Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information for

Rhodium-catalyzed one-pot tandem reductive amination/asymmetric transfer hydrogenation of quinoxaline-2-carbaldehydes and anilines for the efficient synthesis of chiral vicinal diamines

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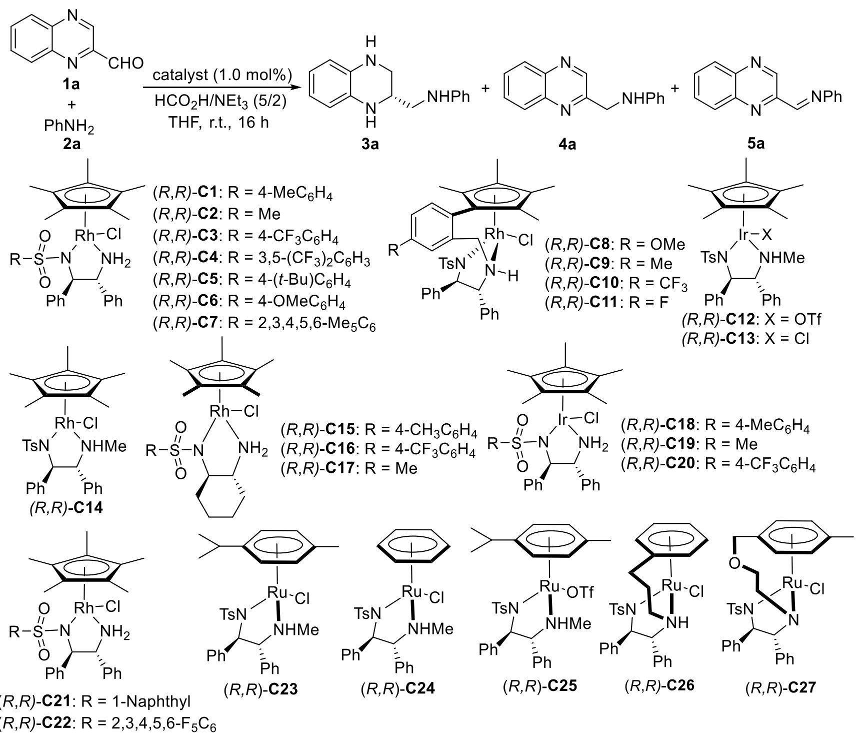
1. General information

Unless otherwise noted, all experiments were carried out under nitrogen atmosphere and all commercially available chemicals including organic solvents were used as received from Aldrich, Acros or Strem without further purification. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Model Advance DMX 400 Spectrometer (^{1}H 400 MHz and ^{13}C{^{1}H} 101 MHz, respectively), Bruker Model Advance DMX 500 Spectrometer (^{1}H 500 MHz and ^{13}C{^{1}H} 126 MHz, respectively) or Bruker Model Advance DMX 600 Spectrometer (^{1}H 600 MHz and ^{13}C{^{1}H} 151 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. Melting points were measured on X-4 melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200-300 mesh). All the quinoxaline-2-carbaldehyde substrates were prepared according to the literature methods.[1]

2. Optimization of reaction conditions

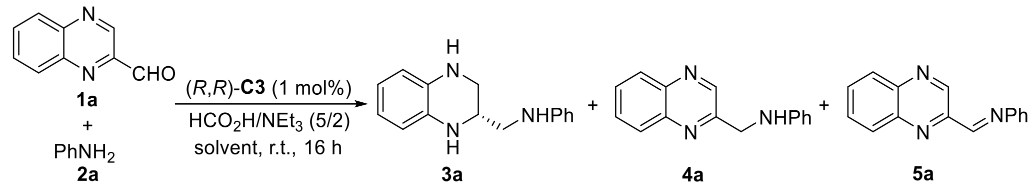
Table S1. Screening of catalysts for the RA/ATH of **1a** and **2a**.[a]



Entry	Catalyst	**3a**/**4a**/**5a** (%)[b]	ee of **3a** (%)[c]
1	(*R*,*R*)-**C1**	91:9:--	54
2	(*R*,*R*)-**C2**	76:24:--	39
3	**(*R*,*R*)-C3**	**93:7:--**	**90**
4	(*R*,*R*)-**C4**	90:10:--	46
5	(*R*,*R*)-**C5**	89:11:--	89
6	(*R*,*R*)-**C6**	90:10:--	72
7	(*R*,*R*)-**C7**	90:10:--	59
8	(*R*,*R*)-**C8**	82:18:--	88
9	(*R*,*R*)-**C9**	80:20:--	87
10	(*R*,*R*)-**C10**	84:16:--	89
11	(*R*,*R*)-**C11**	81:19:--	88
12	(*R*,*R*)-**C12**	92:8:--	77
13	(*R*,*R*)-**C13**	94:6:--	79
14	(*R*,*R*)-**C14**	87:13:--	67
15	(*R*,*R*)-**C15**	44:56:--	23
16	(*R*,*R*)-**C16**	42:58:--	25
17	(*R*,*R*)-**C17**	45:55:--	22
18	(*R*,*R*)-**C18**	95:5:--	66
19	(*R*,*R*)-**C19**	77:23:--	64
20	(*R*,*R*)-**C20**	98:-- :--	78
21	(*R*,*R*)-**C21**	74:26:--	65
22	(*R*,*R*)-**C22**	82:18:--	78
23	(*R*,*R*)-**C23**	22:78:--	48
24	(*R*,*R*)-**C24**	25:75:--	33
25	(*R*,*R*)-**C25**	34:66:--	62
26	(*R*,*R*)-**C26**	--:58:--	--
27	(*R*,*R*)-**C27**	--:58:--	--

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (1.0 mol %), HCO_2H/Et_3N (5:2) (2.4 mmol), THF (1.0 mL), r. t., N_2, 16 h. [b]Determined by ^1H NMR analysis of crude product. [c]Determined by HPLC analysis with a chiral AD-H column.

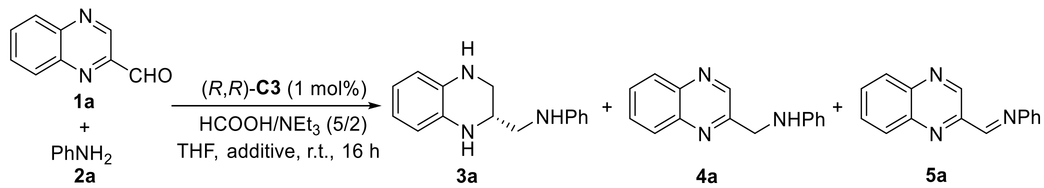
Table S2. Screening of solvents for the RA/ATH of **1a** and **2a**.[a]



Entry	Solvent	**3a**/**4a**/**5a** (%)[b]	ee of **3a** (%)[c]
1	*i*PrOH	70:30:--	64
2	HFIP	--	--
3	EtOAc	64:36:--	54
4	DME	26:74:--	88
5	**THF**	**93:7:--**	**90**
6	1,4-dioxane	82:30:--	85
7	MTBE	88:12:--	83
8	dibutyl ether	80:20:--	84
9	MeOH	61:39:--	73
10	toluene	95:7:--	57
11	$CHCl_3$	96:4:--	66
12	CH_2Cl_2	94:6:--	62

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), (*R*,*R*)-**C3** (1.0 mol %), HCO_2H/Et_3N (5/2) (2.4 mmol), solvent (1.0 mL), r.t., N_2, 16 h. [b]Determined by ^1H NMR analysis of crude product. [c]Determined by HPLC analysis with a chiral AD-H column. HFIP: hexafluoroisopropanol; DME: dimethoxyethane; MTBE: methyl *tert*-butyl ether.

Table S3. Screening of additives for the RA/ATH of **1a** and **2a**.[a]

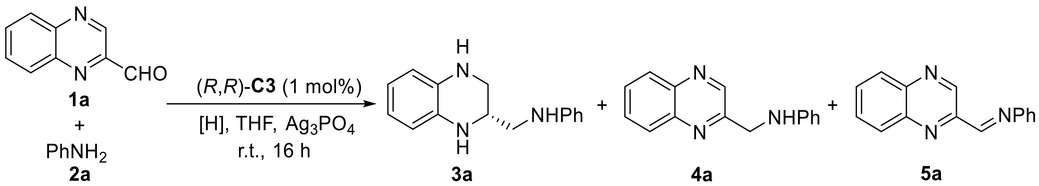


Entry	T (°C)	Additive (mol%)	**3a**/**4a**/**5a** (%)[b]	ee of **3a** (%)[c]
1	r.t.	AgOTf (2)	95:5:--	90
2	r.t.	$AgSbF_6$ (2)	94:6:--	90
3	r.t.	Ag_3PO_4 (2)	92:8:--	92

4	r.t.	Ag_2SO_4 (2)	90:10:--	85
5	r.t.	KI (2)	92:8:--	78
6	**r.t.**	**Ag_3PO_4 (2)**	**96:4:--**	**99**
7	50	Ag_3PO_4 (2)	99:--:--	72
8	r.t.	Ag_3PO_4 (1)	93:7:--	91
9[d]	r.t.	Ag_3PO_4 (2)	77:13:--	91

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), (*R*,*R*)-**C3** (1.0 mol %), HCO_2H/Et_3N (5/2) (2.4 mmol), THF (1.0 mL), r.t., N_2, 16 h. [b]Determined by ^1H NMR analysis of crude product. [c]Determined by HPLC analysis with a chiral AD-H column. [d](*R*,*R*)-**C3** (0.5 mol%) was used.

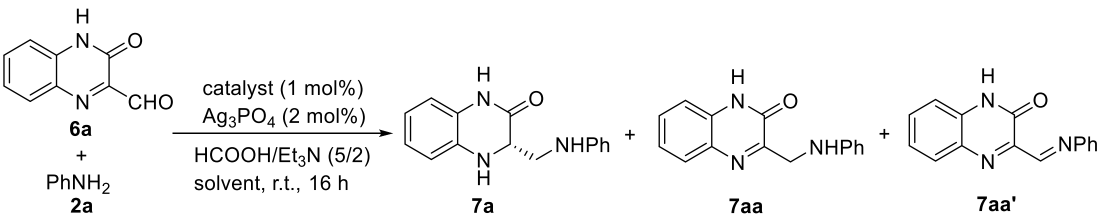
Table S4. Screening of hydrogen donors for the RA/ATH of **1a** and **2a**.[a]



Entry	[H]	**3a**/**4a**/**5a** (%)[b]	ee of **3a** (%)[c]
1	HCO_2H/NEt_3 (1/1)	79:21:--	89
2	HCO_2H/NEt_3 (2/1)	82:18:--	91
3	**HCO_2H/NEt_3 (5/2)**	**95:5:--**	**99**
4	HCO_2H/NEt_3 (3/1)	85:15:--	87
5	HCO_2H	66:34:--	44
6[d]	HCO_2H/NEt_3 (5/2)	94:6:--	96

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), THF (1.0 mL), (*R*,*R*)-**C3** (1.0 mol %), Ag_3PO_4 (2.0 mol %), HCO_2H/Et_3N (5/2) (2.4 mmol), r.t., N_2, 16 h. [b]Determined by ^1H NMR analysis of crude product. [c]Determined by HPLC analysis with a chiral AD-H column. [d]HCO_2H/Et_3N (5/2) (2.0 mmol) was used.

Table S5. Screening of the reaction condition for RA/ATH of **6a** and **2a**.[a]

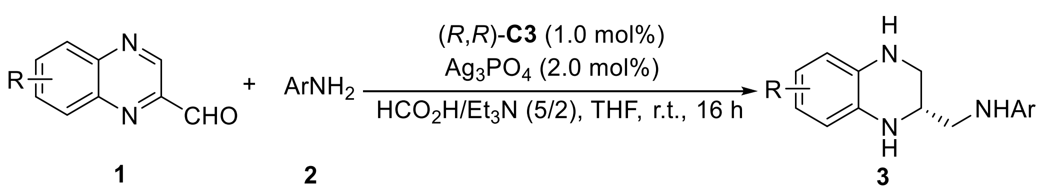


Entry	Catalyst	Solvent	**7a**/**7aa**/**7aa'** (%)[b]	ee of **7a** (%)[c]
1	**(*R*,*R*)-C3**	**THF**	**88:12:--**	**74**

2	(*R*,*R*)-**C8**	THF	80:20:--	74
3	(*R*,*R*)-**C12**	THF	78:22:--	46
4	(*R*,*R*)-**C16**	THF	75:25:--	22
5	(*R*,*R*)-**C18**	THF	70:30:--	36
6	(*R*,*R*)-**C23**	THF	36:52:12	18
7	(*R*,*R*)-**C3**	IPA	79:21:--	68
8	(*R*,*R*)-**C3**	DCE	89:11:--	59
9	(*R*,*R*)-**C3**	1,4-dioxane	85:15:--	72
10	(*R*,*R*)-**C3**	toluene	90:10:--	42
11	(*R*,*R*)-**C3**	$CHCl_3$	89:11:--	37
12[d]	(*R*,*R*)-**C3**	THF	82:18:--	74
13[e]	(*R*,*R*)-**C3**	THF	92:8:--	69
14[f]	(*R*,*R*)-**C3**	THF	94:6:--	62
15[g]	(*R*,*R*)-**C3**	THF	81:19:--	70
16[h]	(*R*,*R*)-**C3**	THF	80:20:--	70
17[i]	(*R*,*R*)-**C3**	THF	87:13:--	72

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (1.0 mol %), HCO_2H/Et_3N (5/2) (2.4 mmol), Ag_3PO_4 (2.0 mol %), Solvent (1.0 mL), r. t., N_2, 16 h. [b]Determined by ^1H NMR analysis of crude product. [c]Determined by HPLC analysis with a chiral OJ-H column. [d]Reaction temperature 0 °C. [e]Reaction temperature 40 °C. [f]Reaction temperature 50 °C. [g] No Ag_3PO_4 was used. [h]HCO_2H/Et_3N (1/1) (2.4 mmol) was used. [i]HCO_2H/Et_3N (3/1) (2.4 mmol) was used.

3. The general procedure

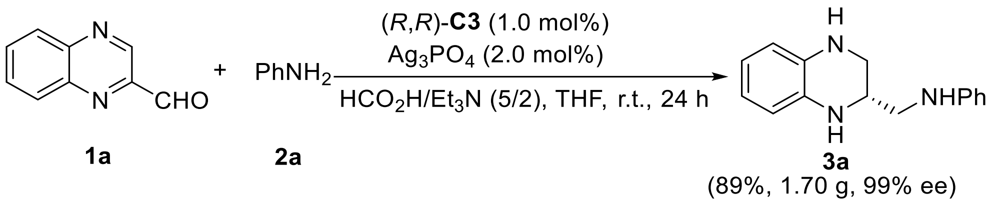


An oven-dried screw-capped pressure tube (25 mL) equipped with a magnetic stirrer bar was charged with quinoxaline-2-carbaldehyde **1** (0.2 mmol), amine **2** (0.2 mmol), Ag_3PO_4 (1.67 mg, 0.004 mmol), (*R*,*R*)-**C3** (1.40 mg, 0.002 mmol),

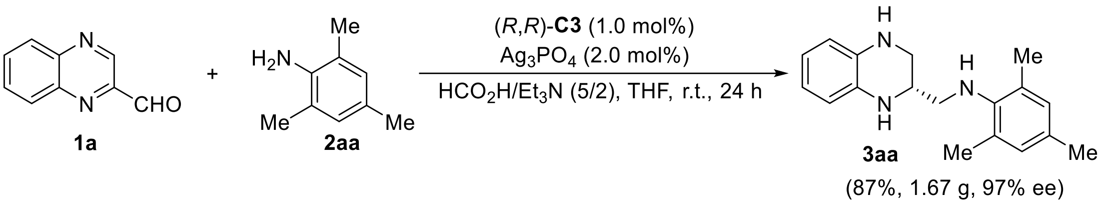
HCO_2H/Et_3N (5/2) (207.6 mg, 2.4 mmol, 0.2 mL) and THF (1.0 mL) under N_2 atmosphere in a glove box. Then the tube was capped and removed from the glovebox. The reaction mixture was stirred vigorously at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was basified with the saturated aqueous $NaHCO_3$ (2.0 mL) and extracted with CH_2Cl_2 (3 × 3.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate to provide product **3**.

4. Synthetic applications

4.1 Scale-up reactions

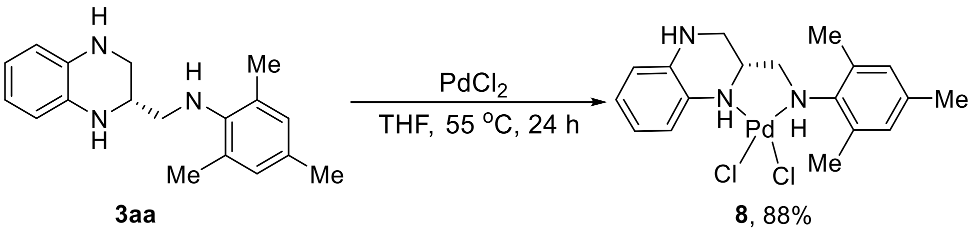


To an oven-dried screw-capped pressure tube (100 mL) equipped with a magnetic stir bar were sequentially added quinoxaline-2-carbaldehyde (**1a**) (1.27 g, 8.0 mmol), aniline (**2a**) (0.75 g, 8.0 mmol), (*R,R*)-**C3** (55.44 mg, 0.08 mmol), Ag_3PO_4 (67.0 mg, 0.16 mmol) and HCO_2H/Et_3N (8.06 mL, 96 mmol) and THF (40 mL) in a nitrogen atmosphere glovebox. Then the tube was capped and removed from the glovebox. The reaction mixture was allowed to stir vigorously at room temperature for 24 h. The solvent was then removed under reduced pressure, and the residue was basified with the saturated aqueous $NaHCO_3$ (100.0 mL) and extracted with CH_2Cl_2 (3 × 50.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (5:1) to provide product **3a** (89%, 1.70 g, 99% ee).



To an oven-dried screw-capped pressure tube (100.0 mL) equipped with a magnetic stir bar were sequentially added quinoxaline-2-carbaldehyde (**1a**) (1.27 g, 8.0 mmol), 2,4,6-trimethylaniline (**2aa**) (1.08 g, 8.0 mmol), (*R,R*)-**C3** (55.44 mg, 0.08 mmol), Ag_3PO_4 (67.0 mg, 0.16 mmol) and HCO_2H/Et_3N (5/2) (8.06 mL, 96 mmol) and THF (40.0 mL) in a nitrogen atmosphere glovebox. Then the tube was capped and removed from the glovebox. The reaction mixture was allowed to stir vigorously at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was basified with the saturated aqueous $NaHCO_3$ (100.0 mL) and extracted with CH_2Cl_2 (3 × 50.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (20:1) to provide product **3aa** (87%, 1.96 g, 97% ee).

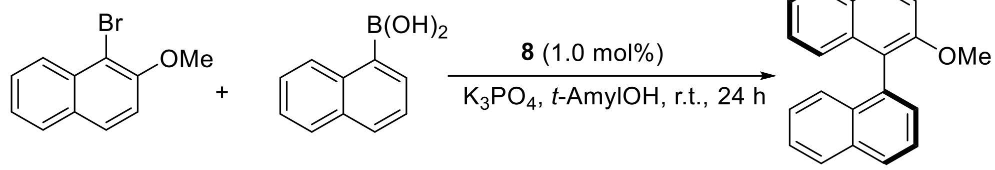
4.2 Synthesis of chiral Pd-diamine complex 8 and its application



To a round bottom flask was added (*R*)-2,4,6-trimethyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (**3aa**) (140.7 mg, 0.5 mmol), $PdCl_2$ (106.4 mg, 0.6 mmol) and dry THF (3.0 mL). Then, the reaction mixture was stirred vigorously at 55 ^{o}C for 24 h. After cooling to room temperature, the resulting mixture was concentrated under vacuum to give an orange-yellow residue, which was recrystallized from CH_2Cl_2/hexane to afford the pure product **8** (201.8 mg, 88%).

8: Orange-yellow solid, 201.8 mg, isolated yield 88%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 4.2 Hz, 1H), 7.24 (dd, *J* = 11.1, 5.1 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.73 – 6.66 (m, 3H), 6.57 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.03 (d, *J* =

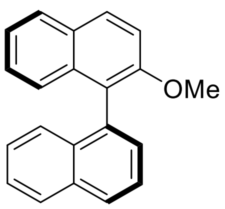
3.3 Hz, 1H), 4.22 (d, J = 12.3 Hz, 1H), 3.18 – 3.05 (m, 2H), 2.76 (dt, J = 12.6, 4.4 Hz, 1H), 2.55 (s, 3H), 2.29 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.57, 140.27, 135.46, 131.40, 131.31, 131.15, 129.37, 129.35, 127.33, 123.66, 117.16, 115.69, 55.93, 55.75, 38.26, 20.63, 19.89, 18.83; HRMS (ESI) calcd. for $C_{21}H_{22}N_3$ [M+Na]$^+$: 480.0196, found: 480.0201.



9 **10** **11**, 81%, 85% ee

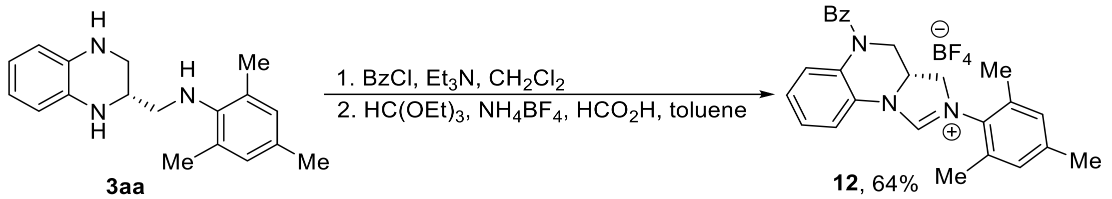
To an oven-dried Schlenk flask containing a magnetic stir bar was added 1-bromo-2-methoxynaphthalene (**9**) (59.3 mg, 0.25 mmol), 1-naphthylboronic acid (**10**) (51.6 mg, 0.30 mmol), **8** (1.1 mg, 0.0025 mmol), K_3PO_4 (106.1 mg, 0.50 mmol) and *t*-AmylOH (1.0 mL) under a nitrogen atmosphere. The reaction mixture was stirred vigorously at 25 °C until the aryl bromide was consumed as indicated by TLC. After filtration and being concentrated, the resulting residue was purified by silical gel column chromatography using hexane/ethyl acetate as eluent to give the pure product **11** (62.0mg, 81%, 85% ee).

(*R*)-2-Methoxy-1,1'-binaphthalene (**11**) [2]



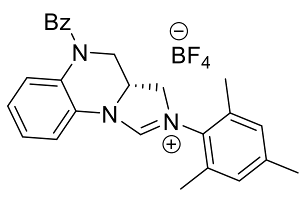
White solid, 62.0 mg, isolated yield 81%; $[\alpha]_D^{20}$ = -22.6 (c = 1.0, $CHCl_3$); Enantiomeric excess; 85%; HPLC (OD-H, elute: hexane/isopropanol = 99/1, flowing rate = 0.4 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 19.097 min (minor), t_{R2} = 20.510 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 3H), 7.77 (dt, J = 8.3, 1.0 Hz, 1H), 7.52 (dd, J = 8.3, 7.0 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.26 – 7.04 (m, 5H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.75, 134.68, 134.40, 133.83, 133.08, 129.60, 129.15, 128.57, 128.36, 127.93, 127.87, 126.51, 126.31, 125.99, 125.82, 125.71, 125.64, 123.70, 123.35, 113.96, 56.89; HRMS (ESI) calcd. for $C_{21}H_{16}NaO$ [M+Na]$^+$: 307.1093, found: 307.1099.

4.3 Synthesis of hindered N-heterocyclic carbene ligand 12



To a solution of **3aa** (281.40 mg, 1.0 mmol) dissolved in CH_2Cl_2 (20.0 mL) was sequentially added BzCl (122 μL, 1.05 mmol) and Et_3N (0.26 mL, 2.0 mmol) at 0 °C. After stirring at room temperature for 1 h, the reaction mixture was poured into water (20.0 mL) and extracted with CH_2Cl_2 (3 × 20.0 mL). The combined extracts were washed with brine, dried with anhydrous magnesium sulfate, and evaporated in vacuo. The crude residue was dissolved in toluene (16.0 mL), and $HC(OEt)_3$ (0.85 mL, 5 mmol), NH_4BF_4 (0.42 g, 4 mmol) and 2 drops of HCO_2H were added. The reaction mixture was heated at 90 °C for 24 h. After cooling to room temperature, the resulting solution was concentrated under vacuum, and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/MeOH = 50:1, v/v) to give the white solid **12** (0.31 g, 64%).

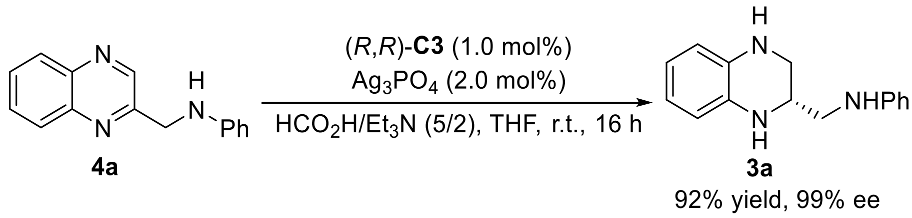
(*S*)-5-Benzoyl-2-mesityl-3,3a,4,5-tetrahydroimidazo[1,5-a]quinoxalin-2-iumtetrafluoroborate (12)



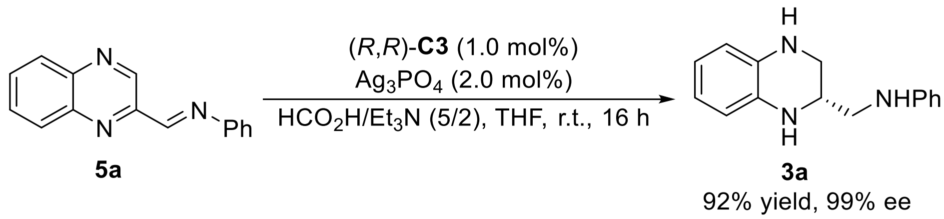
White solid, m.p. 285-287 °C; $[\alpha]_D^{20}$ = -24.8 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.26 – 7.17 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 2H), 7.00 – 6.90 (m, 2H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.71 – 6.56 (m, 3H), 4.35 – 4.13 (m, 2H), 3.57 (dp, *J* = 11.2, 3.8, 3.2 Hz, 1H), 3.39 (dd, *J* = 13.8, 3.0 Hz, 1H), 2.83 (dd, *J* = 12.3, 9.6 Hz, 1H), 2.19 (s, 3H), 2.14 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.49, 160.11, 138.48, 138.13, 136.57, 135.27, 135.22, 134.31, 130.50, 130.33, 130.16, 128.21, 127.72, 126.28, 122.82, 117.76, 117.41, 115.61, 54.04, 51.80, 40.34, 20.96, 18.73, 18.62; HRMS (ESI) calcd. for $C_{26}H_{26}N_3O^+$ $[M-BF_4]^+$: 396.2070, found: 396.2074.

5. Mechanistic Studies

5.1 Control experiments

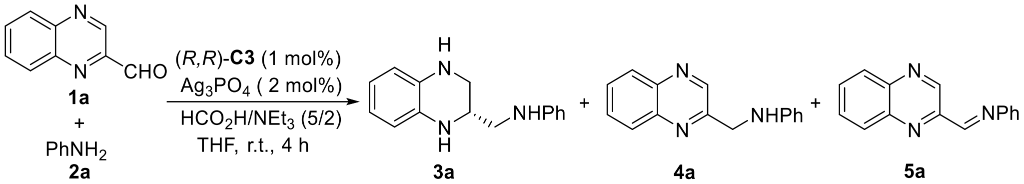


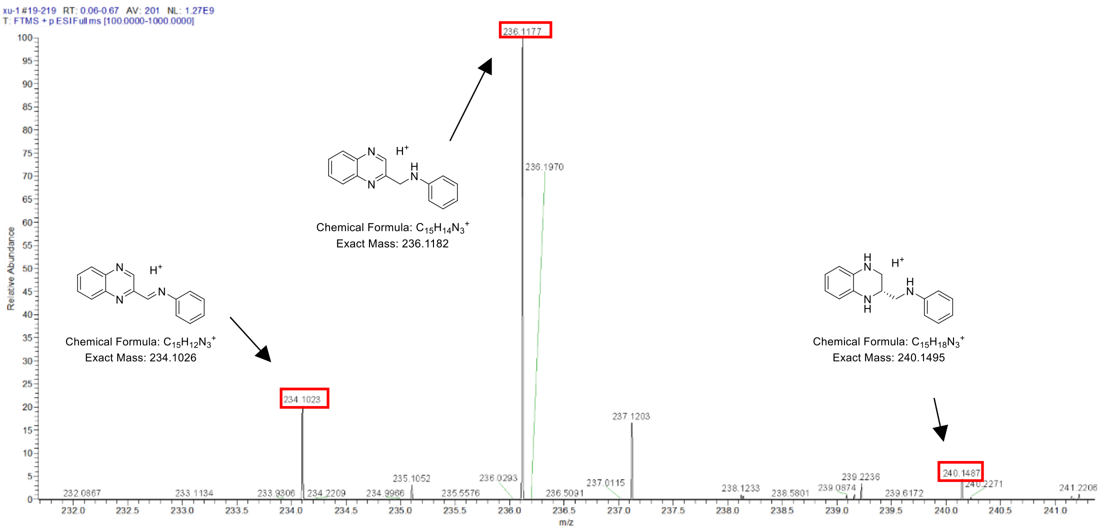
An oven-dried screw-capped pressure tube (25.0 mL) equipped with a magnetic stirrer bar was charged with **4a** (47.1 mg, 0.2 mmol), Ag_3PO_4 (1.7 mg, 0.004 mmol), (*R*,*R*)-**C3** (1.4 mg, 0.002 mmol), HCO_2H/Et_3N (5/2) (207.6 mg, 2.4 mmol, 0.2 mL) and THF (1.0 mL) under N_2 atmosphere in a glove box. The reaction mixture was stirred vigorously at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was basified with the saturated aqueous $NaHCO_3$ (2.0 mL) and extracted with CH_2Cl_2 (3 × 3.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (3/1) to provide product **3a** (44.0 mg, 92%, 99% ee).



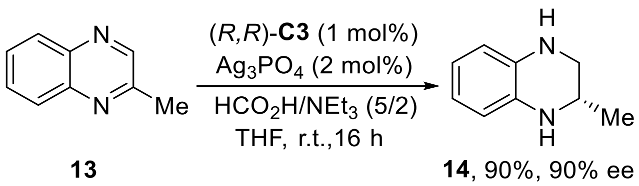
An oven-dried screw-capped pressure tube (25.0 mL) equipped with a magnetic stirrer bar was charged with **5a** (46.7 mg, 0.2 mmol), Ag_3PO_4 (1.7 mg, 0.004 mmol), (*R*,*R*)-**C3** (1.4 mg, 0.002 mmol), HCO_2H/Et_3N (5/2) (207.6 mg, 2.4 mmol, 0.2 mL) and THF (1.0 mL) under N_2 atmosphere in a glove box. The reaction mixture was stirred vigorously at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was basified with the saturated aqueous $NaHCO_3$ (2.0 mL) and extracted with CH_2Cl_2 (3 × 3.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (3/1) to provide product **3a** (44.0 mg, 92%, 99% ee).

5.2 HRMS study



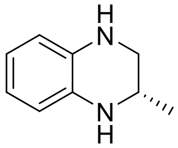


5.3 ATH of 2-methylquinoxaline



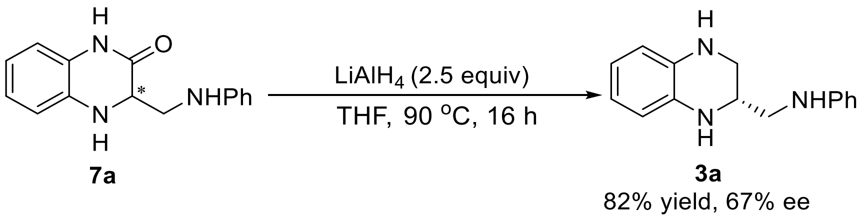
An oven-dried screw-capped pressure tube (25.0 mL) equipped with a magnetic stirrer bar was charged with 2-methylquinoxaline (**13**) (28.8 mg, 0.2 mmol), Ag_3PO_4 (1.7 mg, 0.004 mmol), (*R*,*R*)-**C3** (1.4 mg, 0.002 mmol), HCO_2H/Et_3N (5/2) (207.6 mg, 2.4 mmol, 0.2 mL) and THF (1.0 mL) under N_2 atmosphere in a glove box. The reaction mixture was stirred vigorously at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was basified with the saturated aqueous $NaHCO_3$ (2.0 mL) and extracted with CH_2Cl_2 (3 × 3.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (3/1) to provide product **14** (26.7 mg, 90% ee).

(*S*)-2-methyl-1,2,3,4-tetrahydroquinoxaline (14)[3]

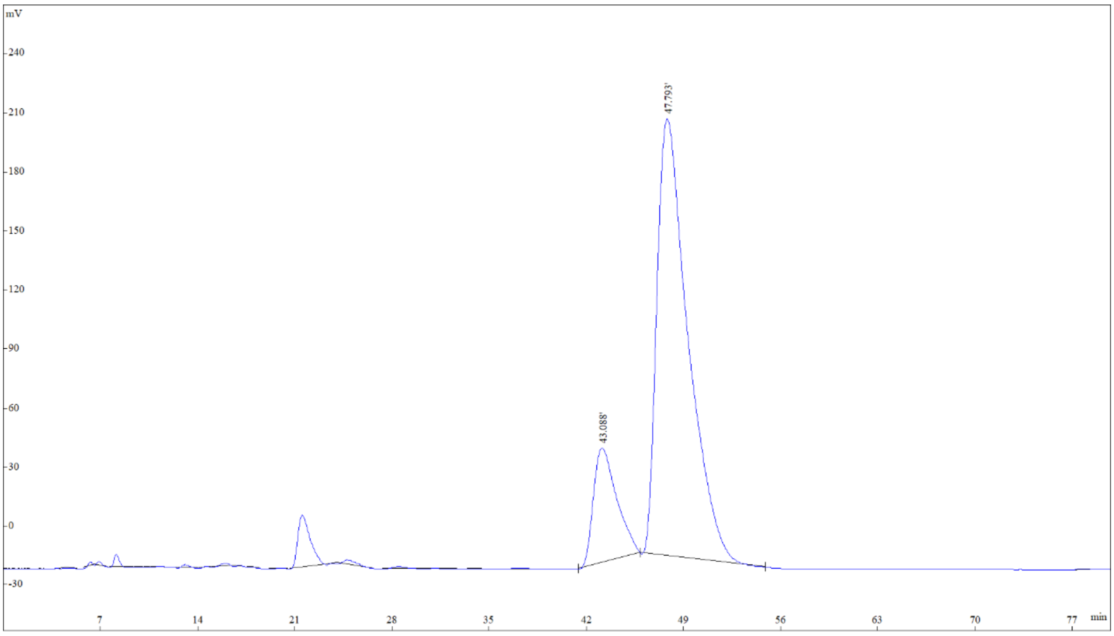


Pale yellow oil, 26.7 mg, isolated yield 90%; $[\alpha]_D^{20}$ = -30.4 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 90%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 10.322 min (minor), t_{R2} = 12.092 min (major); ^{1}H NMR (400 MHz, CDCl3) δ 6.60 (dd, *J* = 5.8, 3.4 Hz, 2H), 6.51 (dt, *J* = 5.8, 3.6 Hz, 2H), 3.71 – 3.43 (m, 3H), 3.32 (dd, *J* = 10.7, 2.9 Hz, 1H), 3.04 (dd, *J* = 10.7, 8.2 Hz, 1H), 1.19 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.67, 133.29, 118.80, 114.58, 114.53, 48.36, 45.82, 20.01 (one carbon was not detected due to overlap of resonances); HRMS (ESI) calcd. for $C_9H_{13}N_2$ $[M+H]^+$: 149.1073, found: 149.1075.

5.4 Verification of 3,4-dihydroquinoxalin-2(1*H*)-one configuration



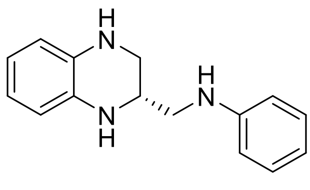
To a 25 mL round-bottom flask in an ice-water bath was sequentially add **7a** (0.2 mmol, 50.7 mg), dry THF (10.0 mL) and $LiAlH_4$ (0.5 mmol, 19.0 mg). The reaction mixture was then vigorously stirred and heated at 90°C for 16 hours. After cooling to room temperature, the excess $LiAlH_4$ was quenched with sat. aq. NH_4Cl. The resulting hydroxide precipitate was filtered, and the filtrate was dried over anhydrous sodium sulfate and concentrated under vacuum. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (3/1) to provide product **3a** (82%, 39.2 mg, 67% ee). The structure of the product was determined to be (*S*) configuration through HPLC analysis.



peak	Ret. Time	Area%	Area
1	43.088	16.58	6885339
2	47.793	83.42	34630701

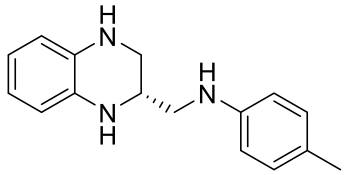
6. Analytic data of products

(*S*)-N-((1,2,3,4-Tetrahydroquinoxalin-2-yl)methyl)aniline (3a)



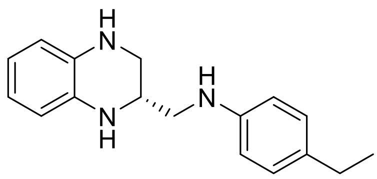
Pale yellow oil, 43.5 mg, isolated yield 91%; $[\alpha]_D^{20}$ = -85.6 (c = 1.0, $CHCl_3$); enantiomeric excess: 99%; HPLC (AD-H elute: hexane/isopropanol = 90/10, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 49.357 min (minor), t_{R2} = 53.587 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 2H), 6.74 (td, J = 7.3, 1.1 Hz, 1H), 6.69 – 6.58 (m, 4H), 6.54 (qt, J = 5.3, 2.7 Hz, 2H), 4.04 – 3.56 (m, 4H), 3.42 (dd, J = 10.9, 3.1 Hz, 1H), 3.35 – 3.21 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.25, 133.40, 132.93, 129.49, 119.17, 118.95, 117.93, 114.93, 114.68, 113.09, 49.69, 47.60, 44.16; HRMS (ESI) calcd. for $C_{15}H_{18}N_3$ $[M+H]^+$: 240.1495, found: 240.1499.

(*S*)-4-Methyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3b)



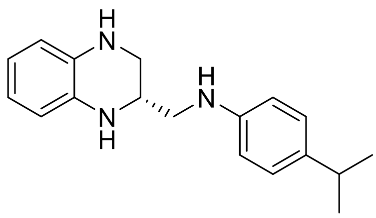
Pale yellow oil, 48.6 mg, isolated yield 96%; $[\alpha]_D^{20}$ = -84.8 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 98%; HPLC (OD-H elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 41.170 min (minor), t_{R2} = 57.908 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.87 (m, 2H), 6.56 – 6.48 (m, 4H), 6.44 (ddt, *J* = 6.6, 2.8, 1.6 Hz, 2H), 3.98 – 3.42 (m, 4H), 3.32 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.24 – 3.08 (m, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.96, 133.41, 132.98, 129.97, 127.18, 119.13, 118.90, 114.88, 114.65, 113.25, 49.72, 47.96, 44.22, 20.50; HRMS (ESI) calcd. for $C_{22}H_{24}N_3$ $[M+H]^+$: 254.1652, found: 254.1656.

(*S*)-4-Ethyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3c)



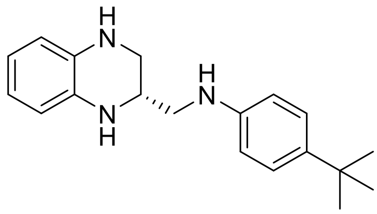
Pale yellow oil, 50.8 mg, isolated yield 95%; $[\alpha]_D^{20}$ = -89.8 (*c* = 1.0, $CHCl_3$); enantiomeric excess; 93%; HPLC (OD-H, elute: hexane/isopropanol = 70/30, flowing rate = 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 20.244 min (minor), t_{R2} = 28.931 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.04 (m, 2H), 6.64 (dt, *J* = 6.5, 2.5 Hz, 4H), 6.55 (dtd, *J* = 6.6, 3.2, 1.5 Hz, 2H), 3.91 – 3.43 (m, 4H), 3.41 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.32 – 3.19 (m, 3H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.14, 133.82, 133.39, 132.97, 128.76, 119.09, 118.86, 114.86, 114.63, 113.22, 49.67, 47.89, 44.19, 28.01, 16.09; HRMS (ESI) calcd. for $C_{17}H_{22}N_3$ $[M+H]^+$: 268.1808, found: 268.1810.

(*S*)-4-Isopropyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3d)



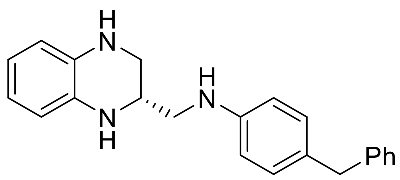
Pale yellow oil, 49.5 mg, isolated yield 88%. $[\alpha]_D^{20}$ = -84.1 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 93%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 13.1 min (minor), t_{R2} = 15.1 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.04 (m, 2H), 6.67 – 6.58 (m, 4H), 6.57 – 6.50 (m, 2H), 4.03 – 3.57 (m, 4H), 3.42 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.35 – 3.18 (m, 3H), 2.84 (p, *J* = 6.9 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.22, 138.53, 133.41, 132.98, 127.33, 119.11, 118.88, 114.87, 114.63, 113.14, 49.67, 47.88, 44.22, 33.28, 24.37; HRMS (ESI) calcd. for $C_{18}H_{24}N_3$ $[M+H]^+$: 282.1965, found: 282.1966

(*S*)-4-(*tert*-Butyl)-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3e)



Pale yellow oil, 56.1 mg, isolated yield 95%, 95% ee. $[\alpha]_D^{20}$ = -88.3 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 95%; HPLC (OJ-H, elute: hexane/isopropanol = 60/40, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} =85.043 min (major), t_{R2} = 135.878 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.65 – 6.59 (m, 4H), 6.55 – 6.50 (m, 2H), 3.72 – 3.66 (m, 1H), 3.42 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.33 – 3.19 (m, 3H), 1.29 (s, 9H) (three active hydrogens were not detected); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 140.82, 133.41, 132.98, 126.27, 119.16, 118.93, 114.91, 114.68, 112.86, 49.69, 47.85, 44.24, 34.01, 31.66; HRMS (ESI) calcd. for $C_{19}H_{26}N_3^+$ $[M+H]^+$: 296.2121, found: 296.2123.

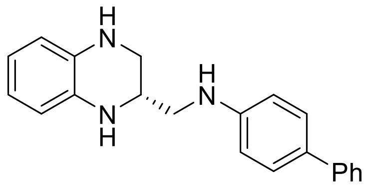
(*S*)-4-Benzyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3f)



Pale yellow oil, 56.6 mg, isolated yield 86%; $[\alpha]_D^{20}$ = -92.7 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 94%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 38.308 min (minor), t_{R2} = 62.957 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.22 (dt, *J* = 7.9, 1.5 Hz, 3H), 7.08 – 7.02 (m, 2H), 6.66 – 6.59 (m, 4H), 6.57 – 6.51 (m, 2H), 4.07 – 3.59 (m, 6H), 3.40 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.32 – 3.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.48, 142.06, 133.38, 132.92, 130.53, 129.92, 128.88, 128.47, 125.94, 119.10, 118.89, 114.87, 114.63, 113.23, 49.62, 47.75, 44.13, 41.11; HRMS (ESI) calcd. for $C_{22}H_{24}N_3$ $[M+H]^+$: 330.1965, found:

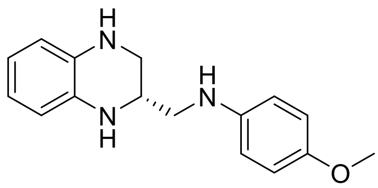
330.1967.

(*S*)-N-((1,2,3,4-Tetrahydroquinoxalin-2-yl)methyl)-[1,1'-biphenyl]-4-amine (3g)



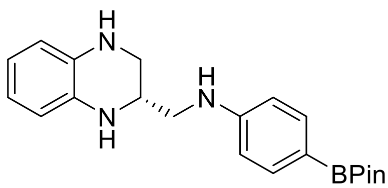
Pale yellow oil, 53.0 mg, isolated yield 84%; $[\alpha]_D^{20}$ = -91.2 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 93%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate = 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 21.7 min (major), t_{R2} = 34.8 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.51 – 7.43 (m, 4H), 7.34 – 7.30 (m, 1H), 6.76 – 6.73 (m, 2H), 6.69 – 6.65 (m, 2H), 6.58 – 6.55 (m, 2H), 4.04 – 3.54 (m, 4H), 3.43 – 3.21 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.62, 141.16, 133.35, 132.84, 130.68, 128.78, 128.08, 126.37, 126.26, 119.13, 118.91, 114.89, 114.66, 113.28, 49.59, 47.48, 44.00; HRMS (ESI) calcd. for $C_{21}H_{22}N_3$ $[M+H]^+$: 316.1808, found: 316.1806.

(*S*)-4-Methoxy-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3h)



White solid, m.p. 46.7-48.9 °C, 50.1 mg, isolated yield 93%; $[\alpha]_D^{20}$ = -84.8 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 96%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate = 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 52.990min (minor), t_{R2} = 75.188 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 – 6.78 (m, 2H), 6.65 – 6.58 (m, 4H), 6.53 (dt, *J* = 6.9, 2.6 Hz, 2H), 3.98 - 3.53 (m, 7H), 3.41 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.29 – 3.16 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.52, 142.44, 133.42, 132.99, 119.13, 118.91, 115.11, 114.88, 114.66, 114.44, 55.96, 49.83, 48.61, 44.28; HRMS (ESI) calcd. for $C_{16}H_{20}N_3O[M+H]^+$: 270.1601, found: 270.1597.

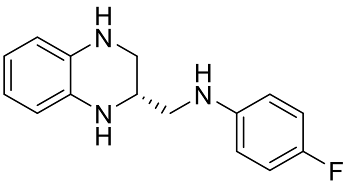
(*S*)-N-((1,2,3,4-Tetrahydroquinoxalin-2-yl)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3i)



Yellow solid, m.p. 56.4-58.6 ℃, 64.1 mg, isolated yield 88%; $[\alpha]_D^{20}$ = -84.8 (*c* = 1.0, $CHCl_3$); enantiomeric excess: >99%; HPLC (OD-H, elute:

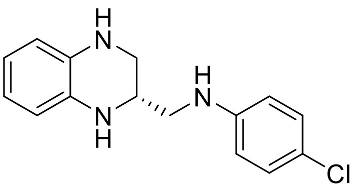
hexane/isopropanol = 80/20, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 32.793min (minor major), t_{R2} =47.341 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 6.63 – 6.61 (m, 4H), 6.54 – 6.52 (m, 2H), 4.21 – 3.55 (m, 4H), 3.43 – 3.21 (m, 4H), 1.34 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.74, 136.54, 133.30, 132.78, 119.15, 118.91, 114.90, 114.65, 112.04, 83.37, 49.51, 46.96, 43.88, 24.95; HRMS (ESI) calcd. for $C_{21}H_{29}BN_3O_2$ $[M+H]^+$: 365.2275, found: 365.2280.

(*S*)-4-Fluoro-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3j)



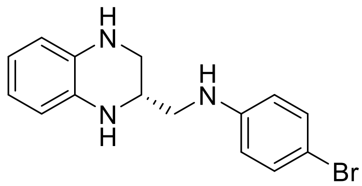
Pale yellow oil, 47.8 mg, isolated yield 93%, 93% ee. $[\alpha]_D^{20}$ = -79.7 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 93%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 18.978 min (minor), t_{R2} = 22.378 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 – 6.88 (m, 2H), 6.64 – 6.57 (m, 4H), 6.55 – 6.53 (m, 2H), 4.17-3.52 (m, 4H), 3.41 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.28 – 3.25 (m, 2H), 3.20 (dd, *J* = 12.8, 7.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.11 (d, *J* = 235.4 Hz), 144.61, 133.39, 132,85, 119.19, 119.01, 115.95, 115.80, 114.83 (d, *J* = 36.6 Hz), 113.94 (d, *J* = 7.5 Hz), 49.71, 48.27, 44.12; HRMS (ESI) calcd. for $C_{15}H_{17}FN_3$ $[M+H]^+$: 258.1401, found: 258.1401.

(*S*)-4-Chloro-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3k)



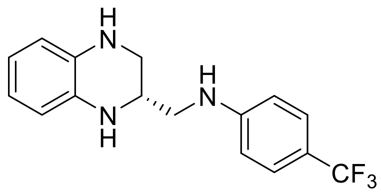
Pale yellow oil, 49.7 mg, isolated yield 91%; $[\alpha]_D^{20}$ = -82.7 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 95%; HPLC (OD-H, elute: hexane/isopropanol = 90/10, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 82.808 min (minor), t_{R2} = 115.401 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.11 (m, 2H), 6.65 – 6.60 (m, 2H), 6.59 – 6.52 (m, 4H), 4.20 – 3.68 (m, 4H), 3.40 (dd, *J* = 10.9, 3.1 Hz, 1H), 3.30 – 3.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.83, 133.34, 132.75, 129.26, 122.41, 119.23, 119.05, 114.97, 114.73, 114.13, 49.61, 47.67, 43.98; HRMS (ESI) calcd. for $C_{15}H_{17}ClN_3[M+H]^+$: 274.1106, found: 274.1104, 276.1074.

(*S*)-4-Bromo-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3l)



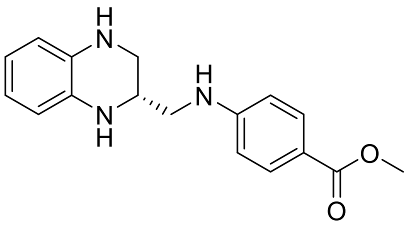
Pale yellow oil, 57.9 mg, isolated yield 91%; $[\alpha]_D^{20}$ = -78.7 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 98%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate = 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 22.4 min (minor), t_{R2} = 31.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 6.65 – 6.59 (m, 2H), 6.56 – 6.49 (m, 4H), 4.23 – 3.52 (m, 4H), 3.40 (dd, *J* = 10.9, 3.1 Hz, 1H), 3.32 – 3.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.26, 133.33, 132.73, 132.14, 119.27, 119.08, 115.00, 114.75, 114.64, 109.44, 49.60, 47.58, 43.97; HRMS (ESI) calcd. for $C_{15}H_{17}BrN_3[M+H]^+$: 318.0600, found: 318.0603, 320.0583.

(*S*)-N-((1,2,3,4-Tetrahydroquinoxalin-2-yl)methyl)-4-(trifluoromethyl)aniline (3m)



Pale yellow oil,50.4 mg, isolated yield 82%; $[\alpha]_D^{20}$ = -72.6 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 99%; HPLC (OD-H, elute: hexane/isopropanol = 90/10, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 72.338 min (minor), t_{R2} = 109.730 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 6.64 (dt, *J* = 7.7, 2.6 Hz, 4H), 6.57 – 6.53 (m, 2H), 4.35 (s, 1H), 3.98 – 3.46 (m, 3H), 3.42 – 3.24 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.73, 133.30, 132.62, 126.78 (q, *J* = 3.8 Hz), 125.04 (q, *J* = 270.2 Hz), 119.27, 119.20 (q, *J* = 32.6 Hz), 119.09, 115.00, 114.75, 112.11, 49.47, 47.01, 43.76; HRMS (ESI) calcd. for $C_{16}H_{17}F_3N_3$ $[M+H]^+$: 308.1369, found: 308.1368.

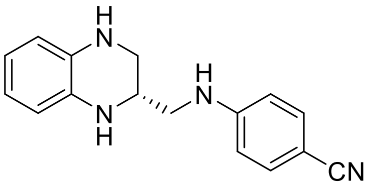
Methyl (*S*)-4-(((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)amino)benzoate (3n)



Pale yellow oil,48.1 mg, isolated yield 81%; $[\alpha]_D^{20}$ = -75,4 (*c* = 1.0, $CHCl_3$); enantiomeric excess: >99%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 63.089 min (minor), t_{R2} = 90.132 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 6.67 – 6.49 (m, 6H), 4.45 (s, 1H), 3.86 (s, 6H), 3.47 –

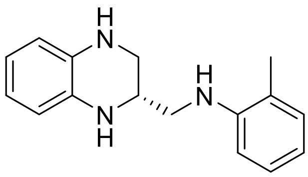
3.21 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.36, 152.01, 133.25, 132.60, 131.72, 119.32, 119.10, 118.86, 115.02, 114.77, 111.77, 51.71, 49.49, 46.90, 43.75; HRMS (ESI) calcd. for $C_{17}H_{20}N_3O_2$ $[M+H]^+$: 298.1550, found: 298.1553.

(S)-4-(((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)amino)benzonitrile (3o)



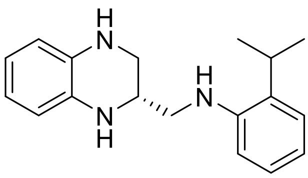
Pale yellow oil, 48.6 mg, isolated yield 92%; $[\alpha]_D^{20}$ = -75.6 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 99%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 59.066 min (minor), t_{R2} = 84.434 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 6.63 (dt, *J* = 7.7, 3.8 Hz, 2H), 6.61 – 6.57 (m, 2H), 6.55 (dq, *J* = 6.2, 3.7 Hz, 2H), 4.68 (d, *J* = 6.1 Hz, 1H), 3.83 (d, *J* = 159.5 Hz, 3H), 3.41 – 3.24 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.47, 133.85, 133.18, 132.45, 120.53, 119.36, 119.14, 115.04, 114.80, 112.48, 99.04, 49.38, 46.73, 43.58; HRMS (ESI) calcd. for $C_{16}H_{17}N_4$ $[M+H]^+$: 265.1448, found: 265.1451.

(*S*)-2-Methyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3p)



Pale yellow oil, 42.0 mg, isolated yield 83%; $[\alpha]_D^{20}$ = -78.4 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 95%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} =50.565 min (minor), t_{R2} = 67.338 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (td, *J* = 7.7, 1.6 Hz, 1H), 7.15 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.80 – 6.67 (m, 4H), 6.62 – 6.55 (m, 2H), 4.04 – 3.62 (m, 4H), 3.48 – 3.28 (m, 4H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.05, 133.35, 132.90, 130.30, 127.23, 122.24, 119.02, 118.82, 117.36, 114.84, 114.58, 109.84, 49.35, 47.43, 44.09, 17.62; HRMS (ESI) calcd. for $C_{16}H_{20}N_3$ $[M+H]^+$: 254.1652, found: 254.1648.

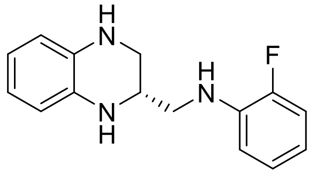
(*S*)-2-Isopropyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3q)



Pale yellow oil, 45.0 mg, isolated yield 80%; $[\alpha]_D^{20}$ = -76.5 (c = 1.0, $CHCl_3$); enantiomeric excess: 96%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate = 1.0

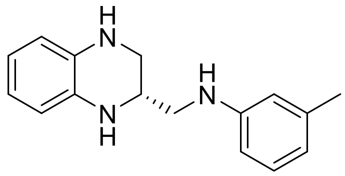
mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 10.562 min (major), t_{R2} = 11.991 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.10 (td, *J* = 7.7, 1.6 Hz, 1H), 6.75 (td, *J* = 7.4, 1.2 Hz, 1H), 6.66 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.62 – 6.57 (m, 2H), 6.51 – 6.48 (m, 2H), 4.05 (d, *J* = 5.8 Hz, 1H), 3.84 (s, 1H), 3.70 (qd, *J* = 6.3, 3.1 Hz, 1H), 3.60 (s, 1H), 3.38 – 3.22 (m, 4H), 2.84 (p, *J* = 6.8 Hz, 1H), 1.24 (dd, *J* = 6.8, 1.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.78, 133.36, 132.91, 132.53, 126.82, 125.16, 119.05, 118.89, 117.75, 114.93, 114.63, 110.59, 49.36, 47.67, 44.16, 27.33, 22.40; HRMS (ESI) calcd. for $C_{18}H_{24}N_3$ $[M+H]^+$: 282.1965, found: 282.1962.

(*S*)-2-Fluoro-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3r)



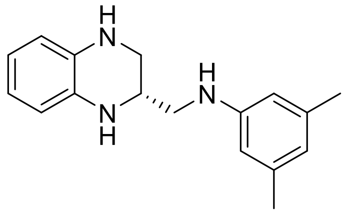
Pale yellow oil, 43.2 mg, isolated yield 84%; $[\alpha]_D^{20}$ = -86.3 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 93%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate = 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} =13.058 min (major), t_{R2} = 18.106min (minor); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 – 7.01 (m, 2H), 6.78 (td, *J* = 8.3, 1.5 Hz, 1H), 6.71 – 6.64 (m, 3H), 6.57 – 6.55 (m, 2H), 4.26 – 4.20 (m, 1H), 3.96 (s, 1H), 3.71 – 3.68 (m, 2H), 3.42 (dd, *J* = 10.9, 3.1 Hz, 1H), 3.34 (dt, *J* = 13.1, 5.4 Hz, 1H), 3.30 – 3.25 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.68 (d, *J* = 238.3 Hz), 136.63 (d, *J* = 11.5 Hz), 133.31, 132.74, 124.72 (d, *J* = 3.7 Hz), 119.13, 118.88, 117.09 (d, *J* = 7.0 Hz), 114.90, 114.64 (d, *J* = 18.4 Hz), 114.63, 112.28 (d, *J* = 3.0 Hz), 49.62, 47.10, 43.89; HRMS (ESI) calcd. for $C_{15}H_{17}FN_3$ $[M+H]^+$: 258.1401, found: 258.1406.

(*S*)-2-Methyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3s)



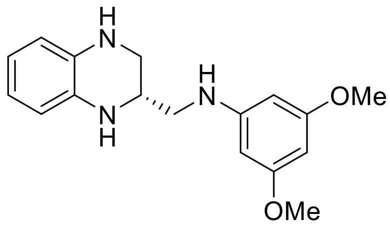
Pale yellow oil, 44.1 mg, isolated yield 87%; $[\alpha]_D^{20}$ = -55.2 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 95%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 0.7 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 51.6 min (minor), t_{R2} = 67.9 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (td, *J* = 7.3, 1.3 Hz, 1H), 6.69 – 6.66 (m, 2H), 6.63 (d, *J* = 7.4 Hz, 1H), 6.57 (dt, *J* = 7.0, 2.5 Hz, 2H), 6.52 (d, *J* = 7.3 Hz, 2H), 3.96-3.92 (m, 2H), 3.71-3.67 (m, 2H), 3.41 (dd, *J* = 10.9, 3.1 Hz, 1H), 3.32-3.22 (m, 3H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.21, 139.20, 133.34, 132.90, 129.27, 119.03, 118.81, 118.72, 114.83, 114.59, 113.76, 110.16, 49.55, 47.46, 44.07, 21.70; HRMS (ESI) calcd. for $C_{16}H_{20}N_3$ $[M+H]^+$: 254.1652, found: 254.1651.

(*S*)-3,5-Dimethyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3t)



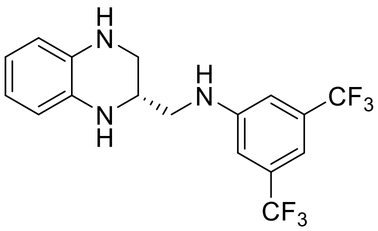
Pale yellow oil, 50.8 mg, isolated yield 95%; $[\alpha]_D^{20}$ = -81.7 (c = 1.0, $CHCl_3$); enantiomeric excess: 94%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 16.685 min (minor), t_{R2} = 18.233 min (major) ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.66 – 6.62 (m, 2H), 6.55 (ddt, J = 6.5, 5.7, 2.9 Hz, 2H), 6.44 (s, 1H), 6.32 (d, J = 1.6 Hz, 2H), 4.06 – 3.54 (m, 4H), 3.42 (dd, J = 10.8, 3.1 Hz, 1H), 3.33 – 3.21 (m, 3H), 2.28 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.29, 139.14, 133.38, 132.95, 119.87, 119.09, 118.86, 114.88, 114.62, 110.99, 49.63, 47.55, 44.17, 21.60; HRMS (ESI) calcd. for $C_{17}H_{22}N_3$ $[M+H]^+$: 268.1808, found: 268.1805.

(*S*)-3,5-Dimethoxy-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3u)



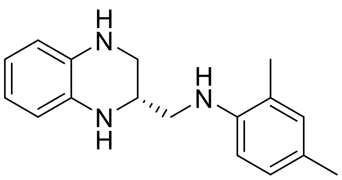
Pale yellow oil, 47.9 mg, isolated yield 80%; $[\alpha]_D^{20}$ = -85.8 (c = 1.0, $CHCl_3$); enantiomeric excess: 96%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 16.7 min (minor), t_{R2} = 18.2 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.64 – 6.61 (m, 2H), 6.53 (dt, J = 7.0, 2.5 Hz, 2H), 5.92 (t, J = 2.2 Hz, 1H), 5.85 (d, J = 2.1 Hz, 2H), 4.09 – 3.65 (m, 3H), 3.76 (s, 6H), 3.67 (tdd, J = 6.6, 5.2, 3.1 Hz, 1H), 3.38 (dd, J = 10.9, 3.1 Hz, 1H), 3.29 – 3.18 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.88, 150.18, 133.35, 132.87, 119.09, 118.86, 114.86, 114.63, 91.88, 90.04, 55.27, 49.53, 47.47, 43.95; HRMS (ESI) calcd. for $C_{17}H_{22}N_3O_2$ $[M+H]^+$: 300.1707, found: 300.1705.

(*S*)-3,5-Dimethoxy-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3v)



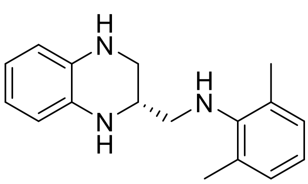
Pale yellow oil, 69.0 mg, isolated yield 92%; $[\alpha]_D^{20}$ = -85.8 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 99%; HPLC (OJ-H, elute: hexane/isopropanol = 60/40, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 12.938 min (major), t_{R2} = 18.399 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.97 (d, *J* = 1.6 Hz, 2H), 6.66 (dd, *J* = 5.8, 3.4 Hz, 2H), 6.59 – 6.53 (m, 2H), 4.55 (t, *J* = 5.8 Hz, 1H), 3.94 – 3.54 (m, 3H), 3.44 – 3.26 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.96, 133.24, 132.61 (q, *J* = 32.7 Hz), 132.44, 123.66 (q, *J* = 272.7 Hz), 119.49, 119.30, 115.19, 114.91, 112.15 (d, *J* = 4.4 Hz), 110.60(m), 49.45, 47.22, 43.62; HRMS (ESI) calcd. for $C_{17}H_{16}F_6N_3$ $[M+H]^+$: 376.1243, found: 376.1245.

(*S*)-3,5-Dimethoxy-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3w)



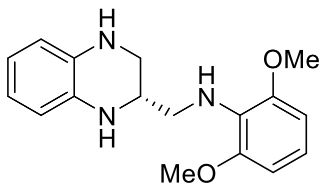
Pale yellow oil, 44.4 mg, isolated yield 83%; $[\alpha]_D^{20}$ = -80.7 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 95%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 11.775 min (major), t_{R2} = 12.872 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.95 (m, 2H), 6.66 – 6.61 (m, 3H), 6.57 – 6.54 (m, 2H), 4.05 – 3.52 (m, 4H), 3.45 (dd, *J* = 10.9, 3.1 Hz, 1H), 3.39 – 3.26 (m, 3H), 2.28 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.78, 133.40, 132.99, 131.24, 127.48, 126.63, 122.46, 119.08, 118.86, 114.88, 114.63, 110.17, 49.49, 47.79, 44.23, 20.42, 17.61; HRMS (ESI) calcd. for $C_{17}H_{22}N_3$ $[M+H]^+$: 268.1808, found: 268.1812.

(*S*)-2,6-Dimethyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3x)



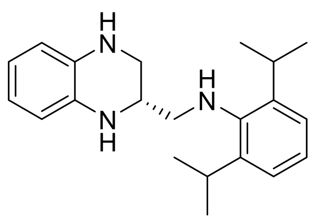
Pale yellow oil, 48.6 mg, isolated yield 91%; $[\alpha]_D^{20}$ = -75.8 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 99%; HPLC (AD-H, elute: hexane/isopropanol = 90/10, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 19.768 min (minor), t_{R2} = 21.784 min (major);^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.56 – 6.49 (m, 2H), 6.48 – 6.39 (m, 2H), 3.78 – 3.48 (m, 4H), 3.29 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.14 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.05 – 2.92 (m, 2H), 2.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.68, 133.46, 133.02, 129.78, 129.07, 122.41, 119.05, 118.88, 114.94, 114.61, 51.55, 51.14, 44.39, 18.63; HRMS (ESI) calcd. for $C_{17}H_{22}N_3$ $[M+H]^+$: 268.1808, found: 268.1805.

(*R*)-2,6-Dimethoxy-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3y)



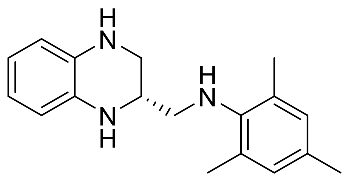
Pale yellow oil, 55.6 mg, isolated yield 93%; $[\alpha]_D^{20}$ = -78.9 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 92%; HPLC (AD-H, elute: hexane/isopropanol = 90/10, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 19.768 min (minor), t_{R2} = 21.784 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (t, *J* = 8.3 Hz, 1H), 6.64 – 6.54 (m, 4H), 6.52-6.49 (m, 2H), 4.40 - 4.91 (m, 2H), 3.87 (s, 6H), 3.71 (s, br, 1H), 3.48 – 3.34 (m, 3H), 3.28 – 3.12 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.32, 133.47, 133.44, 126.17, 120.64, 118.89, 118.47, 114.60, 114.49, 104.77, 55.97, 50.09, 50.00, 44.29; HRMS (ESI) calcd. for $C_{17}H_{22}N_3O_2$ [M+H]+: 300.1707, found: 300.1710.

