Supporting information

Polymer-Bound Chiral Gold-Based Complexes as Efficient Heterogeneous Catalysts for Enantioselectivity Tunable Cycloaddition

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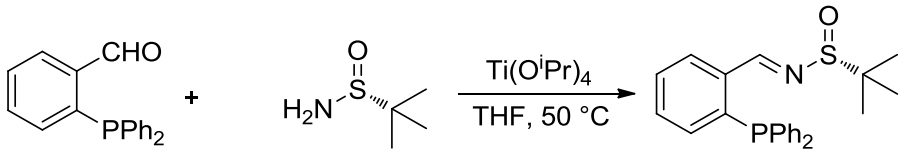
1. General Information

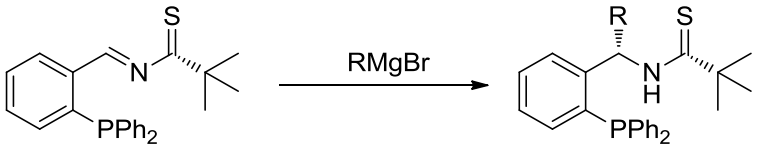
All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. ^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multip let), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. F lash column chromatography was performed over silica gel (300-400 mesh). Dichloromethane, dichloromethane, toluene, acetonitrile were freshly distilled from CaH_2; THF was freshly distilled from sodium metal prior to use. 4 Å molecular sieves purchased from Sinopharm Chemical Reagent Co. Ltd were powdered and dried at 300°C in muffle furnace for 8-10 hours prior to use. The substrates **1a-1g**, **2a - 2h** were synthesized according to the procedure of reference.[1] And the spectral data of the substrates were consisted with the literature. Catalyst loading was analyzed by Optima 7000 DV Inductively coupled plasma optical emission spectroscopy (ICP-OES). GPC was determined by WATER. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range 4000-200cm^{-1}) in KBr pellets

2. General Procedure for the Synthesis of Ligands



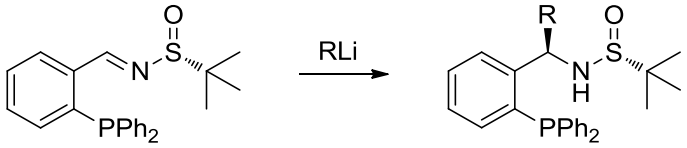
The sulfonyl imine was prepared according to the modified procedure of literature [2] with the use of $Ti(OPr^{i})_4$ instead of $Ti(OEt)_4$.

Method A:



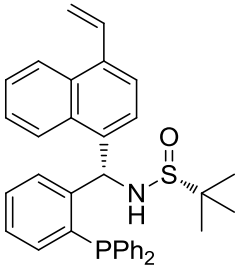
a solution of sulfonyl imine (1.0 equiv) in CH_2Cl_2 at – 48 °C was added Grignard reagent (2.0 equiv) in Et_2O. The mixture was stirred at - 48 °C for 4 -6 h and then was warmed to room temperature with stirring overnight. When completed, the reaction mixture was quenched by the addition of NH_4Cl aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography.

Method B:



To a solution of sulfonyl mine (1.0 equiv) in toluene at – 78 °C was added a solution of organ lithium (2.0 equip) in n-hexane. Stirring was continued at -78 °C for 2-4 h before the mixture was warmed to 0 °C.When completed, the reaction mixture was quenched by the addition of NH_4Cl(aq). and diluted with EtOAc. The organic layer was removed, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO4, filtered, concentrated, and purified by flash chromatography.

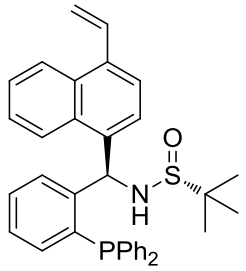
Synthesis of (*S, R*s)-L1.



Using Method A: The reaction of sulfonyl mine (2.0 g, 5 mmol) and (4-vinylnaphthalen-1-yl)magnesium bromide (1.0 equip 10 mmol), after a flash column chromatography (n-hexanes: AcOEt = 5:1) afforded the product (*S, Rs*)-**L1** (1.64 g, 60%) as

a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4, 1H), 7.89 (d, *J* = 8, 1H), 7.91-7.88 (m, 1H), 7.52 – 7.46 (m, 4H), 7.35 - 7.07(m, 12H), 6.96 (t, *J* = 8 Hz, 1H), 6.88 (d, *J* = 7.5Hz, 1H), 6.80 (t, *J* = 8.0 Hz, 2H), 6.68 (t, *J* = 8 Hz, 2H), 5.80 (d, *J* = 16 Hz, 1H), 5.40 (d, *J* = 12 Hz, 1H), 3.77(s, 1H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.94 ($J_{C,P}$ = 23 Hz), 137.23($J_{C,P}$ = 10 Hz), 136.91($J_{C,P}$ = 16 Hz), 136.08($J_{C,P}$ = 12 Hz), 134.72, 134.53, 134.21($J_{C,P}$ = 9 Hz), 133.98($J_{C,P}$ = 20 Hz), 133.46($J_{C,P}$ = 18 Hz), 131.41, 130.56, 128.91, 128.76($J_{C,P}$ = 6 Hz), 128.43, 128.37, 128.29, 128.09, 127.05, 127.65, 127.57, 127.43, 126.68, 125.88, 124.29, 123.95, 122.79, 55.97, 55.39($J_{C,P}$ = 30 Hz), 22.75; ^{31}P NMR (162 MHz, $CDCl_3$) δ -18.74. ESI-MS calculated for $C_{31}H_{32}NNaOPS$: m/z (%): 570.1991($M+Na^+$), found: 570.1987. $[\alpha]_D^{20}$ = -79.5 (*c* = 0.50, $CHCl_3$).

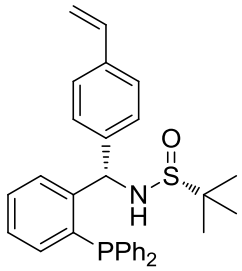
Synthesis of (*R, Rs*)-L1.



Using Method B: The reaction of sulfonyl mine (2.0 g, 5.0 mmol) and (4- vinylnaphthalen-1-yl) lithium (1.0 M in THF, 10.0 mL), after a flash column chromatography (n-hexanes: AcOEt = 5:1) afforded the product (*R, Rs*)-**L1** (1.6 g, 65% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.99(d, *J* = 8.4 Hz, 1H), 7.60 – 7.57(m, 1H), 7.42 -7.19(m, 12H),7.14(t, *J* = 7.5Hz, 1H),7.08 -7.01 (m, *J* = 7.5 Hz, 1H), 6.89(t, *J* = 7.4Hz, 2H), 5.66(dd, J_1= 1.2Hz, J_2 = 1.6Hz, 1H), 5.42(dd, J_1 = 1.2 Hz, J_2 = 1.2Hz, 1H), 3.91(d, *J* = 4.8Hz, 1H), 1.17(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.56 ($J_{C,P}$ = 10 Hz), 136.96 ($J_{C,P}$ = 25 Hz) 136.91, 136.67, 135.95($J_{C,P}$ = 16 Hz), 135.66, 135.05, 134.88($J_{C,P}$ = 9 Hz), 134.52, 133.87($J_{C,P}$ = 12 Hz) , 133.68 ($J_{C,P}$ = 11 Hz), 131.37, 131.09, 129.37, 128.52 ($J_{C,P}$ = 7 Hz), 128.39 ($J_{C,P}$ = 6 Hz), 128,30, 128.01 ($J_{C,P}$ = 4 Hz),

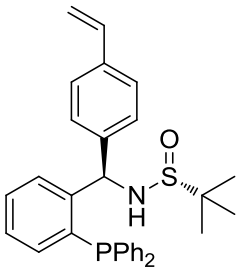
127.84, 126.68, 125.89, 125.66, 124.55 ($J_{C,P}$ = 3 Hz), 124.23, 122.83, 117.18, 56.57 ($J_{C,P}$ = 27 Hz), 56.37, 22.71; ^{31}P NMR (162 MHz, $CDCl_3$) δ -19.11. ESI-MS calculated for $C_{35}H_{34}NNaOPS$: m/z (%): 570.1991($M+Na^+$), found: 570.1996. $[\alpha]_D^{20}$ = 75.6 (*c* = 0.50, $CHCl_3$).

Synthesis of (*S, Rs*)-L2.



Using Method A: The reaction of sulfonyl mine (2.0 g, 5.0 mmol) and (4-vinylphenyl)magnesium bromide (2.0 equip 10 mmol), after a flash column chromatography (*n*-hexanes: AcOEt = 5:1) afforded the product (*S, Rs*)-**L2** (2.0 g, 85% yield) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 1 H), 7.40 -7.37 (m, 4 H), 7.30 – 7.20 (m, 11 H), 7.06 – 7.01(m, 3 H), 6.63 -6.54(m, 2H), 5.62 (d, *J* = 8.96, 1 H), 5.18 (d, *J* = 10.8 1 H), 3.88 (d, *J* = 2.8, 1 H),1.02 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.59 ($J_{C,P}$ = 24 Hz), 141.53, 136.91($J_{C,P}$ = 10 Hz), 136.34, 136.99($J_{C,P}$ = 15 Hz), 135.76($J_{C,P}$ = 9 Hz), 134.97, 133.78($J_{C,P}$ = 2 Hz), 133.60, 129.30, 128.43, 128.34($J_{C,P}$ = 3 Hz), 128.25, 128.25, 128.19, 127.68, 126.20, 113.91, 59.90($J_{C,P}$ = 26 Hz), 56.02, 22.70; ^{31}P NMR (162 MHz, $CDCl_3$) δ -18.18. ESI-MS calculated for $C_{31}H_{32}NNaOPS$: m/z (%): 520.1834 ($M+Na^+$), found: 520.1849. $[\alpha]_D^{20}$ = -45.3, (*c* = 0.50, $CHCl_3$)

Synthesis of (*R, Rs*)-L2.



Using Method B: The reaction of sulfonyl mine (2.0 g, 5.0 mmol) and (4-vinylphenyl) lithium (1.0 M in THF, 10.0 mL), after a flash column chromatography (n-hexanes: AcOEt = 5:1) afforded the product (*R, Rs*)-**L2** (2.0 g, 86% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62（m, 1H, 7.40 -7.36(m, 1H), 7.31-6.97(m, 17H), 6.60-6.48(m, 2H), 5.61(d, *J* = 17.6Hz, 1H), 5.17(d, *J* = 10.9Hz, 1H), 4.04(d, *J* = 4.04Hz, 1H),1.21(s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.22 ($J_{C,P}$ = 24 Hz), 140.34, 136.58, 136.49($J_{C,P}$ = 5 Hz), 136.44, 135.94($J_{C,P}$ = 9 Hz), 135.56($J_{C,P}$ = 16 Hz), 135.10, 133.80 ($J_{C,P}$ = 25 Hz), 129.63, 128.67, 128.66, 128.52($J_{C,P}$ = 7 Hz), 128.35, 128.28, 127.88, 127.75($J_{C,P}$ = 6 Hz), 125.97, 113.75, 59.66($J_{C,P}$ = 25 Hz), 56.07, 22.72; ^{31}P NMR (162 MHz, $CDCl_3$) δ -18.18. ESI-MS calculated for $C_{31}H_{32}NNaOPS$: m/z (%): 520.1834 ($M+Na^+$), found: 520.1849. $[\alpha]_D^{20}$ = -5.5 (*c* = 0.50, $CHCl_3$).

3. General data for polymer

3.1 **Preparation of chiral polystyrene-supported Ming-phos ligand P1**

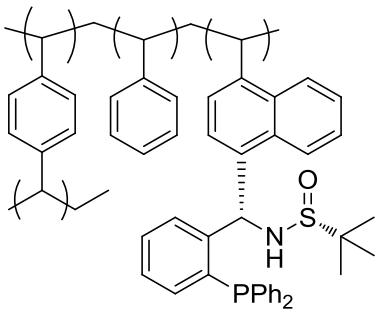
, A solution of styrene (0.7 mL, 20 mmol), phosphorus ligand (0.3 mmol) in toluene (1.6 mL) was added to a sealed tube. With liquid nitrogen freezing to remove oxygen and filling with argon, repeated for three times. AIBN (22 mg) was added to the solution, the sealed tube was sealed safely with full of argon. The solution was heated at 85 ^{o}C for 6 h. the sealed tube put out, and then cooled down to room temperature. THF (25 mL) was added to the mixture and stirred for 24 h, the crude material was added dropwise to a cold (0 ^{o}C) vigorously stirring solution of methanol (150 mL). The white precipitate was filtered and dried to get polymer (430.1 mg, 54% yield).

Typical procedure for washing the polymer.

The polymer (430.1 mg) was partially dissolved in DCE (25 mL) and stirred for 6 h, then hexanes (100 mL) was added slowly, the polymer was precipitated and filtered, repeated for twice time. The

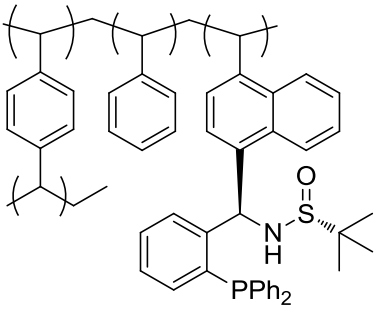
polymer was dried in vacuum for 24 h. the polymer was soluble in DCM, the monomer was detected by TLC until the monomer disappeared, and then the polymer was determined by 1 H NMR and ^{31}P NMR.

Preparation of chiral polystyrene-supported Ming-phos ligand P1.



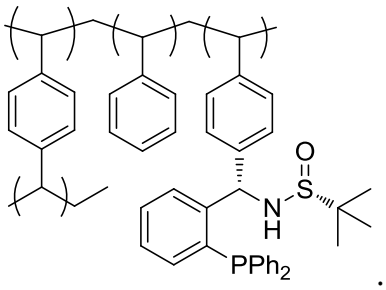
The analytical data for this new material are as follows: Element analysis: Calcd for $[C_6H_5(CH_2CH_2)_2]_{20}[C_6H_5(CH_2CH_3)(CH_2CH_2)]_1[C_{35}H_{35}NOPS]_1$: C 89.09, H 7.42, N 0.53; Element analysis found; C 88.26, H 7.32, N 0.47, Amount of Ming-phos ligand moieties = 0.23 mmol/g from ^{31}P NMR(Triphenylphosphine oxide was conducted as internal standard); ^{31}P NMR (162 MHz, $CDCl_3$) -18.46; IR (film) 3050, 2950, 1490, 1410, 750, 698.

Preparation of chiral polystyrene-supported Ming-phos ligand P5.



The analytical data for this new material are as follows: Element analysis: Cacld for $[C_6H_5(CH_2CH_2)_2]_{20}[C_6H_5(CH_2CH_3)(CH_2CH_2)]_1[C_{35}H_{35}NOPS]_1$: C 89.09, H 7.42, N 0.54; found; C 88.19, H 7.49, N 0.48, Amount of Ming-phos ligand moieties = 0.24 mmol/g from ^{31}P NMR(Triphenylphosphine oxide was conducted as internal standard); ^{31}P NMR (162 MHz, $CDCl_3$) -19.48; IR (film) 3050, 2950, 1490, 1410, 750, 698.

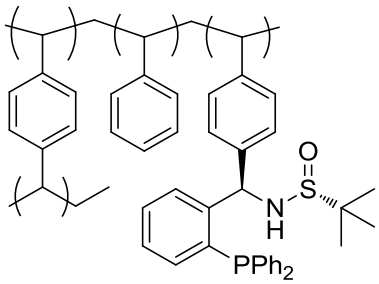
Preparation of chiral polystyrene-supported Ming-phos ligand P7.



The analytical data for this new material are as follows: Element analysis: Cacld for $[C_6H_5(CH_2CH_2)_2]_{20}[C_6H_5(CH_2CH_3)(CH_2CH_2)]_1[C_{31}H_{33}NOPS]_{1:}$ C 89.07, H7.42, N 0.54 found; C 87.79, H 7.57, N 0.50. Amount of Ming-phos ligand moieties = 0.241mmol/g from ^{31}P NMR(Triphenylphosphine oxide was conducted as internal standard); ^{31}P NMR (162 MHz, $CDCl_3$) -18.46; IR (film) 3053, 2950, 1720, 1490, 1410, 750, 698.

P-(0-6) was similarly prepared.

Preparation of chiral polystyrene-supported Ming-phos ligand P6.



The analytical data for this new material are as follows: Cacld for $[C_6H_5(CH_2CH_2)_2]_{20}[C_6H_5(CH_2CH_3)(CH_2CH_2)]_1[C_{31}H_{33}NOPS]_{1:}$ C 89.07, H 7.42, N 0.54, Found for: 87.98, H 7.36, N 0.47, amount of Ming-phos ligand moieties = 0.22 mmol/g from (Triphenylphosphine oxide was conducted as internal standard); ^{31}P NMR (162 MHz, $CDCl_3$) -18.56; IR (film) 3053, 2950, 1720, 1490, 1410, 750, 698.

We attempted to determine the molecular weight, however, the polymer was difficult to dissolve in THF. The polymer was partially dissolve in DMF. GPC: **P7:** Molecular weight (M_w) = 79500 (PDI = 1.34) (on the base of polystyrene calibration); **P6:** Molecular weight (M_w) = 62500 (PDI = 1.34) (on the base of polystyrene calibration); **P1:** not detected; **P5:** 33600(PDI = 2.24). Because the polymer is only partial dissolve in DMF, the data for molecular weight is inaccuracy but only for as a reference.

(1) Preparation of polymer-supported catalyst C1

A mixture of 520 mg of polystyrene-supported Ming-phos ligand **L-1** (amount of ^{31}P: 0.125 mmol) and 45 mg of Me_2SAuCl in DCE (16 mL) was magnetically stirred under nitrogen atmosphere at room temperature for 10 h. Hexanes (100 mL) was slowly added to the mixture, and the precipitated was collected by filtration, washed with n-hexane :toluene (8:1) for twice time. The collected polymer was dried for 12 h. Under nitrogen atmosphere, the collected polymer in DCE (25 mL) was added $AgNTf_2$ at room temperature. The mixture was stirred for 30 min to generate the cationic catalyst, *n*-hexanes was added slowly, and the precipitate was collected by filtration, washed with the solution of n-hexane : toluene (8:1) for twice time. Then collected polymer catalyst was dried for 12 h. (ICP-OES) Anal Calcd: 0.24 mmol/g (Au); found: 0.19 mmol/g (Au); 80% loading. **C-(0-7)** was similar with **C1.**

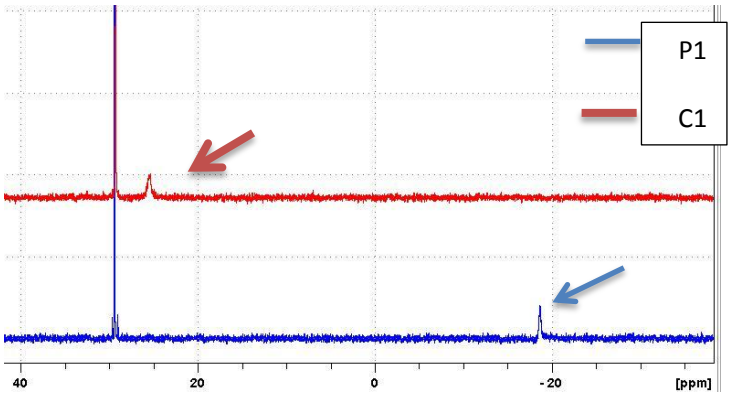


Figure S1. ^{31}NMR of **P1** and **P1**AuCl. triphenylphosphine oxide was conducted as internal standard.

Table S1. Characterization of polymers P1,5-7and Catalyst C

polymers	^{31}P **NMR** (ppm)[a]	Ming-phos moieties (mmol/g of polymer)[b]	Au content[c] (mmol/g)	loading(%)
P-7	-18.46	0.23	0.19	80
P-6	-18.56	0.24	0.19	79
P-5	-18.46	0.21	0.14	67
P-1	-19.48	0.20	0.14	70

[a] Determined by ^{31}P liquid NMR .[b] Determined by ^{31}P liquid NMR; [c] Determined by ICP-OES.

4. Asymmetric cycloaddition catalyzed by chiral polystyrene-supported Ming-phos catalyst.

Asymmetric cycloaddition and recovery of C1.

The polystyrene-supported catalyst M1 was added to the solution of ketone **1** (0.2mmol) and intones **2 (**0.3 mmol) in DCE (2 mL). The reaction was determined by TLC analysis, after the ketone **1** was consumed completely. The *n*-hexane (15 mL) was slowly added to the mixture and stirred for 5 min, and the precipitated polymer-supported catalyst was recovered by filtration, recovered catalyst was dried for 2 h. After removal of the filtrate was evaporated under reduced pressure, the diastereomeric ratio was determined by crude ^{1}H NMR, the resulting crude product was then purified by flash column chromatography on silica gel to afford the desired product. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC using a Chiral Pak AD-H and AS-H. The recovered **C1** was reused next time for reaction under the same conditions.

