Supplementary Information for:

Design of *N*-Sulfinyl Homoallylic Amines as Novel Sulfinamide-Olefin Hybrid Ligands for Asymmetric Catalysis: Application in Rh-Catalyzed Enantioselective 1,4-Additions

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1. General

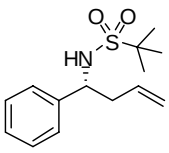
NMR spectra were recorded on a Varian spectrometer (300 MHz for ^{1}H, and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-*d* (δ 77.16) for ^{13}C NMR. HPLC was performed on a JASCO 2000 instrument by using Daicel columns.

2. General procedures for Rh-Catalyzed 1,4-additions.

Under N_2 atmosphere, a solution of $[RhCl(C_2H_4)_2]_2$ (1.5 mg, 0.0075 mmol of Rh), **11** (3.2 mg, 0.0075 mmol), and arylboronic acid (0.60 mmol) in 0.5 mL of dioxane was stirred at 60 °C for 30 min. To this mixture were added the α,β-unsaturated carbonyl compounds (0.25 mmol) and then aqueous K_3PO_4 (83 μL, 1.5M, 0.125 mmol). After being stirred at 60 °C for 1 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product **14**.

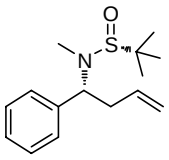
3. Characterization data of new ligand compounds.

Ligands **1**, **5-12** were synthesized according to the procedures[1] we reported before. Ligands **2** was synthesized following the literature[2]. Ligands **3** and **4** were synthesized by general *m*-CPBA epoxidation and MeI/NaH methylation of ligand **1**, respectively.



3

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (s, 9H), 2.59-2.63 (m, 2H), 4.39 (d, *J* = 8.7 Hz, 1H), 4.61-4,68 (m, 1H), 5.13-5.19 (m, 2H), 5.57-5.70 (m, 1H), 7.24-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.25, 42.62, 56.98, 58.94, 118.60, 125.43, 126.53, 127.76, 132.11, 140.92; ESI-MS: 266.2 [M - H]$^-$; HRMS (ESI) for $C_{14}H_{21}NO_2SNa$ [M + Na]$^+$: calcd 290.1191, found 288.1189.



4

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (s, 9H), 2.46 (s, 3H), 2.67-2.88 (m, 2H), 4.43 (t, *J* = 7.5 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 5.11 (d, *J* = 17.1 Hz, 1H), 5.67-5.81 (m, 1H), 7.25-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.99, 26.36, 36.11, 57.94, 66.40, 116.42, 126.84, 127.10, 127.54, 134.41, 138.44; ESI-MS: 265.9 [M + H]$^+$; HRMS (ESI) for $C_{15}H_{23}NOSNa$ [M + Na]$^+$: calcd 288.1398, found 288.1392.

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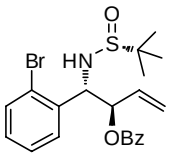
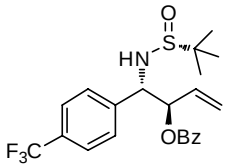
[1] (a) X.-W. Sun, M.-H. Xu, G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979; (b) X.-W. Sun, M. Liu, M.-H. Xu, G.-Q. Lin, *Org. Lett.*, 2008, **10**, 1259; (c) M. Liu, X.-W. Sun, M.-H. Xu G.-Q. Lin, *Chem. Eur. J.*, 2009, ***15***, 10217. (d) M. Liu, A. Shen, X.-W. Sun, F. Deng, M.-H. Xu, G.-Q. Lin, *Chem.Commun.*, 2010, **46**, 8460.

[2] J. T. Colyer, N. G. Andersen, J. S. Tedrow, T. S. Soukup, M. M. Faul, *J. Org. Chem.*, 2006, **71**, 6859.



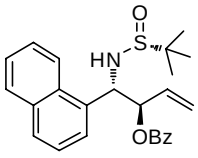
7

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 4.01 (d, *J* = 7.2 Hz, 1H), 5.22-5.26 (m, 1H), 5.32-5.41 (m, 2H), 5.80-5.96 (m, 2H), 7.13-7.19 (m, 1H), 7.32-7.59 (m, 7H), 8.02 (d, *J* = 10.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.69, 55.91, 59.28, 74.51, 118.76, 122.98, 126.73, 127.56, 128.76, 131.06, 132.34, 136.77, 164.18; ESI-MS: 450.0 $[M + H]^+$; HRMS (ESI) for $C_{21}H_{25}BrNO_3S$ $[M + H]^+$: calcd 450.0739, found 450.0748.



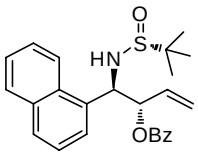
9

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (s, 9H), 3.83 (d, *J* = 5.7 Hz, 1H), 4.84-4.87 (m, 1H), 5.32-5.43 (m, 2H), 5.69-5.80 (m, 1H), 5.92-5.95 (m, 1H), 7.44-7.49 (m, 2H), 7.57-7.66 (m, 5H), 8.00 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.69, 55.88, 60.20, 75.25, 119.03, 124.65, 124.68, 127.52, 127.69, 128.70, 130.76, 132.55, 141.32, 164.52; ESI-MS: 440.0 $[M + H]^+$; HRMS (ESI) for $C_{22}H_{25}F_3NO_3S$ $[M + H]^+$: calcd 440.1507, found 440.1498.



10

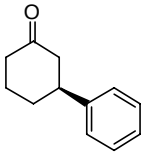
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 9H), 4.07 (d, *J* = 6.6 Hz, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 5.44 (d, *J* = 17.4 Hz, 1H), 5.72-5.83 (m, 2H), 6.01-6.04 (m, 1H), 7.42-7.67 (m, 7H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 2H), 8.46 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.76, 54.87, 55.92, 74.93, 118.63, 122.25, 124.22, 124.64, 125.04, 125.98, 127.57, 127.98, 128.05, 128.82, 129.02, 129.99, 130.64, 132.33, 132.89, 133.37, 164.73; ESI-MS: 422.0 $[M + H]^+$; HRMS (ESI) for $C_{25}H_{28}NO_3S$ $[M + H]^+$: calcd 422.1790, found 422.1800.



11

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 9H), 4.08 (d, *J* = 2.7 Hz, 1H), 5.35 (d, *J* = 10.5 Hz, 1H), 5.46 (d, *J* = 17.1 Hz, 1H), 5.71-5.86 (m, 2H), 6.00-6.02 (m, 1H), 7.40-7.65 (m, 7H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 8.41 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.61, 55.20, 55.87, 75.39, 119.24, 122.12, 124.01, 124.89, 125.16, 125.82, 127.51, 127.83, 127.98, 128.68, 128.75, 128.90, 130.38, 130.54, 132.31, 132.79, 164.74; ESI-MS: 422.0 $[M + H]^+$; HRMS (ESI) for $C_{25}H_{28}NO_3S$ $[M + H]^+$: calcd 422.1790, found 422.1800.

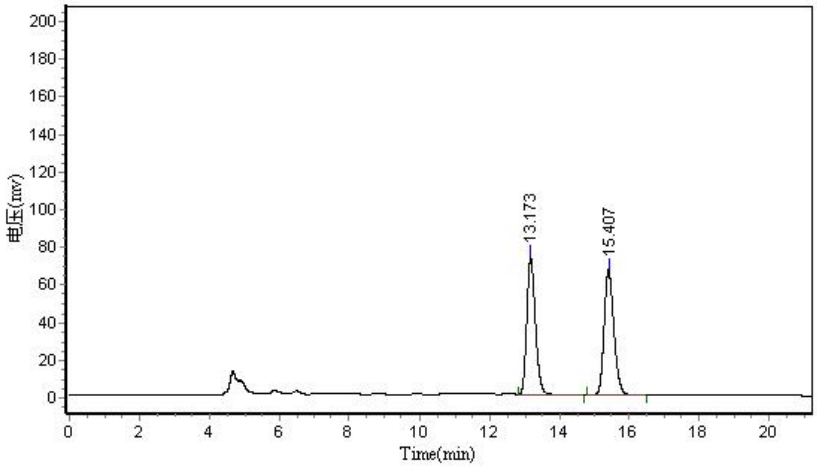
4. Characterization data and HPLC of addition products.



14a

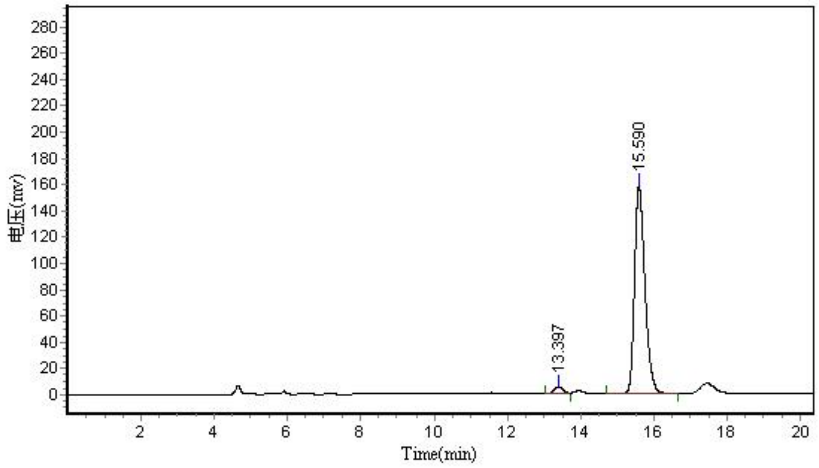
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70-1.92 (m, 2H), 2.05-2.20 (m, 2H), 2.35-2.62 (m, 4H), 2.95-3.08 (m, 1H), 7.19-7.25 (m, 3H), 7.34 (t, *J* = 7.8 Hz, 2H). $[\alpha]_D^{20}$ -18.2 (c 1.01, $CHCl_3$) for 96% ee [Lit. 1: $[\alpha]_D^{23}$ -19.5 (c 0.95, $CHCl_3$) for 93% ee of the *S*-isomer; *Org. Lett.*, **2008**, *10*, 4101; Lit. 2: $[\alpha]_D^{20}$ -21 (c 0.96, $CHCl_3$) for 97% ee of the *S*-isomer; *J. Am. Chem. Soc.* **1998**, *120*, 5579.]

HPLC: Chiracel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 13.4 min, 15.6 min (maj).



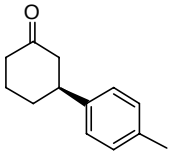
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.173	72456.828	1247548.000	49.1282
2		15.407	66176.023	1291822.500	50.8718
Total			138632.852	2539370.500	100.0000



Results

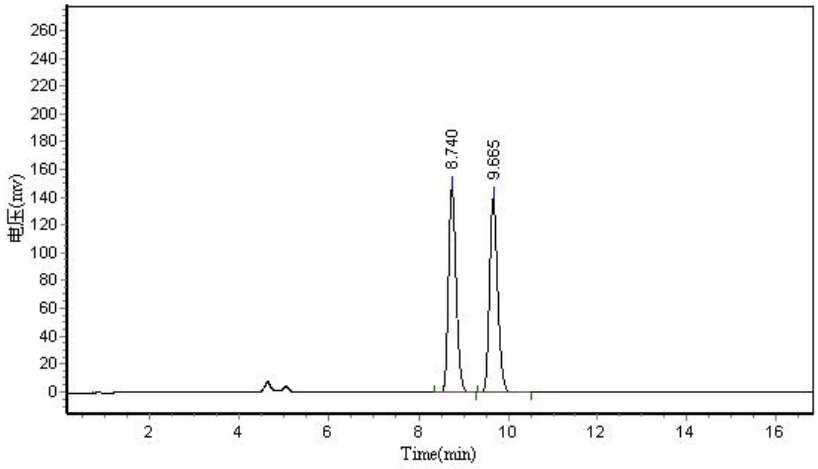
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.397	4830.880	75559.406	2.3753
2		15.590	157861.172	3105463.000	97.6247
Total			162692.052	3181022.406	100.0000



14b

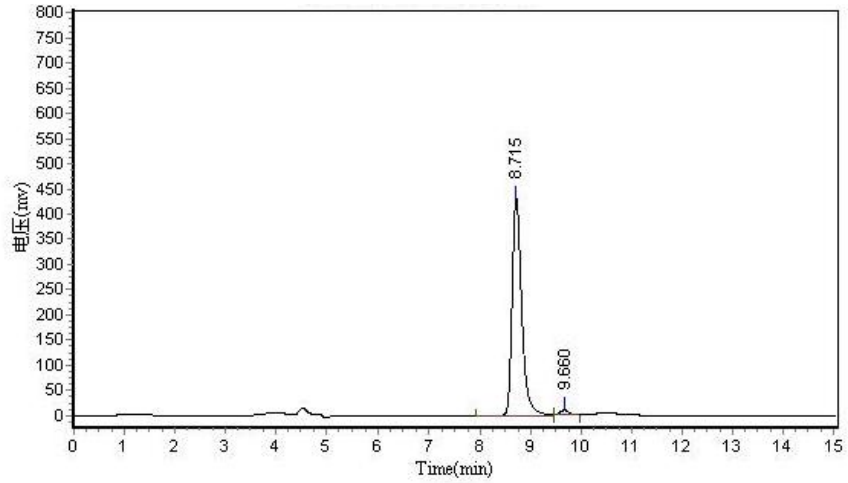
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73-1.94 (m, 2H), 2.05-2.17 (m, 2H), 2.31-2.60 (m, 4H), 2.33 (s, 3H), 2.94-3.02 (m, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H).

HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 8.7 min (maj), 9.7 min.



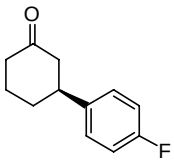
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.740	147199.172	1768476.250	49.9290
2		9.665	138828.344	1773508.750	50.0710
Total			286027.516	3541985.000	100.0000



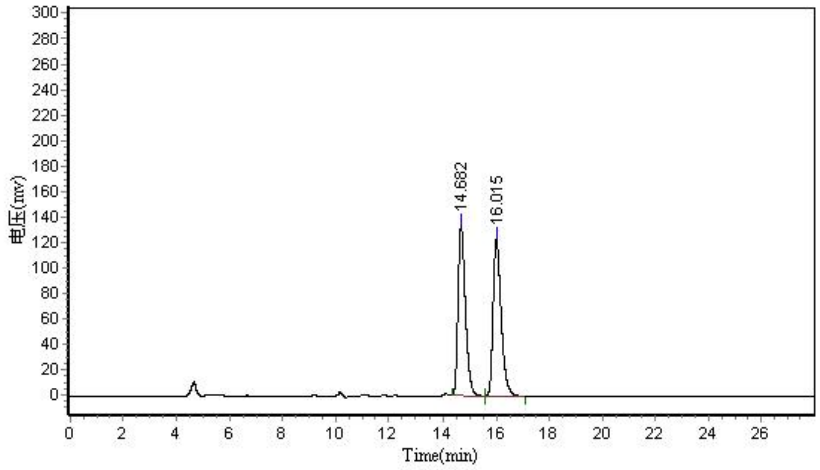
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.715	431277.594	5720740.500	98.1537
2		9.660	8952.486	107606.406	1.8463
Total			440230.080	5828346.906	100.0000



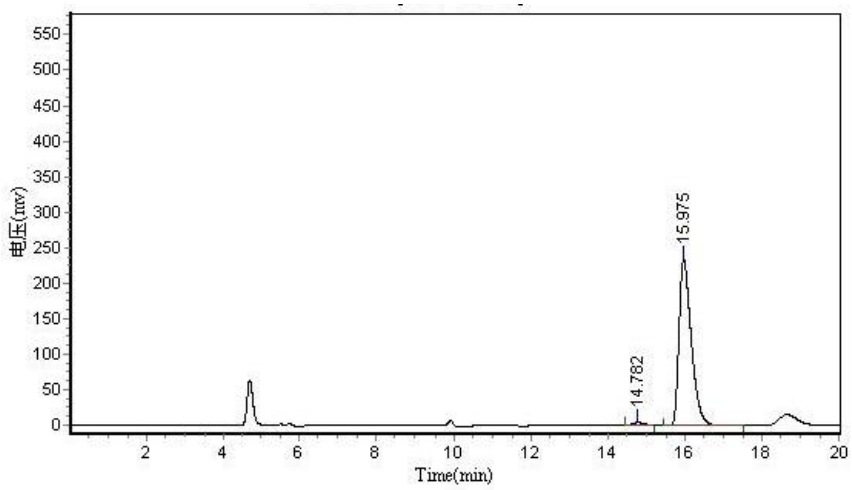
14c

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75-1.89 (m, 2H), 2.05-2.17 (m, 2H), 2.37-2.61 (m, 4H), 2.95-3.04 (m, 1H), 6.99-7.04 (m, 2H), 7.16-7.20 (m, 2H). HPLC: Chiracel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 14.8 min, 16.0 min (maj).



