Catalytic asymmetric construction of C-4 alkenyl substituted pyrazolone derivatives bearing multiple stereoelements

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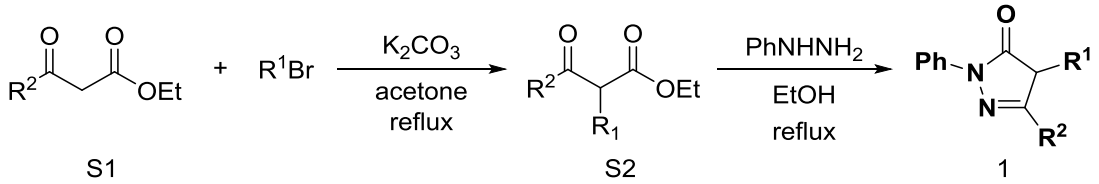
Content

1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200~300mesh). Diastereoisomeric ratios (dr) were determined by ^{1}H NMR (400 MHz). Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral columns as stated at 30 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]^T_D$ (c g/100 mL, solvent). All ^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker Avance Ⅱ 400 MHz and Bruker Avance Ⅲ 471 MHz respectively, ^{13}C NMR spectra were recorded on a Bruker Avance Ⅱ 101 MHz or Bruker Avance Ⅲ 126 MHz with chemical shifts reported as ppm (in $CDCl_3$, TMS as internal standard). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = doublet doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL™). The absolute configuration of 3aj was assigned by the X-ray analysis.

2. General procedures for preparation of pyrazol-5-ones[1]

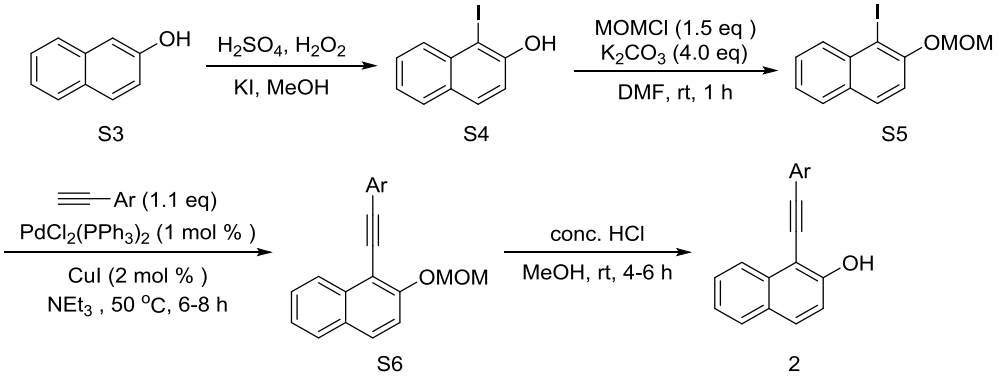


S1 S2 1

A mixture of β-ketoacid ester **S1** (10 mmol) and anhydrous K_2CO_3 (13 mmol) in dry acetone was stirred under argon atmosphere for five minutes. Then, alkyl iodide or corresponding benzyl bromide (13 mmol) was added carefully. The reaction was refluxed overnight. After filtration, the solvent was evaporated. The crude mixture purified by flash chromatography on silica gel with mixture of hexane/ethyl acetate (20:1) affording corresponding pure compound **S2**.

A mixture of **S2** (1.0 eq) and phenylhydrazine (1.0 eq) was refluxed in EtOH until full conversion. The solvent was removed and a residue was crystalized from Et_2O. Solid material was filtered affording corresponding pyrazol-5-ones **1**. NMR data fit with data published in the literature.

3. General Procedure for the synthesis of ortho-alkynyl naphthols[2]



S3 S4 S5 S6 2

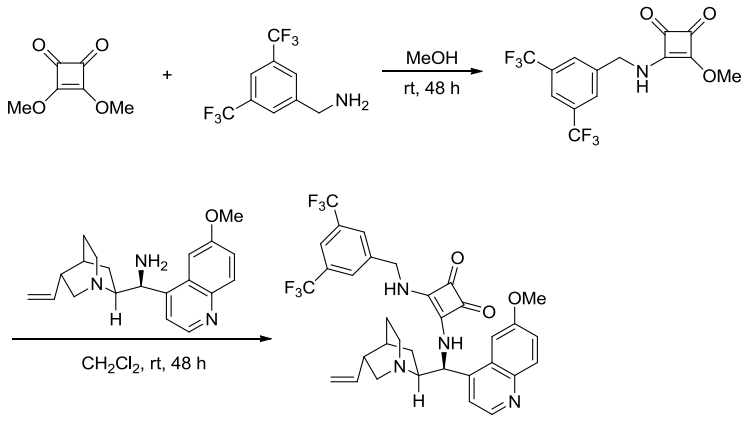
Sulfuric acid (75 mmol) was added to a solution of 2-naphthol **S3** (7.2 g, 50 mmol) and potassium iodide (8.25 g, 1.0 eq) in methanol (200 mL) at 0 °C. When the white precipitate

formed, hydrogen peroxide (30% aqueous solution, 2.0 eq) was added. After 1.5 hours later, the mixture was filtered, and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2, washed with $Na_2S_2O_3$ aq and water, dried over Na_2SO_4, Then, the mixture was filtrated and the colature was evaporated on a rotary evaporator. This material was purified by flash chromatography (PE:EA = 50:1) to provide a white solid **S4**. MOMCl (1.2 g, 1.5 eq) was added to a mixture of **S4** (10 mmol) and K_2CO_3 (5.52, 4.0 eq) in DMF (30 mL) at 25 °C. The mixture was then stirred at room temperature for about 1 h (determined by TLC), the mixture was filtered, quenched with water and extracted with diethyl ether. The organic phase was separated, washed with water and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (PE:EA = 25:1) to afford the MOM protected product **S5**.

To a dry flask under argon atmosphere containing the MOM-protected product **S5** (10 mmol) was sequentially added Et_3N (20 mL), arylacetylene (11.0 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 1 mol%), CuI (38 mg, 2 mol%). The mixture was stirred for 6-8 h at 50 °C in oil bath. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 20:1) to afford the coupling product **S6**.

The above product **S6** (10 mmol) was dissolved in methanol (10 mL), and then hydrochloric acid (36%, 1.0 mL) was slowly added. The resulted mixture was stirred at room temperature until deprotection is complete (usually 4-6 h). The acid was diluted with water. The organic material was extracted with ethyl acetate, and dried over Na_2SO_4. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (PE:EA = 100:1) to afford compound **2** as a pale yellow solid. NMR data fit with data published in the literature.

4. General Procedure for the synthesis of catalyst C5 [3]



C5

Step 1: synthesis of squaric ester monoamide intermediate

To a solution of dimethyl squarate (142 mg, 1.00 mmol) in MeOH (4 mL) was added a solution of 3,5-bis (trifluoromethyl) benzylamine (255 mg, 1.05 mmol) in MeOH (1 mL) and the mixture was stirred at room temperature for 48 h. The reaction mixture was filtered, and the filtrate was washed with 1 M HCl (10 mL), dried with Na_2SO_4, filtered again, and concentrated to afford 3-((3,5-bis(trifluoromethyl) benzyl) amino)-4-methoxycyclobut-3-ene-1,2-dione (309 mg, 87%) as a white solid. All spectroscopic data were identical to those reported in the literature.[3]

Step 2: coupling to final squaramide C5

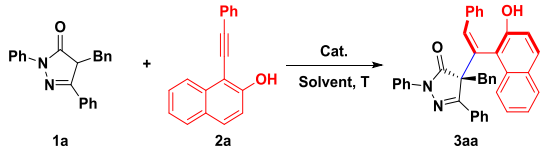
To a solution of previously obtained material (309 mg, 0.87 mmol) in CH_2Cl_2 (10 mL) at room temperature was added a solution of 9-amino-(9-deoxy) epiquinine (236 mg, 0.73 mmol) in MeOH (3 mL). After stirring the mixture for 24 h, the solvent was evaporated under reduced pressure and the residue was purified by non acid column chromatography (50:50 Hex:EtOAc) to afford the desired squaramide **C5** as a white solid (227 mg, 0.35 mmol, 50% yield). All spectroscopic data were identical to those reported in the literature.[3]

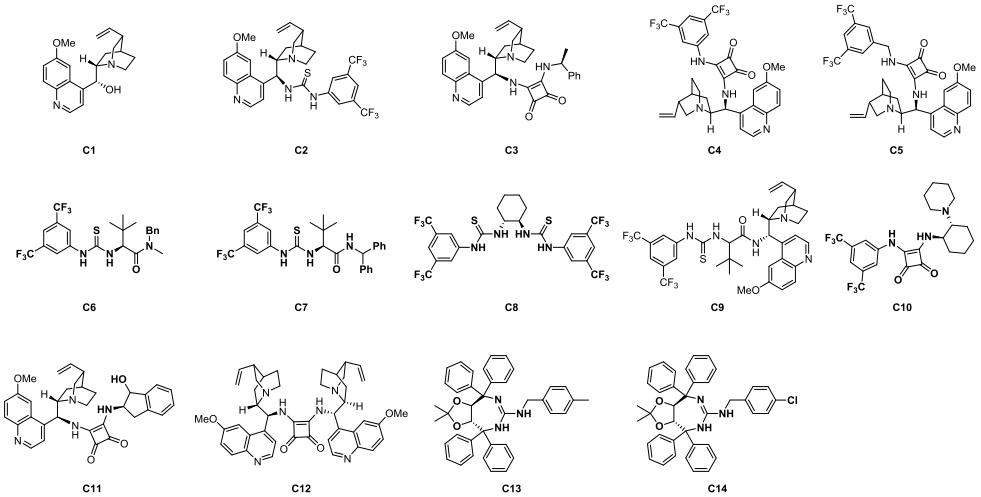
5. General Procedure for the synthesis of racemic products 3

The racemic products **3** were synthesized using 1,4-Diazabicyclo [2.2.2] octane (DABCO) or quinine/quinidine as catalyst. In a Schlenk tube, pyrazol-5-ones **1** (0.12 mmol), DABCO (0.10 mmol) or quinine/quinidine = 1:1 (0.10 mmol) were added into $CHCl_3$ (1 mL) under argon atmosphere. Then ortho-alkynyl naphthol **2** (0.10 mmol) was added in one portion and the reaction solution was stirred at 25 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography on silica gel (unless otherwise noticed, petroleum ether/EtOAc = 10/1 was used as the eluent) directly to give the racemic products **3**.

6. Experimental procedures and characterization of products 3

Table S1. Optimization of reaction conditions[a]



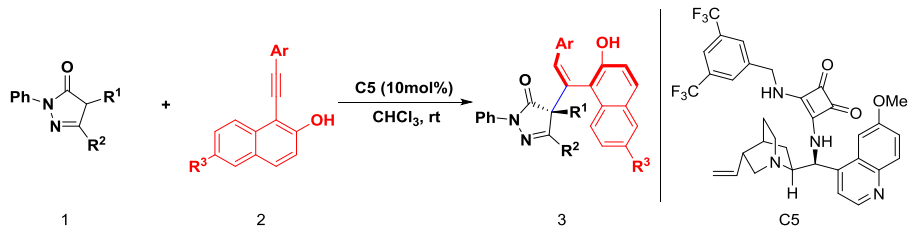


Entry[a]	**Cat.**	solvent	T (°C)	t (h)	Yield[b] (%)	ee[c] (%)
1	**C1**	$CHCl_3$	25	96	70	5
2	**C2**	$CHCl_3$	25	72	46	83
3	**C3**	$CHCl_3$	25	14	88	88
4	**C4**	$CHCl_3$	25	48	54	45
5	**C5**	$CHCl_3$	25	5	99	97

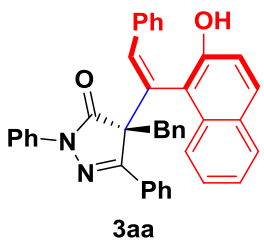
6	**C6**	$CHCl_3$	25	48	0	-
7	**C7**	$CHCl_3$	25	48	0	-
8	**C8**	$CHCl_3$	25	48	0	-
9	**C9**	$CHCl_3$	25	48	0	-
10	**C10**	$CHCl_3$	25	36	82	-64
11	**C11**	$CHCl_3$	25	42	98	72
12	**C12**	$CHCl_3$	25	40	84	74
13	**C13**	$CHCl_3$	25	90	49	11
14	**C14**	$CHCl_3$	25	90	46	17
15	**C5**	CH_2Cl_2	25	5	99	96
16	**C5**	Toluene	25	120	70	77
17	**C5**	CH_3CN	25	120	56	89
18	**C5**	THF	25	120	61	74
19	**C5**	CH_3OH	25	120	19	70
20	**C5**	1,4-dioxane	25	120	44	85
21	**C5**	$CHCl_3$	10	10	98	98
22	**C5**	$CHCl_3$	40	3.5	99	95
23[d]	**C5**	$CHCl_3$	25	7	99	96

[a]The reaction was carried out on a 0.1 mmol scale with **1a** (0.12 mmol), **2a** (0.10 mmol), and **catalyst** (10 mol%) in Solvent（1.0 mL）under Ar. dr > 20 / 1 for all reactions, and the dr was determined by ^{1}H NMR of the crude reaction mixture. [b]Isolated Yield. [c]The ee was determined by chiral HPLC. [d]The load of catalyst was 5 mol%.

General procedure: synthesis of compound 3



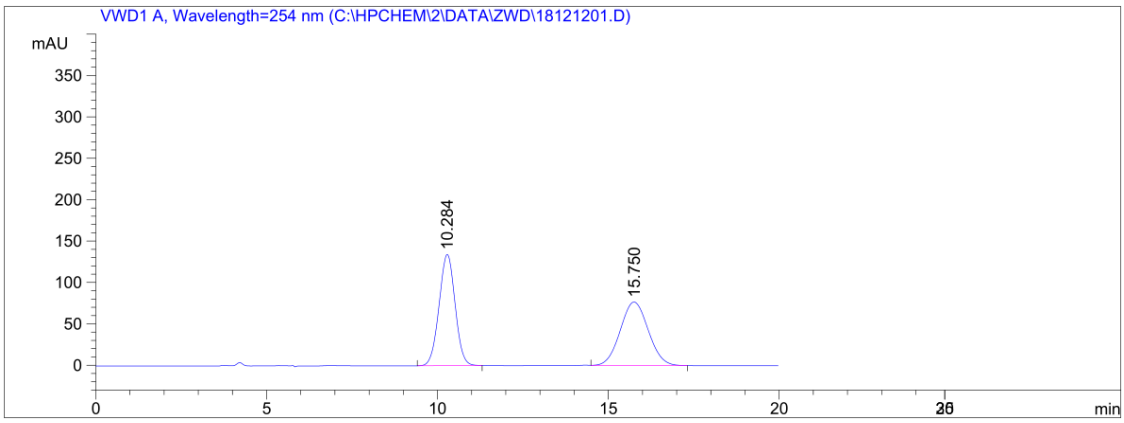
In a Schlenk tube, pyrazol-5-ones 1 (0.24 mmol), C5 (0.02 mmol) were added into $CHCl_3$ (2 mL) under argon atmosphere. Then ortho-alkynyl naphthol 2 (0.20 mmol) was added in one portion and the reaction solution was stirred at 25 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography on silica gel (unless otherwise noticed, petroleum ether/EtOAc = 10/1 was used as the eluent) directly to give the product **3**.



3aa

Prepared according to the procedure within 5 h as white solid (113 mg, 99% yield, dr > 20:1); mp 170-173 °C; $[\alpha]_D^{18}$ = -217.9 (*c* 1.35, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.12–7.68 (m, 6H), 7.61–7.31 (m, 7H), 7.23–7.08 (m, 3H), 6.98–6.72 (m, 10H), 6.63 (s, 1H), 3.55 (d, J = 13.6 Hz, 1H), 3.16 (d, J = 13.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.5, 162.5, 154.6, 137.9, 137.0, 135.2, 133.8, 131.5, 131.3, 131.3, 130.3, 130.1, 129.4, 129.3, 129.1, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 127.6, 126.6, 126.2, 125.6, 123.4, 120.5, 120.4, 115.0, 67.9, 39.5; **HRMS** (ESI)

m/z Calcd. for $C_{40}H_{31}N_2O_2$ ([M+H]$^+$) 571.2380, Found 571.2382; **Enantiomeric excess** was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.9 min, t_{minor} = 15.1 min).



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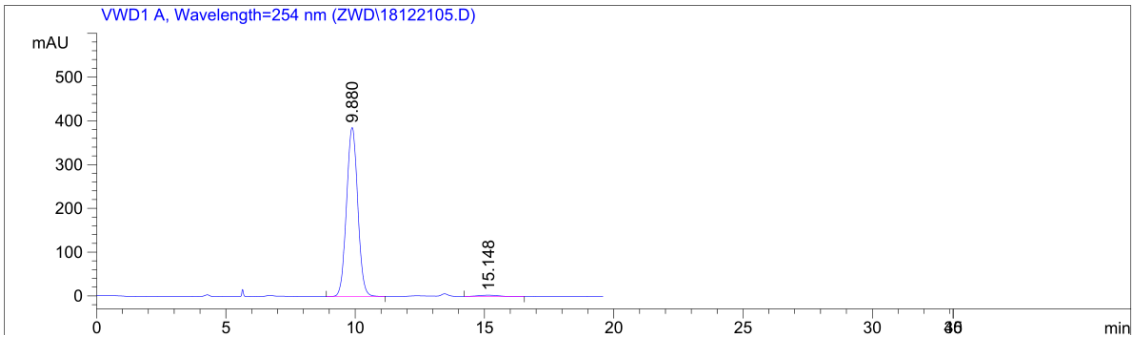

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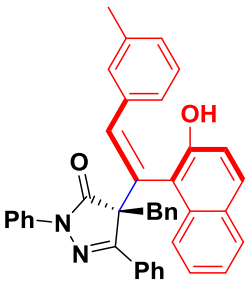
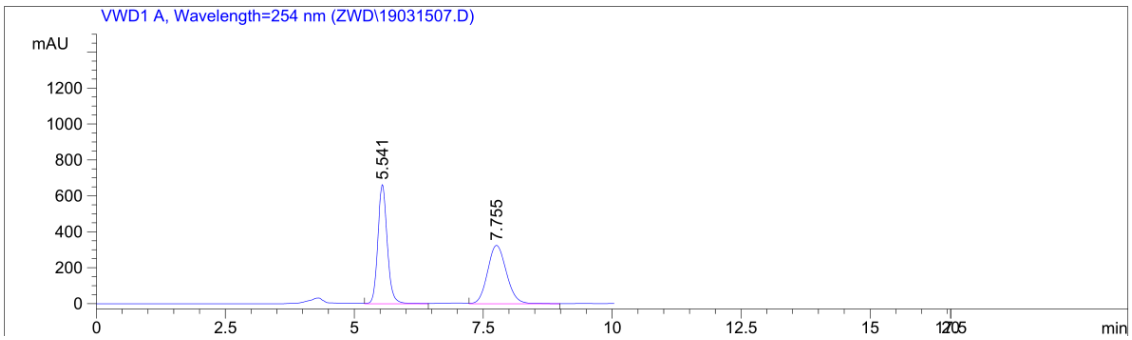


3ab

Prepared according to the procedure within 6 h as white solid (114.5 mg, 98% yield, dr > 20:1); mp 191-194 °C; $[\alpha]_D^{18}$ = -214.9 (c 1.08, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.08–7.74 (m, 6H), 7.54 (m, 7.9 Hz, 2H), 7.46–7.36 (m, 5H), 7.24–7.12 (m, 3H), 7.01–6.85 (m, 5H), 6.72–6.49 (m, 5H), 3.54 (d, J = 13.6 Hz, 1H), 3.18 (d, J = 13.6 Hz, 1H), 1.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.4, 162.5, 154.4, 137.9, 137.4, 137.0, 135.0, 133.7, 131.6, 131.2, 131.1, 130.2, 130.1, 129.9, 129.3, 129.3, 129.0, 128.8, 128.4, 128.4, 128.1, 127.9, 127.4, 126.4, 126.1, 125.8, 125.6, 123.3, 120.4, 120.2, 115.1, 67.8, 39.4, 21.1; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{33}N_2O_2$ ([M+H]$^+$) 585.2537, Found 585.2548; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 5.5 min, t_{minor} = 7.7 min).



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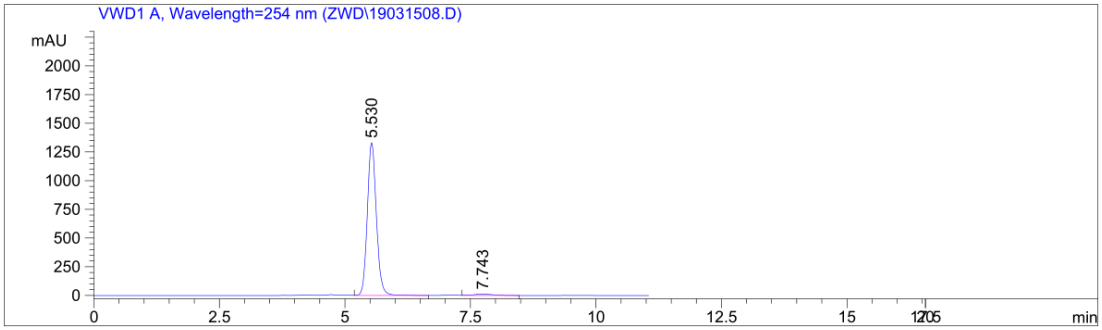

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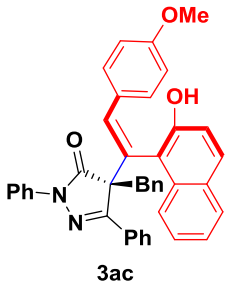
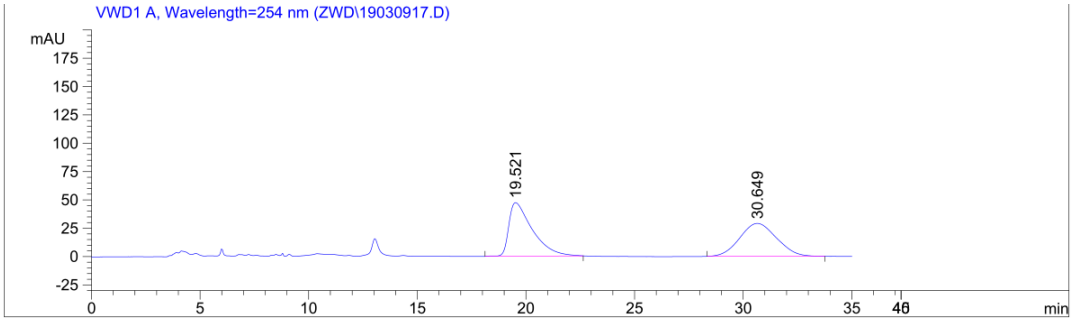


3ac

Prepared according to the procedure within 6 h as white solid (118 mg, 98% yield, dr > 20:1); mp 95-98 °C; $[\alpha]_D^{17}$ = -173.4 (c 1.01, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 8.07–7.74 (m, 6H), 7.61–7.48 (m, 2H), 7.45–7.36 (m, 5H), 7.26–7.15 (m, 3H), 7.00–6.85 (m, 5H), 6.68–6.35 (m, 5H), 3.51 (d, J = 13.6 Hz, 1H), 3.50 (s, 3H), 3.15 (d, J = 13.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.5, 162.5, 159.3, 154.4, 137.2, 137.0, 133.8, 131.6, 131.1, 131.0, 130.6, 130.1, 129.3, 129.3, 129.0, 128.7, 128.5, 128.4, 128.1, 127.8, 127.4, 127.4, 126.4, 126.2, 125.7, 123.3, 120.4, 120.3, 115.1, 113.5, 67.8, 55.0, 39.4; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{33}N_2O_3$ ($[M+H]^+$) 601.2486, Found 601.2489; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 18.4 min, t_{minor} = 30.7 min).



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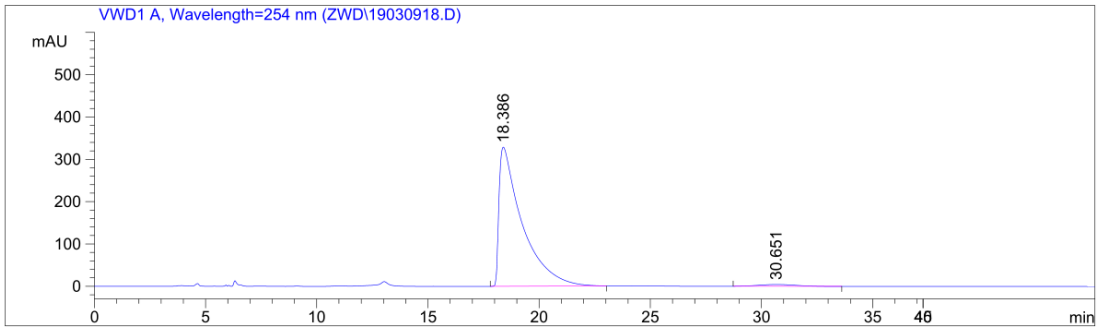

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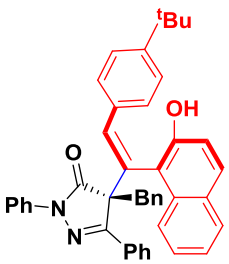
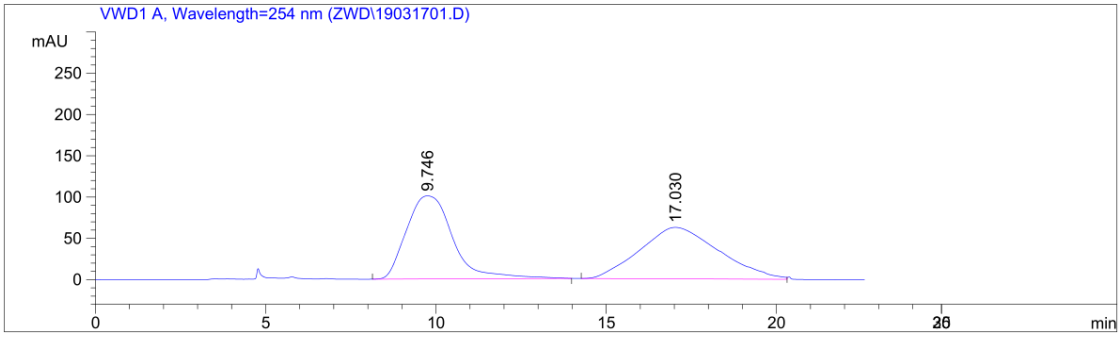


3ad

Prepared according to the procedure within 4 h as white solid (121.6 mg, 97% yield, dr > 20:1); mp 123-126 °C; $[\alpha]_D^{22}$ = -139.7 (*c* 0.54, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.91–7.61 (m, 5H),7.52–7.36 (m, 6H), 7.30–7.17 (m, 3H), 7.02–6.87 (m, 7H), 6.68 (d, *J* = 8.1 Hz, 2H), 6.58 (s, 1H), 3.49 (d, *J* = 13.6 Hz, 1H), 3.17 (d, *J* = 13.7 Hz, 1H), 1.07 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.4, 162.5, 154.1, 151.5, 137.6, 137.0, 133.8, 132.1, 131.8, 131.1, 131.0, 130.2, 129.3, 129.3, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.1, 127.4, 126.4, 126.3, 125.7, 125.1, 123.3, 120.4, 115.2, 68.0, 39.4, 34.5, 31.0; **HRMS** (ESI) m/z Calcd. for $C_{44}H_{39}N_2O_2$ ($[M+H]^+$) 627.3006, Found 627.3014; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 60/1, λ = 254 nm, 30 °C, 0.8 mL/min, t_{minor} = 10 min, t_{major} = 16.8 min).



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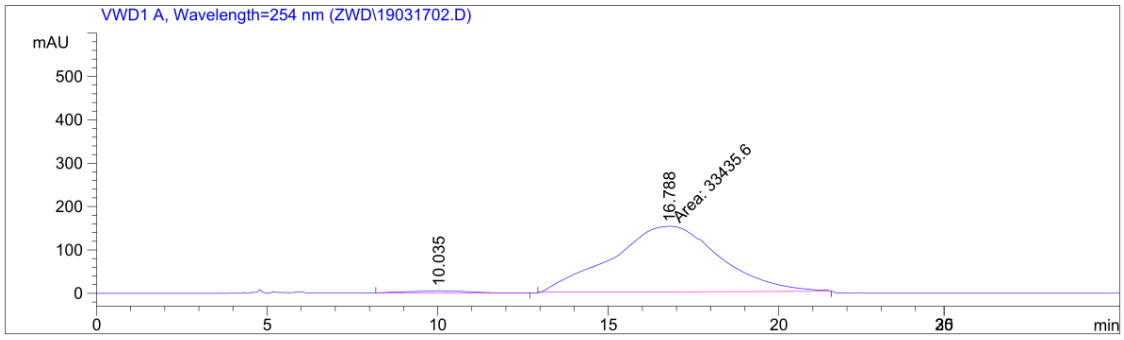

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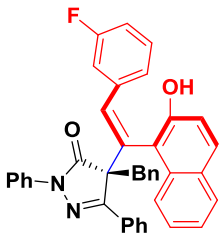
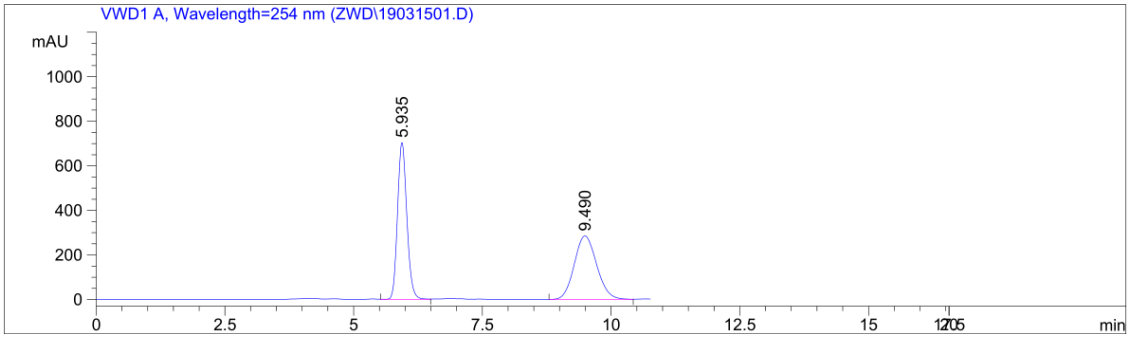
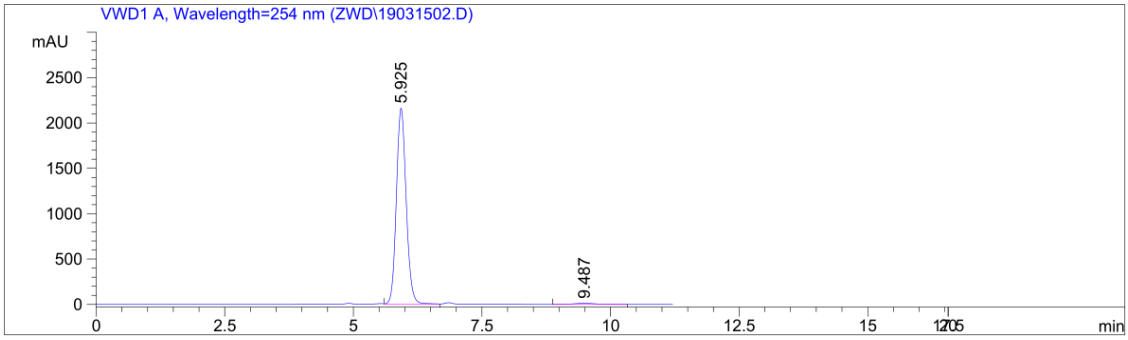


3ae

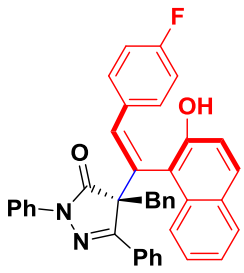
Prepared according to the procedure within 5 h as white solid (116.2 mg, 99% yield, dr > 20:1); mp 87-90 °C; $[\alpha]_D^{19}$ = -204.1 (*c* 1.11, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 8.08–7.72 (m, 6H), 7.55–7.36 (m, 7H), 7.26–7.14 (m, 3H), 7.02–6.76 (m, 6H), 6.61–6.40 (m, 4H), 3.54 (d, *J* = 13.6 Hz, 1H), 3.18 (d, *J* = 13.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2, 162.3, 162.2 (d, *J* = 246.2 Hz), 154.4, 137.2 (d, *J* = 7.9 Hz), 136.9, 136.5 (d, *J* = 2.5 Hz), 133.5, 132.0, 131.4, 131.3, 131.2, 129.9, 129.4 (d, *J* = 8.3 Hz), 129.3, 129.3, 129.0, 128.8, 128.6, 128.4, 128.2, 127.5, 126.4 (d, *J* = 26.7 Hz), 125.2, 124.8 (d, *J* = 2.9 Hz), 123.4, 120.4, 120.3, 115.6, 115.4, 115.1 (d, *J* = 21.3 Hz), 114.4, 67.7, 39.4; **HRMS (ESI)** m/z Calcd. for $C_{40}H_{30}FN_2O_2$ ($[M+H]^+$) 589.2286, Found 589.2290; **Enantiomeric excess** was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 5.9 min, t_{minor} = 9.5 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.935	VV	0.1949	8871.14844	704.97314	50.7447
2	9.490	PV	0.4722	8610.76660	284.76837	49.2553

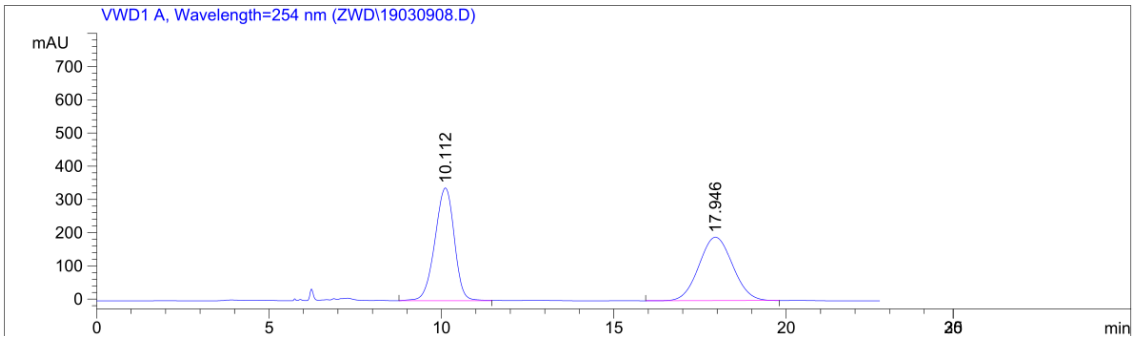


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.925	VV	0.2045	2.87493e4	2164.13843	98.6064
2	9.487	VB	0.4836	406.31927	13.22679	1.3936

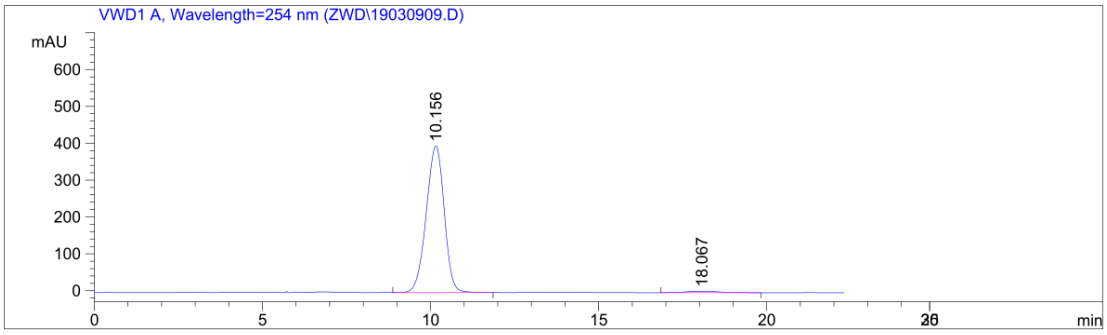


3af

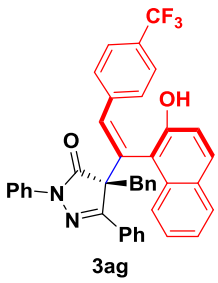
Prepared according to the procedure within 5 h as white solid (117 mg, 99% yield, dr > 20:1); mp 97-100 °C; $[\alpha]_D^{19}$ = -215.5 (*c* 0.52, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.07–7.74 (m, 6H), 7.56–7.51 (m, 2H), 7.48–7.39 (m, 5H), 7.25–7.15 (m, 3H), 7.03–6.86 (m, 5H), 6.73 (m, 2H), 6.59–6.52 (m, 3H), 3.53 (d, *J* = 13.8 Hz, 1H), 3.18 (d, *J* = 13.7 Hz, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -112.33; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.3, 162.3, 162.1 (d, *J* = 250.4 Hz), 154.5, 136.9, 136.4, 133.56, 131.2, 131.3, 131.3, 131.2, 130.7 (d, *J* = 8.1 Hz), 130.0 (d, *J* = 11.5 Hz), 129.3, 129.2, 129.0, 128.7, 128.5, 128.3, 128.1, 127.4, 126.4, 126.2, 125.3, 123.3, 120.3, 120.2, 115.0 (d, *J* = 21.6 Hz), 114.5, 67.6, 39.4; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}FN_2O_2$ ($[M+H]^+$) 589.2286, Found 589.2288; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.2 min, t_{minor} = 18.1 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.112	BB	0.6108	1.33379e4	339.77890	50.6241
2	17.946	PB	1.0720	1.30090e4	191.17874	49.3759

