Supplementary Information for:

Design of *N*-Cinnamyl Sulfinamides as New Sulfur-Containing Olefin Ligands for Asymmetric Catalysis: Achieving Structural Simplicity with a Categorical Linear Framework

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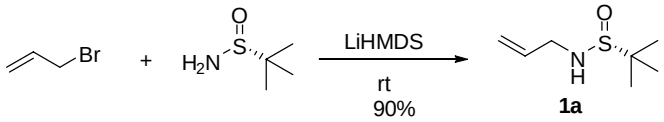
1. General

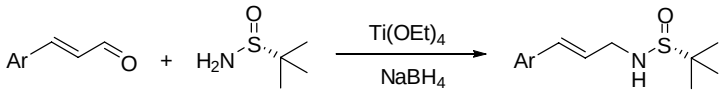
NMR spectra were recorded on a Varian spectrometer (300 MHz for ^{1}H, and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-*d* (δ 77.16) for ^{13}C NMR. HPLC was performed on a JASCO 2000 instrument by using Daicel chiral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

2. Synthesis of ligands.



1a

Under N_2 atmosphere, 2 mL of LiHMDS (1 M in THF, 2 mmol) was added to a solution of (*R*)-*tert*-butanesulfinamide (121 mg, 1 mmol) in 5 mL THF at room temperature. After 15 minutes, allyl bromide (1.6 mL, 2 mmol) was added to the mixture and the reaction was stirred for 2 hours at room temperature. When the reaction was complete, 10 mL of water was added. The solution was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography gave the product **1a** as colorless oil (145 mg, 90% yield).



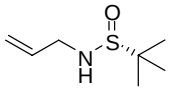
1b-1i

Typical procedure for **1b**: A solution of cinnamaldehyde (1.9 mL, 15 mmol), (*R*)-*tert*-butanesulfinamide (1.21 g, 10 mmol) and $Ti(OEt)_4$ (4.1 mL, 20 mmol) in 30 mL THF was heated to reflux for 4 hours. Then the reaction was cooled to room temperature and $NaBH_4$ (1.52 g, 40 mmol). The mixture was stirred at room temperature for additional 2 hours. When the reaction was complete, methanol was added dropwise until there was no bubble. The mixture was poured to 30 mL of brine, stirred for a while and filtered. The filtrate was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography gave the product **1b** as a white solid (2.15 g, 91% yield).

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

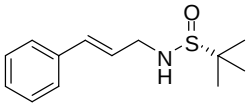
Under N_2 atmosphere, a solution of $[RhCl(C_2H_4)_2]_2$ (1.5 mg, 0.00375 mmol of Rh), **1b** (1.8 mg, 0.0075 mmol), and arylboronic acid (0.60 mmol) in 0.5 mL of dioxane was stirred at 40 ^{o}C for 30 min. To this mixture were added the α,β-unsaturated carbonyl compounds (0.25 mmol) and then aqueous K_3PO_4 (83 μL, 1.5 M, 0.125 mmol). After being stirred at 40 ^{o}C for 0.5-1 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product **3**.

4. Characterization data of ligand compounds.



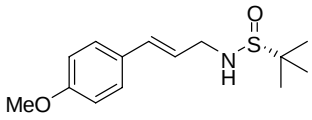
1a

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 9H), 3.29 (s, 1H), 3.67-3.86 (m, 2H), 5.16 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.27 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.85-5.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.67, 48.20, 55.78, 117.12, 135.30; ESI-MS: 162.0 $[M + H]^+$, 322.9 $[2M + H]^+$; HRMS (ESI) for $C_7H_{15}NOSNa$ $[M + Na]^+$: calcd 184.0772, found 184.0764.



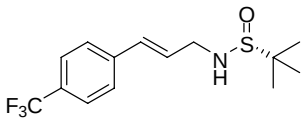
1b

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9H), 3.35 (t, *J* = 5.7 Hz, 1H), 3.82-4.01 (m, 2H), 6.25 (dt, *J* = 15.9, 6.6 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 7.24-7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.74, 47.97, 55.88, 126.55, 127.89, 128.67, 132.66, 136.51; ESI-MS: 238.0 $[M + H]^+$, 475.0 $[2M + H]^+$; HRMS (ESI) for $C_{13}H_{19}NOSNa$ $[M + Na]^+$: calcd 260.1085, found 260.1070.



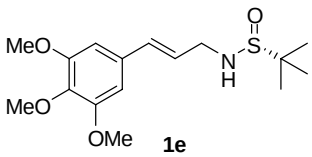
1c

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9H), 3.34 (t, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 3.83-3.98 (m, 2H), 6.11 (dt, *J* = 15.6, 6.6 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.75, 48.13, 55.37, 55.86, 114.07, 124.26, 127.76, 129.29, 132.22, 159.43; ESI-MS: 267.9 $[M + H]^+$, 535.0 $[2M + H]^+$; HRMS (ESI) for $C_{14}H_{22}NO_2S$ $[M + H]^+$: calcd 268.1371, found 268.1360.



1d

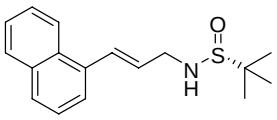
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H), 3.72 (t, *J* = 5.4 Hz, 1H), 3.85-4.03 (m, 2H), 6.36 (dt, *J* = 15.6, 6.3 Hz, 1H), 6.61 (d, *J* = 15.6 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.59, 47.65, 55.89, 125.39, 125.43, 125.46, 126.60, 129.51, 130.86, 140.00; ESI-MS: 306.0 $[M + H]^+$, 610.9 $[2M + H]^+$; HRMS (ESI) for $C_{14}H_{19}F_3NOS$ $[M + H]^+$: calcd 306.1139, found 306.1124.



1e

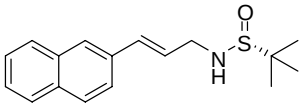
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H), 3.47 (s, 1H), 3.84 (s, 3H), 3.87 (s, 6H), 3.84-4.00 (m, 2H), 6.19 (dt, *J* = 15.6, 6.6 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.61 (s, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 22.62, 47.88, 55.79, 56.02, 60.85, 103.47, 126.01, 132.18, 132.46, 137.84, 153.23; ESI-MS: 327.9 $[M + H]^+$, 655.1 $[2M + H]^+$; HRMS (ESI) for $C_{16}H_{25}NO_4SNa$ $[M + Na]^+$: calcd 350.1402, found 350.1381.



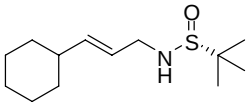
1f

^1H NMR (300 MHz, $CDCl_3$): δ 1.26 (s, 9H), 3.45 (t, *J* = 5.4 Hz, 1H), 3.93-4.15 (m, 2H), 6.28 (dt, *J* = 15.6, 6.3 Hz, 1H), 7.34 (d, *J* = 15.3 Hz, 1H), 7.40-7.59 (m, 4H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.78, 48.17, 55.94, 123.76, 124.08, 125.66, 125.91, 126.25, 128.24, 128.62, 129.81, 129.83, 131.16, 133.65, 134.30; ESI-MS: 288.0 $[M + H]^+$, 575.0 $[2M + H]^+$; HRMS (ESI) for $C_{17}H_{21}NOSNa$ $[M + Na]^+$: calcd 310.1242, found 310.1224.



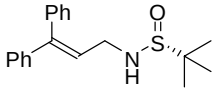
1g

^1H NMR (300 MHz, $CDCl_3$): δ 1.26 (s, 9H), 3.37 (s, 1H), 3.90-4.05 (m, 2H), 6.38 (dt, *J* = 15.6, 6.6 Hz, 1H), 6.74 (d, *J* = 15.6 Hz, 1H), 7.44-7.46 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.73-7.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.80, 48.18, 55.99, 123.63, 126.11, 126.44, 126.64, 126.96, 127.78, 128.11, 128.38, 132.80, 133.17, 133.64, 134.00; ESI-MS: 287.9 $[M + H]^+$, 575.0 $[2M + H]^+$; HRMS (ESI) for $C_{17}H_{22}NOS$ $[M + H]^+$: calcd 288.1422, found 288.1409.



1h

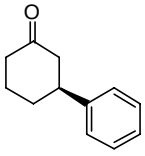
^1H NMR (300 MHz, $CDCl_3$): δ 0.99-1.28 (m, 6H), 1.22 (s, 9H), 1.62-1.72 (m, 4H), 1.91-2.00 (m, 2H), 3.18 (t, *J* = 5.4 Hz, 1H), 3.58-3.78 (m, 2H), 5.45 (dt, *J* = 15.3, 6.3 Hz, 1H), 5.61 (dd, *J* = 15.3, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.72, 26.04, 26.18, 32.80, 32.81, 40.41, 47.99, 55.69, 124.27, 140.17; ESI-MS: 244.1 $[M + H]^+$, 487.1 $[2M + H]^+$; HRMS (ESI) for $C_{13}H_{26}NOS$ $[M + H]^+$: calcd 244.1735, found 244.1722.



1i

^1H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 3.42 (t, *J* = 4.5 Hz, 1H), 3.73-3.92 (m, 2H), 6.14 (t, *J* = 6.6 Hz, 1H), 7.16-7.39 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.65, 44.93, 55.79, 125.63, 127.52, 127.60, 128.18, 128.36, 129.67, 138.89, 141.66, 144.41; ESI-MS: 314.0 $[M + H]^+$, 627.0 $[2M + H]^+$; HRMS (ESI) for $C_{19}H_{24}NOS$ $[M + H]^+$: calcd 314.1579, found 314.1564.

5. Characterization data and HPLC of addition products.

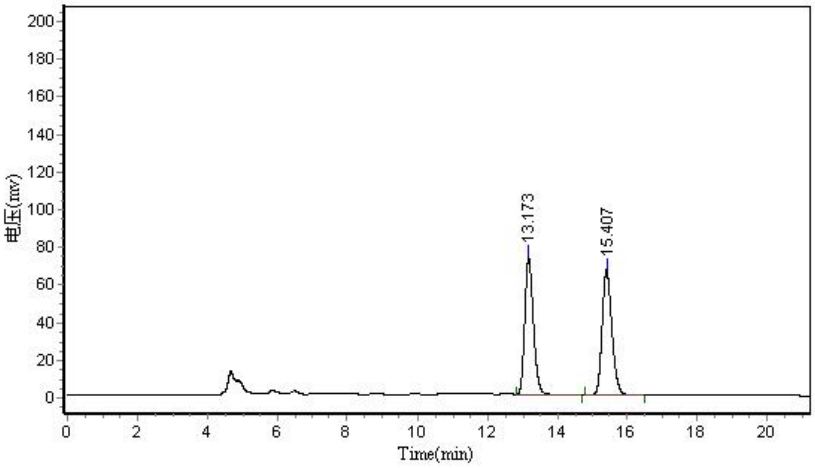


3a

^{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). $[\alpha]_D^{20}$ -19.6 (c 1.30, $CHCl_3$) for 97% 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.]

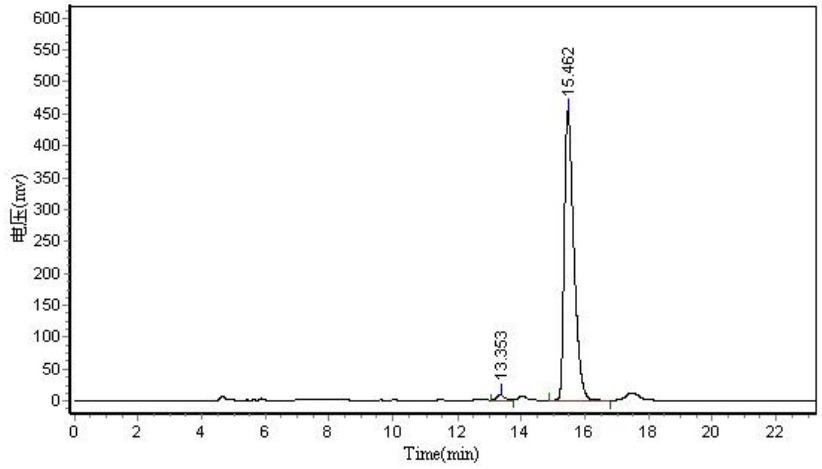
HPLC: Chiralcel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 13.4 min, 15.5 min (maj).

Ref: Takaya, Y.; Ogasawara, M.; Hayashi, T. *J. Am. Chem. Soc.* **1998,** *120,* 5579.



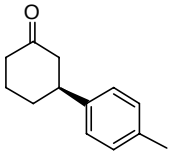
Results

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		13.353	9183.676	152296.094	1.5873
2		15.462	452863.594	9442373.000	98.4127
Total			462047.270	9594669.094	100.0000

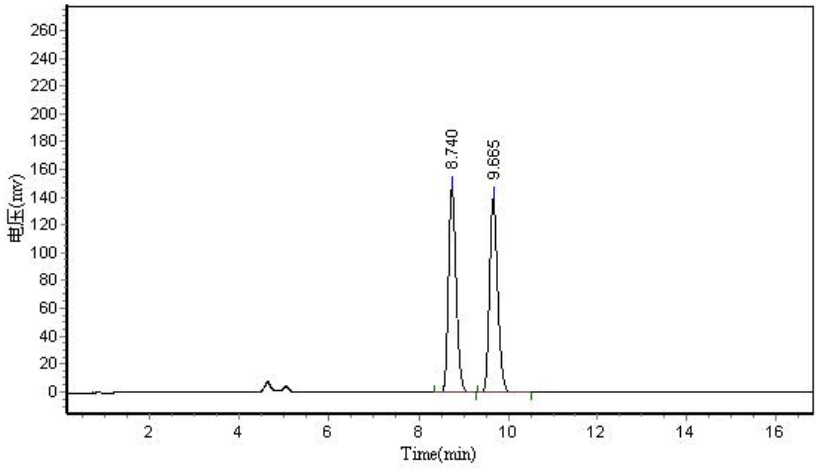


3b

^{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).

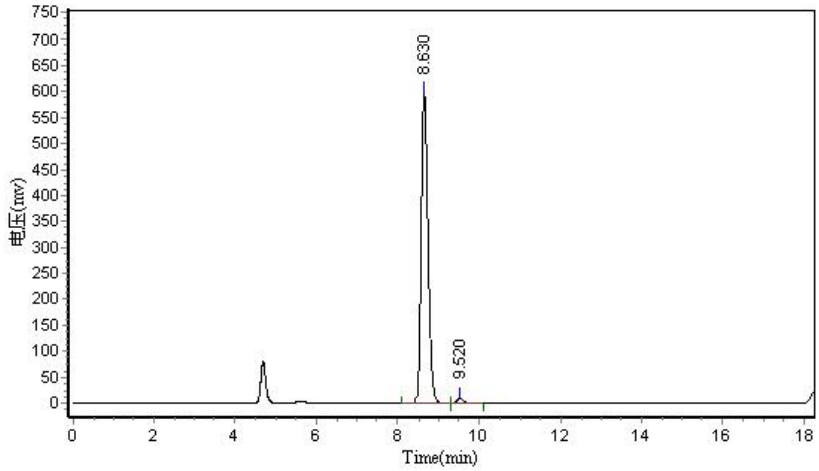
HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 8.6 min (maj), 9.5 min.

Ref: Takaya, Y.; Ogasawara, M.; Hayashi, T. *J. Am. Chem. Soc.* **1998,** *120,* 5579.



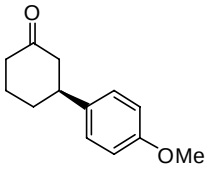
Results

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		8.630	596343.500	6922119.000	98.2153
2		9.520	10202.115	125785.039	1.7847
Total			606545.615	7047904.039	100.0000

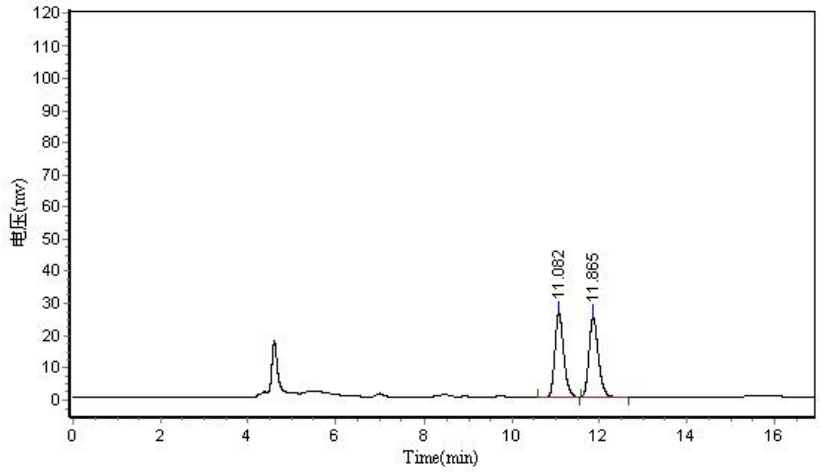


3c

^{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).

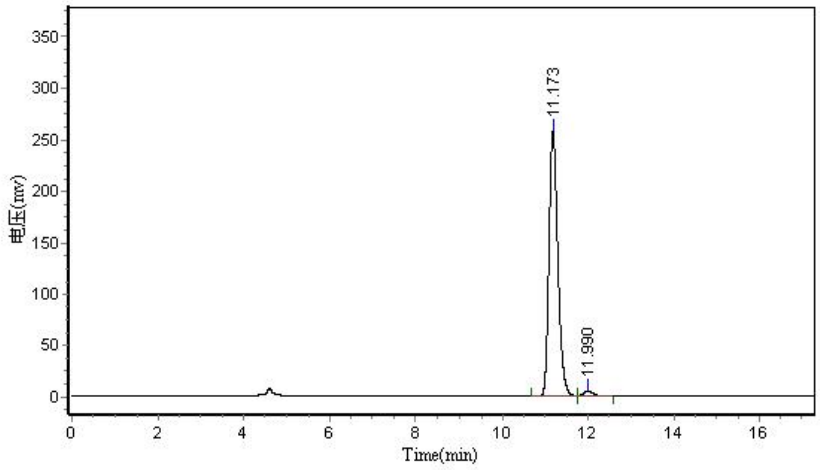
HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 11.2 min (maj), 12.0 min.