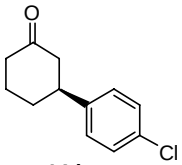
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.682	133924.609	2598232.250	49.7400
2		16.015	123799.938	2625395.500	50.2600
Total			257724.547	5223627.750	100.0000



Results

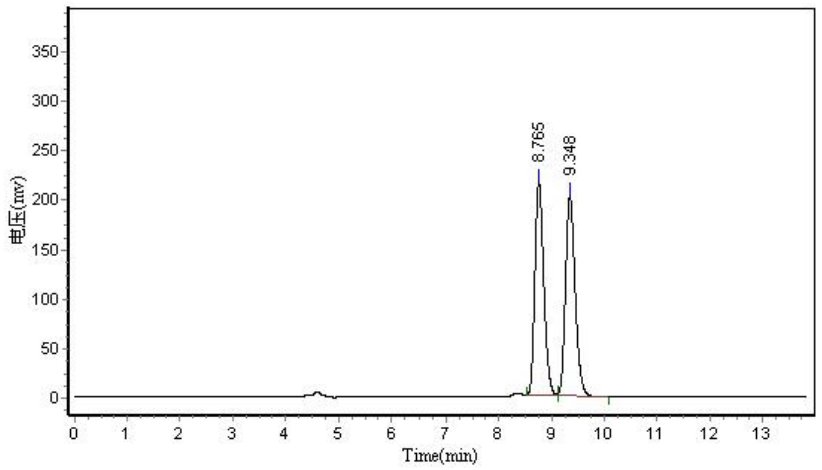
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.782	3928.320	72054.898	1.3782
2		15.975	233349.188	5156141.000	98.6218
Total			237277.508	5228195.898	100.0000



14d

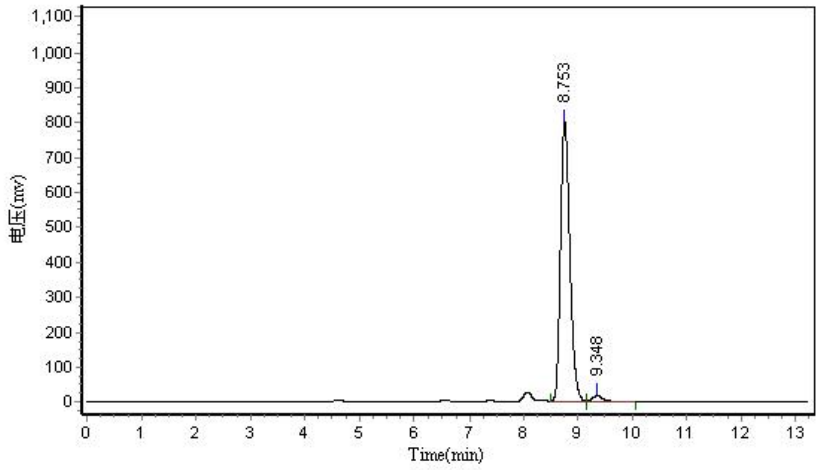
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74-1.89 (m, 2H), 2.05-2.19 (m, 2H), 2.32-2.61 (m, 4H), 2.94-3.04 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H).

HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 8.8 min (maj), 9.3 min.



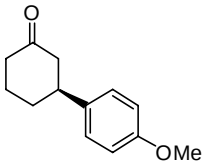
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.765	216798.250	2577154.500	49.7392
2		9.348	202160.531	2604181.000	50.2608
Total			418958.781	5181335.500	100.0000



Results

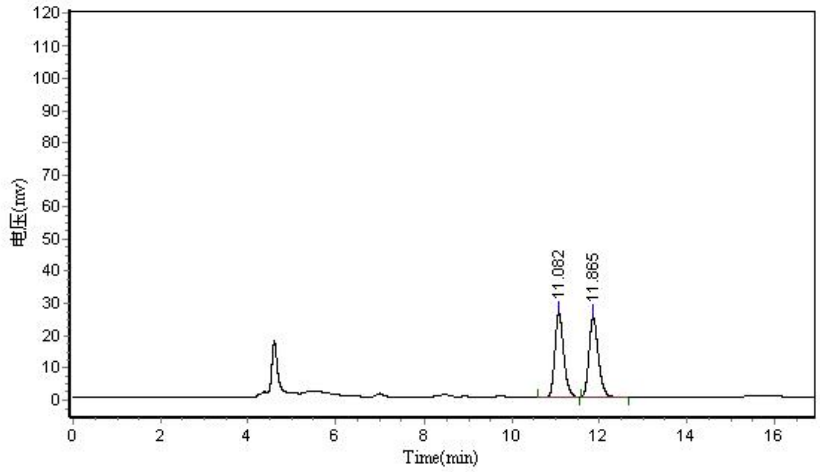
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.753	800116.500	9554647.000	97.4940
2		9.348	16725.496	245593.203	2.5060
Total			816841.996	9800240.203	100.0000



14e

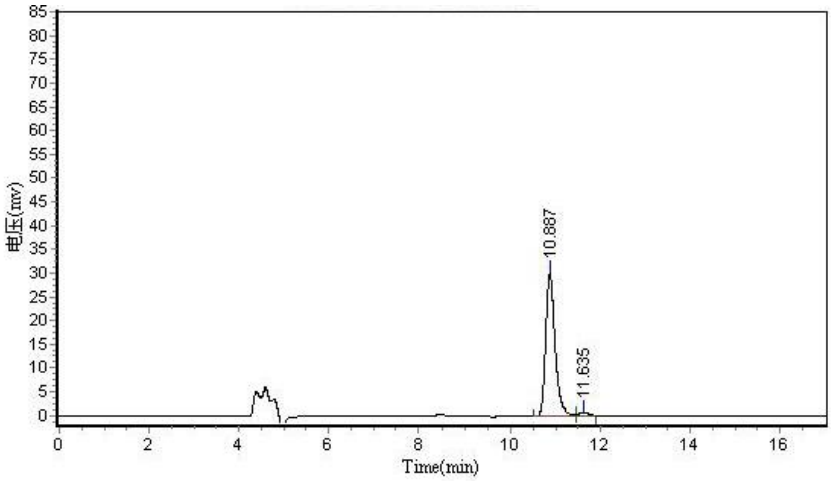
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73-1.88 (m, 2H), 2.05-2.16 (m, 2H), 2.36-2.61 (m, 4H), 2.92-3.01 (m, 1H), 3.80 (s, 3H), 6.87 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H).

HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 10.9 min (maj), 11.6 min.



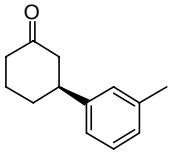
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.082	26127.211	368003.719	49.7049
2		11.865	24887.816	372373.969	50.2951
Total			51015.027	740377.688	100.0000



Results

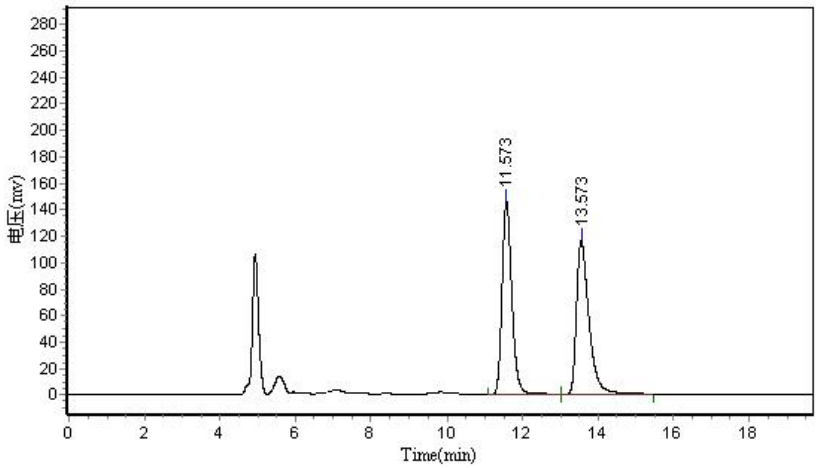
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.887	29978.938	439162.750	97.4335
2		11.635	789.269	11567.850	2.5665
Total			30768.206	450730.600	100.0000



14f

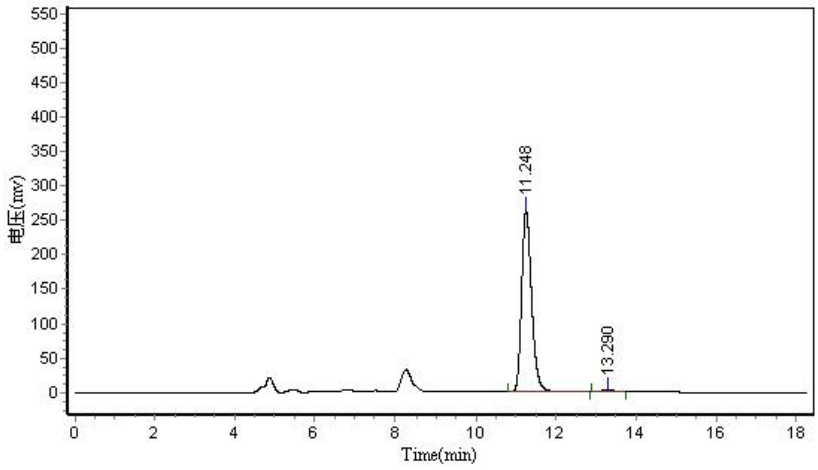
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75-1.91 (m, 2H), 2.05-2.18 (m, 2H), 2.35 (s, 3H), 2.35-2.62 (m, 4H), 2.92-3.01 (m, 1H), 7.01-7.07 (m, 3H), 7.20-7.26 (m, 1H).

HPLC: Chiracel OD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 11.2 min (maj), 13.3 min.



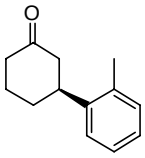
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.573	145153.859	2621532.250	49.5832
2		13.573	115854.695	2665600.500	50.4167
Total			261008.555	5287132.750	100.0000



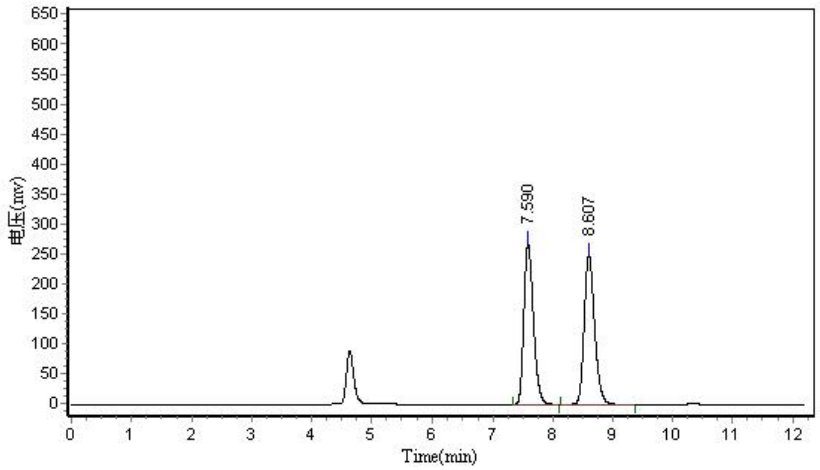
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.248	264353.469	4607014.000	98.8376
2		13.290	2839.830	54182.000	1.1624
Total			267193.299	4661196.000	100.0000



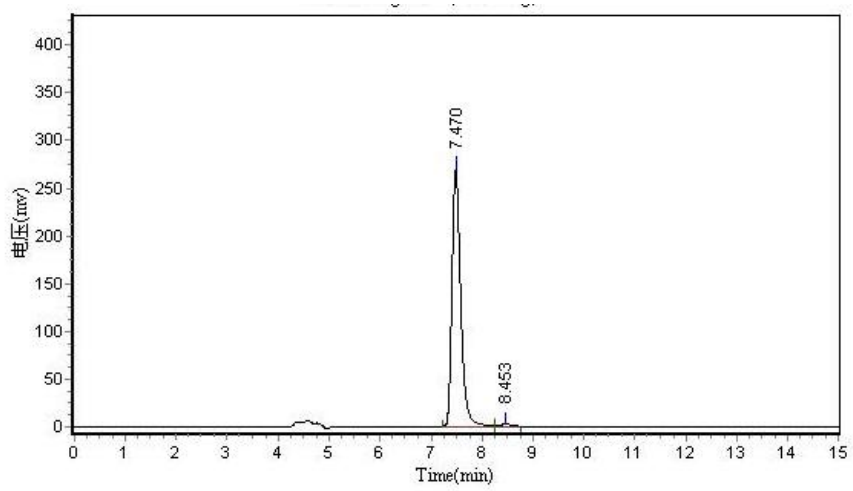
14g

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.77-1.91 (m, 2H), 1.99-2.05 (m, 1H), 2.16-2.20 (m, 1H), 2.32 (s, 3H), 2.37-2.53 (m, 4H), 3.16-3.25 (m, 1H), 7.13-7.25 (m, 4H). HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 7.5 min (maj), 8.5 min.



