Supporting Information

Enantioselective Synthesis of Fluoro-dihydroquinazolones and –benzooxazinones by Fluorination Initiated Asymmetric Cyclization Reactions

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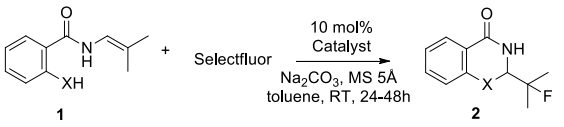
General Information

Unless otherwise noted, all commercial reagents were used without further purification. Dry and degassed THF, dichloromethane, diethyl ether, toluene, triethylamine, and dimethylformamide were obtained by passage through activated alumina columns under argon. All other dried solvents were obtained by storage over 3Å or 4Å molecular sieves (beads, 8-12 mesh) overnight. Selectfluor® (Sigma Aldrich) and anhydrous Na_2CO_3 were ground in a pestle and morter and dried at 80 °C under high vacuum for 30 minutes prior to use. 4Å and 5Å molecular sieves powder (< 50 μm) were dried in an oven overnight prior to use. Fluorination reactions were run in 1 dram (15 mm x 45 mm) vials fitted with a screw cap and stirred using an 8 mm magnetic stirrer bar. It is important to note that, due to the heterogeneous nature of the reactions, fast stirring is required in order to achieve optimal conversions. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates, and visualized under UV. Flash column chromatography was carried out on Merck Silica Gel 60 Å, 230 X 400 mesh or Fuji Silysia Chromatorex NH, 200-350 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-600, AVQ-400, AVB-400, AV-300 and JEOL ECX-400P spectrometers. ^1H and ^{13}C chemical shifts were referenced to ^1H (residual) and ^{13}C signals of the deuterated solvents, respectively.[1] Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectral data were obtained from the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. Diastereomeric ratios were determined by integration of ^{19}F NMR spectra of crude product prior to purification. Enantiomeric excesses were determined on a Shimadzu VP Series Chiral HPLC using IA or IB or IC columns. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The synthesis of PhDAP [2], OCyDAP[3] and C_8-TRIP[4] was previously described. Racemic products were synthesized by carrying out the reaction in toluene in the presence of a previously reported[5] *t*Bu-substituted achiral phosphoric acid catalyst or in acetonitrile in the absence of catalyst and Na_2CO_3. X-ray crystallographic data were collected by Dr. Antonio DiPasquale of the University of California, Berkeley College of Chemistry X-ray Crystallography Facility.

Optimization of Catalysts and Solvent on Fluorocyclization.

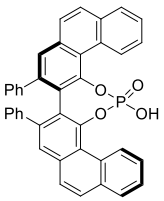
Table S1. Optimization of Catalysts and Solvent on Fluorocyclization

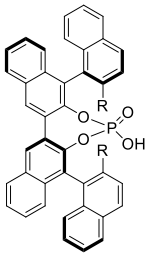


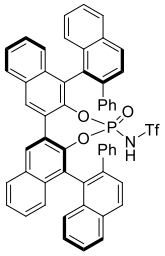
1 **2**

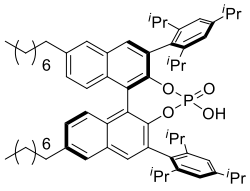
Entry	X	Catalyst	Product	% yield **2**[a]	%ee **2**[b]
1	NH	(S)-VAPOL PA	***ent*-2e**	19	1
2	NH	*(R)*-PhDAP	**2e**	13	87
3	NH	*(R)*-PhDAPNHTf	**2e**	16	54
4	NH	*(R)*-C_8-TRIP	**2e**	18	21
5	NMe	(S)-VAPOL PA	**2f**	59	27
6	NMe	*(R)*-PhDAP	**2f**	72	84
7	NMe	*(R)*-C_8-TRIP	**2f**	65	55
9	NMe	*(R)*-PhDAPNHTf	**2f**	58	55
10	NBn	*(R)*-STRIP	**2g**	60	7
11	NBn	*(R)*-PhDAP	**2g**	61	84
12	NBn	*(R)*-C_8-TRIP	**2g**	78	81
13	NBn	*(R)*-C_8-TRIP[c]	**2g**	83	63
14	NCy	*(R)*-PhDAP	**2h**	34	94
15	NCy	*(R)*-C_8-TRIP	**2h**	28	82
16	NPh	*(R)*-PhDAP	**2i**	90	98
17	NPh	*(R)*-C_8-TRIP	**2i**	84	95
18	NPh	*(R)*-4-Ph-PhDAP	**2i**	90	97
19	N(4-methoxyphenyl)	*(R)*-PhDAP	**2j**	65	97
20	N(4-methoxyphenyl)	*(R)*-C_8-TRIP	**2j**	27	96
21	N(4-nitrophenyl)	*(R)*-PhDAP	**2k**	43	95
22	N(4-nitrophenyl)	*(R)*-C_8-TRIP	**2k**	49	98
23	O	*(R)*-PhDAP	**2l**	84	55
24	O	*(R)*-C_8-TRIP	**2l**	80	36
25	O	*(R)*-TRIP	**2l**	79	17
26	O	*(R)*-4-Ph-PhDAP	**2l**	77	9
27	O	*(R)*-Taddol PA	**2l**	92	67
28	O	*(R)*-OCyDAP	**2l**	71	98
29	O	(S)-VAPOL PA	***ent*-2l**	76	96
30	O	(S)-VANOL PA	***ent*-2l**	83	34

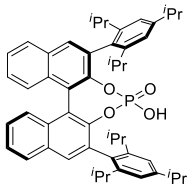
[a] Isolated yields after chromatography on silica gel. [b] Determined by HPLC.
[c] Difluorobenzene was used as a solvent.

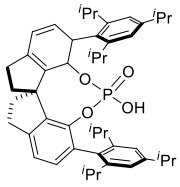

(*S*)-VAPOL PA

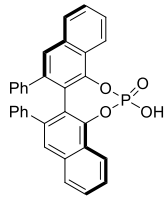

(*R*)-PhDAP R=phenyl
(*R*)-4-Ph-PhDAP R=4-phenyl-phenyl
(*R*)-OCyDAP R=cyclohexanol

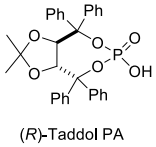

(R)-PhDAPNHTf


(*R*)-C_8-TRIP


(R)-TRIP

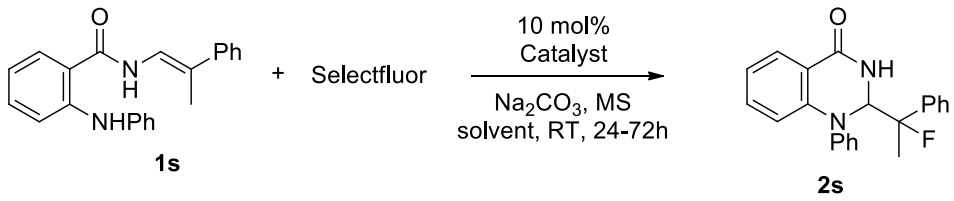

(R)-STRIP


(*S*)-VANOL PA


(*R*)-Taddol PA

Optimization of Condition on Fluoroamination.

Table S2. Optimization of Condition on Fluoroamination



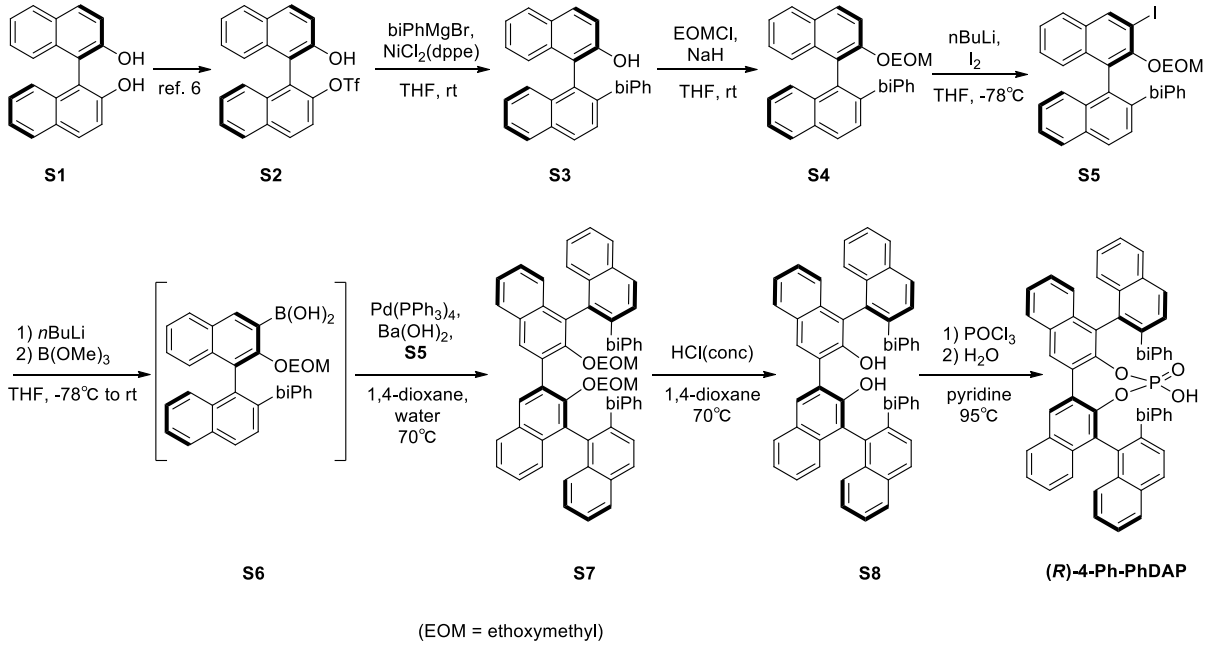
Entry	condition (Cat., MS, solvent, additive)	% yield **2s**[a]	% ee **2s**[b]	dr[c]
1	no catalyst and base, acetonitrile (homogeneous)	39	0	5:2
2	*(R)*-C_8-TRIP, MS 5Å, toluene	52	82	9:1
3	*(R)*-PhDAP, MS 5Å, toluene	58	57	> 20:1
4	*(R)*-4-Ph-PhDAP, MS 5Å, toluene	55	63	> 20:1
5	*(R)*-PhDAP, MS 5Å, 1,2-difluorobenzene	60	33	> 20:1
6	*(R)*-C_8-TRIP, MS 5Å, trifluorotoluene	48	37	2:1
7	*(R)*-C_8-TRIP, MS 3Å, toluene	37	72	10:1
8	*(R)*-4-Ph-PhDAP, MS 5Å, benzene	41	50	> 20:1
9	*(R)*-4-Ph-PhDAP, MS 5Å, trifluorotoluene	45	31	> 20:1
10	*(R)*-4-Ph-PhDAP, MS 5Å, xylene	50	75	> 20:1
11	*(R)*-4-Ph-PhDAP, MS 4Å, xylene	42	87	> 20:1
12	*(R)*-PhDAP, MS 4Å, xylene	74	72	> 20:1
13	*(R)*-4-Ph-PhDAP, MS 4Å, xylene, 3-hexanol (5 eq)	10	85	> 20:1
14	*(R)*-4-Ph-PhDAP, MS 4Å, xylene, water (10 eq)	9	90	> 20:1
15	no catalyst, MS 4Å, xylene	trace	0	-
16	no base, *(R)*-PhDAP, MS 4Å, xylene	trace	41	-

[a] Isolated yields after chromatography on silica gel. [b] Determined by HPLC. [c] Determined by ^{1}H-NMR or ^{19}F-NMR analysis of crude reaction mixture.

Synthesis of (R)-4-Ph-PhDAP

The title compound was prepared following the route shown below.

Scheme S1. Synthesis of (*R*)-4-Ph-PhDAP



***(R)*- 2-([1,1'-biphenyl]-4-yl)-2'-(ethoxymethoxy)-1,1'-binaphthalene (*(R)*-S4)**.

A solution of biphenylmagnesium bromide in THF was first prepared as follows. A 2-necked round bottom flask equipped with a reflux condenser was charged with magnesium turnings (4.37 g, 180 mmol, 6.0 equiv), and the flask was heated under vacuum for 30 min with stirring. THF (40 mL) and 1,2-dibromoethane (650 μL, 7.5 mmol, 0.25 equiv) was then added by cannulation, followed by biphenyl bromide (34.97 g, 150 mmol, 5.0 equiv) in THF (200 mL). The reaction mixture was stirred vigorously under reflux for 2 h, upon which only traces of magnesium metal remained unreacted, and allowed to cool to ambient temperature. A separate round bottom flask was charged with a suspension of ***(R)*-S2** (12.55 g, 30 mmol, 1.0 equiv)[6], methylmagnesium iodide (3M solution in diethylether, 10 mL, 30 mmol, 1.0 equiv) and bis(triphenylphosphine)nickel(II) dichloride (792 mg, 1.5 mmol, 0.04 equiv) in THF (40 mL). The solution of Grignard reagent was cannulated into the stirred suspension over 5 min, during which a significant exotherm was observed. After being stirred for 12 h at room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl (200 mL). The mixture was extracted with EtOAc (3×100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated, and filtered through a pad of silica gel (EtOAc:hexane = 1:9) to give

the crude product **S3** (7.78 g, 18.4 mmol). To the residue of **S3** and EOMCl (3.4 mL, 36.8 mmol, 2.0 equiv) in THF (90 mL), was added NaH (60 % in mineral oil, 1.47 g, 36.8 mmol, 2.0 equiv) dropwise at room temperature. The reaction mixture was stirred for 1 h, water was carefully added and the reaction mixture was extracted with EtOAc 2 times and dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (EtOAc:Hexane = 1:15) to give **S4** as a colorless foam (6.18 g, 12.9 mmol, 43% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 9.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 9.1 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.39 – 7.13 (m, 12H), 5.00 (d, J = 7.0 Hz, 1H), 4.85 (d, J = 6.9 Hz, 1H), 3.37 – 3.24 (m, 2H), 0.98 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.08, 141.26, 140.78, 139.63, 139.04, 134.67, 133.37, 132.97, 132.02, 129.62, 129.43, 129.41, 128.75, 128.35, 128.17, 128.15, 128.06, 128.05, 127.21, 126.97, 126.59, 126.33, 126.12, 125.86, 125.77, 123.88, 122.91, 116.54, 93.64, 63.93, 15.10. m/z HRMS (ESI) found $[M+K]^+$ 519.1720, $C_{35}H_{28}O_2{}^{39}K_1$ requires 519.1721.

***(R)*-2'-([1,1'-biphenyl]-4-yl)-2-(ethoxymethoxy)-3-iodo-1,1'-binaphthalene (*(R)*-S5)**.

To a stirred solution of **S4** (3.50 g, 7.28 mmol, 1.0 equiv) in THF (58 mL) cooled to -78 °C was added *n*-butyllithium (2.5 M solution in hexane, 7.28 mL, 18.2 mmol, 2.5 equiv). After an additional 5 min, the reaction mixture was moved to an ice bath and stirred for 2 h. The reaction mixture was then cooled to -78 °C, iodine (7.39 g, 29.1 mmol, 4.0 equiv) was added in one portion. The reaction mixture was stirred for additional 30 min at -78 °C, subsequently, saturated aqueous Na_2SO_3 (150 mL) was added. The mixture was extracted with EtOAc (3×100 mL). The combined organic layers were dried over Na_2SO_4, concentrated, purified by column chromatography (EtOAc:Hexane = 1:20) to give **S5** (3.60 g, 5.94 mmol, 81 %) as a pale brown foam.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.51 – 7.45 (m, 3H), 7.40 – 7.23 (m, 9H), 7.21 (d, J = 8.5 Hz, 1H), 7.17 – 7.12 (m, 2H), 4.85 – 4.81 (m, 1H), 4.49 – 4.45 (m, 1H), 3.17 – 3.08 (m, 1H), 2.76 – 2.68 (m, 1H), 0.69 (td, J = 7.1, 1.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.41, 140.86, 140.67, 140.39, 139.65, 139.30, 134.59, 133.45, 132.79, 132.02, 131.29, 129.23, 128.87, 128.75, 128.68, 128.46, 128.16, 127.22, 127.10, 127.07 (2 overlapping carbons), 127.01, 126.81, 126.63, 126.29, 125.97, 125.61, 97.47, 92.90, 65.05, 14.59. m/z HRMS (ESI) found $[M+Na]^+$ 629.0950, $C_{35}H_{27}O_2I_1{}^{23}Na_1$ requires 629.0948.

***(R,R)*- 2,2'''-di([1,1'-biphenyl]-4-yl)-[1,1':3',2'':4'',1'''-quaternaphthalene]-2',3''-diol *((R,R)*-S8)**.

To a stirred solution of **S4** (2.50 g, 5.2 mmol, 1.0 equiv) in THF (42 mL) cooled to -78 °C was added *n*-butyllithium (2.5 M solution in hexane, 5.2 ml, 13.0 mmol, 2.5 equiv). The reaction mixture was moved to an ice bath and stirred for 2 h. After cooling to –78 °C, $B(OMe)_3$ (2.95 mL, 26.0 mmol, 5.0 equiv) was added, then the mixture was allowed to warm to room temperature and stirred for 12 h. A solution of 1N HCl (100 mL) was added and the organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 100 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give **S6** as a crude product. The residue was combined with **S5** (3.15 g, 5.2 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (600 mg, 0.52 mmol, 0.1 equiv), $Ba(OH)_2$ (2.67 g, 15.6 mmol, 3.0 equiv) in 1,4-dioxane (60 mL) and water (6 mL). The resulting mixture was heated at 100 °C under argon for 20 h. Water was added and the mixture was extracted with ethyl acetate (3 x 100 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was passed through a short silica gel pad (EtOAc:Hexane = 1:10) to remove polar materials to obtain **S7** as a crude product. To the residue in 1,4-dioxane (100 mL) was added 10 N HCl (20 mL), the mixture was stirred at 70 °C for 20 min. Brine (50 mL) was added and extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ and dried over $MgSO_4$, concentrated and purified by column chromatography (EtOAc:Hexane = 1:8) to afford **S8** as a white powder (2.1 g, 2.49 mmol, 48% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H), 7.84 (s, 2H), 7.79 (dd, J = 11.2, 8.3 Hz, 4H), 7.52 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.35 – 7.00 (m, 26H), 4.58 (s, 2H). ^{13}C NMR (151 MHz, DMSO) δ 151.40, 140.81, 139.65, 139.46, 138.03, 133.34, 133.07, 132.70, 131.24, 130.52, 129.22, 128.77, 128.60, 128.23, 128.21, 128.20, 127.91, 127.74, 127.26, 126.57, 126.41, 126.29, 126.04, 125.74, 125.69, 123.90, 122.70, 118.74. m/z HRMS (ESI) found $[M+Na]^+$ 865.3081, $C_{64}H_{42}O_2{}^{23}Na_1$ requires 865.3077.

(R,R)*-5,9-bis(2-([1,1'-biphenyl]-4-yl)naphthalen-1-yl)-7-hydroxydinaphtho[2,3-d:2',3'-f][1,3,2]dioxaphosphepine 7-oxide (*(R)-4-Ph-PhDAP).

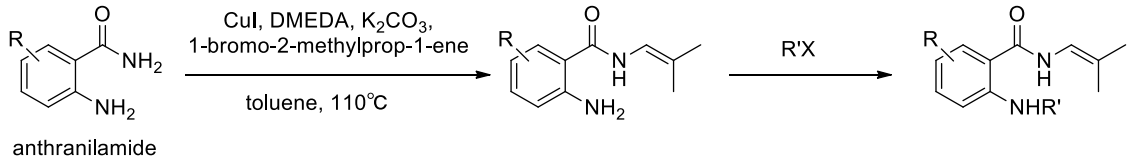
S8 (2.10 g, 2.49 mmol, 1.0 equiv) was suspended in anhydrous pyridine (13 mL). To the mixture was added $POCl_3$ (464 μL, 4.89 mmol, 2.0 equiv) and heated at 95 ºC for 2 h. The resulting solution was cooled to room temperature, and water 13 mL was added. This mixture was then heated at 95 ºC for 2 h and then cooled to room temperature. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with 3N HCl (3 × 50 mL) and then dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was triturated with MeCN to give the title compound as a pale brown powder (1.25 g, 1.38 mmol, 55% yield).

$[\alpha]_D^{20}$ = -174 ° (c = 0.2, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.78 – 7.64 (m, 3H), 7.53 – 6.88 (m, 34H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.67, 141.12, 140.89, 140.11, 138.83, 134.44, 132.98, 132.59, 131.03, 130.20, 129.60, 129.23, 128.85, 128.71, 128.64, 128.35, 128.08, 127.86, 127.49, 127.25, 127.11, 127.01, 126.78, 126.27, 126.16, 126.06, 125.87, 125.71. ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.92 (s). m/z HRMS (ESI) found $[M-H]^-$ 903.2657, $C_{64}H_{40}O_4P_1$ requires 903.2670.

Synthesis of Substrates

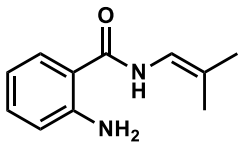
The synthesis of substrates (**1e-1r** other than **1h, 1k** and **1o**) is summarized below. A variety of anthranilamide are commercially available.

Scheme S2.Synthesis of Substrates



R = H, Me, OMe, F, Cl
R' = H, Me, Bn, Ph, 4-methoxyphenyl

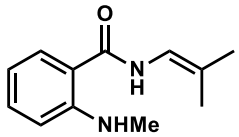
2-amino-N-(2-methylprop-1-en-1-yl)benzamide (1e)



Synthesized according to the previously published procedure.[7] A 20 mL Biotage® tube was charged with anthranilamide (2.0 g, 14.7 mmol, 1.0 equiv), 1-bromo-2-methylprop-1-ene (1.81 mL, 17.6 mmol, 1.2 equiv), DMEDA (316 μL, 2.94 mmol, 0.2 equiv), copper iodide (280 mg, 1.47 mmol, 0.1 equiv), K_2CO_3 (3.0 g, 21.7 mmol, 1.5 equiv) and toluene (10 mL), evacuated and backfilled with N_2. The reaction tube was sealed with cap and stirred for 16 h at 110 ºC in an oil bath. After cooling to ambient temperature, water was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:4) to obtain the title compound as a white solid (1.8 g, 9.5 mmol, 64 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 2H), 7.25 – 7.20 (m, 1H), 6.75 – 6.65 (m, 3H), 5.51 (s, 2H), 1.77 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.91, 149.12, 132.68, 127.02, 117.59, 117.19, 116.85, 116.04, 115.81, 22.71, 16.75. m/z HRMS (ESI) found $[M+H]^+$ 191.1179, $C_{11}H_{15}N_2O_1$ requires 191.1179.

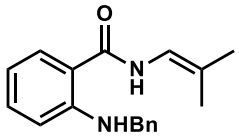
2-(methylamino)-N-(2-methylprop-1-en-1-yl)benzamide (1f)



To a solution of **1e** (500 mg, 2.63 mmol, 1.0 equiv) and K_2CO_3 (727 mg, 5.26 mmol, 2.0 equiv) in DMF (20 mL) was added iodomethane (164 μL, 2.63 mmol, 1.0 equiv) at room temperature. The mixture was stirred for 2 h at 55 ºC. The reaction mixture was diluted with EtOAc (100 mL) and washed with water (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 1:8) to afford the title compound as a white solid (170 mg, 0.83 mmol, 32 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.29 (m, 4H), 6.74 – 6.65 (m, 2H), 6.61 (t, J = 7.5 Hz, 1H), 2.86 (d, J = 5.0 Hz, 3H), 1.77 (s, 3H), 1.69 (d, J = 1.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.44, 150.97, 133.22, 127.03, 117.19, 115.86, 114.76, 114.65, 111.40, 29.80, 22.73, 16.74. m/z HRMS (ESI) found $[M+H]^+$ 205.1336, $C_{12}H_{17}N_2O_1$ requires 205.1335.

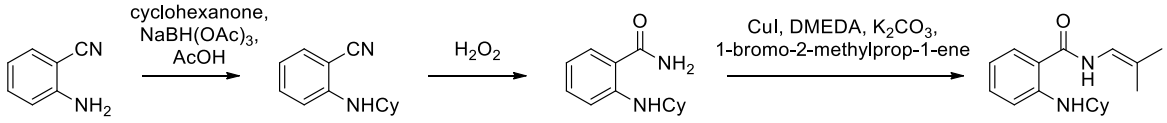
2-(benzylamino)-N-(2-methylprop-1-en-1-yl)benzamide (1g)



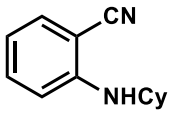
To a solution of **1e** (350 mg, 1.84 mmol, 1.0 equiv) and K_2CO_3 (509 mg, 3.68 mmol, 2.0 equiv) in DMF (45 mL) was added benzylbromide (220 μL, 1.84 mmol, 1.0 equiv) at room temperature. The mixture was stirred for 3 h at 60 ºC. The reaction mixture was diluted with EtOAc (100 mL) and washed with water (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 1:8) to afford the title compound as a white solid (110 mg,0.39 mmol, 21 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.47 – 7.30 (m, 6H), 7.26 (s, 2H), 6.72 (d, J = 10.2 Hz, 1H), 6.68 – 6.59 (m, 2H), 4.42 (s, 2H), 1.78 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.39, 149.87, 139.06, 133.17, 128.71, 127.22, 127.14, 127.11, 117.15, 116.06, 115.19, 114.94, 112.43, 47.27, 22.72, 16.74. m/z HRMS (ESI) found $[M+H]^+$ 281.1648, $C_{18}H_{21}N_2O_1$ requires 281.1648.

2-(cyclohexylamino)-N-(2-methylprop-1-en-1-yl)benzamide was synthesized according to the scheme below.



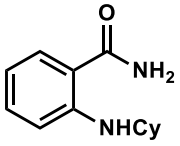
2-(cyclohexylamino)benzamide



To a solution of 2-aminobenzonitrile (5.0 g, 42.3 mmol, 1.2 equiv) in 1,2-dichloroethane (50 mL) was added cyclohexanone (3.7 mL, 36.0 mmol, 1.0 equiv), sodium triacetoxyborohydride (11.4 g, 53.8 mmol, 1.5 equiv) and acetic acid (5 mL) at room temperature. The mixture was stirred for 12 h at 40 ºC. The reaction mixture was diluted with EtOAc (100 mL) and washed with water (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 1:6) to afford the title compound as a white solid (5.0 g, 25.0 mmol, 69 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 6.66 (d, J = 8.4 Hz, 1H), 6.61 (t, J = 7.6 Hz, 1H), 4.50 – 4.36 (m, 1H), 3.40 – 3.28 (m, 1H), 2.09 – 1.97 (m, 2H), 1.85 – 1.74 (m, 2H), 1.71 – 1.63 (m, 1H), 1.45 – 1.19 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.56, 134.24, 133.00, 118.22, 116.03, 111.13, 95.59, 51.48, 33.06, 25.76, 24.91. m/z HRMS (ESI) found $[M+H]^+$ 201.1388, $C_{13}H_{17}N_2$ requires 201.1386.

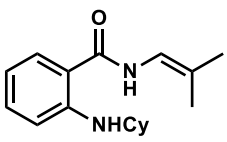
2-(cyclohexylamino)benzamide



To a suspention of 2-(cyclohexylamino)benzamide (2.1 g, 10.5 mmol, 1.0 equiv) and K_2CO_3 (1.5 g, 10.5 mmol, 1.0 equiv) in DMSO (5 mL) was added H_2O_2 (4.0 mL, 35.3 mmol, 3.4 equiv) slowly at ice-cooled temperature. The mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with saturated NH_4Cl (30 mL) and extracted with EtOAc (2 × 50 mL). The organic layer was washed with water (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 1:2) to afford the title compound as a white solid (1.7 g, 7.8 mmol, 74 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 7.1 Hz, 1H), 7.36 (d, J = 7.9 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 6.52 (t, J = 7.6 Hz, 1H), 5.62 (s, 2H), 3.41 – 3.31 (m, 1H), 2.05 – 1.95 (m, 2H), 1.82 – 1.71 (m, 2H), 1.66 – 1.57 (m, 1H), 1.45 – 1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.44, 149.64, 133.49, 128.65, 113.87, 112.67, 112.40, 50.68, 32.92, 26.02, 24.84. m/z HRMS (ESI) found $[M+H]^+$ 219.1492, $C_{13}H_{19}N_2O_1$ requires 219.1492.

2-(cyclohexylamino)-N-(2-methylprop-1-en-1-yl)benzamide (1h)

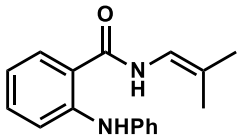


A 20 mL Biotage® tube was charged with 2-(cyclohexylamino)benzamide (400 mg, 1.83 mmol, 1.0 equiv), 1-bromo-2-methylprop-1-ene (205 μL, 2.0

mmol, 1.1 equiv), DMEDA (39 μL, 0.36 mmol, 0.2 equiv), copper iodide (34 mg, 0.18 mmol, 0.1 equiv), K_2CO_3 (380 mg, 2.75 mmol, 1.5 equiv) and toluene (5 mL), evacuated and backfilled with N_2. The reaction tube was sealed with cap and stirred for 24 h at 110 ºC in an oil bath. After cooling to ambient temperature, water (50 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:9) to obtain **1h** as a white solid (270 mg, 0.99 mmol, 54 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.43 – 7.31 (m, 2H), 7.31 – 7.24 (m, 1H), 6.75 – 6.65 (m, 2H), 6.55 (t, J = 7.5 Hz, 1H), 3.39 – 3.29 (m, 1H), 2.05 – 1.95 (m, 2H), 1.82 – 1.71 (m, 5H), 1.69 (s, 3H), 1.65 – 1.56 (m, 1H), 1.44 – 1.20 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.51, 149.30, 133.09, 127.43, 117.28, 115.78, 114.35, 114.29, 112.55, 50.82, 32.90, 26.04, 24.84, 22.73, 16.74. m/z HRMS (ESI) found $[M+H]^+$ 273.1960, $C_{17}H_{25}N_2O_1$ requires 273.1961.

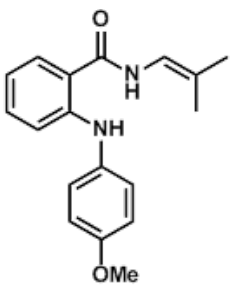
N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1i)



To a solution of **1e** (300 mg, 1.58 mmol, 1.0 equiv) and K_2CO_3 (459 mg, 3.32 mmol, 2.1 equiv) in *t*-Butanol (10 mL) was added bromobenzene (166 μL, 1.58 mmol, 1.0 equiv), $Pd_2(dba)_3$ (14 mg, 0.02 mmol, 0.01 equiv) and 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-Phos, 15 mg, 0.03 mmol, 0.02 equiv) at room temperature. The mixture was refluxed for 12 h under N_2. The reaction mixture was diluted with water (30 mL) and EtOAc (30 mL), extracted with EtOAc (3 × 30 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 1:9) to afford the title compound as a light yellow solid (160 mg,0.60 mmol, 38 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.52 (d, J = 10.2 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.19 (d, J = 7.9 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 10.2 Hz, 1H), 1.78 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.05, 145.87, 141.60, 132.58, 129.43, 127.44, 122.70, 120.94, 118.36, 118.30, 117.07, 116.75, 116.02, 22.75, 16.79. m/z HRMS (ESI) found $[M+H]^+$ 267.1490, $C_{17}H_{19}N_2O_1$ requires 267.1492.

2-((4-methoxyphenyl)amino)-N-(2-methylprop-1-en-1-yl)benzamide (1j)

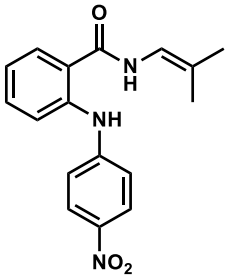


To a solution of **1e** (192 mg, 1.01 mmol, 1.0 equiv) and K_2CO_3 (307 mg, 2.22 mmol, 2.2 equiv) in *t*-Butanol (5 mL) was added 4-bromoanisole (127 μL,

1.01 mmol, 1.0 equiv), $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 0.01 equiv) and 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-Phos, 10 mg, 0.02 mmol, 0.02 equiv) at room temperature. The mixture was refluxed for 12 h under N_2. The reaction mixture was diluted with water (30 mL) and EtOAc (30 mL), extracted with EtOAc (3 × 30 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 1:9) to afford the title compound as a light yellow oil (167 mg,0.56 mmol, 56 % yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.55 – 7.38 (m, 2H), 7.26 – 7.19 (m, 1H), 7.18 – 7.03 (m, 3H), 6.93 – 6.84 (m, 2H), 6.76 – 6.67 (m, 2H), 3.81 (s, 3H), 1.78 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.16, 156.14, 147.72, 134.17, 132.61, 127.27, 124.57, 117.07, 116.95, 116.47, 116.42, 114.66, 114.61, 55.52, 22.67, 16.71. m/z HRMS (ESI) found $[M+H]^+$ 297.1598, $C_{18}H_{21}N_2O_2$ requires 297.1598.

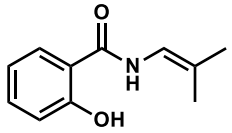
N-(2-methylprop-1-en-1-yl)-2-((4-nitrophenyl)amino)benzamide (1k)



Synthesized using an adaptation of a previously reported procedure.[8] To a solution of anthranilamide (2.0 g, 14.7 mmol, 1.0 equiv) and K_2CO_3 (4.1 g, 29.4 mmol, 2.0 equiv) in *t*-Butanol (50 mL) was added 4-bromonitrobenzene (2.4 g, 11.8 mmol, 0.8 equiv), $Pd_2(dba)_3$ (916 mg, 1.0 mmol, 0.07 equiv) and 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-Phos, 2.0 g, 4.2 mmol, 0.29 equiv) at room temperature. The mixture was refluxed for 12 h under N_2. The reaction mixture was diluted with water (100 mL) and EtOAc (100 mL), extracted with EtOAc (3 × 100 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 3:7) to afford 2-((4-nitrophenyl)amino)benzamide as a light yellow solid (2.6 g, 10.1 mmol). A 20 mL Biotage® tube was charged with the benzamide (1.0 g, 3.89 mmol, 1.0 equiv), 1-bromo-2-methylprop-1-ene (398 μL, 3.89 mmol, 1.0 equiv), DMEDA (84 μL,0.78 mmol, 0.2 equiv), copper iodide (74 mg, 0.39 mmol, 0.1 equiv), K_2CO_3 (806 mg, 5.8 mmol, 1.5 equiv) and toluene (5 mL), evacuated and backfilled with N_2. The reaction tube was sealed with cap and stirred for 24 h at 110 ºC in an oil bath. After cooling to ambient temperature, water (30 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:9) to obtain the title compound as a yellow oil (120 mg, 0.39 mmol, 7 % yield (2 steps)).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.16 – 8.06 (m, 2H), 7.58 – 7.47 (m, 3H), 7.44 (t, J = 7.8 Hz, 1H), 7.17 – 7.08 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 10.2 Hz, 1H), 1.78 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.59, 148.40, 141.98, 140.85, 132.59, 127.65, 126.26, 126.06, 121.85, 121.81, 118.92, 116.66, 116.31, 22.73, 16.83. m/z HRMS (ESI) found $[M+H]^+$ 312.1344, $C_{17}H_{18}N_3O_3$ requires 312.1343.

2-hydroxy-N-(2-methylprop-1-en-1-yl)benzamide (1l)

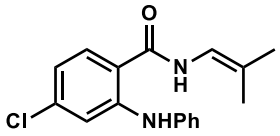


Synthesized using an adaptation of a previously reported procedure.[9] A 20 mL Biotage® tube was charged with salicylamide (1.0 g, 7.3 mmol, 1.0 equiv), 1-bromo-2-methylprop-1-ene (874 μL, 8.5 mmol, 1.17 equiv), DMEDA (237 μL, 2.2 mmol, 0.3 equiv), copper iodide (139 mg, 0.73 mmol, 0.1 equiv), K_2CO_3 (1.7 g, 12.3 mmol, 1.7 equiv) and MeCN (8 mL), evacuated and backfilled with N_2. The reaction tube was sealed with cap and stirred for 72 h at 50 ºC in an oil bath. After cooling to ambient temperature, water was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:4) to give the title compound as a white solid (650 mg, 3.4 mmol, 47 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.11 (s, 1H), 7.57 (s, 1H), 7.45 – 7.34 (m, 2H), 7.00 (d, J = 8.3 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 10.1 Hz, 1H), 1.79 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.55, 161.90, 134.58, 125.20, 118.95, 118.93, 118.19, 116.17, 114.22, 22.73, 16.77. m/z HRMS (ESI) found $[M-H]^-$ 190.0874, $C_{11}H_{12}N_1O_2$ requires 190.0874.

Substrates **1m-1r** were prepared as outlined in the syntheses for substrates **1i**.

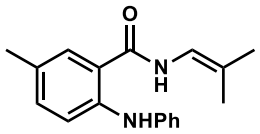
4-chloro-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1m)



Yellow oil, 17 % yield (2 steps from 4-chloroanthranilamide). This compound is unstable especially in solution on bench, should be kept dry in a freezer.

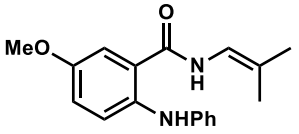
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.40 (d, J = 10.0 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.26 (s, 1H), 7.19 (d, J = 7.9 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 6.72 (dd, J = 8.4, 2.0 Hz, 1H), 6.68 (d, J = 10.2 Hz, 1H), 1.78 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.47, 147.56, 140.52, 138.92, 129.65, 128.48, 123.80, 122.07, 117.82, 117.16, 116.91, 115.71, 114.80, 22.74, 16.83. m/z HRMS (ESI) found $[M+H]^+$ 301.1104, $C_{17}H_{18}{}^{35}Cl_1N_2O_1$ requires 301.1102.

5-methyl-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1n)



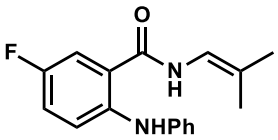
White solid.7 % yield (2 steps from 5-methylanthranilamide). This compound is unstable especially in solution on bench, should be kept dry in a freezer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.21 – 7.12 (m, 3H), 7.01 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 10.3 Hz, 1H), 2.36 (s, 3H), 1.81 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.80, 142.74, 142.46, 133.30, 129.39, 128.56, 127.90, 121.98, 119.79, 117.53, 117.15, 116.67 (2 overlapping aryl carbons), 22.72, 20.71, 16.81. m/z HRMS (ESI) found $[M+H]^+$ 281.1649, $C_{18}H_{21}N_2O_1$ requires 281.1648.

5-methoxy-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1o)



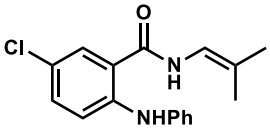
Light yellow solid. 23 % yield (2 steps from 5-methoxyanthranilamide) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, J = 10.3 Hz, 1H), 7.42 (s, 1H), 7.31 (d, J = 3.0 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.00 – 6.89 (m, 4H), 6.68 (d, J = 10.3 Hz, 1H), 3.84 (s, 3H), 1.73 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.30, 154.65, 144.14, 136.70, 129.51, 124.92, 122.91, 121.36, 118.81, 117.95, 117.22, 116.88, 113.57, 56.02, 22.70, 16.73. m/z HRMS (ESI) found $[M+H]^+$ 297.1601, $C_{18}H_{21}N_2O_2$ requires 297.1598.

5-fluoro -N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1p)



Light yellow solid. 10 % yield (2 steps from 5-fluoroanthranilamide) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.35 – 7.24 (m, 4H), 7.14 – 6.94 (m, 4H), 6.72 – 6.62 (m, 1H), 1.77 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.42, 156.09 (d, J_{C-F} = 240.0 Hz), 142.38, 141.30 (d, J_{C-F} = 2.1 Hz), 129.56, 122.43, 121.11 (d, J_{C-F} = 5.6 Hz), 119.78, 119.67 (d, J_{C-F} = 22.7 Hz), 119.54, 117.50, 116.91, 114.10 (d, J_{C-F} = 23.3 Hz), 22.73, 16.81. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.62 (m). m/z HRMS (ESI) found $[M+H]^+$ 285.1401, $C_{17}H_{18}F_1N_2O_1$ requires 285.1398.

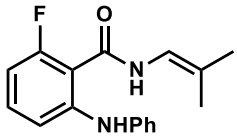
5-chloro-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1q)



Light yellow solid. 12 % yield (2 steps from 5-chloroanthranilamide). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.50 – 7.38 (m, 2H), 7.35 – 7.26 (m, 2H), 7.28 – 7.24 (m, 1H), 7.23 (d, J = 2.3 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.08 – 6.99 (m, 1H), 6.71 – 6.63 (m, 1H), 1.78 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.88, 144.54, 141.17, 132.42, 129.56, 127.05, 123.19, 122.71, 121.16, 119.50, 117.68, 117.38,

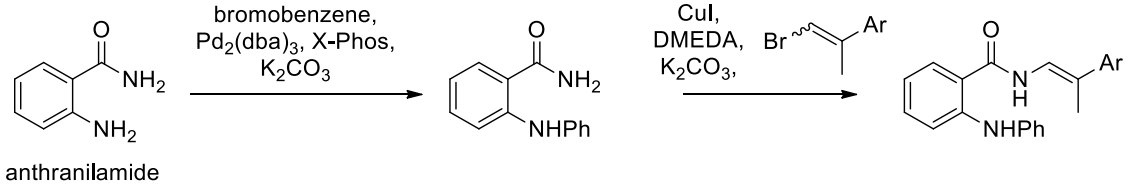
116.84, 22.77, 16.93. m/z HRMS (ESI) found $[M+H]^+$ 301.1105, $C_{17}H_{18}{}^{35}Cl_1N_2O_1$ requires 301.1102.

2-fluoro-N-(2-methylprop-1-en-1-yl)-6-(phenylamino)benzamide (1r)

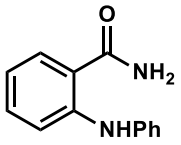


Light yellow oil. 64 % yield (2 steps from 6-fluoroanthranilamide).
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.16 – 8.04 (m, 1H), 7.37 – 7.29 (m, 2H), 7.23 – 7.18 (m, 2H), 7.19 – 7.12 (m, 1H), 7.10 – 7.04 (m, 2H), 6.79 – 6.72 (m, 1H), 6.52 – 6.43 (m, 1H), 1.78 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.81 (d, J_{C-F} = 2.6 Hz), 162.24 (d, J_{C-F} = 243.6 Hz), 149.17 (d, J_{C-F} = 5.5 Hz), 140.98, 132.55 (d, J_{C-F} = 13.0 Hz), 129.47, 123.63, 122.45, 117.26, 116.75, 110.90 (d, J_{C-F} = 2.4 Hz), 104.82 (d, J_{C-F} = 13.8 Hz), 104.27 (d, J_{C-F} = 26.3 Hz), 22.72, 16.82. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.77 (m). m/z HRMS (ESI) found $[M+H]^+$ 285.1397, $C_{17}H_{18}F_1N_2O_1$ requires 285.1398.

Substrates **1s-1w** were synthesized according to the scheme below.



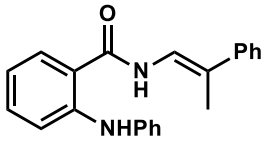
2-(phenylamino)benzamide



According to published procedure,[10] to a solution of anthranilamide (20.0 g, 146.9 mmol, 2.0 equiv) and K_2CO_3 (25.4 g, 183.6 mmol, 2.5 equiv) in *t*-Butanol (500 mL) was added bromobenzene (7.7 mL, 73.5 mmol, 1.0 equiv), $Pd_2(dba)_3$ (1.4 g mg, 1.47 mmol, 0.02 equiv) and 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-Phos, 1.8 g, 3.7 mmol, 0.05 equiv) at room temperature. The mixture was refluxed for 24 h under N_2. The reaction mixture was diluted with water (300 mL) and EtOAc (300 mL), extracted with EtOAc (3 × 150 mL), dried over anhydrous Na_2SO_4, filtered and then concentrated *in vacuo.* Purification by column chromatography (EtOAc:Hexane = 1:3) to give the title compound as a light yellow solid (4.9 g, 23.1 mmol, 31 % yield)
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.37 – 7.18 (m, 6H), 7.04 (t, J = 7.3 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.00 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.03, 146.57,

141.36, 133.03, 129.42, 128.44, 122.98, 121.62, 117.66, 116.07, 115.42. m/z HRMS (ESI) found $[M+H]^+$ 213.1024, $C_{13}H_{13}N_2O_1$ requires 213.1022.

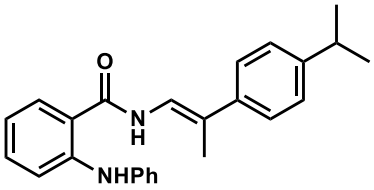
***(E)*-2-(phenylamino)-N-(2-phenylprop-1-en-1-yl)benzamide (1s)**



A 20 mL Biotage® tube was charged with 2-(phenylamino)benzamide (1.0 g, 4.7 mmol, 1.0 equiv), 1-Bromo-2-phenylpropene (prepared according to a previously reported procedure,[11] 928 mg, 4.7 mmol, 1.0 equiv), DMEDA (101 μL, 0.94 mmol, 0.2 equiv), copper iodide (90 mg, 0.47 mmol, 0.1 equiv), K_2CO_3 (1.1 g, 8.0 mmol, 1.7 equiv) and toluene (5 mL), evacuated and backfilled with N_2. The reaction tube was sealed with cap and stirred for 36 h at 110 ºC in an oil bath. After cooling to ambient temperature, water (80 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:50) to afford the title compound as a light yellow solid (480 mg, 1.5 mmol, 31 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.86 (d, J = 10.9 Hz, 1H), 7.55 (dd, J = 8.0, 1.5 Hz, 1H), 7.48 – 7.16 (m, 12H), 7.08 – 6.99 (m, 1H), 6.90 – 6.80 (m, 1H), 2.12 (d, J = 1.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.17, 146.18, 141.50, 141.08, 132.98, 129.50, 128.61, 127.53, 126.88, 125.54, 122.97, 121.20, 119.78, 118.56, 118.46, 117.94, 116.28, 14.68. m/z HRMS (ESI) found $[M+H]^+$ 329.1650, $C_{22}H_{21}N_2O_1$ requires 329.1648.

***(E)*-N-(2-(4-isopropylphenyl)prop-1-en-1-yl)-2-(phenylamino)benz amide (1t)**

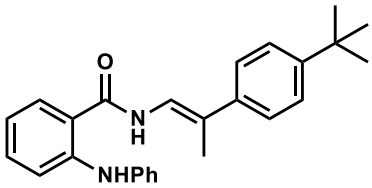


A 20 mL Biotage® tube was charged with 2-(phenylamino)benzamide (1.0 g, 4.7 mmol, 1.0 equiv), 1-Bromo-2-(4-isopropyl)phenylpropene (prepared from 4- isopropyl -α-methylstyrene according to a previously reported procedure,[11] 1.1 g, 4.7 mmol, 1.0 equiv), DMEDA (101 μL, 0.94 mmol, 0.2 equiv), copper iodide (90 mg, 0.47 mmol, 0.1 equiv), K_2CO_3 (1.1 g, 8.0 mmol, 1.7 equiv) and toluene (5 mL), evacuated and backfilled with N_2. The reaction tube was sealed with cap and stirred for 48 h at 120 ºC in an oil bath. After cooling to ambient temperature, water (80 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:50) to afford the title compound as a light yellow solid (120 mg, 0.32 mmol, 7 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.84 (d, J = 10.8 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.41

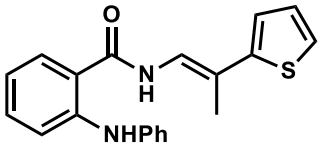
– 7.35 (m, 4H), 7.35 – 7.29 (m, 3H), 7.21 (dd, J = 8.2, 3.6 Hz, 4H), 7.03 (t, J = 7.3 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 2.91 (hept, J = 6.9 Hz, 1H), 2.10 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.10, 147.67, 146.14, 141.51, 138.50, 132.91, 129.48, 127.51, 126.67, 125.47, 122.93, 121.18, 119.15, 118.53, 118.42, 118.01, 116.22, 33.88, 24.11, 14.68. m/z HRMS (ESI) found $[M+H]^+$ 371.2122, $C_{25}H_{27}N_2O_1$ requires 371.2118.

***(E)*-N-(2-(4-(*tert*-butyl)phenyl)prop-1-en-1-yl)-2-(phenylamino)benzamide (1u)**



A 20 mL Biotage® tube was charged with 2-(phenylamino)benzamide (1.0 g, 4.7 mmol, 1.0 equiv), 1-Bromo-2-(4-*tert*-butyl)phenylpropene (prepared from 4-*tert*-butyl-α-methylstyrene according to a previously reported procedure,[11] 1.2 g, 4.7 mmol, 1.0 equiv), DMEDA (101 μL, 0.94 mmol, 0.2 equiv), copper iodide (90 mg, 0.47 mmol, 0.1 equiv), K_2CO_3 (1.1 g, 8.0 mmol, 1.7 equiv) and toluene (5 mL), evacuated and backfilled with N_2. The reaction tube was sealed with cap and stirred for 72 h at 120 ºC in an oil bath. After cooling to ambient temperature, water (80 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:50) to afford the title compound as a light yellow solid (250 mg, 0.65 mmol, 14 % yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.88 (d, J = 10.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.43 – 7.36 (m, 5H), 7.35 – 7.30 (m, 4H), 7.21 (d, J = 7.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 2.11 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.09, 149.90, 146.12, 141.52, 138.06, 132.90, 129.48, 127.54, 125.52, 125.18, 122.92, 121.17, 119.21, 118.44, 118.40, 118.05, 116.25, 34.61, 31.47, 14.60. m/z HRMS (ESI) found $[M+H]^+$ 385.2279, $C_{26}H_{29}N_2O_1$ requires 385.2274.

***(E)*-2-(phenylamino)-N-(2-(thiophen-2-yl)prop-1-en-1-yl)benzamide (1v)**



A 20 mL Biotage® tube was charged with 2-(phenylamino)benzamide (600 mg, 2.8 mmol, 1.0 equiv), 2-(1-bromoprop-1-en-2-yl)thiophene (prepared from 2-acetyl thiophene according to a previously reported procedure,[12] 569 mg, 2.8 mmol, 1.0 equiv), DMEDA (61 μL, 057 mmol, 0.2 equiv), copper iodide (53 mg, 0.28 mmol, 0.1 equiv), K_2CO_3 (663 mg, 4.8 mmol, 1.7 equiv) and toluene (4 mL), evacuated and backfilled with N_2. The reaction tube was sealed

with cap and stirred for 72 h at 120 ºC in an oil bath. After cooling to ambient temperature, water (80 mL) was added and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (EtOAc:Hexane = 1:50) to afford the title compound as a yellow solid (95 mg, 0.28 mmol, 10 % yield).

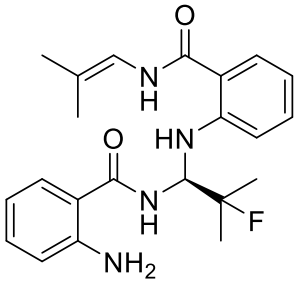
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.89 (d, J = 10.8 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 10.7 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.20 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 4.9 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.85 (t, J = 7.5 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.89, 146.16, 145.31, 141.44, 133.05, 129.49, 127.55, 127.50, 123.05, 123.01, 122.33, 121.19, 118.74, 118.52, 117.78, 116.37, 113.50, 15.05. m/z HRMS (ESI) found $[M+H]^+$ 335.1218, $C_{20}H_{19}N_2O_1S_1$ requires 335.1213.

Synthesis of Products

General procedure for asymmetric fluorcyclization:

To a one dram (15 x 45 mm) vial equipped with an 8 mm magnetic stirrer bar, the substrate (0.1 mmol, 1.0 equiv), 5Å molecular sieves (< 50 μm powder, 30 mg), anhydrous Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv), Selectfluor (57 mg, 0.16 mmol, 1.6 equiv) and the specified catalyst (0.01 mmol, 0.1 equiv) were added. Toluene (2 mL) was added to the mixture and the vial was capped with a screw cap. The reaction mixture was stirred vigorously for 24 h at room temperature. The mixture was poured into saturated $NaHCO_3$ solution, extracted with EtOAc (2 x 5 mL) and the combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash column chromatography, eluting with EtOAc:Hexanes. Most of the products except for **2e, 2k** and **2l** show blue spot on TLC under long wave (365 nm) UV lamp.

(*R*)-2-amino-*N*-(2-fluoro-2-methyl-1-((2-((2-methylprop-1-en-1-yl)carbamoyl)phenyl)amino)propyl)benzamide (2e)

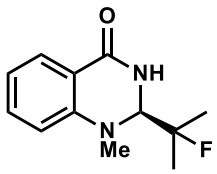


Only compound identification data was provided.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.5 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.33 (ddd, J = 8.6, 7.2, 1.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.19 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.79 – 6.64 (m, 3H), 6.65 – 6.57 (m, 1H), 6.33 (d, J = 9.2 Hz, 1H), 5.67 (dt, J = 20.4, 8.9 Hz, 1H),

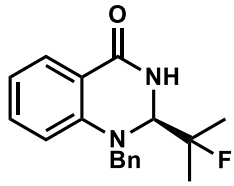
5.52 (s, 2H), 1.77 (s, 3H), 1.71 (s, 3H), 1.60 (d, J = 21.5 Hz, 3H), 1.53 (d, J = 22.0 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ170.53, 167.61, 151.35, 149.04, 133.78, 133.15, 129.38, 129.04, 118.79, 117.69, 117.05, 116.93, 116.84, 116.10, 115.55, 113.72, , 97.91 (d, J = 175.0 Hz), 64.41 (d, J = 21.4 Hz), 24.70 (d, J = 24.2 Hz), 24.05 (d, J = 23.7 Hz)., 23.14, 17.15. ^{19}F NMR (376 MHz, $CDCl_3$) δ -157.81 (m). m/z HRMS (ESI) found $[M+Na]^+$ 421.2010, $C_{22}H_{27}F_1N_4Na_1O_2$requires 421.2010.

***(R)*-2-(2-fluoropropan-2-yl)-1-methyl-2,3-dihydroquinazolin-4(1H)-one (2f)**



Reaction carried out according to the general procedure using **1f** (20.4 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 36 h at room temperature to give **2f** as an white solid (16.0 mg, 0.072 mmol, 72 % yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.45 – 7.32 (m, 1H), 6.85 – 6.70 (m, 1H), 6.60 (d, J = 7.0 Hz, 1H), 4.79 – 4.60 (m, 1H), 3.11 (s, 3H), 1.36 (d, J_{H-F} = 22.4 Hz, 3H), 1.20 (d, J_{H-F} = 21.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.41, 147.58, 134.59, 128.27, 117.43, 115.28, 111.81, 100.00 (d, J_{C-F} = 172.7 Hz), 76.78 (d, J_{C-F} = 29.7 Hz), 39.59 (d, J_{C-F} = 4.5 Hz), 23.03 (d, J_{C-F} = 23.2 Hz), 21.76 (d, J_{C-F} = 24.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.82 (m). m/z HRMS (ESI) found $[M+H]^+$ 223.1242, $C_{12}H_{16}F_1N_2O_1$ requires 223.1241. HPLC (Chiralpak IC column, 85:15 hexanes/isopropanol, 1 ml/min); tr = 11.9 min (major), 12.9 min (minor); 84 % ee.

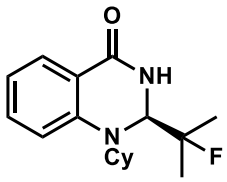
***(R)*-1-benzyl-2-(2-fluoropropan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2g)**



Reaction carried out according to the general procedure using **1g** (28.0 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 48 h at room temperature to give **2g** as an white solid (17.9 mg, 0.060 mmol, 60 % yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, J = 7.7 Hz, J_{H-F} = 1.6 Hz, 1H), 7.48 (d, J = 4.2 Hz, 1H), 7.37 – 7.20 (m, 6H), 6.79 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 4.88 (d, J = 16.2 Hz, 1H), 4.70 (dd, J_{H-F} = 7.4, J = 4.6 Hz, 1H), 4.50 (d, J = 16.2 Hz, 1H), 1.32 (d, J_{H-F} = 22.5 Hz, 3H), 1.26 (d, J_{H-F} = 22.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.27, 147.01, 136.95, 134.37, 128.95, 128.46, 127.78, 127.44, 118.72, 117.16, 114.52, 99.66 (d, J_{C-F} = 172.5 Hz), 74.70 (d, J_{C-F} = 29.2 Hz), 55.87 (d, J_{C-F} = 3.7 Hz), 23.01 (d, J_{C-F} = 23.4 Hz), 22.41 (d, J_{C-F} = 23.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.08 (m). m/z HRMS (ESI) found $[M+H]^+$ 299.1557, $C_{18}H_{20}F_1N_2O_1$ requires 299.1554. HPLC (Chiralpak

IC column, 86:14 hexanes/isopropanol, 1 ml/min); tr = 8.6 min (minor), 10.9 min (major); 84 % ee.

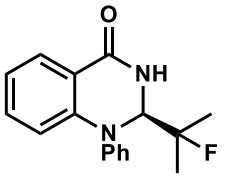
***(R)*-1-cyclohexyl-2-(2-fluoropropan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2h)**



Reaction carried out according to the general procedure using 1h (27.2 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 48 h at room temperature to give **2h** as an white solid (10.0 mg, 0.034mmol, 34 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.82 (m, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.06 – 6.93 (m, 2H), 4.56 (dd, J_{H-F} = 11.6, 4.5 Hz, 1H), 3.39-3.25 (m, 1H), 2.03 (d, J = 12.9 Hz, 1H), 1.95 – 0.99 (m, 15H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.61, 148.92, 133.50, 127.24, 122.52, 121.51, 98.07 (d, J_{C-F} = 172.5 Hz), 69.54 (d, J_{C-F} = 28.7 Hz), 67.36, 33.04, 30.22, 25.67, 26.35 (d, J_{C-F} = 15.5 Hz), 23.65 (d, J_{C-F} = 23.5 Hz), 22.84 (d, J_{C-F} = 23.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.92 (m). m/z HRMS (ESI) found $[M+H]^+$ 291.1867, $C_{17}H_{24}F_1N_2O_1$ requires 291.1867. HPLC (Chiralpak IA column, 87:13 hexanes/isopropanol, 1 ml/min); tr = 8.8 min (major), 14.2 min (minor); 94% ee.

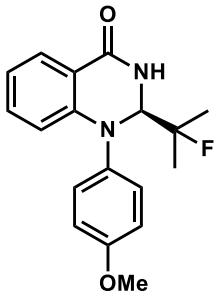
***(R)*-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2i)**



Reaction carried out according to the general procedure using **1i** (26.6 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24 h at room temperature to give **2i** as an white solid (25.6 mg, 0.090 mmol, 90 % yield). By using *(R)*-4-Ph-PhDAP (9.0 mg, 0.01 mmol) as a catalyst, the same product was obtained in 97 % ee and 90 % yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 3.9 Hz, 1H), 7.39 – 7.27 (m, 3H), 7.22 (d, J – 8.5 Hz, 2H), 7.13 (t, 7.6 Hz, 1H), 7.05 (t, 7.5 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 4.96 (dd, J_{H-F} = 10.0, J = 4.7 Hz, 1H), 1.41 (d, J_{H-F} = 21.9 Hz, 3H), 1.37 (d, J_{H-F} = 21.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.12, 149.18, 145.50, 133.50, 129.56, 127.82, 124.75, 123.75, 122.19, 121.61, 121.47, 98.08 (d, J_{C-F} = 174.0 Hz), 77.41 (d, J_{C-F} = 28.9 Hz), 23.69 (d, J_{C-F} = 23.9 Hz), 23.03 (d, J_{C-F} = 24.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.39 (m). m/z HRMS (ESI) found $[M+H]^+$ 285.1397, $C_{17}H_{18}F_1N_2O_1$ requires 285.1398. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 8.9 min (major), 12.1 min (minor); 98 % ee.

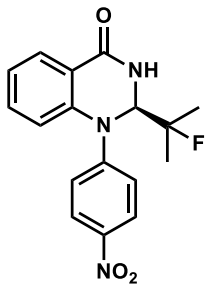
***(R)*-2-(2-fluoropropan-2-yl)-1-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (2j)**



Reaction carried out according to the general procedure using **1j** (29.6 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24 h at room temperature to give **2j** as an yellow solid (20.5 mg, 0.065 mmol, 65 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 4.6 Hz, 1H), 7.94 (dd, J = 7.8, 1.7 Hz, 1H), 7.31-7.27 (m, 1H), 7.22 – 7.17 (m, 2H), 6.97 – 6.92 (m, 1H), 6.87 – 6.83 (m, 2H), 6.77 (d, J =5.2 Hz, 1H), 4.87 (dd, J_{H-F} = 9.6, J = 4.5 Hz, 1H), 3.79 (s, 3H), 1.43 (d, J_{H-F} = 21.9 Hz, 3H), 1.36 (d, J_{H-F} = 21.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.69, 158.26, 147.63, 143.35, 133.81, 128.25 (d, J_{C-F} = 12.9 Hz), 127.43, 122.15 (d, J = 1.2 Hz), 121.67, 121.22, 115.57 , 99.27 (d, J_{C-F} = 175.3 Hz), 78.36 (d, J_{C-F} = 26.4 Hz), 55.90, 24.06 (d, J_{C-F} = 24.0 Hz), 23.20 (d, J_{C-F} = 24.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.27 (m). m/z HRMS (ESI) found $[M+H]^+$ 315.1503, $C_{18}H_{20}F_1N_2O_2$ requires 315.1503. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 11.9 min (major), 15.4 min (minor); 97 % ee.

