Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Enantioselective gold-catalyzed intermolecular [2+2]-cycloadditions of 3-styrylindoles with *N*-allenyl oxazolidinone

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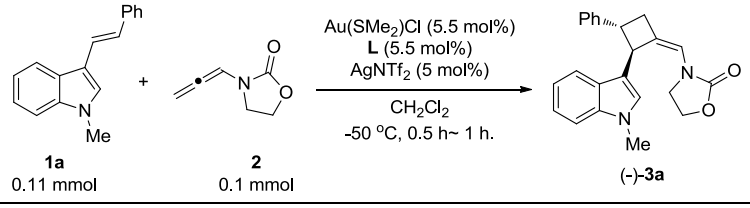
Table Contents

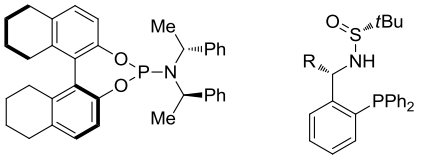
1. General Information

^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.00 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Dichloromethane were freshly distilled from CaH_2; THF was freshly distilled from sodium metal prior to use; AgOTf, $AgNTf_2$, $AgBF_4$, and $AgCH_3O_3S$ were purchased from Alfa-Aesar Company and used directly. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. The ee was recorded using UltiMate 3000 HPLC from Dionex Company.

2. Optimization of conditions

a. Screening of ligands.



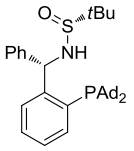


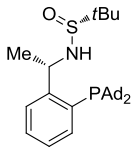
R = Ph, (*S*, R_S)-**M1**, -12% ee, 77% yield

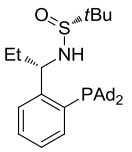
R = 3,5 -di*tert*-butyl-4-methoxyl, (*S*, R_S)-**M2**, -11% ee, 76% yield

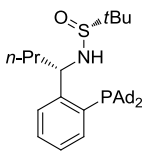
R = 1-nap, (*S*, R_S)-**M3**, -32% ee, 79% yield

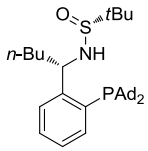
R = Me, (*S*, R_S)-**M4**, 9% ee, 73% yield

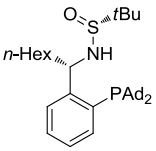

(*S*, R_S)-**X1**
-19% ee, 87% yield

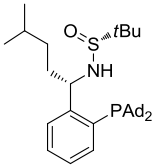

(*S*, R_S)-**X2**
74% ee, 87% yield

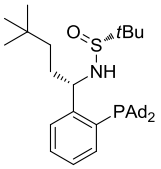

(*S*, R_S)-**X3**
82% ee, 86% yield


(*S*, R_S)-**X4**
83% ee, 85% yield


(*S*, R_S)-**X5**
85% ee, 88% yield

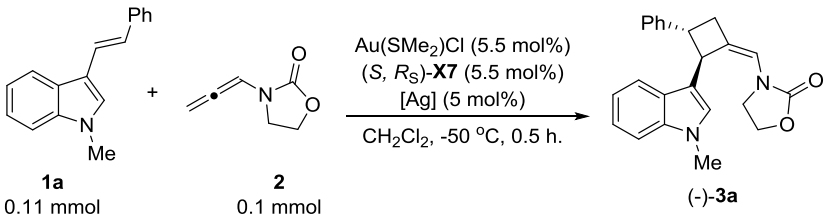

(*S*, R_S)-**X6**
83% ee, 91% yield


(*S*, R_S)-**X7**
88% ee, 92% yield


(*S*, R_S)-**X8**
70% ee, 89% yield

The reactions were carried out in 1.5 mL CH_2Cl_2. Yields of (-)-**3a** were NMR yields, and *ee* values were Determined by chiral HPLC.

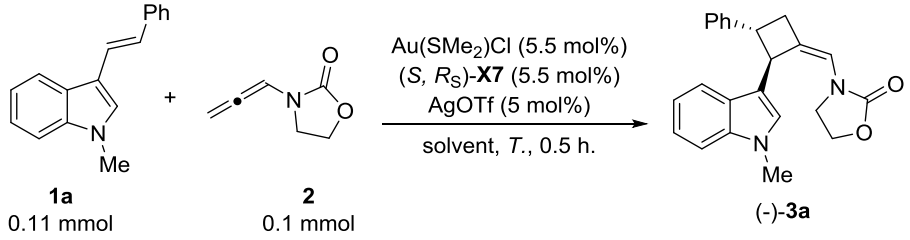
b. Screening of silver salt[a].



Entry	Silver salt	Ee (%)[b]	Yield (%)[c]
1	$AgNTf_2$	88	92
2	$AgC_4F_7O_2$	76	88
3	$AgBF_4$	90	90
4	$AgCH_3O_3S$	78	84
5	**AgOTf**	**91**	**91**
6	$AgSbF_6$	86	89

[a]The reactions were carried out in 1.5 mL CH_2Cl_2. [b]Determined by chiral HPLC. [c]NMR yield.

c. Further Optimization.[a]

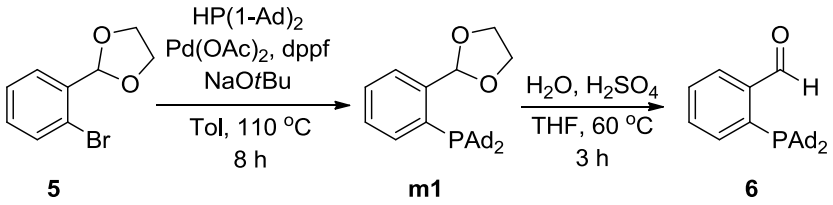


Entry	solvent	*T.* (°C)	Ee (%)[b]	Yield (%)[c]
1	CH_2Cl_2	-50	91	91
2	DCE	-40	78	91
3	$CHCl_3$	-50	87	91
4	CH_2Cl_2	-60	92	90
5	CH_2Cl_2	-70	92	92
6	**CH_2Cl_2**	**-78**	**94**	**92**

[a]The reactions were carried out in 1.5 mL solvent. [b]Determined by chiral HPLC. [c]NMR yield.

3. Synbthesis of Ligands (*S, R*$_s$)-X1-X8

(1) Synthesis of 6.

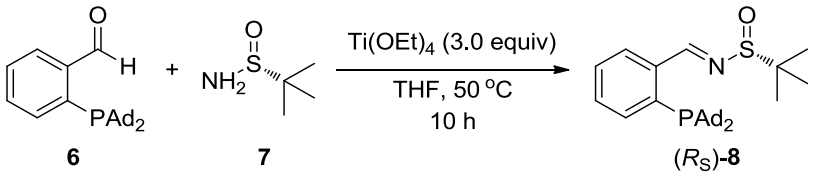


To a solution of 15.1 g HP(1-Ad)$_2$ (50 mmol) in toluene (150 mL), 9 mL 2-(2-Brdmophenyl)-1,3-dioxolane (60 mmol, 1.2 equiv), 600 mg Pd(OAc)$_2$ (2.5 mmol, 5 mol%), 1.65 g dppf (3.0 mmol, 6 mol%) and 5.75 g NaO*t*Bu (60 mmol, 1.0 equiv) was added. The reaction was stirred at 110 °C for 8 h, and then was cooled to ambient temperature. The solid was filtered off by celite and washed with CH_2Cl_2. The filtrate was concentrated in vacuo. The residue was purified by recrystallization and **m1** was obtained in 80% yield: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.70-7.68 (m, 1H), 7.44-7.40 (m, 1H), 7.35-7.31 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.18-4.03 (m, 4H), 2.01-1.98 (m, 6H), 1.89-1.86 (m, 12H), 1.66 (s, 12H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.50. ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (d, J_{CP} = 22.0 Hz), 135.9 (d, J_{CP} = 3.0 Hz), 133.8 (d, J_{CP} = 28.0 Hz), 129.2, 127.1, 126.6 (d, J_{CP} = 7.0 Hz),

101.3 (d, J_{CP} = 38.0 Hz), 65.5, 41.8 (d, J_{CP} = 13.0 Hz), 36.84 (d, J_{CP} = 22.0 Hz), 36.82, 28.7 (d, J_{CP} = 7.0 Hz). MS (70 eV): m/z (%): 376 (M^+, 2.07), 105 (100). HRMS calcd for $C_{29}H_{39}N_2O_2P$: 376.1587, found: 376.1585.

To a solution of 4.5 g **m1** (10 mmol) in 90 mL THF, 20 mL H_2O and 3 mL H_2SO_4 was added. The reaction mixture was heated at 60 ^oC for 3 h, and then was cooled to room temperature. The reaction was quenched by saturated $NaHCO_3$ solution and extracted with EtOAc for 2 times. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (hexane : EtOAc = 20:1) to get **6** as yellow solid (89% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 11.24 (d, *J* = 8.8 Hz, 1H), 7.98-7.95 (m, 1H), 7.90-7.88 (m, 1H), 7.57-7.52 (m, 1H), 7.51-7.47 (m, 1H), 1.98-1.87 (m, 18H), 1.67 (s, 12H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.92. ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6 (d, J_{CP} = 41.0 Hz), 143.6 (d, J_{CP} = 17.0 Hz), 138.4 (d, J_{CP} = 35.0 Hz), 136.8 (d, J_{CP} = 2.0 Hz), 131.4, 129.1-129.0 (m), 127.5 (d, J_{CP} = 6.0 Hz), 41.9 (d, J_{CP} = 12.0 Hz), 37.0 (d, J_{CP} = 22.0 Hz), 36.8, 28.7 (d, J_{CP} = 8.0 Hz). MS (70 eV): m/z (%): 406 (M^+, 40.68), 135 (100). HRMS calcd for $C_{27}H_{35}OP$: 406.2426, found: 406.2423.

(2) Synthesis of (R_s)-8.

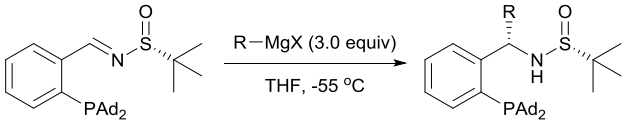


6 **7** (R_S)-**8**

The sulfinyl imine (R_s)-**8** was prepared according to the modified procedure of literature.[1] To a solution of 2.03 g *o*-phosphino aldehyde **6** (5 mmol) in 20 mL THF was added 909 mg (*R*)-(+)-2-methyl-2-propanesulfinamide **7** (7.5 mmol, 1.5 equiv) and 3.1 mL $Ti(OEt)_4$ (15 mmol, 3.0 equiv). The reaction was heated at 50 ^oC for 10 h. When completed, the reaction mixture was quenched by saturated $NaHCO_3$ solution, filtered by celite, and washed with ethyl acetate for twice. The filtrate was extracted with EtOAc, dried over Na_2SO_4, and concentrated in vacuo. Further purification was

accomplished by flash chromatography (hexane : EtOAc = 10:1) to isolate (R_S)-**8** as yellow solid (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (d, *J* = 7.6 Hz, 1H), 8.09-8.06 (m, 1H), 7.87-7.85 (m, 1H), 7.46-7.44 (m, 2H), 1.93-1.87 (m, 18H), 1.70-1.60 (m, 12H), 1.27 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.56. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (d, J_{CP} = 38.0 Hz), 142.1 (d, J_{CP} = 22.0 Hz), 137.7 (d, J_{CP} = 33.0 Hz), 136.7 (d, J_{CP} = 2.0 Hz), 129.6, 128.9, 128.0 (d, J_{CP} = 6.0 Hz), 57.8, 41.8 (d, J_{CP} = 4.0 Hz), 41.6 (d, J_{CP} = 4.0 Hz), 37.2-37.1 (m), 36.9 (d, J_{CP} = 2.0 Hz), 36.8, 28.7 (d, J_{CP} = 9.0 Hz), 22.7. HRMS(ESI) calcd for $C_{31}H_{45}NOPS$ [M+H$^+$]: 510.2954, found: 510.3013. $[\alpha]_D^{20}$ = -155.1 (*c* = 0.3, $CHCl_3$).

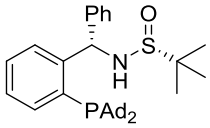
(3) Synthesis of (*S, R*$_S$)-X1-X8.



(R_S)-**8** (S, R_S)-**X1-X8**

General procedure: To a solution of 510 mg (R_S)-**8** (1.0 mmol) in 10 mL CH_2Cl_2 at -55 °C was added Grignard reagent (15 mmol, 3.0 equiv) in THF. The mixture was stirred at - 55 °C for 4-6 h and then was warmed to room temperature with stirring overnight. When completed, the reaction mixture was quenched by the addition of saturated NH_4Cl aolution and diluted with ethyl acetate. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography (hexane : CH_2Cl_2: EtOAc = 6:2:1) to isolated (S, R_S)-**X1-X8** as yellow solid.

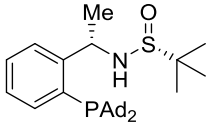
(1) Synthesis of (*S,R*$_S$)-**X1**



(*S,R*$_S$)-**X1**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.46-7.40 (m, 3H), 7.38-7.23 (m, 3H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.07-7.03 (m, 1H), 3.65 (d, *J* = 3.2 Hz, 1H), 2.06-2.00 (m, 3H), 1.95-1.83 (m, 6H), 1.70-1.48 (m, 21H), 1.22 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.47. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (d, J_{CP} = 24.0 Hz), 142.8, 136.7 (d, J_{CP} = 2.0 Hz), 133.6 (d, J_{CP} = 29.0 Hz), 129.3 (d, J_{CP} = 2.0 Hz), 128.7, 128.2, 127.9 (d, J_{CP} = 6.0 Hz), 127.2, 125.4, 59.6 (d, J_{CP} = 34.0 Hz), 55.8, 41.8 (d, J_{CP} = 13.0 Hz), 41.4 (d, J_{CP} = 13.0 Hz), 37.4 (d, J_{CP} = 23.0 Hz), 36.8 (d, J_{CP} = 15.0 Hz), 36.5, 28.7 (d, J_{CP} = 9.0 Hz), 22.7. HRMS(ESI) calcd for $C_{37}H_{50}NOPS$ [M+H$^+$]: 588.3423, found: 588.3497. $[\alpha]_D^{20}$ = -34.2 (*c* = 0.3, $CHCl_3$).

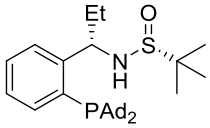
(2) Synthesis of (*S,R*$_S$)-**X2**



(*S,R*$_S$)-**X2**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.47-7.43 (m, 1H), 7.37 (t, *J* = 7.8 Hz , 1H), 7.23-7.20 (m, 1H), 6.00-5.91 (m, 1H), 3.36 (d, *J* = 5.2 Hz, 1H), 2.04-1.84 (m, 18H), 1.68-1.66 (m, 12H), 1.51 (d, *J* = 6.8 Hz, 3H), 1.16 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.87. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (d, *J* = 25.0 Hz), 136.2, 132.1 (d, *J* = 26.0 Hz), 129.2, 126.4 (d, *J* = 5.0 Hz), 125.1, 55.5, 52.5 (d, *J* = 35.0 Hz), 42.0 (d, *J* = 13.0 Hz), 41.7 (d, *J* = 12.0 Hz), 37.2 (d, *J* = 22.4 Hz), 36.9 (d, *J* = 4.0 Hz), 36.6, 28.8 (d, *J* = 4.0 Hz), 28.7 (d, *J* = 4.0 Hz), 25.7, 22.6. HRMS(ESI) calcd for $C_{32}H_{48}NOPS$ [M+H$^+$]: 526.3267, found: 526.3272. $[\alpha]_D^{20}$ = -80.3 (*c* = 0.3, $CHCl_3$).

(3) Synthesis of (*S,R*$_S$)-**X3**

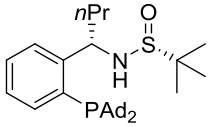


(*S,R*$_S$)-**X3**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8 Hz, 1H), 7.40-7.33 (m, 2H), 7.22-7.18 (m, 1H), 5.76 (s, 1H), 3.45 (s, 1H), 2.00-1.80 (m, 20H), 1.67 (d, *J* = 13.2 Hz, 12H), 1.14 (s, 9H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.13. ^{13}C

NMR (100 MHz, $CDCl_3$) δ 151.7 (d, J_{CP} = 25.0 Hz), 136.4 (m), 132.4 (d, J_{CP} = 27.0 Hz), 128.9, 126.8 (m), 124.9, 55.6, 42.2 (d, J_{CP} = 13.0 Hz), 41.6 (d, J_{CP} = 12.0 Hz), 41.2, 37.3 (d, J_{CP} = 23.0 Hz), 36.9, 36.9 (d, J_{CP} = 24.0 Hz), 28.8, (d, J_{CP} = 9.0 Hz), 28.7 (d, J_{CP} = 9.0 Hz), 22.6, 19.5, 14.2. HRMS(ESI) calcd for $C_{33}H_{50}NOPS$ [M+H$^+$]: 540.3423, found: 540.3439. $[\alpha]_D^{20}$ = -79.2 (*c* = 0.3, $CHCl_3$).

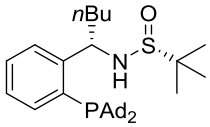
(4) Synthesis of (*S*,R_S)-**X4**



(*S*,R_S)-**X4**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.39-7.33 (m, 2H), 7.23-7.18 (m, 1H), 5.74-5.67 (m, 1H), 3.3 (d, *J* = 5.2 Hz, 1H), 2.01-1.82 (m, 22H), 1.61 (d, *J* = 12.4 Hz, 12H), 1.14 (s, 9H), 0.96-0.93 (t, *J* = 7.6 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.27. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2 (d, J_{CP} = 25.0 Hz), 136.3 (d, J_{CP} = 2.0 Hz), 132.6 (d, J_{CP} = 26.0 Hz), 128.9, 126.8 (d, J_{CP} = 6.0 Hz), 124.9, 58.1 (d, J_{CP} = 32.0 Hz), 55.6, 42.2 (d, J_{CP} = 13.0 Hz), 41.7 (d, J_{CP} = 12.0 Hz), 37.3 (d, J_{CP} = 13.0 Hz), 36.93 (d, J_{CP} = 24.0 Hz), 36.90, 31.8, 28.84 (d, J_{CP} = 8.0 Hz), 28.76 (d, J_{CP} = 9.0 Hz), 22.6, 10.8. HRMS(ESI) calcd for $C_{34}H_{52}NOPS$ [M+H$^+$]: 554.3589, found: 554.3580. $[\alpha]_D^{20}$ = -41.4 (*c* = 0.3, $CHCl_3$).

(5) Synthesis of (*S*,R_S)-**X5**

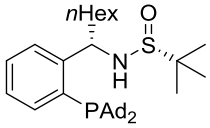


(*S*,R_S)-**X5**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.40-7.33 (m, 2H), 7.23-7.18 (m, 1H), 5.75 (s, 1H), 3.43 (s, 1H), 2.02-1.82 (m, 22H), 1.77 (s, 1H), 1.69-1.64 (m, 12H), 1.44-1.40 (m, 1H), 1.14 (s, 9H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.19. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (d, *J* = 25.0 Hz), 136.4, 132.4 (d, *J* = 26.0 Hz), 128.9, 126.7, 124.9, 55.6, 42.2 (d, *J* = 13.0 Hz), 41.6 (d, *J* = 12.0 Hz), 38.8, 37.3 (d, J = 23.0 Hz), 36.90, 36.87 (d, *J* = 24.0 Hz), 28.8 (d, *J* = 9.0 Hz), 28.7

(d, *J* = 9.0 Hz), 28.5, 22.6, 13.9. HRMS(ESI) calcd for $C_{35}H_{54}NOPS$ [M+H$^+$]: 568.3736, found: 568.3738. $[\alpha]_D^{20}$ = -67.5 (*c* = 0.3, $CHCl_3$).

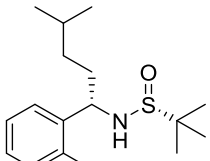
(6) Synthesis of (*S,R*$_S$)-**X6**



(*S,R*$_S$)-**X6**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.40-7.33 (m, 2H), 7.23-7.18 (m, 1H), 5.75 (s, 1H), 3.43 (s, 1H), 2.04-1.82 (m, 22H), 1.70-1.65 (m, 12H), 1.26-1.22 (m, 9H), 1.14 (s, 9H), 0.84 (t, *J* = 1.6 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.19. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6 (d, J_{CP} = 25.0 Hz), 136.3, 132.4 (d, J_{CP} = 27.0 Hz), 128.9, 126.7, 124.9, 55.6, 42.2 (d, J_{CP} = 13.0 Hz), 41.6 (d, J_{CP} = 12.0 Hz), 39.1, 37.2 (d, J_{CP} = 23.0 Hz), 36.9, 36.8 (d, J_{CP} = 24.0 Hz), 31.6, 29.2, 28.8 (d, J_{CP} =9.0 Hz), 28.7 (d, J_{CP} = 9.0 Hz), 26.2, 22.5 (d, J_{CP} = 5.0 Hz), 14.0. HRMS(ESI) calcd for $C_{37}H_{58}NOPS$ [M+H$^+$]: 596.4056, found: 596.4049. $[\alpha]_D^{20}$ = -76.6 (*c* = 0.3, $CHCl_3$).

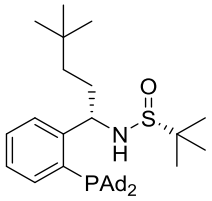
(7) Synthesis of (*S,R*$_S$)-**X7**



(*S,R*$_S$)-**X7**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.40-7.32 (m, 2H), 7.22-7.17 (m, 1H), 5.72 (s, 1H), 3.41 (s, 1H), 2.01-1.79 (m, 22H), 1.65 (d, *J* = 10.8 Hz, 12H), 1.58-1.49 (m, 1H), 1.13 (s, 9H), 0.84 (t, *J* = 6.4 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.18. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (d, J_{CP} = 25.0 Hz), 136.3, 132.4 (d, J_{CP} = 27.0 Hz), 128.9, 126.7 (d, J_{CP} = 6.0 Hz), 124.8, 55.5, 42.2 (d, J_{CP} = 13.0 Hz), 41.6 (d, J_{CP} = 12.0 Hz), 37.2 (d, J_{CP} = 23.0 Hz), 36.87, 36.85 (d, J_{CP} = 24.0 Hz), 35.4, 28.81 (d, J_{CP} = 9.0 Hz), 28.7 (d, J_{CP} = 9.0 Hz), 27.9, 22.6, 22.5, 22.4. HRMS(ESI) calcd for $C_{37}H_{56}NOPS$ [M+H$^+$]: 582.3893, found: 582.3902. $[\alpha]_D^{20}$ = -87.1 (*c* = 0.3, $CHCl_3$).

(8) Synthesis of (S,R_S)-**X8**



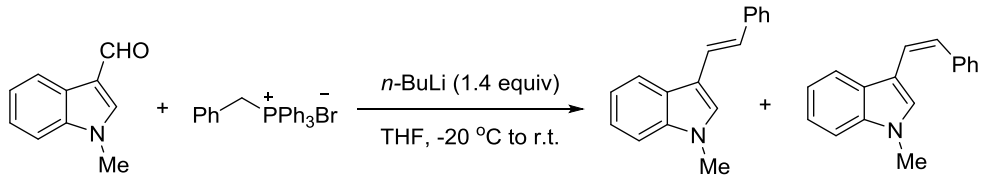
(S,R_S)-**X8**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.41-7.33 (m, 2H), 7.23-7.18 (m, 1H), 5.73 (s, 1H), 3.38 (s, 1H), 2.01-1.81 (m, 20H), 1.65 (d, *J* = 7.8 Hz, 12H), 1.14 (s, 9H), 0.92 (s, 2H), 0.83 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.27. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8 (d, J_{CP} = 24.7 Hz), 136.3, 132.5 (d, J_{CP} = 26.5 Hz), 128.9, 126.6 (d, J_{CP} = 5.8 Hz), 124.9, 60.0, 55.5, 46.5, 42.3 (d, J_{CP} = 12.7 Hz), 41.6 (d, J_{CP} = 12.0 Hz), 40.6, 37.3 (d, J_{CP} = 22.7 Hz), 36.89, 36.88 (d, J_{CP} = 24.1 Hz), 34.4, 30.2, 29.7, 29.2, 28.8 (d, J_{CP} = 9.0 Hz), 28.7 (d, J_{CP} = 9.0 Hz), 22.6. HRMS(ESI) calcd for $C_{37}H_{58}NOPS$ [M+H$^+$]: 596.4049, found: 596.4066. $[\alpha]_D^{20}$ = -84.0 (*c* = 0.3, $CHCl_3$).

4. Synthesis of substrates 1a-1t and 2.

All 3-vinylindole substrates were synthesized according to our previous procedure.[2] The spectra of known compounds such as **1a**, **1b** and **2** are consistent with the literature, which are not included here except **1a** as a typical procedure.

Typical Procedure for synthesis of 3-styrylindoles.

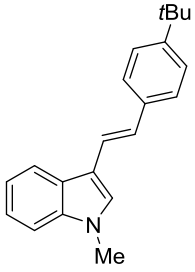


s1 **1a**

n-BuLi (2.5 M in hexane solution) (9.6 mL, 24 mmol) was slowly added to the suspension of RCH_2PPh_3Br (10.39 g, 24 mmol) in dry T HF (130 mL) at -20 °C. The mixture was stirred at room temperature for 2 hours followed by the addition of **S1** (3.18 g, 20 mmol) in THF (20 mL) at -20 °C. Then the mixture was stirred at room

temperature for 2 hours, monitored by TLC and quenched by saturated solution of NH_4Cl at room temperature. The extracts with ethyl acetate were washed by Saturated salt water and dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure. The crude product was purified by column chromatography to give (*E*)-Product (2.70 g, 58%) as a white solid and (*Z*)-product (1.86 g, 40%) as a colorless liquid.

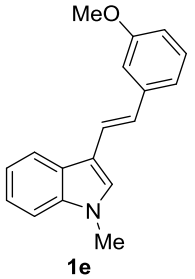
(1) Synthesis of **1d**



1d

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6Hz, 1H), 7.46-7.43 (m, 2H), 7.38-7.36 (m, 2H), 7.32-7.16 (m, 5H), 7.09-7.05 (m, 1H), 3.73 (s, 3H), 1.35-1.31 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 137.6, 135.9, 128.2, 125.5, 125.4, 124.6, 122.1, 120.8, 120.2, 120.0, 114.1, 109.5, 34.5, 32.8, 31.3. MS (70 eV): m/z (%): 289 (M^+, 100). HRMS calcd for $C_{21}H_{23}N$: 289.1830, found: 289.1833.

(2) Synthesis of **1e**

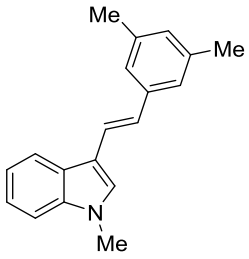


1e

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.31-7.19 (m, 5H), 7.16 (s, 1H), 7.12-7.02 (m, 3H), 3.82 (s, 3H), 6.78-6.73 (m, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 140.2, 137.7, 129.5, 128.6, 126.1, 124.5, 122.2, 121.9, 120.2, 120.0, 118.4, 113.8, 112.1, 110.9, 109.5, 55.2, 32.8. MS (70 eV): m/z (%): 263

(M^+, 100). HRMS calcd for $C_{18}H_{17}NO$: 263.1310, found: 263.1312.

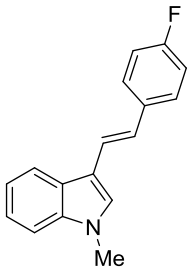
(3) Synthesis of **1f**



1f

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.33-7.17 (m, 5H), 7.14 (s, 2H), 7.03 (d, *J* = 16.4 Hz, 1H), 6.85 (s, 1H), 3.75 (s, 3H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.0, 137.7, 128.3, 128.2, 126.2, 125.0, 123.6, 122.2, 121.2, 120.3, 119.9, 114.1, 109.5, 32.8, 21.3. MS (70 eV): m/z (%): 261 (M^+, 100). HRMS calcd for $C_{19}H_{19}N$: 261.1517, found: 261.1518.

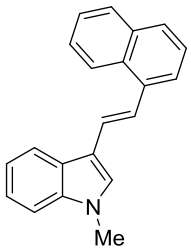
(4) Synthesis of **1i**



1i

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.47-7.40 (m, 2H), 7.34-7.24 (m, 2H), 7.23-7.15 (m, 3H), 7.06-6.98 (m, 3H), 3.75 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.10. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 160.5, 137.7, 134.8 (d, *J* = 3.0 Hz), 128.4, 127.0 (d, *J* = 7.7 Hz), 126.1, 123.6, 122.3, 121.4 (d, *J* = 2.0 Hz), 120.1 (d, *J* = 9.3 Hz), 115.4 (d, *J* = 21.0 Hz), 113.8, 109.6, 32.8. MS (70 eV): m/z (%): 251 (M^+, 100). HRMS calcd for $C_{17}H_{14}NF$: 251.1110, found: 251.1112.

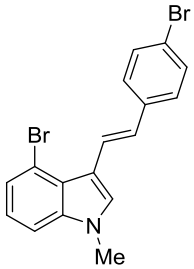
(5) Synthesis of **1k**



1k

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 8.08-8.04 (m, 1H), 7.88-7.81 (m, 2H), 7.77-7.71 (m, 2H), 7.56-7.44 (m, 3H), 7.34-7.23 (m, 4H), 7.19 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.2, 133.8, 131.2, 128.8, 128.5, 126.9, 125.8, 125.6, 124.5, 123.9, 122.6, 122.3, 121.6, 120.3, 120.2, 114.4, 109.6, 32.8. MS (70 eV): m/z (%): 283 (M^+, 100). HRMS calcd for $C_{21}H_{17}N$: 283.1361, found: 283.1364.

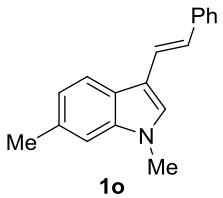
(6) Synthesis of **1m**



1m

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 16.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.33-7.28 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.04-6.97 (m, 1H), 6.65 (d, *J* = 16.4 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.2, 131.5, 127.3, 126.8, 124.8, 124.4, 123.6, 122.5, 122.0, 120.0, 114.8, 114.3, 108.9, 33.1.

(7) Synthesis of **1o**

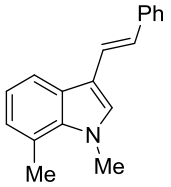


1o

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.34-7.28 (m, 2H), 7.24-7.13 (m, 2H), 7.08-7.01 (m, 4H), 3.65 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.1, 132.0, 128.5, 128.1, 126.3, 125.6, 124.4,

123.9, 121.8, 121.7, 119.9, 113.8, 109.5, 32.7,21.8. MS (70 eV): m/z (%): 247(M^+, 100). HRMS calcd for $C_{18}H_{17}N$: 247.1361, found: 247.1362.

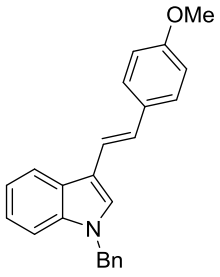
(8) Synthesis of **1p**



1p

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.33-7.27 (m, 2H), 7.23-7.14 (m, 2H), 7.08 (s, 1H), 7.06-6.94 (m, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 4.00 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.3, 129.7, 128.6, 127.4, 126.4, 125.7, 124.9, 121.5, 121.3, 120.2, 118.1, 113.6, 37.0, 19.7. MS (70 eV): m/z (%): 247 (M^+, 100). HRMS calcd for $C_{18}H_{17}N$: 247.1361, found: 247.1363.

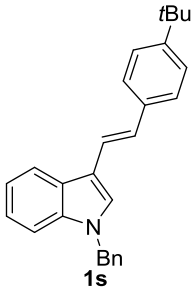
(9) Synthesis of **1r**



1r

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.96 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.34-7.18 (m, 10H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.30 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 137.2, 137.1, 131.4, 128.8, 127.7, 127.2, 126.84, 126.81, 126.4, 124.9, 122.3, 120.3, 120.1, 119.4, 114.8, 114.1, 110.0, 55.3, 50.1. MS (70 eV): m/z (%): 339 (M^+, 100). HRMS calcd for $C_{24}H_{21}NO$: 339.1623, found: 339.1621.

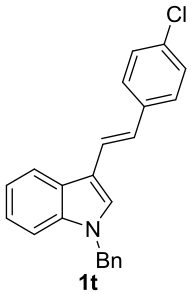
(10)Synthesis of **1s**



1s

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.98 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.28-7.17 (m, 8H), 7.13-7.05 (m, 3H), 5.20 (s, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 137.2, 137.0, 135.8, 128.8, 127.7, 127.5, 126.8, 126.4, 125.5, 125.4, 125.0, 122.3, 120.7, 120.3, 120.2, 114.7, 110.0, 50.0, 34.5, 31.3. MS (70 eV): m/z (%): 365 (M^+, 100). HRMS calcd for $C_{27}H_{27}N$: 365.2144, found: 365.2146.

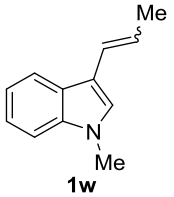
(11)Synthesis of **1t**



1t

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.94 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34-7.20 (m, 10H), 7.16-7.10 (m, 2H), 7.03 (d, *J* = 16.8 Hz, 1H), 5.29 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 137.1, 136.9, 131.9, 128.8, 128.7, 128.0, 127.8, 126.9, 126.8, 126.3, 123.8, 122.5, 122.1, 120.4, 120.3, 114.3, 110.1, 50.1. MS (70 eV): m/z (%): 343 (M^+, 100). HRMS calcd for $C_{23}H_{18}NCl$: 343.1128, found: 343.1125.

(12) Synthesis of **1w**

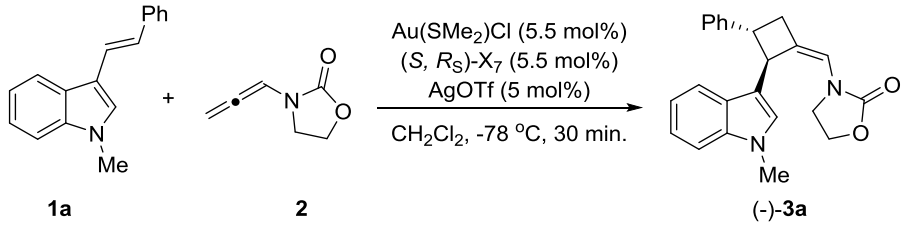


1w

Yellow liquid. (mixture, E: Z = 1.56: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ [7.82 (d, *J* = 8.2 Hz,

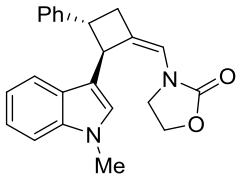
0.39H), 7.66 (d, *J* = 8.2 Hz, 0.61H)], [7.34-7.11 (m, 3H)], [7.12 (s, 0.61H),7.00 (s, 0.39H)], [6.66-6.61 (m, 0.61H), 6.57-6.53 (m, 0.39H)], [6.24-6.10 (m, 0.39H), 5.77-5.66 (m, 0.61H)], [3.78 (s, 1.83H), 3.72 (s, 1.17H)], [1.96-1.87 (m, 3H)]. ^{13}C NMR (100 MHz, $CDCl_3$) δ [137.4, 136.2], [127.9, 127.4], [126.6, 126.2], [123.2, 122.6], [122.0, 121.9], [121.8, 120.5], [120.0, 119.3], [119.5, 119.1], [114.1, 112.4], [109.3, 109.1], [32.8, 32.6], [18.9, 15.6]. MS (70 eV): m/z (%): 171 (M^+, 100). HRMS calcd for $C_{12}H_{13}N$: 171.1048, found: 171.1045.

5. General procedure for the [2+2] cycloaddition and copies of HPLC data



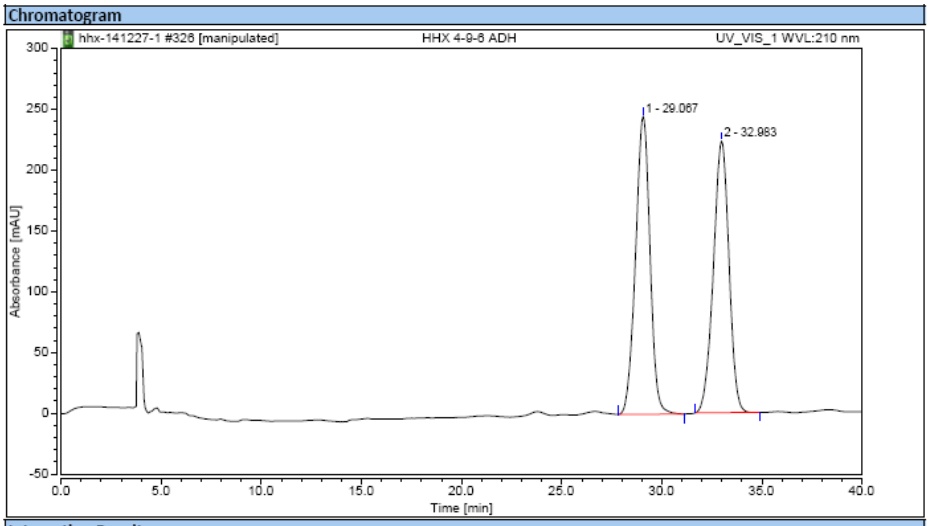
The solution of (*S,R*$_S$)-**X8** (0.012 mmol, 6 mol %) and Au(SMe_2)Cl (0.01 mmol, 5 mol%) in 1 mL CH_2Cl_2 was stirred at rt for 2 hours, and then remove the solvent. After completion, the gold complex and AgOTf (0.01 mmole, 5 mol %) in CH_2Cl_2 (1 mL) was stirred at rt for 15 min., Then the above catalyst solution then was added to the solution of **1a** (0.22 mmol, 1.1 equiv) and **2** (0.2 mmol) in DCM (3 mL) at -78 ^{o}C. The reaction was determined by TLC, after the less component was consumed, the solution was removed under reduced pressure. The diastereomeric ratio was determined by crude 1H NMR, the resulting crude mixture was purified by flash column chromatography on silica gel with petroleum ether/ ethyl acetate (3:1) as the solvent to afford product. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralpak such as AD-H, AS-H, OD-H, etc.

(1) Synthesis of **3a**



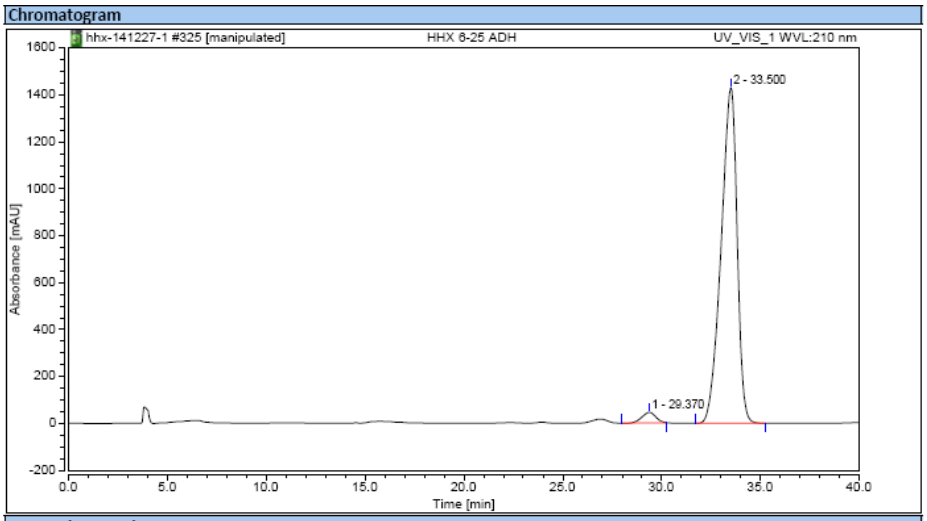
3a

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.39-7.29 (m, 5H), 7.28-7.21 (m, 2H), 7.10-7.03 (m, 1H), 6.98 (s, 1H), 6.54 (d, *J* = 2.0 Hz, 1H). 4.48-4.43 (m, 1H), 4.07-4.00 (m, 1H), 3.88 (dd, *J* = 16.8, 8.8 Hz 1H), 3.78 (s, 3H), 3.55-3.30 (m, 4H), 3.00-2.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.8, 137.5, 128.5, 126.5, 126.4, 126.0, 123.2, 121.9, 119.5, 119.1, 117.6, 117.0, 109.4, 62.1, 47.6, 46.4, 44.2, 33.6, 32.8. MS (70 eV): m/z (%): 358 (M^+, 72.16), 271 (100). HRMS calcd for $C_{23}H_{22}N_2O_2$: 356.1681, found: 358.1685. $[\alpha]_D^{20}$ = -11.1 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 0.8 mL/min, 233 nm; t_r (minor) = 29.37 min, t_r (major) = 33.50 min, 95% *ee*.



