Supporting Information for

# Asymmetric Hydrogenation of 2- and 2,3-Substituted Quinoxalines with Chiral Cationic Ruthenium Diamine Catalysts

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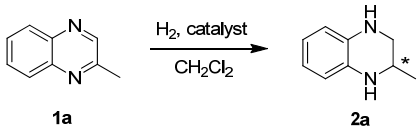
## Contents

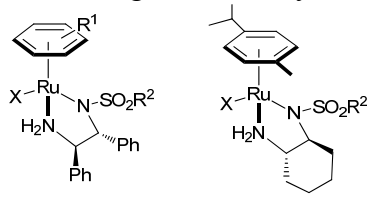
## 1. General information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled 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 PerkinElmer 341 polarimeter. High resolution MS (P-ESI HRMS) were obtained on Bruker Apex IV FTMS spectrometer. HPLC analyses were performed on a Varian Prostar 210 liqiud chromatograph. All organic solvents were dried using standard, published methods and were distilled before use. All other chemicals were used as received from Aldrich or Acros without further purification. The catalysts were prepared according to the published method.[1] 2-Methylquinoxaline **1a** was purchased from Aldrich and used without further purification. 2- and 2,3-substituted quinoxalines were synthesized according to published literature method.

## 2. Optimization of conditions for asymmetric hydrogenation

***Table S1*:** Asymmetric hydrogenation of **1a**: screening of the catalysts[a]




X = OTf (**a**); $BF_4$ (**b**); $PF_6$ (**c**); $SbF_6$ (**d**); BArF (**e**)

(*R*,*R*)-**7**: $\eta^6$-arene = *p*-cymene; $R^2$ = 4-$CH_3C_6H_4$

(*R*,*R*)-**8**: $\eta^6$-arene = *p*-cymene; $R^2$ = $CH_3$

(*S*,*S*)-**9**: $R^2$ = 4-$CF_3C_6H_4$

(*S*,*S*)-**10**: $R^2$ = 4-$CH_3C_6H_4$

(*R*,*R*)-**11**:$\eta^6$-arene = *p*-cymene; $R^2$ = 2,4,6-($^i$Pr)$_3C_6H_2$

(*R*,*R*)-**12**: $\eta^6$-arene = *p*-cymene; $R^2$ = $CF_3$

(*R*,*R*)-**13**: $\eta^6$-arene = *p*-cymene; $R^2$ = 4-$CF_3C_6H_4$

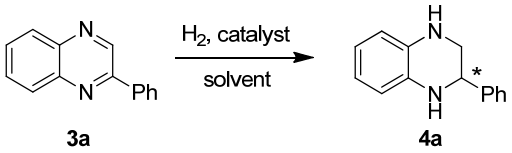
(*R*,*R*)-**14**: $\eta^6$-arene = 1,2,3,4,5,6-$(CH_3)_6$-benzene; $R^2$ = 4-$CH_3C_6H_4$

(*R*,*R*)-**15**: $\eta^6$-arene = 1,2,3,4,5,6-$(CH_3)_6$-benzene; $R^2$ = $CH_3$

| Entry | Catalyst | $R^2$ | Anion ($[X]^-$) | Conv. (%)[b] | Ee (%)[c, d] |
|---|---|---|---|---|---|
| 1 | **(*R*,*R*)-7a** | 4-$CH_3C_6H_4$ | $[OTf]^-$ | >99 | 75 (*R*) |
| 2 | (*R*,*R*)-**8a** | $CH_3$ | $[OTf]^-$ | >99 | 69 (*R*) |
| 3 | (*S*,*S*)-**10a** | 4-$CH_3C_6H_4$ | $[OTf]^-$ | 47 | 56 (*S*) |
| 4 | (*R*,*R*)-**11a** | 2,4,6-($^i$Pr)$_3C_6H_2$ | $[OTf]^-$ | 25 | 32 (*S*) |
| 5 | **(*R*,*R*)-14a** | 4-$CH_3C_6H_4$ | $[OTf]^-$ | 47 | 58 (*R*) |
| 6 | **(*R*,*R*)-7e** | 4-$CH_3C_6H_4$ | $[BArF]^-$ | >99 | 97 (*R*) |
| **7** | **(*R*,*R*)-8e** | **$CH_3$** | **$[BArF]^-$** | **>99** | **98 (*R*)** |
| 8 | (*S*,*S*)-**9e** | 4-$CF_3C_6H_4$ | $[BArF]^-$ | >99 | 95(*S*) |
| 9 | (*R*,*R*)-**8b** | $CH_3$ | $[BF_4]^-$ | >99 | 87 (*R*) |
| 10 | **(*R*,*R*)-8c** | $CH_3$ | $[PF_6]^-$ | >99 | 90 (*R*) |
| 11 | **(*R*,*R*)-8d** | $CH_3$ | $[SbF_6]^-$ | >99 | 91 (*R*) |

[a] Reaction conditions: **1a** (0.2 mmol) in dichloromethane (2 mL), catalyst (1.0 mol %), $H_2$ (50 atm), stirred at 40 °C for 20 h. [b] The conversions were determined by $^1$H NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by chiral HPLC with a chiral OD-H column. [d] The absolute configurations of the products were assigned by comparison of the optical rotations with those in the published literature.[4]

***Table S2:*** Asymmetric hydrogenation of **3a**: screening of the catalysts and reaction conditions[a]

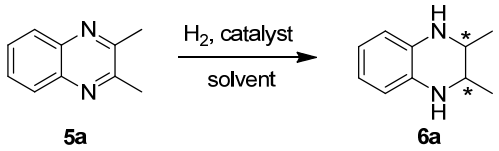



**3a** **4a**

| Entry | Catalyst | solvent | $H_2$ (atm); Temp. ($^oC$) | Conv. (%)[b] | Ee (%)[c, d] |
|---|---|---|---|---|---|
| 1 | (*R*,*R*)-**8a** (OTf) | DCE | 50 ; 40 | >99 | 67 (*R*) |
| 2 | (*R*,*R*)-**8e** (BArF) | DCE | 50 ; 40 | >99 | 84 (*R*) |
| 3 | (*R*,*R*)-**7e** (BArF) | DCE | 50 ; 40 | >99 | 78 (*R*) |
| 4 | (*S*,*S*)-**9e** (BArF) | DCE | 50 ; 40 | >99 | 91 (*S*) |
| 5 | (*R*,*R*)-**12e** (BArF) | DCE | 50 ; 40 | >99 | 88 (*R*) |
| 6 | (*R*,*R*)-**13e** (BArF) | DCE | 50 ; 40 | >99 | 87 (*R*) |
| 7 | (*R*,*R*)-**15e** (BArF) | DCE | 50 ; 40 | >99 | 60 (*R*) |
| 8 | (*S*,*S*)-**9e** (BArF) | DCM | 50 ; 40 | >99 | 82 (*S*) |
| 9 | (*S*,*S*)-**9e** (BArF) | toluene | 50 ; 40 | >99 | 93 (*S*) |
| 10 | (*S*,*S*)-**9e** (BArF) | DCE | 10 ; 40 | >99 | 88 (*S*) |
| 11 | (*S*,*S*)-**9e** (BArF) | DCE | 80 ; 40 | >99 | 92 (*S*) |
| 12 | (*S*,*S*)-**9e** (BArF) | DCE | 50 ; 20 | >99 | 92 (*S*) |
| 13 | (*S*,*S*)-**9e** (BArF) | DCE | 50 ; 60 | >99 | 89 (*S*) |
| **14** | **(*S*,*S*)-9e (BArF)** | **DCE** | **80 ; 20** | **>99** | **94 (*S*)** |
| 15 | (*S*,*S*)-**9e** (BArF) | toluene | 80 ; 20 | >99 | 94 (*S*) |

[a] Reaction conditions: **3a** (0.2 mmol) in solvent (1 mL), catalyst (1.0 mol %), stirred for 16 h. [b] The conversions were determined by $^1H$ NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by chiral HPLC with a chiral OD-H column. [d] The absolute configurations of the products were assigned by comparison of the optical rotations with those in the published literature.[7]

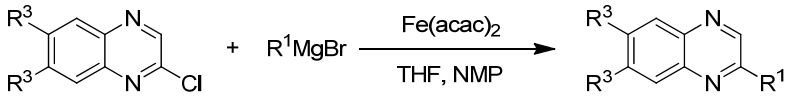
***Table S3:*** Asymmetric hydrogenation of **5a**: screening of the catalysts and reaction conditions[a]



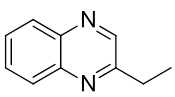

| Entry | Catalyst (Anion) | solvent | $H_2$ (atm); Temp. ($^oC$) | Conv. (%)[b] | Dr. (*trans* : *cis*)[c] | Ee (%)[d] |
|---|---|---|---|---|---|---|
| 1 | (*R*,*R*)-**8a** (OTf) | DCE | 50 ; 40 | >99 | 16 : 84 | 98 |
| 2 | (*R*,*R*)-**8b** ($BF_4$) | DCE | 50 ; 40 | >99 | 22 : 78 | 97 |
| 3 | (*R*,*R*)-**8c** ($PF_6$) | DCE | 50 ; 40 | >99 | 42 : 58 | 99 |
| 4 | (*R*,*R*)-**8d** ($SbF_6$) | DCE | 50 ; 40 | >99 | 51 : 49 | 99 |
| 5 | (*R*,*R*)-**8e** (BArF) | DCE | 50 ; 40 | >99 | 72 : 28 | 99 |
| 6 | (*S*,*S*)-**7e** (BArF) | DCE | 50 ; 40 | >99 | 70 : 30 | 99 |
| 7 | (*S*,*S*)-**9e** (BArF) | DCE | 50 ; 40 | >99 | 76 : 24 | 99 |
| 8 | (*R*,*R*)-**12e** (BArF) | DCE | 50 ; 40 | >99 | 77 : 23 | 99 |
| 9 | (*R*,*R*)-**13e** (BArF) | DCE | 50 ; 40 | >99 | 68 : 32 | 99 |
| 10 | (*R*,*R*)-**15e** (BArF) | DCE | 50 ; 40 | 53 | 59 : 41 | 99 |
| 11 | (*R*,*R*)-**8e** (BArF) | DCM | 50 ; 40 | 90[e] | 71 : 29 | 99 |
| **12** | **(*R*,*R*)-8e (BArF)** | **toluene** | **50 ; 40** | **80**[e] | **80 : 20** | **99** |
| 13 | (*R*,*R*)-**8e** (BArF) | toluene | 10 ; 40 | 53[e] | 80 : 20 | 99 |
| 14 | (*R*,*R*)-**8e** (BArF) | toluene | 80 ; 40 | 85[e] | 79 : 21 | 99 |
| 15 | (*R*,*R*)-**8e** (BArF) | toluene | 50 ; 20 | 69[e] | 80 : 20 | 99 |
| 16 | (*R*,*R*)-**8e** (BArF) | toluene | 50 ; 60 | 84[e] | 79 : 21 | 99 |

[a] Reaction conditions: **5a** (0.2 mmol) in solvent (1 mL), catalyst (1.0 mol %), stirred for 9 h. [b] The conversions were determined by $^1$H NMR spectroscopy of the crude reaction mixture. [c] The *trans*:*cis* ratio were determined by $^1$H NMR spectroscopy and HPLC. [d] The enantiomeric excesses were determined by chiral HPLC with a chiral OD-H column. [e] The reaction time was 2 h.

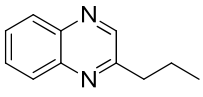
## 3. General procedure for the synthesis of substrates



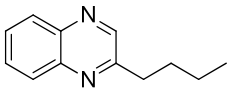

**2-Alkyl-substituted quinoxalines:** 2-Alkyl-substituted quinoxalines **1b**~**1h** and **1j**~**1l** were prepared by the iron-catalyzed Kumada reaction with 2-chloroquinoxalines according to the methods previously reported in the literature.[2] Under $N_2$ atmosphere, 2-chloroquinoxaline (1.15 g, 6.99 mmol) and iron(II) acetylacetonate (125 mg, 0.35 mmol) were dissolved in 50 mL dry THF and 4 mL *N*-methyl-2-pyrrolidone was added. A Grignard solution (8.39 mmol) was added dropwise at room temperature over 10 min. After stirred for 20 min, the reaction mixture was diluted with ether (50 mL) and quenched with 1M aqueous HCl solution (15 mL). The ether layer was separated, washed with water and brine, dried over $Na_2SO_4$, and the solvent was removed under vacuum. Further purification was performed by a silica gel column eluted with petroleum ether/ethyl acetate (10/1, V/V) to give the pure product.



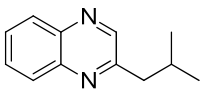

**2-ethylquinoxaline (1b):** (known compound, see: Jones, Z.; Groneberg, R.; Drew, M.; Eary, C. T. U.S. Patent 20050282812, **2005**). Orange liquid; 75% yield; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.72 (s, 1H), 8.05-7.99 (m, 2H), 7.72-7.62 (m, 2H), 3.05-2.97 (q, $J$ = 7.6 Hz, 2H), 1.42-1.37 (t , $J$ = 7.7 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.5, 145.6, 142.2, 141.3, 129.9, 129.2, 128.9, 128.9, 29.7, 13.4.



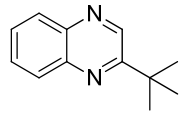
**2-propylquinoxaline (1c):** (known compound, see: Murata, S.; Sugimoto, T.; Matsuura, S. *Heterocycles* **1987**, *26*, 763). Orange liquid; 70% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.71 (s, 1H), 8.06-8.00 (m, 2H), 7.73-7.63 (m, 2H), 2.99-2.94 (t, *J* = 7.7 Hz, 2H), 1.92-1.80 (m, 2H), 1.04-0.99 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.0, 145.5, 141.9, 140.9, 129.4, 128.9, 128.6, 128.4, 38.0, 22.4, 13.6.



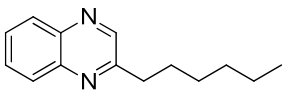
**2-butylquinoxaline (1d):** (known compound, see: Fontana, F.; Minisci, F.; Barbosa, N. M. C.; Vismara, E. *Tetrahedron* **1990**, *46*, 2525). Orange liquid; 85% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.68 (s, 1H), 8.03-7.97 (m, 2H), 7.69-7.59 (m, 2H), 2.98-2.93 (t, *J* = 7.8 Hz, 2H), 1.83-1.72 (m, 2H), 1.46-1.34 (m, 2H), 0.94-0.89 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.7, 145.9, 142.2, 141.2, 129.9, 129.2, 128.9, 128.9, 36.3, 31.6, 22.6, 13.9.



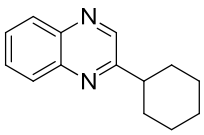
**2-isobutylquinoxaline (1e):** (known compound, see: Fontana, F.; Minisci, F.; Barbosa, N. M. C.; Vismara, E. *Tetrahedron* **1990**, *46*, 2525). Orange liquid; 73% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.68 (s, 1H), 8.06-8.00 (m, 2H), 7.73-7.63 (m, 2H), 2.87-2.84 (d, *J* = 7.2 Hz, 2H), 2.29-2.15 (m, 1H), 0.98-0.96 (d, *J* = 6.6 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.0, 146.3, 142.4, 141.3, 129.9, 129.3, 129.0, 129.0, 45.5, 29.4, 22.6.



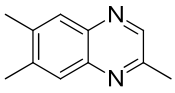
**2-(*tert*-butyl)quinoxaline (1f):** (known compound, see: Fontana, F.; Minisci, F.; Barbosa, N. M. C. and Vismara, E. *Tetrahedron* **1990**, *46*, 2525). Orange liquid; 83% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.98 (s, 1H), 8.07-8.03 (m, 2H), 7.74-7.64 (m, 2H), 1.50 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 163.8, 143.5, 141.7, 140.9, 129.7, 129.4, 129.0, 129.0, 37.3, 29.9.



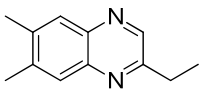
**2-hexylquinoxaline (1g):** (known compound, see: Tan, J.; Tang, W.; Sun, Y.; Jiang, Z.; Chen, F.; Xu, L.; Fan, Q.; Xiao, J. *Tetrahedron* **2011**, *67*, 6206). Yellow liquid; 79% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.73 (s, 1H), 8.07-8.01 (m, 2H), 7.75-7.65 (m, 2H), 3.02-2.97 (d, $J$ = 7.8 Hz, 2H), 1.88-1.78 (m, 2H), 1.44-1.30 (m, 6H), 0.89-0.85 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.8, 146.0, 142.4, 141.3, 130.0, 129.3, 129.0, 129.0, 36.7, 31.7, 29.6, 29.2, 22.7, 14.2.



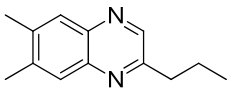
**2-cyclohexylquinoxaline (1h):** (known compound, see: Dong, Z.; G. C.; Wunderlich, S. H.; Unsinn, A.; Li, J.; Knoche, P. *Chem.-Eur. J.* **2009**, *15*, 457). Brown solid; m.p. 44-46 $^{o}$C; 60% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.76 (s, 1H), 8.07-8.02 (m, 2H), 7.74-7.65 (m, 2H), 2.99-2.91 (m, 1H), 2.06-2.01 (m, 2H), 1.95-1.89 (m, 2H), 1.82-1.68 (m, 3H), 1.50-1.32 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 161.2, 145.1, 142.3, 141.6, 129.9, 129.24, 129.15, 128.9, 45.2, 32.4, 26.5, 26.0.



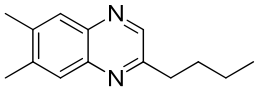
**2,6,7-trimethylquinoxaline (1i):** (known compound, see: Landquist, J. K.; Stacey, G. J. *J. Chem. Soc.* **1953**, 2822. Compound **1i** was prepared according to the method previously reported in the literature[3]). White solid; m.p. 112-114 $^{o}$C; 90% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.63 (s, 1H), 7.80-7.75 (d, 2H), 2.73 (s, 3H), 2.48 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.8, 145.1, 141.1, 140.5, 140.0, 139.3, 128.3, 127.9, 22.5, 20.4, 20.3.



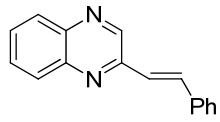
**2-ethyl-6,7-dimethylquinoxaline (1j):** (known compound, see: Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). White solid; m.p. 115-116 $^{o}$C; 82% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 7.74-7.72 (d, 2H), 3.00-2.92 (q, $J$ = 7.6 Hz, 2H), 2.41 (s, 6H), 1.40-1.35 (t, $J$ = 7.7 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.5, 144.6, 141.1, 140.3, 140.2, 139.2, 128.3, 128.0, 29.6, 20.3, 20.2, 13.5.



**6,7-dimethyl-2-propylquinoxaline (1k):** Orange liquid; 83% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.63 (s, 1H), 7.80-7.79 (m, 2H), 2.98-2.93 (t, $J$ = 7.7 Hz, 2H), 2.48 (s, 6H), 1.93-1.81 (m, 2H), 1.05-1.01 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.3, 144.8, 141.1, 140.1, 139.1, 128.1, 127.9, 38.3, 22.8, 20.2, 20.1, 13.8. HRMS-ESI exact mass calcd. for $C_{13}H_{17}N_2^+$ ($[M+H]^+$) requires m/z 201.13862, found m/z 201.13811.

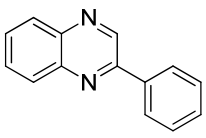


**2-butyl-6,7-dimethylquinoxaline (1l):** (known compound, see: Cartigny, D.; Nagano, T.; Ayad, T.; Genet, J.-P.; Ohshima, T.; Mashima, K.; Ratovelomanana-Vidal, V. *Adv. Synth. Catal.* **2010**, *352*, 1886). Orange liquid; 70% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.53 (s, 1H), 7.67 (s, 2H), 2.90-2.85 (m, 2H), 2.35 (s, 6H), 1.77-1.68 (m, 2H), 1.39-1.33 (m, 2H), 0.91-0.85 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.5, 144.8, 141.1, 140.1, 139.0, 128.2, 127.9, 36.1, 31.6, 22.5, 20.2, 20.1, 13.8.



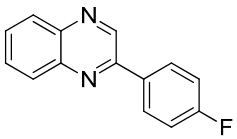
**2-styrylquinoxaline (1m):** (known compound, see: Jones, Z.; Groneberg, R.; Drew, M.; Eary, C. T. U.S. Patent 20050282812, **2005**. Compound **1m** was prepared according to the methods previously reported in the literature[4]). White solid; 70% yield; m.p. 113-1115 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.04 (s, 1H), 8.09-8.06 (d, $J$ = 8.7 Hz, 2H), 7.90-7.85 (d, $J$ = 16.2 Hz, 1H), 7.79-7.65 (m, 4H), 7.45-7.36 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.6, 144.4, 142.4, 141.6, 136.5, 136.0, 130.3, 129.3, 129.2, 129.1, 128.9, 127.5, 125.3.

**2-Aryl-substituted quinoxalines:** 2-Aryl-substituted quinoxalines **3a~3g** were prepared according to the methods previously reported in the literature.[5]

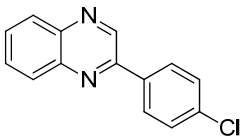


**2-phenylquinoxaline (3a):** (known compound, see: Grovenstein, E. J.; Postman, W.; Taylor, J. W. *J. Org. Chem.* **1960**, *25*, 68). Yellow solid; m.p. 78-79 $^{o}$C; 70% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.33 (s, 1H),

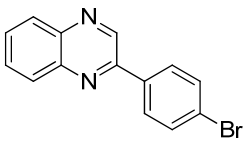
8.22-8.11 (m, 4H), 7.81-7.71 (m, 2H), 7.60-7.52 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.0, 143.5, 142.5, 141.7, 136.9, 130.4, 130.3, 129.8, 129.7, 129.3, 127.7.



**2-(4-fluorophenyl)quinoxaline (3b):** (known compound, see: Cho, C. S.; Oh, S. G. *J. Mol. Catal. A Chem.* **2007**, *276*, 205). Yellow solid; m.p. 120-122 $^{o}$C; 75% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.28 (s, 1H), 8.21-8.09 (m, 4H), 7.80-7.71 (m, 2H), 7.27-7.21 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 166.0, 162.7, 150.8, 143.0, 142.3, 141.6, 133.1, 133.0, 130.5, 129.7, 129.7, 129.6, 129.3, 116.5, 116.2.

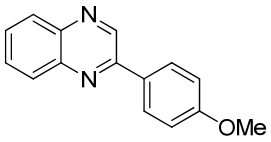


**2-(4-chlorophenyl)quinoxaline (3c):** (known compound, see: Martin, L. J.; Marzinzik, A. L.; Ley, S. V.; Baxendale, I. R. *Org. Lett.* **2011**, *13*, 320). Yellow solid; m.p. 132-134 $^{o}$C; 68% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.29 (s, 1H), 8.17-8.10 (m, 4H), 7.81-7.73 (m, 2H), 7.55-7.52 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.7, 143.0, 142.4, 141.8, 136.7, 135.3, 130.6, 129.9, 129.7, 129.5, 129.3, 128.9.

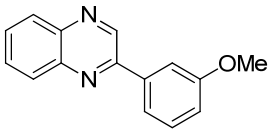


**2-(4-bromophenyl)quinoxaline (3d):** (known compound, see: Madhav, B.; Murthy, S. N.; Reddy, V. P.; Rao, K. R., Nageswar, Y. V. D. *Tetrahedron Lett.* **2009**, *50*, 6025). Yellow solid; m.p. 136-138 $^{o}$C; 72% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.29 (s, 1H), 8.15-8.07 (m, 4H), 7.81-7.67 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.8, 142.9, 142.4, 141.9,

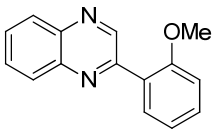
135.8, 132.5, 130.6, 129.9, 129.8, 129.3, 129.1, 125.1.



**2-(4-methoxyphenyl)quinoxaline (3e):** (known compound, see: Madhav, B.; Murthy, S. N.; Reddy, V. P.; Rao, K. R., Nageswar, Y. V. D. *Tetrahedron Lett.* **2009**, *50*, 6025). Yellow solid; 70% yield; m.p. 99-100 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.27 (s, 1H), 8.18-8.15 (d, *J* = 8.7 Hz, 2H), 8.12-8.06 (m, 2H), 7.76-7.66 (m, 2H), 7.08-7.05 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 161.6, 151.5, 143.2, 142.4, 141.3, 130.2, 129.5, 129.4, 129.2, 129.1, 129.1, 114.7, 55.5.



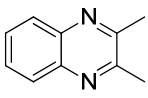
**2-(3-methoxyphenyl)quinoxaline (3f):** (known compound, see: Cho, C.S.; Oh, S.G. *J. Mol. Catal. A Chem.* **2007**, *276*, 205). Yellow solid; m.p. 87-88 $^{o}$C; 75% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.31 (s, 1H), 8.18-8.10 (m, 2H), 7.80-7.71 (m, 4H), 7.50-7.44 (t, *J* = 8.0 Hz, 1H), 7.08-7.05 (m, 1H), 3.94 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 160.5, 151.8, 143.6, 142.4, 141.8, 138.3, 130.4, 130.3, 129.8, 129.7, 129.3, 120.1, 116.4, 112.9, 55.6.



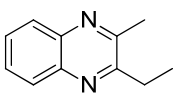
**2-(2-methoxyphenyl)quinoxaline (3g):** (known compound, see: Cho, C. S.; Oh, S. G. *Tetrahedron Lett.* **2006**, *47*, 5633.). Yellow solid; 71% yield; m.p. 109-110 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.34 (s, 1H), 8.17-8.10 (m, 2H), 7.92-7.89 (m, 1H), 7.77-7.70 (m, 2H), 7.50-7.44 (m, 1H), 7.18-7.13 (t, *J* = 7.5 Hz, 1H), 7.07-7.04 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H); $^{13}$C NMR

(75 MHz, $CDCl_3$): δ (ppm) 157.5, 152.3, 147.4, 142.8, 141.2, 131.7, 131.5, 129.8, 129.6, 129.4, 129.2, 126.7, 121.6, 111.5, 55.7.

**2,3-Dialkyl quinoxalines**: 2,3-Dialkyl quinoxalines **5a-5h** were prepared according to the method previously reported in the literature:[3] To a stirred solution of 2,3-dione (13 mmol) in 50 mL of methanol was added benzene-1,2-diamine (10 mmol) and ammonium chloride (50 mol%). The mixture was stirred at room tempreture for 1 h. The reaction mixture was washed with water (200 mL) and extracted by $CH_2Cl_2$. The organic phase was evaporated under reduced pressure and the pure product was obtained without any further purification.

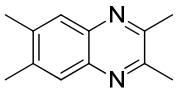


**2,3-dimethylquinoxaline (5a):** (known compound, see: Darabi, H. R.; Tahoori, F.; Aghapoor, K.; Taala F.; Mohsenzadeh, F. *J. Braz. Chem. Soc.*, **2008**, *19*, 1646). White solid; m.p. 105-106 $^oC$; 92% yield; $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 7.92-7.86 (m, 2H), 7.59-7.54 (m, 2H), 2.62 (s, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ (ppm) 153.4, 141.1, 128.8, 128.3, 23.2.

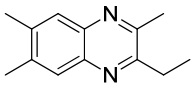


**2-ethyl-3-methylquinoxaline (5b):** (known compound, see: Kaiser, E. M. Petty, J. D. *J. Organomet. Chem.* **1976**, *108*, 139). White solid; m.p. 53-54 $^oC$; 94% yield; $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 8.01-7.94 (m, 2H), 7.65-7.62 (m, 2H), 3.05-2.97 (q, $J$ = 7.4 Hz, 2H), 2.74 (s, 3H), 1.42-1.37 (t, $J$ = 7.5 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ (ppm) 157.7, 153.2, 141.3, 141.0, 128.9, 128.8,

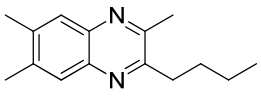
128.7, 128.4, 29.1, 22.8, 12.1.



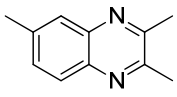
**2,3,6,7-tetramethylquinoxaline (5c):** (known compound, see: Raghuveerachary, P.; Devanna, N. *Asian J. Chem.* **2011**, *23*, 1628). White solid; m.p. 211-212 $^{o}$C; 94% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.69 (s, 2H), 2.67 (s, 6H), 2.43 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.4, 140.1, 139.1, 127.6, 23.2, 20.3.



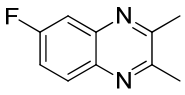
**2-ethyl-3,6,7-trimethylquinoxaline (5d):** White solid; m.p. 139-140 $^{o}$C; 91% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.74 (s, 1H), 7.69 (s, 1H), 3.01-2.93 (q, $J$ = 7.5 Hz, 2H), 2.70 (s, 3H), 2.43 (s, 6H), 1.40-1.35 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.6, 152.0, 140.2, 139.9, 139.0, 139.0, 127.9, 127.6, 29.0, 22.7, 20.3, 20.3, 12.2. HRMS-ESI exact mass calcd. for $C_{13}H_{17}N_2^+$ ($[M+H]^+$) requires m/z 201.13862, found m/z 201.13825.



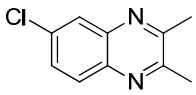
**2-butyl-3,6,7-trimethylquinoxaline (5e):** White solid; m.p. 88-89 $^{o}$C; 93% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.73 (s, 1H), 7.69 (s, 1H), 2.96-2.91 (t, $J$ = 8.0 Hz, 2H), 2.70 (s, 3H), 2.43 (s, 6H), 1.82-1.72 (m, 2H), 1.54-1.41 (m, 2H), 1.00-0.95 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 155.9, 152.1, 140.2, 139.9, 139.0, 139.0, 127.8, 127.6, 35.7, 30.5, 23.0, 22.8, 20.3, 20.3, 14.1. HRMS-ESI exact mass calcd. for $C_{15}H_{21}N_2^+$ ($[M+H]^+$) requires m/z 229.16993, found m/z 229.16966.



**2,3,6-trimethylquinoxaline (5f):** (known compound, see: Darabi, H. R.; Tahoori, F.; Aghapoor, K.; Taala F.; Mohsenzadeh, F. *J. Braz. Chem. Soc.*, **2008**, *19*, 1646). White solid; m.p. 104-106 $^{o}$C; 95% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86-7.83 (d, *J* = 8.7 Hz, 1H), 7.73 (s, 1H), 7.49-7.46 (m, 1H), 2.70 (s, 6H), 2.54 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 153.4, 152.6, 141.3, 139.6, 139.2, 131.1, 128.0, 127.5, 23.3, 23.2, 21.9.



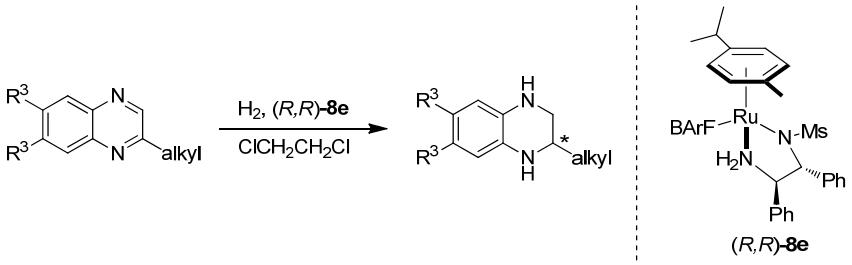
**6-fluoro-2,3-dimethylquinoxaline (5g):** (known compound, see: Zhang, L.; Qiu, B.; Li, Xin.; Wang, Xin.; Li, J.; Zhang, Y.; Liu, J.; Li, J.; Shen, J. *Molecules* **2006**, *11*, 988). White solid; 90% yield; m.p. 108-110 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.89-7.84 (m, 1H), 7.53-7.49 (m, 1H), 7.38-7.31 (m, 1H), 2.63 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 163.8, 160.5, 154.4, 152.8, 152.7, 141.8, 141.7, 138.2, 130.4, 130.2, 119.0, 118.7, 112.2, 111.9, 23.2, 23.0.



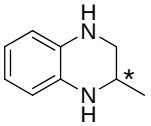
**6-chloro-2,3-dimethylquinoxaline (5h):** (known compound, see: Darabi, H. R.; Tahoori, F.; Aghapoor, K.; Taala F.; Mohsenzadeh, F. *J. Braz. Chem. Soc.*, **2008**, *19*, 1646). White solid; m.p. 89-91 $^{o}$C; 90% yield; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.91 (s, 1H), 7.86-7.83 (d, J = 8.7 Hz 1H), 7.56-7.53 (d, *J* = 8.7 Hz, 1H), 2.67 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 154.6, 153.8, 141.5, 139.6, 134.4, 129.8, 129.7, 127.5, 23.3, 23.2.

## 4. General procedure for the asymmetric hydrogenation of quinoxalines

### (1) Typical procedure for the asymmetric hydrogenation of 2-alkyl substituted quinoxalines:

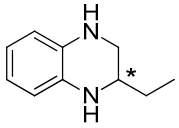



A 50 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ru-catalyst (*R*,*R*)-**8e** (0.002 mmol) and the corresponding quinoxaline (0.2 mmol) in DCE (1 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 40 $^{o}$C for 8 h. Then the hydrogen gas was carefully released and the conversion was determined by $^{1}$H NMR spectroscopy after the solvent was evaporated under reduced pressure. The reaction mixture was filtered through a short pad of silica eluted with DCM to give the pure products. The enantiomeric excess of the product was determined by HPLC with a chiral OD-H column.

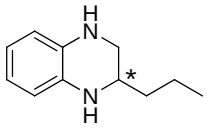



**(*R*)-2-methyl-1,2,3,4-tetrahydroquinoxaline (2a)**: (known compound, see: George, H. F.; Harry, P. S. *J. Org. Chem.* **1974**, *39*, 635). White solid; m.p. 71-72 $^{o}$C; isolated yield 95%, 98% ee, $[\alpha]_D^{20}$ = +3.7 (*c* 0.5, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -34.4 (c 0.065, $CH_2Cl_2$), 93% ee, (*S*)]; $^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm)

6.59-6.49 (m, 4H), 3.55 (b, 2H), 3.34-3.31 (m, 1H), 3.05 (b, 1H), 1.20-1.18 (d, *J* = 6.30 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 133.6, 133.3, 118.7, 114.52, 114.47, 48.3, 45.8, 19.9. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) $t_1$ = 9.9 min (major), (*S*) $t_2$ =11.8 min (minor).

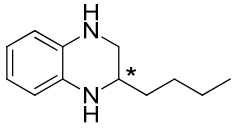


**(*R*)-2-ethyl-1,2,3,4-tetrahydroquinoxaline (2b)**: (known compound, see: Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). White solid; m.p. 67-69 $^{o}$C; isolated yield 90%, 99% ee, $[\alpha]_D^{20}$ = +36.0 (*c* 1.0, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -30.1 (c 0.105, $CH_2Cl_2$), 89% ee, (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.60-6.49 (m, 4H), 3.61 (bs, 2H), 3.40-3.36 (m, 1H), 3.33-3.26 (m, 1H), 3.10-3.04 (m, 1H), 1.58-1.48 (m, *J* = 7.3 Hz, 2H), 1.04-0.99 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 133.6, 133.5, 118.8, 118.7, 114.5, 114.5, 51.8, 46.4, 27.2, 10.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 9.9 min (major), (*S*) $t_2$ =12.5 min (minor).

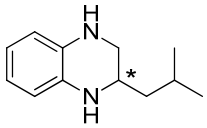


**(*R*)-2-propyl-1,2,3,4-tetrahydroquinoxaline (2c)**: (known compound, see: Murata, S.; Sugimoto, T.; Matsuura, S. *Heterocycles* **1987**, *26*, 763). White solid; m.p. 87-88 $^{o}$C; isolated yield 98%, 98% ee, $[\alpha]_D^{20}$ = +43.5 (*c* 1.0, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -30.1 (c 0.105, $CH_2Cl_2$) (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.61-6.49 (m, 4H), 3.62 (b, 2H), 3.38-3.34 (m, 2H), 3.10-3.04 (m, 1H), 1.51-1.41 (m, 4H), 1.01-0.97 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$):

δ (ppm) 133.6, 133.5, 118.6, 118.5, 114.5, 114.4, 50.0, 46.7, 36.5, 18.9, 14.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 9.0 min (major), (*S*) $t_2$ =11.7 min (minor).

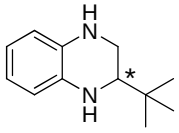


**(*R*)-2-butyl-1,2,3,4-tetrahydroquinoxaline (2d)**: (known compound, see: Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). White solid; 58-59 m.p. $^{o}$C; isolated yield 92%, 99% ee, $[\alpha]_D^{20}$ = +32.0 (*c* 0.5, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -30.4 (c 0.150, $CH_2Cl_2$), 93% ee, (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.61-6.49 (m, 4H), 3.64 (b, 2H), 3.38-3.35 (m, 2H), 3.10-3.04 (m, 1H), 1.50-1.37 (m, 6H), 0.97-0.92 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 133.6, 133.5, 118.8, 118.7, 114.6, 114.5, 50.4, 46.8, 34.1, 27.9, 22.9, 14.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 60 / 40, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 6.1 min (major), (*S*) $t_2$ =7.7 min (minor).

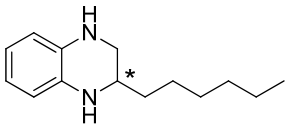


**(*R*)-2-isobutyl-1,2,3,4-tetrahydroquinoxaline (2e)**: (known compound, see: Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). White solid; m.p. 69-70 $^{o}$C; isolated yield 97%, 98% ee, $[\alpha]_D^{20}$ = +47.5 (*c* 1.0, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -43.5 (c 0.135, $CH_2Cl_2$), 94% ee, (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.65-6.52 (m, 4H), 3.65 (b, 2H), 3.48-3.45 (m, 1H), 3.38-3.34 (m, 1H), 3.10-3.03 (m, 1H), 1.83-1.74 (m, 1H), 1.43-1.35 (m, 2H), 1.03-0.99 (m, 6H); $^{13}$C

NMR (75 MHz, $CDCl_3$): δ (ppm) 133.5, 118.7, 118.7, 114.6, 114.5, 48.2, 47.1, 43.4, 24.5, 23.2, 22.6. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 8.4 min (major), (*S*) $t_2$ =12.1 min (minor).