***(R)*-2-(2-fluoropropan-2-yl)-1-(4-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (2k)**

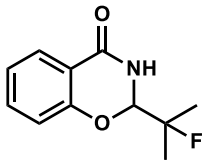


Reaction carried out according to the general procedure using **1k** (31.1 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24 h at room temperature to give **2k** as an yellow solid (14.3 mg, 0.043 mmol, 43 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 8.05 (dd, J = 7.8, 1.6 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.31 – 7.21 (m, 3H), 7.19-7.13 (m, 2H), 5.11 (dd, J_{H-F} = 9.5, J = 5.1 Hz, 1H), 1.44 (d, J_{H-F} = 21.9 Hz, 3H), 1.31 (d, J_{H-F} = 21.7 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 162.77, 154.91, 143.32, 143.26, 133.93, 128.70, 126.18, 125.39 (d, J_{C-F} = 2.0 Hz), 125.27, 123.80, 120.35 (d, J_{C-F} = 2.0 Hz), 99.23 (d, J_{C-F} = 177.2 Hz), 76.27 (d, J_{C-F} = 24.7 Hz), 24.34 (d, J_{C-F} = 24.1 Hz), 23.33 (d, J_{C-F} = 24.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.50 (m). m/z HRMS (ESI) found $[M+H]^+$ 330.1249,

$C_{17}H_{17}F_1N_3O_3$ requires 330.1248. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 16.8 min (major), 24.7 min (minor); 95% ee.

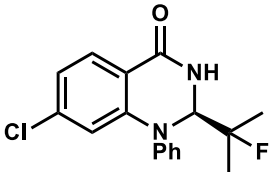
2-(2-fluoropropan-2-yl)-2H-benzo[e][1,3]oxazin-4(3H)-one (2l)



Reaction carried out according to the general procedure using **1l** (9.6 mg, 0.05 mmol, 1.0 equiv) as substrate, toluene (0.5 ml) as solvent and *(R)*-OCyDAP (4.0 mg, 0.005 mmol, 0.1 equiv) as catalyst, with Selectfluor (21 mg, 0.06 mmol, 1.2 equiv), 5Å molecular sieves (15 mg) and Na_2CO_3 (7 mg, 0.065 mmol, 1.3 equiv) by stirring for 24 h at room temperature to give **2l** as an white solid (7.4 mg, 0.035 mmol, 71 % yield). By using *(S)*-VAPOL Phosphoric acid (3.0 mg, 0.005 mmol, 0.1 equiv) as a catalyst, enantiomer of the product (***ent*-2l)** was obtained in 96 % ee and 76 % yield. This reaction could compete with fluorohydration reaction if the reaction mixture contains water. Using dry solvent, Selectfluor, Na_2CO_3 and molecular sieves is important to obtain high yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.8, 1.7 Hz, 1H), 7.53 – 7.43 (m, 1H), 7.13 (td, J = 7.5, 1.1 Hz, 1H), 6.98 (dd, J = 8.1, 0.9 Hz, 1H), 6.37 (s, 1H), 5.29 (d, J_{H-F} = 3.6 Hz, 1H), 1.55 (t, J_{H-F} = 22.2 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 162.07, 156.69, 134.31, 127.18, 122.09, 118.19, 116.16, 95.16 (d, J_{C-F} = 174.4 Hz), 86.08 (d, J_{C-F} = 25.7 Hz), 21.94 (d, J_{C-F} = 8.7 Hz), 21.79 (d, J_{C-F} = 8.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -153.54 (m). m/z HRMS (ESI) found $[M+H]^+$ 210.0927, $C_{11}H_{13}F_1N_1O_2$ requires 210.0925. HPLC (Chiralpak IA column, 96:04 hexanes/isopropanol, 1 ml/min); tr = 14.4 min (major), 16.4 min (minor); 98% ee.

***(R)*-7-chloro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2m)**

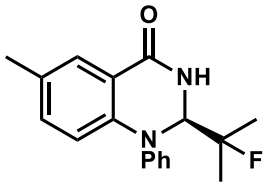


Reaction carried out according to the general procedure using **1m** (30.1 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24 h at room temperature to give **2m** as an white solid (26.9 mg, 0.084 mmol, 84 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 4.1 Hz, 1H), 7.87 (dd, J = 8.4 Hz, 1.1 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.28 – 7.15 (m, 3H), 6.96 (dd, J = 8.4, 1.9 Hz, 1H), 6.91-6.86 (m, 1H), 4.93 (dd, J_{H-F} = 9.5 Hz, J = 4.6 Hz, 1H), 1.44 (d, J_{H-F} = 21.9 Hz, 3H), 1.35 (d, J_{H-F} = 21.7 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 162.78, 149.48, 147.77, 138.99, 130.66, 130.13, 126.08, 125.04, 122.62, 121.81 (d, J_{C-F} = 1.8 Hz), 121.25, 99.51 (d, J_{C-F} = 176.6 Hz), 77.99 (d, J_{C-F} = 25.1 Hz), 24.23 (d, J_{C-F} = 24.0

Hz), 23.26 (d, J_{C-F} = 24.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.59 (m). m/z HRMS (ESI) found $[M+H]^+$ 319.1007, $C_{17}H_{17}Cl_1F_1N_2O_1$ requires 319.1008. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 7.8 min (major), 8.8 min (minor); 89 % ee.

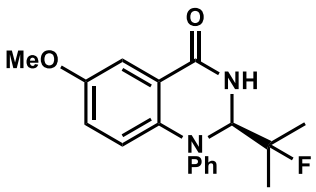
***(R)*-2-(2-fluoropropan-2-yl)-6-methyl-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2n)**



Reaction carried out according to the general procedure using **1n** (28.4 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 18 h at room temperature to give **2n** as an white solid (23.2 mg, 0.078 mmol, 78 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.55 (d, J = 5.0 Hz, 1H), 7.34-7.23 (m, 2H), 7.23-7.12 (m, 3H), 7.09 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 4.94 (dd, J_{H-F} = 10.5, J = 4.8 Hz, 1H), 2.33 (s, 3H), 1.40 (d, J_{H-F} = 22.0 Hz, 3H), 1.39 (d, J_{H-F} = 21.7 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 163.55, 150.86, 143.61, 134.60, 132.74, 130.28, 128.31, 124.57, 124.02, 123.22, 123.12, 99.14 (d, J_{C-F} = 175.8 Hz), 77.91 (d, J_{C-F} = 25.8 Hz), 24.27 (d, J_{C-F} = 24.1 Hz), 23.53 (d, J_{C-F} = 24.0 Hz), 20.90. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.62 (m). m/z HRMS (ESI) found $[M+H]^+$ 299.1553, $C_{18}H_{20}F_1N_2O_1$ requires 299.1554. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 9.6 min (major), 10.7 min (minor); 97 % ee.

***(R)*-2-(2-fluoropropan-2-yl)-6-methoxy-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2o)**

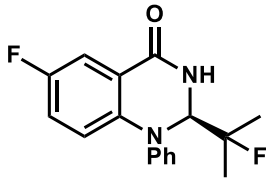


Reaction carried out according to the general procedure using **1o** (29.6 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24h at room temperature to give **2o** as an white solid (17.3 mg, 0.055 mmol, 55 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 4.8 Hz, 1H), 7.50 (d, J = 2.9 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.17 – 7.04 (m, 3H), 7.03 – 6.92 (m, 2H), 4.97 (dd, J_{H-F} = 10.9, J = 4.8 Hz, 1H), 3.86 (s, 3H), 1.43 (d, J_{H-F} = 21.6 Hz, 3H), 1.39 (d, J_{H-F} = 22.0 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 163.15, 156.59, 151.44, 139.02, 130.28, 125.71 (d, J_{C-F} = 1.7 Hz), 125.40, 124.21, 122.55, 121.35, 110.91, 98.98 (d, J_{C-F} = 175.7 Hz), 78.06 (d, J_{C-F} = 25.7 Hz), 56.03, 24.21 (d, J_{C-F} = 24.4 Hz), 23.73 (d, J_{C-F} = 24.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.10 (m). m/z HRMS (ESI) found $[M+H]^+$ 315.1503,

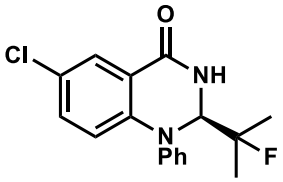
$C_{18}H_{20}F_1N_2O_2$ requires 315.1503. HPLC (Chiralpak IB column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 7.9 min (major), 9.1 min (minor); 94 % ee.

***(R)*-6-fluoro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2p)**



Reaction carried out according to the general procedure using **1p** (28.4 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24h at room temperature to give **2p** as an white solid (28.2 mg, 0.093 mmol, 93 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J_{H-F} = 8.5, J = 3.1 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.21 (d, J = 4.7 Hz, 1H), 7.19 – 7.05 (m, 4H), 6.95 (dd, J = 8.9, J_{H-F} = 4.5 Hz, 1H), 4.92 (dd, J_{H-F} = 10.9, J = 4.8 Hz, 1H), 1.40 (d, J_{H-F} = 21.6 Hz, 3H), 1.39 (d, J_{H-F} = 21.9 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 162.46 (d, J_{C-F} = 2.3 Hz), 159.08 (d, J_{C-F} = 240.4 Hz), 150.77, 142.41 (d, J_{C-F} = 2.2 Hz), 130.43, 125.78 (dd, J_{C-F} = 7.3, 2.0 Hz), 125.45 (d, J_{C-F} = 7.5 Hz), 124.96, 123.38 (d, J_{C-F} = 1.6 Hz), 121.03 (d, J_{C-F} = 23.7 Hz), 113.72 (d, J_{C-F} = 23.8 Hz), 99.25 (d, J_{C-F} = 176.6 Hz), 77.96 (d, J_{C-F} = 24.7 Hz), 24.23 (d, J_{C-F} = 24.2 Hz), 23.53 (d, J_{C-F} = 23.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.31 (m), -144.22 (m). m/z HRMS (ESI) found $[M+H]^+$ 303.1304, $C_{17}H_{17}F_2N_2O_1$ requires 303.1303. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 9.0 min (major), 9.9 min (minor); 96 % ee.

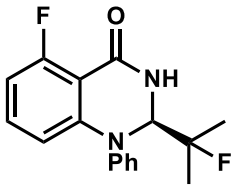
***(R)*-6-chloro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2q)**



Reaction carried out according to the general procedure using **1q** (30.1 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24h at room temperature to give **2q** as an white solid (23.6 mg, 0.074 mmol, 74 % yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, 4.4 Hz, 1H), 7.93 (d, 2.5 Hz, 1H), 7.38 – 7.26 (m, 3H), 7.23-7.12 (m, 3H), 6.90 (d, J = 8.7 Hz, 1H), 4.95 (dd, J_{H-F} = 11.0 Hz, J = 4.8 Hz, 1H), 1.45 (d, J_{H-F} = 21.9 Hz, 3H), 1.36 (d, J_{H-F} = 21.7 Hz, 3H). ^{13}C NMR (151 MHz, Acetone d-6) δ 162.45, 149.89, 145.07, 133.59, 130.50, 127.65, 127.45, 125.50, 124.97 (d, J_{C-F} = 1.9 Hz), 124.36, 124.14, 99.42 (d, J_{C-F} = 176.8 Hz), 77.79 (d, J_{C-F} = 24.7 Hz), 24.24 (d, J_{C-F} = 24.2 Hz), 23.34 (d, J_{C-F} = 24.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.36 (m). m/z HRMS (ESI) found $[M+H]^+$ 319.1007,

$C_{17}H_{17}Cl_1F_1N_2O_1$ requires 319.1008. HPLC (Chiralpak IC column, 88:12 hexanes/isopropanol, 1 ml/min); tr = 6.4 min (minor), 7.0 min (major); 97 % ee.

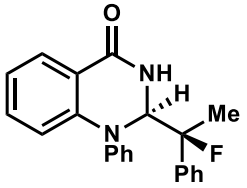
***(R)*-5-fluoro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2r)**



Reaction carried out according to the general procedure using **1r** (28.4 mg, 0.1 mmol, 1.0 equiv) as substrate, toluene (2.0 ml) as solvent and *(R)*-PhDAP (7.5 mg, 0.01 mmol, 0.1 equiv) as catalyst, with Selectfluor (57 mg, 0.16 mmol, 1.6 equiv), 5Å molecular sieves (30 mg) and Na_2CO_3 (17 mg, 0.16 mmol, 1.6 equiv) by stirring for 24h at room temperature to give **2r** as an white solid (25.3 mg, 0.084 mmol, 84 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 5.3 Hz, 1H), 7.37 – 7.20 (m, 5H), 7.18 – 7.12 (m, 1H), 6.77 – 6.65 (m, 2H), 4.92 (dd, J_{H-F} = 11.7, J = 5.3 Hz, 1H), 1.48 (d, J_{H-F} = 21.8 Hz, 3H), 1.36 (d, J_{H-F} = 21.7 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 162.95 (d, J_{C-F} = 259.7 Hz), 160.70 (d, J_{C-F} = 2.7 Hz), 149.94, 148.45 (d, J_{C-F} = 2.8 Hz), 134.17 (d, J_{C-F} = 10.9 Hz), 130.40, 125.32, 123.97, 118.61 (d, J_{C-F} = 3.8 Hz), 113.01 (d, J_{C-F} = 8.9 Hz), 110.62 (d, J_{C-F} = 21.5 Hz), 99.24 (d, J_{C-F} = 176.7 Hz), 77.50 (d, J_{C-F} = 24.7 Hz), 24.33 (d, J_{C-F} = 24.2 Hz), 23.35 (d, J_{C-F} = 24.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.71 (m), -144.38 (m). m/z HRMS (ESI) found $[M+H]^+$ 303.1303, $C_{17}H_{17}F_2N_2O_1$ requires 303.1303. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 9.7 min (major), 12.5 min (minor); 92 % ee.

(*R*)-2-((*S*)-1-fluoro-1-phenylethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2s)

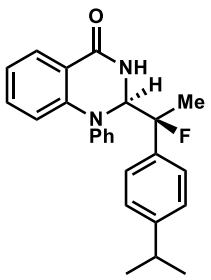


Reaction carried out according to the general procedure using **1s** (16.4 mg, 0.05 mmol, 1.0 equiv) as substrate, xylene (1.0 ml, mixture of isomers) as solvent and *(R)*-PhDAP (3.8 mg, 0.005 mmol, 0.1 equiv) as catalyst, with Selectfluor (28.3 mg, 0.08 mmol, 1.6 equiv), 4Å molecular sieves (15 mg) and Na_2CO_3 (8.5 mg, 0.08 mmol, 1.6 equiv) by stirring for 72 h at room temperature to give **2s** as an white solid (12.9 mg, 0.037 mmol, 74 % yield). By using *(R)*-biPhDAP (4.5 mg, 0.005 mmol, 0.1 equiv) as a catalyst, the same product was obtained in 87 % ee and 42 % yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 1H), 7.39 – 7.24 (m, 8H), 7.19 – 7.06 (m, 3H), 6.95 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.15 – 6.07 (m, 1H), 5.05 (dd, J_{H-F} = 10.0, J = 4.6 Hz, 1H), 1.81 (d, J_{H-F} = 23.3 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 163.31, 150.59, 146.68, 141.87 (d, J_{C-F} = 22.1 Hz), 133.46, 130.22, 129.08 (d, J_{C-F} = 1.4 Hz), 129.03 (d, J_{C-F} = 1.4 Hz), 128.21, 126.94 (d,

J_{C-F} = 9.3 Hz), 125.30, 124.26, 123.98 (d, J_{C-F} = 2.5 Hz), 122.68, 122.62, 101.65 (d, J_{C-F} = 182.7 Hz), 79.02 (d, J_{C-F} = 25.5 Hz), 22.95 (d, J_{C-F} = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -148.04 (m). m/z HRMS (ESI) found $[M+H]^+$ 347.1552, $C_{22}H_{20}F_1N_2O_1$ requires 347.1554. HPLC (Chiralpak IC column, 88:12 hexanes/isopropanol, 1 ml/min); tr = 12.0 min (minor), 14.0 min (major); 72 % ee.

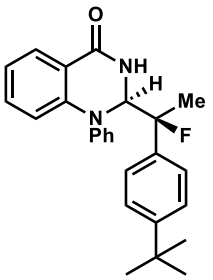
(*R*)-2-((*S*)-1-fluoro-1-(4-isopropylphenyl)ethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2t)



Reaction carried out according to the general procedure using **1t** (18.5 mg, 0.05 mmol, 1.0 equiv) as substrate, xylene (1.0 ml, mixture of isomers) as solvent and *(R)*-PhDAP (3.8 mg, 0.005 mmol, 0.1 equiv) or as catalyst, with Selectfluor (28.3 mg, 0.08 mmol, 1.6 equiv), 4Å molecular sieves (15 mg) and Na_2CO_3 (8.5 mg, 0.08 mmol, 1.6 equiv) by stirring for 72 h at room temperature to give **2t** as an white solid (8.9 mg, 0.023 mmol, 46 % yield). By using *(R)*-biPhDAP (4.5 mg, 0.005 mmol, 0.1 equiv) as a catalyst, the same product was obtained in 77 % ee and 49 % yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.7 Hz, 1H), 7.54 (s, 1H), 7.31 – 7.19 (m, 5H), 7.17-7.05 (m, 3H), 6.96-6.88 (m, J = 3H), 6.84 (d, J = 8.1 Hz, 1H), 5.05 (dd, J_{H-F} = 12.1, J = 4.6 Hz, 1H), 2.94-2.76 (m, 1H), 1.85 (d, J_{H-F} = 23.2 Hz, 3H), 1.22 (d, J = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, Acetone-d6) δ 163.26 (d, J_{C-F} = 9.1 Hz), 150.58, 149.70, (d, J_{C-F} = 1.3 Hz), 146.69, 139.01 (d, J_{C-F} = 22.1 Hz), 133.34, 130.20, 128.16 (d, J_{C-F} = 1.9Hz), 127.10 (d, J_{C-F} = 8.9 Hz), 126.98, 126.97, 125.36, 124.48, 123.81, 122.47 (d, J_{C-F} = 11.3 Hz), 101.38 (d, J_{C-F} = 181.7 Hz), 79.05 (d, J_{C-F} = 26.6 Hz), 34.74, 24.46 (d, J_{C-F} = 24.5 Hz), 22.98 (d, J_{C-F} = 22.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -147.34 (m). m/z HRMS (ESI) found $[M+H]^+$ 389.2034, $C_{25}H_{26}F_1N_2O_1$ requires 389.2024. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 8.4 min (minor), 9.9 min (major); 70 % ee.

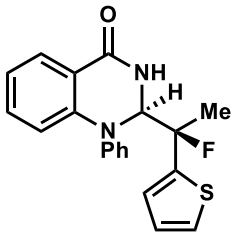
(*R*)-2-((*S*)-1-(4-(tert-butyl)phenyl)-1-fluoroethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2u)



Reaction carried out according to the general procedure using **1u** (19.2 mg, 0.05 mmol, 1.0 equiv) as substrate, xylene (1.0 ml, mixture of isomers) as solvent and *(R)*-PhDAP (3.8 mg, 0.005 mmol, 0.1 equiv) or as catalyst, with Selectfluor (28.3 mg, 0.08 mmol, 1.6 equiv), 4Å molecular sieves (15 mg) and Na_2CO_3 (8.5 mg, 0.08 mmol, 1.6 equiv) by stirring for 72 h at room temperature to give **2u** as an white solid (11.1 mg, 0.028 mmol, 55 % yield). By using *(R)*-biPhDAP (4.5 mg, 0.005 mmol, 0.1 equiv) as a catalyst, the same product was obtained in 84 % ee and 40 % yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 1H), 7.31 – 7.24 (m, 7H), 7.14 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.9 Hz, 2H), 6.90 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.32 (d, J = 4.5 Hz, 1H), 5.05 (dd, J_{H-F} = 9.5, J = 4.4 Hz, 1H), 1.83 (d, J_{H-F} = 23.2 Hz, 3H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, Acetone-d6) δ 163.34, 151.83, 150.57, 146.69, 138.54 (d, J_{C-F} = 22.2 Hz), 133.31, 130.19, 128.16, 126.84 (d, J_{C-F} = 8.9 Hz), 125.82, 125.39, 124.55, 123.76 (d, J_{C-F} = 2.3 Hz), 122.47, 122.40, 101.30 (d, J_{C-F} = 181.5 Hz), 79.13 (d, J_{C-F} = 26.7 Hz), 35.21, 31.75, 22.99 (d, J_{C-F} = 22.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -147.34 (m). m/z HRMS (ESI) found $[M+H]^+$ 403.2184, $C_{26}H_{28}F_1N_2O_1$ requires 403.2180. HPLC (Chiralpak IC column, 88:12 hexanes/isopropanol, 1 ml/min); tr = 12.5 min (minor), 13.9 min (major); 86 % ee.

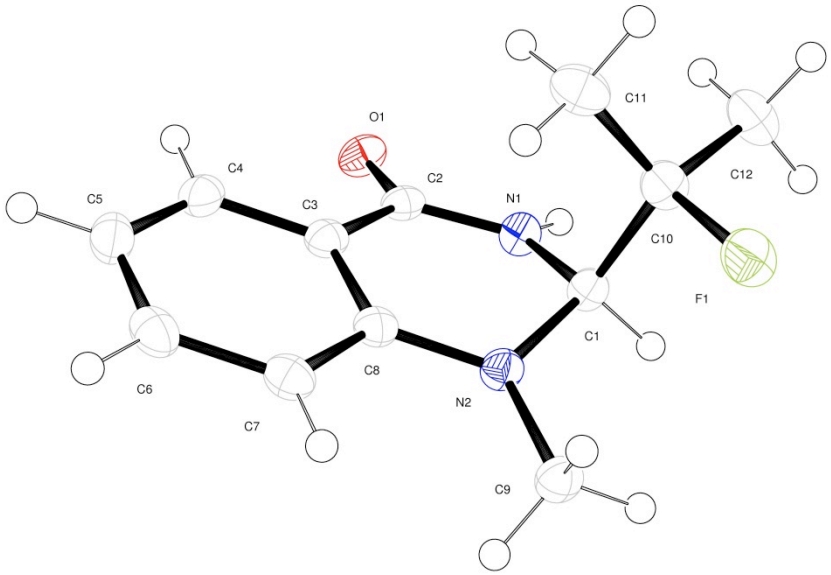
(*R*)-2-((*R*)-1-fluoro-1-(thiophen-2-yl)ethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2v)



Reaction carried out according to the general procedure using **1v** (16.7 mg, 0.05 mmol, 1.0 equiv) as substrate, xylene (1.0 ml, mixture of isomers) as solvent and *(R)*-PhDAP (3.8 mg, 0.005 mmol, 0.1 equiv) or as catalyst, with Selectfluor (28.3 mg, 0.08 mmol, 1.6 equiv), 5Å molecular sieves (15 mg) and Na_2CO_3 (8.5 mg, 0.08 mmol, 1.6 equiv) by stirring for 72 h at room temperature to give **2v** as an white solid (9.0 mg, 0.026 mmol, 51 % yield). By using *(R)*-4-Ph-PhDAP (4.5 mg, 0.005 mmol, 0.1 equiv) as a catalyst, the same product was obtained in 58 % ee and 53 % yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, J_{H-F} = 7.8, J = 1.6 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.19 – 7.13 (m, 3H), 7.05-7.01 (m, 1H), 7.01 – 6.97 (m, 1H), 6.97 – 6.93 (m, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.35 (d, J = 4.6 Hz, 1H), 5.14 (dd, J_{H-F} = 9.4, J = 4.6 Hz, 1H), 1.82 (d, J_{H-F} = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d6) δ 163.11, 150.48, 146.35, 144.57 (d, J_{C-F} = 1.2 Hz), 144.40, 133.52, 130.33, 128.31, 127.70, 126.96 (d, J_{C-F} = 5.4 Hz), 125.31, 124.02, 123.73 (d, J_{C-F} = 2.4 Hz), 122.82, 122.72, 100.42 (d, J_{C-F} = 180.2 Hz), 79.00 (d, J_{C-F} = 27.2 Hz), 23.52 (d, J_{C-F} = 21.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.69 (m). m/z HRMS (ESI) found $[M+H]^+$ 353.1122, $C_{20}H_{18}F_1N_2O_1S_1$ requires 353.1118. HPLC (Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min); tr = 10.1 min (minor), 11.2 min (major); 72 % ee.

X-Ray Crystal Structure Data for 2f



A colorless rod 0.140 x 0.040 x 0.040 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 67.000° in θ. A total of 19143 reflections were collected covering the indices, -9<=*h*<=9, -7<=*k*<=7, -14<=*l*<=14. 2020 reflections were found to be symmetry independent, with an R_{int} of 0.0265. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2013. Absolute stereochemistry was unambiguously determined to be *R* at C1.

Table S3. Crystal data and structure refinement for 2f.

X-ray ID	toste80	
Sample/notebook ID	ken4-150-3	
Empirical formula	C12 H15 F N2 O	
Formula weight	222.26	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.6084(2) Å	α= 90°.
	b = 6.4312(2) Å	β= 103.6270(10)°.
	c = 11.7689(3) Å	γ = 90°.
Volume	559.66(3) $Å^3$	
Z	2	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.799 mm^{-1}	
F(000)	236	
Crystal size	0.140 x 0.040 x 0.040 mm^3	
Crystal color/habit	colorless rod	
Theta range for data collection	3.865 to 68.289°.	
Index ranges	-9<=h<=9, -7<=k<=7, -14<=l<=14	
Reflections collected	19143	
Independent reflections	2020 [R(int) = 0.0265]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.858	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2020 / 1 / 148	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0685	
R indices (all data)	R1 = 0.0258, wR2 = 0.0687	
Absolute structure parameter	0.01(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.211 and -0.136 $e.Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2f. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7165(2)	4726(3)	7618(1)	21(1)
C(2)	9813(2)	6655(3)	8780(1)	21(1)
C(3)	9580(2)	8121(3)	7794(2)	21(1)
C(4)	10523(2)	9994(3)	7919(2)	25(1)
C(5)	10429(2)	11308(3)	6974(2)	28(1)
C(6)	9359(2)	10727(3)	5894(2)	26(1)
C(7)	8389(2)	8892(3)	5749(2)	23(1)
C(8)	8477(2)	7551(3)	6704(2)	20(1)
C(9)	6591(2)	4936(3)	5454(1)	24(1)
C(10)	5376(2)	5494(3)	7896(2)	26(1)
C(11)	5226(3)	7826(3)	7999(2)	32(1)
C(12)	4979(3)	4338(4)	8926(2)	34(1)
N(1)	8682(2)	5017(2)	8620(1)	21(1)
N(2)	7571(2)	5678(2)	6591(1)	20(1)
O(1)	11021(2)	6836(2)	9690(1)	26(1)
F(1)	4015(1)	4893(2)	6902(1)	34(1)

Table S5. Bond lengths [Å] and angles [°] for 2f.

C(1)-N(2)	1.451(2)	C(7)-H(7)	0.9500
C(1)-N(1)	1.455(2)	C(8)-N(2)	1.379(2)
C(1)-C(10)	1.553(2)	C(9)-N(2)	1.451(2)
C(1)-H(1)	1.0000	C(9)-H(9A)	0.9800
C(2)-O(1)	1.241(2)	C(9)-H(9B)	0.9800
C(2)-N(1)	1.345(2)	C(9)-H(9C)	0.9800
C(2)-C(3)	1.473(2)	C(10)-F(1)	1.421(2)
C(3)-C(4)	1.392(3)	C(10)-C(11)	1.512(3)
C(3)-C(8)	1.406(2)	C(10)-C(12)	1.512(3)
C(4)-C(5)	1.385(3)	C(11)-H(11A)	0.9800
C(4)-H(4)	0.9500	C(11)-H(11B)	0.9800
C(5)-C(6)	1.390(3)	C(11)-H(11C)	0.9800
C(5)-H(5)	0.9500	C(12)-H(12A)	0.9800
C(6)-C(7)	1.381(3)	C(12)-H(12B)	0.9800
C(6)-H(6)	0.9500	C(12)-H(12C)	0.9800
C(7)-C(8)	1.406(2)	N(1)-H(1A)	0.8800
N(2)-C(1)-N(1)	109.67(13)	C(6)-C(5)-H(5)	120.7
N(2)-C(1)-C(10)	114.22(14)	C(7)-C(6)-C(5)	121.59(17)
N(1)-C(1)-C(10)	110.85(14)	C(7)-C(6)-H(6)	119.2
N(2)-C(1)-H(1)	107.3	C(5)-C(6)-H(6)	119.2
N(1)-C(1)-H(1)	107.3	C(6)-C(7)-C(8)	120.13(17)
C(10)-C(1)-H(1)	107.3	C(6)-C(7)-H(7)	119.9
O(1)-C(2)-N(1)	120.91(16)	C(8)-C(7)-H(7)	119.9
O(1)-C(2)-C(3)	123.15(16)	N(2)-C(8)-C(3)	119.55(15)
N(1)-C(2)-C(3)	115.86(14)	N(2)-C(8)-C(7)	122.03(16)
C(4)-C(3)-C(8)	120.28(16)	C(3)-C(8)-C(7)	118.37(16)
C(4)-C(3)-C(2)	120.46(16)	N(2)-C(9)-H(9A)	109.5
C(8)-C(3)-C(2)	119.15(16)	N(2)-C(9)-H(9B)	109.5
C(5)-C(4)-C(3)	121.02(17)	H(9A)-C(9)-H(9B)	109.5
C(5)-C(4)-H(4)	119.5	N(2)-C(9)-H(9C)	109.5
C(3)-C(4)-H(4)	119.5	H(9A)-C(9)-H(9C)	109.5
C(4)-C(5)-C(6)	118.59(18)	H(9B)-C(9)-H(9C)	109.5
C(4)-C(5)-H(5)	120.7	F(1)-C(10)-C(11)	106.37(16)

F(1)-C(10)-C(12)	106.37(15)
C(11)-C(10)-C(12)	112.96(17)
F(1)-C(10)-C(1)	104.19(13)
C(11)-C(10)-C(1)	114.77(16)
C(12)-C(10)-C(1)	111.30(15)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(2)-N(1)-C(1)	125.01(15)
C(2)-N(1)-H(1A)	117.5
C(1)-N(1)-H(1A)	117.5
C(8)-N(2)-C(9)	120.86(14)
C(8)-N(2)-C(1)	119.22(14)
C(9)-N(2)-C(1)	117.74(14)

Symmetry transformations used to generate equivalent atoms:

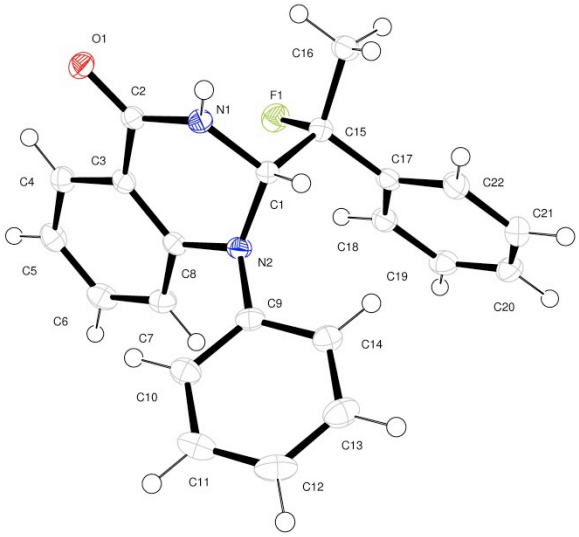
Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for t2f. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	23(1)	19(1)	18(1)	1(1)	2(1)	-1(1)
C(2)	19(1)	21(1)	21(1)	-4(1)	4(1)	4(1)
C(3)	19(1)	22(1)	23(1)	-3(1)	6(1)	3(1)
C(4)	23(1)	24(1)	30(1)	-6(1)	8(1)	0(1)
C(5)	26(1)	21(1)	41(1)	-1(1)	14(1)	-1(1)
C(6)	27(1)	23(1)	32(1)	6(1)	15(1)	6(1)
C(7)	23(1)	25(1)	23(1)	2(1)	7(1)	5(1)
C(8)	18(1)	20(1)	23(1)	-1(1)	7(1)	4(1)
C(9)	24(1)	26(1)	20(1)	-2(1)	2(1)	-1(1)
C(10)	21(1)	35(1)	19(1)	0(1)	1(1)	-2(1)
C(11)	27(1)	37(1)	34(1)	0(1)	11(1)	8(1)
C(12)	28(1)	46(1)	31(1)	6(1)	11(1)	0(1)
N(1)	22(1)	21(1)	18(1)	3(1)	1(1)	1(1)
N(2)	22(1)	22(1)	16(1)	0(1)	2(1)	-1(1)
O(1)	25(1)	27(1)	23(1)	-4(1)	-2(1)	2(1)
F(1)	22(1)	53(1)	26(1)	-4(1)	1(1)	-4(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2f.

	x	y	z	U(eq)
H(1)	7036	3198	7466	25
H(4)	11242	10377	8664	30
H(5)	11083	12580	7063	34
H(6)	9293	11613	5239	31
H(7)	7662	8535	5002	28
H(9A)	5488	5762	5186	36
H(9B)	6268	3472	5514	36
H(9C)	7355	5074	4894	36
H(11A)	4043	8179	8142	48
H(11B)	5352	8484	7272	48
H(11C)	6184	8328	8651	48
H(12A)	5885	4705	9637	51
H(12B)	5020	2837	8790	51
H(12C)	3774	4723	9018	51
H(1A)	8875	4047	9163	25

X-Ray Crystal Structure Data for 2s



A colorless prism 0.100 x 0.080 x 0.060 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 99.9% complete to 67.000° in θ. A total of 58533 reflections were collected covering the indices, -16<=*h*<=16, -15<=*k*<=15, -23<=*l*<=20. 3151 reflections were found to be symmetry independent, with an R_{int} of 0.0207. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P b c a (No. 61). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2013.

Table S8. Crystal data and structure refinement for 2s.

X-ray ID	toste82	
Sample/notebook ID	ken4-153-9	
Empirical formula	C22 H19 F N2 O	
Formula weight	346.39	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 13.5231(9) Å	α= 90°.
	b = 13.1489(9) Å	β= 90°.
	c = 19.3467(14) Å	γ = 90°.
Volume	3440.1(4) $Å^3$	
Z	8	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	0.730 mm^{-1}	
F(000)	1456	
Crystal size	0.100 x 0.080 x 0.060 mm^3	
Crystal color/habit	colorless prism	
Theta range for data collection	4.571 to 68.335°.	
Index ranges	-16<=h<=16, -15<=k<=15, -23<=l<=20	
Reflections collected	58533	
Independent reflections	3151 [R(int) = 0.0207]	
Completeness to theta = 67.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.880	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3151 / 0 / 236	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0946	
R indices (all data)	R1 = 0.0371, wR2 = 0.0948	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.475 and -0.322 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2s. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-122(1)	1466(1)	3698(1)	17(1)
C(2)	844(1)	1231(1)	4766(1)	17(1)
C(3)	1414(1)	2142(1)	4558(1)	18(1)
C(4)	2289(1)	2394(1)	4904(1)	21(1)
C(5)	2782(1)	3283(1)	4743(1)	24(1)
C(6)	2415(1)	3918(1)	4228(1)	25(1)
C(7)	1558(1)	3671(1)	3876(1)	22(1)
C(8)	1044(1)	2782(1)	4044(1)	18(1)
C(9)	-621(1)	3279(1)	3686(1)	19(1)
C(10)	-655(1)	4067(1)	4168(1)	23(1)
C(11)	-1394(1)	4797(1)	4132(1)	29(1)
C(12)	-2117(1)	4739(1)	3627(1)	31(1)
C(13)	-2099(1)	3948(1)	3157(1)	29(1)
C(14)	-1352(1)	3222(1)	3181(1)	23(1)
C(15)	404(1)	847(1)	3125(1)	19(1)
C(16)	137(1)	-273(1)	3174(1)	24(1)
C(17)	198(1)	1292(1)	2417(1)	20(1)
C(18)	885(1)	1924(1)	2097(1)	22(1)
C(19)	690(1)	2330(1)	1449(1)	26(1)
C(20)	-195(1)	2121(1)	1118(1)	27(1)
C(21)	-892(1)	1509(1)	1438(1)	28(1)
C(22)	-693(1)	1094(1)	2084(1)	24(1)
N(1)	46(1)	1015(1)	4376(1)	17(1)
N(2)	152(1)	2538(1)	3701(1)	18(1)
O(1)	1059(1)	726(1)	5285(1)	22(1)
F(1)	1431(1)	915(1)	3253(1)	26(1)

Table S10. Bond lengths [Å] and angles [°] for 2s.

C(1)-N(2)	1.4576(16)	C(11)-H(11)	0.9500
C(1)-N(1)	1.4581(16)	C(12)-C(13)	1.381(2)
C(1)-C(15)	1.5489(18)	C(12)-H(12)	0.9500
C(1)-H(1)	1.0000	C(13)-C(14)	1.391(2)
C(2)-O(1)	1.2390(16)	C(13)-H(13)	0.9500
C(2)-N(1)	1.3471(17)	C(14)-H(14)	0.9500
C(2)-C(3)	1.4796(18)	C(15)-F(1)	1.4135(15)
C(3)-C(8)	1.3954(19)	C(15)-C(17)	1.5149(18)
C(3)-C(4)	1.3995(18)	C(15)-C(16)	1.5188(18)
C(4)-C(5)	1.382(2)	C(16)-H(16A)	0.9800
C(4)-H(4)	0.9500	C(16)-H(16B)	0.9800
C(5)-C(6)	1.393(2)	C(16)-H(16C)	0.9800
C(5)-H(5)	0.9500	C(17)-C(18)	1.3907(19)
C(6)-C(7)	1.383(2)	C(17)-C(22)	1.392(2)
C(6)-H(6)	0.9500	C(18)-C(19)	1.389(2)
C(7)-C(8)	1.3979(19)	C(18)-H(18)	0.9500
C(7)-H(7)	0.9500	C(19)-C(20)	1.384(2)
C(8)-N(2)	1.4129(17)	C(19)-H(19)	0.9500
C(9)-C(14)	1.3915(19)	C(20)-C(21)	1.385(2)
C(9)-C(10)	1.3952(19)	C(20)-H(20)	0.9500
C(9)-N(2)	1.4300(16)	C(21)-C(22)	1.390(2)
C(10)-C(11)	1.387(2)	C(21)-H(21)	0.9500
C(10)-H(10)	0.9500	C(22)-H(22)	0.9500
C(11)-C(12)	1.385(2)	N(1)-H(1A)	0.8800
N(2)-C(1)-N(1)	110.50(10)	C(8)-C(3)-C(4)	120.12(12)
N(2)-C(1)-C(15)	113.26(10)	C(8)-C(3)-C(2)	119.66(12)
N(1)-C(1)-C(15)	111.01(10)	C(4)-C(3)-C(2)	120.10(12)
N(2)-C(1)-H(1)	107.3	C(5)-C(4)-C(3)	120.02(13)
N(1)-C(1)-H(1)	107.3	C(5)-C(4)-H(4)	120.0
C(15)-C(1)-H(1)	107.3	C(3)-C(4)-H(4)	120.0
O(1)-C(2)-N(1)	121.83(12)	C(4)-C(5)-C(6)	119.76(13)
O(1)-C(2)-C(3)	122.18(12)	C(4)-C(5)-H(5)	120.1
N(1)-C(2)-C(3)	115.90(11)	C(6)-C(5)-H(5)	120.1

C(7)-C(6)-C(5)	120.75(13)	C(15)-C(16)-H(16C)	109.5
C(7)-C(6)-H(6)	119.6	H(16A)-C(16)-H(16C)	109.5
C(5)-C(6)-H(6)	119.6	H(16B)-C(16)-H(16C)	109.5
C(6)-C(7)-C(8)	119.85(13)	C(18)-C(17)-C(22)	118.94(12)
C(6)-C(7)-H(7)	120.1	C(18)-C(17)-C(15)	120.72(12)
C(8)-C(7)-H(7)	120.1	C(22)-C(17)-C(15)	120.32(12)
C(3)-C(8)-C(7)	119.48(12)	C(19)-C(18)-C(17)	120.35(13)
C(3)-C(8)-N(2)	120.23(11)	C(19)-C(18)-H(18)	119.8
C(7)-C(8)-N(2)	120.28(12)	C(17)-C(18)-H(18)	119.8
C(14)-C(9)-C(10)	119.11(12)	C(20)-C(19)-C(18)	120.28(13)
C(14)-C(9)-N(2)	119.85(12)	C(20)-C(19)-H(19)	119.9
C(10)-C(9)-N(2)	121.05(12)	C(18)-C(19)-H(19)	119.9
C(11)-C(10)-C(9)	120.28(14)	C(19)-C(20)-C(21)	119.86(13)
C(11)-C(10)-H(10)	119.9	C(19)-C(20)-H(20)	120.1
C(9)-C(10)-H(10)	119.9	C(21)-C(20)-H(20)	120.1
C(12)-C(11)-C(10)	120.36(14)	C(20)-C(21)-C(22)	119.88(14)
C(12)-C(11)-H(11)	119.8	C(20)-C(21)-H(21)	120.1
C(10)-C(11)-H(11)	119.8	C(22)-C(21)-H(21)	120.1
C(13)-C(12)-C(11)	119.61(13)	C(21)-C(22)-C(17)	120.68(13)
C(13)-C(12)-H(12)	120.2	C(21)-C(22)-H(22)	119.7
C(11)-C(12)-H(12)	120.2	C(17)-C(22)-H(22)	119.7
C(12)-C(13)-C(14)	120.51(14)	C(2)-N(1)-C(1)	122.82(11)
C(12)-C(13)-H(13)	119.7	C(2)-N(1)-H(1A)	118.6
C(14)-C(13)-H(13)	119.7	C(1)-N(1)-H(1A)	118.6
C(13)-C(14)-C(9)	120.12(13)	C(8)-N(2)-C(9)	118.69(10)
C(13)-C(14)-H(14)	119.9	C(8)-N(2)-C(1)	116.02(10)
C(9)-C(14)-H(14)	119.9	C(9)-N(2)-C(1)	118.20(10)
F(1)-C(15)-C(17)	108.34(10)		
F(1)-C(15)-C(16)	106.47(10)		
C(17)-C(15)-C(16)	112.81(11)		
F(1)-C(15)-C(1)	106.97(10)		
C(17)-C(15)-C(1)	111.07(10)		
C(16)-C(15)-C(1)	110.87(11)		
C(15)-C(16)-H(16A)	109.5		
C(15)-C(16)-H(16B)	109.5		
H(16A)-C(16)-H(16B)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2s. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(1)	15(1)	17(1)	1(1)	-1(1)	-1(1)
C(2)	19(1)	16(1)	16(1)	-2(1)	3(1)	3(1)
C(3)	19(1)	18(1)	17(1)	-3(1)	4(1)	1(1)
C(4)	19(1)	23(1)	20(1)	-3(1)	1(1)	2(1)
C(5)	19(1)	26(1)	28(1)	-6(1)	0(1)	-2(1)
C(6)	23(1)	20(1)	33(1)	-2(1)	5(1)	-5(1)
C(7)	24(1)	18(1)	25(1)	2(1)	2(1)	0(1)
C(8)	18(1)	17(1)	18(1)	-3(1)	2(1)	1(1)
C(9)	19(1)	16(1)	22(1)	4(1)	4(1)	-1(1)
C(10)	24(1)	20(1)	26(1)	0(1)	4(1)	-2(1)
C(11)	29(1)	19(1)	40(1)	-3(1)	10(1)	0(1)
C(12)	22(1)	22(1)	48(1)	7(1)	6(1)	5(1)
C(13)	21(1)	28(1)	38(1)	8(1)	-2(1)	1(1)
C(14)	25(1)	21(1)	24(1)	3(1)	0(1)	0(1)
C(15)	20(1)	18(1)	19(1)	0(1)	0(1)	1(1)
C(16)	33(1)	18(1)	21(1)	-1(1)	2(1)	0(1)
C(17)	27(1)	15(1)	17(1)	-2(1)	2(1)	2(1)
C(18)	26(1)	19(1)	22(1)	-1(1)	1(1)	0(1)
C(19)	34(1)	21(1)	23(1)	3(1)	5(1)	1(1)
C(20)	41(1)	23(1)	19(1)	2(1)	-2(1)	5(1)
C(21)	33(1)	28(1)	24(1)	-2(1)	-7(1)	-1(1)
C(22)	30(1)	21(1)	22(1)	0(1)	-1(1)	-4(1)
N(1)	19(1)	16(1)	16(1)	2(1)	1(1)	-2(1)
N(2)	19(1)	14(1)	20(1)	1(1)	-1(1)	0(1)
O(1)	25(1)	21(1)	18(1)	4(1)	-3(1)	-2(1)
F(1)	24(1)	28(1)	24(1)	1(1)	0(1)	3(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2s.

	x	y	z	U(eq)
H(1)	-849	1430	3605	20
H(4)	2544	1953	5250	25
H(5)	3370	3461	4984	29
H(6)	2757	4527	4116	31
H(7)	1318	4105	3521	27
H(10)	-170	4104	4522	28
H(11)	-1405	5339	4457	35
H(12)	-2622	5240	3603	37
H(13)	-2601	3900	2815	35
H(14)	-1341	2685	2852	28
H(16A)	-584	-347	3175	36
H(16B)	410	-558	3601	36
H(16C)	413	-636	2776	36
H(18)	1489	2079	2324	27
H(19)	1166	2754	1231	31
H(20)	-324	2396	673	33
H(21)	-1504	1373	1216	34
H(22)	-1171	672	2301	29
H(1A)	-393	582	4538	20

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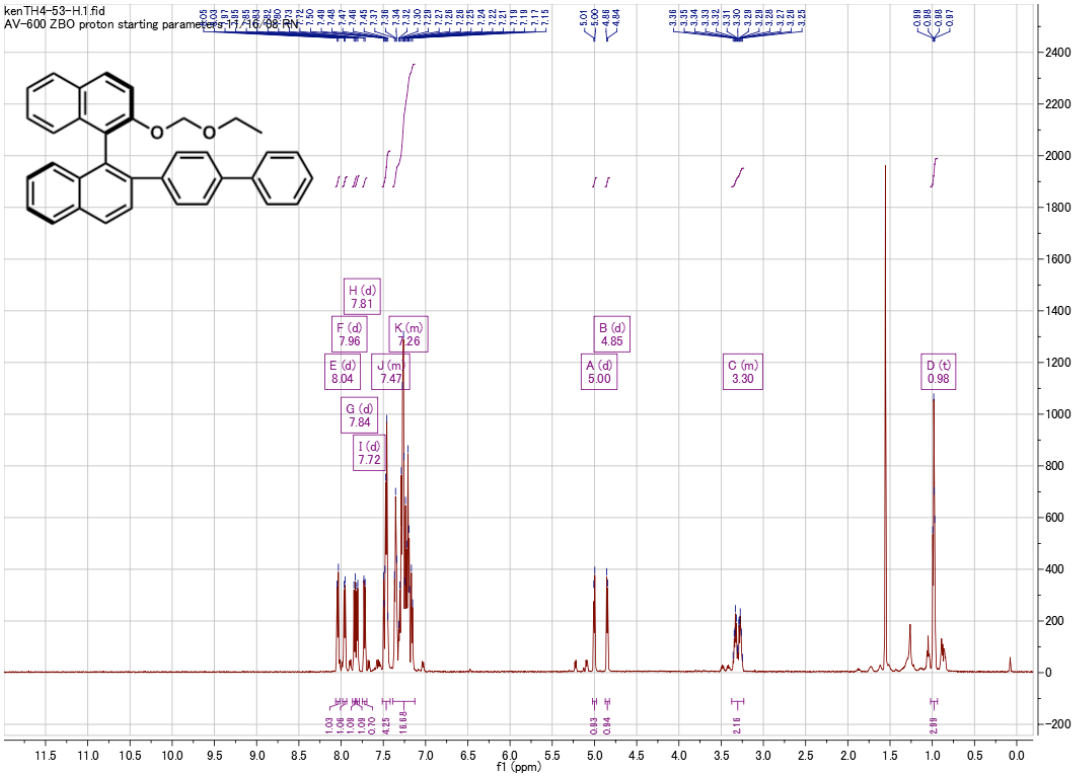
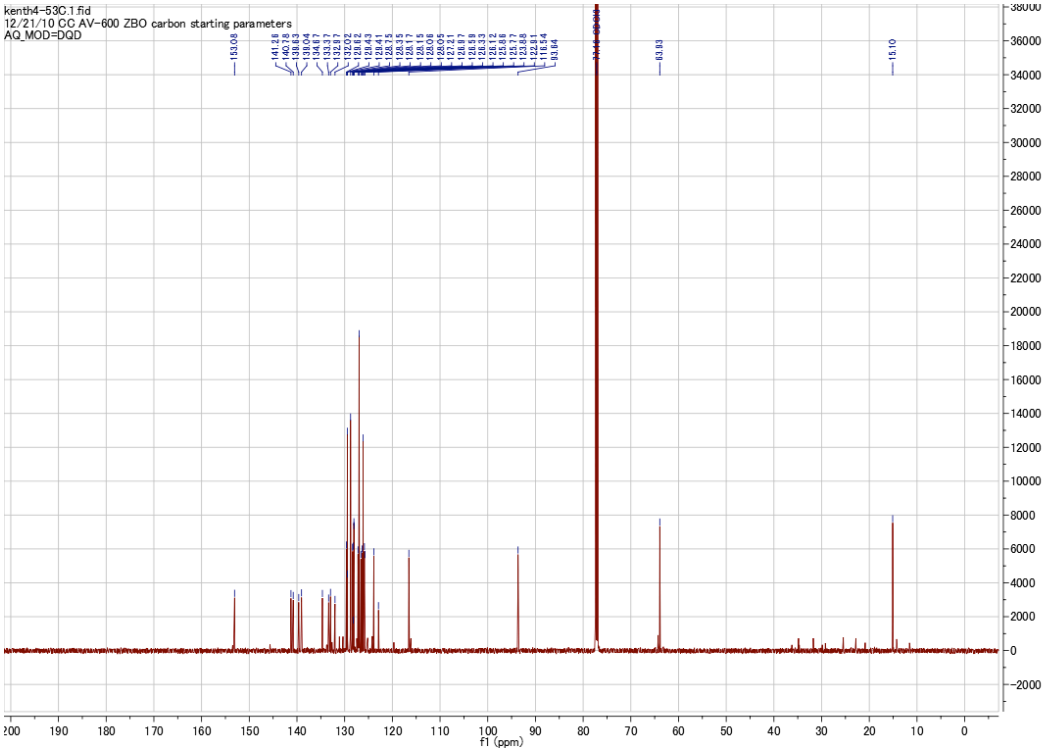
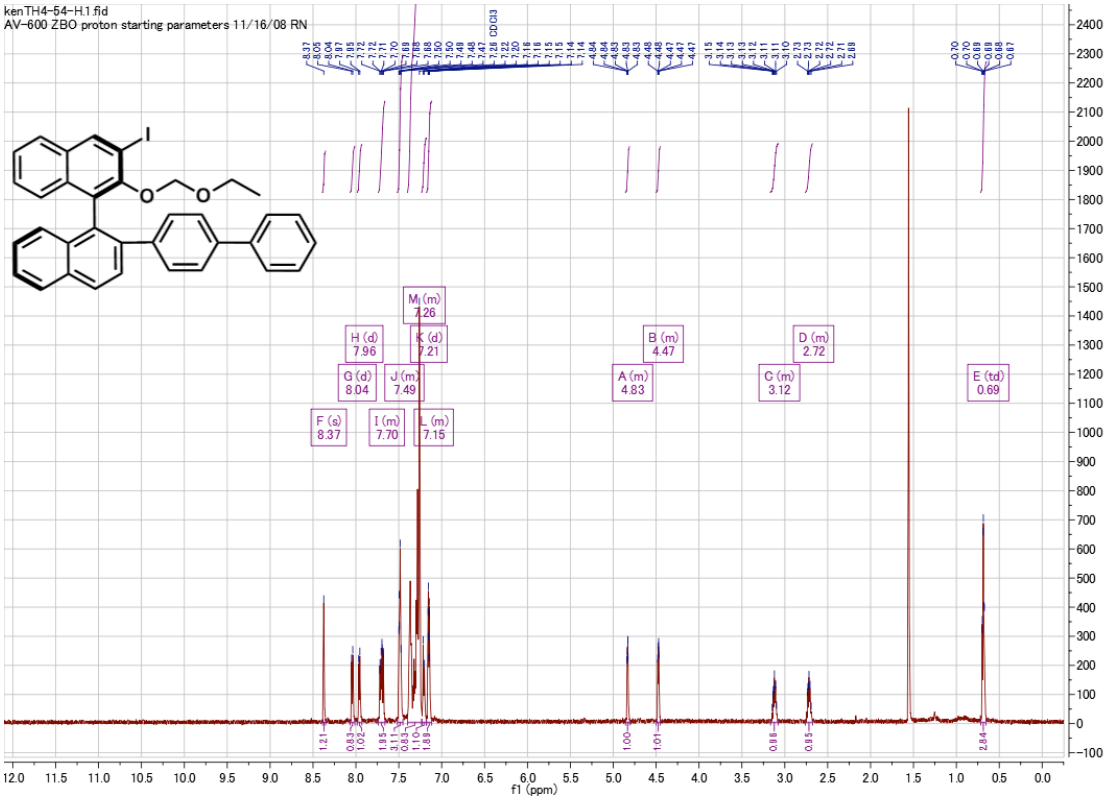
NMR Spectra

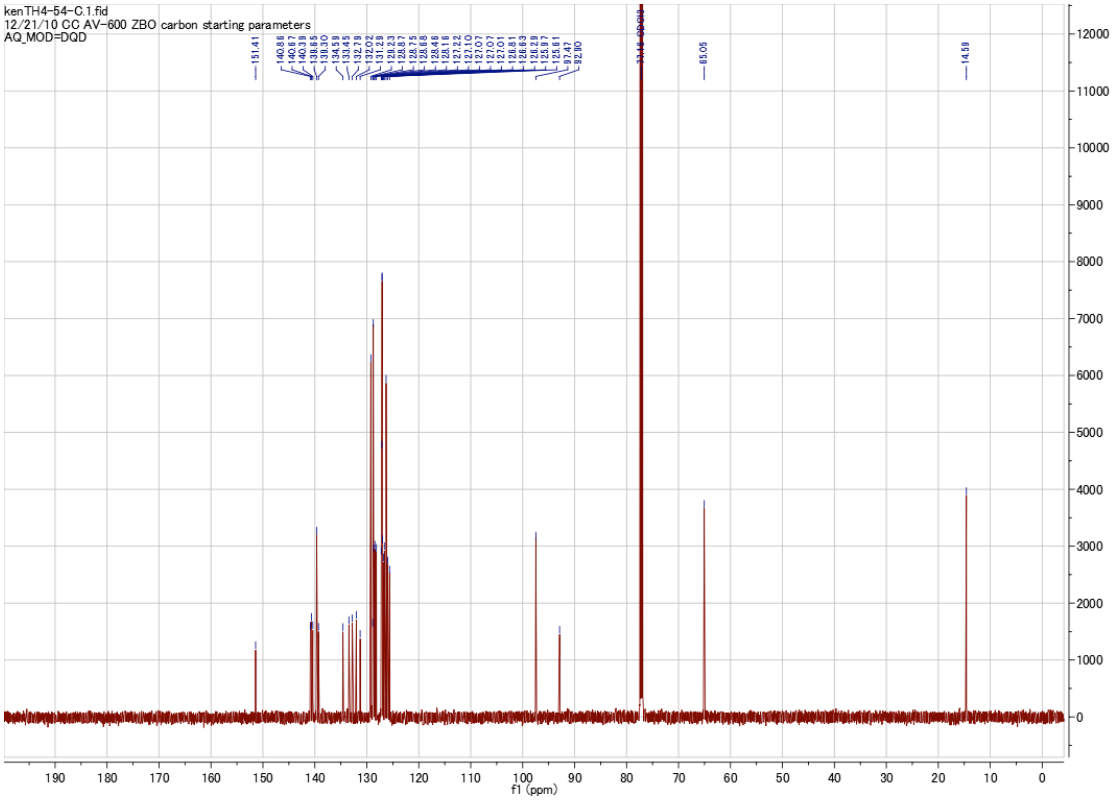
_(R)_- 2-([1,1'-biphenyl]-4-yl)-2'-(ethoxymethoxy)-1,1'-binaphthalene (_(R)_-S4).



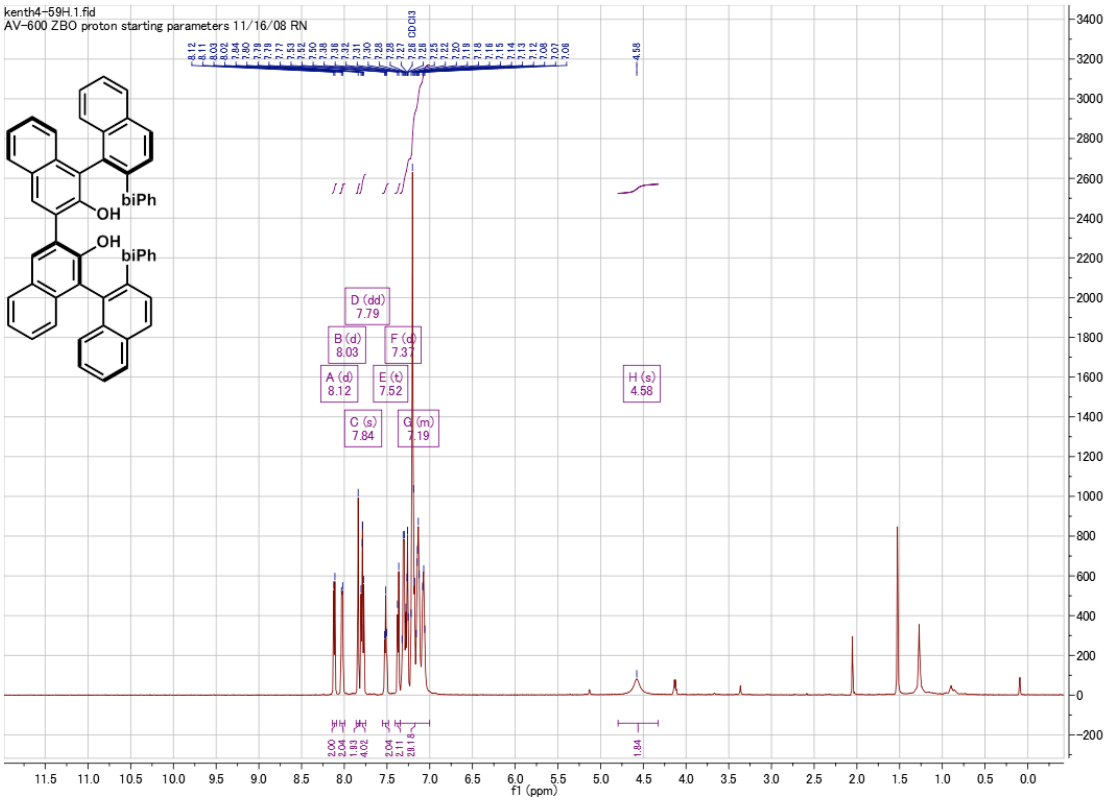


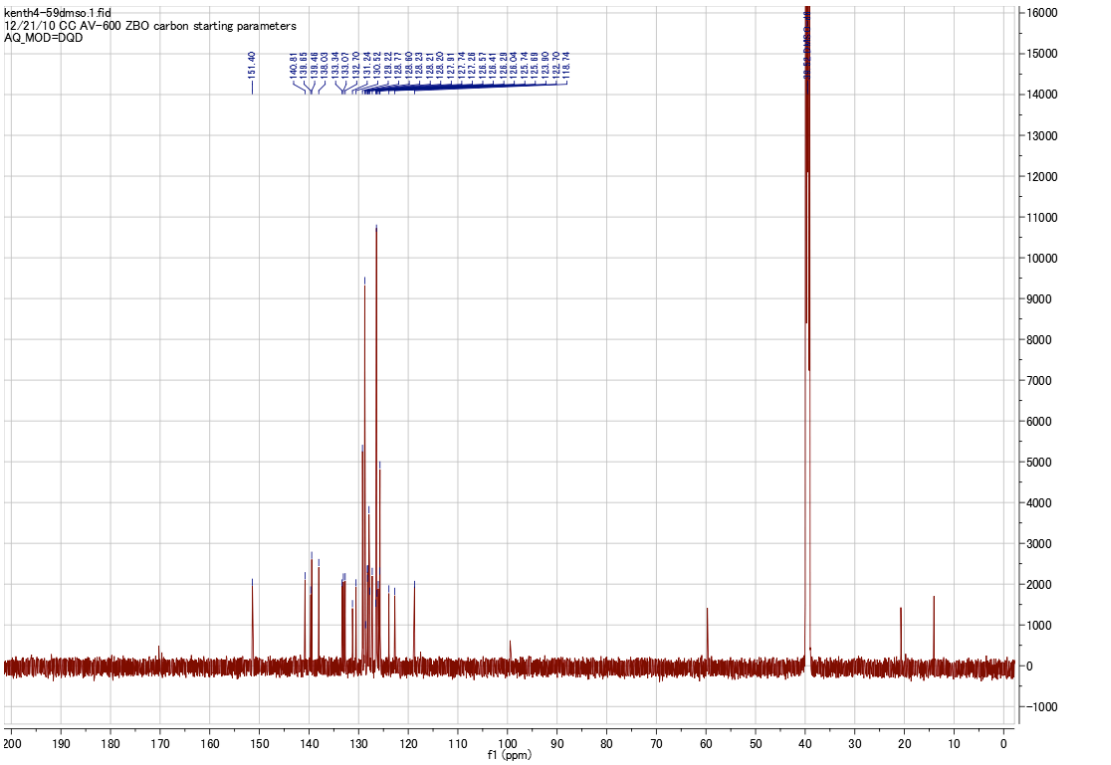
***(R)*-2'-([1,1'-biphenyl]-4-yl)-2-(ethoxymethoxy)-3-iodo-1,1'-binaphthalene (*(R)*-S5)**.