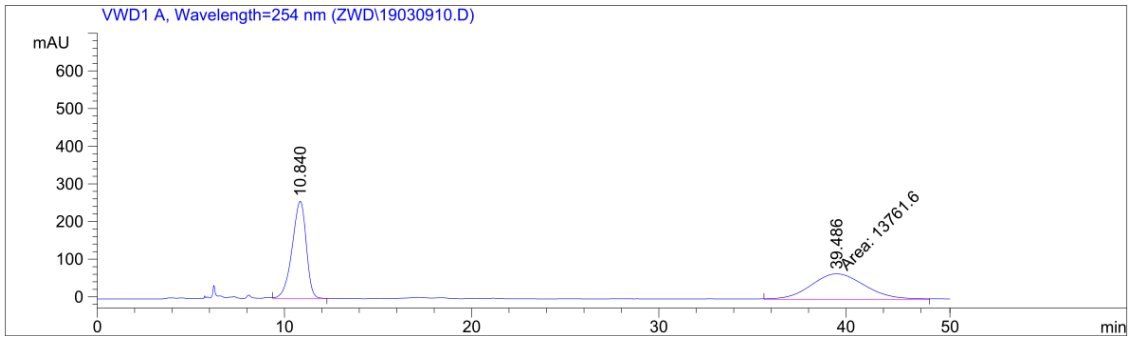


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.156	VB	0.5833	1.48231e4	397.70624	98.2051
2	18.067	BB	0.8109	270.92508	3.97620	1.7949

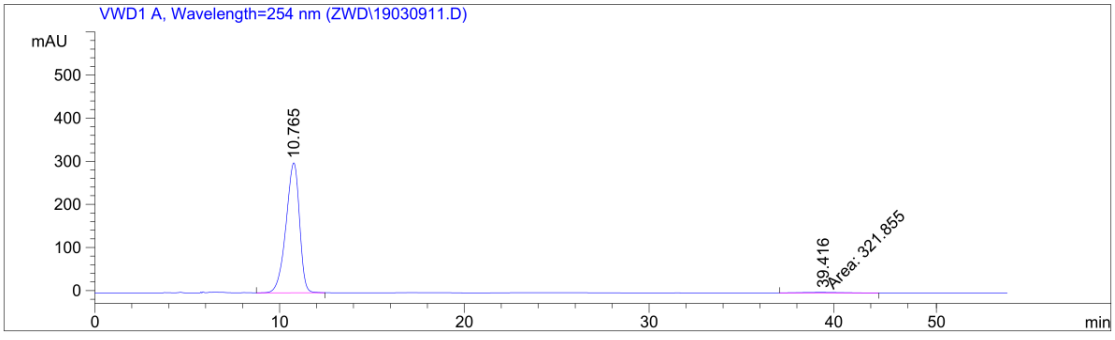


3ag

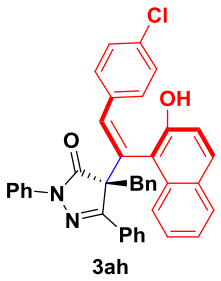
Prepared according to the procedure within 5 h as white solid (124 mg, 97% yield, dr > 20:1); mp 174-176 °C; $[\alpha]_D^{20}$ = -195.6 (*c* 0.98, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.13–7.73 (m, 6H), 7.58–7.35 (m, 7H), 7.31–7.09 (m, 5H), 6.94 (m, 7H), 6.71–6.64 (m, 1H), 3.58 (d, *J* = 13.4 Hz, 1H), 3.22 (d, *J* = 13.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 162.3, 154.5, 138.5, 136.8, 136.3, 133.4 (q, *J* = 4.6 Hz), 131.6, 131.4, 131.2, 129.9, 129.7 (q, *J* = 33.4 Hz), 129.3, 129.3, 129.1, 129.0, 128.9, 128.7, 128.4, 128.2, 127.6, 126.6, 126.4, 125.2, 125.0, 125.0, 125.0, 123.8 (q, *J* = 272.8 Hz), 123.5, 120.4, 114.3, 67.9, 39.4; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{30}F_3N_2O_2$ ($[M+H]^+$) 639.2254, Found 639.2255; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.8 min, t_{minor} = 39.4 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.840	VB	0.8027	1.35220e4	258.40549	49.5609
2	39.486	MM	3.3704	1.37616e4	68.05173	50.4391

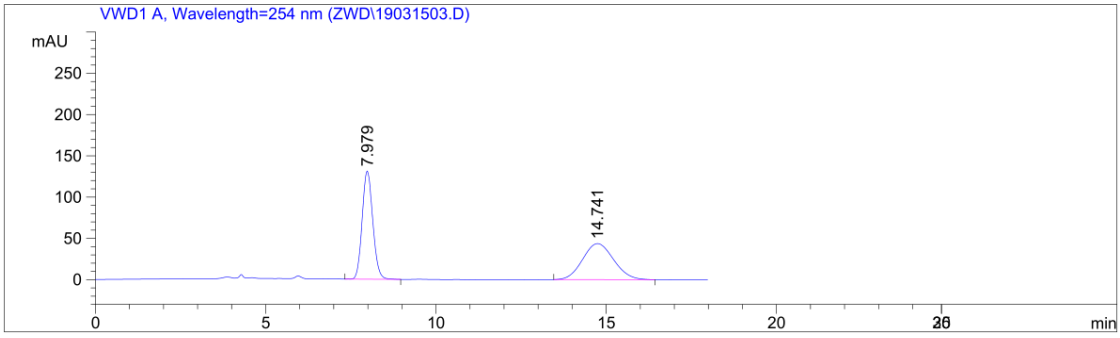


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.765	VB	0.7838	1.53149e4	301.29510	97.9417
2	39.416	MM	3.2172	321.85464	1.66734	2.0583

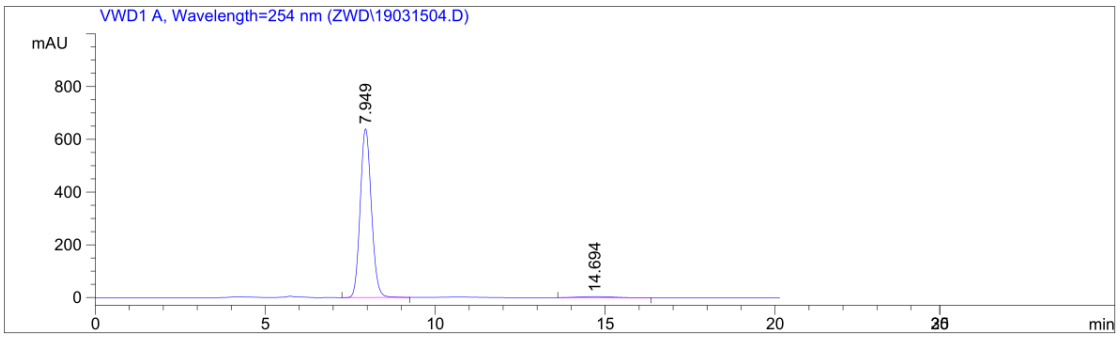


3ah

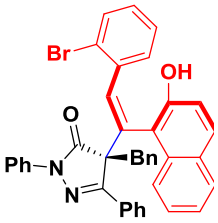
Prepared according to the procedure within 5 h as white solid (119.7 mg, 99% yield, dr > 20:1); mp 95-98 °C; $[\alpha]_D^{20}$ = -202.3 (*c* 1.13, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.80–7.74 (m, 3H), 7.56–7.38 (m, 7H), 7.27–7.14 (m, 3H), 7.04–6.95 (m, 3H), 6.90–6.80 (m, 4H), 6.68 (d, *J* = 8.3 Hz, 2H), 6.57 (s, 1H), 3.53 (d, *J* = 13.7 Hz, 1H), 3.17 (d, *J* = 13.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2, 162.3, 154.4, 136.8, 136.4, 133.9, 133.6, 133.5, 131.3, 131.2, 131.2, 131.1, 130.1, 129.9, 129.3, 129.2, 129.0, 128.8, 128.6, 128.3, 128.2, 128.1, 127.5, 126.5, 126.2, 125.2, 123.4, 120.3, 120.2, 114.4, 67.7, 39.4; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}ClN_2O_2$ ($[M+H]^+$) 605.1990, Found 605.1993; **Enantiomeric excess** was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.9 min, t_{minor} = 14.7 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.979	BB	0.3367	2851.47021	131.11531	50.6480
2	14.741	BB	0.9817	2778.50854	43.71678	49.3520

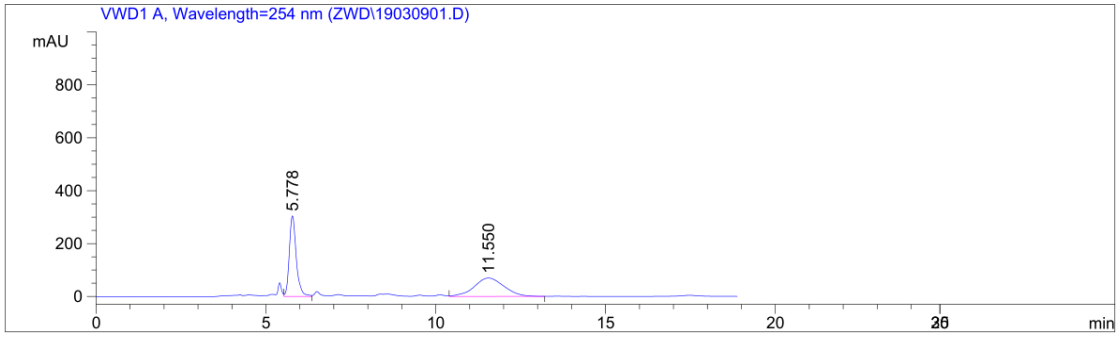


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.949	VB	0.3538	1.46137e4	639.99133	98.3523
2	14.694	BP	0.7680	244.82127	3.85047	1.6477

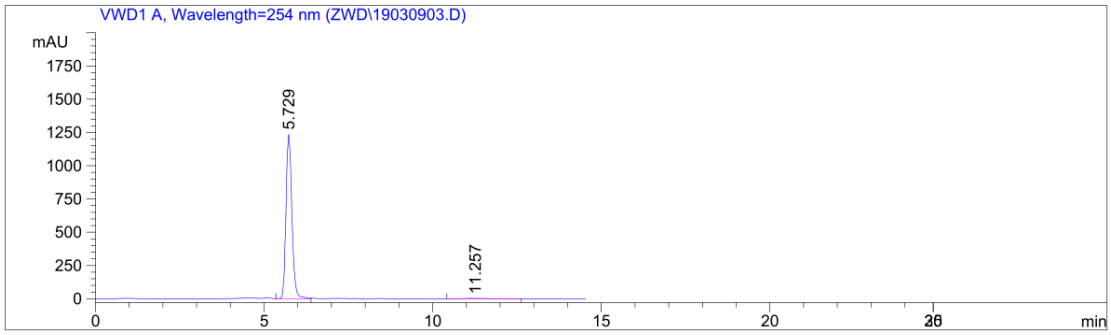


3ai

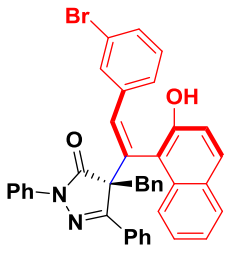
Prepared according to the procedure within 12 h as white solid (122 mg, 94% yield, dr > 20:1); mp 183-186 °C; $[\alpha]_D^{21}$ = -333.4 (*c* 1.06, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 8.10 (d, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 8.6 Hz, 3H), 7.68–7.44 (m, 5H), 7.42–7.33 (m, 3H), 7.24–7.15 (m, 4H), 7.04–6.93 (m, 5H), 6.83–6.61 (m, 4H), 3.56 (d, *J* = 13.7 Hz, 1H), 3.25 (d, *J* = 13.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.0, 162.4, 155.1, 138.3, 136.8, 135.6, 133.5, 132.5, 131.8, 131.8, 131.2, 131.0, 130.2, 129.8, 129.3, 129.2, 129.0, 128.7, 128.6, 128.3, 128.2, 127.5, 126.7, 126.5, 125.9, 125.3, 123.7, 123.1, 120.5, 119.8, 114.2, 67.5, 39.7; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}BrN_2O_2$ ($[M+H]^+$) 649.1485, Found 649.1484; **Enantiomeric excess** was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 5.7 min, t_{minor} = 11.3 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.778	VV	0.2177	4358.87549	305.01349	50.4191
2	11.550	VB	0.9340	4286.40576	69.60310	49.5809



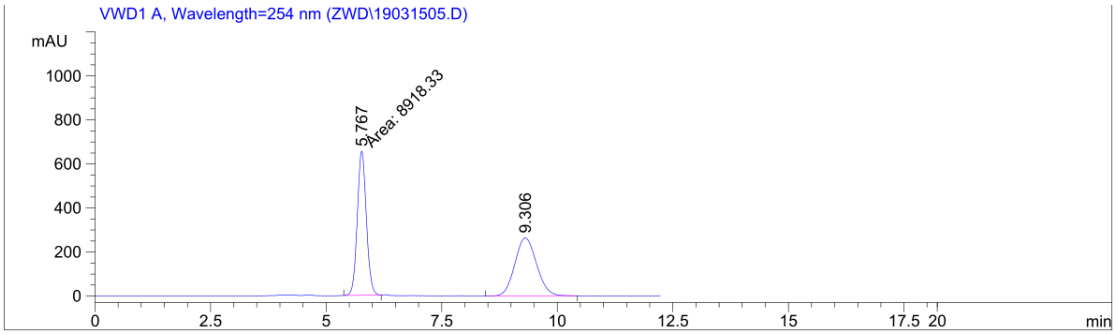
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.729	VV	0.1880	1.51515e4	1237.00391	98.9850
2	11.257	BP	0.6615	155.36160	3.00455	1.0150



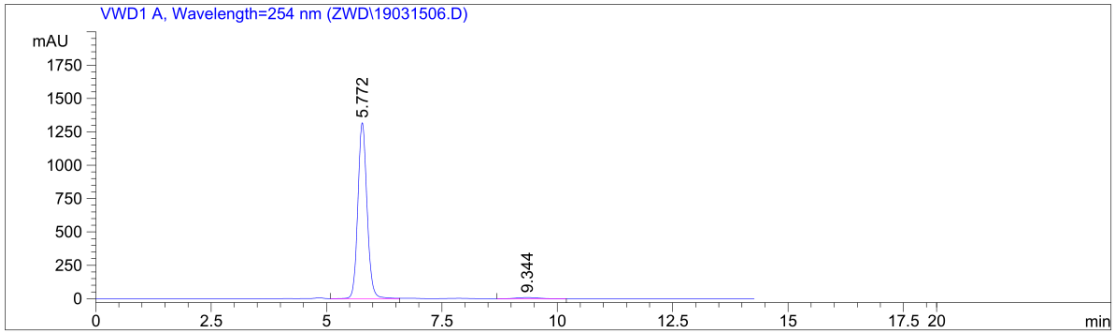
3aj

Prepared according to the procedure within 5 h as white solid (119.8 mg, 92% yield, dr > 20:1); mp 199-202 °C; $[\alpha]_D^{21}$ = -206.0 (*c* 1.12, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.07–7.74 (m, 6H), 7.56–7.37 (m, 7H), 7.26–7.15 (m, 3H), 7.03–6.85 (m, 7H), 6.67–6.53 (m, 3H), 3.54 (d, *J* = 13.7 Hz, 1H), 3.19 (d, *J* = 13.7 Hz, 1H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 162.2, 154.5, 137.1, 136.8, 136.1, 133.5, 132.3, 132.2, 131.4, 131.3, 131.2, 131.0, 129.8, 129.5, 129.3, 129.2, 129.0, 128.8, 128.6, 128.3, 128.2, 127.5, 126.9, 126.5, 126.3, 125.1, 123.4, 121.9, 120.3, 120.3, 114.3, 67.7, 39.4; **HRMS** (ESI) m/z

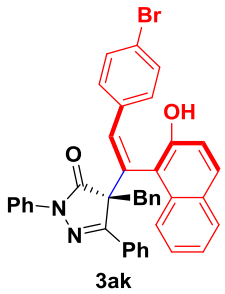
Calcd. for $C_{40}H_{30}BrN_2O_2$ ([M+H]$^+$) 649.1485, Found 649.1490; **Enantiomeric excess** was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 5.8 min, t_{minor} = 9.3 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.767	MM	0.2268	8918.33203	655.34711	50.9042
2	9.306	VB	0.5093	8601.51758	263.29315	49.0958

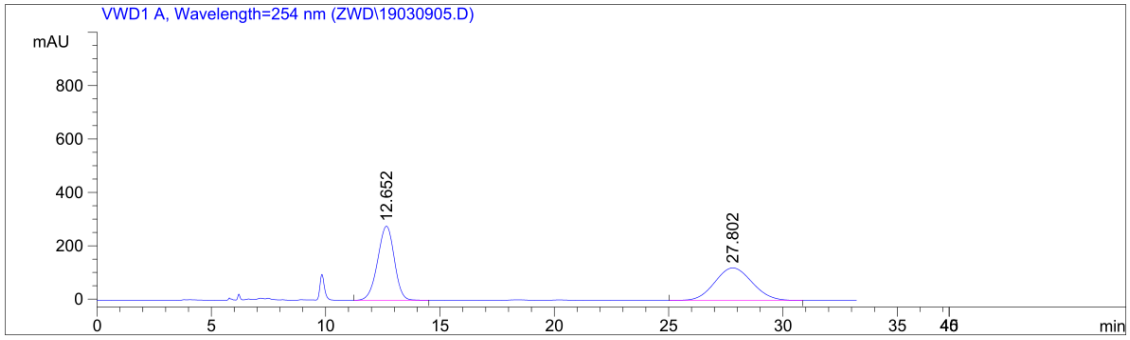


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.772	VV	0.2130	1.83296e4	1319.40625	98.3753
2	9.344	VB	0.5064	302.72653	9.23091	1.6247

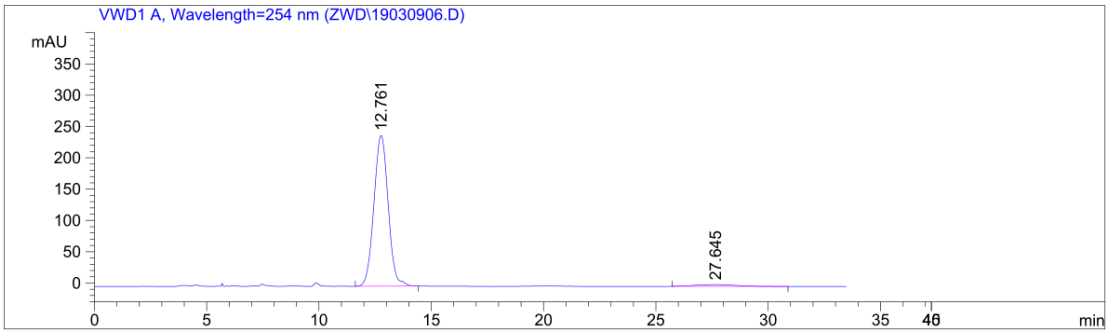


3ak

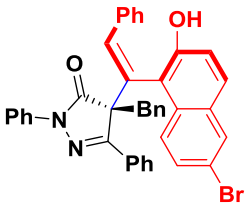
Prepared according to the procedure within 7 h as white solid (108 mg, 83% yield, dr > 20:1); mp 83-86 °C; $[\alpha]_D^{21}$ = -162.4 (*c* 1.01, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.80–7.74 (m, 3H), 7.54–7.38 (m, 7H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 6.0 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.01–6.86 (m, 7H), 6.61 (d, *J* = 8.2 Hz, 2H), 6.55 (s, 1H), 3.52 (d, *J* = 13.6 Hz, 1H), 3.17 (d, *J* = 13.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 162.2, 154.4, 136.8, 136.5, 134.0, 133.5, 131.3, 131.3, 131.2, 131.1, 130.4, 129.9, 129.3, 129.2, 129.0, 128.8, 128.6, 128.3, 128.1, 127.5, 126.5, 126.3, 125.2, 123.4, 122.3, 120.3, 120.3, 114.4, 67.7, 39.4; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}BrN_2O_2$ ([M+H]$^+$) 649.1485, Found 649.1490; **Enantiomeric excess** was determined to be 93% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.8 min, t_{minor} = 27.7 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.652	PB	0.7897	1.41215e4	277.77914	50.1770
2	27.802	BB	1.7488	1.40219e4	122.37407	49.8230

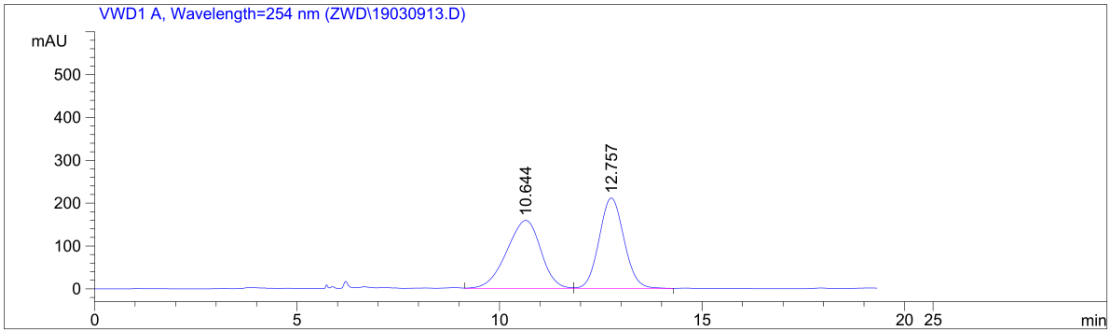


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.761	BB	0.6871	1.06382e4	240.85709	96.7091
2	27.645	BP	1.5475	362.01059	2.75249	3.2909

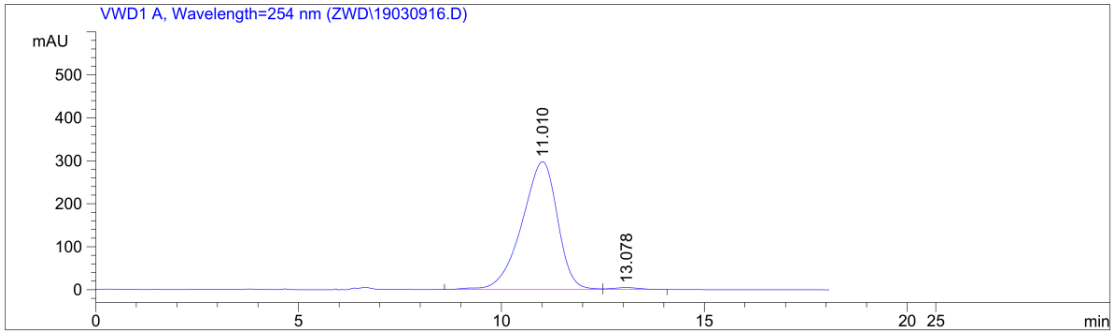


3al

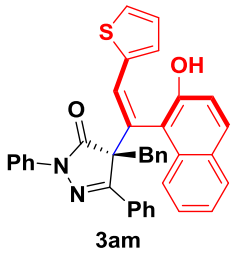
Prepared according to the procedure within 4 h as white solid (188 mg, 96% yield, dr > 20:1); mp 108-110 °C; $[\alpha]_D^{18}$ = -117.7 (*c* 1.81, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 8.06–7.70 (m, 6H), 7.53–7.35 (m, 7H), 7.23–7.17 (m, 2H), 7.01–6.83 (m, 8H), 6.73 (d, *J* = 7.5 Hz, 2H), 6.62 (s, 1H), 3.52 (d, *J* = 13.7 Hz, 1H), 3.15 (d, *J* = 13.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.3, 162.4, 155.0, 138.2, 136.9, 134.9, 133.5, 131.4, 130.5, 130.5, 130.3, 130.1, 130.0, 129.8, 129.3, 129.0, 129.0, 128.9, 128.4, 128.3, 128.2, 128.2, 127.6, 127.3, 126.6, 121.6, 120.4, 117.1, 115.2, 67.7, 39.4; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}BrN_2O_2$ ($[M+H]^+$) 649.1485, Found 649.1486; **Enantiomeric excess** was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.0 min, t_{minor} = 13.1 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.644	VV	0.9299	9393.21191	159.23003	50.8762
2	12.757	VB	0.6692	9069.66406	211.47977	49.1238

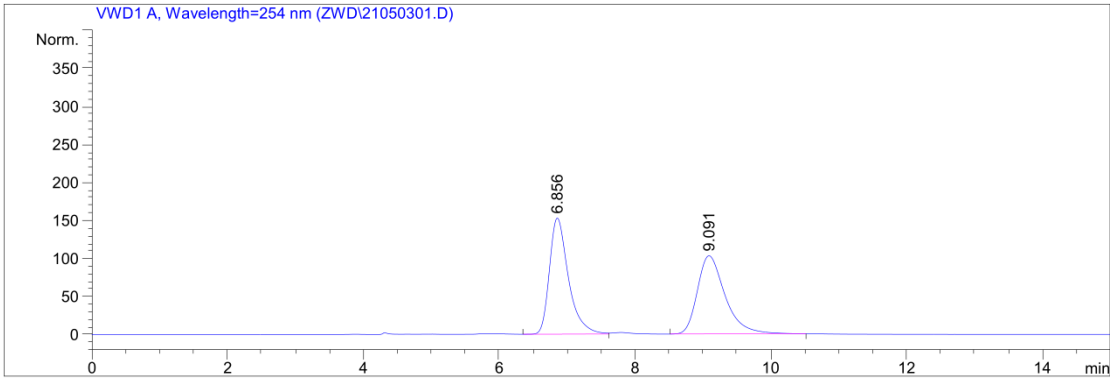


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.010	BV	0.9273	1.81964e4	297.62833	98.8486
2	13.078	VB	0.6613	211.94911	4.61224	1.1514

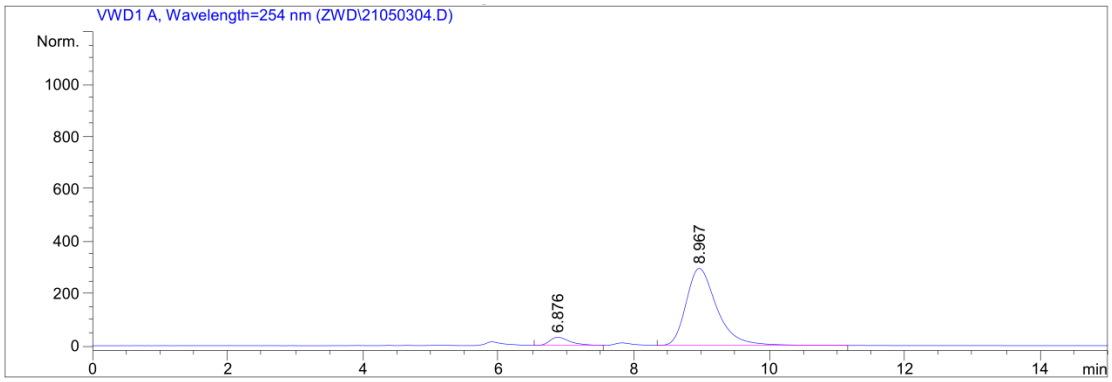


3am

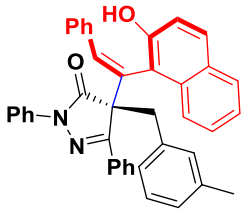
Prepared according to the procedure within 24 h as white solid (67 mg, 39% yield, dr > 20:1); mp 225-226 °C; $[\alpha]_D^{11}$ = -109.5 (*c* 0.20, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.60–7.29 (m, 8H), 7.08–6.61 (m, 10H), 3.48 (d, *J* = 13.7 Hz, 1H), 3.28 (d, *J* = 13.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2, 162.1, 154.4, 138.4, 137.0, 133.6, 132.7, 131.7, 131.2, 130.9, 130.7, 130.3, 129.7, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 128.2, 127.5, 127.0, 126.4, 125.6, 125.1, 123.5, 120.8, 120.3, 114.2, 67.6, 39.9; **HRMS** (ESI) m/z Calcd. for $C_{38}H_{29}N_2O_2S$ ($[M+H]^+$) 577.1944, Found 577.1926; **Enantiomeric excess** was determined to be 86% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{minor} = 6.9 min), t_{major} = 9.0 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.856	VV	0.2946	2980.47070	152.75111	50.4729
2	9.091	PB	0.4304	2924.62061	102.95380	49.5271

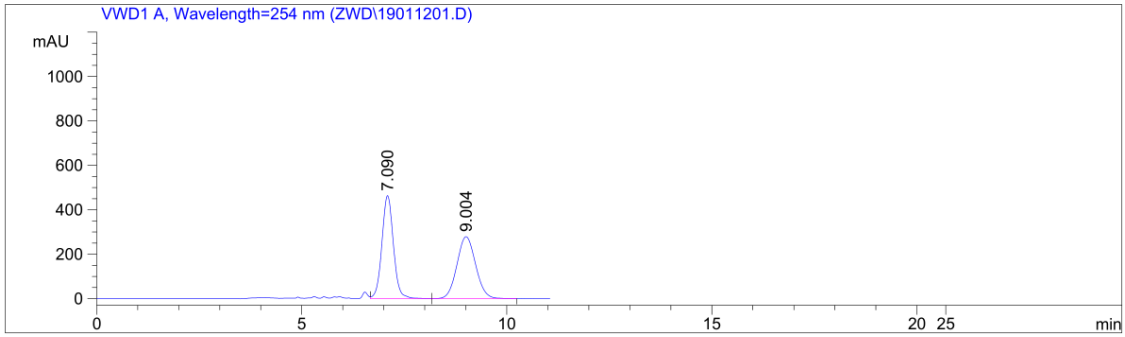


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.876	VV	0.3284	695.09583	31.90995	6.9096
2	8.967	VB	0.4803	9364.69922	295.59076	93.0904

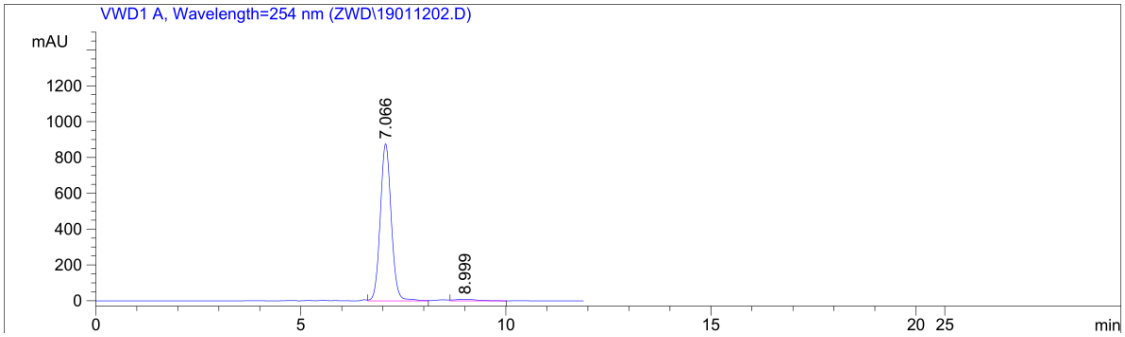


3ba

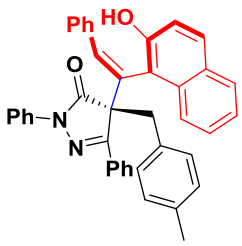
Prepared according to the procedure within 7 h as white solid (106 mg, 91% yield, dr > 20:1); mp 198-200 °C; $[\alpha]_D^{20}$ = -226.3 (*c* 0.40, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.06–7.75 (m, 6H), 7.58–7.50 (m, 2H), 7.46–7.39 (m, 5H), 7.24 (m, 2H), 7.18–7.13 (m, 1H), 6.95–6.81 (m, 5H), 6.78–6.70 (m, 3H), 6.63–6.60 (m, 2H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 1.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.5, 162.5, 154.4, 137.8, 137.6, 136.9, 135.1, 133.5, 131.4, 131.1, 130.2, 130.1, 130.0, 129.2, 129.0, 128.9, 128.6, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 126.4, 126.1, 126.0, 125.5, 123.2, 120.4, 120.2, 114.9, 67.7, 39.3, 21.0; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{33}N_2O_2$ ($[M+H]^+$) 585.2537, Found 585.2542; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.1 min, t_{minor} = 9.0 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.090	VV	0.3024	9148.93359	464.92157	50.5022
2	9.004	VB	0.4974	8966.97754	280.01254	49.4978

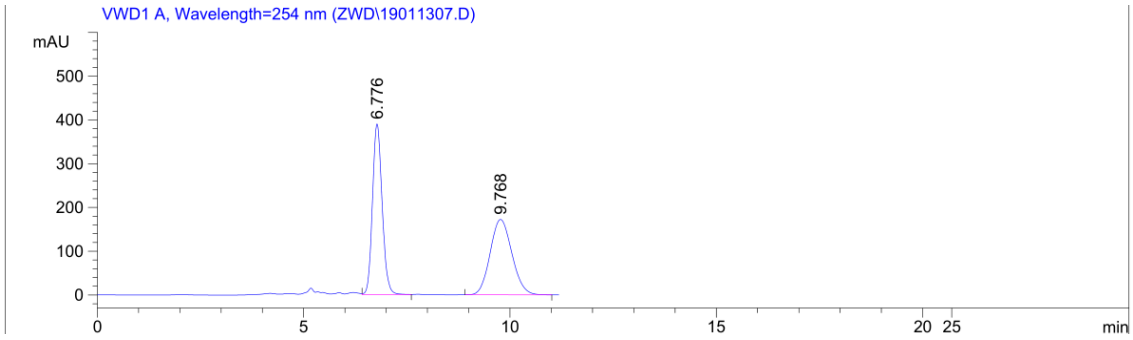


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.066	VV	0.2878	1.63817e4	877.15027	97.9032
2	8.999	VV	0.5462	350.84537	9.52421	2.0968

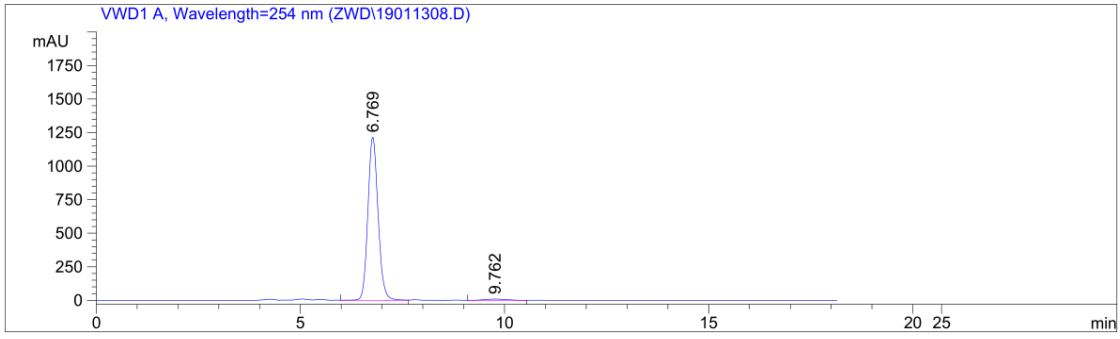


3ca

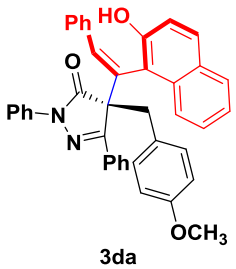
Prepared according to the procedure within 9 h as white solid (116 mg, 99% yield, dr > 20:1); mp 117-120 °C; $[\alpha]_D^{19}$ = -229.4 (*c* 1.06, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 8.09–7.74 (m, 6H), 7.57–7.36 (m, 7H), 7.25–7.09 (m, 3H), 6.93–6.71 (m, 9H), 6.62 (s, 1H), 3.51 (d, *J* = 13.8 Hz, 1H), 3.14 (d, *J* = 13.7 Hz, 1H), 2.09 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.45, 162.54, 154.43, 137.74, 137.00, 136.94, 135.10, 131.43, 131.13, 131.08, 130.52, 130.27, 130.07, 129.27, 129.06, 128.96, 128.84, 128.72, 128.45, 128.38, 128.13, 128.01, 126.39, 126.07, 125.50, 123.25, 120.39, 120.23, 114.96, 67.84, 39.03, 21.01; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{33}N_2O_2$ ($[M+H]^+$) 585.2537, Found 585.2539; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 6.8 min, t_{minor} = 9.8 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.776	VB	0.2534	6385.18701	390.44424	50.2381
2	9.768	VB	0.5722	6324.67236	172.38377	49.7619

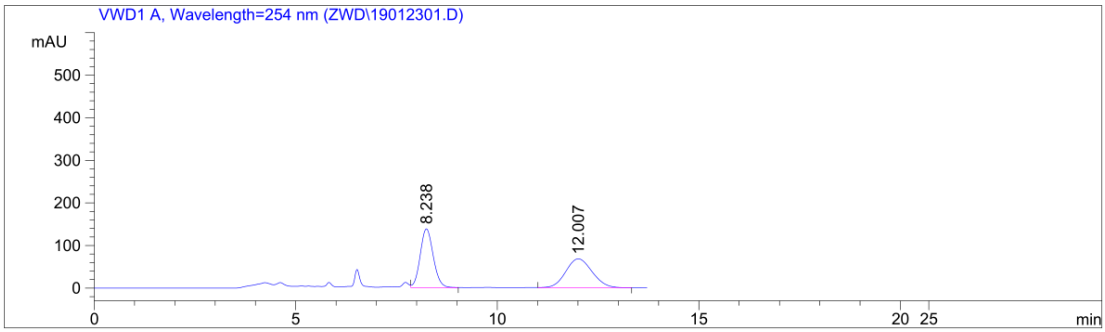


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.769	VV	0.2687	2.11955e4	1216.88818	98.1672
2	9.762	VV	0.6292	395.71576	9.60375	1.8328