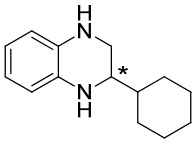


**(*R*)-2-(*tert*-butyl)-1,2,3,4-tetrahydroquinoxaline (2f)**: (known compound, see: Sakata, T.; Tanaka, D.; Takahashi, M.; Sakaguchi, T. Oka, R.; Nishiyama, T. *Tech. Rep. Kan. Univ.* **2005**, *47*, 39.). White solid; m.p. 95-96 $^oC$; isolated yield 96%, 95% ee, $[\alpha]_D^{20}$ = +26.9 (*c* 1.0, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -18.9 (c 0.090, $CH_2Cl_2$), 85% ee, (*S*)]; $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 6.67-6.51 (m, 4H), 3.64 (b, 2H), 3.41-3.33 (m, 1H), 3.20-3.13 (m, 2H), 1.03 (s, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ (ppm) 134.6, 133.5, 118.9, 118.3, 114.4, 114.3, 59.1, 42.6, 32.8, 26.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 6.8 min (major), (*S*) $t_2$ =10.0 min (minor).

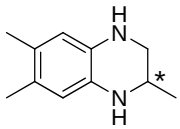


**(*R*)-2-hexyl-1,2,3,4-tetrahydroquinoxaline (2g)**: (known compound, see: Tan, J.; Tang, W.; Sun, Y.; Jiang, Z.; Chen, F.; Xu, L.; Fan, Q.; Xiao, J. *Tetrahedron* **2011**, *67*, 6206). White solid; m.p. 74-76 $^oC$; isolated yield 95%, 99% ee, $[\alpha]_D^{20}$ = +37.5 (*c* 1.0, $CH_2Cl_2$); $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 6.62-6.50 (m, 4H), 3.64 (b, 2H), 3.39-3.35 (m, 2H), 3.10-3.04 (m, 1H), 1.49-1.34 (m, 10H), 0.95-0.91 (m, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ (ppm) 133.6, 133.5, 118.8, 118.6, 114.5, 114.5, 50.4, 46.8, 34.4, 31.9, 29.5, 25.7, 22.7, 14.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL /

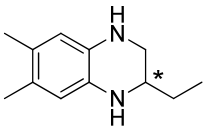
min ), (*R*) $t_1$ = 7.3 min (major), (*S*) $t_2$ =10.2 min (minor).



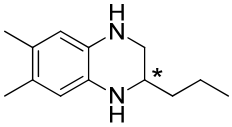
**(*R*)-2-cyclohexyl-1,2,3,4-tetrahydroquinoxaline (2h)**: (known compound, see: Tan, J.; Tang, W.; Sun, Y.; Jiang, Z.; Chen, F.; Xu, L.; Fan, Q.; Xiao, J. *Tetrahedron* **2011**, *67*, 6206). White solid; m.p. 105-106 $^{o}$C; isolated yield 95%, 97% ee, $[\alpha]_D^{20}$ = +43.7 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.61-6.49 (m, 4H), 3.67 (b, 2H), 3.39-3.36 (m, 1H), 3.22-3.13 (m, 2H), 1.92-1.71 (m, 5H), 1.47-1.04 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 133.9, 133.6, 118.8, 118.4, 114.4, 55.3, 44.1, 40.8, 29.3, 29.0, 26.6, 26.3, 26.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 8.5 min (major), (*S*) $t_2$ =10.7 min (minor).



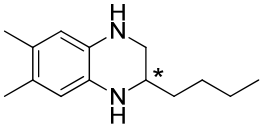
**(*R*)-2,6,7-trimethyl-1,2,3,4-tetrahydroquinoxaline (2i)**: (known compound, see: Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). White solid; m.p. 118-119 $^{o}$C; isolated yield 94%, 99% ee, $[\alpha]_D^{20}$ = +6.2 (*c* 0.5, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -26.5 (c 0.150, $CH_2Cl_2$), 87% ee, (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.36-6.35 (m, 2H), 3.45 (b, 3H), 3.32-3.28 (m, 1H), 3.04-2.98 (m, 1H), 2.13 (s, 6H), 1.21-1.18 (d, *J* = 6.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 131.5, 131.1, 126.5, 126.5, 116.4, 48.7, 46.1, 20.0, 18.9. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 7.7 min (major), (*S*) $t_2$ =10.4 min (minor).



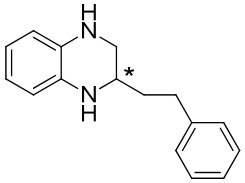
**(*R*)-2-ethyl-6,7-dimethyl-1,2,3,4-tetrahydroquinoxaline (2j)**: (known compound, see: Tang, W.; Xu, L.; Fan, Q. H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K. H.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). White solid; m.p. 122-123 $^{o}$C; isolated yield 93%, 99% ee, $[\alpha]_D^{20}$ = +22.8 (*c* 0.5, $CH_2Cl_2$), [Lit.[4] $[\alpha]_D^{20}$ = -35.5 (c 0.150, $CH_2Cl_2$), 91% ee, (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$, $D_2O$ was added): δ (ppm) 6.34 (s, 2H), 3.35-3.31 (m, 1H), 3.22 (b, 1H), 3.04-3.01 (m, 1H), 2.09 (s, 6H), 1.55-1.46 (m, 2H), 1.01-0.97 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 131.4, 131.3, 126.6, 126.3, 116.4, 52.1 46.7, 27.1, 18.9, 10.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 7.5 min, (*S*) $t_2$ =10.6 min.



**(*R*)-6,7-dimethyl-2-propyl-1,2,3,4-tetrahydroquinoxaline (2k)**: White solid; m.p. 115-116 $^{o}$C; isolated yield 95%, 99% ee, $[\alpha]_D^{20}$ = +26.9 (*c* 0.5, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$, $D_2O$ was added): δ (ppm) 6.33 (s, 2H), 3.30 (b, 2H), 3.01-2.96 (m, 1H), 2.09 (s, 6H), 1.46-1.38 (m, 4H), 0.98-0.94 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 131.5, 131.3, 126.6, 126.4, 116.5, 50.4, 47.1, 36.5, 19.0, 14.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) $t_1$ = 7.3 min (major), (*S*) $t_2$ =10.3 min (minor). HRMS-ESI exact mass calcd. for $C_{13}H_{21}N_2^+$ ($[M+H]^+$) requires m/z 205.16993, found m/z 205.16930.

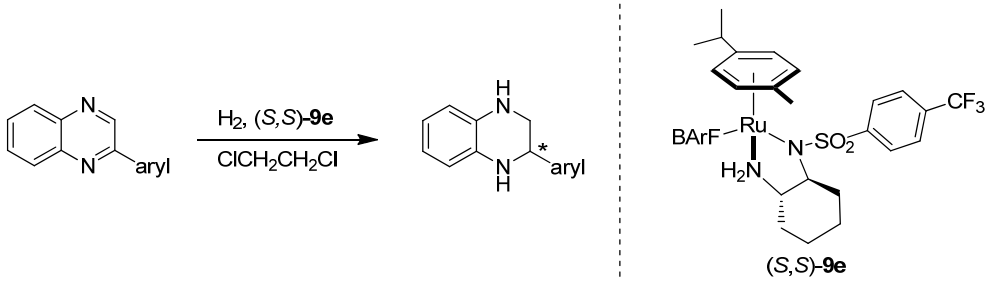


**(*R*)-2-butyl-6,7-dimethyl-1,2,3,4-tetrahydroquinoxaline (2l)**: (known compound, see: Cartigny, D.; Nagano, T.; Ayad, T.; Genêt, J.-P.; Ohshima, T.; Mashima, K.; Ratovelomanana-Vidal, V. *Adv. Synth. Catal.* **2010**, *352*, 1886). White solid; m.p. 102-103 $^{o}$C; isolated yield 92%, 98% ee, $[\alpha]_D^{20}$ = +32.8 (*c* 0.5, $CH_2Cl_2$), [Lit.[6] $[\alpha]_D^{20}$ = -38.4 (c 1.0, $CH_2Cl_2$), (*S*).]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.33 (s, 2H), 3.30 (b, 2H), 3.01 (b, 1H), 2.09 (s, 6H), 1.46-1.36 (m, 6H), 0.95-0.90 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 131.5, 131.3, 126.6, 126.3, 116.4, 50.7, 47.1, 34.0, 28.0, 22.9, 18.9, 14.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 7.0 min (major), (*S*) $t_2$ =10.5 min (minor).

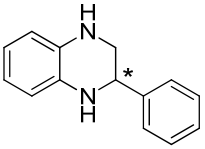


**(*R*)-2-phenethyl-1,2,3,4-tetrahydroquinoxaline (2m)**: (known compound, see: Cartigny, D.; Nagano, T.; Ayad, T.; Genêt, J.-P.; Ohshima, T.; Mashima, K.; Ratovelomanana-Vidal, V. *Adv. Synth. Catal.* **2010**, *352*, 1886). White solid; m.p. 68-69 $^{o}$C; isolated yield 90%, 98% ee, $[\alpha]_D^{20}$ = +49.8 (*c* 1.0, $CH_2Cl_2$), [Lit.[6] $[\alpha]_D^{20}$ = -46.3 (c 1.0, $CH_2Cl_2$), 91% ee, (*S*).]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.32-7.20 (m, 5H), 6.60-6.45 (m, 4H), 3.62 (b, 2H), 3.44-3.36 (m, 2H), 3.15-3.08 (m, 1H), 2.80-2.72 (m, 2H), 1.87-1.80 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 141.6, 133.4, 133.4, 128.6, 128.4, 126.1, 118.8, 118.7, 114.6, 114.5, 49.9, 46.5, 35.9, 32.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 15.4 min (major), (*S*) $t_2$ =20.7 min (minor).

**(2) Typical procedure for asymmetric hydrogenation of 2-aryl substituted quinoxalines:**

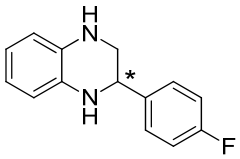



A 50 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ru-catalyst (*S*,*S*)-**9e** (0.002 mmol) and the corresponding quinoxaline (0.2 mmol) in DCE (1 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 80 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at room temperature for 16 h. Then the hydrogen gas was carefully released and the conversion was determined by $^1$H NMR spectroscopy after the solvent was evaporated under reduced pressure. The reaction mixture was filtered through a short pad of silica gel eluted with DCM to give the pure products. The enantiomeric excess of the product was determined by HPLC with a chiral OD-H column.

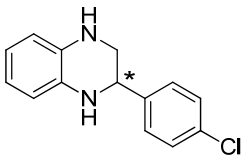


**(*S*)-2-phenyl-1,2,3,4-tetrahydroquinoxaline (4a)**: (known compound, see: Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). Yellow solid; m.p. 121-123 $^o$C; isolated yield 90%, 94% ee, $[\alpha]_D^{20}$ = +96.3 (*c* 1.0, $CHCl_3$), [Lit.[7] $[\alpha]_D^{20}$ = -98.6 (c 1.0, $CHCl_3$), 90% ee, (*R*).]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42-7.33 (m, 5H), 6.70-6.59 (m, 4H), 4.51-4.48 (dd, *J* = 3.1, 8.1

Hz, 1H), 3.74 (b, 2H), 3.50-3.45 (m, 1H), 3.38-3.31 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.0, 134.2, 132.9, 128.7, 128.0, 127.1, 119.0, 118.9, 114.8, 114.6, 54.8, 49.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 14.3 min (minor), (*S*) $t_2$ = 18.6 min (major).

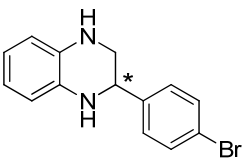


**(*S*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoxaline (4b)**: (known compound, see: Chen, Q.-A.; Wang, D.-S.; Zhou, Y.-G.; Duan, Y.; Fan, H.-J.; Yang, Y.; Zhang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 6126). Yellow solid; m.p. 103-104 $^{o}$C; isolated yield 92%, 94% ee, $[\alpha]_D^{20}$ = +92.5 (*c* 1.0, $CHCl_3$), [Lit.[7] $[\alpha]_D^{20}$ = -91.3 (c 0.9, $CHCl_3$), 89% ee, (*R*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39-7.34 (m, 2H), 7.09-7.03 (m, 2H), 6.72-6.58 (m, 4H), 4.52-4.48 (dd, *J* = 2.4, 8.1 Hz, 1H), 4.06 (b, 2H), 3.48-3.43 (m, 1H), 3.32-3.26 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 137.4, 137.4, 134.3, 131.7, 128.8, 128.7, 119.9, 119.1, 115.8, 115.5, 114.8, 54.0, 49.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 17.4 min (minor), (*S*) $t_2$ = 16.7 min (major).

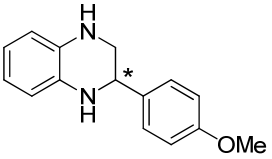


**(*S*)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroquinoxaline (4c)**: (known compound, see: Chen, Q.-A.; Wang, D.-S.; Zhou, Y.-G.; Duan, Y.; Fan, H.-J.; Yang, Y.; Zhang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 6126). Yellow solid; m.p. 104-105 $^{o}$C; isolated yield 94%, 96% ee, $[\alpha]_D^{20}$ = +93.8 (*c* 1.0, $CHCl_3$), [Lit.[7] $[\alpha]_D^{20}$ = -92.7 (c 0.96, $CHCl_3$), 87% ee, (*R*)]; $^1$H NMR

(300 MHz, $CDCl_3$): δ (ppm) 7.37-7.31 (m, 4H), 6.68-6.57 (m, 4H), 4.48-4.45 (dd, *J* = 3.0, 8.0 Hz, 1H), 3.58 (b, 2H), 3.46-3.41 (m, 1H), 3.31-3.25 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ (ppm) 140.6, 133.9, 133.7, 132.8, 128.9, 128.4, 119.1, 119.1, 114.9, 114.6, 54.2, 49.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 19.6 min (minor), (*S*) $t_2$ = 32.0 min (major).

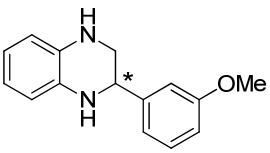


**(*S*)-2-(4-bromophenyl)-1,2,3,4-tetrahydroquinoxaline (4d)**: (known compound, see: Chen, Q.-A.; Wang, D.-S.; Zhou, Y.-G.; Duan, Y.; Fan, H.-J.; Yang, Y.; Zhang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 6126). Yellow solid; m.p. 144-146 °C; isolated yield 95%, 95% ee, $[\alpha]_D^{20}$ = +85.6 (*c* 1.0, $CHCl_3$), [Lit.[7] $[\alpha]_D^{20}$ = -76.1 (c 1.12, $CHCl_3$), 87% ee, (*R*)]; $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42-7.37 (m, 2H), 7.19-7.14 (m, 2H), 6.59-6.47 (m, 4H), 4.35-4.31 (dd, *J* = 3.0, 7.8 Hz, 1H), 3.57 (b, 2H), 3.35-3.29 (m, 1H), 3.21-3.12 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ (ppm) 141.1, 133.8, 132.8, 131.8, 128.8, 121.7, 119.1, 119.1, 114.9, 114.6, 54.2, 49.0. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 21.0 min (minor), (*S*) $t_2$ = 34.3 min (major).

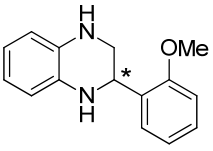


**(*S*)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline (4e)**: (known compound, see: Rueping, M.; Tato, F.; Schoepke, F. R. *Chem. Eur. J.* **2010**, *16*, 2688). Yellow solid; m.p. 63-65 °C; isolated yield 90%, 94% ee, $[\alpha]_D^{20}$ = +90.1 (*c* 1.0, $CHCl_3$), [Lit.[8] $[\alpha]_D^{20}$ = -83.2 (c 1.0, $CHCl_3$), 94% ee, (*R*)];

$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.34-7.31 (m, 2H), 6.95-6.92 (m, 2H), 6.68-6.56 (m, 4H), 4.45-4.42 (dd, *J* = 2.7, 7.8 Hz, 1H), 3.84 (s, 3H), 3.68 (b, 2H), 3.45-3.40 (m, 1H), 3.34-3.28 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.4, 134.3, 134.0, 132.9, 128.2, 118.9, 118.8, 114.7, 114.5, 114.1, 55.4, 54.2, 49.3. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*R*) $t_1$ = 17.5 min (minor), (*S*) $t_2$ = 23.7 min (major).



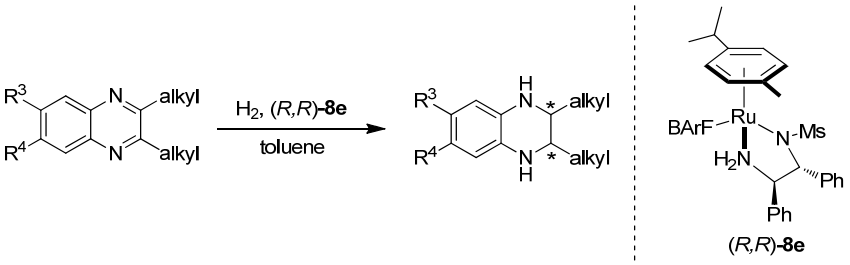

**(*S*)-2-(3-methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline (4f)**: (known compound, see: Cartigny, D.; Nagano, T.; Ayad, T.; Genêt, J.-P.; Ohshima, T.; Mashima, K.; Ratovelomanana-Vidal, V. *Adv. Synth. Catal.* **2010**, *352*, 1886). Yellow solid; m.p. 89-90 $^o$C; isolated yield 95%, 94% ee, $[\alpha]_D^{20}$ = +81.8 (*c* 1.0, $CHCl_3$), [Lit.[6] $[\alpha]_D^{20}$ = -2.8 (c 1.22, $CHCl_3$), 87% ee, (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33-7.28 (m, 1H), 7.01-6.98 (m, 2H), 6.90-6.86 (m, 1H), 6.68-6.58 (m, 4H), 4.48-4.44 (dd, *J* = 2.7, 8.1 Hz, 1H), 3.83 (s, 3H), 3.68 (b, 2H), 3.49-3.44 (m, 1H), 3.36-3.30 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 160.0, 143.6, 134.2, 132.8, 129.7, 119.4, 119.1, 118.9, 114.9, 114.6, 113.4, 112.5, 55.3, 54.7, 49.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) $t_1$ = 19.4 min (minor), (*S*) $t_2$ = 28.3 min (major).




**(*S*)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline (4g)**: (known compound, see: Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.;

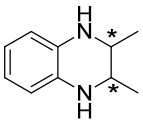
Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135). Yellow solid; m.p. 89-90 $^{o}$C; isolated yield 91%, 89% ee, $[\alpha]_D^{20}$ = +82.5 (*c* 1.0, $CHCl_3$), [Lit.[4] $[\alpha]_D^{20}$ = -18.1 (c 0.1, $CH_2Cl_2$), 84% ee, (*S*)]; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47-7.44 (m, 1H), 7.33-7.28 (m, 1H), 7.03-6.92 (m, 2H), 6.69-6.59 (m, 4H), 4.95-4.93 (m, 1H), 3.88 (s, 3H), 3.70 (b, 2H), 3.59-3.56 (m, 1H), 3.34-3.28 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.6, 134.6, 133.0, 130.2, 128.5, 127.1, 120.9, 119.0, 118.6, 115.0, 114.6, 110.3, 55.4, 47.9, 46.8. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), (*S*) $t_1$ = 14.4 min (major), (*R*) $t_2$ =17.9 min (minor).

**(3) Typical procedure for the asymmetric hydrogenation of 2,3-dialkyl substituted quinoxalines:**



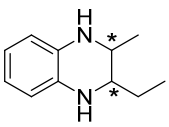

A 50 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ru-catalyst (*R*,*R*)-**8e** (0.002 mmol) and the corresponding quinoxaline (0.2 mmol) in toluene (1 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 40 $^{o}$C for 8 h. Then the hydrogen gas was carefully released and the conversion was determined by $^1$H NMR spectroscopy after the solvent was

evaporated under reduced pressure. The diastereomeric excess was determined by $^1$H NMR spectroscopy and HPLC. The *trans* isomer and *cis* isomer were separated by a silica gel column eluted with petroleum ether/ethyl acetate (10/1, V/V). The enantiomeric excess of the product was determined by HPLC with a chiral OD-H, AD-H or OB-H column.



**(+)-*trans*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (6a)**: (known compound, see: Murata, S.; Sugimoto, T.; Matsuura, S. *Heterocycles* **1987**, *26*, 763). White solid; m.p. 105-106 $^o$C; 99% ee, $[\alpha]_D^{20}$ = +65.1 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.63-6.49 (m, 4H), 3.48 (b, 2H), 3.08-2.99 (m, 2H), 1.19-1.17 (d, *J* = 5.7 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 133.6, 118.6, 114.0, 52.1, 19.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), $t_1$ = 6.5 min (mojor), $t_2$ =8.6 min (minor).

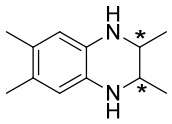
*Cis* isomer: White solid; m.p. 112-113 $^o$C; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.65-6.52 (m, 4H), 3.59 (s, 2H), 3.54-3.48 (m, 2H), 1.17-1.14 (d, *J* = 6.3 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 132.8, 118.6, 114.5, 49.1, 17.3. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), t = 9.8 min.



**(+)-*trans*-2-ethyl-3-methyl-1,2,3,4-tetrahydroquinoxaline (6b)**: Yellow oil; 99% ee, $[\alpha]_D^{20}$ = +94.9 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.59-6.49 (m, 4H), 3.45 (b, 2H), 3.18 (b, 1H), 2.89 (b, 1H), 1.78-1.64 (m, 1H), 1.53-1.38 (m, 1H), 1.21-1.19 (d, *J* = 6.3 Hz, 3H), 1.06-1.01 (t, *J* =

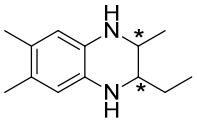
7.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 133.5, 133.2, 118.7, 118.5, 114.1, 57.3, 49.8, 25.7, 19.5, 9.6. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), $t_1$ = 6.0 min (major), $t_2$ =7.6 min (minor). HRMS-ESI exact mass calcd. for $C_{11}H_{17}N_2^+$ ($[M+H]^+$) requires m/z 177.13862, found m/z 177.13819.

*Cis* isomer: White solid; m.p. 79-80 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.58-6.49 (m, 4H), 3.54-3.52 (m, 1H), 3.25 (s, 1H), 1.48-1.44 (m, 2H), 1.14-1.12 (d, *J* = 6.6 Hz, 3H), 1.02-0.97 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 132.9, 132.6, 118.8, 118.8, 114.8, 114.5, 55.2, 48.4, 24.1, 16.7, 10.5. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), $t_1$ = 9.0 min, $t_2$ = 10.9 min.



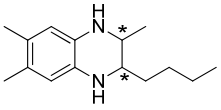
**(+)-*trans*-2,3,6,7-tetramethyl-1,2,3,4-tetrahydroquinoxaline (6c)**: White solid; m.p. 128-129 °C; 99% ee, $[\alpha]_D^{20}$ = +71.5 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.33 (s, 2H), 2.97 (b, 2H), 2.79 (b, 2H), 2.10 (b, 6H), 1.16-1.14 (d, *J* = 6.0 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 131.5, 126.3, 116.0, 52.4, 19.0. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), $t_1$ = 6.1 min (major), $t_2$ = 8.4 min (minor). HRMS-ESI exact mass calcd. for $C_{12}H_{19}N_2^+$ ($[M+H]^+$) requires m/z 191.15428, found m/z 191.15380.

*Cis* isomer: White solid; m.p. 135-136 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.35 (s, 2H), 3.46-3.45 (m, 2H), 3.29 (b, 2H), 2.12 (s, 6H), 1.14-1.12 (d, *J* = 6.6 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 130.5, 126.4, 116.4, 49.4, 19.0, 17.2.



**(+)-*trans*-2-ethyl-3,6,7-trimethyl-1,2,3,4-tetrahydroquinoxaline (6d)**: Yellow oil; 99% ee, $[\alpha]_D^{20}$ = +99.8 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.40-6.37 (d, 2H), 3.39 (b, 2H), 3.19 (b, 1H), 2.89 (b, 1H), 2.16 (s, 6H), 1.78-1.65 (m, 1H), 1.55-1.40 (m, 1H), 1.23-1.21 (d, *J* = 6.3 Hz, 3H), 1.08-1.03 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 131.1, 130.9, 126.1, 115.9, 57.4, 49.9, 25.6, 19.5, 18.9, 9.6. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), $t_1$ = 5.5 min (mojor), $t_2$ = 6.5 min (minor). HRMS-ESI exact mass calcd. for $C_{13}H_{21}N_2^+$ ($[M+H]^+$) requires m/z 205.16993, found m/z 205.16940.

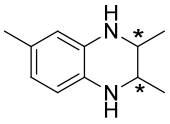
*Cis* isomer: yellow oil; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.34-6.33 (d, 2H), 3.48 (b, 3H), 3.20 (b, 1H), 2.11 (s, 6H), 1.50-1.40 (m, 2H), 1.13-1.11 (d, *J* = 6.6 Hz, 3H), 1.01-0.96 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 130.7, 126.4, 116.5, 116.3, 55.6, 48.6, 24.0, 19.0, 16.7, 10.5. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), $t_1$ = 6.7 min, $t_2$ = 8.4 min.



**(+)-*trans*-2-butyl-3,6,7-trimethyl-1,2,3,4-tetrahydroquinoxaline (6e)**: Yellow oil; 99% ee, $[\alpha]_D^{20}$ = +87.6 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.39-6.37 (d, 2H), 3.41 (b, 2H), 3.16 (b, 1H), 2.93 (b, 1H), 2.16 (s, 6H), 1.67-1.64 (m, 1H), 1.60-1.33 (m, 5H), 1.22-1.20 (d, *J* = 6.0 Hz, 3H), 1.02-0.97 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 130.9, 126.1, 116.0, 56.2, 50.3, 32.7, 27.6, 22.9, 19.5, 18.9, 14.1. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), $t_1$ = 4.8 min (major), $t_2$ =

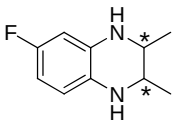
5.7 min (minor). HRMS-ESI exact mass calcd. for $C_{15}H_{25}N_2^+$ ($[M+H]^+$) requires m/z 233.20123, found m/z 233.20075.

*Cis* isomer: yellow oil; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.34-6.33 (d, 2H), 3.47-3.45 (m, 1H), 3.28 (b, 3H), 2.11 (s, 6H), 1.44-1.29 (m, 6H), 1.13-1.11 (d, $J$ = 6.3 Hz, 3H), 0.96-0.91 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 130.7, 130.6, 126.4, 126.4, 116.6, 116.3, 53.9, 48.9, 30.9, 28.4, 22.9, 19.0, 16.8, 14.2. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min ), $t_1$ = 6.5 min, $t_2$ = 8.1 min.



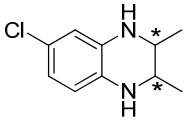
**(+)-*trans*-2,3,6-trimethyl-1,2,3,4-tetrahydroquinoxaline (6f)**: White solid; m.p. 72-73 °C; 99% ee, $[\alpha]_D^{20}$ = +75.1 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.48-6.42 (m, 2H), 6.37, (s 1H), 3.41(b, 2H), 3.03 (b, 2H), 2.23 (s, 3H), 1.20-1.18 (d, $J$ = 5.7 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 133.6, 131.0, 128.1, 118.9, 114.7, 114.2, 52.2, 52.1, 20.7, 19.1, 19.0. HPLC (AD-H, elute: Hexane / *i*-PrOH = 95 / 5, detector: 254 nm, flow rate: 1 mL / min), $t_1$ = 10.7 min (major), $t_2$ =11.8 min (minor). HRMS-ESI exact mass calcd. for $C_{11}H_{17}N_2^+$ ($[M+H]^+$) requires m/z 177.13862, found m/z 177.13823.

*Cis* isomer: White solid; m.p. 125-126 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.45-6.39 (m, 2H), 6.34, (s 1H), 3.52-3.43 (m, 4H), 2.20 (s, 3H), 1.14-1.12 (d, $J$ = 6.3 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 132.8, 130.2, 128.2, 119.0, 115.2, 114.8, 49.3, 49.2, 20.8, 17.3. HPLC (AD-H, elute: Hexane / *i*-PrOH = 95 / 5, detector: 254 nm, flow rate: 1 mL / min), $t_1$ = 13.4 min, $t_2$ = 13.7 min.



**(+)-*trans*-6-fluoro-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (6g)**: White solid; m.p. 151-152 $^{o}$C; 99% ee, $[\alpha]_D^{20}$ = +90.3 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.42-6.38 (m, 1H), 6.29-6.20, (m, 2H), 3.44 (b, 2H), 3.06-2.91 (m, 2H), 1.17-1.14 (dd, *J* = 2.1 Hz, 6.0 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.5, 155.4, 134.8, 134.7, 129.3, 114.4, 114.3, 103.9, 103.6, 100.8, 100.4, 52.2, 51.9, 19.0, 18.9. HPLC (AD-H, elute: Hexane / *i*-PrOH = 95 / 5, detector: 254 nm, flow rate: 1 mL / min), $t_1$ = 13.2 min (major), $t_2$ =13.9 min (minor). HRMS-ESI exact mass calcd. for $C_{10}H_{14}FN_2^+$ ($[M+H]^+$) requires m/z 181.11355, found m/z 181.11323.

*Cis* isomer: White solid; m.p. 172-173 $^{o}$C; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.42-6.37 (m, 1H), 6.29-6.19 (m, 2H), 3.51-3.39 (m, 4H), 1.12-1.10 (d, *J* = 6.3 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.6, 155.5, 134.0, 133.9, 128.4, 115.0, 114.8, 104.0, 103.7, 101.2, 100.9, 49.2, 49.0, 17.2, 17.2. HPLC (AD-H, elute: Hexane / *i*-PrOH = 95 / 5, detector: 254 nm, flow rate: 1 mL / min), $t_1$ = 15.9 min, $t_2$ = 18.4 min.



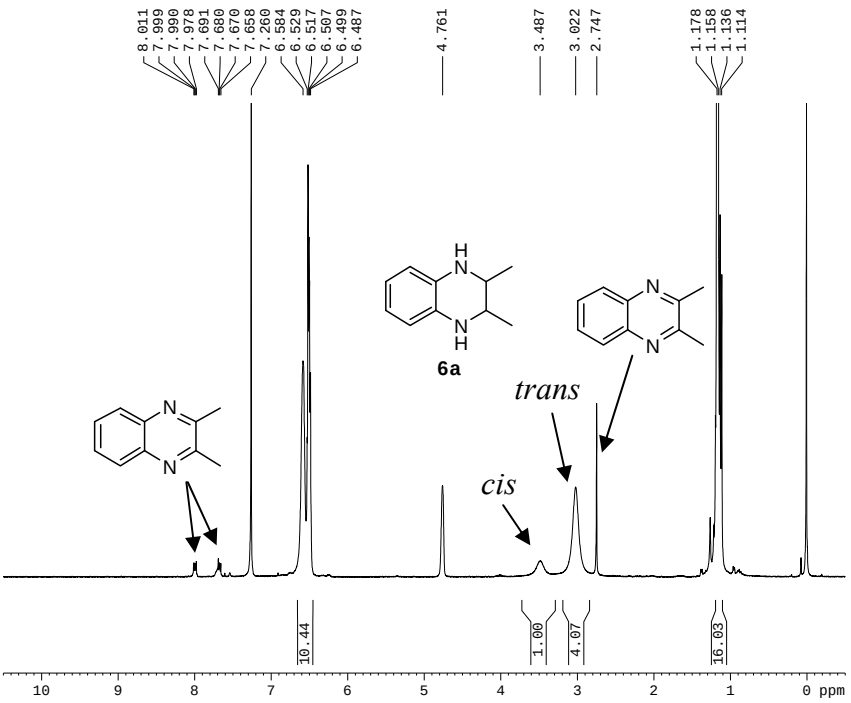
**(+)-*trans*-6-chloro-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (6h)**: White solid; m.p. 113-114 $^{o}$C; 99% ee, $[\alpha]_D^{20}$ = +84.6 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.53-6.50 (m, 1H), 6.45-6.44, (m, 1H), 6.39-6.37, (m, 1H), 3.49 (b, 2H), 3.01-2.95 (m, 2H), 1.16-1.14 (d, *J* = 4.5 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 134.6, 132.0, 122.9, 117.7, 114.5, 113.2, 51.9,

51.8, 19.0, 19.0. HPLC (OB-H, elute: Hexane / *i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), $t_1$ = 19.8 min (major), $t_2$ =24.8 min (minor). HRMS-ESI exact mass calcd. for $C_{10}H_{14}ClN_2^+$ ($[M+H]^+$) requires m/z 197.08400, found m/z 197.08343.

*Cis* isomer: White solid; m.p. 172-173 $^oC$; $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 6.53-6.49 (m, 1H), 6.45-6.44 (m, 1H), 6.39-6.36 (m, 1H), 3.47-3.45 (m, 4H), 1.12-1.10 (d, *J* = 6.3 Hz, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ (ppm) 133.9, 131.2, 123.1, 117.9, 115.0, 113.8, 49.0, 49.0, 17.3, 17.2.

## 5. Determination of the *trans*/*cis* ratio of dialkyl-substituted products

According to the published method,[9] the *trans*/*cis* ratio of dialkyl-substituted product was determined by $^1H$ NMR of the crude reaction mixture. For example, after hydrogenation of **5a**, the solvent was evaporated under reduced pressure, and the metal catalyst was removed by a short silica gel column eluted with DCM. Then, the diastereomeric excess (*trans*/*cis* ratio) was determined by $^1H$ NMR spectroscopy according to the corresponding signals from the C-2 and C-3 protons (*cis*, 3.49 ppm, and *trans*, 3.02 ppm).[9a] The *trans* (racemic) and *cis* (meso) configurations were further confirmed by HPLC with a chiral OD-H column.

