Supporting Information for:

Enantioselective construction of substituted hydantoins *via* chiral phosphoric acid catalyzed annulation/Heyns rearrangement of aryl-substituted ureas with glyoxals

Yong Wang,[a] Jingyuan Li,[b] Yanyan Li,[a] Chao Pi,[a] Yangjie Wu,[a] and Xiuling Cui*[a]

[a] *Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450052, China*
[b] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

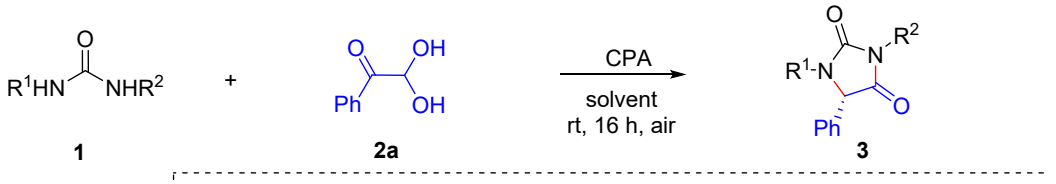
*E-mail: cuixl@zzu.edu.cn

Table of Contents:

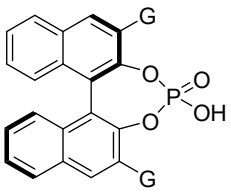
I. General Information

Unless otherwise noted, substrates, catalysts and solvents were obtained from commercial suppliers and used without further purification. The urea **1e**, **1i-1k** were prepared according to the literatures.[1] Products **3** were visualized by UV-light at 254 nm. Flash chromatography was conducted on silica gel (200–300 mesh). The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained using a Bruker AVANCE III spectrometer at 400, 100 and 376 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. Peak multiplicity is indicated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, and broad = b. Enantiomeric excesses values were determined with HPLC on Chiral Daicel Chiralpak AS-H and AD-H (mobile phase: hexane/^{i}PrOH). Optical rotation were measured on a Anton Paar MCP 4100 polarimeter and reported as follows: [α]D 20 (c = g/100 mL, solvent). Melting points were uncorrected. All high-resolution mass spectra were obtained on an TOF LC/MS equipped with an ESI source.

II. Optimization of the Reaction Conditions



1a, R^1 = Ph, R^2 = H
1b, R^1 = , R^2 = Ph
1c, R^1 = , R^2 = Bn
1d, R^1 = , R^2 = ^{t}Bu



4a, G = 2,4,6-^{i}Pr$_3$C$_6$H$_2$
4b, G = 1-naphthyl
4c, G = 1-pyrenyl
4d, G = 2,4,6-Me$_3$C$_6$H$_2$
4e, G = 3,5-(CF$_3$)$_2$C$_6$H$_3$
4f, G = 4-NO$_2$C$_6$H$_4$
4g, G = 4-Ad-2,6-^{i}Pr$_2$C$_6$H$_2$

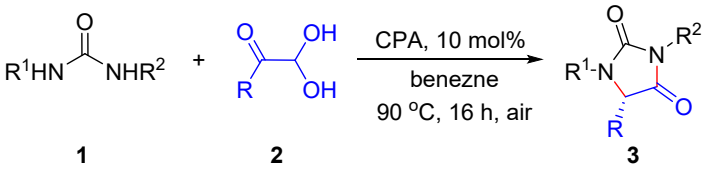
4h, G = 3,5-Ph$_2$C$_6$H$_3$
4i, G = 3,5-Me$_2$C$_6$H$_3$
4j, G = 9-phenanthryl
4k, G = 1-naphthyl
4l, G = 4-ClC$_6$H$_4$
4m, G = 2,4,6-(cyclohexyl)$_3$C$_6$H$_2$
4n, G = 2-naphthyl
4o, G = 4-OMeC$_6$H$_4$

entry	CPA	**1/3**	solvent	yield (%)[b]	ee (%)[c]
1	**4a**	**1a/3aa**	toluene	61	14
2	**4a**	**1b/3ba**	toluene	23	92
3	**4a**	**1c/3ca**	toluene	50	0
4	**4a**	**1d/3da**	toluene	quant.	28
5	**4b**	**1b/3ba**	toluene	80	78
6	**4c**	**1b/3ba**	toluene	87	89
7	**4d**	**1b/3ba**	toluene	45	89
8	**4e**	**1b/3ba**	toluene	41	-68
9	**4f**	**1b/3ba**	toluene	quant.	-38
10	**4h**	**1b/3ba**	toluene	27	33
11	**4i**	**1b/3ba**	toluene	98	78
12	**4j**	**1b/3ba**	toluene	48	86
13	**4k**	**1b/3ba**	toluene	80	78

14	**4l**	**1b/3ba**	toluene	quant.	-33
15	**4m**	**1b/3ba**	toluene	18	92
16	**4n**	**1b/3ba**	toluene	93	48
17	**4o**	**1b/3ba**	toluene	quant.	45
18[d]	**4a**	**1b/3ba**	PhCl	quant.	91
19[d]	**4a**	**1b/3ba**	*o*-xylene	97	91
20[d]	**4a**	**1b/3ba**	*m*-xylene	85	85
21[d]	**4a**	**1b/3ba**	*p*-xylene	89	75
22[d]	**4a**	**1b/3ba**	benzene	73	95
23[d]	**4a**	**1b/3ba**	CCl_4	quant.	94
24[d]	**4a**	**1b/3ba**	mesitylene	51	93
25[d]	**4a**	**1b/3ba**	$PhCF_3$	quant.	90
26[e]	**4a**	**1b/3ba**	benzene	quant.	95
27[e]	**4g**	**1b/3ba**	benzene	quant.	96

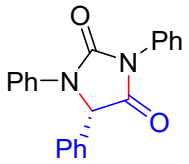
[a]Reaction conditions: **1** (0.05 mmol), **2a** (0.075 mmol), CPA (10 mol %), solvent (2 mL), rt, 16 h, air. [b]Isolated yields, quant. = quantitative yield. [c]Determined by chiral HPLC. [d]90 °C. [e]**1b** (0.12 mmol), **2a** (0.1 mmol), CPA (10 mol %), solvent (2 mL), 90 °C, 16 h, air.

III. General Procedure and Characterization of Products 3



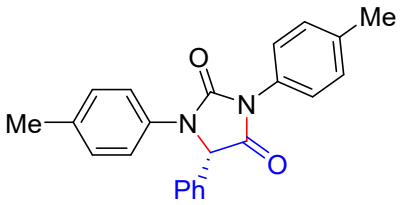
1 **2** **3**

The urea **1** (0.12 mmol), glyoxal hydrate **2** (0.1 mmol) and **CPA** (10 mol %) was dissolved in benezne (2 mL). The reaction mixture was stirred at 90 °C for 16 h. The crude product was separated by flash column chromatography on silica gel to afford target products **3**.



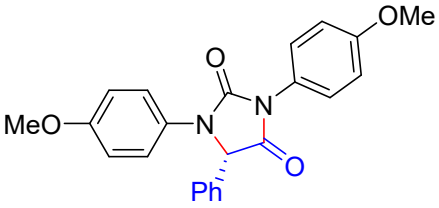
(*S*)-1,3,5-triphenylimidazolidine-2,4-dione (3ba).[2]

Product **3ba** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 35.4 mg, 96% ee. M.p.: 124-125 °C. ^{1}H NMR ($CDCl_3$) δ: 7.53 (d, J = 7.9 Hz, 2H), 7.50-7.43 (m, 4H), 7.43-7.33 (m, 6H), 7.30 (t, J = 8.4 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 5.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.9, 153.6, 136.3, 132.9, 131.4, 129.3, 129.2, 129.1, 129.1, 128.4, 126.8, 126.5, 126.3, 125.0, 120.6, 64.1; $[\alpha]^{20}_D$ = +25.9 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AD-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 36.0 min (minor), 77.4 min (major).



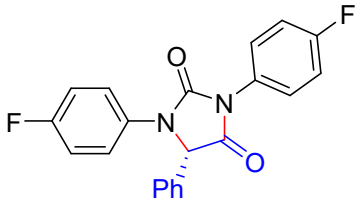
(*S*)-5-phenyl-1,3-di-*p*-tolylimidazolidine-2,4-dione (3ea).

Product **3ea** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 36.7 mg, 95% ee. M.p.: 166-168 °C. ^{1}H NMR ($CDCl_3$) δ: 7.43-7.29 (m, 9H), 7.29-7.23 (m, 2H), 7.09 (d, J = 8.3 Hz, 2H), 5.56 (s, 1H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 169.2, 153.8, 138.5, 134.8, 133.8, 133.1, 129.8, 129.7, 129.3, 129.2, 128.8, 126.9, 126.2, 120.8, 64.3, 21.2, 20.8; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O_2^+$ $(M+H)^+$ 357.1598, found 357.1597. $[\alpha]^{20}_D$ = +25.2 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AD-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 42.8 min (minor), 69.2 min (major).



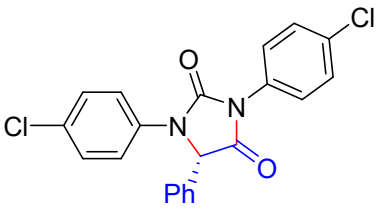
(*S*)-1,3-bis(4-methoxyphenyl)-5-phenylimidazolidine-2,4-dione (3fa).

Product **3fa** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 42.9 mg, 90% ee. M.p.: 68-70 °C. ^{1}H NMR ($CDCl_3$) δ: 7.41-7.28 (m, 9H), 7.00-6.93 (m, 2H), 6.85-6.79 (m, 2H), 5.52 (s, 1H), 3.81 (s, 3H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$) δ:169.4, 159.4, 157.0, 154.1, 133.2, 129.3, 129.2, 127.7, 127.1, 124.2, 123.0, 114.4, 114.4, 64.7, 55.5, 55.4; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O_4^+$ $(M+H)^+$ 389.1496, found 389.1496. $[\alpha]^{20}_D$ = +32.3 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 37.0 min (minor), 123.2 min (major).



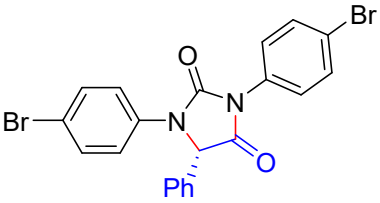
(*S*)-1,3-bis(4-fluorophenyl)-5-phenylimidazolidine-2,4-dione (3ga).

Product **3ga** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 37.1 mg, 93% ee. M.p.: 131-133 °C. ^{1}H NMR ($CDCl_3$) δ: 7.50-7.41 (m, 4H), 7.41-7.30 (m, 5H), 7.20-7.10 (m, 2H), 7.04-6.91 (m, 2H), 5.56 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.8, 163.4, 161.0, (d, J = 19.0 Hz), 158.7, 153.6, 132.5, 132.2 (d, J = 2.9 Hz), 129.5, 128.2 (d, J = 8.8 Hz), 127.3 (d, J = 3.1 Hz), 126.9, 122.8 (d, J = 8.1 Hz), 116.3 (d, J = 11.5 Hz), 116.0 (d, J = 11.2 Hz), 64.5; ^{19}F NMR ($CDCl_3$): -112.2, -116.4. HRMS (ESI) m/z calcd for $C_{21}H_{15}F_2N_2O_2^+$ $(M+H)^+$ 365.1096, found 365.1098. $[\alpha]^{20}_D$ = +32.0 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; R = 21.7 min (minor), 30.4 min (major).



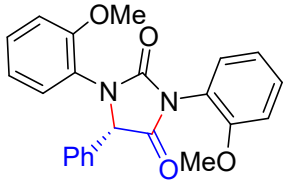
(*S*)-1,3-bis(4-chlorophenyl)-5-phenylimidazolidine-2,4-dione (3ha).

Product **3ha** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 42.2 mg, 95% ee. M.p.: 158-161 °C. ^{1}H NMR ($CDCl_3$) δ: 7.49-7.32 (m, 11H), 7.29-7.21 (m, 2H), 5.56 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.4, 153.2, 134.8, 134.4, 132.3, 130.5, 129.8, 129.6, 129.4, 129.3, 127.5, 126.8, 121.8, 64.1; HRMS (ESI) m/z calcd for $C_{21}H_{14}Cl_2N_2O_2Na^+$ $(M+Na)^+$ 419.0325, found 419.0324. $[\alpha]^{20}_D$ = +16.8 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 24.7 min (minor), 45.5 min (major).



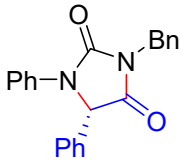
(*S*)-1,3-bis(4-bromophenyl)-5-phenylimidazolidine-2,4-dione (3ia).

Product **3ia** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 52.8 mg, 98% ee. M.p.: 207-208 °C. ^{1}H NMR ($CDCl_3$) δ: 7.62-7.56 (m, 2H), 7.44-7.31 (m, 11H), 5.55 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.3, 153.1, 135.3, 132.4, 132.3, 132.2, 130.3, 129.6, 127.7, 126.7, 122.4, 122.0, 118.2, 64.0; HRMS (ESI) m/z calcd for $C_{21}H_{14}Br_2N_2O_2Na^+$ $(M+Na)^+$ 506.9314, found 506.9311. $[\alpha]^{20}_D$ = +22.1 (*c* 0.5, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 23.4 min (minor), 49.6 min (major).



(*S*)-1,3-bis(2-methoxyphenyl)-5-phenylimidazolidine-2,4-dione (3ja).

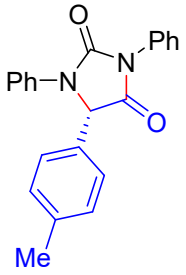
Product **3ja** was obtained by flash chromatography (PE:EA = 2:1) in 93% yield as white solid. 35.9 mg, 68% ee. M.p.: 75-76 °C. ^{1}H NMR ($CDCl_3$) δ: 7.43-7.26 (m, 7H), 7.23-7.15 (m, 2H), 7.10-6.98 (m, 2H), 6.92-6.79 (m, 2H), 5.68 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 170.9, 155.2, 154.9, 154.9, 134.2, 130.8, 130.1, 130.0, 129.1, 129.0, 128.9, 128.2, 123.8, 121.0, 120.8, 120.6, 112.2, 111.9, 66.2, 56.0, 55.7; HRMS (ESI) m/z calcd for $C_{23}H_{20}N_2O_4Na^+$ $(M+Na)^+$ 411.1315, found 411.1313. $[\alpha]^{20}_D$ = +5.5 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 13.9 min (minor), 28.2 min (major).



(*S*)-3-benzyl-1,5-diphenylimidazolidine-2,4-dione (3ka).[3]

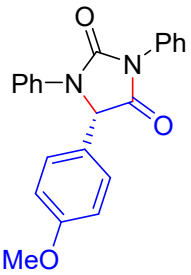
Product **3ka** was obtained by flash chromatography (PE:EA = 10:1) in quantitative yield as white

solid. 76 % ee. M.p.: 183-185 °C. ^{1}H NMR ($CDCl_3$) δ: 7.48-7.40 (m, 4H), 7.36-7.21 (m, 10H), 7.06 (t, J = 7.4 Hz, 1H), 5.44 (s, 1H), 4.76 (q, J = 17.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 169.7, 154.4, 136.4, 135.8, 132.8, 129.3, 129.2, 129.1, 128.8, 128.1, 126.7, 124.7, 120.2, 64.2, 42.9; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2O_2^+$ $(M+H)^+$ 343.1441, found 343.1442. $[\alpha]^{20}_D$ = +46.6 (c 0.4, DCM). Chiral HPLC: Chiralpak AD-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 254 nm; tR = 19.2 min (minor), 26.2 min (major).



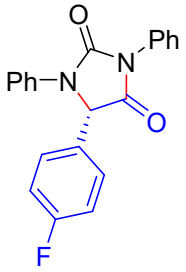
(*S*)-1,3-diphenyl-5-(*p*-tolyl)imidazolidine-2,4-dione (3bb).

Product **3bb** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as colorless oil. 34.9 mg. 83% ee. ^{1}H NMR ($CDCl_3$) δ: 7.56-7.50 (m, 2H), 7.50-7.42 (m, 4H), 7.41-7.34 (m, 1H), 7.33-7.25 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 5.57 (s, 1H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 169.2, 153.7, 139.3, 136.4, 131.5, 130.1, 129.9, 129.2, 129.1, 128.5, 126.8, 126.4, 125.0, 120.7, 64.0, 29.7, 21.2; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2O_2^+$ $(M+H)^+$ 343.1441, found 343.1442. $[\alpha]^{20}_D$ = +29.8 (c 0.3, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 254 nm; tR = 20.6 min (minor), 31.5 min (major).



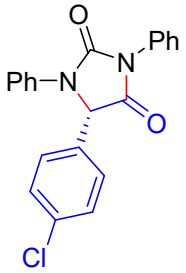
(*S*)-5-(4-methoxyphenyl)-1,3-diphenylimidazolidine-2,4-dione (3bc).

Product **3bc** was obtained by flash chromatography (PE:EA = 5:1) in 97% yield as white solid. 34.6 mg. 87% ee. M.p.: 56-58 °C. ^{1}H NMR ($CDCl_3$) δ: 7.55-7.50 (m, 2H), 7.50-7.43 (m, 4H), 7.42-7.36 (m, 1H), 7.36-7.28 (m, 4H), 7.12 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 5.57 (s, 1H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 169.3, 160.3, 153.6, 136.4, 131.5, 129.2, 129.1, 128.5, 128.1, 126.4, 125.0, 124.8, 120.8, 114.9, 63.7, 55.3; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2O_3^+$ $(M+H)^+$ 359.1390, found 359.1390. $[\alpha]^{20}_D$ = +17.3 (c 0.3, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 34.0 min (minor), 41.3 min (major).



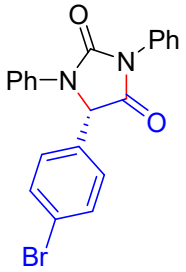
(*S*)-5-(4-fluorophenyl)-1,3-diphenylimidazolidine-2,4-dione (3bd).

Product **3bd** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 35.3 mg. 95% ee. M.p.: 55-57 °C. ^{1}H NMR ($CDCl_3$) δ: 7.54-7.42 (m, 6H), 7.50-7.43 (m, 4H), 7.42-7.35 (m, 3H), 7.35-7.27 (m, 2H), 7.13 (tt, J = 7.4, 0.9 Hz, 1H), 7.10-7.02 (m, 2H), 5.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.8, 163.1 (d, J = 248.8 Hz), 153.5, 136.2, 131.3, 129.2 (d, J = 9.9 Hz), 129.0, 128.8, 128.7, 128.6, 128.6, 126.3, 125.2, 120.7, 116.5 (d, J = 22.0 Hz), 63.4; ^{19}F NMR ($CDCl_3$): -111.8. HRMS (ESI) m/z calcd for $C_{21}H_{16}FN_2O_2^+$ $(M+H)^+$ 347.1190, found 347.1190. $[\alpha]^{20}_D$ = +32 (c 0.1, DCM). Chiral HPLC: Chiralpak AD-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 33.5 min (minor), 84.4 min (major).



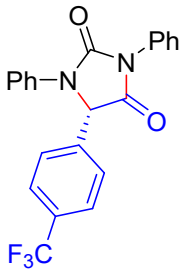
(*S*)-5-(4-chlorophenyl)-1,3-diphenylimidazolidine-2,4-dione (3be).

Product **3be** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 40.5 mg. 86% ee. M.p.: 149-150 °C. ^{1}H NMR ($CDCl_3$) δ: 7.53-7.37 (m, 7H), 7.36-7.27 (m, 6H), 7.13 (t, J = 7.4 Hz, 1H), 5.59 (s, 1H); ^{13}C NMR ($CDCl_3$) δ:168.6, 153.5, 136.1, 135.3, 131.4, 131.3, 129.7, 129.3, 129.2, 128.6, 128.2, 126.3, 125.2, 120.6, 63.4. HRMS (ESI) m/z calcd for $C_{21}H_{16}ClN_2O_2^+$ $(M+H)^+$ 363.0895, found 363.0895. $[\alpha]^{20}_D$ = +34.3 (c 0.3, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 25.7 min (minor), 61.7 min (major).



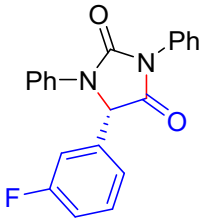
(*S*)-5-(4-bromophenyl)-1,3-diphenylimidazolidine-2,4-dione (3bf).

Product **3bf** was obtained by flash chromatography (PE:EA = 5:1) in 88% yield as white solid. 35.6 mg. 75% ee. M.p.: 166-168 °C. ^{1}H NMR ($CDCl_3$) δ: 7.54-7.36 (m, 9H), 7.35-7.25 (m, 4H), 7.13 (t, J = 7.4 Hz, 1H), 5.57 (s, 1H); ^{13}C NMR ($CDCl_3$) δ:168.4, 153.5, 136.1, 132.6, 131.9, 131.3, 129.3, 129.2, 128.8, 128.6, 128.5, 126.3, 125.3, 123.5, 120.6, 63.5. HRMS (ESI) m/z calcd for $C_{21}H_{15}BrN_2O_2Na^+$ $(M+Na)^+$ 429.0209, found 429.0209. $[\alpha]^{20}_D$ = +27.2 (c 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 254 nm; tR = 23.5 min (minor), 35.8 min (major).



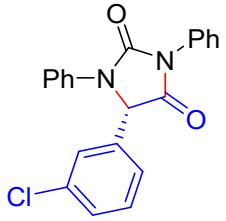
(*S*)-1,3-diphenyl-5-(4-(trifluoromethyl)phenyl)imidazolidine-2,4-dione (3bg).

Product **3bg** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as colorless oil. 40.1 mg. 60% ee. ^{1}H NMR ($CDCl_3$) δ: 7.55-7.49 (m, 2H), 7.49-7.27 (m, 8H), 7.21 (d, J = 7.8 Hz, 1H), 7.17-7.09 (m, 2H), 7.084 (td, J = 8.4, 2.2 Hz, 1H), 5.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ:168.4, 163.2 (d, J = 248.2 Hz), 153.5, 136.2, 135.3 (d, J = 7.3 Hz), 131.3, 131.1 (d, J = 8.2 Hz), 129.3 (d, J = 12.8 Hz), 128.6, 126.3, 125.2, 122.6 (d, J = 3.0 Hz), 120.6, 116.4 (d, J = 21.2 Hz), 114.1 (d, J = 23.0 Hz), 63.5 (d, J = 1.6 Hz); ^{19}F NMR ($CDCl_3$): -110.9. HRMS (ESI) m/z calcd for $C_{22}H_{16}F_3N_2O_2^+$ $(M+H)^+$ 397.1158, found 397.1155. $[\alpha]^{20}_D$ = +22.6 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 16.8 min (minor), 24.7 min (major).



(*S*)-5-(3-fluorophenyl)-1,3-diphenylimidazolidine-2,4-dione (3bh).

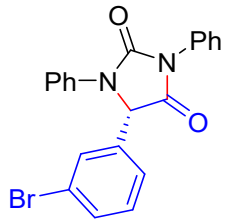
Product **3bh** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as colorless oil. 35.7 mg. 91% ee. ^{1}H NMR ($CDCl_3$) δ: 7.55-7.49 (m, 2H), 7.49-7.27 (m, 8H), 7.21 (d, J = 7.8 Hz, 1H), 7.17-7.09 (m, 2H), 7.04 (td, J = 8.4, 2.2 Hz, 1H), 5.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.4, 163.2 (d, J = 248.2 Hz), 153.5, 136.2, 135.3 (d, J = 7.3 Hz), 131.3, 131.1 (d, J = 8.2 Hz), 129.3, 129.2, 128.6, 126.3, 125.2, 122.6 (d, J = 3.0 Hz), 120.6, 116.4 (d, J = 21.1 Hz), 114.1 (d, J = 23.0 Hz), 63.5 (d, J = 1.5 Hz); ^{19}F NMR ($CDCl_3$): -110.9. HRMS (ESI) m/z calcd for $C_{21}H_{16}FN_2O_2^+$ $(M+H)^+$ 347.1190, found 347.1187. $[\alpha]^{20}_D$ = +25.7 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 22.3 min (minor), 48.9 min (major).



(*S*)-5-(3-chlorophenyl)-1,3-diphenylimidazolidine-2,4-dione (3bi).

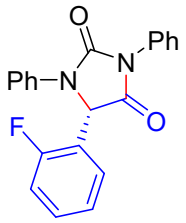
Product **3bh** was obtained by flash chromatography (PE:EA = 5:1) in 95% yield as white solid. 34.3 mg. 85% ee. M.p.: 135-136 ^{o}C. ^{1}H NMR ($CDCl_3$) δ: 7.56-7.36 (m, 8H), 7.36-7.26 (m, 5H), 7.17-7.11 (m, 1H), 5.58 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.3, 153.5, 136.1, 135.4, 134.9, 131.3, 130.7, 129.6, 129.4, 129.2, 128.6, 127.2, 126.3, 125.3, 125.0, 120.6, 63.5. HRMS (ESI) m/z calcd for $C_{21}H_{16}ClN_2O_2^+$ $(M+H)^+$ 363.0895, found 363.0894. $[\alpha]^{20}_D$ = +27.5 (*c* 0.4, DCM). Chiral HPLC:

Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 26.8 min (minor), 42.1 min (major).



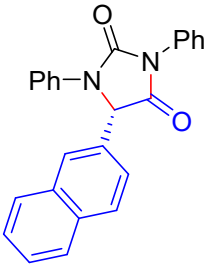
(*S*)-5-(3-bromophenyl)-1,3-diphenylimidazolidine-2,4-dione (3bj).

Product **3bj** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 41.0 mg. 81% ee. M.p.: 138-139 °C. ^{1}H NMR ($CDCl_3$) δ: 7.58 (t, J = 1.7 Hz, 1H), 7.54-7.36 (m, 8H), 7.36-7.28 (m, 3H), 7.25 (t, J = 7.8 Hz, 1H), 7.17-7.10 (m, 1H), 5.57 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.3, 153.5, 136.1, 135.1, 132.6, 131.3, 130.9, 130.0, 129.4, 129.2, 128.6, 126.3, 125.4, 125.3, 123.5, 120.6, 63.4. HRMS (ESI) m/z calcd for $C_{21}H_{16}BrN_2O_2^+$ $(M+H)^+$ 407.0390, found 407.0387. $[\alpha]^{20}_D$ = +25.7 (*c* 0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 254 nm; tR = 26.6 min (minor), 56.3 min (major).



(*S*)-5-(2-fluorophenyl)-1,3-diphenylimidazolidine-2,4-dione (3bk).

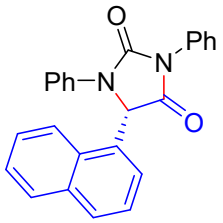
Product **3bk** was obtained by flash chromatography (PE:EA = 5:1) in quantitative yield as white solid. 35.2 mg. 80% ee. M.p.: 74-74 °C. ^{1}H NMR ($CDCl_3$) δ: 7.53-7.44 (m, 6H), 7.44-7.37 (m, 1H), 7.35-7.26 (m, 4H), 7.15-7.06 (m, 3H), 5.86 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.7, 163.2 (d, J = 249.5 Hz), 153.6, 135.8, 131.5, 131.4 (d, J = 8.4 Hz), 129.6 (d, J = 2.8 Hz), 129.2, 129.2, 128.6, 126.5, 125.6, 124.9 (d, J = 3.6 Hz), 121.6, 116.5 (d, J = 20.8 Hz), 59.8 (d, J = 1.5 Hz); ^{19}F NMR ($CDCl_3$): -117.9. $[\alpha]^{20}_D$ = +20.0 (*c* 0.1, DCM). Chiral HPLC: Chiralpak AD-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 254 nm; tR = 38.4 min (minor), 89.6 min (major).



(*S*)-5-(naphthalen-2-yl)-1,3-diphenylimidazolidine-2,4-dione (3bl).

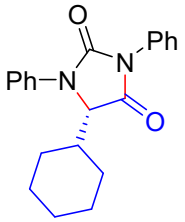
Product **3bl** was obtained by flash chromatography (PE:EA = 5:1) in 98% yield as white solid. 37.2 mg. 71% ee. M.p.: 158-160 °C. ^{1}H NMR ($CDCl_3$) δ: 7.89 (s, 1H), 7.86 (t, J = 8.5 Hz, 1H), 7.83-7.77 (m, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.52-7.41 (m, 7H), 7.41-7.33 (m, 1H), 7.30-7.21 (m, 2H), 7.07 (t, J = 7.3 Hz, 1H), 5.75 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 169.0, 153.7, 136.4, 133.6, 133.3, 131.5, 130.4, 129.6, 129.2, 129.2, 128.5, 128.1, 127.9, 127.1, 126.9, 126.8, 126.4, 125.1, 123.4, 120.7, 64.4. HRMS (ESI) m/z calcd for $C_{25}H_{18}N_2O_2Na^+$ $(M+Na)^+$ 401.1260, found 401.1258. $[\alpha]^{20}_D$ = +8.8 (*c*

0.4, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 28.1 min (minor), 50.1 min (major).



(*S*)-5-(naphthalen-1-yl)-1,3-diphenylimidazolidine-2,4-dione (3bm).

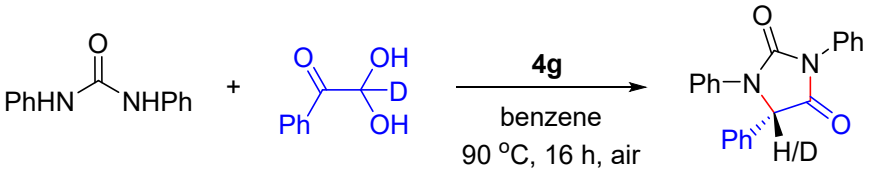
Product **3bm** was obtained by flash chromatography (PE:EA = 5:1) in 86% yield as white solid. 32.5 mg. 60% ee. M.p.: 170-171 °C. ^{1}H NMR ($CDCl_3$) δ: 8.36 (br, s, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.70-7.61 (m, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.54-7.42 (m, 7H), 7.41-7.35 (m, 2H), 7.22 (t, J = 8.4 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.51 (br, s, 1H), 5.75 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.8, 153.8, 136.4, 134.5, 131.5, 131.3, 129.9, 129.2, 129.1, 128.5, 127.2, 126.4, 126.4, 125.4, 124.9, 123.4, 120.0, 59.9. HRMS (ESI) m/z calcd for $C_{25}H_{19}N_2O_2^+$ $(M+H)^+$ 379.1441, found 379.1443. $[\alpha]^{20}_D$ = +37.8 (*c* 0.3, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 270 nm; tR = 22.2 min (minor), 33.6 min (major).



(S)-5-cyclohexyl-1,3-diphenylimidazolidine-2,4-dione (3bn).