Ref: Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 883.



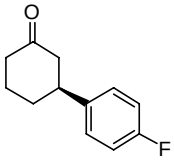
Results

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		11.173	257124.875	3695915.000	97.7735
2		11.990	5318.716	84164.773	2.2265
Total			262443.591	3780079.773	100.0000

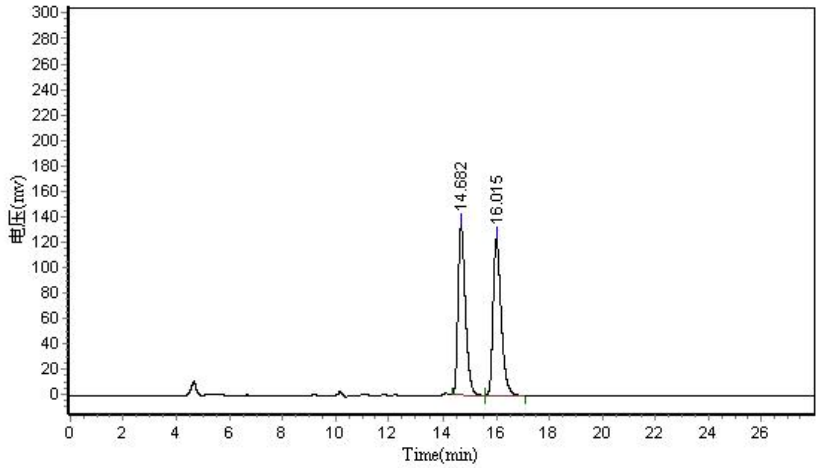


3d

^{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).

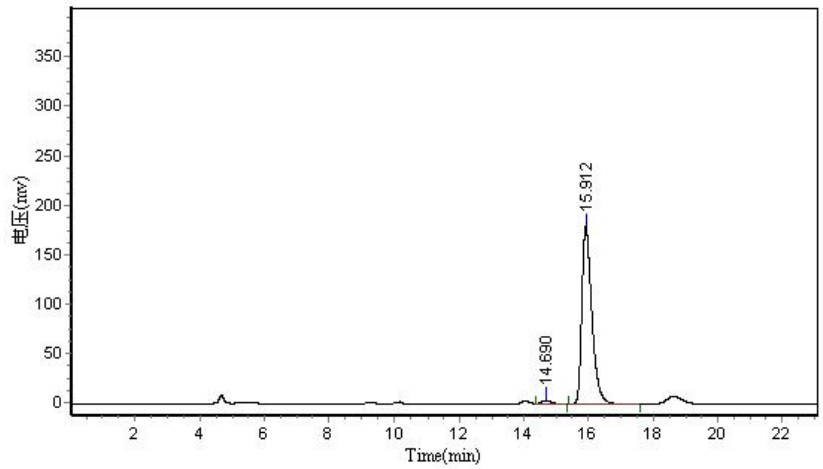
HPLC: Chiralcel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 14.7 min, 15.9 min (maj).

Ref: Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002,** *124*, 5052.



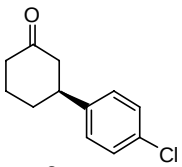
Results

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		14.690	3343.608	59528.695	1.5290
2		15.912	179016.031	3833900.750	98.4710
Total			182359.640	3893429.445	100.0000

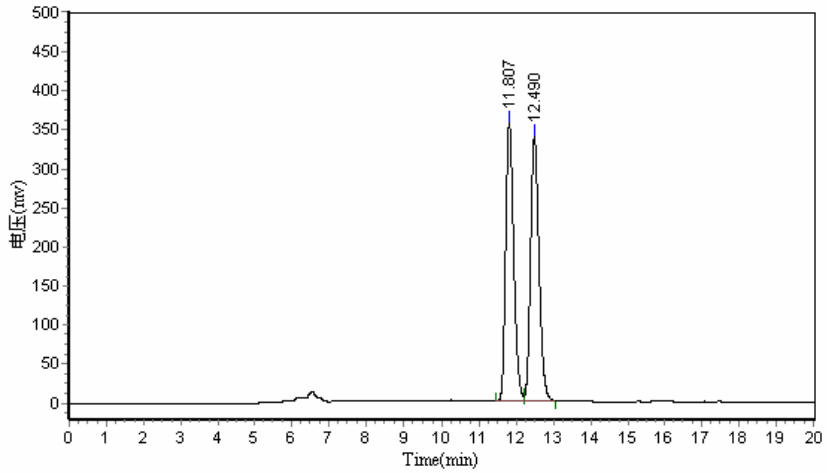


3e

^{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).

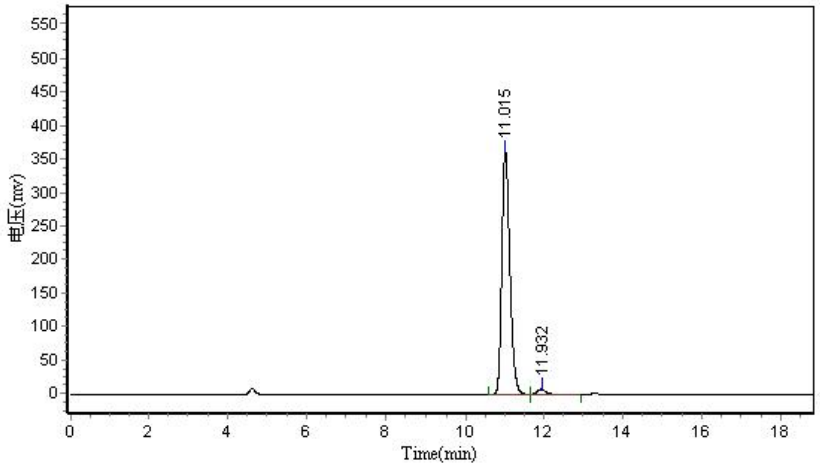
HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 11.0 min (maj), 11.9 min.

Ref: Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 883.



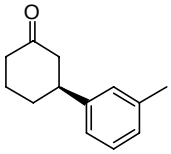
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.807	354797.813	5362085.000	49.7534
2		12.490	338781.063	5415236.000	50.2466
Total			693578.875	10777321.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.015	361329.688	5109656.000	97.7947
2		11.932	7515.633	115224.148	2.2053
Total			368845.321	5224880.148	100.0000

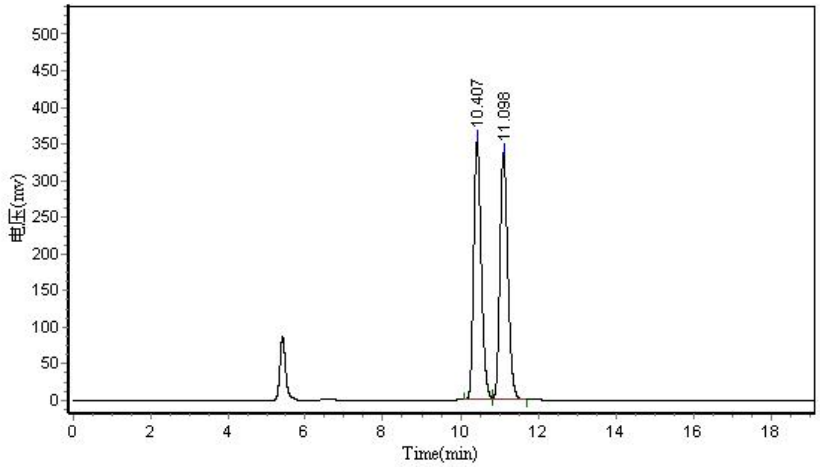


3f

^{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).

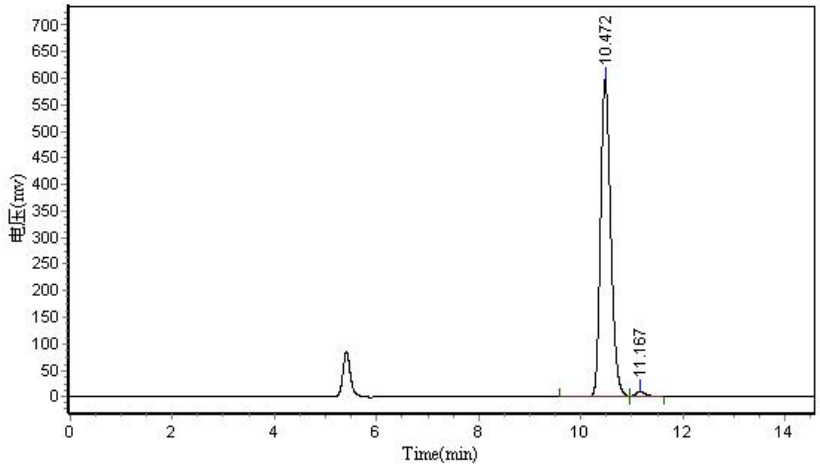
HPLC: Chiralcel OD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 10.5 min (maj), 11.2 min.

Ref: Boiteau, J.; Imbos, R.; Minnaard, A.; Feringa, B. *Org. Lett*., **2003,** *5*, 681.



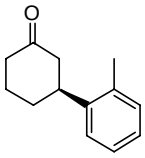
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.407	353720.344	4834028.000	50.0232
2		11.098	336994.813	4829541.500	49.9768
Total			690715.156	9663569.500	100.0000



Results

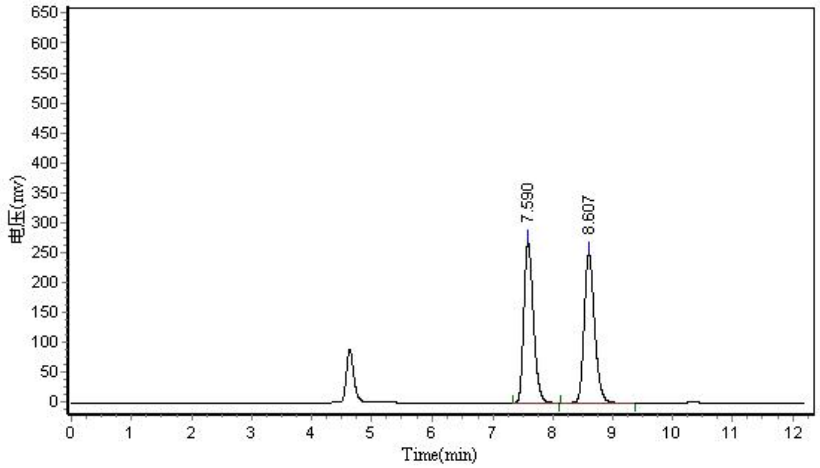
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.472	597986.125	8297507.000	98.3749
2		11.167	9457.029	137071.641	1.6251
Total			607443.154	8434578.641	100.0000



3g

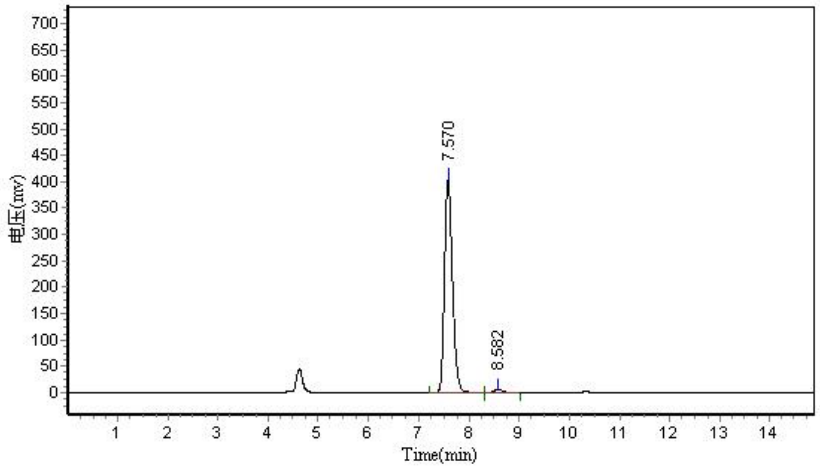
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.77-1.91 (m, 2H), 1.99-2.05 (m, 1H), 2.16-2.20 (m, 1H), 2.32 (s, 3H), 2.37-2.53 (m, 4H), 3.16-3.25 (m, 1H), 7.13-7.25 (m, 4H). HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 7.6 min (maj), 8.6 min.

Ref: Hayashi, T.; Tokunaga, N.; Yoshida, K.; and Han,J.-W. *J. Am. Chem. Soc.*, **2002,** *124*, 12102.



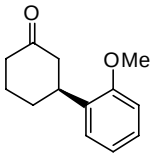
Results

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		7.570	403765.344	4486009.000	98.4075
2		8.582	6142.053	72595.547	1.5925
Total			409907.396	4558604.547	100.0000

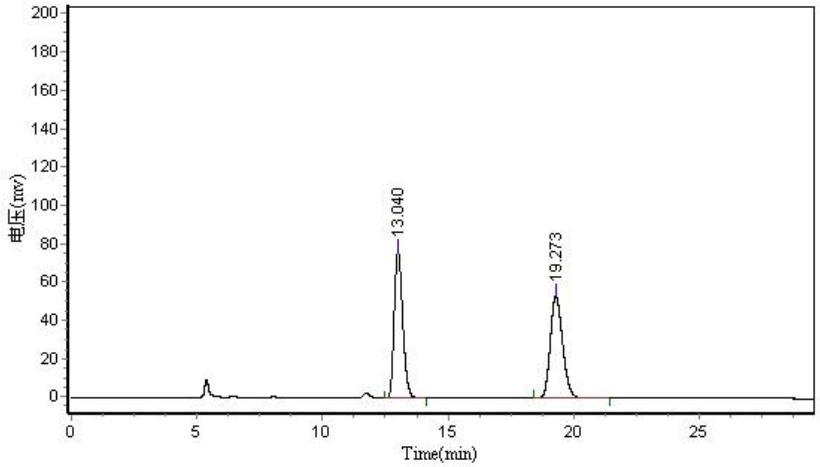


3h

^{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).

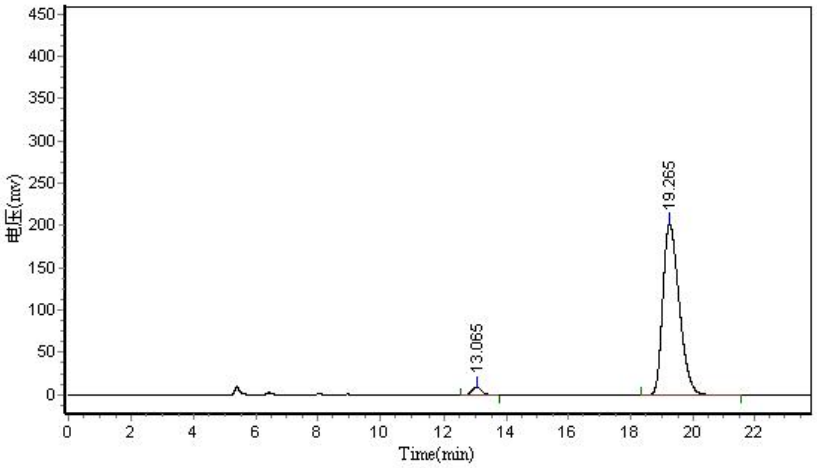
HPLC: Chiralpak AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.6 mL/min; Retention time: 13.1 min, 19.3 min (maj).

Ref: Boiteau, J.; Imbos, R.; Minnaard, A.; Feringa, B. *Org. Lett.*, **2003**, *5*, 681.



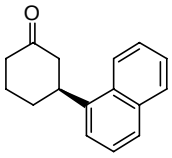
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.040	76358.797	1800745.750	49.6646
2		19.273	53523.621	1825068.875	50.3354
Total			129882.418	3625814.625	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.065	9349.227	221788.297	2.9117
2		19.265	201976.641	7395476.500	97.0883
Total			211325.867	7617264.797	100.0000

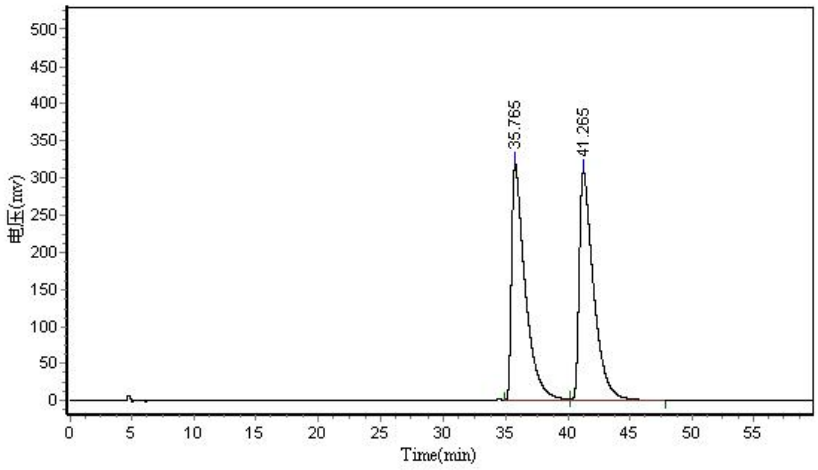


3i

^{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).

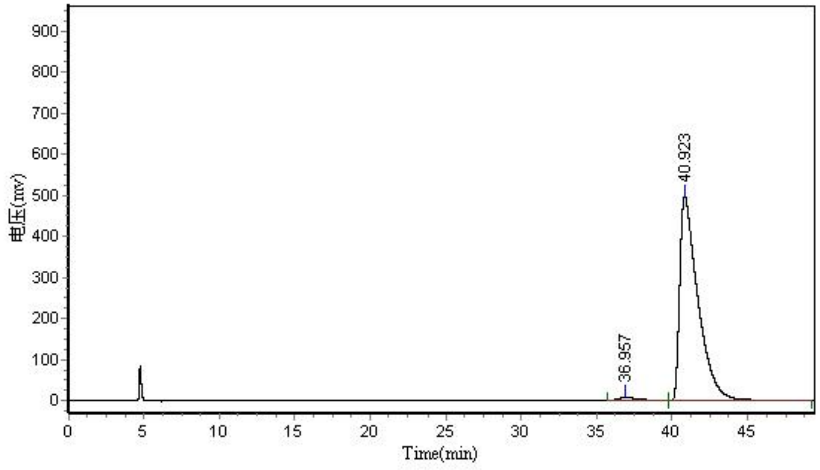
HPLC: Chiralcel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 37.0 min, 40.9 min (maj).