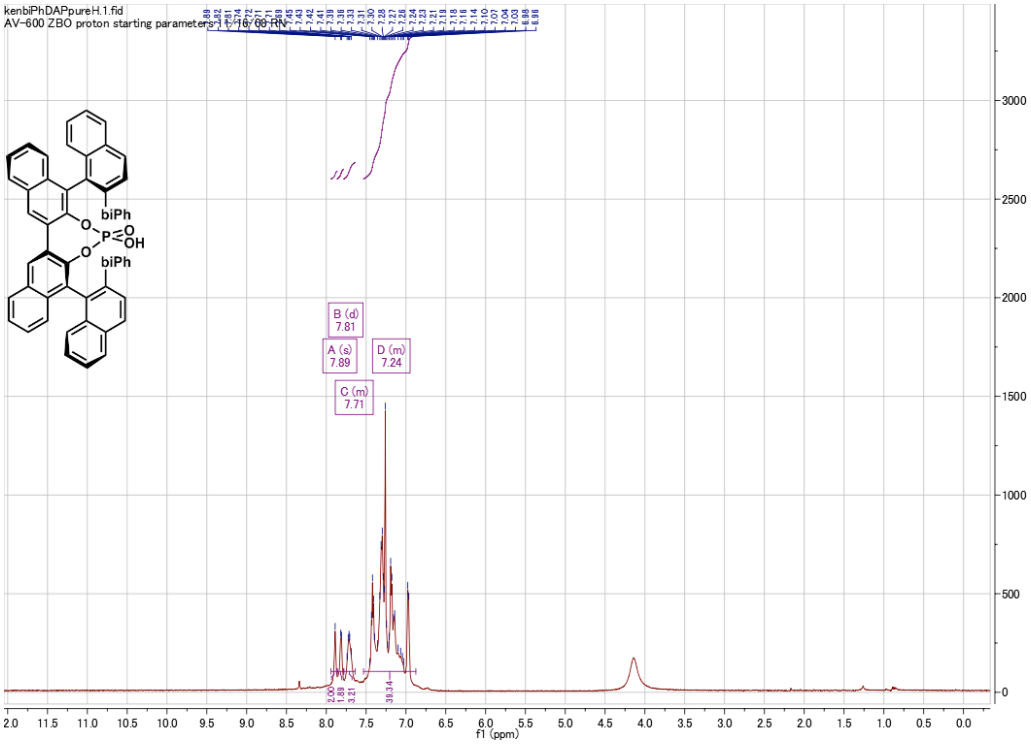


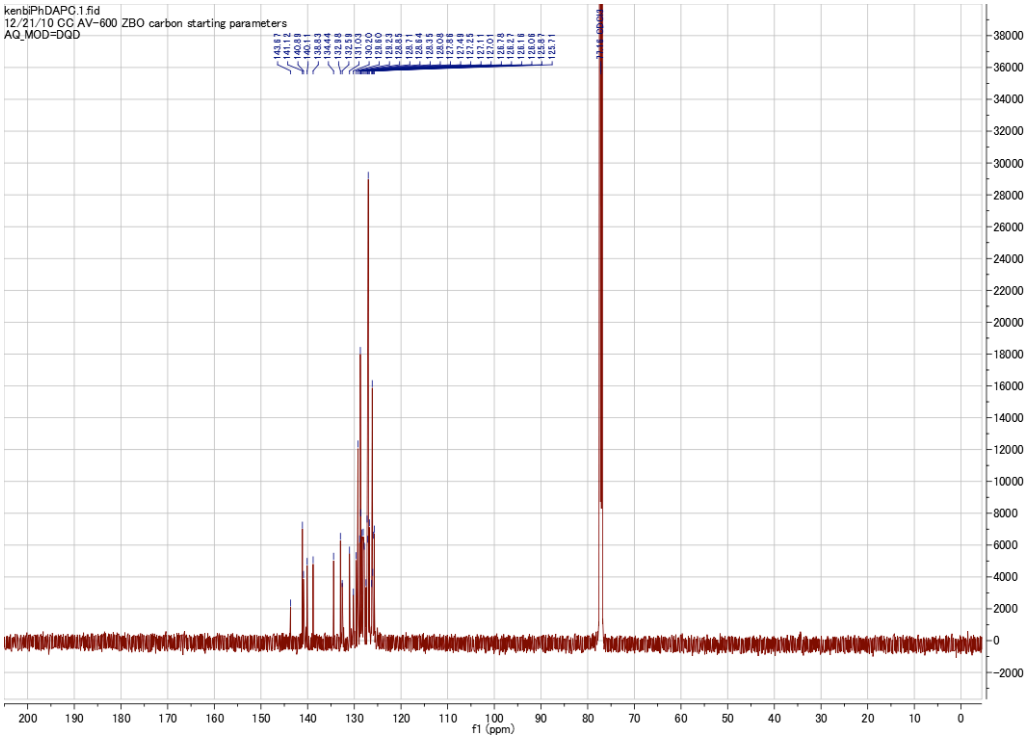
***(R,R)*- 2,2'''-di([1,1'-biphenyl]-4-yl)-[1,1':3',2'':4'',1'''-quaternaphthalene]-2',3''-diol (*(R,R)*-S8)**.

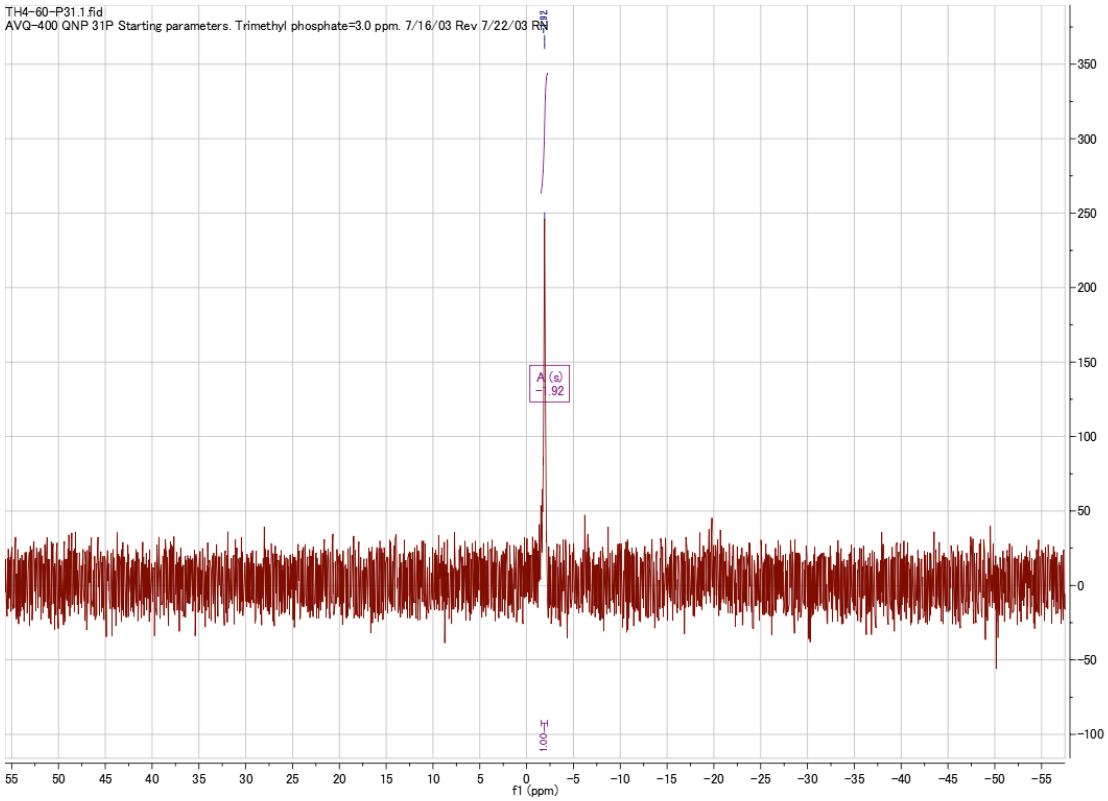




(R,R)*-5,9-bis(2-([1,1'-biphenyl]-4-yl)naphthalen-1-yl)-7-hydroxydinaphtho[2,3-d:2',3'-f][1,3,2]dioxaphosphepine 7-oxide (*(R,R)-4-Ph-PhDAP).



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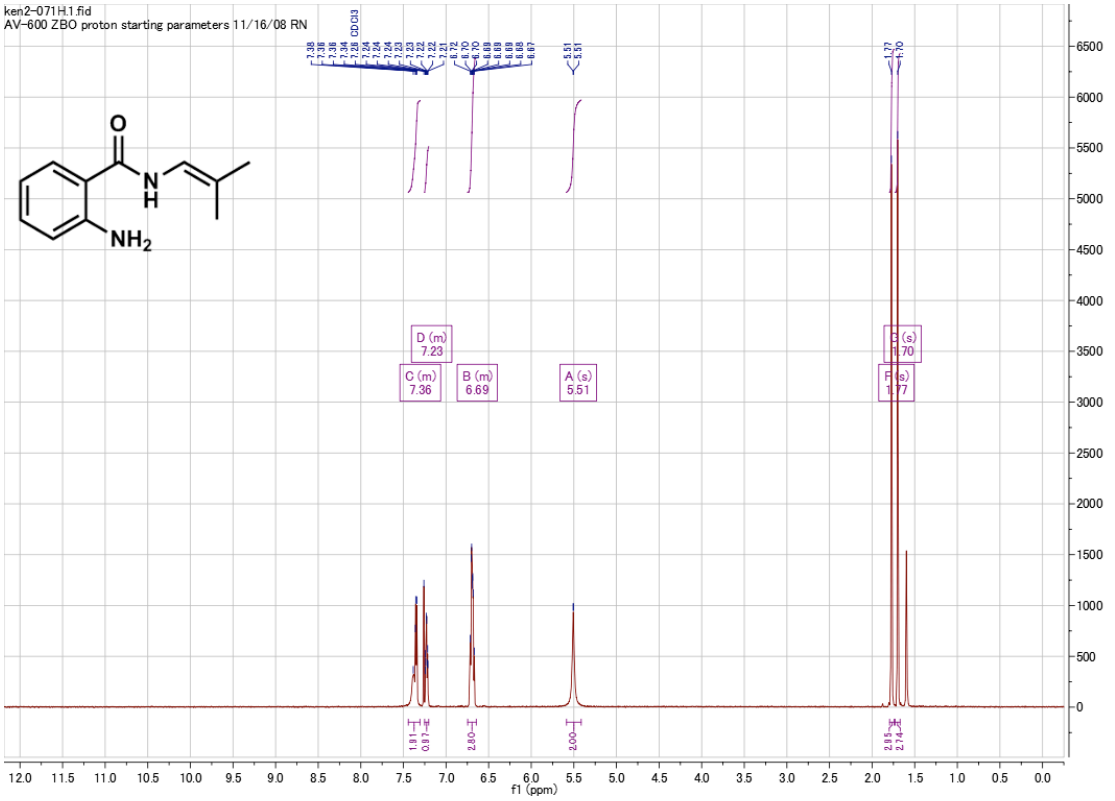
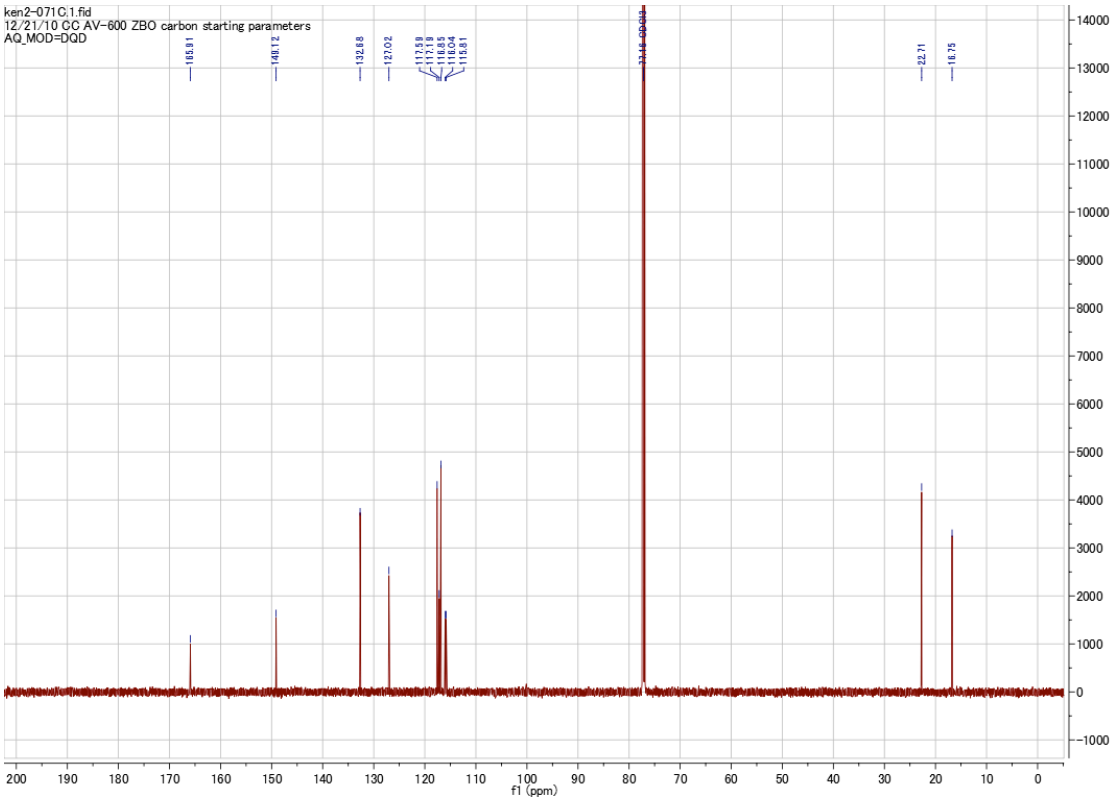
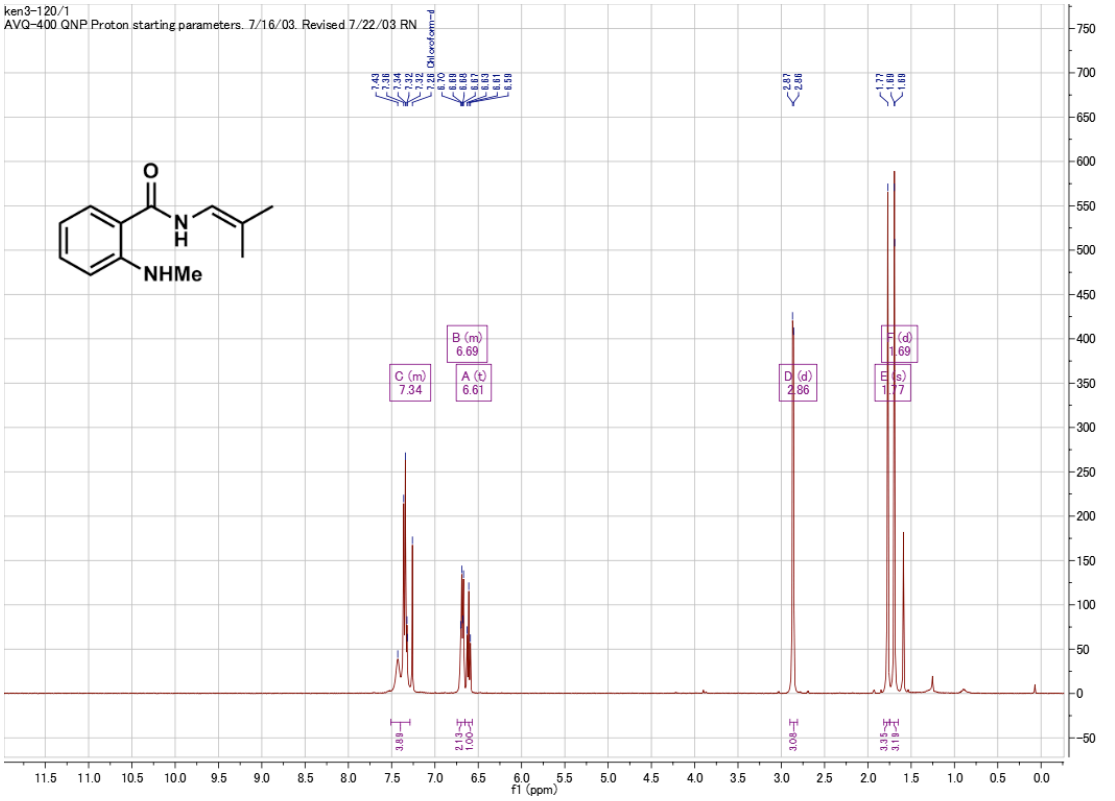
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RM
A (s)
1.92
1.00
f1 (ppm)

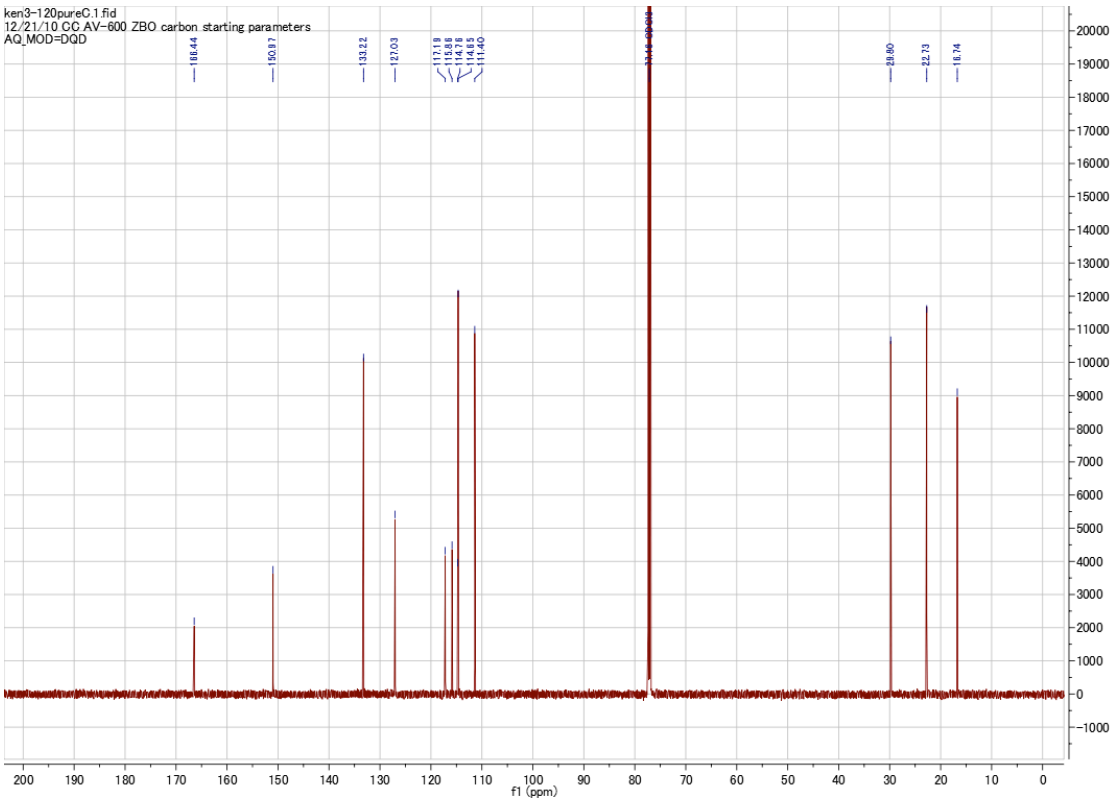
2-amino-N-(2-methylprop-1-en-1-yl)benzamide (1e)



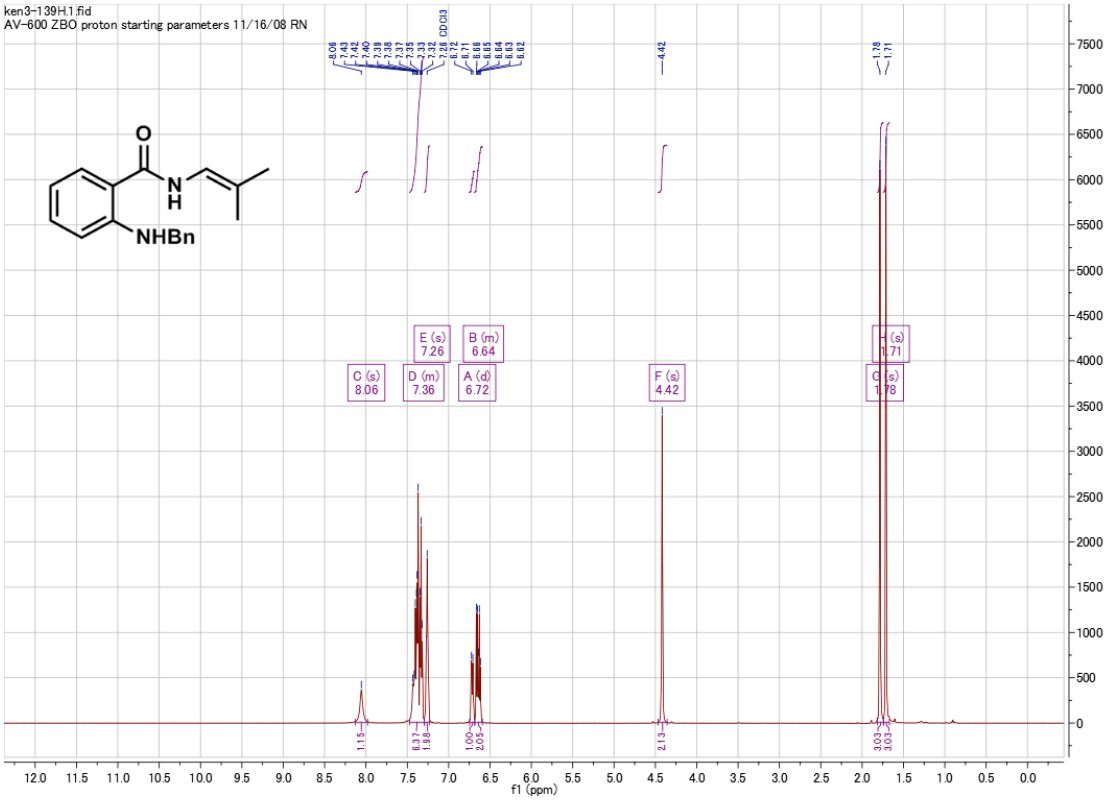


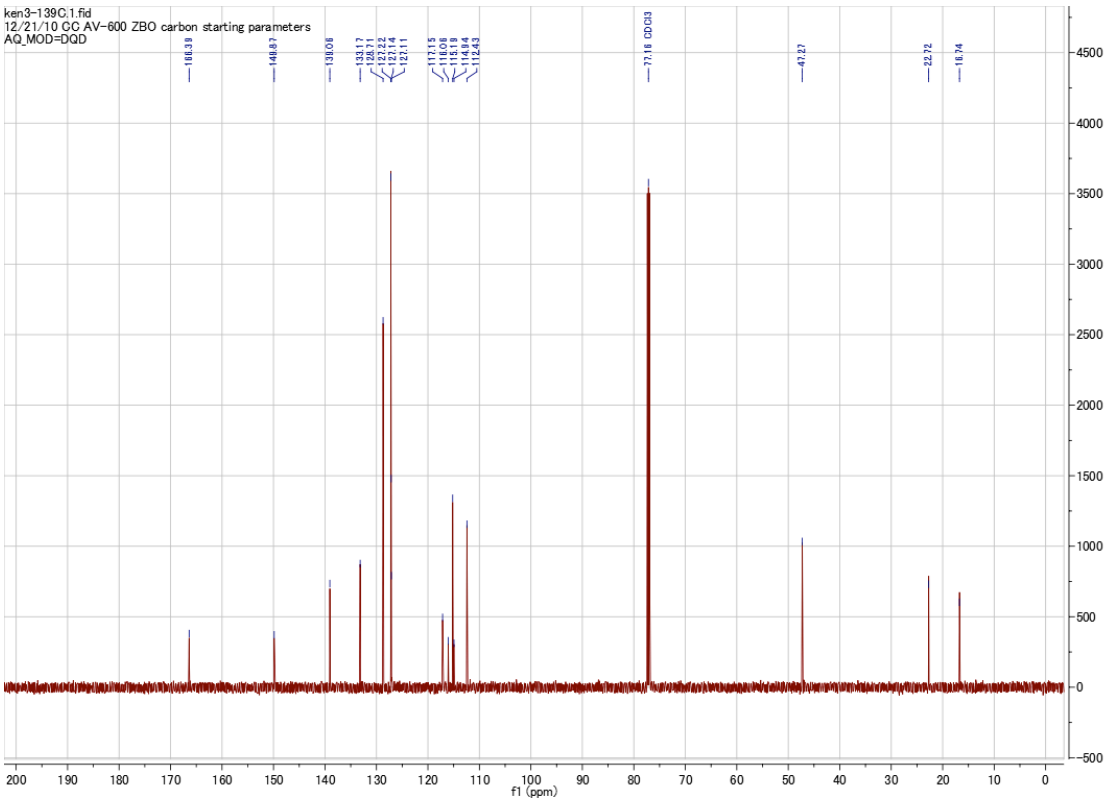
2-(methylamino)-N-(2-methylprop-1-en-1-yl)benzamide (1f)



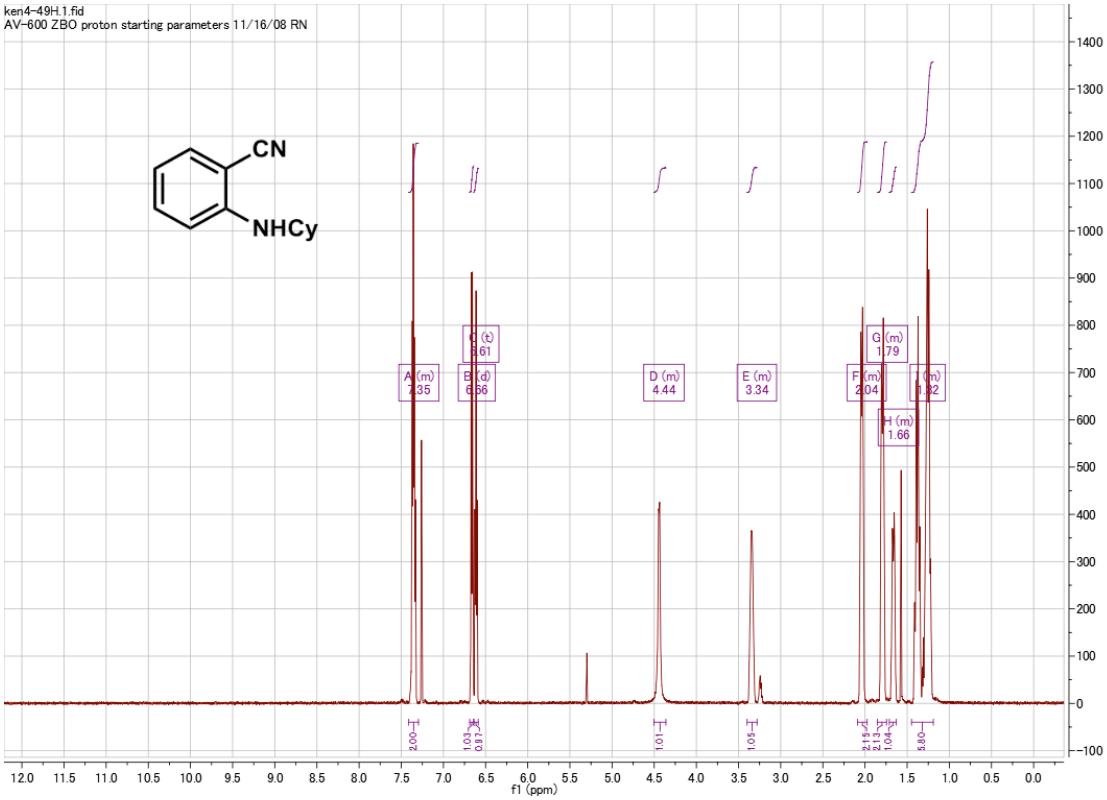


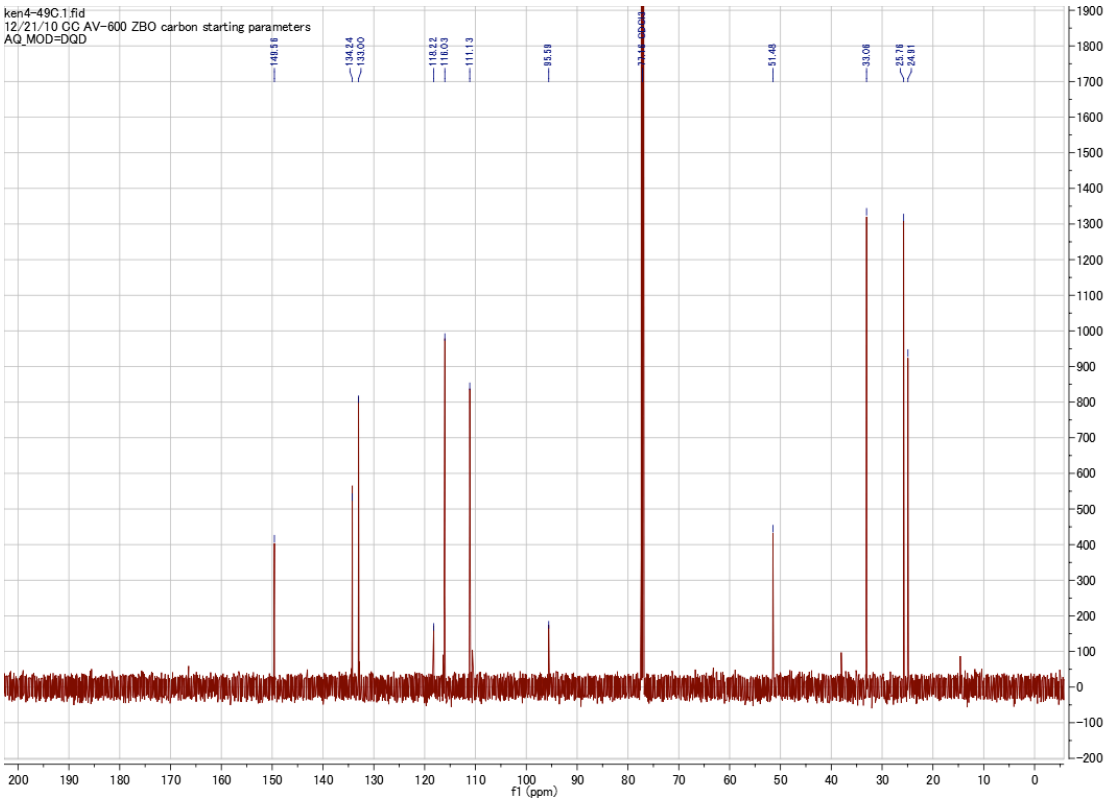
2-(benzylamino)-N-(2-methylprop-1-en-1-yl)benzamide (1g)



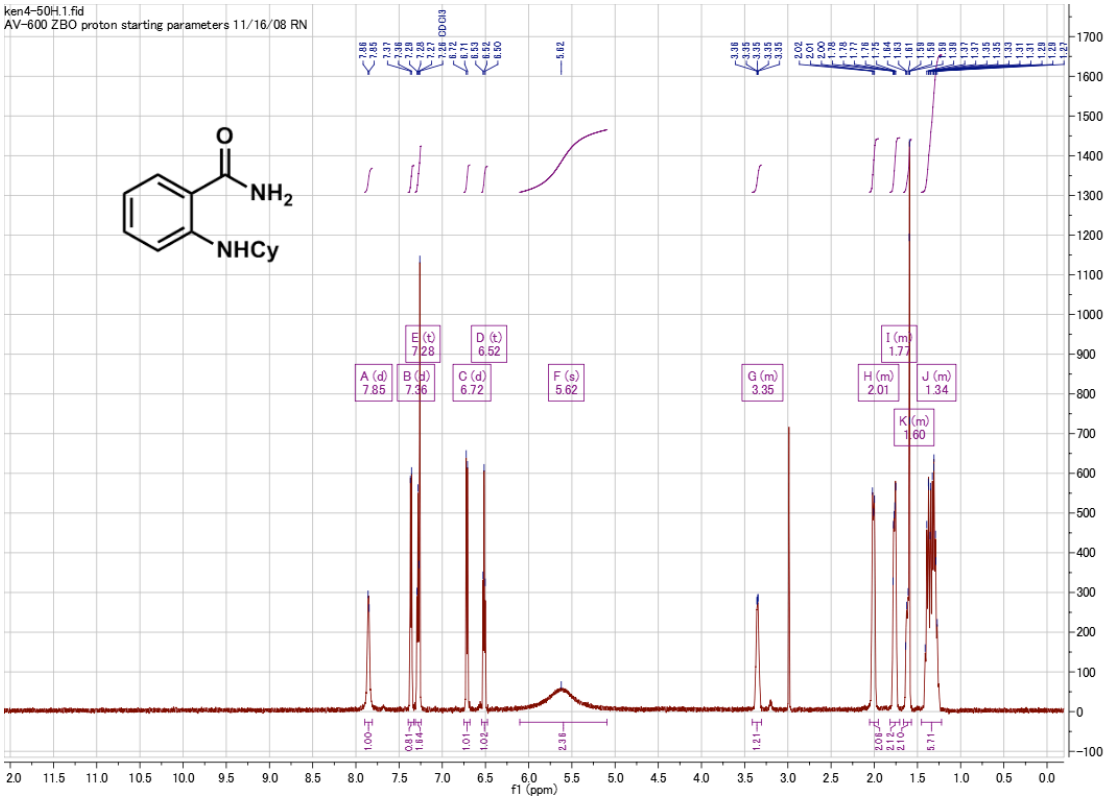


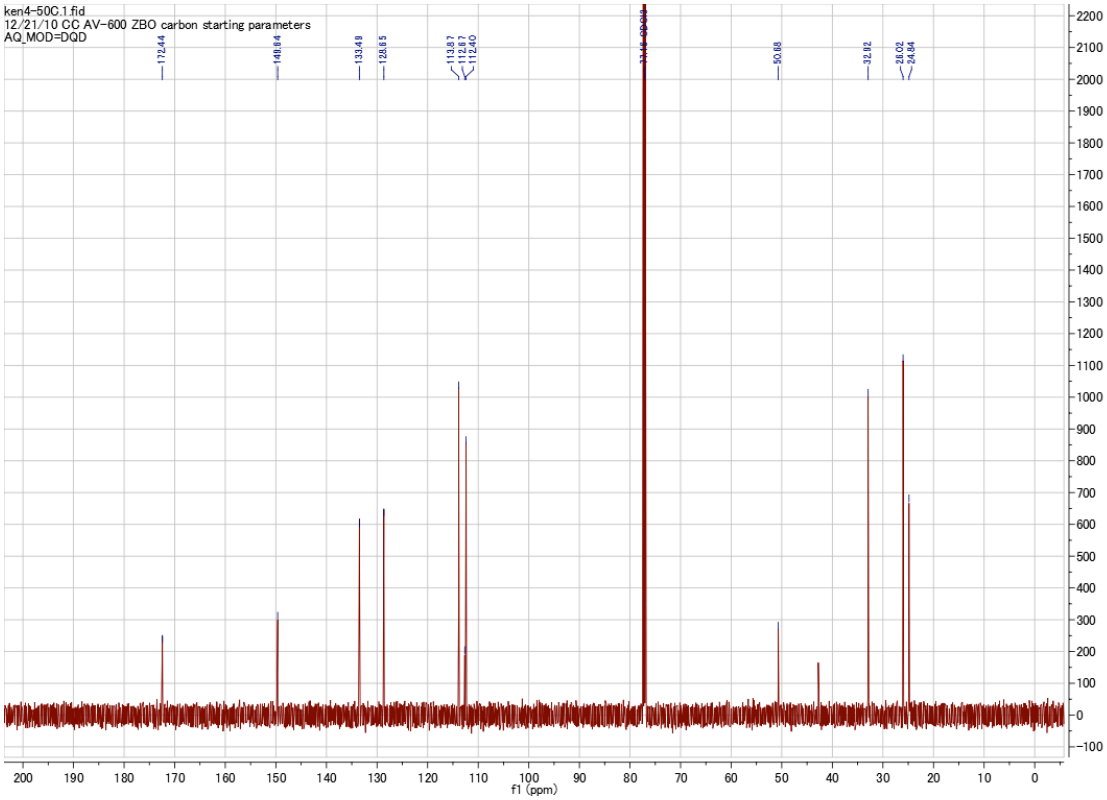
2-(cyclohexylamino)benzamide



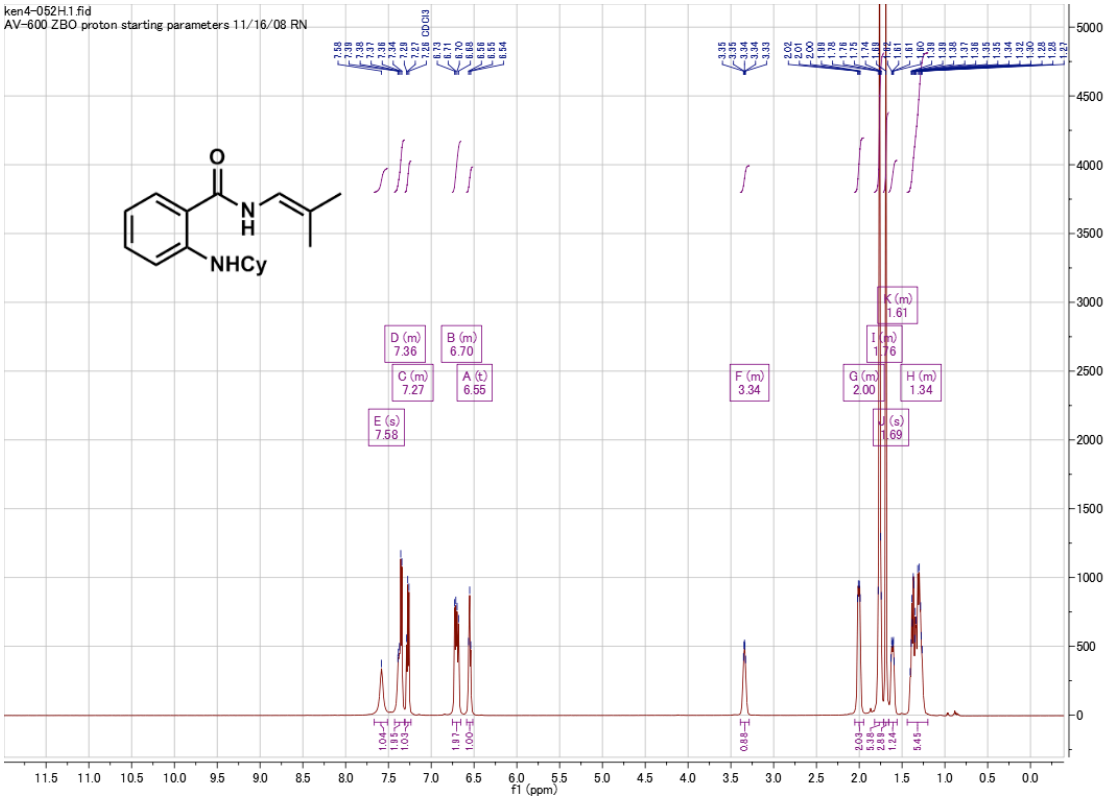


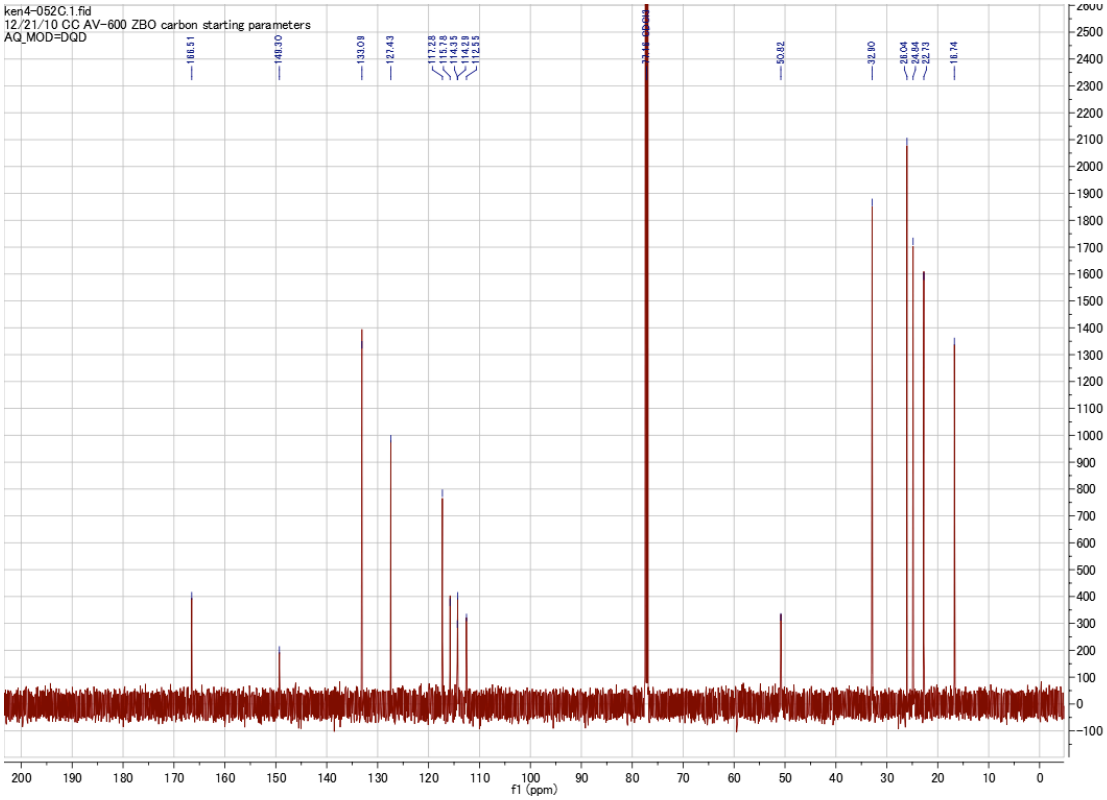
2-(cyclohexylamino)benzamide



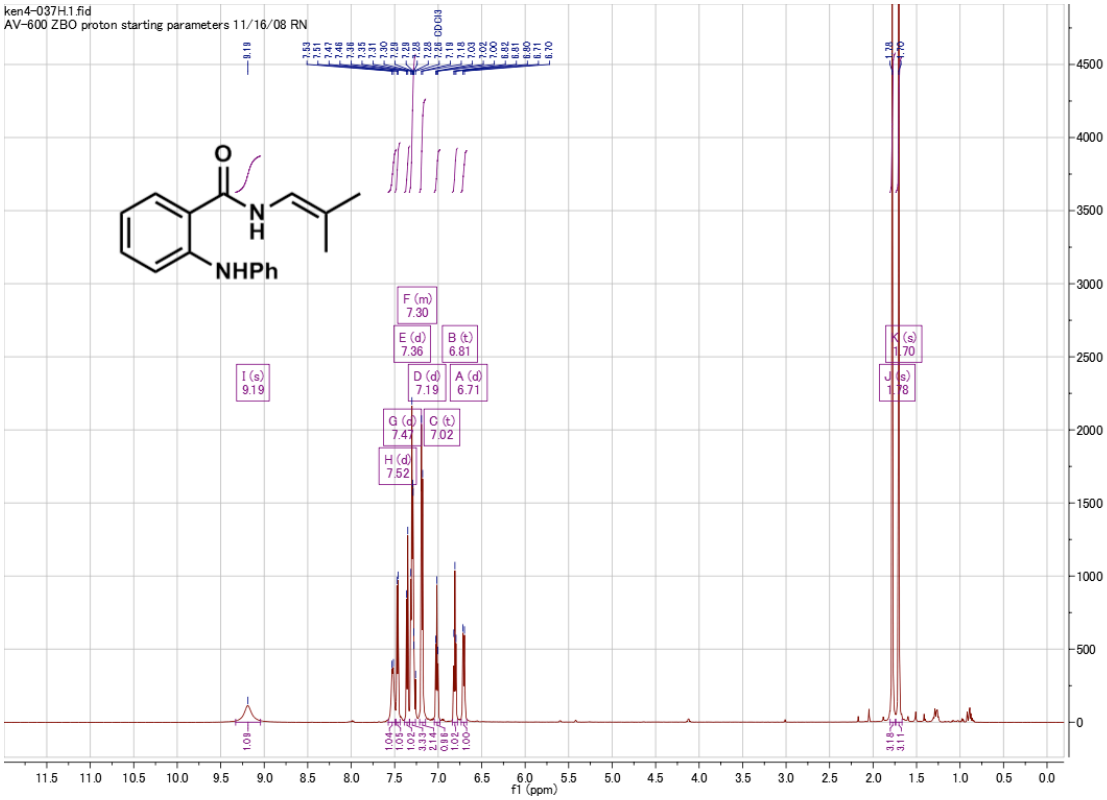


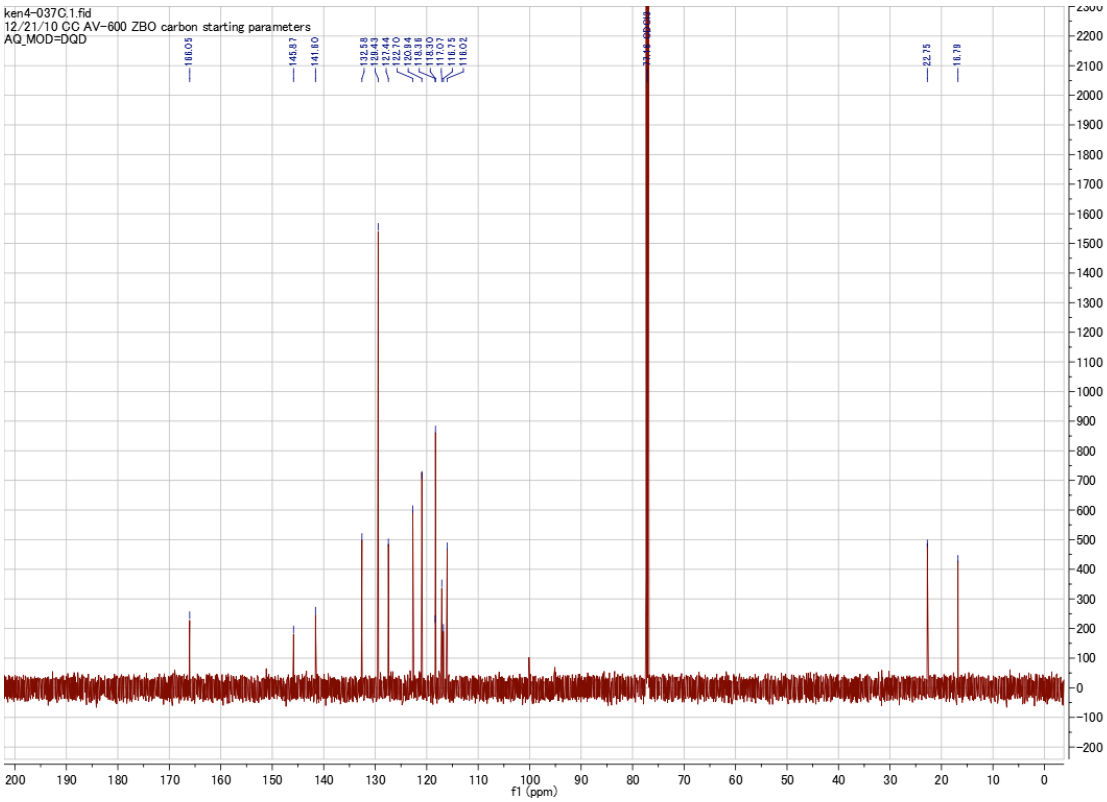
2-(cyclohexylamino)-N-(2-methylprop-1-en-1-yl)benzamide (1h)



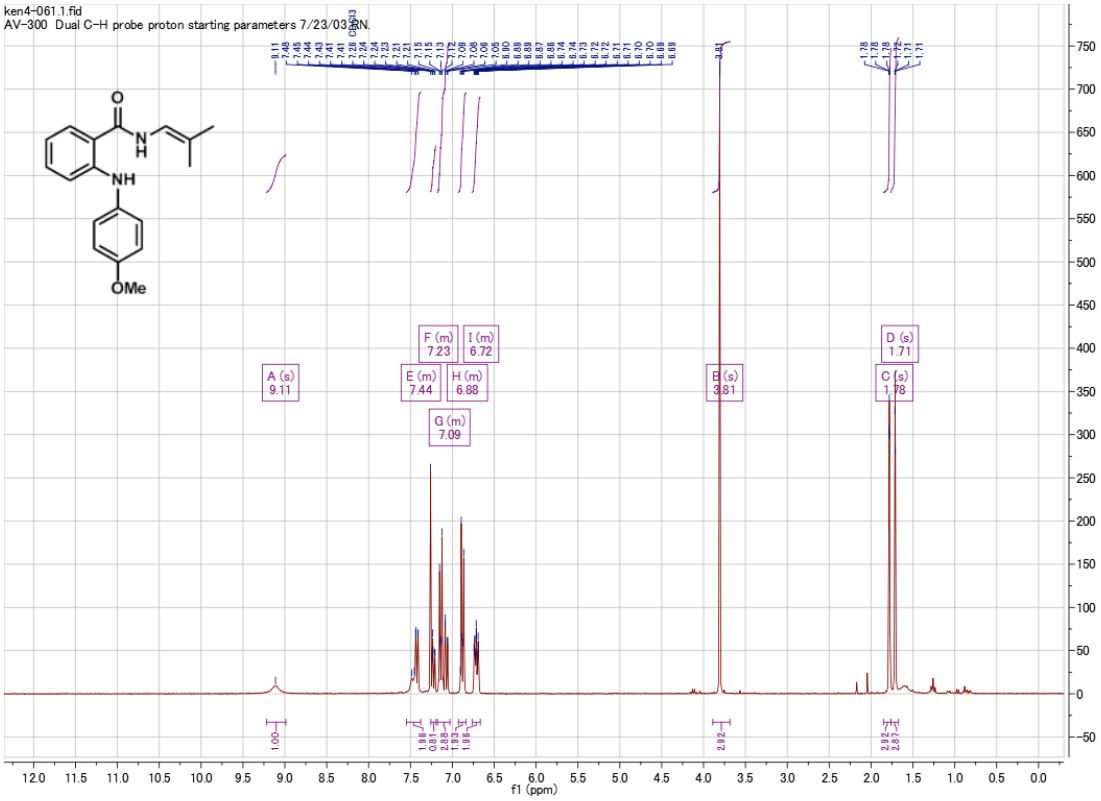


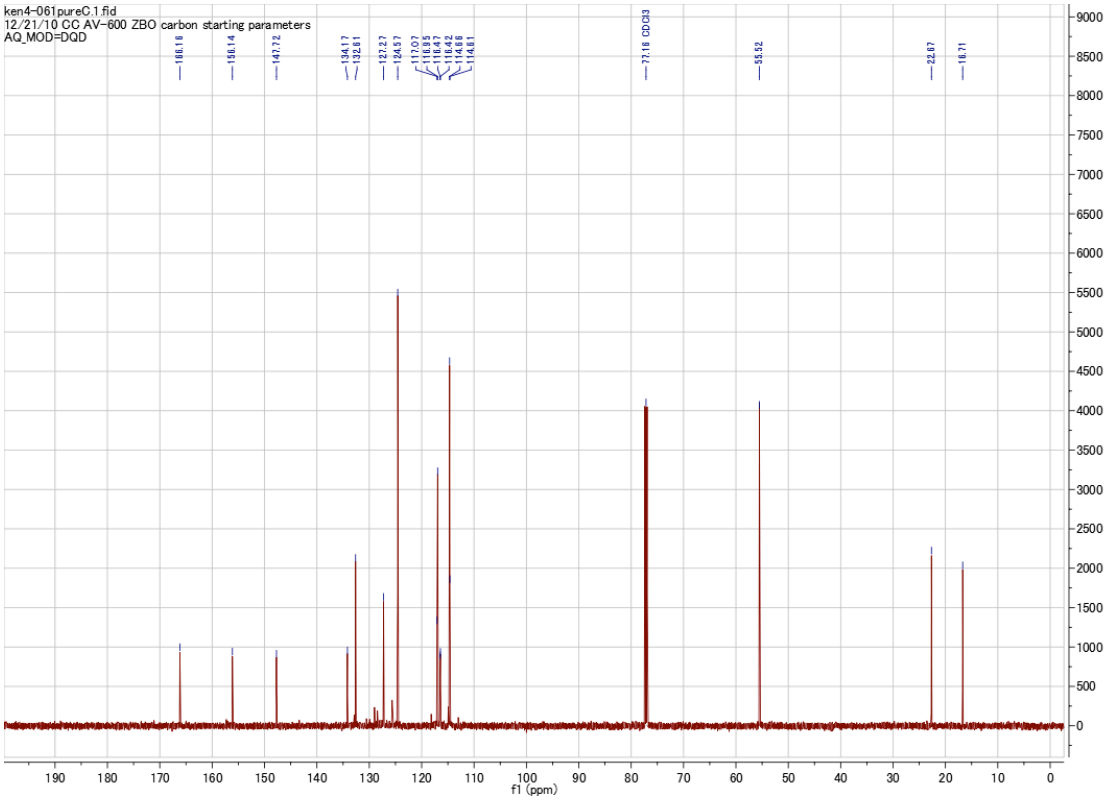
N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1i)



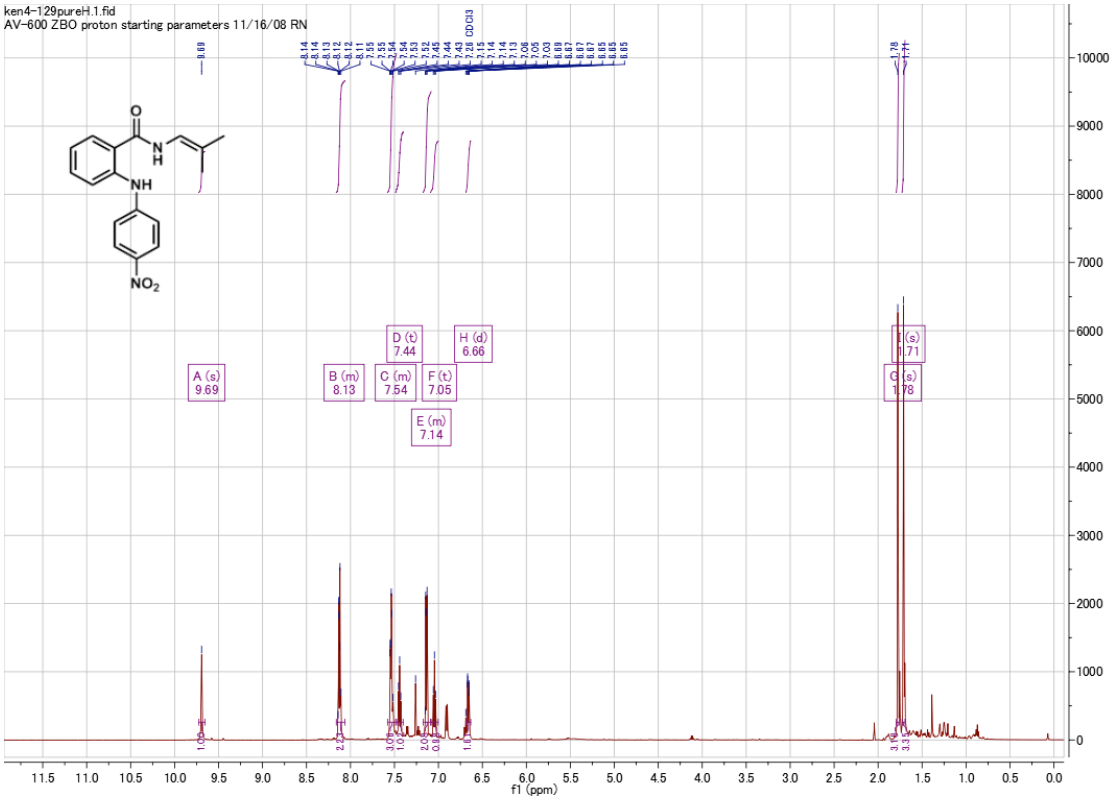


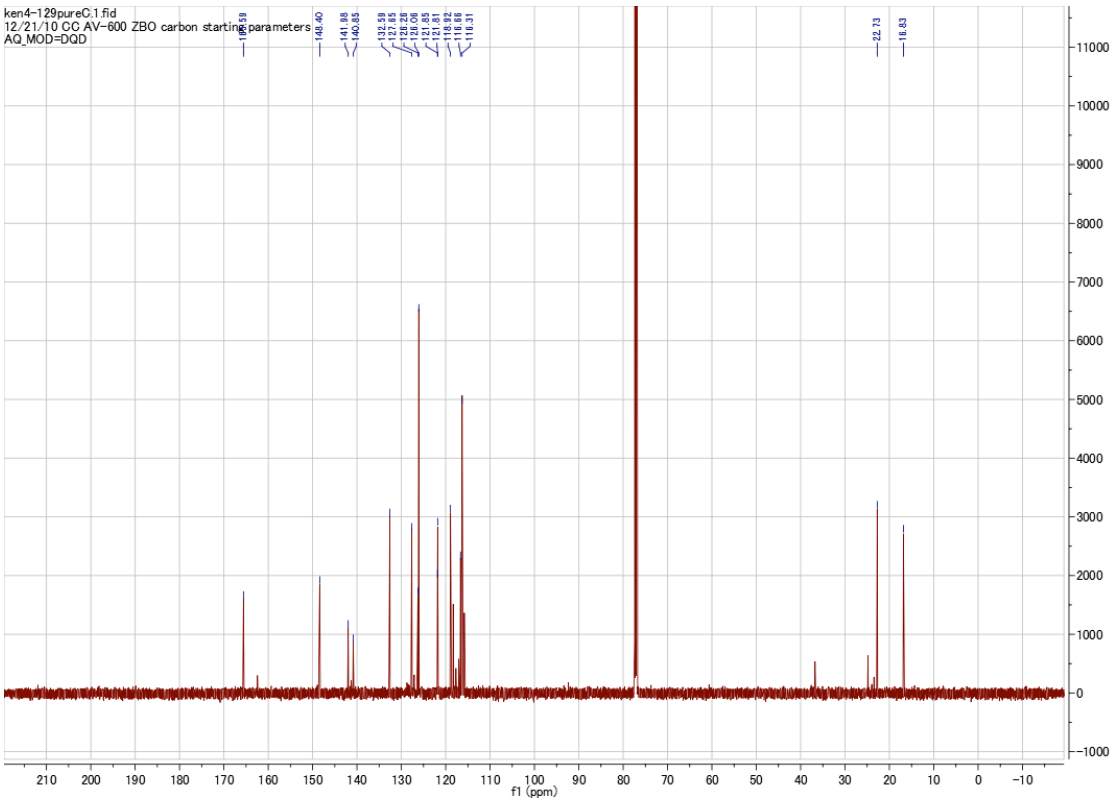
2-((4-methoxyphenyl)amino)-N-(2-methylprop-1-en-1-yl)benzamide (1j)



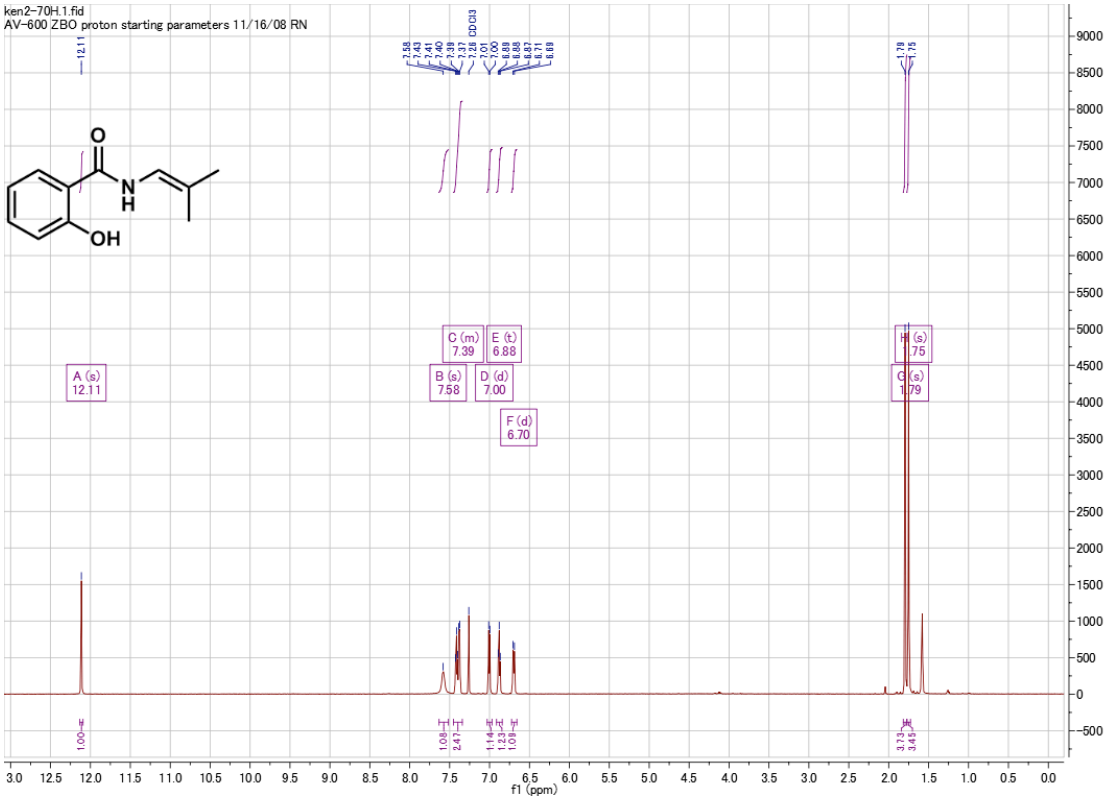


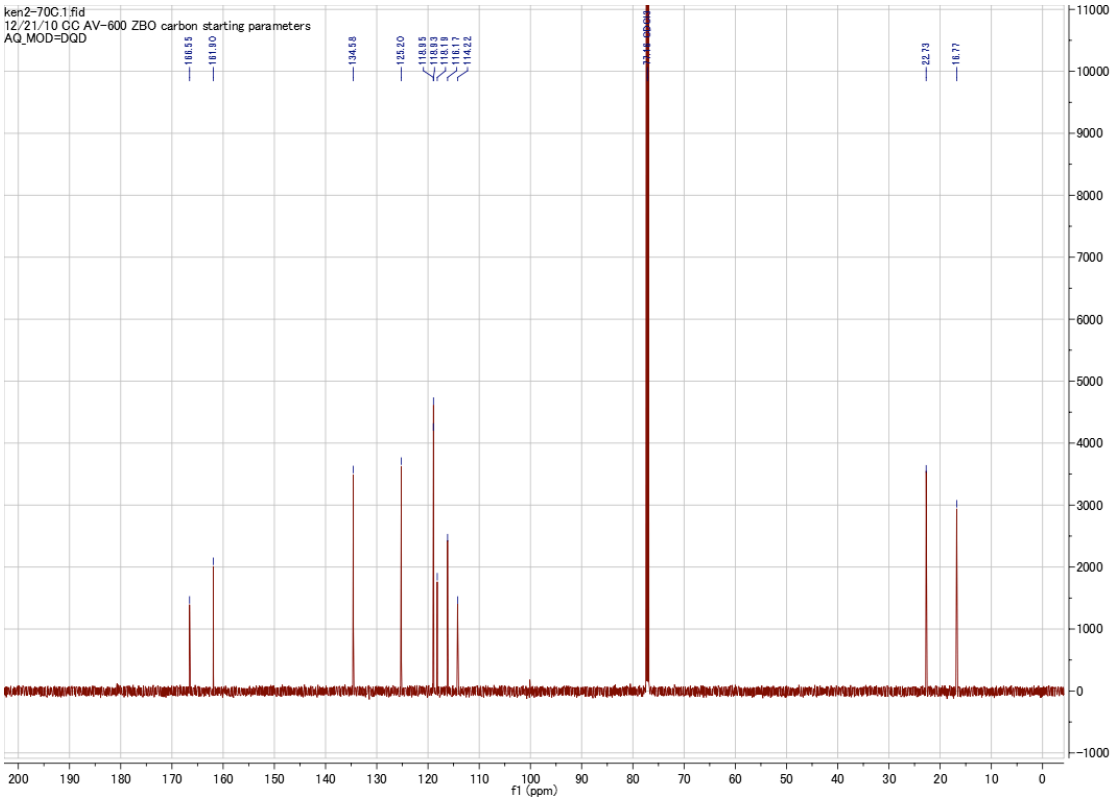
N-(2-methylprop-1-en-1-yl)-2-((4-nitrophenyl)amino)benzamide (1k)



