Supporting Information for

Efficient asymmetric hydrogenation of quinolines in neat water catalyzed by chiral cationic Ru-diamine complexes

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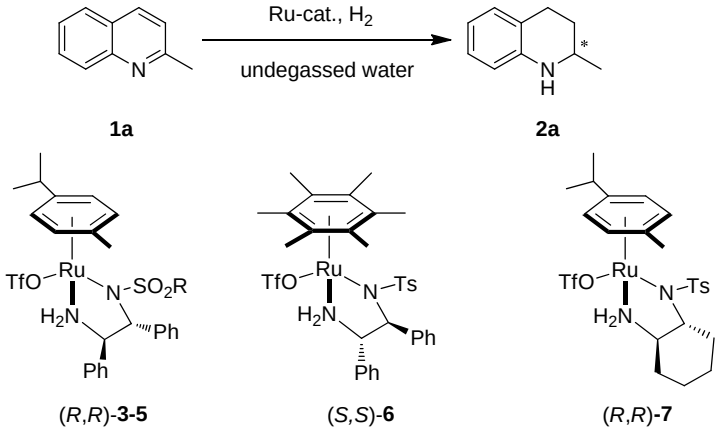
Contents

1. General information

Unless otherwise noted, all experiments were carried out by using standard Schlenk techniques in undegassed water without the use of glovebox. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 300 Spectrometer (^{1}H 300 MHz and ^{13}C 75 MHz, respectively). Chemical shifts (δ) were given in ppm and were referenced to residual solvent or TMS peaks. Optical rotations were measured with Rudolph Autopl Ⅵ polarimeter. HPLC analyses were performed on a VARIAN PROSTAR 210 liqiud chromatograph. The water was purified by ULUPURE UPHW-Ⅲ-90T ultra-pure grade water system. All other chemicals were used as received from Aldrich or Acros without further purification. The catalysts were prepared according to the published method.[1] Quinolines **1a-1k** were prepared according to the literature procedure and their ^{1}H and ^{13}C NMR data are consistent with the literature data. [1]

2. Optimization of conditions for asymmetric hydrogenation of 1a

***Table S1*:** Optimization of reaction conditions for the asymmetric hydrogenation of **1a** in water.[a]

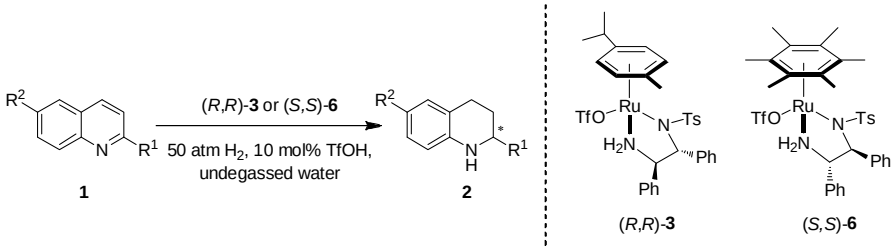


R = 4-$CH_3C_6H_4$ (**3**); CH_3 (**4**); 4-$CF_3C_6H_4$ (**5**)

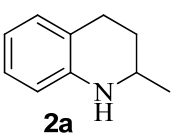
Entry	Catalyst	H_2 (atm); T (^oC)	TfOH (equiv)	Time (h)	Conv. (%)[b]	Ee (%)[c]
1[d]	(*R*,*R*)-**3**	50; 30	0	3	26	95
2[d]	(*R*,*R*)-**3**	50; 30	10	3	71	94
3	(*R*,*R*)-**3**	50; 30	5	3	>99	95
4	(*R*,*R*)-**3**	50; 30	10	3	>99	95
5	(*R*,*R*)-**3**	50; 30	10	0.5	30	95
6	(*R*,*R*)-**3**	50; 30	20	3	>99	94
7	(*R*,*R*)-**3**	10; 30	10	3	64	95
8	(*R*,*R*)-**3**	30; 30	10	3	>99	96
9	(*R*,*R*)-**3**	80; 30	10	3	>99	96
10	(*R*,*R*)-**3**	50; 20	10	3	>99	95
11	(*R*,*R*)-**3**	50; 50	10	3	>99	94
12	(*R*,*R*)-**4**	50; 30	10	3	>99	92
13	(*R*,*R*)-**5**	50; 30	10	3	>99	94
14	(*S*,*S*)-**6**	50; 30	10	3	>99	99
15	(*S*,*S*)-**6**	50; 30	10	3	>99	99
16	(*R*,*R*)-**7**	50; 30	10	3	>99	82
17[f]	(*R*,*R*)-**3**	50; 50	10	12	>99	94
18[f]	(*S*,*S*)-**6**	50; 50	10	12	87	98

[a] Reaction conditions: **1a** (0.2 mmol) in undegassed water (1 mL), Ru-cat. (1.0 mol %), reaction for 3 h. All manipulations were conducted in air, and the autoclave was purged with H_2 three times before reaction. [b] The conversions were determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by HPLC with a chiral OJ-H column. [d] All manipulations were conducted under anaerobic conditions (with the use of degassed methanol and glovebox), and the autoclave was purged with H_2 three times before reaction. [e] All manipulations were conducted in air, without purging the autoclave with H_2 before reaction. [f] Substrate/catalyst = 500 (143 mg substrate in 5 mL H_2O).

3. Asymmetric hydrogenation of quinolines in undegassed water



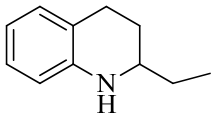
Typical procedure for the asymmetric hydrogenation of quinolones in water: quinolines **1** (0.20 mmol), (*R*,*R*)-**3** or (*S*,*S*)-**6** (0.002 mmol, 1.0 mol%), undegassed water (1 mL) and undegassed TfOH (3.0 mg, 0.02 mmol, 10 mol%) were added to a glass tube in air. Then, the tube was placed into a 30 mL stainless steel autoclave and the autoclave was purged with hydrogen gas for 3 times before pressurized with H_2 to 50 atm. The hydrogenation was performed at 30 ^{o}C or 50 ^{o}C for the specified period of time. After careful releasing of the hydrogen, the reaction mixture was diluted with ethyl acetate (3 mL) and saturated sodium carbonate aqueous solution (2 mL), then stirred for 2 min. The aqueous layer was extracted with ethyl acetate (3 x 3 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated to afford the crude product. The conversion of the reaction was based on ^{1}H NMR spectra. Purification was performed by a silica gel column eluted with petroleum ether/triethylamine (95:5, *v*/*v*) to give the pure product. The enantiomeric excesses were determined by chiral HPLC with a chiral column.



2a

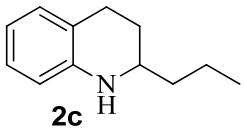
(*S*)-2-Methyl-1,2,3,4-tetrahydroquinoline (2a). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*.

2011, *133*, 9878-9891). Isolated yield 95%, 99% ee, $[\alpha]_D^{25}$ = -81.0 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +84.3 (*c* 0.20, $CHCl_3$) 99% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.04-7.00 (m, 2H), 6.60 (t, *J* = 7.35 Hz, 1H), 6.53-6.50 (m, 1H), 3.74 (b, 1H), 3.50-3.39 (m, 1H), 2.95-2.73 (m, 2H), 2.02-1.94 (m, 1H), 1.71-1.58 (m, 1H), 1.26 (d, *J* = 6.30 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.83, 129.35, 126.77, 121.19, 117.07, 114.11, 47.24, 30.21, 26.68, 22.69; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 10.1 min (major), t_{R2} = 11.3 min (minor).



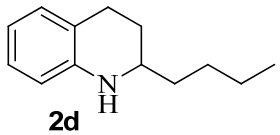
2b

(*R*)-2-Ethyl-1,2,3,4-tetrahydroquinoline (2b). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 95%, 94% ee, $[\alpha]_D^{25}$ = +73.0 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +80.3 (*c* 0.19, $CHCl_3$) 99% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.99 (t, *J* = 7.05, 2H), 6.63 (t, *J* = 7.20 Hz, 1H), 6.51 (d, *J* = 8.10 Hz, 1H), 3.78 (b, 1H), 3.24-3.16 (m, 1H), 2.89-2.73 (m, 2H), 2.05-1.96 (m, 1H), 1.69-1.51 (m, 3H), 1.02 (t, *J* = 7.50 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.84, 129.34, 126.82, 121.51, 116.99, 114.12, 53.15, 29.51, 27.69, 26.53, 10.17; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 9.4 min (minor), t_{R2} = 10.3 min (major).



2c

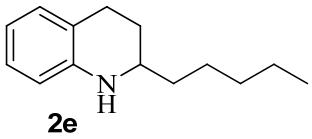
(*R*)-2-Propyl-1,2,3,4-tetrahydroquinoline (2c). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 93%, 94% ee, $[\alpha]_D^{25}$ = +78.6 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +89.0 (*c* 0.16, $CHCl_3$) 99% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.99 (t, *J* = 7.05 Hz, 2H), 6.62 (t, *J* = 7.20 Hz, 1H), 6.50 (d, *J* = 8.10 Hz, 1H), 3.77 (b, 1H), 3.28 (d, *J* = 6.00 Hz 1H), 2.90-2.71 (m, 2H), 2.01-1.94 (m, 1H), 1.69-1.43 (m, 5H), 1.00 (d, *J* = 7.20 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.84, 129.37, 126.81, 121.50, 116.99, 114.15, 51.42, 39.01, 28.24, 26.55, 19.02, 14.32; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 8.7 min (minor), t_{R2} = 10.9 min (major).



2d

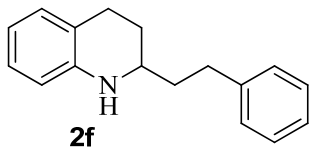
(*R*)-2-Butyl-1,2,3,4-tetrahydroquinoline (2d). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 96%, 93% ee, $[\alpha]_D^{25}$ = +73.0 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +90.4 (*c* 0.19, $CHCl_3$) 99% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.00 (t, *J* = 7.05 Hz, 2H), 6.64 (t, *J* = 7.35 Hz, 1H), 6.51 (d, *J* = 8.1 0Hz, 1H), 3.79 (b, 1H), 3.29-3.25 (m, 1H), 2.86-2.78 (m, 2H), 2.03-1.96 (m, 1H), 1.67-1.40 (m, 7H), 0.98 (t, *J* = 6.90 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.84, 129.34, 126.79, 121.47, 116.96, 114.12, 51.68, 36.53, 28.23, 28.03, 26.55, 22.96, 14.21; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H

column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 7.6 min (minor), t_{R2} = 8.7 min (major).



2e

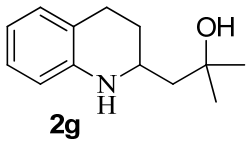
(*R*)-2-Pentyl-1,2,3,4-tetrahydroquinoline (2e). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 91%, 95% ee, $[\alpha]_D^{25}$ = +106.0 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +87.3 (*c* 0.20, $CHCl_3$) 99% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.99 (t, *J* = 7.05 Hz, 2H), 6.63 (t, *J* = 7.20 Hz, 1H), 6.51 (d, *J* = 8.10 Hz, 1H), 3.77 (b, 1H), 3.31-3.23 (m, 1H), 2.89-2.71 (m, 2H), 2.04-1.95 (m, 1H), 1.70-1.37 (m, 9H), 0.95 (t, *J* = 6.75 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.83, 129.35, 126.80, 121.50, 116.99, 114.15, 51.71, 36.80, 32.08, 28.23, 26.56, 25.52, 22.77, 14.18; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 6.8 min (minor), t_{R2} = 7.4 min (major).



2f

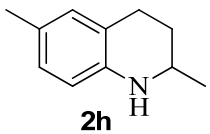
(*R*)-2-Phenethyl-1,2,3,4-tetrahydroquinoline (2f). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 95%, 93% ee, $[\alpha]_D^{25}$ = +78.6 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +88.9 (*c* 0.27, $CHCl_3$) 99% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.31-7.19 (m, 5H), 6.95 (t, *J* = 7.05 Hz, 2H), 6.59 (t, *J* = 7.35 Hz 1H), 6.43 (d, *J* = 7.80 Hz, 1H), 3.72 (b, 1H), 3.32-3.23 (m, 1H), 2.80-2.69 (m, 4H),

2.02-1.93 (m, 1H), 1.85-1.78 (m, 2H), 1.72-1.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.60, 141.95, 129.36, 128.59, 128.46, 126.84, 126.07, 121.39, 117.14, 114.25, 51.22, 38.35, 32.27, 28.07, 26.32; The enantiomeric excess was determined by HPLC on Chiralcel AS-H column (hexane : isopropanol = 95 : 5, flowing rate = 0.6 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 9.4 min (minor), t_{R2} = 10.5 min (major).



2g

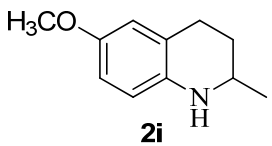
(*S*)-2-methyl-1-(1,2,3,4-tetrahydroquinolin-2-yl)propan-2-ol (2g). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 92%, 93% ee, $[\alpha]_D^{25}$ = +52.6 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +80.3 (*c* 0.19, $CHCl_3$) 99% ee for *S* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.96 (t, *J* = 7.20 Hz, 2H), 6.60 (t, *J* = 7.35 Hz, 1H), 6.49 (d, *J* = 7.80 Hz, 1H), 3.62-3.53 (m, 2H), 2.89-2.83 (m, 1H), 2.78-2.71 (m, 1H), 1.88-1.82 (m, 1H), 1.77-1.57 (m, 2H), 1.33-1.28 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.70, 129.35, 126.81, 121.01, 116.80, 114.54, 72.08, 48.91, 48.50, 32.92, 29.88, 27.90, 26.69; The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 95 : 5, flowing rate = 0.8 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 13.0 min (major), t_{R2} = 15.7 min (minor).



2h

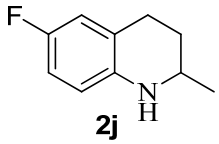
(*S*)-2,6-Dimethyl-1,2,3,4-tetrahydroquinoline (2h). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*,

9878-9891). Isolated yield 94%, 99% ee, $[\alpha]_D^{25}$ = -81.4 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +80.3 (*c* 0.19, $CHCl_3$) 98% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.81 (d, *J* = 6.60 Hz, 2H), 6.44 (d, *J* = 8.40 Hz, 1H), 3.59 (b, 1H), 3.42-3.36 (m, 1H), 2.91-2.68 (m, 2H), 2.24 (s, 3H), 1.99-1.90 (m, 1H), 1.67-1.56 (m, 1H), 1.23 (d, *J* = 6.30 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.55, 129.93, 127.32, 126.34, 121.32, 114.35, 47.42, 30.46, 26.70, 22.71, 20.52; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 12.1 min (major), t_{R2} = 15.0 min (minor).



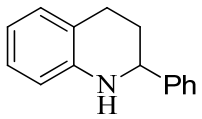
2i

(*S*)- 6-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (2i). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 94%, 99% ee, $[\alpha]_D^{25}$ = -81.0 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +80.3 (*c* 0.19, $CHCl_3$) 99% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.61 (t, *J* = 8.55 Hz, 2H), 6.45 (d, *J* = 8.40 Hz, 1H), 3.73 (s, 3H), 3.49-3.28 (m, 2H), 2.91-2.67 (m, 2H), 1.96-1.88 (m, 1H), 1.65-1.51 (m, 1H), 1.20 (d, *J* = 6.30 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.98, 139.04, 122.64, 115.44, 114.76, 112.97, 55.93, 47.61, 30.45, 27.05, 22.69; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 8.2 min (minor), t_{R2} = 9.0 min (major).



2j

(*S*)-6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (2j). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 94%, 99% ee, $[\alpha]_D^{25}$ = -81.2 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +80.3 (*c* 0.19, $CHCl_3$) 98% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.71-6.65 (m, 2H), 6.43-6.38 (m, 1H), 3.54 (b, 1H), 3.40-3.31 (m, 1H), 2.89-2.66 (m, 2H), 1.96-1.88 (m, 1H), 1.63-1.50 (m, 1H), 1.21 (d, *J* = 6.30 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 154.07, 141.09, 122.64, 122.55, 115.65, 115.37, 114.88, 114.78, 113.42, 113.13, 47.43, 30.01, 26.84, 22.62; The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm) t_{R1} = 5.2 min (minor), t_{R2} = 5.9 min (major).