Ref: Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 883.



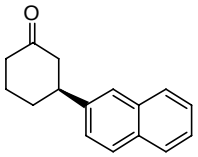
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		35.765	318032.375	24419586.000	49.4730
2		41.265	308339.406	24939842.000	50.5270
Total			626371.781	49359428.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		36.957	7349.875	633098.000	1.4928
2		40.923	497348.656	41777472.000	98.5072
Total			504698.531	42410570.000	100.0000

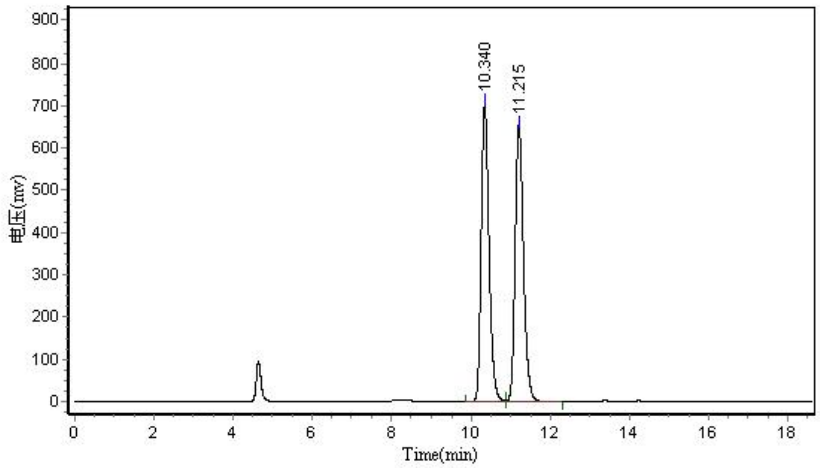


3j

^{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).

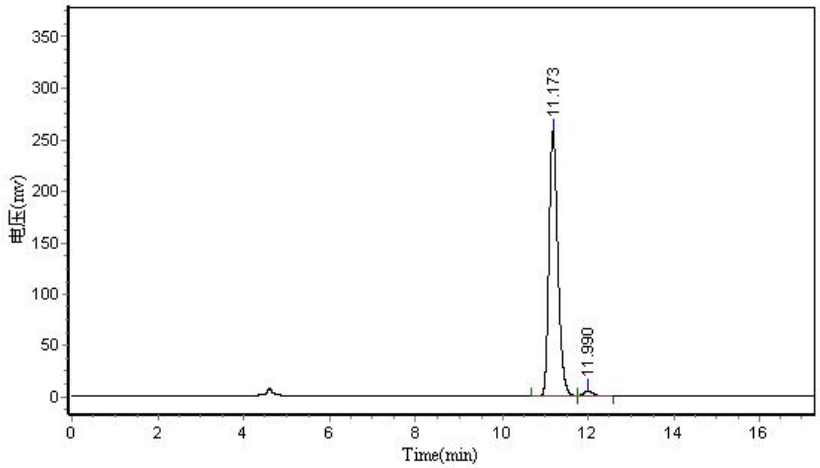
HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 11.2 min (maj), 12.0 min.

Ref: Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1999**, *40*, 6957.



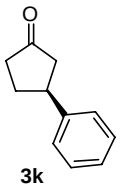
Results

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

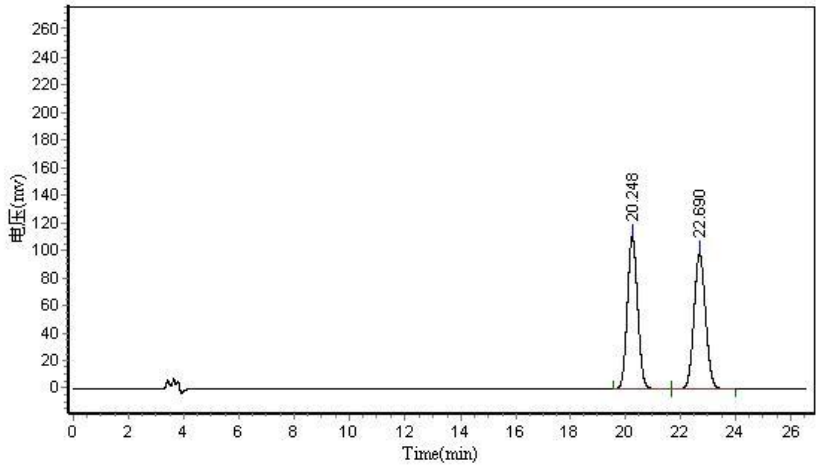
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.173	257124.875	3695915.000	97.7735
2		11.990	5318.716	84164.773	2.2265
Total			262443.591	3780079.773	100.0000



3k

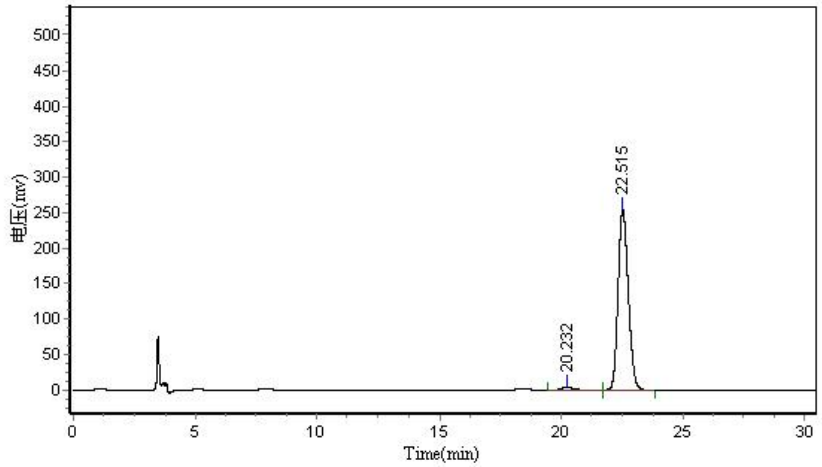
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90-2.08 (m, 1H), 2.22-2.54 (m, 4H), 2.67 (dd, *J* = 18.3, 7.8 Hz, 1H), 3.35-3.49 (m, 1H), 7.22-7.30 (m, 3H), 7.31-7.39 (m, 2H).
HPLC: Chiralcel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 20.2 min, 22.5 min (maj).

Ref: Takaya, Y.; Ogasawara, M.; Hayashi, T. *J. Am. Chem. Soc.* **1998,** *120,* 5579.



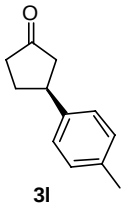
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.248	110518.664	2858506.500	49.7971
2		22.690	98116.148	2881800.500	50.2029
Total			208634.813	5740307.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.232	4411.511	130115.297	1.7292
2		22.515	254086.938	7394305.500	98.2708
Total			258498.449	7524420.797	100.0000

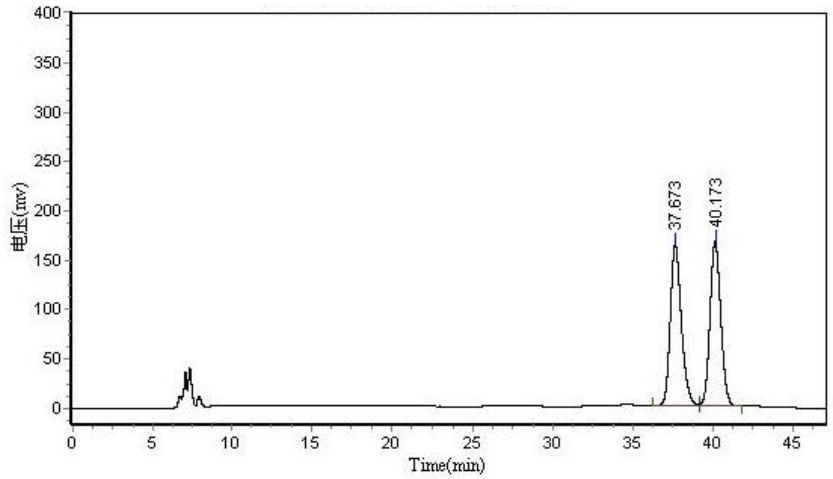


3l

^{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).

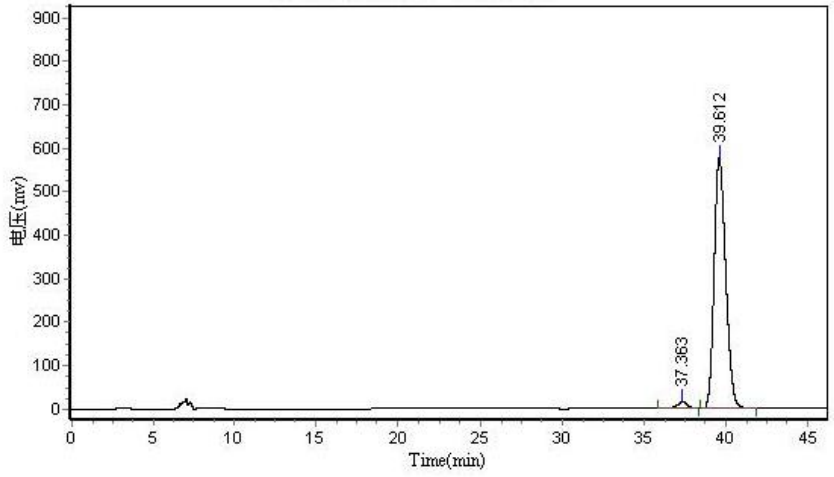
HPLC: Chiralcel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 99/1; flow = 0.5 mL/min; Retention time: 37.4 min, 39.6 min (maj).

Ref: Feng, C.-G.; Wang, Z.-Q.; Tian, P.; Xu, M.-H.; Lin, G.-Q. *Chem. Asian J.* **2008**, *3*, 1511.



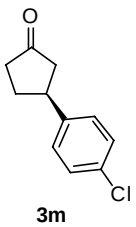
Results

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		37.363	14115.769	641547.938	2.2055
2		39.612	576989.188	28447320.000	97.7945
Total			591104.956	29088867.938	100.0000

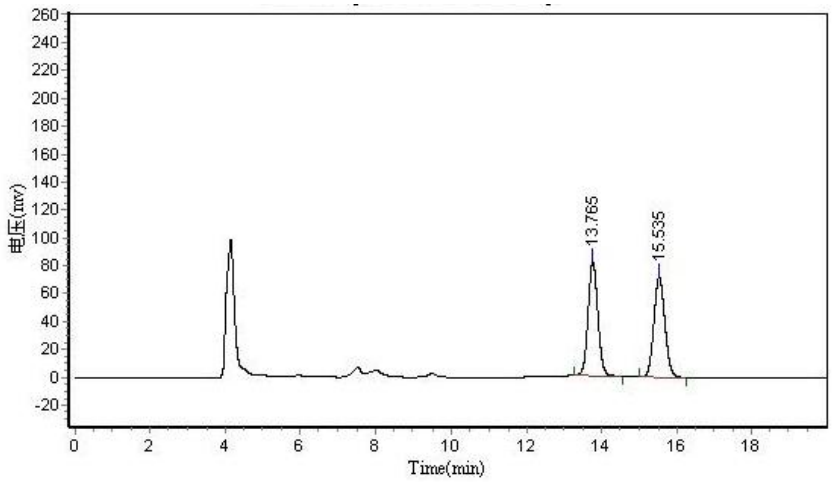


3m

^{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).

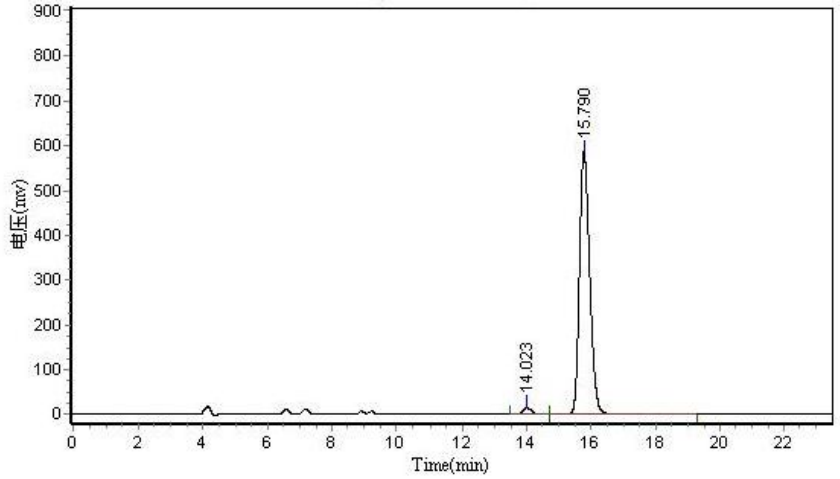
HPLC: Chiralcel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 14.0 min, 15.8 min (maj).

Ref: Feng, C.-G.; Wang, Z.-Q.; Tian, P.; Xu, M.-H.; Lin, G.-Q. *Chem. Asian J.* **2008**, *3*, 1511.



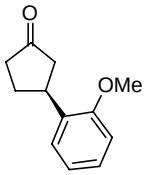
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.765	81739.070	1477601.375	50.2198
2		15.535	71823.234	1464669.750	49.7802
Total			153562.305	2942271.125	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.023	14759.937	279404.594	2.0989
2		15.790	586391.375	13032714.000	97.9011
Total			601151.312	13312118.594	100.0000

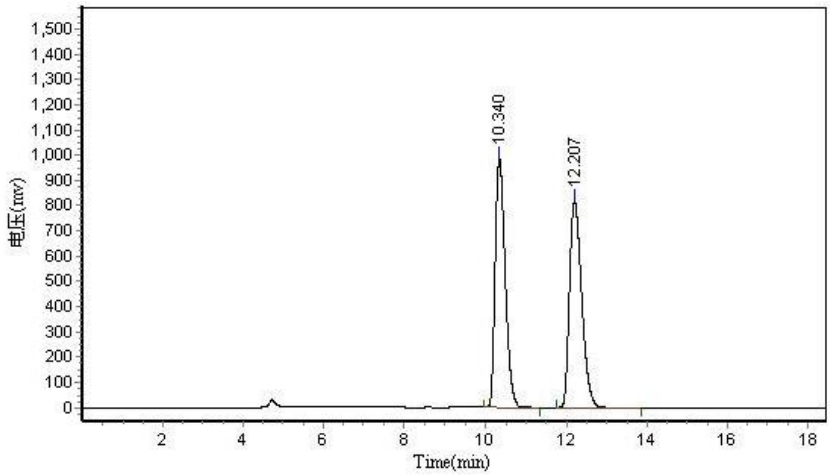


3n

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00-2.11 (m, 1H), 2.23-2.48 (m, 4H), 2.64 (dd, *J* = 18.0, 7.5 Hz, 1H), 3.63-3.74 (m, 1H), 3.84 (s, 3H), 6.88-6.97 (m, 2H), 7.17-7.26 (m, 2H).

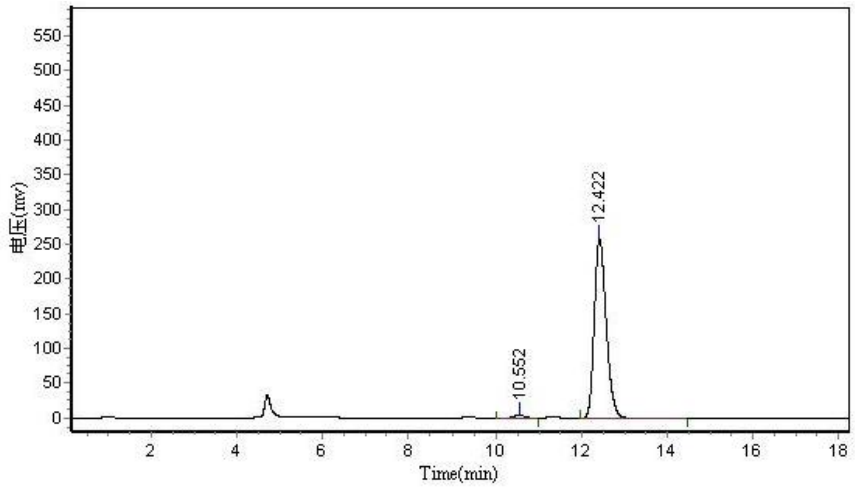
HPLC: Chiralcel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 10.6 min, 12.4 min (maj).

Ref: Yelb, Q.; Grunewald, G. L. *J. Med. Chem.* **1989**, *32*, 478.



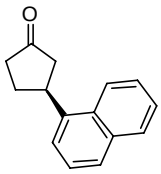
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.340	984275.938	17040330.000	49.7884
2		12.207	816781.125	17185192.000	50.2116
Total			1801057.063	34225522.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.552	4394.226	72993.188	1.4469
2		12.422	258378.578	4971777.000	98.5531
Total			262772.804	5044770.188	100.0000

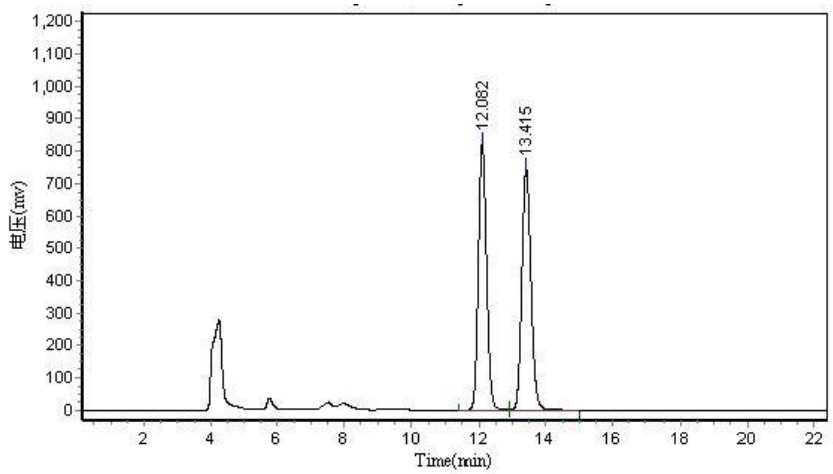


3o

^{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).