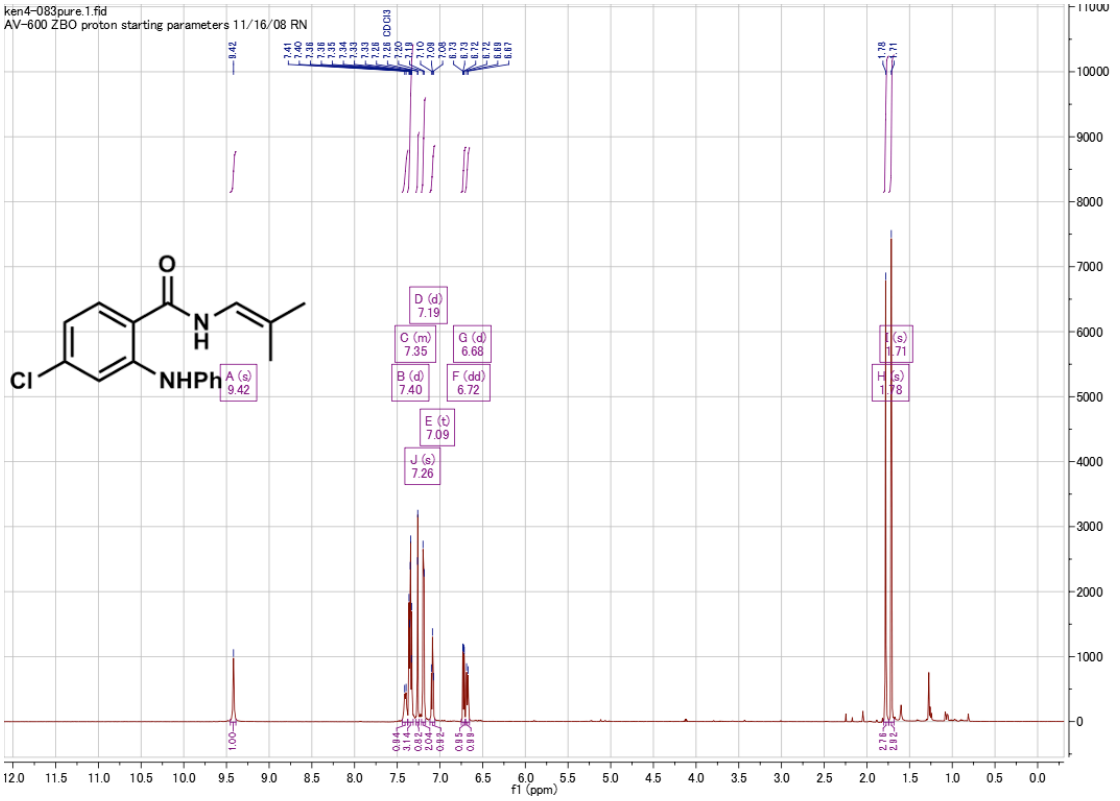


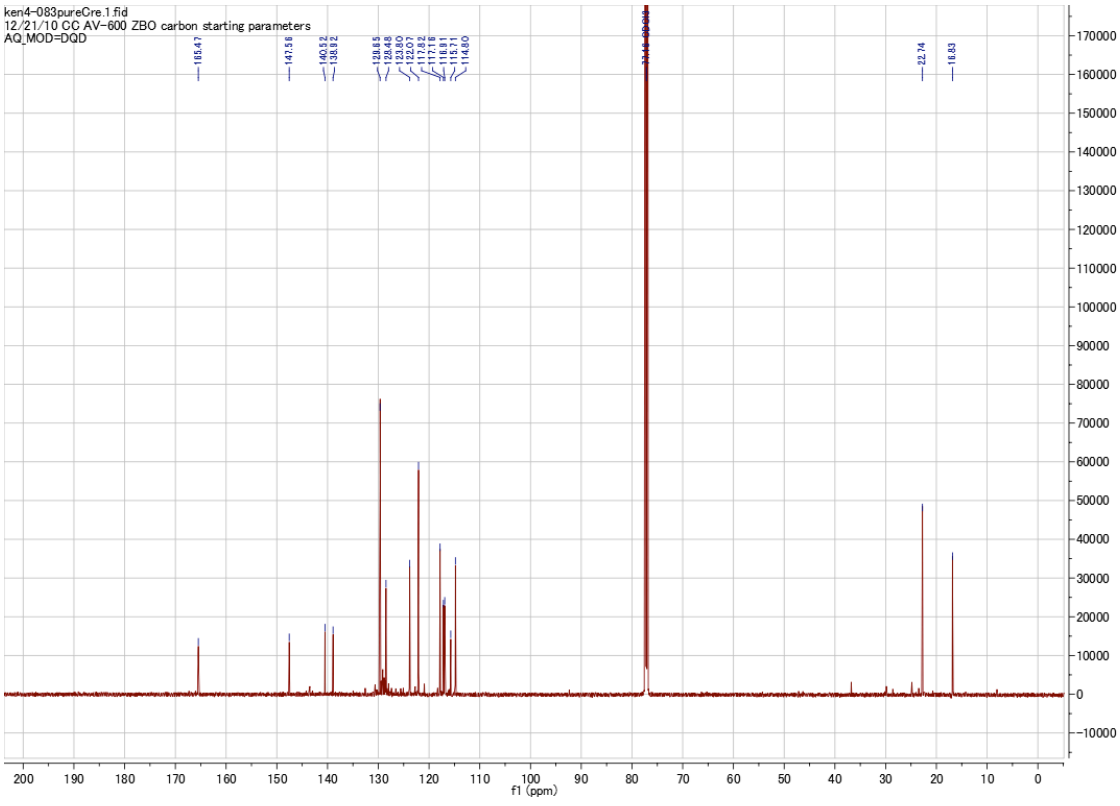
2-hydroxy-N-(2-methylprop-1-en-1-yl)benzamide (1l)



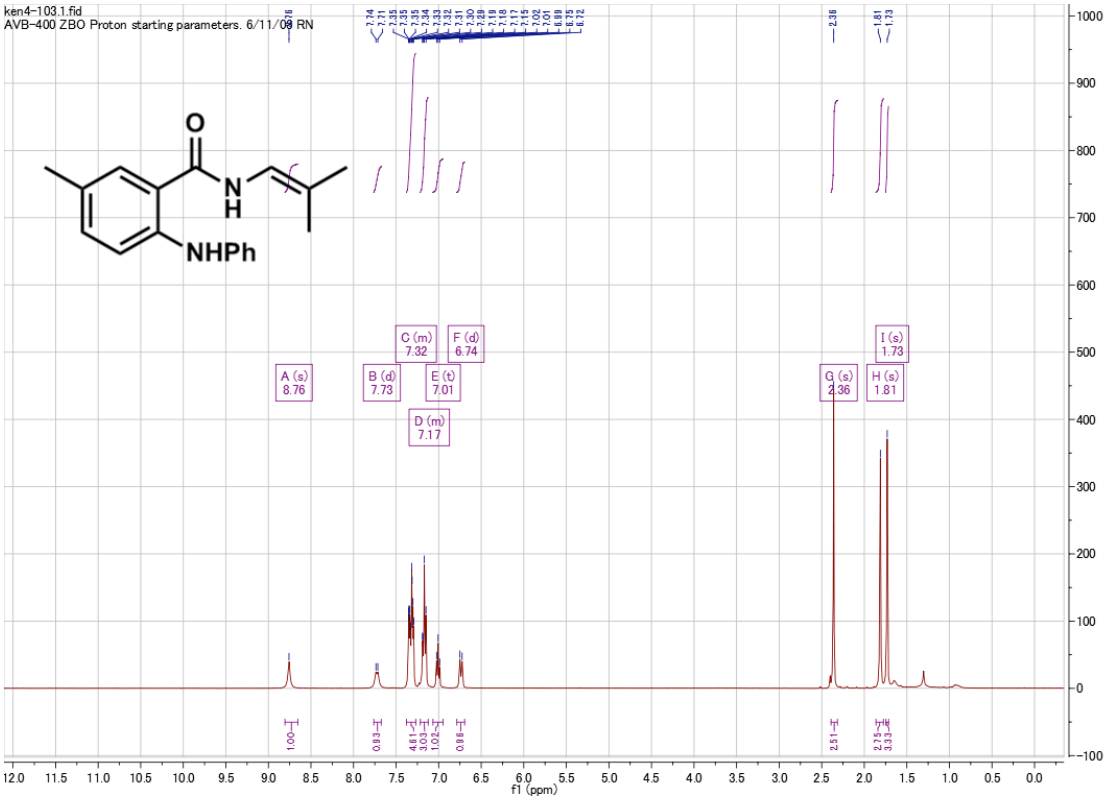


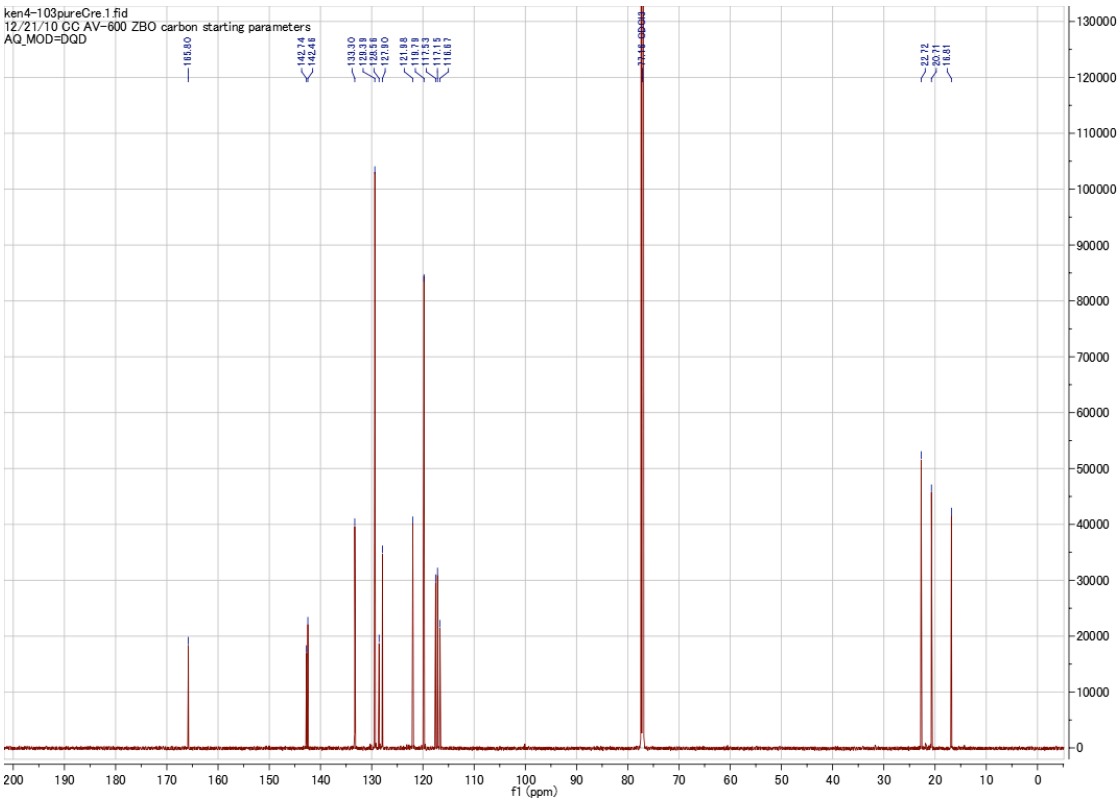
4-chloro-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1m)



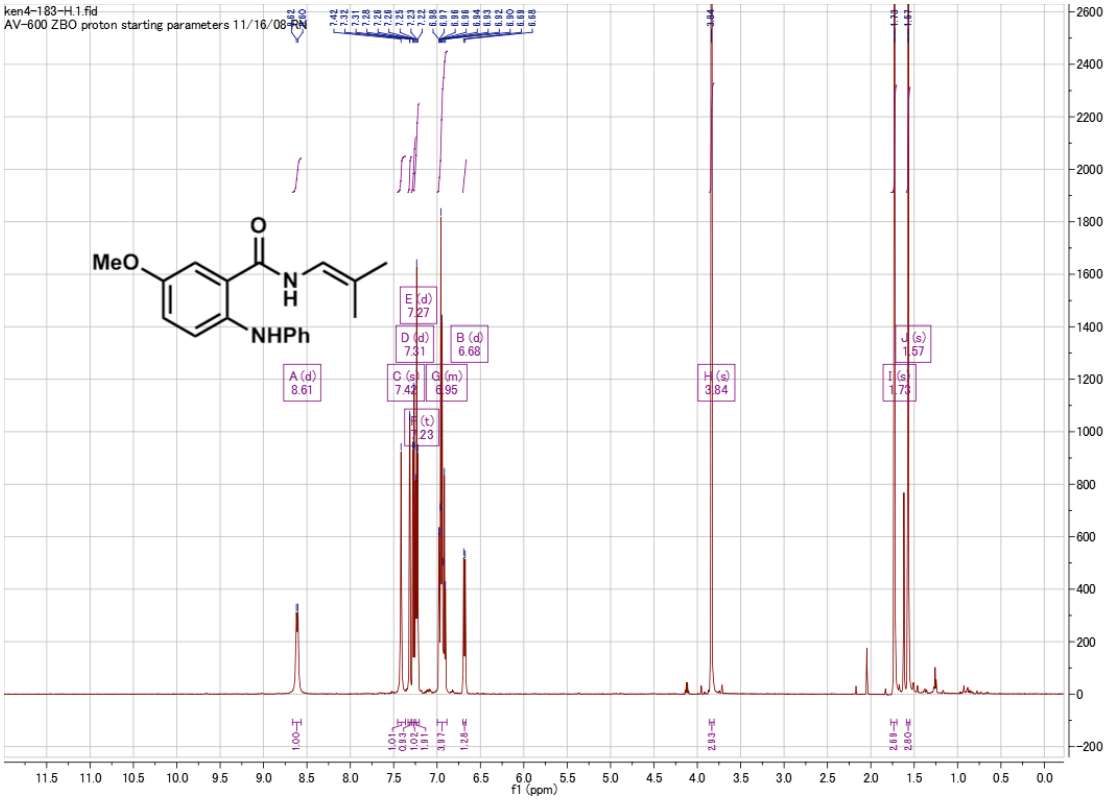


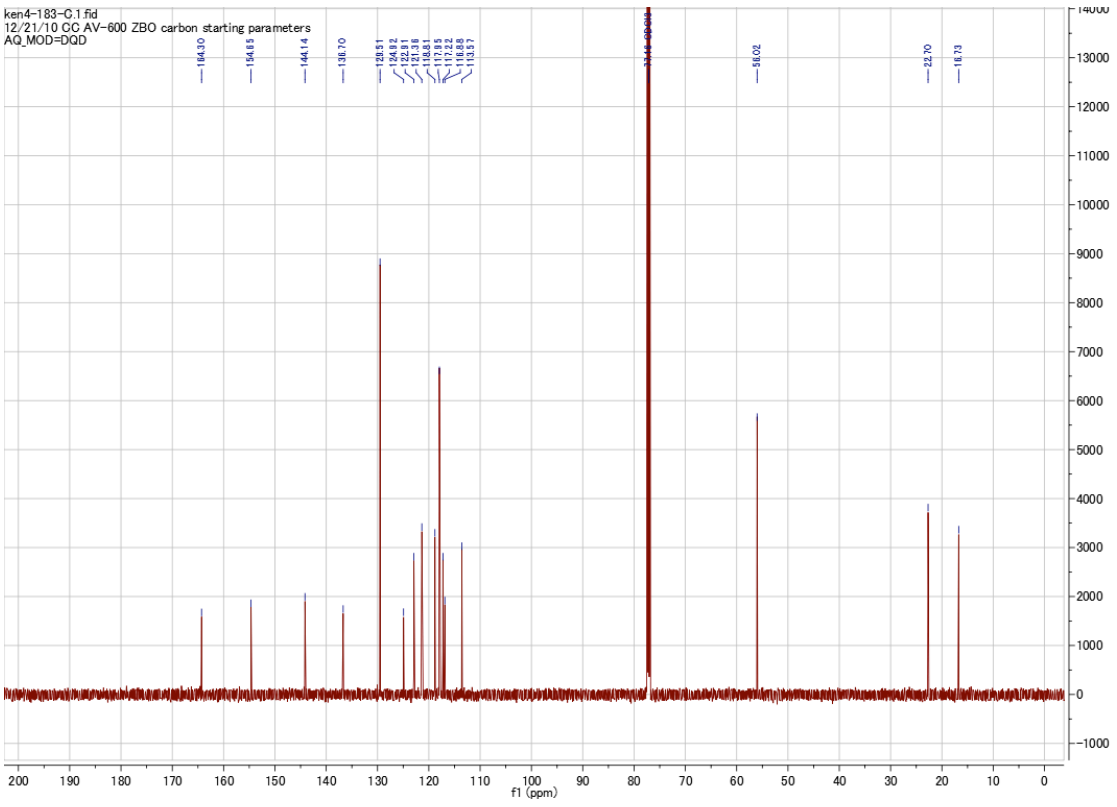
5-methyl-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1n)



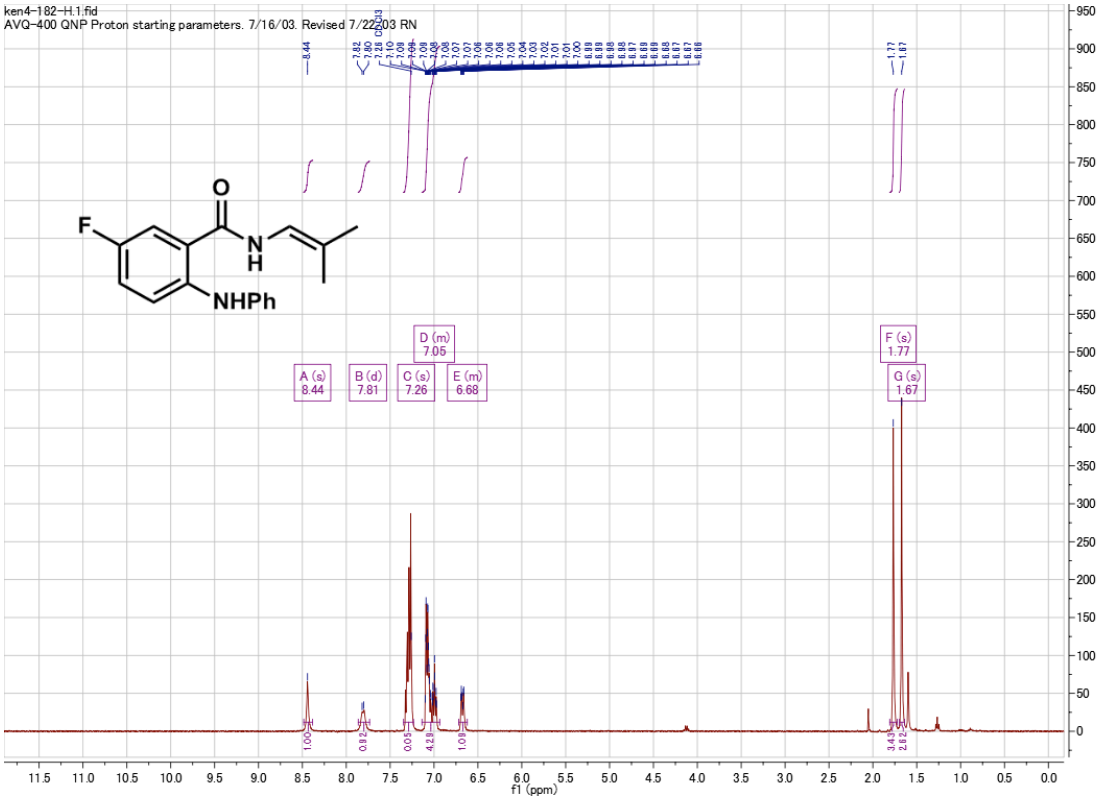


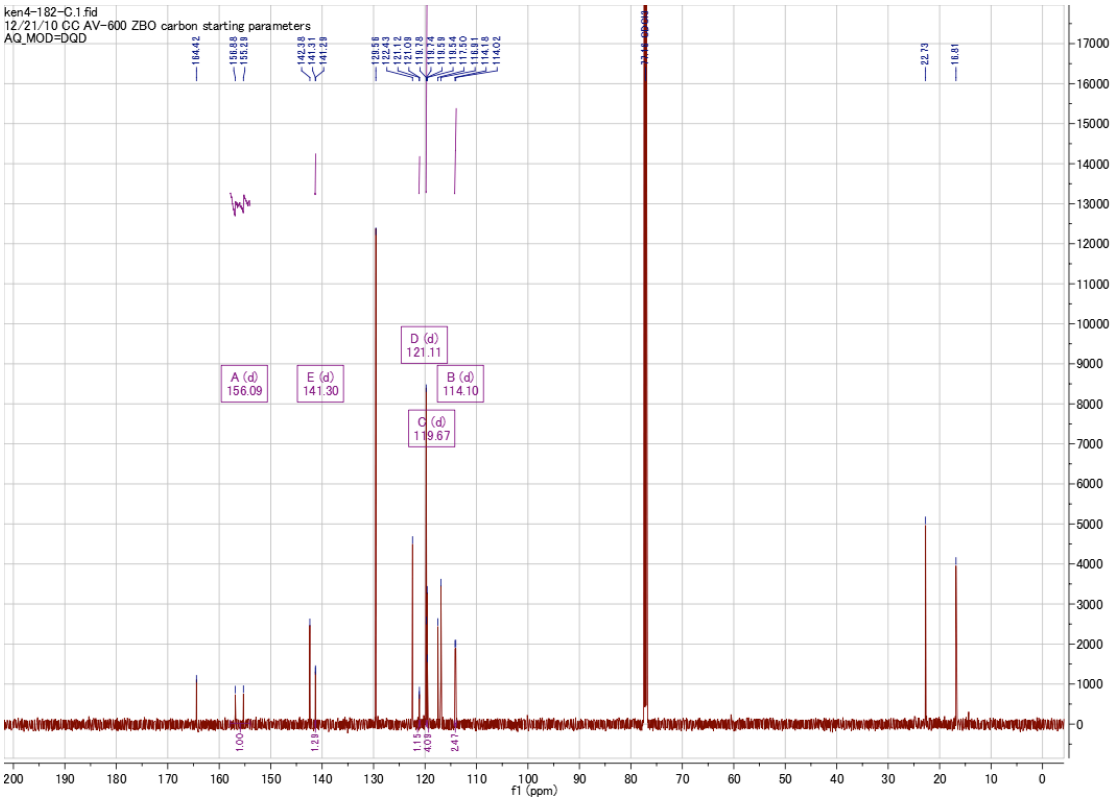
5-methoxy-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1o)

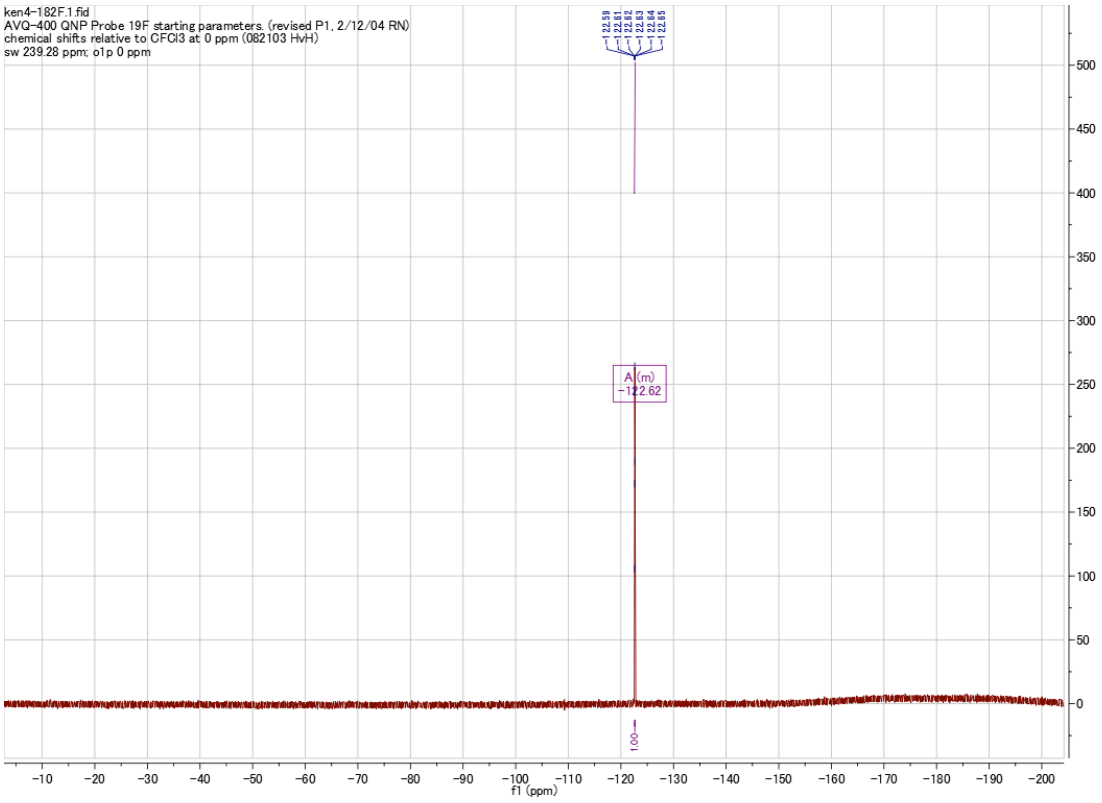




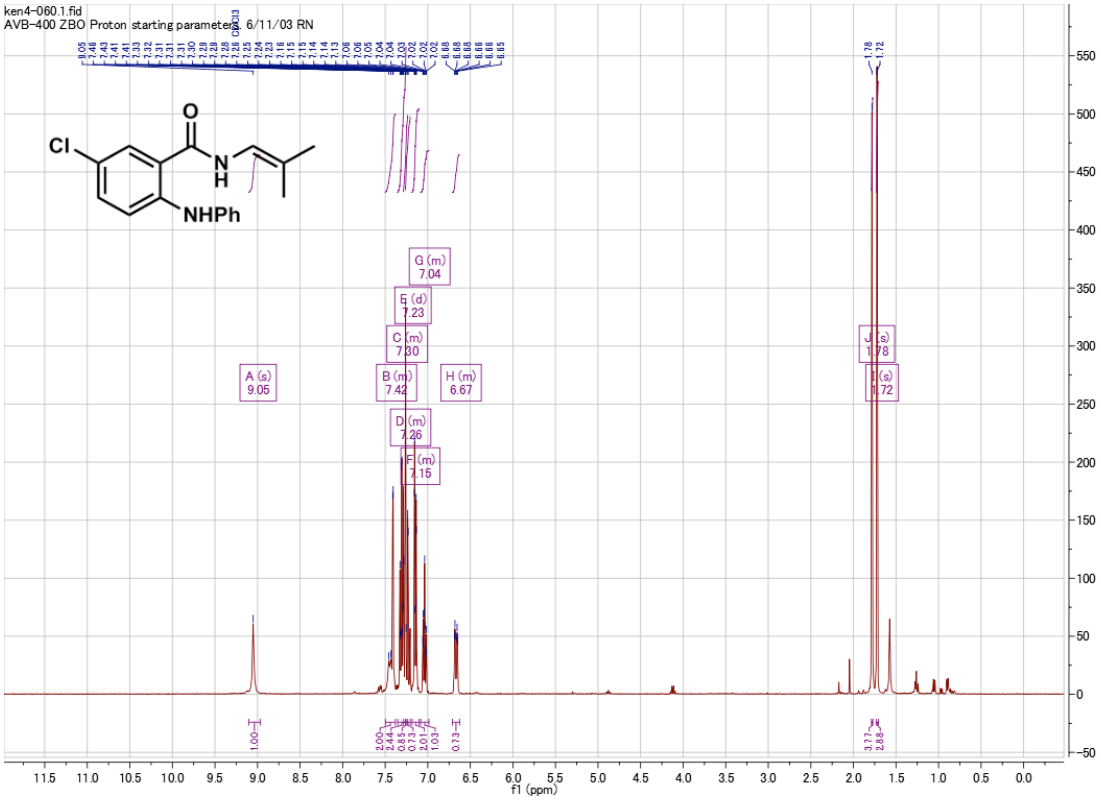
5-fluoro -N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1p)

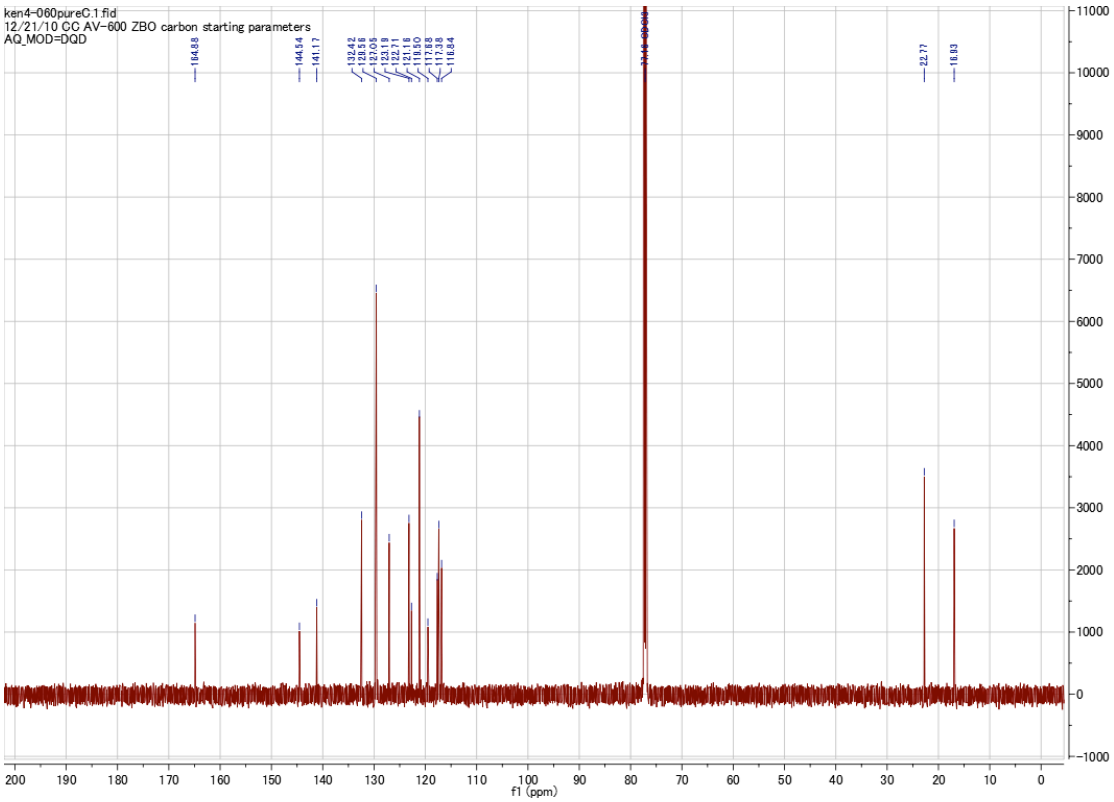




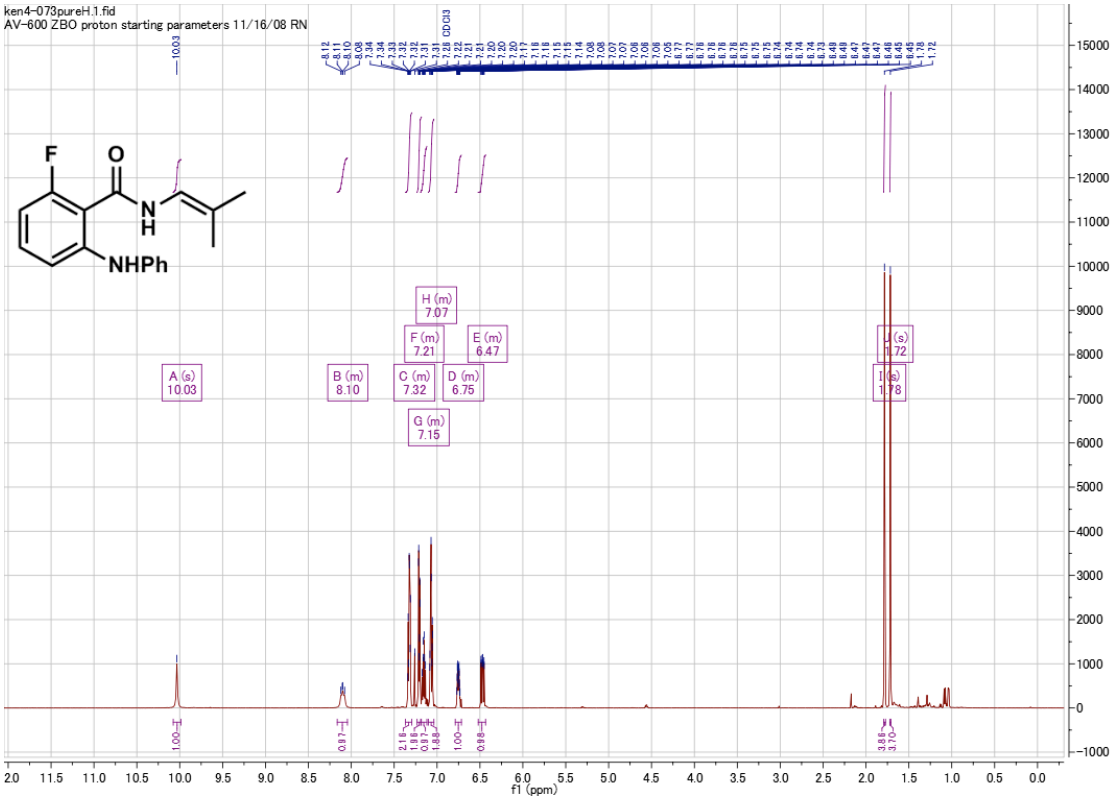

ken4-182F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A (m)
-122.62
1.00
f1 (ppm)

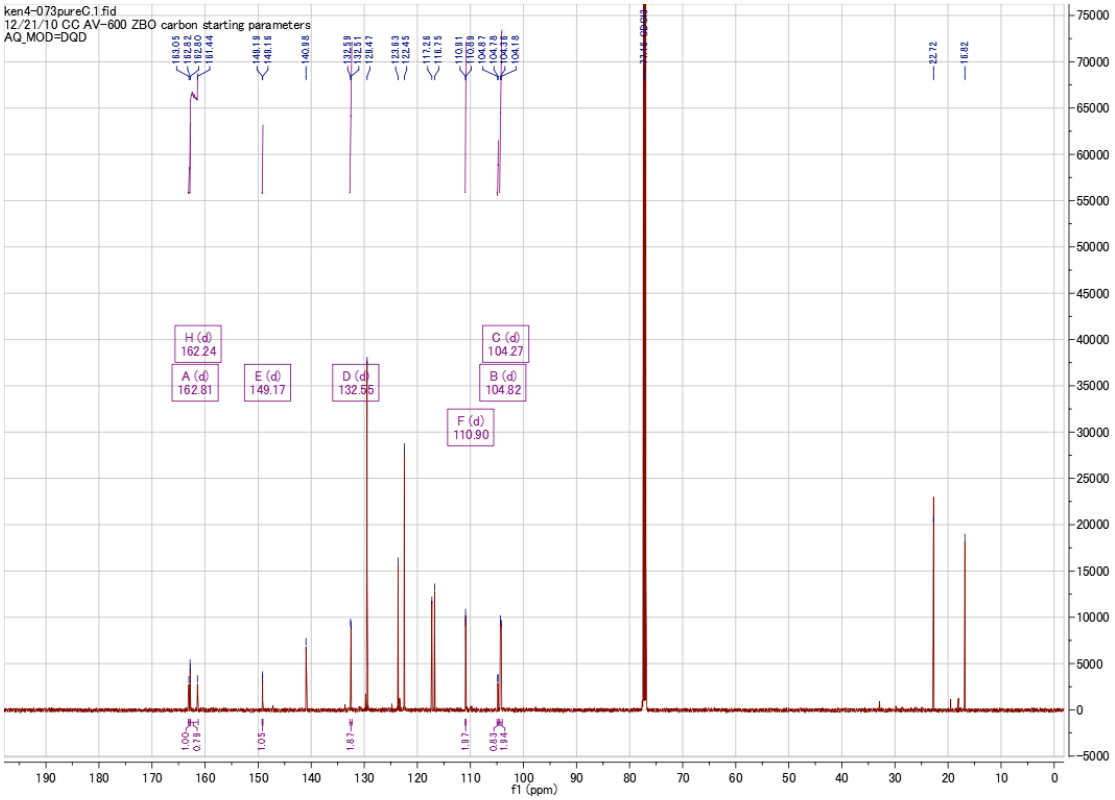
5-chloro-N-(2-methylprop-1-en-1-yl)-2-(phenylamino)benzamide (1q)

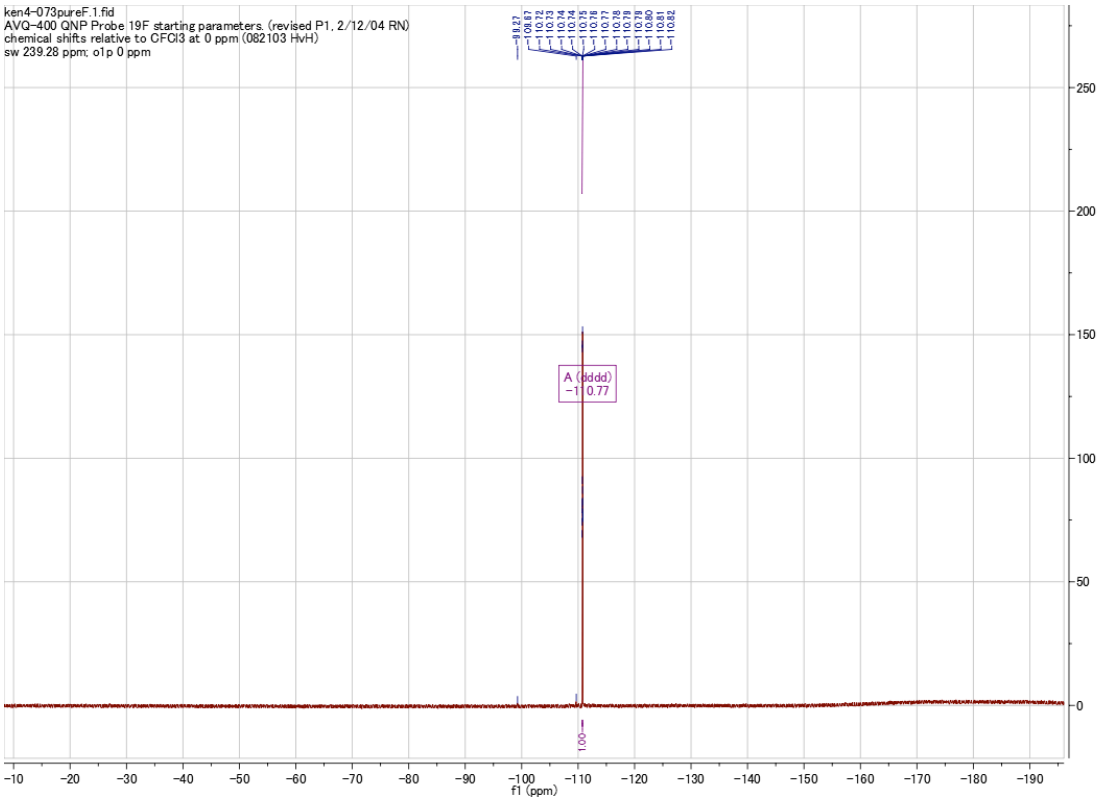




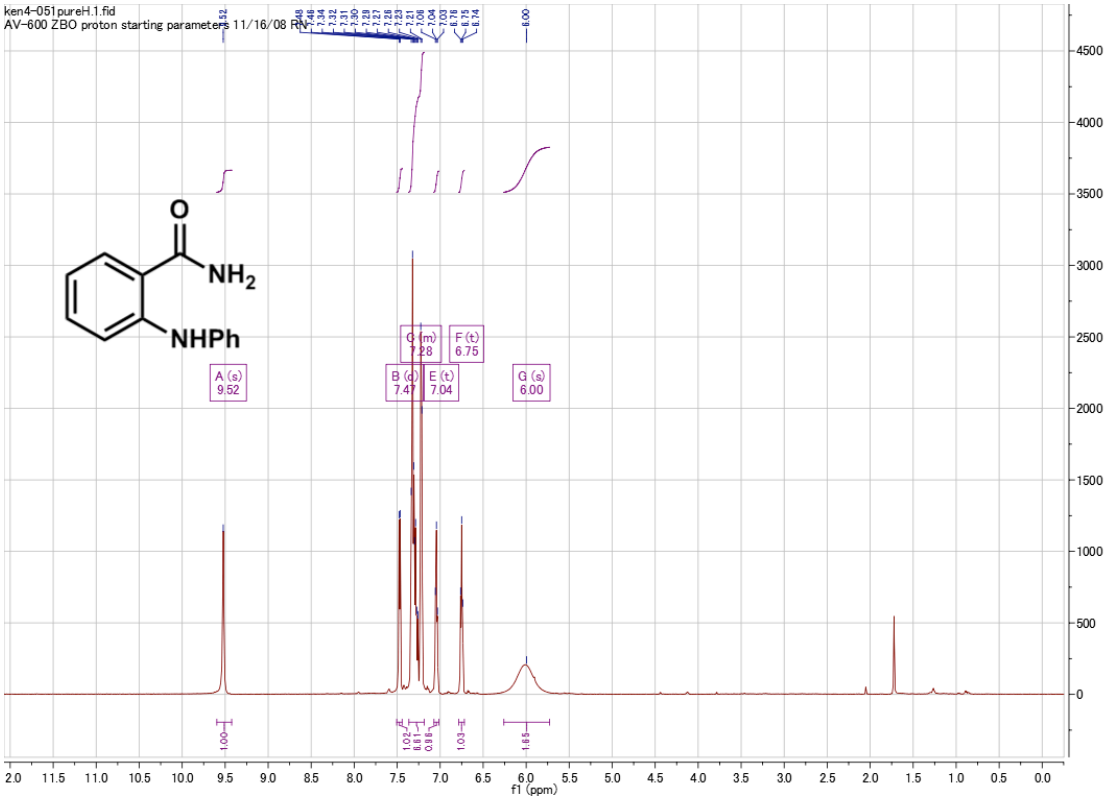
2-fluoro-N-(2-methylprop-1-en-1-yl)-6-(phenylamino)benzamide (1r)

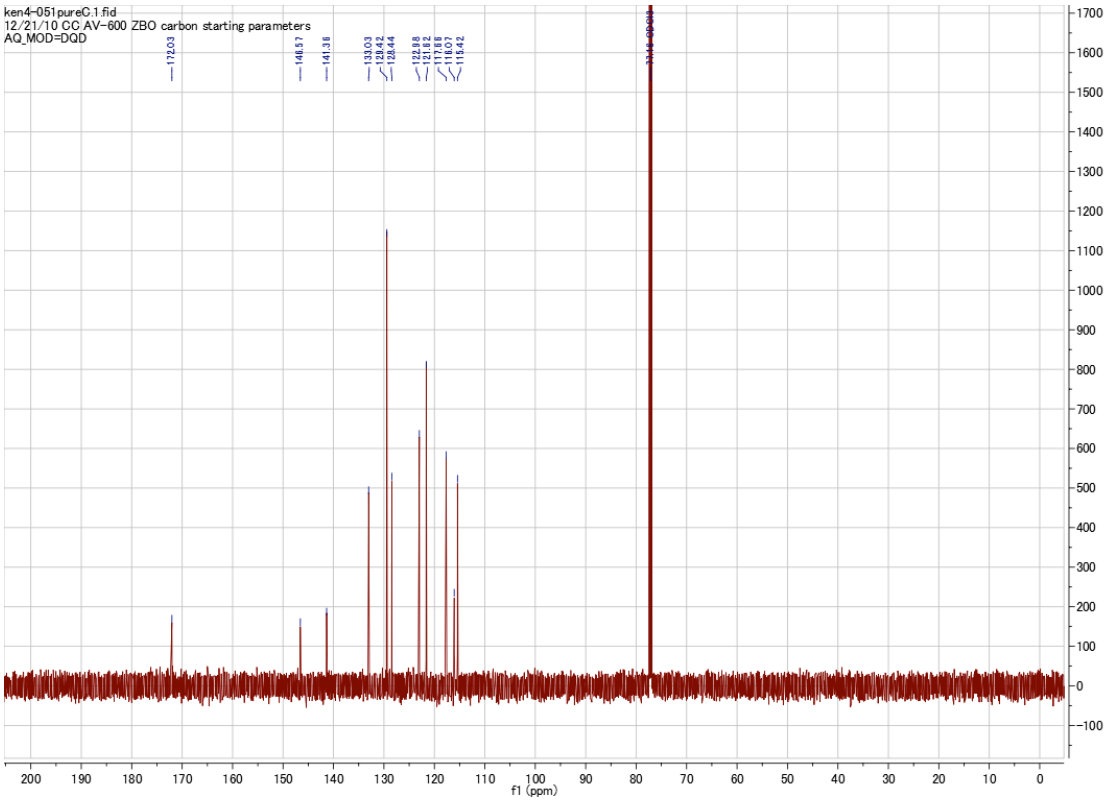




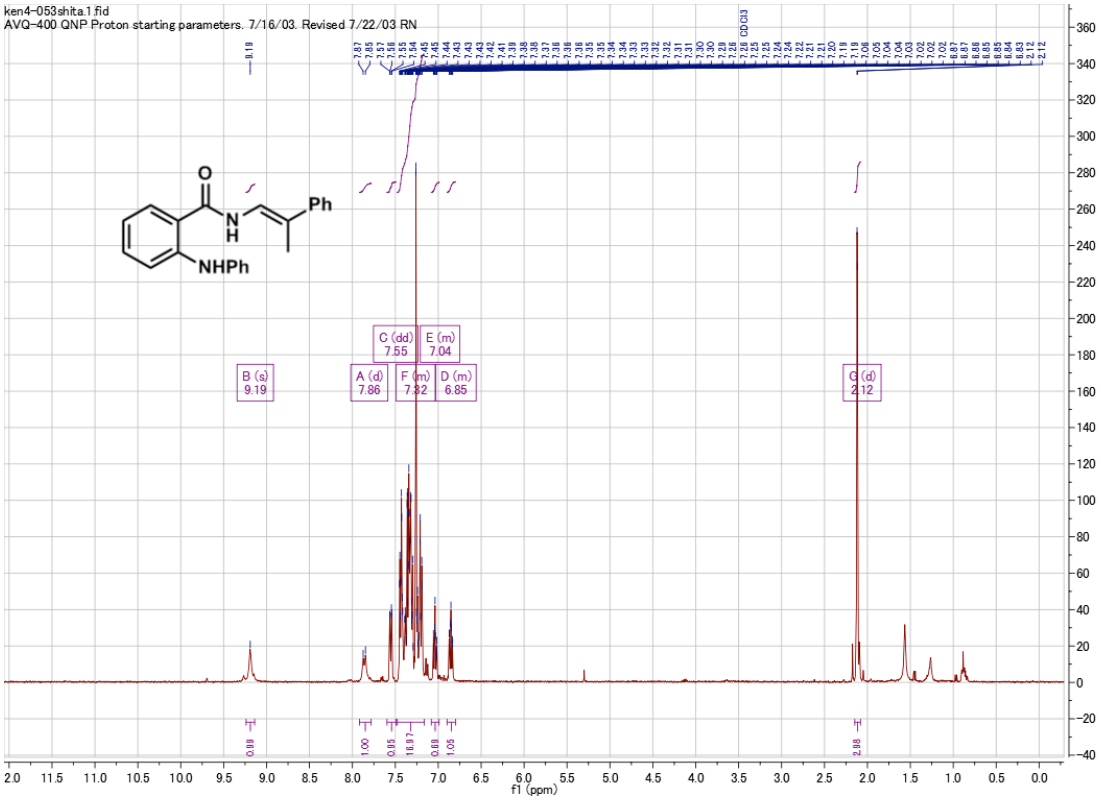

ken4-073pureF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-109.27
-109.67
-110.72
-110.73
-110.74
-110.74
-110.75
-110.76
-110.77
-110.78
-110.78
-110.79
-110.79
-110.80
-110.81
-110.82
A (dddd)
-110.77
1.00
250
200
150
100
50
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

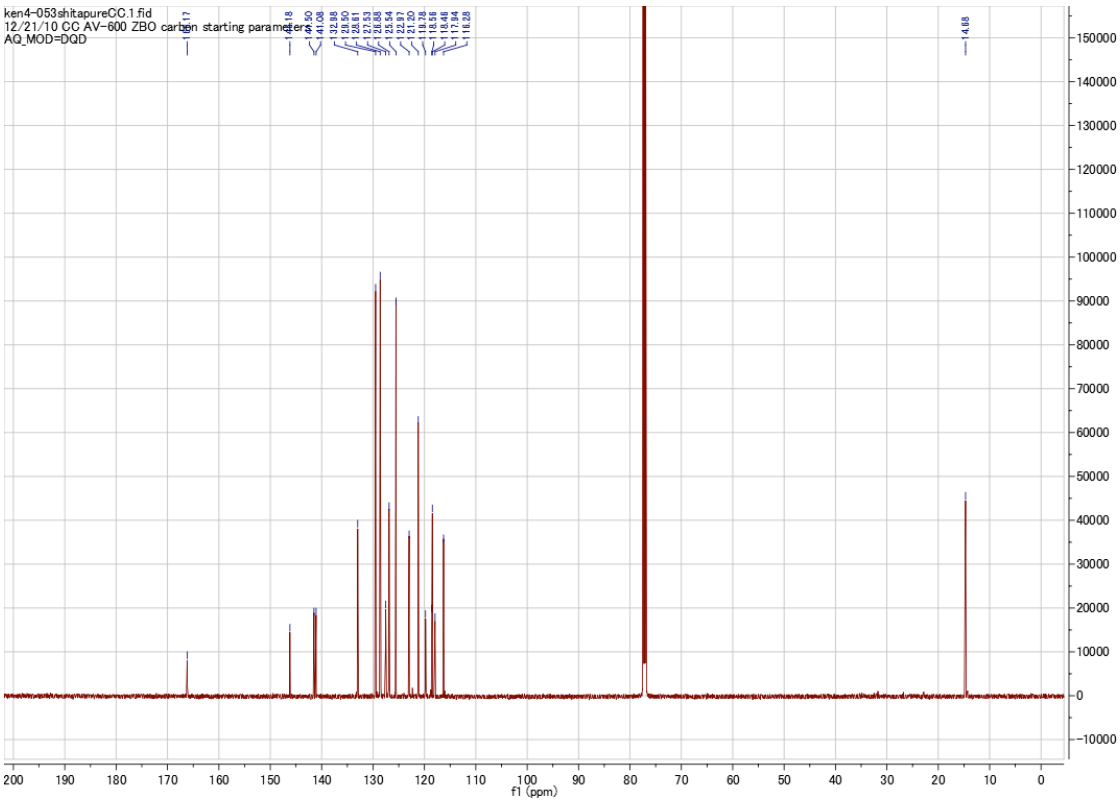
2-(phenylamino)benzamide



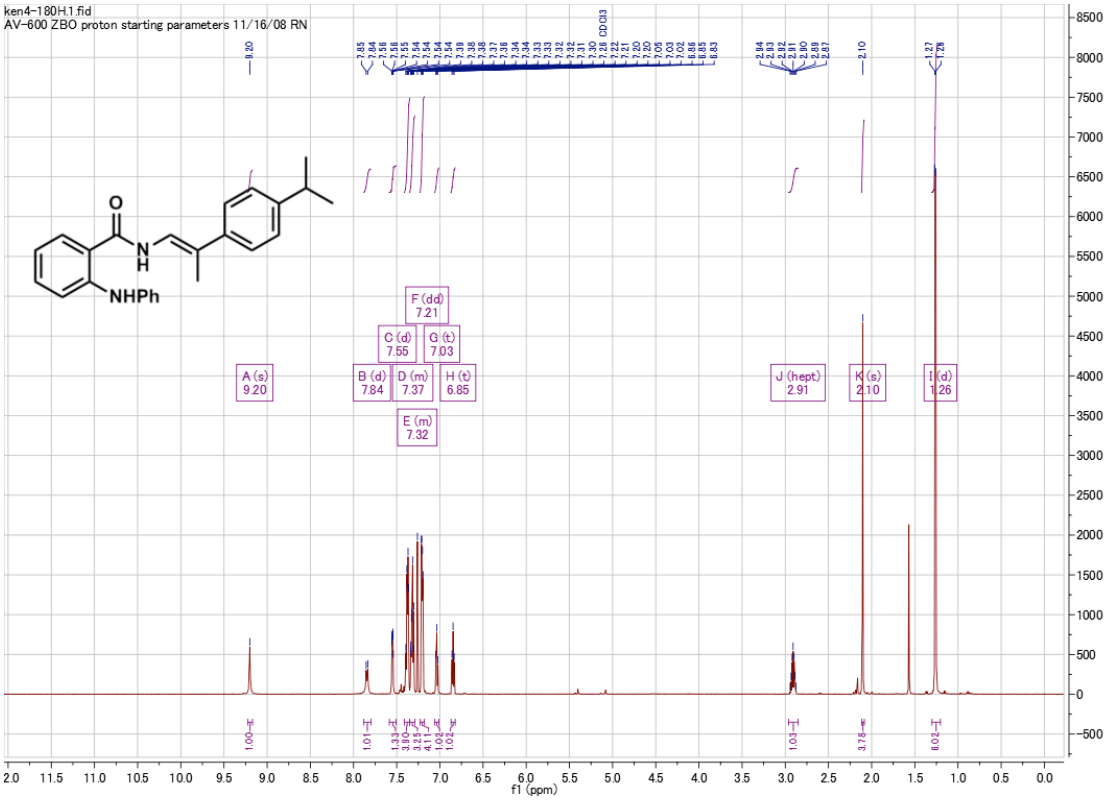


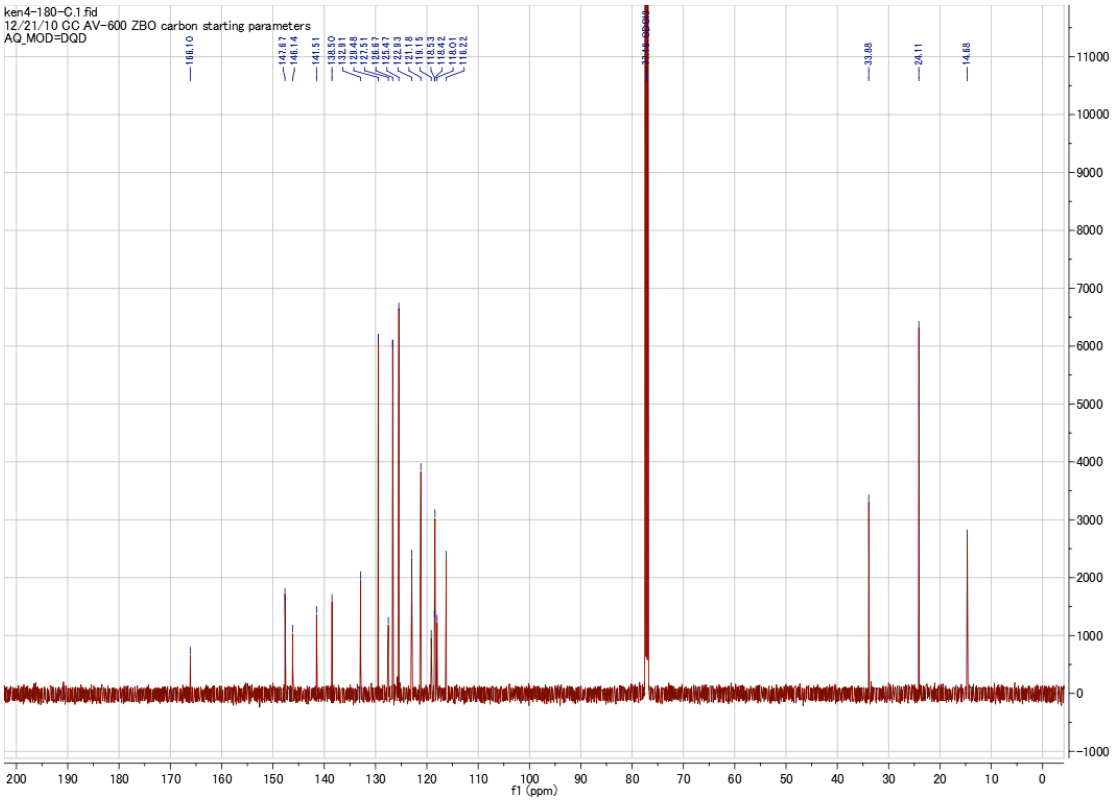
(E)-2-(phenylamino)-N-(2-phenylprop-1-en-1-yl)benzamide (1s)