Integration Results

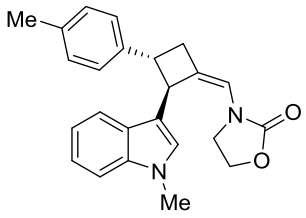
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.067	205.277	245.192	50.44	52.32	n.a.
2		32.983	201.689	223.467	49.56	47.68	n.a.
Total:			**406.965**	**468.659**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.370	36.109	44.517	2.62	3.02	n.a.
2		33.500	1342.804	1431.725	97.38	96.98	n.a.
Total:			**1378.913**	**1476.242**	**100.00**	**100.00**	

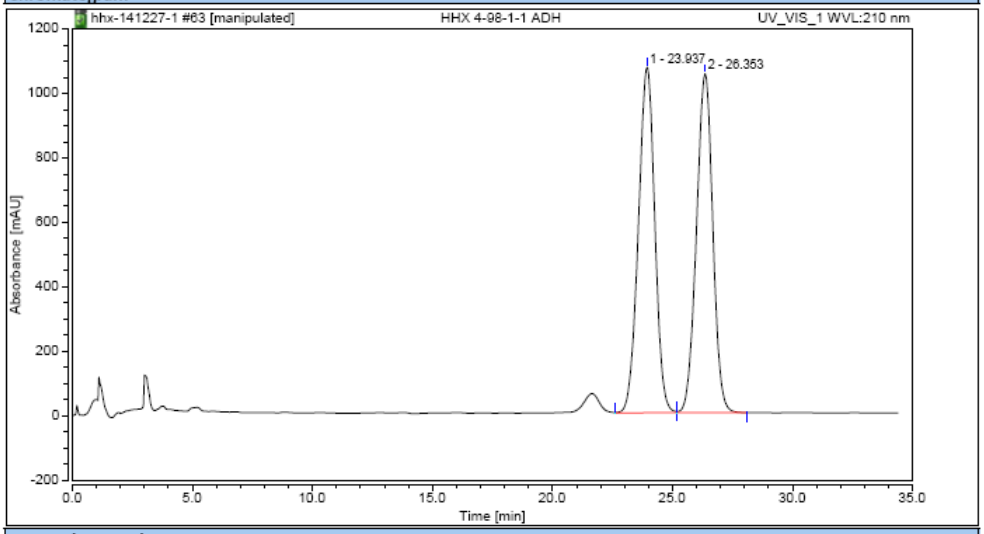
(2) Synthesis of **3b**



3b

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H) 7.31 (d, *J* = 8.4 Hz, 1H), 7.28-7.20 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09-7.04 (m, 1H), 6.96 (s, 1H), 6.54-6.52 (d, *J* = 2.4 Hz, 1H), 4.42-4.38 (m, 1H), 4.06-3.98 (m, 1H), 3.91-3.86 (m, 1H), 3.76 (s, 3H), 3.54-3.26 (m, 4H), 2.96-2.90 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 141.8, 137.5, 135.9, 129.2, 126.4, 126.3, 126.0, 123.3, 121.9, 119.5, 119.1, 117.5, 117.1, 109.3, 62.1, 47.7, 46.0, 44.2, 33.7, 32.7, 21.0. MS (70 eV): m/z (%): 372 (M^+, 100). HRMS calcd for $C_{24}H_{24}N_2O_2$: 372.1838, found: 372.1837. $[\alpha]_D^{20}$ = 26.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 1.0 mL/min, 233 nm; tr (minor) = 24.47 min, tr (major) = 26.97 min, 92% *ee*.

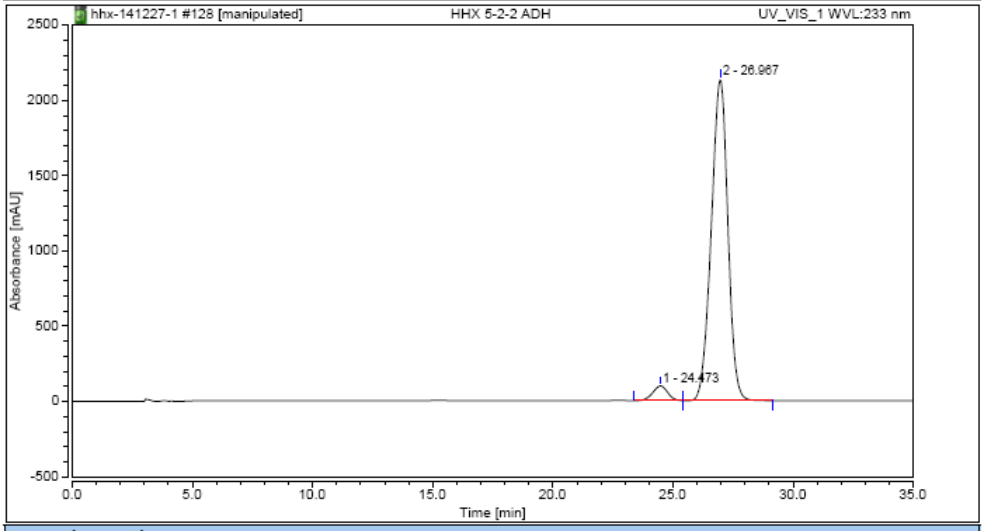
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.937	851.540	1073.403	50.69	50.49	n.a.
2		26.353	828.222	1052.732	49.31	49.51	n.a.
Total:			**1679.763**	**2126.135**	**100.00**	**100.00**	

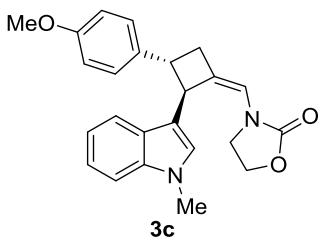
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.473	69.439	96.802	3.91	4.34	n.a.
2		26.967	1705.001	2134.497	96.09	95.66	n.a.
Total:			**1774.440**	**2231.298**	**100.00**	**100.00**	

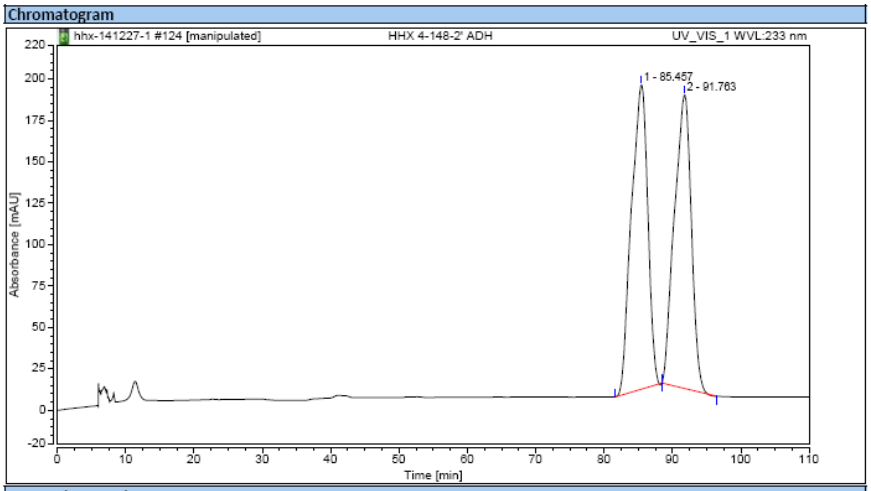
(3) Synthesis of **3c**



3c

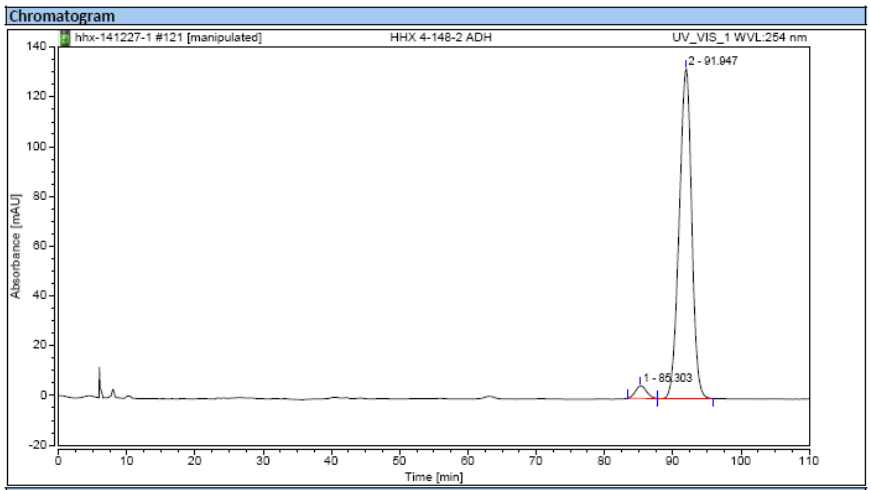
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz,

1H), 7.27-7.23 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.53 (s, 1H), 4.40-4.37 (m, 1H), 4.04 (dd, *J* = 14.8, 8.8 Hz, 1H), 3.90 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.54-3.26 (m, 4H), 2.95-2.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 156.3, 137.4, 137.0, 127.5, 126.3, 125.9, 123.2, 121.9, 119.5, 119.1, 117.5, 117.1, 113.9, 109.3, 62.1, 55.3, 47.9, 45.8, 44.2, 33.8, 32.8. MS (70 eV): m/z (%): 388 (M^+, 26.8), 263 (100). $[\alpha]_D^{20}$ = 7.9 (*c* = 0.3, $CHCl_3$). HRMS calcd for $C_{24}H_{24}N_2O_3$: 388.1787, found: 388.1789. HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 0.5 mL/min, 233 nm; tr (minor) = 85.30 min, tr (major) = 91.95 min, 93% *ee*.



Integration Results

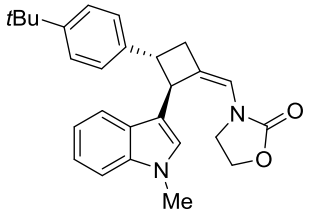
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		85.457	509.732	183.938	50.13	50.91	n.a.
2		91.763	507.102	177.340	49.87	49.09	n.a.
Total:			**1016.834**	**361.278**	**100.00**	**100.00**	



Integration Results

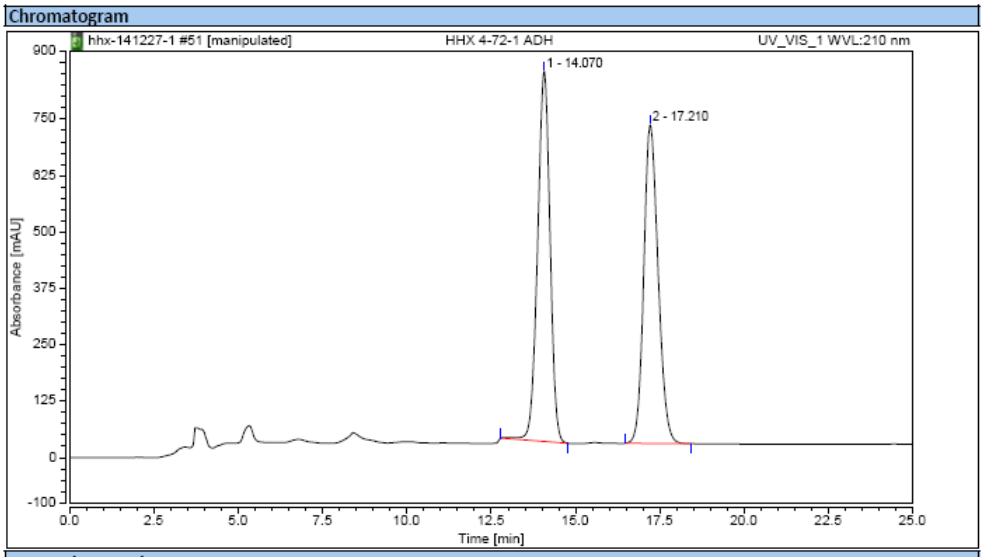
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		85.303	9.658	5.050	3.32	3.67	n.a.
2		91.947	280.858	132.692	96.68	96.33	n.a.
Total:			**290.516**	**137.742**	**100.00**	**100.00**	

(4) Synthesis of **3d**



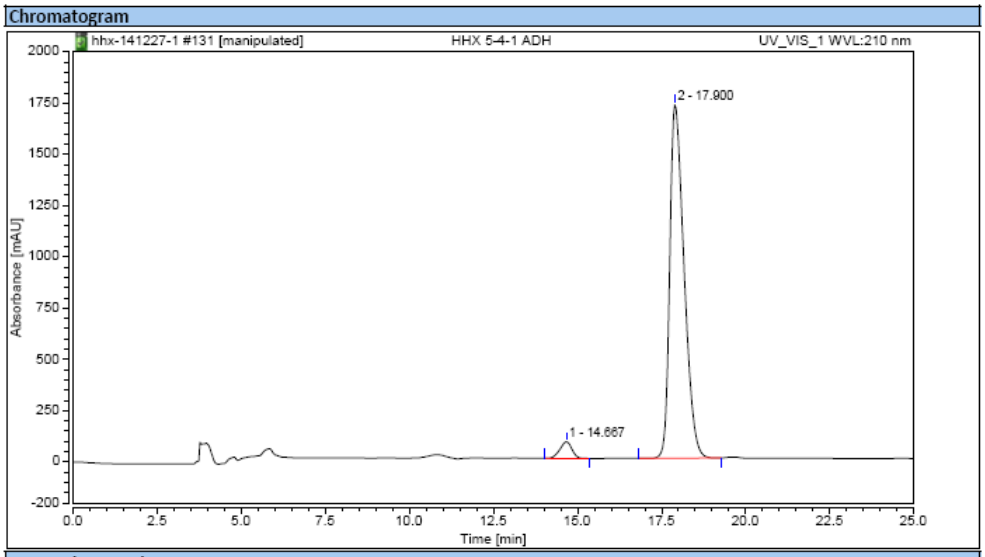
3d

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.41-7.22 (m, 6H), 7.11-7.06 (m, 1H), 6.97 (s, 1H), 6.52 (d, J = 2.4 Hz, 1H), 4.45-4.41 (m, 1H), 4.07-4.00 (m, 1H), 3.89 (dd, *J* = 16.8, 8.8 Hz 1H), 3.77 (s, 3H), 3.56-3.30 (m, 4H), 2.98-2.93 (m, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 149.2, 141.8, 137.5, 126.3, 126.1, 126.0, 125.4, 123.4, 121.9, 119.5, 119.1, 117.5, 117.2, 109.3, 62.1, 47.5, 45.8, 44.2, 34.4, 33.6, 32.8, 31.4. MS (70 eV): m/z (%): 414 (M+, 35.0), 44 (100). HRMS calcd for $C_{27}H_{30}N_2O_2$: 414.2307, found: 414.2309. $[\alpha]_D^{20}$ = 32.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10, 0.8 mL/min, 210 nm; tr (minor) = 14.67 min, tr (major) = 17.9 min, 92% ee.



Integration Results

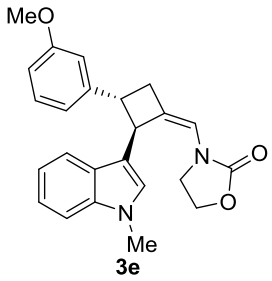
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.070	350.185	820.930	50.14	53.74	n.a.
2		17.210	348.250	706.610	49.86	46.26	n.a.
Total:			**698.435**	**1527.540**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.667	33.891	81.672	3.82	4.52	n.a.
2		17.900	852.577	1724.393	96.18	95.48	n.a.
Total:			886.468	1806.065	100.00	100.00	

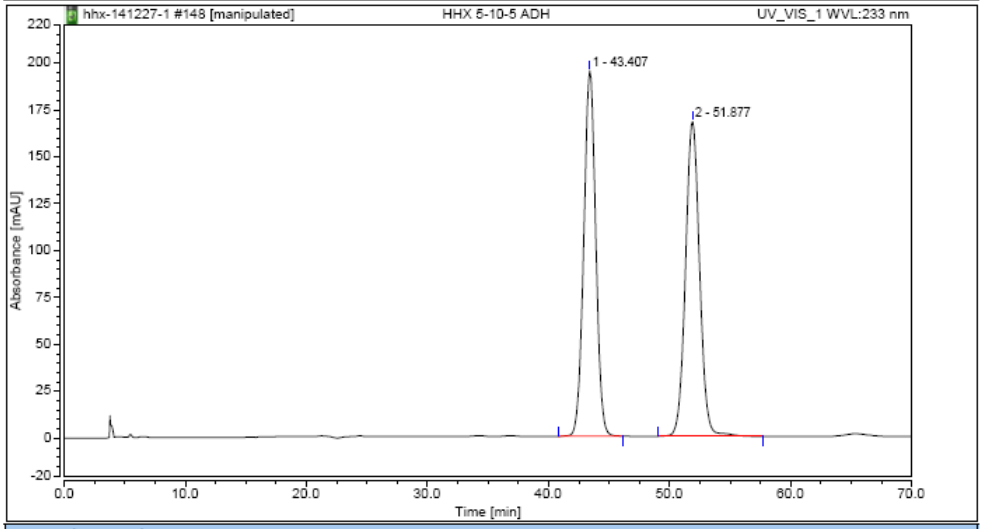
(5) Synthesis of **3e**



3e

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.31-7.29 (m, 1H), 7.27-7.18 (m, 2H), 7.10-7.04 (m, 1H), 6.96 (s, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.80-6.76 (m, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 4.46-4.42 (m, 1H), 4.05-3.98 (m, 1H), 3.86 (dd, *J* = 16.8, 8.8 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.54-3.27 (m, 4H), 3.02-2.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.3, 146.5, 137.5, 129.5, 126.3, 126.0, 123.0, 122.0, 119.5, 119.1, 118.9, 117.6, 117.0, 112.4, 111.6, 109.4, 62.1, 55.2, 47.5, 46.4, 44.2, 33.5, 32.8. MS (70 eV): m/z (%): 388 (M^+, 44.58), 301 (100). HRMS calcd for $C_{24}H_{24}N_2O_3$: 388.1787, found: 388.1784. $[\alpha]_D^{20}$ = 6.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 0.8 mL/min, 233 nm; tr (minor) = 43.56 min, tr (major) = 52.79 min, 91% *ee*.

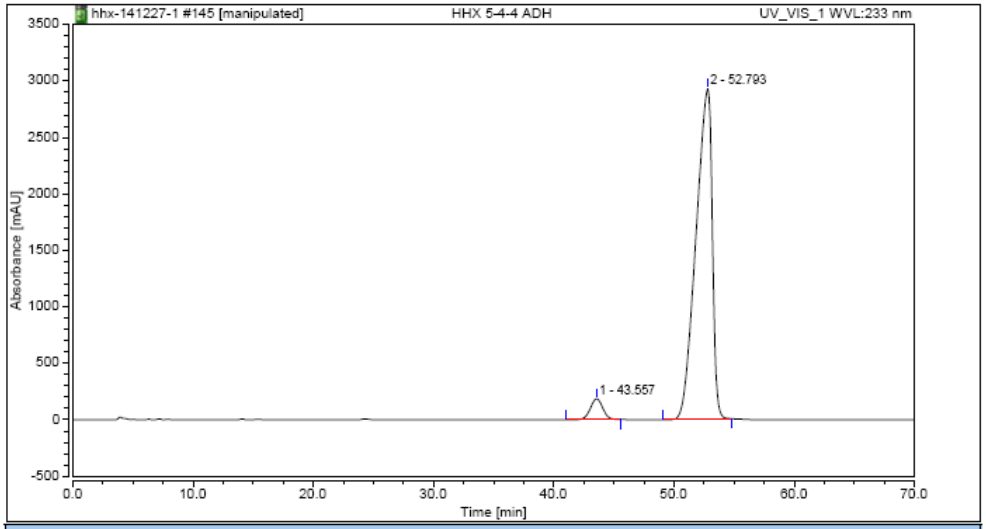
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		43.407	222.925	194.744	49.61	53.72	n.a.
2		51.877	226.412	167.788	50.39	46.28	n.a.
Total:			**449.336**	**362.532**	**100.00**	**100.00**	

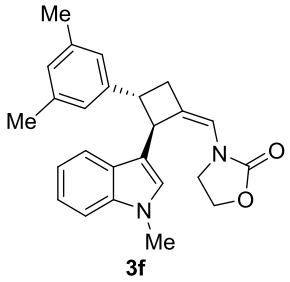
Chromatogram



Integration Results

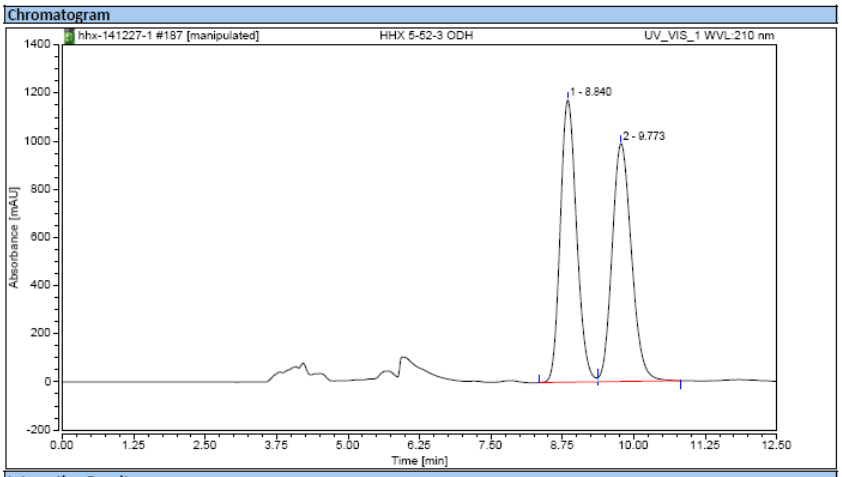
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		43.557	223.583	185.887	4.64	5.96	n.a.
2		52.793	4597.985	2933.891	95.36	94.04	n.a.
Total:			**4821.568**	**3119.777**	**100.00**	**100.00**	

(6) Synthesis of **3f**



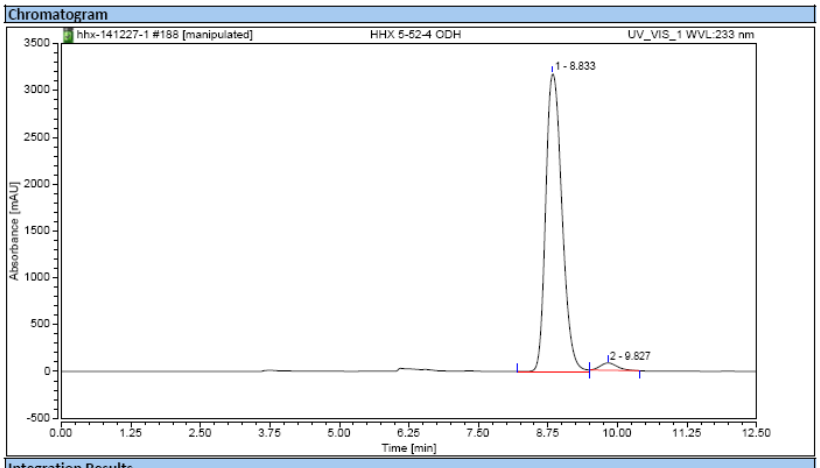
3f

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28-7.22 (m, 1H), 7.11-7.03 (m, 1H), 6.99-6.93 (m, 3H), 6.88 (s, 1H), 6.52 (d, *J* = 2.0, 1H), 4.45-4.42 (m, 1H), 4.05-3.99 (m, 1H), 3.87 (dd, *J* = 16.4, 8.8 Hz, 1H), 3.77 (s, 3H), 3.53-3.26 (m, 4H), 3.01-2.92 (m, 1H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.7, 137.9, 137.5, 128.0, 126.3, 126.0, 124.3, 123.5, 121.9, 119.6, 119.0, 117.5, 117.1, 109.3, 62.0, 47.5, 46.3, 44.2, 33.6, 32.7, 21.3. MS (70 eV): m/z (%): 386 (M^+, 99.68), 44 (100). HRMS calcd for $C_{25}H_{26}N_2O_2$: 386.1994, found: 386.1996. $[\alpha]_D^{20}$ = 8.1 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 70: 30, 0.8 mL/min, 210 nm); tr (major) = 8.83 min, tr (minor) = 9.83 min, 95% *ee*.



Integration Results

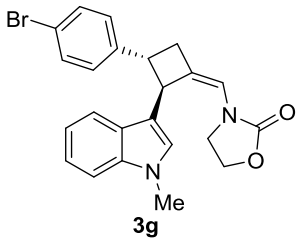
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.840	388.746	1173.634	50.09	54.24	n.a.
2		9.773	387.425	989.997	49.91	45.76	n.a.
Total:			**776.170**	**2163.632**	**100.00**	**100.00**	



Integration Results

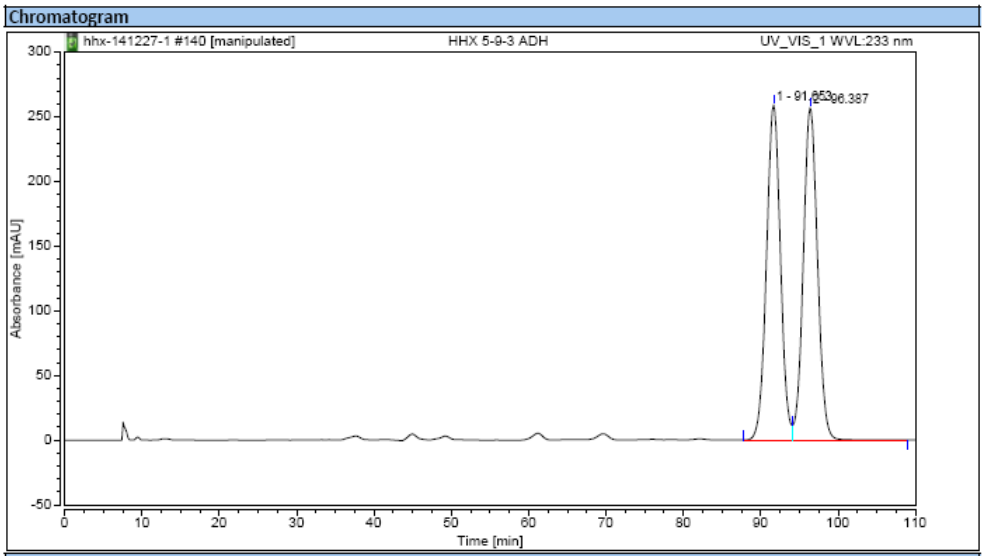
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.833	1078.223	3180.371	97.47	97.60	n.a.
2		9.827	27.973	78.154	2.53	2.40	n.a.
Total:			**1106.196**	**3258.525**	**100.00**	**100.00**	

(7) Synthesis of **3g**



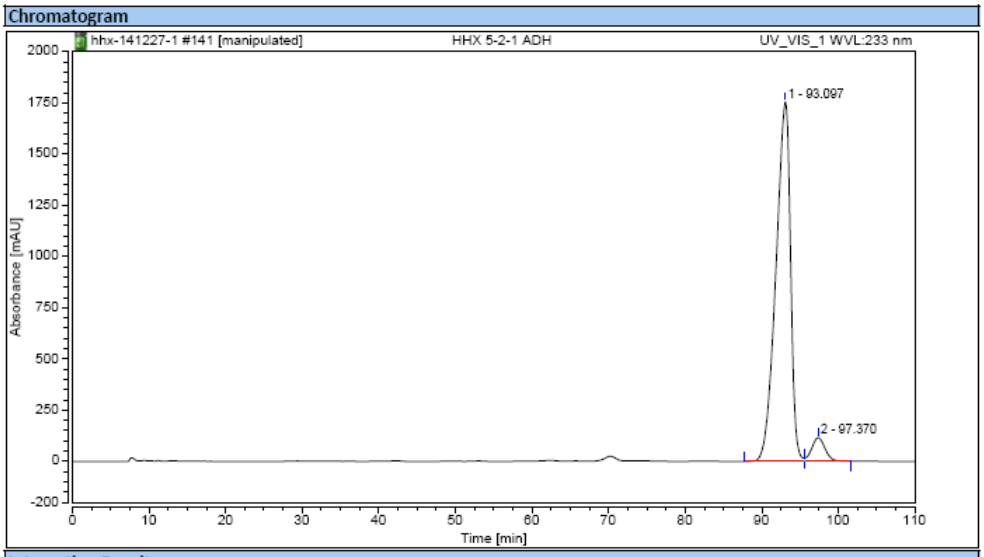
3g

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.47-7.43 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28-7.23 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.11-7.04 (m, 1H), 6.96 (s, 1H), 6.53 (dd, *J* = 4.4, 2.4 Hz, 1H), 4.40-4.36 (m, 1H), 4.06-3.99 (m, 1H), 3.89 (dd, J = 16.8, 9.2 Hz, 1H), 3.78 (s, 3H), 3.53-3.30 (m, 4H), 2.96-2.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 143.8, 137.4, 131.6, 128.3, 126.2, 126.0, 122.4, 122.0, 119.3, 119.2, 117.8, 116.7, 109.4, 62.1, 47.7, 45.9, 44.2, 33.5, 32.8. MS (70 eV): m/z (%): 436 (M^+, 100), 438 ($[M+2]^+$, 99.16). HRMS calcd for $C_{23}H_{21}N_2O_2Br$: 436.0786, found: 436.0787. $[\alpha]_D^{20}$ = 57.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 0.4 mL/min, 233 nm; tr (major) = 93.10 min, tr (minor) = 97.37 min, 89% *ee*.



Integration Results

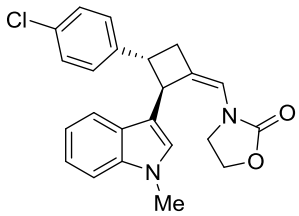
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		91.653	542.570	259.343	49.78	50.20	n.a.
2		96.387	547.390	257.270	50.22	49.80	n.a.
Total:			**1089.960**	**516.613**	**100.00**	**100.00**	



Integration Results

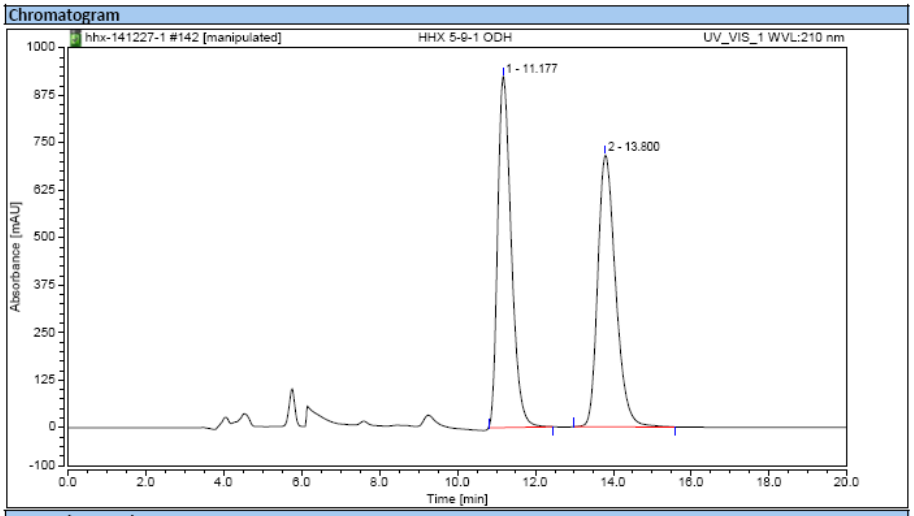
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		93.097	3874.604	1754.695	94.29	93.83	n.a.
2		97.370	234.728	115.351	5.71	6.17	n.a.
Total:			**4109.332**	**1870.046**	**100.00**	**100.00**	

(8) Synthesis of **3h**



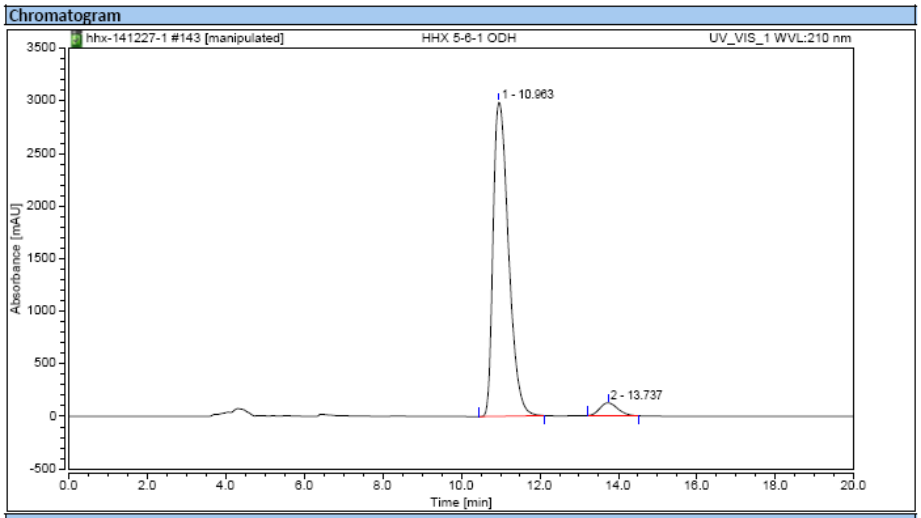
3h

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.41 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28-7.15 (m, 3H), 7.11-7.05 (m, 1H), 6.96 (s, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 4.42-4.37 (m, 1H), 4.06-3.99 (m, 1H), 3.86 (dd, *J* = 16.4, 8.4 Hz, 1H), 3.77 (s, 3H), 3.53-3.27 (m, 4H), 2.96-2.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 143.8, 137.5, 131.6, 128.2, 126.2, 126.0, 122.5, 122.0, 120.0, 119.3, 119.2, 117.8, 116.7, 109.4, 62.1, 47.7, 45.9, 44.2, 33.5, 32.8. MS (70 eV): m/z (%): 392 (M^+, 99.52), 394 ([M+2]$^+$, 35.32), 305 (100). HRMS calcd for $C_{23}H_{21}N_2O_2Cl$: 392.1295, found: 392.1292. $[\alpha]_D^{20}$ = 21.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak OD-H, hexane/2-propanol = 95: 5, 0.8 mL/min, 210 nm; tr (major) = 10.96 min, tr (minor) = 13.74 min, 91% *ee*.



Integration Results

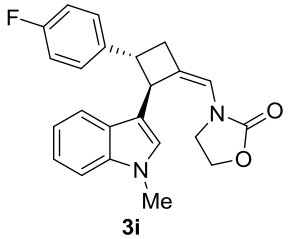
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.177	374.608	924.642	49.61	56.36	n.a.
2		13.800	380.462	716.100	50.39	43.64	n.a.
Total:			**755.071**	**1640.742**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.963	1358.751	2991.939	95.47	96.08	n.a.
2		13.737	64.422	122.021	4.53	3.92	n.a.
Total:			**1423.173**	**3113.960**	**100.00**	**100.00**	

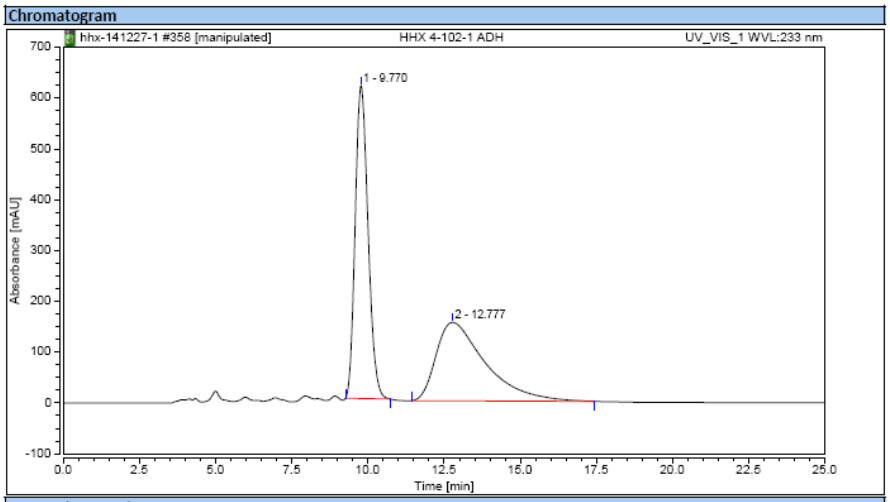
(9) Synthesis of **3i**



3i

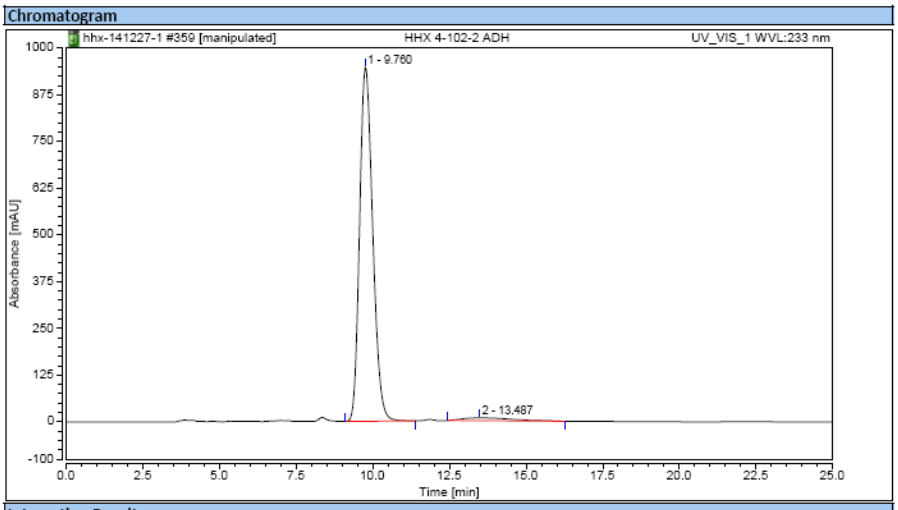
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.35-7.22 (m, 4H), 7.11-6.95 (m, 4H), 6.53 (dd, *J* = 4.4, 2.4 Hz, 1H), 4.40-4.36 (m, 1H), 4.06-3.98 (m, 1H),

3.94-3.85 (m, 1H), 3.78 (s, 3H), 3.55-3.31 (m, 4H), 2.95-2.87 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.71. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 160.3, 156.3, 140.5 (d, *J* = 3.0 Hz), 137.5, 127.9 (d, *J* = 8 Hz), 126.3, 126.0, 122.9, 122.0, 119.3 (d, *J* = 15.0 Hz), 117.7, 116.8, 115.3 (d, *J* = 21.0 Hz), 109.4, 62.1, 47.9, 45.8, 44.2, 33.8, 32.8. MS (70 eV): m/z (%): 376 (M^+, 2.07), 105 (100). HRMS calcd for $C_{23}H_{21}N_2O_2F$: 376.1587, found: 376.1585. $[\alpha]_D^{20}$ = -10.3 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 70: 30, 0.8 mL/min, 233 nm); tr (major) = 9.76 min, tr (minor) = 13.49 min, 94% *ee*.