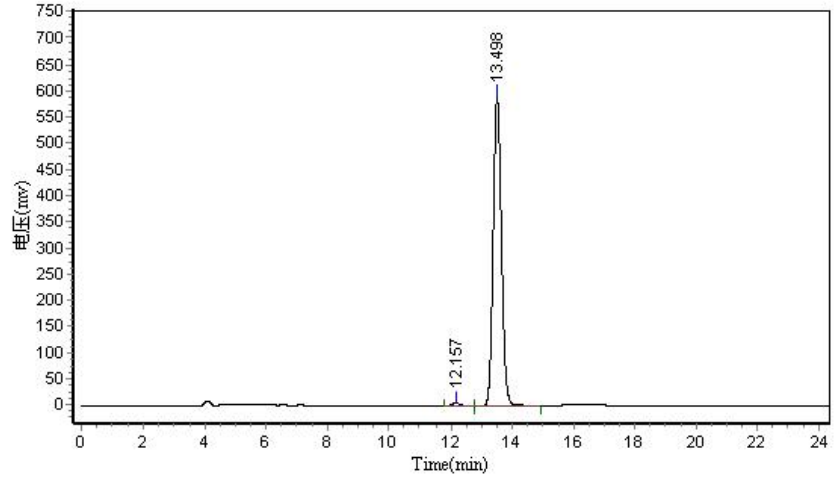
HPLC: Chiralcel OZ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.8 mL/min; Retention time: 12.2 min, 13.5 min (maj).

Ref: Feng, C.-G.; Wang, Z.-Q.; Tian, P.; Xu, M.-H.; Lin, G.-Q. *Chem. Asian J.* **2008**, *3*, 1511.



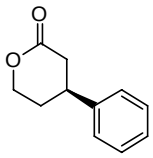
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.082	819691.438	14235402.000	49.7535
2		13.415	743597.813	14376469.000	50.2465
Total			1563289.250	28611871.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.157	6026.279	98504.047	0.8873
2		13.498	588155.063	11003387.000	99.1127
Total			594181.342	11101891.047	100.0000

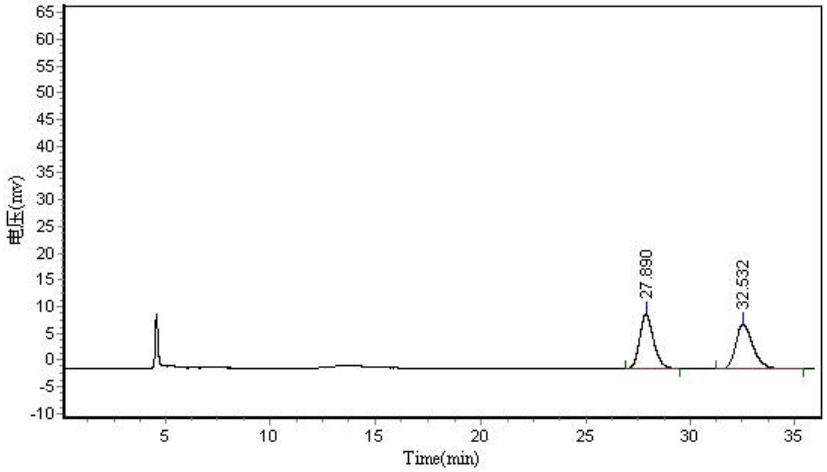


3p

^{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).

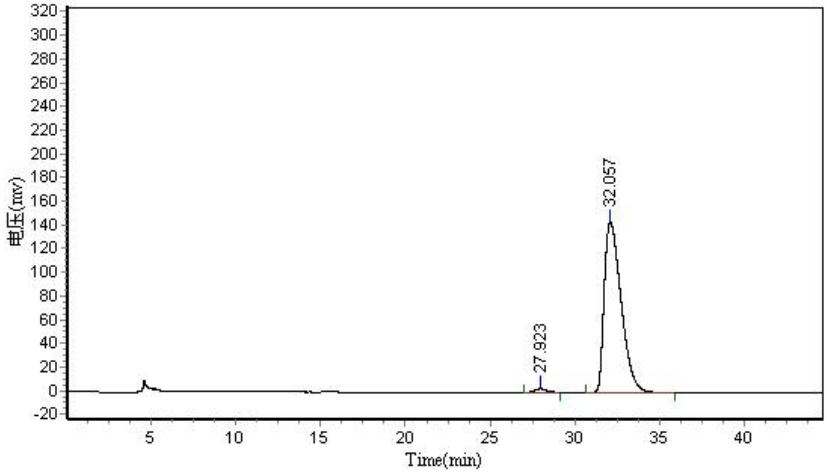
HPLC: Chiralpak AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 27.9 min, 32.1 min (maj).

Ref: Boiteau, J.; Imbos, R.; Minnaard, A.; Feringa, B. *Org. Lett*., **2003,** *5*, 681.



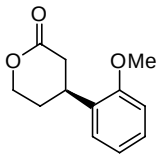
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.890	10121.000	467127.906	49.3439
2		32.532	8297.507	479549.625	50.6561
Total			18418.507	946677.531	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.923	2991.538	136785.297	1.3569
2		32.057	143439.203	9944130.000	98.6431
Total			146430.741	10080915.297	100.0000

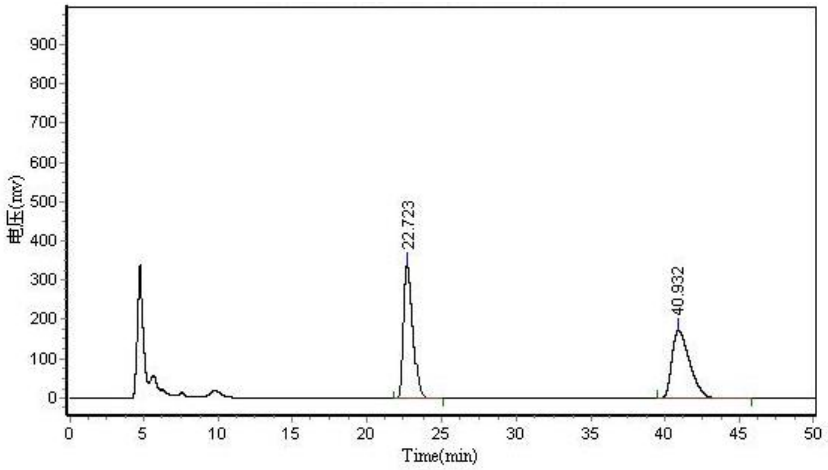


3q

^{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).

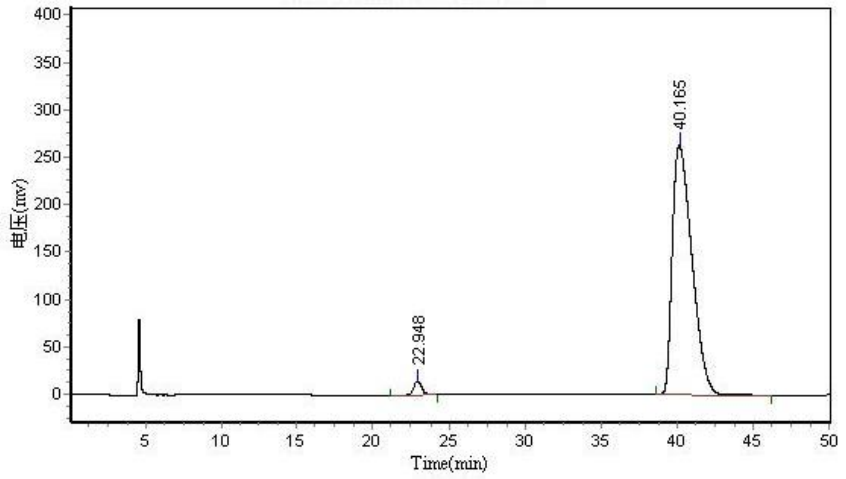
HPLC: Chiralpak AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 22.9 min, 40.2 min (maj).

Ref: Jin, S.-S.; Wang, H.; Xu, M.-H. *Chem.Common*, **2011**, *47*, 7230.



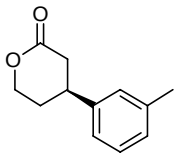
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.723	339878.156	14363554.000	49.8841
2		40.932	172196.016	14430269.000	50.1158
Total			512074.172	28793823.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.948	15013.800	546834.875	2.2484
2		40.165	263545.156	23773702.000	97.7516
Total			278558.956	24320536.875	100.0000

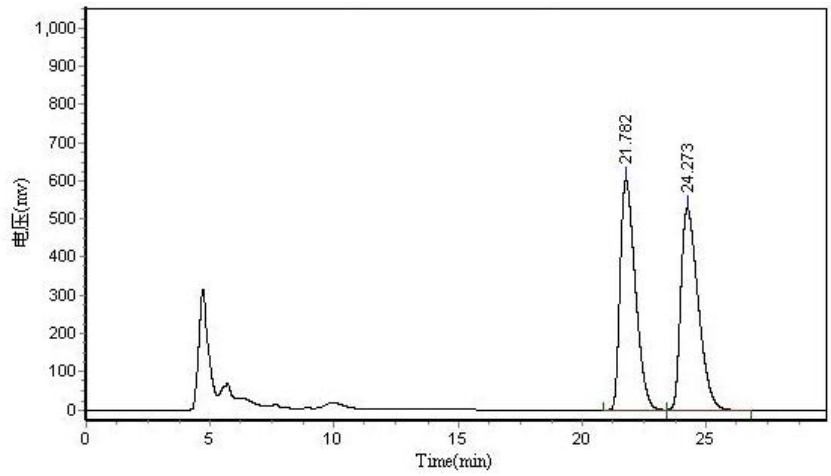


3r

^{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).

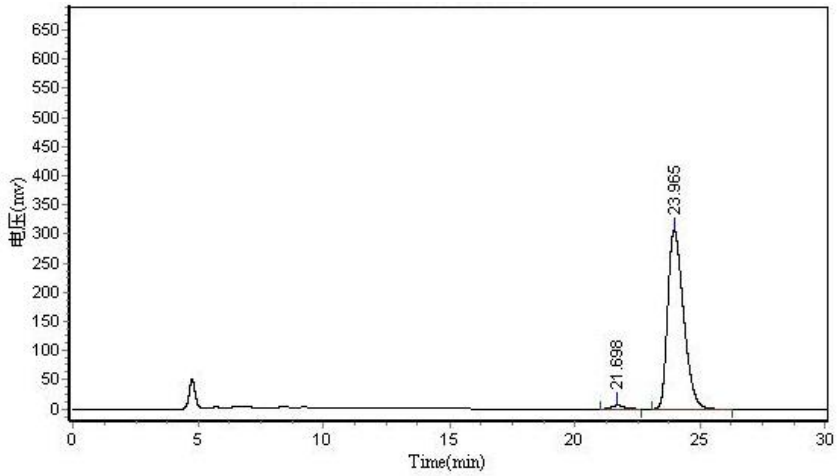
HPLC: Chiralpak AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 21.7 min, 24.0 min (maj).

Ref: Bürgi, J. J.; Mariz, R.; Gatti, M.; Drinkel, E.; Luan, X.; Blumentritt, S.; Linden, A.; Dorta, R. A*ngew. Chem. Int. Ed.* **2009**, *48*, 2768.



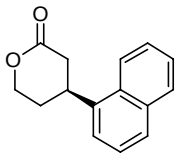
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.782	603203.188	25727878.000	49.8811
2		24.273	529131.063	25850572.000	50.1189
Total			1132334.250	51578450.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.698	5937.079	206019.344	1.5079
2		23.965	306201.344	13456970.000	98.4921
Total			312138.422	13662989.344	100.0000

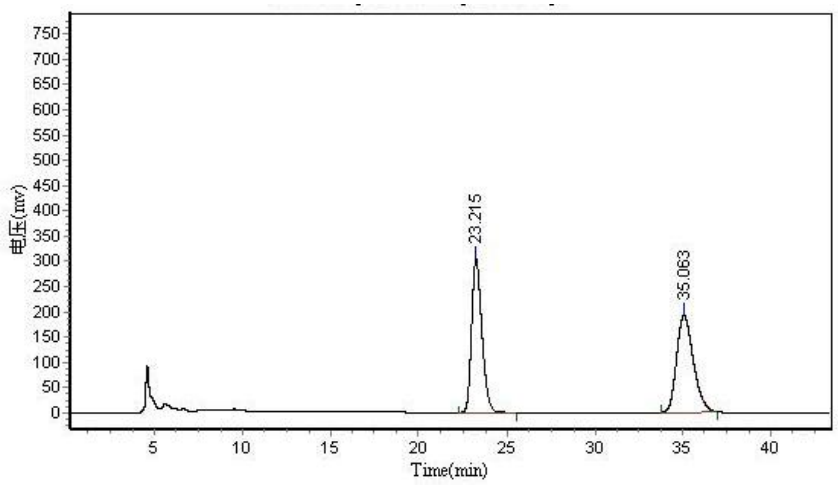


3s

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10-2.23 (m, 1H), 2.30-2.36 (m, 1H), 2.76 (dd, *J* = 17.7, 9.9 Hz, 1H), 3.08 (dd, *J* = 17.7, 6.0 Hz, 1H), 4.02-4.12 (m, 1H), 4.46-4.50 (m, 2H), 7.00-7.02 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.45-7.58 (m, 3H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H).

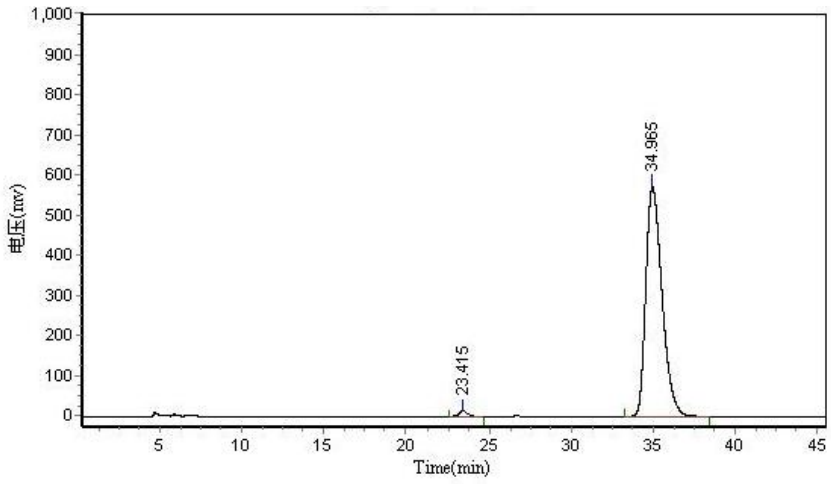
HPLC: Chiralpak AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 23.4 min, 35.0 min (maj).

Ref: Gendrineau, T.; Chuzel, O.; Eijsberg, H.; Genet, J-P.; Darses, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 7669.



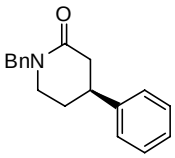
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.215	303003.219	12386152.000	49.3491
2		35.063	192336.625	12712914.000	50.6509
Total			495339.844	25099066.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.415	14369.841	547620.938	1.3785
2		34.965	570955.188	39177276.000	98.6215
Total			585325.028	39724896.938	100.0000

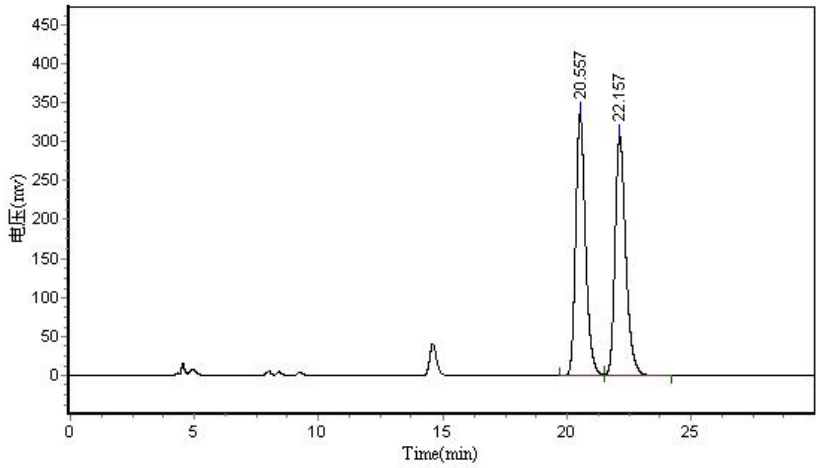


3t

^{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).

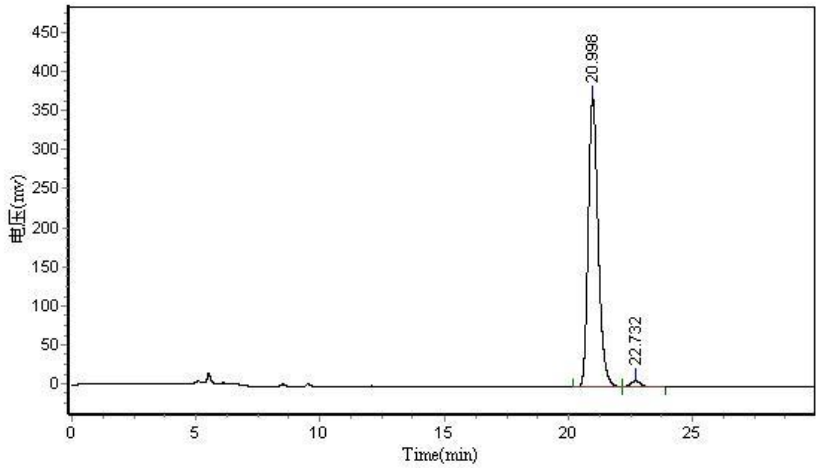
HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 21.0 min (maj), 22.7 min.