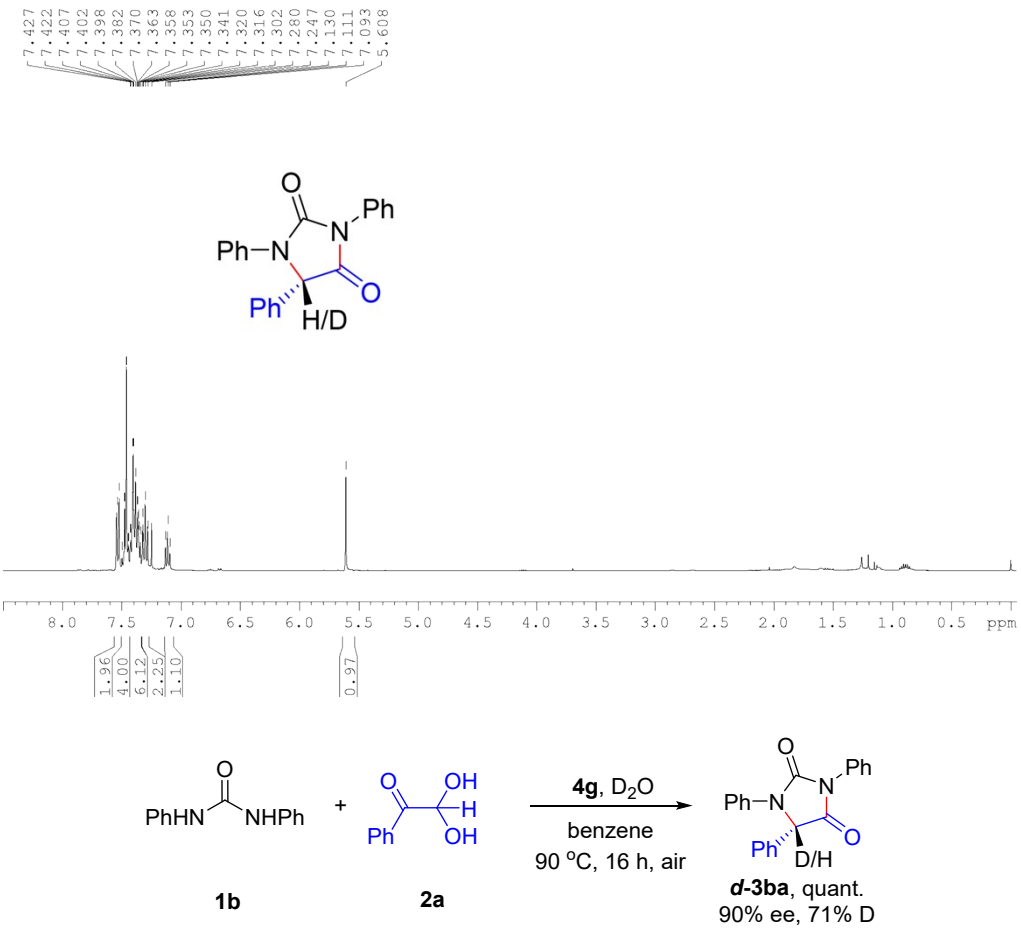
Product **3bn** was obtained by flash chromatography (PE:EA = 5:1) in 98% yield as colorless oil. 32.8 mg. 92% ee. ^{1}H NMR ($CDCl_3$) δ: 7.51-7.34 (m, 9H), 7.29-7.24 (m, 1H), 4.58 (d, J = 2.8 Hz, 1H), 2.03-1.92 (m, 1H), 1.84-1.59 (m, 6H), 1.28-0.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ: 170.5, 153.7, 135.7, 132.0, 131.5, 129.4, 129.1, 128.4, 126.4, 125.9, 122.9, 64.5, 39.0, 27.9, 26.8, 26.2, 25.9. $[\alpha]^{20}_D$ = +6.7 (*c* 0.1, DCM). Chiral HPLC: Chiralpak AD-H, hexane:^{i}PrOH = 60:40, 0.5 mL/min, 254 nm; tR = 26.1 min (major), 35.9 min (minor).

IV. Control experiments

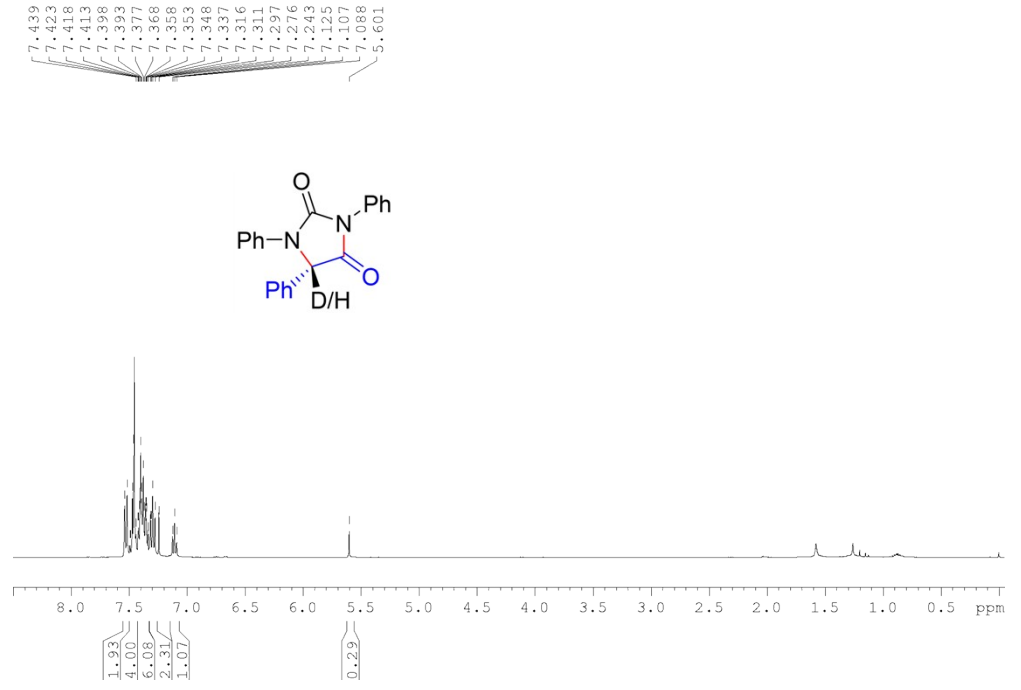


1b ***d*-2a** ***d*-3ba**, quant. 78%ee, <5% D

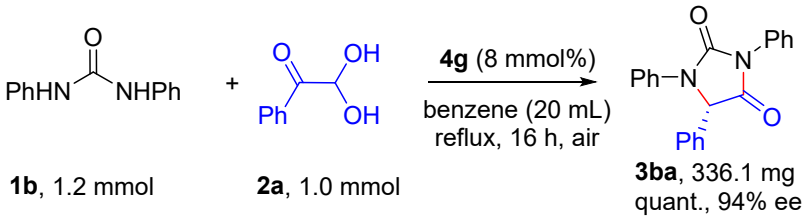
The 1-deuterated phenylglyoxal monohydrate (***d*-2a**) was synthesized according to reference.[4] The urea **1b** (1.2 mmol), ***d*-2a** (0.1 mmol) and **4g** (10 mol %) was dissolved in benzene (2 mL). The reaction mixture was stirred at 90 °C for 16 h. The product was separated by flash column chromatography (PE:EA = 5:1) on silica gel to afford compound ***d*-3ba** (35.1 mg, <5%D) in quant yield.



The urea **1b** (1.2 mmol), **2a** (0.1 mmol) and **4g** (10 mol %) was dissolved in benzene (2 mL). The D_2O (4.0 equiv) was added into the mixture. The reaction mixture was stirred at 90 °C for 16 h. The product was separated by flash column chromatography (PE:EA = 5:1) on silica gel to afford compound ***d*-3ba** (33.4 mg, 71%D) in quant yield.

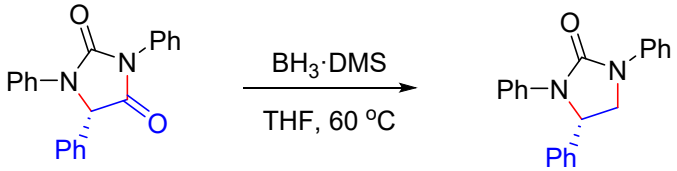


V. Gram-scale Synthesis and Further Chemical Transformations



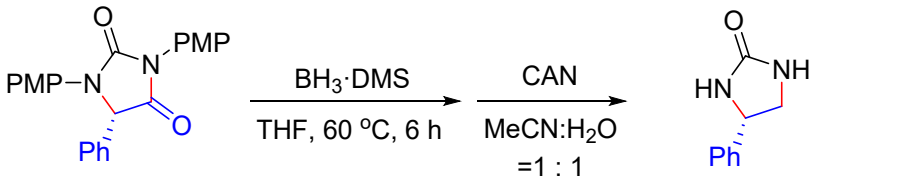
1b, 1.2 mmol **2a**, 1.0 mmol **3ba**, 336.1 mg quant., 94% ee

The *N*,*N*'-diphenylurea **1b** (1.2 mmol), **2a** (1.0 mmol) and **4g** (8 mol %) was dissolved in benzene (20 mL). The reaction mixture was refluxed for 16 h. Then solvent was removed in vacuo and the crude product was separated by flash column chromatography on silica gel (PE:EA = 5:1) to afford products **3ba** in quantitative yield with 94% ee.



3ba, 94% ee **4**, 78% yield 94% ee

A solution of **3ba** (0.1 mmol) in THF (0.5 mL) was treated with borane-dimethyl sulfide complex (2 M in THF, 2 equiv) at 0 °C under N_2. The resulting mixture was heated at 60 °C for 6 h and then cooled to 0 °C. The reaction was then quenched with MeOH (0.5 mL) at 0 °C. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (PE:EA = 5:1) to afford white solid (24.6 mg) in 78% yield. **(*S*)-1,3,4-triphenylimidazolidin-2-one (4)**: white solid, m.p.: 150-152 °C, 94% ee; ^{1}H NMR ($CDCl_3$) δ: 7.58 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.40-7.31 (m, 6H), 7.30-7.19 (m, 3H), 7.08 (t, J = 7.3 Hz, 1H), 7.01 (t, J = 7.3 Hz, 1H), 5.32 (dd, J = 9.2, 5.9 Hz, 1H), 4.33 (t, J = 9.0 Hz, 1H), 3.72 (dd, J = 9.0, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 155.5, 140.0, 139.8, 138.7, 129.2, 128.9, 128.7, 128.4, 126.2, 123.7, 123.2, 120.8, 118.2, 57.3, 51.6. HRMS (ESI) m/z calcd for $C_{21}H_{19}N_2O^+$ $(M+H)^+$ 315.1492, found 315.1493. $[\alpha]^{20}_D$ = -30.5 (*c* 0.2, DCM). Chiral HPLC: Chiralpak AS-H, hexane:^{i}PrOH = 80:20, 1.0 mL/min, 254 nm; tR = 12.5 min (major), 14.3 min (minor).



3fa, 90% ee **6**, 63% yield (2 setps), 81% ee

A solution of **3fa** (0.1 mmol) in THF (0.5 mL) was treated with borane-dimethyl sulfide complex (2 M in THF, 2 equiv) at 0 °C under N_2. The resulting mixture was heated at 60 °C for 6 h and then cooled to 0 °C. The reaction was then quenched with MeOH (0.5 mL) at 0 °C. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column

chromatography (PE:EA = 3:1) to afford white solid. To a solution of the white solid in MeCN (1.5 mL), was added a solution of CAN in water (1.5 mL) slowly in 30 min at 0 °C. Then the solution was extracted with EA, and dried with Na_2SO_4. Then solvent was removed in vacuo and the crude product was separated by flash column chromatography on silica gel (DCM:MeOH = 95:5) to afford products **6** in 63% yield with 81% ee. **(*S*)-4-phenylimidazolidin-2-one (6)**:[5] yellow solid, m.p.: 126-128 °C, 81% ee; ^{1}H NMR ($CDCl_3$) δ: 7.42-7.29 (m, 5H), 5.09 (br, s, 1H), 4.93 (br, s, 1H), 4.88 (t, J = 8.2 Hz, 1H), 3.87 (t, J = 8.8 Hz, 1H), 3.35 (t, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 141.3, 128.9, 128.3, 126.1, 56.7, 49.6. $[\alpha]^{20}_D$ = +19.3 (*c* 0.1, DCM). Chiral HPLC: Chiralpak IB-3, hexane:^{i}PrOH = 80:20, 1.0 mL/min, 210 nm; tR = 9.0 min (major), 9.8 min (minor).

VI. References

(1) Wang, M.; Han, J.; Si, X.; Hu, Y.; Zhu, J.; Sun, X., Effective approach to ureas through organocatalyzed one-pot process. *Tetrahedron Lett.* **2018,** *59*, 1614-1618.

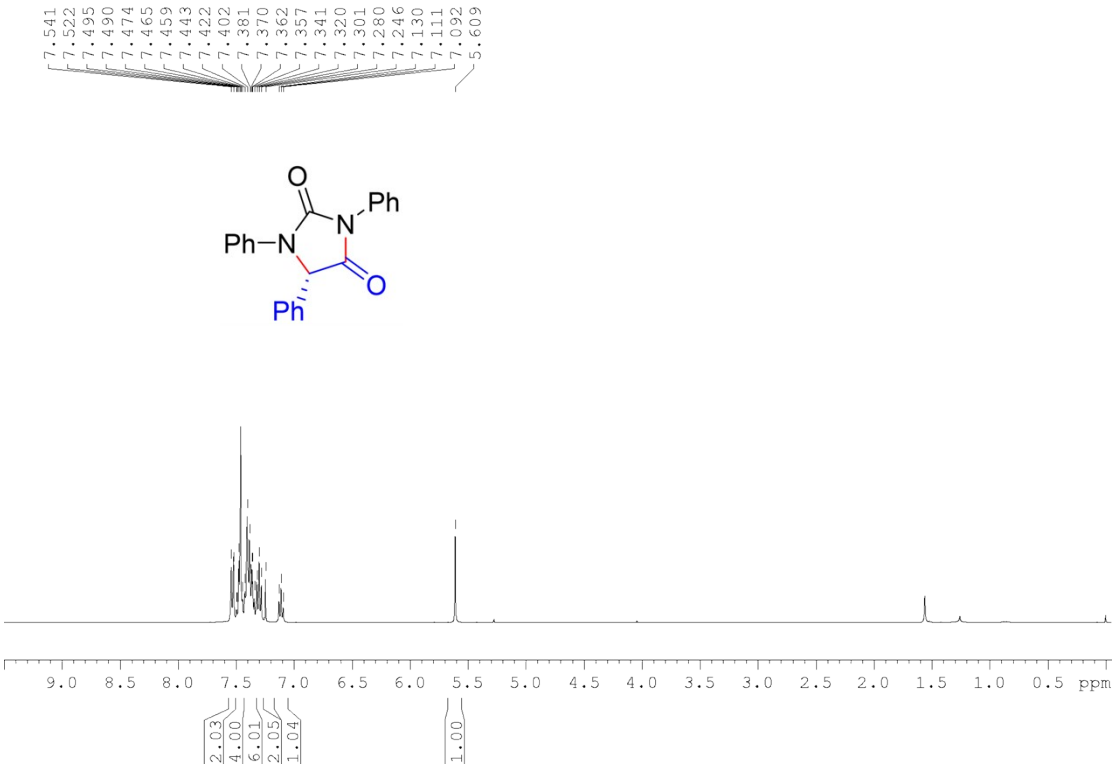
(2) Han, G. H.; Kim, S. Y.; Lee, H. R.; Lee, J. S.; Park, Y. S., A Convenient One-Pot Synthesis of Both Enantiomers of 1,3,5-Trisubstituted Hydantoins. *Synlett* **2020,** *31*, 171-174.

(3) Xu, Z.-G.; Ding, Y.; Meng, J.-P.; Tang, D.-Y.; Li, Y.; Lei, J.; Xu, C.; Chen, Z.-Z., Facile Construction of Hydantoin Scaffolds via a Post-Ugi Cascade Reaction. *Synlett* **2018,** *29*, 2199-2202.

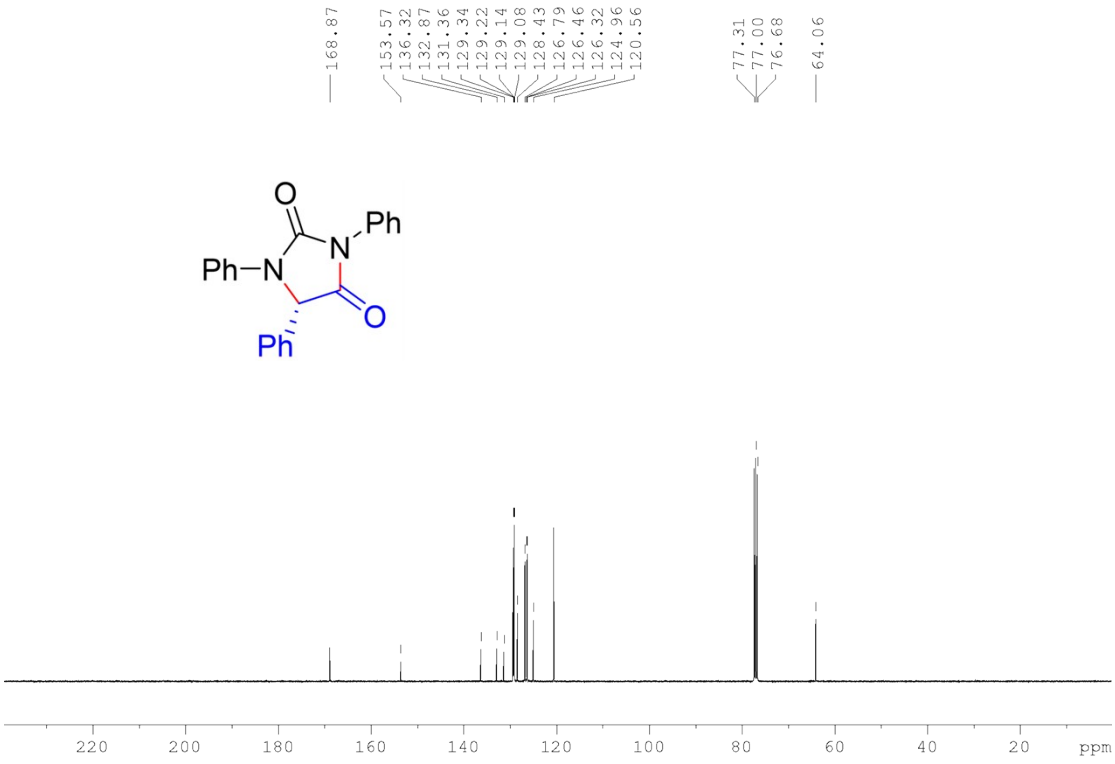
(4) Marchand, N. J.; Grée, D. M.; Martelli, J. T.; Grée, R. L.; Toupet, L. J., Synthesis and Reactivity of Cross-Conjugated Polyenones with a Planar Chirality. *J. Org. Chem.* **1996,** *61*, 5063-5072.

(5) Zhou, Z.; Tan, Y.; Yamahira, T.; Ivlev, S.; Xie, X.; Riedel, R.; Hemming, M.; Kimura, M.; Meggers, E., Enantioselective Ring-Closing C–H Amination of Urea Derivatives. *Chem* **2020,** *6*, 2024-2034.

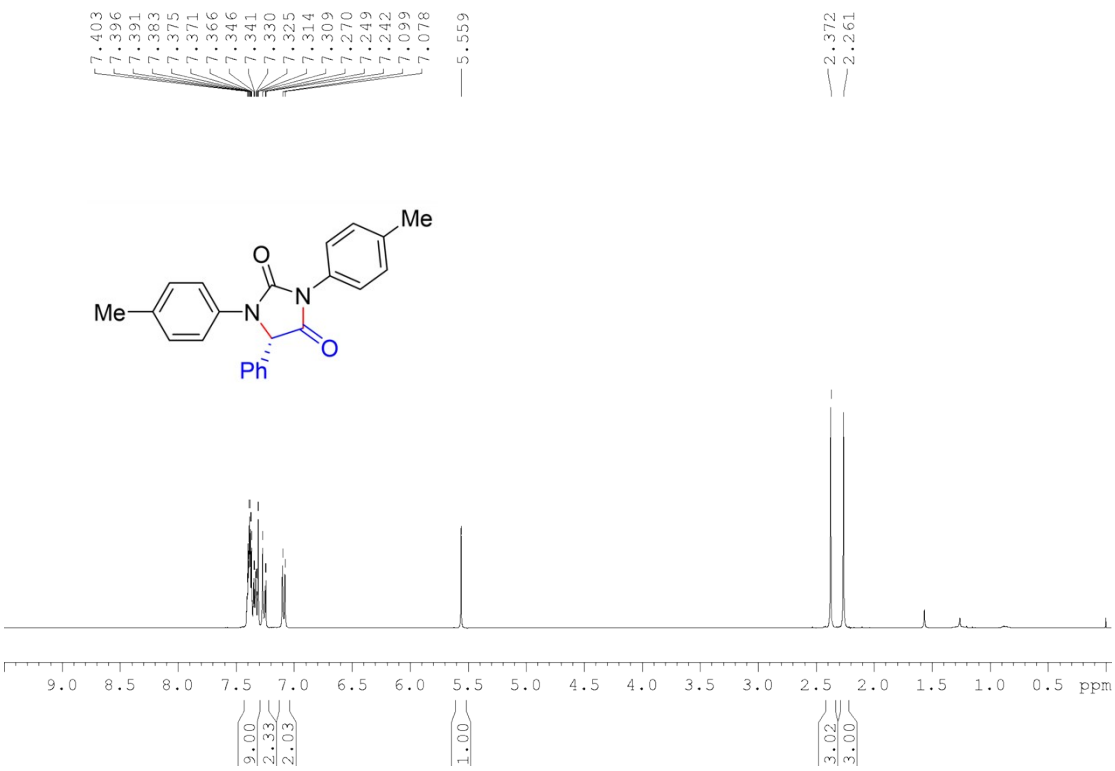
VII. Copies of NMR Spectra



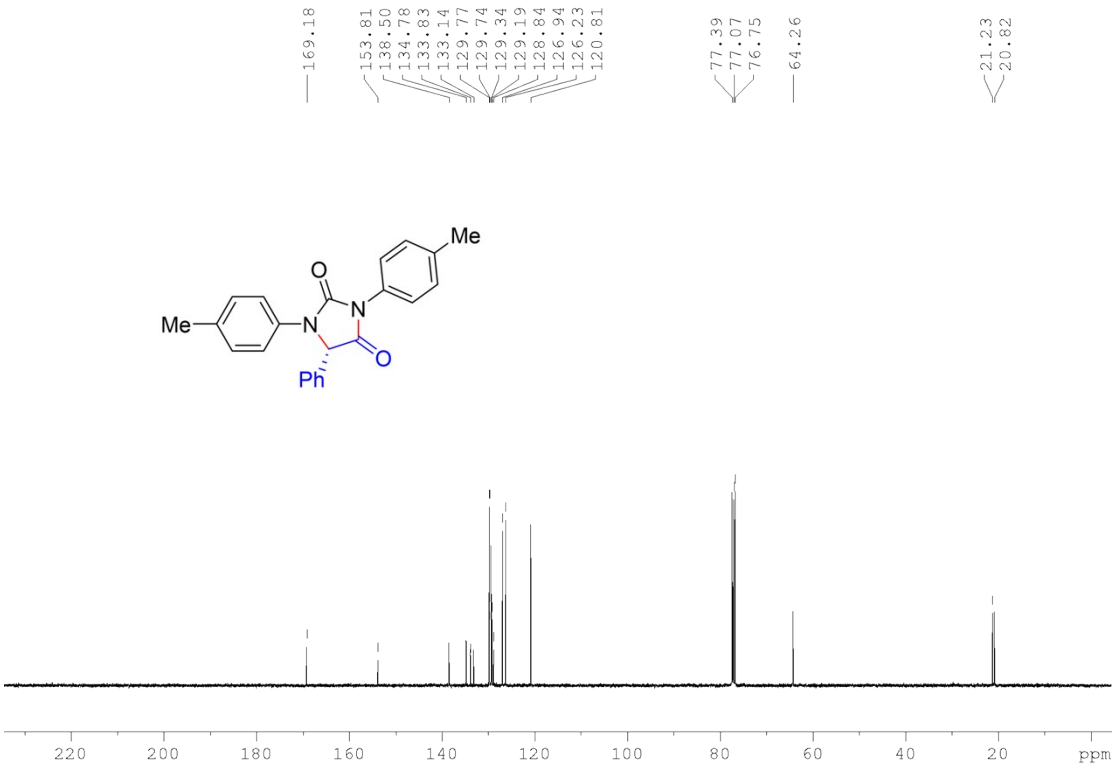
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



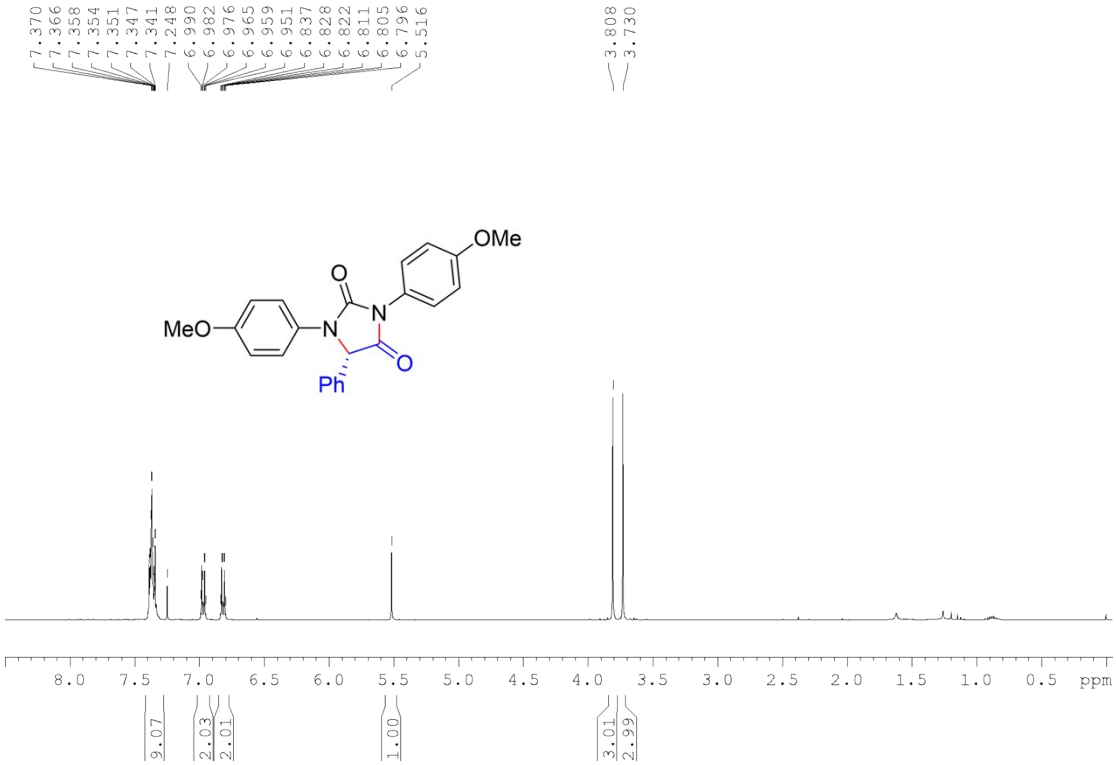
^{13}C NMR (100 MHz, $CDCl_3$) of **3ba**



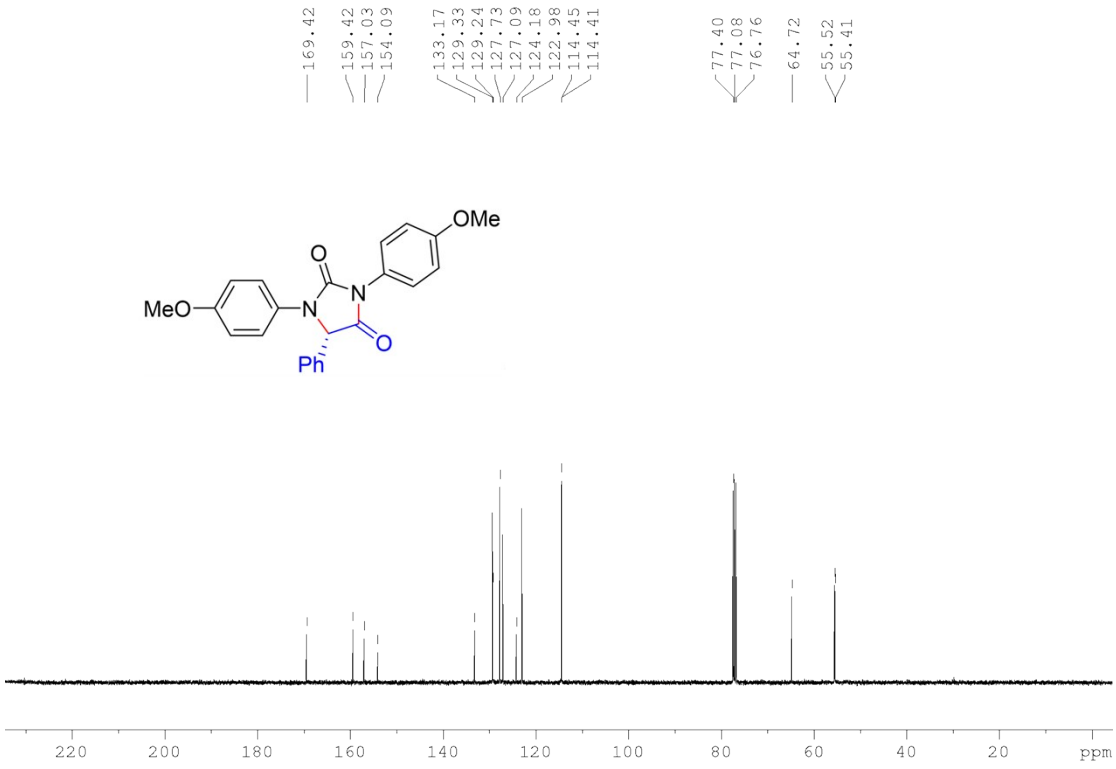
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



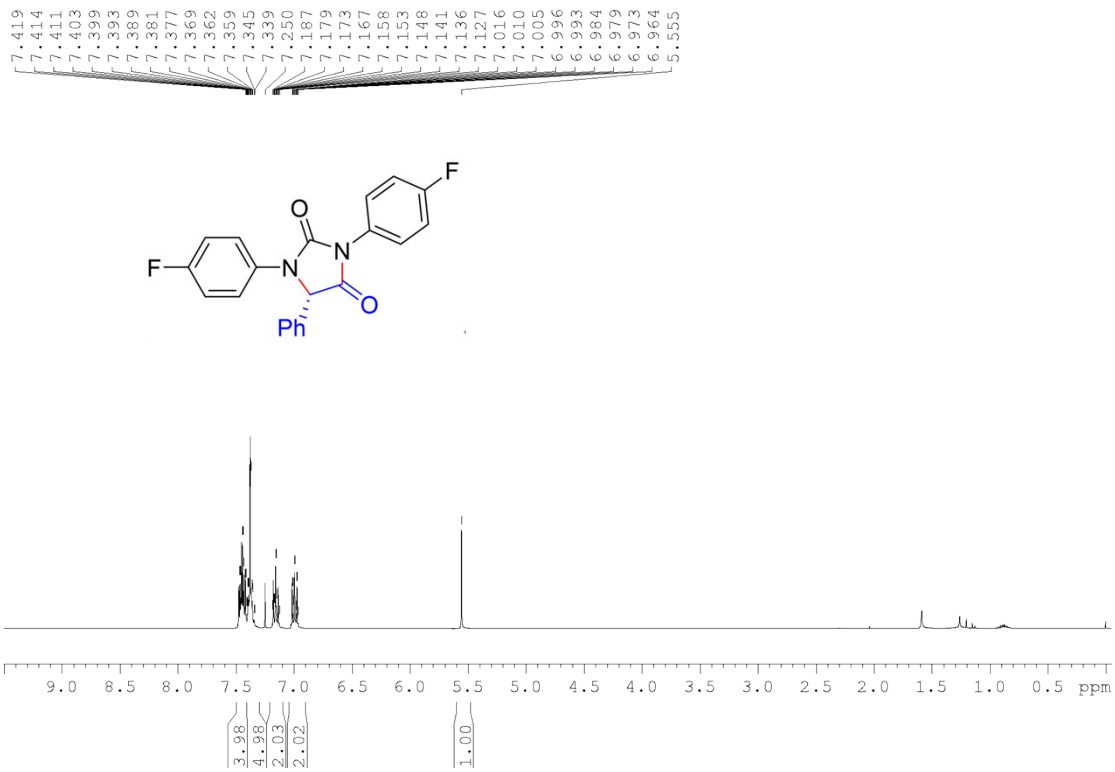
^{13}C NMR (100 MHz, $CDCl_3$) of **3ea**