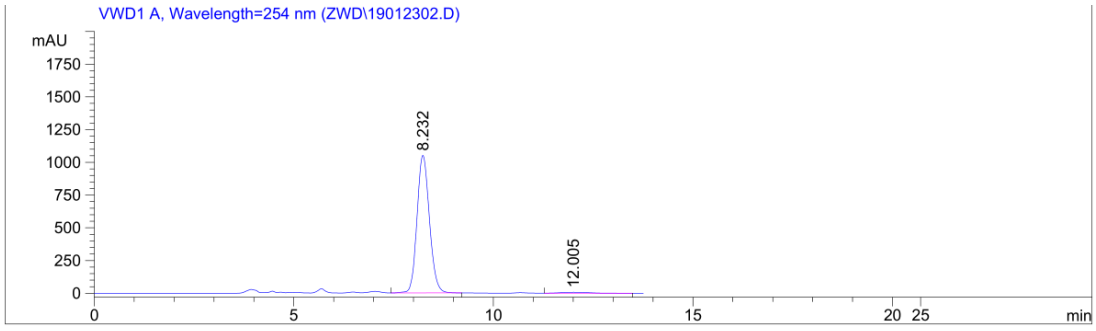


3da

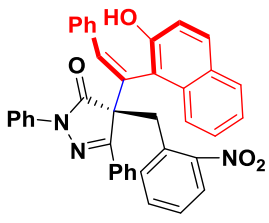
Prepared according to the procedure within 12 h as white solid (118 mg, 98% yield, dr > 20:1); mp 107-109 °C; $[\alpha]_D^{18}$ = -217.5 (*c* 0.48, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.90–7.74 (m, 4H), 7.57–7.37 (m, 7H), 7.26–7.11 (m, 3H), 6.90-6.73 (m, 7H), 6.62 (s, 1H), 6.48 (d, *J* = 8.1 Hz, 2H), 3.56 (s, 3H), 3.48 (d, *J* = 13.9 Hz, 1H), 3.13 (d, *J* = 13.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.4, 162.5, 158.7, 154.4, 137.8, 137.0, 135.1, 131.4, 131.1, 131.1, 130.3, 130.2, 130.1, 129.3, 129.0, 128.7, 128.4, 128.3, 128.1, 128.0, 126.4, 126.1, 125.6, 125.5, 123.3, 120.4, 120.2, 115.0, 113.5, 67.9, 55.0, 38.6; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{33}N_2O_3$ ($[M+H]^+$) 601.2486, Found 601.2496; **Enantiomeric excess** was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 8.2 min, t_{minor} = 12.0 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.238	VB	0.3502	3113.99365	138.24484	50.0373
2	12.007	BB	0.7117	3109.35205	67.92660	49.9627

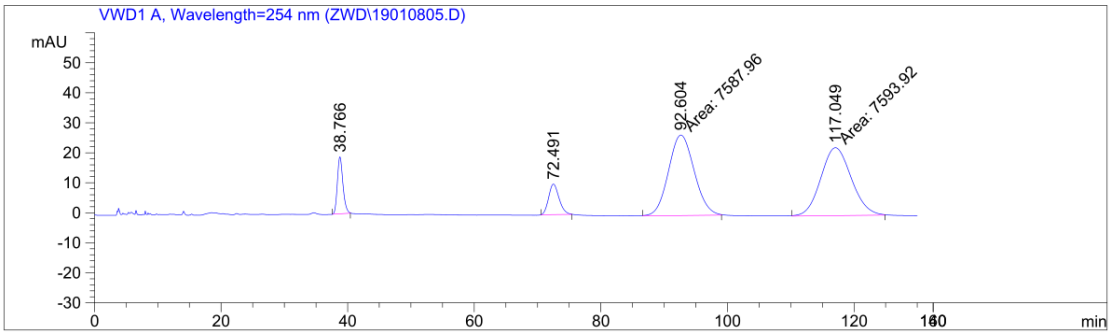


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.232	VB	0.3354	2.27396e4	1051.05920	98.5335
2	12.005	VB	0.7395	338.45093	7.29217	1.4665

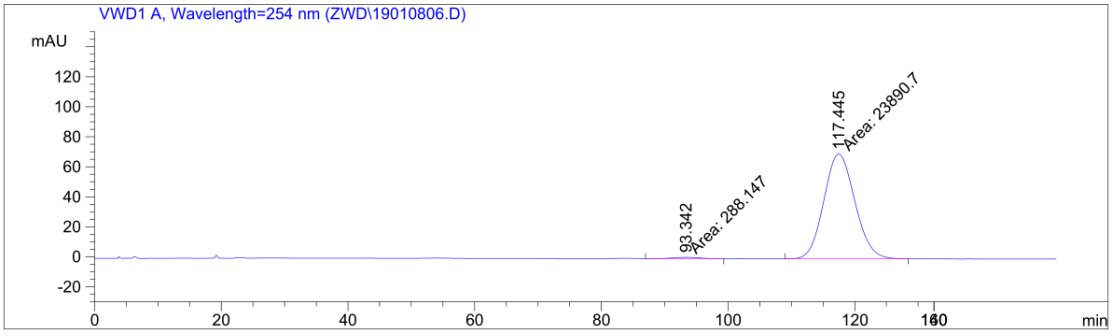


3ea

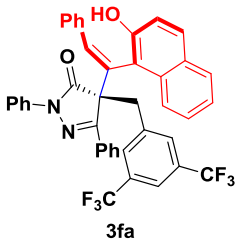
Prepared according to the procedure within 6 h as white solid (169 mg, 91% yield, dr > 20:1); mp 106-109 °C; $[\alpha]_D^{20}$ = -200.6 (*c* 1.02, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.10–7.75 (m, 6H), 7.59–7.35 (m, 8H), 7.25–7.05 (m, 6H), 6.91–6.70 (m, 5H), 6.60 (s, 1H), 3.99 (d, *J* = 14.5 Hz, 1H), 3.82 (d, *J* = 14.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.8, 162.3, 154.6, 150.2, 137.9, 136.8, 134.9, 132.3, 132.1, 131.7, 131.6, 131.3, 130.0, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 126.6, 126.2, 125.4, 124.9, 123.4, 120.2, 120.0, 114.4, 66.9, 33.8; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}N_3O_4$ ($[M+H]^+$) 616.2231, Found 616.2233; **Enantiomeric excess** was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{minor} = 93.3 min, t_{major} = 117.4 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.766	BB	0.9378	1168.57397	18.98912	6.6695
2	72.491	BB	1.4330	1170.78711	10.18351	6.6821
3	92.604	MM	4.7136	7587.95557	26.83012	43.3072
4	117.049	MM	5.5918	7593.92236	22.63398	43.3412



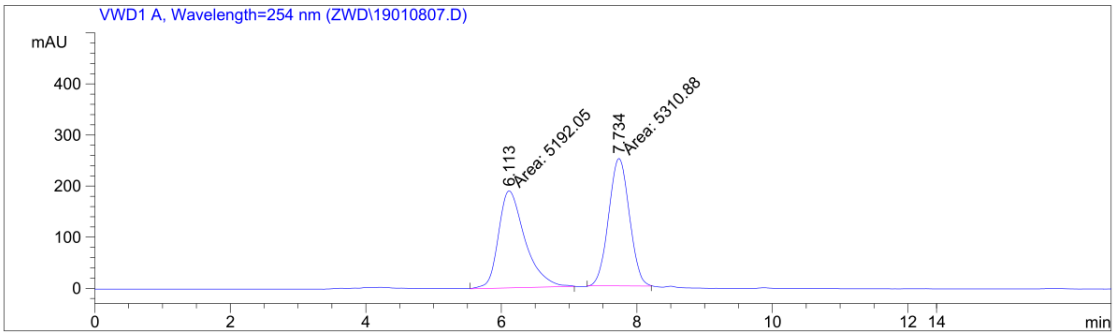
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	93.342	MM	5.0186	288.14679	9.56934e-1	1.1917
2	117.445	MM	5.6971	2.38907e4	69.89099	98.8083



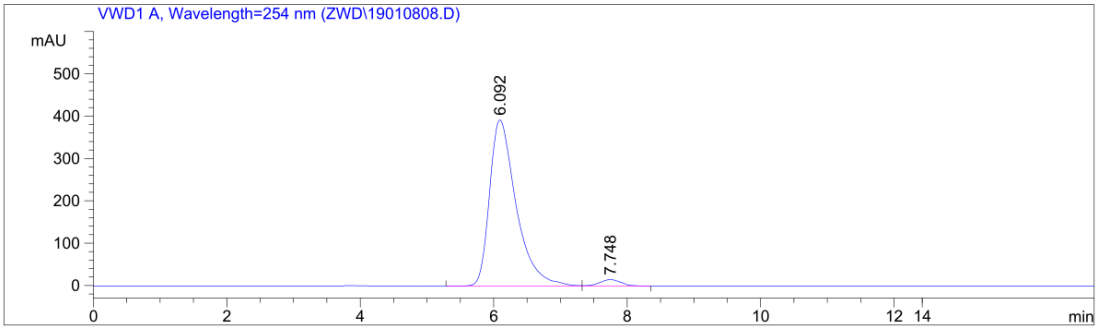
3fa

Prepared according to the procedure within 23 h as white solid (129 mg, 91% yield, dr > 20:1); mp 73-76 °C; $[\alpha]_D^{17}$ = -202.6 (*c* 3.31, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.02 (d, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.83–7.78 (m, 3H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.58–7.54 (m, 2H), 7.47–7.41 (m, 5H), 7.31–7.19 (m, 5H), 6.96–6.87 (m, 3H), 6.80 (d, *J* = 7.3 Hz, 2H), 6.69 (s, 1H), 3.69 (d, *J* = 13.7 Hz, 1H), 3.25 (d, *J* = 13.7 Hz, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$) δ -63.26; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.6, 161.7, 154.4,

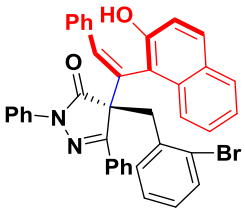
138.1, 136.5, 136.4, 134.8, 131.7, 131.50, 131.4, 131.2, 131.1, 129.6 (q, J = 2.8 Hz), 129.2 (q, J = 30.1 Hz), 129.1, 129.0, 129.0, 128.6, 128.4, 128.1, 127.9, 126.7, 126.3, 125.3, 123.5, 122.74 (q, J = 280.1 Hz), 121.4, 120.1, 119.9, 114.3, 67.0, 38.7; **HRMS** (ESI) m/z Calcd. for $C_{42}H_{29}F_6N_2O_2$ ([M+H]$^+$) 707.2128, Found 707.2128; **Enantiomeric excess** was determined to be 94% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 6.1 min, t_{minor} = 7.7 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.113	MM	0.4552	5192.04785	190.11078	49.4343
2	7.734	MM	0.3547	5310.88232	249.55434	50.5657

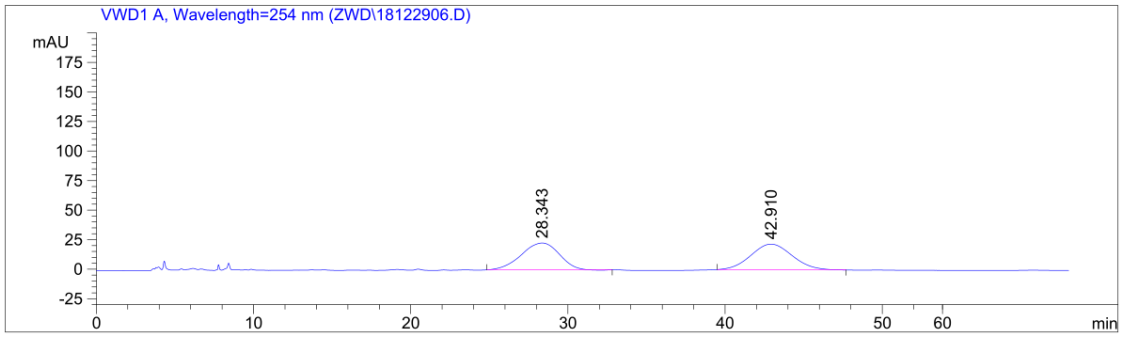


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.092	BV	0.4163	1.08595e4	392.12042	96.9900
2	7.748	VP	0.3378	337.01279	15.08564	3.0100

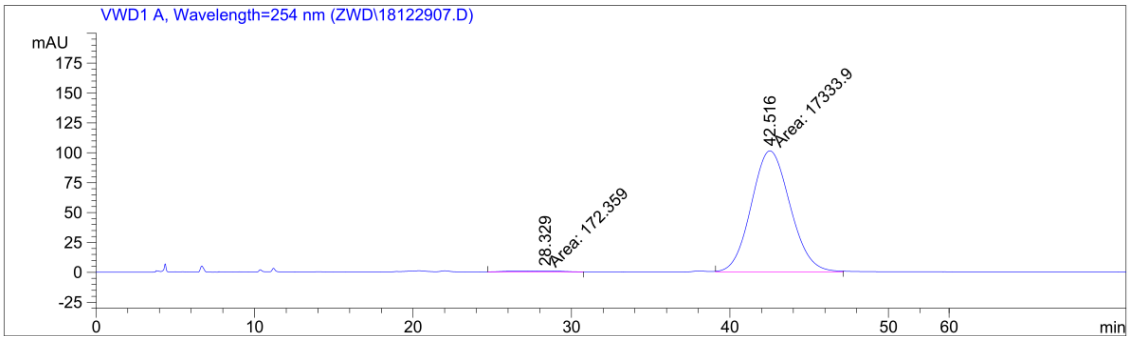


3ga

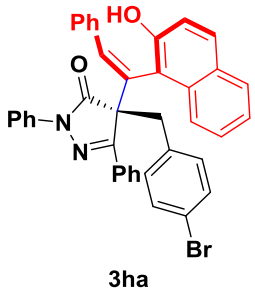
Prepared according to the procedure within 1 h as white solid (129.3 mg, 99% yield, dr > 20:1); mp 189-190 °C; $[\alpha]_D^{20}$ = -171.5 (c 0.40, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.03 (d, J = 7.6 Hz, 2H), 7.89-7.85 (m, 3H), 7.77 (d, J = 8.0 Hz, 1H), 7.55–7.39 (m, 7H), 7.32–7.22 (m, 3H), 7.13 (t, J = 7.7 Hz, 1H), 7.03–6.83 (m, 6H), 6.76 (d, J = 7.6 Hz, 2H), 6.65 (s, 1H), 3.83 (d, J = 14.8 Hz, 1H), 3.45 (d, J = 14.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.0, 162.7, 154.5, 137.7, 137.0, 135.0, 133.9, 133.2, 131.6, 131.2, 131.2, 130.6, 130.4, 130.0, 129.3, 129.0, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2, 128.0, 127.1, 126.4, 126.1, 125.3, 125.2, 123.3, 120.3, 120.1, 114.8, 66.6, 37.6; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}BrN_2O_2$ ([M+H]$^+$) 649.1485, Found 649.1488; **Enantiomeric excess** was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{minor} = 28.3 min, t_{major} = 42.5 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.343	BP	2.0102	3793.62842	22.70831	48.7089
2	42.910	BB	2.1695	3994.73779	21.77478	51.2911

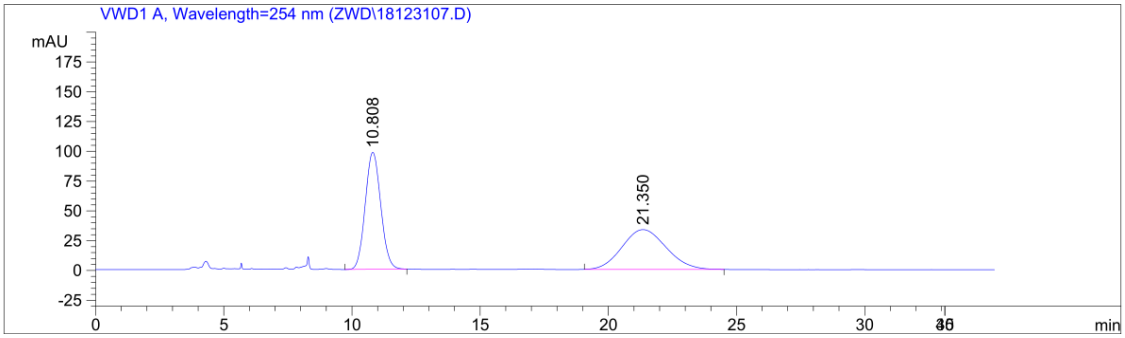


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.329	MM	3.1431	172.35883	9.13955e-1	0.9846
2	42.516	MM	2.8490	1.73339e4	101.40337	99.0154

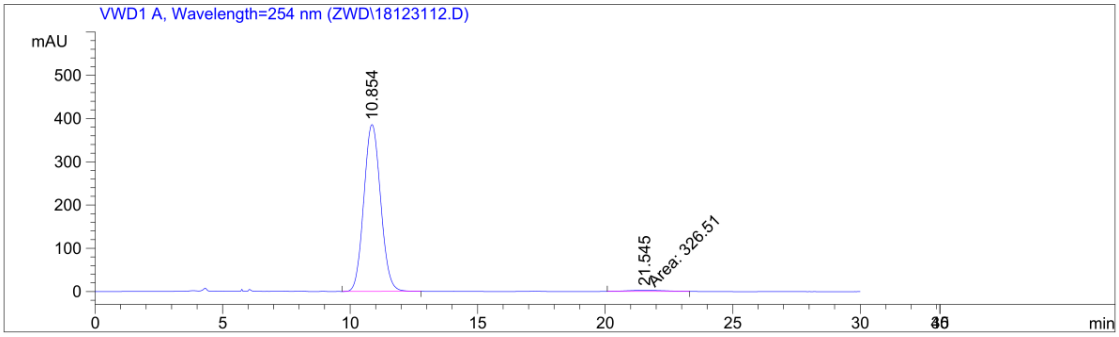


3ha

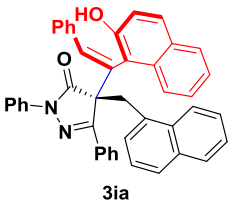
Prepared according to the procedure within 10 h as white solid (119 mg, 92% yield, dr > 20:1); mp 118-120 °C; $[\alpha]_D^{20}$ = -204.6 (*c* 0.54, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.07–7.73 (m, 6H), 7.48 (m, 7H), 7.24–7.03 (m, 5H), 6.94–6.68 (m, 7H), 6.63 (s, 1H), 3.49 (d, *J* = 13.8 Hz, 1H), 3.11 (d, *J* = 13.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 162.2, 154.4, 137.9, 136.8, 135.0, 132.8, 131.4, 131.3, 131.3, 131.2, 131.0, 129.8, 129.7, 129.3, 129.1, 129.0, 128.8, 128.5, 128.3, 128.2, 128.0, 126.6, 126.2, 125.4, 123.4, 121.6, 120.3, 120.2, 114.7, 67.4, 38.7; **HRMS** (ESI) m/z Calcd. for $C_{40}H_{30}BrN_2O_2$ ($[M+H]^+$) 649.1485, Found 649.1486; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.9 min, t_{minor} = 21.5 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.808	VB	0.6565	4142.15381	98.22169	50.7201
2	21.350	BB	1.7031	4024.53101	33.49734	49.2799

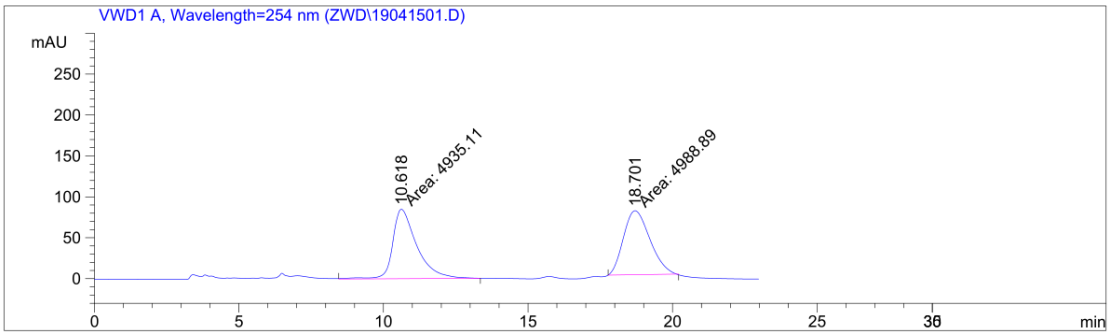


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.854	VB	0.7154	1.76952e4	386.01068	98.1882
2	21.545	MM	1.9334	326.51001	2.81470	1.8118

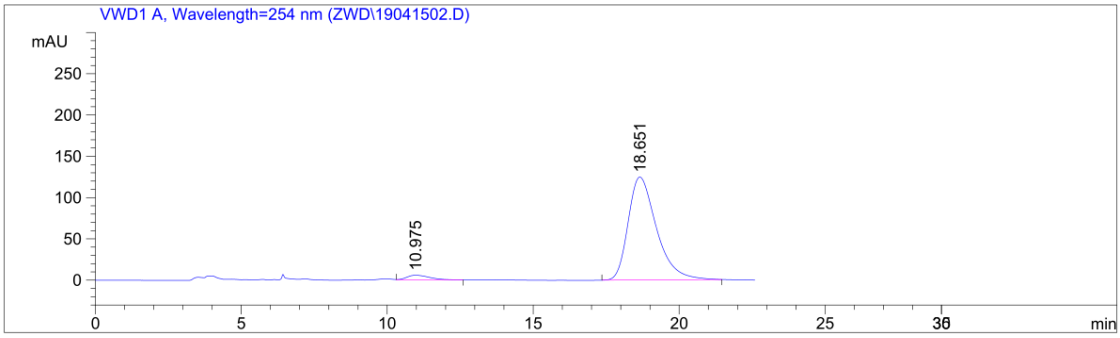


3ia

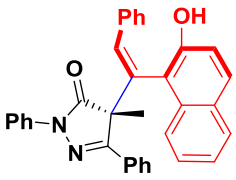
Prepared according to the procedure within 72 h as white solid (79 mg, 64% yield, dr > 20:1); mp 208-211 °C; $[\alpha]_D^{20}$ = -157.2 (*c* 0.47, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.09–7.78 (m, 5H), 7.66-7.61 (m, 2H), 7.55–7.41 (m, 5H), 7.36–7.31 (m, 4H), 7.26–7.08 (m, 5H), 7.01–6.77 (m, 7H), 6.63 (s, 1H), 4.27 (d, *J* = 14.3 Hz, 1H), 3.49 (d, *J* = 14.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.5, 162.6, 154.7, 138.1, 136.5, 135.1, 133.6, 131.8, 131.4, 131.3, 131.1, 130.7, 130.1, 130.0, 129.4, 129.0, 128.8, 128.7, 128.6, 128.4, 128.4, 128.3, 128.2, 128.0, 127.8, 126.3, 126.1, 125.7, 125.6, 125.5, 124.4, 124.0, 123.3, 120.3, 120.3, 114.9, 67.2, 34.4; **HRMS** (ESI) m/z Calcd. for $C_{44}H_{32}N_2NaO_2$ ($[M+Na]^+$) 643.2356, Found 643.2359; **Enantiomeric excess** was determined to be 92% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{minor} = 10.9 min, t_{major} = 18.7 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.618	MM	0.9693	4935.11133	84.85335	49.7291
2	18.701	MM	1.0626	4988.88672	78.25082	50.2709

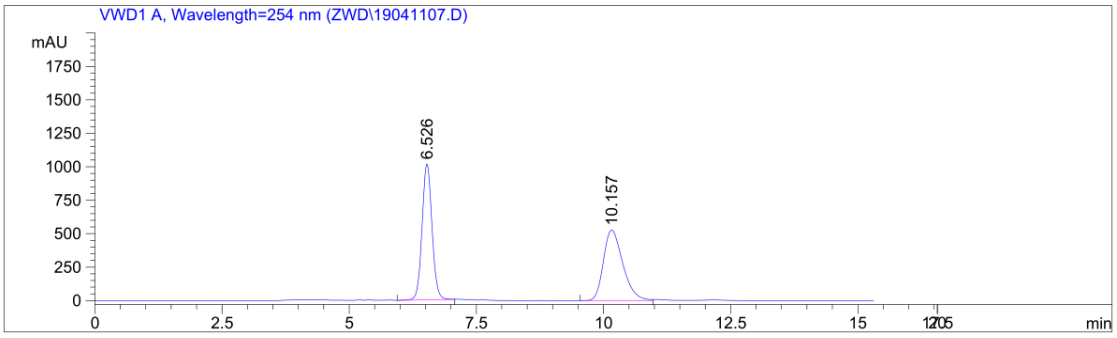


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.975	VB	0.7864	333.48544	5.92339	3.8043
2	18.651	BB	1.0303	8432.59570	124.74757	96.1957

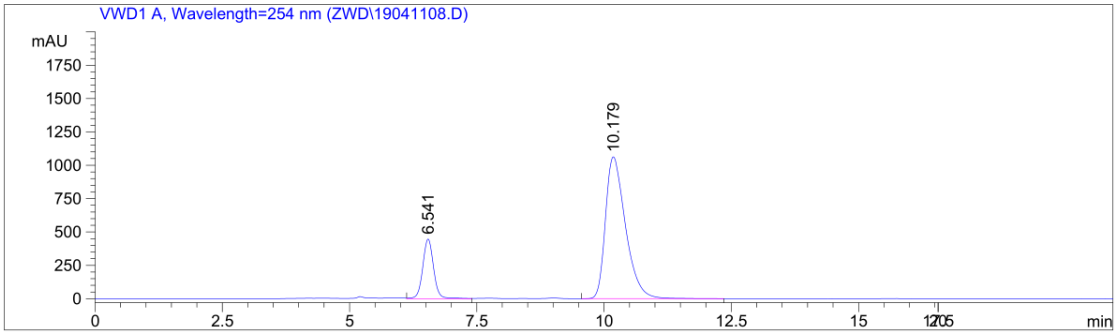


3ja

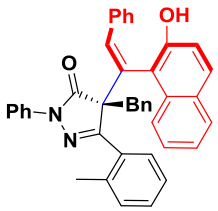
Prepared according to the procedure within 8 h as white solid (92.3 mg, 93% yield, dr > 20:1); mp 203-206 °C; $[\alpha]_D^{21}$ = -107.0 (*c* 1.20, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.51–7.34 (m, 6H), 7.28–7.15 (m, 3H), 7.02–6.80 (m, 4H), 6.73 (d, *J* = 7.4 Hz, 2H), 6.59 (s, 1H), 1.58 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.0, 165.1, 154.0, 137.6, 137.4, 135.1, 131.7, 131.1, 130.9, 130.3, 129.8, 129.2, 129.2, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 126.2, 126.2, 125.1, 123.2, 120.1, 119.7, 115.0, 61.7, 19.7; **HRMS** (ESI) m/z Calcd. for $C_{34}H_{27}N_2O_2$ ($[M+H]^+$) 495.2067, Found 495.2072; **Enantiomeric excess** was determined to be 63% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{minor} = 6.5 min, t_{major} = 10.2 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.526	VB	0.2122	1.39003e4	1015.17383	49.8736
2	10.157	BV	0.4065	1.39707e4	527.65601	50.1264

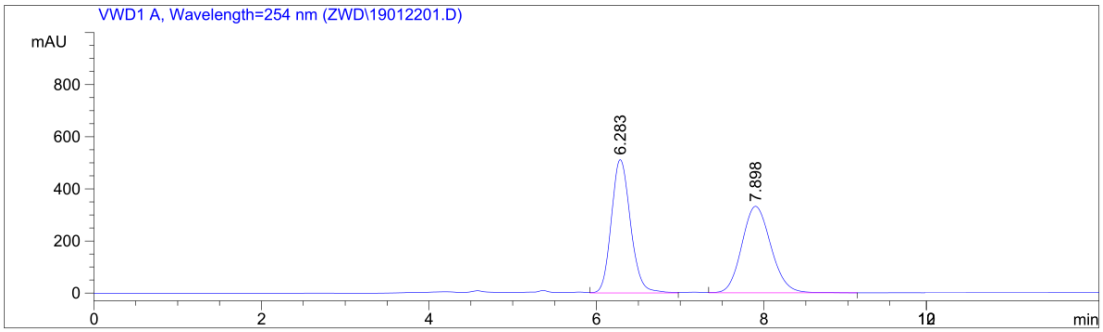


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.541	VV	0.2313	6687.86035	447.12073	18.6921
2	10.179	BB	0.4166	2.90913e4	1063.69214	81.3079

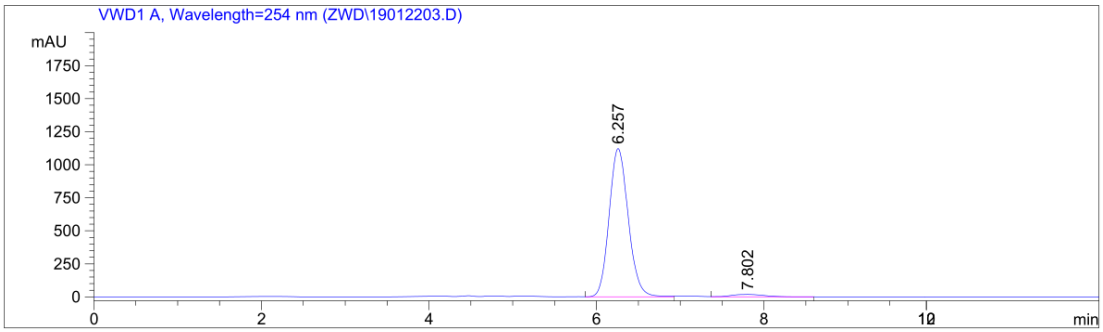


3ka

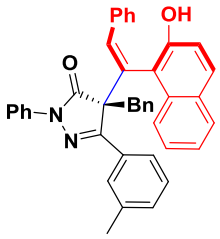
Prepared according to the procedure within 36 h as white solid (116 mg, 99% yield, dr > 20:1); mp 97-100 °C; $[\alpha]_D^{20}$ = -230.8 (*c* 0.45, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 3H), 7.77–7.74 (m, 3H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.43–7.32 (m, 5H), 7.24–7.18 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.01–6.82 (m, 8H), 6.74 (d, *J* = 7.0 Hz, 2H), 6.62 (s, 1H), 3.54 (d, *J* = 13.6 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.3, 162.6, 154.5, 138.6, 137.8, 136.9, 135.1, 133.7, 132.1, 131.5, 131.1, 130.2, 130.1, 129.3, 129.0, 128.9, 128.7, 128.5, 128.4, 128.1, 128.0, 127.4, 126.4, 126.4, 125.8, 125.2, 123.2, 120.4, 120.2, 115.0, 67.8, 39.4, 21.6; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{33}N_2O_2$ ($[M+H]^+$) 585.2537, Found 585.2546; **Enantiomeric excess** was determined to be 94% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 6.3 min, t_{minor} = 7.8 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.283	VV	0.2472	8163.64063	511.83102	50.3632
2	7.898	VP	0.3757	8045.89502	332.26428	49.6368

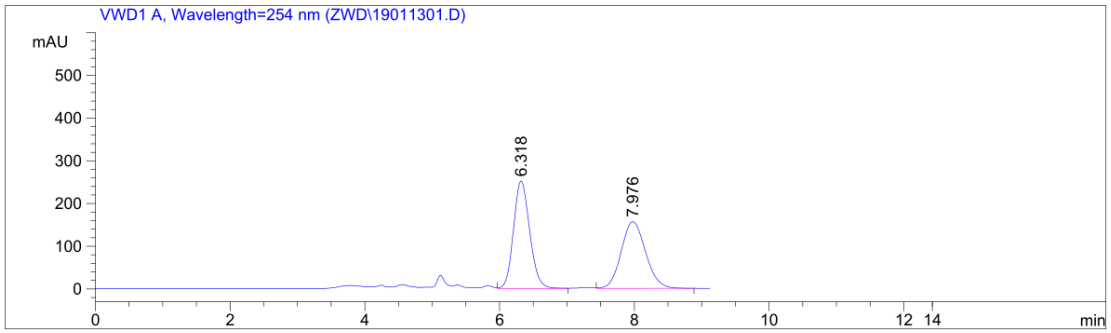


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.257	VV	0.2467	1.78486e4	1122.17419	97.1935
2	7.802	VB	0.4532	515.37982	17.93664	2.8065

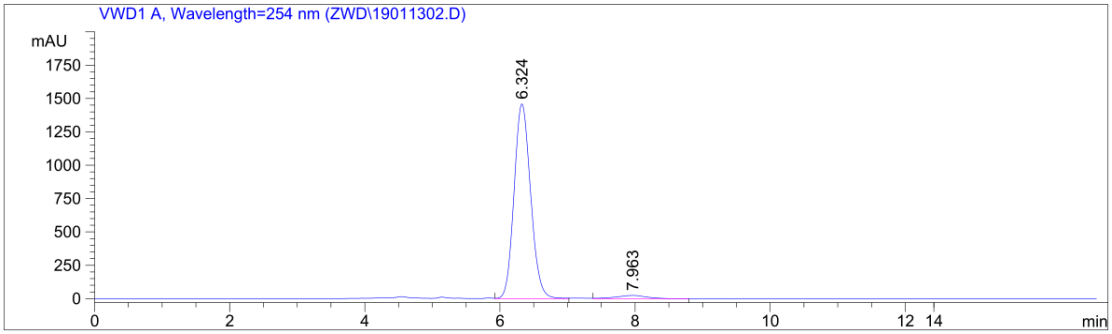


3la

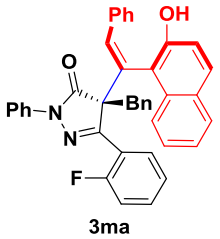
Prepared according to the procedure within 12 h as white solid (116 mg, 99% yield, dr > 20:1); mp 98-101 °C; $[\alpha]_D^{20}$ = -218.2 (*c* 0.62, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 3H), 7.77–7.74 (m, 3H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.44–7.31 (m, 5H), 7.24–7.10 (m, 3H), 7.01–6.81 (m, 8H), 6.74 (d, *J* = 7.6 Hz, 2H), 6.63 (s, 1H), 3.54 (d, *J* = 13.6 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.3, 162.6, 154.5, 138.6, 137.8, 136.9, 135.1, 133.7, 132.1, 131.5, 131.1, 130.2, 130.1, 129.3, 129.0, 128.9, 128.7, 128.5, 128.4, 128.1, 128.0, 127.4, 126.4, 126.4, 125.8, 125.2, 123.2, 120.4, 120.3, 115.0, 67.8, 39.4, 21.6; **HRMS** (ESI) m/z Calcd. for $C_{41}H_{33}N_2O_2$ ($[M+H]^+$) 585.2537, Found 585.2543; **Enantiomeric excess** was determined to be 94% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 6.3 min, t_{minor} = 8.0 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.318	VB	0.2591	4204.78955	251.57463	51.6161
2	7.976	VB	0.3935	3941.49194	156.16393	48.3839



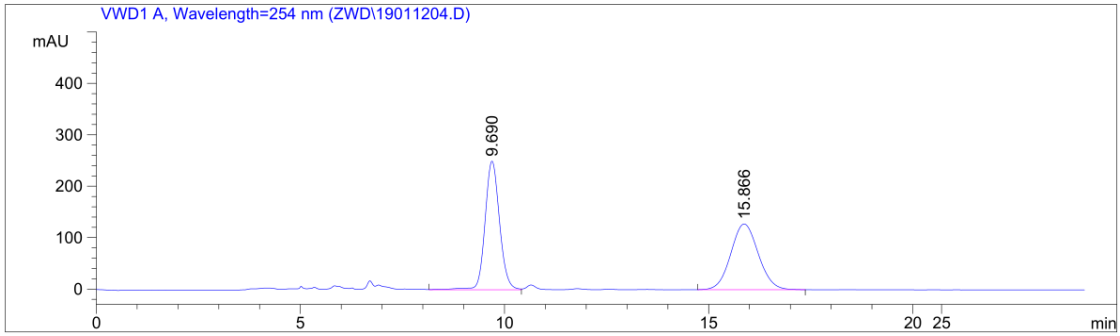
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.324	VV	0.2643	2.48718e4	1459.87610	97.0345
2	7.963	VB	0.4713	760.10895	24.19756	2.9655



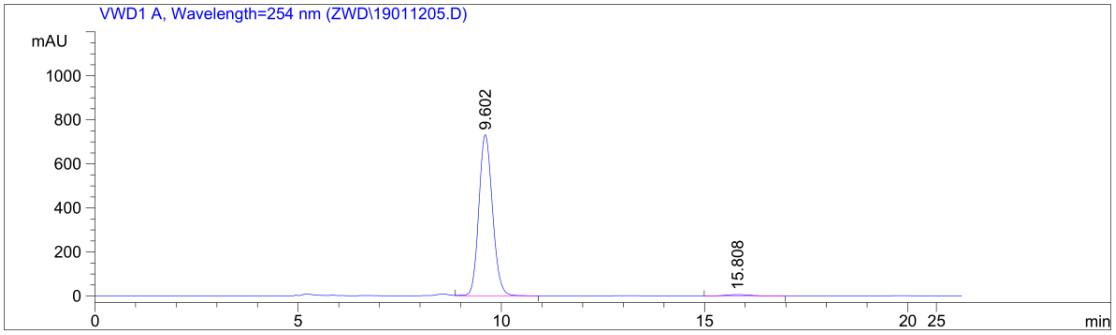
3ma

Prepared according to the procedure within 11 h as white solid (117 mg, 99% yield, dr > 20:1); mp 192-193 °C; $[\alpha]_D^{20}$ = -119.8 (*c* 0.77, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.95–7.66 (m, 5H), 7.55–7.33 (m, 4H), 7.27–7.13 (m, 5H), 7.03 (m, 6H), 6.87 (m, 3H), 6.75–6.65 (m, 3H), 3.41 (d, *J* = 13.8 Hz, 1H), 3.30 (d, *J* = 13.8 Hz, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$) δ -105.80; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.0, 160.7 (d, *J* = 252.1 Hz), 153.9, 138.3, 136.8, 135.0, 133.8, 132.6 (d, *J* = 8.8 Hz), 131.9, 131.4, 131.3, 131.0, 130.0, 129.3, 129.1, 129.0, 128.9, 128.4, 128.3, 128.2, 128.1, 128.1, 127.6, 126.3 (d, *J* = 40.3 Hz),