The preparation **of C-(2-4)** is similar with **C-1**

Table S2. Recovery of Catalysis Reaction

run	Yield (%)[a]	Ee (%)[b]	Time (%)	Recovery of catalyst (%)[c]	leaching of gold (%)[d]
1	96	94	3	97	1.8
2	92	94	6	96	1.5
3	84	95	12	95	1.1
4	82	95	24	94	1.0
5	82	94	37	95	1.0
6[e]	89	93	6	92	0.9
7	83	93	12	92	0.9
8	75	92	35	91	0.8

[a] Isolated yield. [b] Determined by HPLC analysis. [c] The gold content in the reaction filtrate compared with that of previous time. [d] Gold leaching compared with that of previous time. [e] 50% of the initial amount of $AgNTf_2$ was added to regenerate the cationic gold catalyst.

(a) (b)

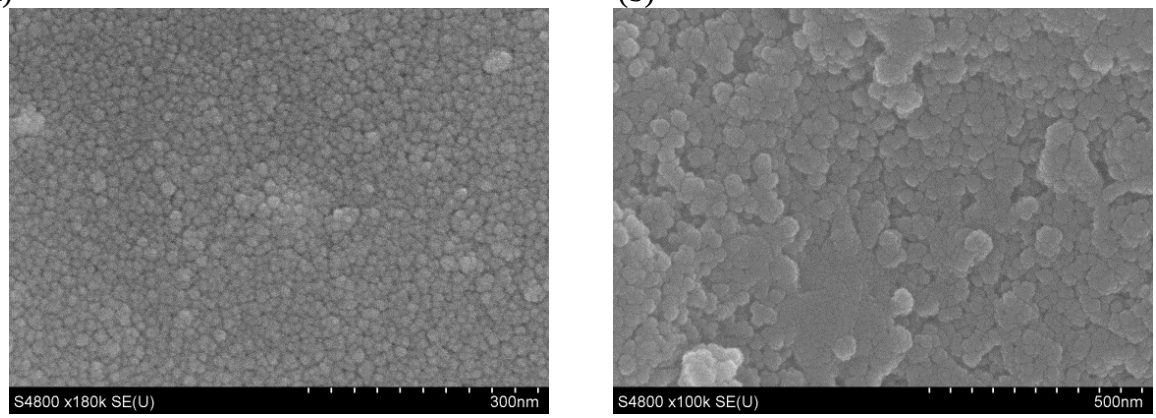
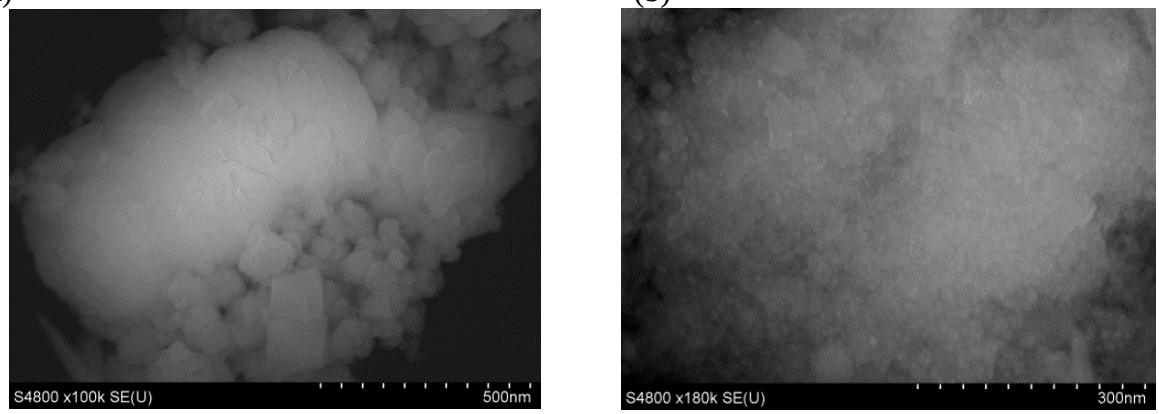


Figure S2. SEM image: catalyst **C1** (a) and (b) after 8 times recycle

(a) (b)



(t-8) (t-8)

Figure S3.TEM image : catalyst C1 (a) and (b) after 8 times recycle

5. General data for products 3a-3g

Asymmetric cycloaddition and recovery of C-1.

The polystyrene-supported catalyst was added to the solution of ketone **1** (0.2 mmol) and introne **2 (**0.3 mmol) in DCE (2 mL). The reaction was determined by TLC analysis, after the ketone **1** was consumed completely. *n*-hexanes (15 mL) was slowly added to the mixture and stirred for 5min, and the precipitated polymer-supported catalyst was recovered by filtration, recovered catalyst was dried for 2 h. After removal of the filtrate, the re-

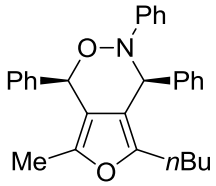
action mixture was evaporated under reduced pressure; the diastereomeric ratio was determined by crude ^{1}H NMR, the resulting crude product was then purified by flash column chromatography on silica gel to afford the desired product. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralpak AD-H and AS-H. The recovered M1 was reused for next time under the same conditions.

Condition A: the catalyst was the polymer **C5**

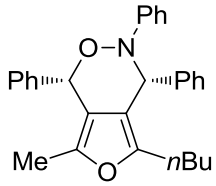
Condition B: the catalyst was the polymer **C1**

Compounds *ent*-**3a-f** and **3a-f** has been reported, the data is consistent with our previous reported.[1]

1. Synthesis of *ent*-4a and 3a.[1]

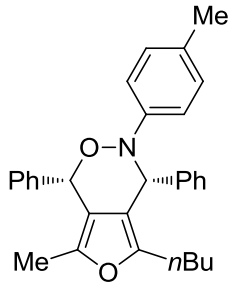


Under conditions A: The reaction of ketone **1a** (45 mg, 0.2 mmol) and introne **2a** (60.0 mg, 0.30 mmol), after a flash column chromatography (n-hexanes: AcOEt = 20:1) afforded the product *ent*-**3a** as a pale yellow liquid (74.2 mg, 92% yield) with 95% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:5, 0.8 mL/min, 230 nm); minor enantiomer tr = 6.2 min, major enantiomer tr = 6.7 min.

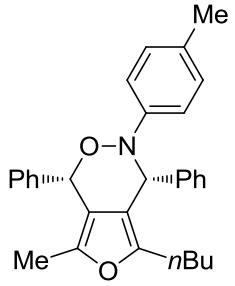


Under conditions B: The product **3a** was obtained (4 mg, 86% yield) with 94% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 90:10, 0.8 mL/min, 230 nm); minor enantiomer tr =6.7 min, major enantiomer tr = 6.2 min.

2. Synthesis of *ent*-3b and 3b.[1]

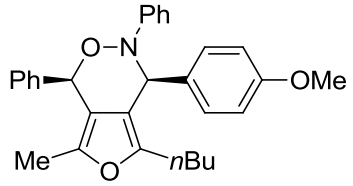


Under conditions A: The reaction of ketone **1a** (25.0 mg, 0.1 mmol) and introne **2b** (30 mg, 0.15 mmol), after a flash column chromatography (n-hexanes: AcOEt = 20:1) afforded the product *ent*-**3b** as a pale yellow liquid (39.2mg, 85% yield) with 95% ee; Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:5, 0.8 mL/min, 230 nm); minor enantiomer tr = 7.5 min, major enantiomer tr = 9.1 min.



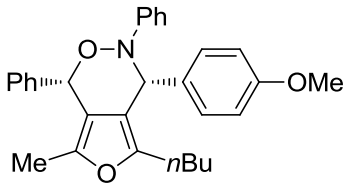
Under conditions B: The product **3b** was obtained (148 mg, 85% yield) with 97% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:05, 0.8 mL/min, 230 nm); minor enantiomer tr = 7.5 min, major enantiomer tr = 9.1 min.

3. Synthesis of *ent*-3c and 3c.[1]



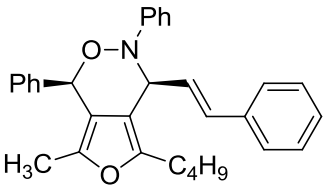
Under conditions A: The reaction of ketone **1a** (22.1 mg, 0.1 mmol) and introne **2d** (29.1 mg, 0.15 mmol), after a flash column chromatography (n-hexanes: AcOEt = 20:1) afforded the productt *ent*-**3c** as a pale yellow liquid (37.7 mg, 96% yield) with 95% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (n-hexanes: 2-propanol =

95:05, 0.8 mL/min, 230 nm); minor enantiomer tr = 8.3 min, major enantiomer tr = 7.8 min.

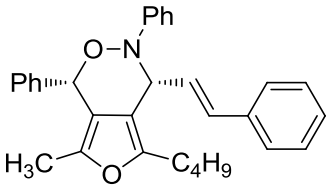


Under conditions B: The product **3c** was obtained (39.4 mg, 87% yield) with 99% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (n-hexanes: 2-propanol = 95: 5, 0.8 mL/min, 230 nm); minor enantiomer tr = 7.7 min, major enantiomer tr = 8.4 min.

4. Synthesis of *ent*-3d and 3d.[1]

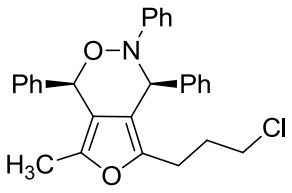


Under conditions A: The reaction of ketone **1a** (22.3 mg, 0.10 mmol) and introne **2f** (30.0mg, 0.15 mmol), after a flash column chromatography (n-hexanes: AcOEt = 20:1) afforded the product *ent*-**3d** as a pale yellow liquid (38.0 mg, 85% yield) with 99% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:05, 0.8 mL/min, 230 nm); minor enantiomer tr = 5.8 min, major enantiomer tr = 9.1 min.

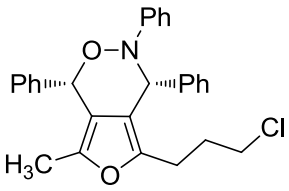


Under conditions B: The product **3d** was obtained (34.1 mg, 74.4% yield) with 90% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:05, 0.8 mL/min, 230 nm); minor enantiomer tr = 9.0 min, major enantiomer tr = 5.8 min

5. Synthesis of *ent*-3e and 3e.[1]

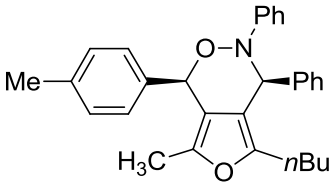


Under conditions A: The reaction of ketone **1** (25 mg, 0.10 mmol) and introne **2a** (30 mg, 0.15 mmol), after a flash column chromatography (n-hexanes: AcOEt =30: 1) afforded the product *ent*-**3e** as a white liquid (36.2 mg, 81% yield) with 90% ee. [1]Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:5, 0.8mL/min, 230 nm); minor enantiomer tr = 8.2 min, major enantiomer tr = 10.1 min.



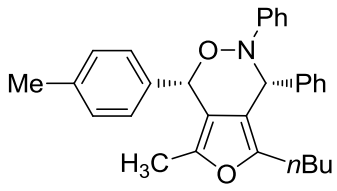
Under conditions B: The reaction of ketone **1** (25 mg, 0.10 mmol) and introne **2a** (30 mg, 0.15 mmol), after a flash column chromatography (n-hexanes: AcOEt = 30 : 1) afforded the product *ent*-**3e** as a white liquid (36.2 mg, 81% yield) with 90% ee. [1]Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:5, 0.8 mL/min, 230 nm); minor enantiomer tr = 8.2 min, major enantiomer tr = 10.1 min.

6. Synthesis of *ent*-3f and 3f.[1]



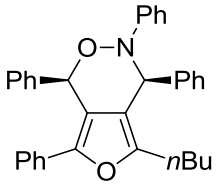
Under conditions A: The reaction of ketone **1f** (23.5 mg, 0.10 mmol) and introne **2a** (30 mg, 0.15 mmol), after a flash column chromatography (n-hexanes: AcOEt = 40:1) afforded the product *ent*-**3f** as a white liquid (35.1 mg, 78.5% yield) with 96% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol =

95:05, 0.8 mL/min, 230 nm); minor enantiomer tr = 6.0 min, major enantiomer tr = 8.8 min.

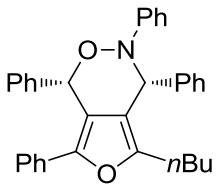


Under conditions B: The product **3f** was obtained liquid (39.1 mg, 87% yield) with 96% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95 :05, 0.8 mL/min, 230 nm); minor enantiomer tr = 11.2 min, major enantiomer tr = 6.8 min

7. Synthesis of *ent*-3g and 3g.[1]



Under conditions A: The reaction of ketone **1f** (26.2 mg, 0.10 mmol) and introne **2a** (30 mg, 0.15 mmol), after a flash column chromatography (n-hexanes: AcOEt = 80:1) afforded the product *ent*-**3g** as a yellow liquid (35.1 mg, 78.5% yield) with 95% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54(m, 2H), 7.34-7.23(m, 7H), 7.15-7.12(m, 7H), 7.05(t, *J* = 20Hz), 6.96-6.90(m, 3H), 6.28(s, 1H), 5.58(s, 1H), 2.35-2.30(m, 2H), 1.54-1.44(m, 1H), 1.40-1.29(m, 1H), 1.21-1.18 (m, 2H), 0.82-0.78(m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.15, 148.31, 144.82, 138.99, 138.17, 130.64, 129.62, 129.55, 128.60, 128.39, 128.32, 128.15, 127.95, 127.67, 126.39, 124.80, 124.20, 123.73, 120.40, 118.14, 79.28, 64.07, 29.99, 26.46, 22.32, 13.77; MS (APCI): (M+H) (%) = 485.45; HRMS calculated for [$C_{34}H_{31}NO_2$] 485.2355, found: 485.2352; Enantiomeric excess was determined by HP LC with a Chiral pak AS-H column (n-hexanes: 2-propanol = 95:05, 0.5 mL/min, 230 nm); minor enantiomer tr = 7.8 min, major enantiomer tr = 11.6 min..



Under conditions B: The product **3g** was obtained liquid (39.1 mg, 81% yield) with 95% ee. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (n-hexanes: 2-propanol = 95:05, 0.8 mL/min, 230 nm); minor enantiomer tr = 7.8 min, major enantiomer tr = 11.8 min.

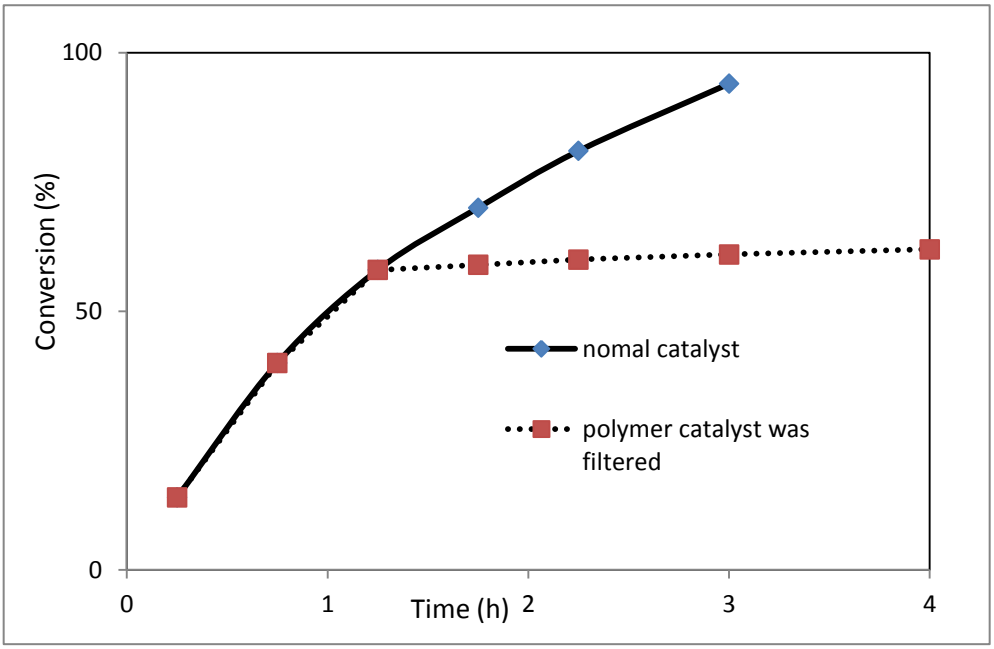


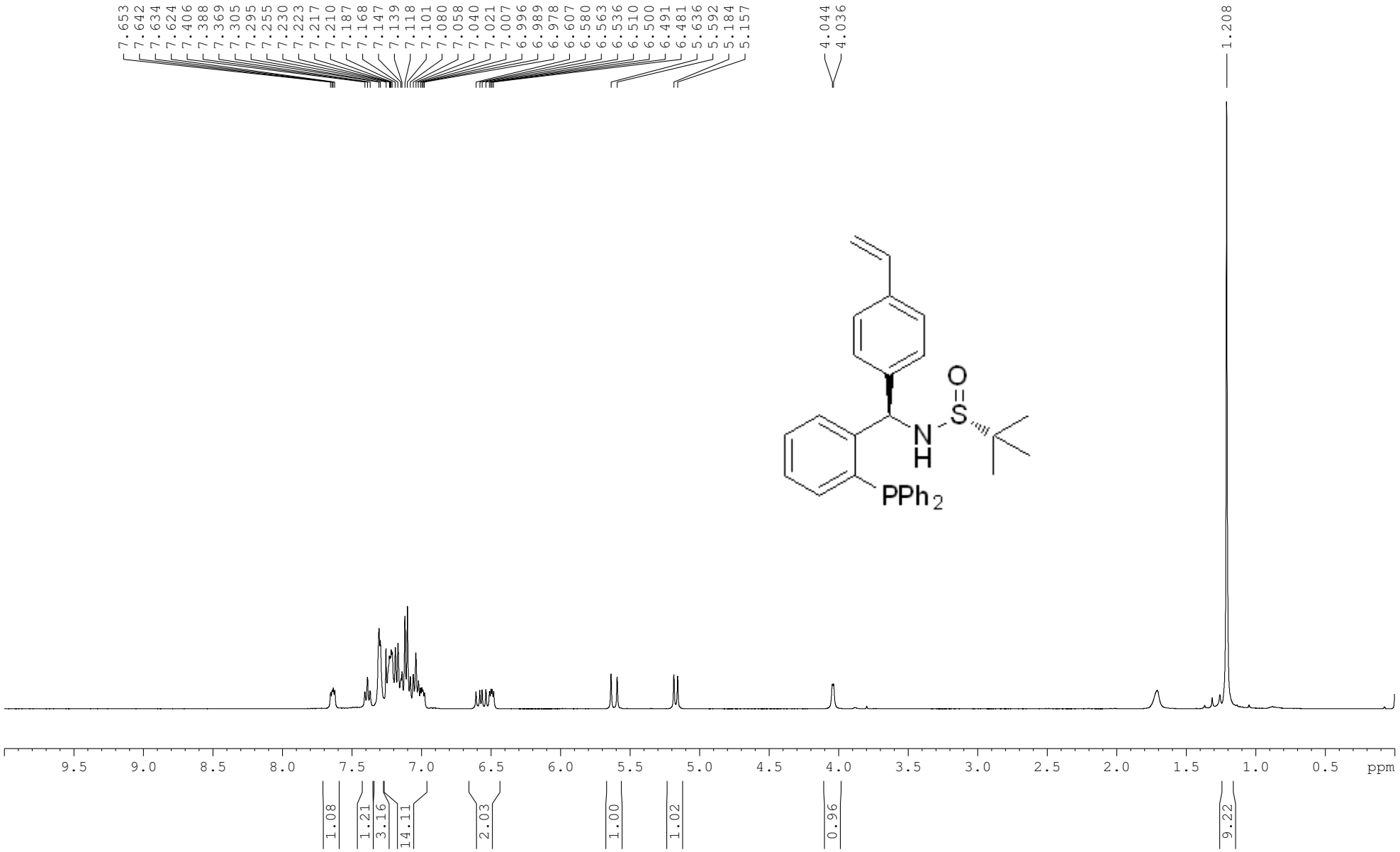
Figure S4 the normal reaction kinetic curve (no filtration) versus the polymer catalyst was filtrated(filtration)

6. References

1. Z.-M. Zhang, P. Chen, W. Li, Y, Niu, X.-L. Zhao, J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *126*, 4439.

2. (a) L. B. Schenkel, J. A. Ellman, *Org. Lett.* **2003**, *5*, 545. (b) D. A. Cogan, G. Liu, J. A. Ellman, *Tetrahedron* **1999**, *55*, 8883.