(*S*)-2,6-Diisopropyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3z)



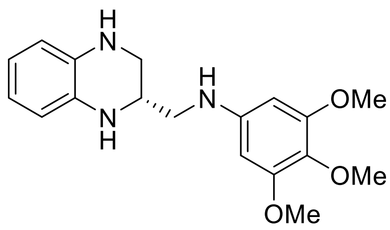
Pale yellow oil, 51.1 mg, isolated yield 79%; $[\alpha]_D^{20}$ = -86.9 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 91%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 5.64 min (major), t_{R2} = 4.63 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, 3H), 6.70 – 6.60 (m, 3H), 6.56 – 6.54 (m, 1H), 3.72 – 3.66 (m, 1H), 3.48 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.35 – 3.26 (m, 3H), 3.08 – 2.96 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 6H), 1.24 (d, *J* = 6.9 Hz, 6H) (three active hydrogens were not detected due to overlap); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.89, 142.79, 133.49, 133.00, 124.32, 123.72, 119.08, 118.95, 115.05, 114.66, 54.90, 51.06, 44.56, 27.73, 24.43, 24.20; HRMS (ESI) calcd. for $C_{21}H_{30}N_3$ $[M+H]^+$: 324.2434, found: 324.2434.

(*S*)-2,4,6-Trimethyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3aa)



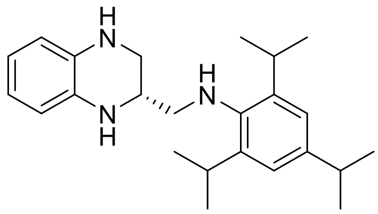
Pale yellow oil, 50.6 mg, isolated yield 90%; $[\alpha]_D^{20}$ = -83.2 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 97%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 25.481 min (major), t_{R2} = 27.658 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 (s, 2H), 6.70 – 6.66 (m, 2H), 6.61 – 6.60 (m, 1H), 6.58 – 6.55 (m, 1H), 4.17 (s, br, 1H), 3.66 – 3.61 (m, 1H), 3.43 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.28 (dd, *J* = 10.8, 6.9 Hz, 1H), 3.12 – 3.03 (m, 2H), 2.34 (s, 6H), 2.31 (s, 3H), (two active hydrogens were not detected); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.01, 133.44, 133.05, 131.82, 130.08, 129.60, 118.93, 118.76, 114.83, 114.53, 51.80, 51.05, 44.43, 20.63, 18.38; HRMS (ESI) calcd. for $C_{18}H_{24}N_3$ $[M+H]^+$: 282.1965, found: 282.1969.

(*S*)-3,4,5-Trimethoxy-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3ab)



Pale yellow oil, 62.5 mg, isolated yield 95%; $[\alpha]_D^{20}$ = -84.6 (*c* = 1.0, $CHCl_3$); enantiomeric excess: >99%; HPLC (OD-H, elute: hexane/isopropanol = 60/40, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} =27.638 min (minor), t_{R2} = 43.175 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 – 6.58 (m, 2H), 6.57 – 6.49 (m, 2H), 5.89 (s, 2H), 4.01- 3.74(m, 12H), 3.70 – 3.64 (m, 1H), 3.41 (dd, J = 10.8, 3.1 Hz, 1H), 3.32 – 3.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.09, 145.15, 133.34, 132.84, 130.40, 119.17, 118.93, 114.91, 114.66, 90.67, 61.19, 56.06, 49.99, 48.05, 44.02; HRMS (ESI) calcd. for $C_{18}H_{24}N_3O_3$ $[M+H]^+$: 330.1812, found: 330.1816.

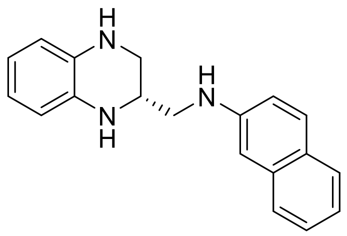
(*S*)-2,4,6-Triisopropyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3ac)



Pale yellow oil, 51.1 mg, isolated yield 79%; $[\alpha]_D^{20}$ = -82.1 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 82%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 5.996 min (major), t_{R2} = 8.270 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.64 – 6.58 (m, 3H), 6.54 – 6.52 (m, 1H), 4.04 – 3.04 (m, 9H), 3.02 (dd,

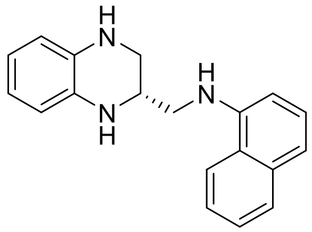
J = 11.9, 4.4 Hz, 1H), 2.95 – 2.85 (m, 2H), 1.26 (dd, J = 6.9, 2.8 Hz, 12H), 1.21 (d, J = 6.9 Hz, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.44, 142.78, 140.40, 133.55, 133.14, 121.62, 119.08, 118.91, 114.99, 114.65, 55.04, 51.13, 44.71, 34.10, 27.83, 24.54, 24.30, 24.28, 24.25; HRMS (ESI) calcd. for $C_{24}H_{36}N_3$ $[M+H]^+$: 366.2904, found: 366.2908.

(*S*)-N-((1,2,3,4-Tetrahydroquinoxalin-2-yl)methyl)naphthalen-2-amine (3ad)



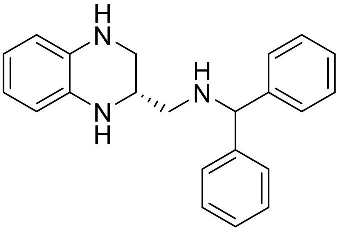
Pale yellow oil, 53.2 mg, isolated yield 92%, $[\alpha]_D^{20}$ = -90.4 (c = 1.0, $CHCl_3$); enantiomeric excess: 92%; HPLC (hexane : isopropanol = 70 : 30, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} =19.899 min (major), t_{R2} = 22.135 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 1H), 7.67 (dd, J = 12.8, 8.5 Hz, 2H), 7.43 (ddd, J = 8.1, 6.7, 1.3 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.92 – 6.87 (m, 2H), 6.70 – 6.67 (m, 2H), 6.58 – 6.55 (m, 2H), 4.27 – 3.56 (m, 4H), 3.41 – 3.26 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.85, 135.17, 133.33, 132.85, 129.10, 127.73, 127.66, 126.53, 126.00, 122.24, 119.11, 118.90, 118.06, 114.91, 114.66, 104.62, 49.46, 47.42, 44.02; HRMS (ESI) calcd. for $C_{19}H_{20}N_3$ $[M+H]^+$: 290.1652, found: 290.1658

(*S*)-N-((1,2,3,4-Tetrahydroquinoxalin-2-yl)methyl)naphthalen-1-amine (3ae)



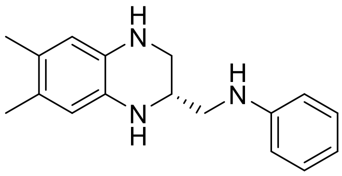
Pale yellow oil, 53.8 mg, isolated yield 93%; $[\alpha]_D^{20}$ = -93.7 (c = 1.0, $CHCl_3$); enantiomeric excess: 90%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} =13.478 min (minor), t_{R2} = 17.233 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 2H), 7.34 – 7.30 (m, 2H), 7.22 (tdt, J = 7.4, 3.5, 1.7 Hz, 1H), 7.14 (dt, J = 7.3, 2.7 Hz, 1H), 6.51 (tdd, J = 7.5, 4.7, 2.8 Hz, 3H), 6.39 (dd, J = 5.9, 3.4 Hz, 2H), 4.58 (t, J = 5.6 Hz, 1H), 3.75 (s, 1H), 3.63 (qq, J = 6.2, 3.1 Hz, 1H), 3.48 (s, 1H), 3.25 – 3.15 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.35, 134.38, 133.33, 132.95, 128.76, 126.62, 125.92, 124.91, 123.60, 120.02, 119.10, 118.90, 117.78, 114.96, 114.65, 104.57, 49.18, 47.62, 44.18; HRMS (ESI) calcd. for $C_{19}H_{20}N_3$ $[M+H]^+$: 290.1652, found: 290.1654.

(*S*)-1,1-Diphenyl-N-((1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)methanamine (3af)



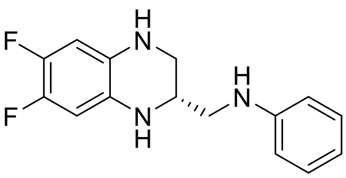
Pale yellow oil, 54.0 mg, isolated yield 82%; $[\alpha]_D^{20}$ = -93.7 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 90%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 35.366 min (minor), t_{R2} = 46.663 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 4H), 7.33 (td, *J* = 7.6, 3.1 Hz, 4H), 7.27 – 7.24 (m, 2H), 6.66 – 6.50 (m, 4H), 4.87 (s, 1H), 3.53 – 3.32 (m, 5H), 3.13 (dd, *J* = 10.7, 7.2 Hz, 1H), 2.77 (dd, *J* = 11.8, 4.5 Hz, 1H), 2.65 (dd, *J* = 11.8, 8.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.93, 143.50, 133.40, 133.28, 128.69, 128.65, 127.37, 127.32, 127.25, 119.05, 118.65, 114.71, 114.63, 67.49, 51.23, 50.33, 44.79; HRMS (ESI) calcd. for $C_{22}H_{24}N_3$ $[M+H]^+$: 330.1965, found: 330.1968.

(*S*)-N-((6,7-Dimethyl-1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3ba)



Pale yellow oil, 49.2 mg, isolated yield 92%; $[\alpha]_D^{20}$ = -87.3 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 92%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 22.263 min (major), t_{R2} = 24.300 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 6.77 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.71 – 6.65 (m, 2H), 6.38 (d, *J* = 1.8 Hz, 2H), 3.76 – 3.41 (m, 4H), 3.39 (dd, *J* = 10.9, 3.0 Hz, 1H), 3.33 – 3.21 (m, 3H), 2.15 (t, *J* = 1.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.26, 131.12, 130.65, 129.41, 126.94, 126.67, 117.75, 116.72, 116.49, 113.01, 49.85, 47.40, 44.43, 18.99, 18.98; HRMS (ESI) calcd. for $C_{17}H_{22}N_3$ $[M+H]^+$: 268.1808, found: 268.1810.

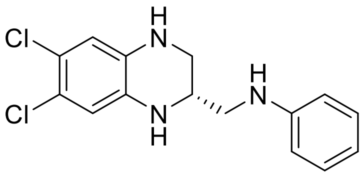
(*S*)-N-((6,7-Difluoro-1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3ca)



Pale yellow oil, 47.9 mg, isolated yield 87%; $[\alpha]_D^{20}$ = -78.5 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 95%; HPLC (AD-H, elute: hexane/isopropanol = 80/10, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 16.498 min (minor), t_{R2} = 18.8 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.76 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.68 – 6.65 (m, 2H), 6.31 (ddd, *J* = 11.5, 7.7, 1.7

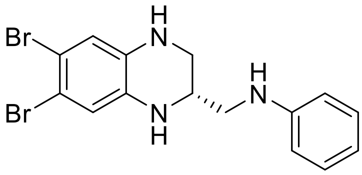
Hz, 2H), 3.78 (s, br, 3H), 3.62 (dddd, J = 7.9, 6.5, 5.0, 3.1 Hz, 1H), 3.36 (dd, J = 11.0, 3.1 Hz, 1H), 3.29 (dd, J = 13.1, 5.0 Hz, 1H), 3.23 – 3.17 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.92, 143.26 (dd, J = 10.3, 5.4 Hz), 141.02 (dd, J = 11.6, 4.4 Hz), 128.38, 127.95 (dd, J = 7.8, 2.4 Hz), 127.50 (dd, J = 7.9, 2.5 Hz), 116.96, 111.94, 102.13 (d, J = 20.0 Hz), 101.87 (d, J = 20.6 Hz), 48.29, 46.19, 42.76; HRMS (ESI) calcd. for $C_{15}H_{16}F_2N_3$ $[M+H]^+$: 276.1307, found: 276.1304.

(*S*)-N-((6,7-Dichloro-1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3da)



Pale yellow oil, 55.9 mg, isolated yield 91%; $[\alpha]_D^{20}$ = -79.7 (c = 1.0, $CHCl_3$); enantiomeric excess: 94%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 31.657 min (major), t_{R2} = 37.644 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 6.77 (tt, J = 7.3, 1.1 Hz, 1H), 6.66 (dt, J = 7.7, 1.1 Hz, 2H), 6.52 (d, J = 1.8 Hz, 2H), 4.04 (s, br, 1H), 3.89 (s, br, 1H), 3.71 (s, br, 1H), 3.63 – 3.57 (m, 1H), 3.36 (dd, J = 11.0, 3.1 Hz, 1H), 3.28 (dd, J = 13.2, 5.0 Hz, 1H), 3.18 (dt, J = 11.2, 5.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.95, 133.04, 132.55, 129.52, 120.60, 120.45, 118.12, 115.10, 114.80, 113.05, 49.16, 47.28, 43.48; HRMS (ESI) calcd. for $C_{15}H_{16}Cl_2N_3$ $[M+H]^+$: 308.0716, found: 308.0718, 312.0660.

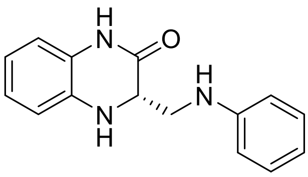
(*S*)-N-((6,7-Dibromo-1,2,3,4-tetrahydroquinoxalin-2-yl)methyl)aniline (3ea)



Pale yellow oil, 67.1 mg, isolated yield 85%; $[\alpha]_D^{20}$ = -76.2 (c = 1.0, $CHCl_3$); enantiomeric excess: 87%; HPLC (AD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 21.664 min (minor), t_{R2} = 23.526 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 6.77 (ddt, J = 8.4, 7.3, 1.1 Hz, 1H), 6.70 – 6.64 (m, 4H), 4.07 – 3.68 (m, 3H), 3.63 – 3.56 (m, 1H), 3.35 (dd, J = 11.0, 3.2 Hz, 1H), 3.28 (dd, J = 13.2, 5.0 Hz, 1H), 3.23 – 3.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.93, 133.84, 133.35, 129.53, 118.16, 118.09, 117.78, 113.07, 111.72, 111.56, 49.13, 47.30, 43.41; HRMS (ESI) calcd. for $C_{15}H_{16}Br_2N_3$ $[M+H]^+$:

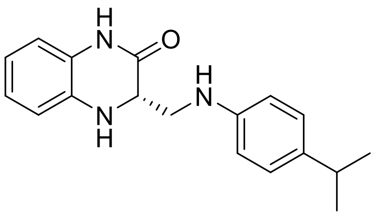
395.9705, found: 395.9708, 399.9662.

(*S*)-3-((Phenylamino)methyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7a)



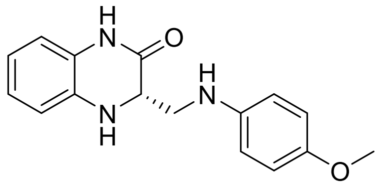
Pale yellow oil, 41.5 mg, isolated yield 82%; $[\alpha]_D^{20}$ = -67.3 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 74%; HPLC (OJ-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 29.4 min (major), t_{R2} = 37.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.22 – 7.16 (m, 2H), 6.91 (td, *J* = 7.5, 1.6 Hz, 1H), 6.80 – 6.67 (m, 6H), 4.23 (s, 1H), 4.21-4.17 (m, 1H), 4.11 (s, 1H), 3.68 (dd, *J* = 13.6, 4.4 Hz, 1H), 3.51 (dd, *J* = 13.5, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.59, 147.57, 132.84, 129.58, 125.18, 124.28, 119.85, 118.46, 115.53, 114.62, 113.35, 55.43, 45.78; HRMS (ESI) calcd. for $C_{15}H_{16}N_3O$ $[M+H]^+$: 254.1288, found: 254.1290.

(*S*)-3-(((4-Isopropylphenyl)amino)methyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7b)



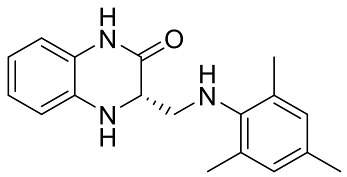
Pale yellow oil, 47.2 mg, isolated yield 80%; $[\alpha]_D^{20}$ = -67.3 (*c* = 1.0, $CHCl_3$); enantiomeric excess: 72%; HPLC (OJ-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 23.872 min (major), t_{R2} = 37.258 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.11 – 7.03 (m, 2H), 6.90 (ddd, *J* = 7.8, 5.2, 3.7 Hz, 1H), 6.76 (dd, *J* = 4.2, 1.0 Hz, 2H), 6.71 – 6.61 (m, 3H), 4.33 (s, 1H), 4.23 – 4.15 (m, 1H), 3.67 (dd, *J* = 13.5, 4.3 Hz, 1H), 3.49 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.83 (hept, *J* = 6.8 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 6H) (one active hydrogen was not detected); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.25, 145.54, 139.04, 132.86, 127.40, 125.23, 124.21, 119.71, 115.74, 114.51, 113.46, 55.34, 46.04, 33.28, 24.34; HRMS (ESI) calcd. for $C_{18}H_{22}N_3O$ $[M+H]^+$: 296.1757, found: 296.175

(*S*)-3-(((4-Methoxyphenyl)amino)methyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7c)



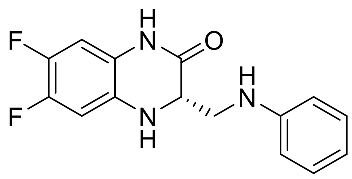
Pale yellow oil, 48.3 mg, isolated yield 85%; $[\alpha]_D^{20}$ = -70.2 (c = 1.0, $CHCl_3$); enantiomeric excess: 69%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 17.802 min (minor), t_{R2} = 22.677 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 6.90 (ddd, J = 7.7, 6.3, 2.6 Hz, 1H), 6.82 – 6.73 (m, 4H), 6.70 – 6.63 (m, 3H), 4.30 (s, 1H), 4.17 (ddd, J = 8.2, 4.3, 1.7 Hz, 1H), 3.85 (s, 1H), 3.75 (s, 3H), 3.62 (dd, J = 13.3, 4.4 Hz, 1H), 3.45 (dd, J = 13.3, 8.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.07, 152.81, 141.67, 132.87, 125.22, 124.20, 119.71, 115.66, 115.12, 114.81, 114.50, 55.91, 55.43, 46.81; HRMS (ESI) calcd. for $C_{16}H_{18}N_3O_2$ $[M+H]^+$: 284.1394, found: 284.1395.

(*S*)-3-((Mesitylamino)methyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7d)



Colorless oil, 45.5 mg, isolated yield 77%, 46% ee. $[\alpha]_D^{20}$ = -55.4 (c = 1.0, $CHCl_3$); enantiomeric excess: 46%; HPLC (OJ-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 11.748 min (minor), t_{R2} = 13.783 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 6.91 (ddd, J = 7.8, 6.4, 2.5 Hz, 1H), 6.83 (s, 2H), 6.79 – 6.73 (m, 2H), 6.71 – 6.66 (m, 1H), 4.34 (s, 1H), 4.12 (ddd, J = 6.8, 4.5, 1.9 Hz, 1H), 3.53 – 3.05 (m, 3H), 2.28 (s, 6H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.28, 142.45, 133.06, 132.28, 130.49, 129.71, 125.33, 124.15, 119.73, 115.67, 114.55, 56.94, 49.83, 20.69, 18.40; HRMS (ESI) calcd. for $C_{18}H_{22}N_3O$ $[M+H]^+$: 296.1757, found: 296.1753

(*S*)-6,7-Difluoro-3-((phenylamino)methyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7e)



Yellow solid, 48.6 mg, isolated yield 84%; $[\alpha]_D^{20}$ = -65.2 (c = 1.0, $CHCl_3$); enantiomeric excess: 70%; HPLC (OD-H, elute: hexane/isopropanol = 80/20, flowing rate: 1.0 mL/min, 25 ºC, UV detection at λ = 254 nm), t_{R1} = 15.111 min (major), t_{R2} = 17.573 min (minor); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 7.11 – 7.05 (m, 2H), 6.70 (td, J = 8.1, 3.6 Hz, 2H), 6.64 – 6.59 (m, 2H), 6.56 (tt, J = 7.3, 1.1 Hz, 1H), 6.28 (d, J = 2.0 Hz, 1H), 5.61 (t, J = 6.1 Hz, 1H), 3.96 (ddd, J = 7.4, 4.1, 1.9 Hz, 1H), 3.35 (s, 1H), 3.24 (dt, J = 13.6, 7.1 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.69, 148.81, 145.23 (dd, J = 224.1, 12.7 Hz), 141.95 (dd, J = 220.4, 12.1 Hz), 130.97 (d, J = 6.8 Hz), 129.38, 122.27 (d, J = 6.3 Hz), 116.67, 112.79, 103.84 (d, J = 21.9 Hz), 102.35 (d, J = 21.9 Hz), 54.86, 45.27; HRMS (ESI) calcd. for $C_{15}H_{14}F_2N_3O$ [M+H]$^+$: 290.1099, found: 290.1095.

7. References

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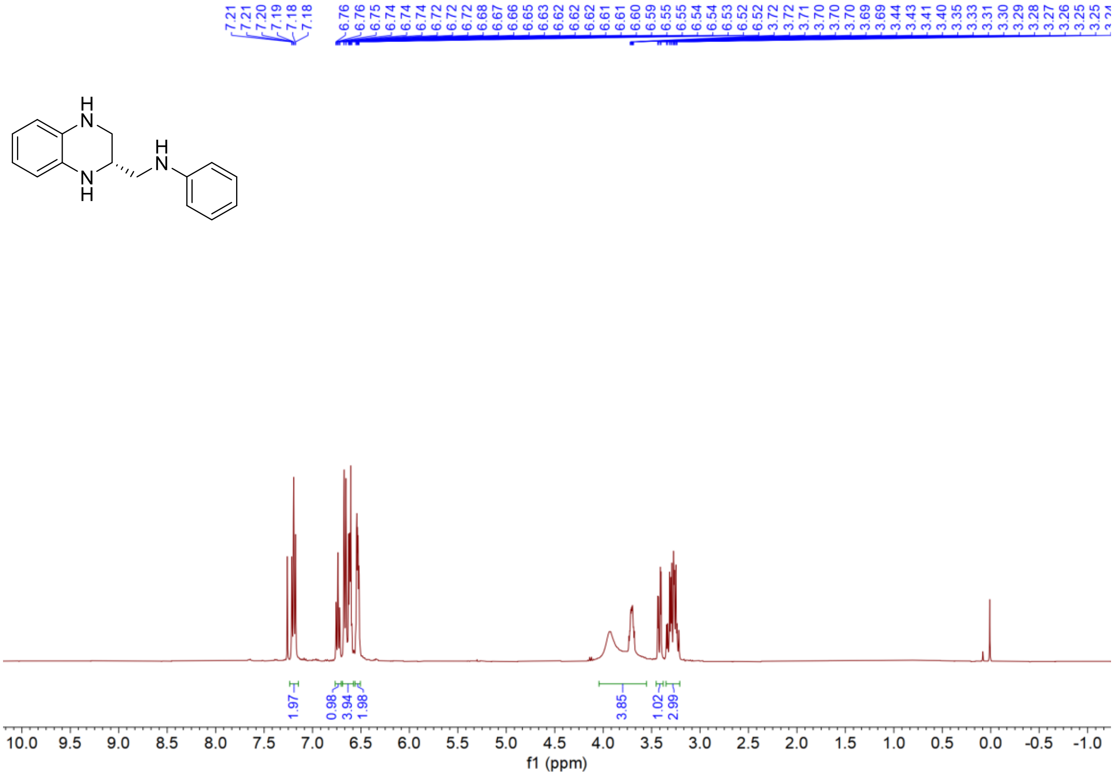
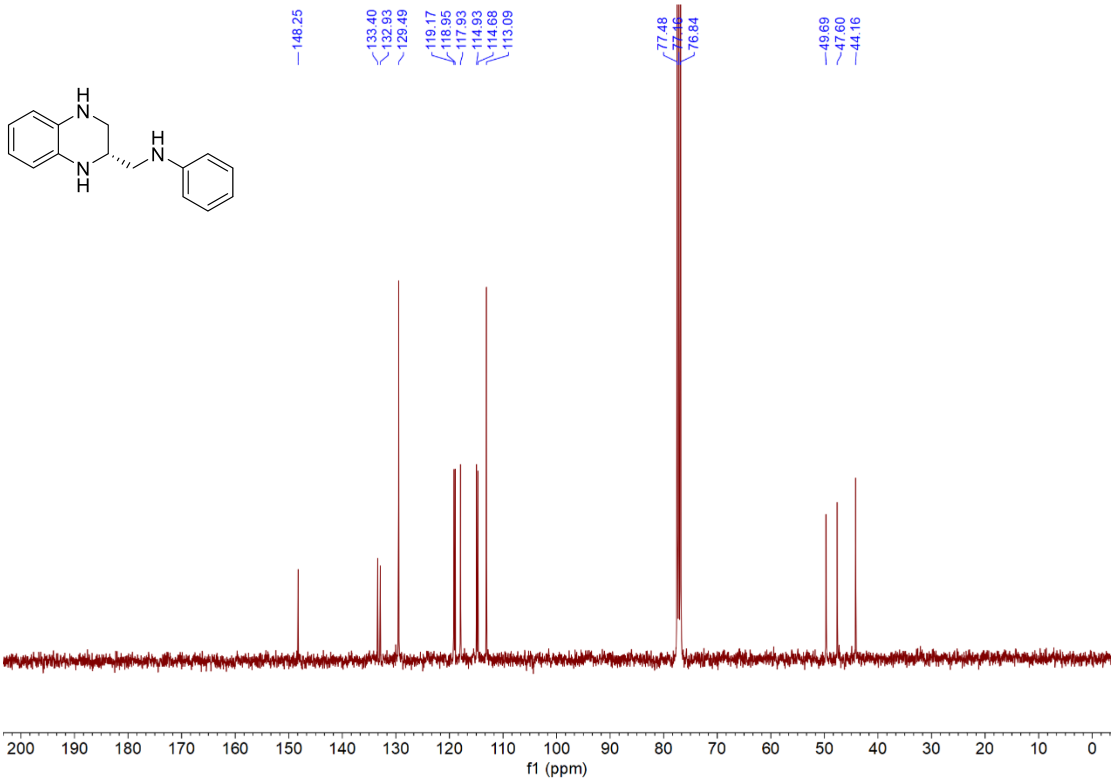
2. M. Koichi, M. Takashi, H. Manabu, *Chem. Commun.* **2004**, 2082-2083.

3. N. Arai, Y. Saruwatari, K. Isobe, Takeshi Ohkuma, *Adv. Synth. Catal*. **2013**, *355*, 2769–2774.

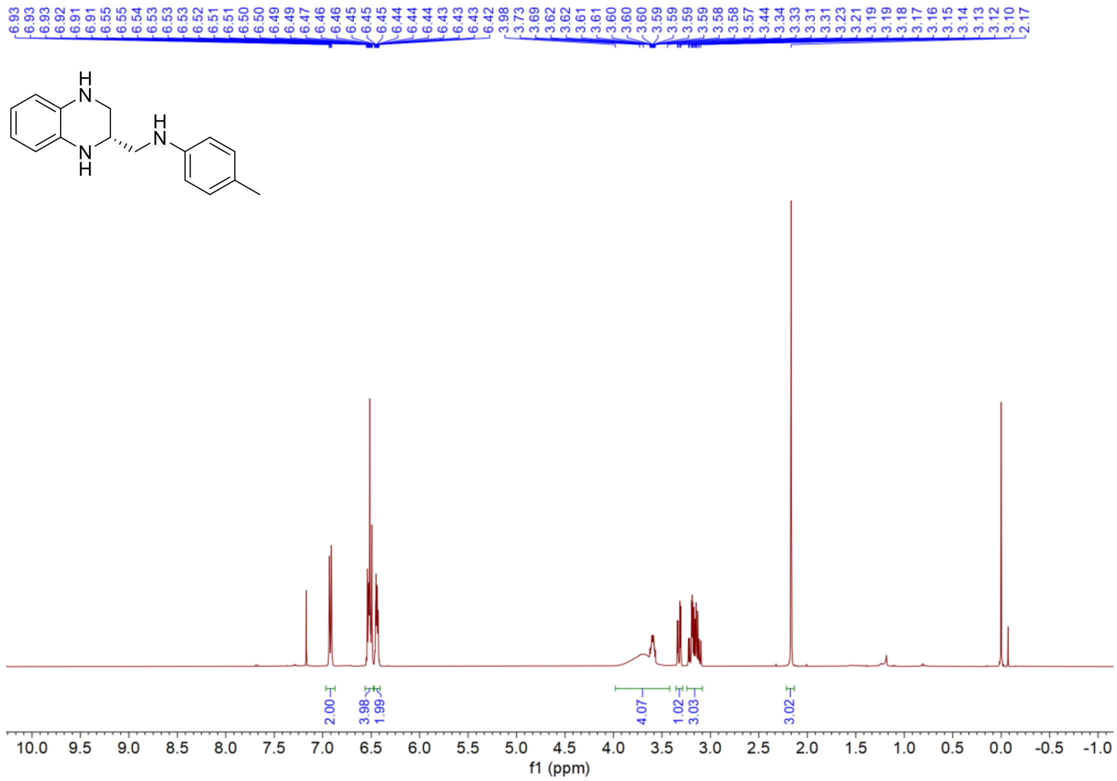
8. ^{1}H and ^{13}C{^{1}H} NMR spectra of the products

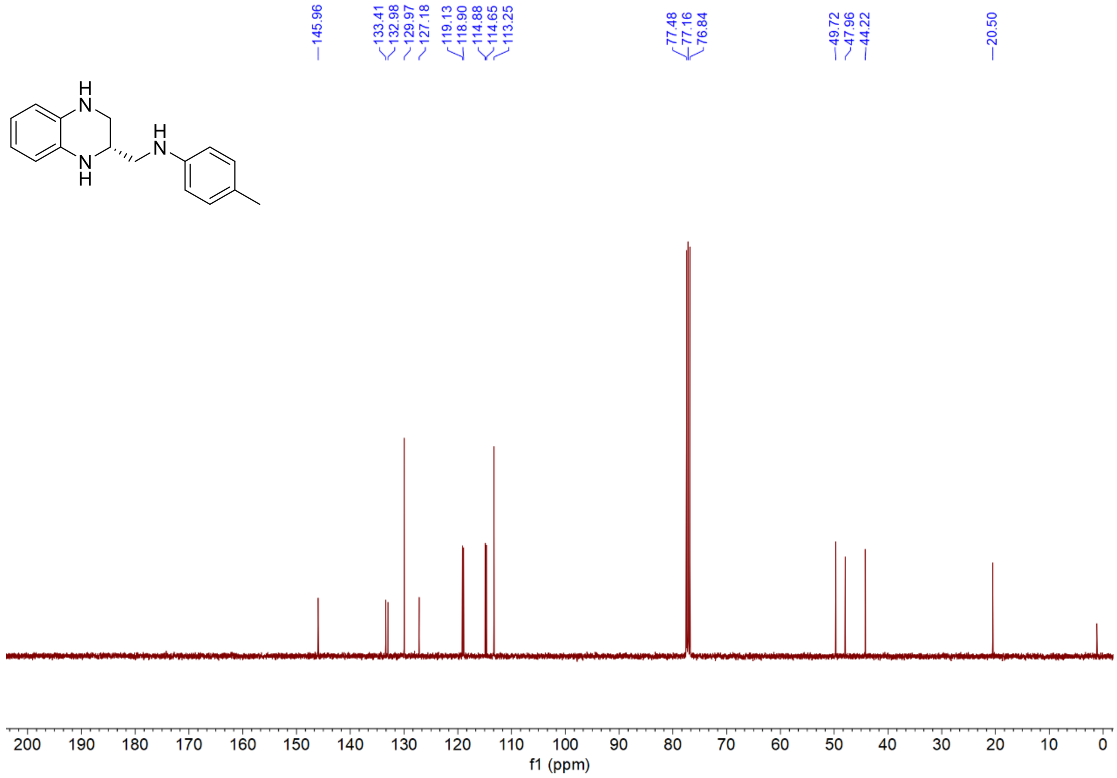
^{1}H and ^{13}C{^{1}H} NMR spectra of compound **3a** in $CDCl_3$



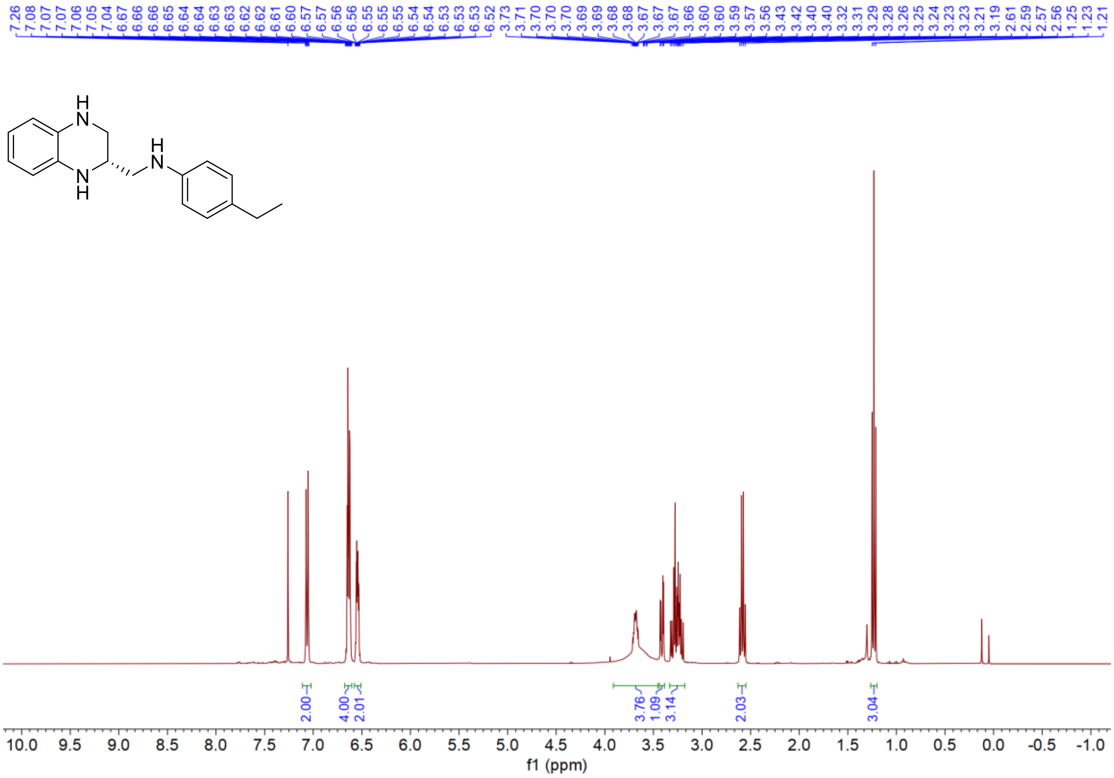


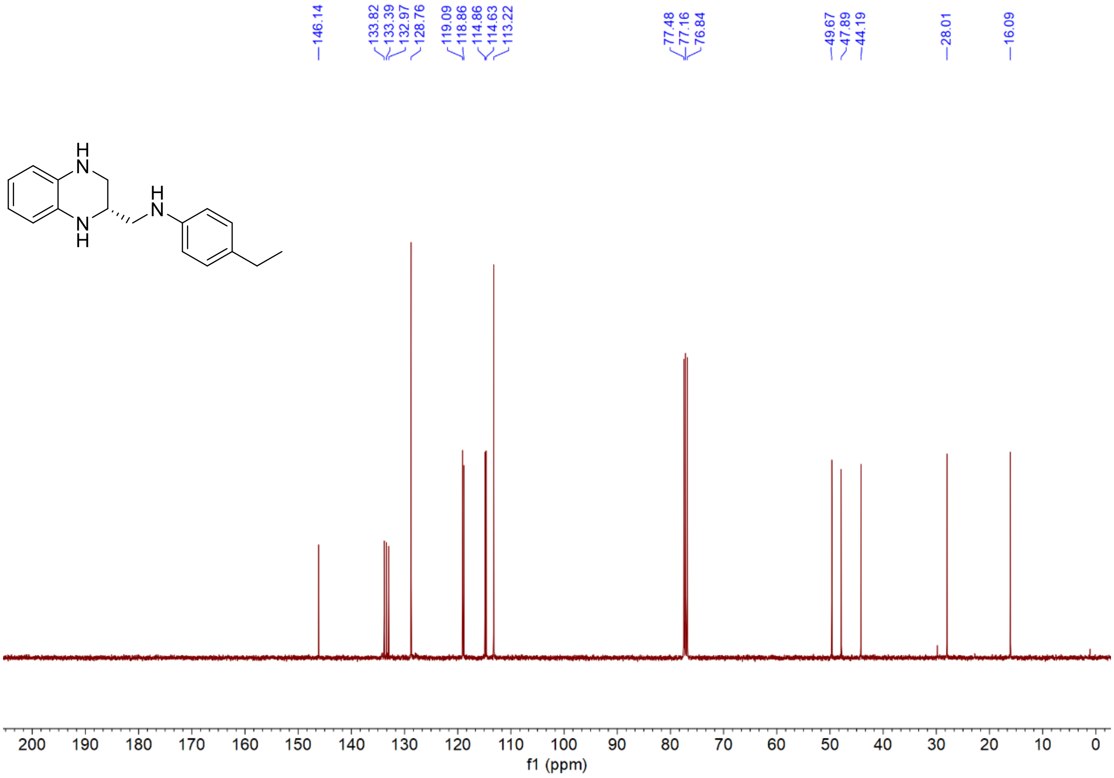
[1]H and [13]C{[1]H} NMR spectra of compound **3b** in $CDCl_3$



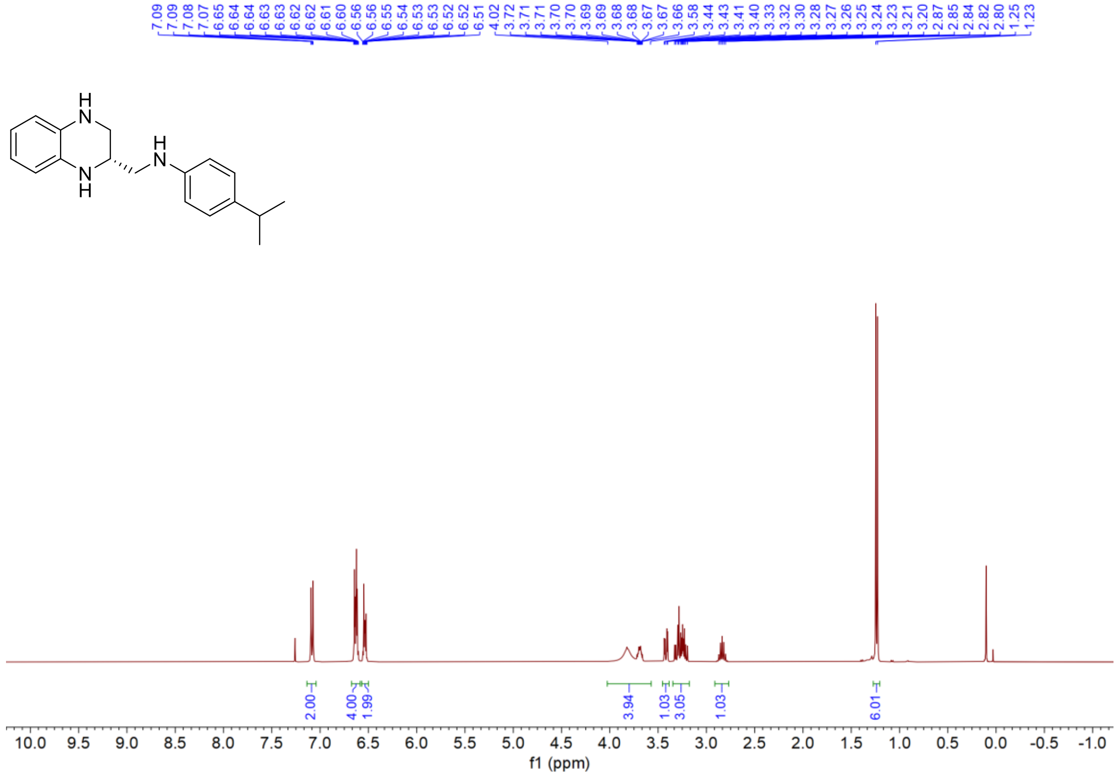


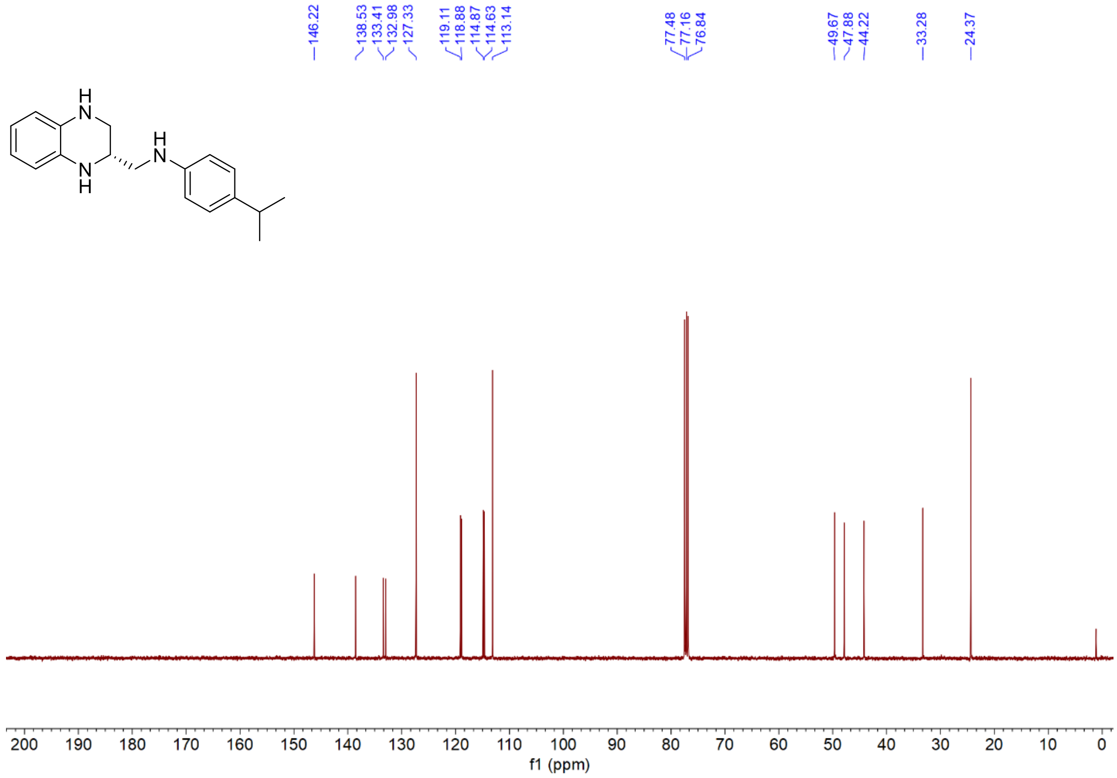
[1]H and [13]C{[1]H} NMR spectra of compound **3c** in $CDCl_3$



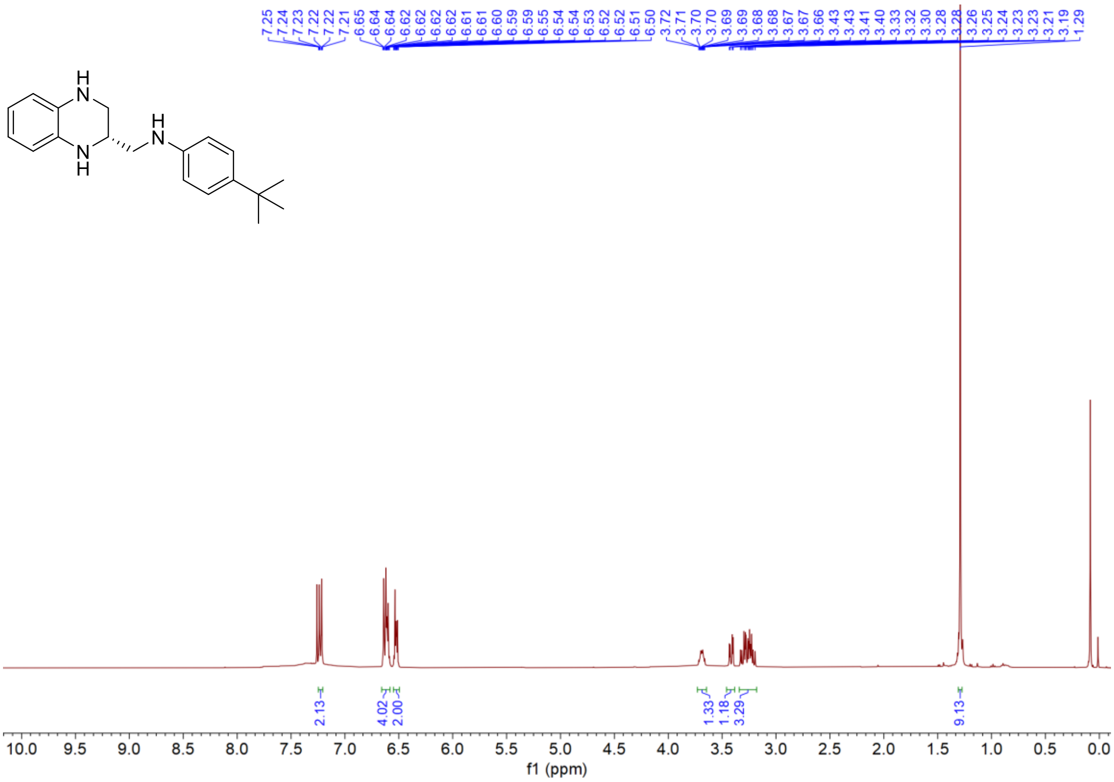


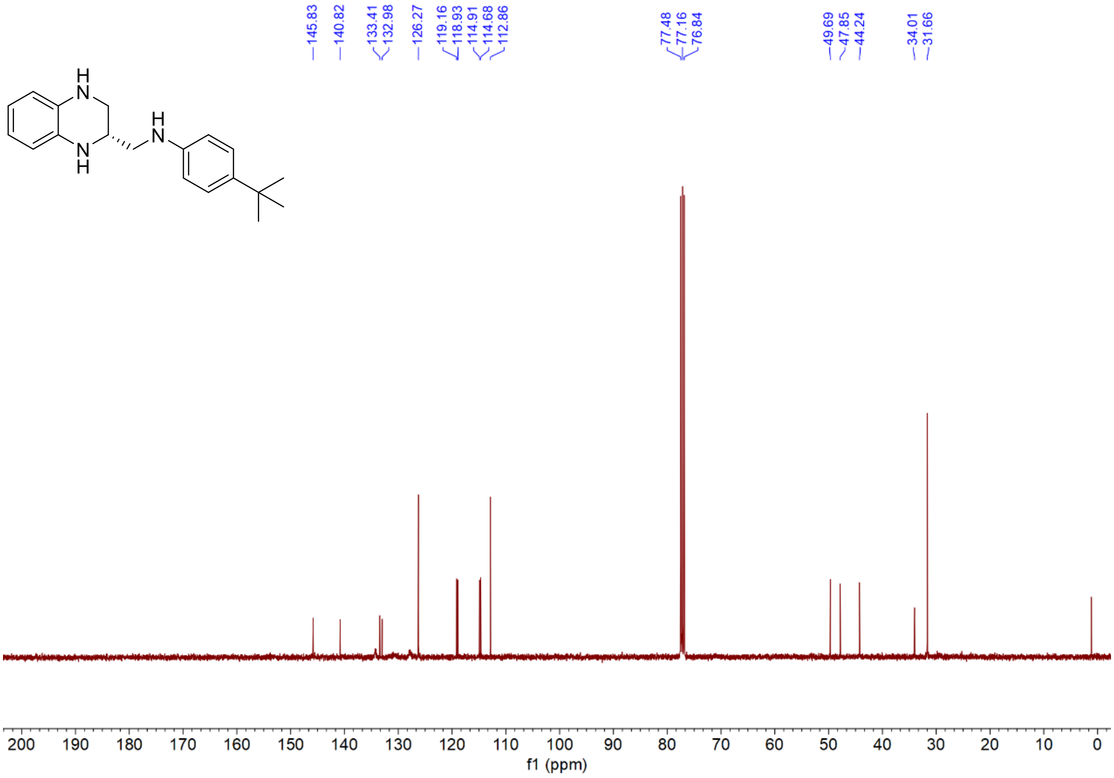
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3d** in $CDCl_3$



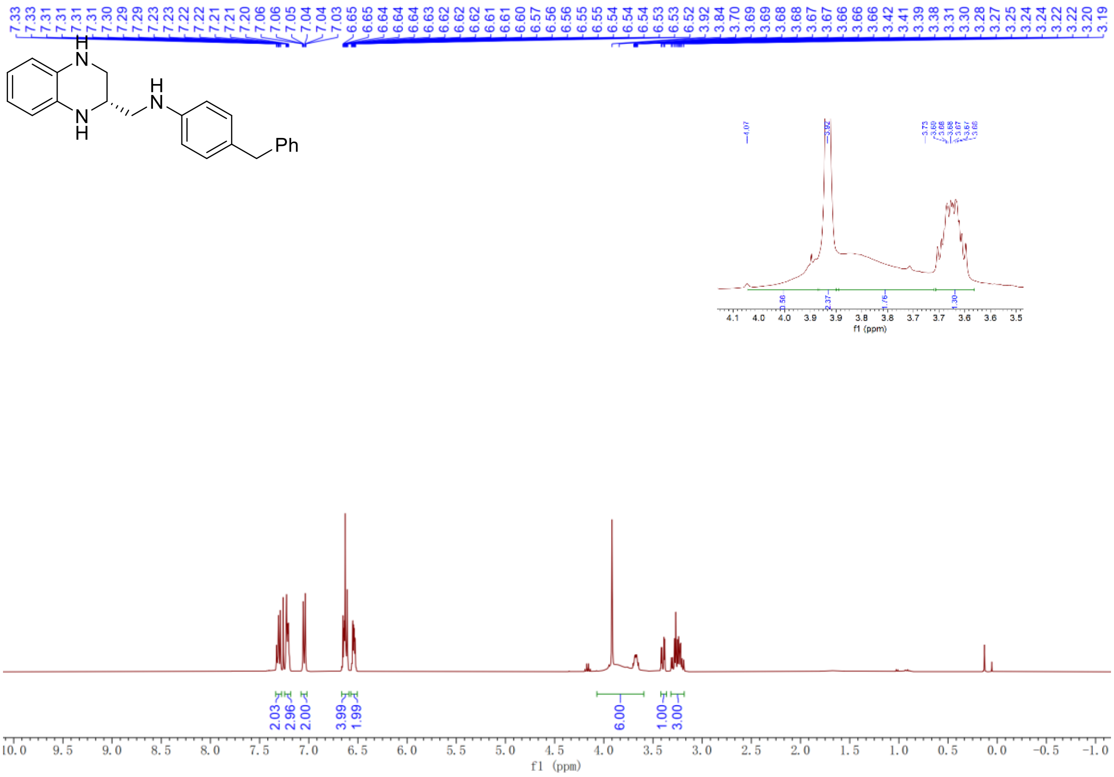


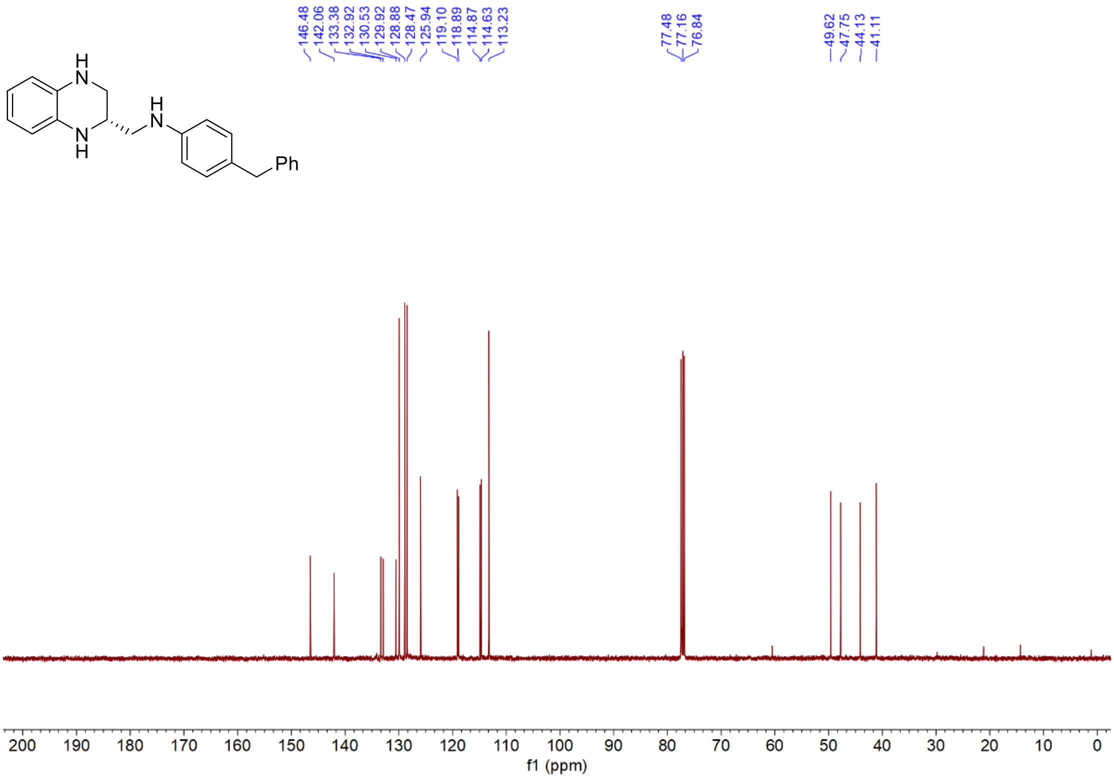
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3e** in $CDCl_3$



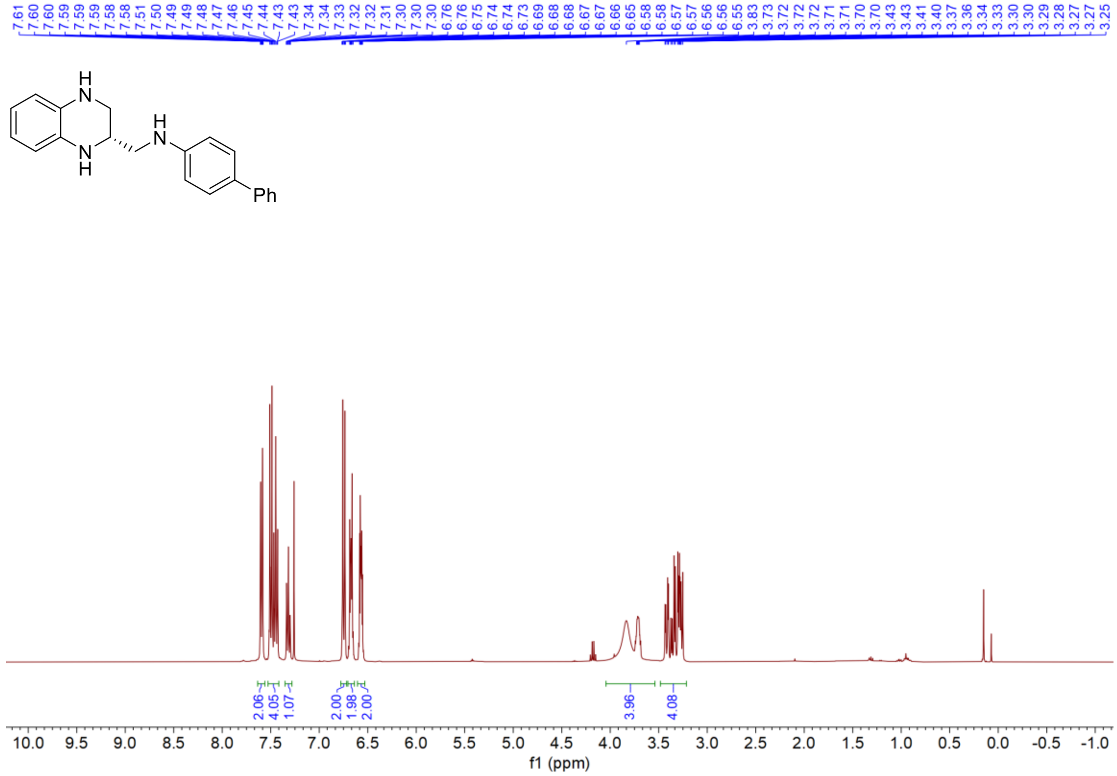


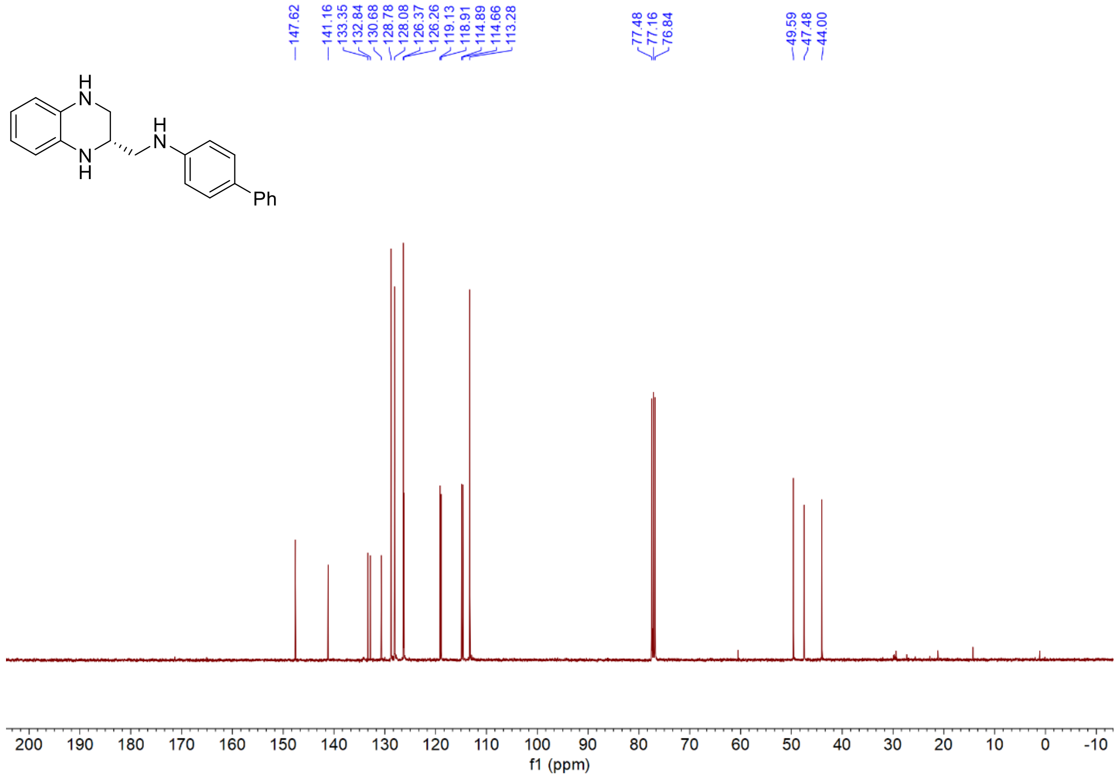
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3f** in $CDCl_3$



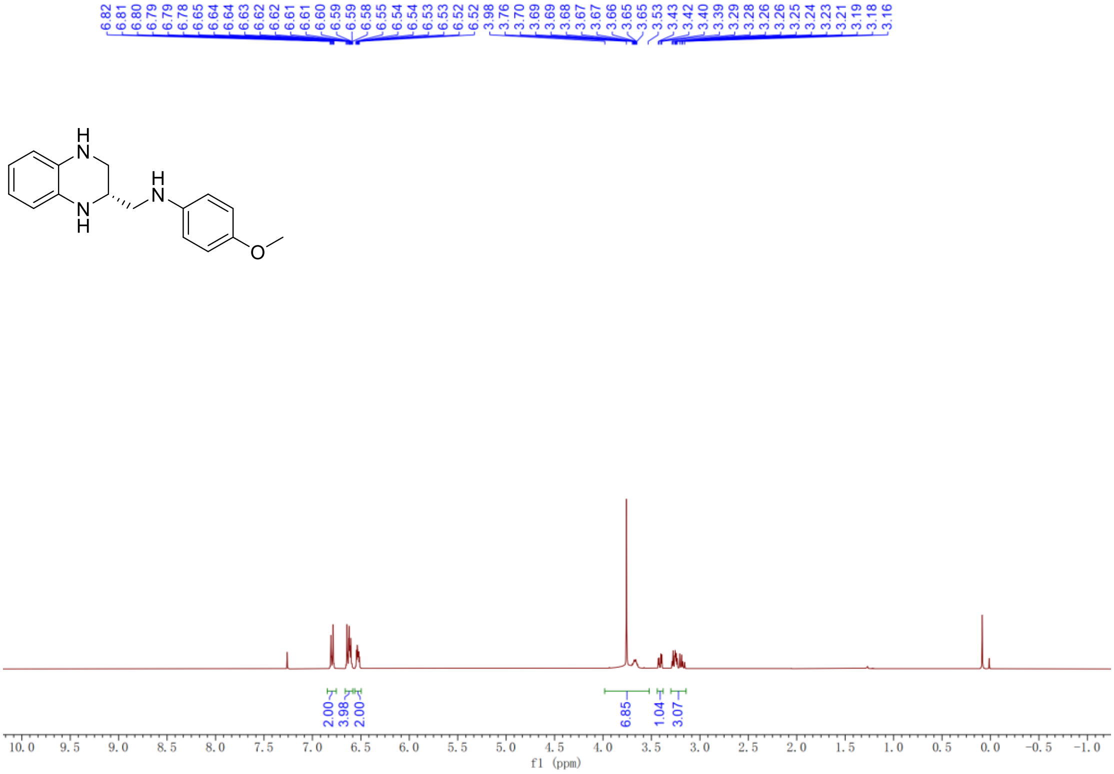


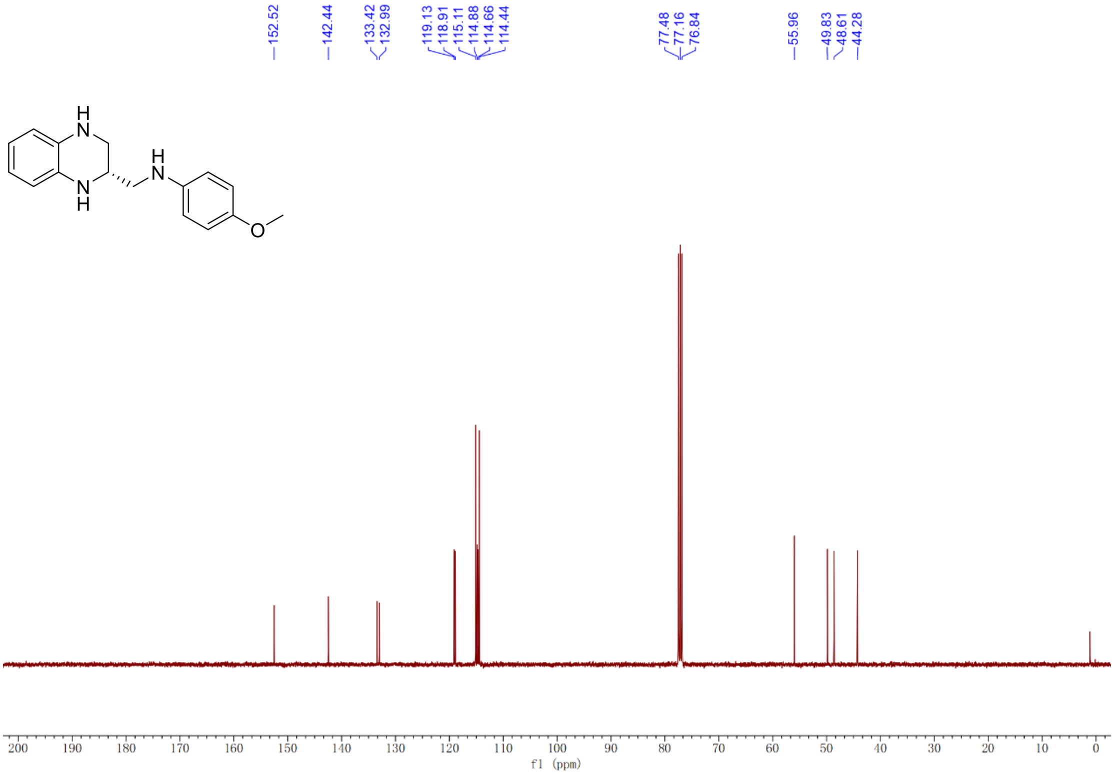
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3g** in $CDCl_3$