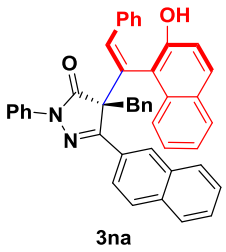
124.7, 124.5 (d, J = 3.5 Hz), 123.3, 120.3, 120.0, 119.4 (d, J = 11.3 Hz), 117.3 (d, J = 22.7 Hz), 115.1, 68.7, 39.2 (d, J = 5.8 Hz); **HRMS** (ESI) m/z Calcd. for $C_{40}H_{29}FN_2NaO_2$ ($[M+Na]^+$) 611.2105, Found 611.2107; **Enantiomeric excess** was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.6 min, t_{minor} = 15.8 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.690	VV	0.3823	6199.50586	250.12845	50.8249
2	15.866	BB	0.7307	5998.27686	127.88545	49.1751

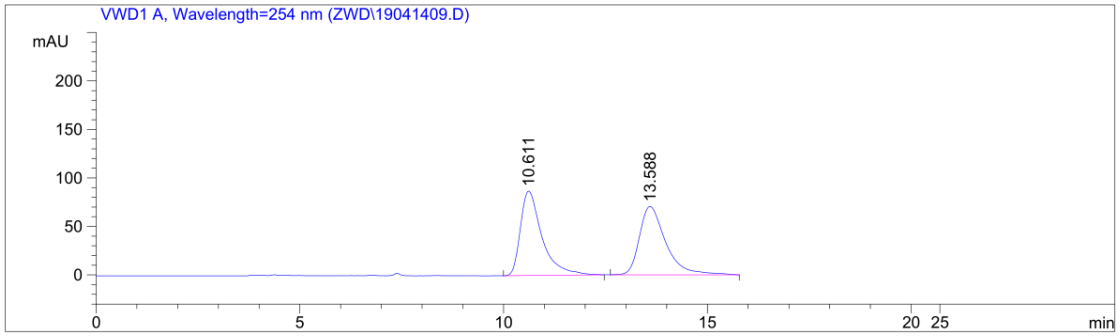


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.602	VB	0.3640	1.71856e4	732.35138	98.2260
2	15.808	BB	0.6924	310.37088	6.97448	1.7740

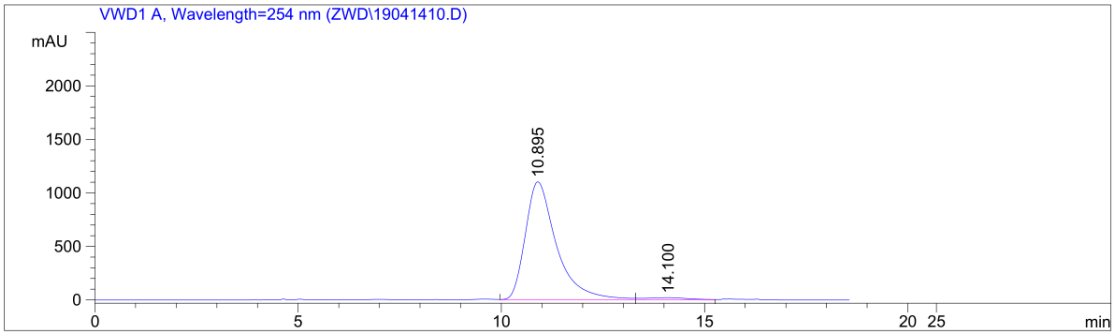


3na

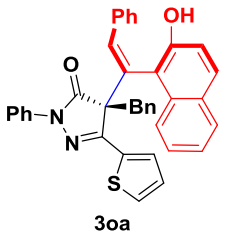
Prepared according to the procedure within 6 h as white solid (122.7 mg, 99% yield, dr > 20:1); mp 109-112 °C; $[\alpha]_D^{20}$ = -312.5 (c 1.07, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.48 (d, J = 3.7 Hz, 1H), 8.43–8.26 (m, 2H), 7.95–7.88 (m, 3H), 7.82–7.79 (m, 3H), 7.68–7.38 (m, 7H), 7.29–7.18 (m, 2H), 7.07–6.69 (m, 12H), 3.65 (d, J = 13.6, 2.7 Hz, 1H), 3.32 (d, J = 13.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.49, 162.35, 154.67, 137.84, 136.93, 135.09, 134.58, 133.70, 132.55, 131.50, 131.27, 130.37, 129.41, 129.30, 129.08, 129.03, 129.00, 128.95, 128.72, 128.64, 128.18, 128.15, 128.00, 127.96, 127.84, 127.44, 127.39, 126.79, 126.78, 126.55, 125.29, 124.21, 123.23, 120.51, 120.36, 114.89, 67.72, 39.69; **HRMS** (ESI) m/z Calcd. for $C_{44}H_{33}N_2O_2$ ($[M+H]^+$) 621.2537, Found 621.2538; **Enantiomeric excess** was determined to be 94% (determined by HPLC using chiral IC-H column, hexane/2-propanol = 60/1, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.9 min, t_{minor} = 14.1 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.611	PB	0.5502	3204.32959	87.06305	50.1858
2	13.588	BBA	0.6746	3180.60864	70.53582	49.8142

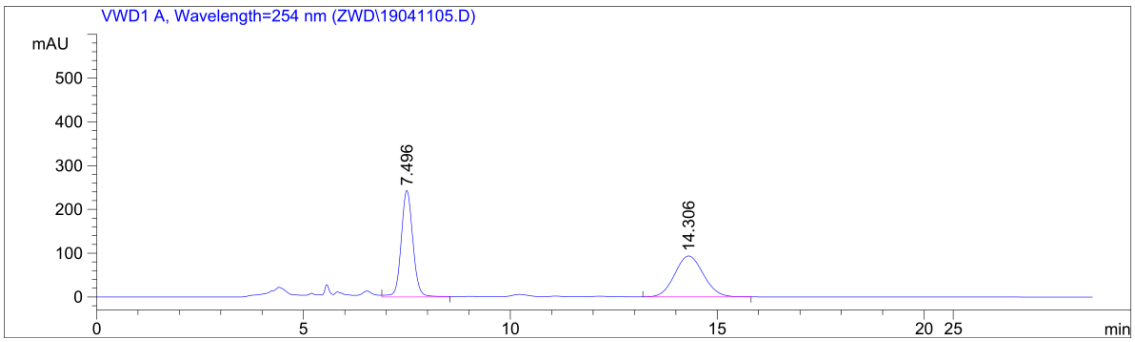


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.895	VB	0.7897	5.91353e4	1103.50232	97.2484
2	14.100	BV	1.0672	1673.18726	21.14826	2.7516

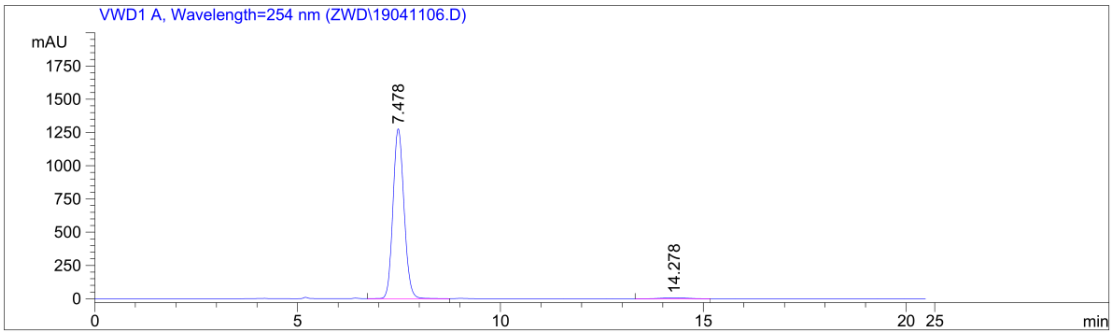


3oa

Prepared according to the procedure within 6 h as white solid (108 mg, 94% yield, dr > 20:1); mp 182-184 °C; $[\alpha]_D^{21}$ = -251.3 (*c* 0.96, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.87–7.62 (m, 6H), 7.51–7.34 (m, 4H), 7.25–7.10 (m, 4H), 7.03–6.96 (m, 3H), 6.93–6.84 (m, 5H), 6.80–6.68 (m, 3H), 3.49 (d, *J* = 13.6 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.6, 158.8, 154.3, 137.8, 136.7, 135.0, 133.9, 133.6, 131.5, 131.1, 130.4, 130.2, 129.6, 129.3, 129.1, 129.0, 128.6, 128.3, 128.2, 128.1, 127.6, 127.5, 126.5, 126.3, 125.2, 123.4, 120.4, 120.3, 115.1, 67.9, 39.2; **HRMS** (ESI) m/z Calcd. for $C_{38}H_{29}N_2O_2S$ ($[M+H]^+$) 577.1944, Found 577.1949; **Enantiomeric excess** was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.5 min, t_{minor} = 14.3 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.496	VB	0.3034	4810.35742	243.39771	51.4837
2	14.306	BB	0.7547	4533.10107	93.53902	48.5163



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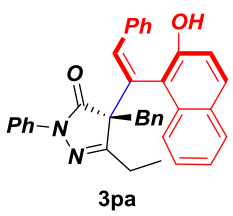
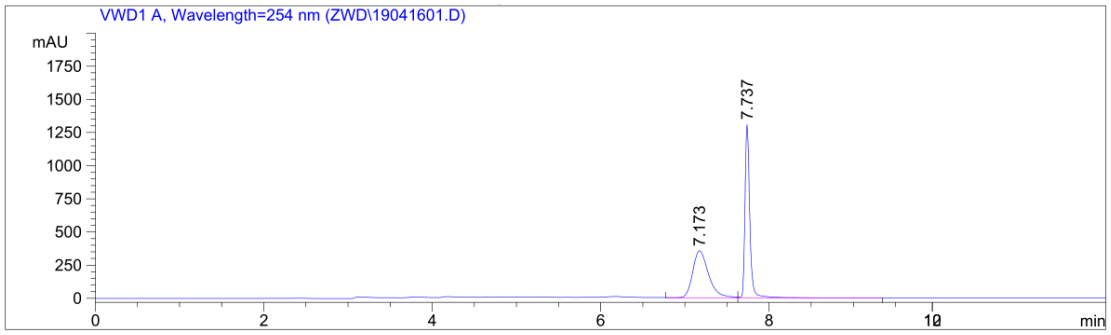
1	7.478	VB	0.2943	2.42658e4	1278.25842	98.6672
2	14.278	BV	0.7328	327.79517	6.90631	1.3328

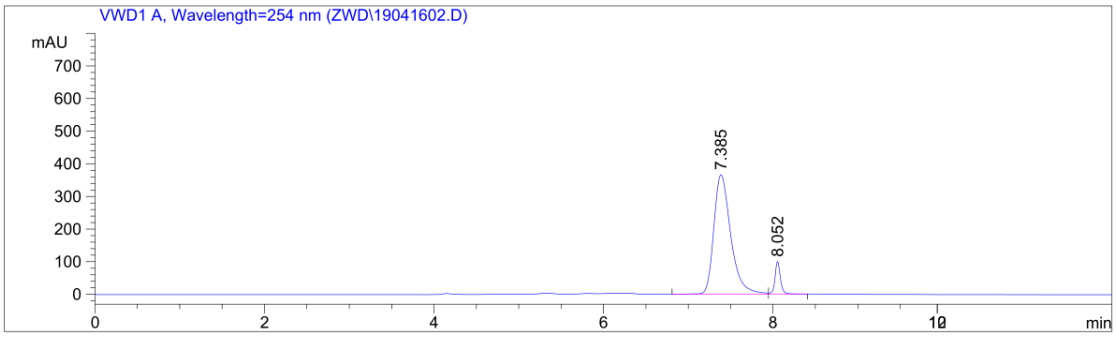


3pa

Prepared according to the procedure within 24 h as white solid (90 mg, 86% yield, dr > 20:1); mp 209-212 °C; $[\alpha]_D^{20}$ = -69.5 (*c* 1.56, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.87–7.65 (m, 5H), 7.39–7.35 (m, 4H), 7.23–7.08 (m, 5H), 7.00–6.75 (m, 7H), 6.54 (s, 1H), 3.13 (d, *J* = 13.5 Hz, 1H), 3.06–3.03 (m, 1H), 2.83–2.73 (m, 1H), 2.66 (d, *J* = 13.6 Hz, 1H), 1.41 (d, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.02, 168.03, 153.61, 137.27, 137.06, 134.79, 133.73, 132.86, 130.72, 130.36, 129.00, 128.88, 128.86, 128.75, 128.26, 128.18, 127.46, 127.00, 126.03, 123.25, 123.04, 120.35, 120.05, 115.52, 68.70, 38.84, 22.56, 9.27; **HRMS** (ESI) m/z Calcd. for $C_{36}H_{30}N_2NaO_2$ ($[M+Na]^+$) 545.2199, Found 545.2204; **Enantiomeric excess** was determined to be 84% (determined by HPLC using chiral IC-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.4 min, t_{minor} = 8.1 min).

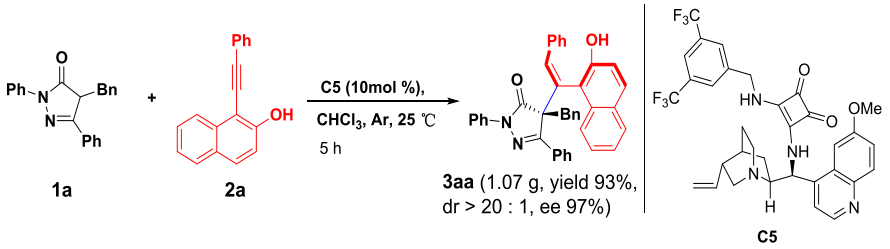


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.173	VV	0.2035	4806.06982	357.33591	47.1140
2	7.737	VB	0.0626	5394.87549	1310.58862	52.8860



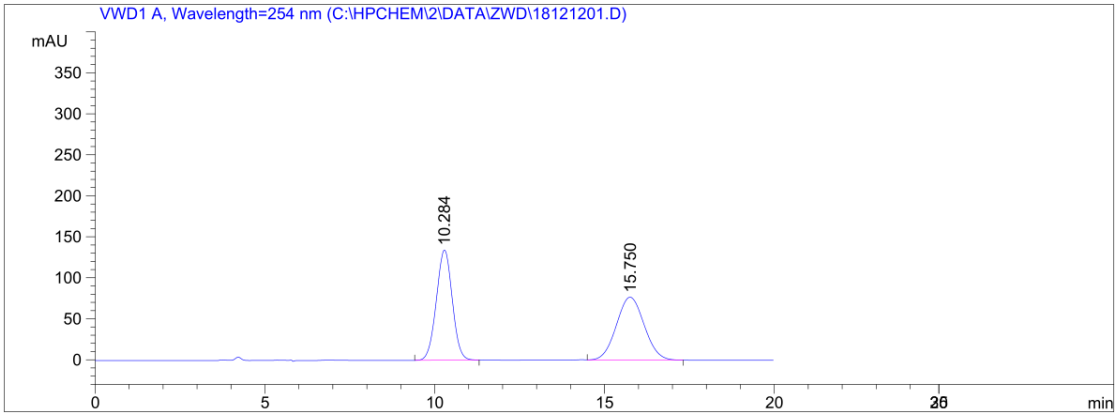
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.385	VV	0.2112	5074.84521	366.23849	91.9729
2	8.052	VB	0.0679	442.91916	99.55677	8.0271

Gram scale synthesis of compound 3aa



In a Schlenk tube, pyrazol-5-ones **1a** (783.4 mg, 2.4 mmol, 1.2 eq), **C5** (129 mg, 0.2 mmol, 0.1 eq) were added into $CHCl_3$ (20 mL) under argon atmosphere. Then ortho-alkynyl naphthol **2a** (488.6 mg,2.0 mmol,1.0 eq) was added in one portion and the reaction solution was stirred at 25 °C. After the reaction was complete (monitored by TLC), the solvent was removed under vacuum, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1 was used as the eluent) directly to give the product **3aa** (93% yield).

Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.9 min, t_{minor} = 15.0 min).



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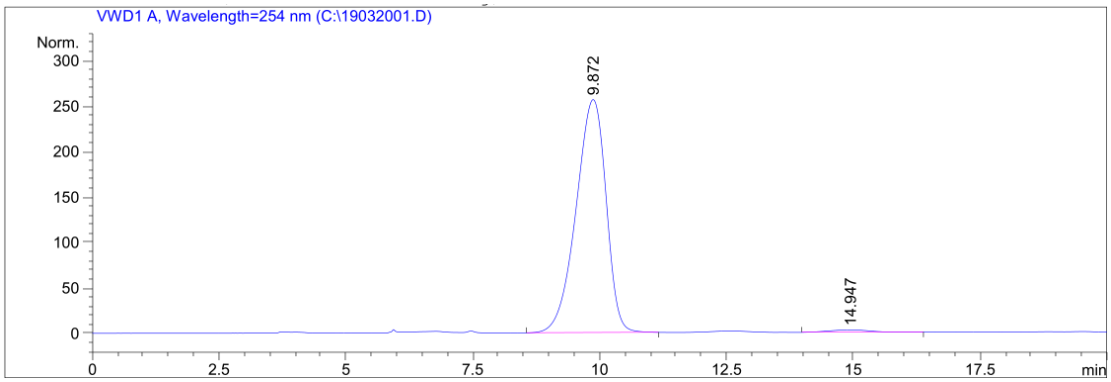
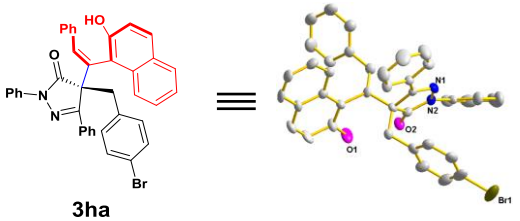
1	10.284	BB	0.5081	4396.92383	134.47589	49.9789
2	15.750	VB	0.8964	4400.63086	76.88025	50.0211



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.872	BB	0.6454	1.05649e4	256.32065	98.6260
2	14.947	BP	0.6569	147.18102	2.66723	1.3740

X-ray structures of 3ha



3ha

CCDC deposition number: 2012517

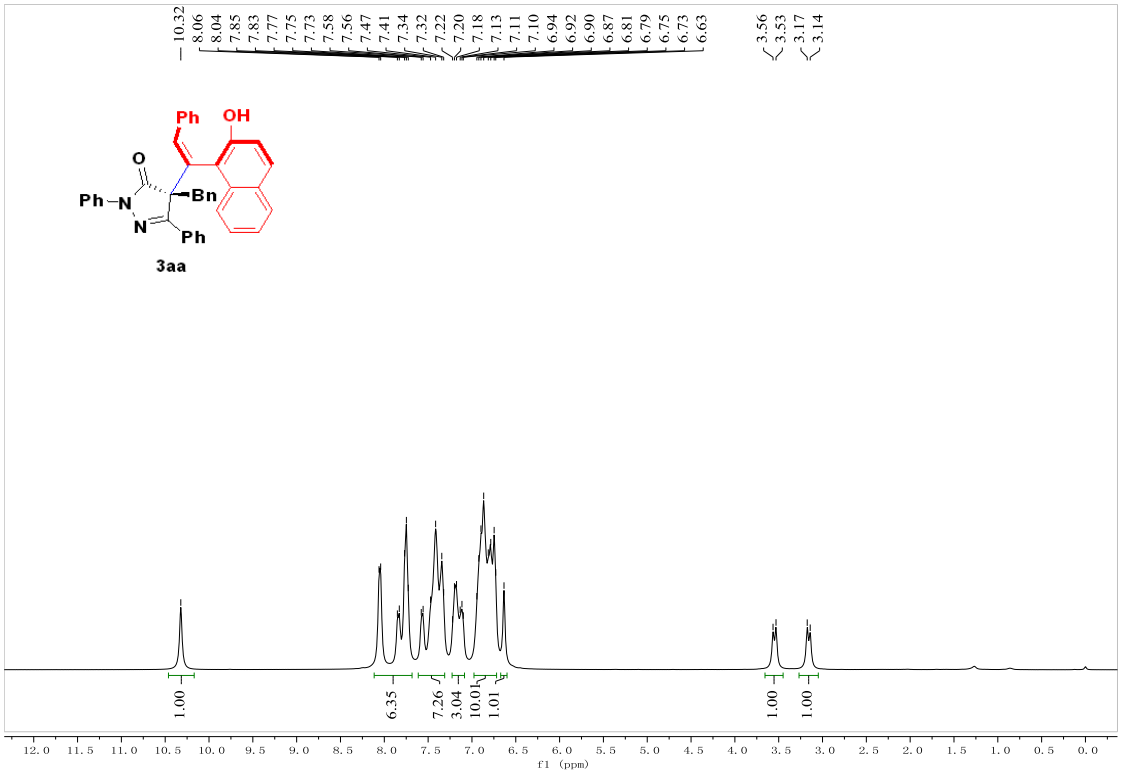
7. References

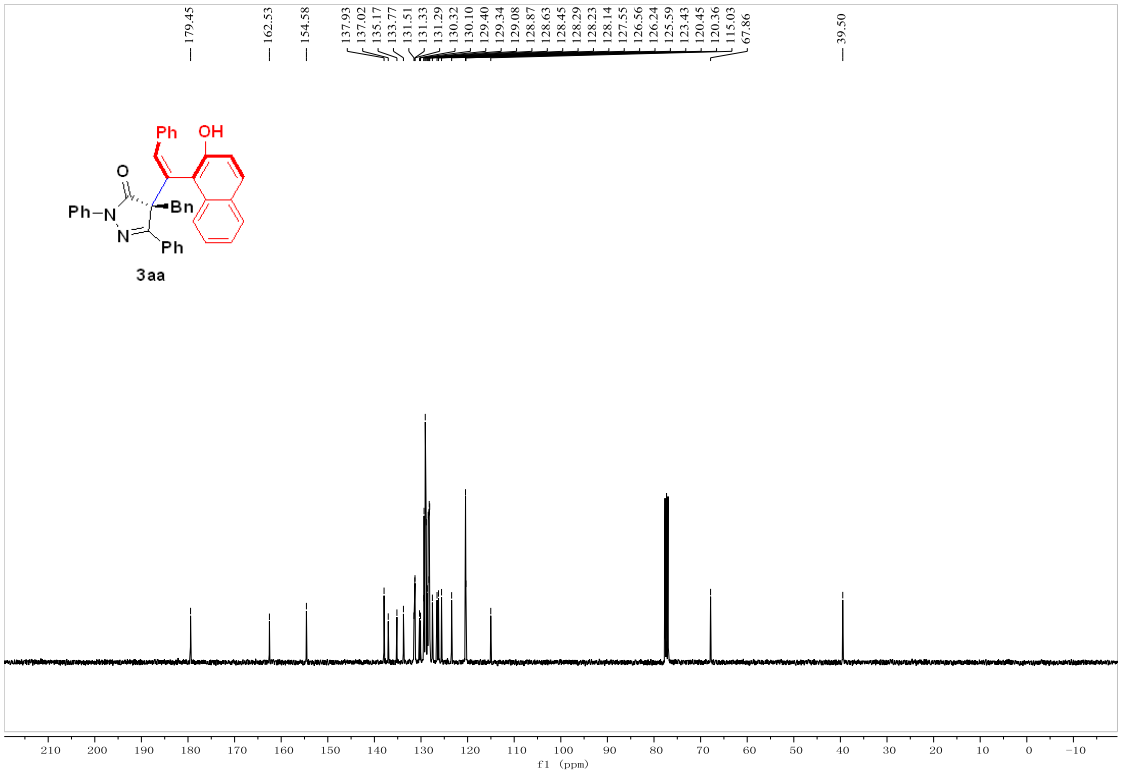
1. (a) P. E. Gagnon, J. L. Boivin, R. J. Paquin, *Can. J. Chem.*, 1953, **31**, 1025-1039; (b) H. Nakagawa, R. Ohyama, A. Kimata, T. Suzuki and N. Miyata, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 5939-5942; (c) Y.-H. Liao, W.-B. Chen, Z.-J. Wu, X.-L. Du, L.-F. Cun, X.-M. Zhang and W.-C. Yuan, *Adv. Synth. Catal.*, 2010, **352**, 827-832; (d) Z. Wang, Z. Yang, D. Chen, X. Liu, L. Lin and X. Feng, *Angew. Chem., Int. Ed.*, 2011, **50**, 4928-4932; (e) X. Bao, S. Wei, L. Zou, Y. He, F. Xue, J. Qu, and B. Wang, 2016, **52**, 11426-11429; (f) X. Sheng, J. Zhang, H. Yang and G. Jiang, *Org. Lett.*, 2017, **19**, 2618-2621.

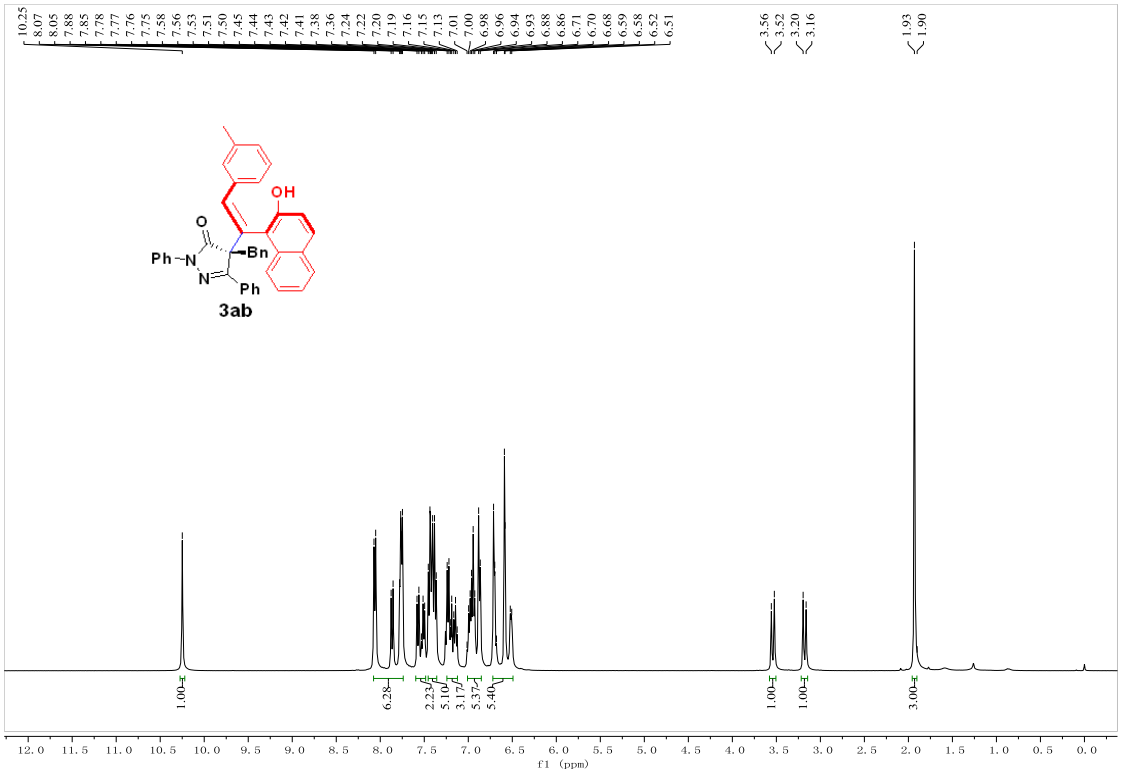
2. (a) S. Jia, Z. Chen, N. Zhang, Y. Tan, Y. Liu, J. Deng and H. Yan, *J. Am. Chem. Soc.*, 2018, **140**, 7056-7060; (b) D. Li, Y. Tan, L. Peng, S. Li, N. Zhang, Y. Liu and H. Yan, *Org. lett.*, 2018, **20**, 4959-4963; (c) A. Huang, L. Zhang, D. Li, Y. Liu, H. Yan and W. Li, *Org. lett.*, 2019, **21**, 95-99; (d) Y.-B. Wang, P. Yu, Z.-P. Zhou, J. Zhang, J. Wang, S.-H. Luo, Q.-S. Gu, K. N. Houk and B. Tan, *Nat. Catal.*, 2019, **2**, 504-513; (e) T. Xu, K. Chen, H.-Y. Zhu, W.-J. Hao, S.-J. Tu and B. Jiang, *Org. lett.*, 2020, 22, 2414-2418.