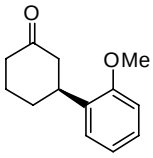
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.590	268902.563	2969217.750	49.7755
2		8.607	249240.563	2996002.750	50.2245
Total			518143.125	5965220.500	100.0000



Results

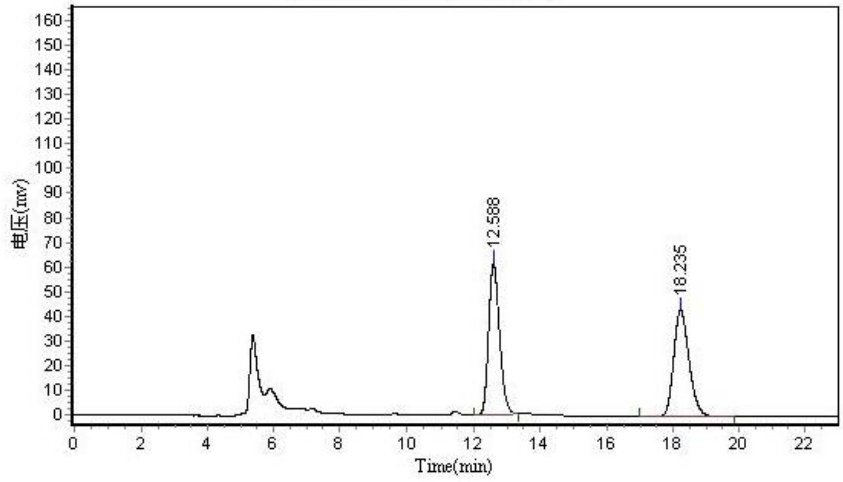
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.470	269233.875	3252994.000	98.7885
2		8.453	2745.774	39892.641	1.2115
Total			271979.649	3292886.641	100.0000



14h

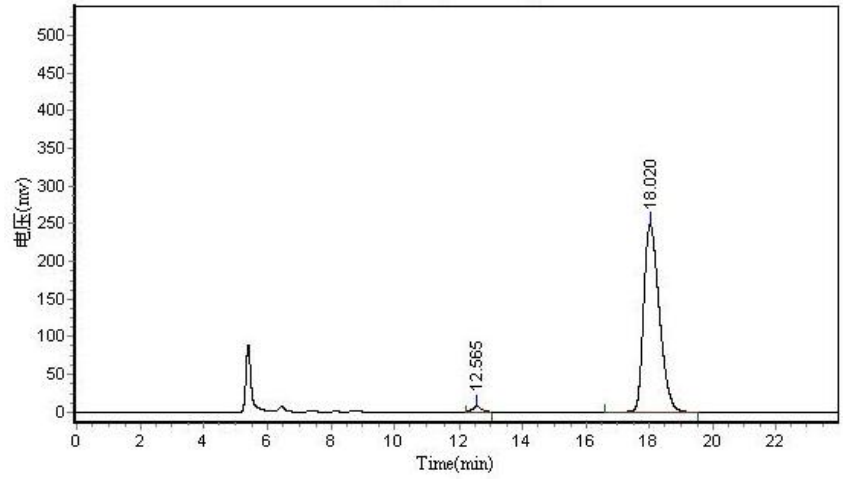
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75-1.93 (m, 2H), 2.01-2.16 (m, 2H), 2.34-2.61 (m, 4H), 3.37-3.46 (m, 1H), 3.82 (s, 3H), 6.86-6.97 (m, 2H), 7.18-7.26 (m, 2H).

HPLC: Chiracel AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.6 mL/min; Retention time: 12.6 min, 18.0 min (maj).



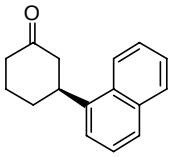
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.588	61001.832	1400663.375	50.3000
2		18.235	42966.145	1383954.000	49.7000
Total			103967.977	2784617.375	100.0000



Results

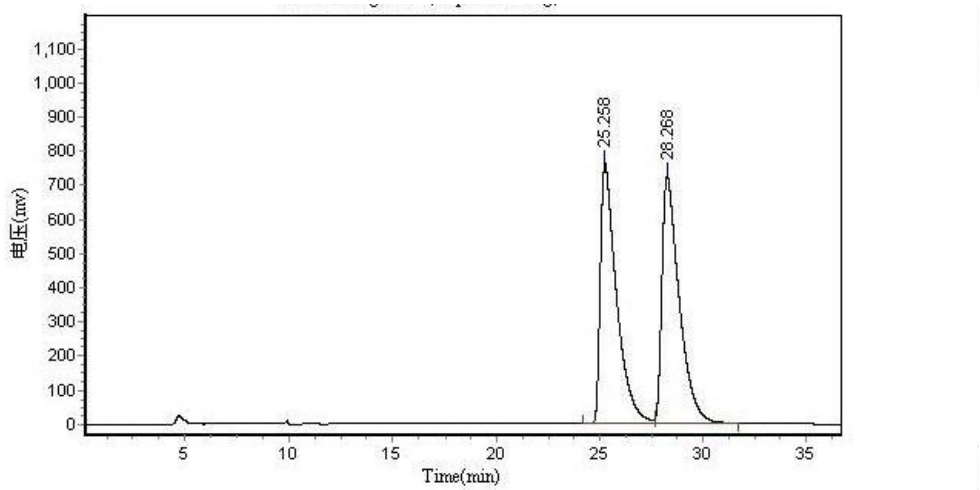
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.565	6957.111	147213.906	1.7008
2		18.020	248969.828	8508237.000	98.2992
Total			255926.939	8655450.906	100.0000



14i

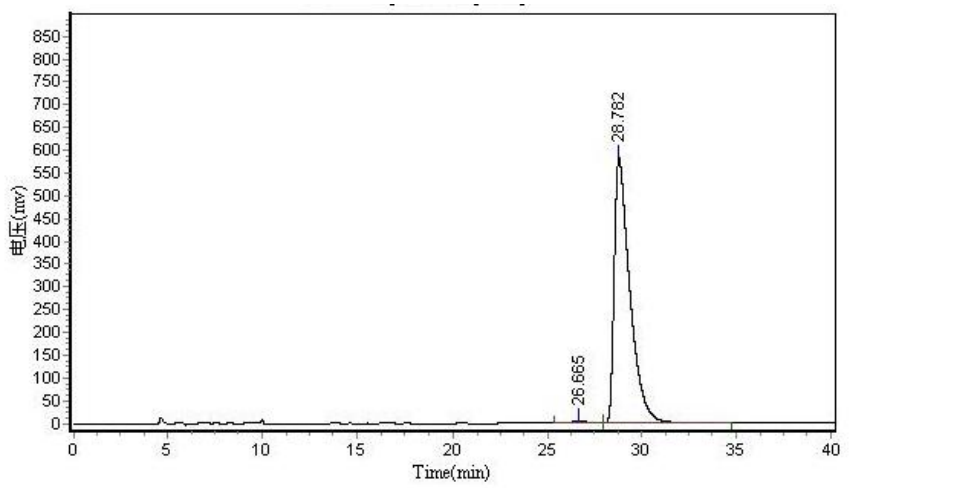
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89-2.07 (m, 2H), 2.19-2.27 (m, 2H), 2.41-2.79 (m, 4H), 3.81-3.90 (m, 1H), 7.39-7.56 (m, 4H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H).

HPLC: Chiracel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 26.7 min, 28.8 min (maj).



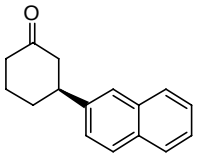
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.258	760713.625	41566560.000	49.6772
2		28.268	725356.688	42106672.000	50.3228
Total			1486070.313	83673232.000	100.0000



Results

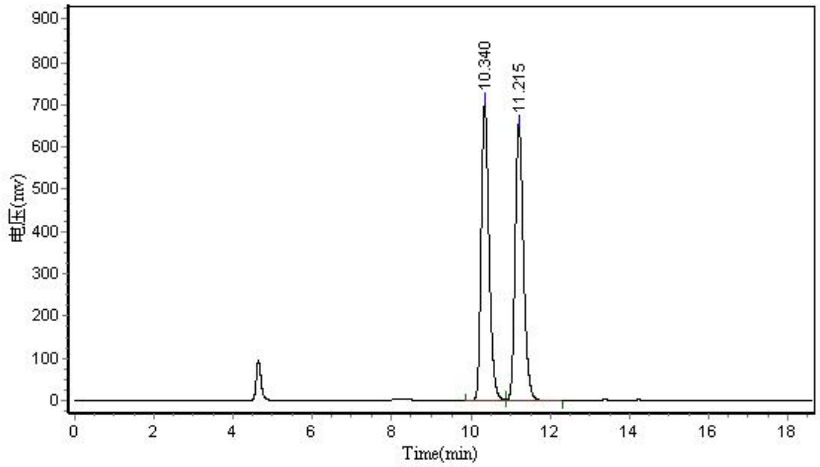
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.665	4907.527	318376.906	0.9361
2		28.782	581520.375	33691380.000	99.0639
Total			586427.902	34009756.906	100.0000



14j

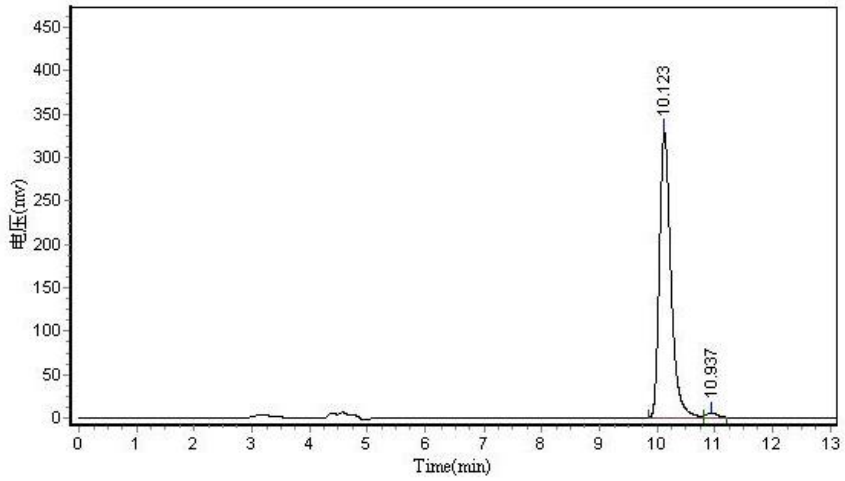
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81-2.04 (m, 2H), 2.15-2.23 (m, 2H), 2.37-2.53 (m, 2H), 2.59-2.71 (m, 2H), 3.14-3.22 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.45-7.47 (m, 2H), 7.64 (s, 1H), 7.79-7.83 (m, 3H).

HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 10.1 min (maj), 10.9min.



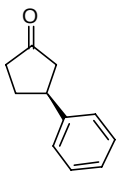
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.340	700643.750	9661382.000	50.1977
2		11.215	652979.500	9585274.000	49.8023
Total			1353623.250	19246656.000	100.0000



Results

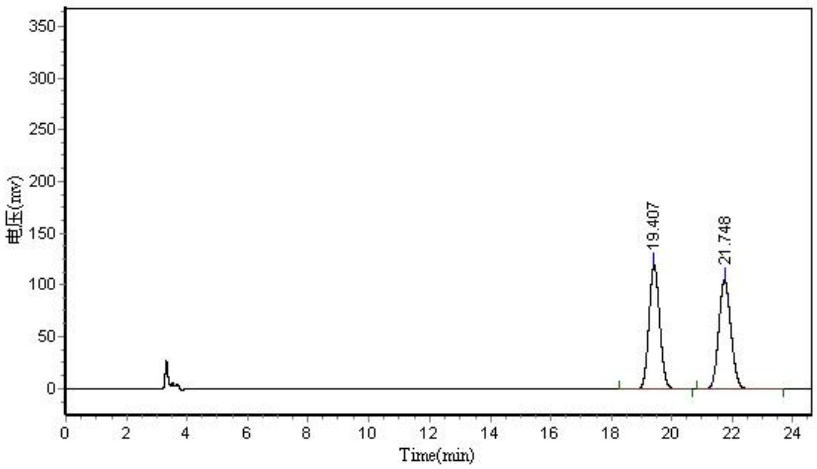
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.123	329012.938	4567270.000	98.3265
2		10.937	5712.250	77732.328	1.6735
Total			334725.187	4645002.328	100.0000



14k

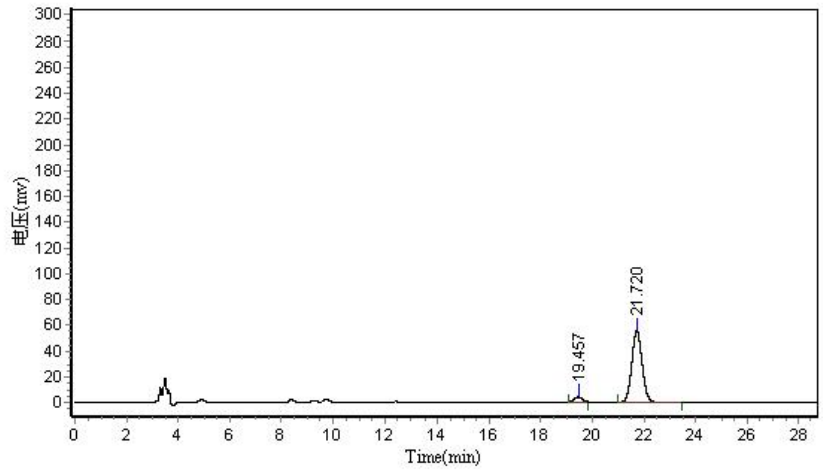
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90-2.08 (m, 1H), 2.22-2.54 (m, 4H), 2.67 (dd, *J* = 18.3, 7.8 Hz, 1H), 3.35-3.49 (m, 1H), 7.22-7.30 (m, 3H), 7.31-7.39 (m, 2H). $[\alpha]_D^{20}$ -81.2 (c 0.81, $CHCl_3$) for 90% ee [Lit. 1: $[\alpha]_D^{24}$ -73.8 (c 1.21, $CHCl_3$) for 80% ee of the *S*-isomer; *Org. Lett.*, **2008**, *10*, 4101; Lit. 2: $[\alpha]_D^{20}$ -92 (c 0.82, $CHCl_3$) for 97% ee of the *S*-isomer; *J. Am. Chem. Soc.* **1998**, *120*, 5579.]

HPLC: Chiracel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 19.5 min, 21.7 min (maj).



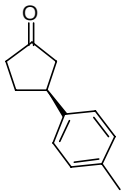
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.407	120187.859	2974788.250	49.7440
2		21.748	105346.766	3005400.750	50.2560
Total			225534.625	5980189.000	100.0000



Results

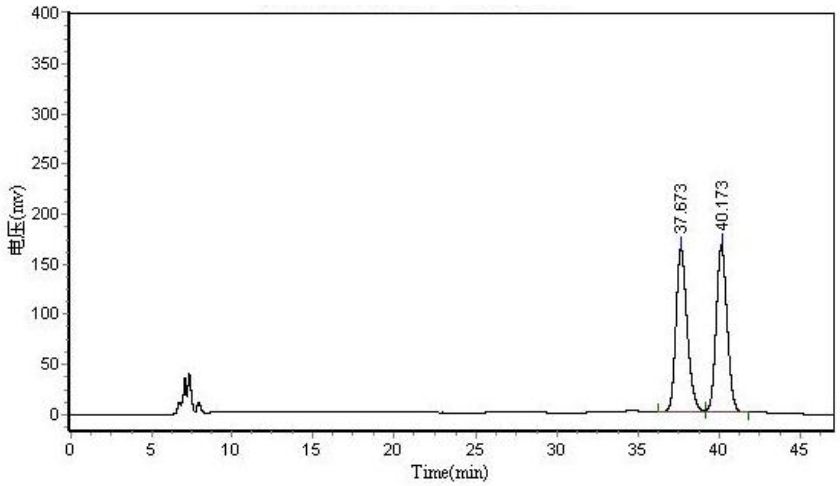
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.457	3680.409	83031.703	5.1053
2		21.720	55607.699	1543348.875	94.8947
Total			59288.108	1626380.578	100.0000



14l

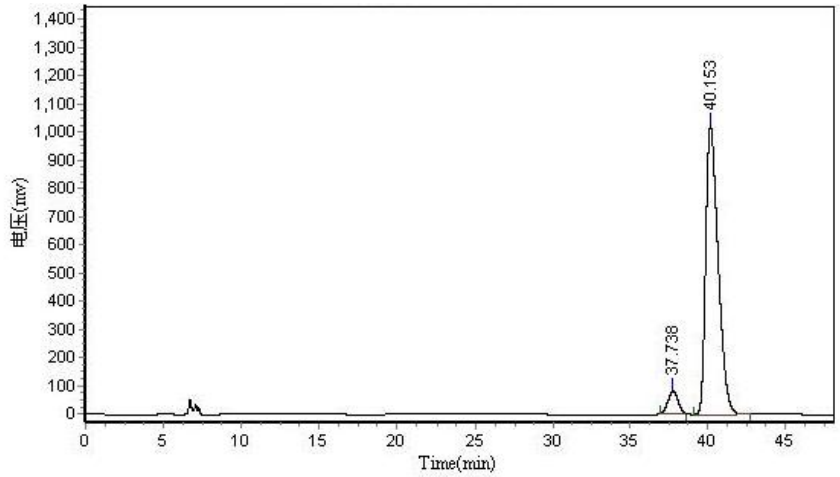
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90-2.04 (m, 1H), 2.27-2.51 (m, 4H), 2.34 (s, 3H), 2.66 (dd, *J* = 18.0, 7.5 Hz, 1H), 3.33-3.45 (m, 1H), 7.16 (s, 4H).