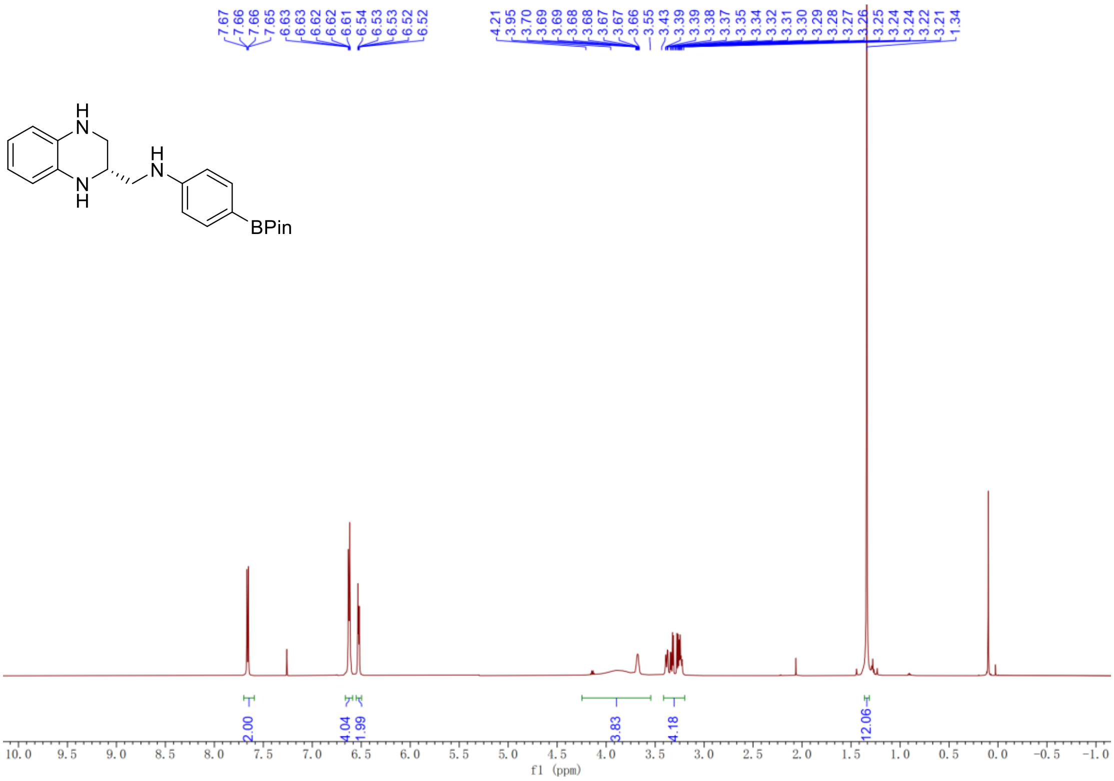


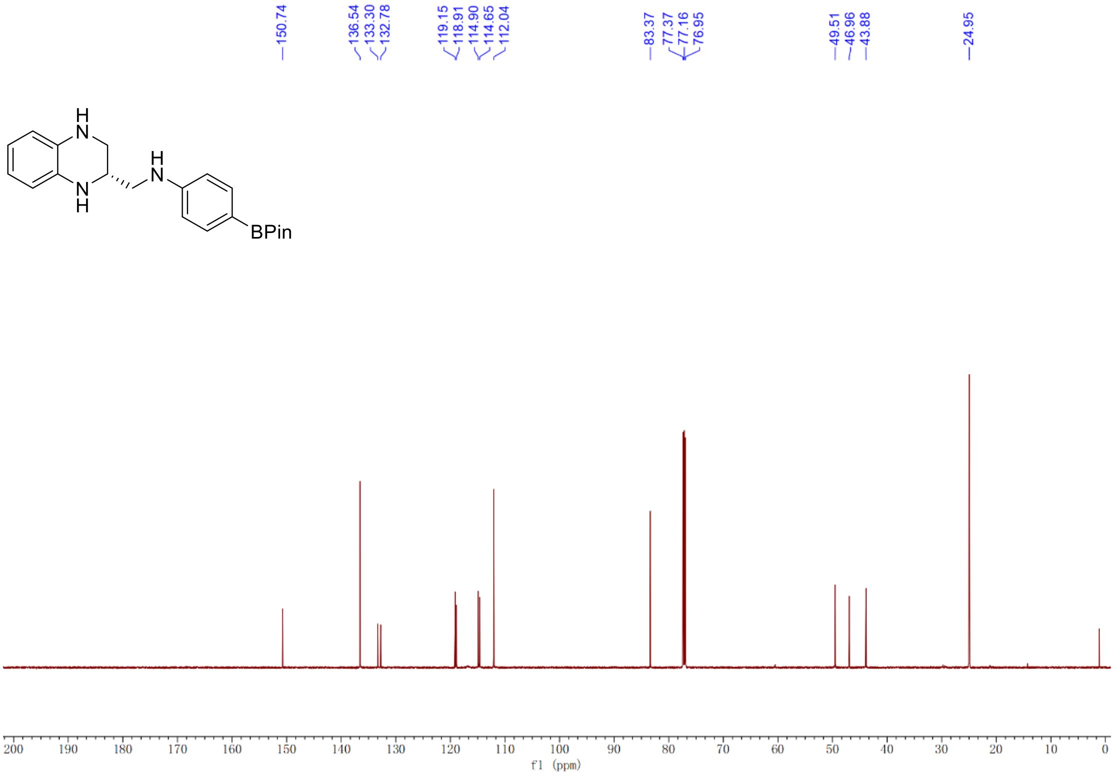
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3g** in $CDCl_3$



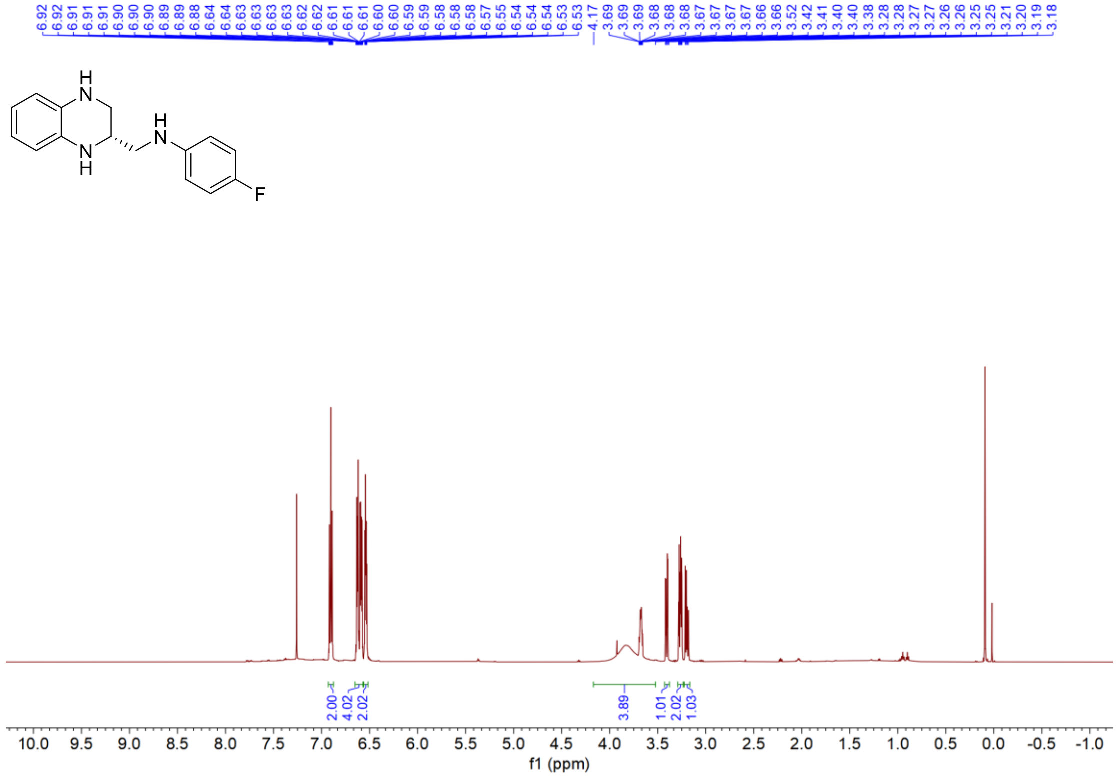


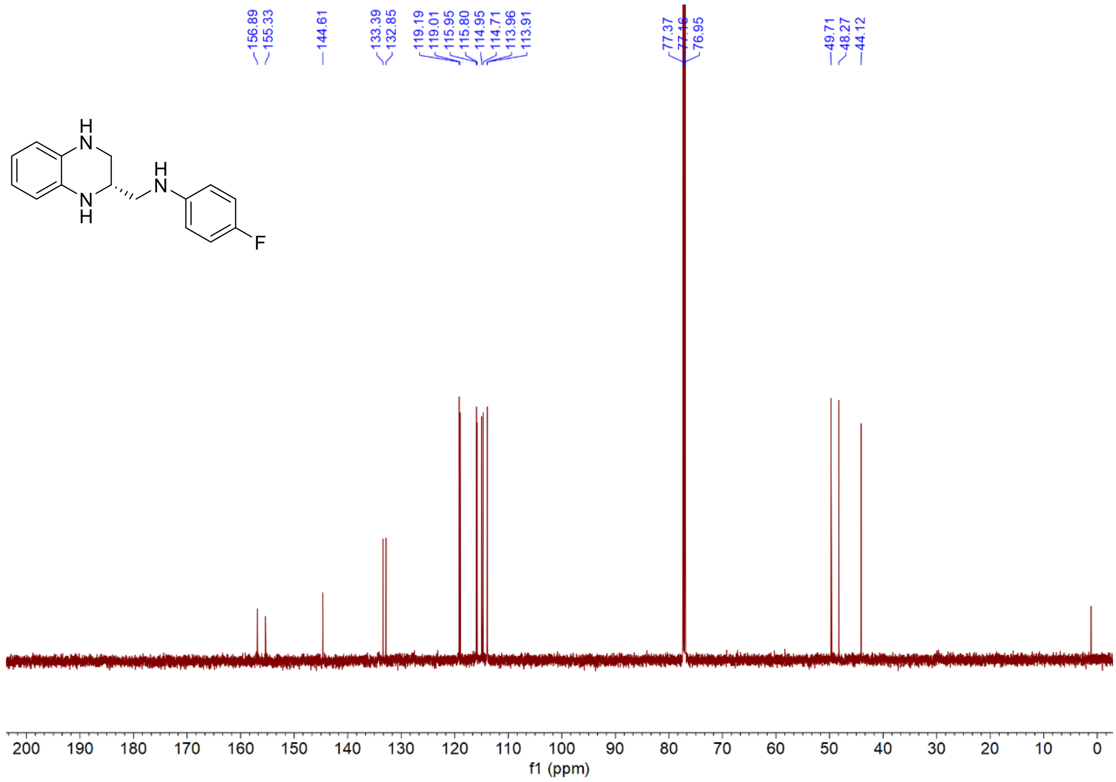
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3i** in $CDCl_3$



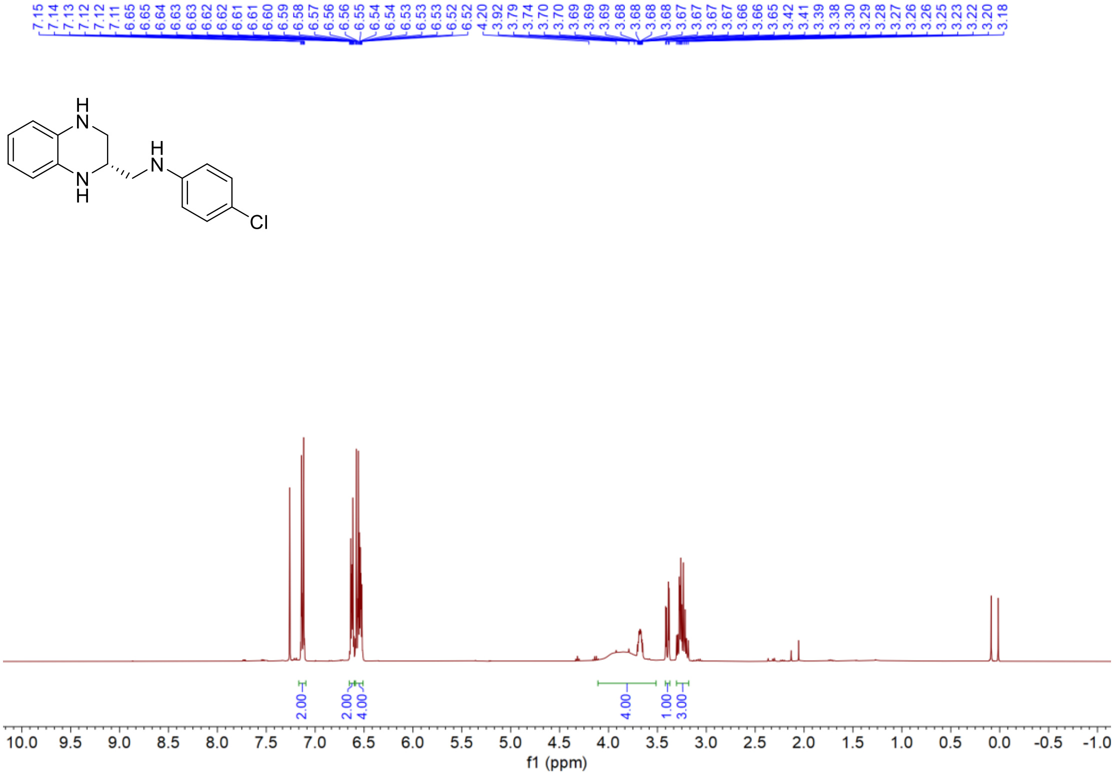


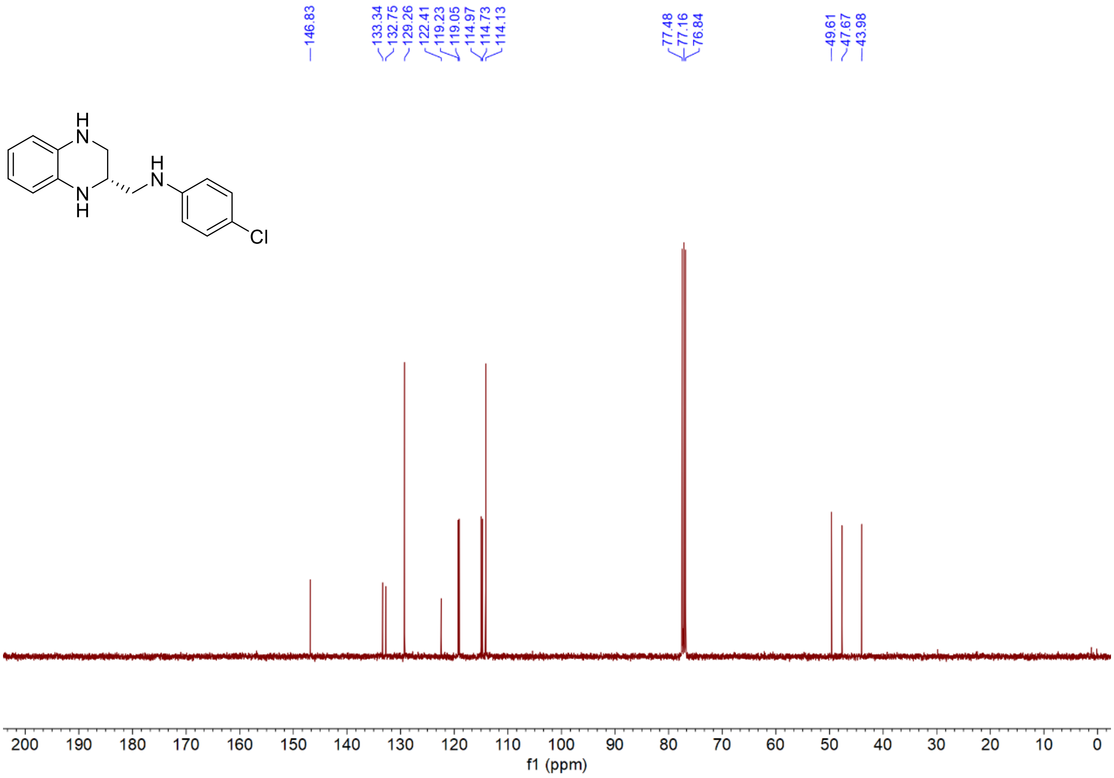
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3j** in $CDCl_3$



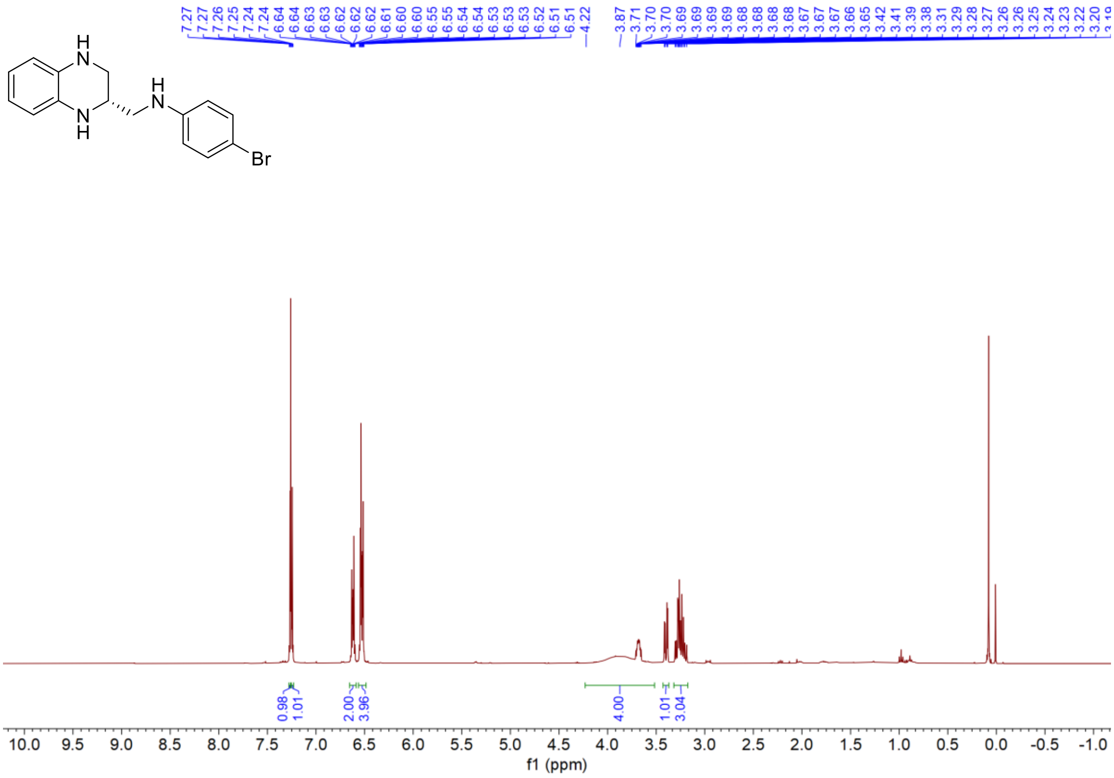


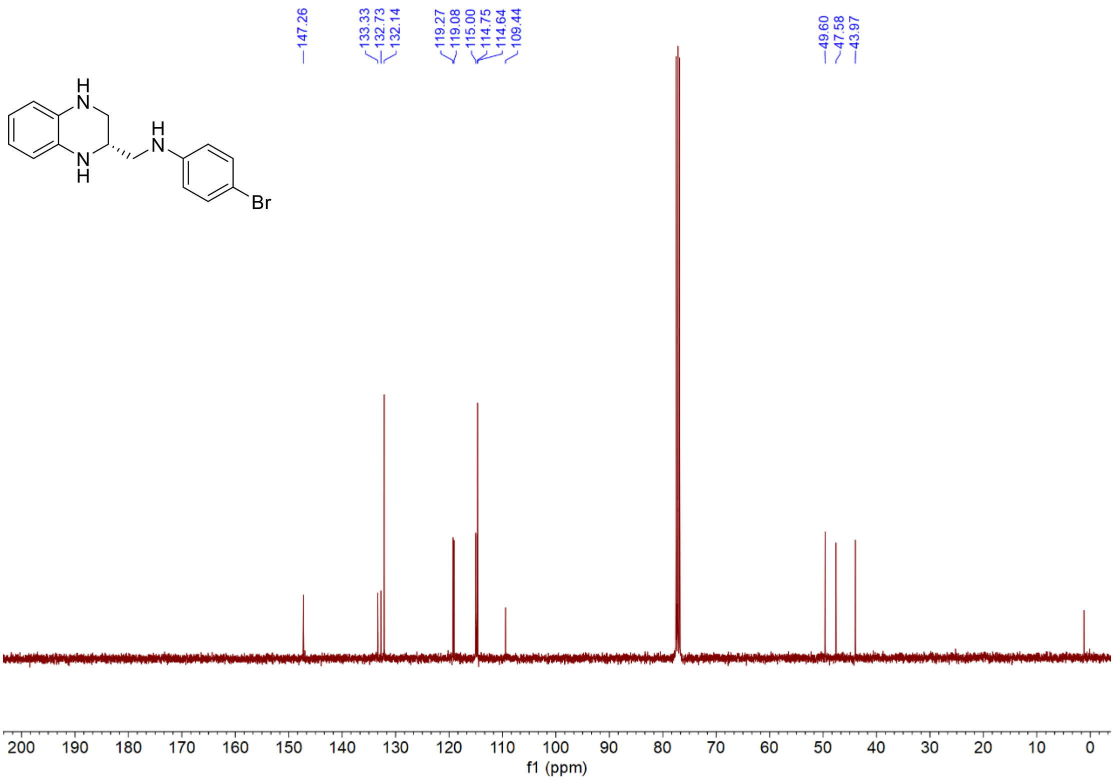
^{1}H and ^{13}C{^{1}H} NMR spectra of compound **3k** in $CDCl_3$



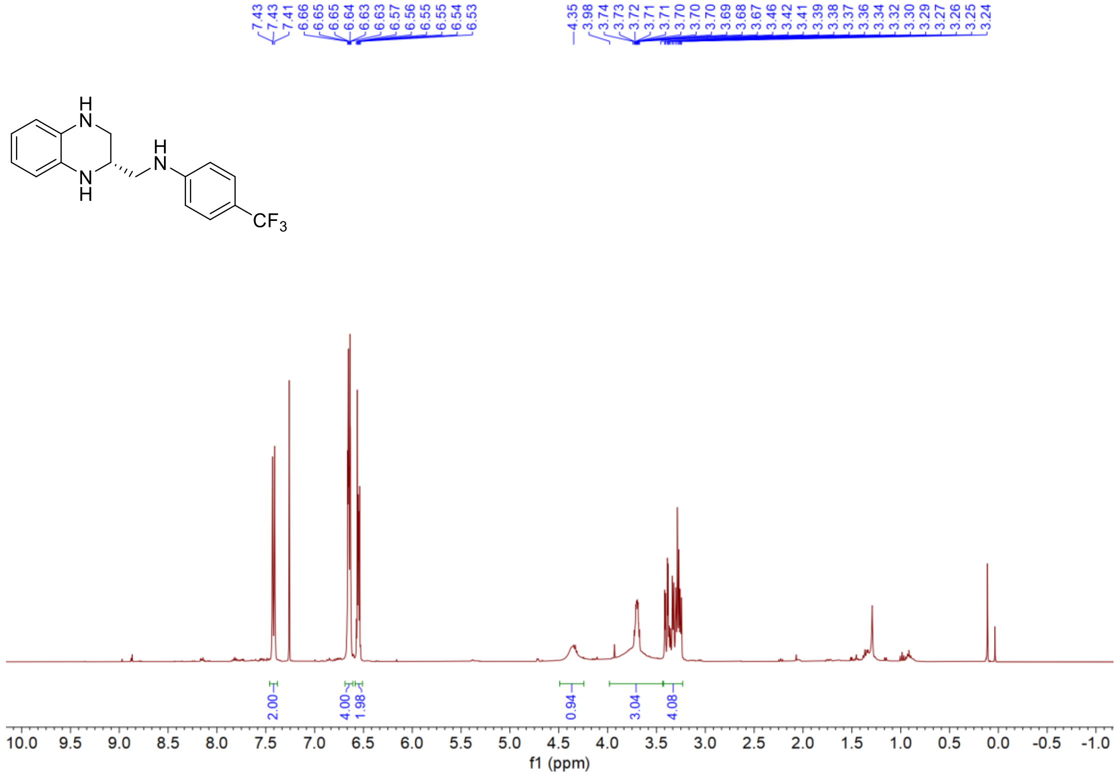


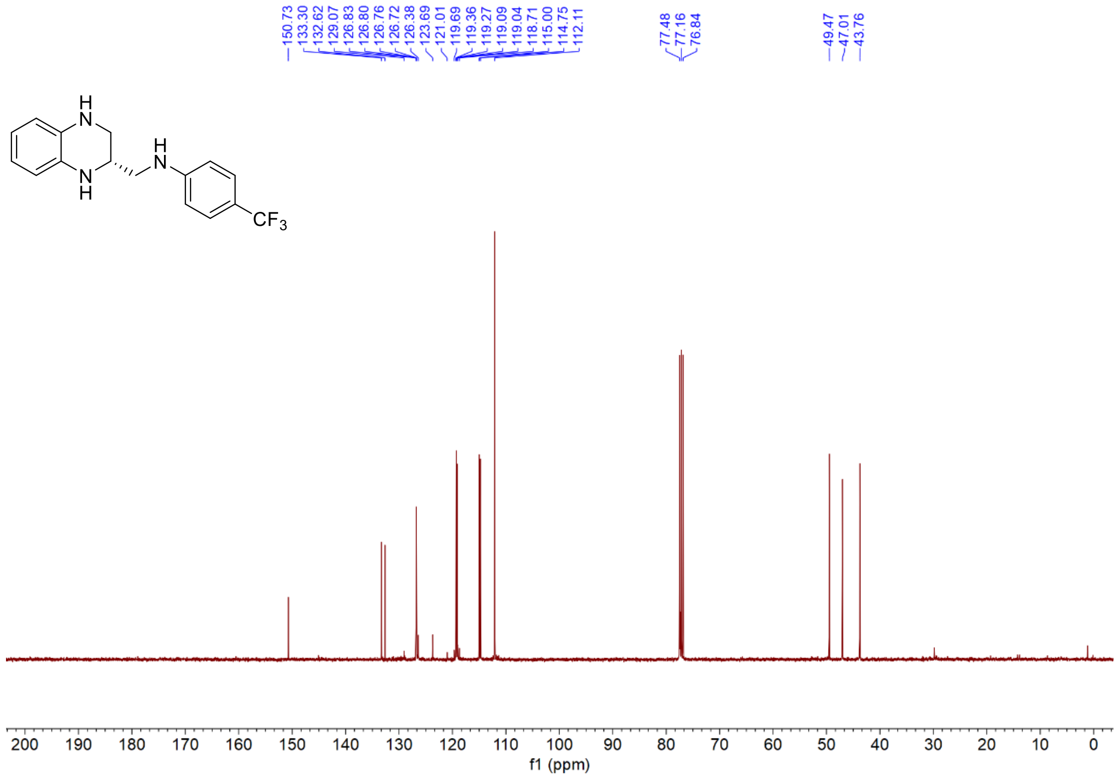
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3l** in $CDCl_3$



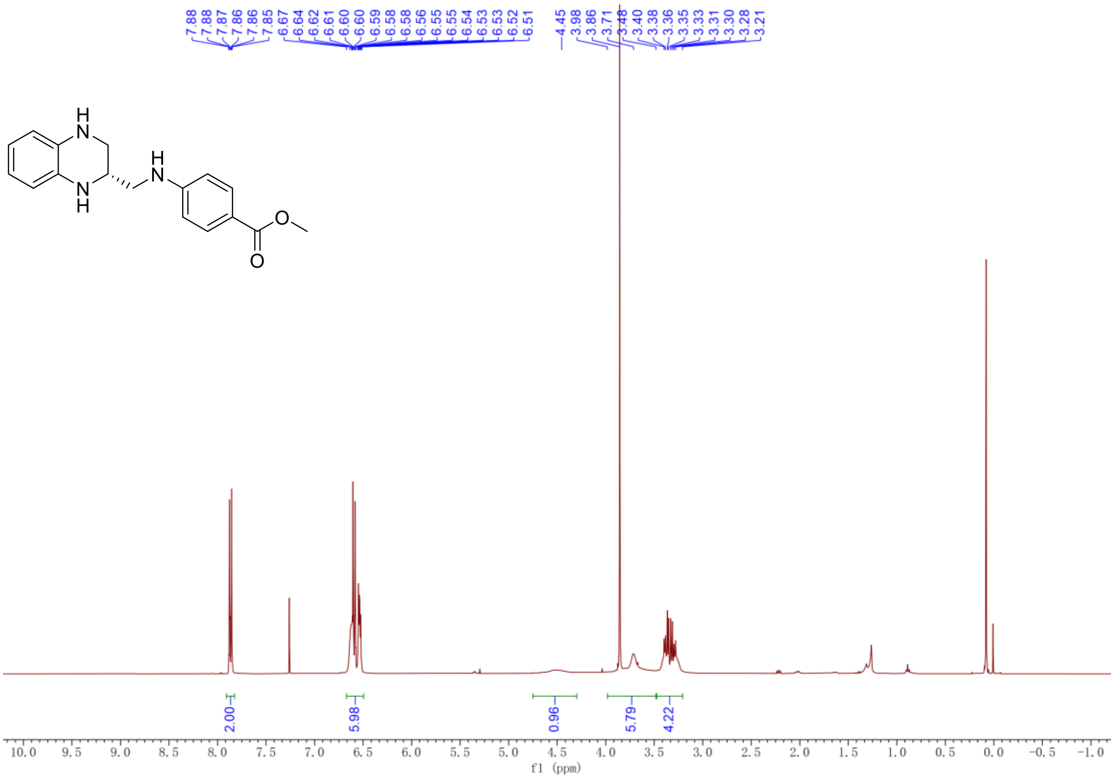


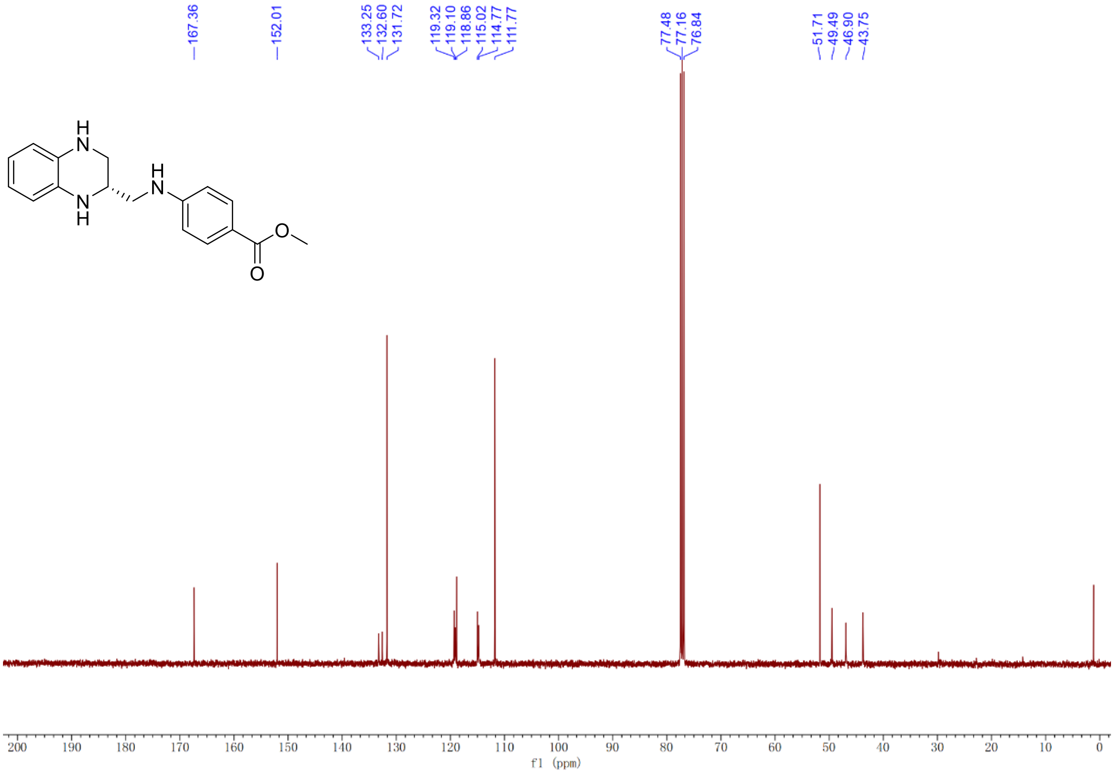
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3m** in $CDCl_3$



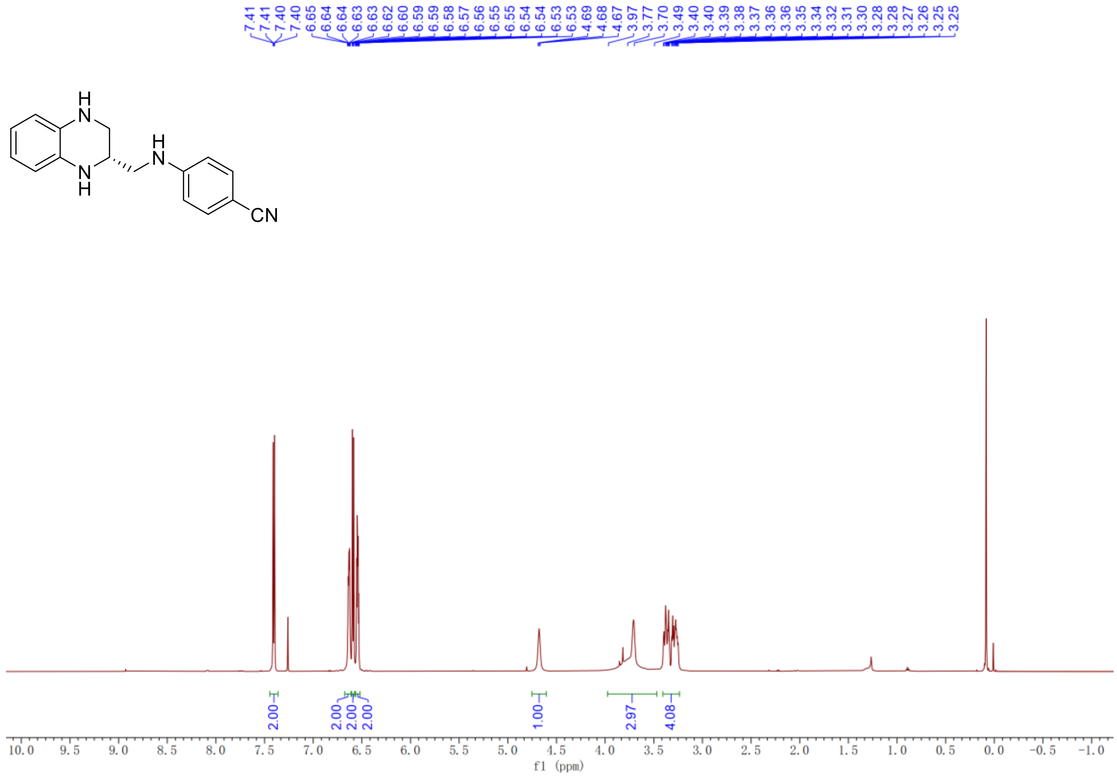


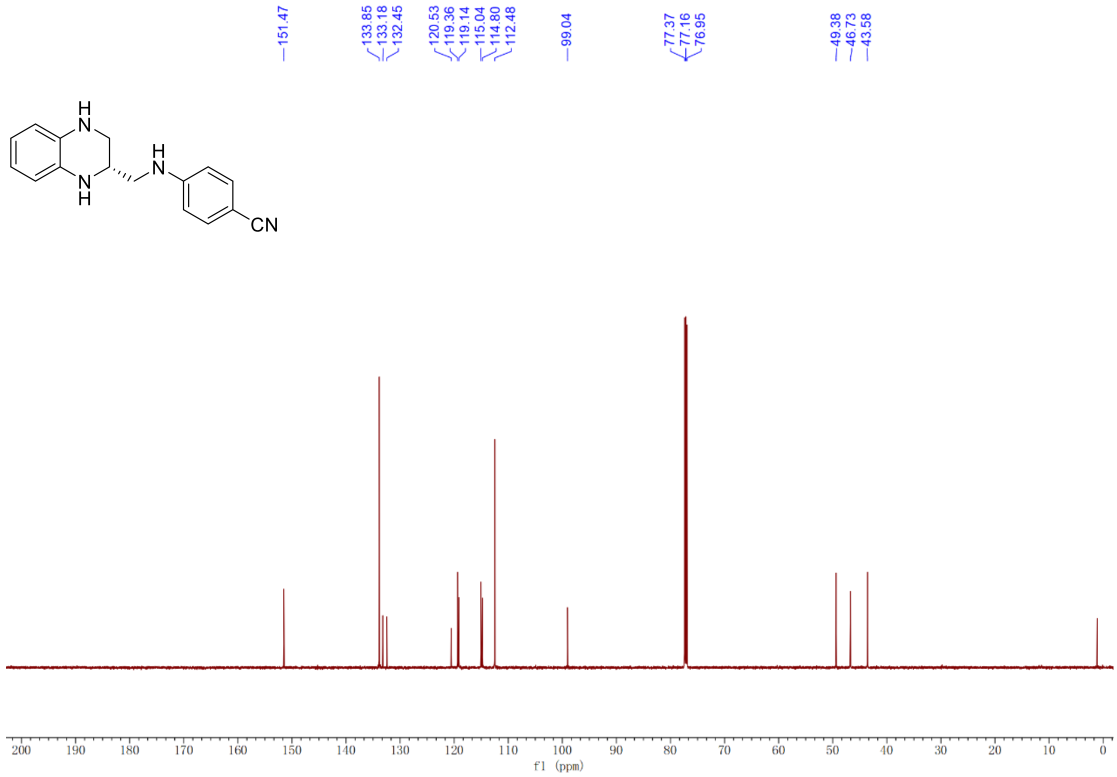
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3n** in $CDCl_3$



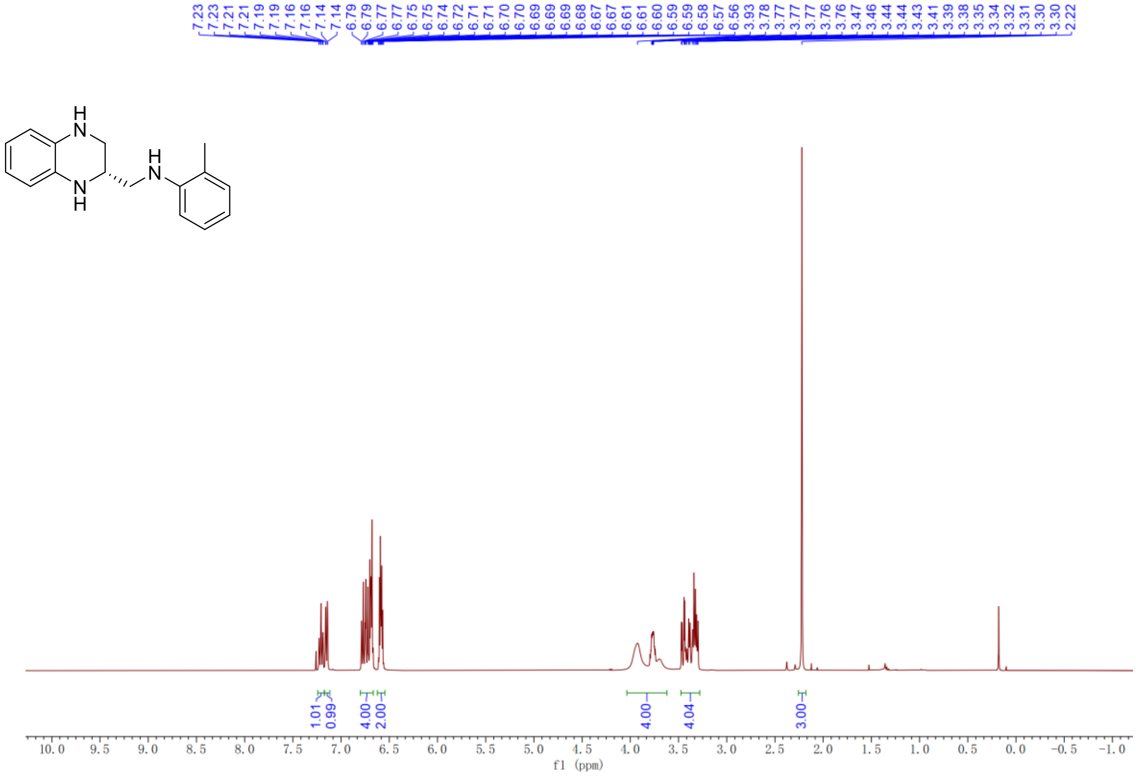


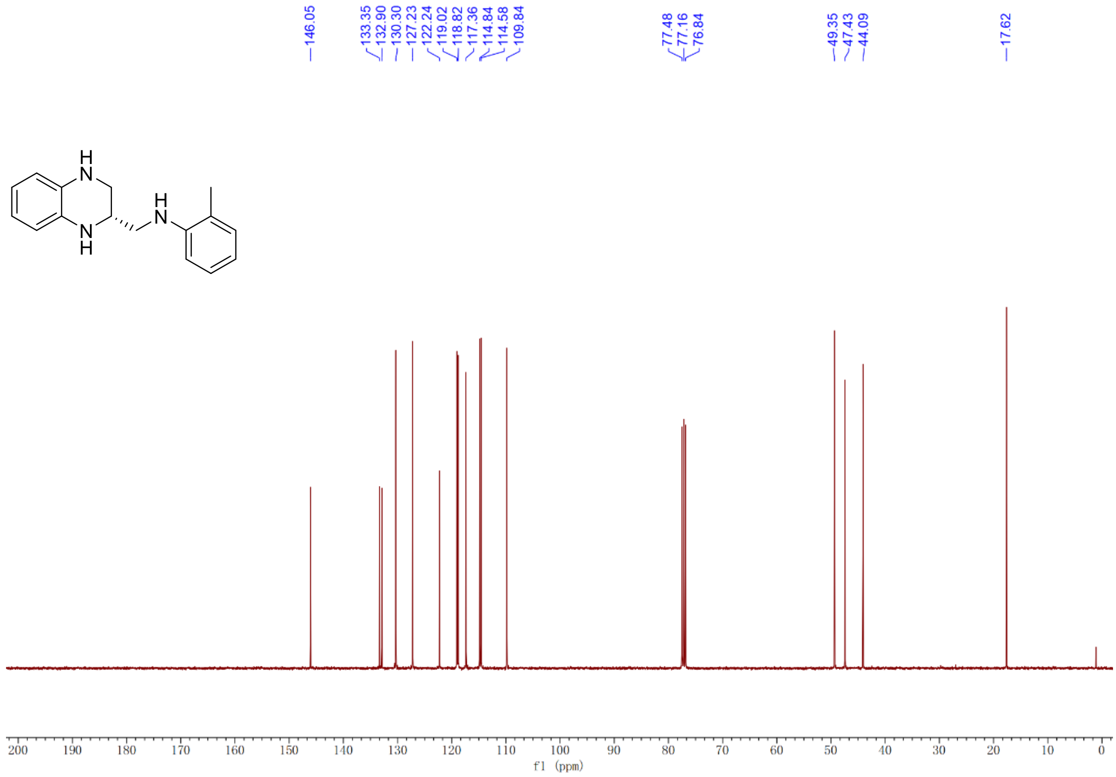
[1]H and [13]C{[1]H} NMR spectra of compound **3o** in $CDCl_3$



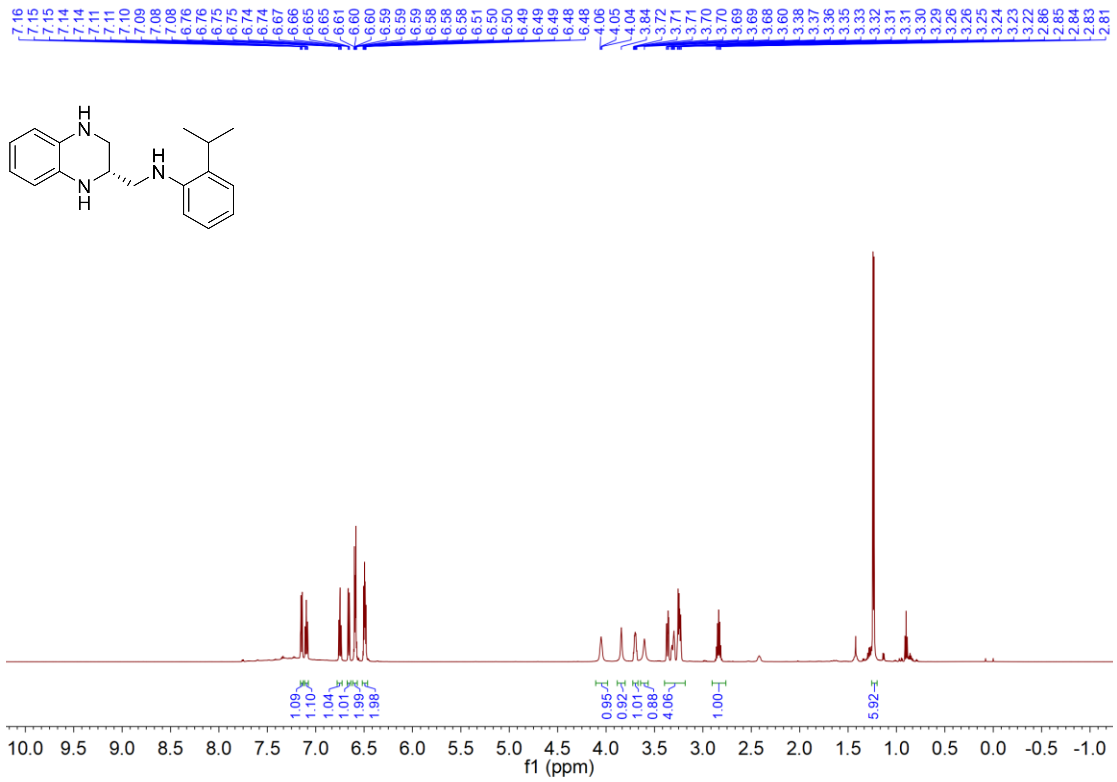


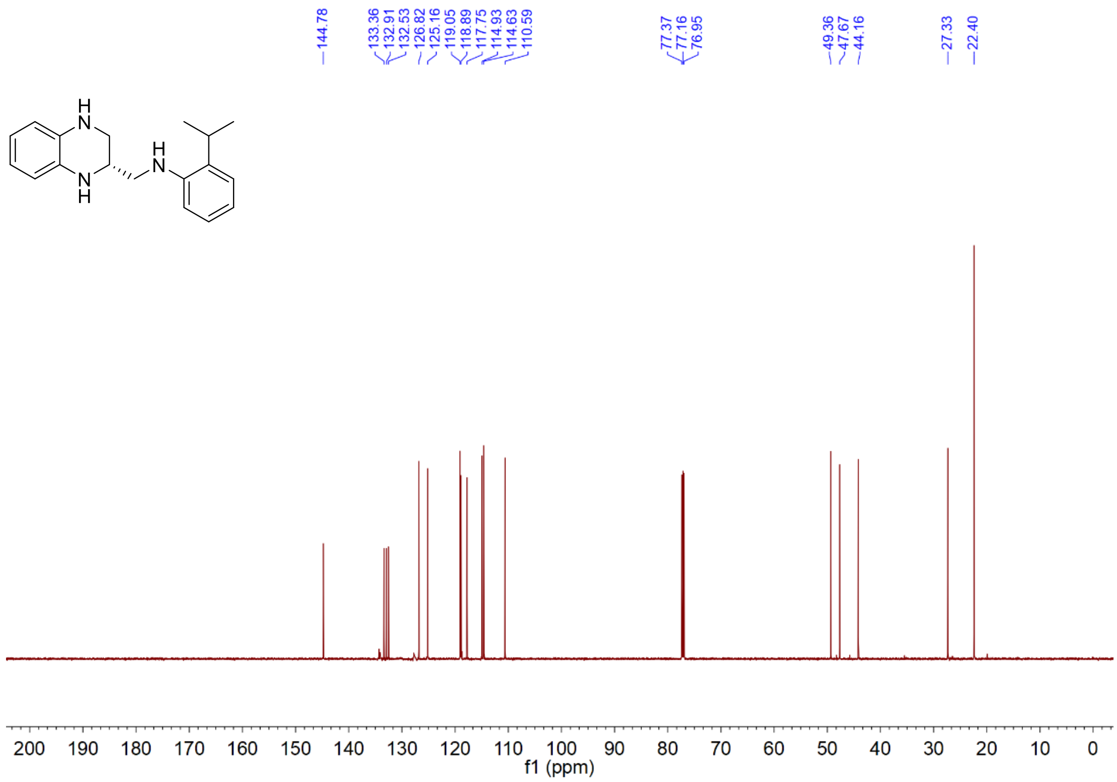
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3p** in $CDCl_3$



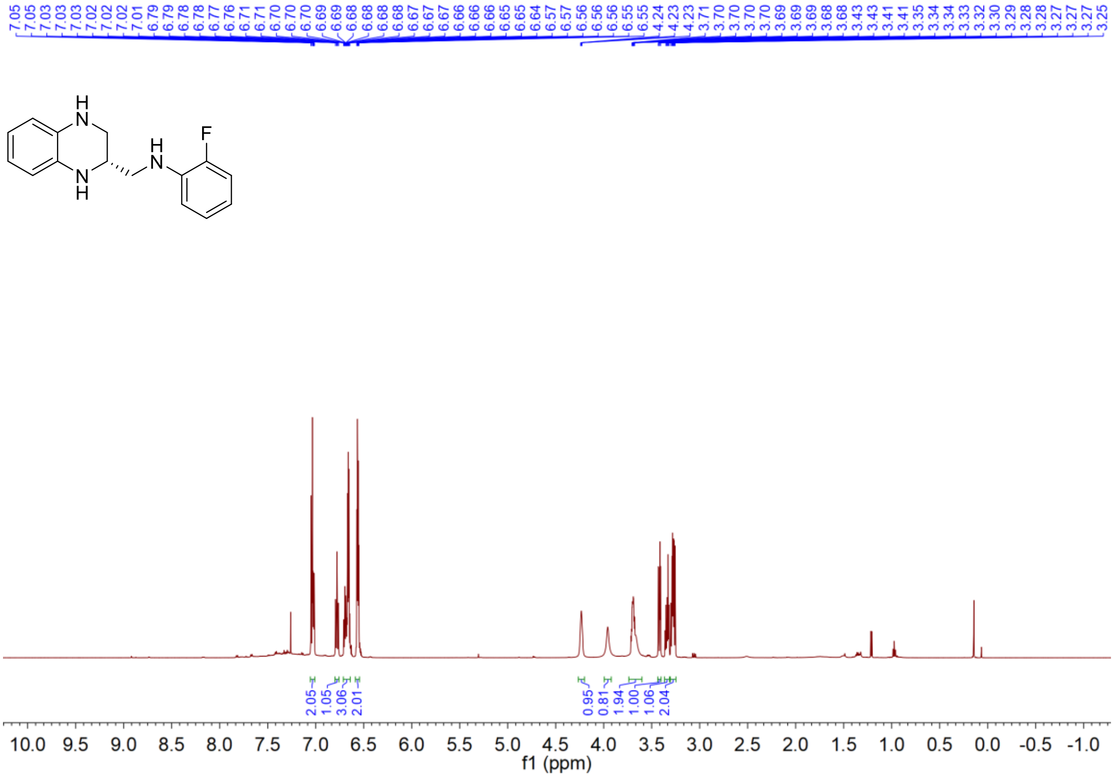


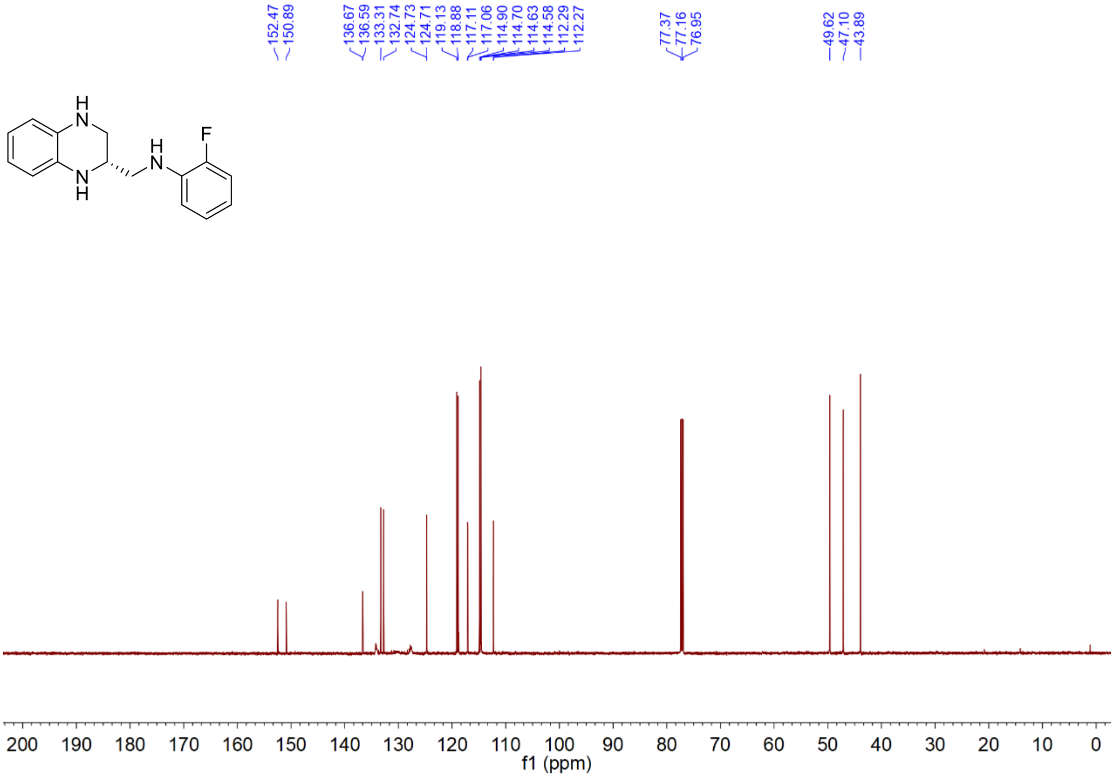
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3q** in $CDCl_3$



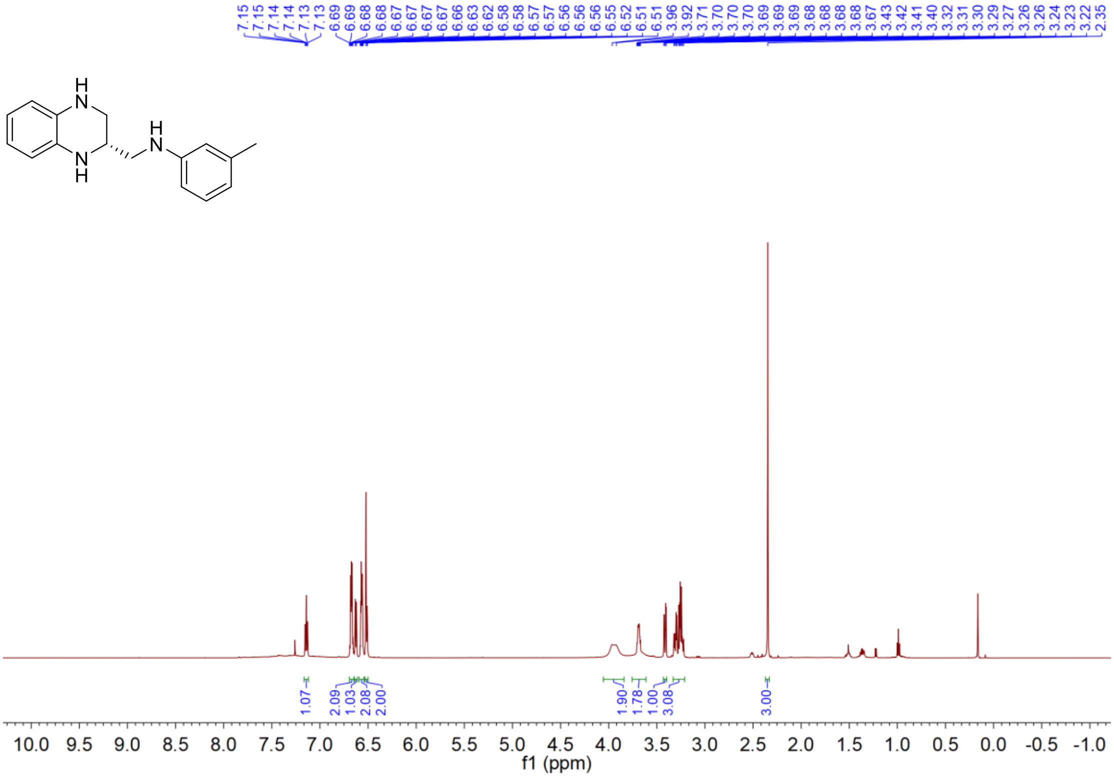


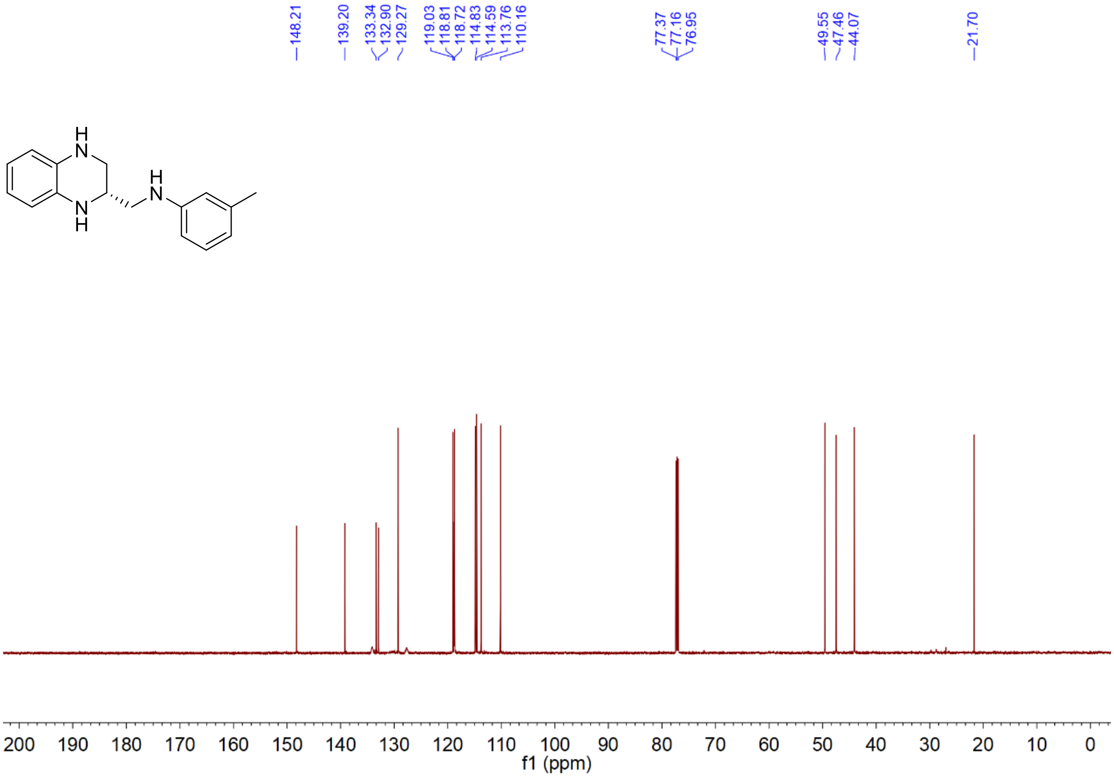
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3r** in $CDCl_3$



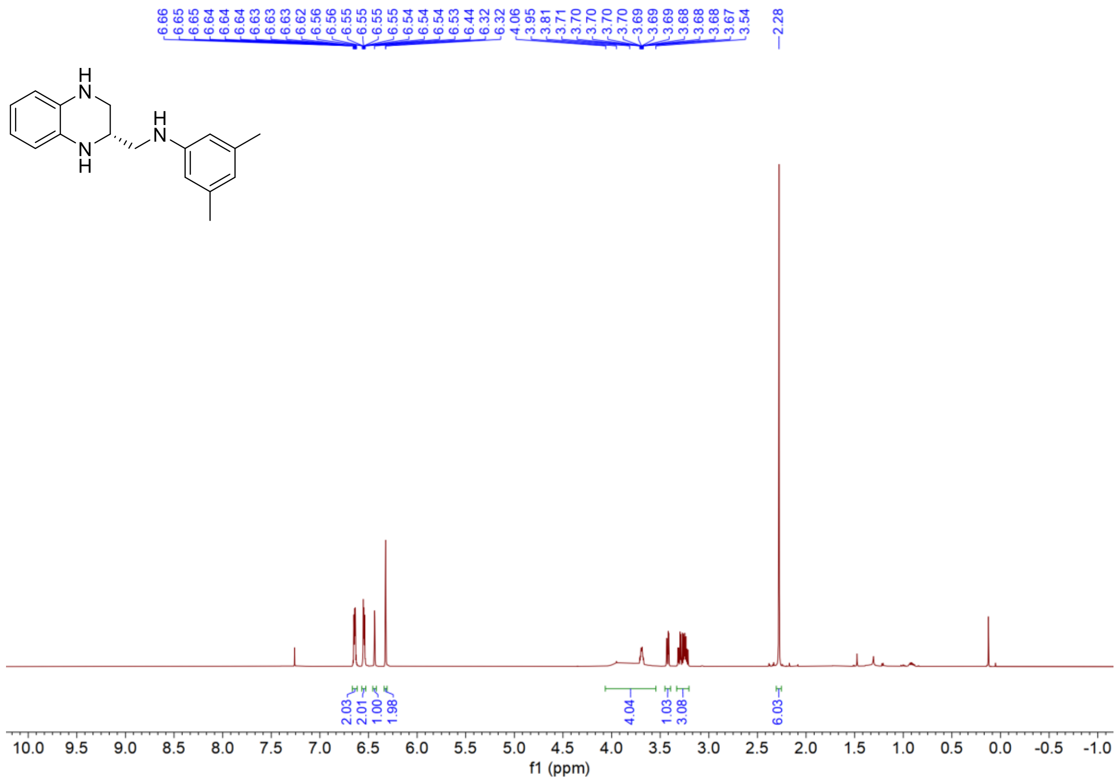


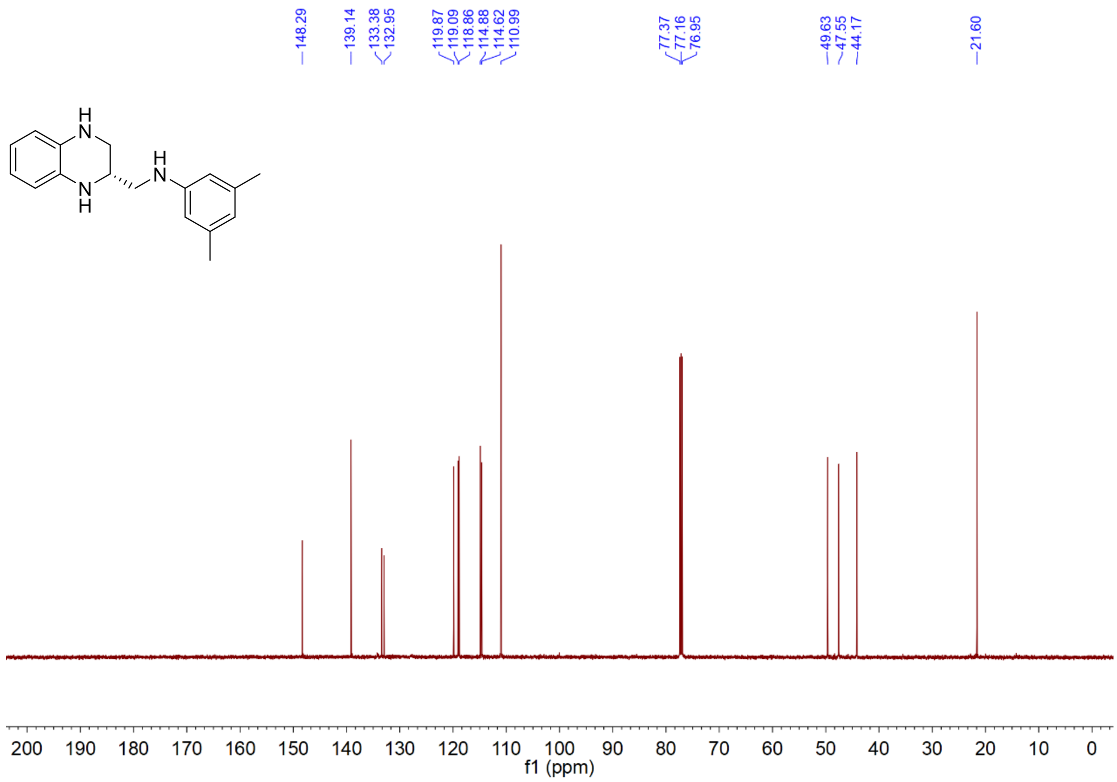
[1]H and [13]C{[1]H} NMR spectra of compound **3s** in $CDCl_3$



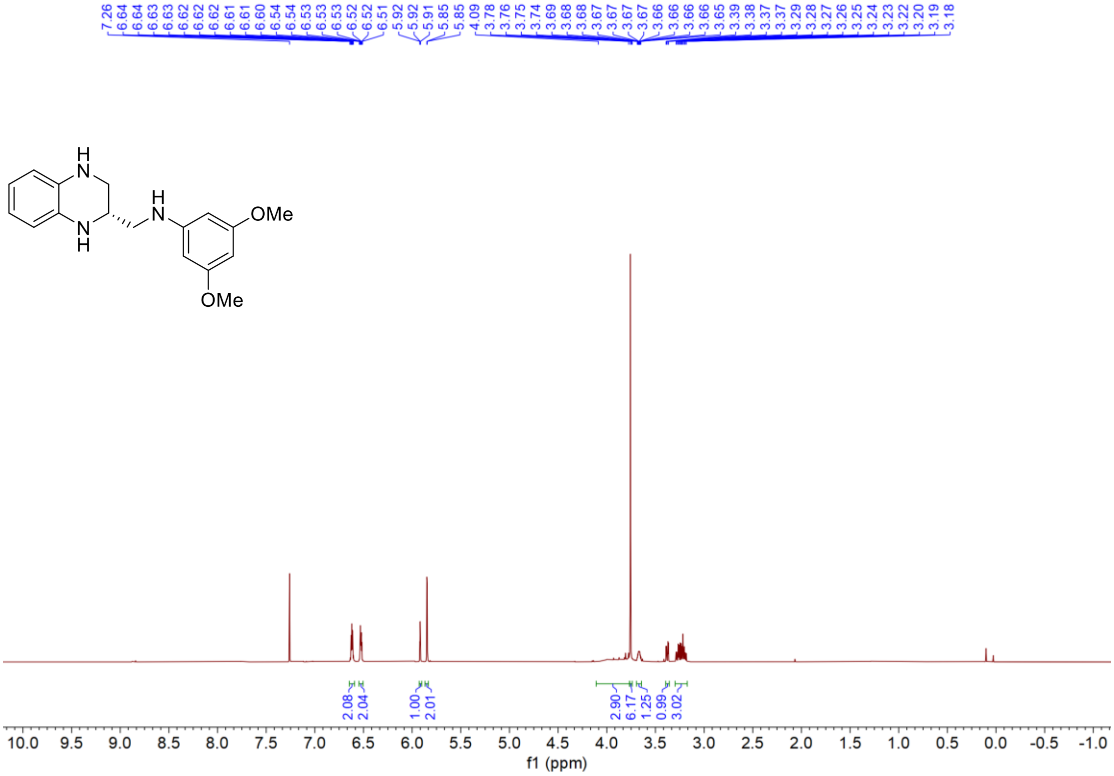


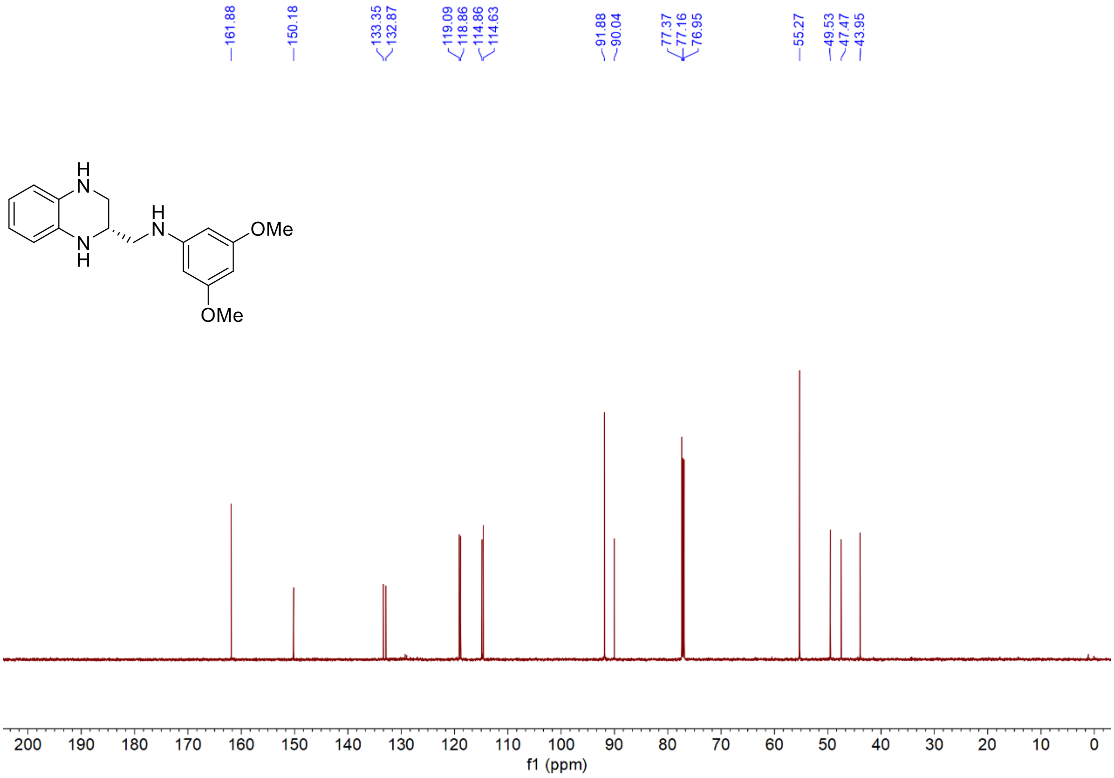
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3t** in $CDCl_3$