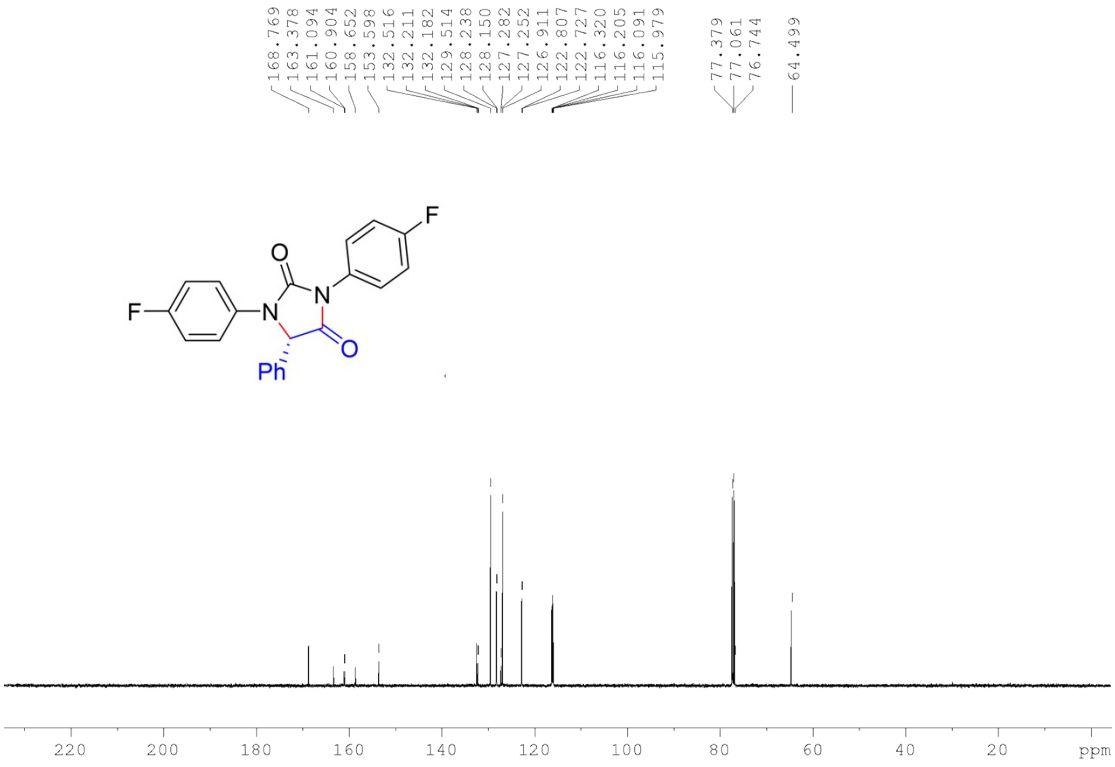
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



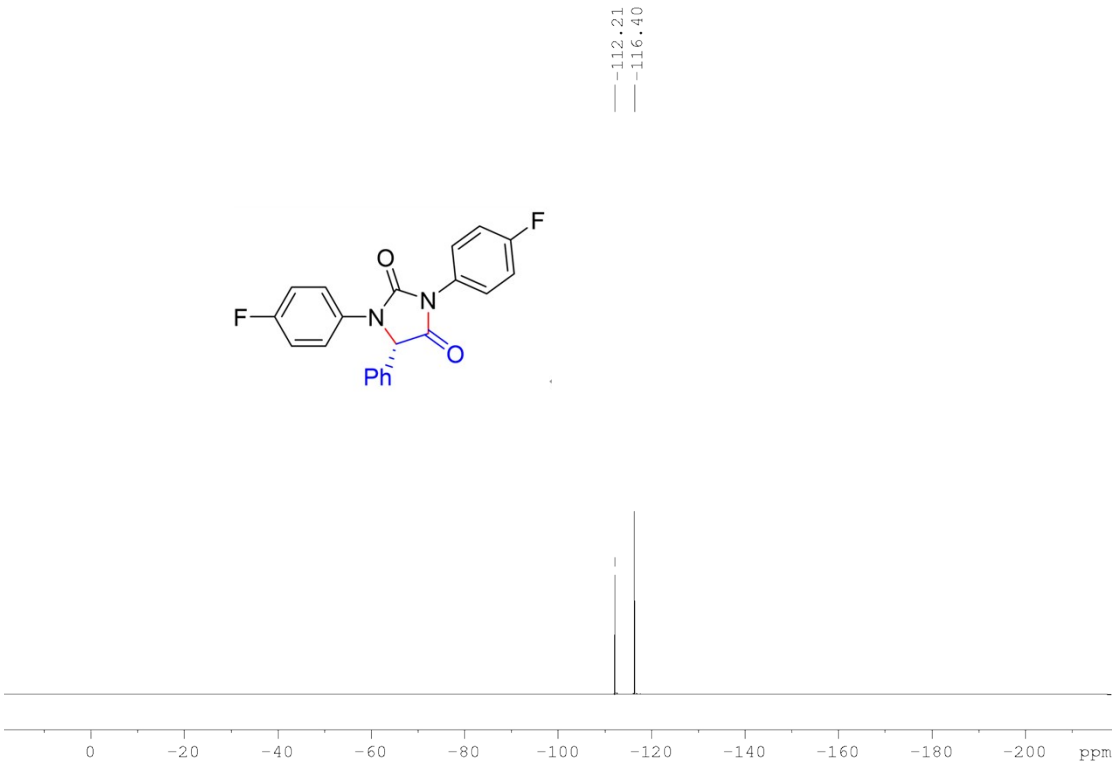
^{13}C NMR (100 MHz, $CDCl_3$) of **3fa**



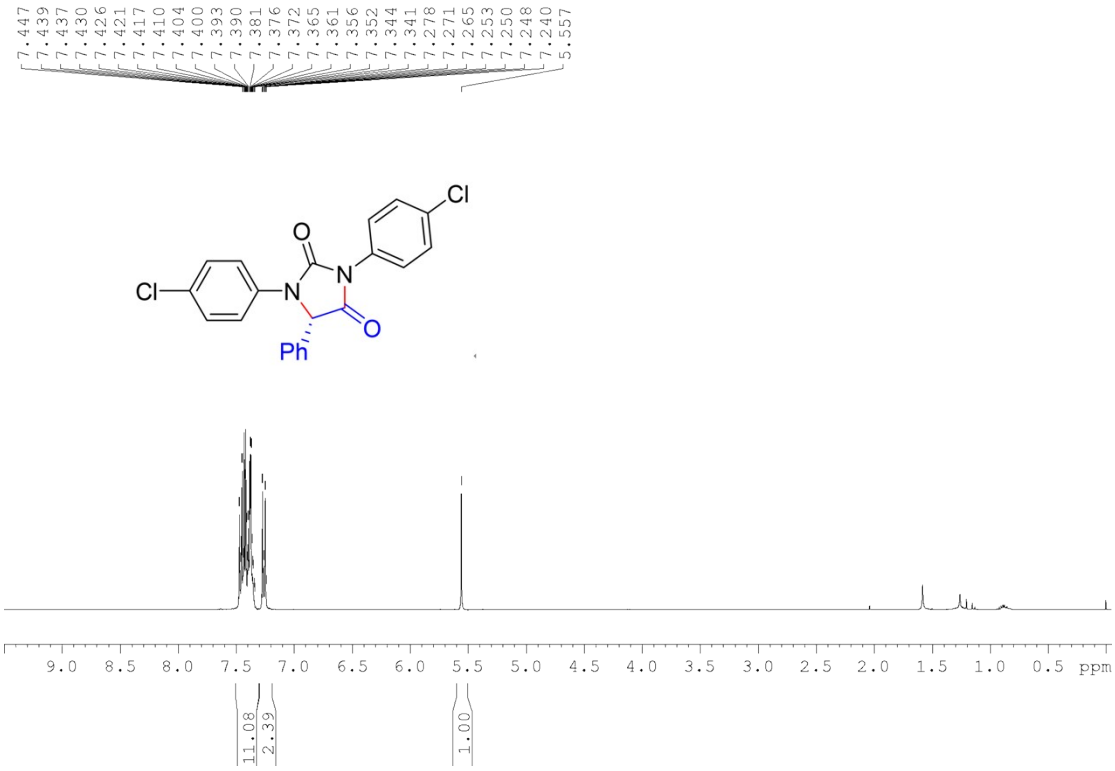
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



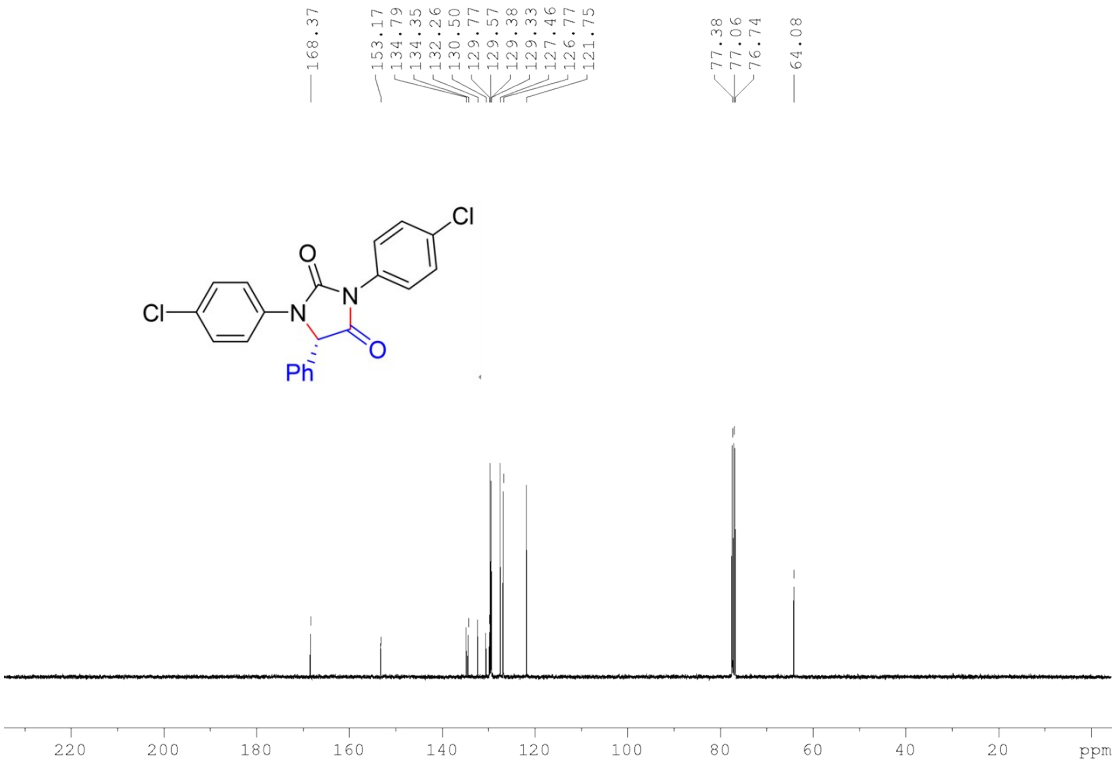
^{13}C NMR (100 MHz, $CDCl_3$) of **3ga**



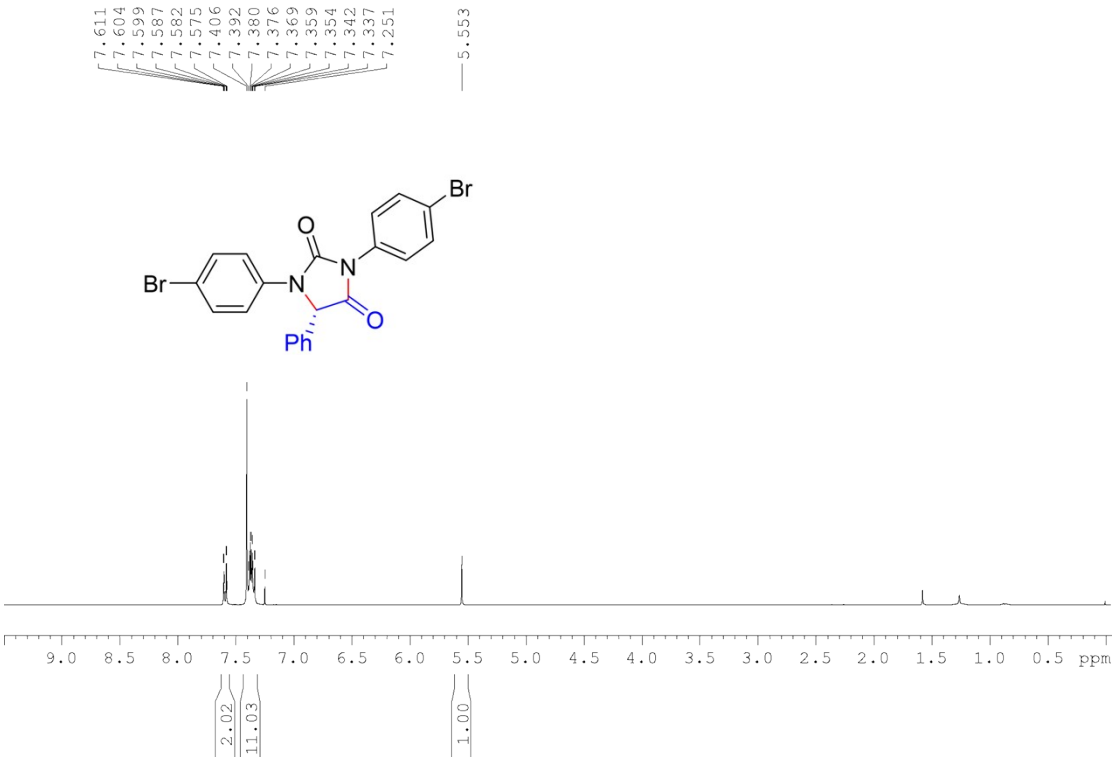
^{19}F NMR (376 MHz, $CDCl_3$) of **3ga**



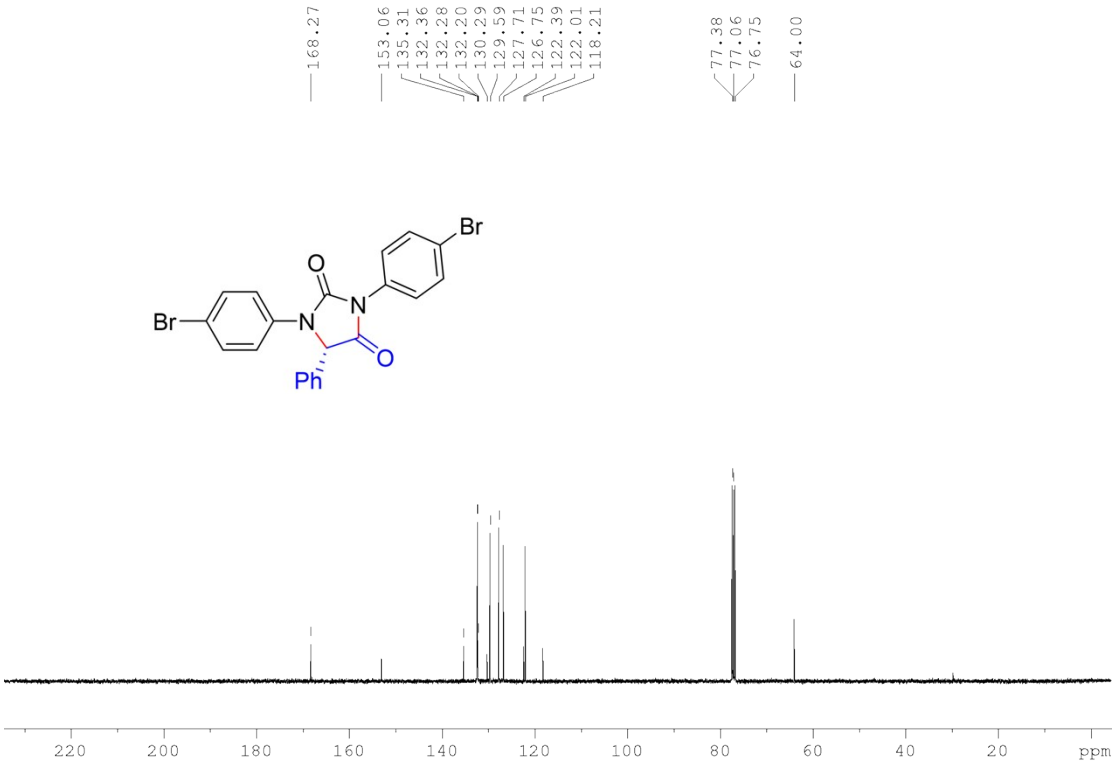
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



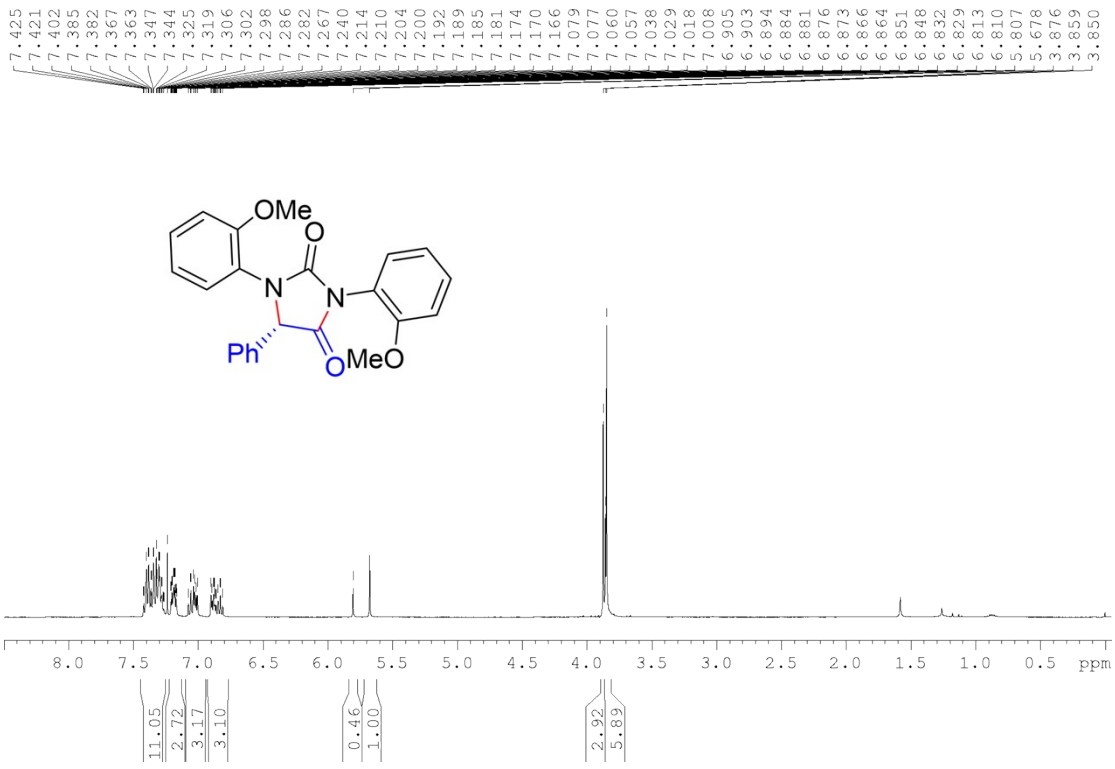
^{13}C NMR (100 MHz, $CDCl_3$) of **3ha**



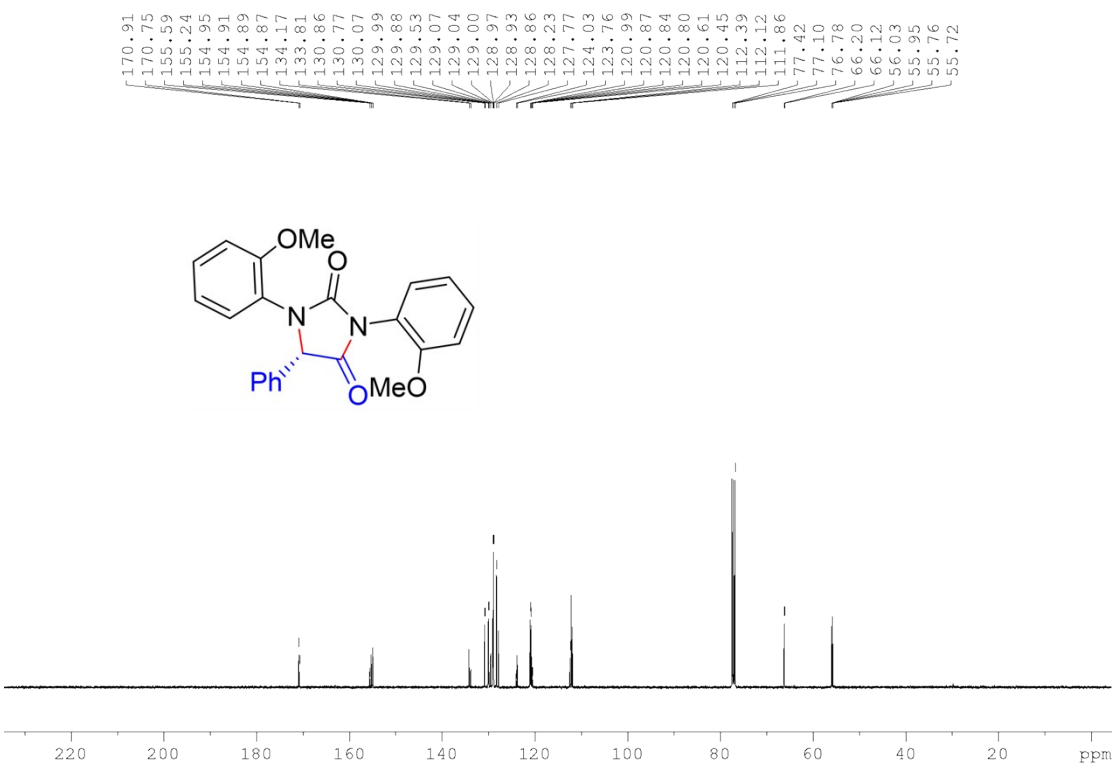
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



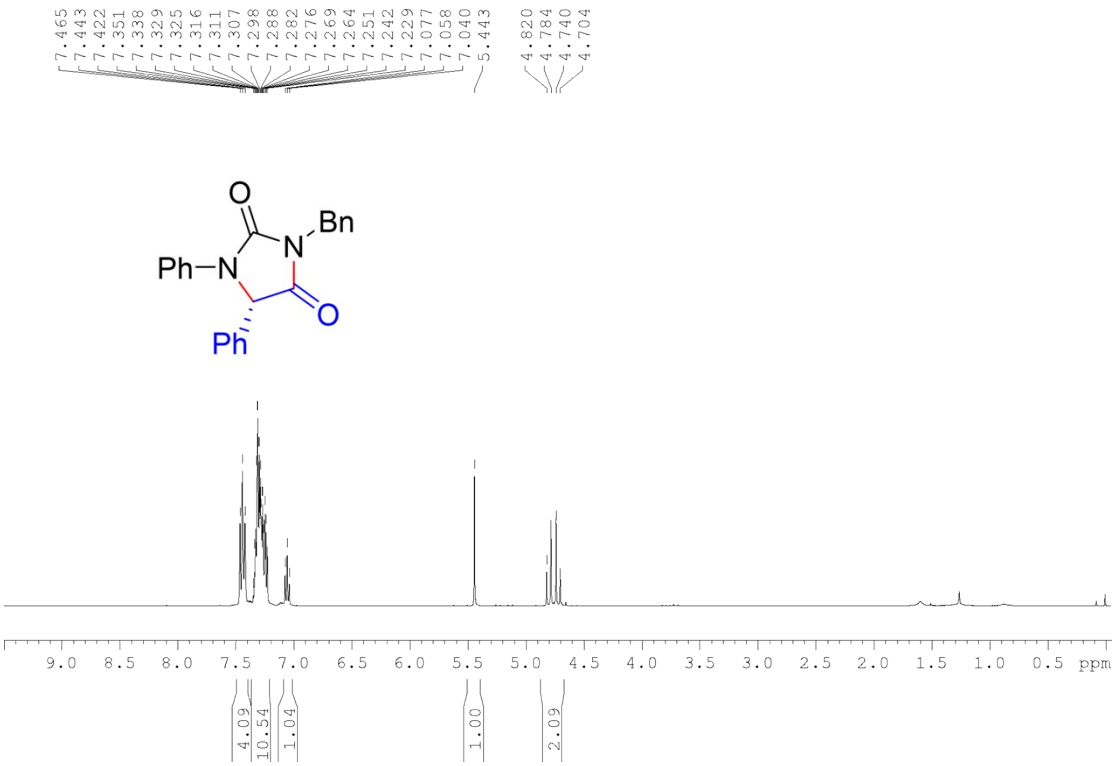
^{13}C NMR (100 MHz, $CDCl_3$) of **3ia**



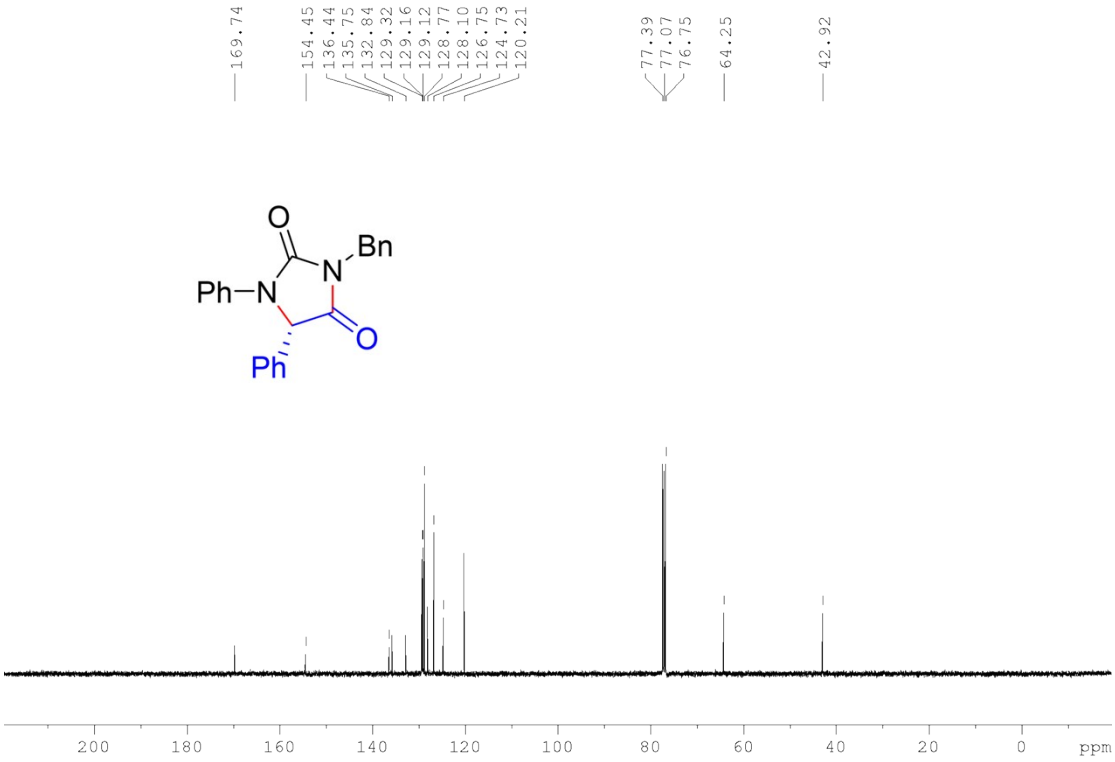
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**



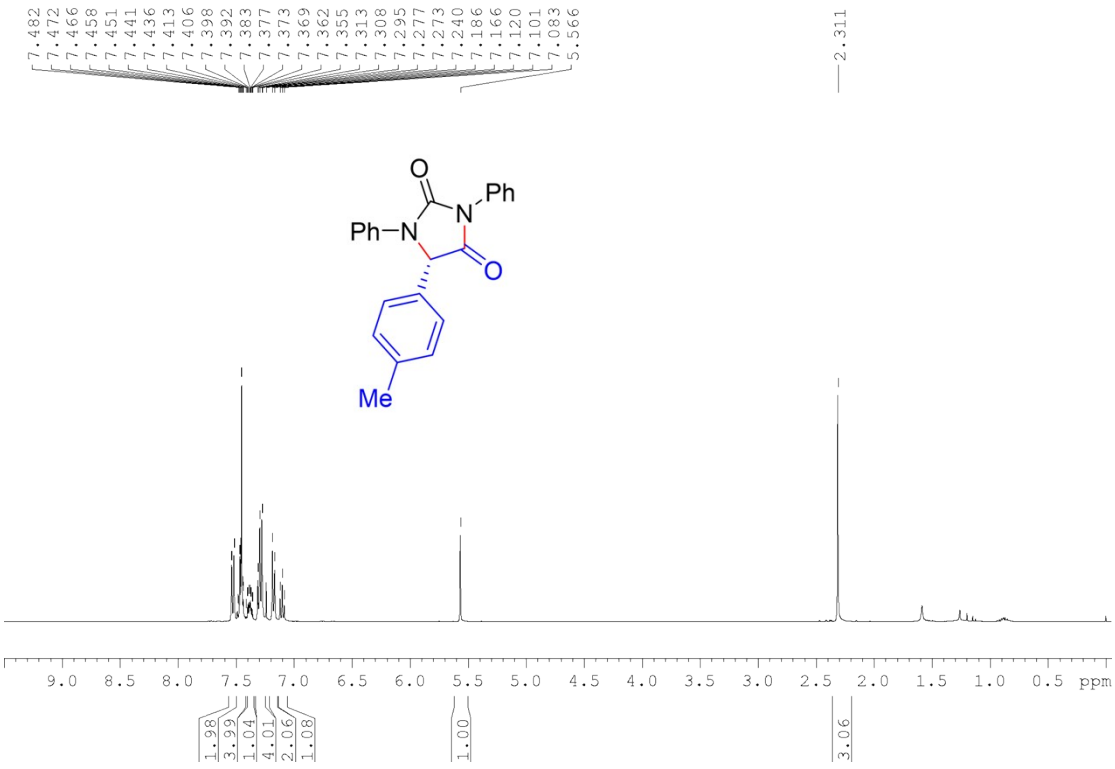
^{13}C NMR (100 MHz, $CDCl_3$) of **3ja**



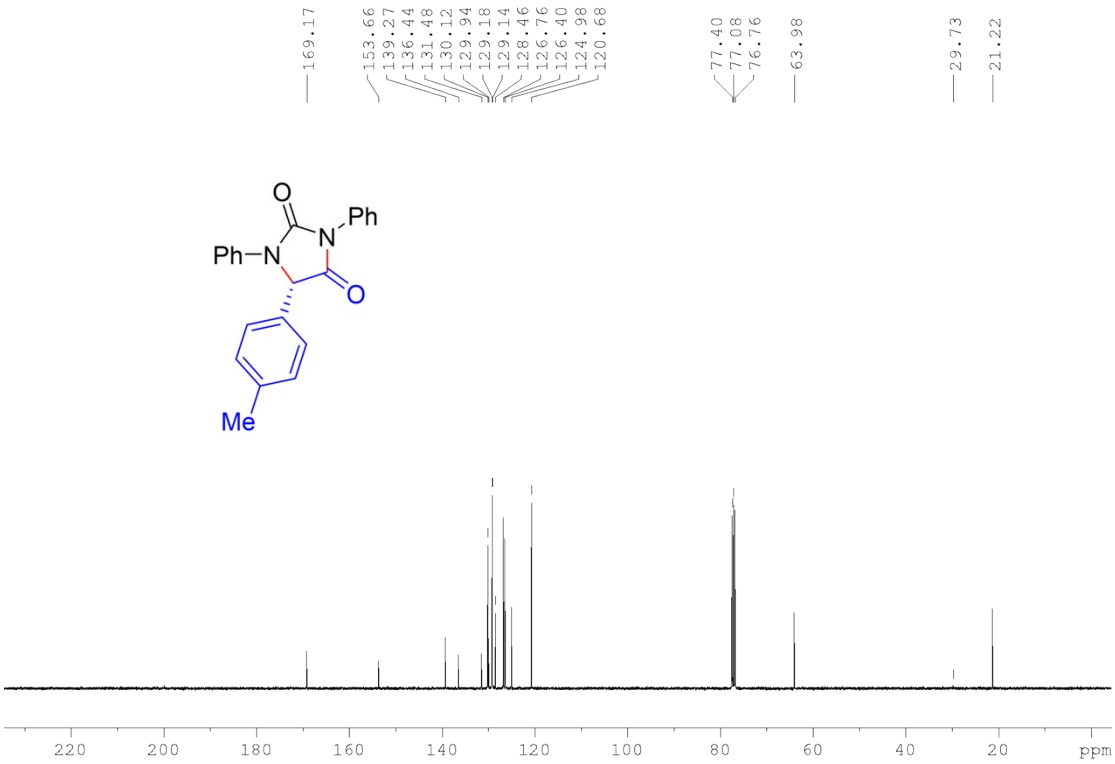
^{1}H NMR (400 MHz, $CDCl_3$) of **3ka**



