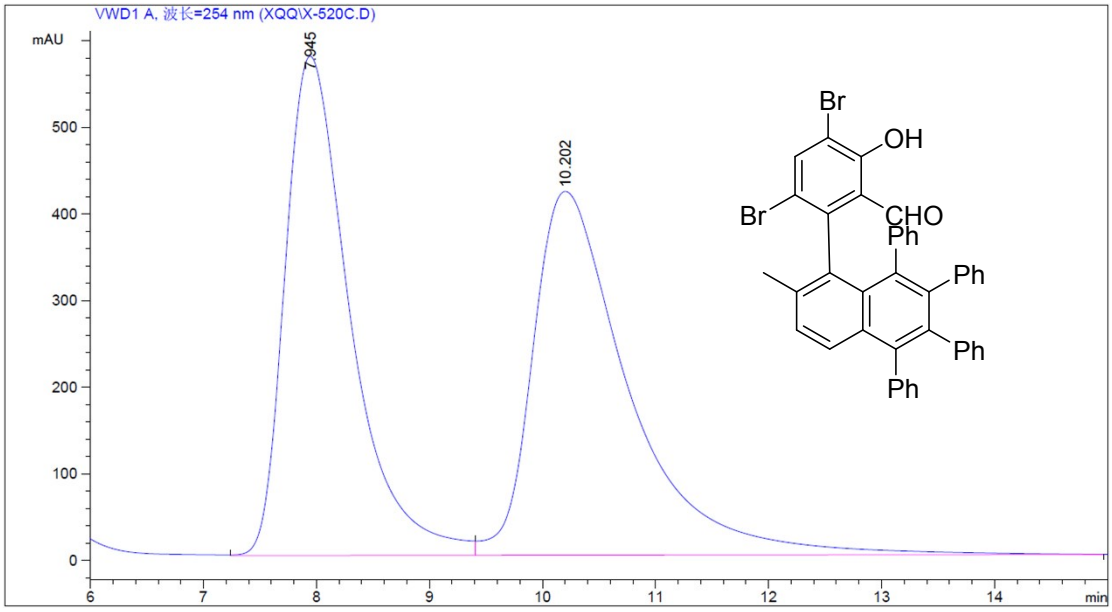
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.367 | VV | 0.5054 | 6808.41357 | 203.45636 | 47.8982 |
| 2 | 6.757 | VB | 0.3922 | 7405.91650 | 280.76282 | 52.1018 |




Area Percent Report

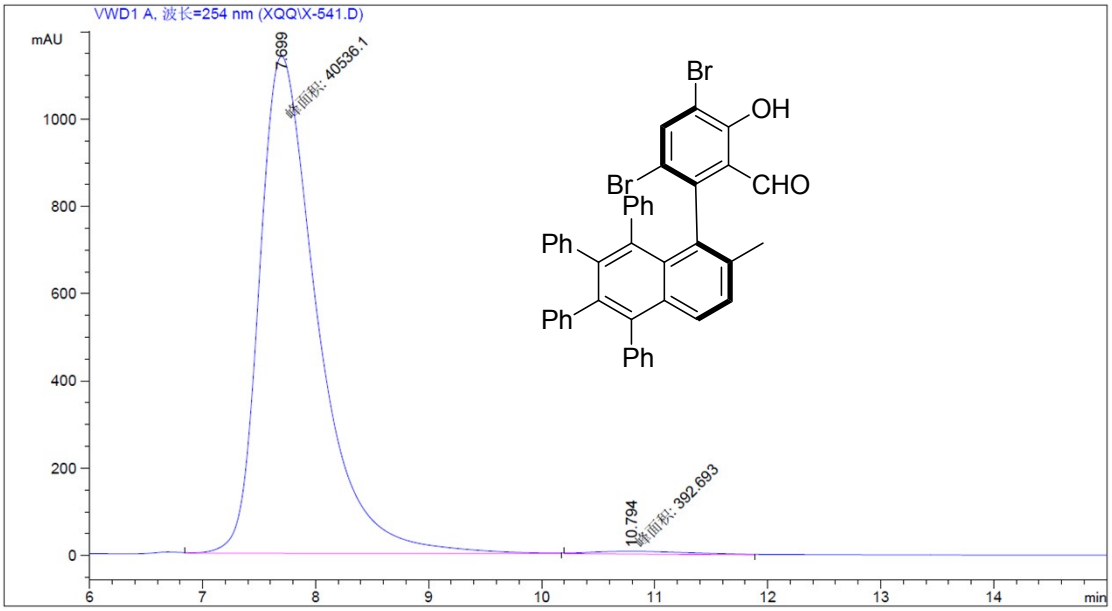
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.455 | MM | 0.6184 | 413.17612 | 11.13528 | 0.8250 |
| 2 | 6.981 | VV | 0.5054 | 4.96686e4 | 1506.98193 | 99.1750 |