Ref: Senda, T. Ogasawara, M. Gayashi, T. *J. Org. Chem.* **2001**, *66*, 6852.



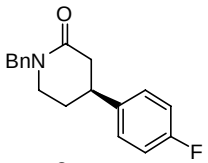
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.557	334979.313	9202285.000	50.0283
2		22.157	306399.969	9191888.000	49.9717
Total			641379.281	18394173.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.998	369601.469	10355180.000	97.7039
2		22.732	8081.784	243349.547	2.2961
Total			377683.253	10598529.547	100.0000

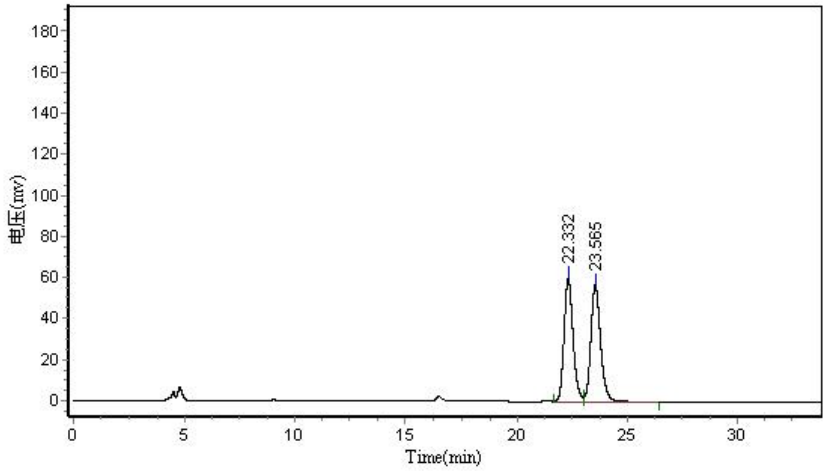


3u

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83-2.08 (m, 2H), 2.54 (dd, *J* = 17.7, 11.1 Hz, 1H), 2.80 (dd, *J* = 17.1, 4.8 Hz, 1H), 3.05-3.13 (m, 1H), 3.27-3.31 (m, 2H), 4.55 (d, *J* = 15.0 Hz, 1H), 4.74 (d, *J* = 14.7 Hz, 1H), 7.00 (t, *J* = 8.4 Hz, 2H), 7.13-7.17 (m, 2H), 7.27-7.36 (m, 5H).

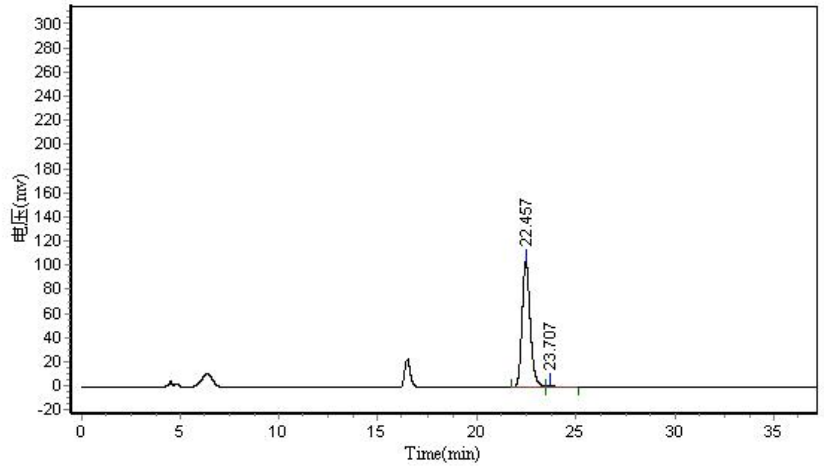
HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 22.5 min (maj), 23.7 min.

Ref: Senda, T. Ogasawara, M. Gayashi, T. *J. Org. Chem.* **2001,** *66,* 6852.



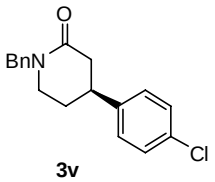
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.332	60270.293	1712624.375	49.1633
2		23.565	56922.777	1770919.625	50.8367
Total			117193.070	3483544.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.457	104505.273	3043873.500	98.3001
2		23.707	1331.457	52636.516	1.6999
Total			105836.730	3096510.016	100.0000

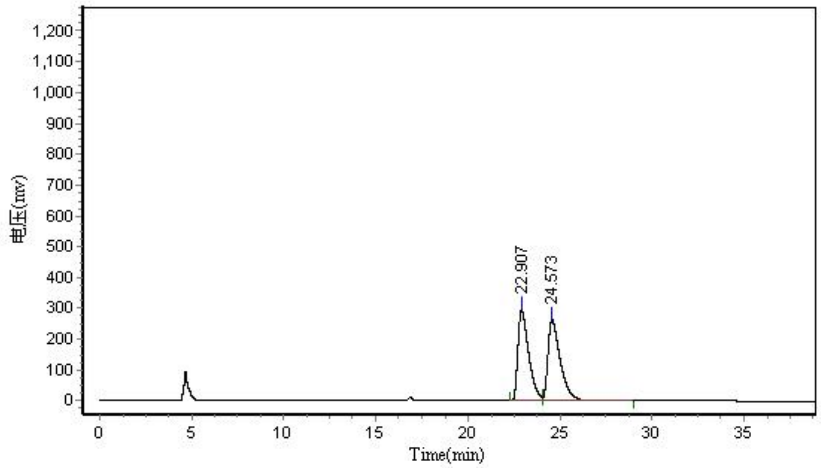


3v

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.84-2.07 (m, 2H), 2.53 (dd, *J* = 17.4, 11.1 Hz, 1H), 2.79 (dd, *J* = 17.4, 5.4 Hz, 1H), 3.03-3.13 (m, 1H), 3.23-3.33 (m, 2H), 4.54 (d, *J* = 14.7 Hz, 1H), 4.73 (d, *J* = 15.0 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.27-7.36 (m, 7H).

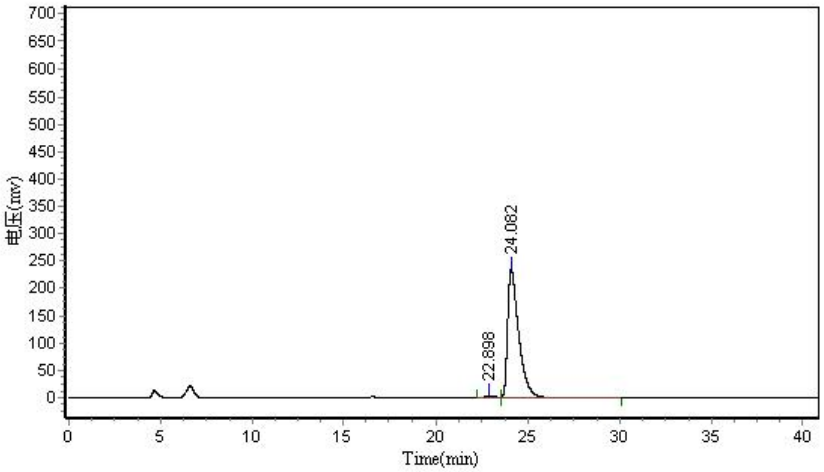
HPLC: Chiralcel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 22.9 min, 24.1 min (maj).

Ref: Senda, T. Ogasawara, M. Gayashi, T. *J. Org. Chem.* **2001,** *66,* 6852.



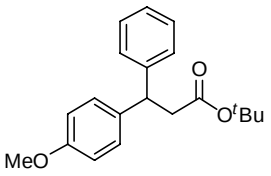
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.907	295153.563	12051471.000	49.3264
2		24.573	264422.188	12380626.000	50.6736
Total			559575.750	24432097.000	100.0000



Results

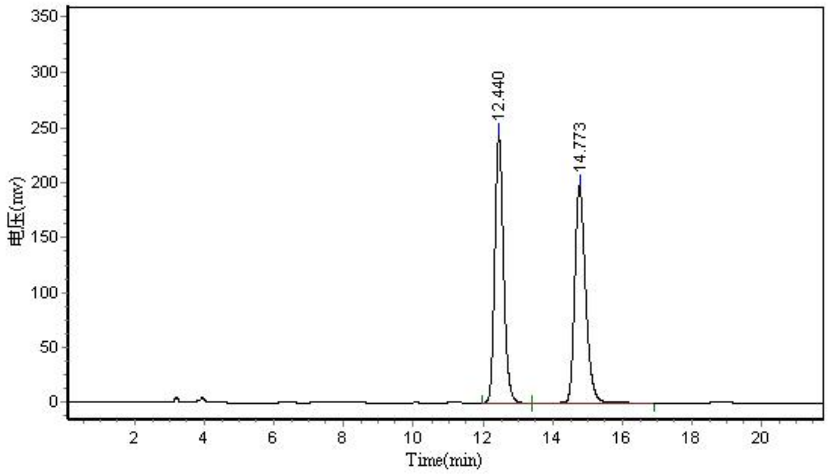
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.898	3690.359	126109.734	1.2565
2		24.082	234475.859	9910202.000	98.7435
Total			238166.219	10036311.734	100.0000



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (s, 9H), 2.93 (d, *J* = 8.1 Hz, 2H), 3.76 (s, 3H), 4.43 (t, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 2H), 7.14-7.29 (m, 7H).

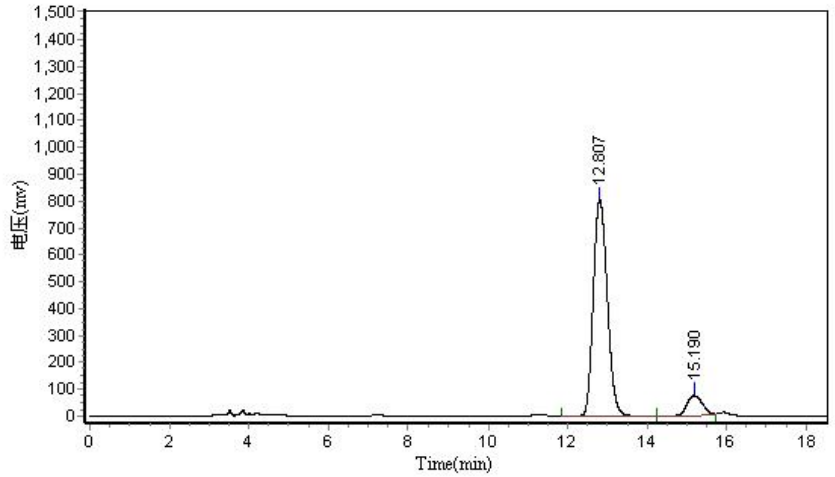
HPLC: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 12.8 min (maj), 15.2 min.

Ref: Paquin, J.-F.; Stephenson, C. R. J.; Defieber, C.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 3821.



Results

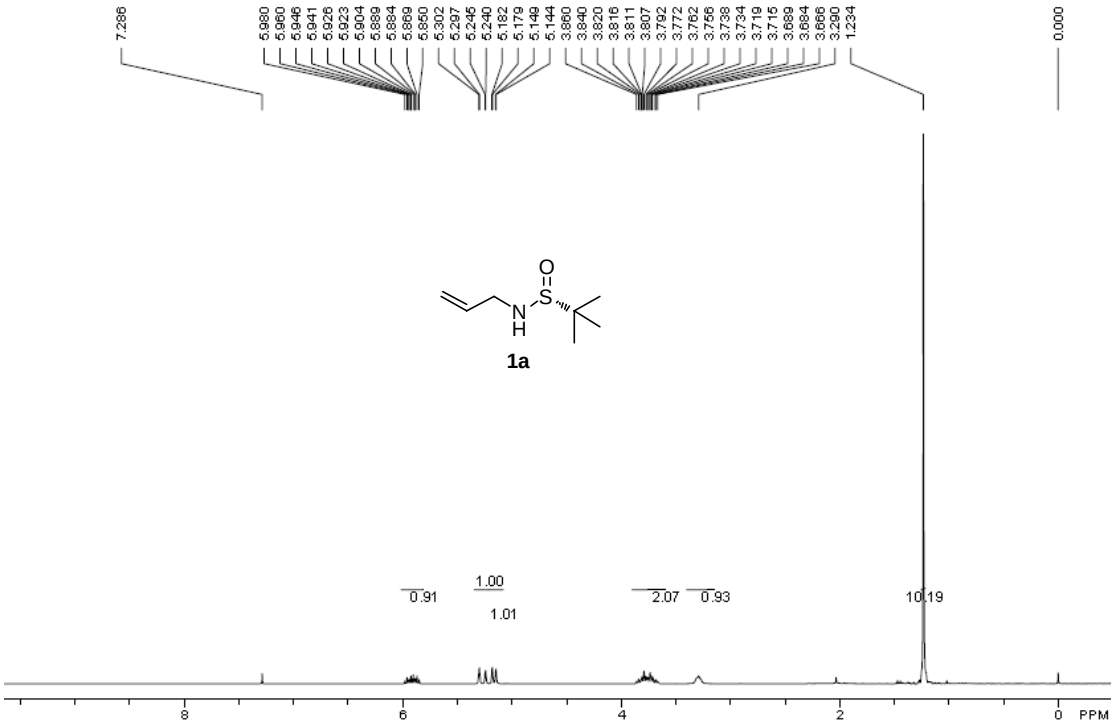
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.440	242398.125	4249242.000	49.8165
2		14.773	196375.469	4280554.000	50.1835
Total			438773.594	8529796.000	100.0000



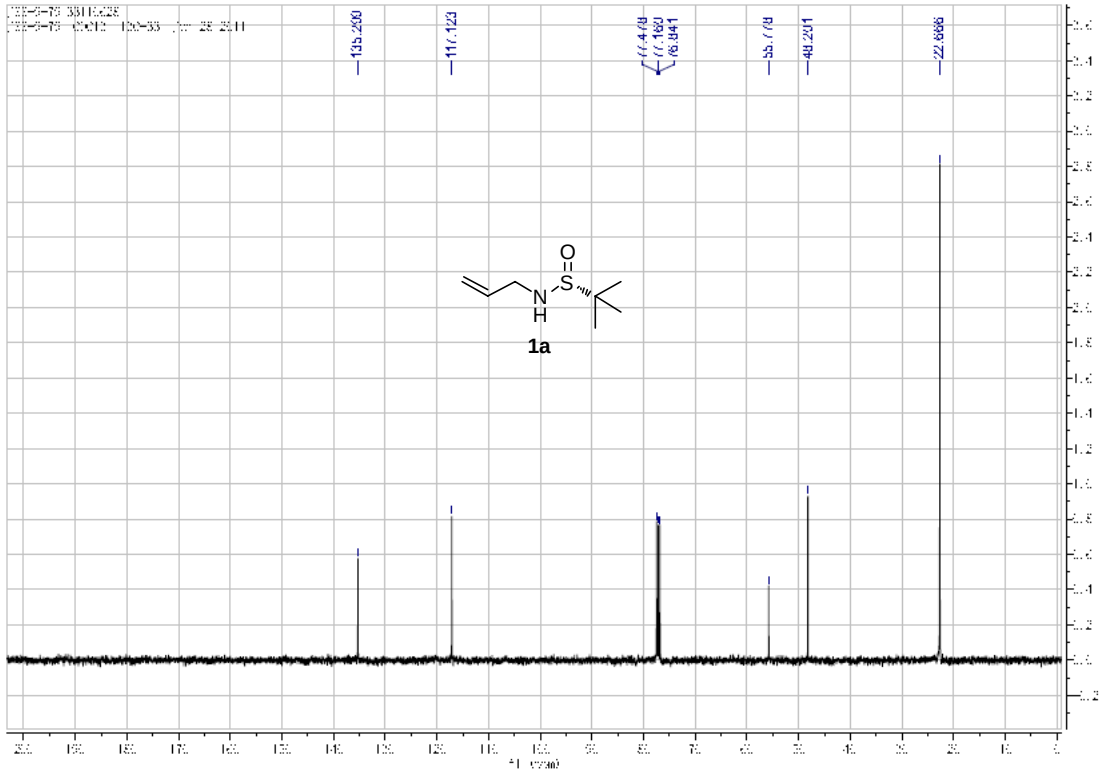
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.807	803266.188	19676904.000	90.1318
2		15.190	75416.281	2154347.750	9.8682
Total			878682.469	21831251.750	100.0000

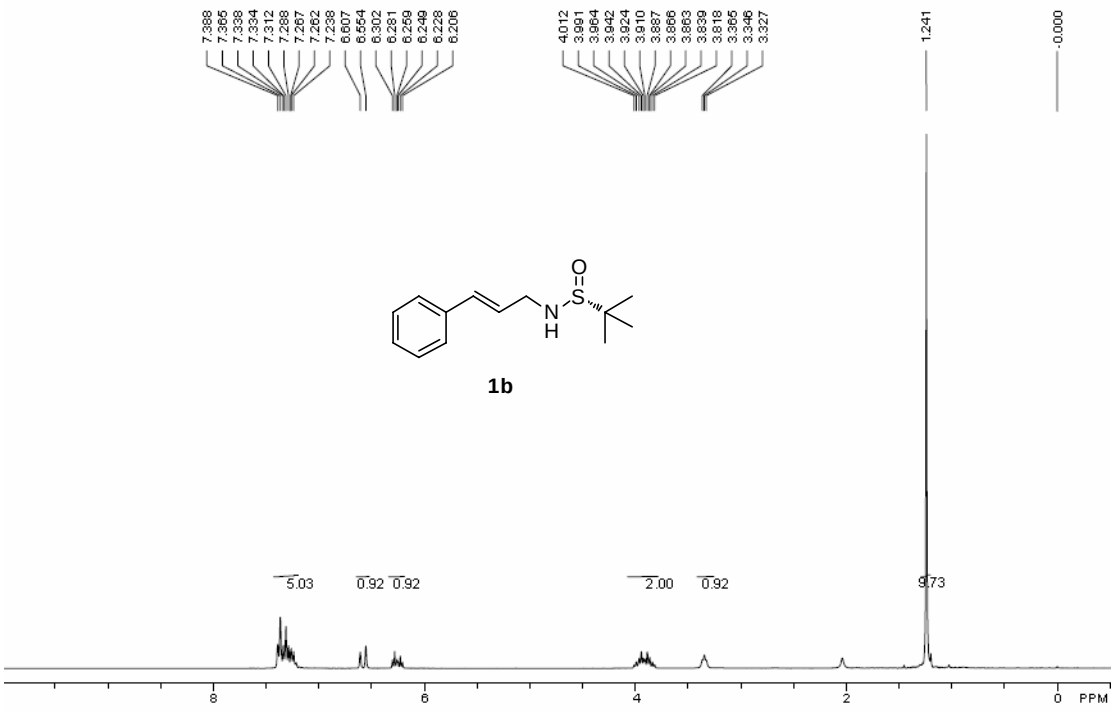
6. Copies of ^{1}H and ^{13}C NMR for ligand compounds.



