

# Supporting Information

## Iminosugar-phosphine as organocatalysts in the [3 + 2] cycloaddition of allenates and *N*-tosylimines

Pilar Elías-Rodríguez, Ana T. Carmona, Antonio J. Moreno-Vargas and Inmaculada Robina

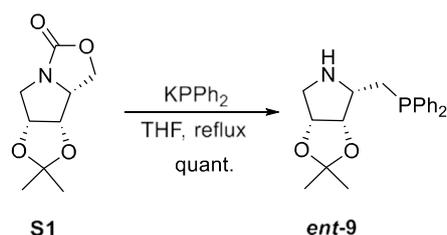
*Departamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, Sevilla, c/ Profesor García González 1, Sevilla 41012, Spain*

*\*Correspondence: anatere@us.es and robina@us.es*

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## 1. Synthesis of compound *ent-9*



**(2*R*,3*S*,4*R*)-2-Diphenylphosphinomethyl-3,4-*O*-isopropylidene-pyrrolidine-3,4-diol (*ent-9*).** To a solution of **S1**<sup>1</sup> (223.1 mg, 1.12 mmol) in anhydrous THF (9 mL) at 0 °C was slowly added KPPH<sub>2</sub> (0.5 M in THF, 4.5 mL, 2.24 mmol). The mixture was heated at reflux for 2 h and then warmed to room temperature. IRA-120H<sup>+</sup> was added, and the resulting mixture was filtered through Celite and washed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was evaporated, and the residue was purified by chromatography column on silica gel (CH<sub>2</sub>Cl<sub>2</sub>:cyclohexane, 5:1 → CH<sub>2</sub>Cl<sub>2</sub> → CH<sub>2</sub>Cl<sub>2</sub>:acetone, 5:1, 0.5% Et<sub>3</sub>N) to give **ent-9** (399 mg, 1.17 mmol, quant.) as a colorless oil. NMR and IR data are in accordance with those of its enantiomer **9**.<sup>2</sup> [ $\alpha$ ]<sub>D</sub><sup>23</sup> – 51.8 (c 0.78, CH<sub>2</sub>Cl<sub>2</sub>). HRMS (ESI) *m/z* found 356.1759, calc. for C<sub>21</sub>H<sub>27</sub>NO<sub>2</sub>P [M+H]<sup>+</sup>: 356.1774.

## 2. Synthesis of enantiomeric 3-pyrrolines *ent*-(21a-f)

*General procedure:* To a solution of the imine **19a-d** (1.0 equiv, 0.154 mmol) and phosphine **ent-9** (0.2 equiv, 0.03 mmol, 11 mg) in Et<sub>2</sub>O (0.6 mL) cooled at 0 °C (R = H, Me) or in toluene (0.6 mL) at r.t. (R = <sup>t</sup>Bu), the allenolate **20a-c** (1.2 equiv, 0.185 mmol) was added dropwise in Et<sub>2</sub>O (0.6 mL) (R = H, Me) or in toluene (0.6 mL) (R = <sup>t</sup>Bu). The reaction mixture was stirred for the specified time at specific temperature. Then, the solvent was concentrated and the resulting residue was purified by chromatography column on silica gel to give pure **ent-21**. Enantiomeric ratios were determined by HPLC analysis. Diastereomeric ratios were determined by analysis of <sup>1</sup>H NMR reaction crudes. Racemic samples were prepared with PPh<sub>3</sub> or PBu<sub>3</sub> (20 mol%) in toluene at r.t. following this general procedure.

**(2*S*,5*R*) Ethyl 2-Phenyl-5-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-carboxylate (*ent-21a*).** Reaction of imine **19a**<sup>3</sup> (40 mg, 0.15 mmol), **ent-9** (11 mg, 0.03 mmol) and allenolate **20a**<sup>4</sup> (24 mg, 0.19 mmol) in Et<sub>2</sub>O (1.2 mL) for 30 h at 0 °C and chromatography column (toluene:acetone, 60:1), afforded **ent-21a** (53 mg, 0.14 mmol, 90%, 60% ee, dr 94:6 *cis/trans*) as a pale yellow oil. NMR and IR data are in accordance with those of its enantiomer **21a**. [ $\alpha$ ]<sub>D</sub><sup>23</sup> +94.5 [c 1.0, CHCl<sub>3</sub>, 60% ee, (2*S*,5*R*)]. Lit.<sup>5</sup> [ $\alpha$ ]<sub>D</sub><sup>20</sup> +159.7 [c 1.0, CHCl<sub>3</sub>, 97% ee (2*S*,5*R*)]. The enantiomeric ratios were determined by HPLC using a

Chiralpak ID column [*n*-hexanes/*i*PrOH (70:30)]; flow rate 1.0 mL/min,  $\lambda$  = 210 nm, T= 30 °C;  $t_R$  ((2*S*,5*R*), major) = 15.7 min,  $t_R$  ((2*R*,5*S*), minor) = 24.7 min.

**(2*S*) Ethyl 2-Phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-carboxylate (*ent*-21*b*).** Reaction imine **19a**<sup>3</sup> (40 mg, 0.15 mmol), *ent*-**9** (11 mg, 0.03 mmol) and allenolate **20b**<sup>6</sup> (21 mg, 0.19 mmol) in Et<sub>2</sub>O (1.2 mL) for 38 h at 0 °C and chromatography column (EtOAc:cyclohexane, 1:5), afforded *ent*-**21b** (47 mg, 0.13 mmol, 81%, 31% ee (2*S*)) as a colourless oil. NMR and IR data are in accordance with those of its enantiomer **21b**.  $[\alpha]_D^{24} +49.1$  [*c* 1.0, CHCl<sub>3</sub>, 31% ee (2*S*)]. Lit.<sup>5</sup>  $[\alpha]_D^{20} +147.4$  [*c* 1.0, CHCl<sub>3</sub>, 72% ee (2*S*)]. The enantiomeric ratios were determined by HPLC using a Chiralpak IC column [*n*-hexanes/*i*PrOH (50:50)]; flow rate 1.0 mL/min,  $\lambda$  = 210 nm, T= 30 °C;  $t_R$  (2*S*, minor) = 15.2 min,  $t_R$  (2*R*, major) = 22.3 min.

**(2*S*,5*S*) Ethyl 5-(*tert*-Butyl)-2-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-carboxylate (*ent*- 21*c*).** Reaction of imine **19a**<sup>3</sup> (40 mg, 0.15 mmol), *ent*-**9** (11 mg, 0.03 mmol) and allenolate **20c**<sup>6</sup> (31 mg, 0.19 mmol) in toluene (1.2 mL) for 48 h at r.t. and chromatography column (EtOAc:cyclohexane, 1:8), afforded *ent*-**21c** (59 mg, 0.14 mmol, 90%, dr 100:0 *cis/trans*, 59% ee (2*S*,5*S*)) as a pale yellow oil. NMR and IR data are in accordance with those of its enantiomer **21c**.  $[\alpha]_D^{23} +68.2$  (*c* 1.0, CHCl<sub>3</sub>, 59% ee (2*S*,5*S*)). Lit.<sup>5</sup>  $[\alpha]_D^{20} +109.8$  [*c* 1.0, CHCl<sub>3</sub>, 99% ee (2*S*,5*S*)]. The enantiomeric ratios were determined by HPLC using a Chiralpak IA column [*n*-hexanes/*i*PrOH (80:20)]; flow rate 1.0 mL/min,  $\lambda$  = 210 nm, T= 30 °C;  $t_R$  ((2*S*,5*S*), minor) = 5.0 min,  $t_R$  ((2*R*,5*R*), major) = 6.1 min.

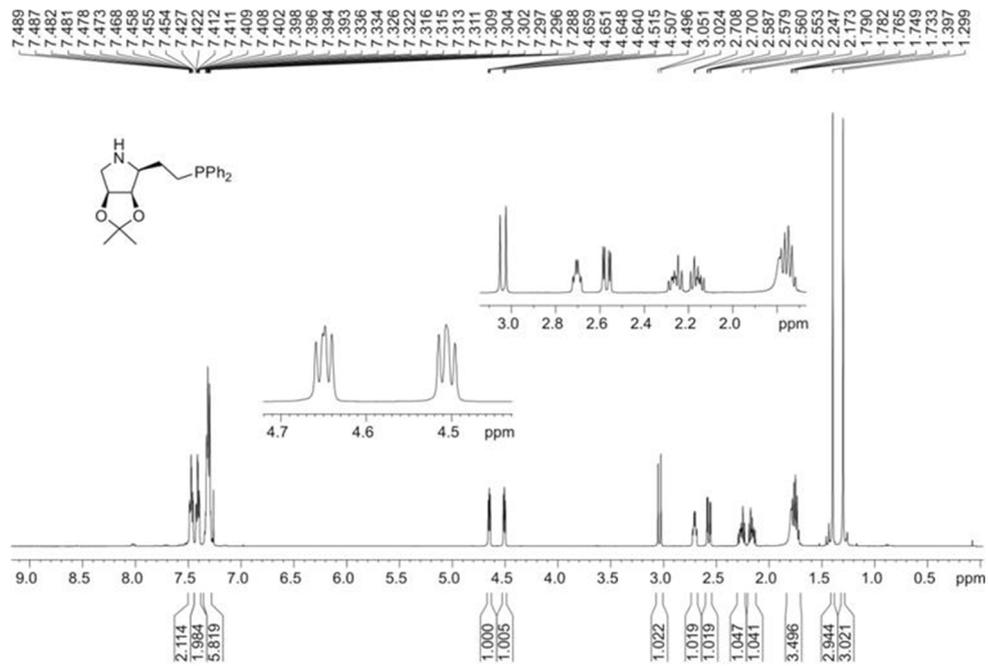
**(2*S*,5*R*) Ethyl 5-Methyl-2-(4-methoxyphenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-carboxylate (*ent*-21*d*).** Reaction of imine **19b**<sup>7</sup> (45 mg, 0.15 mmol), *ent*-**9** (11 mg, 0.03 mmol) and allenolate **20a**<sup>4</sup> (24 mg, 0.19 mmol) in Et<sub>2</sub>O (1.2 mL) for 44 h at 0 °C and chromatography column (Toluene:acetone, 50:1), afforded *ent*-**21d** (35 mg, 0.08 mmol, 55%, dr 94:6 *cis/trans*, 60% ee (2*S*,5*R*)) as a pale yellow oil. NMR and IR data are in accordance with those of its enantiomer **21d**.  $[\alpha]_D^{23} +101.1$  [*c* 1.0, CHCl<sub>3</sub>, 60% ee (2*S*,5*R*)]. The enantiomeric ratios were determined by HPLC using a Chiralpak IF column [*n*-hexanes/*i*PrOH (70:30)]; flow rate 1.0 mL/min,  $\lambda$  = 210 nm, T= 30 °C;  $t_R$  ((2*S*,5*R*), minor) = 17.0 min,  $t_R$  ((2*R*,5*S*), major) = 21.3 min.