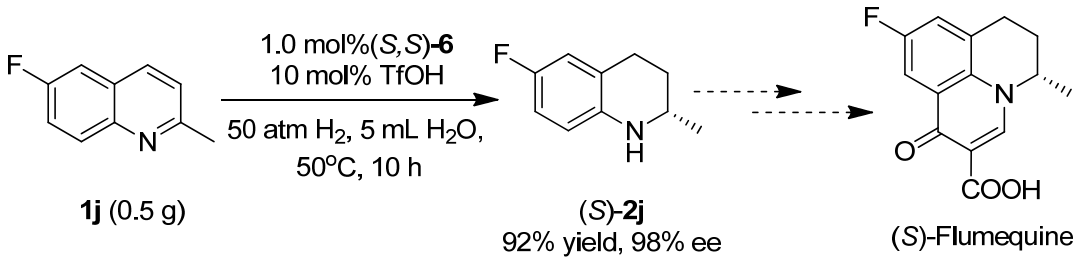


2k

(*S*)-2-Phenyl-1,2,3,4-tetrahydroquinoline (2k). (Known compound, see: T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891). Isolated yield 92%, 63% ee, $[\alpha]_D^{25}$ = -35.6 (*c* 0.50, $CHCl_3$), [Lit.[1] $[\alpha]_D^{RT}$ = +36.8 (*c* 0.95, $CHCl_3$) 92% ee for *R* enantiomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44-7.32 (m, 5H), 7.05 (t, *J* = 6.90 Hz, 2H), 6.69 (t, *J* = 7.35 Hz, 1H), 6.57 (d, *J* = 8.10 Hz, 1H), 4.49-4.45 (m, 1H), 4.06 (b, 1H), 2.96-2.91 (m, 1H), 2.81-2.73 (m, 1H), 2.19-2.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.93, 144.84, 129.41, 128.69, 127.55, 127.02, 126.66, 120.98, 117.26, 114.09, 56.36, 31.10, 26.50; The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10,

flowing rate = 0.6 mL/min, 25 °C, UV detection at λ = 254 nm) t_{R1} = 15.4 min (major), t_{R2} = 20.8 min (minor).

4. Scaled-up synthesis of 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline



1j (0.5 g) (*S*)-**2j** 92% yield, 98% ee (*S*)-Flumequine

Quinoline **1j** (0.5 g, 3.10 mmol), (*S*,*S*)-**6** (0.031 mmol, 1.0 mol%), undegassed water (5 mL) and undegassed CF_3SO_3H (46.5 mg, 0.31mmol, 10 mol%) were added to a glass tube in air. Then, the tube was placed into a 30 mL stainless steel autoclave and the autoclave was purged with hydrogen gas for 3 times before pressurized with H_2 to 50 atm. The hydrogenation was performed at 50 °C for 10 h. After careful releasing of the hydrogen, the reaction mixture was diluted with ethyl acetate (3 mL) and saturated sodium carbonate aqueous solution (2 mL), then stirred for 2 min. The aqueous layer was extracted with ethyl acetate (3 x 3 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated to afford the crude product. The full conversion of the reaction was based on ^{1}H NMR spectra. Purification was performed by a silica gel column eluted with petroleum ether/triethylamine (95:5, v/v) to give the pure product as a yellow solid (460 mg, 92% yield, 98% ee). The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm) t_{R1} = 5.2 min (minor), t_{R2} = 5.9 min (major).

5. The determination of substrate solubility in water

5.1 The determination of solubilities for quinolines 1a and 1j:

2-Methylquinoline (**1a**) (27 μL, 0.2 mmol) and D_2O (1 mL) were added to a glass tube and stirred for 30 min at 20 ^oC. Then, the reaction mixture was standed overnight. After that, 0.5 mL clear solution was carefully transferred into a NMR tube, then 1.12 mg isopropanol was added into the NMR tube as an internal standard. The solubility of **1a** (4.04 mg/mL) was obtained based on its ^1H NMR spectrum.

The solubility of 6-fuoro-2-methylquinoline (**1j**) (0.84 mg/mL) was obtained with the same method described above.

5.2 The determination of solubilities for TfOH protonated quinoline salts:

The TfOH protonated 2-methylquinoline salt was added into 0.2 mL deionized water in pertions until the salt was undissolved and the solubility was obtained as 5.68 g/mL.

The solubility of TfOH protonated 6-fuoro-2-methylquinoline salt (2.12 g/mL) was obtained with the same method described above.

5.3 The difference between oil substrate 1a and solid substrate 1j:

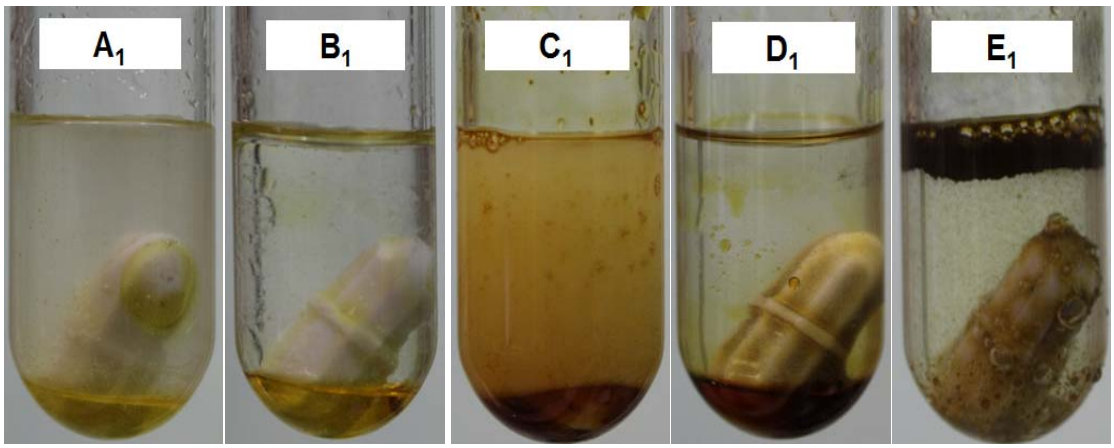


Figure 1. Unless noted otherwise, 500 mg 2-methylquinoline in 5 mL deionized water. A_1: stirred at room temperature; B_1: added 10 mol% CF_3SO_3H; C_1: added 10 mol% TfOH and 1 mol% catalyst; D_1: heated in an oil bath at 50 °C for 0.5 h; E_1: reacted with 50 atm hydrogen at 50 °C for 6 h.

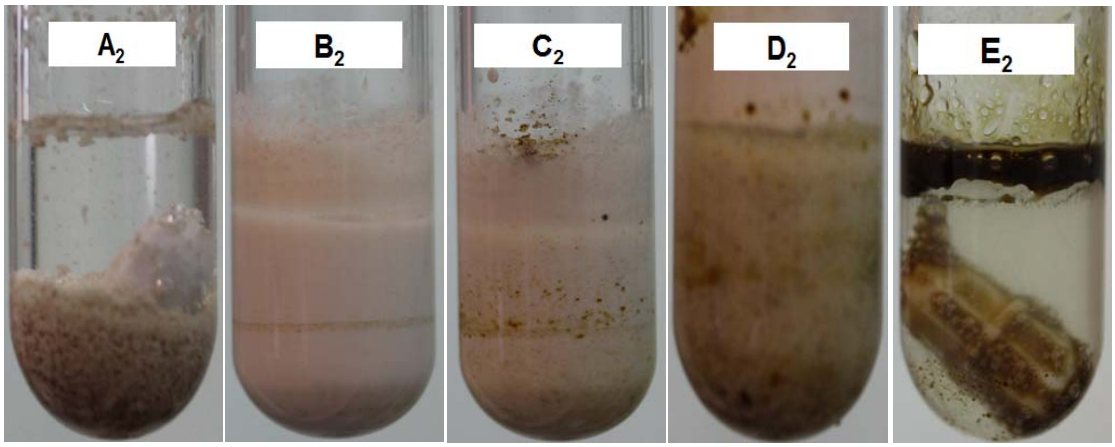
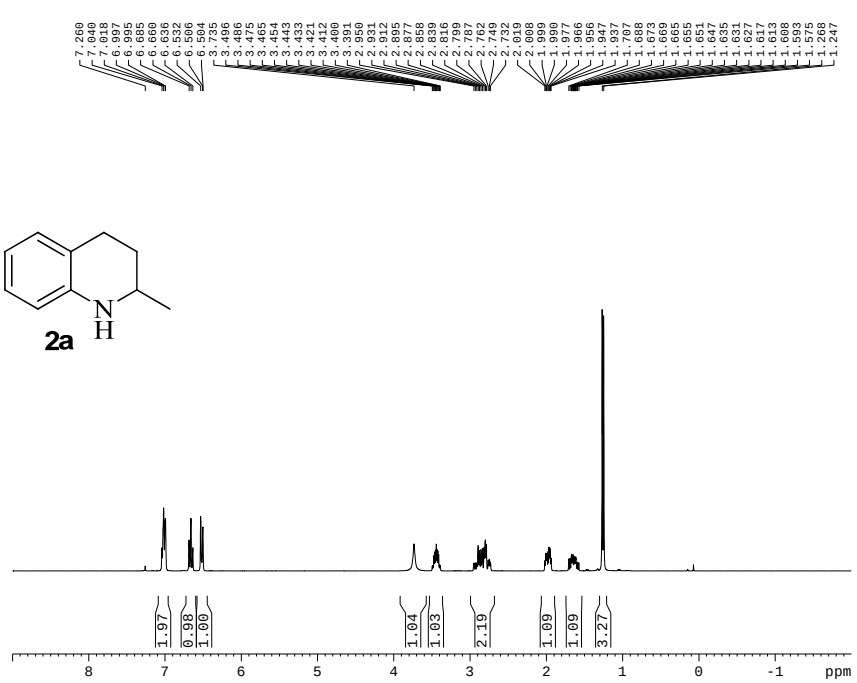


Figure 2. Unless noted otherwise, 500 mg 6-fuoro-2-methylquinoline in 5 mL deionized water. A_2: stirred at room temperature. B_2: added 10 mol% TfOH; C_2: added 1 mol% catalyst; D_2: heated in an oil bath at 50 °C for 0.5 h; E_2: reacted with 50 atm hydrogen at 50 °C for 6 h.

6. Reference

[1] T. Wang, L. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*. **2011**, *133*, 9878-9891.

7. ^{1}H and ^{13}C NMR of products

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PROCNO                1

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PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                    57
DW                55.600 usec
DE                 6.50 usec
TE                296.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300067 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
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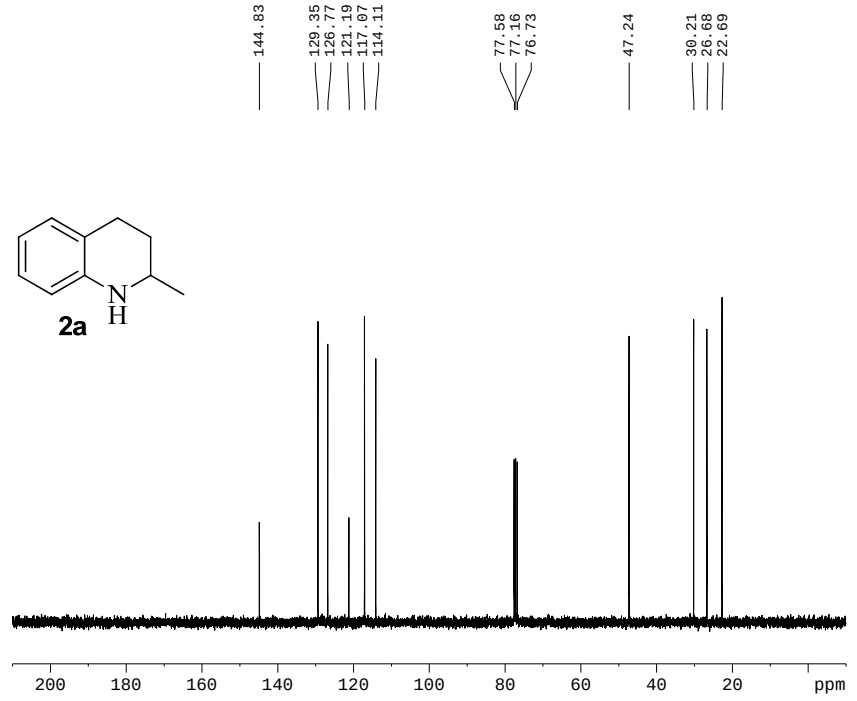


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Current Data Parameters
NAME      yzs-c-2-025-1
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
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Time               12.56
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    40
DS                     4
SWH           17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   512
DW                27.800 usec
DE                 6.50 usec
TE                296.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
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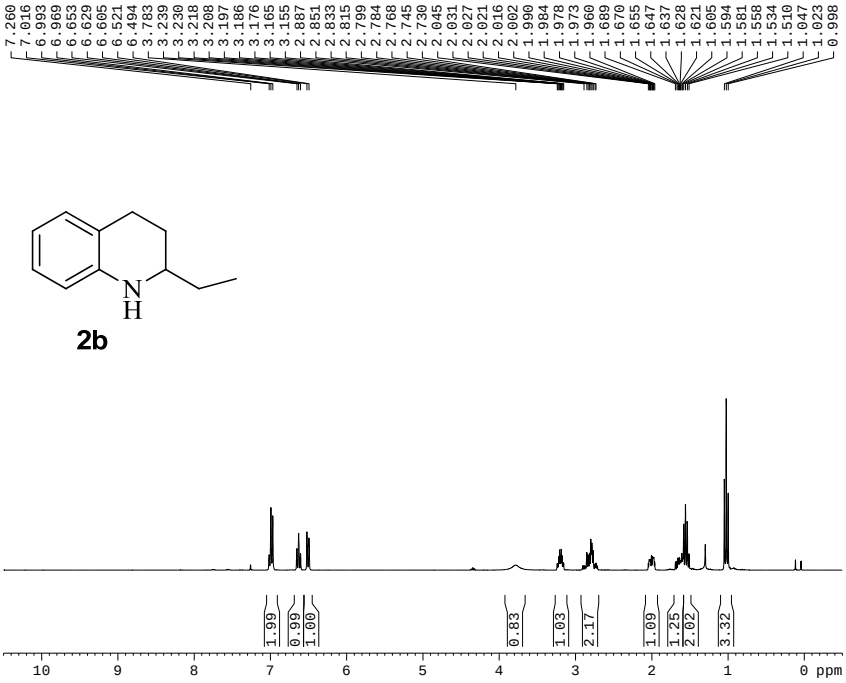


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Current Data Parameters
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EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20131202
Time              21.28
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.274439 Hz
AQ           1.8219508 sec
RG                 71.8
DW               55.600 usec
DE                6.50 usec
TE                297.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300067 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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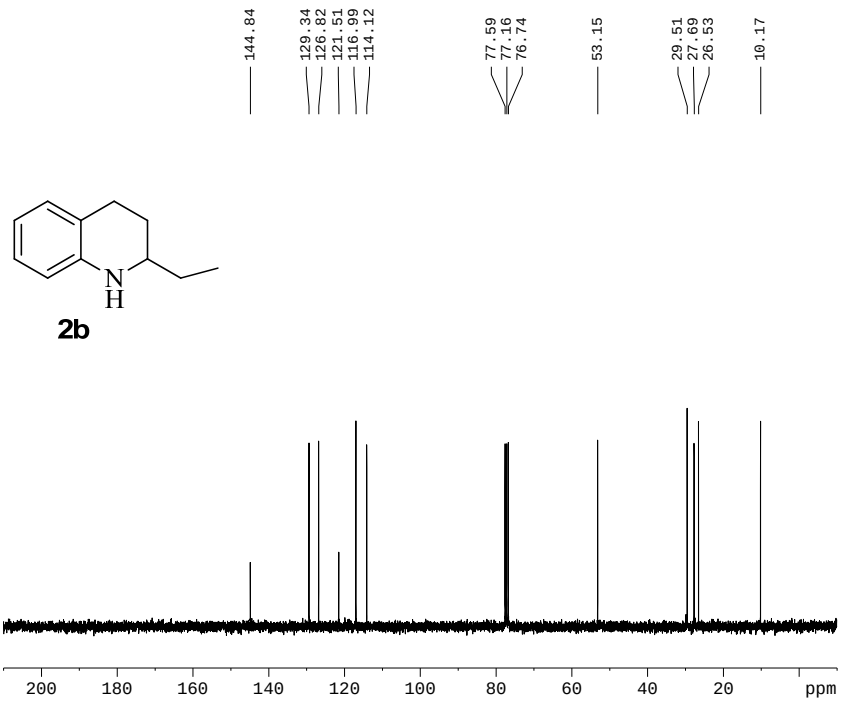