3. S. D. Pozo, S. Vera, M. Oiarbide and C. Palomo, *J. Am. Chem. Soc.*, 2017, **139**, 15308-15311.

8. NMR spectra for compounds



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Ph
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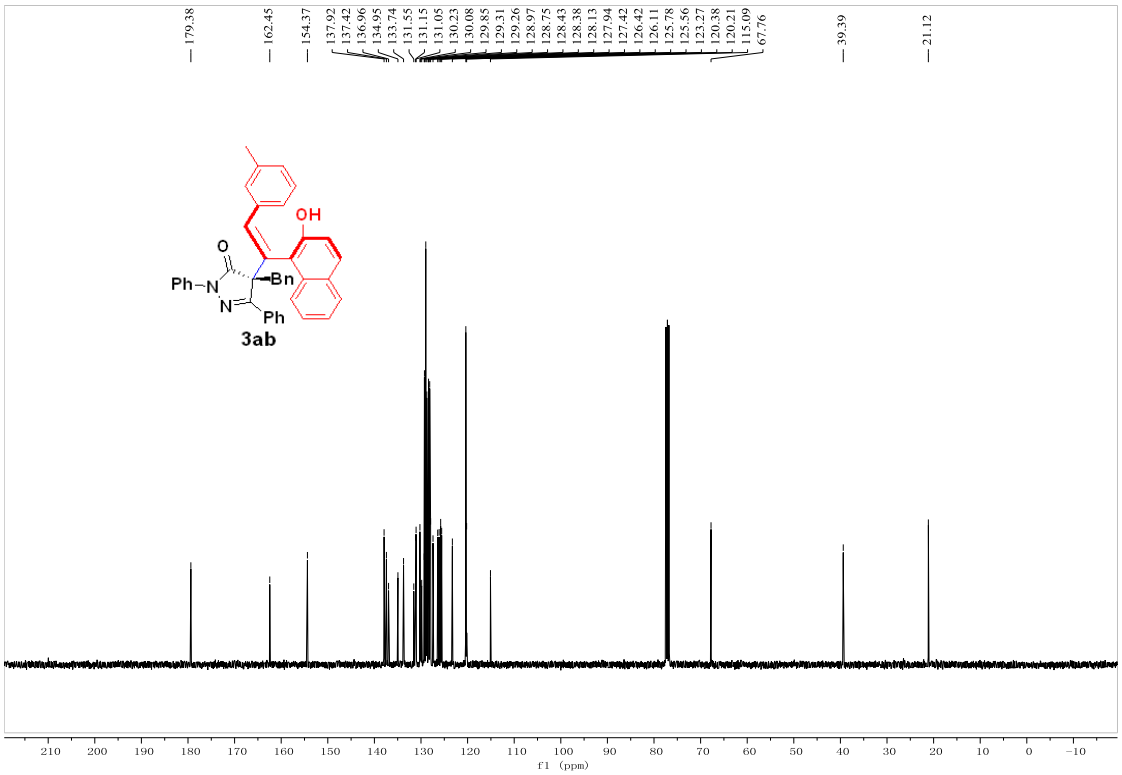
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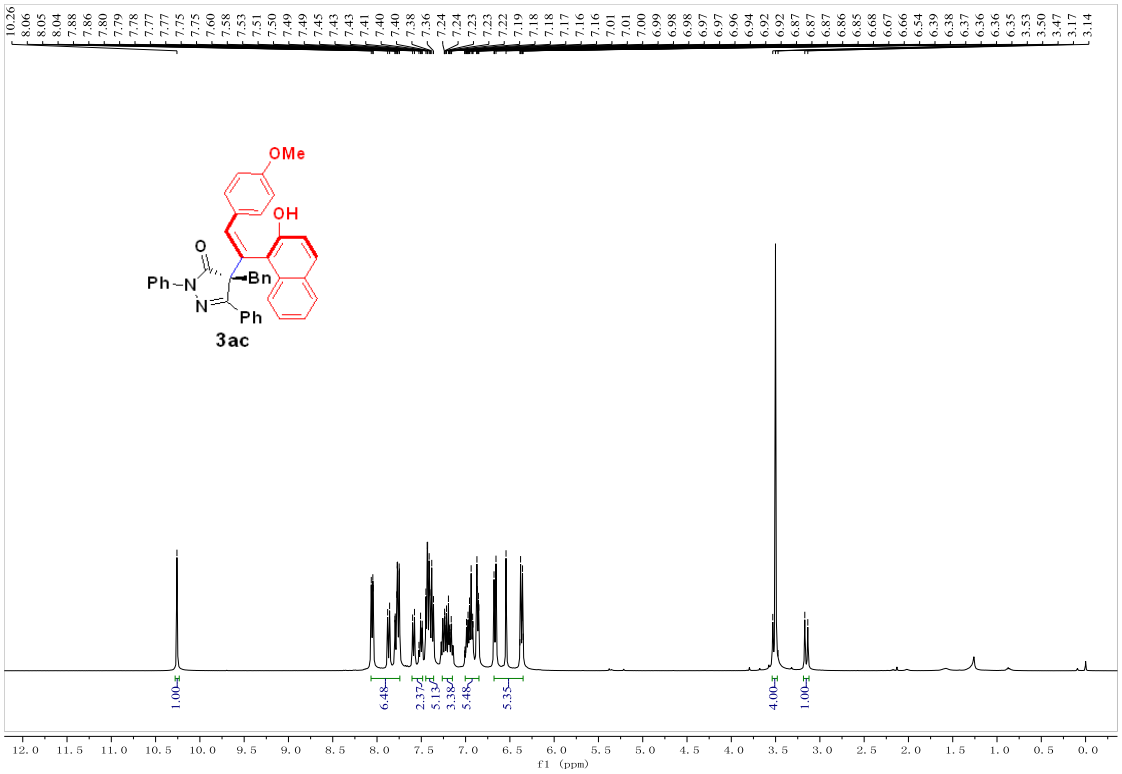
f1 (ppm)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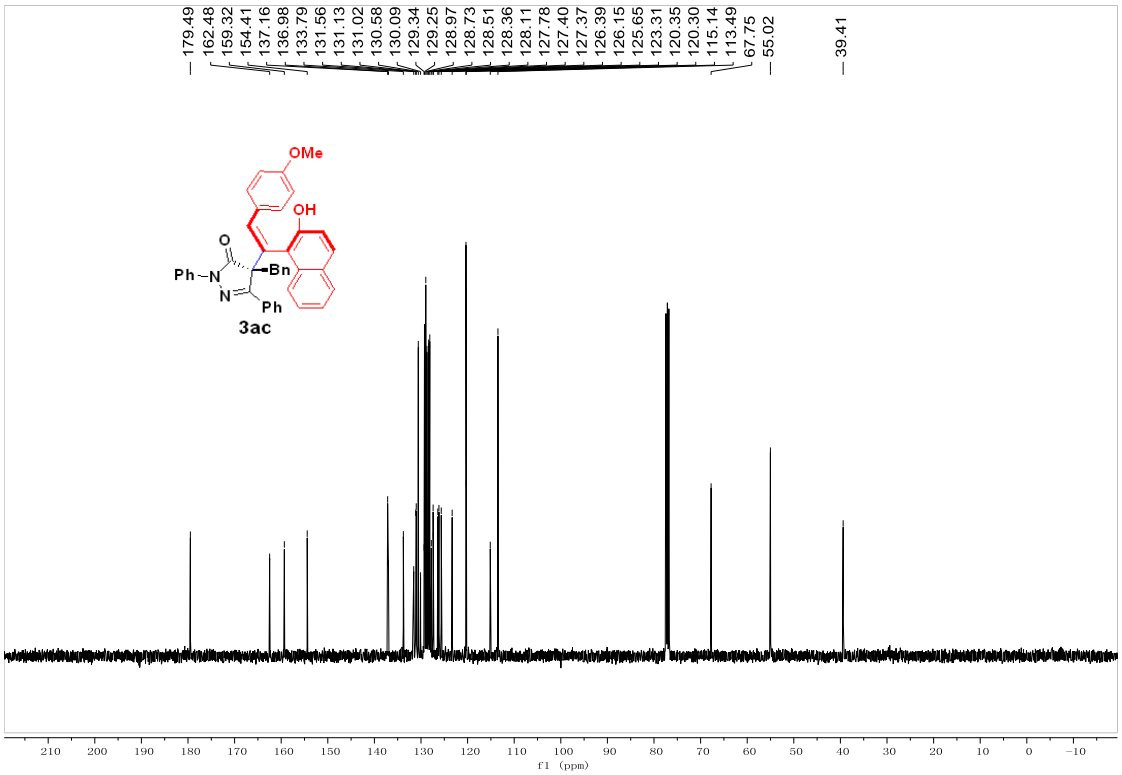
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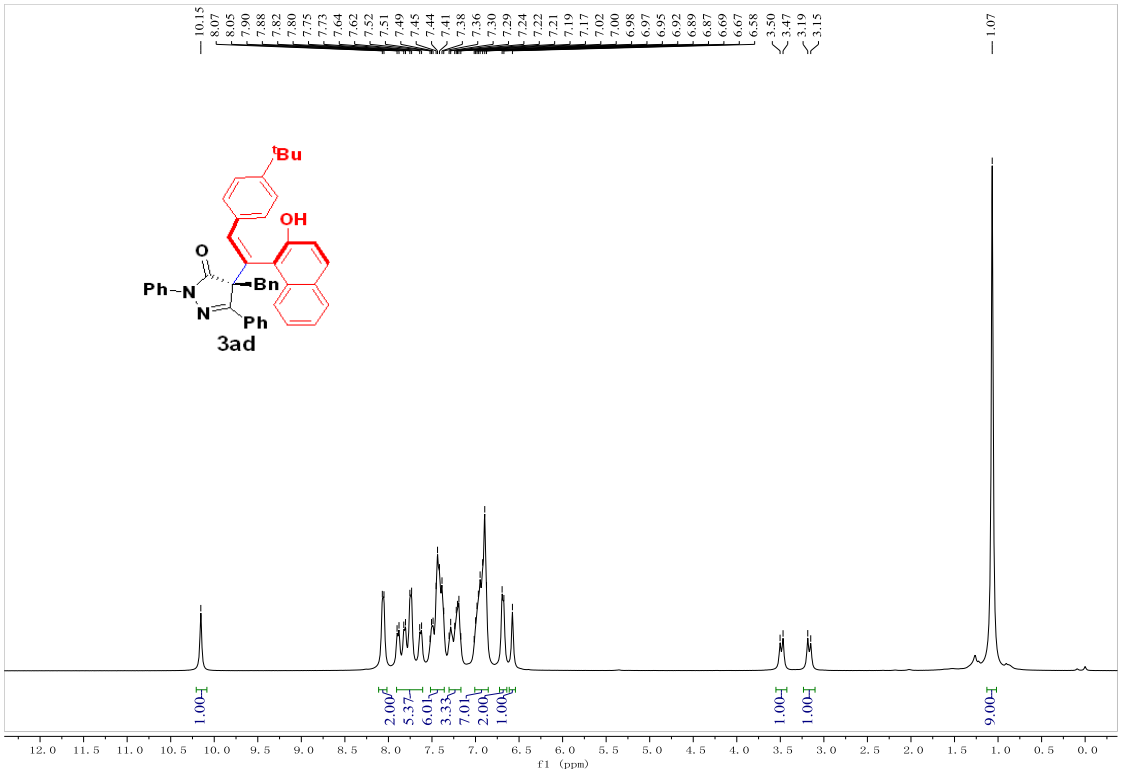
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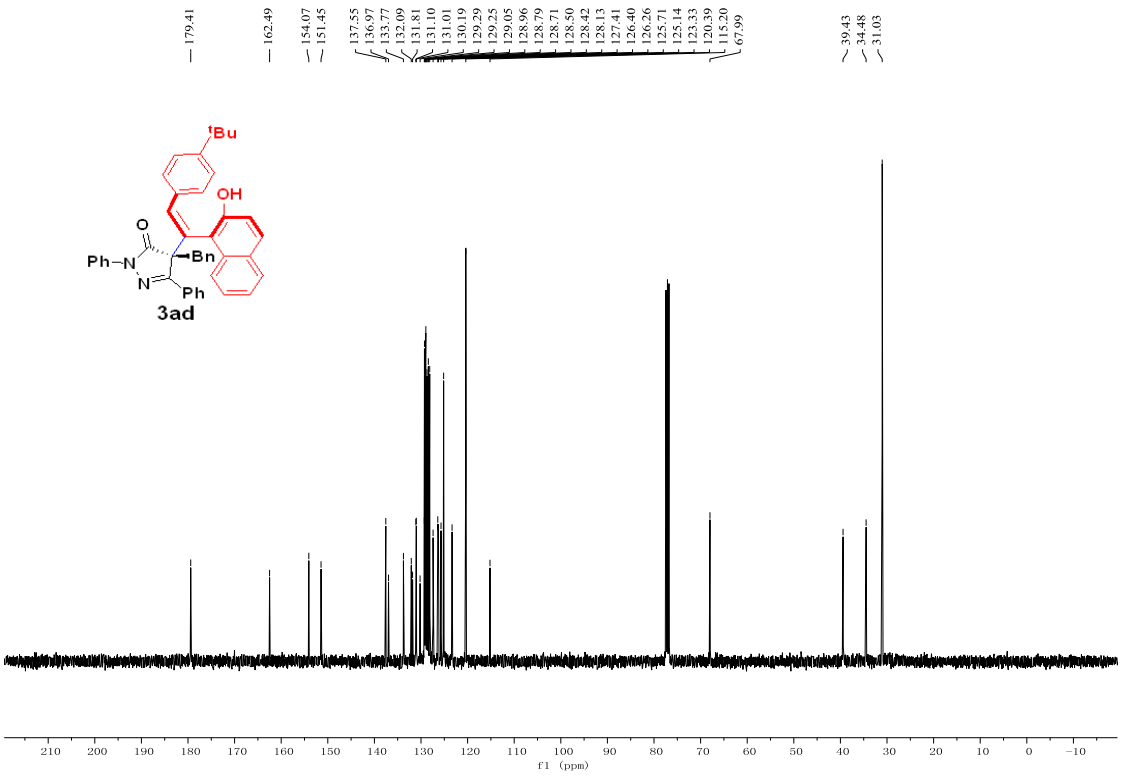
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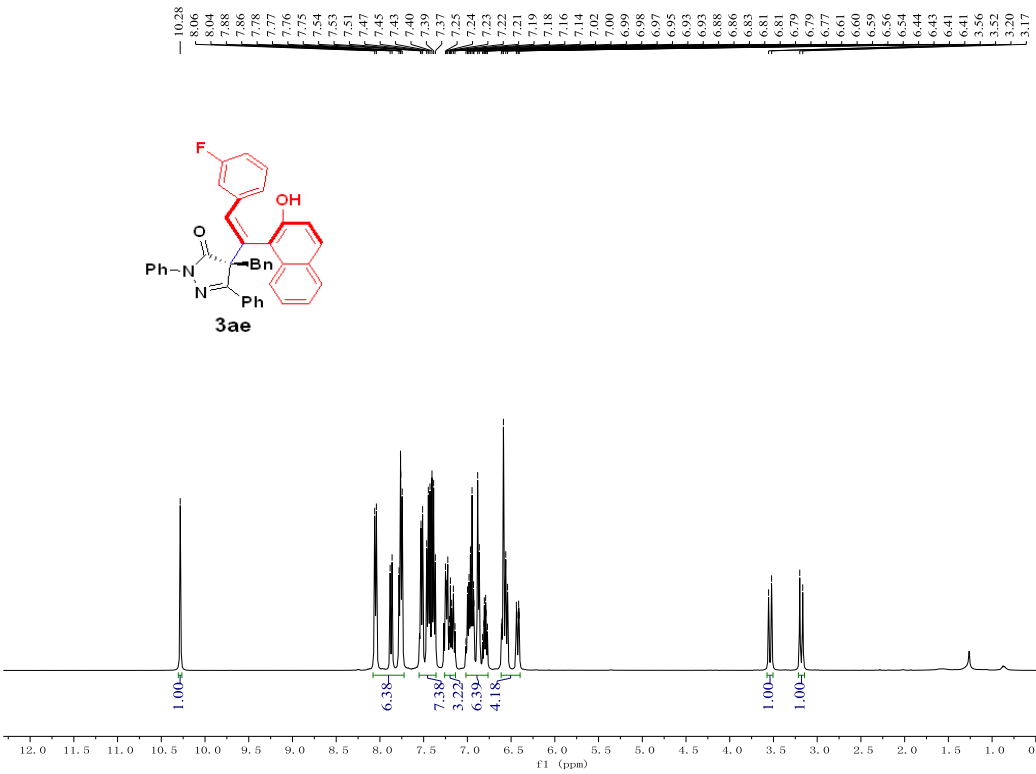
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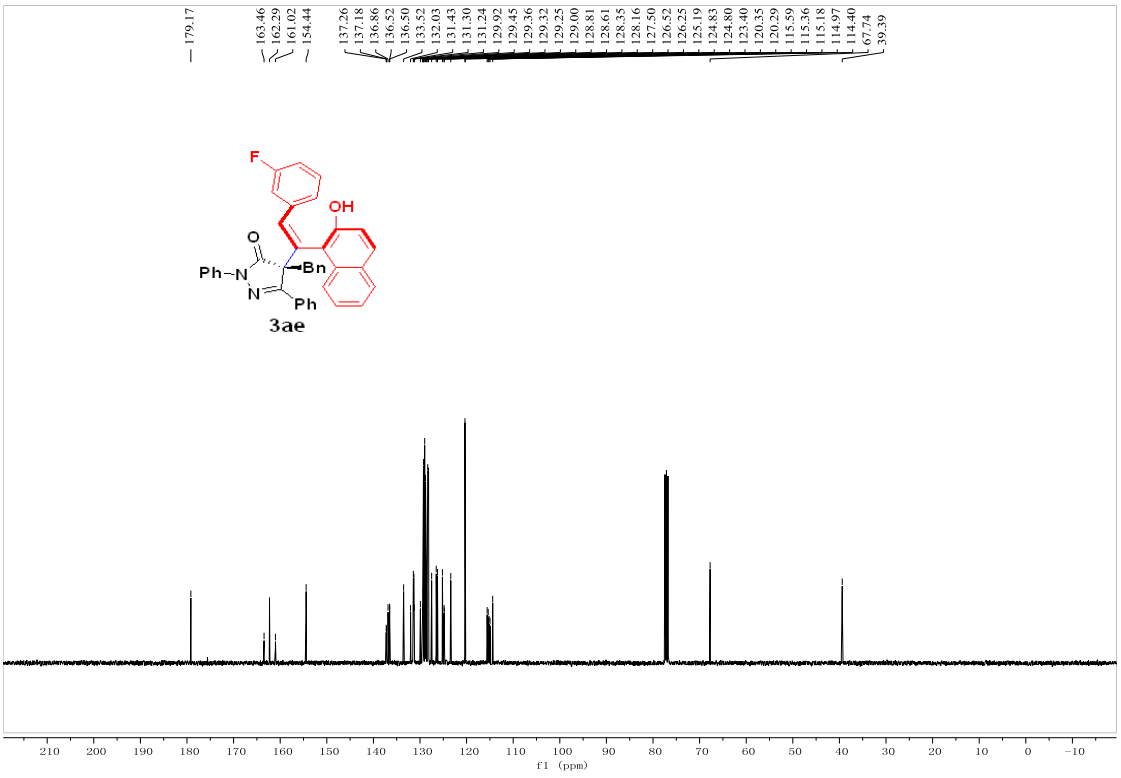
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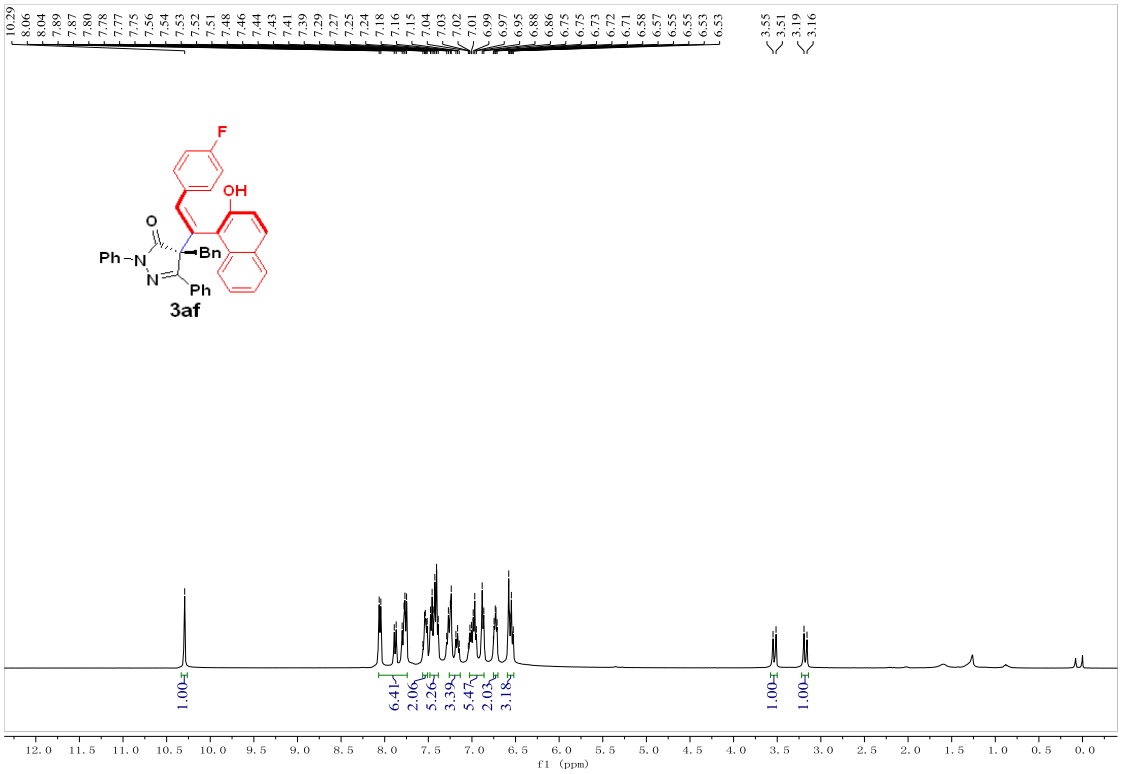
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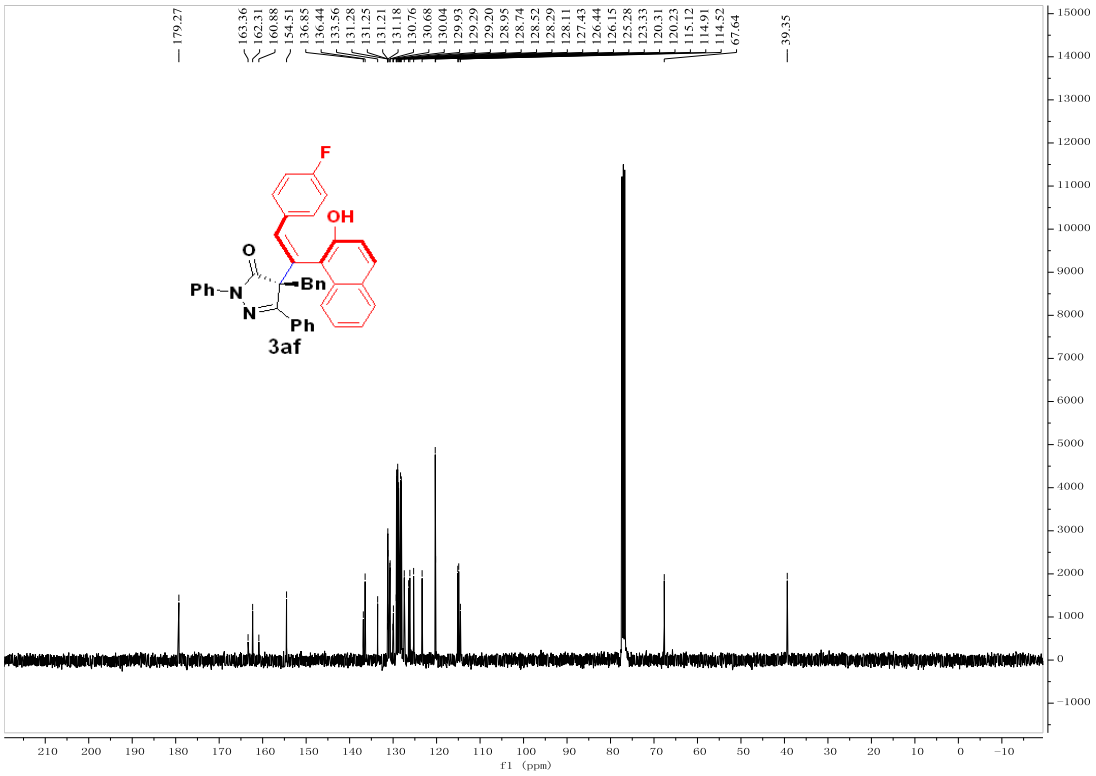
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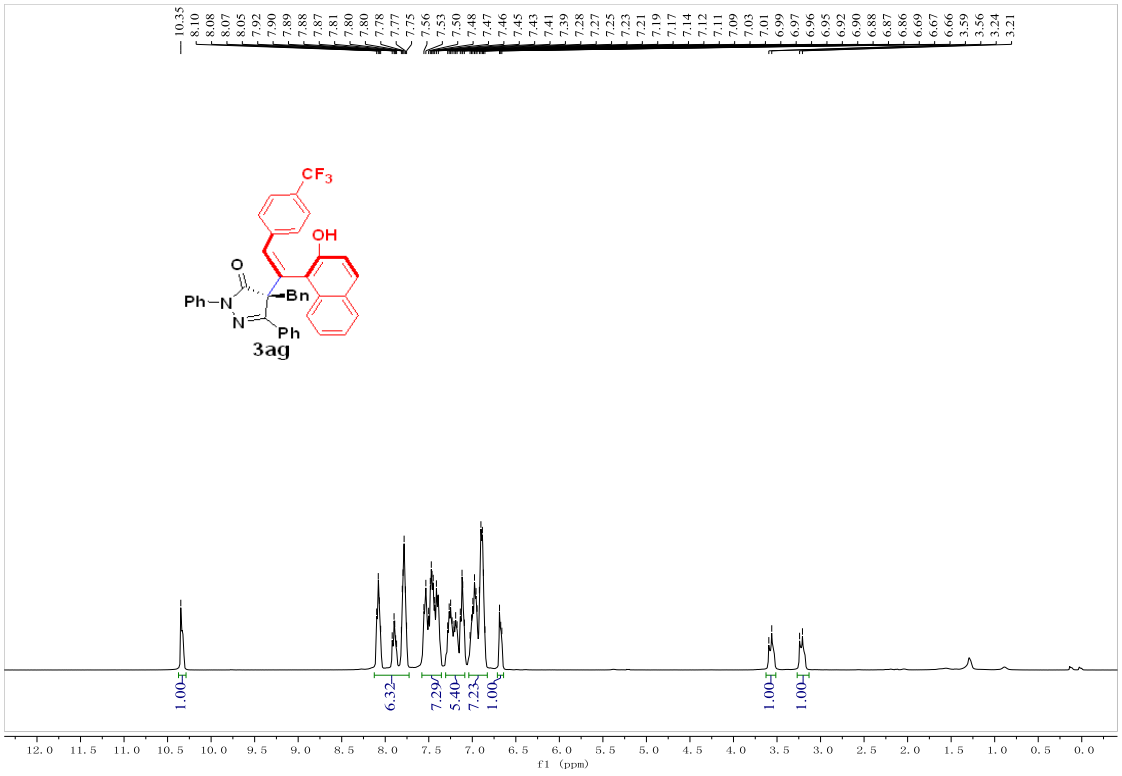
f1 (ppm)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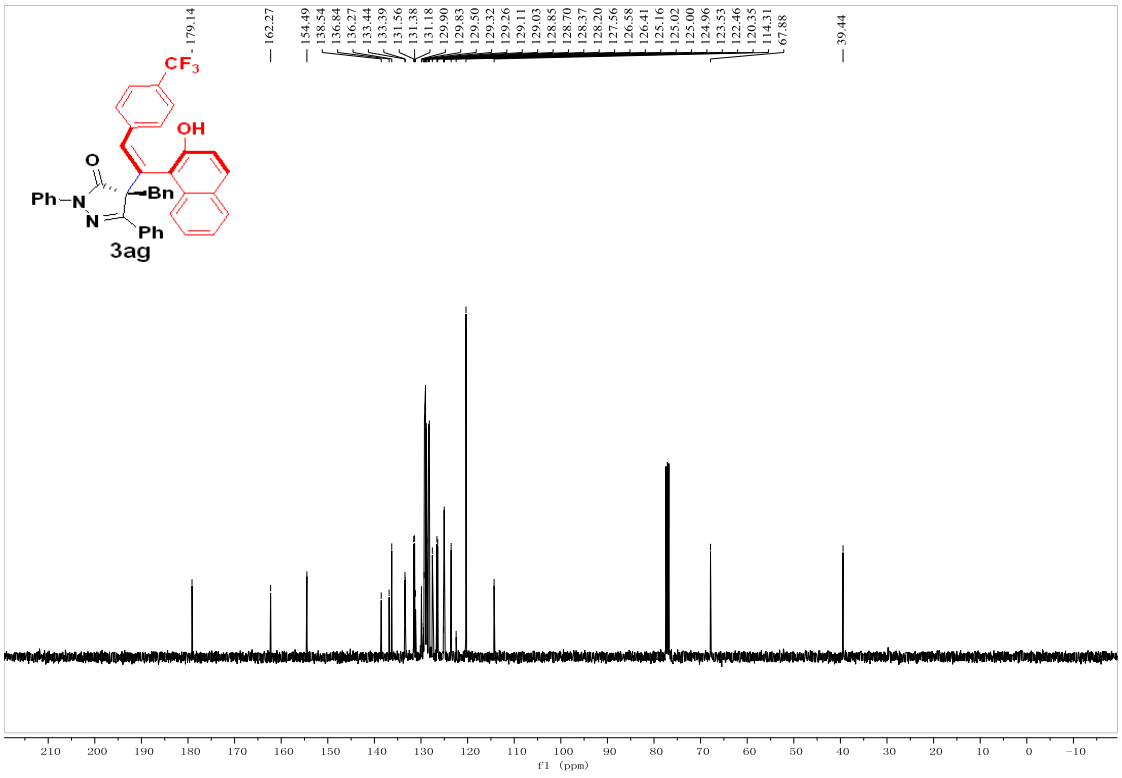
8.07
8.05
7.92
7.90
7.89
7.88
7.87
7.81
7.80
7.80
7.78
7.77
7.75
7.56
7.53
7.50
7.48
7.47
7.46
7.45
7.43
7.41
7.39
7.28
7.27
7.25
7.23
7.21
7.19
7.17
7.14
7.12
7.11
7.09
7.03
7.01
6.99
6.97
6.96
6.95
6.92
6.90
6.88
6.87
6.86
6.69
6.67
6.66
3.59
3.56
3.24
3.21
CF3
OH
O
Ph–N
N
Bn
Ph
3ag
1.00
6.32
7.29
5.40
7.23
1.00
1.00
1.00
f1 (ppm)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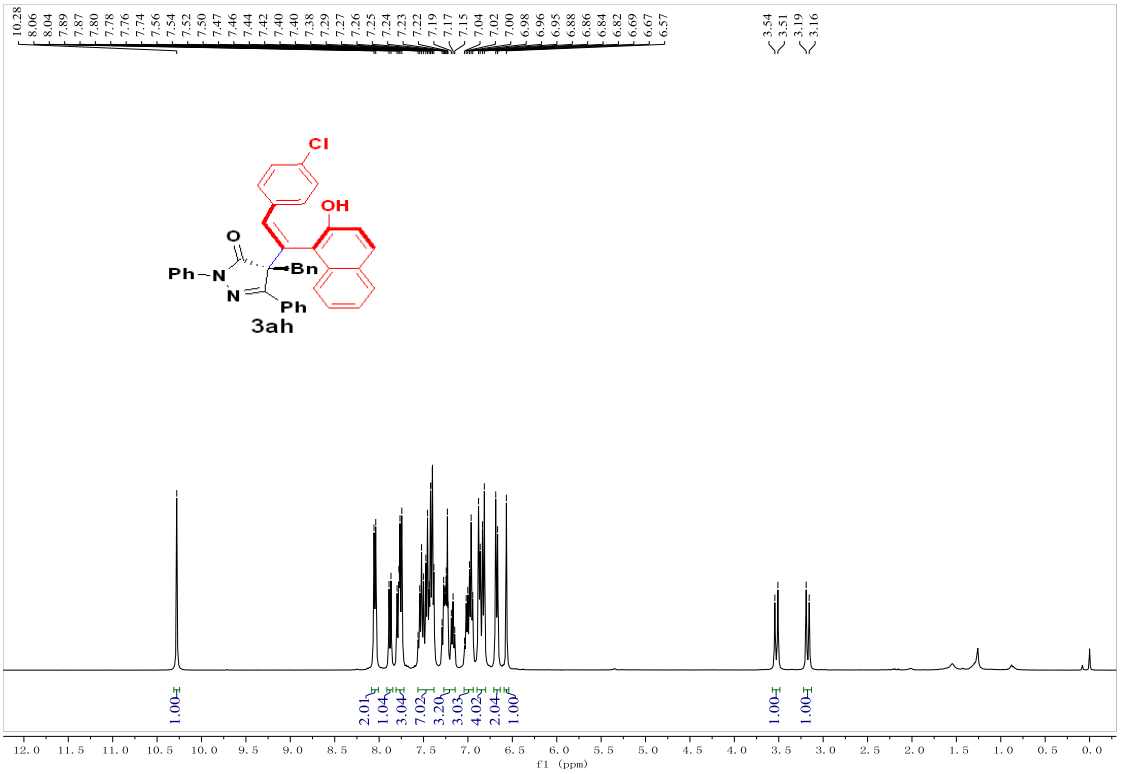
133.39
131.56
131.38
131.18
129.90
129.83
129.50
129.32
129.26
129.11
129.03
128.85
128.70
128.37
128.20
127.56
126.58
126.41
125.16
125.02
125.00
124.96
123.53
122.46
120.35
114.31
67.88
39.44
CF3
OH
O
Ph–N
N
Bn
Ph
3ag
f1 (ppm)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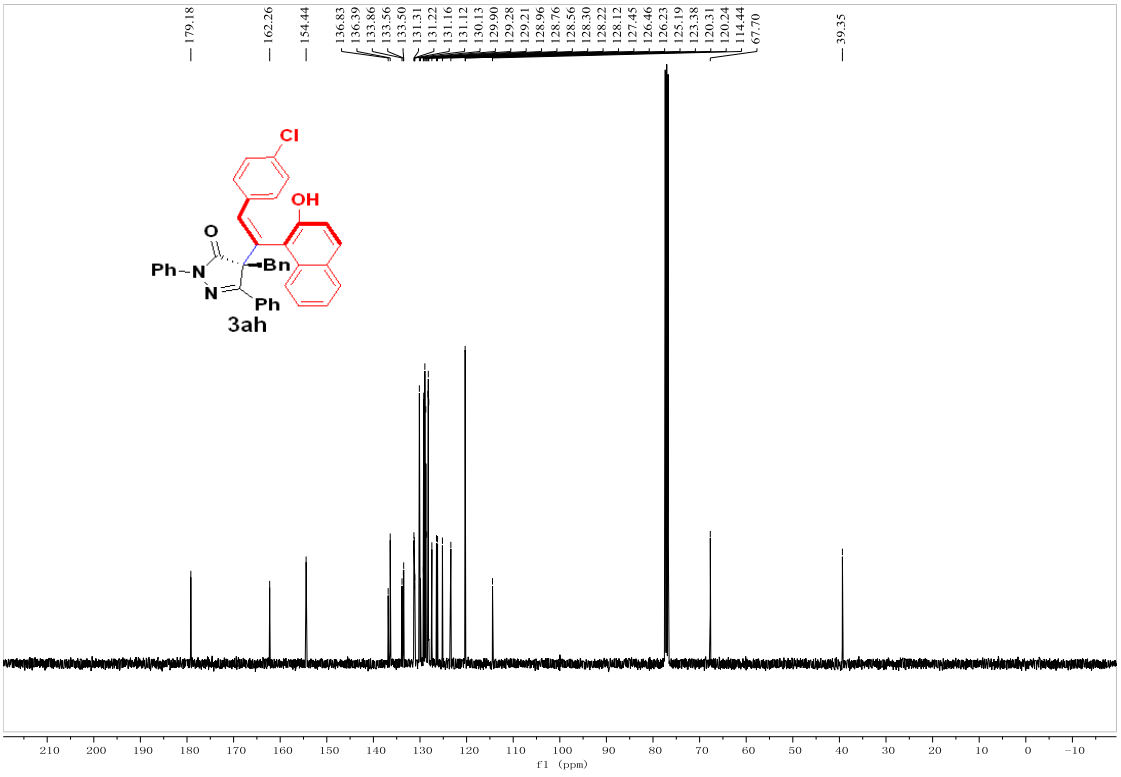
OH
O
Ph
N
N
Bn
Ph
3ah
f1 (ppm)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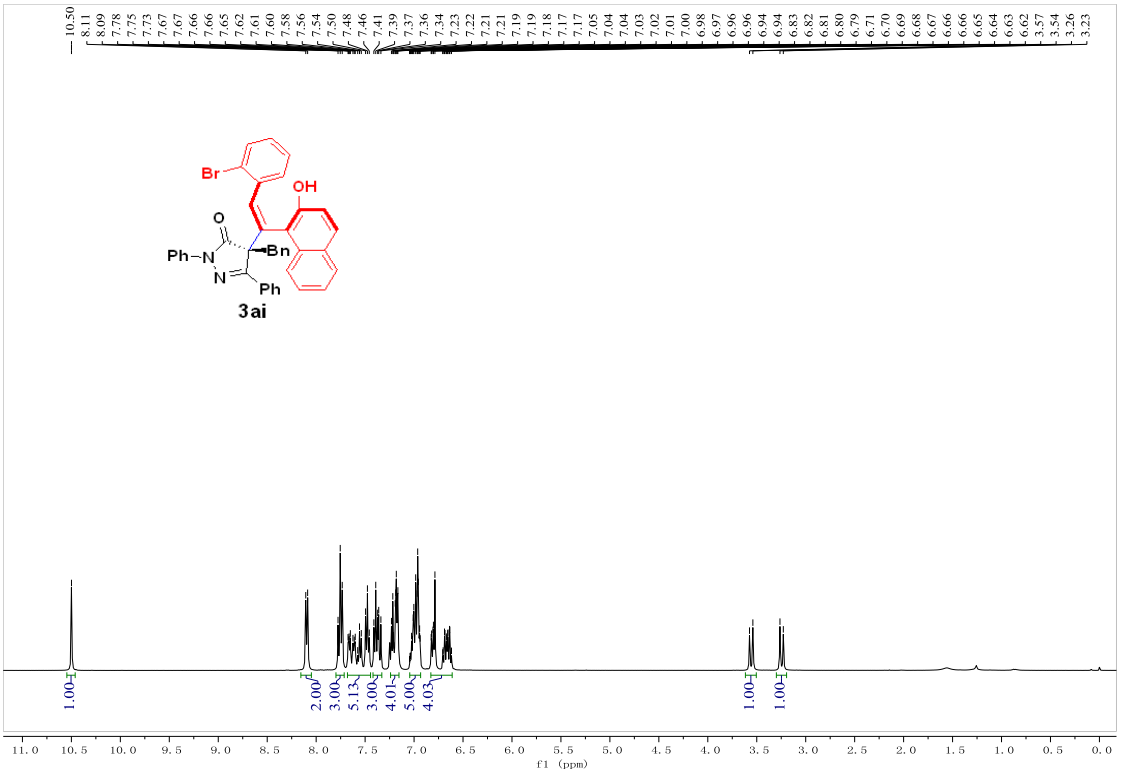
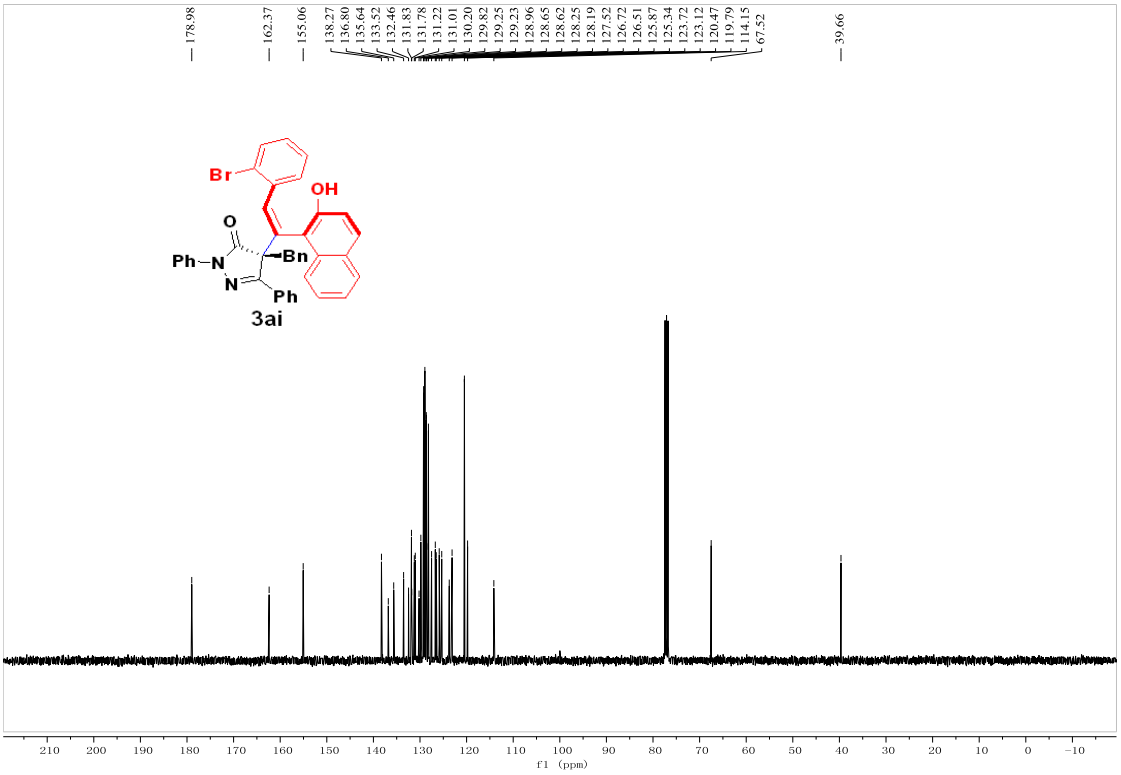
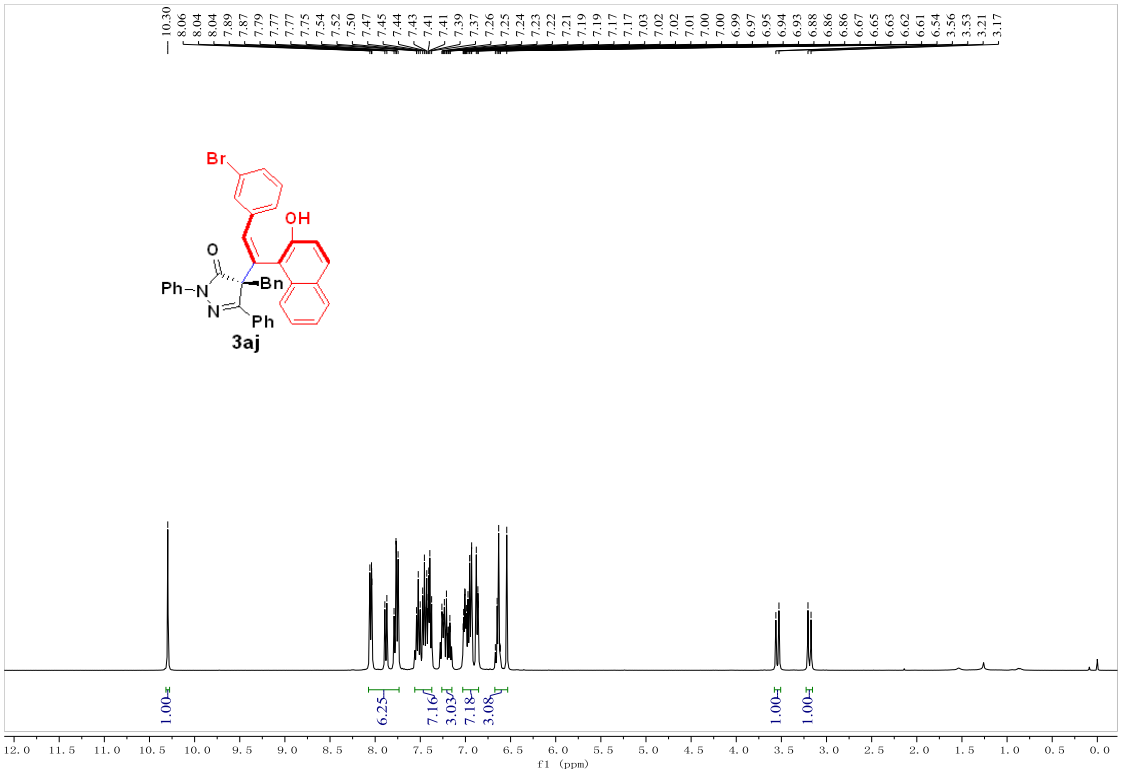
OH
O
Ph
N
N
Bn
Ph
3ah
f1 (ppm)


Br
OH
O
Ph–N
N
Bn
Ph
3ai
f1 (ppm)


