Electronic Supplementary Material (ESI) for ChemComm.

C6’ steric bulk of the Cinchona alkaloid enables an enantioselective Michael addition/annulation sequence toward pyranopyrazoles

Xiaoze Bao, Shiqiang Wei, Jingping Qu and Baomin Wang*

State Key Laboratory of Fine Chemicals, School of Pharmaceutical Science and Technology, Dalian University of Technology, Dalian 116024, P. R. China

E-mail: bmwang@dlut.edu.cn

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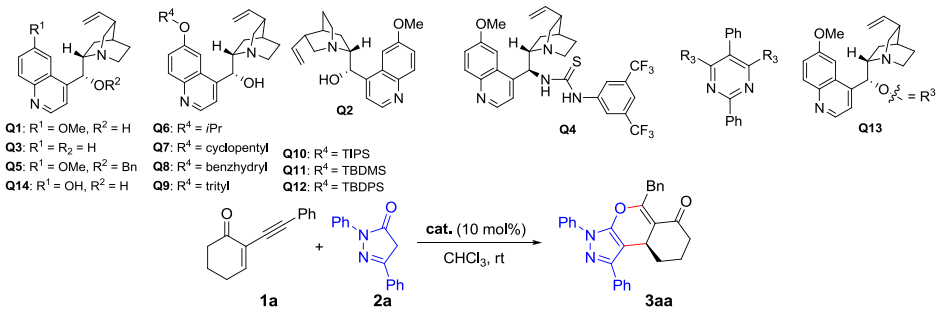
1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (100~200 mesh). 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 370 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 = double doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM). The absolute configuration of **3ad** was assigned by the X-ray analysis.

Cyclic 2-(1-alkynyl)-2-alken-1-ones **1a-j** were prepared according to the literature.[1] Pyrazolones **2a-l** were prepared from *β*-keto esters according to the literature.[2] The catalysts **Q4-10** were prepared from quinine according to the literature.[3] The racemic products were synthesized using tetramethyl guanidine (TMG) as the catalyst.

2. Screening of reaction conditions

Table S1. Optimization of reaction conditions.



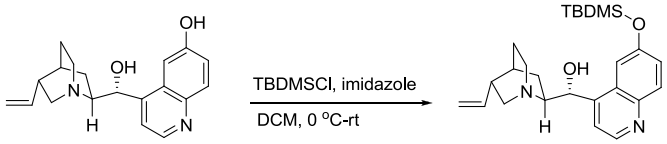
Entry[a]	Solvent	**Cat.**	*t* (h)	Yield (%)[b]	ee [%][c]
1	$CHCl_3$	**Q1**	1	93	61
2	$CHCl_3$	**Q2**	1	93	-54
3	$CHCl_3$	**Q3**	1	95	30
4	$CHCl_3$	**Q4**	24	66	-47
5	$CHCl_3$	**Q5**	24	57	37
6	$CHCl_3$	**Q13**	24	55	17
7	$CHCl_3$	**Q14**	12	90	56
8	$CHCl_3$	**Q6**	1	93	79
9	$CHCl_3$	**Q7**	1	93	78
10	$CHCl_3$	**Q8**	1	90	75
11	$CHCl_3$	**Q9**	3	93	83
12	$CHCl_3$	**Q10**	3	95	86
13	$CHCl_3$	**Q11**	3	95	86
14	$CHCl_3$	**Q12**	3	95	85
15	DCM	**Q10**	3	95	81
16	DCE	**Q10**	3	94	81
17	CCl_4	**Q10**	3	92	84
18	toluene	**Q10**	3	89	76

19	EtOAc	**Q10**	8	78	71
20	Et_2O	**Q10**	8	76	74
21[d]	$CHCl_3$	**Q10**	12	95	91
22[e]	$CHCl_3$	**Q10**	24	95	92
23[e]	$CHCl_3$	**Q11**	24	95	91

[a] Unless otherwise noted, reactions were conducted with **1a** (0.1 mmol), **cat.** (10 mol %), **2a** (0.12 mmol) in solvent (1.0 mL) at rt. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was performed at -20 °C for 12 h, and then stirred at rt for 3 h. [e] The reaction was performed at -30 °C for 24 h, and then stirred at rt for 3 h.

3. Experimental procedures and characterization of compounds

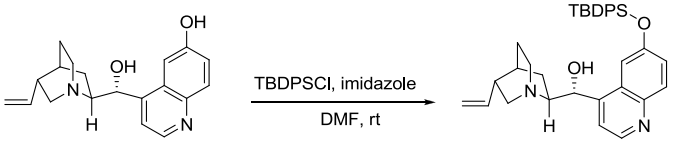
Synthesis of catalyst Q11



Cupreine **Q11**

A Schlenk tube equipped with a magnetic stir bar was charged with cupreine (1.0 mmol) under argon. After the addition of anhydrous DCM (5 mL), the resulting mixture was cooed to 0 °C. TBDMSCl (2.0 mmol) and imidazole (2.0 mmol) were added in sequence. The mixture was then warmed to rt, stirred for 1 h. DCM (15 mL) was added to the mixture, then washed with diluted $NaHCO_3$ solution and brine, dried over Na_2SO_4, concentrated. The crude mixture was purified by column chromatography (EtOAc/MeOH/$NH_3.H_2O$ = 10:1:0.1) on silica gel to give the product **Q11** as white foam (260 mg, yield 60%). mp 67.3-70.1 °C; $[\alpha]_D^{25}$= -52.4 (*c* 0.43, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 4.5 Hz, 1H), 7.38 (d, *J* = 2.3 Hz, 1H), 7.21 (dd, *J* = 9.0, 2.3 Hz, 1H), 5.81-5.65 (m, 1H), 5.44 (d, *J* = 4.3 Hz, 1H), 4.92 (dd, *J* = 17.9, 13.8 Hz, 2H), 4.58 (brs, 1H), 3.47 (d, *J* = 13.6 Hz, 1H), 3.18-2.95 (m, 2H), 2.73-2.53 (m, 2H), 2.24 (s, 1H), 1.78 (s, 1H), 1.75-1.65 (m, 2H), 1.58-1.37 (m, 2H), 1.01 (s, 9H), 0.26 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 148.0, 147.7, 144.2, 142.0, 131.3, 126.7, 125.0, 118.6, 114.2, 110.5, 72.3, 60.0, 57.1, 43.2, 40.0, 27.9, 27.7, 25.7, 22.0, 18.3, -4.3; HRMS (ESI) m/z Calcd. for $C_{25}H_{37}N_2O_2Si$ ($[M+H]^+$) 425.2619, Found; 425.2613.

Synthesis of catalyst Q12

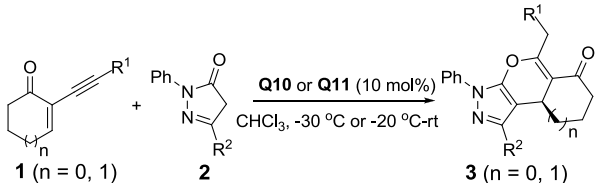


Cupreine **Q12**

A Schlenk tube equipped with a magnetic stir bar was charged with cupreine (1.0 mmol) under argon. After the addition of anhydrous DMF (5 mL), TBDPSCl (2.0 mmol) and imidazole (2.0 mmol) were added in sequence. The mixture was then stirred at rt overnight. Water (20 mL) was added to the mixture, the mixture was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with diluted $NaHCO_3$ solution and brine, dried over Na_2SO_4, concentrated. The crude mixture was purified by column chromatography (EtOAc/MeOH/ $NH_3.H_2O$ = 10:1:0.1) on silica gel to give the product **Q12** as white foam (400 mg, yield 73%). mp 68.3-70.5 °C; $[\alpha]_D^{25}$ = -50.9 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 12.2, 7.1 Hz, 4H), 7.42-7.30 (m, 7H), 7.27-7.22 (m, 2H), 5.80-5.59 (m, 1H), 5.06-4.80 (m, 3H), 3.53 (brs, 1H), 2.99-2.83 (m, 3H), 2.48-2.28 (m, 2H), 2.16 (s, 1H), 1.69 (s, 1H), 1.60-1.28 (m, 4H), 1.14 (s, 9H); ^{13}C

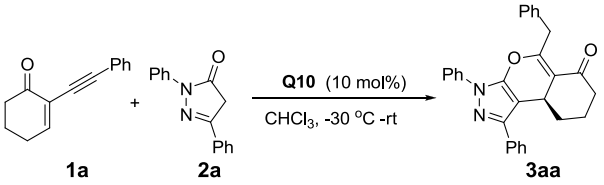
NMR (101 MHz, $CDCl_3$) δ 153.7, 147.8, 147.7, 144.2, 142.1, 135.6, 135.5, 132.6, 132.4, 131.3, 130.1, 128.0, 127.9, 127.0, 124.6, 118.7, 114.2, 110.2, 71.6, 60.1, 56.6, 42.6, 40.0, 27.8, 27.7, 26.6, 23.6, 19.5; HRMS (ESI) m/z Calcd. for $C_{35}H_{41}N_2O_2Si$ ($[M+H]^+$) 549.2932, Found 549.2912.

General procedure: synthesis of compounds 3aa-3ja, 3ab-3al



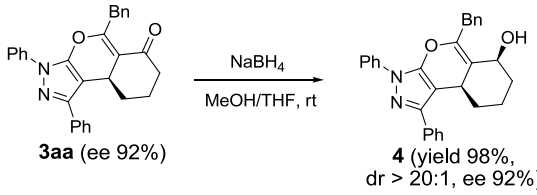
A Schlenk tube equipped with a magnetic stir bar was charged with enynone **1** (0.2 mmol) and Q**10** or **Q11** (0.02 mmol), followed with $CHCl_3$ (2 mL). After cooled to -30 ℃ or -20 ℃ for 15 min, the pyrazolone **2** (0.24 mmol) was added in one portion. The reaction was detected by TLC. After 24-120 h, the reaction mixture was warmed to rt, then stirred for 1-5 h. The mixture was purified by column chromatography on silica gel directly to give the product **3**.

Gram scale synthesis of the product 3aa



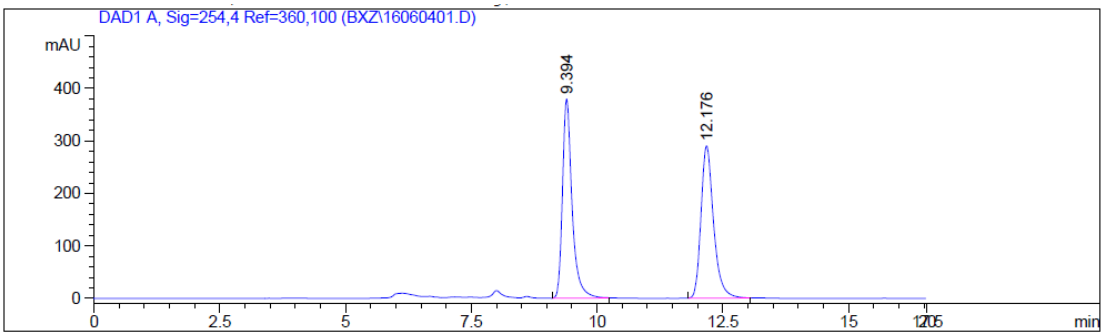
A solution of **1a** (3.0 mmol, 1.0 eq.) and **Q10** (0.3 mmol, 0.1 eq.) in $CHCl_3$ (30 mL) was cooled to -30 ^oC. After 15 min, **2a** (3.6 mmol, 1.2 eq.) was added in one portion. The resulting mixture was stirred at -30 ^oC for 48 h, and then warmed to rt, stirred for 3 h. The solvent was removed under vacuum, then the crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/8) to give **3aa** as white solid (1.24 g, 96% yield, 92% ee)

Synthesis of (6*S*,9a*R*)-5-benzyl-1,3-diphenyl-3,6,7,8,9,9a-hexahydroisochromeno[3,4-*c*] pyrazol-6-ol (4)



3aa (0.1 mmol) was suspended in a 1:1 mixture of THF and MeOH (2.0 mL). $NaBH_4$ (0.2 mmol, 2.0 equiv.) was added in one portion at rt. After 10 min, the mixture turned to be clear (TLC detected the starting material was consumed). The solvent was evaporated, and then the crude mixture was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/4) to give **4** as white solid (42 mg, 98% yield, 92% ee). The absolute configuration was determined by 1D NOE (see page S55). mp 101.9-104.1 ^oC; $[\alpha]_D^{25}$ = -142.8 (*c* 0.41, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.44-7.28 (m, 9H), 7.23-7.17 (m, 2H), 4.30 (d, *J* = 9.3 Hz, 1H), 4.11 (s, 2H), 3.53 (dd, *J* = 11.7, 2.4 Hz, 1H), 2.12 (s, 1H), 2.08-2.00 (m, 1H), 1.96-1.88 (m, 1H), 1.82-1.73 (m, 1H), 1.68-1.54 (m, 1H), 1.32-1.22 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 146.9, 142.2, 139.4, 138.4, 134.0, 129.0, 128.7, 128.6, 128.5, 127.9, 126.7, 126.3, 125.9, 120.7, 115.5, 97.3, 73.0, 38.0, 36.4, 35.9, 35.1, 24.1; HRMS (ESI) m/z Calcd. for $C_{29}H_{27}N_2O_2$ ($[M+H]^+$) 435.2067, Found

435.2061; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 13.0 min, t_{minor} = 11.5 min).



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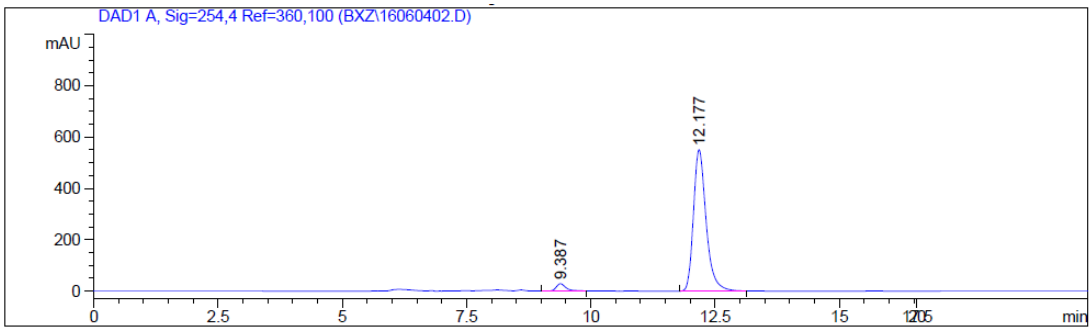

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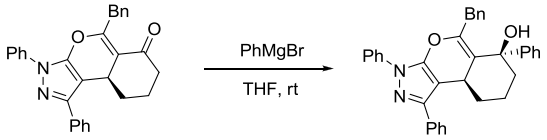
2	12.177	BB	0.2688	9773.40820	551.36127	96.1617

Synthesis of (6*R*,9a*R*)-5-benzyl-1,3,6-triphenyl-3,6,7,8,9,9a-hexahydroisochromeno[3,4-*c*] pyrazol-6-ol (5)

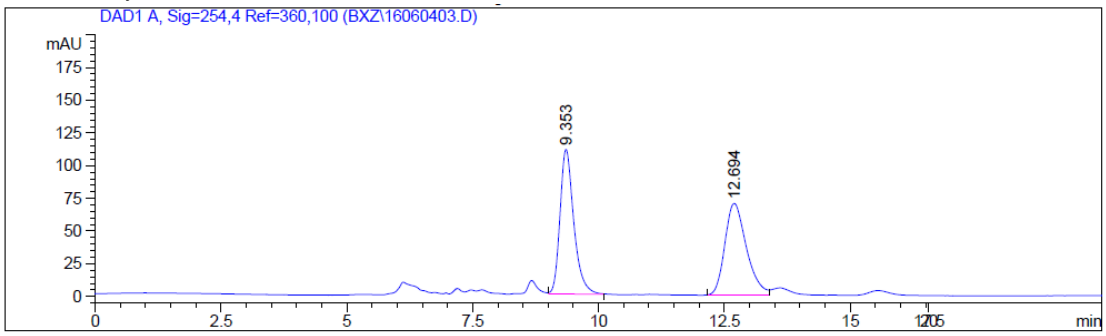


3aa (ee 92%)

5 (yield 80%, dr > 20:1, ee 92%)

3aa (0.1 mmol) was dissolved in anhydrous THF (1.0 mL) under argon. 0.5 mL (5.0 eq.) of PhMgBr (1.0 M) was added dropwise to the solution at rt. After 30 min, another 0.5 mL (5.0 eq.) of PhMgBr (1.0 M) was added. The resulting mixture was stirred overnight. Saturated NH_4Cl aq. (5 mL) was added to quench the mixture, and then extracted with EtOAc (10 mL × 2). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated. The crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/15) on silica gel to give the product **5** as white foam (41 mg, yield 80%). The absolute configuration was assigned by analogy to **4**. mp 75.3-78.4 °C $[\alpha]_D^{25}$ = -85.0 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.55 (m, 6H), 7.43-7.21 (m, 14H), 4.07 (d, *J* = 15.3 Hz, 1H), 3.97 (d, *J* = 15.2 Hz, 1H), 3.79 (dd, *J* = 11.9, 3.7 Hz, 1H), 2.57-2.44 (m, 1H), 2.03 (brs, 2H), 1.98-1.89 (m, 1H), 1.88-1.78 (m, 1H), 1.72-1.44 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 147.0, 146.6, 145.4, 138.6, 138.2, 133.9, 123.0, 129.0, 128.9, 128.4, 127.9, 127.8, 126.9, 126.4,

126.0, 125.8, 120.8, 117.6, 115.3, 97.6, 40.4, 37.5, 33.6, 32.8, 20.3; HRMS (ESI) m/z Calcd. for $C_{35}H_{31}N_2O_2$ ([M+H]$^+$) 511.2380, Found 511.2371; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 12.7 min, t_{minor} = 9.4 min).



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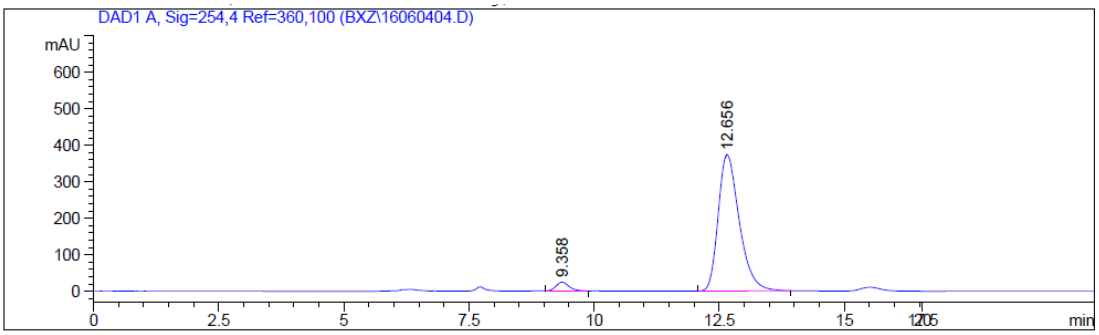
2	12.694	BV	0.4479	2092.74023	70.17435	49.7916



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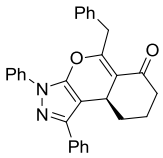
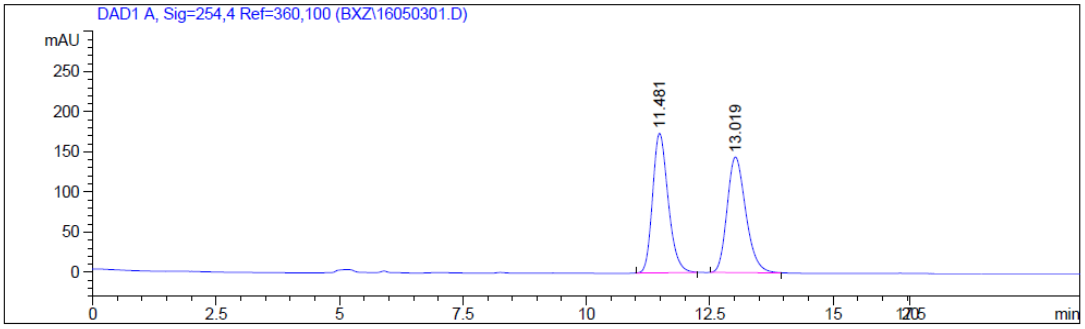
2	12.656	BB	0.4499	1.09572e4	373.90375	96.1491

Characterization of products 3aa-3al

(*S*)-5-benzyl-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3aa)


3aa

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (82 mg, 95% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 159.8-162.2 °C; $[\alpha]_D^{22}$ = -133.6 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-.63 (m, 2H), 7.61-7.55 (m, 2H), 7.46-7.30 (m, 9H), 7.29-7.20 (m, 2H), 4.10 (dd, *J* = 11.7, 3.8 Hz, 1H), 3.98 (d, *J* = 14.7 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 2.65 (dt, *J* = 15.8, 4.7 Hz, 1H), 2.52-2.39 (m, 1H), 2.24-2.14 (m, 1H), 2.01-1.84 (m, 2H), 1.70-1.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 153.8, 148.1, 145.4, 137.9, 137.0, 133.7, 129.4, 129.0, 128.7, 128.6, 128.2, 127.1, 126.9, 126.5, 121.0, 114.7, 97.7, 42.3, 36.7, 34.9, 32.0, 23.0; HRMS (ESI) m/z Calcd. for $C_{29}H_{25}N_2O_2$ ([M+H]$^+$) 433.1911, Found 433.1909; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.6 mL/min, t_{major} = 13.0 min, t_{minor} = 11.5 min).



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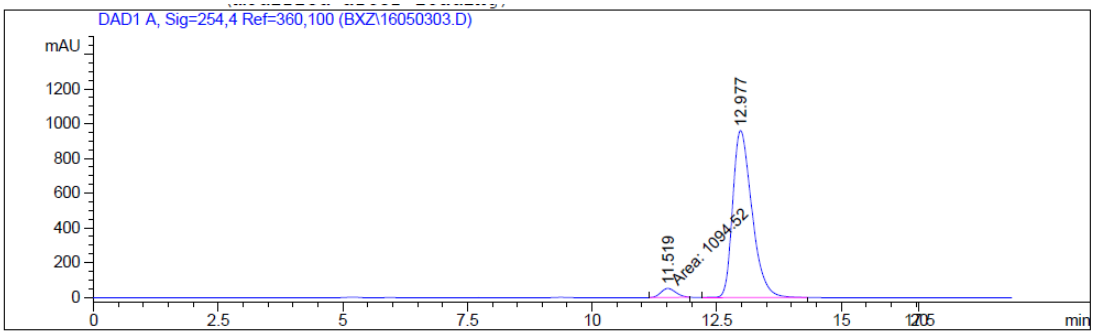
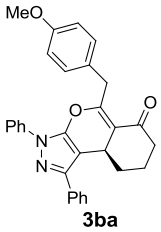
1	11.481	BB	0.3366	3824.14648	173.90144	50.1708
2	13.019	BB	0.4055	3798.11157	144.08389	49.8292



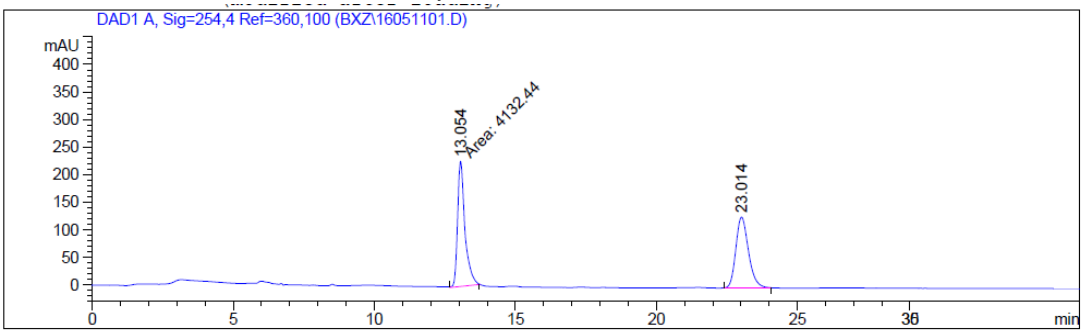
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.519	MM	0.3494	1094.51538	52.21276	4.0584
2	12.977	BB	0.4137	2.58748e4	962.16998	95.9416

(*S*)-5-(4-methoxybenzyl)-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ba)

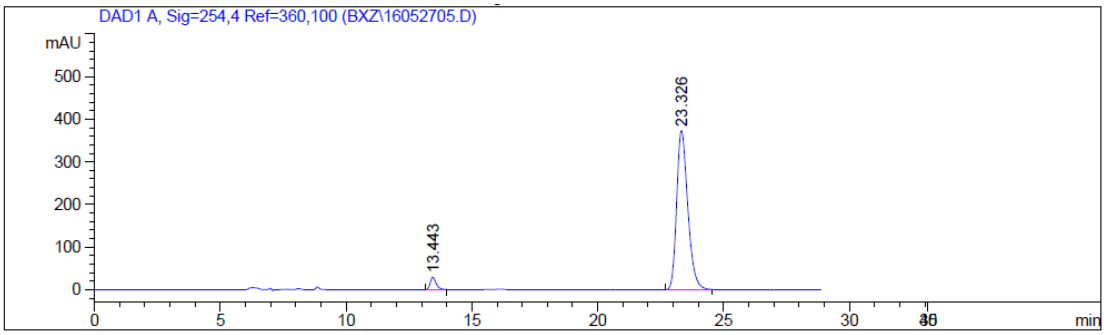


3ba

Prepared according to the general procedure at -30 °C for 48 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (90 mg, 98% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 117.3-119.0 °C; $[\alpha]_D^{21}$ = -104.0 (*c* 0.90, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.45-7.29 (m, 7H), 7.24 (d, *J* = 9.7 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.08 (dd, *J* = 11.7, 3.7 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 3.83 (d, *J* = 14.7 Hz, 1H), 3.77 (s, 3H), 2.64 (dt, *J* = 15.8, 4.8 Hz, 1H), 2.52-2.37 (m, 1H), 2.23-2.14 (m, 1H), 2.00-1.85 (m, 2H), 1.70-1.57 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 158.6, 154.2, 148.1, 145.4, 137.9, 133.7, 130.4, 129.0, 128.6, 128.2, 127.1, 126.5, 121.0, 114.3, 114.0, 97.7, 55.3, 42.3, 35.9, 34.8, 32.0, 23.0; HRMS (ESI) m/z Calcd. for $C_{30}H_{27}N_2O_3$ ($[M+H]^+$) 463.2016, Found 463.2016; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 23.3 min, t_{minor} = 13.4 min).

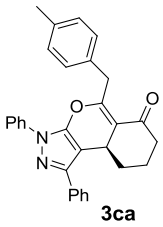


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.054	MM	0.3030	4132.43604	227.33954	50.8083
2	23.014	BB	0.4790	4000.94458	128.58113	49.1917



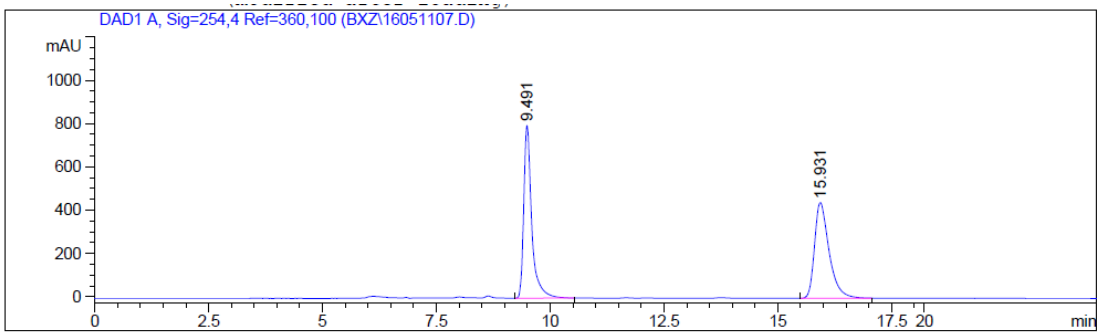
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.443	BB	0.2504	498.32336	29.59588	4.1546
2	23.326	BB	0.4690	1.14960e4	373.57315	95.8454

(*S*)-5-(4-methylbenzyl)-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ca)

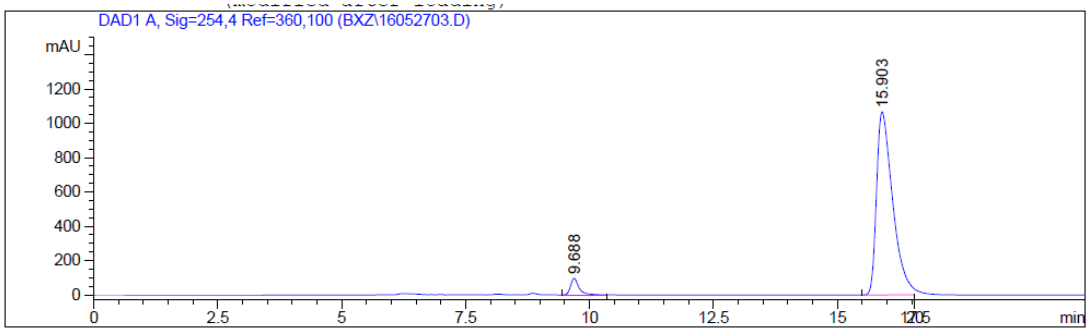


3ca

Prepared according to the general procedure at -30 °C for 48 h with **Q10** as the catalyst, then stirred at rt for 3 h, as light yellow solid (83 mg, 93% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 173.9-175.6 °C; $[\alpha]_D^{21}$ = -113.1 (*c* 0.82, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.44-7.31 (m, 5H), 7.30-7.20 (m, 3H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.08 (dd, *J* = 11.7, 3.7 Hz, 1H), 3.93 (d, *J* = 14.6 Hz, 1H), 3.87 (d, *J* = 14.6 Hz, 1H), 2.64 (dt, *J* = 15.8, 4.8 Hz, 1H), 2.52-2.40 (m, 1H), 2.32 (s, 3H), 2.24-2.14 (m, 1H), 2.01-1.83 (m, 2H), 1.71-1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 154.1, 148.1, 145.4, 137.9, 136.47, 133.9, 133.7, 129.3, 129.0, 128.7, 128.2, 127.2, 126.4, 121.0, 114.4, 97.7, 42.3, 36.3, 34.9, 32.0, 23.0, 21.2; HRMS (ESI) m/z Calcd. for $C_{30}H_{27}N_2O_2$ ($[M+H]^+$) 447.2067, Found 447.2064; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 15.9 min, t_{minor} = 9.7 min).

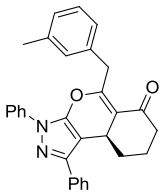


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.491	PB	0.1826	9750.29297	797.48956	49.8650
2	15.931	BB	0.3344	9803.08398	442.58325	50.1350



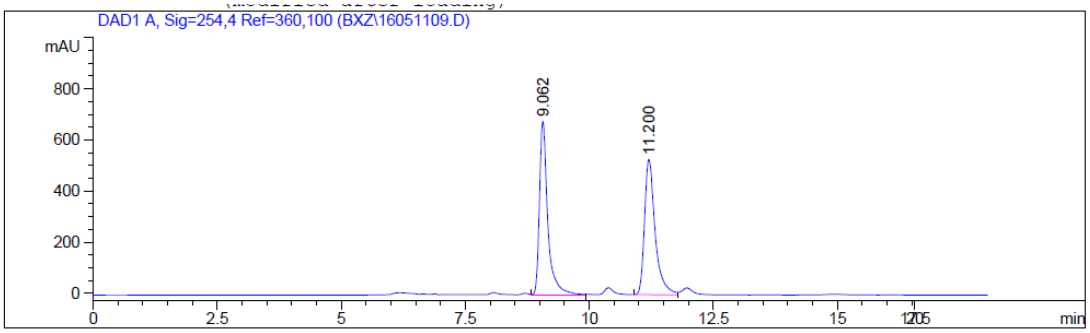
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.688	PB	0.1787	1146.37646	96.44128	4.4791
2	15.903	BB	0.3270	2.44478e4	1068.13647	95.5209

(*S*)-5-(3-methylbenzyl)-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3da)

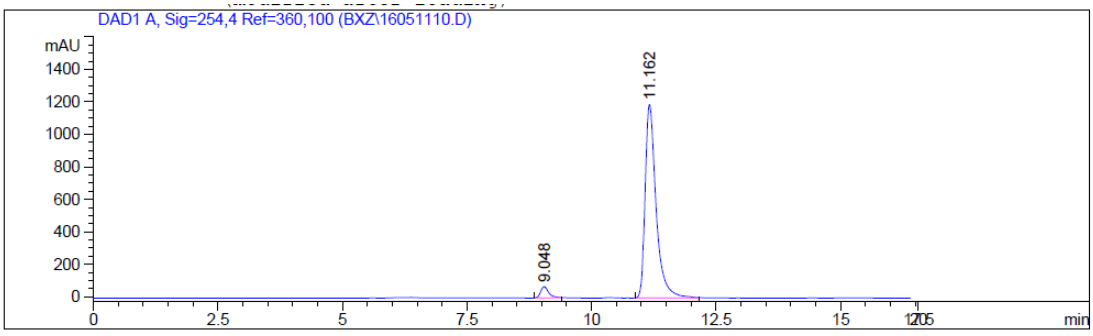


3da

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 3 h, as light yellow foam (86 mg, 96% yield) after silica gel chromatography (EtOAc/petroleum ether). $[\alpha]_D^{21}$ = -131.0 (*c* 0.81, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.64 (m, 2H), 7.63-7.57 (m, 2H), 7.45-7.31 (m, 5H), 7.27-7.16 (m, 4H), 7.07 (d, *J* = 7.0 Hz, 1H), 4.09 (dd, *J* = 11.8, 3.8 Hz, 1H), 3.95 (d, *J* = 14.4 Hz, 1H), 3.86 (d, *J* = 14.6 Hz, 1H), 2.65 (dt, *J* = 16.1, 4.8 Hz, 1H), 2.52-2.41 (m, 1H), 2.34 (s, 3H), 2.24-2.14 (m, 1H), 2.00-1.85 (m, 2H), 1.70-1.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 153.9, 148.1, 145.4, 138.2, 137.9, 136.9, 133.7, 130.2, 129.0, 128.7, 128.5, 128.2, 127.7, 127.1, 126.5, 126.4, 121.0, 114.5, 97.7, 42.4, 36.6, 34.9, 32.0, 23.1, 21.5; HRMS (ESI) m/z Calcd. for $C_{30}H_{27}N_2O_2$ ($[M+H]^+$) 447.2067, Found 447.2072; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 11.2 min, t_{minor} = 9.0 min).

