Supplementary Information

Asymmetric cyclopropanation of electron-rich alkenes by the racemic diene rhodium catalyst: the chiral poisoning approach

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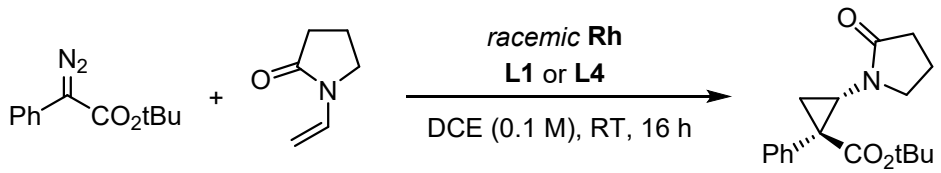
General information

Unless stated otherwise, all reactions were carried out under argon in oven-dried glassware. The solvents used for the reactions were purified by distillation over the drying agents indicated and were stored under argon: hexane, THF, toluene, 1,4-dioxane – Na; CH_2Cl_2 (DCM), $C_2H_4Cl_2$ (DCE) – CaH_2; MeCN – P_2O_5. Other solvents were purchased from the local suppliers and were used as received.

Racemic and enantiopure complexes rac-**Rh**, *R,R*-**Rh**, *S,S*-**Rh**,[1] S-Salox ligand sodium salt (**L1**)[1], S-N-(tert-butylsulfinyl)benzamide (**L4H**),[2] N-methylpyrrolidine-borane adduct **3**,[3] benzyl vinyl ether[4] and diazo compounds **1a-e**[5,6] were synthesized according to the literature procedures. All other reagents were obtained from commercial sources and used without further purification. Macherey-Nagel silica gel 60 (230–400 mesh) was used for column chromatography. Reactions were monitored by thin-layer chromatography on Macherey-Nagel POLYGRAM SIL G/UV_{254} pre-coated polyester TLC plates (0.2 mm) which were rendered visible by ultraviolet and spraying with solution of phosphomolybdic acid (10%) in ethanol followed by heating. The 3Å molecular sieves were pre-dried for 15 min in MW (750W), then dried in vacuo and stored under argon atmosphere. NMR spectra were measured on Bruker Avance 400 and Varian Inova 400 spectrometers. Chemical shifts (δ) are given in ppm relative to the internal solvent signal (^{1}H and ^{13}C), $CFCl_3$ (^{19}F) or $BF_3{\cdot}Et_2O$ (^{11}B). High-resolution mass spectra were recorded on Bruker microTOF II instrument using electrospray ionization (ESI). Enantiomeric excess values of the products were measured using Shimadzu HPLC equipped with Chiralpak IA-3 (4.6 × 150 mm), Chiralpak IB-3 (4.6 x 150 mm), or Chiralpak IJ-3 (4.6 x 150 mm) column and diode array detector. Unless stated otherwise, flow rate 1 mL/min was adjusted in all experiments.

Optimization of cyclopropanation reaction conditions



1a **6a**

In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar the racemic catalyst **Rh** was placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1.0 ml of DCE and **L1** (sodium salt, 0.1085M stock solution in THF) or **L4** (freshly generated sodium salt, 0.0500M stock solution in THF, see details below) were added to the reaction vessel. The resulting mixture was stirred at ambient temperature for 1 hour. After that, the diazo compound **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and 1-vinyl-2-pyrrolidone (13.3 mg, 0.12 mmol, 1.2 eq.) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After full consumption of the starting diazo compound **1a** (monitored by TLC) the minimum amount of SiO_2 was added to this mixture and the solvent was removed in vacuo. Subsequent purification on silica gel column afforded the desired cyclopropane product **6a**. Quantities of the racemic catalyst **Rh** (molar %, referring to a rhodium content) and the corresponding chiral additive are indicated in the Table S1.

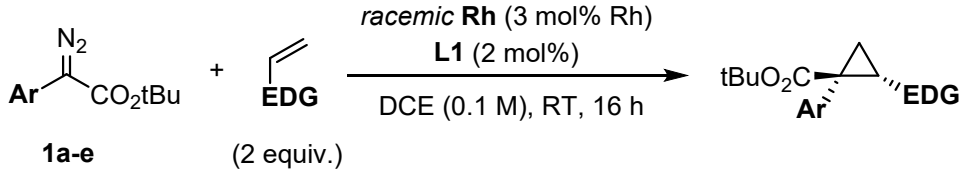
Table S1

entry	temperature	catalyst loading	additive	additive loading	yield, %	ee, %
1	r.t.	5 mol % Rh	**L1**	4 mol %	58	95
2	r.t.	4 mol % Rh	**L1**	3.2 mol %	68	95
3	r.t.	3 mol % Rh	**L1**	2 mol %	73	92
4[a]	r.t.	2.5 mol % Rh	**L1**	2 mol %	69	96
5[b]	50°C	3 mol % Rh	**L1**	2 mol %	77	85
6	r.t.	5 mol % Rh	**L4**	4 mol %	61	93
7	r.t.	4 mol % Rh	**L4**	3.2 mol %	66	94
8	r.t.	3 mol % Rh	**L4**	2 mol %	62	95
9[c]	r.t.	2.5 mol % Rh	**L4**	2 mol %	66	85

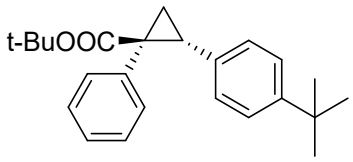
All reactions were performed with 1.2 eq of N-vinyl pyrrolidone for 16 hours;[a, c] reaction time of 113 hours was required for full consumption of **1a**; [b] 2.0 eq of N-vinylpyrrolidone were used

L4 sodium salt generation: in a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar NaH (60% dispersion in mineral oil, 2.4 mg, 0.06 mmol, 1.5 eq.) was placed. The flask was subjected to a vacuum and refilled with argon three times. Then 0.800 ml of THF was added via syringe. Under intensive stirring S-N-(tert-butylsulfinyl)benzamide (**L4H**) (9.0 mg, 0.04 mmol, 1.0 eq) was added to the reaction mixture. The resulting suspension was stirred for 30 minutes until the gas evolution was over, then the magnetic stirrer was turned off to allow the solids to settle for additional 30 minutes. The obtained solution was used immediately on the next step without any purification.

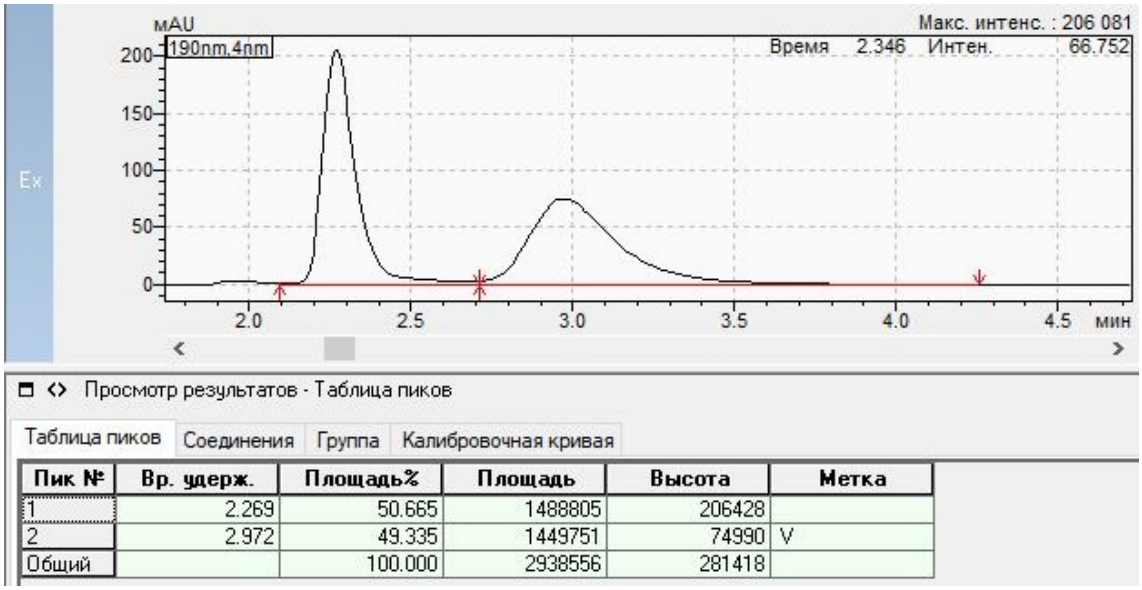
General procedure for Rh-catalyzed asymmetric alkene cyclopropanation



In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar racemic catalyst **Rh** (2.0 mg, 2.25 mmol, 1.5 mol %) was placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1.5 ml of DCE and stock solution of **L1** in THF (0.028 ml of 0.1085M solution, 0.003 mmol, 2.0 mol %) were added to the reaction vessel. The resulting mixture was stirred at ambient temperature for 1 hour. After that, diazo compound **1a-e** (0.15 mmol, 1.0 eq.) and corresponding alkene (0.3 mmol, 2.0 eq.) were added to the reaction mixture. The resulting mixture was stirred overnight at ambient temperature, unless stated otherwise. After full consumption of the starting diazo compound (monitored by TLC) the minimum amount of SiO_2 was added to this mixture and the solvent was removed in vacuo. Subsequent purification on silica gel column afforded the desired cyclopropane product **4b-7d**.



4b. **Yield** 28.0 mg, 53%, 77% *ee* (98% *ee* with enantiomerically pure *S,S*-**Rh** as a catalyst); white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.12 – 7.09 (m, 3H, CH^{Ph}), 7.06 (d, *J* = 8.0 Hz, 2H, CH^{Ar}), 7.03 – 7.01 (m, 2H, CH^{Ph}), 6.67 (d, *J* = 8.0 Hz, 2H, CH^{Ar}), 2.96 (dd, appears as t, *J* = 8.3, 8.3 Hz, 1H, CH), 2.05 (dd, *J* = 9.4, 4.7 Hz, 1H, CH), 1.75 (dd, *J* = 7.2, 4.9 Hz, 1H, CH), 1.39 (s, 9H, CH^3), 1.21 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.97, 149.08, 135.64, 133.94, 132.07, 127.76, 127.50, 126.69, 124.63, 80.86, 38.56, 34.39, 32.13, 31.40, 28.11, 20.05. **HRMS** (ESI-TOF, m/z) calcd for $C_{24}H_{30}O_2$ $[M+H]^+$: 351.2319; Found: 351.2316.
HPLC conditions: IJ-3 (4.6 x 150 mm), Heptane/i-PrOH = 90/10, t_R = 2.27 min for *1R,2S*-**4b**, t_R = 2.97 min for *1S,2R*-**4b**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	2.269	50.665	1488805	206428	
2	2.972	49.335	1449751	74990	V
Общий		100.000	2938556	281418	

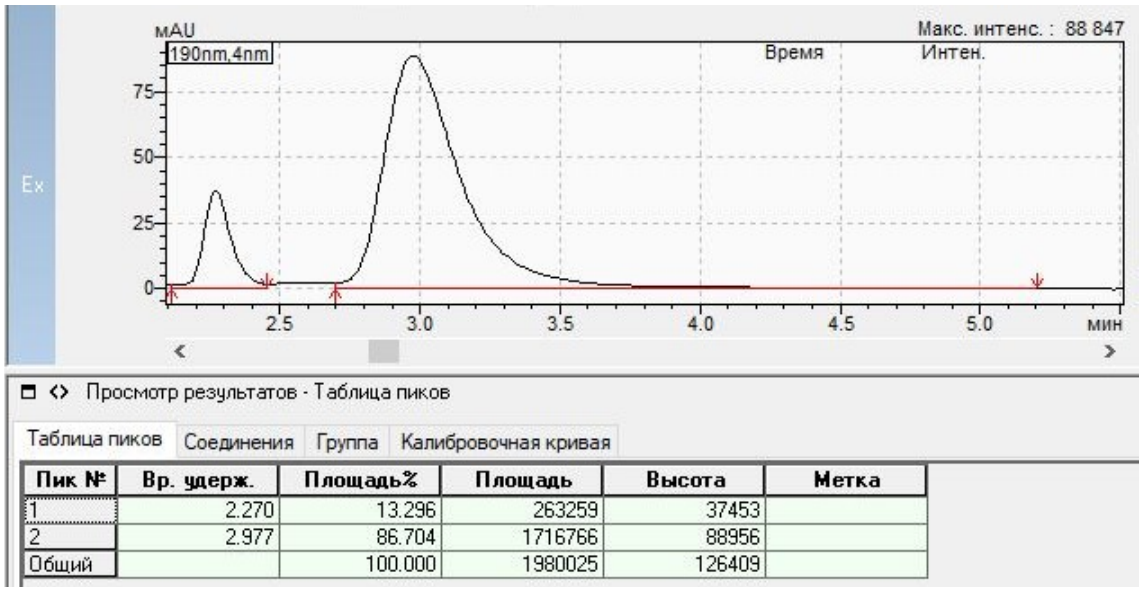


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Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	2.270	13.296	263259	37453	
2	2.977	86.704	1716766	88956	
Общий		100.000	1980025	126409	

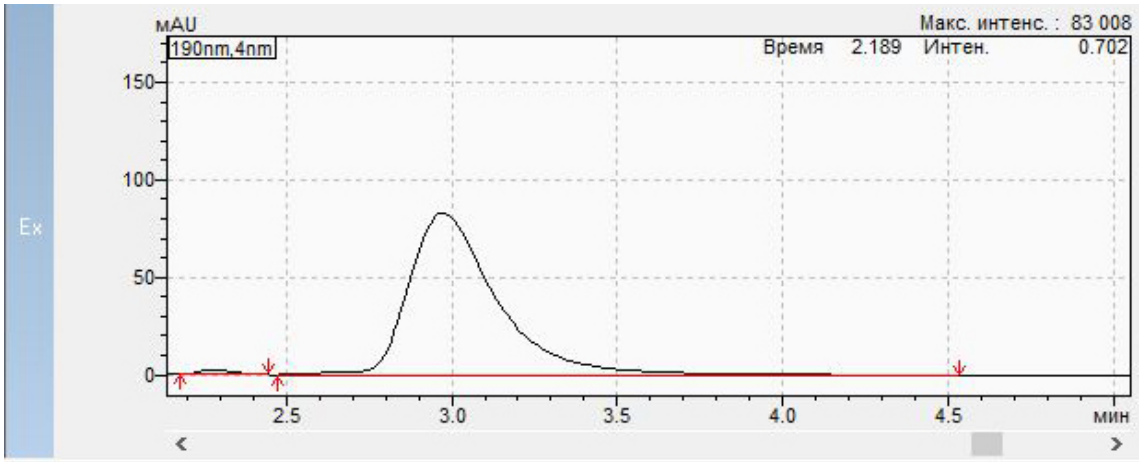

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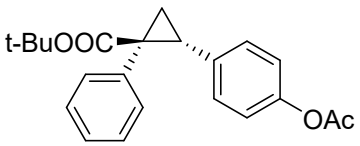
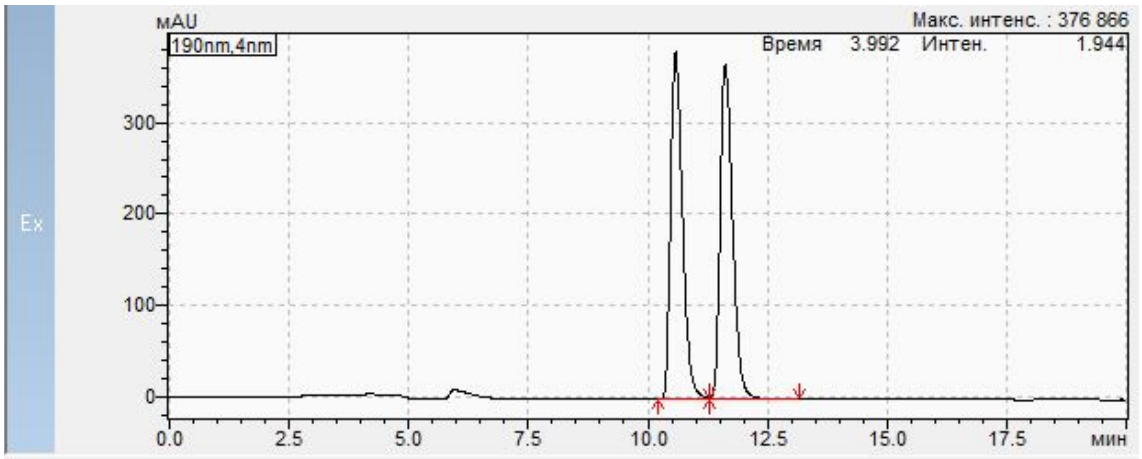
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	2.283	0.890	14102	2355	M
2	2.972	99.110	1570734	83339	S
Общий		100.000	1584836	85694	



4c. Reaction was performed on a 0.1 mmol scale. **Yield** 21.5 mg, 61%, 70% *ee* (96% *ee* with enantiomerically pure *S,S*-**Rh** as a catalyst); white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.13 – 7.10 (m, 3H, CH^{Ar}), 7.04 – 6.98 (m, 2H, CH^{Ar}), 6.80 – 6.72 (m, 4H, CH^{Ar}), 3.00 (dd, *J* = 9.3, 7.2 Hz, 1H, CH), 2.22 (s, 3H, CH_3), 2.06 (dd, *J* = 9.3, 4.9 Hz, 1H, CH), 1.76 (dd, *J* = 7.0, 5.0 Hz, 1H, CH), 1.39 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.08, 139.01, 135.24, 134.66, 131.96, 129.00, 127.68, 126.90, 120.80, 81.07, 38.67, 31.78, 28.10, 21.24, 20.01. **HRMS** (ESI-TOF, m/z) calcd for $C_{22}H_{24}O_4$ $[M+H]^+$: 353.1753; found: 353.1748.

HPLC conditions: Chiralpak IB-3 (4.6 x 150 mm), Heptane/i-PrOH = 99/1, flow rate 0.5 mL/min, t_R = 10.55 min for *1S,2R*-**4c**, t_R = 11.62 min for *1R,2S*-**4c**.



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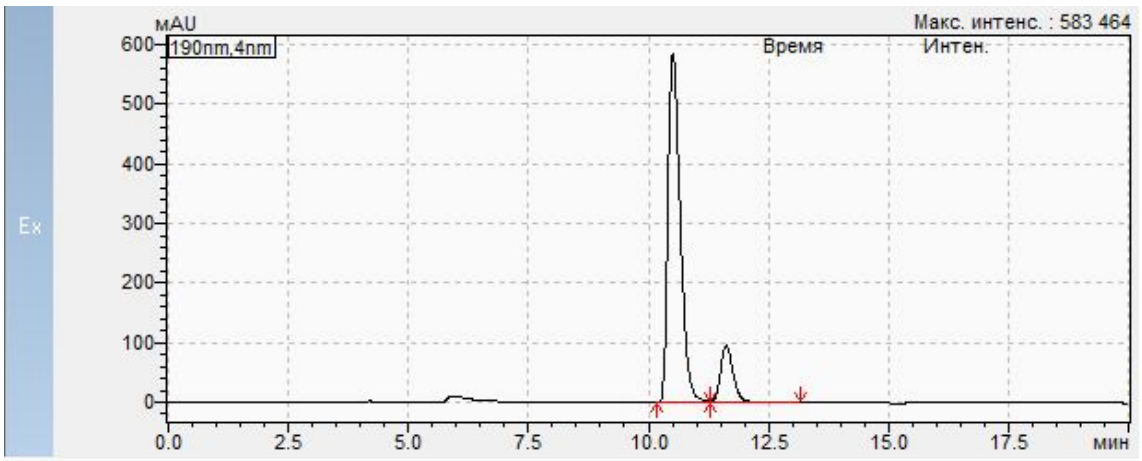
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	10.578	49.753	6630609	380381	
2	11.619	50.247	6696342	367832	SV
Общий		100.000	13326951	748212	



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Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	10.510	85.327	10438016	584264	
2	11.621	14.673	1794936	95857	V
Общий		100.000	12232952	680121	

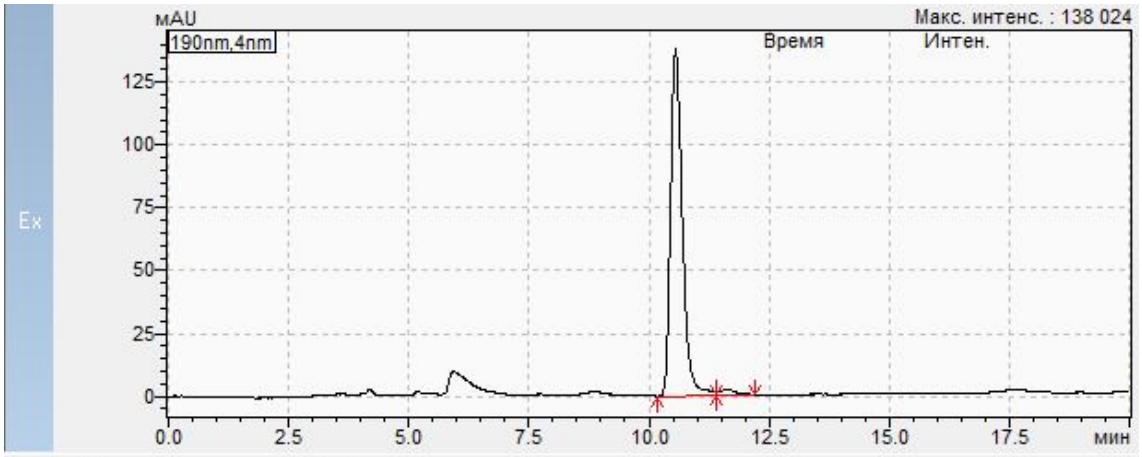

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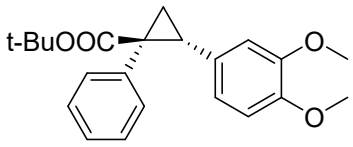
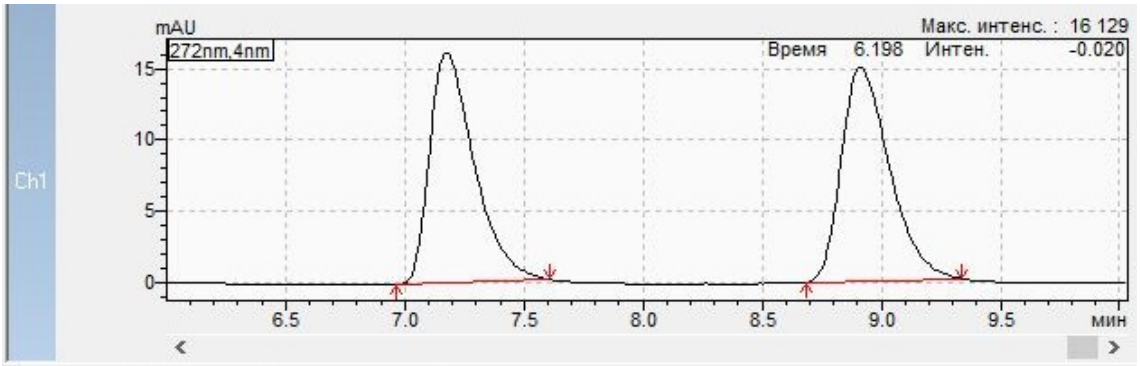
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	10.555	98.032	2347179	137881	M
2	11.639	1.968	47130	2197	V M
Общий		100.000	2394309	140078	



4d. **Yield** 32.8 mg, 62%, 84% *ee*; white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 – 7.08 (m, 3H, CH^{Ph}), 7.07 – 7.01 (m, 2H, CH^{Ph}), 6.60 (d, *J* = 8.3 Hz, 1H, CH^{Ar}), 6.49 (dd, *J* = 8.3, 1.9 Hz, 1H, CH^{Ar}), 5.99 (d, *J* = 1.9 Hz, 1H, CH^{Ar}), 3.77 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 2.94 (dd, *J* = 9.3, 7.2 Hz, 1H, CH), 2.06 (dd, *J* = 9.4, 4.9 Hz, 1H, CH), 1.70 (dd, *J* = 7.0, 5.0 Hz, 1H, CH), 1.39 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.83, 148.10, 147.42, 135.66, 131.97, 129.56, 127.69, 126.76, 120.78, 110.71, 110.38, 80.94, 55.80, 55.58, 38.40, 32.12, 28.09, 20.39. **HRMS** (ESI-TOF, m/z) calcd for $C_{22}H_{26}O_4$ $[M+Na]^+$: 377.1723; Found: 377.1721.

HPLC conditions: Chiralpak IB-3 (4.6 x 150 mm), Heptane/i-PrOH = 99/1, t_R = 7.17 min for *1S,2R*-**4d**, t_R = 8.97 min for *1R,2S*-**4d**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	7.174	50.025	210397	16126	
2	8.914	49.975	210183	14936	
Общий		100.000	420580	31062	

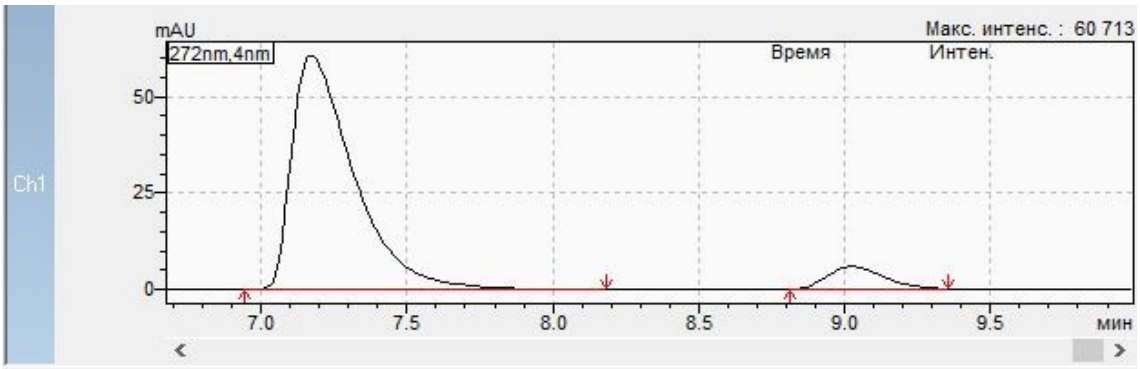


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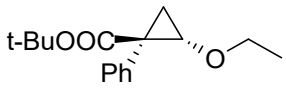
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	7.173	91.953	897600	60752	M
2	9.024	8.047	78549	5877	
Общий		100.000	976148	66629	



5a. **Yield** 33.6 mg, 76%, 81% *ee* (96% *ee* of the opposite enantiomer with the enantiomerically pure *R*,*R*-**Rh** as a catalyst); colorless oil. NMR spectra and the specific rotation angle match to the data reported previously for *(1R,2S)* product **5a**.[7]

Control experiment with enantiomerically pure (ee > 99%) catalyst: 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar *R,R*-**Rh** (0.9 mg, 0.01 mmol, 2 mol % Rh) was placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1.0 ml of DCE, diazo compound **1a** (21.8 mg, 0.1 mmol, 1.0 eq.) and vinyl ethyl ether (0.019 ml, 0.2 mmol, 2.0 eq.) were added to the reaction mixture. The resulting mixture was stirred overnight at ambient temperature. After full consumption of the starting diazo compound (monitored by TLC) the minimum amount of SiO_2 was added to this mixture and the solvent was removed in vacuo. Subsequent purification on silica gel column afforded the desired cyclopropane product **5a** with ee = 96%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 4H, CH^{Ph}), 7.26 – 7.21 (m, 1H, CH^{Ph}), 3.86 (dd, *J* = 7.0, 4.5 Hz, 1H, CH), 3.55 (q, *J* = 7.0 Hz, 2H, CH_2), 1.70 (dd, *J* = 7.0, 5.7 Hz, 1H, CH), 1.56 (dd, *J* = 5.7, 4.5 Hz, 1H, CH), 1.38 (s, 9H, CH_3), 0.98 (t, *J* = 7.0 Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.19, 134.96, 131.47, 127.75, 126.93, 80.89, 66.56, 64.29, 36.20, 28.13, 20.17, 15.00. **$[\alpha]^{20}_D$** = – 49.2 (c 0.37, $CHCl_3$).

HPLC conditions: Chiralpak IJ-3, Heptane/i-PrOH = 99/1, t_R = 4.15 min for *1S,2R*-**5a**, t_R = 6.42 min for *1R,2S*-**5a**.

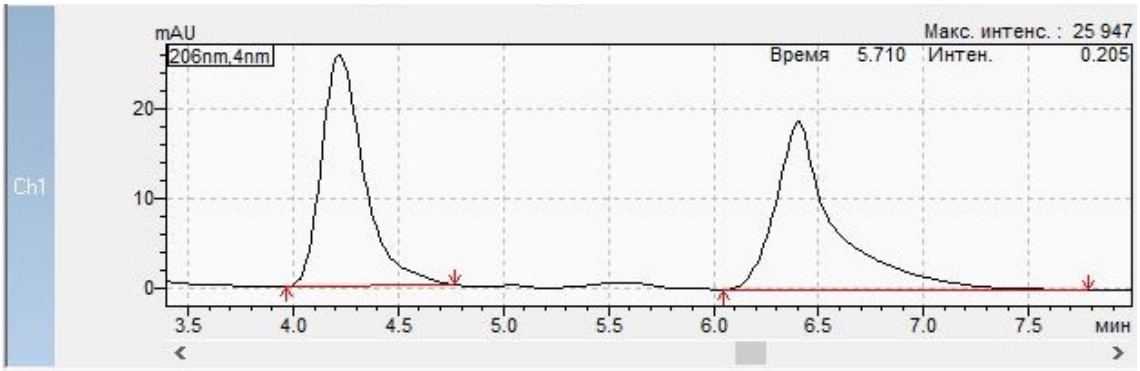


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Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.220	49.495	362973	25794	
2	6.405	50.505	370382	18834	M
Общий		100.000	733356	44628	

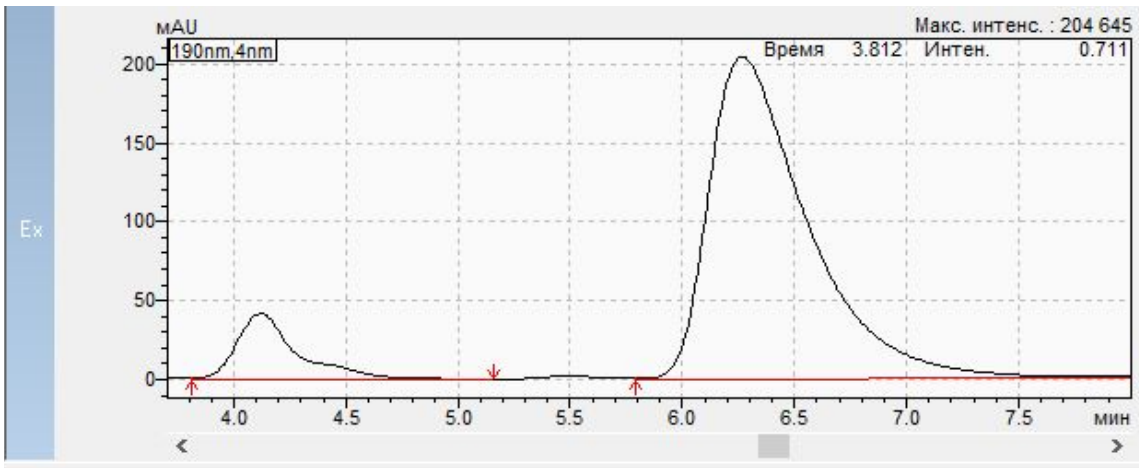

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Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.122	11.233	785135	41776	
2	6.266	88.767	6204142	204052	
Общий		100.000	6989277	245828	

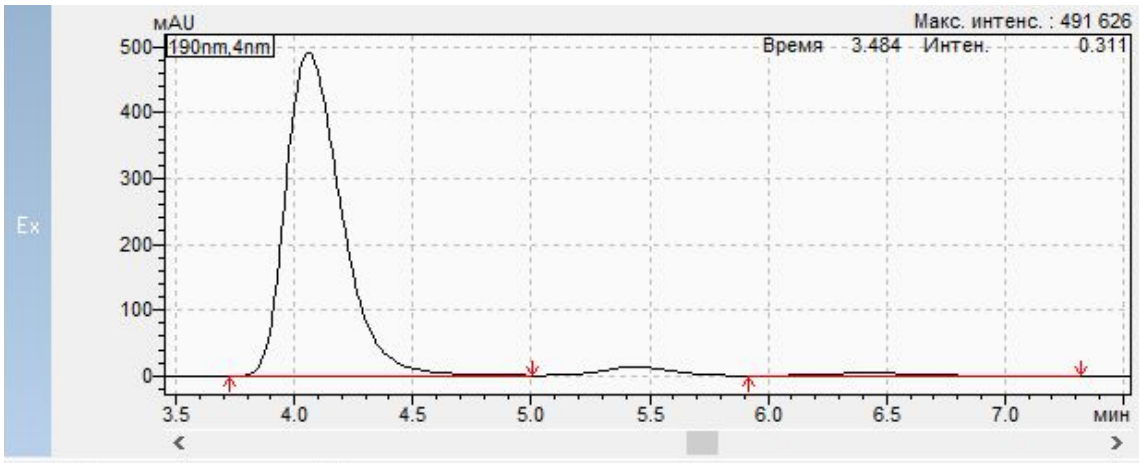

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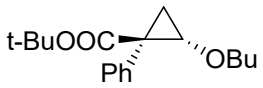
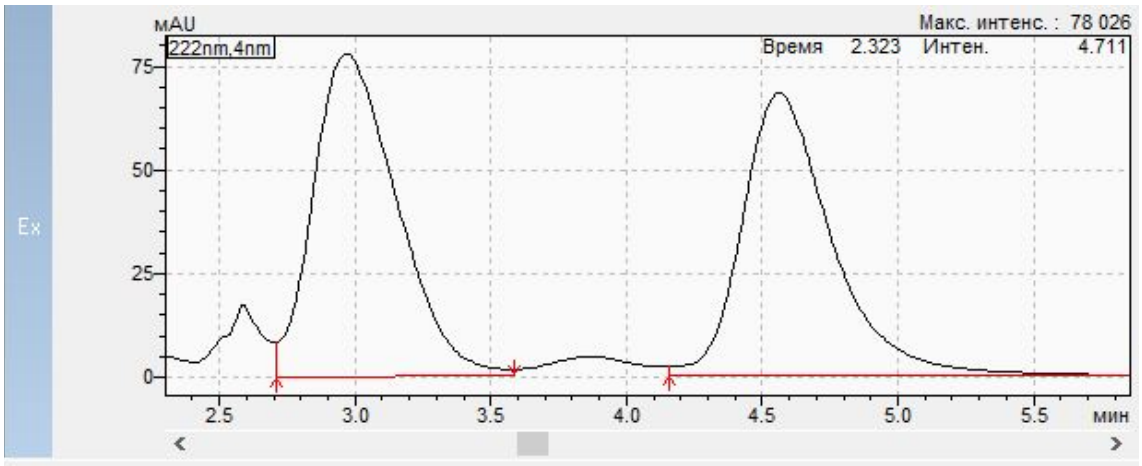
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.059	97.845	8067859	492410	
2	6.426	2.155	177673	4938	
Общий		100.000	8245532	497347	



5b. **Yield** 25.0 mg, 59%, 69% *ee* (88% *ee* with enantiomerically pure *S,S*-**Rh** as a catalyst); yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.21 (m, 5H, Ph), 3.85 (dd, *J* = 6.9, 4.4 Hz, 1H, CH), 3.52 – 3.40 (m, 2H, OCH_2), 1.69 (dd, *J* = 6.9, 5.7 Hz, 1H, CH), 1.58 (dd, *J* = 5.7, 4.5 Hz, 1H, CH), 1.38 (s, 9H), 1.35 – 1.25 (m, 2H, CH_2), 1.12 – 1.03 (m, 2H, CH_2), 0.75 (t, *J* = 7.3 Hz, 3H, CH_3).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.22, 134.85, 131.49, 127.68, 126.88, 80.88, 70.86, 64.49, 36.25, 31.61, 28.13, 20.12, 19.10, 13.91. **HRMS** (ESI-TOF, m/z) calcd for $C_{18}H_{26}O_3$ $[M+H]^+$: 291.1955; found: 291.1968.