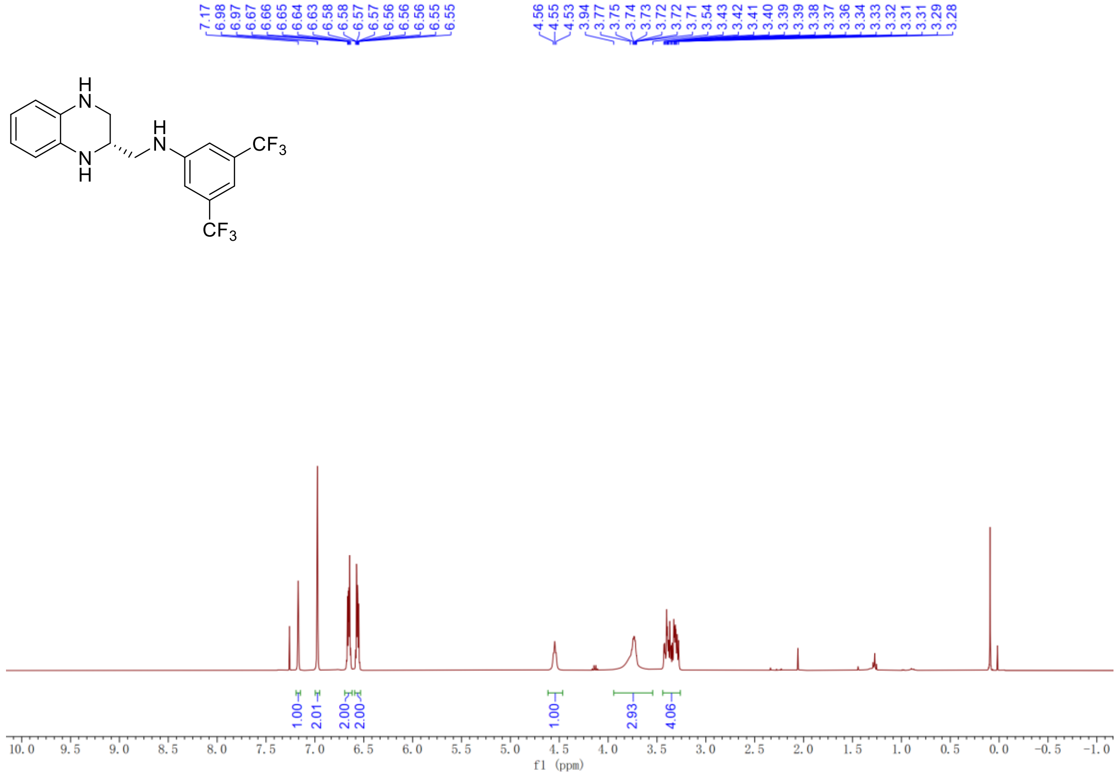


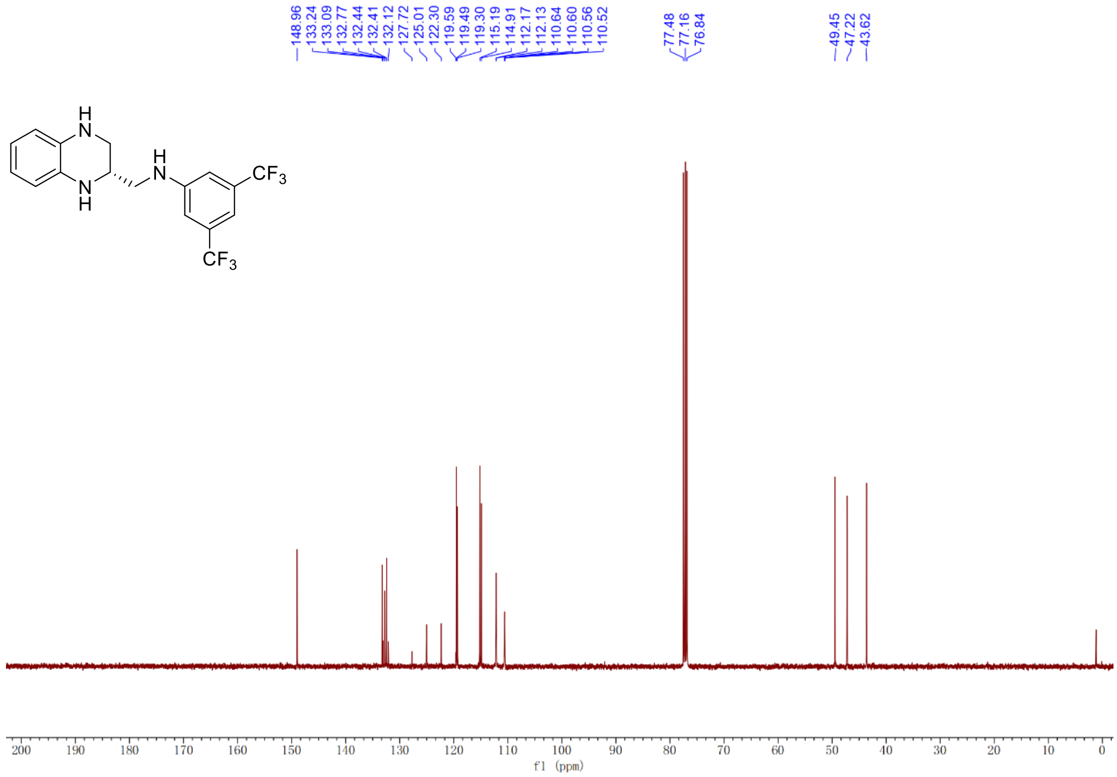
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3u** in $CDCl_3$



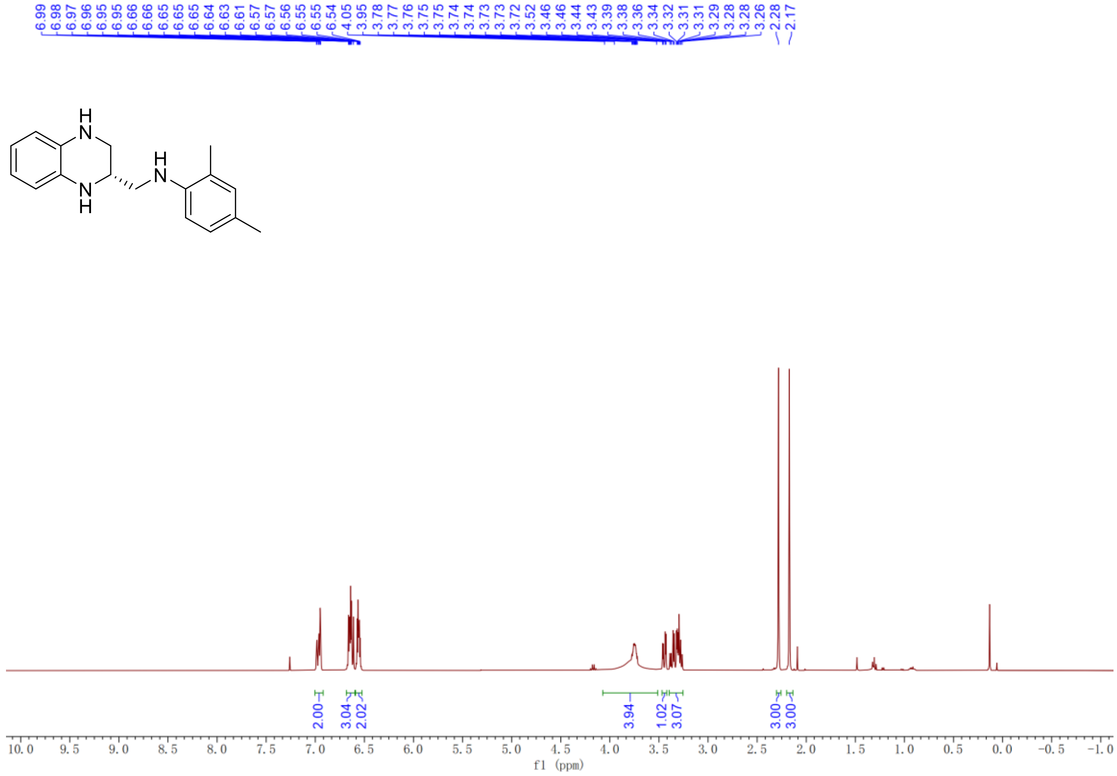


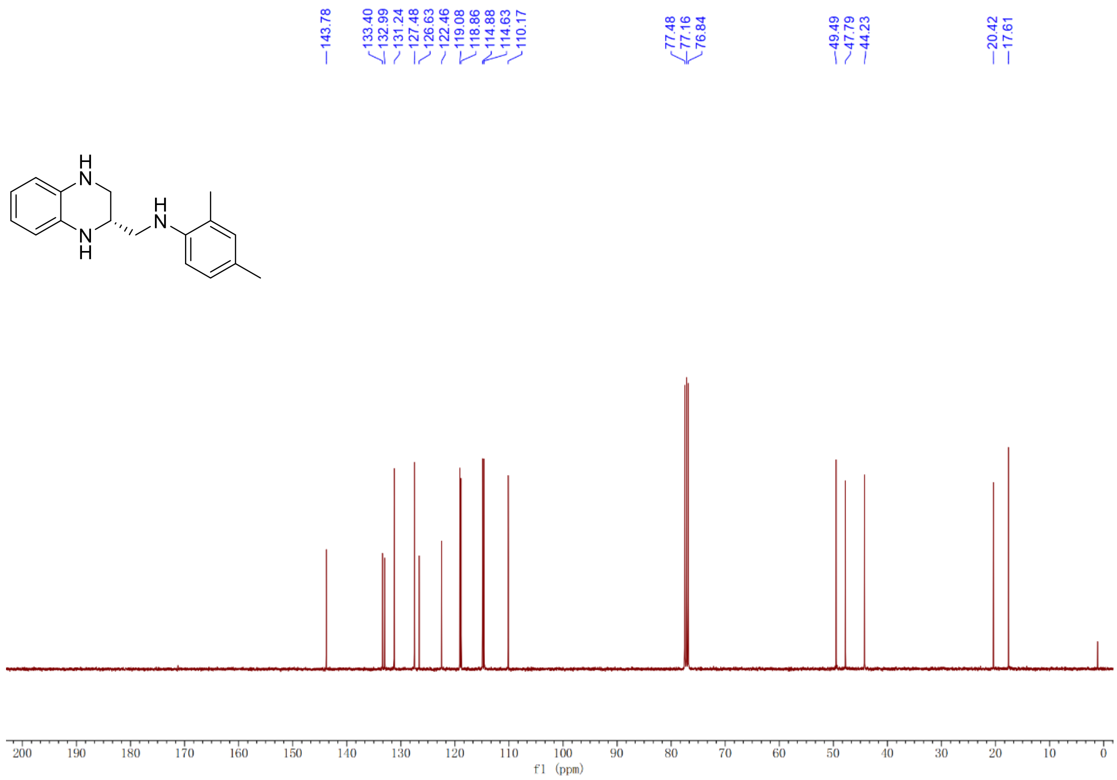
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3v** in $CDCl_3$



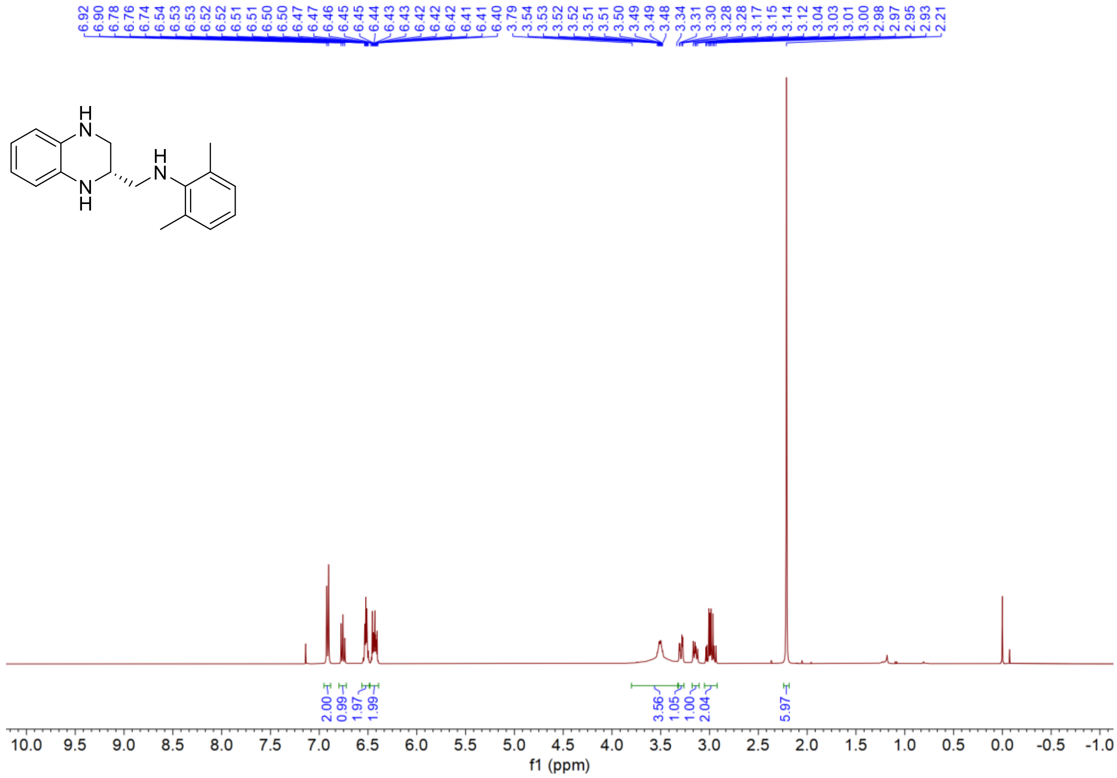


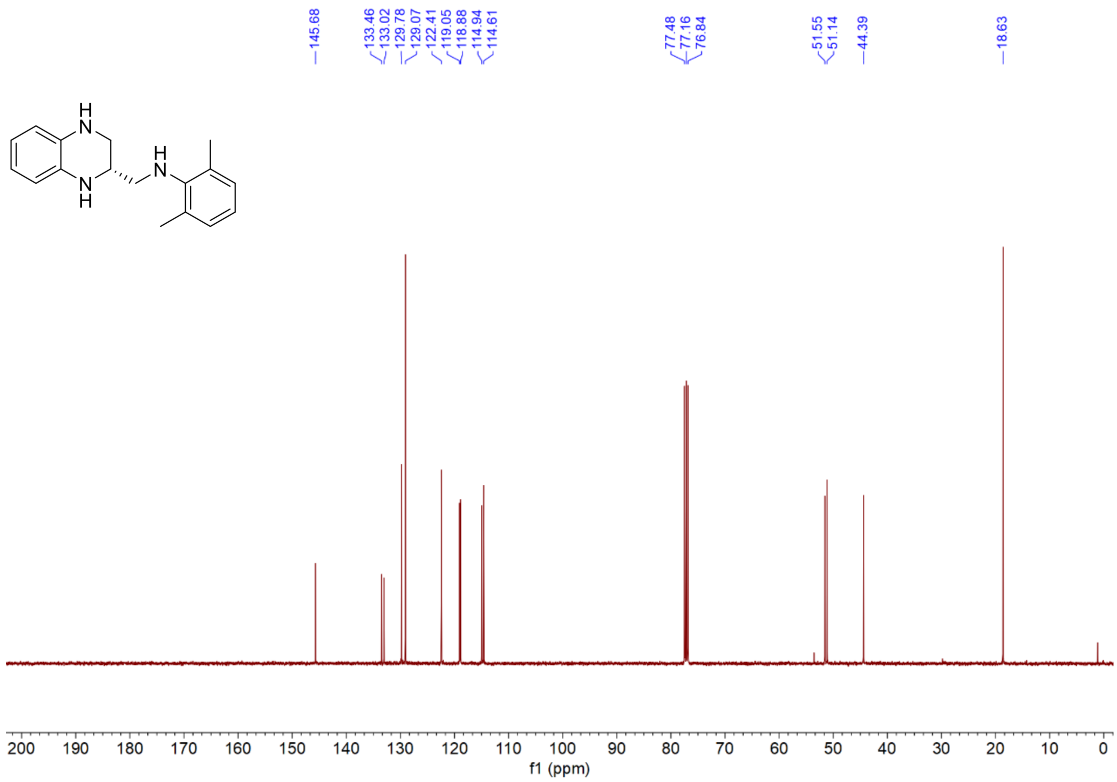
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3w** in $CDCl_3$



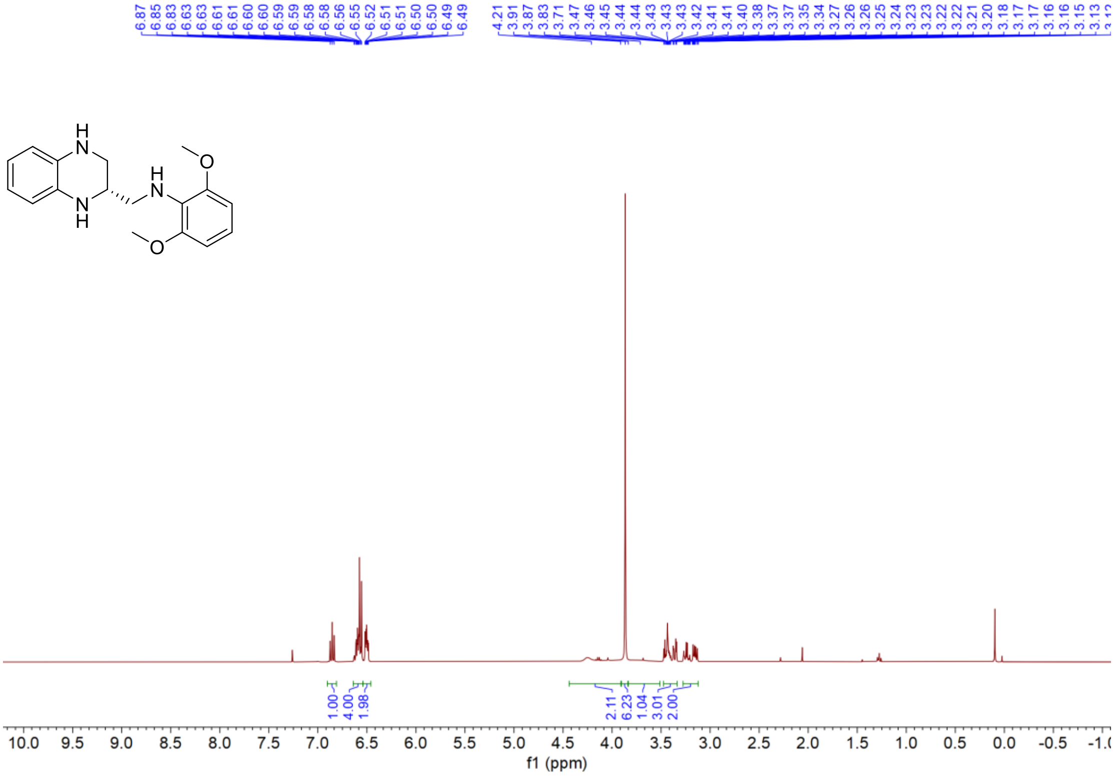


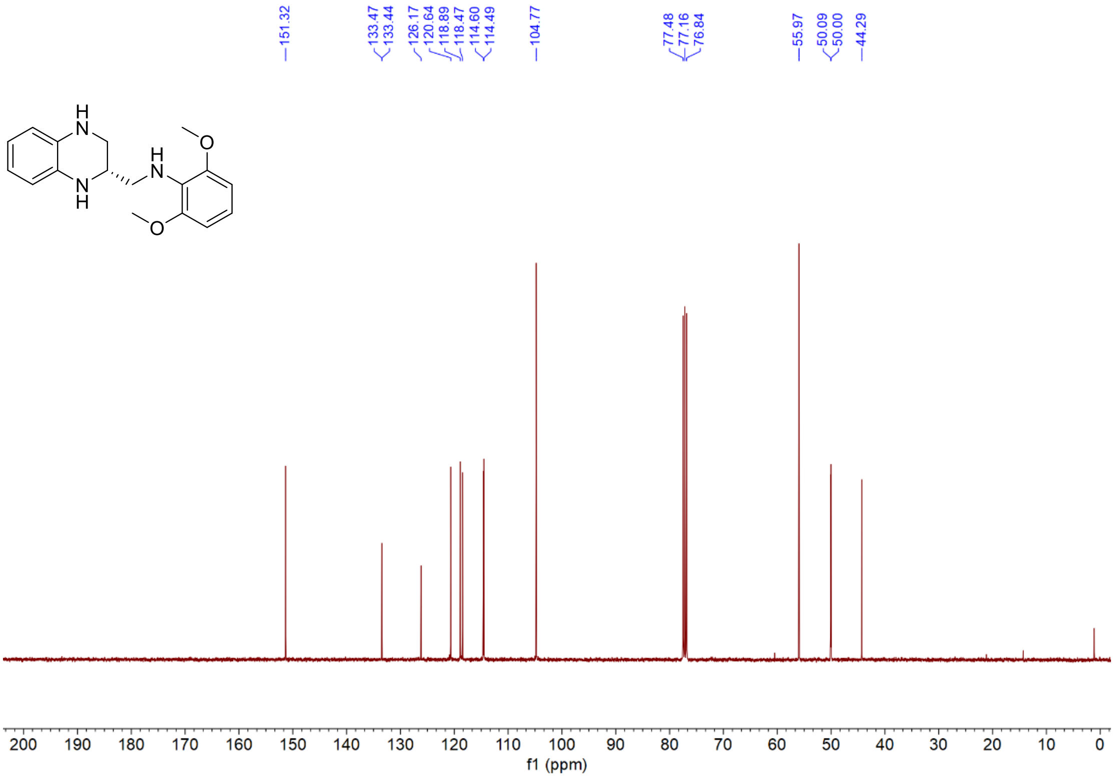
^{1}H and ^{13}C{^{1}H} NMR spectra of compound **3x** in $CDCl_3$



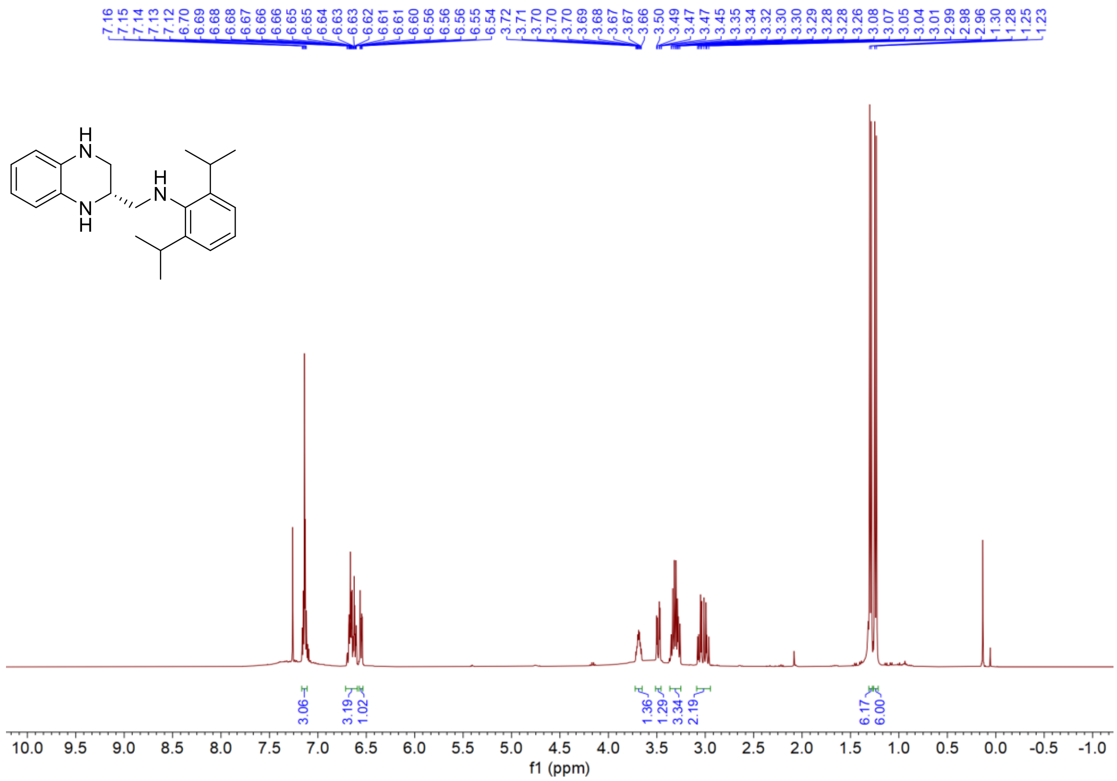


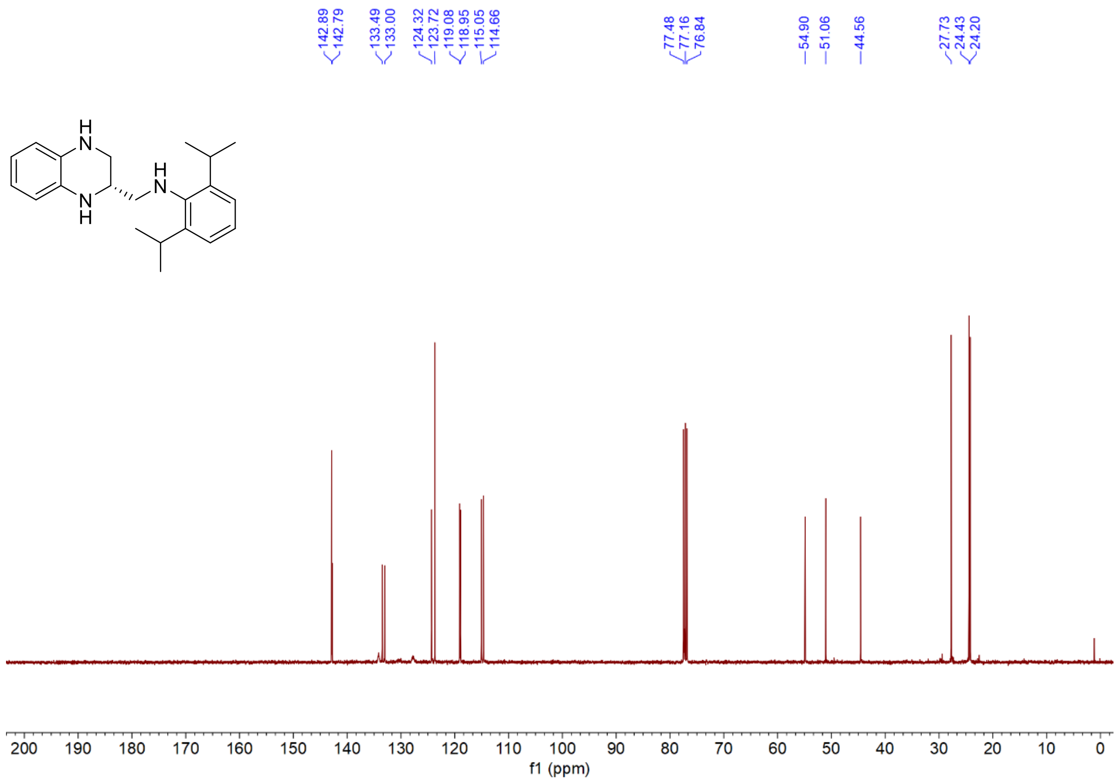
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3y** in $CDCl_3$



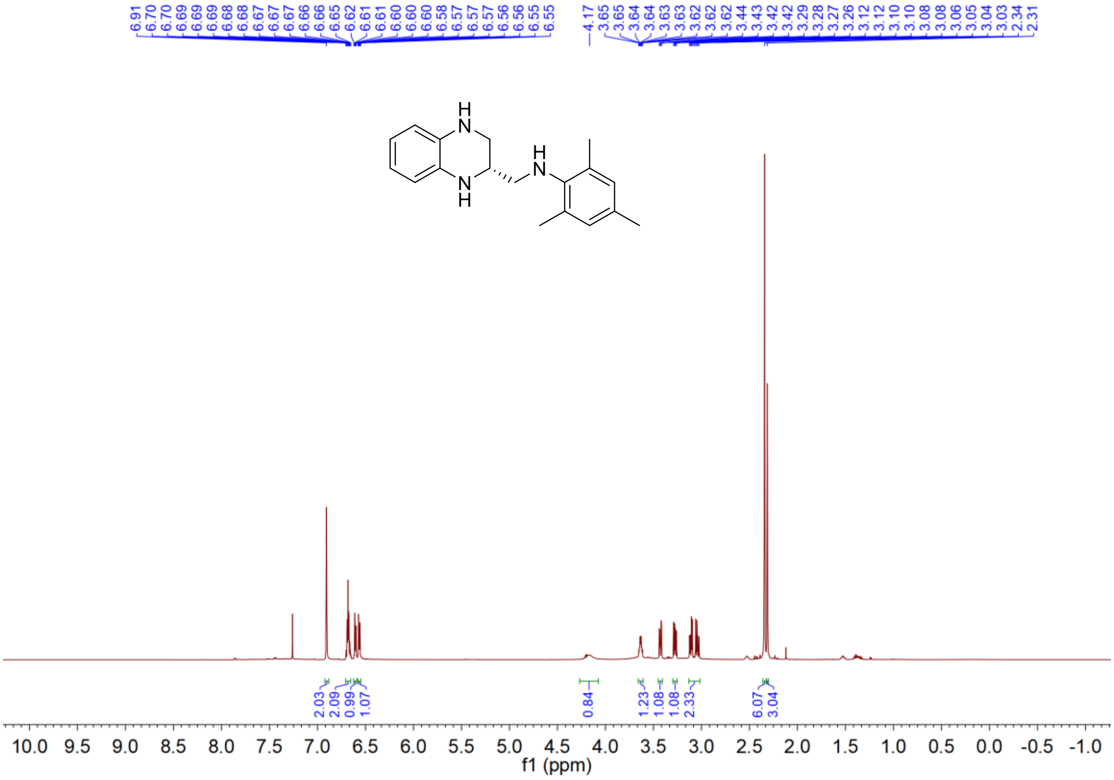


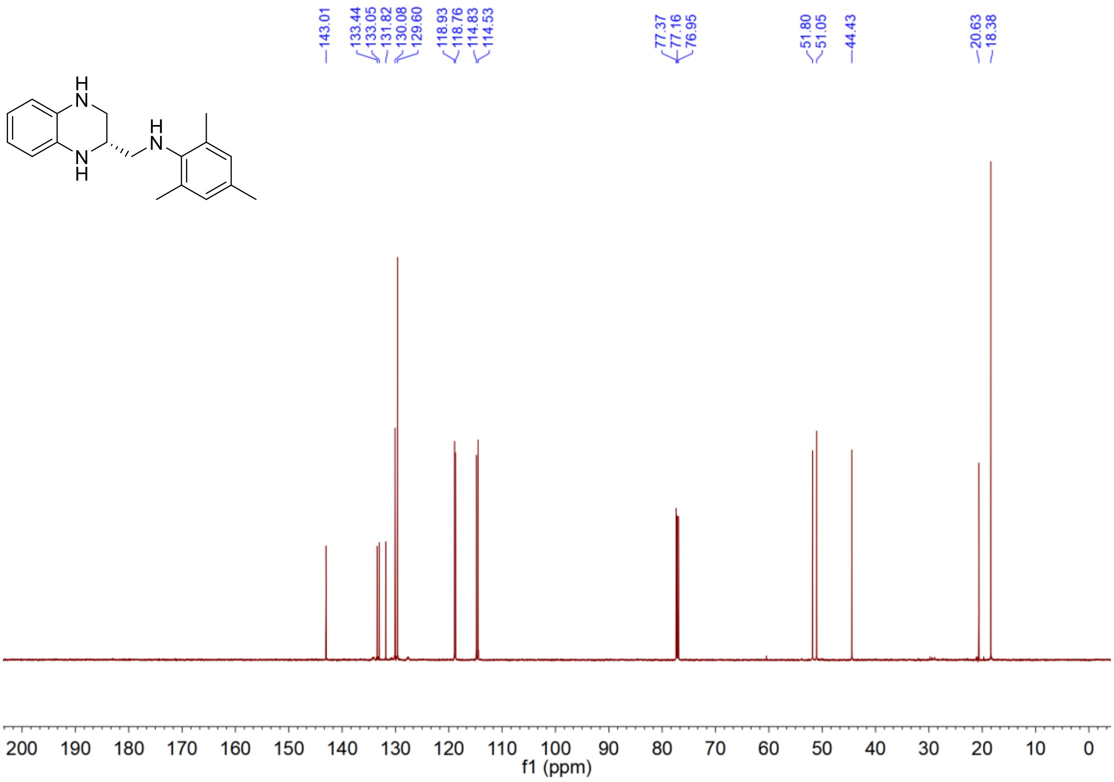
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3z** in $CDCl_3$



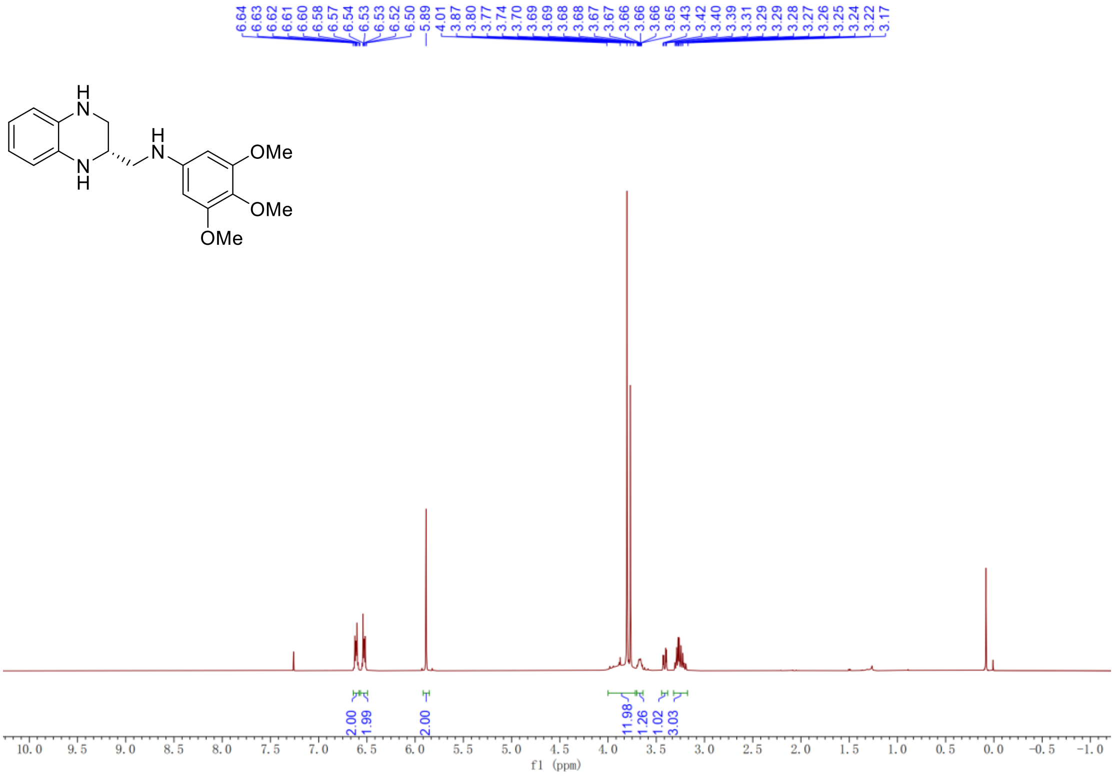


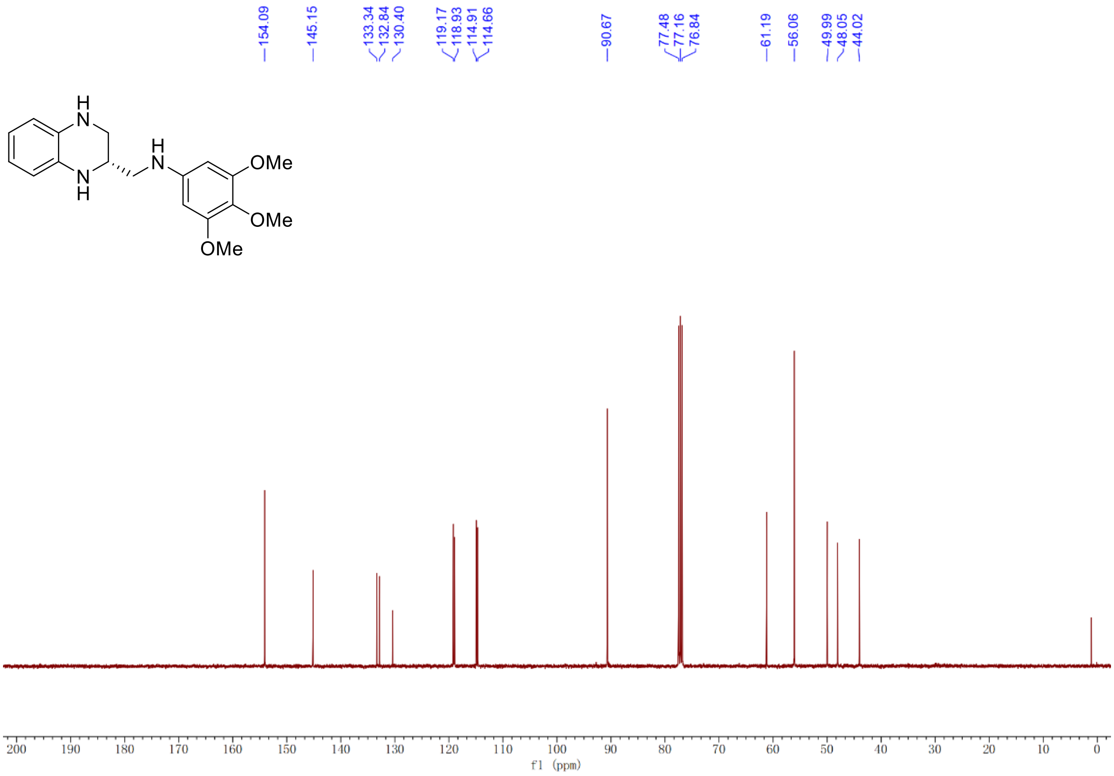
^{1}H and ^{13}C{^{1}H} NMR spectra of compound **3aa** in $CDCl_3$



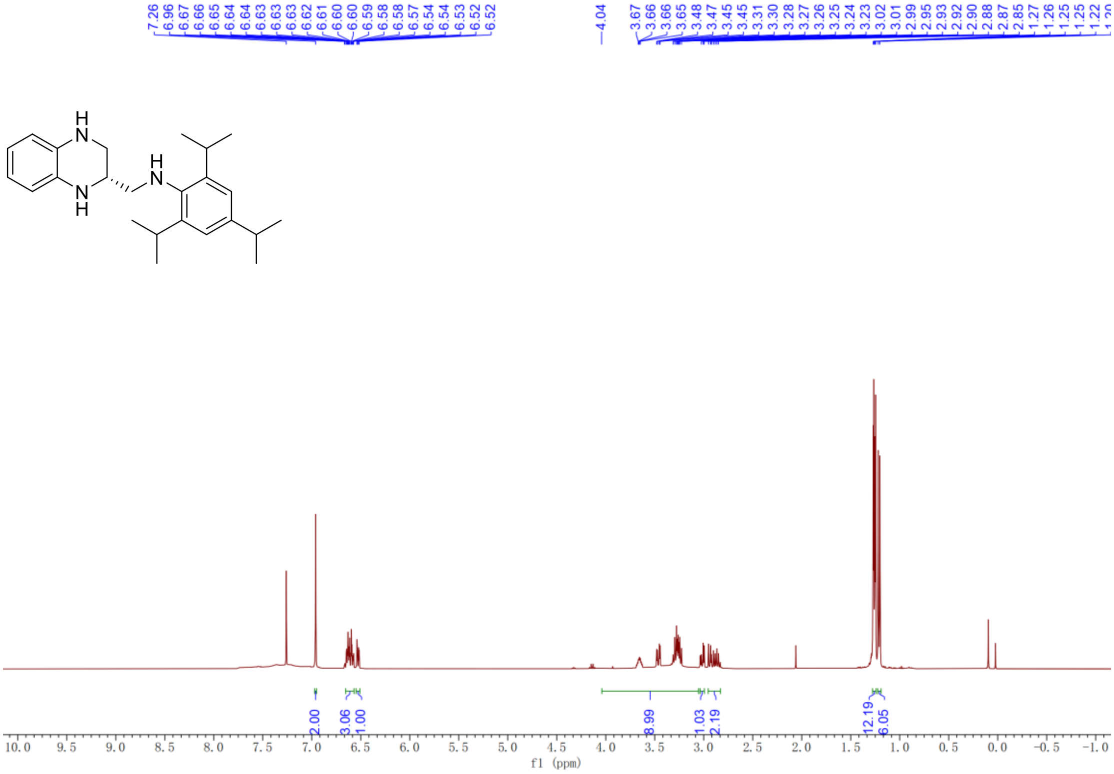


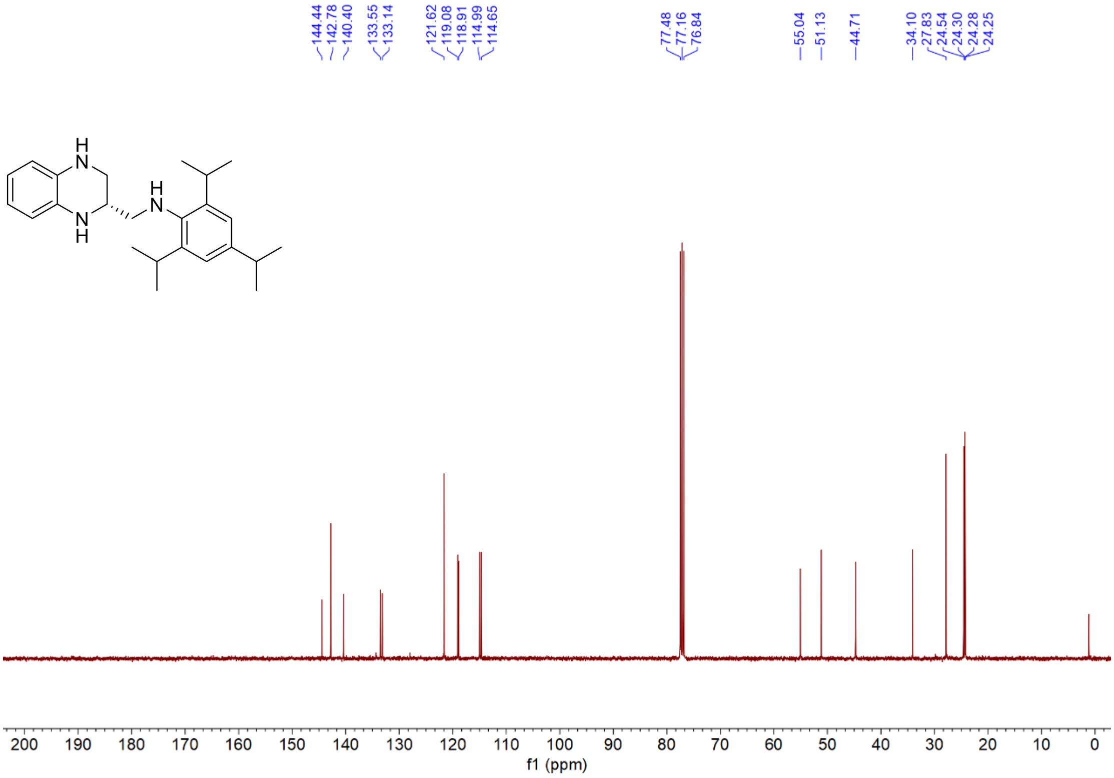
[1]H and [13]C{[1]H} NMR spectra of compound **3ab** in $CDCl_3$



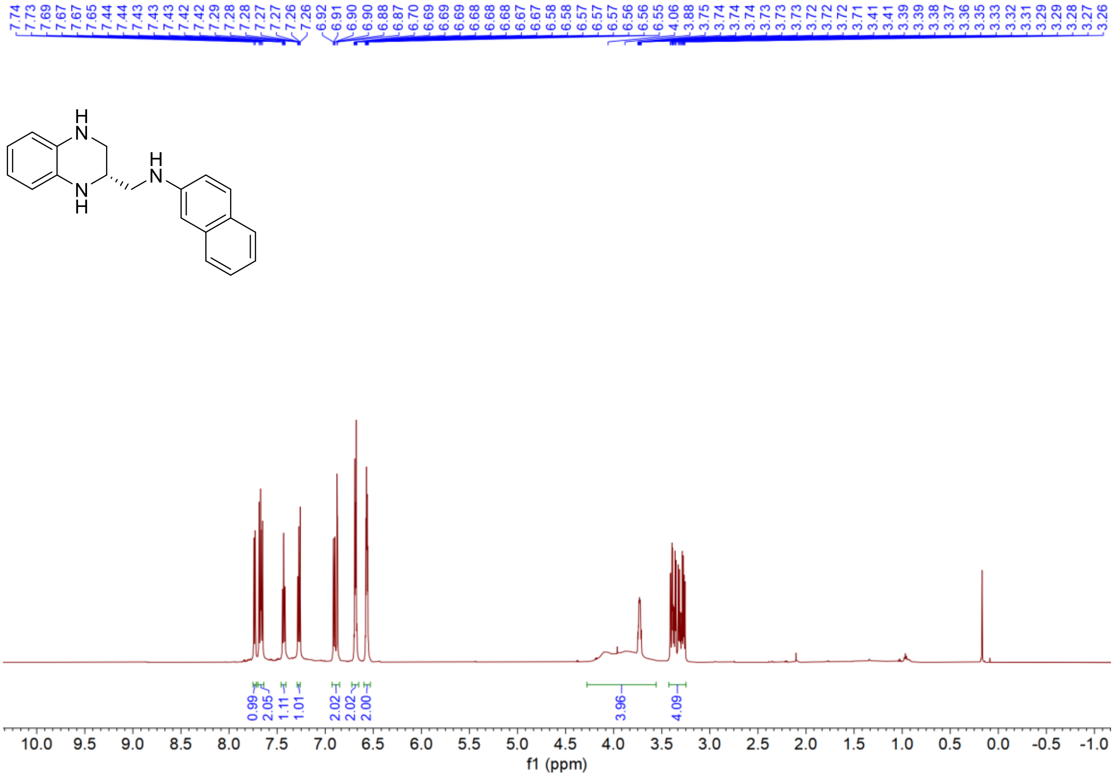


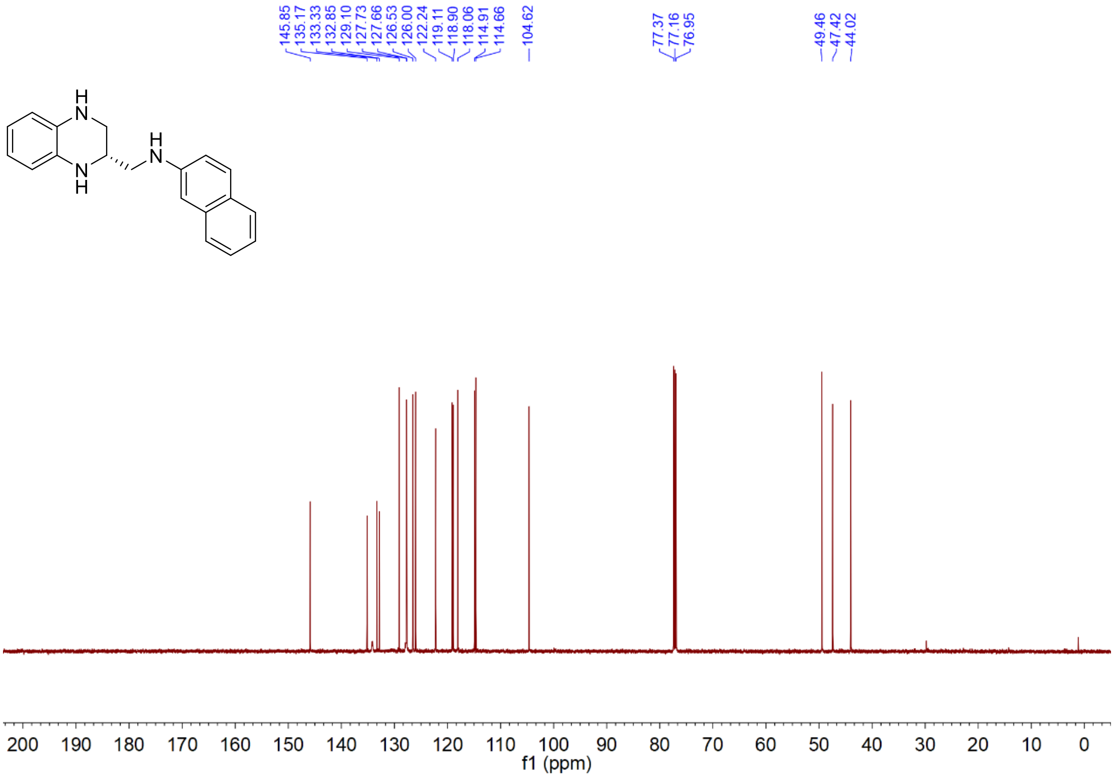
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3ac** in $CDCl_3$



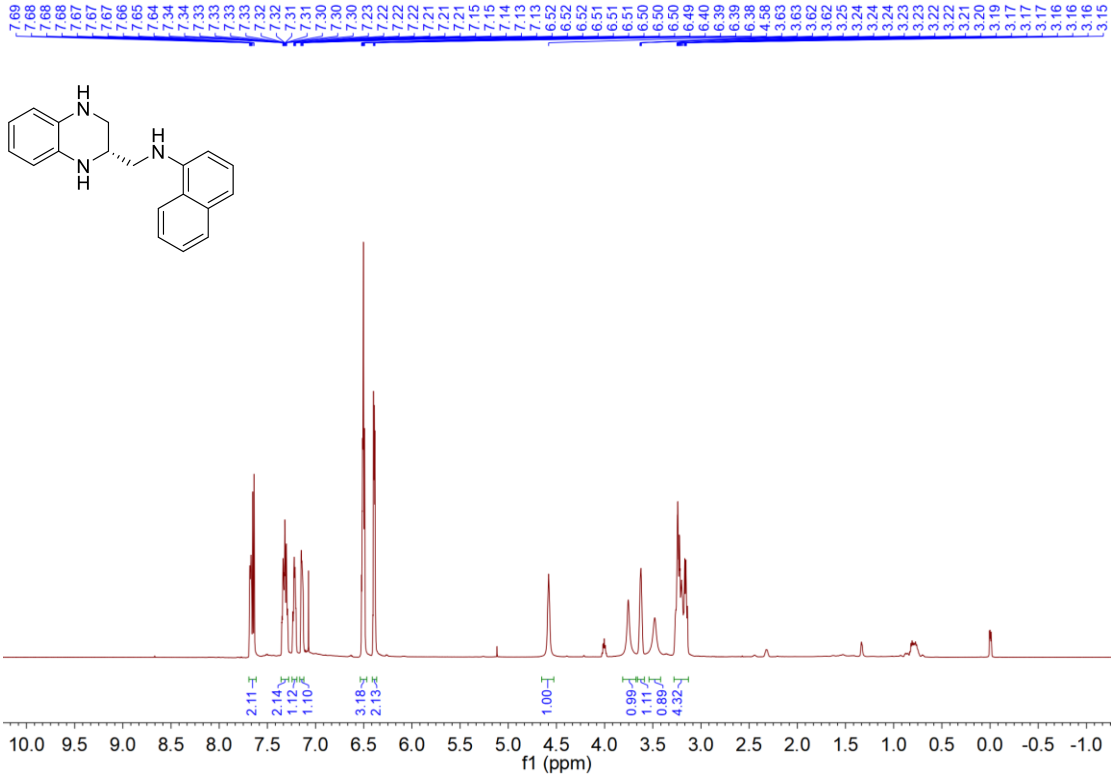


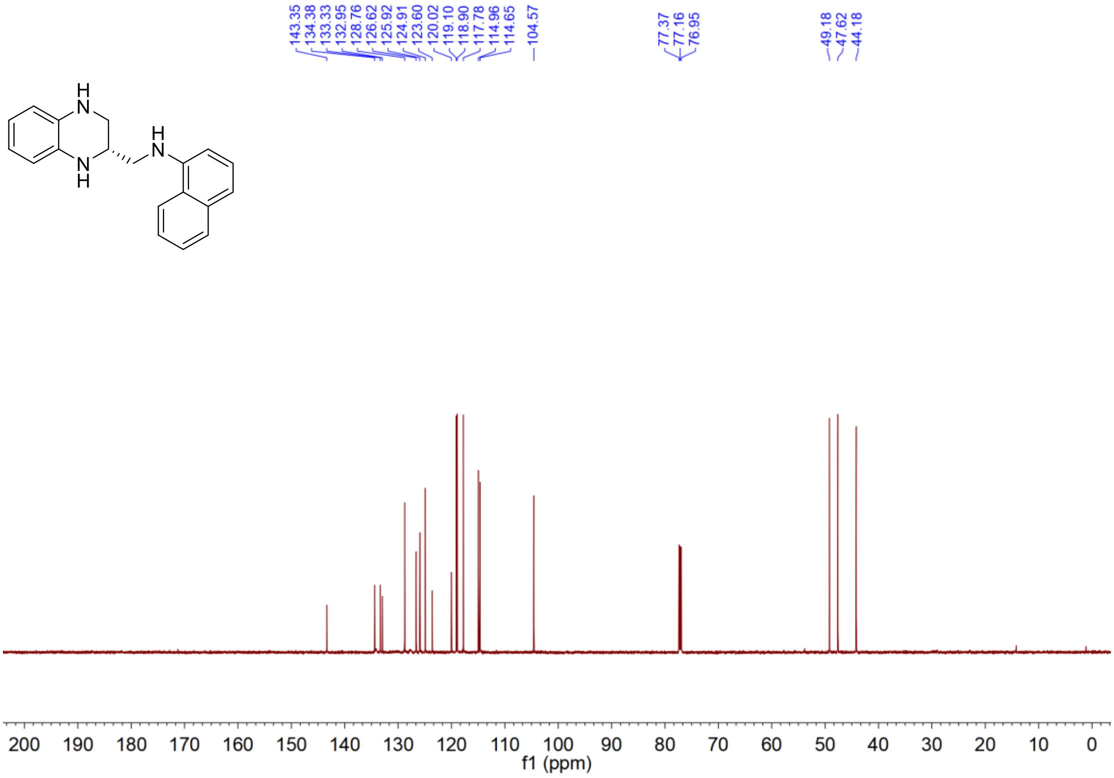
[1]H and [13]C{[1]H} NMR spectra of compound **3ad** in $CDCl_3$



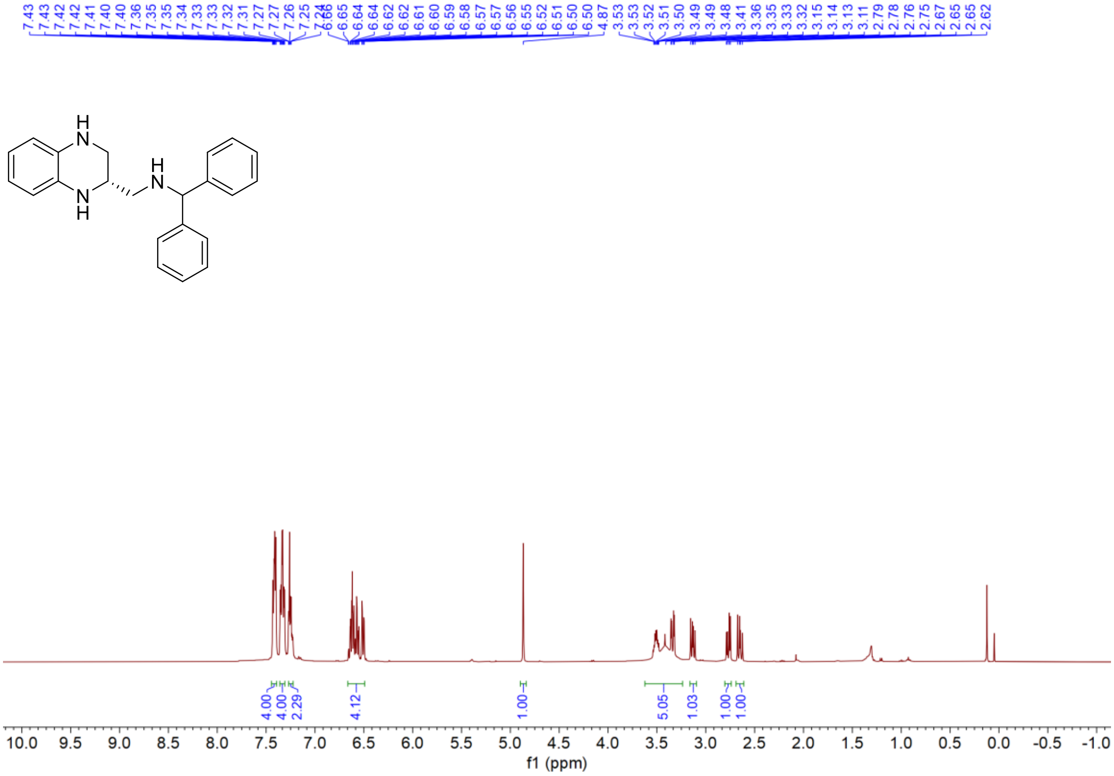


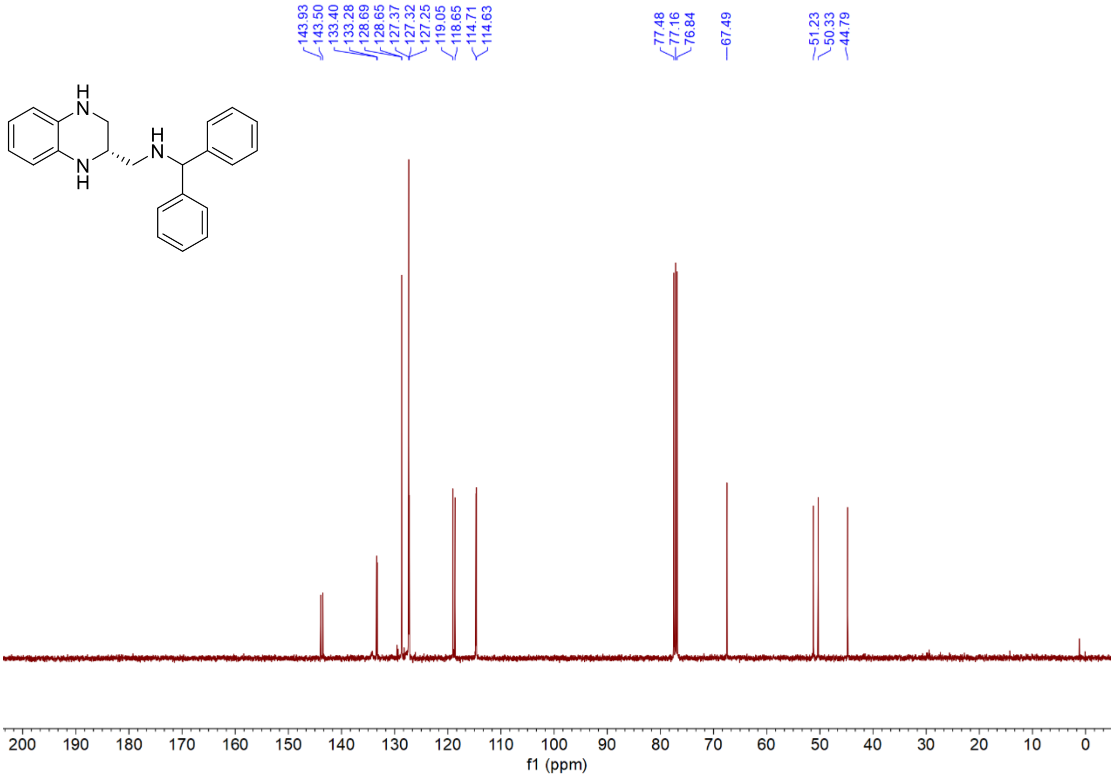
[1]H and [13]C{[1]H} NMR spectra of compound **3ae** in $CDCl_3$



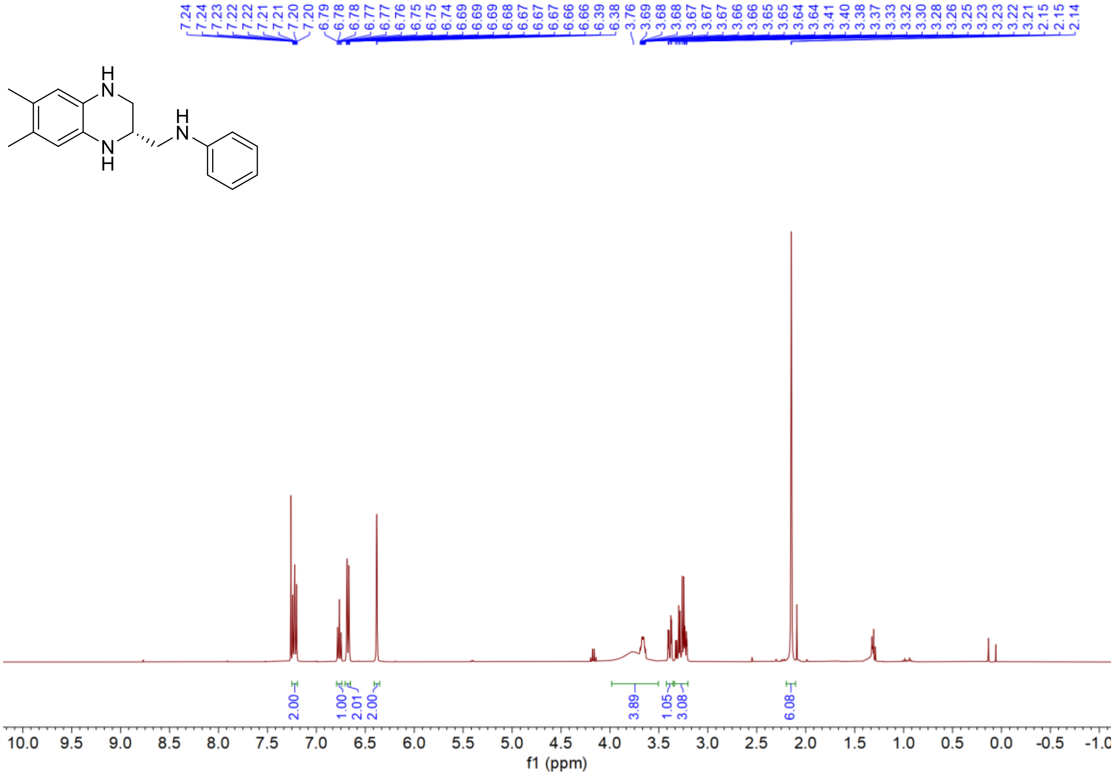


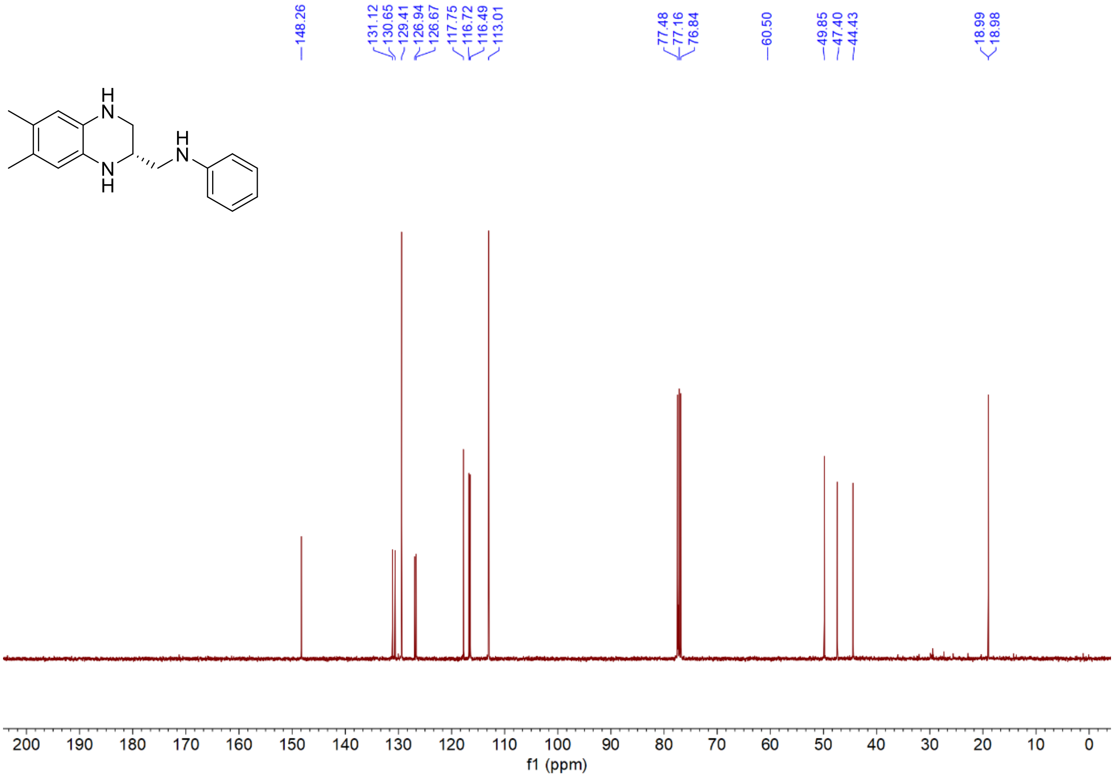
[1]H and [13]C{[1]H} NMR spectra of compound **3af** in $CDCl_3$