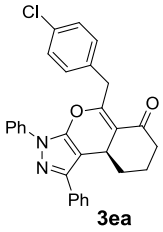


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.062	VB	0.1732	7879.21777	679.80365	49.9499
2	11.200	BV	0.2214	7895.03027	531.13947	50.0501



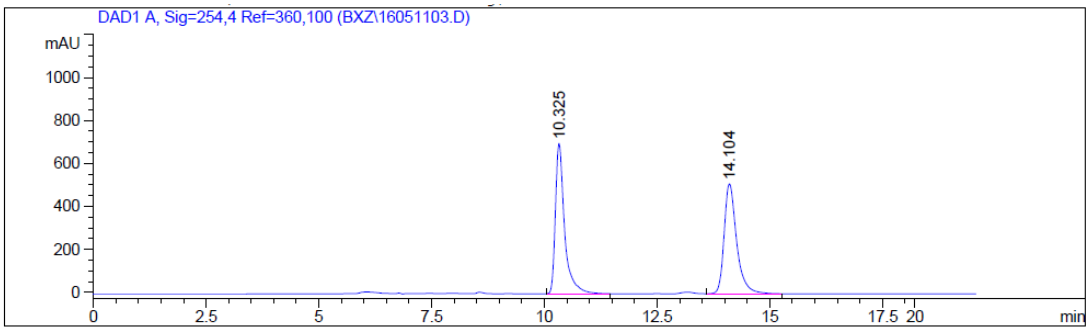
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.048	BB	0.1685	776.28271	69.41628	4.0939
2	11.162	BB	0.2303	1.81858e4	1189.76660	95.9061

(*S*)-5-(4-chlorobenzyl)-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ea)

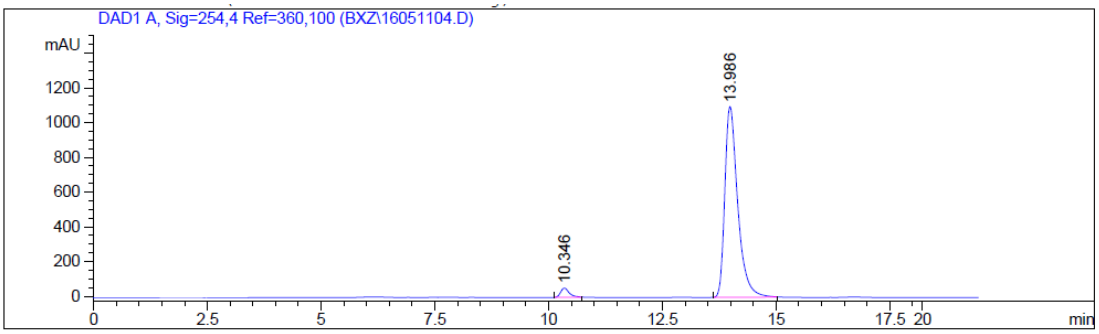


3ea

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (85 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 153.1-155.6 °C; $[\alpha]_D^{22}$ = -103.0 (*c* 0.80, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.44-7.21 (m, 10H), 4.08 (dd, *J* = 11.7, 3.7 Hz, 1H), 3.96 (d, *J* = 14.6 Hz, 1H), 3.82 (d, *J* = 14.7 Hz, 1H), 2.64 (dt, *J* = 15.9, 5.0 Hz, 1H), 2.50-2.36 (m, 1H), 2.24-2.14 (m, 1H), 2.00-1.84 (m, 2H), 1.70-1.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 153.3, 148.1, 145.2, 137.8, 135.5, 133.6, 132.8, 130.7, 129.1, 128.7, 128.2, 127.1, 126.6, 121.0, 114.9, 97.7, 42.2, 36.2, 34.8, 31.9, 22.9; HRMS (ESI) m/z Calcd. for $C_{29}H_{24}ClN_2O_2$ ($[M+H]^+$) 467.1521, Found 467.1524; 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, 0.5 mL/min, t_{major} = 14.0 min, t_{minor} = 10.3 min).



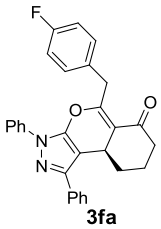
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.325	PB	0.2093	9918.23535	700.02948	50.0458
2	14.104	VB	0.2896	9900.08691	511.97269	49.9542



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.346	BB	0.2009	714.42285	53.80969	3.1904
2	13.986	BB	0.2981	2.16787e4	1099.01758	96.8096

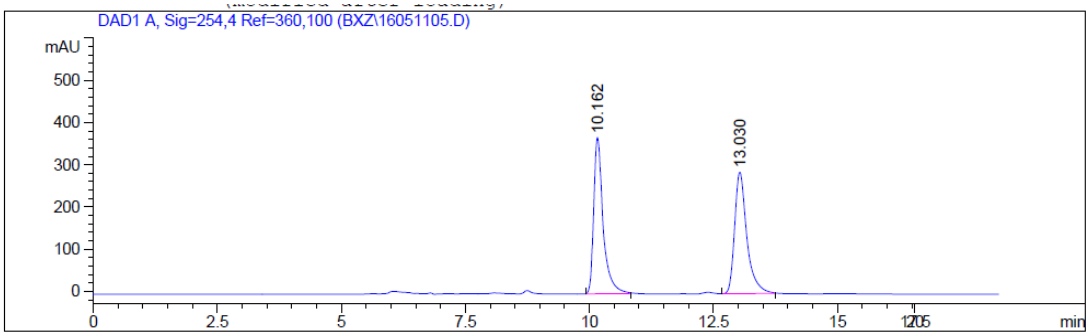
(*S*)-5-(4-fluorobenzyl)-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3fa)

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (81 mg, 90% yield) after silica gel chromatography (EtOAc/petroleum ether).

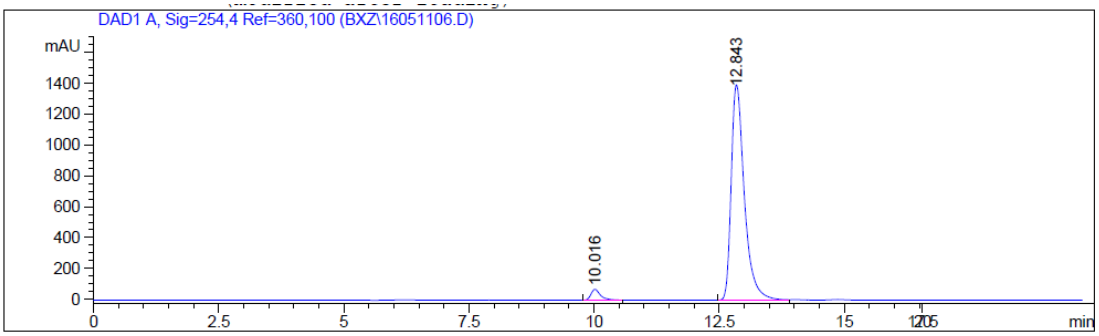


3fa

mp 146.3-149.0 °C; $[\alpha]_D^{21}$ = -111.4 (*c* 0.80, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.45-7.31 (m, 7H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 8.6 Hz, 2H), 4.09 (dd, *J* = 11.8, 3.8 Hz, 1H), 3.97 (d, *J* = 14.6 Hz, 1H), 3.82 (d, *J* = 14.6 Hz, 1H), 2.64 (dt, *J* = 15.9, 4.9 Hz, 1H), 2.53-2.37 (m, 1H), 2.27-2.14 (m, 1H), 2.03-1.82 (m, 2H), 1.71-1.55 (m, 1H); ^{19}F NMR (370 MHz, $CDCl_3$) δ -116.03; ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 162.0 (d, *J* = 246.0 Hz), 153.6, 148.1, 145.3, 137.9, 133.6, 132.7 (d, *J* = 3.3 Hz), 130.9 (d, *J* = 8.1 Hz), 129.1, 128.7, 128.2, 127.1, 126.6, 121.0, 115.3 (d, *J* = 21.4 Hz), 114.7, 97.7, 42.2, 36.0, 34.8, 31.9, 22.9; HRMS (ESI) m/z Calcd. for $C_{29}H_{24}FN_2O_2$ ($[M+H]^+$) 451.1816, Found 451.1817; Enantiomeric excess was determined to be 93% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 12.8 min, t_{minor} = 10.0 min).

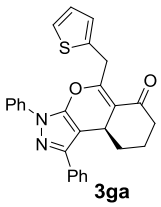


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.162	BB	0.1975	4875.26758	370.61945	49.6590
2	13.030	VB	0.2561	4942.22949	288.21173	50.3410



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.016	PB	0.1964	932.86438	70.48771	3.5168
2	12.843	BB	0.2756	2.55935e4	1397.98523	96.4832

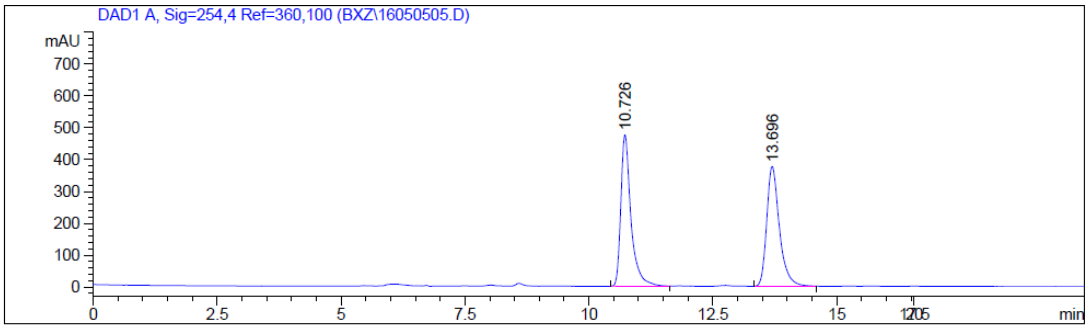
(*S*)-1,3-diphenyl-5-(thiophen-2-ylmethyl)-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ga)



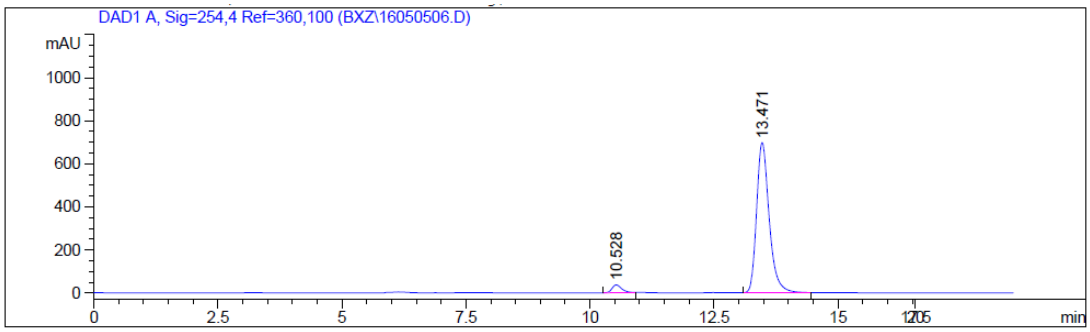
3ga

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 1 h, as white solid (79 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 166.0-168.3 °C; $[\alpha]_D^{22}$ = -134.6 (*c* 0.79, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.44-7.38 (m, 4H), 7.38-7.31 (m, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.17 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.13 (s, 2H), 4.09

(dd, *J* = 11.8, 3.9 Hz, 1H), 2.64 (dt, *J* = 15.9, 4.8 Hz, 1H), 2.51-2.39 (m, 1H), 2.24-2.12 (m, 1H), 1.99-1.83 (m, 2H), 1.70-1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 153.1, 148.1, 145.3, 138.7, 137.9, 133.6, 129.1, 128.7, 128.2, 127.2, 126.9, 126.7, 126.5, 124.7, 121.1, 114.5, 97.8, 42.1, 34.7, 31.7, 31.2, 22.8; HRMS (ESI) m/z Calcd. for $C_{27}H_{23}N_2O_2S$ ($[M+H]^+$) 439.1475, Found 439.1470; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 13.5 min, t_{minor} = 10.5 min).

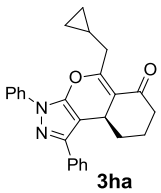


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.726	BB	0.2104	6783.56787	475.63092	50.2954
2	13.696	BB	0.2699	6703.88477	376.17636	49.7046



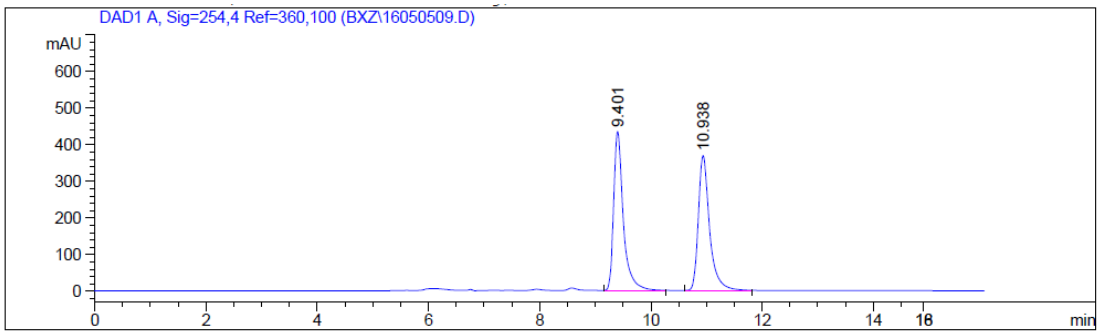
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.528	BB	0.2078	513.91327	37.04564	4.0102
2	13.471	BB	0.2699	1.23011e4	696.99561	95.9898

(*S*)-5-(cyclopropylmethyl)-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ha)

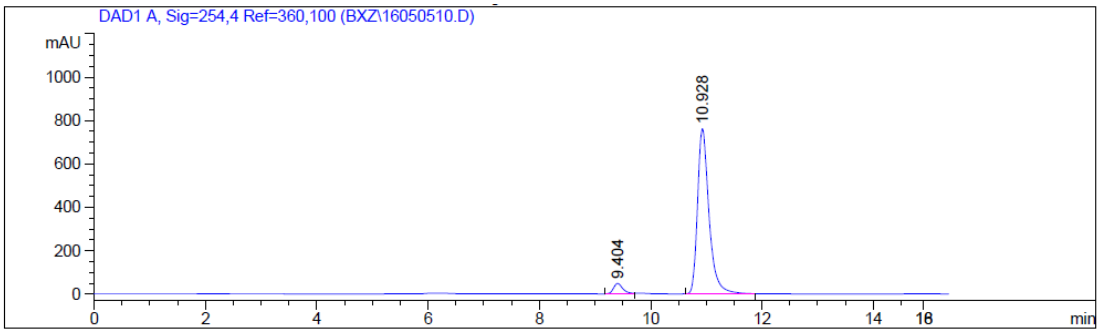


3ha

Prepared according to the general procedure at -30 °C for 72 h with **Q10** as the catalyst, then stirred at rt for 5 h, as light yellow solid (71 mg, 89% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 107.4-109.5 °C; $[\alpha]_D^{22}$ = -96.7 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.80 (m, 2H), 7.73-7.67 (m, 2H), 7.49-7.40 (m, 4H), 7.39-7.32 (m, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 4.09 (dd, *J* = 11.7, 3.8 Hz, 1H), 2.69-2.53 (m, 2H), 2.48-2.33 (m, 2H), 2.27-2.14 (m, 1H), 1.99-1.83 (m, 2H), 1.71-1.58 (m, 1H), 1.15-1.01 (m, 1H), 0.57-0.45 (m, 2H), 0.40-0.29 (m, 1H), 0.25-0.16 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 155.4, 148.1, 145.6, 138.1, 133.7, 129.1, 128.6, 128.2, 127.1, 126.5, 121.0, 114.0, 97.8, 42.3, 35.3, 34.8, 32.0, 23.1, 9.4, 4.5; HRMS (ESI) m/z Calcd. for $C_{26}H_{25}N_2O_2$ ($[M+H]^+$) 397.1911, Found 397.1909; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 10.9 min, t_{minor} = 9.4 min).

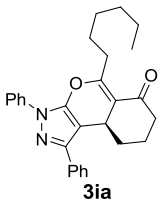


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.401	PB	0.1792	5253.99658	434.21024	50.4070
2	10.938	BB	0.2097	5169.15088	368.48993	49.5930



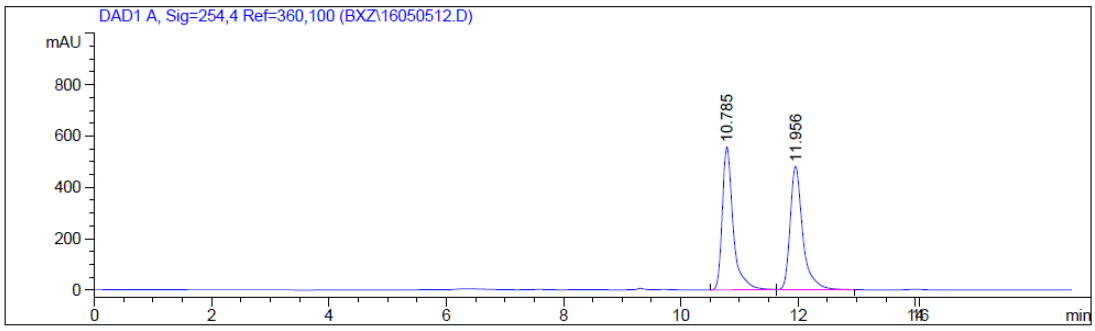
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.404	BV	0.1775	567.20215	48.10886	4.9444
2	10.928	BB	0.2151	1.09044e4	761.27087	95.0556

(*S*)-5-hexyl-1,3-diphenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ia)

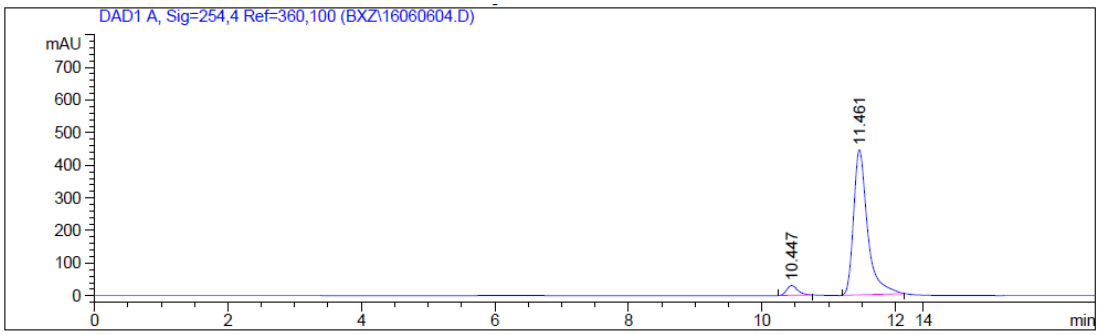


3ia

Prepared according to the general procedure at -30 °C for 120 h with **Q10** as the catalyst, then stirred at rt for 5 h, as light yellow solid (76 mg, 89% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 73.3-75.2 °C; $[\alpha]_D^{22}$ = -77.3 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.77 (m, 2H), 7.74-7.66 (m, 2H), 7.49-7.40 (m, 4H), 7.39-7.32 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 4.08 (dd, *J* = 11.7, 3.9 Hz, 1H), 2.69-2.54 (m, 3H), 2.45-2.37 (m, 1H), 2.23-2.14 (m, 1H), 1.96-1.85 (m, 2H), 1.72-1.56 (m, 3H), 1.41-27 (m, 6H), 0.93-0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 156.2, 148.1, 145.6, 138.1, 133.7, 129.2, 128.6, 128.2, 127.1, 126.5, 121.0, 114.0, 97.9, 42.2, 34.6, 32.0, 31.5, 30.9, 28.8, 27.5, 22.9, 22.6, 14.1; HRMS (ESI) m/z Calcd. for $C_{28}H_{31}N_2O_2$ ($[M+H]^+$) 427.2380, Found 427.2378; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 11.5 min, t_{minor} = 10.4 min).

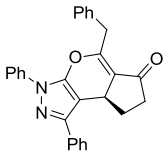


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.785	BV	0.1931	7215.78271	557.11121	49.9911
2	11.956	VB	0.2250	7218.34375	481.25952	50.0089



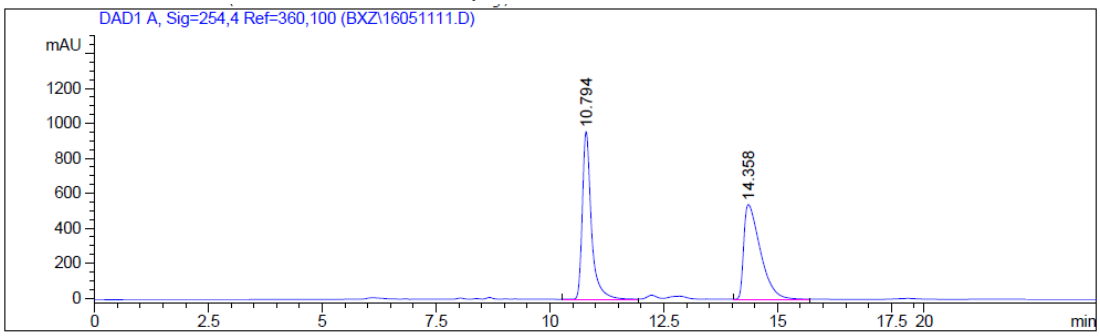
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.447	BB	0.1755	348.14990	29.97339	5.0898
2	11.461	BB	0.2182	6491.94678	444.93619	94.9102

(*S*)-compound (3ja)

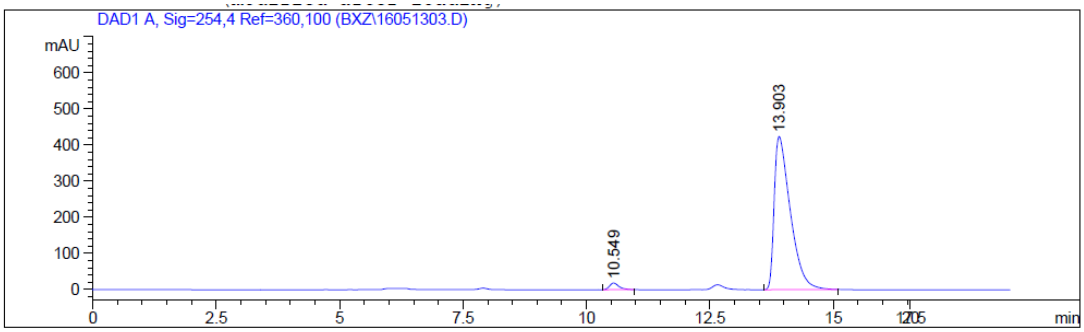


3ja

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (80 mg, 96% yield, 85% ee) after silica gel chromatography (EtOAc/petroleum ether); after recrystallization from Et_2O/hexane (59 mg, 70% yield, 95% ee). mp 142.3-145.8 °C; $[\alpha]_D^{22}$ = -132.4 (*c* 0.59, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.47-7.22 (m, 11H), 4.32 (d, *J* = 14.6 Hz, 1H), 4.20-4.10 (m, 2H), 2.66-2.55 (m, 1H), 2.48-2.38 (m, 2H), 1.74-1.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 154.1, 148.1, 145.4, 137.9, 136.47, 133.9, 133.7, 129.3, 129.0, 128.7, 128.2, 127.2, 126.4, 121.0, 114.4, 97.7, 42.3, 36.3, 34.9, 32.0, 23.0, 21.2; HRMS (ESI) m/z Calcd. for $C_{28}H_{31}N_2O_2$ ($[M+H]^+$) 427.2380, Found 427.2378; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 13.9 min, t_{minor} = 10.5 min).

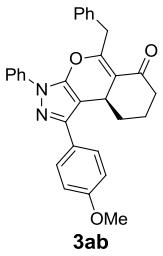


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.794	BB	0.2052	1.32639e4	959.82703	49.2645
2	14.358	VB	0.3919	1.36599e4	542.33618	50.7355



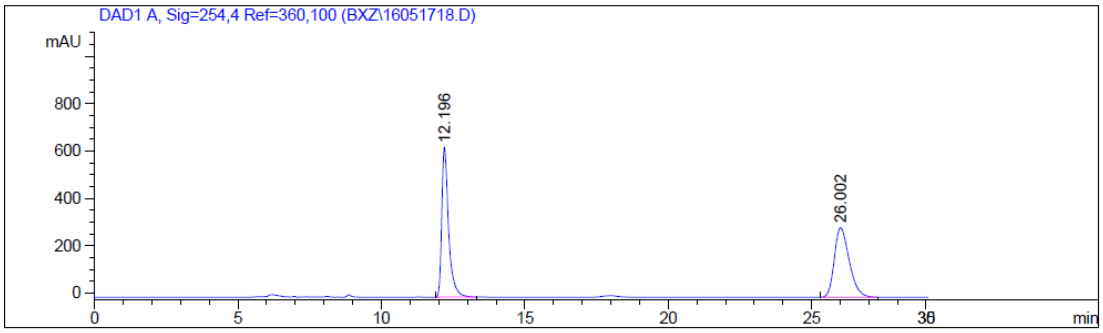
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.549	BB	0.2004	248.70316	18.55514	2.5157
2	13.903	BB	0.3430	9637.31543	424.21173	97.4843

(*S*)-5-benzyl-1-(4-methoxyphenyl)-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ab)

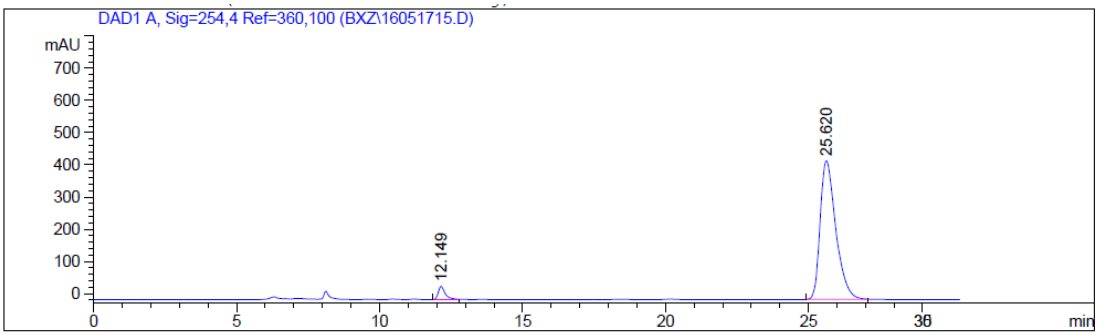


3ab

Prepared according to the general procedure at -30 °C for 36 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (91 mg, 98% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 150.1-152.8 °C; $[\alpha]_D^{22}$ = -110.5 (*c* 0.87, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.8 Hz, 4H), 7.43-7.17 (m, 8H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.05 (dd, *J* = 11.7, 3.5 Hz, 1H), 3.97 (d, *J* = 14.6 Hz, 1H), 3.91 (d, *J* = 14.6 Hz, 1H), 3.80 (s, 3H), 2.64 (dt, *J* = 15.8, 4.8 Hz, 1H), 2.55-2.39 (m, 1H), 2.27-2.13 (m, 1H), 1.99-1.84 (m, 1H), 1.69-1.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 159.7, 153.8, 147.9, 145.3, 137.9, 137.0, 129.4, 129.0, 128.6, 128.4, 126.9, 126.3, 126.2, 120.9, 114.7, 114.1, 97.3, 55.3, 42.3, 36.7, 34.9, 31.9, 23.0; HRMS (ESI) m/z Calcd. for $C_{30}H_{27}N_2O_3$ ($[M+H]^+$) 463.2016, Found 463.2017; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 25.6 min, t_{minor} = 12.1 min).

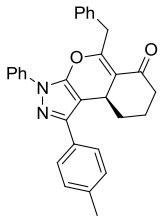


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.196	PB	0.2467	1.04818e4	634.69708	49.6676
2	26.002	BB	0.5532	1.06221e4	294.24759	50.3324



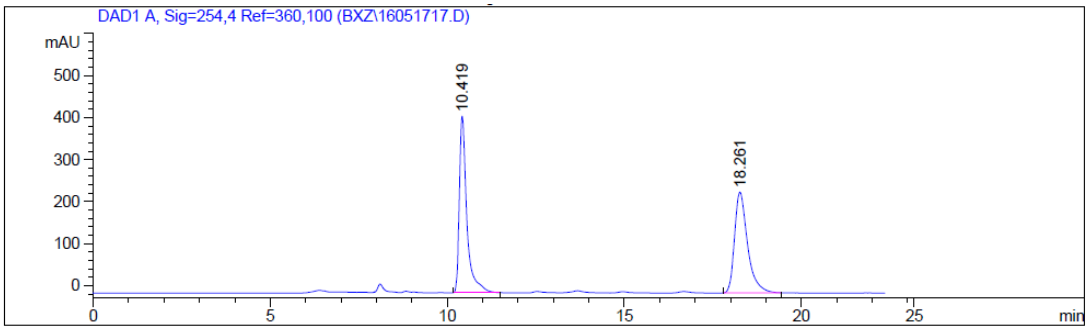
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.149	BB	0.2433	665.61810	40.59055	3.9133
2	25.620	BB	0.5832	1.63435e4	430.21353	96.0867

(*S*)-5-benzyl-3-phenyl-1-p-tolyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ac)

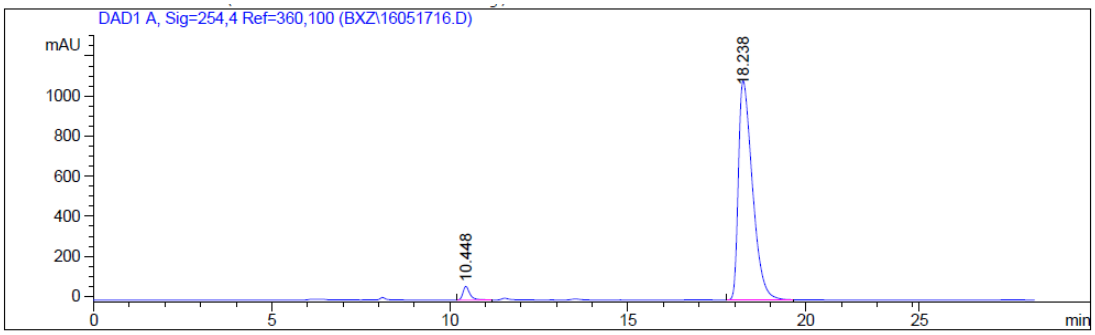


3ac

Prepared according to the general procedure at -30 °C for 36 h with **Q10** as the catalyst, then stirred at rt for 3 h, as light yellow solid (87 mg, 98% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 131.2-134.4 °C; $[\alpha]_D^{20}$ = -121.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.6 Hz, 4H), 7.42-7.30 (m, 6H), 7.25 (dd, *J* = 14.9, 7.3 Hz, 4H), 4.10 (dd, *J* = 11.7, 3.7 Hz, 1H), 3.98 (d, *J* = 14.7 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 2.66 (dt, *J* = 15.8, 4.8 Hz, 1H), 2.53-2.41 (m, 1H), 2.38 (s, 3H), 2.27-2.17 (m, 1H), 1.02-1.86 (m, 2H), 1.72-1.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 153.8, 148.1, 145.3, 138.0, 137.9, 137.0, 130.8, 129.3, 129.0, 128.5, 127.0, 126.9, 126.3, 121.0, 114.7, 97.5, 42.3, 36.7, 34.9, 31.9, 23.0, 21.3; HRMS (ESI) m/z Calcd. for $C_{30}H_{27}N_2O_2$ ($[M+H]^+$) 447.2067, Found 447.2062; 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, 0.5 mL/min, t_{major} = 18.2 min, t_{minor} = 10.4 min).

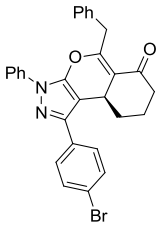


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.419	BB	0.2156	6187.61328	420.59561	50.1774
2	18.261	BB	0.3864	6143.87109	240.21918	49.8226



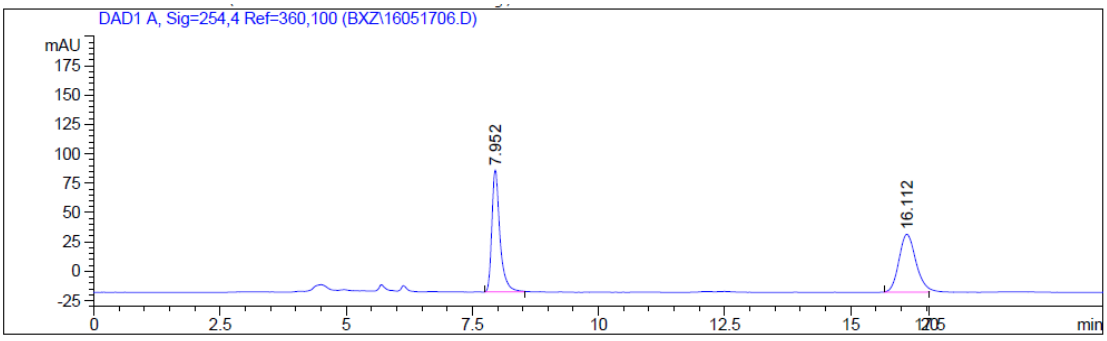
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.448	BB	0.2035	938.56671	68.66446	3.0426
2	18.238	BB	0.4210	2.99094e4	1093.92883	96.9574

(*S*)-5-benzyl-1-(4-bromophenyl)-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-*c*]pyrazol-6(3*H*)-one (3ad)

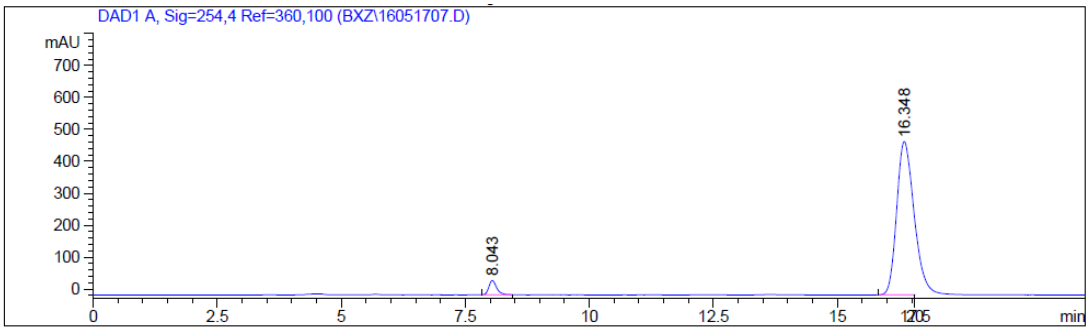


3ad

Prepared according to the general procedure at -30 °C for 40 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (98 mg, 96% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 153.2-156.7 °C; $[\alpha]_D^{21}$ = -93.8 (*c* 0.98, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.48 (m, 6H), 7.41-7.29 (m, 6H), 7.28-7.20 (m, 2H), 4.03 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.97 (d, *J* = 14.7 Hz, 1H), 3.90 (d, *J* = 14.6 Hz, 1H), 2.64 (dt, *J* = 15.8, 4.8 Hz, 1H), 2.53-2.40 (m, 1H), 2.20-2.08 (m, 1H), 2.03-1.82 (m, 2H), 1.70-1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 153.7, 146.9, 145.5, 137.7, 136.9, 132.6, 131.8, 129.4, 129.1, 128.6, 128.6, 127.0, 126.6, 122.3, 121.0, 114.5, 97.7, 42.2, 36.7, 34.8, 32.0, 22.9; HRMS (ESI) m/z Calcd. for $C_{29}H_{24}BrN_2O_2$ ($[M+H]^+$) 511.1016, Found 511.1008; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.7 mL/min, t_{major} = 16.3 min, t_{minor} = 8.0 min).

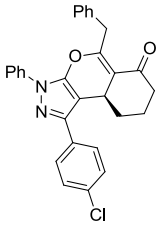


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.952	BB	0.1662	1159.76892	103.95145	49.9224
2	16.112	BB	0.3612	1163.37537	49.31961	50.0776



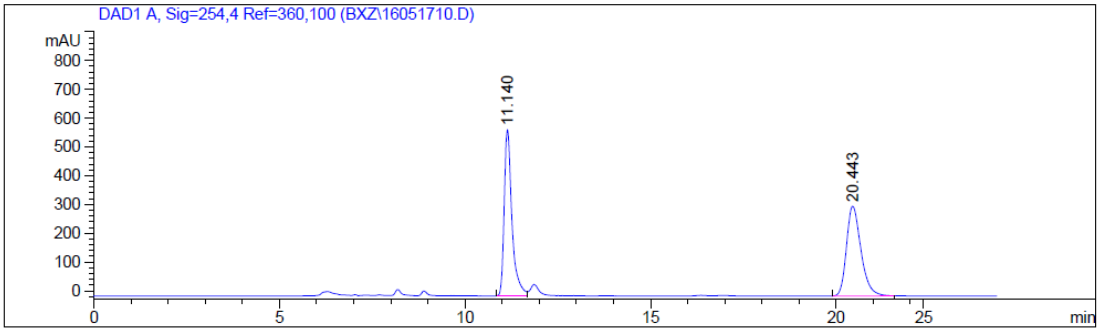
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.043	BB	0.1656	489.91135	44.79923	3.9945
2	16.348	BB	0.3783	1.17746e4	479.76050	96.0055

(*S*)-5-benzyl-1-(4-chlorophenyl)-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3ae)

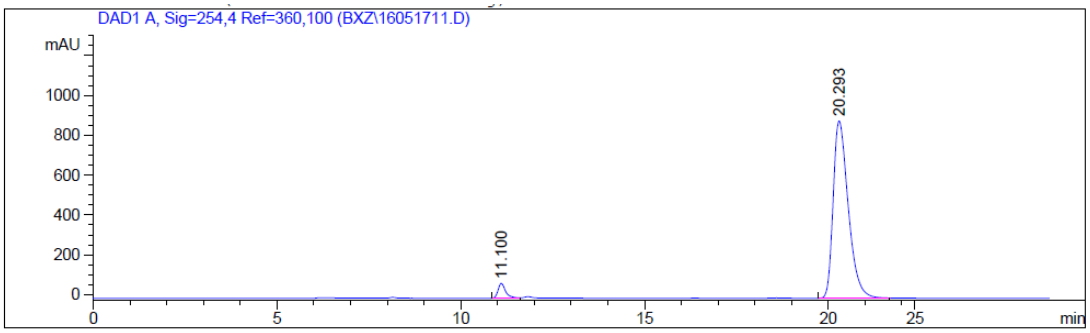


3ae

Prepared according to the general procedure at -30 °C for 40 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (90 mg, 96% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 152.7-154.0 °C; $[\alpha]_D^{21}$ = -115.1 (*c* 0.84, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 11.4, 8.4 Hz, 4H), 7.41 -7.20 (m, 10H), 4.04 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.97 (d, *J* = 14.7 Hz, 1H), 3.90 (d, *J* = 14.6 Hz, 1H), 2.65 (dt, *J* = 15.9, 4.9 Hz, 1H), 2.52-2.40 (m, 1H), 2.20-2.10 (m, 1H), 2.02-1.83 (m, 2H), 1.72-1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 153.8, 146.9, 145.5, 137.7, 136.9, 134.1, 132.2, 129.4, 129.1, 128.9, 128.6, 128.4, 127.0, 126.6, 121.0, 114.5, 97.7, 42.2, 36.7, 34.8, 32.0, 22.9; HRMS (ESI) m/z Calcd. for $C_{29}H_{24}ClN_2O_2$ ($[M+H]^+$) 467.1521, Found 467.1528; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 20.3 min, t_{minor} = 11.1 min).