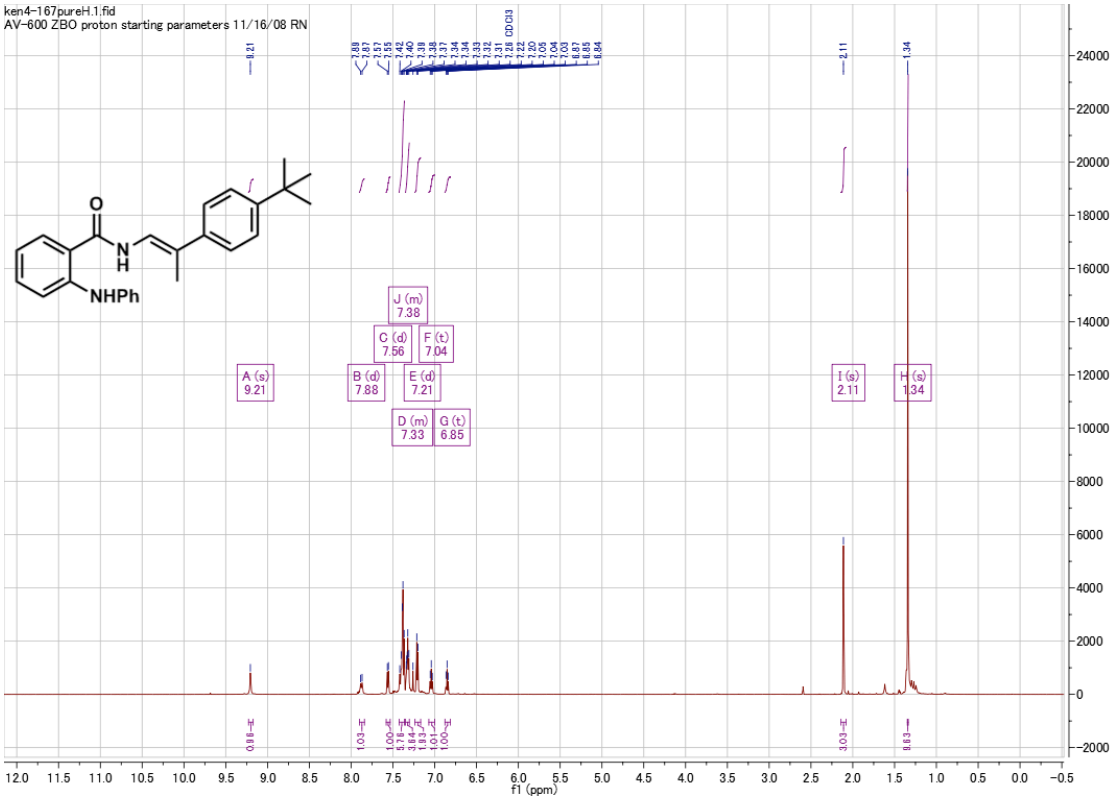


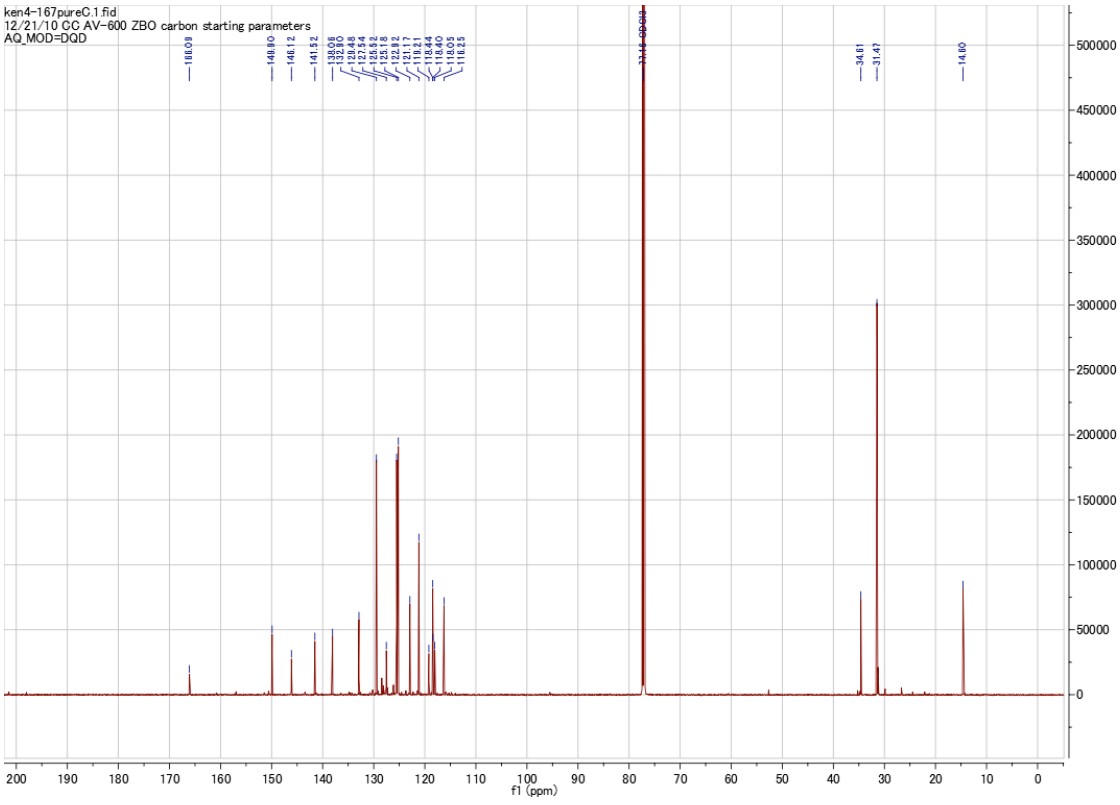
(E)-N-(2-(4-isopropylphenyl)prop-1-en-1-yl)-2-(phenylamino)benzamide (1t)



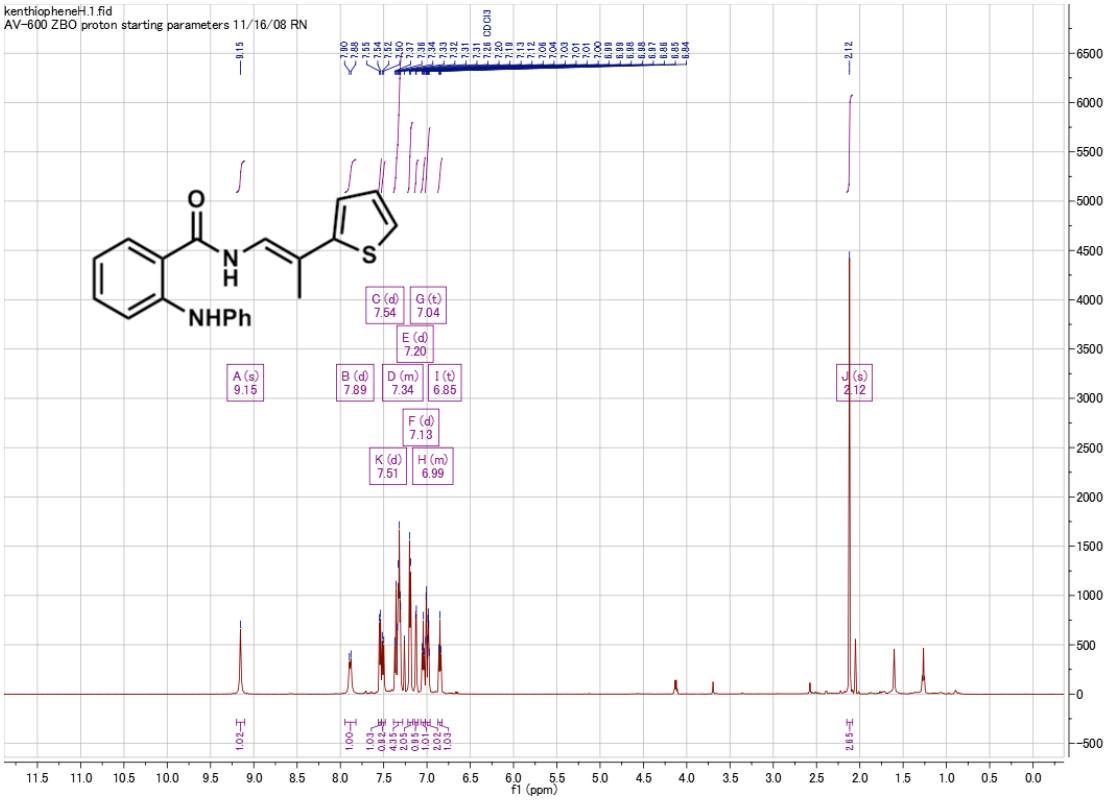


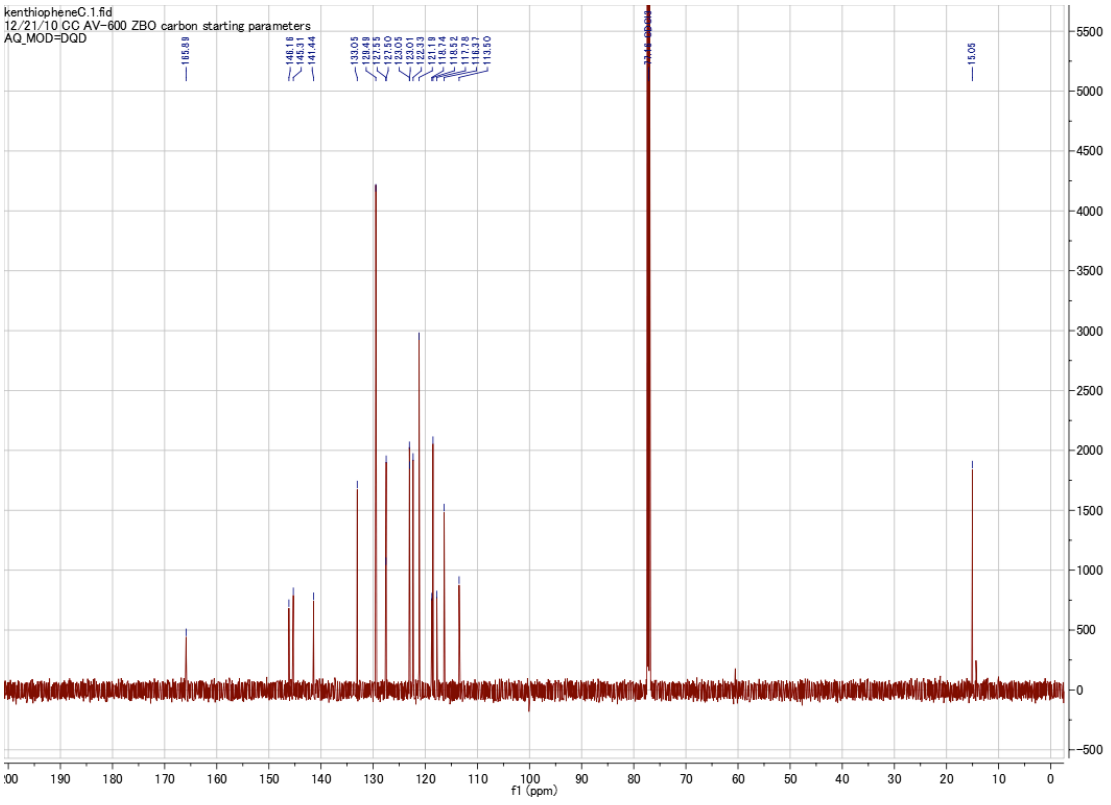
***(E)*-N-(2-(4-(*tert*-butyl)phenyl)prop-1-en-1-yl)-2-(phenylamino)benzamide (1u)**



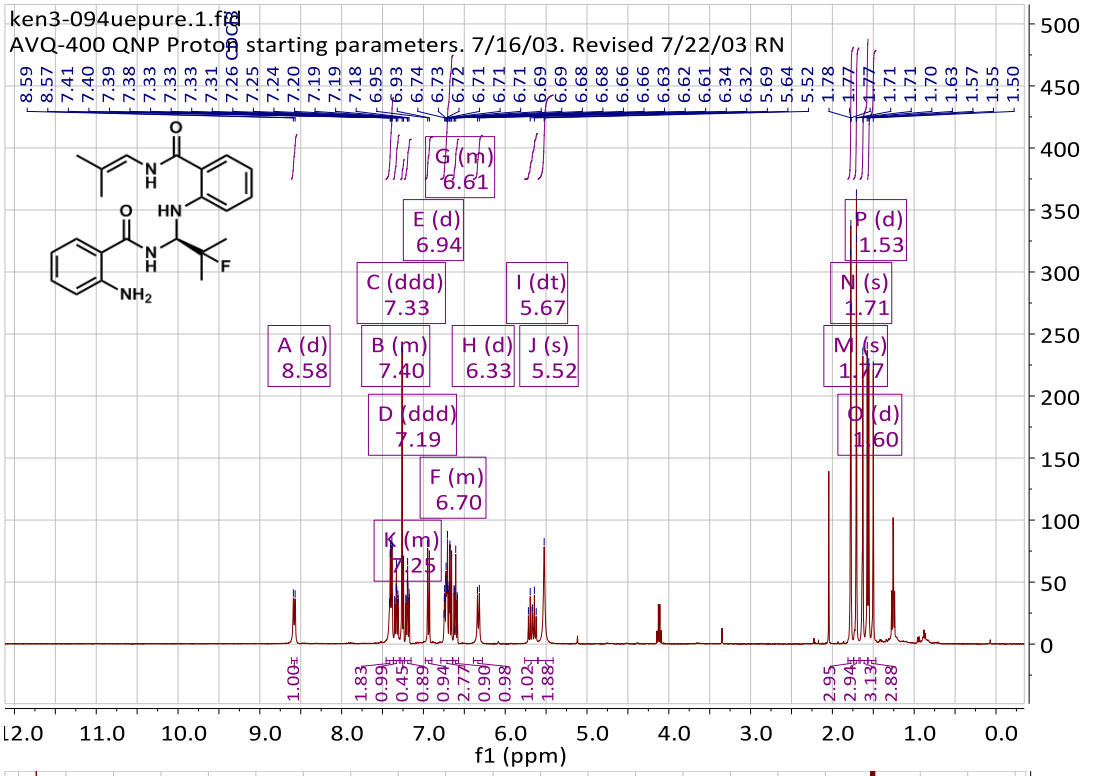


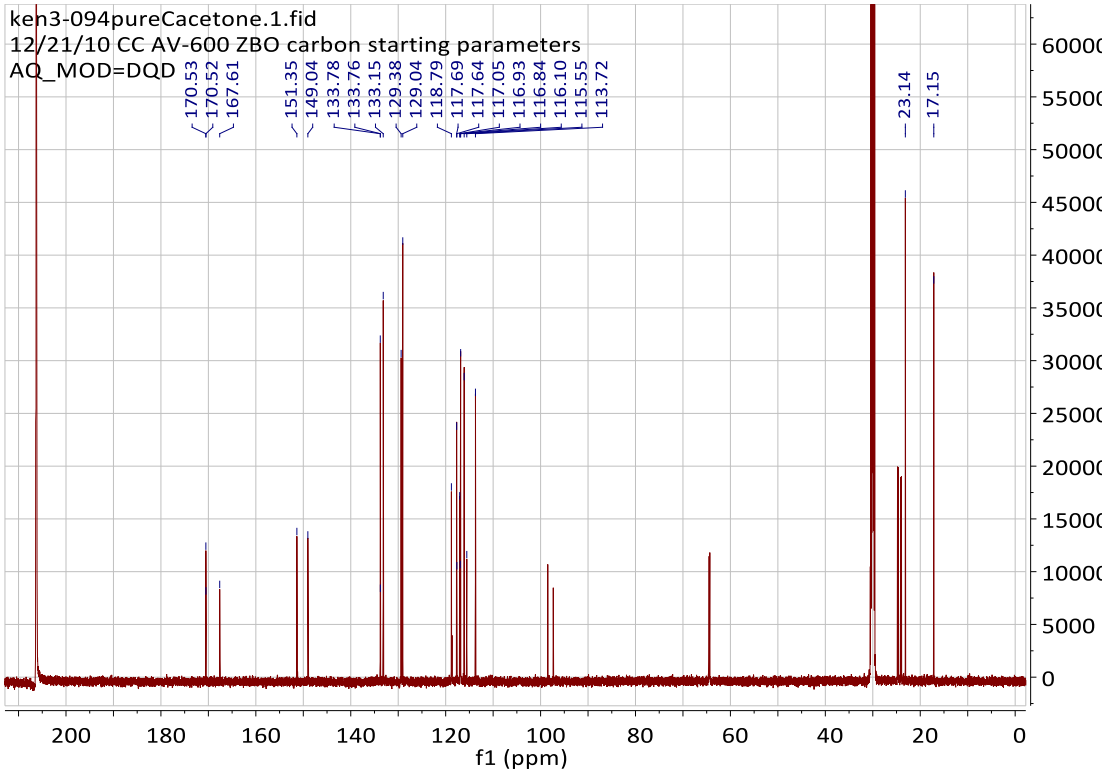
***(E)*-2-(phenylamino)-N-(2-(thiophen-2-yl)prop-1-en-1-yl)benzamide (1v)**

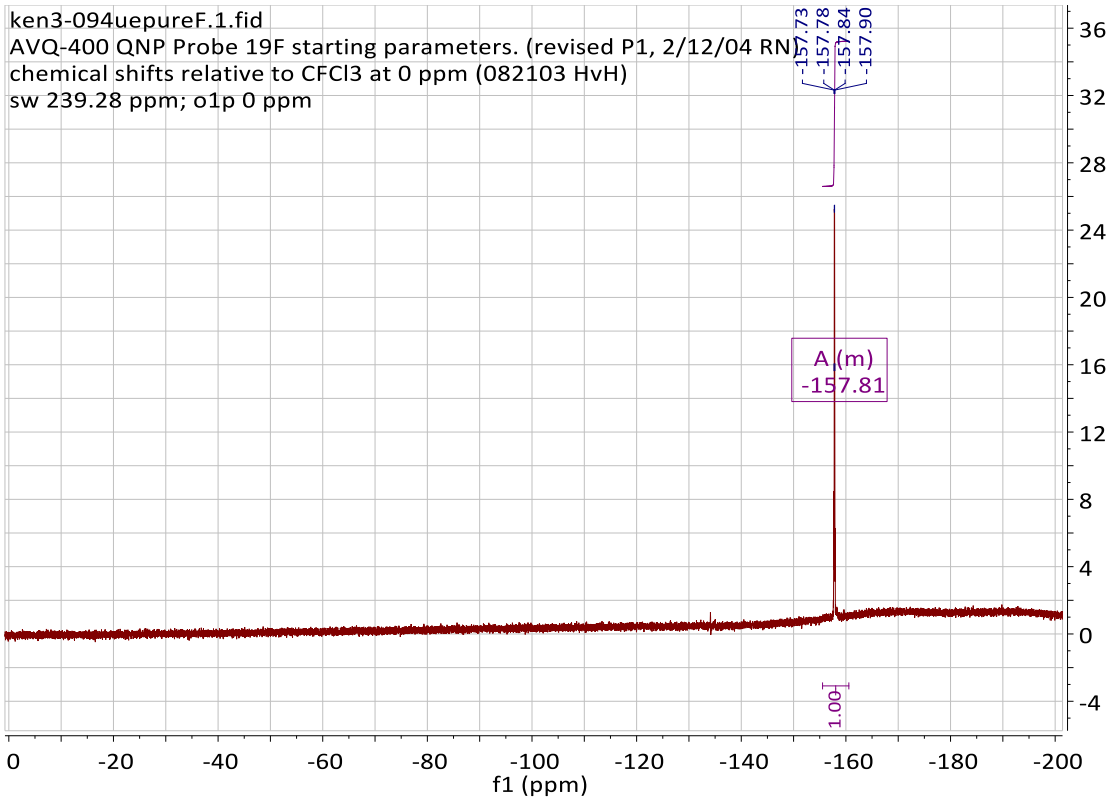




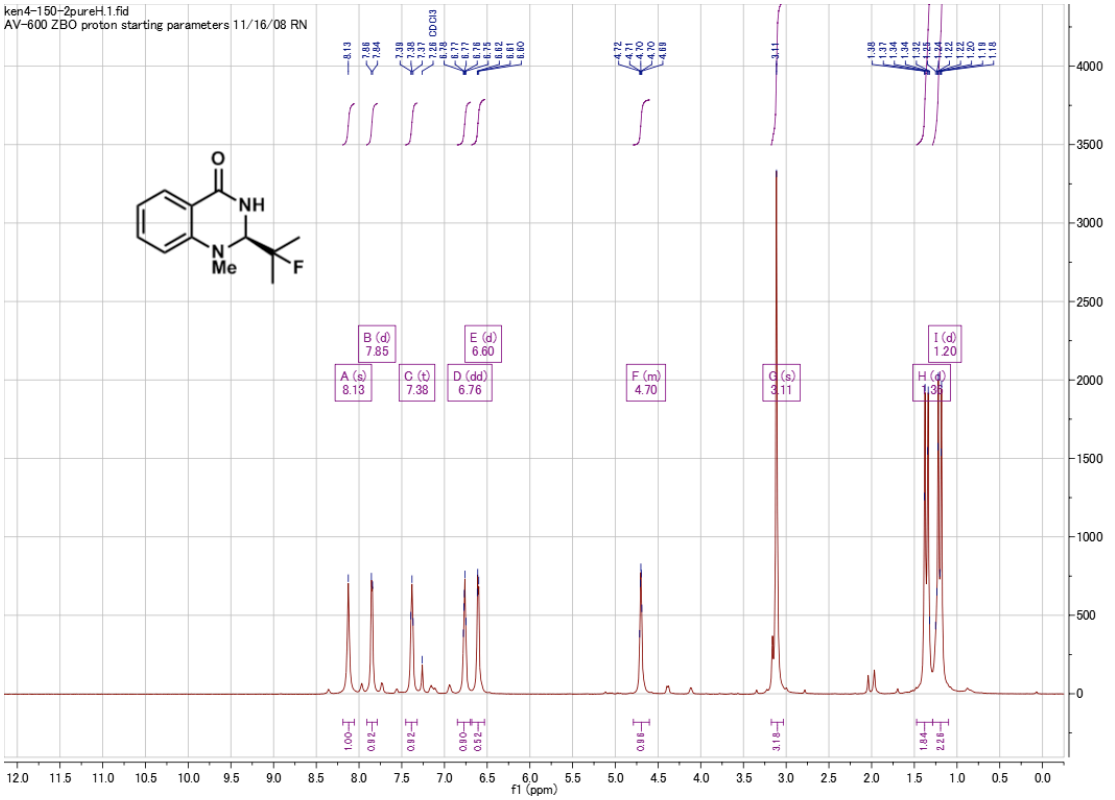
(*R*)-2-amino-*N*-(2-fluoro-2-methyl-1-((2-((2-methylprop-1-en-1-yl)carbamoyl)phenyl)amino)propyl)benzamide (2e)

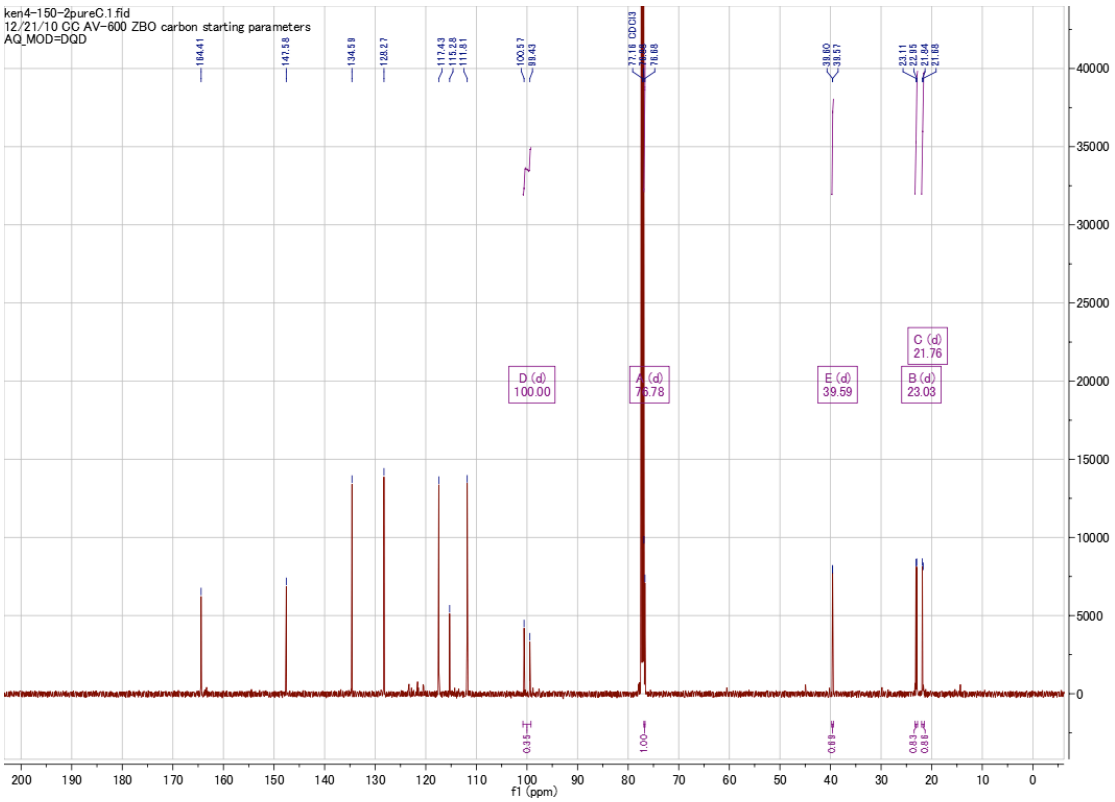


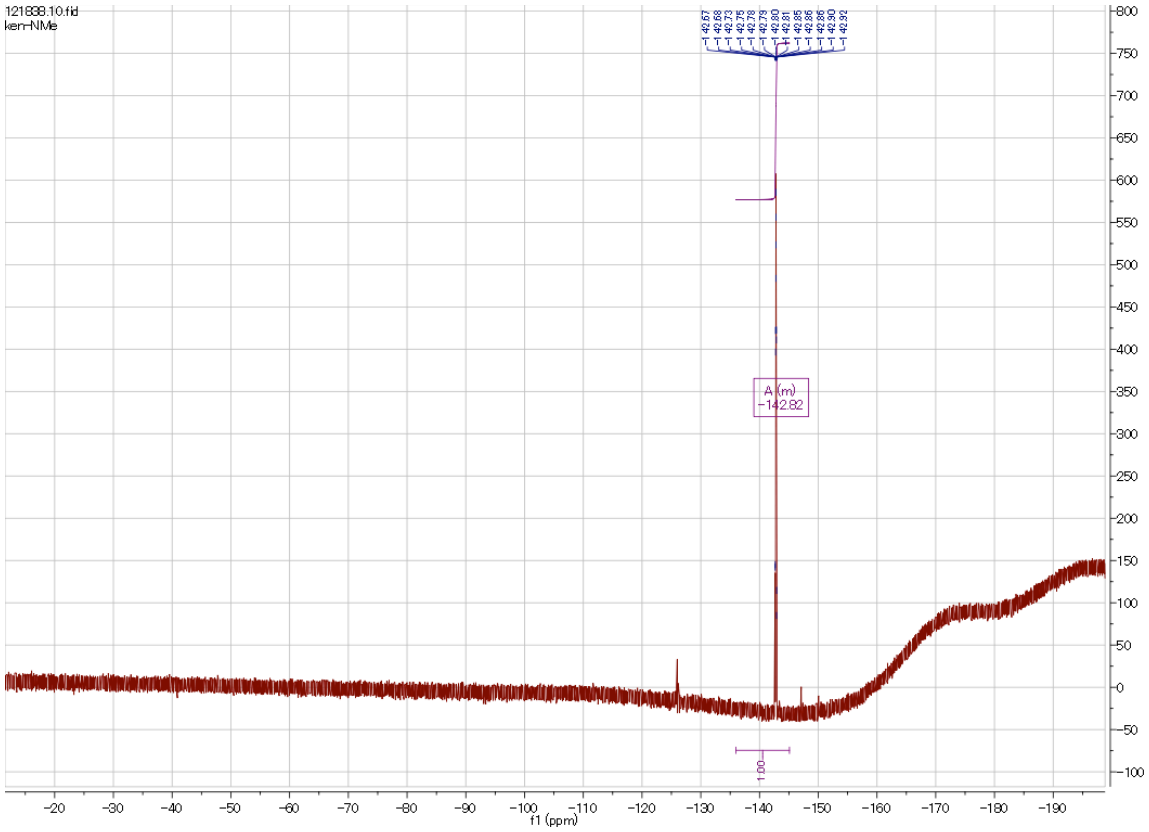



ken3-094uepureF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-157.73
-157.78
-157.84
-157.90
A (m)
-157.81
1.00
36
32
28
24
20
16
12
8
4
0
-4
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

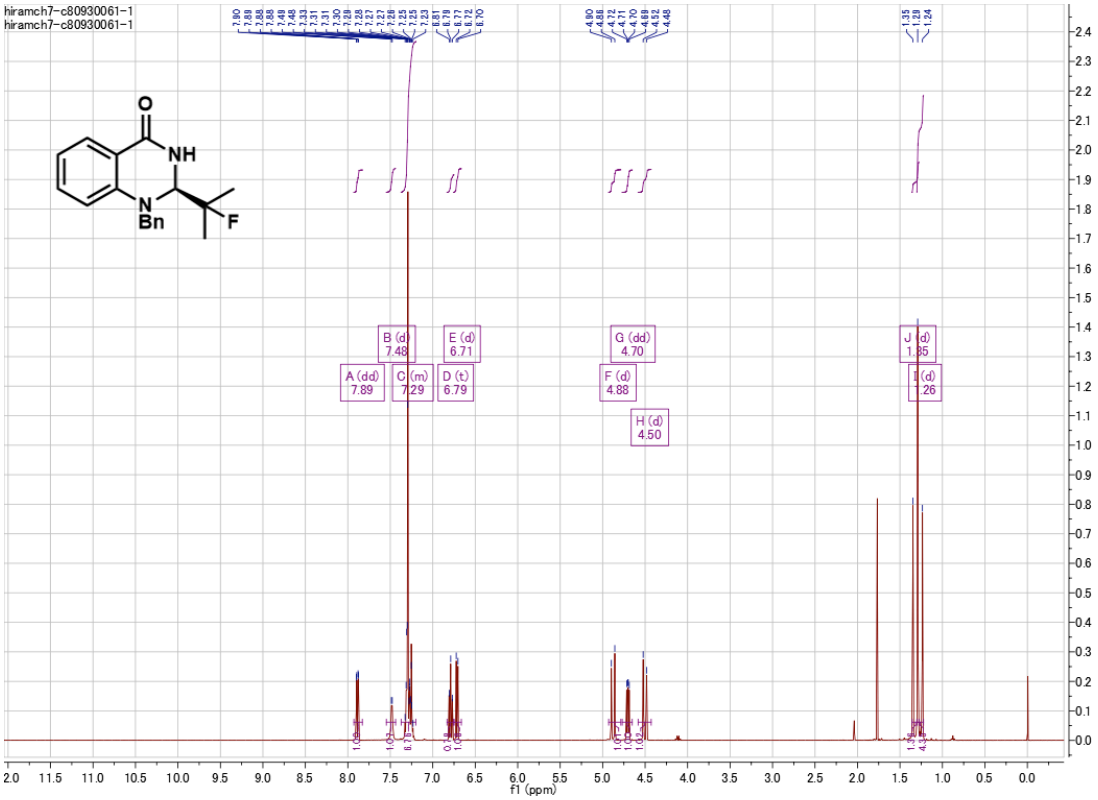
***(R)*-2-(2-fluoropropan-2-yl)-1-methyl-2,3-dihydroquinazolin-4(1H)-one (2f)**

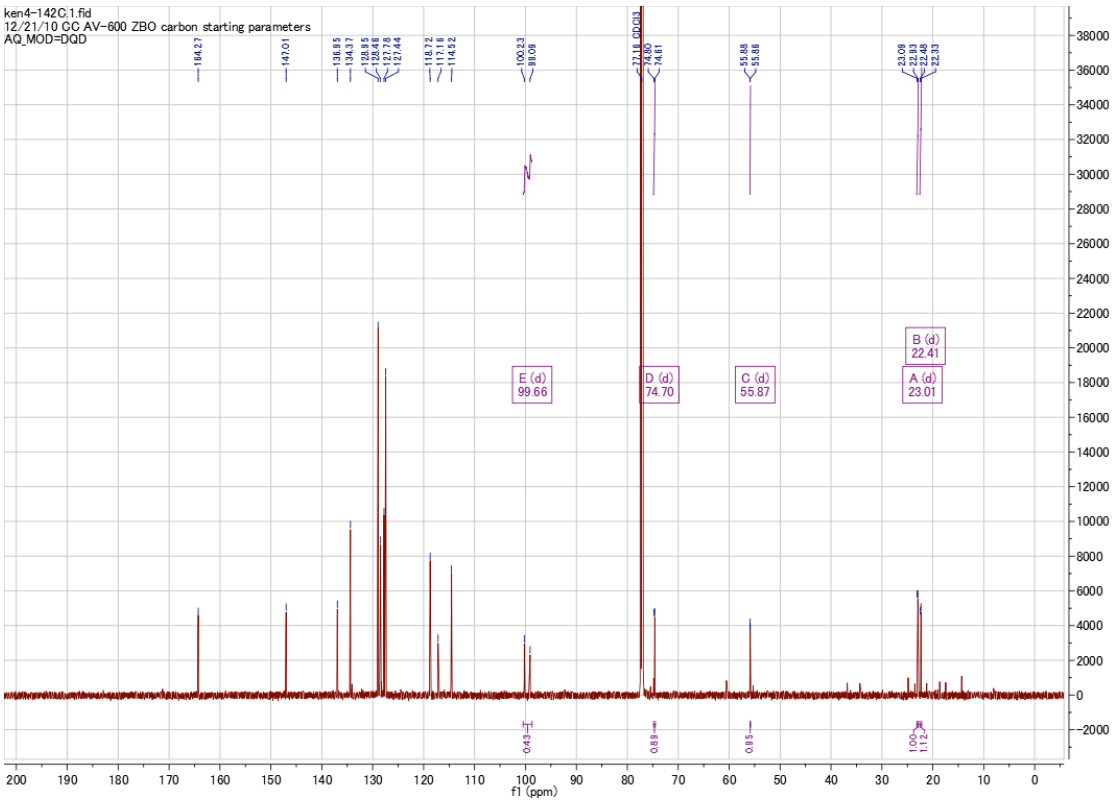


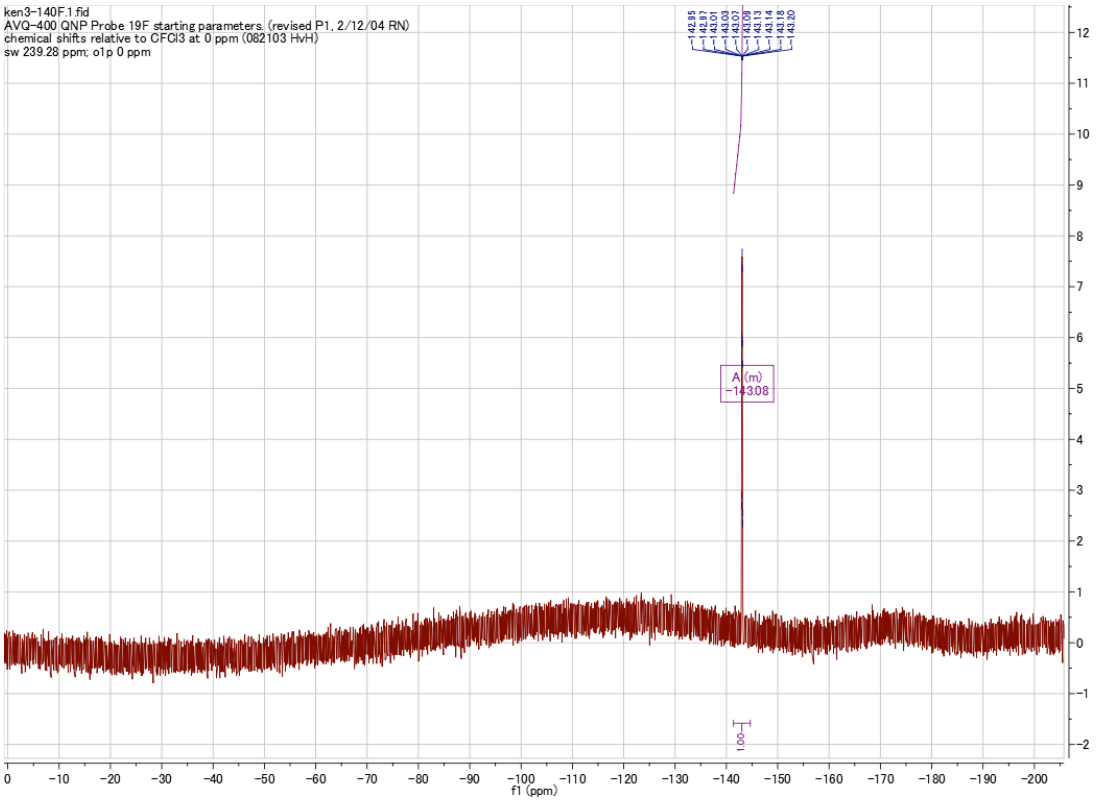



121838.10.fid
ken-NMe
A (m)
-142.82
1.00
f1 (ppm)

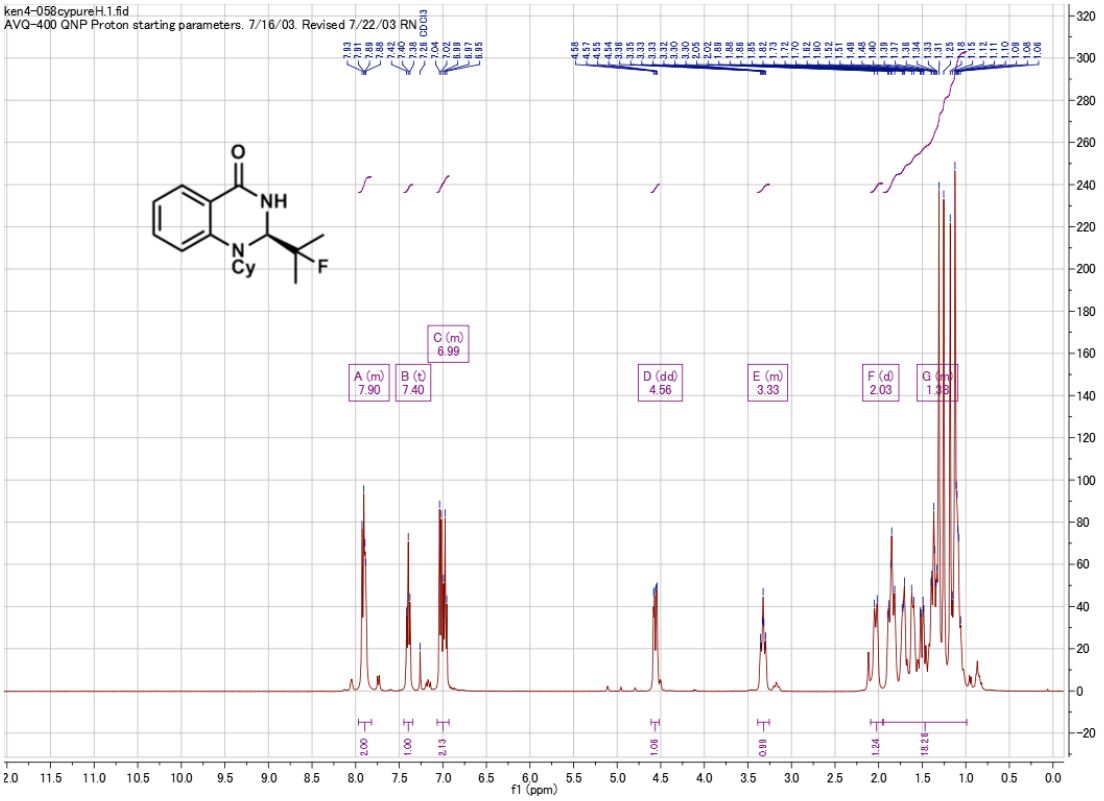
***(R)*-1-benzyl-2-(2-fluoropropan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2g)**

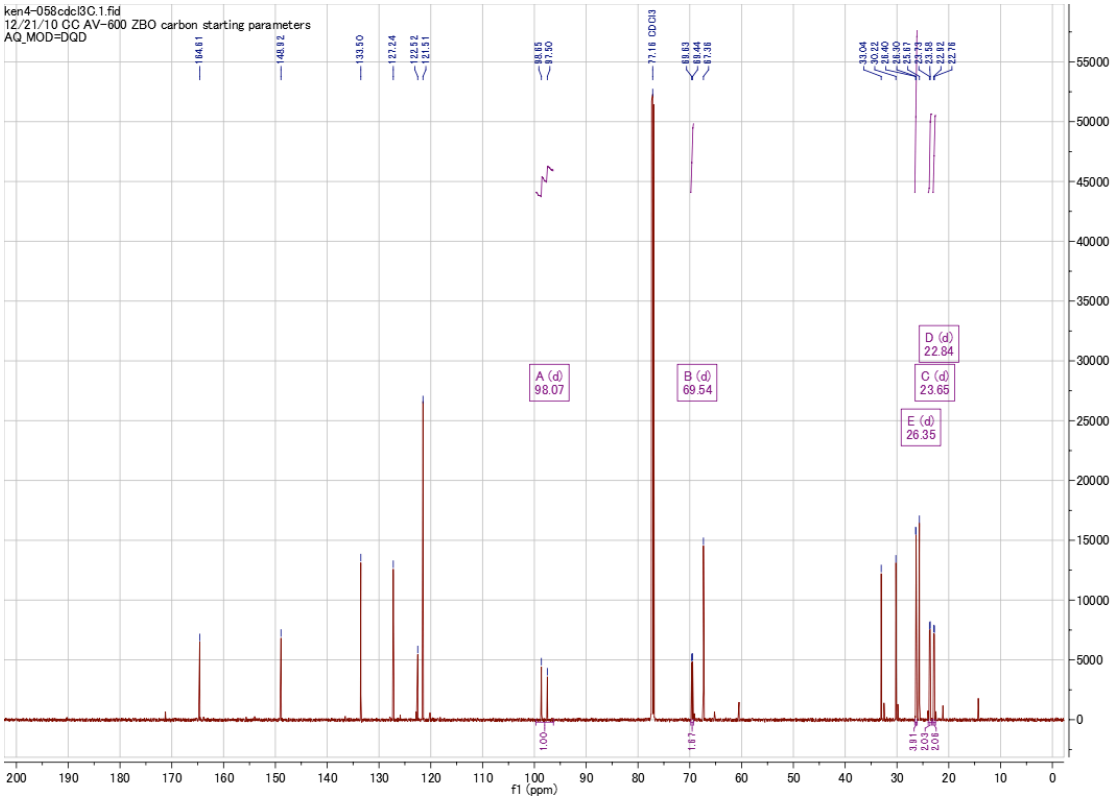


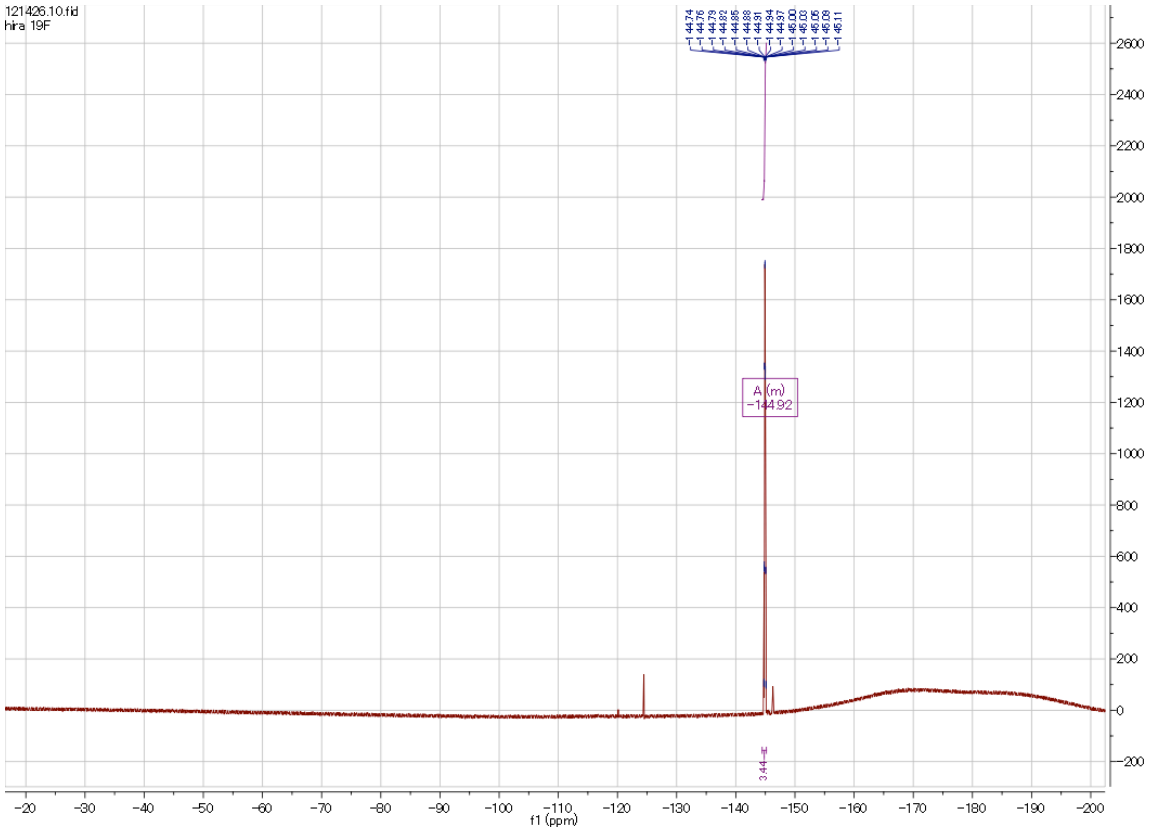



ken3-140F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-142.85
-142.97
-143.01
-143.03
-143.07
-143.09
-143.13
-143.14
-143.18
-143.20
A (m)
-143.08
1.00
f1 (ppm)

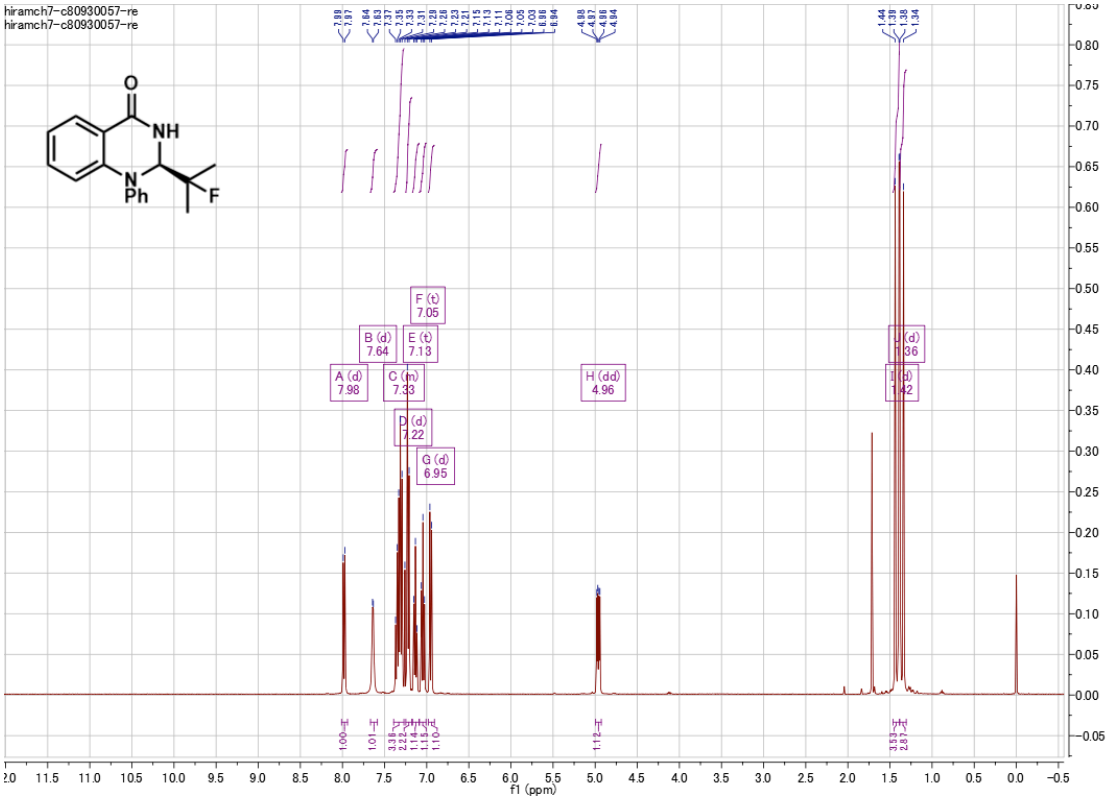
***(R)*-1-cyclohexyl-2-(2-fluoropropan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2h)**

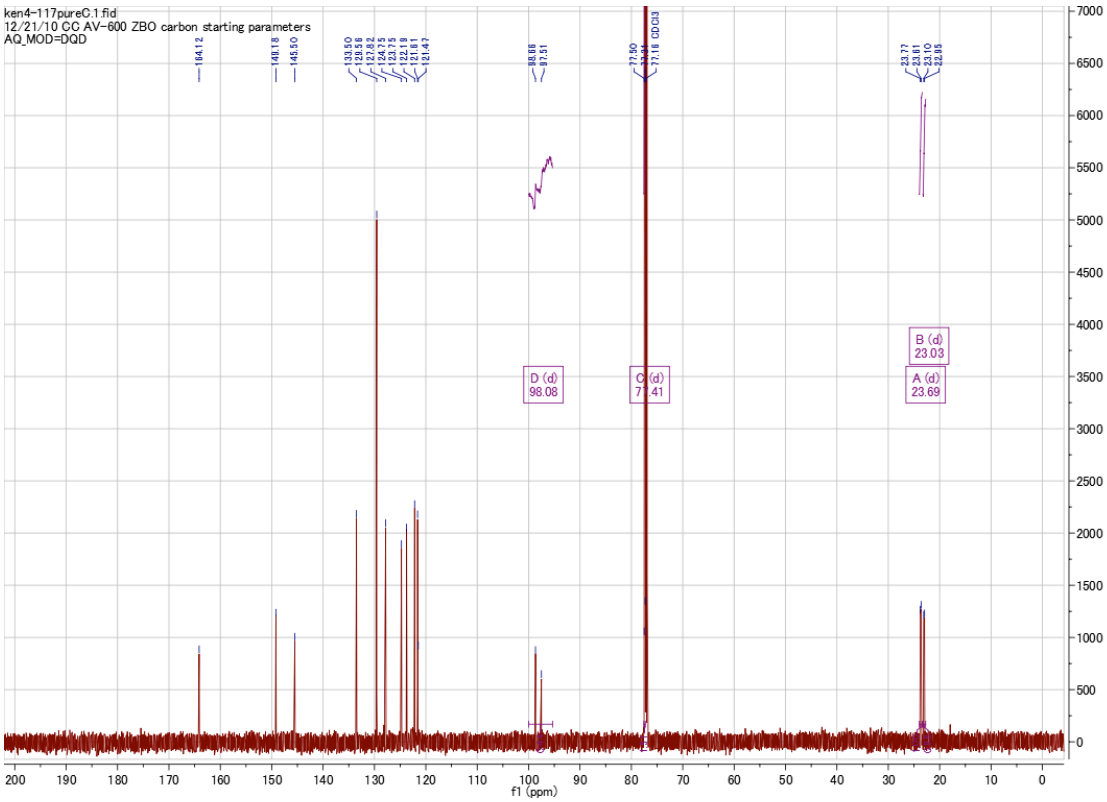


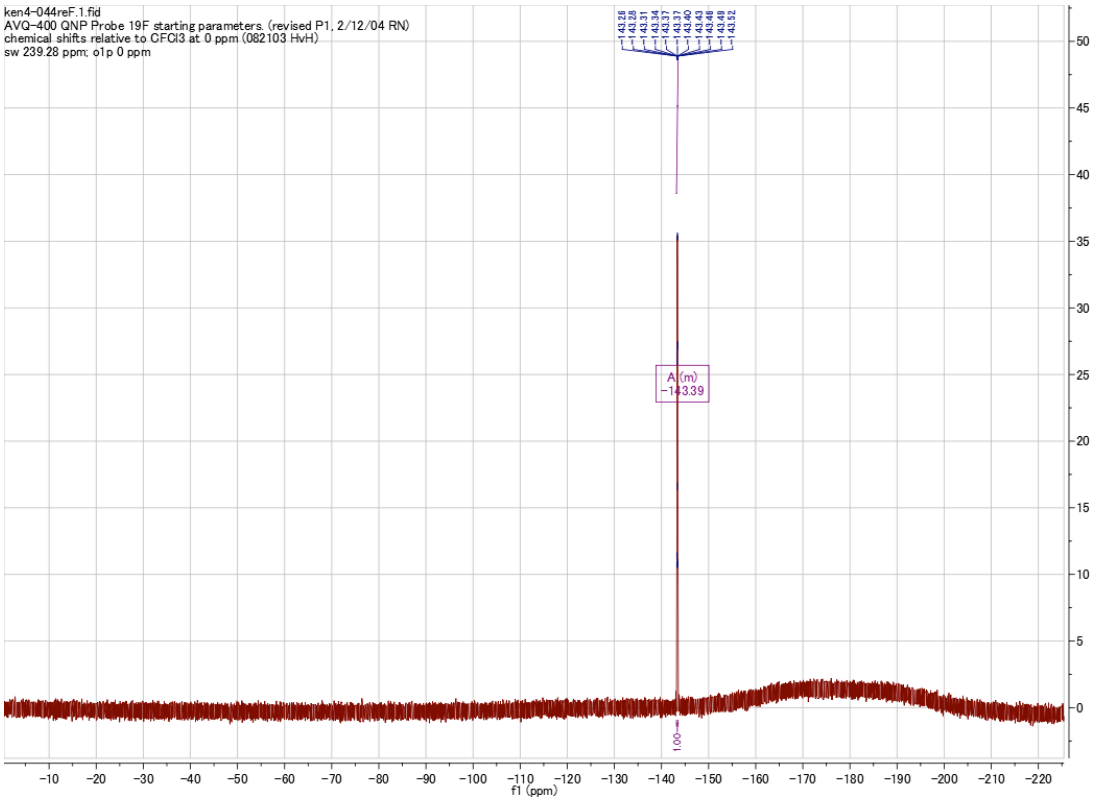



121426.10.fid
hira 19F
-144.74
-144.76
-144.79
-144.82
-144.85
-144.88
-144.91
-144.94
-144.97
-145.00
-145.03
-145.06
-145.09
-145.11
A (m)
-144.92
3.444E
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

***(R)*-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2i)**

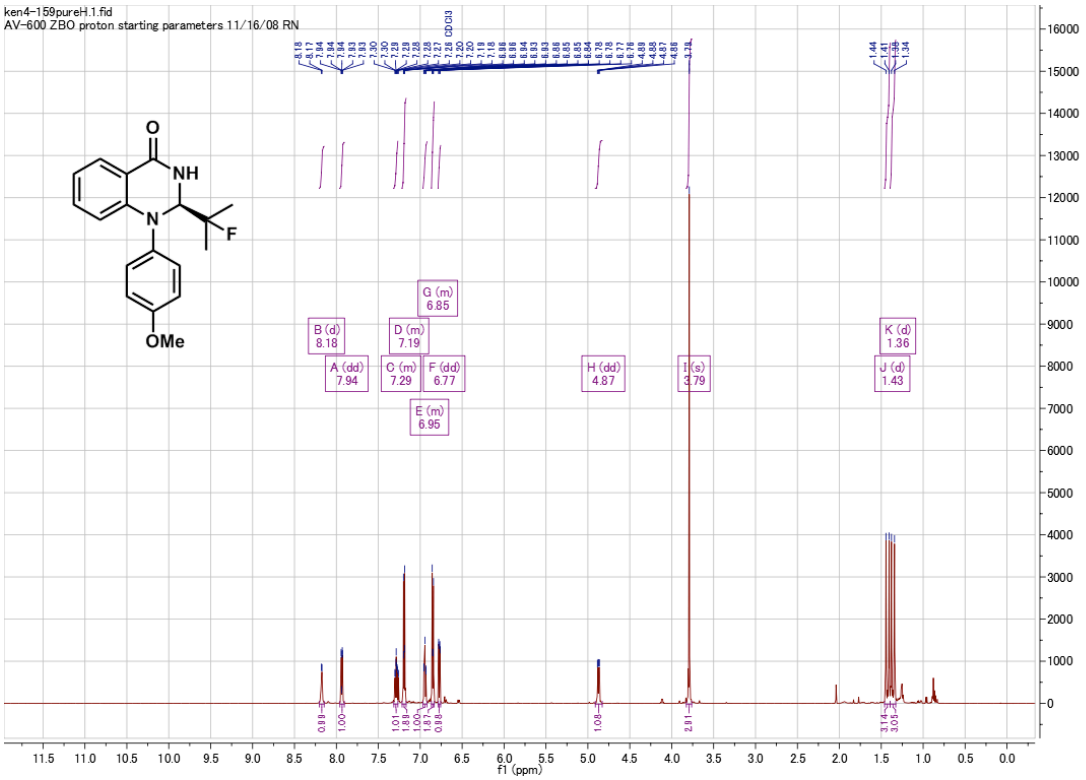


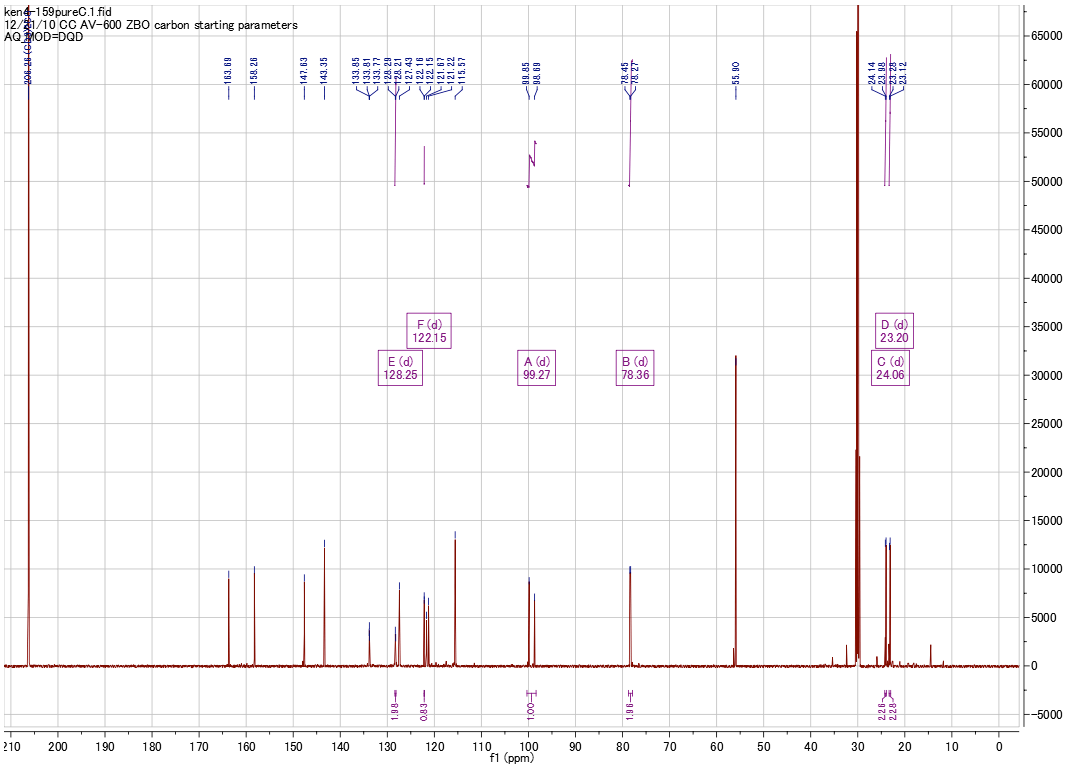


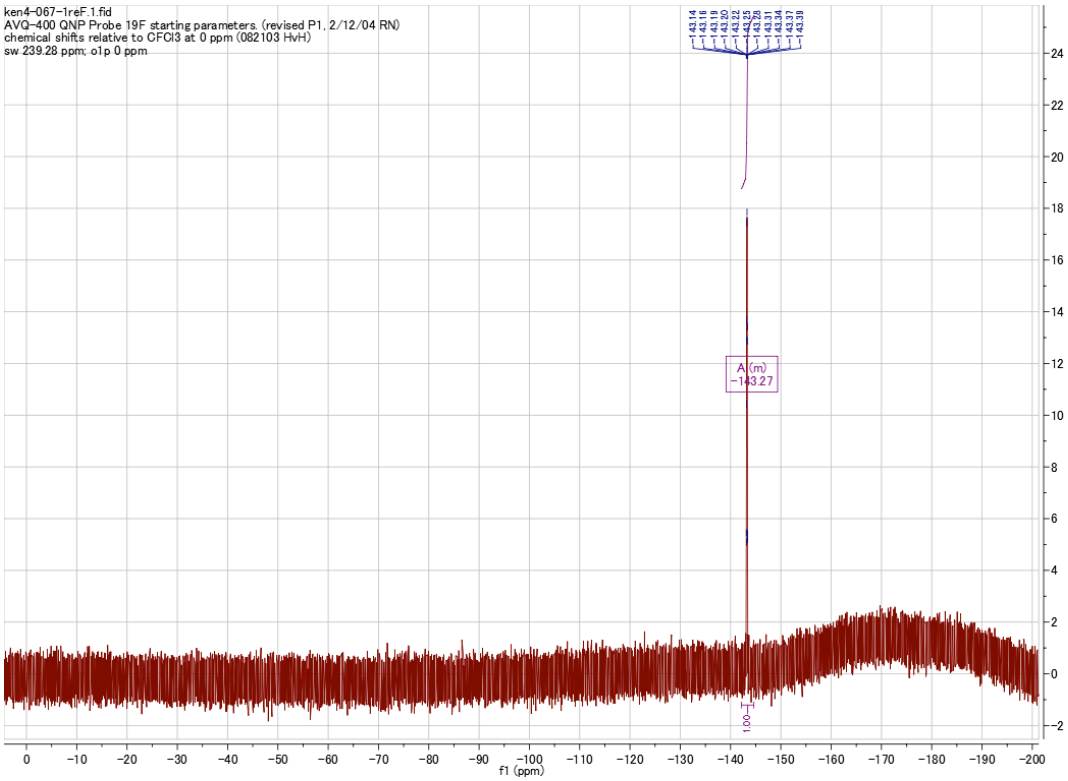

ken4-044reF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-143.28
-143.28
-143.31
-143.34
-143.37
-143.37
-143.40
-143.43
-143.46
-143.49
-143.52
A (m)
-143.39
1.00
f1 (ppm)

***(R)*-2-(2-fluoropropan-2-yl)-1-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one**

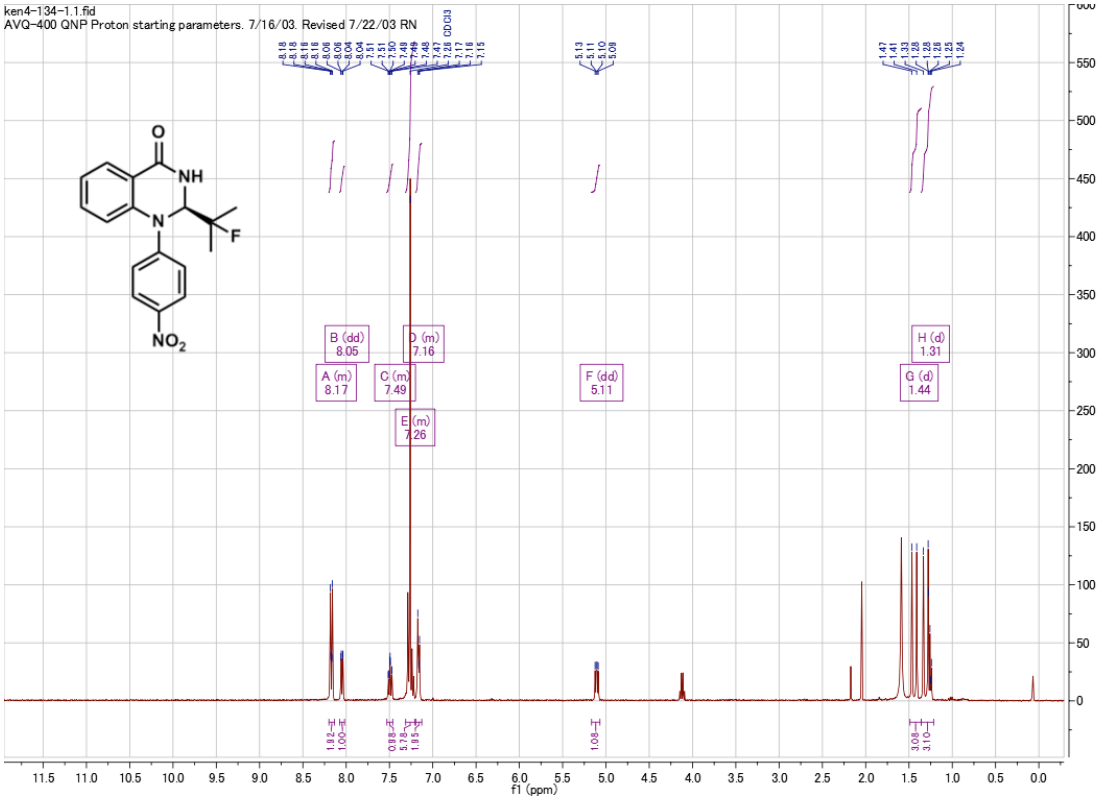
(2j)