HPLC: Chiracel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 99/1; flow = 0.5 mL/min; Retention time: 37.7 min, 40.2 min (maj).



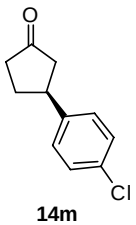
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		37.673	163888.156	7968155.500	49.9028
2		40.173	167311.484	7999200.000	50.0972
Total			331199.641	15967355.500	100.0000



Results

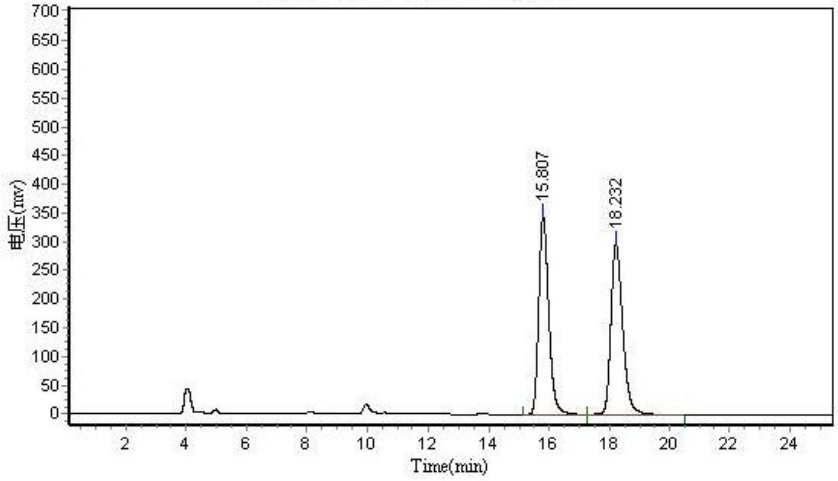
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		37.738	80246.055	3657647.500	6.0533
2		40.153	1023675.750	56766132.000	93.9467
Total			1103921.805	60423779.500	100.0000



14m

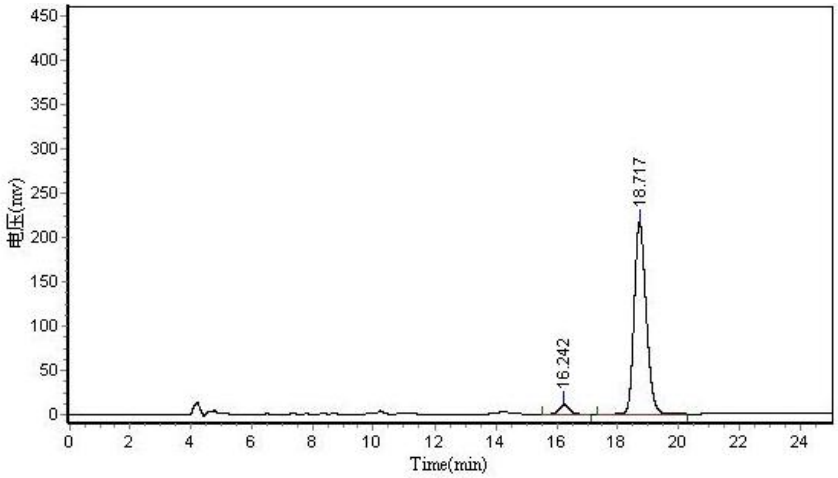
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88-2.02 (m, 1H), 2.24-2.51 (m, 4H), 2.66 (dd, *J* = 18.0, 7.5 Hz, 1H), 3.34-3.45 (m, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H).

HPLC: Chiracel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 16.2 min, 18.7 min (maj).



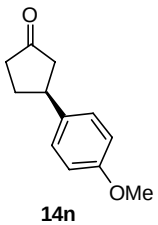
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.807	346445.969	8030962.500	49.7680
2		18.232	297831.906	8105829.000	50.2320
Total			644277.875	16136791.500	100.0000



Results

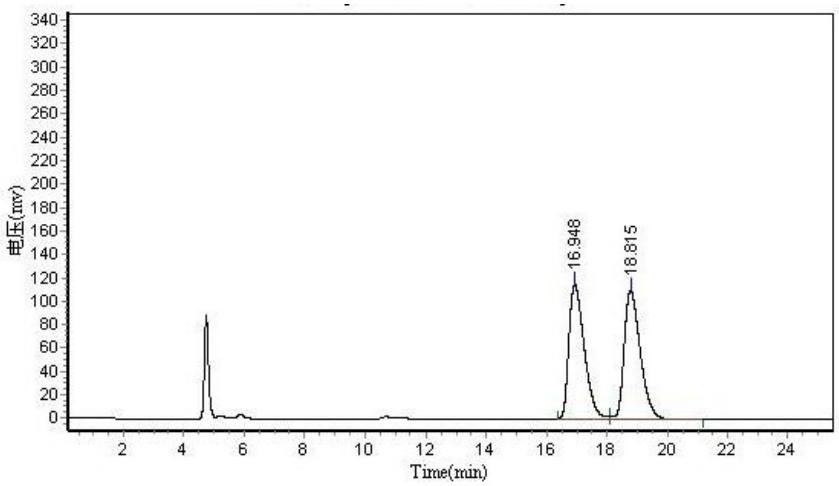
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.242	11058.124	246867.031	4.0098
2		18.717	216801.609	5909662.000	95.9902
Total			227859.733	6156529.031	100.0000



14n

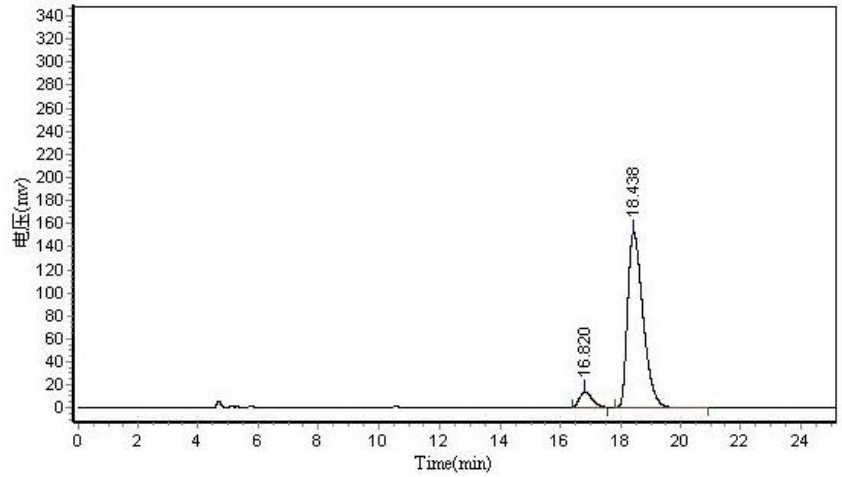
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88-2.02 (m, 1H), 2.22-2.50 (m, 4H), 2.64 (dd, *J* = 18.0, 7.5 Hz, 1H), 3.31-3.43 (m, 1H), 3.80 (s, 3H), 6.88 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H).

HPLC: Chiracel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 99/1; flow = 0.5 mL/min; Retention time: 16.8 min, 18.4 min (maj).



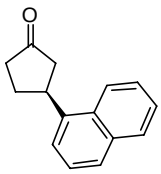
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.948	115365.813	4145231.500	50.1130
2		18.815	110029.117	4126538.750	49.8870
Total			225394.930	8271770.250	100.0000



Results

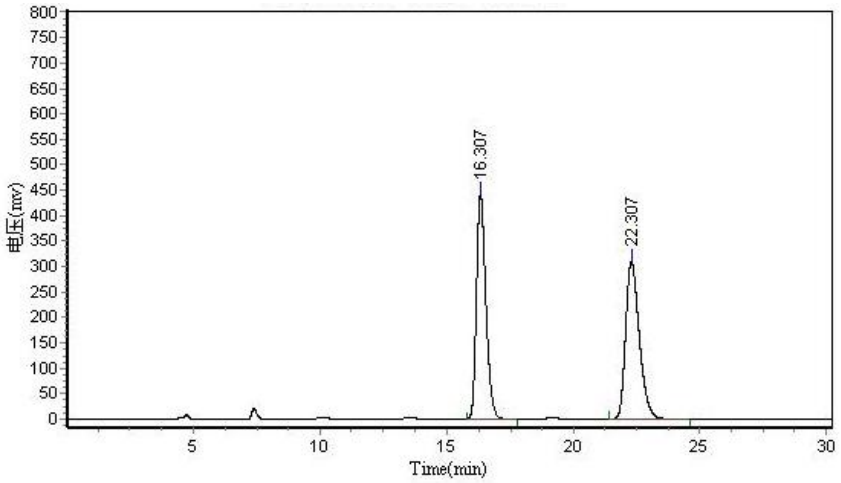
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.820	13220.216	385383.406	6.6354
2		18.438	152133.375	5422572.500	93.3646
Total			165353.591	5807955.906	100.0000



14o

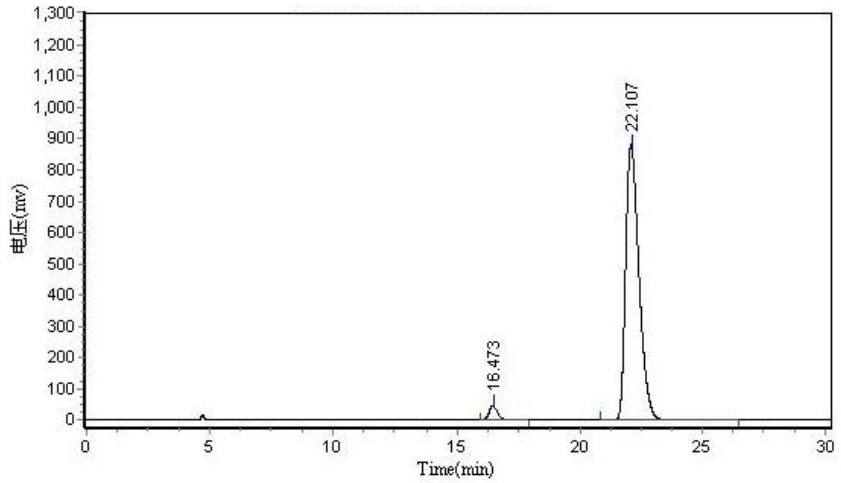
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10-2.23 (m, 1H), 2.31-2.59 (m, 4H), 2.80 (dd, *J* = 18.0, 7.2 Hz, 1H), 4.15-4.25 (m, 1H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.42-7.58 (m, 3H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H).

HPLC: Chiracel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 16.5 min, 22.1 min (maj).



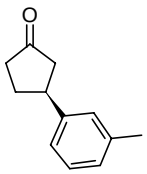
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.307	441572.125	11484082.000	49.6569
2		22.307	310135.531	11642778.000	50.3431
Total			751707.656	23126860.000	100.0000



Results

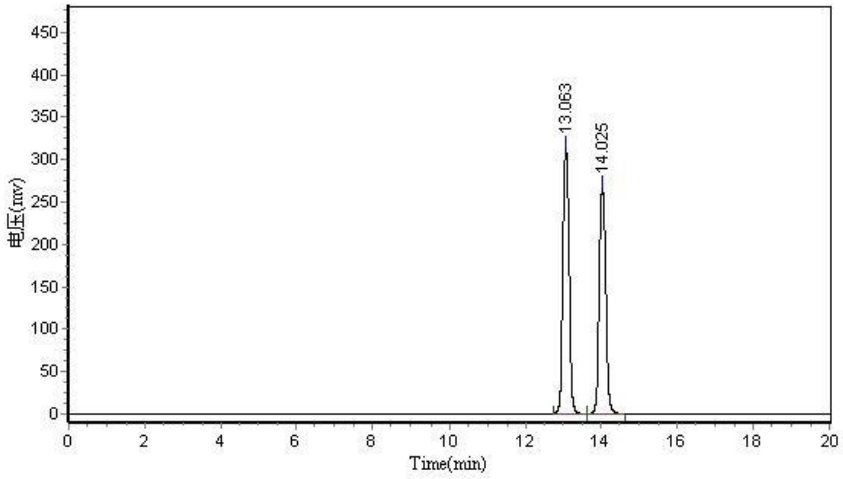
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.473	45993.500	1173993.125	3.4237
2		22.107	879358.438	33115880.000	96.5763
Total			925351.938	34289873.125	100.0000



14p

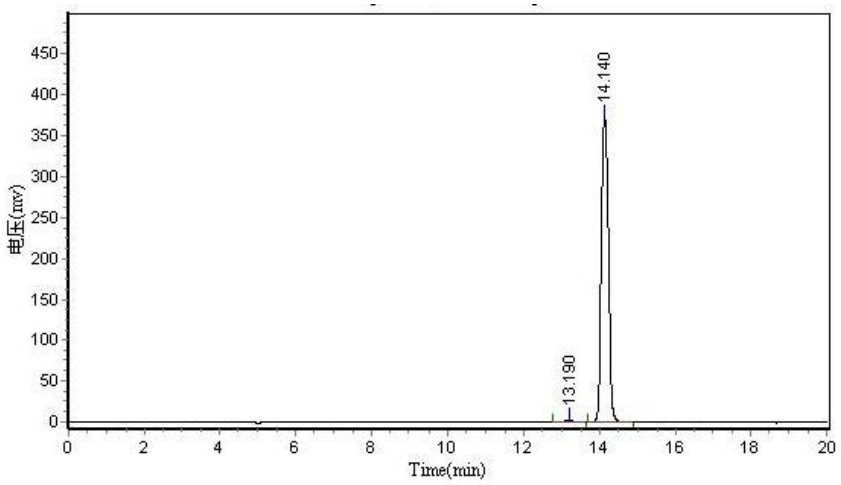
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83-2.05 (m, 1H), 2.17-2.51 (m, 4H), 2.35 (s, 3H), 2.65 (dd, *J* = 18.0, 7.5 Hz, 1H), 3.27-3.44 (m, 1H), 6.94-7.12 (m, 3H), 7.21-7.26 (m, 1H).

HPLC: Chiracel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 13.2 min, 14.1 min (maj).