1a



1a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6.607
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6.302
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6.259
6.249
6.228
6.206
4.012
3.991
3.964
3.942
3.924
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3.887
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3.863
3.839
3.818
3.365
3.346
3.327
1.241
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O
S
N
H
5.03
0.92
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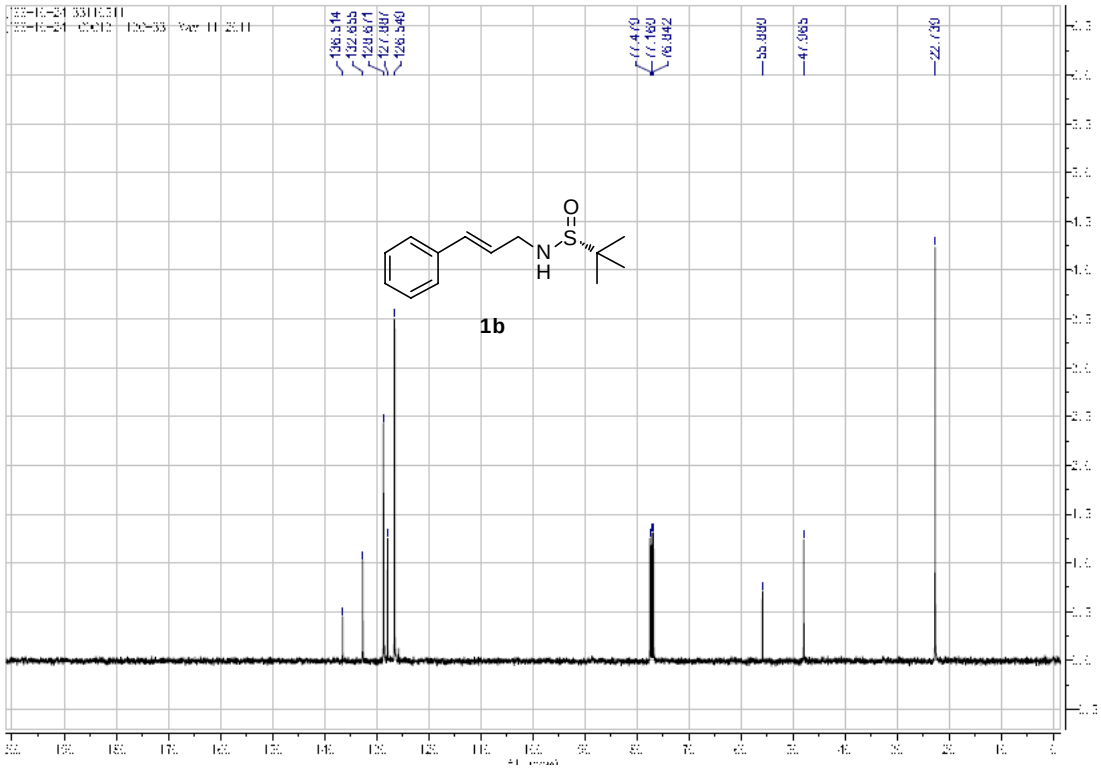
2.00
0.92
9.73
8
6
4
2
0
PPM

1b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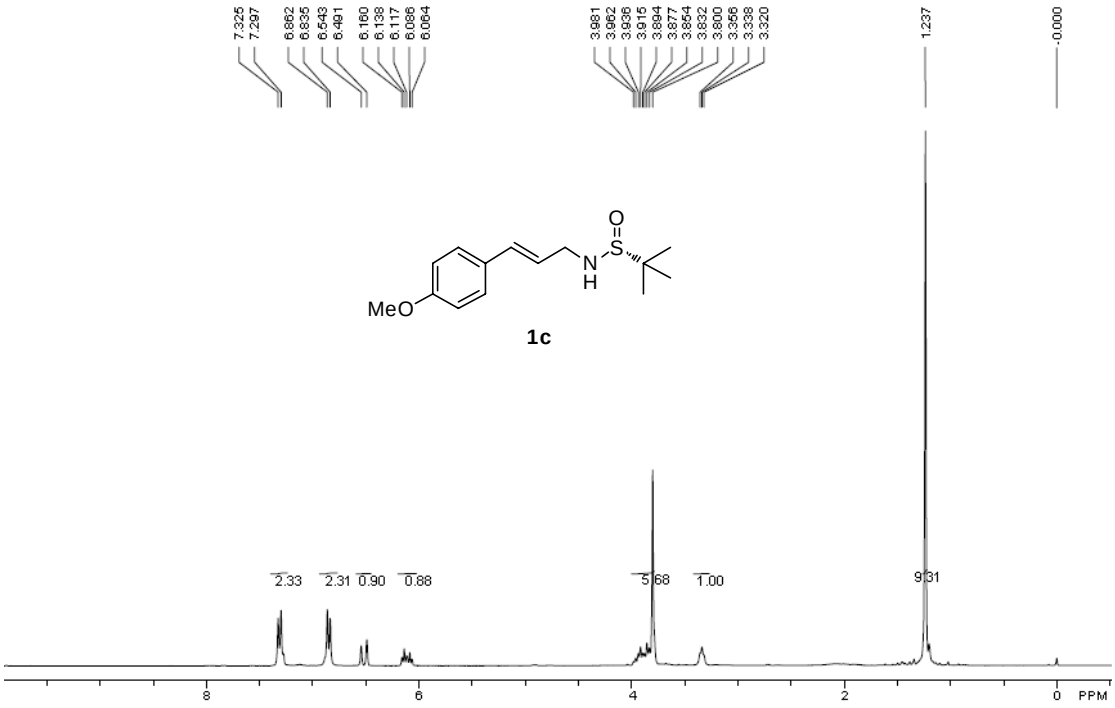
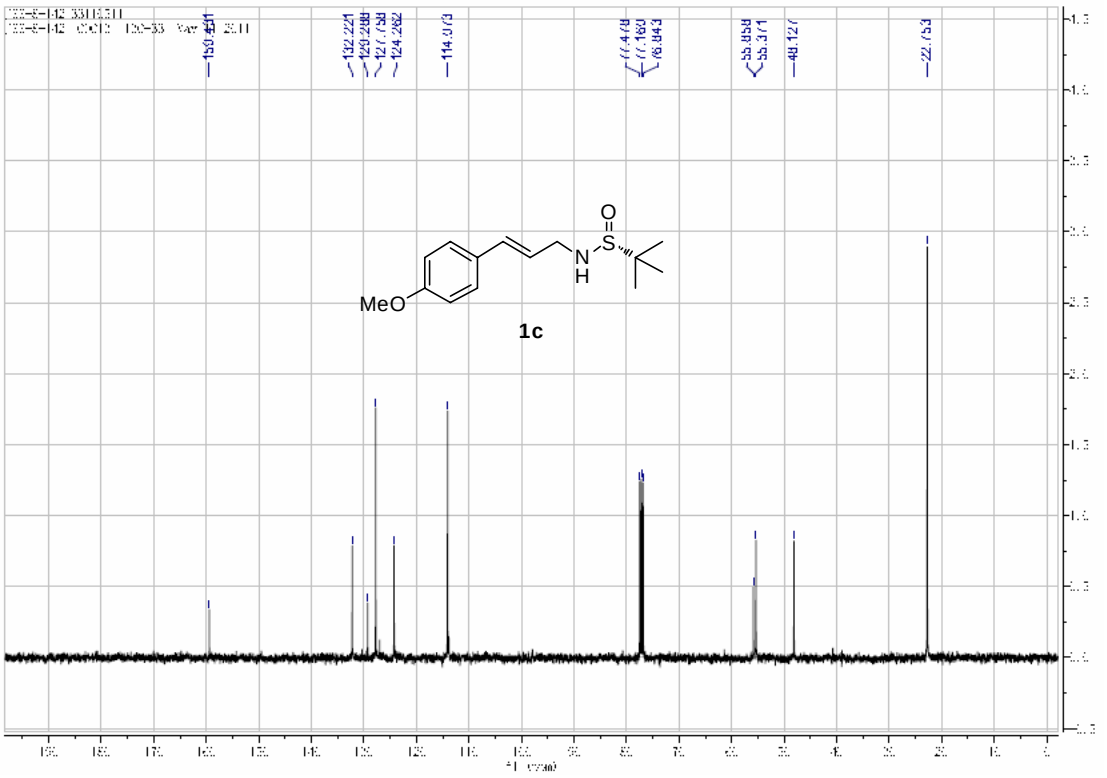
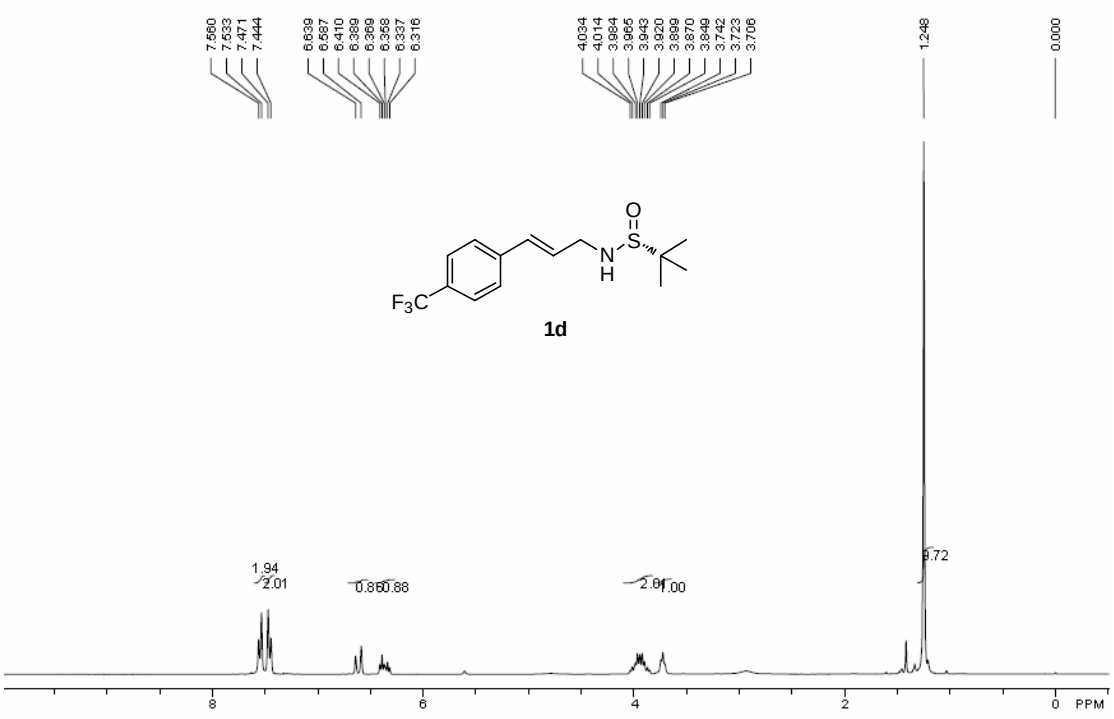
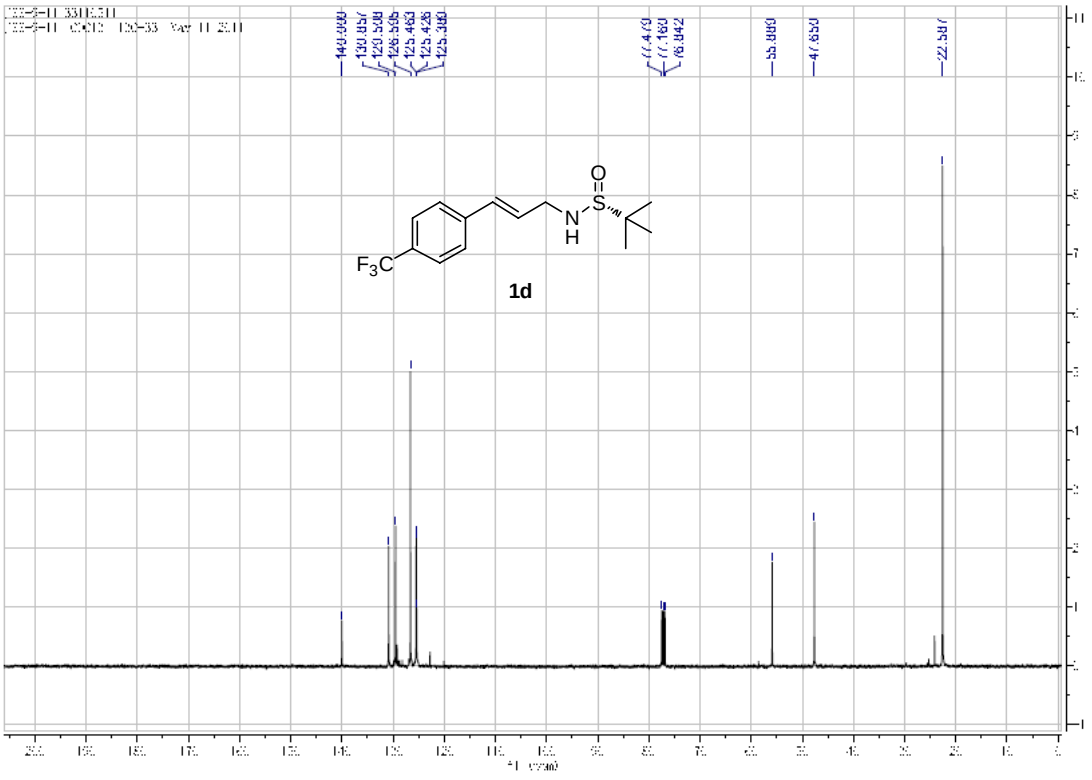
132.655
129.871
127.080
126.940
77.484
77.160
76.842
55.880
47.085
22.730
O
S
N
H