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PROCNO                1

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PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   13
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                  256
DW               55.600 usec
DE                8.00 usec
TE                297.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
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SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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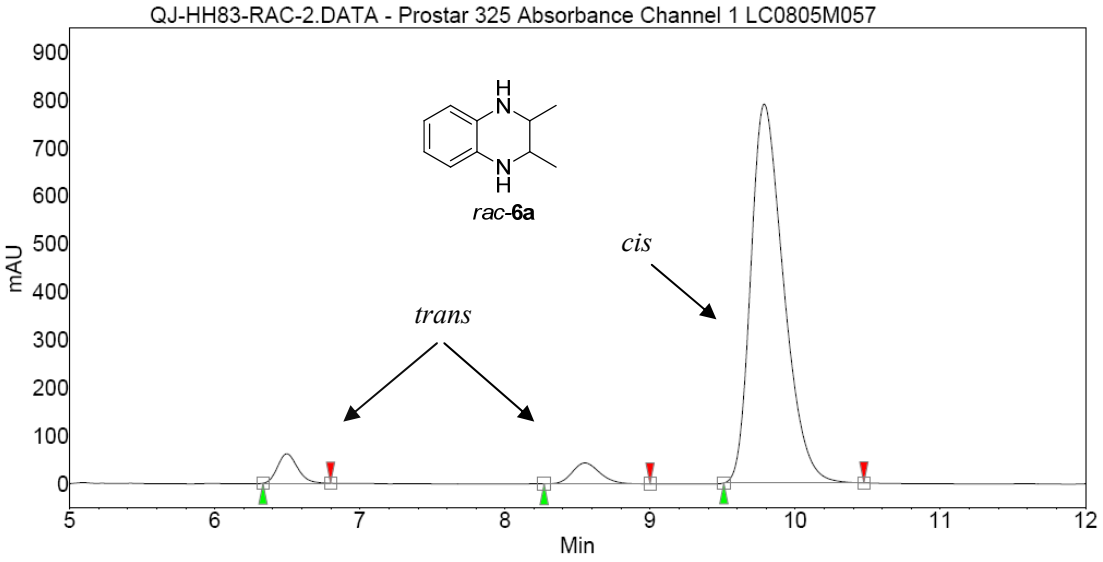
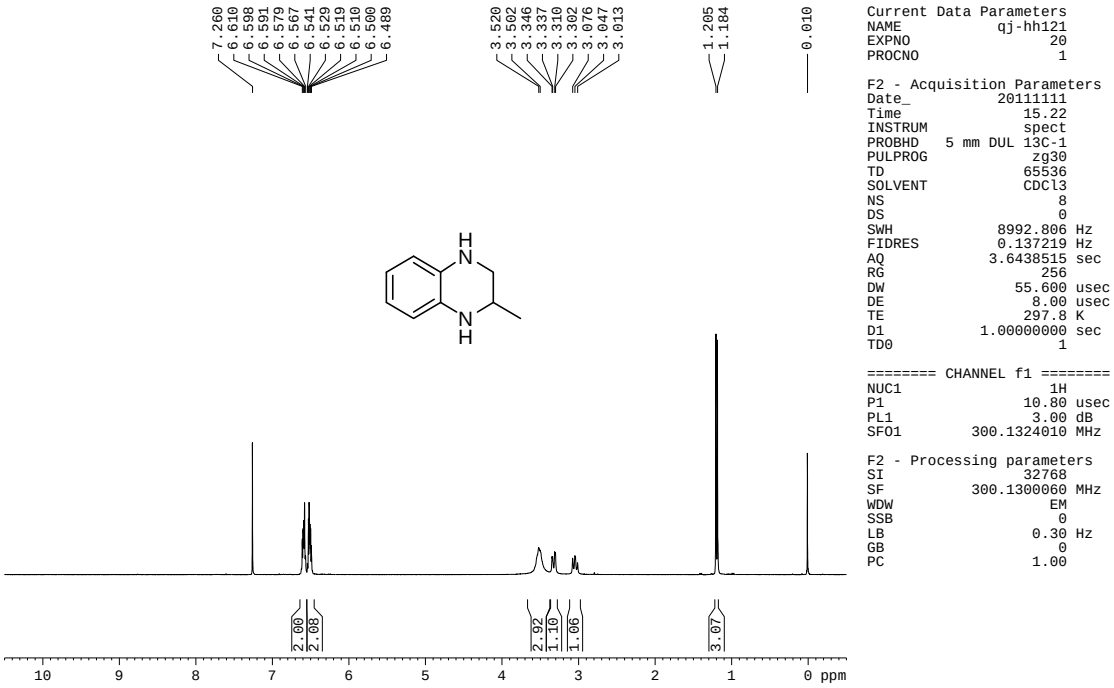
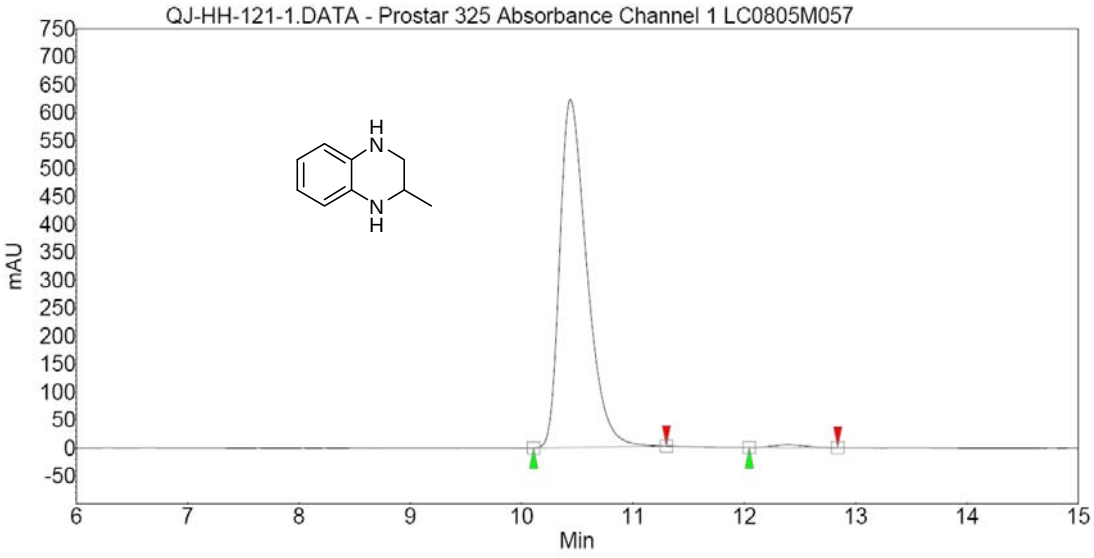



| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 6.49 | 4.31 | 61.3 | 9.7 | 4.311 |
| 1 | 未知 | 8.55 | 4.25 | 43.6 | 9.6 | 4.252 |
| 3 | 未知 | 9.79 | 91.44 | 789.6 | 206.6 | 91.437 |
| | | | | | | |
| Total | | | 100.00 | 894.5 | 226.0 | 100.000 |

## 6. Asymmetric hydrogenation of 2-methylquinoxaline on gram scale

A 50 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with 0.1 mol % Ru-catalyst (*R*,*R*)-**8e** (20 mg, 0.014 mmol) and 2-methylquinoxaline **1a** (2.0 g, 14 mmol) in DCE (14 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 40 $^{o}$C for 24 h. Then the hydrogen gas was carefully released and the conversion was determined by $^{1}$H NMR spectroscopy after the solvent was evaporated under reduced pressure. The crude pruduct was purified by a silica gel column eluted with DCM to give 1.9 g pure product in 95% yield with 98% ee.






| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 10.44 | 99.12 | 623.3 | 175.5 | 99.125 |
| 1 | 未知 | 12.39 | 0.88 | 5.0 | 1.5 | 0.875 |
| | | | | | | |
| Total | | | 100.00 | 628.3 | 177.0 | 100.000 |

## 7. References


1) (a) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem. Int. Ed.* **1997**, *36*, 285. (b) Chen, F.; Wang, T.; He, Y.; Ding, Z.; Li, Z.; Xu, L.; Fan, Q.-H. *Chem.-Eur. J.* **2011**, *17*, 1109. (c) Chen, F.; Ding, Z., Qin, J.; Wang, T.; He, Y.; Fan, Q.-H. *Org. Lett.*, **2011**, *13*, 4348.
2) Jones, Z.; Groneberg, R.; Drew, M.; Eary, C. T. U.S. Patent 20050282812, **2005**.
3) Darabi, H. R.; Tahoori, F.; Aghapoor, K.; Taala F.; Mohsenzadeh, F. *J. Braz. Chem. Soc.*, **2008**, *19*, 1646.
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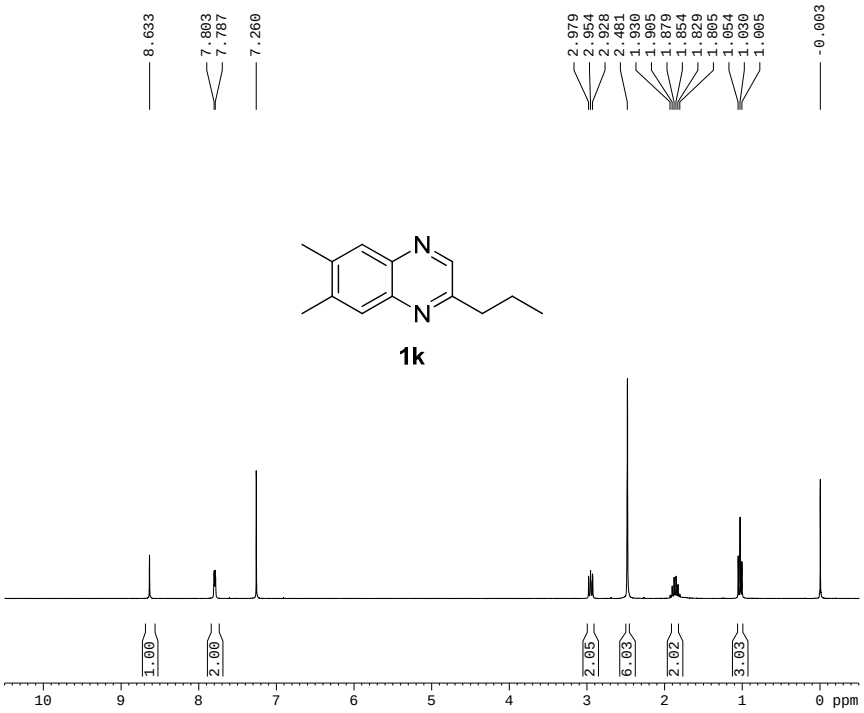
5) Ding, C.-J.; Wang, Y.; Zhang W.-W.; Liu, L.; Liang, Y.-J.; Dong, D.-W. *Chem. Res. Chinese Universities* **2009**, *25*, l74.
6) Cartigny, D.; Nagano, T.; Ayad, T.; Genêt, J.-P.; Ohshima, T.; Mashima, K.; Ratovelomanana-Vidal, V. *Adv. Synth. Catal.* **2010**, *352*, 1886.
7) Chen, Q.-A.; Wang, D.-S.; Zhou, Y.-G.; Duan, Y.; Fan, H.-J.; Yang, Y.; Zhang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 6126.
8) Rueping, M.; Tato, F.; Schoepke, F. R. *Chem.-Eur. J.* **2010**, *16*, 2688.
9) (a) Gibson, C. S. *J. Chem. Soc.* **1927**, 342. (b) Archer, R. A.; Mosher, H. S. *J. Org. Chem.*, **1967**, *32*, 1378.

# 8. Copy of NMR and HRMS spectra for new substrates and products

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EXPNO                       40
PROCNO                       1

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Date_                 20111012
Time                     16.34
INSTRUM                  spect
PROBHD   5 mm DUL 13C-1
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         11
DS                          0
SWH                  8992.806 Hz
FIDRES               0.137219 Hz
AQ                   3.6438515 sec
RG                       456.1
DW                      55.600 usec
DE                       8.00 usec
TE                      300.2 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       10.80 usec
PL1                       3.00 dB
SFO1               300.1324010 MHz

F2 - Processing parameters
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WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
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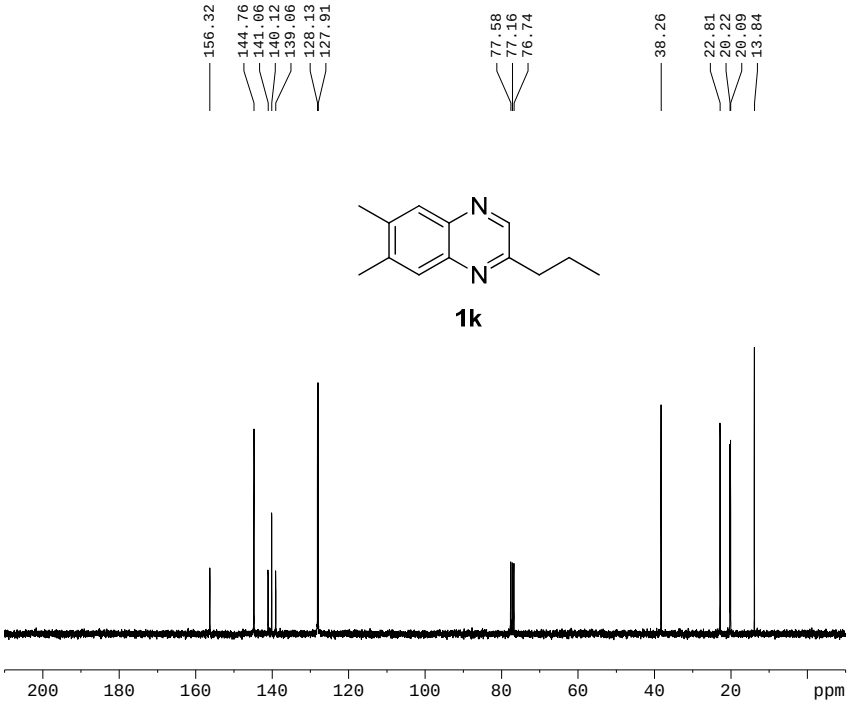


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EXPNO                       20
PROCNO                       1

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TD                      65536
SOLVENT                 CDCl3
NS                         66
DS                          4
SWH                 17985.611 Hz
FIDRES               0.274439 Hz
AQ                   1.8219508 sec
RG                       812.7
DW                      27.800 usec
DE                       6.50 usec
TE                      300.1 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

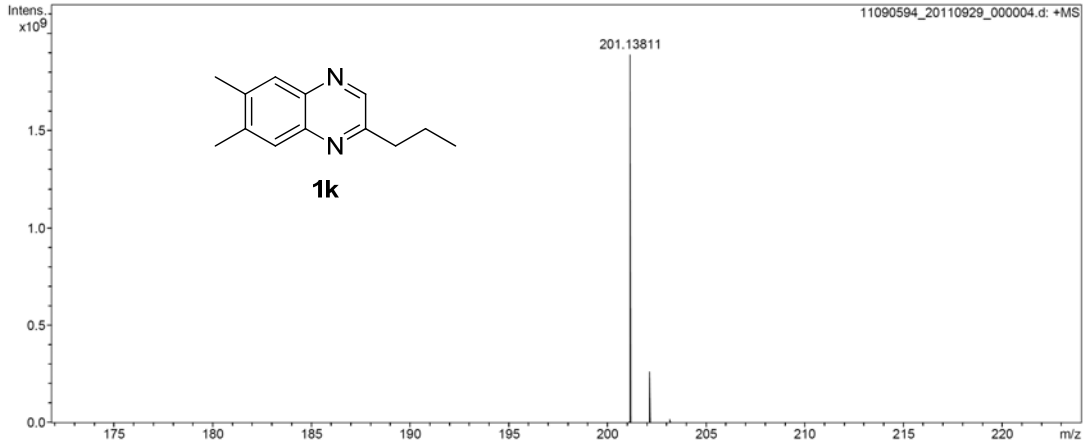
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                   100.00 usec
PL2                       3.00 dB
PL12                     22.33 dB
PL13                     23.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                       32768
```

# Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000004.d | Acquisition Date | 9/29/2011 1:41:00 PM |
| Sample | QJ-1 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |






**1k**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
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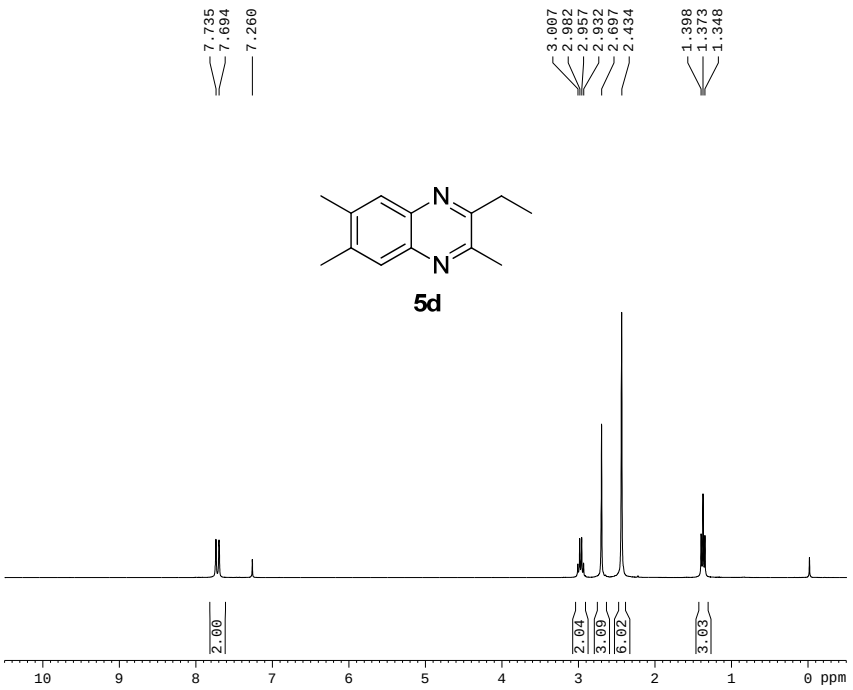


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EXPNO                10
PROCNO                1

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Date_          20110802
Time              10.44
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    6
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ            3.6438515 sec
RG                  128
DW               55.600 usec
DE                8.00 usec
TE               300.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300061 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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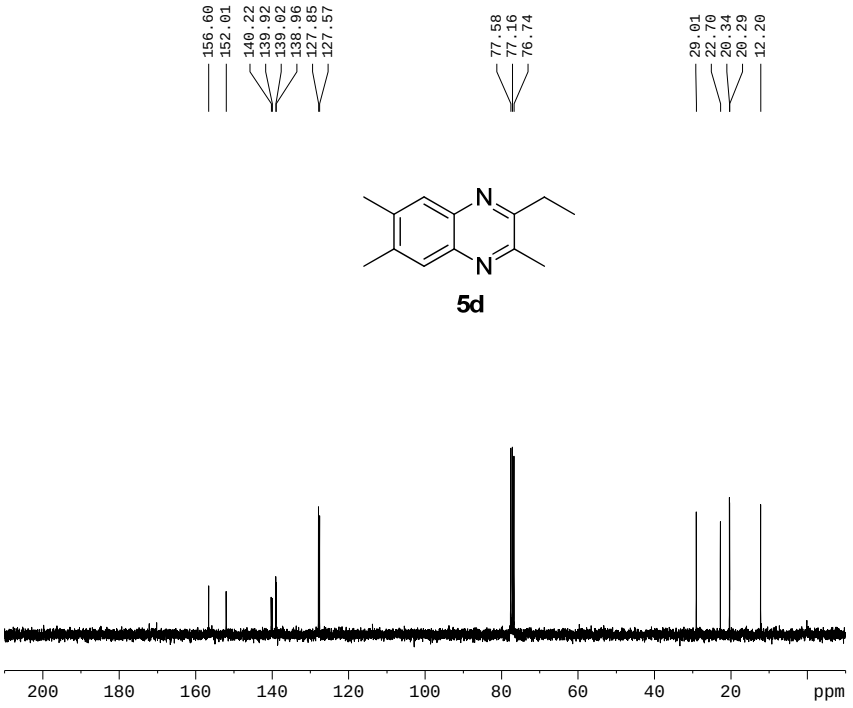


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PROCNO                1

F2 - Acquisition Parameters
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   57
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               300.5 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

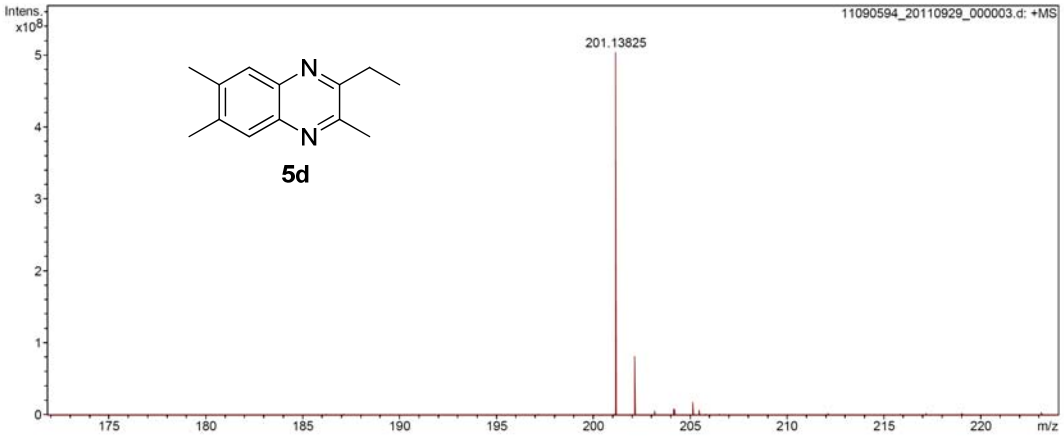
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

## Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000003.d | Acquisition Date | 9/29/2011 1:39:28 PM |
| Sample | QJ-2 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |




**5d**

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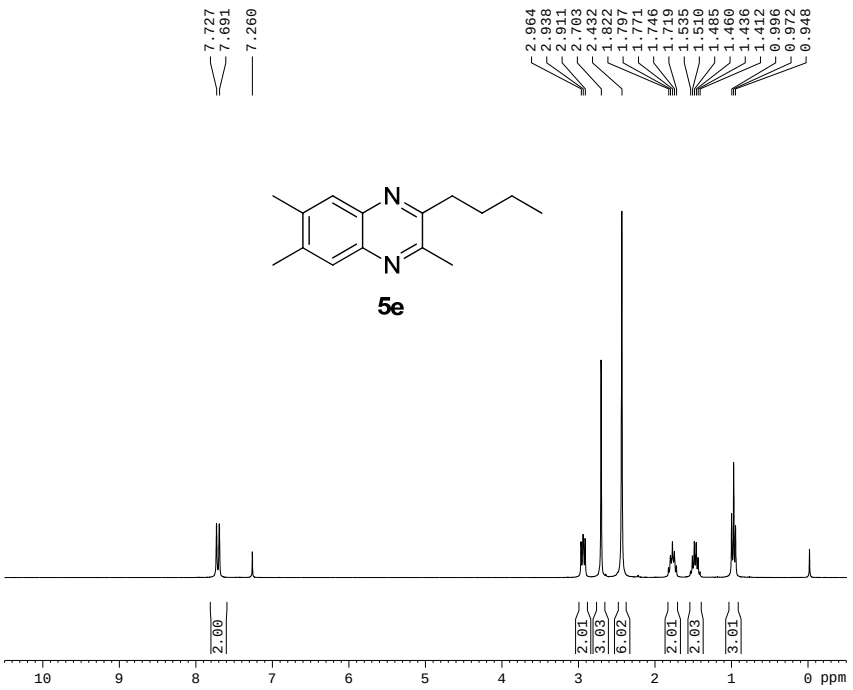


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PROCNO                1

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PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    6
DS                    0
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FIDRES         0.137219 Hz
AQ            3.6438515 sec
RG                  128
DW               55.600 usec
DE                8.00 usec
TE               300.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300061 MHz
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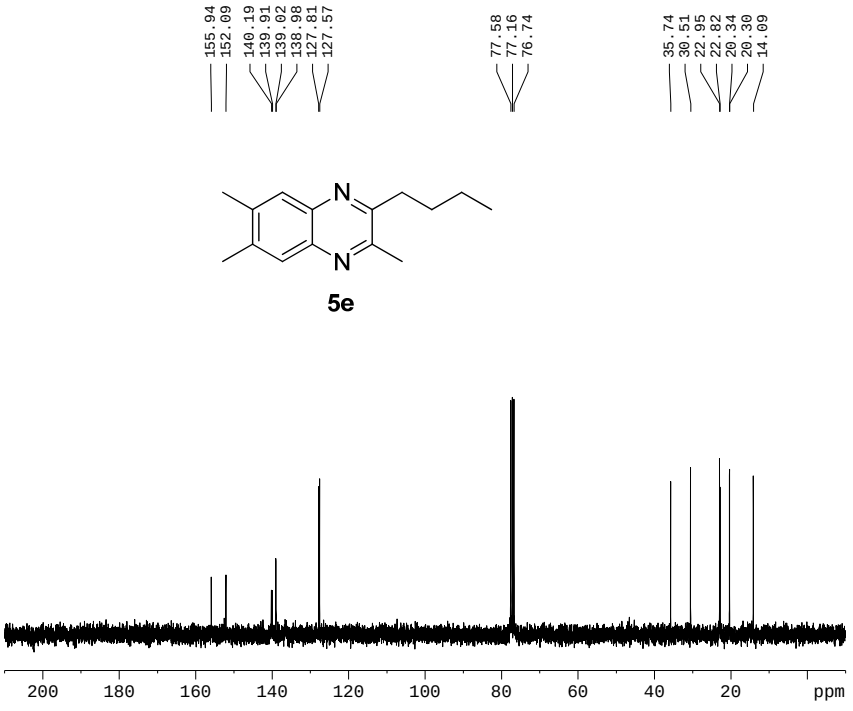


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PROCNO                1

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NS                   31
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FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                574.7
DW               27.800 usec
DE                6.50 usec
TE               300.4 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              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
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# Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

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|---|---|---|---|
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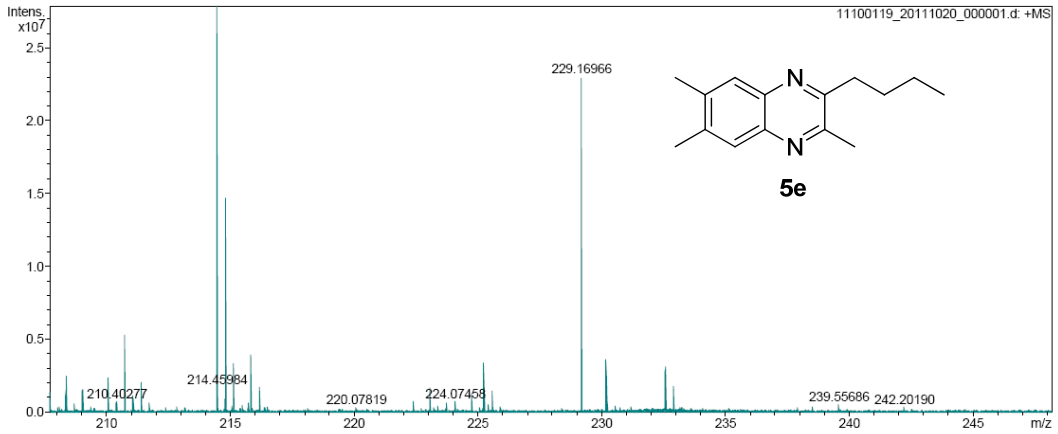
| Sample | QJ-12 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |




**5e**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
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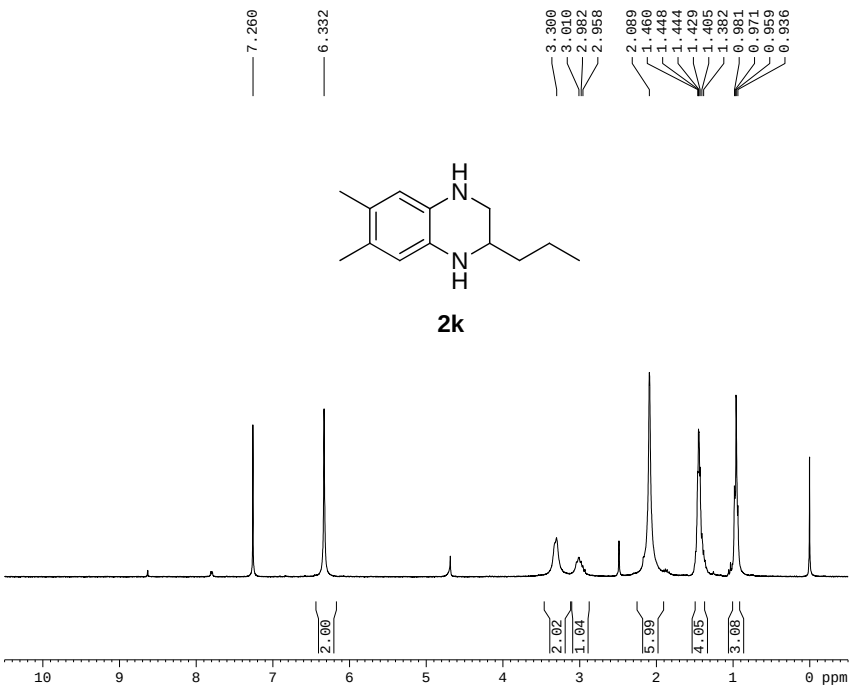


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PROCNO                1

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NS                    13
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FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   512
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DE                 8.00 usec
TE                300.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
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P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
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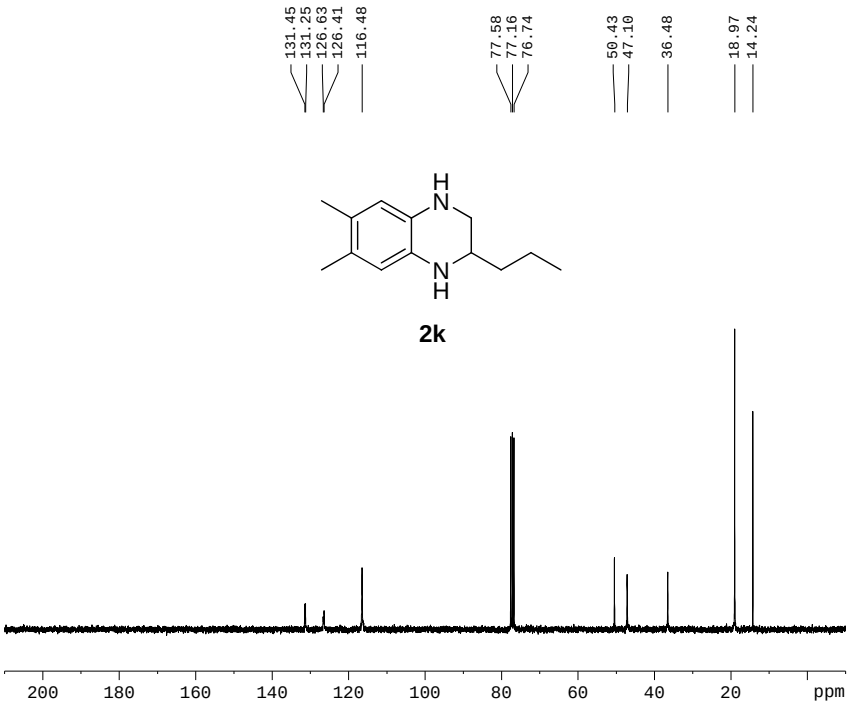


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PROCNO                1

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TD                 65536
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SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                1290.2
DW                27.800 usec
DE                 6.50 usec
TE                301.2 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

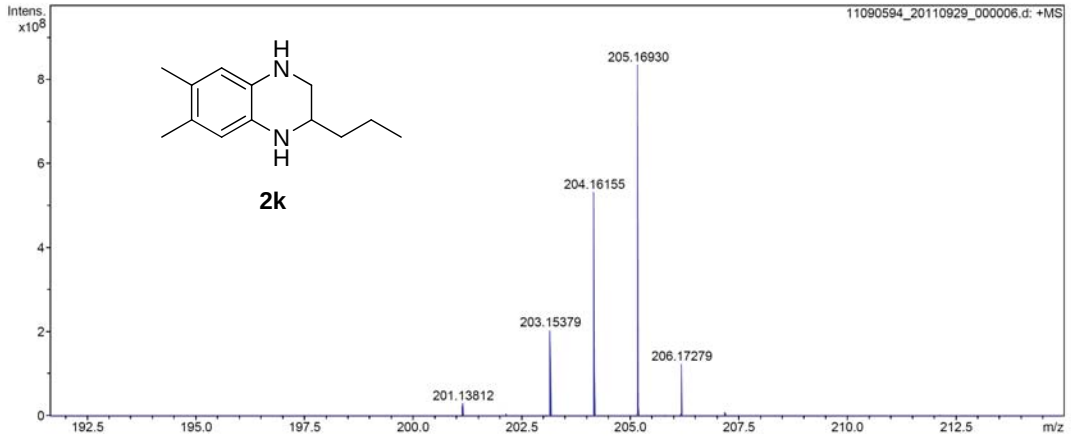
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

# Peking University Mass Spectrometry Sample Analysis Report

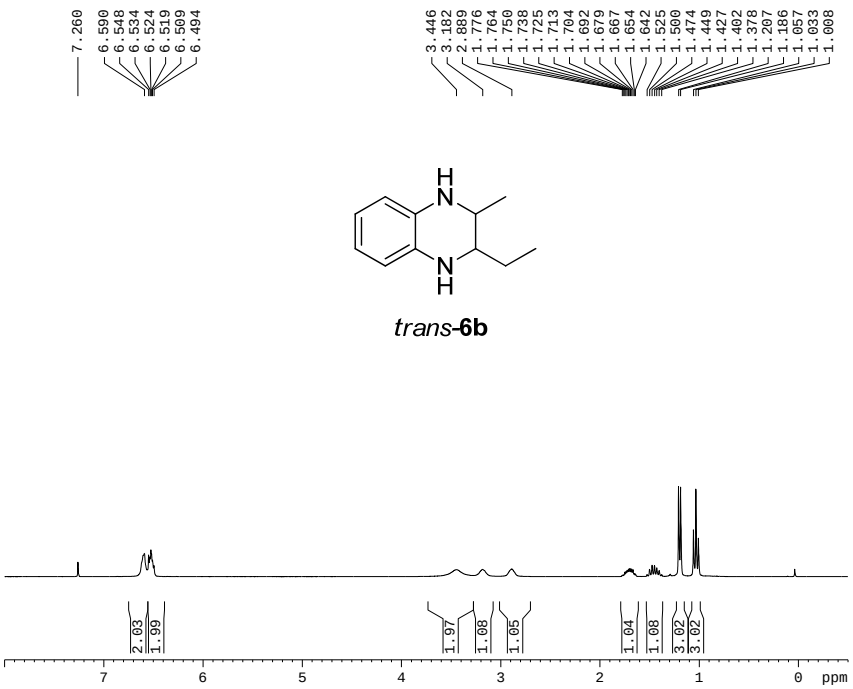
**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000006.d | Acquisition Date | 9/29/2011 1:43:24 PM |
| Sample | QJ-4 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |




**2k**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 203.15379 | 1 | C 13 H 19 N 2 | 100.00 | 203.15428 | 0.5 | 2.4 | 85.6 | 5.5 | even | ok |
| 204.16155 | 1 | C 13 H 20 N 2 | 100.00 | 204.16210 | 0.5 | 2.7 | 85.6 | 5.0 | odd | ok |
| 205.16930 | 1 | C 13 H 21 N 2 | 100.00 | 205.16993 | 0.6 | 3.0 | 0.1 | 4.5 | even | ok |



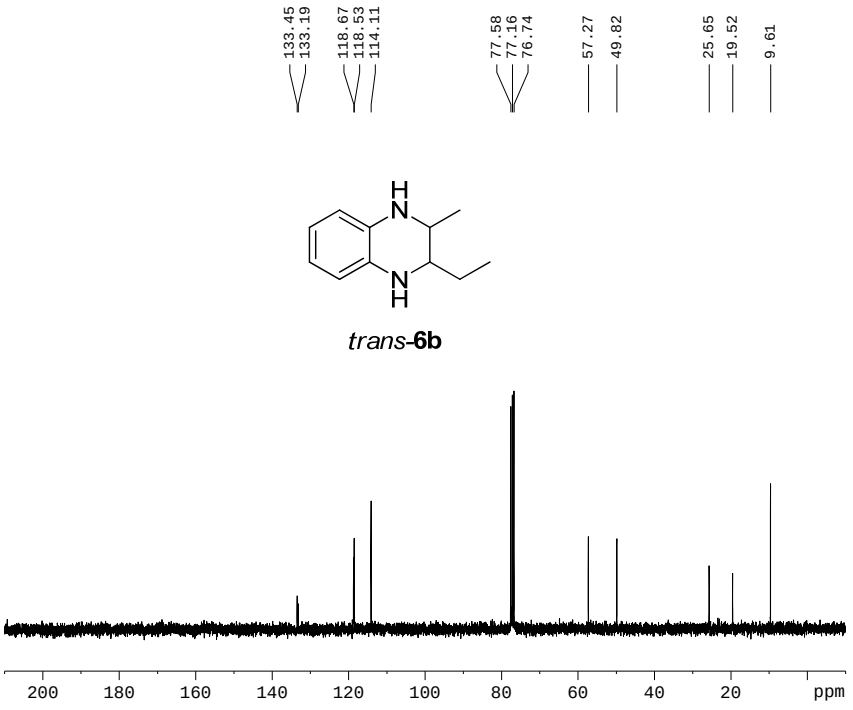

*trans*-**6b**

```
Current Data Parameters
NAME         qj-hh115-1
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20110913
Time              19.55
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                298.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300063 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




*trans*-**6b**

```
Current Data Parameters
NAME         qj-hh115-1
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_          20110913
Time              19.23
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgig30
TD                 32768
SOLVENT            CDCl3
NS                   115
DS                     0
SWH            18832.393 Hz
FIDRES          0.574719 Hz
AQ              0.8700404 sec
RG                9195.2
DW                26.550 usec
DE                 8.00 usec
TE                299.0 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

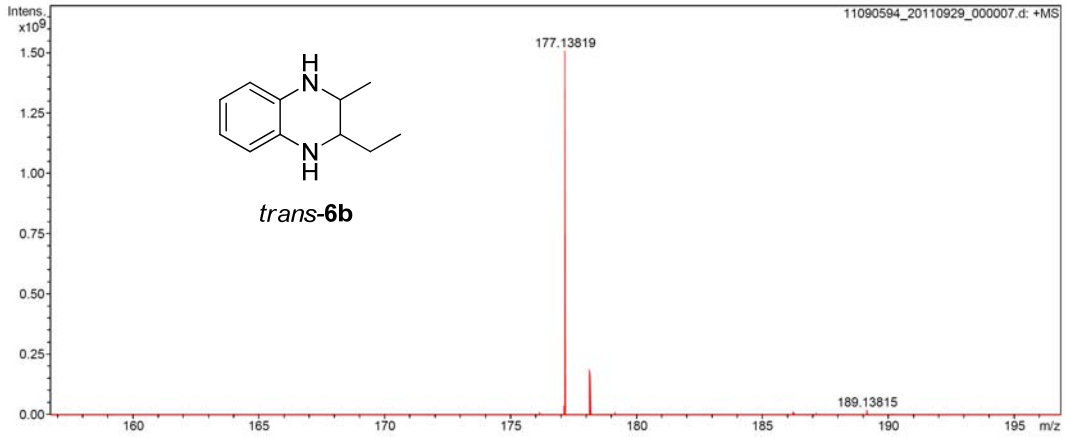
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677409 MHz
```

## Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

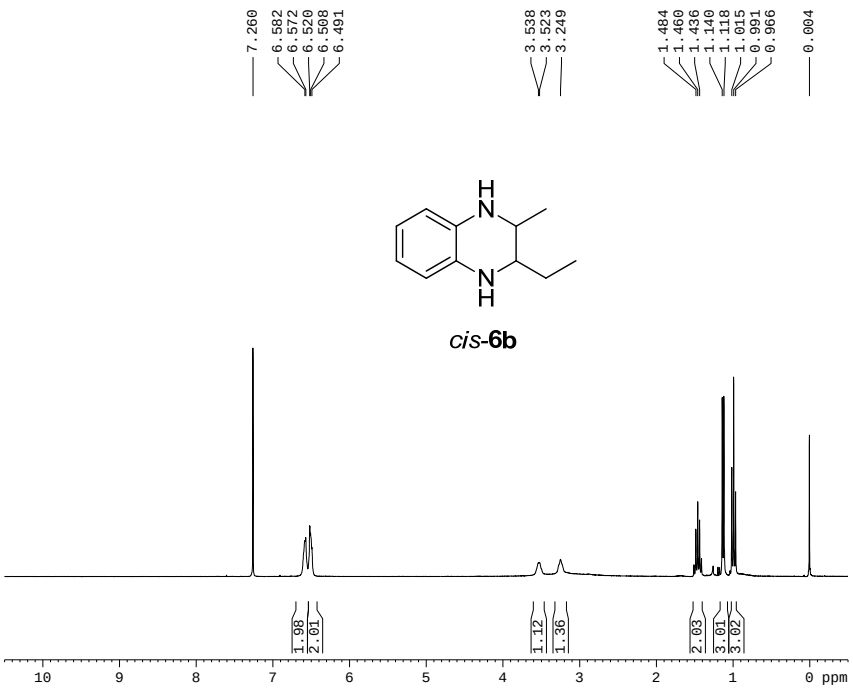
| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000007.d | Acquisition Date | 9/29/2011 1:45:11 PM |
| Sample | QJ-5 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |






*trans*-**6b**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 177.13819 | 1 | C 11 H 17 N 2 | 100.00 | 177.13862 | 0.4 | 2.5 | 1.0 | 4.5 | even | ok |