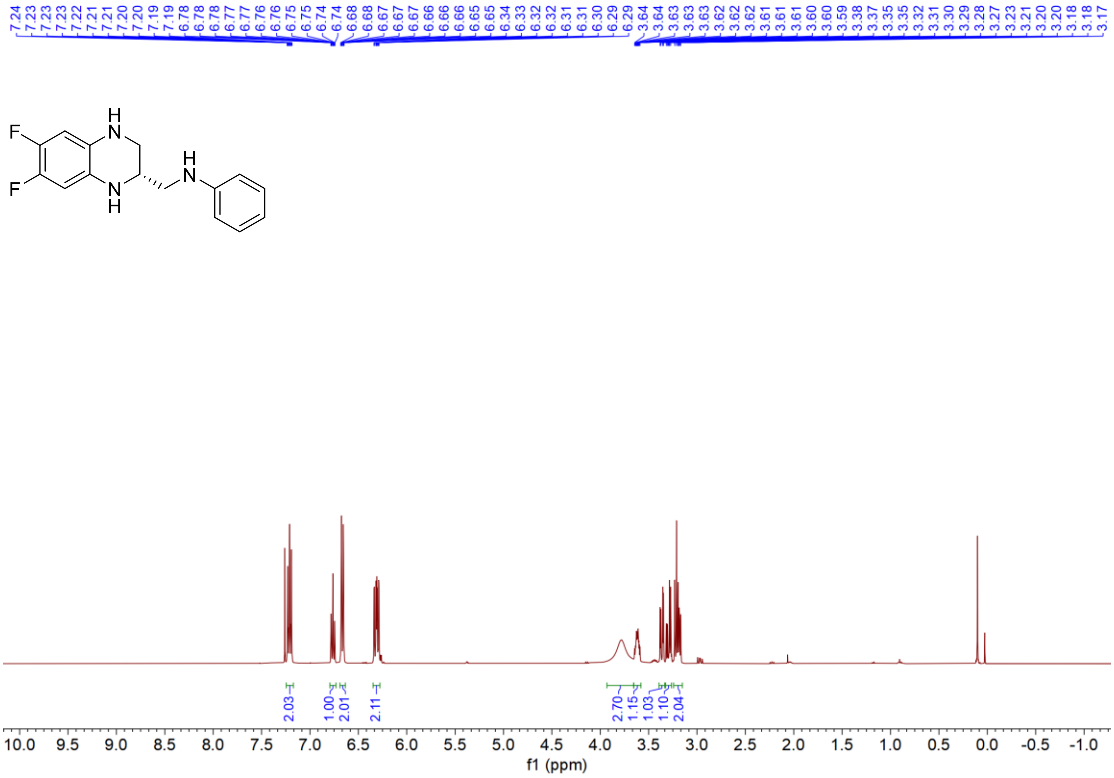


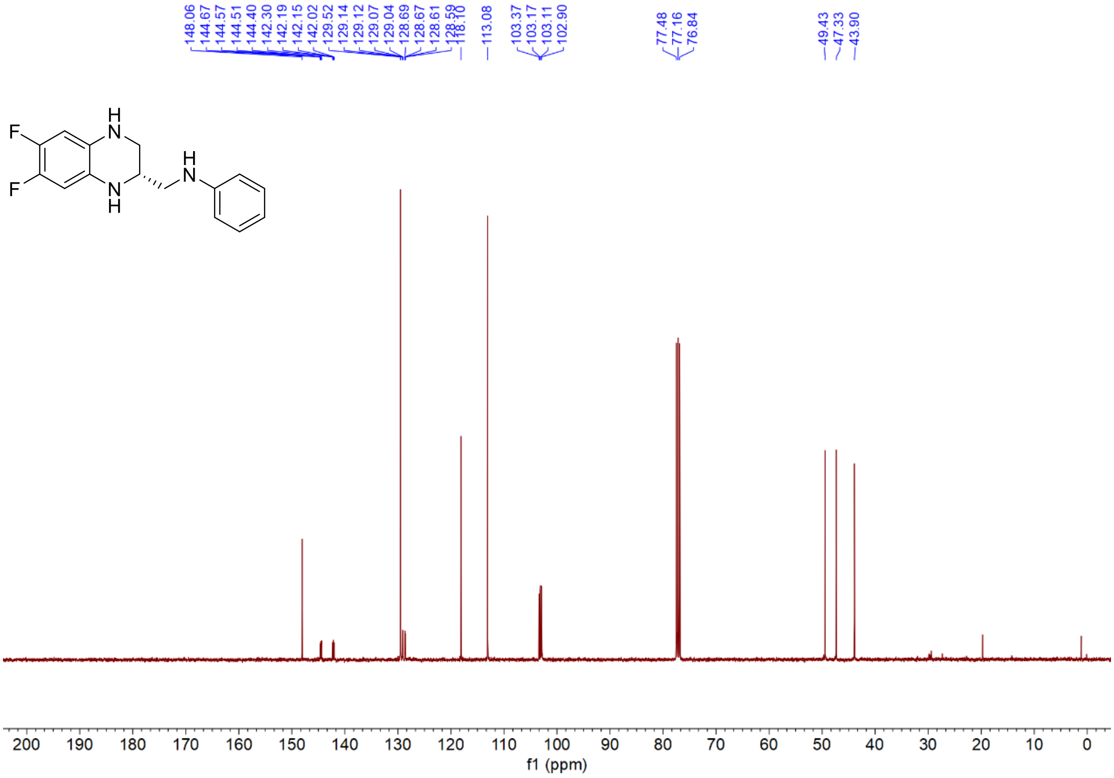
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ba** in $CDCl_3$



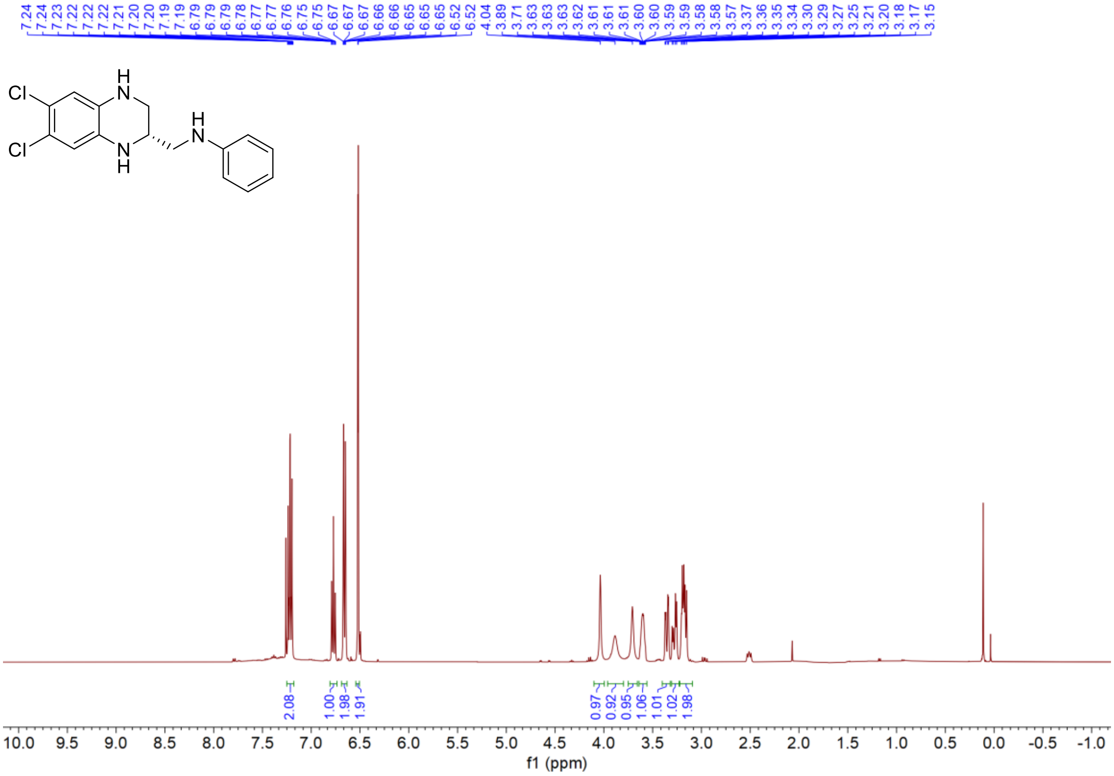


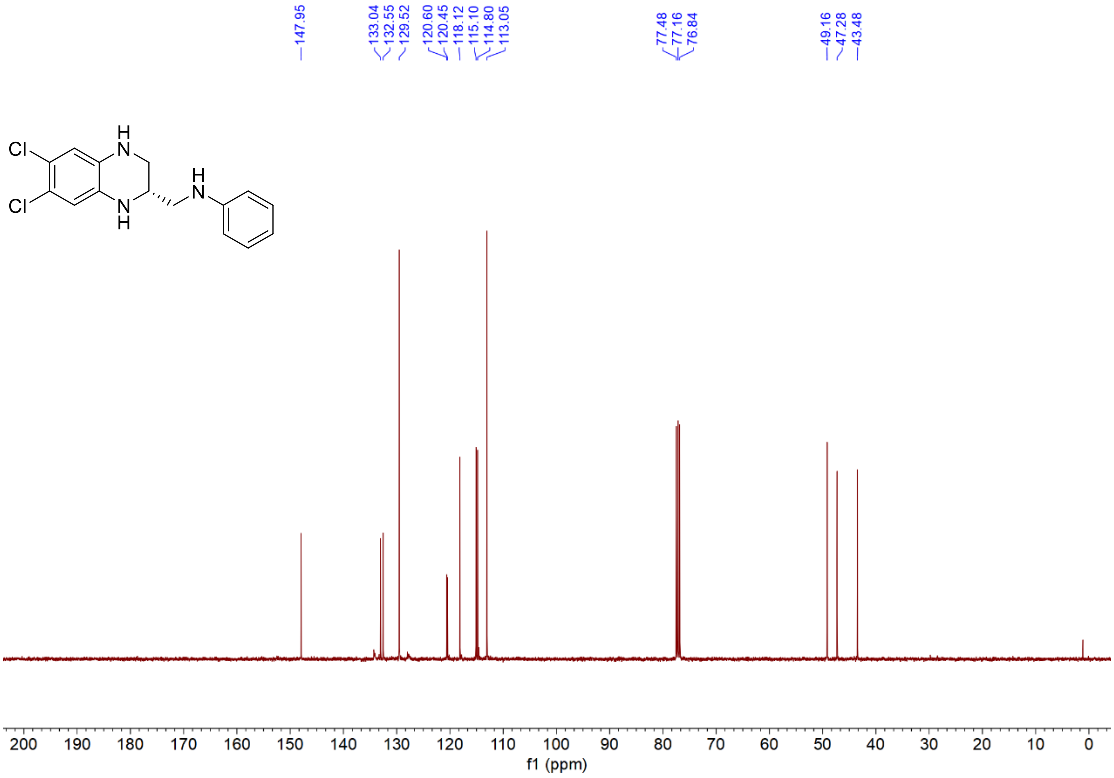
[1]H and [13]C{[1]H} NMR spectra of compound **3ca** in $CDCl_3$



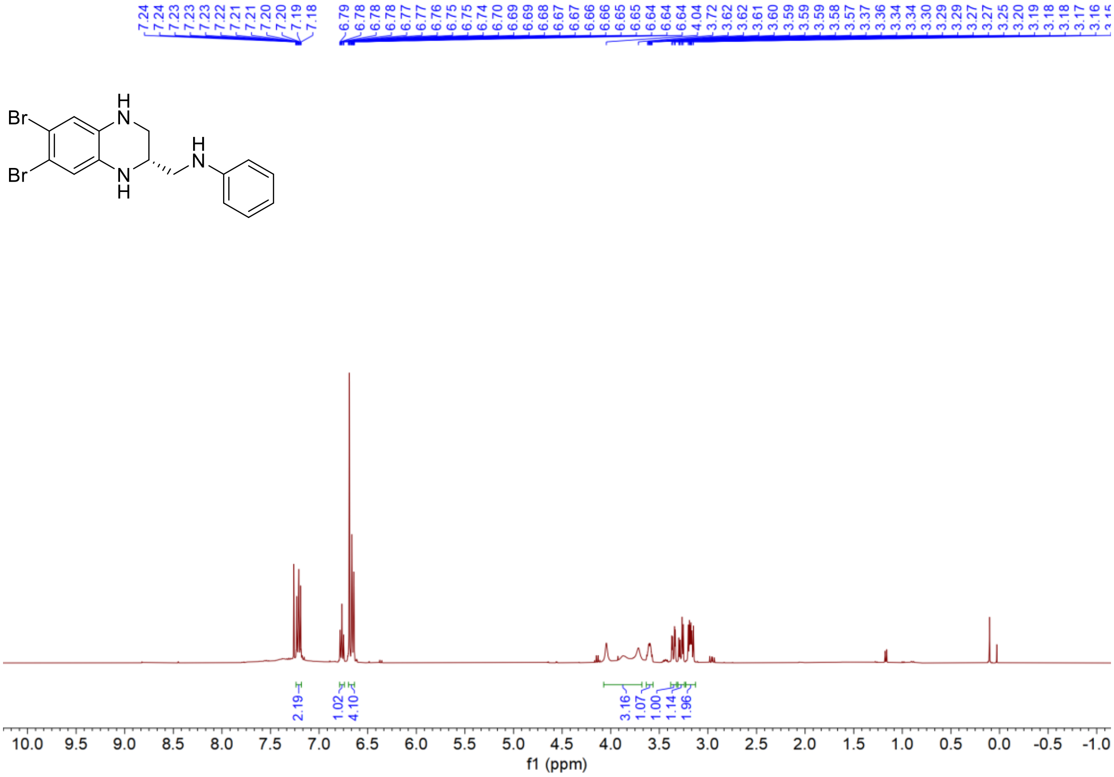


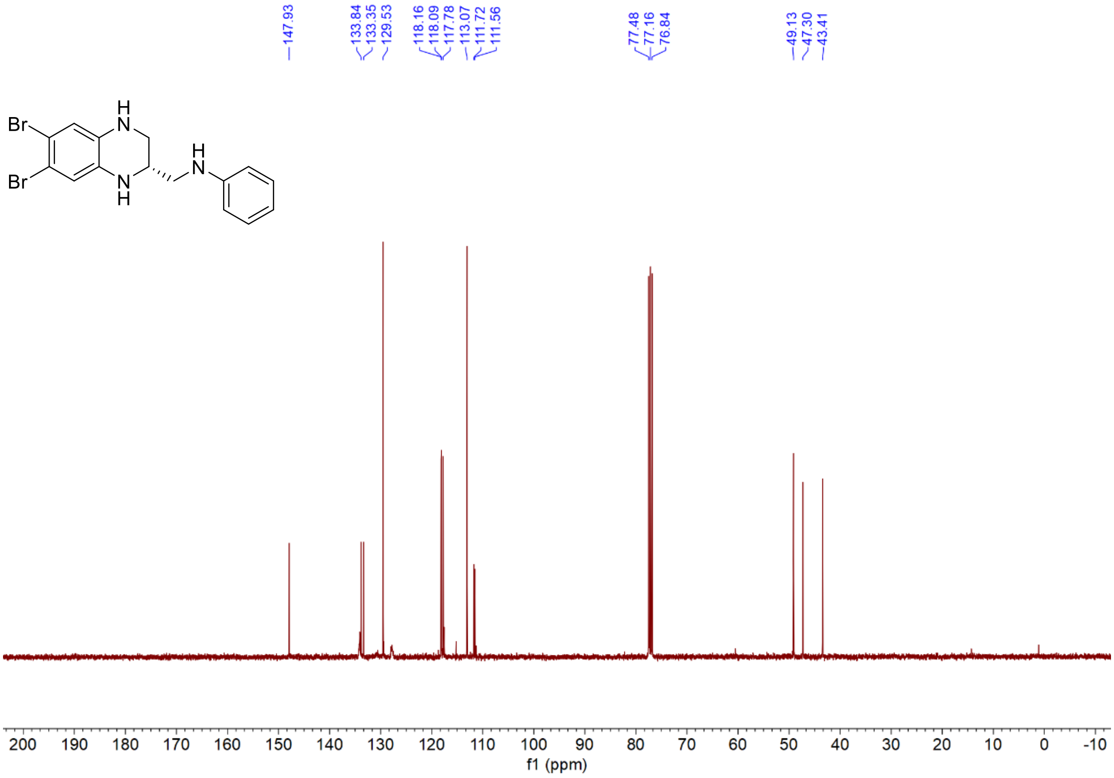
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **3da** in $CDCl_3$



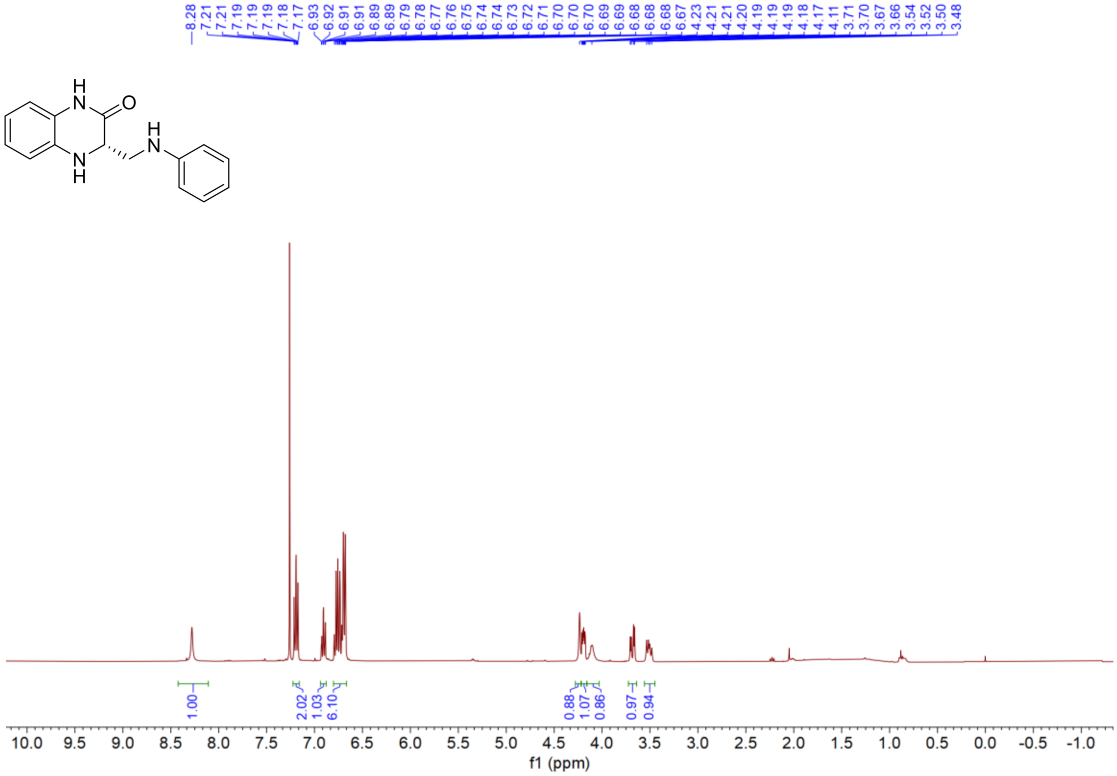


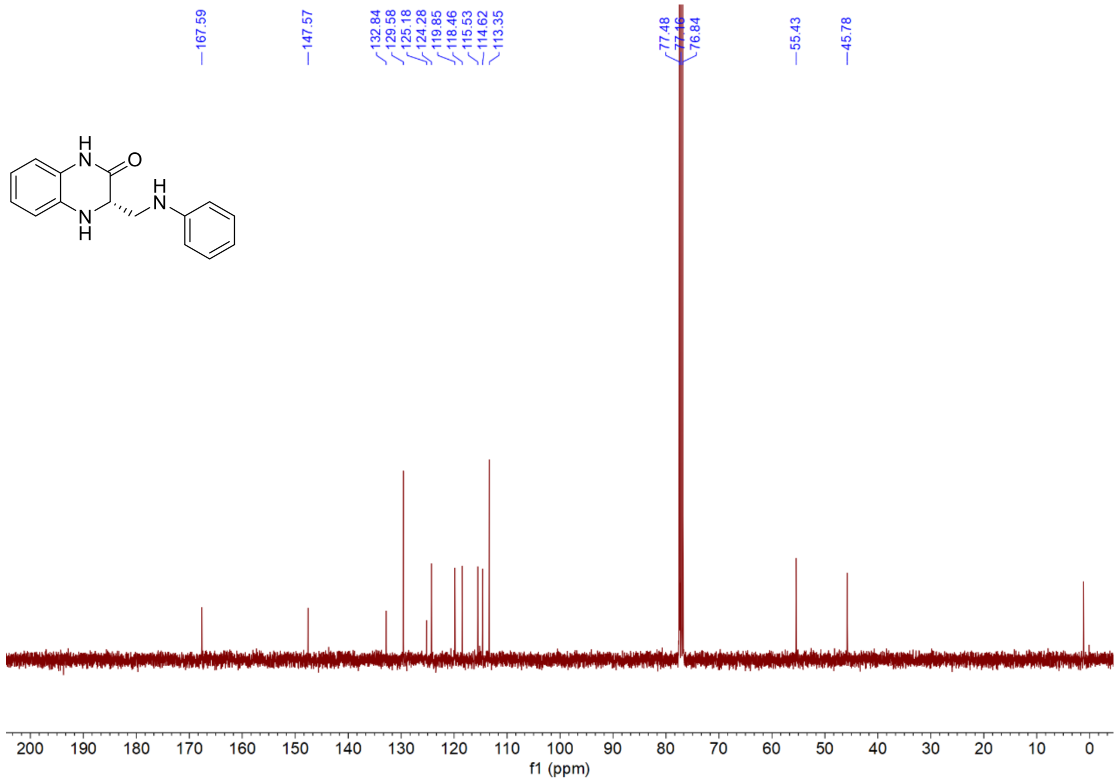
^{1}H and ^{13}C{^{1}H} NMR spectra of compound **3ea** in $CDCl_3$



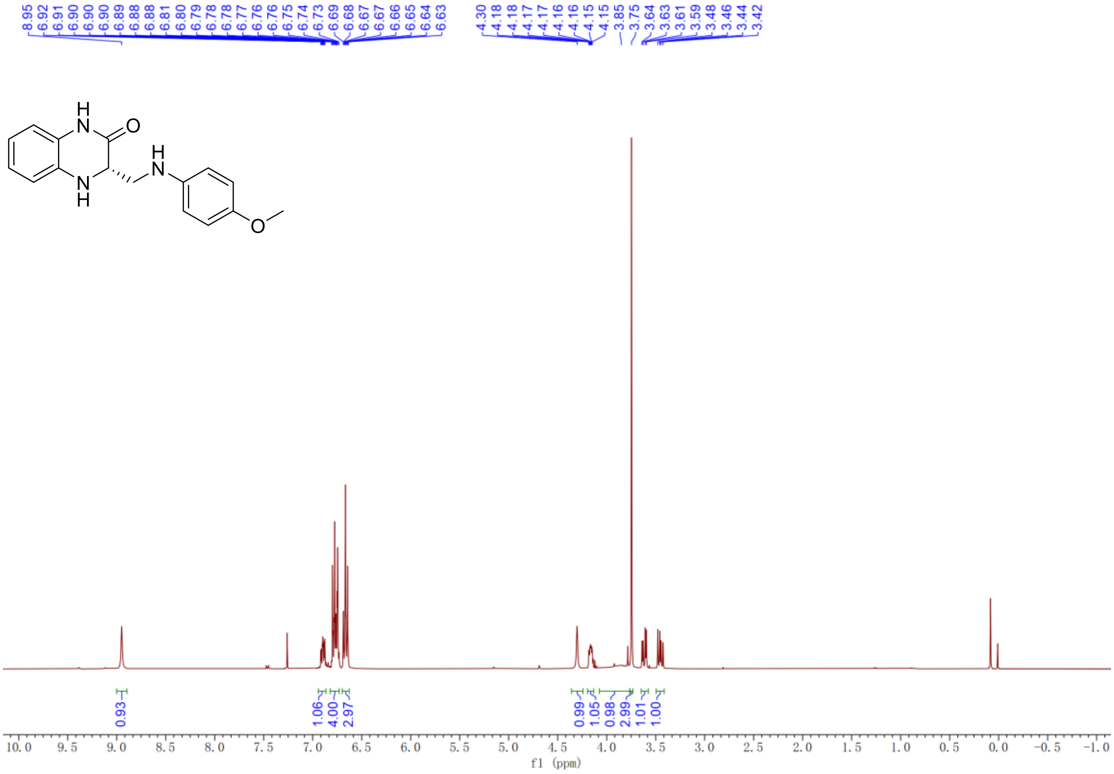


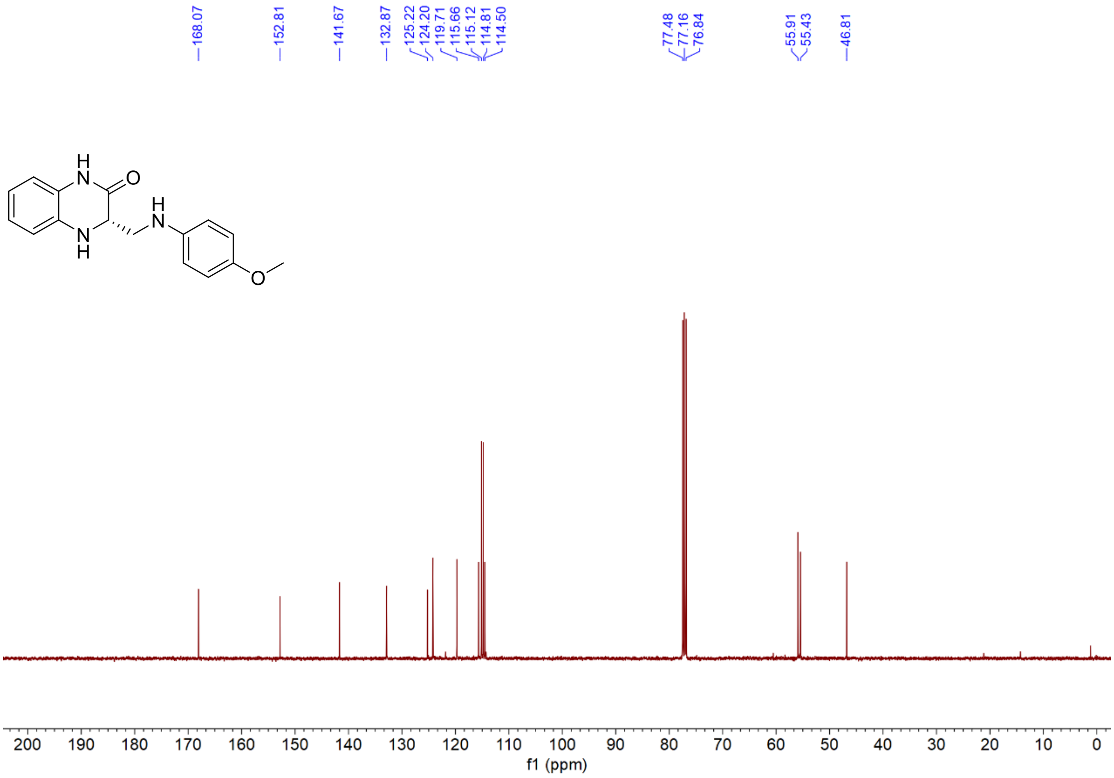
^1H and $^{13}C\{^1H\}$ NMR spectra of compound **7a** in $CDCl_3$



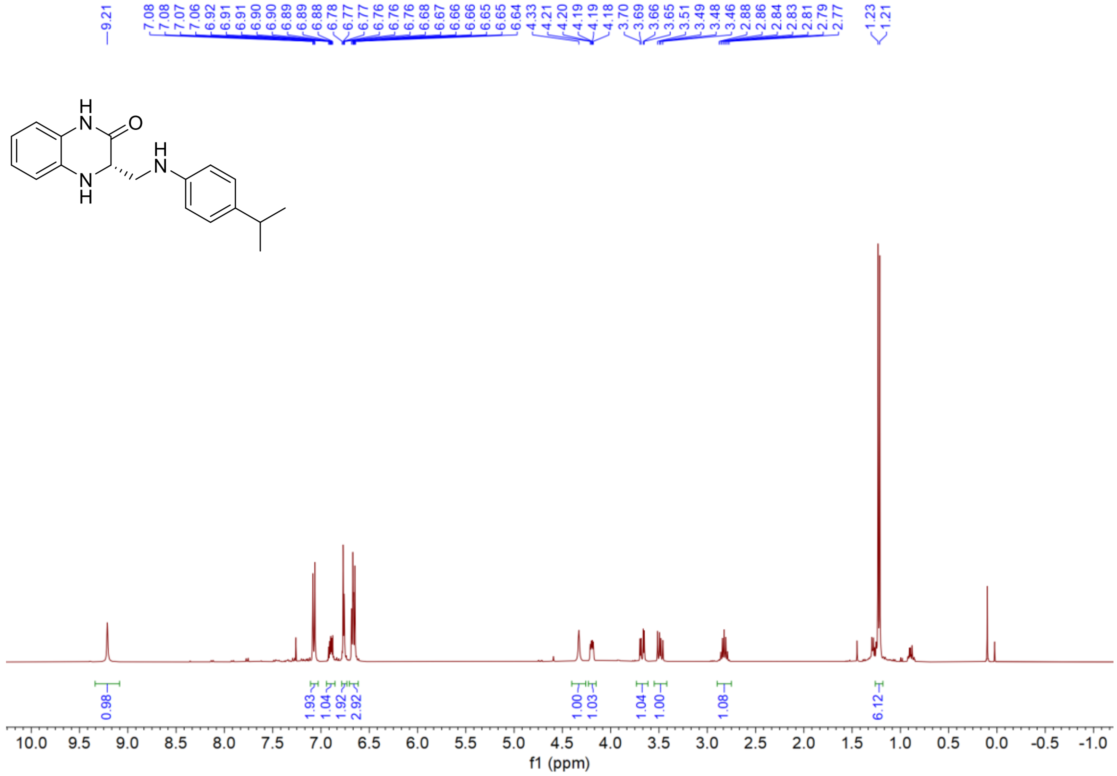


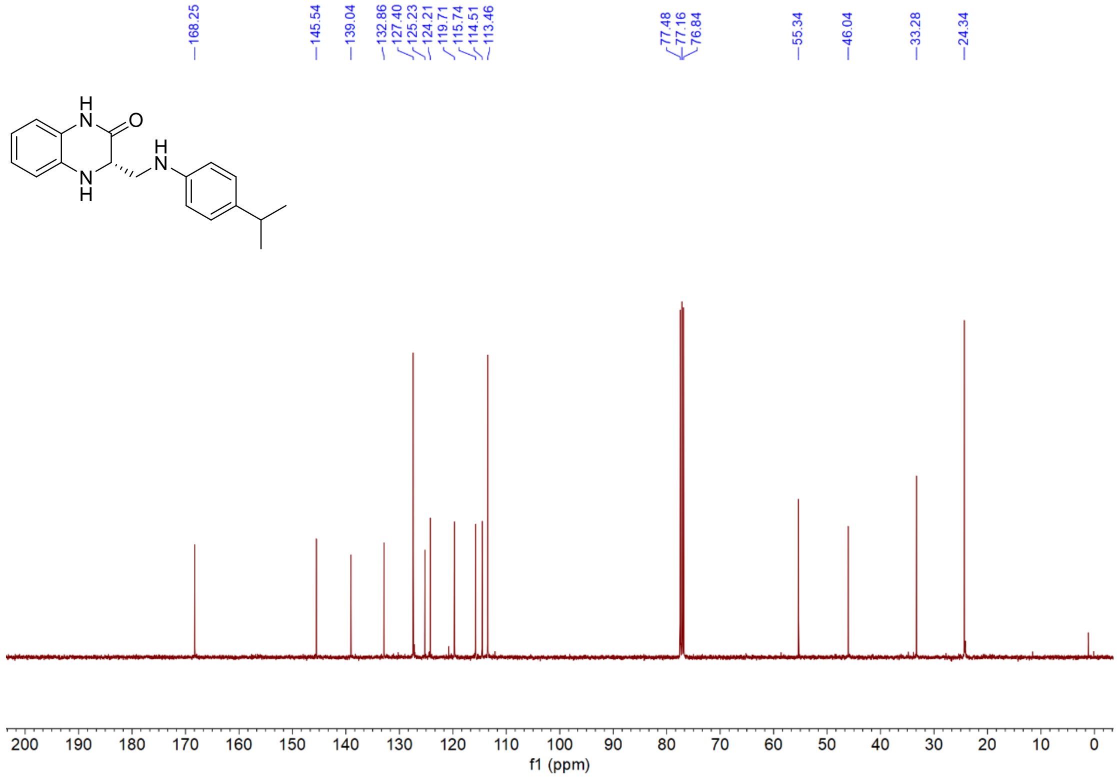
¹H and $^{13}C\{^1H\}$ NMR spectra of compound **7b** in $CDCl_3$



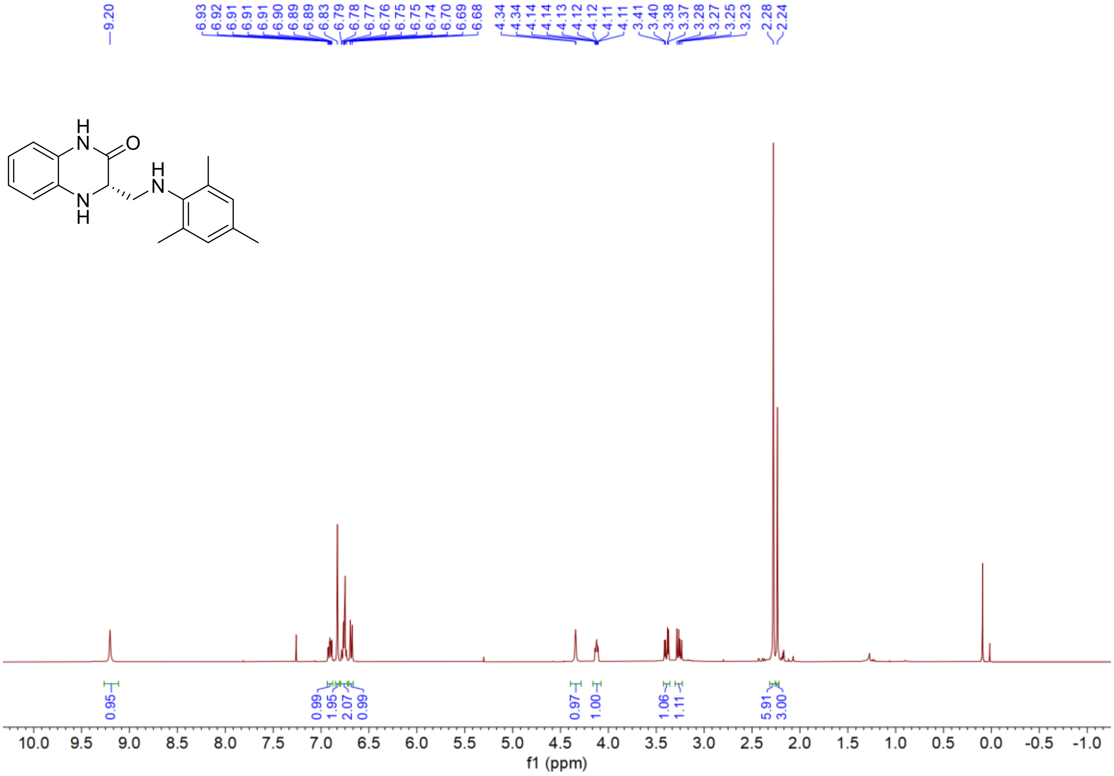


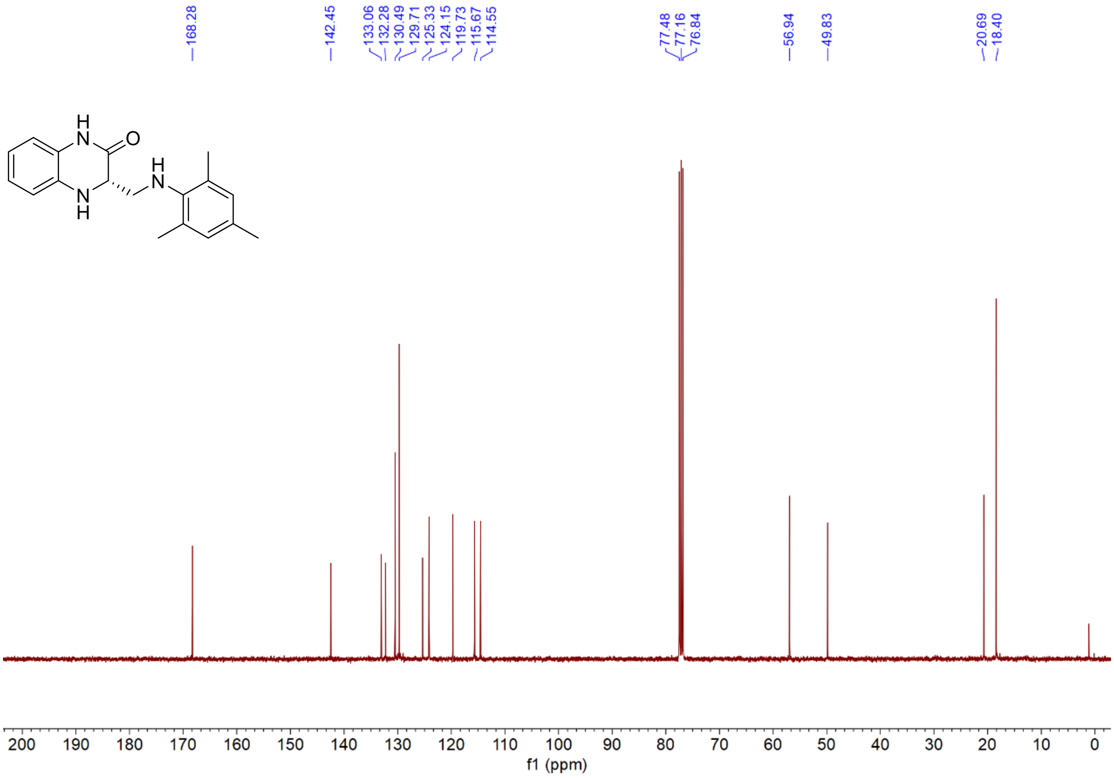
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **7c** in $CDCl_3$



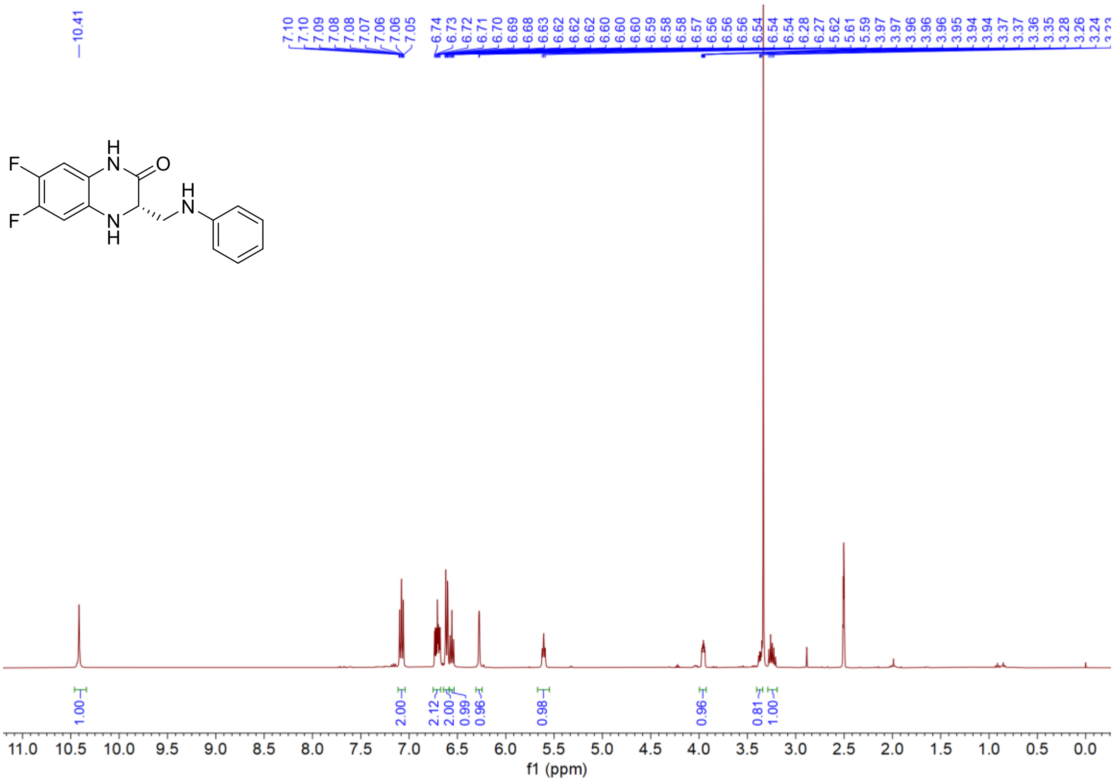


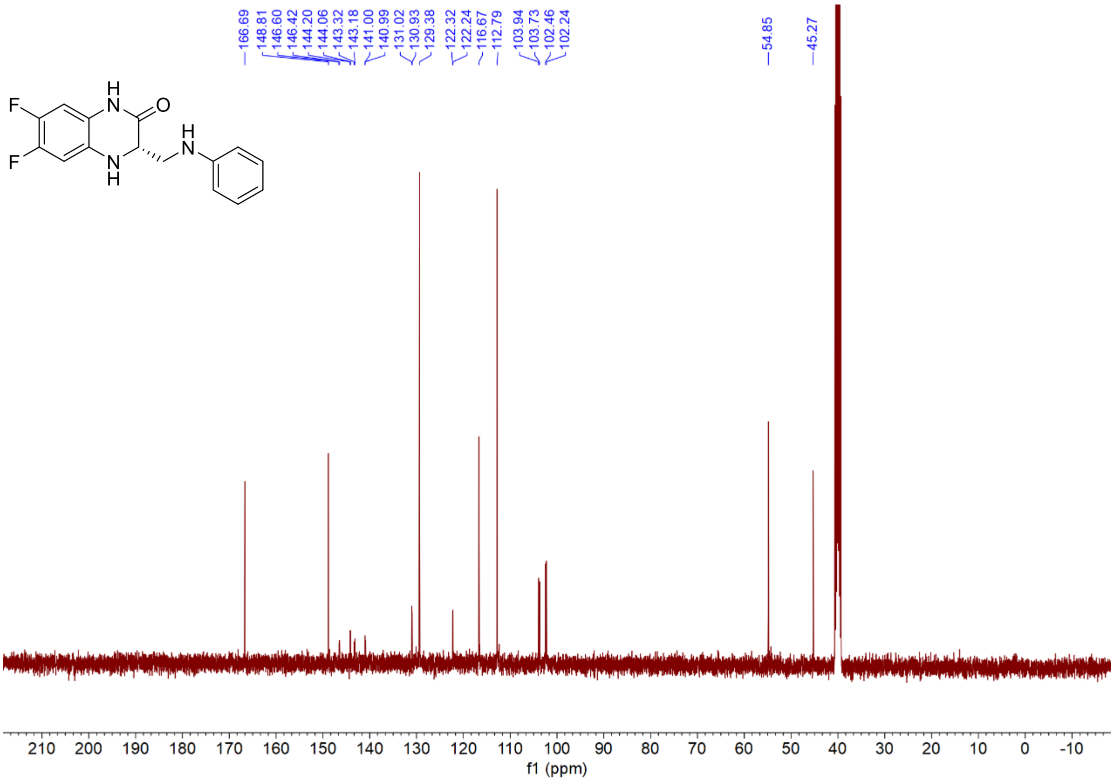
^{1}H and ^{13}C{^{1}H} NMR spectra of compound **7d** in $CDCl_3$



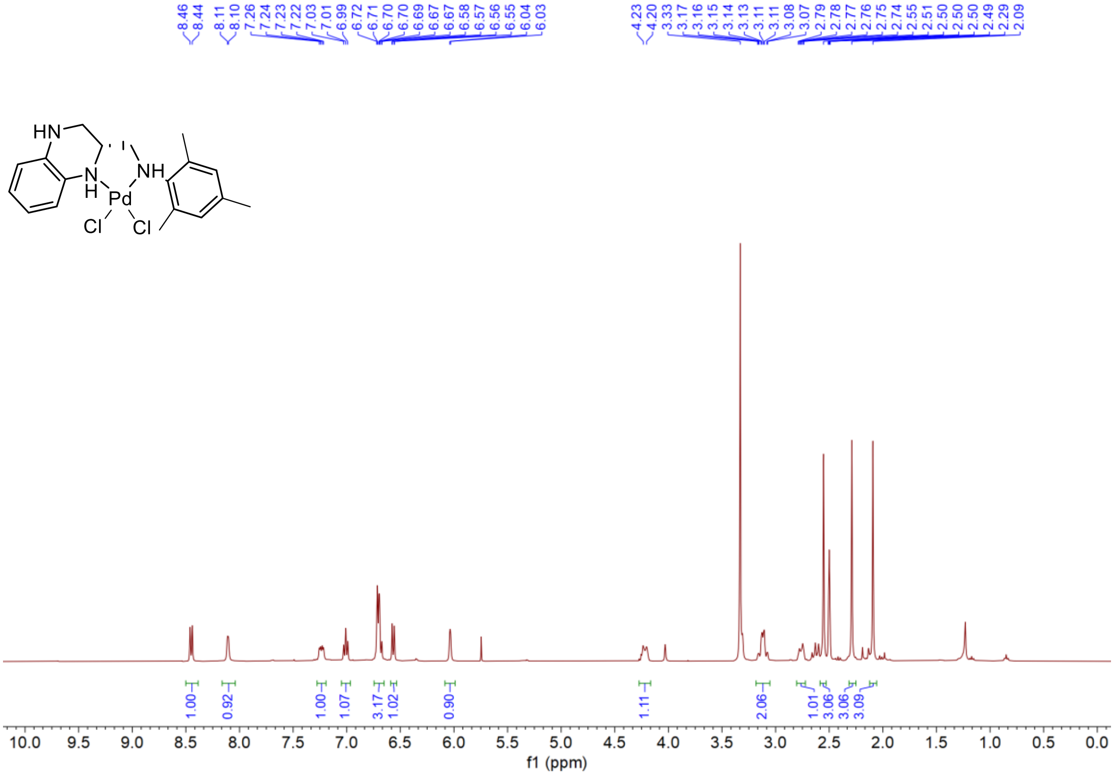


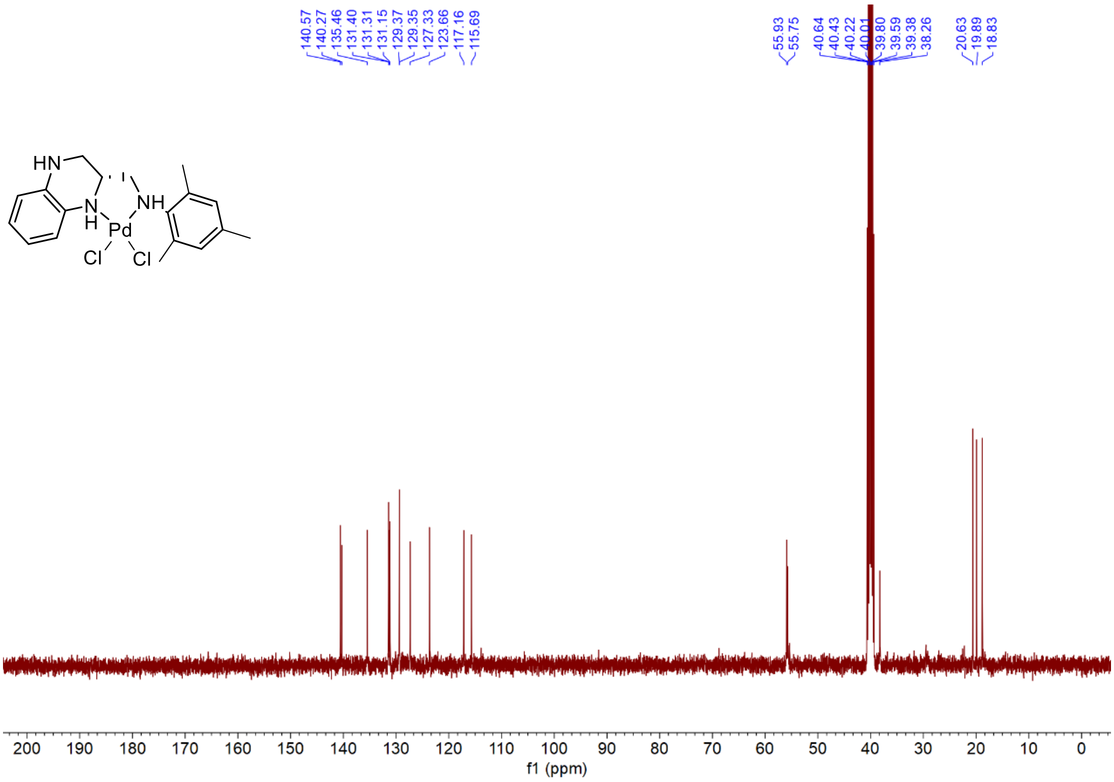
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **7e** in $CDCl_3$



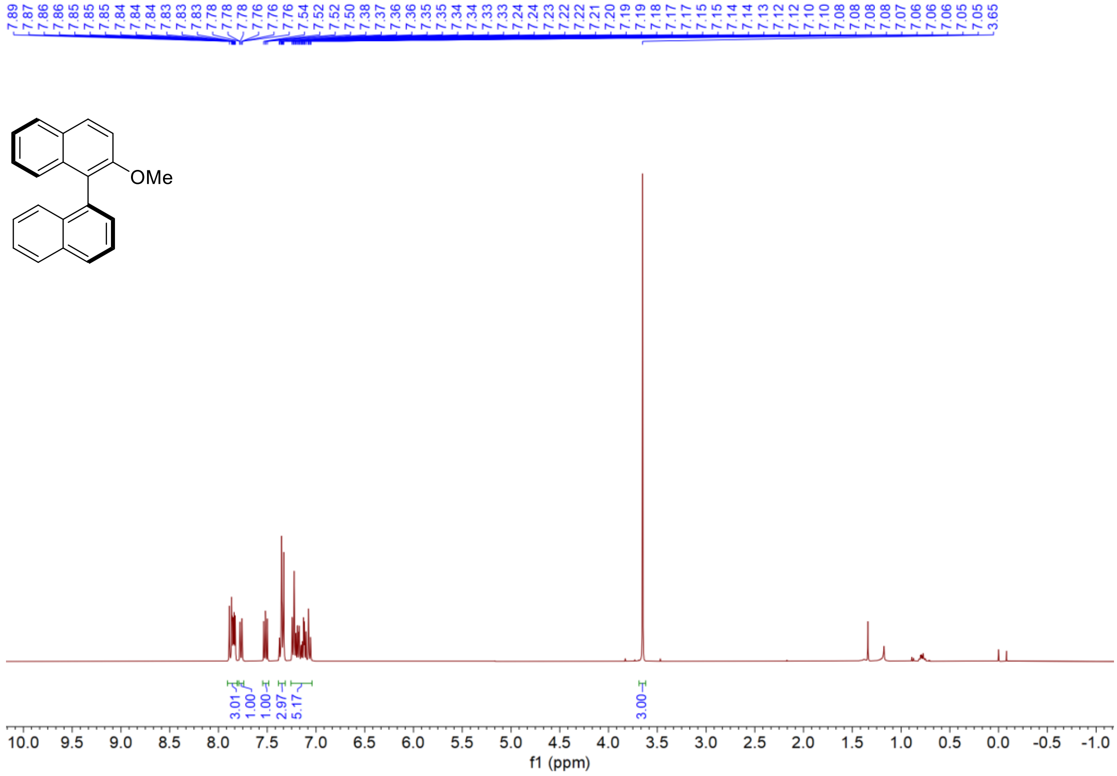


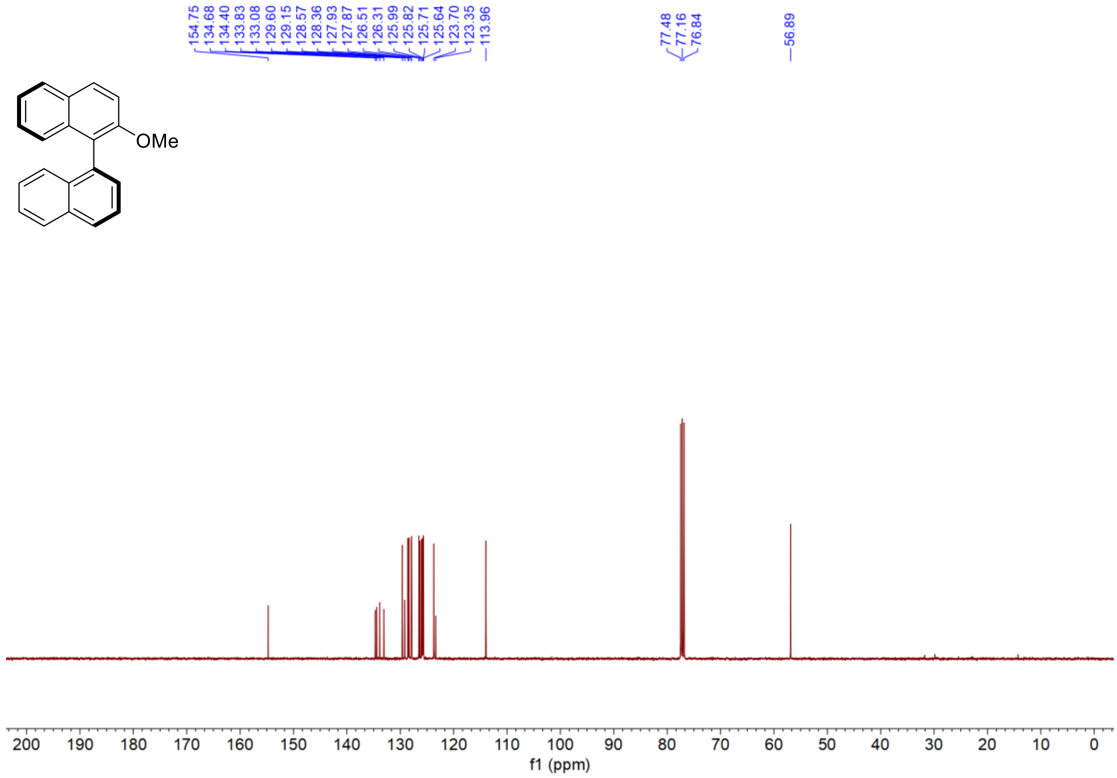
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **12** in DMSO-d_6



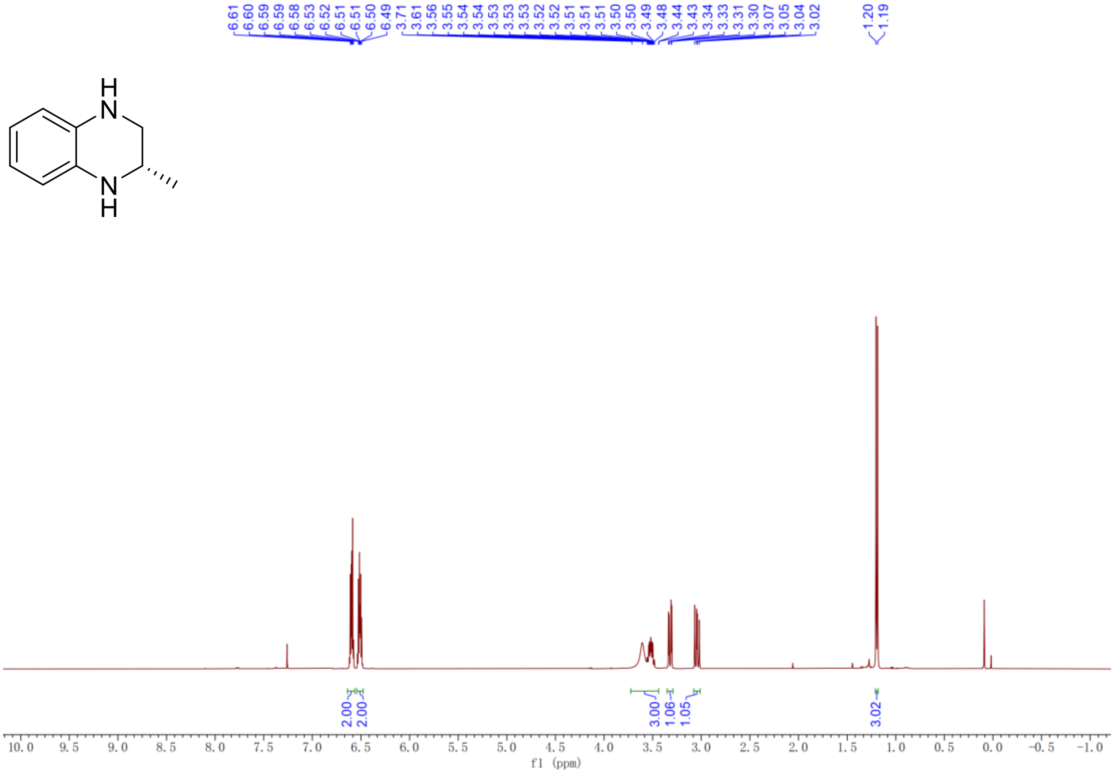


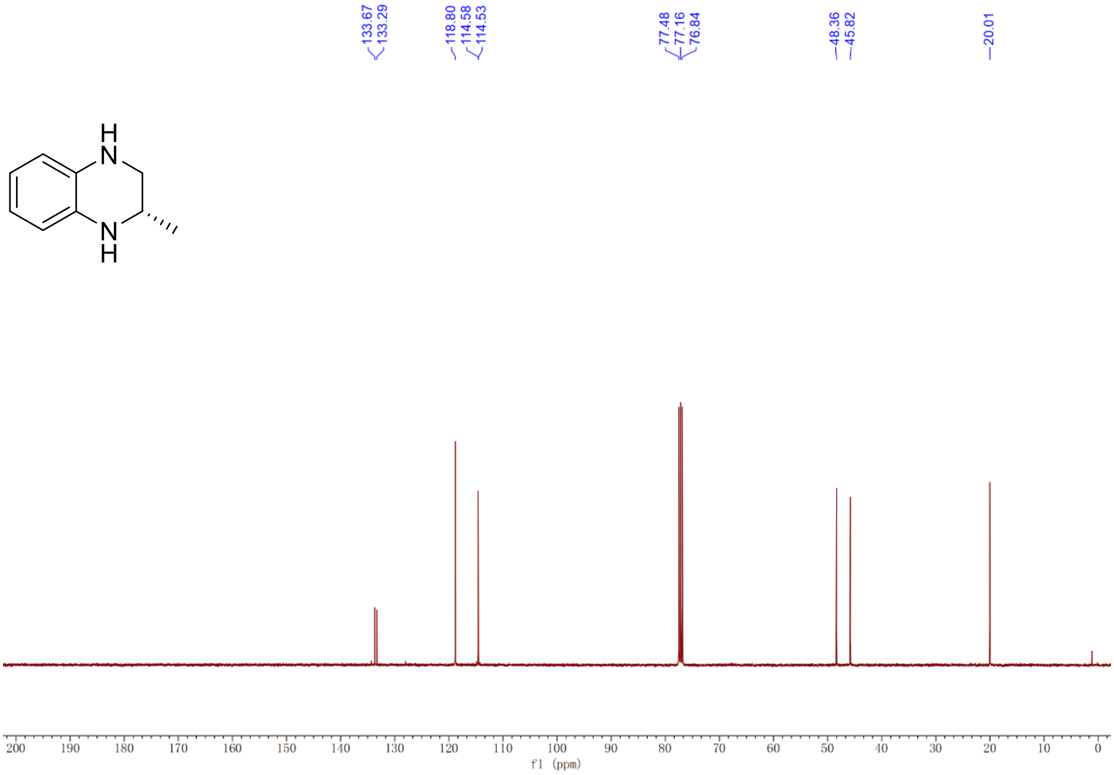
[1]H and $^{13}C\{^{1}H\}$ NMR spectra of compound **11** in $CDCl_3$



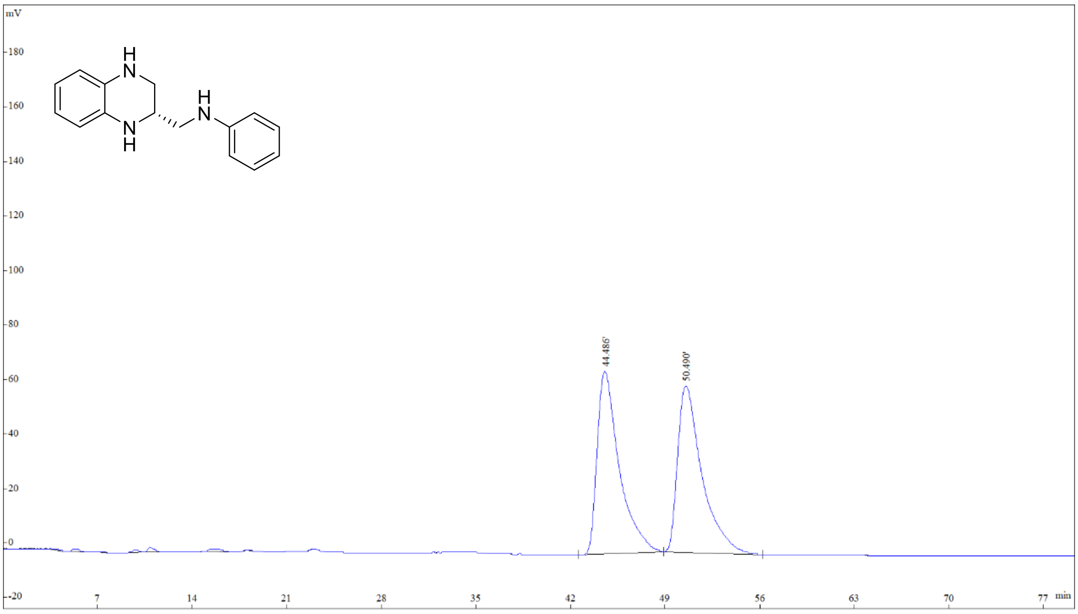


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **14** in $CDCl_3$

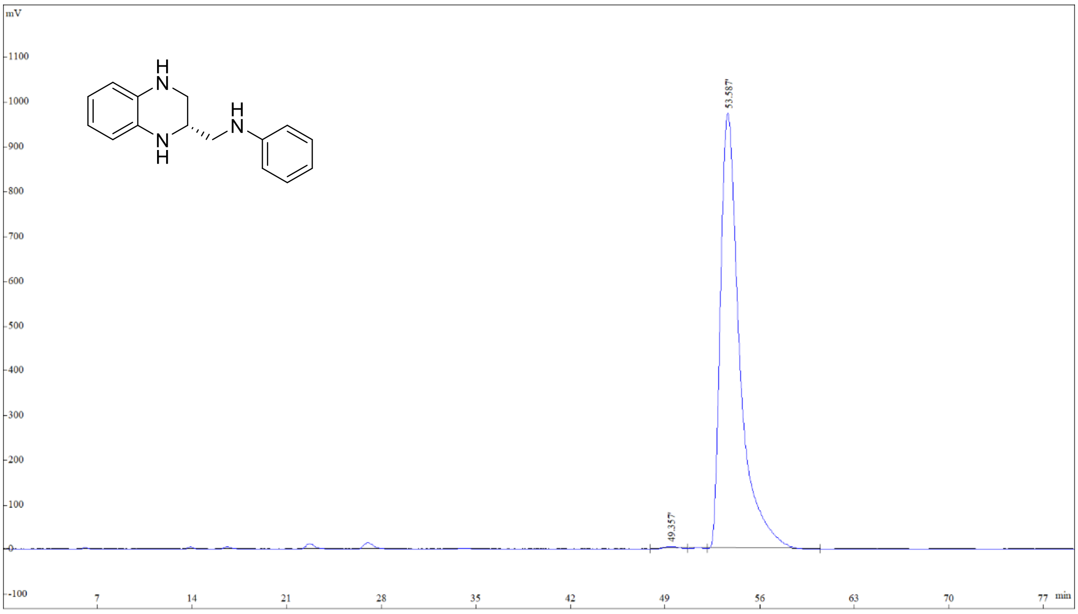




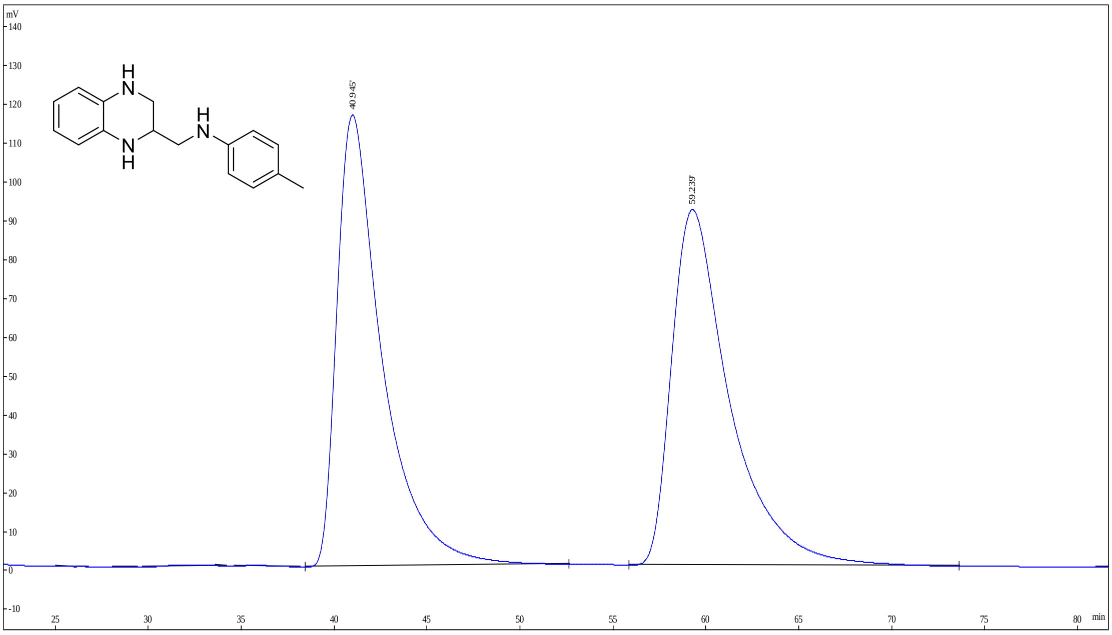
9. Copy of HPLC spectra of the racemic and chiral products