Integration Results

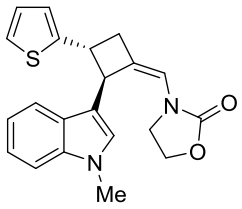
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.770	302.070	616.042	51.12	79.96	n.a.
2		12.777	288.820	154.388	48.88	20.04	n.a.
Total:			**590.890**	**770.430**	**100.00**	**100.00**	



Integration Results

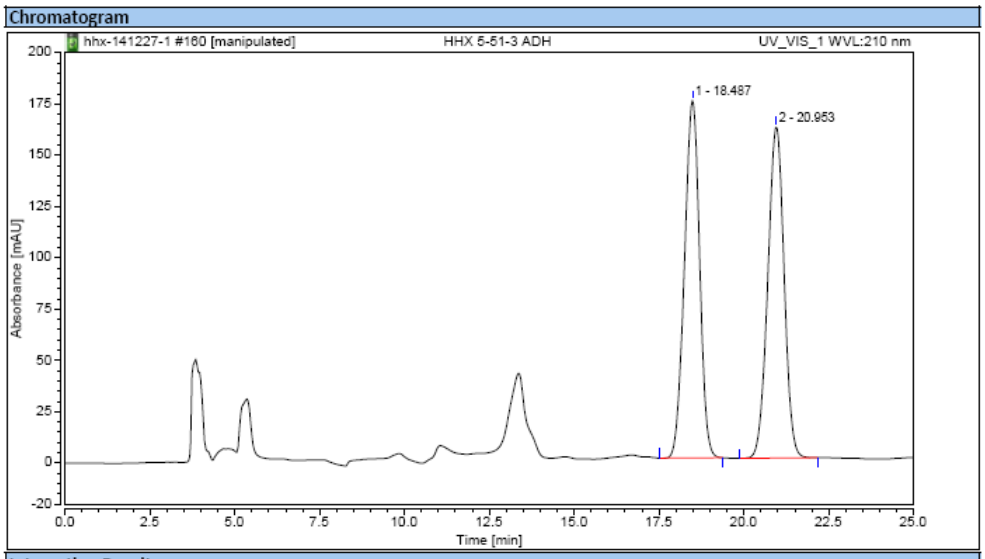
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.760	468.955	947.547	96.92	99.17	n.a.
2		13.487	14.897	7.955	3.08	0.83	n.a.
Total:			**483.852**	**955.502**	**100.00**	**100.00**	

(10) Synthesis of **3j**



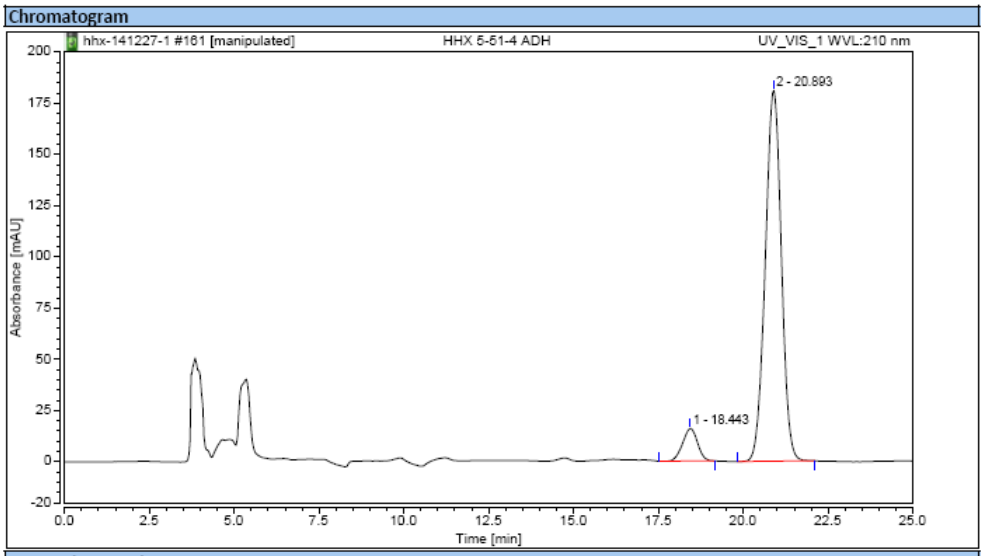
3j

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32-7.25 (m, 1H), 7.23-7.20 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.01-6.97 (m, 2H), 6.93 (d, *J* = 4.2 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 4.56-4.50 (m, 1H), 4.13-4.04 (m, 1H), 3.93 (dd, *J* = 16.8, 8.8 Hz,1H), 3.81 (s, 3H), 3.77-3.71 (m, 1H), 3.57-3.41 (m, 3H), 3.06-2.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 148.7, 137.5, 126.9, 126.2, 126.1, 123.2, 123.1 122.0, 121.8, 119.5, 119.2, 118.0, 116.4, 109.4, 62.1, 49.1, 44.1, 42.1, 35.3, 32.8. MS (70 eV): m/z (%): 364 (M^+, 6.37), 119 (100). HRMS calcd for $C_{21}H_{20}N_2O_2S$: 364.1245, found: 364.1248. $[\alpha]_D^{20}$ = 3.2 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10,, 0.8 mL/min, 210 nm); tr (minor) = 18.44 min, tr (major) = 20.89 min, 85% ee.



Integration Results

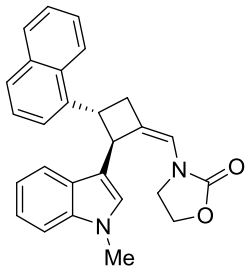
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.487	89.897	174.393	50.00	51.90	n.a.
2		20.953	89.883	161.602	50.00	48.10	n.a.
Total:			**179.780**	**335.995**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.443	8.044	15.897	7.49	8.07	n.a.
2		20.893	99.315	181.128	92.51	91.93	n.a.
Total:			**107.359**	**197.024**	**100.00**	**100.00**	

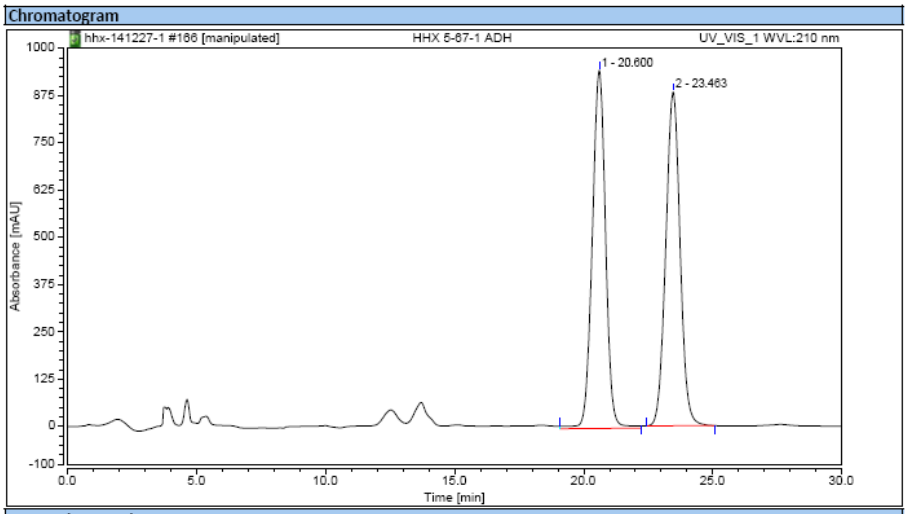
(11) Synthesis of **3k**



3k

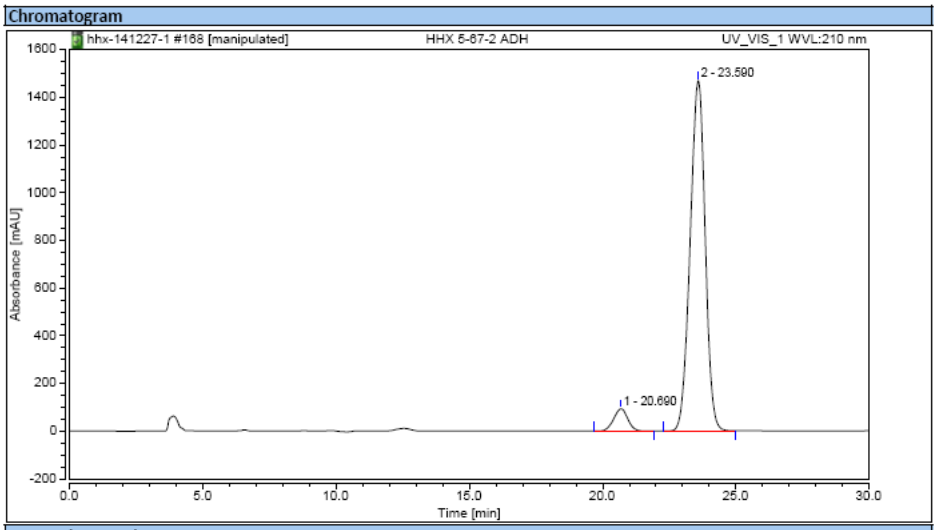
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.79-7.70 (m, 3H), 7.58-7.49 (m, 2H), 7.46-7.40 (m, 1H), 7.37-7.22 (m, 3H), 7.08-7.00 (m, 2H), 6.54 (dd, *J* = 4.4, 2.0 Hz, 1H), 4.76-4.71 (m, 1H), 4.35-4.26 (m, 1H), 4.04-3.96 (m, 1H), 3.93-3.85 (m, 1H), 3.78 (s, 3H), 3.65-3.36 (m, 3H), 3.09-3.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 139.9, 137.4, 133.9, 131.5, 128.6, 126.9, 126.6, 126.4, 125.64, 125.59, 125.5, 124.2, 123.5, 122.1, 121.9, 119.6, 119.2, 117.6, 116.9, 109.4, 62.1, 45.1, 44.3, 43.0, 34.0, 32.8. MS (70 eV): m/z (%): 408 (M^+, 41.13), 44 (100). HRMS calcd for $C_{27}H_{24}N_2O_2$: 408.1838, found: 408.1833. $[\alpha]_D^{20}$ = -62.0 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10, 0.8 mL/min, 210 nm); tr (minor) = 20.69 min, tr

(major) = 23.59 min, 89% *ee*.



Integration Results

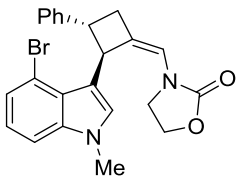
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.600	567.815	947.146	50.00	51.76	n.a.
2		23.463	567.781	882.881	50.00	48.24	n.a.
Total:			**1135.596**	**1830.027**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.690	57.706	93.926	5.66	6.00	n.a.
2		23.590	962.046	1470.558	94.34	94.00	n.a.
Total:			**1019.752**	**1564.484**	**100.00**	**100.00**	

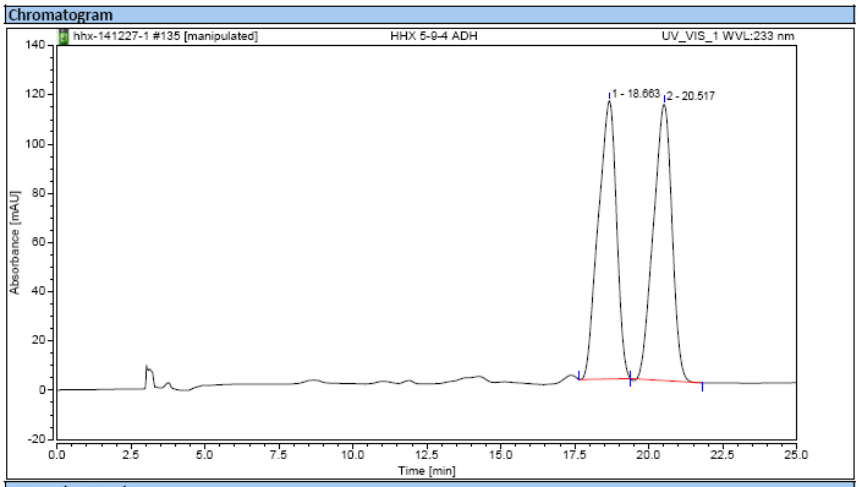
(12) Synthesis of **3l**



3l

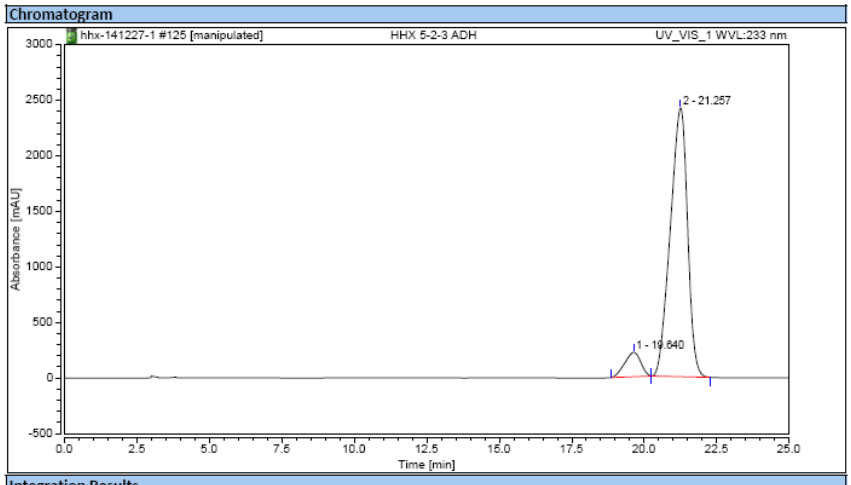
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.33-7.20 (m, 3H),

7.24-7.14 (m, 3H), 7.06-7.01 (m, 1H), 6.55 (s, 1H), 5.24-5.16 (m, 1H), 4.15 (dd, *J* = 14,8, 8.8 Hz, 1H), 3.93 (dd, *J* = 16.8, 8.8 Hz, 1H), 3.78 (s, 3H), 3.72 (dd, J = 17.2, 8.8 Hz, 1H), 3.59-3.49 (m, 1H), 3.42-3.33 (m, 2H), 2.85-2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.7, 138.4, 128.5, 128.2, 126.9, 126.2, 124.2, 123.7, 122.5, 117.9, 117.1, 118.0, 113.9, 108.7, 62.2, 48.3, 46.0, 44.1, 34.4, 33.1. MS (70 eV): m/z (%): 436 (M^+, 70.75), 438 (M^++2, 70.09), 349 (100). HRMS calcd for $C_{23}H_{21}N_2O_2Br$: 346.0786, found: 346.0783. $[\alpha]_D^{20}$ = -41.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 1.0 mL/min, 233 nm; tr (minor) = 19.64 min, tr (major) = 21.26 min, 84% *ee*.



Integration Results

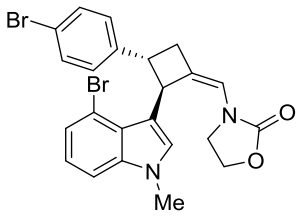
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.663	80.746	113.136	49.69	50.16	n.a.
2		20.517	81.752	112.403	50.31	49.84	n.a.
Total:			**162.498**	**225.540**	**100.00**	**100.00**	



Integration Results

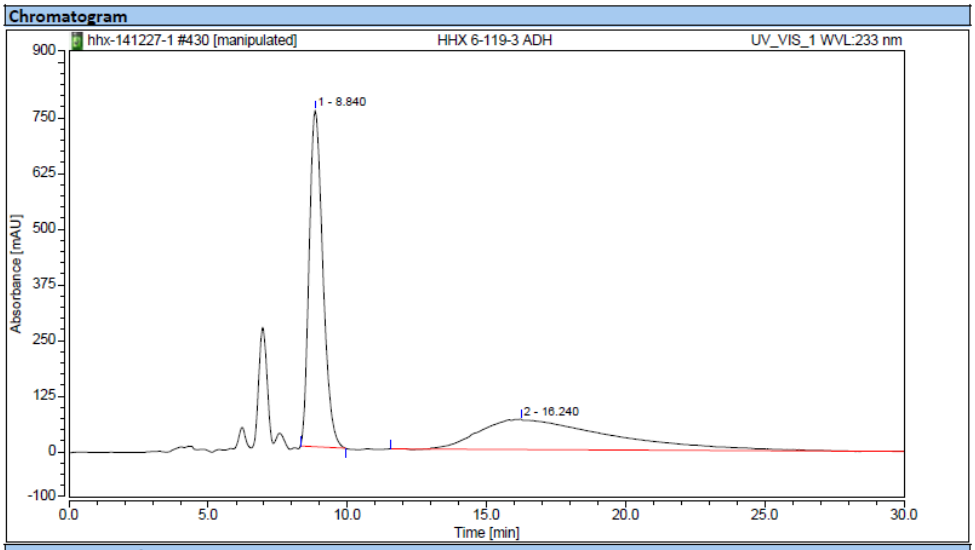
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.640	140.819	219.794	7.79	8.32	n.a.
2		21.257	1667.625	2421.084	92.21	91.68	n.a.
Total:			**1808.444**	**2640.878**	**100.00**	**100.00**	

(13) Synthesis of **3m**



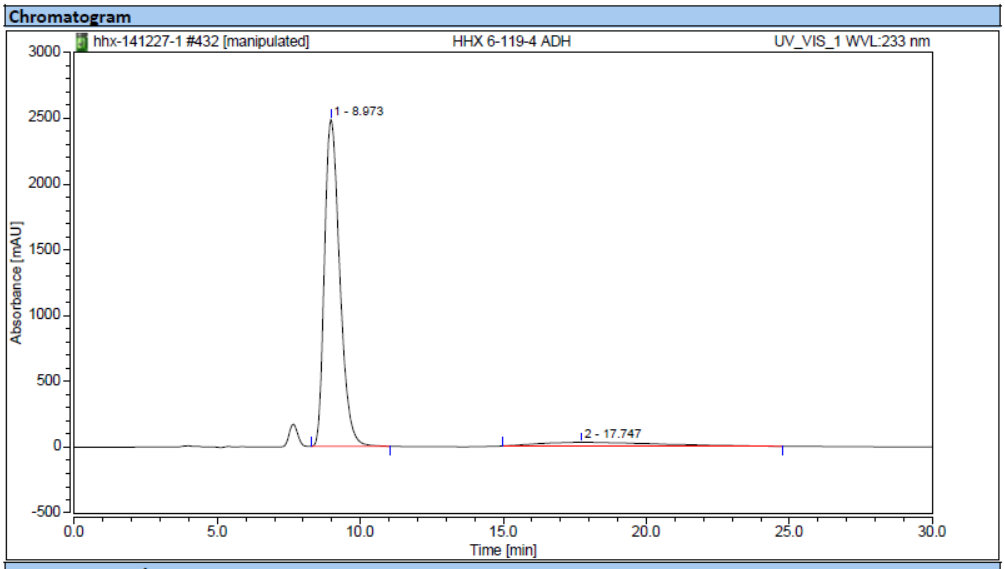
3m

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.30-7.16 (m, 5H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 5.16-5.10 (m, 1H), 4.21 (dd, *J* = 15.2, 8.8 Hz, 1H), 3.99 (dd, *J* = 16.4, 8.8 Hz, 1H), 3.80 (s, 3H), 3.76-3.70 (m, 1H), 3.58-3.49 (m, 1H), 3.41-3.26 (m, 2H), 2.78-2.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 143.8, 138.4, 131.3, 128.7, 128.4, 123.7, 122.7, 119.8, 117.5, 113.8, 108.7, 62.2, 47.6, 46.0, 43.9, 34.4, 33.2. HRMS (ESI) calcd for $C_{23}H_{20}N_2O_2Br_2$ [M+Na$^+$]: 536.9784, found: 536.9778. $[\alpha]_D^{20}$ = 1.7 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 70: 30, 0.8 mL/min, 233 nm; tr (major) = 8.97 min, tr (minor) = 17.75 min, 84% *ee*.



Integration Results

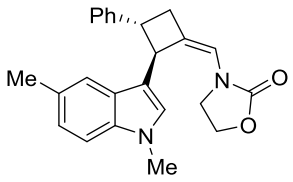
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.840	430.237	755.000	53.89	91.72	n.a.
2		16.240	368.055	68.138	46.11	8.28	n.a.
Total:			**798.293**	**823.138**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.973	1539.436	2487.762	91.76	98.89	n.a.
2		17.747	138.271	27.964	8.24	1.11	n.a.
Total:			**1677.707**	**2515.726**	**100.00**	**100.00**	

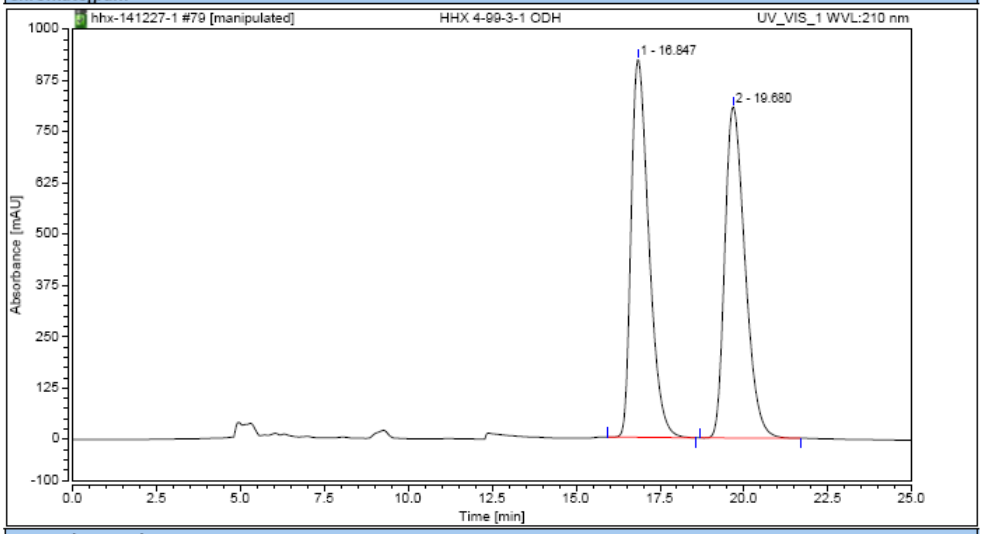
(14) Synthesis of **3n**



3n

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.33 (m, 4H), 7.32-7.22 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 4.46-4.44 (m, 1H), 4.11-4.02 (m, 1H), 3.93 (dd, *J* = 16.8, 8.8 Hz, 1H), 3.78 (s, 3H), 3.61-3.33 (m, 4H), 3.03-2.96 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.9, 135.9, 128.5, 128.4, 126.5, 126.3, 126.1, 123.6, 123.2, 119.1, 117.5, 116.5, 109.0, 62.1, 47.7, 46.3, 44.2, 33.5, 32.8, 21.4. MS (70 eV): m/z (%): 372 (M^+, 100). HRMS calcd for $C_{24}H_{24}N_2O_2$: 372.1838, found: 372.1835. $[\alpha]_D^{20}$ = -5.1 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak OD-H, hexane/2-propanol = 80: 20, 0.6 mL/min, 210 nm; tr (major) = 16.92 min, tr (minor) = 19.70 min, 85% *ee*.

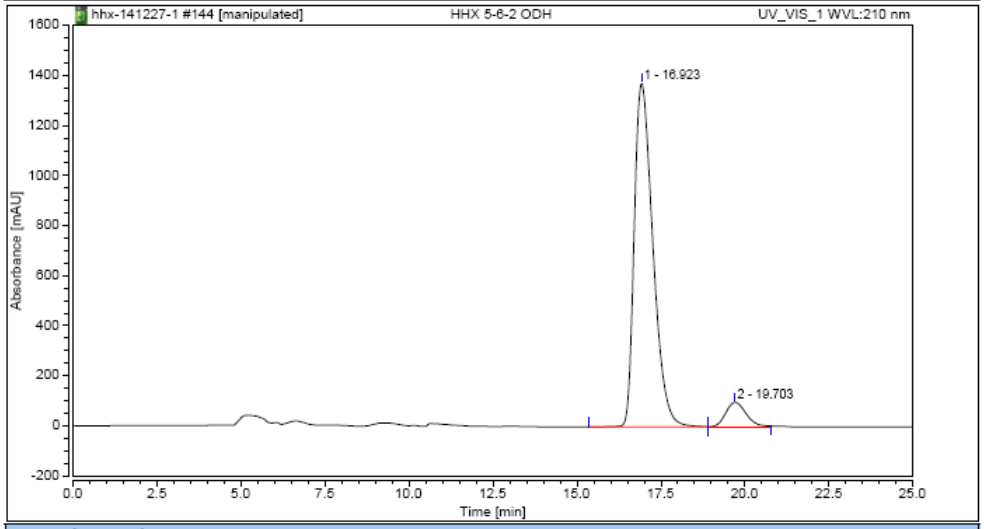
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.847	562.501	921.876	49.97	53.30	n.a.
2		19.680	563.226	807.792	50.03	46.70	n.a.
Total:			**1125.727**	**1729.667**	**100.00**	**100.00**	

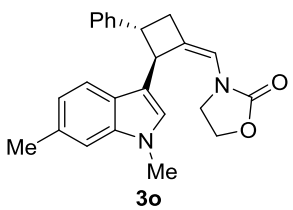
Chromatogram



Integration Results

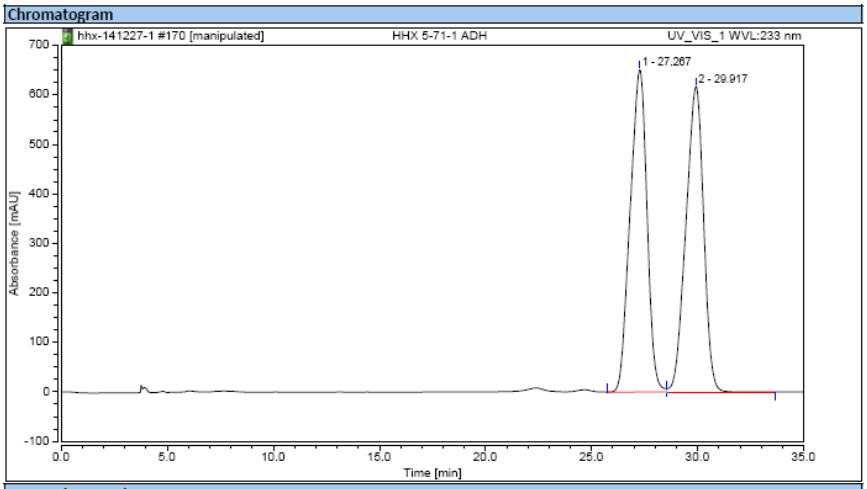
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.923	882.215	1373.250	92.65	93.33	n.a.
2		19.703	69.999	98.212	7.35	6.67	n.a.
Total:			**952.214**	**1471.462**	**100.00**	**100.00**	

(15) Synthesis of **3o**



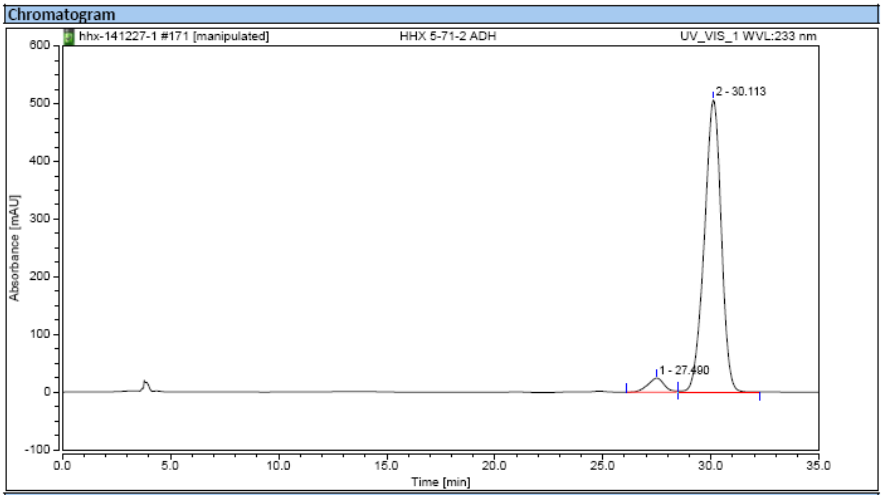
3o

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.31 (m, 5H), 7.29-7.21 (m, 1H), 7.12 (s, 1H), 7.04 -6.87 (m, 2H), 6.55 (s, 1H), 4.51-4.40 (m, 1H), 4.10-4.02 (m, 1H), 3.90 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.74 (s, 3H), 3.59-3.28 (m, 4H), 3.07-2.93 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.9, 137.9, 131.9, 128.5, 126.5, 126.3, 125.4, 124.17, 123.0, 120.9, 119.2, 117.6, 117.0, 109.4, 62.1, 47.7, 46.4, 44.2, 33.5, 32.7, 21.8. MS (70 eV): m/z (%): 372 (M^+, 100). HRMS calcd for $C_{24}H_{24}N_2O_2$: 372.1838, found: 372.1844. $[\alpha]_D^{20}$ = 0.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 0.8 mL/min, 233 nm; tr (minor) = 27.49 min, tr (major) = 30.11 min, 91% *ee*.



Integration Results

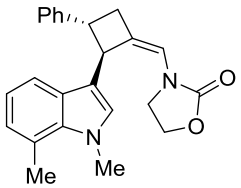
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.267	599.044	652.458	50.02	51.35	n.a.
2		29.917	598.481	618.074	49.98	48.65	n.a.
Total:			**1197.525**	**1270.532**	**100.00**	**100.00**	



Integration Results

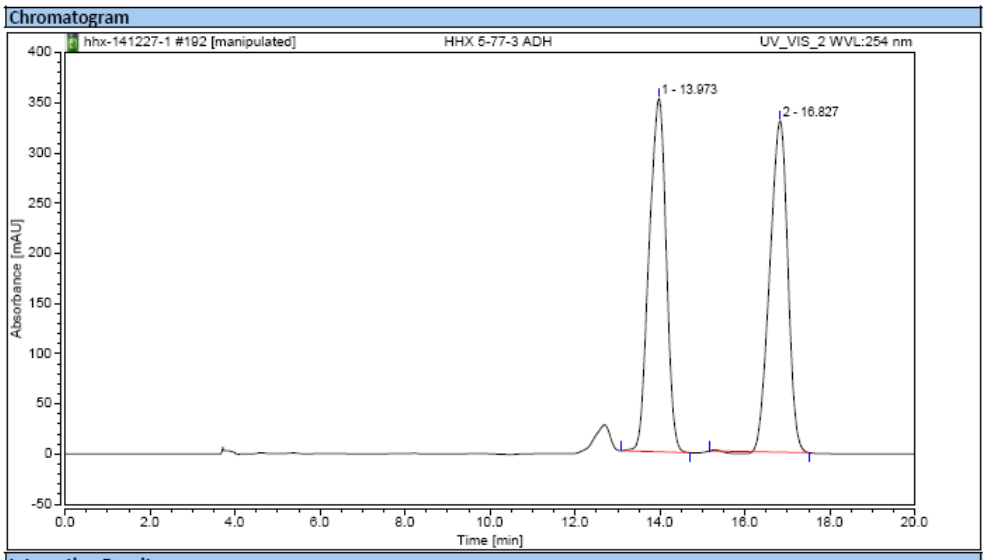
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.490	21.527	24.263	4.47	4.57	n.a.
2		30.113	460.062	506.850	95.53	95.43	n.a.
Total:			**481.589**	**531.113**	**100.00**	**100.00**	

(16) Synthesis of **3p**



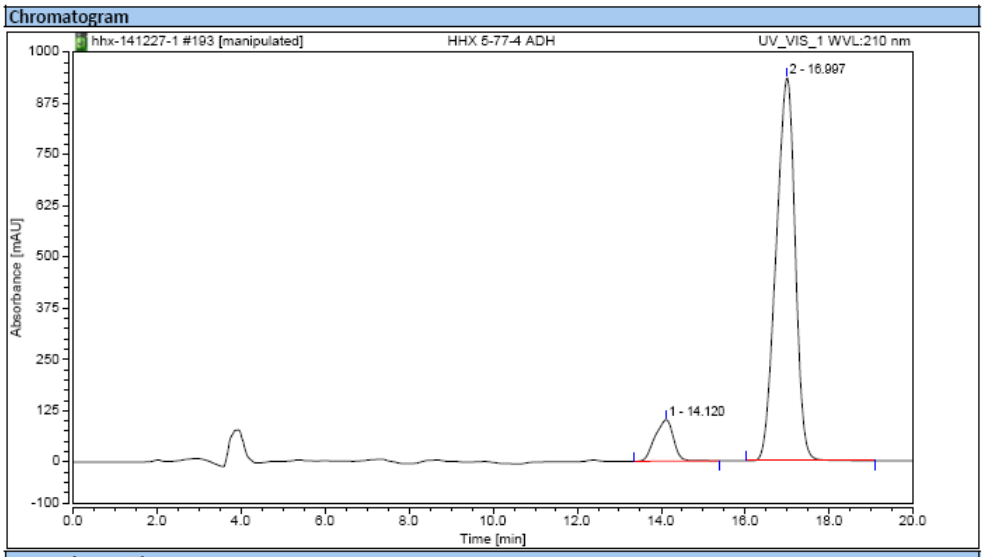
3p

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 4H), 7.22-7.12 (m, 2H), 6.85-6.82 (m, 2H), 6.78 (s, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 4.37-4.31 (m, 1H), 4.02-3.93 (m, 1H), 3.96 (s, 3H), 3.85 (dd, *J* = 16.8, 8.8 Hz, 1H), 3.49-3.33 (m, 3H), 3.30-3.21 (m, 1H), 2.91-2.82 (m, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 145.0, 136.2, 128.5, 127.6, 127.3, 126.5, 126.3, 124.6, 122.9, 121.4, 119.4, 117.6, 117.5, 116.8, 62.1, 47.4, 46.4, 44.1, 36.7, 33.6, 19.7. MS (70 eV): m/z (%): 372 (M^+, 81.09), 285 (100). HRMS calcd for $C_{24}H_{24}N_2O_2$: 372.1838, found: 372.1835. $[\alpha]_D^{20}$ = -23.5 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10, 0.8 mL/min, 254 nm; tr (minor) = 14.12 min, tr (major) = 17.00 min, 81% *ee*.



Integration Results

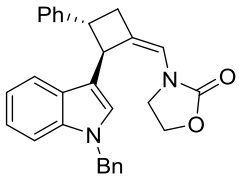
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.973	163.899	352.282	50.41	51.58	n.a.
2		16.827	161.205	330.713	49.59	48.42	n.a.
Total:			**325.104**	**682.995**	**100.00**	**100.00**	



Integration Results

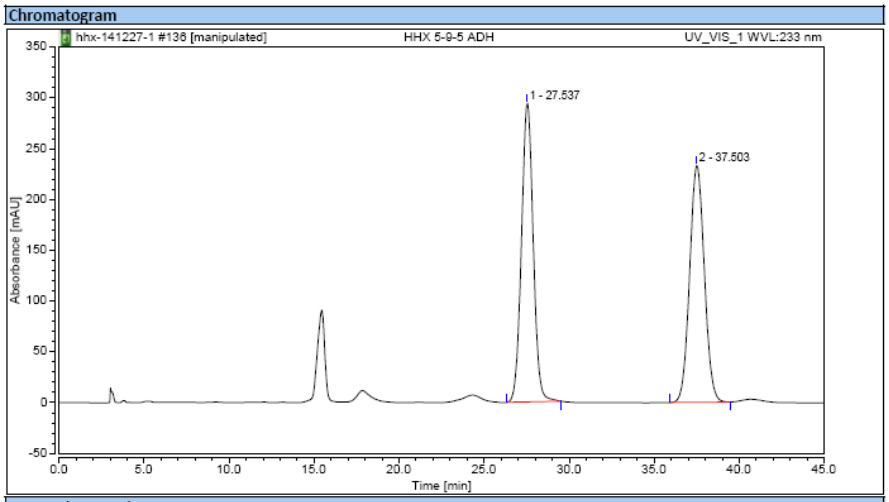
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.120	51.824	101.197	9.54	9.76	n.a.
2		16.997	491.278	935.298	90.46	90.24	n.a.
Total:			543.102	1036.495	100.00	100.00	

(17) Synthesis of **3q**



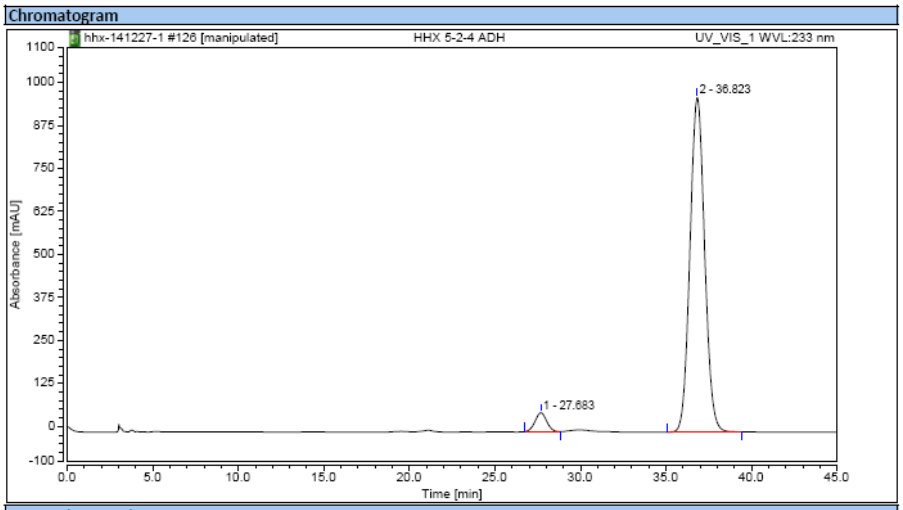
3q

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.37-7.14 (m, 10H), 7.12-7.09 (m, 2H), 7.08-7.04 (m, 2H), 6.49 (dd, *J* = 4.4, 2.4 Hz, 1H), 5.28 (dd, *J* = 22.4, 16 Hz, 2H), 4.47-4.42 (m, 1H), 3.96-3.90 (m, 1H), 3.67 (dd, *J* = 16.8, 8.8 Hz, 1H), 3.62-3.53 (m, 1H), 3.43-3.25 (m, 3H), 3.03-2.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 144.7, 137.6, 137.0, 128.8, 128.5, 127.8, 126.8, 126.52, 126.48, 126.4, 125.3, 123.3, 122.2, 119.6, 119.4, 117.6, 109.9, 61.9, 50.0, 47.7, 46.3, 44.3, 33.5. MS (70 eV): m/z (%): 434 (M^+, 59.67), 91 (100). HRMS calcd for $C_{29}H_{26}N_2O_2$: 434.1994, found: 434.1999. $[\alpha]_D^{20}$ = -7.7 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 95: 5, 1.0 mL/min, 233 nm; tr (minor) = 27.68 min, tr (major) = 36.82 min, 92% *ee*.



Integration Results

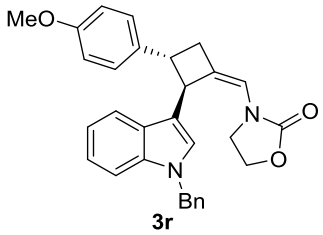
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.537	235.926	294.468	50.25	55.80	n.a.
2		37.503	233.559	233.247	49.75	44.20	n.a.
Total:			**469.486**	**527.715**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.683	42.833	54.708	4.25	5.33	n.a.
2		36.823	965.308	971.744	95.75	94.67	n.a.
Total:			**1008.141**	**1026.452**	**100.00**	**100.00**	

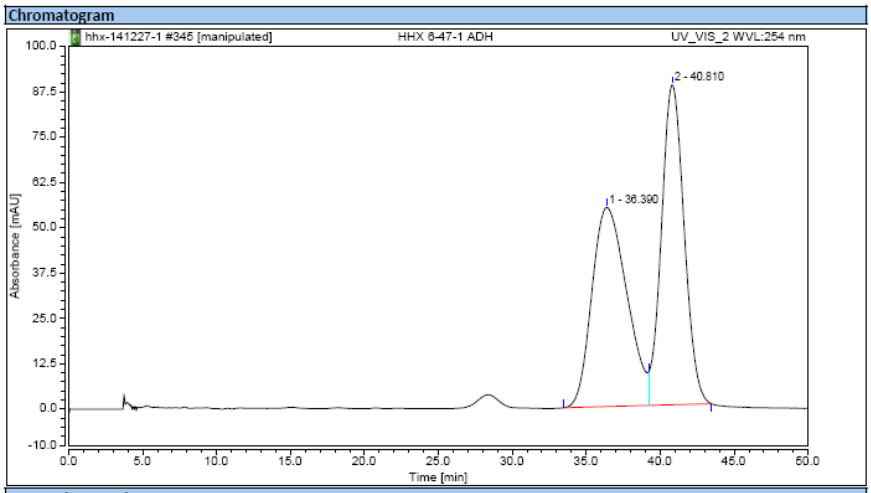
(18) Synthesis of **3r**



3r

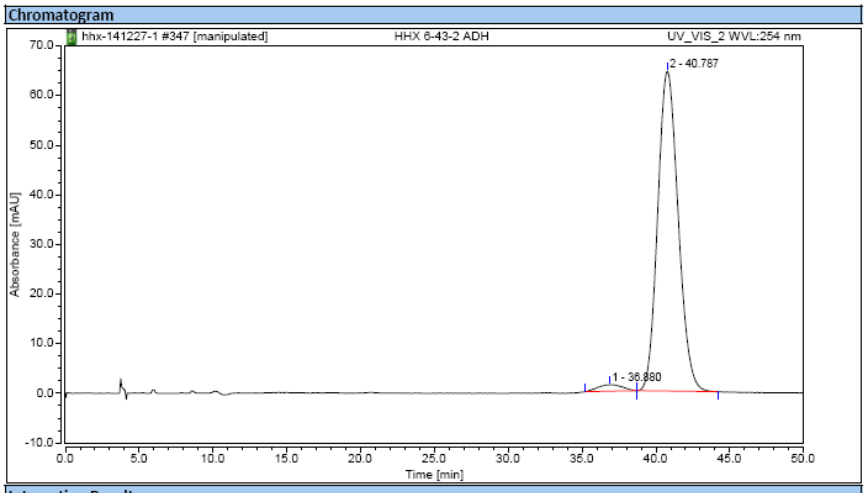
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.34-7.18 (m, 7H),

7.14-7.03 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 2.0 Hz, 1H), 5.28 (dd, *J* = 20.4, 16.0 Hz, 2H), 4.42-4.37 (m, 1H), 3.99-3.89 (m, 1H), 3.81 (s, 3H), 3.67 (dd, *J* = 17.2, 8.4 Hz, 1H), 3.51 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.45-3.22 (m, 3H), 2.99-2.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 156.3, 137.6, 137.0, 136.9, 128.8, 127.8, 127.5, 126.8, 126.6, 125.3, 123.5, 122.2, 119.6, 119.4, 117.7, 117.6, 113.9, 109.9, 61.9, 55.3, 50.0, 47.9, 45.8, 44.4, 33.8. MS (70 eV): m/z (%): 464 (M^+, 55.59), 91 (100). HRMS calcd for $C_{30}H_{28}N_2O_3$: 464.2100, found: 464.2096. $[\alpha]_D^{20}$ = 20.7 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10, 0.8 mL/min, 254 nm); tr (minor) = 36.88 min, tr (major) = 40.79 min, 95% *ee*.