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Current Data Parameters
NAME      yzs-c-2-023-2
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20131202
Time              21.32
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   55
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                1625.5
DW               27.800 usec
DE                6.50 usec
TE                297.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
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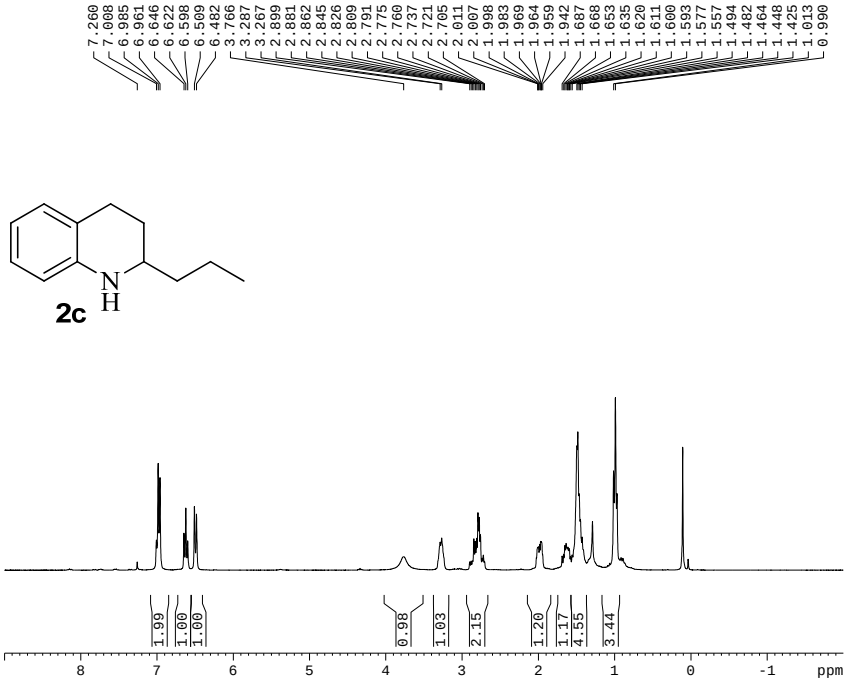


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Current Data Parameters
NAME      yzs-c-2-023-3
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_           20131213
Time               21.02
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                  71.8
DW                55.600 usec
DE                 6.50 usec
TE                295.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300072 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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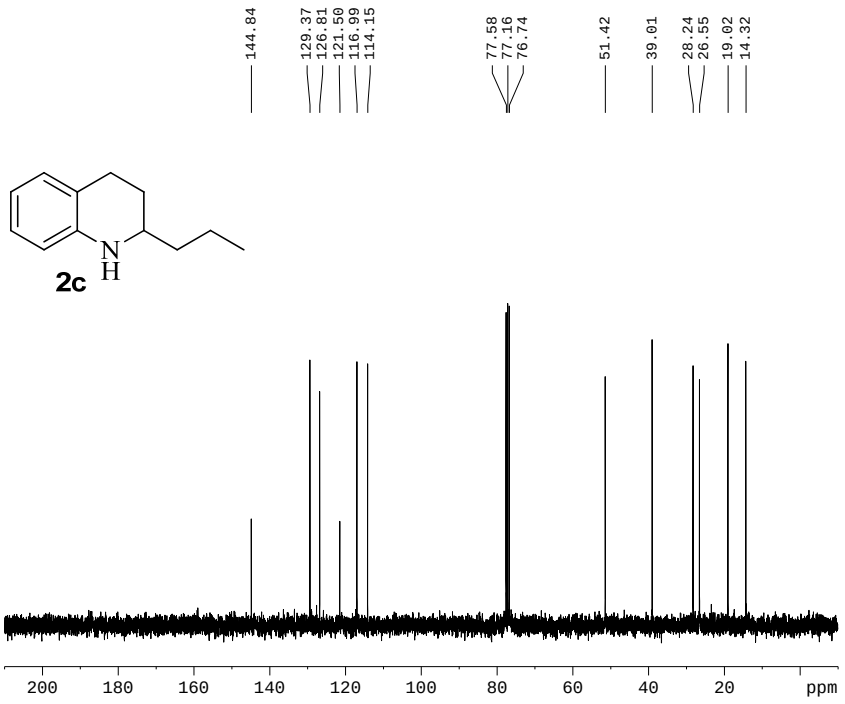


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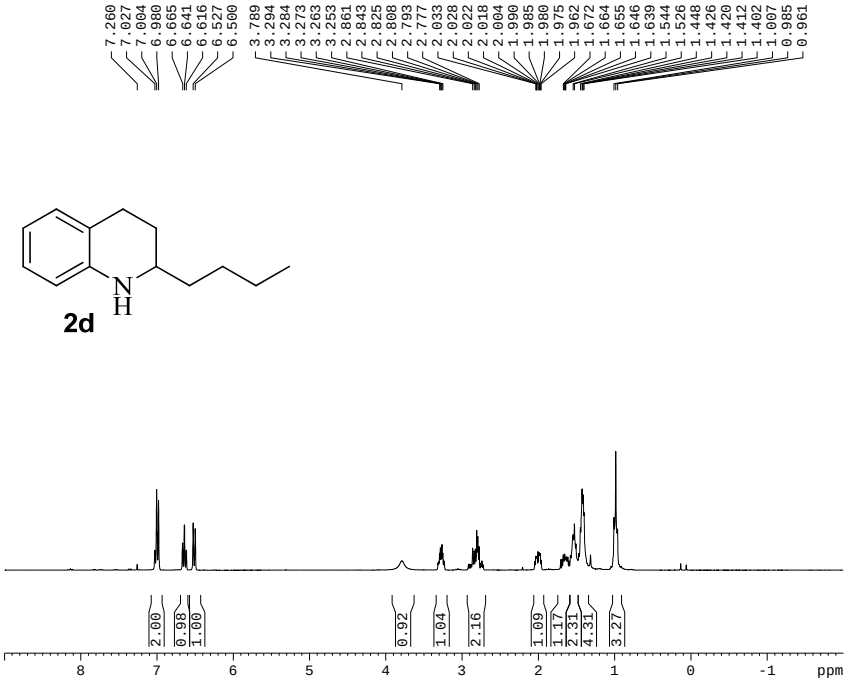
Current Data Parameters
NAME      yzs-c-2-023-3
EXPNO                21
PROCNO                1

F2 - Acquisition Parameters
Date_           20131202
Time               21.53
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    45
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                1625.5
DW                27.800 usec
DE                 6.50 usec
TE                297.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

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Current Data Parameters
NAME      yzs-c-2-025-4
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20131211
Time              11.55
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.274439 Hz
AQ           1.8219508 sec
RG                 40.3
DW               55.600 usec
DE                6.50 usec
TE                296.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300067 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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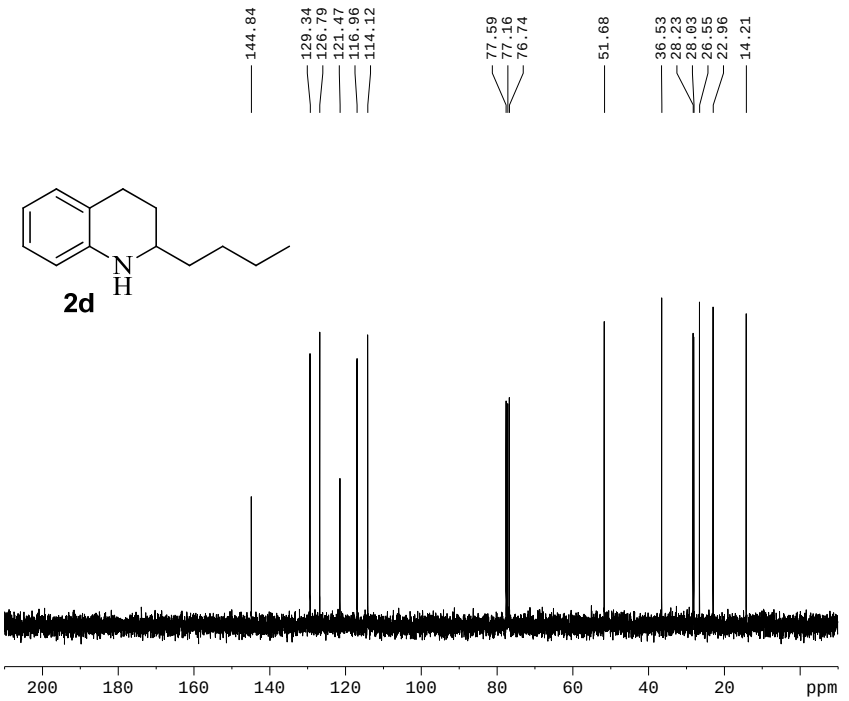


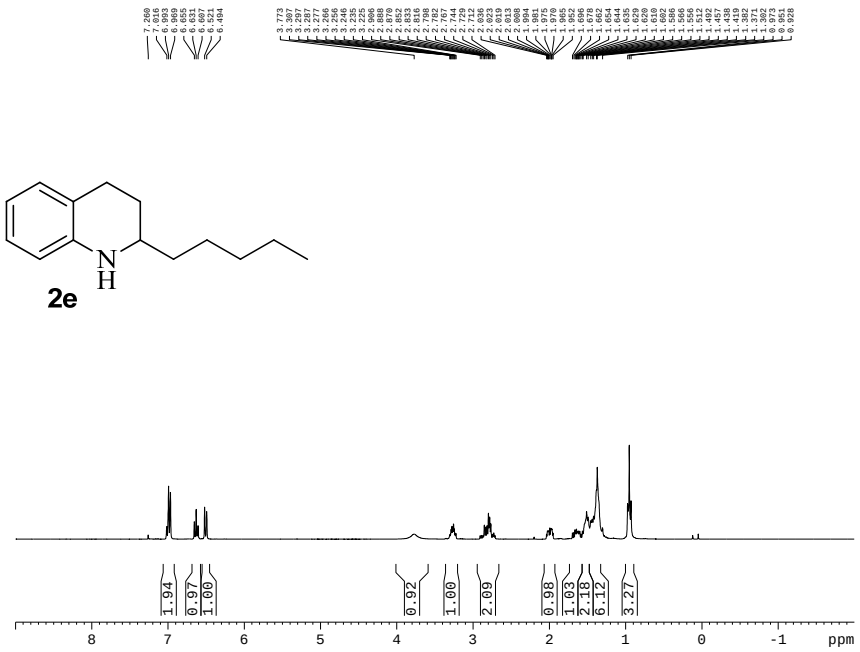

```
Current Data Parameters
NAME      YZS-C-2-026-2
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20131211
Time              22.29
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   15
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ           1.8219508 sec
RG                574.7
DW               27.800 usec
DE                6.50 usec
TE                296.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

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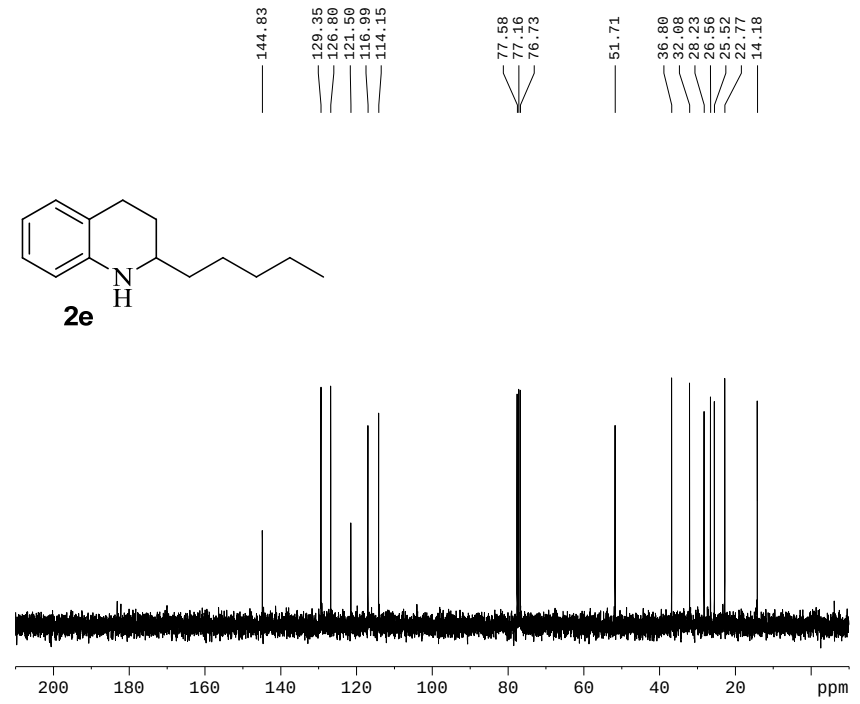
Current Data Parameters
NAME      yzs-c-2-025-5
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_           20131211
Time               22.18
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                    57
DW               55.600 usec
DE                6.50 usec
TE                296.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300067 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




```
Current Data Parameters
NAME      yzs-c-2-025-5
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20131211
Time               22.23
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    19
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                 1149.4
DW               27.800 usec
DE                6.50 usec
TE                296.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
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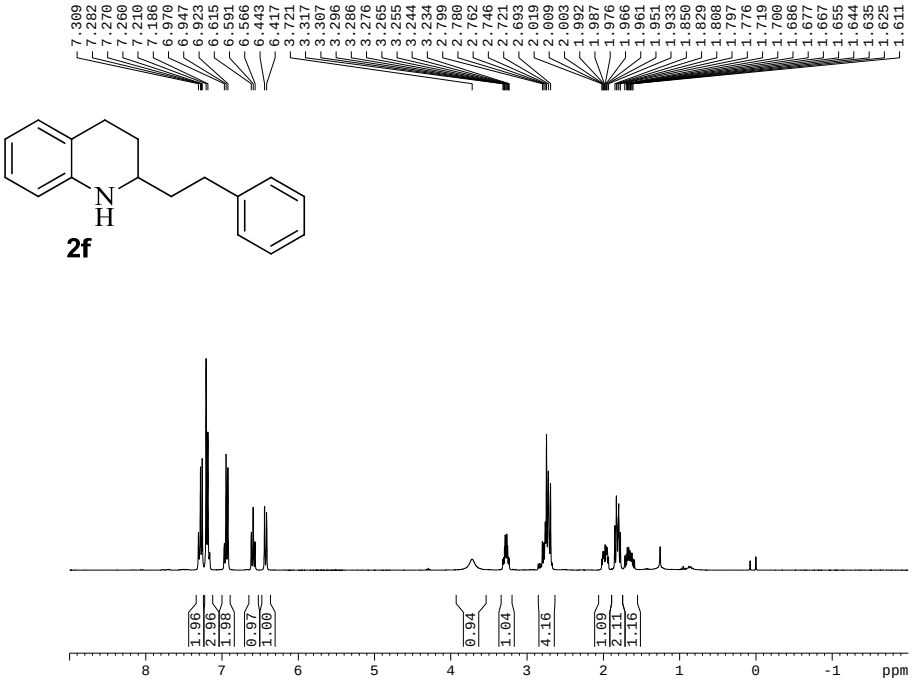