Br
OH
O
Ph–N
N
Bn
Ph
3ai
f1 (ppm)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OH
O
Ph–N
Bn
N
Ph
3aj
1.00
6.25
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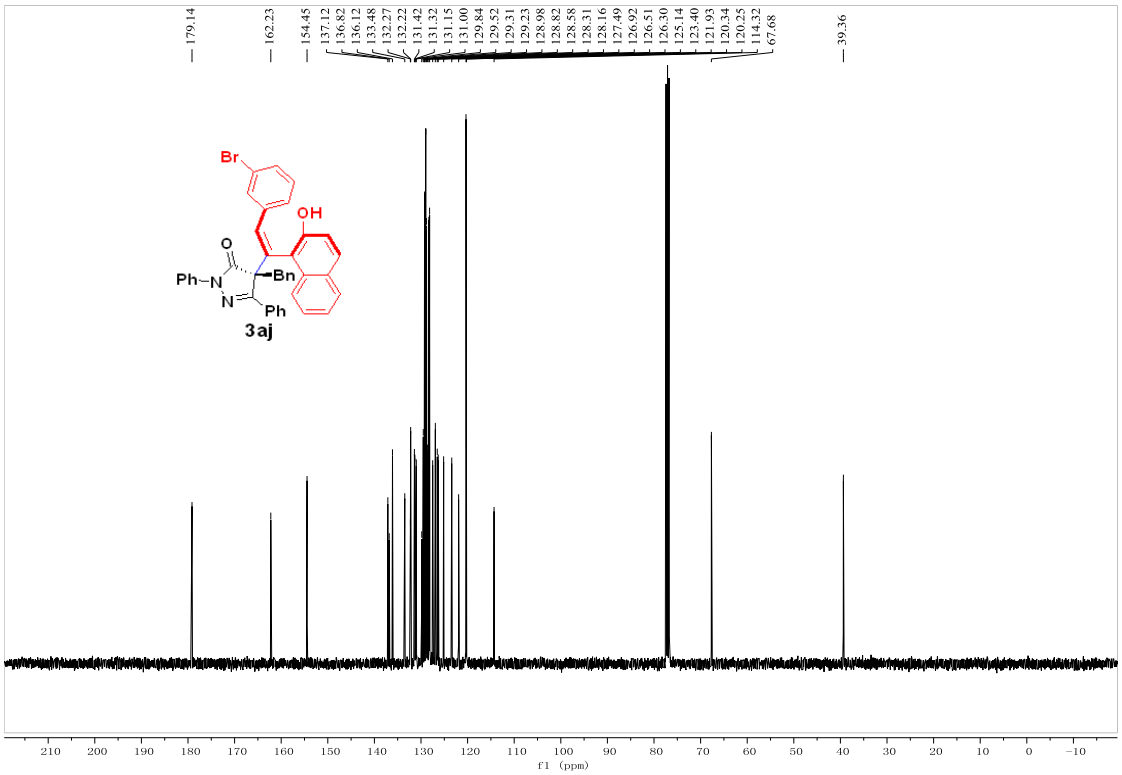
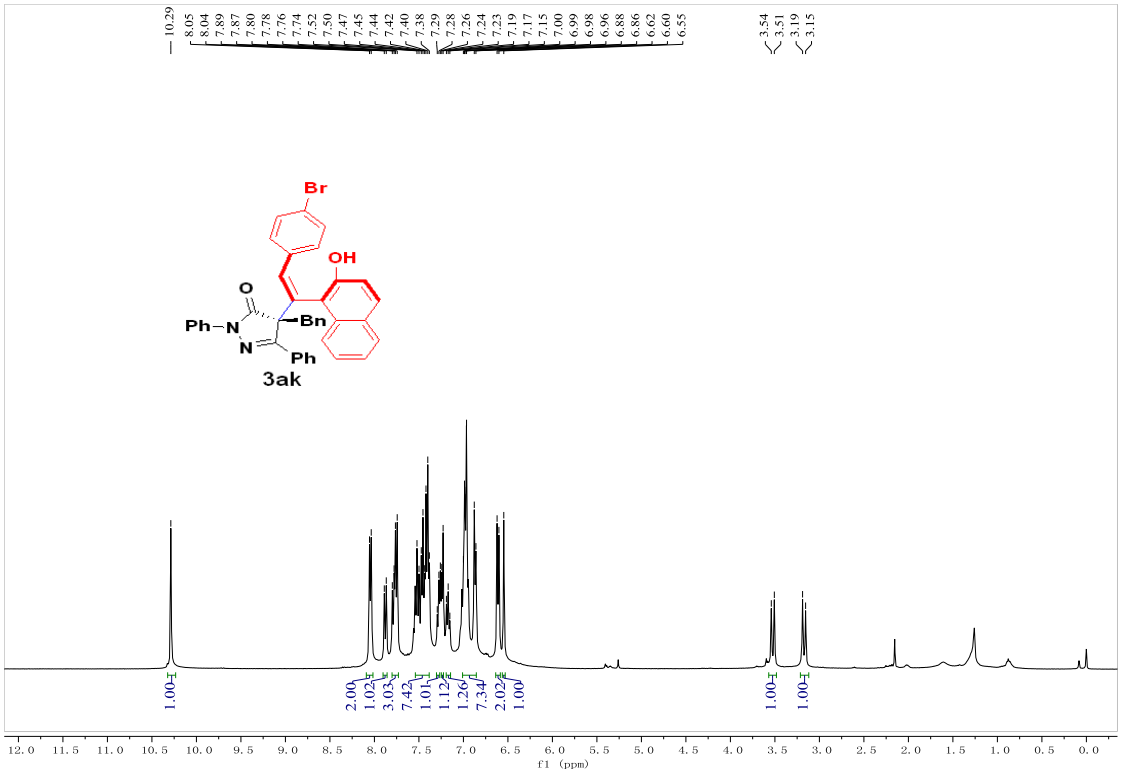
3.03
7.18
3.08
1.00
1.00
f1 (ppm)


Br
OH
O
Ph–N
Bn
N
Ph
3aj
f1 (ppm)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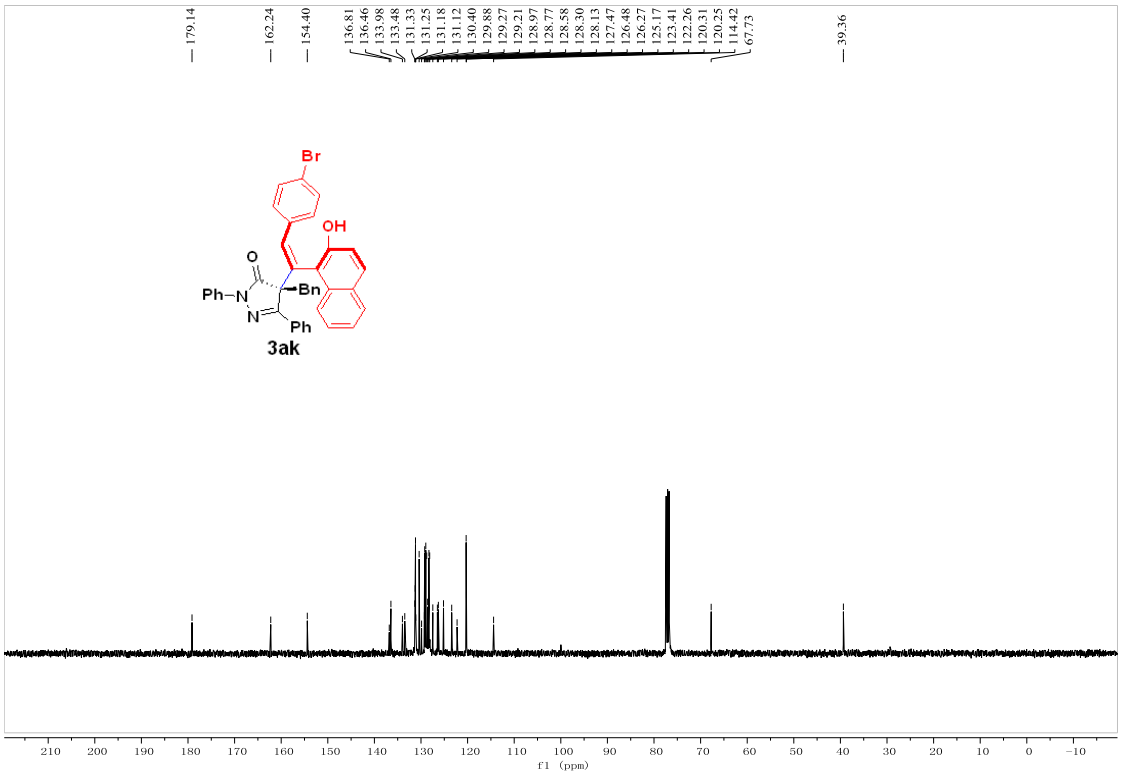
7.47
7.45
7.44
7.42
7.40
7.38
7.29
7.28
7.26
7.24
7.23
7.19
7.17
7.15
7.00
6.99
6.98
6.96
6.88
6.86
6.62
6.60
6.55
3.54
3.51
3.19
3.15
Br
OH
O
Ph–N
N
Bn
Ph
3ak
1.00
2.00
1.02
3.03
7.42
1.01
1.12
1.26
7.34
2.02
1.00
1.00
1.00
f1 (ppm)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131.18
131.12
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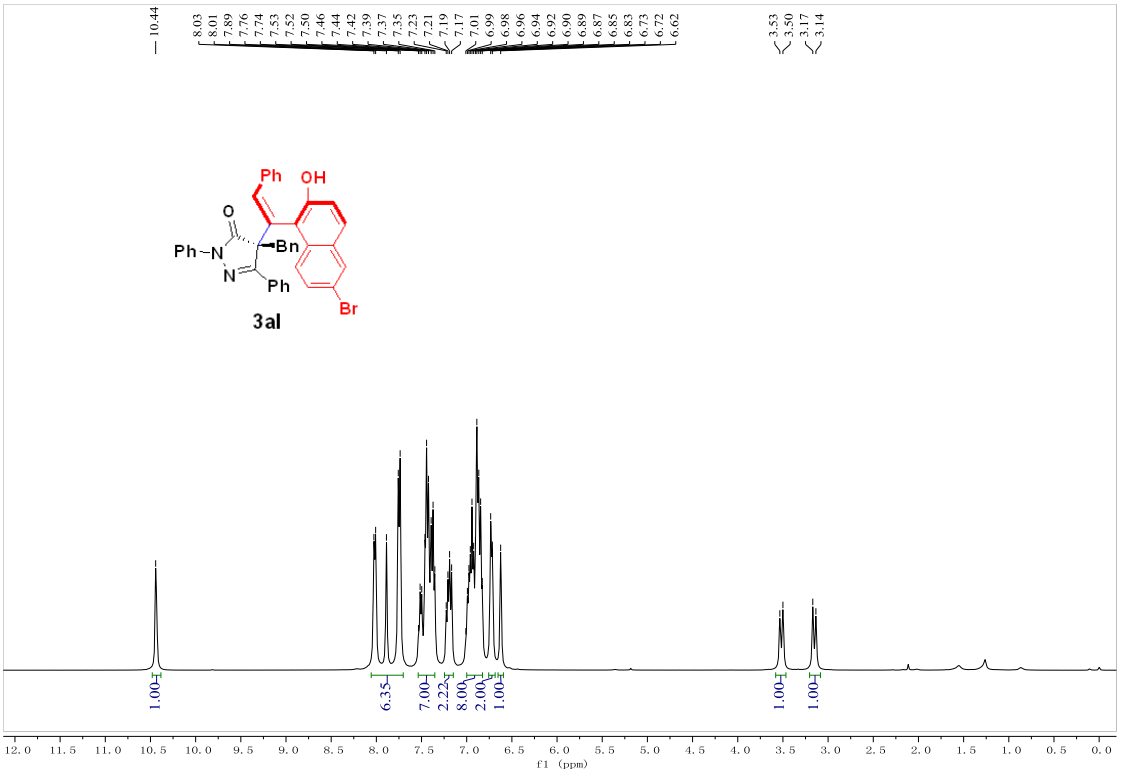
129.88
129.27
129.21
128.97
128.77
128.58
128.30
128.13
127.47
126.48
126.27
125.17
123.41
122.26
120.31
120.25
114.42
67.73
39.36
Br
OH
O
Ph–N
N
Bn
Ph
3ak
f1 (ppm)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7.74
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7.52
7.50
7.46
7.44
7.42
7.39
7.37
7.35
7.23
7.21
7.19
7.17
7.01
6.99
6.98
6.96
6.94
6.92
6.90
6.89
6.87
6.85
6.83
6.73
6.72
6.62
3.53
3.50
3.17
3.14
Ph
OH
O
Ph–N
Bn
N
Ph
Br
3al
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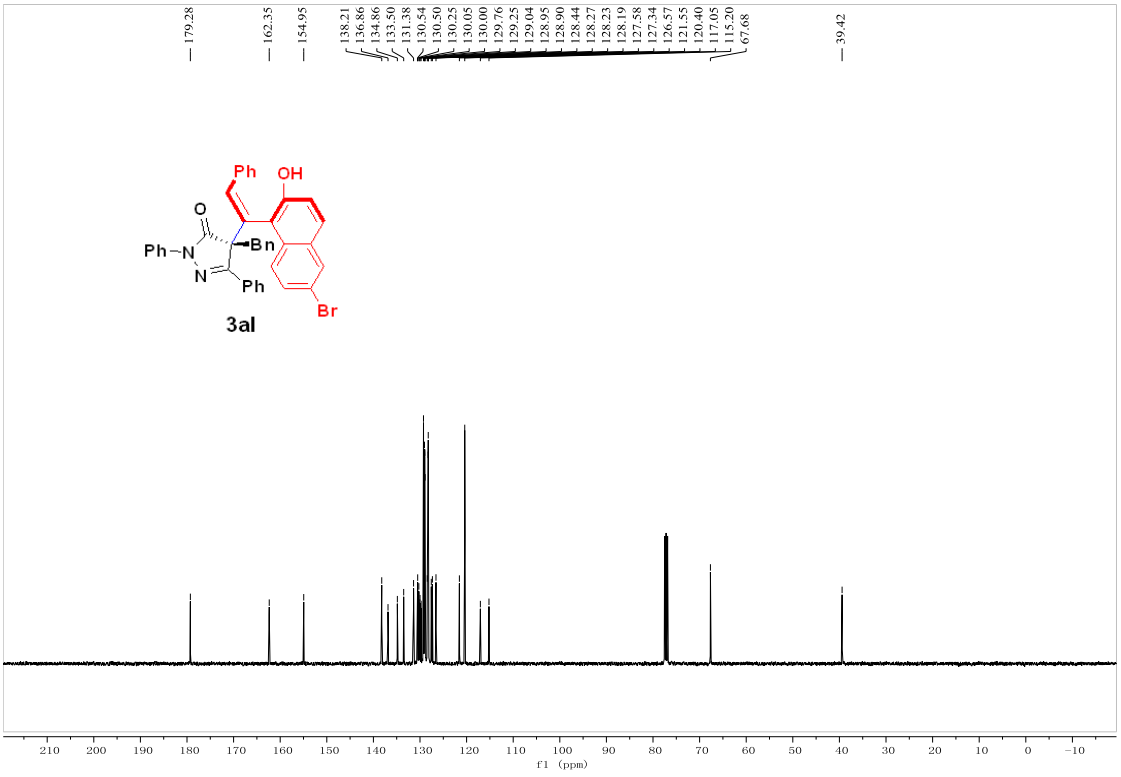
6.35
7.00
2.22
8.00
2.00
1.00
1.00
1.00
f1 (ppm)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134.86
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131.38
130.54
130.50
130.25
130.05
130.00
129.76
129.25
129.04
128.95
128.90
128.44
128.27
128.23
128.19
127.58
127.34
126.57
121.55
120.40
117.05
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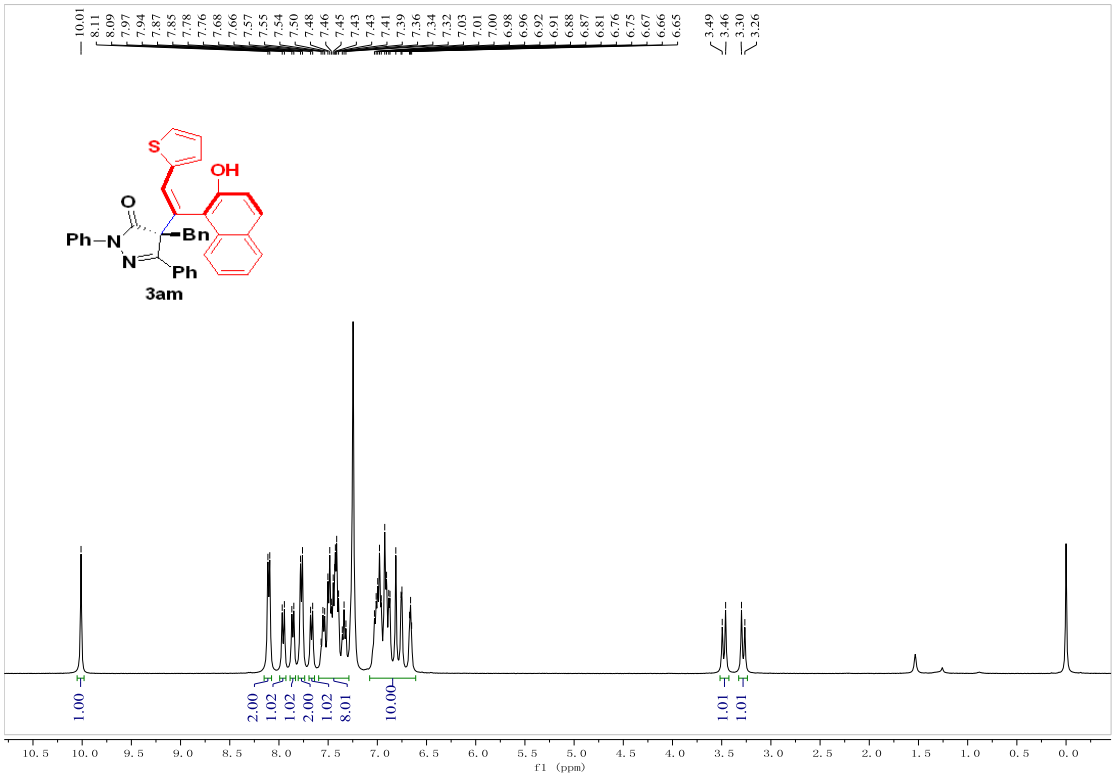
67.68
39.42
Ph
OH
O
Ph–N
Bn
N
Ph
Br
3al
f1 (ppm)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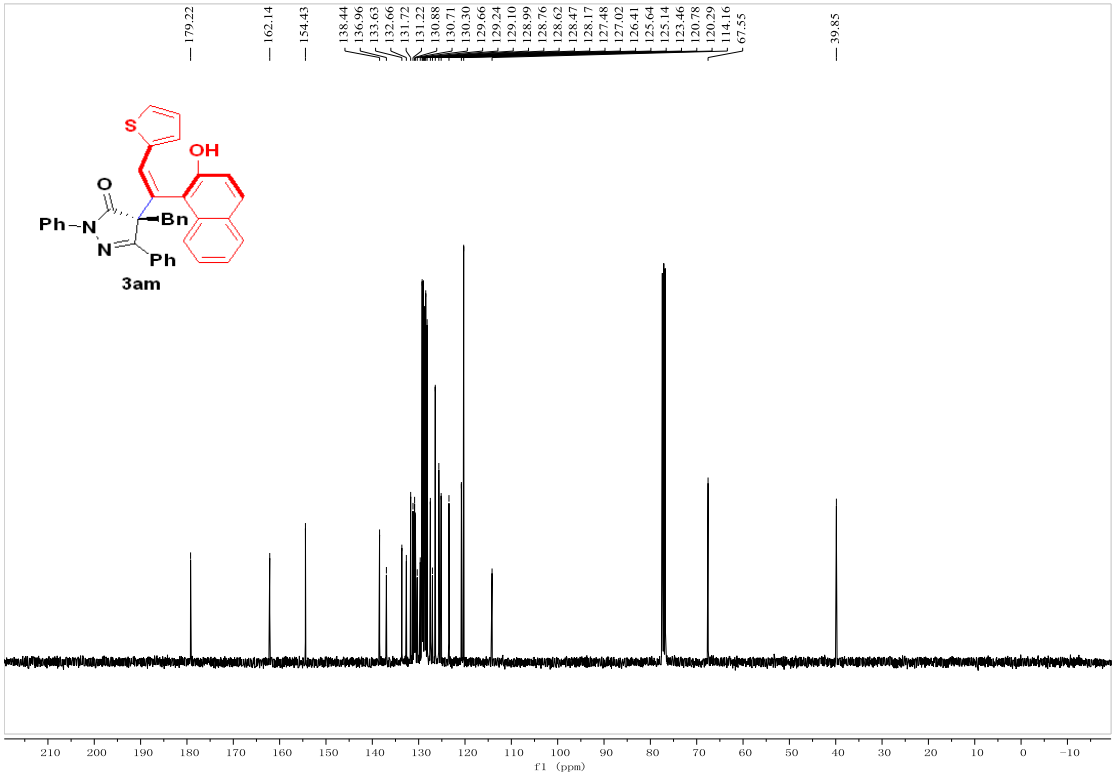
7.87
7.85
7.78
7.76
7.68
7.66
7.57
7.55
7.54
7.50
7.48
7.46
7.45
7.43
7.41
7.39
7.36
7.34
7.32
7.03
7.01
7.00
6.98
6.96
6.92
6.91
6.88
6.87
6.81
6.76
6.75
6.67
6.66
6.65
3.49
3.46
3.30
3.26
S
OH
O
Ph
N
Bn
N
Ph
3am
1.00
2.00
1.02
1.02
2.00
1.02
8.01
10.00
1.01
1.01
f1 (ppm)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133.63
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131.22
130.88
130.71
130.30
129.66
129.24
129.10
128.99
128.76
128.62
128.47
128.17
127.48
127.02
126.41
125.64
125.14
123.46
120.78
120.29
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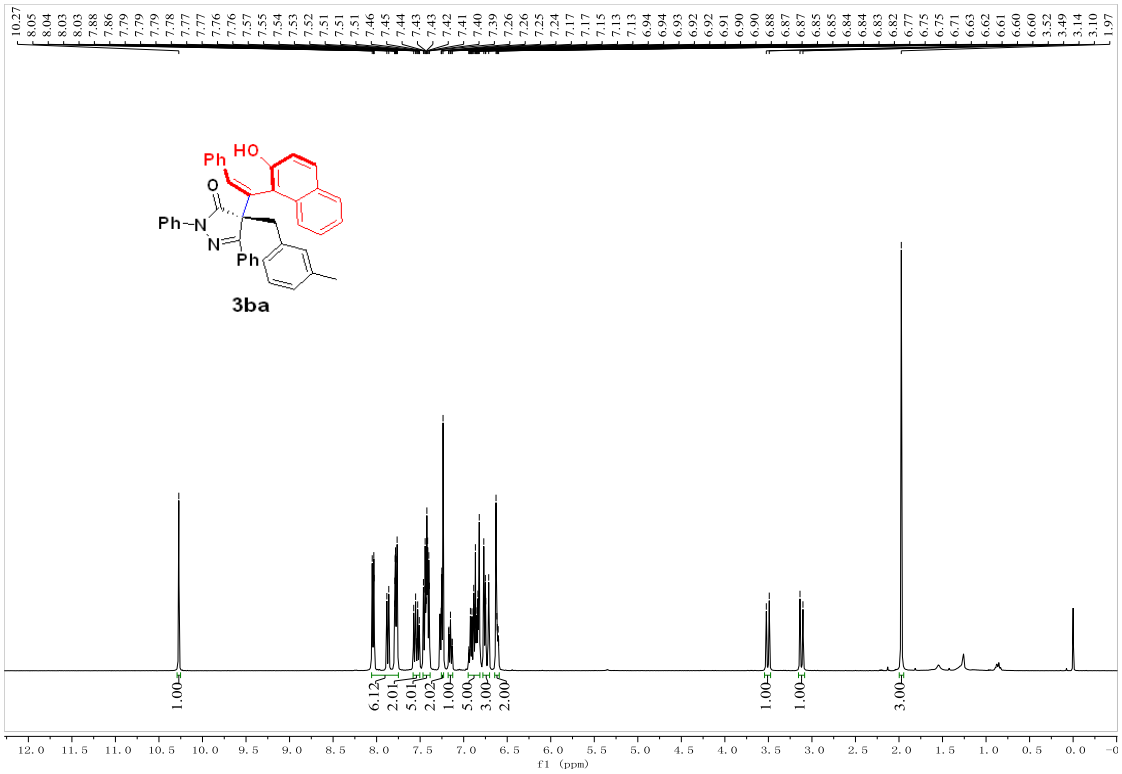
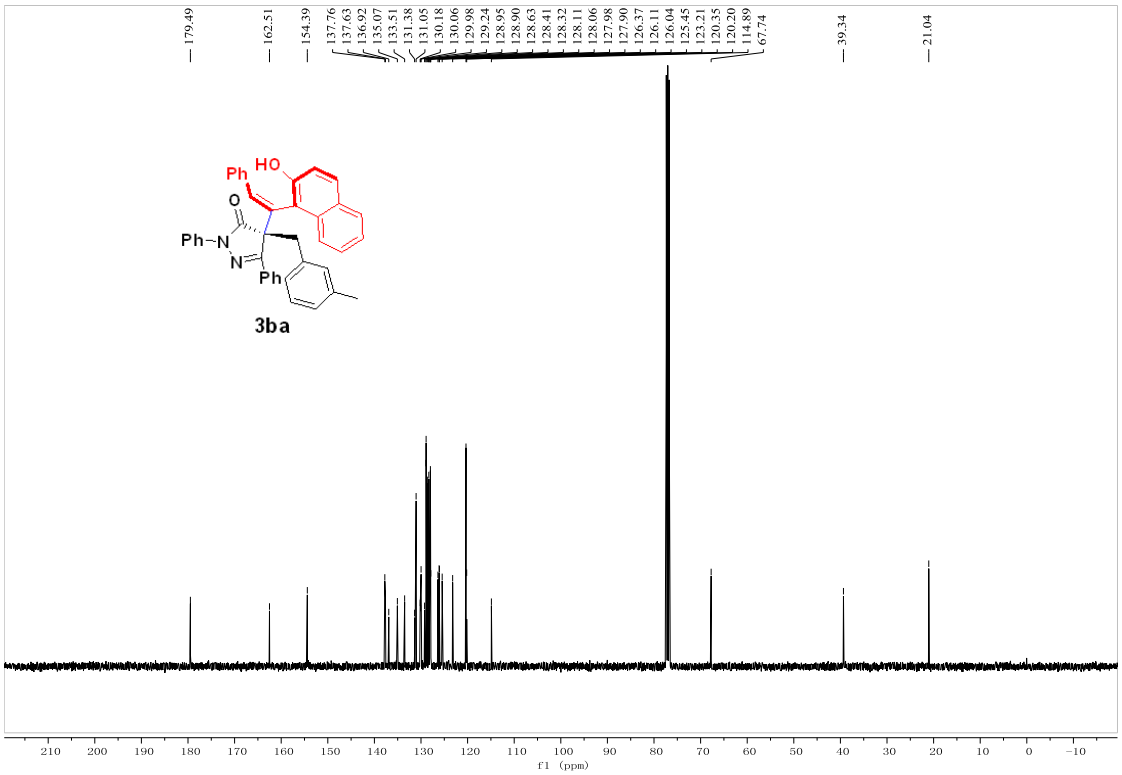
67.55
39.85
S
OH
O
Ph
N
Bn
N
Ph
3am
f1 (ppm)