Integration Results

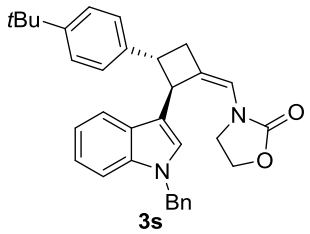
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		36.390	150.592	54.969	48.91	38.37	n.a.
2		40.810	157.328	88.278	51.09	61.63	n.a.
Total:			**307.919**	**143.247**	**100.00**	**100.00**	



Integration Results

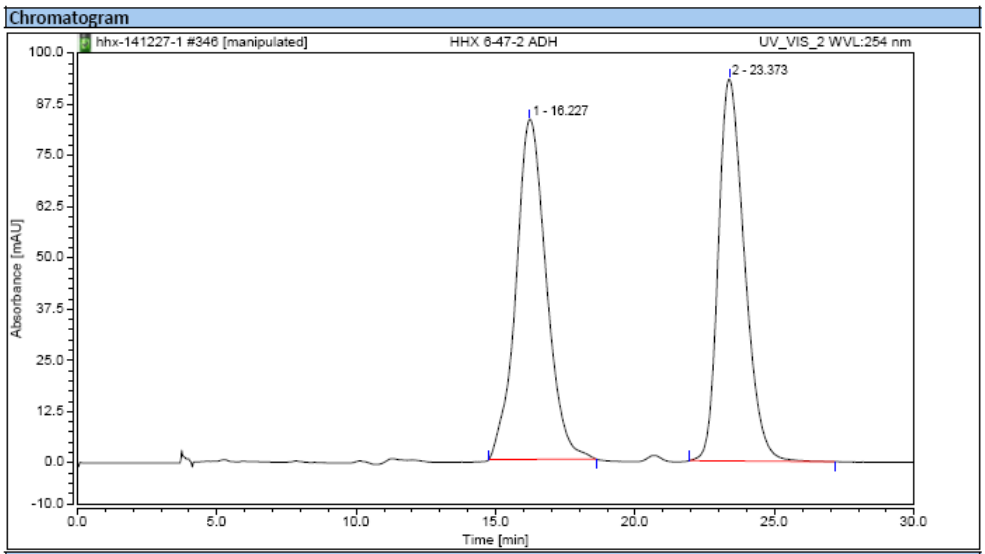
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		36.880	2.486	1.322	2.34	2.01	n.a.
2		40.787	103.661	64.513	97.66	97.99	n.a.
Total:			**106.147**	**65.835**	**100.00**	**100.00**	

(19) Synthesis of **3s**



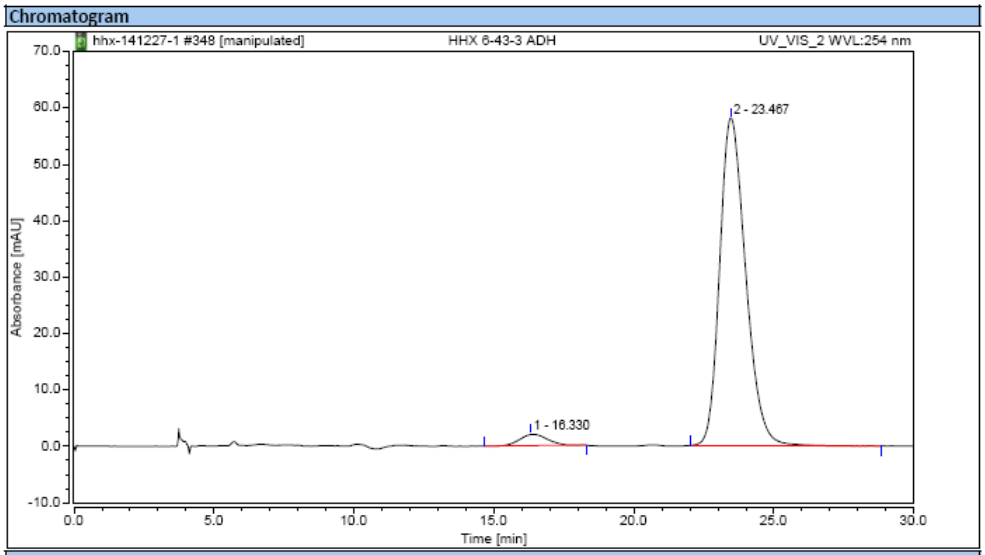
3s

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.38-7.32 (m, 2H), 7.31-7.22 (m, 6H), 7.21-7.18 (m, 1H), 7.12-7.03 (m, 4H), 6.49 (d, *J* = 2.0 Hz, 1H), 5.28 (dd, *J* = 20.4, 16.0 Hz, 2H), 4.47-4.42 (m, 1H), 3.97-3.92 (m, 1H), 3.69 (dd, *J* = 17.2, 8.8 Hz, 1H), 3.59-3.53 (m, 1H), 3.44-3.37 (dd, *J* = 15.2, 8.8 Hz, 1H), 3.37-3.25 (m, 2H), 3.00-2.94 (m, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.2, 141.7, 137.6, 137.0, 128.8, 127.8, 126.8, 126.6, 126.2, 125.3, 123.5, 122.2, 119.6, 119.4, 117.7, 117.5, 109.8, 61.9, 55.3, 50.0, 47.9, 45.8, 44.4, 33.8. MS (70 eV): m/z (%): 490 (M^+, 55.59), 91 (100). HRMS calcd for $C_{33}H_{34}N_2O_2$: 490.2620, found: 490.2617. $[\alpha]_D^{20}$ = 37.5 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10, 0.8 mL/min, 254 nm; tr (minor) = 16.33 min, tr (major) = 23.47 min, 93% *ee*.



Integration Results

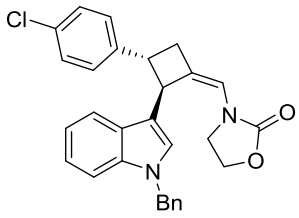
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.227	104.993	83.063	50.90	47.12	n.a.
2		23.373	101.293	93.226	49.10	52.88	n.a.
Total:			**206.286**	**176.290**	**100.00**	**100.00**	



Integration Results

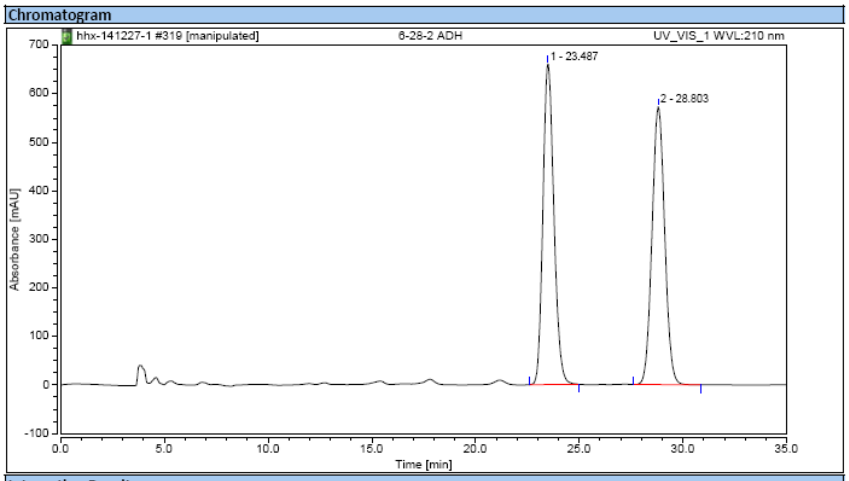
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.330	2.268	2.021	3.50	3.35	n.a.
2		23.467	62.440	58.204	96.50	96.65	n.a.
Total:			**64.708**	**60.224**	**100.00**	**100.00**	

(20) Synthesis of **3t**



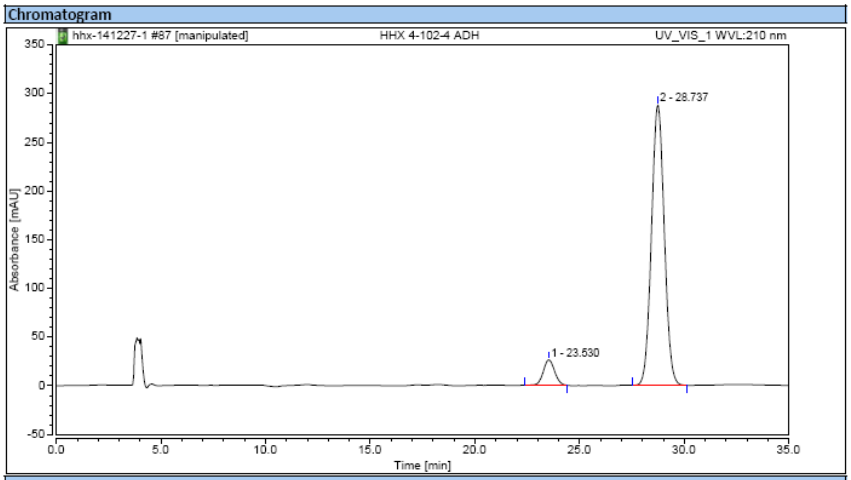
3t

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.39-7.14 (m, 9H), 7.13-7.04 (m, 4H), 6.51 (d, *J* = 2.4 Hz, 1H), 5.32 (dd, *J* = 23.6, 16.0 Hz, 2H), 4.42-4.37 (m, 1H), 3.98-3.91 (m, 1H), 3.72-3.64 (m, 1H), 3.58-3.52 (m, 1H), 3.47-3.28 (m, 3H), 2.98-2.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 143.1, 137.5, 137.0, 132.0, 128.8, 128.6, 127.9, 127.8, 126.7, 126.4, 125.3, 122.7, 122.3, 119.5, 119.4, 117.8, 117.3, 109.9, 61.9, 50.0, 47.8, 45.8, 44.3, 33.5. MS (70 eV): m/z (%): 468 (M^+, 27.43), 91 (100). HRMS calcd for $C_{29}H_{25}N_2O_2Cl$: 468.1605, found: 468.1602. $[\alpha]_D^{20}$ = 36.9 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10, 0.8 mL/min, 210 nm); tr (minor) = 23.63 min, tr (major) = 28.74 min, 85% *ee*.



Integration Results

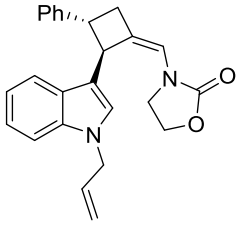
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.487	404.357	660.973	49.96	53.57	n.a.
2		28.803	404.942	572.864	50.04	46.43	n.a.
Total:			**809.298**	**1233.837**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.530	16.417	26.181	7.43	8.33	n.a.
2		28.737	204.637	288.244	92.57	91.67	n.a.
Total:			**221.054**	**314.425**	**100.00**	**100.00**	

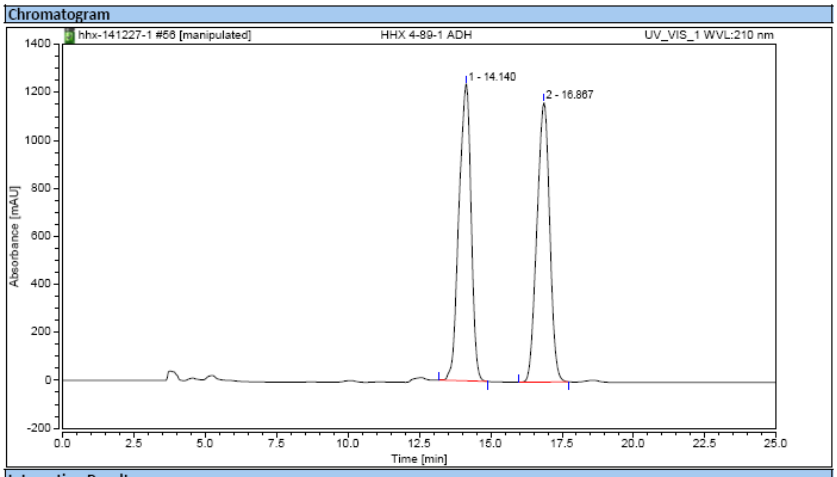
(21) Synthesis of **3u**



3u

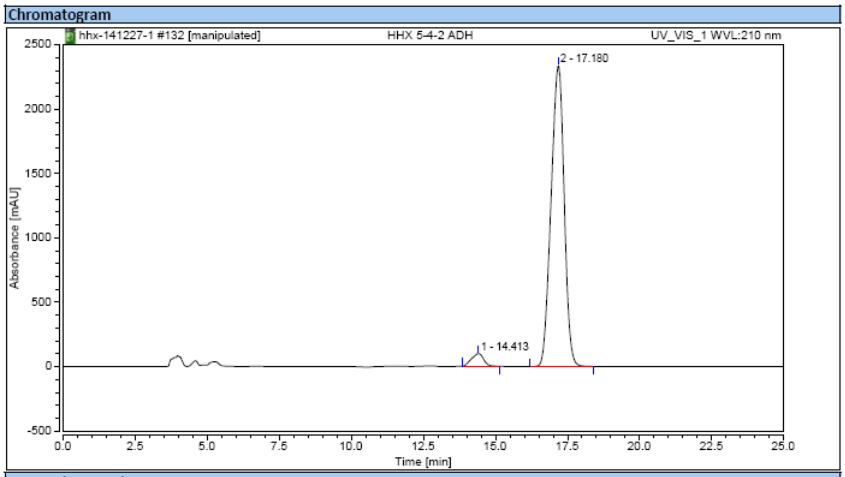
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.37-7.27 (m, 5H), 7.26-7.16 (m, 2H), 7.09-7.01 (m, 2H), 6.52 (dd, *J* = 4.4, 2.0 Hz, 1H), 6.04-5.92 (m, 1H), 5.19(dd, *J* = 10.4, 1.2 Hz, 1H), 5.04 (dd, *J* = 16.8, 1.2 Hz, 1H), 4.74-4.69 (m, 2H),

4.46-4.42 (m, 1H), 4.03-3.97 (m, 1H), 3.87-3.80 (m, 1H), 3.61-3.28 (m, 4H), 3.03-2.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 144.7, 136.8, 133.4, 128.5, 126.4, 126.3, 125.0, 123.4, 122.0, 119.5, 119.4, 117.5, 117.3, 117.1, 109.7, 62.0, 48.7, 47.6, 46.3, 44.2, 33.6. MS (70 eV): m/z (%): 384 (M^+, 100). HRMS calcd for $C_{25}H_{24}N_2O_2$: 384.1838, found: 384.1840. $[\alpha]_D^{20}$ = -18.5 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak AD-H, hexane/2-propanol = 90: 10, 0.8 mL/min, 210 nm; tr (minor) = 14.41 min, tr (major) = 17.18 min, 93% *ee*.



Integration Results

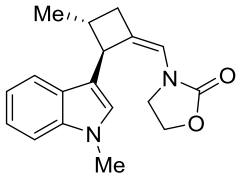
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.140	607.810	1237.926	50.15	51.52	n.a.
2		16.867	604.063	1164.911	49.85	48.48	n.a.
Total:			**1211.873**	**2402.837**	**100.00**	**100.00**	



Integration Results

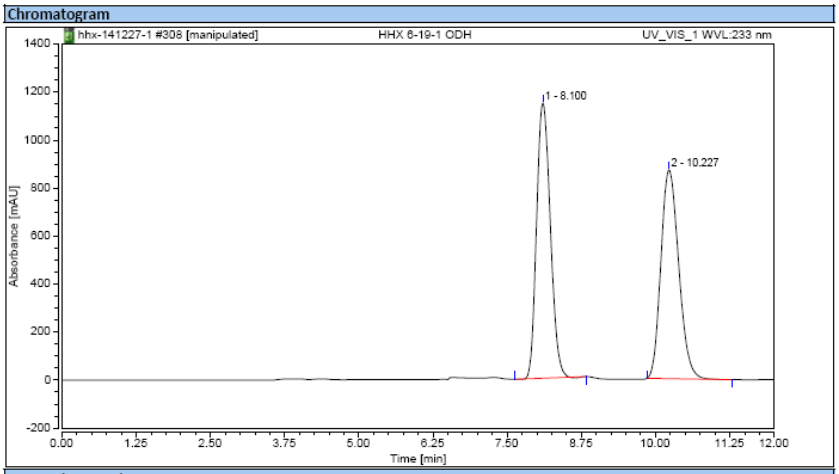
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.413	47.712	98.991	3.74	4.06	n.a.
2		17.180	1228.661	2337.773	96.26	95.94	n.a.
Total:			**1276.374**	**2436.764**	**100.00**	**100.00**	

(22) Synthesis of **3w**



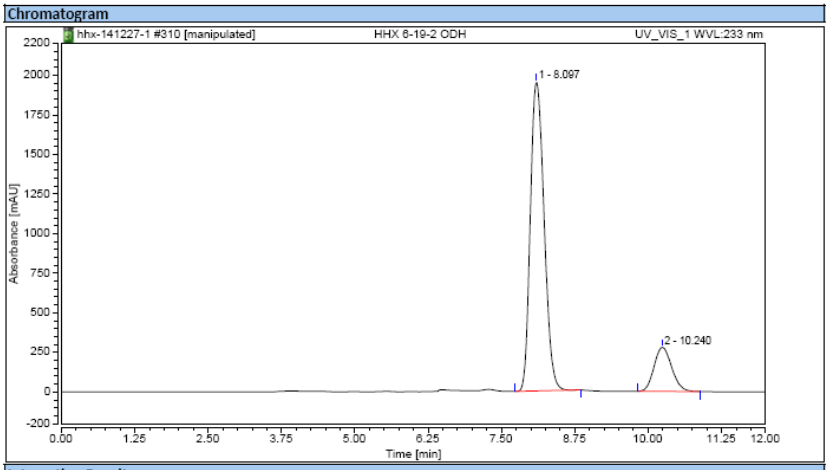
3w

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.38-7.22 (m, 2H), 7.19-7.13 (m, 1H), 6.94 (s, 1H), 6.46 (s, 1H), 4.21-4.06 (m, 1H), 4.01-3.91 (m, 2H), 3.79 (s, 3H), 3.62-3.49 (m, 2H), 3.11-3.05 (m, 1H), 2.43-2.32 (m, 2H), 1.36 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 137.4, 126.4, 125.7, 123.7, 121.8, 119.1, 118.9, 117.5, 117.4, 109.3, 62.1, 45.9, 44.1, 36.8, 33.8, 32.7, 21.4. MS (70 eV): m/z (%): 296 (M^+, 24.35), 57 (100). HRMS calcd for $C_{18}H_{20}N_2O_2$: 296.1525, found: 196.1528. $[\alpha]_D^{20}$ = -30.5 (*c* = 0.3, $CHCl_3$). HPLC conditions: Chiralpak OD-H, hexane/2-propanol = 70: 30, 0.8 mL/min, 233 nm); tr (minor) = 8.10 min, tr (major) = 10.24 min, 69% *ee*.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.100	307.470	1148.578	50.40	56.87	n.a.
2		10.227	302.632	871.250	49.60	43.13	n.a.
Total:			**610.103**	**2019.828**	**100.00**	**100.00**	



Integration Results

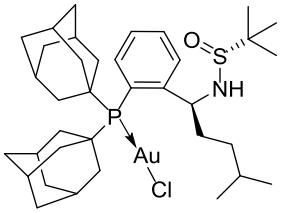
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.097	530.636	1950.353	84.56	87.52	n.a.
2		10.240	96.908	278.066	15.44	12.48	n.a.
Total:			627.544	2228.419	100.00	100.00	

6. References

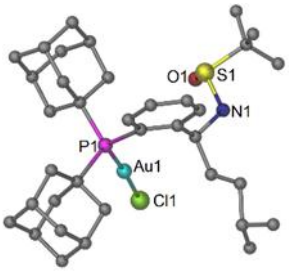
1 (a) L. B. Schenkel and J. A. Ellman, *Org. Lett.,* **2003**, *5*, 545. (b) Z.-M. Zhang, P. Chen, W. Li, Y. Niu, X.-L. Zhao and J. Zhang, *Angew. Chem. Int. Ed.*, **2014**, *53*, 4350.

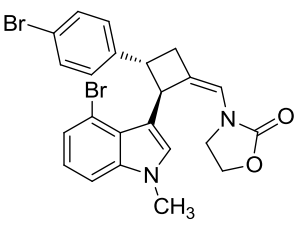
2 (a) H. Gao, X. Wu, J. Zhang, *Chem. Eur. J.,* **2011**, *17*, 2838. (b) Y. Wang, P. Zhang, Y. Liu, F. Xia and J. Zhang, *Chem. Sci.*, **2015**, *6*, 5564.

7. X-ray crystal data

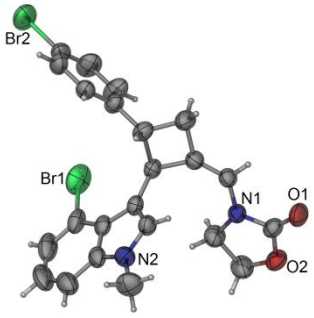


(S, R_S)-**X7***AuCl

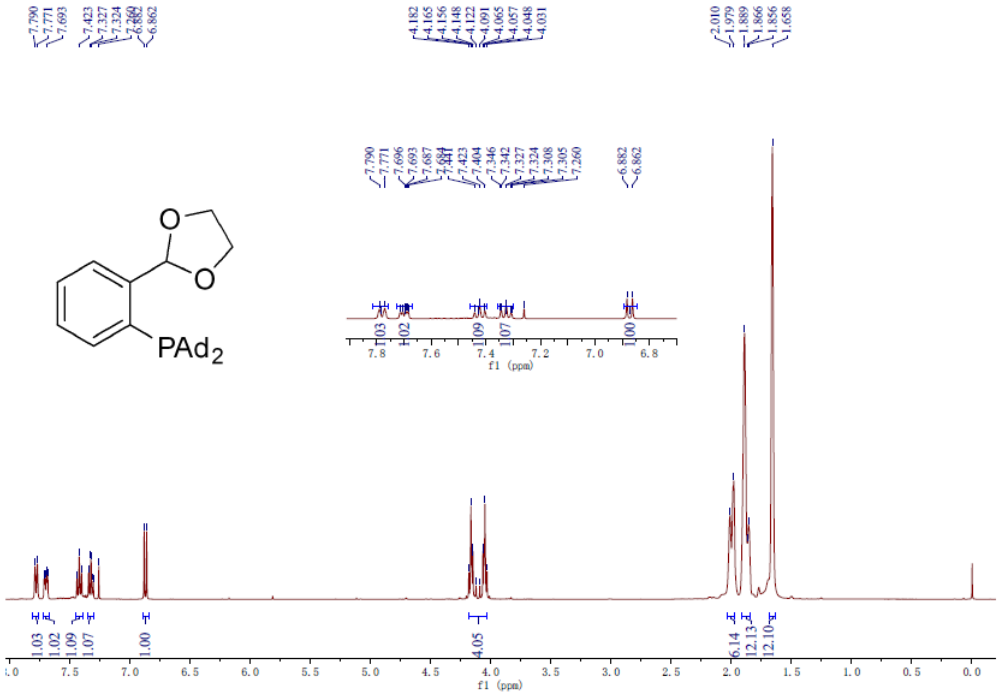


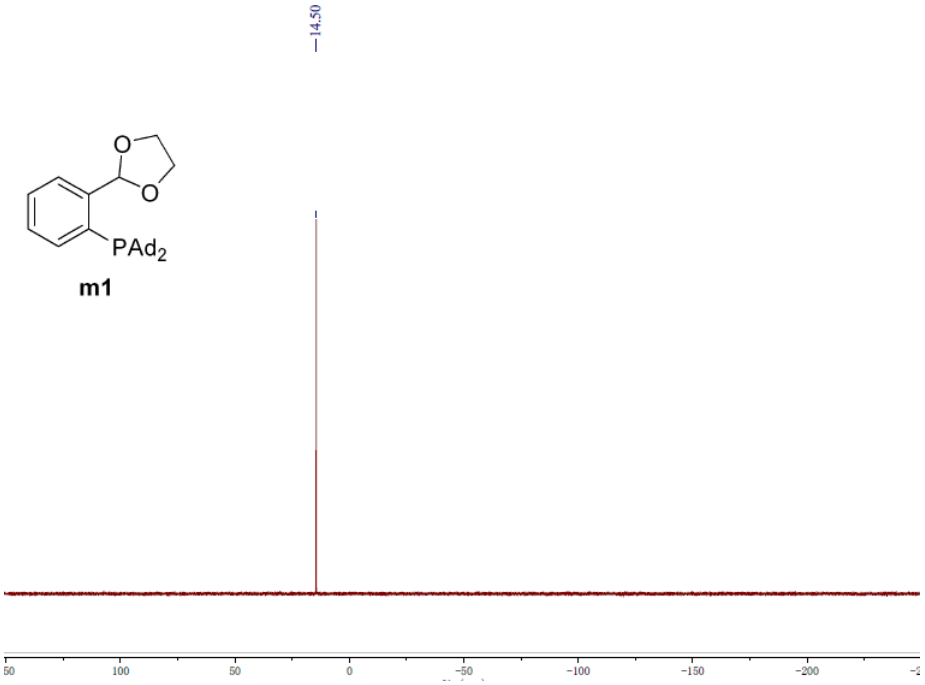


3m

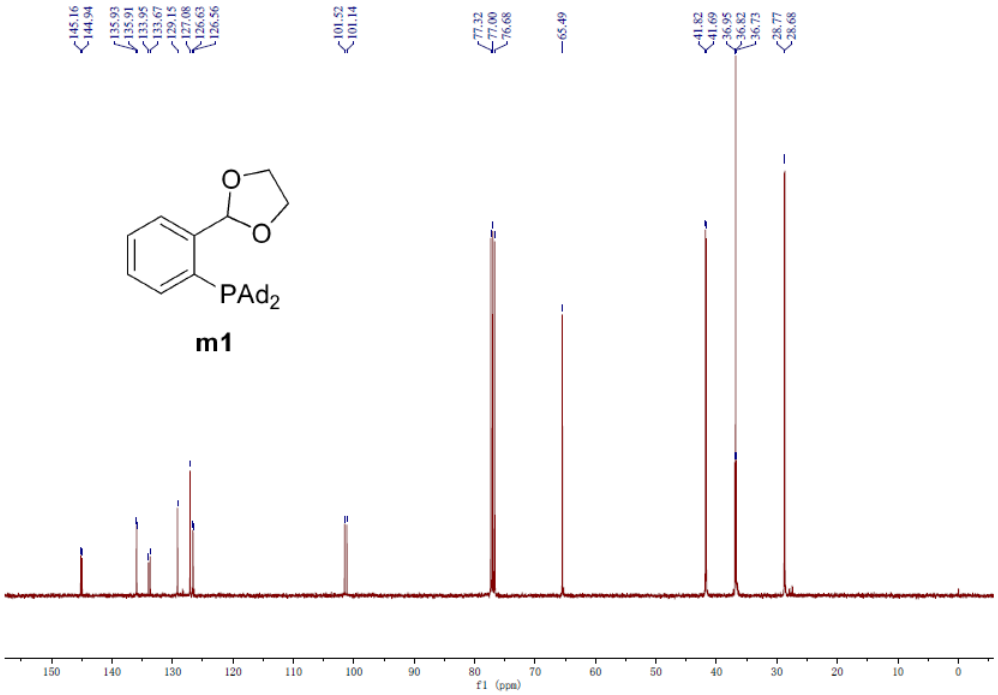


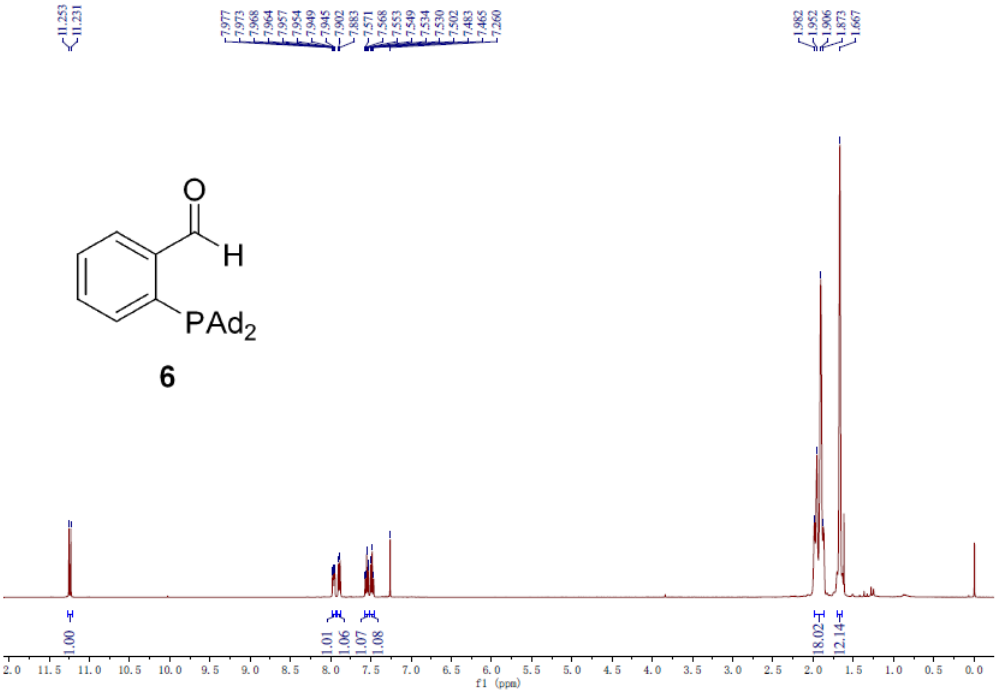
8. Copies of NMR Spectra for [2+2] adducts

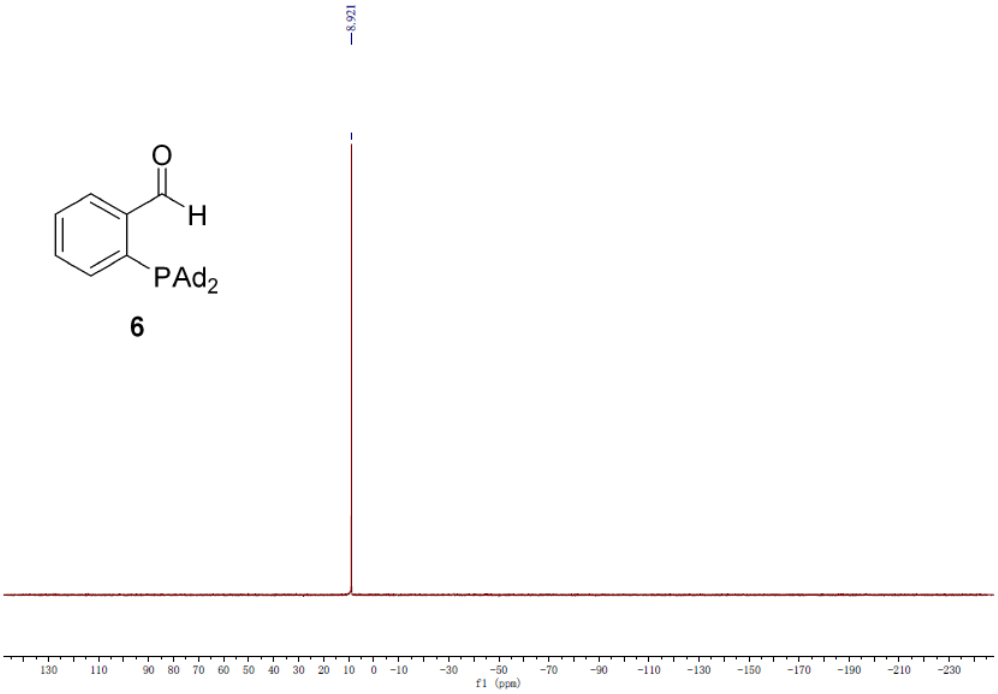


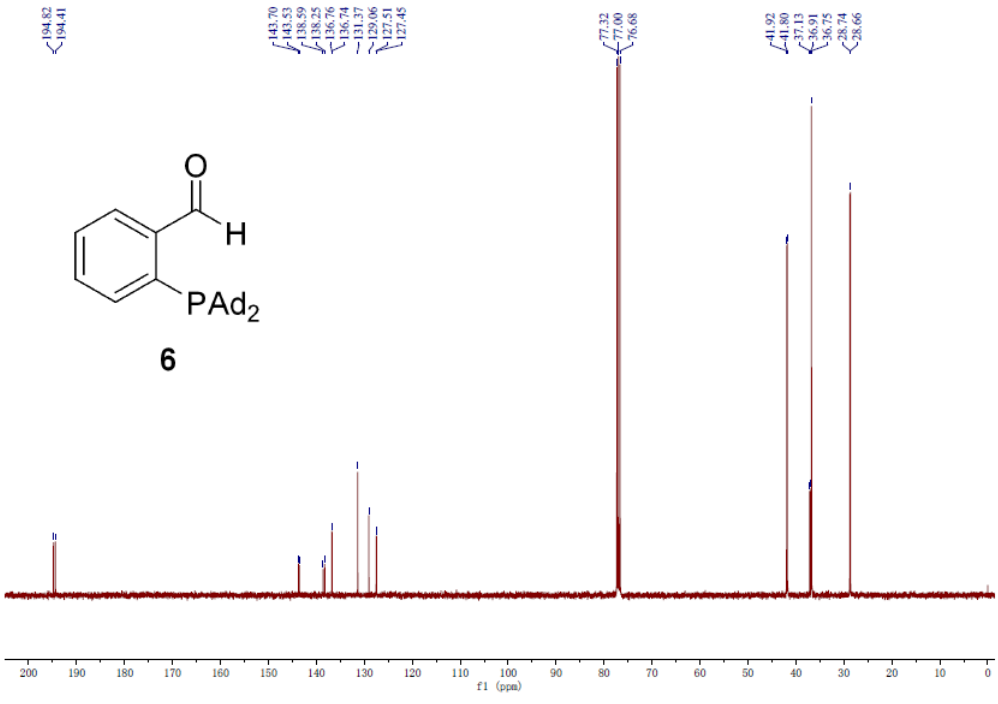


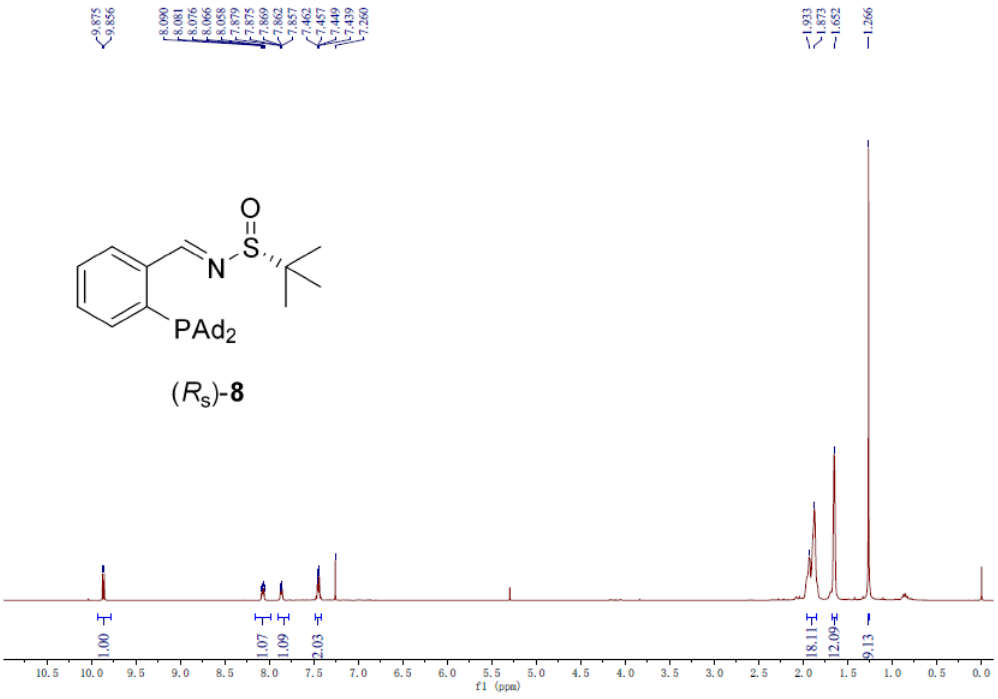
m1


145.16
144.94
135.93
135.91
133.95
133.67
129.15
127.08
126.63
126.56
101.52
101.14
77.32
77.00
76.68
65.49
41.82
41.69
36.95
36.82
36.73
28.77
28.68
O
O
PAd2
m1
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

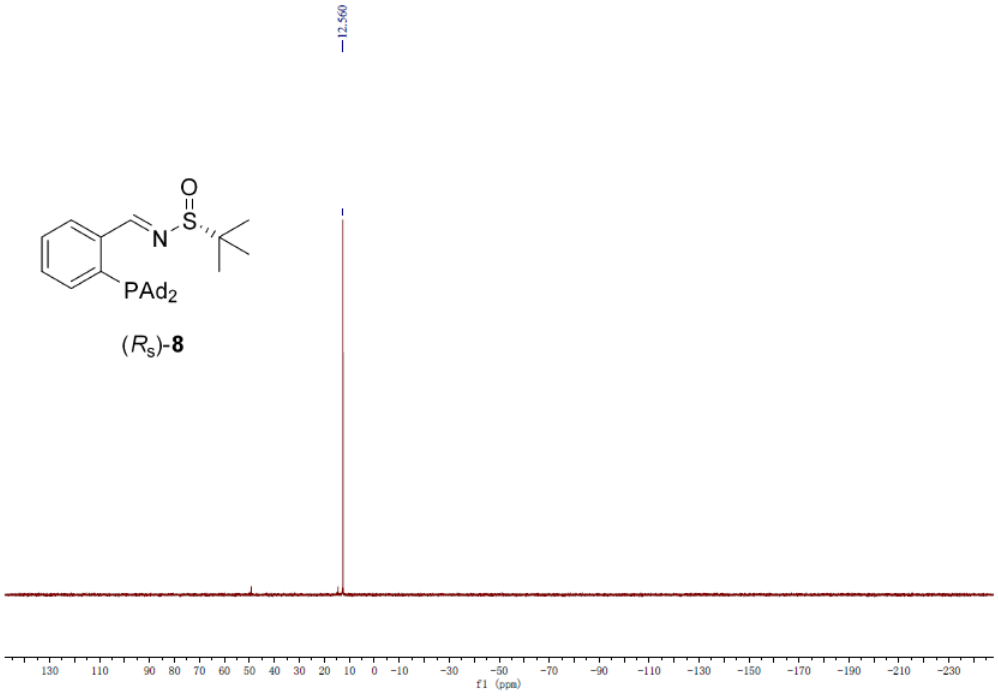

11.253
11.231
7.977
7.973
7.968
7.964
7.957
7.954
7.949
7.945
7.902
7.883
7.571
7.568
7.553
7.549
7.534
7.530
7.502
7.483
7.465
7.260
1.982
1.952
1.906
1.873
1.667
O
H
PAd2
6
1.00
1.01
1.06
1.07
1.08
18.02
12.14
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


8.921
O
H
PAd2
6
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

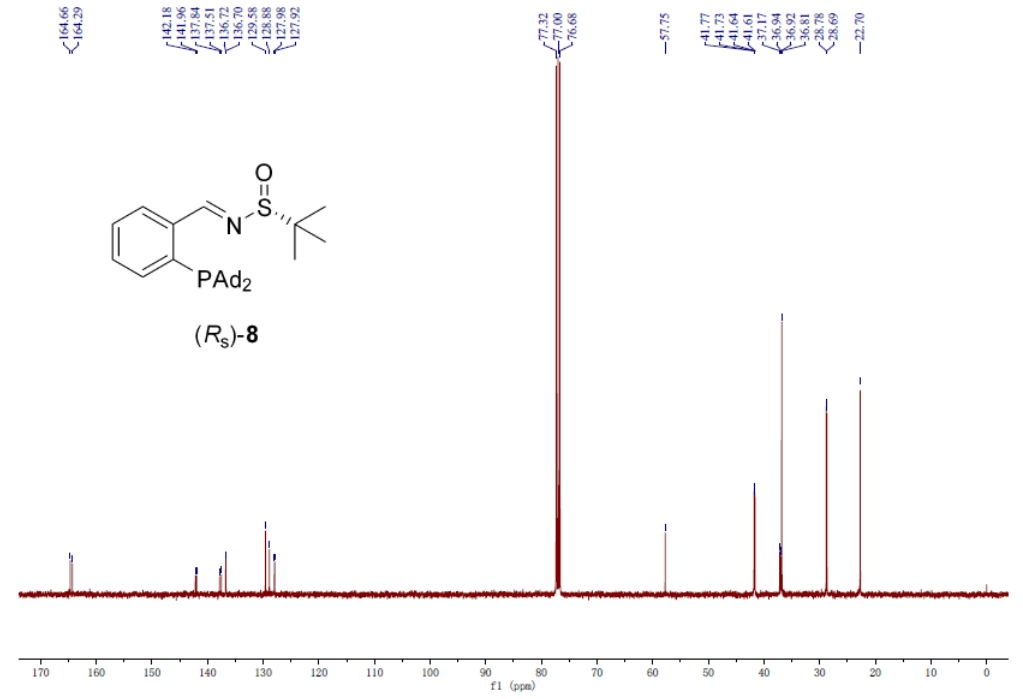

194.82
194.41
143.70
143.53
138.59
138.25
136.76
136.74
131.37
129.06
127.51
127.45
77.32
77.00
76.68
41.92
41.80
37.13
36.91
36.75
28.74
28.66
O
H
PAd2
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