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Current Data Parameters
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EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_           20131210
Time               19.46
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                    64
DW                55.600 usec
DE                 6.50 usec
TE                296.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300291 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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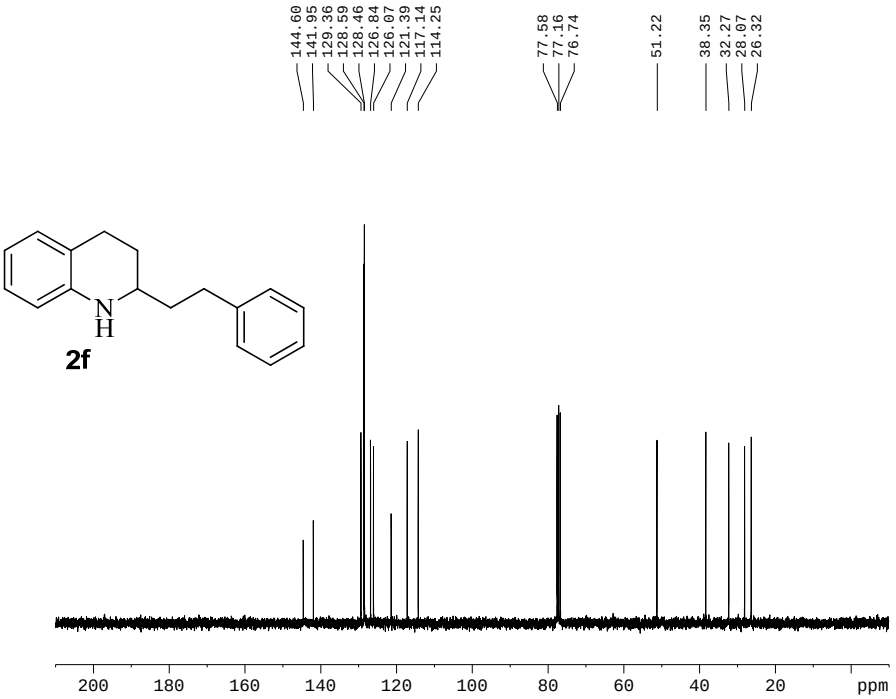


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Current Data Parameters
NAME      yzs-c-2-024-6
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20131210
Time               19.54
INSTRUM            spect
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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    45
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                   512
DW                27.800 usec
DE                 6.50 usec
TE                297.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
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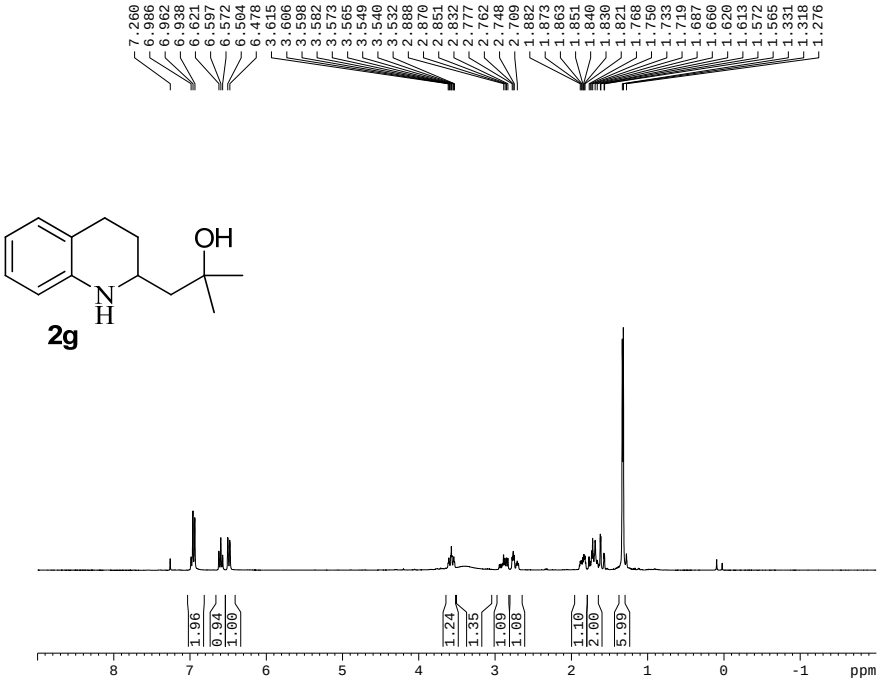


```
Current Data Parameters
NAME      yzs-c-2-026-7
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_          20131214
Time               11.02
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                  71.8
DW                55.600 usec
DE                 6.50 usec
TE                295.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300067 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
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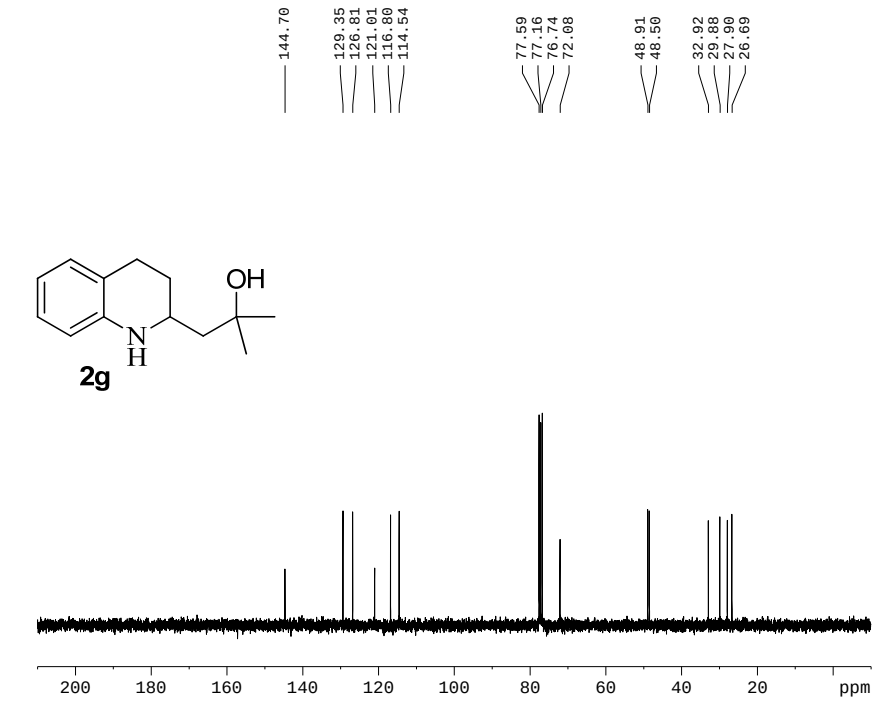


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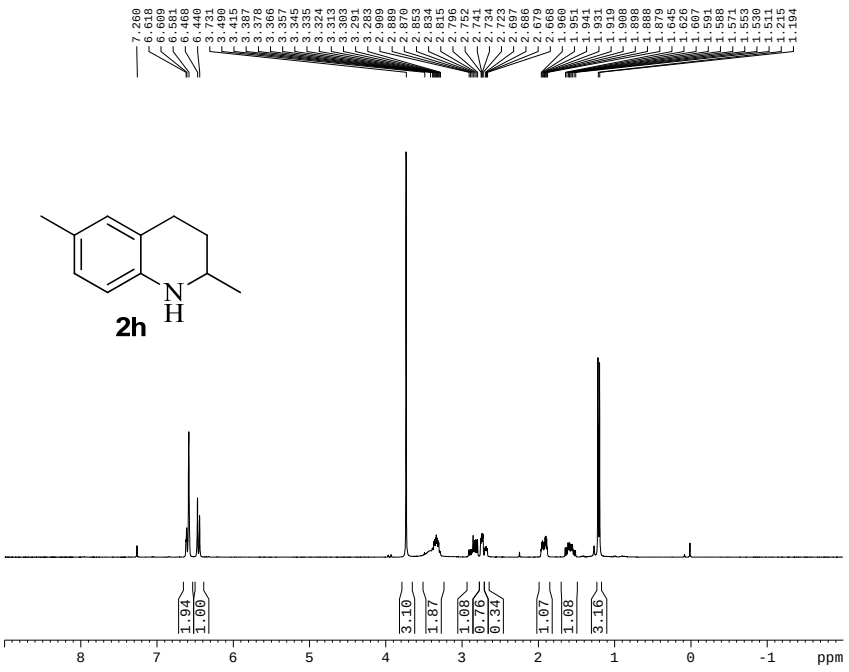
Current Data Parameters
NAME      yzs-c-2-026-7
EXPNO                31
PROCNO                1

F2 - Acquisition Parameters
Date_          20131214
Time               11.05
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    40
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                   362
DW                27.800 usec
DE                 6.50 usec
TE                295.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

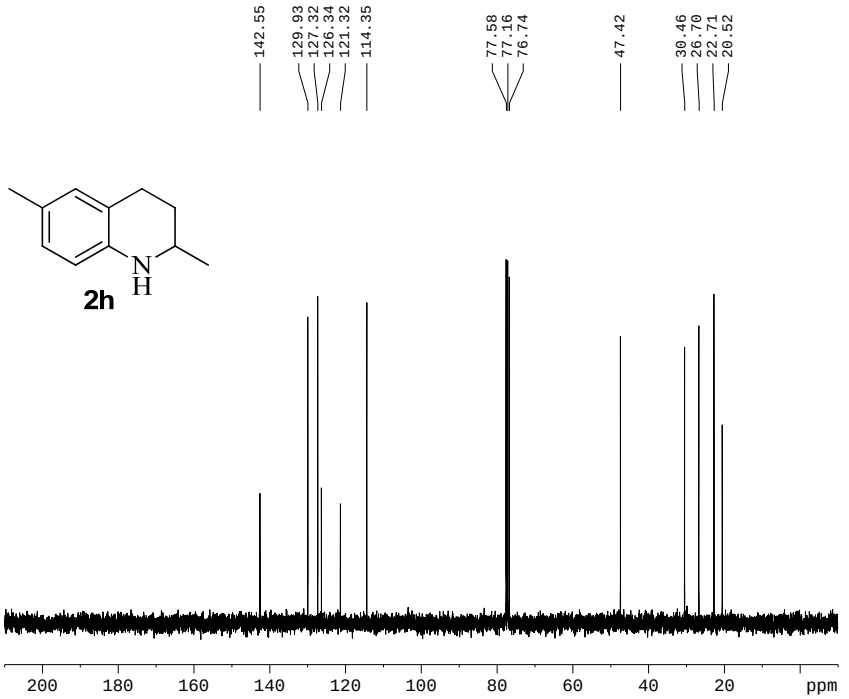



```
Current Data Parameters
NAME      yzs-c-2-026-3
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20131211
Time              22.04
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                  181
DW               55.600 usec
DE                6.50 usec
TE               296.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300067 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



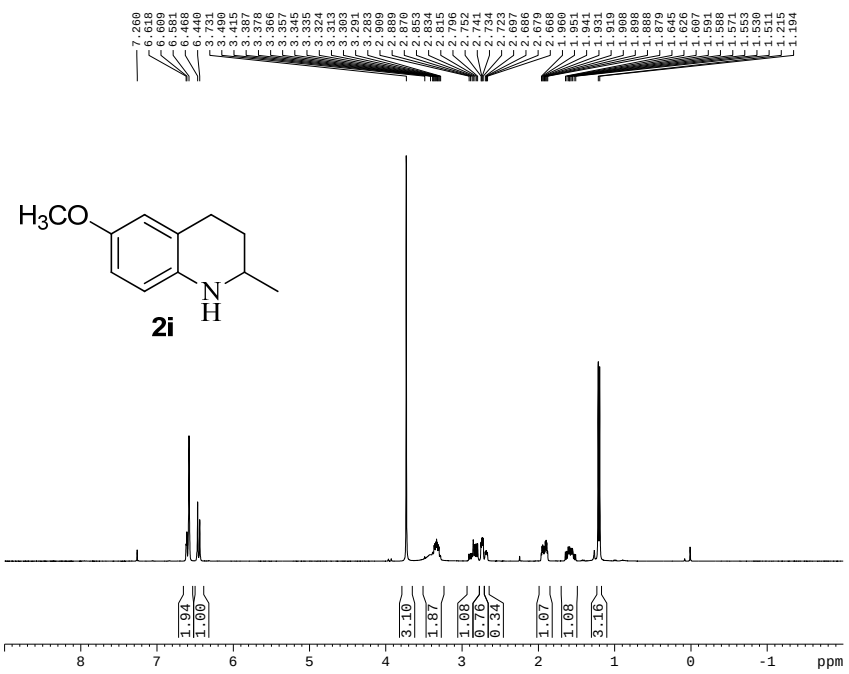

```
Current Data Parameters
NAME      YZS-C-2-026-1
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20131211
Time              21.34
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   41
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                  512
DW               27.800 usec
DE                6.50 usec
TE               296.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

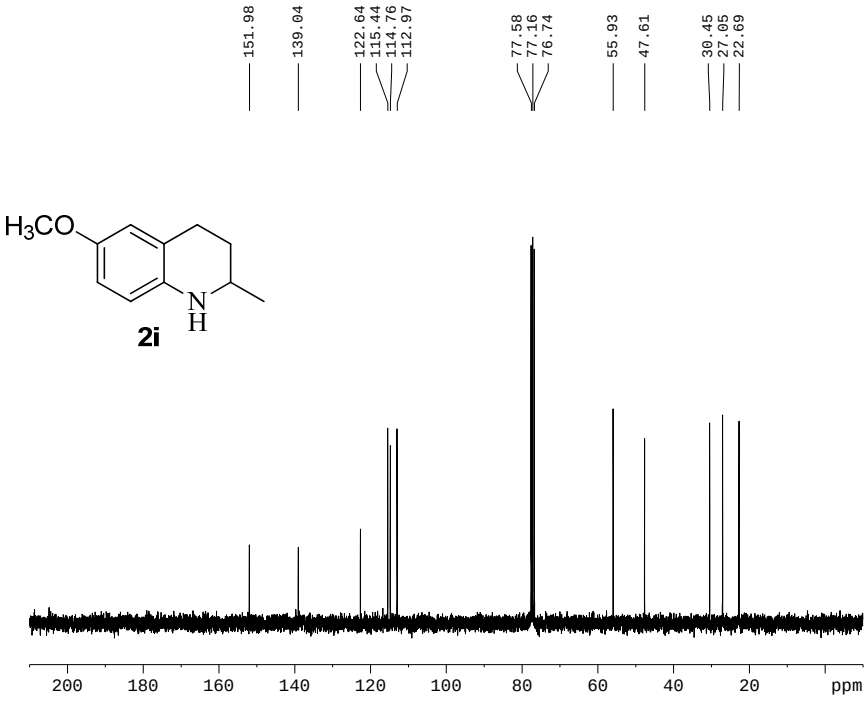



```
Current Data Parameters
NAME      yzs-c-2-026-3
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_           20131211
Time               22.04
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                   181
DW                55.600 usec
DE                 6.50 usec
TE                296.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300067 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



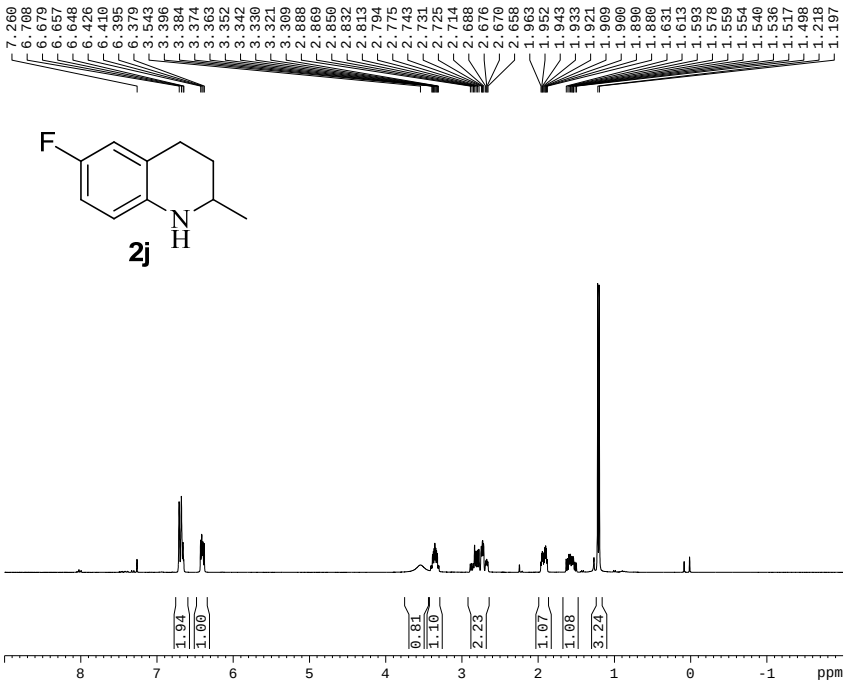

```
Current Data Parameters
NAME      yzs-c-2-026-3
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20131211
Time               22.07
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    82
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                   512
DW                27.800 usec
DE                 6.50 usec
TE                296.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

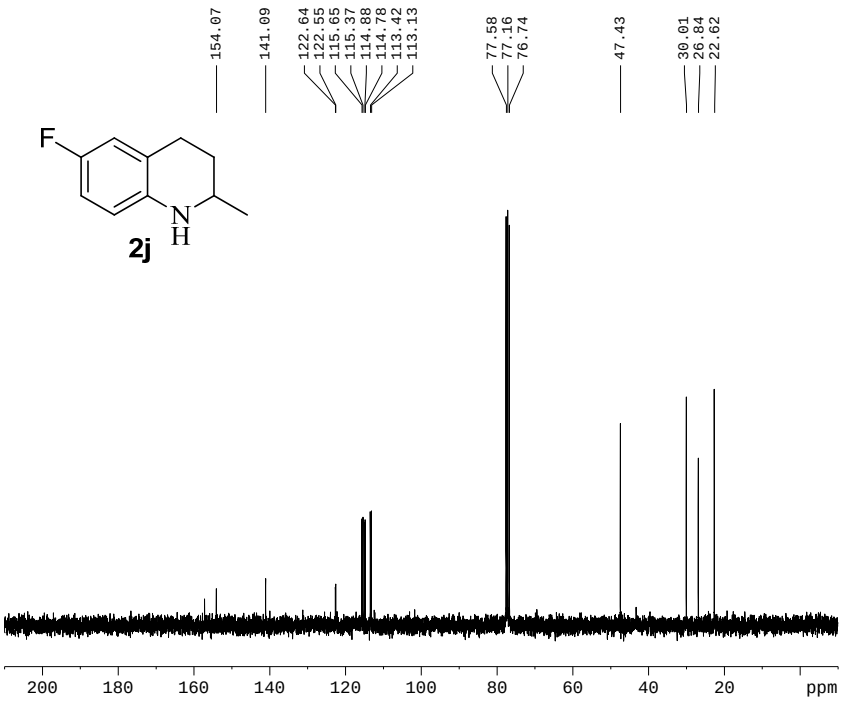