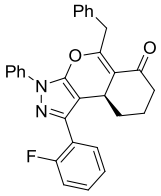


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.140	BV	0.2168	8362.03809	577.83588	49.7541
2	20.443	BB	0.4118	8444.69043	312.02054	50.2459



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.100	BV	0.2160	1080.41431	75.04544	4.0828
2	20.293	BB	0.4347	2.53824e4	890.16949	95.9172

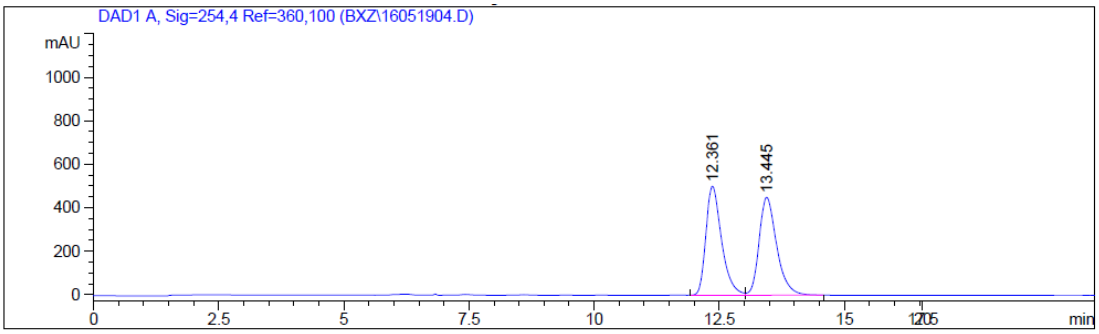
(*S*)-5-benzyl-1-(2-fluorophenyl)-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3af)



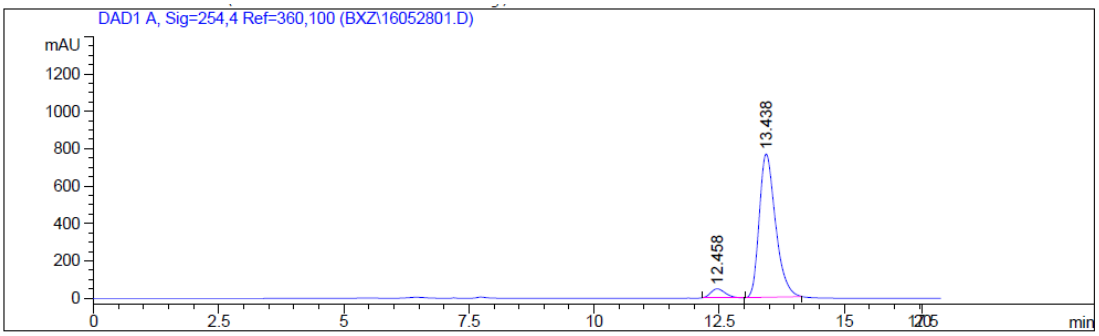
3af

Prepared according to the general procedure at -30 °C for 48 h with **Q10** as the catalyst, then stirred at rt for 3 h, as light yellow solid (87 mg, 96% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 108.0-110.8 °C; $[\alpha]_D^{21}$ = -119.5 (*c* 0.83, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.9

Hz, 2H), 7.42-7.29 (m, 7H), 7.28-7.16 (m, 3H), 7.15-7.08 (m, 1H), 4.08-3.90 (m, 3H), 2.67-2.57 (m, 1H), 2.50-2.37 (m, 1H), 1.99-1.82 (m, 3H), 1.67-1.53 (m, 1H); ^{19}F NMR (370 MHz, $CDCl_3$) δ -116.18; ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 160.1 (d, J = 248.9 Hz), 154.1, 145.2, 143.7, 137.8, 137.1, 130.7 (d, J = 3.3 Hz), 130.3 (d, J = 8.1 Hz), 129.4, 129.1, 128.6, 126.9, 126.6, 124.5 (d, J = 3.3 Hz), 121.7 (d, J = 14.4 Hz), 121.1, 115.8 (d, J = 21.7 Hz), 114.7, 99.7, 42.4, 36.8, 34.8, 34.7, 31.8, 23.2; HRMS (ESI) m/z Calcd. for $C_{29}H_{24}FN_2O_2$ ([M+H]$^+$) 451.1816, Found 451.1814; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 12.4 min, t_{minor} = 13.4 min).

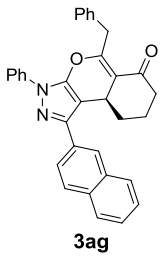


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.361	BV	0.3327	1.09547e4	501.74875	49.7682
2	13.445	VB	0.3724	1.10568e4	450.43445	50.2318



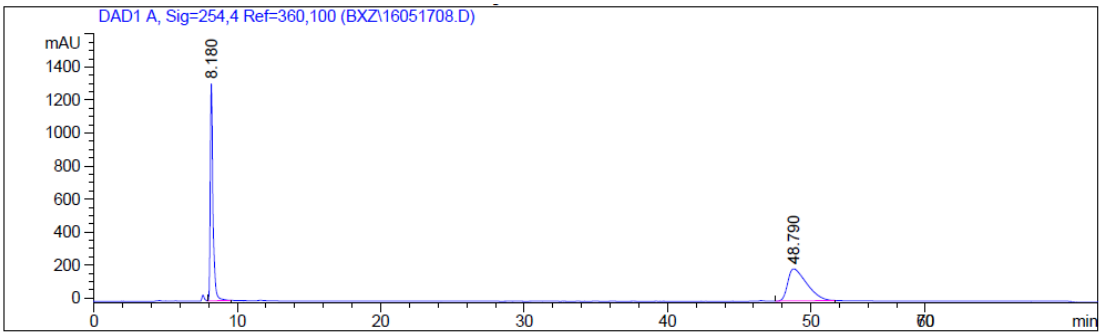
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.458	BP	0.3113	958.13226	48.32341	5.2293
2	13.438	BB	0.3441	1.73644e4	766.98279	94.7707

(*S*)-5-benzyl-1-(naphthalen-2-yl)-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3ag)

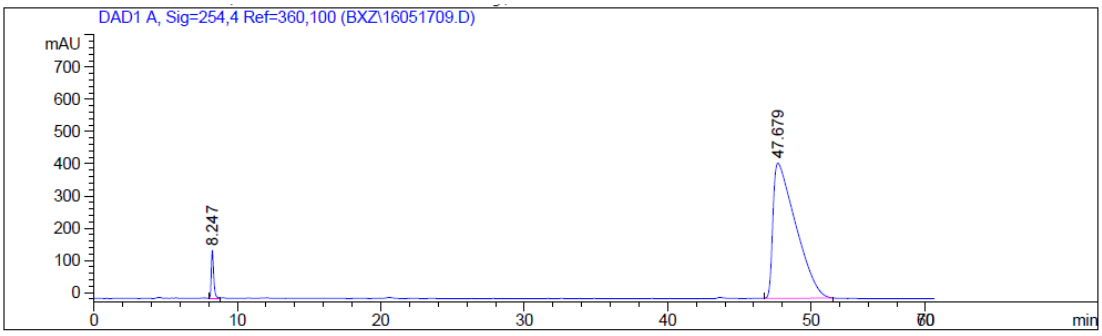


3ag

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 3 h, as light yellow solid (92 mg, 95% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 159.1-162.2 °C; $[\alpha]_D^{21}$ = -135.0 (*c* 0.90, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.90-7.79 (m, 4H), 7.61 (d, J = 8.2 Hz, 2H), 7.50-7.29 (m, 8H), 7.25 (dd, J = 13.2, 7.0 Hz, 2H), 4.14 (dd, J = 11.7, 3.5 Hz, 1H), 3.98 (d, J = 14.6 Hz, 1H), 3.93 (d, J = 14.7 Hz, 1H), 2.64 (dt, J = 15.9, 4.7 Hz, 1H), 2.51-2.39 (m, 1H), 2.25-2.15 (m, 1H), 1.96-1.82 (m, 2H), 1.69-1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 153.8, 148.0, 145.5, 137.9, 137.0, 133.4, 133.1, 131.1, 129.4, 129.1, 128.6, 128.3, 128.3, 127.8, 127.0, 126.5, 126.4, 126.3, 126.2, 125.0, 121.1, 114.7, 97.9, 42.3, 36.7, 35.0, 32.1, 23.0; HRMS (ESI) m/z Calcd. for $C_{33}H_{27}N_2O_2$ ([M+H]$^+$) 483.2067, Found 483.2070; Enantiomeric excess was determined to be 93% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.7 mL/min, t_{major} = 47.7 min, t_{minor} = 8.2 min).

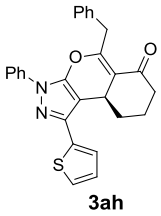


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.180	VB	0.1955	1.73077e4	1315.57874	49.1590
2	48.790	BB	1.2910	1.78999e4	194.62134	50.8410



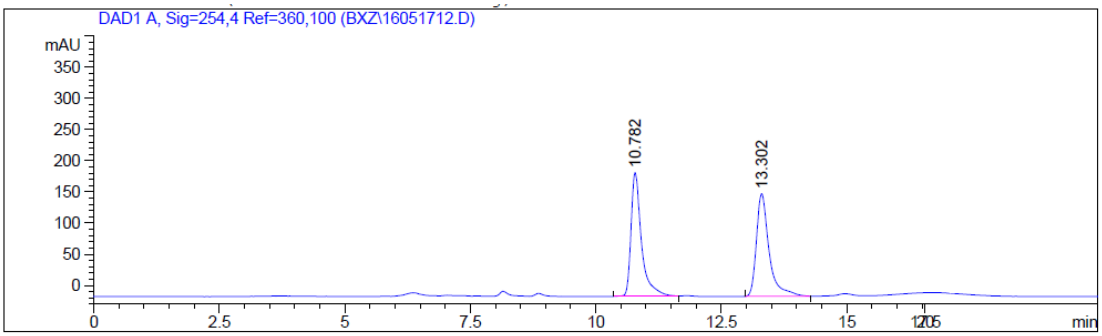
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.247	VB	0.1738	1733.52966	148.98088	3.6176
2	47.679	BB	1.4607	4.61864e4	419.43921	96.3824

(*S*)-5-benzyl-3-phenyl-1-(thiophen-2-yl)-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3ah)

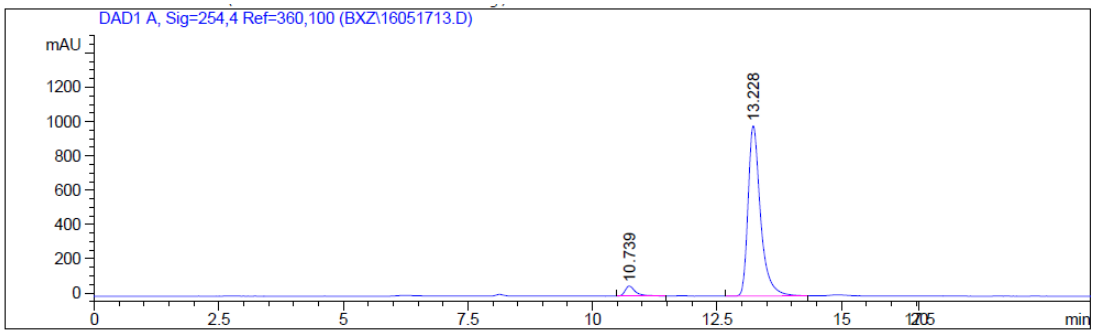


3ah

Prepared according to the general procedure at -30 °C for 24 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (85 mg, 97% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 142.0-144.7 °C; $[\alpha]_D^{21}$ = -117.6 (*c* 0.82, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.41-7.18 (m, 10H), 7.09-7.03 (m, 1H), 4.02-3.86 (m, 3H), 2.67 (dt, *J* = 16.1, 5.0 Hz, 1H), 2.54-2.39 (m, 2H), 2.08-1.87 (m, 2H), 1.79-1.64 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 153.5, 145.4, 143.1, 137.7, 136.9, 135.8, 129.4, 129.1, 128.6, 127.5, 127.0, 126.5, 125.5, 125.3, 121.0, 114.8, 97.4, 42.2, 36.7, 34.5, 31.9, 22.9; HRMS (ESI) m/z Calcd. for $C_{27}H_{23}N_2O_2S$ ($[M+H]^+$) 439.1475, Found 439.1472; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 13.2 min, t_{minor} = 10.7 min).

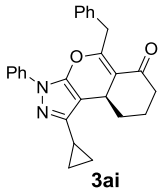


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.782	BB	0.2170	2917.38525	199.03740	50.1922
2	13.302	BB	0.2589	2895.04321	164.87874	49.8078



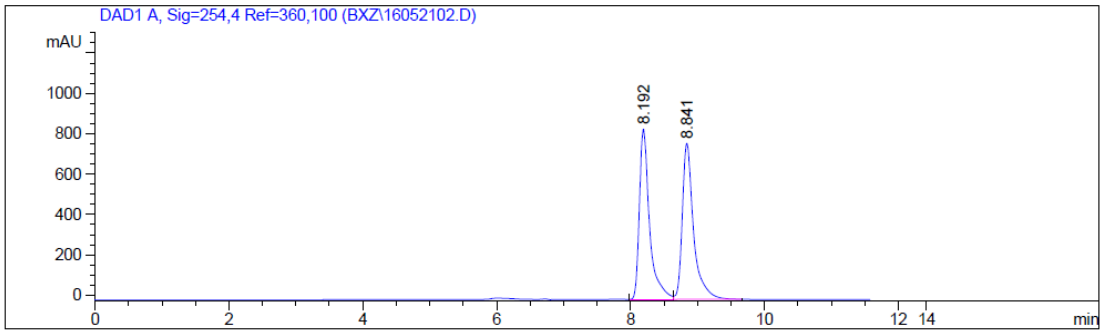
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.739	BB	0.2202	884.92896	59.25995	4.8668
2	13.228	BB	0.2631	1.72980e4	993.45398	95.1332

(*S*)-5-benzyl-1-cyclopropyl-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3ai)

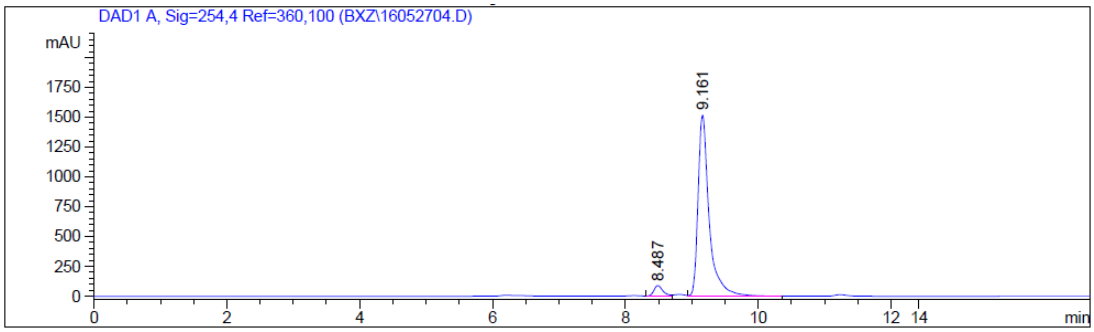


3ai

Prepared according to the general procedure at -30 °C for 48 h with **Q10** as the catalyst, then stirred at rt for 3 h, as white solid (76 mg, 96% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 81.8-84.9 °C; $[\alpha]_D^{25}$ = -44.1 (*c* 0.39, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.39-7.29 (m, 6H), 7.25 (t, *J* = 6.0 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 4.02-3.80 (m, 3H), 2.66 (dt, *J* = 15.8, 4.8 Hz, 1H), 2.61-2.44 (m, 2H), 2.16-1.94 (m, 2H), 1.94-1.71 (m, 2H), 1.07-0.99 (m, 1H), 0.94-0.80 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 154.4, 150.8, 144.8, 138.0, 137.1, 129.3, 128.9, 128.5, 126.8, 125.9, 120.5, 114.4, 98.7, 42.3, 36.8, 34.1, 32.4, 23.2, 8.6, 7.6, 6.1; HRMS (ESI) m/z Calcd. for $C_{27}H_{23}N_2O_2S$ ($[M+H]^+$) 439.1475, Found 439.1472; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 9.2 min, t_{minor} = 8.5 min).

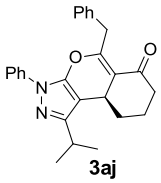


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.192	VV	0.1572	8922.43164	844.61688	49.6205
2	8.841	VB	0.1727	9058.90430	773.40399	50.3795



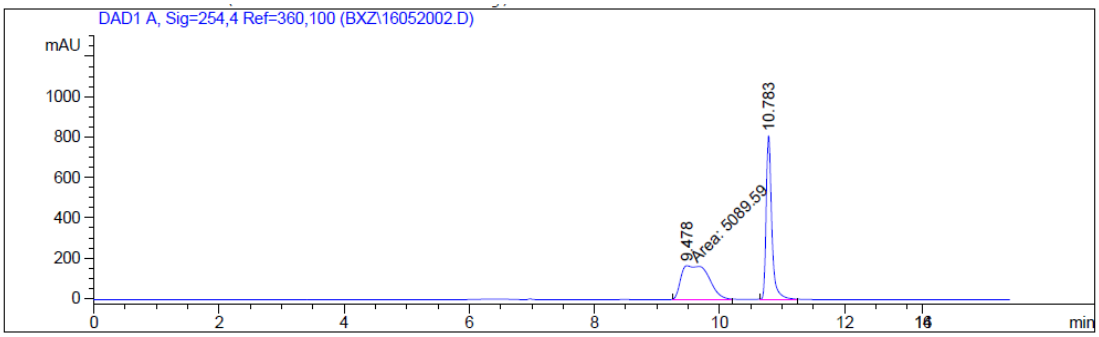
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.487	VV	0.1467	864.49200	89.45777	4.6559
2	9.161	VB	0.1720	1.77033e4	1518.95947	95.3441

(*S*)-5-benzyl-1-isopropyl-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3aj)

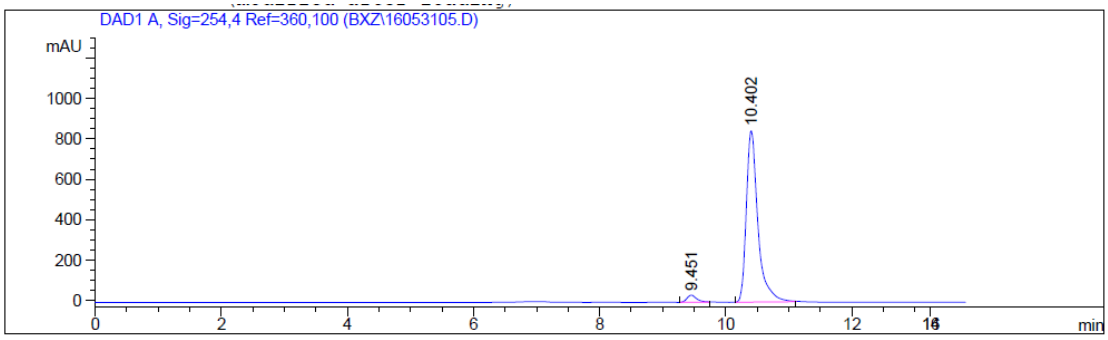


3aj

Prepared according to the general procedure at -30 °C for 48 h with **Q11** as the catalyst, then stirred at rt for 3 h, as light yellow solid (78 mg, 97% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 77.6-79.8 °C; $[\alpha]_D^{25}$ = -54.1 (*c* 0.74, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (d, *J* = 8.5, 2H), 7.40-7.28 (m, 6H), 7.26-7.16 (m, 2H), 3.96 (d, *J* = 14.6 Hz, 1H), 3.87 (d, *J* = 14.4 Hz, 1H), 3.81 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.02- 2.90 (m, 1H), 2.64 (dt, *J* = 15.7, 4.8 Hz, 1H), 2.53-2.37 (m, 2H), 2.15-1.91 (m, 2H), 1.89-1.77 (m, 1H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 155.0, 154.3, 144.8, 138.1, 137.1, 129.3, 128.9, 128.5, 126.8, 125.9, 120.8, 114.3, 96.9, 42.1, 36.8, 34.3, 32.4, 28.0, 23.0, 22.3, 21.0; HRMS (ESI) m/z Calcd. for $C_{26}H_{27}N_2O_2$ ([M+H]$^+$) 399.2067, Found 399.2065; 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, 0.5 mL/min, t_{major} = 10.4 min, t_{minor} = 9.5 min).

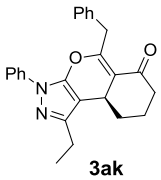


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.478	MM	0.5103	5089.59424	166.23579	49.9935
2	10.783	BB	0.0952	5090.92383	811.35278	50.0065



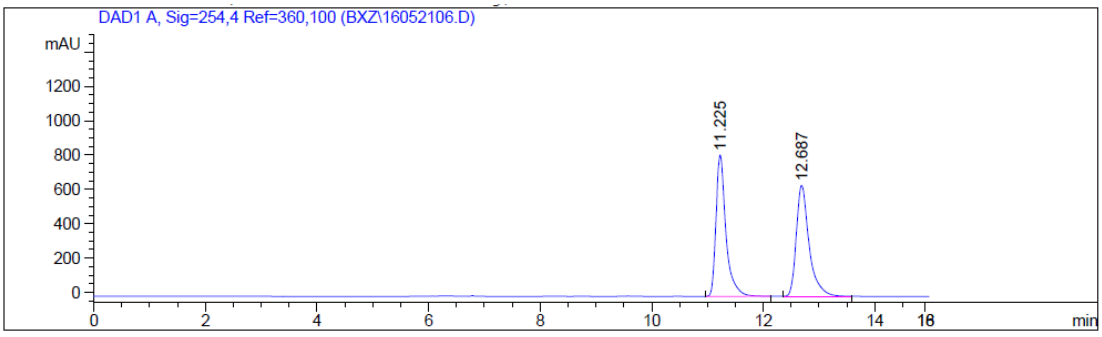
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.451	BB	0.1623	373.40994	35.05546	3.3289
2	10.402	PB	0.1912	1.08439e4	847.78790	96.6711

(*S*)-5-benzyl-1-ethyl-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3ak)

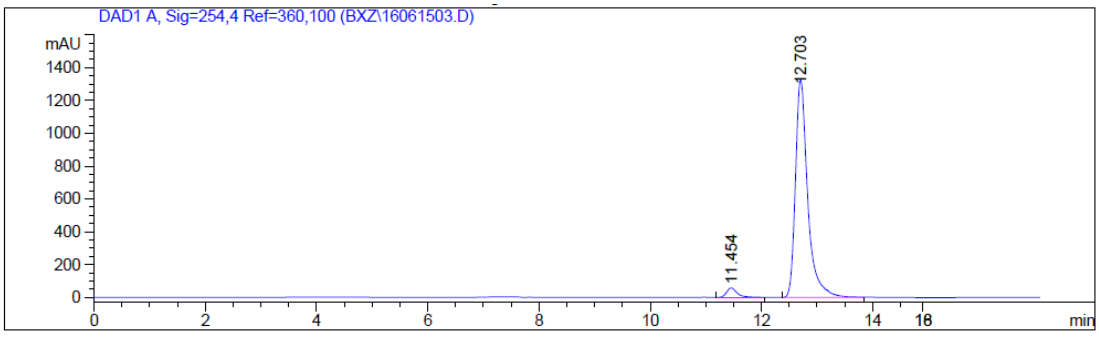


3ak

Prepared according to the general procedure at -20 °C for 48 h with **Q11** as the catalyst, then stirred at rt for 5 h, as light yellow solid (70 mg, 92% yield) after silica gel chromatography (EtOAc/petroleum ether). mp 70.9-72.9 °C; $[\alpha]_D^{23}$ = -60.9 (*c* 0.64, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.39-7.27 (m, 6H), 7.27-7.17 (m, 2H), 3.97 (d, *J* = 14.6 Hz, 1H), 3.88 (d, *J* = 14.6 Hz, 1H), 3.79 (dd, *J* = 11.7, 4.0 Hz, 1H), 2.69-2.58 (m, 3H), 2.53-2.44 (m, 1H), 2.41-2.31 (m, 1H), 2.12 -1.93 (m, 2H), 1.88-1.76 (m, 1H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 154.5, 151.2, 144.9, 138.0, 137.1, 129.3, 129.0, 128.5, 126.8, 125.9, 120.7, 114.3, 97.5, 42.2, 36.8, 34.1, 32.2, 23.1, 21.8, 13.1; HRMS (ESI) m/z Calcd. for $C_{25}H_{25}N_2O_2$ ($[M+H]^+$) 385.1911, Found 385.1905; 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, 0.5 mL/min, t_{major} = 12.7 min, t_{minor} = 11.5 min).

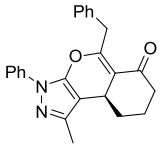


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.225	BB	0.1845	1.02233e4	825.28253	49.7109
2	12.687	PB	0.2407	1.03422e4	646.42383	50.2891



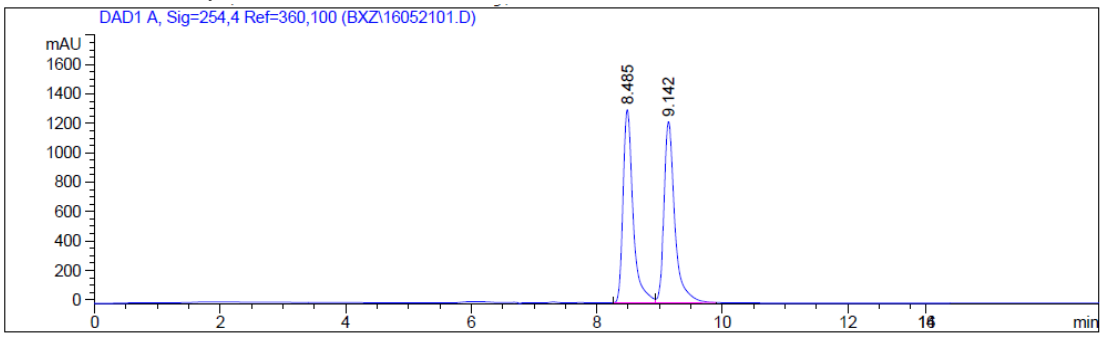
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.454	VB	0.1995	769.77026	57.75057	3.6543
2	12.703	PB	0.2303	2.02951e4	1328.25208	96.3457

(*S*)-5-benzyl-1-methyl-3-phenyl-7,8,9,9a-tetrahydroisochromeno[3,4-c]pyrazol-6(3*H*)-one (3al)

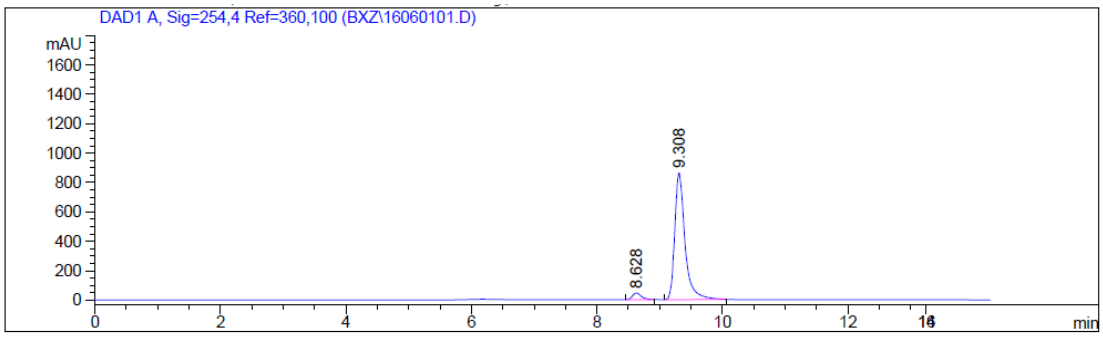


3al

Prepared according to the general procedure at -20 °C for 48 h with **Q10** as the catalyst, then stirred at rt for 3 h, as colorless oil (71 mg, 96% yield) after silica gel chromatography (EtOAc/petroleum ether); $[\alpha]_D^{25}$ = -52.3 (*c* 0.69, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.39-7.28 (m, 6H), 7.28-7.17 (m, 2H), 3.96 (d, *J* = 14.7 Hz, 1H), 3.89 (d, *J* = 14.6 Hz, 1H), 3.76 (dd, *J* = 11.8, 4.1 Hz, 1H), 2.64 (dt, *J* = 15.8, 4.5 Hz, 1H), 2.54-2.43 (m, 1H), 2.41-2.31 (m, 1H), 2.26 (s, 3H), 2.14-1.90 (m, 2H), 1.88-1.75 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 154.5, 145.9, 145.0, 137.9, 137.0, 129.3, 129.0, 128.5, 126.9, 126.0, 120.5, 114.3, 98.2, 42.3, 36.8, 34.0, 32.0, 23.1, 13.8; HRMS (ESI) m/z Calcd. for $C_{24}H_{23}N_2O_2$ ($[M+H]^+$) 371.1754, Found 371.1749; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 9.3 min, t_{minor} = 8.6 min).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.485	BV	0.1677	1.46075e4	1314.22583	49.7563
2	9.142	VB	0.1796	1.47506e4	1232.32825	50.2437



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.628	BB	0.1524	461.90714	45.52400	4.4978
2	9.308	BB	0.1705	9807.76758	863.41589	95.5022

4. The X-ray structure of 3ad

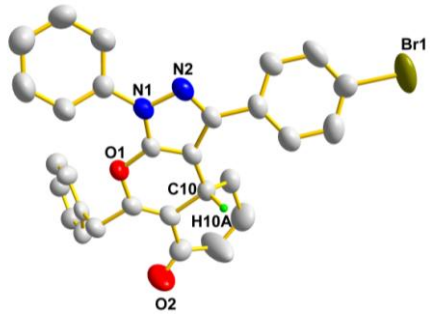
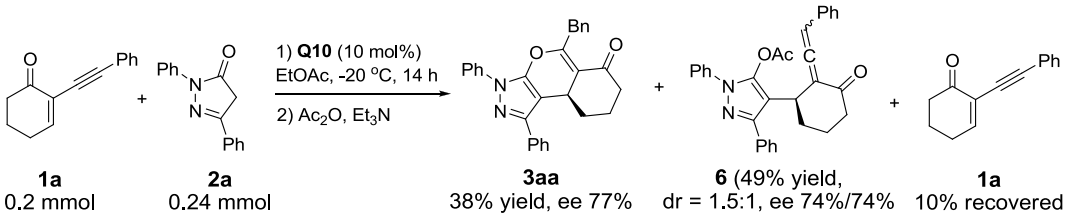


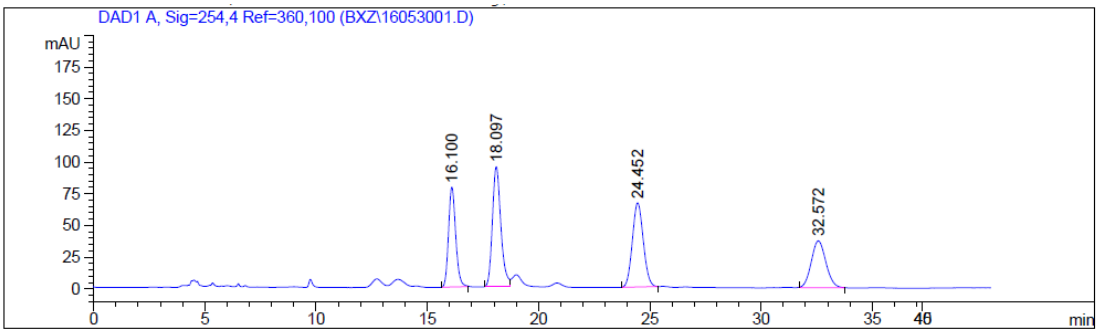
Figure S1. The X-ray structure of **3ad**.

5. Mechanism study

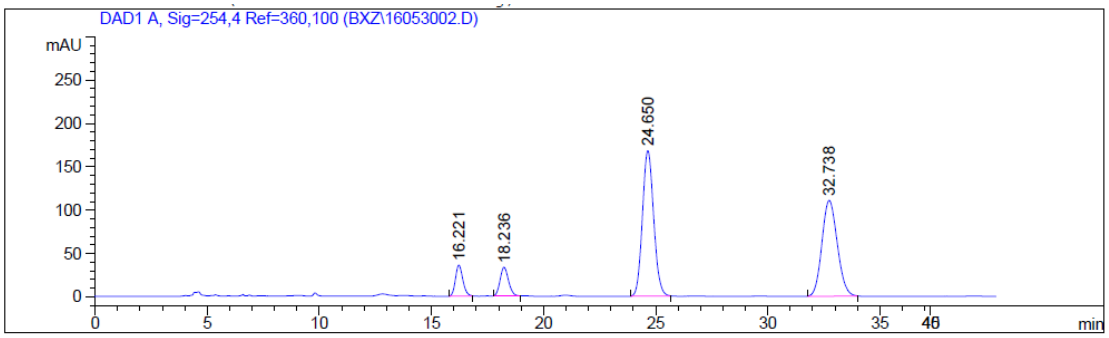
The capture of the intermediate with acetic anhydride



A solution of **1a** (0.2 mmol, 1.0 eq.) and **Q10** (0.02 mmol, 0.1 eq.) in EtOAc (2.0 mL) was cooled to -20 °C. After 10 min, **2a** (0.24 mmol, 1.2 eq.) was added in one portion. The resulting mixture was stirred at -20 °C for 14 h. Ac_2O (0.3 mmol, 1.5 eq.) was added dropwise, followed with the dropwise addition of a solution of Et_3N (0.3 mmol, 1.5 eq.) in EtOAc (0.5 mL) at -20 °C. After 1 h, the solvent was removed under vacuum. The crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/15 to 1/4) on silica gel to give **3aa** (32 mg, yield 38%, 77% ee), **6** as light yellow oil (47 mg, yield 49%, dr = 1.5:1, 74%/74% ee) and **1a** (3.9 mg, 10% recovered). The following is the data of the intermediate **6** (the dr value was determined by ^{1}H NMR, the racemic product was prepared using a 1:1 mixture of quinine and quinidine as the catalyst). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.39-7.33 (m, 4H), 7.29-7.24 (m, 2H), 7.24-7.17 (m, 3H), 6.55 (d, J = 3.9 Hz, 1H), 4.27-4.18 (m, 1H), 2.63 (dt, J = 17.1, 5.5 Hz, 1H), 2.56-2.46 (m, 1H), 2.17 (s, 3H), 2.09-1.80 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.9, 198.8, 167.3, 150.2, 142.2, 138.0, 133.4, 131.8, 129.2, 128.7, 128.5, 128.4, 128.2, 127.8, 127.7, 127.5, 123.1, 111.4, 110.6, 100.0, 40.4, 35.2, 30.0, 21.4, 20.4; HRMS (ESI) m/z Calcd. for $C_{31}H_{27}N_2O_3$ ($[M+H]^+$) 475.2016, Found 475.2022; Enantiomeric excess was determined to be 74% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 90/10, λ = 254 nm, 30 °C, 0.7 mL/min, t_{major} = 24.7 and 32.7 min, t_{minor} = 18.2 and 16.2 min).