Ph
HO
O
Ph–N
N
Ph
3ba
1.00
6.12
2.01
5.01
2.02
1.00
5.00
3.00
2.00
1.00
1.00
3.00
f1 (ppm)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135.07
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131.38
131.05
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130.06
129.98
129.24
128.95
128.90
128.63
128.41
128.32
128.11
128.06
127.98
127.90
126.37
126.11
126.04
125.45
123.21
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120.20
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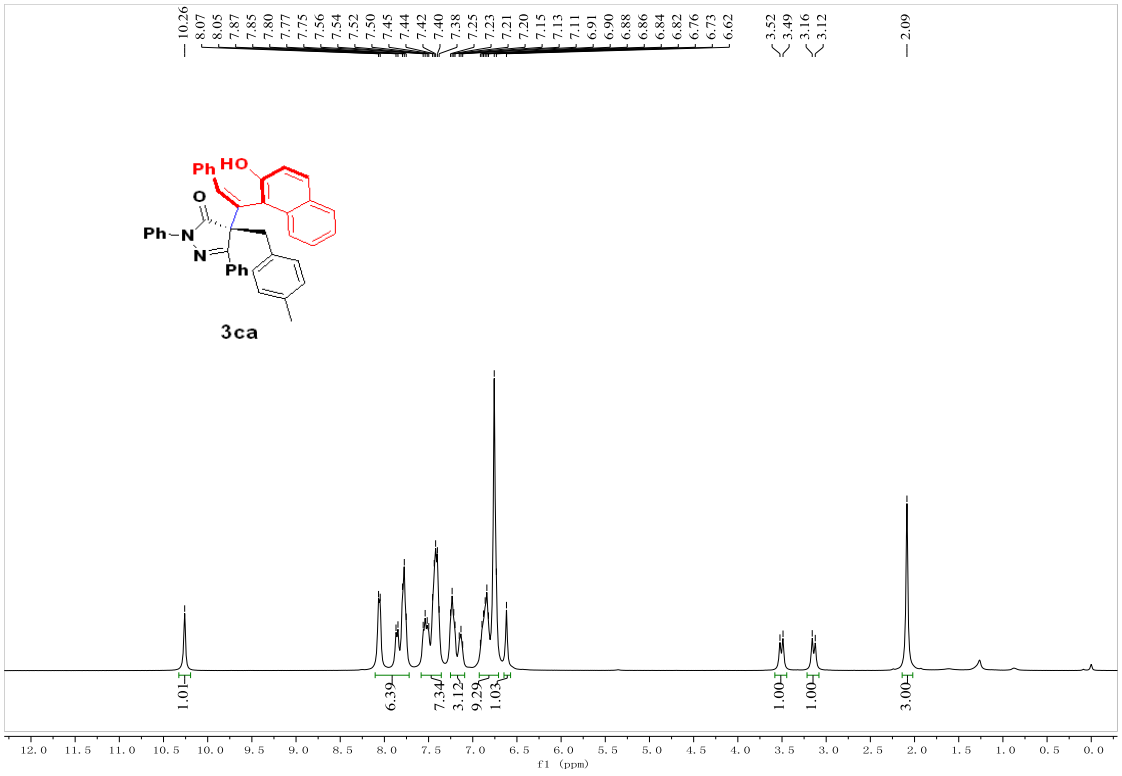
67.74
39.34
21.04
Ph
HO
O
Ph–N
N
Ph
3ba
f1 (ppm)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7.54
7.52
7.50
7.45
7.44
7.42
7.40
7.38
7.25
7.23
7.21
7.20
7.15
7.13
7.11
6.91
6.90
6.88
6.86
6.84
6.82
6.76
6.73
6.62
3.52
3.49
3.16
3.12
2.09
Ph
HO
O
Ph–N
N
Ph
3ca
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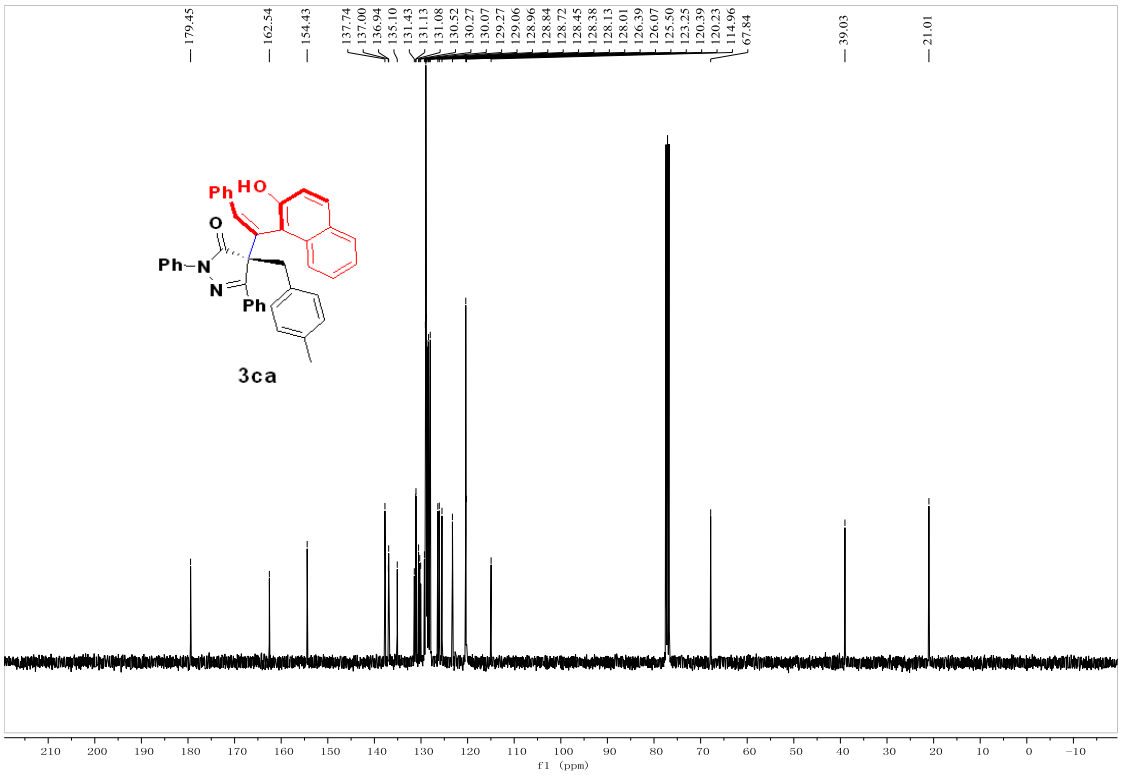
6.39
7.34
3.12
9.29
1.03
1.00
1.00
3.00
f1 (ppm)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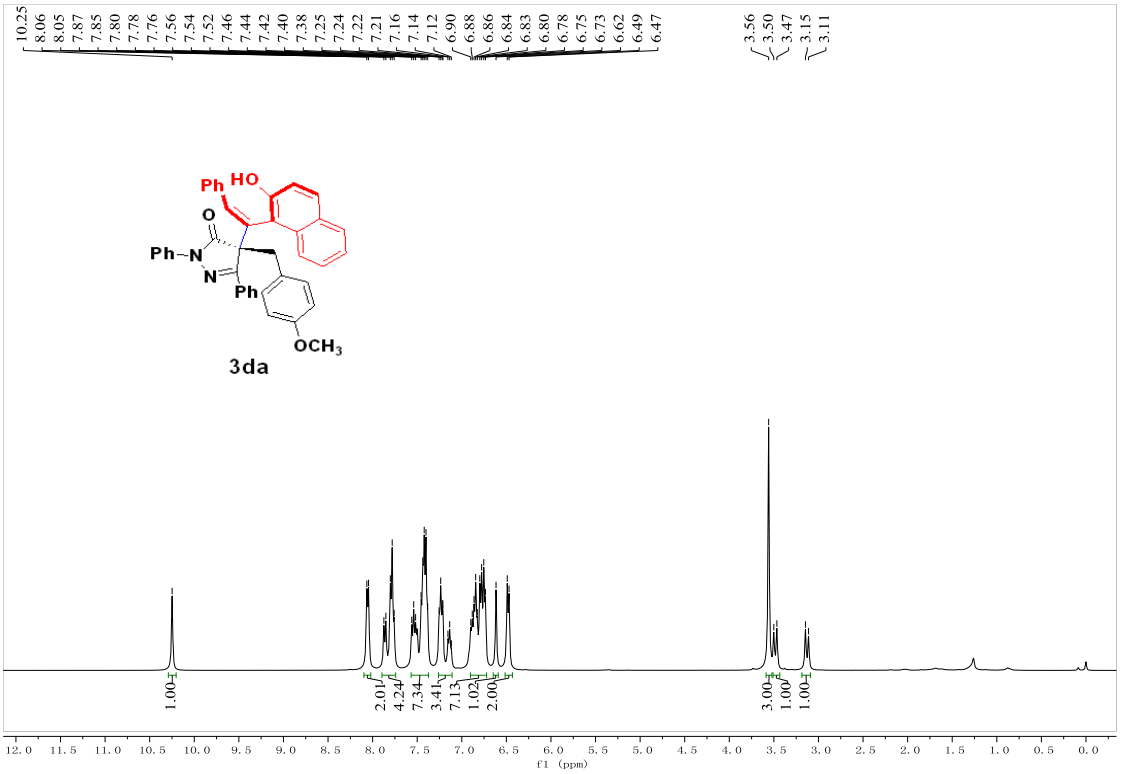
130.27
130.07
129.27
129.06
128.96
128.84
128.72
128.45
128.38
128.13
128.01
126.39
126.07
125.50
123.25
120.39
120.23
114.96
67.84
39.03
21.01
Ph
HO
O
Ph–N
N
Ph
3ca
f1 (ppm)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7.76
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7.54
7.52
7.46
7.44
7.42
7.40
7.38
7.25
7.24
7.22
7.21
7.16
7.14
7.12
6.90
6.88
6.86
6.84
6.83
6.80
6.78
6.75
6.73
6.62
6.49
6.47
3.56
3.50
3.47
3.15
3.11
Ph
HO
O
Ph–N
N
Ph
OCH3
3da
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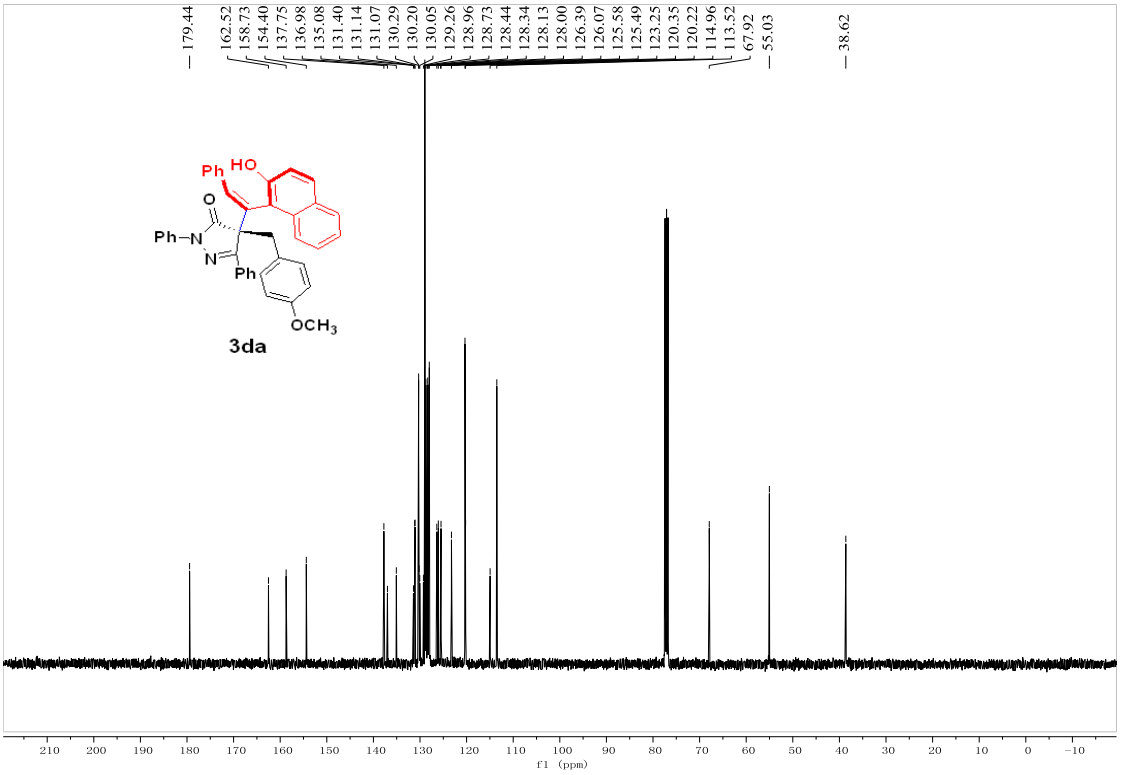
7.34
3.41
7.13
1.02
2.00
3.00
1.00
1.00
f1 (ppm)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130.05
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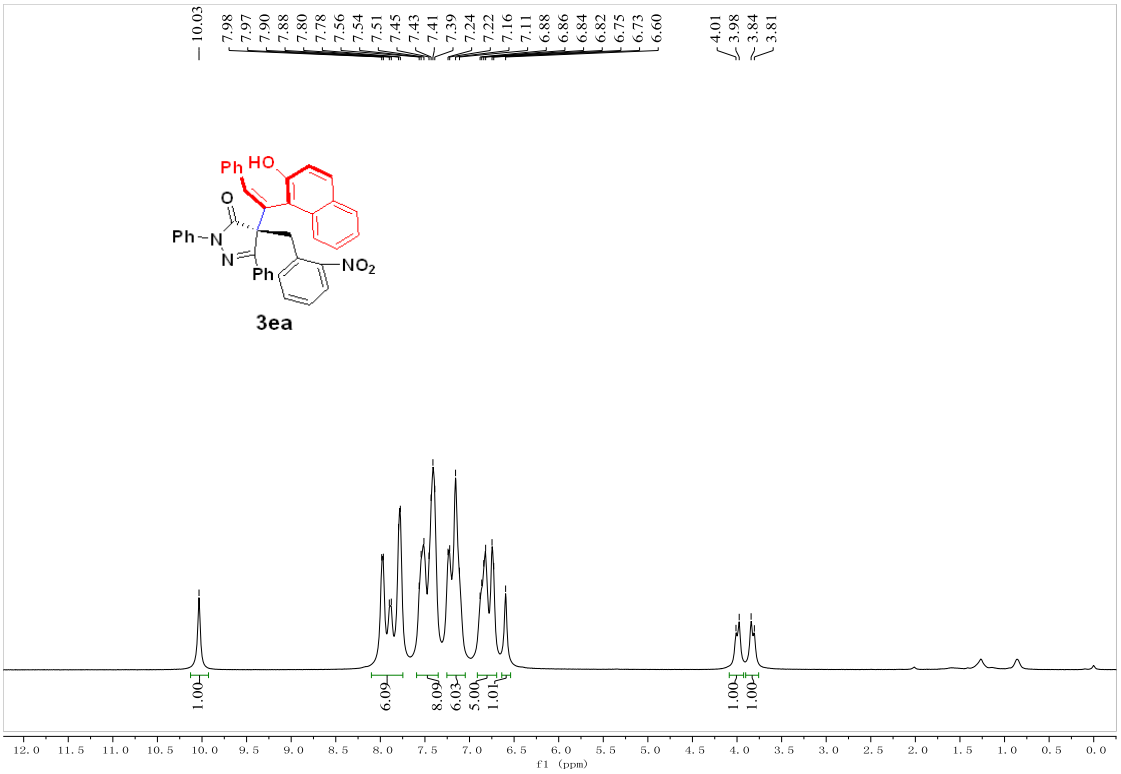
128.96
128.73
128.44
128.34
128.13
128.00
126.39
126.07
125.58
125.49
123.25
120.35
120.22
114.96
113.52
67.92
55.03
38.62
Ph
HO
O
Ph–N
N
Ph
OCH3
3da
f1 (ppm)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7.56
7.54
7.51
7.45
7.43
7.41
7.39
7.24
7.22
7.16
7.11
6.88
6.86
6.84
6.82
6.75
6.73
6.60
4.01
3.98
3.84
3.81
Ph
HO
O
Ph–N
N
Ph
NO2
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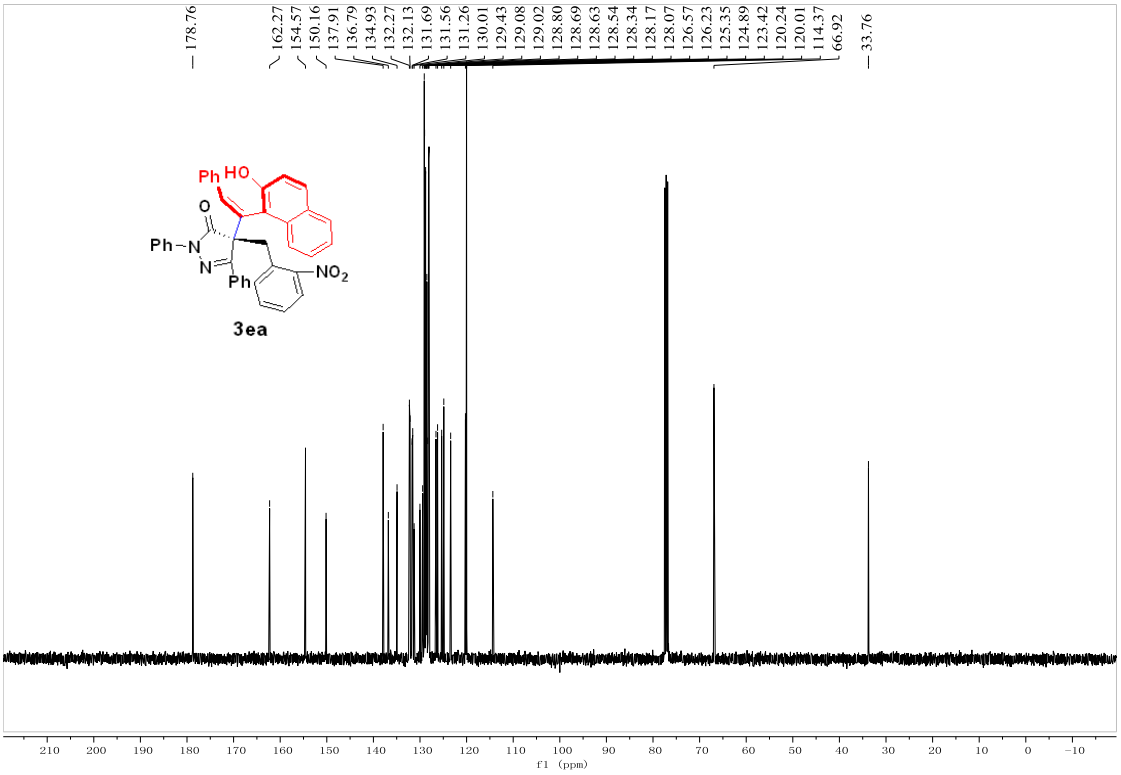
1.00
6.09
8.09
6.03
5.00
1.01
1.00
1.00
f1 (ppm)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132.27
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131.69
131.56
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130.01
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129.08
129.02
128.80
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128.63
128.54
128.34
128.17
128.07
126.57
126.23
125.35
124.89
123.42
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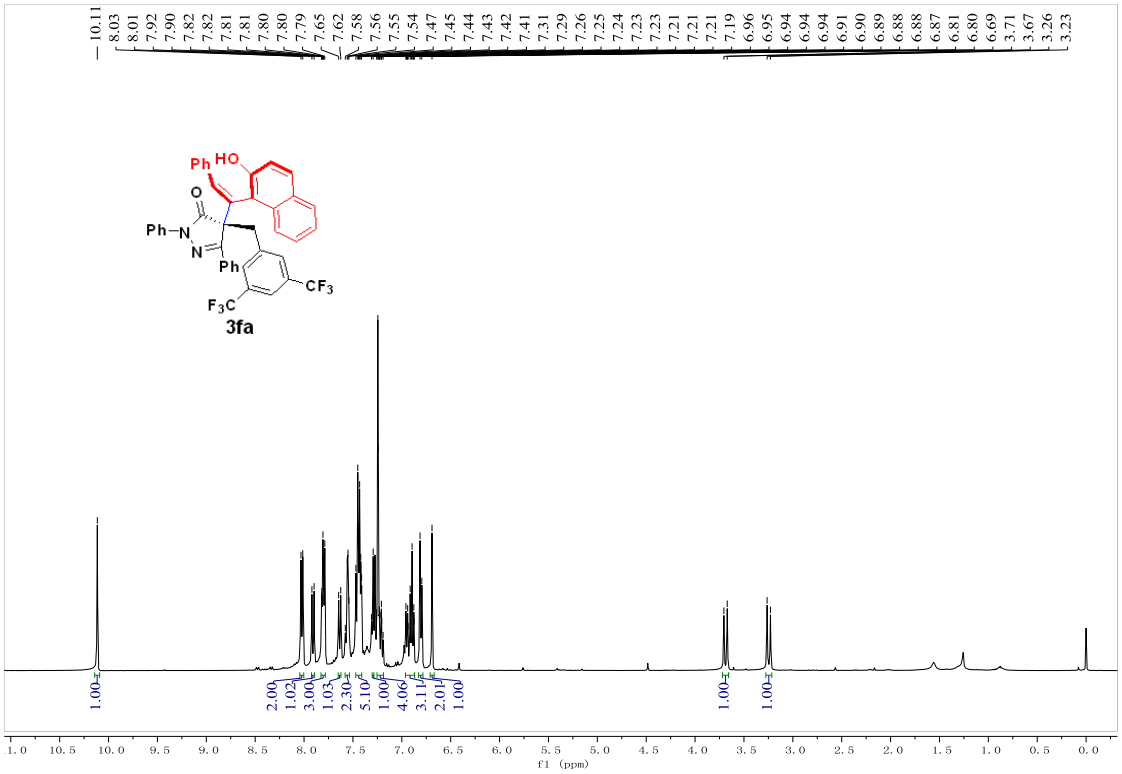
114.37
66.92
33.76
Ph
HO
O
Ph–N
N
Ph
NO2
3ea
f1 (ppm)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7.80
7.79
7.65
7.62
7.58
7.56
7.55
7.54
7.47
7.45
7.44
7.43
7.42
7.41
7.31
7.29
7.26
7.25
7.24
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7.21
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6.95
6.94
6.94
6.94
6.91
6.90
6.89
6.88
6.88
6.87
6.81
6.80
6.69
3.71
3.67
3.26
3.23
Ph
HO
O
Ph–N
N
Ph
CF3
F3C
3fa
1.00
2.00
1.02
3.00
1.03
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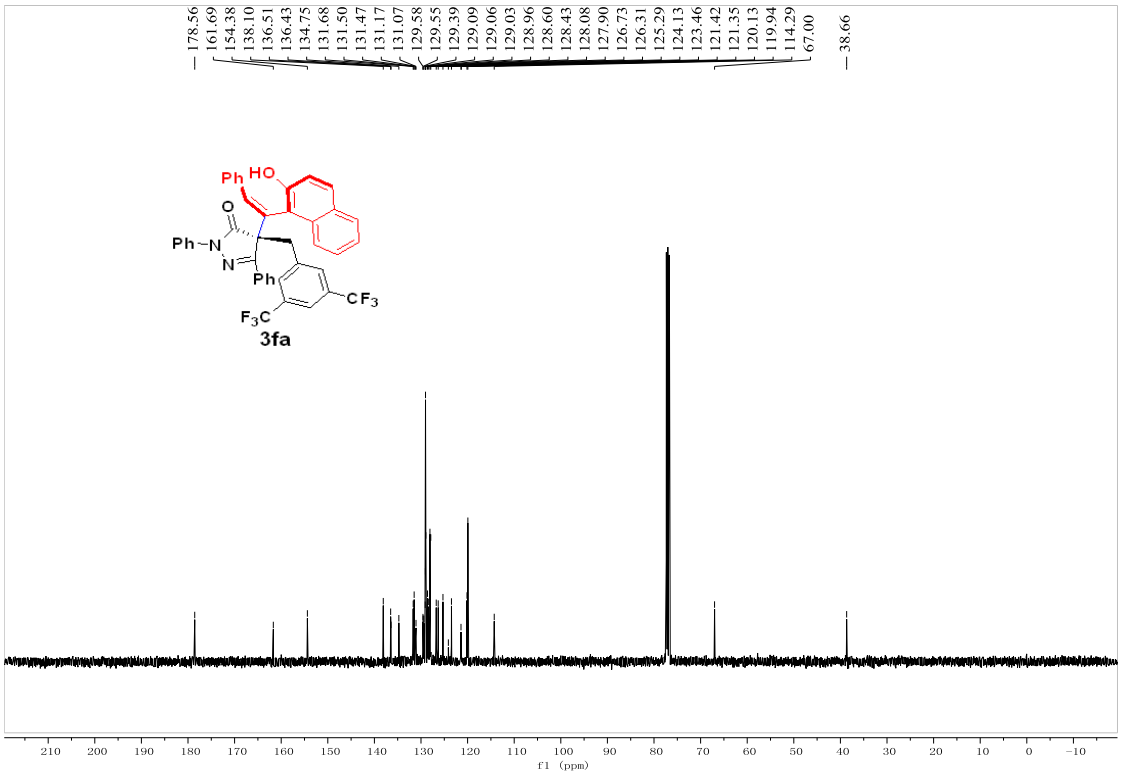
5.10
1.00
4.06
3.11
2.01
1.00
1.00
1.00
f1 (ppm)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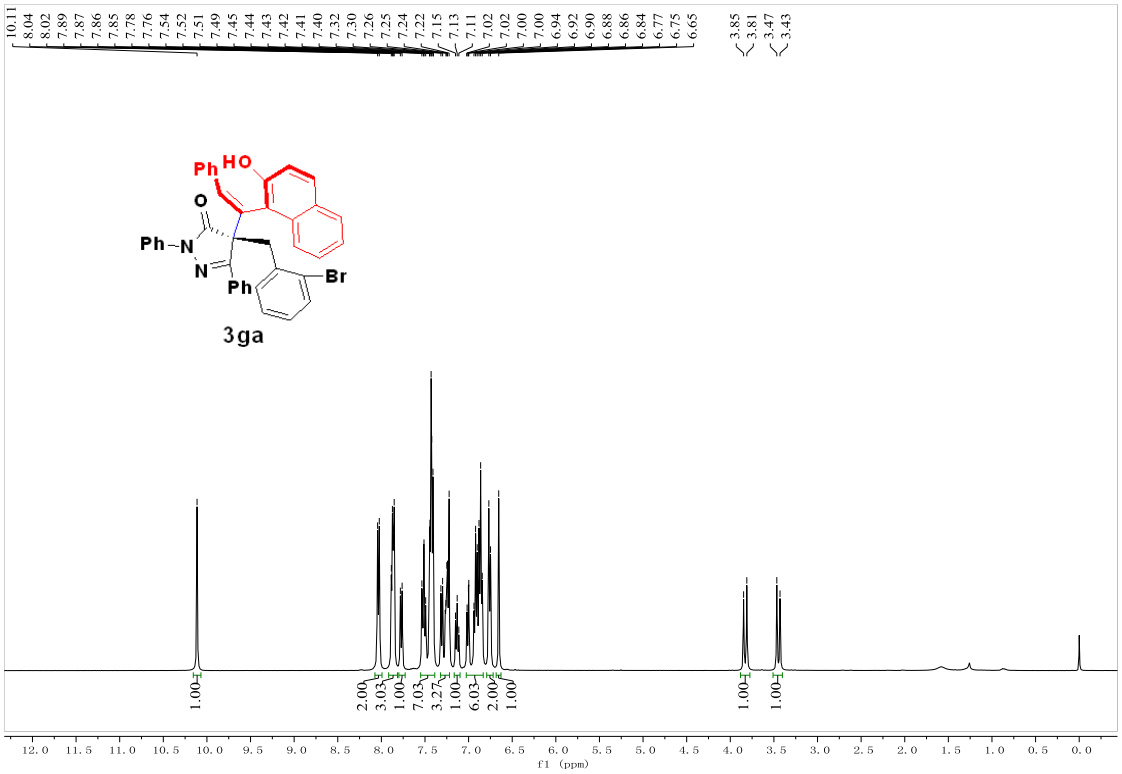
131.47
131.17
131.07
129.58
129.55
129.39
129.09
129.06
129.03
128.96
128.60
128.43
128.08
127.90
126.73
126.31
125.29
124.13
123.46
121.42
121.35
120.13
119.94
114.29
67.00
38.66
Ph
HO
O
Ph–N
N
Ph
CF3
F3C
3fa
f1 (ppm)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7.86
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7.76
7.54
7.52
7.51
7.49
7.45
7.44
7.43
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7.41
7.40
7.32
7.30
7.26
7.25
7.24
7.22
7.15
7.13
7.11
7.02
7.02
7.00
7.00
6.94
6.92
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6.86
6.84
6.77
6.75
6.65
3.85
3.81
3.47
3.43
Ph
HO
O
Ph–N
N
Ph
Br
3ga
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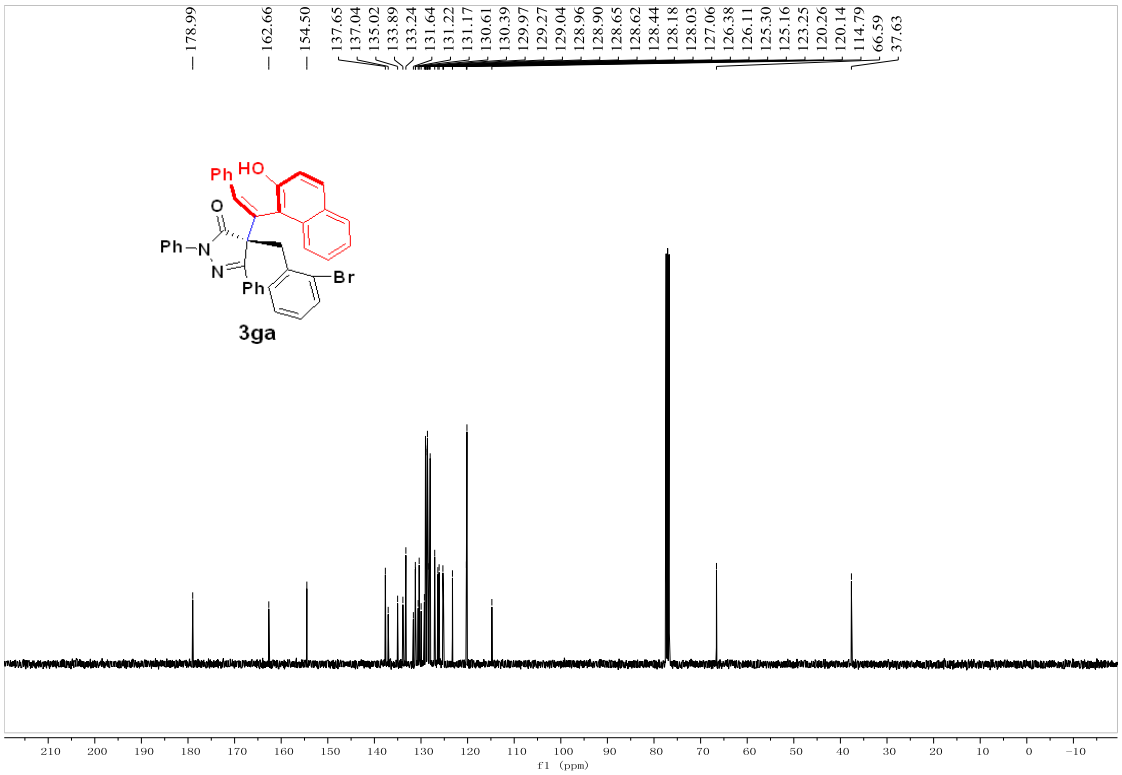
2.00
3.03
1.00
7.03
3.27
1.00
6.03
2.00
1.00
1.00
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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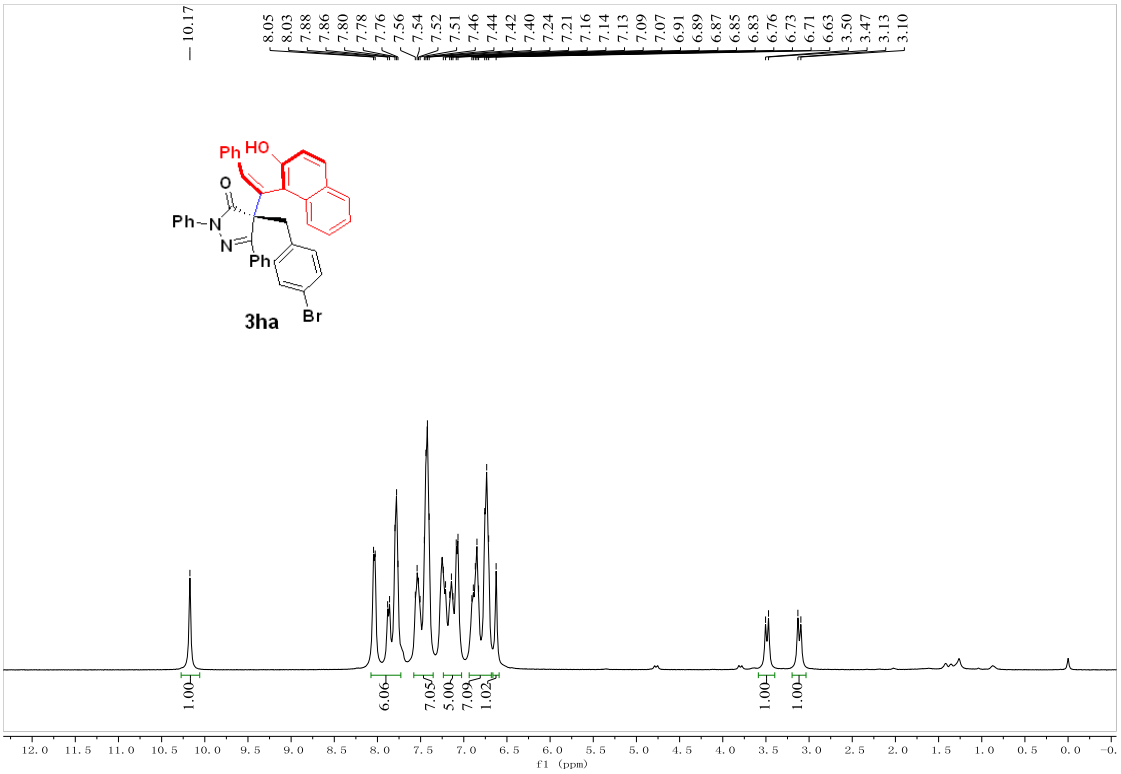
129.27
129.04
128.96
128.90
128.65
128.62
128.44
128.18
128.03
127.06
126.38
126.11
125.30
125.16
123.25
120.26
120.14
114.79
66.59
37.63
Ph
HO
O
Ph–N
N
Ph
Br
3ga
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.76
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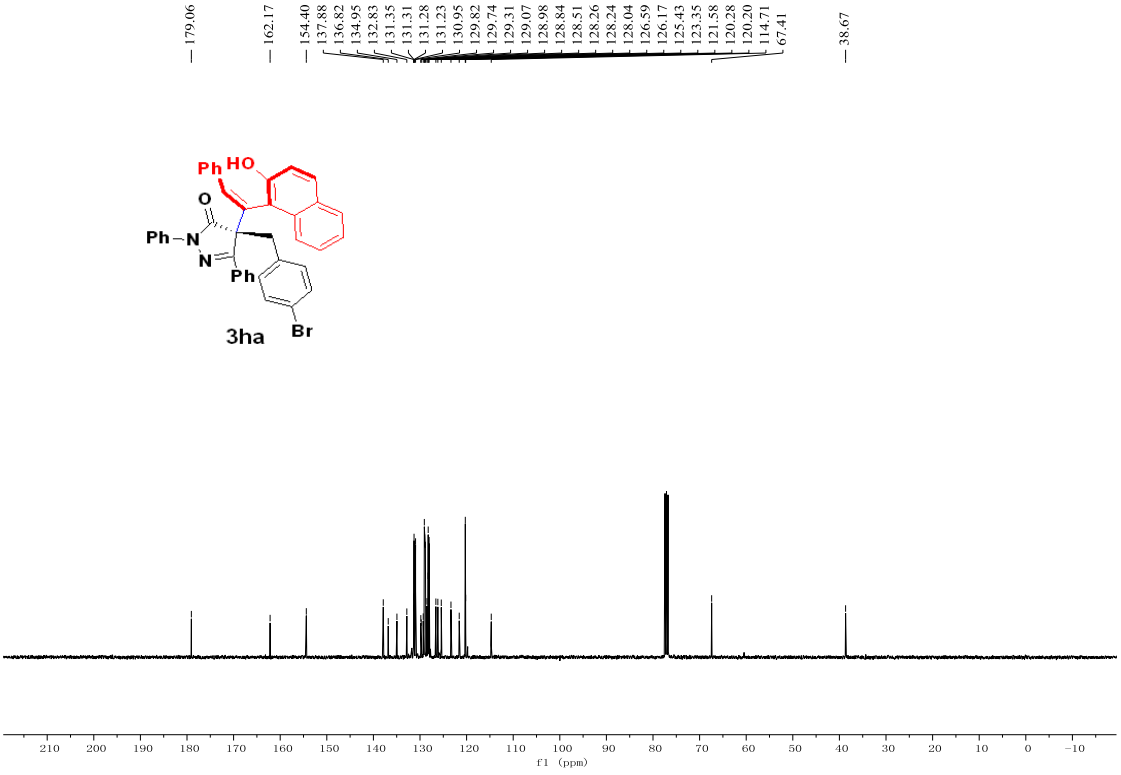
7.52
7.51
7.46
7.44
7.42
7.40
7.24
7.21
7.16
7.14
7.13
7.09
7.07
6.91
6.89
6.87
6.85
6.83
6.76
6.73
6.71
6.63
3.50
3.47
3.13
3.10
Ph
HO
O
Ph
N
N
Ph
Br
3ha
1.00
6.06
7.05
5.00
7.09
1.02
1.00
1.00
f1 (ppm)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129.31
129.07
128.98
128.84
128.51
128.26
128.24
128.04
126.59
126.17
125.43
123.35
121.58
120.28
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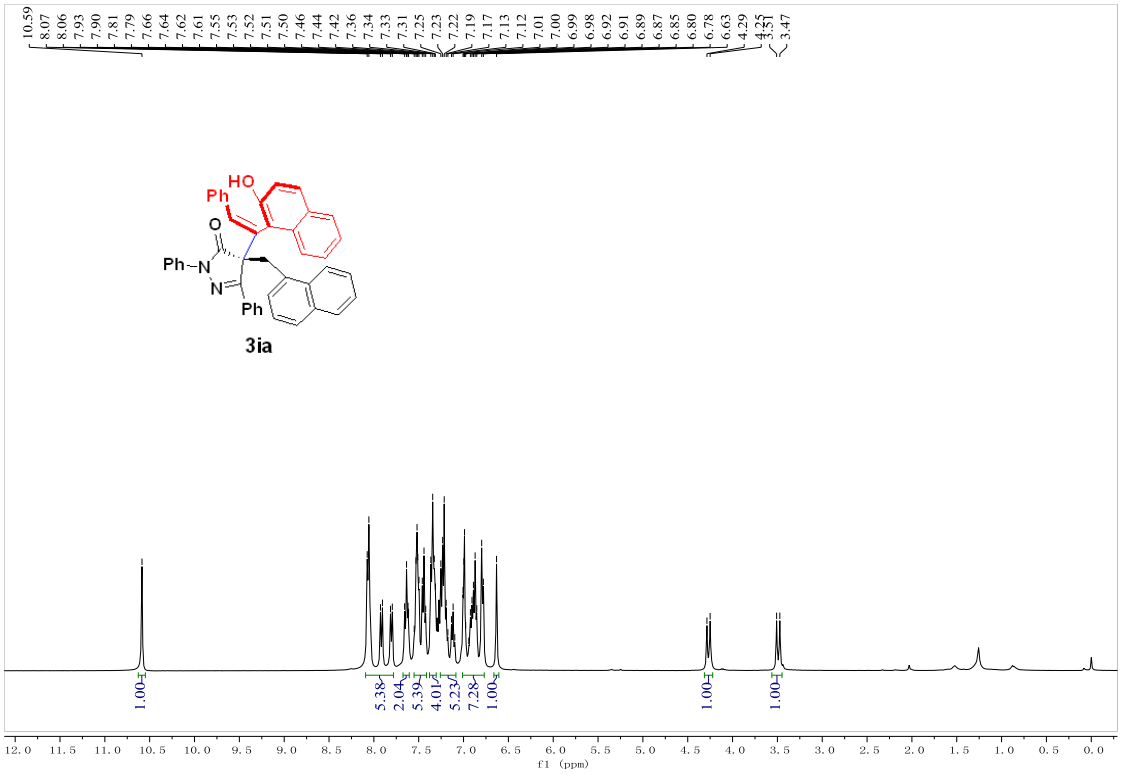
114.71
67.41
38.67
Ph
HO
O
Ph
N
N
Ph
Br
3ha
f1 (ppm)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7.62
7.61
7.55
7.53
7.52
7.51
7.50
7.46
7.44
7.42
7.36
7.34
7.33
7.31
7.25
7.23
7.22
7.19
7.17
7.13
7.12
7.01
7.00
6.99
6.98
6.92
6.91
6.89
6.87
6.85
6.80
6.78
6.63
4.29
3.47
HO
Ph
O
Ph–N
N
Ph
3ia
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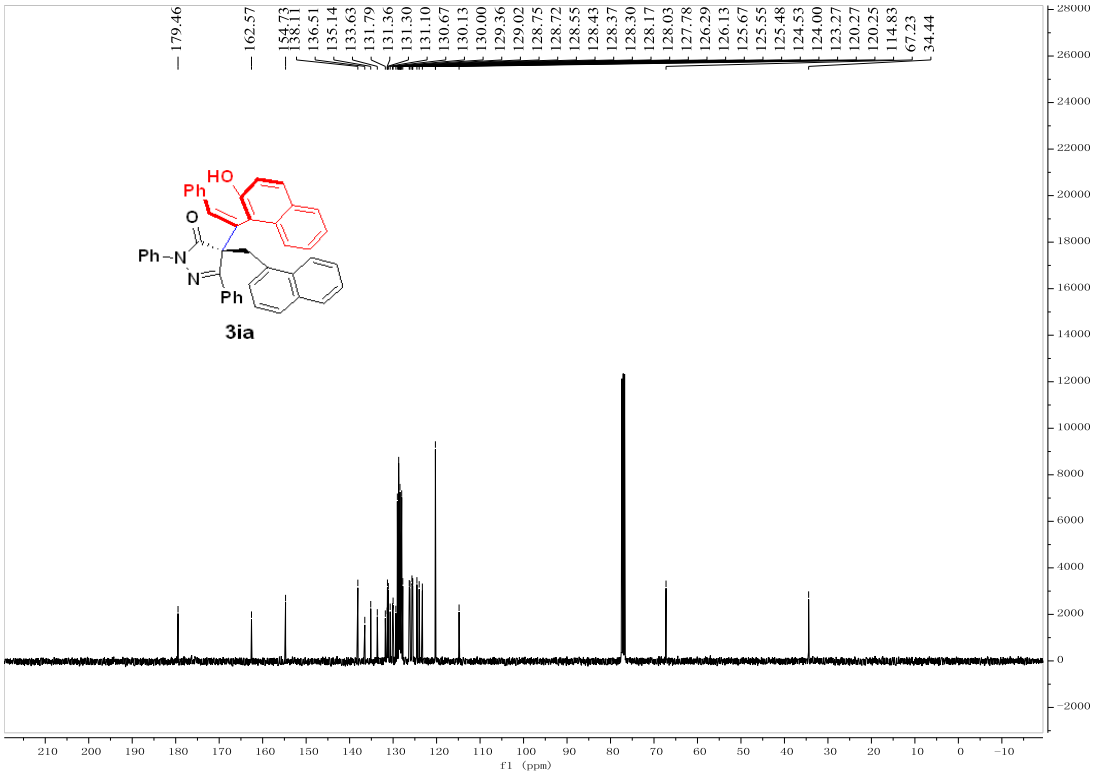
2.04
5.39
4.01
5.23
7.28
1.00
1.00
1.00
f1 (ppm)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129.36
129.02
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128.72
128.55
128.43
128.37
128.30
128.17
128.03
127.78
126.29
126.13
125.67
125.55
125.48
124.53
124.00