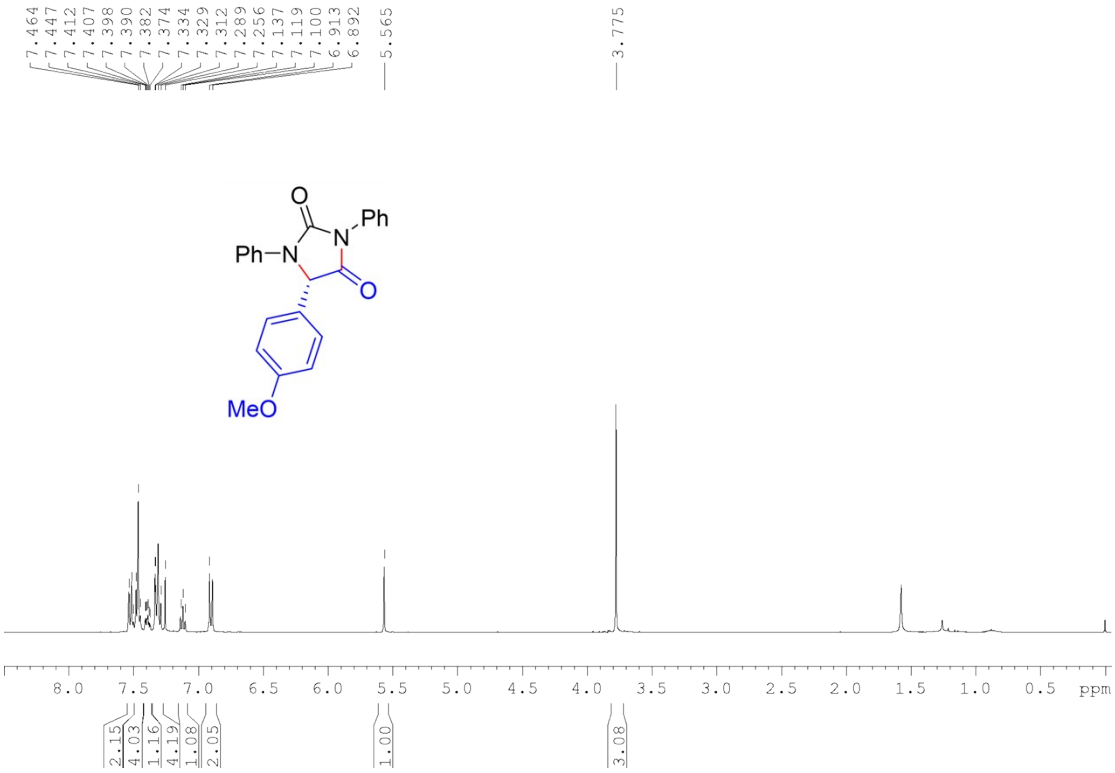
^{13}C NMR (100 MHz, $CDCl_3$) of **3ka**



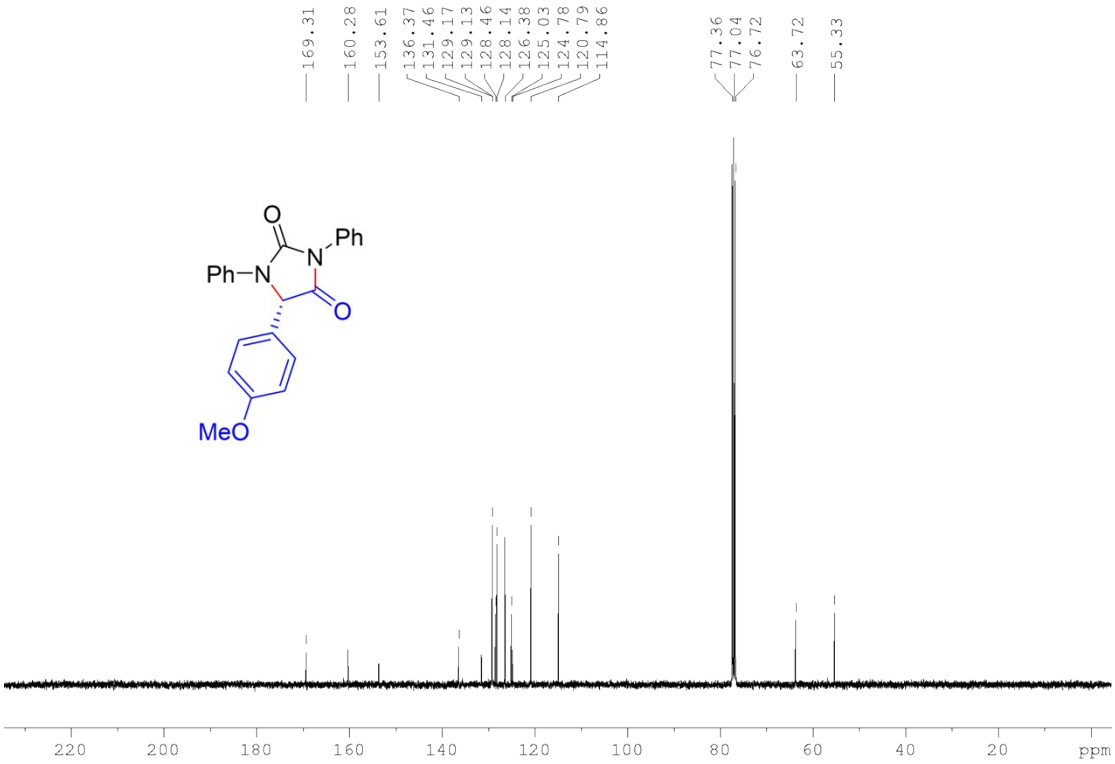
^{1}H NMR (400 MHz, $CDCl_3$) of **3bb**



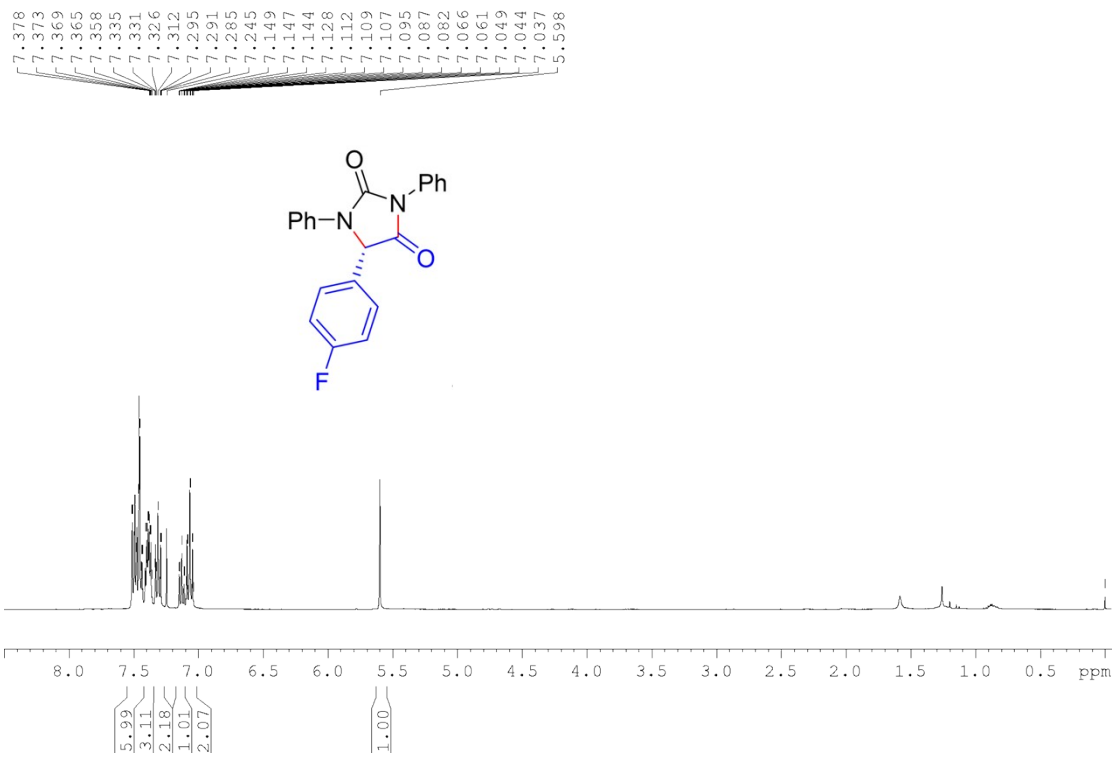
^{13}C NMR (100 MHz, $CDCl_3$) of **3bb**



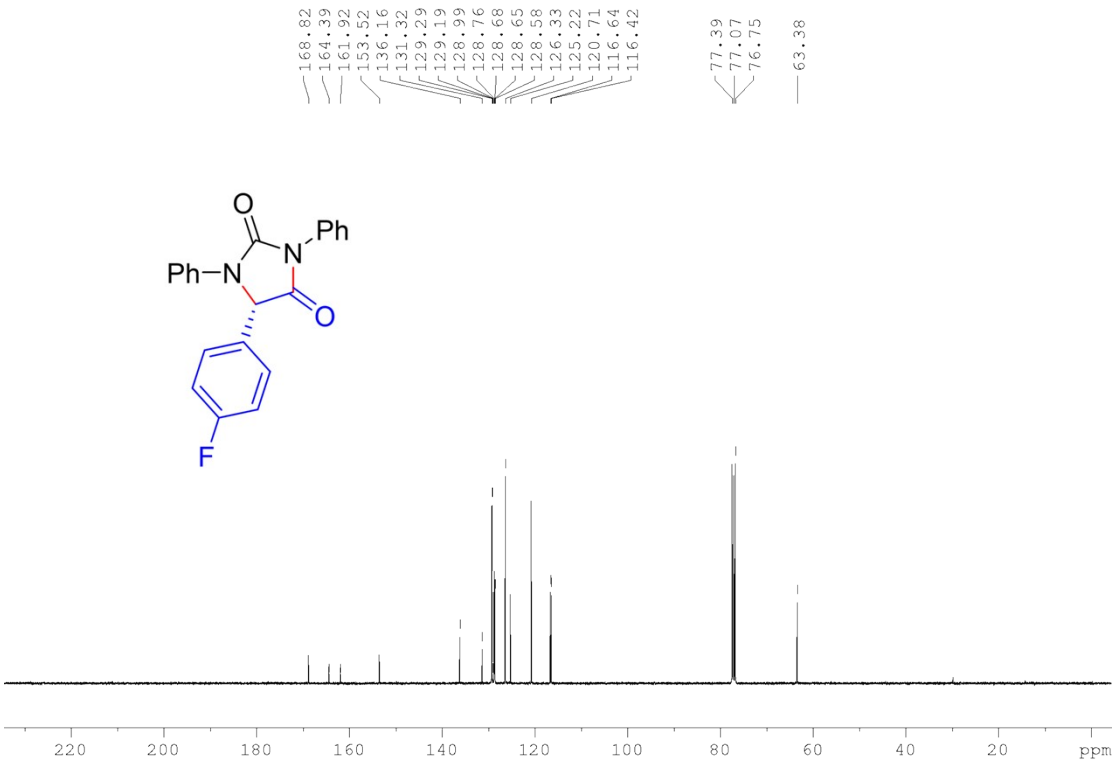
^{1}H NMR (400 MHz, $CDCl_3$) of **3bc**



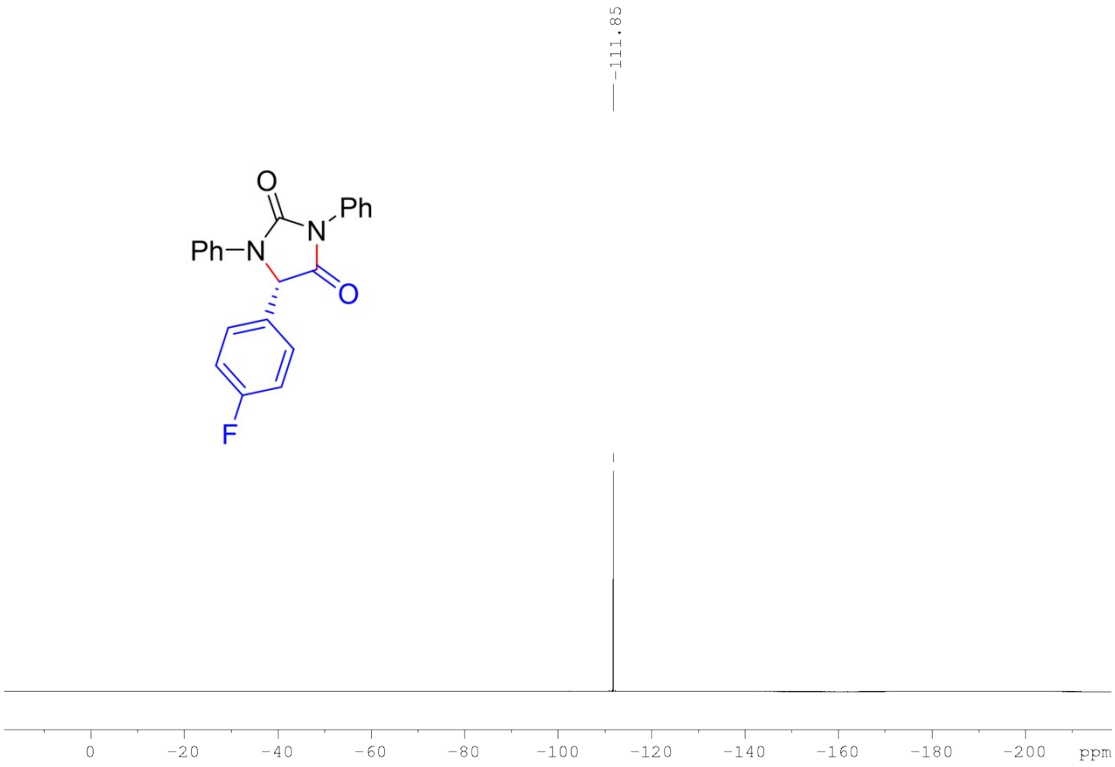
^{13}C NMR (100 MHz, $CDCl_3$) of **3bc**



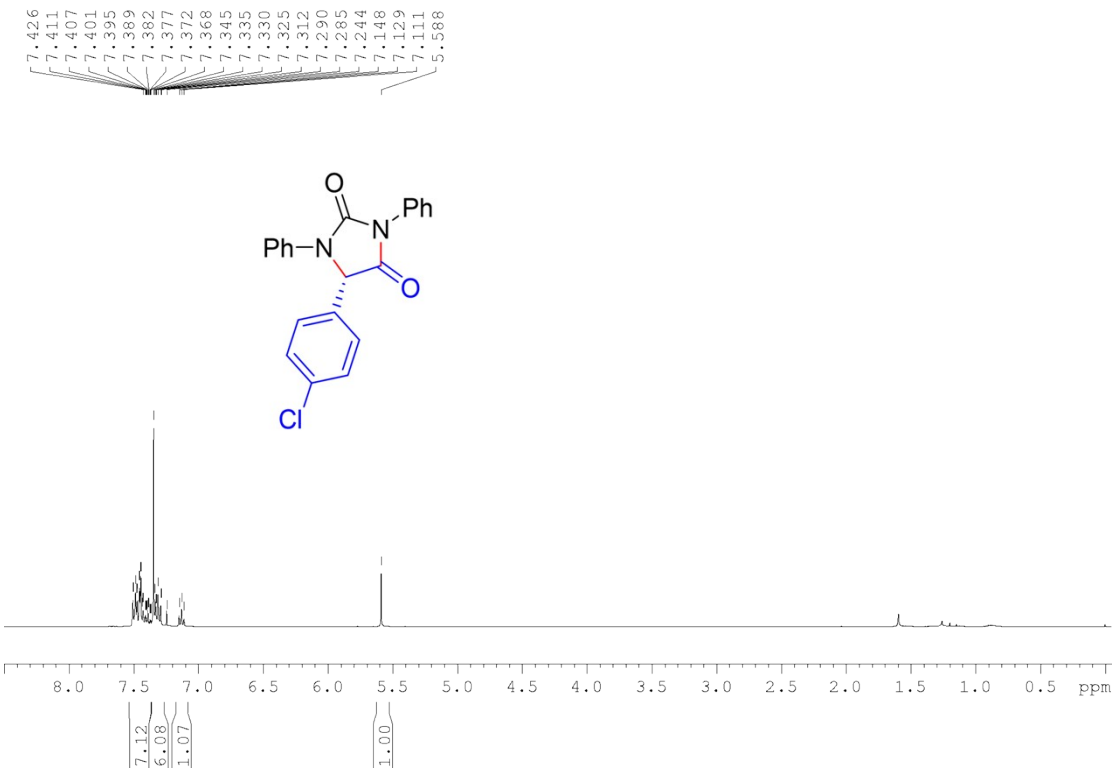
^{1}H NMR (400 MHz, $CDCl_3$) of **3bd**



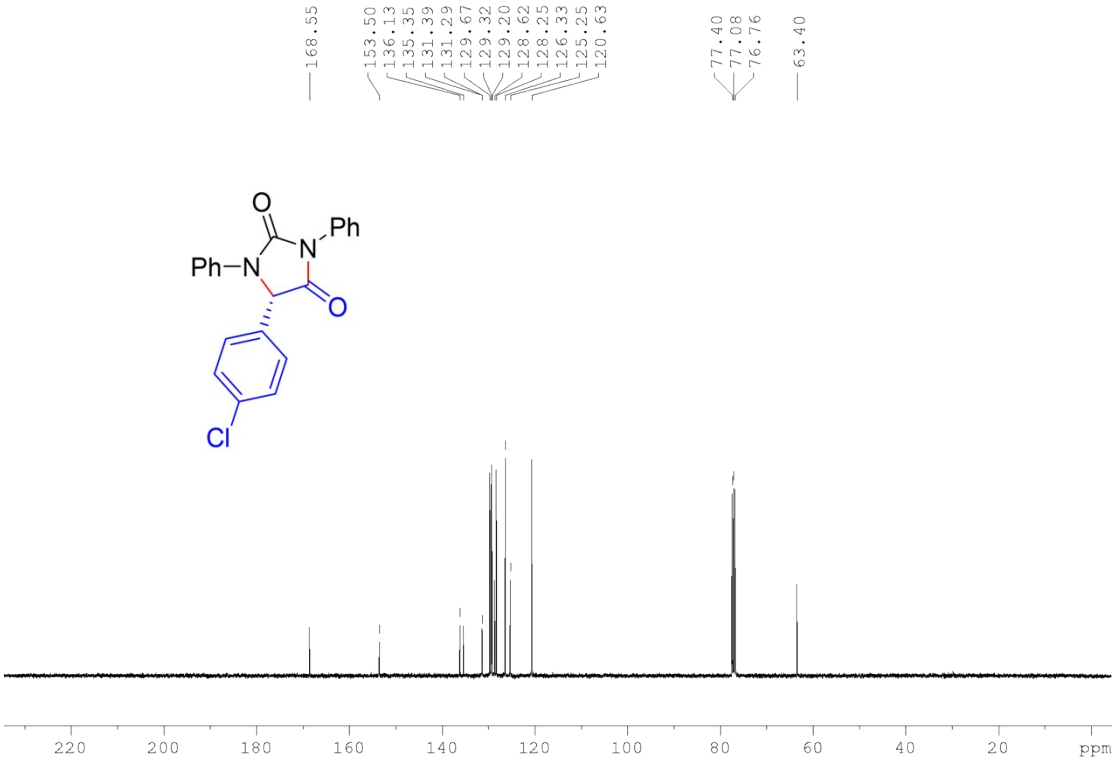
^{13}C NMR (100 MHz, $CDCl_3$) of **3bd**



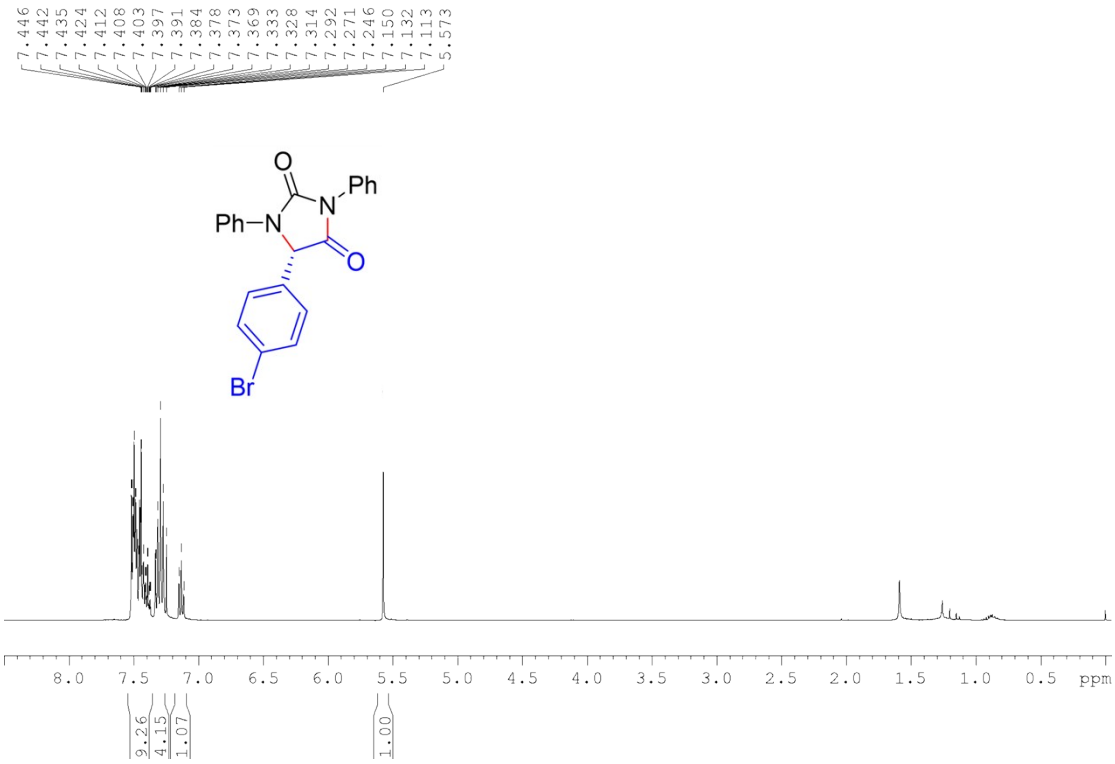
^{19}F NMR (376 MHz, $CDCl_3$) of **3bd**



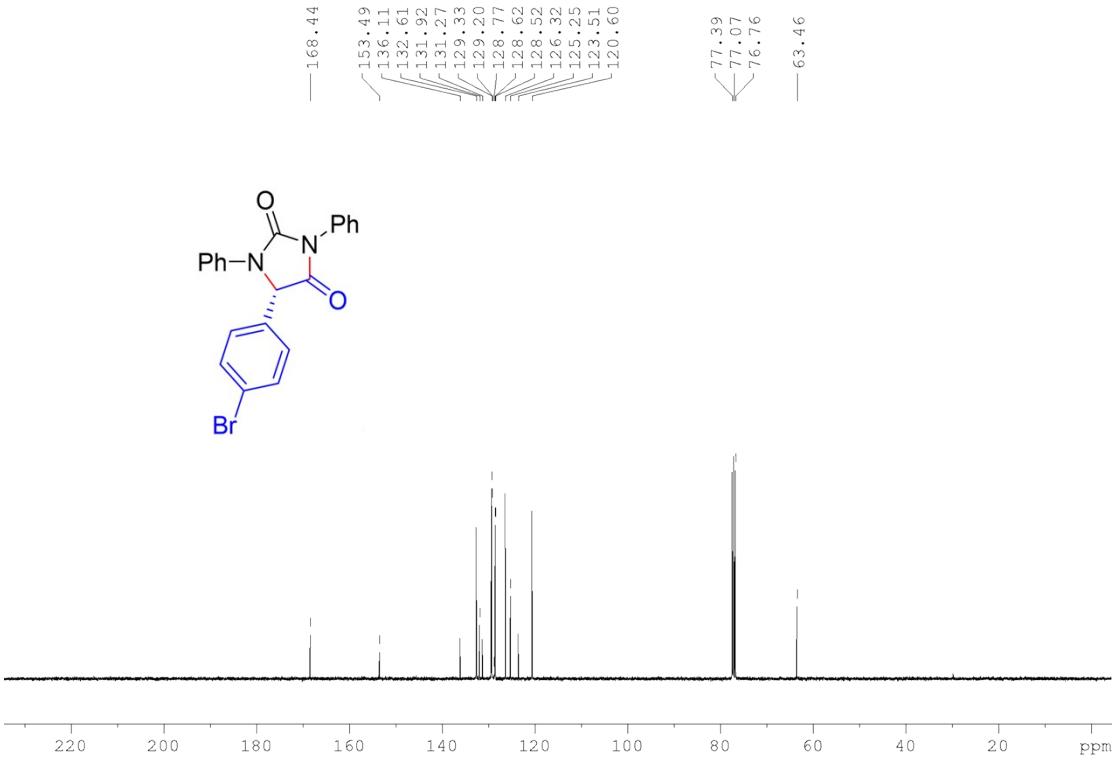
^{1}H NMR (400 MHz, $CDCl_3$) of **3be**



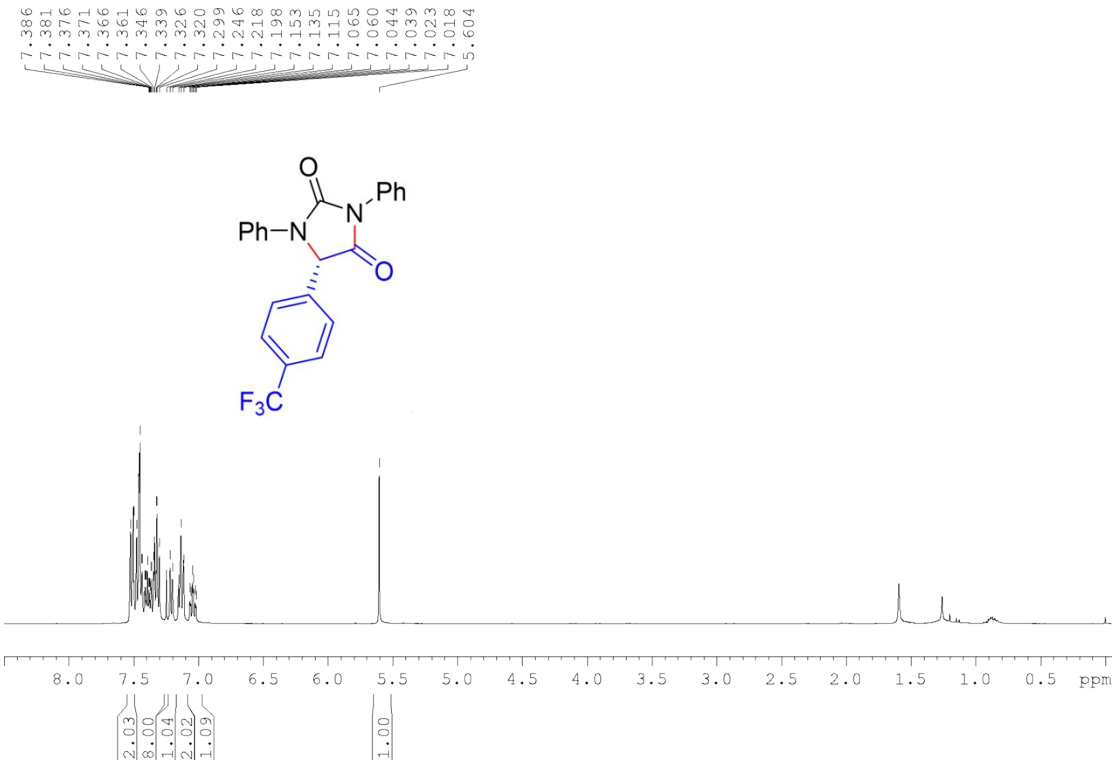
^{13}C NMR (100 MHz, $CDCl_3$) of **3be**



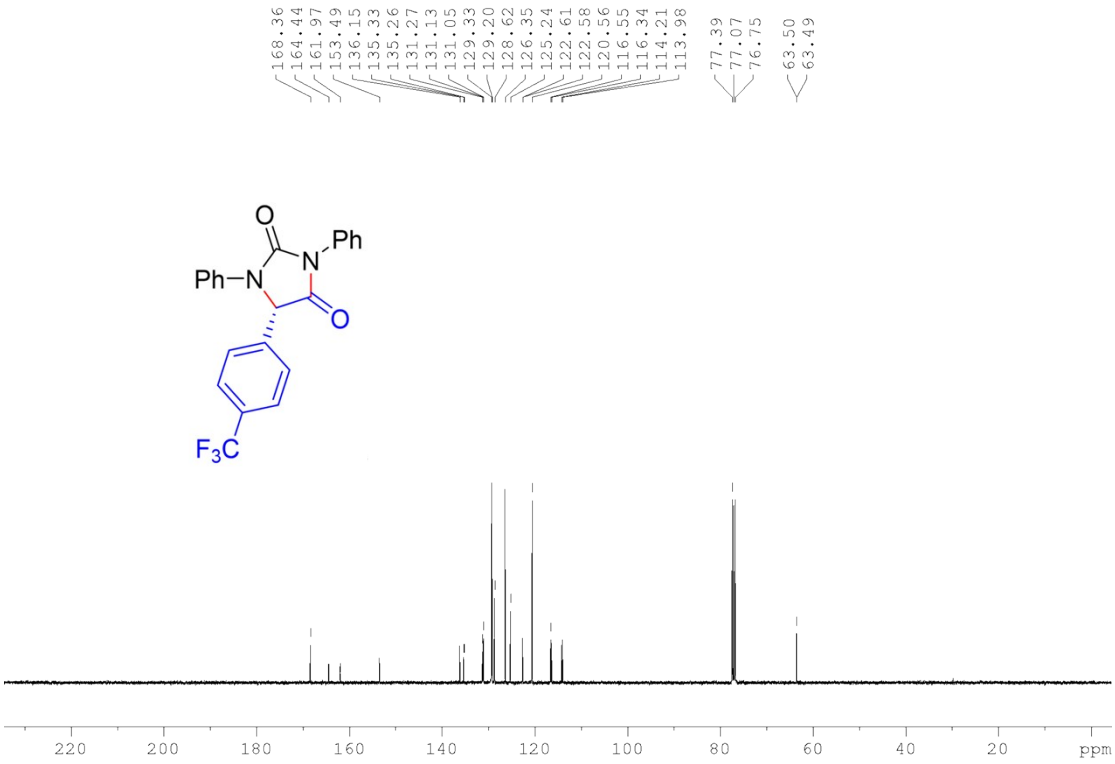
^{1}H NMR (400 MHz, $CDCl_3$) of **3bf**



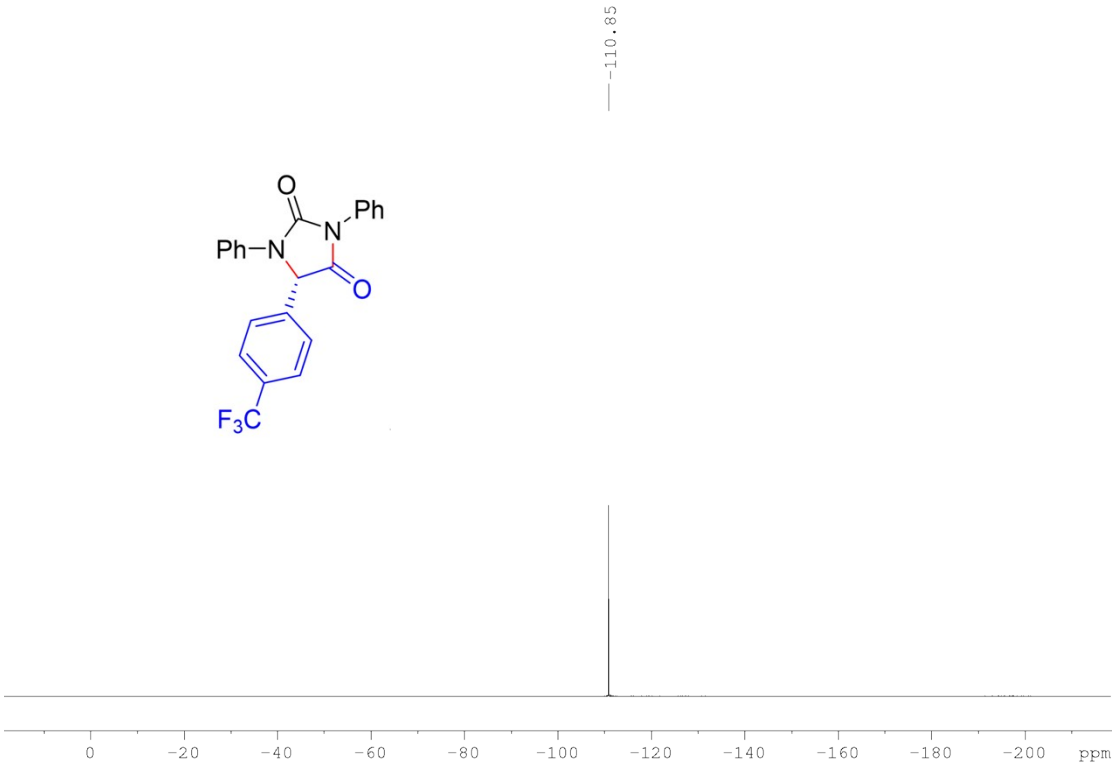
^{13}C NMR (100 MHz, $CDCl_3$) of **3bf**