**(2*S*,5*R*) Ethyl 2-(4-Chlorophenyl)-5-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-carboxylate (*ent*-21*e*).** Reaction of imine **19c**<sup>7</sup> (46 mg, 0.15 mmol), *ent*-**9** (11 mg, 0.03 mmol) and allenolate **20a**<sup>4</sup> (24 mg, 0.19 mmol) in Et<sub>2</sub>O (1.2 mL) for 38 h at 0 °C and chromatography column (Toluene:acetone, 50:1), afforded *ent*-**21e** (40 mg, 0.01 mmol,

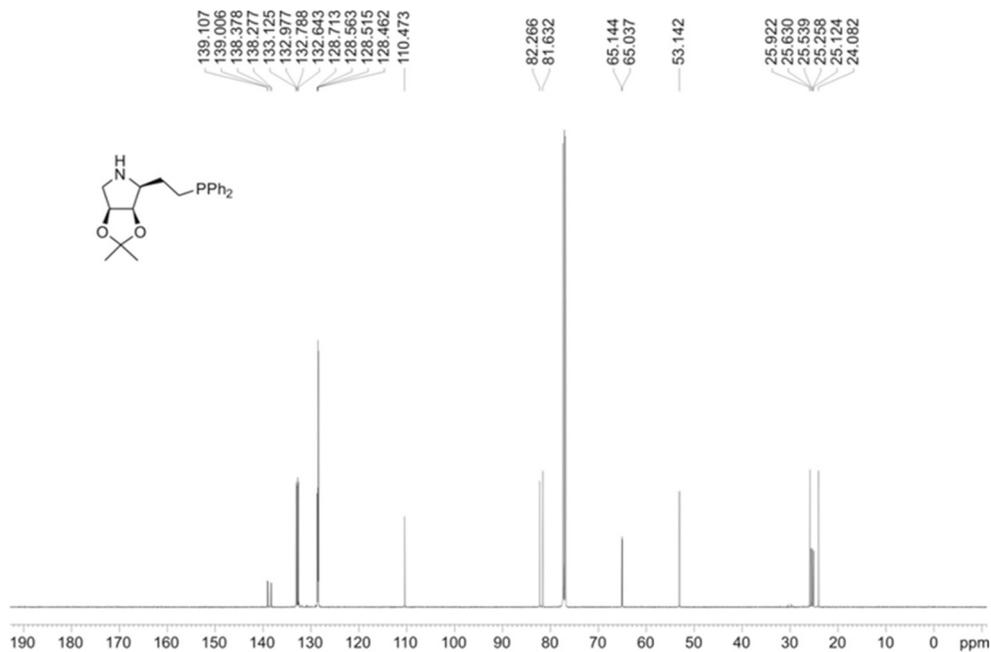
78%, dr 93:7 *cis/trans*, 62% ee (2*S*,5*R*) as a colourless oil. NMR and IR data are in accordance with those of its enantiomer **21e**.  $[\alpha]_D^{24} +113.0$  [c 1.0, CHCl<sub>3</sub>, 62% ee (2*S*,5*R*)]. The enantiomeric ratios were determined by HPLC using a Chiralpak IC column [*n*-hexanes/*i*PrOH (90:10)]; flow rate 1.0 mL/min,  $\lambda = 210$  nm, T= 30 °C;  $t_R$  ((2*S*,5*R*), minor) = 30.2 min,  $t_R$  ((2*R*,5*S*), major) = 41.8 min.

**(2*S*,5*R*) Ethyl 5-Methyl-2-(4-nitrophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-carboxilate (*ent*-**21f**)**. Reaction of imine **19d**<sup>7</sup> (47 mg, 0.15 mmol), *ent*-**9** (11 mg, 0.03 mmol) and allenoate **20a**<sup>4</sup> (24 mg, 0.19 mmol) in Et<sub>2</sub>O (1.2 mL) for 16 h at 0 °C and chromatography column (Toluene:acetone, 50:1), afforded *ent*-**21f** (42 mg, 0.10 mmol, 63%, dr 88:12 *cis/trans*, 34% ee (2*S*,5*R*)) as a colourless oil. NMR and IR data are in accordance with those of its enantiomer **21f**.  $[\alpha]_D^{25} +68.6$  [c 1.0, CHCl<sub>3</sub>, 34% ee (2*S*,5*R*)]. The enantiomeric ratios were determined by HPLC using a Chiralpak IC column [*n*-hexanes/*i*PrOH (70:30)]; flow rate 1.0 mL/min,  $\lambda = 210$  nm, T= 30 °C;  $t_R$  ((2*S*,5*R*), minor) = 25.5 min,  $t_R$  ((2*R*,5*S*), major) = 32.0 min.

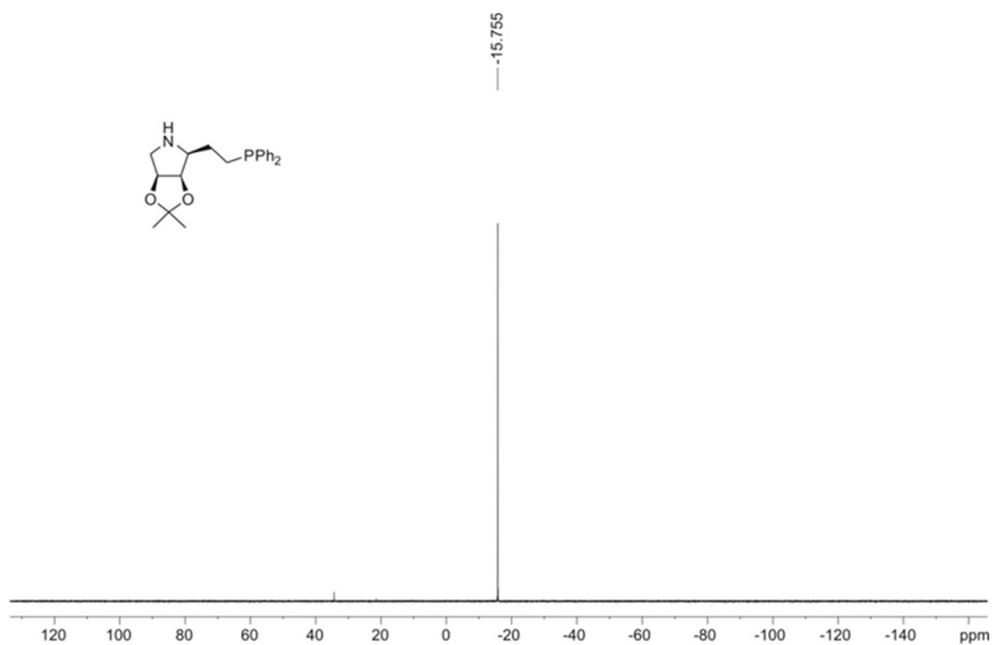
### 3. Copies of $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR Spectra



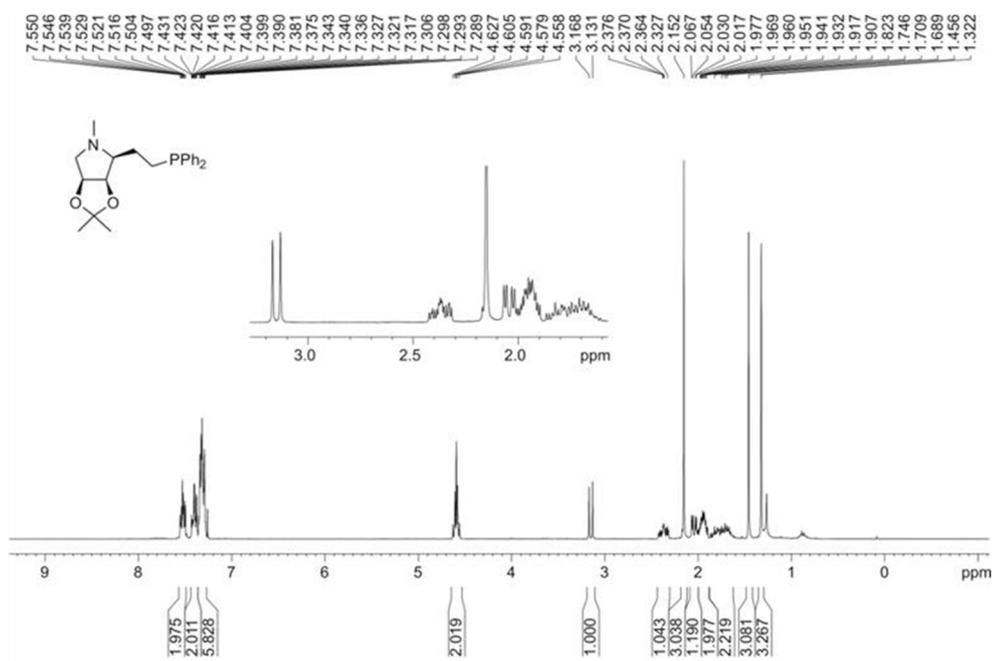
$^1\text{H}$  NMR spectrum of compound 1 (300 MHz,  $\text{CDCl}_3$ )



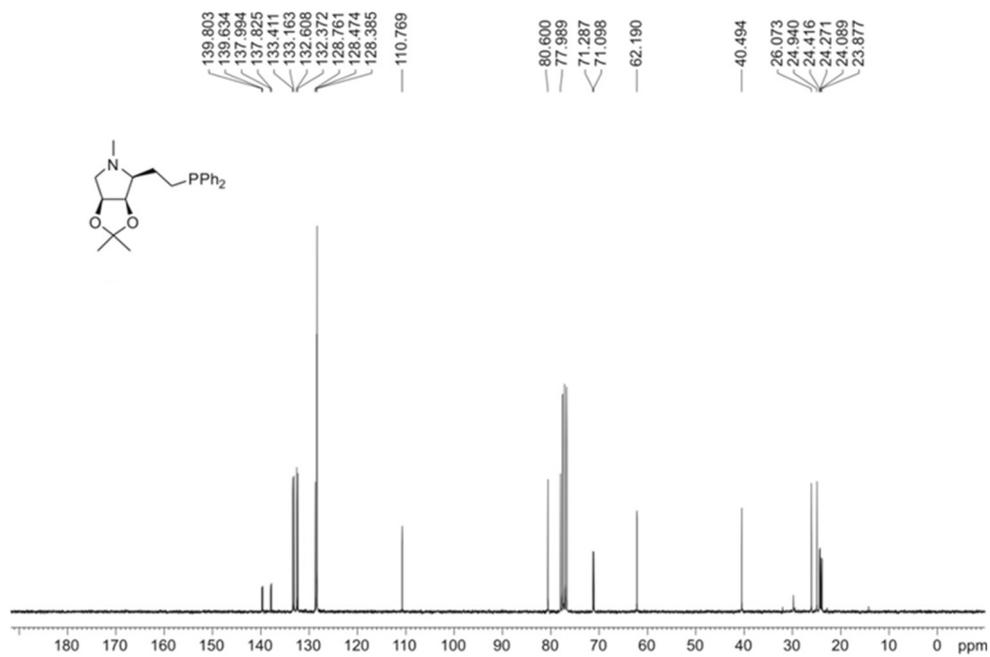
$^{13}\text{C}$  NMR spectrum of compound 1 (75.4 MHz,  $\text{CDCl}_3$ )



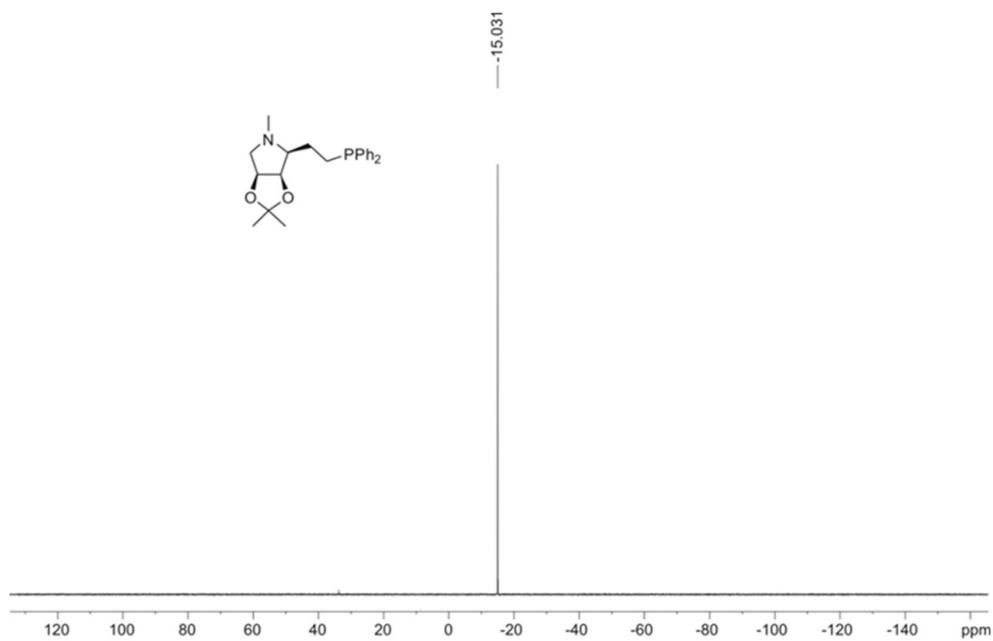
$^{31}\text{P}$  NMR spectrum of compound 1 (121.5 MHz,  $\text{CDCl}_3$ )