cmj-1-146-b H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7.217
7.210
7.187
7.168
7.147
7.139
7.118
7.101
7.080
7.058
7.040
7.021
7.007
6.996
6.989
6.978
6.607
6.580
6.563
6.536
6.510
6.500
6.491
6.481
5.636
5.592
5.184
5.157
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4.036
1.208
O
S
N
H
PPh2
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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
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1.5
1.0
0.5
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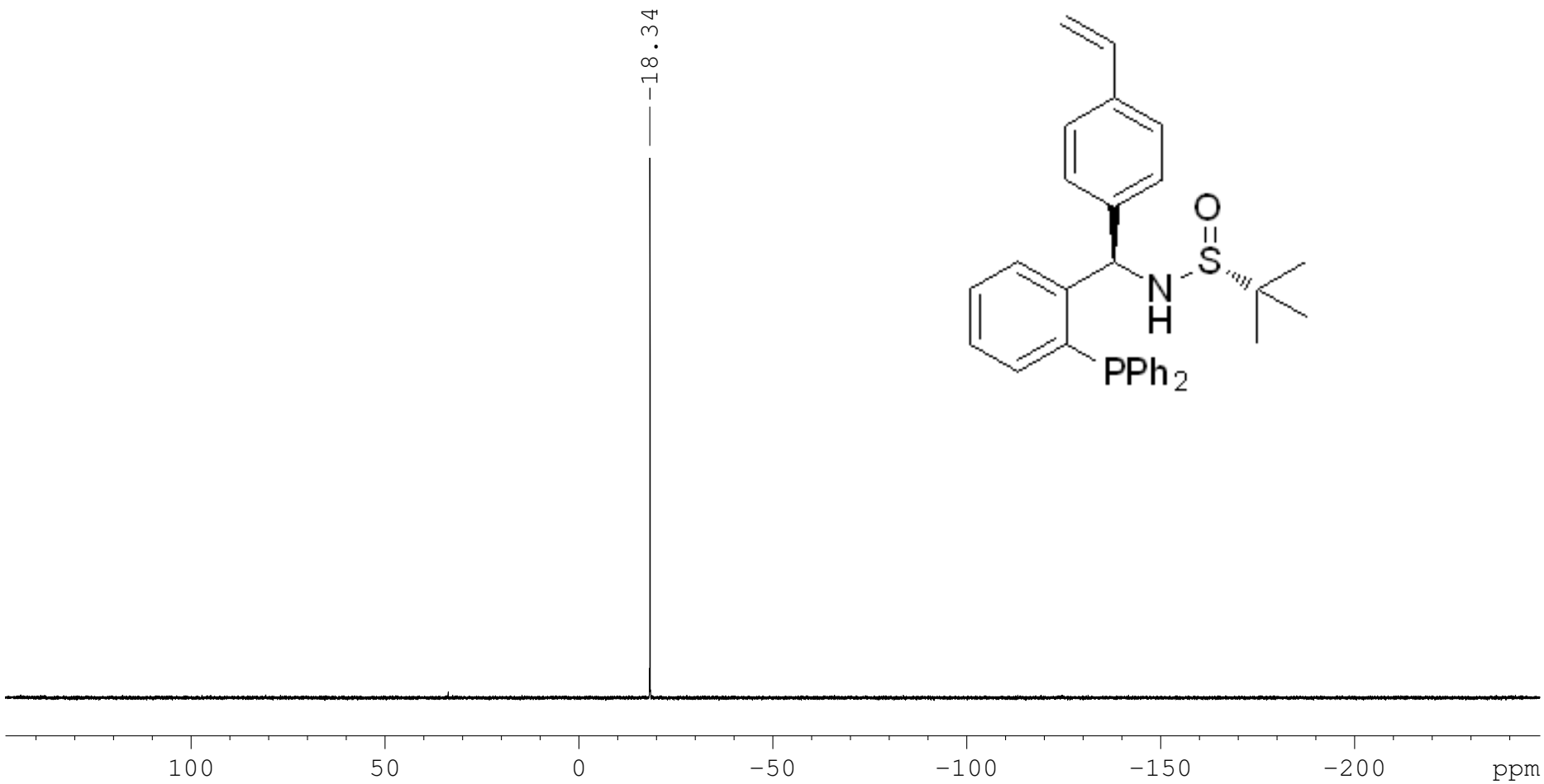
1.02
0.96
9.22

cmj-1-146-b P



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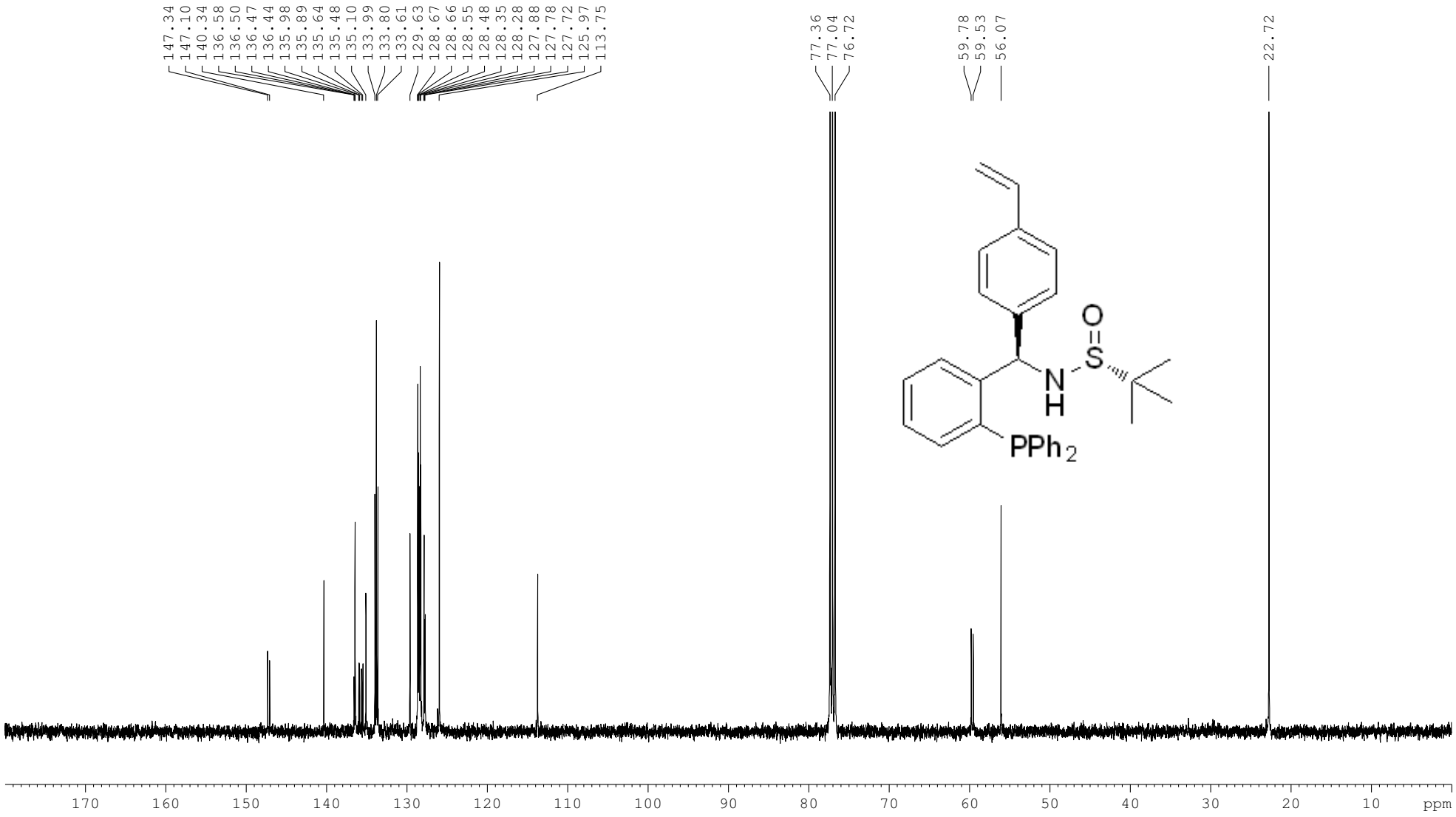
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135.10
133.99
133.80
133.61
129.63
128.67
128.66
128.55
128.48
128.35
128.28
127.88
127.78
127.72
125.97
113.75
77.36
77.04
76.72
59.78
59.53
56.07
22.72
O
S
N
H
PPh2
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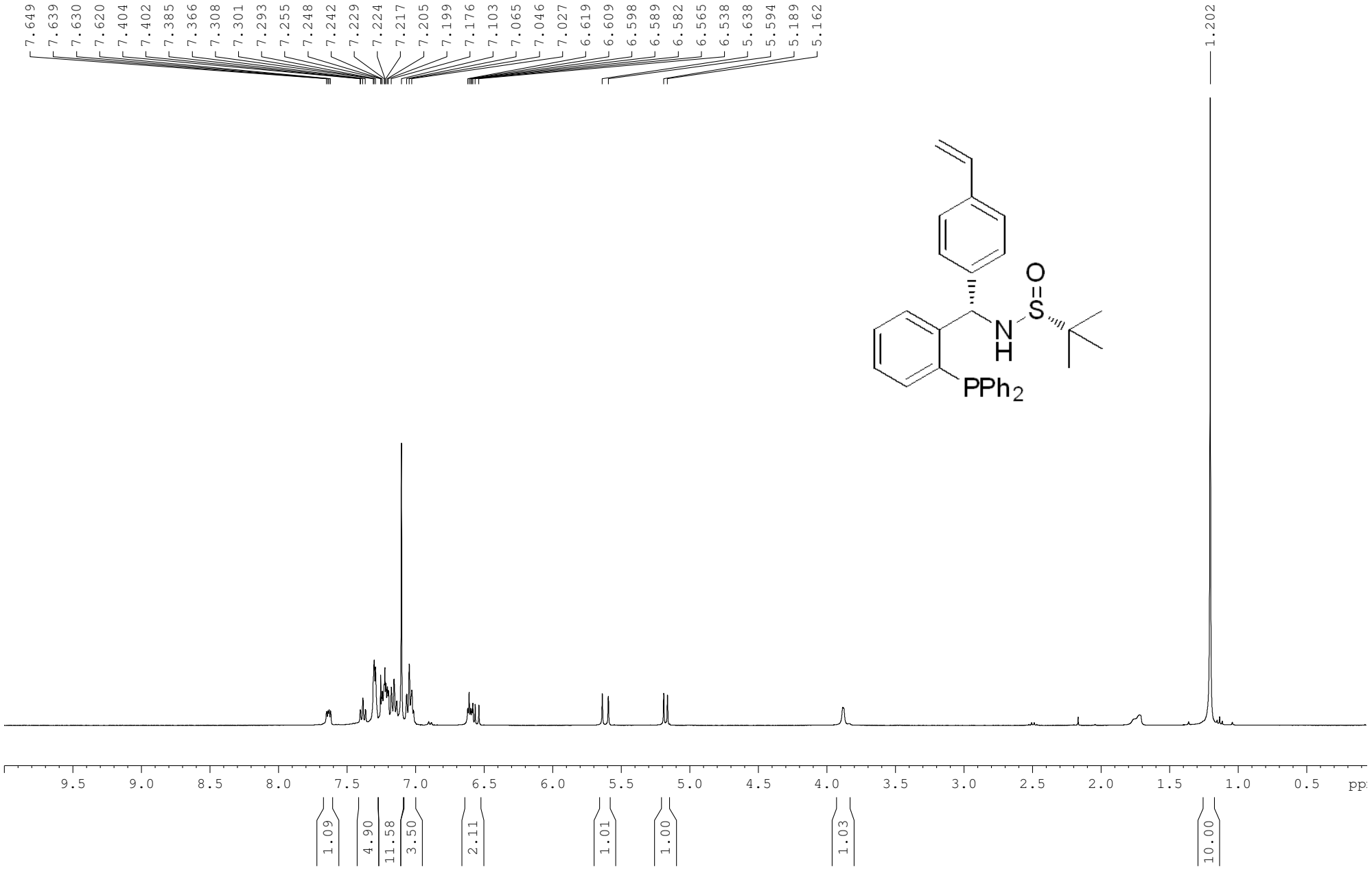
10
ppm

cmj-2-10-3 H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7.205
7.199
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7.046
7.027
6.619
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6.598
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6.565
6.538
5.638
5.594
5.189
5.162
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S
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H
PPh2
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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
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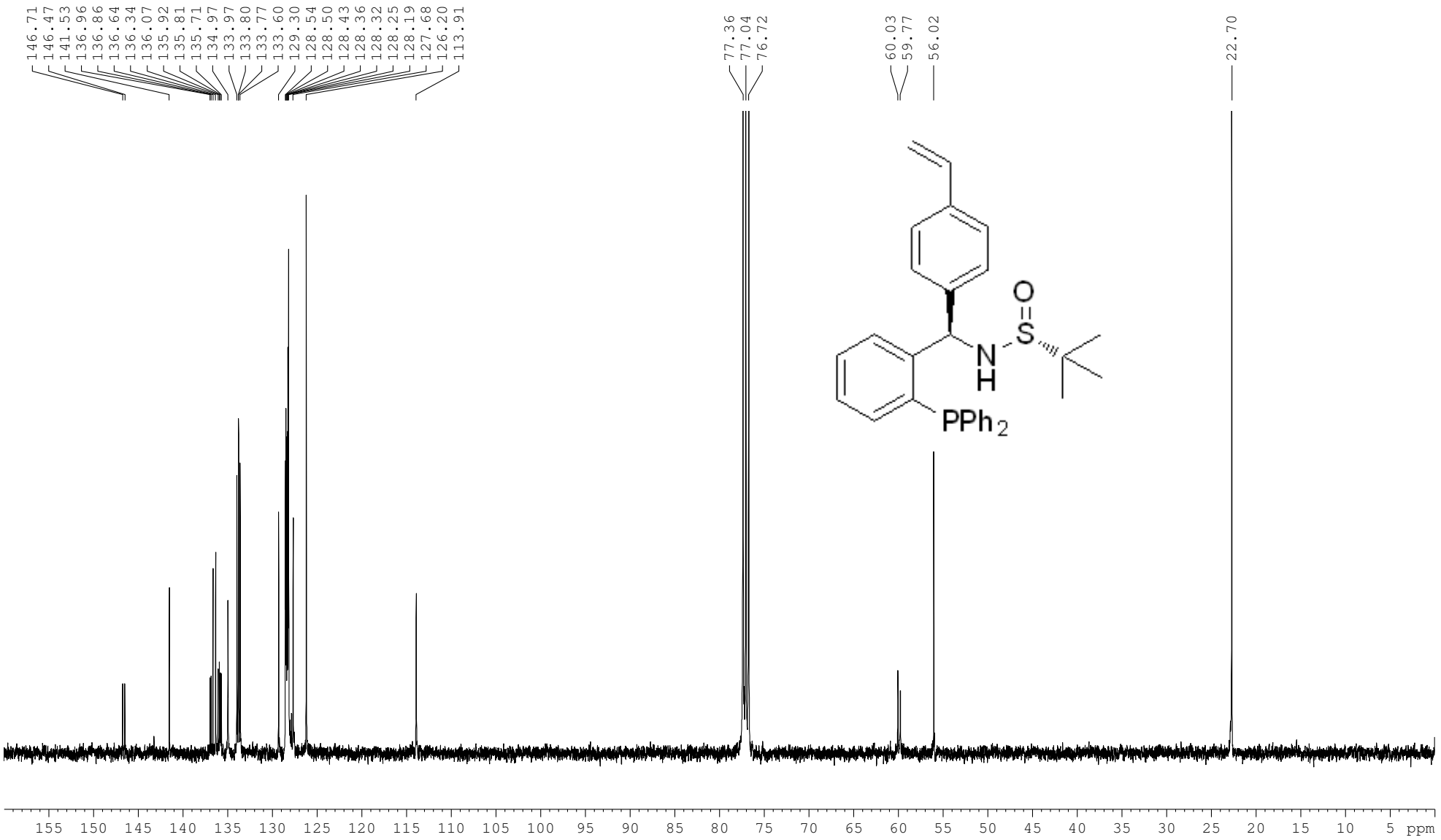
cmj-2-10-3 C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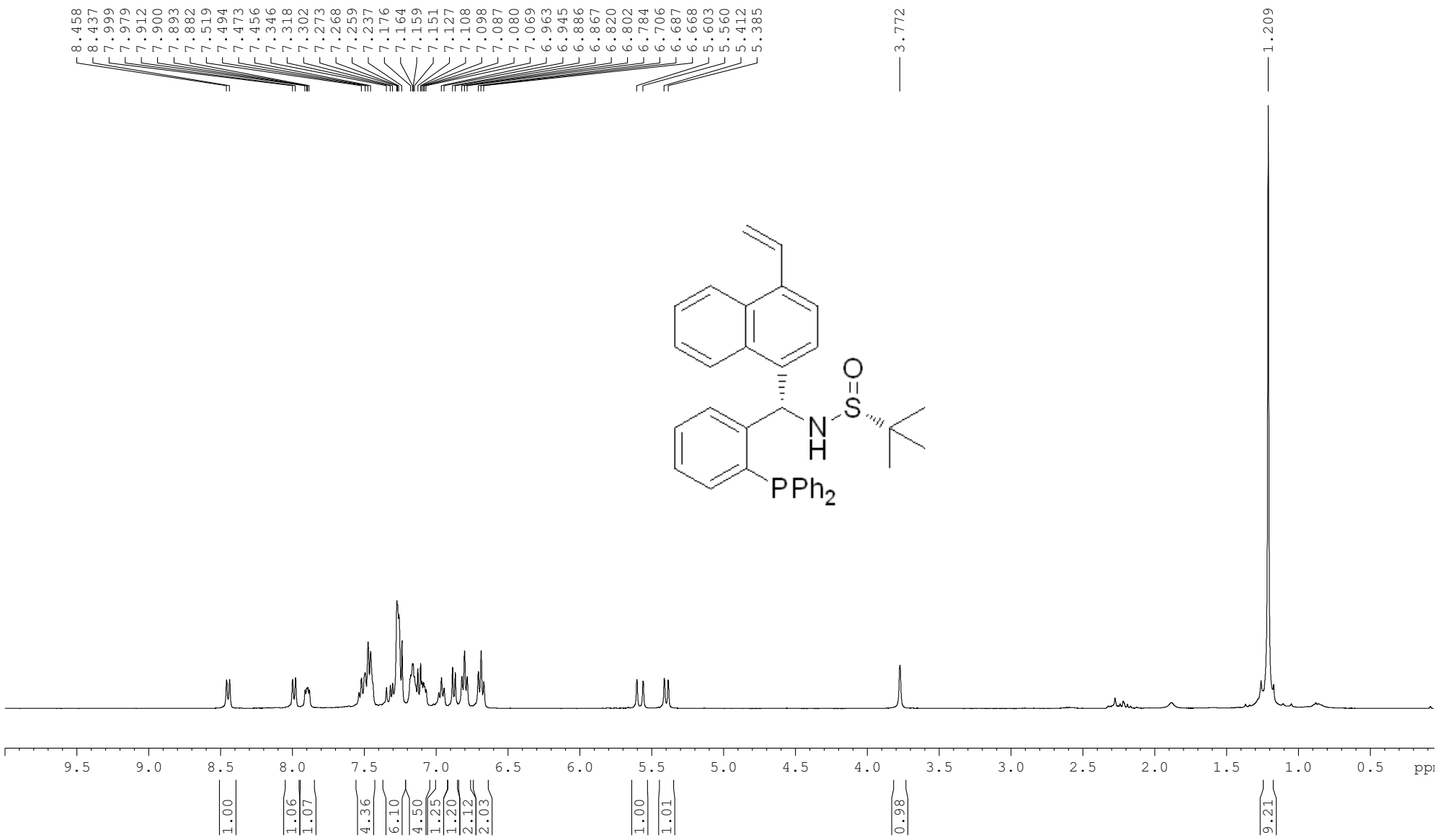
133.80
133.77
133.60
129.30
128.54
128.50
128.43
128.36
128.32
128.25
128.19
127.68
126.20
113.91
77.36
77.04
76.72
60.03
59.77
56.02
22.70
O
S
N
H
PPh2
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