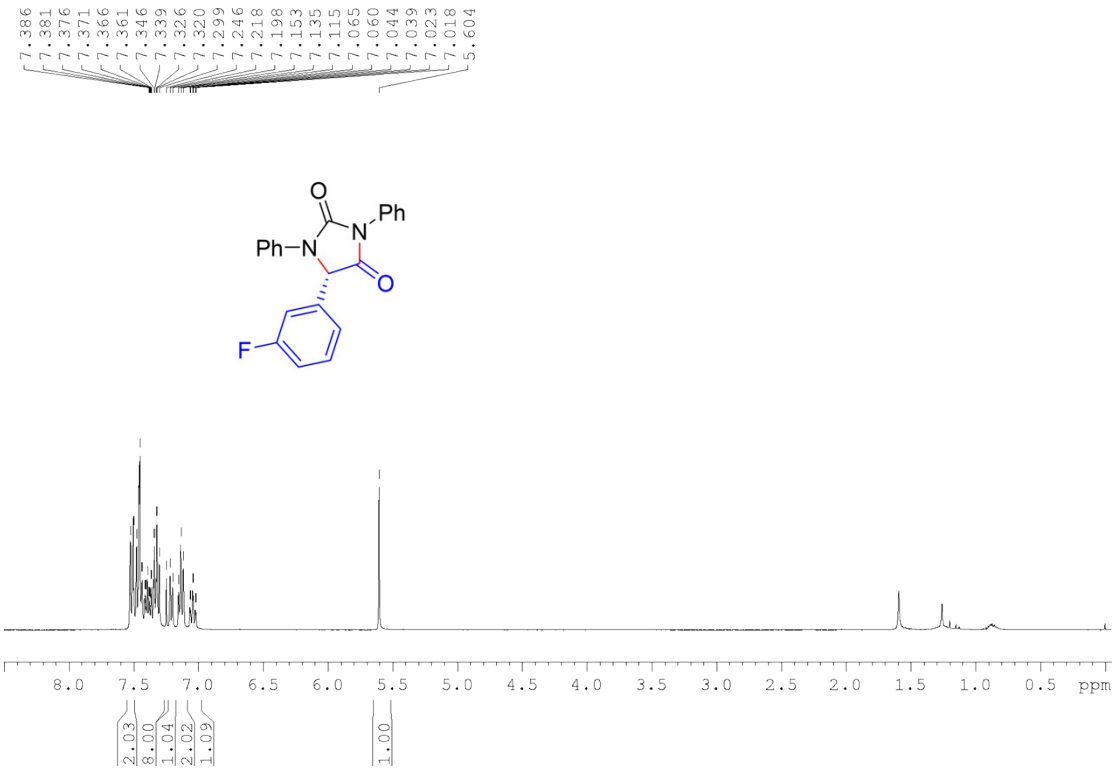
^{1}H NMR (400 MHz, $CDCl_3$) of **3bg**



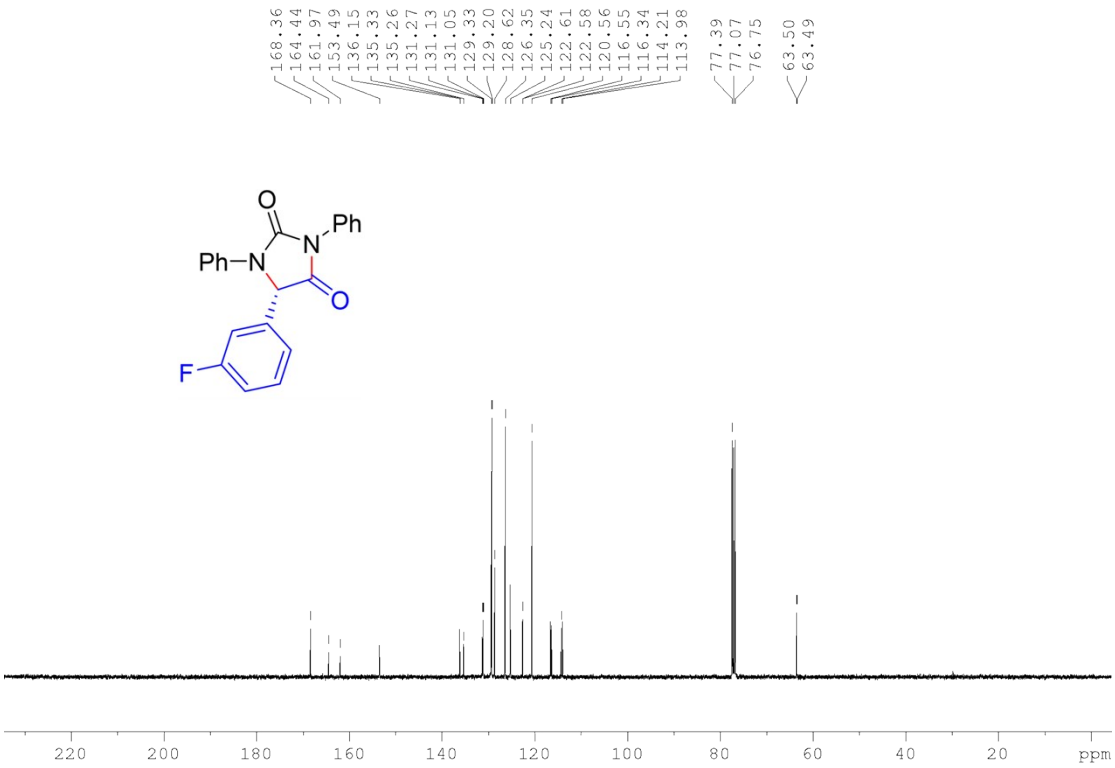
^{13}C NMR (100 MHz, $CDCl_3$) of **3bg**



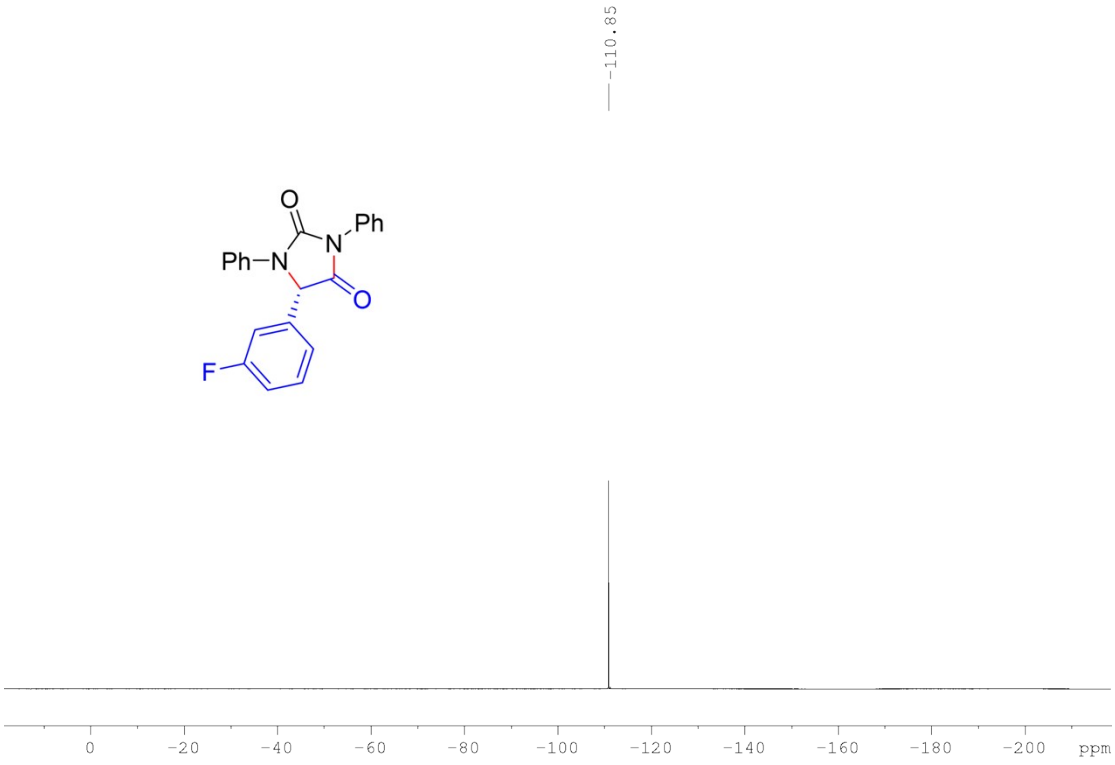
^{19}F NMR (376 MHz, $CDCl_3$) of **3bg**



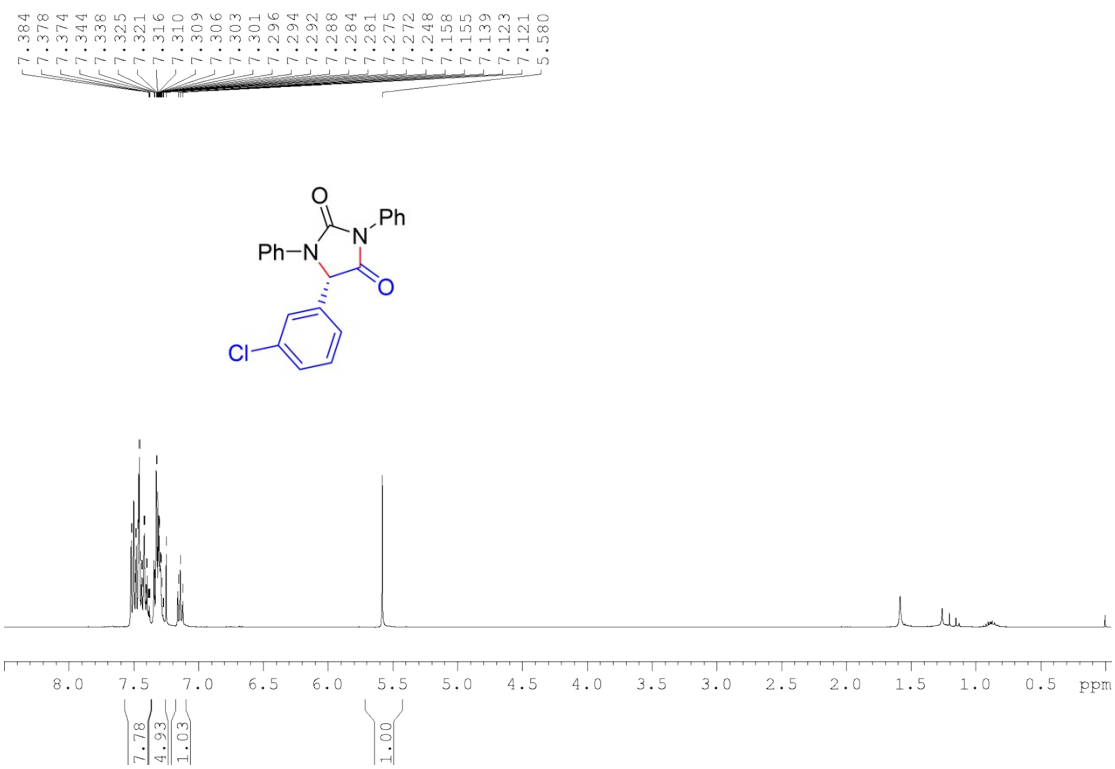
^{1}H NMR (400 MHz, $CDCl_3$) of **3bh**



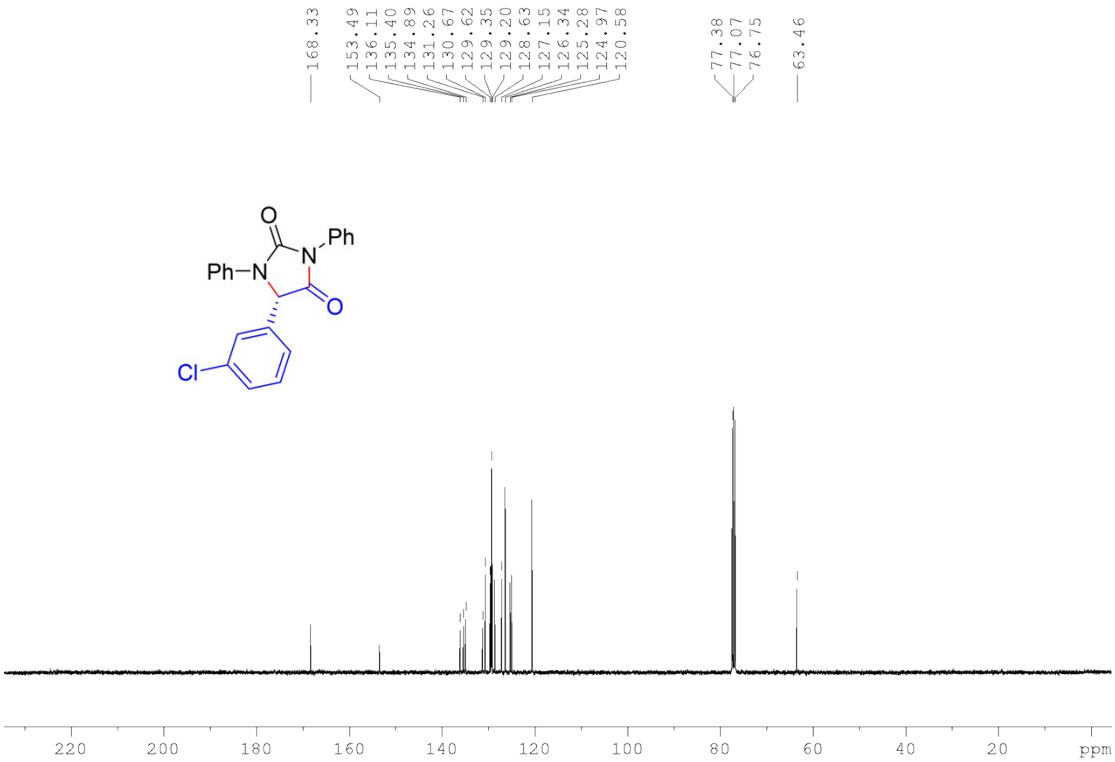
^{13}C NMR (100 MHz, $CDCl_3$) of **3bh**



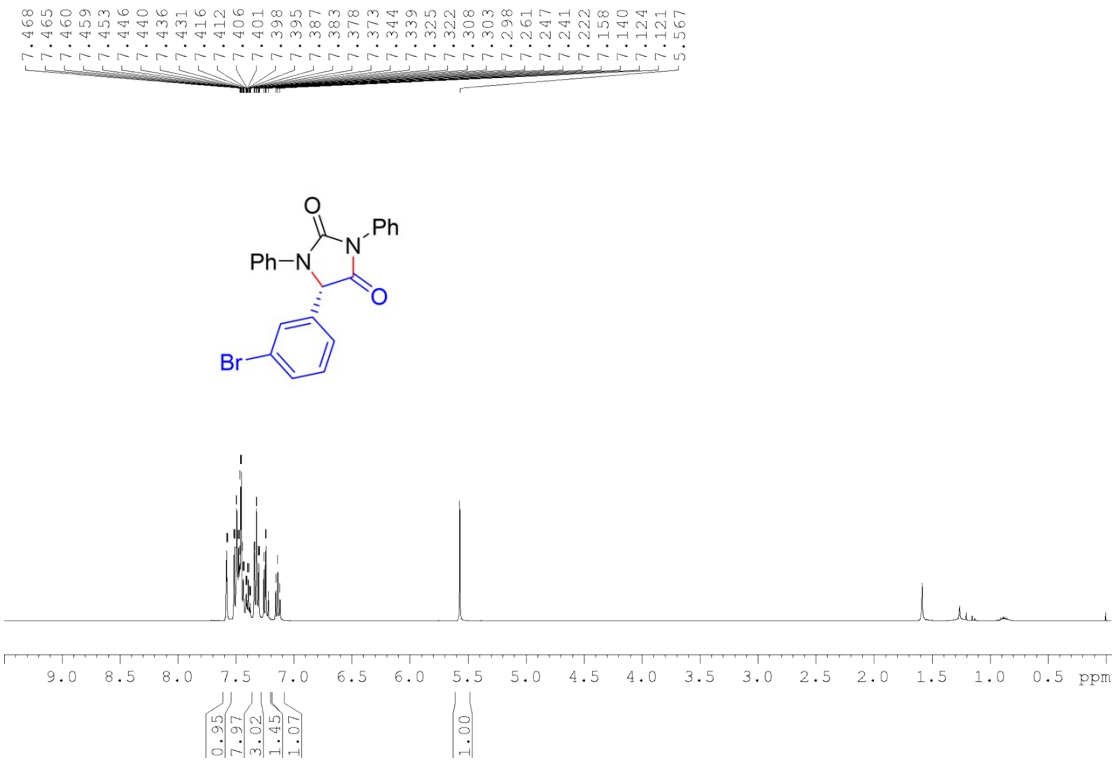
^{19}F NMR (376 MHz, $CDCl_3$) of **3bh**



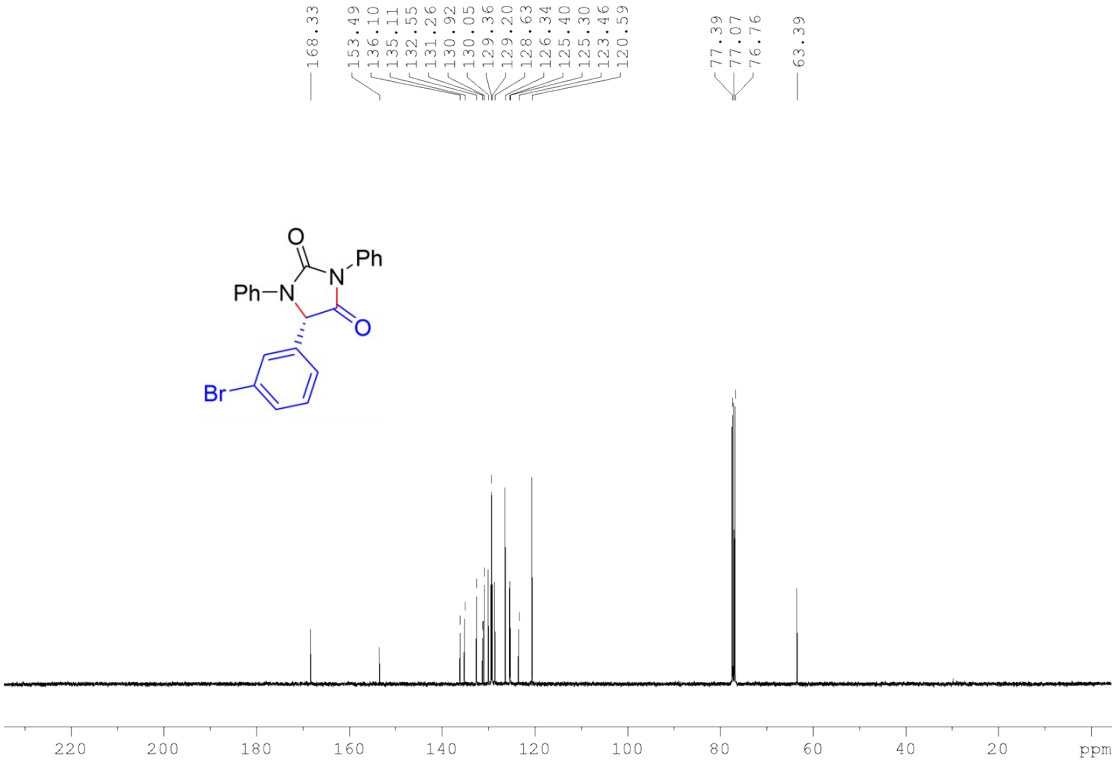
^{1}H NMR (400 MHz, $CDCl_3$) of **3bi**



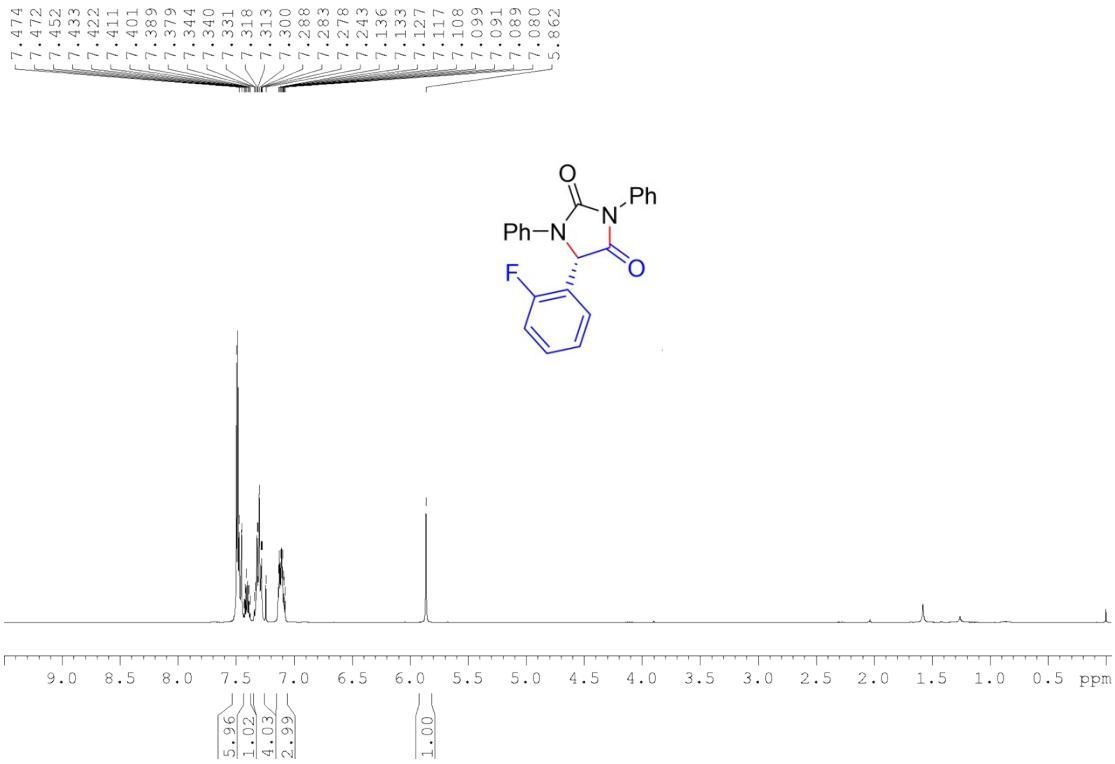
^{13}C NMR (100 MHz, $CDCl_3$) of **3bi**



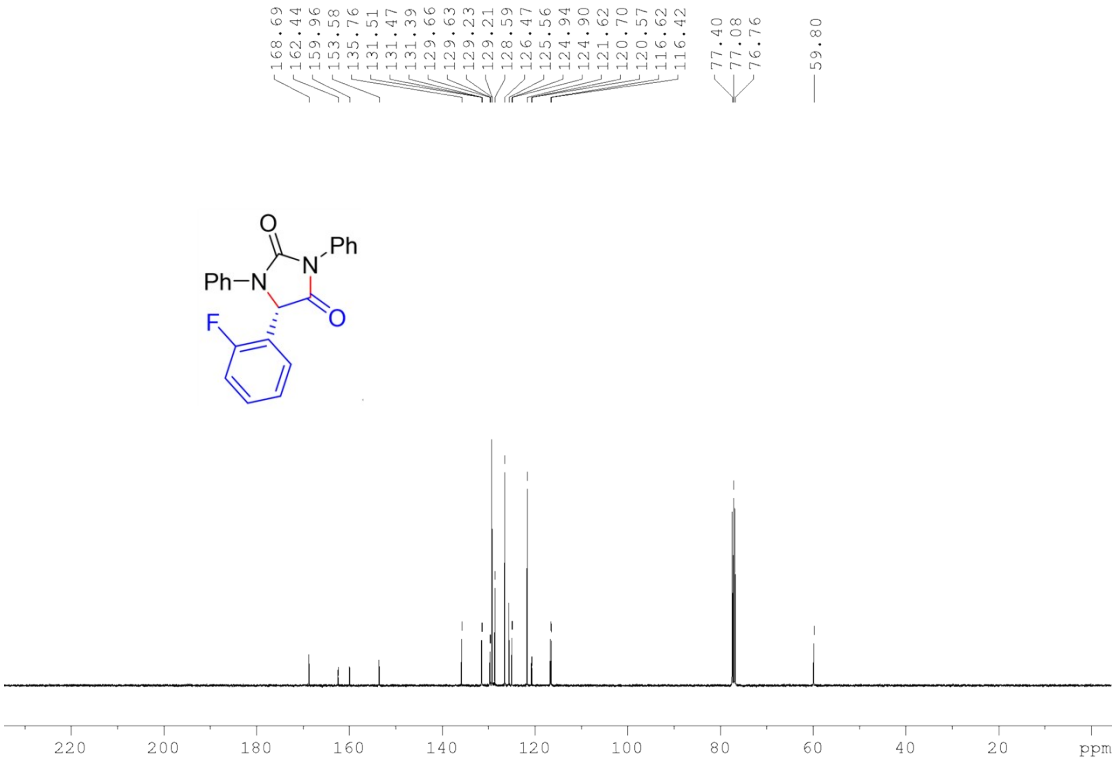
^{1}H NMR (400 MHz, $CDCl_3$) of **3bj**



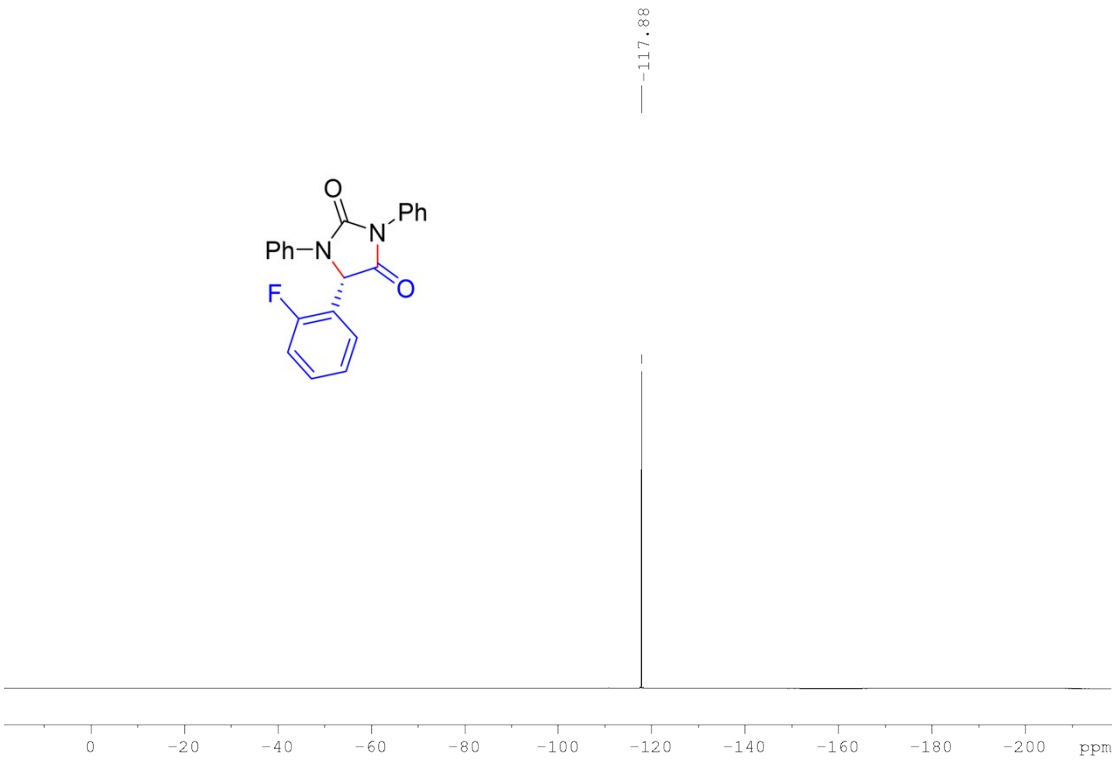
^{13}C NMR (100 MHz, $CDCl_3$) of **3bj**



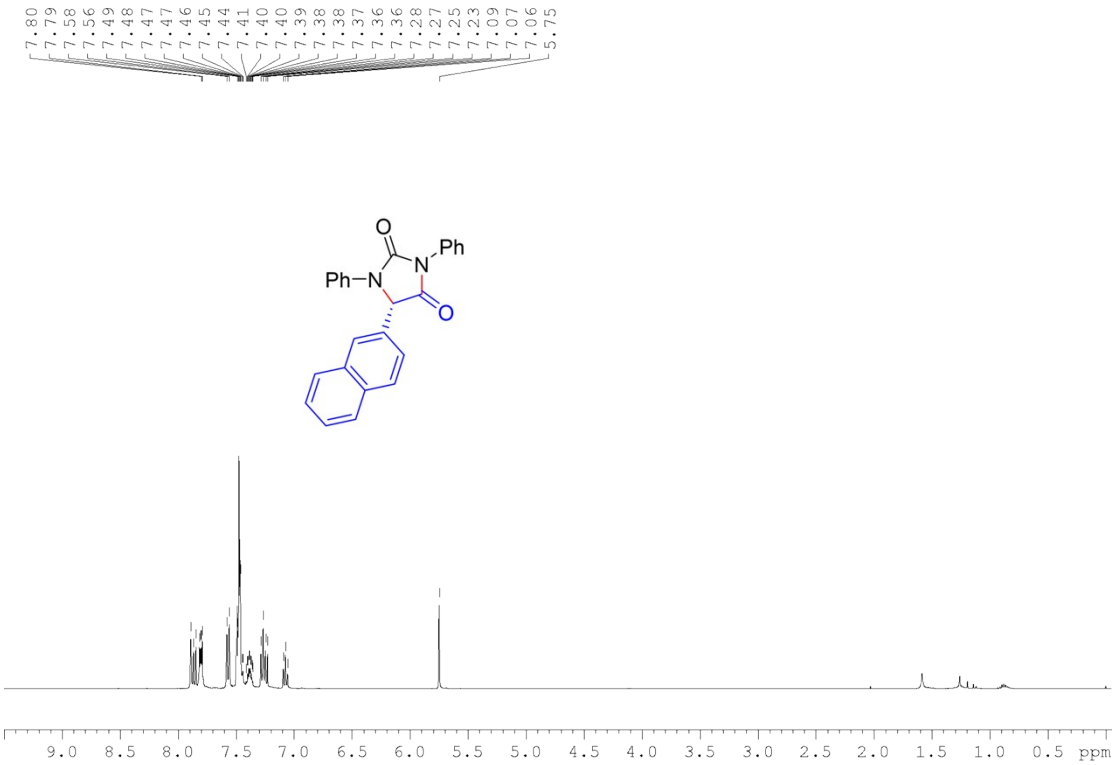
^{1}H NMR (400 MHz, $CDCl_3$) of **3bk**