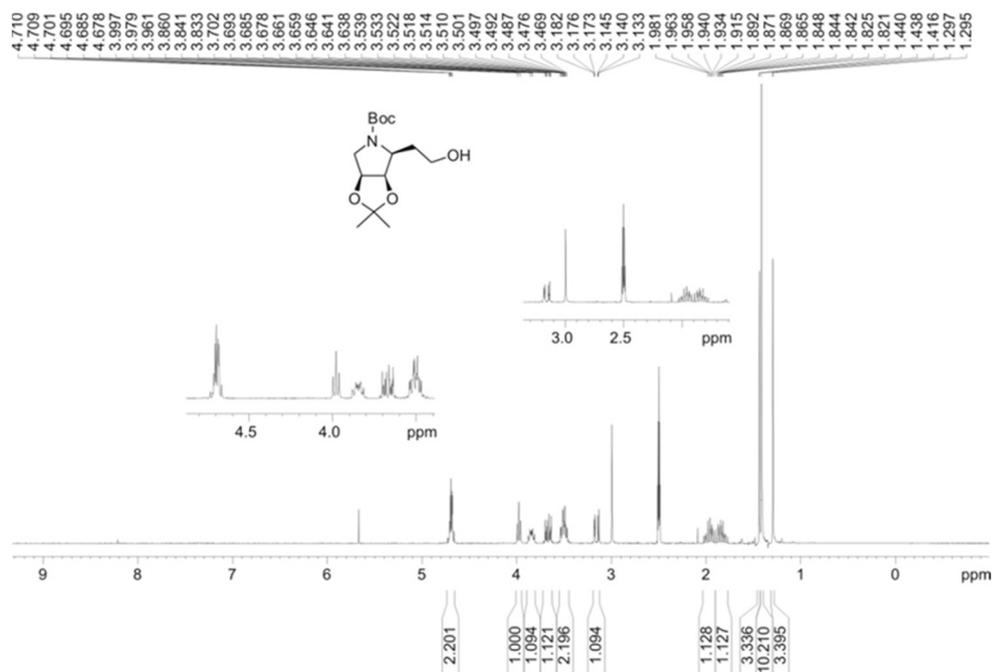
$^1\text{H}$  NMR spectrum of compound 2 (300 MHz,  $\text{CDCl}_3$ )



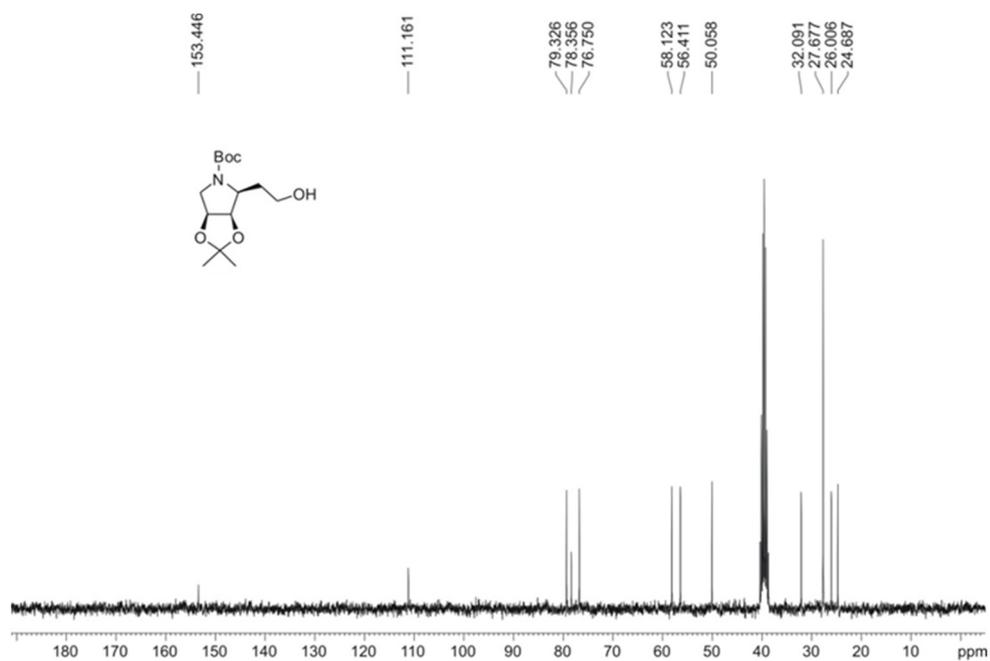
<sup>13</sup>C NMR spectrum of compound **2** (75.4 MHz, CDCl<sub>3</sub>)



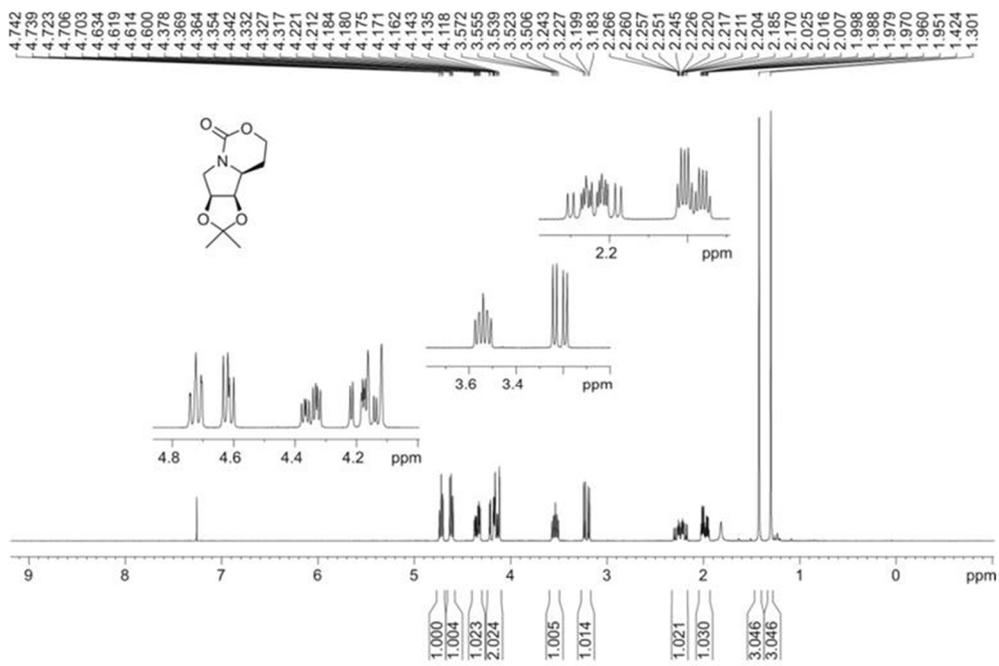
<sup>31</sup>P NMR spectrum of compound **2** (121.5 MHz, CDCl<sub>3</sub>)



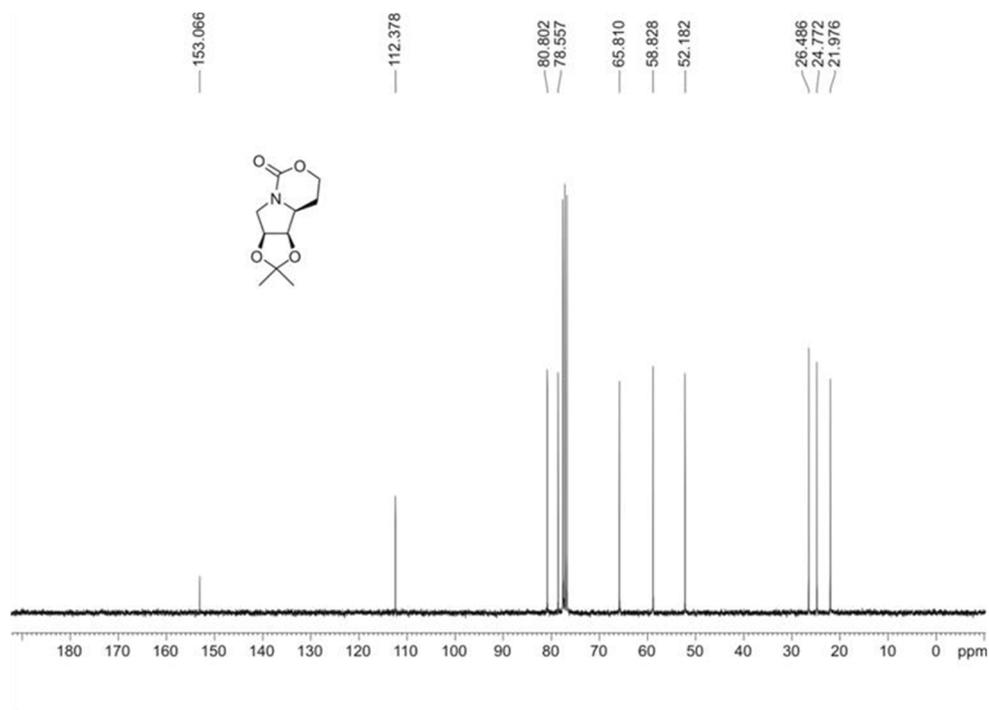
<sup>1</sup>H NMR spectrum of compound 4 (300 MHz, DMSO-*d*<sub>6</sub>, 363 K)



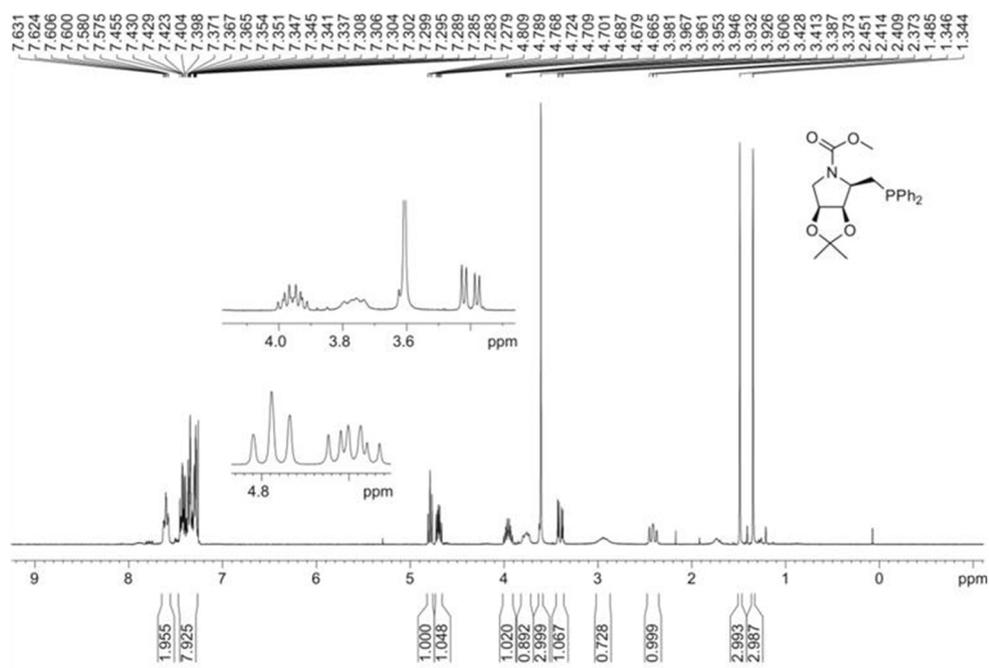
<sup>13</sup>C NMR spectrum of compound 4 (75.4 MHz, DMSO-*d*<sub>6</sub>, 363 K)