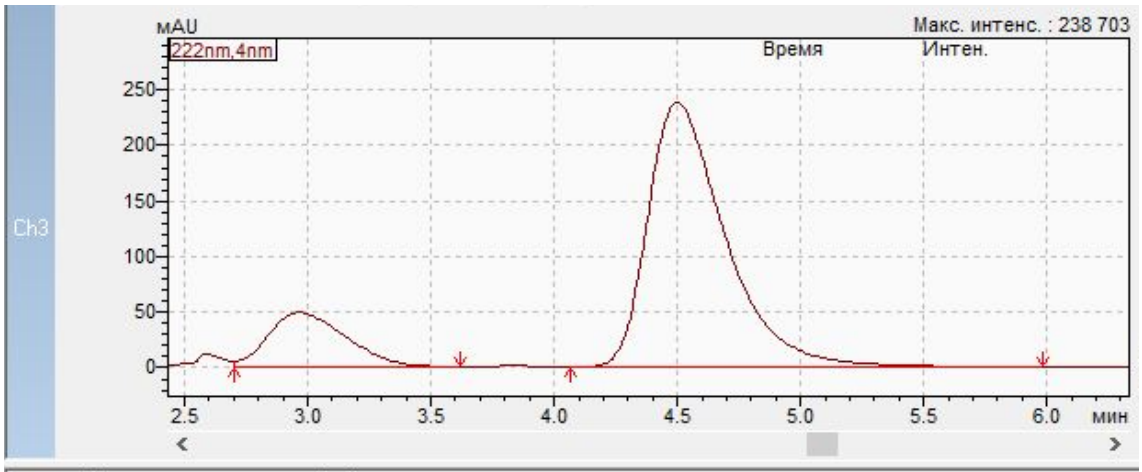
HPLC conditions: Chiralpak IJ-3 (4.6 x 150 mm), Heptane/i-PrOH = 99/1, t_R = 2.97 min for *1S,2R*-**5b**, t_R = 4.53 min for *1R,2S*-**5b.**



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

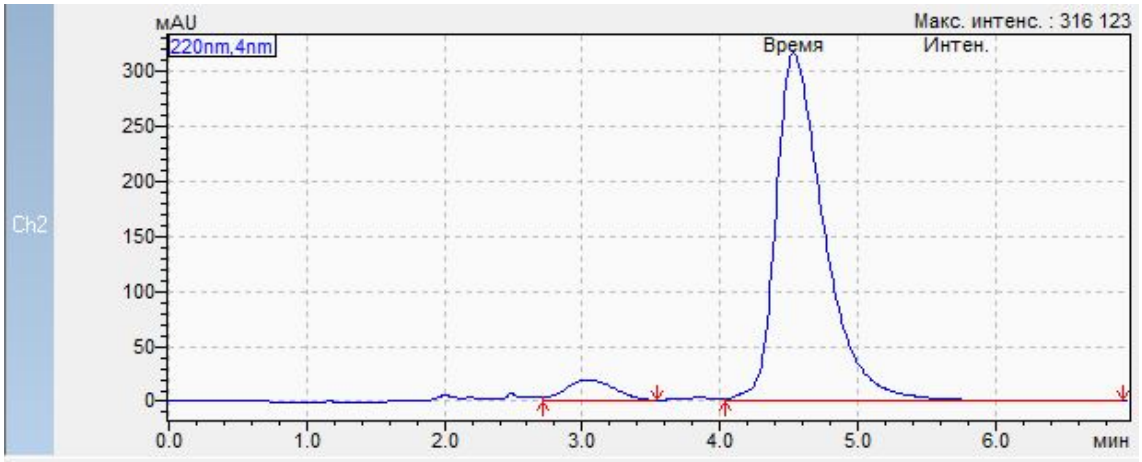
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	2.968	51.697	1667723	77872	
2	4.562	48.303	1558221	68097	
Общий		100.000	3225944	145969	



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

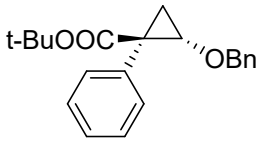
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	2.966	17.318	1089459	49431	
2	4.500	82.682	5201602	238132	
Общий		100.000	6291061	287563	



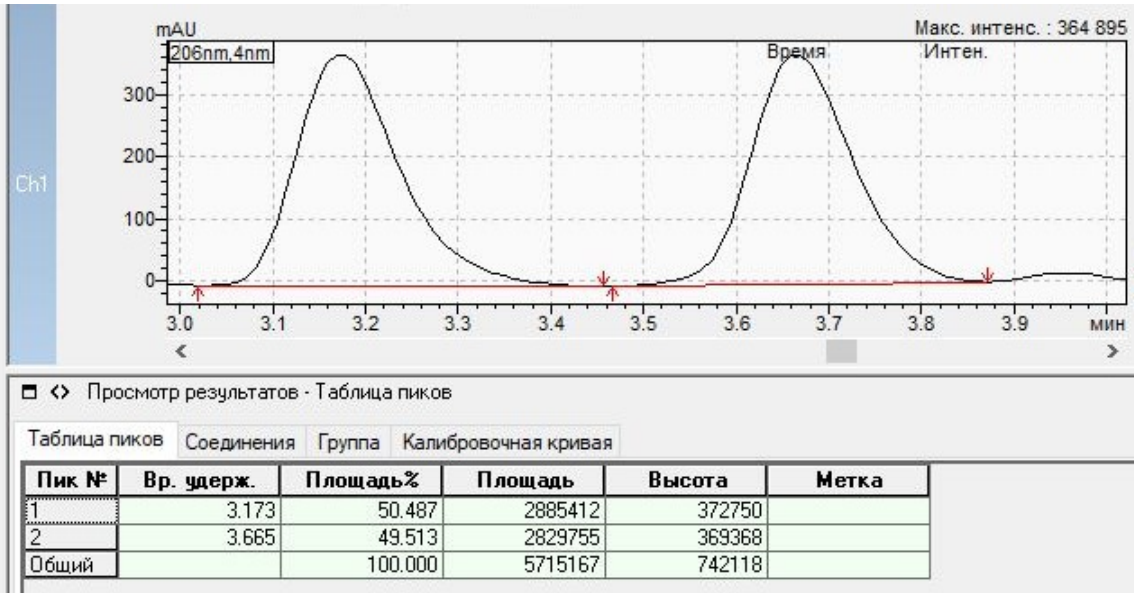
Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	3.039	6.075	502924	19695	
2	4.537	93.925	7775119	315863	
Общий		100.000	8278043	335558	

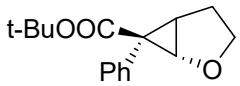


5c. Reaction was carried out at 50 ºC. **Yield** 19.0 mg, 39%, 66% *ee*; yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H, Ph), 7.34 (t, *J* = 7.4 Hz, 2H, Ph), 7.30 – 7.27 (m, 1H, Ph), 7.25 – 7.21 (m, 3H, Ph), 6.98 (dd, *J* = 6.6, 3.0 Hz, 2H, Ph), 4.53 (d, *J* = 11.3 Hz, 1H, OCH_2), 4.48 (d, *J* = 11.3 Hz, 1H, OCH_2), 3.98 (dd, *J* = 6.9, 4.4 Hz, 1H, CH), 1.72 (t, *J* = 6.4 Hz, 1H, CH), 1.68 – 1.65 (m, 1H, CH), 1.39 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.04, 137.42, 134.69, 131.54, 128.40, 127.96, 127.85, 127.06, 81.05, 72.89, 64.02, 36.46, 28.14, 20.11. **HRMS** (ESI-TOF, m/z) calcd for $C_{21}H_{24}O_3$ $[M+Na]^+$: 347.1618; found: 347.1616.
HPLC conditions: Chiralpak IB-3, Heptane/i-PrOH = 99/1, t_R = 3.18 min for *1S,2R*-**5c**, t_R = 3.68 min for *1R,2S*-**5c.**



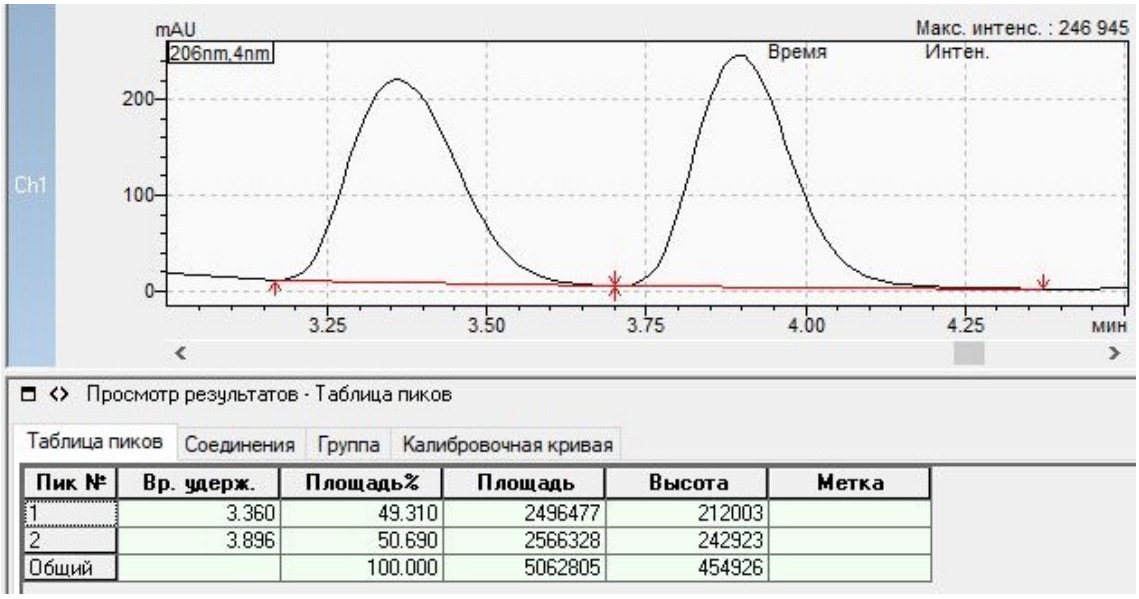
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	3.173	50.487	2885412	372750	
2	3.665	49.513	2829755	369368	
Общий		100.000	5715167	742118	

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	3.184	17.034	696599	77534	
2	3.692	82.966	3392975	396330	
Общий		100.000	4089573	473864	



5d. **Yield** 24.1 mg, 62%, 83% *ee*, white solid. NMR spectra and the specific rotation angle match data reported previously for the (1S,6R) product.[7] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H, Ph), 4.46 (d, *J* = 5.7 Hz, 1H, CH), 3.76 (ddd, *J* = 10.1, 8.5, 3.5 Hz, 1H, CH_2), 2.56 (dd, appears as t, *J* = 5.9, 5.9 Hz, 1H, CH_2), 2.40 (ddd appears as q, *J* = 8.7, 8.7, 8.7 Hz, 1H, CH), 2.29 – 2.15 (m, 1H, CH_2), 1.84 (ddd, *J* = 12.6, 8.7, 3.5 Hz, 1H, CH_2), 1.32 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.60, 133.02, 131.43, 128.35, 127.20, 80.83, 70.09, 69.37, 39.18, 31.49, 28.08, 26.39. **$[\alpha]^{20}_D$** = + 33.3 (c 0.33, $CHCl_3$).

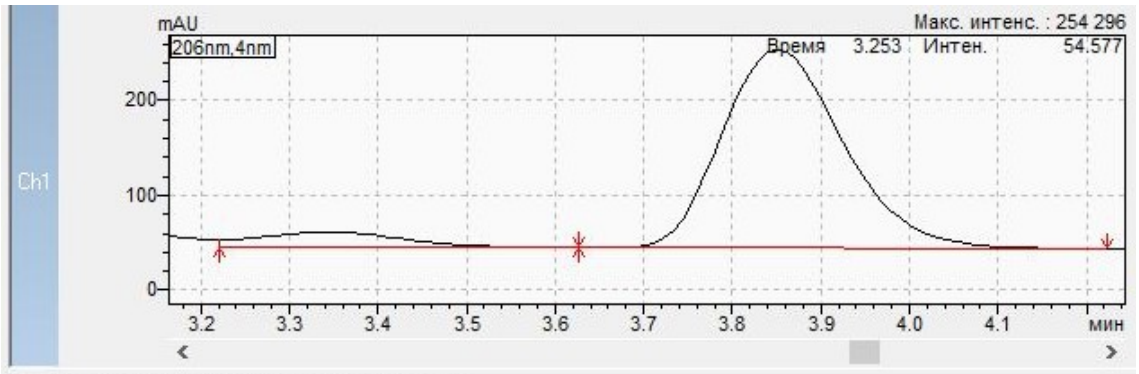
HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 99/1, t_R = 3.35 min for *1R,6S*-**5d**, t_R = 3.87 min for *1S,6R*-**5d**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

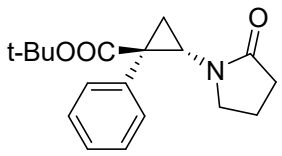
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	3.360	49.310	2496477	212003	
2	3.896	50.690	2566328	242923	
Общий		100.000	5062805	454926	



Просмотр результатов - Таблица пиков

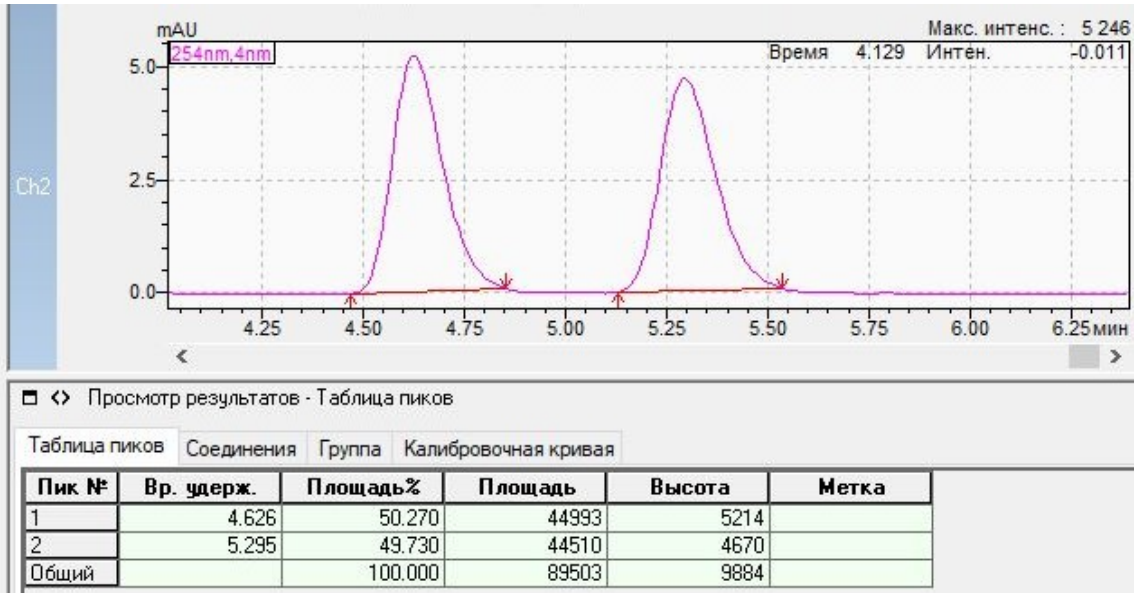
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	3.341	8.398	182578	16143	
2	3.851	91.602	1991402	209643	
Общий		100.000	2173979	225787	



6a. **Yield** 33.0 mg, 73%; 92% *ee*, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 5H, Ph), 3.79 (dd, *J* = 8.9, 6.0 Hz, 1H, CH), 2.99 (td, *J* = 8.7, 5.4 Hz, 1H, CH_2), 2.32 – 2.08 (m, 3H, CH_2), 1.99 (dd, *J* = 8.8, 6.1 Hz, 1H, CH), 1.78 (t, *J* = 6.0 Hz, 1H, CH), 1.75 – 1.62 (m, 1H, CH_2), 1.50 – 1.42 (m, 1H, CH_2), 1.38 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.65, 171.48, 134.78, 131.33, 128.11, 127.46, 81.33, 46.77, 39.59, 34.33, 31.74, 28.08, 18.30, 17.80. **Anal. Calcd** for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.61; H, 7.54; N, 4.74.

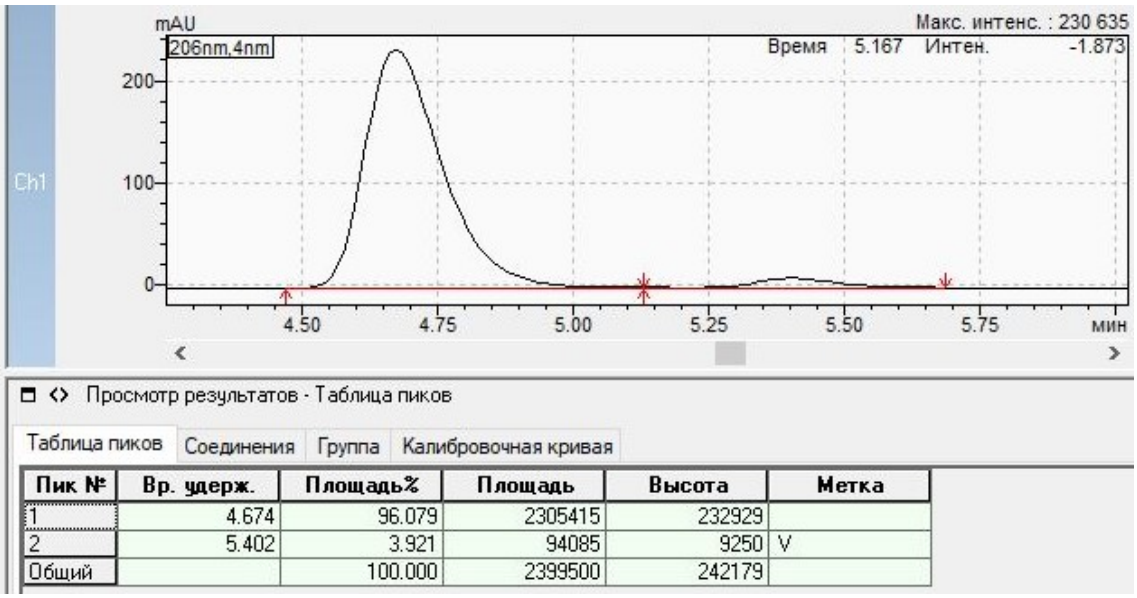
HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 90/10, t_R = 4.65 min for *1R,2S*-**6a**, t_R = 5.35 min for *1S,2R*-**6a**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

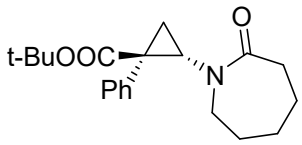
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.626	50.270	44993	5214	
2	5.295	49.730	44510	4670	
Общий		100.000	89503	9884	



Просмотр результатов - Таблица пиков

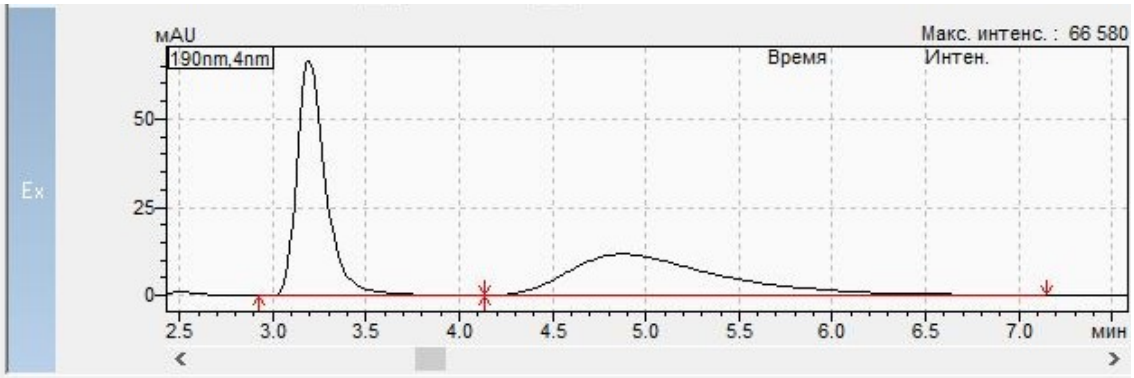
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.674	96.079	2305415	232929	
2	5.402	3.921	94085	9250	V
Общий		100.000	2399500	242179	



6b. **Yield** 39.4 mg, 80%, 94% *ee*; white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.18 (m, 5H, CH^{Ph}), 3.74 (dd, *J* = 8.7, 6.3 Hz, 1H, CH), 3.15 (dd, *J* = 15.4, 10.2 Hz, 1H, CH_2), 2.92 (dd, *J* = 15.2, 6.8 Hz, 1H, CH_2), 2.45 – 2.31 (m, 2H, CH_2), 1.93 (dd, *J* = 8.7, 6.1 Hz, 1H, CH), 1.71 (dd, appears as t, *J* = 6.2, 6.2 Hz, 1H, CH), 1.53 – 1.45 (m, 2H, CH_2), 1.40 (s, 9H, CH_3), 1.32 – 1.21 (m, 2H, CH_2), 1.04 – 0.91 (m, 1H, CH_2), 0.37 – 0.20 (m, 1H, CH_2). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.83, 171.78, 135.05, 131.82, 127.76, 127.30, 81.11, 48.87, 46.39, 37.97, 37.11, 29.70, 28.07, 27.39, 22.52, 18.26. **HRMS** (ESI-TOF, m/z) calcd for $C_{20}H_{27}NO_3$ $[M+Na]^+$: 352.1883; Found: 352.1875.

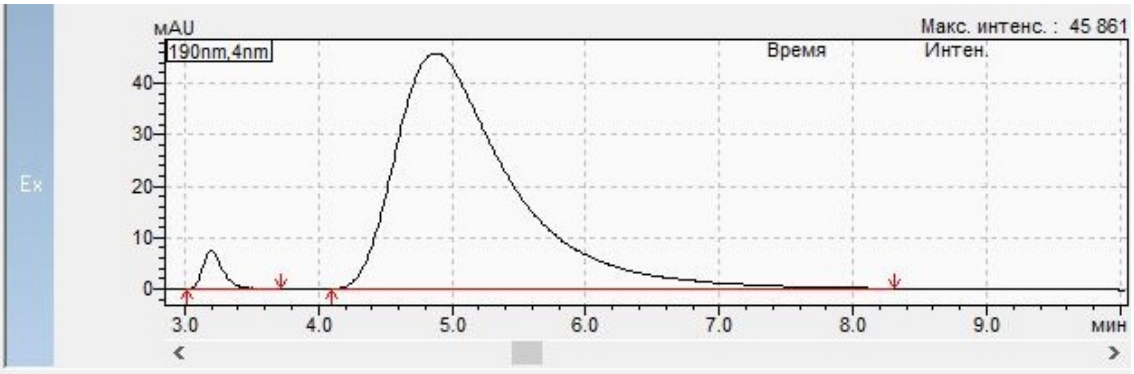
HPLC conditions: Chiralpak IJ-3 (4.6 x 150 mm), Heptane/i-PrOH = 90/10, t_R = 3.20 min for *1S,2R*-**6b**, t_R = 4.88 min for *1R,2S*-**6b**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

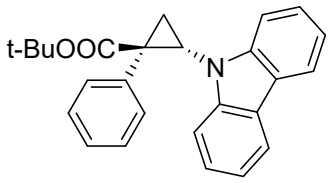
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	3.192	51.270	722511	66717	S
2	4.875	48.730	686727	11898	SV
Общий		100.000	1409239	78615	



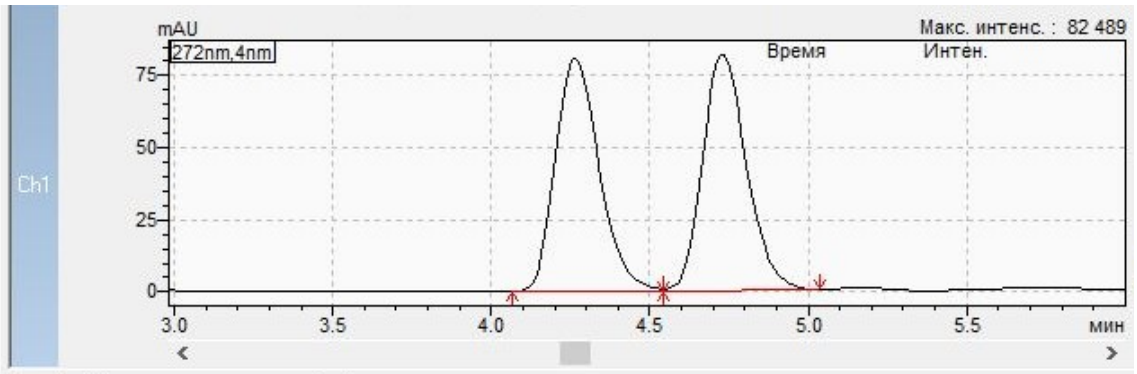
Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	3.198	2.883	81277	7603	
2	4.877	97.117	2737440	45890	SV
Общий		100.000	2818717	53494	



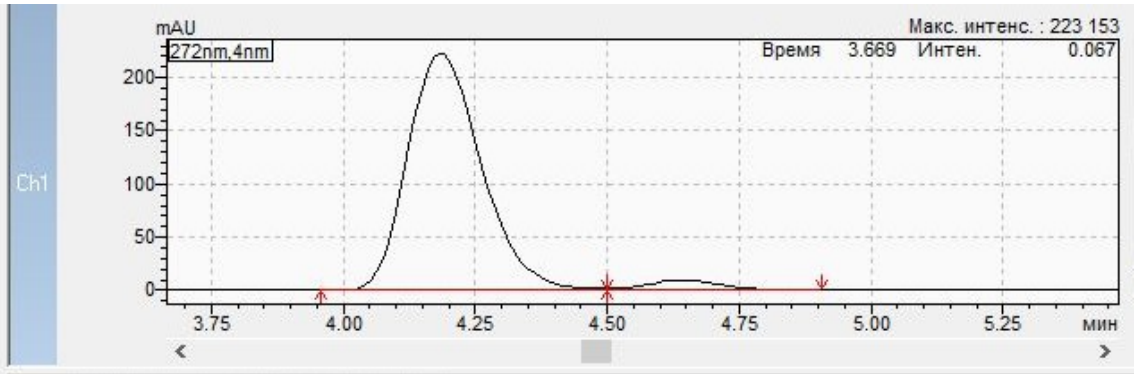
6c. **Yield** 45.8 mg, 80%, 92% *ee*; white viscous oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.7 Hz, 2H, CH^{Ar}), 7.57 (d, *J* = 8.2 Hz, 2H, CH^{Ar}), 7.40 (t, *J* = 7.7 Hz, 2H, CH^{Ar}), 7.17 (t, *J* = 7.5 Hz, 2H, CH^{Ar}), 7.11 (d, *J* = 7.5 Hz, 2H, CH^{Ph}), 6.91 – 6.82 (m, 3H, CH^{Ph}), 4.36 – 4.23 (m, 1H, CH), 2.82 (dd appears as t, *J* = 5.9 Hz, 1H, CH), 2.52 – 2.41 (m, 1H, CH), 1.56 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.60, 141.37, 132.99, 130.00, 127.34, 127.09, 125.60, 123.41, 120.18, 119.59, 110.27, 81.90, 40.61, 36.66, 28.23, 19.62. **HRMS** (ESI-TOF, m/z) calcd for $C_{26}H_{25}NO_2$ $[M+H]^+$: 384.1964; found: 384.1958. HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 99/1, t_R = 4.22 min for *1R,2S*-**6c**, t_R = 4.69 min for *1S,2R*-**6c**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

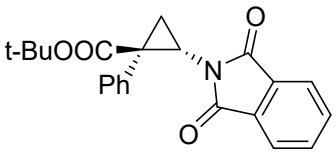
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.264	49.814	780258	81024	
2	4.730	50.186	786073	81876	V
Общий		100.000	1566331	162900	



Просмотр результатов - Таблица пиков

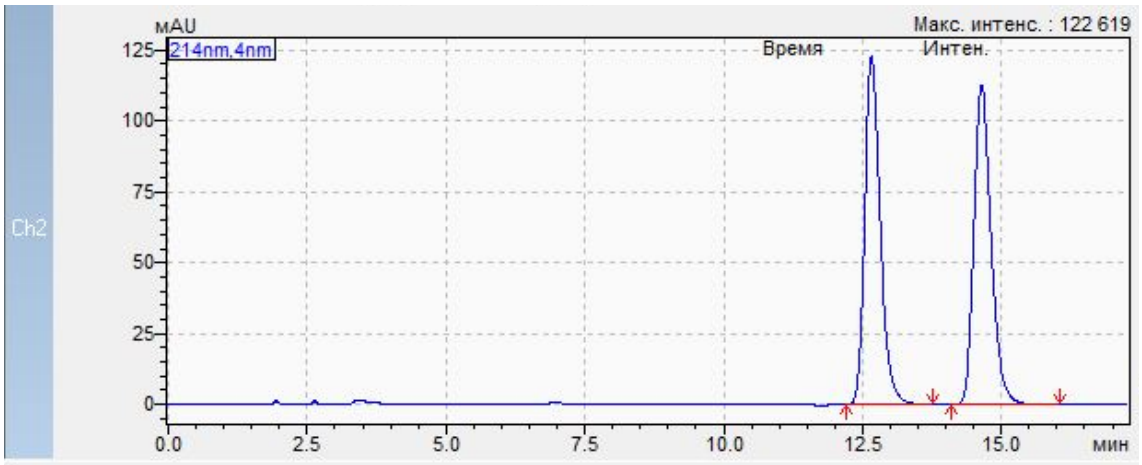
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.185	95.795	2169960	223057	
2	4.641	4.205	95248	9670	V
Общий		100.000	2265208	232727	



6d. Reaction was performed on a 0.1 mmol scale. **Yield** 18.2 mg, 50%; 48% *ee* (95% *ee* with the enantiomerically pure *S*,*S*-**Rh** as a catalyst); white solid. NMR spectra match data reported previously.[7] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.54 (m, 2H, CH^{Ar}), 7.63 – 7.56 (m, 2H, CH^{Ar}), 7.26 – 7.25 (m, 2H, CH^{Ph}), 7.15 – 7.11 (m, 2H, CH^{Ph}), 7.08 – 7.04 (m, 1H, CH^{Ph}), 3.84 – 3.67 (m, 1H, CH), 3.08 (dd, appears as t, *J* = 5.8, 5.8 Hz, 1H, CH), 2.17 – 2.03 (m, 1H, CH), 1.43 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.60, 168.49, 134.10, 133.55, 131.34, 131.22, 127.90, 127.49, 123.13, 81.68, 36.58, 35.38, 28.11, 16.21.