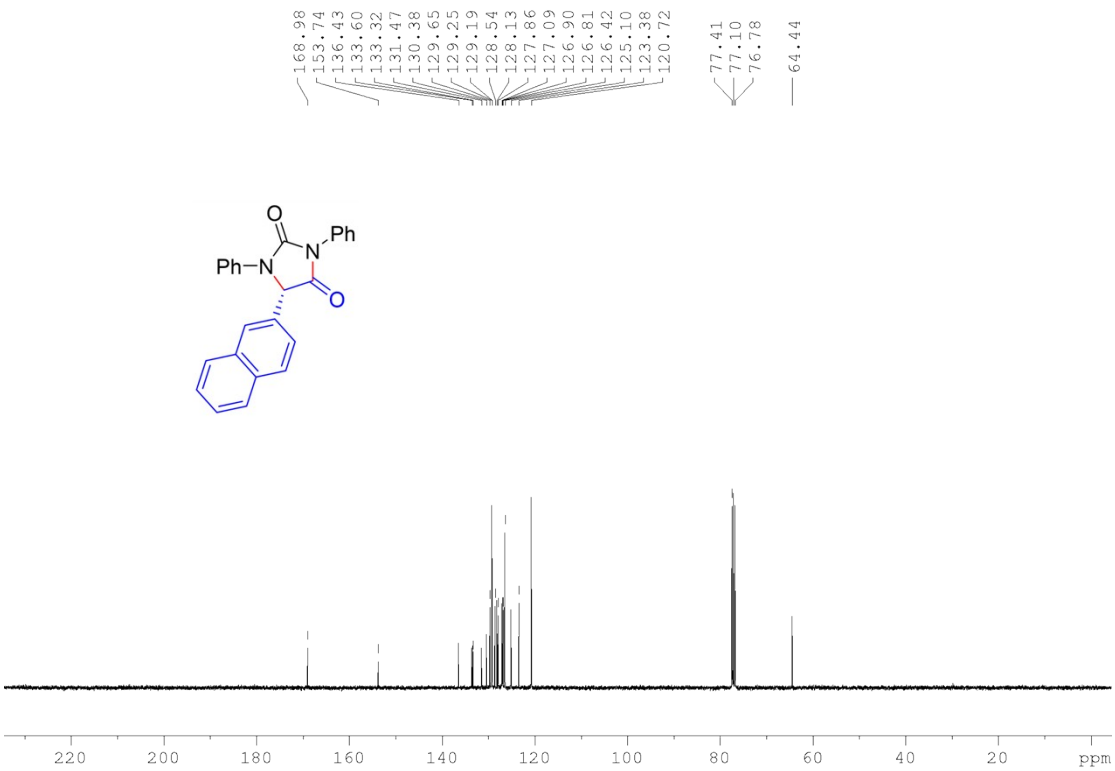
^{13}C NMR (100 MHz, $CDCl_3$) of **3bk**



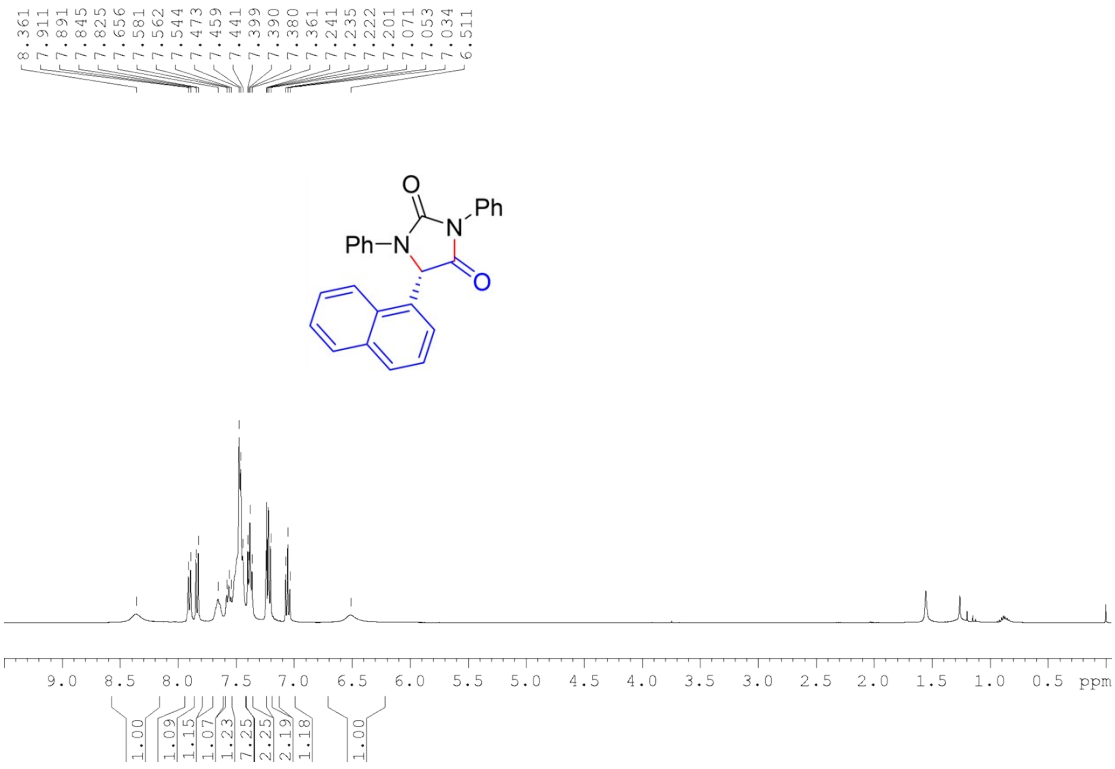
^{19}F NMR (376 MHz, $CDCl_3$) of **3bk**



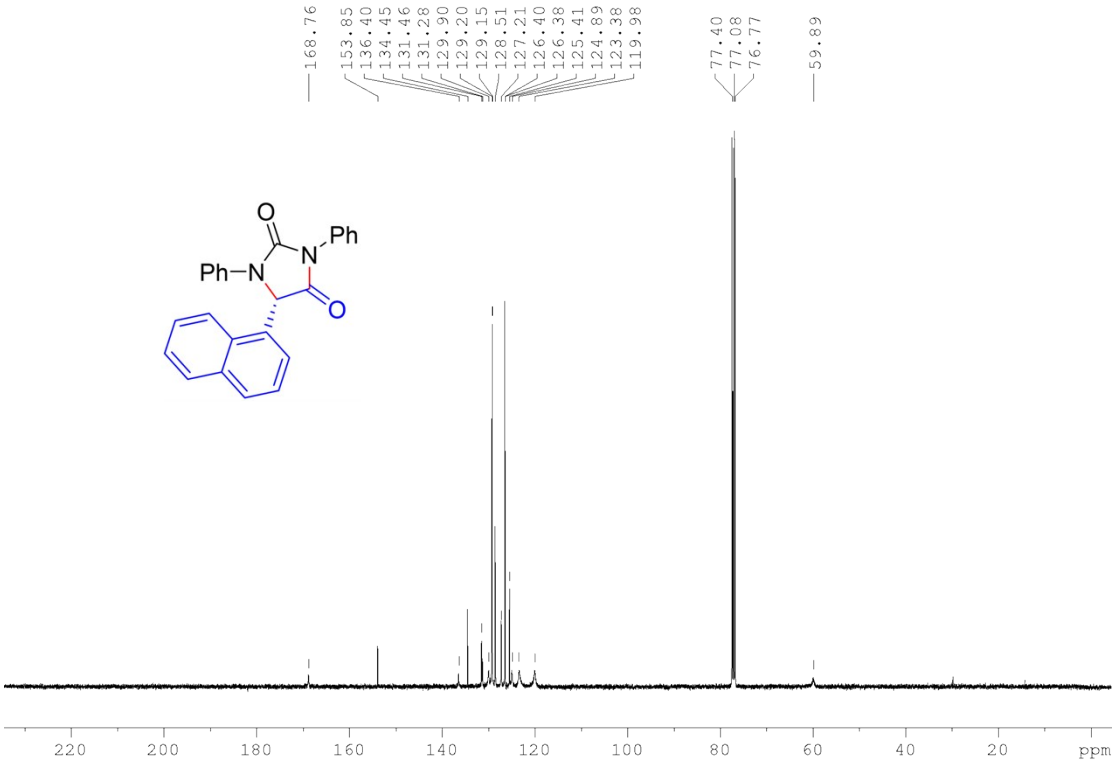
^{1}H NMR (400 MHz, $CDCl_3$) of **3bl**



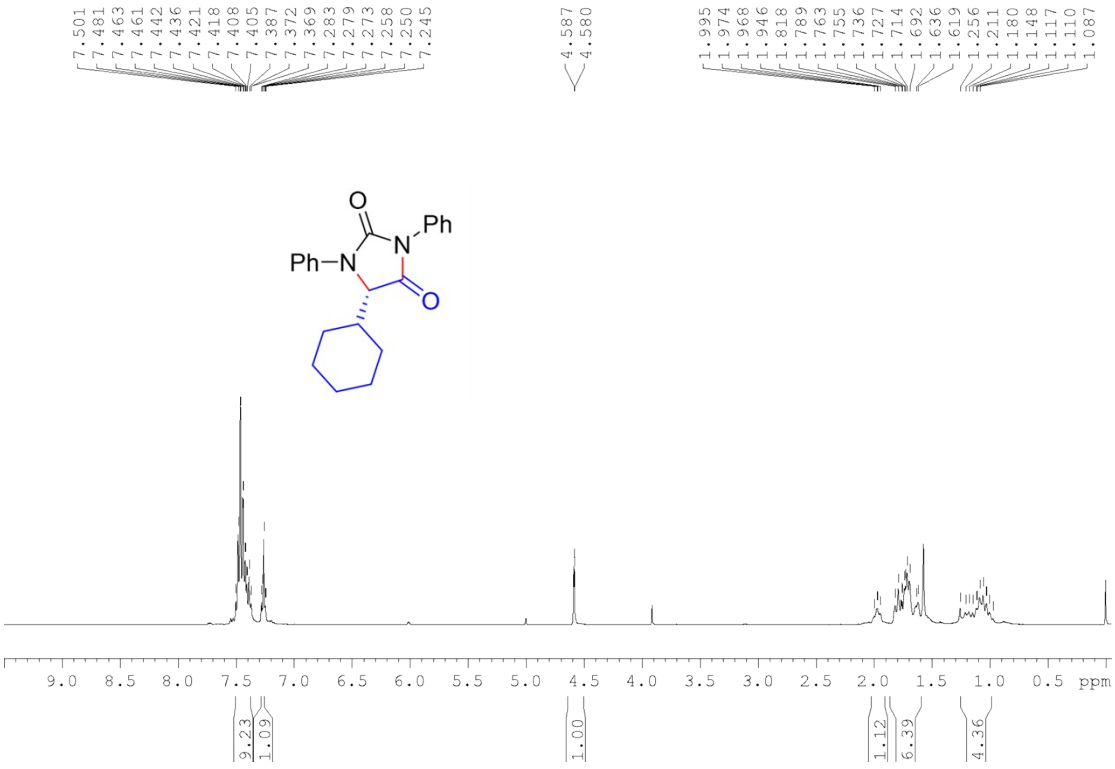
^{13}C NMR (100 MHz, $CDCl_3$) of **3bl**



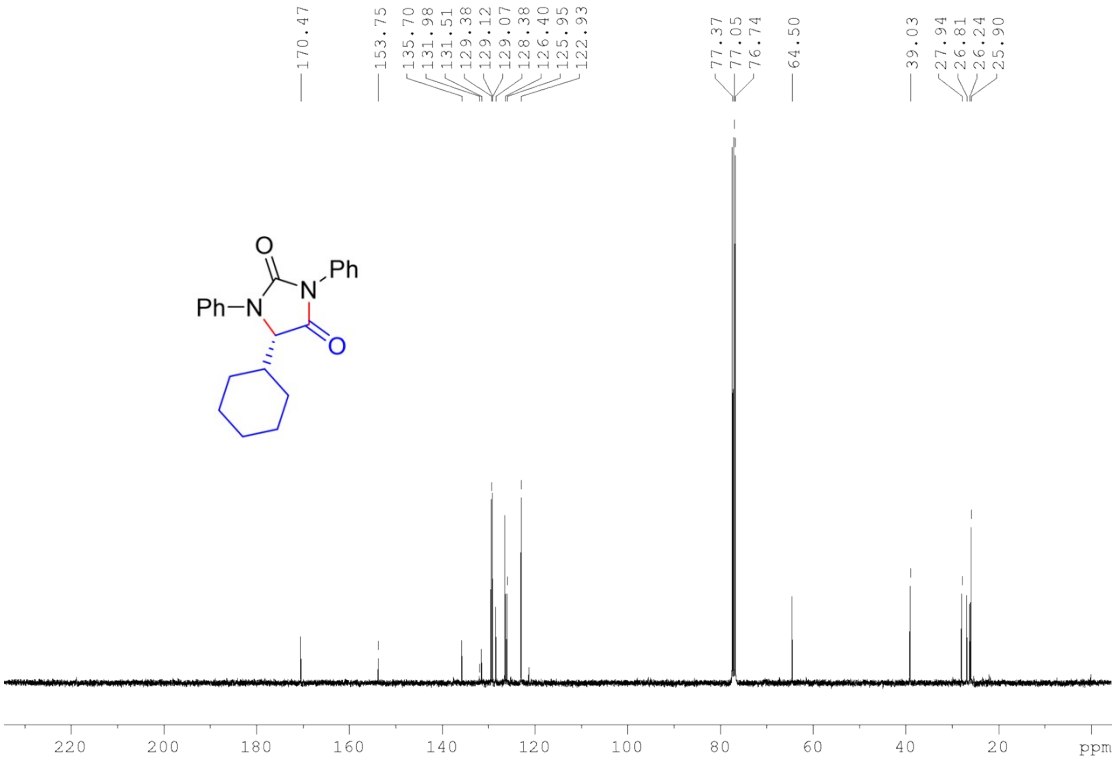
^{1}H NMR (400 MHz, $CDCl_3$) of **3bm**



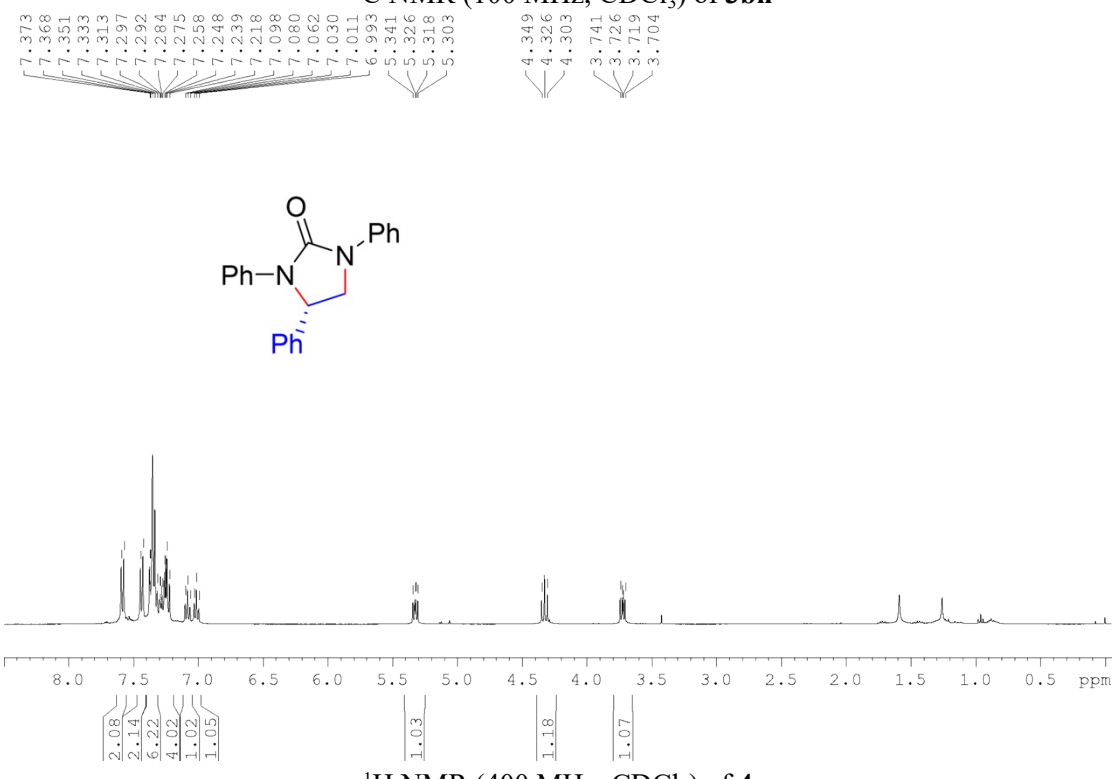
^{13}C NMR (100 MHz, $CDCl_3$) of **3bm**



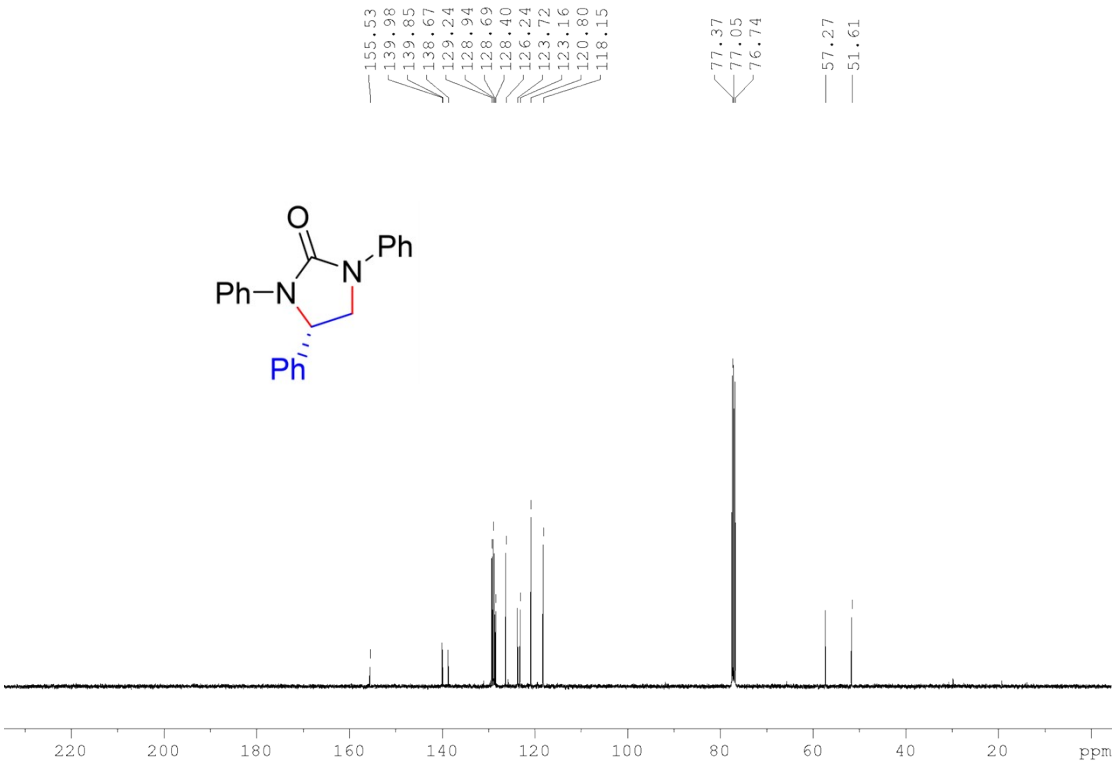
^{1}H NMR (400 MHz, $CDCl_3$) of **3bn**



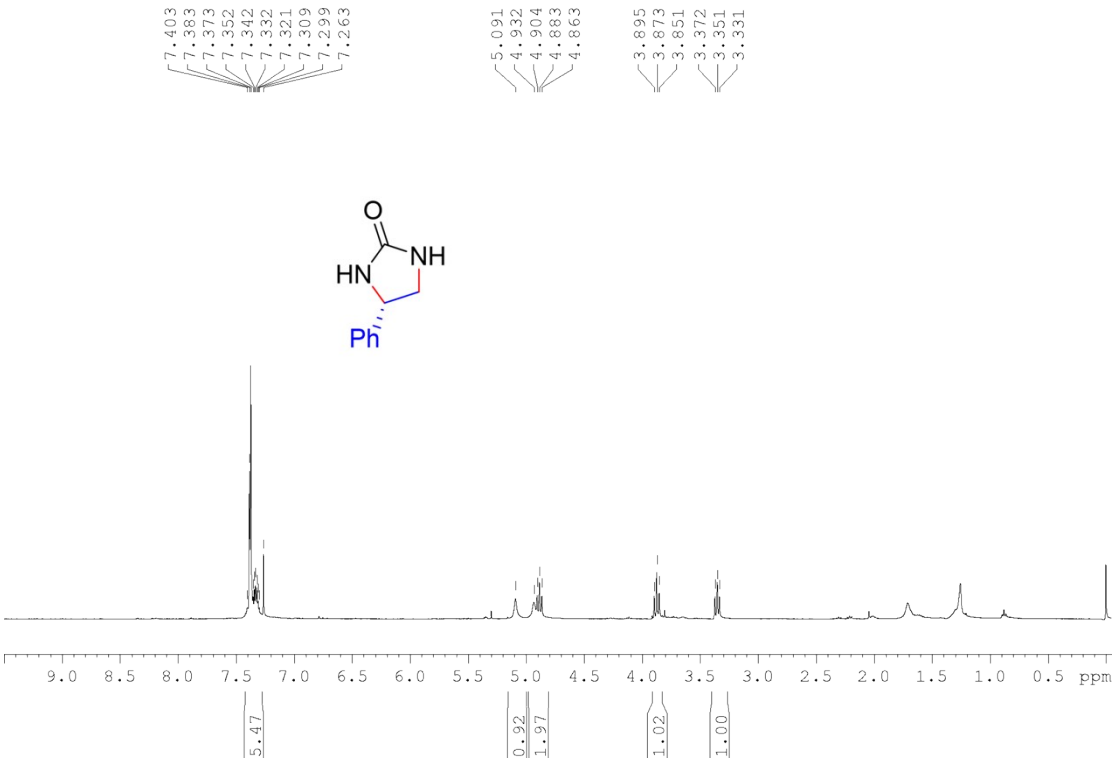
^{13}C NMR (100 MHz, $CDCl_3$) of **3bn**



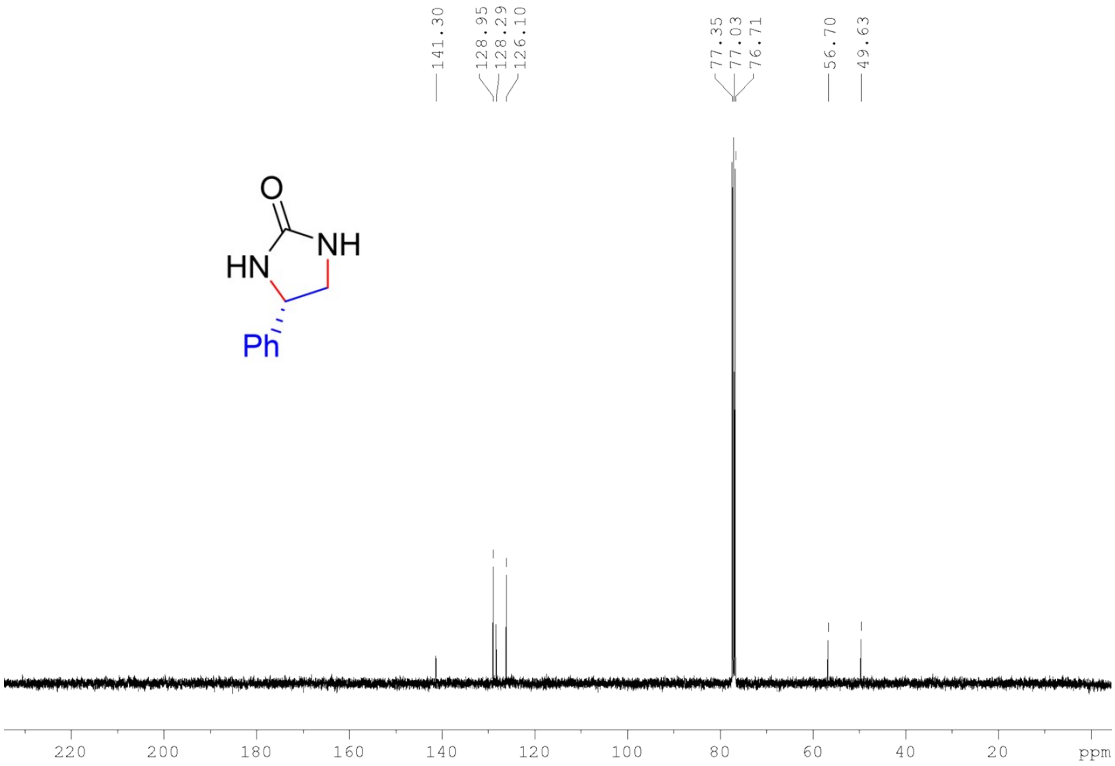
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



^{13}C NMR (100 MHz, $CDCl_3$) of **4**



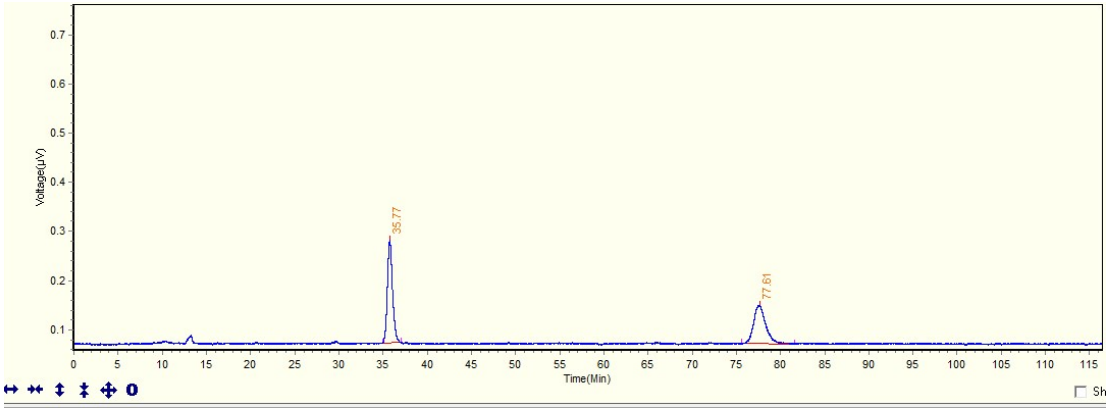
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



^{13}C NMR (100 MHz, $CDCl_3$) of **6**

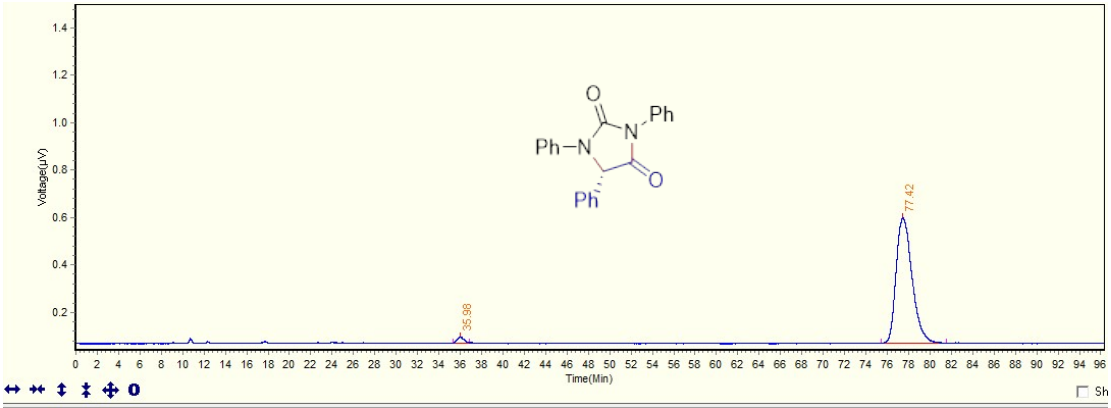
VIII. Copies of HPLC Spectra

HPLC spectra of **3ba**



Integration Result | Calculation Result | TimeTable

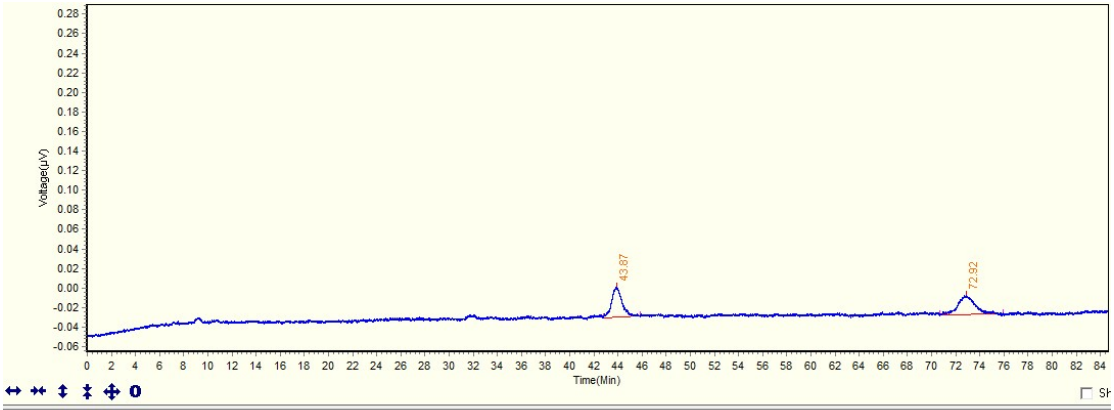
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	35.77	4239890	105012	53.32%	2.104	BB
2	77.61	3711527	39396	46.68%	5.988	BB
Total		7,951,417	144,408	100.00%		



Integration Result | Calculation Result | TimeTable

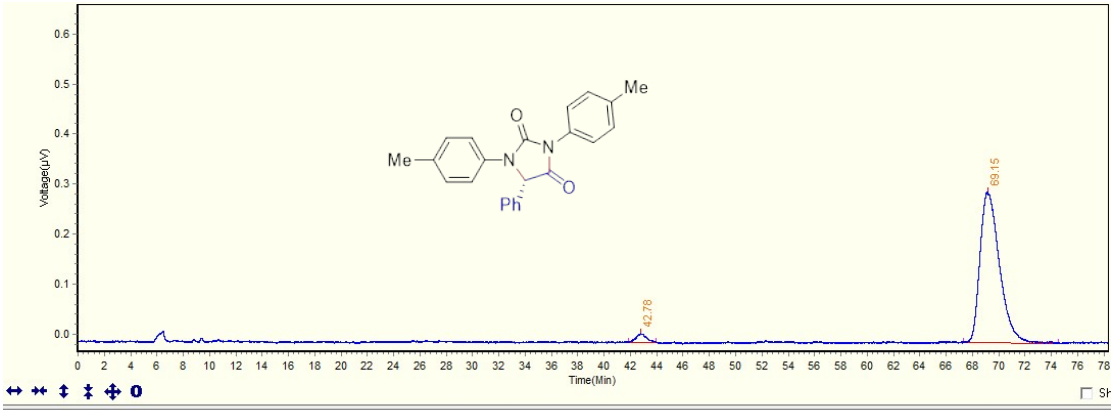
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	35.98	538024	12959	1.92%	1.497	BB
2	77.42	27417723	264349	98.08%	6.11	BB
Total		27,955,747	277,308	100.00%		

HPLC spectra of **3ea**



Integration Result | Calculation Result | TimeTable

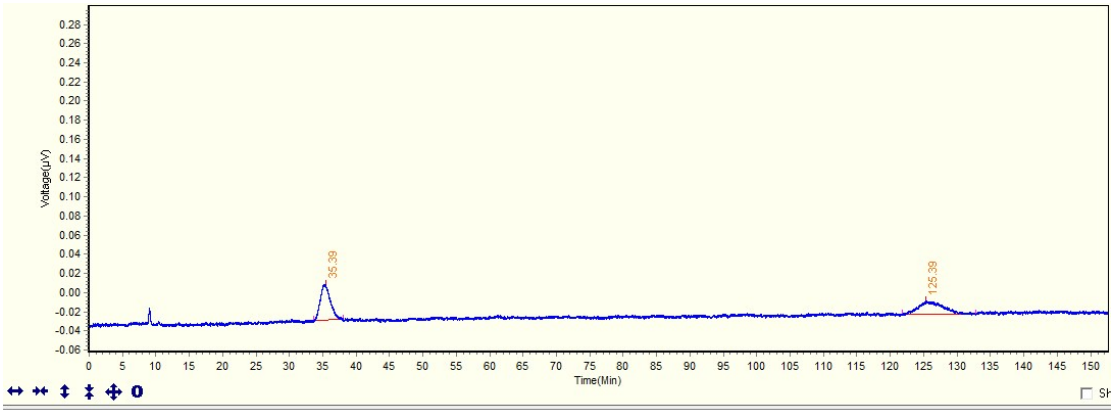
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	43.87	887224	15000	49.64%	3.047	BB
2	72.92	899991	9455	50.36%	5.232	BB
Total		1,787,215	24,455	100.00%		