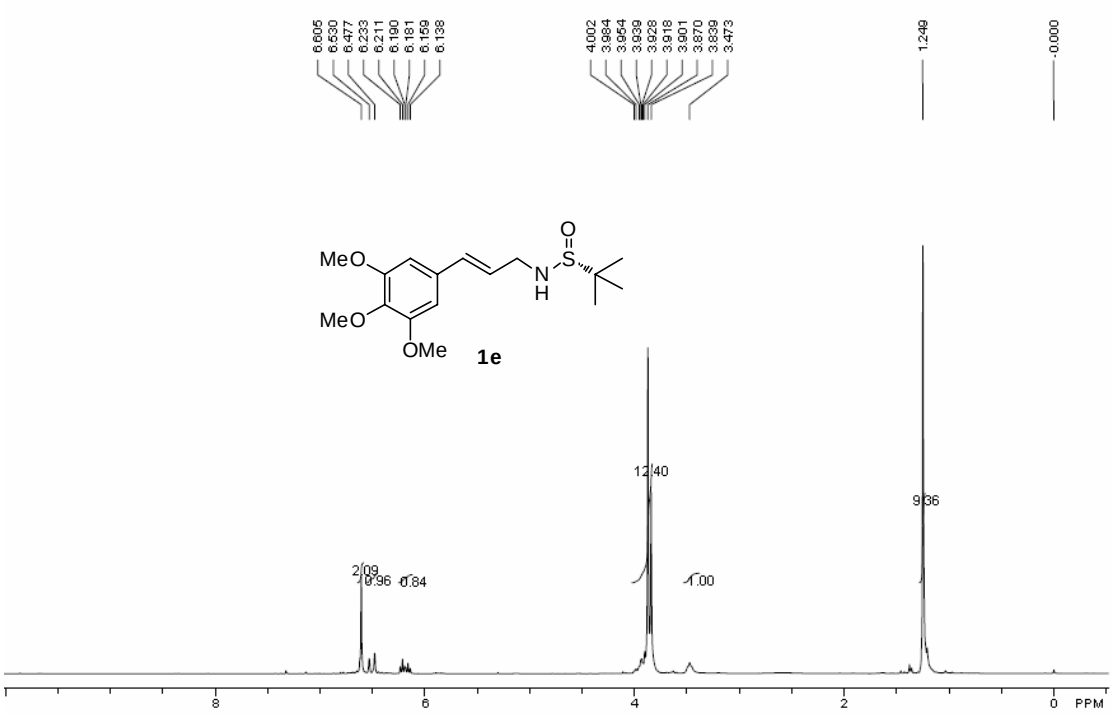
1b

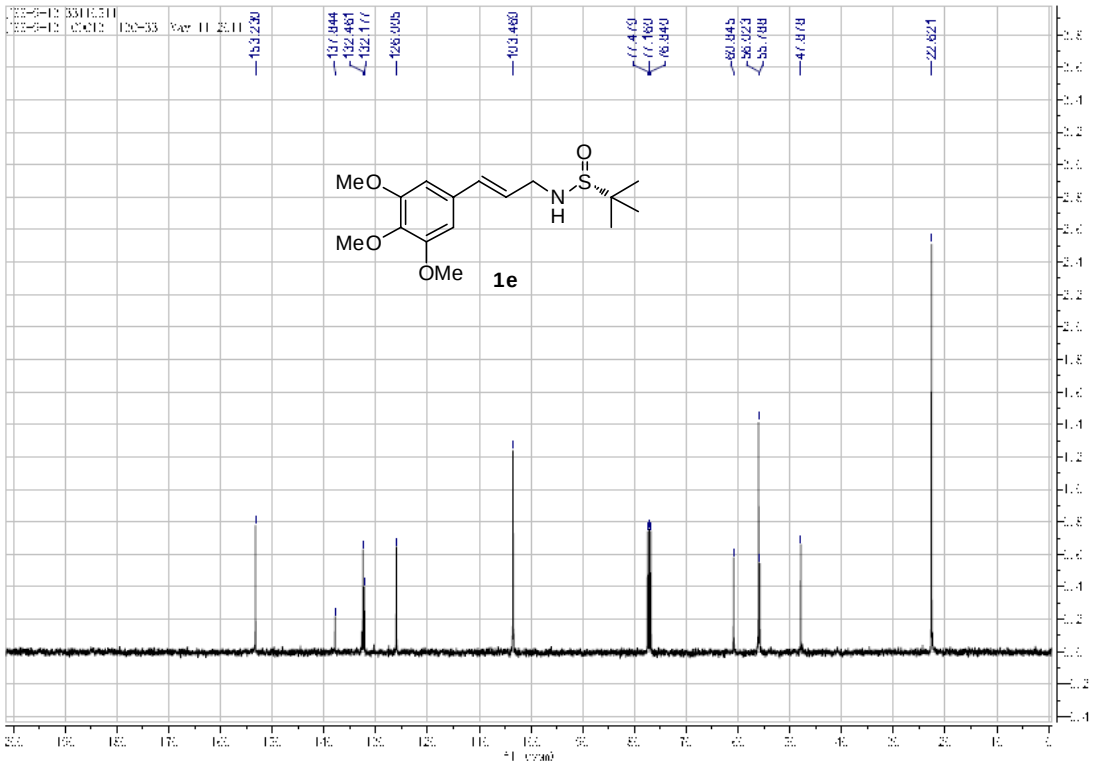

7.325
7.297
6.862
6.835
6.543
6.491
6.160
6.138
6.117
6.086
6.064
3.981
3.962
3.936
3.915
3.894
3.877
3.854
3.832
3.800
3.356
3.338
3.320
1.237
-0.000
MeO
1c
2.33
2.31
0.90
0.88
5.68
1.00
9.31
8
6
4
2
0
PPM

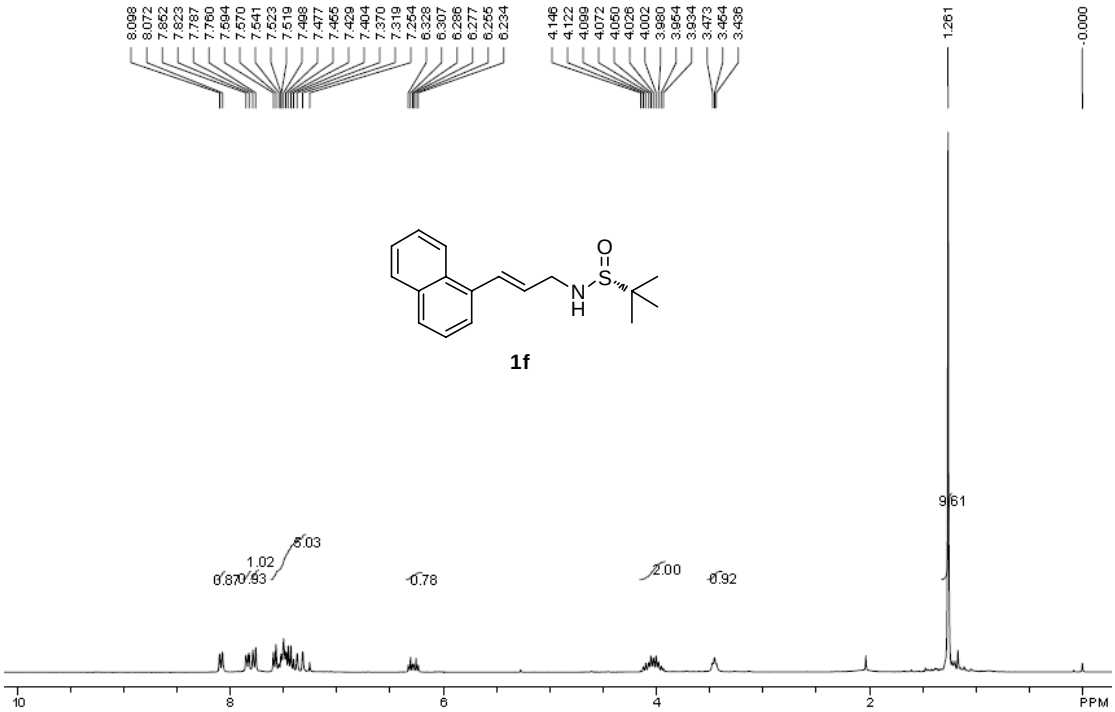

MeO
1c


7.560
7.533
7.471
7.444
6.639
6.587
6.410
6.389
6.369
6.368
6.337
6.316
4.034
4.014
3.984
3.965
3.943
3.920
3.899
3.870
3.849
3.742
3.723
3.706
1.248
0.000
1.94
2.01
0.86
0.88
2.01
1.00
9.72
8
6
4
2
0
PPM
F3C
N
H
O
S
1d


F3C
N
H
O
S
1d



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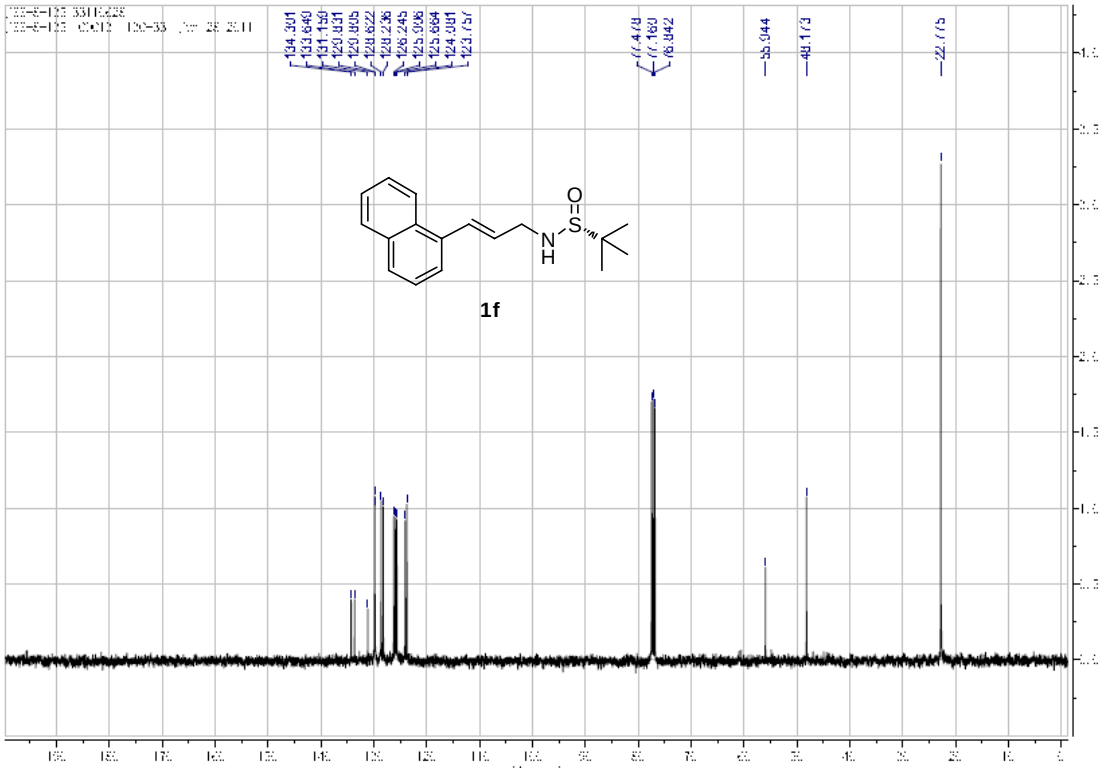
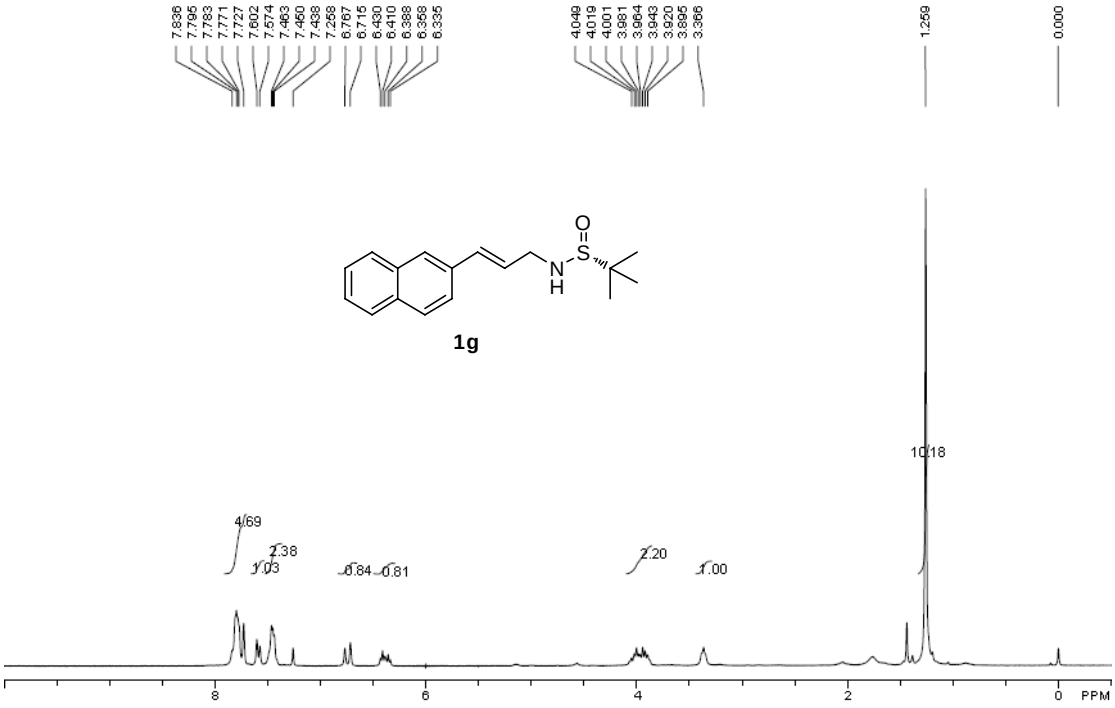
8.072
7.862
7.823
7.787
7.760
7.694
7.670
7.541
7.523
7.519
7.498
7.477
7.455
7.429
7.404
7.370
7.319
7.254
6.328
6.307
6.286
6.277
6.255
6.234
4.146
4.122
4.099
4.072
4.050
4.026
4.002
3.980
3.964
3.934
3.473
3.454
3.436
1.261
-0.000
1f
9.61
6.03
1.02
0.87
0.93
0.78
2.00
0.92
10
8
6
4
2
PPM


1f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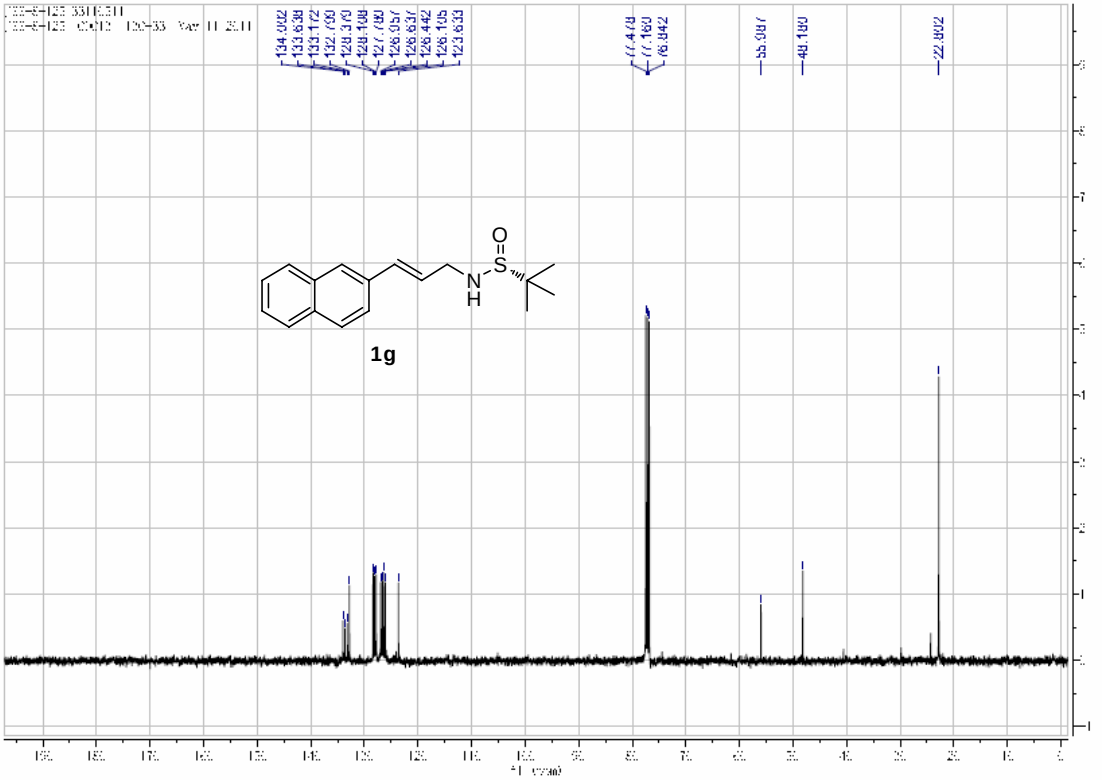
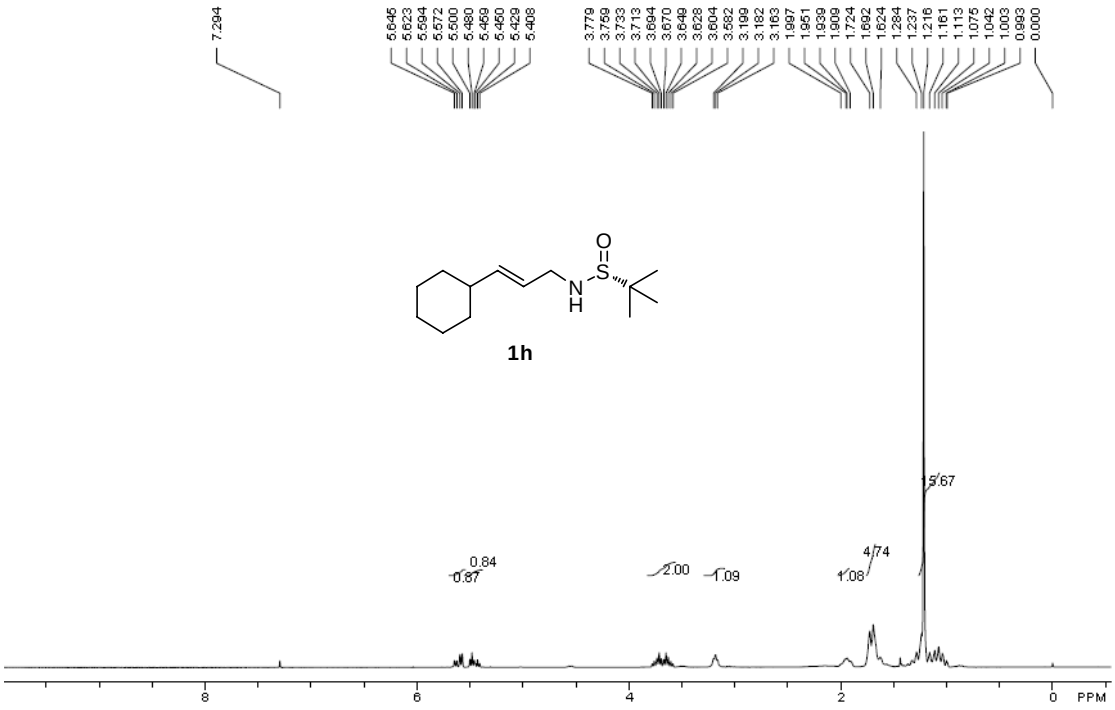
7.783
7.771
7.727
7.602
7.574
7.463
7.460
7.438
7.258
6.767
6.715
6.430
6.410
6.388
6.368
6.335
4.049
4.019
4.001
3.981
3.964
3.943
3.920
3.895
3.366
1.259
0.000
1g
10.18
4.69
2.38
1.03
0.84
0.81
2.20
1.00
8
6
4
2
0
PPM