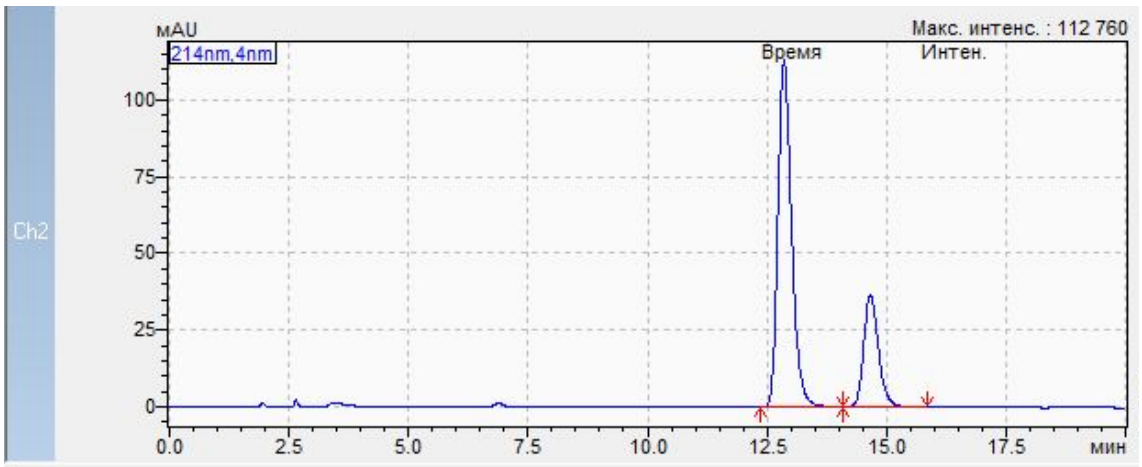
HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 99/1, t_R = 12.83 min for *1R,2S*-**6b**, t_R = 14.64 min for *1S,2R*-**6b**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

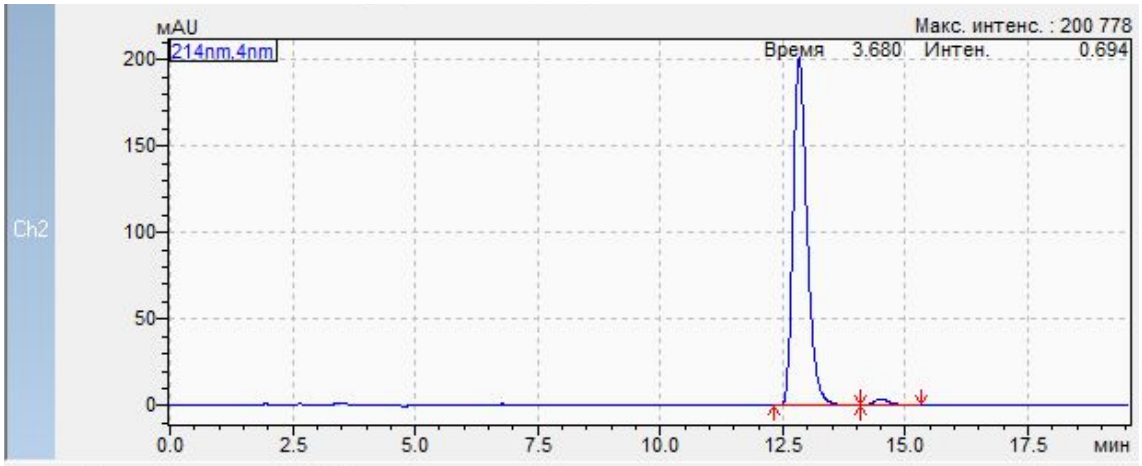
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	12.663	49.507	2388191	122720	
2	14.644	50.493	2435742	112827	
Общий		100.000	4823933	235546	



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

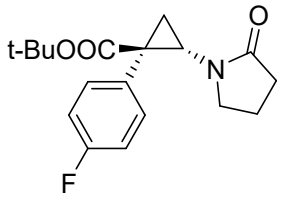
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	12.856	73.998	2254871	112906	
2	14.665	26.002	792314	36720	V
Общий		100.000	3047185	149626	



Просмотр результатов - Таблица пиков

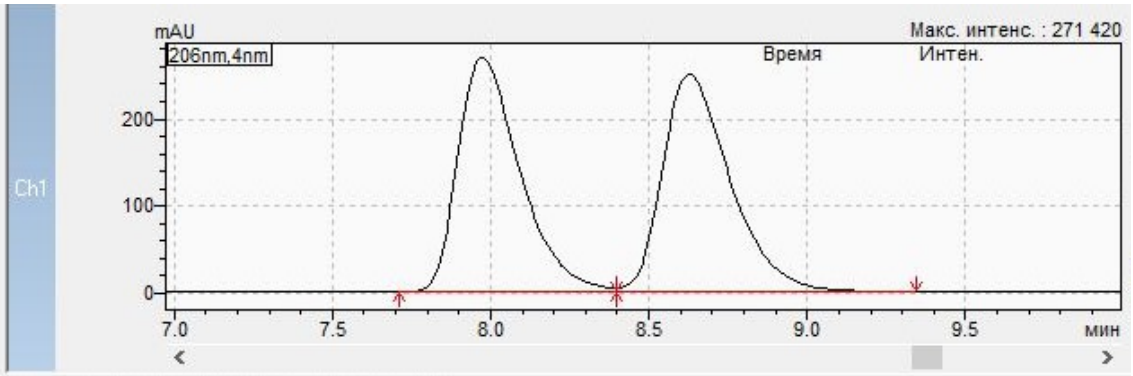
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	12.832	97.593	3997477	200907	
2	14.495	2.407	98611	4064	V
Общий		100.000	4096088	204971	



7a. **Yield** 38.8 mg, 81%, 90% *ee*; white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.20 (m, 2H, CH^{Ar}), 7.10 – 6.91 (m, 2H, CH^{Ar}), 3.77 (dd, *J* = 8.9, 5.9 Hz, 1H, CH), 3.07 – 3.02 (m, 1H, CH_2), 2.30 (ddd, *J* = 15.6, 9.4, 6.3 Hz, 2H, CH_2), 2.16 (ddd, *J* = 16.8, 9.4, 7.0 Hz, 1H, CH_2), 2.01 (dd, *J* = 8.9, 6.1 Hz, 1H, CH), 1.82 – 1.69 (m, 2H, CH_2 and CH), 1.58 – 1.48 (m, 1H, CH_2), 1.39 (s, 9H, CH_3). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -114.79. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.70, 171.25, 162.15 (d, *J* = 246.9 Hz), 133.01 (d, *J* = 8.2 Hz), 130.67 (d, *J* = 2.6 Hz), 115.06 (d, *J* = 21.2 Hz), 81.51, 46.87, 39.64, 33.72, 31.69, 28.05, 18.31, 18.06. **Anal. Calcd** for $C_{18}H_{23}NO_3$: C, 67.69; H, 6.94; N, 4.39; found: C, 67.69; H, 7.01; N, 4.51.

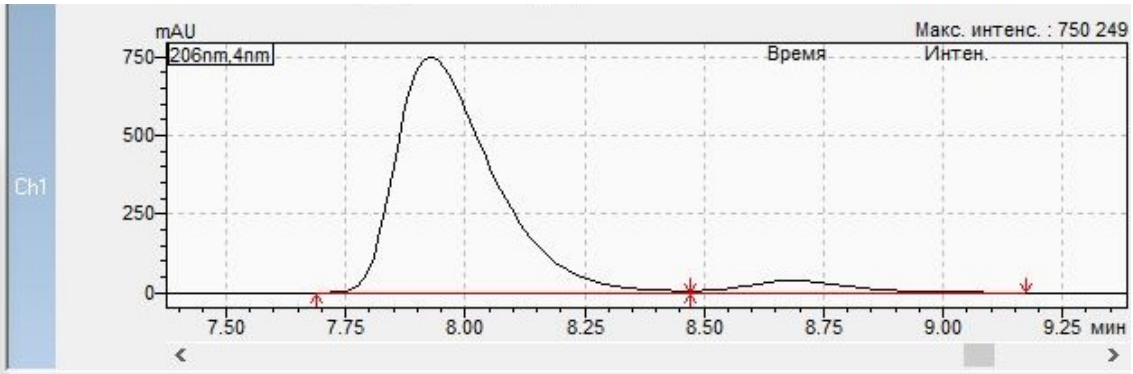
HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 95/5, t_R = 7.95 min for *1R,2S*-**7a**, t_R = 8.66 min for *1S,2R*-**7a**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

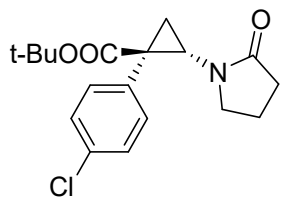
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	7.973	49.813	3697608	270737	
2	8.628	50.187	3725365	249835	V
Общий		100.000	7422973	520572	



Просмотр результатов - Таблица пиков

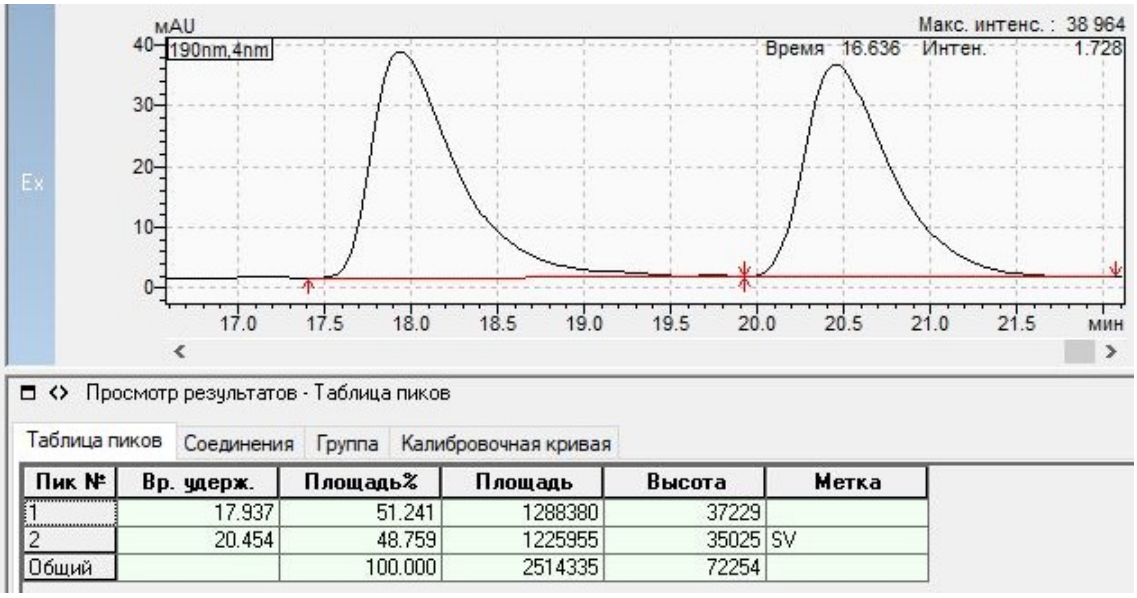
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	7.928	94.879	10469755	748704	
2	8.683	5.121	565152	37296	V
Общий		100.000	11034907	786000	



7b. **Yield** 43.9 mg, 87%, 96% *ee*; white solid; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.3 Hz, 2H, CH^{Ar}), 7.21 (d, *J* = 8.6 Hz, 2H, CH^{Ar}), 3.74 (dd, *J* = 8.9, 6.0 Hz, 1H, CH), 3.03 (td, *J* = 8.7, 5.3 Hz, 1H, CH_2), 2.33 – 2.23 (m, 2H, CH_2), 2.15 (ddd, *J* = 16.8, 9.4, 7.0 Hz, 1H, CH_2), 1.99 (dd, *J* = 8.9, 6.2 Hz, 1H, CH), 1.80 – 1.70 (m, 2H, CH and CH_2), 1.52 (ddt, *J* = 21.6, 13.9, 7.3 Hz, 1H, CH_2), 1.36 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.76, 170.99, 133.46, 133.40, 132.75, 128.36, 81.66, 46.92, 39.74, 33.90, 31.68, 28.07, 18.33, 17.97. **HRMS** (ESI-TOF, m/z) calcd for $C_{18}H_{22}ClNO_3$ $[M+H]^+$: 336.1366; found: 336.1363.

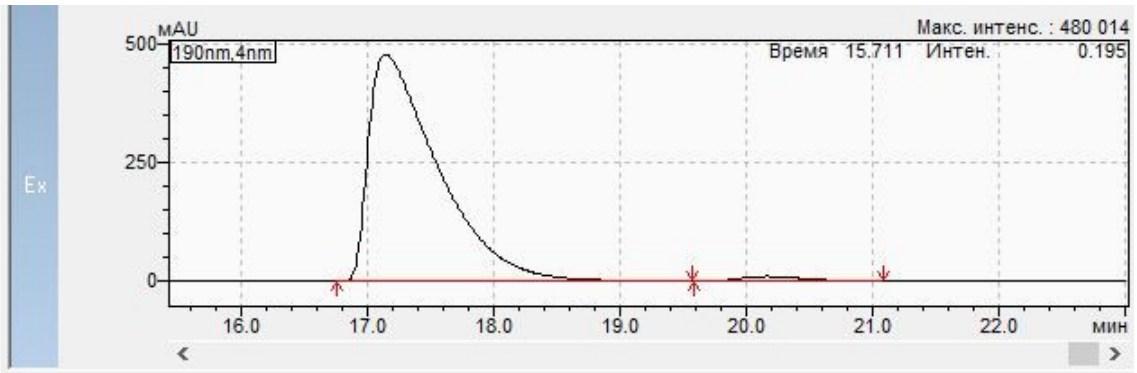
HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 98/2, t_R = 17.54 min for *1R,2S*-**7b**, t_R = 20.30 min for *1S,2R*-**7b**.



Просмотр результатов - Таблица пиков

Таблица пиков | Соединения | Группа | Калибровочная кривая

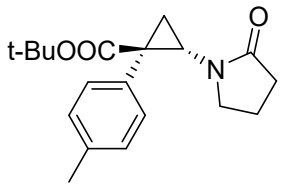
Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	17.937	51.241	1288380	37229	
2	20.454	48.759	1225955	35025	SV
Общий		100.000	2514335	72254	



Просмотр результатов - Таблица пиков

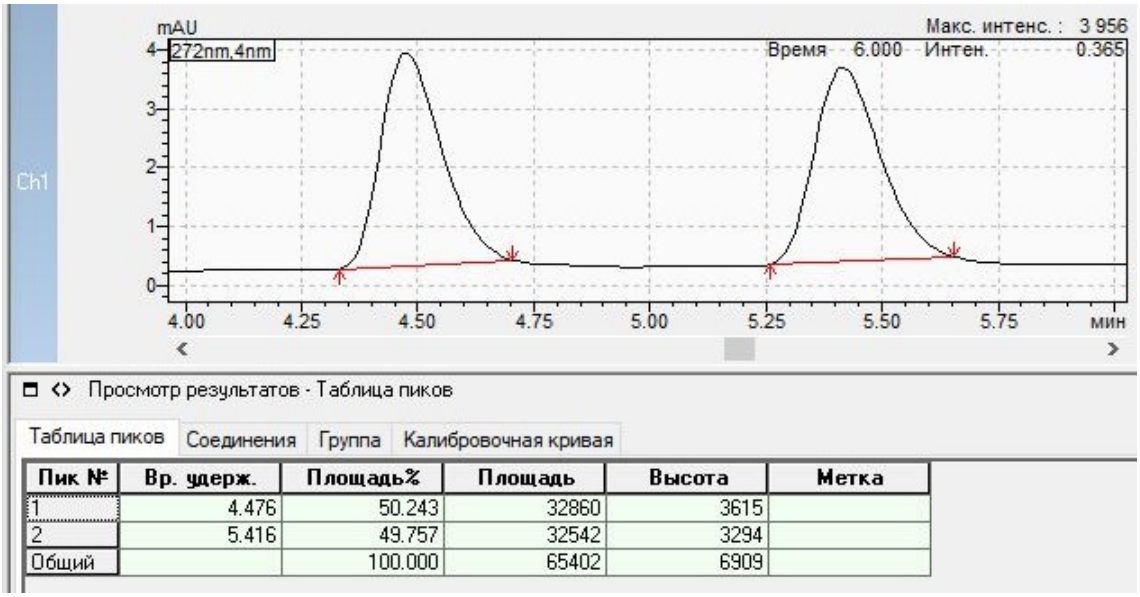
Таблица пиков | Соединения | Группа | Калибровочная кривая

Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	17.142	98.092	18304673	479874	M
2	20.154	1.908	356013	10281	
Общий		100.000	18660686	490155	

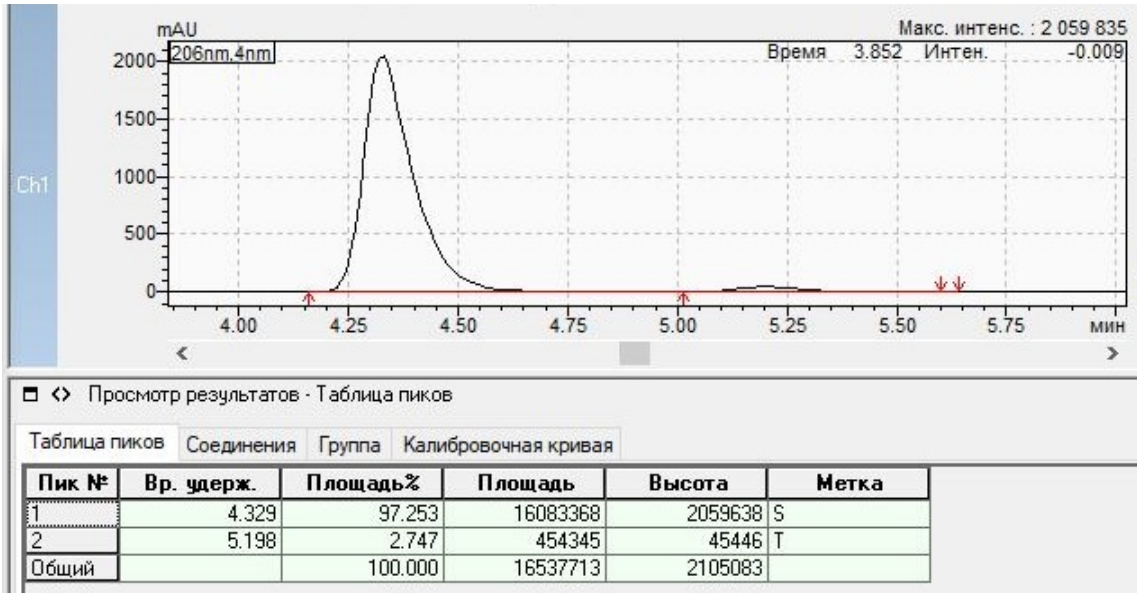


7c. **Yield** 34.7 mg, 73%, 95% *ee*, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 7.8 Hz, 2H, CH^{tol}), 7.07 (d, *J* = 7.7 Hz, 2H, CH^{tol}), 3.75 (dd, *J* = 9.0, 5.9 Hz, 1H, CH), 3.01 – 2.95 (m, 1H CH_2), 2.31 (s, 3H, CH_3^{tol}), 2.27 – 2.22 (m, 2H, CH_2), 2.18 – 2.10 (m, 1H, CH_2), 1.95 (dd, *J* = 9.0, 6.0 Hz, 1H, CH), 1.75 – 1.71 (m, 1H, CH), 1.69 – 1.63 (m, 1H, CH_2), 1.54 – 1.43 (m, 1H, CH_2), 1.37 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.64, 171.64, 137.02, 131.60, 131.11, 128.83, 81.17, 46.77, 39.51, 33.92, 31.75, 28.06, 21.31, 18.30, 17.76. **HRMS** (ESI-TOF, m/z) calcd for $C_{19}H_{25}NO_3$ $[M+H]^+$: 316.1907; found: 316.1906.

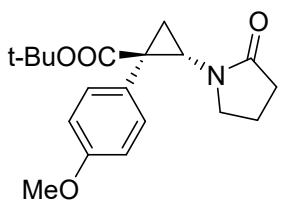
HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 90/10, t_R = 4.40 min for *1R,2S*-**7c**, t_R = 5.31 min for *1S,2R*-**7c**.



Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.476	50.243	32860	3615	
2	5.416	49.757	32542	3294	
Общий		100.000	65402	6909	

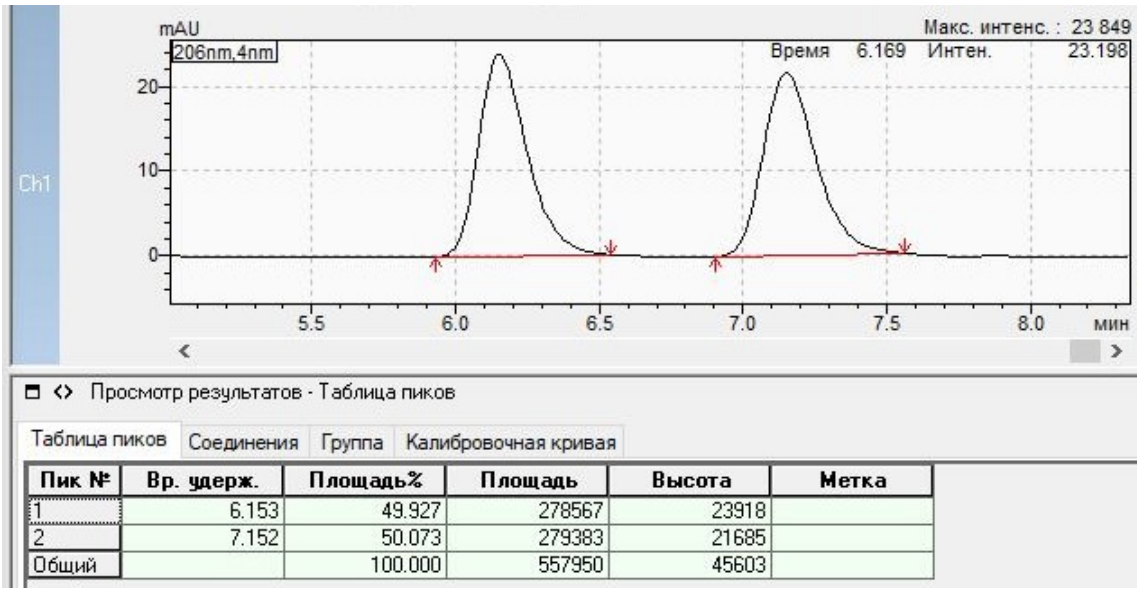


Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	4.329	97.253	16083368	2059638	S
2	5.198	2.747	454345	45446	T
Общий		100.000	16537713	2105083	

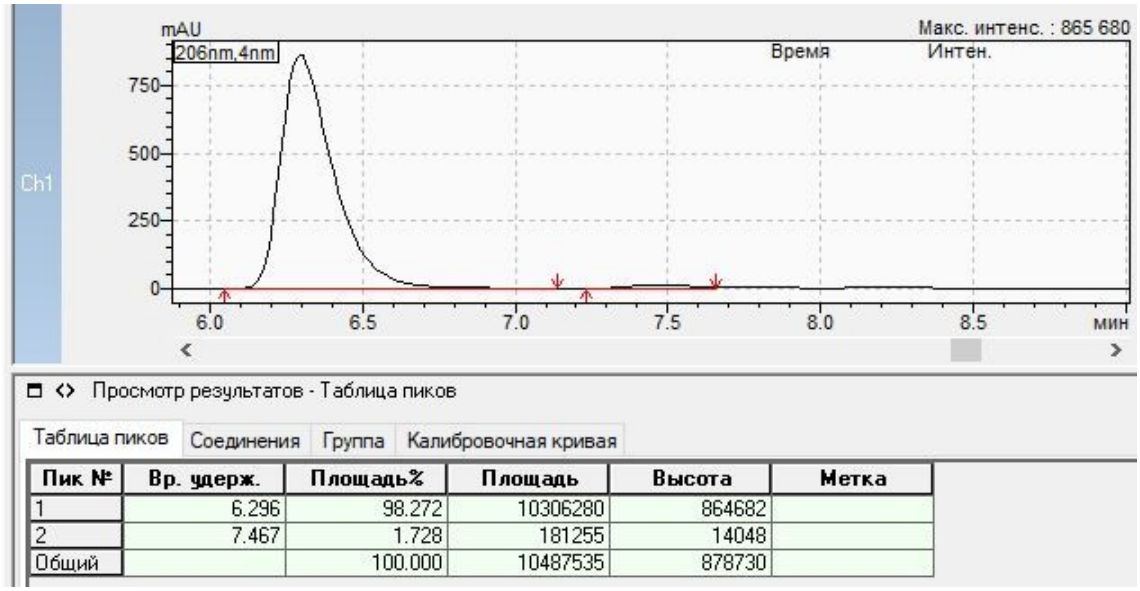


7d. **Yield** 22.4 mg, 68%, 97% *ee*, white solid; reaction was performed on a 0.1 mmol scale. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.3 Hz, 2H, CH^{Ar}), 6.81 (d, *J* = 8.4 Hz, 2H, CH^{Ar}), 3.78 (s, 3H, OCH_3), 3.74 (dd, *J* = 8.7, 6.0 Hz, 1H, CH), 3.02 – 2.97 (m, 1H, CH_2), 2.31 – 2.21 (m, 2H, CH_2), 2.14 (ddd, *J* = 16.8, 9.4, 7.1 Hz, 1H, CH_2), 1.95 (dd, *J* = 8.9, 6.0 Hz, 1H, CH), 1.74 – 1.68 (m, 1H, CH and 1H, CH_2), 1.54 – 1.44 (m, 1H, CH_2), 1.37 (s, 9H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.68, 171.75, 158.83, 132.39, 126.82, 113.52, 81.21, 55.30, 46.85, 39.59, 33.60, 31.77, 28.09, 18.35, 17.94. **HRMS** (ESI-TOF, m/z) calcd for $C_{19}H_{25}NO_4$ $[M+Na]^+$: 354.1676; Found: 354.1672.

HPLC conditions: Chiralpak IA-3 (4.6 x 150 mm), Heptane/i-PrOH = 90/10, t_R = 6.22 min for *1R,2S*-**7d**, t_R = 7.31 min for *1S,2R*-**7d**.

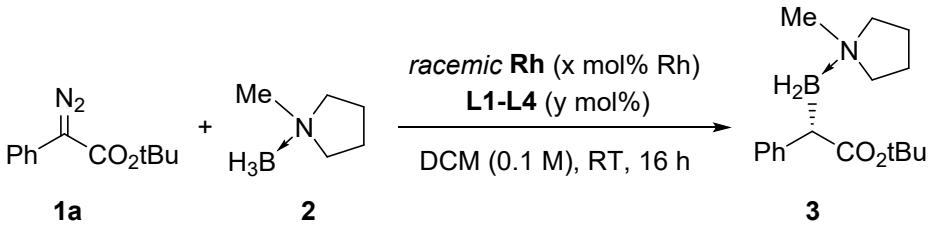


Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	6.153	49.927	278567	23918	
2	7.152	50.073	279383	21685	
Общий		100.000	557950	45603	



Пик №	Вр. удерж.	Площадь%	Площадь	Высота	Метка
1	6.296	98.272	10306280	864682	
2	7.467	1.728	181255	14048	
Общий		100.000	10487535	878730	

BH-insertion reactions



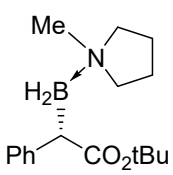
BH-insertion reaction in the presence of L1

In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar racemic catalyst **Rh** and a portion of dried 3Å molecular sieves were placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1ml of DCM and indicated quantity of 0.1085M stock solution of **L1** in THF were added to the reaction vessel. The resulting mixture was stirred at ambient temperature for 0.5 hour, covered by aluminum foil. After that, diazo compound **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and amine-borane adduct **2** (14.9 mg, 0.15 mmol, 1.5 eq) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After full consumption of the starting diazo compound (monitored by TLC) the reaction mixture was opened to air, molecular sieves were removed by filtration through a short celite layer in DCM. Subsequent purification on silica gel column (hexane/EA 10:1 → hexane/EA 1:1) afforded the desired B-H insertion product **3**. See Table **S2** for details on the corresponding catalyst and chiral additive loadings.

Table S2

entry	temperature	catalyst loading	**L1** loading	yield, %	ee, %
1[a]	r.t.	5 mol % Rh	4 mol %	90	94
2[a]	r.t.	5 mol % Rh	3 mol %	87	90
3	r.t.	5 mol % Rh	3 mol %	93	87
4	r.t.	2.5 mol % Rh	2 mol %	79	88
5[b]	r.t.	5 mol % Rh	4 mol %	97	96
6[b]	r.t.	5 mol % Rh	3 mol %	94	96
7[c]	r.t.	5 mol % Rh	3 mol %	88	87
8[b,c]	r.t.	5 mol % Rh	3 mol %	98	87

[a] Racemic catalyst was stirred overnight with the additive **L1** before adding the substrates; [b] 0.010 ml of dry NEt_3 was added to the reaction mixture simultaneously with the solvent; [c] DCE was used instead of DCM



3. NMR spectra are consistent with the previously reported data.[3]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.6 Hz, 2H, CH^{Ph}), 7.22 (t, *J* = 7.6 Hz, 2H, CH^{Ph}), 7.08 (t, *J* = 7.3 Hz, 1H, CH^{Ph}), 3.22 (dt, *J* = 11.7, 8.0 Hz, 1H, CH_2), 3.11 (t, appears as br.s, 1H, CH), 2.96 (dt, *J* = 12.0, 7.9 Hz, 1H,

CH_2), 2.82 (dt, J = 11.9, 6.5 Hz, 1H, CH_2), 2.60 – 2.52 (m, 1H, CH_2), 2.52 (s, 3H, CH_3), 2.35 – 1.70 (m, 6H, CH_2 and BH_2), 1.42 (s, 9H, CH_3); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.98, 144.82, 129.33, 127.72, 124.57, 78.63, 61.73, 61.69, 47.95, 28.43, 22.51, 22.36. **^{11}B{^{1}H} NMR** (128 MHz, Chloroform-*d*) δ -1.74.

BH-insertion reaction in the presence of L2

In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar racemic catalyst **Rh** and a portion of dried 3Å molecular sieves were placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1.0 ml of DCM and **L2** (freshly generated sodium salt, 0.0500M stock solution in THF) were added to the reaction vessel. The resulting mixture was stirred at ambient temperature for 30 minutes. After that, diazo compound **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and amine-borane adduct **2** (14.9 mg, 0.15 mmol, 1.5 eq) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After full consumption of the starting diazo compound (monitored by TLC) the minimum amount of SiO_2 was added to this mixture and the solvent was removed in vacuo. Subsequent purification on silica gel column afforded the desired B-H insertion product **3**. See Table **S3** for details on the corresponding catalyst and chiral additive loadings.

Generation of the sodium salt of L2: in a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar NaH (60% dispersion in mineral oil, 2.4 mg, 0.06 mmol, 1.5 eq.) was placed. The flask was subjected to a vacuum and refilled with argon three times. Then 0.800 ml of THF was added via syringe. Upon strong stirring (R)-2-(phenyl((1-phenylethyl)imino)methyl)phenol (**L2H**)[8] (12.2 mg, 0.04 mmol, 1.0 eq) was added to the reaction mixture. The resulting suspension was stirred for 30 minutes until the gas evolution was over, then the magnetic stirrer was turned off to allow the solids to settle for additional 30 minutes. The obtained solution was used immediately on the next step without any purification.

Table S3

entry	temperature	catalyst loading	**L2** loading	yield, %	ee, %
1	r.t.	5 mol % Rh	4 mol %	93	12
2	r.t.	5 mol % Rh	3 mol %	96	8

BH-insertion reaction in the presence of L3.

In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar racemic catalyst **Rh** and a portion of dried 3Å molecular sieves were placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1.0 ml of DCM and **L3** (freshly generated sodium salt, 0.0500M stock solution in THF) were added to the reaction vessel. The resulting mixture was stirred at ambient temperature for 30 minutes. After that, diazo compound **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and amine-borane adduct **2** (14.9 mg, 0.15 mmol, 1.5 eq) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After full consumption of the starting diazo compound (monitored by TLC) the minimum amount of SiO_2 was added to this mixture and the solvent was removed in vacuo. Subsequent purification on silica gel column afforded the desired B-H insertion product **3**. See Table **S4** for details on the corresponding catalyst and chiral additive loadings.

Generation of the sodium salt of L3[9]: in a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar NaH (60% dispersion in mineral oil, 2.4 mg, 0.06 mmol, 1.5 eq.) was placed. The flask was subjected to a vacuum and refilled with argon three times. Then 0.800 ml of THF was added via syringe. Upon strong stirring (S)-N-(2-hydroxybenzylidene)-2-methylpropane-2-sulfinamide (**L3H**) (9.0 mg, 0.04 mmol, 1.0 eq) was added to the reaction mixture. The resulting suspension was stirred for 30 minutes until the gas evolution was over, then the magnetic stirrer was turned off to allow the solids to settle for additional 30 minutes. The obtained solution was used immediately on the next step without any purification.

Table S4

entry	temperature	catalyst loading	**L3** loading	yield, %	ee, %
1[a]	r.t.	5 mol % Rh	4 mol %	80	- 8
2	r.t.	5 mol % Rh	4 mol %	78	- 60
3	r.t.	5 mol % Rh	3 mol %	86	- 62

[a] (S)-N-(2-hydroxybenzylidene)-2-methylpropane-2-sulfinamide (**L3H**) (0.9 mg, 0.004 mmol) was used as a chiral additive in the presence of K_3PO_4 (0.8 mg, 0.004 mmol); **L3H** and K_3PO_4 were stirred together in the reaction vessel for 15 min prior to addition of the racemic catalyst.

BH-insertion reaction in the presence of L4.

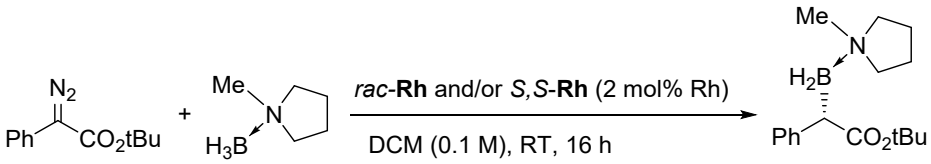
In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar racemic catalyst **Rh** and a portion of dried 3Å molecular sieves were placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1.0 ml of DCM and **L4** (freshly generated sodium salt, 0.0500M stock solution in THF, see details below) were added to the reaction vessel. The resulting mixture was stirred at ambient temperature for 30 minutes. After that, diazo compound **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and amine-borane adduct **2** (14.9 mg, 0.15 mmol, 1.5 eq) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After full consumption of the starting diazo compound (monitored by TLC) the minimum amount of SiO_2 was added to this mixture and the solvent was removed in vacuo. Subsequent purification on silica gel column afforded the desired B-H insertion product **3**. See Table **S5** for details on the corresponding catalyst and chiral additive loadings.

Generation of the sodium salt of L4: in a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar NaH (60% dispersion in mineral oil, 2.4 mg, 0.06 mmol, 1.5 eq.) was placed. The flask was subjected to a vacuum and refilled with argon three times. Then 0.800 ml of THF was added via syringe. Upon strong stirring S-N-(tert-butylsulfinyl)benzamide (**L4H**) (9.0 mg, 0.04 mmol, 1.0 eq) was added to the reaction mixture. The resulting suspension was stirred for 30 minutes until the gas evolution was over, then the magnetic stirrer was turned off to allow the solids to settle for additional 30 minutes. The obtained solution was used immediately on the next step without any purification.