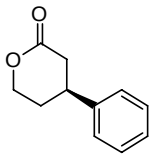
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.063	312533.469	3600191.250	52.6386
2		14.025	266207.906	3239260.750	47.3614
Total			578741.375	6839452.000	100.0000



Results

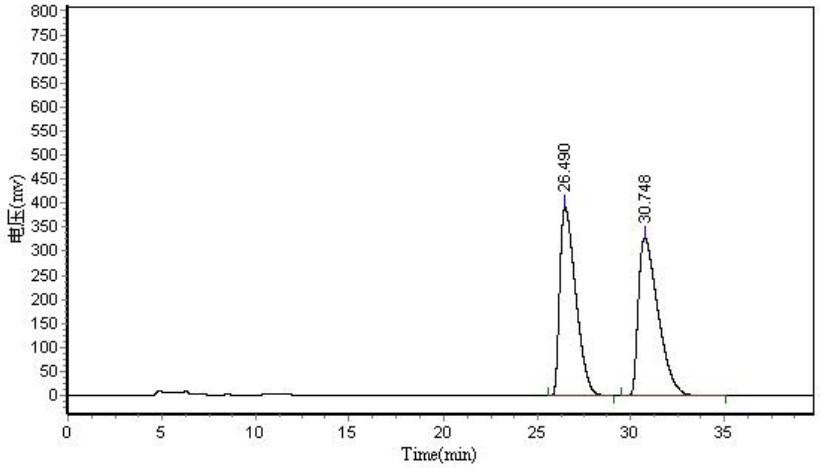
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.190	2646.842	42952.875	0.8728
2		14.140	372361.844	4878500.500	99.1272
Total			375008.686	4921453.375	100.0000



14q

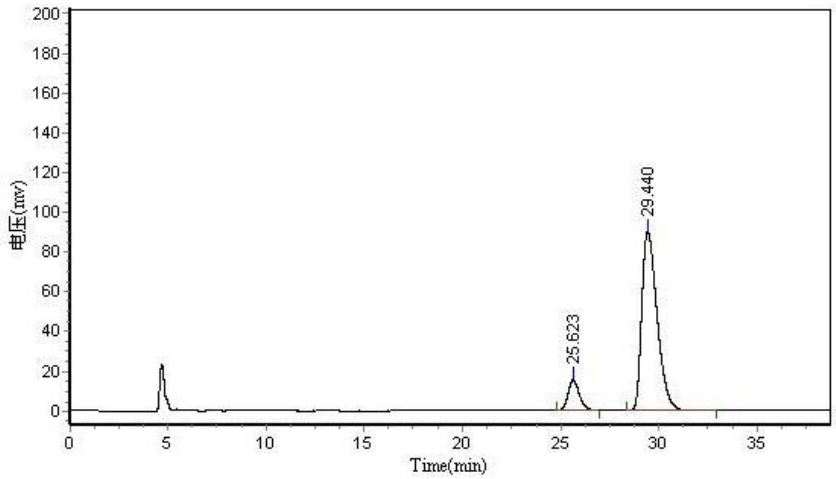
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.97-2.10 (m, 1H), 2.15-2.21 (m, 1H), 2.63 (dd, *J* = 17.7, 10.8 Hz, 1H), 2.92 (dd, *J* = 17.7, 5.7 Hz, 1H), 3.19-3.29 (m, 1H), 4.35-4.43 (m, 1H), 4.48-4.54 (m, 1H), 7.20-7.39 (m, 5H).

HPLC: Chiracel AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 25.6 min, 29.4 min (maj).



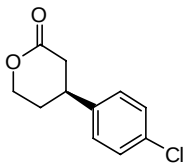
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.490	393225.031	23275850.000	49.1991
2		30.748	328169.500	24033634.000	50.8009
Total			721394.531	47309484.000	100.0000



Results

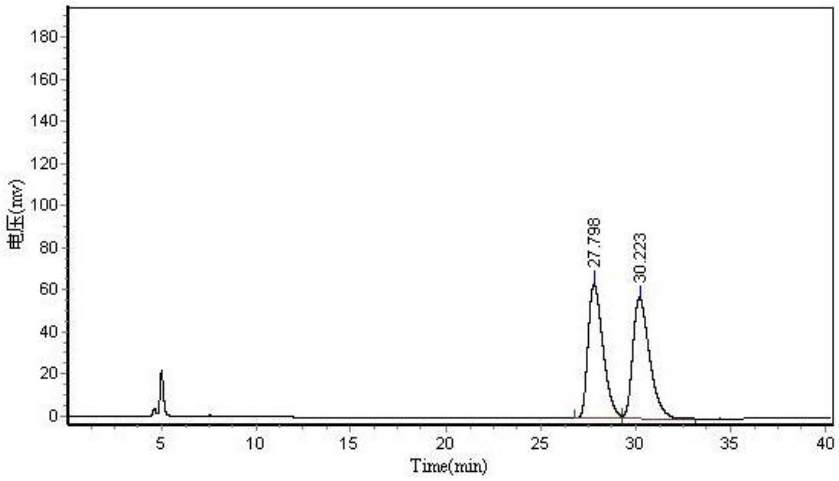
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.623	15323.409	613707.188	11.0983
2		29.440	90187.141	4916041.000	88.9017
Total			105510.550	5529748.188	100.0000



14r

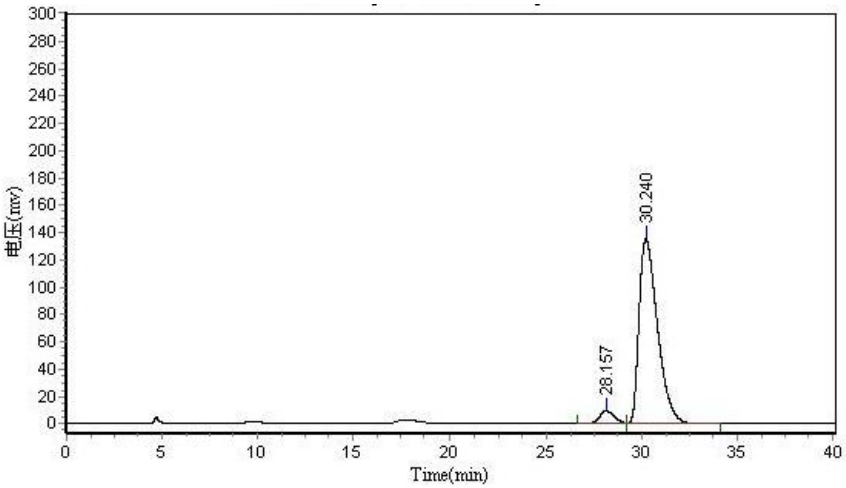
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.94-2.07 (m, 1H), 2.14-2.20 (m, 1H), 2.58 (dd, *J* = 17.7, 10.8 Hz, 1H), 2.91 (dd, *J* = 17.7, 5.7 Hz, 1H), 3.18-3.28 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.17, 36.90, 37.40, 68.52, 127.85, 129.12, 132.98, 141.23, 170.32; EI-MS: 210.0 M^+; HRMS (ESI) for $C_{11}H_{11}ClO_2$ M^+: calcd 210.0448, found 210.0450.

HPLC: Chiracel AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 28.2 min, 30.2 min (maj).



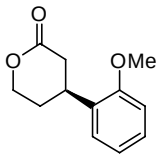
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.798	64055.973	3524530.500	49.8980
2		30.223	57505.371	3538945.500	50.1020
Total			121561.344	7063476.000	100.0000



Results

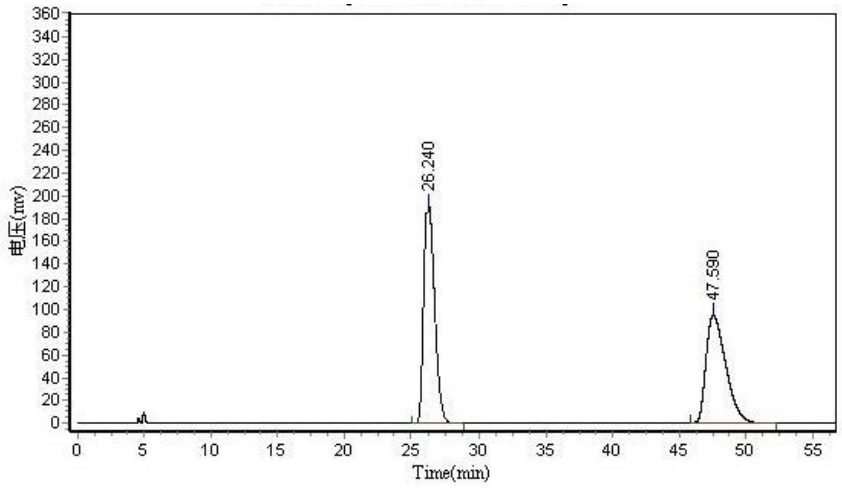
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.157	9410.521	508643.000	5.3157
2		30.240	135018.609	9060136.000	94.6843
Total			144429.131	9568779.000	100.0000



14s

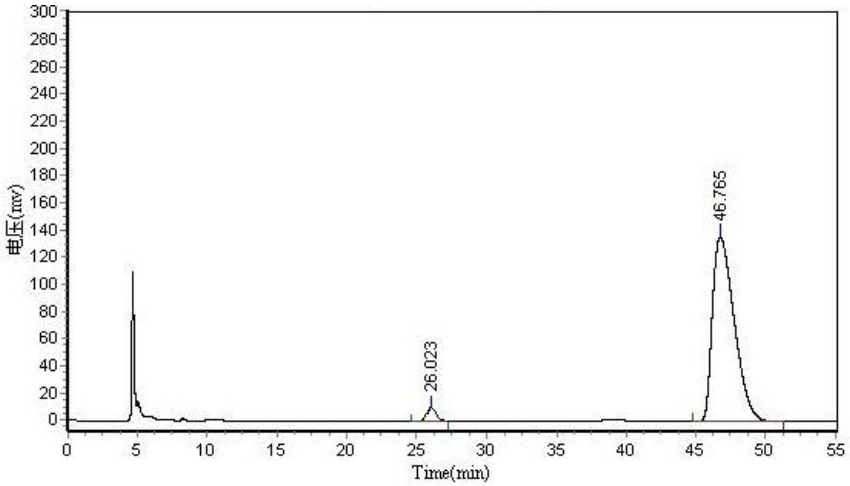
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05-2.13 (m, 1H), 2.64 (dd, *J* = 14.4, 9.9 Hz, 1H), 2.91 (dd, *J* = 14.4, 6.3 Hz, 1H), 3.49-3.59 (m, 1H), 3.84 (s, 3H), 4.33-4.52 (m, 2H), 6.88-6.98 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.23-7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.45, 32.17, 35.93, 55.16, 68.68, 110.69, 120.77, 126.88, 128.19, 130.85, 156.88, 171.65; EI-MS: 206.1 M^+; HRMS (ESI) for $C_{12}H_{14}O_3$ M^+: calcd 206.0943, found 206.0946.

HPLC: Chiracel AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 26.0 min, 46.8 min (maj).



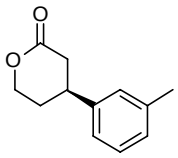
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.240	190609.375	9727790.000	49.8817
2		47.590	94399.805	9773941.000	50.1183
Total			285009.180	19501731.000	100.0000



Results

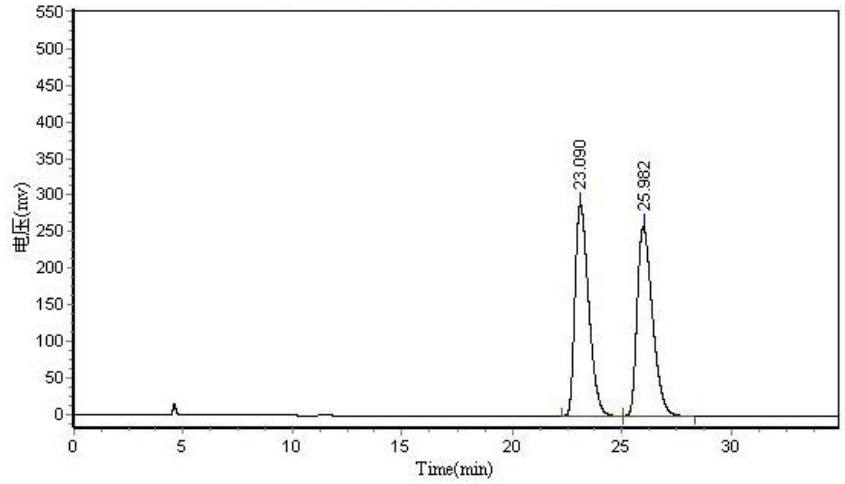
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.023	10274.346	470445.406	3.0819
2		46.765	135238.391	14794375.000	96.9181
Total			145512.736	15264820.406	100.0000



14t

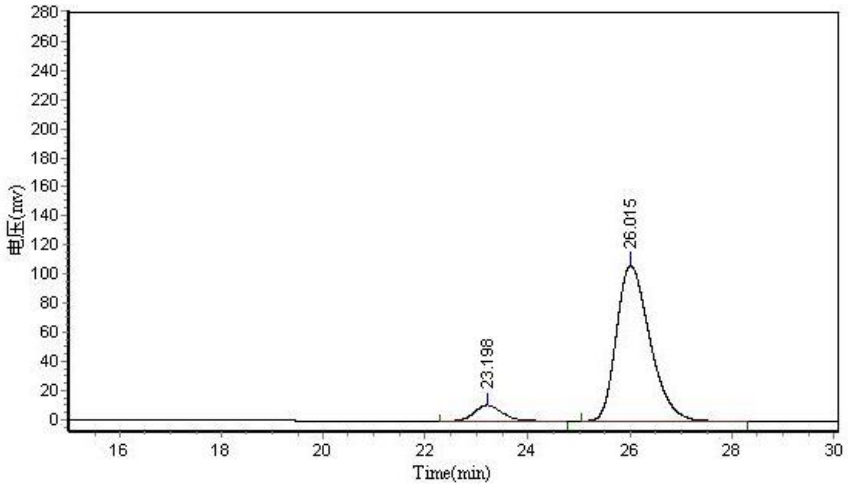
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96-2.09 (m, 1H), 2.12-2.20 (m, 1H), 2.36 (s, 3H), 2.63 (dd, *J* = 17.7, 10.8 Hz, 1H), 2.90 (dd, *J* = 18.0, 6.0 Hz, 1H), 3.15-3.25 (m, 1H), 4.34-4.42 (m, 1H), 4.47-4.54 (m, 1H), 7.00-7.02 (m, 2H), 7.08-7.10 (d, *J* = 7.8 Hz, 1H), 7.22-7.27 (m, 1H).

HPLC: Chiracel AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 23.2 min, 26.0 min (maj).