Integration Result | Calculation Result | TimeTable

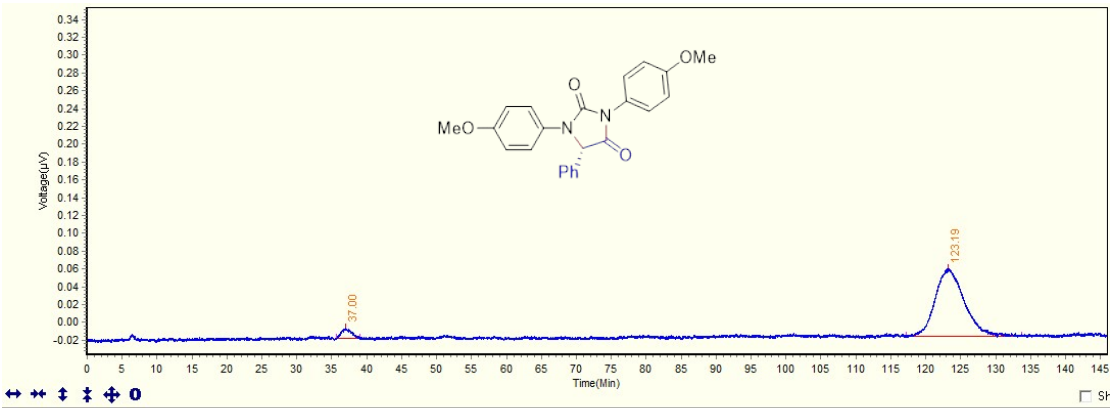
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	42.78	496510	8854	3.11%	2.085	BB
2	69.15	15443610	150774	96.89%	7.253	BB
Total		15,940,120	159,628	100.00%		

HPLC spectra of **3fa**



Integration Result | Calculation Result | TimeTable

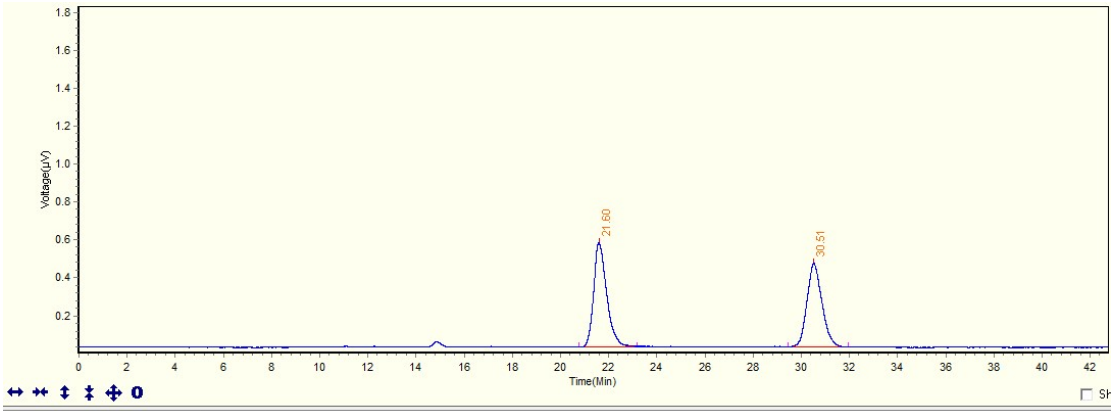
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	35.39	1967807	18807	51.65%	4.353	BB
2	125.39	1842391	7100	48.35%	10.989	BB
Total		3,810,198	25,907	100.00%		



Integration Result | Calculation Result | TimeTable

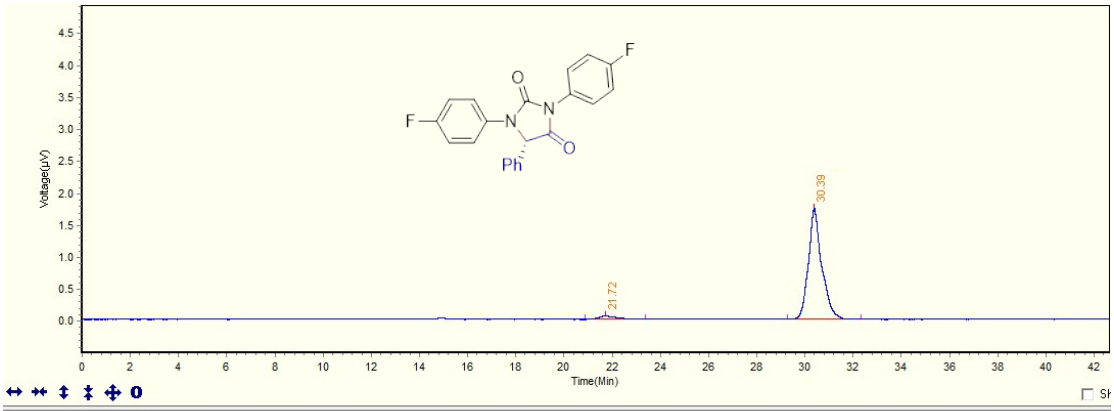
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	37.00	596958	5939	5.19%	3.309	BB
2	123.19	10897784	37750	94.81%	16.549	BB
Total		11,494,742	43,689	100.00%		

HPLC spectra of **3ga**



Integration Result | Calculation Result | TimeTable

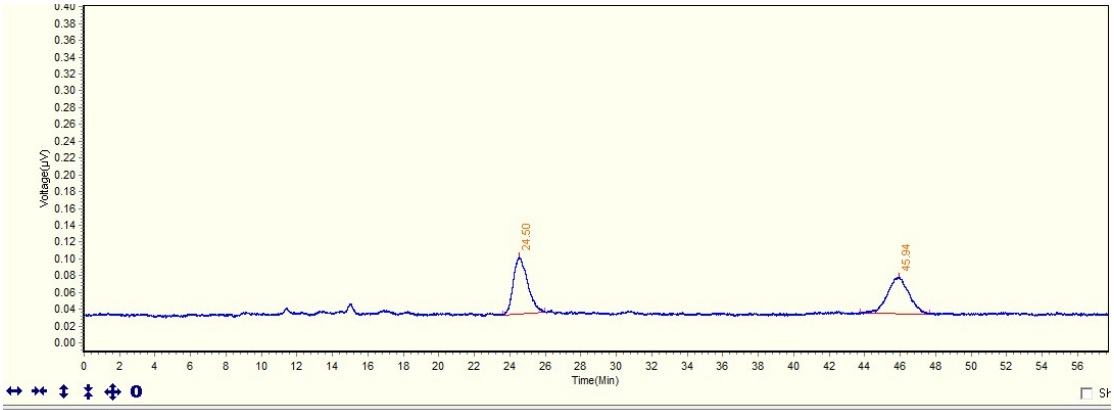
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	21.60	10251663	275847	51.93%	2.385	BB
2	30.51	9489614	220592	48.07%	2.508	BB
Total		19,741,277	496,439	100.00%		



Integration Result | Calculation Result | TimeTable

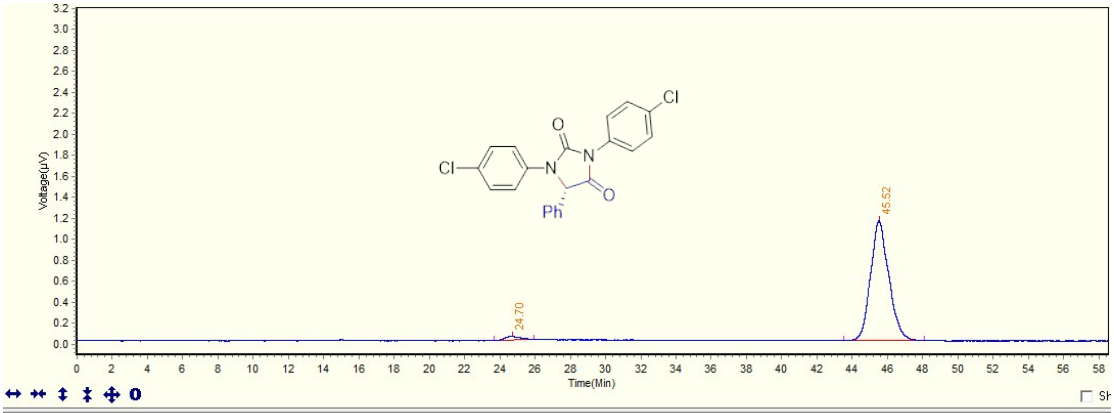
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	21.72	1239018	24268	3.60%	2.51	BB
2	30.39	33155529	867230	96.40%	3.056	BB
Total		34,394,547	891,498	100.00%		

HPLC spectra of **3ha**



Integration Result | Calculation Result | TimeTable

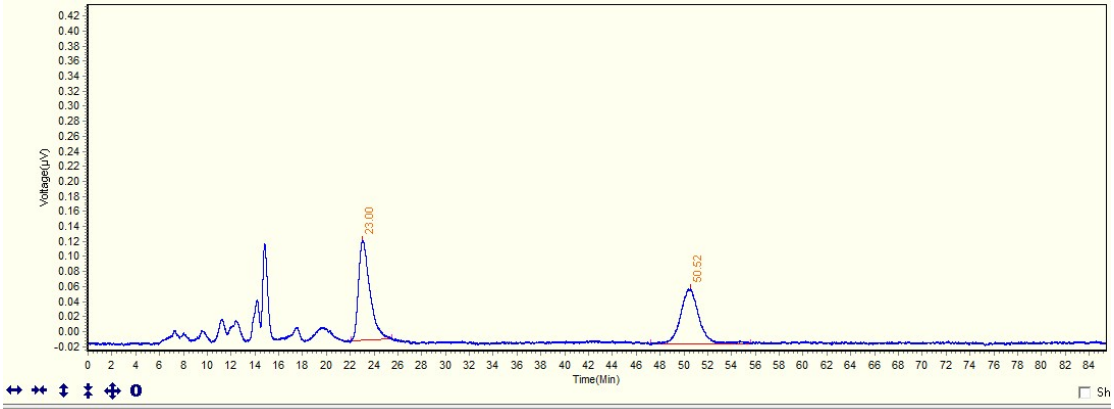
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	24.50	1889833	34039	50.98%	2.389	BB
2	45.94	1817421	21713	49.02%	3.883	BB
Total		3,707,254	55,752	100.00%		



Integration Result | Calculation Result | TimeTable

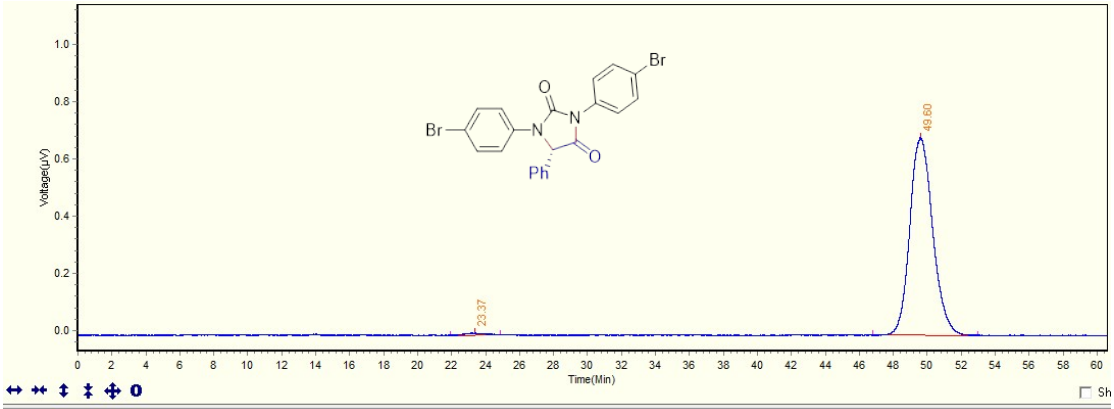
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	24.70	1053234	16989	2.49%	2.278	BB
2	45.52	41170486	571119	97.51%	4.613	BB
Total		42,223,720	588,108	100.00%		

HPLC spectra of **3ia**



Integration Result | Calculation Result | TimeTable

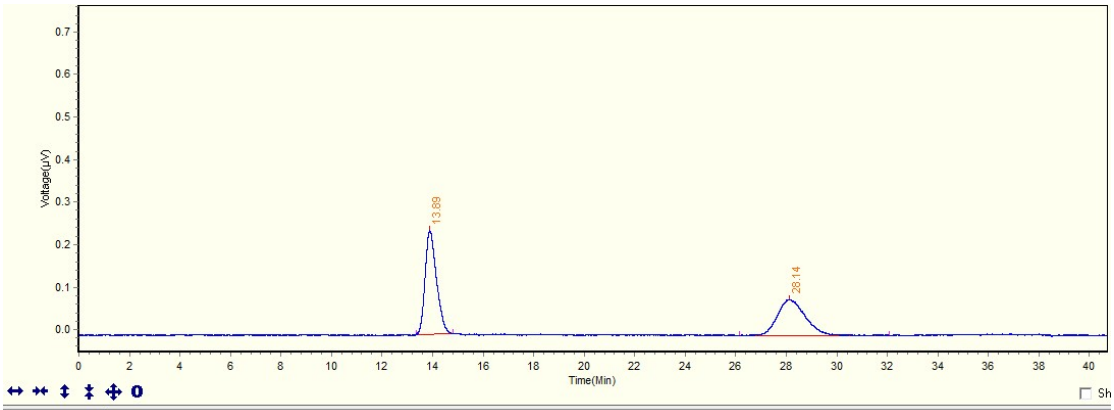
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.00	4383004	66546	53.20%	3.413	BB
2	50.52	3855442	36231	46.80%	8.385	BB
Total		8,238,446	102,777	100.00%		



Integration Result | Calculation Result | TimeTable

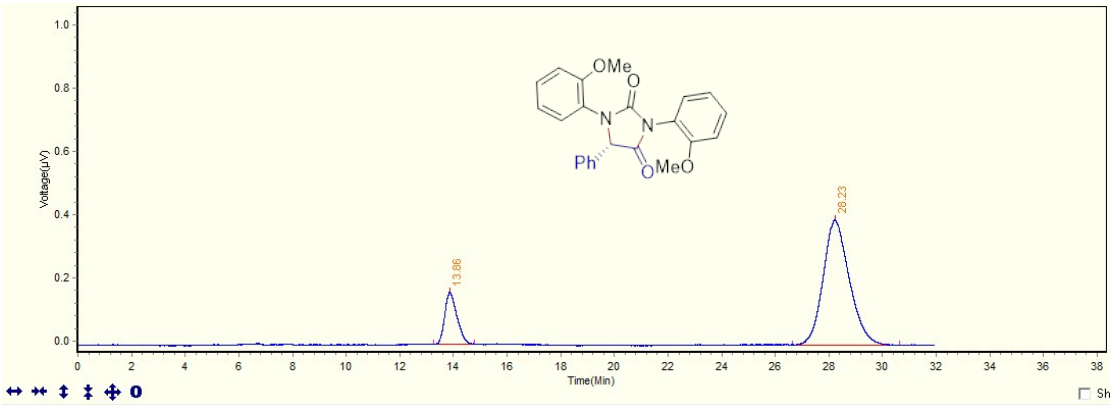
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.37	293559	3831	0.90%	2.955	BB
2	49.60	32263951	345512	99.10%	6.198	BB
Total		32,557,510	349,343	100.00%		

HPLC spectra of **3ja**



Integration Result | Calculation Result | TimeTable

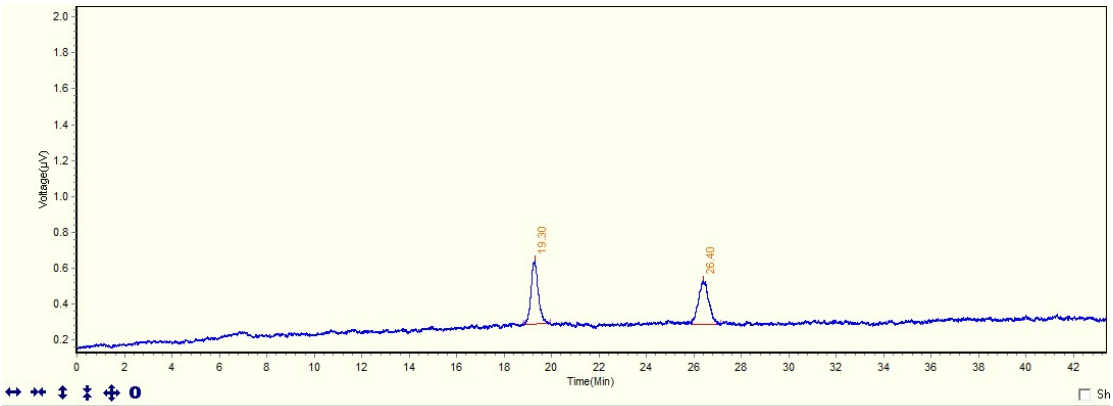
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	13.89	3798177	121464	52.62%	1.458	BB
2	28.14	3420007	42595	47.38%	5.91	BB
Total		7,218,184	164,059	100.00%		



Integration Result | Calculation Result | TimeTable

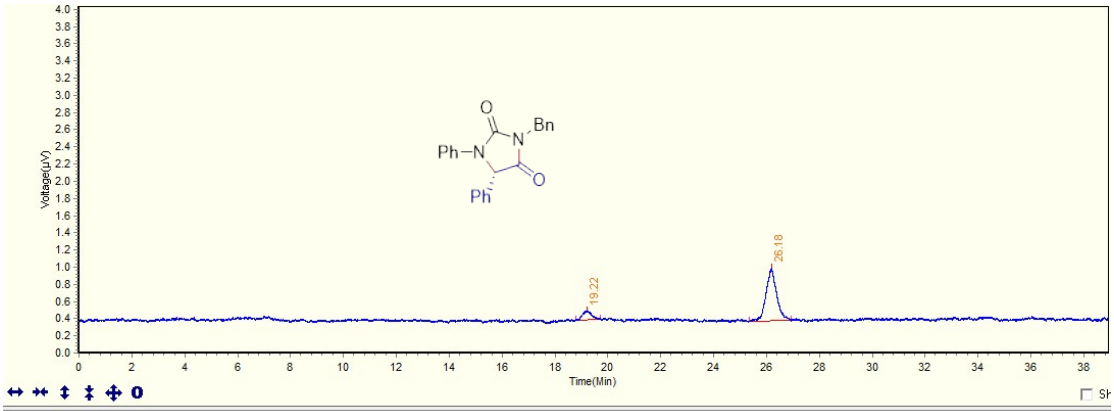
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	13.86	2564242	81718	16.06%	1.515	BB
2	28.23	13401586	197806	83.94%	3.968	BB
Total		15,965,828	279,524	100.00%		

HPLC spectra of **3ka**



Integration Result | Calculation Result | TimeTable

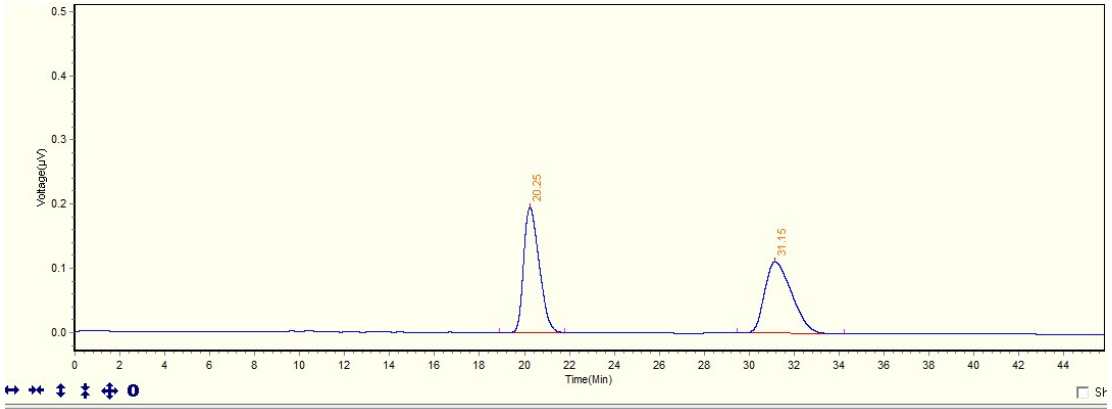
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	19.30	3739153	179544	50.00%	1.126	BB
2	26.40	3739817	121828	50.00%	1.22	BB
Total		7,478,970	301,372	100.00%		



Integration Result | Calculation Result | TimeTable

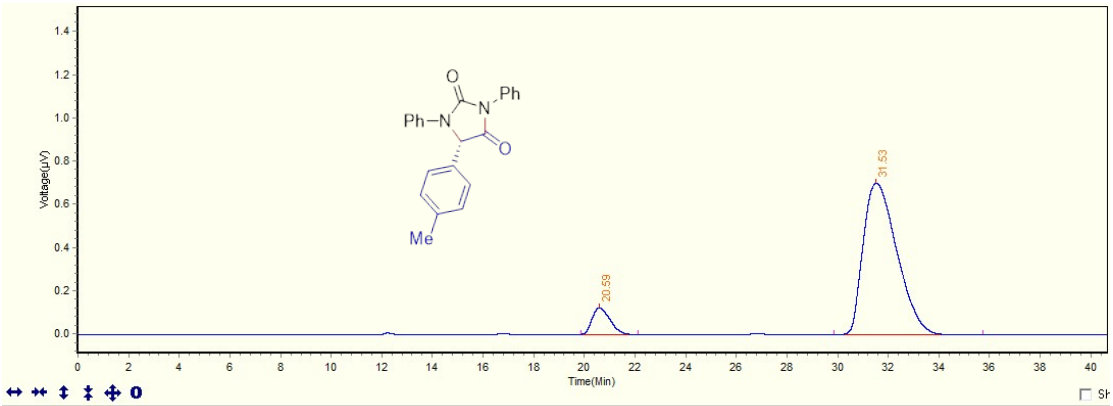
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	19.22	1141047	49795	11.92%	0.923	BB
2	26.18	8434944	308821	88.08%	1.598	BB
Total		9,575,991	358,616	100.00%		

HPLC spectra of **3bb**



Integration Result | Calculation Result | TimeTable

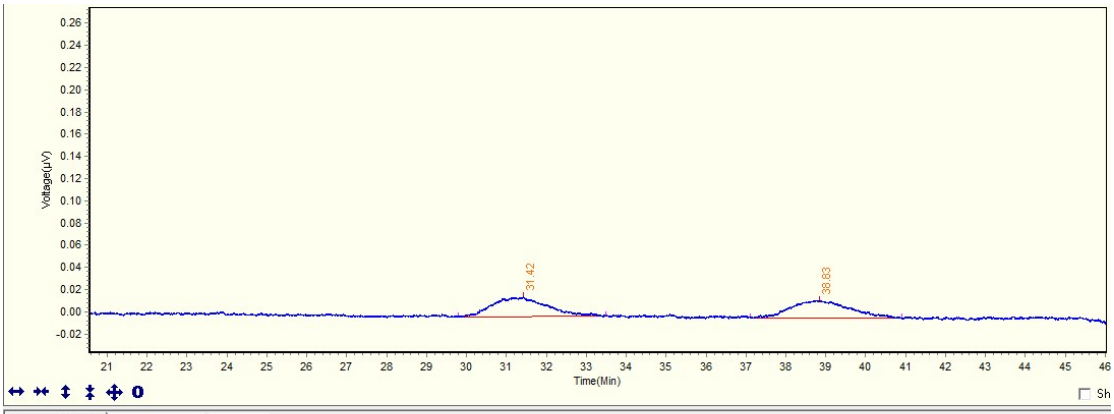
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	20.25	4654078	97257	49.91%	2.904	BB
2	31.15	4670555	55924	50.09%	4.768	BB
Total		9,324,633	153,181	100.00%		



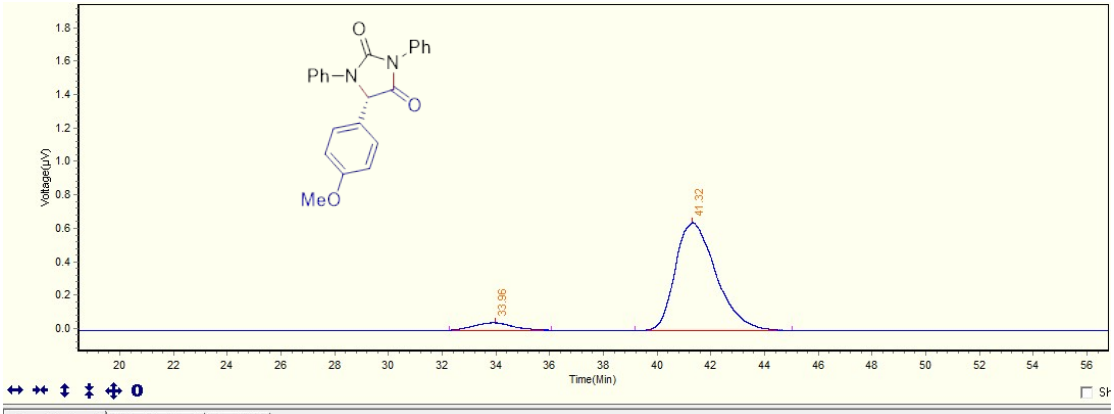
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	20.59	2982754	61566	8.41%	2.272	BB
2	31.53	32469709	350690	91.59%	5.897	BB
Total		35,452,463	412,256	100.00%		

HPLC spectra of **3bc**

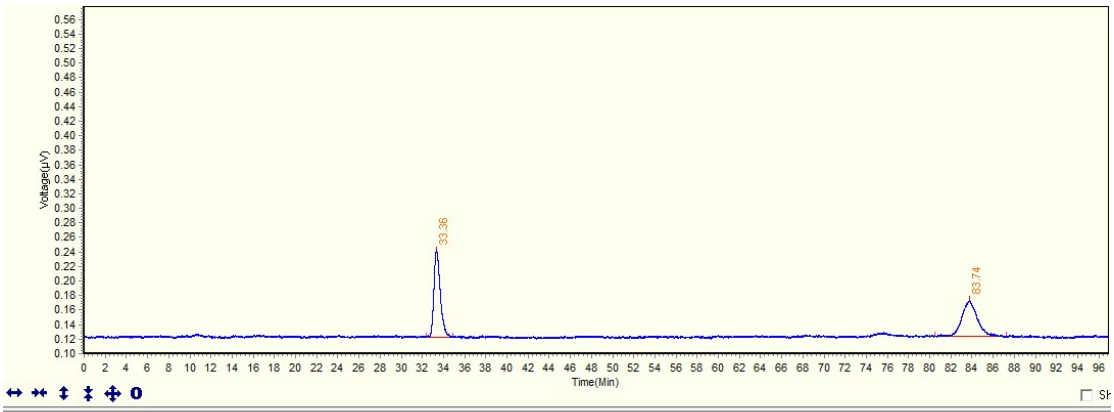


Integration Result	Calculation Result	TimeTable				
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	31.42	807743	8710	50.70%	3.693	BB
2	38.83	785337	7825	49.30%	3.783	BB
Total		1,593,080	16,535	100.00%		

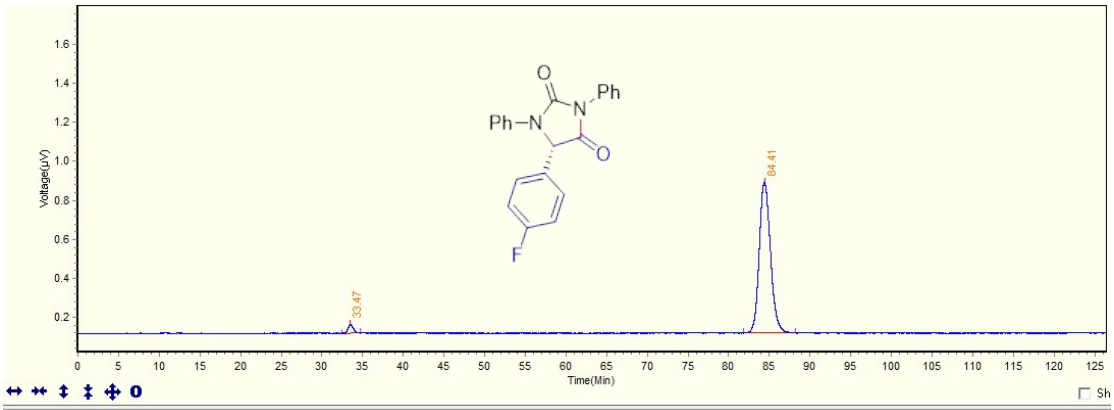


Integration Result	Calculation Result	TimeTable				
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	33.96	2268656	22675	6.26%	3.785	BB
2	41.32	33994372	323000	93.74%	5.858	BB
Total		36,263,028	345,675	100.00%		

HPLC spectra of **3bd**



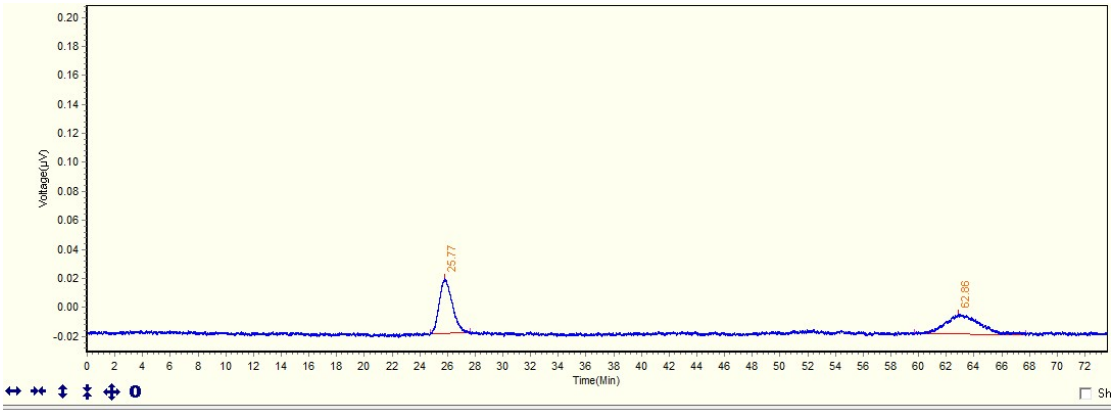
Integration Result	Calculation Result	TimeTable				
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	33.36	2481544	59245	50.08%	2.479	BB
2	83.74	2473830	24920	49.92%	6.762	BB
Total		4,955,374	84,165	100.00%		



Integration Result | Calculation Result | TimeTable

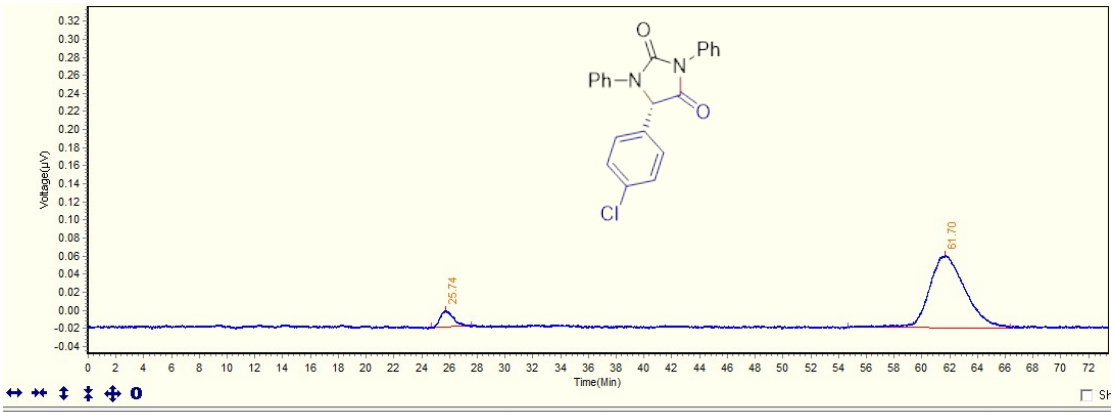
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	33.47	1002349	22185	2.63%	2.245	BB
2	84.41	37072879	385801	97.37%	6.369	BB
Total		38,075,228	407,986	100.00%		

HPLC spectra of **3be**



Integration Result | Calculation Result | TimeTable

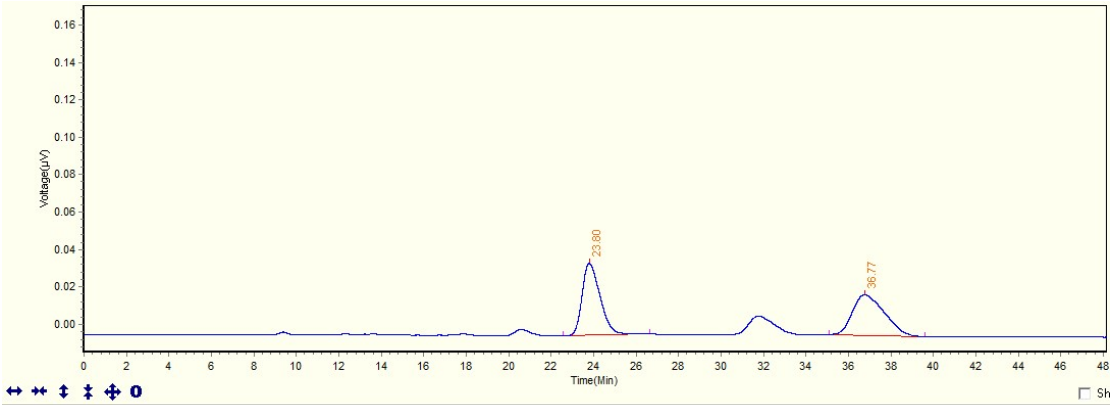
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	25.77	1223979	18944	50.65%	2.898	BB
2	62.86	1192334	6896	49.35%	8.053	BB
Total		2,416,313	25,840	100.00%		