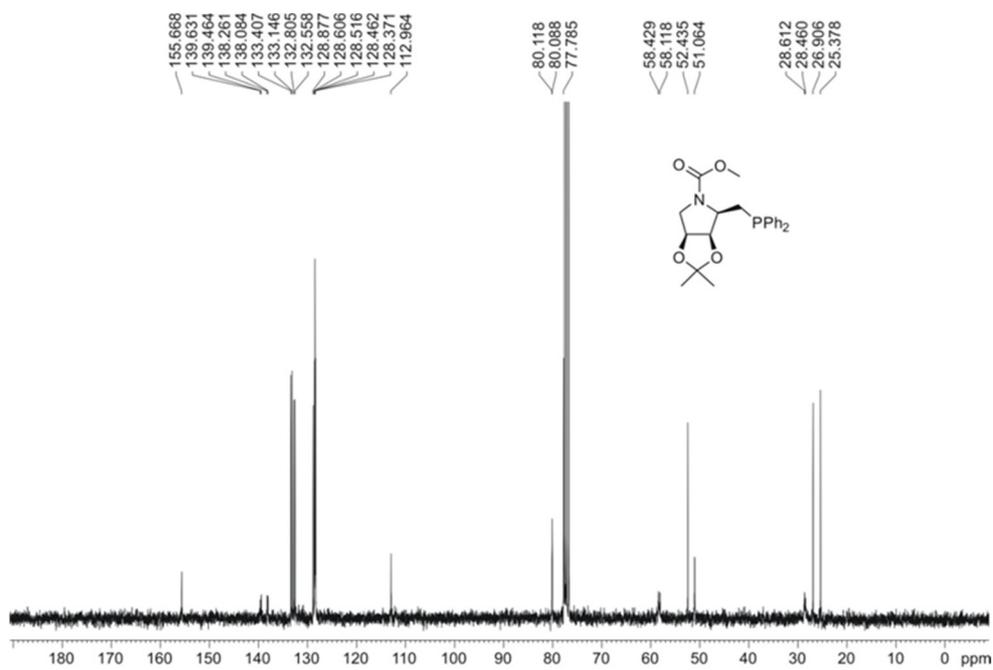
<sup>1</sup>H NMR spectrum of compound 5 (300 MHz, CDCl<sub>3</sub>)



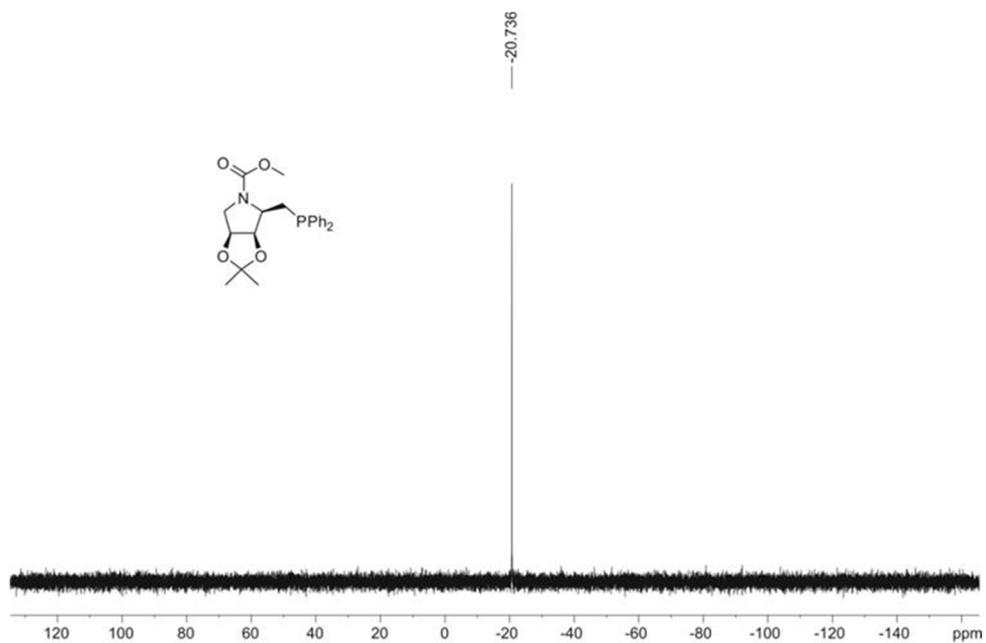
<sup>13</sup>C NMR spectrum of compound 5 (75.4 MHz, CDCl<sub>3</sub>)



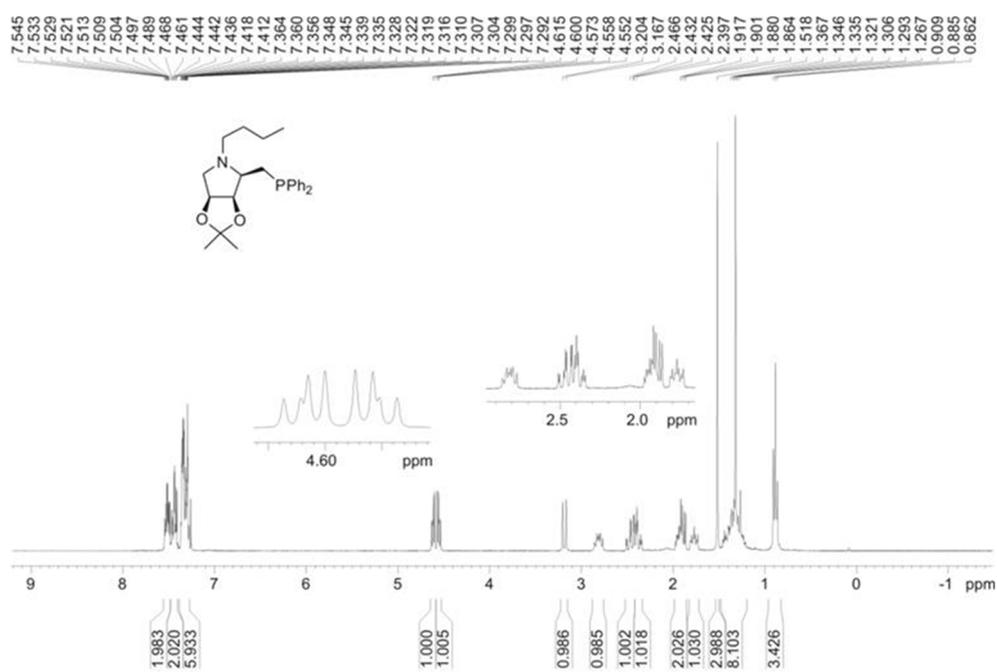
$^1\text{H}$  NMR spectrum of compound **8** (300 MHz,  $\text{CDCl}_3$ )



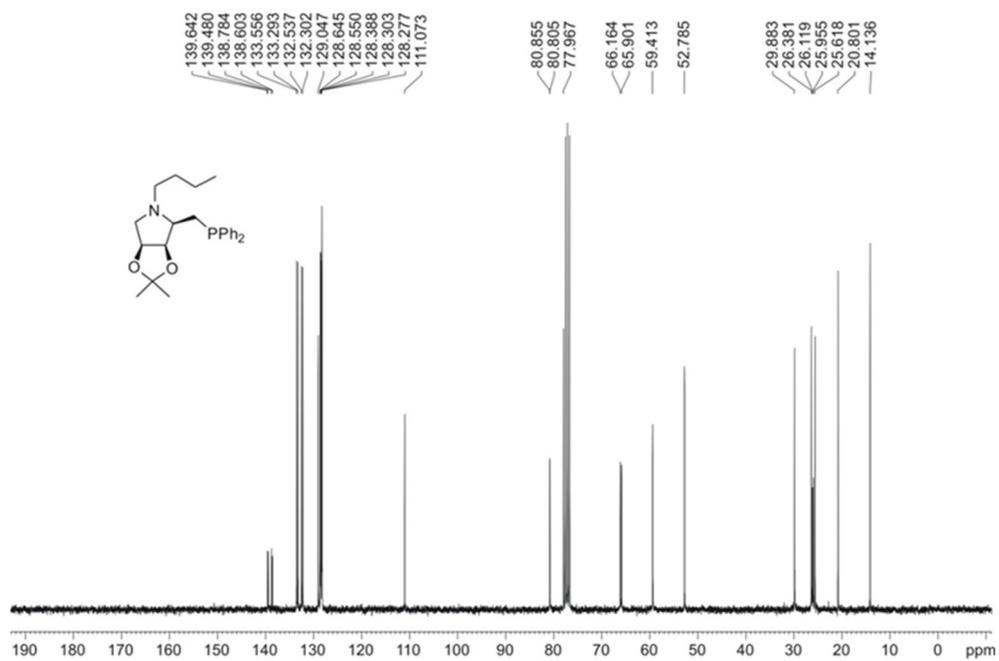
$^{13}\text{C}$  NMR spectrum of compound **8** (75.4 MHz,  $\text{CDCl}_3$ )



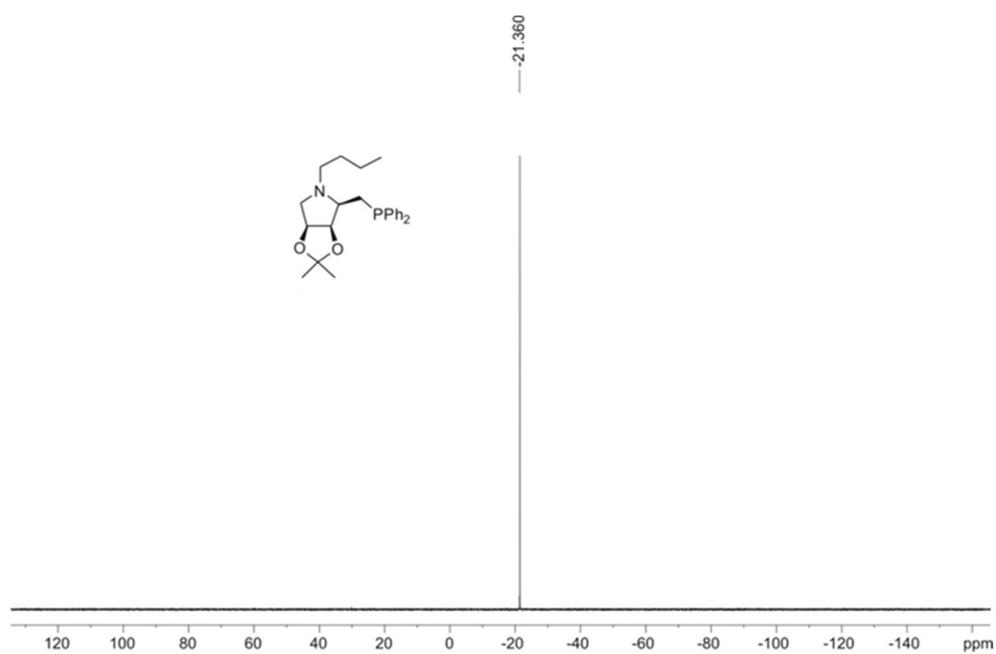
$^{31}\text{P}$  NMR spectrum of compound **8** (121.5 MHz,  $\text{CDCl}_3$ )



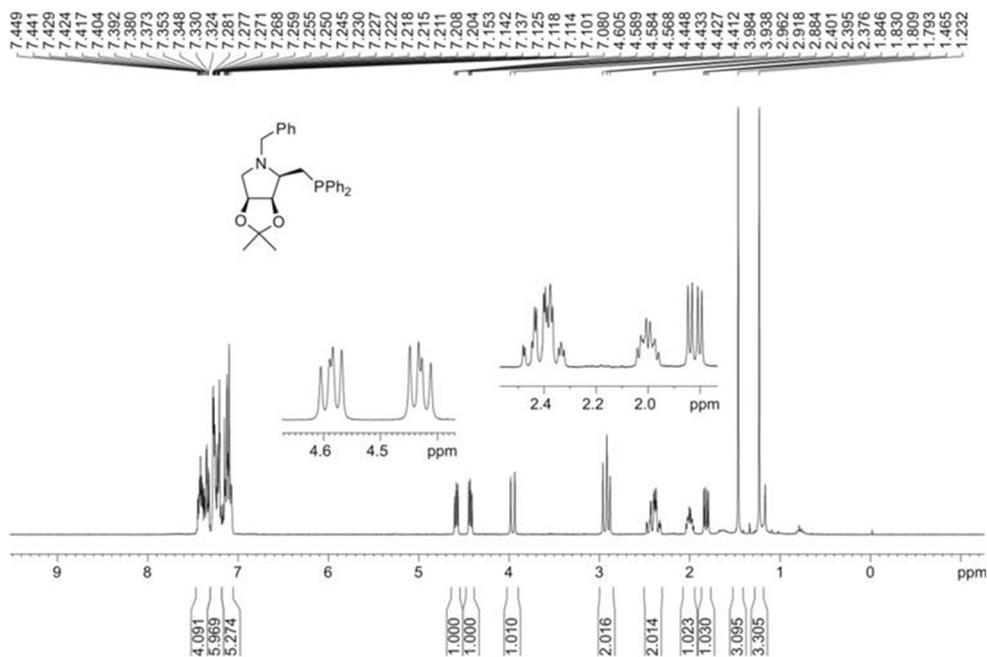
$^1\text{H}$  NMR spectrum of compound **10** (300 MHz,  $\text{CDCl}_3$ )