cmj-4-30-2 h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7.318
7.302
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7.268
7.259
7.237
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7.151
7.127
7.108
7.098
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7.080
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6.945
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S
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H
PPh2
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2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.06
1.07
4.36
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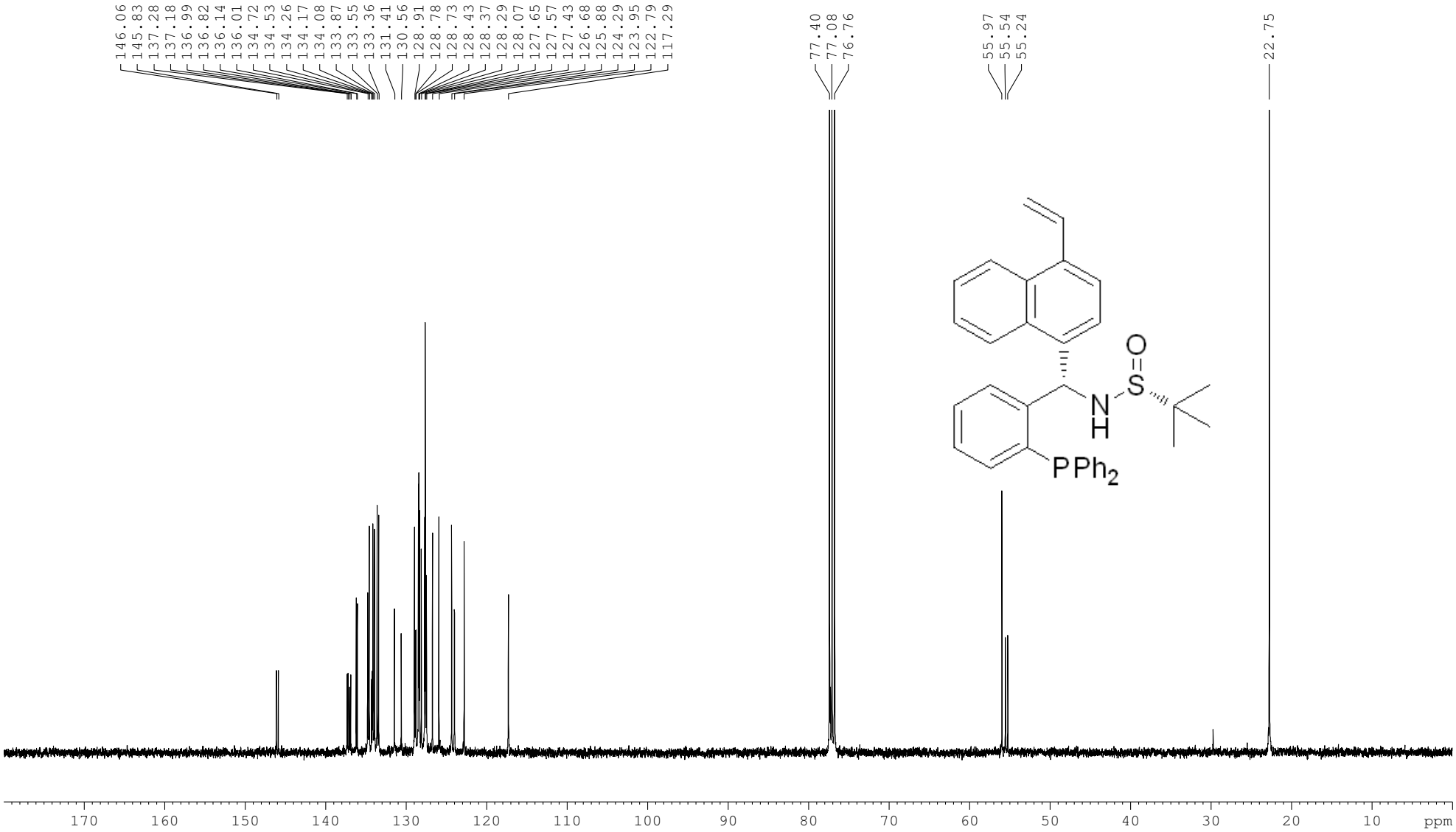
cmj-4-30-2 c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133.87
133.55
133.36
131.41
130.56
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128.78
128.73
128.43
128.37
128.29
128.07
127.65
127.57
127.43
126.68
125.88
124.29
123.95
122.79
117.29
77.40
77.08
76.76
55.97
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55.24
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O
S
N
H
PPh2
170
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30
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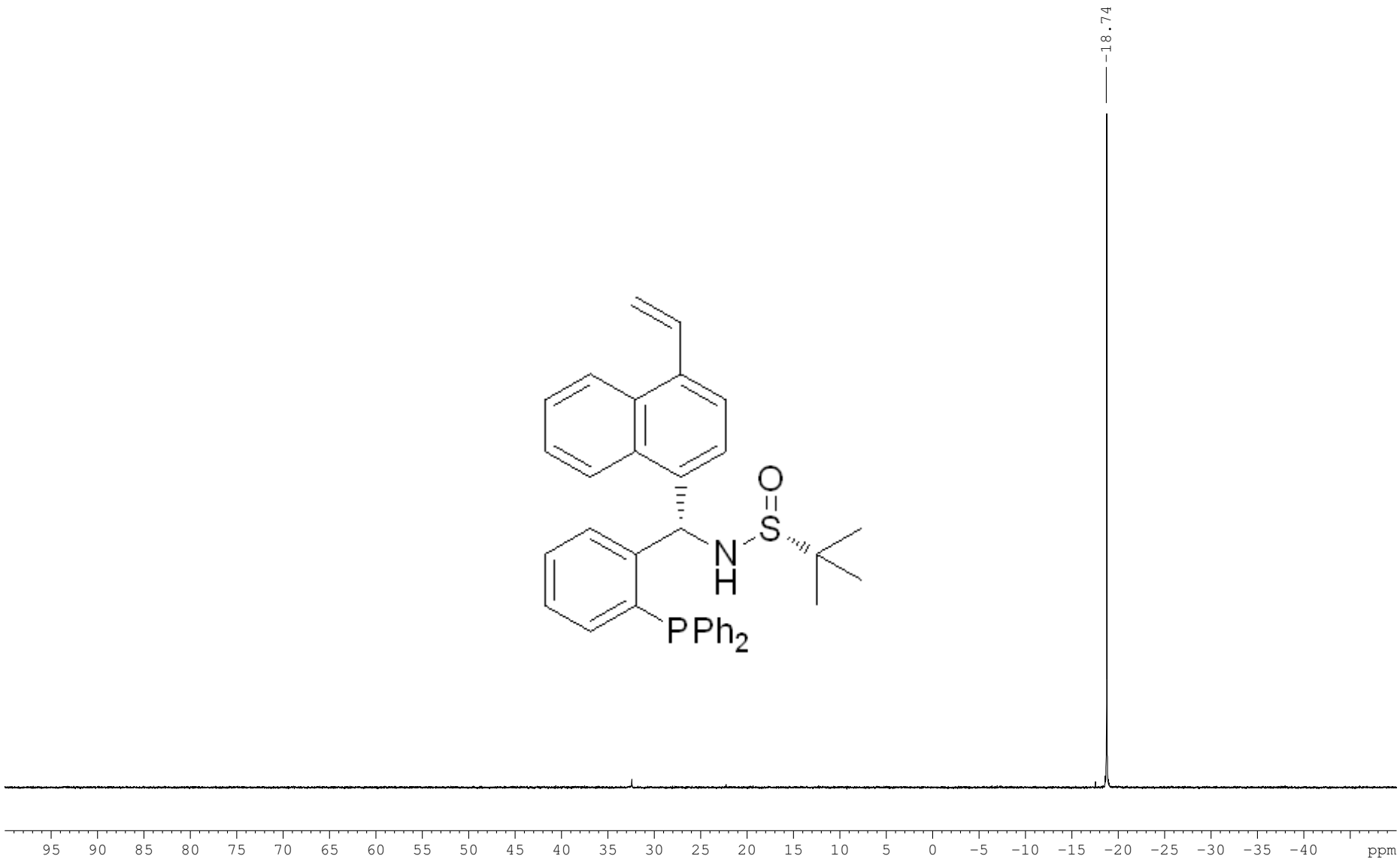
10
ppm

cmj-4-30-2 p


-18.74
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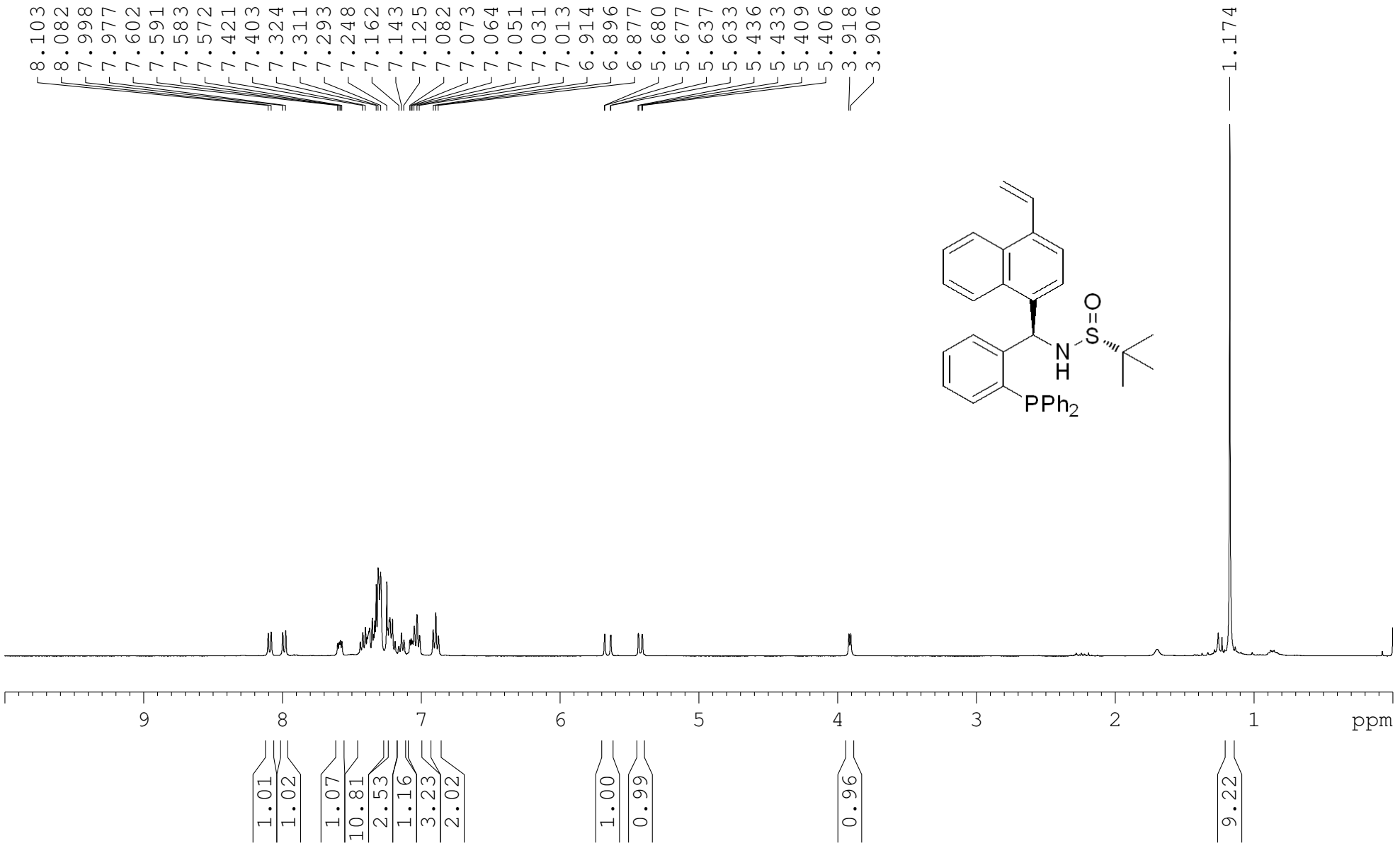
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
ppm

cmj-4-36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3
2
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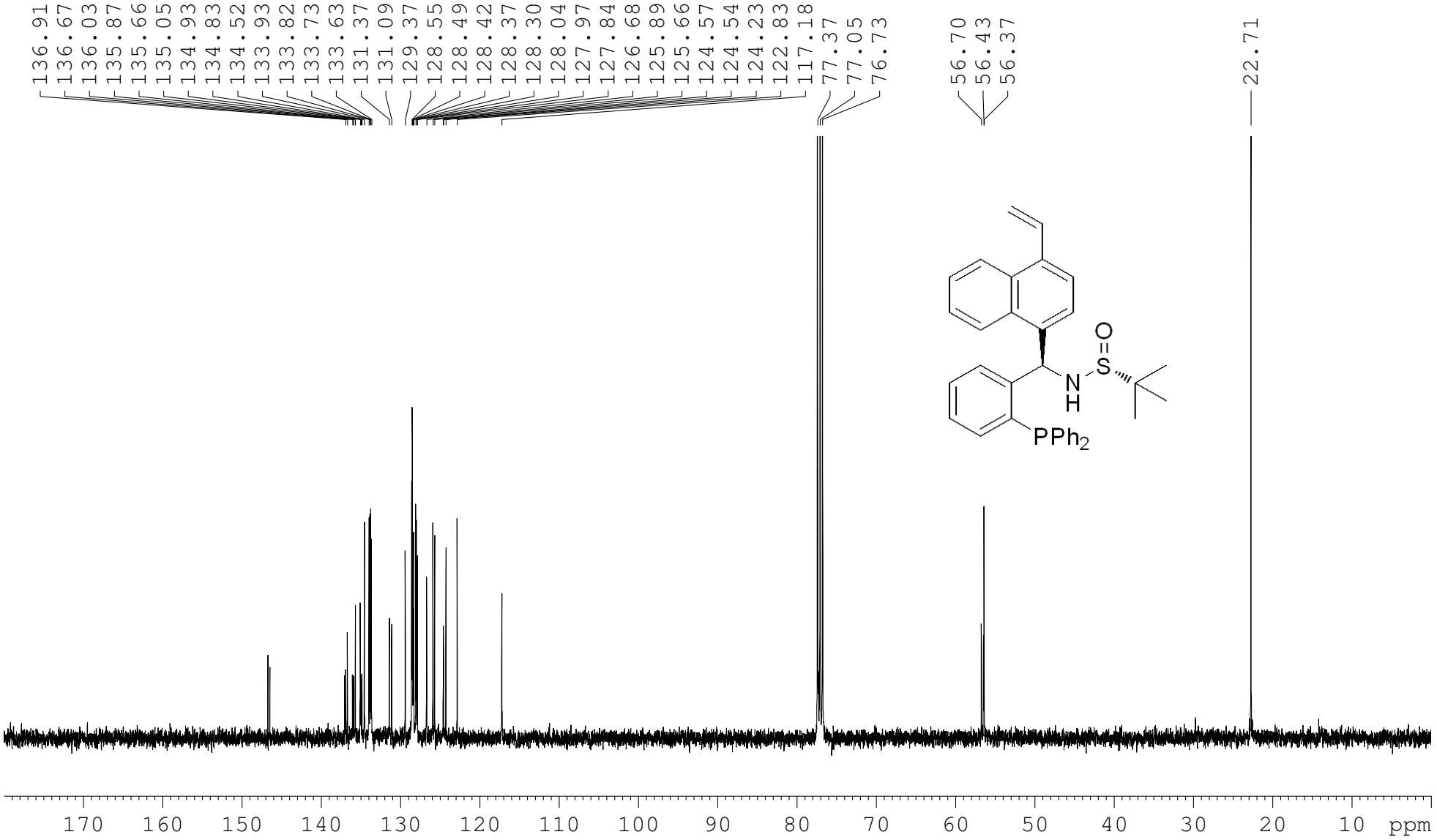
cmj-4-36 c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128.49
128.42
128.37
128.30
128.04
127.97
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126.68
125.89
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117.18
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77.05
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56.70
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S
N
H
PPh2
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120
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100
90
80
70
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30
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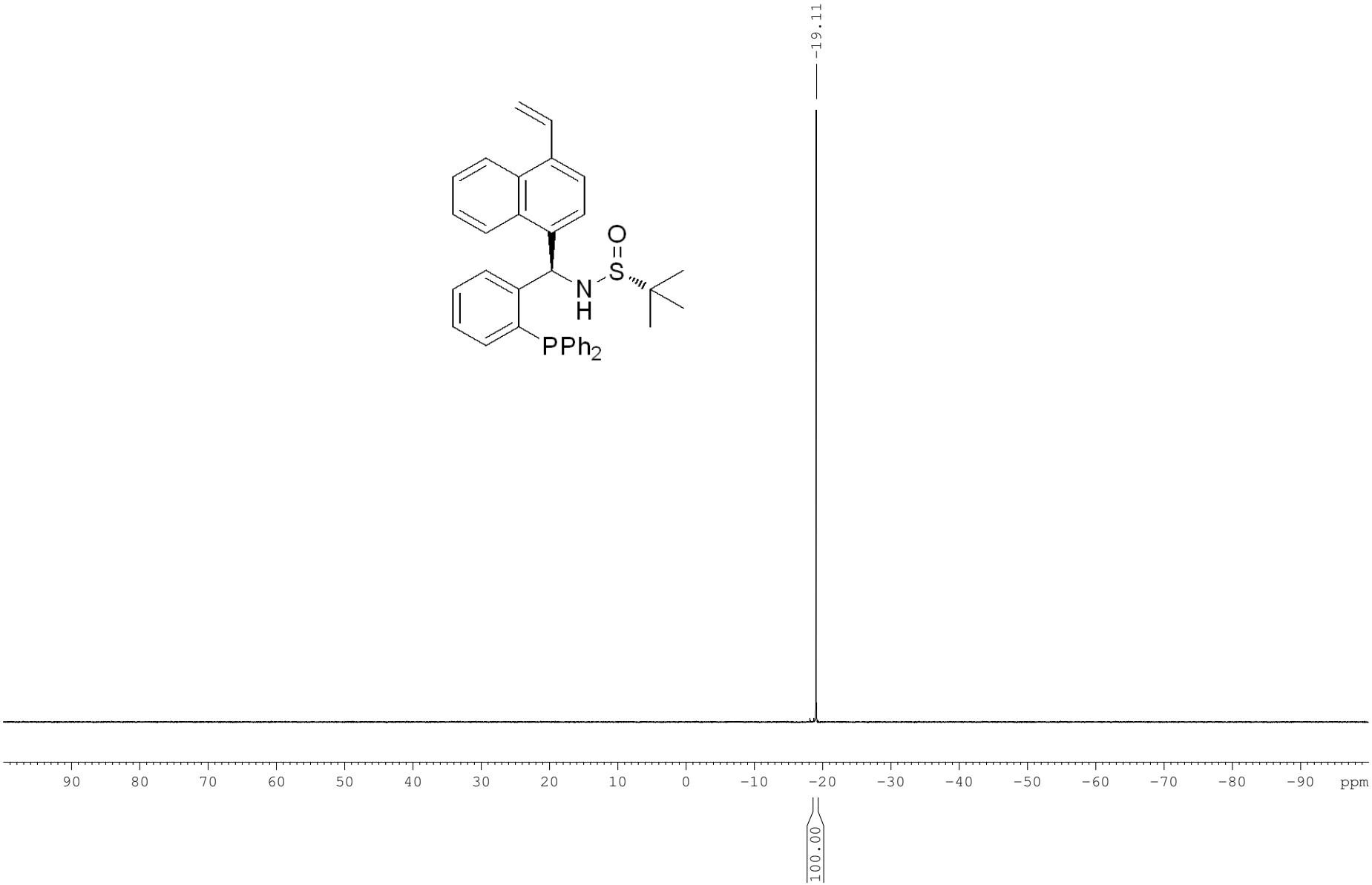
10
ppm