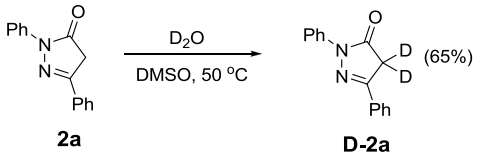


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.100	BB	0.3453	1765.53345	78.84264	21.4356
2	18.097	BV	0.4038	2514.40308	94.69556	30.5277
3	24.452	BB	0.5126	2268.39722	66.38800	27.5409
4	32.572	BB	0.6907	1688.13855	36.97324	20.4959



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.221	BB	0.3537	823.02411	35.86411	6.4307
2	18.236	BP	0.3987	857.63733	33.05950	6.7011
3	24.650	BB	0.5409	5852.94824	167.79897	45.7319
4	32.738	BB	0.7397	5264.79102	110.53192	41.1363

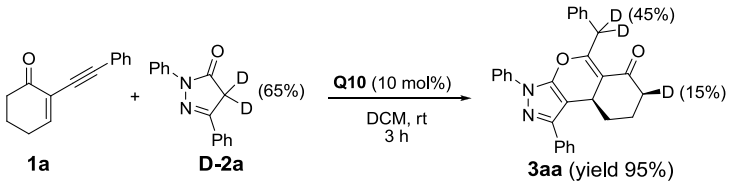
The preparation of the deuterated pyrazolone D-2a



2a **D-2a**

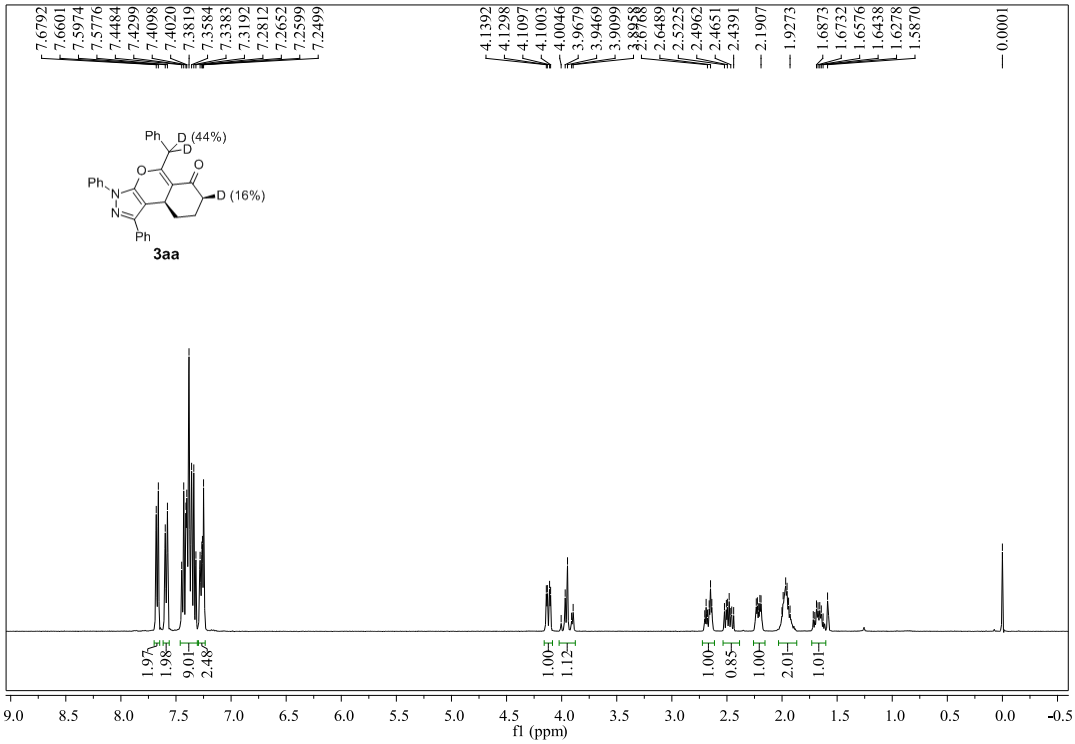
To a solution of **2a** (200 mg) in DMSO (2 mL) was added D_2O (1 mL). The resulting mixture was heated to 50 °C, and then stirred for 12 h. After cooled to rt, the mixture was kept overnight. The crystals were filtrated, then dried to give deuterated pyrazolone **2a** (100 mg, yield 50%, 65% deuteration). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.81-7.75 (m, 2H), 7.49-7.39 (m, 5H), 7.22 (t, J = 7.4 Hz, 1H), 3.87-3.81 (m, 0.7H).

Deuterium-labeling experiment (Table 3, entry 1)



1a **D-2a** **3aa** (yield 95%)

To a solution of **1a** (0.1 mmol, 1.0 eq.) and **Q10** (0.01 mmol, 0.1 eq.) in anhydrous DCM (1.0 mL) was added **2a** (0.12 mmol, 1.2 eq.). The resulting mixture was stirred at rt for 3 h. The solvent was removed under vacuum, then the crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/8) to give **3aa** as white solid (41 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.7 Hz, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.39 (qd, J = 15.6, 7.5 Hz, 9H), 7.26 (dd, J = 7.3, 5.2 Hz, 2H), 4.12 (dd, J = 11.8, 3.8 Hz, 1H), 4.02-3.88 (m, 1.12 H), 2.67 (dt, J = 15.8, 4.8 Hz, 1H), 2.54-2.43 (m, 0.85 H), 2.26-2.15 (m, 1H), 2.03-1.87 (m, 2H), 1.73-1.60 (m, 1H).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7.4098
7.4020
7.3819
7.3584
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7.3192
7.2812
7.2652
7.2599
7.2499
4.1392
4.1298
4.1097
4.1003
4.0046
3.9679
3.9469
3.9099
2.6489
2.5225
2.4962
2.4651
2.4391
2.1907
1.9273
1.6873
1.6732
1.6576
1.6438
1.6278
1.5870
0.0001
Ph
D (44%)
D
O
O
Ph
N
N
D (16%)
Ph
3aa
1.97
1.98
9.01
2.48
1.00
1.12
1.00
0.85
1.00
2.01
1.01
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 -0.5
f1 (ppm)

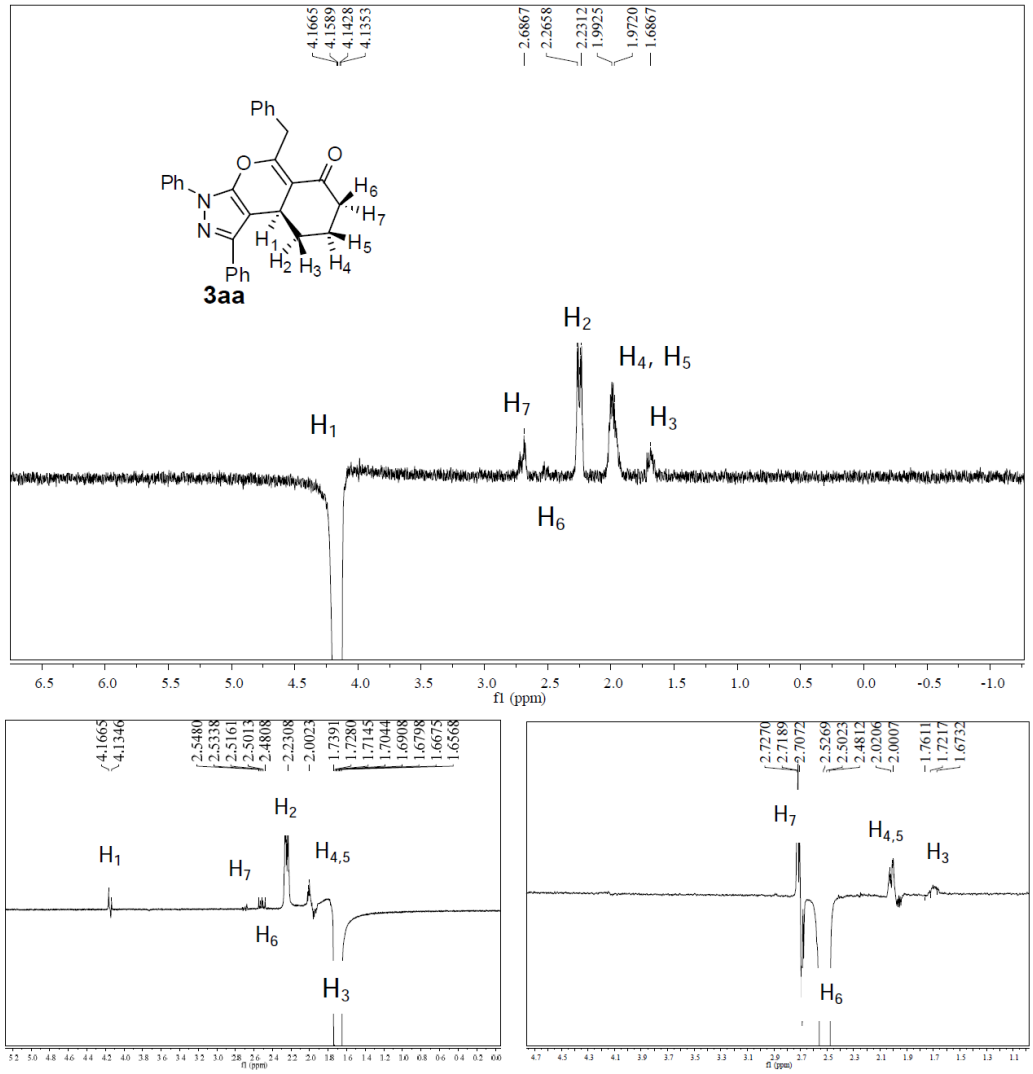
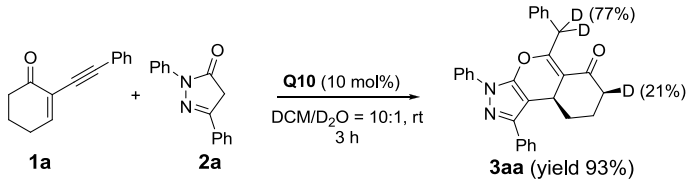
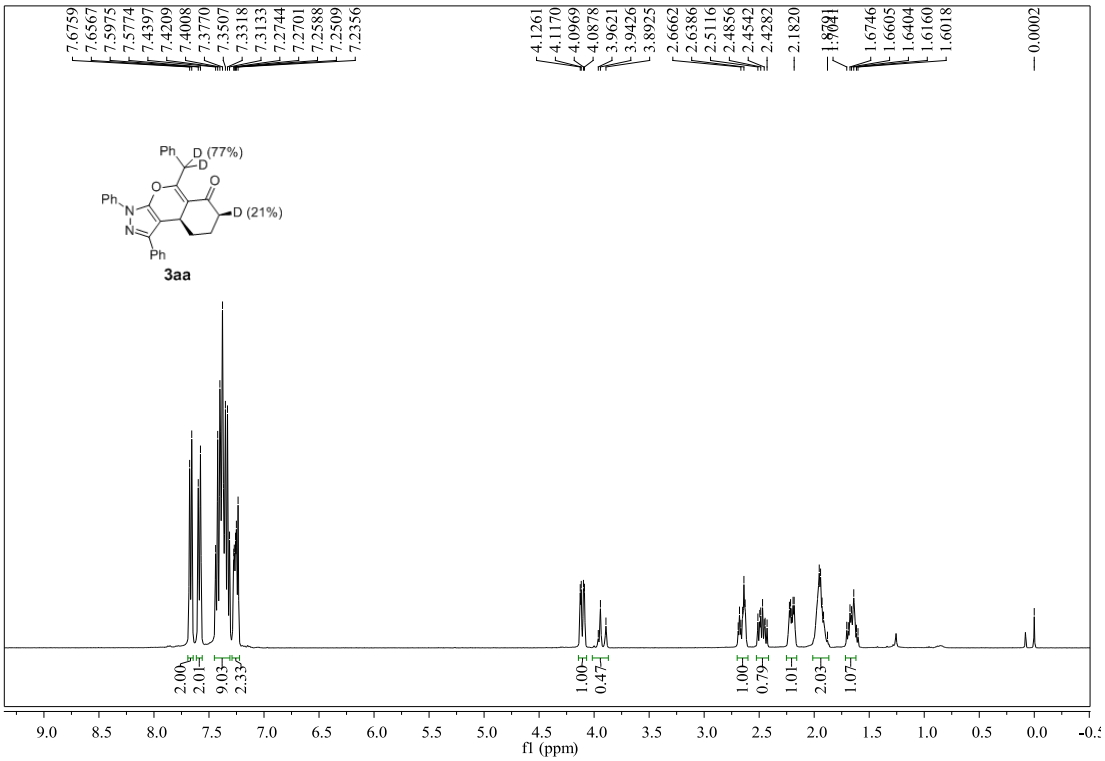


Figure S2. The NOESY (1D) spectrum of the product **3aa**.

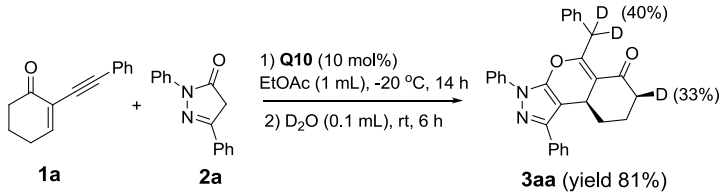
Deuterium-labeling experiment (Table 3, entry 2)



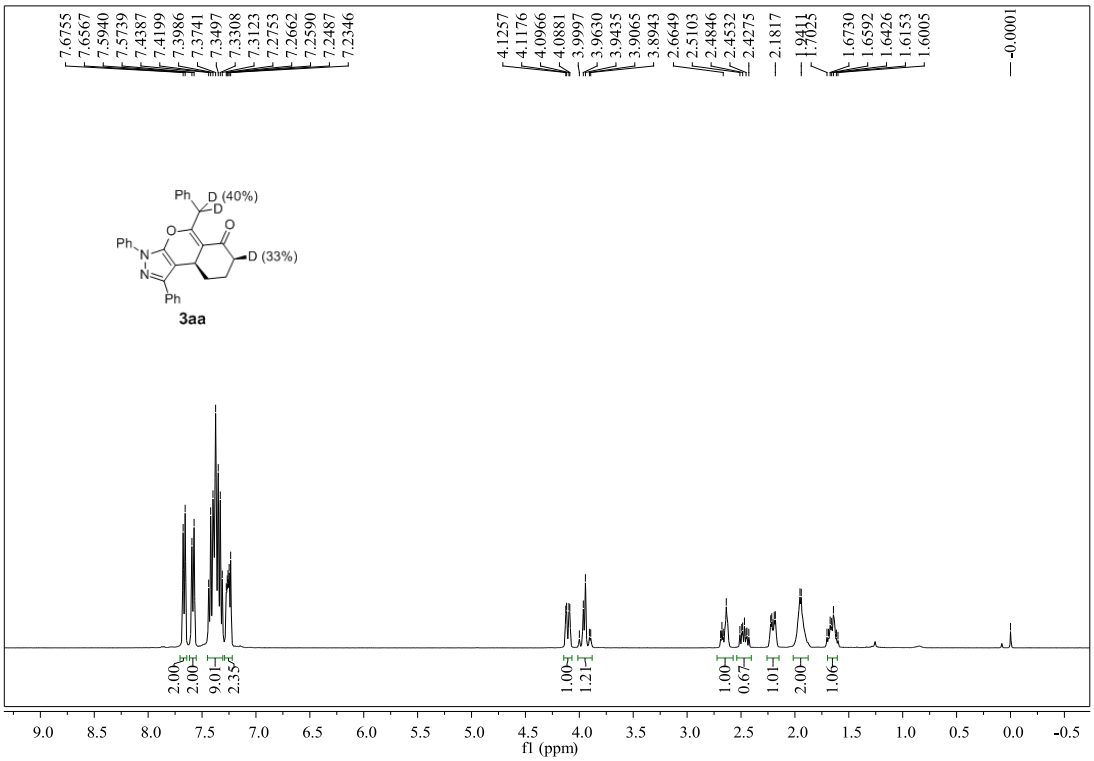
To a solution of **1a** (0.1 mmol, 1.0 eq.) and **Q10** (0.01 mmol, 0.1 eq.) in a mixture of DCM (1.0 mL) and D_2O (0.1 mL) was added **2a** (0.12 mmol, 1.2 eq.). The resulting mixture was stirred at rt for 3 h. The solvent was removed under vacuum, then the crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/8) to give **3aa** as white solid (40 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.7 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.45-7.31 (m, 9H), 7.29-7.22 (m, 2H), 4.11 (dd, J = 11.7, 3.6 Hz, 1H), 4.02-3.87 (m, 0.47 H), 2.66 (dt, J = 15.4, 4.6 Hz, 1H), 2.53-2.41 (m, 0.79H), 2.25-2.16 (m, 1H), 2.01-1.87 (m, 2H), 1.72-1.62 (m, 1H).



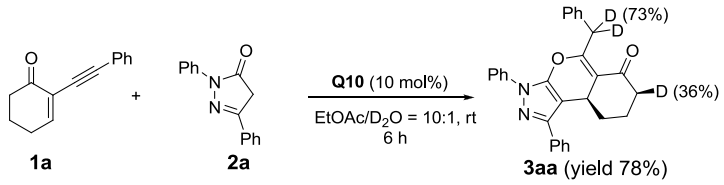
Deuterium-labeling experiment (Table 3, entry 3)



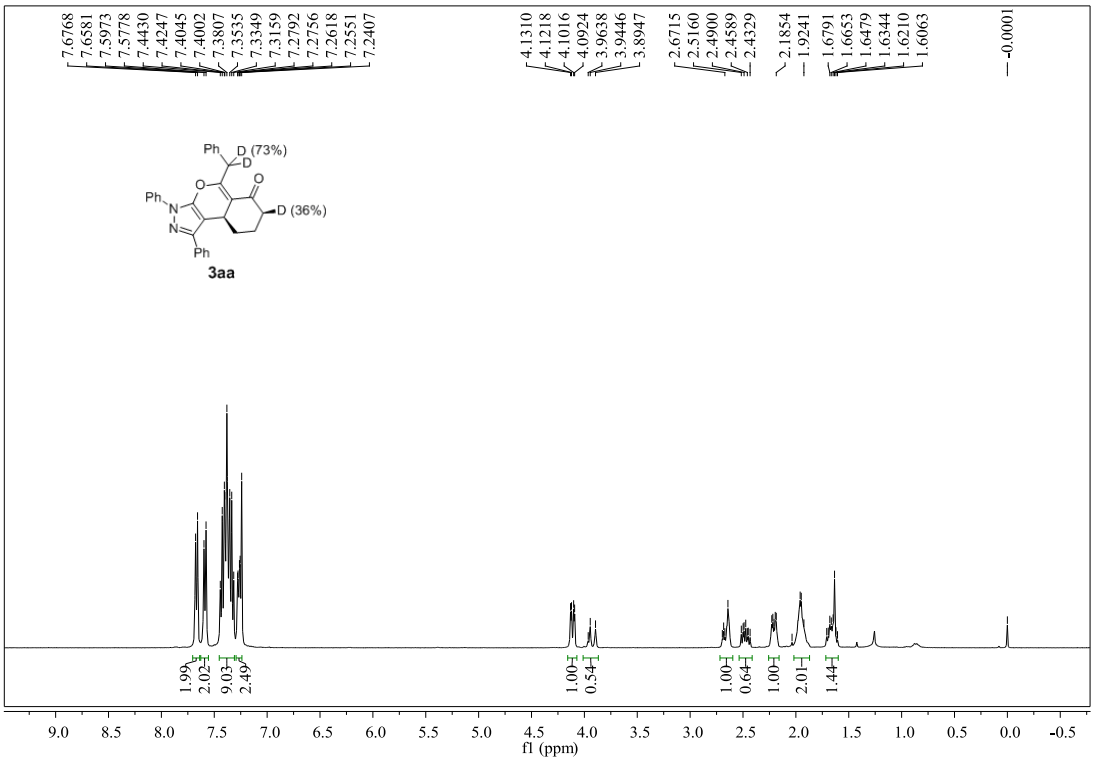
A solution of **1a** (0.1 mmol, 1.0 eq.) and **Q10** (0.01 mol, 0.1 eq.) in EtOAc (1.0 mL) was cooled to -20 ^{o}C. After 10 min, **2a** (0.12 mmol, 1.2 eq.) was added in one portion. The resulting mixture was stirred at -20 ^{o}C for 14 h. After the addition of D_2O (0.1 mL), the mixture was warmed to rt, and then stirred for 6 h. The solvent was removed under vacuum and the crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/8) on silica gel to give **3aa** 35 mg (yield 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.45-7.30 (m, 9H), 7.29-7.22 (m, 2H), 4.11 (dd, J = 11.7, 3.3 Hz, 1H), 4.01-3.88 (m, 1.21 H), 2.67 (dt, J = 15.3, 4.6 Hz, 1H), 2.54-2.40 (m, 0.67 H), 2.26-2.15 (m, 1H), 2.02-1.87 (m, 2H), 1.70-1.61 (m, 1H).



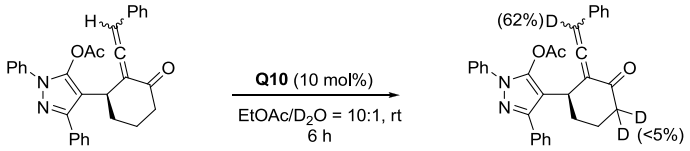
Deuterium-labeling experiment (Table 3, entry 4)



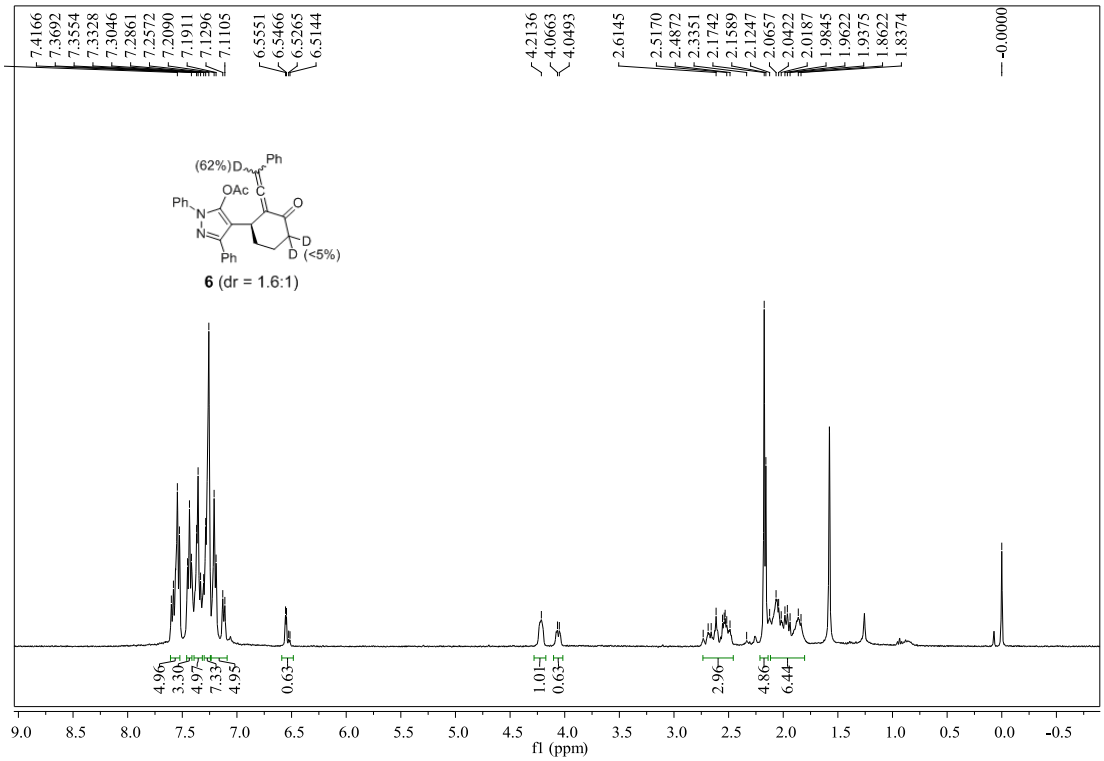
To a solution of **1a** (0.1 mmol, 1.0 eq.) and **Q10** (0.01 mmol, 0.1 eq.) in a mixture of EtOAc (1.0 mL) and D_2O (0.1 mL) was added **2a** (0.12 mmol, 1.2 eq.). The resulting mixture was stirred at rt for 6 h. The solvent was removed under vacuum, then the crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/8) to give **3aa** as white solid (33 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.45-7.31 (m, 9H), 7.29-7.24 (m, 2H), 4.11 (dd, J = 11.7, 3.7 Hz, 1H), 4.00-3.87 (m, 0.54H), 2.71-2.60 (m, 1H), 2.54-2.41 (m, 0.64 H), 2.26-2.16 (m, 1H), 2.02-1.87 (m, 2H), 1.72-1.60 (m, 1H).



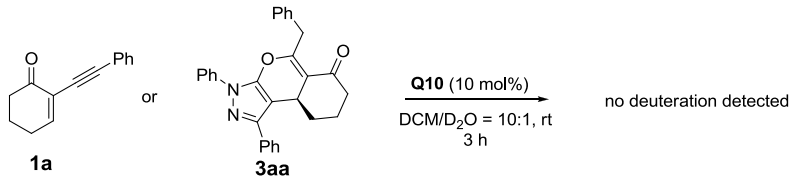
Deuterium-labeling experiment (eq. a)



A solution of **6** (12.0 mg, 1.0 eq., dr = 10:1) and **Q10** (1.2 mg, 0.1 eq.) in a mixture of EtOAc (0.3 mL) and D_2O (30 μL) was stirred at rt for 6 h. The solvent was removed under vacuum, then the crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/4) to give the deuterated **6** (12 mg, yield 99%, dr = 1.6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.52 (m, 4.9H), 7.47-7.41 (m, 3.3H), 7.39-7.31 (m, 4.9H), 7.30-7.24 (m, 6.6H), 7.23-7.10 (m, 4.9H), 6.58-6.51 (m, 0.63H), 4.27-4.18 (m, 1H), 4.10-4.02 (m, 0.63H), 2.77-2.41 (m, 3.0 H), 2.17 (s, 4.9H), 2.11-1.80 (m, 6.4H).



Deuterium-labeling experiment for 1a and 3aa



A solution of **1a** (0.1 mmol, 1.0 eq.) and **Q10** (0.01 mmol, 0.1 eq.) or a solution of **3aa** (0.1 mmol, 1.0 eq.) and **Q10** (0.01 mmol, 0.1 eq.) in a mixture of DCM (1.0 mL) and D_2O (0.1 mL) was stirred at rt for 3 h. The solvent was removed under vacuum, then the crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/8). No deuteration of **1a** and **3aa** was detected by ^1H NMR.

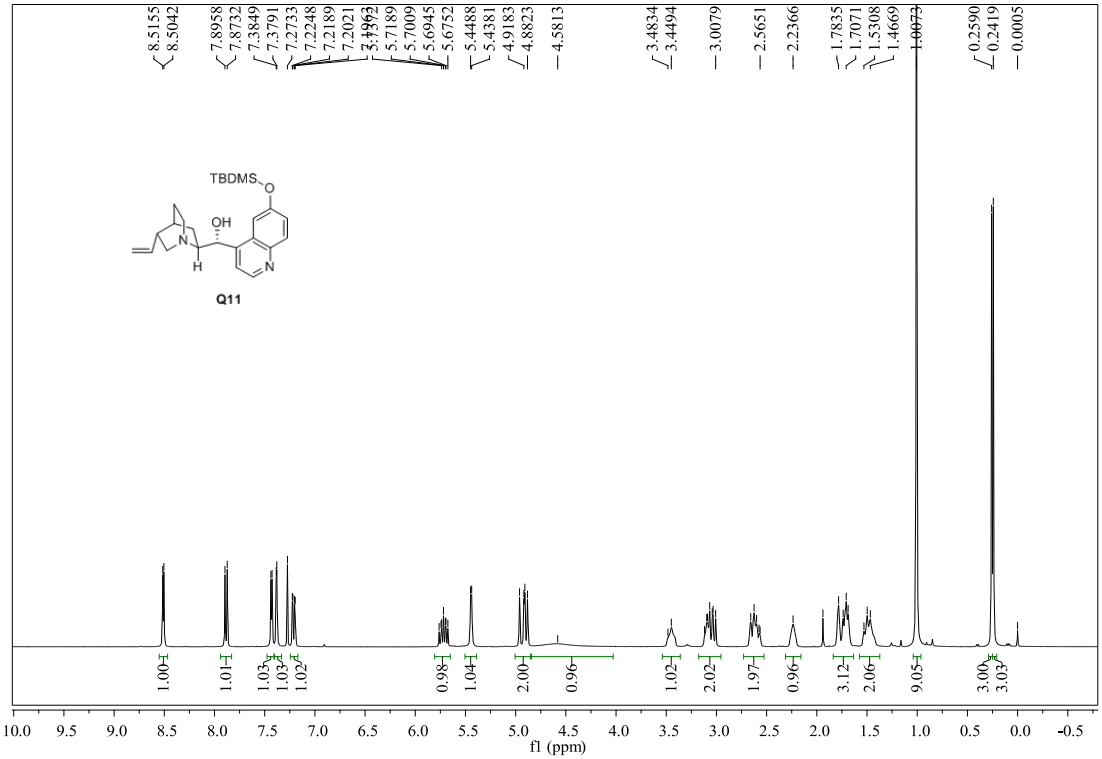
6. Reference

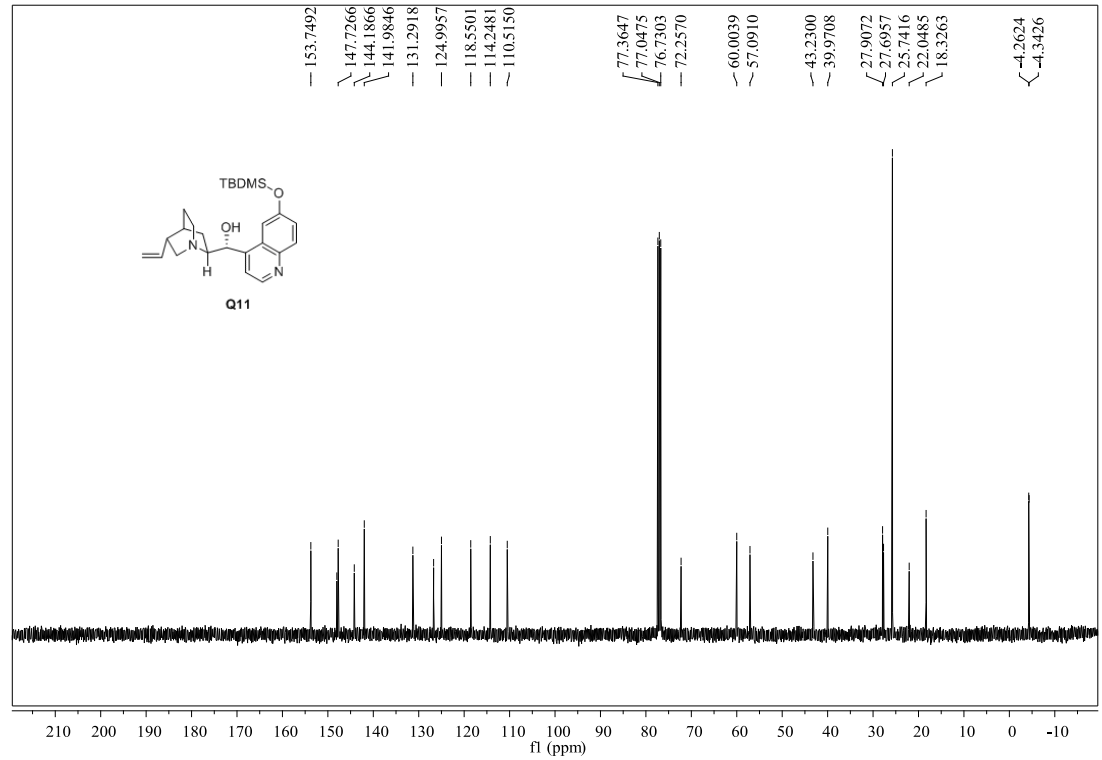
[1] Yao, T.; Zhang, X.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 7679.

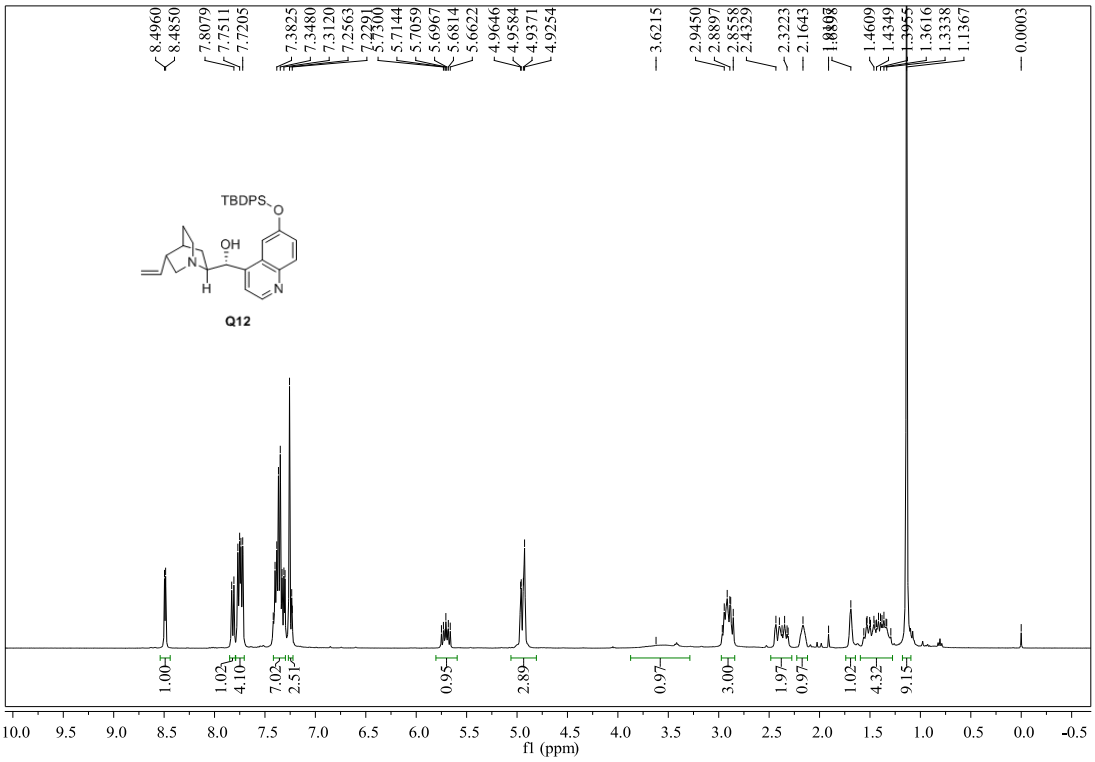
[2] Li, F.; Sun, L.; Teng, Y.; Yu, P.; Zhao, J. C.; Ma, J. *Chem. Eur. J.* **2012**, *18*, 14255.

[3] a) Du, T.; Du, F.; Ning, Y.; Peng, Y. *Org. Lett.* **2015**, *17*, 1308; b) Zhang, T.; He, W.; Zhao, X.; Jin, Y. *Tetrahedron* **2013**, *69*, 7416; c) Li, H.; Wang, B.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 732.