134.002
133.639
133.172
132.790
129.370
129.148
127.780
126.957
126.837
126.442
126.105
123.633
77.479
77.160
76.842
55.597
48.190
22.892
1g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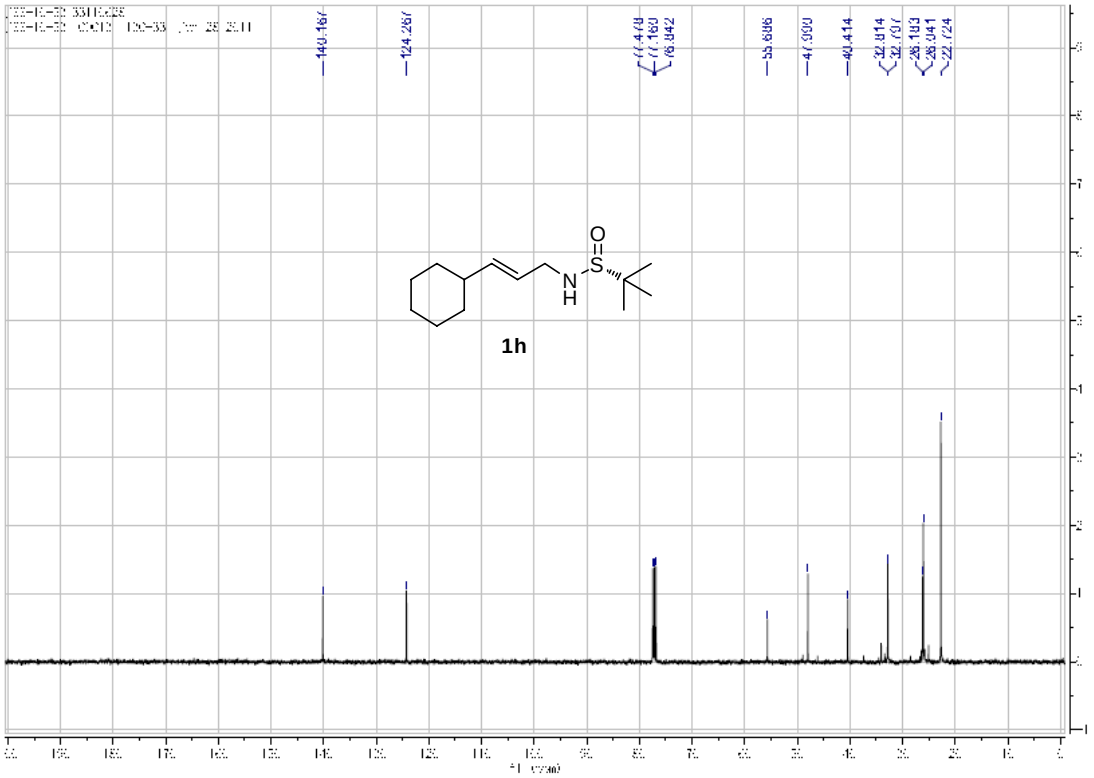
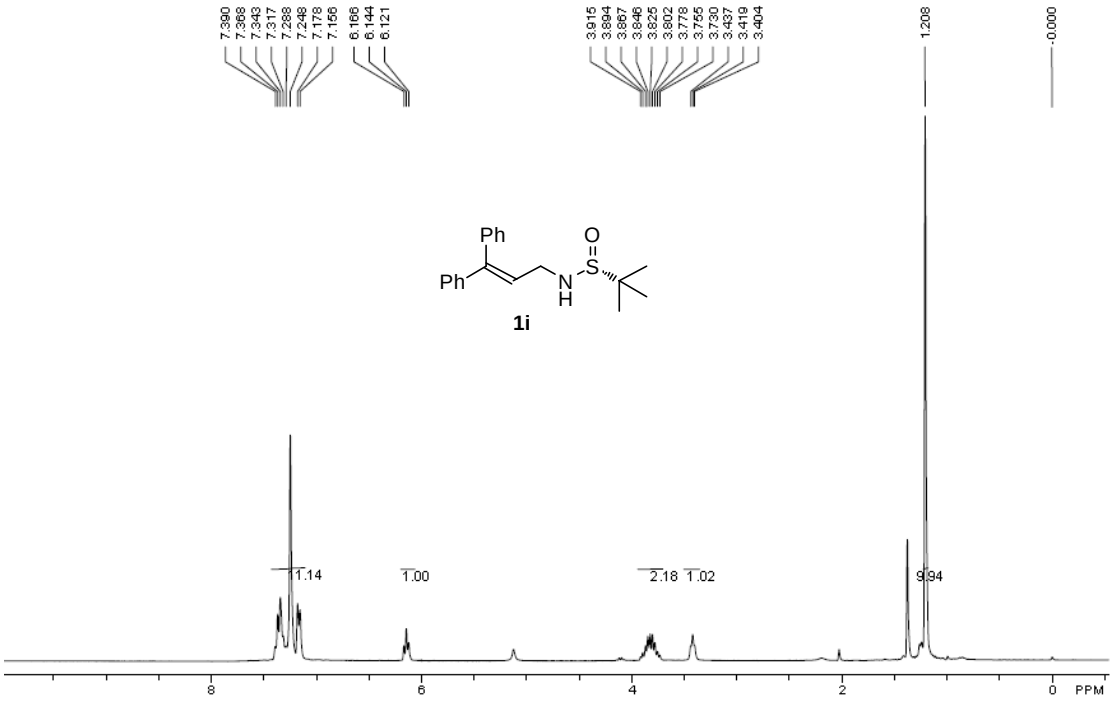
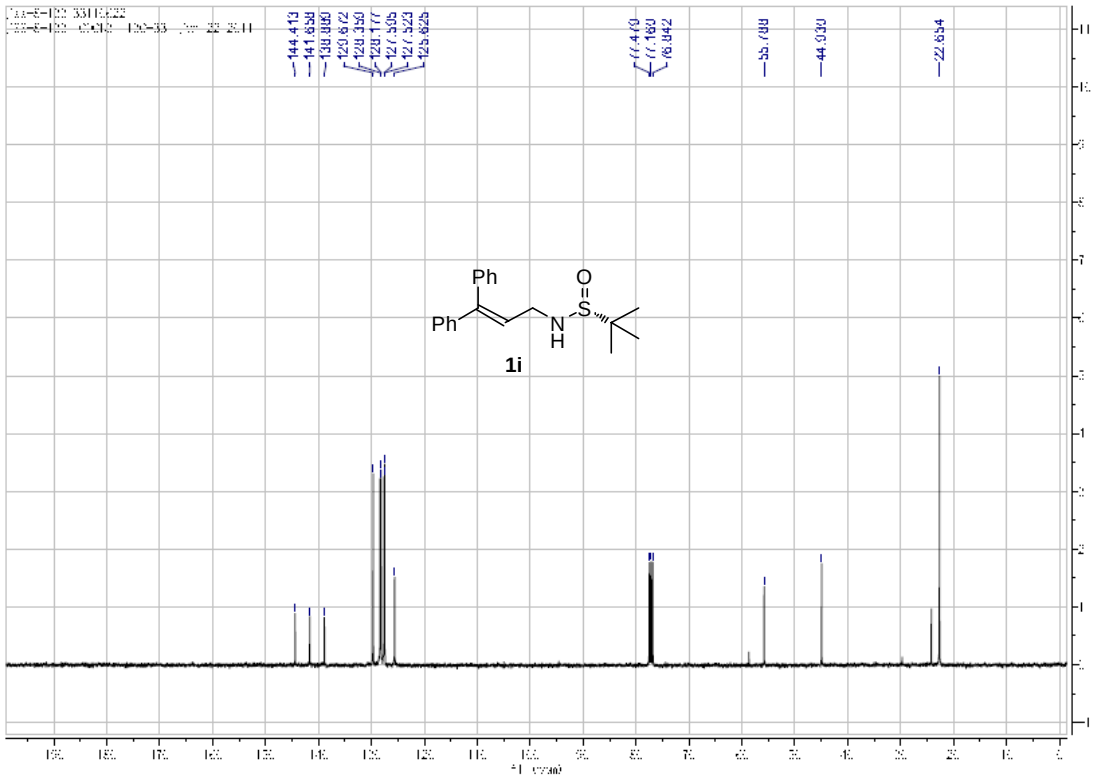
5.645
5.623
5.594
5.572
5.500
5.480
5.459
5.450
5.429
5.408
3.779
3.759
3.733
3.713
3.694
3.670
3.649
3.628
3.604
3.582
3.199
3.182
3.163
1.997
1.951
1.939
1.909
1.724
1.692
1.624
1.284
1.237
1.216
1.161
1.113
1.075
1.042
1.003
0.993
0.000
O
S
N
H
1h
15.67
0.84
0.87
2.00
1.09
4.74
1.08
8
6
4
2
0
PPM


140.167
124.267
77.440
77.160
76.842
55.686
47.900
40.414
32.014
22.791
26.193
26.041
22.724
O
S
N
H
1h


7.390
7.368
7.343
7.317
7.288
7.248
7.178
7.156
6.166
6.144
6.121
3.915
3.894
3.867
3.846
3.825
3.802
3.778
3.755
3.730
3.437
3.419
3.404
1.208
-0.000
Ph
Ph
O
S
N
H
1i
1.14
1.00
2.18
1.02
9.94
8
6
4
2
0
PPM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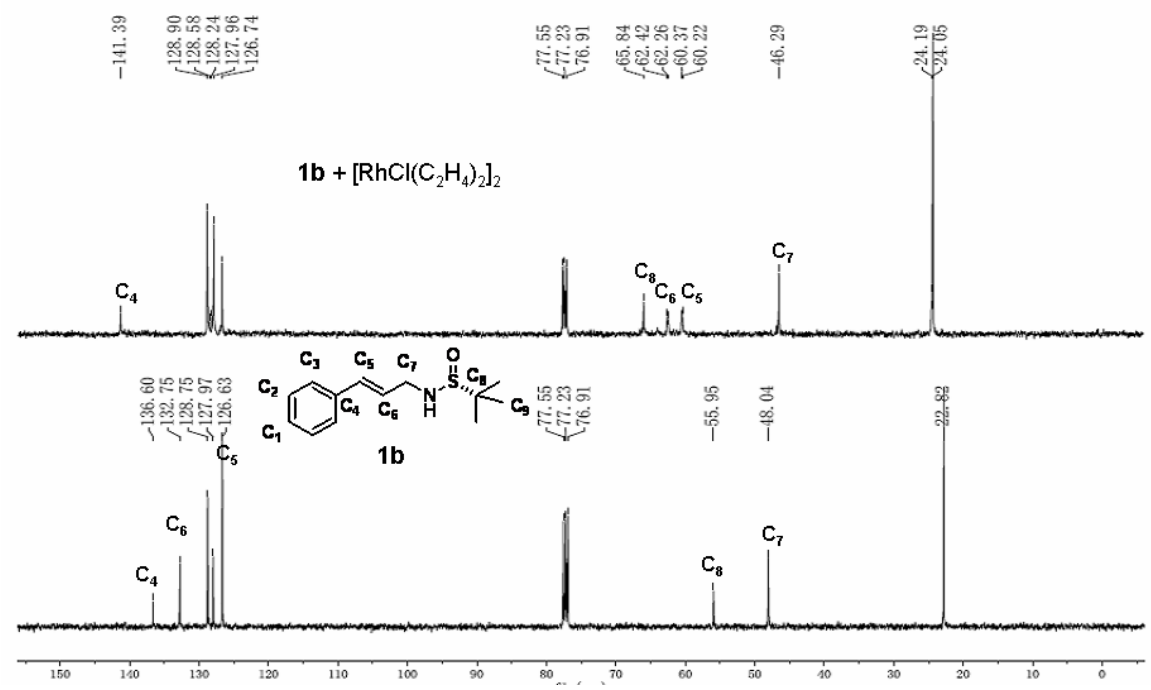
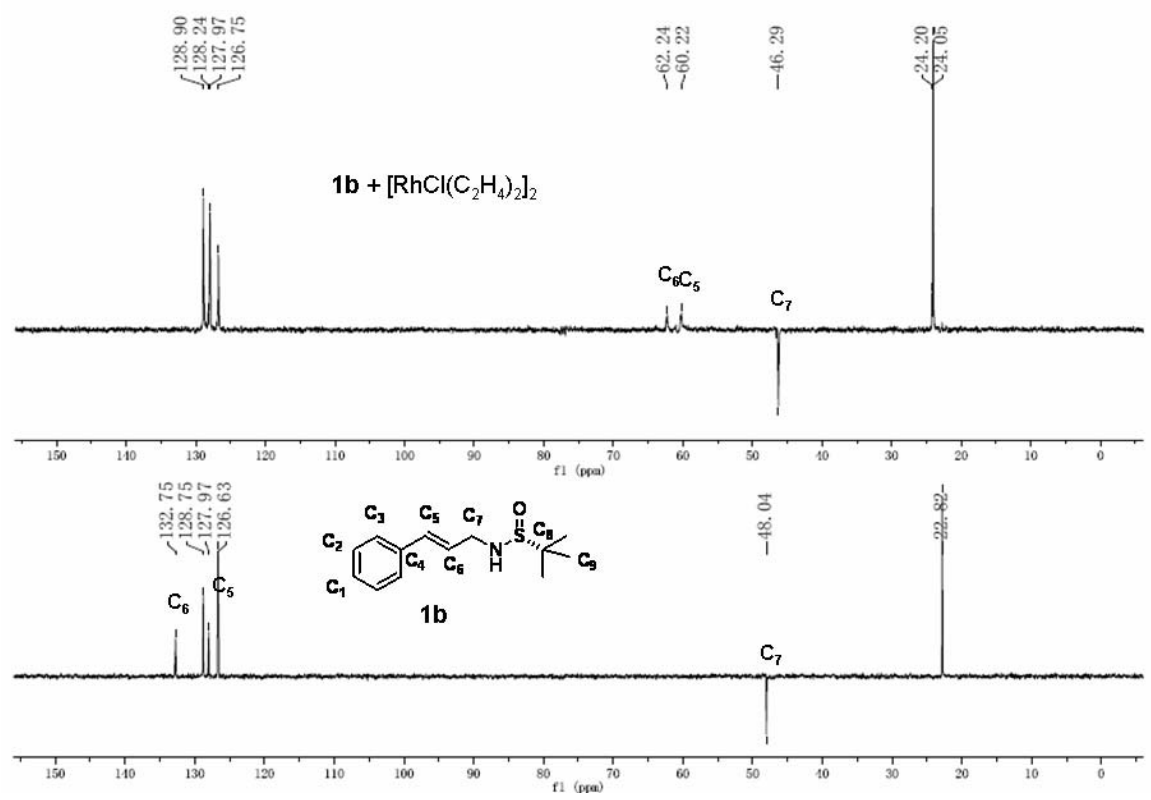
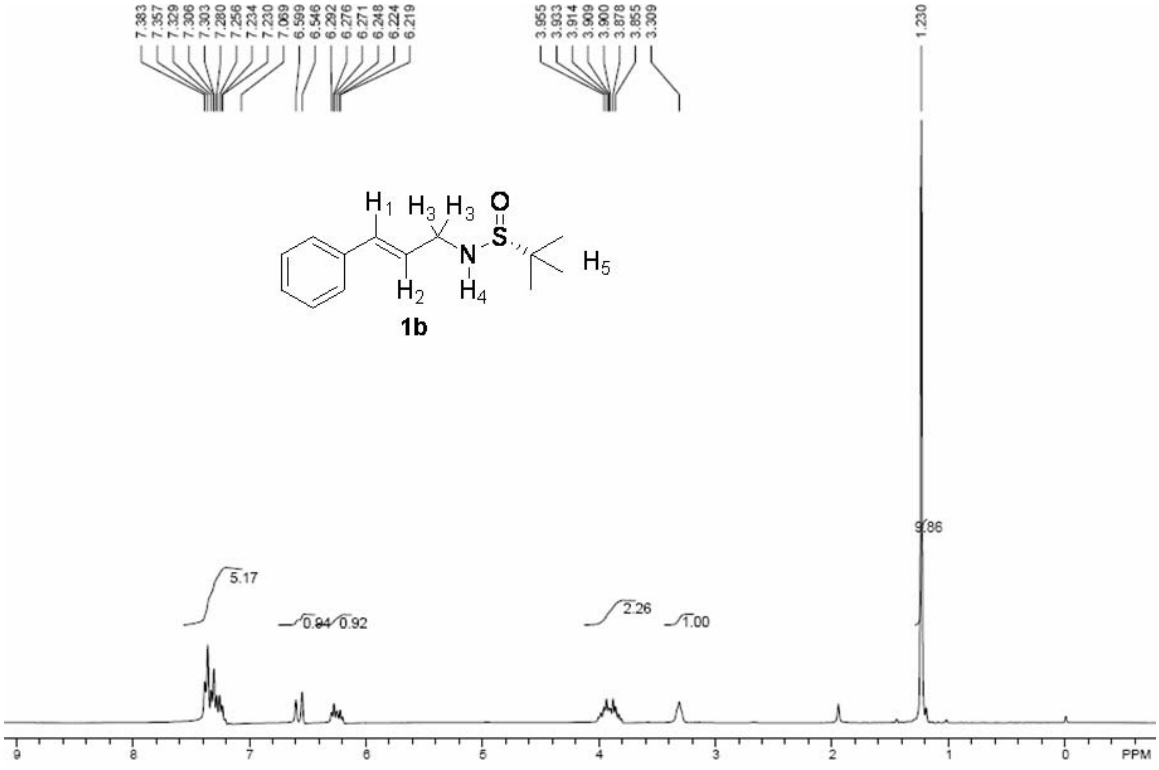
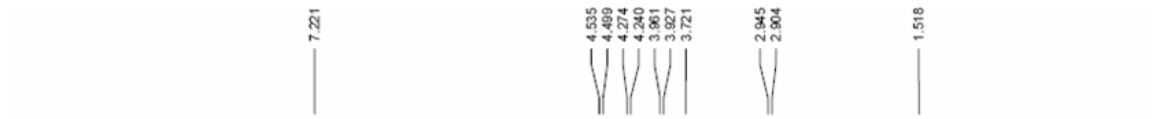
141.829
139.986
129.672
128.950
128.177
127.595
127.523
125.825
77.419
77.160
76.902
55.700
44.930
22.654
Ph
Ph
O
S
N
H
1i

7. Copies of ^{1}H and ^{13}C NMR for ligand 1b-Rh complex









1b + $[RhCl(C_2H_4)_2]_2$