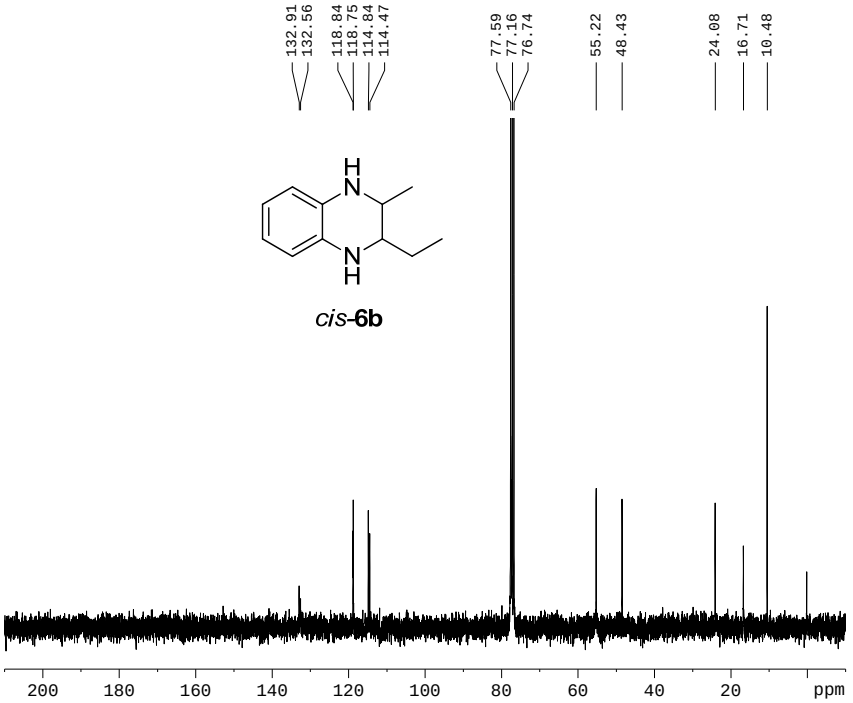

*cis*-**6b**

```
Current Data Parameters
NAME          qj-hh115-1
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110913
Time               19.40
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     9
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                   362
DW                55.600 usec
DE                 8.00 usec
TE                298.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300063 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




*cis*-**6b**

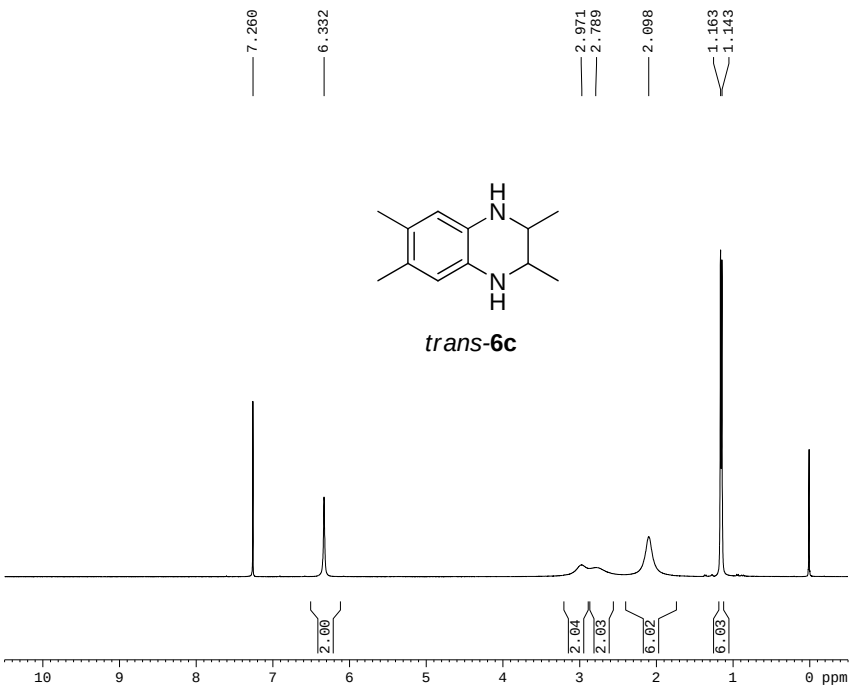
```
Current Data Parameters
NAME          qj-hh115-1
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110914
Time               11.18
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   586
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 322.5
DW                27.800 usec
DE                 6.50 usec
TE                299.4 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               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



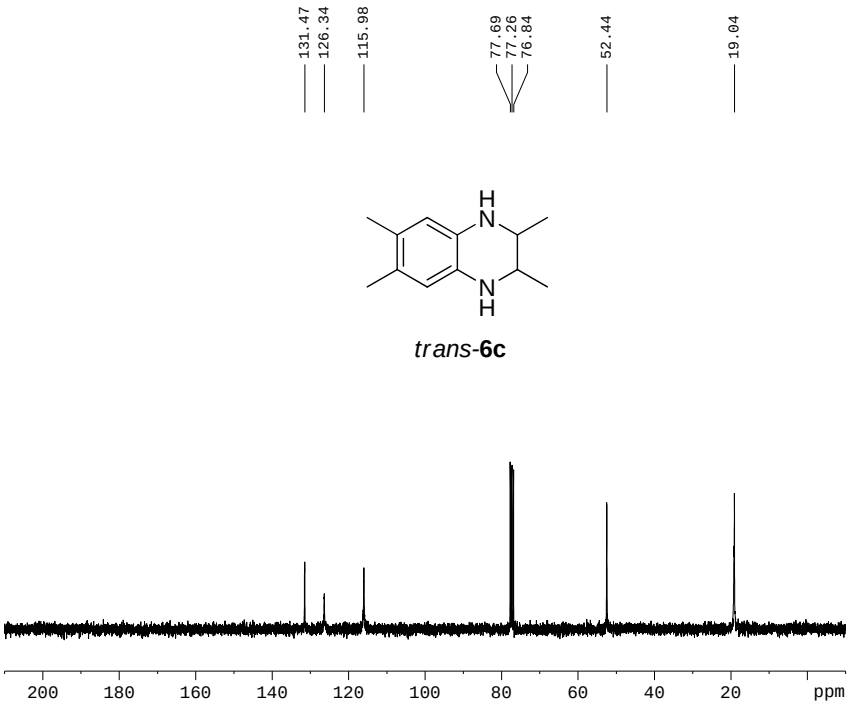

*trans*-**6c**

```
Current Data Parameters
NAME          qj-hh115-3
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110913
Time               22.04
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   256
DW                55.600 usec
DE                 8.00 usec
TE                298.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




*trans*-**6c**

```
Current Data Parameters
NAME          qj-hh115-3
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110913
Time               19.50
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgig30
TD                 32768
SOLVENT            CDCl3
NS                    62
DS                     0
SWH            18832.393 Hz
FIDRES          0.574719 Hz
AQ              0.8700404 sec
RG                 11585.2
DW                26.550 usec
DE                 8.00 usec
TE                299.0 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

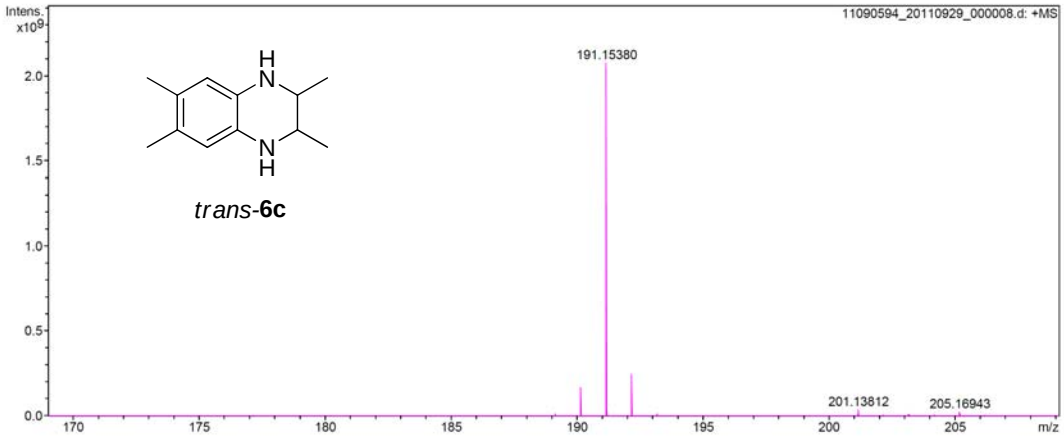
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677425 MHz
```

## Peking University Mass Spectrometry Sample Analysis Report

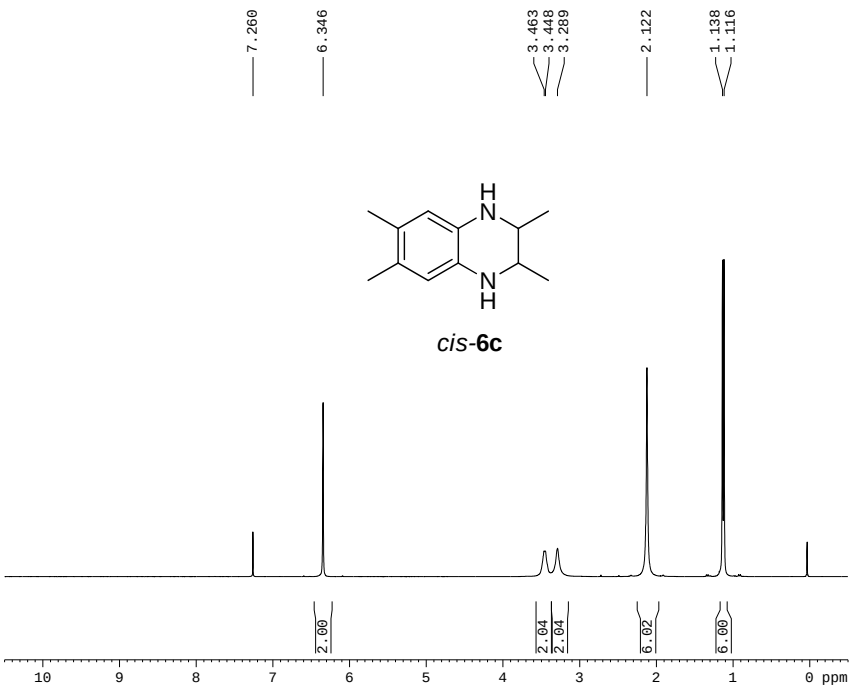
**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000008.d | Acquisition Date | 9/29/2011 1:46:17 PM |
| Sample | QJ-6 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |




*trans*-**6c**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 191.15380 | 1 | C 12 H 19 N 2 | 100.00 | 191.15428 | 0.5 | 2.5 | 9.1 | 4.5 | even | ok |



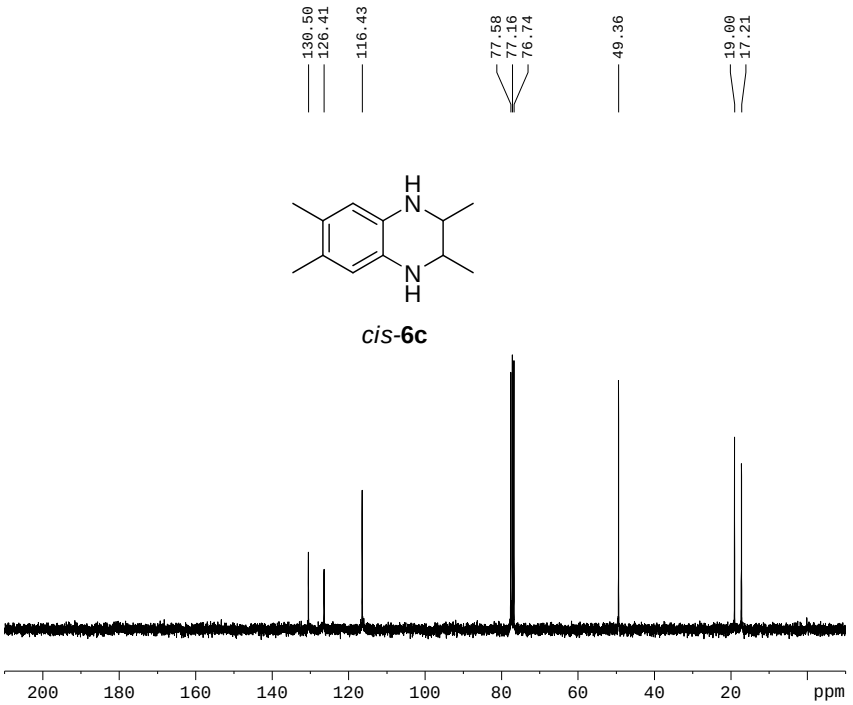

*cis*-**6c**

```
Current Data Parameters
NAME          qj-hh115-3
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110913
Time               22.12
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                298.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




*cis*-**6c**

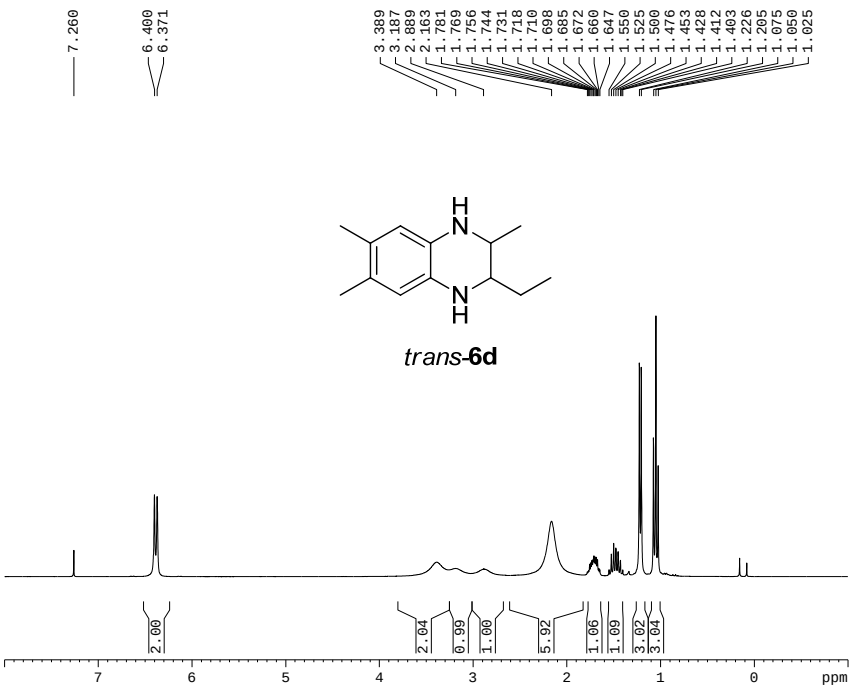
```
Current Data Parameters
NAME          qj-hh115-3
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110913
Time               22.16
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    75
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                299.1 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               22.33 dB
PL13               23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



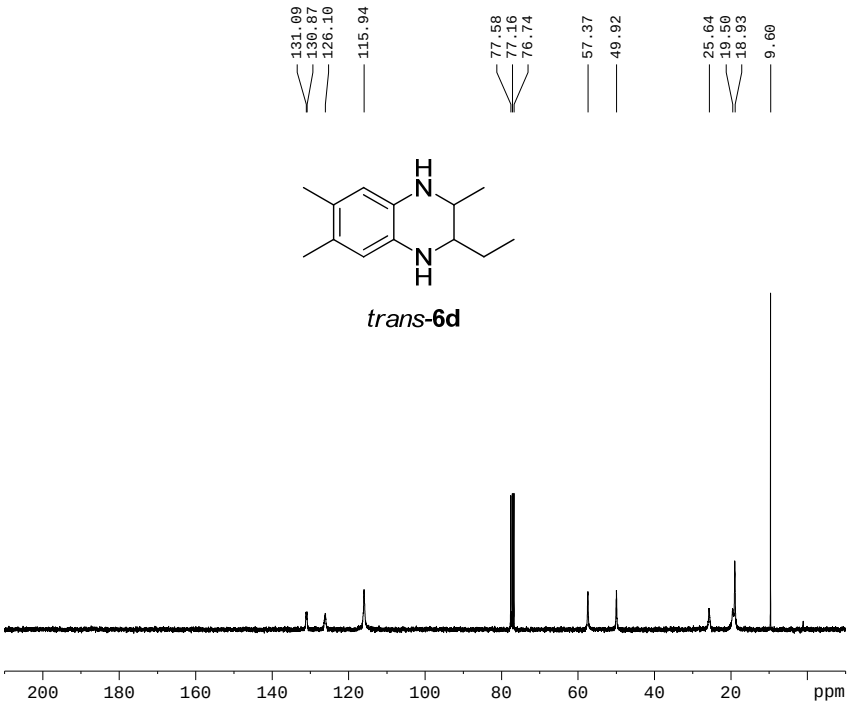

*trans*-**6d**

```
Current Data Parameters
NAME          qj-hh115-4
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110915
Time               13.10
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    10
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                  35.9
DW                55.600 usec
DE                 8.00 usec
TE                299.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




*trans*-**6d**

```
Current Data Parameters
NAME          qj-hh115-4
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110915
Time               13.14
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   215
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 456.1
DW                27.800 usec
DE                 6.50 usec
TE                299.5 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               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

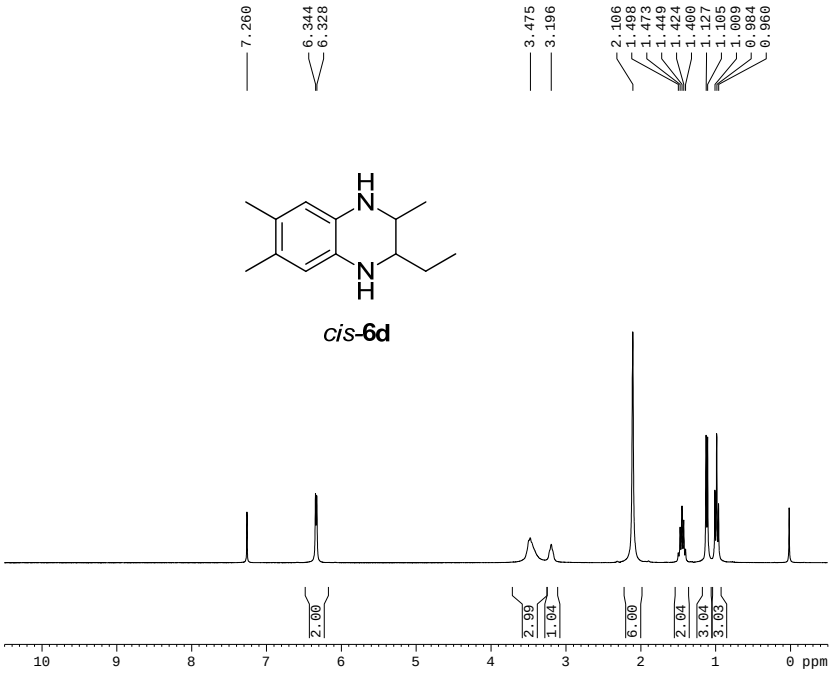
## Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000009.d | Acquisition Date | 9/29/2011 1:47:35 PM |
| Sample | QJ-7 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |


*trans*-**6d**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 205.16940 | 1 | C 13 H 21 N 2 | 100.00 | 205.16993 | 0.5 | 2.6 | 10.0 | 4.5 | even | ok |



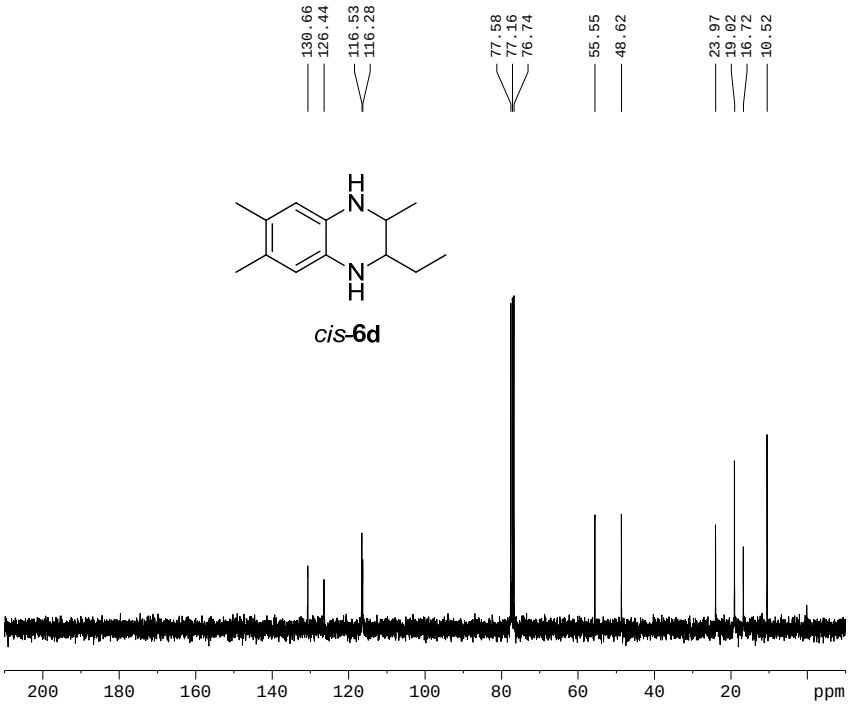

*cis*-**6d**

```
Current Data Parameters
NAME     qj-hh-MeMeMeEt-Q-NaBH4
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110810
Time              11.21
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    6
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                  181
DW               55.600 usec
DE                8.00 usec
TE                300.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300060 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




*cis*-**6d**

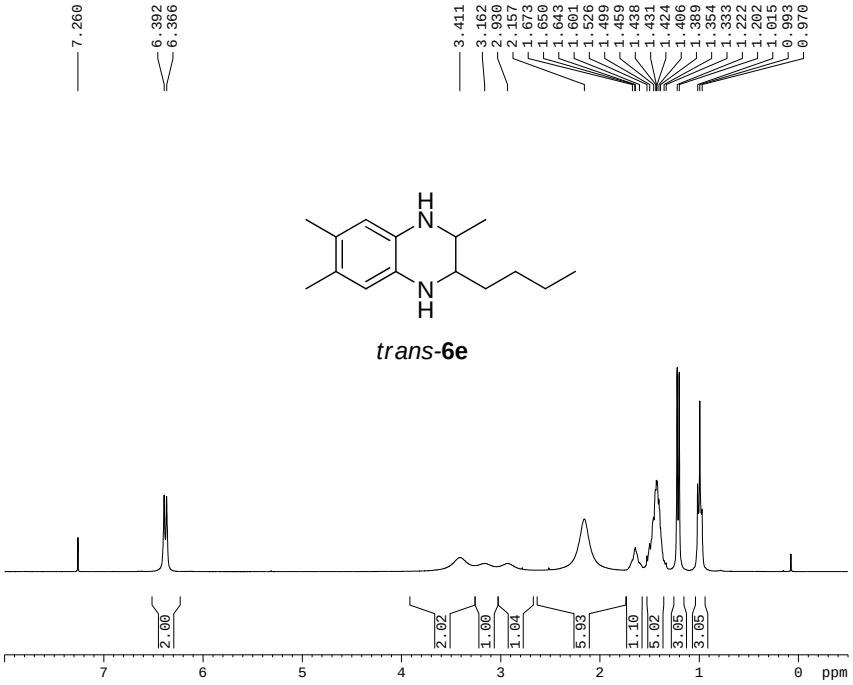
```
Current Data Parameters
NAME     qj-hh-MeMeMeEt-Q-Na
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110810
Time              11.25
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                  107
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                300.3 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              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```



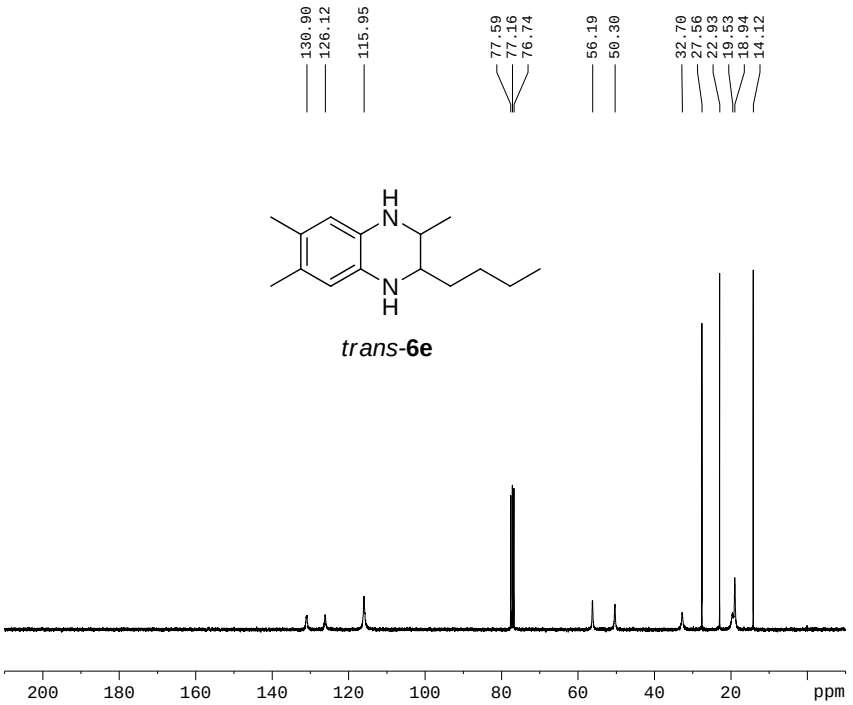

*trans*-**6e**

```
Current Data Parameters
NAME         qj-hh115-5
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20110915
Time              13.30
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     9
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                  35.9
DW                55.600 usec
DE                 8.00 usec
TE                299.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




*trans*-**6e**

```
Current Data Parameters
NAME         qj-hh115-5
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20110915
Time              13.34
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   417
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 456.1
DW                27.800 usec
DE                 6.50 usec
TE                299.5 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

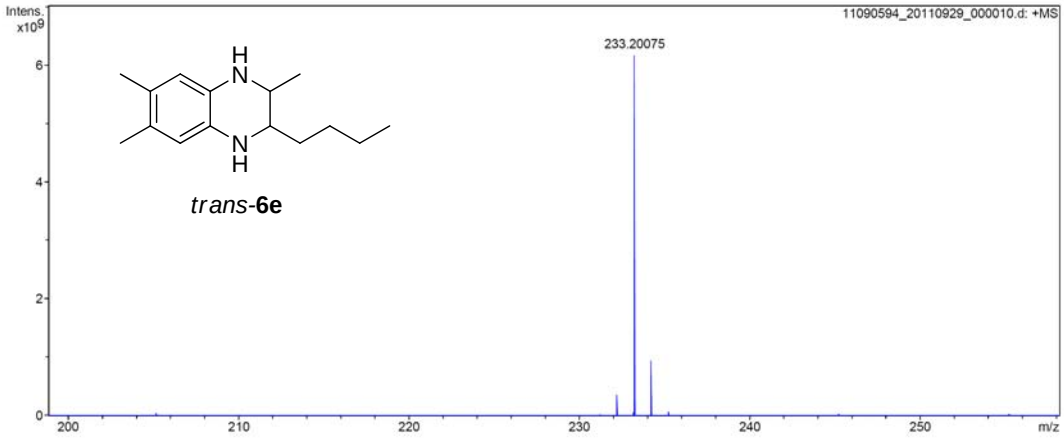
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

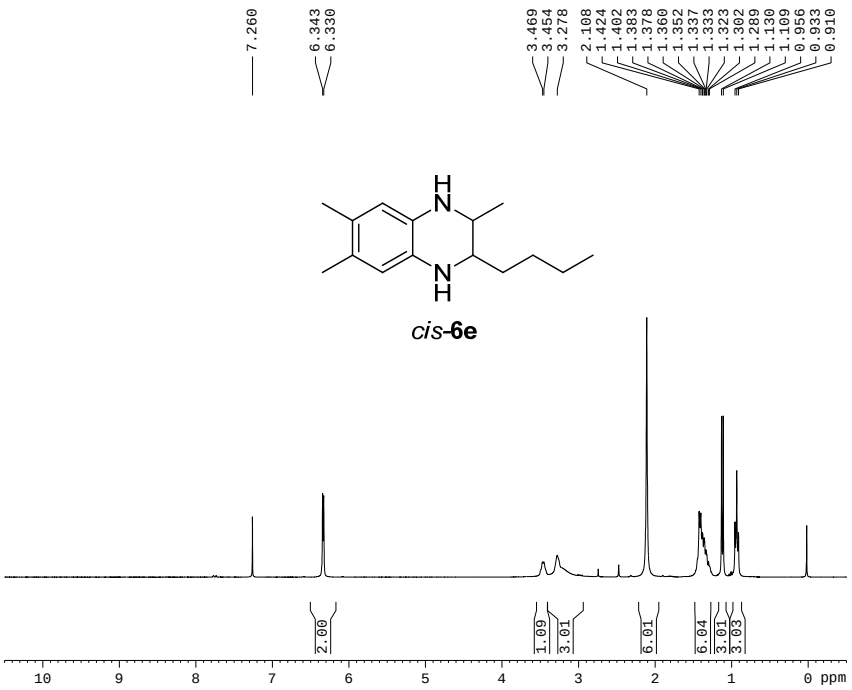
| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000010.d | Acquisition Date | 9/29/2011 1:48:57 PM |
| Sample | QJ-8 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |






*trans*-**6e**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 233.20075 | 1 | C 15 H 25 N 2 | 100.00 | 233.20123 | 0.5 | 2.1 | 11.0 | 4.5 | even | ok |



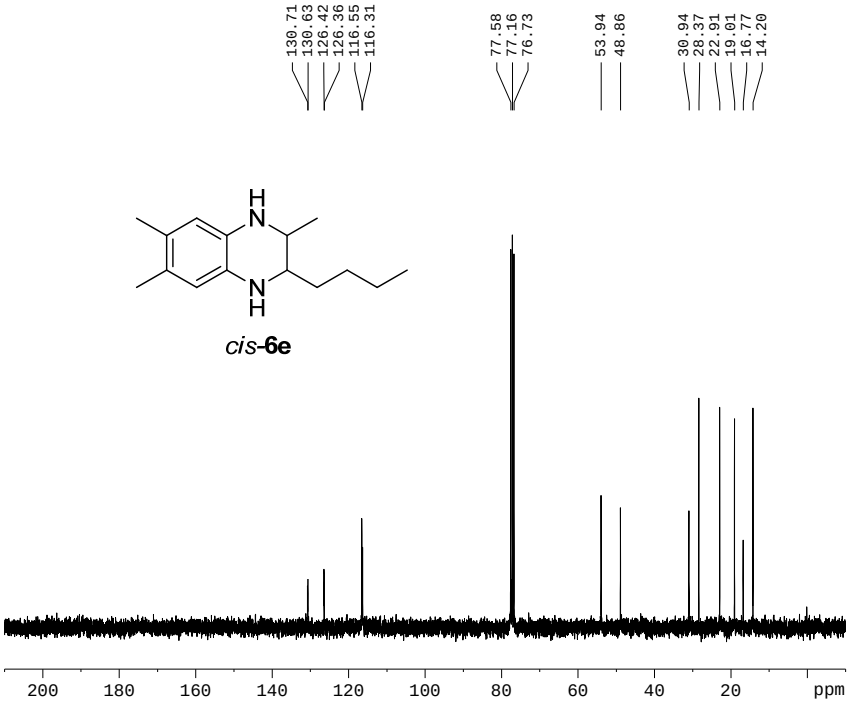

*cis*-**6e**

```
Current Data Parameters
NAME          qj-hh115-5
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110929
Time               20.05
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                299.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




*cis*-**6e**

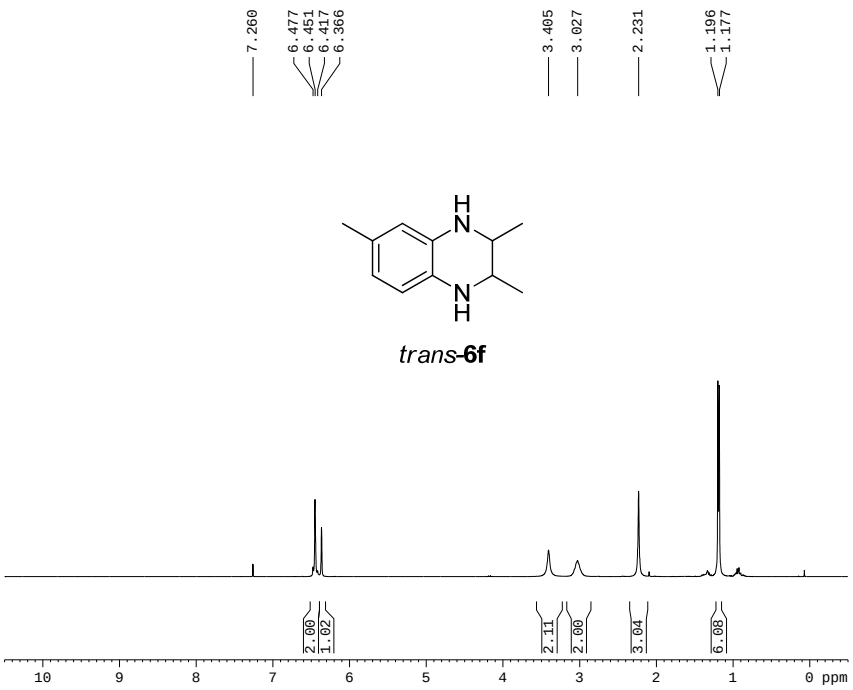
```
Current Data Parameters
NAME          qj-hh115-5
EXPNO                 41
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110929
Time               20.08
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    86
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                299.6 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              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



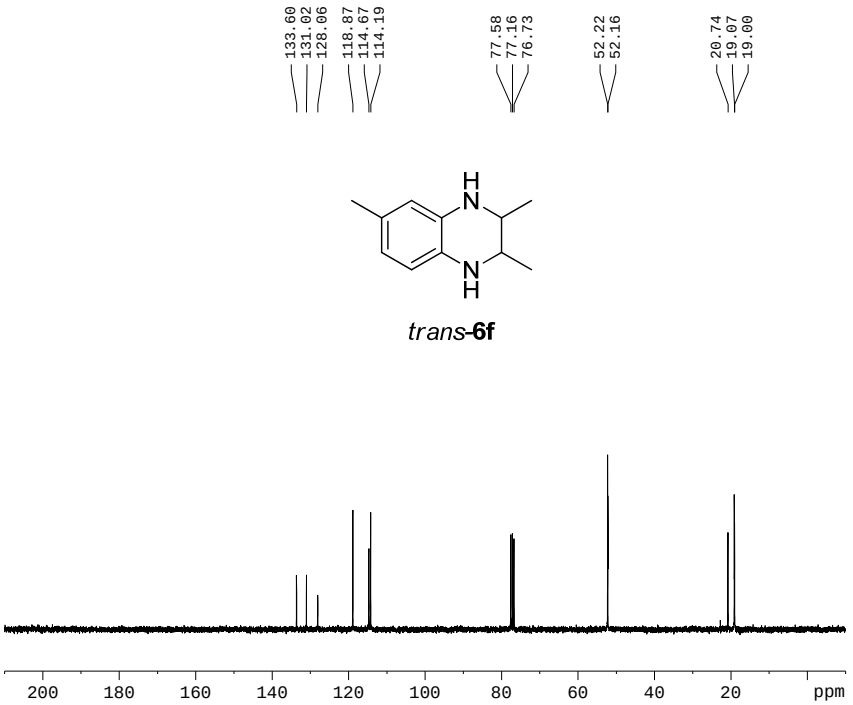

*trans*-**6f**

```
Current Data Parameters
NAME          qj-hh115-6
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110915
Time               20.20
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    10
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                  40.3
DW                55.600 usec
DE                 8.00 usec
TE                299.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




*trans*-**6f**

```
Current Data Parameters
NAME          qj-hh115-6
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110915
Time               20.24
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    47
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                299.8 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

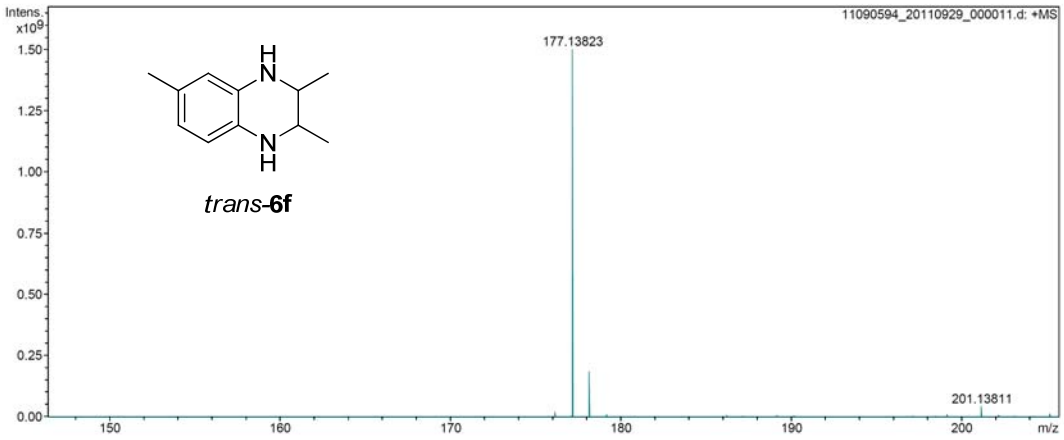
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

## Peking University Mass Spectrometry Sample Analysis Report

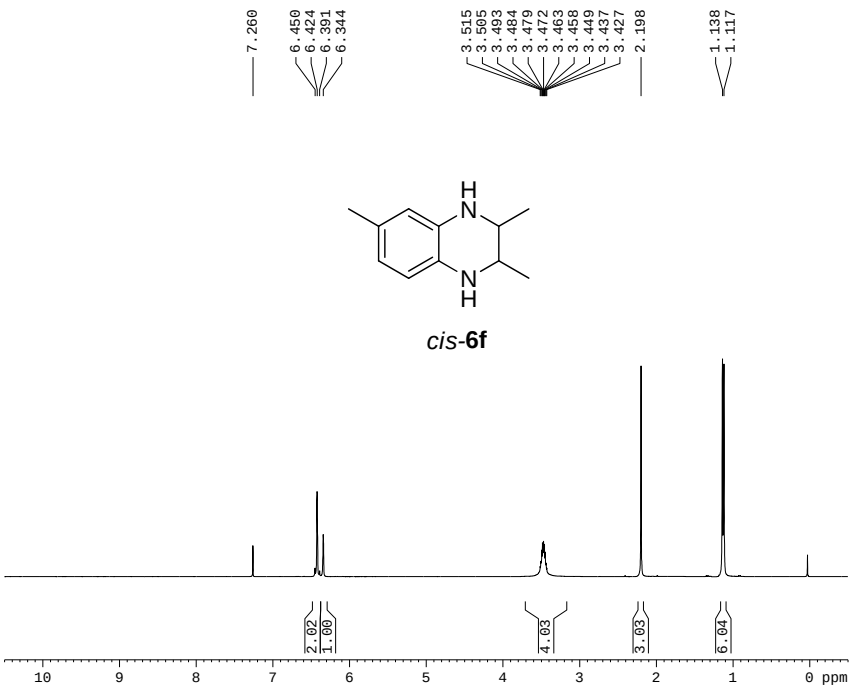
**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000011.d | Acquisition Date | 9/29/2011 1:49:53 PM |
| Sample | QJ-9 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |




*trans*-**6f**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 177.13823 | 1 | C 11 H 17 N 2 | 100.00 | 177.13862 | 0.4 | 2.2 | 1.0 | 4.5 | even | ok |



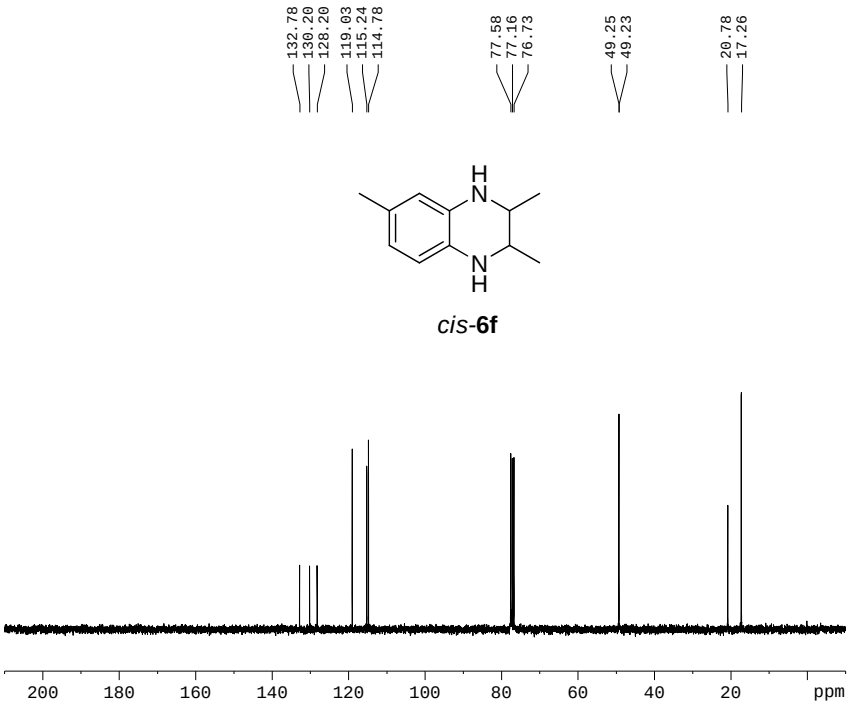

*cis*-**6f**