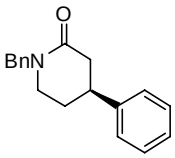
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.090	288161.063	12513641.000	49.9545
2		25.982	257744.453	12536435.000	50.0455
Total			545905.516	25050076.000	100.0000



Results

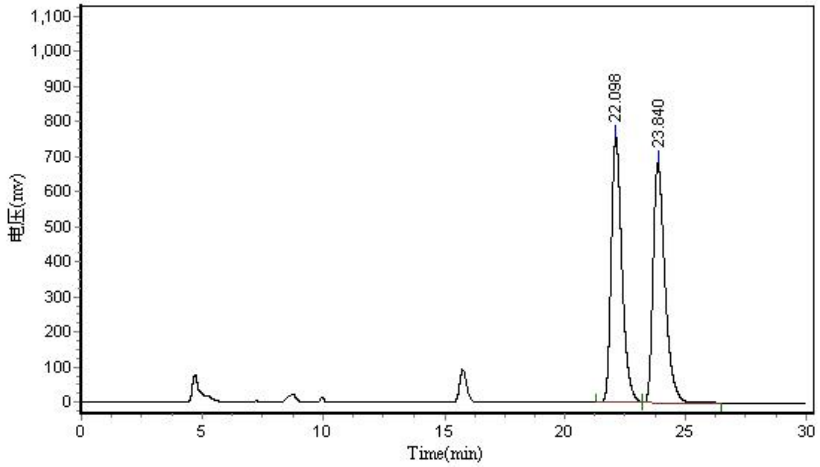
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.198	10866.930	416308.594	7.8454
2		26.015	106997.242	4890095.000	92.1546
Total			117864.172	5306403.594	100.0000



14u

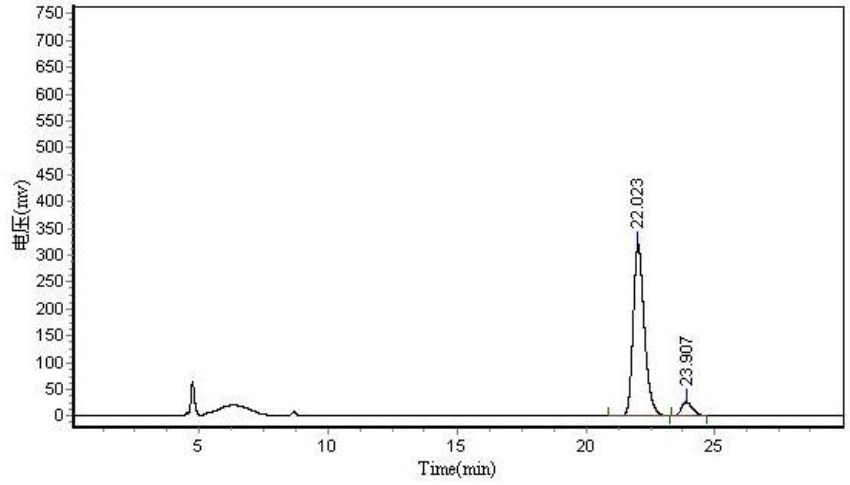
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.85-2.09 (m, 2H), 2.59 (dd, *J* = 17.4, 10.8 Hz, 1H), 2.82 (dd, *J* = 17.4, 4.8 Hz, 1H), 3.05-3.12 (m, 1H), 3.27-3.35 (m, 2H), 4.55 (d, *J* = 15.0 Hz, 1H), 4.74 (d, *J* = 14.7 Hz, 1H), 7.17-7.33 (m, 10H).

HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 22.0 min (maj), 23.9 min.



Results

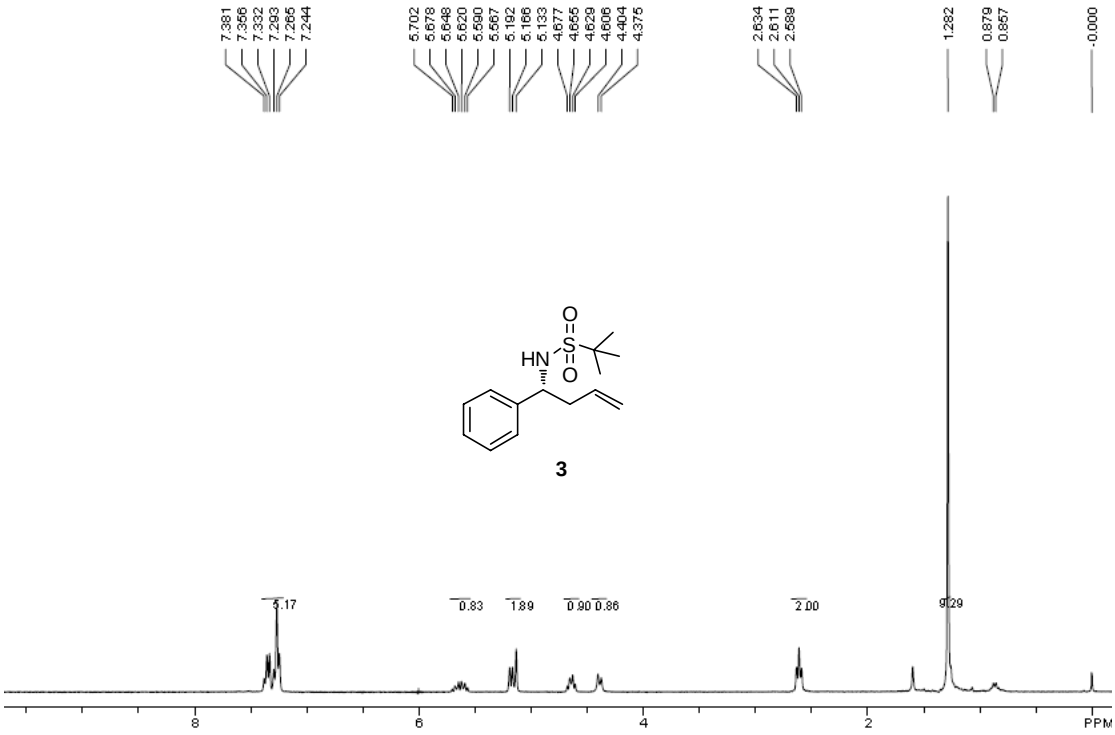
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.098	755555.500	23352180.000	50.0597
2		23.840	683160.688	23296440.000	49.9403
Total			1438716.188	46648620.000	100.0000

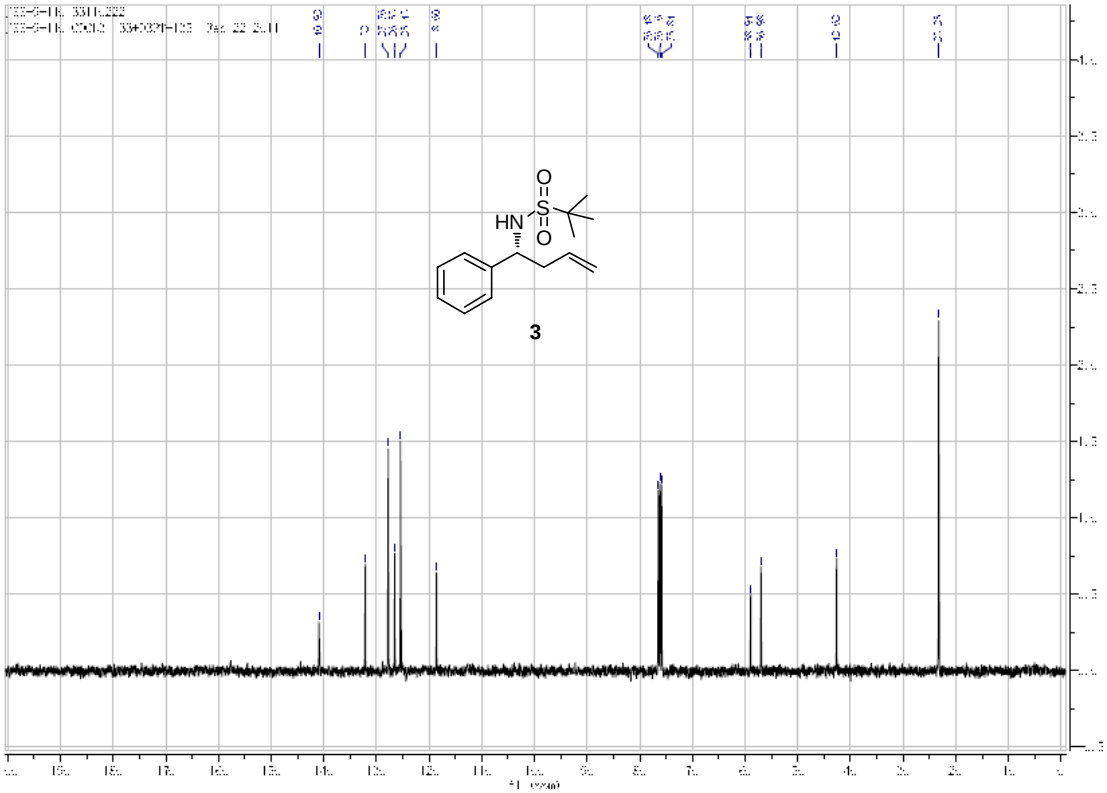


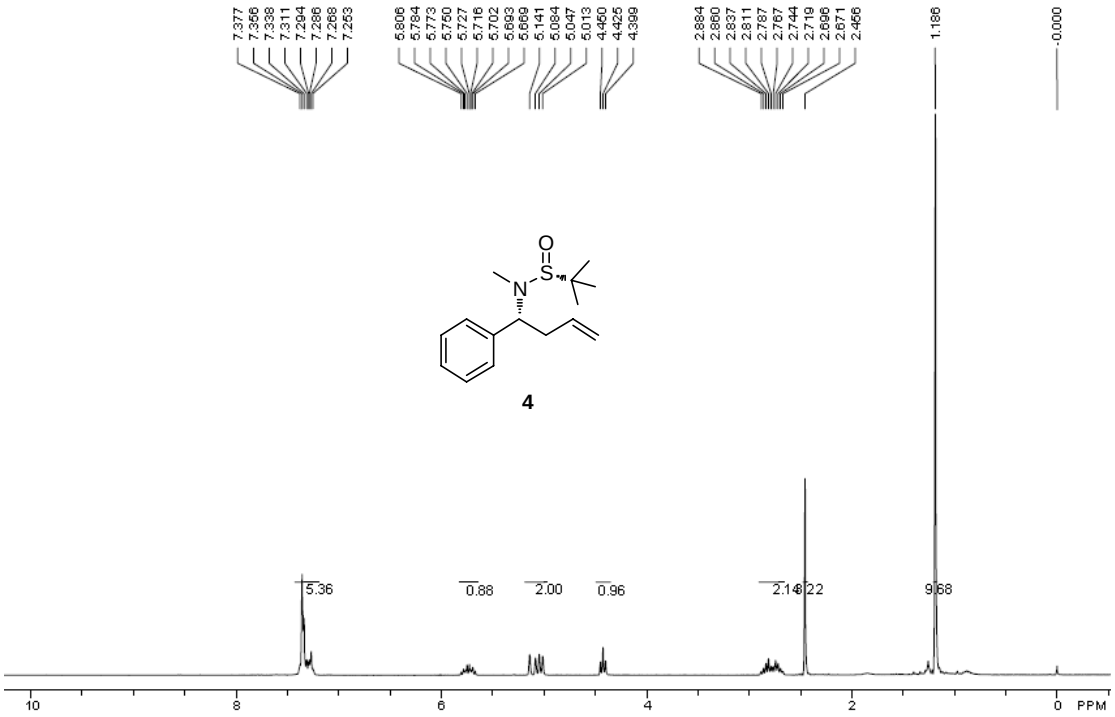
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.023	319866.000	9748744.000	92.4560
2		23.907	25411.340	795450.188	7.5440
Total			345277.340	10544194.188	100.0000

5. Copies of ^{1}H and ^{13}C NMR for new compounds.



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5.702
5.693
5.669
5.141
5.084
5.047
5.013
4.450
4.425
4.399
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2.860
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2.811
2.787
2.767
2.744
2.719
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2.671
2.456
1.186
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0.96
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8
6
4
2
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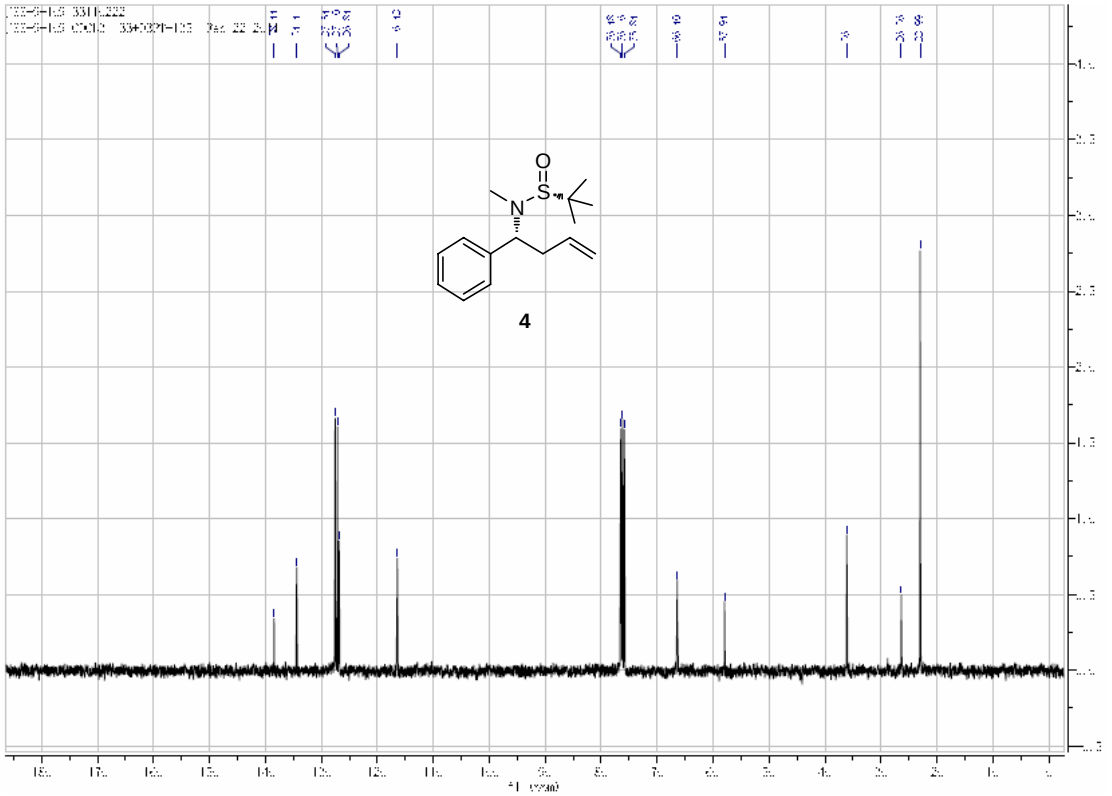
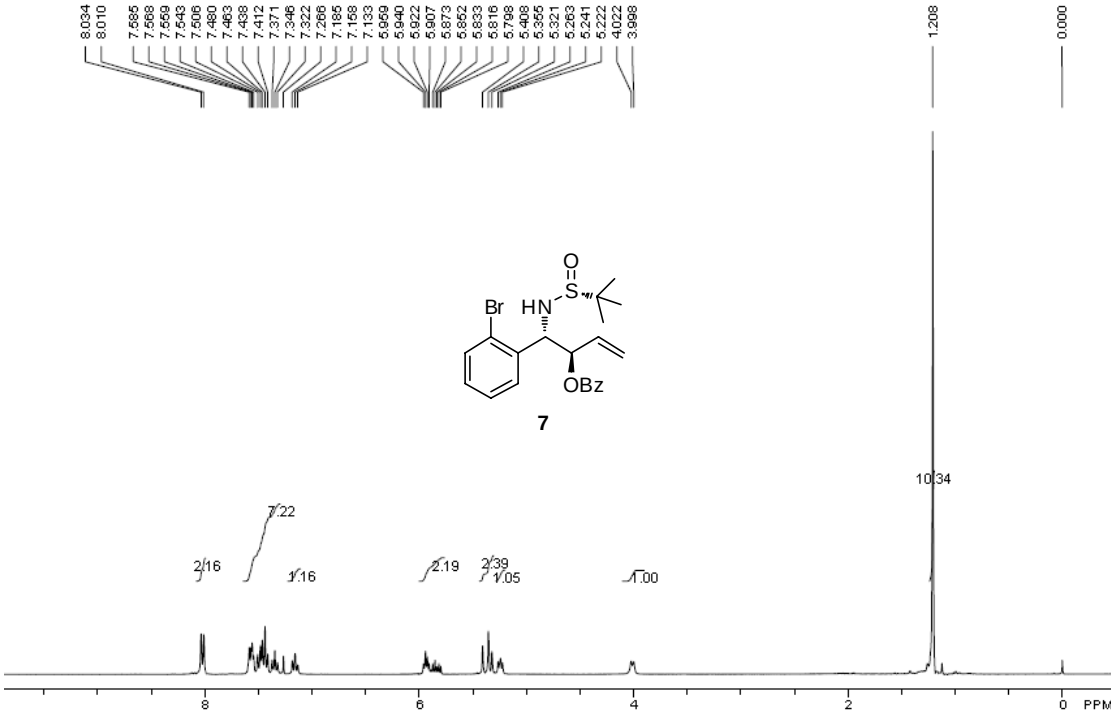
PPM