cmj-4-36-2 p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-70
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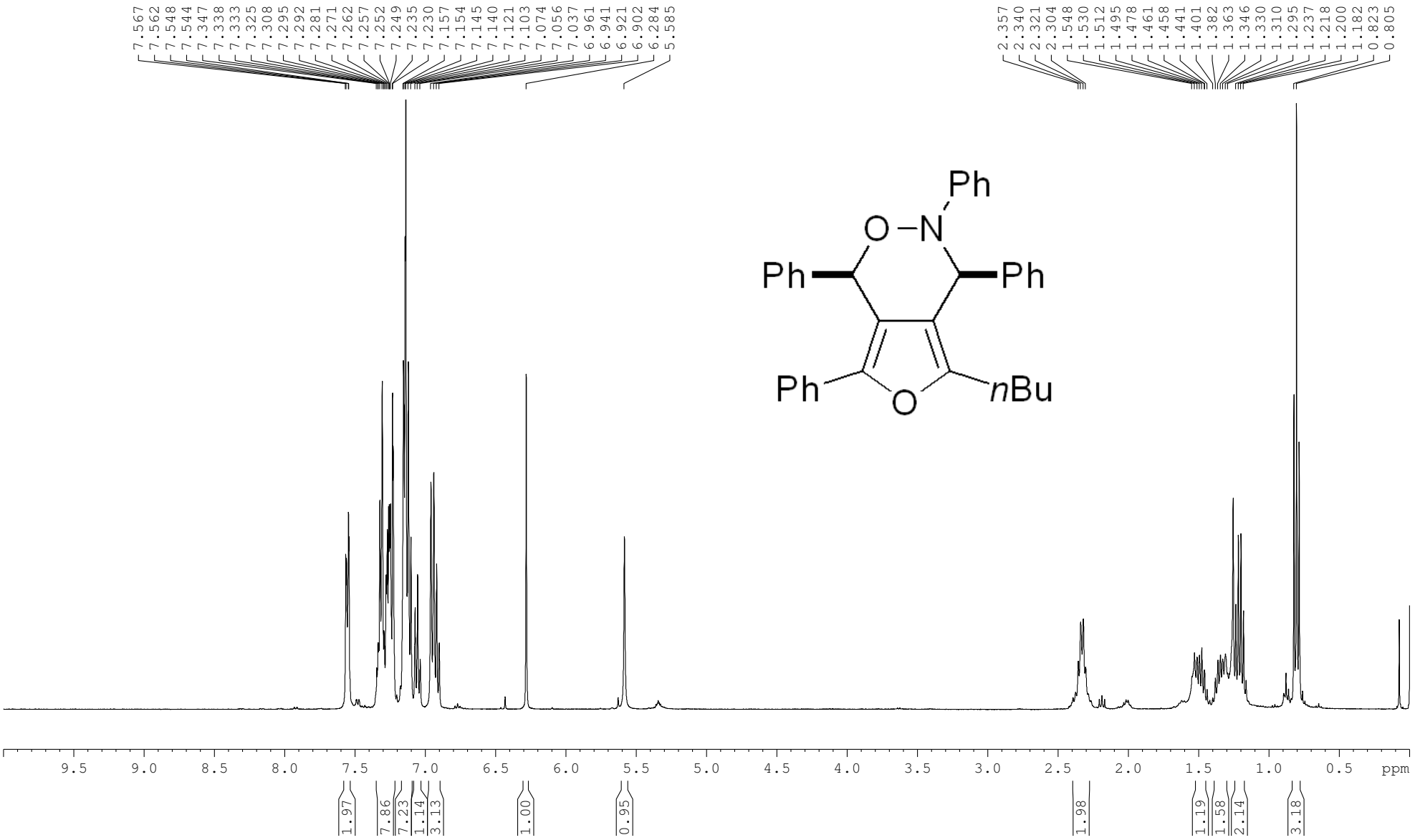
100.00

cmj-4-113-b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7.037
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1.330
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1.295
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1.200
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Ph
O
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8.5
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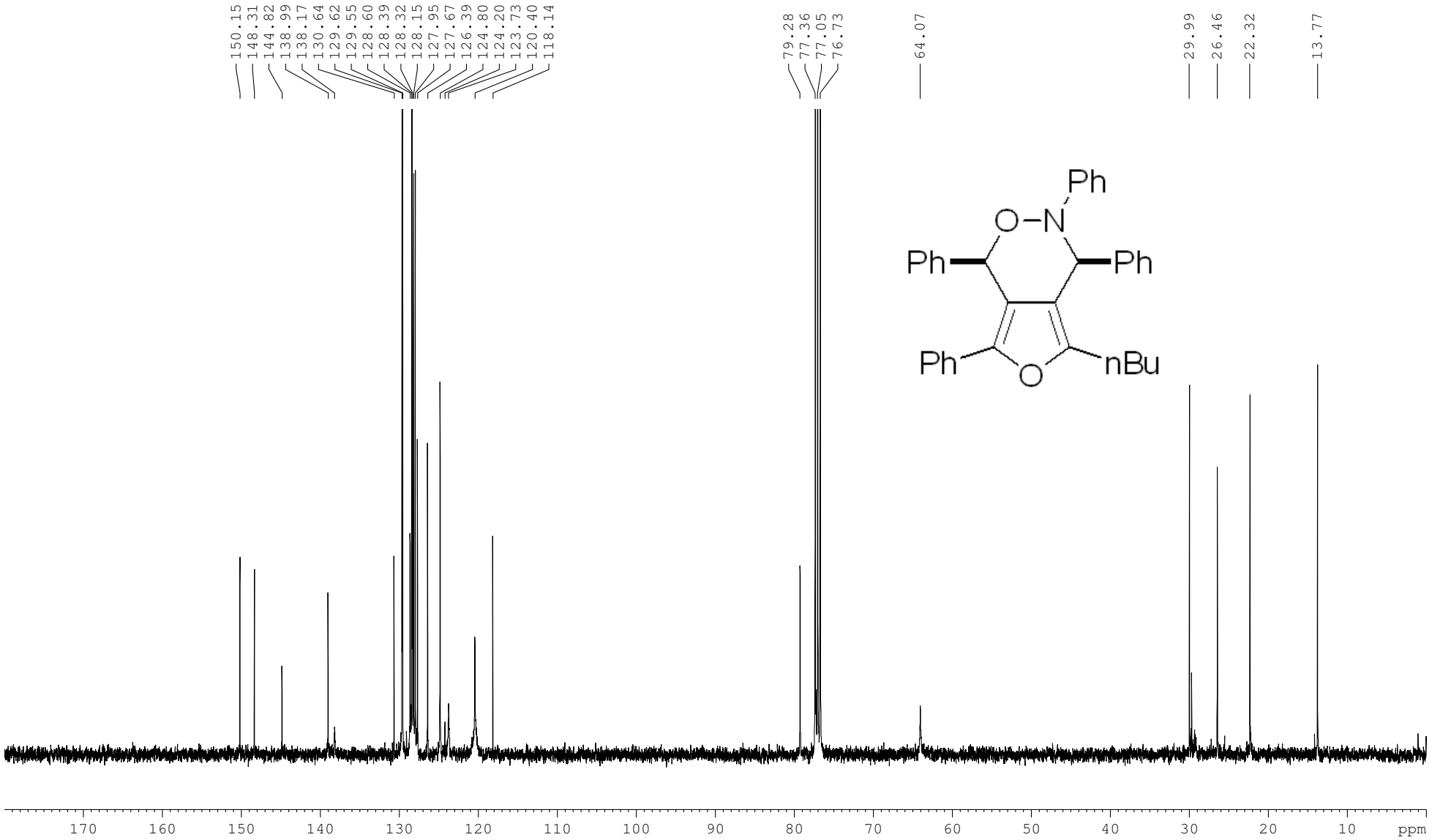
cmj-4-113-b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124.20
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120.40
118.14
79.28
77.36
77.05
76.73
64.07
29.99
26.46
22.32
13.77
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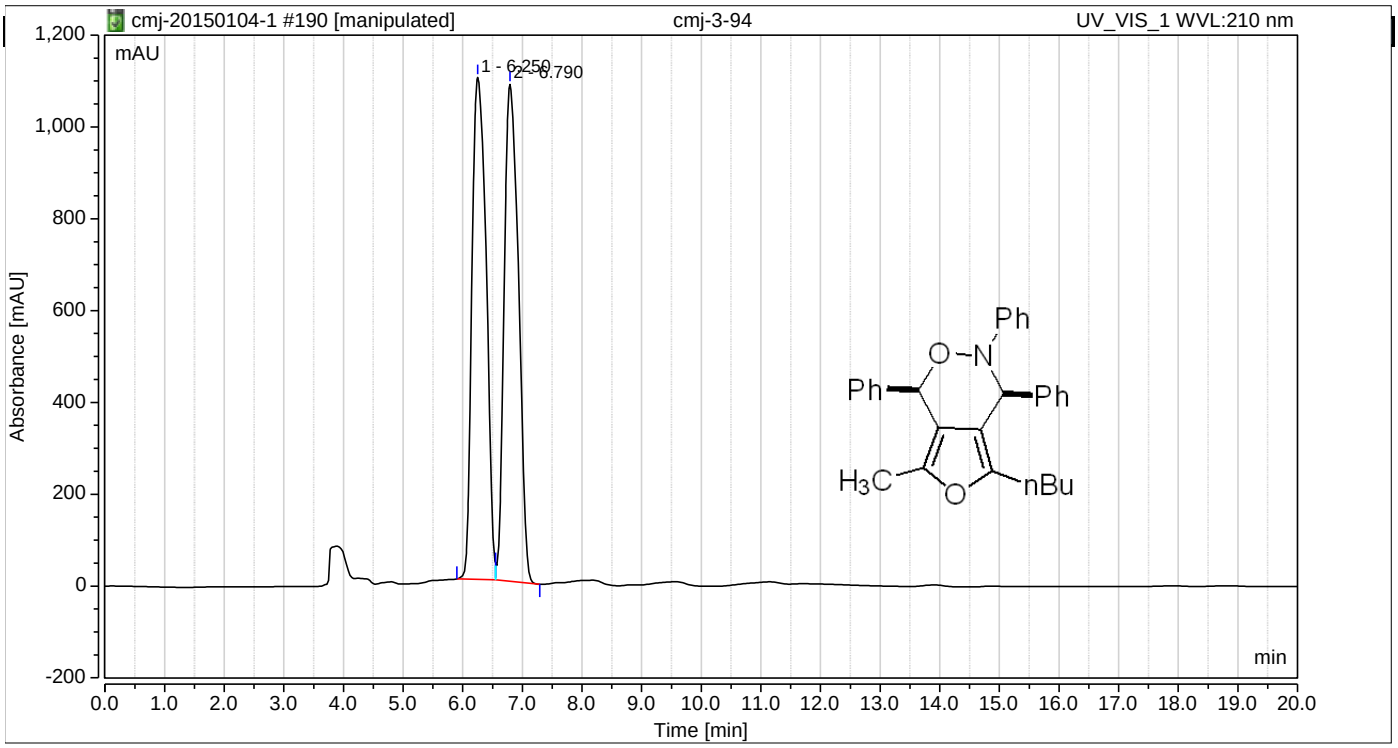
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Chromatogram and Results

Injection Details

Injection Name:	**cmj-3-94**	*Run Time (min):*	**20.00**
Vial Number:	**RA8**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.8ml-210254200-25-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/6月/15 01:15**	*Sample Weight:*	**1.0000**



Integration Results

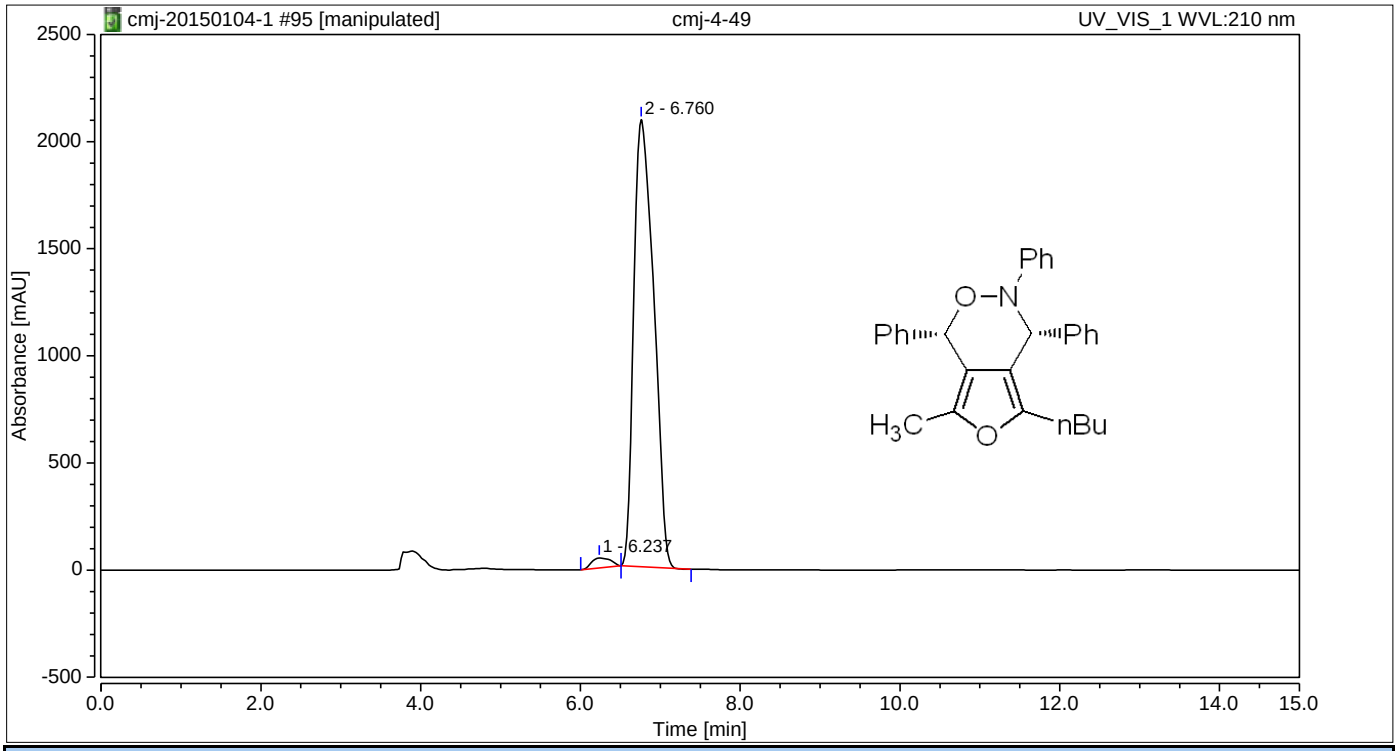
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.250	303.393	1093.261	50.08	50.26	n.a.
2		6.790	302.416	1081.960	49.92	49.74	n.a.
Total:			**605.809**	**2175.221**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-49**	*Run Time (min):*	**15.00**
Vial Number:	**BC8**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**06/5月/15 02:04**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

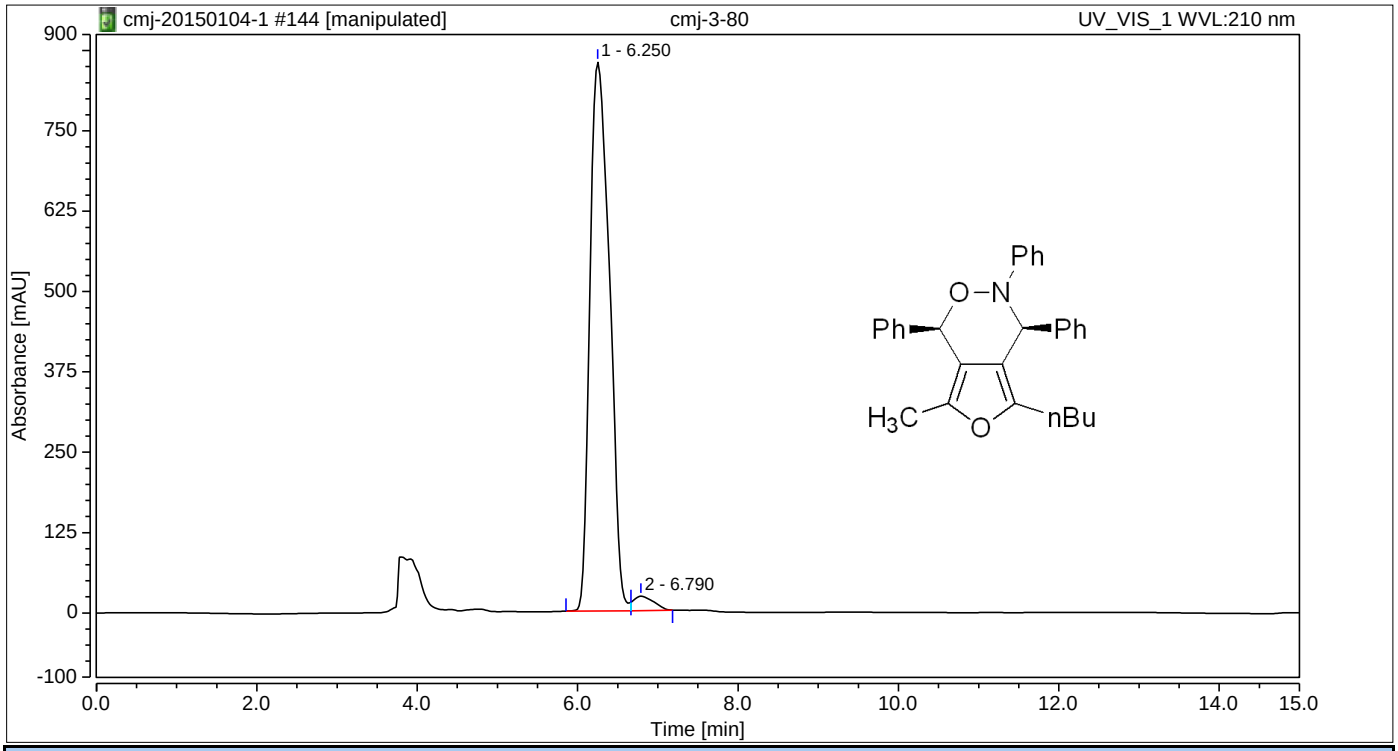
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.237	12.454	46.273	2.02	2.17	n.a.
2		6.760	604.037	2086.069	97.98	97.83	n.a.
Total:			**616.492**	**2132.342**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-3-80**	*Run Time (min):*	**15.00**
Vial Number:	**BB2**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**26/5月/15 21:08**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

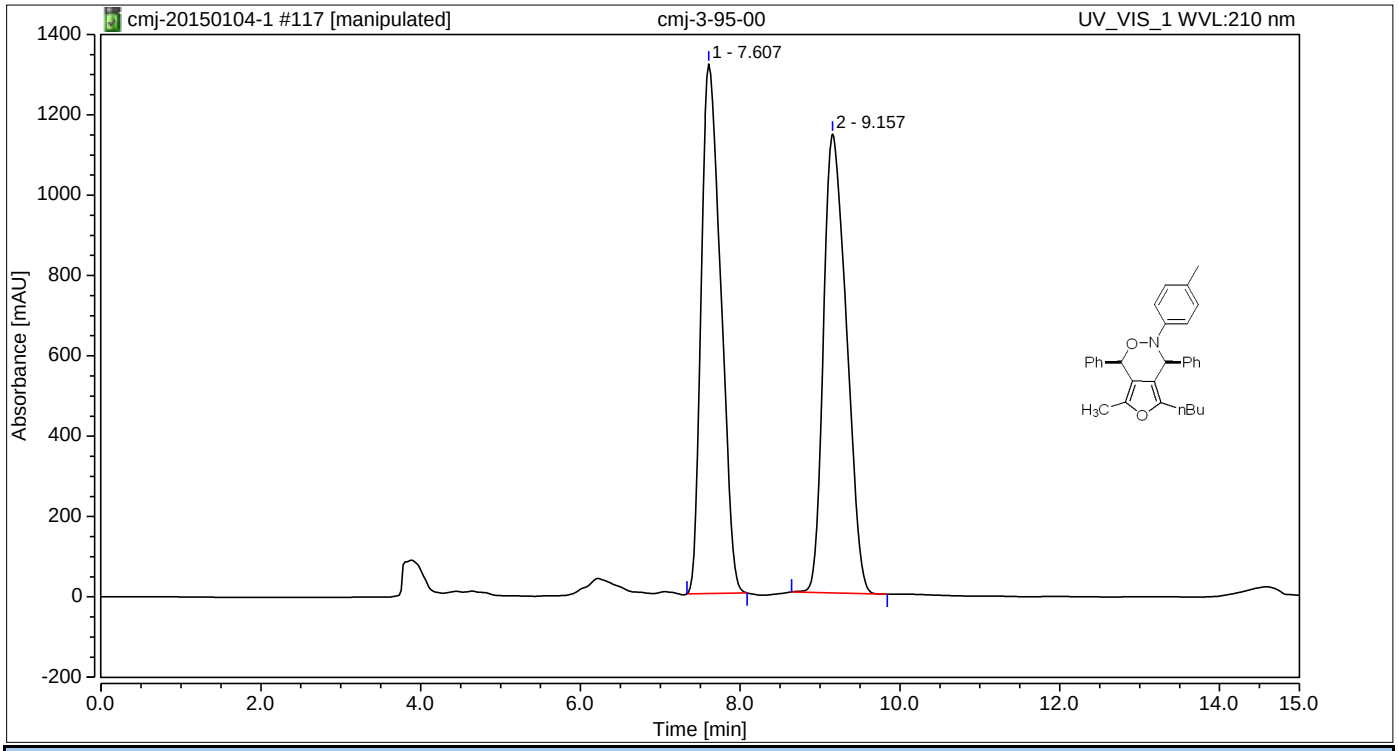
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.250	242.689	853.818	97.40	97.44	n.a.
2		6.790	6.486	22.418	2.60	2.56	n.a.
Total:			**249.175**	**876.236**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-3-95-00**	*Run Time (min):*	**15.00**
Vial Number:	**RC5**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/5月/15 23:37**	*Sample Weight:*	**1.0000**