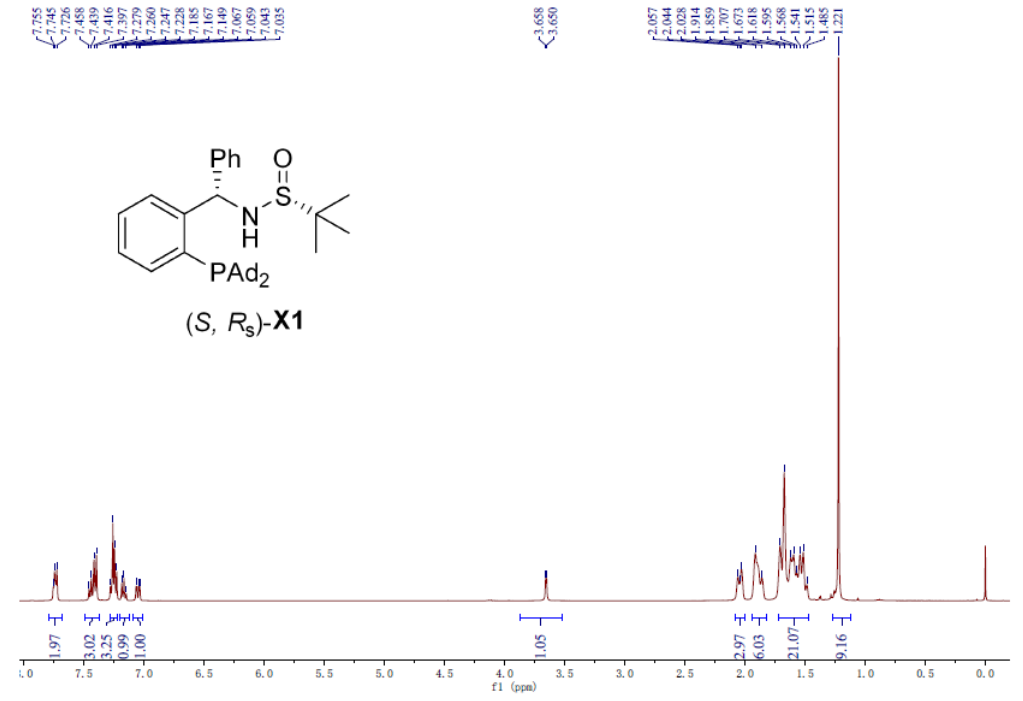

9.875
9.856
8.090
8.081
8.076
8.066
8.058
7.879
7.875
7.869
7.862
7.857
7.462
7.457
7.449
7.439
7.260
1.933
1.873
1.652
1.266
O
S
N
PAd2
1.00
1.07
1.09
2.03
18.11
12.09
9.13
f1 (ppm)

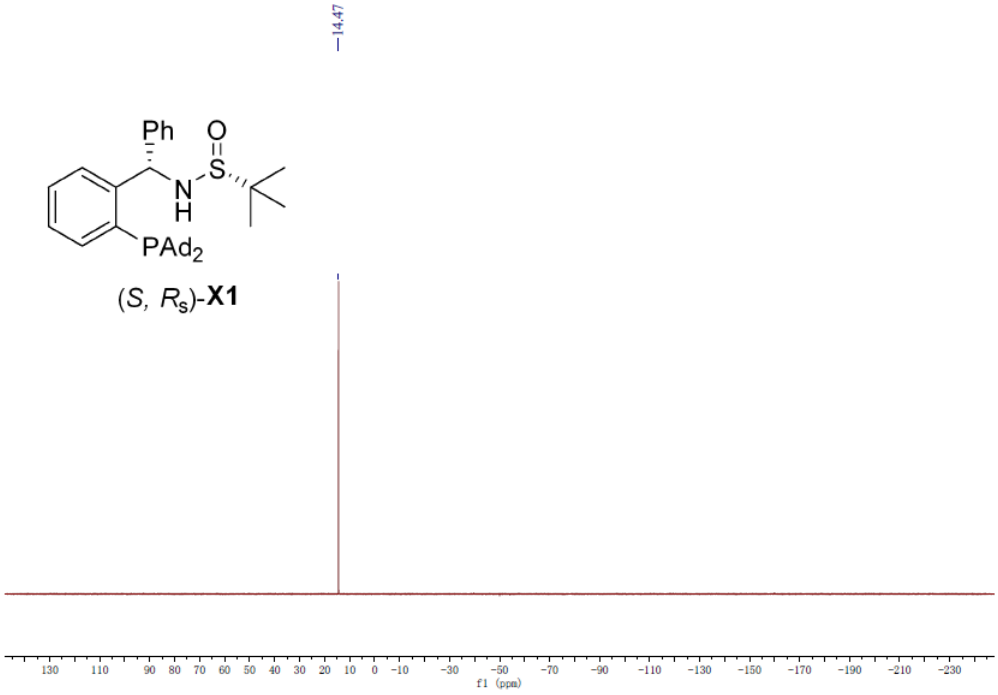
(R_S)-**8**

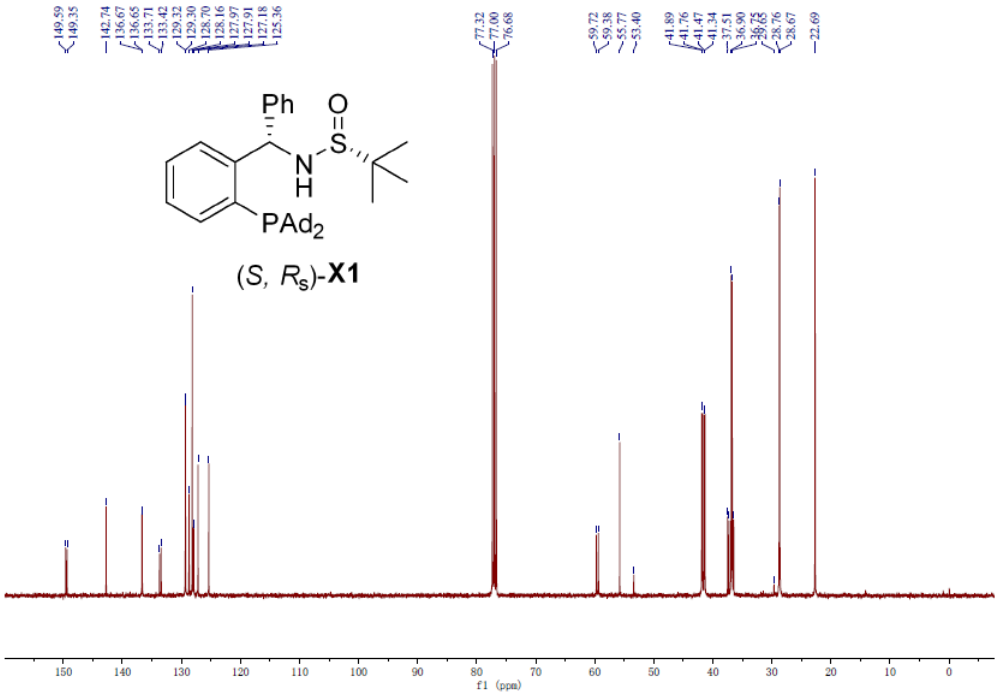

12.560
O
S
N
PAd2
f1 (ppm)

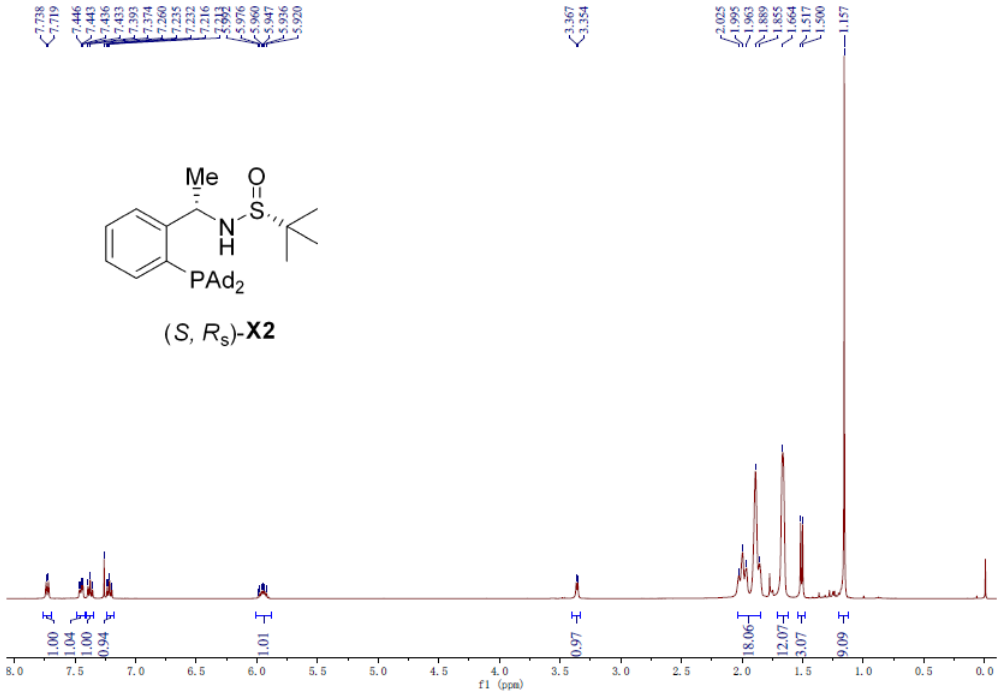
(R_S)-**8**


164.66
164.29
142.18
141.96
137.84
137.51
136.72
136.70
129.58
128.88
127.98
127.92
77.32
77.00
76.68
57.75
41.77
41.73
41.64
41.61
37.17
36.94
36.92
36.81
28.78
28.69
22.70
O
S
N
PAd2
(Rs)-8
f1 (ppm)

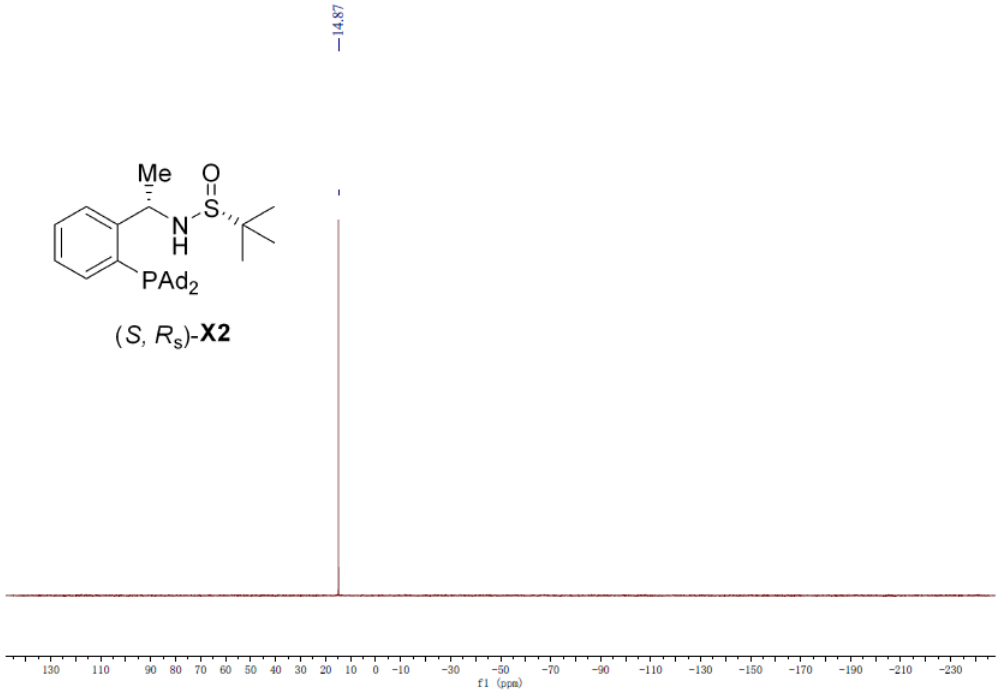

7.755
7.745
7.726
7.458
7.439
7.416
7.397
7.279
7.260
7.247
7.228
7.165
7.167
7.149
7.067
7.059
7.043
7.035
3.658
3.650
2.057
2.044
2.028
1.914
1.859
1.707
1.673
1.618
1.595
1.568
1.541
1.515
1.485
1.221
Ph
O
S
N
H
PAd2
(S, Rs)-X1
1.97
3.02
3.25
0.99
1.00
1.05
2.97
6.03
21.07
9.16
f1 (ppm)


14.47
Ph
O
S
N
H
PAd2
(S, Rs)-X1
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

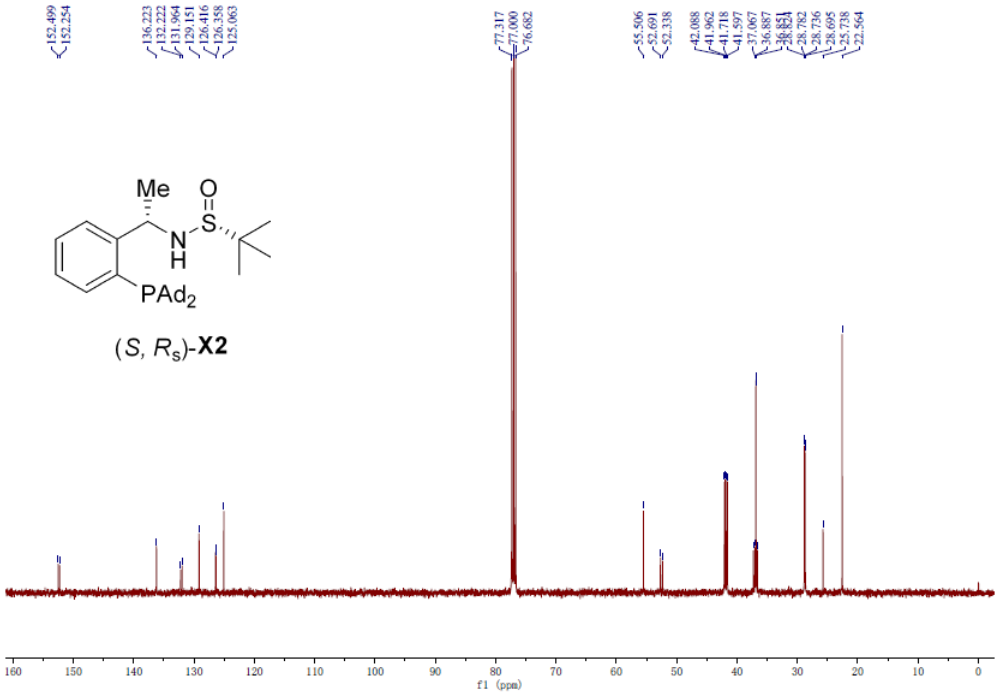

149.59
149.35
142.74
136.67
136.65
133.71
133.42
129.32
129.30
128.70
128.16
127.97
127.91
127.18
125.36
77.32
77.00
76.68
59.72
59.38
55.77
53.40
41.89
41.76
41.47
41.34
37.51
36.90
28.65
28.63
28.76
28.67
22.69
Ph
O
S
N
H
PAd2
(S, Rs)-X1
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.738
7.719
7.446
7.443
7.436
7.433
7.393
7.374
7.260
7.235
7.232
7.216
7.213
5.992
5.976
5.960
5.947
5.936
5.920
3.367
3.354
2.025
1.995
1.963
1.889
1.855
1.664
1.517
1.500
1.157
Me
O
S
N
H
PAd2
1.00
1.04
1.00
0.94
1.01
0.97
18.06
12.07
3.07
9.09
f1 (ppm)

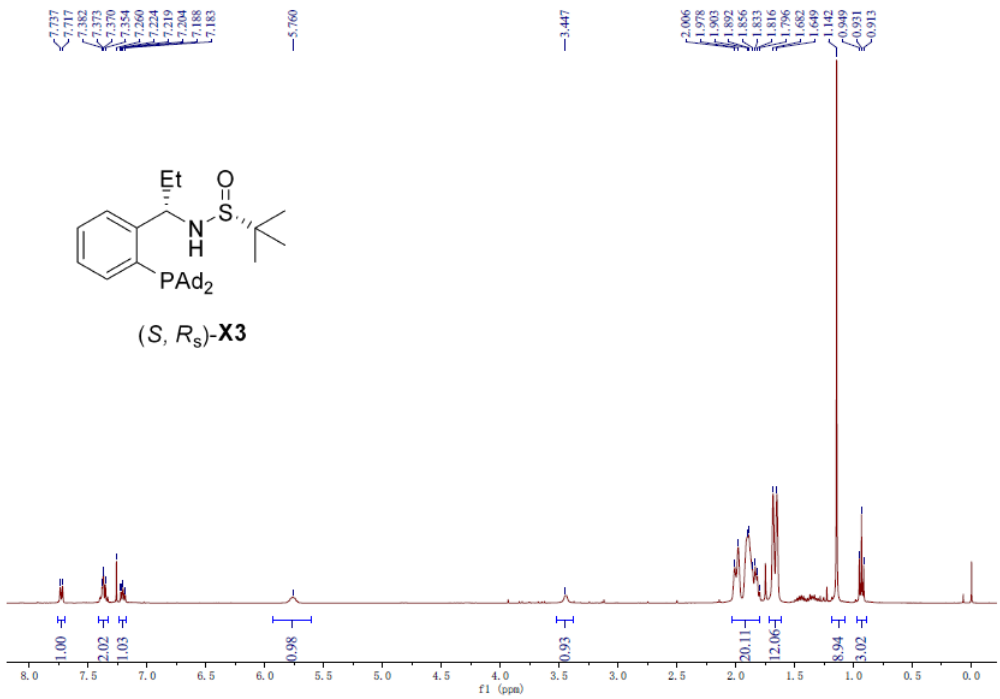
(S, R_s)-**X2**


14.87
Me
O
S
N
H
PAd2
f1 (ppm)

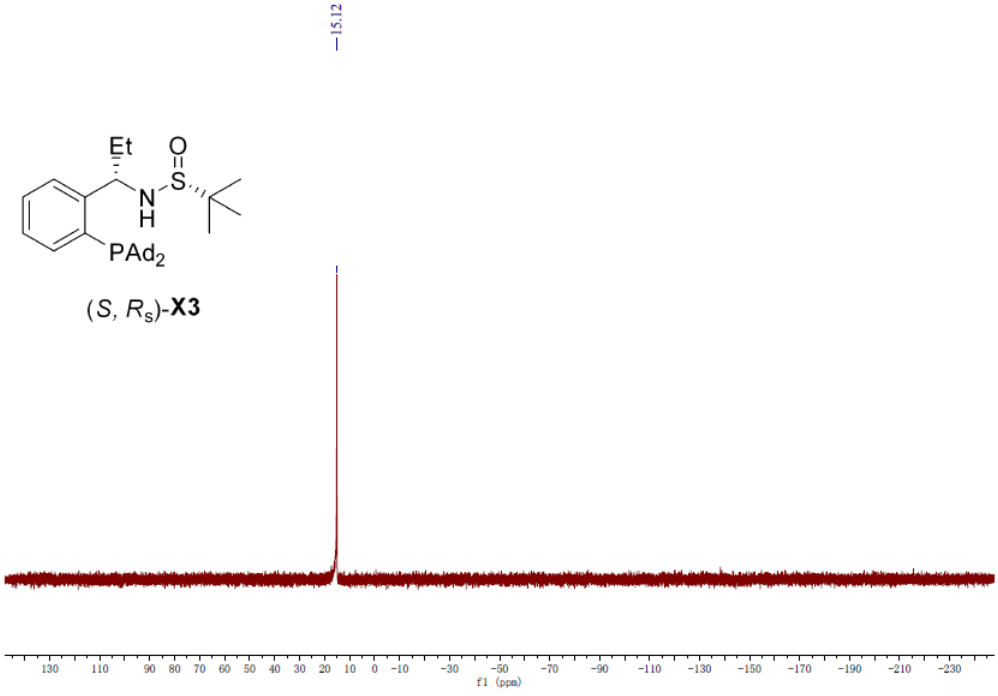
(S, R_s)-**X2**



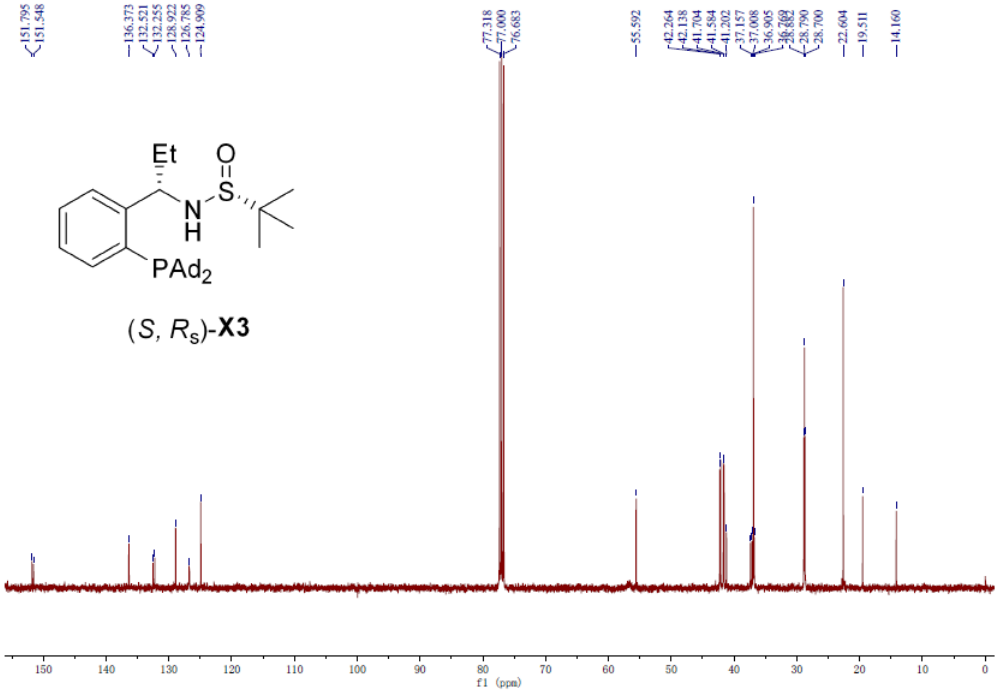
(S, R_S)-**X2**



(S, R_S)-**X3**


15.12
Et
O
S
N
H
PAd2
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

(*S*, R_s)-**X3**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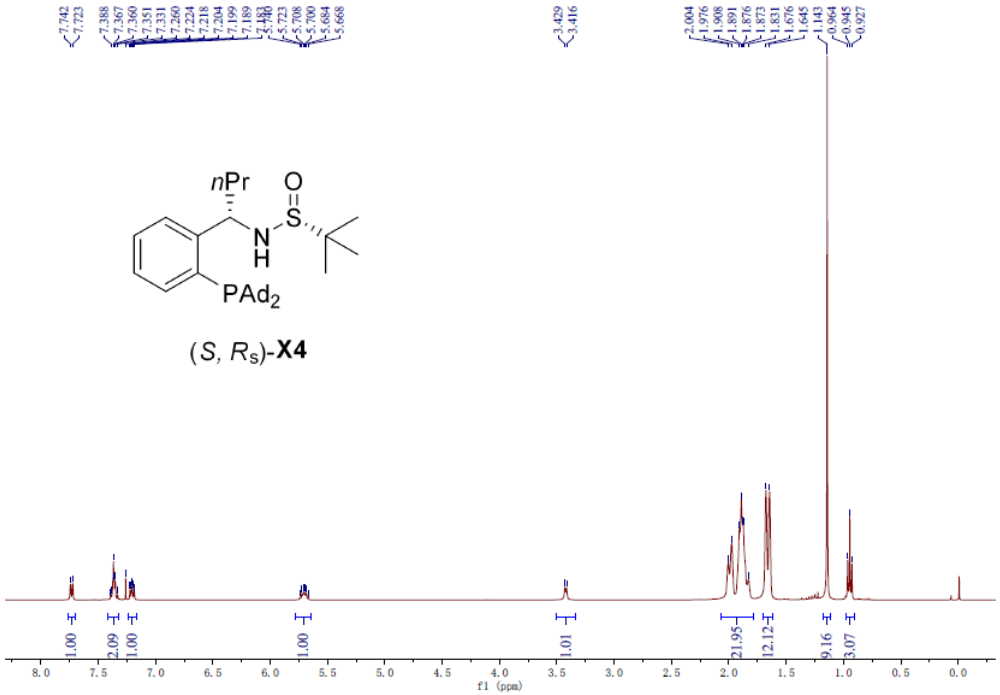
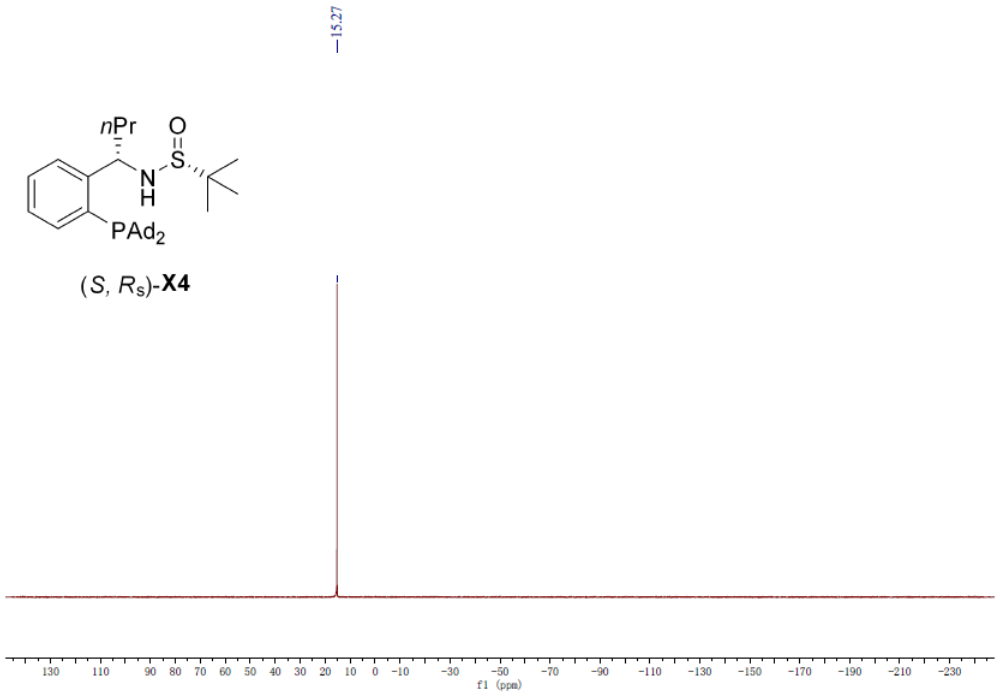
151.548
136.373
132.521
132.255
128.922
126.785
124.909
77.318
77.000
76.683
55.592
42.264
42.138
41.704
41.584
41.202
37.157
37.008
36.905
28.790
28.700
22.604
19.511
14.160
Et
O
S
N
H
PAd2
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

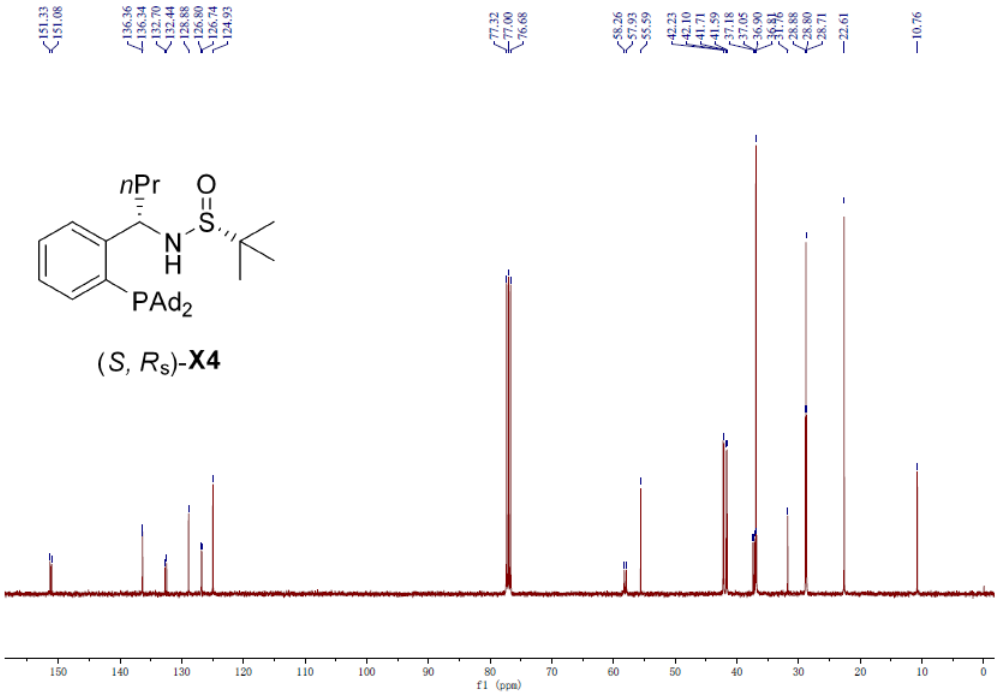
(*S*, R_s)-**X3**


7.742
7.723
7.388
7.367
7.360
7.351
7.331
7.260
7.224
7.218
7.204
7.199
7.189
5.723
5.708
5.700
5.684
5.668
3.429
3.416
2.004
1.976
1.908
1.891
1.876
1.873
1.831
1.676
1.645
1.143
0.964
0.945
0.927
nPr
O
S
N
H
PAd2
1.00
2.09
1.00
1.00
1.01
21.95
12.12
9.16
3.07
f1 (ppm)

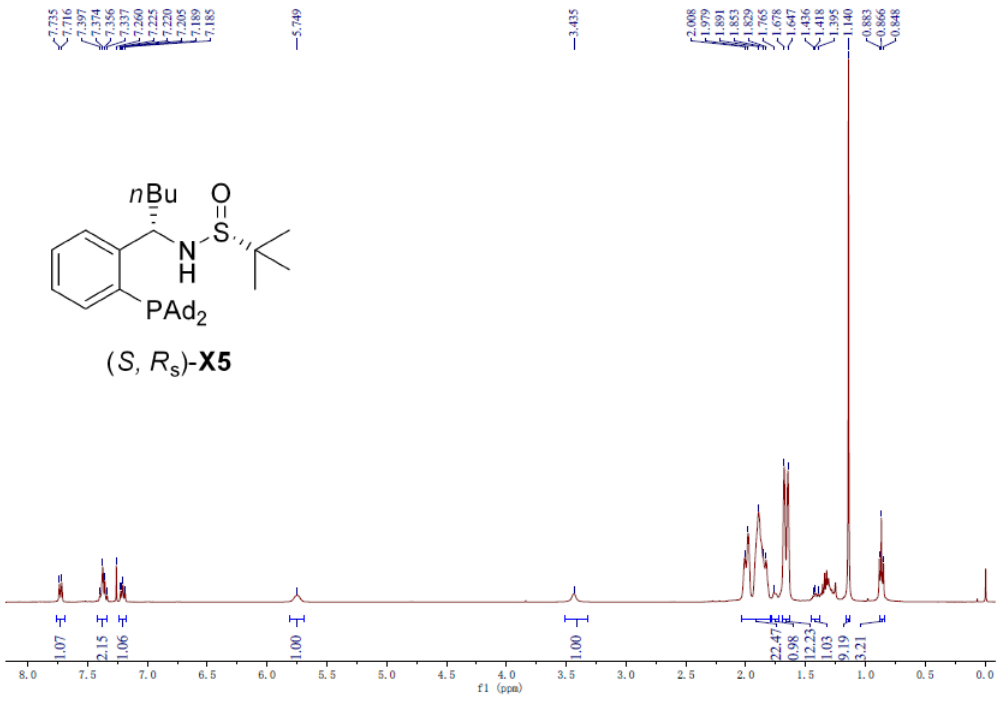
(S, R_s)-**X4**


15.27
nPr
O
S
N
H
PAd2
f1 (ppm)

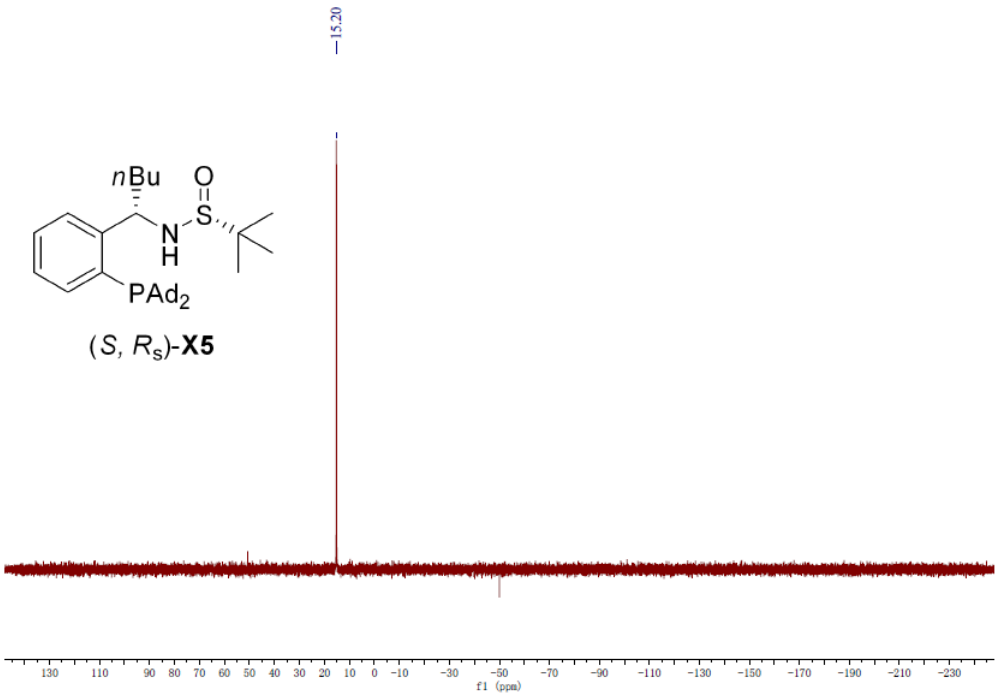
(S, R_s)-**X4**


151.33
151.08
136.36
136.34
132.70
132.44
128.88
126.80
126.74
124.93
77.32
77.00
76.68
58.26
57.93
55.59
42.23
42.10
41.71
41.59
37.18
37.05
36.90
36.81
36.66
28.88
28.80
28.71
22.61
10.76
nPr
O
S
N
H
PAd2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

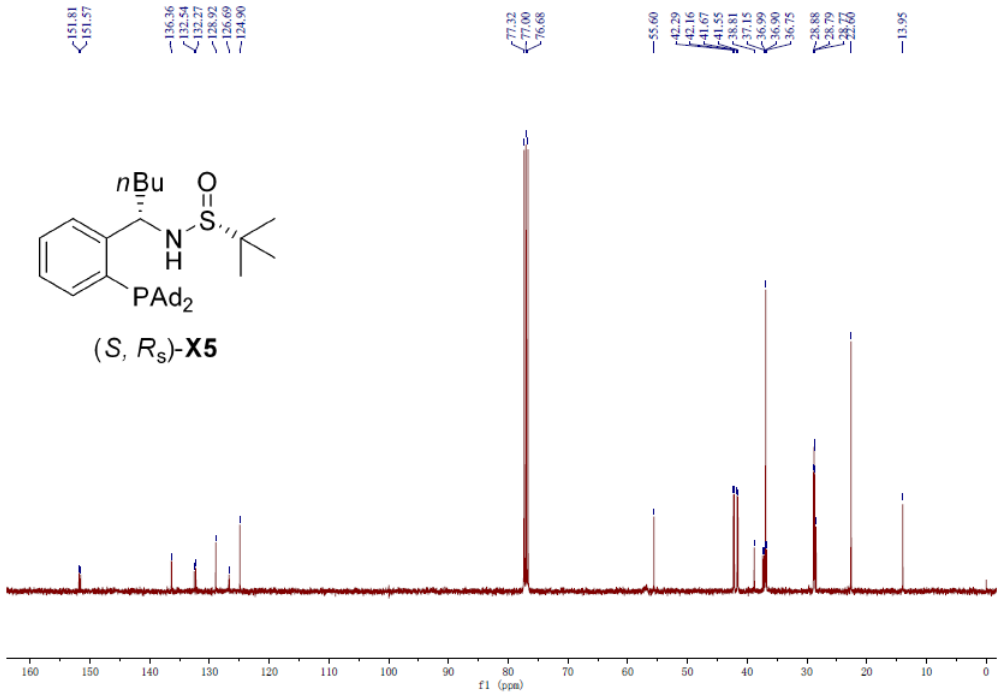
(*S*, *R*$_s$)-**X4**


7.735
7.716
7.397
7.374
7.356
7.337
7.260
7.225
7.220
7.205
7.189
7.185
5.749
3.435
2.008
1.979
1.891
1.853
1.829
1.765
1.678
1.647
1.436
1.418
1.395
1.140
0.883
0.866
0.848
nBu
O
S
N
H
PAd2
1.07
2.15
1.06
1.00
1.00
22.47
0.98
12.23
1.03
9.19
3.21
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)

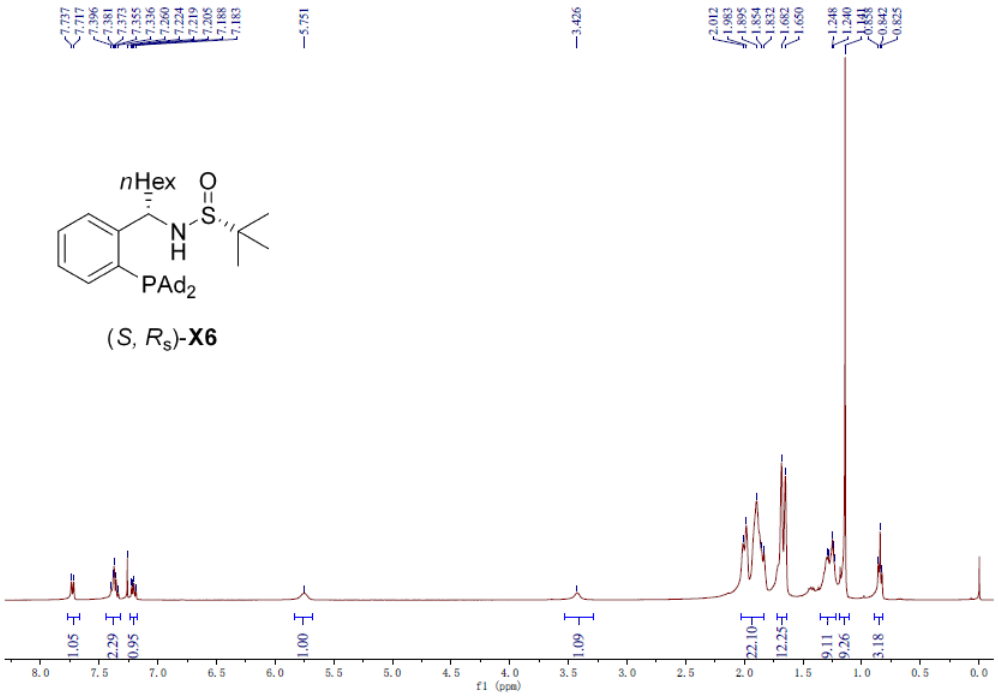
(*S*, *R*$_s$)-**X5**


15.20
nBu
O
S
N
H
PAd2
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

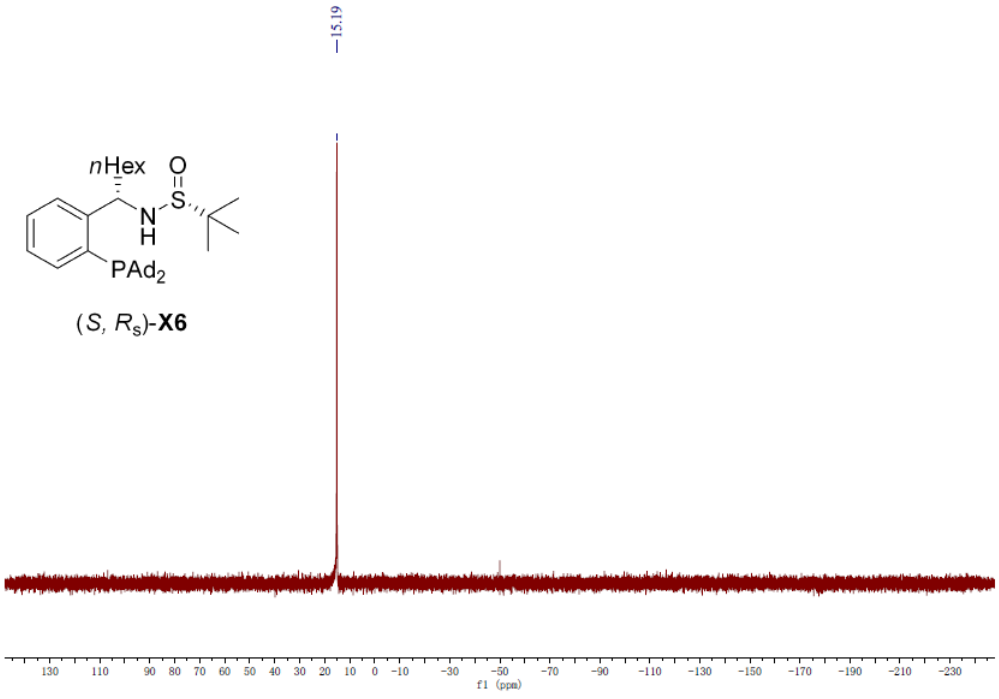
(*S*, R_s)-**X5**


151.81
151.57
136.36
132.54
132.27
128.92
126.69
124.90
77.32
77.00
76.68
55.60
42.29
42.16
41.67
41.55
38.81
37.15
36.99
36.90
36.75
28.88
28.79
28.77
22.68
13.95
nBu
O
S
N
H
PAd2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