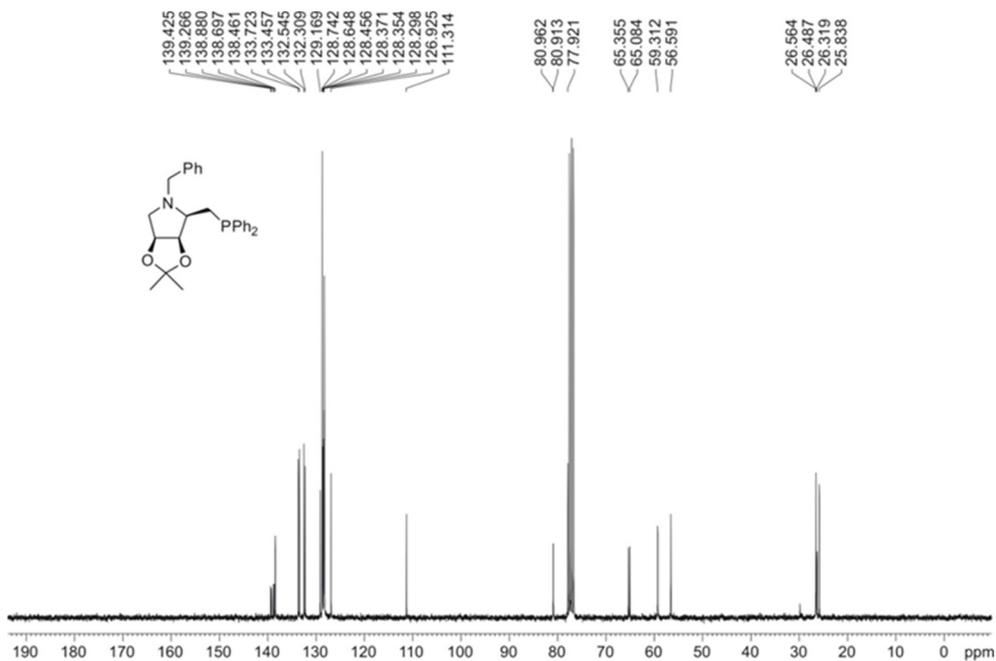
<sup>13</sup>C NMR spectrum of compound **10** (75.4 MHz, CDCl<sub>3</sub>)



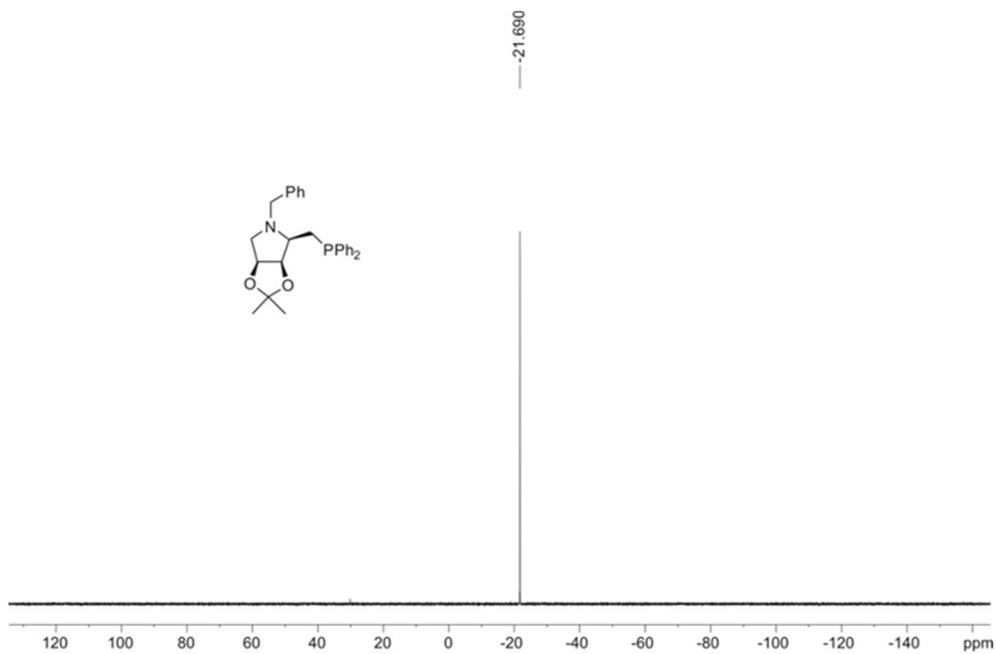
<sup>31</sup>P NMR spectrum of compound **10** (121.5 MHz, CDCl<sub>3</sub>)



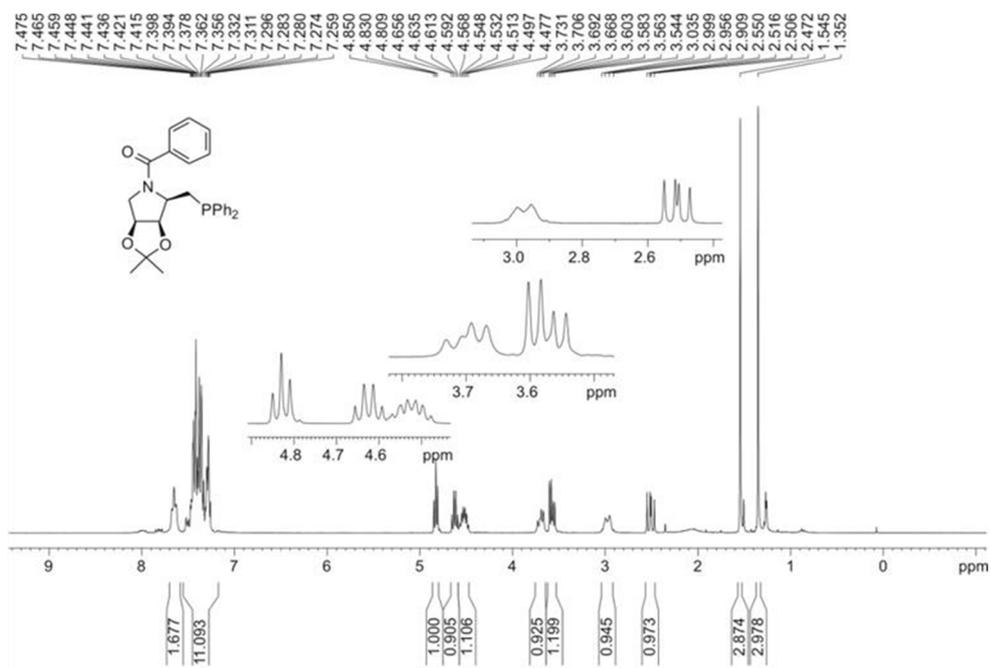
<sup>1</sup>H NMR spectrum of compound **11** (300 MHz, CDCl<sub>3</sub>)



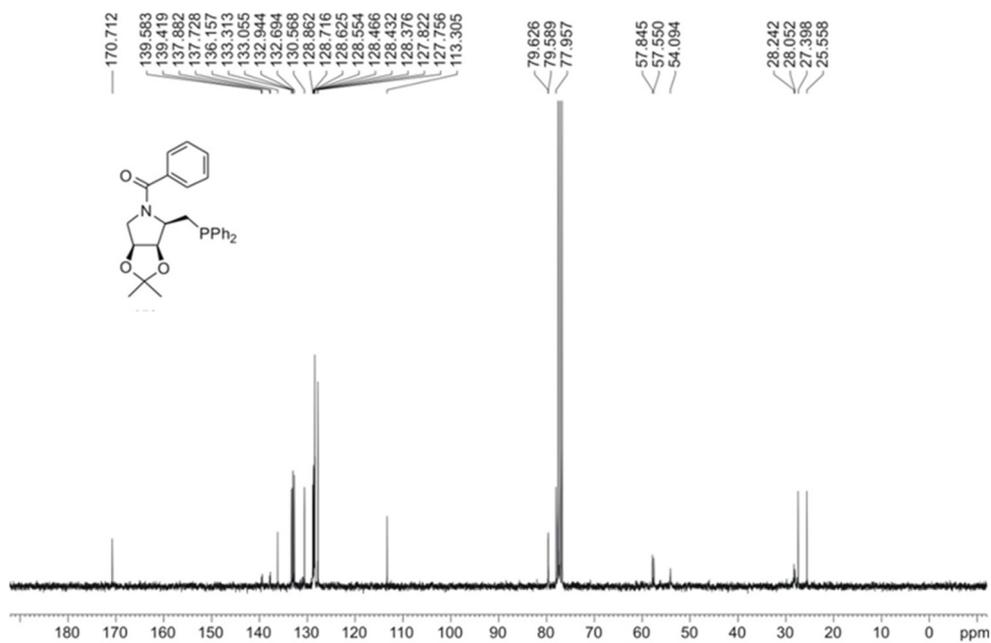
<sup>13</sup>C NMR spectrum of compound **11** (75.4 MHz, CDCl<sub>3</sub>)



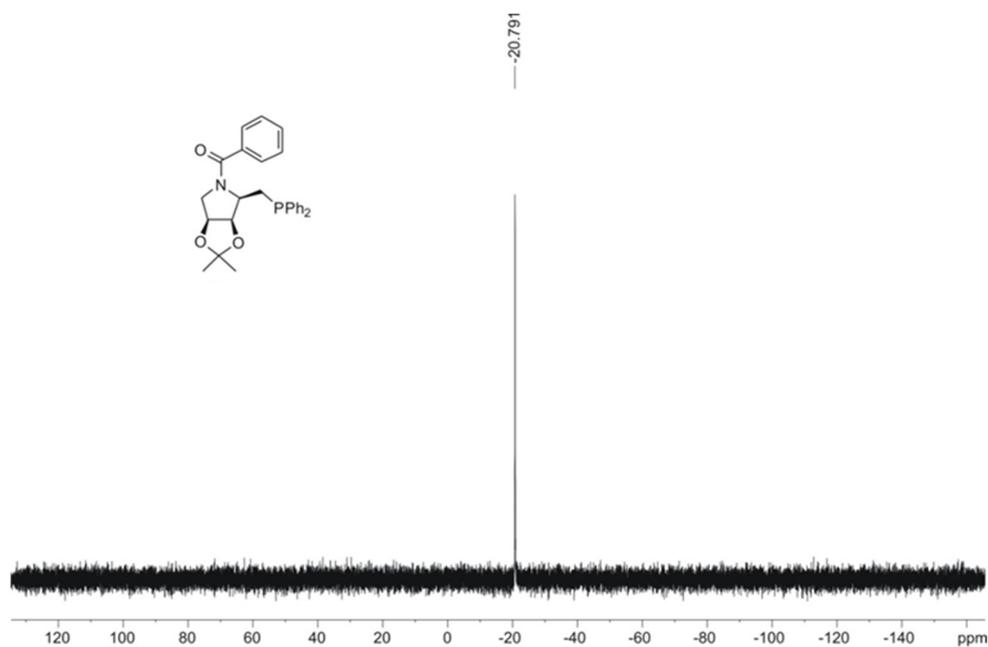
$^{31}\text{P}$  NMR spectrum of compound **11** (121.5 MHz,  $\text{CDCl}_3$ )