Chromatogram



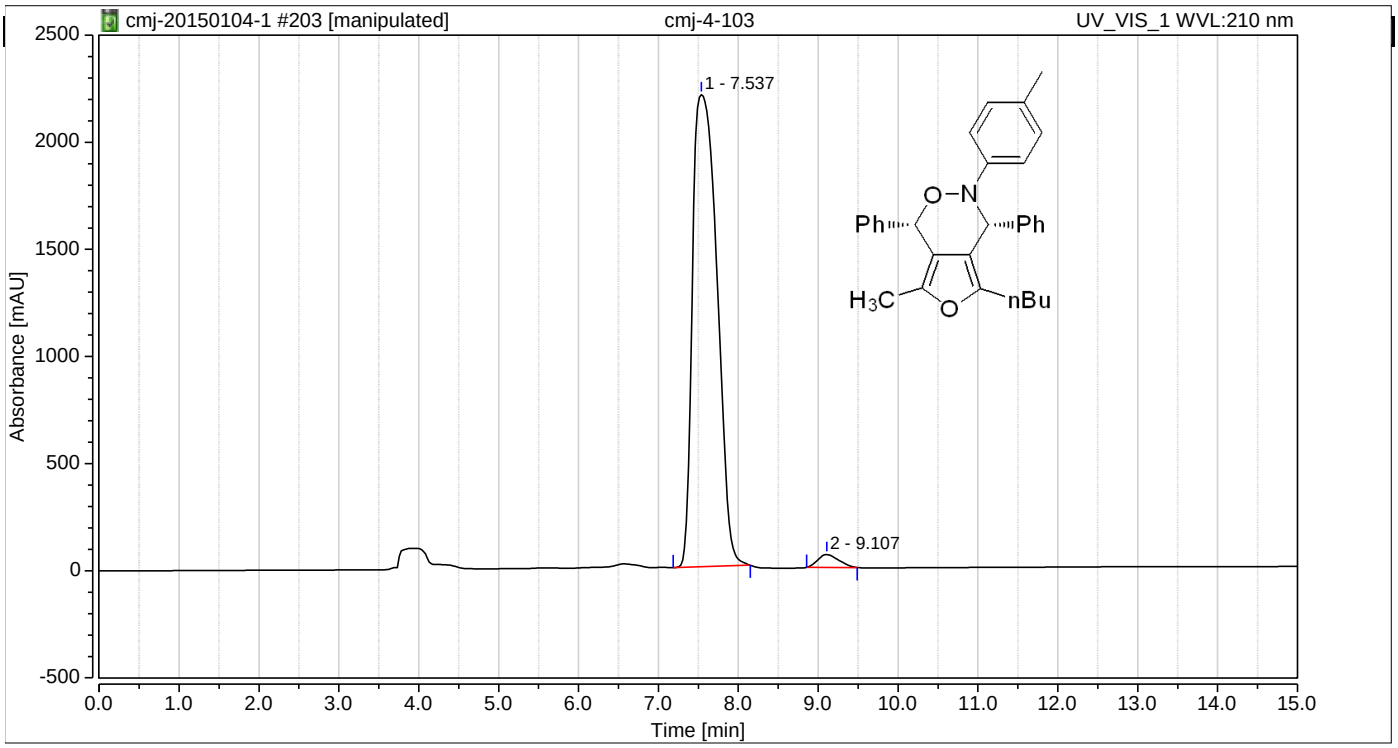
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.607	374.952	1318.392	49.62	53.58	n.a.
2		9.157	380.702	1142.016	50.38	46.42	n.a.
Total:			**755.654**	**2460.408**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-103**	*Run Time (min):*	**15.00**
Vial Number:	**GA4**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**233.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**20/6月/15 15:05**	*Sample Weight:*	**1.0000**



Integration Results

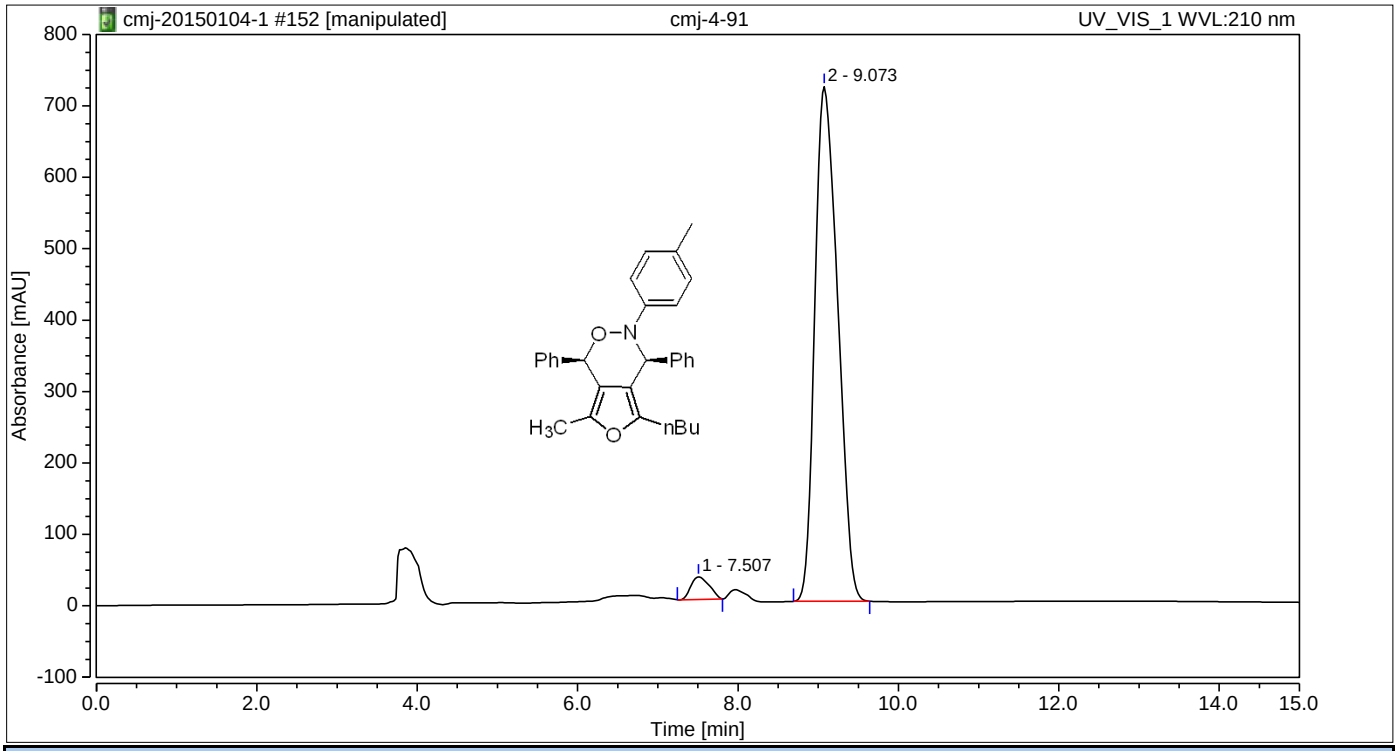
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.537	782.208	2203.102	97.74	97.35	n.a.
2		9.107	18.086	59.914	2.26	2.65	n.a.
Total:			**800.294**	**2263.017**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-91**	*Run Time (min):*	**15.00**
Vial Number:	**RD1**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**03/6月/15 10:26**	*Sample Weight:*	**1.0000**

Chromatogram



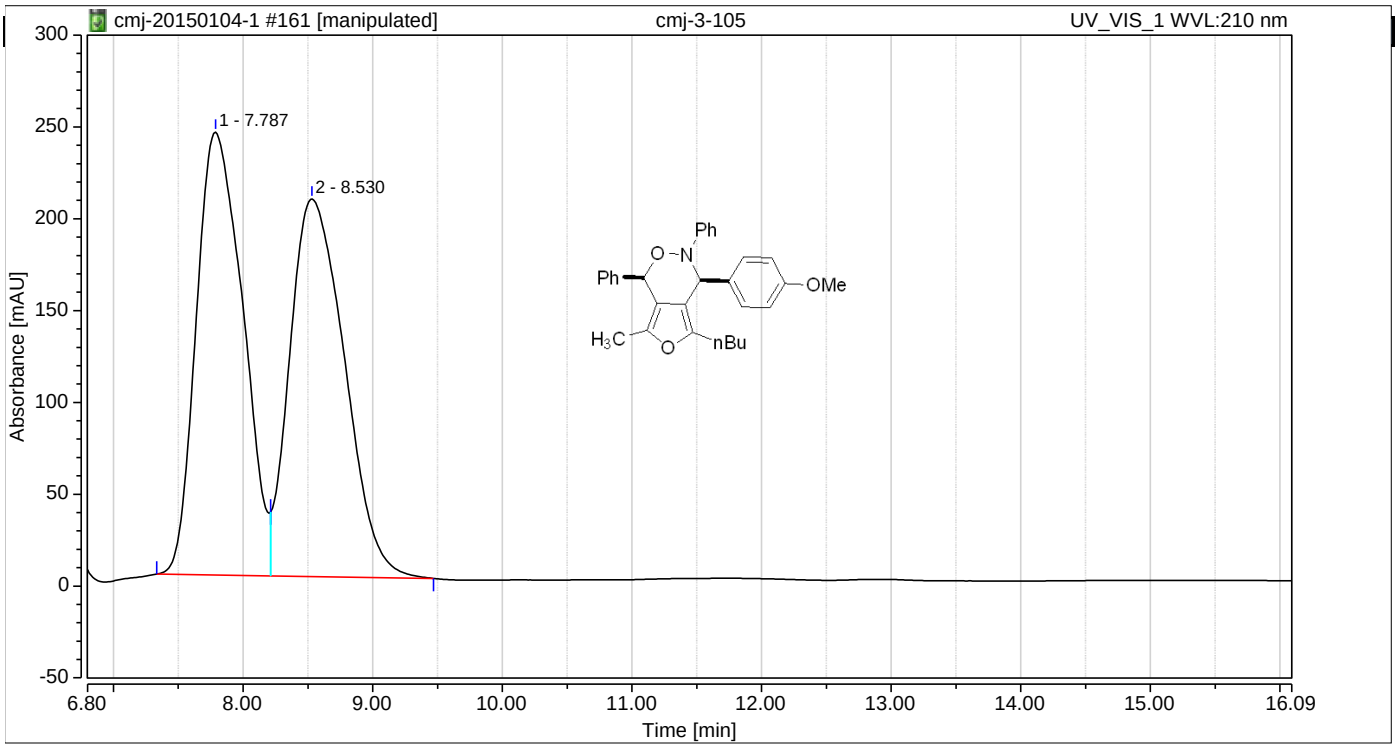
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.507	8.405	31.737	3.41	4.22	n.a.
2		9.073	238.078	720.892	96.59	95.78	n.a.
Total:			**246.483**	**752.629**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-3-105**	*Run Time (min):*	**16.09**
Vial Number:	**GB7**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.5ml-A5B95C0D0-ASH-25**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**06/6月/15 20:54**	*Sample Weight:*	**1.0000**



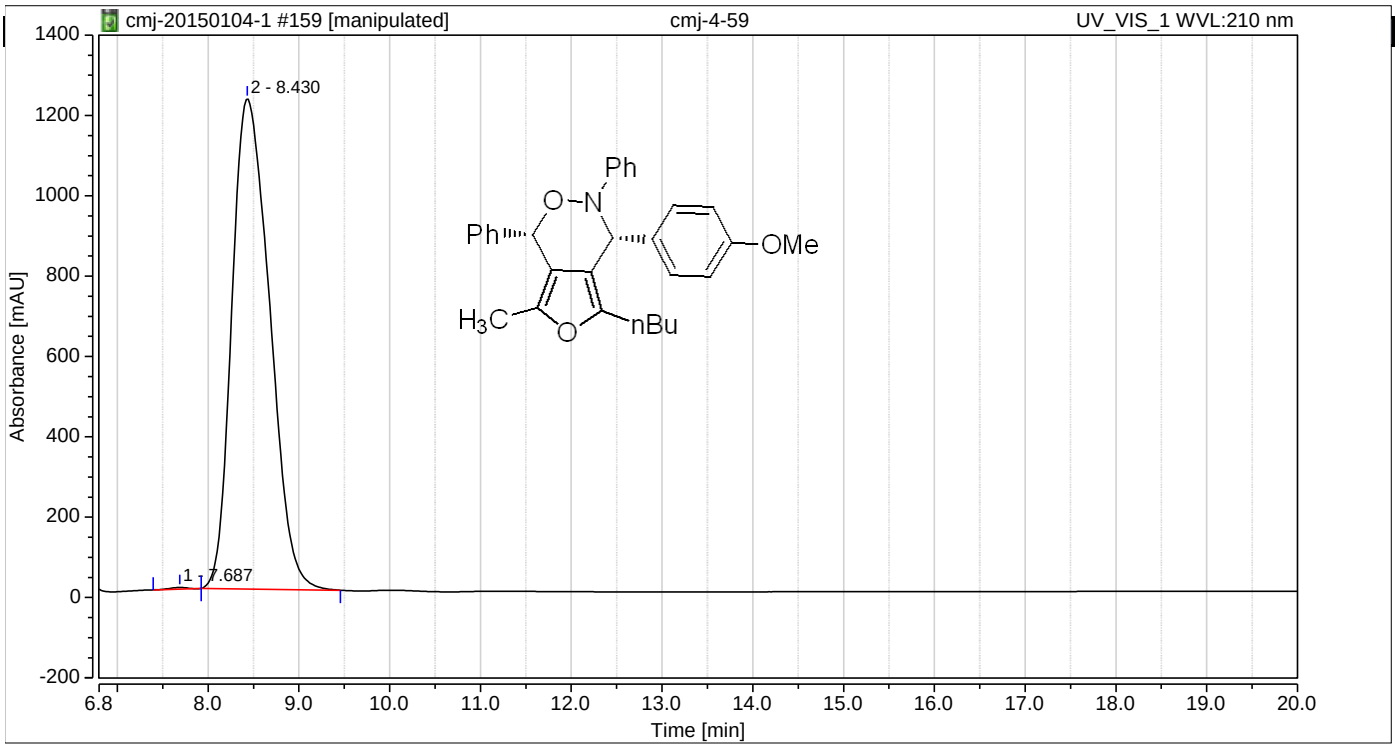
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.787	100.437	241.160	49.94	53.97	n.a.
2		8.530	100.684	205.672	50.06	46.03	n.a.
Total:			**201.121**	**446.832**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-59**	*Run Time (min):*	**20.00**
Vial Number:	**GA7**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.5ml-A5B95C0D0-ASH-25**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**06/6月/15 20:15**	*Sample Weight:*	**1.0000**



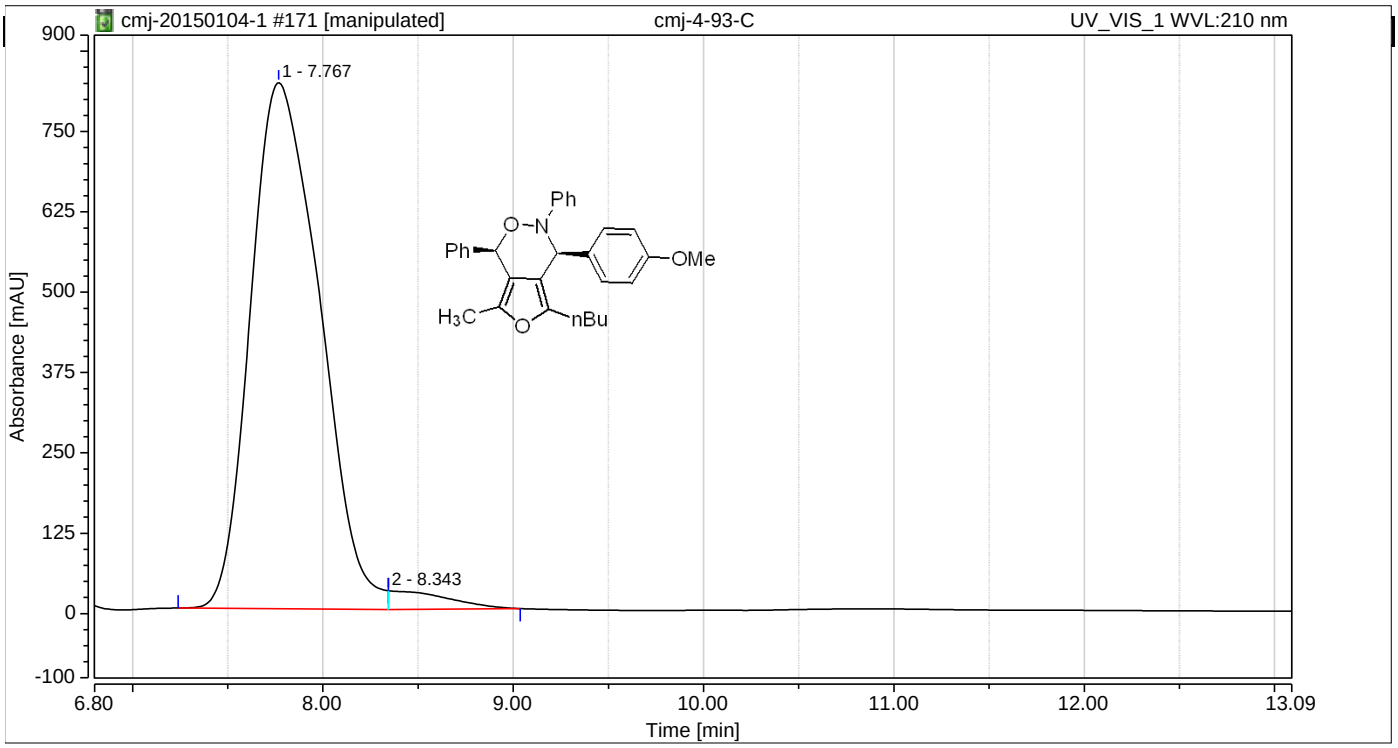
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.687	0.831	4.038	0.14	0.33	n.a.
2		8.430	587.748	1220.539	99.86	99.67	n.a.
Total:			**588.579**	**1224.577**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-93-C**	*Run Time (min):*	**13.09**
Vial Number:	**GA2**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.5ml-A5B95C0D0-ASH-25**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**11/6月/15 18:31**	*Sample Weight:*	**1.0000**



Integration Results

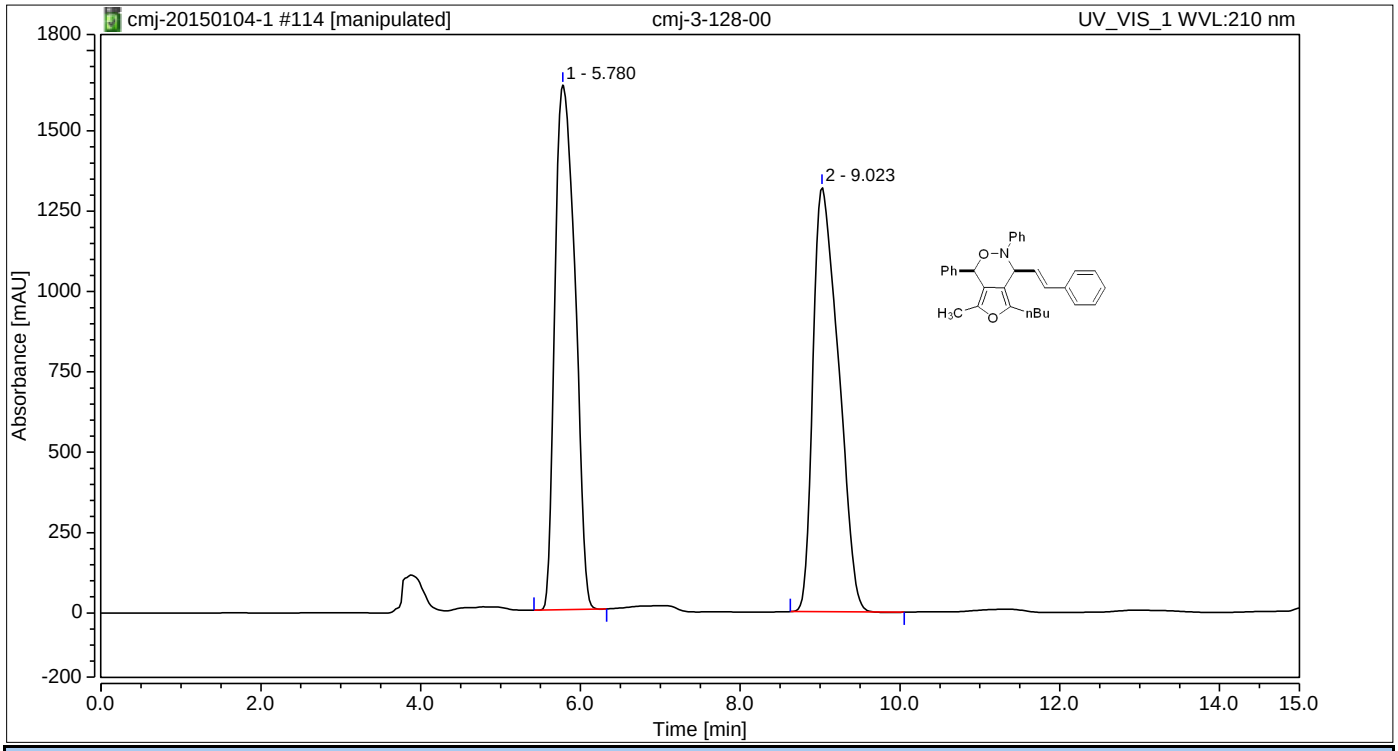
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.767	343.928	818.323	97.13	96.56	n.a.
2		8.343	10.153	29.182	2.87	3.44	n.a.
Total:			**354.082**	**847.505**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-3-128-00**	*Run Time (min):*	**15.00**
Vial Number:	**RC3**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/5月/15 23:05**	*Sample Weight:*	**1.0000**