7. NMR spectra for compounds



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5.6967
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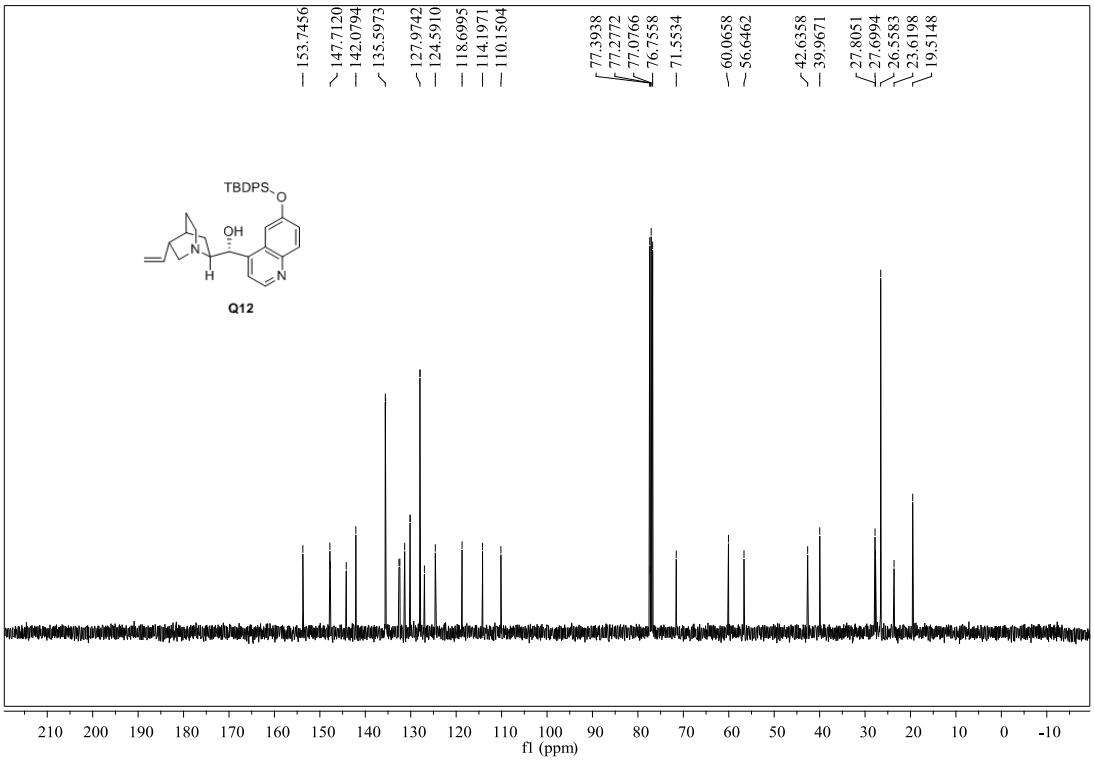
0.97
1.02
4.32
9.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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H
N
Q12
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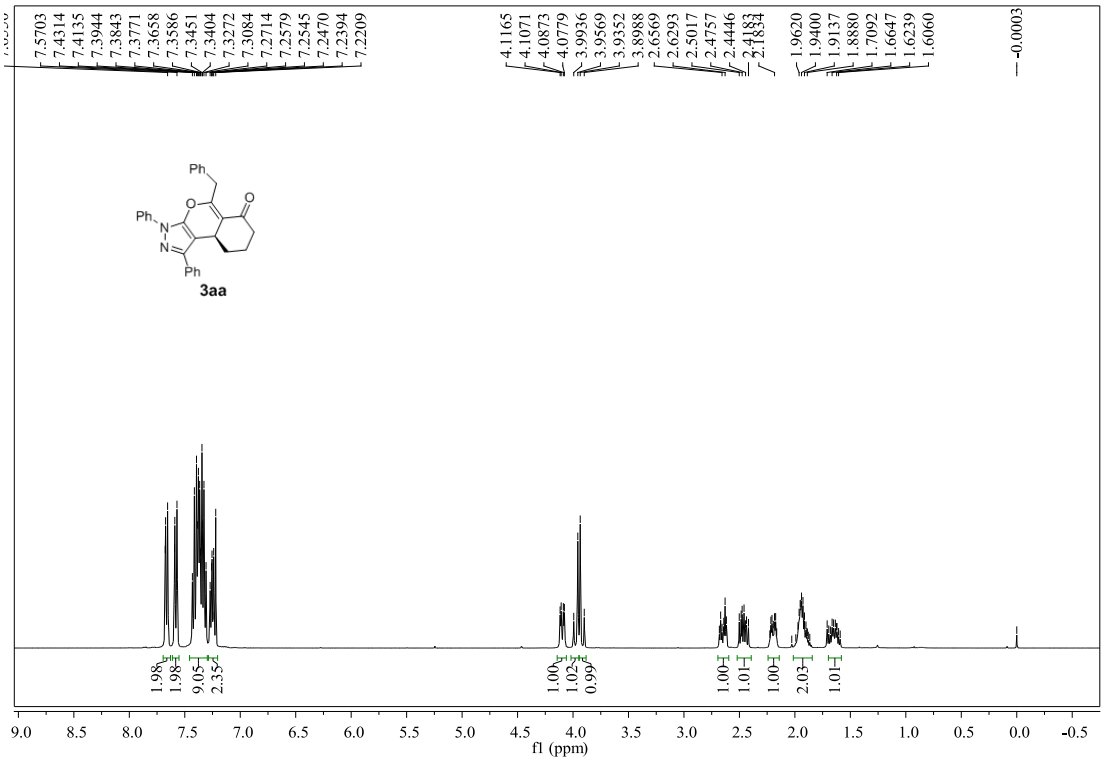
f1 (ppm)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Ph
N
N
Ph
3aa
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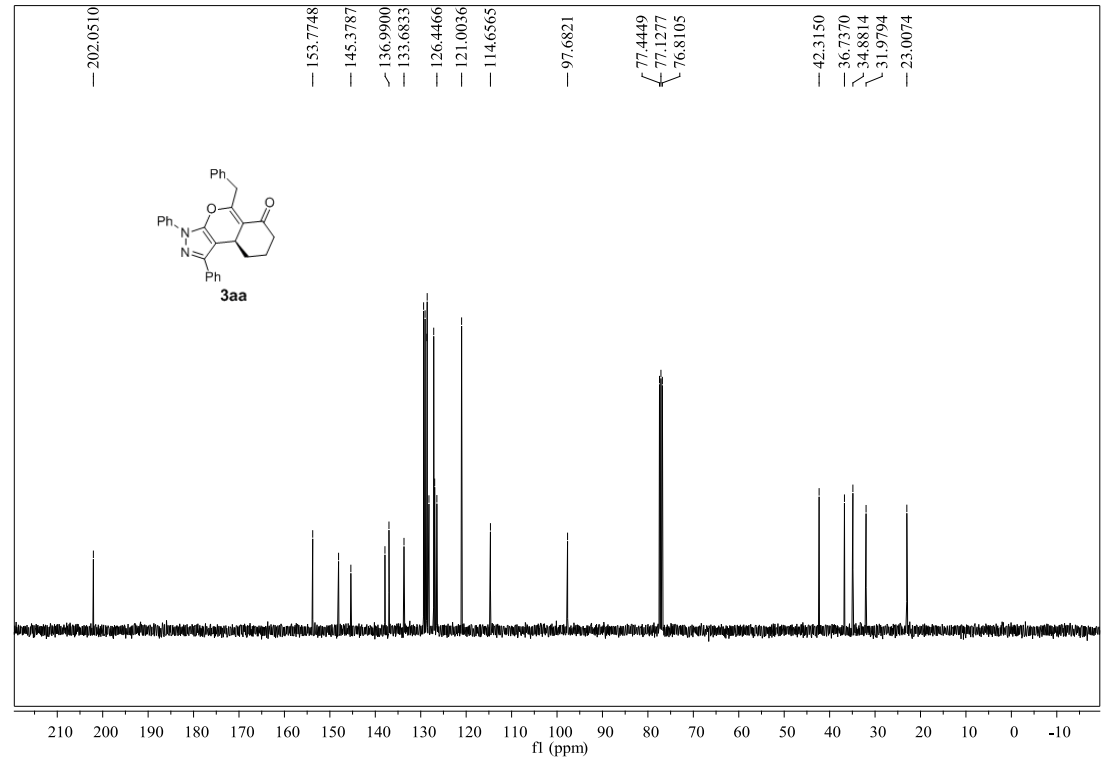
1.98
9.05
2.35
1.00
1.02
0.99
1.00
1.01
1.00
2.03
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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Ph
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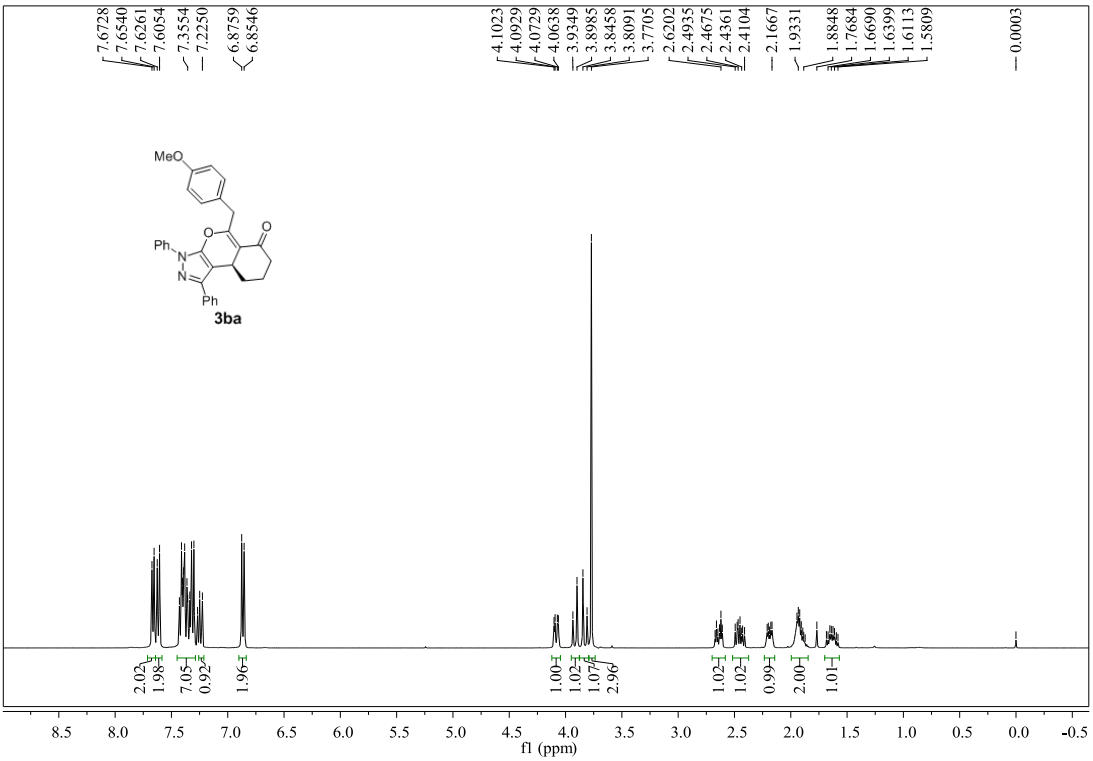
f1 (ppm)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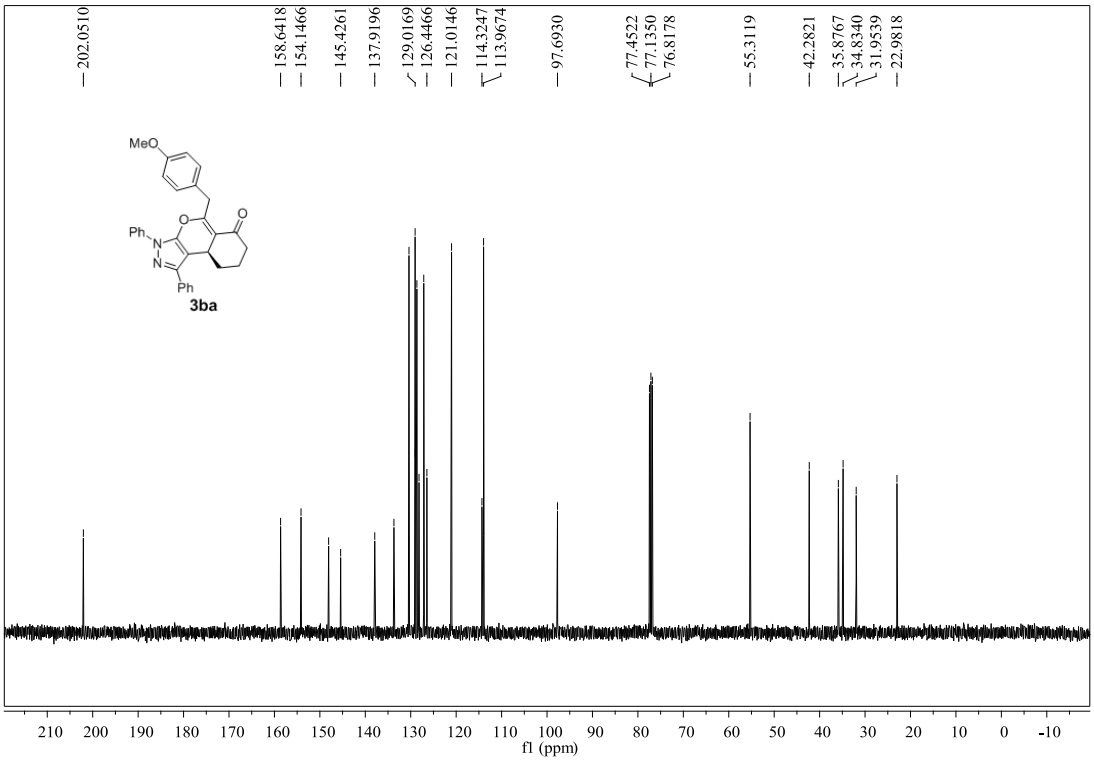
2.00
1.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.4466
121.0146
114.3247
113.9674
97.6930
77.4522
77.1350
76.8178
55.3119
42.2821
35.8767
34.8340
31.9539
22.9818
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Ph
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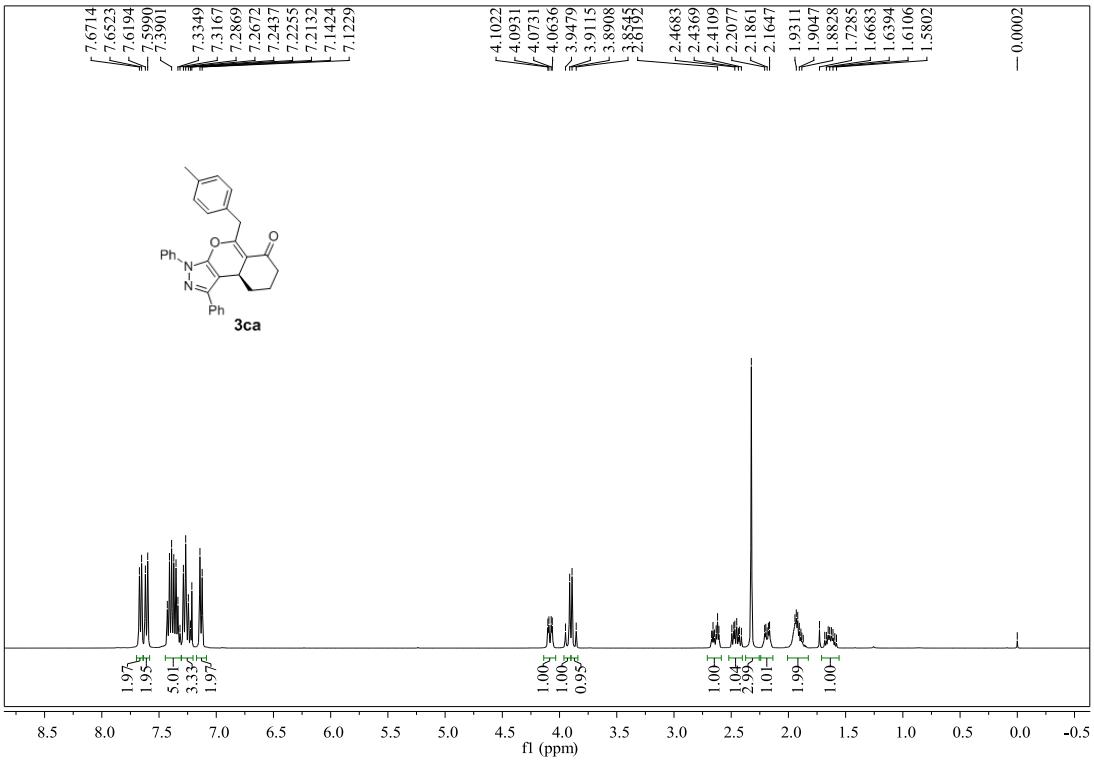
N
O
O
Ph
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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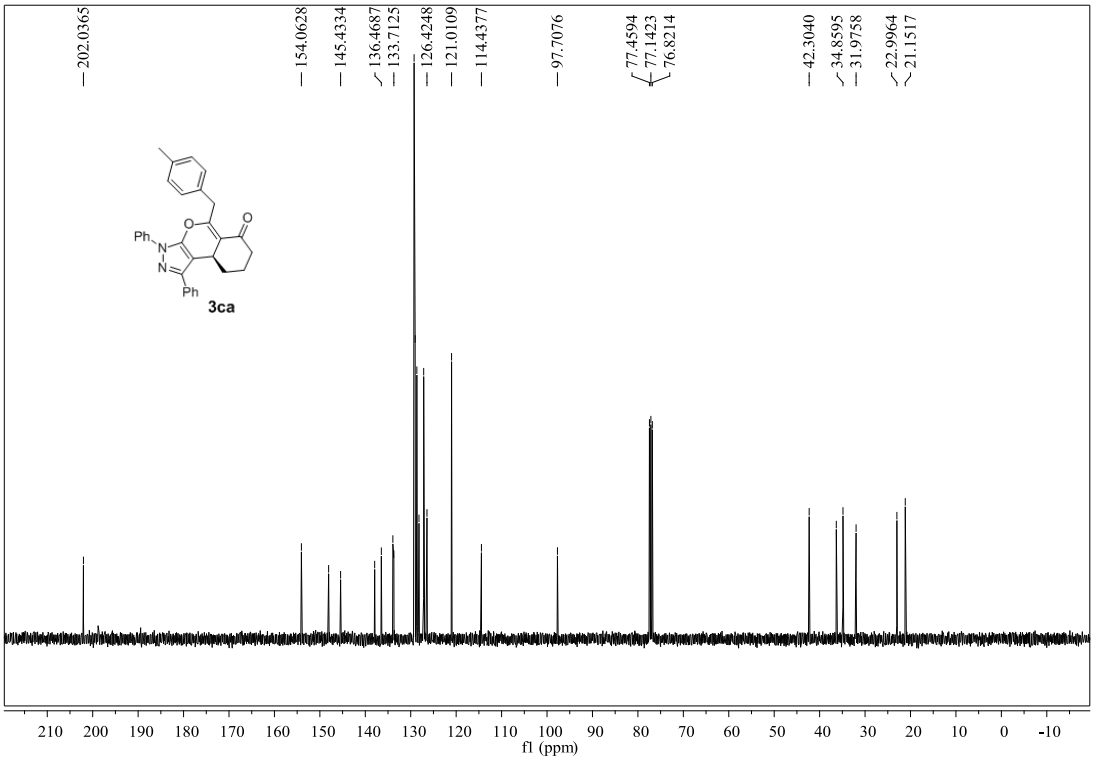
7.2672
7.2437
7.2255
7.2132
7.1424
7.1229
4.1022
4.0931
4.0731
4.0636
3.9479
3.9115
3.8908
3.8545
3.8192
2.4683
2.4369
2.4109
2.2077
2.1861
2.1647
1.9311
1.9047
1.8828
1.7285
1.6683
1.6394
1.6106
1.5802
0.0002
Ph
N
N
O
O
Ph
3ca
1.97
1.95
5.01
3.33
1.97
1.00
1.00
0.95
1.00
1.04
2.99
1.01
1.99
1.00
8.5 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 -0.5
f1 (ppm)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76.8214
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34.8595
31.9758
22.9964
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O
O
Ph
3ca
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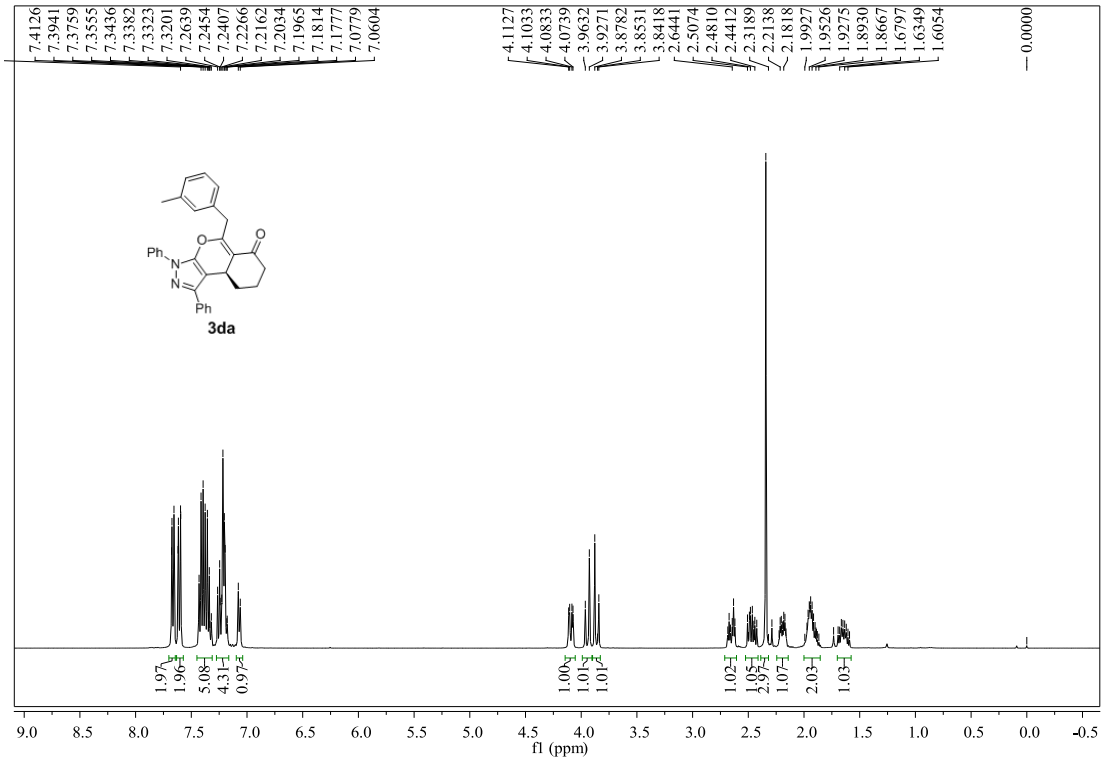
f1 (ppm)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7.3201
7.2639
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7.2407
7.2266
7.2162
7.2034
7.1965
7.1814
7.1777
7.0779
7.0604
4.1127
4.1033
4.0833
4.0739
3.9632
3.9271
3.8782
3.8531
3.8418
2.6441
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2.4810
2.4412
2.3189
2.2138
2.1818
1.9927
1.9526
1.9275
1.8930
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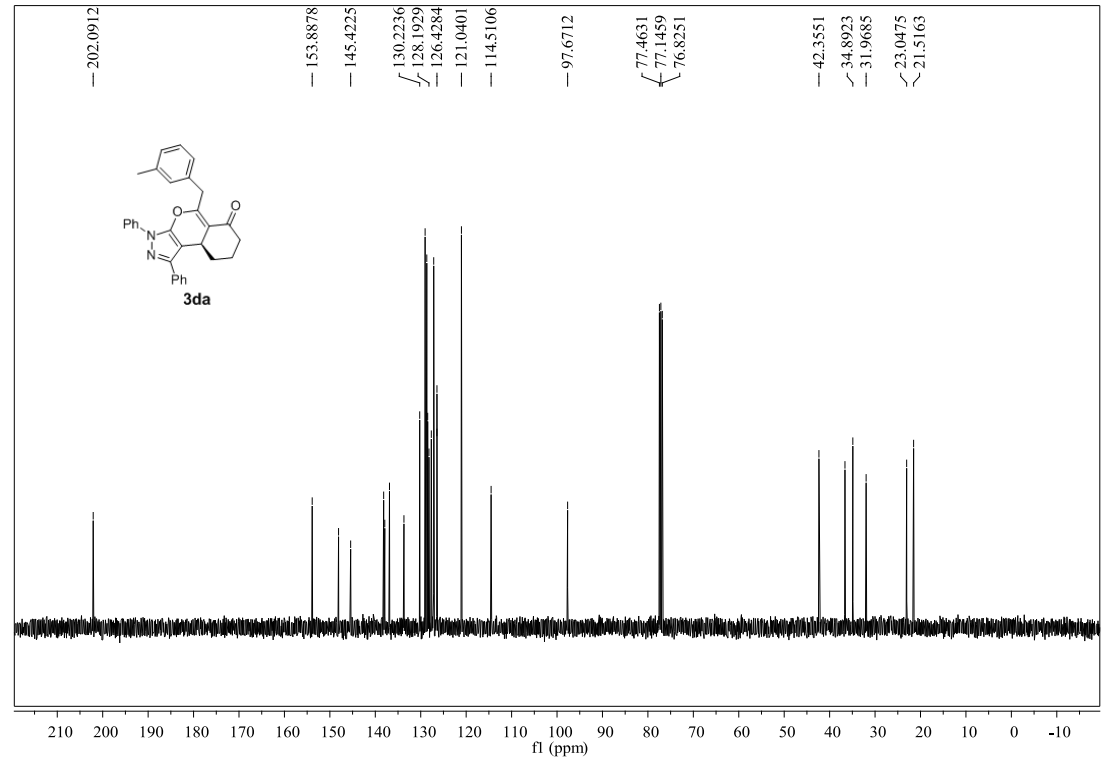
1.6797
1.6349
1.6054
0.0000
Ph
N
N
O
O
Ph
3da
1.97
1.96
5.08
4.31
0.97
1.00
1.01
1.01
1.02
1.05
2.97
1.07
2.03
1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.1459
76.8251
42.3551
34.8923
31.9685
23.0475
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O
Ph
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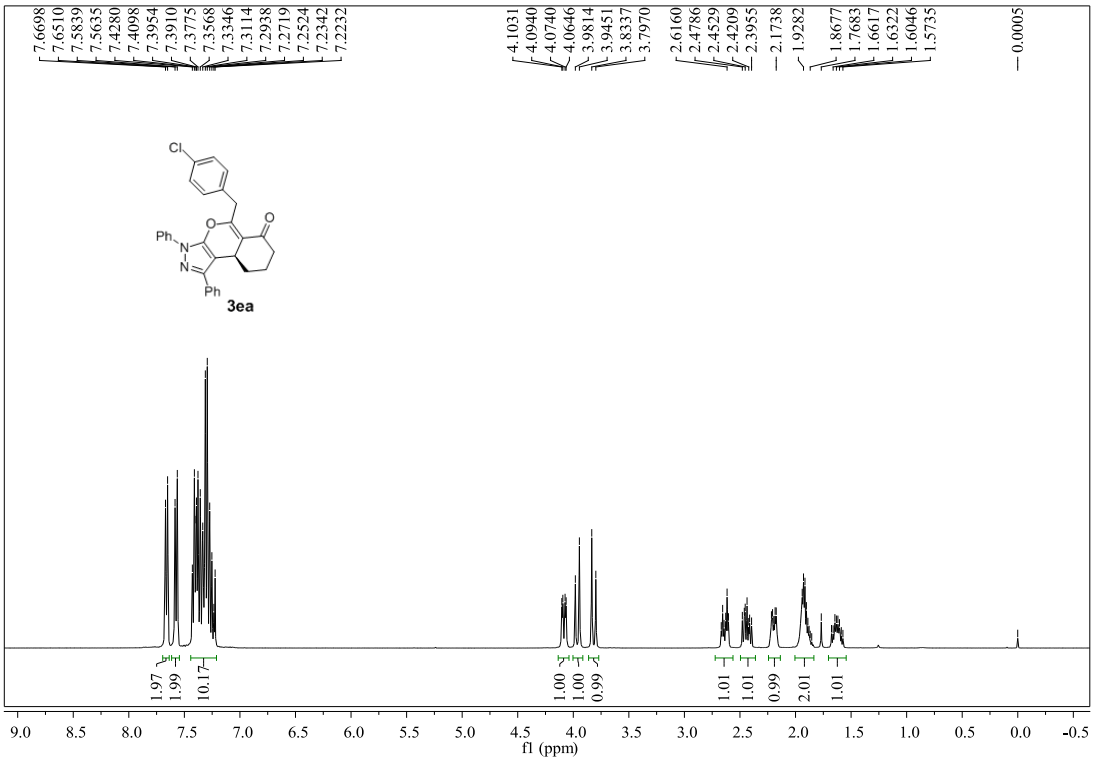
f1 (ppm)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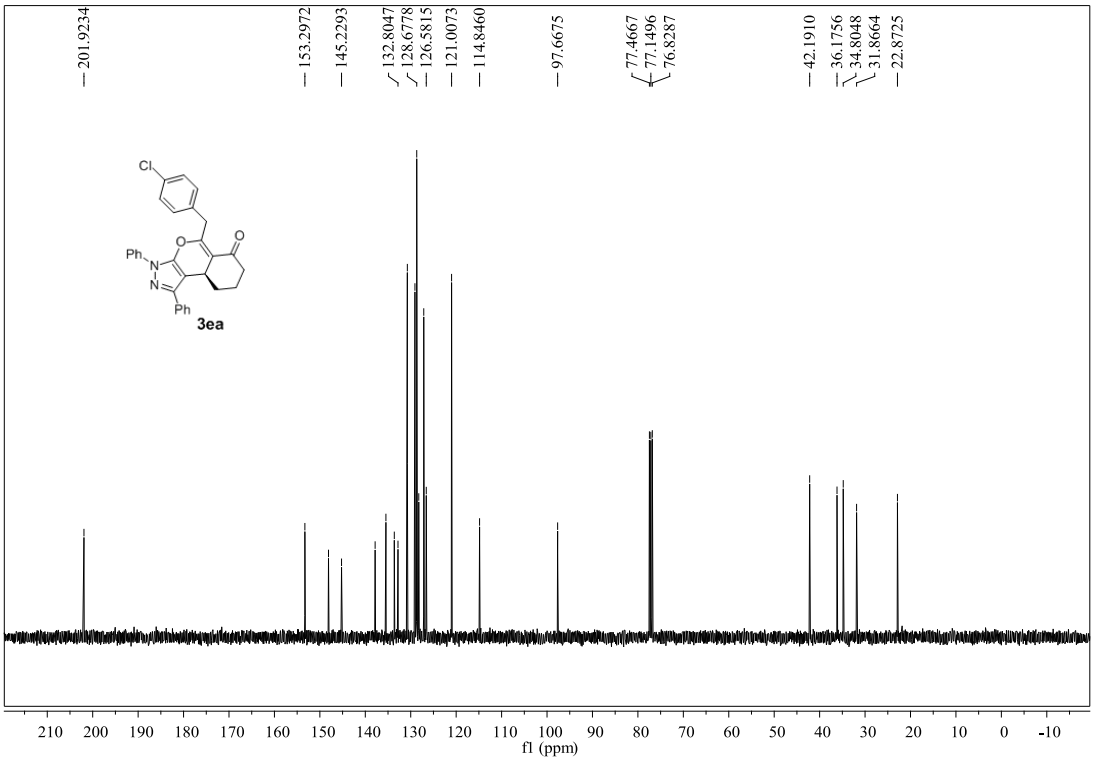
7.3775
7.3568
7.3346
7.3114
7.2938
7.2719
7.2524
7.2342
7.2232
4.1031
4.0940
4.0740
4.0646
3.9814
3.9451
3.8337
3.7970
2.6160
2.4786
2.4529
2.4209
2.3955
2.1738
1.9282
1.8677
1.7683
1.6617
1.6322
1.6046
1.5735
0.0005
Cl
Ph
N
N
O
O
Ph
3ea
1.97
1.99
10.17
1.00
1.00
0.99
1.01
1.01
0.99
2.01
1.01
9.0
8.5
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
-0.5
f1 (ppm)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76.8287
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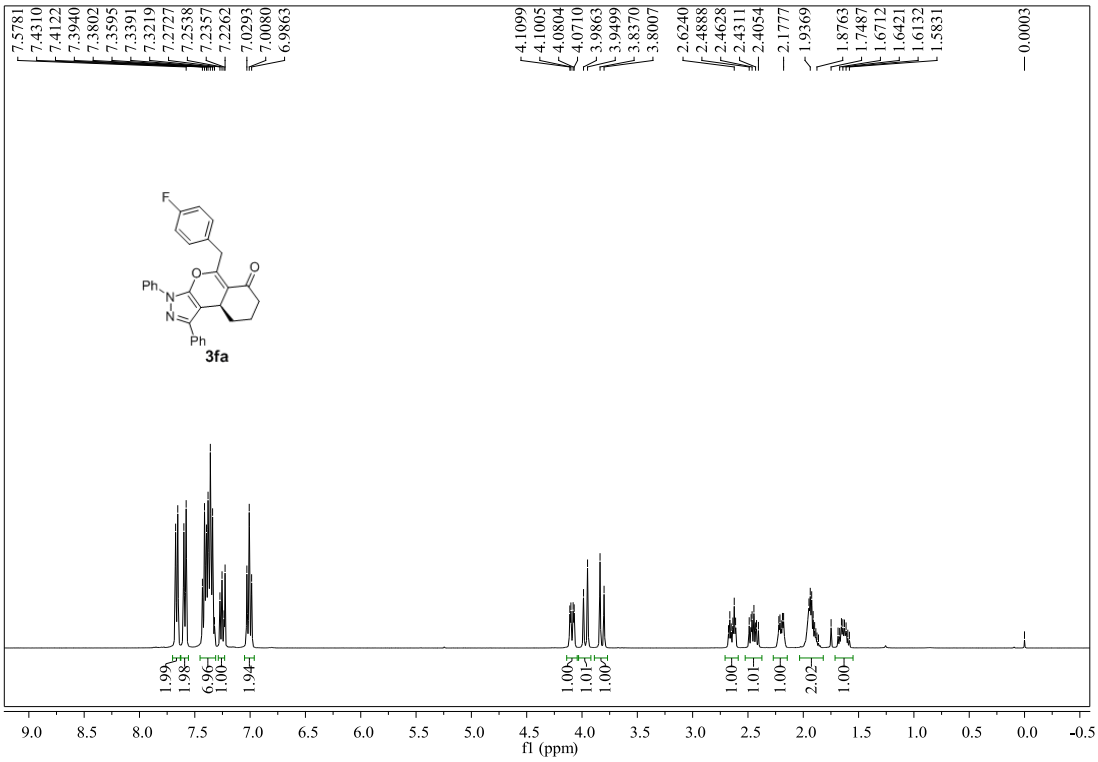
36.1756
34.8048
31.8664
22.8725
Cl
Ph
N
N
O
O
Ph
3ea
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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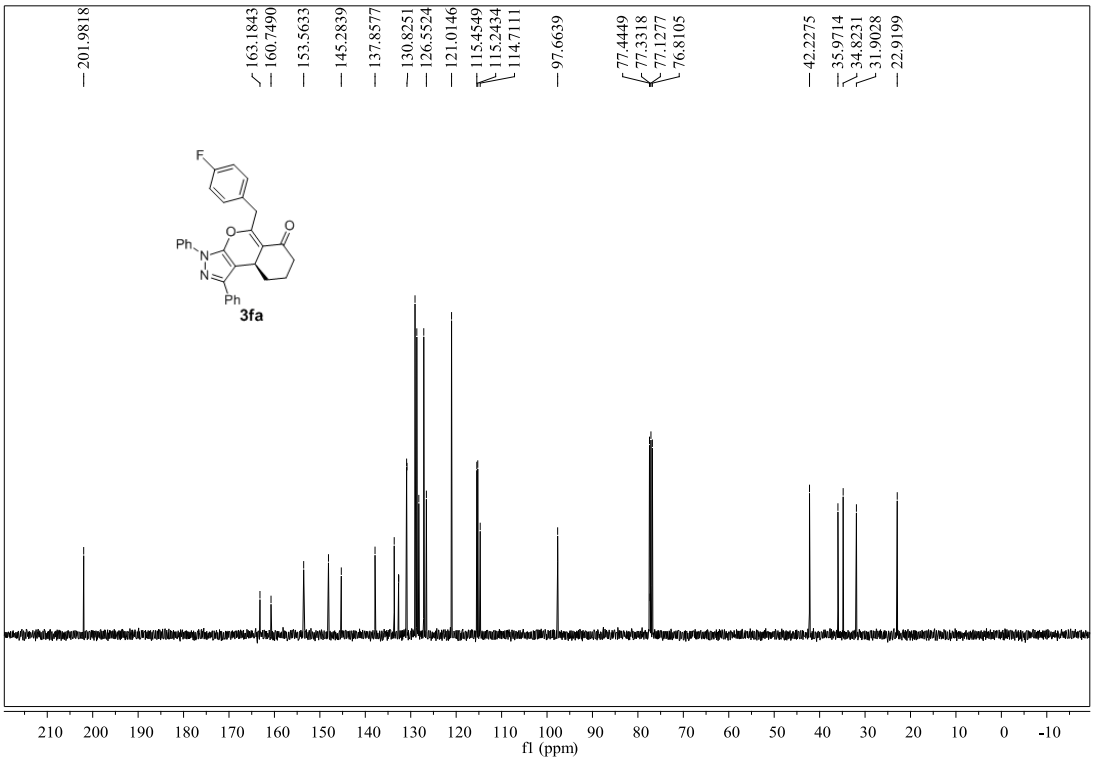
7.3219
7.2727
7.2538
7.2357
7.2262
7.0293
7.0080
6.9863
4.1099
4.1005
4.0804
4.0710
3.9863
3.9499
3.8370
3.8007
2.6240
2.4888
2.4628
2.4311
2.4054
2.1777
1.9369
1.8763
1.7487
1.6712
1.6421
1.6132
1.5831
0.0003
F
O
Ph
N
N
Ph
3fa
1.99
1.98
6.96
1.00
1.94
1.00
1.01
1.00
1.00
1.01
1.00
2.02
1.00
9.0 8.5 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 -0.5
f1 (ppm)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97.6639
77.4449
77.3318
77.1277
76.8105
42.2275
35.9714
34.8231
31.9028
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F
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Ph
N
N
Ph
3fa
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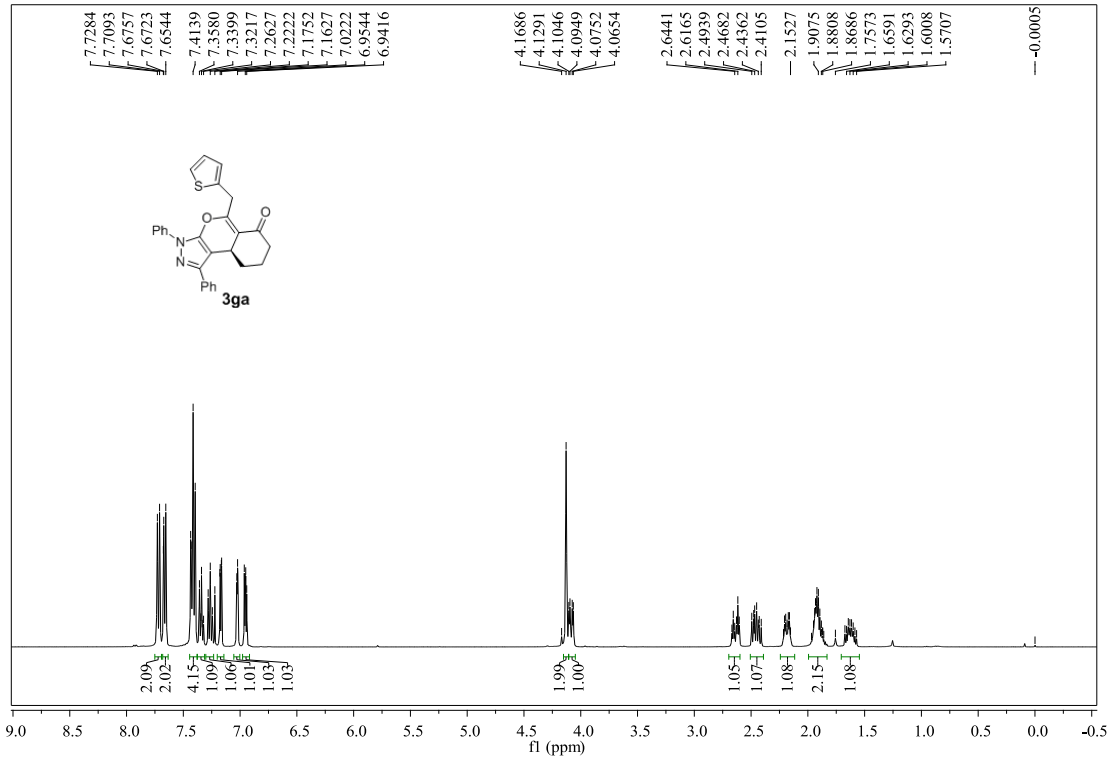
f1 (ppm)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7.3217
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7.1752