Table S5

entry	temperature	catalyst loading	**L4** loading	yield, %	ee, %
1	r.t.	5 mol % Rh	4 mol %	88	-95
2	r.t.	5 mol % Rh	3 mol %	98	-90

Nonlinear effect in B-H insertion reaction studies

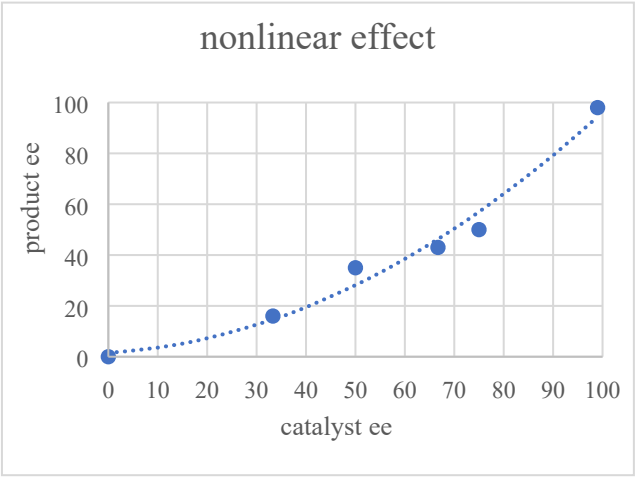


1a **2** **3**

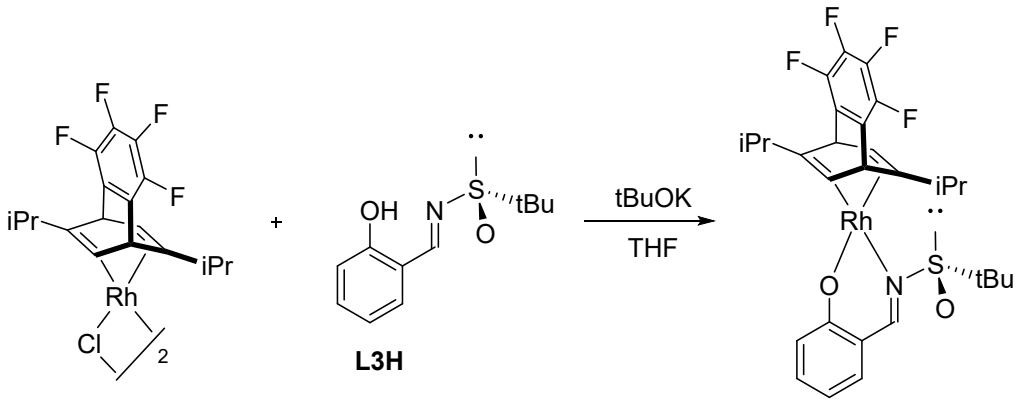
In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar the racemic catalyst **Rh** and the enantiomerically pure catalyst *S,S*-**Rh** (ee > 99%) were placed (total amount equals to 2 mol% Rh) and a portion of dried 3Å molecular sieves was added. The flask was subjected to a vacuum and refilled with argon five times. After that dry DCM was added to the reaction vessel, amount of the solvent adjusted to 0.1M concentration of the starting diazo compound **1a**. Then diazo compound **1a** (1.0 eq.) and amine-borane adduct **2** (1.5 eq) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After full consumption of the starting diazo compound (monitored by TLC) the reaction mixture was opened to air, molecular sieves were removed by filtration through a short celite layer in DCM. Subsequent purification on silica gel column (hexane/EA 10:1 → hexane/EA 1:1) afforded the desired insertion product **3**. Enantiomeric excesses data of the obtained products are provided in the table **S6**.

Table S6

catalyst ee, %	product ee, %
0	0
33	16
50	35
67	43
75	50
99	98



Synthesis of the complex *S,S*-Rh-L3

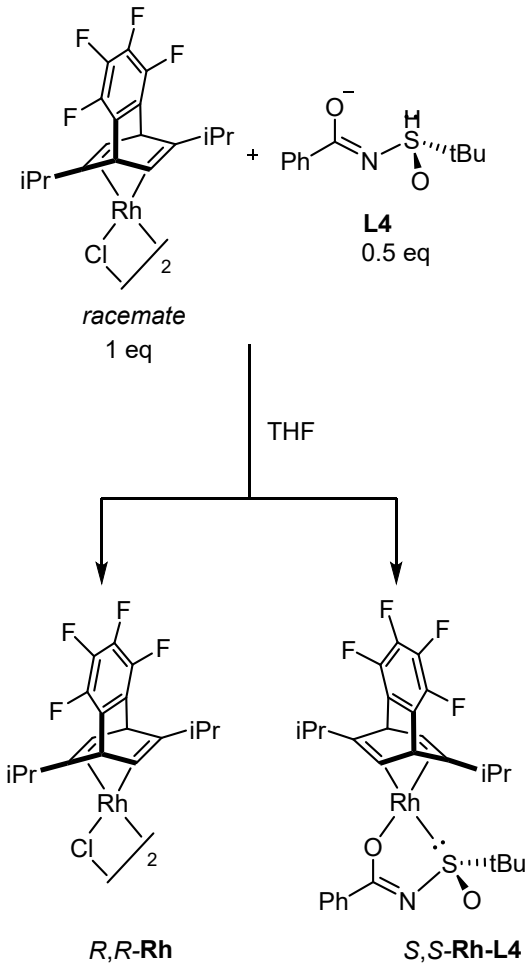


racemate *S,S*-**Rh-L3**

In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar racemic complex **Rh** (44.9 mg, 0.05 mmol, 0.05 eq), tBuOK (16.8 mg, 0.15 mmol, 1.5 eq), **L3H** (24.8 mg, 0.11 mmol, 1.1 eq) were placed. The flask was subjected to a vacuum and refilled with argon three times. Then THF (1.0 ml) was added via syringe and the reaction mixture was strirred overnight at r.t. After that the solvent was removed in vacuo. Subsequent purification on silica gel column (gradient elution with n-Hexane/EtOAc mixture with 1% NEt_3, from 20:1 to 10:1) afforded the desired complex *S,S*-**Rh-L3** as an orange solid. The product was additionally purified by recrystallization (slow gas diffusion of pentane into concentrated DCM solution of the product).

Yield 18.6 mg, 0.03 mmol, 30% (from max. 50% for 1 diastereomer). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H, CH=N), 7.45 – 7.31 (m, 2H, CH^{Ar}), 6.84 (d, *J* = 8.6 Hz, 1H, CH^{Ar}), 6.62 (t, *J* = 7.4 Hz, 1H, CH^{Ar}), 5.22 (t, *J* = 6.0 Hz, 2H, CH), 3.63 (d, *J* = 6.0 Hz, 1H, CH), 3.34 (d, *J* = 5.4 Hz, 1H, CH), 2.18 (hept, *J* = 6.8 Hz, 1H, CH), 1.81 (hept, *J* = 6.7 Hz, 1H, CH), 1.44 (s, 9H, CH_3), 1.41 (d, *J* = 6.8 Hz, 3H, CH_3), 1.35 (d, *J* = 6.8 Hz, 3H, CH_3), 0.91 (d, *J* = 6.9 Hz, 3H, CH_3), 0.69 (d, *J* = 6.8 Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.59, 136.87, 136.37, 122.70, 118.31, 115.41, 61.34, 54.31 (d, *J* = 9.2 Hz), 41.97 (d, *J* = 10.3 Hz), 41.36, 38.60, 38.56, 32.32, 31.50, 23.30, 20.94, 20.71, 20.58. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -147.09 (t, *J* = 18.5 Hz, 1F), -147.77 (t, *J* = 20.5 Hz, 1F), -159.55 – -159.74 (m, 2F). **Anal**. **Calcd**. for $C_{29}H_{32}F_4NO_2RhS$: C, 54.63; H, 5.06; N, 2.20; found C, 54,52; H, 5.21; N, 2.19.

Evaluation of diastereomeric products ratio in reaction of racemic complex Rh with L4



The racemic complex **Rh** (5.0 mg, 0.0056 mmol, 1 eq. of Rh) was placed in a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar. The flask was subjected to a vacuum and refilled with argon three times. Then 1 ml of THF was added and the obtained solution was stirred for 10 minutes. After that, **L4** (freshly generated sodium salt solution, 0.028M, 0.200 ml, 0.0056 mmol, 0.5 eq.) was added to the reaction mixture upon strong stirring. The flask was capped with a stopper, and the obtained solution was allowed to stir overnight. Then it was exposed to air and the solvent evaporated on a rotavap. After that the residue was redissolved in $CDCl_3$ (0.6 ml), transferred to an NMR tube and analyzed via ^{1}H, ^{19}F NMR. Only one diastereomer of the product was detected in the ^{1}H, ^{19}F NMR spectra of the reaction mixture, the ratio *S,S*-**Rh-L4** : *R,R*-**Rh** = 1.00 : 1.07 (see ^{1}H NMR spectrum for characteristic signals of S,S-product at 5.61 (d, J = 5.9 Hz, 1H, CH), 5.53 (d, J = 5.6 Hz, 1H, CH), 4.77 (d, J = 5.9 Hz, 1H, CH); according to ^{19}F NMR spectrum, the ratio *S,S*-**Rh-L4** : *R,R*-**Rh** = 1.00 : 0.99

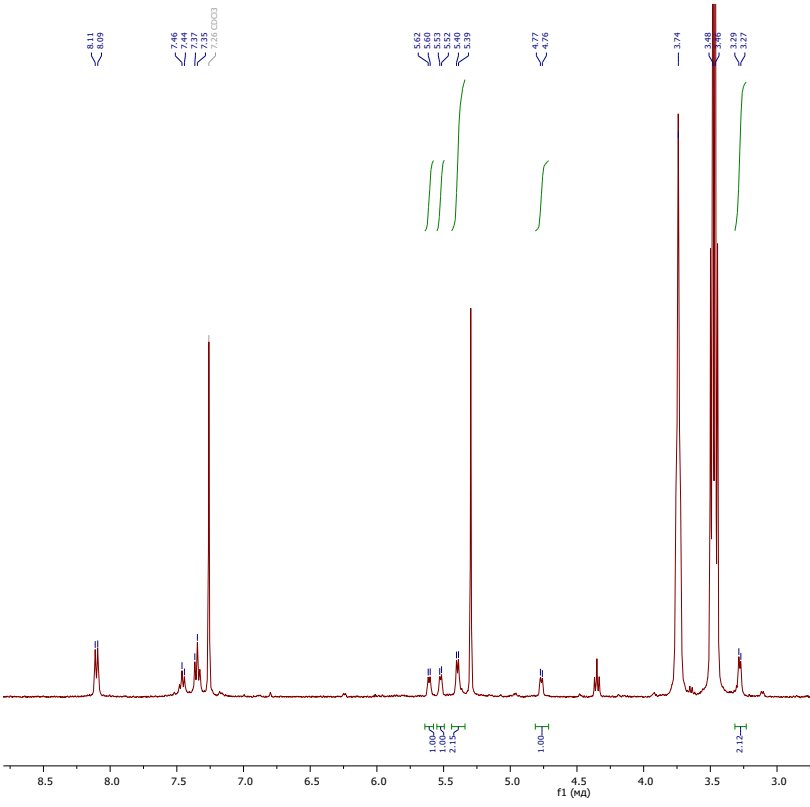


Figure S1. Representative ^{1}H NMR spectrum of the reaction mixture after treatment with **L4** overnight.

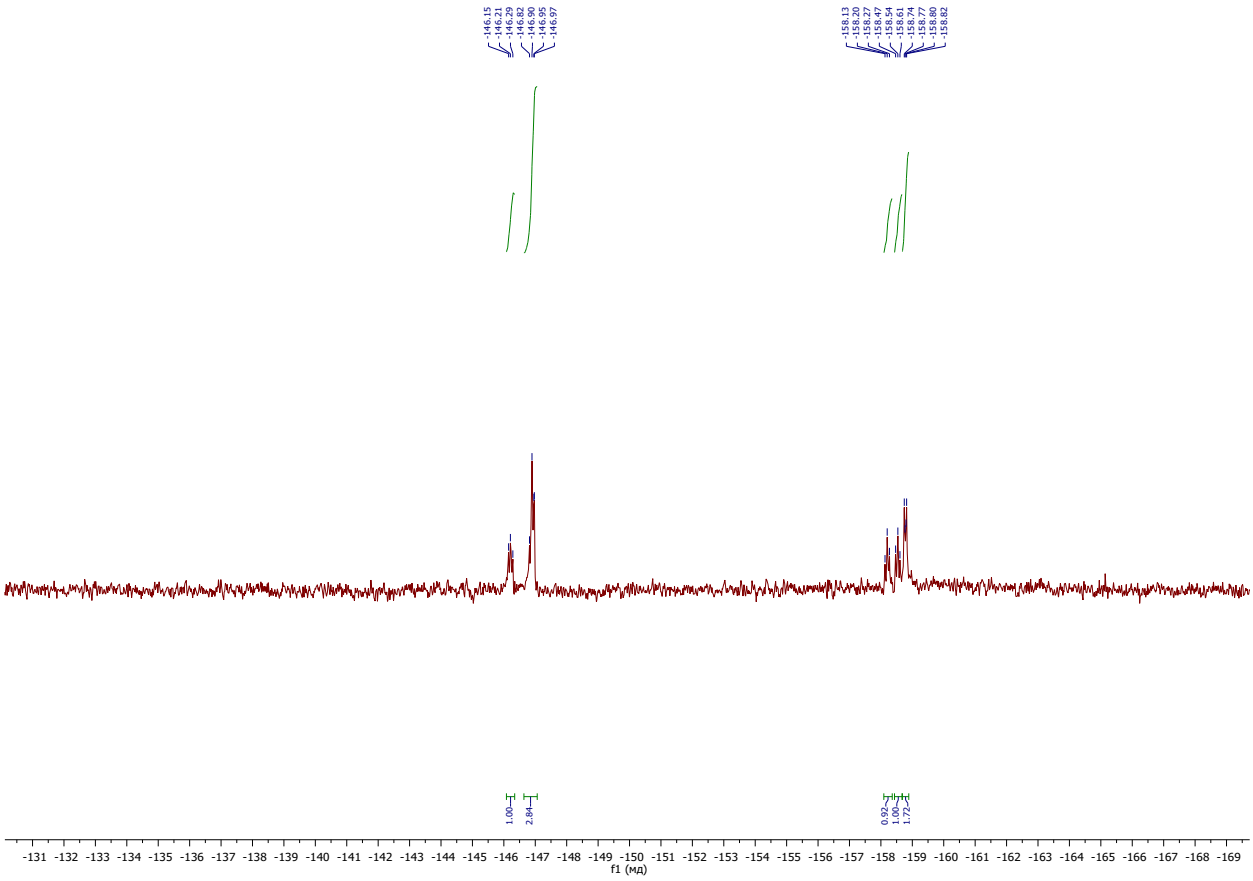
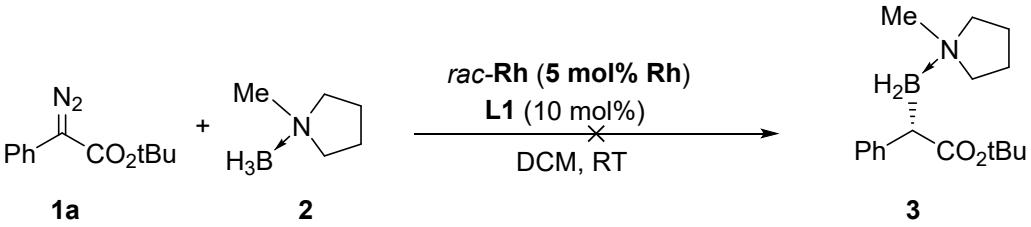


Figure S2. Representative ^{19}F NMR spectrum of the reaction mixture after treatment with **L4** overnight.

B-H insertion reaction in the presence of an excess of L1



1a **2** **3**

In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar racemic catalyst **Rh** (2.2 mg, 0.0025 mmol, 0.025 eq) was placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1ml of DCM and **L1** (0.092 ml of 1085M sodium salt stock solution in THF, 0.010 mmol, 0.10 eq) were added to the reaction vessel. The resulting mixture was stirred at ambient temperature for 0.5 hour. After that, diazo compound **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and amine-borane adduct **2** (14.9 mg, 0.15 mmol, 1.5 eq) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature, covered with aluminum foil. After 5 days the reaction mixture was opened to air, the solvent was evaporated and the residue was analyzed by ^{1}H NMR (400 MHz, Chloroform-*d*, T_1 = 15 s) in the presence of 1,3,5-tribromobenzene (10.5 mg, 0.033 mmol) as internal standard. Product **3** signals were not present in the resulting spectrum.

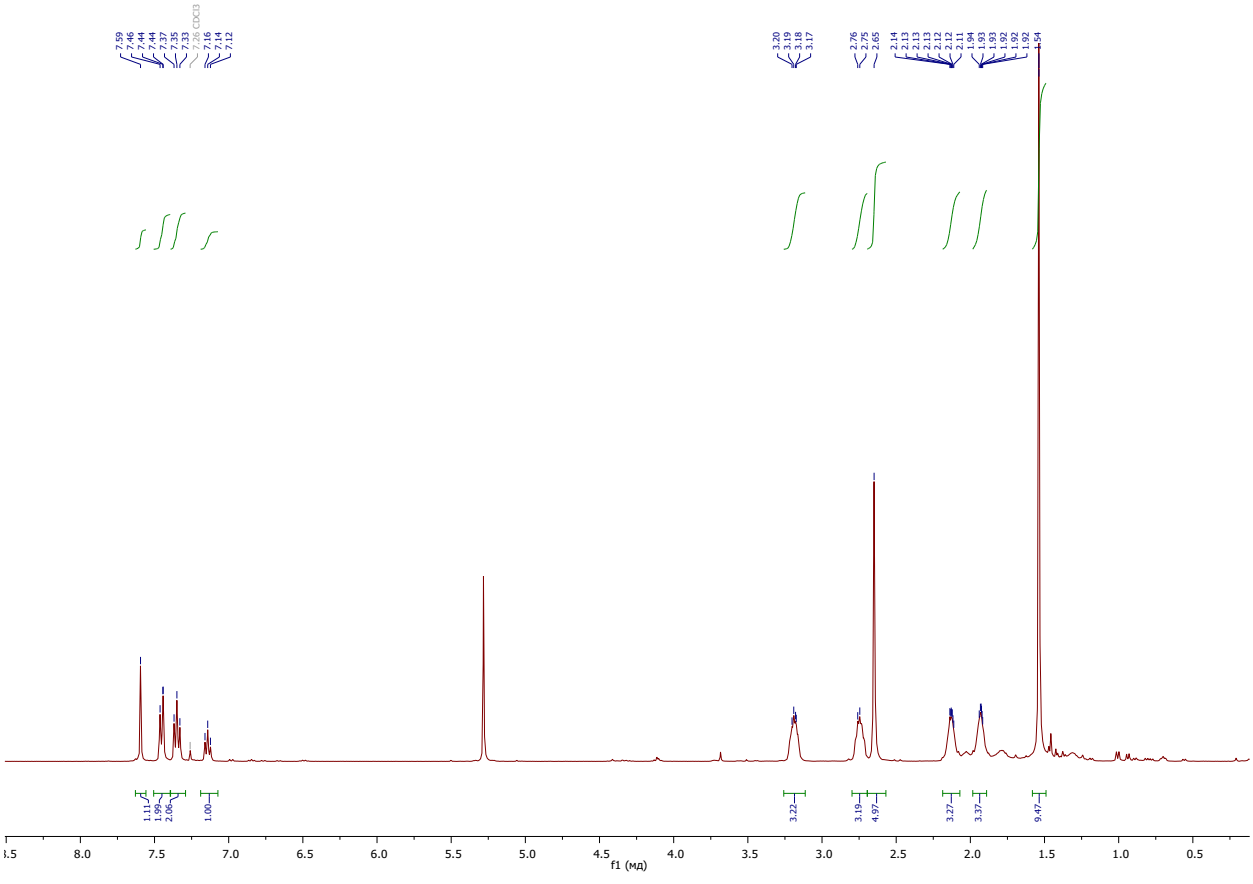
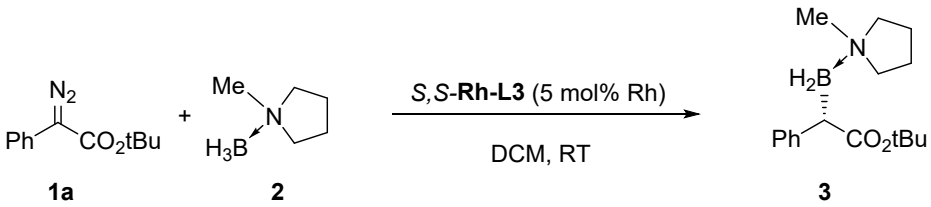


Figure S3. Representative ^{1}H NMR spectrum of the reaction mixture. The product and starting compounds concentrations are determined relative to 1,3,5-tribromobenzene ^{1}H protons (7.59 ppm).

B-H insertion reaction in the presence of complex *S,S*-Rh-L3



In a 10 ml Schlenk flask equipped with PTFE coated magnetic stir bar complex *S,S*-**Rh-L3** (3.2 mg, 0.005 mmol, 0.05 eq) was placed. The flask was subjected to a vacuum and refilled with argon five times. After that 1ml of DCM, diazo compound **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and amine-borane adduct **2** (14.9 mg, 0.15 mmol, 1.5 eq) were added to the reaction mixture. The resulting mixture was stirred at ambient temperature, covered with aluminum foil. After 24 hour the reaction mixture was opened to air, the solvent was evaporated and the residue was analyzed by ^{1}H NMR (400 MHz, Chloroform-*d*, T_1 = 15 s) in the presence of 1,3,5-tribromobenzene (10.5 mg, 0.033 mmol) as internal standard. Conversion of the starting diazo compound **1a** to the product **3** was ~65%.

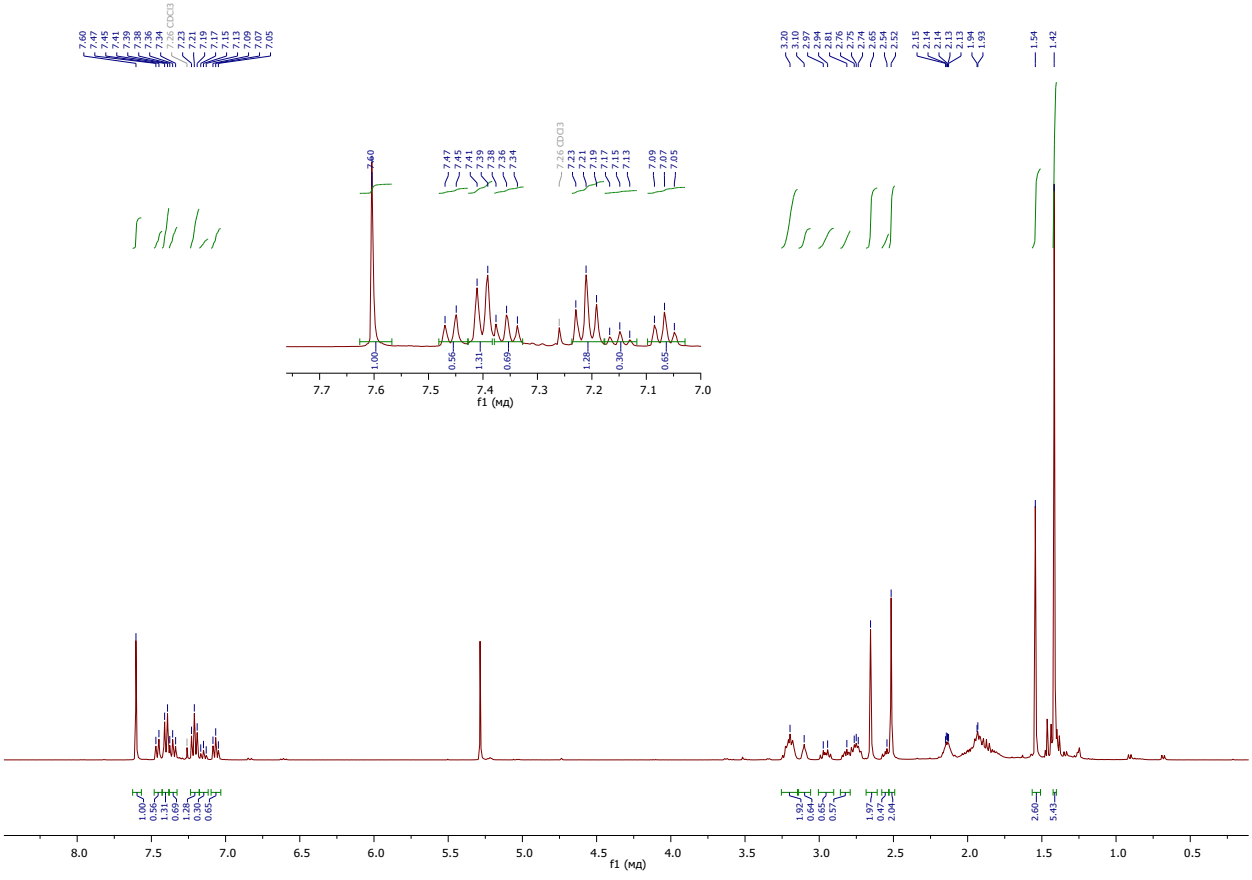


Figure S4. Representative ^{1}H NMR spectrum of the reaction mixture. The product and starting compounds concentrations are determined relative to 1,3,5-tribromobenzene ^{1}H protons (7.60 ppm).

Crystallographic details

X-ray diffraction data for *S,S*-**Rh-L3** were collected at 100 K with a Bruker Quest D8 CMOS diffractometer, using graphite monochromated Mo-Kα radiation (lλ = 0.71073 Å, ω-scans). X-ray diffraction data for **6a** were collected at 120 K at the protein station of urchatov Centre for Synchrotron radiation (λ = 0.745 Å). Structures were solved using Intrinsic Phasing with the ShelXT[10] structure solution program in Olex2[11] and then refined with the XL[12] refinement package using Least-Squares minimization against F^2 in the anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Table S1. CCDC 2159993 and 2159992 contain the supplementary crystallographic data for *S,S*-**Rh-L3** and **6a**, respectively.

Table S7. Crystal data and structure refinement parameters for *S,S*-**Rh-L3** and **6a**.

	S,S-**Rh-L3**	**6a**
Empirical formula	$C_{29}H_{32}F_4NO_2RhS$	$C_{18}H_{23}NO_3$
Formula weight	637.52	301.37
T, K	100	120
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Z	4	2
a, Å	10.8702(10)	9.1340(18)
b, Å	14.0428(12)	6.2150(12)
c, Å	18.3564(16)	14.976(3)
α, °	90	90
β, °	90	106.66(3)
γ, °	90	90
V, Å^3	2802.1(4)	814.5(3)
D_{calc} (g cm^{-1})	1.511	1.229
Linear absorption, μ (cm^{-1})	7.37	0.92
F(000)	1304	324
$2\theta_{max}$, °	56	62
Reflections measured	34930	8466
Independent reflections	6771	4400
Observed reflections [$I > 2\sigma(I)$]	6433	4250
Parameters	350	206
R1	0.0250	0.0590
wR2	0.0631	0.1530
GOF	1.039	1.035
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.312/-0.374	0.474/-0.249

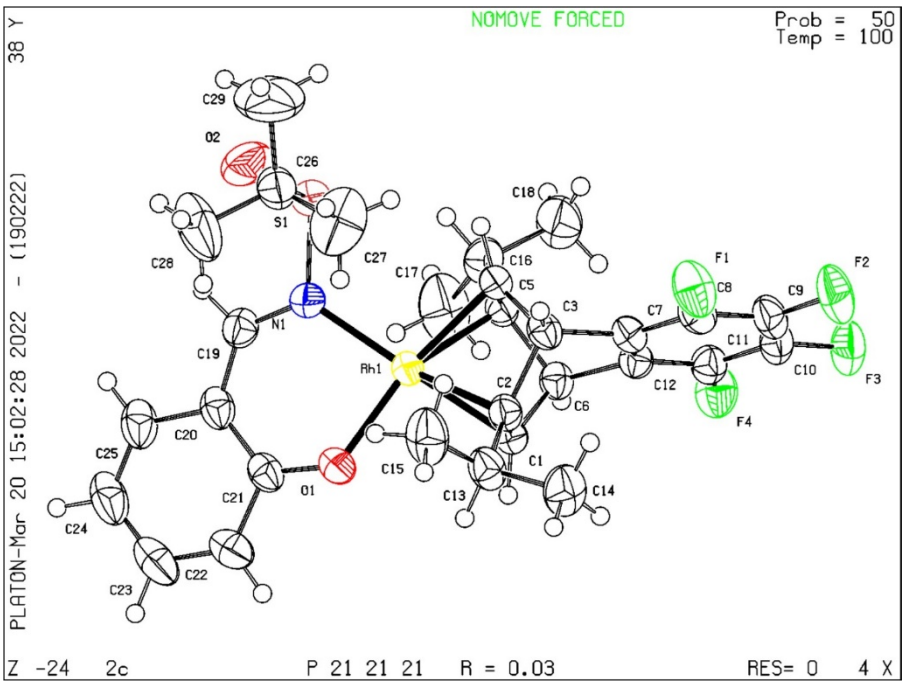


Figure S5. Crystal structure of *S,S*-**Rh-L3** with thermal ellipsoids at 50% probability level (CCDC 2159993).

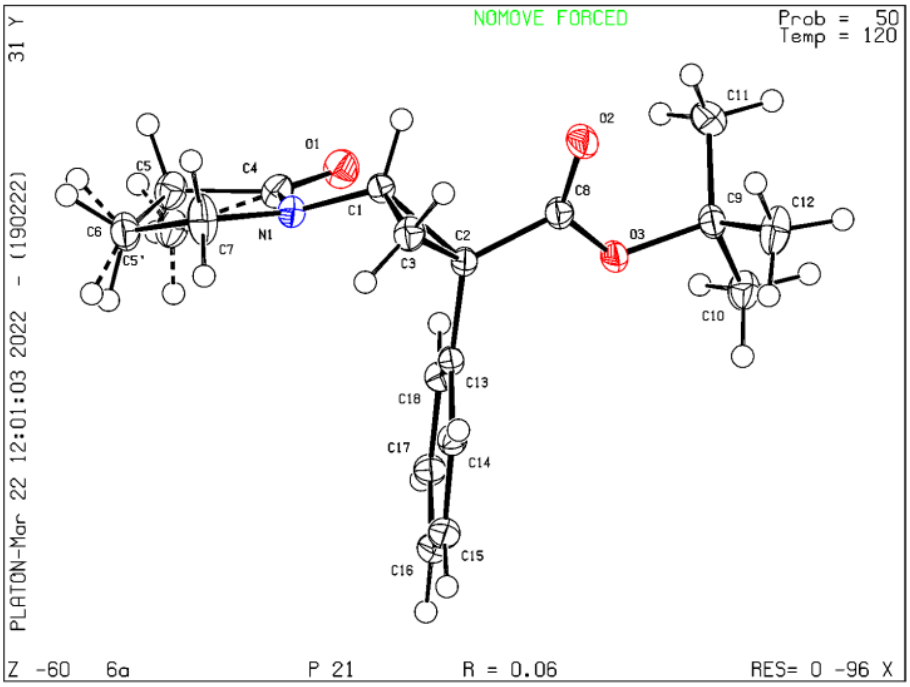
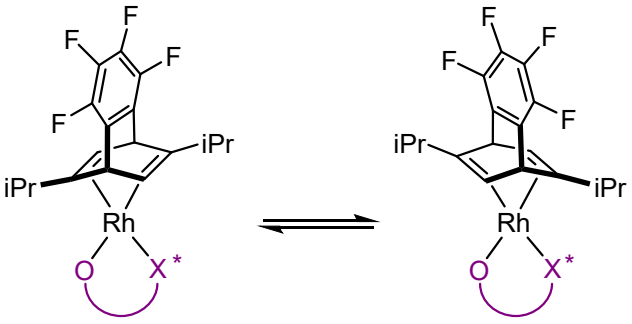


Figure S6. Crystal structure of **6a** with thermal ellipsoids at 50% probability level (CCDC 2159992).

Computational details

Initial geometry optimizations were performed using Priroda 16 software[13] (2016.10.30) at PBE/3z level, which gave appropriate coordinates for further calculations. Additional geometry optimizations and subsequent single-point and frequency calculations were carried out using Gaussian 09 package.[14] For all Rh-containing structures and transition states M06L[15] functional was employed with QZVP[16] basis set for Rh and TZVP[17] basis set for other atoms with the adjustment of corresponding ECP for Rh.[18] For catalytic species, solvation energy corrections were calculated using the SMD solvation model with DCM as the solvent.[19] Geometry optimizations and single-point energy calculations of alkenes were performed with the use of MP2[20] method with 6-311G+(d,p)[21] basis set. The optimized geometries were verified to have no negative frequencies for all intermediates and only one negative frequency for transition states. Cartesian coordinates of the optimized structures are available through separate .xyz file in Supplementary section.



R,R-**Rh-L** *S,S*-**Rh-L**

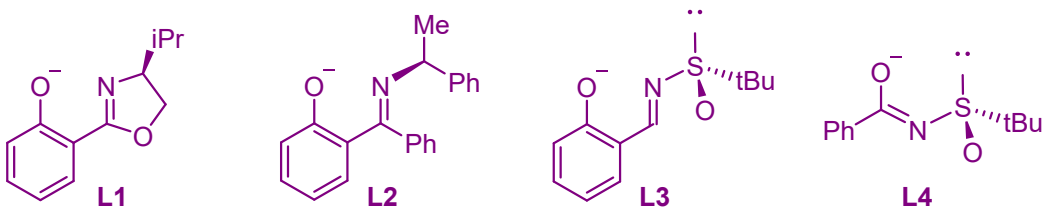
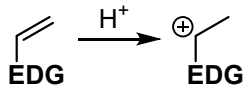


Table S8. Electronic and free energies for diastereomeric complexes *R,R*-**Rh-L** and *S,S*-**Rh-L** (M06L/TZVP//QZVP(ECP)).

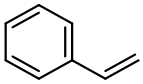
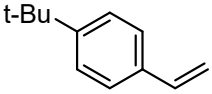
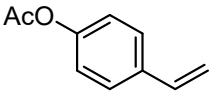
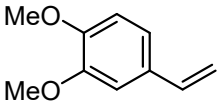
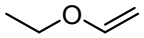
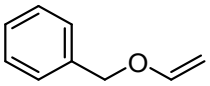
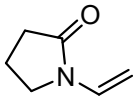
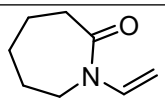
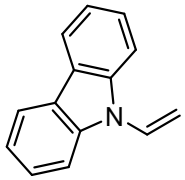
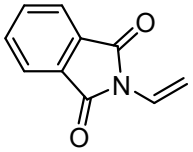
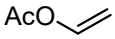
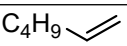
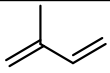
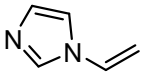
Complex	E + ZPE, a. u.	G, a. u.	ΔG, kcal mol^{-1}
R,R-**Rh-L1**	-1877.543026	-1877.609847	3.91
S,S-**Rh-L1**	-1877.537884	-1877.603616	
R,R-**Rh-L2**	-2147.609406	-2147.680831	0.45
S,S-**Rh-L2**	-2147.608400	-2147.680120	
R,R-**Rh-L3**	-2237.581562	-2237.649711	-4.89
S,S-**Rh-L3**	-2237.590079	-2237.657500	
R,R-**Rh-L4**	-2237.588916	-2237.657886	-2.79
S,S-**Rh-L4**	-2237.593578	-2237.662331	

Proton affinity energies (E_{PA}) for the alkenes were calculated as follows:



$$E_{PA} = -(E_{protonated\ form} - E_{alkene})$$

Table S9. Electronic energies and calculated E_{PA} values for the alkenes (MP2/6-311G+(d,p)).