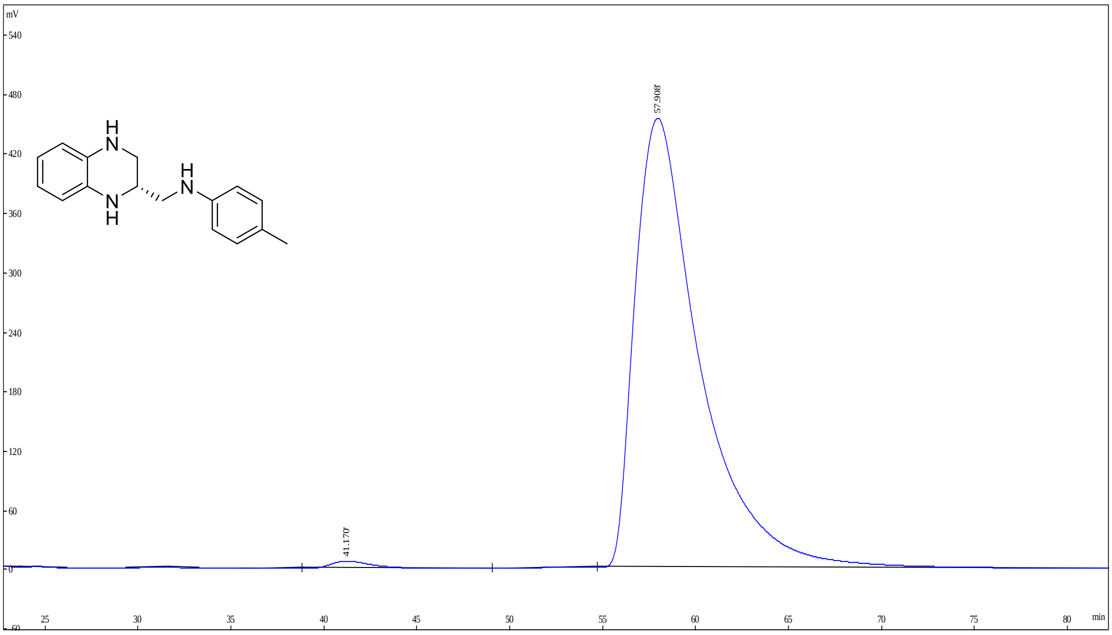
peak	Ret. Time	Area%	Area
1	44.486	49.95	7738251
2	50.490	50.05	7753558



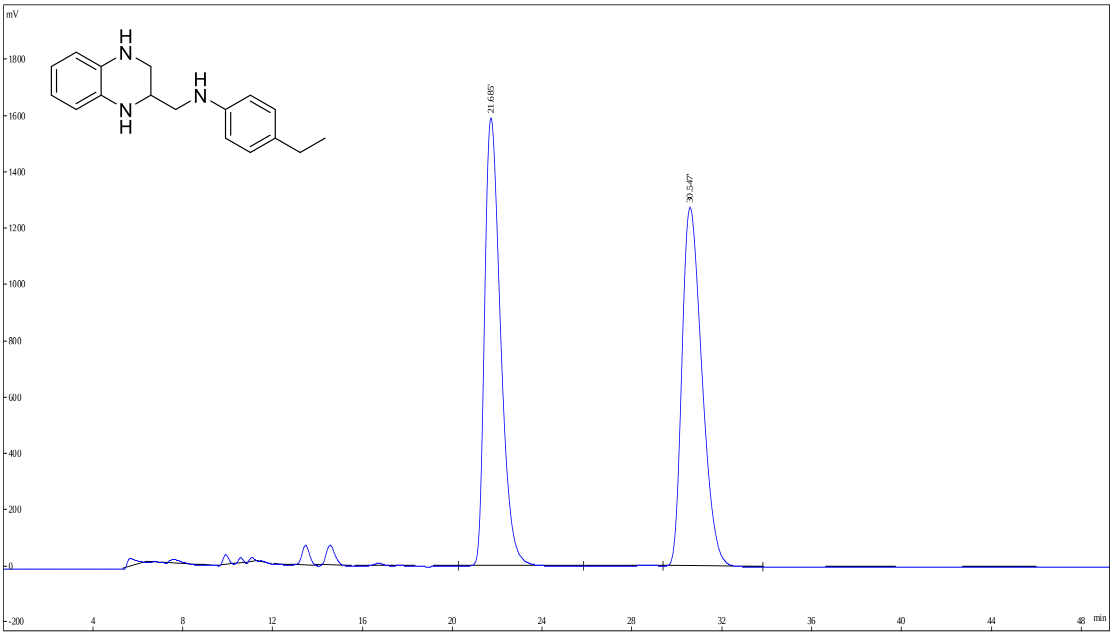
peak	Ret. Time	Area%	Area
1	49.357	0.48	471024
2	53.587	99.52	96375642



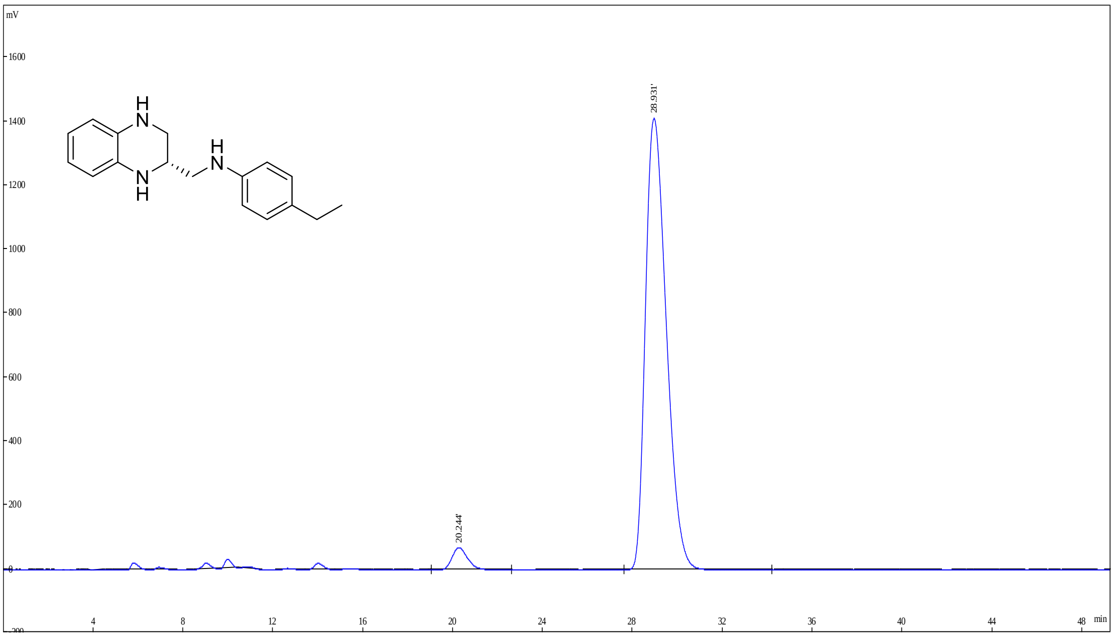
peak	Ret. Time	Area%	Area
1	40.945	49.70	19683021
2	59.239	50.30	19921142



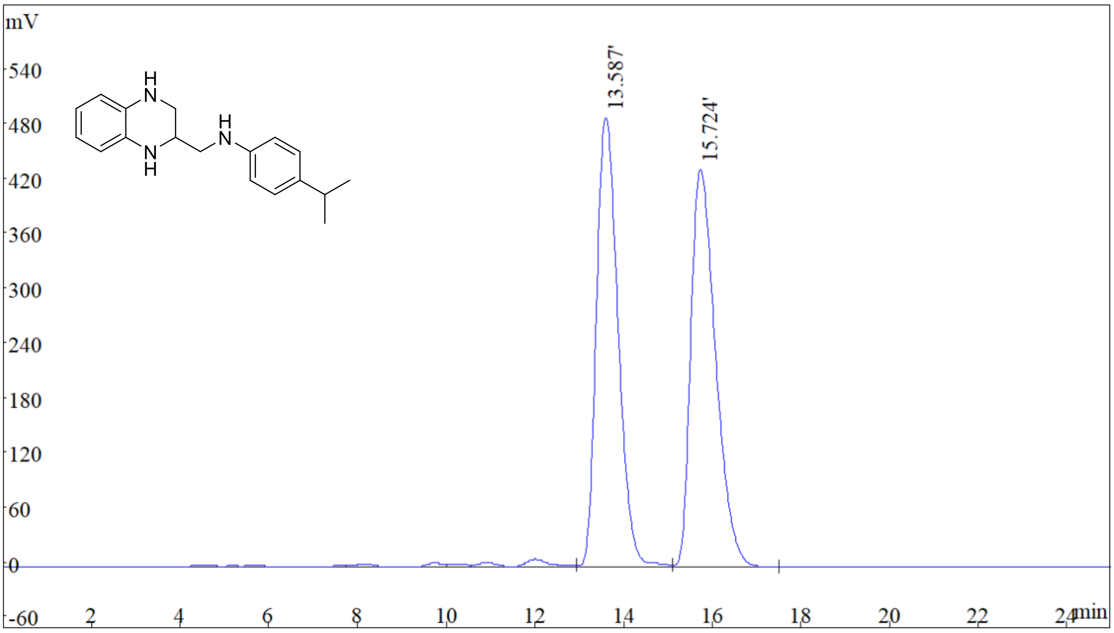
peak	Ret. Time	Area%	Area
1	41.170	1.09	1212964
2	57.908	98.91	110249267



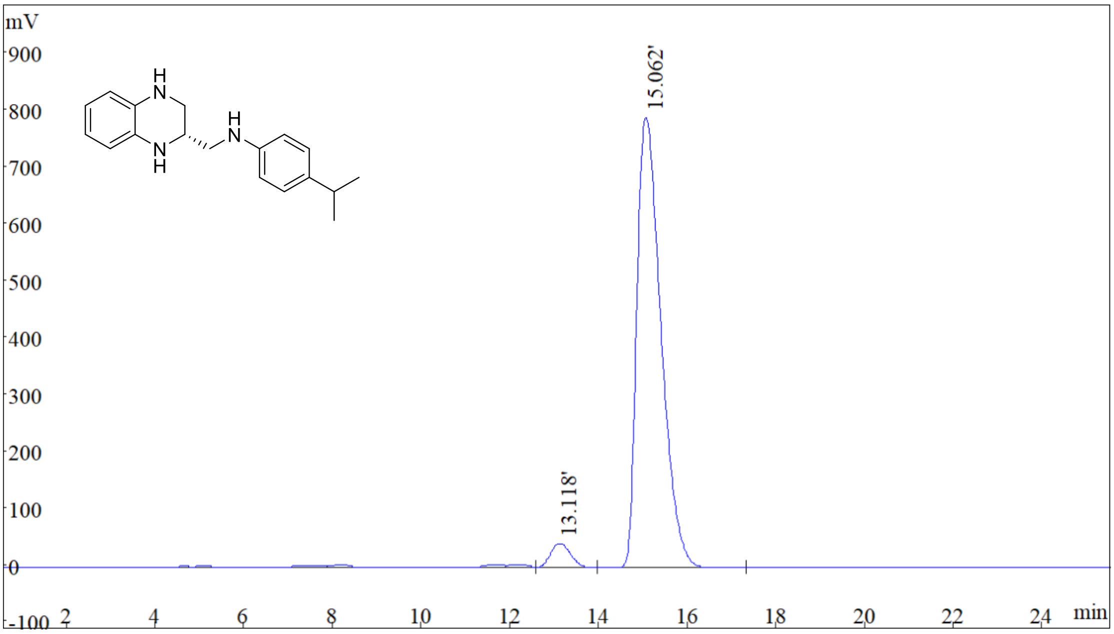
peak	Ret. Time	Area%	Area
1	21.685	50.10	78916480
2	30.547	49.90	78603936



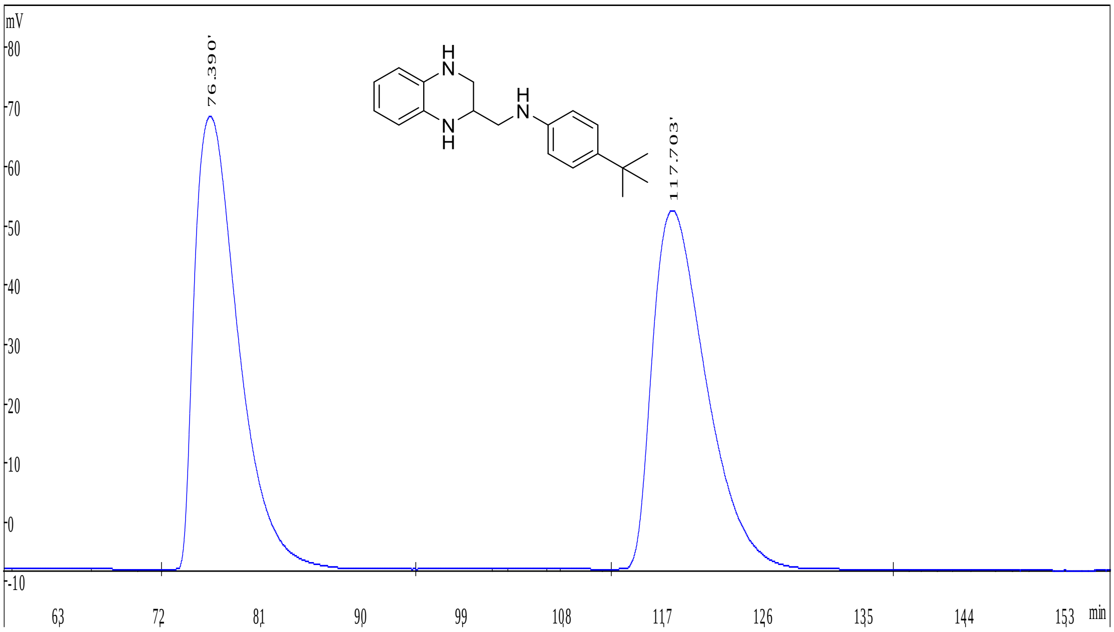
peak	Ret. Time	Area%	Area
1	20.244	3.63	3422859
2	28.931	96.37	91016320



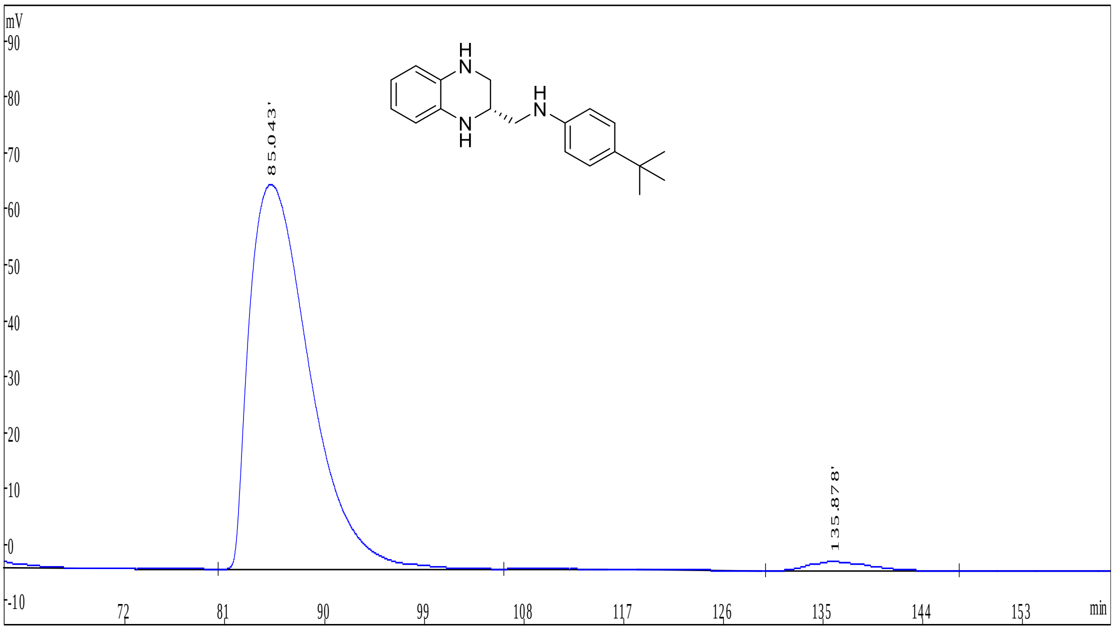
peak	Ret. Time	Area%	Area
1	13.587	49.44	16459510
2	15.724	50.56	16833976



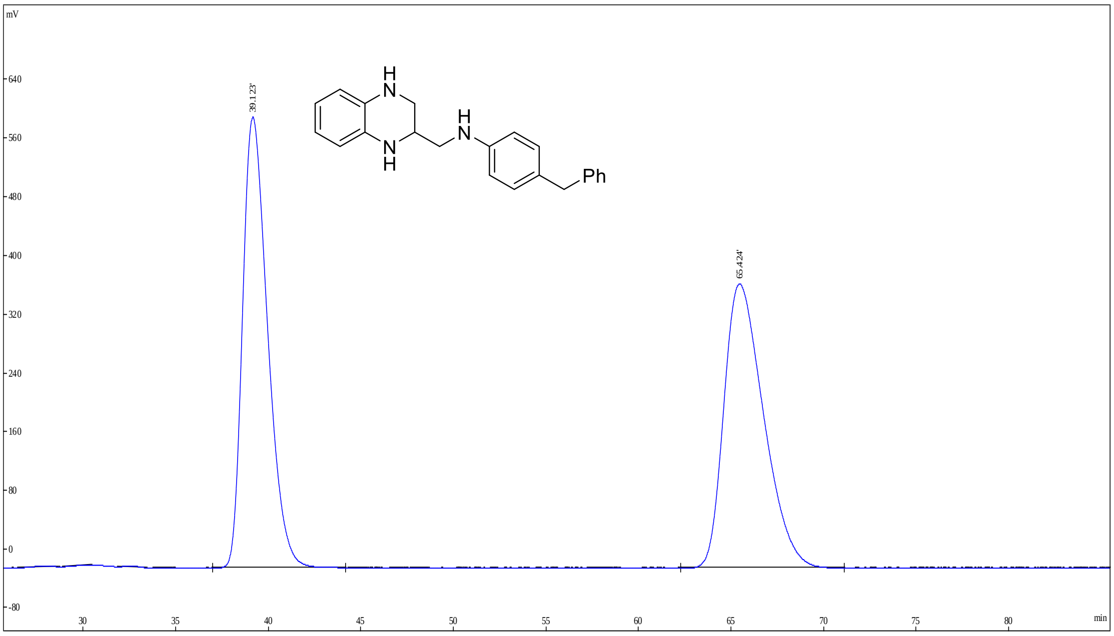
peak	Ret. Time	Area%	Area
1	13.118	3.71	1460084
2	15.062	96.29	29516333



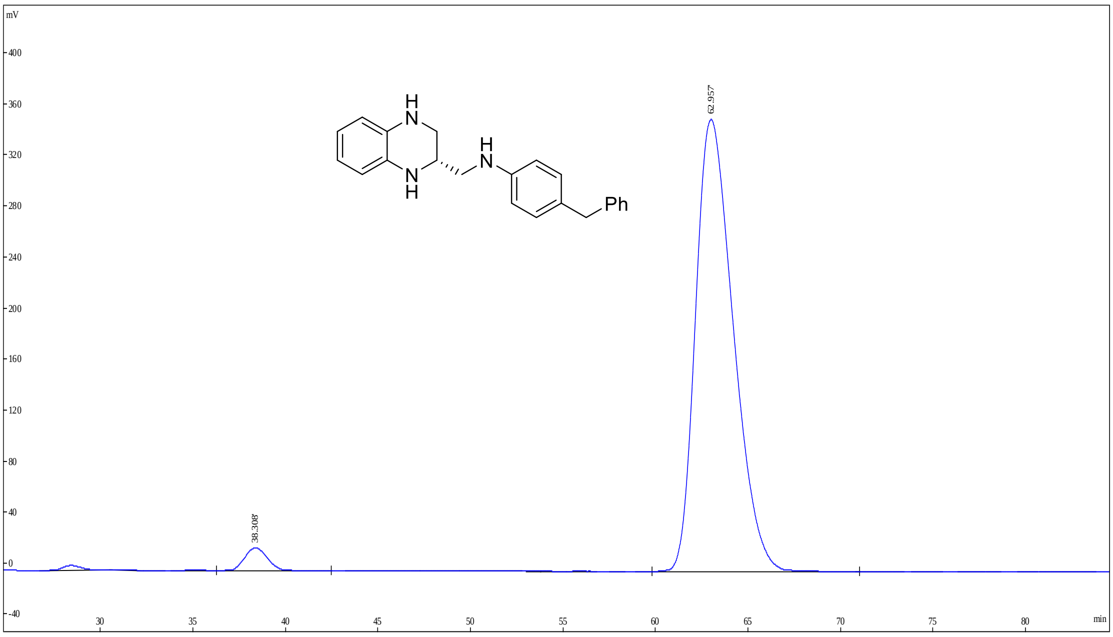
peak	Ret. Time	Area%	Area
1	76.390	50.69	21154221
2	117.703	49.31	20578342



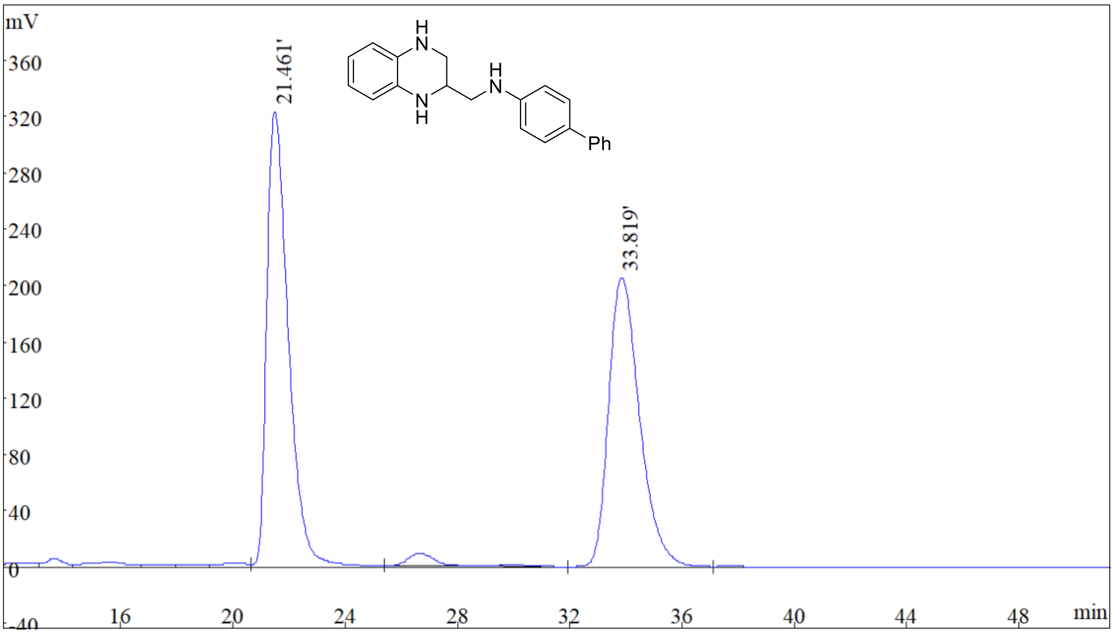
peak	Ret. Time	Area%	Area
1	85.043	97.28	25900382
2	135.878	2.72	725515



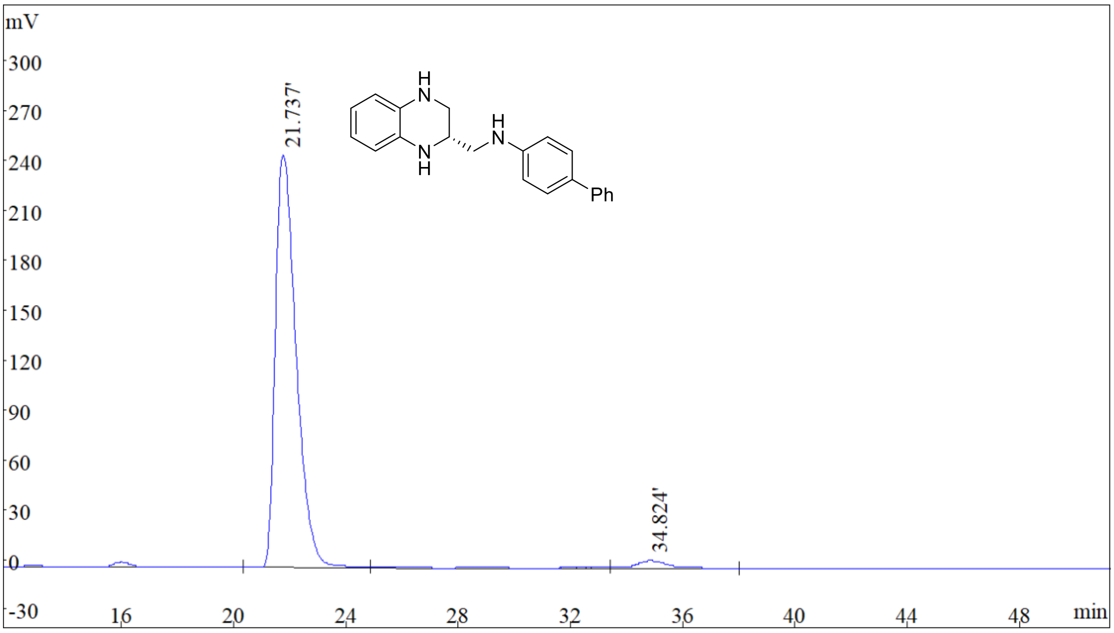
peak	Ret. Time	Area%	Area
1	39.123	49.94	57506797
2	65.424	50.06	57648416



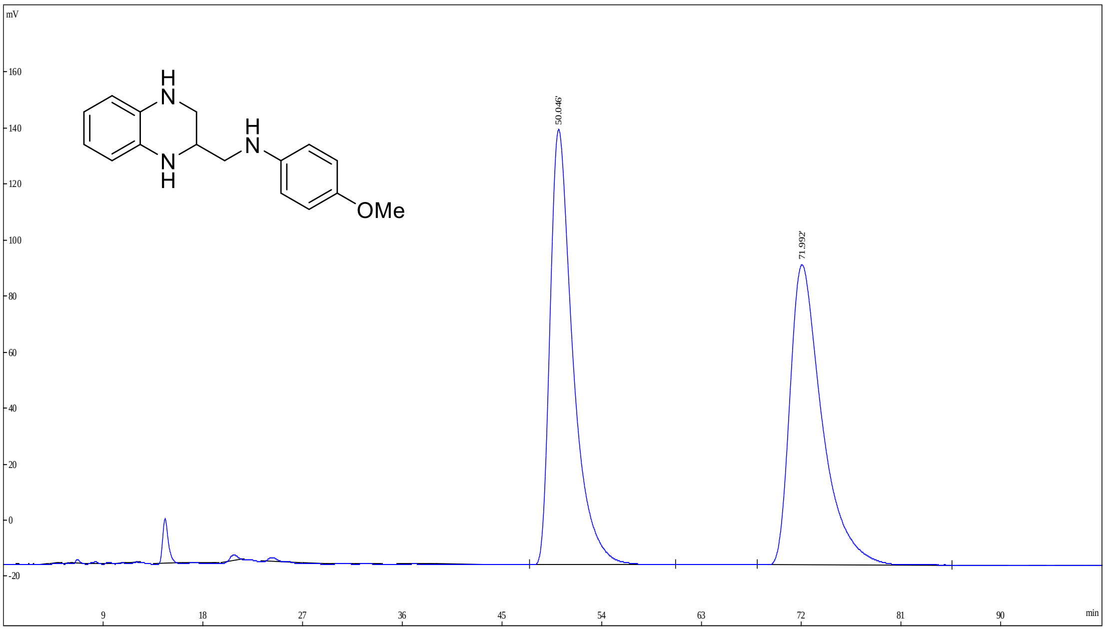
peak	Ret. Time	Area%	Area
1	38.308	3.19	1663099
2	62.957	96.81	50354141



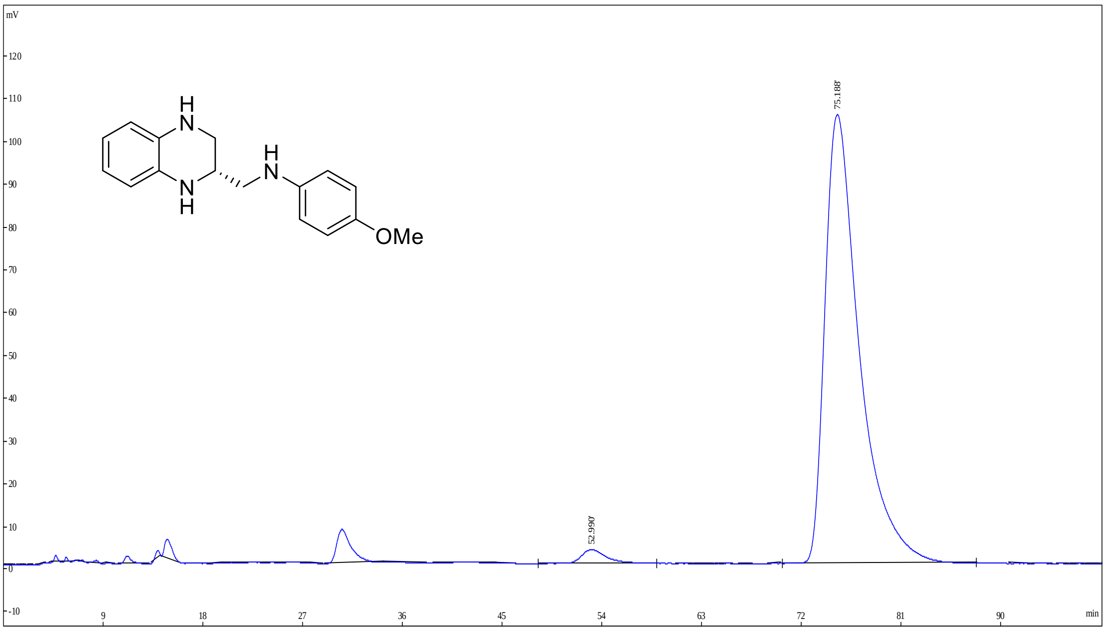
peak	Ret. Time	Area%	Area
1	21.461	52.57	17756973
2	33.819	47.43	16019179



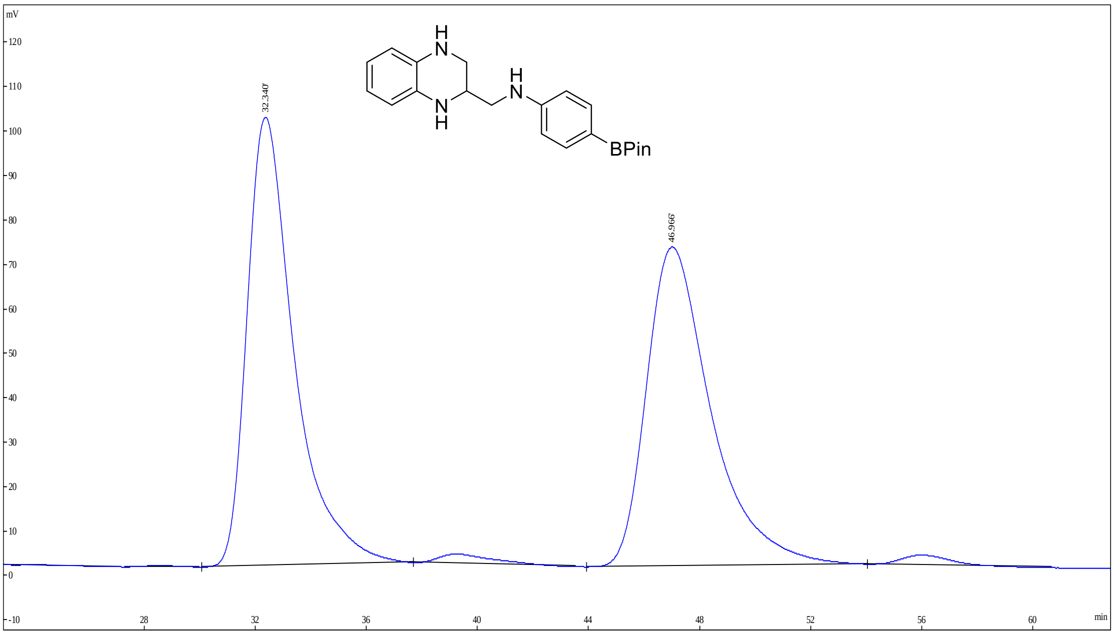
peak	Ret. Time	Area%	Area
1	21.737	96.57	12622021
2	34.824	3.43	448097



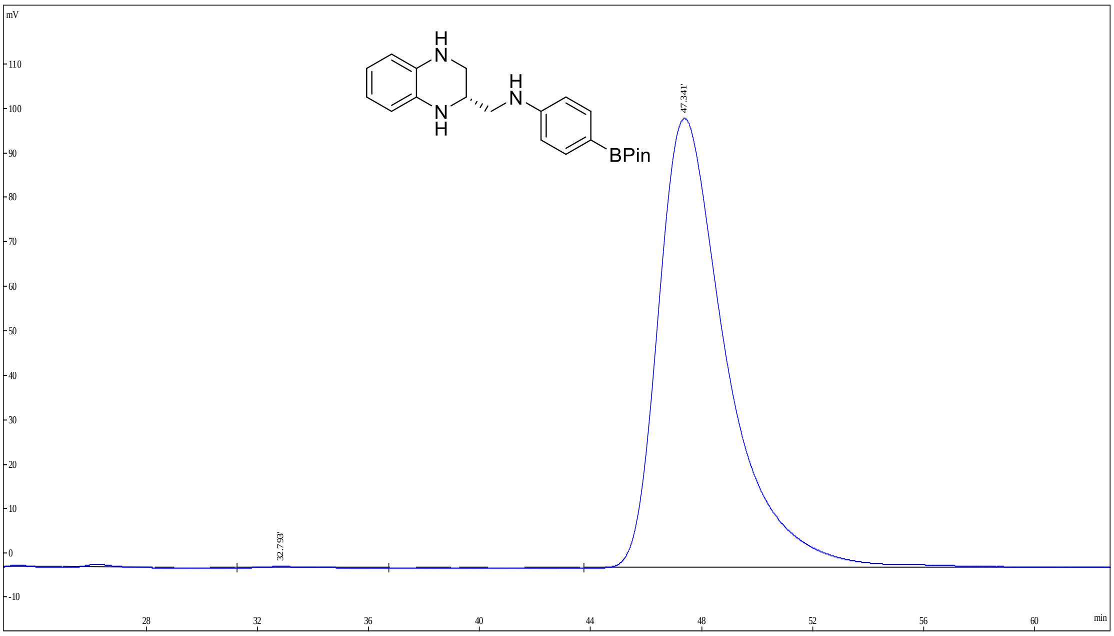
peak	Ret. Time	Area%	Area
1	50.046	50.71	22221195
2	71.992	49.29	21596002



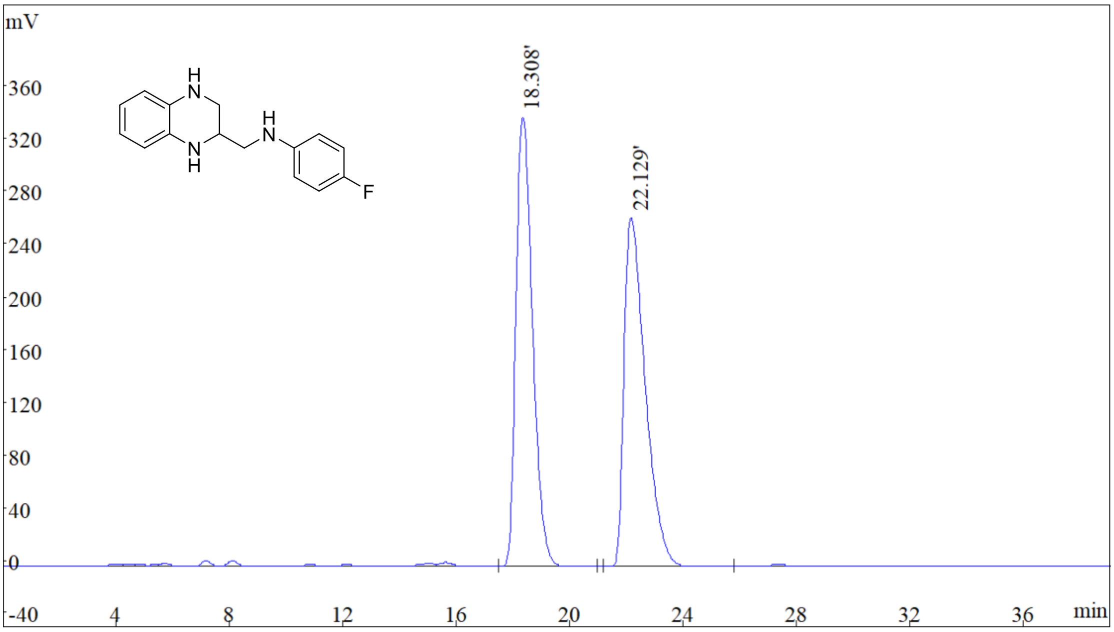
peak	Ret. Time	Area%	Area
1	52.990	2.22	513331
2	75.188	97.78	22601061



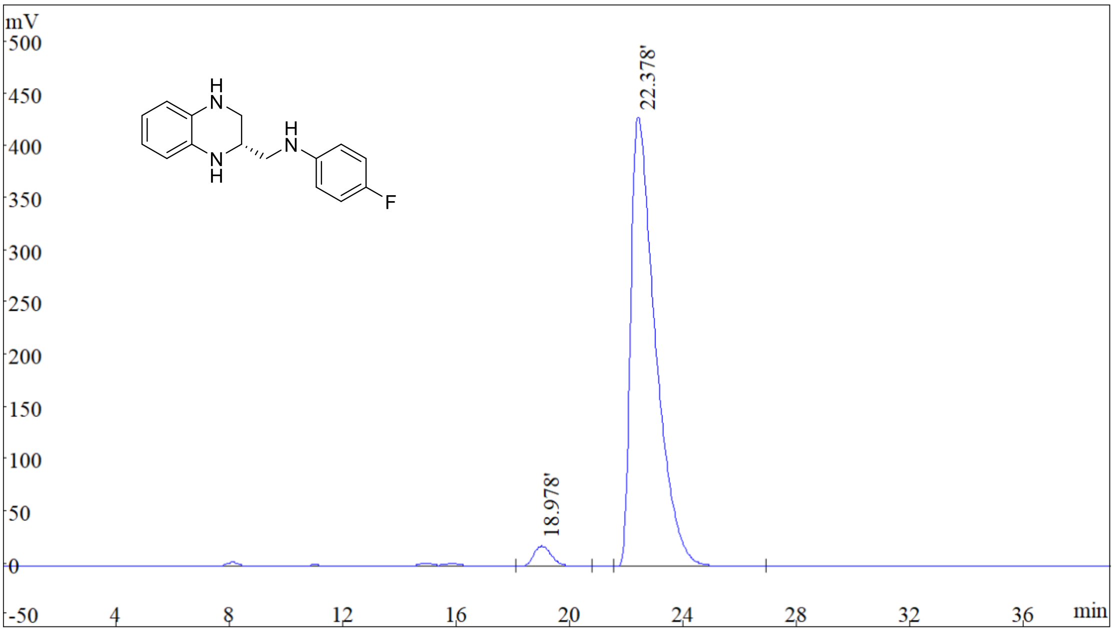
peak	Ret. Time	Area%	Area
1	32.340	50.56	11864045
2	46.966	49.44	11602403



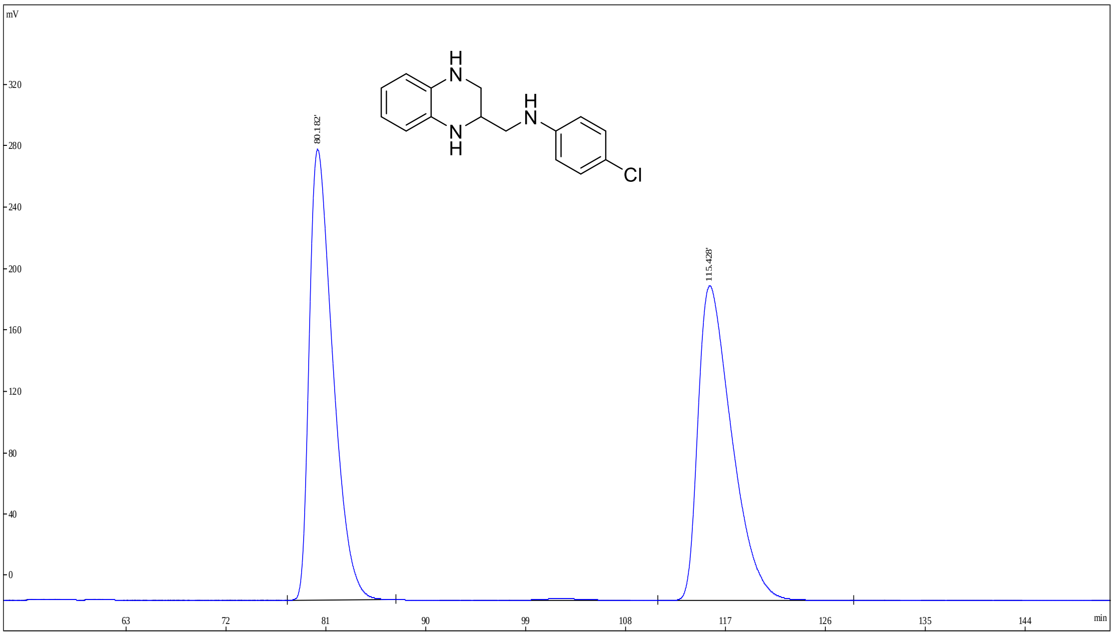
peak	Ret. Time	Area%	Area
1	32.793	0.22	39164
2	47.341	99.78	17326587



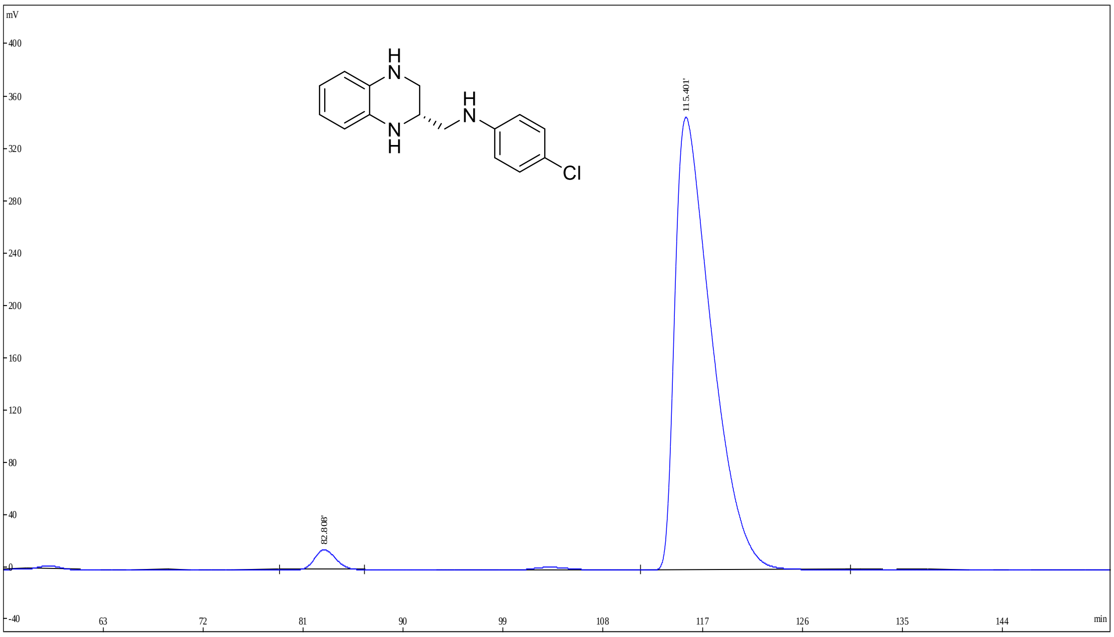
peak	Ret. Time	Area%	Area
1	18.308	49.89	13431256
2	22.129	50.11	13490176



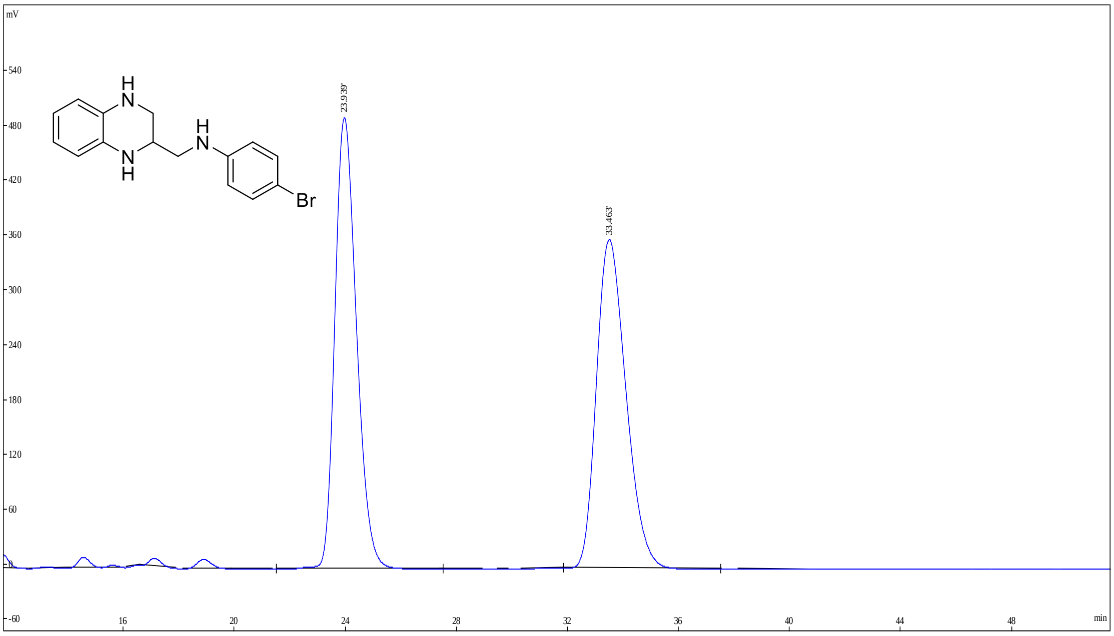
peak	Ret. Time	Area%	Area
1	18.978	3.61	957938
2	22.378	96.39	25602045



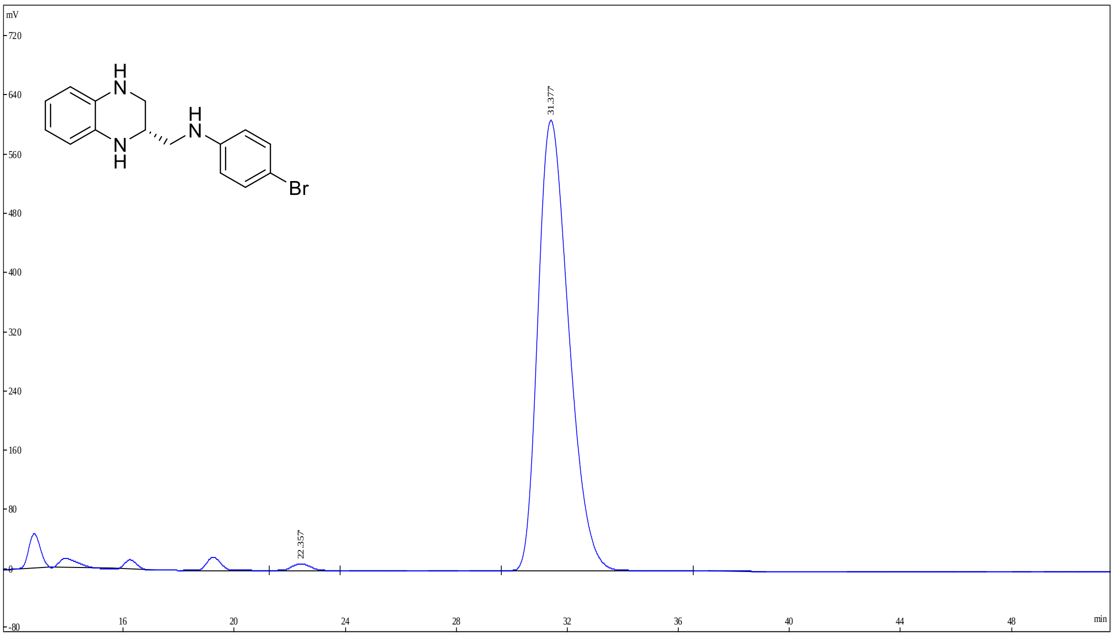
peak	Ret. Time	Area%	Area
1	80.182	50.09	43494454
2	115.428	49.91	43339994



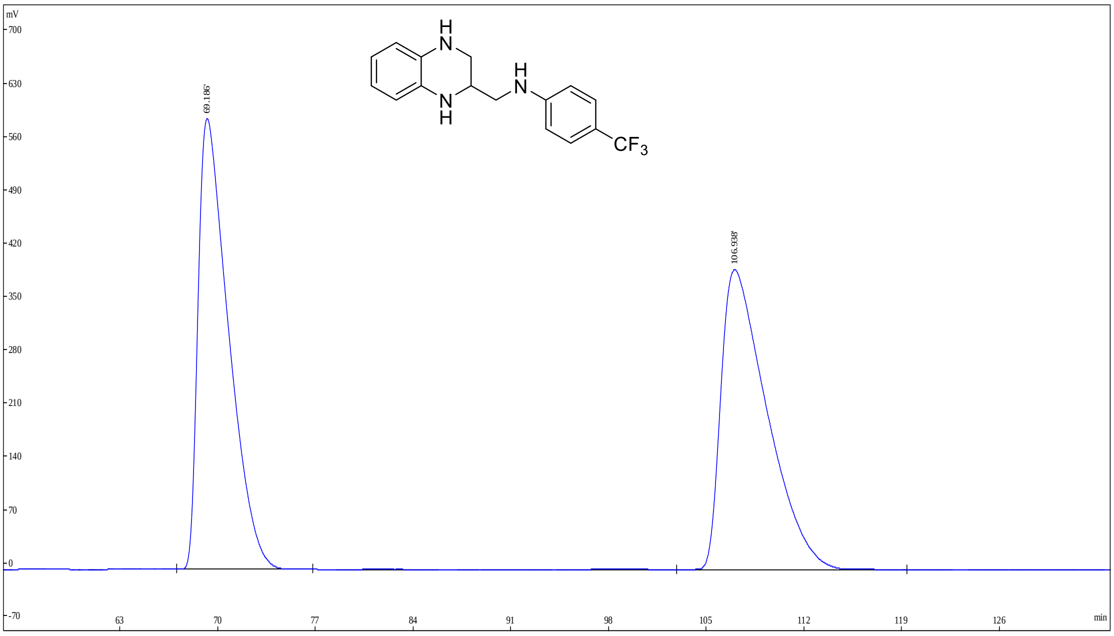
peak	Ret. Time	Area%	Area
1	82.808	2.54	2073665
2	115.401	97.45	79482086



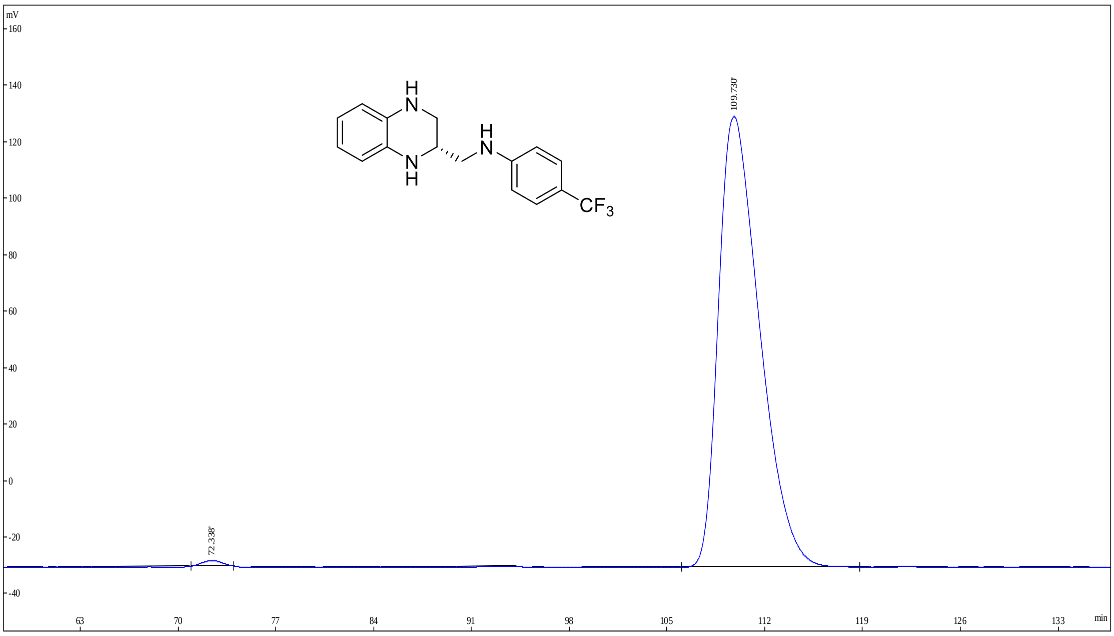
peak	Ret. Time	Area%	Area
1	23.939	50.13	26763835
2	33.463	49.87	26628296



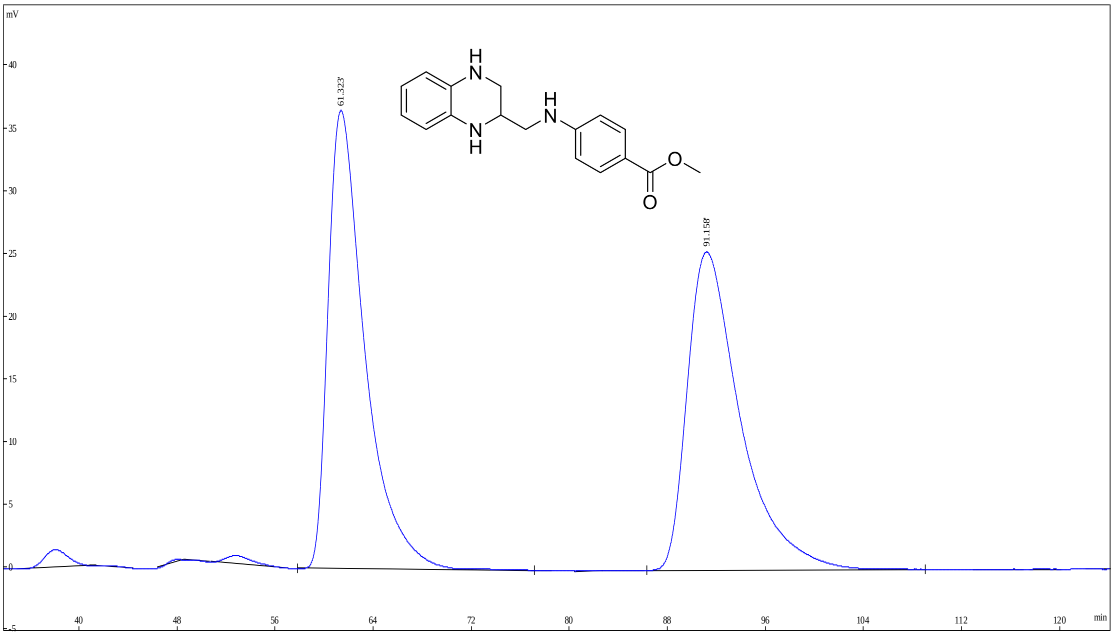
peak	Ret. Time	Area%	Area
1	22.357	1.17	560223
2	31.377	98.83	47261530



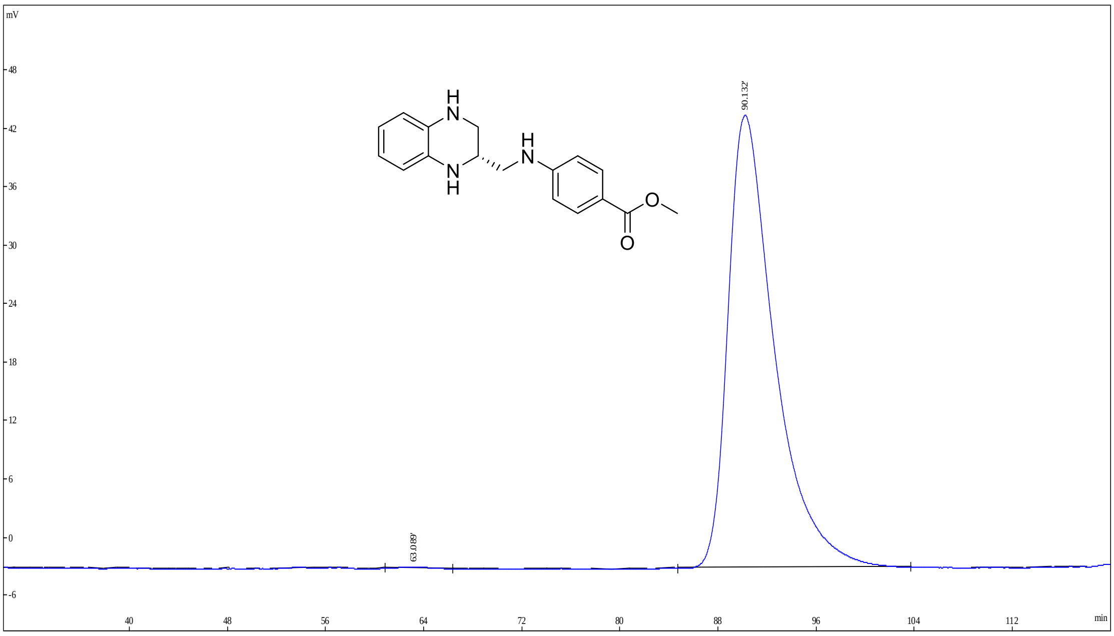
peak	Ret. Time	Area%	Area
1	69.186	49.76	90029293
2	106.938	50.24	90905766



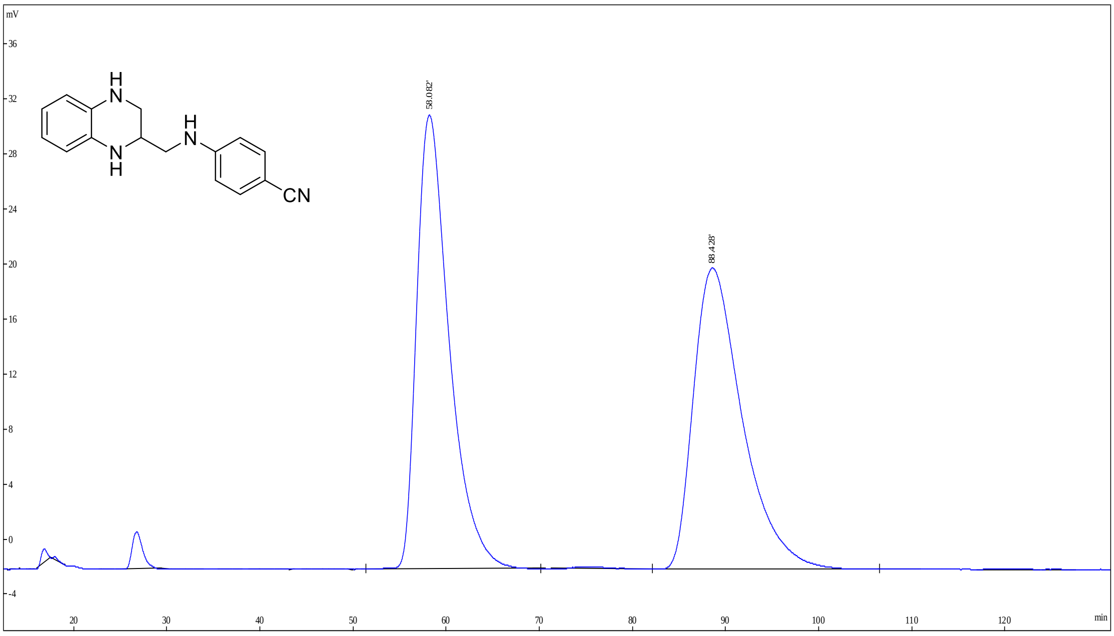
peak	Ret. Time	Area%	Area
1	72.338	0.60	196440
2	109.730	99.40	32667997



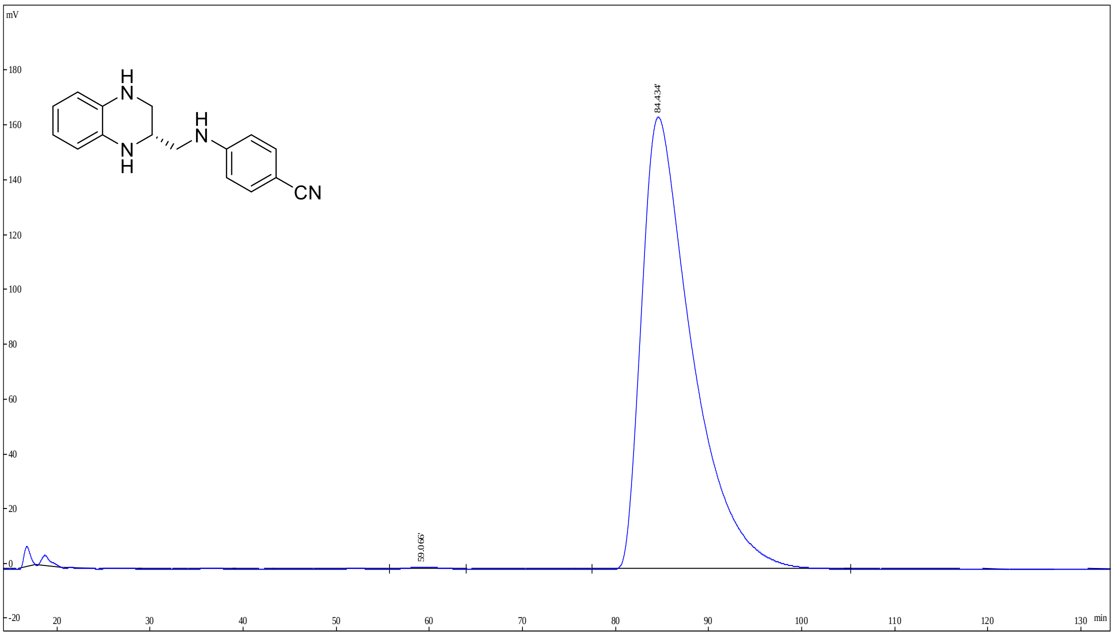
peak	Ret. Time	Area%	Area
1	61.323	49.79	7663944
2	91.158	50.21	7727725



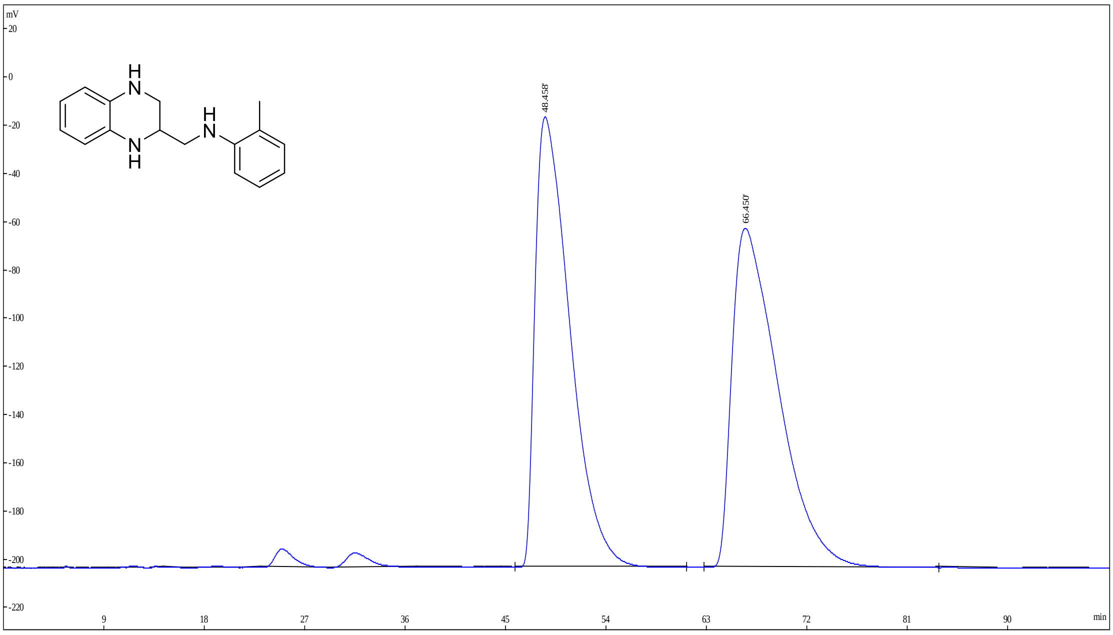
peak	Ret. Time	Area%	Area
1	63.089	0.27	33237
2	90.132	99.73	12269723