```
Current Data Parameters
NAME      YZS-C-2-026-2
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20131211
Time              21.41
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                  181
DW               55.600 usec
DE                6.50 usec
TE                296.8 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300067 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



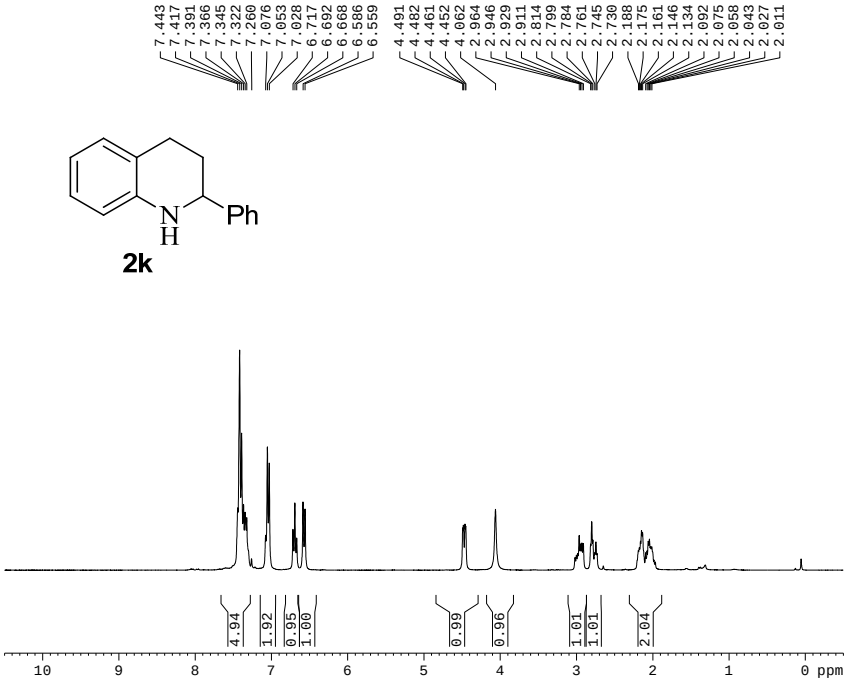

```
Current Data Parameters
NAME      YZS-C-2-026-2
EXPNO                21
PROCNO                1

F2 - Acquisition Parameters
Date_          20131211
Time              21.55
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   92
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG               1149.4
DW               27.800 usec
DE                6.50 usec
TE                297.1 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

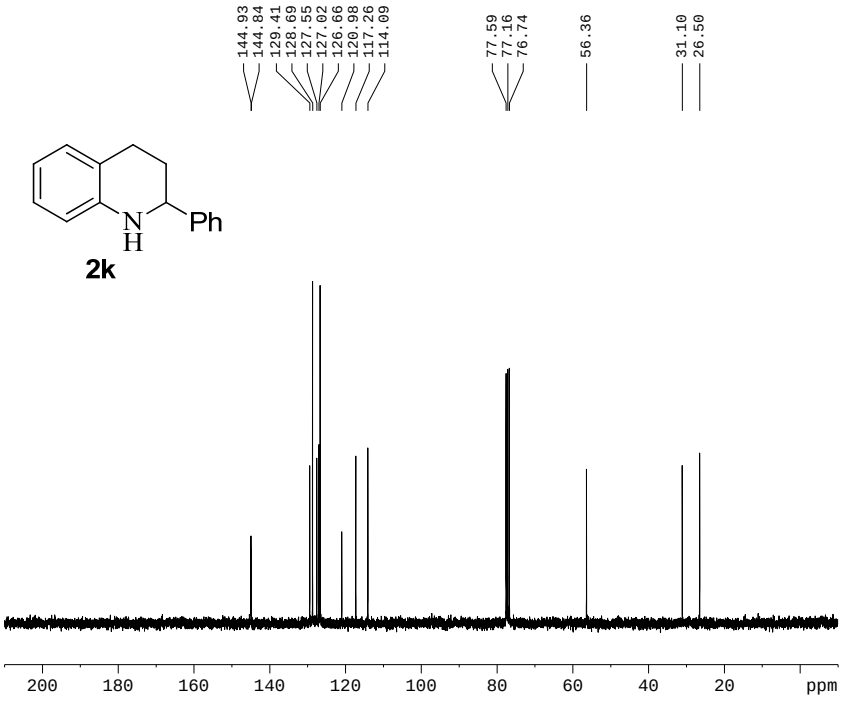



```
Current Data Parameters
NAME       yzs-c-2-ph-r
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_           20140121
Time               14.35
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                   128
DW                55.600 usec
DE                 6.50 usec
TE                295.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300070 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME       yzs-c-2-ph-r
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20140121
Time               14.45
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   103
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                2580.3
DW                27.800 usec
DE                 6.50 usec
TE                296.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

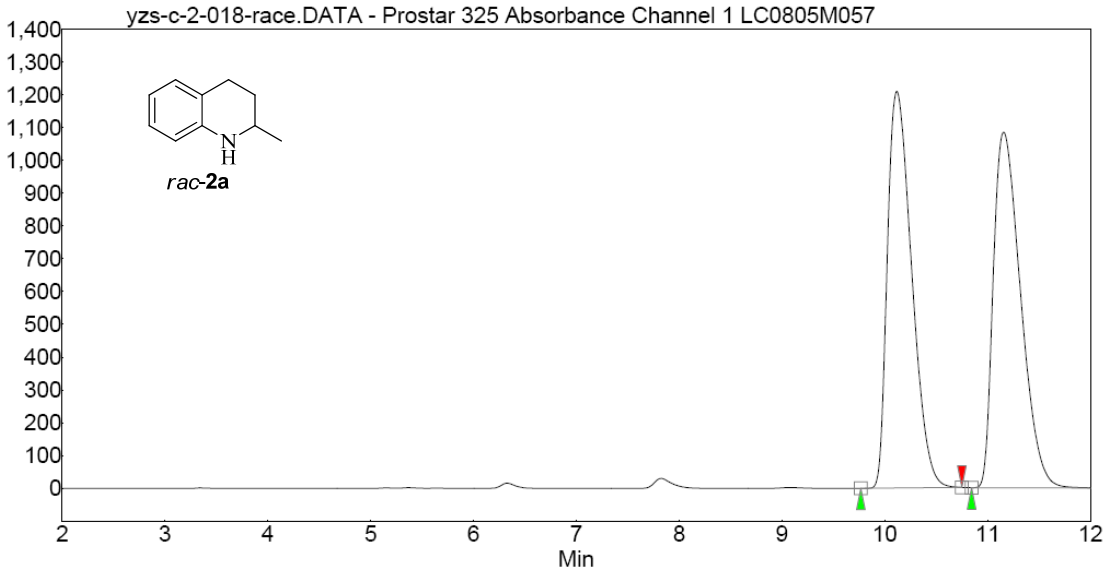
======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