Name	Structure	Energy of alkene, a. u.	Energy of the protonated alkene, a. u.	E_{PA}, kcal mol^{-1}
styrene		-307.654223349	-308.001975828	218.214680573
4-tertutylstyrene		-463.825273601	-464.185435886	226.001833838
4-acetoxystyrene		-534.344679522	-534.709429399	228.880547818
3,4-dimethoxystyrene		-535.467587045	-535.838727729	232.89077921
ethyl vinyl ether		-231.017516514	-231.375660351	224.735257718
butyl vinyl ether		-309.105199184	-309.466077290	226.451011515
benzyl vinyl ether		-421.562017492	-421.926907902	228.968732275
2,3-dihydrofuran		-229.848130342	-230.203427987	222.949272238
N-vinylpyrrolidone		-361.853121647	-362.216415990	227.967200232
N-vinylcaprolactam		-439.923575108	-440.294887036	232.99823482
N-vinylcarbazole		-591.129863303	-591.504690122	235.203828923
N-vinylphthalimide		-587.091046917	-587.437548744	217.429896442
vinyl acetate		-304.762551903	-305.088836656	204.743682508
hexene		-234.232284023	-234.549902908	199.305850338
isoprene		-194.006977282	-194.339973199	208.954937918
N-vinylimidazole		-301.763834555	-302.104000782	213.454307442

We conducted a series of calculations in order to explain the observed stereoselectivity. Based on our previous studies and assuming that rhodium carbenoid **C1** contributes >98% of the total products distribution, only transformations of this intermediate through four different transition states **TS1**-**TS4** were considered. As in our previous work,[1] all attempts to determine the exact structure of the following intermediates led to the formation of weakly coordinated η^2-arene complexes [(*S,S*-iPr$_2$-TFB)RhCl(**5a**)] with the total free energy close to that of free *S,S*-**Rh**-monomer and ethyl vinyl ether combined (these data are not included in Table S9).

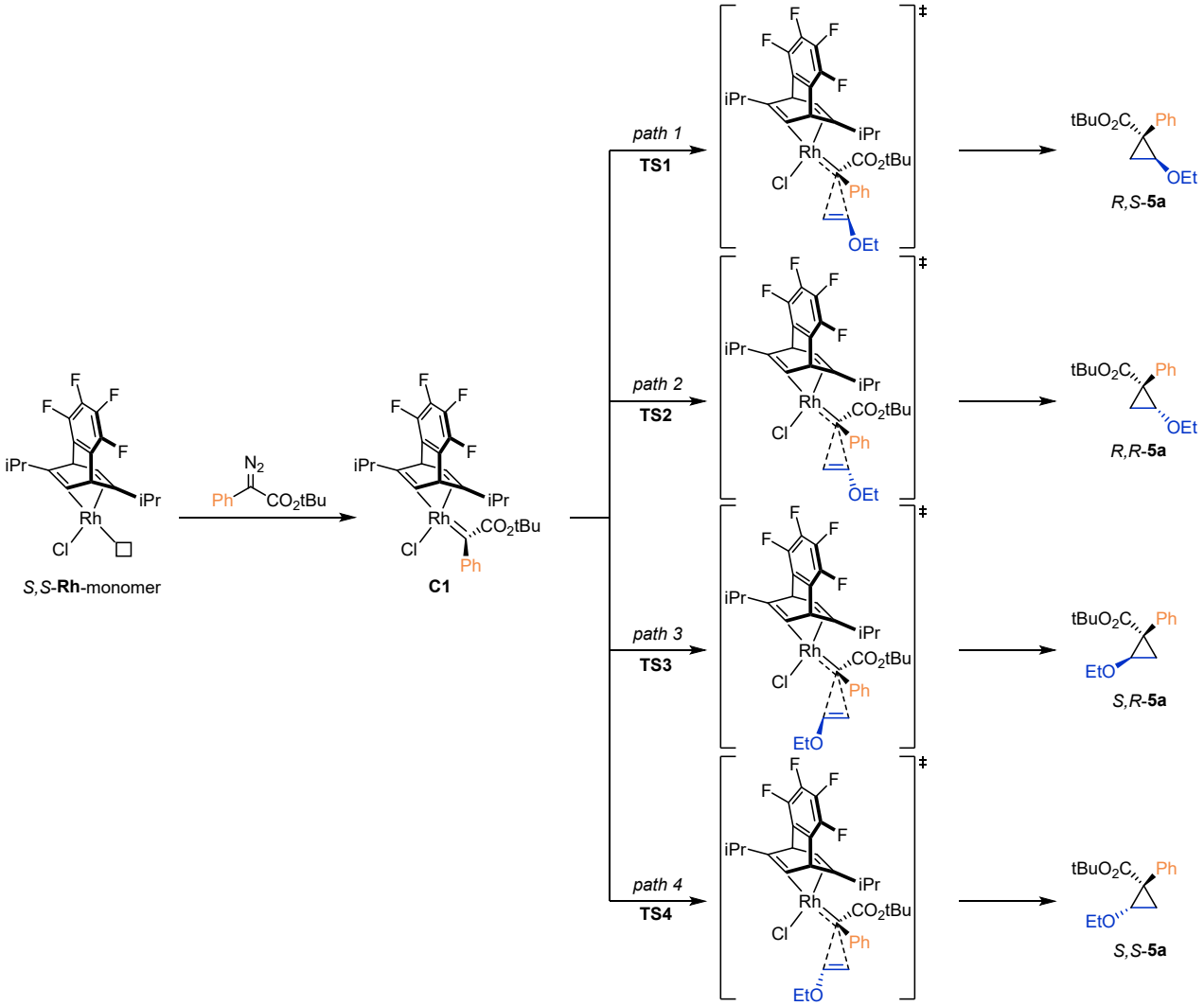


Figure S7. The proposed mechanism for cyclopropanation of ethyl vinyl ether.

Table S10. Free energies for the transition states (M06L/TZVP//QZVP(ECP)) in DCE.

Species	G, a.u.	ΔG, kcal mol^{-1}	Imaginary frequency, cm^{-1}
ethyl vinyl ether	-232.393351	-	-
C1[a]	-2283.077129	-	-
TS1	-2515.446684	14.93	-390.4
TS2	-2515.442553	17.52	-414.6
TS3	-2515.442757	17.40	-411.6
TS4	-2515.439610	19.37	-244.9

[a] The structure of the opposite enantiomer was previously calculated,[1] the exact same free energy of that species is provided here.

Copies of NMR Spectra

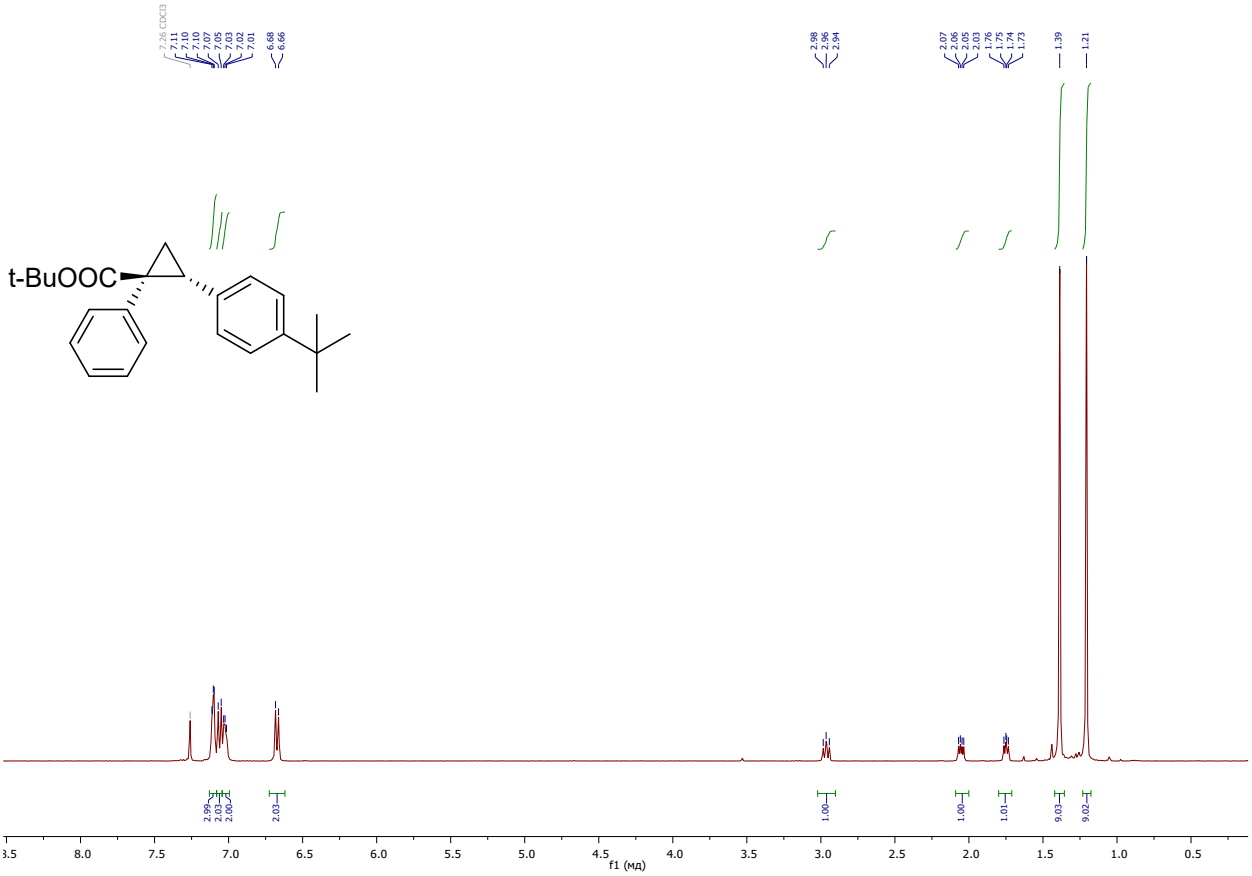


Figure S8. ^{1}**H** spectrum of **4b**.

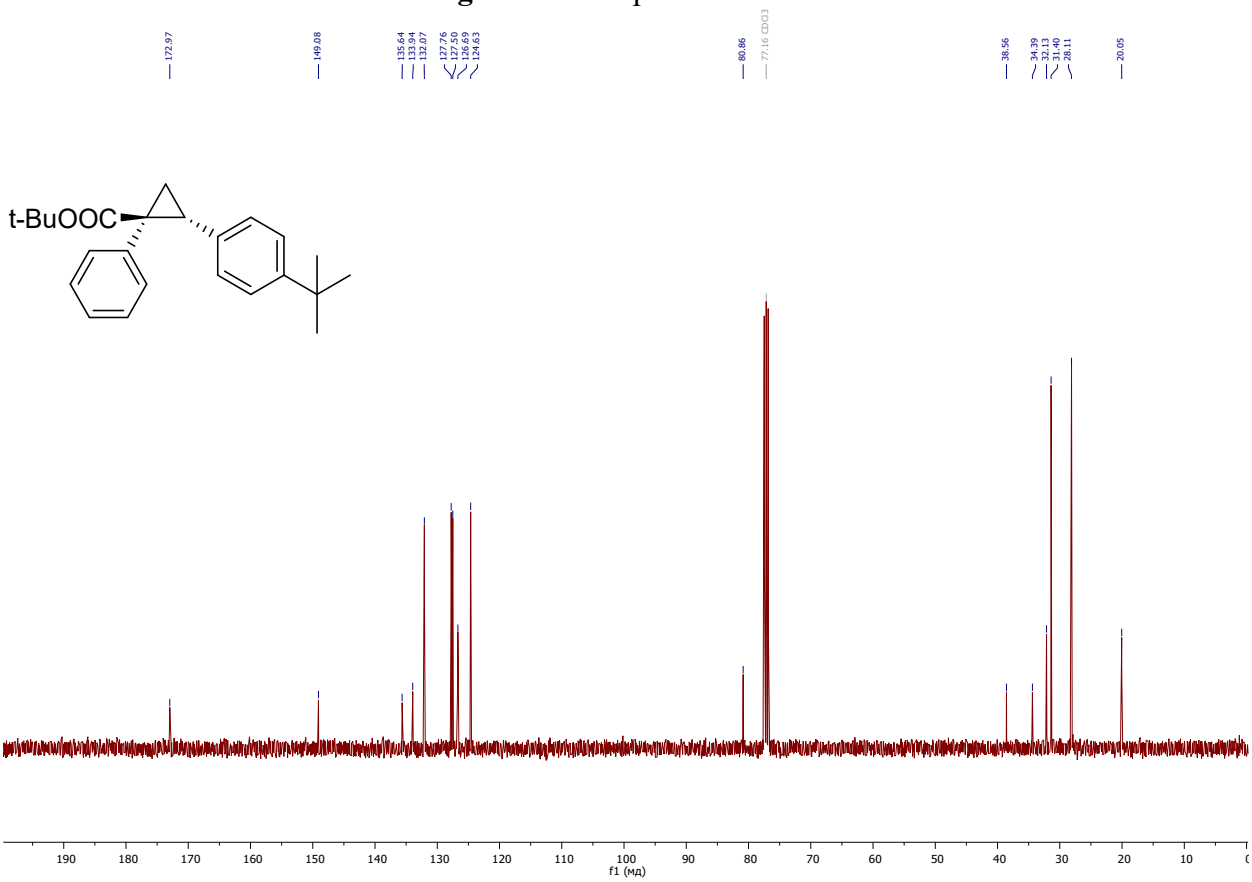


Figure S9. ^{13}**C** spectrum of **4b**.

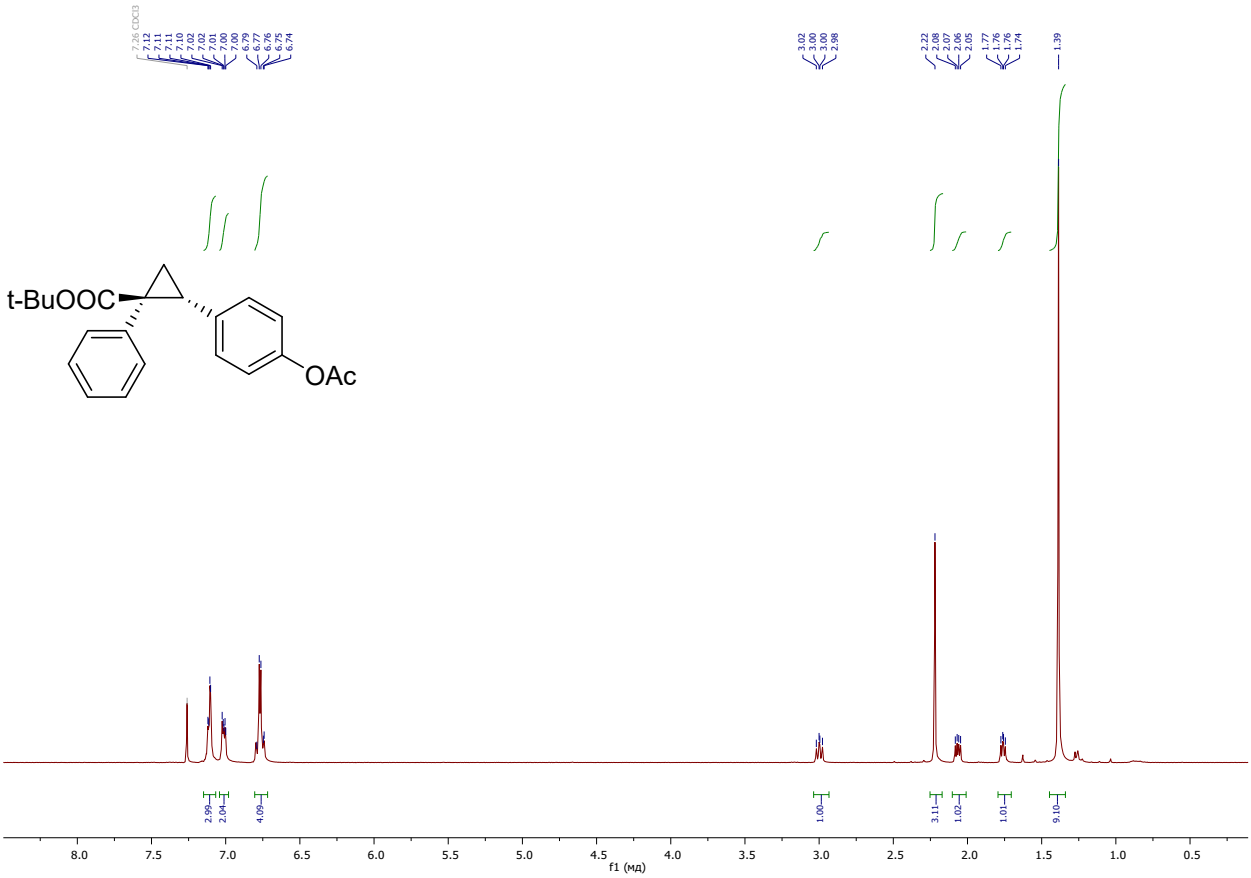


Figure S10. ^{1}**H** spectrum of **4c**.

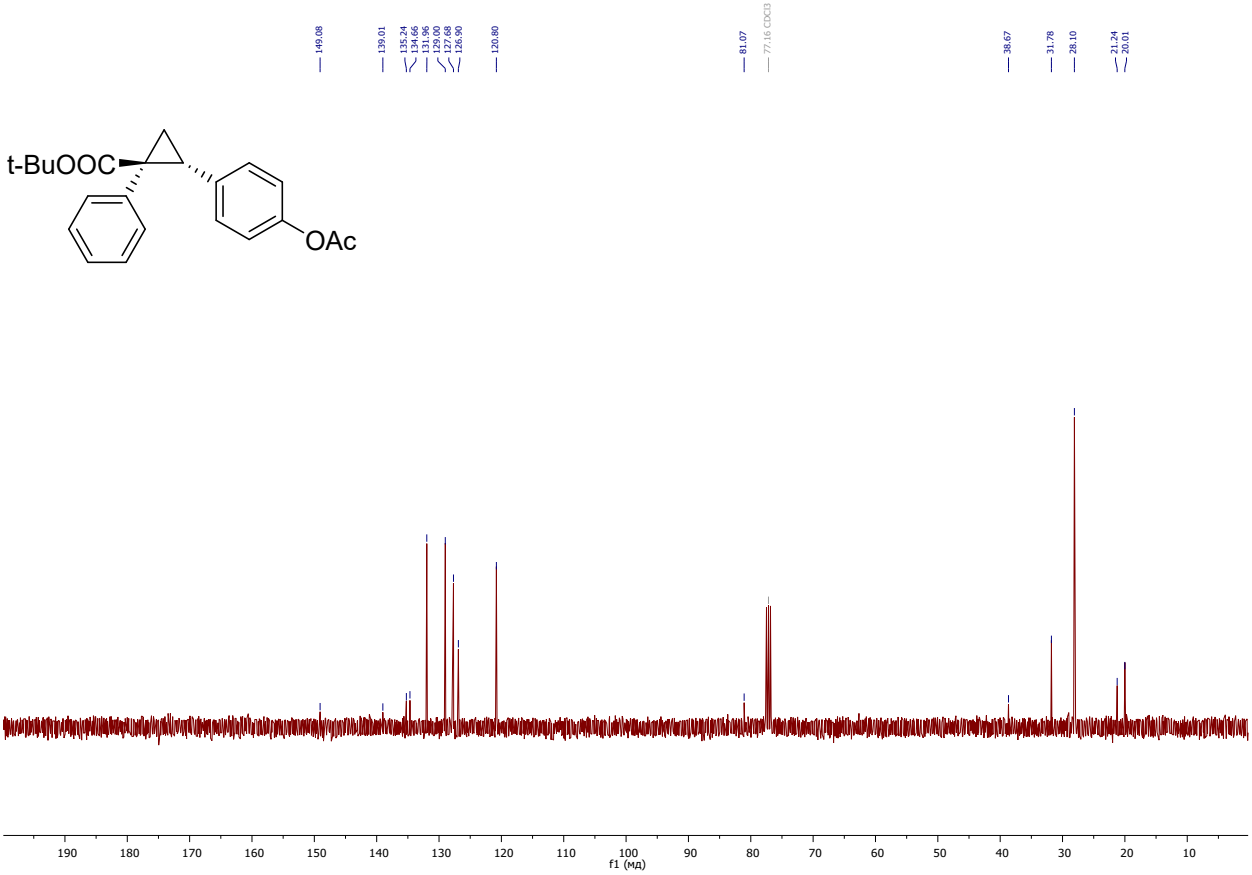


Figure S11. ^{13}**C** spectrum of **4c**.

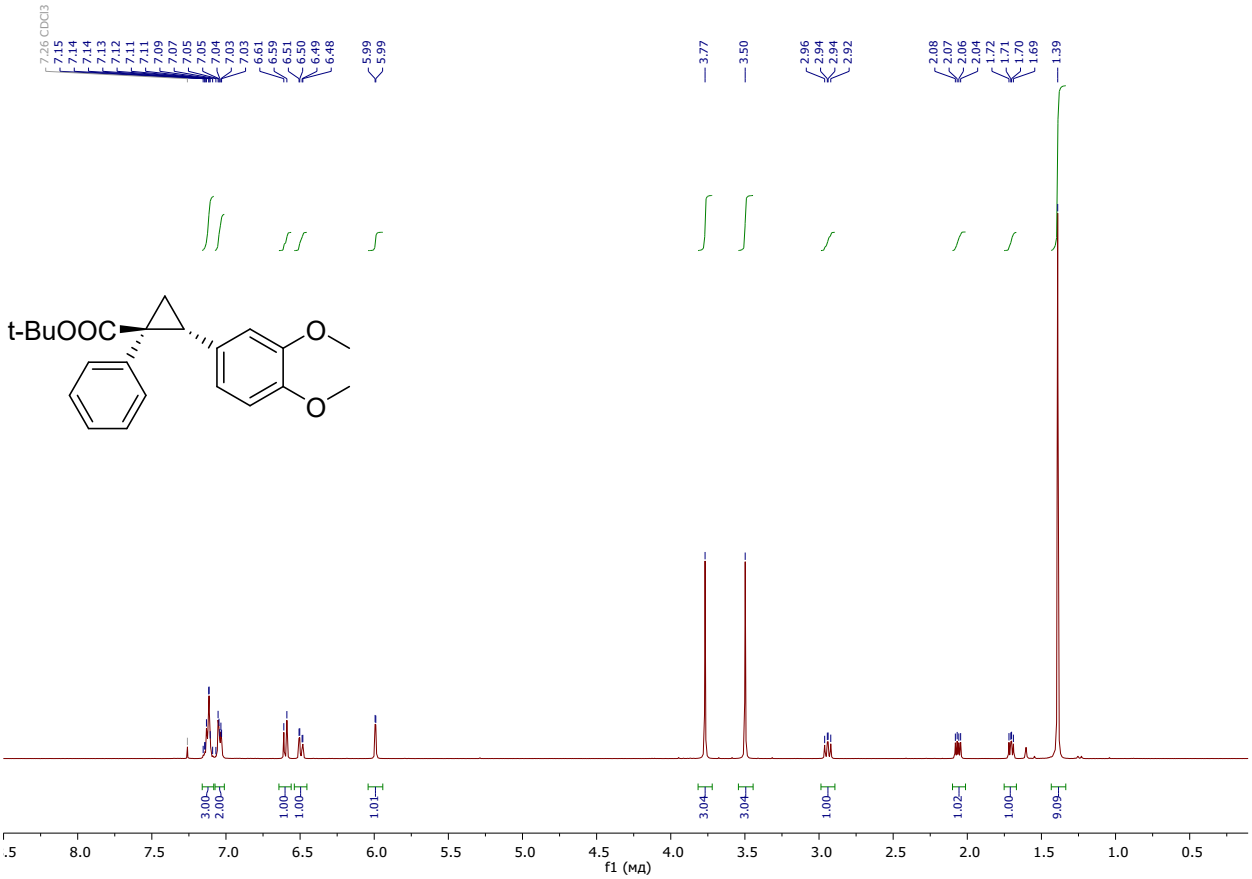


Figure S12. ^{1}**H** spectrum of **4d**.

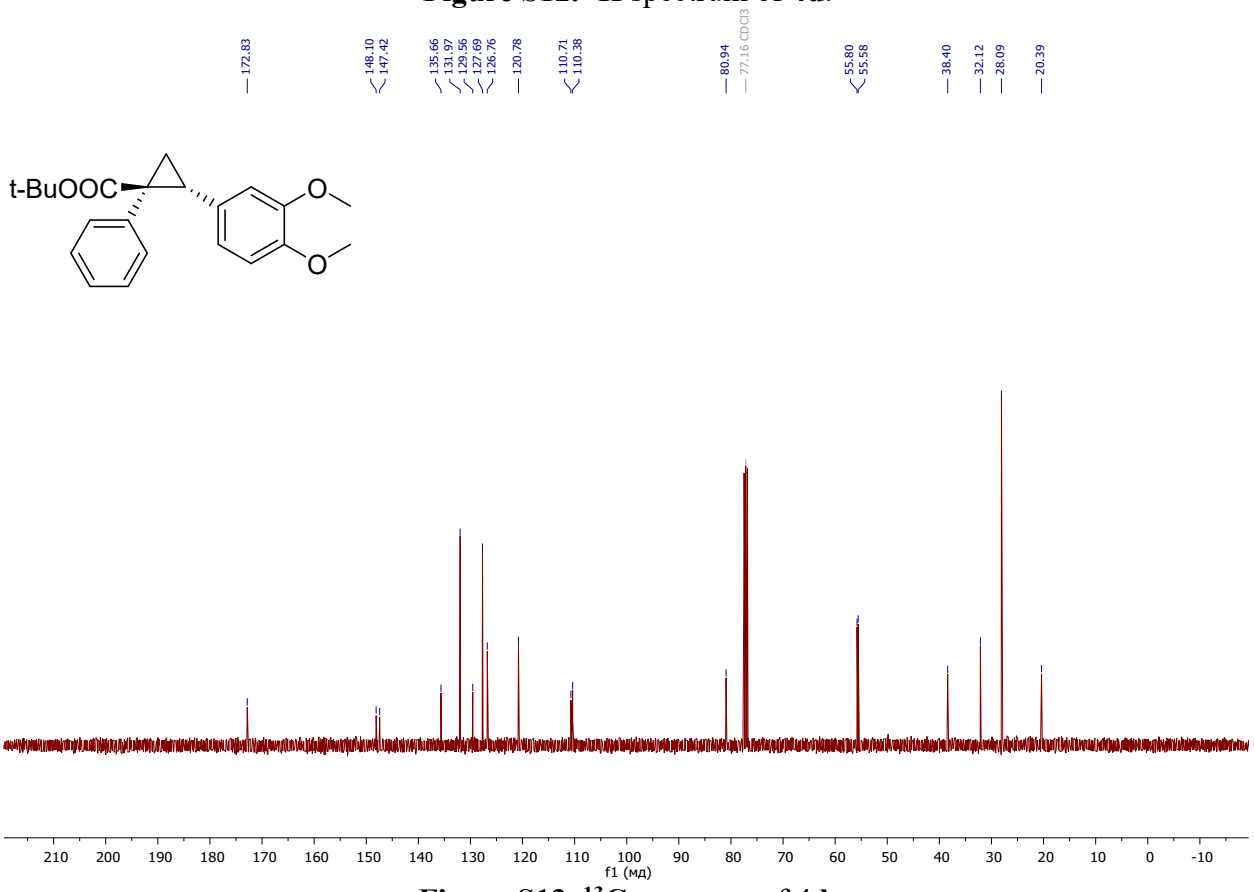


Figure S13. ^{13}**C** spectrum of **4d**.

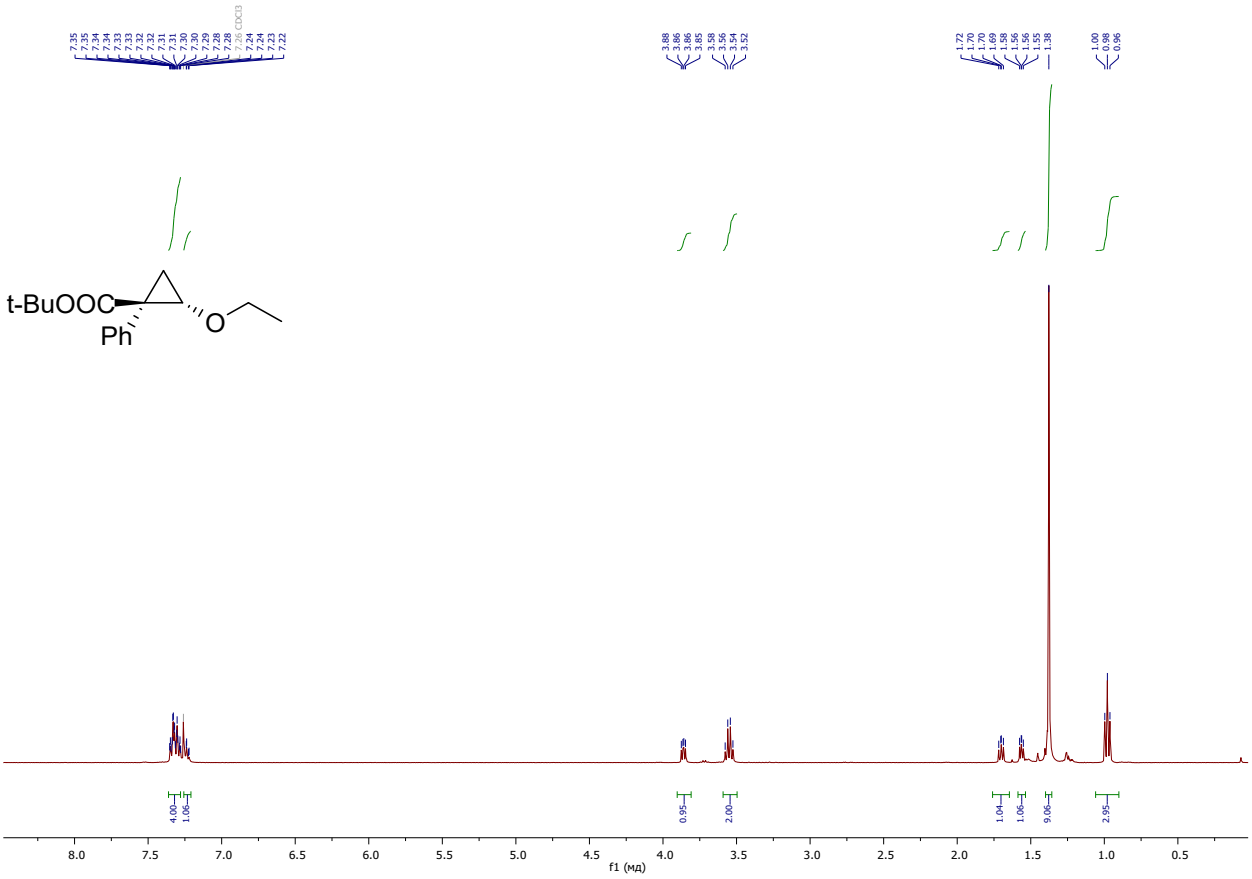


Figure S14. ^{1}**H** spectrum of **5a**.

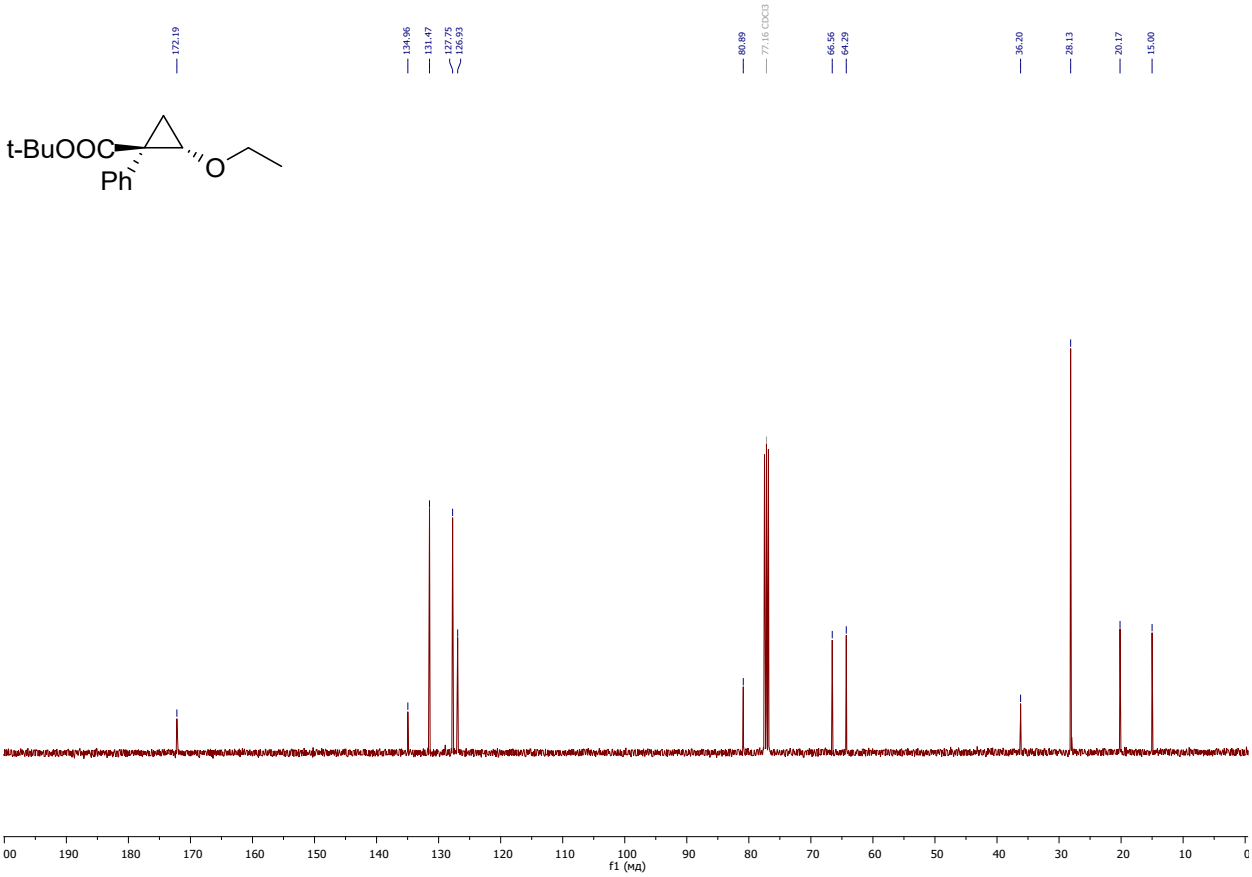


Figure S15. ^{13}**C** spectrum of **5a**.