Chromatogram



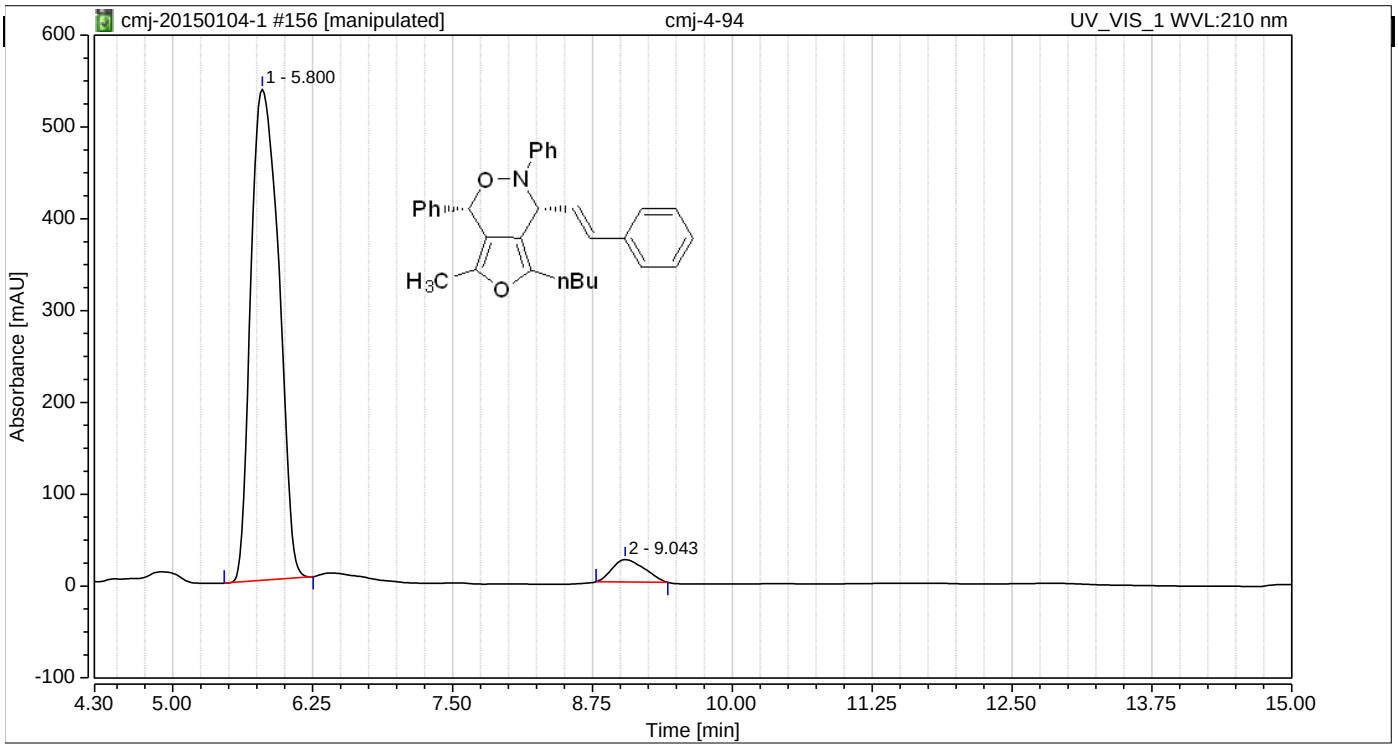
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.780	478.124	1632.580	49.57	55.27	n.a.
2		9.023	486.420	1321.161	50.43	44.73	n.a.
Total:			**964.544**	**2953.741**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-94**	*Run Time (min):*	**15.00**
Vial Number:	**GA8**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**05/6月/15 22:03**	*Sample Weight:*	**1.0000**



Integration Results

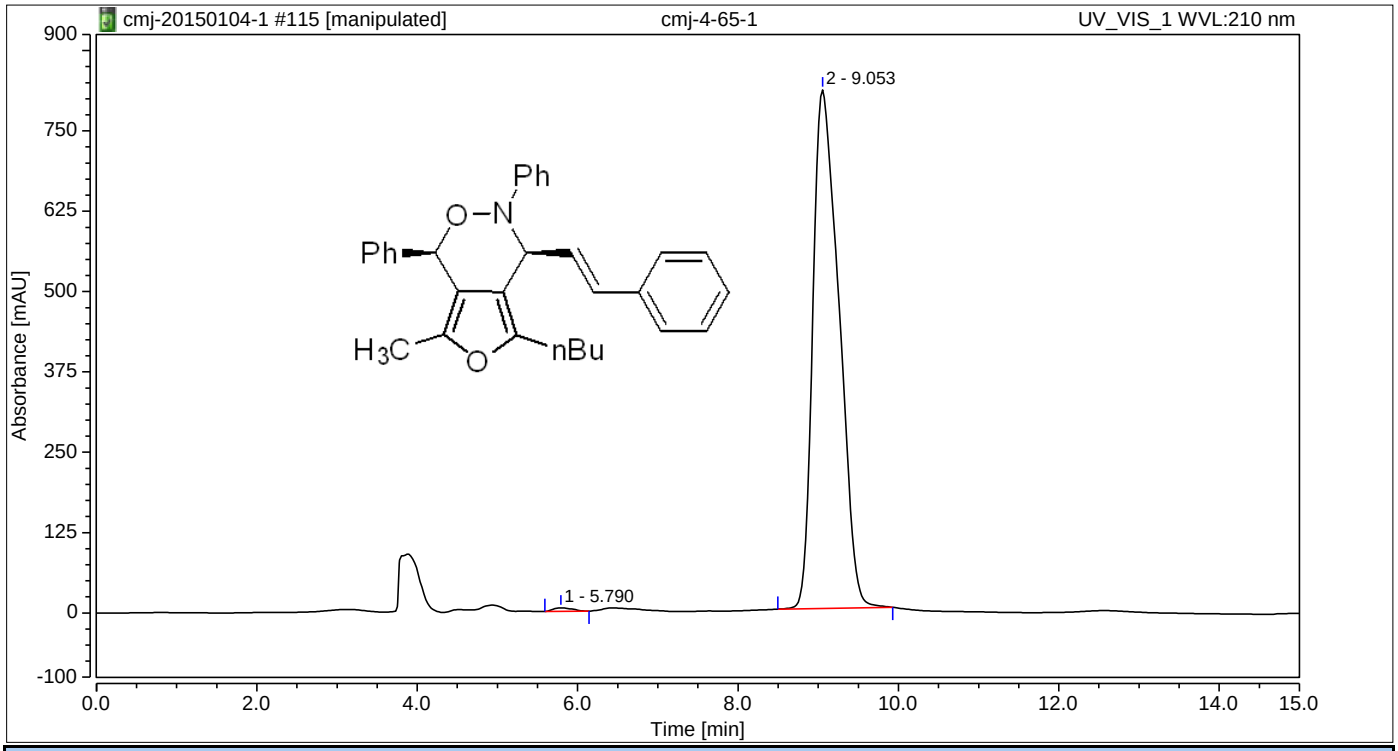
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.800	155.360	534.941	95.01	95.62	n.a.
2		9.043	8.164	24.532	4.99	4.38	n.a.
Total:			**163.524**	**559.473**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-65-1**	*Run Time (min):*	**15.00**
Vial Number:	**RC4**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/5月/15 23:21**	*Sample Weight:*	**1.0000**

Chromatogram



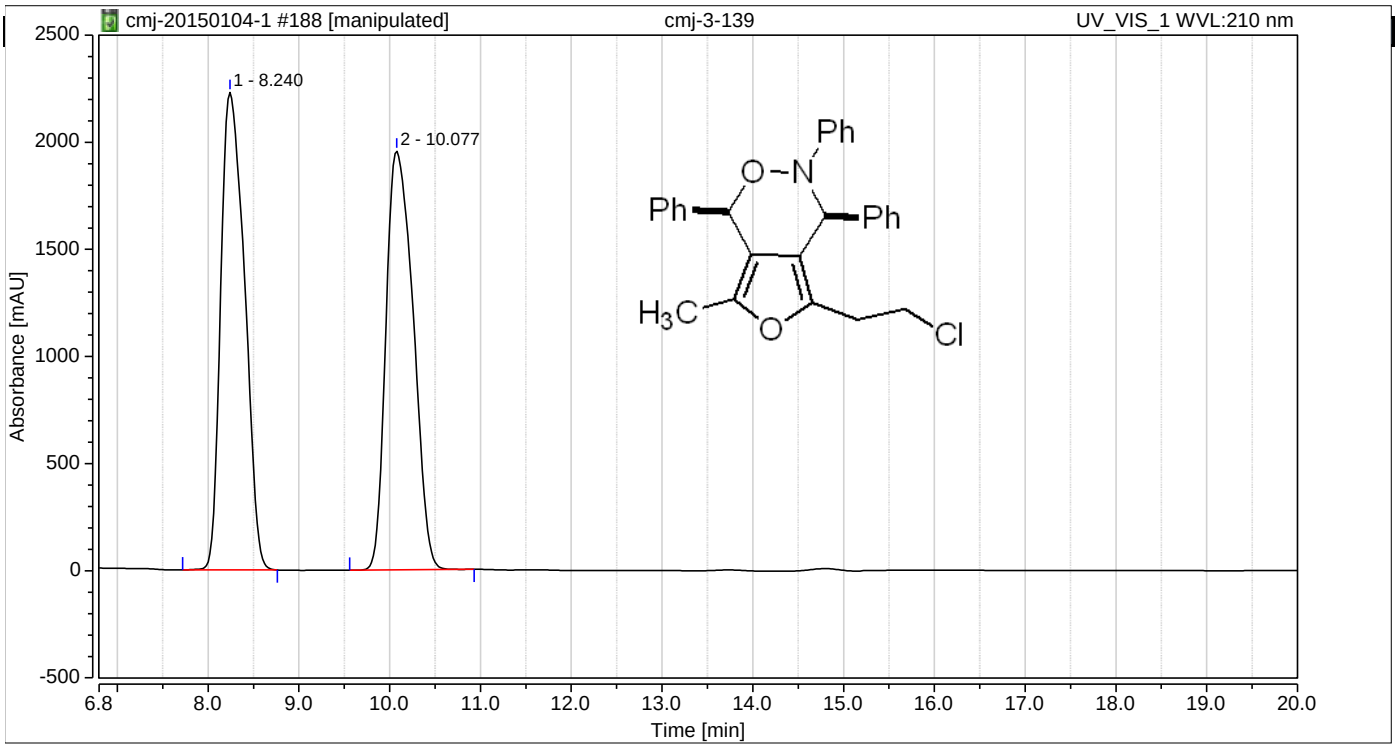
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.790	1.449	5.291	0.47	0.65	n.a.
2		9.053	303.820	807.044	99.53	99.35	n.a.
Total:			**305.269**	**812.335**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-3-139**	*Run Time (min):*	**20.00**
Vial Number:	**RA6**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.8ml-210254200-25-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/6月/15 00:33**	*Sample Weight:*	**1.0000**



Integration Results

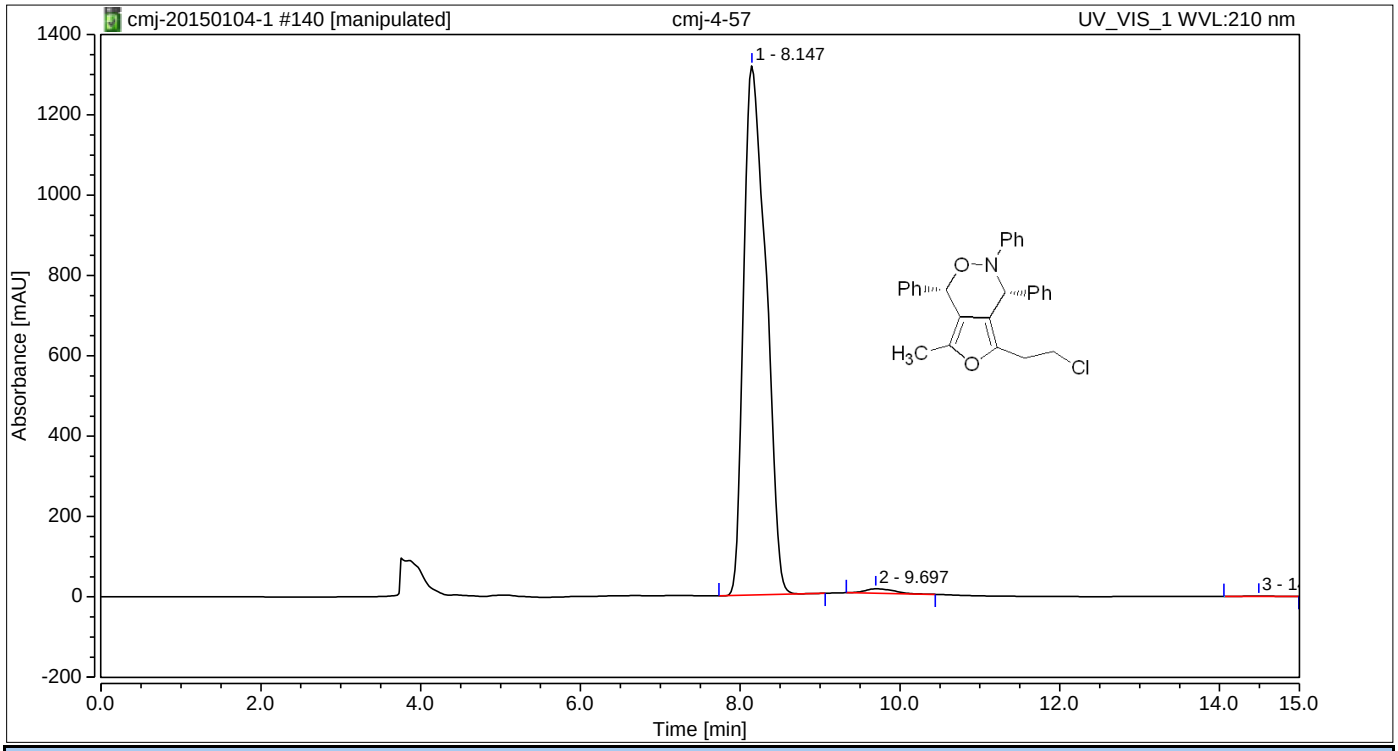
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.240	676.474	2229.437	49.90	53.28	n.a.
2		10.077	679.071	1954.920	50.10	46.72	n.a.
Total:			**1355.545**	**4184.357**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-57**	*Run Time (min):*	**15.00**
Vial Number:	**GB8**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**26/5月/15 03:20**	*Sample Weight:*	**1.0000**

Chromatogram



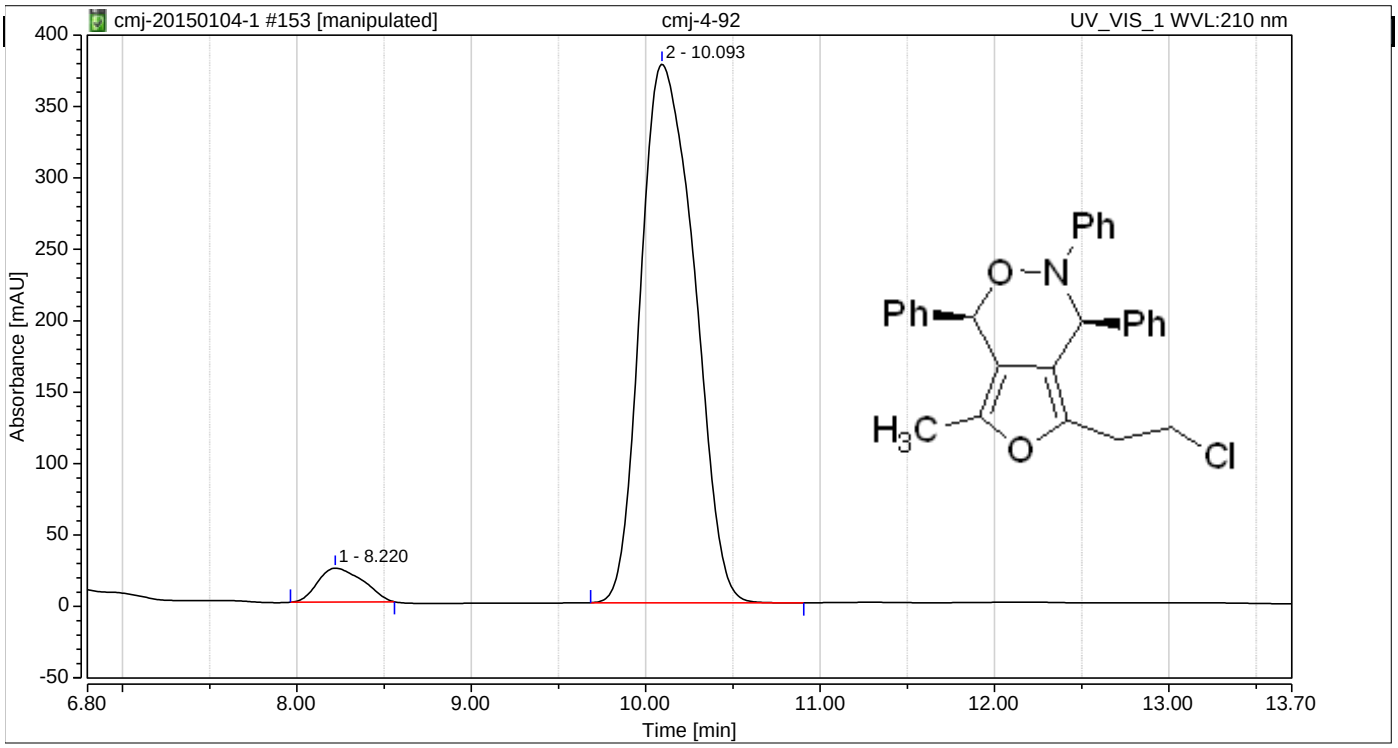
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.147	425.921	1317.273	98.84	99.12	n.a.
2		9.697	4.655	11.123	1.08	0.84	n.a.
3		14.490	0.351	0.616	0.08	0.05	n.a.
Total:			**430.927**	**1329.012**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-92**	*Run Time (min):*	**13.70**
Vial Number:	**RD2**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**03/6月/15 10:42**	*Sample Weight:*	**1.0000**