7.1627
7.0222
6.9544
6.9416
4.1686
4.1291
4.1046
4.0949
4.0752
4.0654
2.6441
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2.4362
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1.8808
1.8686
1.7573
1.6591
1.6293
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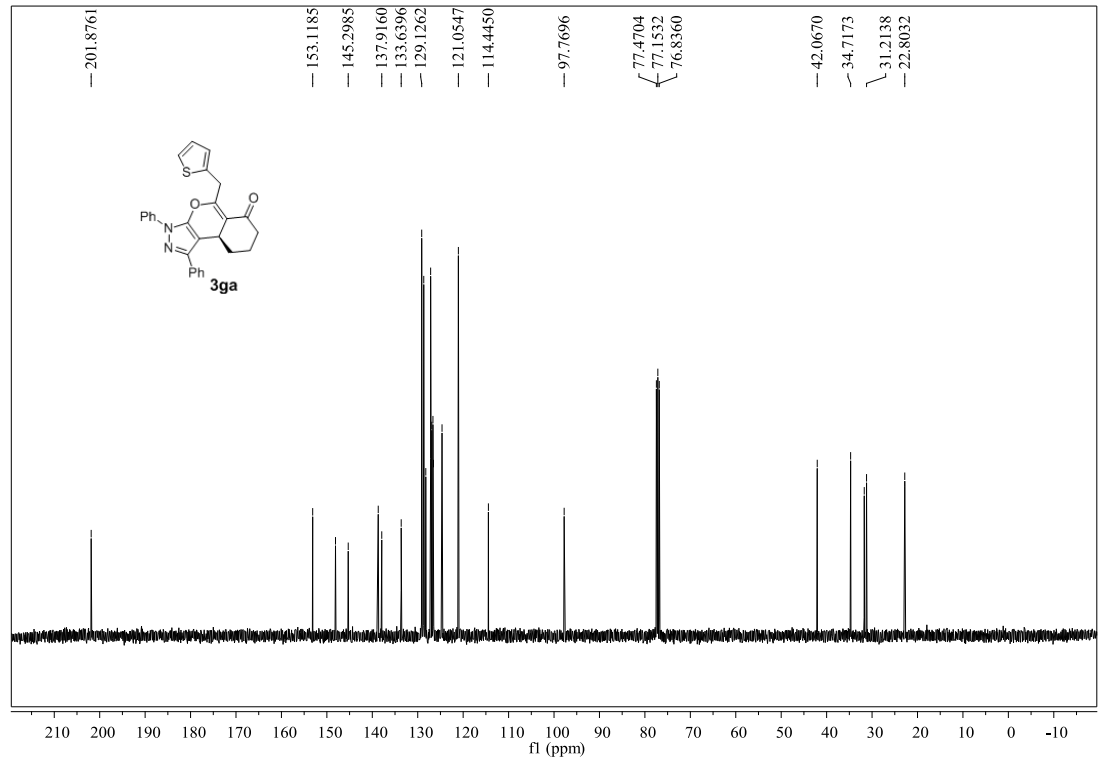
1.5707
0.0005
3ga
2.09
2.02
4.15
1.09
1.06
1.01
1.03
1.03
1.99
1.00
1.05
1.07
1.08
2.15
1.08
f1 (ppm)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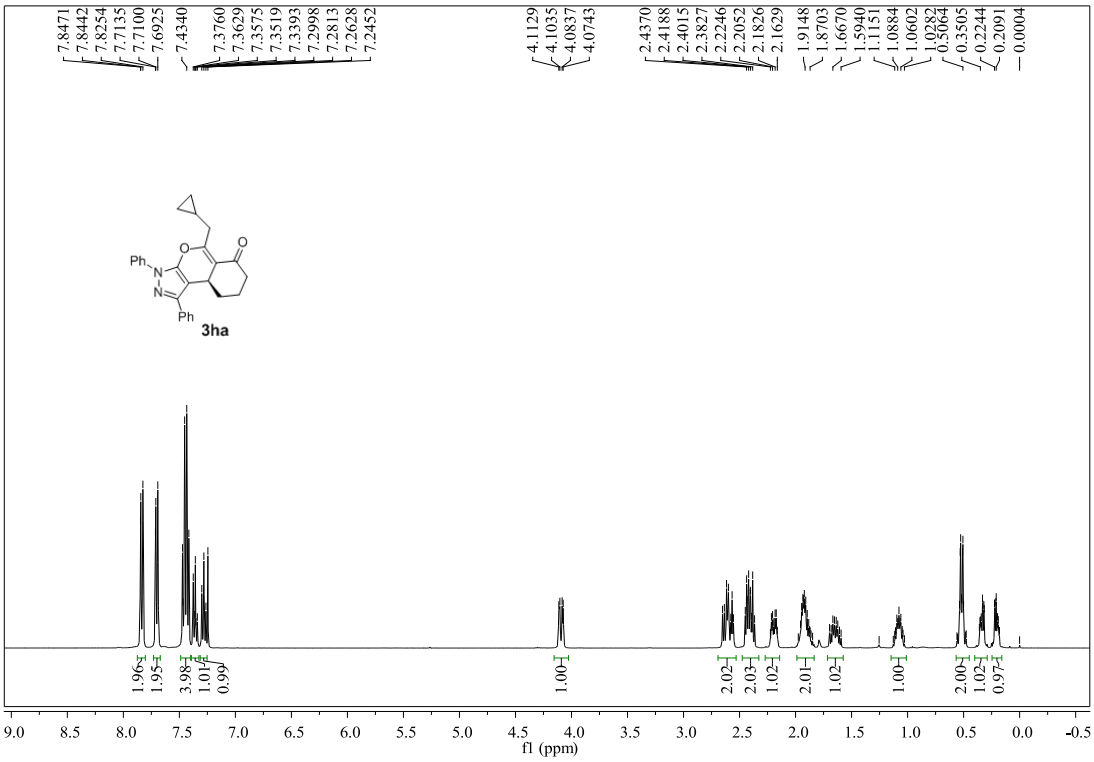
31.2138
22.8032
3ga
f1 (ppm)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7.4340
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7.3629
7.3575
7.3519
7.3393
7.2998
7.2813
7.2628
7.2452
4.1129
4.1035
4.0837
4.0743
2.4370
2.4188
2.4015
2.3827
2.2246
2.2052
2.1826
2.1629
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1.8703
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1.1151
1.0884
1.0602
1.0282
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0.3505
0.2244
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Ph
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N
O
O
Ph
3ha
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1.95
3.98
1.01
0.99
1.00
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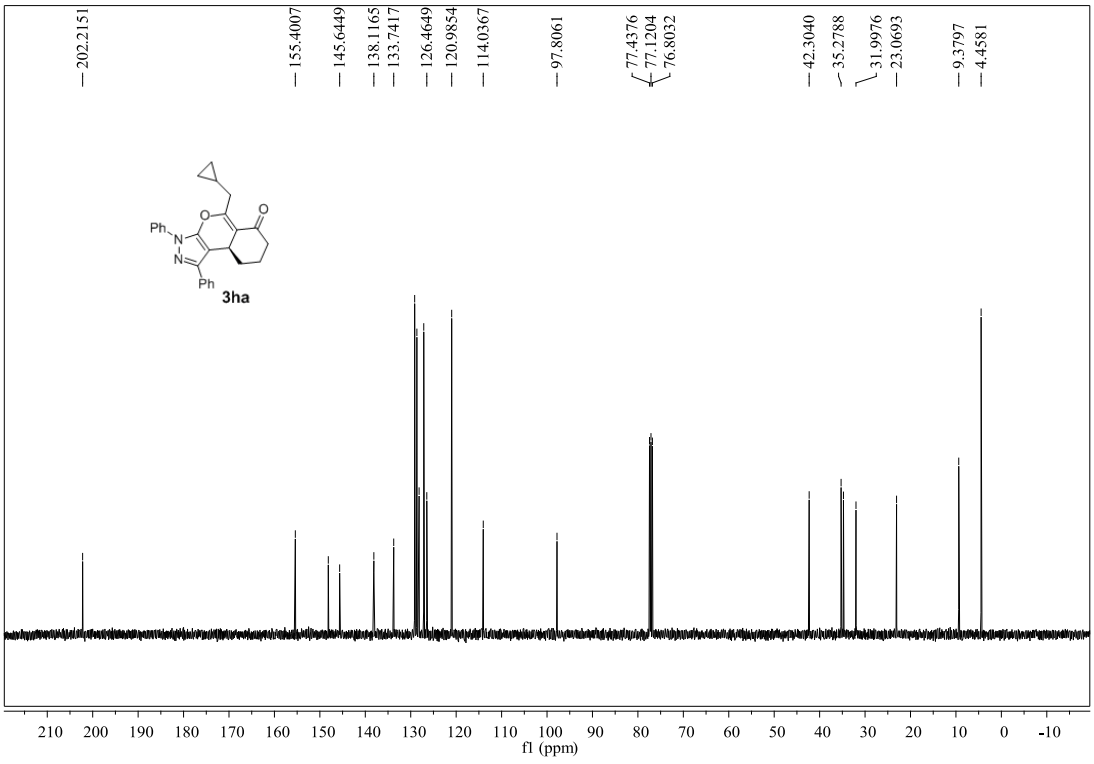
2.03
1.02
2.01
1.02
1.00
2.00
1.02
0.97
fl (ppm)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76.8032
42.3040
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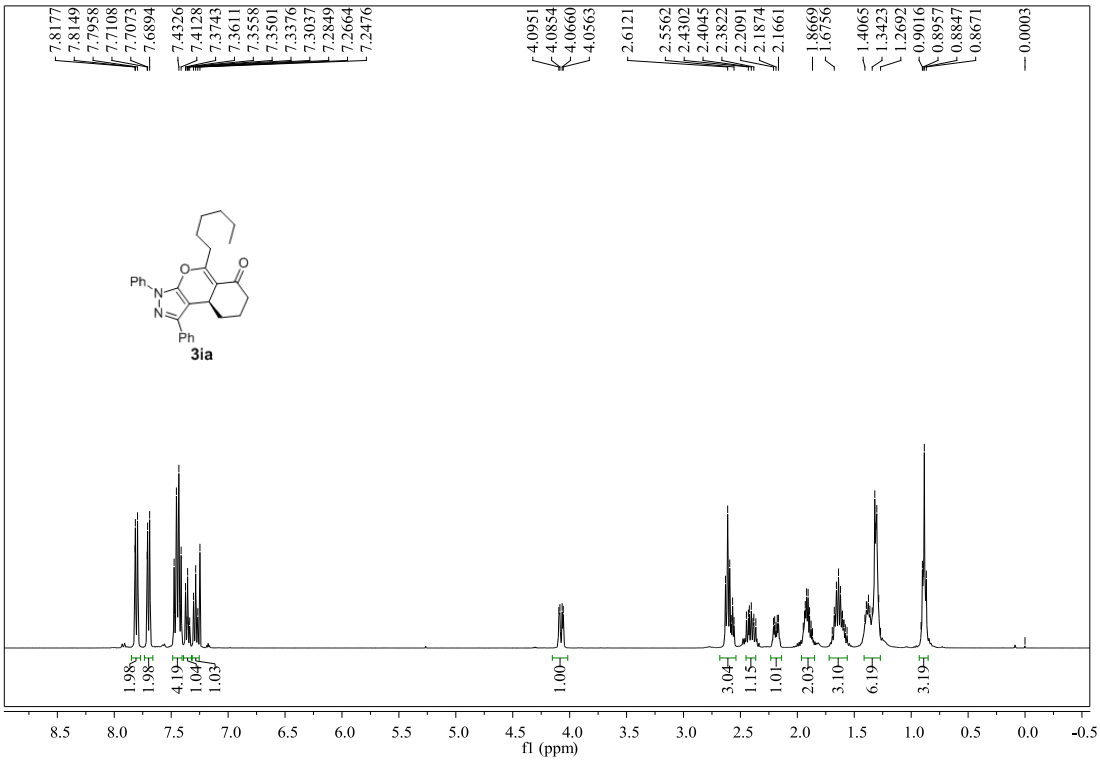
23.0693
9.3797
4.4581
Ph
N
N
O
O
Ph
3ha
fl (ppm)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7.3558
7.3501
7.3376
7.3037
7.2849
7.2664
7.2476
4.0951
4.0854
4.0660
4.0563
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2.4302
2.4045
2.3822
2.2091
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2.1661
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1.6756
1.4065
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N
O
O
Ph
3ia
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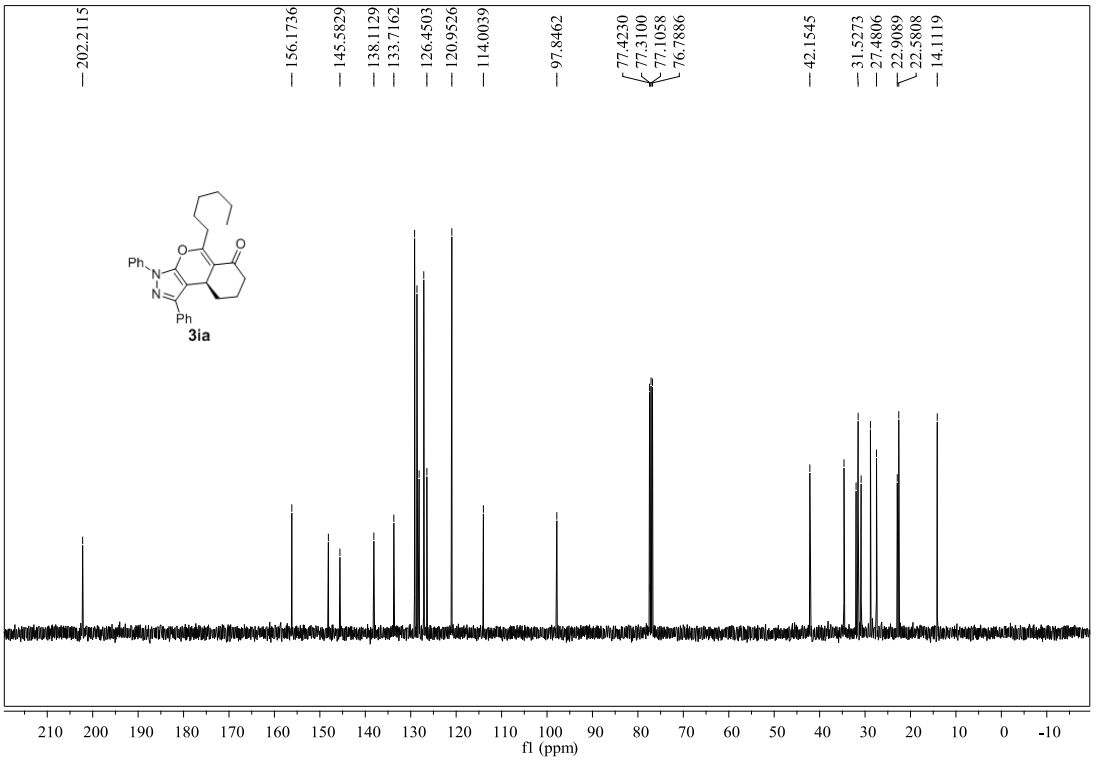
1.98
4.19
1.04
1.03
1.00
3.04
1.15
1.01
2.03
3.10
6.19
3.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.4230
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77.1058
76.7886
42.1545
31.5273
27.4806
22.9089
22.5808
14.1119
Ph
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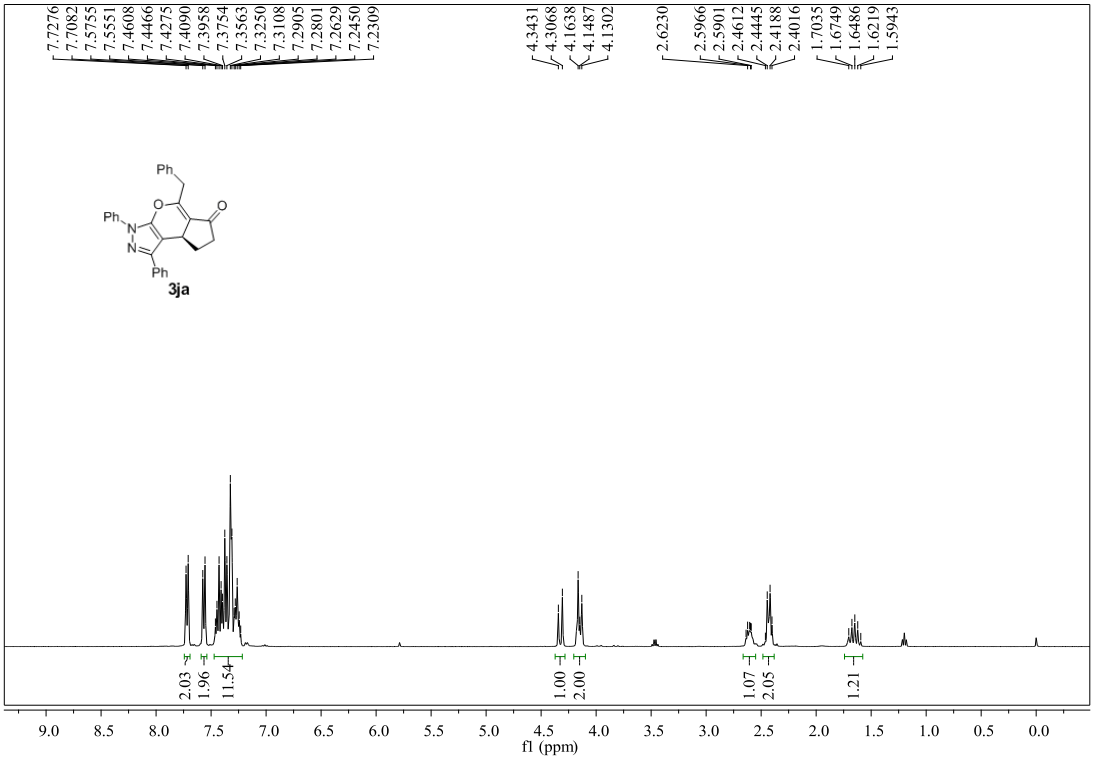
N
O
O
Ph
3ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3754
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7.3250
7.3108
7.2905
7.2801
7.2629
7.2450
7.2309
4.3431
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4.1638
4.1487
4.1302
2.6230
2.5966
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2.4445
2.4188
2.4016
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1.6749
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1.6219
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O
Ph
N
N
Ph
O
3ja
2.03
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11.54
1.00
2.00
1.07
2.05
1.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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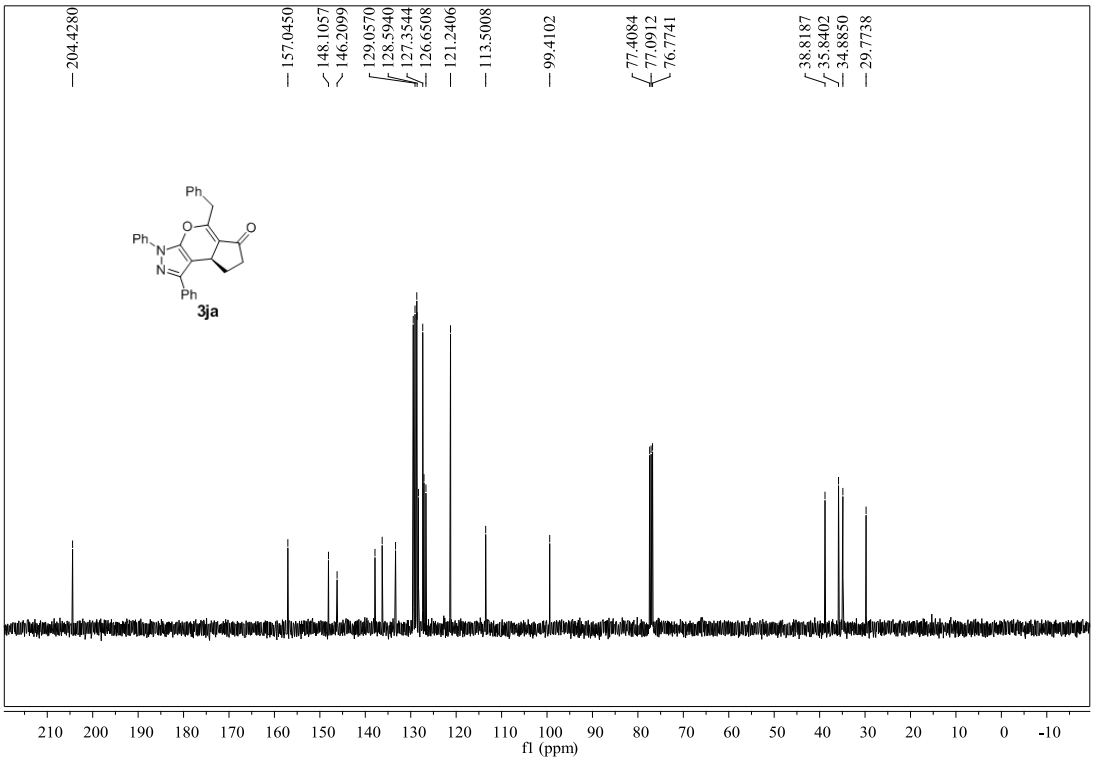
0.0
f1 (ppm)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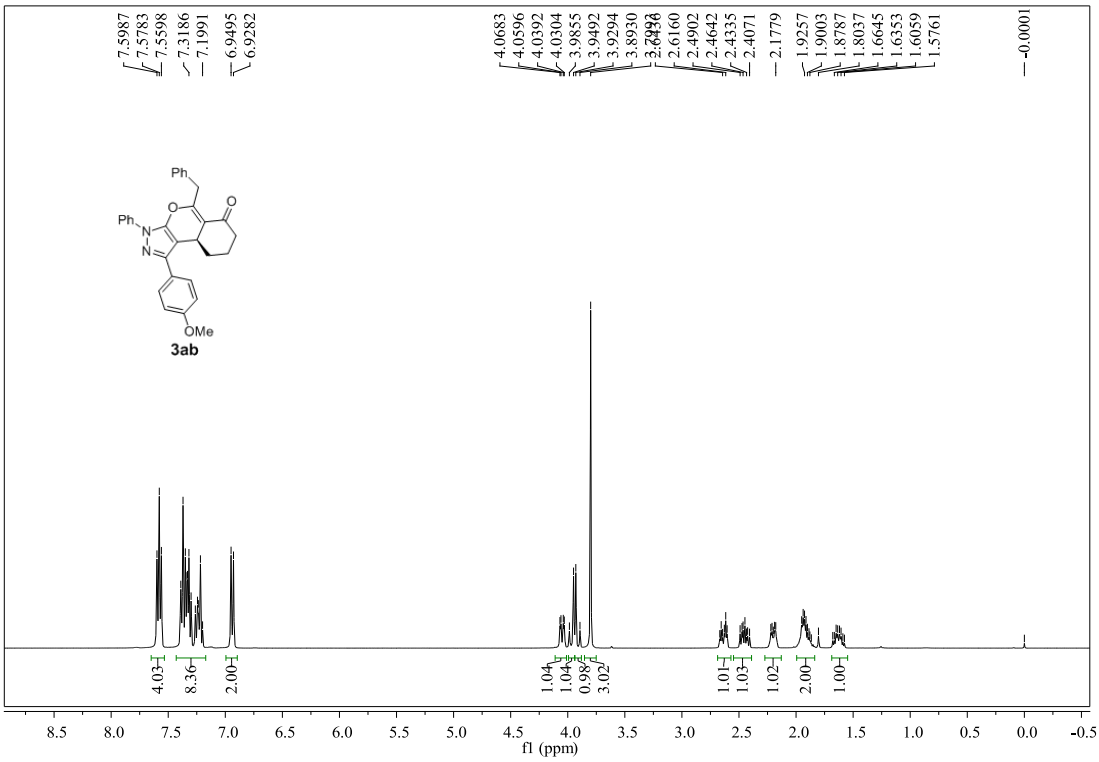
77.4084
77.0912
76.7741
38.8187
35.8402
34.8850
29.7738
Ph
O
Ph
N
N
Ph
O
3ja
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.4902
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1.9003
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1.5761
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Ph
N
N
OMe
3ab
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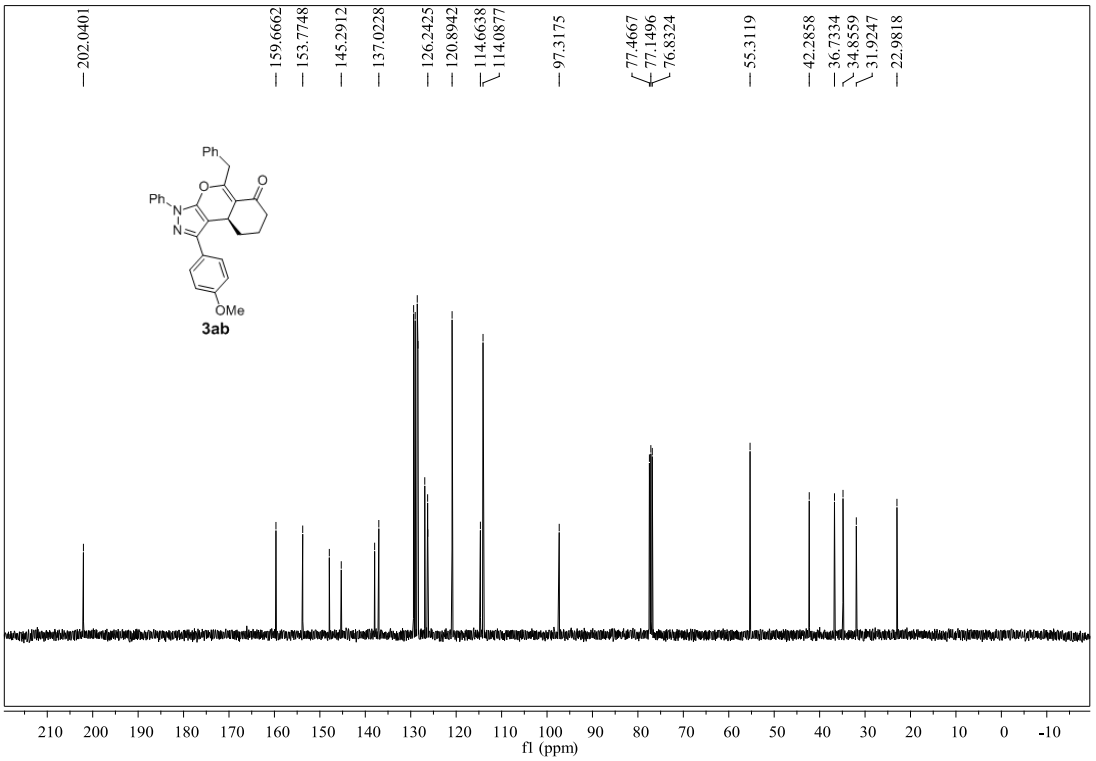
8.36
2.00
1.04
1.04
0.98
3.02
1.01
1.03
1.02
2.00
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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76.8324
55.3119
42.2858
36.7334
34.8559
31.9247
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Ph
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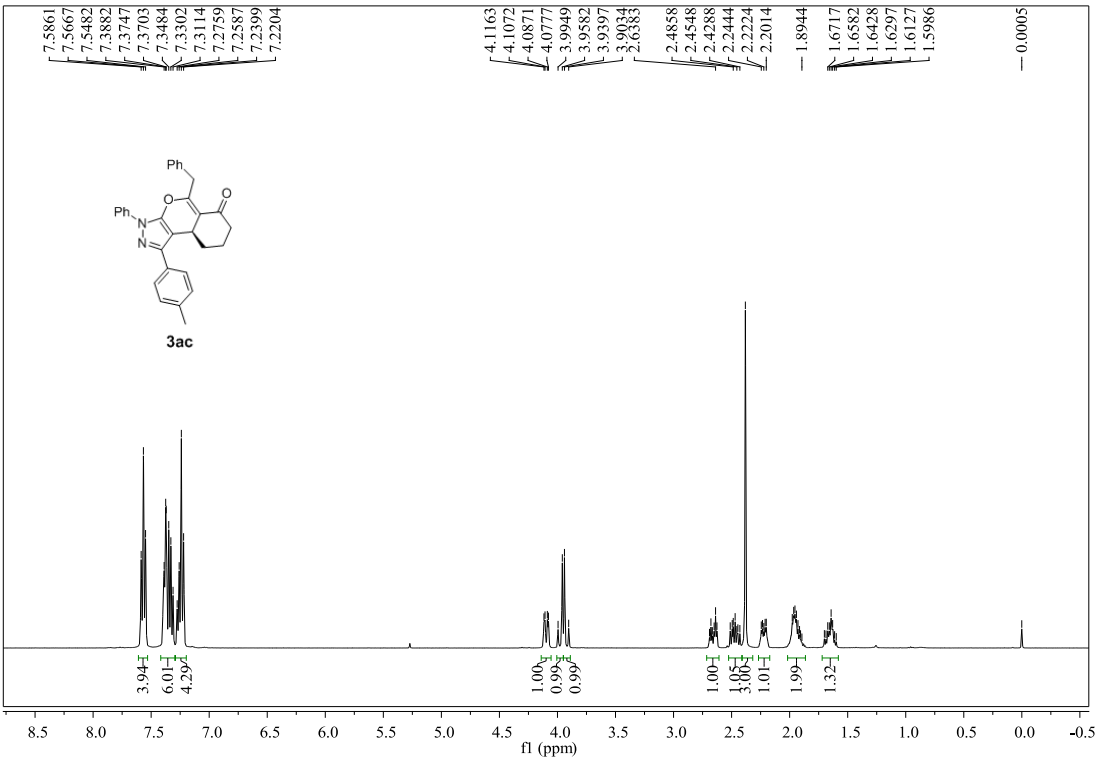
Ph
N
N
OMe
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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1.6428
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1.6127
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Ph
Ph
N
N
O
O
3ac
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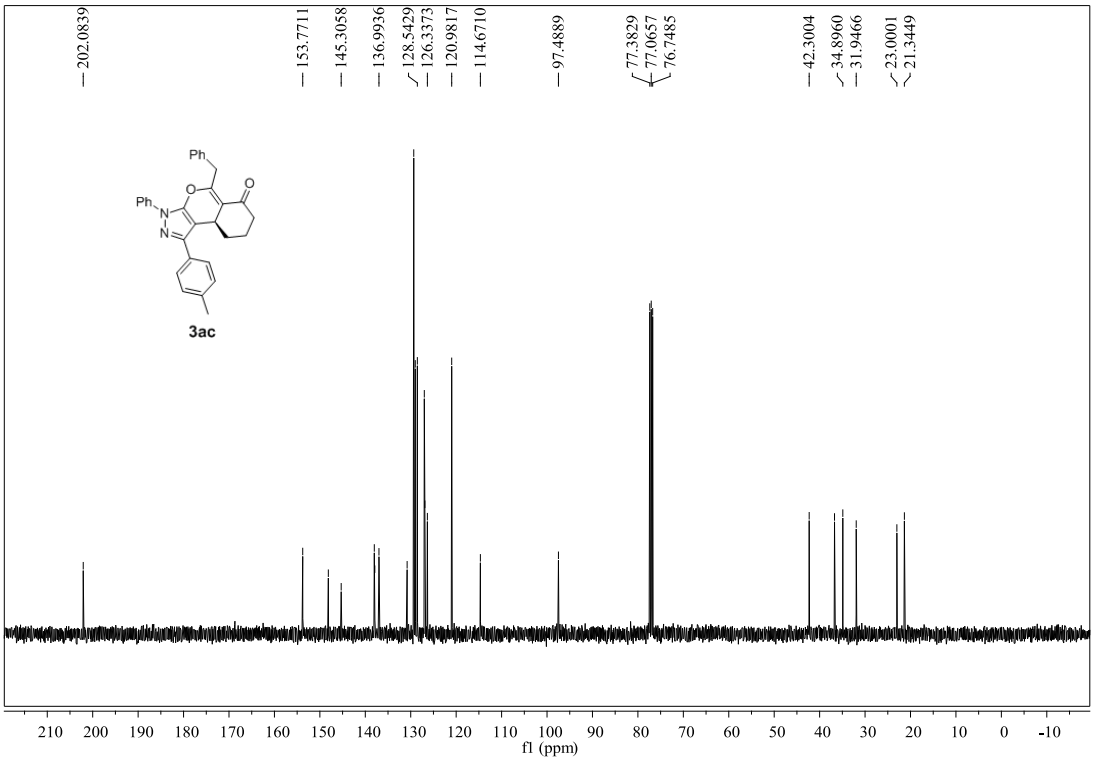
6.01
4.29
1.00
0.99
0.99
1.00
1.05
3.06
1.01
1.99
1.32
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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120.9817
114.6710