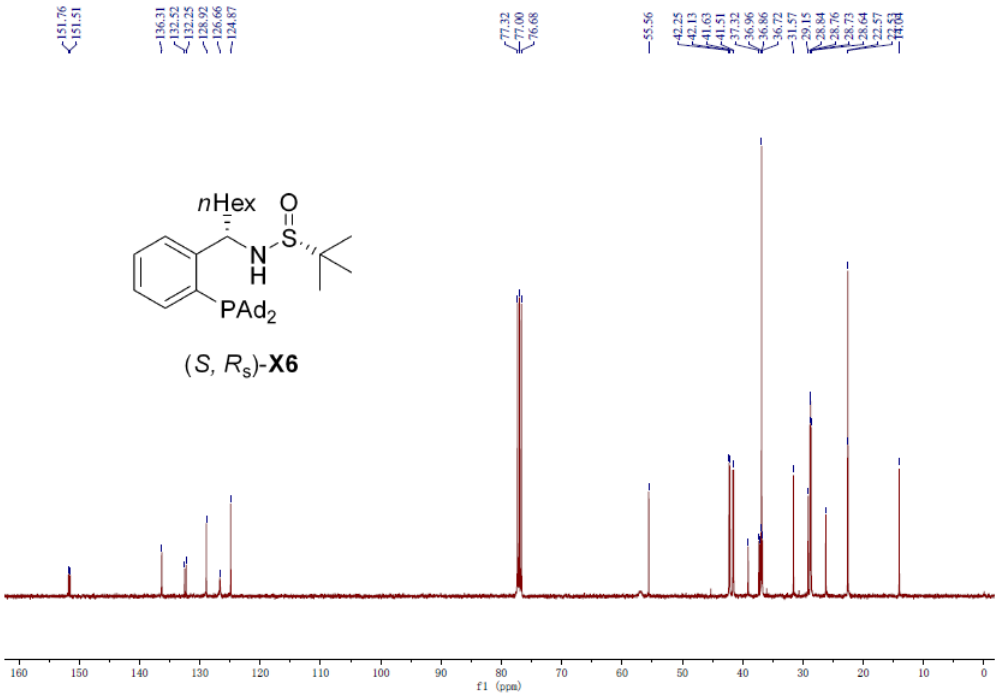
(*S*, R_s)-**X5**

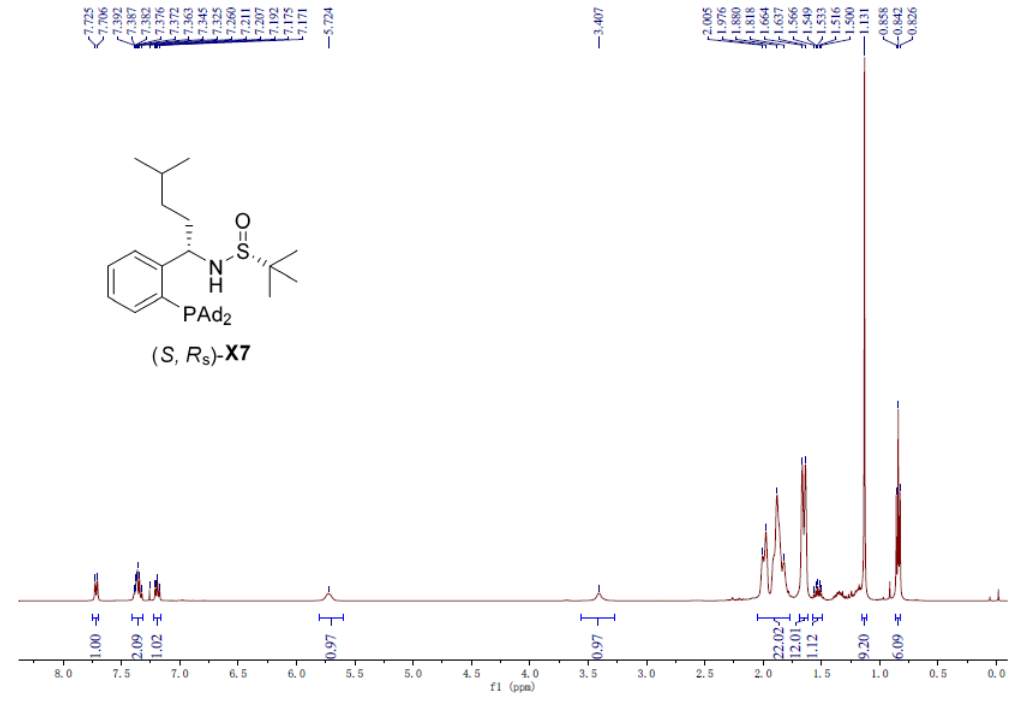

7.737
7.717
7.396
7.381
7.373
7.355
7.336
7.260
7.224
7.219
7.205
7.188
7.183
5.751
3.426
2.012
1.983
1.895
1.854
1.832
1.682
1.650
1.248
1.240
0.858
0.842
0.825
nHex
O
S
N
H
PAd2
1.05
2.29
0.95
1.00
1.09
22.10
12.25
9.11
9.26
3.18
f1 (ppm)

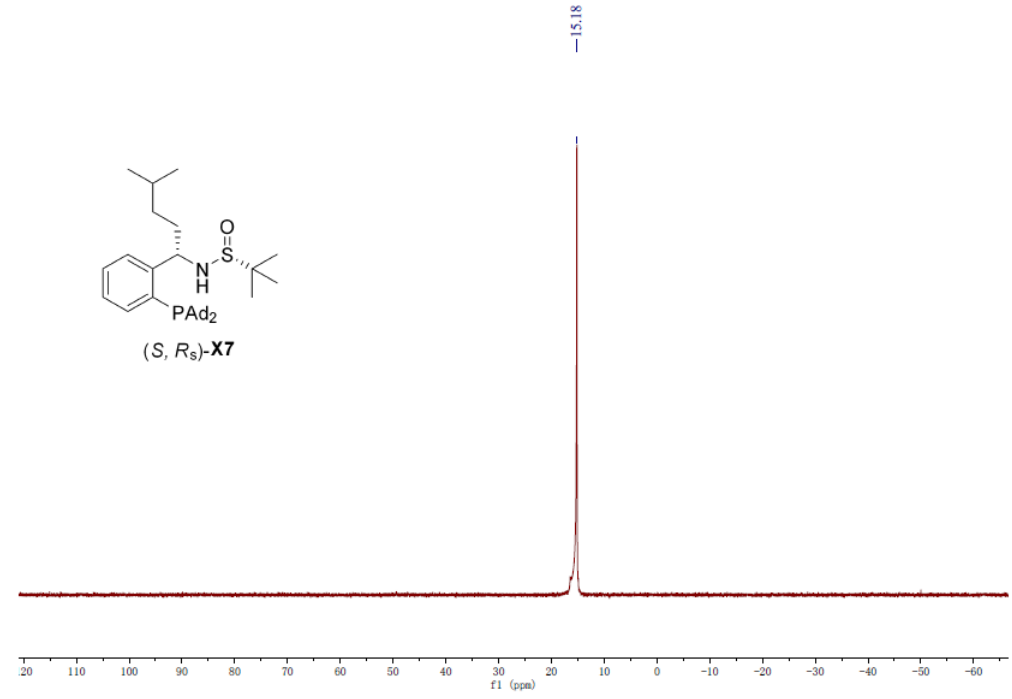
(S, R_s)-**X6**

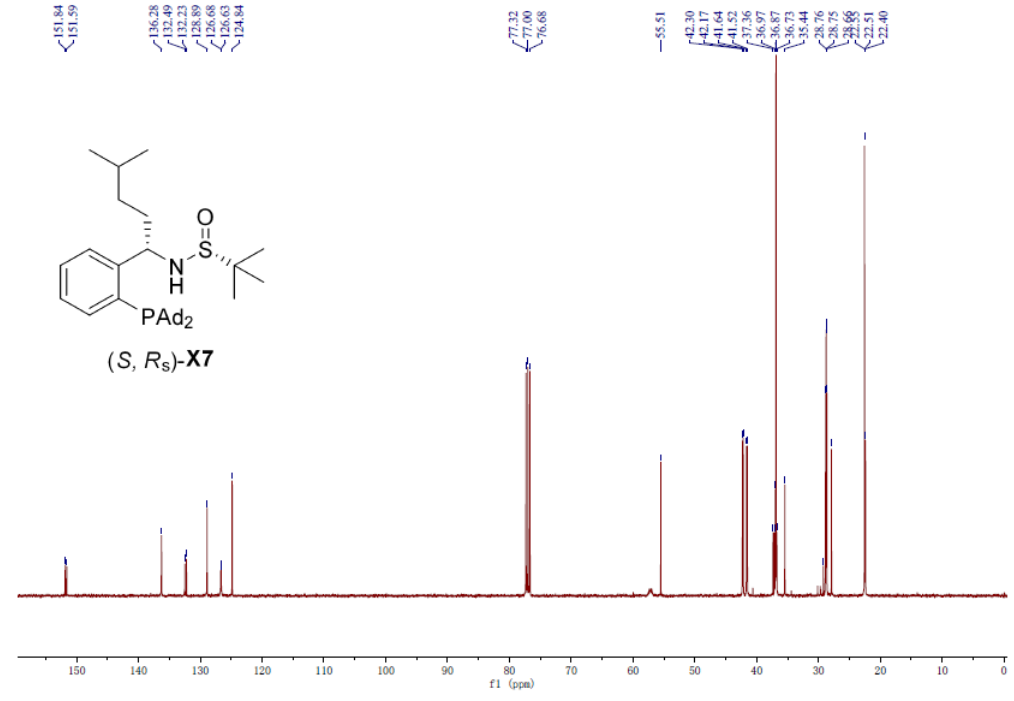

15.19
nHex
O
S
N
H
PAd2
f1 (ppm)

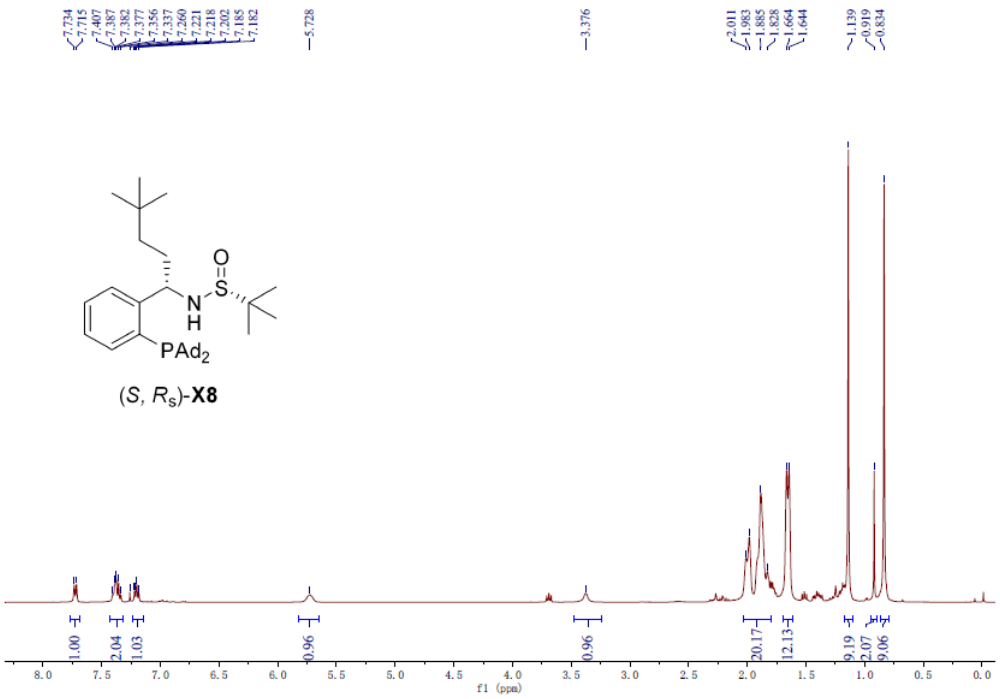
(S, R_s)-**X6**


151.76
151.51
136.31
132.52
132.25
128.92
126.66
124.87
77.32
77.00
76.68
55.56
42.25
42.13
41.63
41.51
37.32
36.96
36.86
36.72
31.57
29.15
28.84
28.76
28.73
28.64
22.57
13.84
nHex
O
S
N
H
PAd2
(S, Rs)-X6
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.725
7.706
7.392
7.387
7.382
7.376
7.372
7.363
7.345
7.325
7.260
7.211
7.207
7.192
7.175
7.171
5.724
3.407
2.005
1.976
1.880
1.818
1.664
1.637
1.566
1.549
1.533
1.516
1.500
1.131
0.858
0.842
0.826
O
S
N
H
PAd2
(S, Rs)-X7
1.00
2.09
1.02
0.97
0.97
22.02
12.01
1.12
9.20
6.09
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)

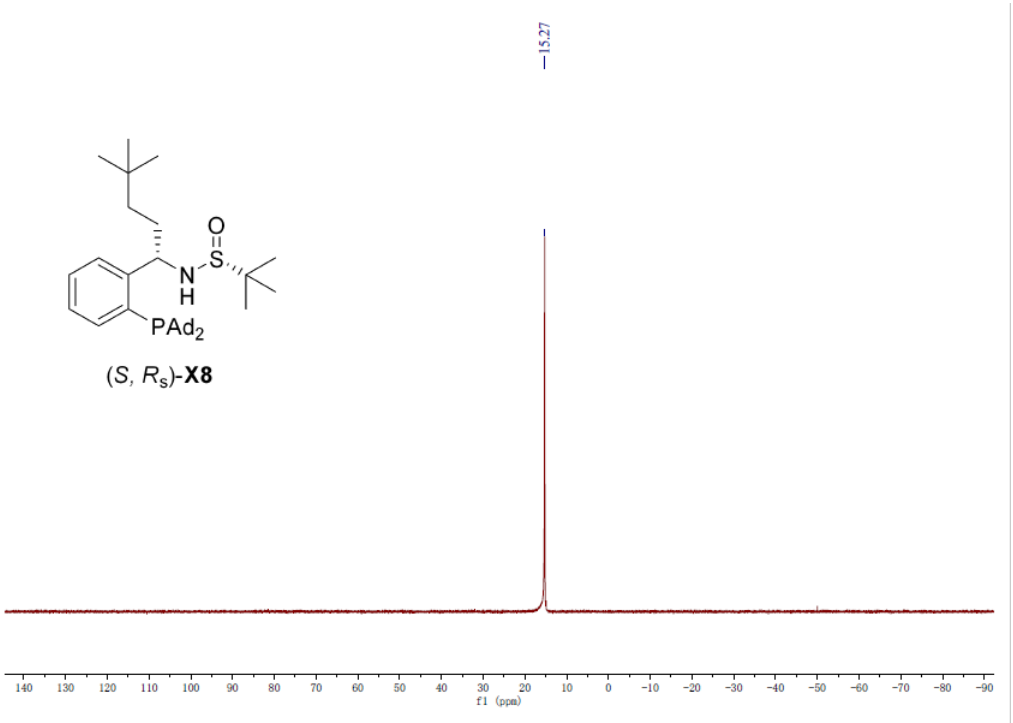

15.18
PAd2
(S, Rs)-X7
f1 (ppm)


151.84
151.59
136.28
132.49
132.23
128.89
126.68
126.63
124.84
77.32
77.00
76.68
55.51
42.30
42.17
41.64
41.52
37.36
36.97
36.87
36.73
35.44
28.76
28.75
28.66
28.65
22.51
22.40
PAd2
(S, Rs)-X7
f1 (ppm)


7.734
7.715
7.407
7.387
7.382
7.377
7.356
7.337
7.260
7.221
7.218
7.202
7.185
7.182
5.728
3.376
2.011
1.983
1.885
1.828
1.664
1.644
1.139
0.919
0.834
1.00
2.04
1.03
0.96
0.96
20.17
12.13
9.19
2.07
9.06
f1 (ppm)

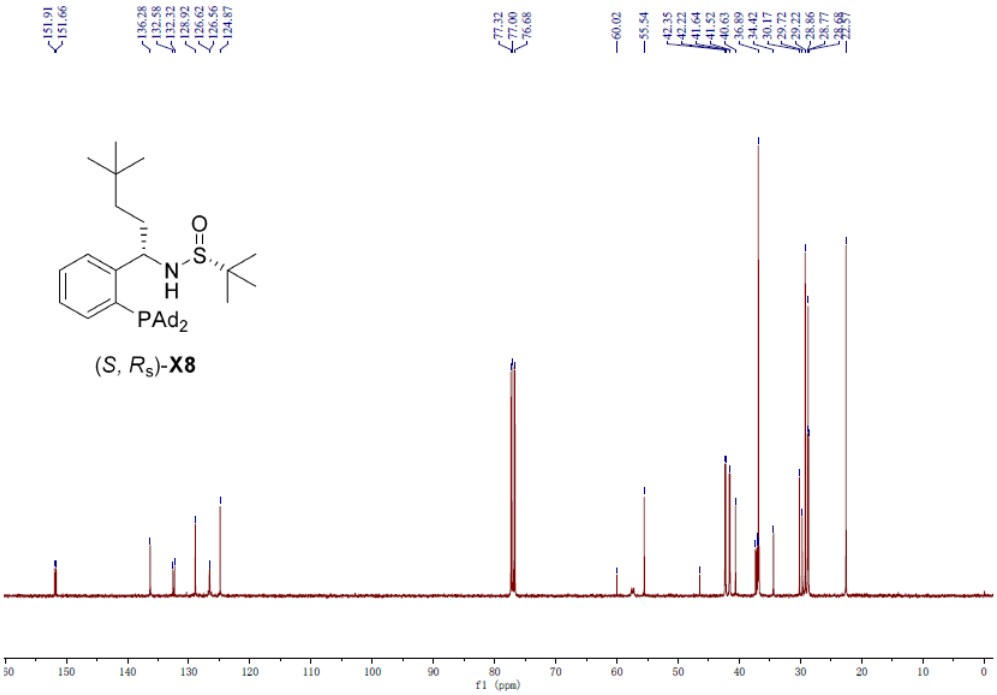
O
S
N
H
PAd2

(*S*, R_s)-**X8**

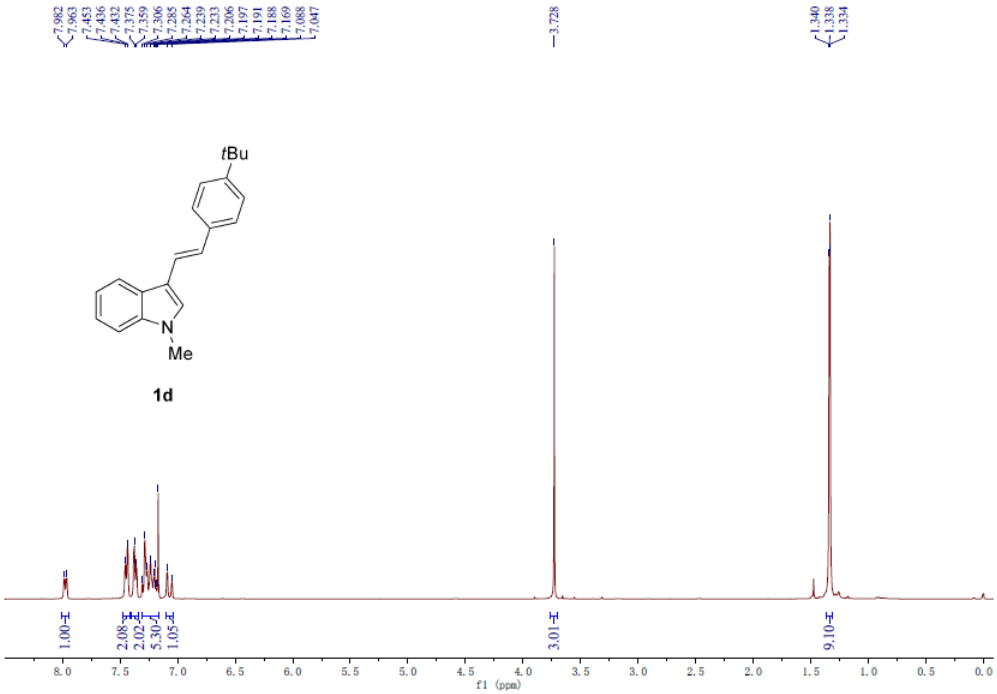

15.27
f1 (ppm)

O
S
N
H
PAd2

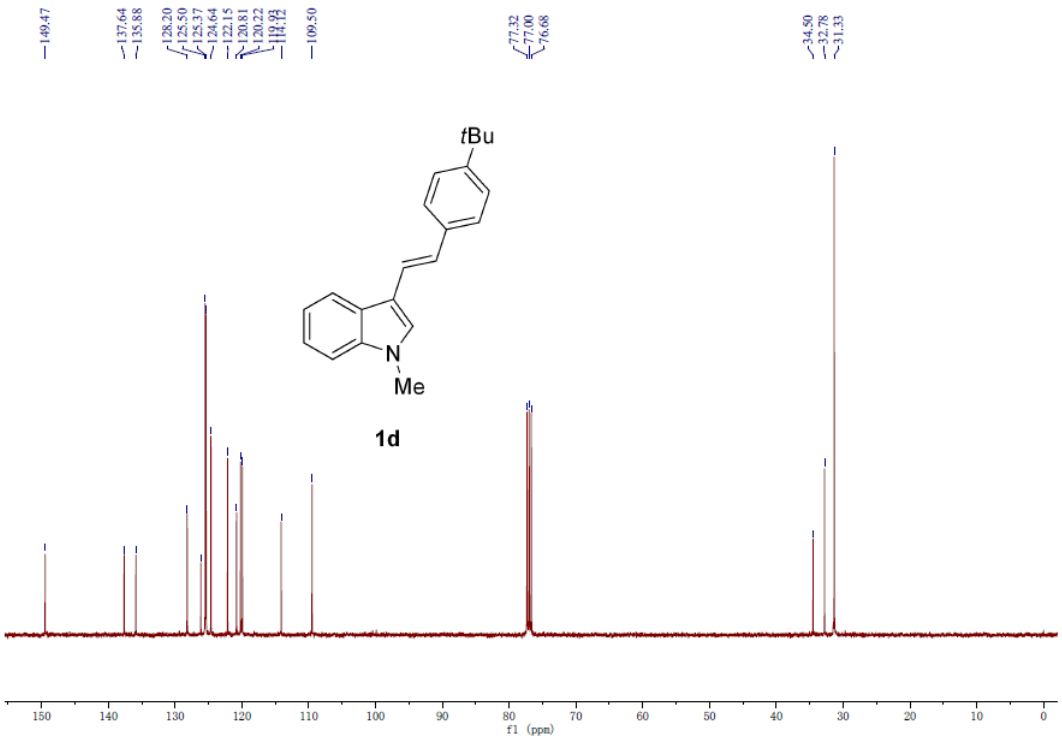
(*S*, R_s)-**X8**

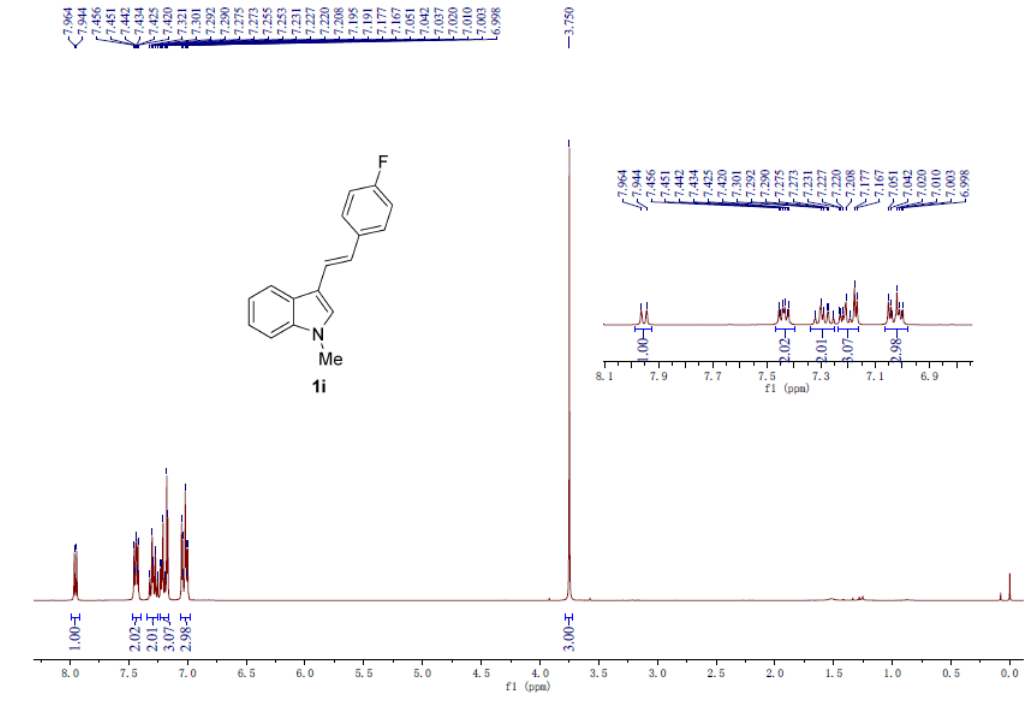

151.91
151.66
136.28
132.58
132.32
128.92
126.62
126.56
124.87
77.32
77.00
76.68
60.02
55.54
42.35
42.22
41.64
41.52
40.63
36.89
34.42
30.17
29.72
29.22
28.86
28.77
f1 (ppm)

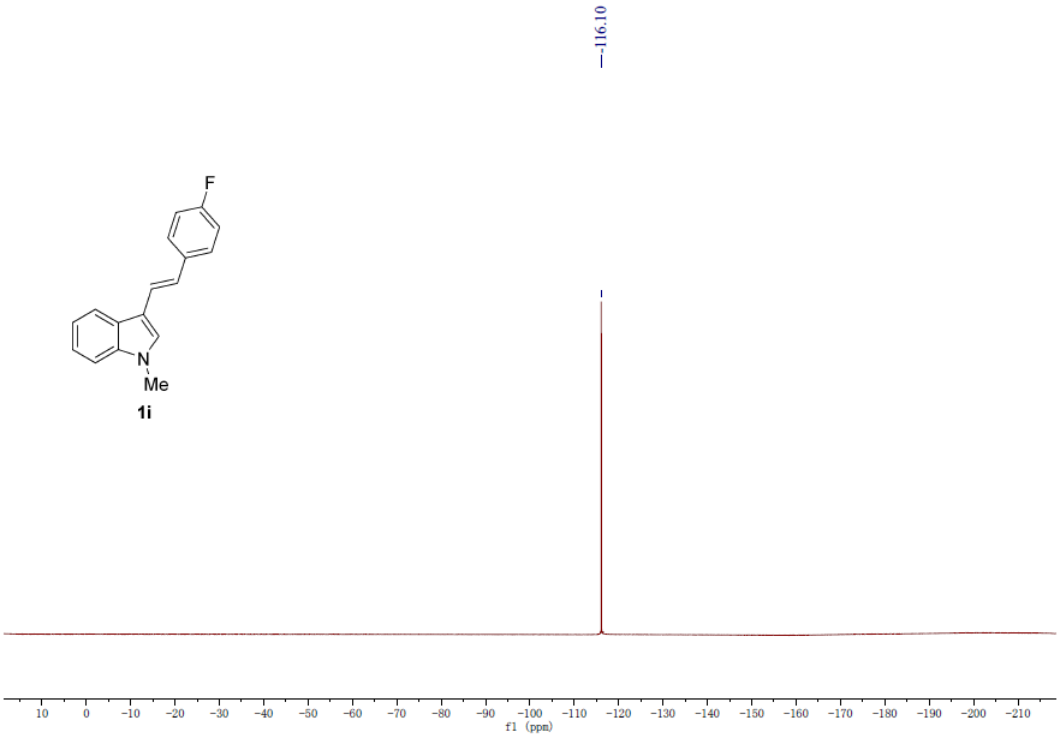
(S, R_S)-**X8**

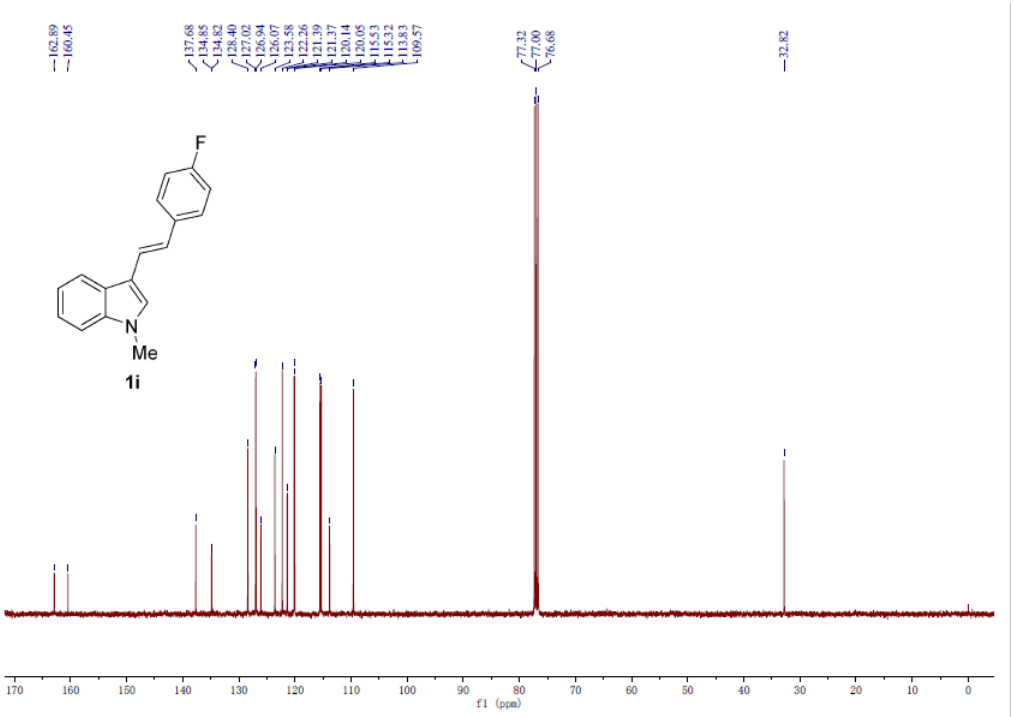

7.982
7.963
7.453
7.436
7.432
7.375
7.359
7.306
7.285
7.264
7.239
7.233
7.206
7.197
7.191
7.188
7.169
7.088
7.047
3.728
1.340
1.338
1.334
tBu
N
Me
1.00
2.08
2.02
5.30
1.05
3.01
9.10
f1 (ppm)

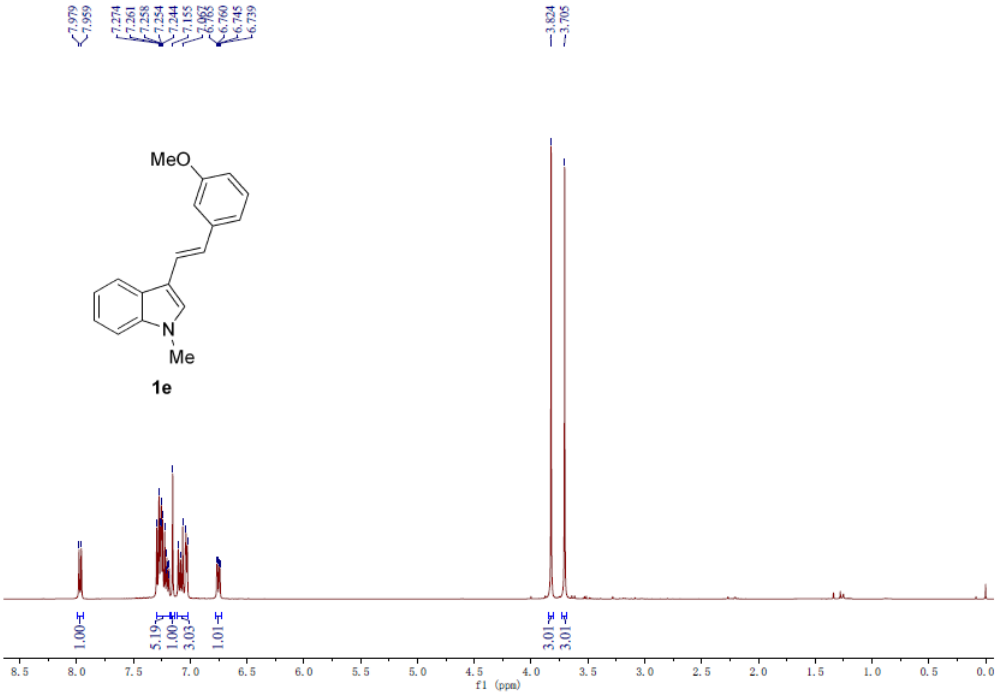
1d

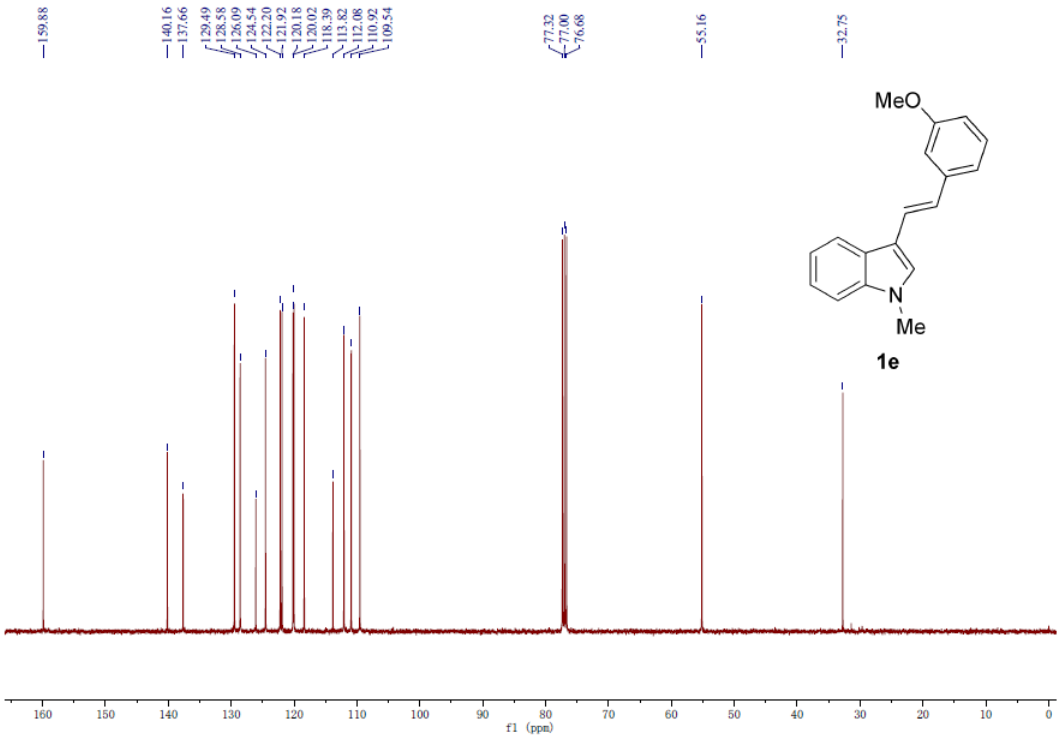

149.47
137.64
135.88
128.20
125.50
125.37
124.64
122.15
120.81
120.22
114.12
109.50
77.32
77.00
76.68
34.50
32.78
31.33
tBu
N
Me
1d
f1 (ppm)

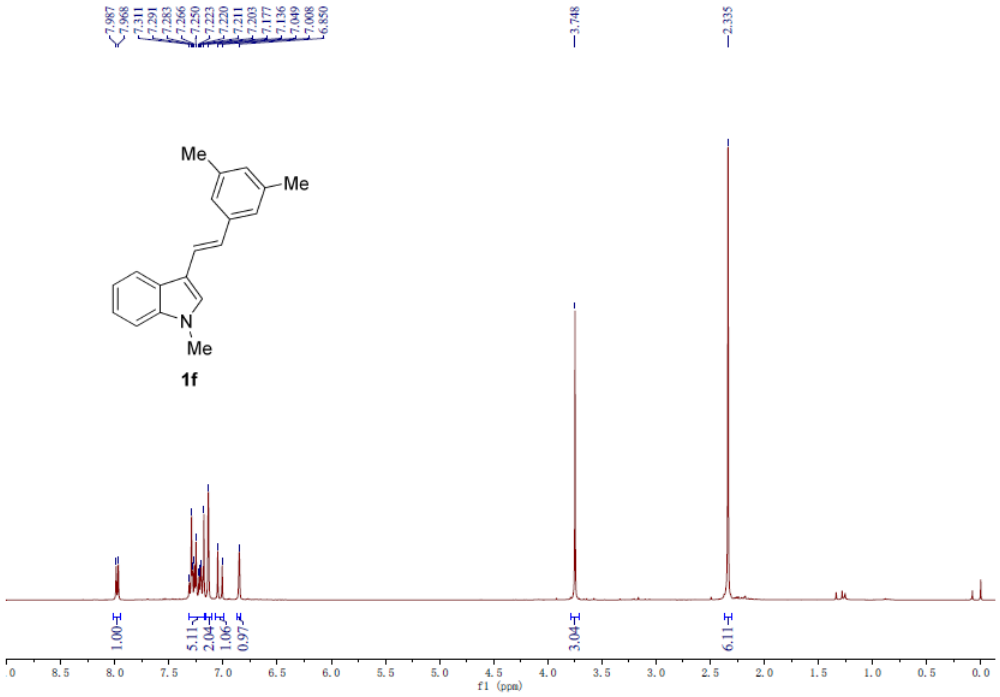

7.964
7.944
7.456
7.451
7.442
7.434
7.425
7.420
7.321
7.301
7.292
7.290
7.275
7.273
7.255
7.253
7.231
7.227
7.220
7.208
7.195
7.191
7.177
7.167
7.051
7.042
7.037
7.020
7.010
7.003
6.998
3.750
F
N
Me
1i
1.00
2.02
2.01
3.07
2.98
3.00
f1 (ppm)