```
Current Data Parameters
NAME          qj-hh115-6
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110915
Time               20.30
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                299.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




*cis*-**6f**

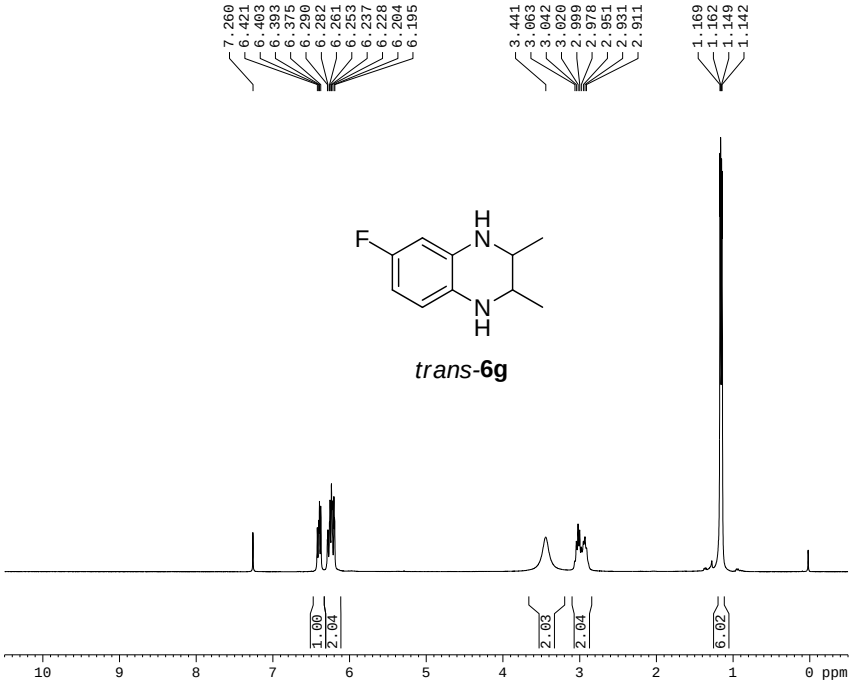
```
Current Data Parameters
NAME          qj-hh115-6
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110915
Time               20.32
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    76
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 322.5
DW                27.800 usec
DE                 6.50 usec
TE                299.7 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               22.33 dB
PL13               23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



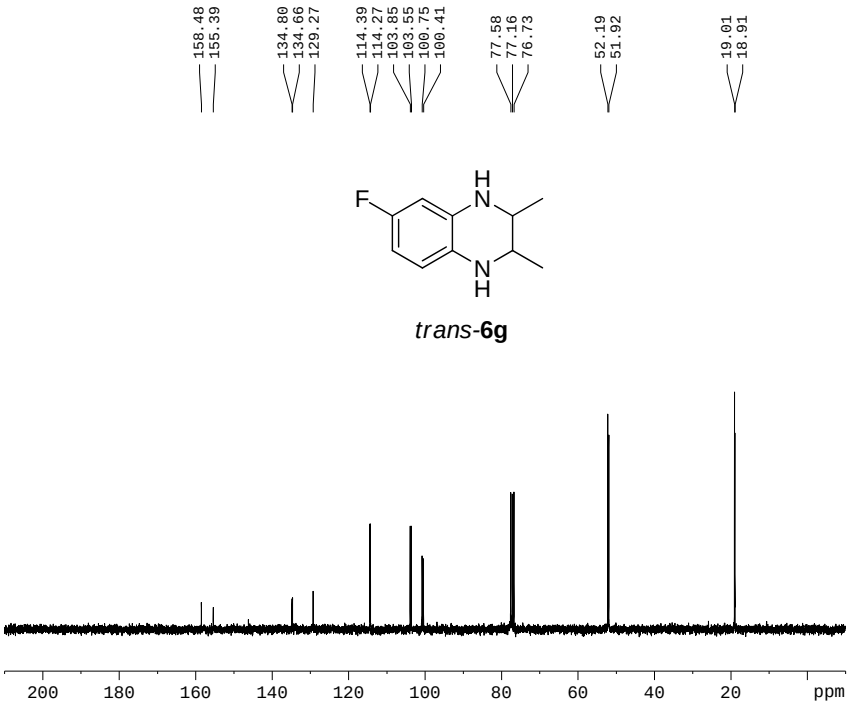

*trans*-**6g**

```
Current Data Parameters
NAME         qj-hh115-7
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20110922
Time              19.57
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                 71.8
DW               55.600 usec
DE                8.00 usec
TE                299.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300060 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




*trans*-**6g**

```
Current Data Parameters
NAME         qj-hh115-7
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20110922
Time              20.00
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   52
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                299.5 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

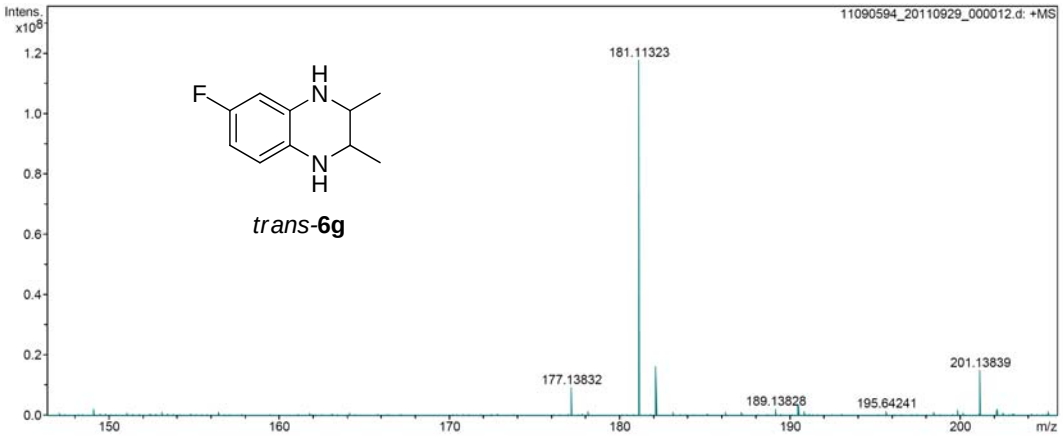
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

## Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**

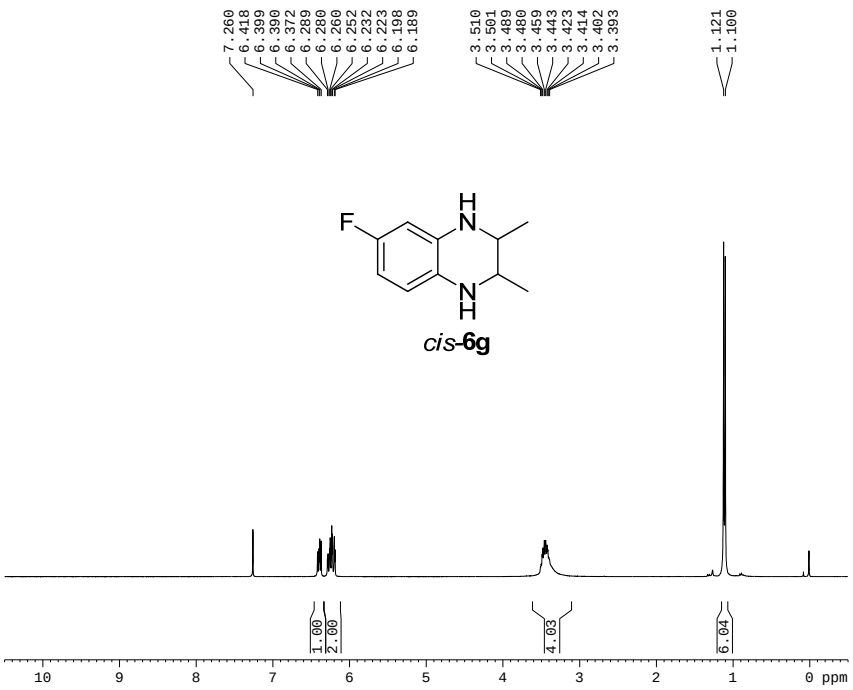
| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000012.d | Acquisition Date | 9/29/2011 1:51:01 PM |
| Sample | QJ-10 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |






*trans*-**6g**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 181.11323 | 1 | C 10 H 14 F N 2 | 100.00 | 181.11355 | 0.3 | 1.8 | 13.5 | 4.5 | even | ok |



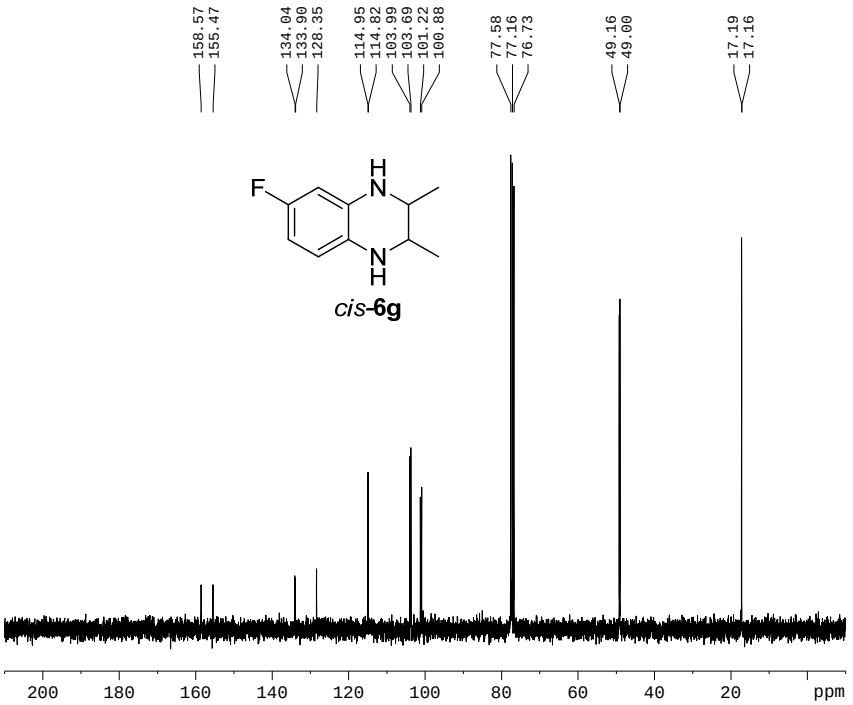

*cis*-**6g**

```
Current Data Parameters
NAME          qj-hh115-7
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110925
Time                8.40
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                298.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




*cis*-**6g**

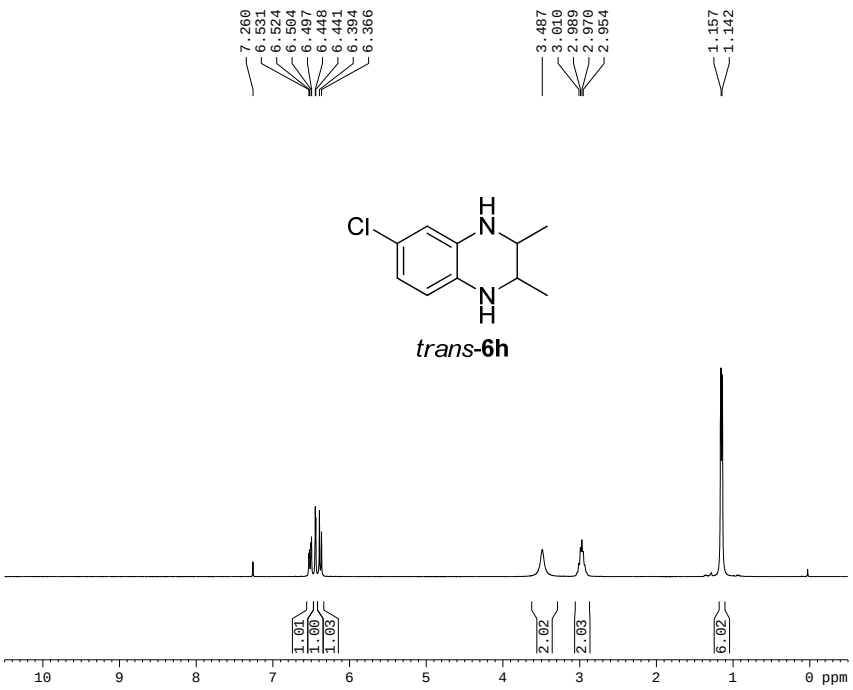
```
Current Data Parameters
NAME          qj-hh115-7
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110925
Time                8.43
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    78
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                298.7 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              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



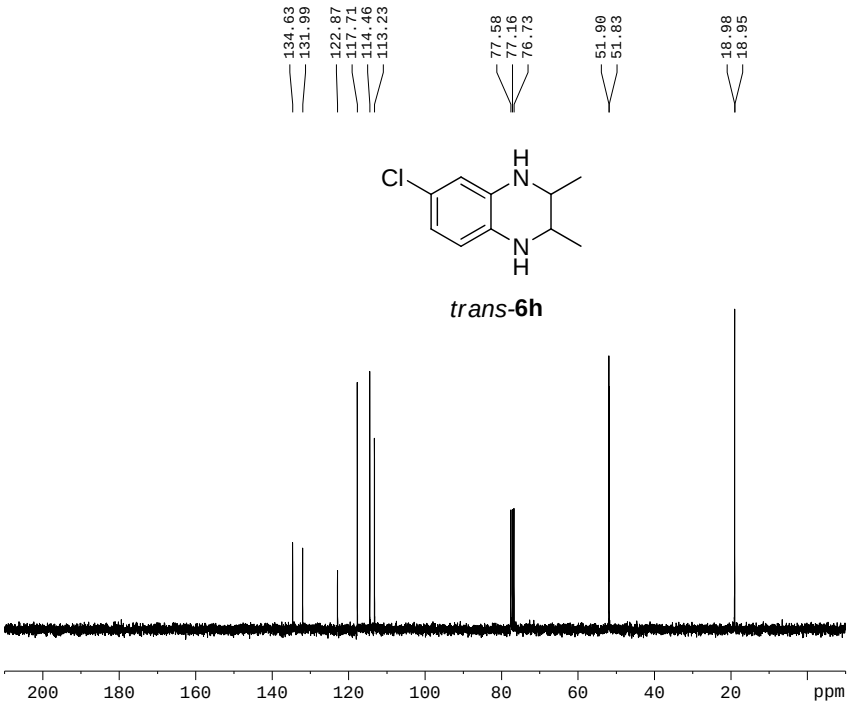

*trans*-**6h**

```
Current Data Parameters
NAME          qj-hh115-8
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110922
Time               20.10
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                    64
DW                55.600 usec
DE                 8.00 usec
TE                299.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




*trans*-**6h**

```
Current Data Parameters
NAME          qj-hh115-8
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110922
Time               20.12
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    25
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                299.5 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

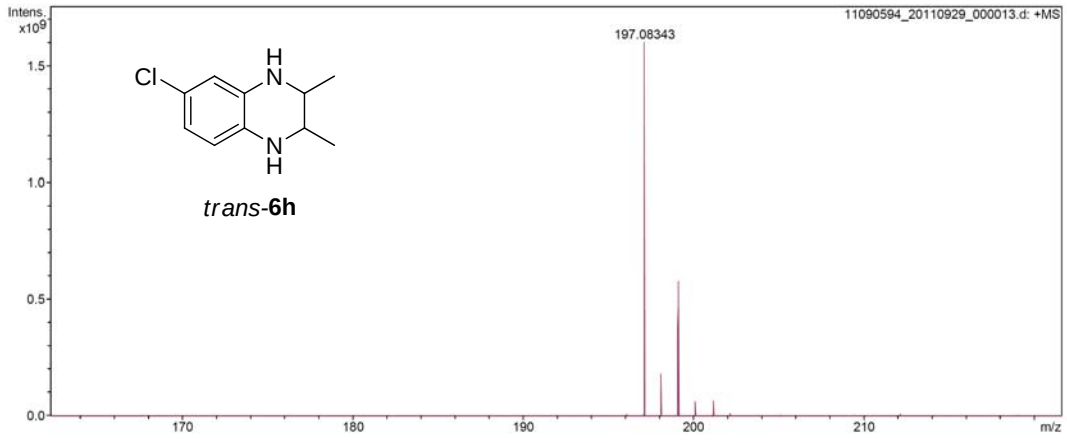
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

## Peking University Mass Spectrometry Sample Analysis Report

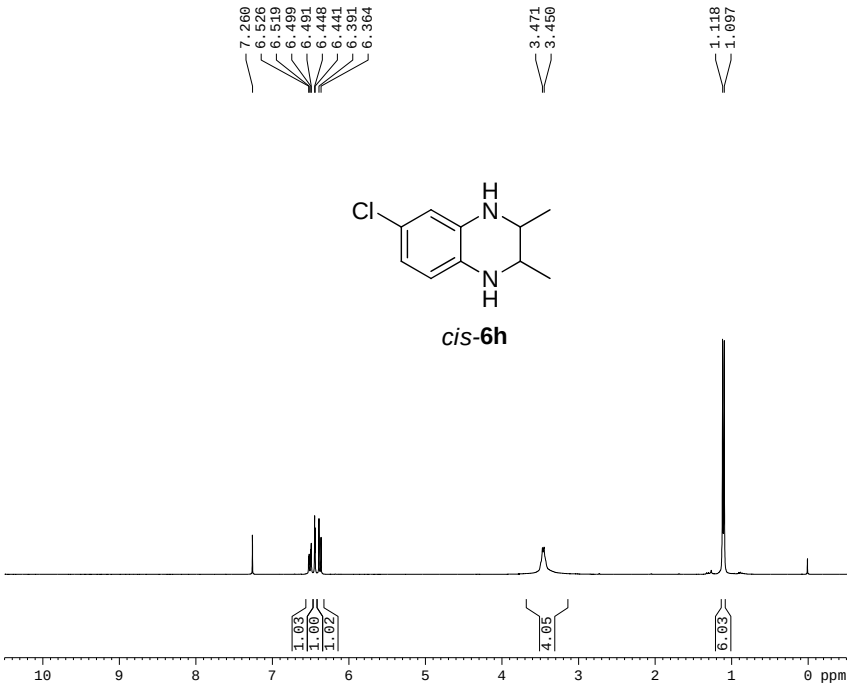
**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | 11090594_20110929_000013.d | Acquisition Date | 9/29/2011 1:52:21 PM |
| Sample | QJ-11 | Instrument | Bruker Apex IV FTMS |
| Comment | | Operator | Peking University |




*trans*-**6h**

| Meas. m/z | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 197.08343 | 1 | C 10 H 14 Cl N 2 | 100.00 | 197.08400 | 0.6 | 2.9 | 18.5 | 4.5 | even | ok |



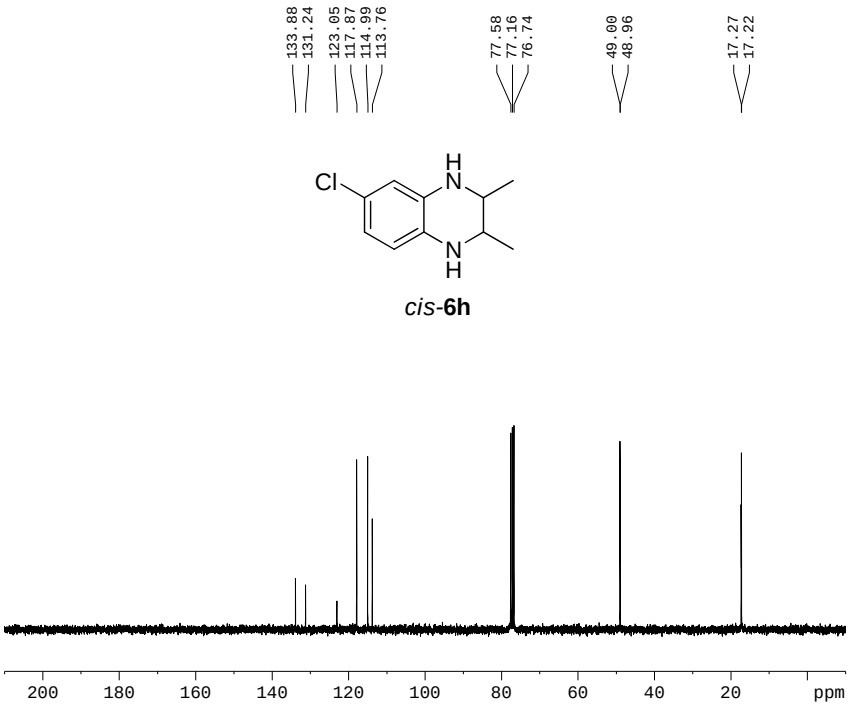

*cis*-**6h**

```
Current Data Parameters
NAME         qj-hh115-8
EXPNO                60
PROCNO                1

F2 - Acquisition Parameters
Date_          20111009
Time               8.41
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   13
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ            3.6438515 sec
RG                  128
DW               55.600 usec
DE                8.00 usec
TE                299.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300060 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