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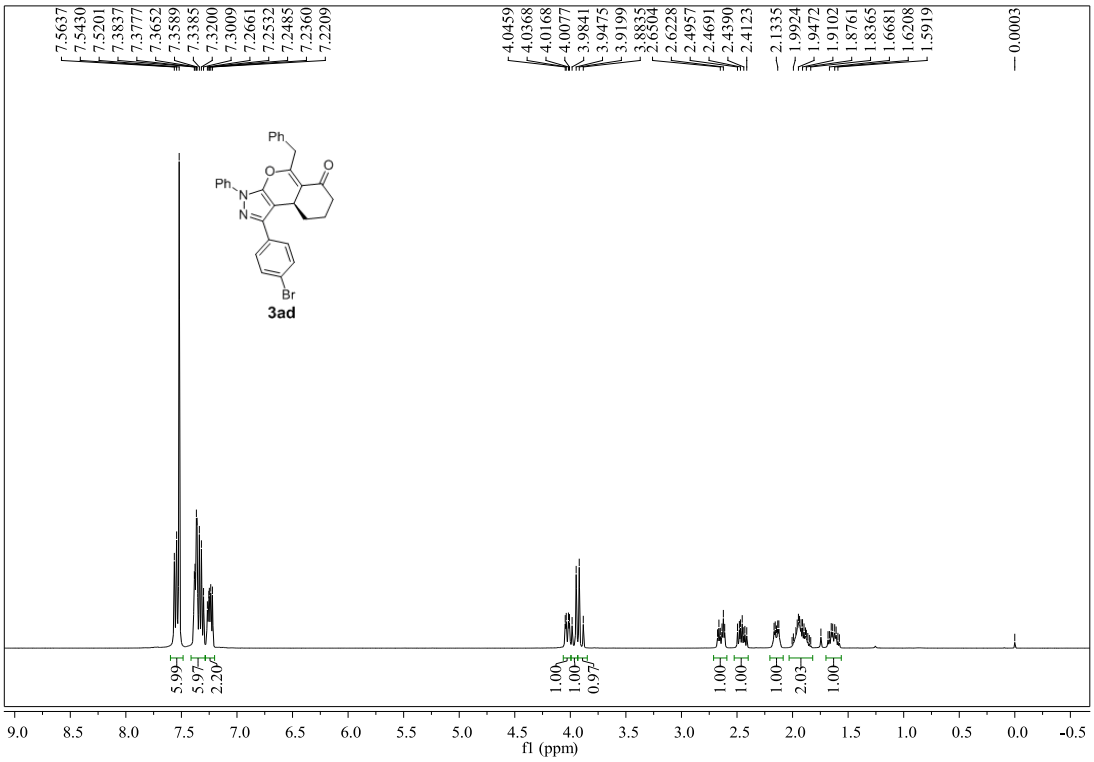
77.3829
77.0657
76.7485
42.3004
34.8960
31.9466
23.0001
21.3449
Ph
Ph
N
N
O
O
3ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3200
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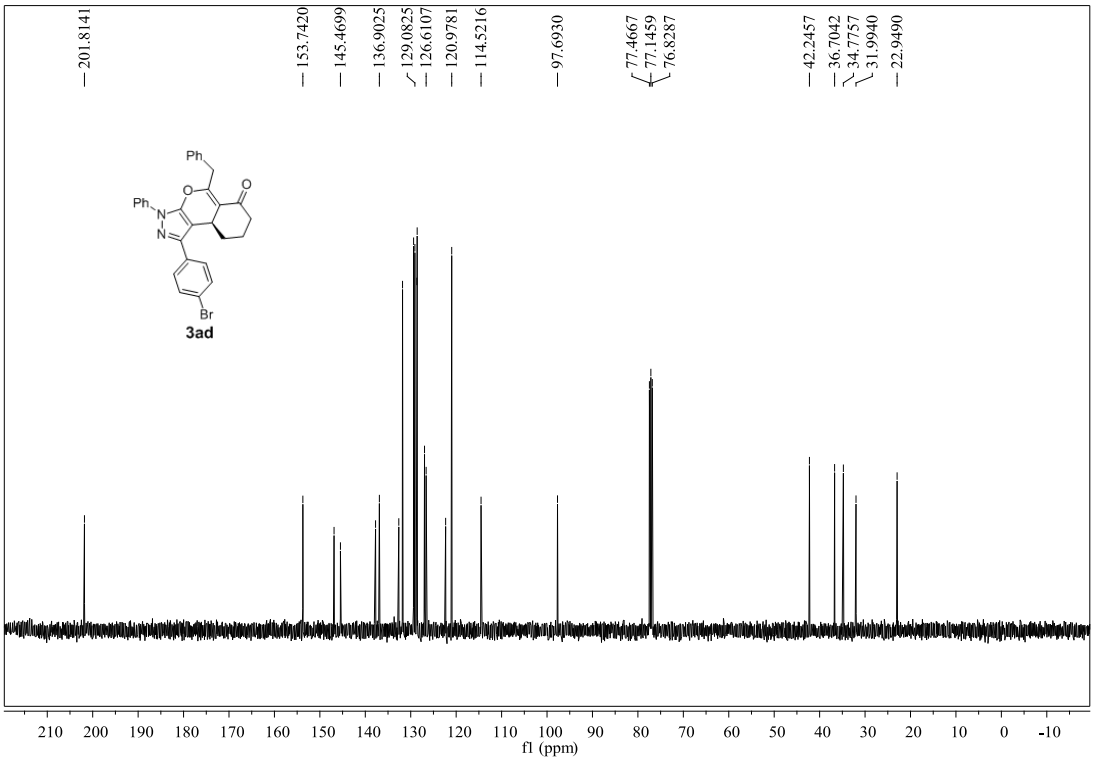
7.2661
7.2532
7.2485
7.2360
7.2209
4.0459
4.0368
4.0168
4.0077
3.9841
3.9475
3.9199
3.8835
2.6504
2.6228
2.4957
2.4691
2.4390
2.4123
2.1335
1.9924
1.9472
1.9102
1.8761
1.8365
1.6681
1.6208
1.5919
0.0003
Ph
O
Ph
N
N
O
Br
3ad
5.99
5.97
2.20
1.00
1.00
0.97
1.00
1.00
1.00
2.03
1.00
9.0 8.5 8.0 7.5 7.0 6.5 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 -0.5
f1 (ppm)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42.2457
36.7042
34.7757
31.9940
22.9490
Ph
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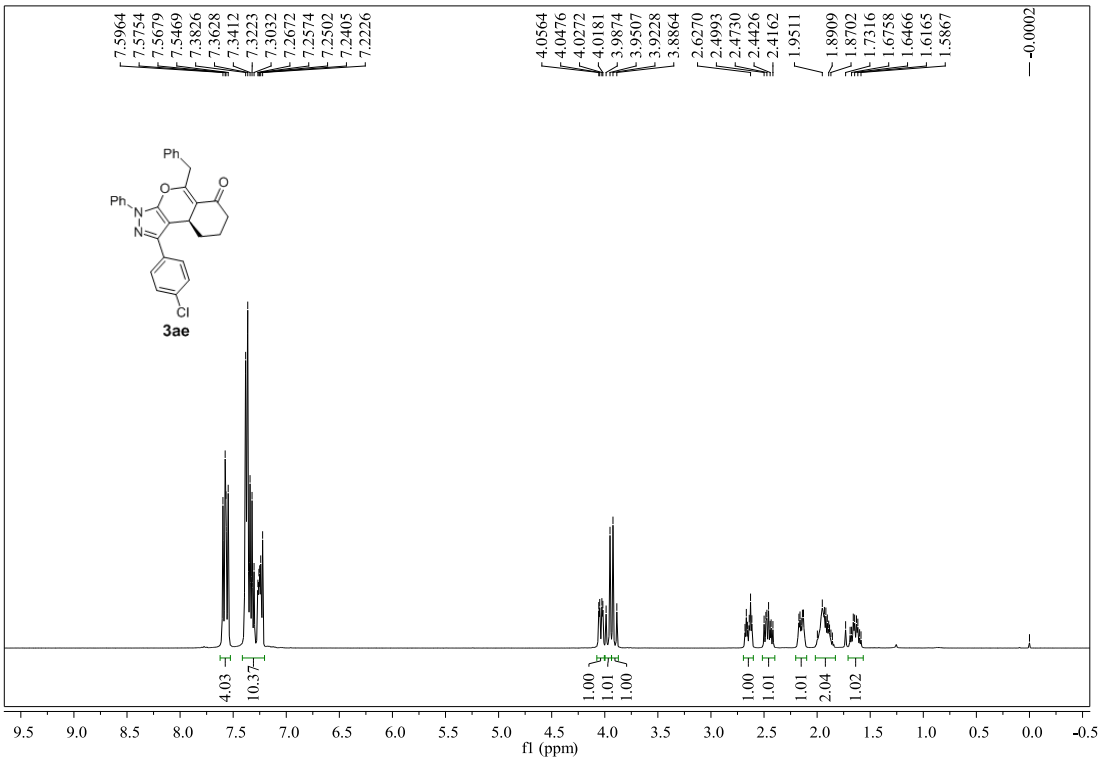
Ph
N
N
O
Br
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2574
7.2502
7.2405
7.2226
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4.0476
4.0272
4.0181
3.9874
3.9507
3.9228
3.8864
2.6270
2.4993
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2.4426
2.4162
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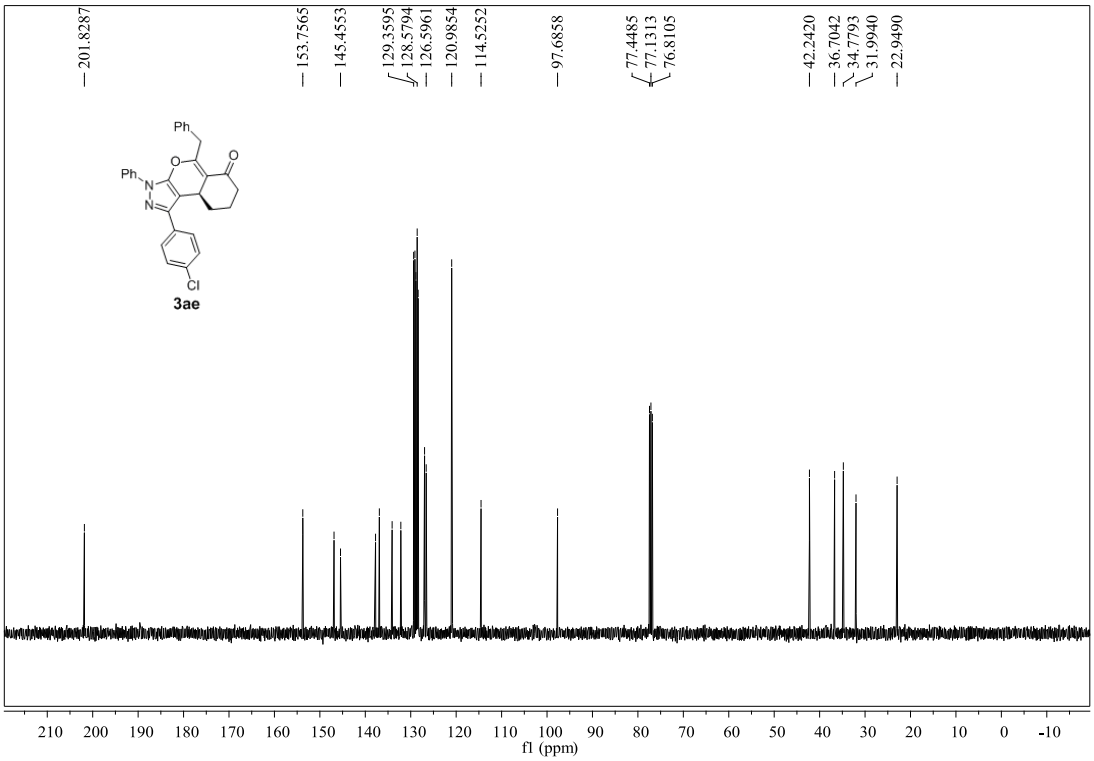
1.8909
1.8702
1.7316
1.6758
1.6466
1.6165
1.5867
-0.0002
Ph
Ph
N
N
O
O
Cl
3ae
4.03
10.37
1.00
1.01
1.00
1.00
1.01
1.01
2.04
1.02
f1 (ppm)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77.1313
76.8105
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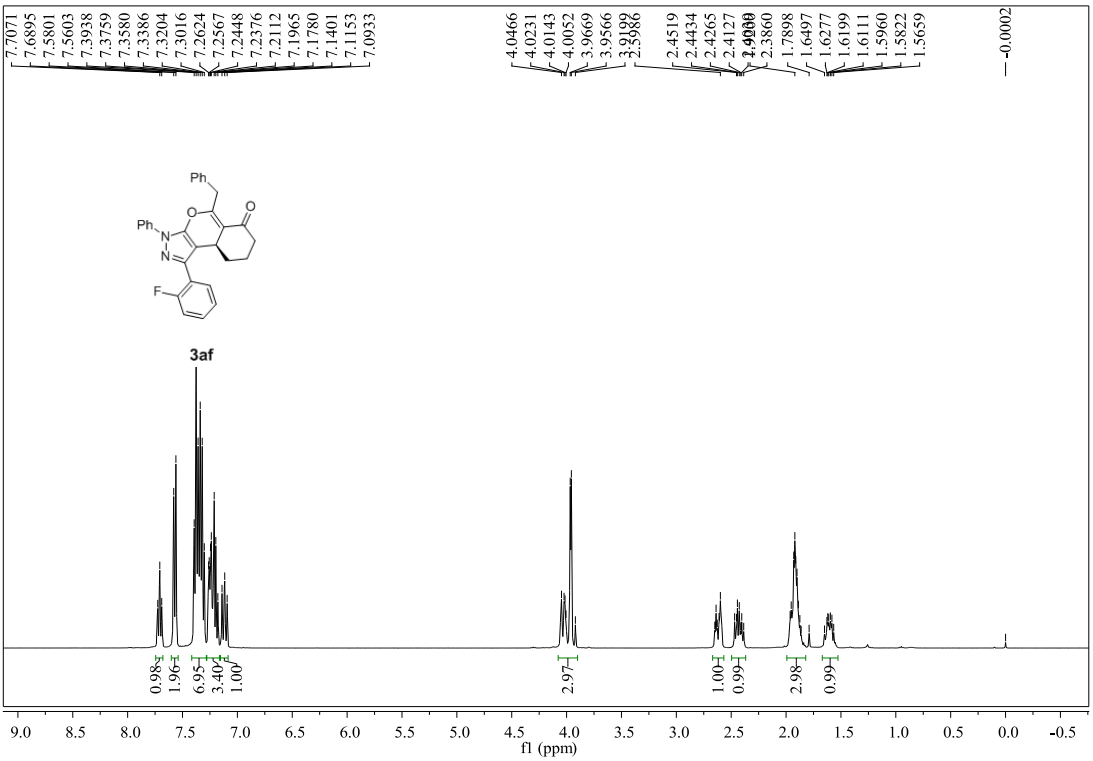
31.9940
22.9490
Ph
Ph
N
N
O
O
Cl
3ae
f1 (ppm)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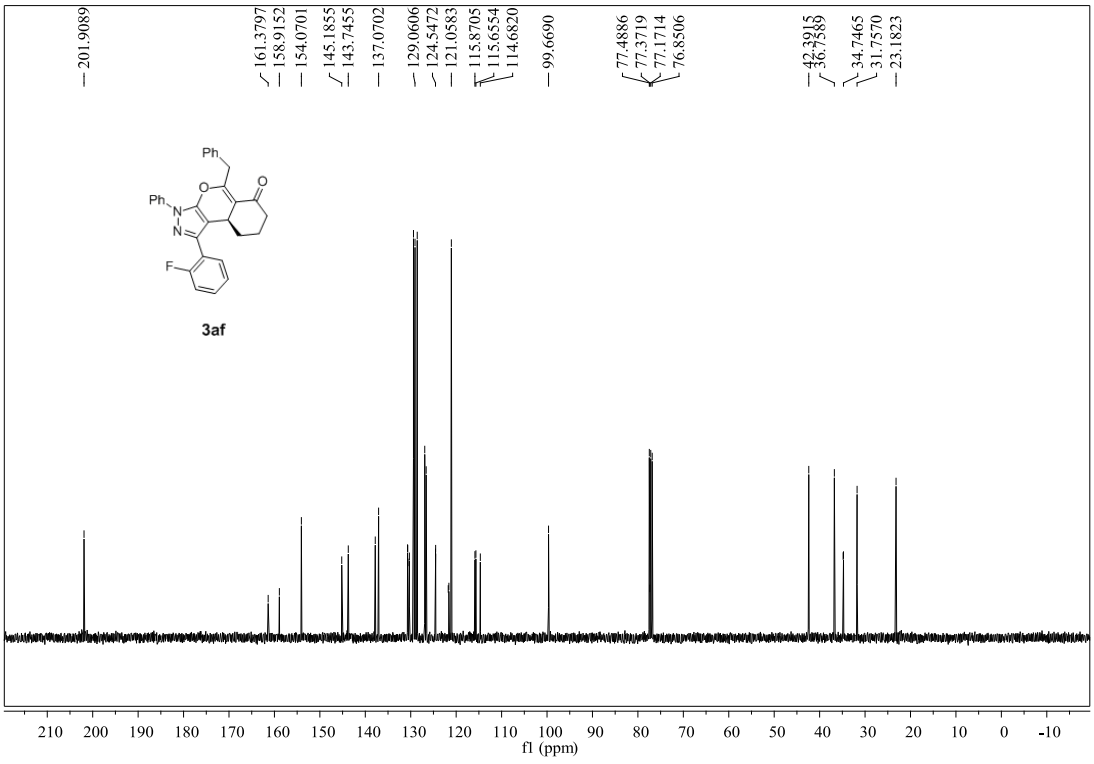
7.2624
7.2567
7.2448
7.2376
7.2112
7.1965
7.1780
7.1401
7.1153
7.0933
4.0466
4.0231
4.0143
4.0052
3.9669
3.9566
2.5986
2.4519
2.4434
2.4265
2.4127
2.3860
1.7898
1.6497
1.6277
1.6199
1.6111
1.5960
1.5822
1.5659
-0.0002
Ph
O
Ph
N
N
O
F
3af
0.98
1.96
6.95
3.40
1.00
2.97
1.00
0.99
2.98
0.99
9.0 8.5 8.0 7.5 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 -0.5
f1 (ppm)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137.0702
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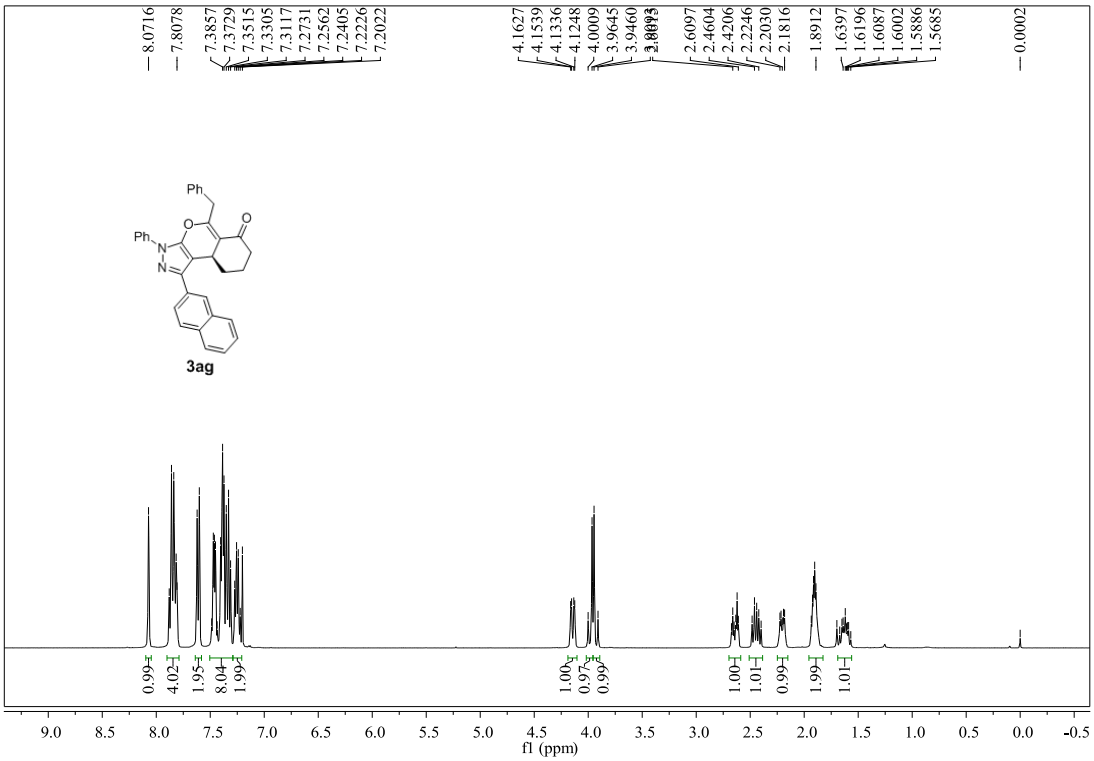
115.8705
115.6554
114.6820
99.6690
77.4886
77.3719
77.1714
76.8506
42.3915
36.7589
34.7465
31.7570
23.1823
Ph
O
Ph
N
N
O
F
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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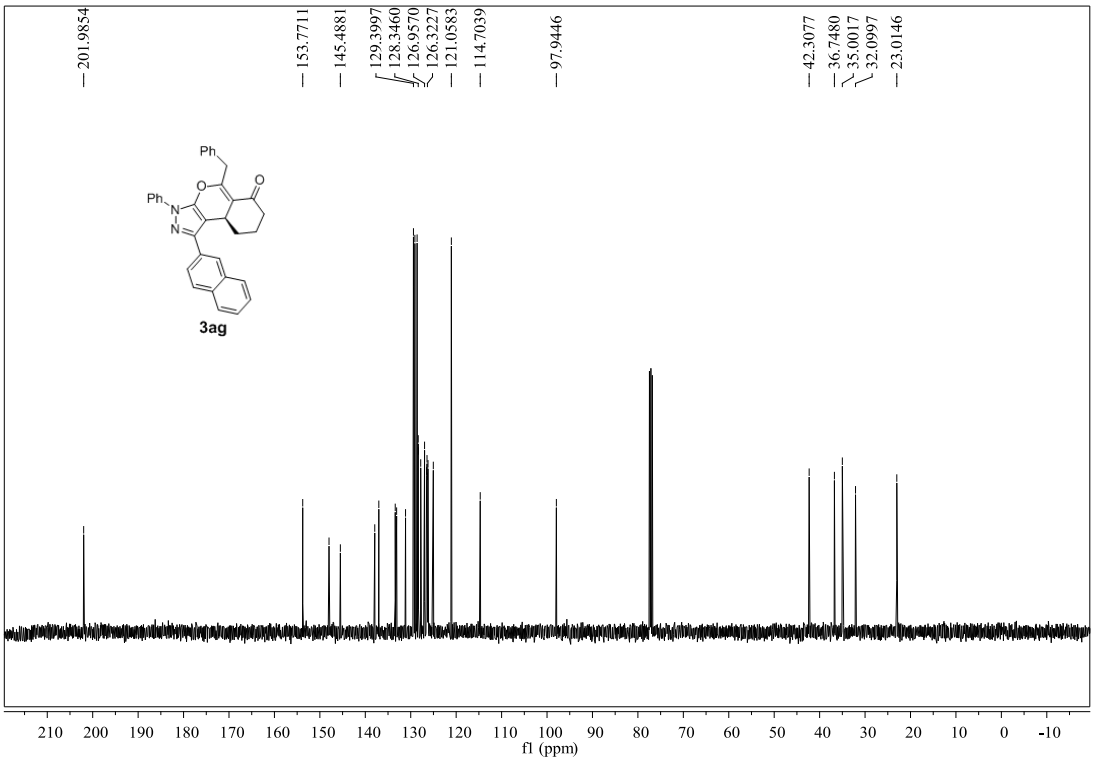
7.2562
7.2405
7.2226
7.2022
4.1627
4.1539
4.1336
4.1248
4.0009
3.9645
3.9460
2.6097
2.4604
2.4206
2.2246
2.2030
2.1816
1.8912
1.6397
1.6196
1.6087
1.6002
1.5886
1.5685
0.0002
Ph
Ph
N
N
O
O
3ag
0.99
4.02
1.95
8.04
1.99
1.00
0.97
0.99
1.00
1.01
0.99
1.99
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.3227
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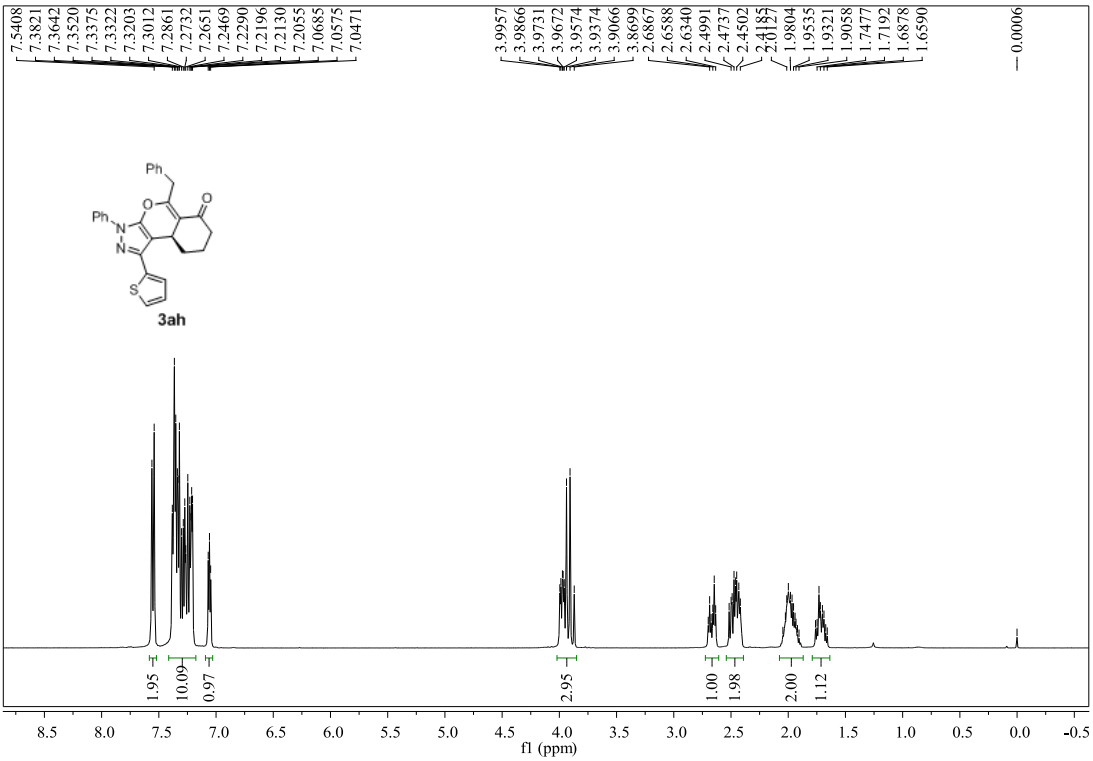
114.7039
97.9446
42.3077
36.7480
35.0017
32.0997
23.0146
Ph
Ph
N
N
O
O
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2651
7.2469
7.2290
7.2196
7.2130
7.2055
7.0685
7.0575
7.0471
3.9957
3.9866
3.9731
3.9672
3.9574
3.9374
3.9066
3.8699
2.6867
2.6588
2.6340
2.4991
2.4737
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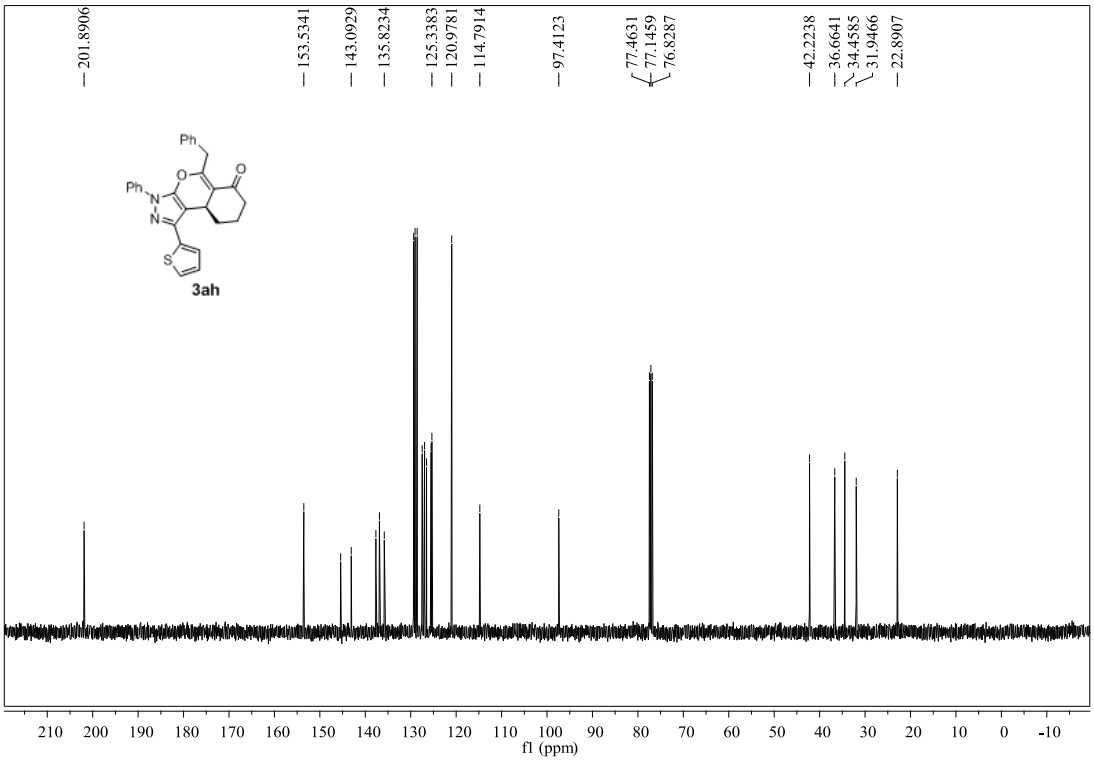
2.4185
2.0127
1.9804
1.9535
1.9321
1.9058
1.7477
1.7192
1.6878
1.6590
0.0006
Ph
O
Ph
N
N
S
3ah
1.95
10.09
0.97
2.95
1.00
1.98
2.00
1.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.1459
76.8287
42.2238
36.6641
34.4585
31.9466
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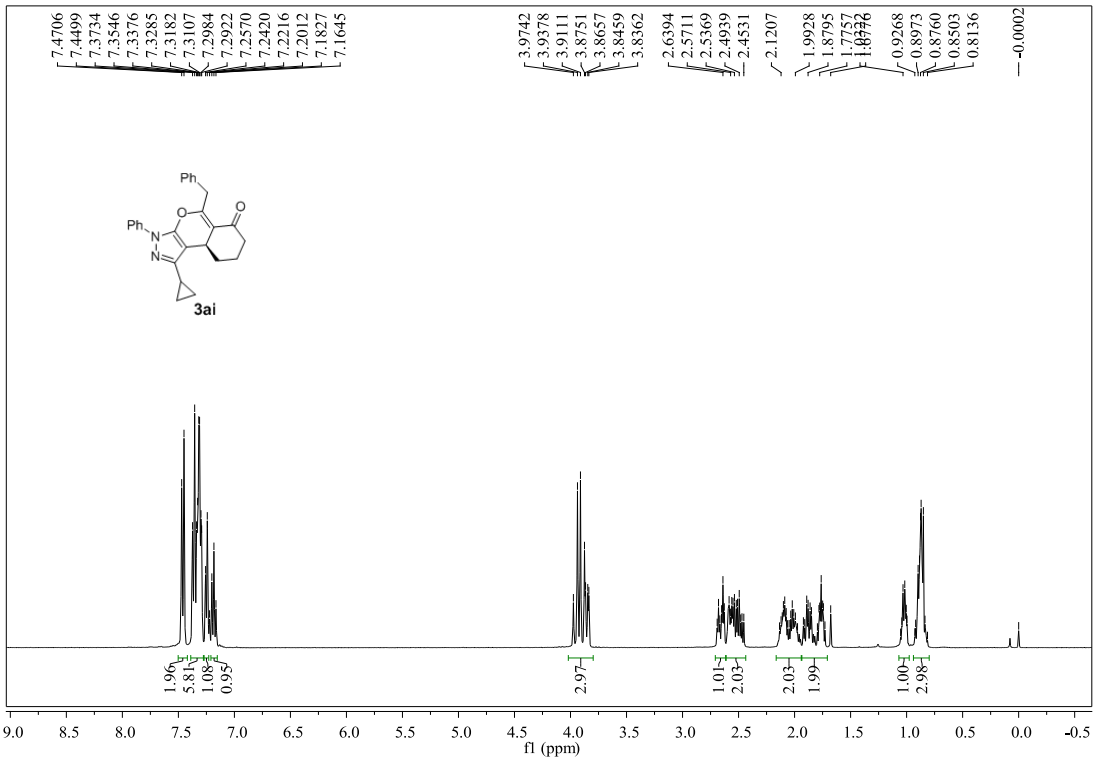
Ph
O
Ph
N
N
S
3ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3182
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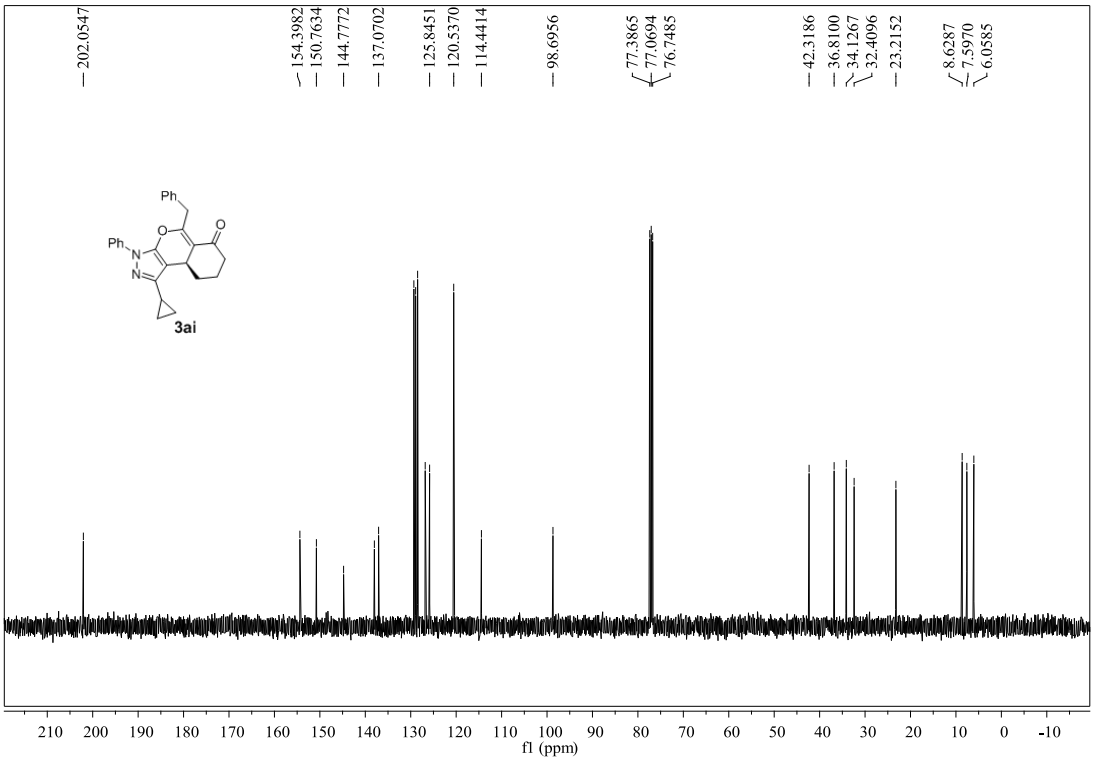
7.2922
7.2570
7.2420
7.2216
7.2012
7.1827
7.1645
3.9742
3.9378
3.9111
3.8751
3.8657
3.8459
3.8362
2.6394
2.5711
2.5369
2.4939
2.4531
2.1207
1.9928
1.8795
1.7757
1.0327
0.9268
0.8973
0.8760
0.8503
0.8136
-0.0002
Ph
O
Ph
N
N
O
3ai
1.96
5.81
1.08
0.95
2.97
1.01
2.03
2.03
1.99
1.00
2.98
9.0 8.5 8.0 7.5 7.0 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 -0.5
f1 (ppm)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76.7485
42.3186
36.8100
34.1267
32.4096
23.2152
8.6287
7.5970
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Ph
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Ph
N
N
O
3ai
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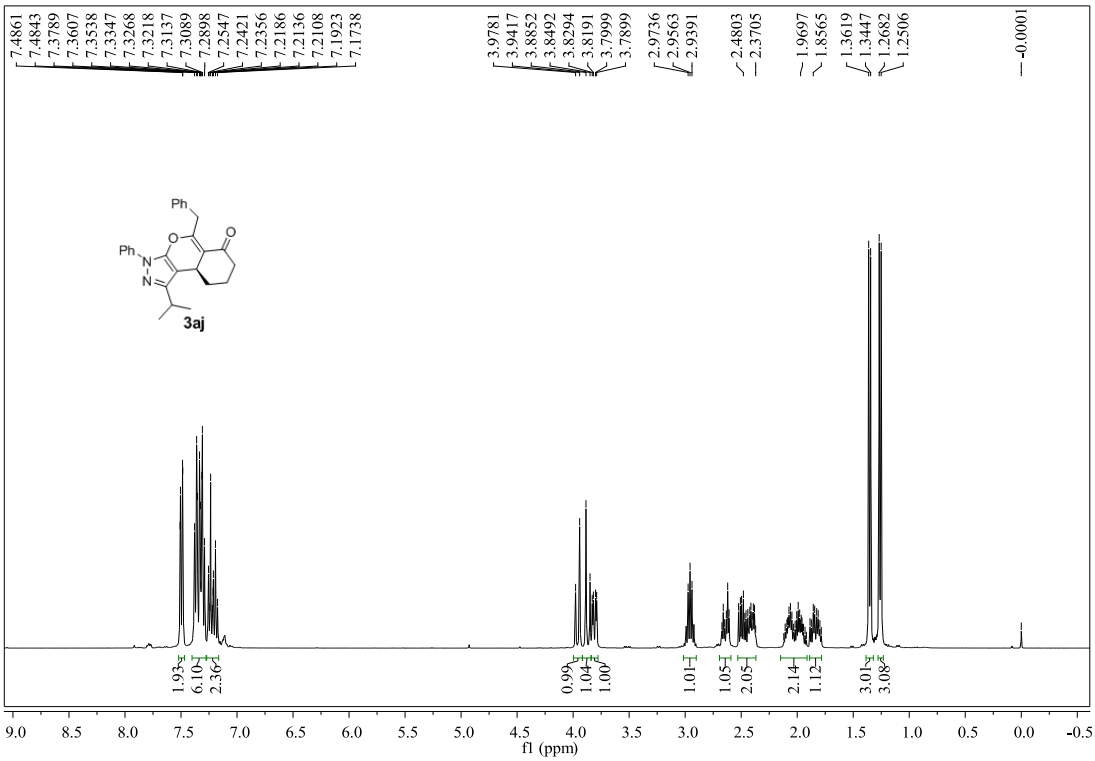
f1 (ppm)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7.2547
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7.2356