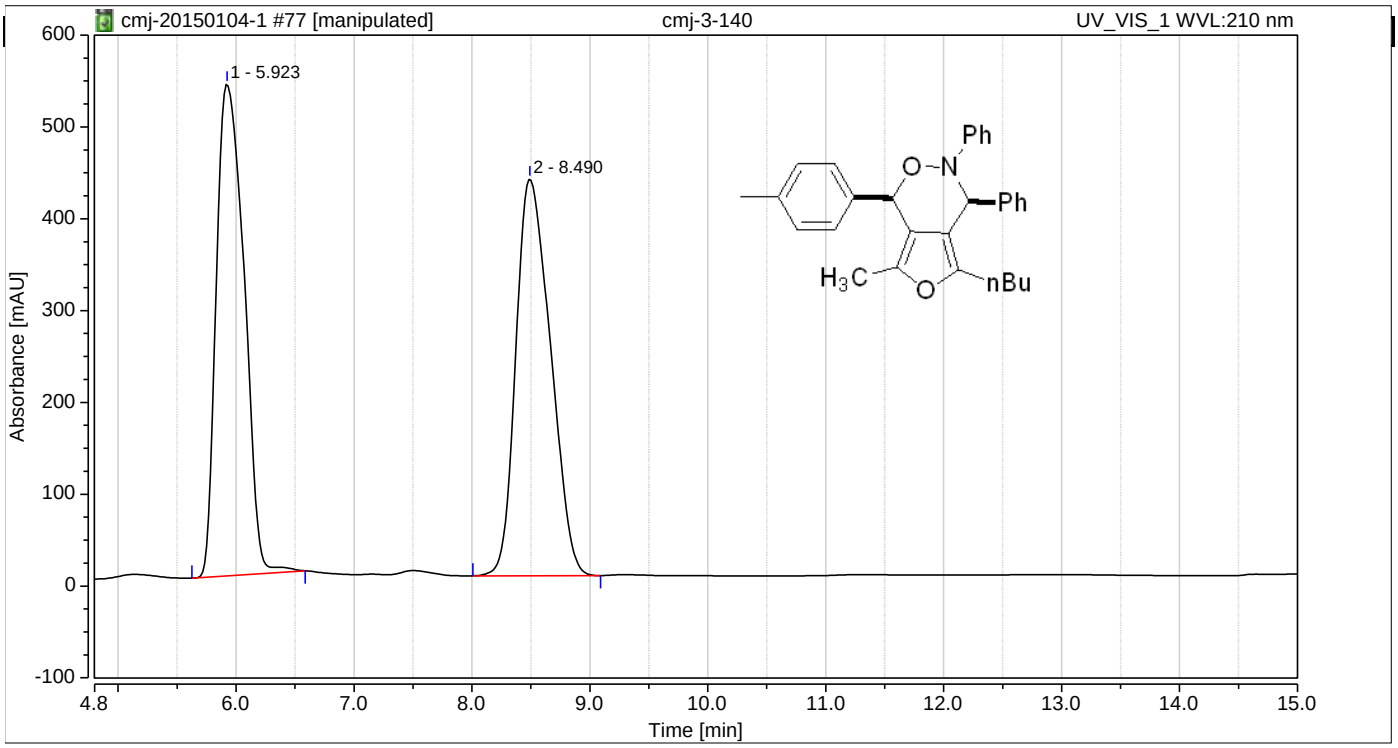
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.220	7.107	23.731	5.02	5.92	n.a.
2		10.093	134.571	377.026	94.98	94.08	n.a.
Total:			**141.678**	**400.757**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-3-140**	*Run Time (min):*	**15.00**
Vial Number:	**RA1**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**13/4月/15 10:06**	*Sample Weight:*	**1.0000**



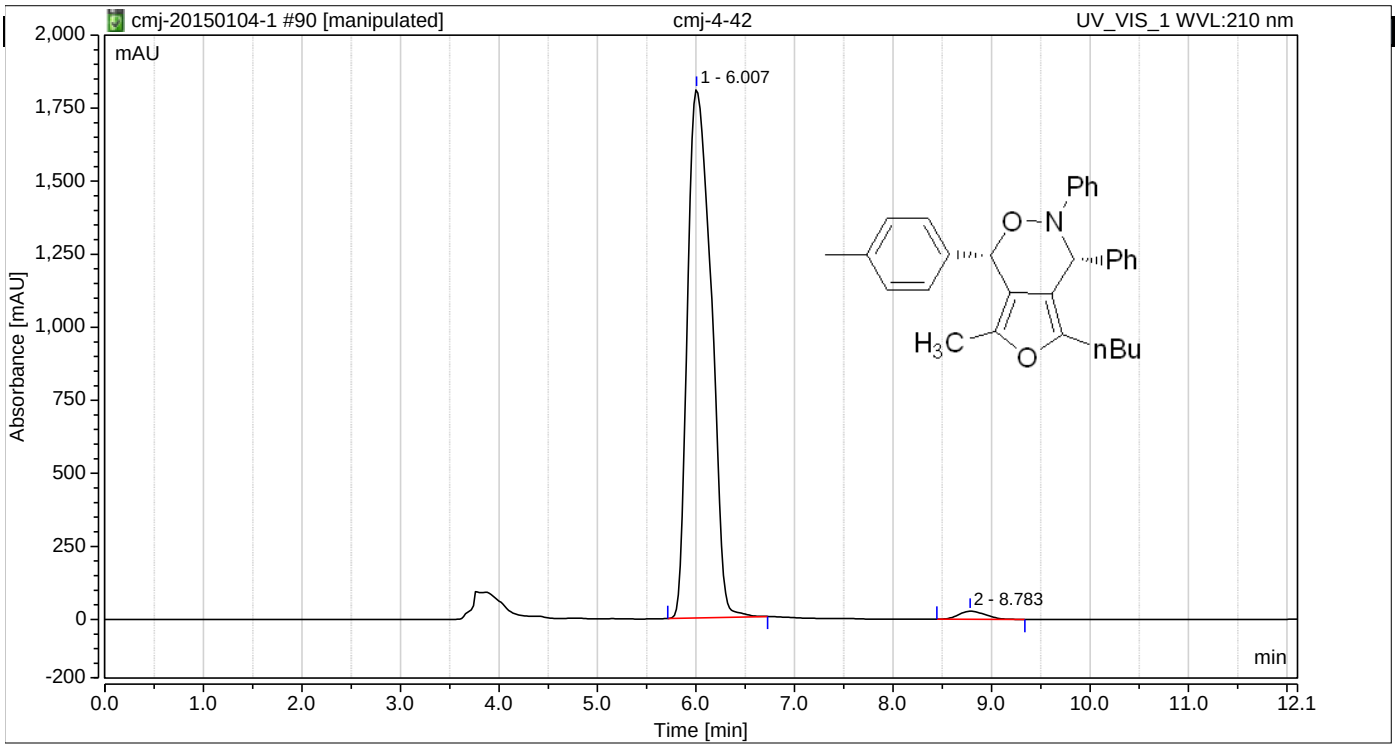
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.923	146.209	535.633	49.91	55.34	n.a.
2		8.490	146.738	432.208	50.09	44.66	n.a.
Total:			**292.947**	**967.842**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-42**	*Run Time (min):*	**12.11**
Vial Number:	**BE7**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**03/5月/15 14:05**	*Sample Weight:*	**1.0000**



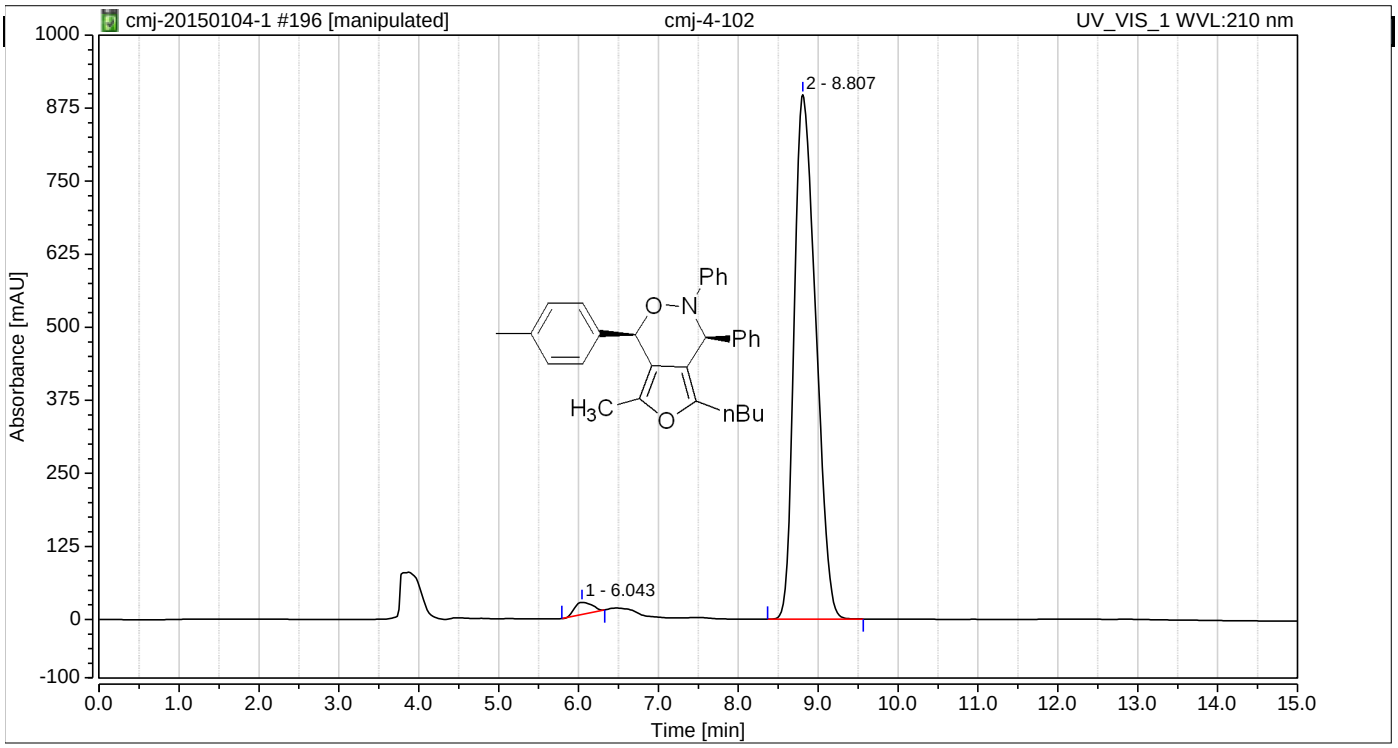
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.007	503.428	1809.589	98.33	98.51	n.a.
2		8.783	8.565	27.448	1.67	1.49	n.a.
Total:			**511.992**	**1837.037**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-102**	*Run Time (min):*	**15.00**
Vial Number:	**RB7**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**15min-0.8ml-210254200-A5B95C0D0**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/6月/15 12:55**	*Sample Weight:*	**1.0000**



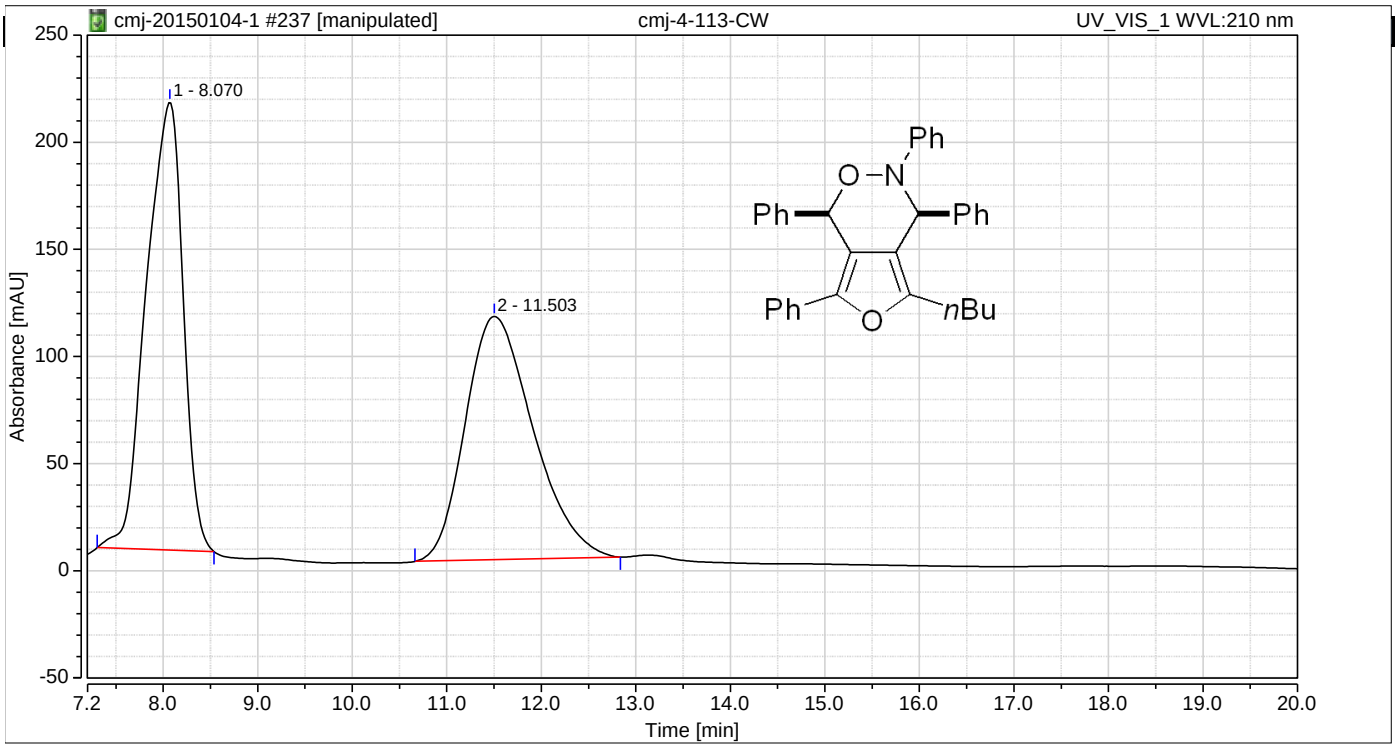
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.043	5.233	20.740	1.83	2.26	n.a.
2		8.807	281.350	897.513	98.17	97.74	n.a.
Total:			**286.582**	**918.253**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-113-CW**	*Run Time (min):*	**20.00**
Vial Number:	**GE5**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.5ml-A5B95C0D0-ASH-25**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**18/7月/15 21:45**	*Sample Weight:*	**1.0000**



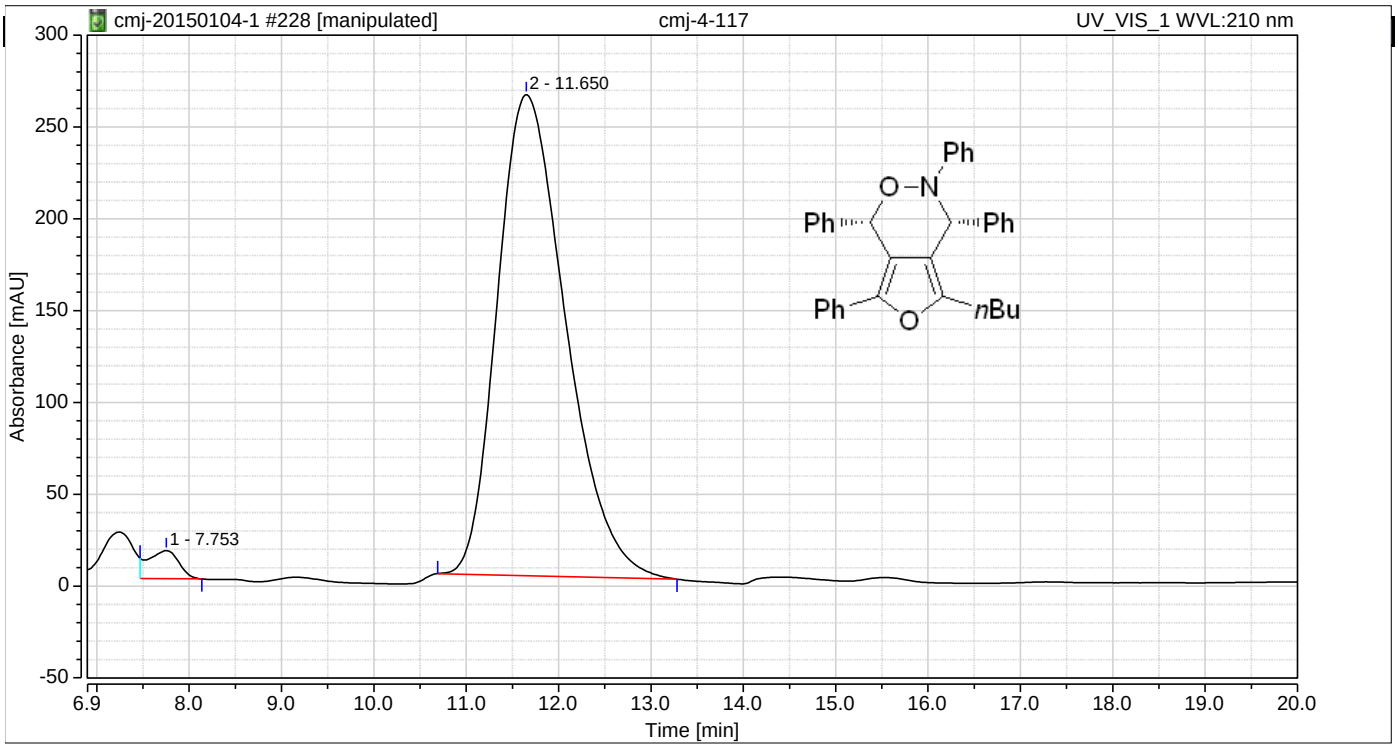
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.070	94.004	209.133	49.94	64.82	n.a.
2		11.503	94.237	113.528	50.06	35.18	n.a.
Total:			**188.241**	**322.662**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-117**	*Run Time (min):*	**20.00**
Vial Number:	**GE2**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.5ml-A5B95C0D0-ASH-25**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/7月/15 00:18**	*Sample Weight:*	**1.0000**



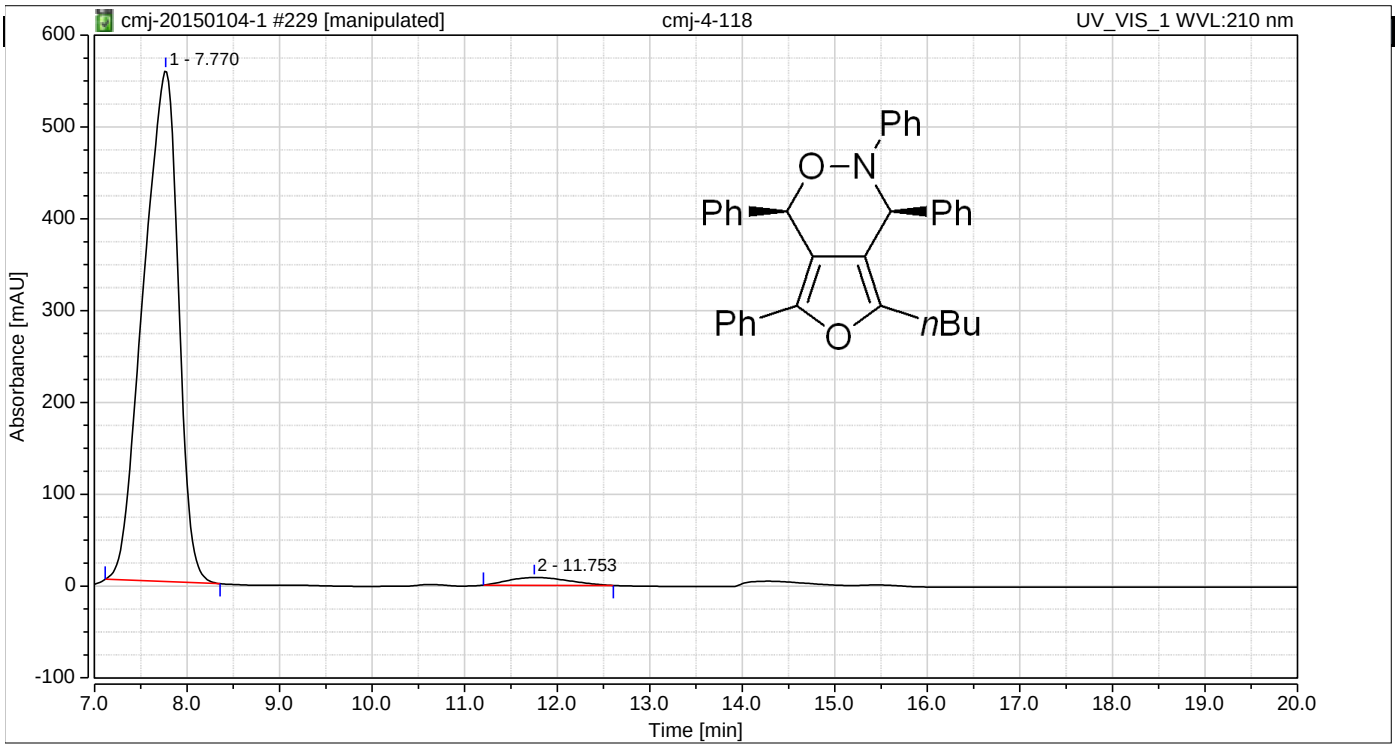
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.753	5.937	15.284	2.58	5.51	n.a.
2		11.650	224.385	261.916	97.42	94.49	n.a.
Total:			**230.322**	**277.199**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**cmj-4-118**	*Run Time (min):*	**20.00**
Vial Number:	**GE3**	*Injection Volume:*	**20.00**
Injection Type:	**Check Standard**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**210.0**
Instrument Method:	**20min-0.5ml-A5B95C0D0-ASH-25**	*Bandwidth:*	**4**
Processing Method:	**zzm-141115**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/7月/15 00:39**	*Sample Weight:*	**1.0000**



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.770	243.015	556.665	97.45	98.52	n.a.
2		11.753	6.363	8.373	2.55	1.48	n.a.
Total:			**249.378**	**565.037**	**100.00**	**100.00**	