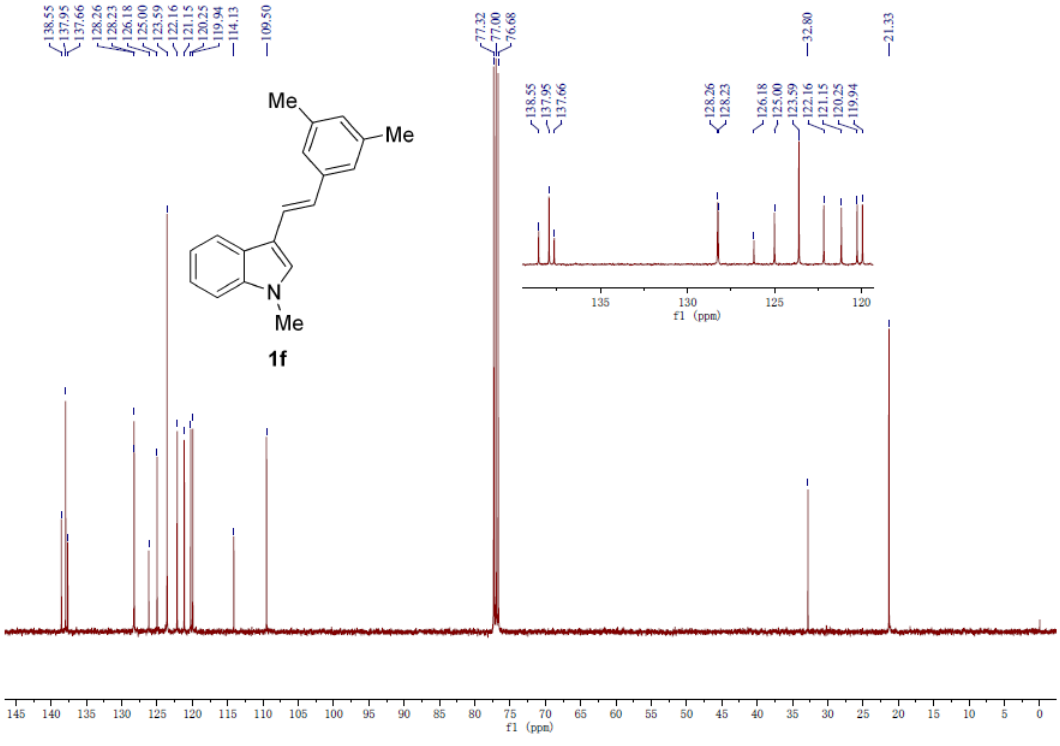

-116.10
F
N
Me
1i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

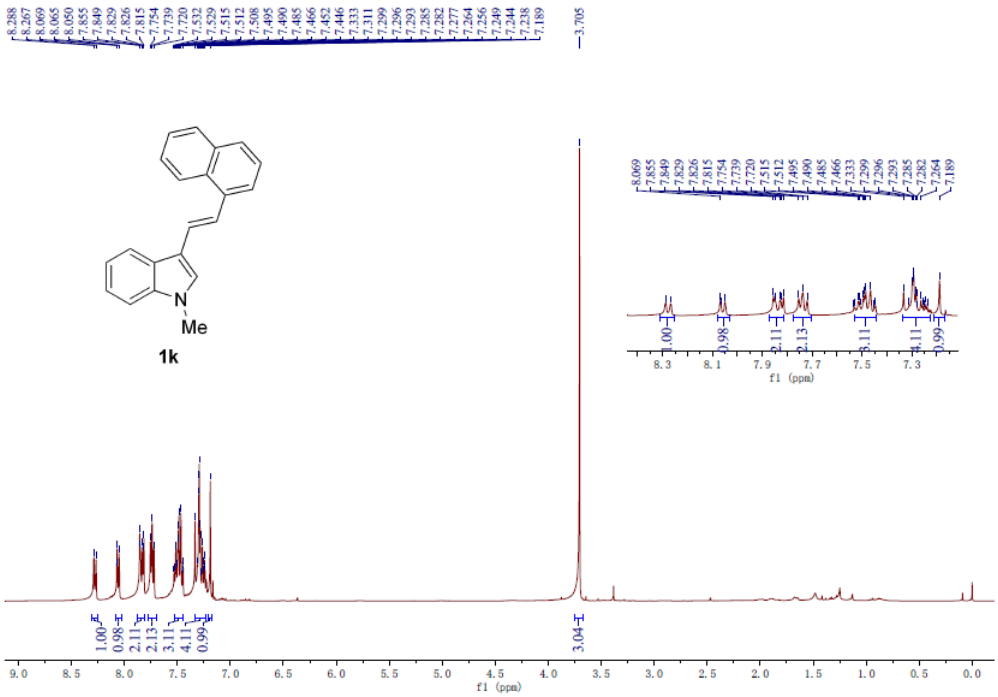

162.89
160.45
137.68
134.85
134.82
128.40
127.02
126.94
126.07
123.58
122.26
121.39
121.37
120.14
120.05
115.53
115.32
113.83
109.57
77.32
77.00
76.68
32.82
F
N
Me
1i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

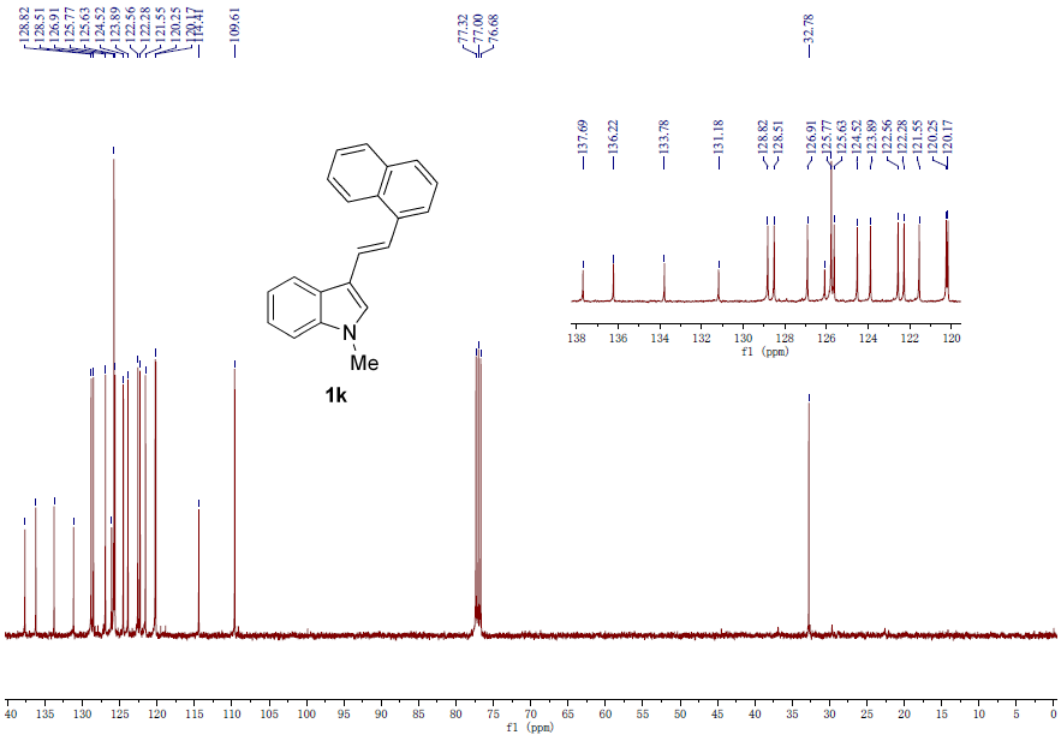

7.979
7.959
7.274
7.261
7.258
7.254
7.244
7.155
7.067
6.783
6.760
6.745
6.739
3.824
3.705
MeO
N
Me
1e
1.00
5.19
1.00
3.03
1.01
3.01
3.01
f1 (ppm)

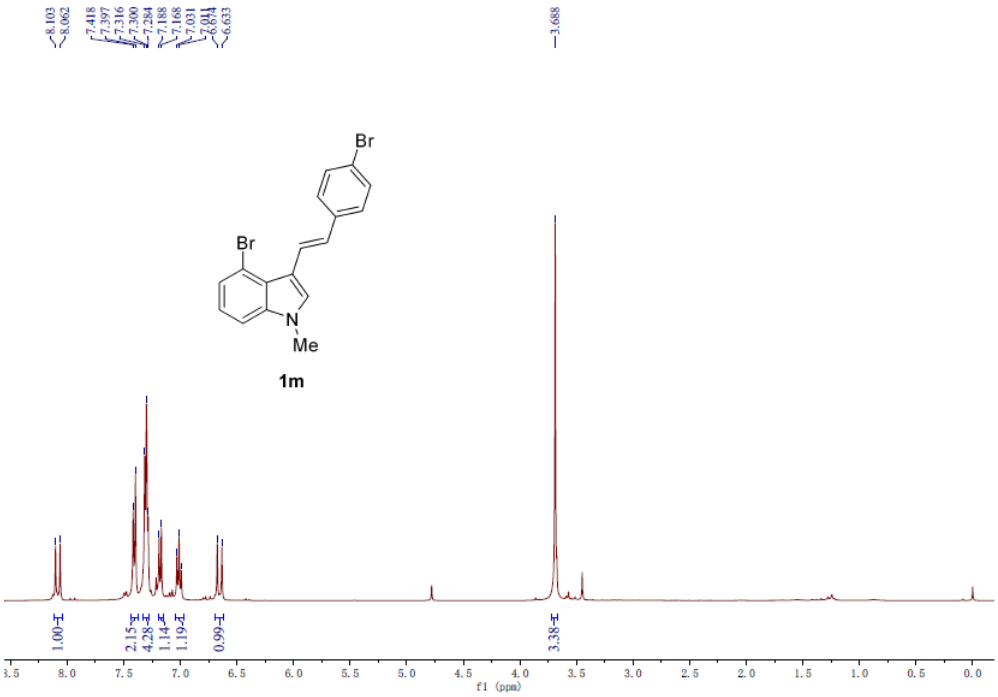

159.88
140.16
137.66
129.49
128.58
126.09
124.54
122.20
121.92
120.18
120.02
118.39
113.82
112.08
110.92
109.54
77.32
77.00
76.68
55.16
32.75
MeO
N
Me
1e
f1 (ppm)

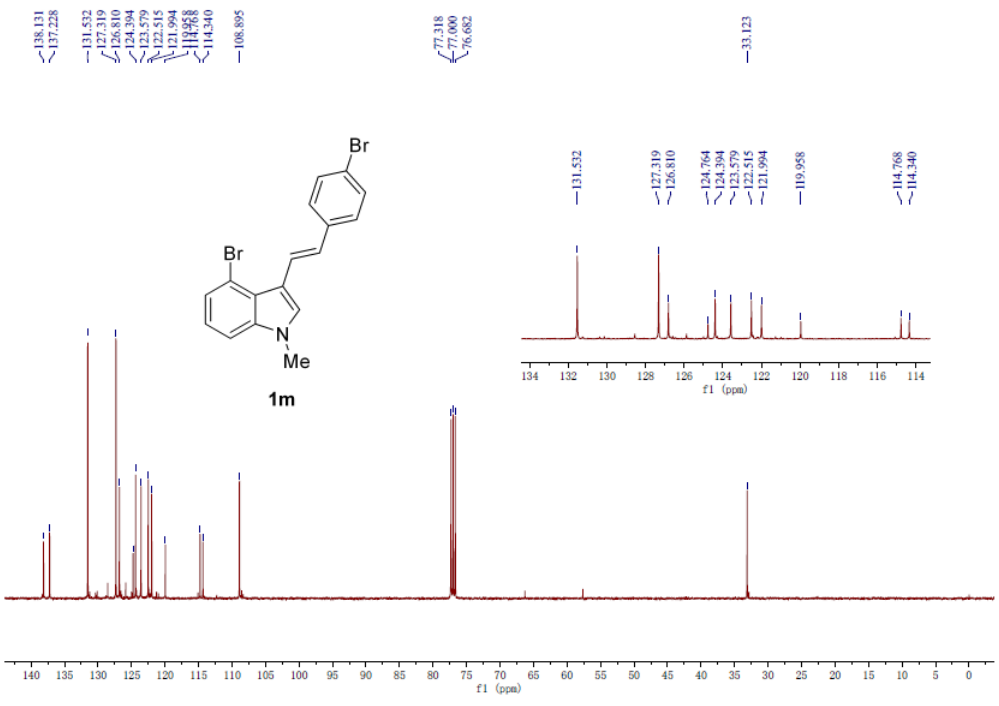

7.987
7.968
7.311
7.291
7.283
7.266
7.250
7.223
7.220
7.211
7.203
7.177
7.136
7.049
7.008
6.850
3.748
2.335
Me
Me
N
Me
1f
1.00
5.11
2.04
1.06
0.97
3.04
6.11
f1 (ppm)

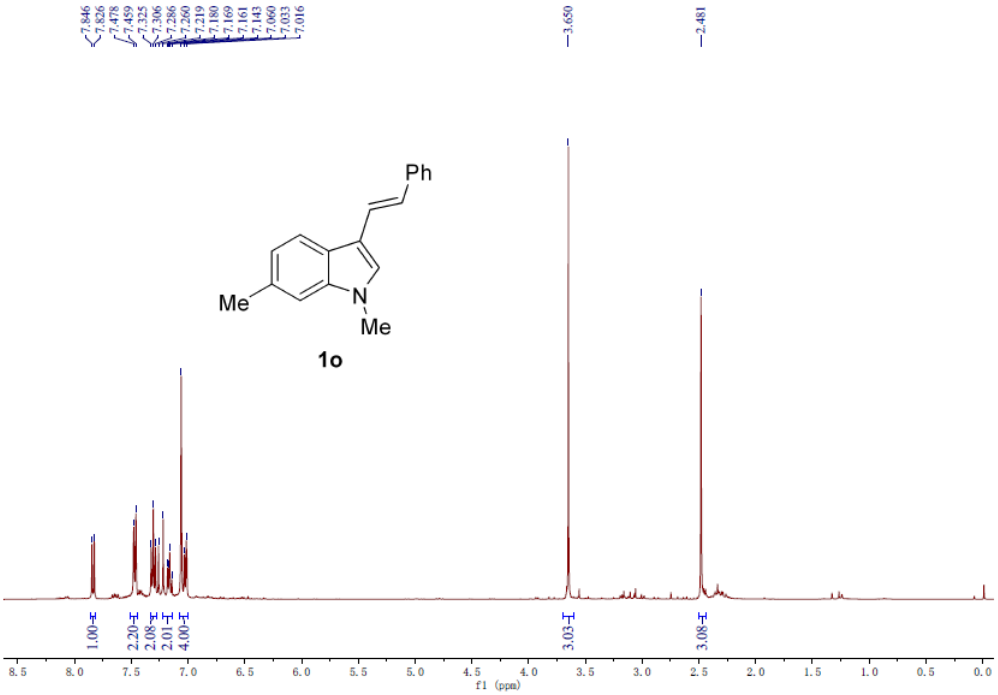

138.55
137.95
137.66
128.26
128.23
126.18
125.00
123.59
122.16
121.15
120.25
119.94
114.13
109.50
77.32
77.00
76.68
32.80
21.33
Me
Me
N
Me
1f
f1 (ppm)

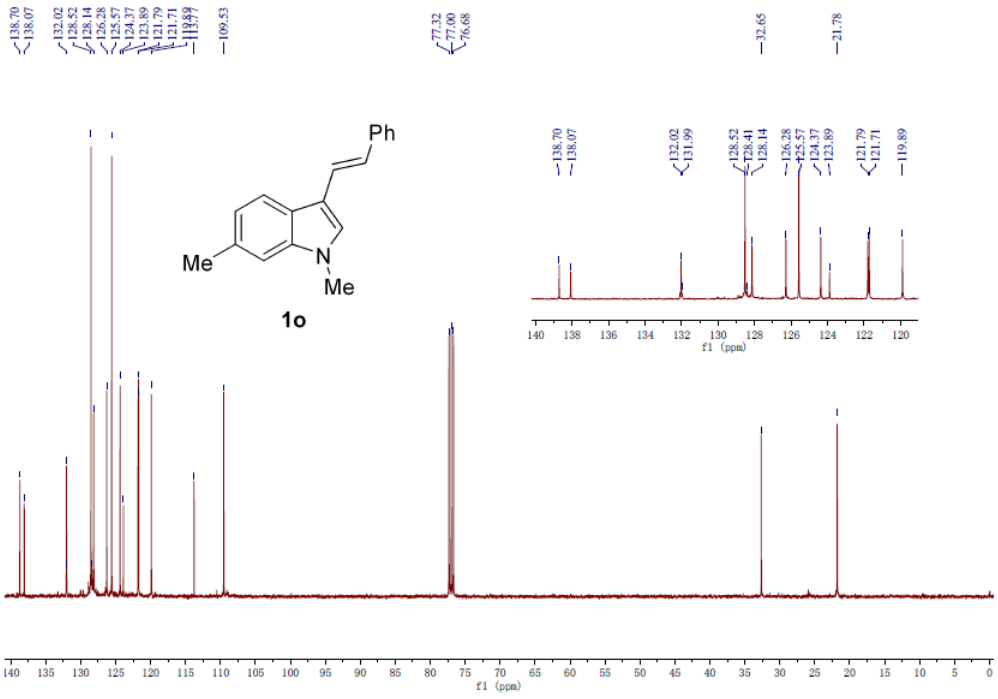

8.288
8.267
8.069
8.065
8.050
7.855
7.849
7.829
7.826
7.815
7.754
7.739
7.720
7.532
7.529
7.515
7.512
7.508
7.495
7.490
7.485
7.466
7.452
7.446
7.333
7.311
7.299
7.296
7.293
7.285
7.282
7.277
7.264
7.256
7.249
7.244
7.238
7.189
3.705
N
Me
1k
1.00
0.98
2.11
2.13
3.11
4.11
0.99
3.04
f1 (ppm)

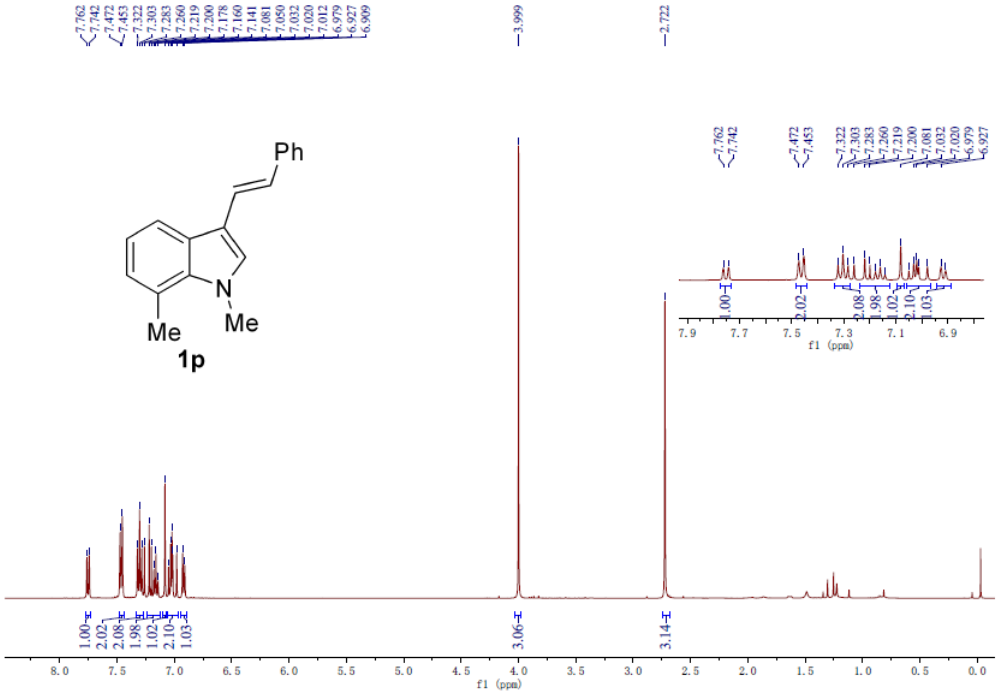

128.82
128.51
126.91
125.77
125.63
124.52
123.89
122.56
122.28
121.55
120.25
120.17
109.61
77.32
77.00
76.68
32.78
N
Me
1k
f1 (ppm)

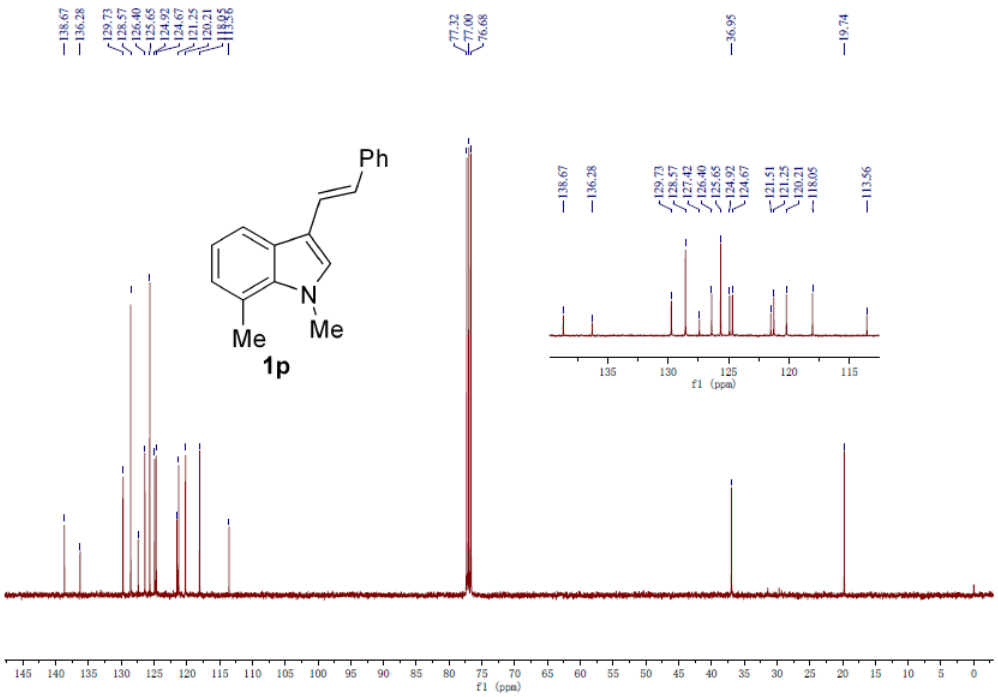

8.103
8.062
7.418
7.397
7.316
7.300
7.284
7.188
7.168
7.031
7.011
6.674
6.633
3.688
Br
Br
N
Me
1m
1.00
2.15
4.28
1.14
1.19
0.99
3.38
f1 (ppm)

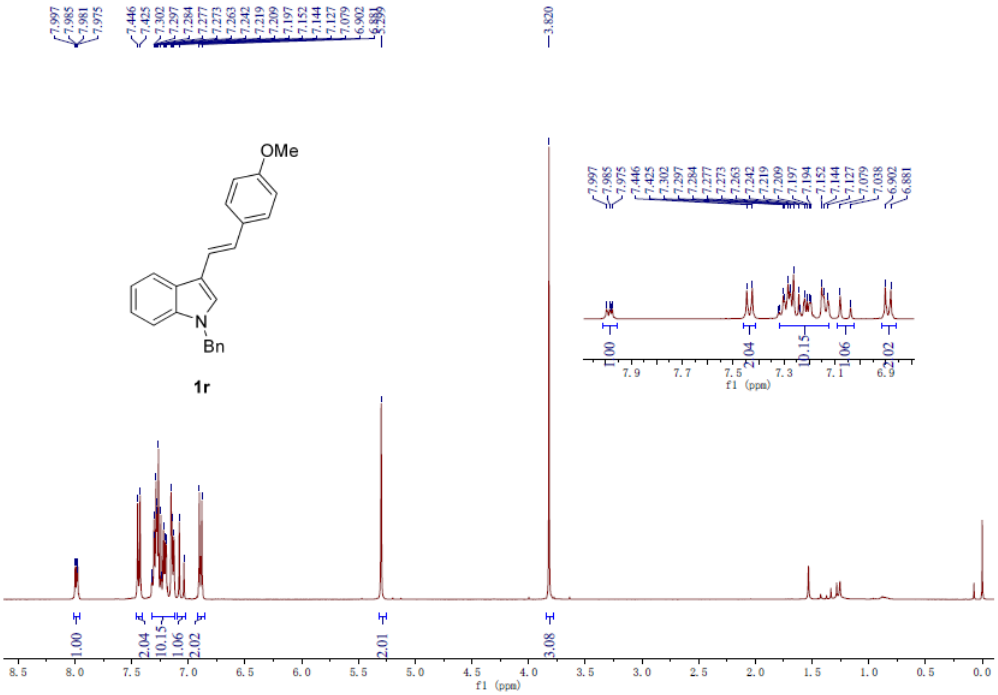

138.131
137.228
131.532
127.319
126.810
124.394
123.579
122.515
121.994
114.340
108.895
77.318
77.000
76.682
33.123
Br
Br
N
Me
1m
131.532
127.319
126.810
124.764
124.394
123.579
122.515
121.994
119.958
114.768
114.340
f1 (ppm)

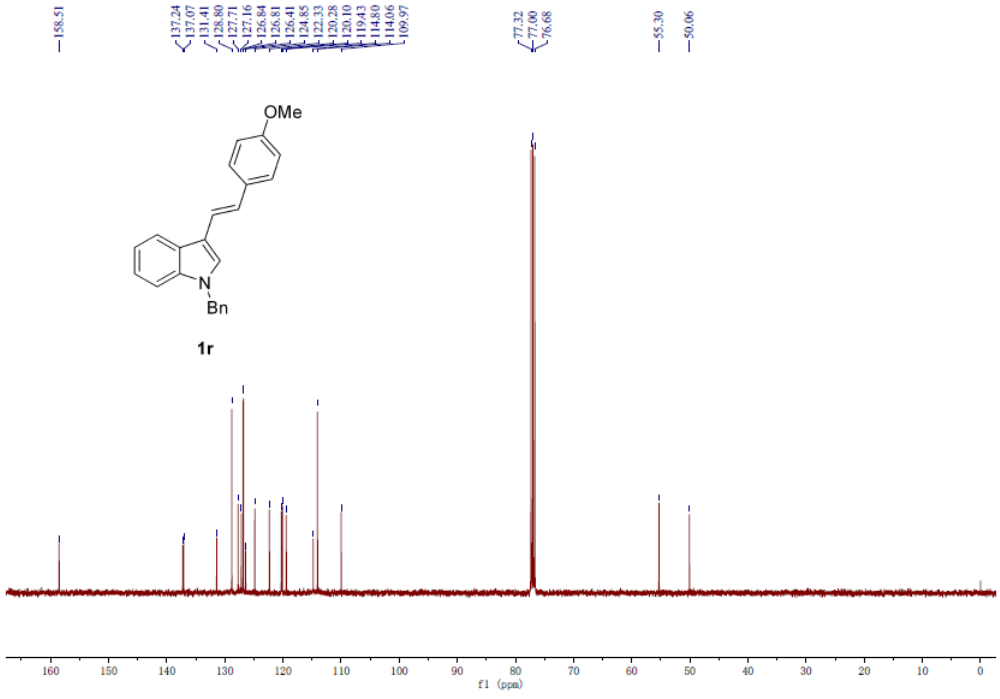

7.846
7.826
7.478
7.459
7.325
7.306
7.286
7.260
7.219
7.180
7.169
7.161
7.143
7.060
7.033
7.016
3.650
2.481
Ph
Me
N
Me
1o
1.00
2.20
2.08
2.01
4.00
3.03
3.08
f1 (ppm)

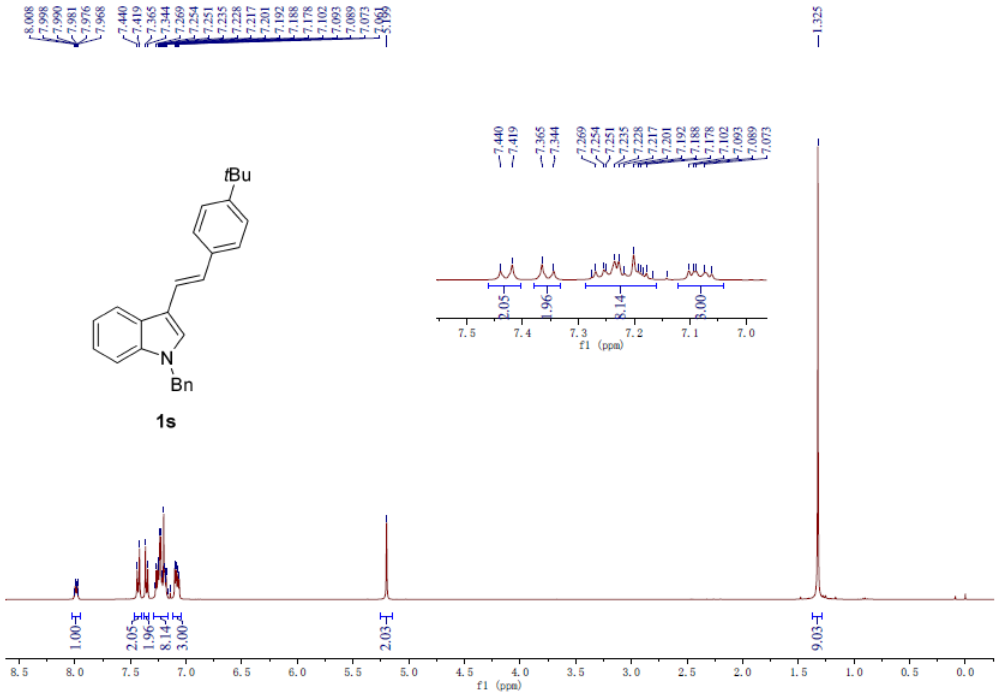

138.70
138.07
132.02
128.52
128.14
126.28
125.57
124.37
123.89
121.79
121.71
119.89
109.53
77.32
77.00
76.68
32.65
21.78
Ph
Me
N
Me
1o
f1 (ppm)

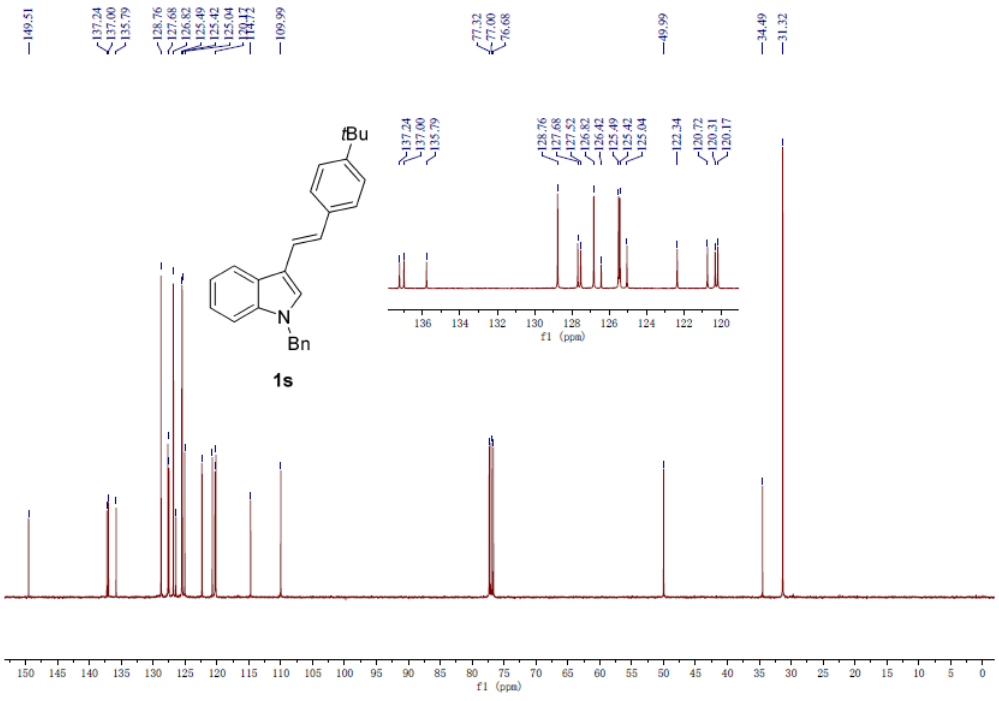

Ph
N
Me
Me
1p
f1 (ppm)

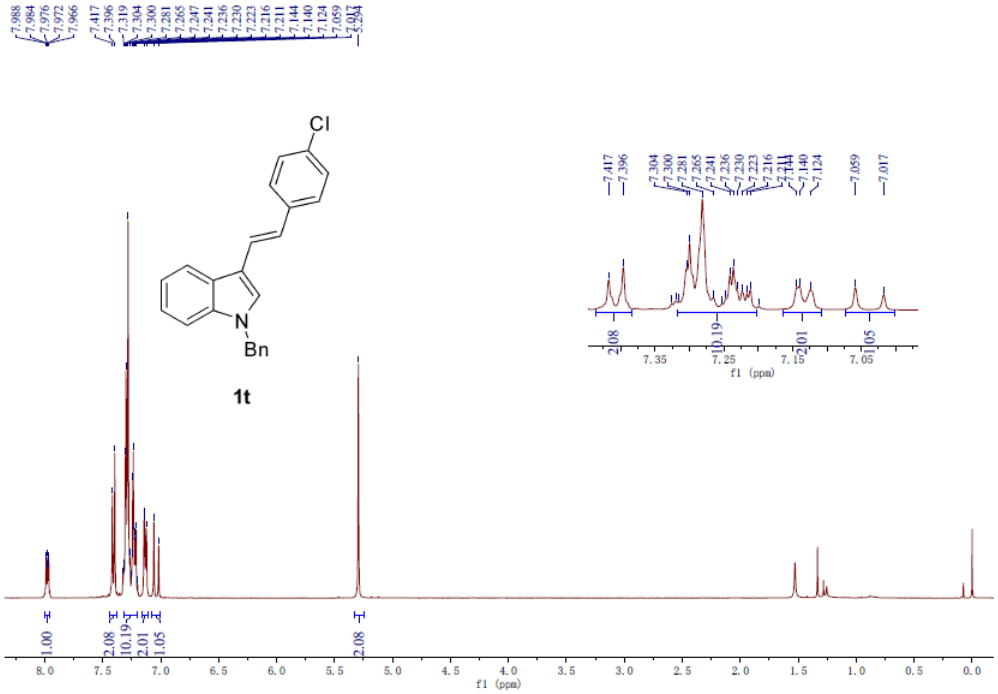

Ph
N
Me
Me
1p
f1 (ppm)

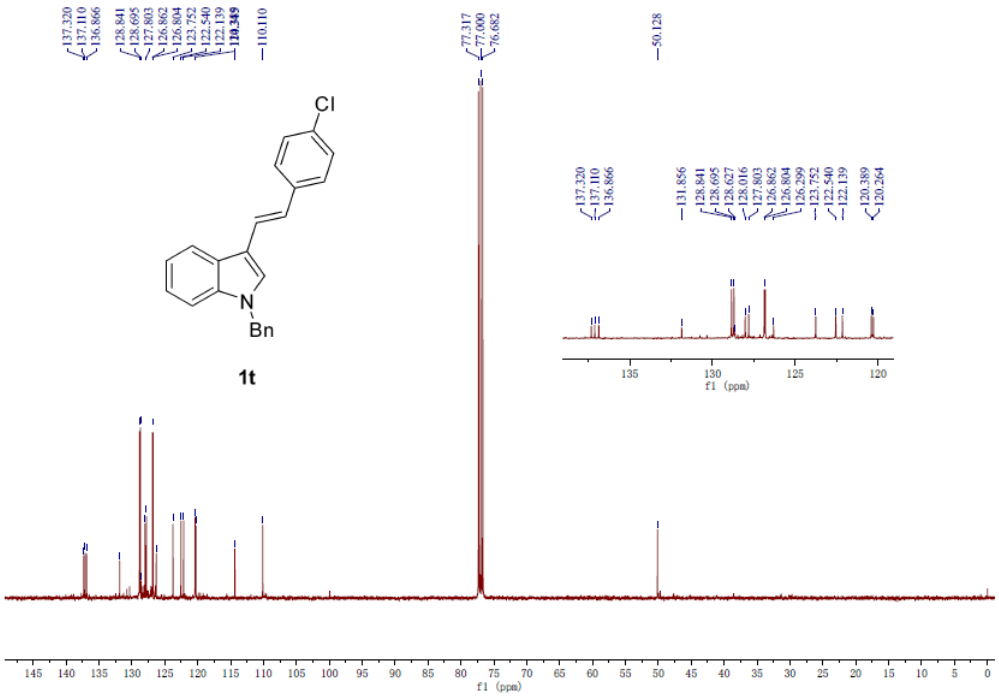

OMe
N
Bn
1r
f1 (ppm)

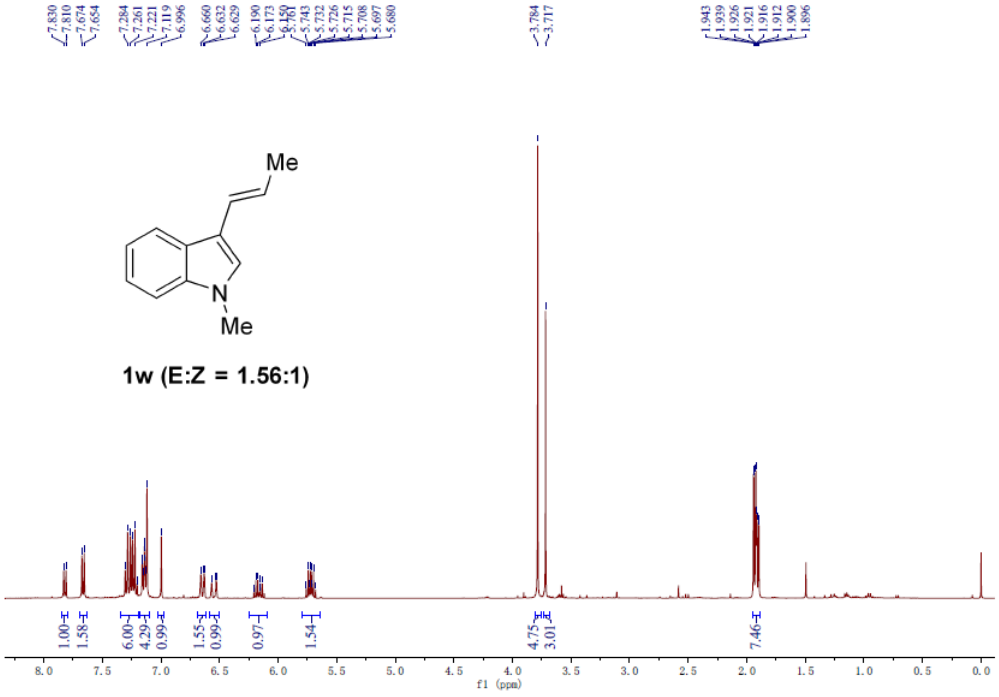

OMe
N
Bn
1r
f1 (ppm)

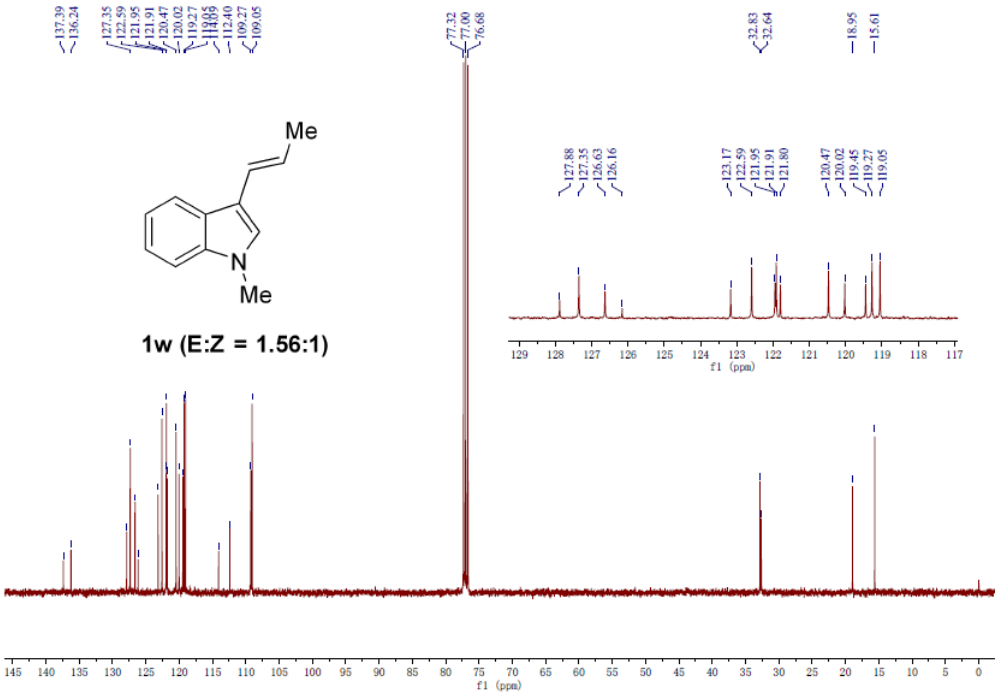

tBu
N
Bn
1s
f1 (ppm)