7.2186
7.2136
7.2108
7.1923
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3.9417
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3.8492
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3.8191
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2.9563
2.9391
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2.3705
1.9697
1.8565
1.3619
1.3447
1.2682
1.2506
-0.0001
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Ph
O
N
N
O
3aj
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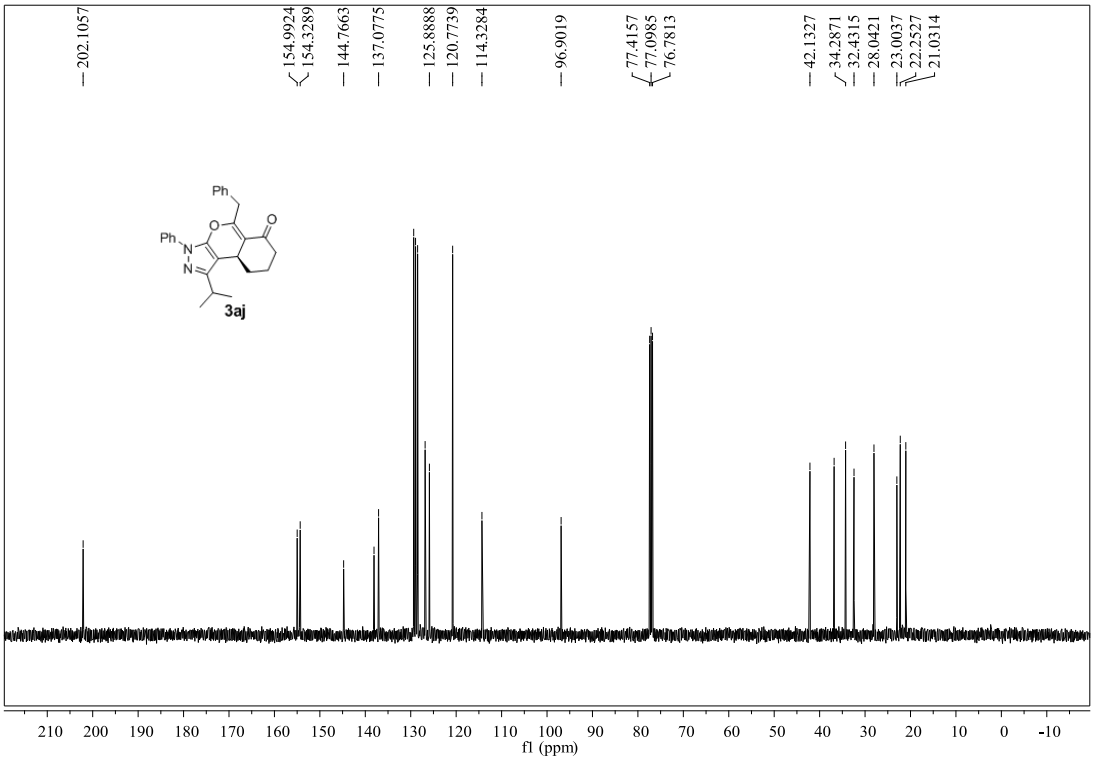
6.10
2.36
0.99
1.04
1.00
1.01
1.05
2.05
2.14
1.12
3.01
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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76.7813
42.1327
34.2871
32.4315
28.0421
23.0037
22.2527
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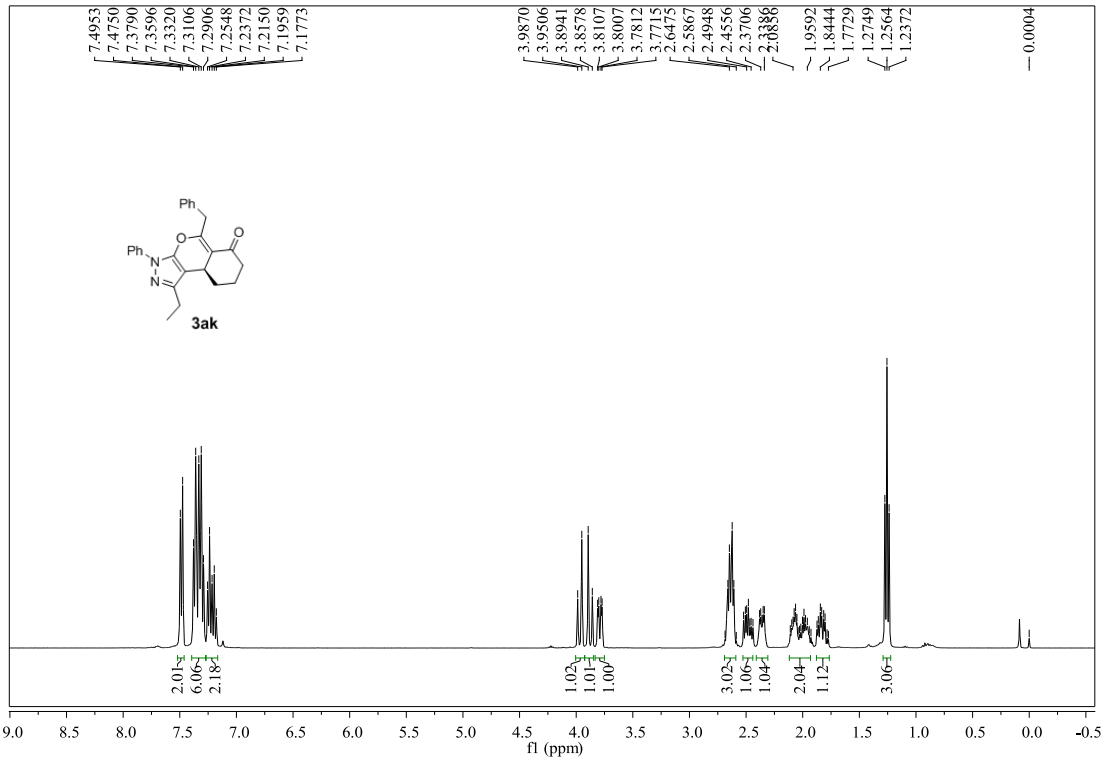
Ph
Ph
O
N
N
O
3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.8941
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Ph
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O
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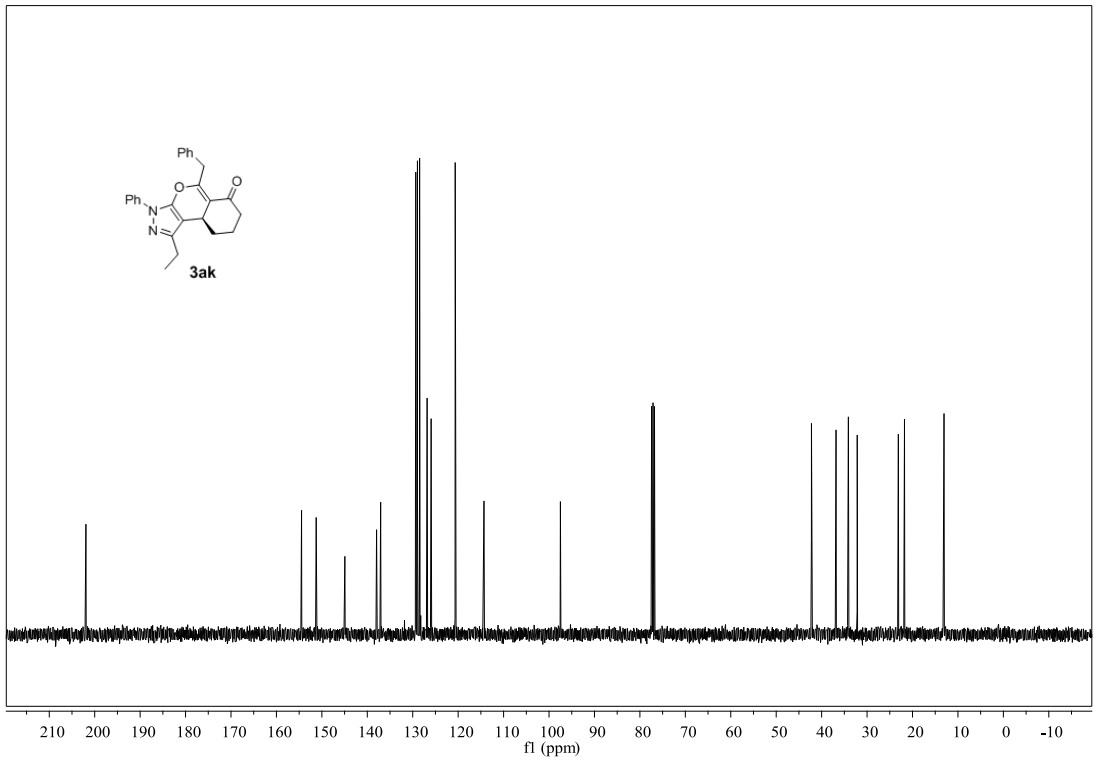
6.06
2.18
1.02
1.01
1.00
3.02
1.06
1.04
2.04
1.12
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Ph
Ph
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N
O
O
3ak
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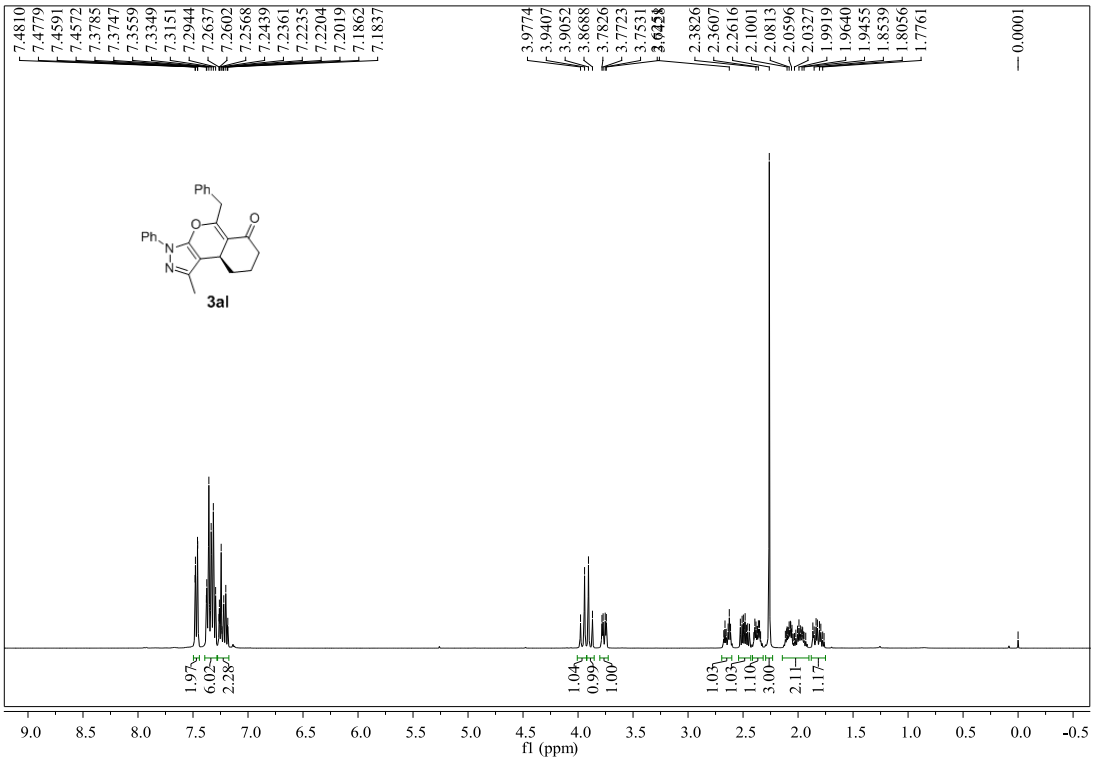
f1 (ppm)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7.2439
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7.2235
7.2204
7.2019
7.1862
7.1837
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3.9407
3.9052
3.8688
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3.7723
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2.0327
1.9919
1.9640
1.9455
1.8539
1.8056
1.7761
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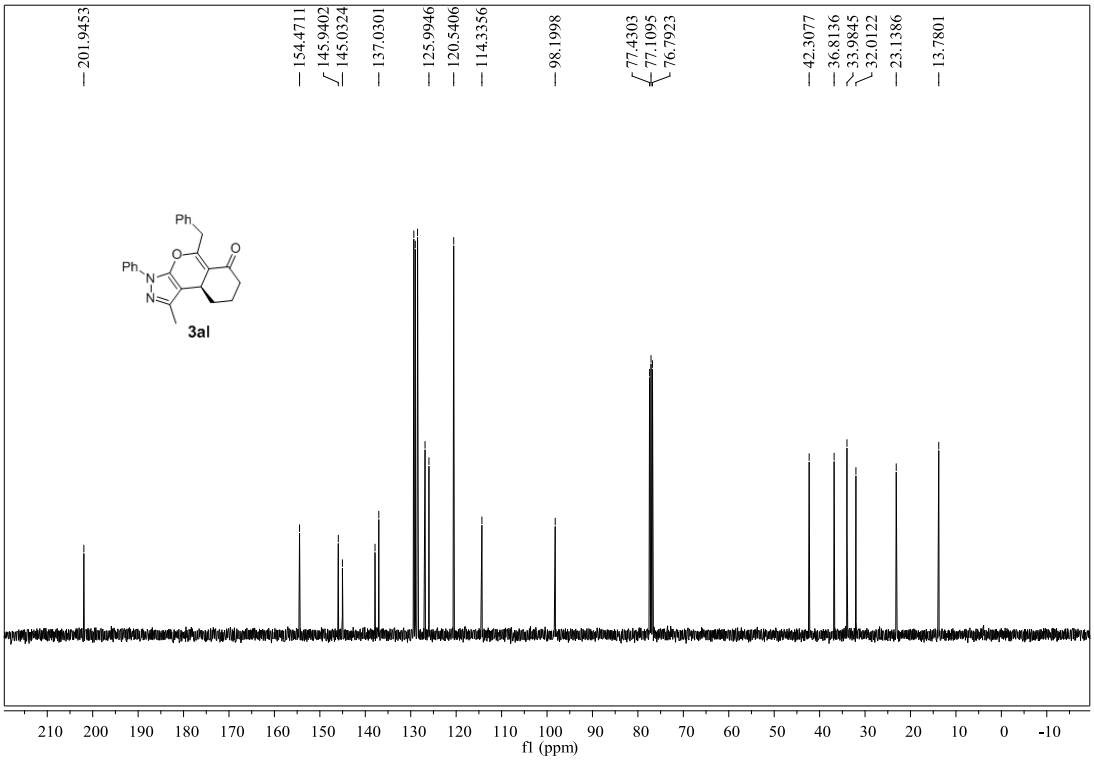
Ph
Ph
N
N
O
O
3al
1.97
6.02
2.28
1.04
0.99
1.00
1.03
1.03
1.10
3.00
2.11
1.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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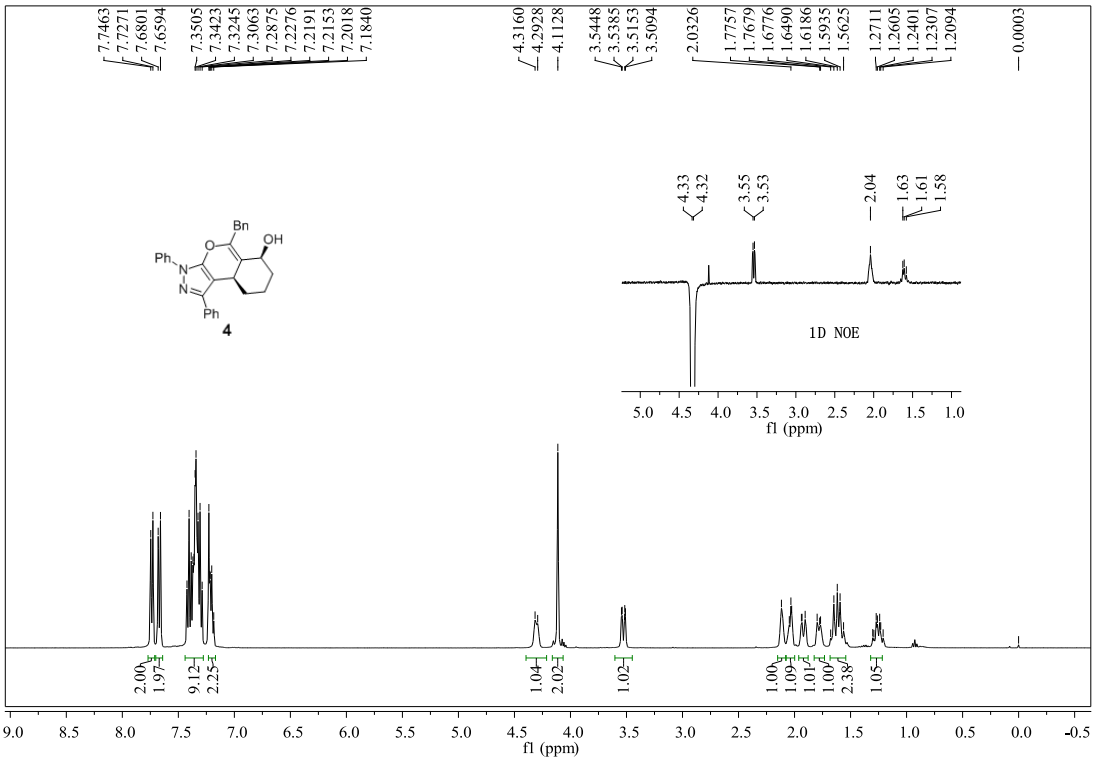
42.3077
36.8136
33.9845
32.0122
23.1386
13.7801
Ph
Ph
N
N
O
O
3al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.5153
3.5094
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1.7679
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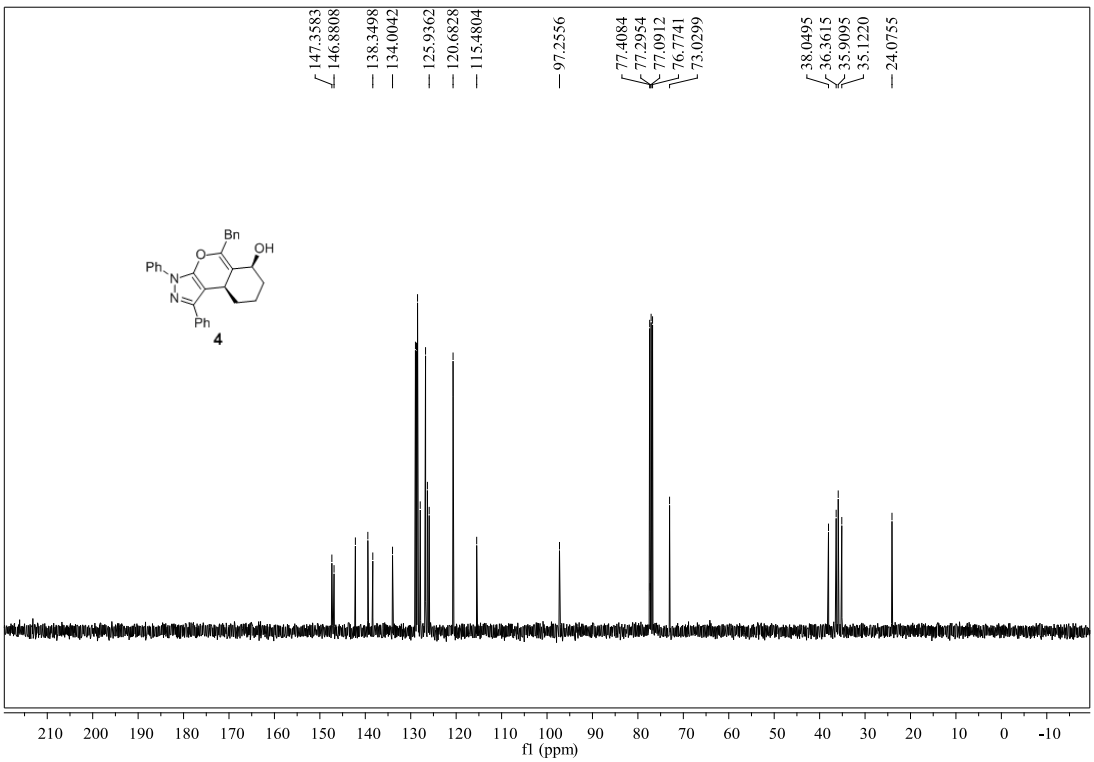
1.5935
1.5625
1.2711
1.2605
1.2401
1.2307
1.2094
0.0003
Bn
OH
Ph
N
N
O
Ph
4
4.33
4.32
3.55
3.53
2.04
1.63
1.61
1.58
1D NOE
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)
2.00
1.97
9.12
2.25
1.04
2.02
1.02
1.00
1.09
1.01
1.00
2.38
1.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.2954
77.0912
76.7741
73.0299
38.0495
36.3615
35.9095
35.1220
24.0755
Bn
OH
Ph
N
N
O
Ph
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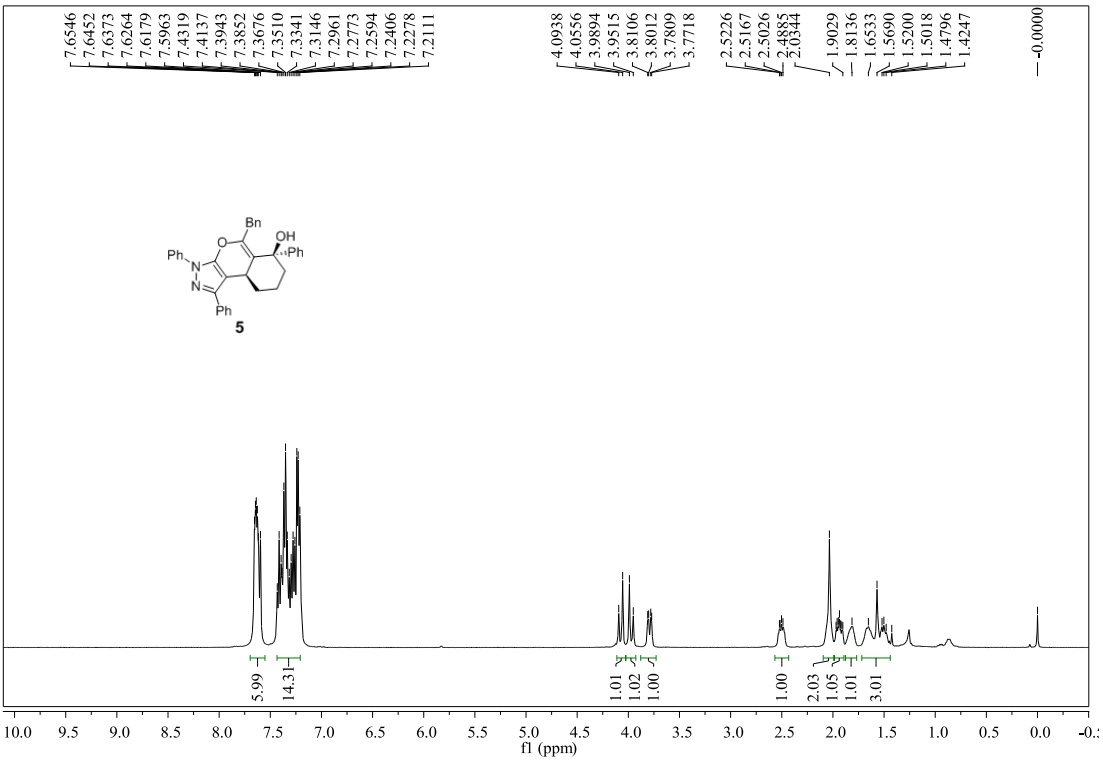
f1 (ppm)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7.2406
7.2278
7.2111
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4.0556
3.9894
3.9515
3.8106
3.8012
3.7809
3.7718
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2.5167
2.5026
2.4885
2.0344
1.9029
1.8136
1.6533
1.5690
1.5200
1.5018
1.4796
1.4247
-0.0000
Bn
OH
Ph
Ph
N
N
O
Ph
5
5.99
14.31
1.01
1.02
1.00
1.00
2.03
1.05
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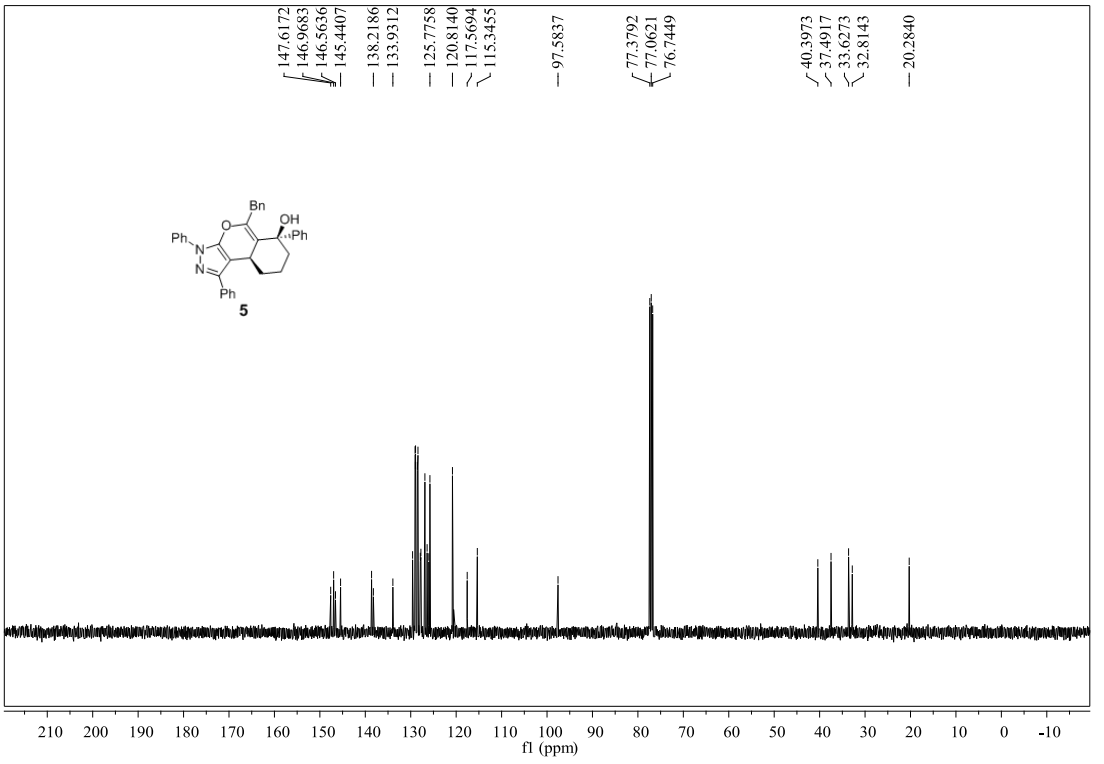
3.01
fl (ppm)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146.5636
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125.7758
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77.3792
77.0621
76.7449
40.3973
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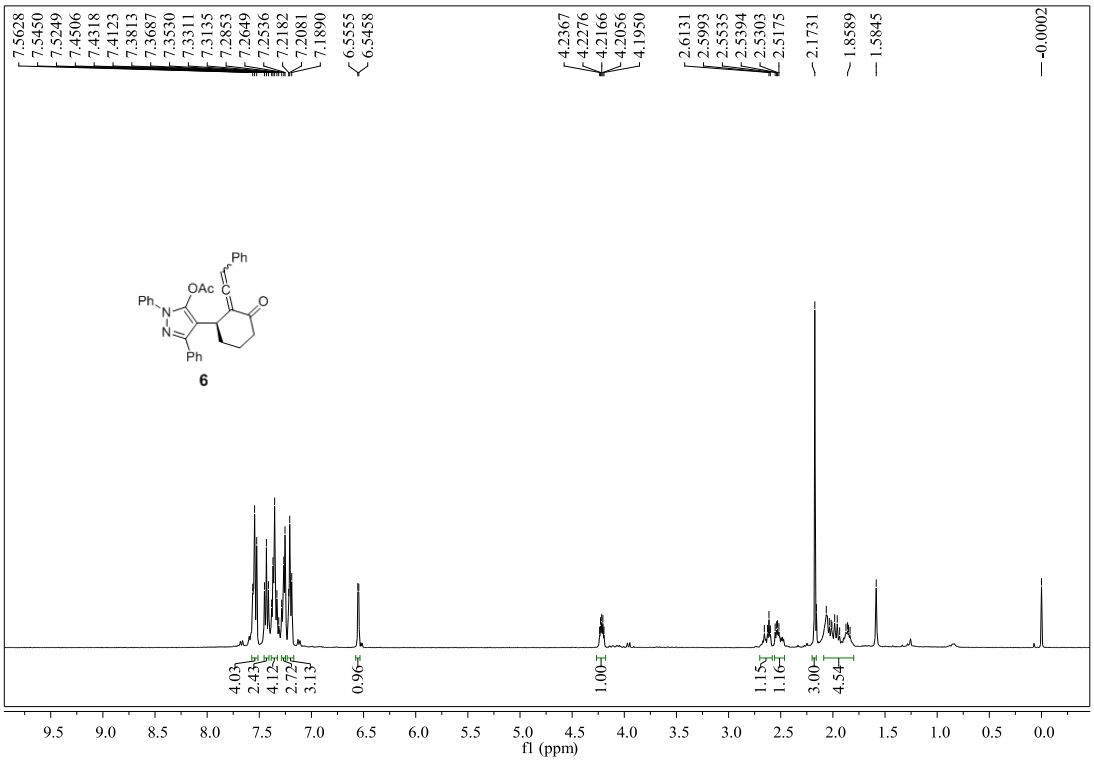
20.2840
Bn
OH
Ph
Ph
N
N
O
Ph
5
fl (ppm)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7.4318
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7.3530
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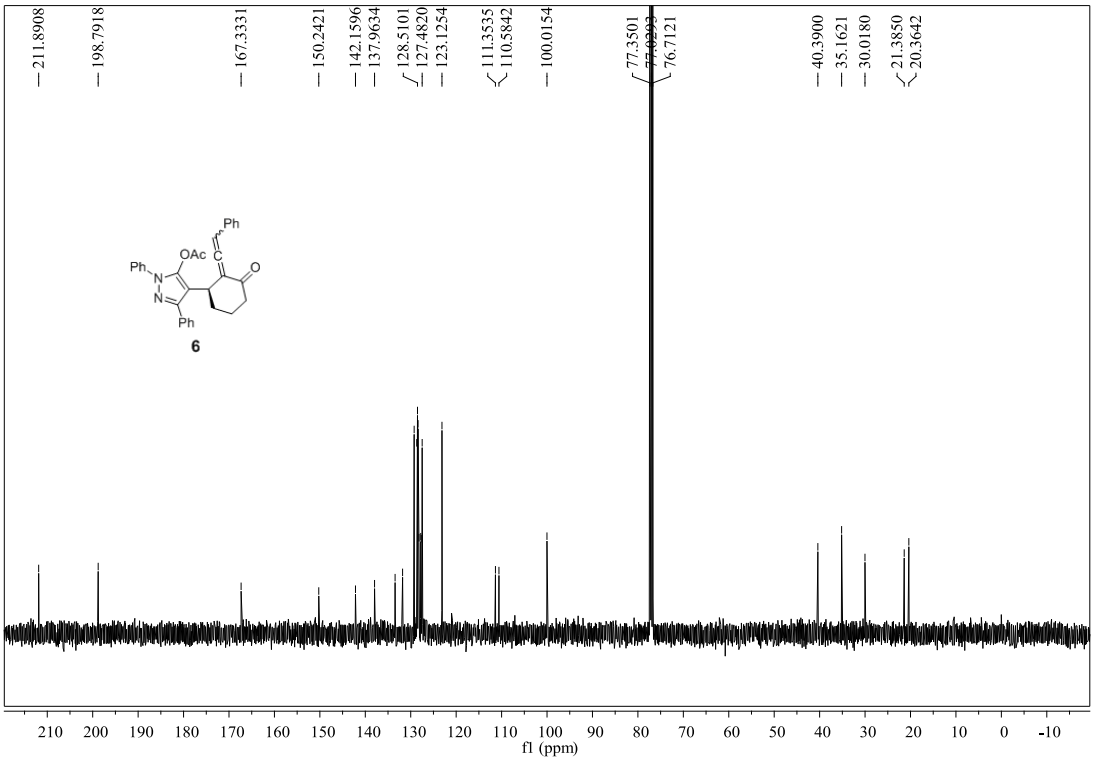
7.3135
7.2853
7.2649
7.2536
7.2182
7.2081
7.1890
6.5555
6.5458
4.2367
4.2276
4.2166
4.2056
4.1950
2.6131
2.5993
2.5535
2.5394
2.5303
2.5175
2.1731
1.8589
1.5845
0.0002
4.03
2.43
4.12
2.72
3.13
0.96
1.00
1.15
1.16
3.00
4.54
Ph
OAc
Ph
N
N
Ph
O
6
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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100.0154
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76.7121
40.3900
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30.0180
21.3850
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Ph
OAc
Ph
N
N
Ph
O
6
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)