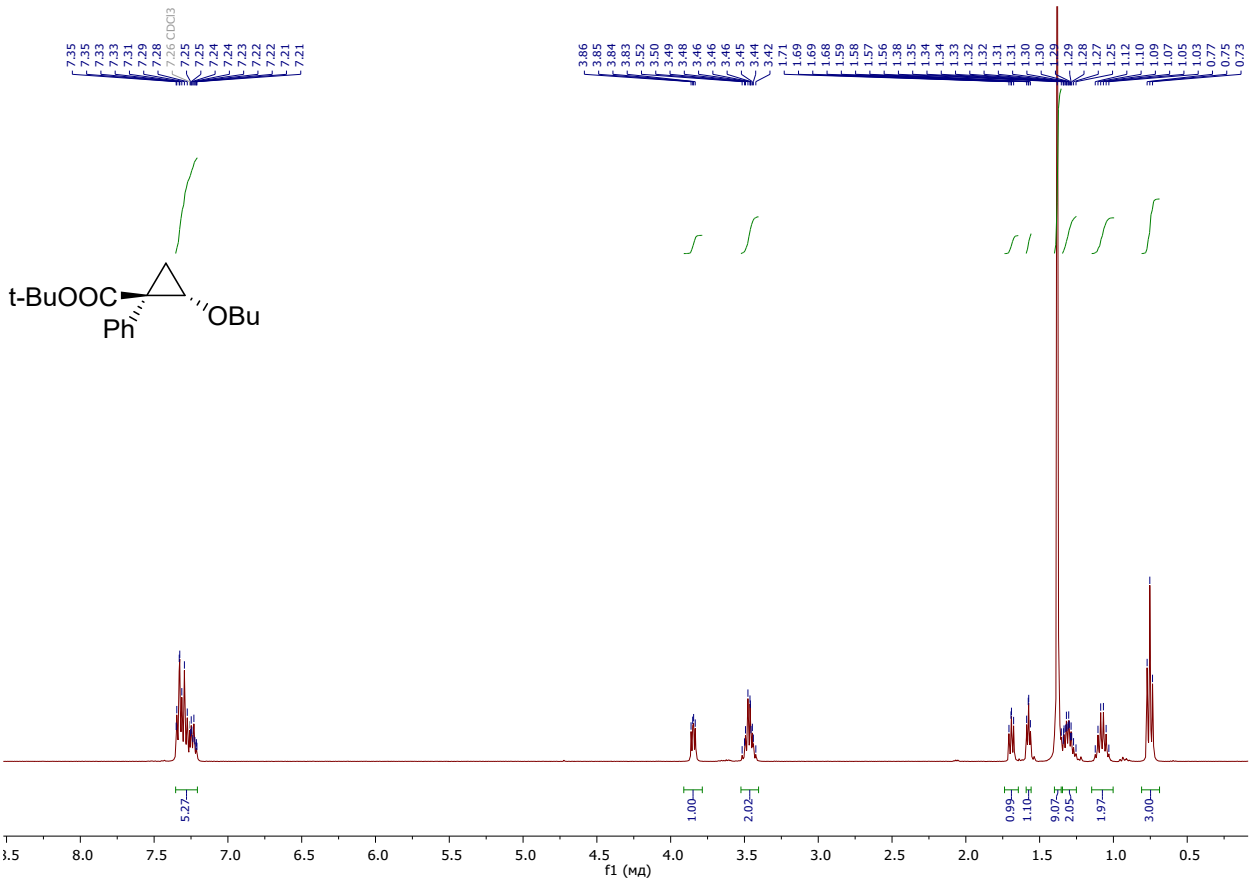


Figure S16. ^{1}**H** spectrum of **5b**.

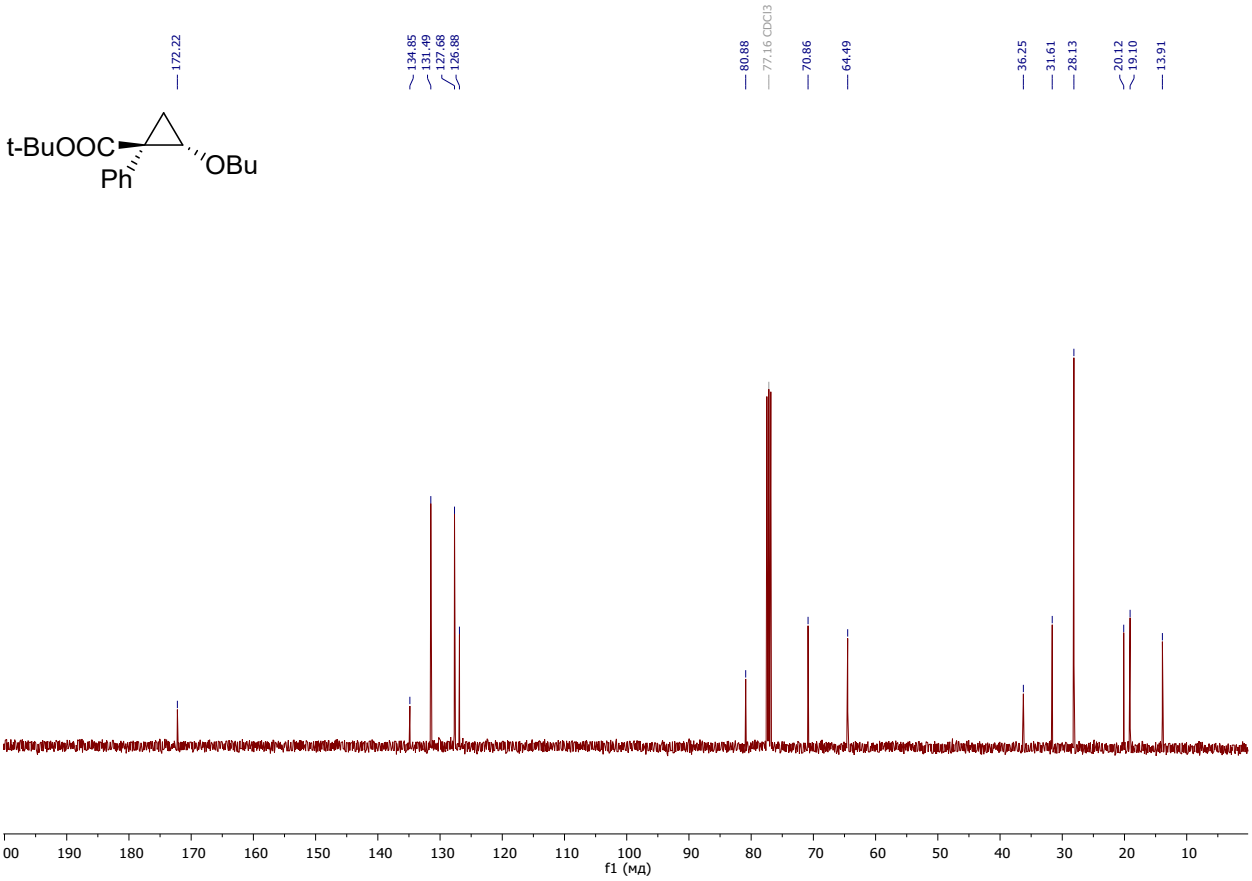


Figure S17. ^{13}**C** spectrum of **5b**.

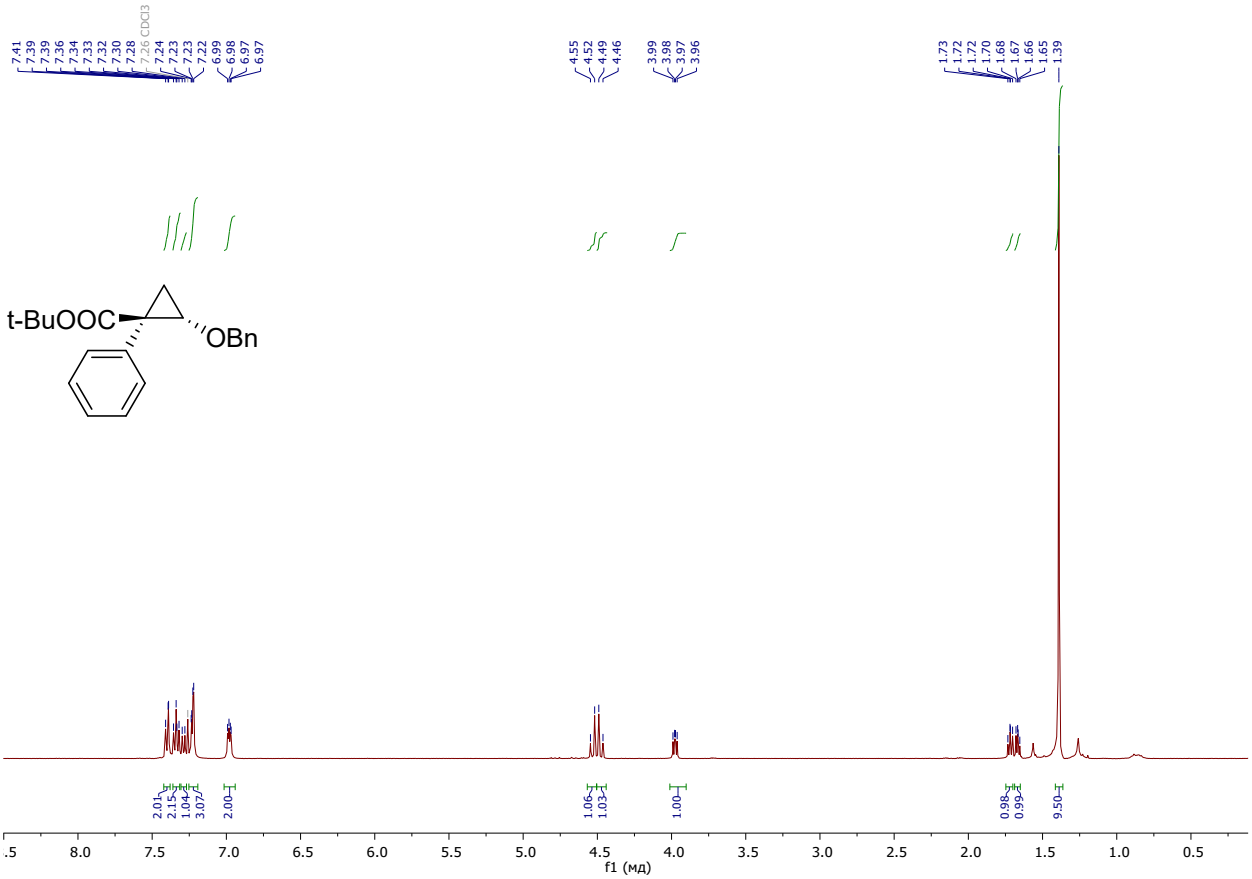


Figure S18. ^{1}**H** spectrum of **5c**.

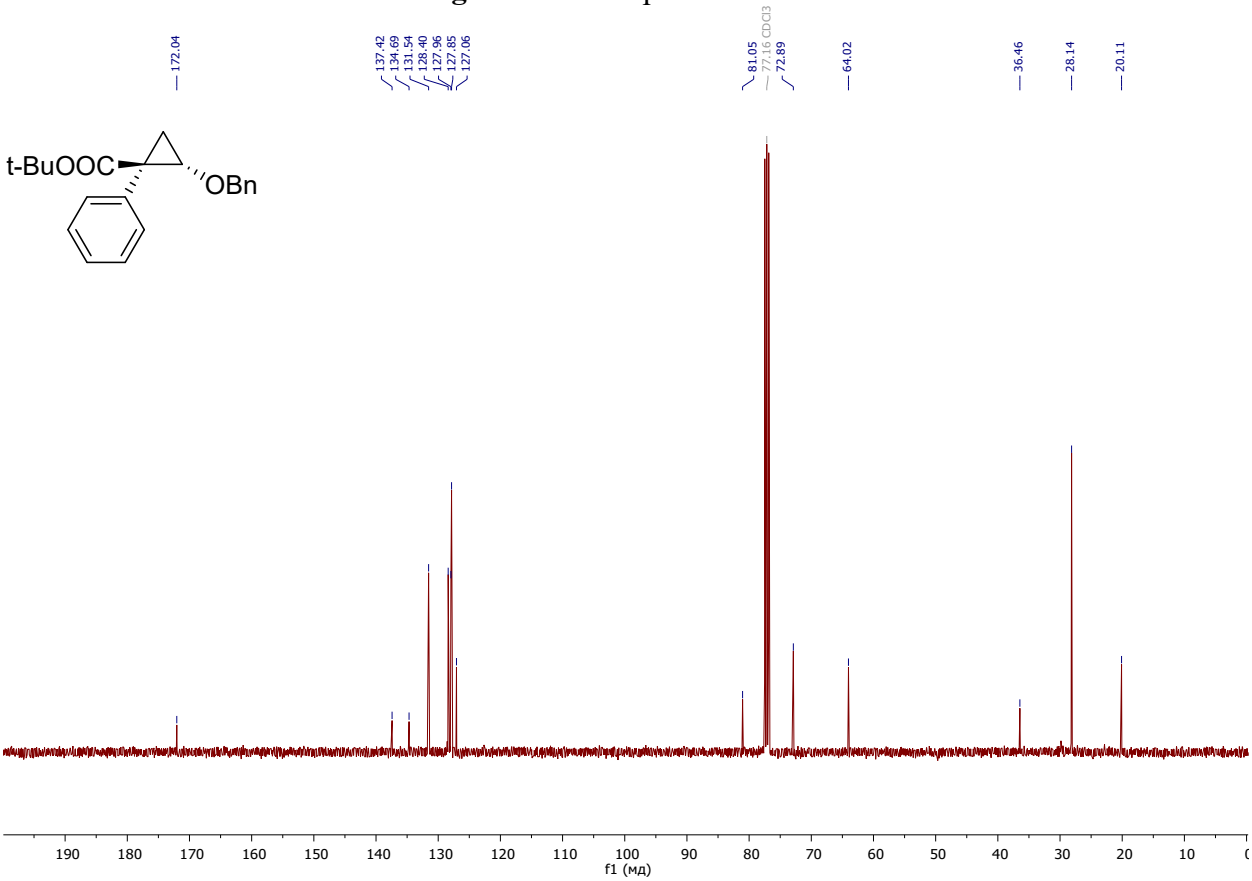


Figure S19. ^{13}**C** spectrum of **5c**.

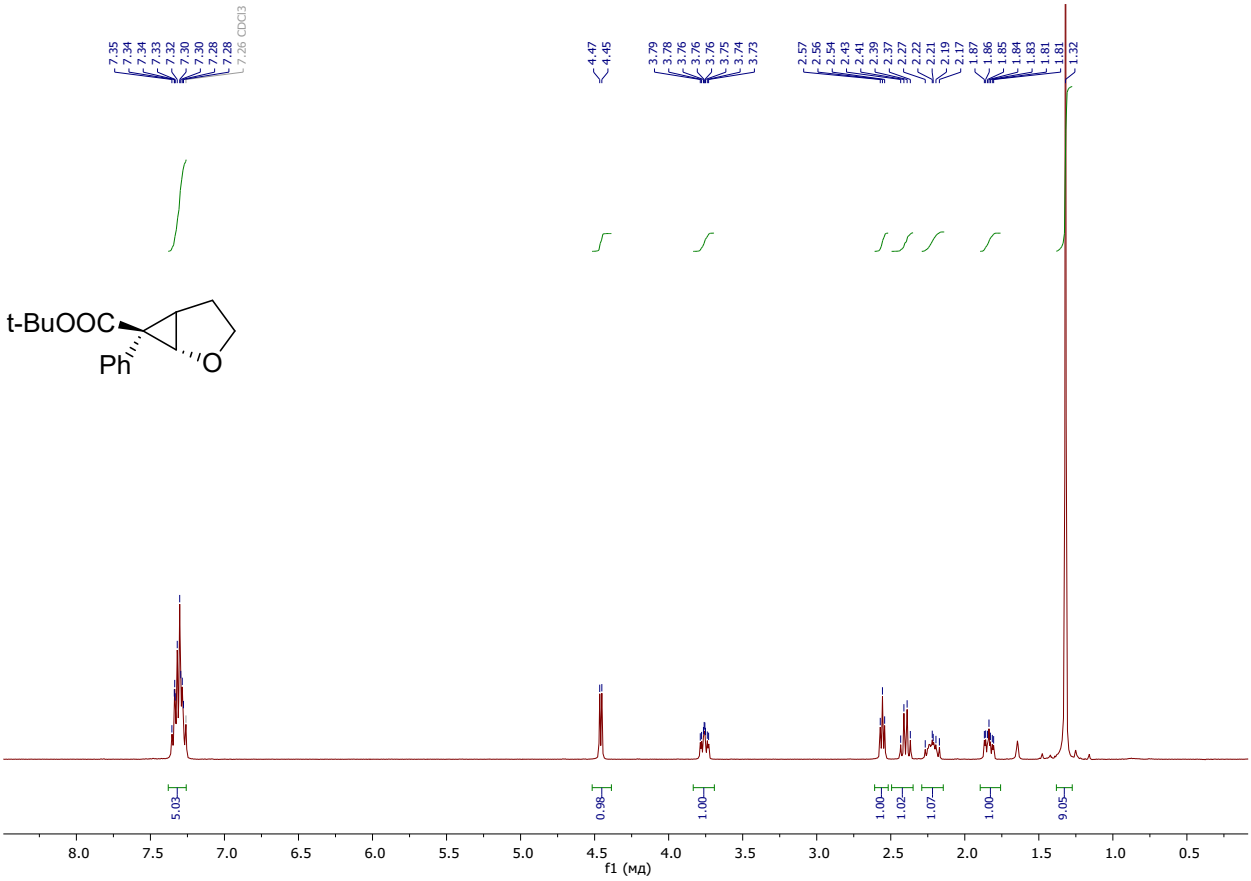


Figure S20. ^{1}**H** spectrum of **5d**.

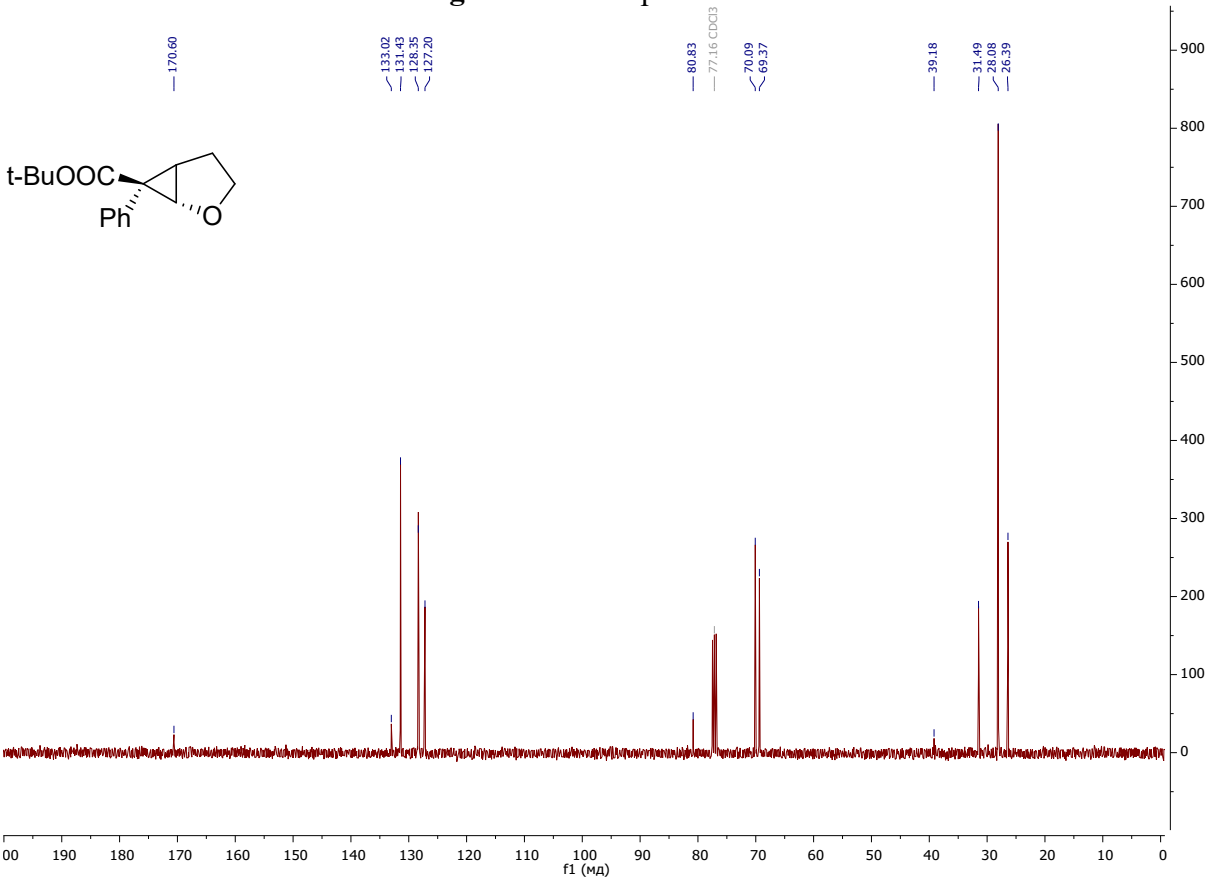


Figure S21. ^{13}**C** spectrum of **5d**.

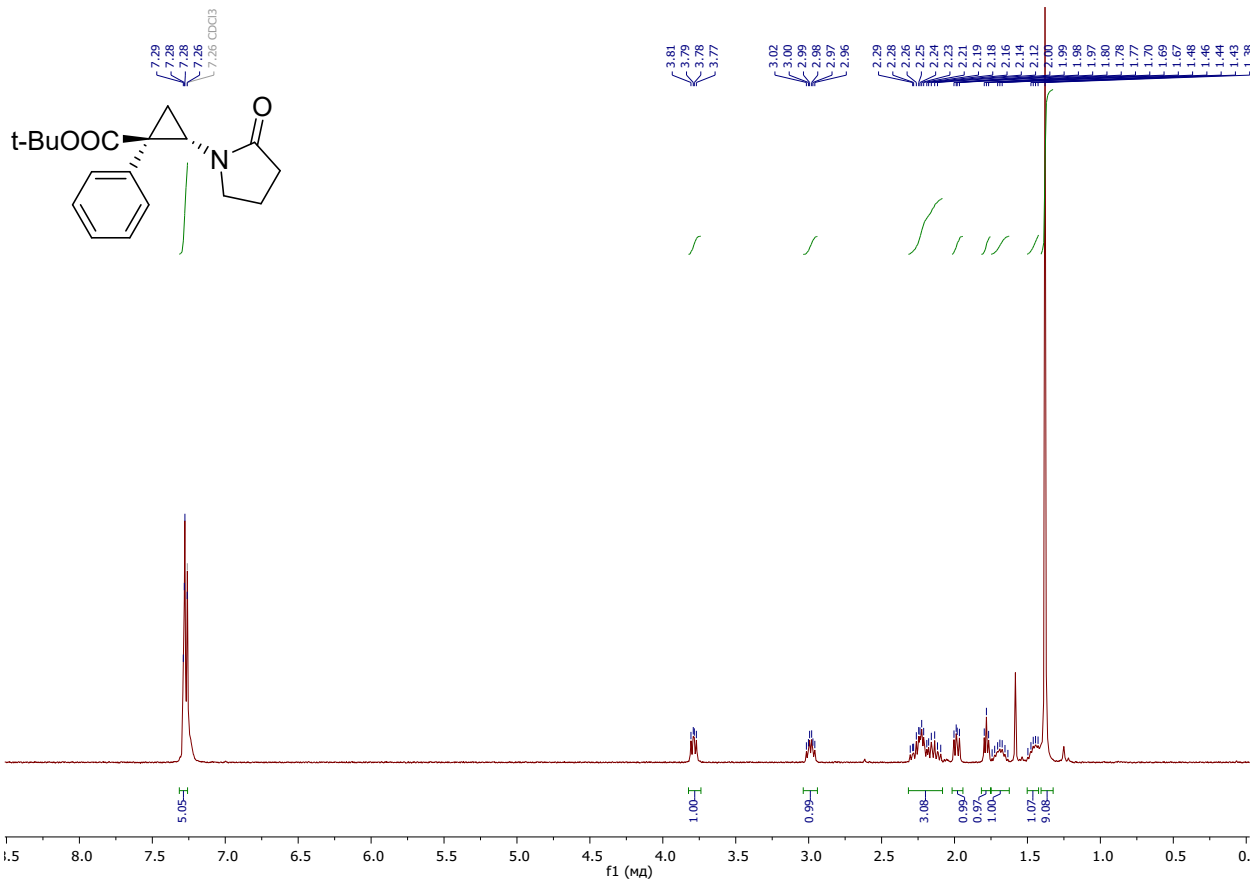


Figure S22. ^{1}**H** spectrum of **6a**.

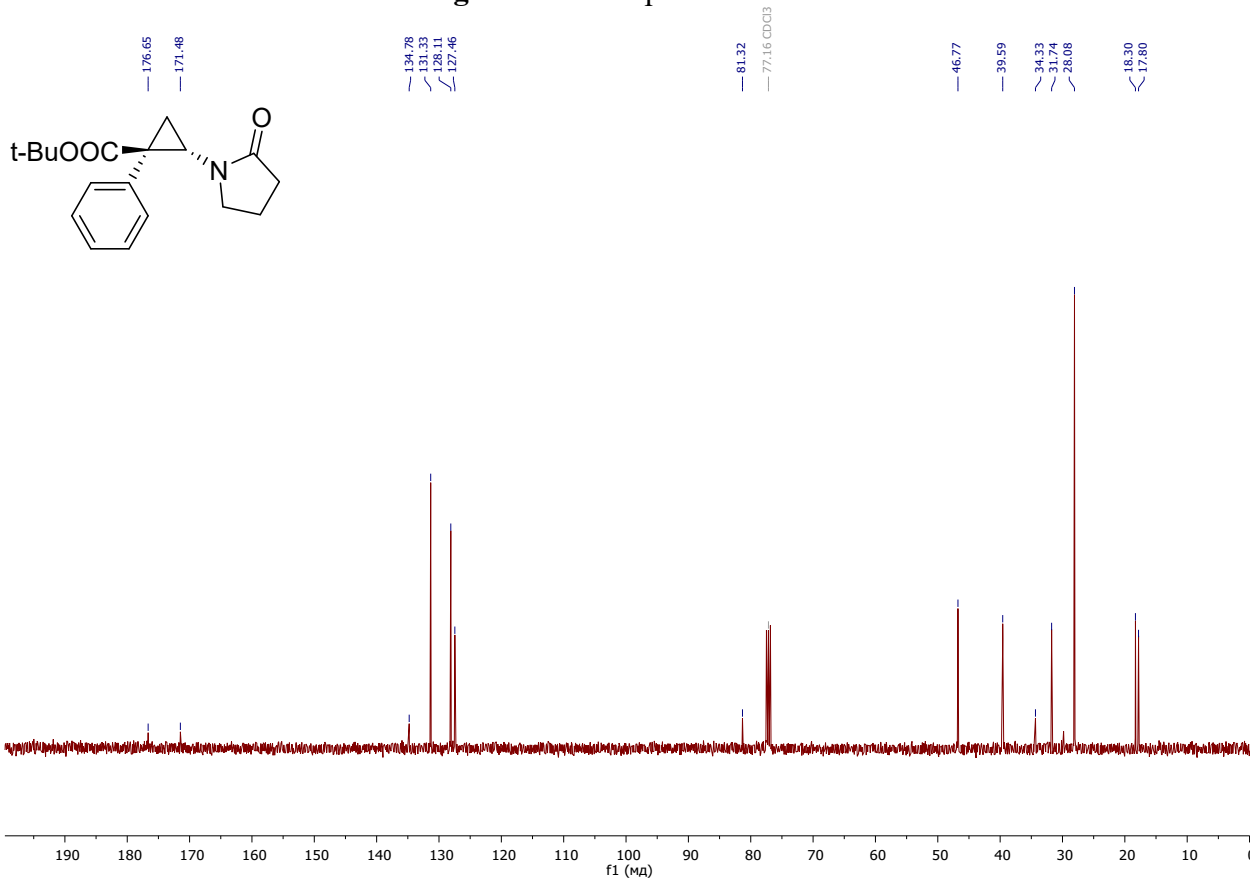


Figure S23. ^{13}**C** spectrum of **6a**.

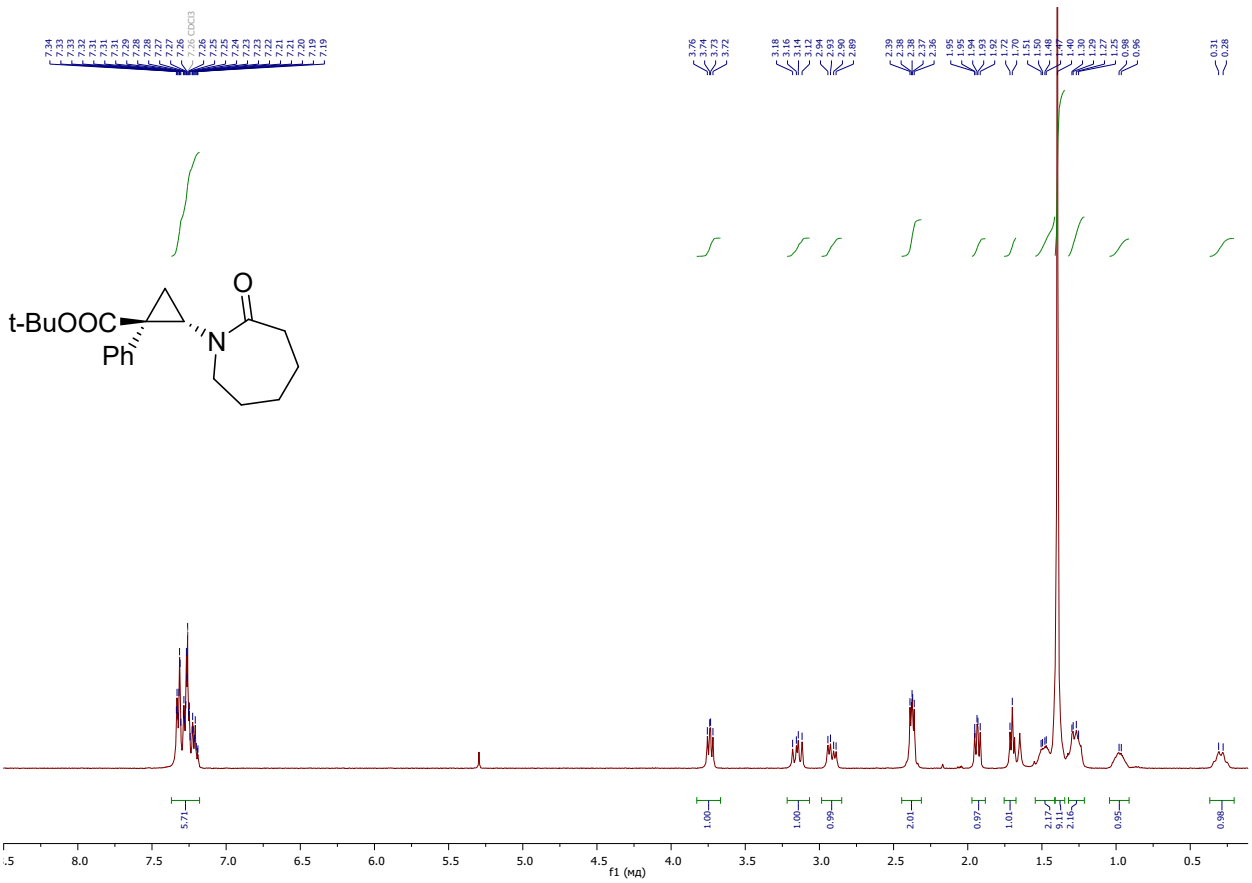


Figure S24. ^{1}**H** spectrum of **6b**.

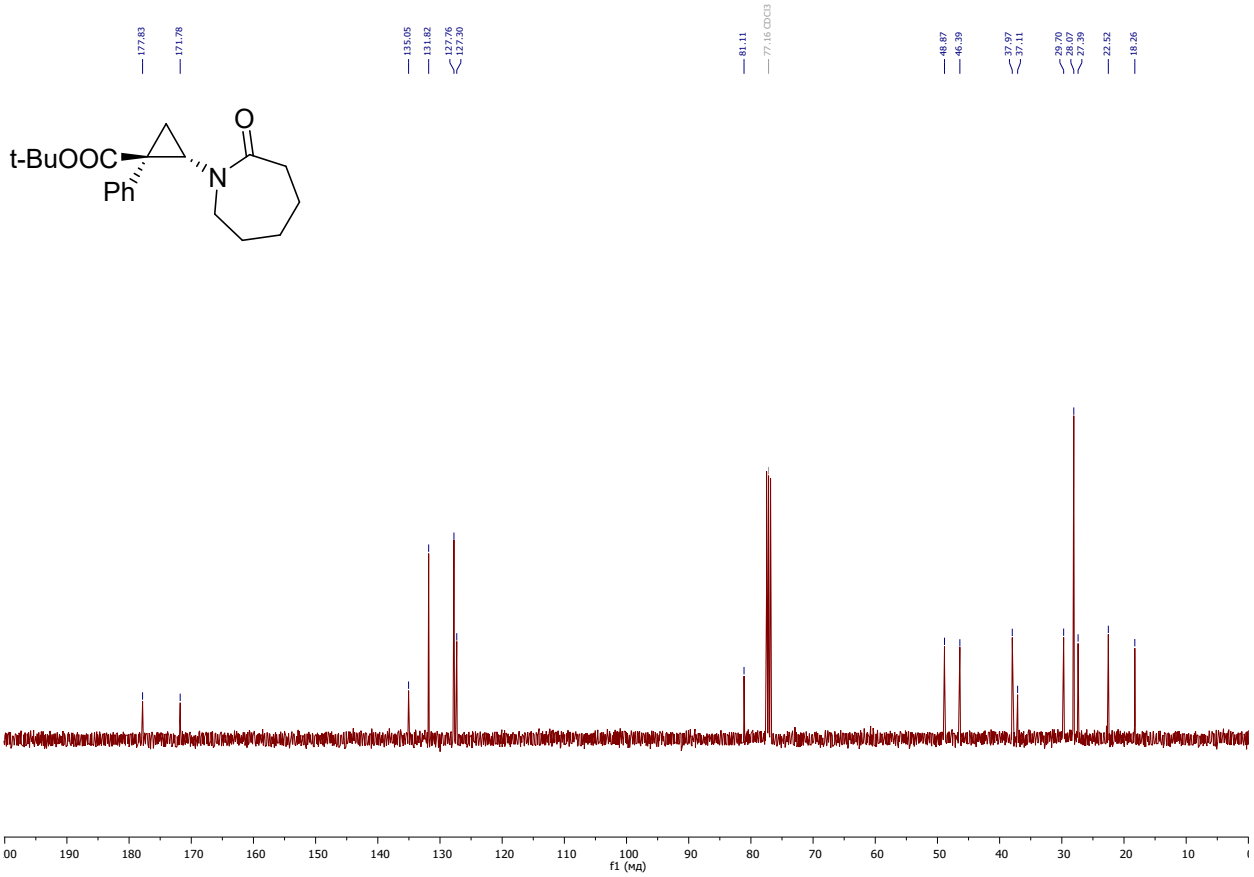


Figure S25. ^{13}**C** spectrum of **6b**.