*cis*-**6h**

```
Current Data Parameters
NAME         qj-hh115-8
EXPNO                61
PROCNO                1

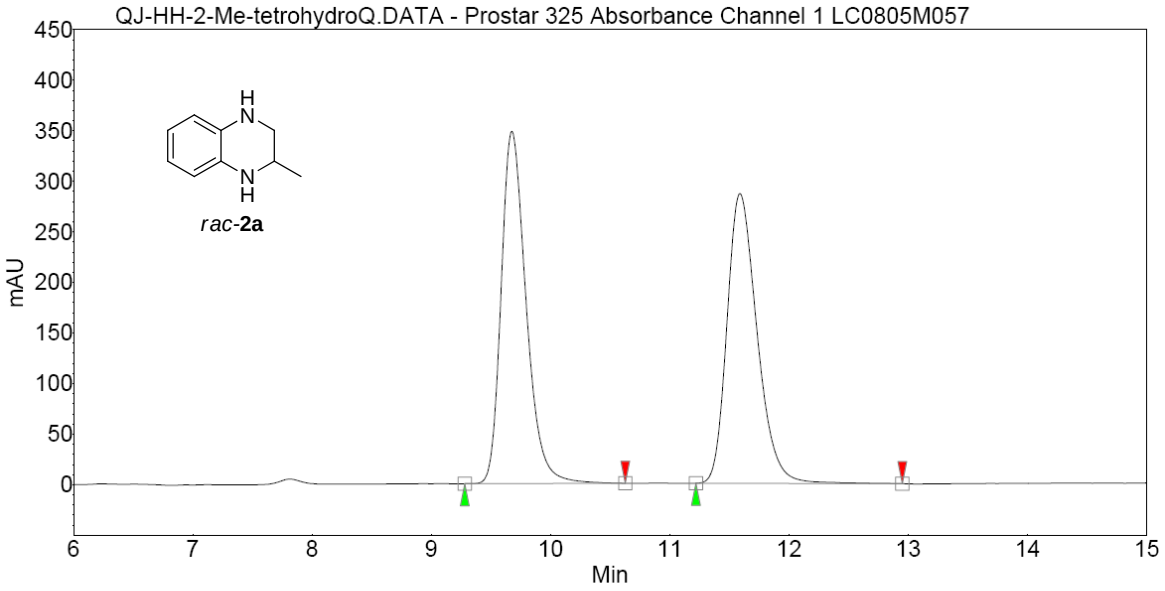
F2 - Acquisition Parameters
Date_          20111009
Time               8.45
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  157
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                812.7
DW               27.800 usec
DE                6.50 usec
TE                299.3 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

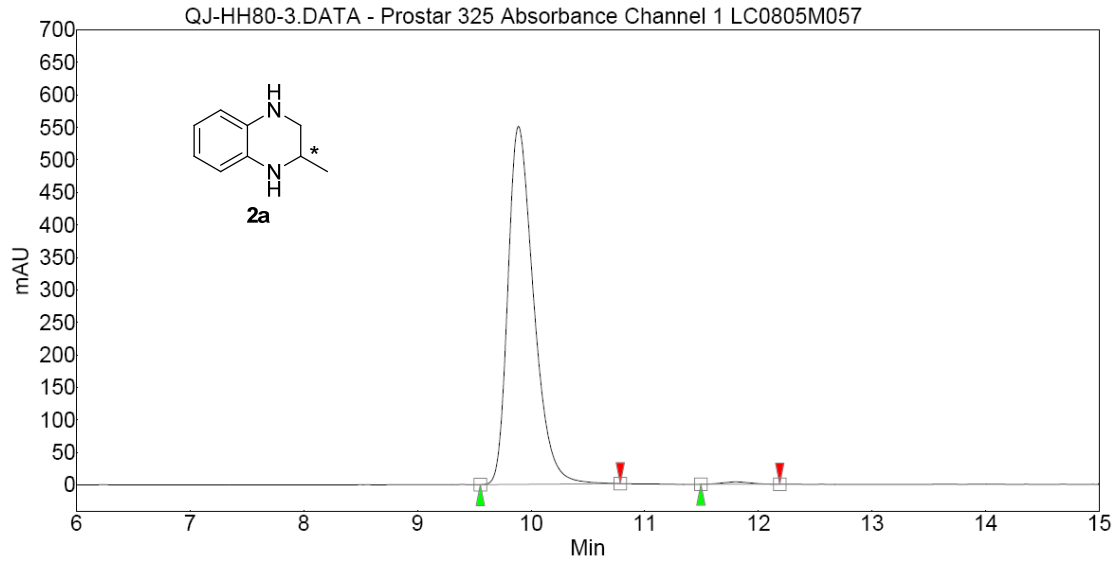
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

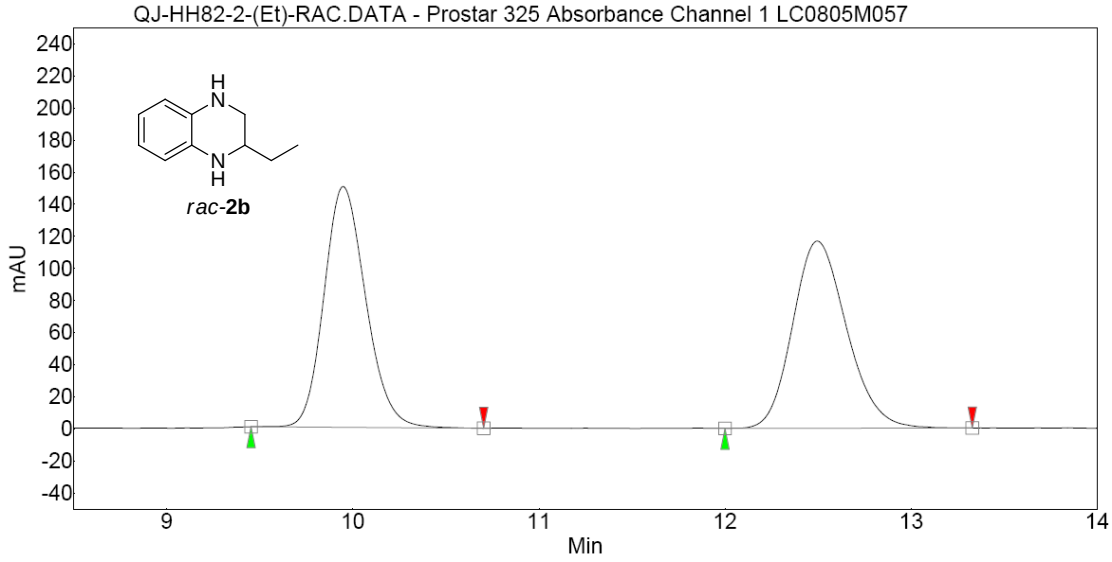
# 7. Copy of HPLC spectra of the racemic and chiral products



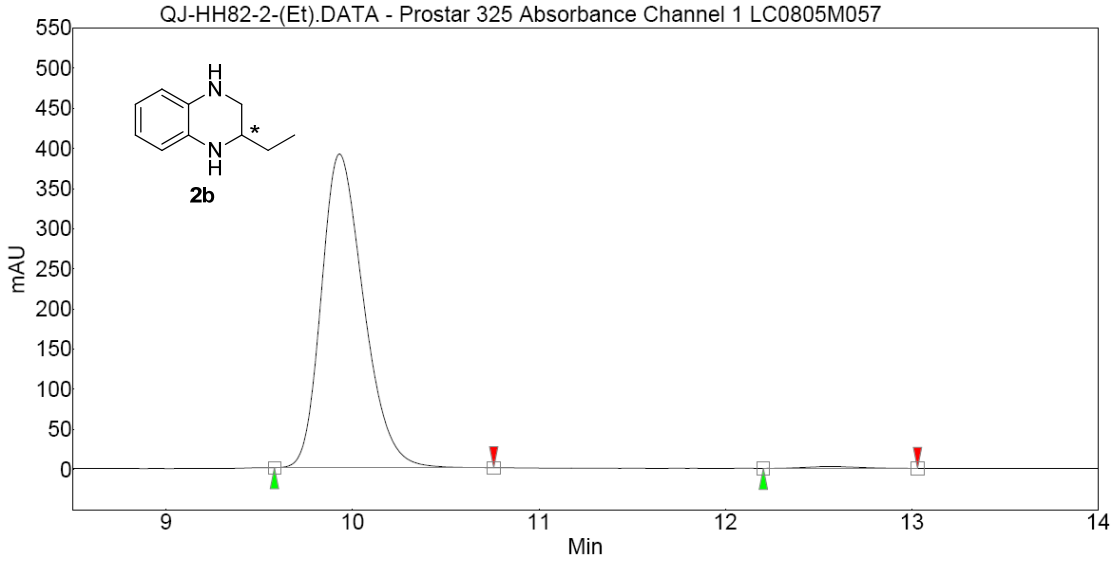

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 9.67 | 50.22 | 348.5 | 84.5 | 50.223 |
| 2 | 未知 | 11.59 | 49.78 | 286.6 | 83.7 | 49.777 |
| | | | | | | |
| Total | | | 100.00 | 635.1 | 168.2 | 100.000 |



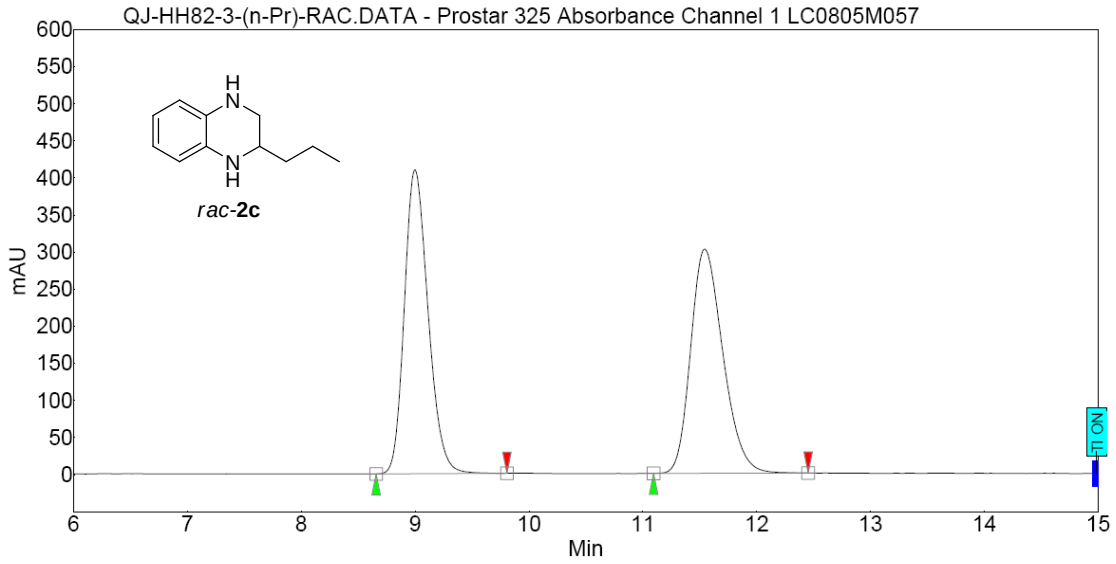

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 9.89 | 99.26 | 550.6 | 144.3 | 99.259 |
| 1 | 未知 | 11.80 | 0.74 | 3.6 | 1.1 | 0.741 |
| | | | | | | |
| Total | | | 100.00 | 554.2 | 145.4 | 100.000 |



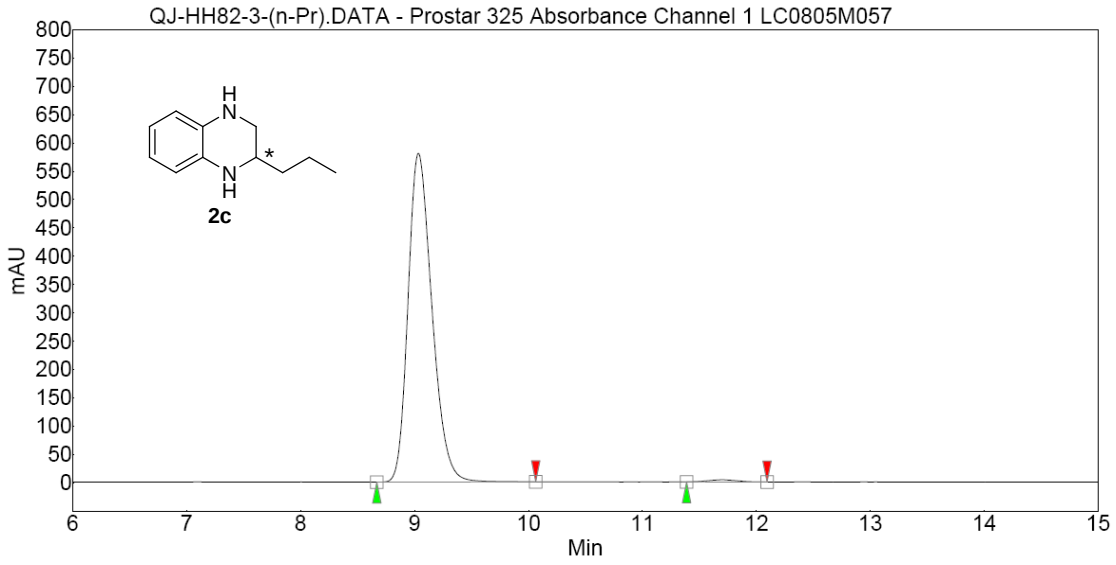

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 9.95 | 49.94 | 150.2 | 39.1 | 49.936 |
| 1 | 未知 | 12.49 | 50.06 | 116.7 | 39.2 | 50.064 |
| | | | | | | |
| Total | | | 100.00 | 266.9 | 78.2 | 100.000 |



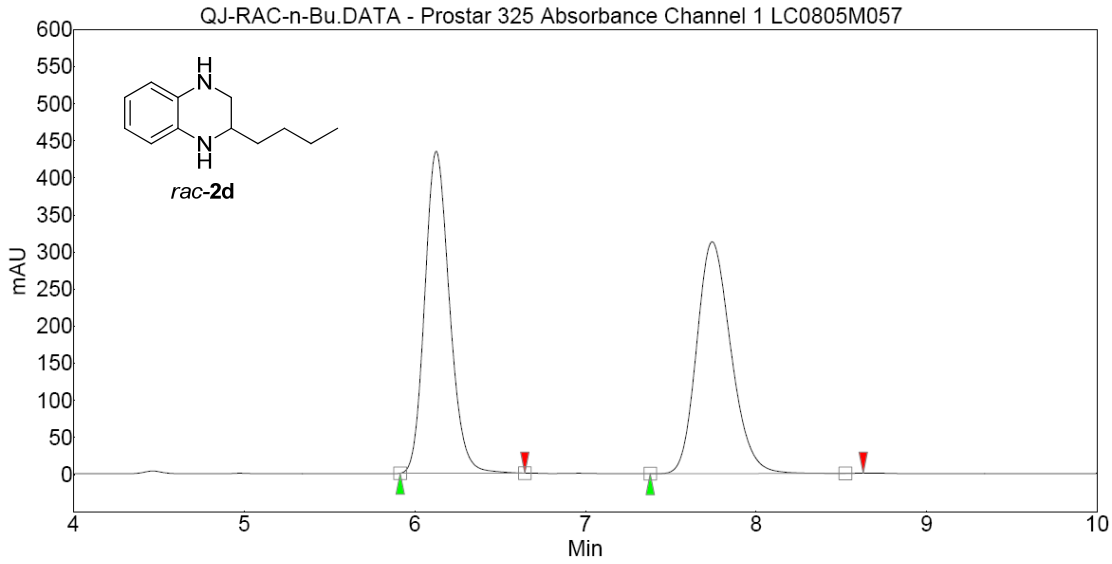

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 9.93 | 99.29 | 390.7 | 102.7 | 99.290 |
| 2 | 未知 | 12.54 | 0.71 | 2.2 | 0.7 | 0.710 |
| | | | | | | |
| Total | | | 100.00 | 392.9 | 103.5 | 100.000 |



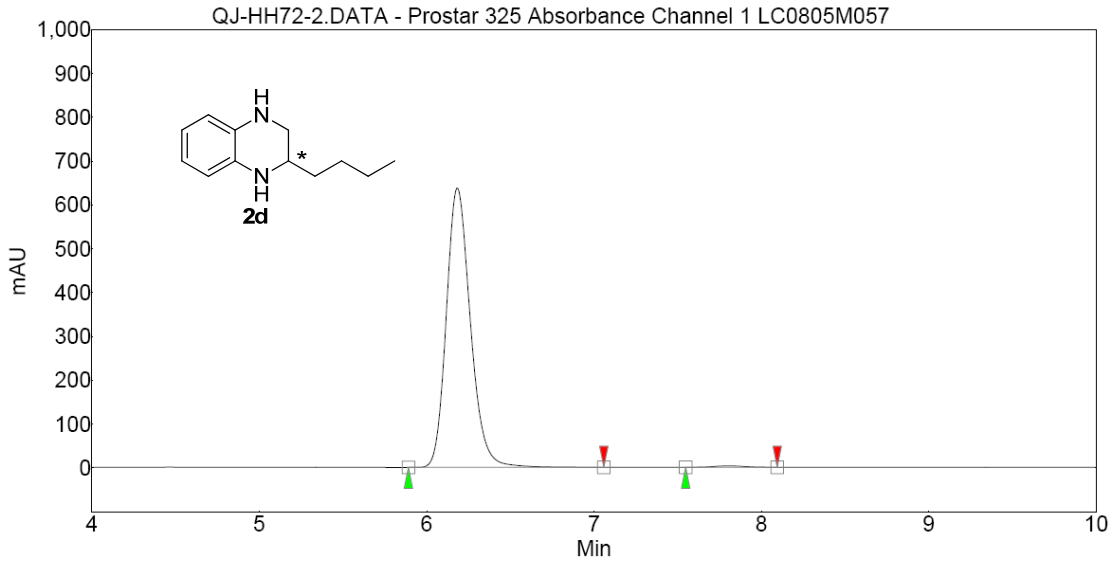

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 9.00 | 49.99 | 409.8 | 99.0 | 49.994 |
| 1 | 未知 | 11.54 | 50.01 | 302.3 | 99.1 | 50.006 |
| | | | | | | |
| Total | | | 100.00 | 712.1 | 198.1 | 100.000 |



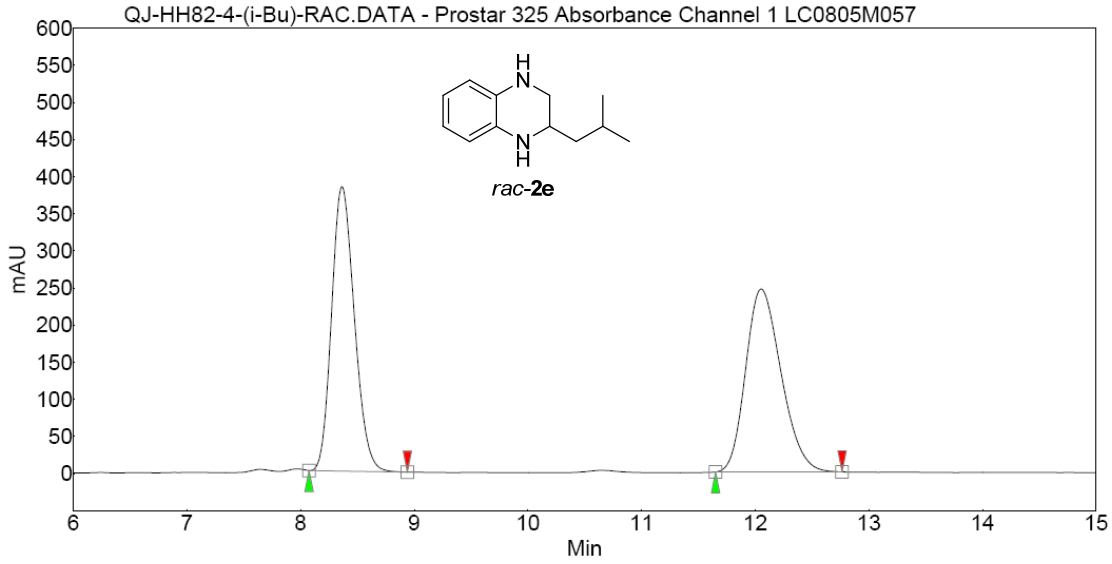

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 9.03 | 99.20 | 580.7 | 141.1 | 99.200 |
| 1 | 未知 | 11.70 | 0.80 | 3.7 | 1.1 | 0.800 |
| | | | | | | |
| Total | | | 100.00 | 584.4 | 142.2 | 100.000 |



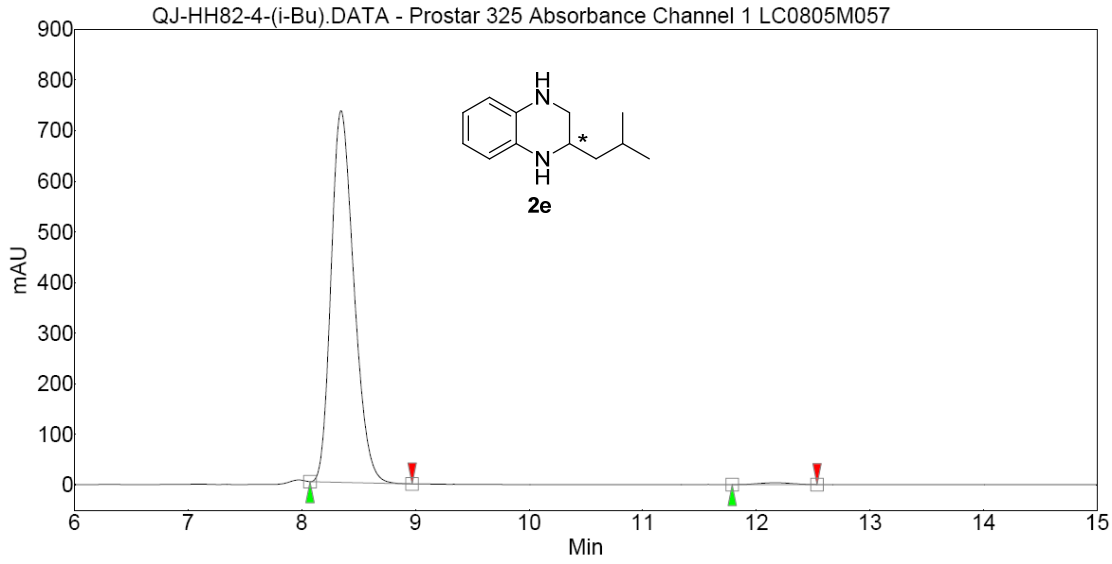

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 6.13 | 50.06 | 434.3 | 72.9 | 50.060 |
| 1 | 未知 | 7.74 | 49.94 | 312.6 | 72.8 | 49.940 |
| | | | | | | |
| Total | | | 100.00 | 747.0 | 145.7 | 100.000 |



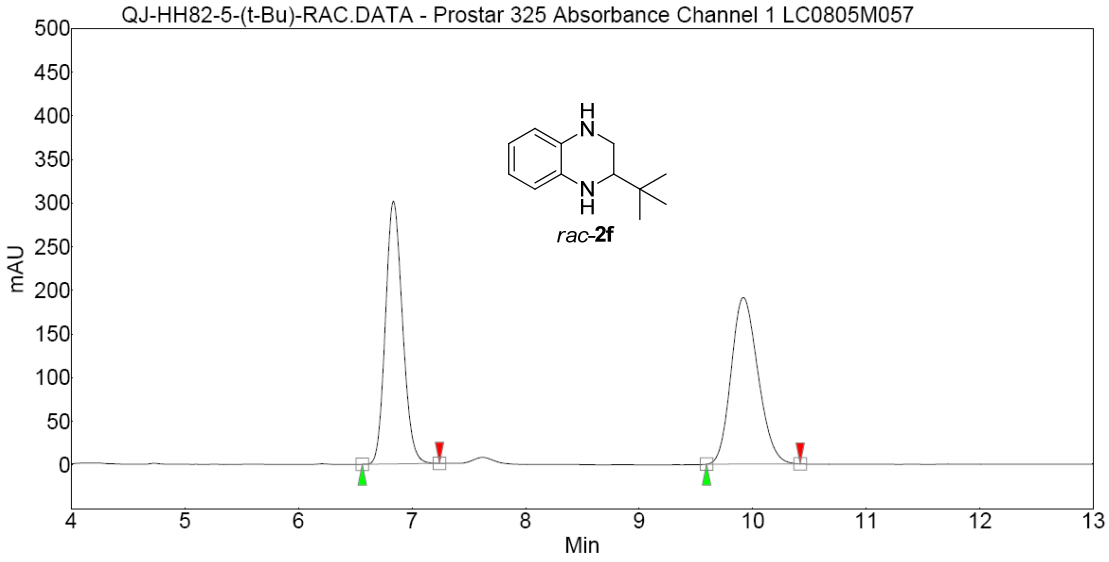

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 6.18 | 99.33 | 637.8 | 106.3 | 99.329 |
| 1 | 未知 | 7.81 | 0.67 | 3.3 | 0.7 | 0.671 |
| | | | | | | |
| Total | | | 100.00 | 641.1 | 107.0 | 100.000 |



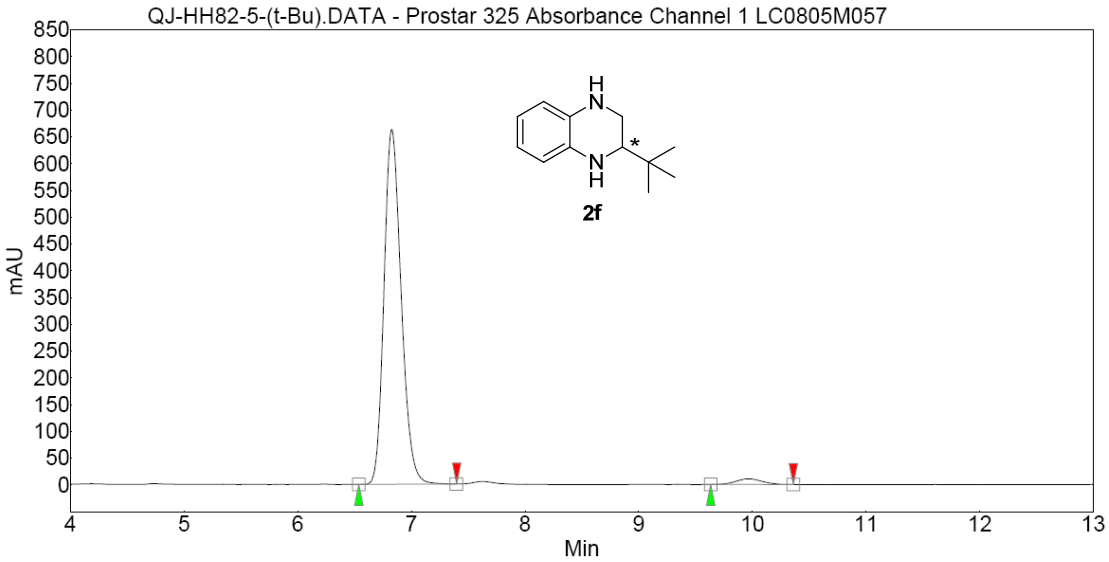

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 8.37 | 49.99 | 383.3 | 89.0 | 49.987 |
| 2 | 未知 | 12.05 | 50.01 | 246.7 | 89.1 | 50.013 |
| | | | | | | |
| Total | | | 100.00 | 629.9 | 178.1 | 100.000 |



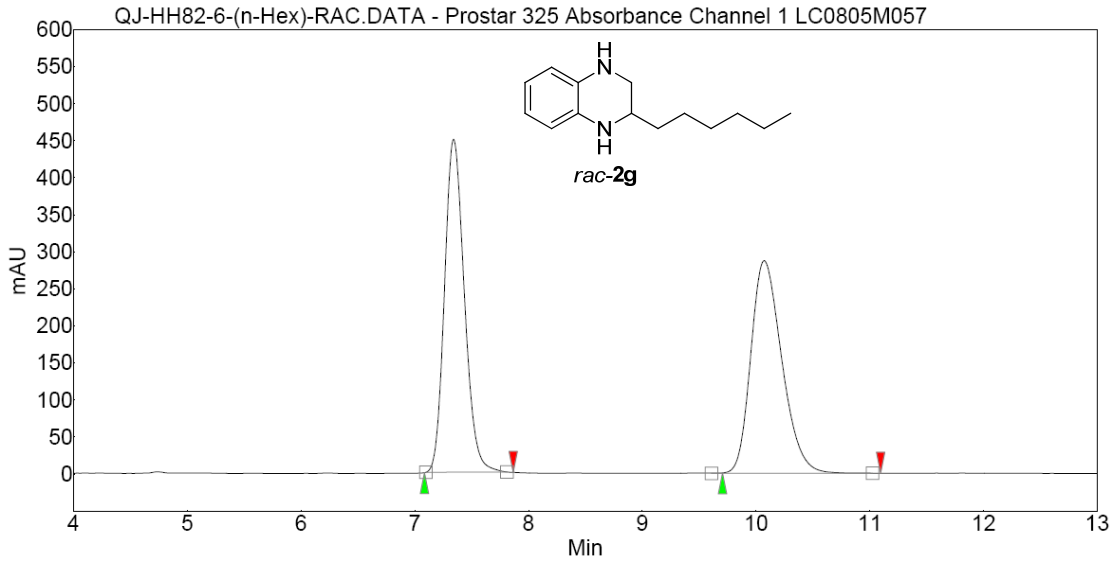

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 8.35 | 99.26 | 734.6 | 171.2 | 99.259 |
| 1 | 未知 | 12.15 | 0.74 | 3.7 | 1.3 | 0.741 |
| | | | | | | |
| Total | | | 100.00 | 738.4 | 172.5 | 100.000 |



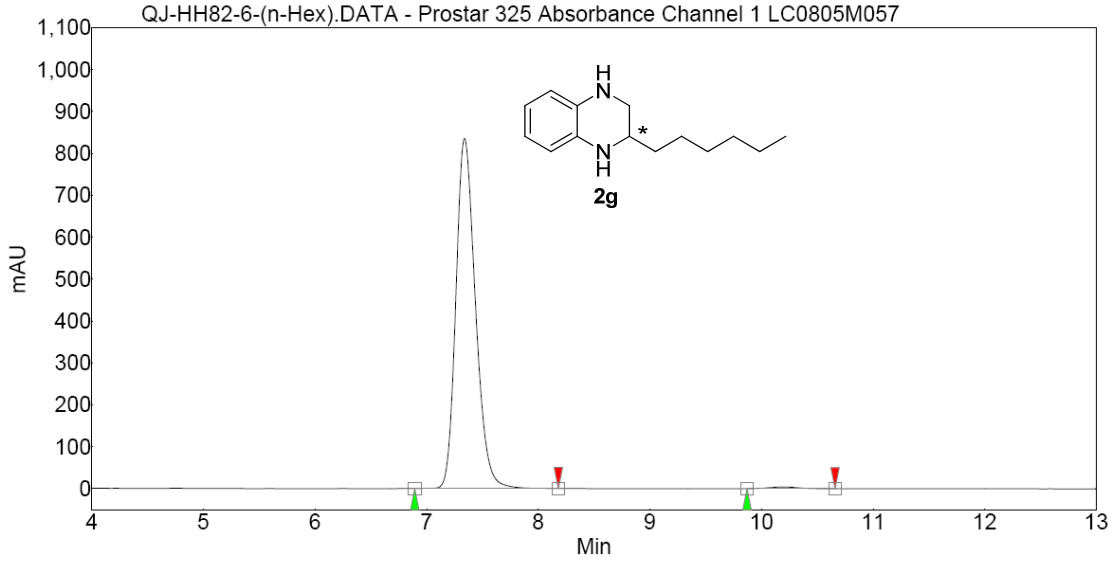

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 6.83 | 50.06 | 301.1 | 52.5 | 50.062 |
| 1 | 未知 | 9.92 | 49.94 | 190.9 | 52.4 | 49.938 |
| | | | | | | |
| Total | | | 100.00 | 492.0 | 104.8 | 100.000 |



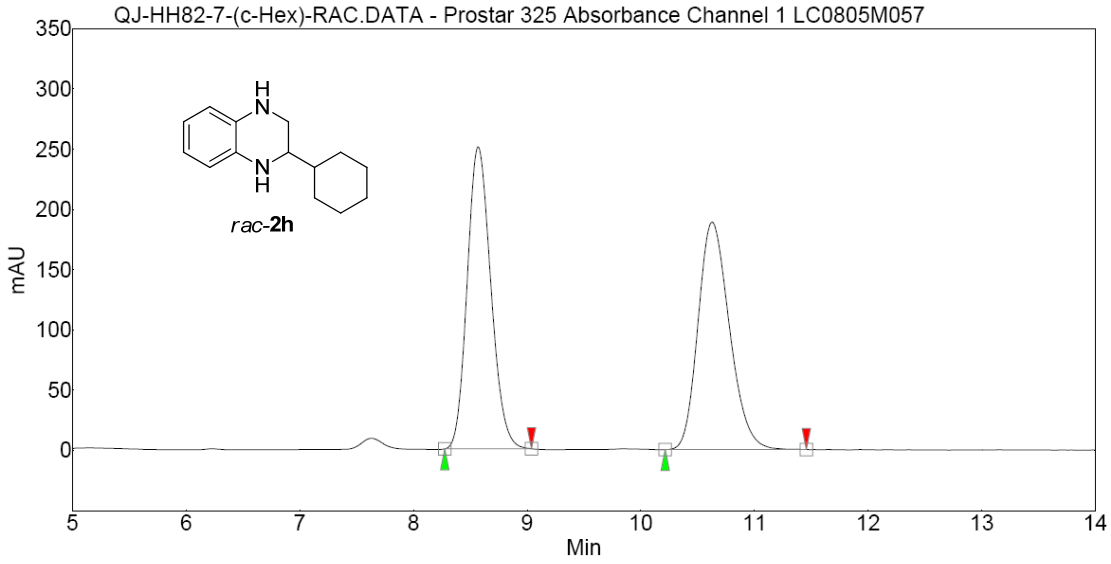

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 6.83 | 97.65 | 663.0 | 116.3 | 97.653 |
| 1 | 未知 | 9.97 | 2.35 | 10.4 | 2.8 | 2.347 |
| | | | | | | |
| Total | | | 100.00 | 673.4 | 119.1 | 100.000 |



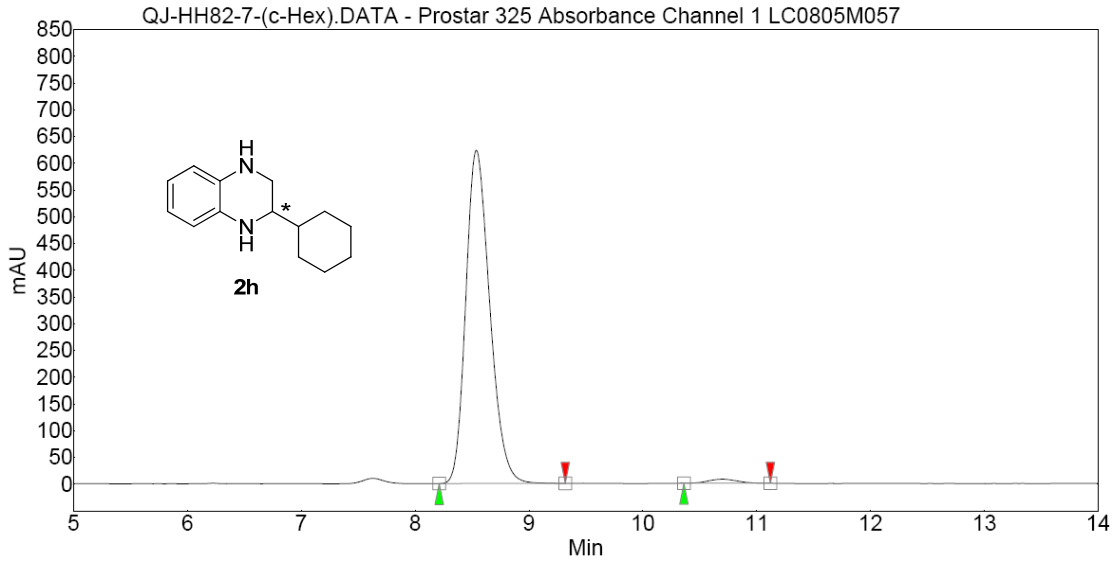

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 7.34 | 50.06 | 449.8 | 90.8 | 50.061 |
| 1 | 未知 | 10.07 | 49.94 | 287.1 | 90.6 | 49.939 |
| | | | | | | |
| Total | | | 100.00 | 736.9 | 181.5 | 100.000 |



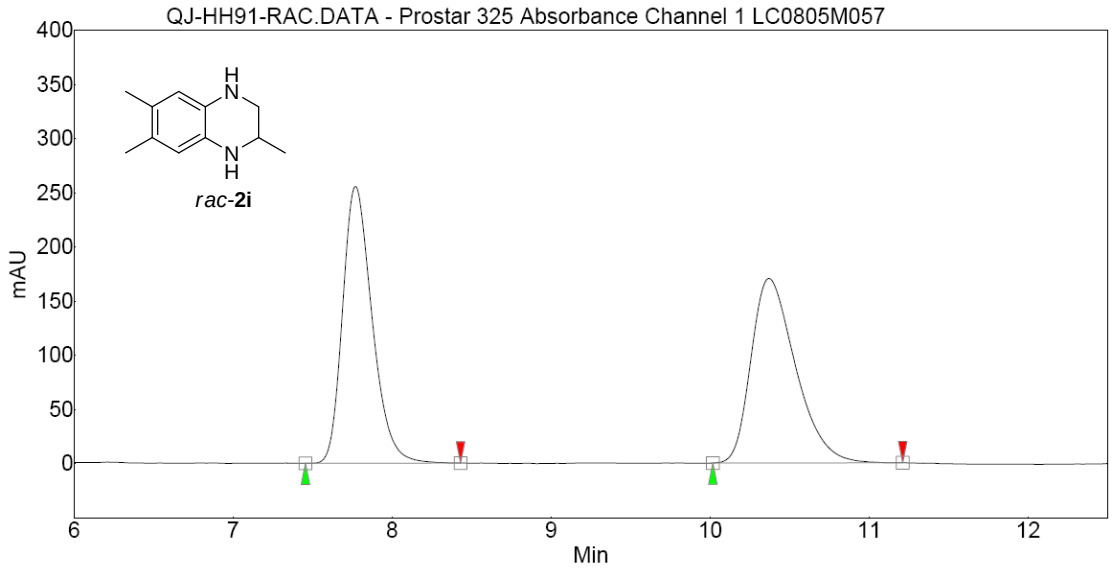

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 7.34 | 99.30 | 835.5 | 169.6 | 99.296 |
| 1 | 未知 | 10.19 | 0.70 | 4.0 | 1.2 | 0.704 |
| | | | | | | |
| Total | | | 100.00 | 839.5 | 170.8 | 100.000 |



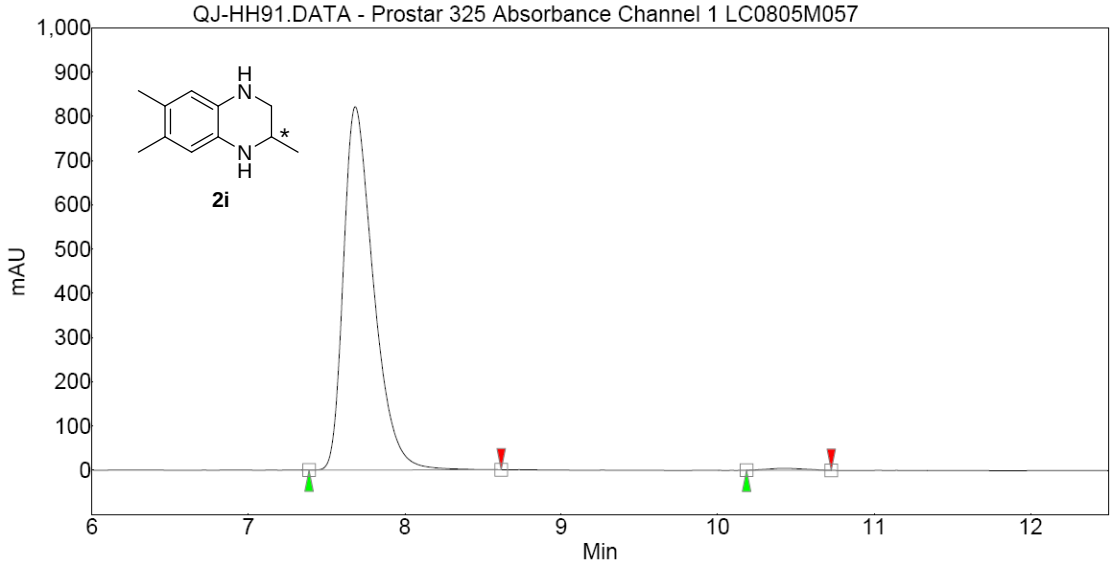

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 8.57 | 50.00 | 250.8 | 60.4 | 49.997 |
| 1 | 未知 | 10.63 | 50.00 | 188.9 | 60.4 | 50.003 |
| | | | | | | |
| Total | | | 100.00 | 439.6 | 120.9 | 100.000 |



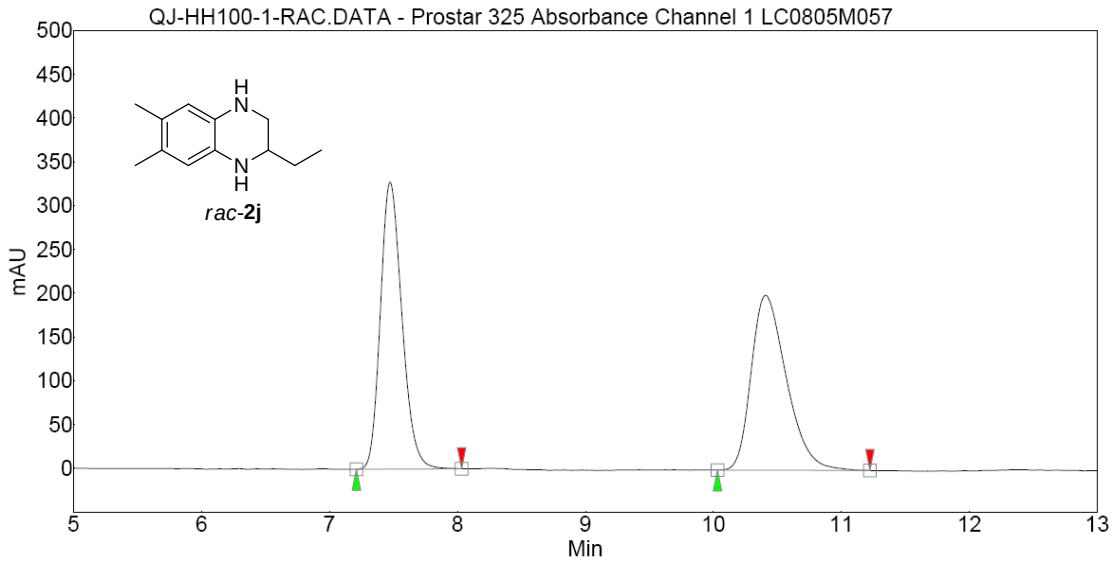

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 8.53 | 98.51 | 622.9 | 152.1 | 98.514 |
| 1 | 未知 | 10.70 | 1.49 | 7.7 | 2.3 | 1.486 |
| | | | | | | |
| Total | | | 100.00 | 630.6 | 154.4 | 100.000 |



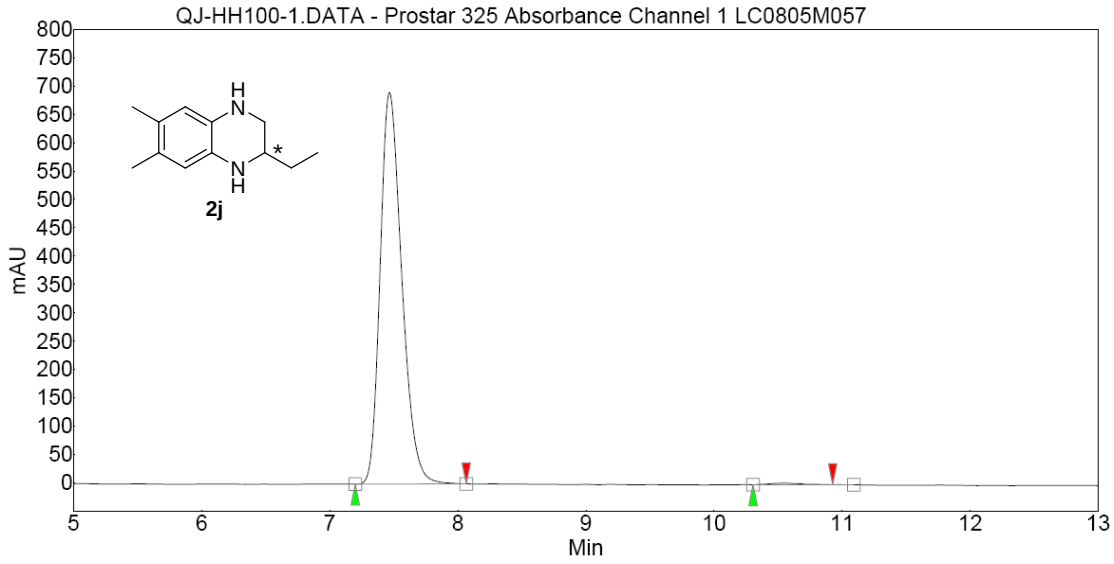

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 7.77 | 49.97 | 255.6 | 55.0 | 49.965 |
| 2 | 未知 | 10.37 | 50.03 | 170.3 | 55.1 | 50.035 |
| | | | | | | |
| Total | | | 100.00 | 425.9 | 110.1 | 100.000 |



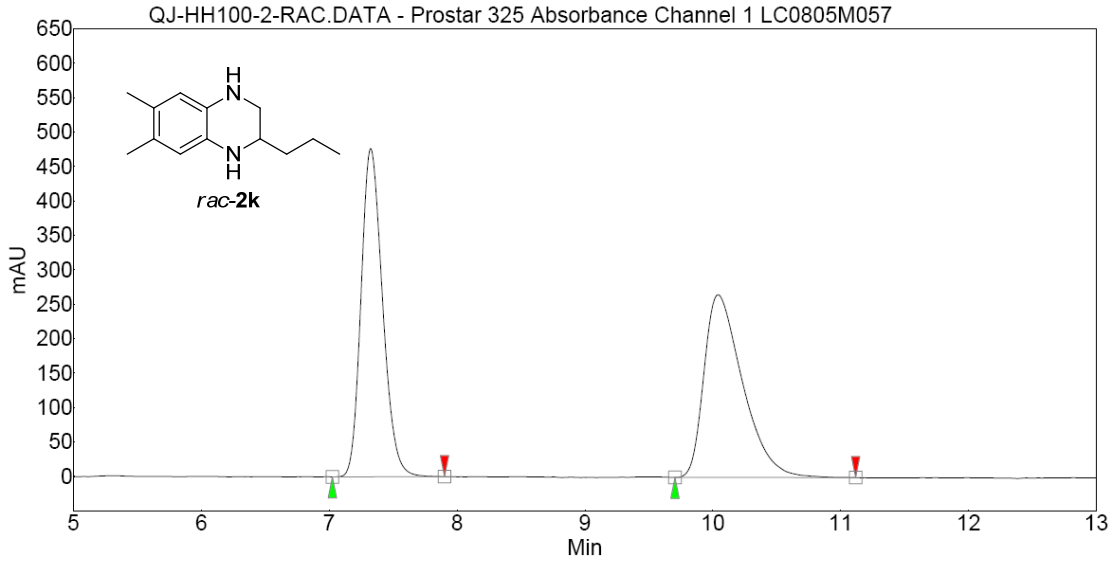

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 7.68 | 99.35 | 821.4 | 182.6 | 99.351 |
| 1 | 未知 | 10.42 | 0.65 | 4.2 | 1.2 | 0.649 |
| | | | | | | |
| Total | | | 100.00 | 825.7 | 183.8 | 100.000 |