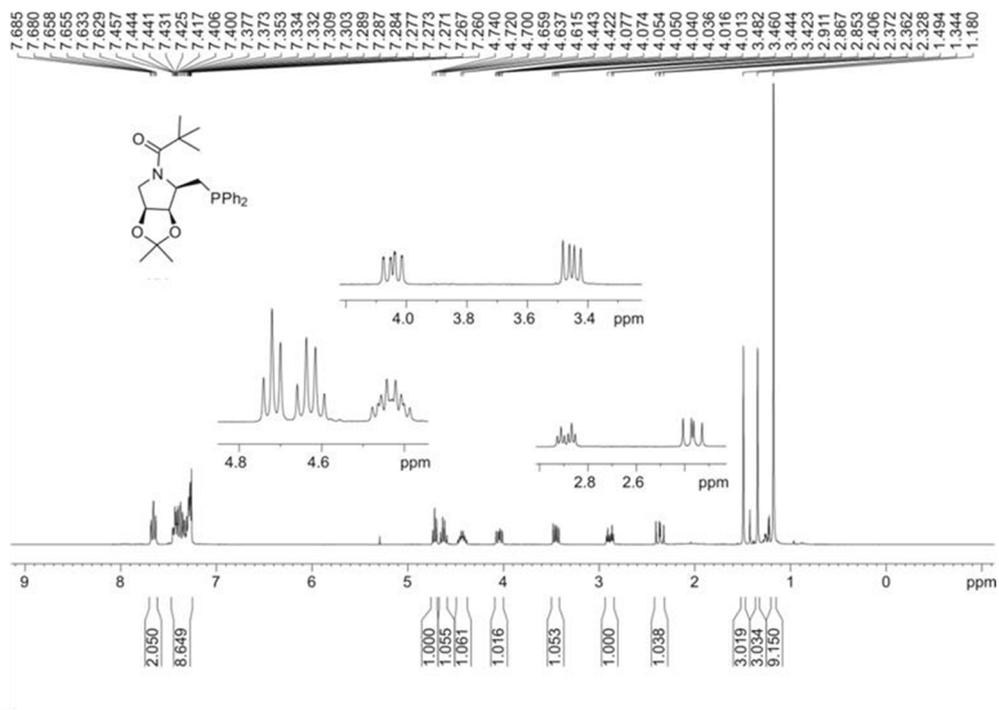
$^1\text{H}$  NMR spectrum of compound **12** (300 MHz,  $\text{CDCl}_3$ )



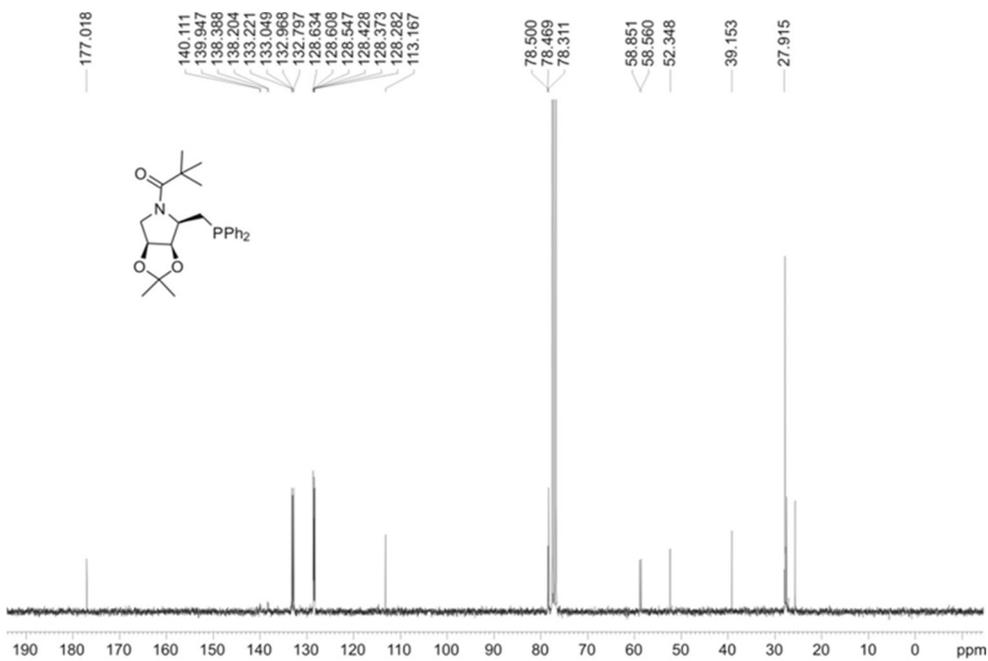
<sup>13</sup>C NMR spectrum of compound **12** (75.4 MHz, CDCl<sub>3</sub>)



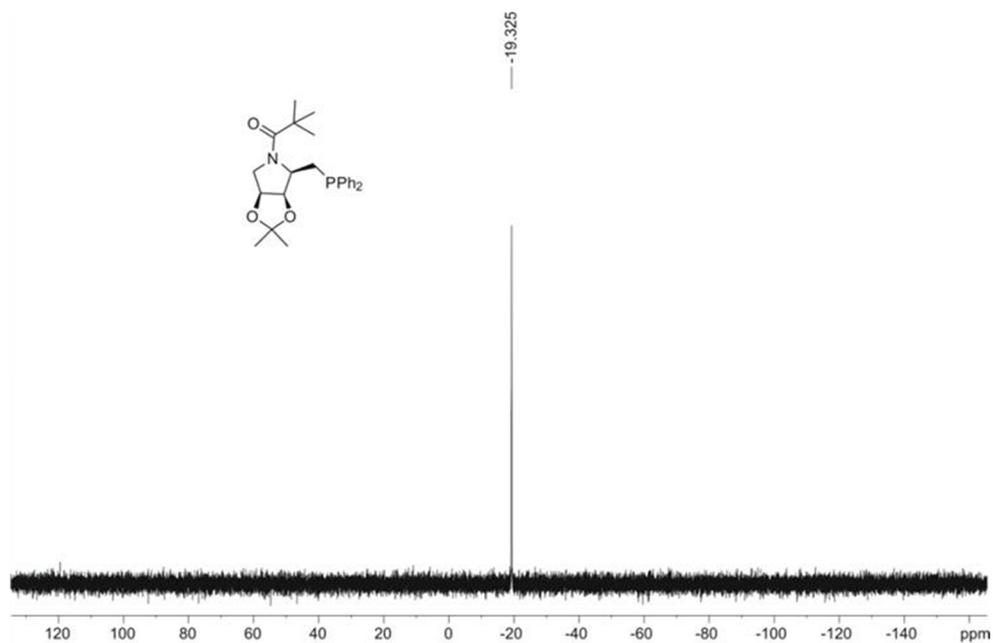
<sup>31</sup>P NMR spectrum of compound **12** (121.5 MHz, CDCl<sub>3</sub>)



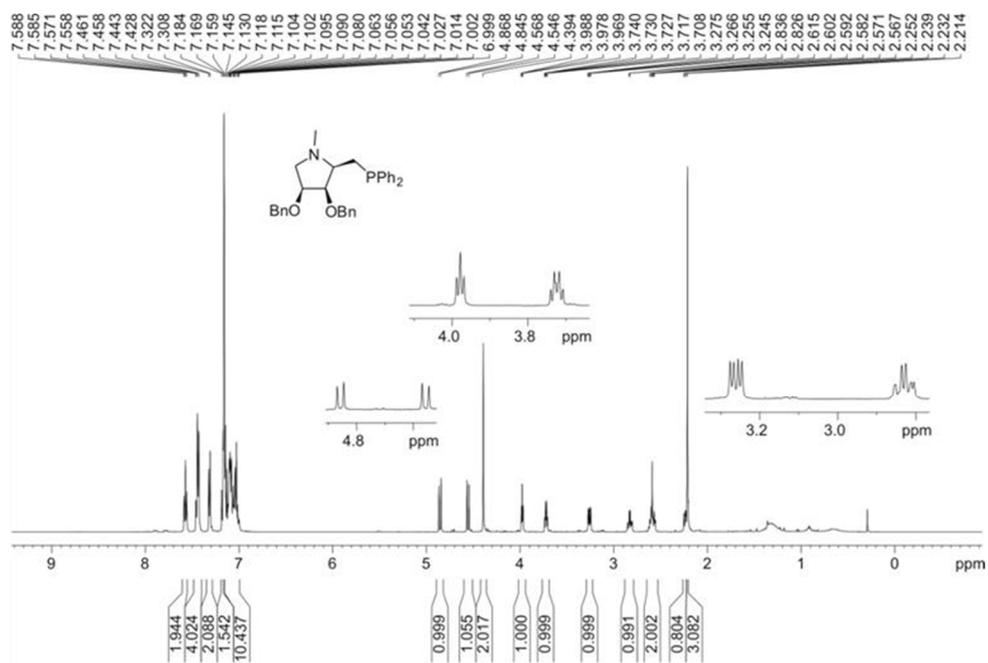
**<sup>1</sup>H NMR spectrum of compound **13** (300 MHz, CDCl<sub>3</sub>)**



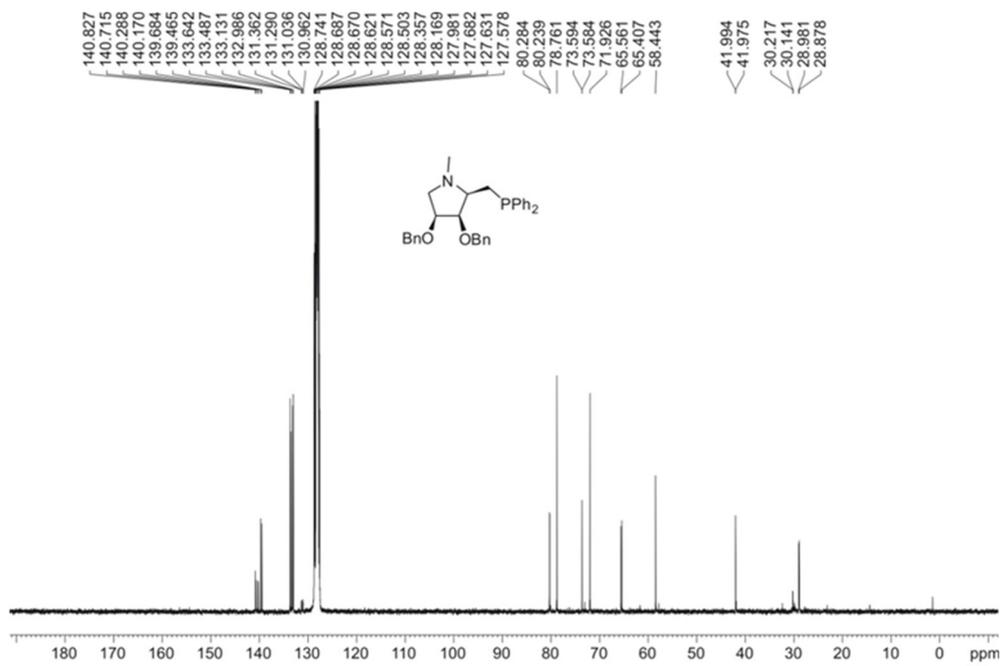
**<sup>13</sup>C NMR spectrum of compound **13** (75.4 MHz, CDCl<sub>3</sub>)**



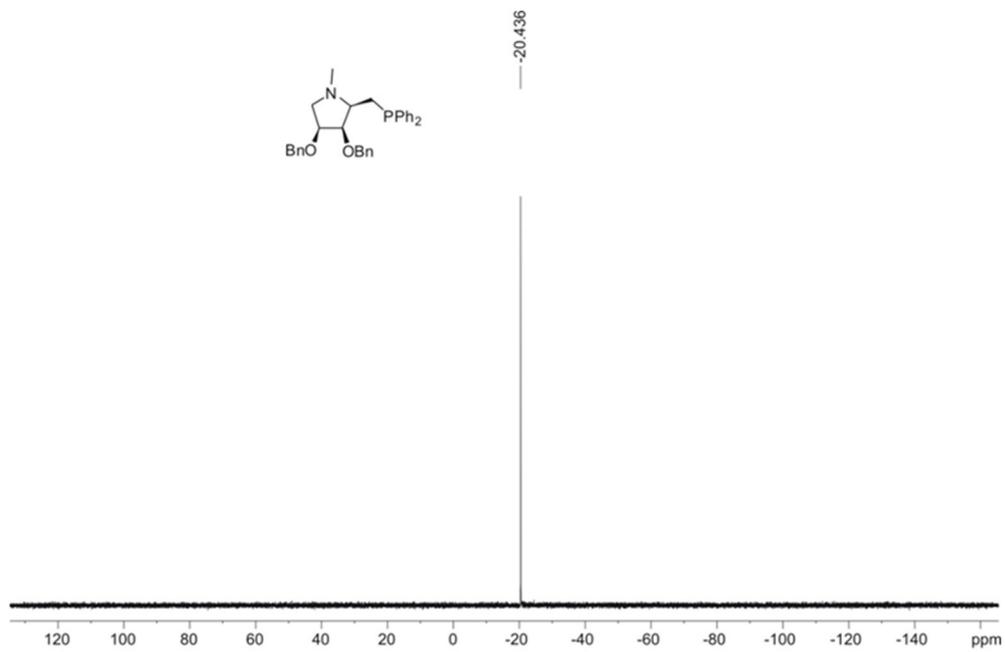
$^{31}\text{P}$  NMR spectrum of compound **13** (121.5 MHz,  $\text{CDCl}_3$ )