4



4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7.266
7.185
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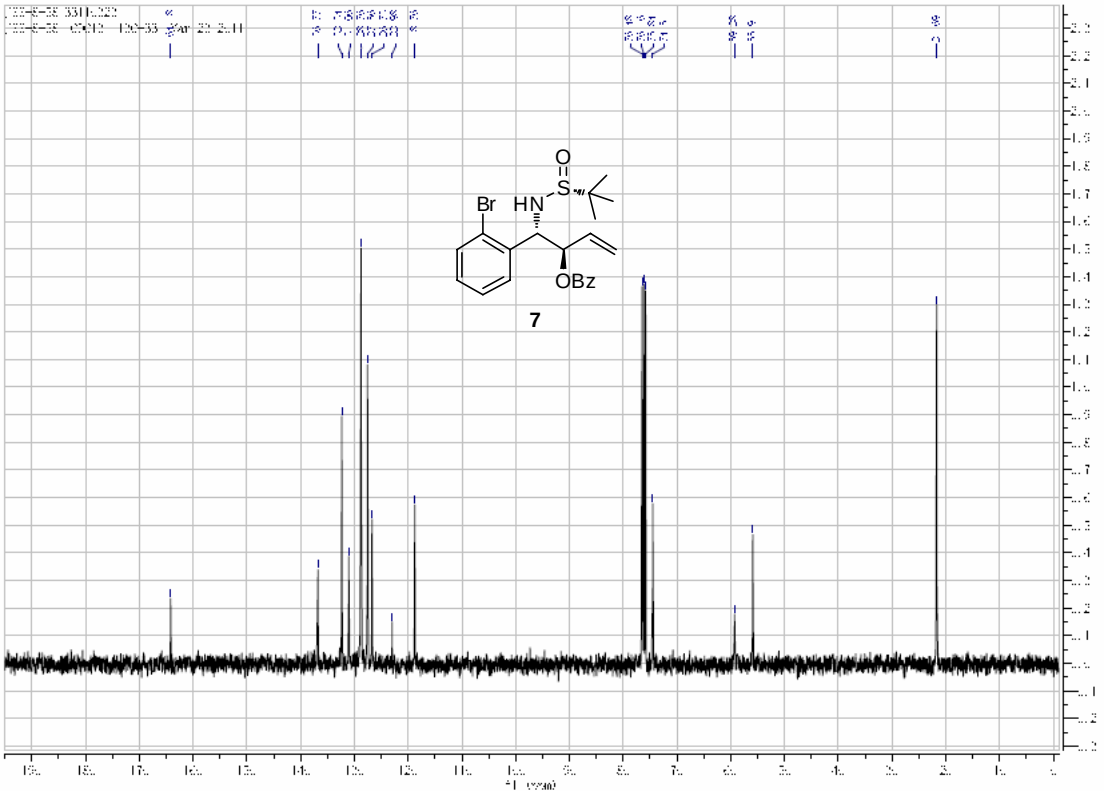
PPM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OBz
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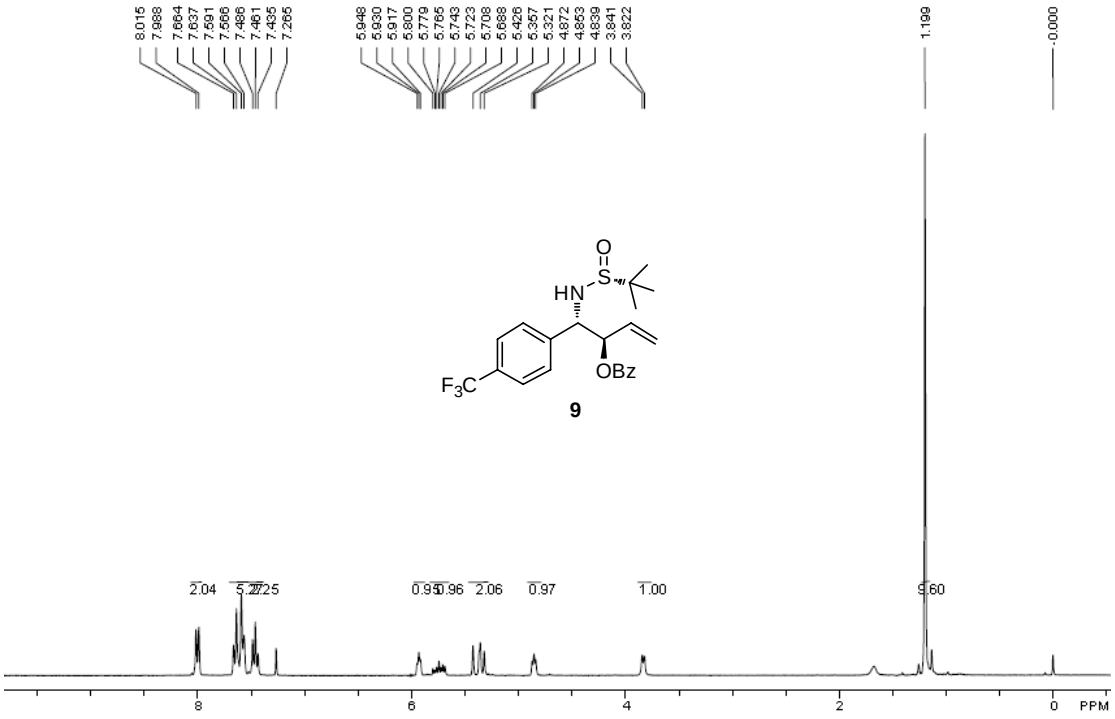
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5.917
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O
S
OBz
F3C
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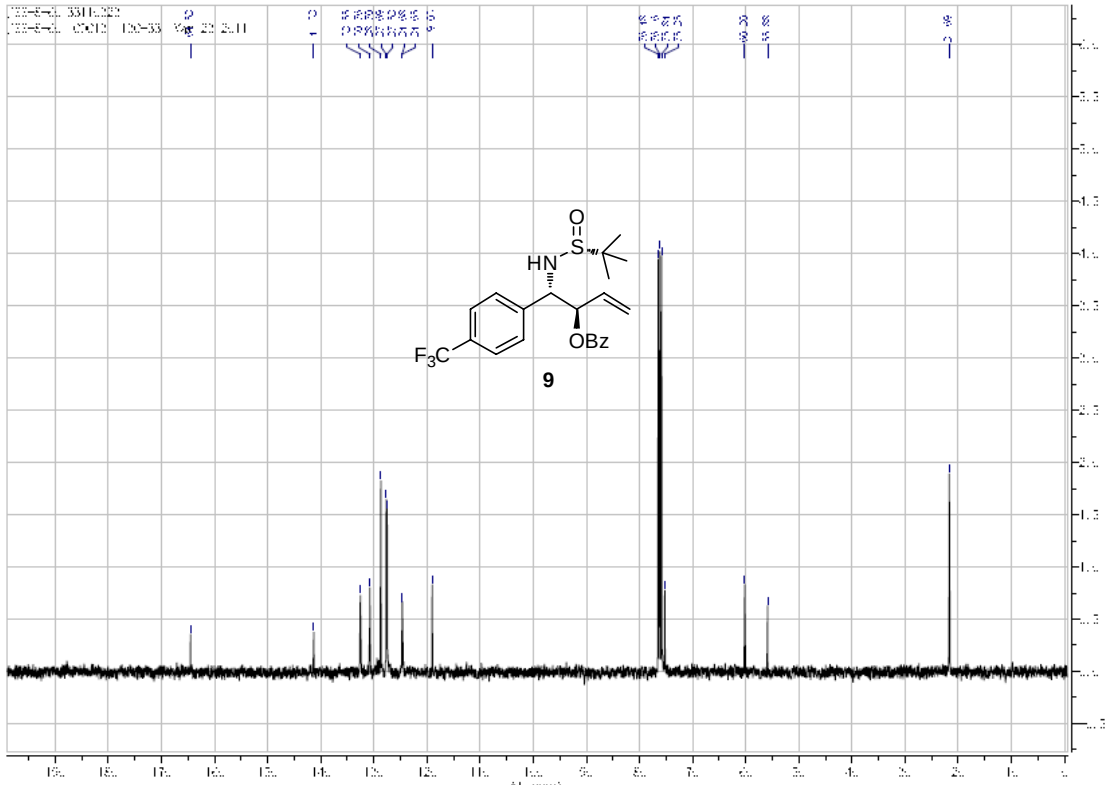
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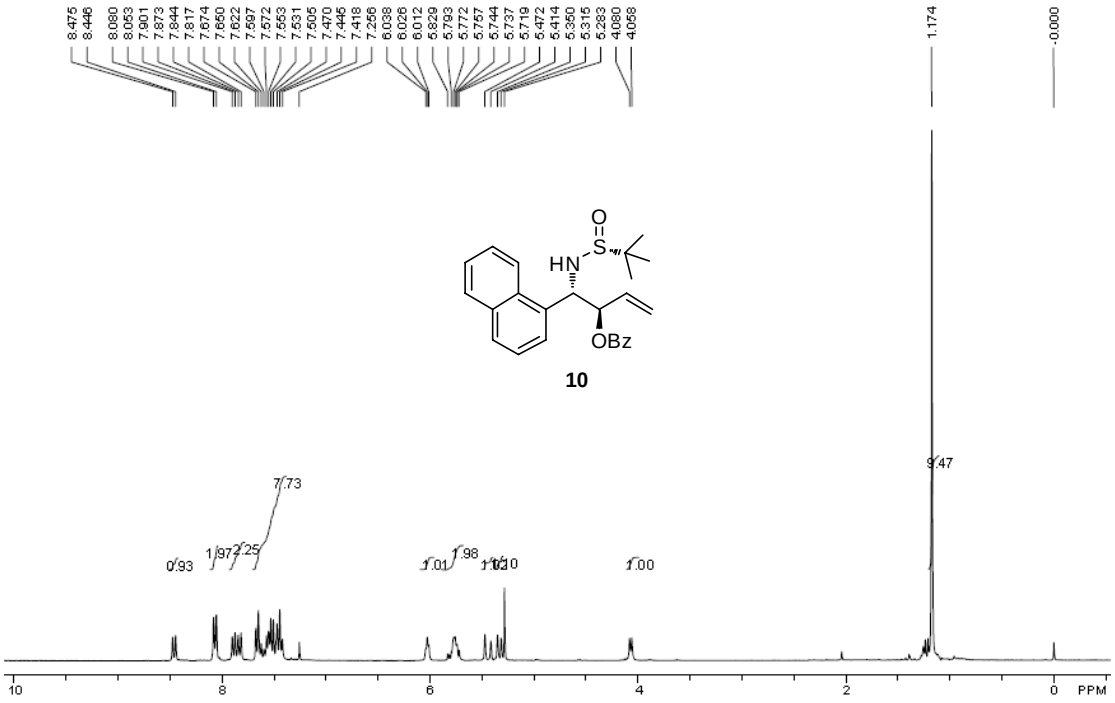
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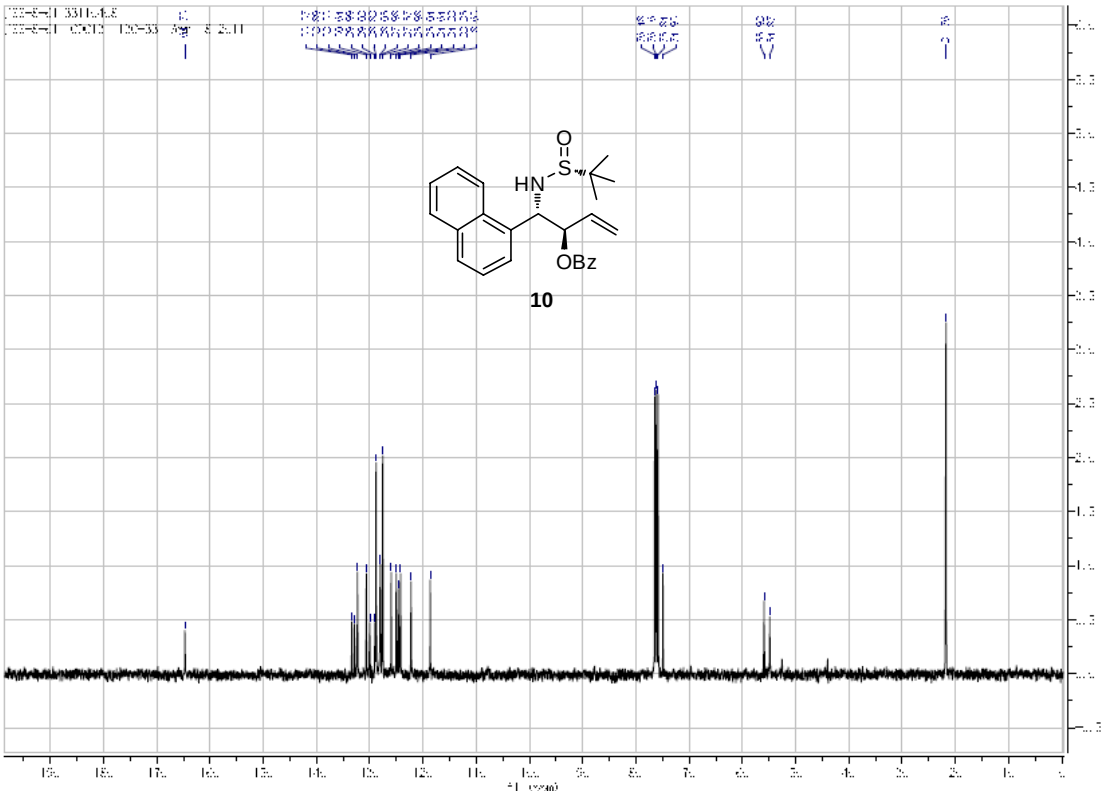
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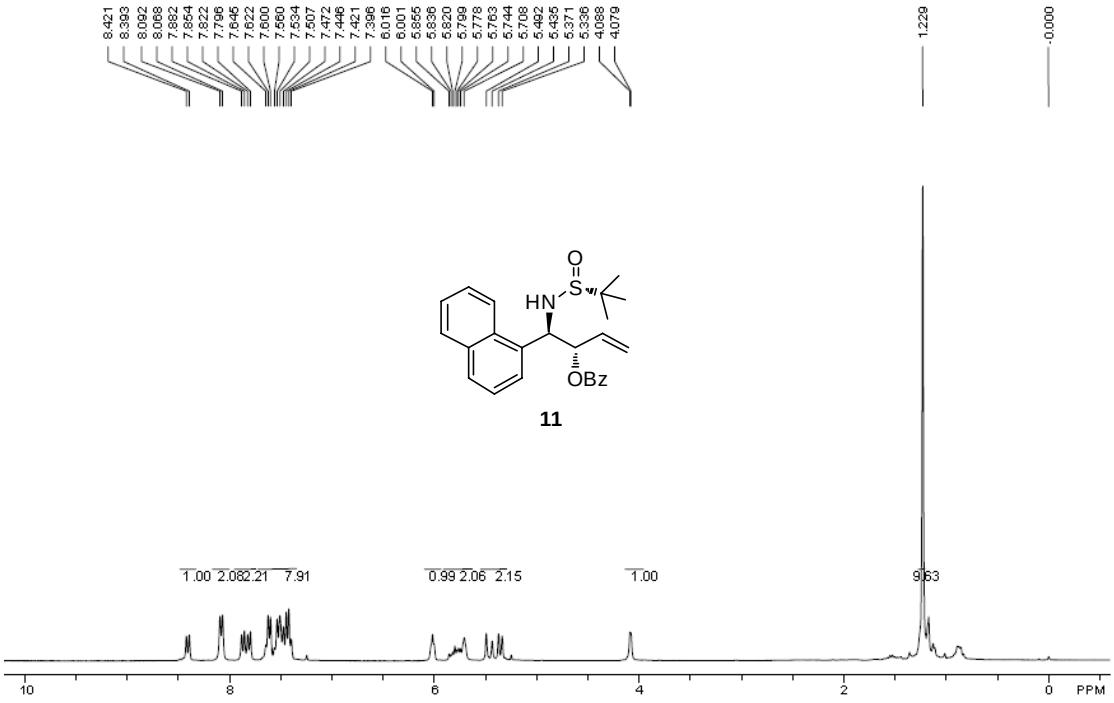