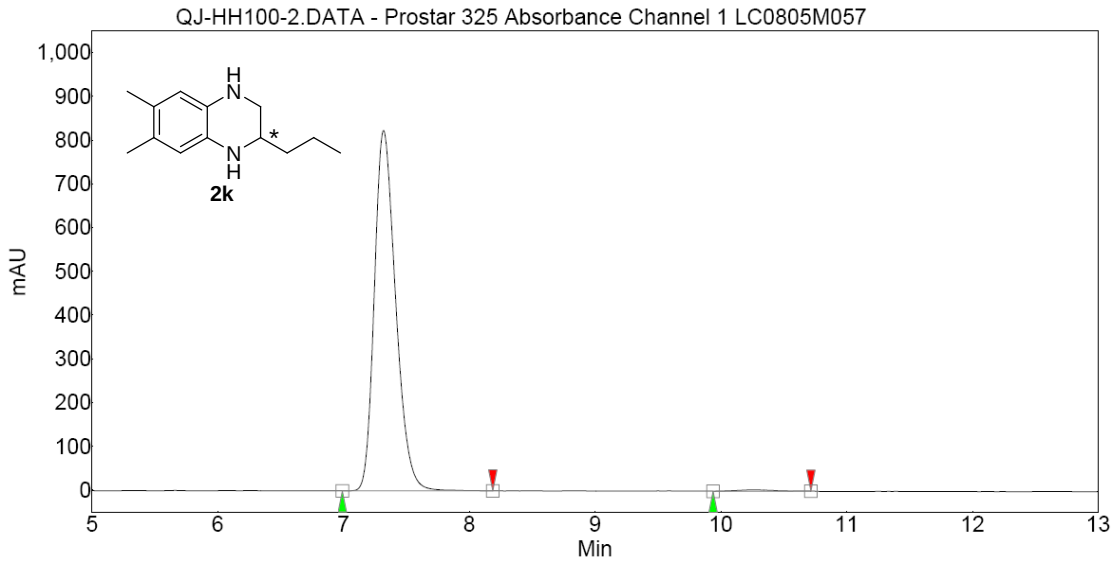

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 7.47 | 50.11 | 328.1 | 64.0 | 50.107 |
| 1 | 未知 | 10.41 | 49.89 | 199.9 | 63.7 | 49.893 |
| | | | | | | |
| Total | | | 100.00 | 527.9 | 127.8 | 100.000 |



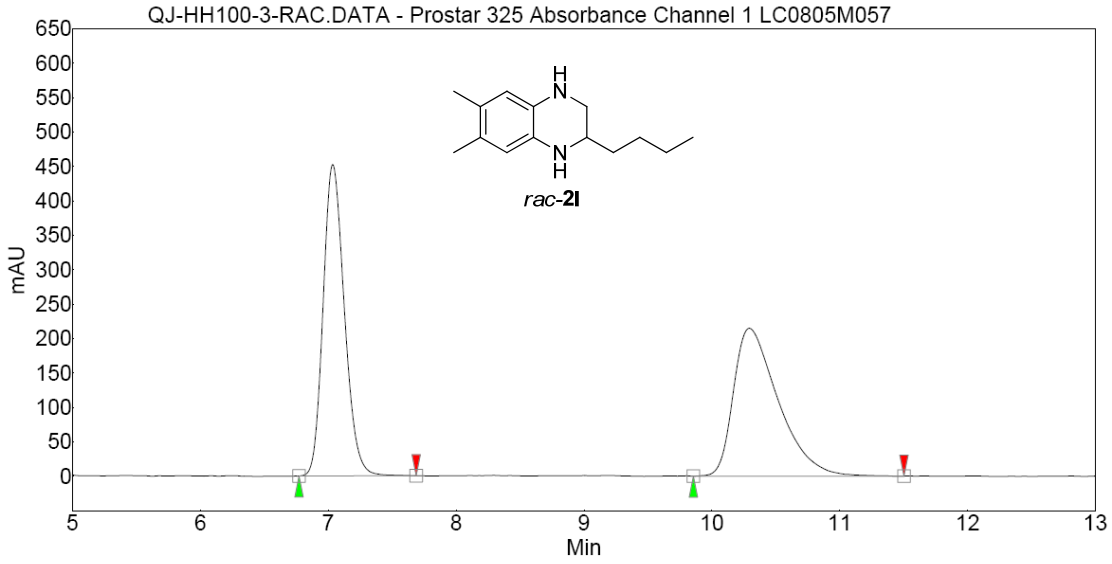

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 7.47 | 99.41 | 691.6 | 135.4 | 99.409 |
| 2 | 未知 | 10.55 | 0.59 | 2.8 | 0.8 | 0.591 |
| | | | | | | |
| Total | | | 100.00 | 694.4 | 136.2 | 100.000 |



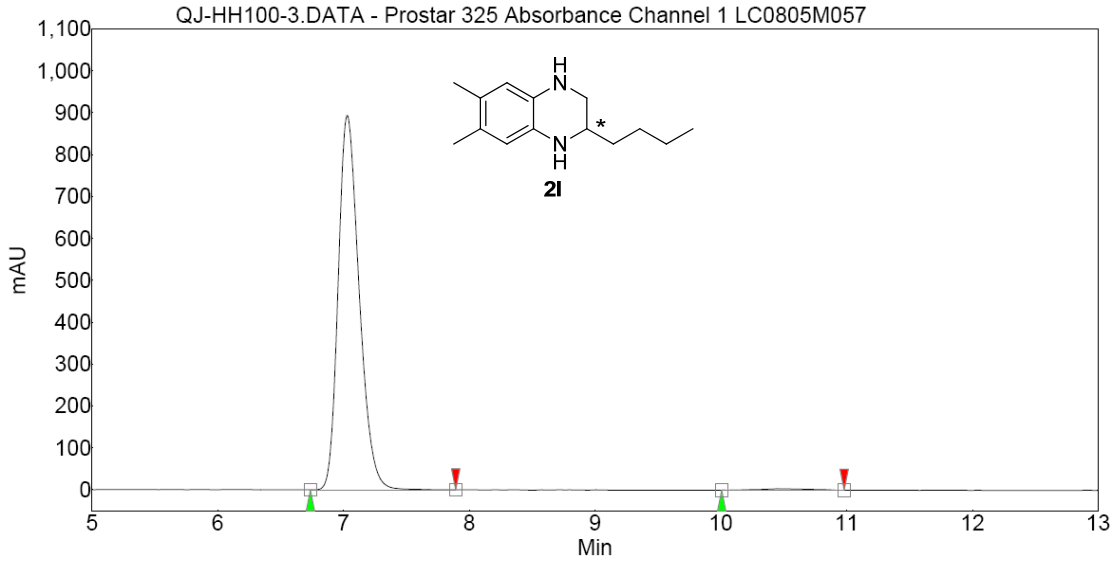

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 7.33 | 50.05 | 476.5 | 93.1 | 50.054 |
| 2 | 未知 | 10.04 | 49.95 | 265.4 | 92.9 | 49.946 |
| | | | | | | |
| Total | | | 100.00 | 742.0 | 185.9 | 100.000 |



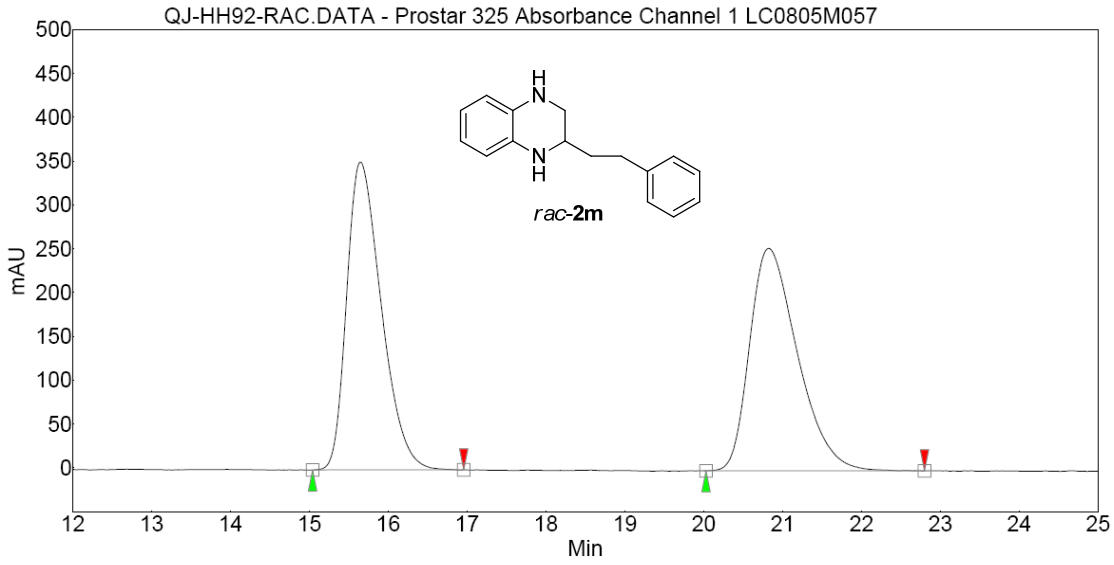

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 7.32 | 99.40 | 823.7 | 161.9 | 99.402 |
| 2 | 未知 | 10.27 | 0.60 | 3.0 | 1.0 | 0.598 |
| | | | | | | |
| Total | | | 100.00 | 826.7 | 162.9 | 100.000 |



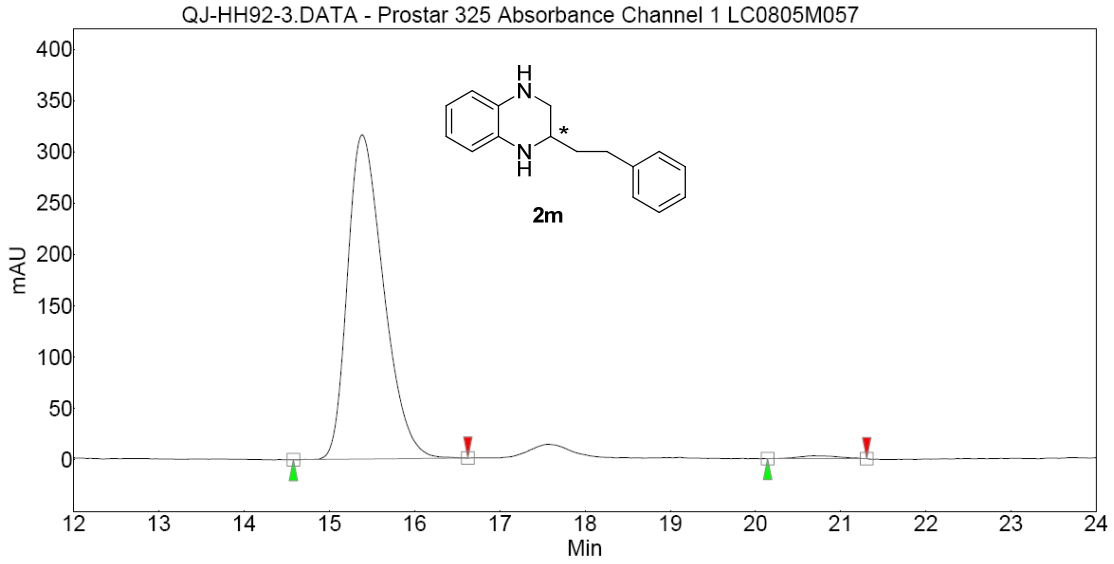

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 7.03 | 50.07 | 452.5 | 87.2 | 50.069 |
| 1 | 未知 | 10.29 | 49.93 | 214.8 | 86.9 | 49.931 |
| | | | | | | |
| Total | | | 100.00 | 667.3 | 174.1 | 100.000 |



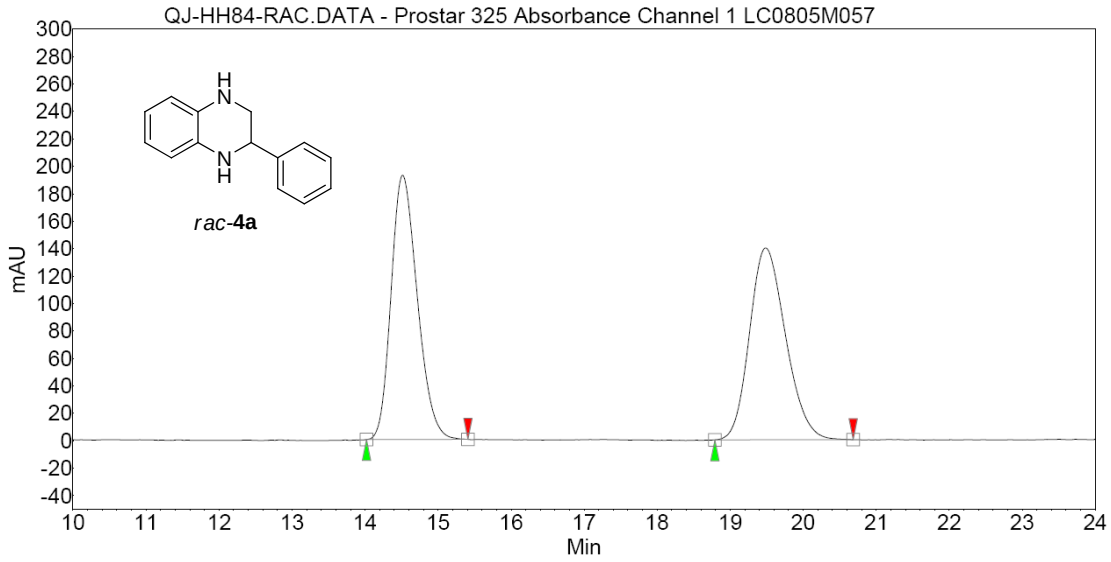

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 7.03 | 99.16 | 893.8 | 173.1 | 99.159 |
| 1 | 未知 | 10.45 | 0.84 | 3.3 | 1.5 | 0.841 |
| | | | | | | |
| Total | | | 100.00 | 897.1 | 174.6 | 100.000 |



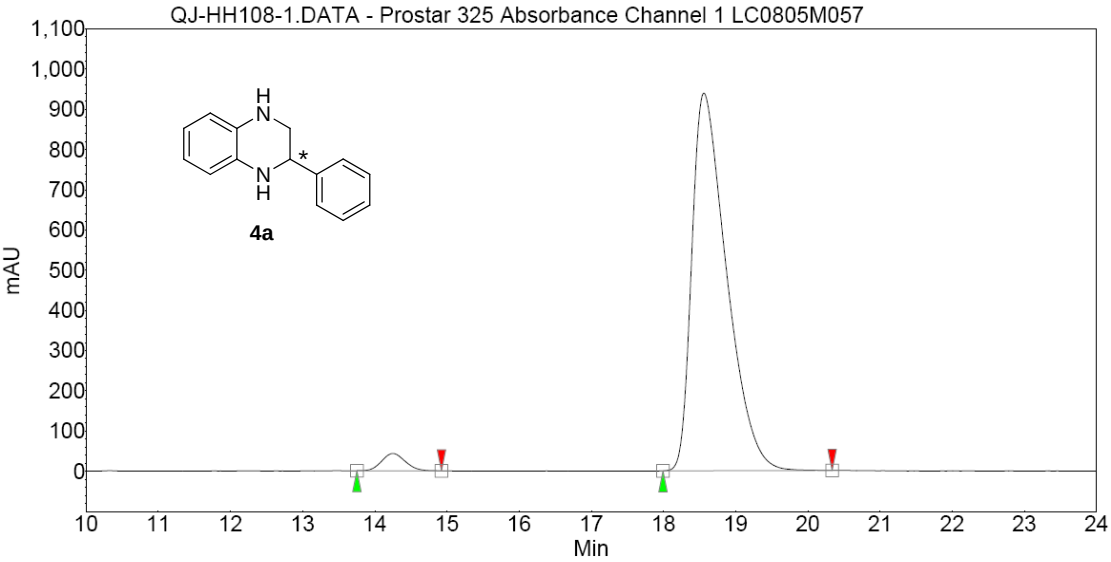

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 15.65 | 50.04 | 351.4 | 178.6 | 50.039 |
| 2 | 未知 | 20.82 | 49.96 | 253.8 | 178.3 | 49.961 |
| | | | | | | |
| Total | | | 100.00 | 605.2 | 356.9 | 100.000 |



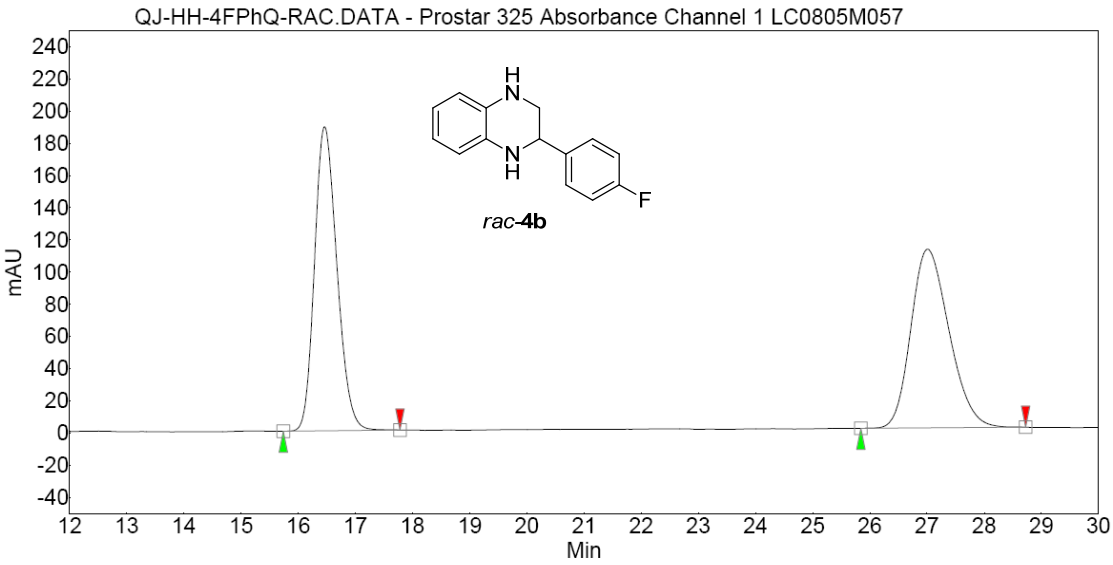

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 15.39 | 98.96 | 315.8 | 154.9 | 98.958 |
| 2 | 未知 | 20.69 | 1.04 | 2.9 | 1.6 | 1.042 |
| | | | | | | |
| Total | | | 100.00 | 318.6 | 156.5 | 100.000 |



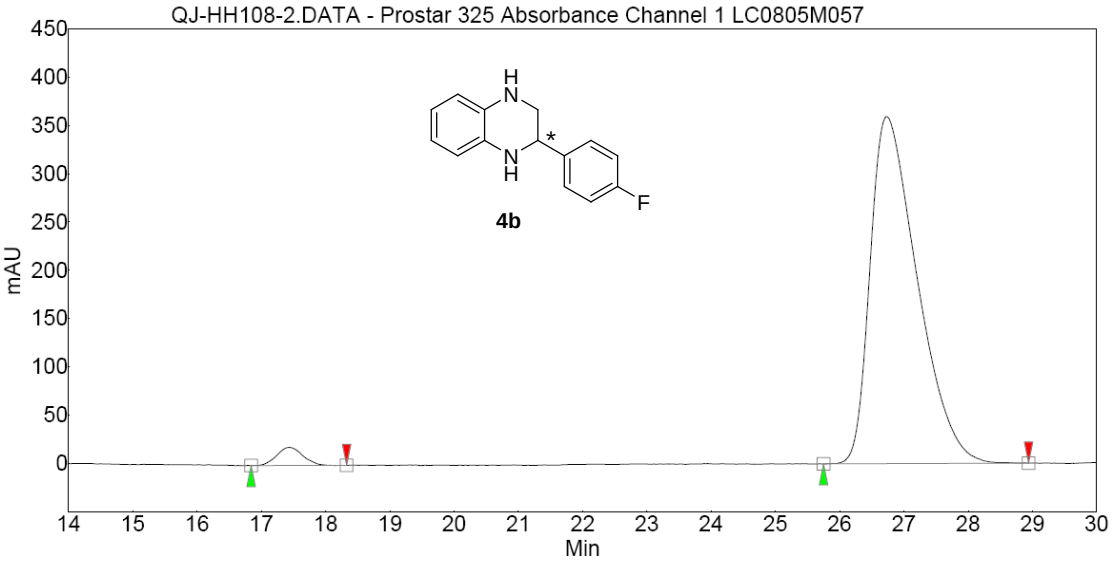

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 14.51 | 50.03 | 192.5 | 80.0 | 50.034 |
| 1 | 未知 | 19.49 | 49.97 | 139.8 | 79.9 | 49.966 |
| | | | | | | |
| Total | | | 100.00 | 332.3 | 159.9 | 100.000 |



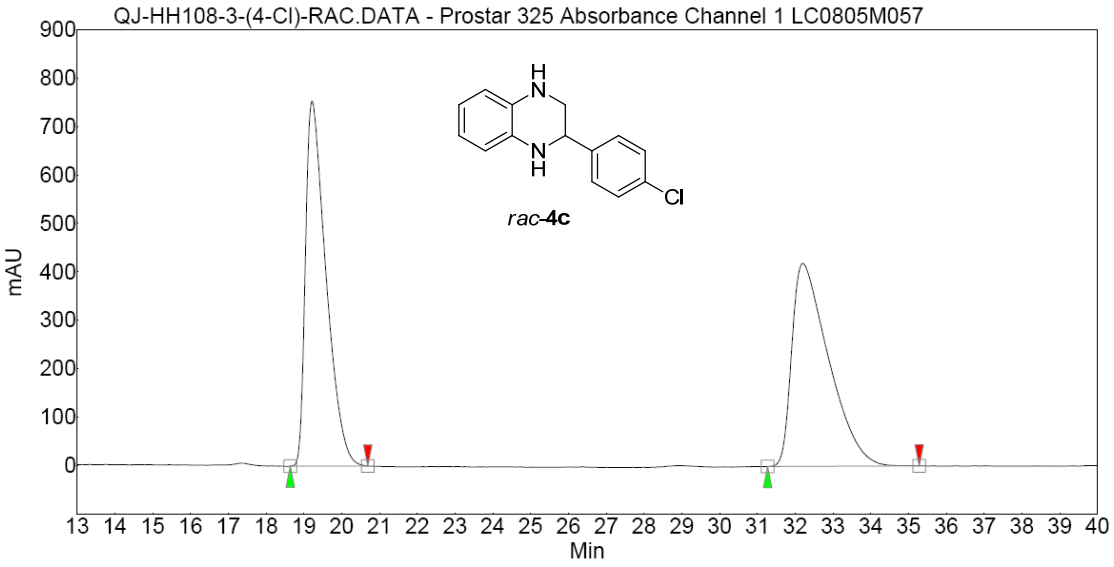

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 14.25 | 3.03 | 43.2 | 16.4 | 3.028 |
| 2 | 未知 | 18.56 | 96.97 | 939.0 | 523.6 | 96.972 |
| | | | | | | |
| Total | | | 100.00 | 982.2 | 540.0 | 100.000 |



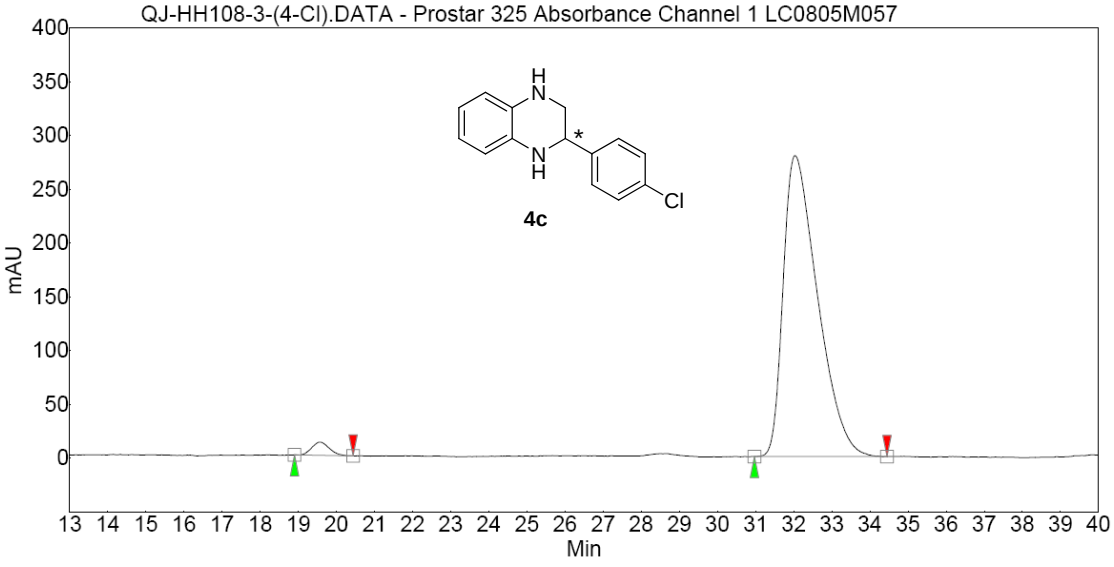

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 16.46 | 50.02 | 189.0 | 86.0 | 50.020 |
| 2 | 未知 | 27.01 | 49.98 | 111.0 | 85.9 | 49.980 |
| | | | | | | |
| Total | | | 100.00 | 300.1 | 171.9 | 100.000 |



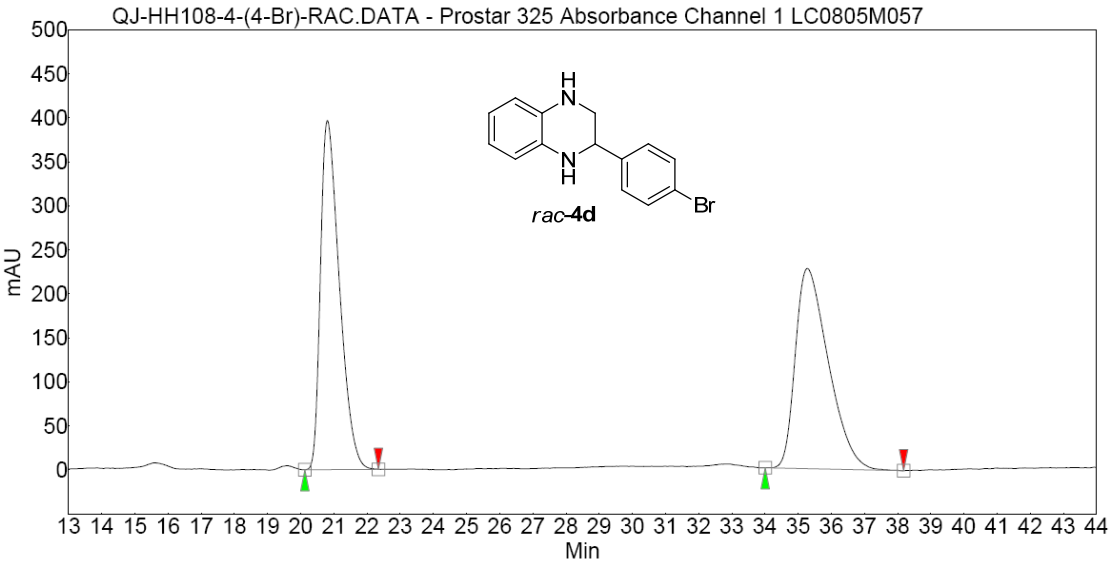

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 17.43 | 2.81 | 18.7 | 8.8 | 2.807 |
| 2 | 未知 | 26.73 | 97.19 | 359.4 | 304.5 | 97.193 |
| | | | | | | |
| Total | | | 100.00 | 378.1 | 313.3 | 100.000 |



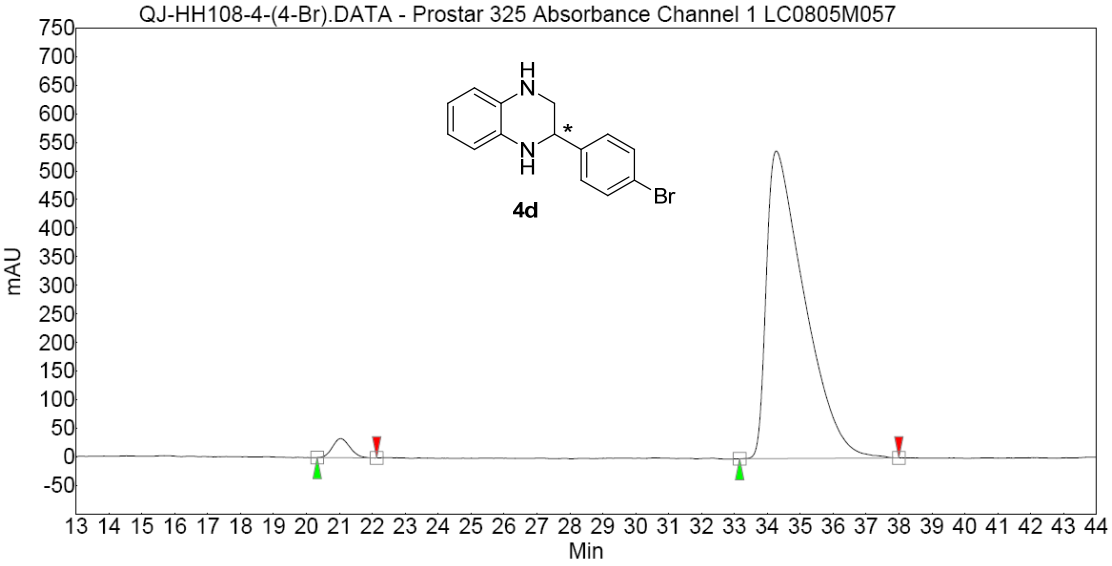

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 19.21 | 50.08 | 753.9 | 473.9 | 50.078 |
| 2 | 未知 | 32.20 | 49.92 | 419.4 | 472.4 | 49.922 |
| | | | | | | |
| Total | | | 100.00 | 1173.3 | 946.2 | 100.000 |



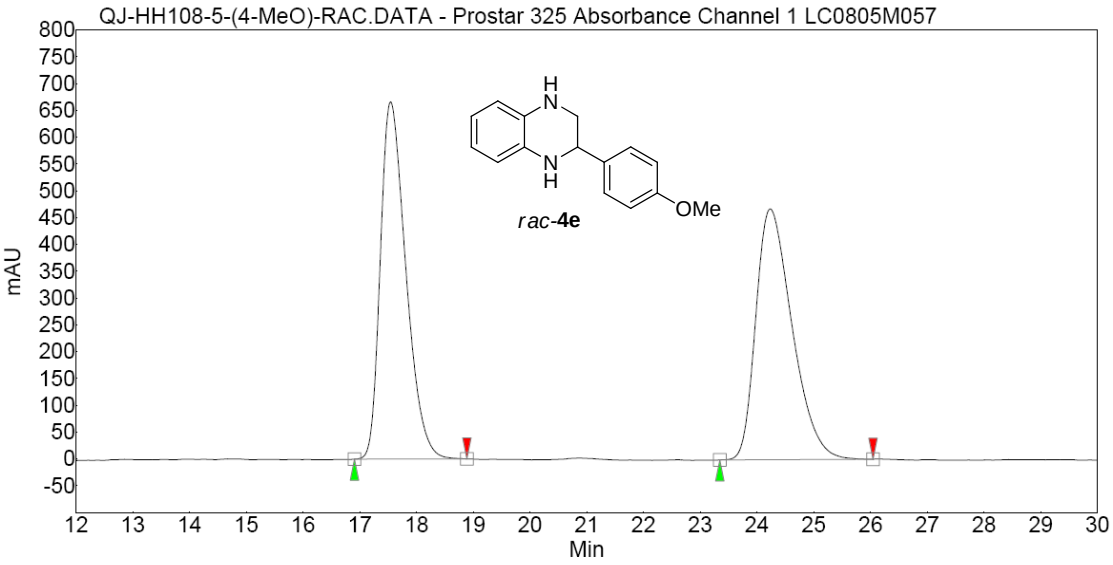

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 19.59 | 2.19 | 12.2 | 6.5 | 2.186 |
| 1 | 未知 | 32.03 | 97.81 | 279.8 | 291.9 | 97.814 |
| | | | | | | |
| Total | | | 100.00 | 292.1 | 298.4 | 100.000 |



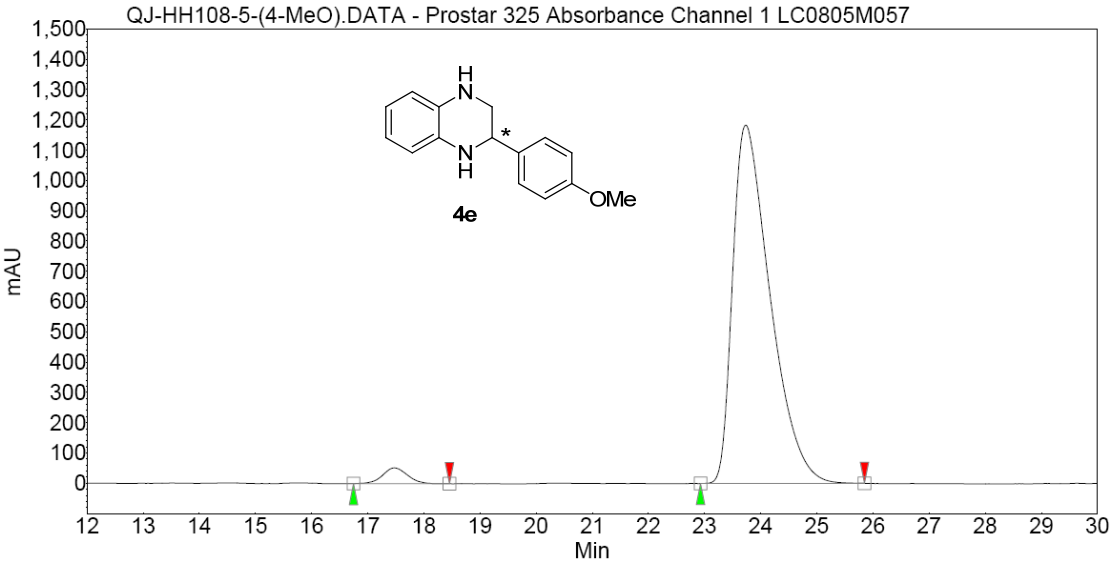

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 20.81 | 49.97 | 396.8 | 262.4 | 49.971 |
| 2 | 未知 | 35.27 | 50.03 | 227.5 | 262.7 | 50.029 |
| | | | | | | |
| Total | | | 100.00 | 624.3 | 525.1 | 100.000 |



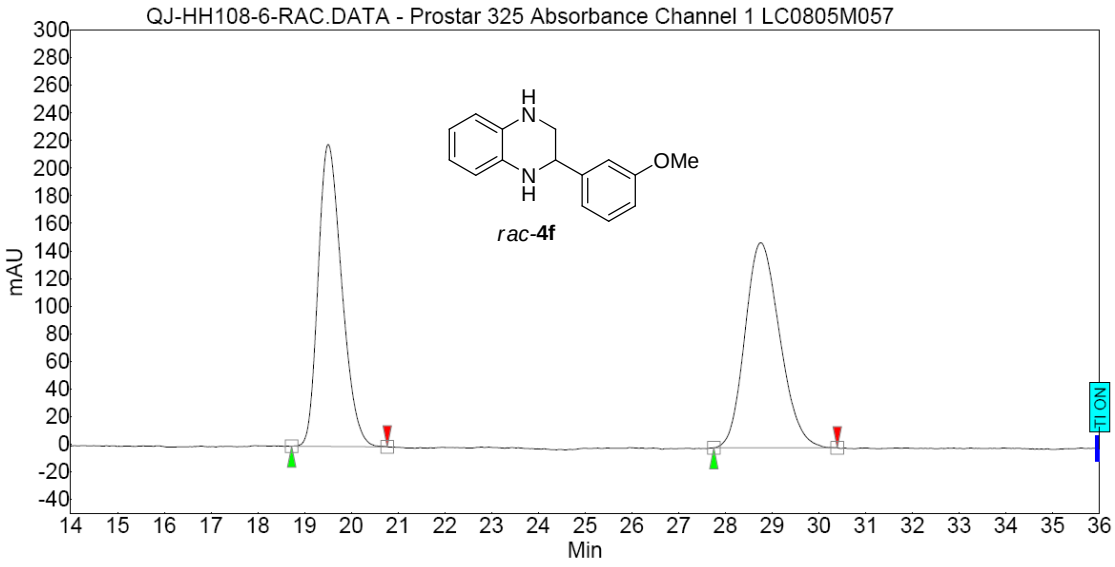

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 21.04 | 2.77 | 33.5 | 20.5 | 2.768 |
| 2 | 未知 | 34.27 | 97.23 | 538.2 | 719.6 | 97.232 |
| | | | | | | |
| Total | | | 100.00 | 571.8 | 740.1 | 100.000 |



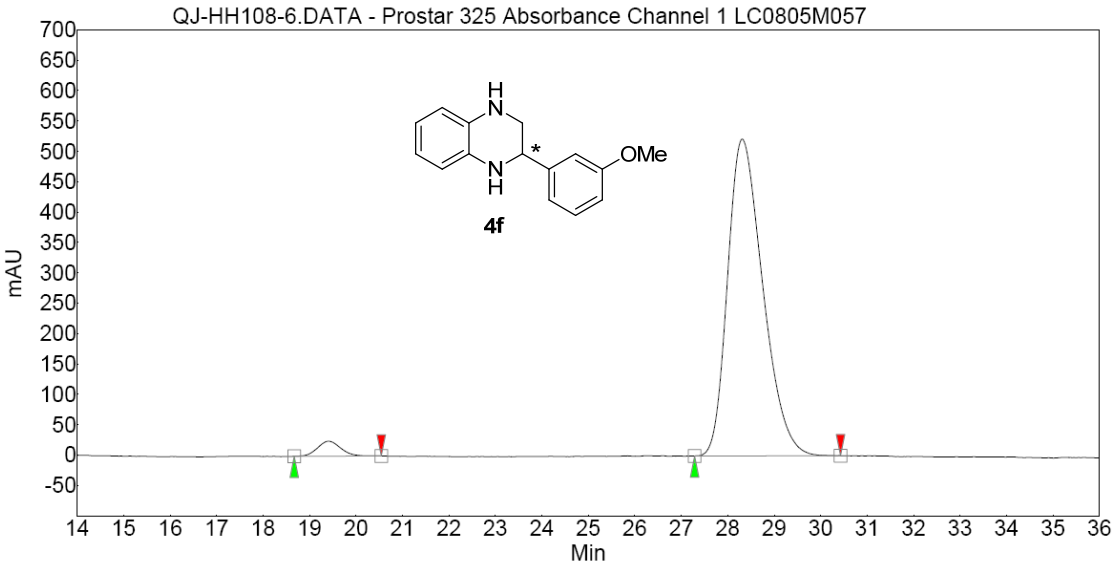

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 17.54 | 50.07 | 666.1 | 346.8 | 50.069 |
| 2 | 未知 | 24.23 | 49.93 | 467.6 | 345.8 | 49.931 |
| | | | | | | |
| Total | | | 100.00 | 1133.7 | 692.6 | 100.000 |



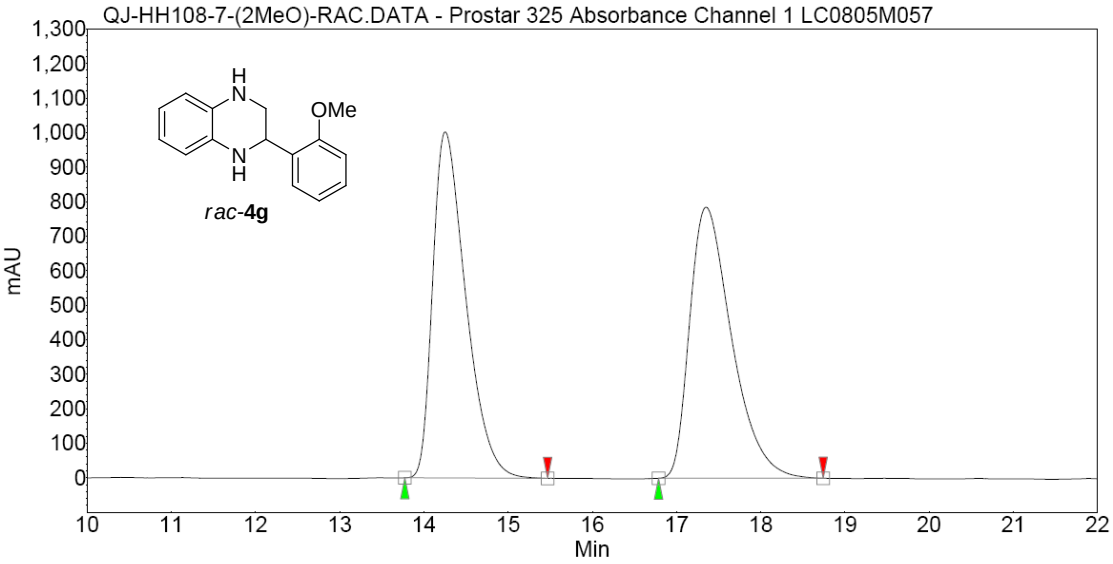

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 17.47 | 2.81 | 51.9 | 26.4 | 2.805 |
| 1 | 未知 | 23.73 | 97.19 | 1183.3 | 913.9 | 97.195 |
| | | | | | | |
| Total | | | 100.00 | 1235.2 | 940.2 | 100.000 |



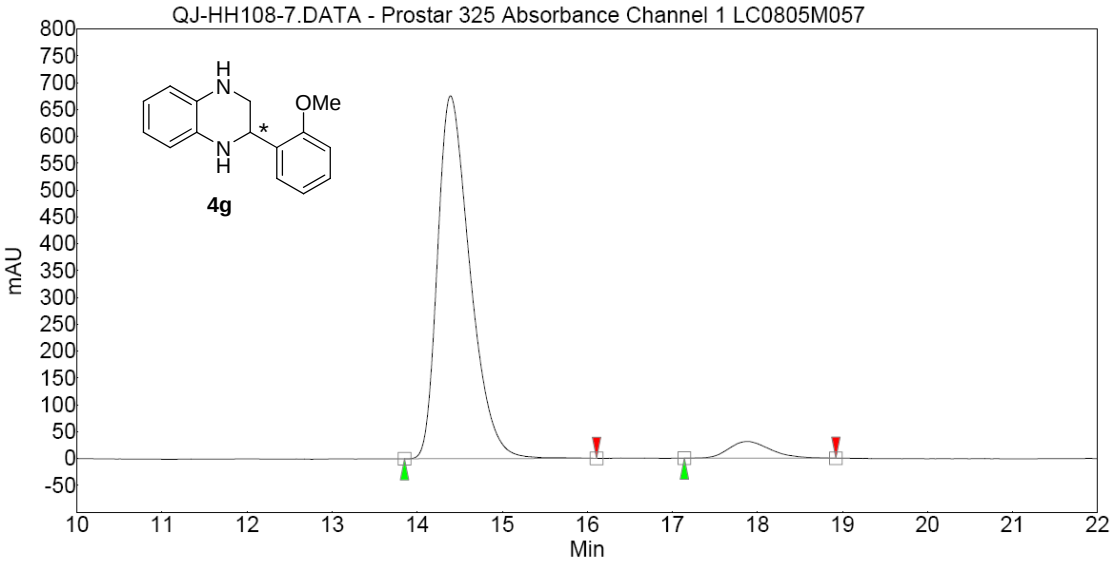

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 19.51 | 50.02 | 218.7 | 128.1 | 50.016 |
| 2 | 未知 | 28.75 | 49.98 | 148.6 | 128.1 | 49.984 |
| | | | | | | |
| Total | | | 100.00 | 367.3 | 256.2 | 100.000 |



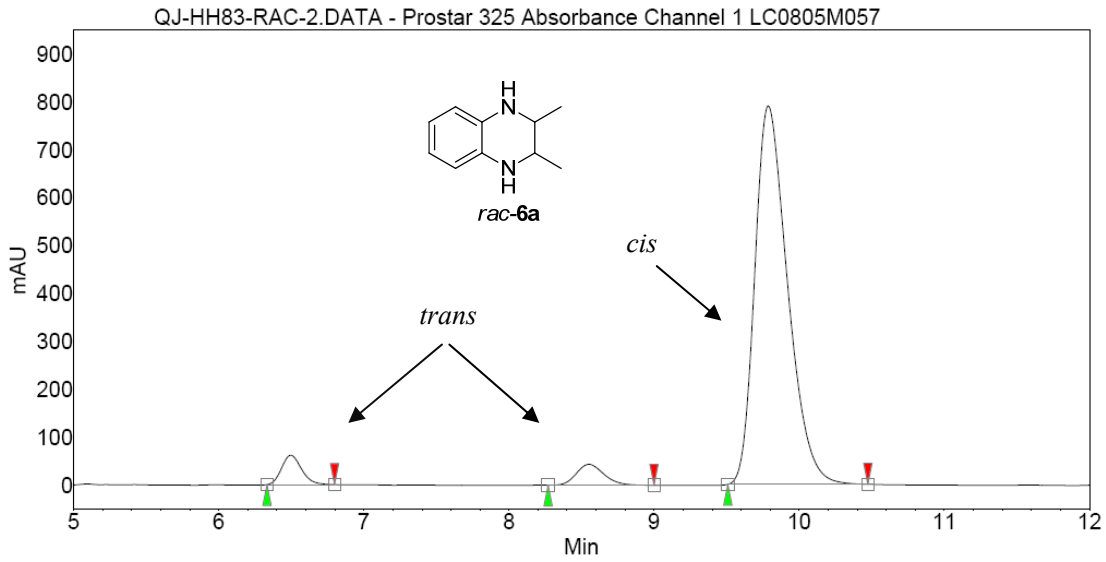

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 19.41 | 3.01 | 24.5 | 14.2 | 3.015 |
| 2 | 未知 | 28.31 | 96.99 | 521.6 | 456.8 | 96.985 |
| | | | | | | |
| Total | | | 100.00 | 546.2 | 471.0 | 100.000 |



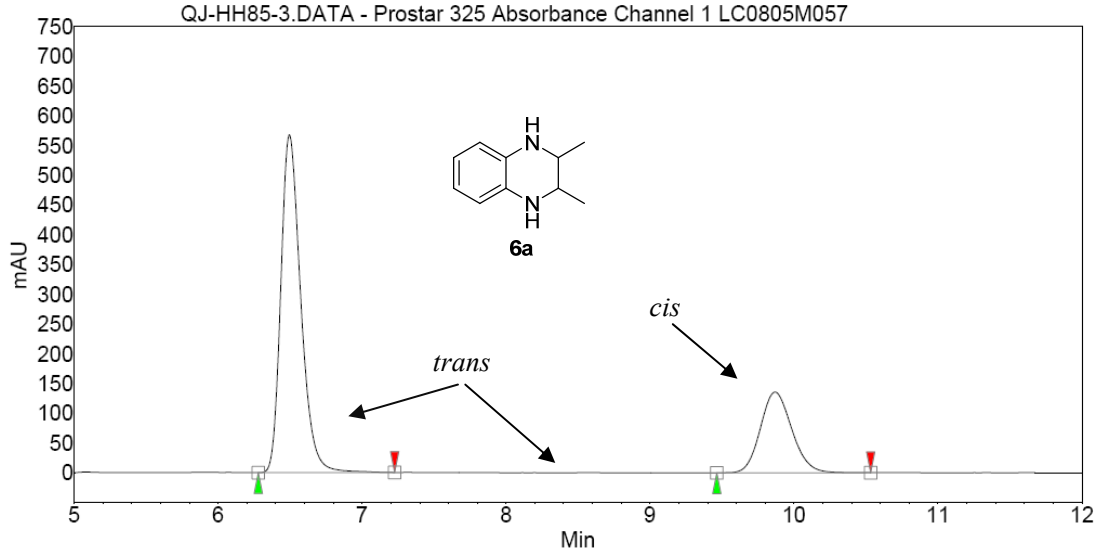

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 14.25 | 50.07 | 1002.8 | 455.0 | 50.069 |