## 11: OD-H, Hexane:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm




Area Percent Report

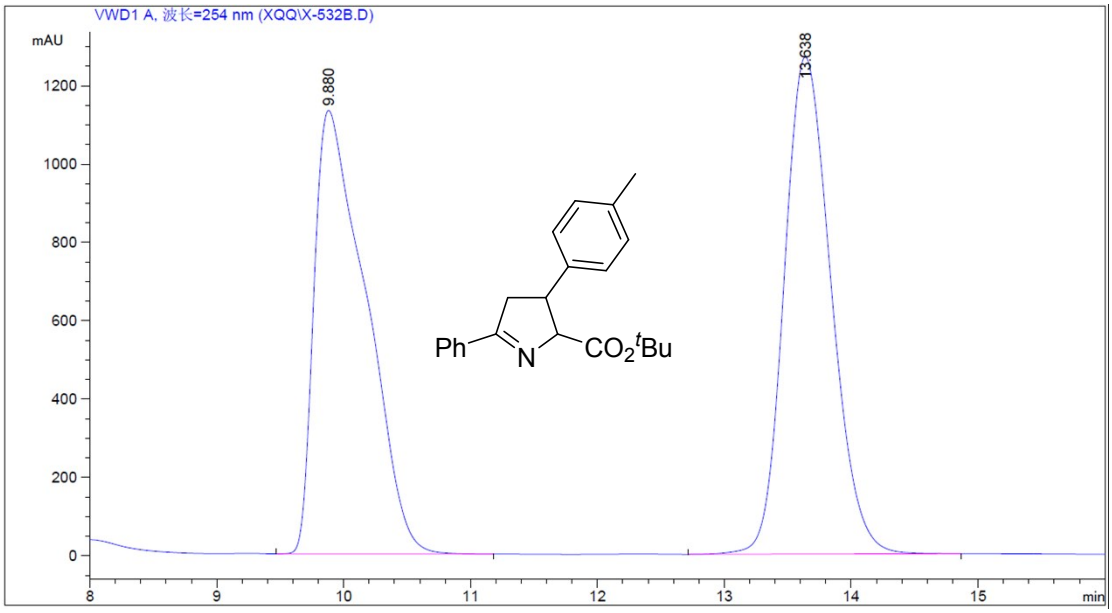
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.945 | BV | 0.6102 | 2.30230e4 | 576.29065 | 47.9915 |
| 2 | 10.202 | VB | 0.8780 | 2.49501e4 | 419.98795 | 52.0085 |




Area Percent Report

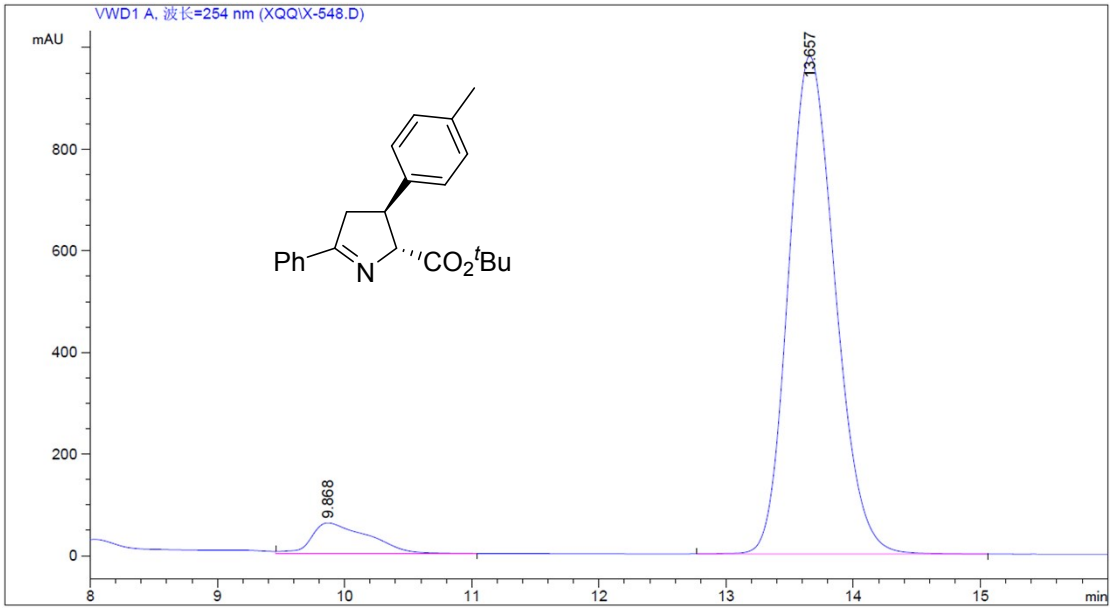
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.699 | MM | 0.5931 | 4.05361e4 | 1139.02344 | 99.0405 |
| 2 | 10.794 | MM | 1.0412 | 392.69305 | 6.28618 | 0.9595 |

## 14: IC, Hexane:*i*-PrOH = 9:1, 1.0 mL/min, 254 nm




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.880 | VB | 0.3974 | 3.20914e4 | 1133.13464 | 49.6066 |
| 2 | 13.638 | VB | 0.4001 | 3.26004e4 | 1269.41614 | 50.3934 |




Area Percent Report

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU *s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.868 | VB | 0.4302 | 1891.76953 | 60.52865 | 7.0357 |
| 2 | 13.657 | BB | 0.3966 | 2.49963e4 | 979.83728 | 92.9643 |