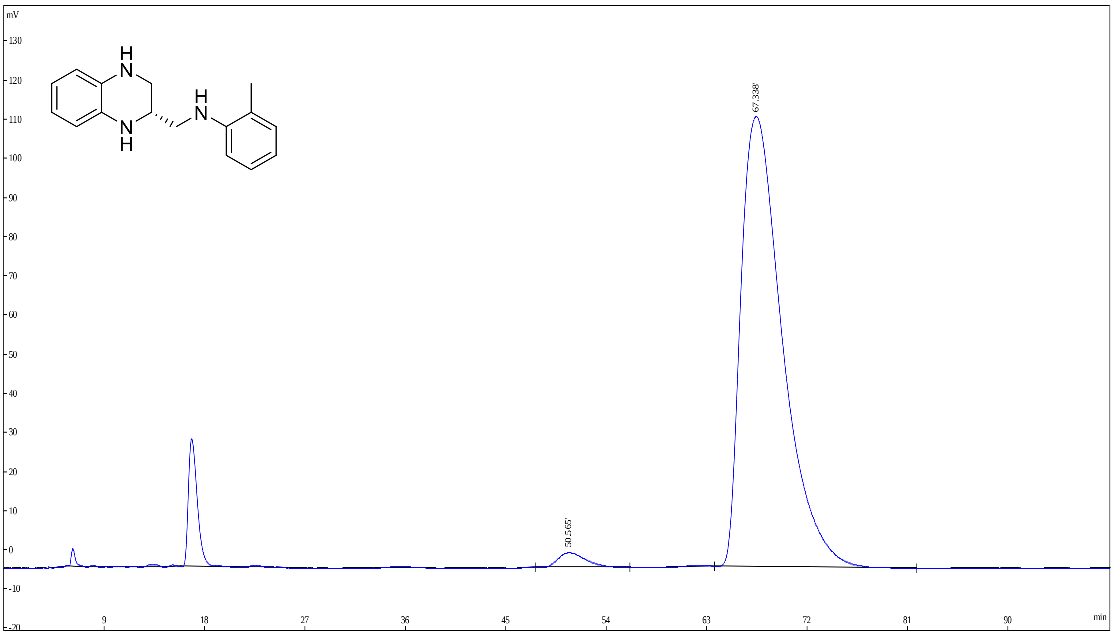
peak	Ret. Time	Area%	Area
1	58.082	50.08	8045229
2	88.428	49.92	8020582



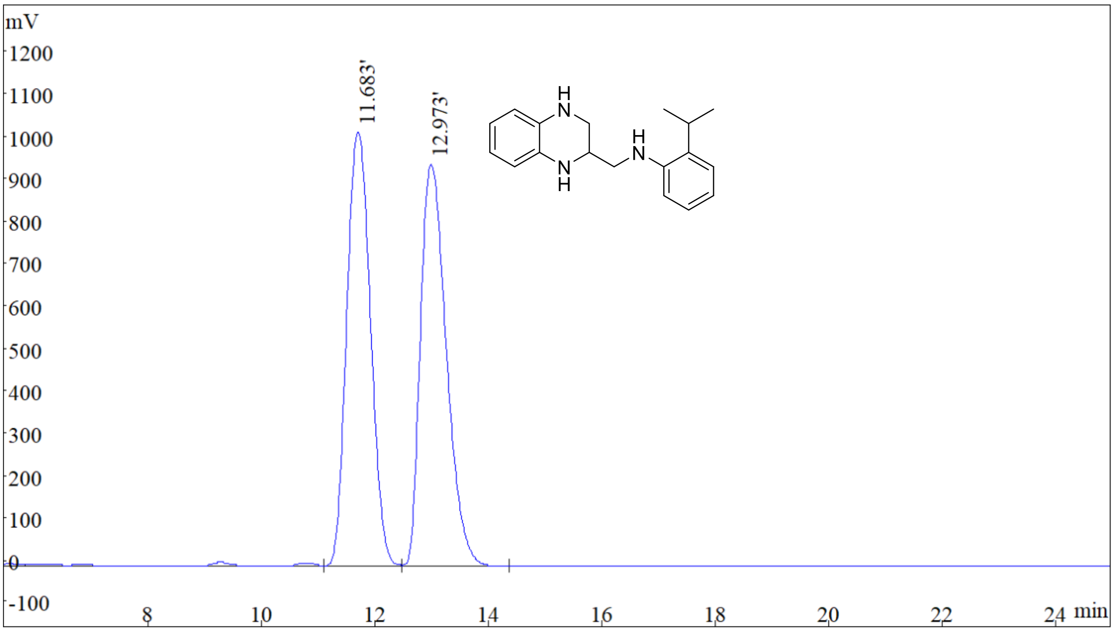
peak	Ret. Time	Area%	Area
1	59.066	0.30	182445
2	84.434	99.70	61910362



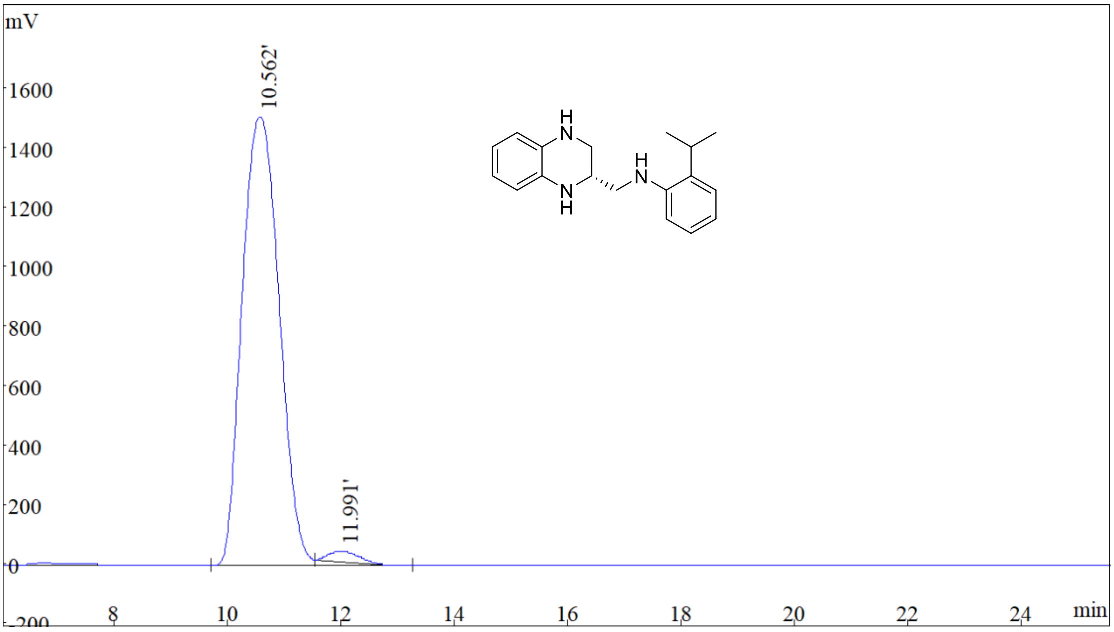
peak	Ret. Time	Area%	Area
1	48.458	49.95	40493251
2	66.450	50.05	40574954



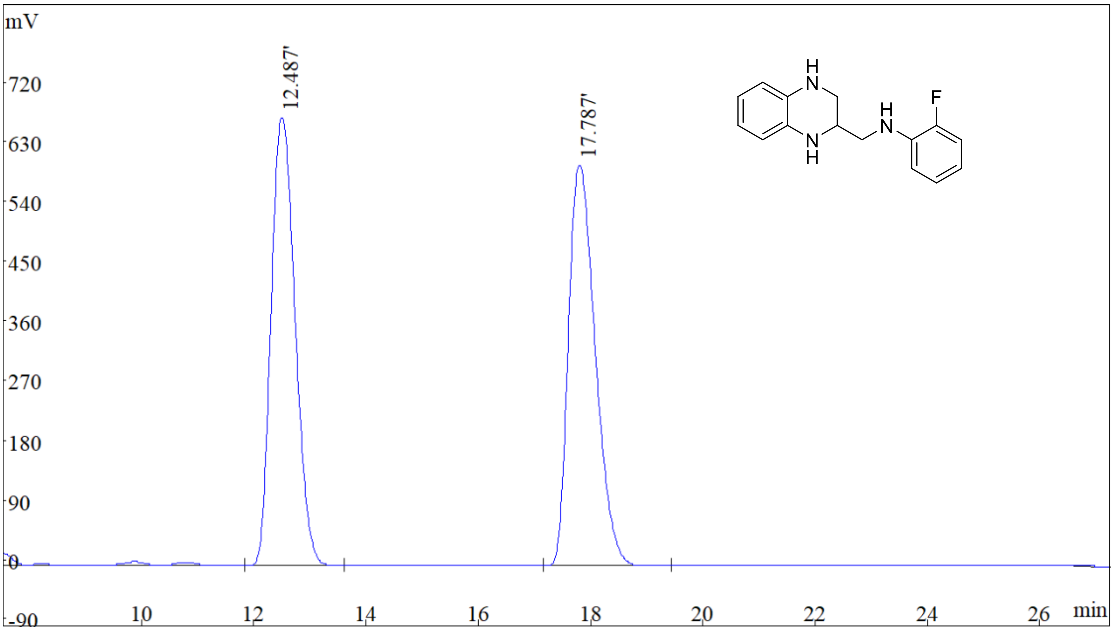
peak	Ret. Time	Area%	Area
1	50.565	2.35	712063
2	67.338	97.65	29612512



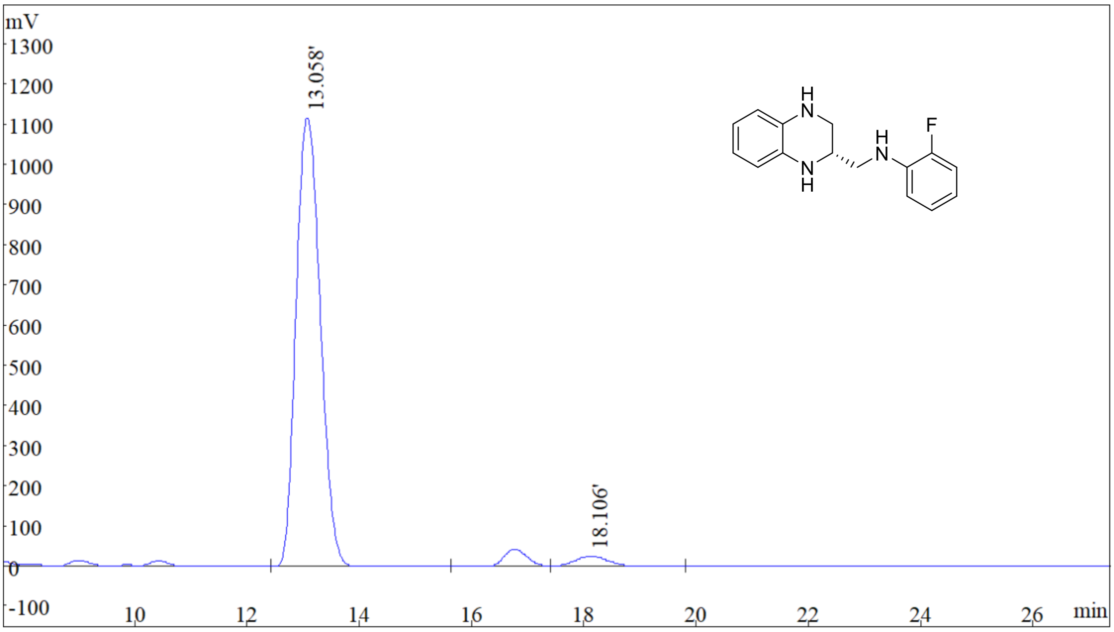
peak	Ret. Time	Area%	Area
1	11.683	49.64	29098573
2	12.973	50.36	29525741



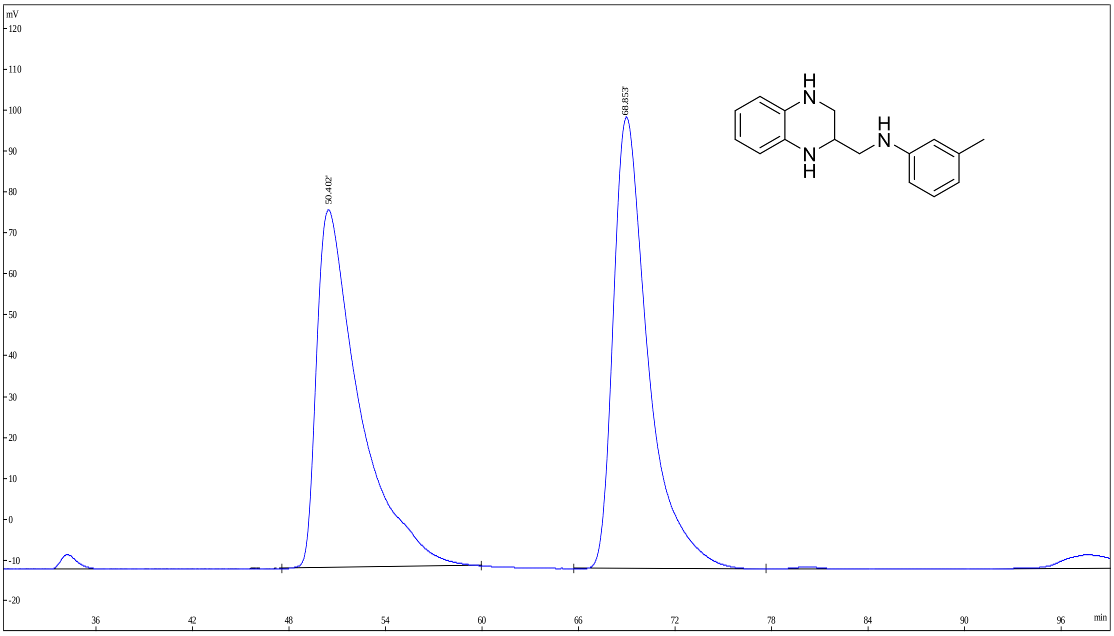
peak	Ret. Time	Area%	Area
1	10.562	98.11	68470899
2	11.991	1.89	1317610



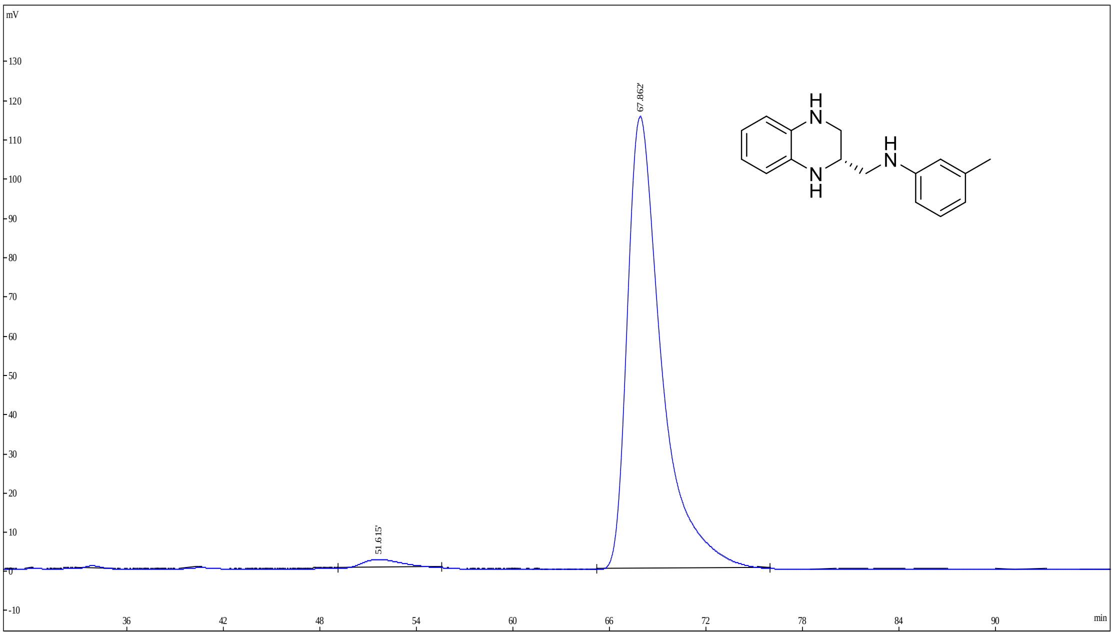
peak	Ret. Time	Area%	Area
1	12.487	49.97	19743235
2	17.787	50.03	19769798



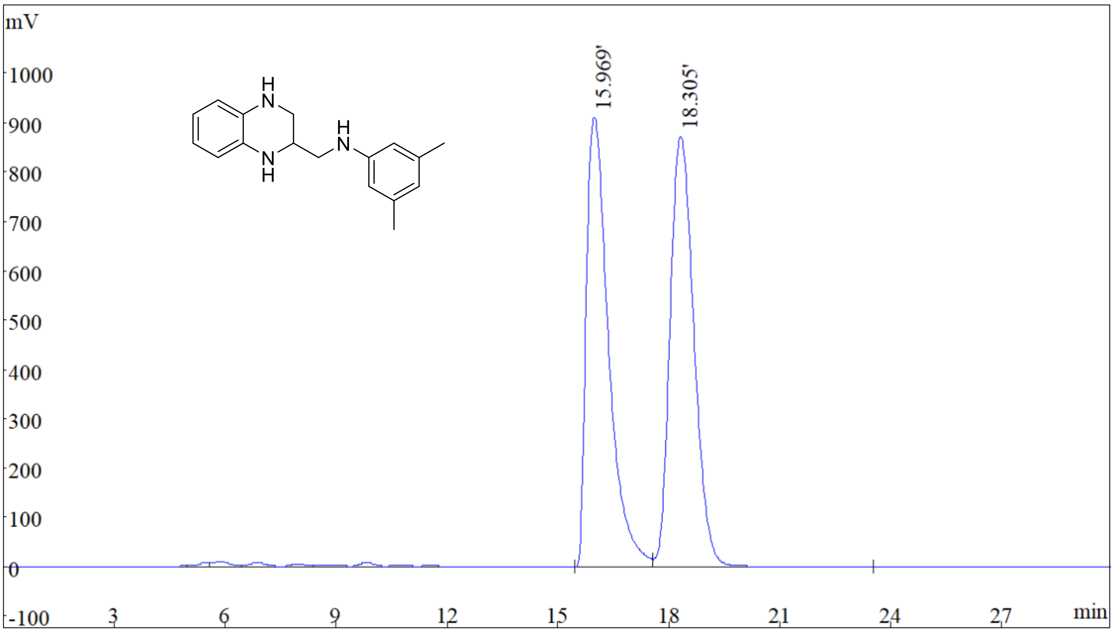
peak	Ret. Time	Area%	Area
1	13.058	96.29	32810906
2	18.106	3.71	1265367



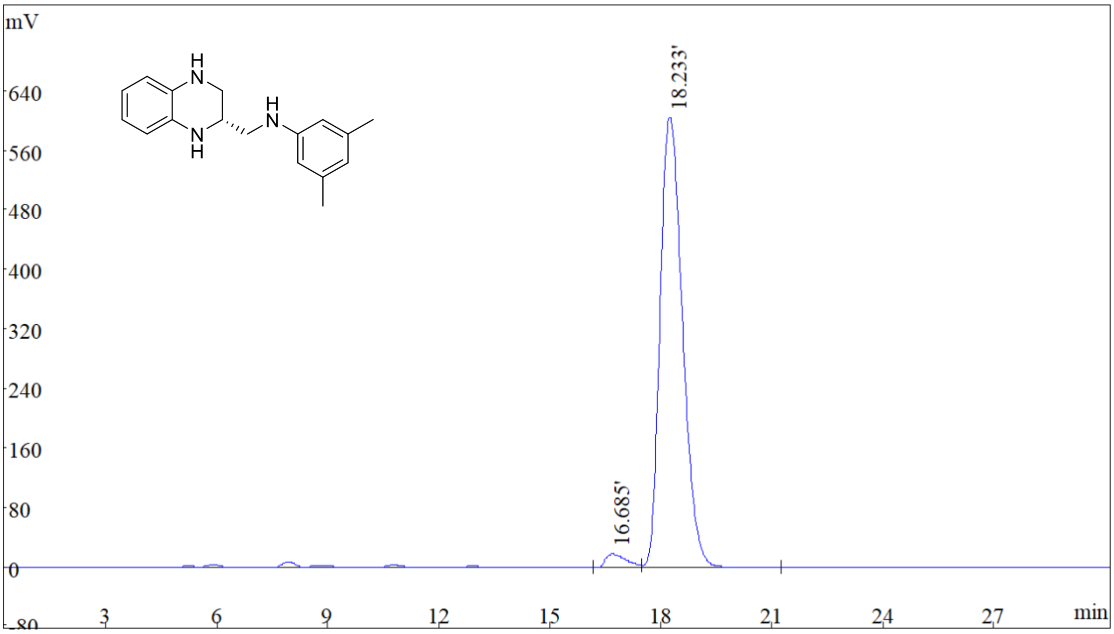
peak	Ret. Time	Area%	Area
1	50.402	49.32	16237766
2	68.853	50.68	16684450



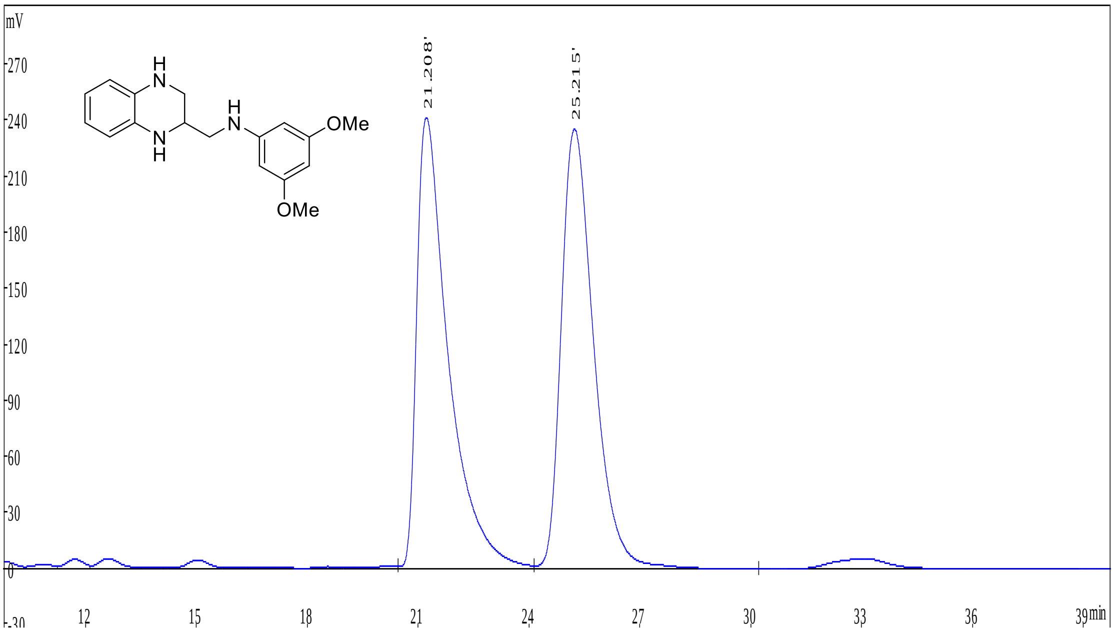
peak	Ret. Time	Area%	Area
1	51.615	2.26	395221
2	67.862	97.74	17105026



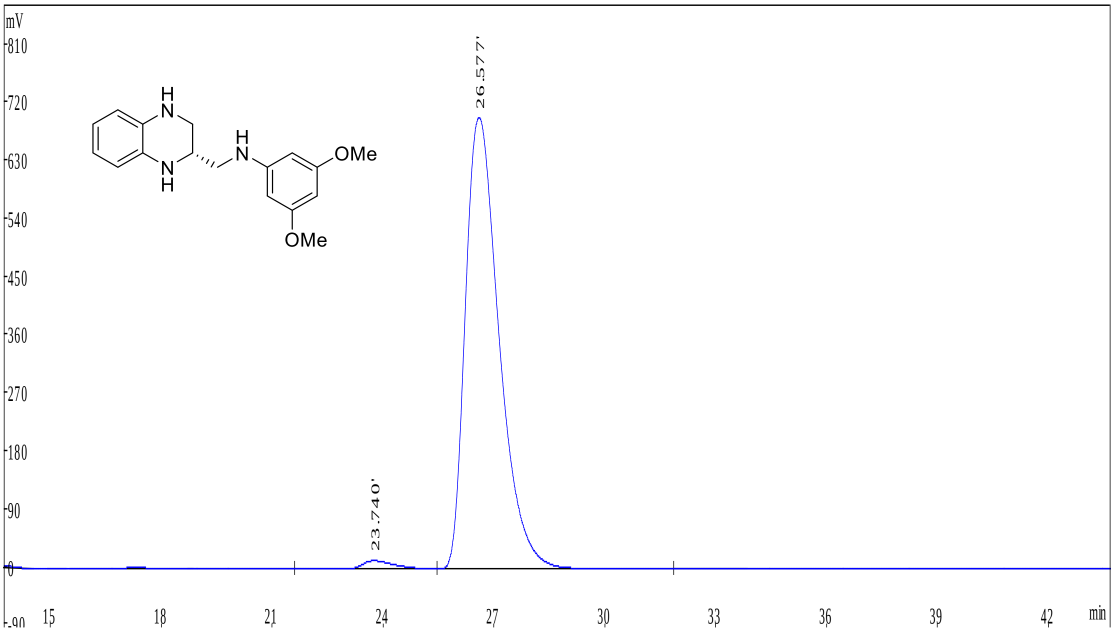
peak	Ret. Time	Area%	Area
1	15.969	49.11	37405632
2	18.305	50.89	38761741



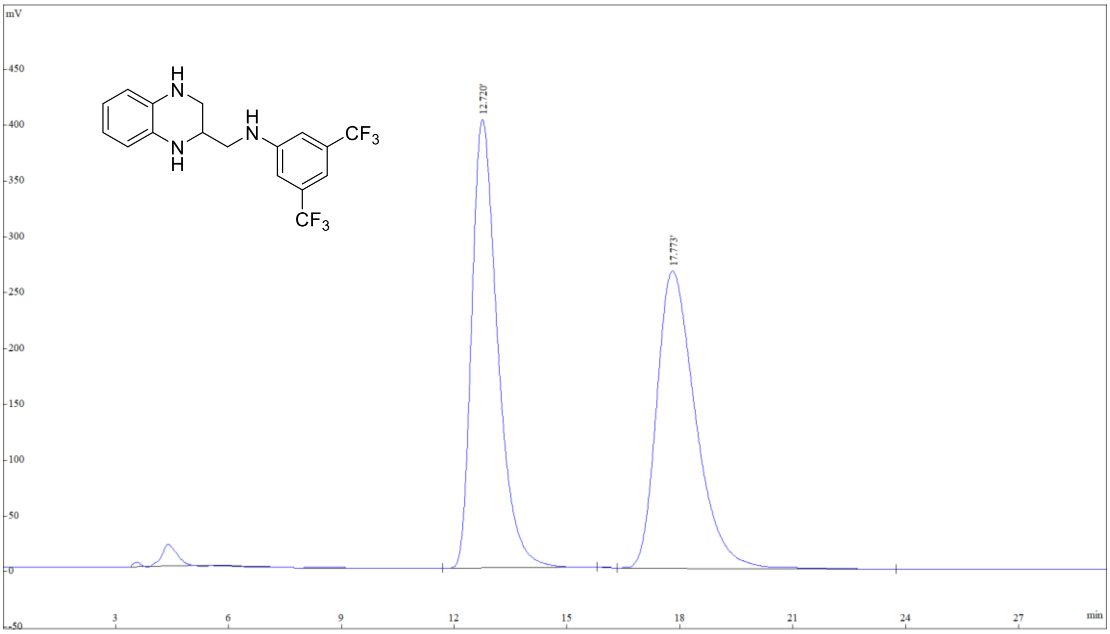
peak	Ret. Time	Area%	Area
1	16.685	2.95	760309
2	18.233	97.05	25039357



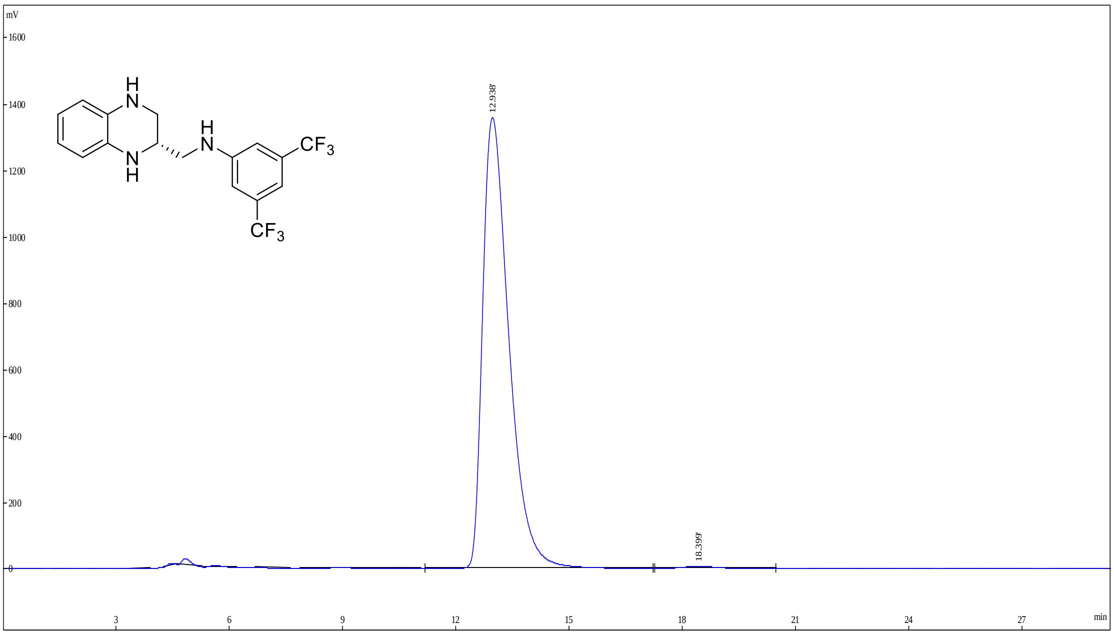
peak	Ret. Time	Area%	Area
1	21.208	49.99	14127504
2	25.215	50.01	14135251



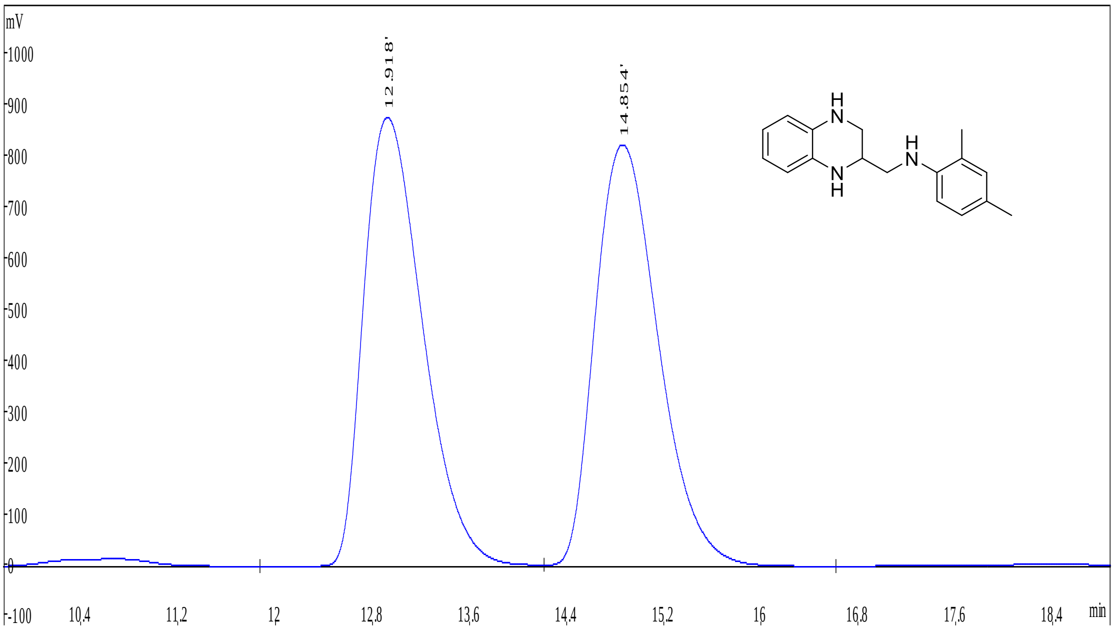
peak	Ret. Time	Area%	Area
1	23.740	2.12	952778
2	26.577	97.88	43948483



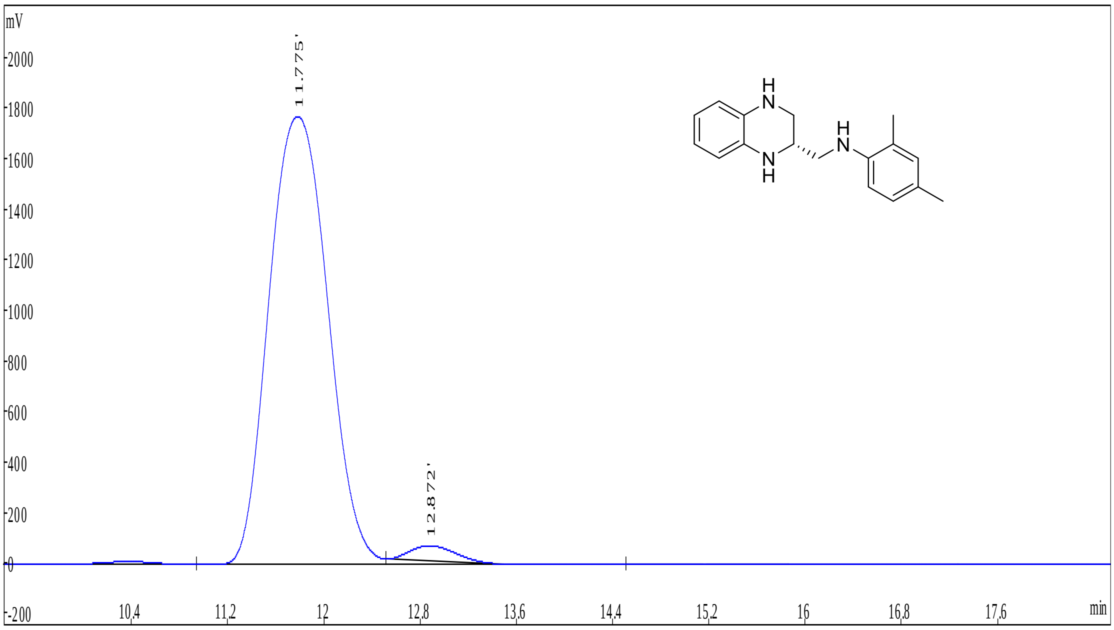
peak	Ret. Time	Area%	Area
1	12. 720	50. 21	19354056
2	17. 773	49. 79	19191038



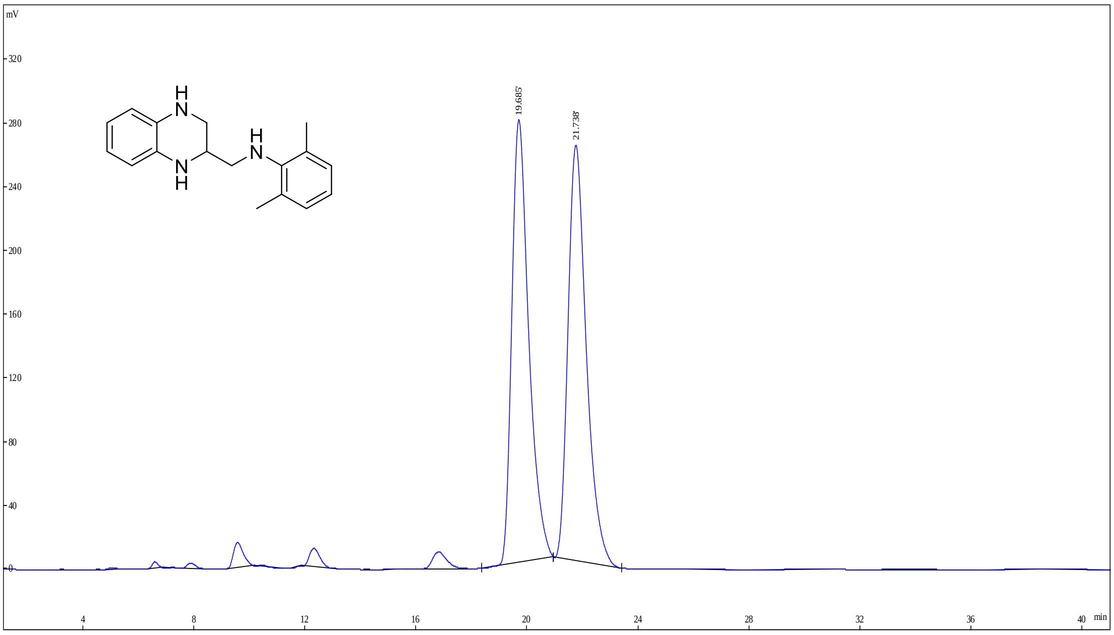
peak	Ret. Time	Area%	Area
1	12. 938	99. 32	65617075
2	18. 399	0. 68	450055



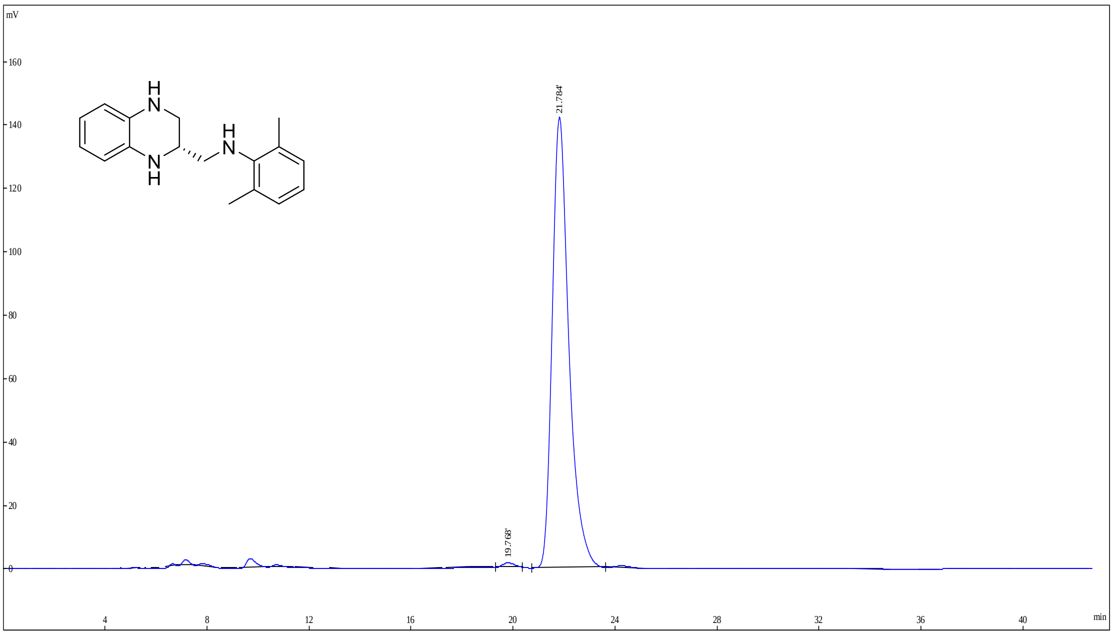
peak	Ret. Time	Area%	Area
1	12.918	49.83	29736230
2	14.854	50.17	29941536



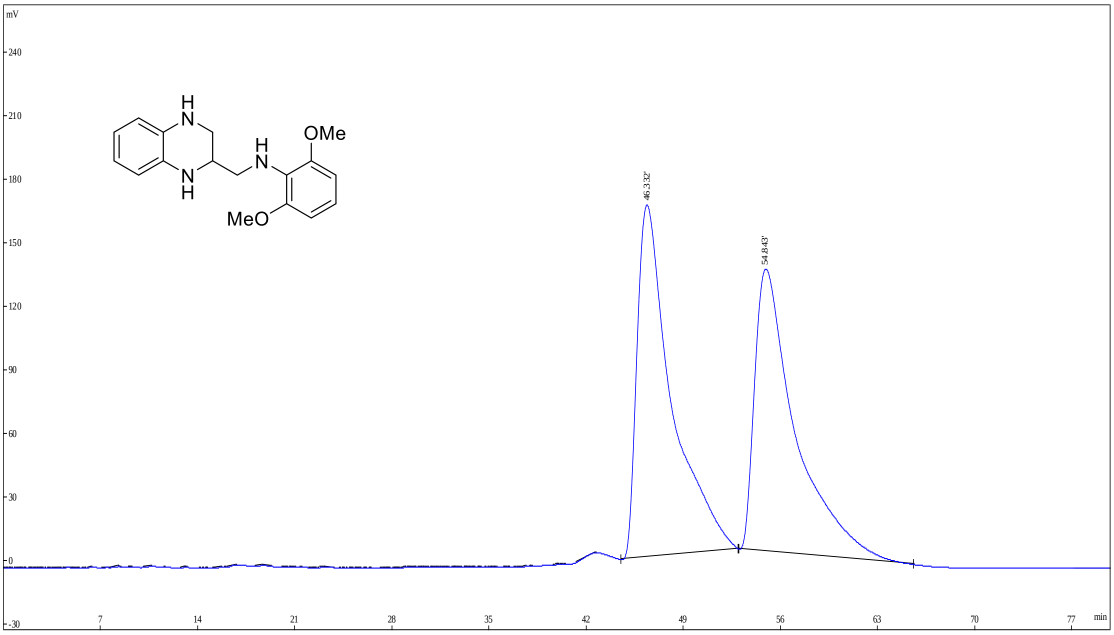
peak	Ret. Time	Area%	Area
1	11.775	97.48	60753984
2	12.872	2.52	1570750



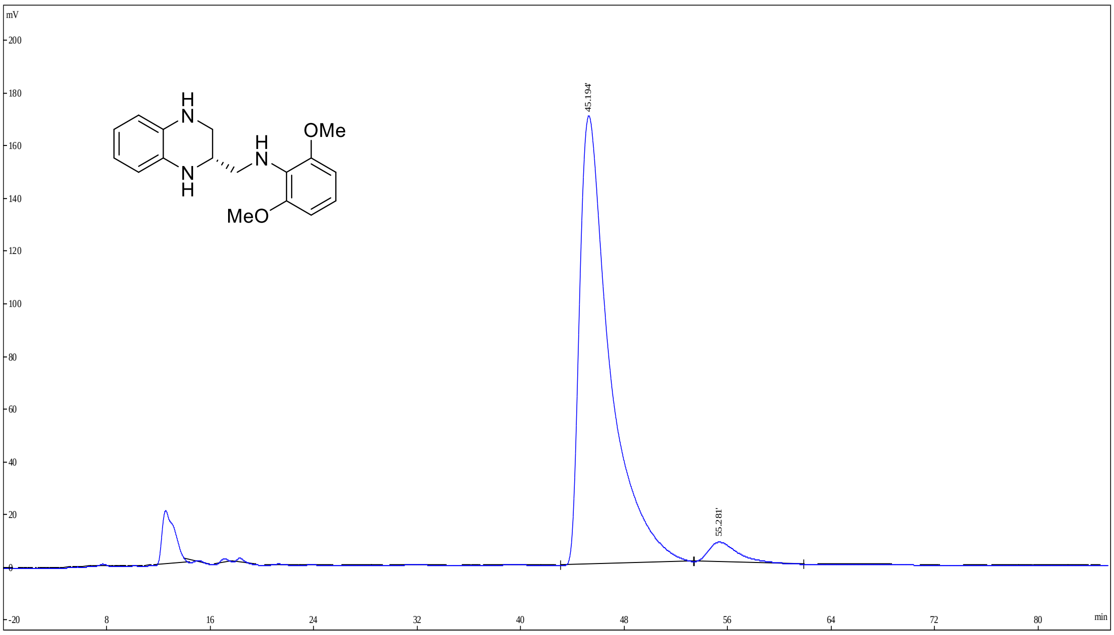
peak	Ret. Time	Area%	Area
1	19.685	49.68	11823673
2	21.738	50.32	11975219



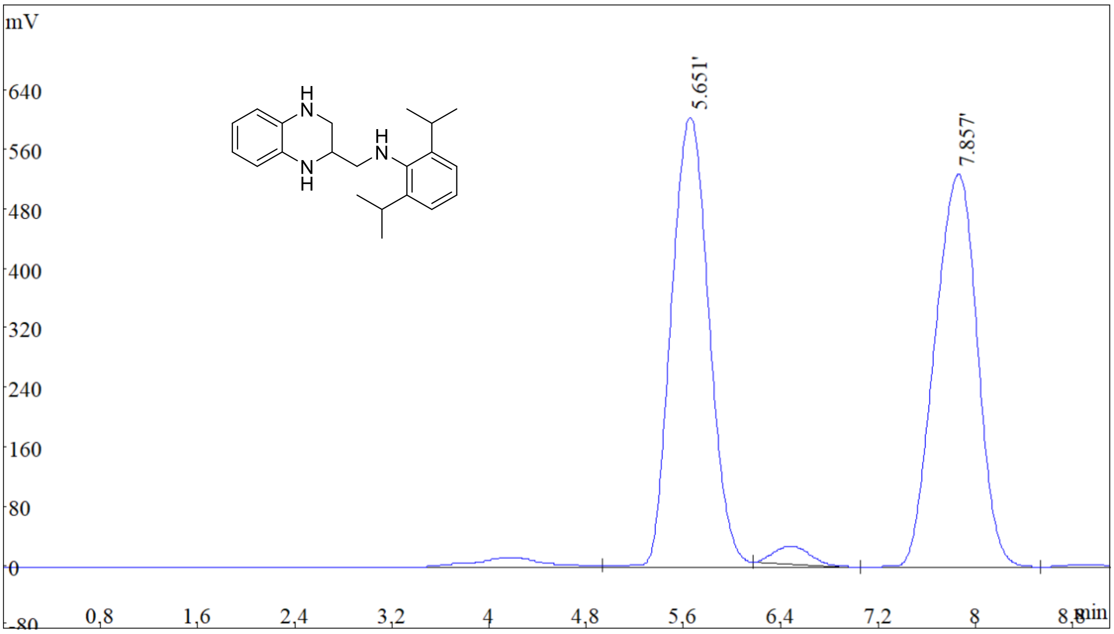
peak	Ret. Time	Area%	Area
1	19.768	0.73	47927
2	21.784	99.27	6471942



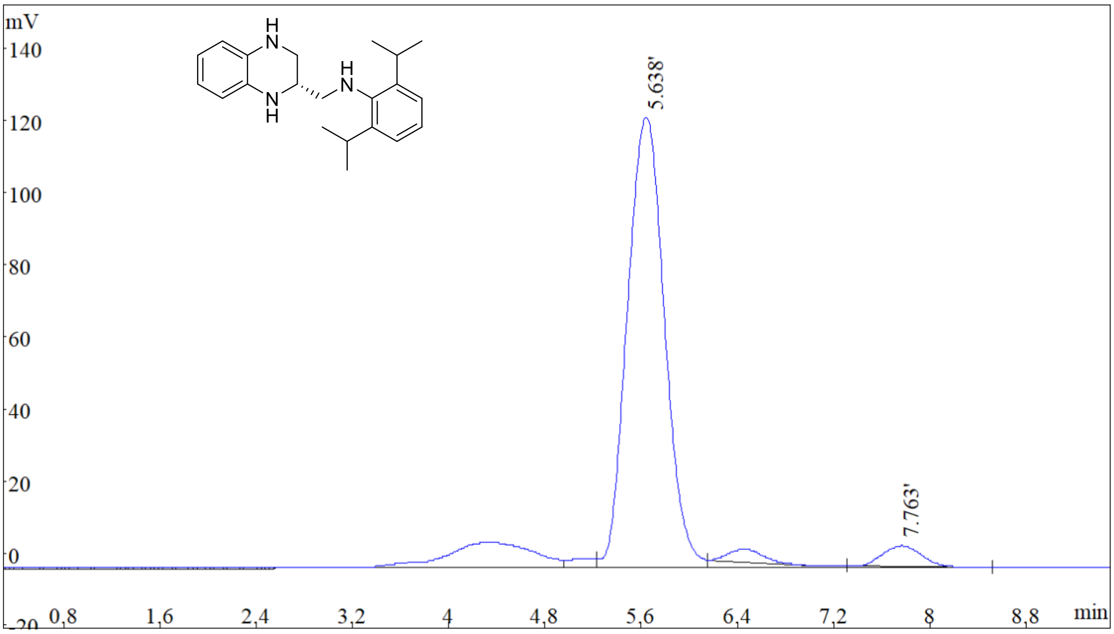
peak	Ret. Time	Area%	Area
1	46.332	51.34	28653834
2	54.843	48.66	27159917



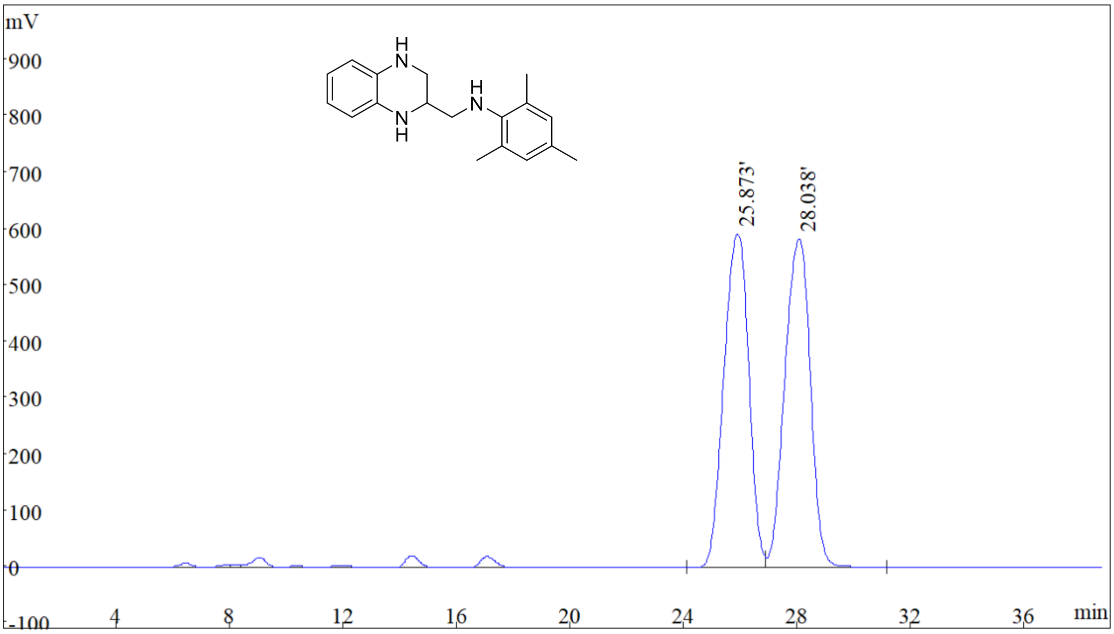
peak	Ret. Time	Area%	Area
1	45.194	95.85	27654784
2	55.281	4.15	1199281



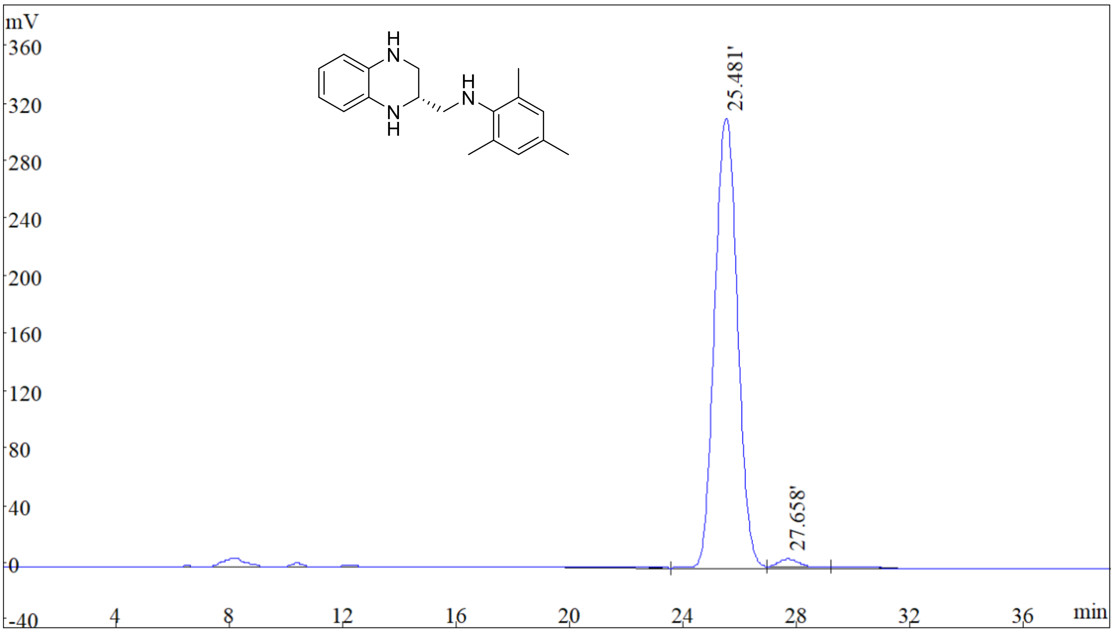
peak	Ret. Time	Area%	Area
1	5.651	50.57	13270950
2	7.857	49.43	12971438



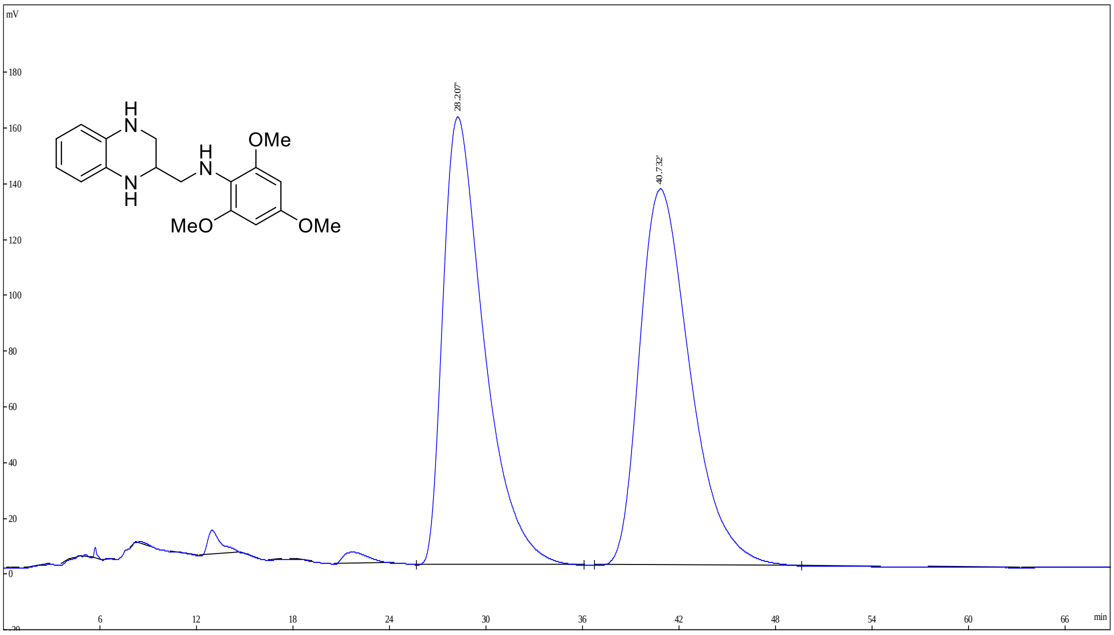
peak	Ret. Time	Area%	Area
1	5.638	95.37	2746539
2	7.763	4.63	133476



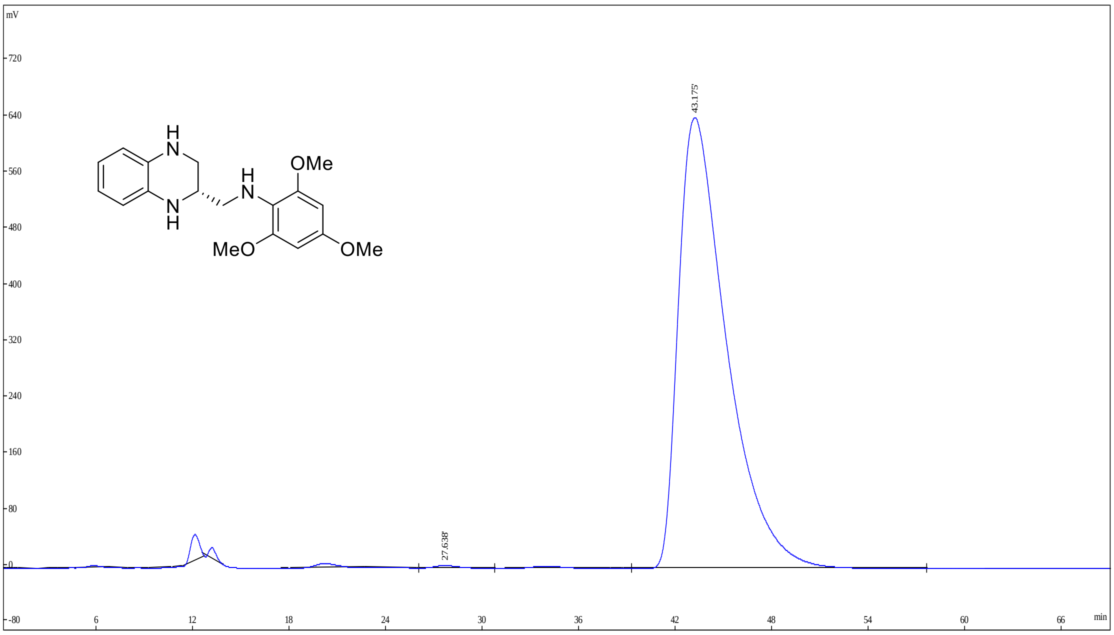
peak	Ret. Time	Area%	Area
1	25.873	49.69	35471120
2	28.038	50.31	35919875



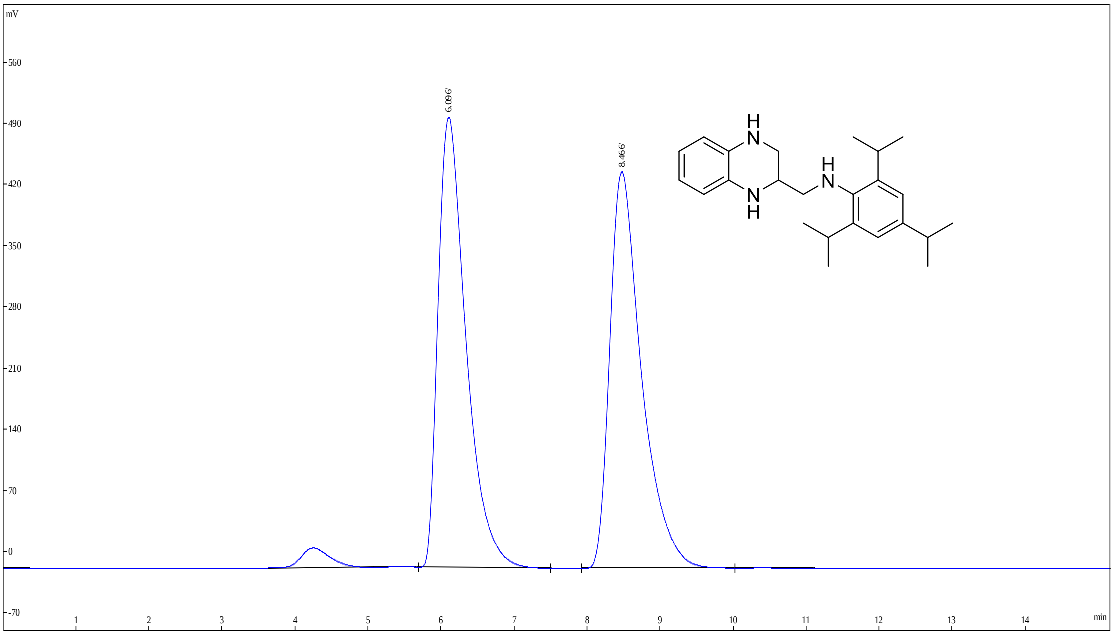
peak	Ret. Time	Area%	Area
1	25.481	98.40	17438259
2	27.658	1.60	284103



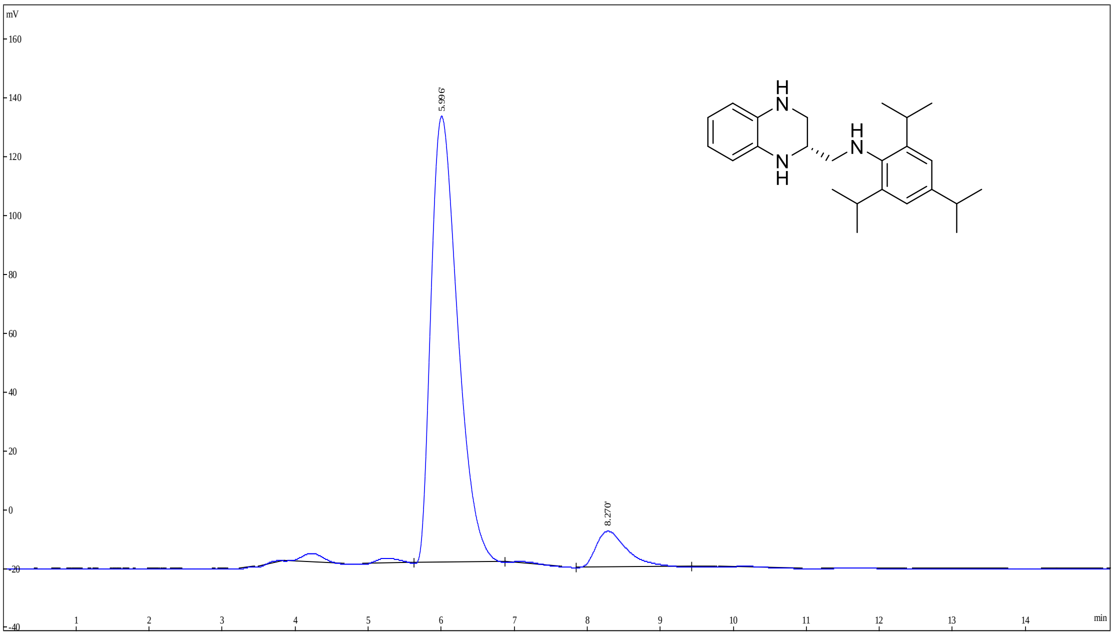
peak	Ret. Time	Area%	Area
1	28.207	49.02	28363296
2	40.732	50.98	29499005



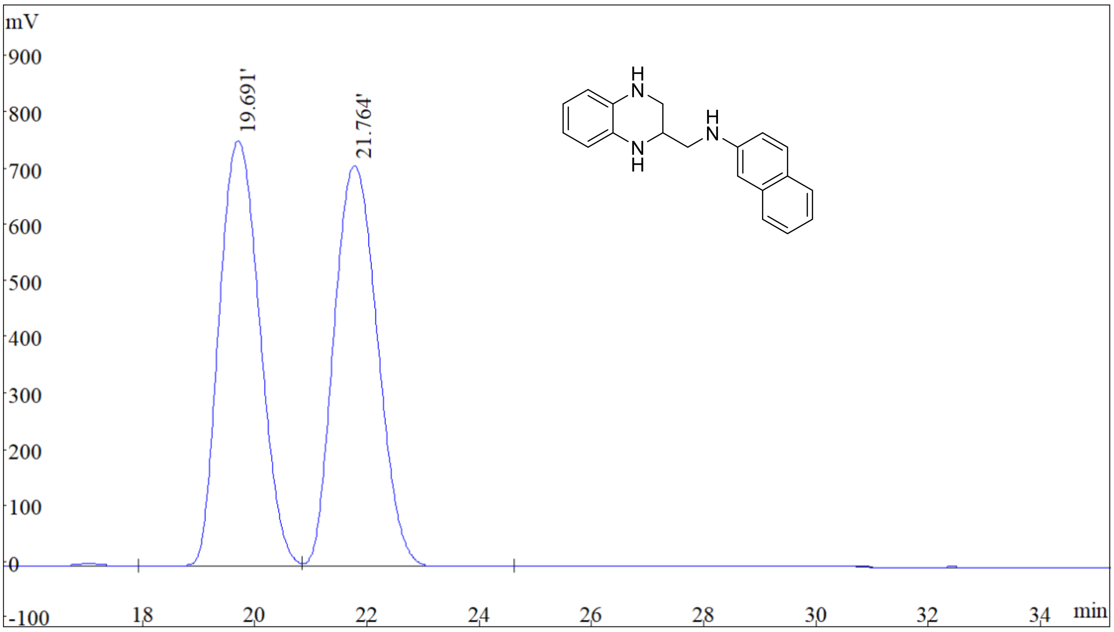
peak	Ret. Time	Area%	Area
1	27.638	0.31	423869
2	43.175	99.69	133705024