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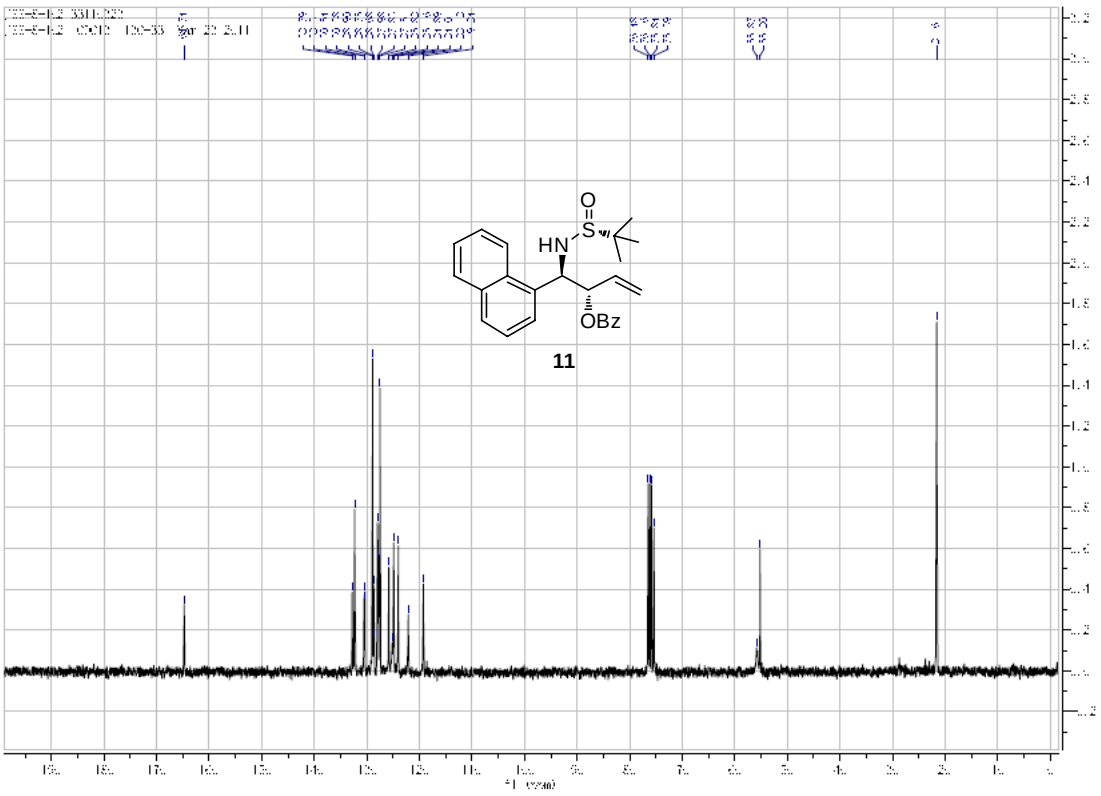
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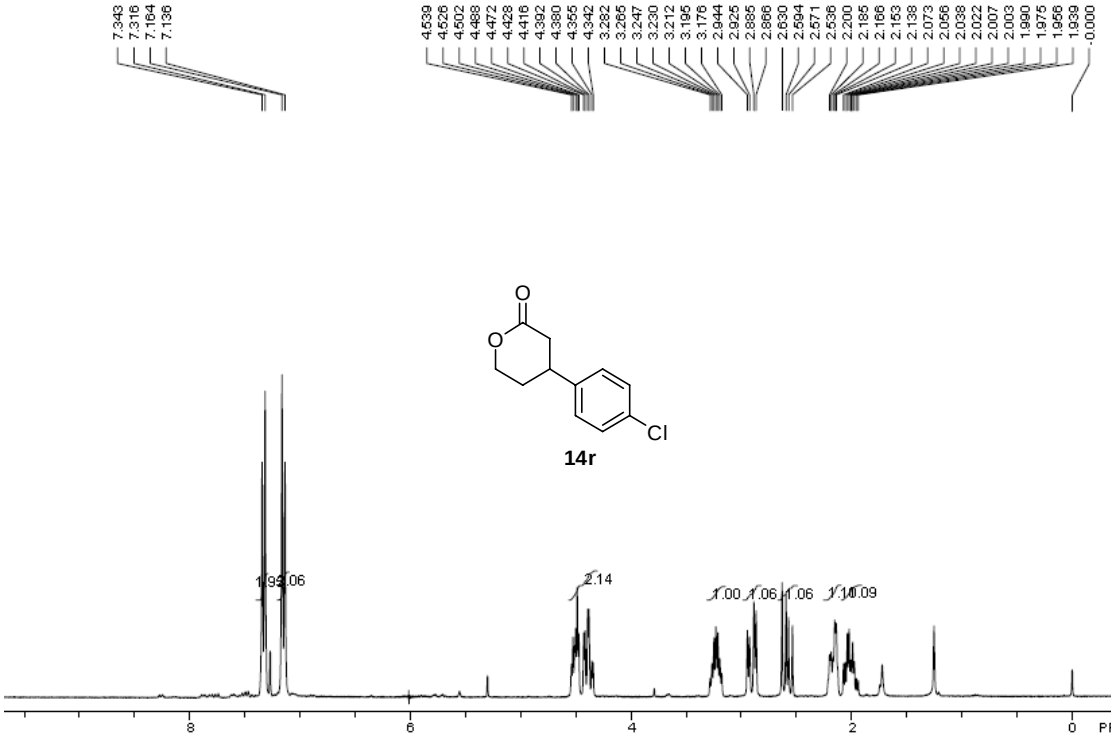
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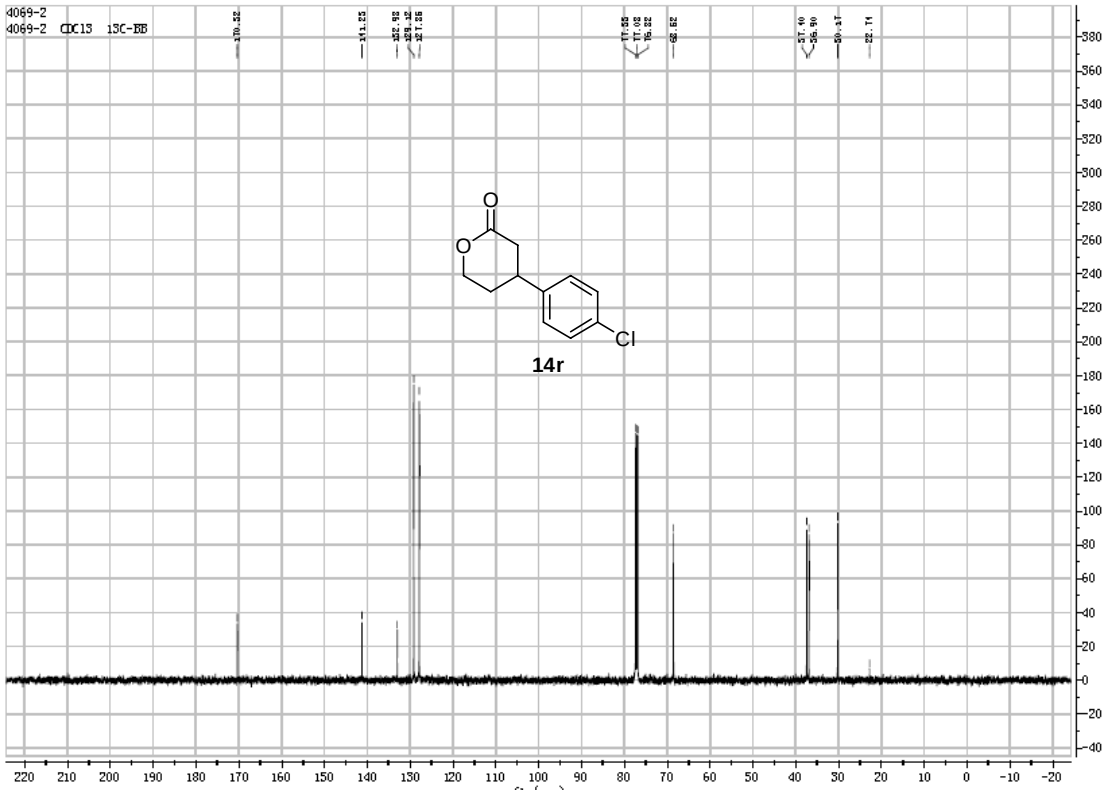
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Cl
14r
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200
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180
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120
110
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90
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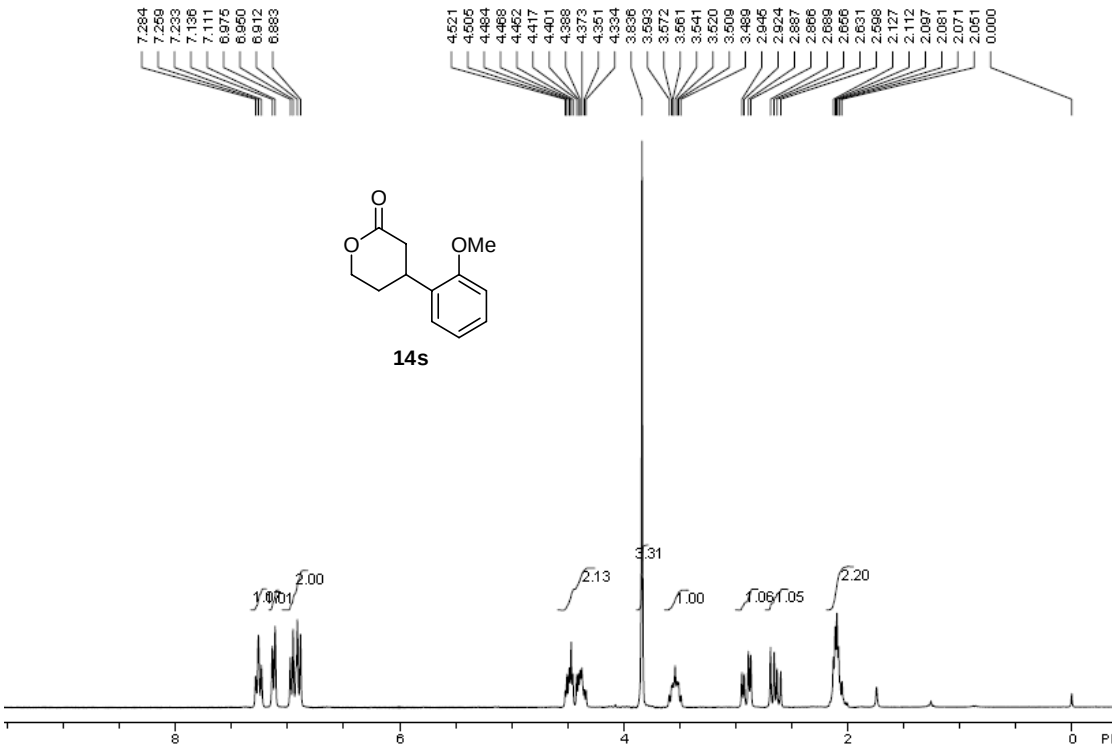
-20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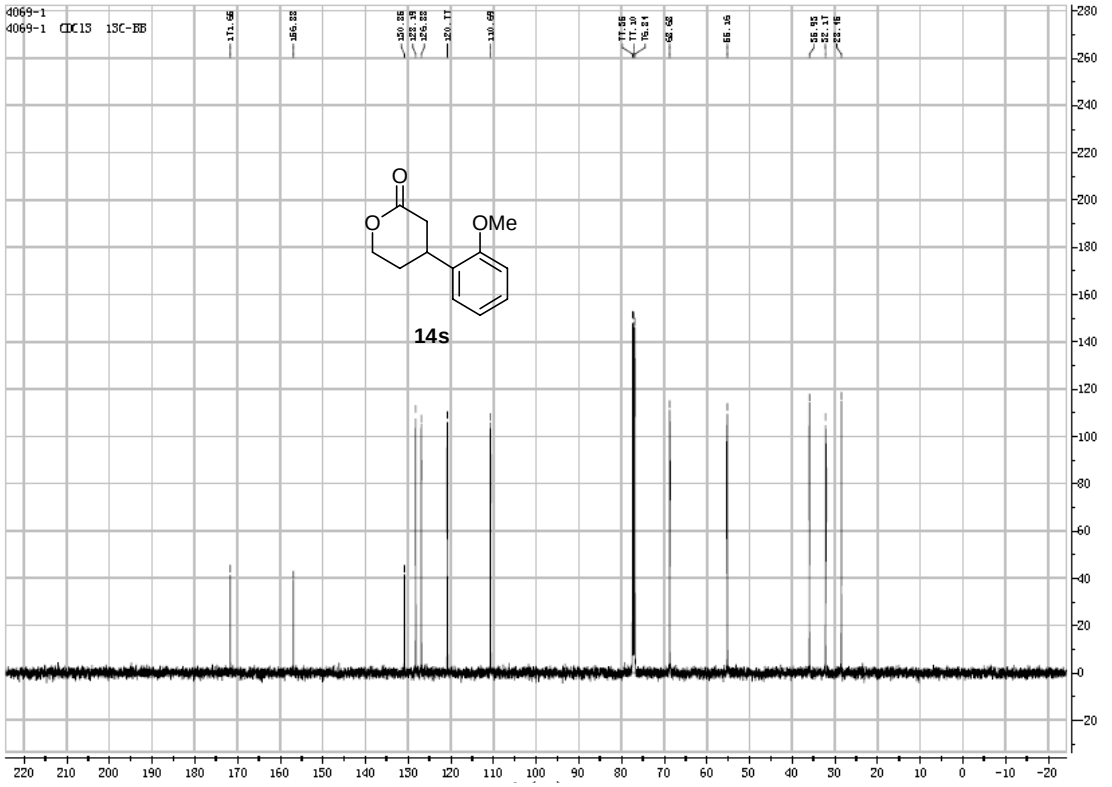
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OMe
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