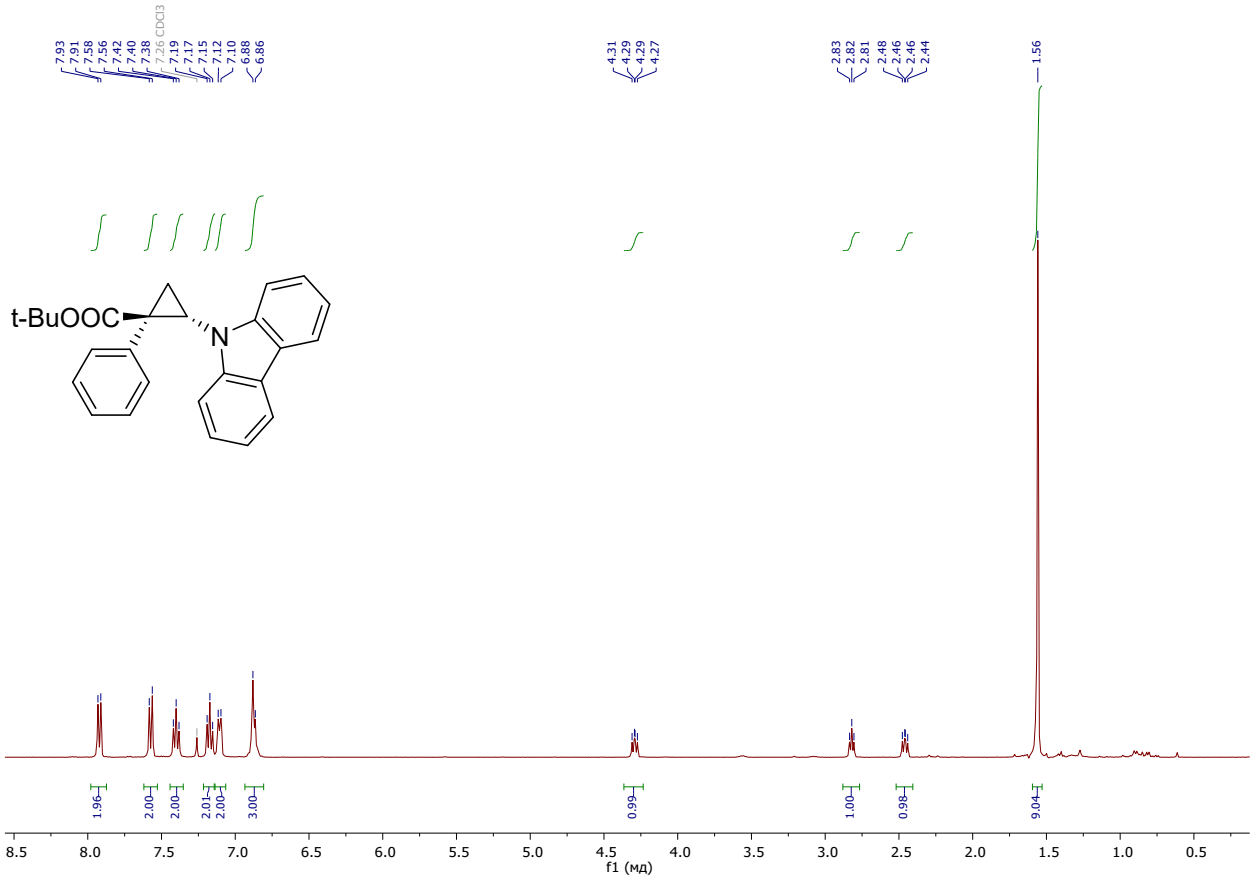


Figure S26. ^{1}**H** spectrum of **6c**.

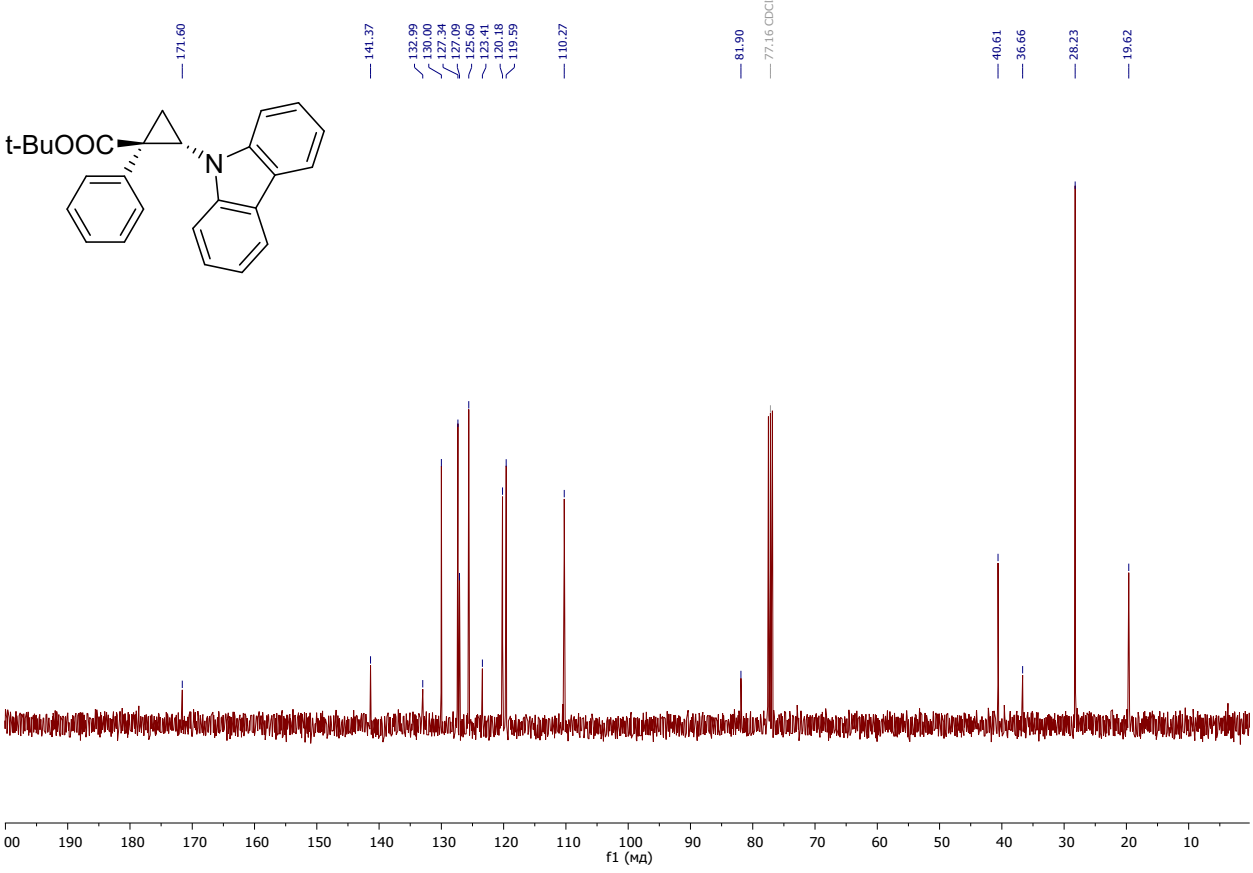


Figure S27. ^{13}**C** spectrum of **6c**.

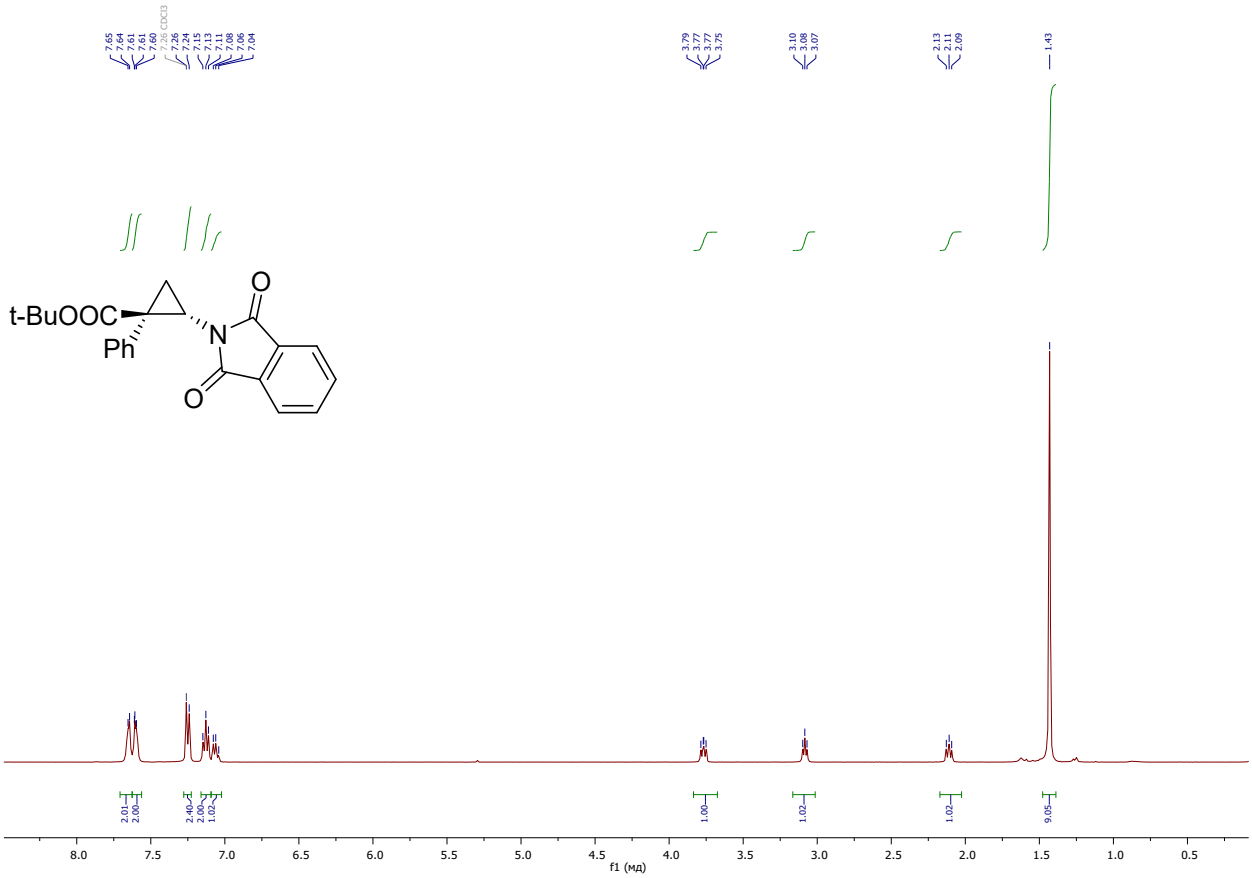


Figure S28. ^{1}**H** spectrum of **6d**.

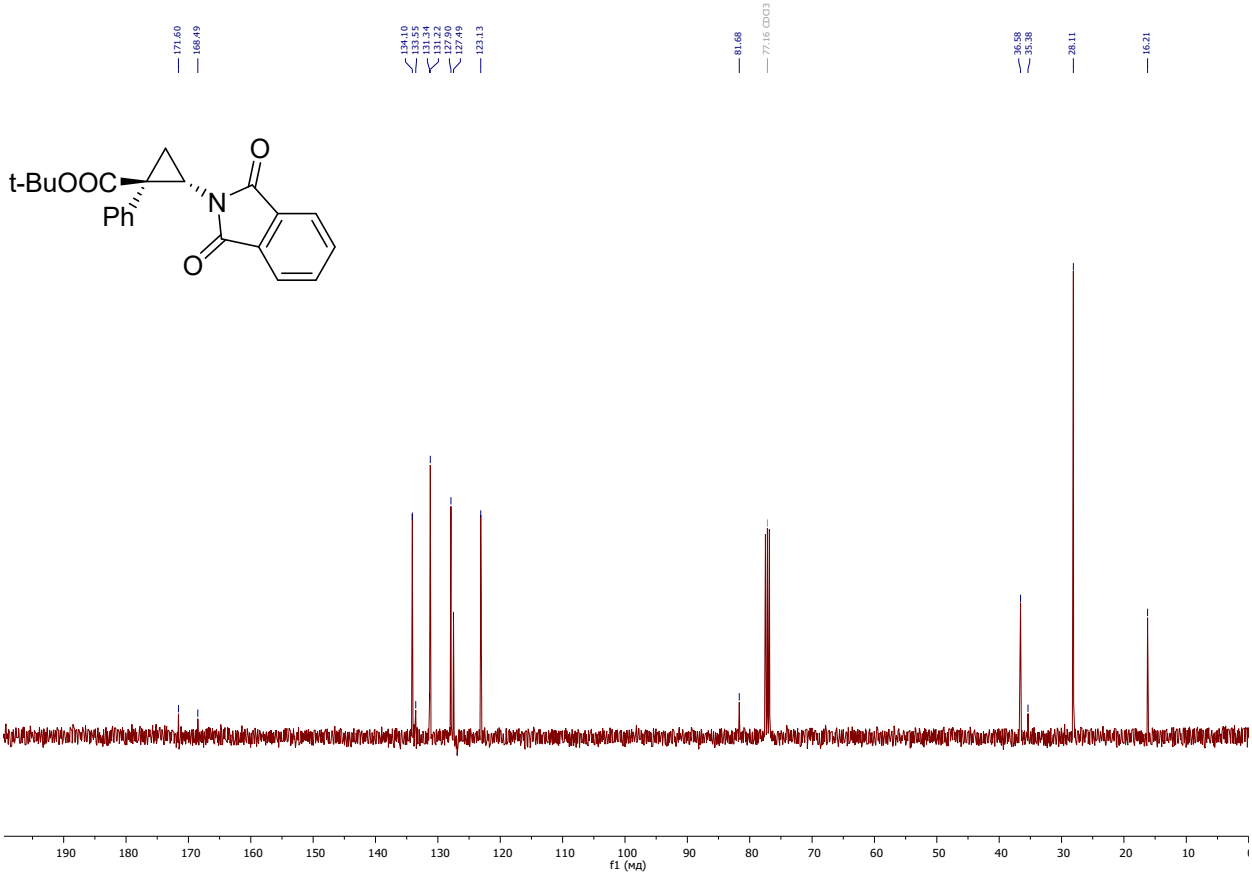


Figure S29. ^{13}**C** spectrum of **6d**.

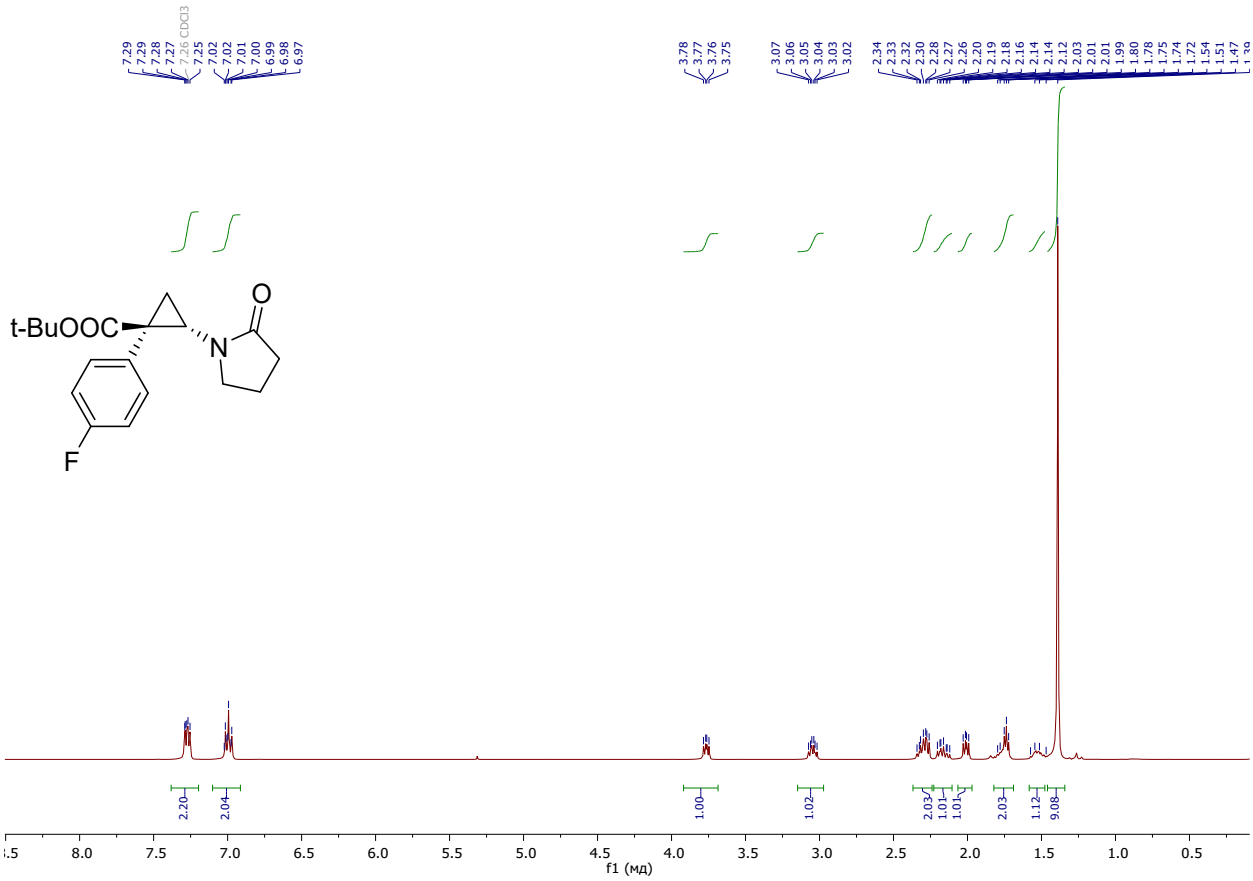


Figure S30. ^{1}**H** spectrum of **7a**.

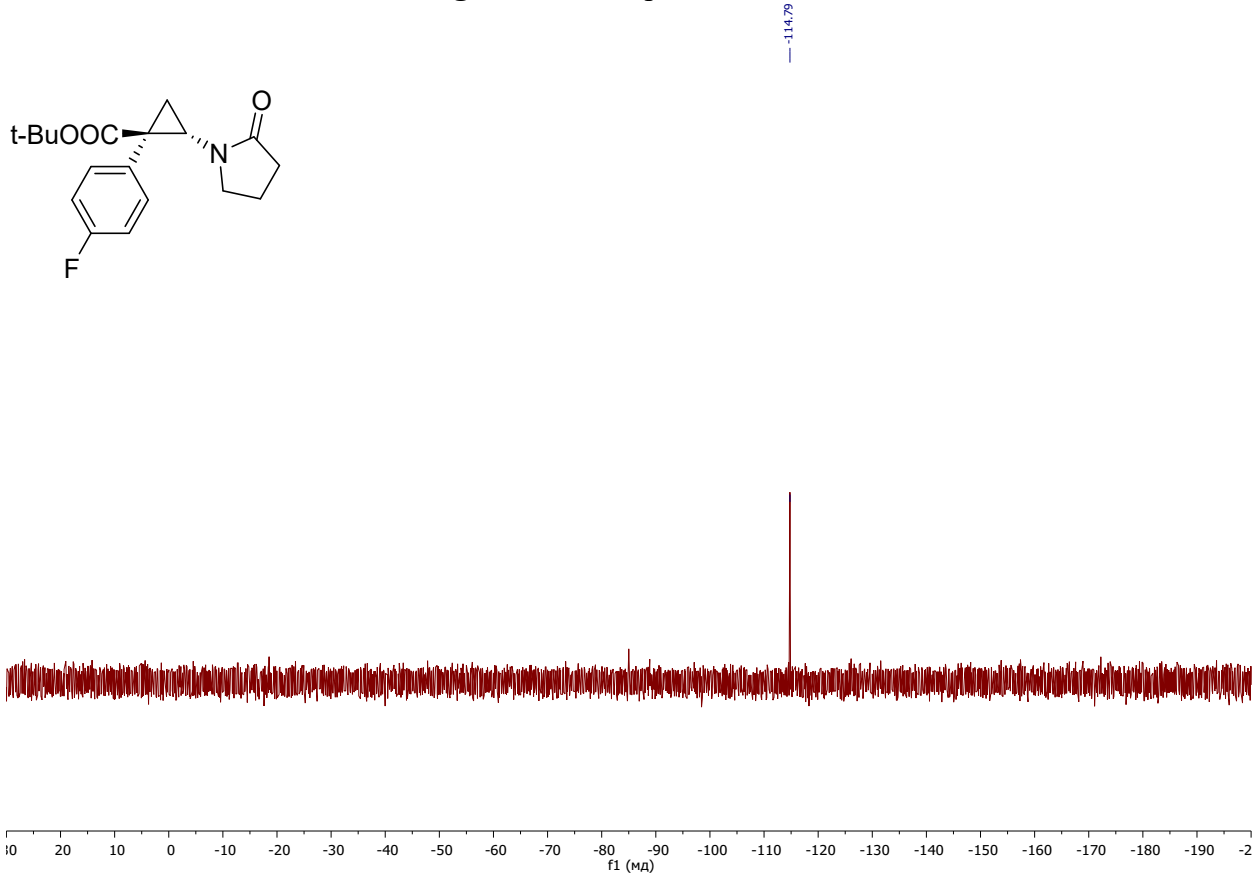


Figure S31. ^{19}**F** spectrum of **7a**.

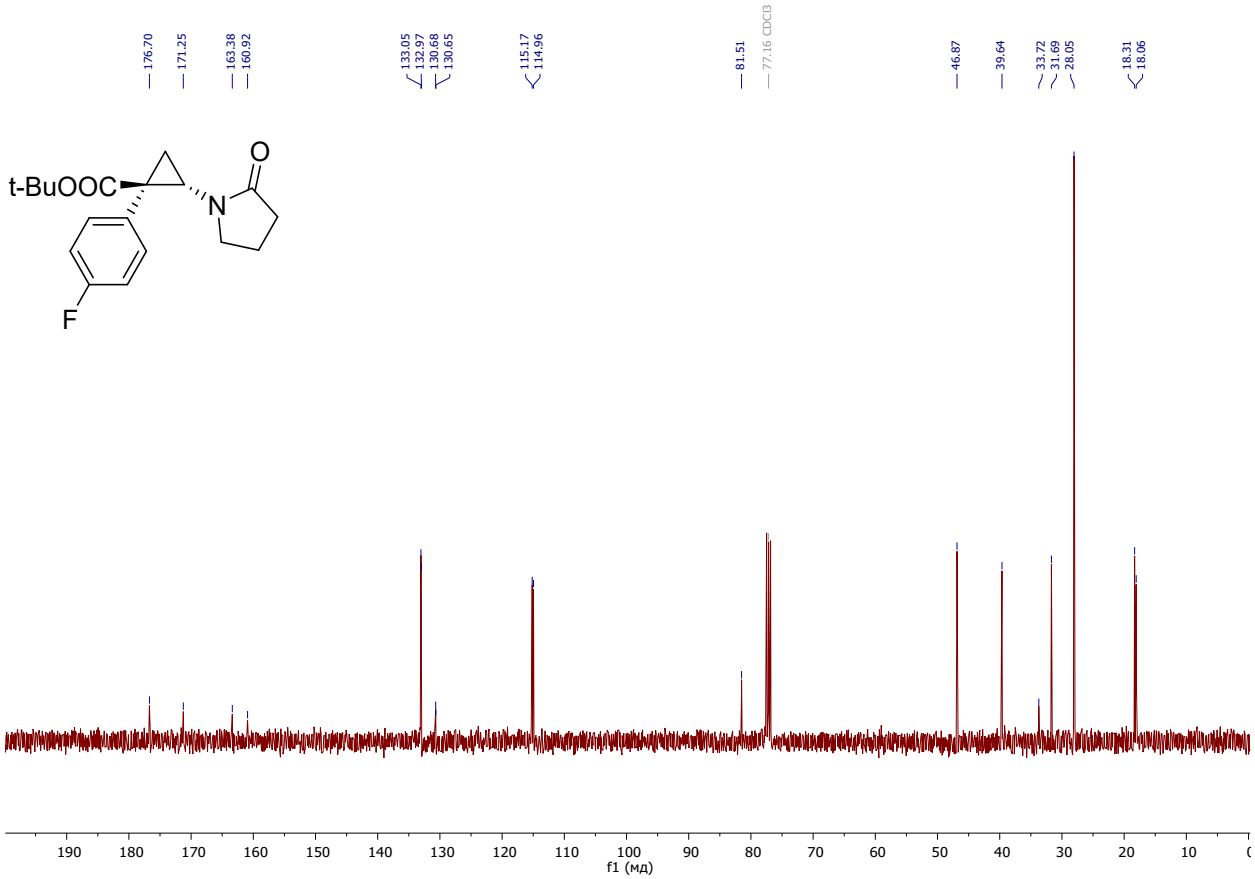


Figure S32. ^{13}**C** spectrum of **7a**.

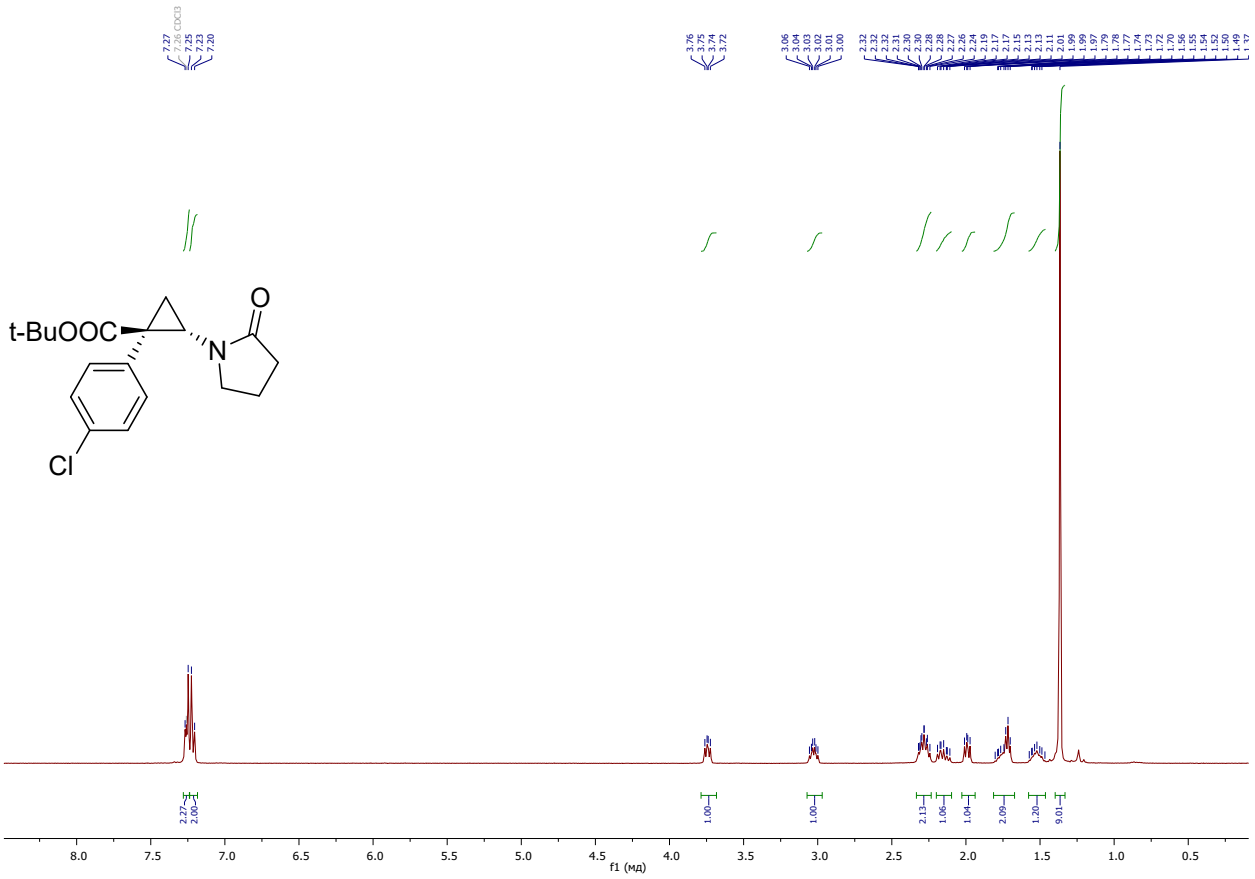


Figure S33. ^{1}**H** spectrum of **7b**.

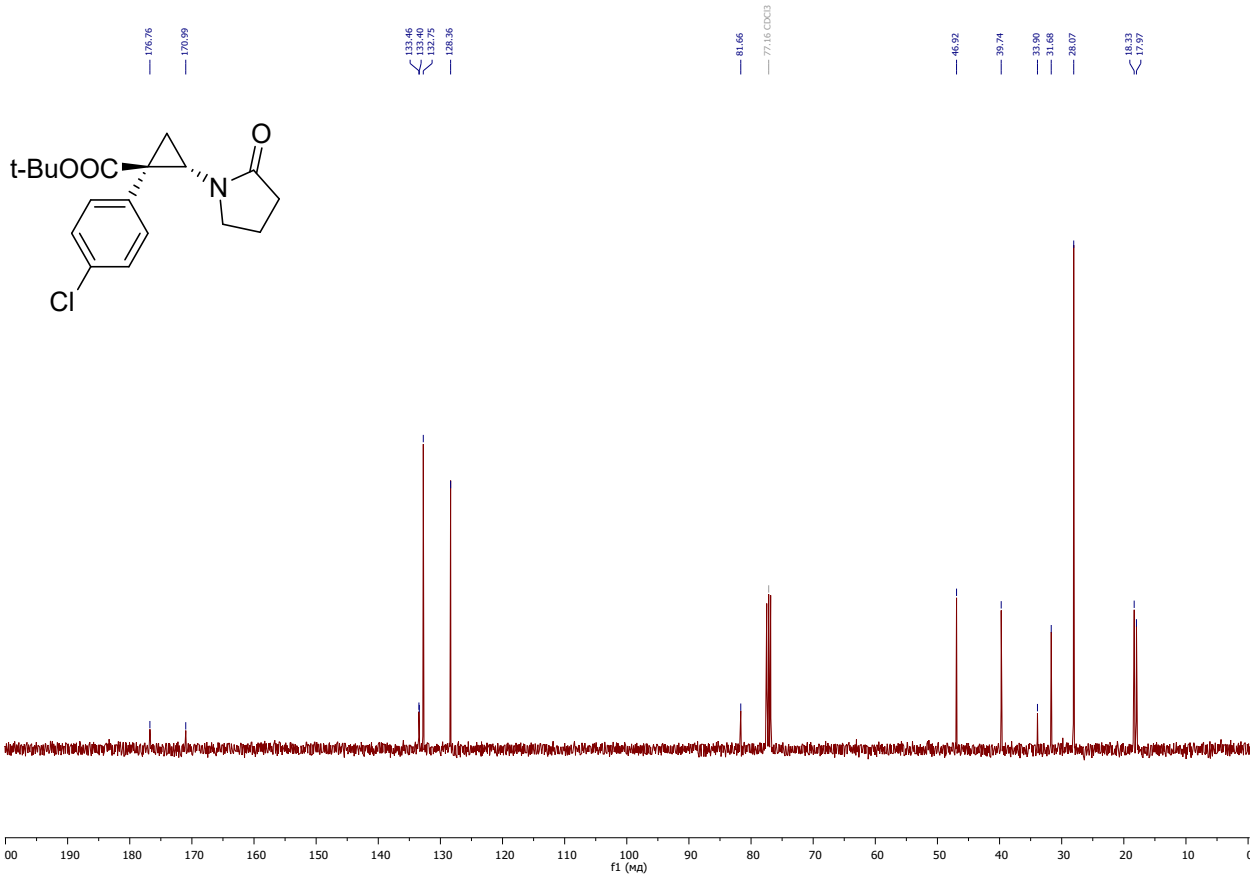


Figure S34. ^{13}**C** spectrum of **7b**.