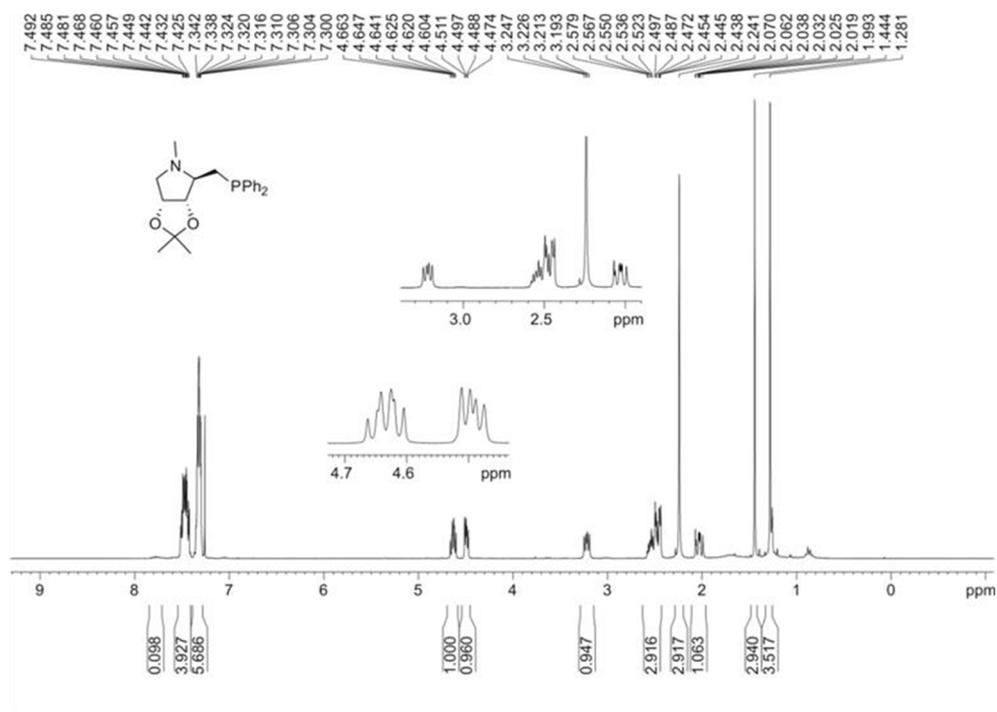
$^1\text{H}$  NMR spectrum of compound **16** (500 MHz,  $\text{C}_6\text{D}_6$ )



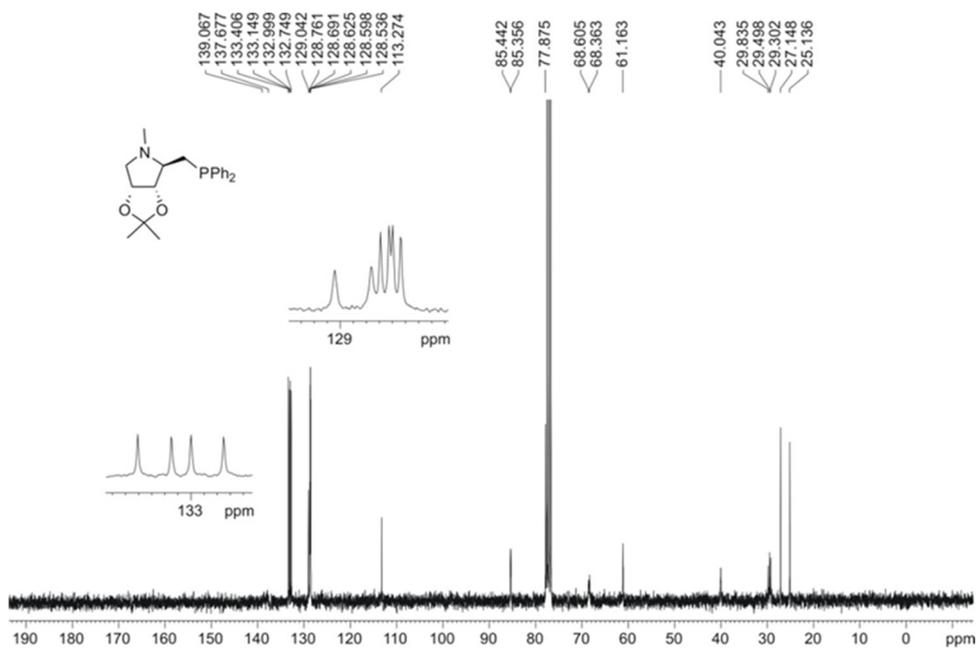
<sup>13</sup>C NMR spectrum of compound **16** (125.7 MHz, C<sub>6</sub>D<sub>6</sub>)



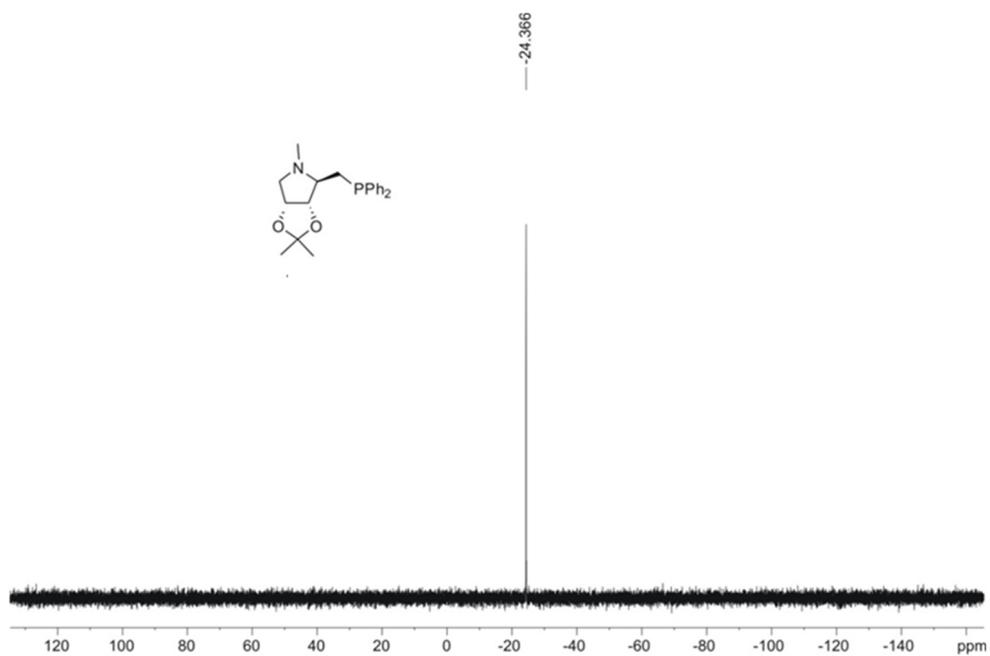
<sup>31</sup>P NMR spectrum of compound **16** (121.5 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>1</sup>H NMR spectrum of compound 18 (300 MHz, CDCl<sub>3</sub>)



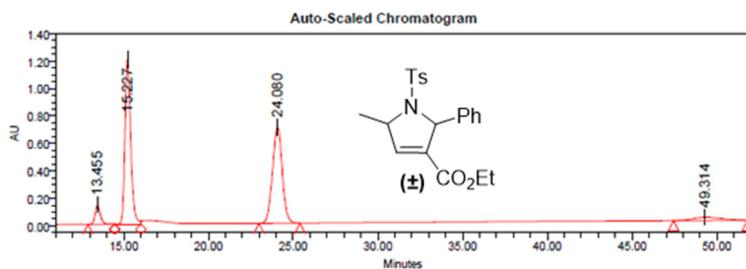
<sup>13</sup>C NMR spectrum of compound 18 (75.4 MHz, CDCl<sub>3</sub>)



$^{31}\text{P}$  NMR spectrum of compound **18** (121.5 MHz,  $\text{CDCl}_3$ )

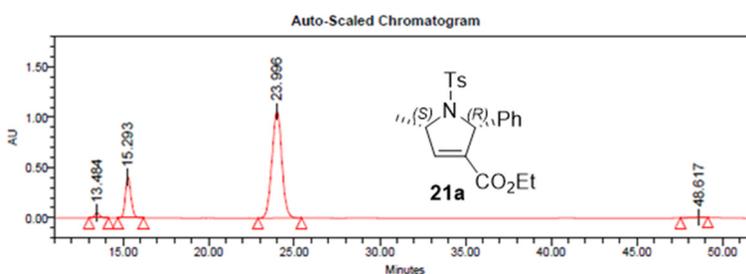
#### 4. HPLC traces

- Compounds **21a** and **ent-21a**



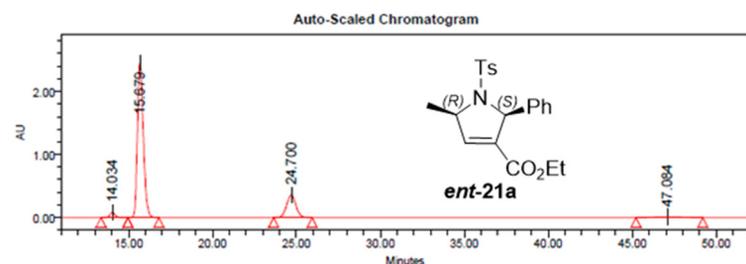
Processed Channel: PDA 210.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 210.0 nm	13.455	2990192	4.82	141519
2	PDA 210.0 nm	15.227	28457512	45.85	1201933
3	PDA 210.0 nm	24.080	27914017	44.97	700119
4	PDA 210.0 nm	49.314	2708908	4.36	23298



Processed Channel: PDA 210.0 nm

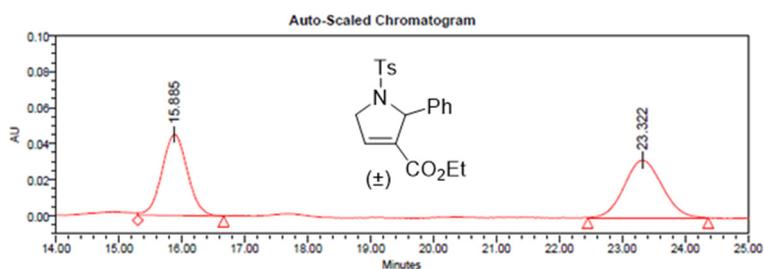
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 210.0 nm	13.484	1078565	2.03	51373
2	PDA 210.0 nm	15.293	9365680	17.61	407579
3	PDA 210.0 nm	23.996	42625126	80.17	1058313
4	PDA 210.0 nm	48.617	101441	0.19	1897



Processed Channel: PDA 210.0 nm

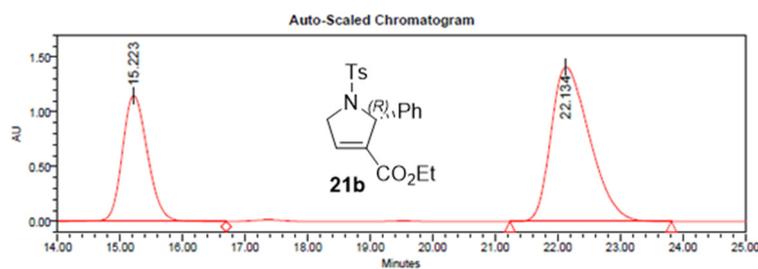
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 210.0 nm	14.034	1806306	2.35	83751
2	PDA 210.0 nm	15.679	59640909	77.45	2443359
3	PDA 210.0 nm	24.700	13982016	18.16	357208
4	PDA 210.0 nm	47.084	1571580	2.04	13901

- Compounds **21b** and **ent-21b**



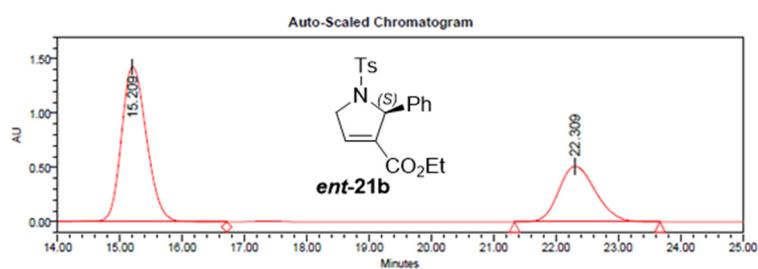
Processed Channel: PDA 210.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 210.0 nm	15.885	1261410	48.49	45025
2	PDA 210.0 nm	23.322	1340212	51.51	31970