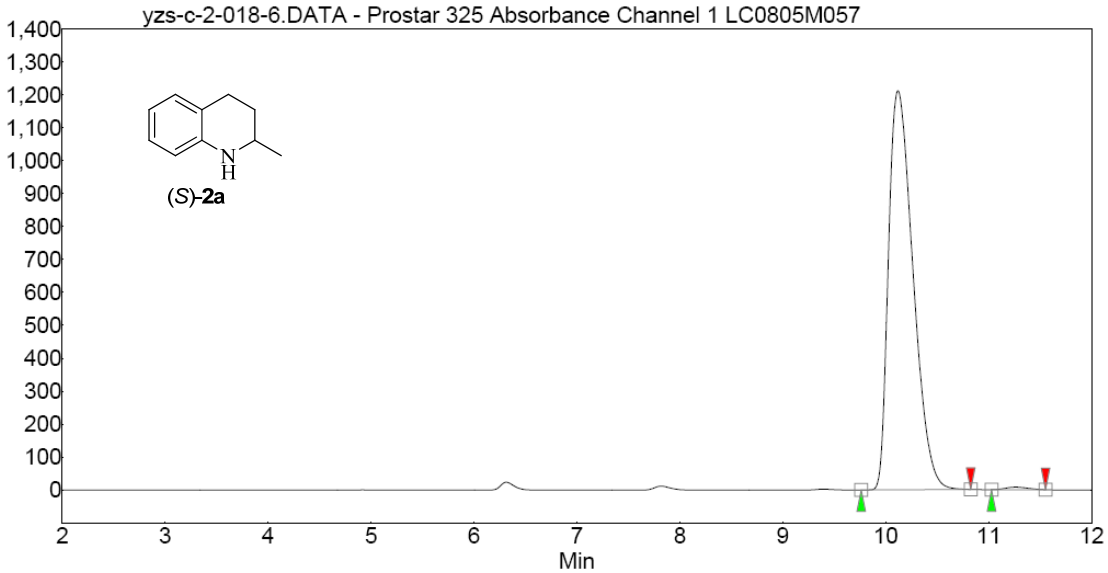
F2 - Processing parameters
SI                 32768
```

8. HPLC spectra of products catalyzed by (*S*,*S*)-6

7.1 HPLC spectra of 2a catalyzed by (*S*,*S*)-6

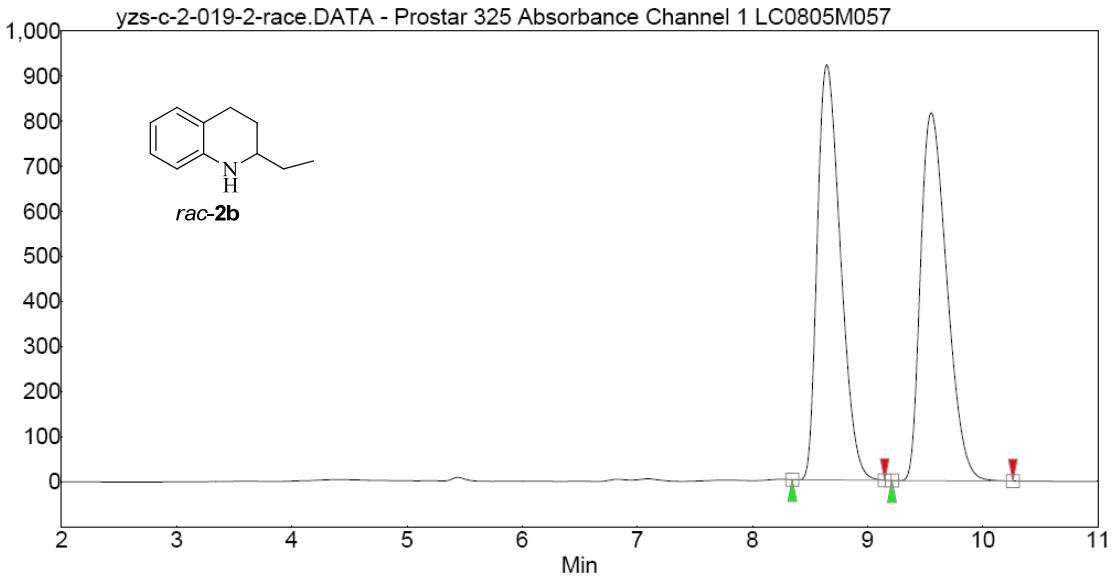


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.11	49.84	1208.8	331.2	49.836
2	未知	11.15	50.16	1083.9	333.4	50.164
Total			100.00	2292.7	664.6	100.000

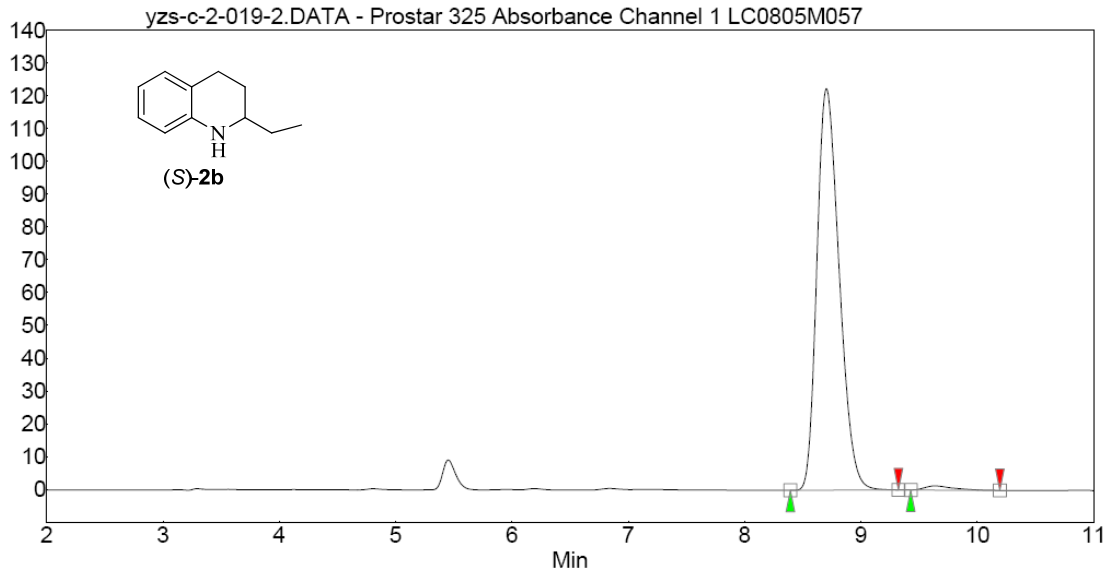


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.12	99.42	1211.7	334.5	99.421
2	未知	11.26	0.58	7.7	1.9	0.579
Total			100.00	1219.4	336.5	100.000

HPLC spectra of 2b catalyzed by (*S*,*S*)-6

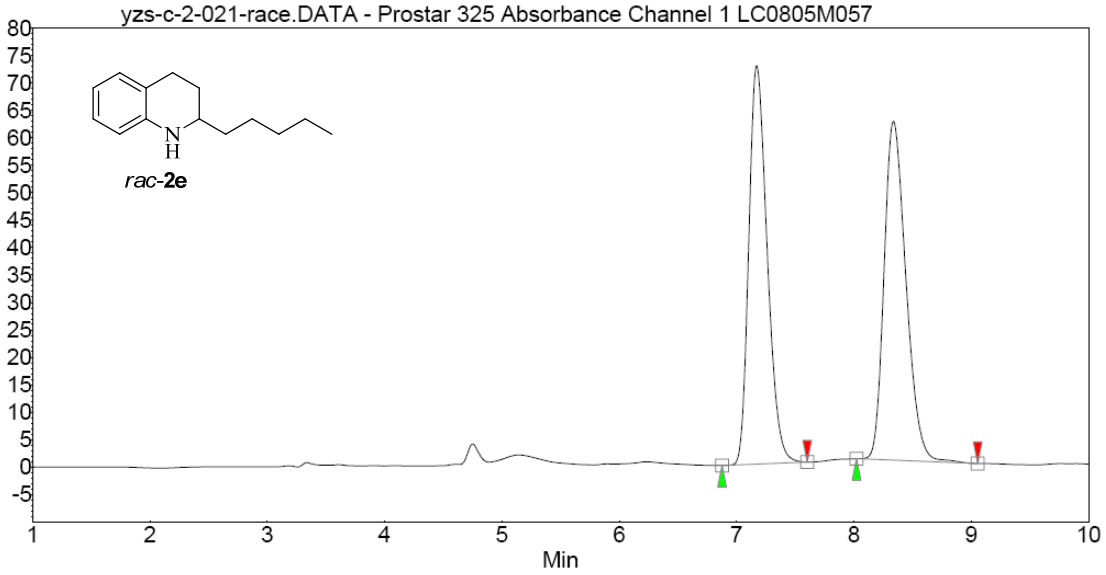


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.65	49.84	920.1	214.2	49.836
2	未知	9.55	50.16	816.0	215.7	50.164
Total			100.00	1736.0	429.9	100.000

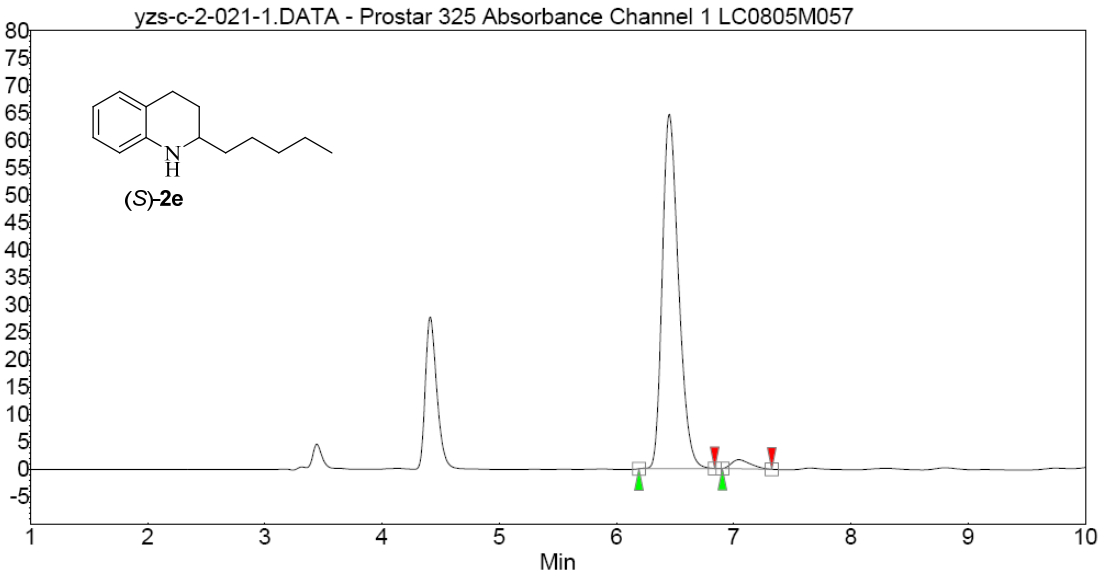


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.70	98.68	122.3	27.2	98.685
2	未知	9.64	1.32	1.3	0.4	1.315
Total			100.00	123.6	27.6	100.000

HPLC spectra of 2e catalyzed by (*S*,*S*)-6

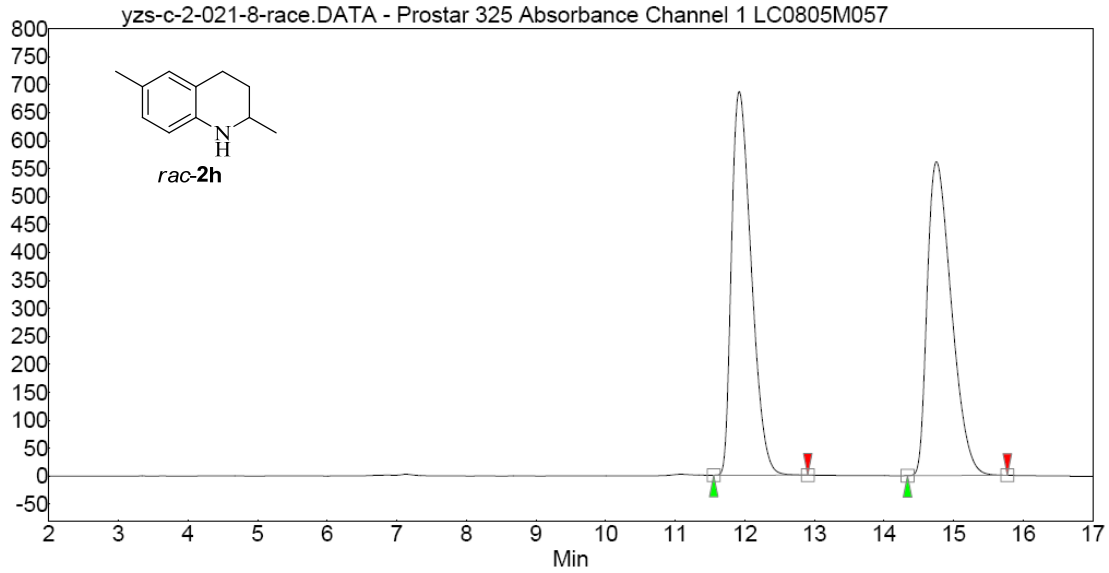


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	7.17	49.66	72.6	13.2	49.662
2	未知	8.33	50.34	61.7	13.3	50.338
Total			100.00	134.3	26.5	100.000

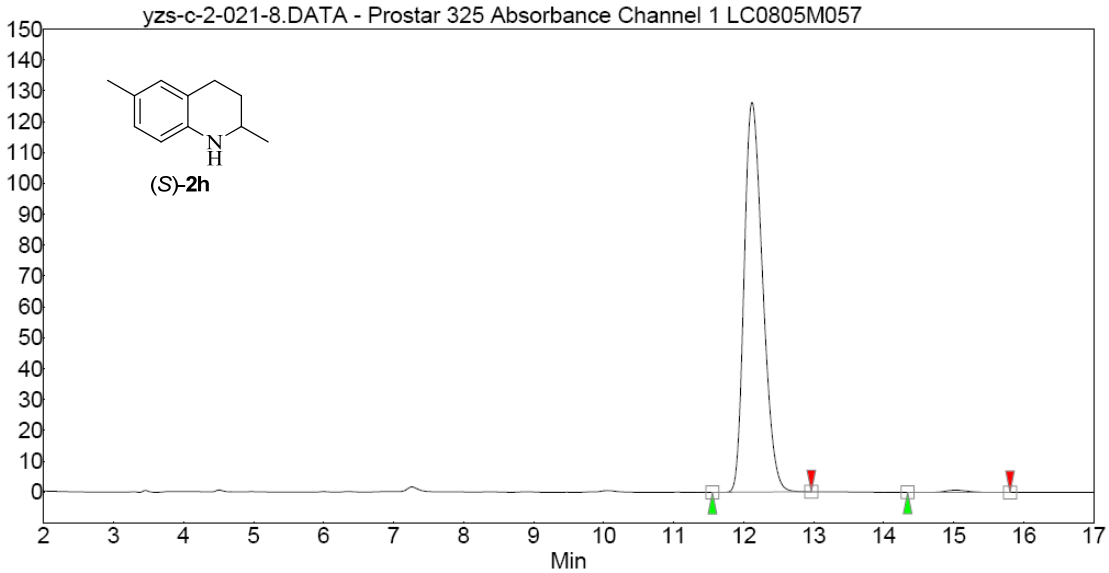


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.45	97.11	64.6	10.4	97.109
2	未知	7.05	2.89	1.7	0.3	2.891
Total			100.00	66.2	10.7	100.000

HPLC spectra of 2h catalyzed by (*S*,*S*)-6

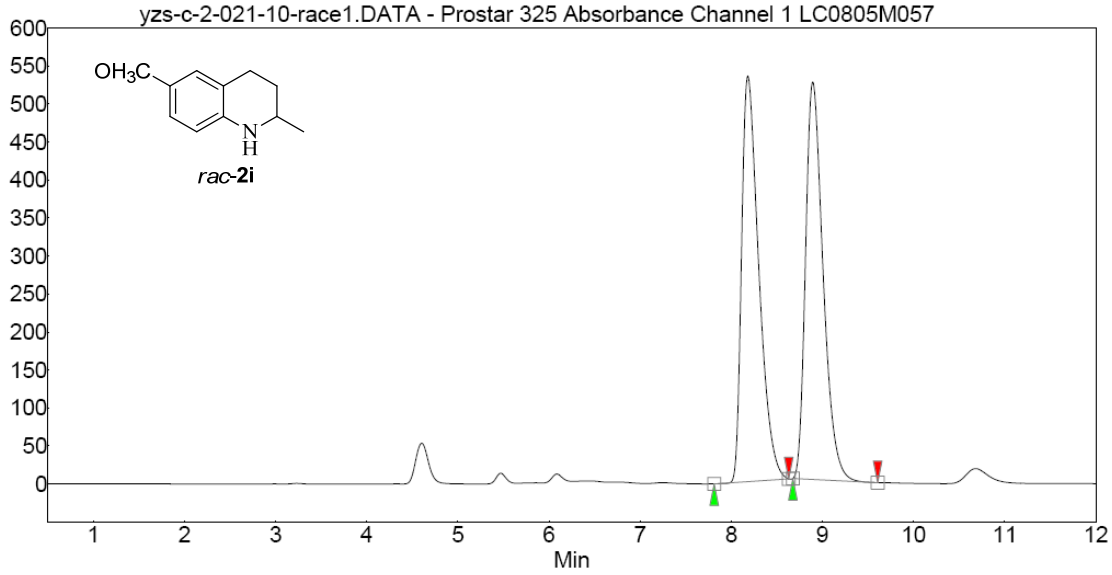


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.12	99.32	126.3	38.7	99.325
2	未知	15.02	0.68	0.7	0.3	0.675
Total			100.00	127.1	38.9	100.000

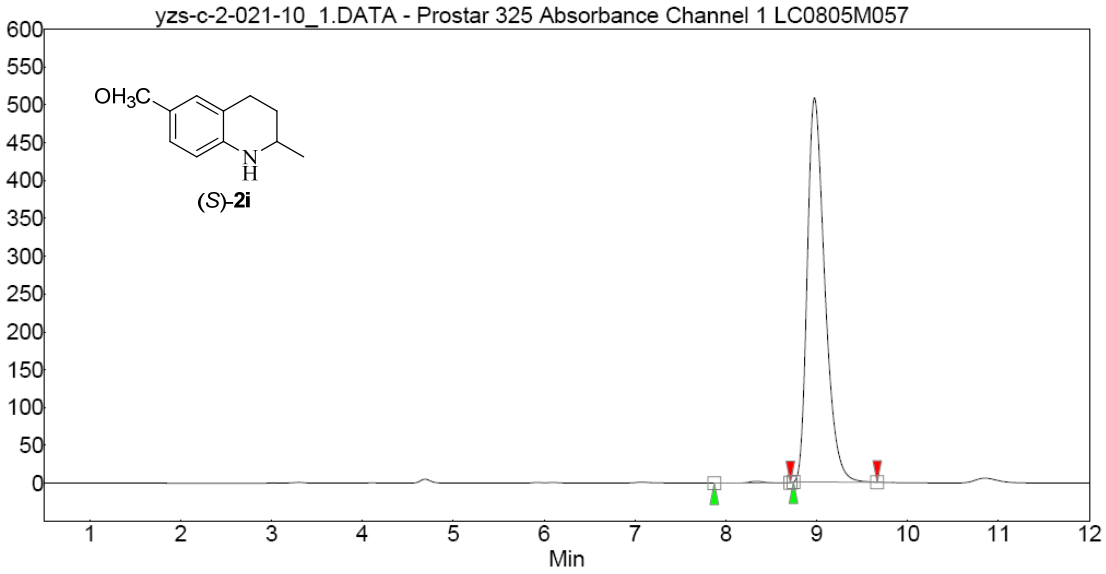


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.12	99.32	126.3	38.7	99.325
2	未知	15.02	0.68	0.7	0.3	0.675
Total			100.00	127.1	38.9	100.000

HPLC spectra of 2i catalyzed by (*S*,*S*)-6