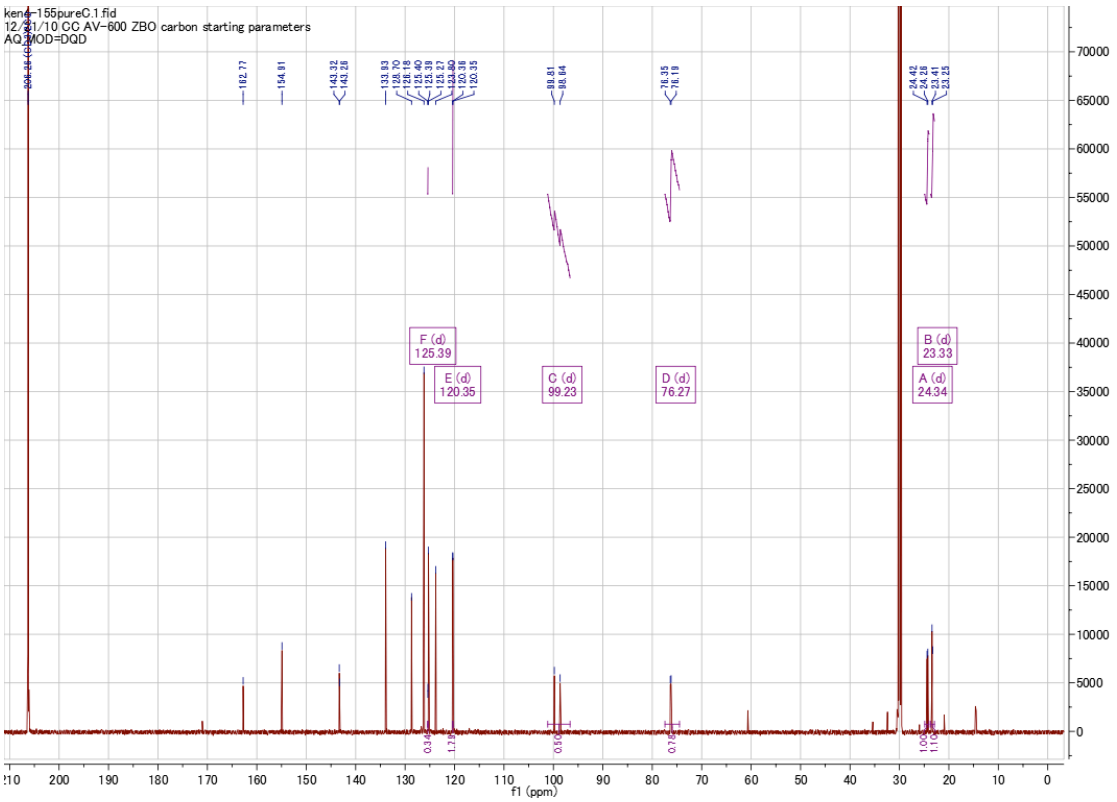


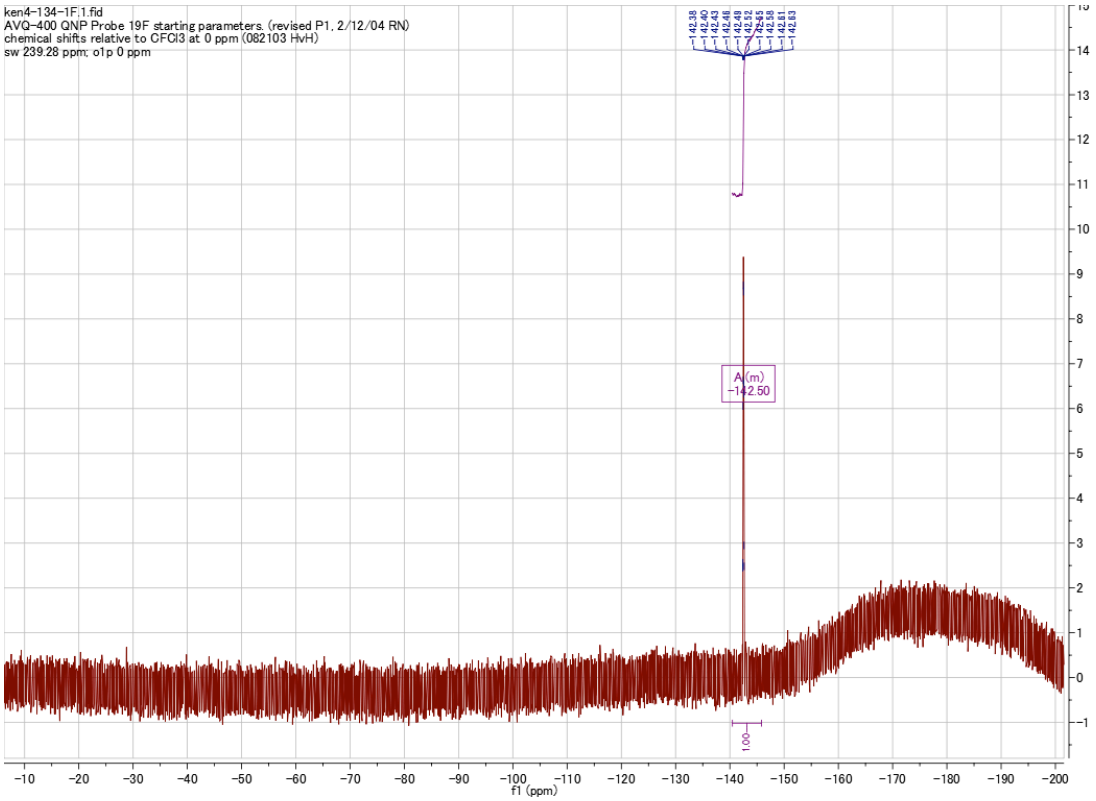

ken4-159pureC.1.fid
12/31/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
F (d)
122.15
E (d)
128.25
A (d)
99.27
B (d)
78.36
D (d)
23.20
C (d)
24.06
f1 (ppm)


ken4-067-1reF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A (m)
-143.27
f1 (ppm)

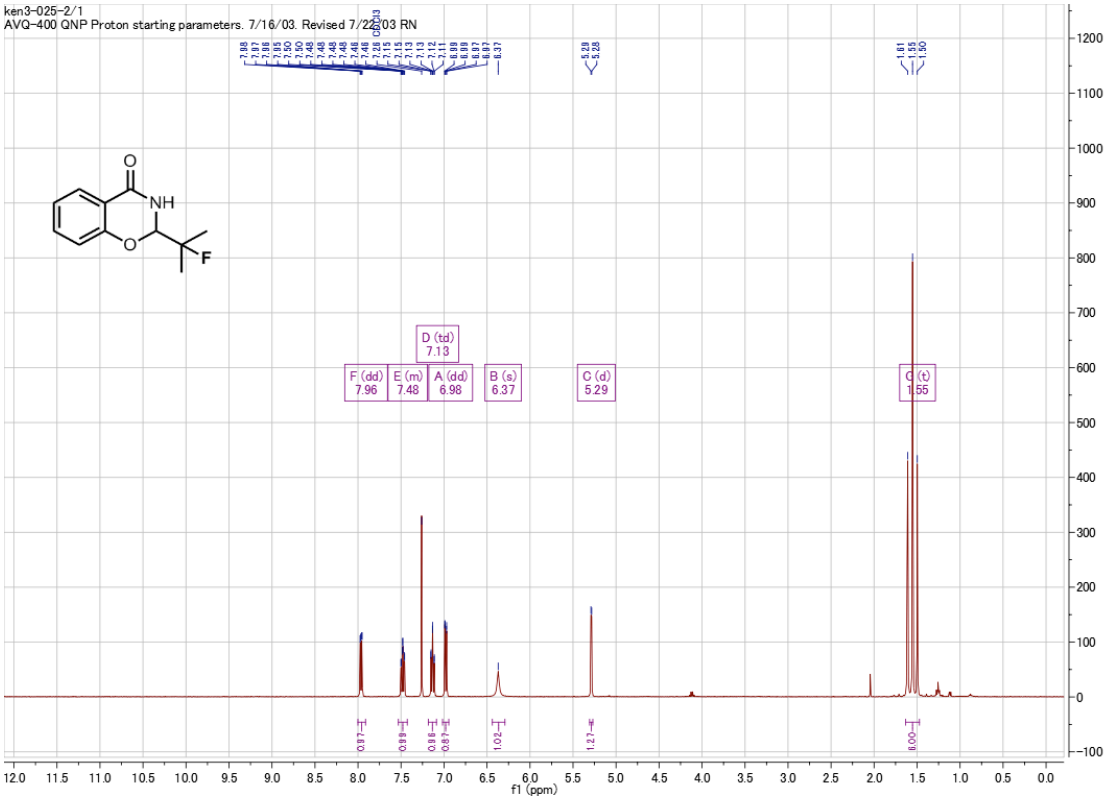
(R)-2-(2-fluoropropan-2-yl)-1-(4-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (2k)

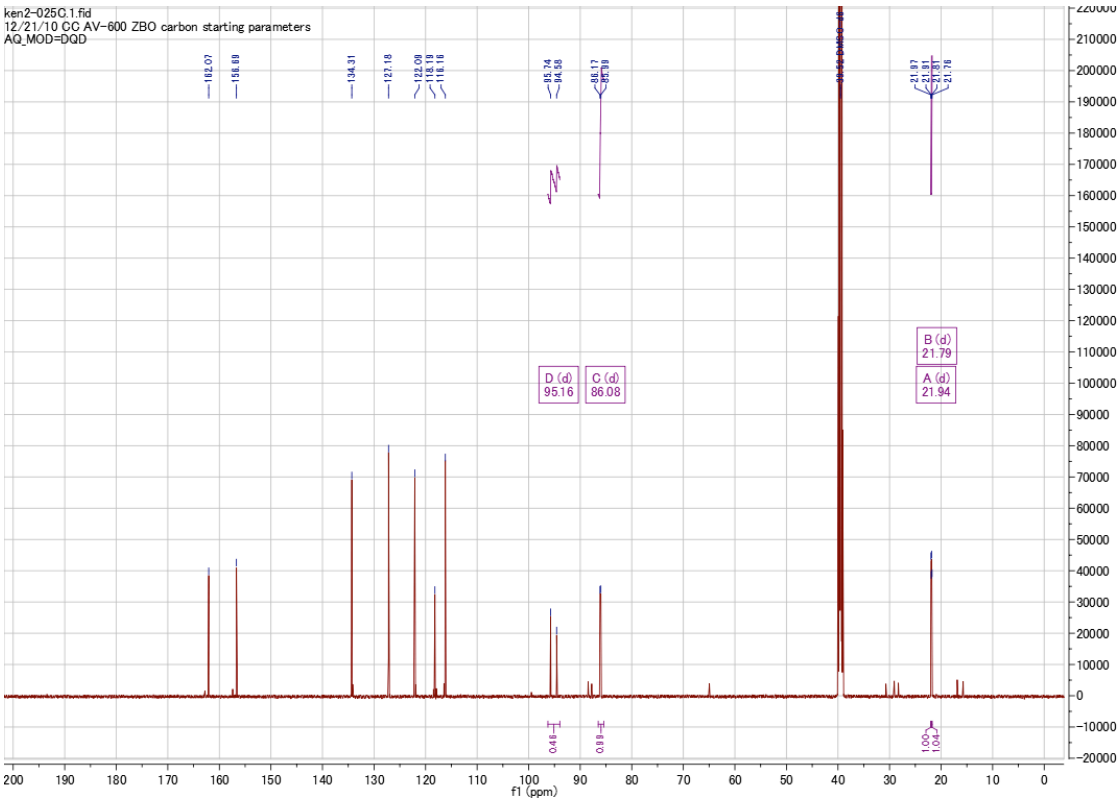


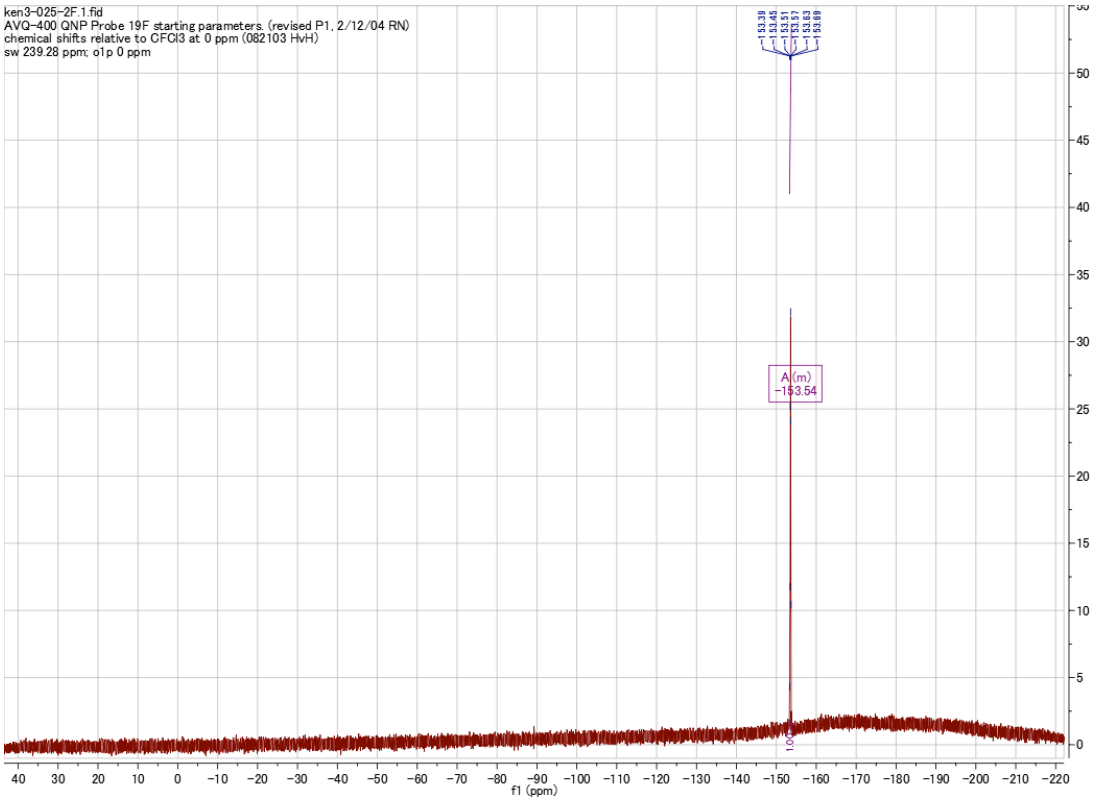



ken4-134-1F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A(m)
-142.50
1.00
f1 (ppm)

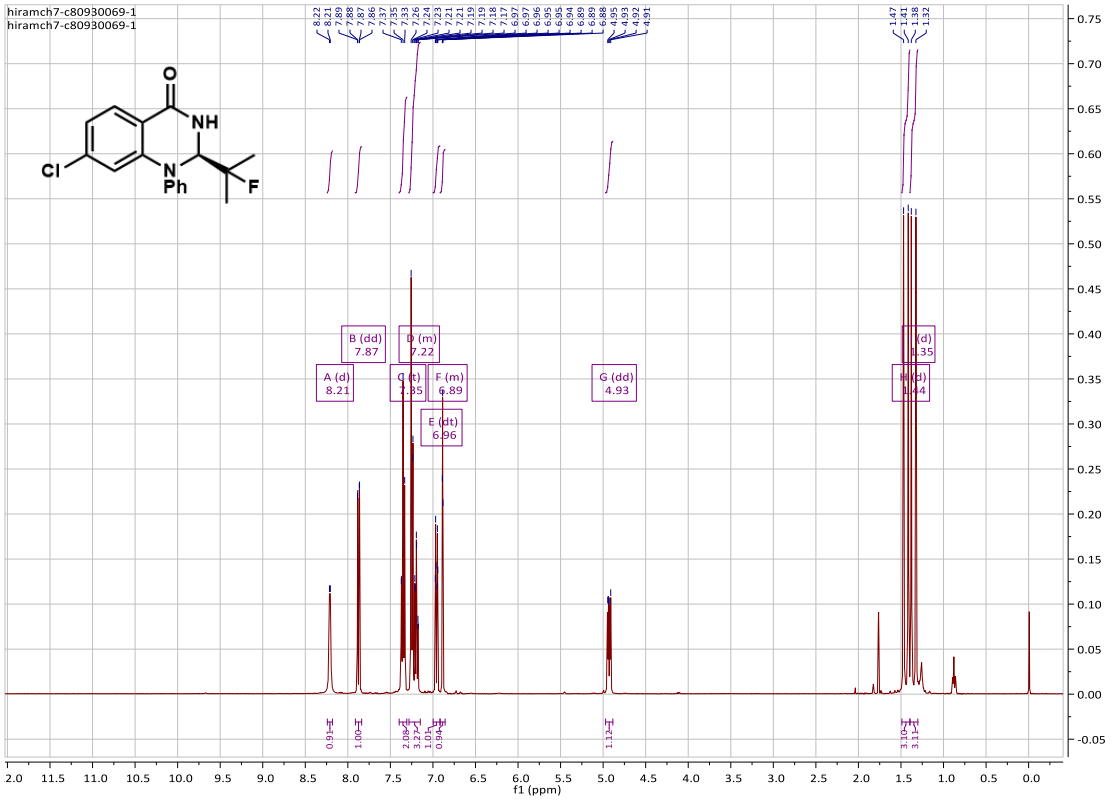
2-(2-fluoropropan-2-yl)-2H-benzo[e][1,3]oxazin-4(3H)-one (2l)

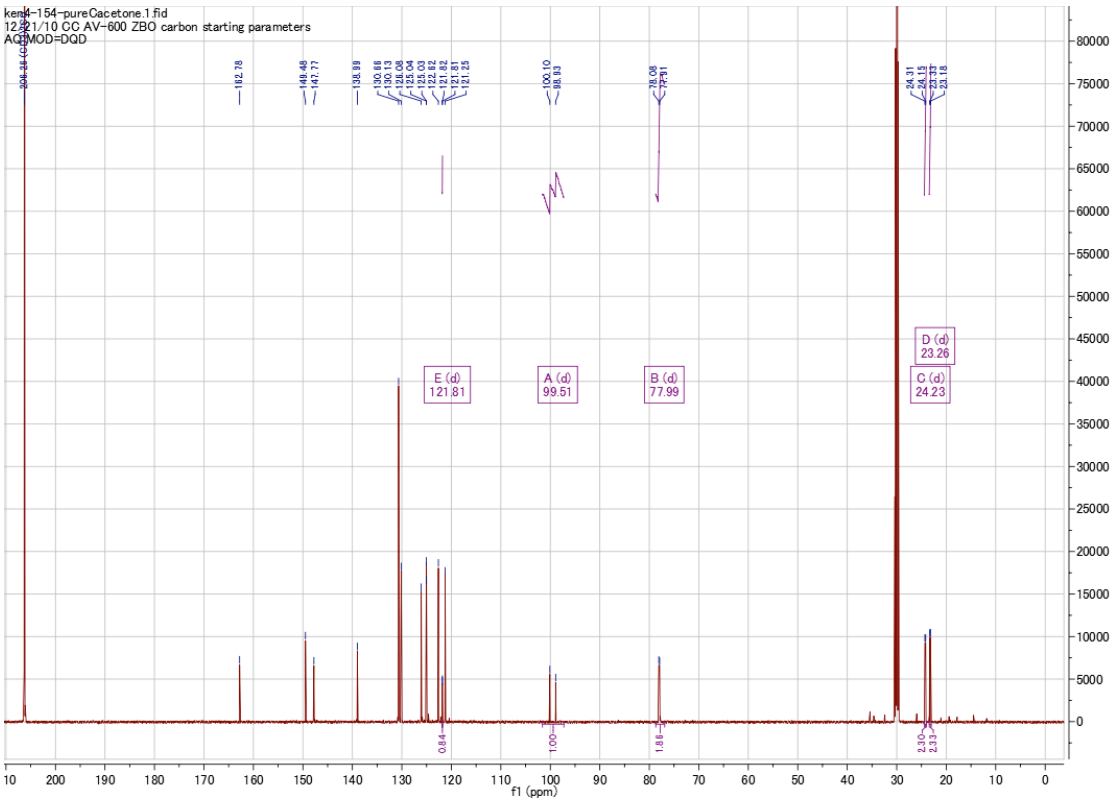


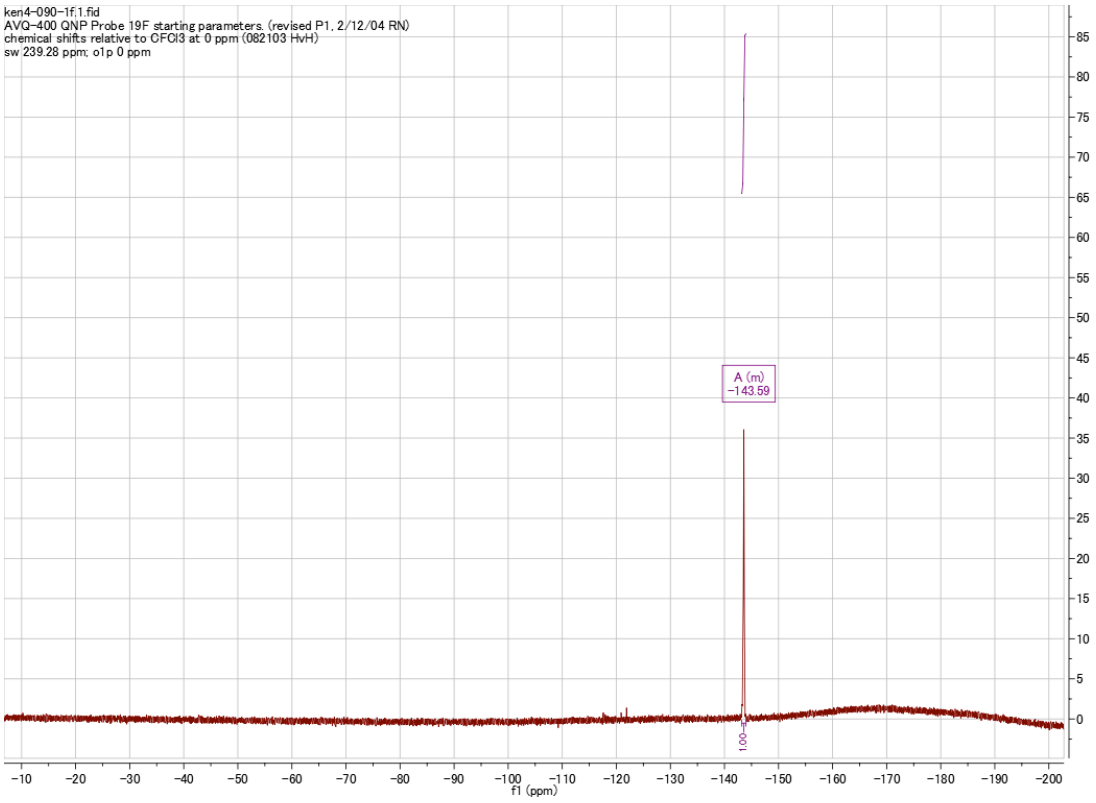



ken3-025-2F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A(m)
-153.54
f1 (ppm)

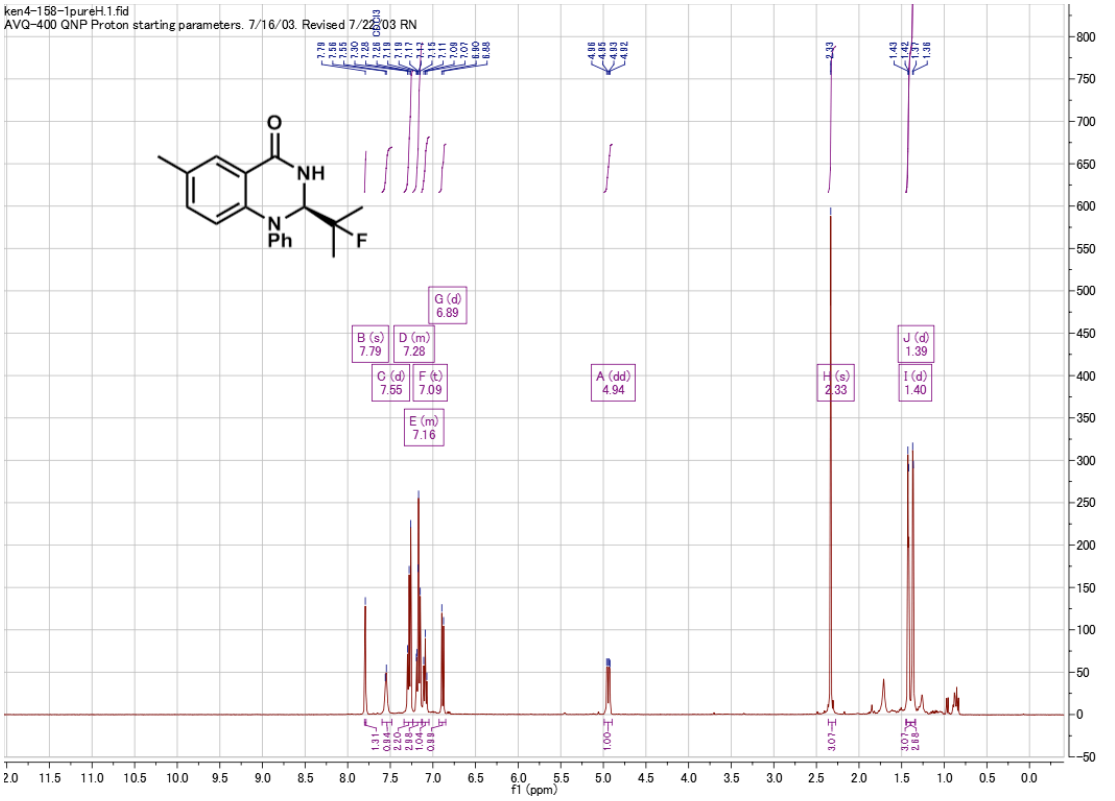
_(R)_-7-chloro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2m)

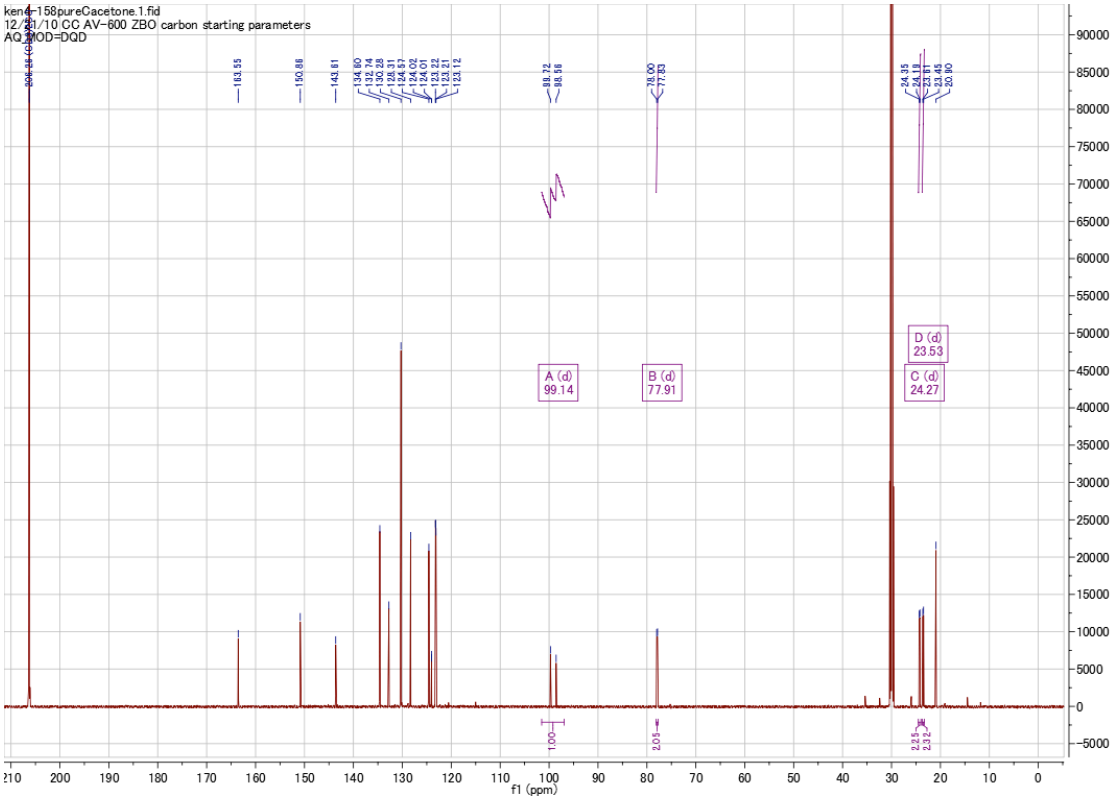


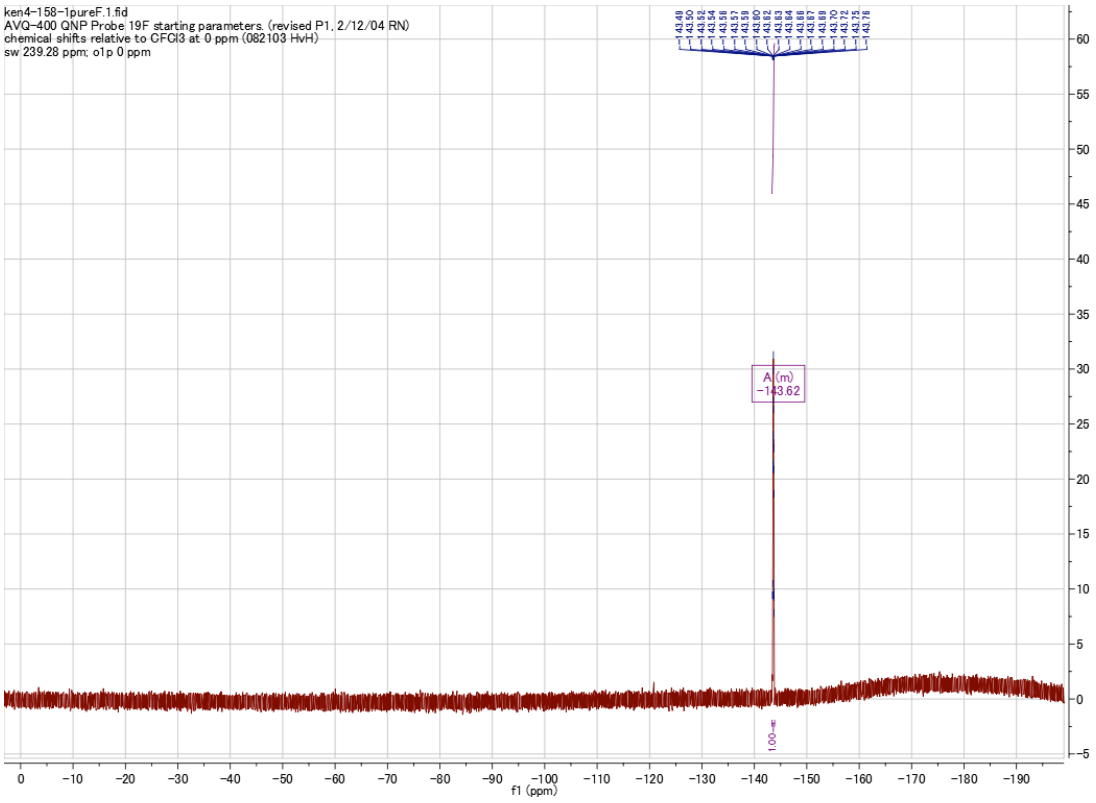



ken4-090-1f.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A (m)
-143.59
1.00
f1 (ppm)

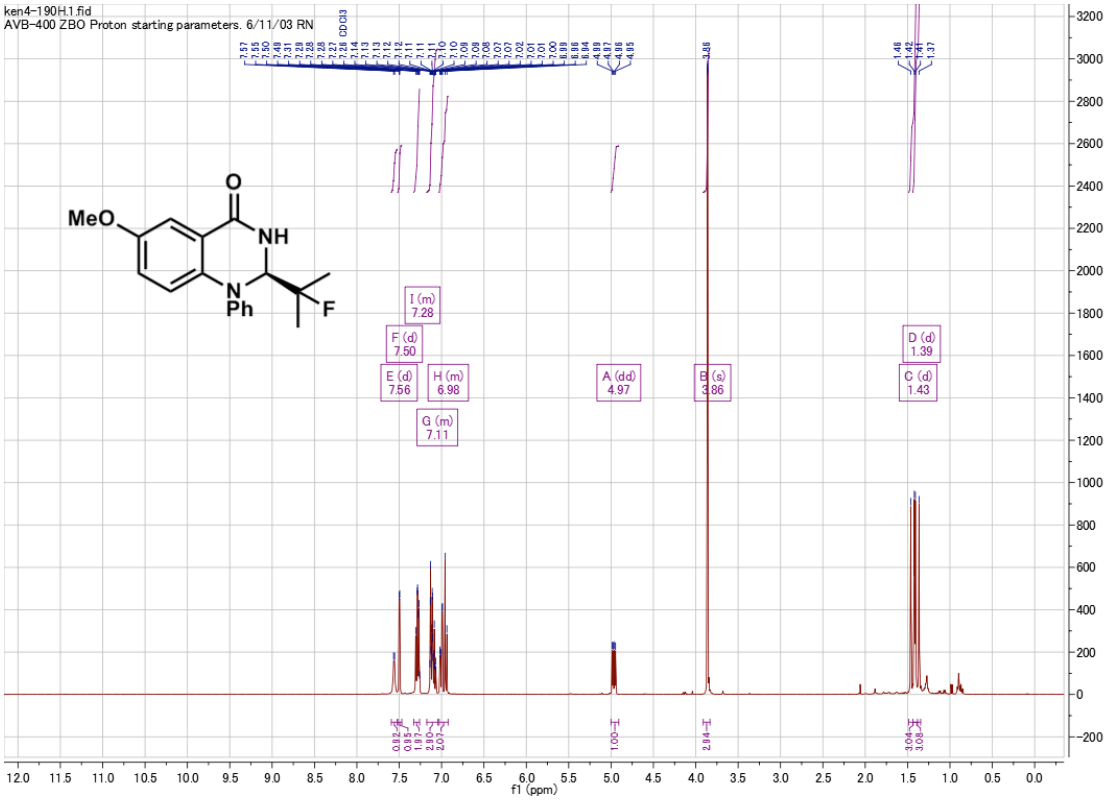
(R)-2-(2-fluoropropan-2-yl)-6-methyl-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2n)

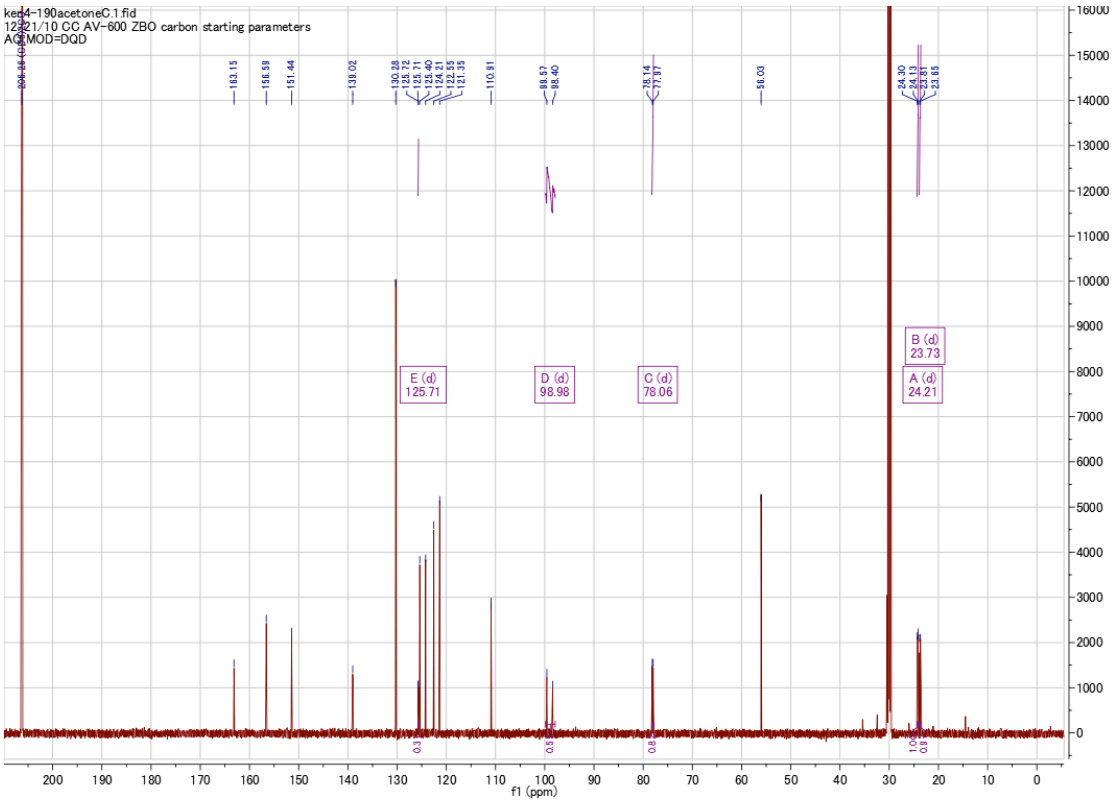


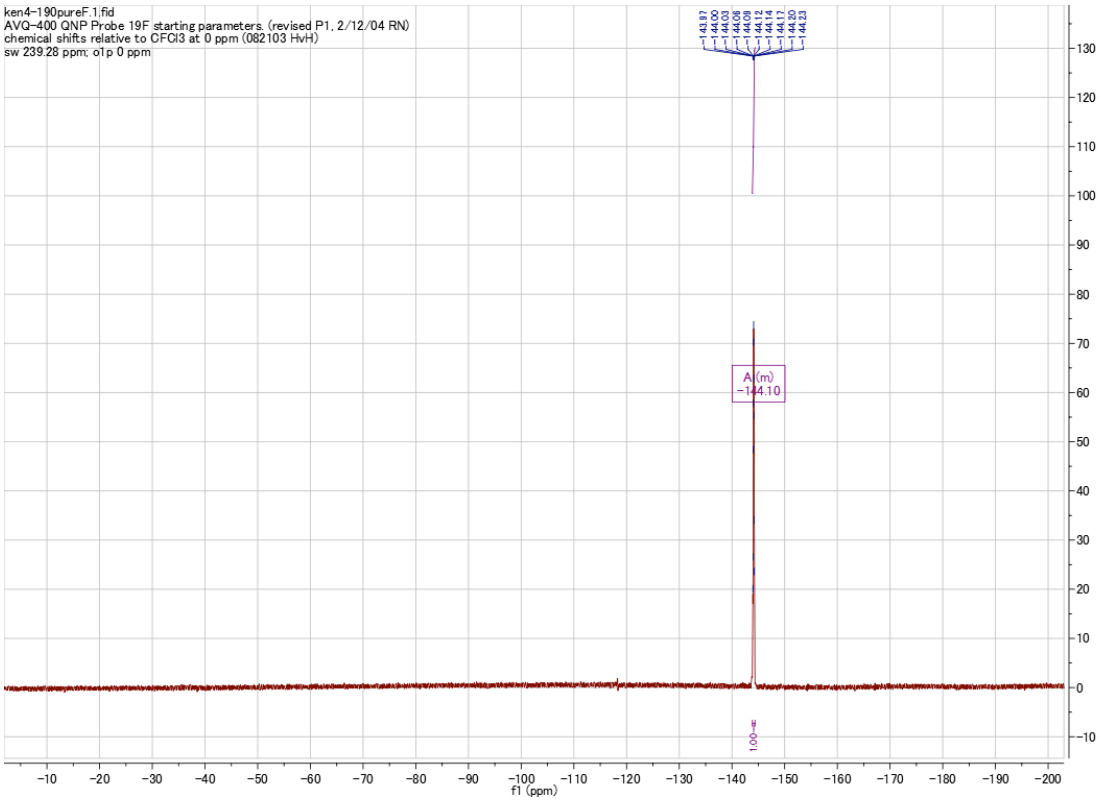



ken4-158-1pureF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A (m)
-143.62
1.00
f1 (ppm)

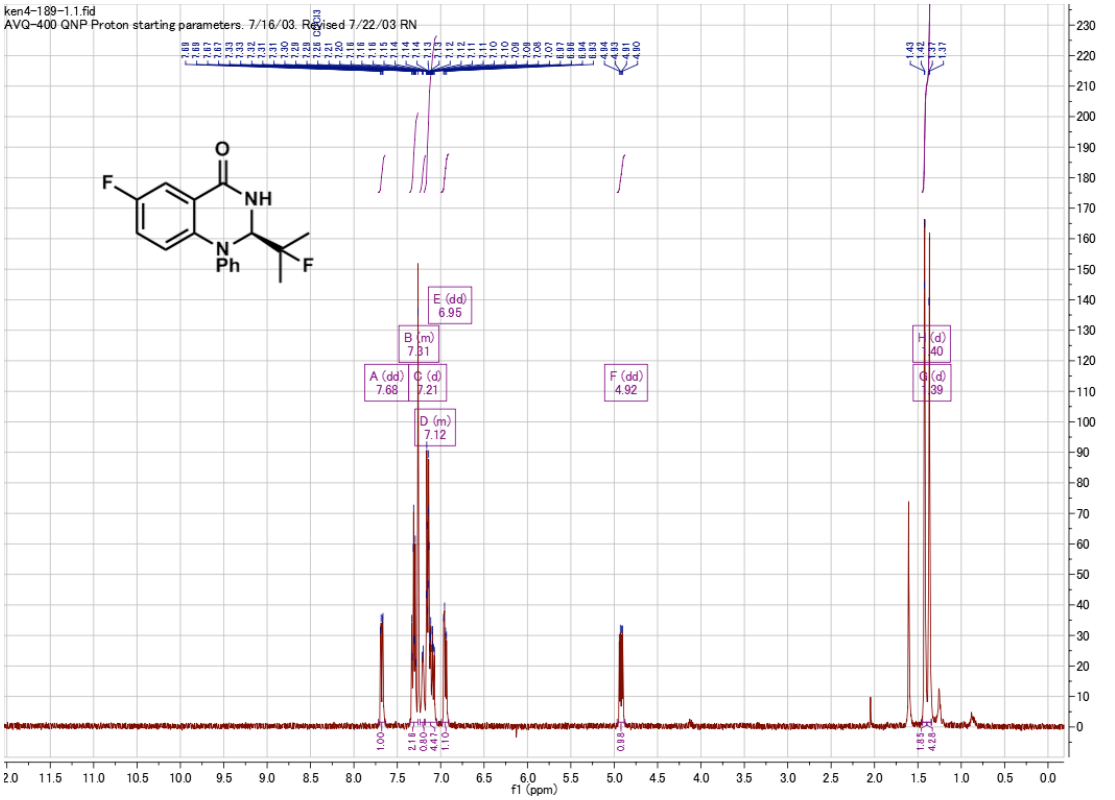
***(R)*-2-(2-fluoropropan-2-yl)-6-methoxy-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2o)**

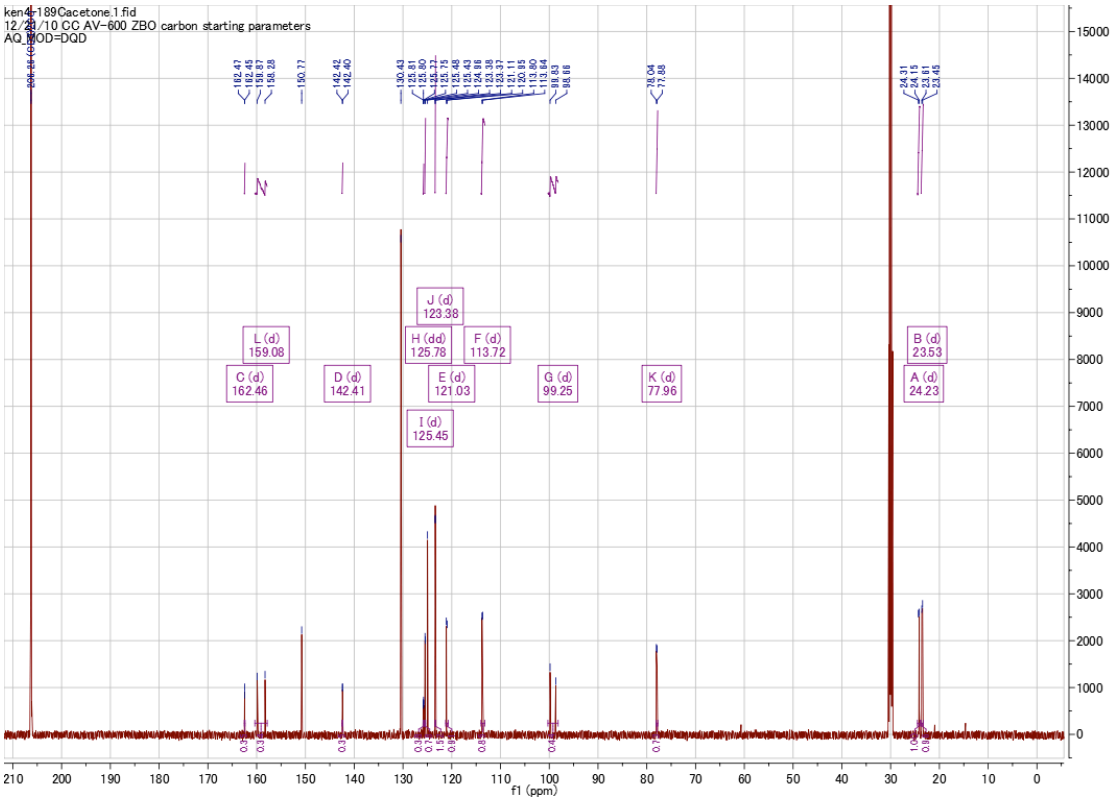


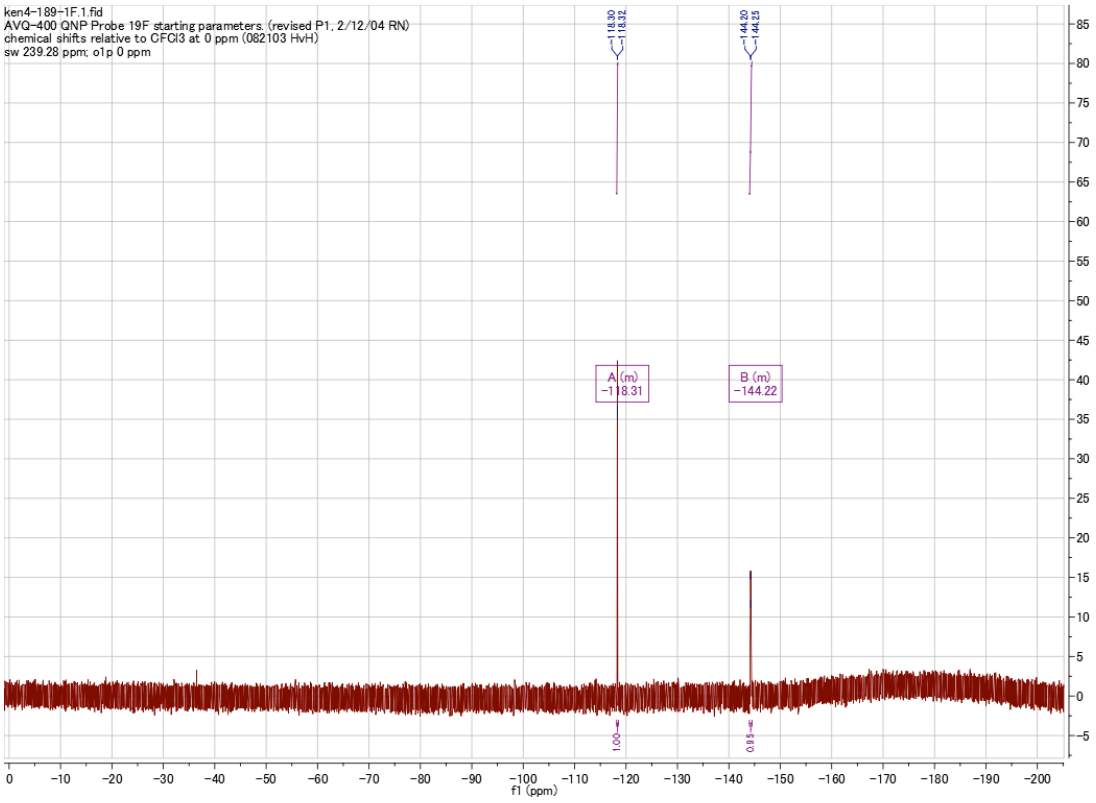



ken4-190pureF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-143.97
-144.00
-144.03
-144.06
-144.09
-144.12
-144.14
-144.17
-144.20
-144.23
A (m)
-144.10
1.00
f1 (ppm)

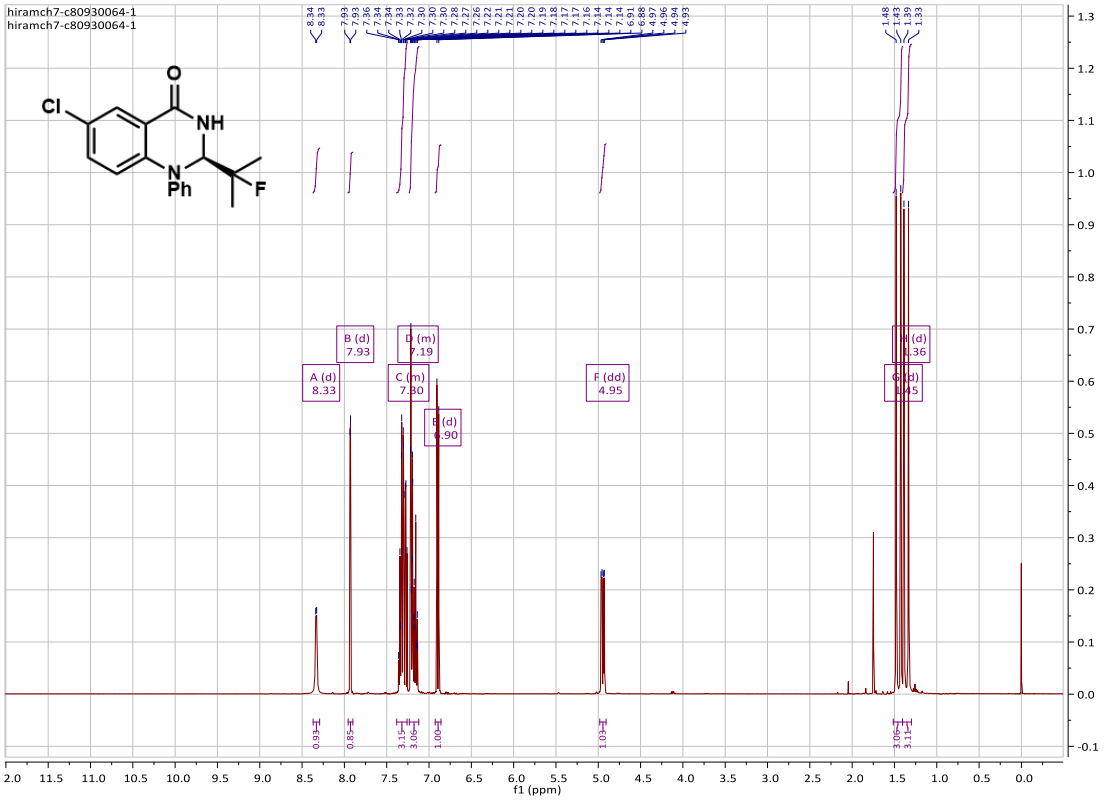
***(R)*-6-fluoro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2p)**

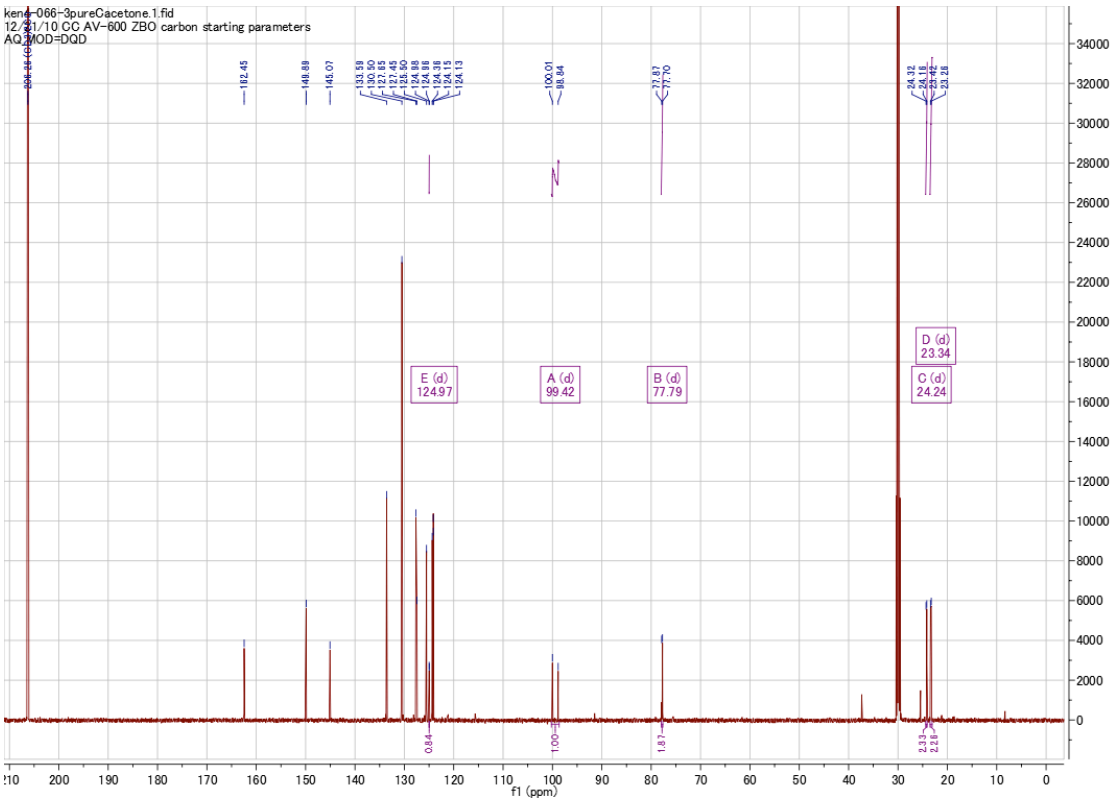


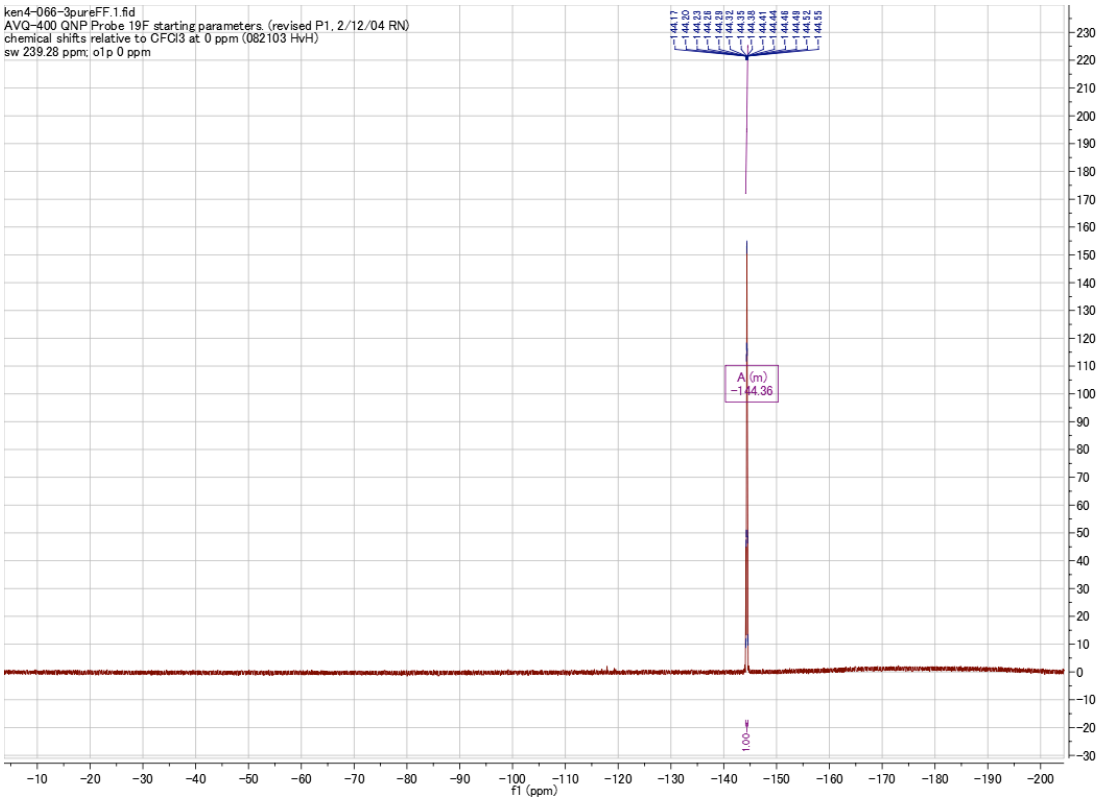



ken4-189-1F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-118.30
-118.32
-144.20
-144.25
A (m)
-118.31
B (m)
-144.22
1.00
0.81
f1 (ppm)

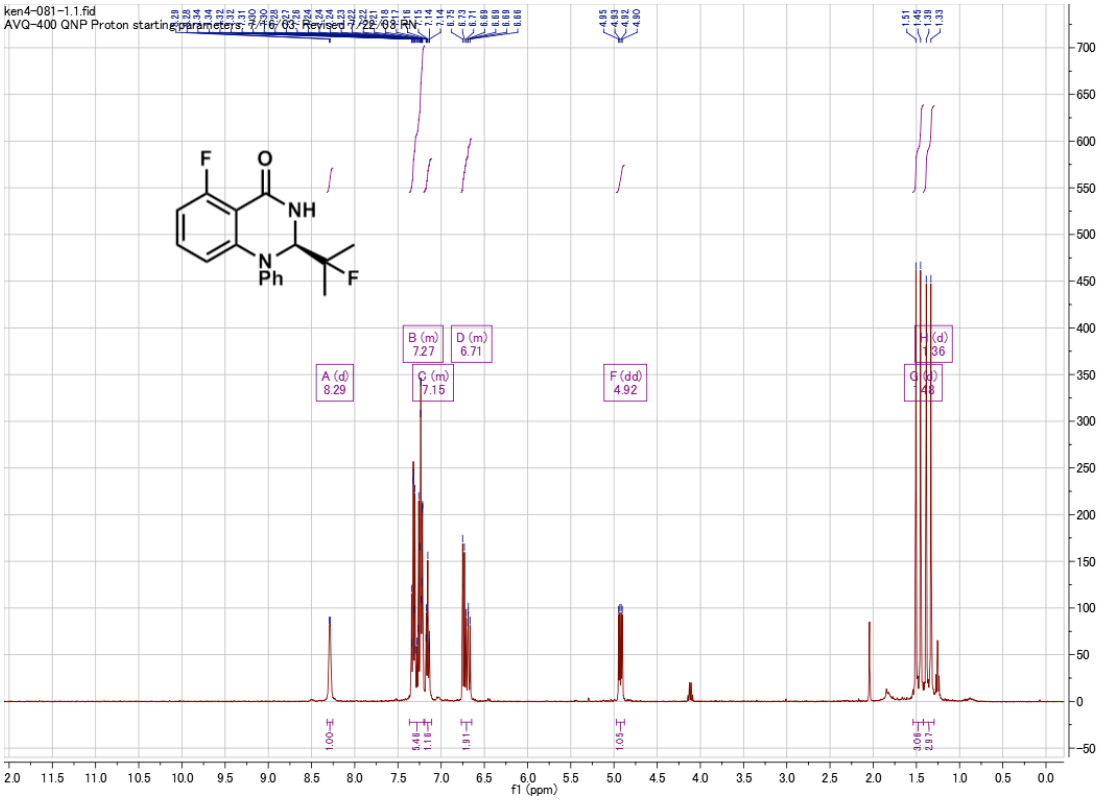
(R)-6-chloro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2q)