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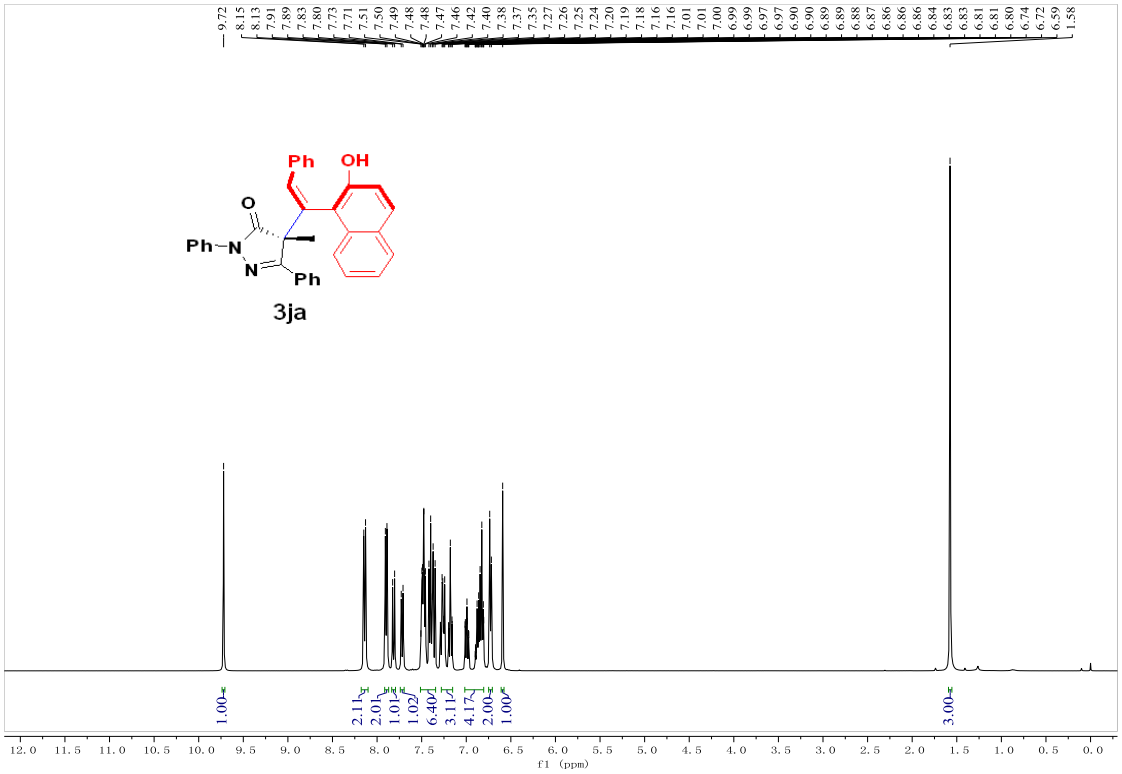
120.27
120.25
114.83
67.23
34.44
HO
Ph
O
Ph–N
N
Ph
3ia
f1 (ppm)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7.50
7.49
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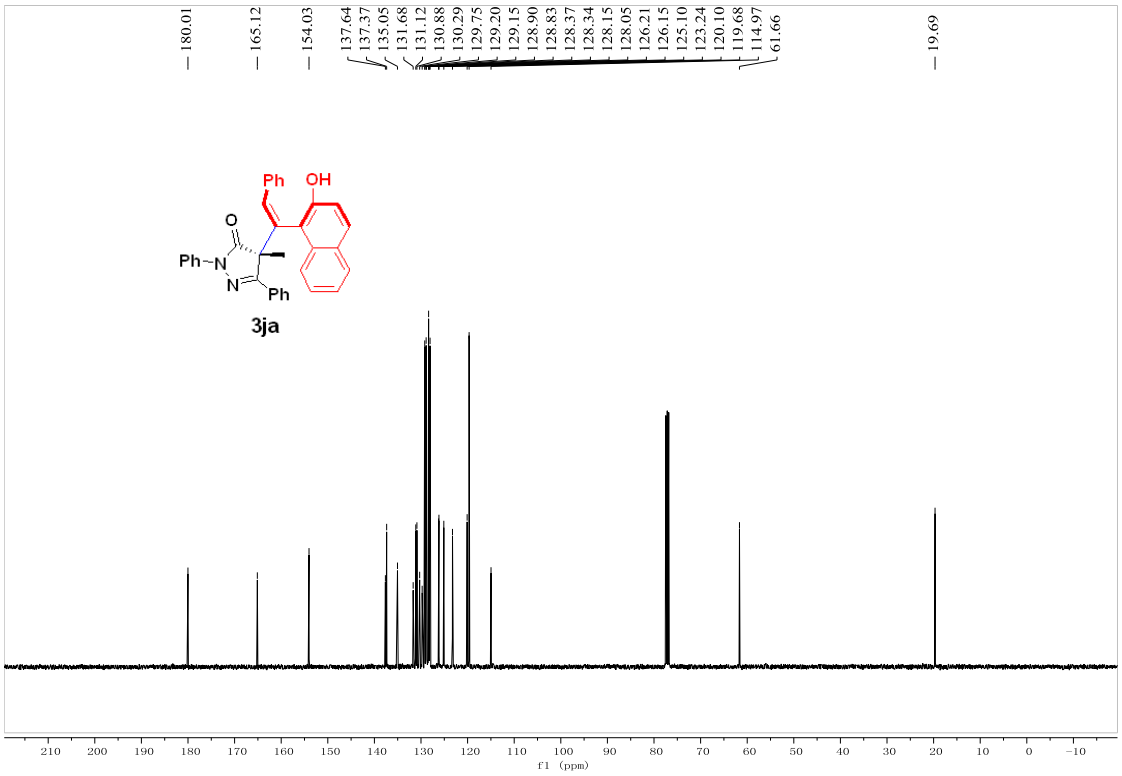
7.48
7.47
7.46
7.42
7.40
7.38
7.37
7.35
7.27
7.26
7.25
7.24
7.20
7.19
7.18
7.16
7.16
7.01
7.01
7.00
6.99
6.99
6.97
6.97
6.90
6.90
6.89
6.89
6.88
6.87
6.86
6.86
6.86
6.84
6.83
6.83
6.81
6.81
6.80
6.74
6.72
6.59
1.58
Ph
OH
O
Ph
N
N
Ph
3ja
1.00
2.11
2.01
1.01
1.02
6.40
3.11
4.17
2.00
1.00
3.00
f1 (ppm)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135.05
131.68
131.12
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130.29
129.75
129.20
129.15
128.90
128.83
128.37
128.34
128.15
128.05
126.21
126.15
125.10
123.24
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114.97
61.66
19.69
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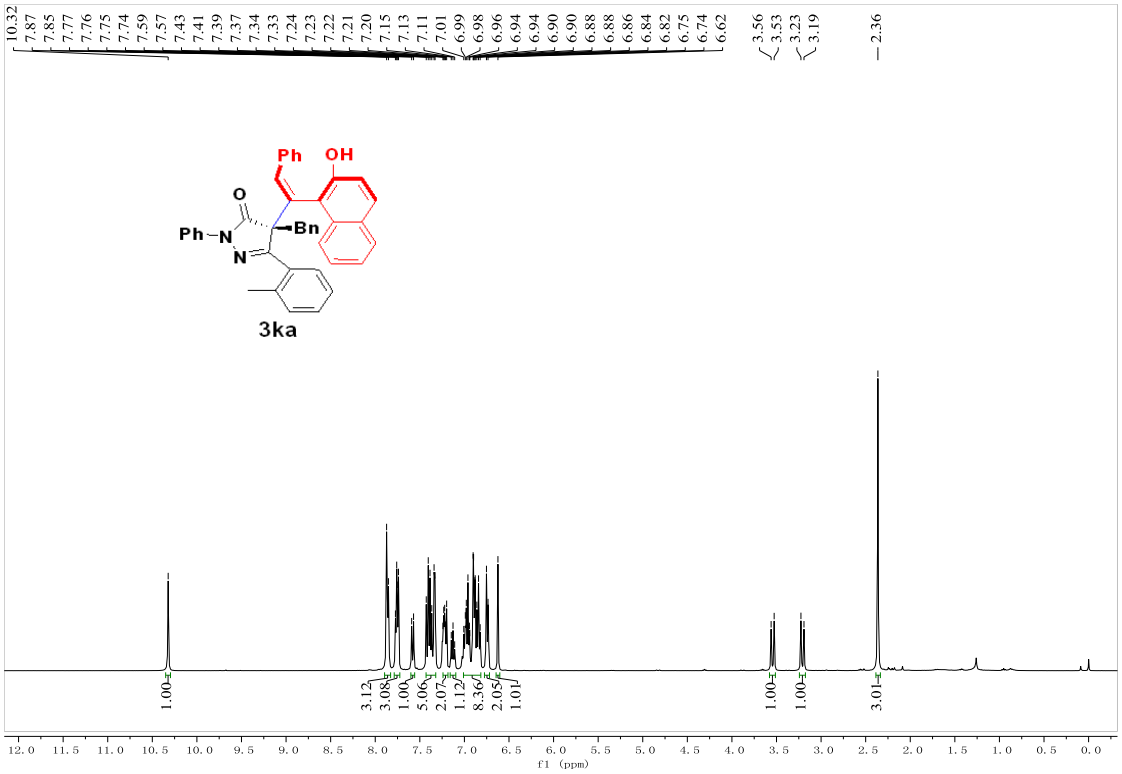
OH
O
Ph
N
N
Ph
3ja
f1 (ppm)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7.41
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7.37
7.34
7.33
7.24
7.23
7.22
7.21
7.20
7.15
7.13
7.11
7.01
6.99
6.98
6.96
6.94
6.94
6.90
6.90
6.88
6.88
6.86
6.84
6.82
6.75
6.74
6.62
3.56
3.53
3.23
3.19
2.36
Ph
OH
O
Ph
N
N
Bn
3ka
1.00
3.12
3.08
1.00
5.06
2.07
1.12
8.36
2.05
1.01
1.00
1.00
3.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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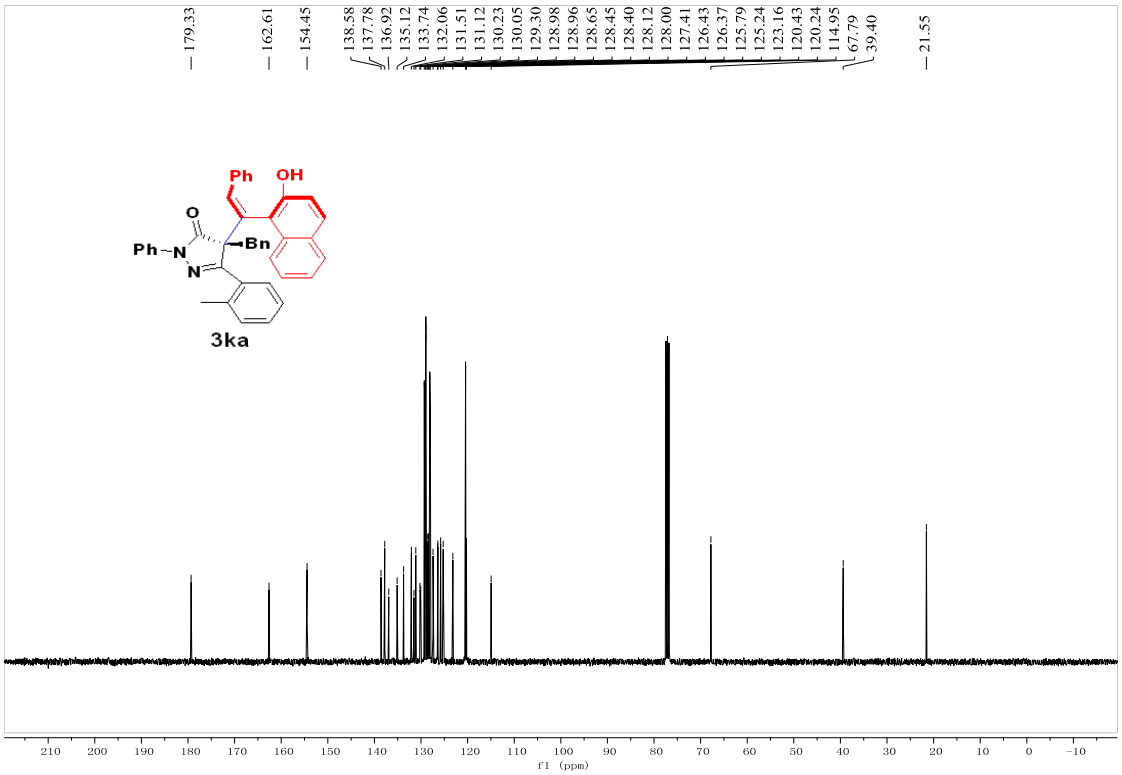
1.0
0.5
0.0
f1 (ppm)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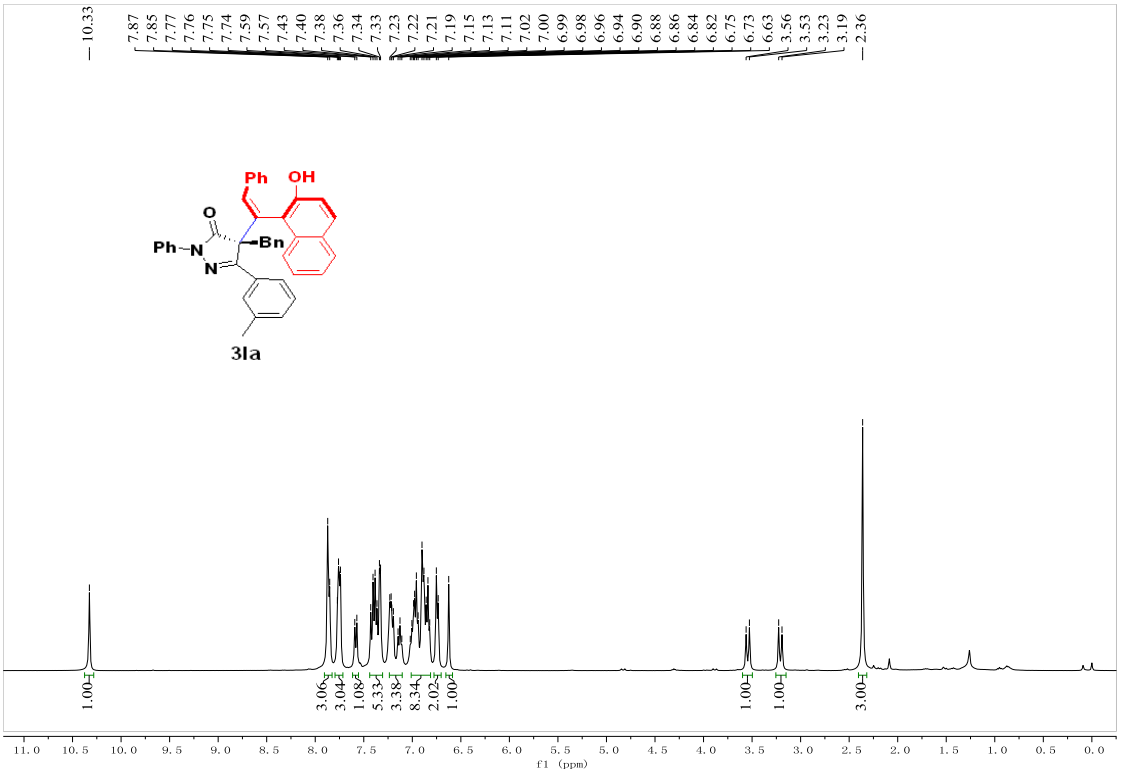
129.30
128.98
128.96
128.65
128.45
128.40
128.12
128.00
127.41
126.43
126.37
125.79
125.24
123.16
120.43
120.24
114.95
67.79
39.40
21.55
Ph
OH
O
Ph
N
N
Bn
3ka
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.77
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7.75
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7.57
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7.40
7.38
7.36
7.34
7.33
7.23
7.22
7.21
7.19
7.15
7.13
7.11
7.02
7.00
6.99
6.98
6.96
6.94
6.90
6.88
6.86
6.84
6.82
6.75
6.73
6.63
3.56
3.53
3.23
3.19
2.36
Ph
OH
O
Ph–N
N
Bn
3la
1.00
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8.34
2.02
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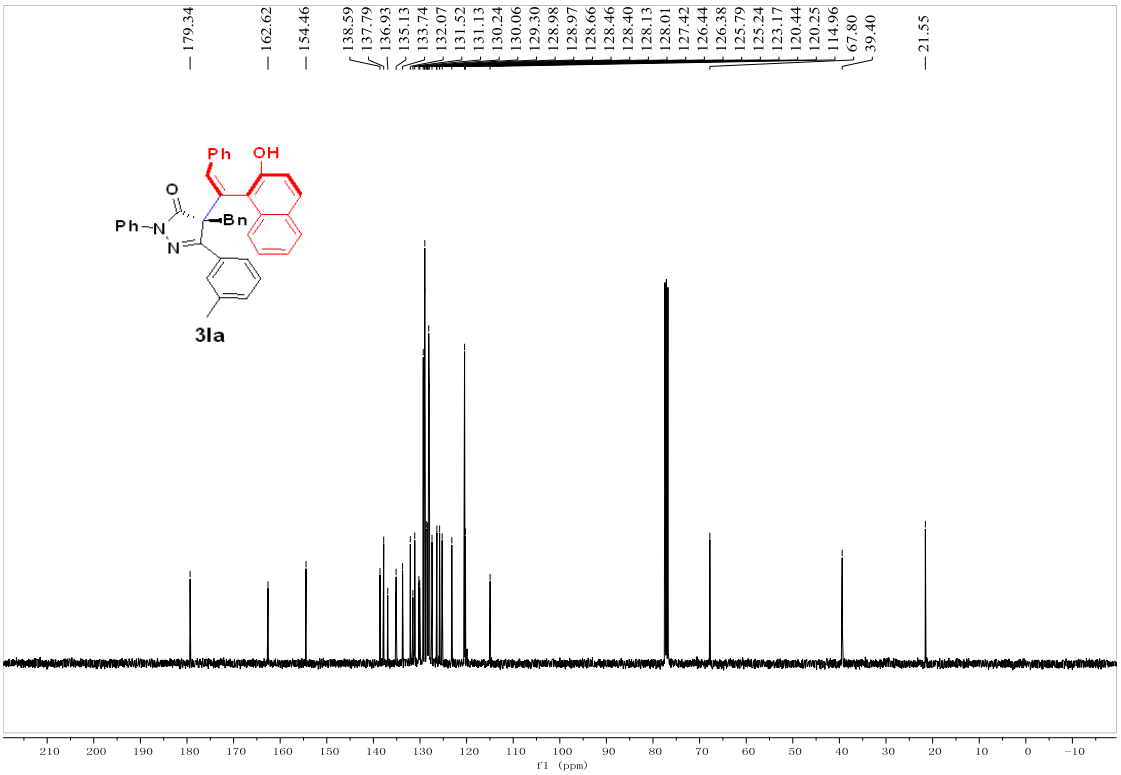
1.00
1.00
3.00
f1 (ppm)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129.30
128.98
128.97
128.66
128.46
128.40
128.13
128.01
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126.44
126.38
125.79
125.24
123.17
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67.80
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21.55
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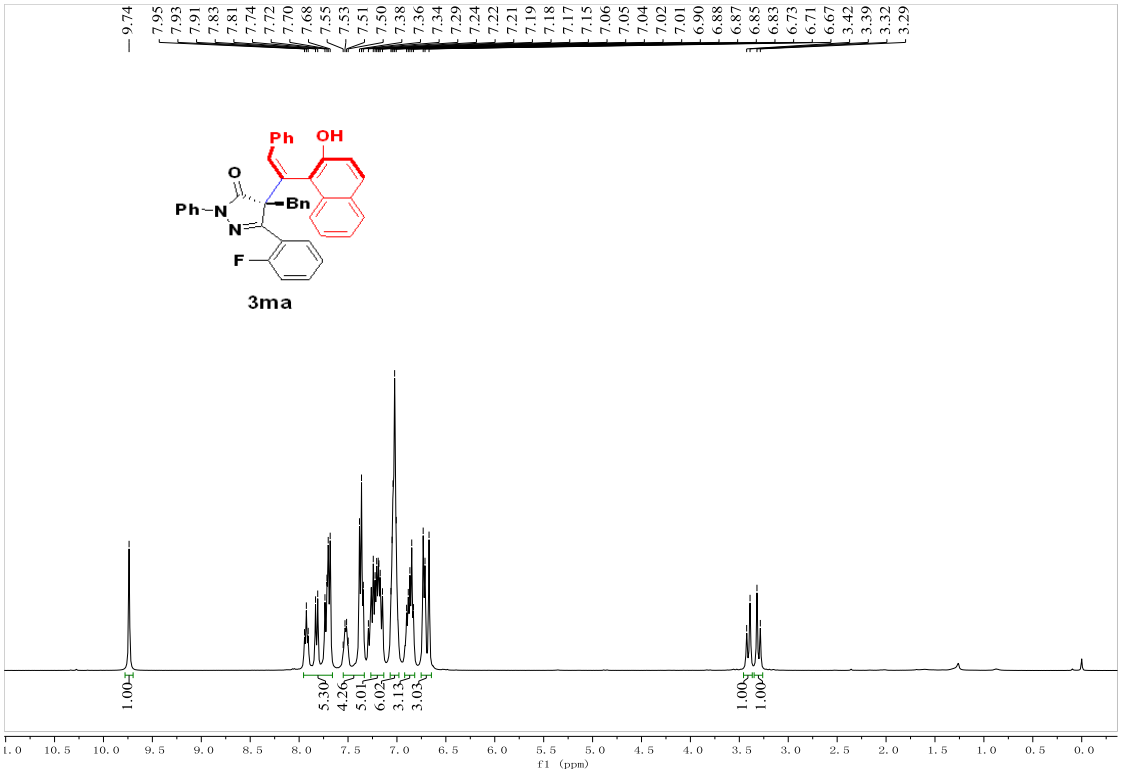
OH
O
Ph–N
N
Bn
3la
f1 (ppm)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7.36
7.34
7.29
7.24
7.22
7.21
7.19
7.18
7.17
7.15
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7.01
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6.85
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6.73
6.71
6.67
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3.39
3.32
3.29
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OH
O
Ph–N
N
Bn
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6.02
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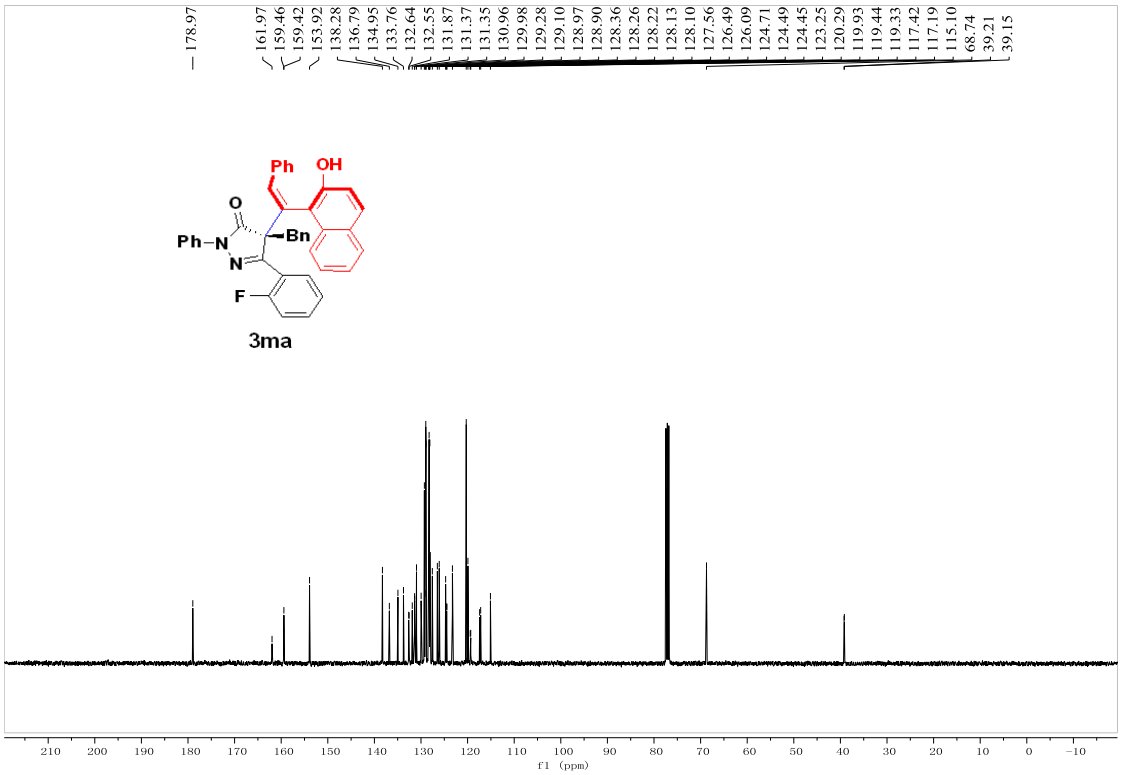
1.00
f1 (ppm)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129.98
129.28
129.10
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128.90
128.36
128.26
128.22
128.13
128.10
127.56
126.49
126.09
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124.49
124.45
123.25
120.29
119.93
119.44
119.33
117.42
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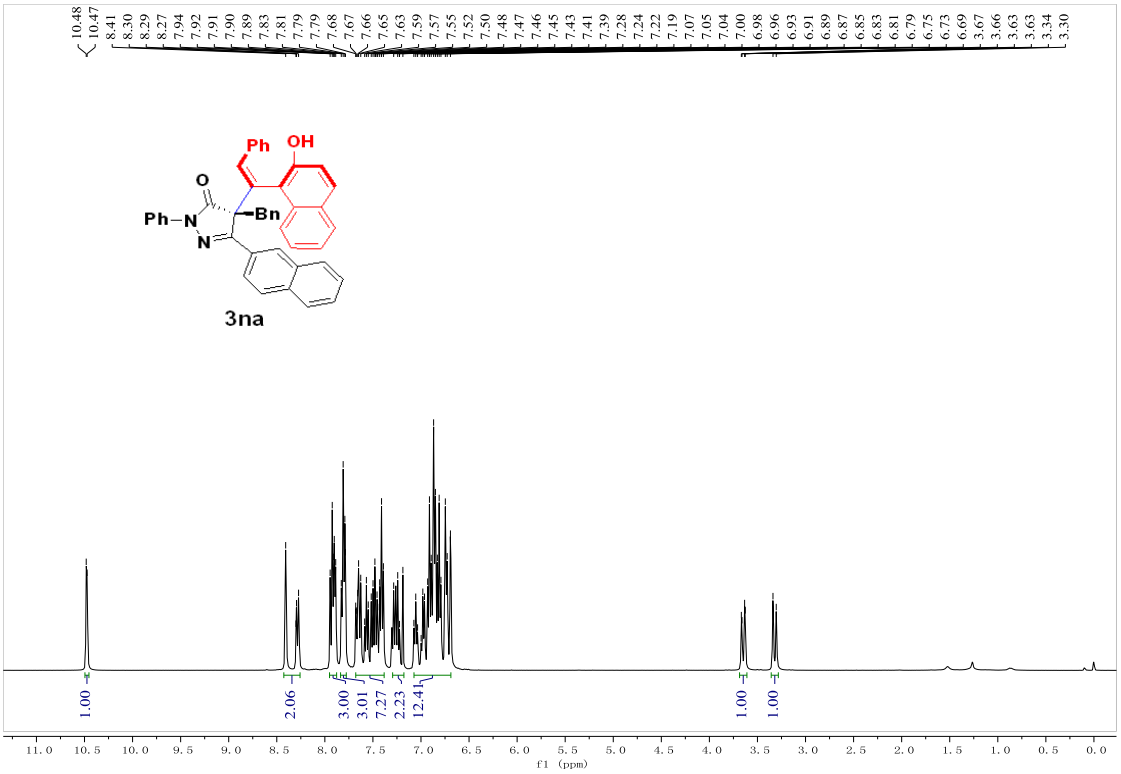
115.10
68.74
39.21
39.15
Ph
OH
O
Ph–N
N
Bn
F
3ma
f1 (ppm)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Ph–N
N
Bn
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3.01
7.27
2.23
12.41
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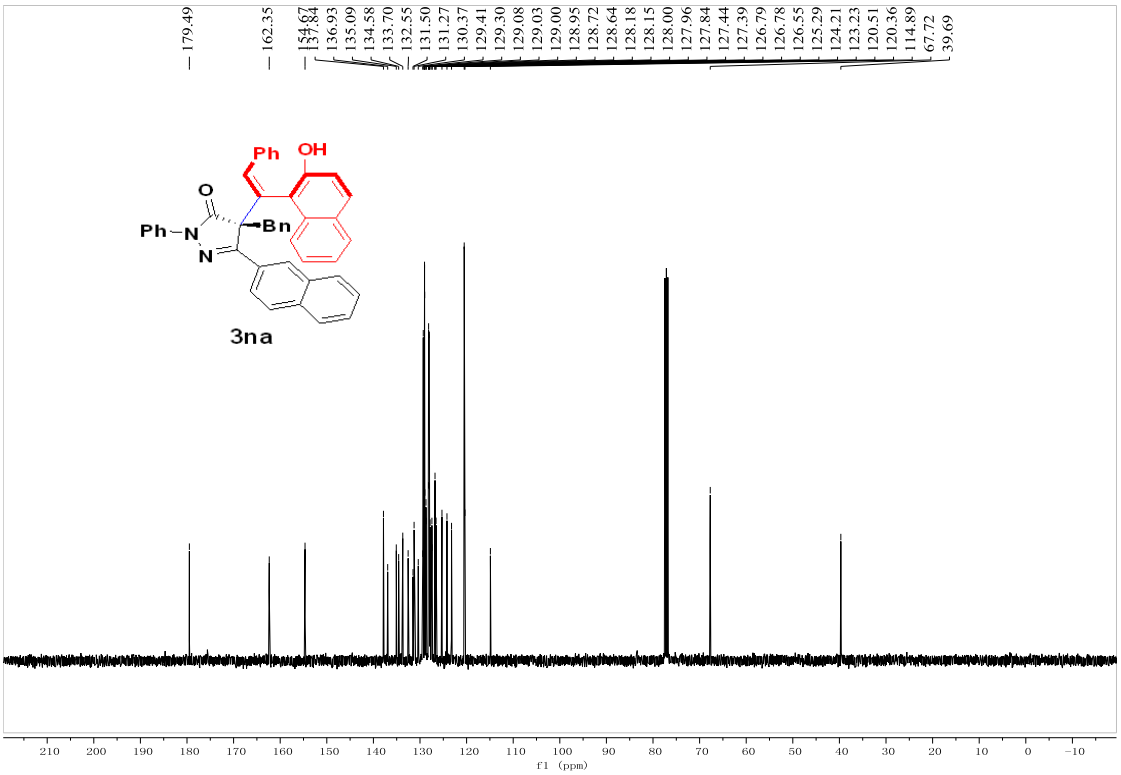
1.00
f1 (ppm)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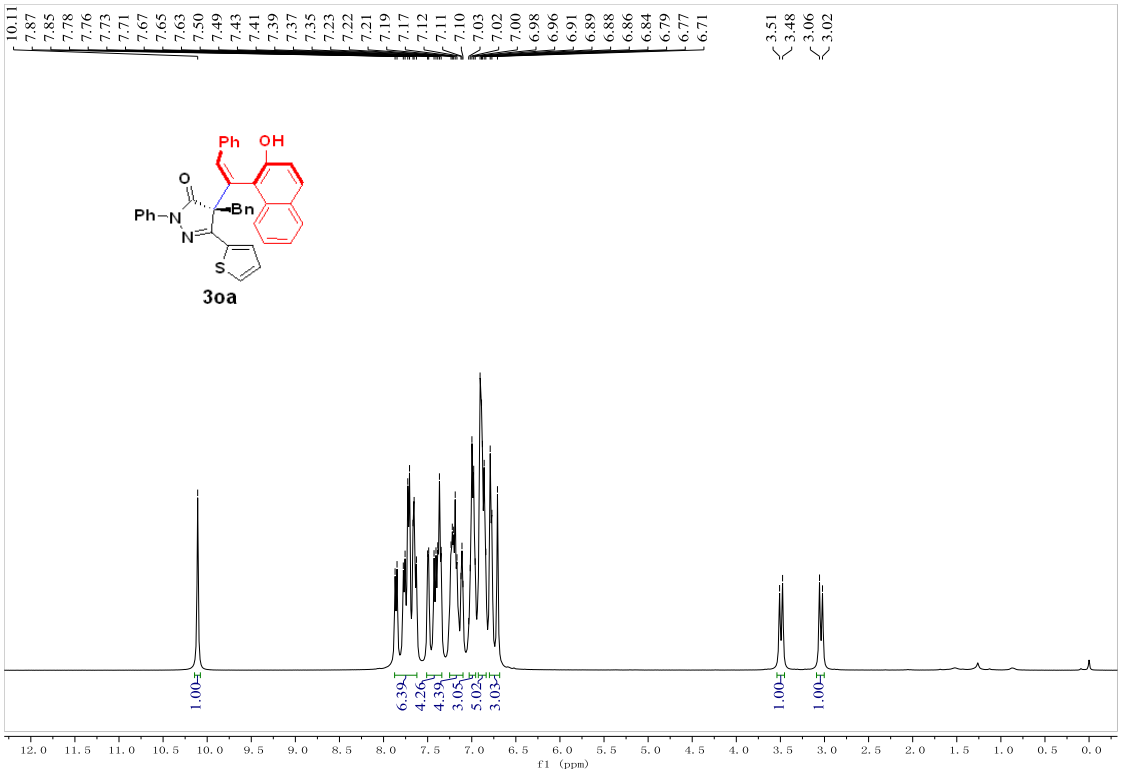
f1 (ppm)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7.37
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7.23
7.22
7.21
7.19
7.17
7.12
7.11
7.10
7.03
7.02
7.00
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6.96
6.91
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6.86
6.84
6.79
6.77
6.71
3.51
3.48
3.06
3.02
Ph
OH
O
Ph–N
N
Bn
S
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3.05
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3.03
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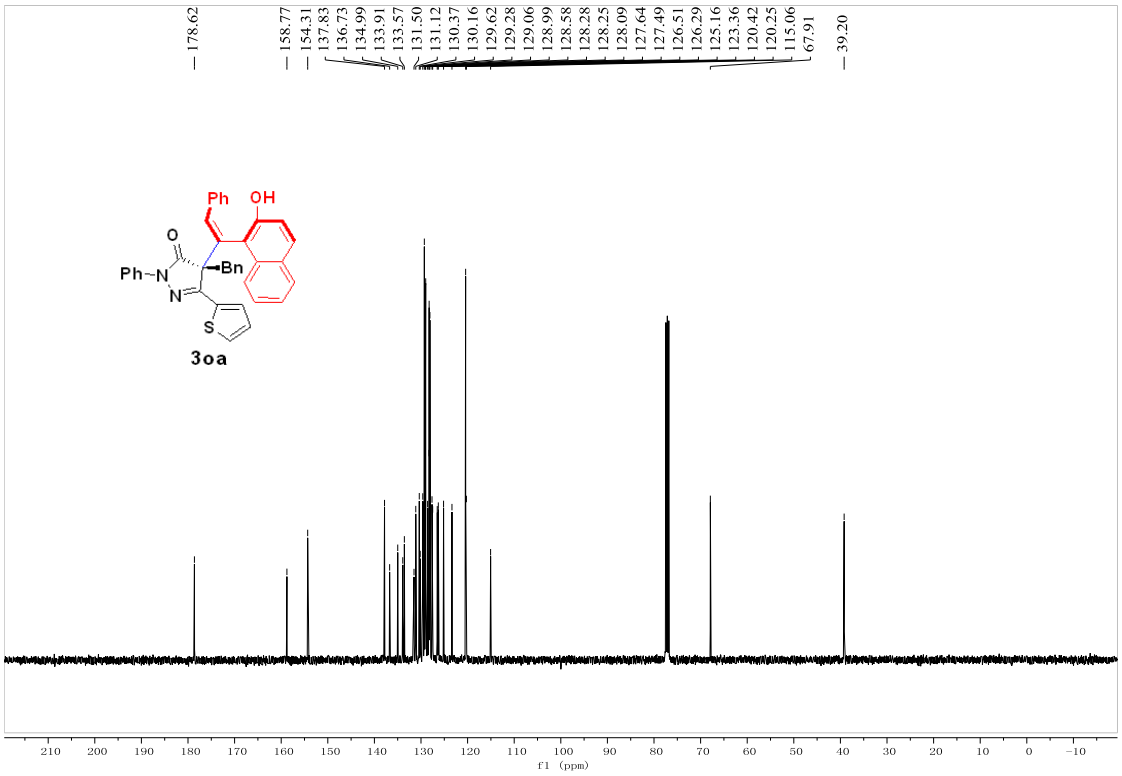
1.00
f1 (ppm)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129.28
129.06
128.99
128.58
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128.25
128.09
127.64
127.49
126.51
126.29
125.16
123.36
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67.91
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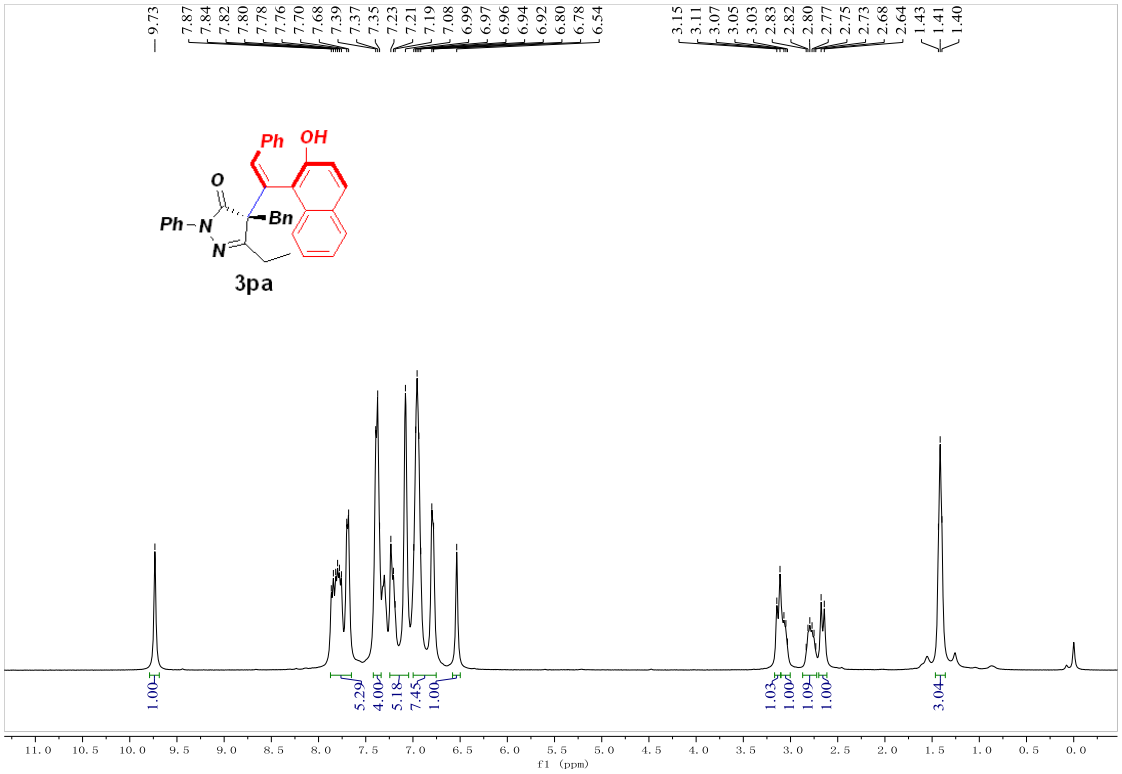
OH
O
Ph–N
N
Bn
S
3oa
f1 (ppm)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7.08
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6.96
6.94
6.92
6.80
6.78
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3.15
3.11
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3.05
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2.83
2.82
2.80
2.77
2.75
2.73
2.68
2.64
1.43
1.41
1.40
Ph
OH
O
Ph–N
N
Bn
3pa
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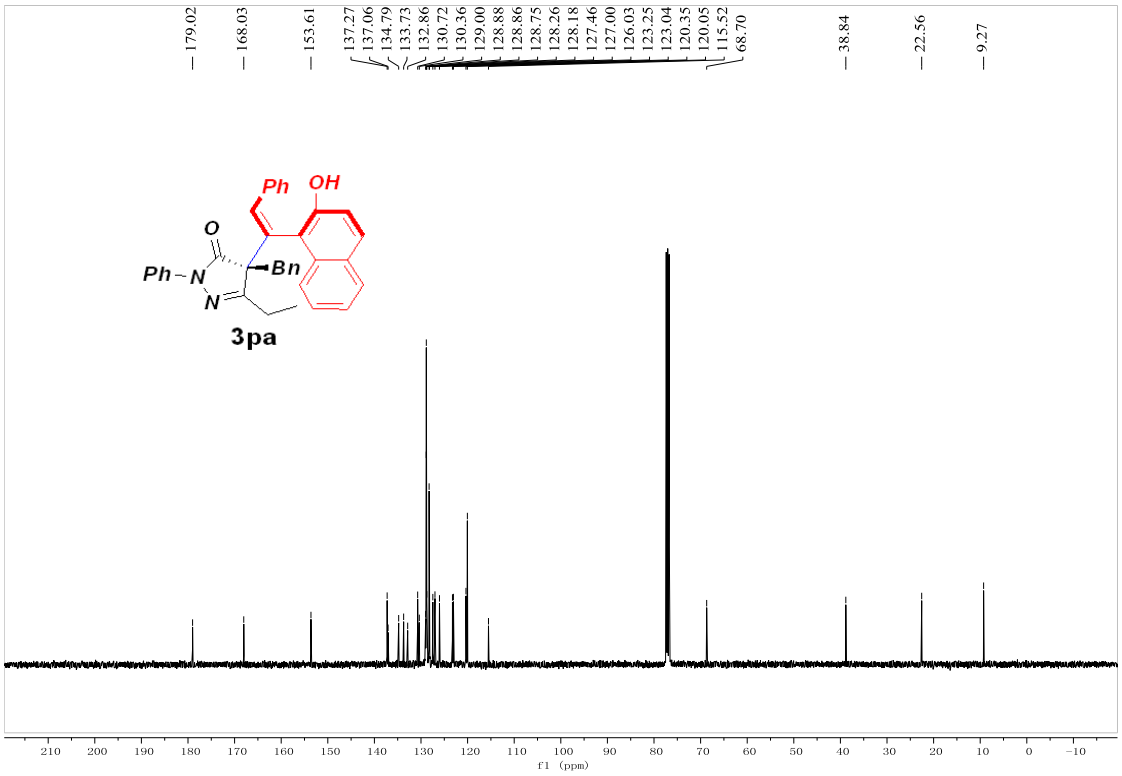
5.18
7.45
1.00
1.03
1.00
1.09
1.00
3.04
f1 (ppm)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128.86
128.75
128.26
128.18
127.46
127.00
126.03
123.25
123.04
120.35
120.05
115.52
68.70
38.84
22.56
9.27
Ph
OH
O
Ph–N
N
Bn
3pa
f1 (ppm)