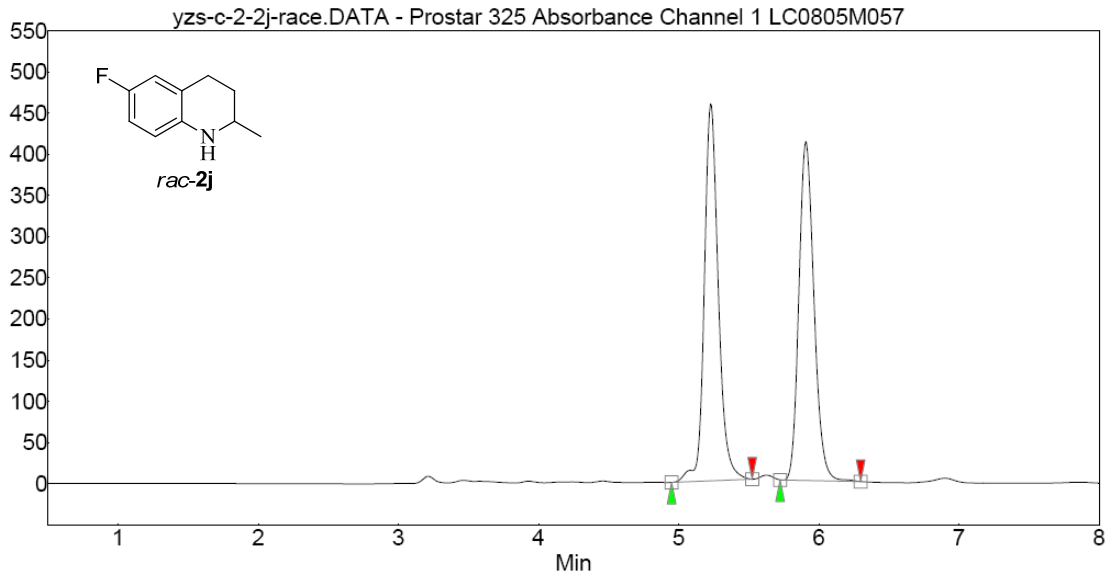


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.18	49.97	533.8	116.5	49.965
2	未知	8.89	50.03	523.1	116.6	50.035
Total			100.00	1056.9	233.1	100.000

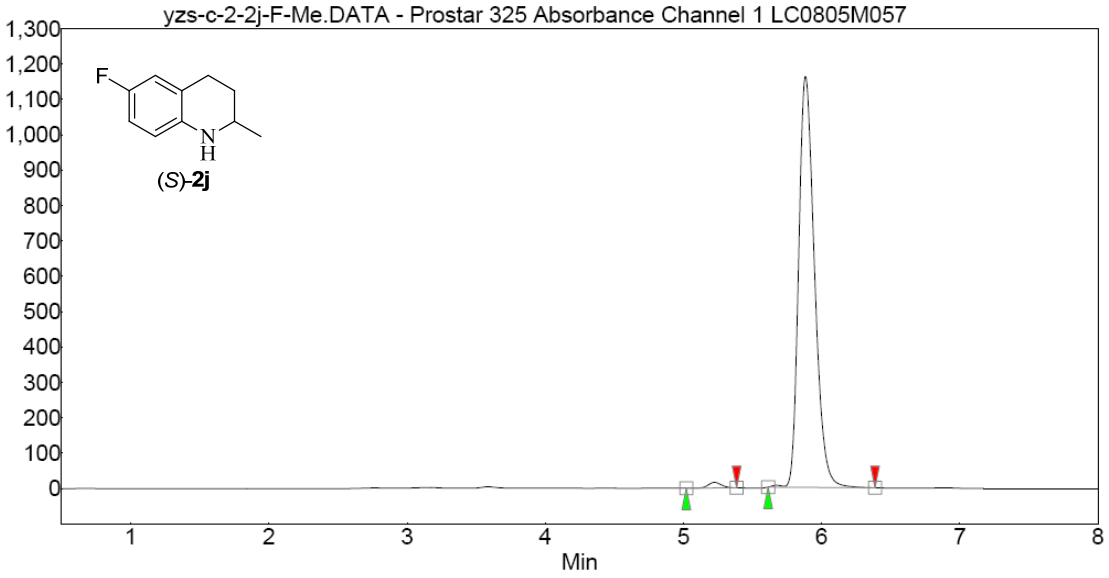


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.33	0.31	2.3	0.4	0.311
2	未知	8.97	99.69	507.8	113.5	99.689
Total			100.00	510.1	113.8	100.000

HPLC spectra of 2j catalyzed by (*S*,*S*)-6



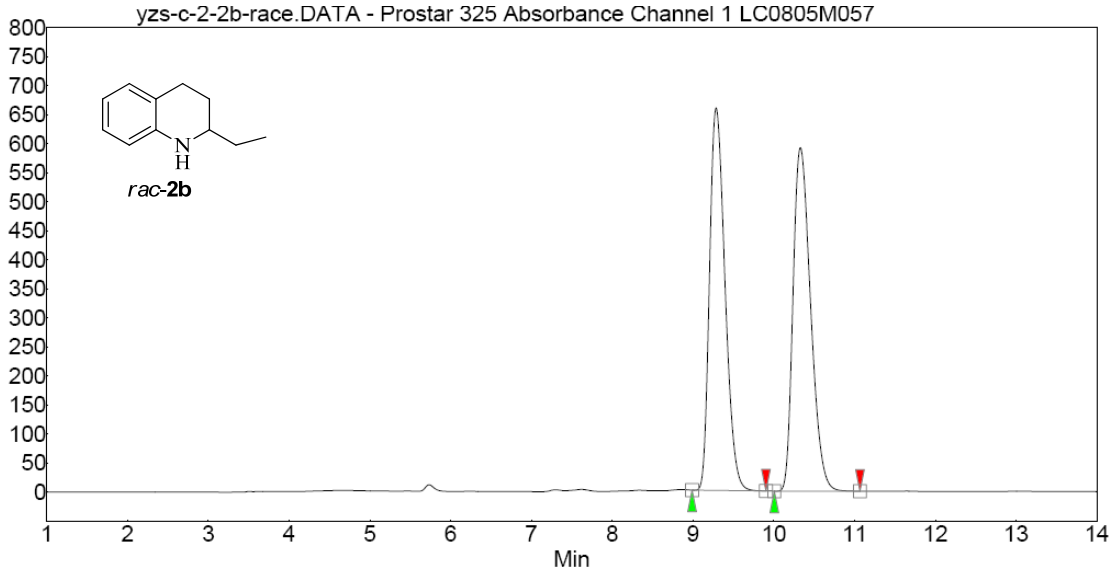
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	5.23	50.85	457.6	53.1	50.853
2	未知	5.91	49.15	411.7	51.3	49.147
Total			100.00	869.2	104.4	100.000



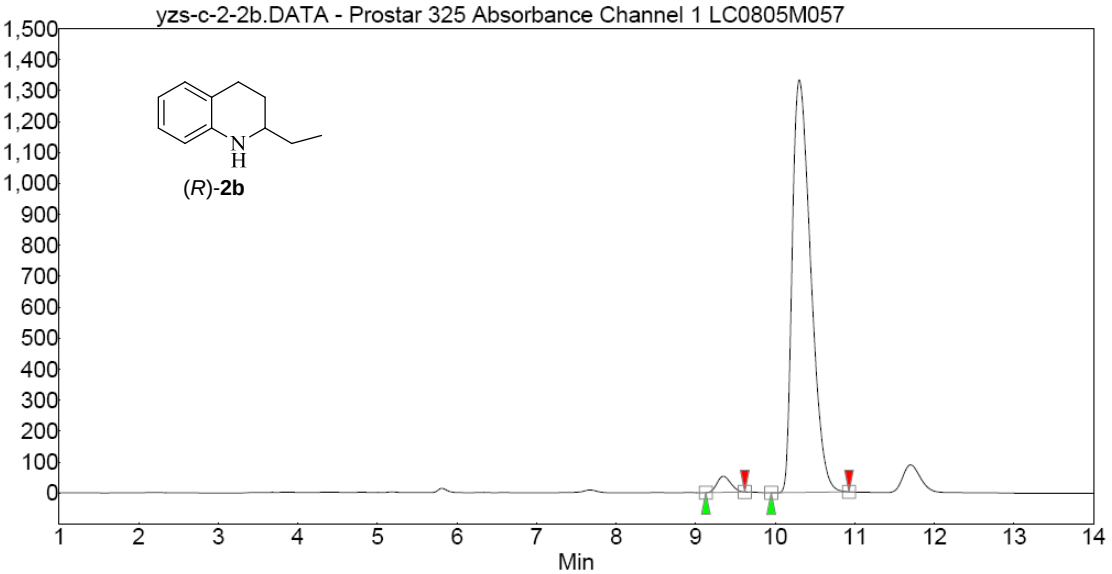
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	5.23	1.13	16.0	1.8	1.125
2	未知	5.88	98.87	1161.0	154.8	98.875
Total			100.00	1177.0	156.6	100.000

8.2 HPLC spectra of products catalyzed by (*R*,*R*)-3

HPLC spectra of 2b catalyzed by (*R*,*R*)-3

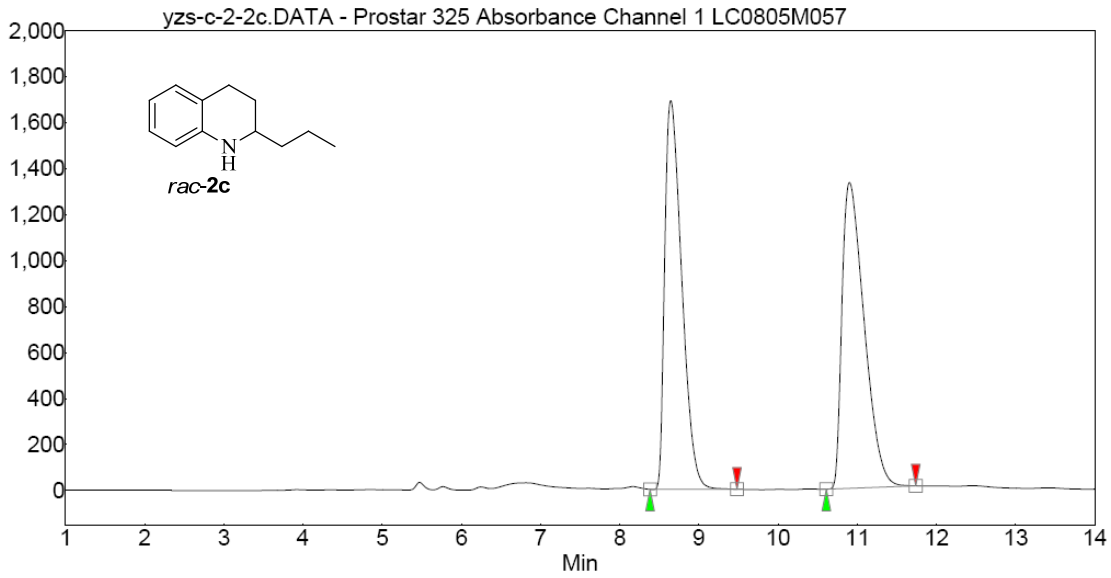


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.29	49.50	658.5	146.1	49.501
2	未知	10.33	50.50	591.5	149.0	50.499
Total			100.00	1249.9	295.1	100.000

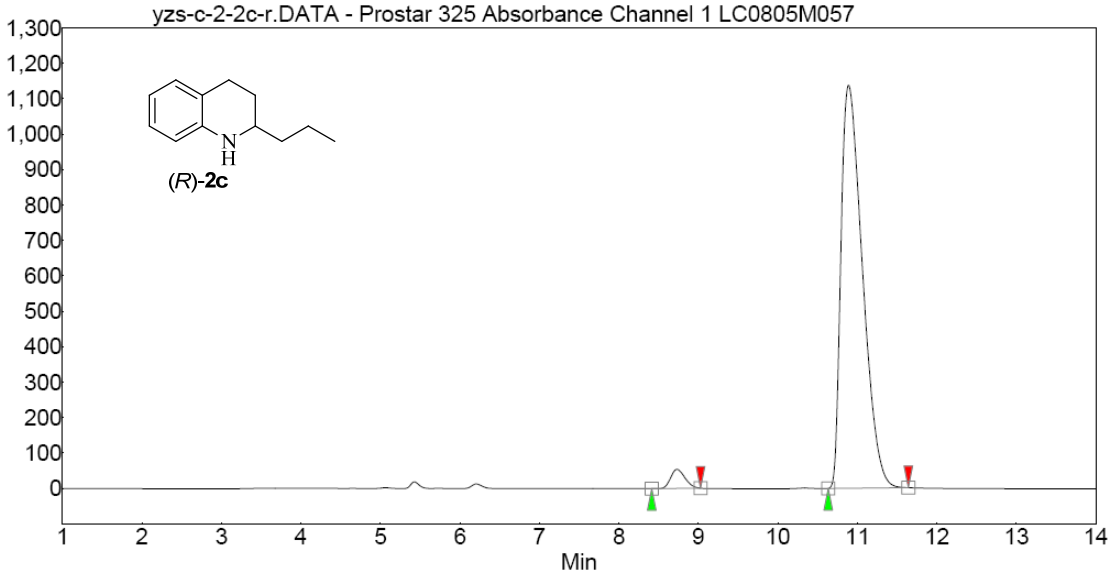


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.35	2.84	52.2	10.5	2.839
2	未知	10.30	97.16	1332.9	359.1	97.161
Total			100.00	1385.1	369.6	100.000

HPLC spectra of 2c catalyzed by (*R*,*R*)-3

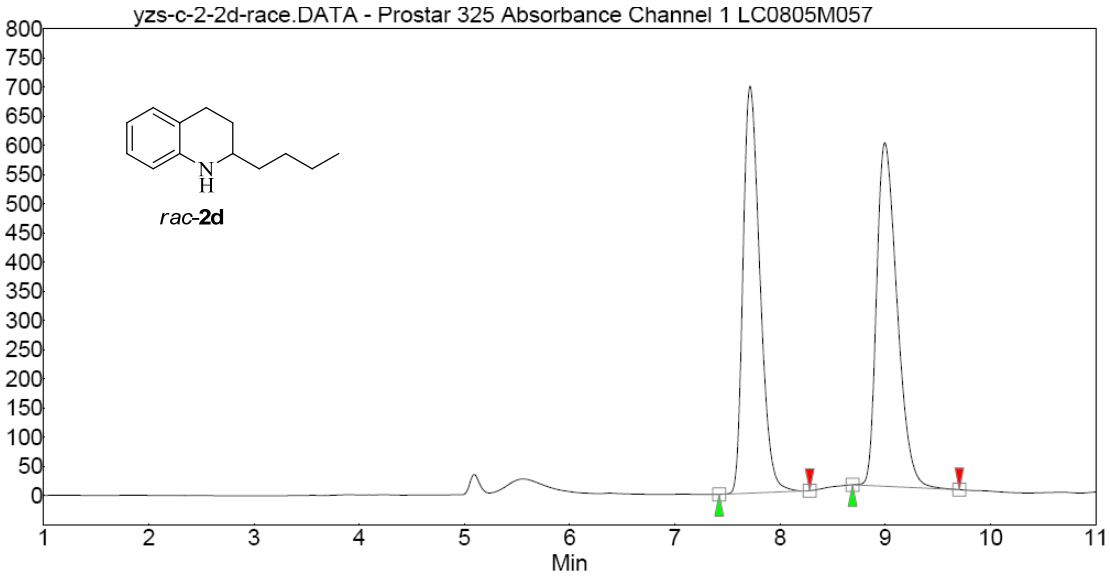


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.65	49.42	1690.7	421.4	49.420
2	未知	10.90	50.58	1330.2	431.3	50.580
Total			100.00	3020.8	852.8	100.000

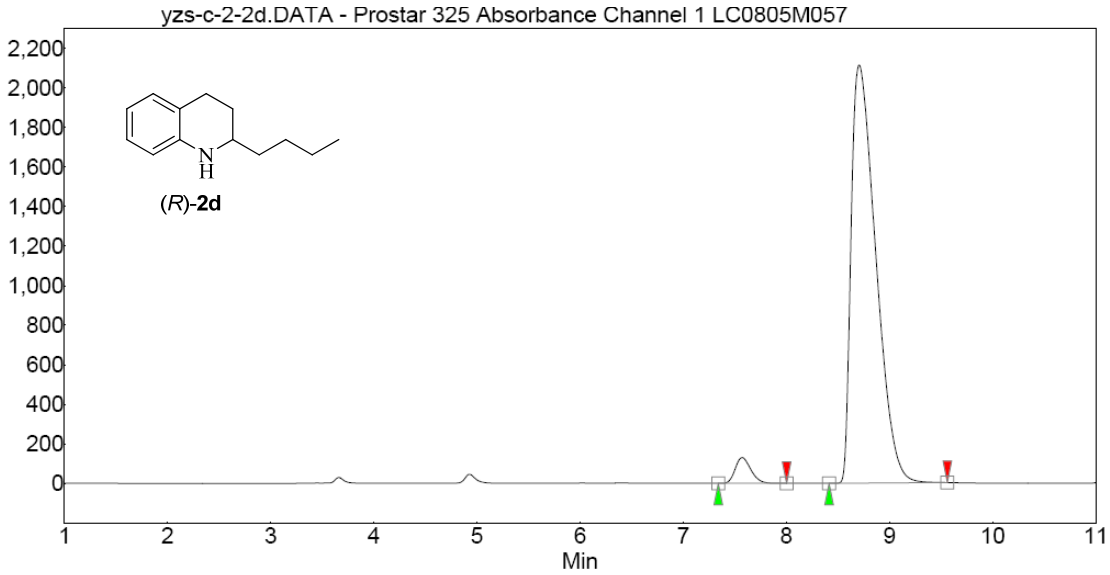


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.73	3.05	53.8	11.2	3.050
2	未知	10.89	96.95	1137.9	356.0	96.950
Total			100.00	1191.7	367.2	100.000

HPLC spectra of 2d catalyzed by (*R*,*R*)-3

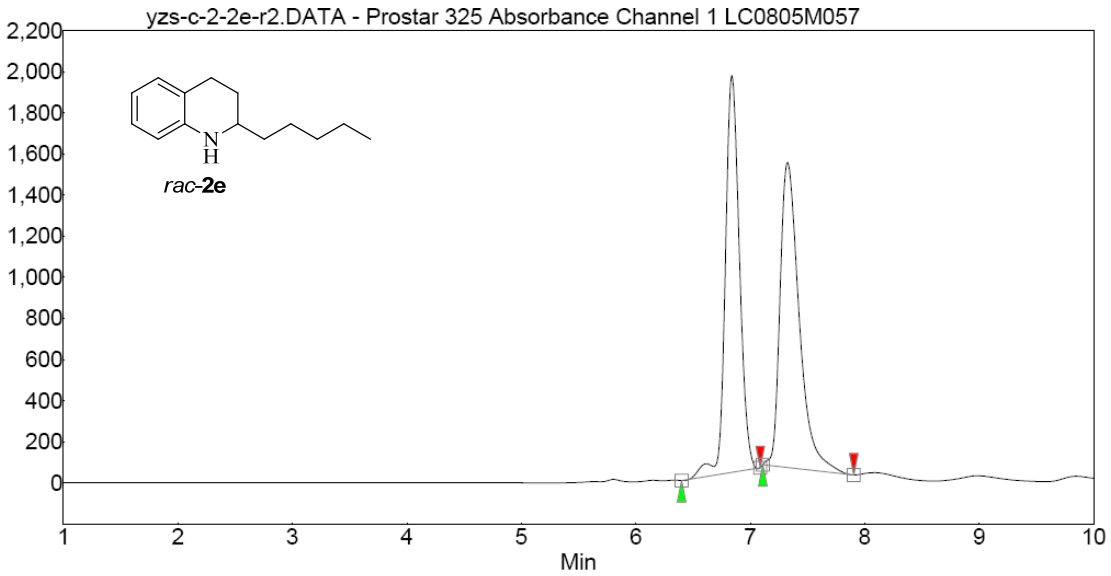


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	7.71	49.36	697.3	129.4	49.365