| 2 | 未知 | 17.35 | 49.93 | 785.4 | 453.7 | 49.931 |
| | | | | | | |
| Total | | | 100.00 | 1788.2 | 908.7 | 100.000 |



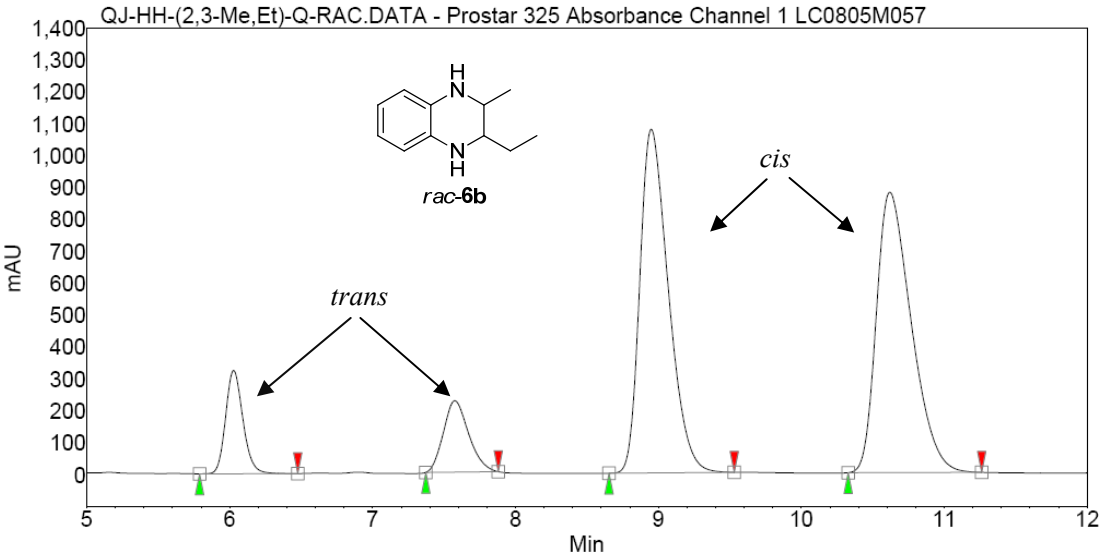

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 14.39 | 94.40 | 675.7 | 298.6 | 94.399 |
| 1 | 未知 | 17.89 | 5.60 | 31.2 | 17.7 | 5.601 |
| | | | | | | |
| Total | | | 100.00 | 706.9 | 316.4 | 100.000 |



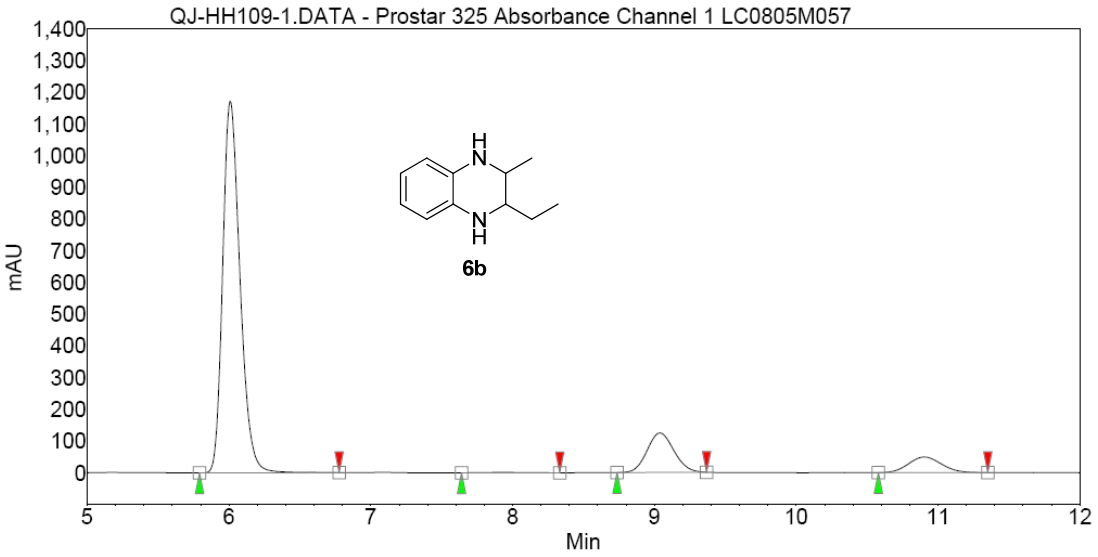

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 6.49 | 4.31 | 61.3 | 9.7 | 4.311 |
| 1 | 未知 | 8.55 | 4.25 | 43.6 | 9.6 | 4.252 |
| 3 | 未知 | 9.79 | 91.44 | 789.6 | 206.6 | 91.437 |
| | | | | | | |
| Total | | | 100.00 | 894.5 | 226.0 | 100.000 |



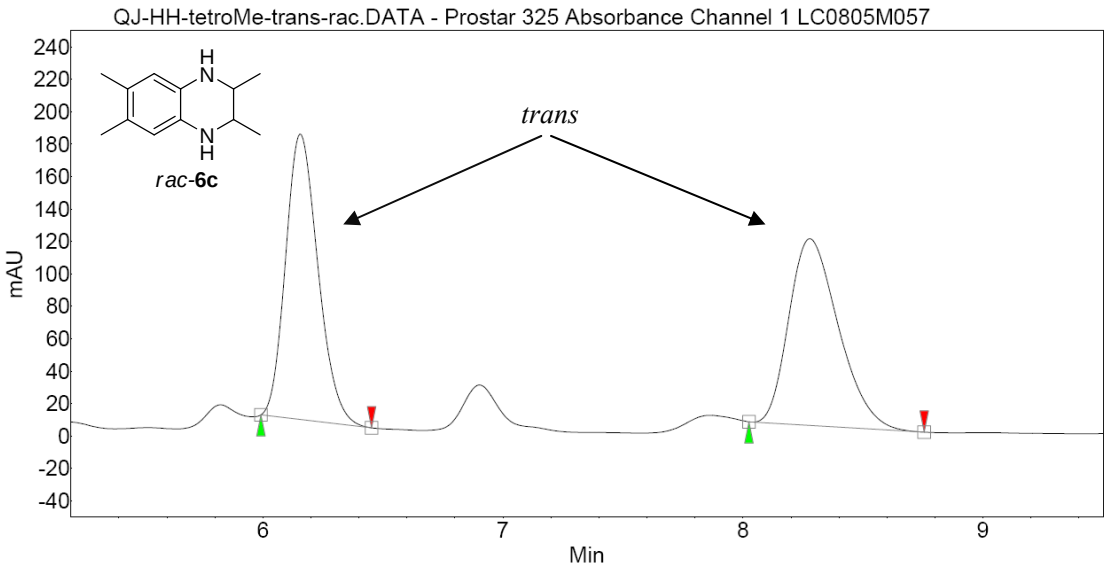

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 6.49 | 72.62 | 567.8 | 91.0 | 72.620 |
| 2 | 未知 | 9.87 | 27.38 | 135.6 | 34.3 | 27.380 |
| | | | | | | |
| Total | | | 100.00 | 703.4 | 125.3 | 100.000 |



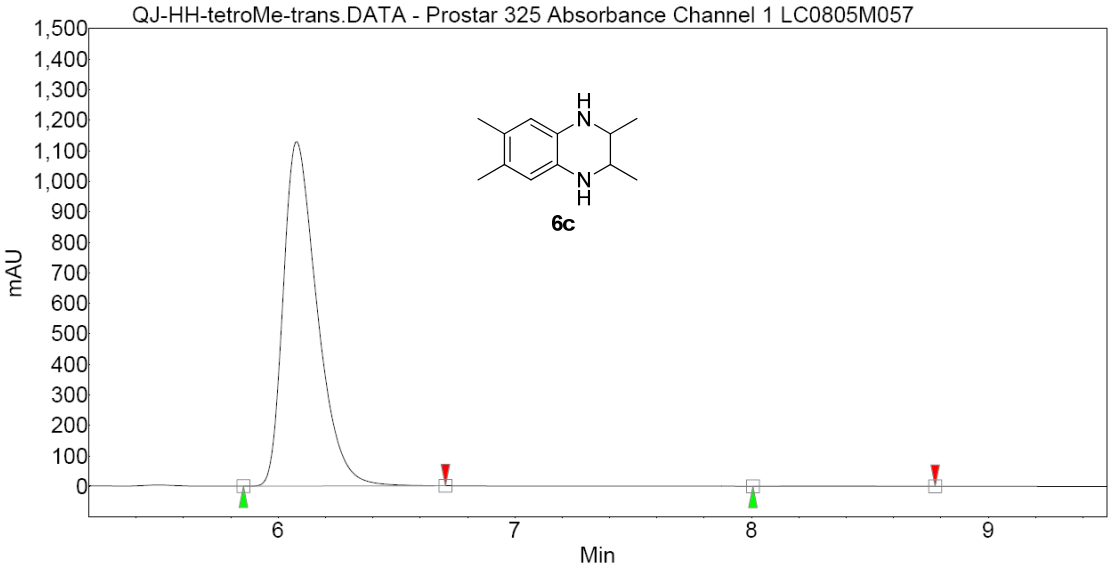

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 6.03 | 7.72 | 324.3 | 45.5 | 7.725 |
| 4 | 未知 | 7.57 | 7.79 | 223.9 | 45.9 | 7.785 |
| 2 | 未知 | 8.95 | 42.30 | 1077.1 | 249.2 | 42.299 |
| 3 | 未知 | 10.62 | 42.19 | 879.0 | 248.5 | 42.191 |
| | | | | | | |
| Total | | | 100.00 | 2504.2 | 589.0 | 100.000 |



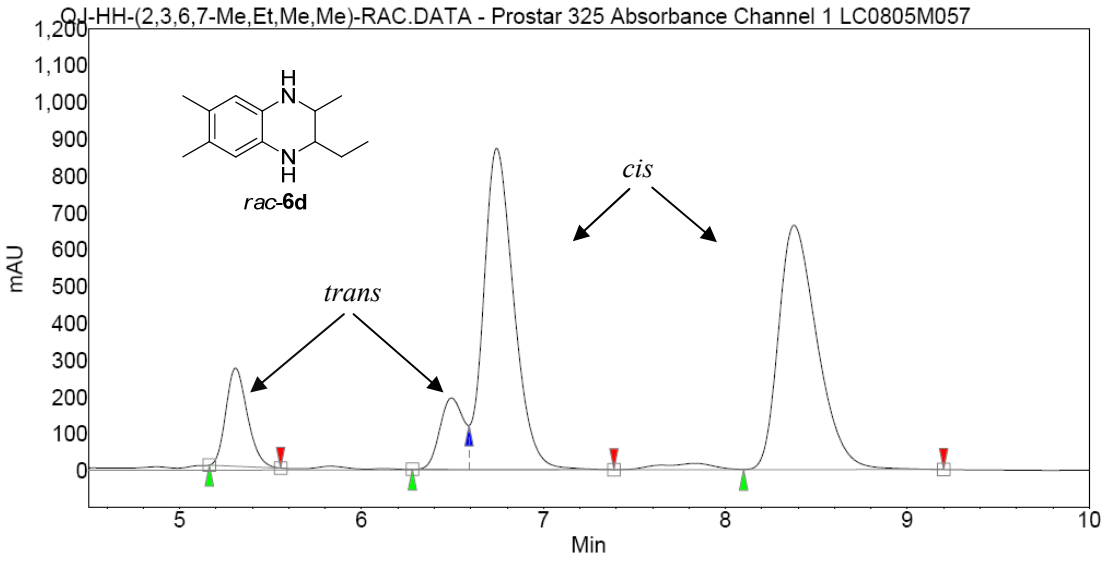

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 3 | 未知 | 6.01 | 80.17 | 1172.2 | 165.6 | 80.174 |
| 4 | 未知 | 7.94 | 0.16 | 1.2 | 0.3 | 0.161 |
| 1 | 未知 | 9.04 | 13.24 | 124.5 | 27.3 | 13.237 |
| 2 | 未知 | 10.90 | 6.43 | 49.3 | 13.3 | 6.429 |
| | | | | | | |
| Total | | | 100.00 | 1347.2 | 206.5 | 100.000 |



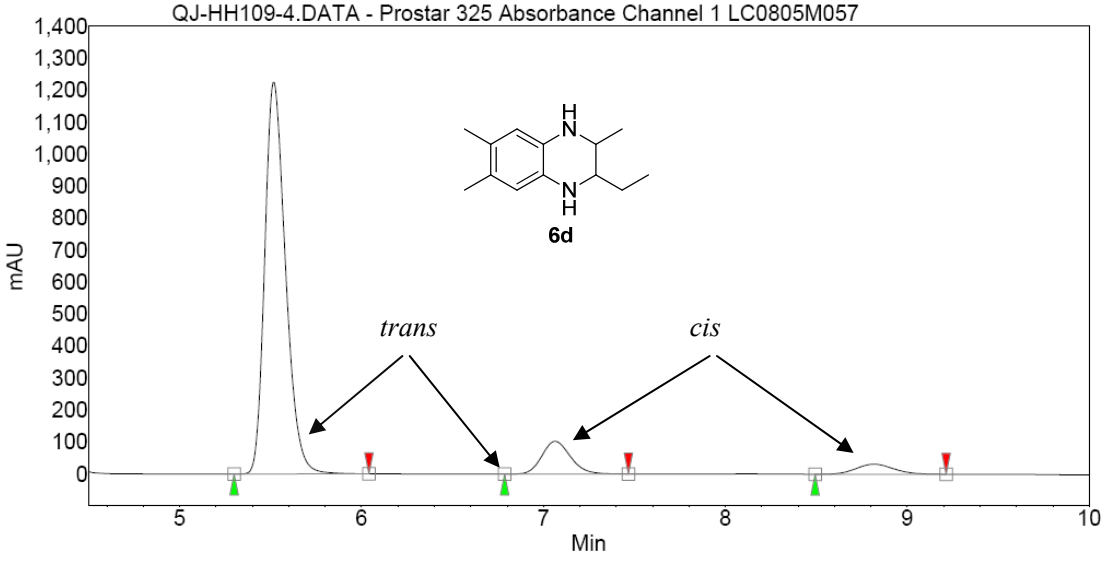

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 6.15 | 50.01 | 176.1 | 27.6 | 50.006 |
| 1 | 未知 | 8.28 | 49.99 | 115.2 | 27.5 | 49.994 |
| | | | | | | |
| Total | | | 100.00 | 291.3 | 55.1 | 100.000 |



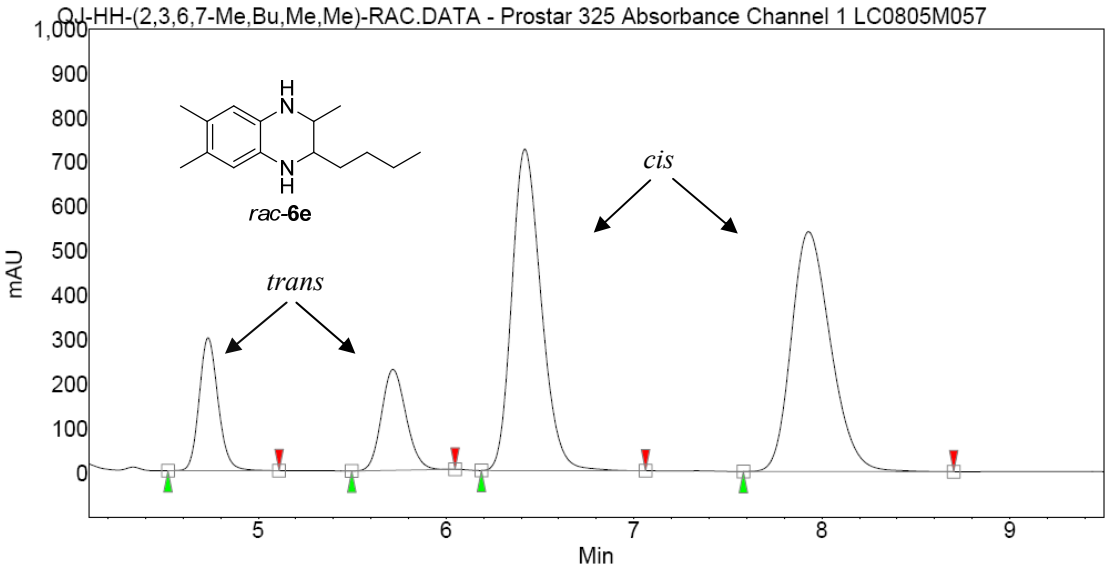

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 6.08 | 99.87 | 1128.2 | 187.2 | 99.870 |
| 2 | 未知 | 8.35 | 0.13 | 0.9 | 0.2 | 0.130 |
| | | | | | | |
| Total | | | 100.00 | 1129.1 | 187.4 | 100.000 |



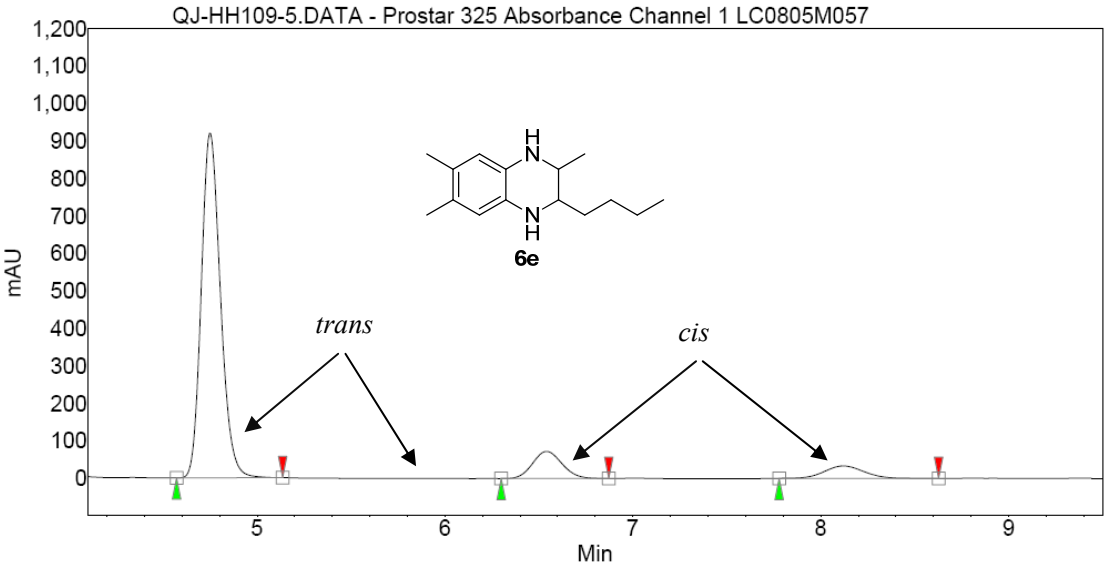

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 4 | 未知 | 5.31 | 9.17 | 266.8 | 36.4 | 9.172 |
| 2 | 未知 | 6.49 | 7.41 | 193.9 | 29.4 | 7.405 |
| 3 | 未知 | 6.74 | 42.19 | 872.3 | 167.5 | 42.190 |
| 1 | 未知 | 8.38 | 41.23 | 663.9 | 163.7 | 41.233 |
| | | | | | | |
| Total | | | 100.00 | 1997.0 | 397.0 | 100.000 |



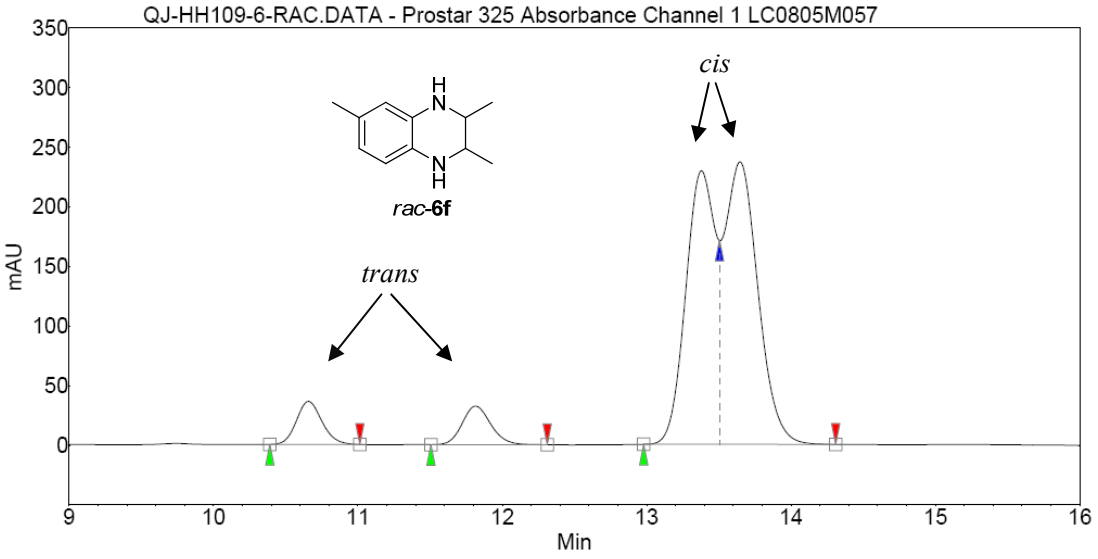

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 3 | 未知 | 5.52 | 86.13 | 1224.7 | 162.5 | 86.135 |
| 1 | 未知 | 7.07 | 9.86 | 102.2 | 18.6 | 9.859 |
| 2 | 未知 | 8.81 | 4.01 | 31.4 | 7.6 | 4.006 |
| | | | | | | |
| Total | | | 100.00 | 1358.3 | 188.6 | 100.000 |



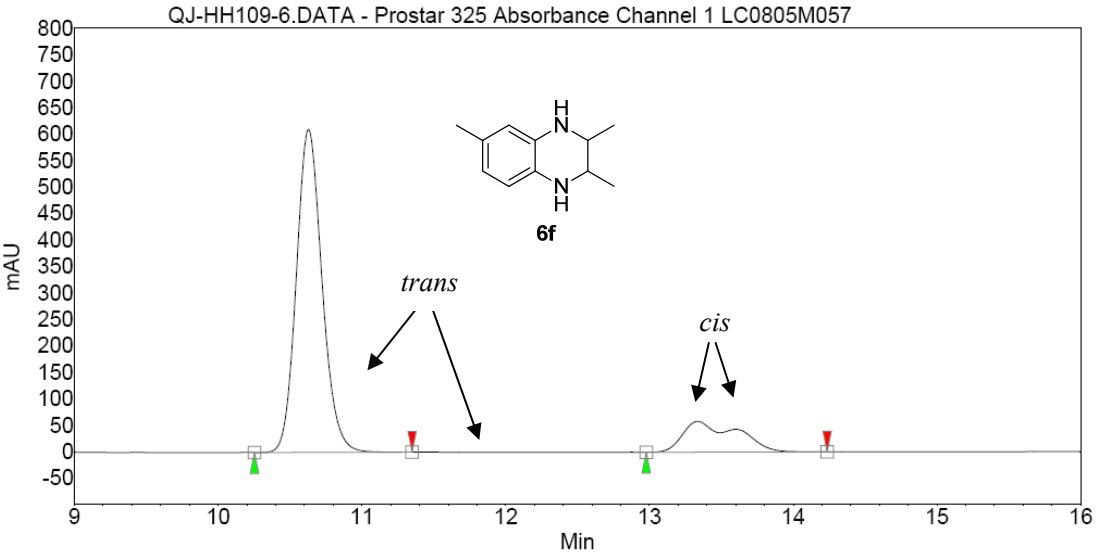

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 4.73 | 10.58 | 300.0 | 35.1 | 10.578 |
| 2 | 未知 | 5.72 | 10.38 | 227.2 | 34.4 | 10.379 |
| 3 | 未知 | 6.42 | 39.56 | 724.4 | 131.1 | 39.563 |
| 4 | 未知 | 7.93 | 39.48 | 540.3 | 130.8 | 39.480 |
| | | | | | | |
| Total | | | 100.00 | 1792.0 | 331.4 | 100.000 |



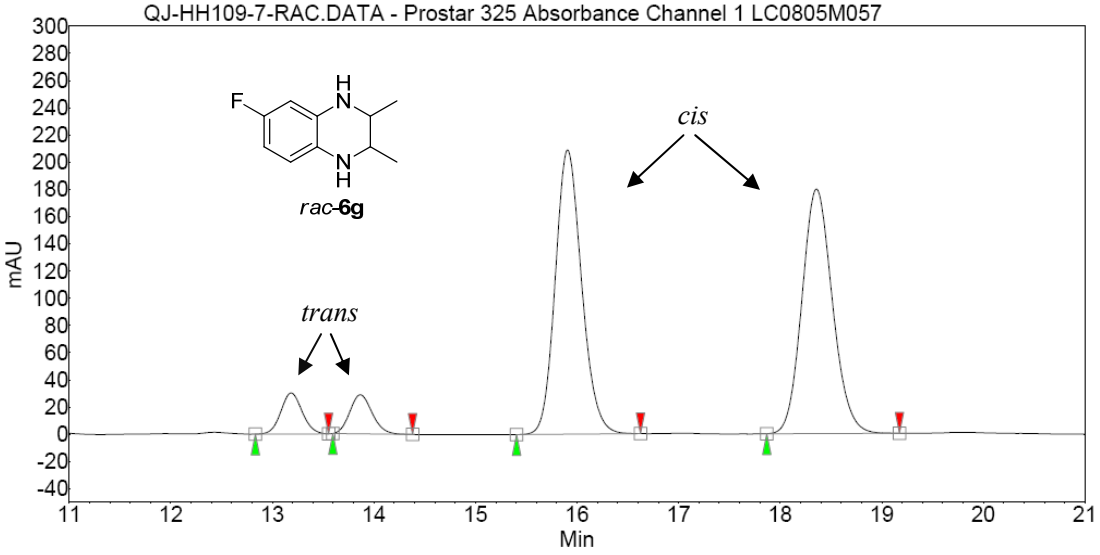

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 3 | 未知 | 4.75 | 83.62 | 920.0 | 108.7 | 83.618 |
| 1 | 未知 | 6.54 | 10.12 | 72.6 | 13.2 | 10.124 |
| 2 | 未知 | 8.12 | 6.26 | 33.2 | 8.1 | 6.258 |
| | | | | | | |
| Total | | | 100.00 | 1025.8 | 130.0 | 100.000 |



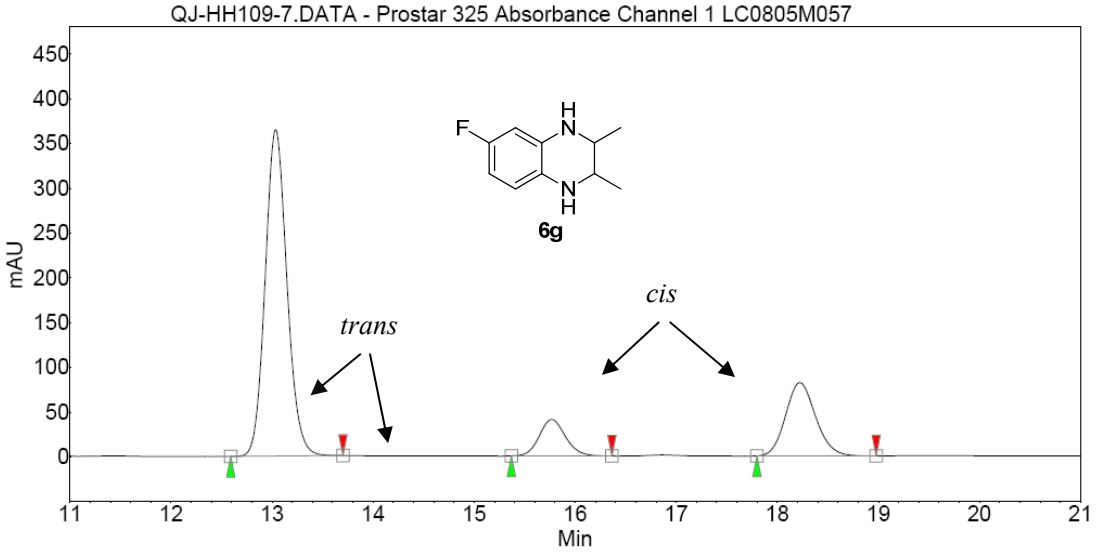

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 2 | 未知 | 10.66 | 5.58 | 36.1 | 7.4 | 5.581 |
| 1 | 未知 | 11.81 | 5.56 | 32.3 | 7.4 | 5.564 |
| 3 | 未知 | 13.38 | 40.62 | 229.4 | 53.9 | 40.619 |
| 4 | 未知 | 13.65 | 48.24 | 237.0 | 64.0 | 48.236 |
| | | | | | | |
| Total | | | 100.00 | 534.8 | 132.6 | 100.000 |



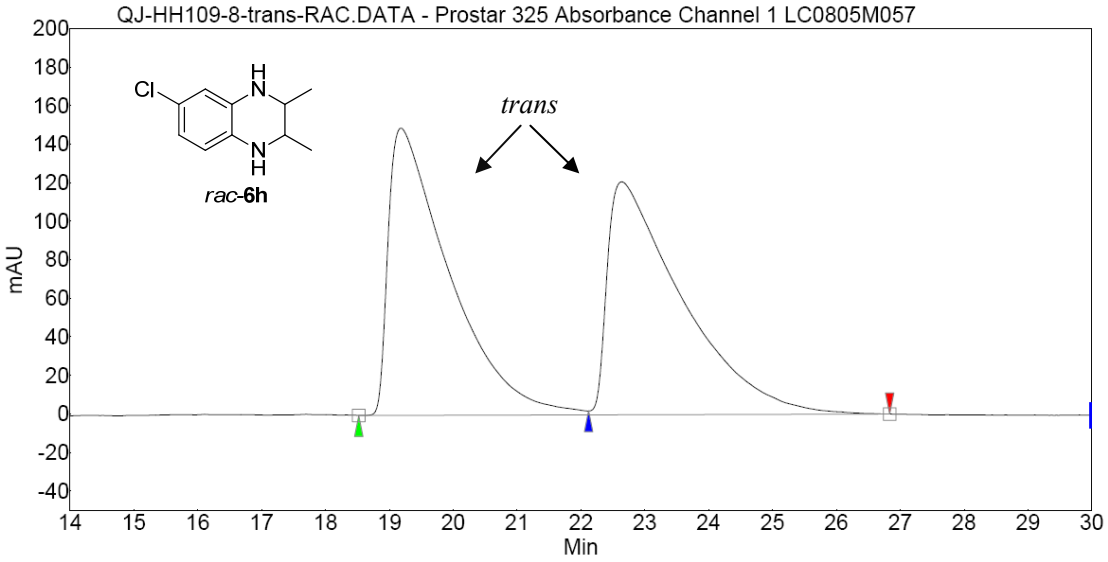

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 10.63 | 83.30 | 610.4 | 126.6 | 83.303 |
| 2 | 未知 | 13.33 | 16.70 | 58.1 | 25.4 | 16.697 |
| | | | | | | |
| Total | | | 100.00 | 668.6 | 152.0 | 100.000 |



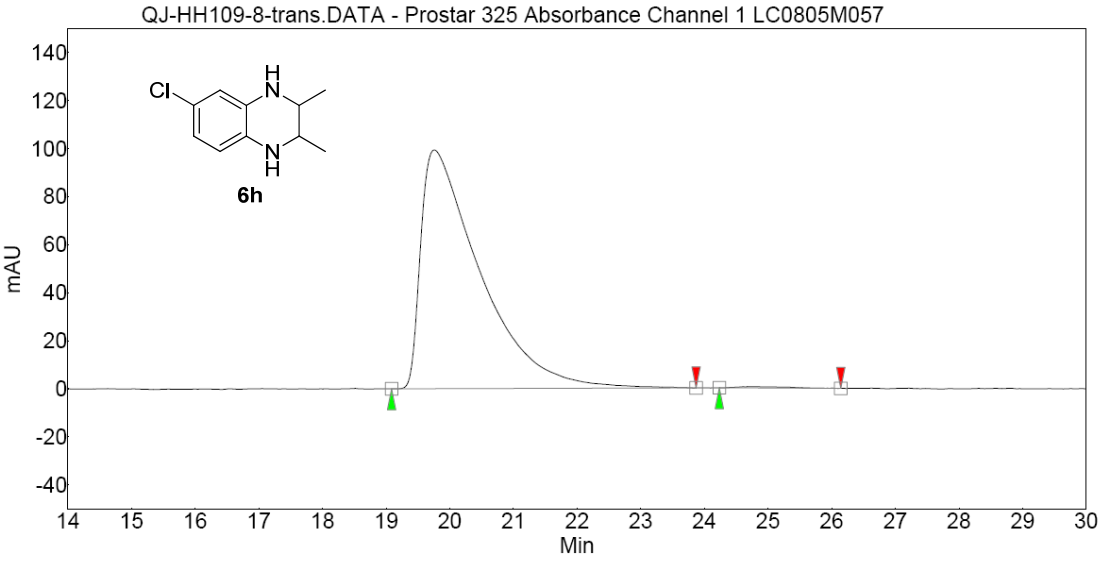

| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 13.19 | 5.26 | 30.2 | 7.4 | 5.256 |
| 2 | 未知 | 13.87 | 5.22 | 28.7 | 7.3 | 5.222 |
| 3 | 未知 | 15.91 | 44.90 | 208.9 | 62.9 | 44.899 |
| 4 | 未知 | 18.36 | 44.62 | 179.7 | 62.5 | 44.623 |
| | | | | | | |
| Total | | | 100.00 | 447.5 | 140.1 | 100.000 |




| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 3 | 未知 | 13.03 | 69.31 | 364.4 | 91.1 | 69.307 |
| 1 | 未知 | 15.77 | 9.27 | 40.7 | 12.2 | 9.265 |
| 2 | 未知 | 18.22 | 21.43 | 81.8 | 28.2 | 21.428 |
| | | | | | | |
| Total | | | 100.00 | 486.9 | 131.4 | 100.000 |




| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 19.18 | 50.11 | 149.1 | 164.7 | 50.105 |
| 2 | 未知 | 22.64 | 49.89 | 120.9 | 164.0 | 49.895 |
| | | | | | | |
| Total | | | 100.00 | 270.0 | 328.8 | 100.000 |




| Index | 文件名 | 时间 [Min] | 数量 [% 面积] | 高度 [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | 未知 | 19.75 | 99.51 | 99.4 | 107.0 | 99.513 |
| 2 | 未知 | 24.75 | 0.49 | 0.5 | 0.5 | 0.487 |
| | | | | | | |
| Total | | | 100.00 | 100.0 | 107.5 | 100.000 |