Processed Channel: PDA 209.9 nm

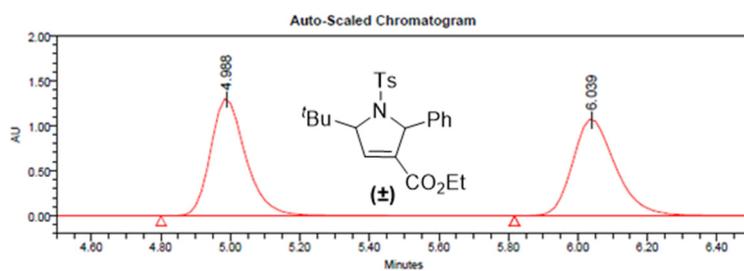
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.9 nm	15.223	32143444	34.68	1149147
2	PDA 209.9 nm	22.134	60540540	65.32	1410495



Processed Channel: PDA 209.9 nm

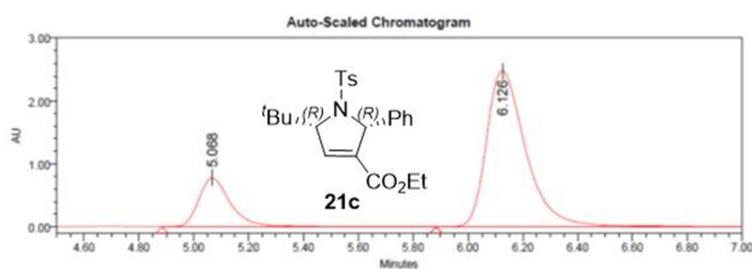
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.9 nm	15.209	39985082	65.54	1430446
2	PDA 209.9 nm	22.309	21027954	34.46	512224

- Compounds **21c** and **ent-21c**



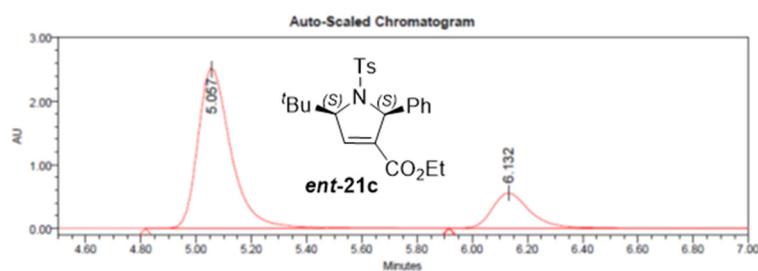
Processed Channel: PDA 240.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 240.0 nm	4.988	9177338	49.80	1300939
2	PDA 240.0 nm	6.039	9249680	50.20	1075607



Processed Channel: PDA 240.0 nm

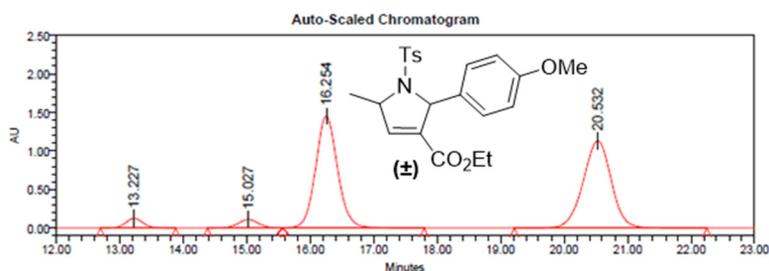
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 240.0 nm	5.068	6335126	20.34	781854
2	PDA 240.0 nm	6.126	24811064	79.66	2482395



Processed Channel: PDA 240.0 nm

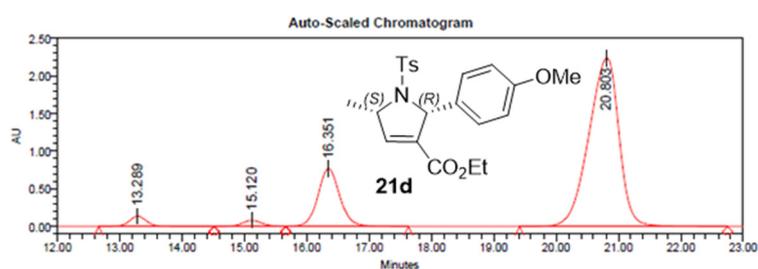
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 240.0 nm	5.057	21044957	79.74	2534651
2	PDA 240.0 nm	6.132	5346442	20.26	555387

- Compounds **21d** and **ent-21d**



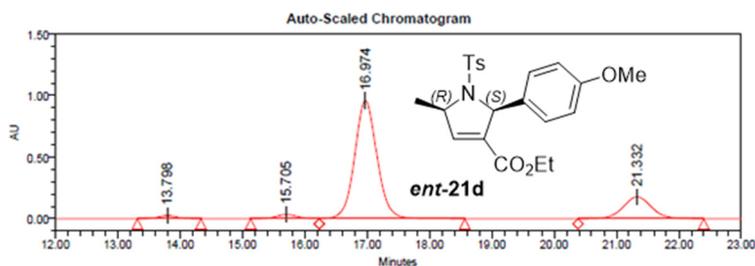
Processed Channel: PDA 210.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 210.0 nm	13.227	2455922	3.26	127107
2	PDA 210.0 nm	15.027	2567526	3.41	111685
3	PDA 210.0 nm	16.254	35190564	46.71	1453585
4	PDA 210.0 nm	20.532	35116805	46.62	1133992



Processed Channel: PDA 210.0 nm

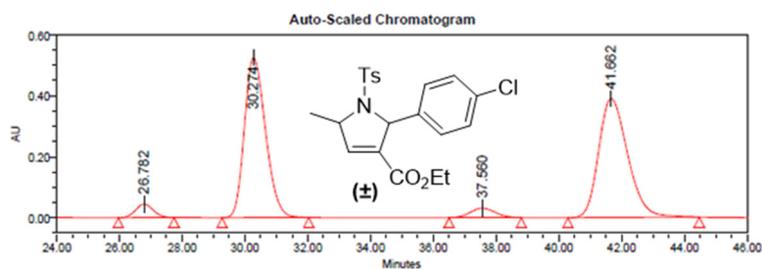
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 210.0 nm	13.289	2750161	2.78	137799
2	PDA 210.0 nm	15.120	1891382	1.91	83002
3	PDA 210.0 nm	16.351	18889356	19.07	768340
4	PDA 210.0 nm	20.803	75514337	76.24	2230208



Processed Channel: PDA 210.0 nm

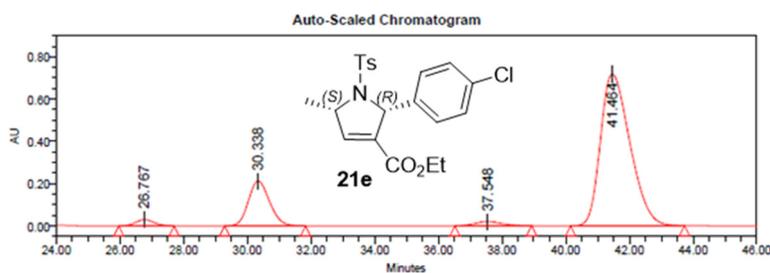
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 210.0 nm	13.798	494507	1.61	25304
2	PDA 210.0 nm	15.705	761115	2.48	32991
3	PDA 210.0 nm	16.974	23842756	77.80	958990
4	PDA 210.0 nm	21.332	5549403	18.11	175992

- Compounds **21e** and **ent-21e**



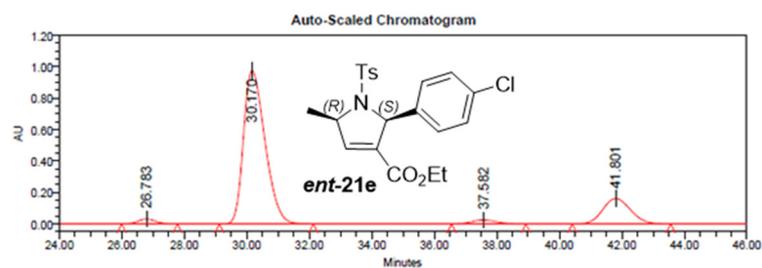
Processed Channel: PDA 230.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 230.0 nm	26.782	1697430	3.21	43742
2	PDA 230.0 nm	30.274	24425861	46.25	524983
3	PDA 230.0 nm	37.560	1699329	3.22	30928
4	PDA 230.0 nm	41.662	24988655	47.32	389885



Processed Channel: PDA 230.0 nm

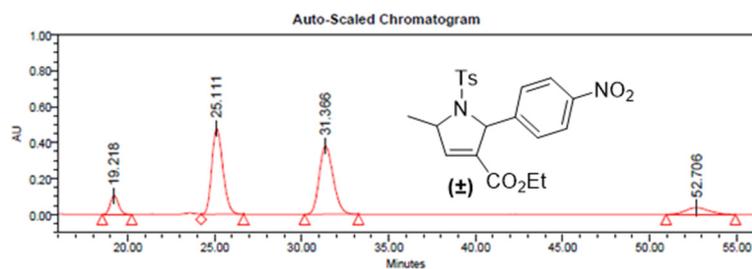
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 230.0 nm	26.767	1169142	2.01	29718
2	PDA 230.0 nm	30.338	9775590	16.81	211980
3	PDA 230.0 nm	37.548	1141374	1.96	20073
4	PDA 230.0 nm	41.464	46075742	79.22	717522



Processed Channel: PDA 230.0 nm

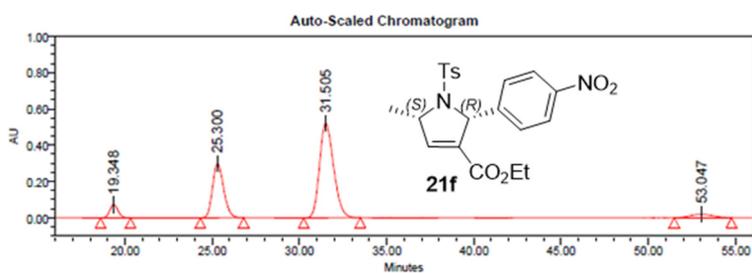
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 230.0 nm	26.783	1242769	2.10	31673
2	PDA 230.0 nm	30.170	46556519	78.54	976169
3	PDA 230.0 nm	37.582	1376512	2.32	25193
4	PDA 230.0 nm	41.801	10102295	17.04	162556

- Compounds **21f** and **ent-21f**



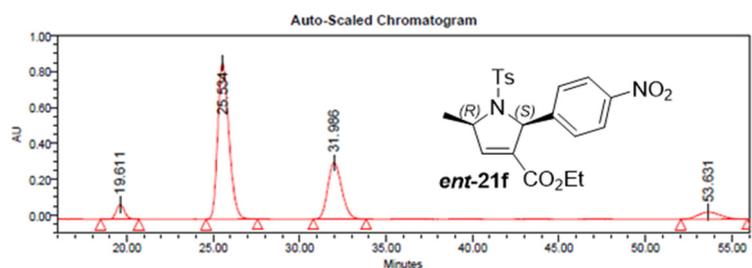
Processed Channel: PDA 209.9 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.9 nm	19.218	3432191	6.99	104496
2	PDA 209.9 nm	25.111	21130698	43.02	475335
3	PDA 209.9 nm	31.366	21197644	43.16	379884
4	PDA 209.9 nm	52.706	3352523	6.83	36419



Processed Channel: PDA 209.9 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.9 nm	19.348	2420151	5.22	72774
2	PDA 209.9 nm	25.300	13230301	28.51	297619
3	PDA 209.9 nm	31.505	29132062	62.78	520160
4	PDA 209.9 nm	53.047	1622201	3.50	18210



Processed Channel: PDA 209.9 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.9 nm	19.611	2747663	4.33	81914
2	PDA 209.9 nm	25.534	39325075	62.02	870167
3	PDA 209.9 nm	31.986	17729920	27.96	314817
4	PDA 209.9 nm	53.631	3601462	5.68	39113

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