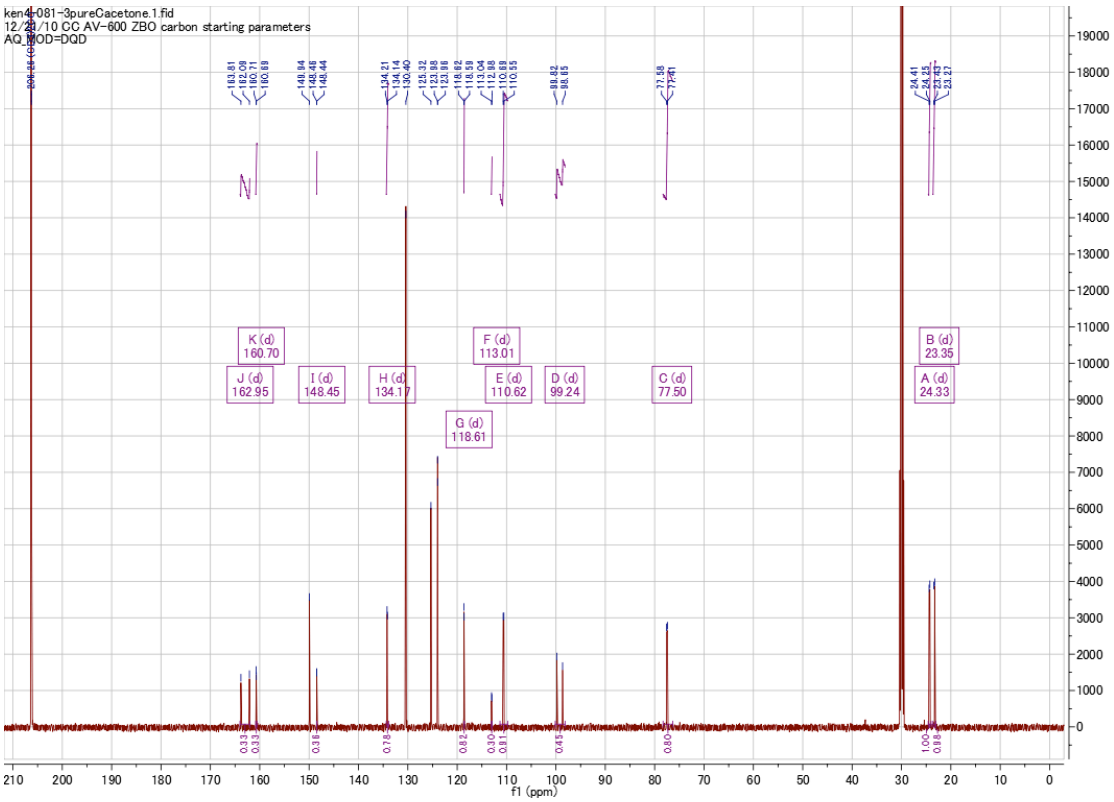


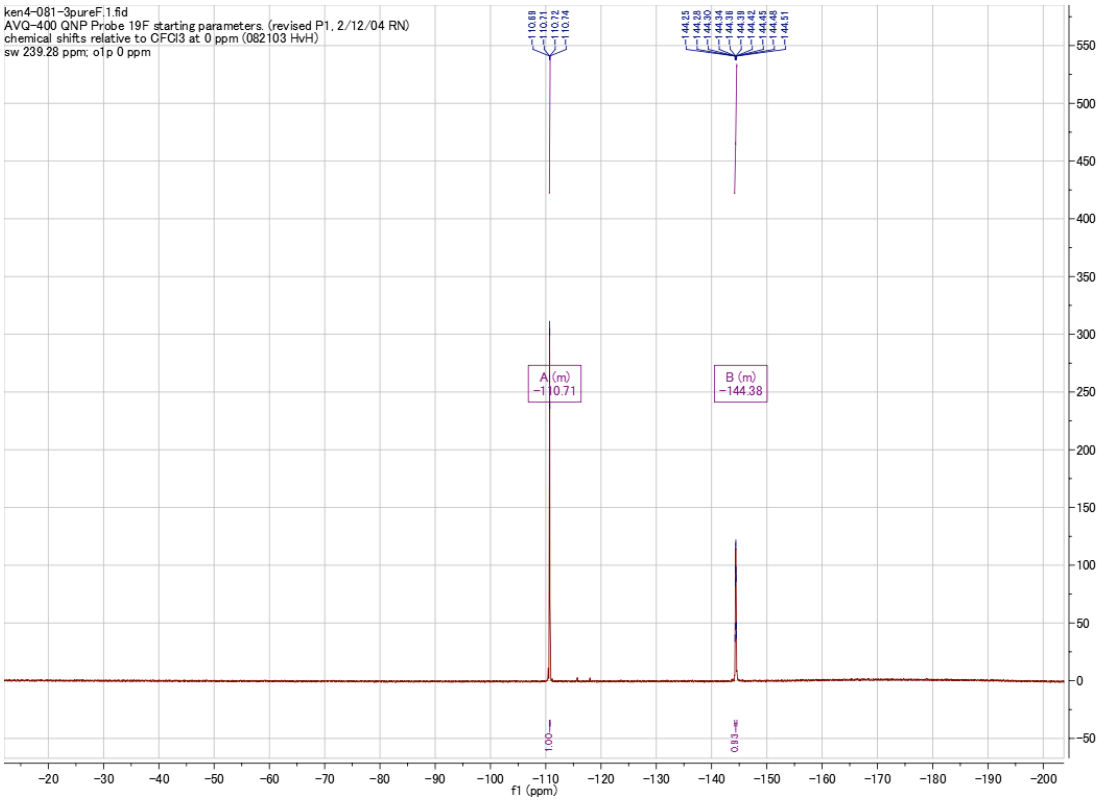



ken4-066-3pureFF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A (m)
-144.36
1.00
f1 (ppm)

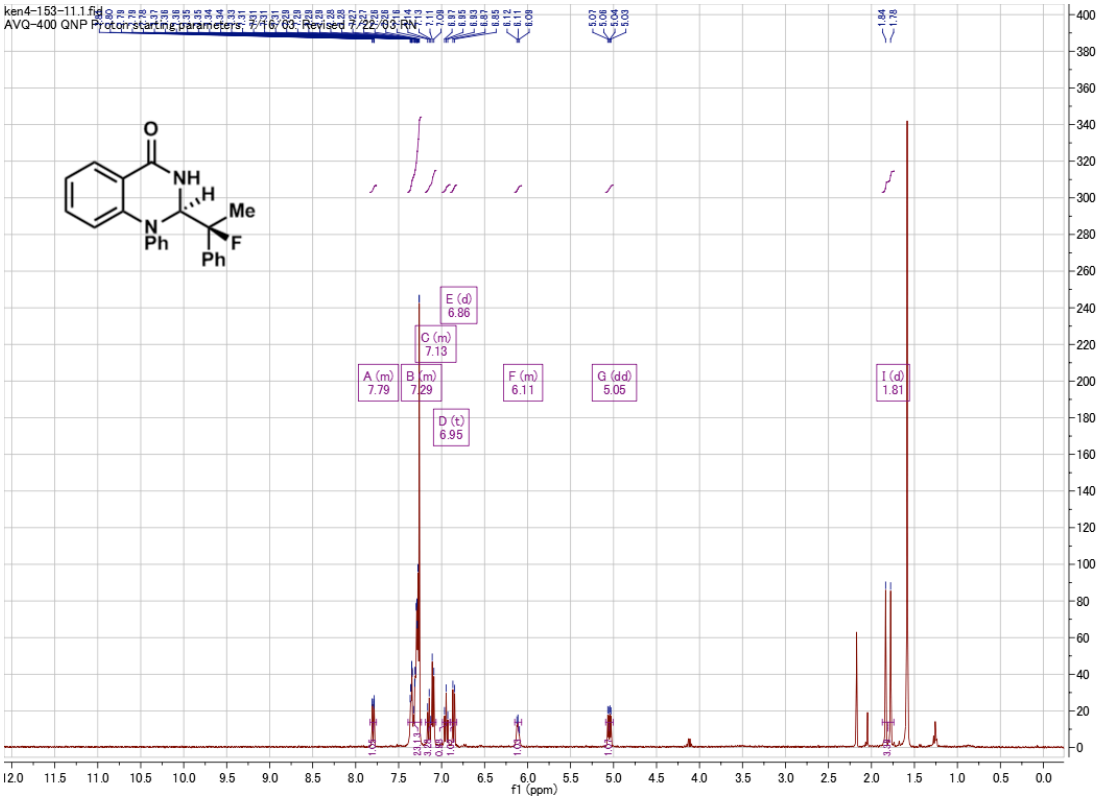
***(R)*-5-fluoro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2r)**

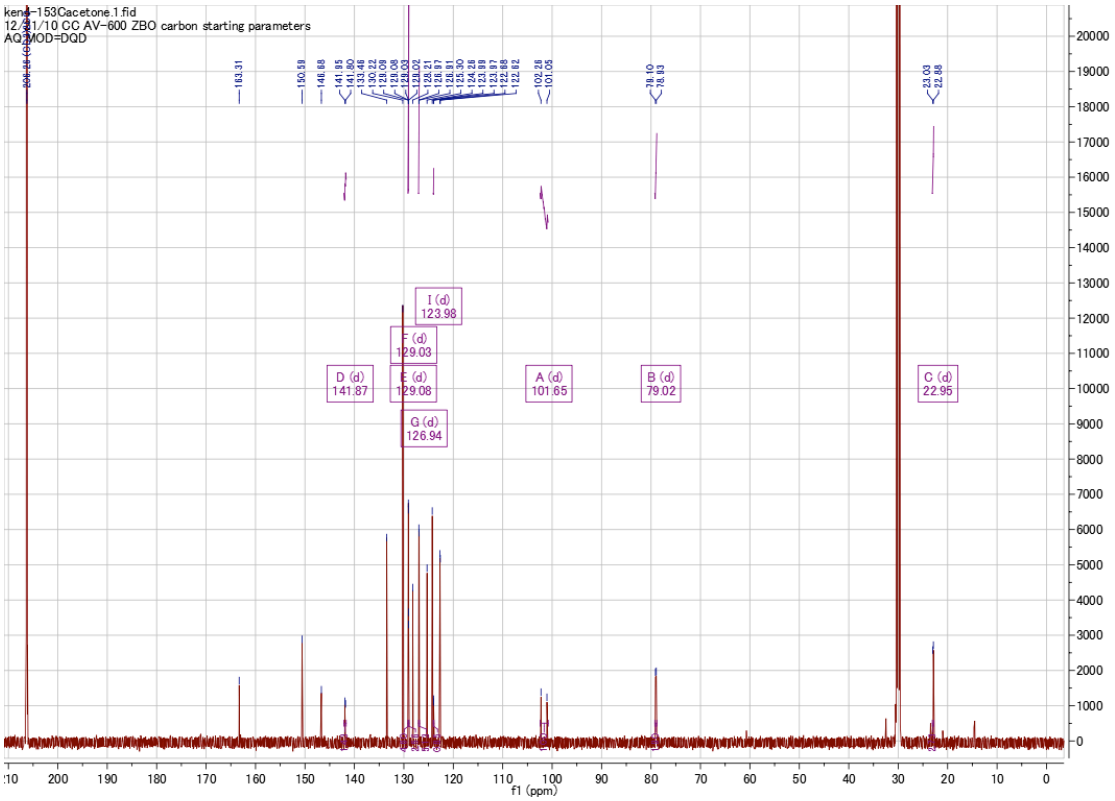


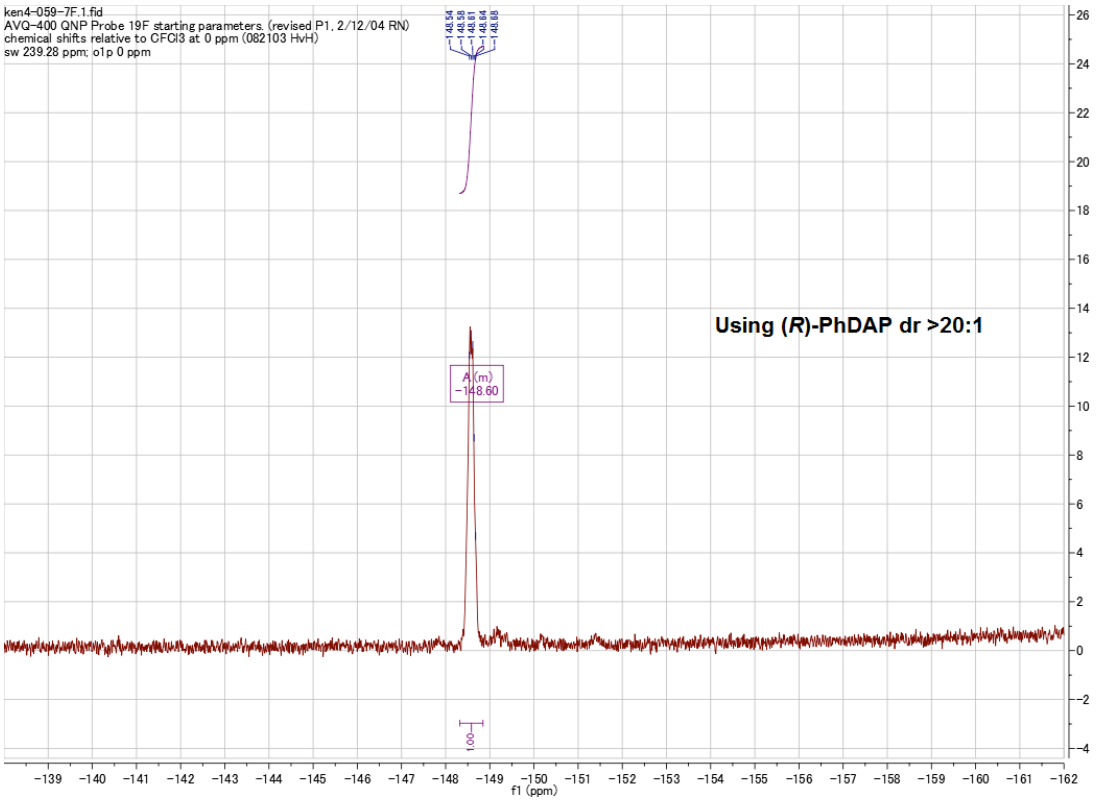


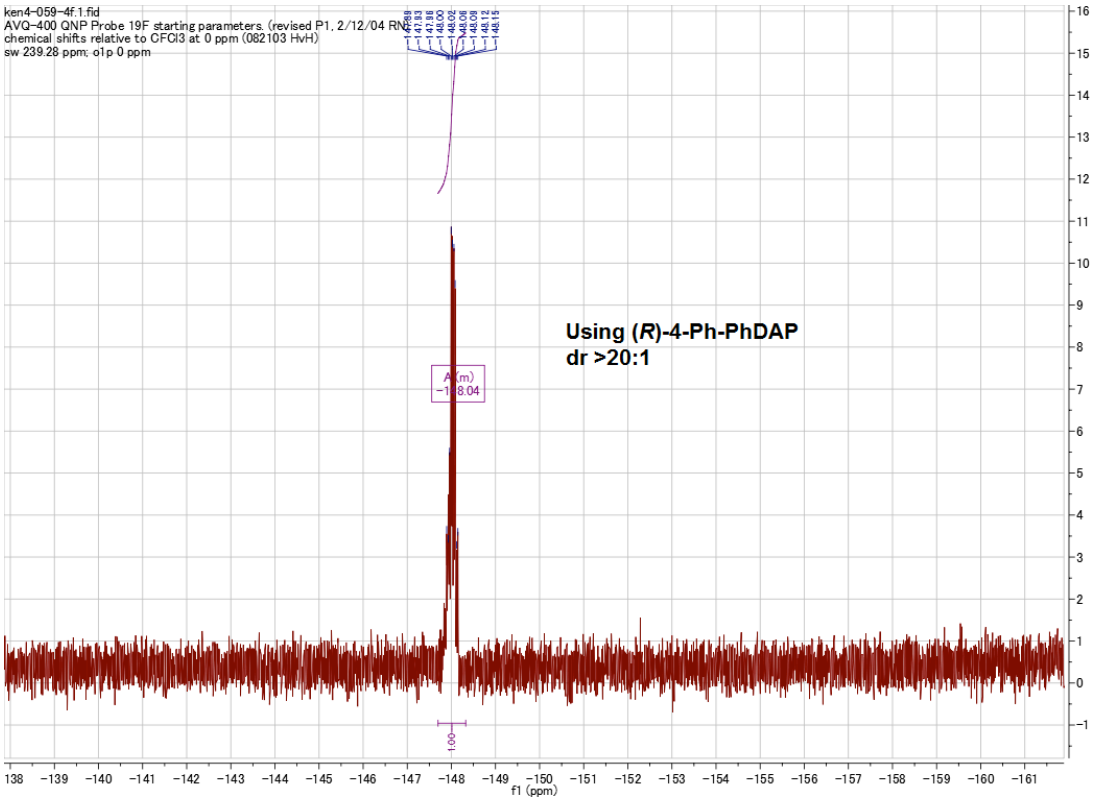

ken4-081-3pureF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
A (m)
-110.71
B (m)
-144.38
1.00
0.83
f1 (ppm)

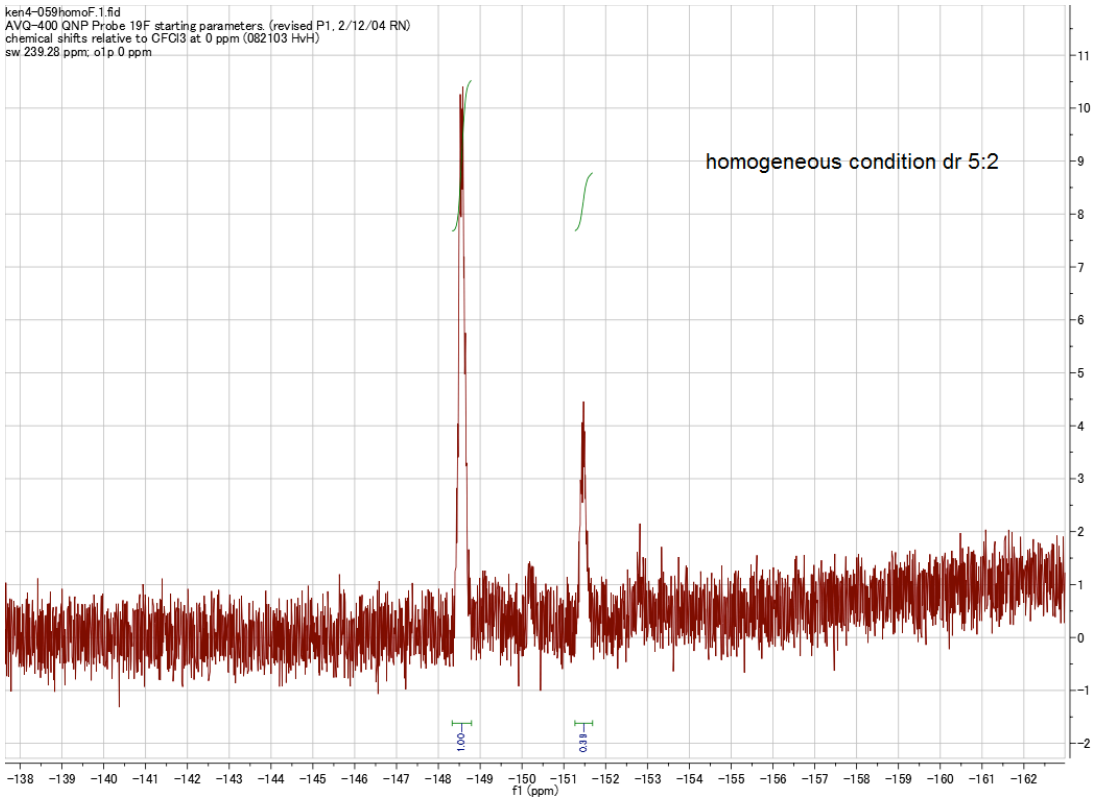
(*R*)-2-((*S*)-1-fluoro-1-phenylethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2s)



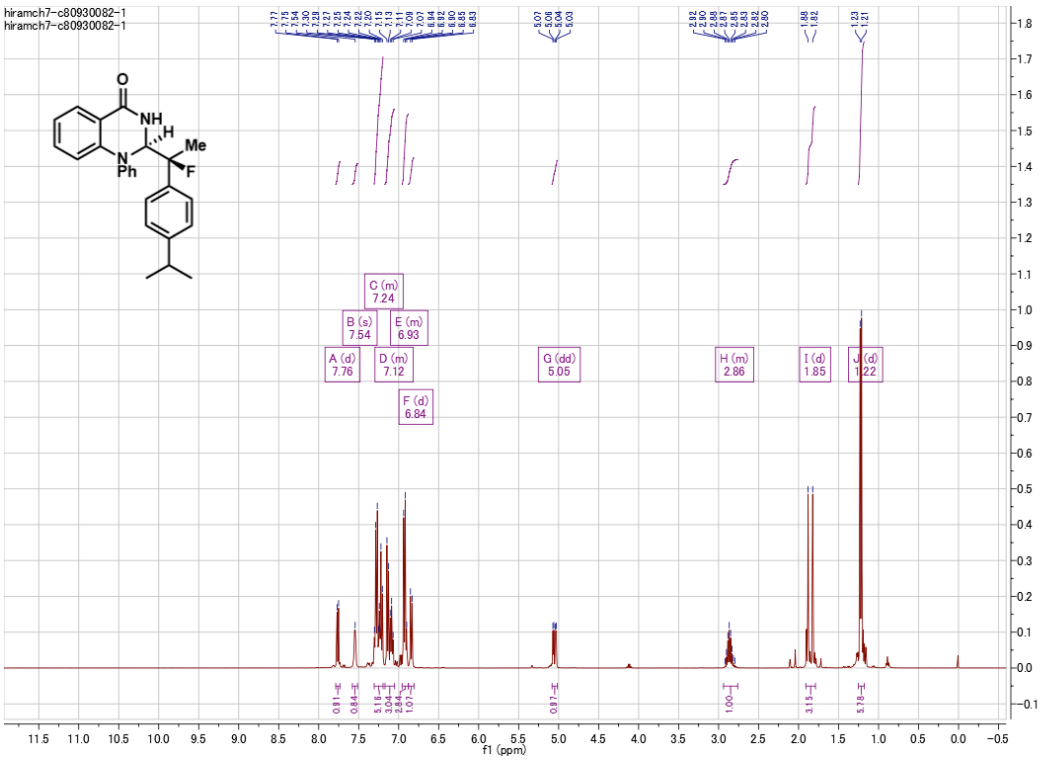


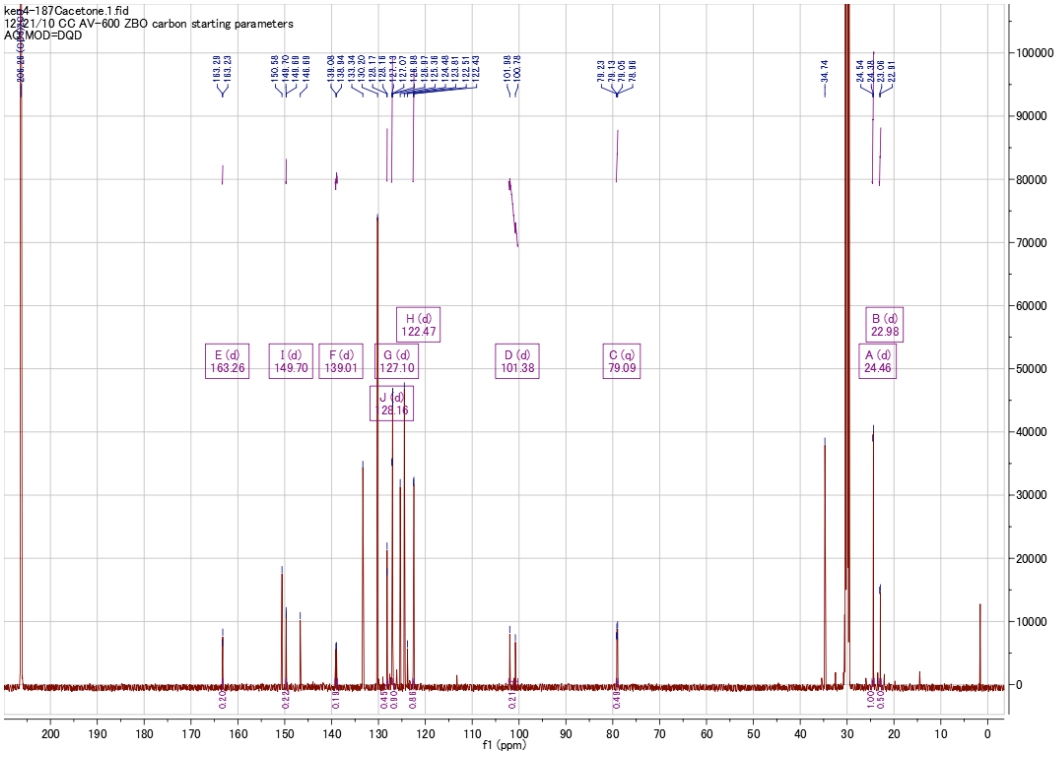

ken4-059-7F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using (R)-PhDAP dr >20:1
f1 (ppm)

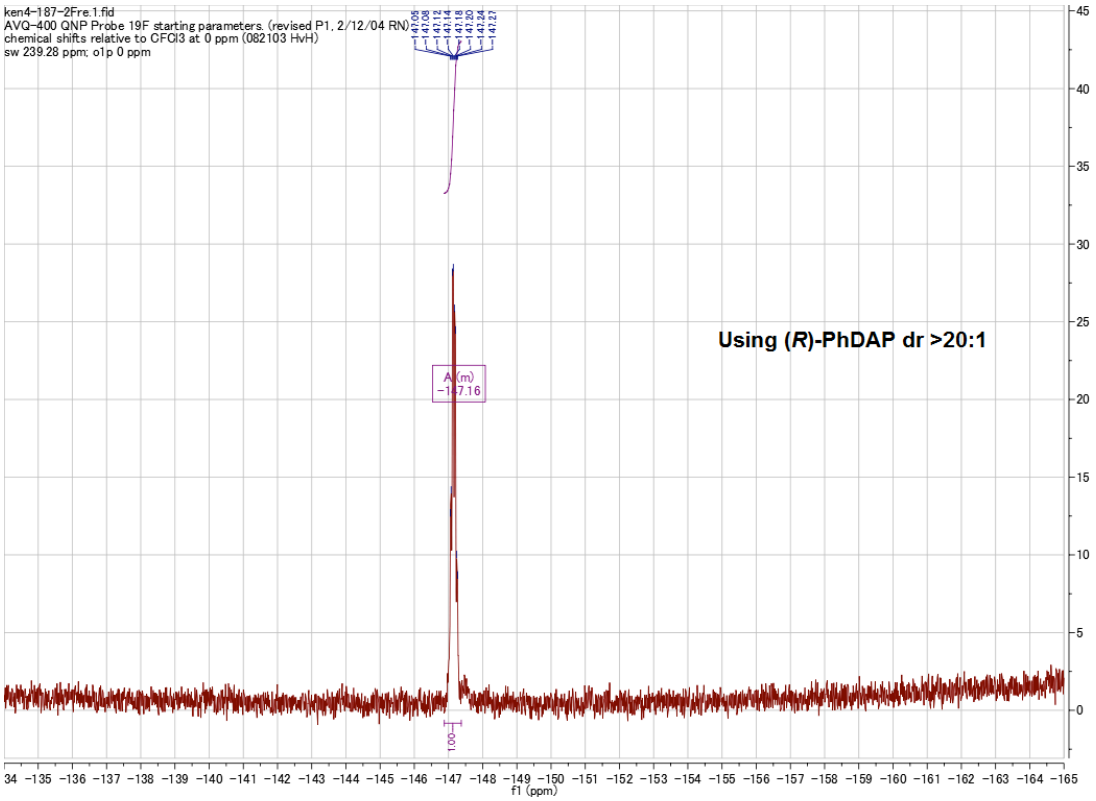

ken4-059-4f.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using (R)-4-Ph-PhDAP
dr >20:1
f1 (ppm)

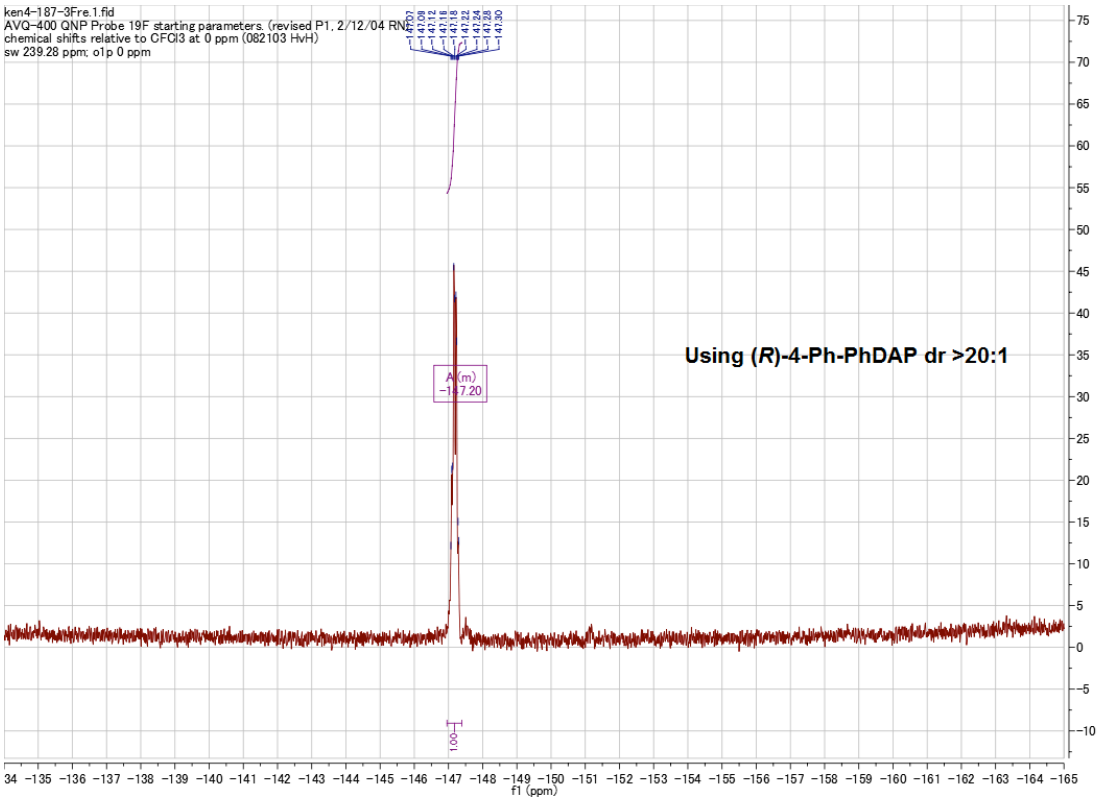

ken4-059homoF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
homogeneous condition dr 5:2
1.00
0.88
f1 (ppm)

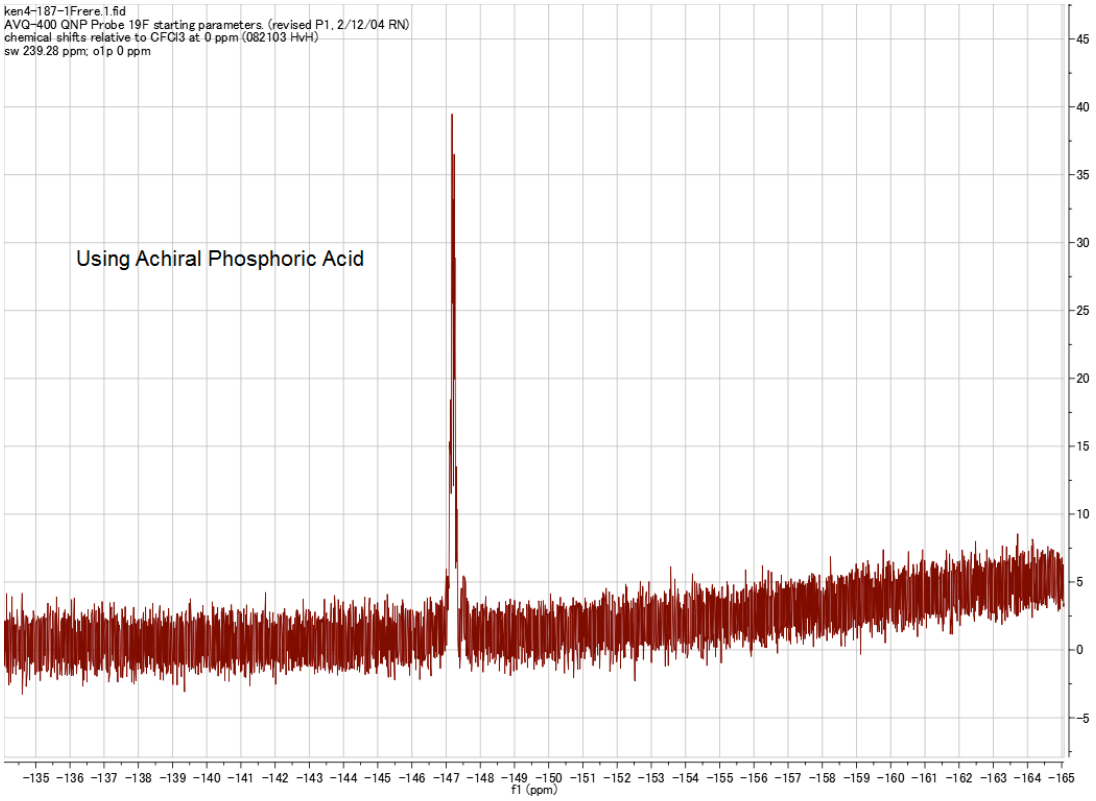
(*R*)-2-((*S*)-1-fluoro-1-(4-isopropylphenyl)ethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2t)



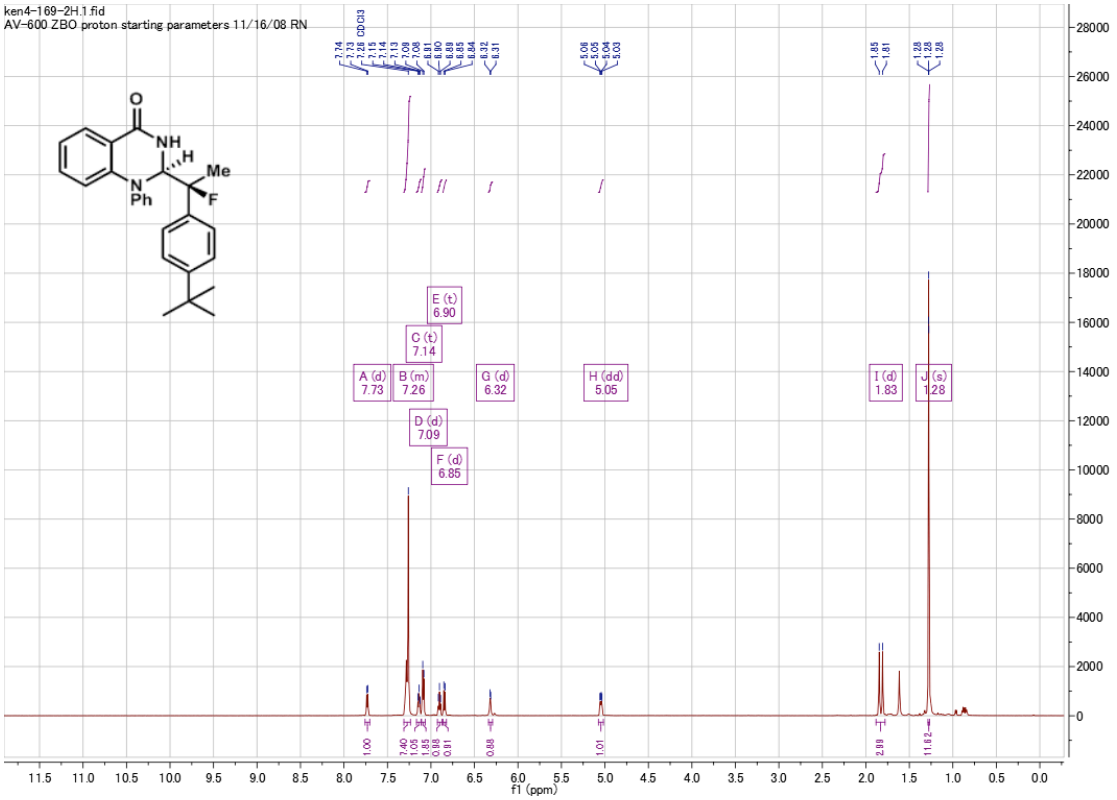


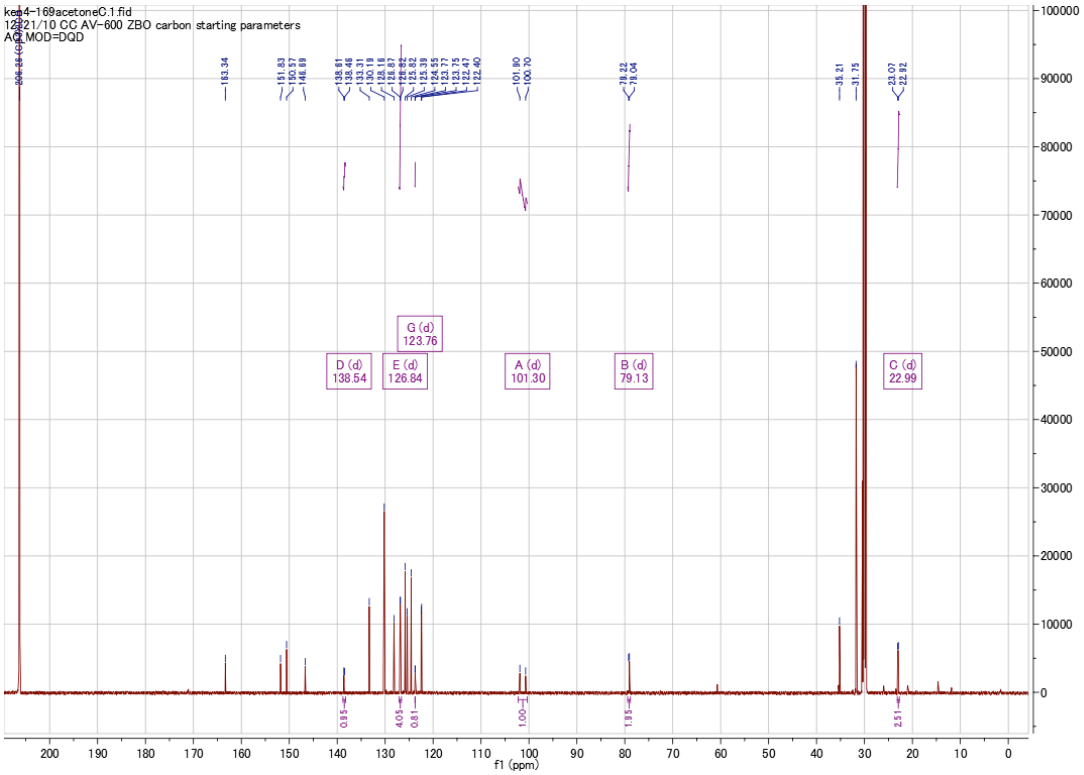

ken4-187-2Fre.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using (R)-PhDAP dr >20:1
f1 (ppm)

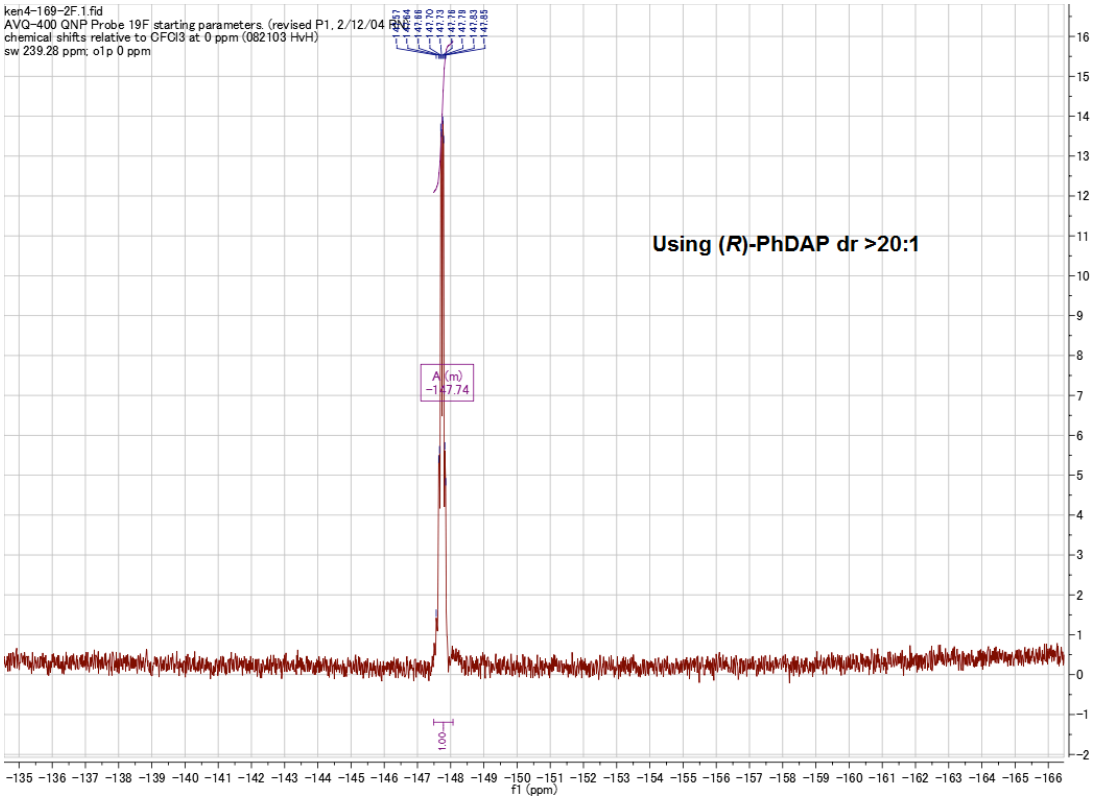

ken4-187-3Fre.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using (R)-4-Ph-PhDAP dr >20:1
f1 (ppm)

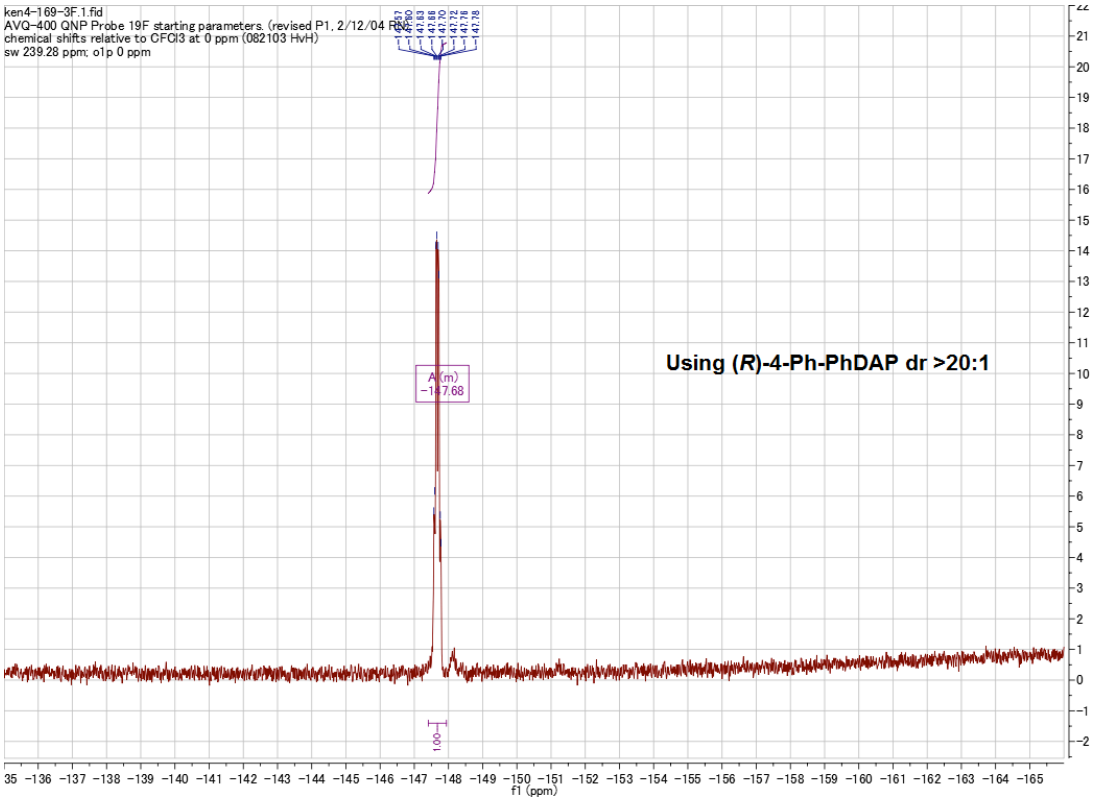

ken4-187-1Frere.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using Achiral Phosphoric Acid
45
40
35
30
25
20
15
10
5
0
-5
-135 -136 -137 -138 -139 -140 -141 -142 -143 -144 -145 -146 -147 -148 -149 -150 -151 -152 -153 -154 -155 -156 -157 -158 -159 -160 -161 -162 -163 -164 -165
f1 (ppm)

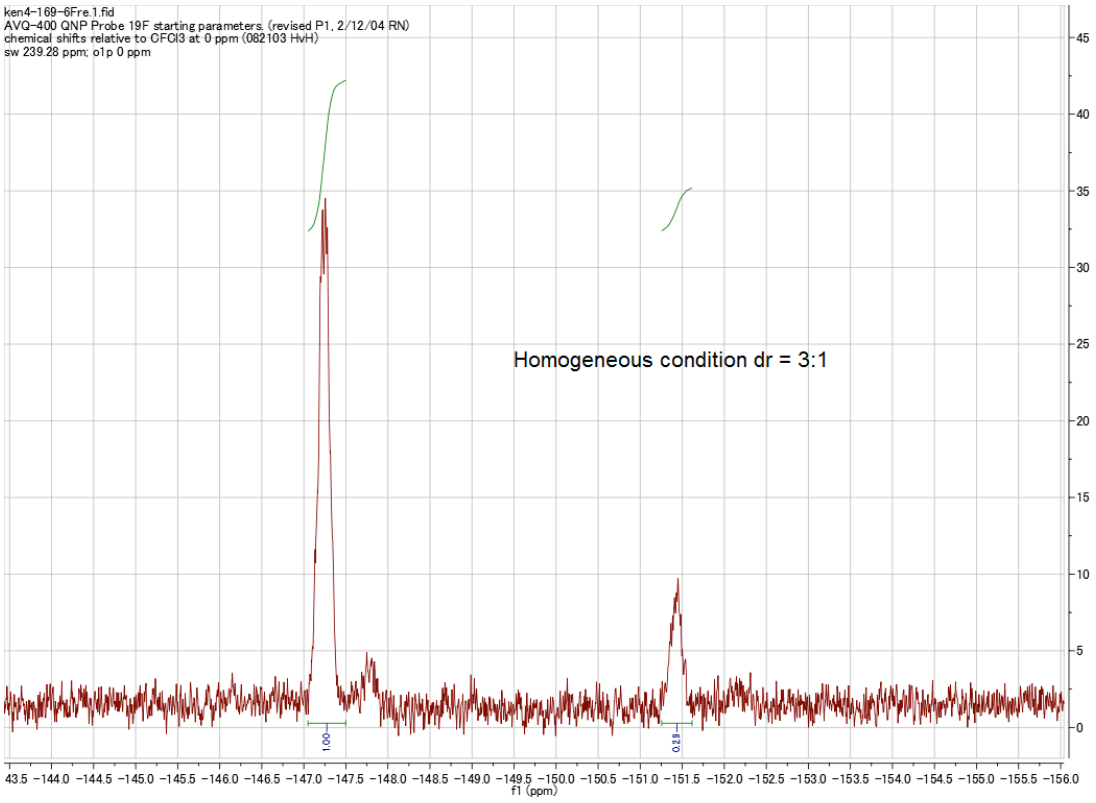
(*R*)-2-((*S*)-1-(4-(tert-butyl)phenyl)-1-fluoroethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2u)





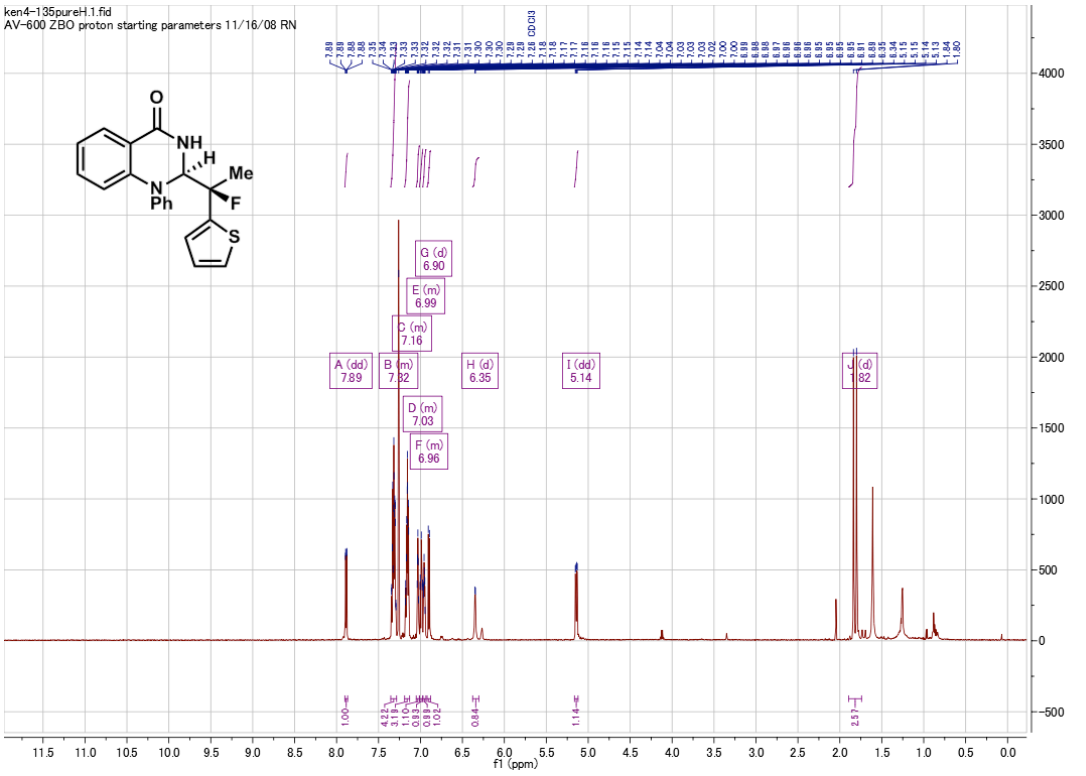

ken4-169-2F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RH)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using (R)-PhDAP dr >20:1
A(m)
-147.74
1.00
f1 (ppm)

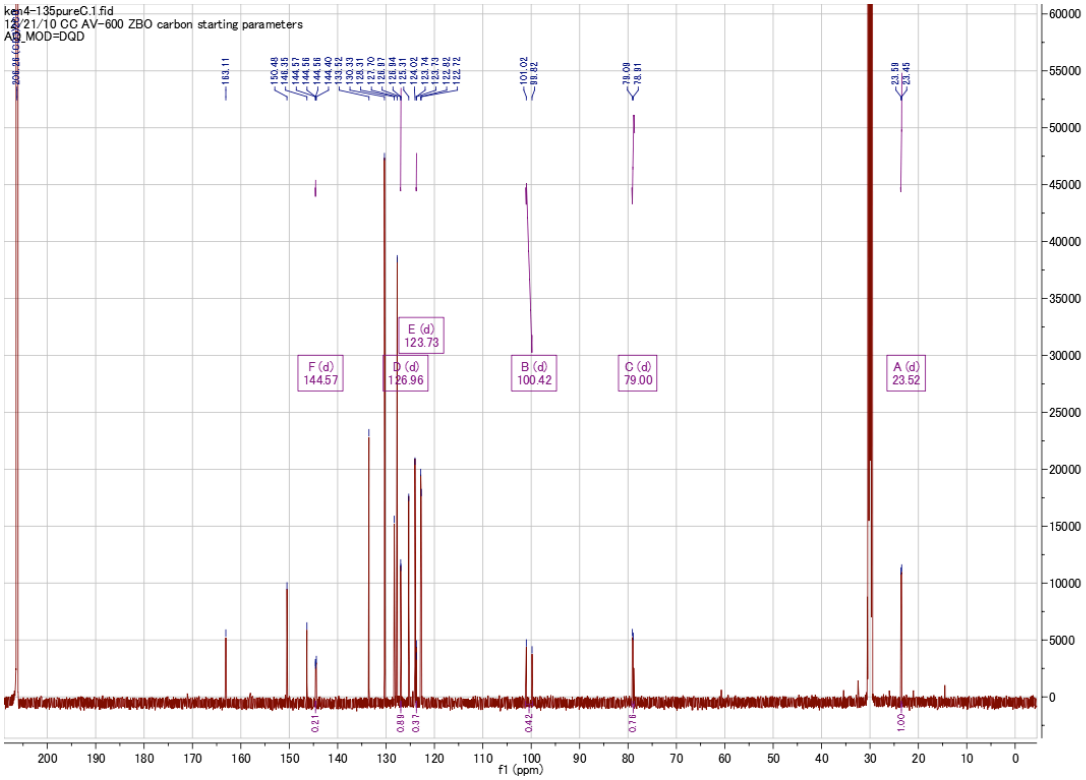

ken4-169-3F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RH)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using (R)-4-Ph-PhDAP dr >20:1
A(m)
-147.68
1.00
f1 (ppm)

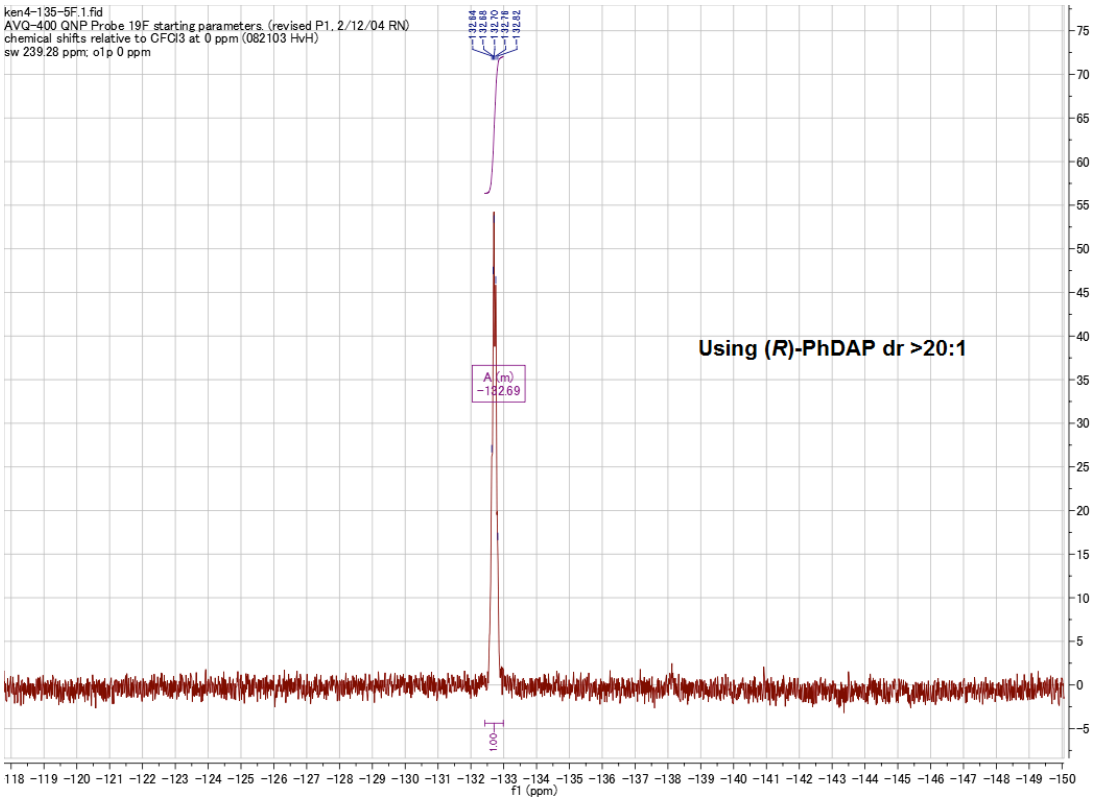

ken4-169-6Fre.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Homogeneous condition dr = 3:1
1.00
0.81
f1 (ppm)

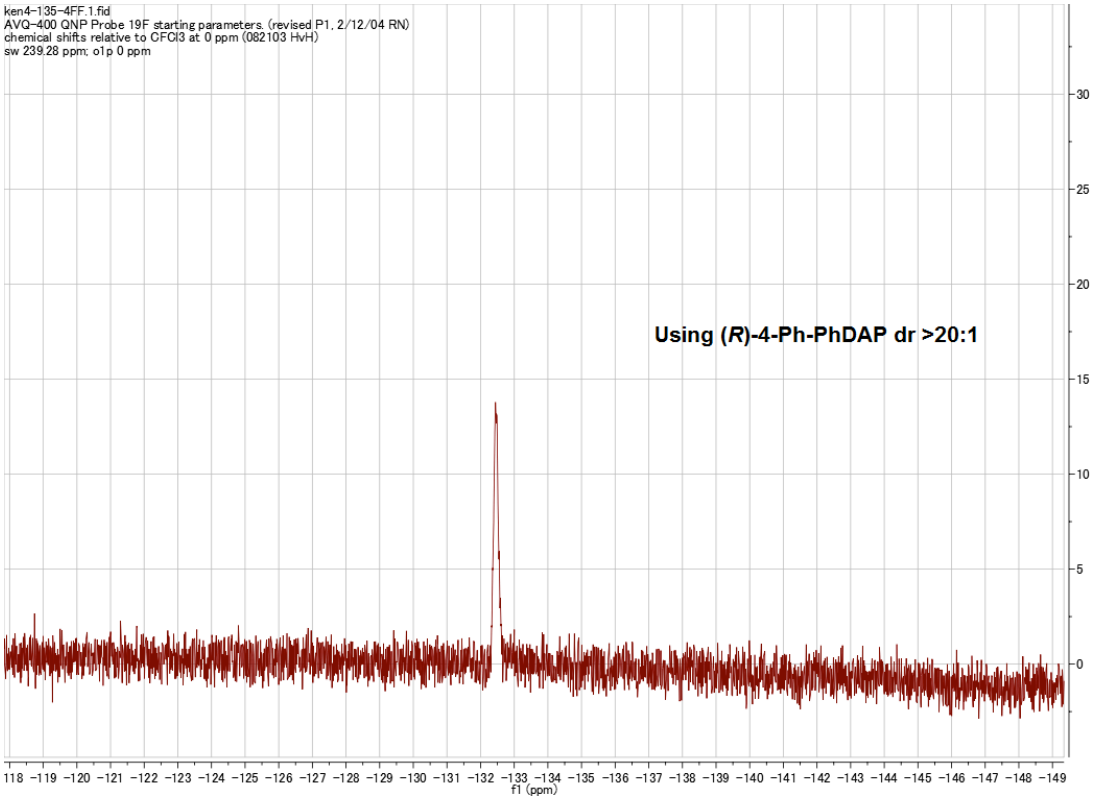
(*R*)-2-((*R*)-1-fluoro-1-(thiophen-2-yl)ethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one

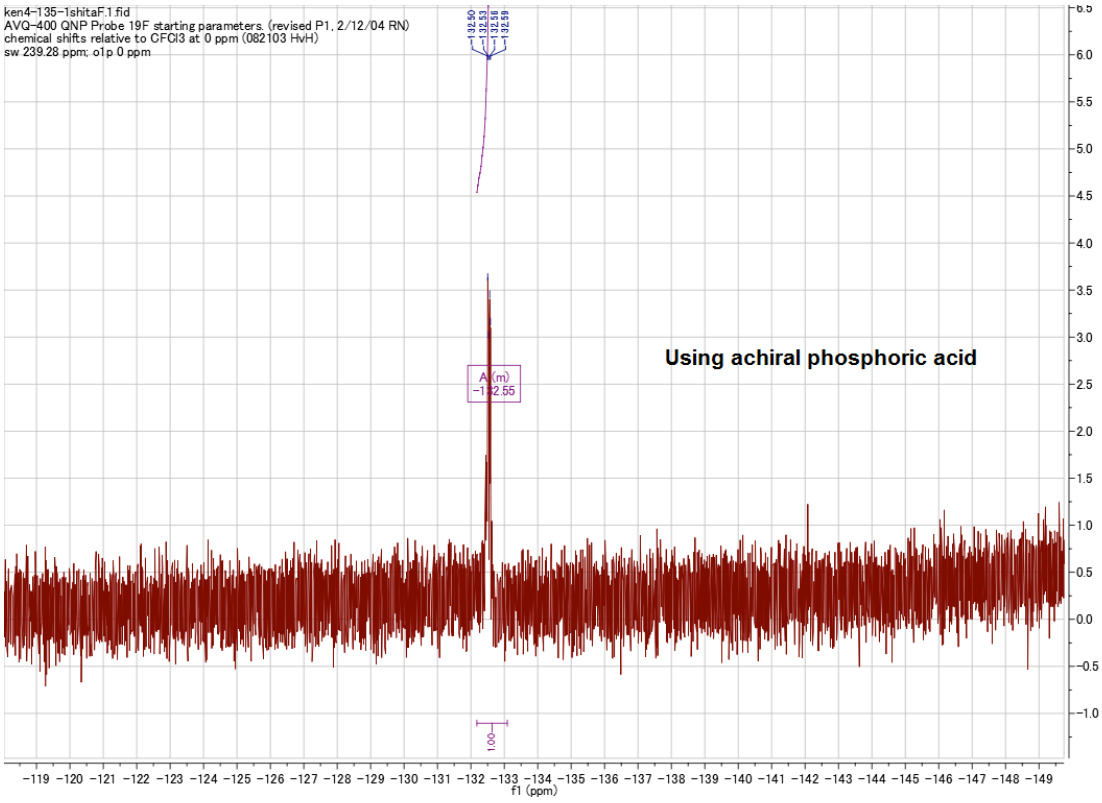
(2v)