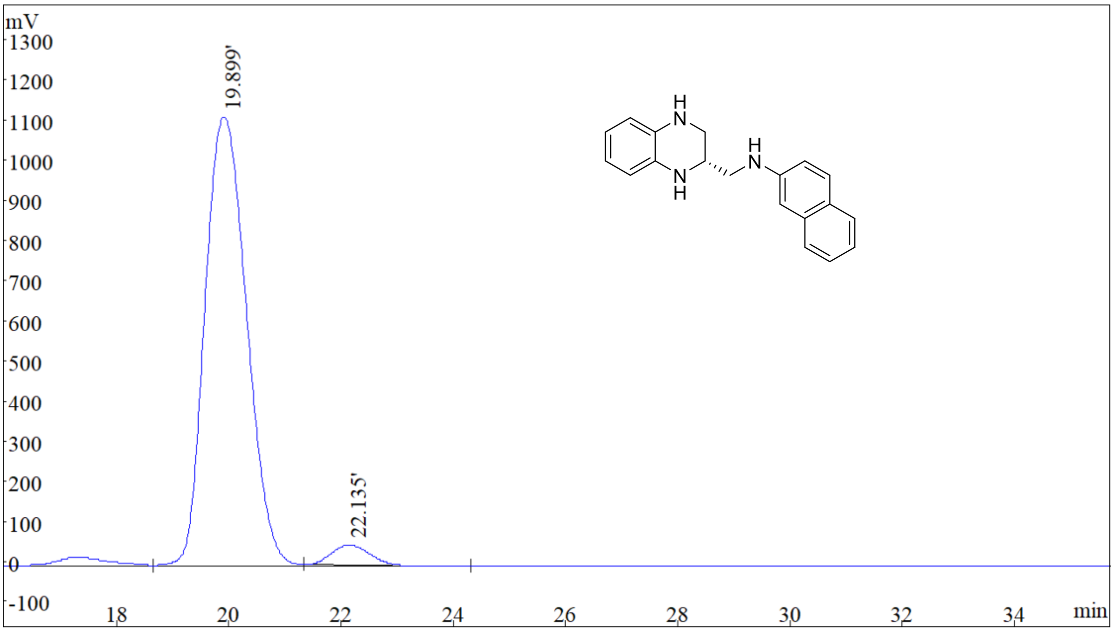
peak	Ret. Time	Area%	Area
1	6.096	50.02	13714690
2	8.466	49.98	13704176



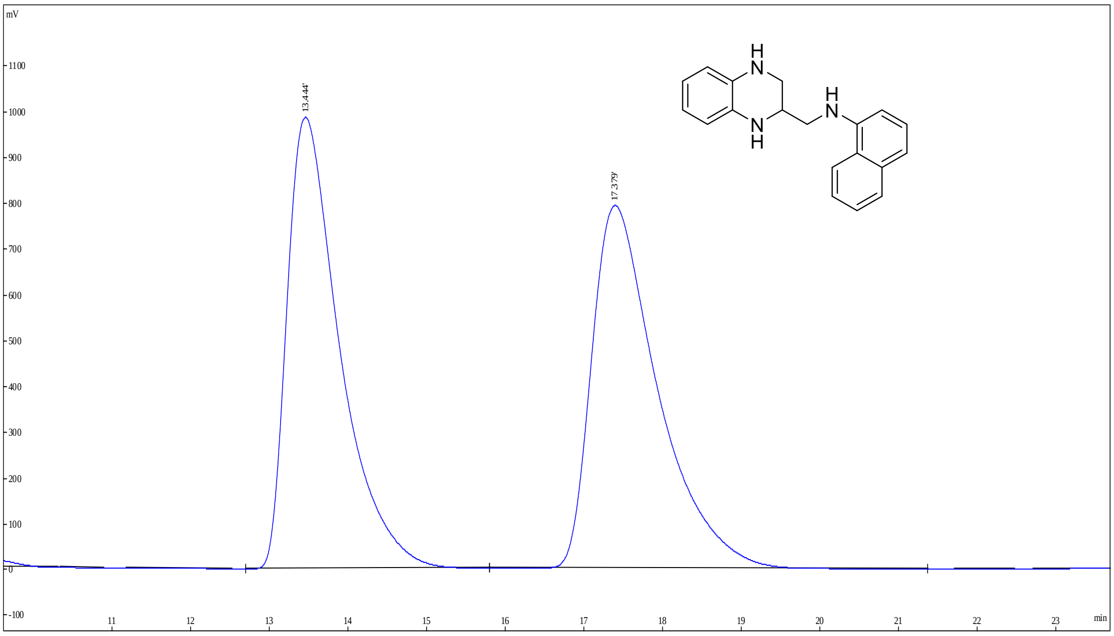
peak	Ret. Time	Area%	Area
1	5.996	91.19	3858241
2	8.270	8.81	372824



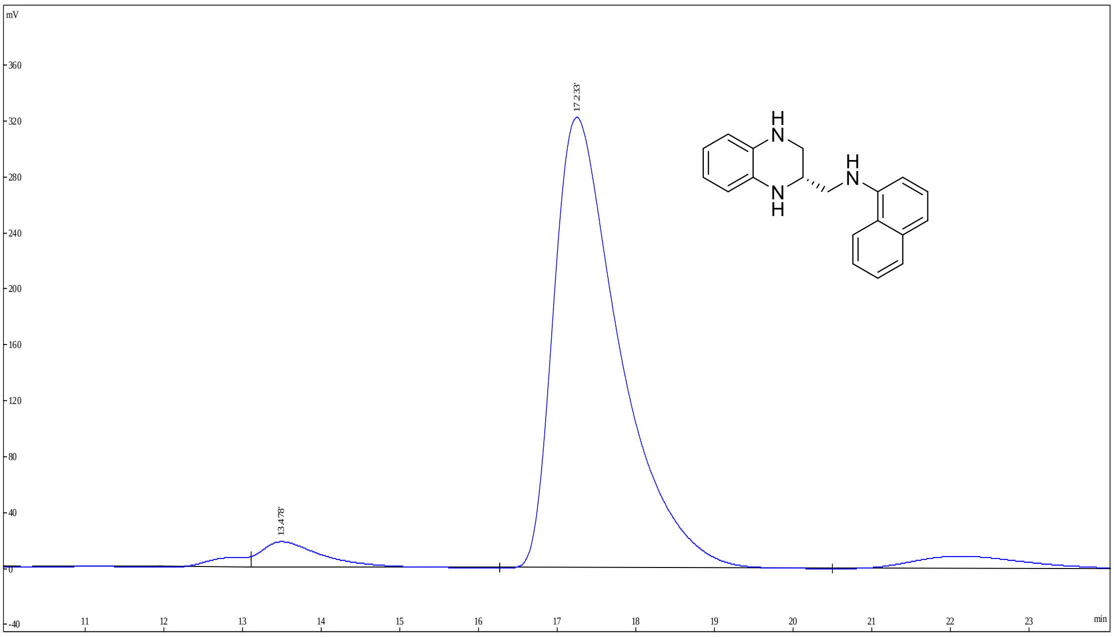
peak	Ret. Time	Area%	Area
1	19.691	49.70	37788051
2	21.764	50.30	38240522



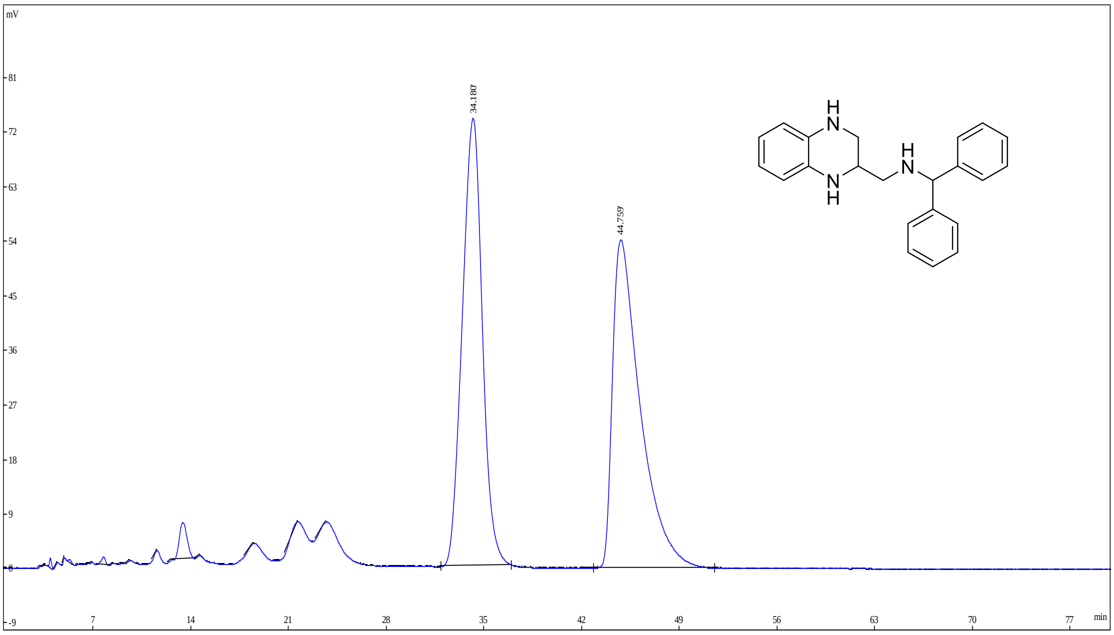
peak	Ret. Time	Area%	Area
1	19.899	96.01	57513184
2	22.135	3.99	2387447



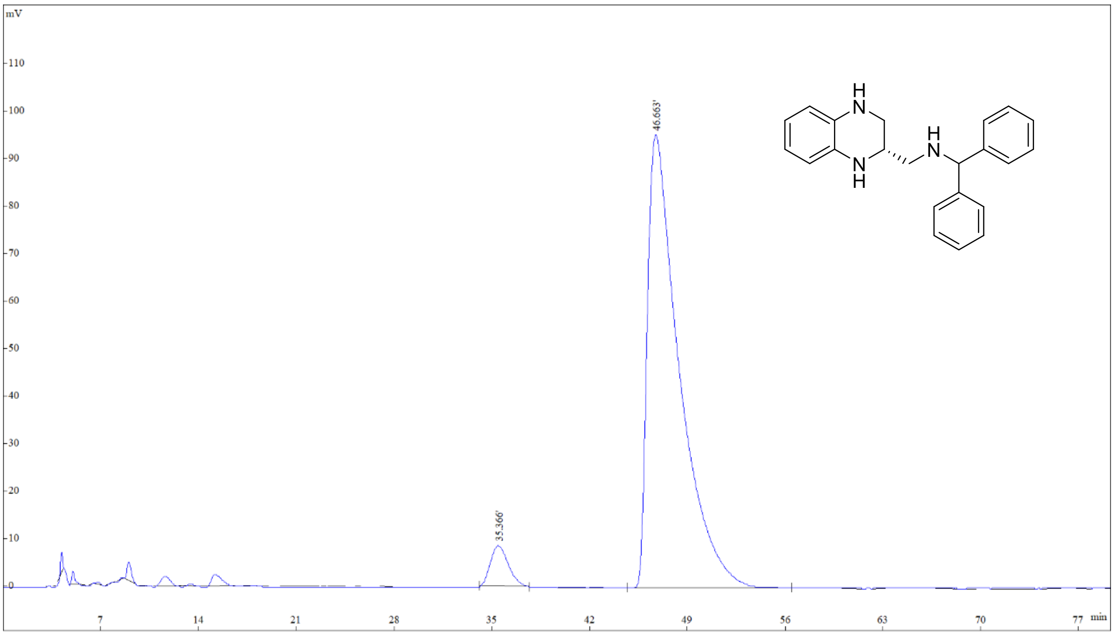
peak	Ret. Time	Area%	Area
1	13.444	49.64	45613546
2	17.379	50.36	46275738



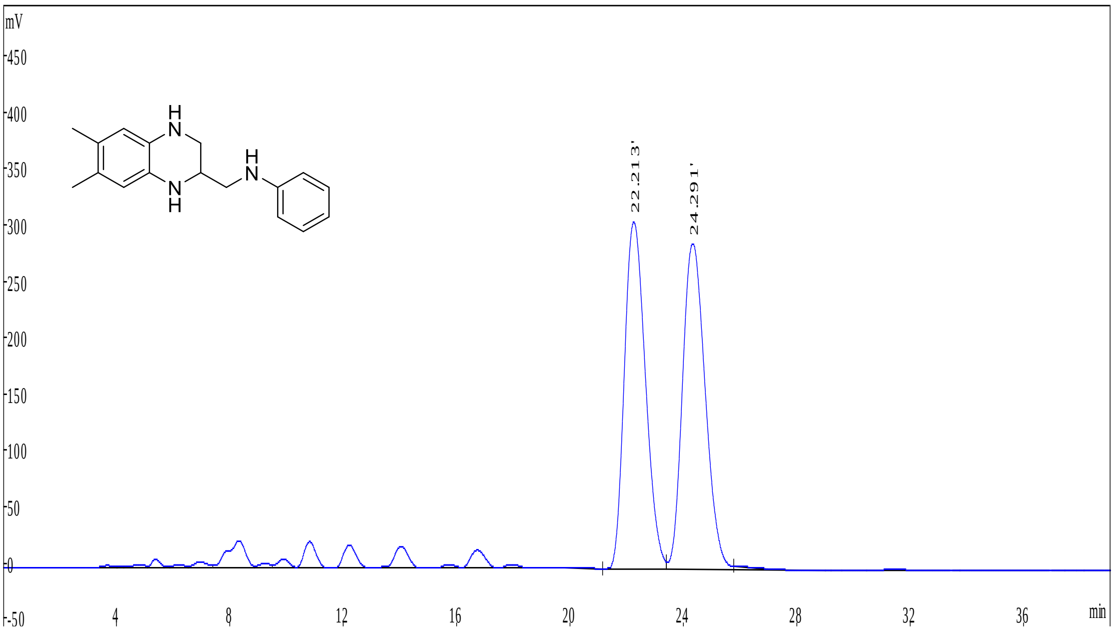
peak	Ret. Time	Area%	Area
1	13.478	5.11	1010773
2	17.233	94.89	18744413



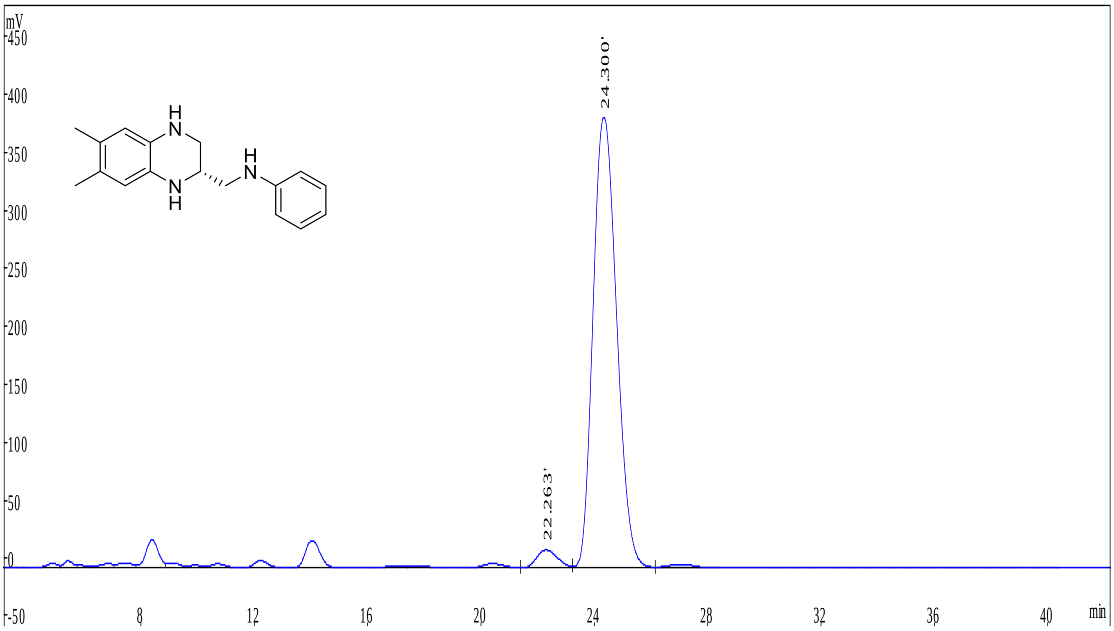
peak	Ret. Time	Area%	Area
1	34.180	49.67	7356882
2	44.759	50.33	7454782



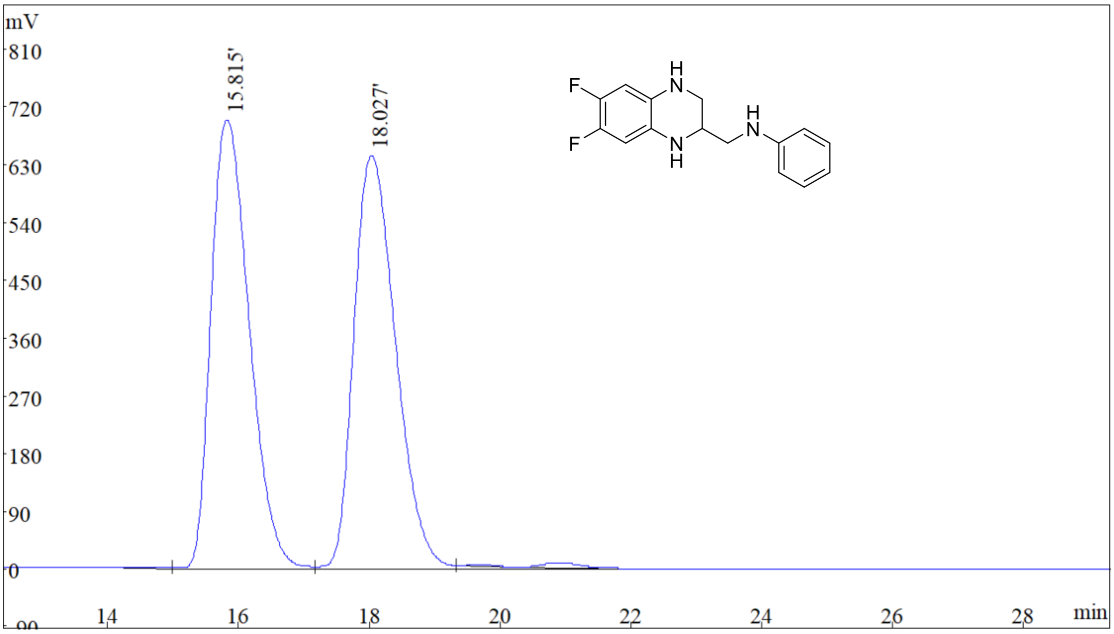
peak	Ret. Time	Area%	Area
1	35.366	4.882	780086
2	46.663	95.12	15199670



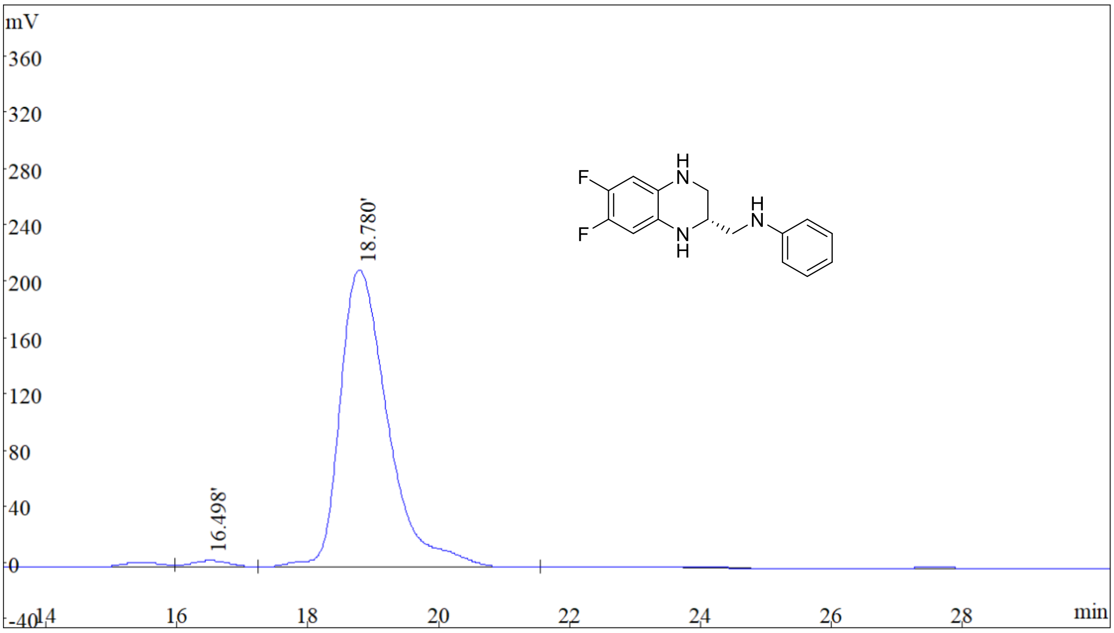
peak	Ret. Time	Area%	Area
1	18.398	48.79	23194963
2	19.768	51.21	24346309



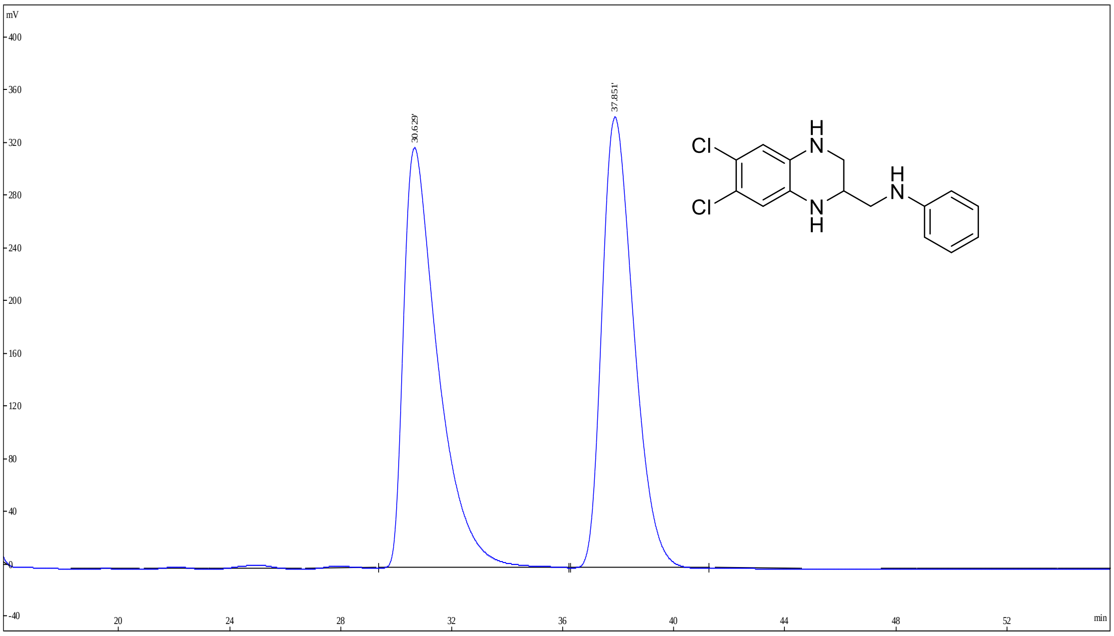
peak	Ret. Time	Area%	Area
1	22.263	3.79	875940
2	24.300	96.21	22207747



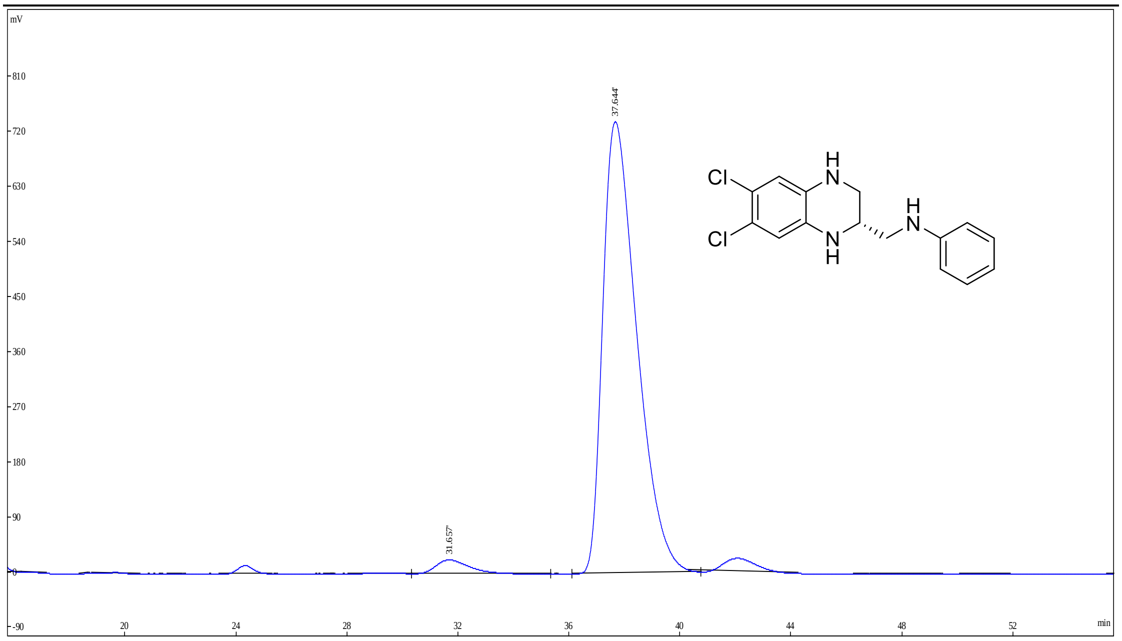
peak	Ret. Time	Area%	Area
1	15.815	49.39	28080246
2	18.027	50.61	28772870



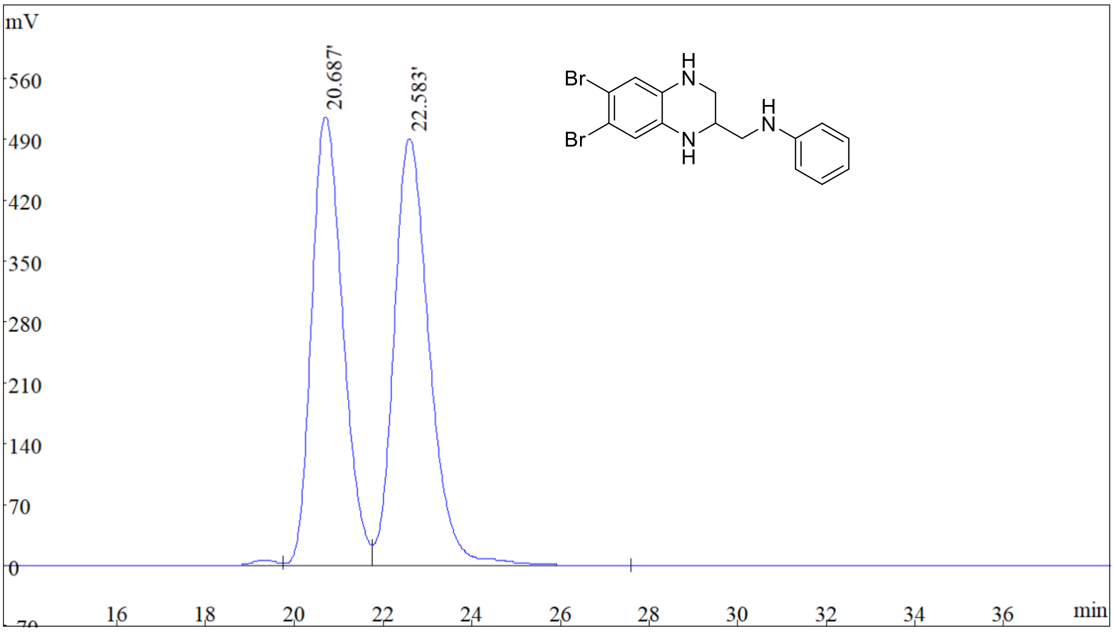
peak	Ret. Time	Area%	Area
1	16.498	2.34	258447
2	18.780	97.66	10805015



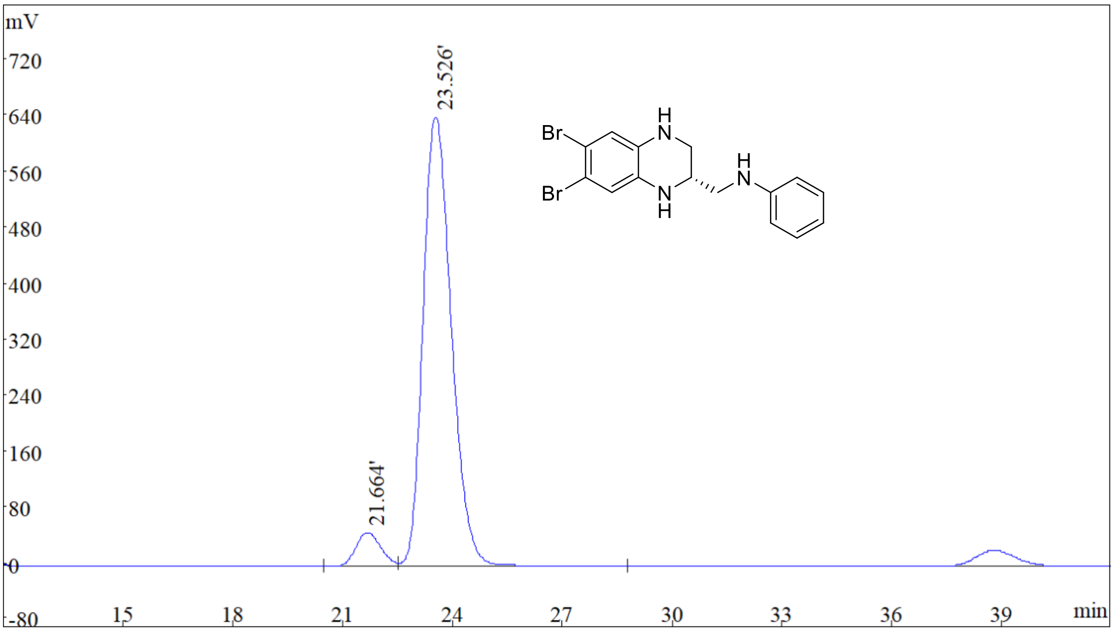
peak	Ret. Time	Area%	Area
1	30.629	50.22	27458054
2	37.851	49.78	27221453



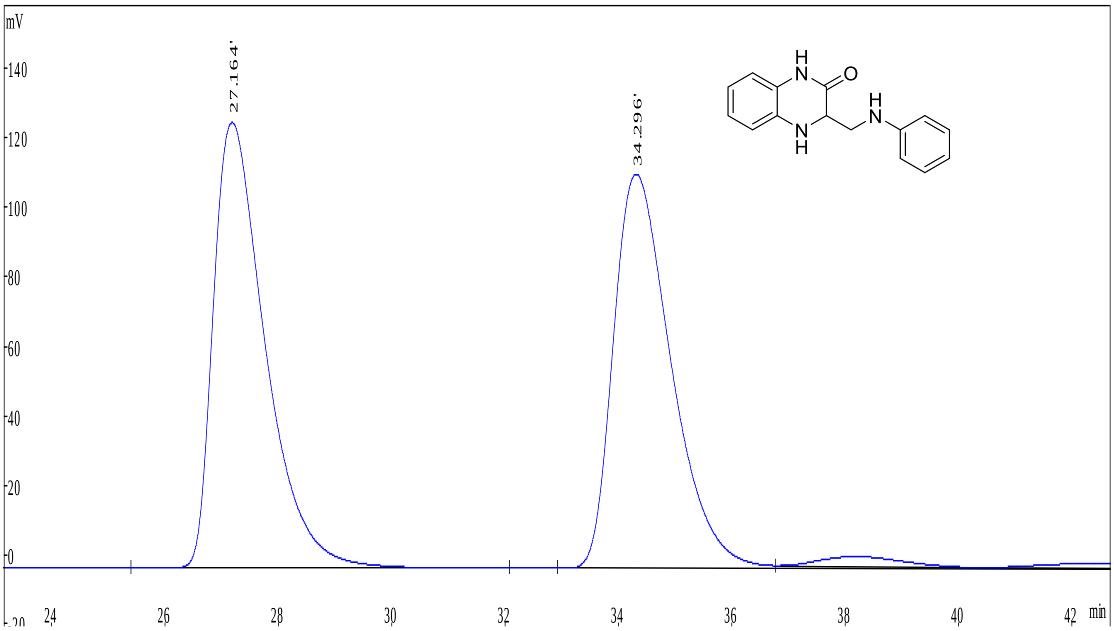
peak	Ret. Time	Area%	Area
1	31.657	2.99	1937312
2	37.644	97.01	62741581



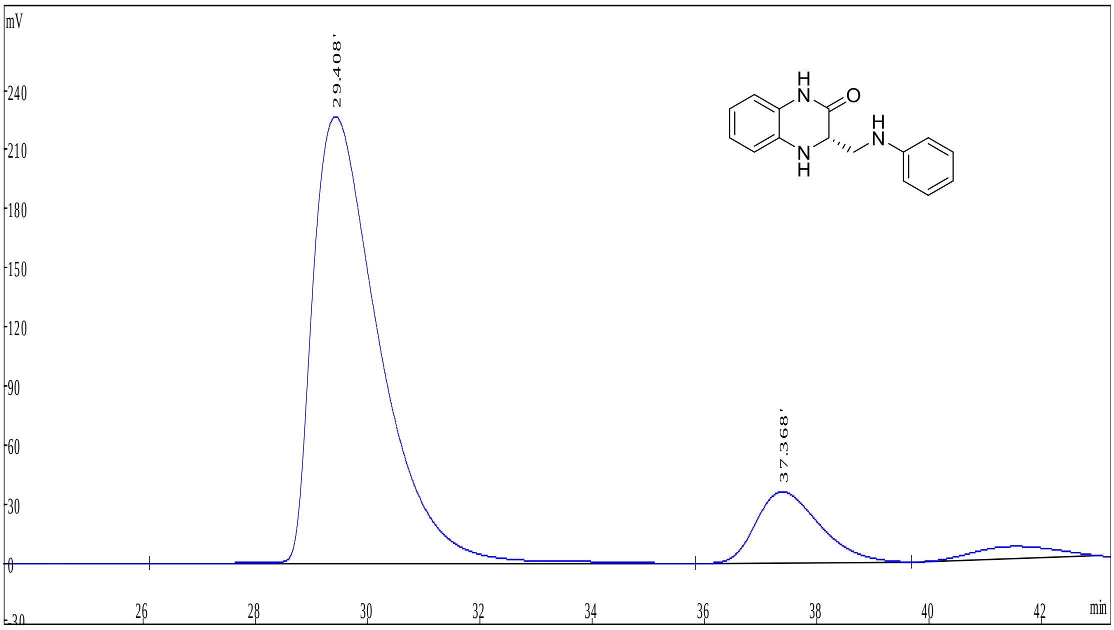
peak	Ret. Time	Area%	Area
1	20.687	47.69	24890597
2	22.583	52.31	27306957



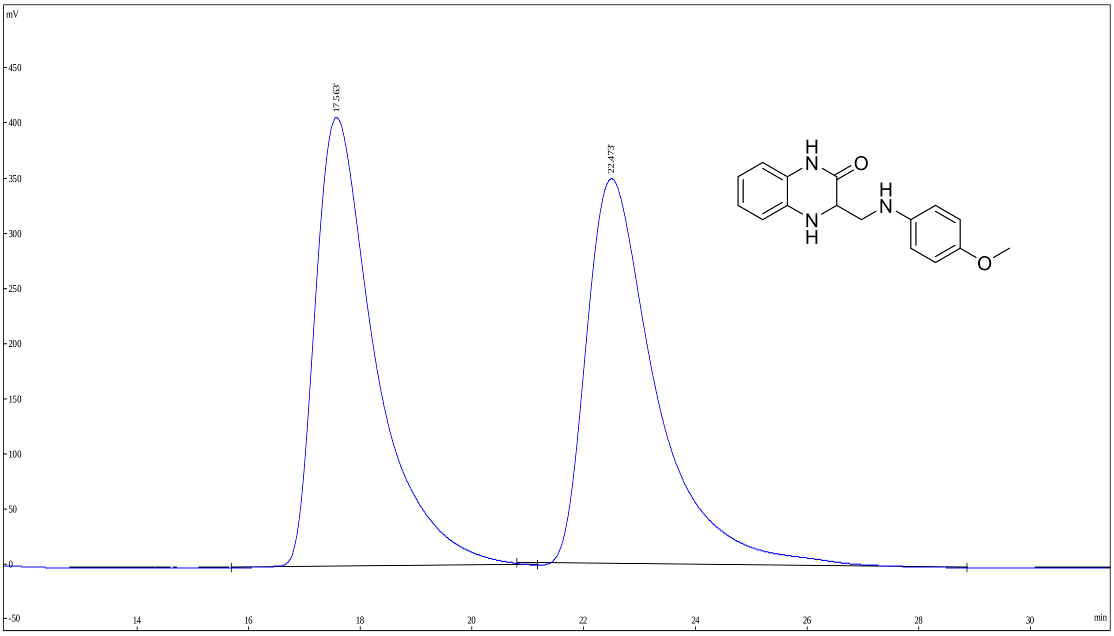
peak	Ret. Time	Area%	Area
1	21.664	6.42	2335235
2	23.526	93.58	34048016



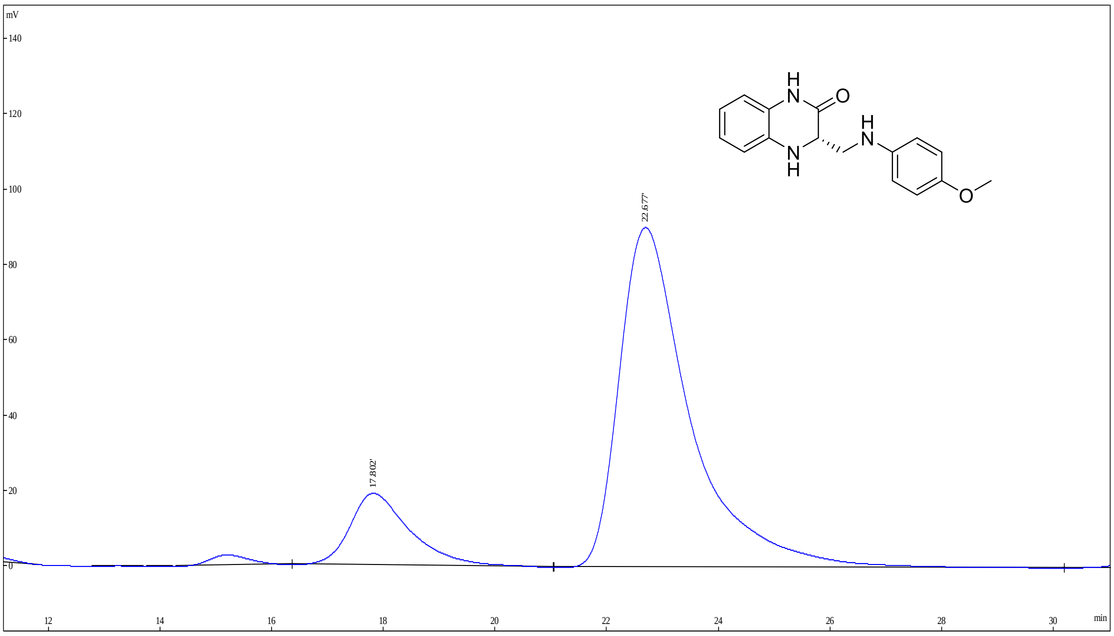
peak	Ret. Time	Area%	Area
1	21.664	6.42	2335235
2	23.526	93.58	34048016



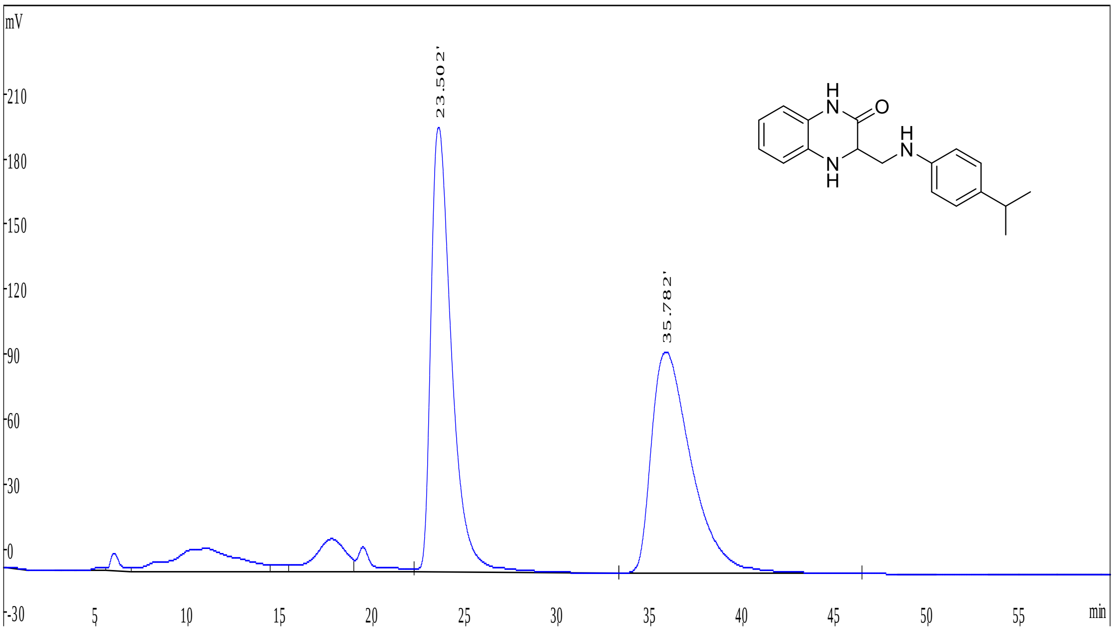
peak	Ret. Time	Area%	Area
1	29.408	86.81	18487262
2	37.368	13.19	2807877



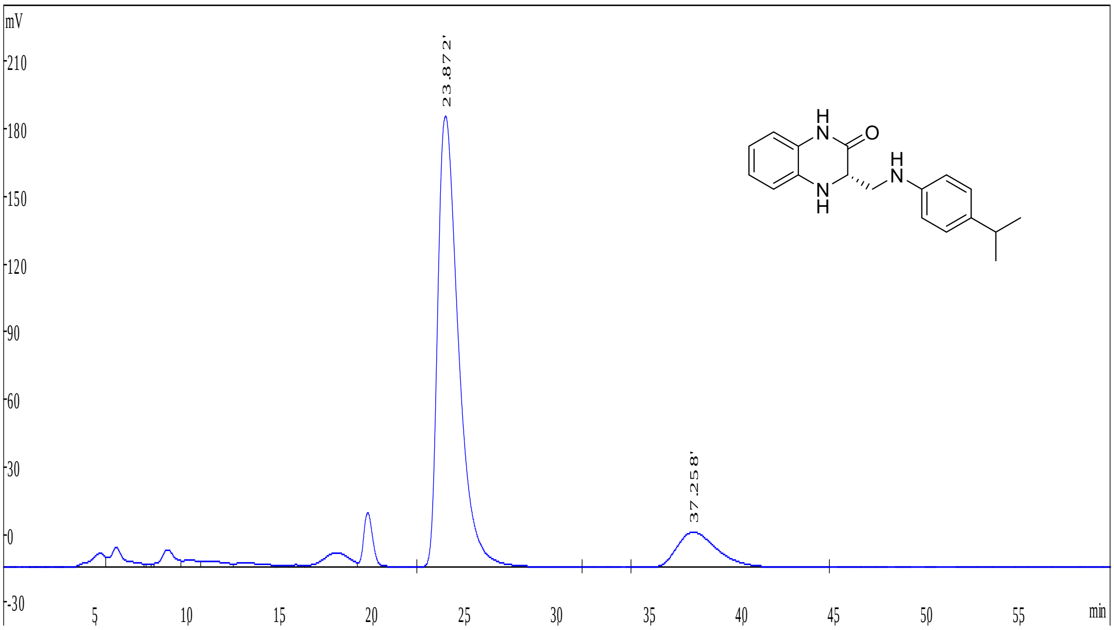
peak	Ret. Time	Area%	Area
1	17.563	50.14	30512227
2	22.473	49.86	30344816



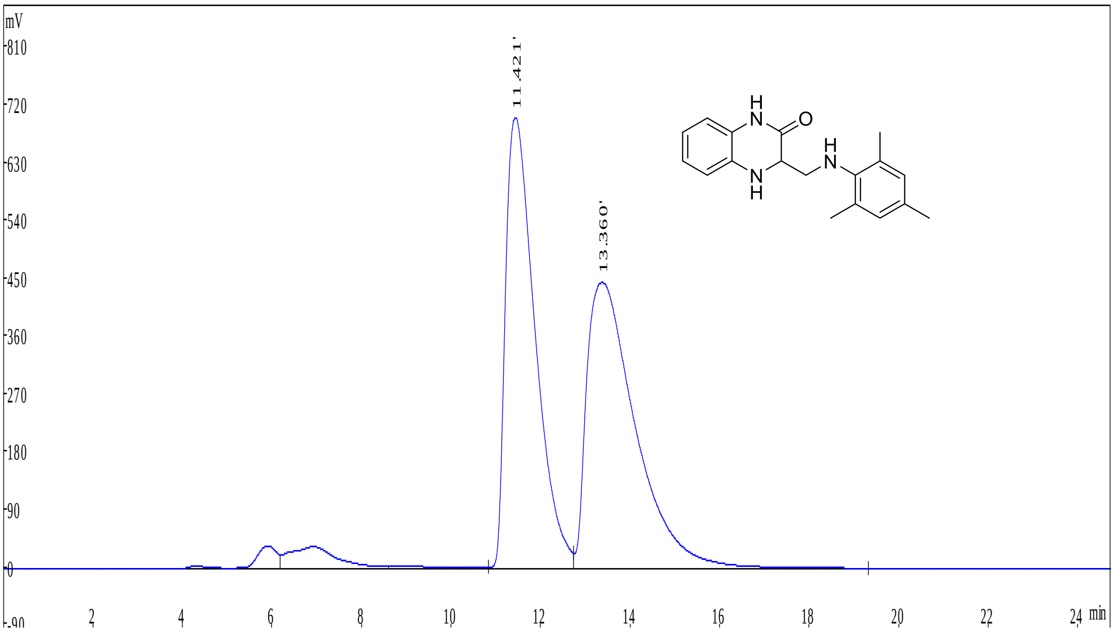
peak	Ret. Time	Area%	Area
1	17.802	15.48	1468165
2	22.677	84.52	8013068



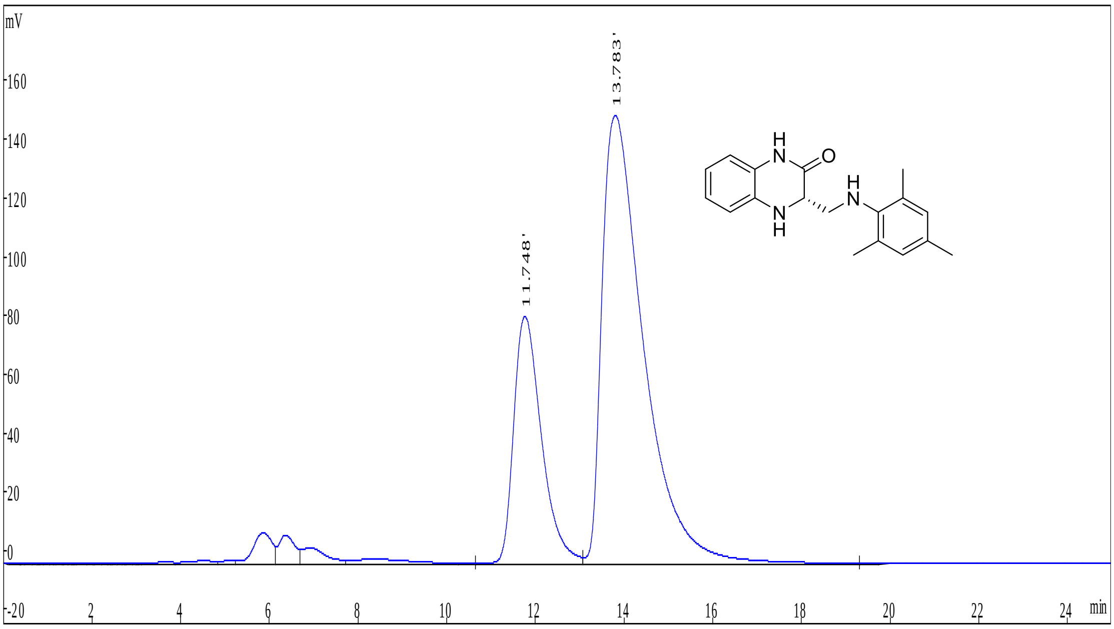
peak	Ret. Time	Area%	Area
1	23.502	50.66	15748410
2	35.782	49.34	15340491



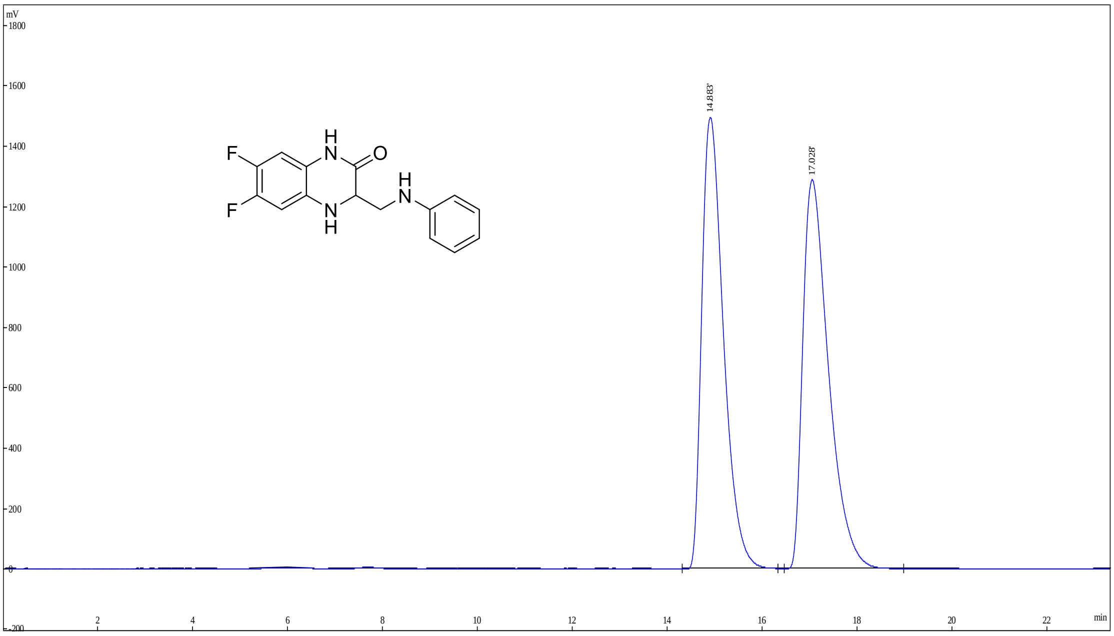
peak	Ret. Time	Area%	Area
1	23.872	85.93	15220325
2	37.258	14.07	2492371



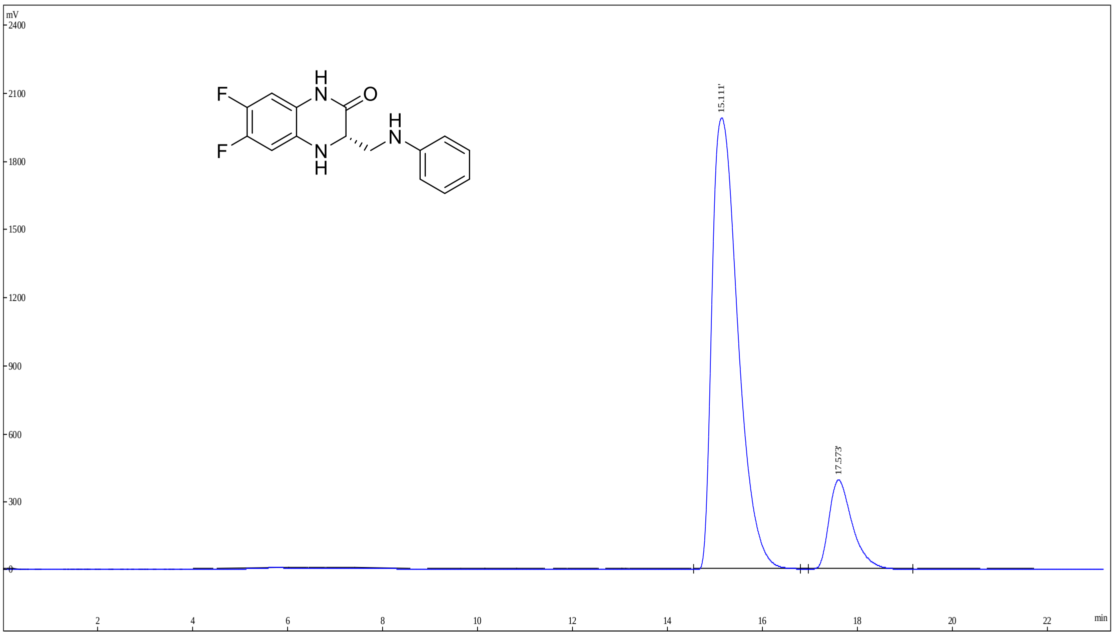
peak	Ret. Time	Area%	Area
1	11.421	48.3	31731526
2	13.360	51.7	33970560



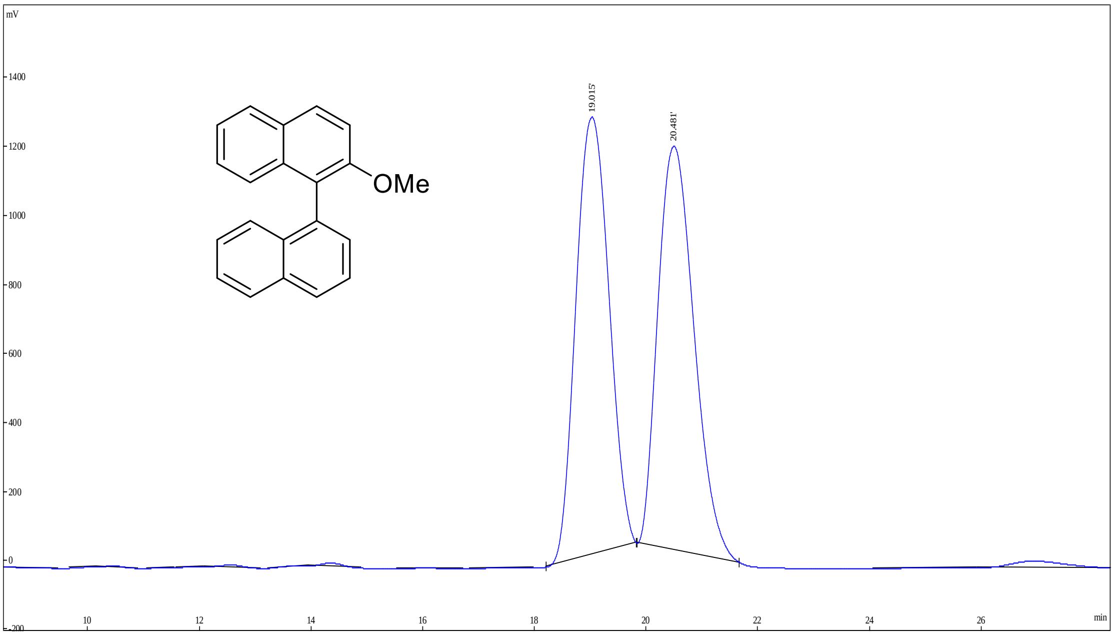
peak	Ret. Time	Area%	Area
1	11.748	26.78	3663020
2	13.783	73.22	10016661



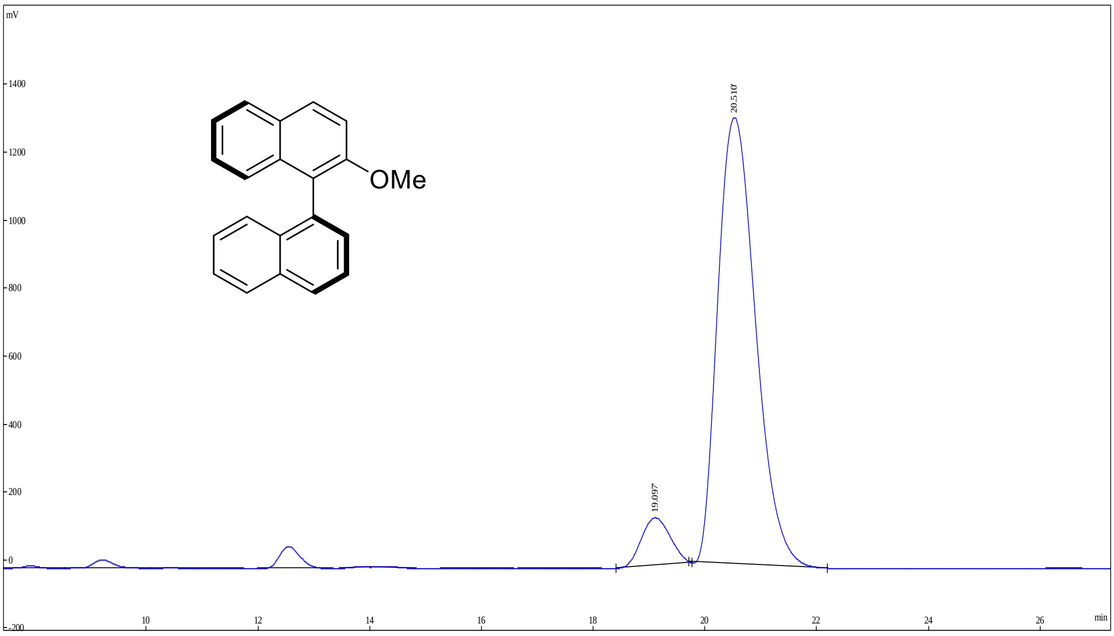
peak	Ret. Time	Area%	Area
1	14.883	49.56	47461581
2	17.028	50.44	48296243



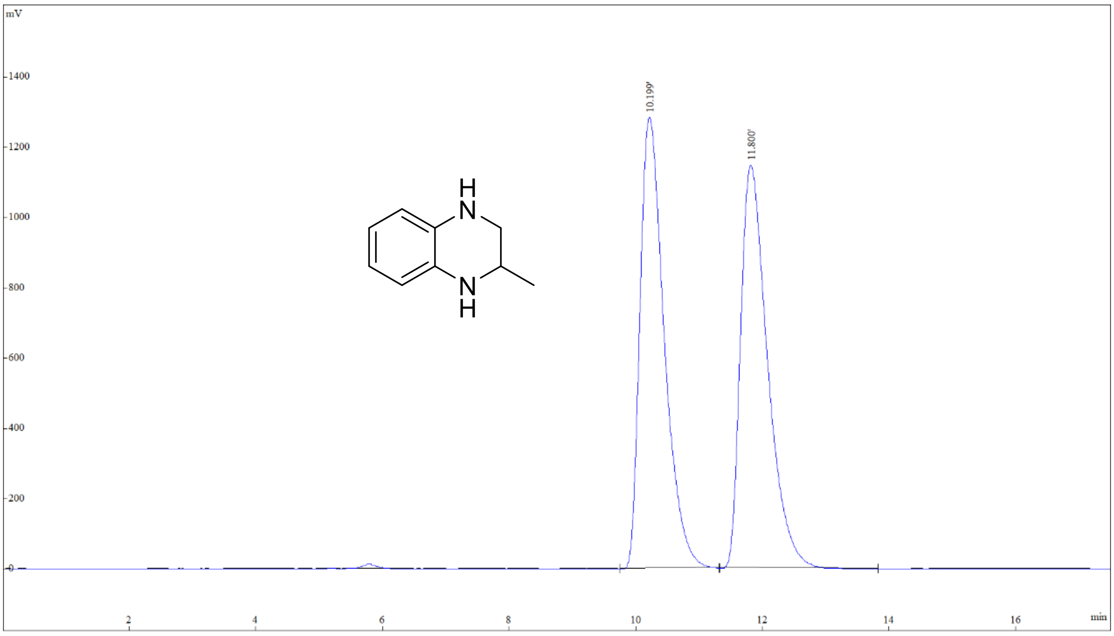
peak	Ret. Time	Area%	Area
1	15.111	84.97	75436134
2	17.573	15.03	13345085



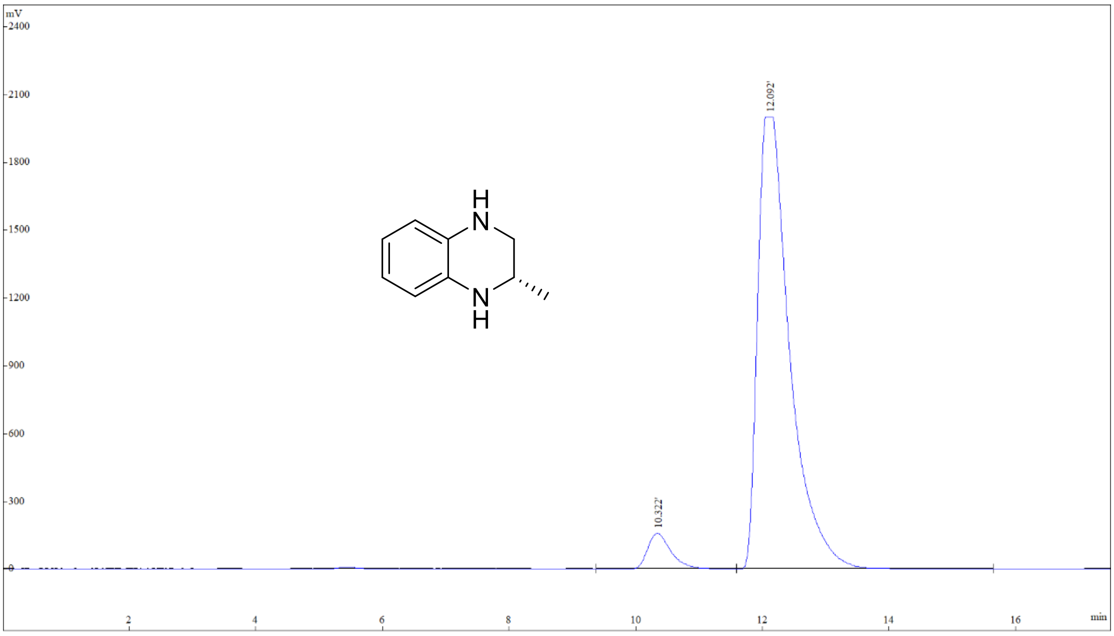
peak	Ret. Time	Area%	Area
1	19.015	49.86	52380122
2	20.481	50.14	52663792



peak	Ret. Time	Area%	Area
1	19.097	7.62	5094608
2	20.510	92.38	61718694



peak	Ret. Time	Area%	Area
1	10.199	50.18	34220595
2	11.800	49.82	33971718

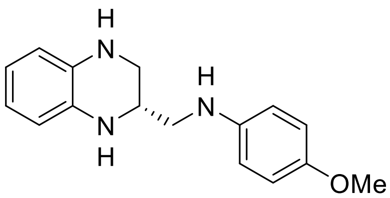


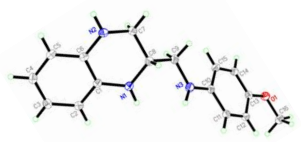
peak	Ret. Time	Area%	Area
1	10.322	5.54	4150719
2	12.092	94.46	70762490

9.X-Ray Crystal Data for Compounds 3h and 3i

Single crystal of **3h** was obtained by slow diffusion of ether into a chloroform solution at room temperature.

Single crystal diffraction data for **3h** was collected at 253 K. All single crystal diffraction data were collected using an IμS micro-focus sealed X-ray tube with Mo Kα radiation (λ = 0.71073 Å) on a Bruker D8 venture Kappa Duo diffractometer equipped with a PHOTON 100 detector. Low-temperature holding was achieved by a Cryostream Cooler (Oxford Cryosystems). All the data were collected 0.5 degree per step and using the ω scan mode. Frames were integrated using the Bruker SAINT software. Semiempirical absorption correction was applied with the SADABS program.





3h (CCDC 2404774)

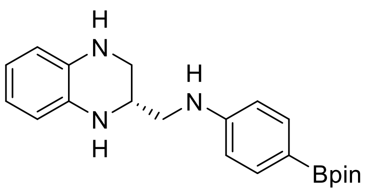
Table 1 Crystal data and structure refinement for TX15347_auto.

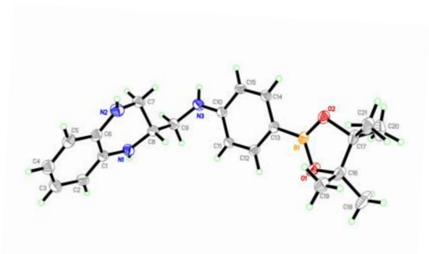
Identification code	TX15347_auto
Empirical formula	$C_{16}H_{19}N_3O$
Formula weight	269.34
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	I2
a/Å	11.61718(18)
b/Å	5.70808(9)
c/Å	21.0321(3)
α/°	90
β/°	101.6542(15)
γ/°	90
Volume/Å^3	1365.92(4)
Z	4
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	0.666
F(000)	576.0
Crystal size/mm^3	0.27 × 0.25 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.082 to 154.532
Index ranges	$-14 \leq h \leq 14$, $-6 \leq k \leq 6$, $-24 \leq l \leq 25$
Reflections collected	8987
Independent reflections	2662 [R_{int} = 0.0209, R_{sigma} = 0.0191]

Data/restraints/parameters	2662/1/183
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0936
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0944
Largest diff. peak/hole / e Å^{-3}	0.33/-0.33
Flack parameter	-0.12(9)

Single crystal of **3i** was obtained by slow diffusion of ether into a chloroform solution at room temperature.

Single crystal diffraction data for **3i** was collected at 253 K. All single crystal diffraction data were collected using an IμS micro-focus sealed X-ray tube with Mo Kα radiation (λ = 0.71073 Å) on a Bruker D8 venture Kappa Duo diffractometer equipped with a PHOTON 100 detector. Low-temperature holding was achieved by a Cryostream Cooler (Oxford Cryosystems). All the data were collected 0.5 degree per step and using the ω scan mode. Frames were integrated using the Bruker SAINT software. Semiempirical absorption correction was applied with the SADABS program.





3i (CCDC 2431788)

Table 1 Crystal data and structure refinement for fx1252.

Identification code	fx1252
Empirical formula	$C_{21}H_{28}BN_3O_2$
Formula weight	365.27
Temperature/K	170.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.3685(2)
b/Å	13.5410(4)
c/Å	14.1637(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1988.58(8)
Z	4
ρ_{calc}g/cm^3	1.220
μ/mm^{-1}	0.618
F(000)	784.0
Crystal size/mm^3	0.6 × 0.3 × 0.2
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	9.036 to 151.94
Index ranges	$-8 \leq h \leq 12$, $-16 \leq k \leq 17$, $-17 \leq l \leq 17$
Reflections collected	12470
Independent reflections	4002 [R_{int} = 0.0338, R_{sigma} = 0.0306]
Data/restraints/parameters	4002/0/249
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.1055
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.1084
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.21
Flack parameter	-0.09(11)