2	未知	8.99	50.64	588.2	132.7	50.635
Total			100.00	1285.5	262.2	100.000

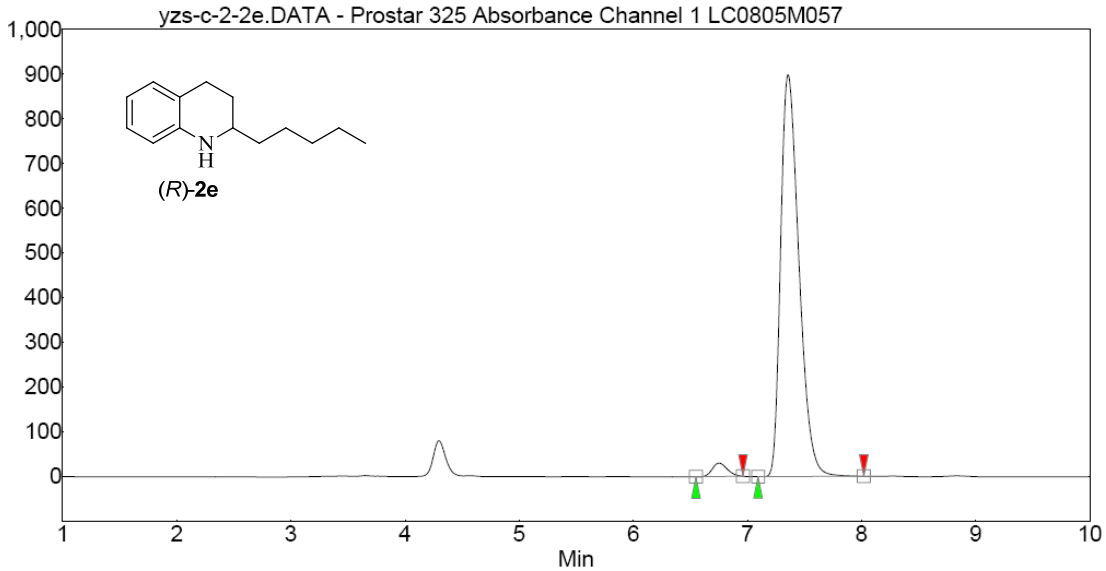


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	7.57	3.77	130.1	22.9	3.766
2	未知	8.71	96.23	2113.7	584.4	96.234
Total			100.00	2243.8	607.2	100.000

HPLC spectra of 2e catalyzed by (*R*,*R*)-3

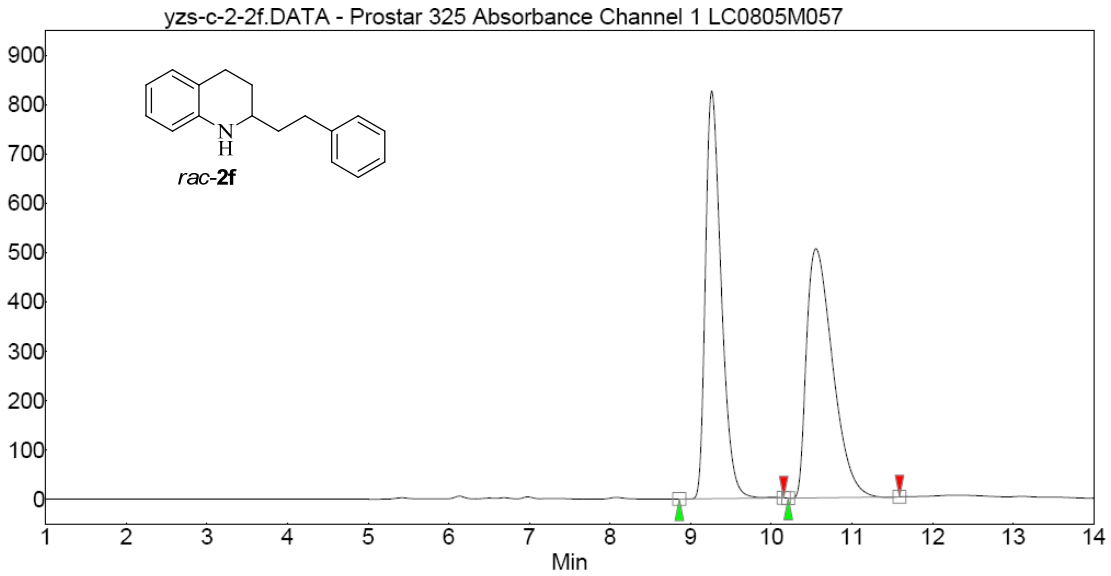


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.84	49.08	1929.8	277.1	49.077
2	未知	7.33	50.92	1483.1	287.5	50.923
Total			100.00	3413.0	564.6	100.000

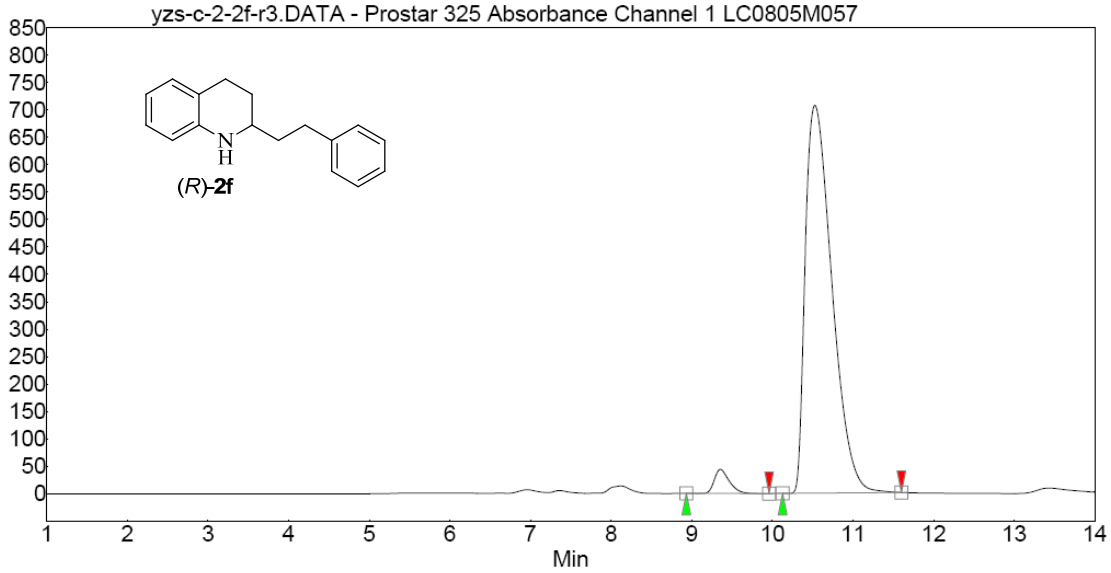


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.75	2.68	30.1	4.6	2.676
2	未知	7.35	97.32	898.2	166.8	97.324
Total			100.00	928.3	171.4	100.000

HPLC spectra of 2f catalyzed by (*R*,*R*)-3

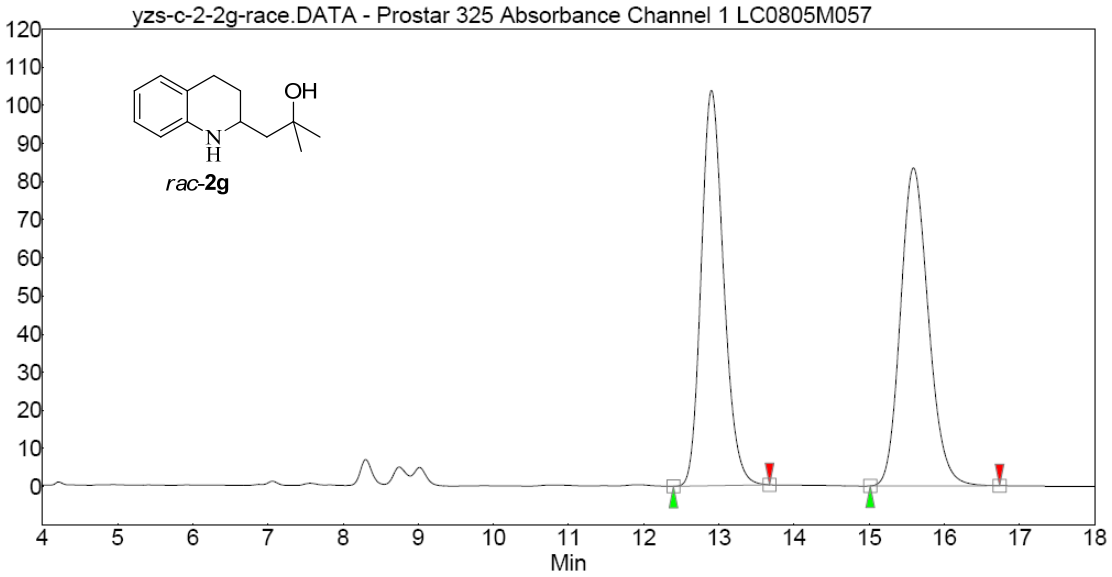


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.26	49.66	826.3	187.0	49.664
2	未知	10.55	50.34	504.9	189.5	50.336
Total			100.00	1331.2	376.5	100.000

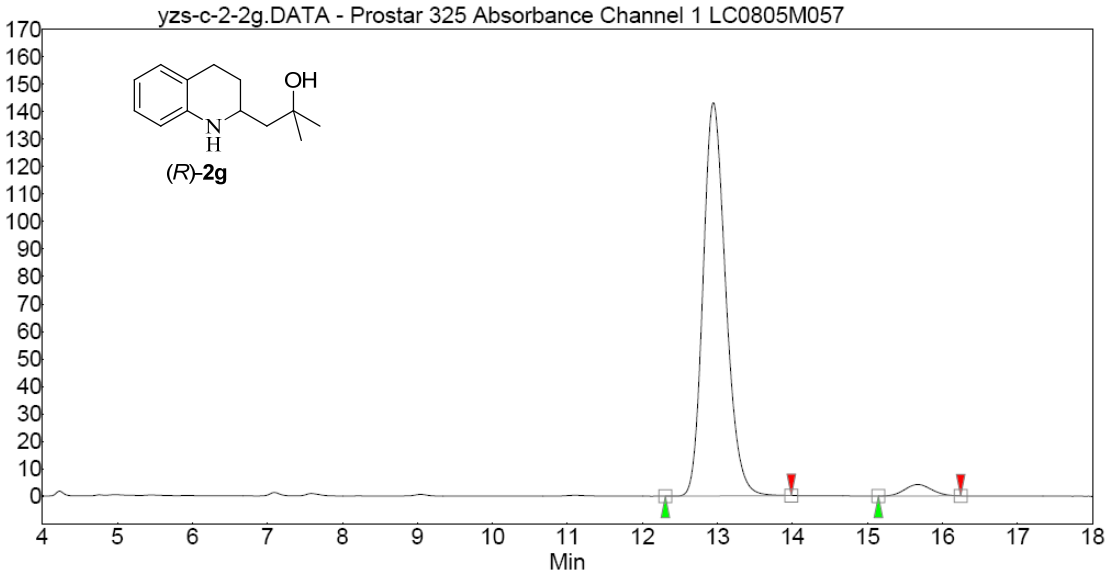


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.35	3.35	44.0	9.4	3.349
2	未知	10.53	96.65	707.2	270.7	96.651
Total			100.00	751.2	280.1	100.000

HPLC spectra of 2g catalyzed by (*R*,*R*)-3

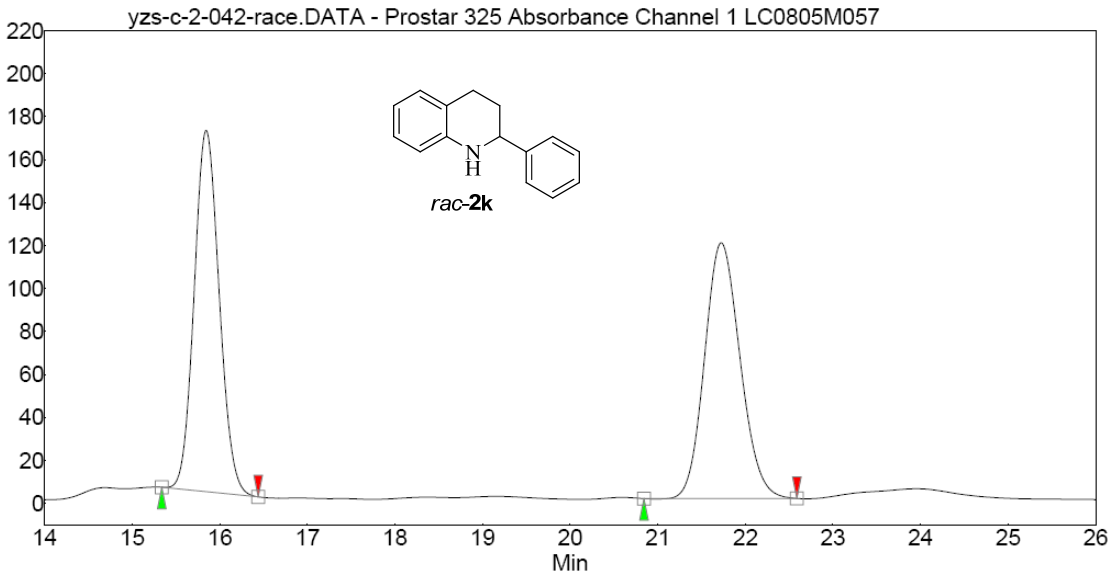


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.90	49.91	103.7	35.8	49.914
2	未知	15.59	50.09	83.4	36.0	50.086
Total			100.00	187.1	71.8	100.000

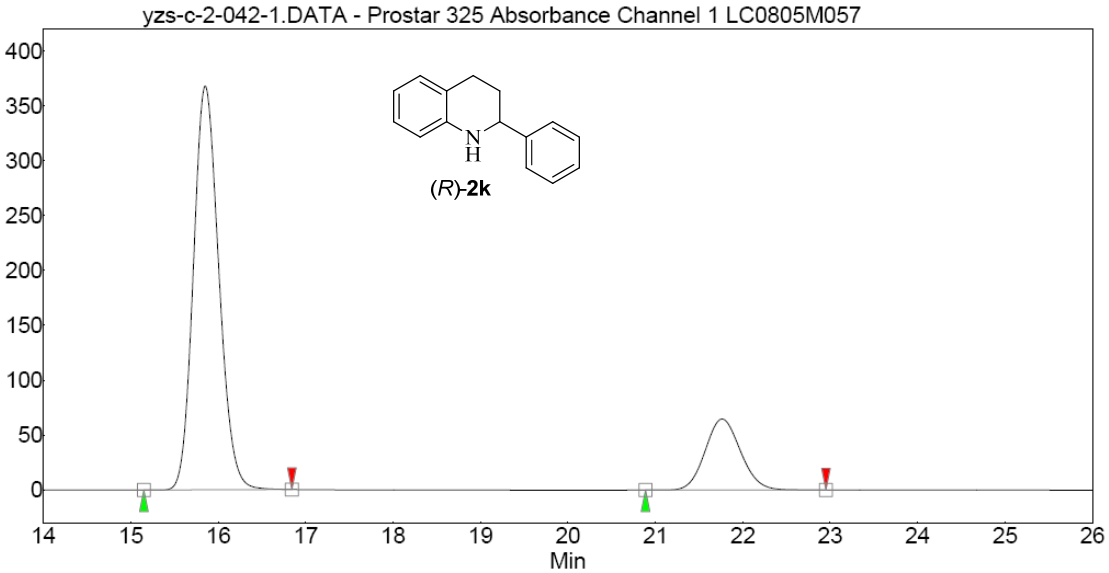


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.95	96.61	143.1	50.0	96.613
2	未知	15.67	3.39	4.2	1.8	3.387
Total			100.00	147.3	51.8	100.000

HPLC spectra of 2k catalyzed by (*R*,*R*)-3



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	15.35	49.64	462.4	150.3	49.645
2	未知	20.74	50.36	333.8	152.5	50.355
Total			100.00	796.2	302.8	100.000



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	15.39	81.63	1211.4	409.8	81.629
2	未知	20.83	18.37	205.7	92.2	18.371
Total			100.00	1417.2	502.0	100.000