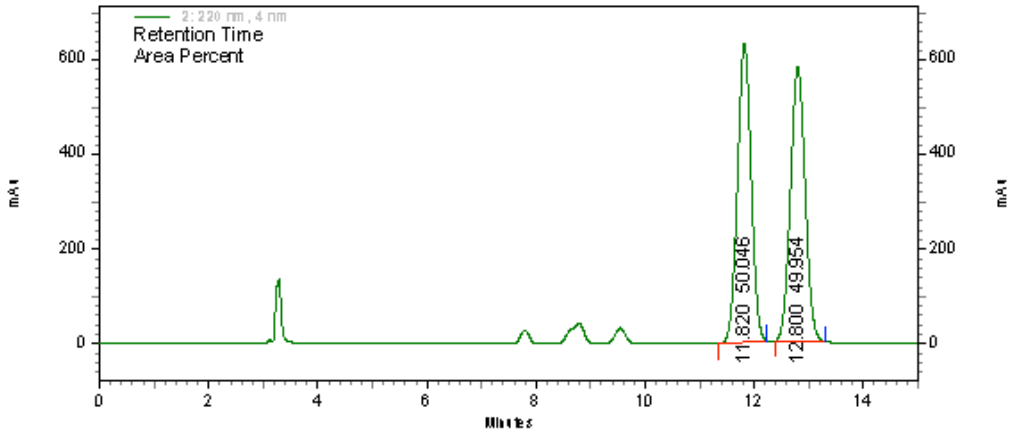

ken4-135-5F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-132.64
-132.66
-132.70
-132.76
-132.82
A (m)
-132.69
1.00
Using (R)-PhDAP dr >20:1
f1 (ppm)


ken4-135-4FF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
Using (R)-4-Ph-PhDAP dr >20:1
f1 (ppm)


ken4-135-1shitaF.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-132.50
-132.53
-132.56
-132.59
A (m)
-132.55
Using achiral phosphoric acid
1.00
f1 (ppm)

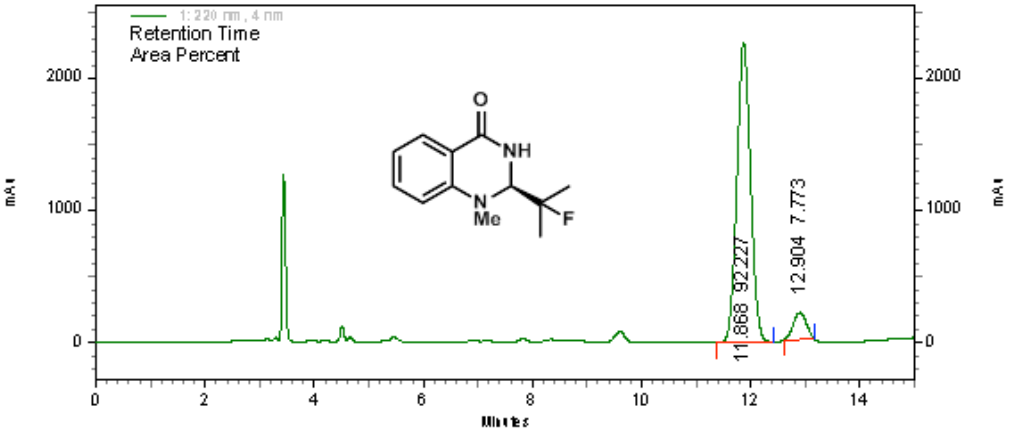
HPLC Traces

(*R*)-2-(2-fluoropropan-2-yl)-1-methyl-2,3-dihydroquinazolin-4(1H)-one (2f)



2: 220 nm, 4 nm
Results

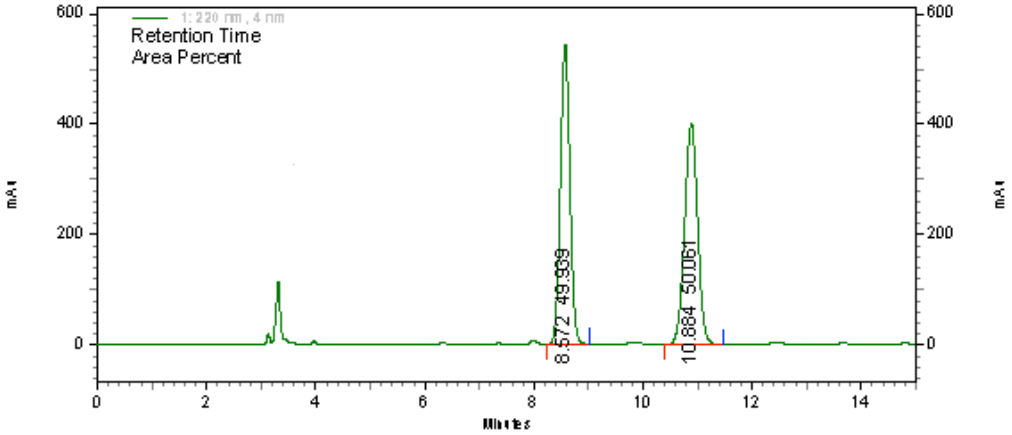
Pk #	Retention Time	Area Percent	Lambda Max
1	11.820	50.046	223
2	12.800	49.954	223



1: 220 nm, 4 nm
Results

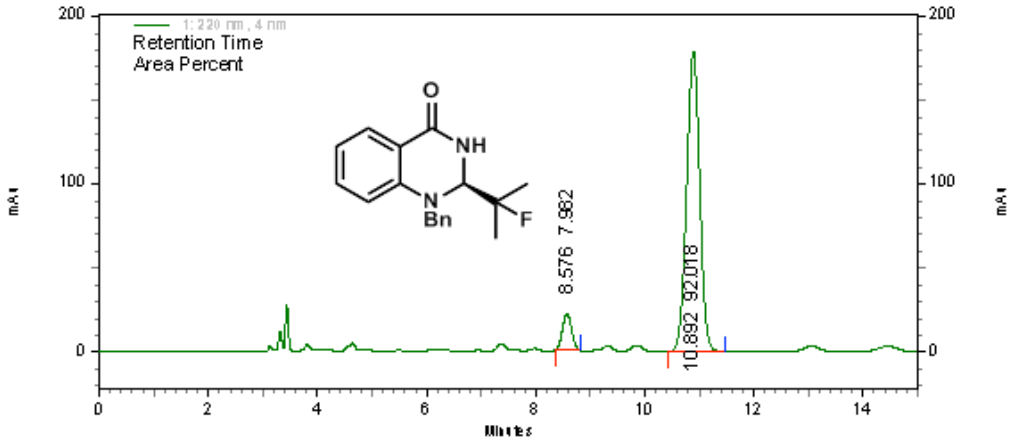
Pk #	Retention Time	Area Percent	Lambda Max
1	11.868	92.227	200
2	12.904	7.773	224

***(R)*-1-benzyl-2-(2-fluoropropan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2g)**



1: 220 nm, 4 nm
Results

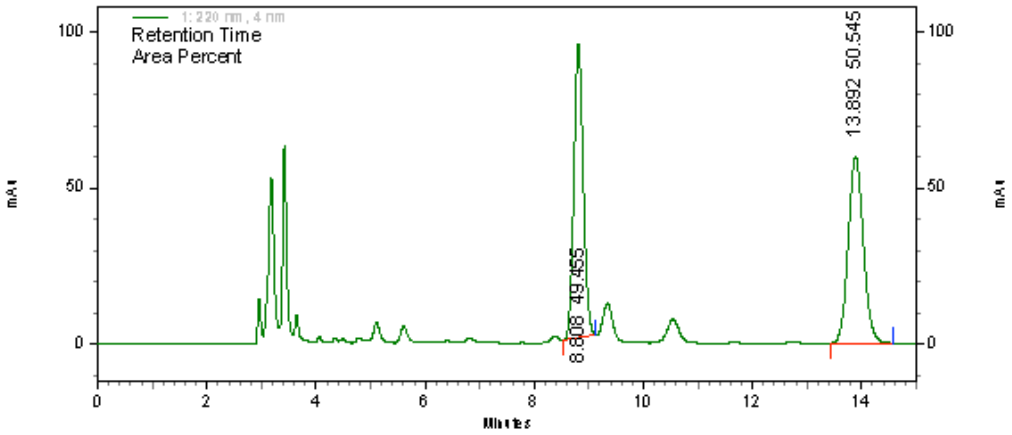
Pk #	Retention Time	Area Percent	Lambda Max
1	8.572	49.939	223
2	10.884	50.061	223



1: 220 nm, 4 nm
Results

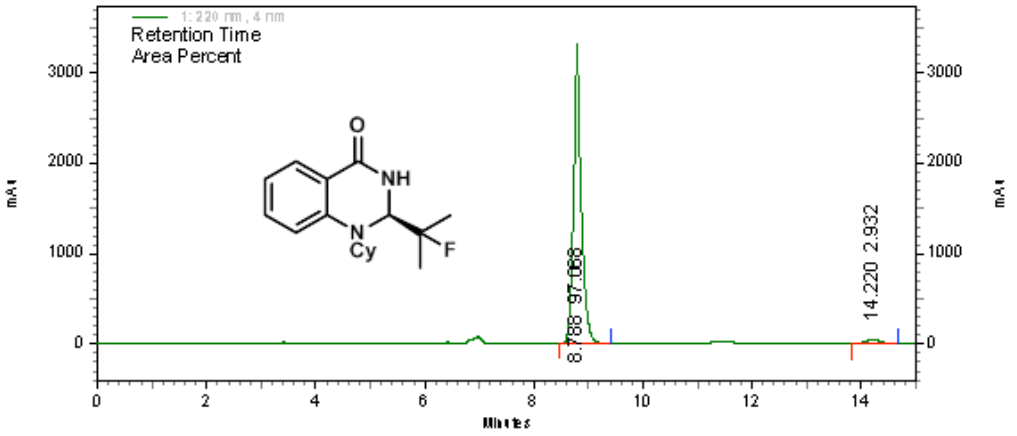
Pk #	Retention Time	Area Percent	Lambda Max
1	8.576	7.982	200
2	10.892	92.018	223

***(R)*-1-cyclohexyl-2-(2-fluoropropan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2h)**



1: 220 nm, 4 nm
Results

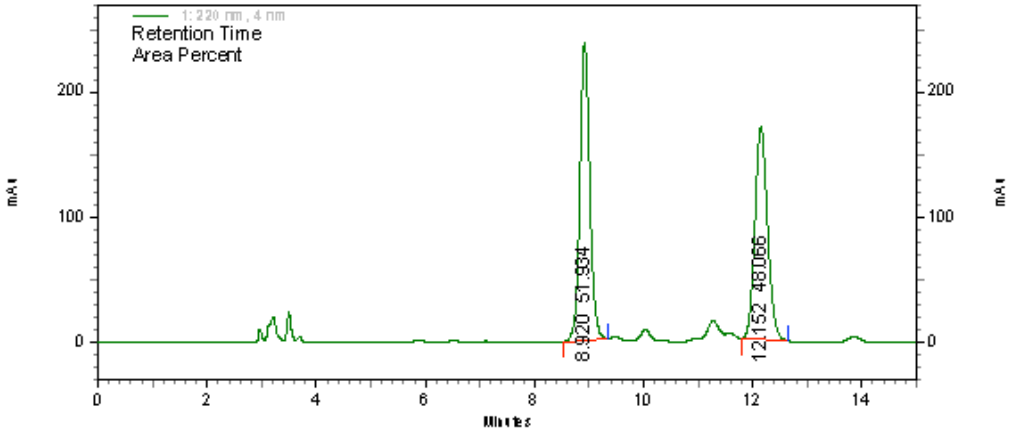
Pk #	Retention Time	Area Percent	Lambda Max
1	8.808	49.455	225
2	13.892	50.545	225



1: 220 nm, 4 nm
Results

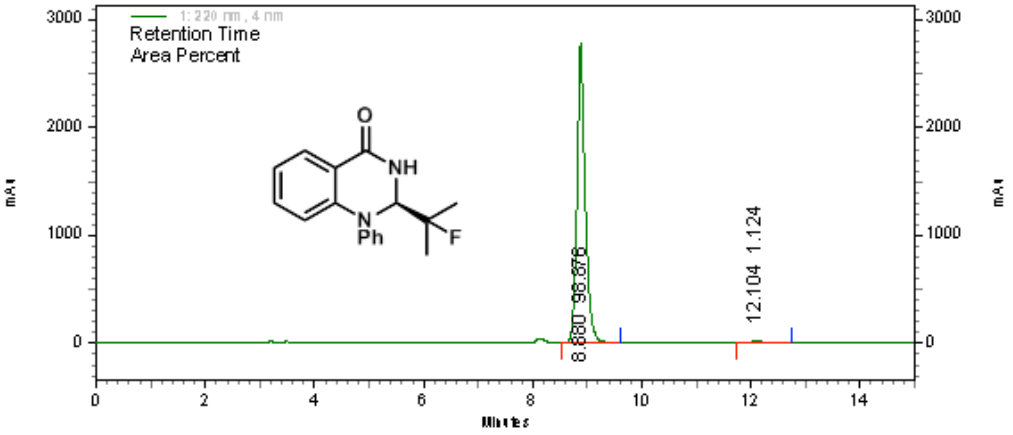
Pk #	Retention Time	Area Percent	Lambda Max
1	8.788	97.068	222
2	14.220	2.932	225

***(R)*-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2i)**



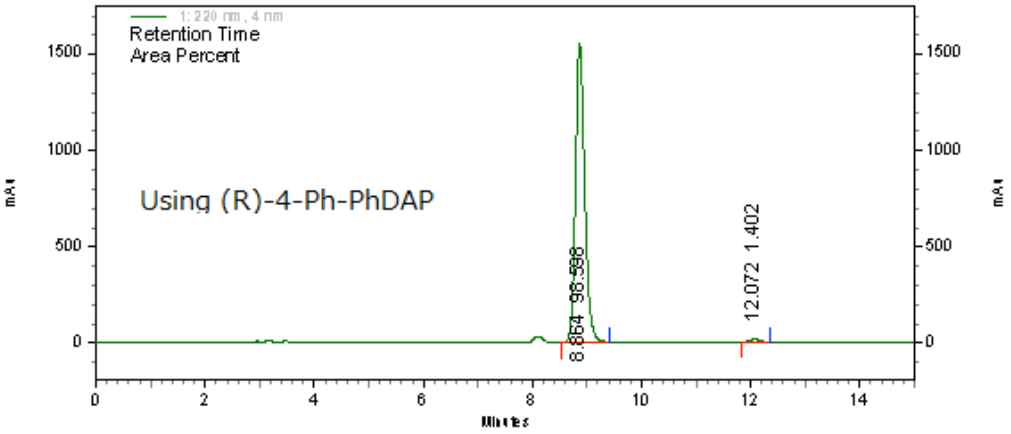
1: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.920	51.934	223
2	12.152	48.066	223



1: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.880	98.876	209
2	12.104	1.124	223

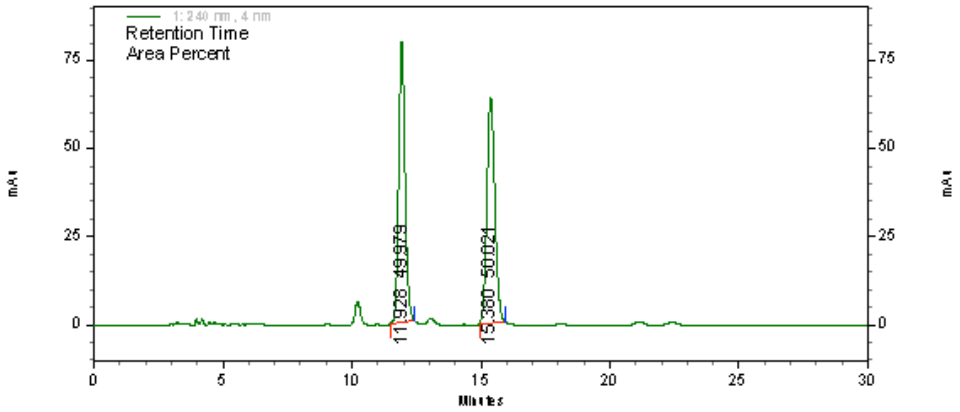


1: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.864	98.598	205
2	12.072	1.402	223

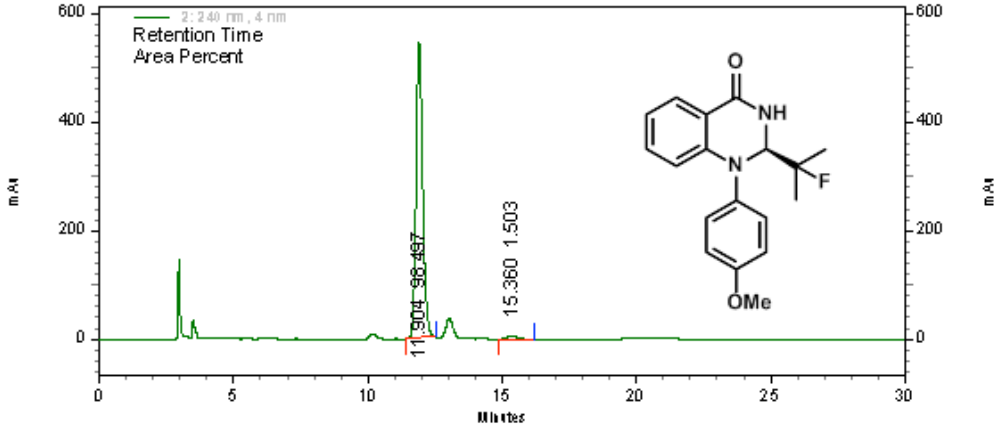
***(R)*-2-(2-fluoropropan-2-yl)-1-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one**

(2j)



1: 240 nm, 4 nm
Results

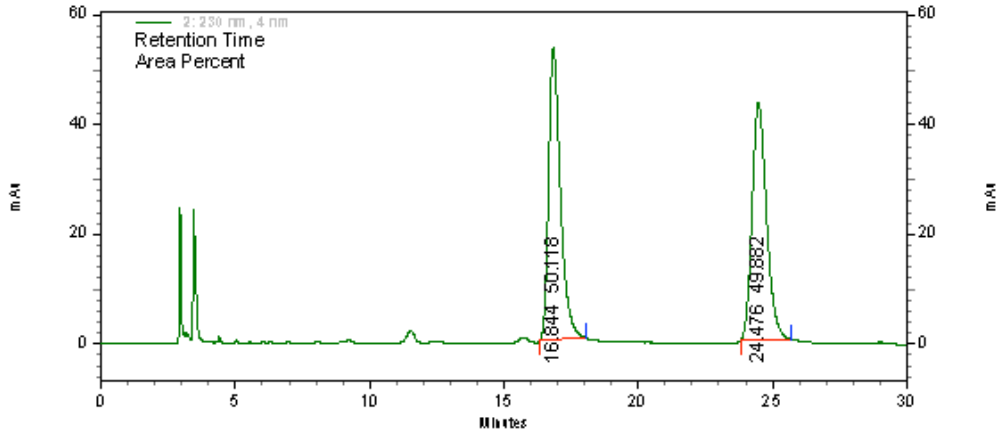
Pk #	Retention Time	Area Percent	Lambda Max
1	11.928	49.979	274
2	15.380	50.021	274



2: 240 nm, 4 nm
Results

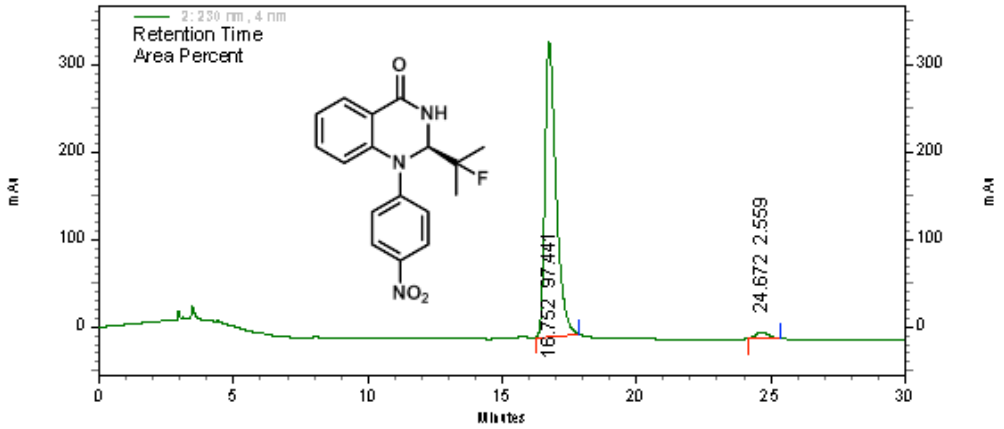
Pk #	Retention Time	Area Percent	Lambda Max
1	11.904	98.497	200
2	15.360	1.503	275

***(R)*-2-(2-fluoropropan-2-yl)-1-(4-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (2k)**



2: 230 nm, 4 nm
Results

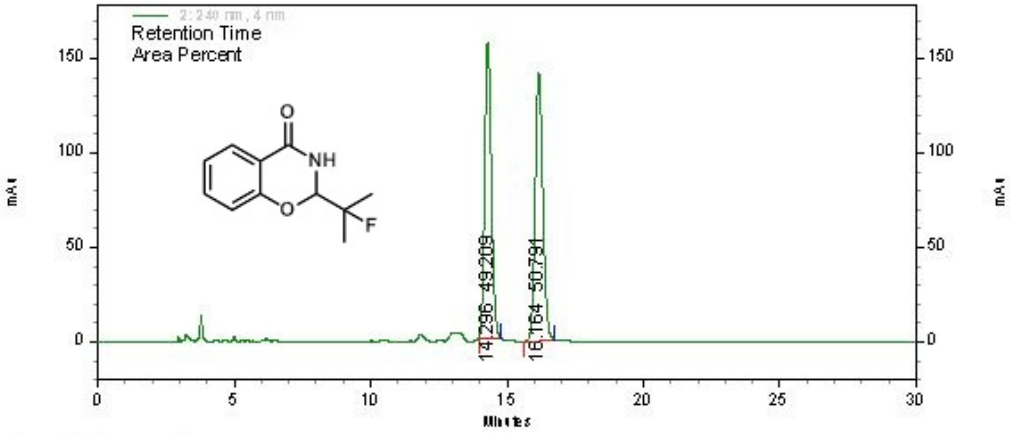
Pk #	Retention Time	Area Percent	Lambda Max
1	16.844	50.118	204
2	24.476	49.882	204



2: 230 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	16.752	97.441	357
2	24.672	2.559	357

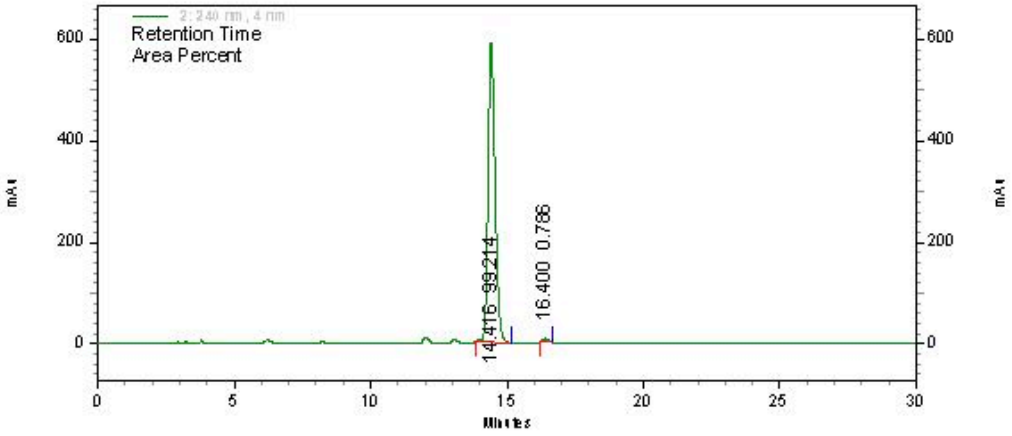
2-(2-fluoropropan-2-yl)-2H-benzo[e][1,3]oxazin-4(3H)-one (2l)



2: 240 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	14.296	49.209	207
2	16.164	50.791	207

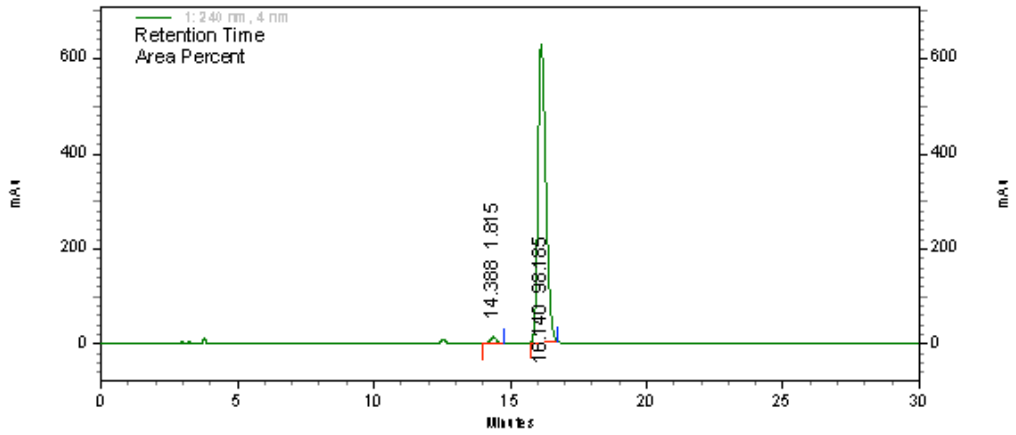
Using (*R)*-OCyDAP (2l)



2: 240 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	14.416	99.214	198
2	16.400	0.786	206

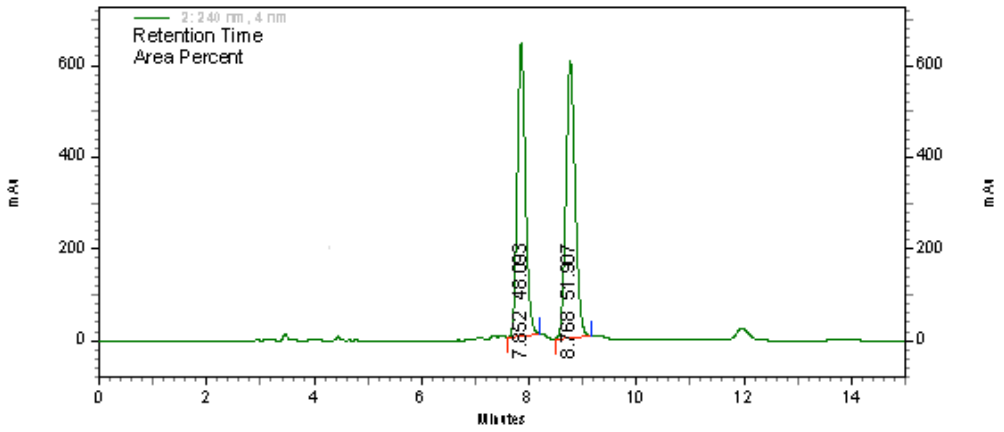
Using (*S*)-VAPOL PA (*ent*-2l)



1: 240 nm, 4 nm
Results

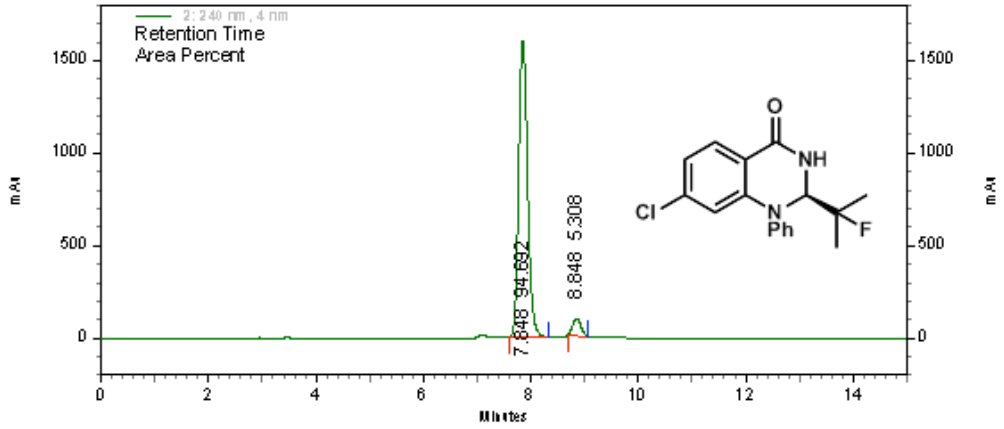
Pk #	Retention Time	Area Percent	Lambda Max
1	14.388	1.815	206
2	16.140	98.185	200

***(R)*-7-chloro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2m)**



2: 240 nm, 4 nm
Results

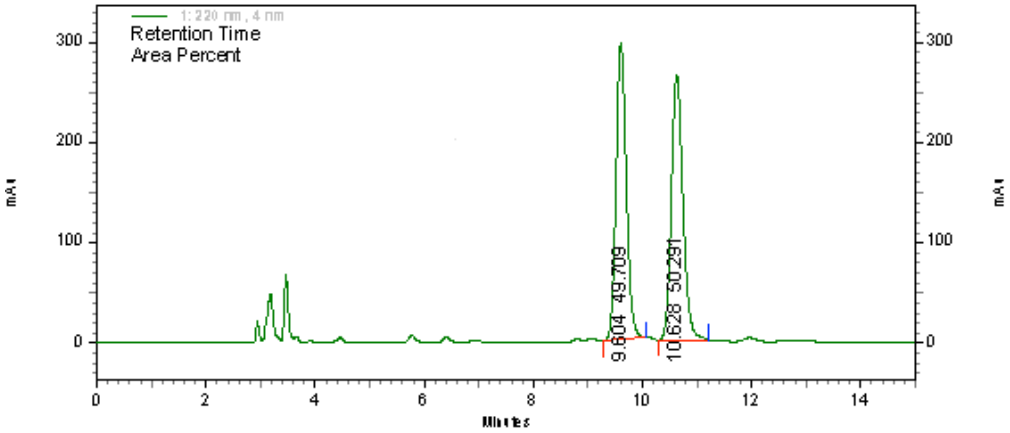
Pk #	Retention Time	Area Percent	Lambda Max
1	7.852	48.093	196
2	8.768	51.907	195



2: 240 nm, 4 nm
Results

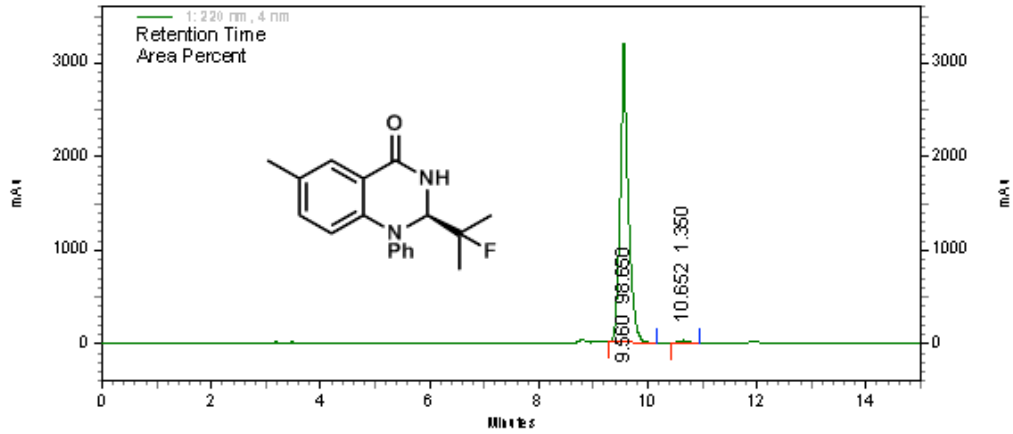
Pk #	Retention Time	Area Percent	Lambda Max
1	7.848	94.692	225
2	8.848	5.308	224

***(R)*-2-(2-fluoropropan-2-yl)-6-methyl-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2n)**



1: 220 nm, 4 nm
Results

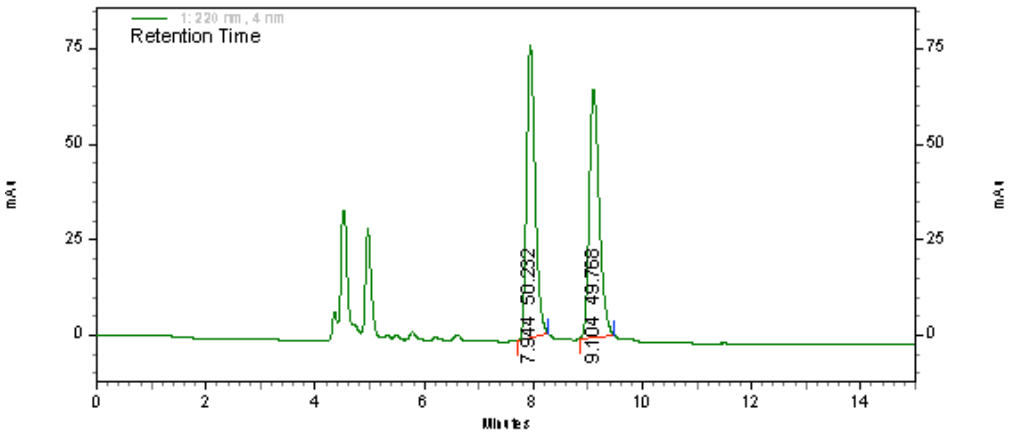
Pk #	Retention Time	Area Percent	Lambda Max
1	9.604	49.709	204
2	10.628	50.291	205



1: 220 nm, 4 nm
Results

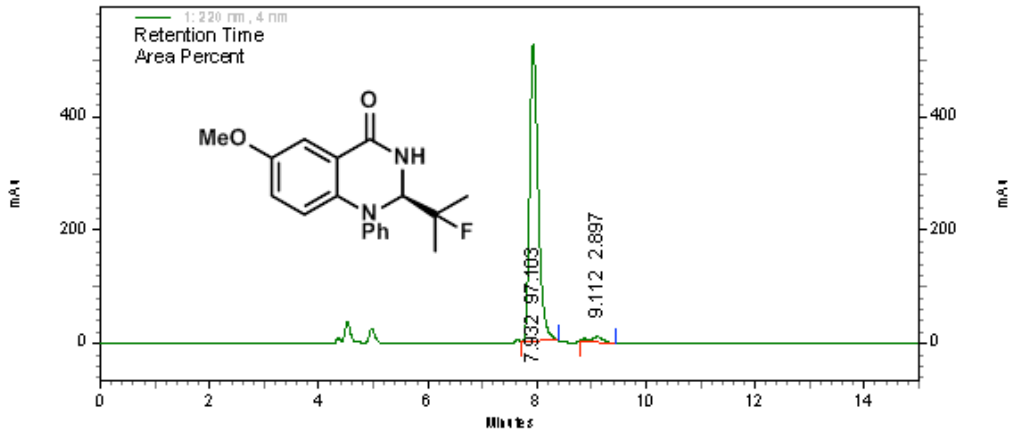
Pk #	Retention Time	Area Percent	Lambda Max
1	9.560	98.650	223
2	10.652	1.350	206

***(R)*-6-methoxy-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2o)**



1: 220 nm, 4 nm
Results

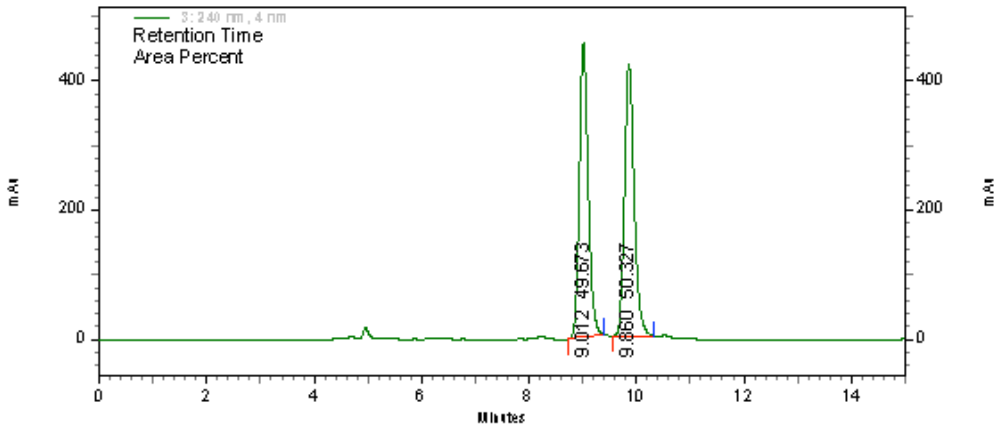
Pk #	Retention Time	Area Percent	Lambda Max
1	7.944	50.232	208
2	9.104	49.768	208



1: 220 nm, 4 nm
Results

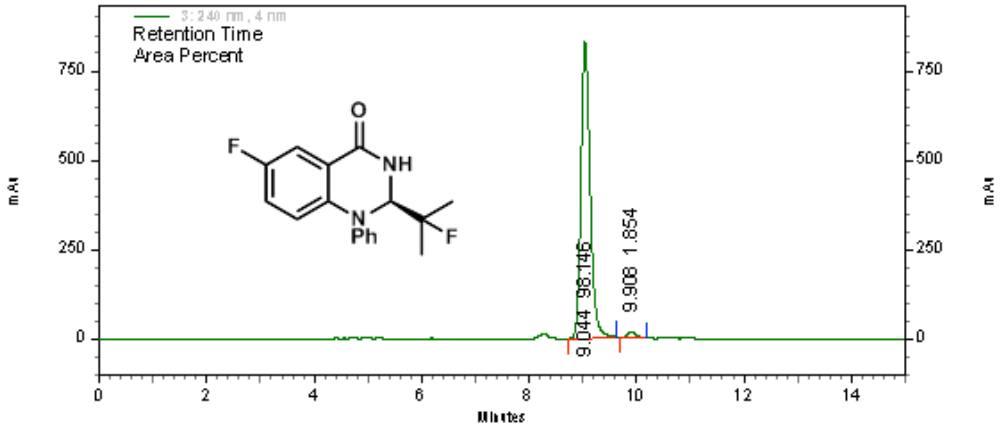
Pk #	Retention Time	Area Percent	Lambda Max
1	7.932	97.103	195
2	9.112	2.897	208

***(R)*-6-fluoro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2p)**



3: 240 nm, 4 nm
Results

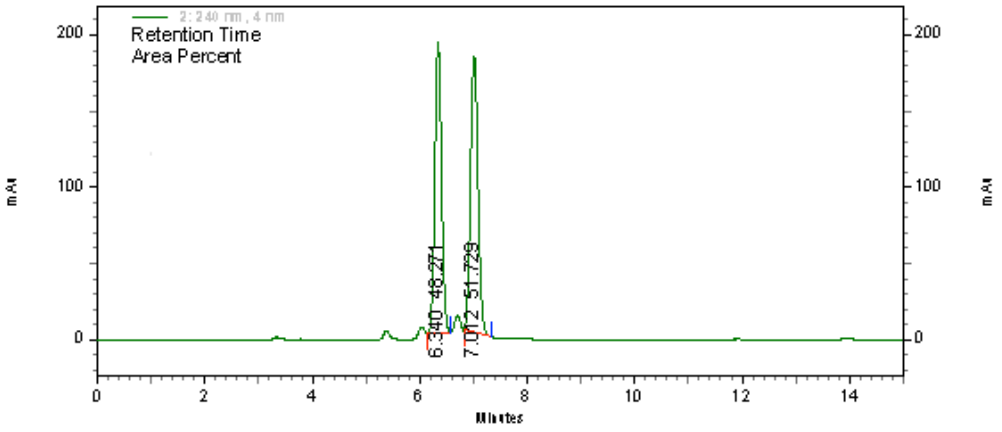
Pk #	Retention Time	Area Percent	Lambda Max
1	9.012	49.673	201
2	9.860	50.327	200



3: 240 nm, 4 nm
Results

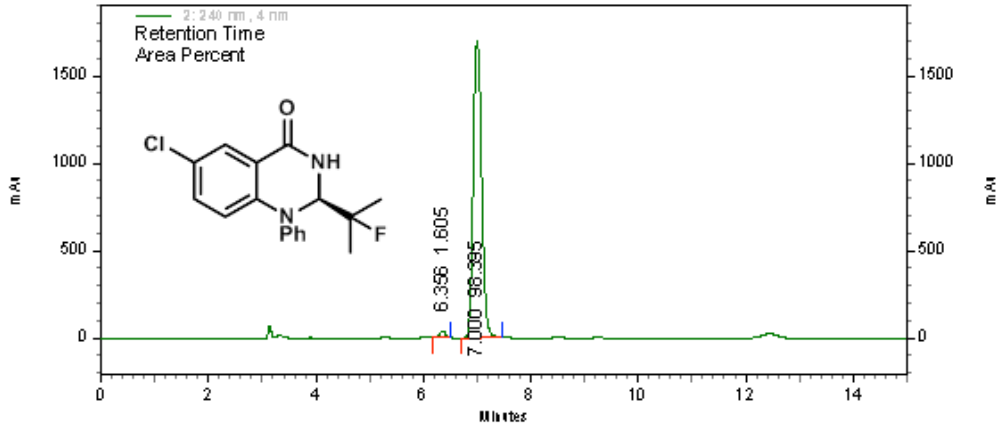
Pk #	Retention Time	Area Percent	Lambda Max
1	9.044	98.146	207
2	9.908	1.854	220

***(R)*-6-chloro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2q)**



2: 240 nm, 4 nm
Results

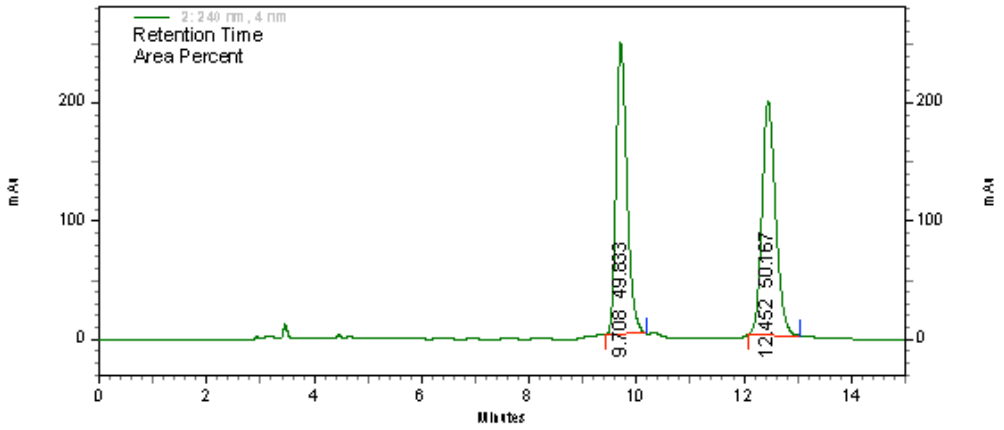
Pk #	Retention Time	Area Percent	Lambda Max
1	6.340	48.271	223
2	7.012	51.729	223



2: 240 nm, 4 nm
Results

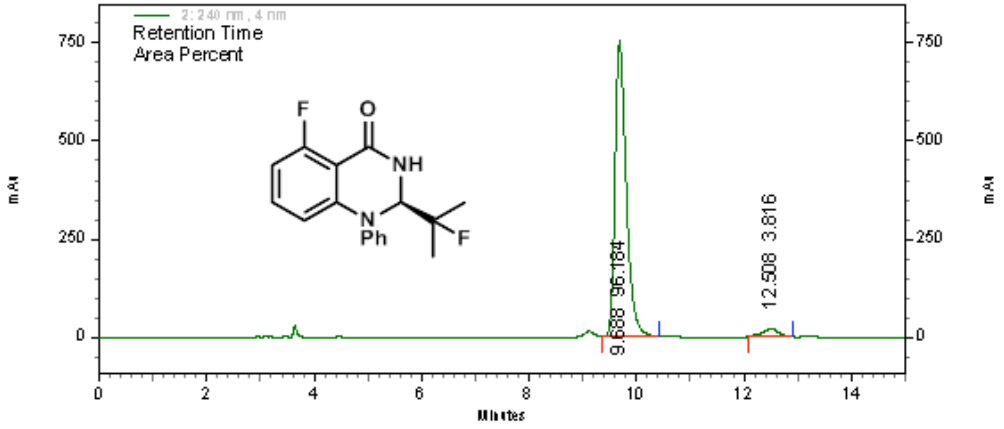
Pk #	Retention Time	Area Percent	Lambda Max
1	6.356	1.605	207
2	7.000	98.395	223

***(R)*-5-fluoro-2-(2-fluoropropan-2-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2r)**



2: 240 nm, 4 nm
Results

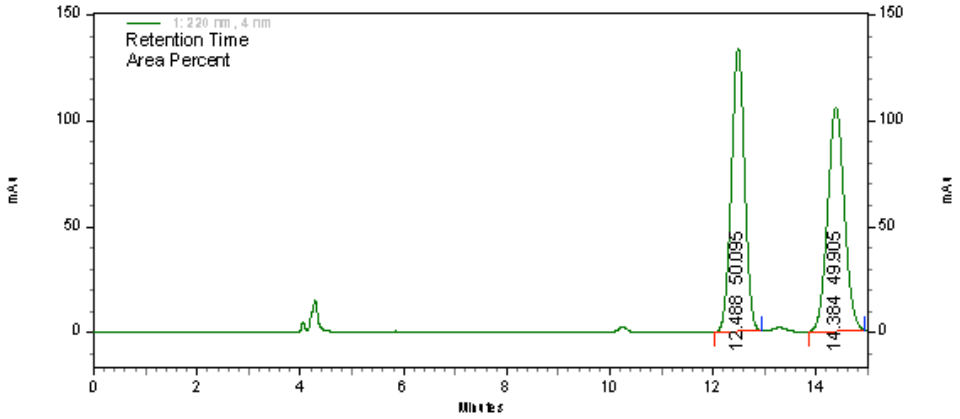
Pk #	Retention Time	Area Percent	Lambda Max
1	9.708	49.833	271
2	12.452	50.167	271



2: 240 nm, 4 nm
Results

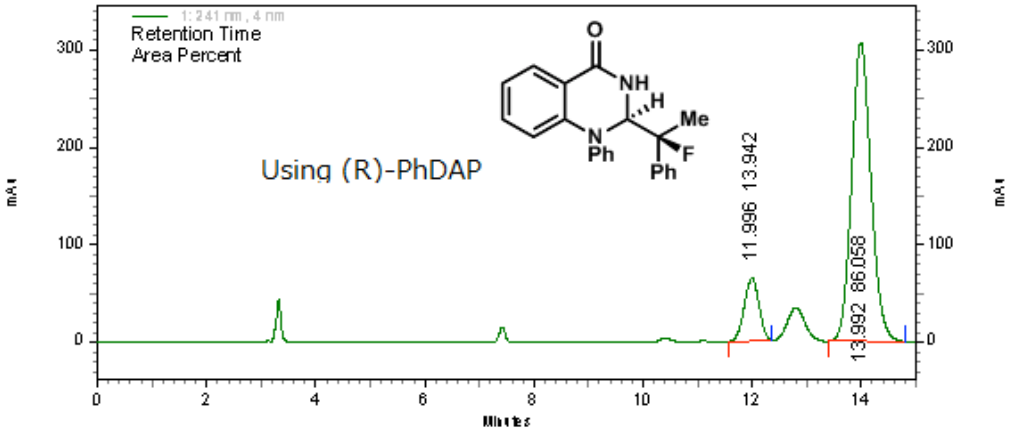
Pk #	Retention Time	Area Percent	Lambda Max
1	9.688	96.184	204
2	12.508	3.816	271

(*R*)-2-((*S*)-1-fluoro-1-phenylethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2s)



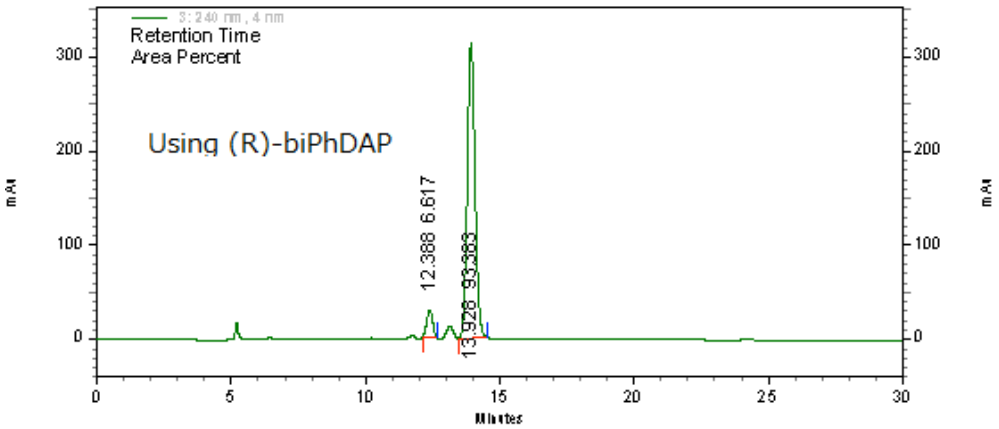
1: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	12.488	50.095	204
2	14.384	49.905	205



1: 241 nm, 4 nm
Results

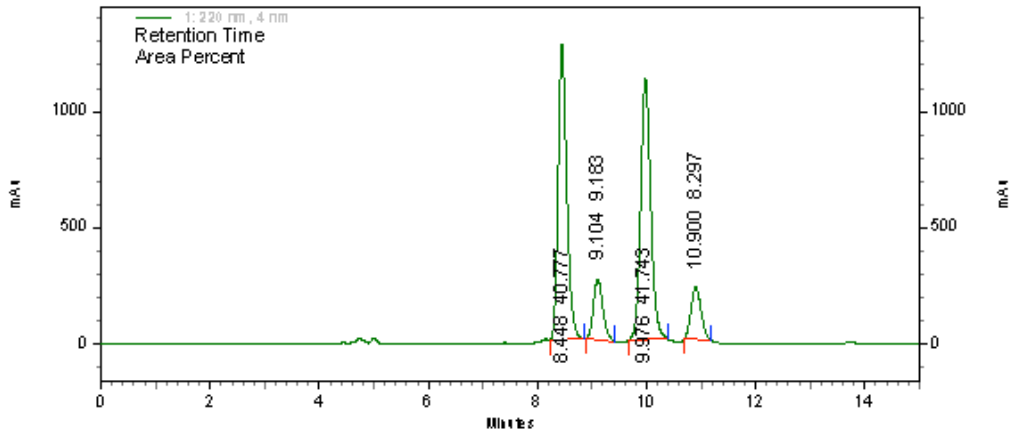
Pk #	Retention Time	Area Percent	Lambda Max
1	11.996	13.942	205
2	13.992	86.058	194



3: 240 nm, 4 nm
Results

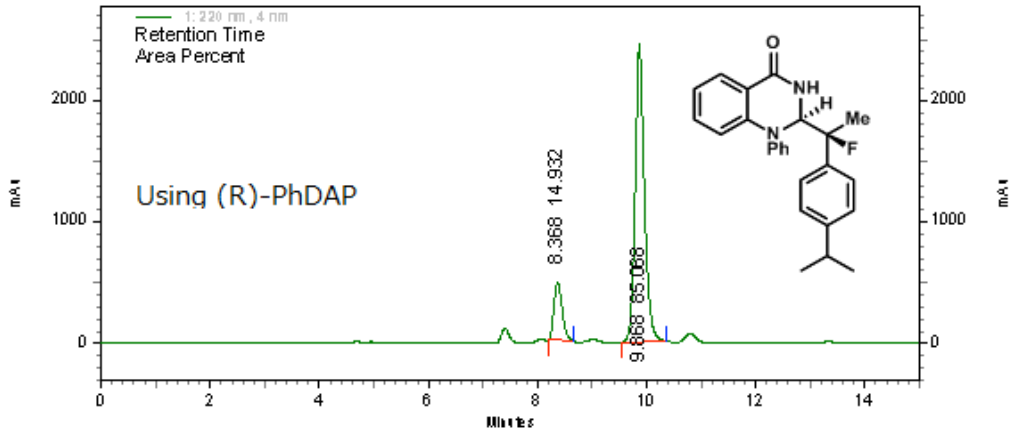
Pk #	Retention Time	Area Percent	Lambda Max
1	12.388	6.617	205
2	13.928	93.383	194

(*R*)-2-((*S*)-1-fluoro-1-(4-isopropylphenyl)ethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2t)



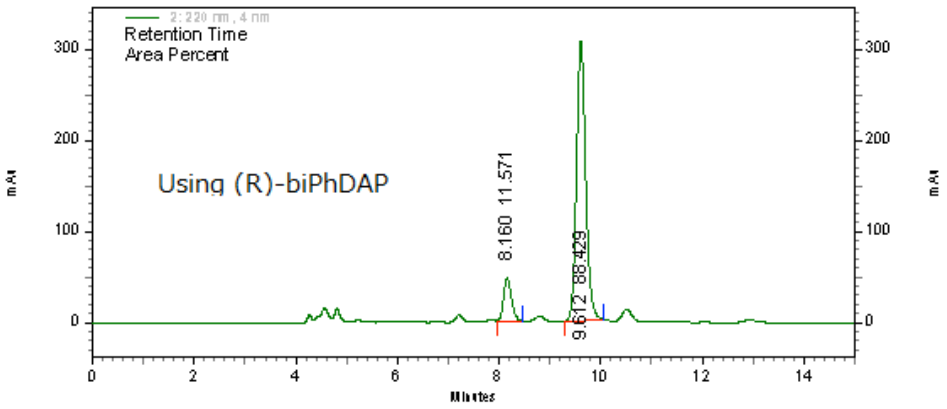
1: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.448	40.777	204
2	9.104	9.183	333
3	9.976	41.743	202
4	10.900	8.297	333



1: 220 nm, 4 nm
Results

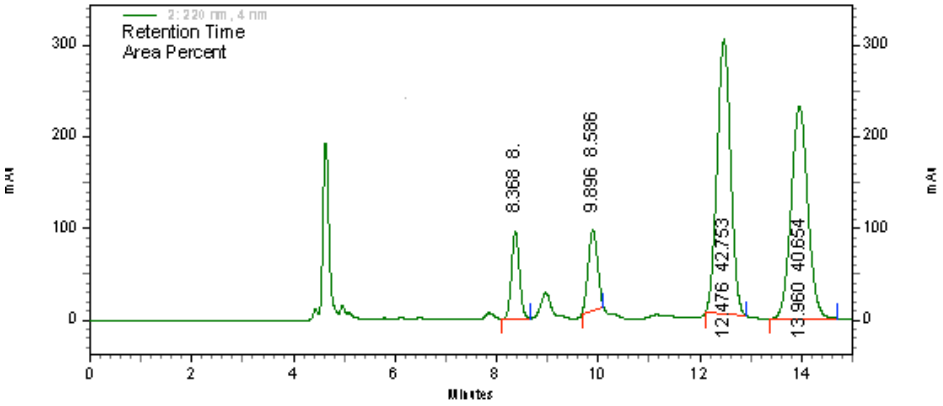
Pk #	Retention Time	Area Percent	Lambda Max
1	8.368	14.932	191
2	9.868	85.068	210



2: 220 nm, 4 nm
Results

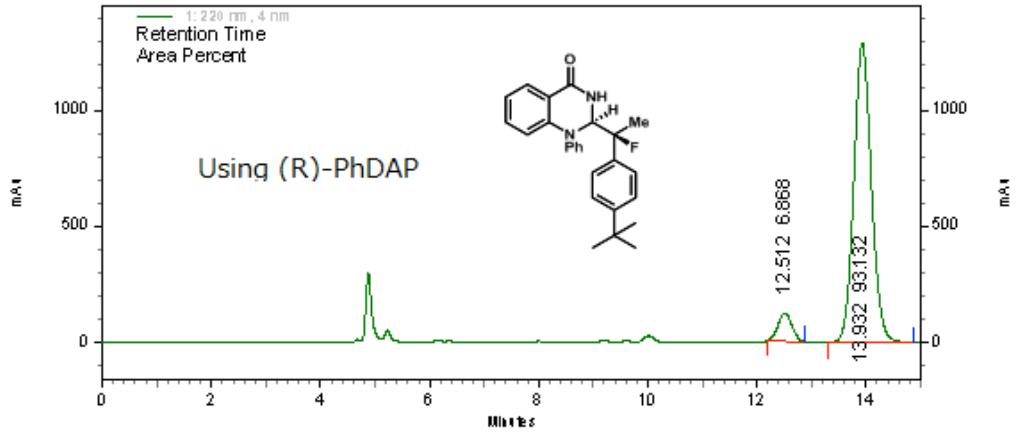
Pk #	Retention Time	Area Percent	Lambda Max
1	8.160	11.571	271
2	9.612	88.429	271

(*R*)-2-((*S*)-1-(4-(tert-butyl)phenyl)-1-fluoroethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one (2u)



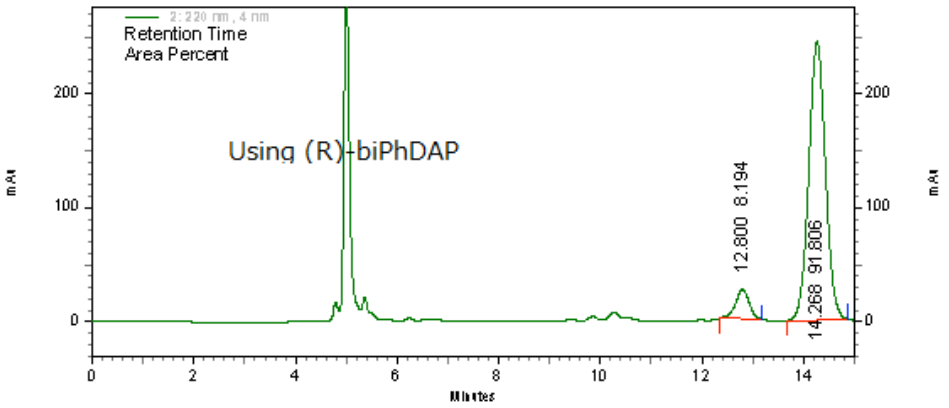
2: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.368	8.007	275
2	9.896	8.586	275
3	12.476	42.753	271
4	13.960	40.654	271



1: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	12.512	6.868	271
2	13.932	93.132	203

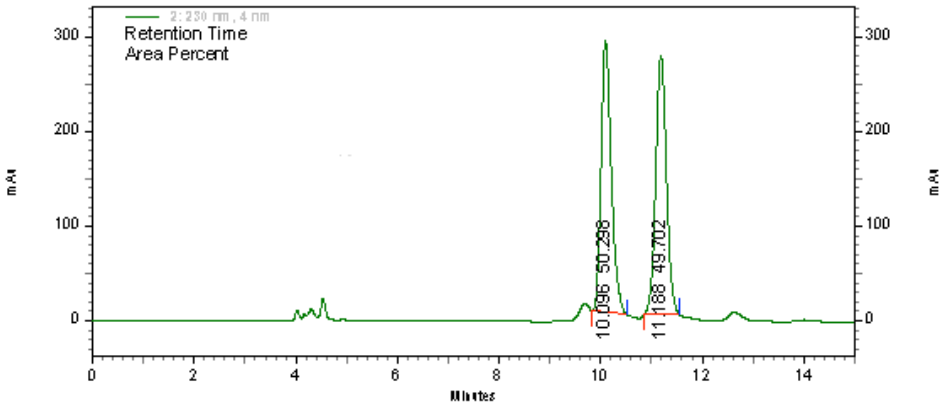


2: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	12.800	8.194	270
2	14.268	91.806	271

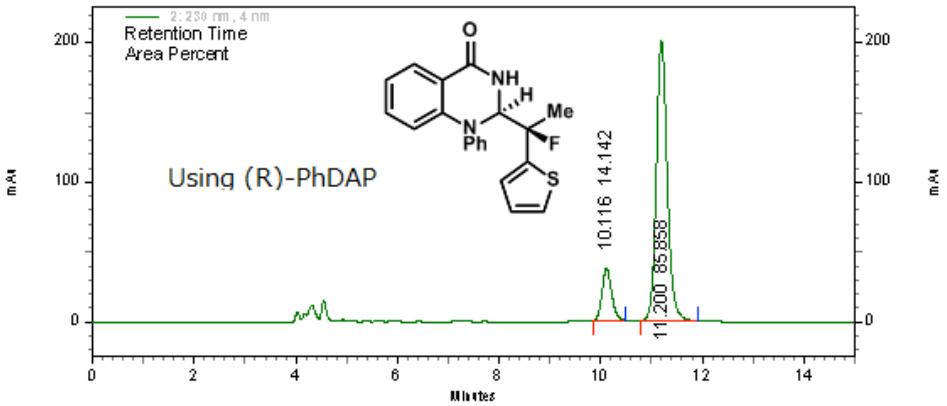
(*R*)-2-((*R*)-1-fluoro-1-(thiophen-2-yl)ethyl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one

(2v)



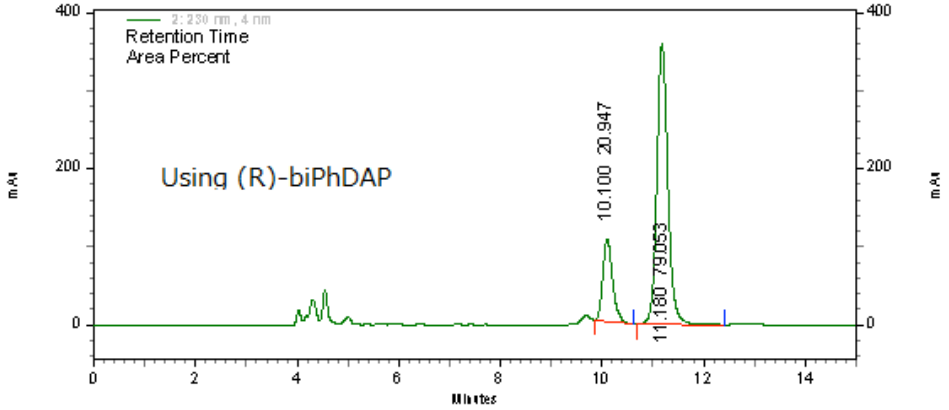
2: 230 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10.096	50.298	224
2	11.188	49.702	224



2: 230 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10.116	14.142	224
2	11.200	85.858	224



2: 230 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10.100	20.947	224
2	11.180	79.053	224