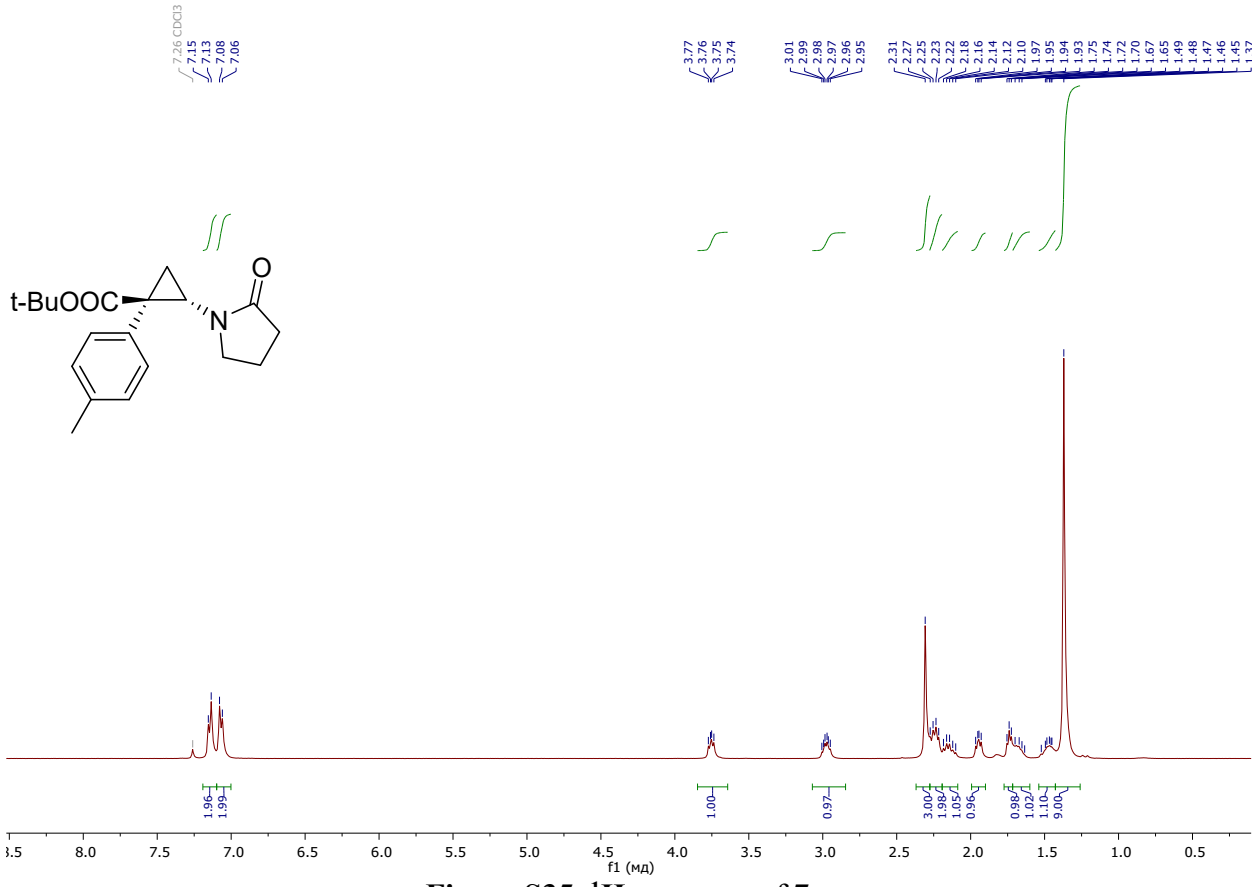


Figure S35. ^{1}**H** spectrum of **7c**.

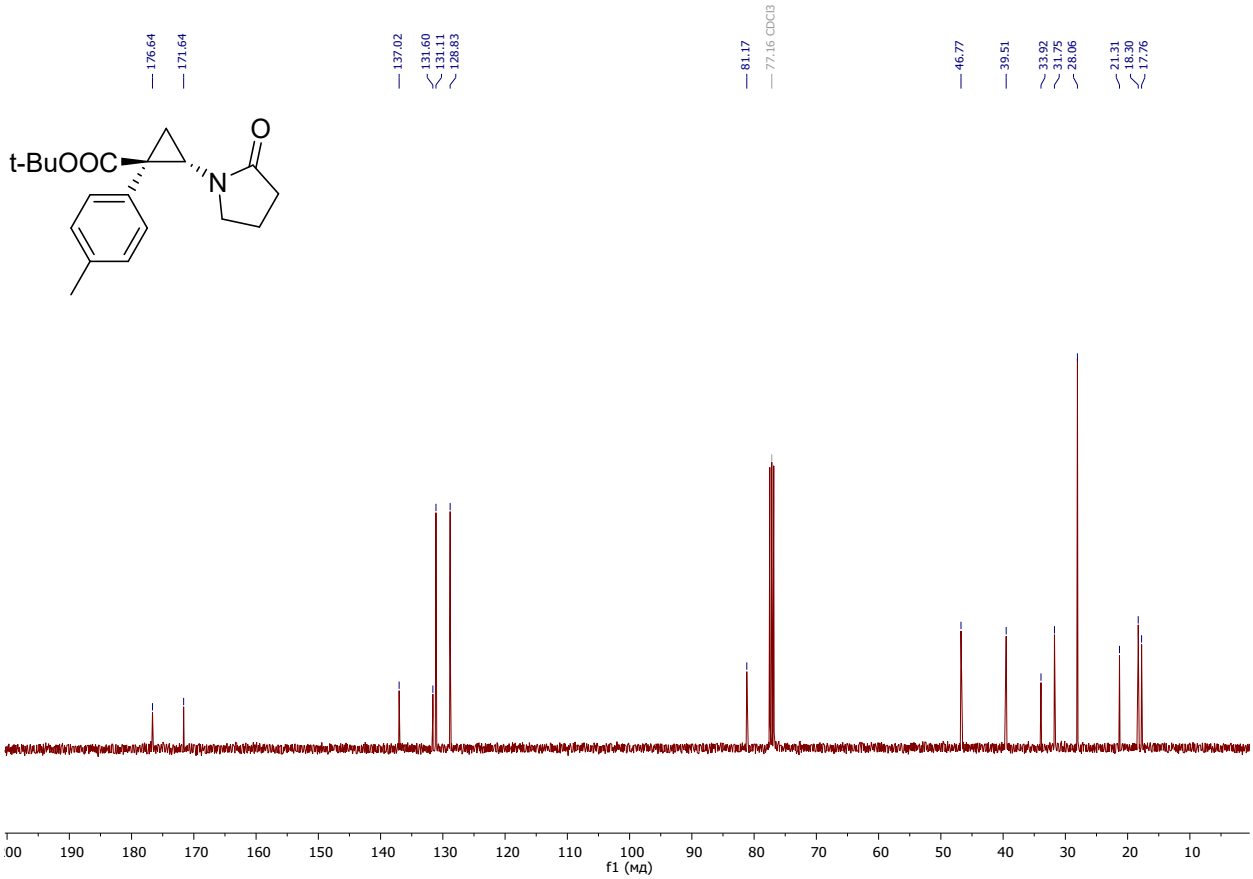


Figure S36. ^{13}**C** spectrum of **7c**.

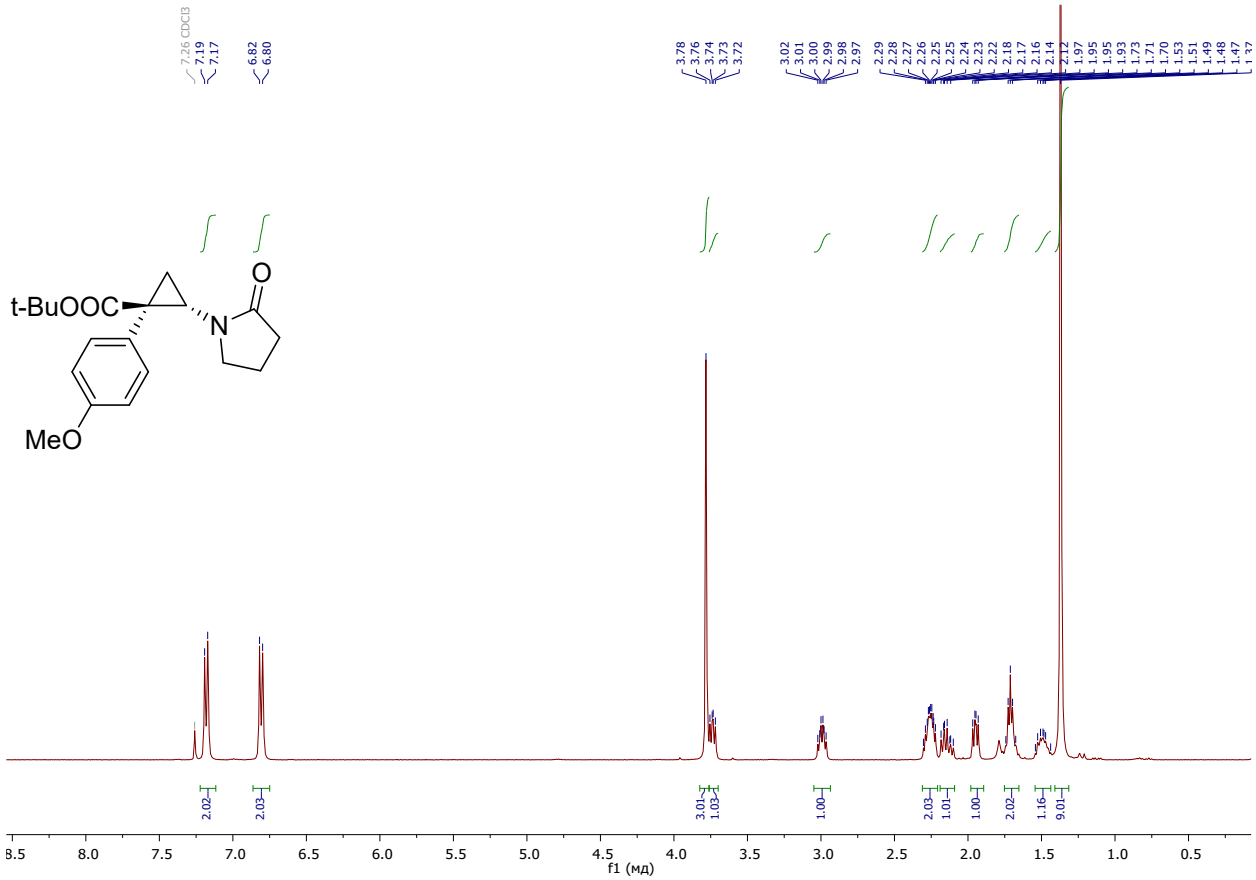


Figure S37. ^{1}**H** spectrum of **7d**.

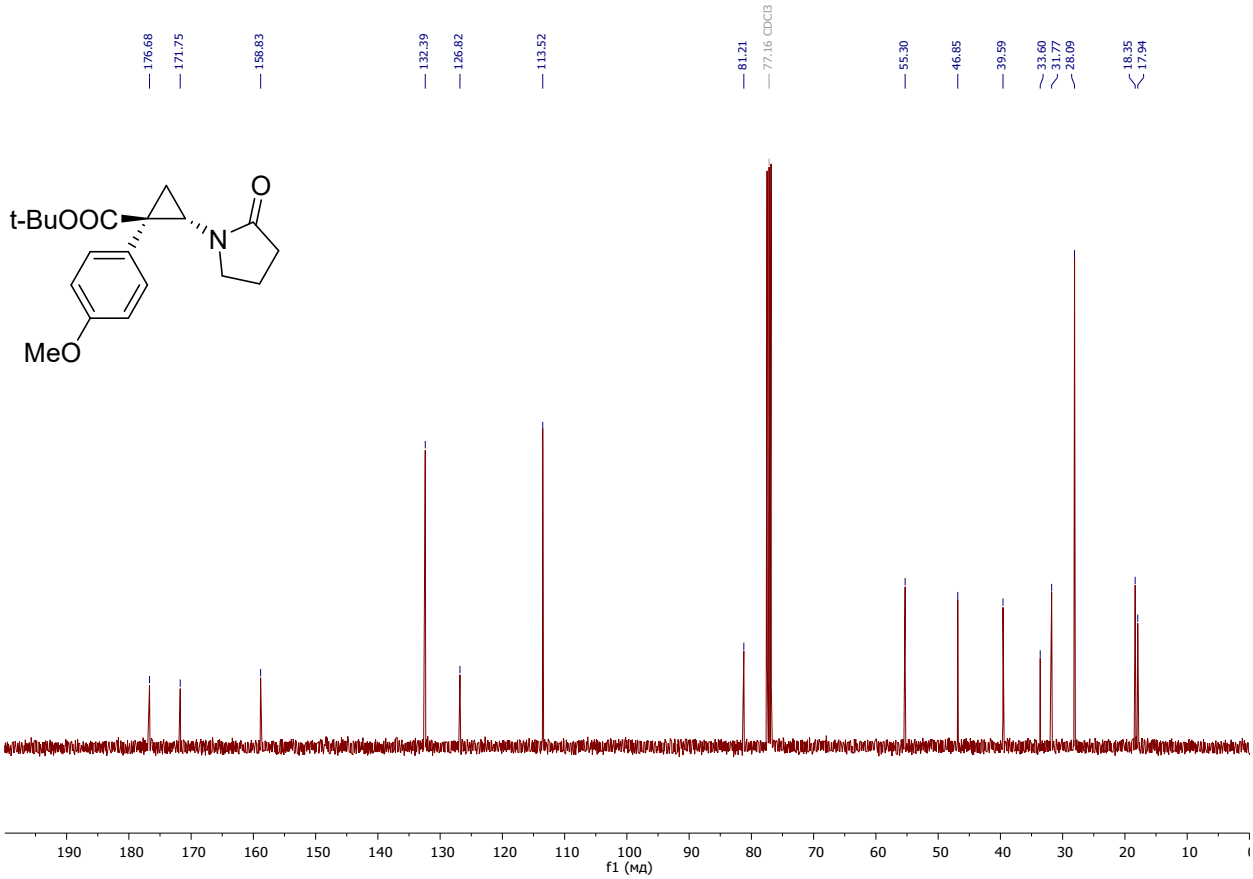


Figure S38. ^{13}**C** spectrum of **7d**.

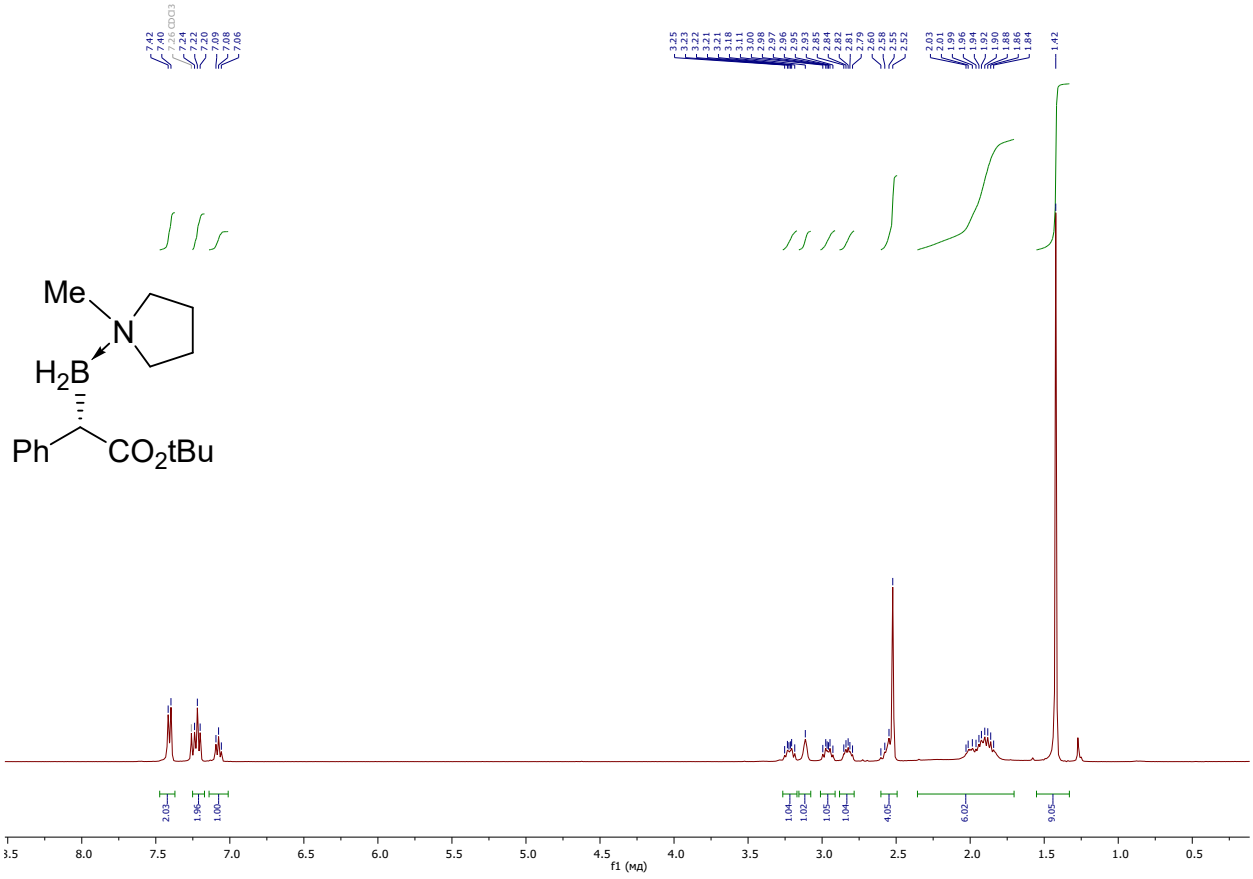


Figure S39. ^{1}**H** spectrum of **3**.

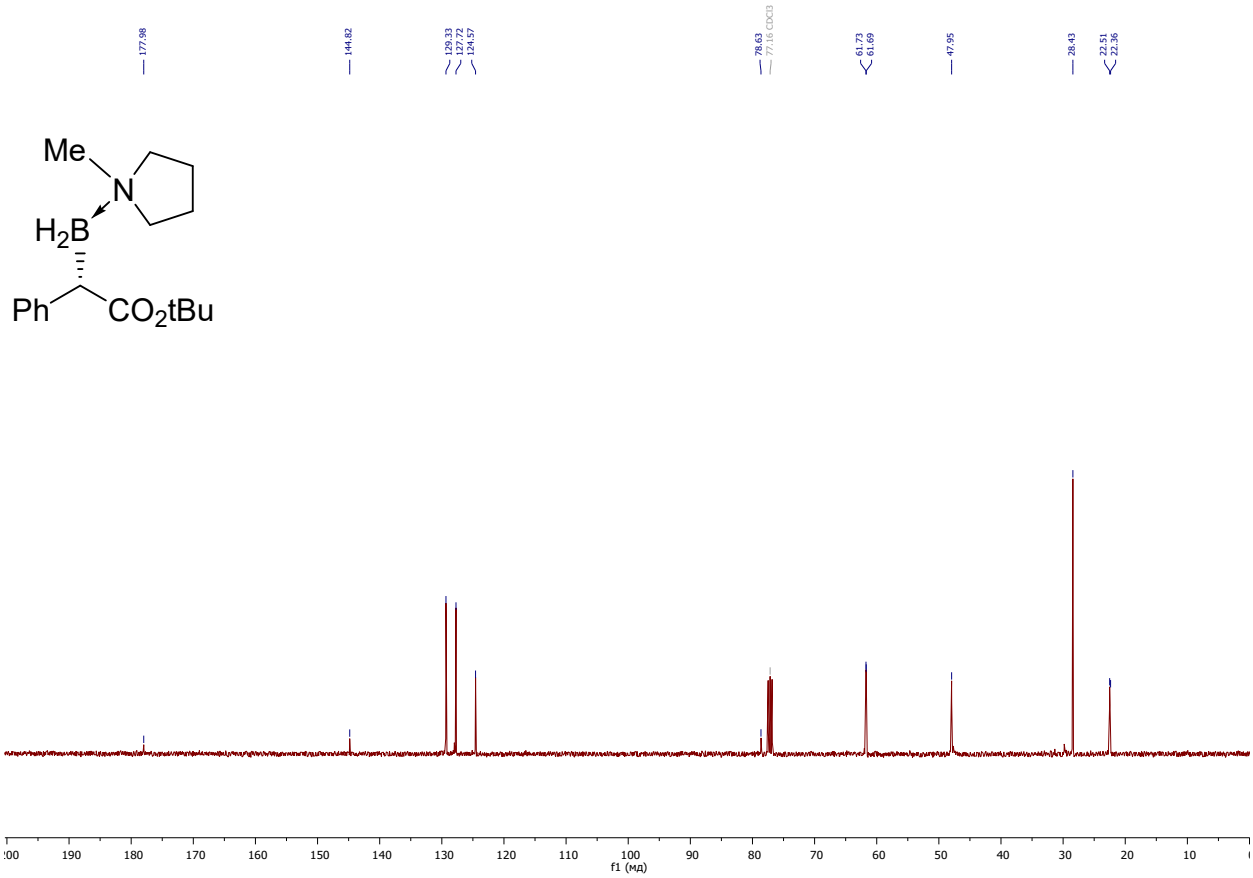


Figure S40. ^{13}**C** spectrum of **3**.

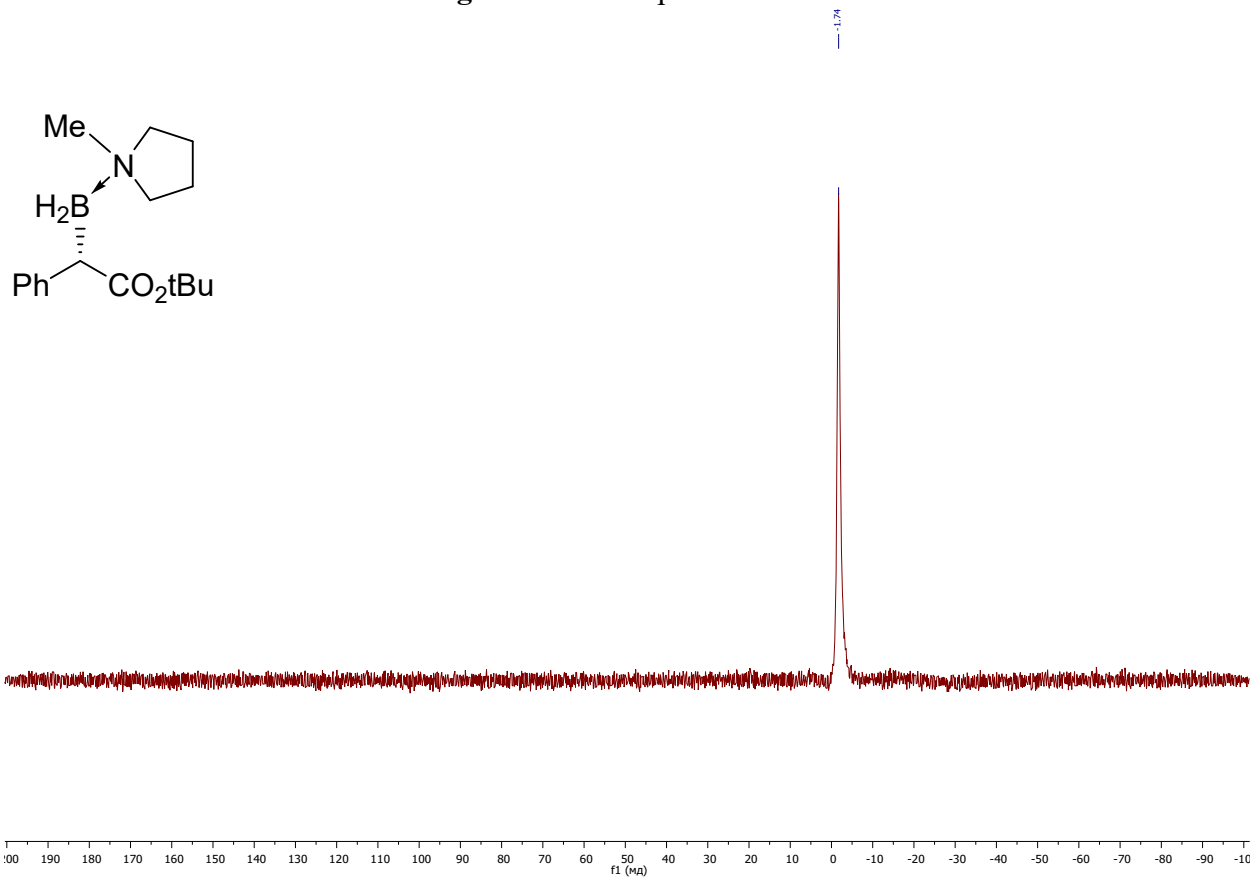


Figure S41. ^{11}**B{**^{1}**H}** spectrum of **3**.

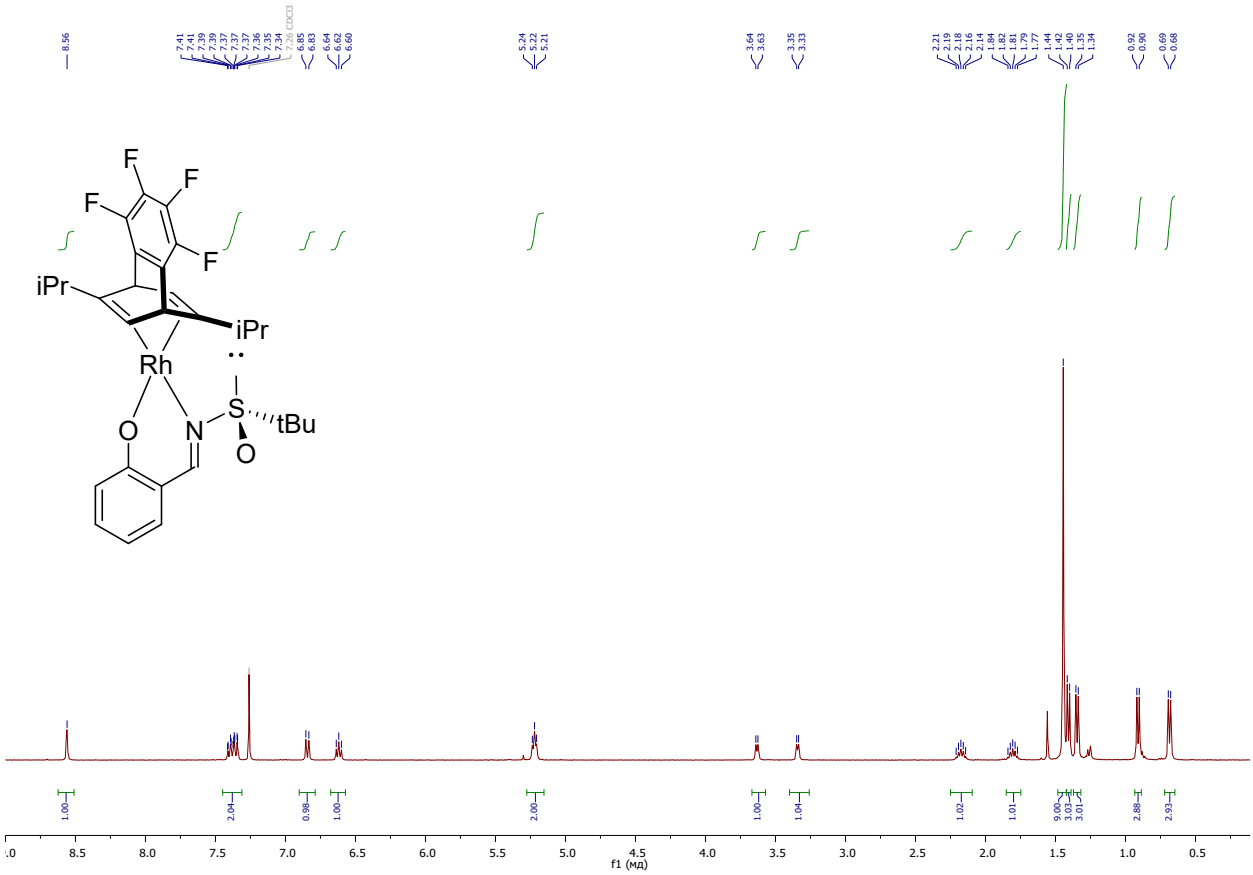


Figure S42. ^{1}**H** spectrum of *S,S*-**Rh-L3**.

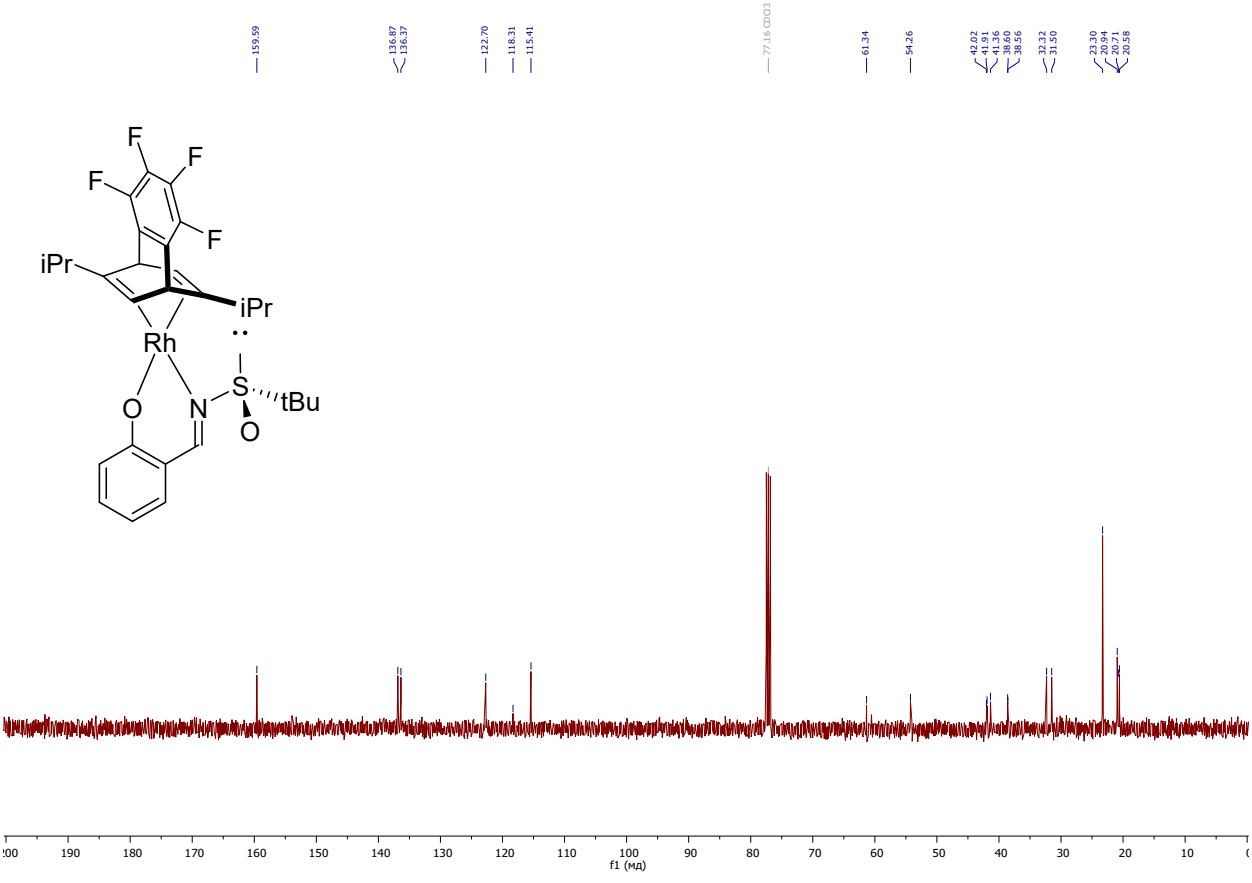


Figure S43. ^{13}**C** spectrum of *S,S*-**Rh-L3**.

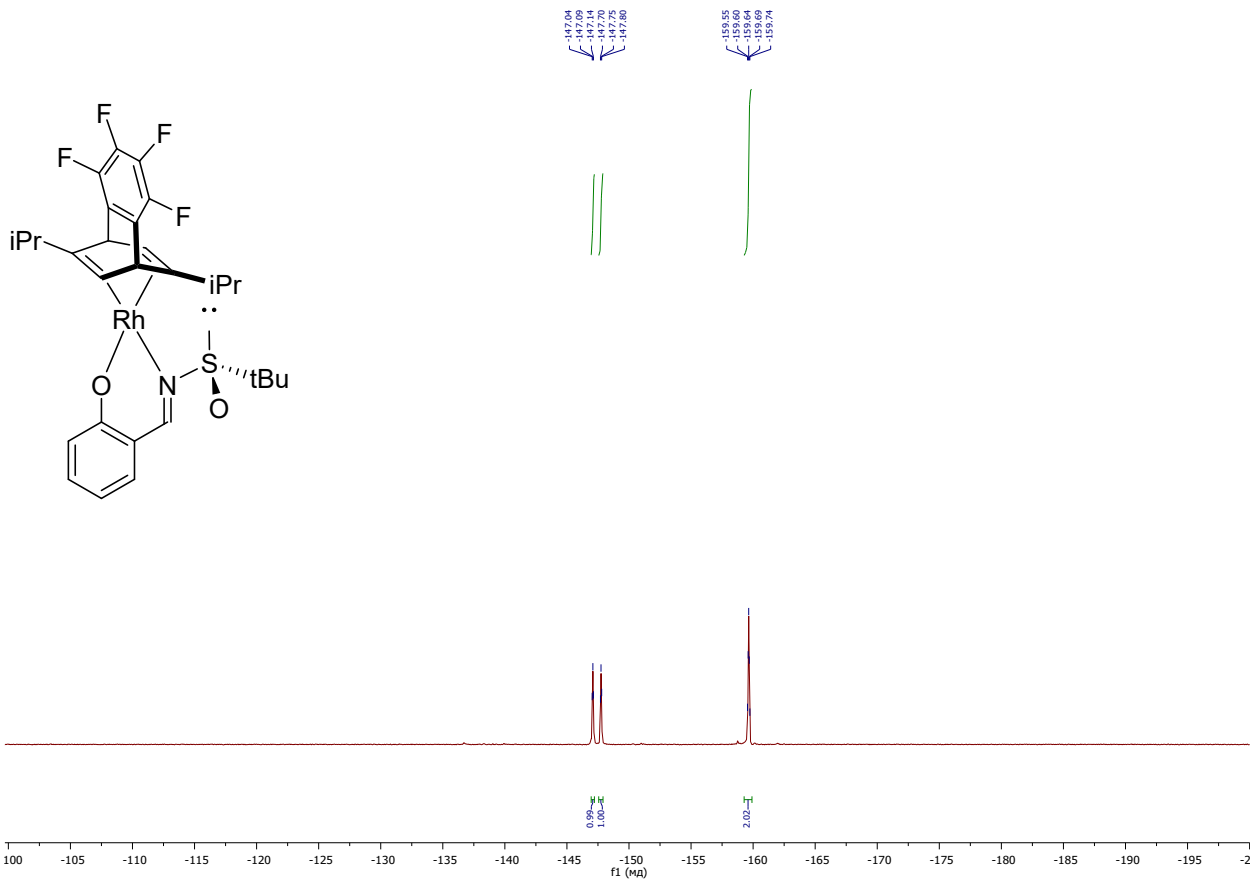


Figure S44. ^{19}**F** spectrum of *S,S*-**Rh-L3**.

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