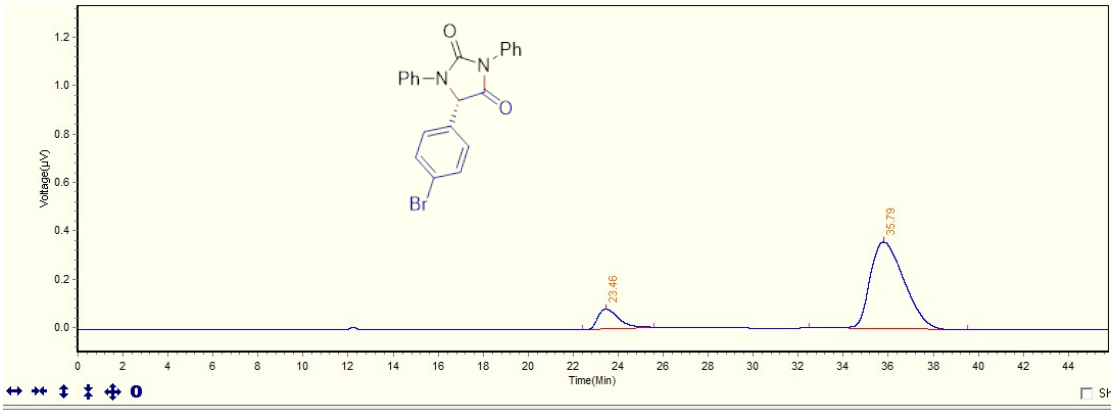
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	25.74	565716	9016	7.44%	2.89	BB
2	61.70	7040405	39649	92.56%	11.684	BB
Total		7,606,121	48,665	100.00%		

HPLC spectra of **3bf**

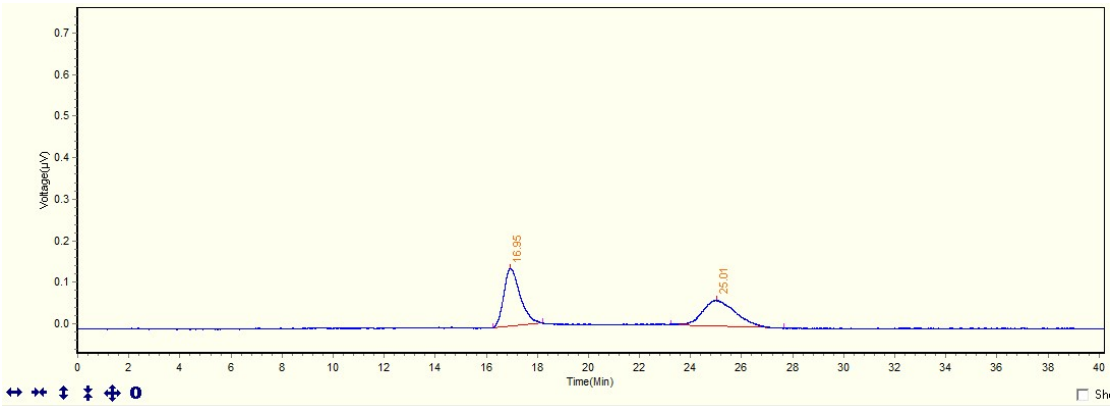


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.80	1126120	19113	49.89%	4.065	BB
2	36.77	1131021	10817	50.11%	4.526	BB
Total		2,257,141	29,930	100.00%		

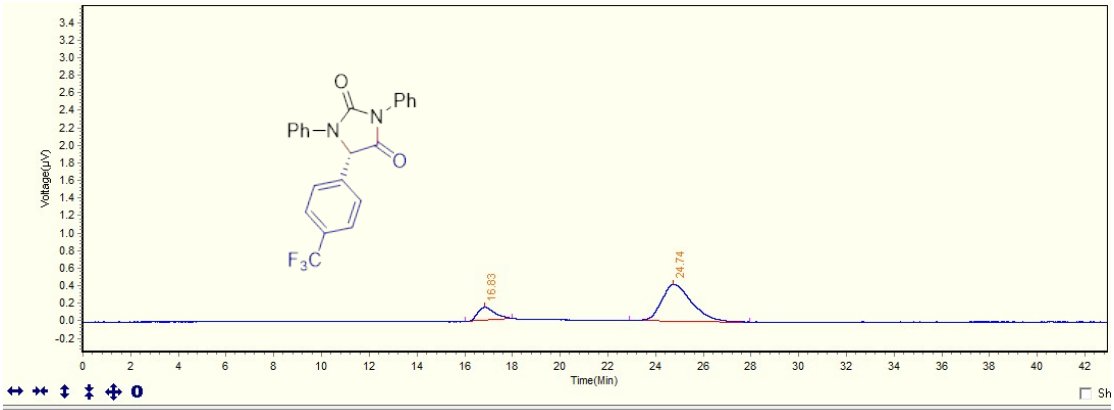


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.46	2633902	41242	12.22%	3.165	BB
2	35.79	18924508	179430	87.78%	7.043	BB
Total		21,558,410	220,672	100.00%		

HPLC spectra of **3bg**



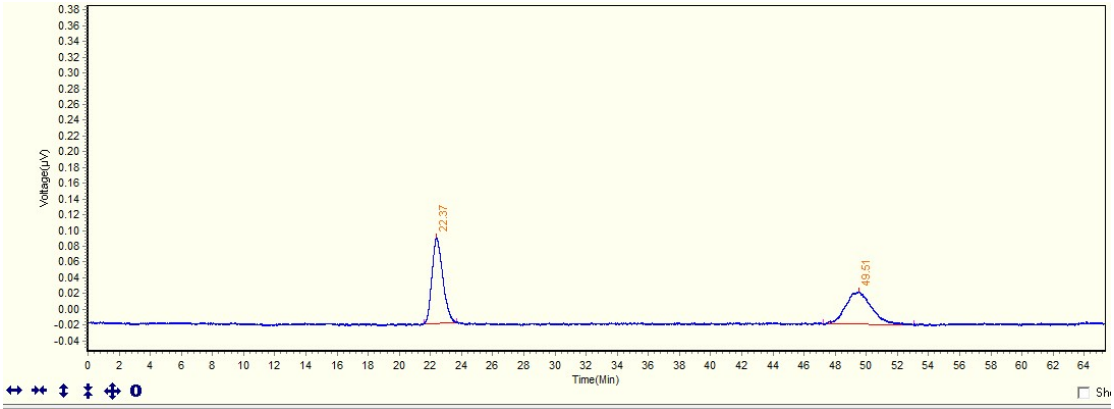
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	16.95	3054828	68908	52.93%	1.932	BB
2	25.01	2716191	30710	47.07%	4.442	BB
Total		5,771,019	99,618	100.00%		



Integration Result | Calculation Result | TimeTable

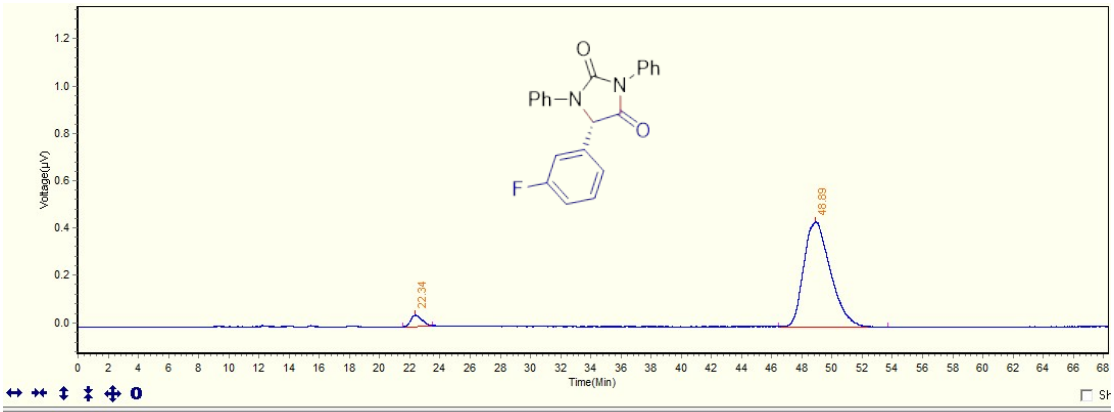
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	16.83	3691257	73590	17.07%	1.935	BB
2	24.74	17934114	206958	82.93%	5.045	BB
Total		21,625,371	280,548	100.00%		

HPLC spectra of **3bh**



Integration Result | Calculation Result | TimeTable

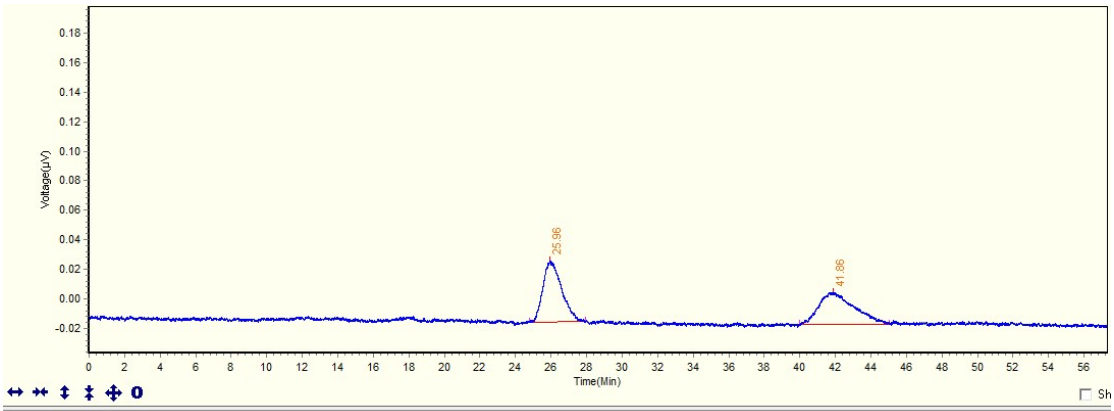
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	22.37	2619940	53922	52.74%	2.099	BB
2	49.51	2348117	20517	47.26%	5.835	BB
Total		4,968,057	74,439	100.00%		



Integration Result | Calculation Result | TimeTable

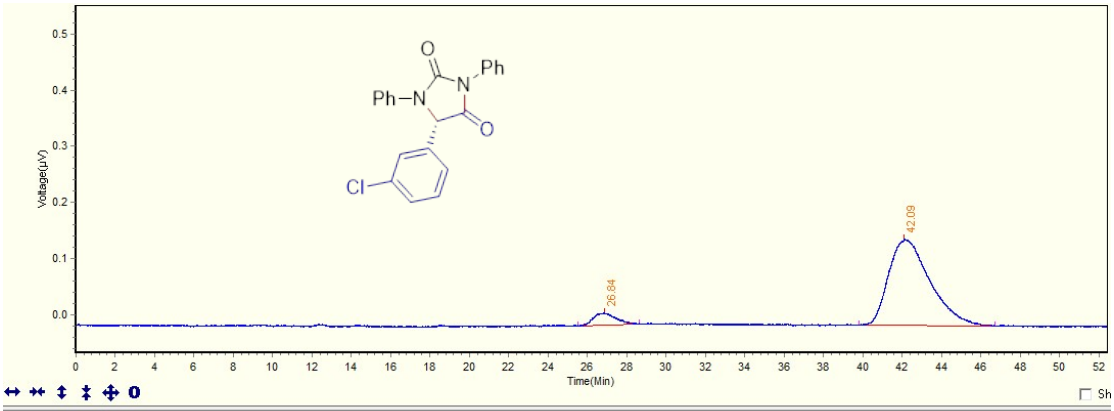
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	22.34	1230163	24048	4.30%	1.988	BB
2	48.89	27383569	221808	95.70%	7.234	BB
Total		28,613,732	245,856	100.00%		

HPLC spectra of **3bi**



Integration Result | Calculation Result | TimeTable

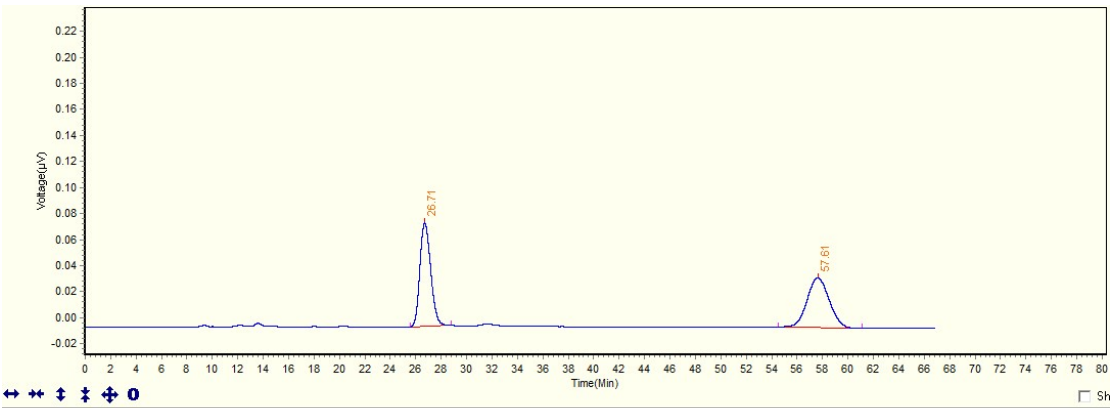
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	25.96	1476927	20407	49.86%	3.174	BB
2	41.86	1485017	10798	50.14%	5.036	BB
Total		2,961,944	31,205	100.00%		



Integration Result | Calculation Result | TimeTable

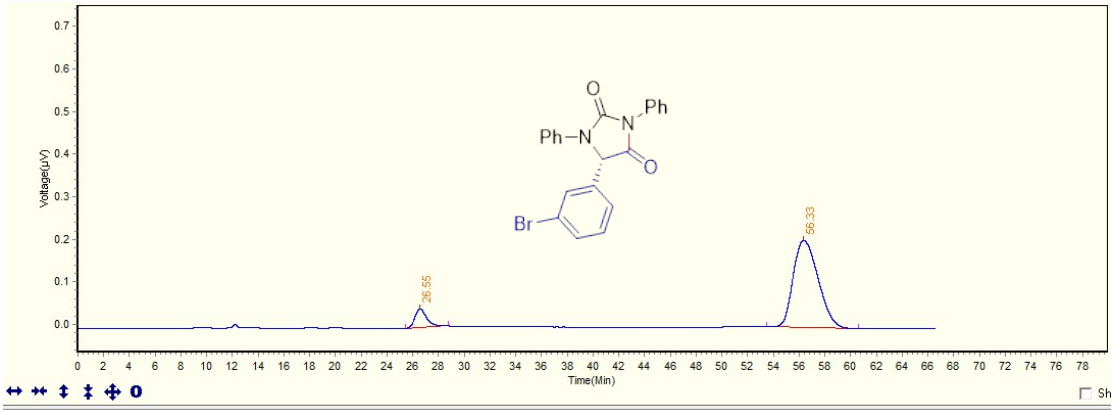
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.84	843501	10639	7.07%	3.147	BB
2	42.09	11082226	76303	92.93%	6.899	BB
Total		11,925,727	86,942	100.00%		

HPLC spectra of **3bj**



Integration Result | Calculation Result | TimeTable

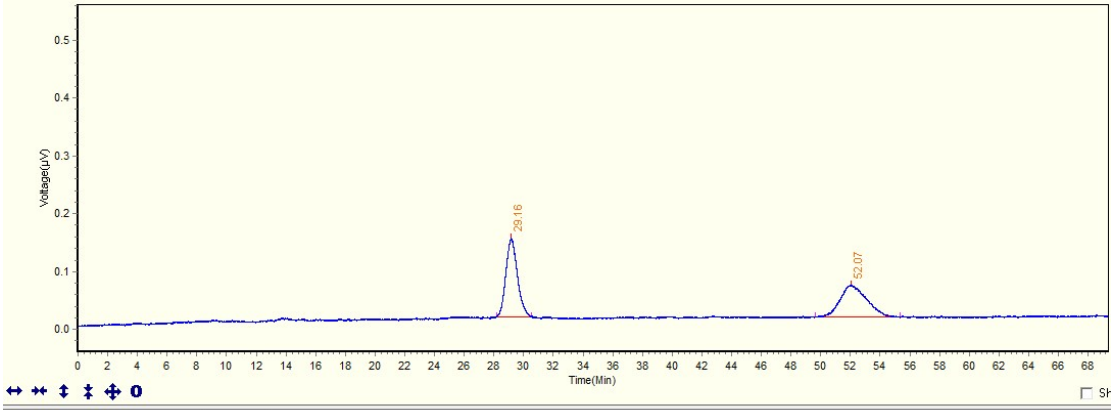
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.71	2356120	39752	50.71%	3.216	BB
2	57.61	2290425	19126	49.29%	6.593	BB
Total		4,646,545	58,878	100.00%		



Integration Result | Calculation Result | TimeTable

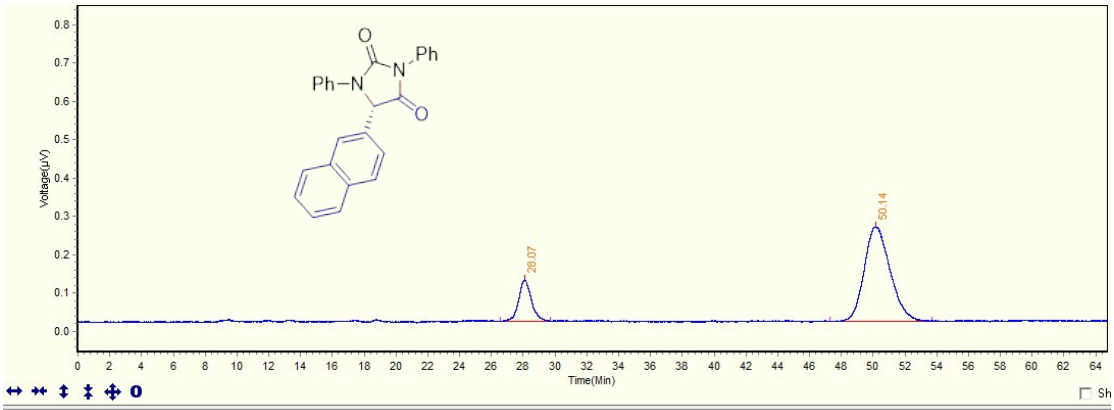
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.55	1376722	21772	9.11%	3.277	BB
2	56.33	13735827	101781	90.89%	7.134	BB
Total		15,112,549	123,553	100.00%		

HPLC spectra of **3bl**



Integration Result | Calculation Result | TimeTable

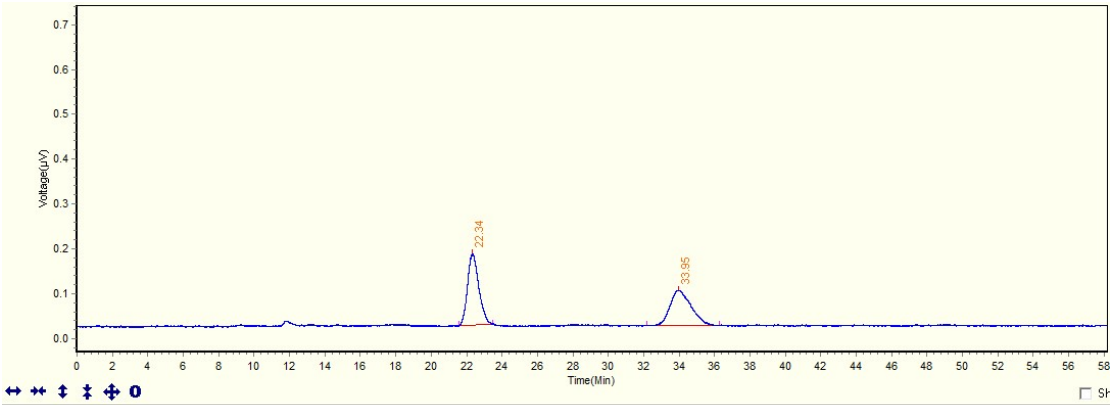
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	29.16	3648534	67928	51.64%	2.383	BB
2	52.07	3417394	27507	48.36%	5.734	BB
Total		7,065,928	95,435	100.00%		



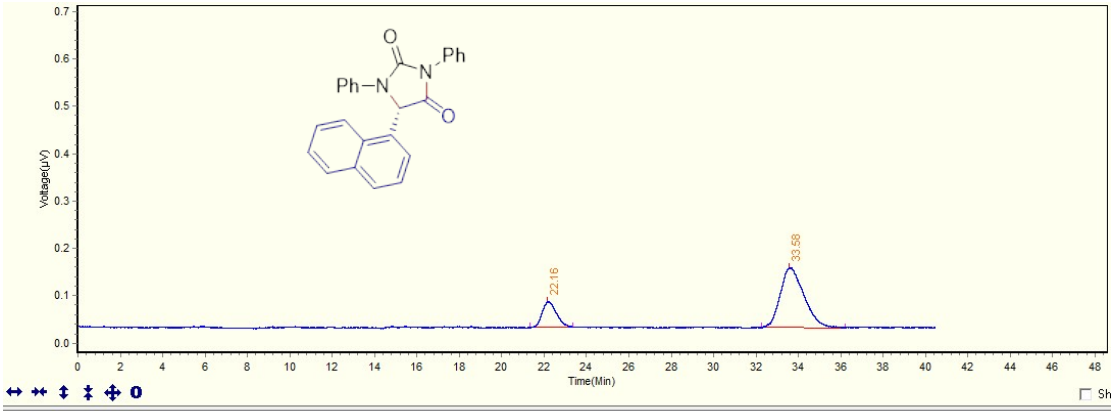
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	28.07	2966354	53935	17.51%	3.178	BB
2	50.14	13972256	123609	82.49%	6.447	BB
Total		16,938,610	177,544	100.00%		

HPLC spectra of **3bm**

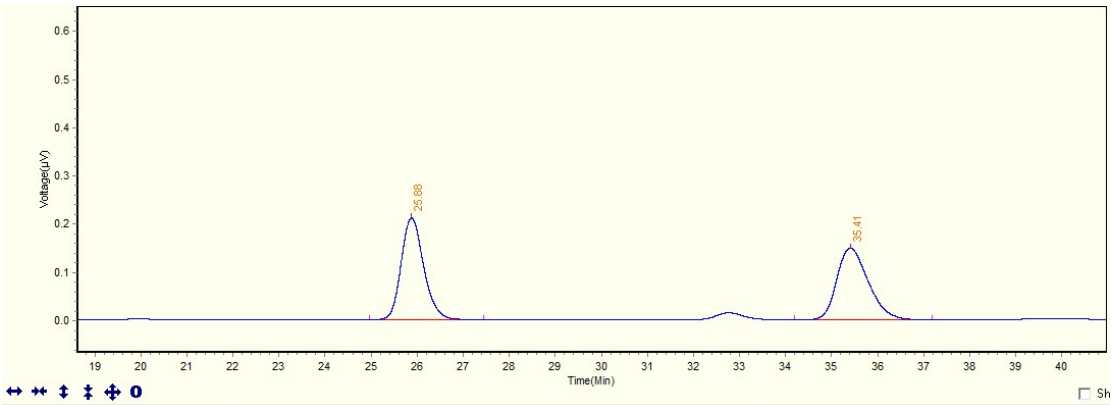


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	22.34	3541333	79182	51.95%	1.928	BB
2	33.95	3276023	39459	48.05%	4.06	BB
Total		6,817,356	118,641	100.00%		

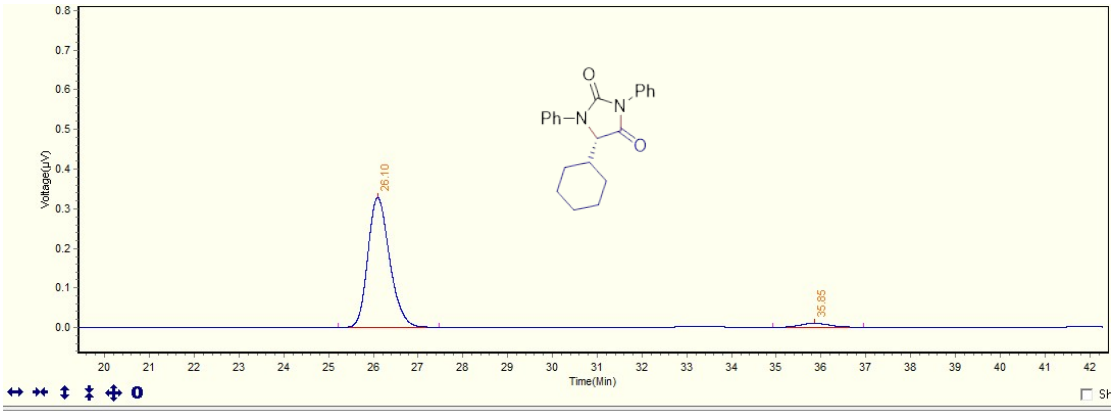


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	22.16	1245908	27243	20.15%	2.008	BB
2	33.58	4938447	63381	79.85%	3.909	BB
Total		6,184,355	90,624	100.00%		

HPLC spectra of **3bn**



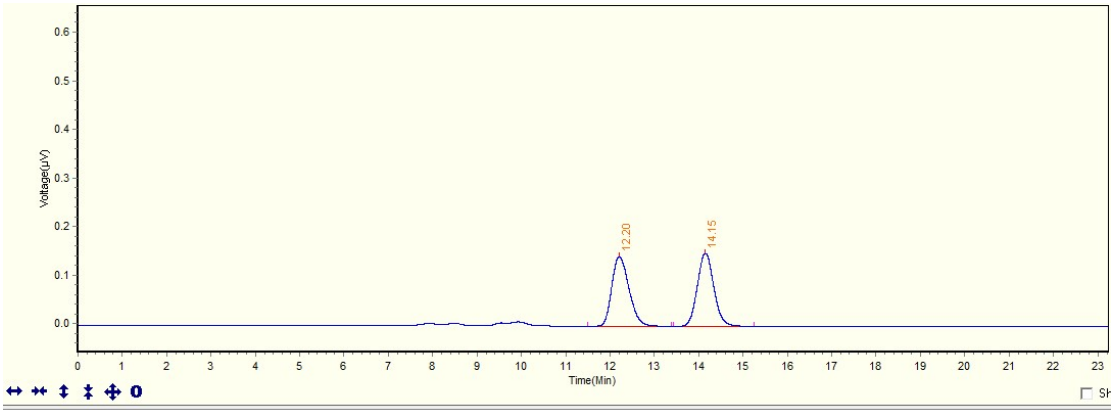
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	25.88	3558137	105232	50.28%	2.473	BB
2	35.41	3519163	74109	49.72%	2.992	BB
Total		7,077,300	179,341	100.00%		



Integration Result | Calculation Result | TimeTable

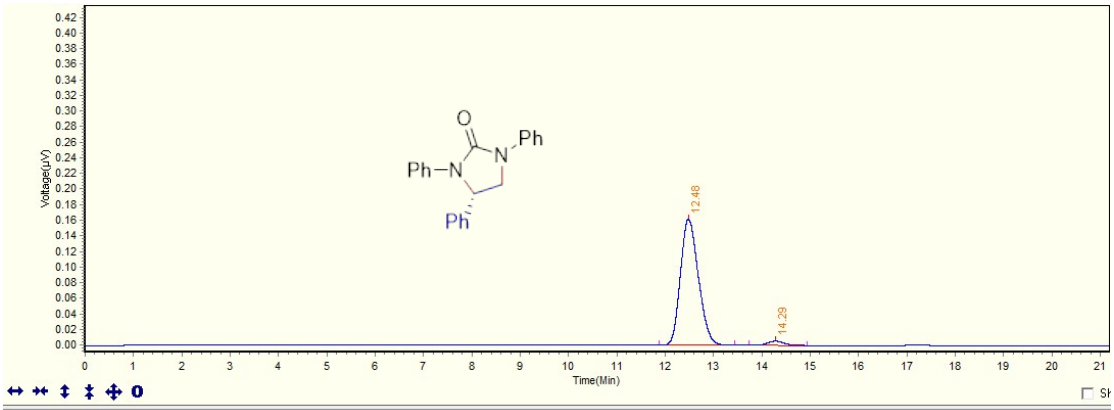
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.10	5507470	163335	96.08%	2.241	BB
2	35.85	224440	5017	3.92%	2.025	BB
Total		5,731,910	168,352	100.00%		

HPLC spectra of **4**



Integration Result | Calculation Result | TimeTable

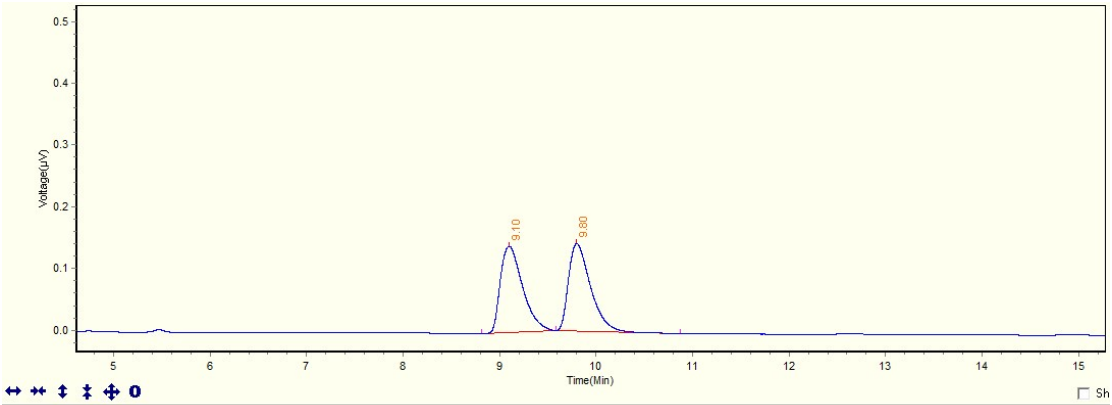
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.20	1932100	71520	49.89%	1.891	BB
2	14.15	1940552	74957	50.11%	1.807	BB
Total		3,872,652	146,477	100.00%		



Integration Result | Calculation Result | TimeTable

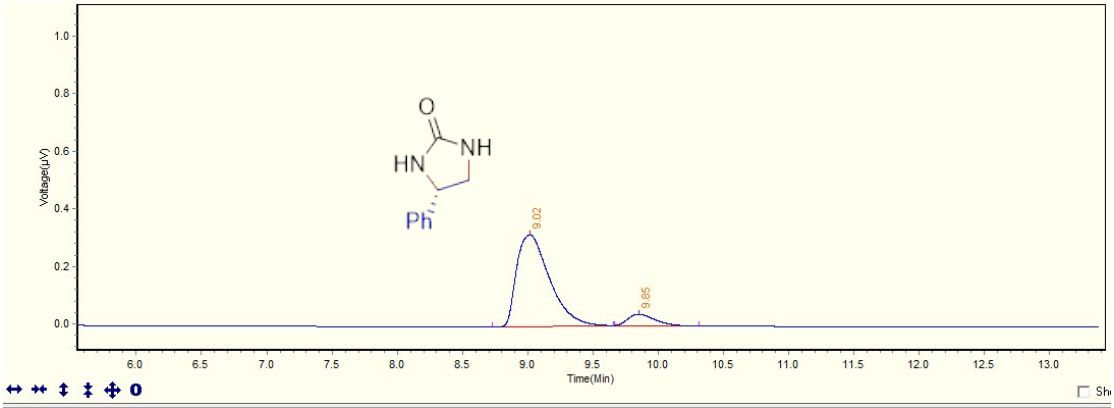
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.48	2083817	80833	97.01%	1.549	BB
2	14.29	64261	2709	2.99%	1.198	BB
Total		2,148,078	83,542	100.00%		

HPLC spectra of **6**



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.80	1118122	70709	50.17%	1.283	BB
2	9.10	1110619	69652	49.83%	0.767	BB
Total		2,228,741	140,361	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	9.02	2774987	158986	90.66%	0.93	BB
2	9.85	285848	19917	9.34%	0.648	BB
Total		3,060,835	178,903	100.00%		