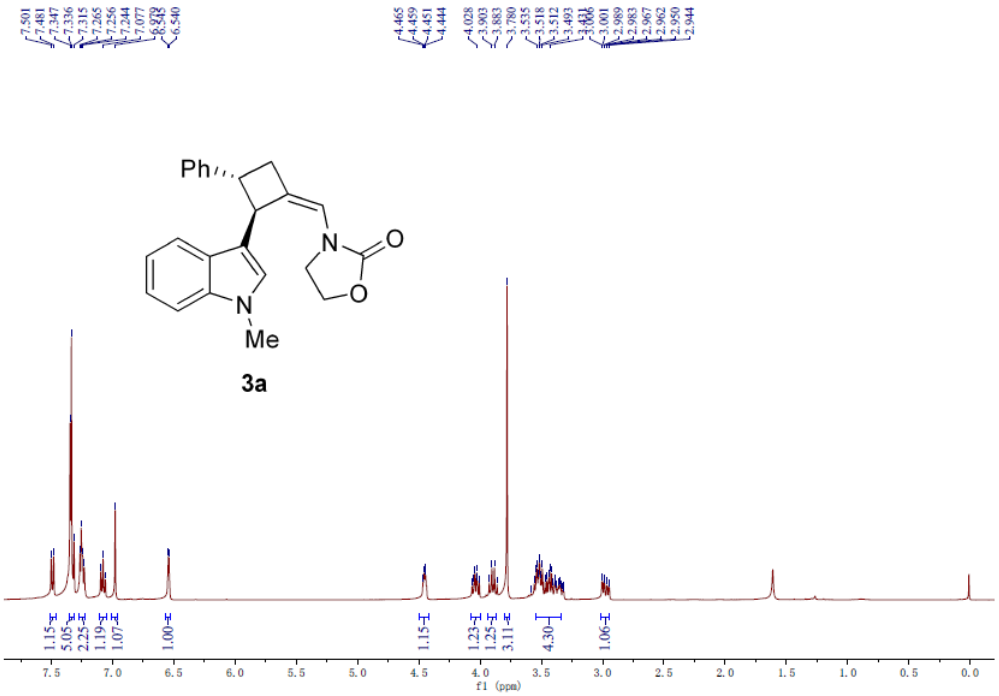

tBu
N
Bn
1s
f1 (ppm)


Cl
N
Bn
1t
f1 (ppm)


Cl
N
Bn
1t
f1 (ppm)


Me
N
Me
1w (E:Z = 1.56:1)


Me
N
Me
1w (E:Z = 1.56:1)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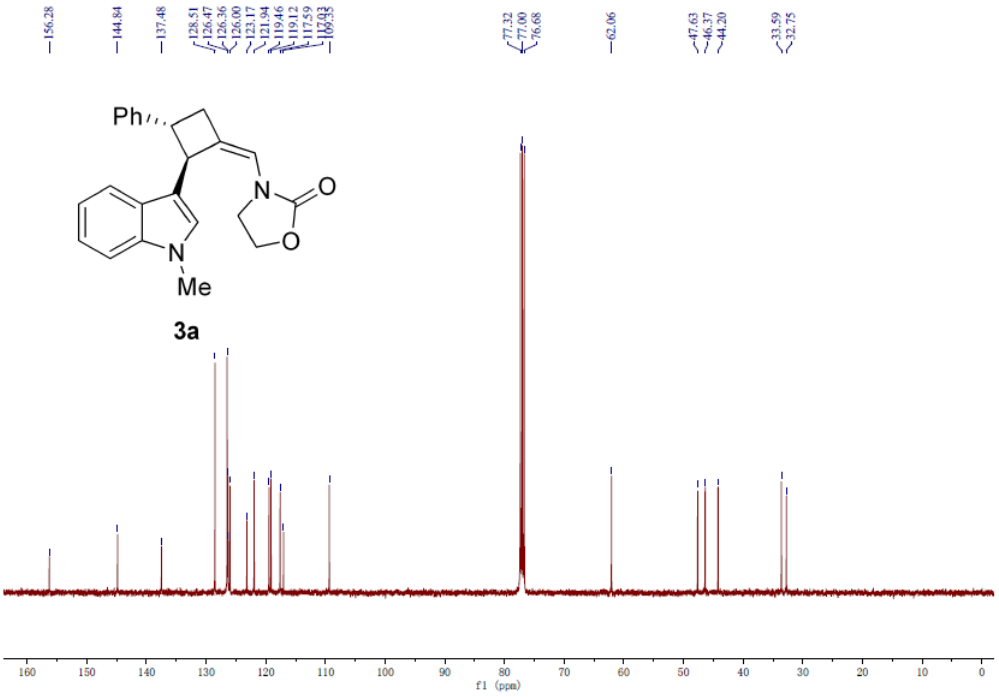
7.265
7.256
7.244
7.077
6.540
4.465
4.459
4.451
4.444
4.028
3.903
3.883
3.780
3.535
3.518
3.512
3.493
3.001
2.989
2.983
2.967
2.962
2.950
2.944
Ph
N
O
N
Me
3a
1.15
5.05
2.25
1.19
1.07
1.00
1.15
1.23
1.25
3.11
4.30
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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137.48
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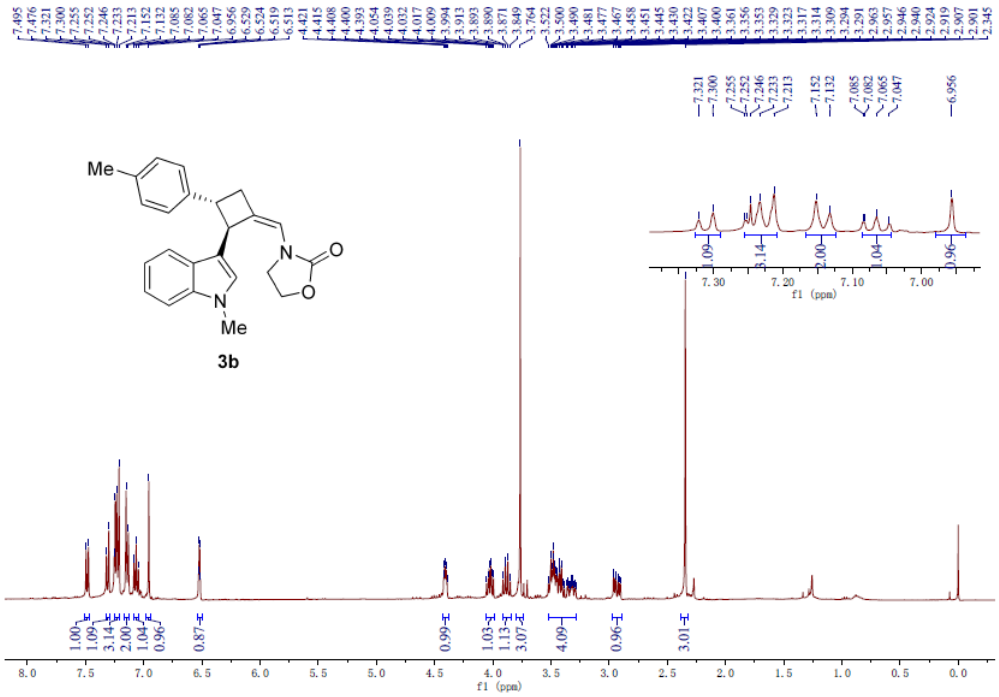
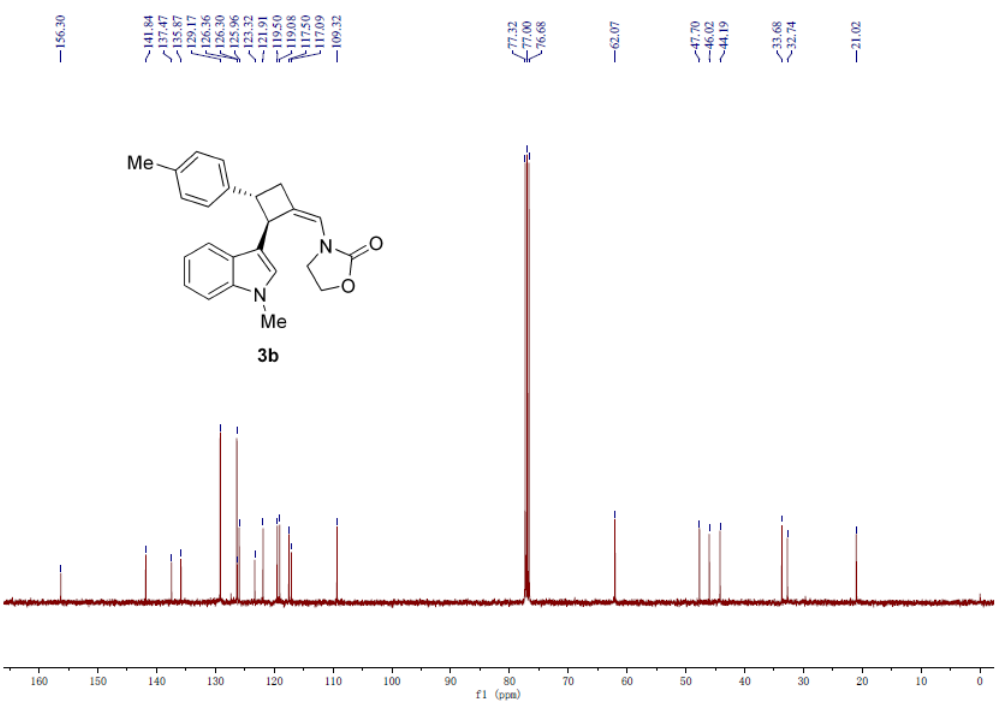
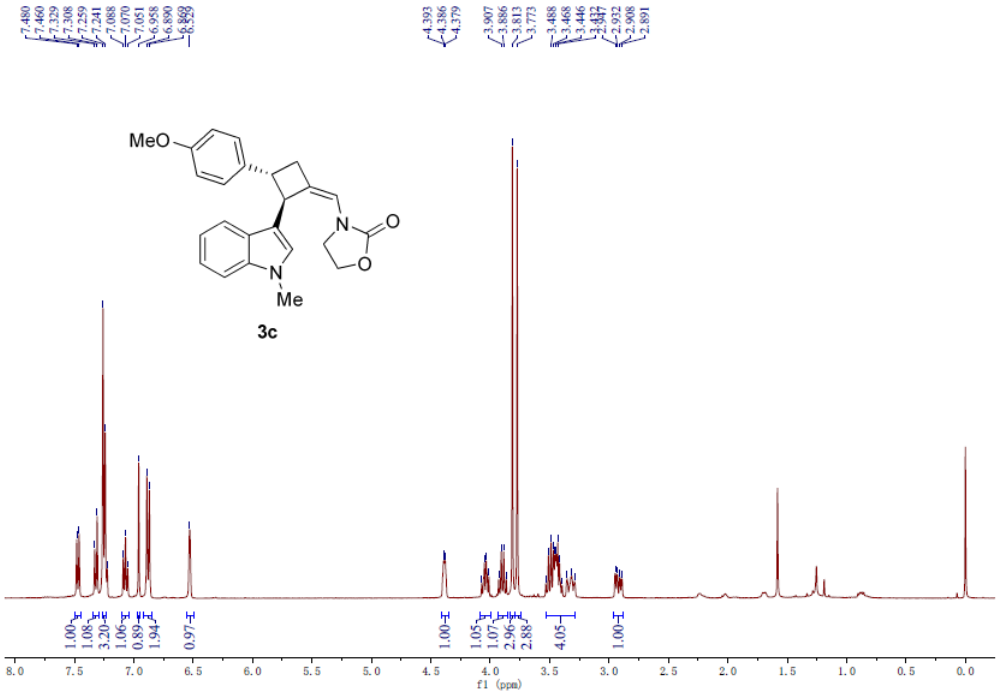
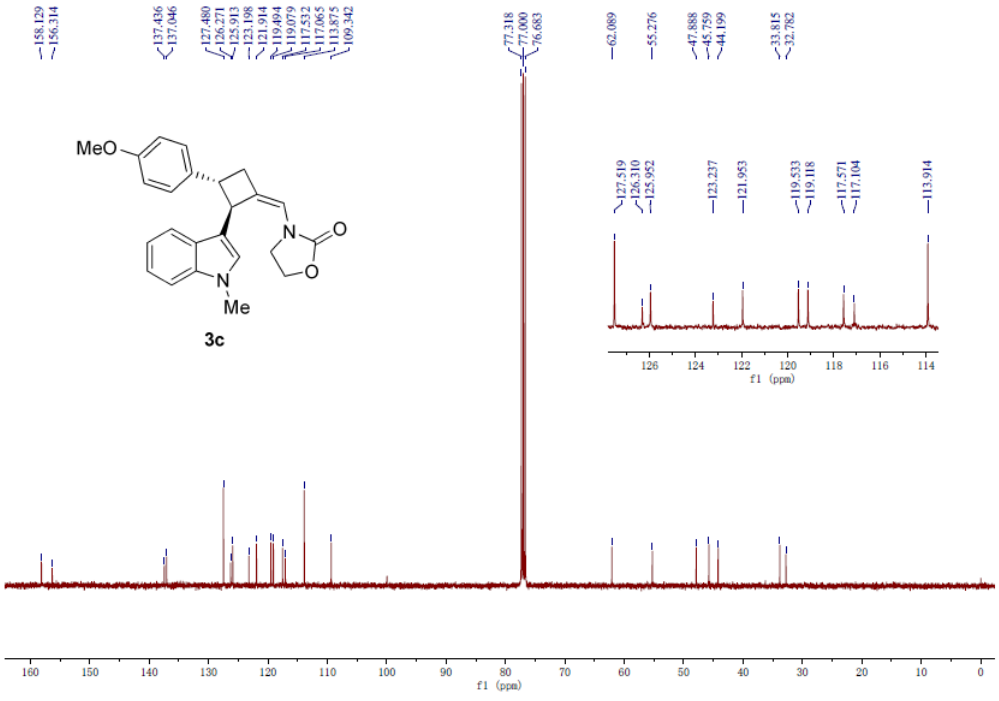
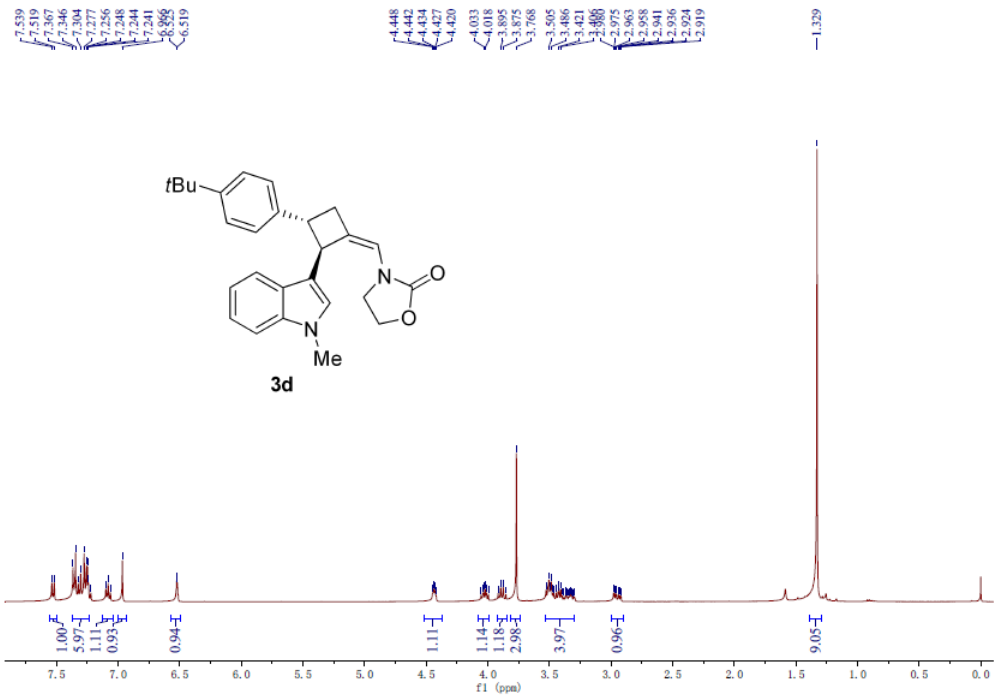
126.36
126.00
123.17
121.94
119.46
119.12
117.59
110.93
77.32
77.00
76.68
62.06
47.63
46.37
44.20
33.59
32.75
Ph
N
O
N
Me
3a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
N
O
N
Me
3b
f1 (ppm)


Me
N
O
N
Me
3b
f1 (ppm)


MeO
N
O
N
Me
3c


MeO
N
O
N
Me
3c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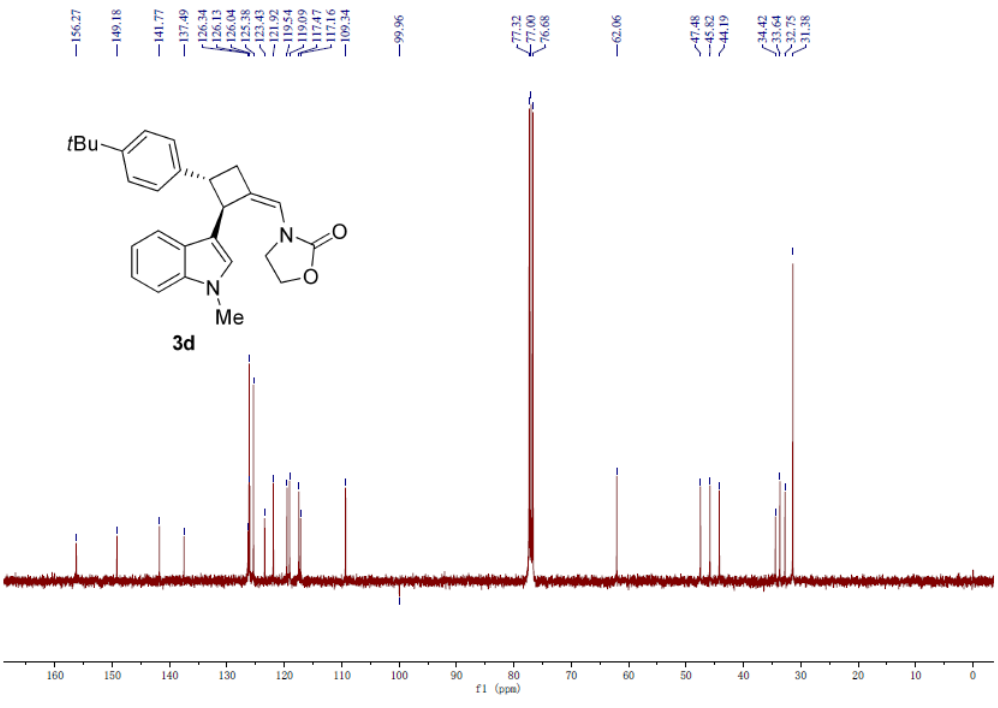
7.277
7.256
7.248
7.244
7.241
6.866
6.525
6.519
4.448
4.442
4.434
4.427
4.420
4.033
4.018
3.895
3.875
3.768
3.505
3.486
3.421
2.975
2.963
2.958
2.941
2.936
2.924
2.919
1.329
tBu
N
O
O
N
Me
3d
1.00
5.97
1.11
0.93
0.94
1.11
1.14
1.18
2.98
3.97
0.96
9.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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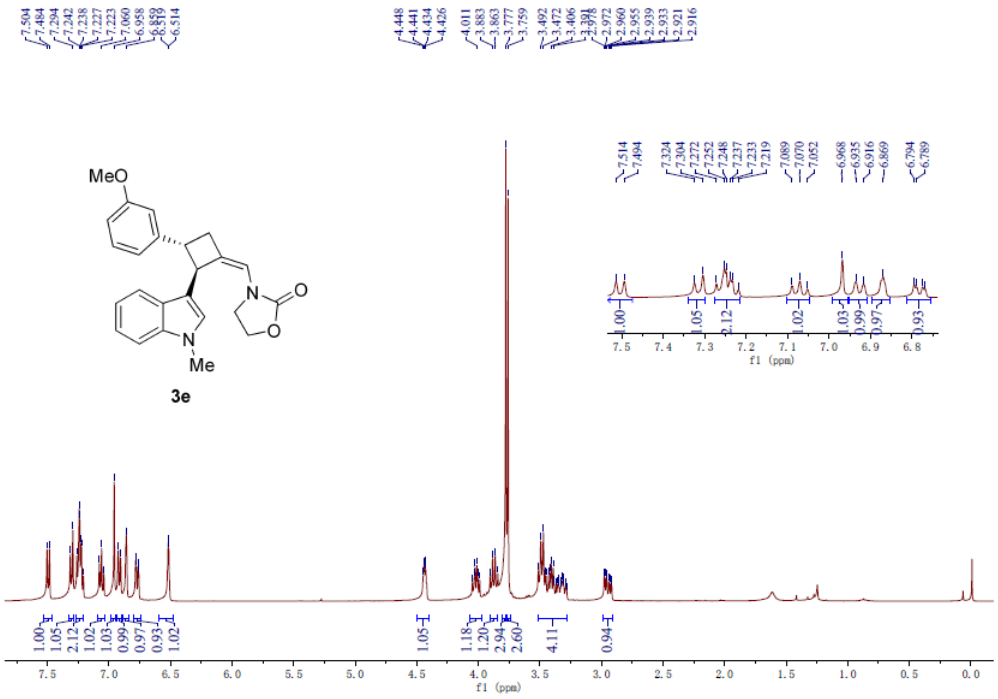
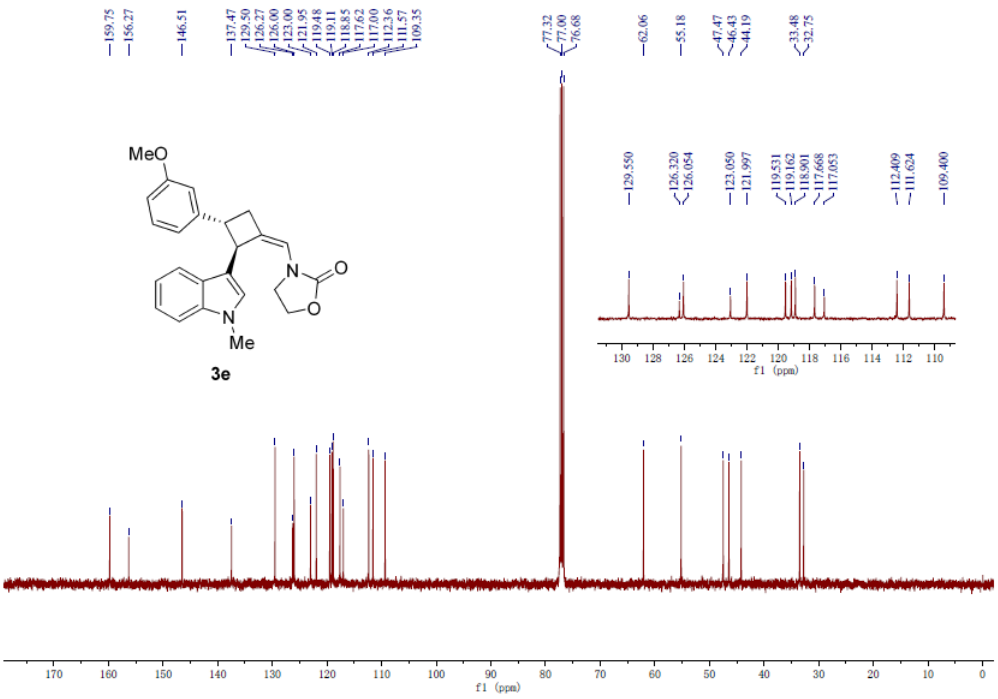
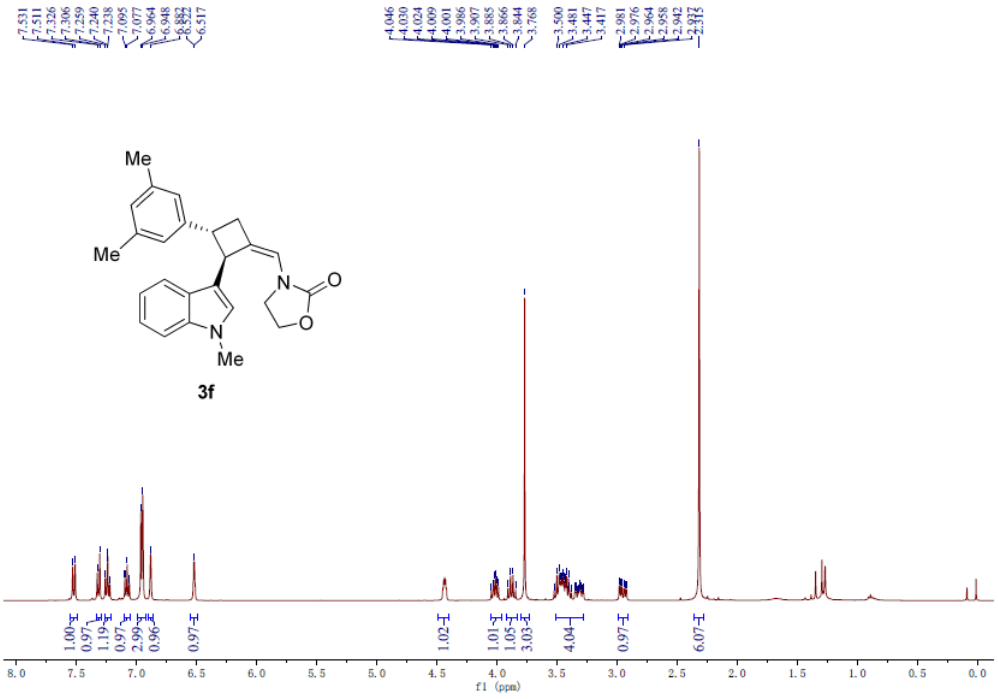
149.18
141.77
137.49
126.34
126.13
126.04
125.38
123.43
121.92
119.54
119.09
117.47
117.16
109.34
99.96
77.32
77.00
76.68
62.06
47.48
45.82
44.19
34.42
33.64
32.75
31.38
tBu
N
O
O
N
Me
3d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
N
O
N
Me
3e


MeO
N
O
N
Me
3e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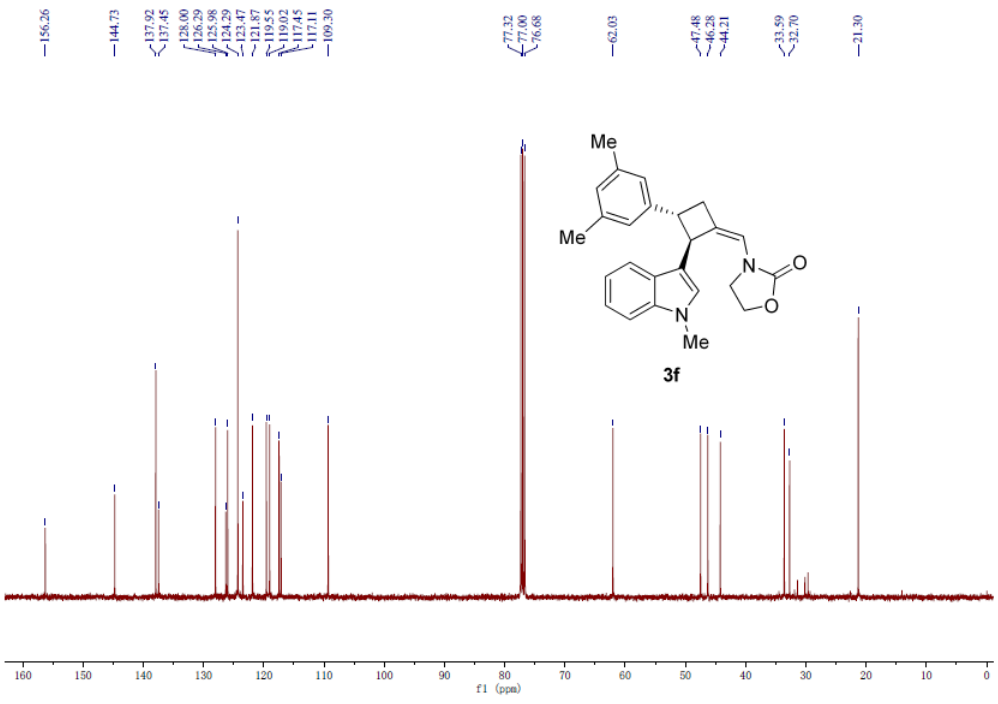
7.306
7.259
7.240
7.238
7.095
7.077
6.964
6.948
6.852
6.832
6.517
4.046
4.030
4.024
4.009
4.001
3.986
3.907
3.885
3.866
3.844
3.768
3.500
3.481
3.447
3.417
2.981
2.976
2.964
2.958
2.942
2.937
2.915
Me
Me
N
O
O
N
Me
3f
1.00
0.97
1.19
0.97
2.99
0.96
0.97
1.02
1.01
1.05
3.03
4.04
0.97
6.07
8.0
7.5
7.0
6.5
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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137.92
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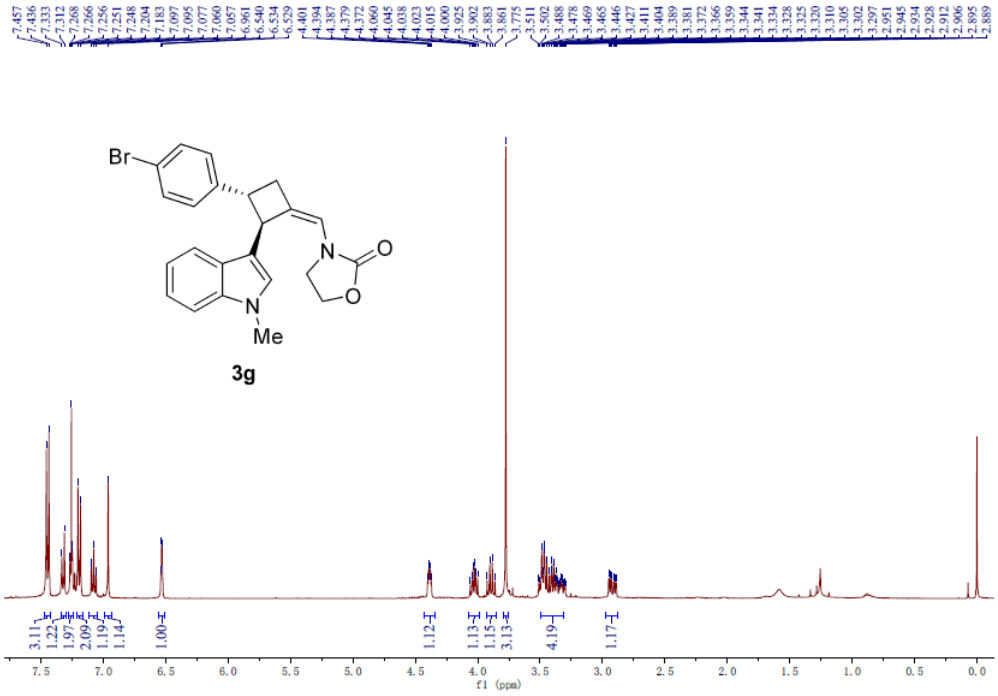
126.29
125.98
124.29
123.47
121.87
119.55
119.02
117.45
117.11
109.30
77.32
77.00
76.68
62.03
47.48
46.28
44.21
33.59
32.70
21.30
Me
Me
N
O
O
N
Me
3f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
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O
N
O
Me
3g
3.11
1.22
1.97
2.09
1.19
1.14
1.00
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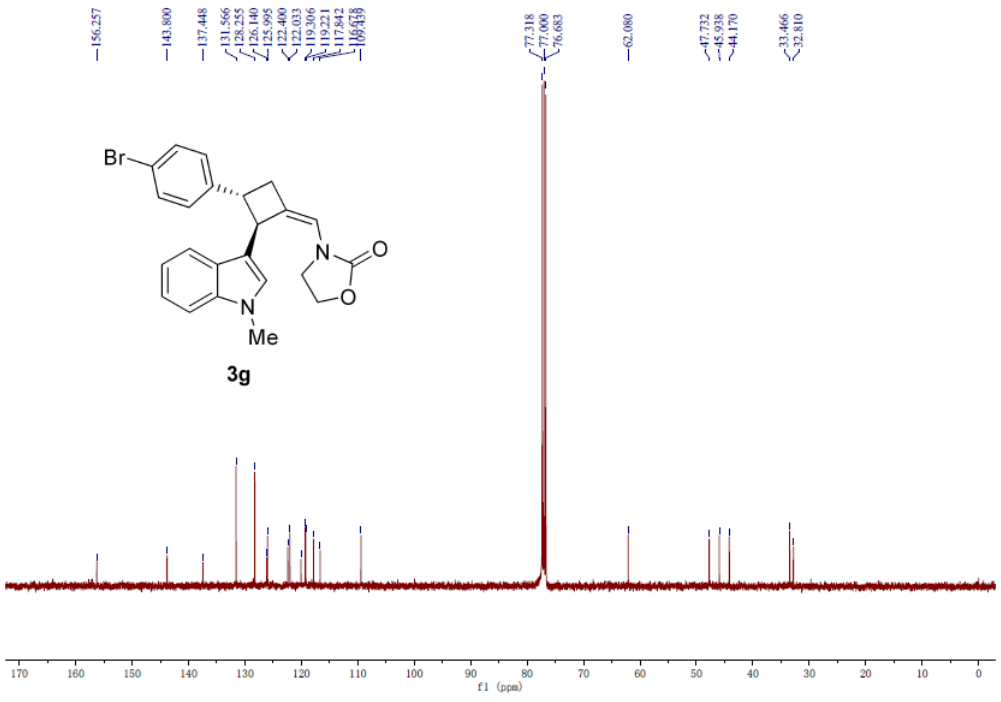
1.15
3.13
4.19
1.17
f1 (ppm)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137.448
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128.255
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125.995
122.400
122.033
119.306
119.221
117.842
77.318
77.000
76.683
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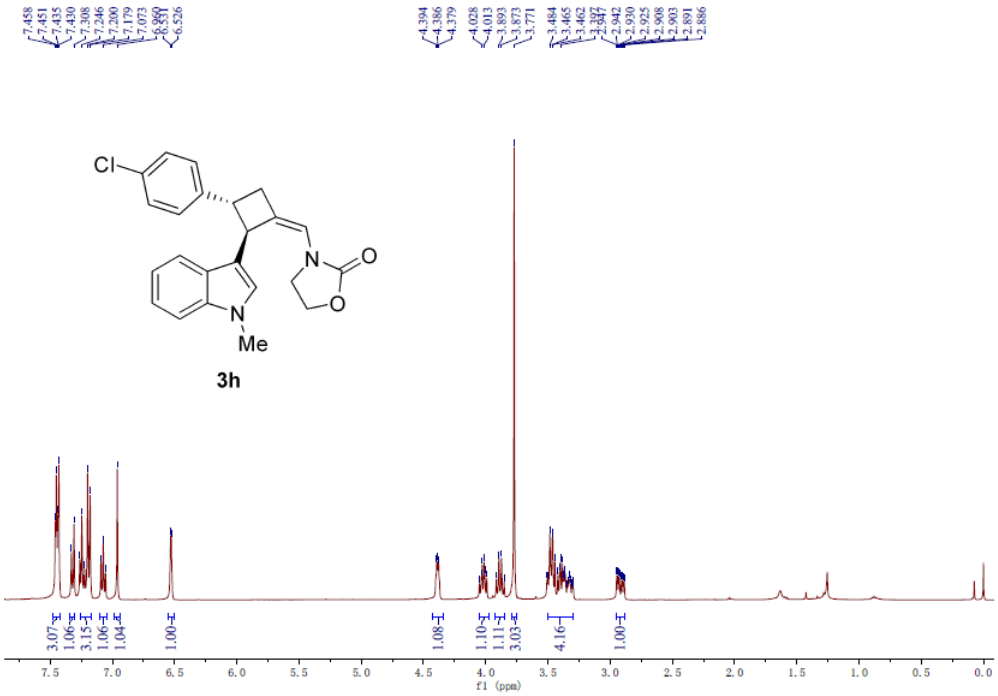
44.170
33.466
32.810
Br
N
O
N
O
Me
3g
f1 (ppm)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7.308
7.246
7.200
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7.073
6.880
6.526
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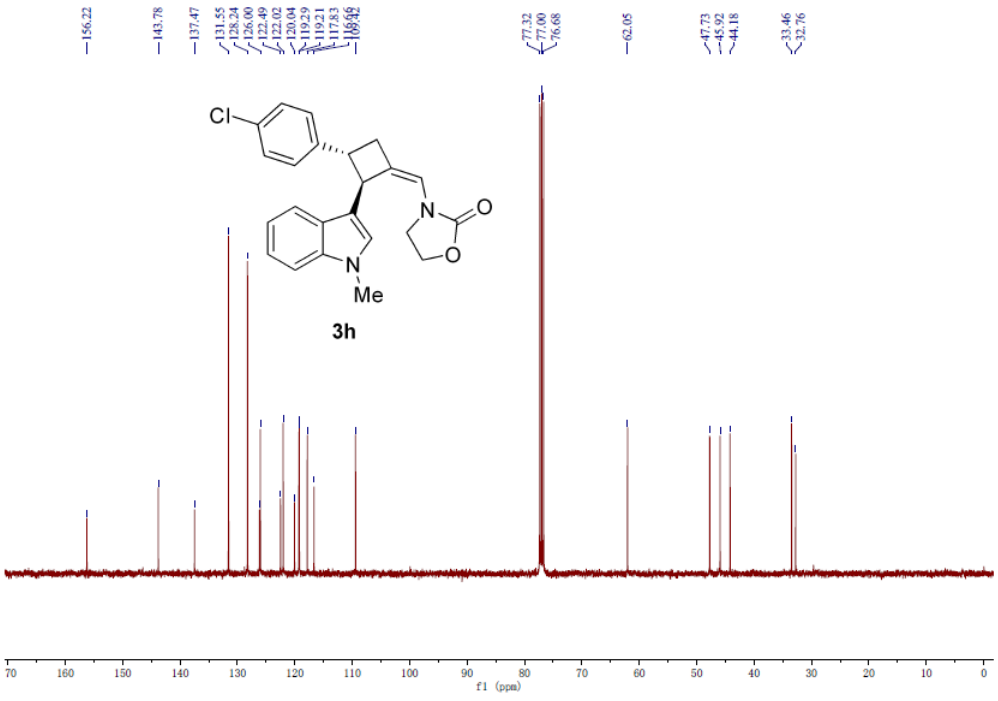
4.386
4.379
4.028
4.013
3.893
3.873
3.771
3.484
3.465
3.462
3.337
2.947
2.942
2.930
2.925
2.908
2.903
2.891
2.886
Cl
N
O
N
Me
3h
3.07
1.06
3.15
1.06
1.04
1.00
1.08
1.10
1.11
3.03
4.16
1.00
f1 (ppm)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122.02
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119.29
119.21
117.83
109.46
77.32
77.00
76.68
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45.92
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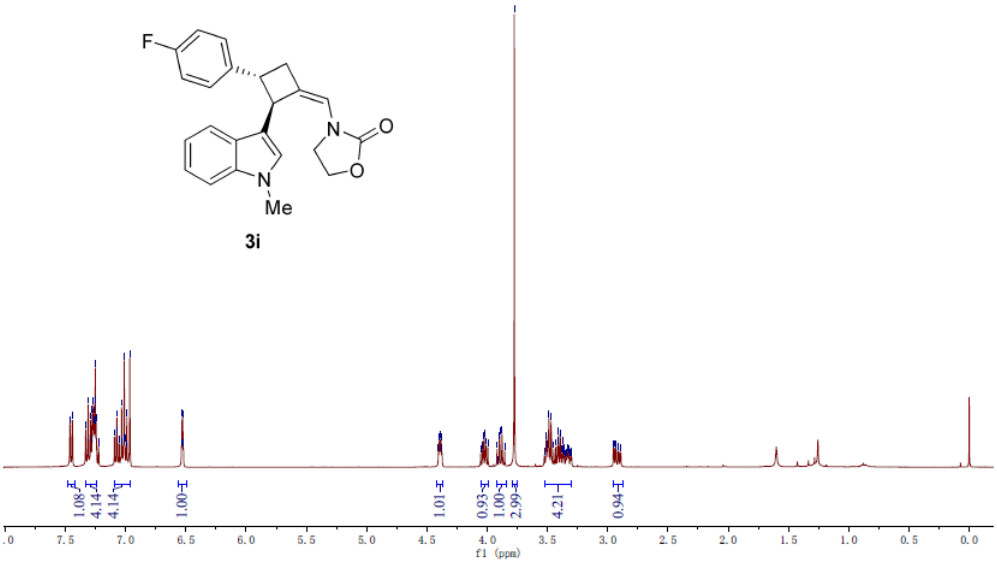
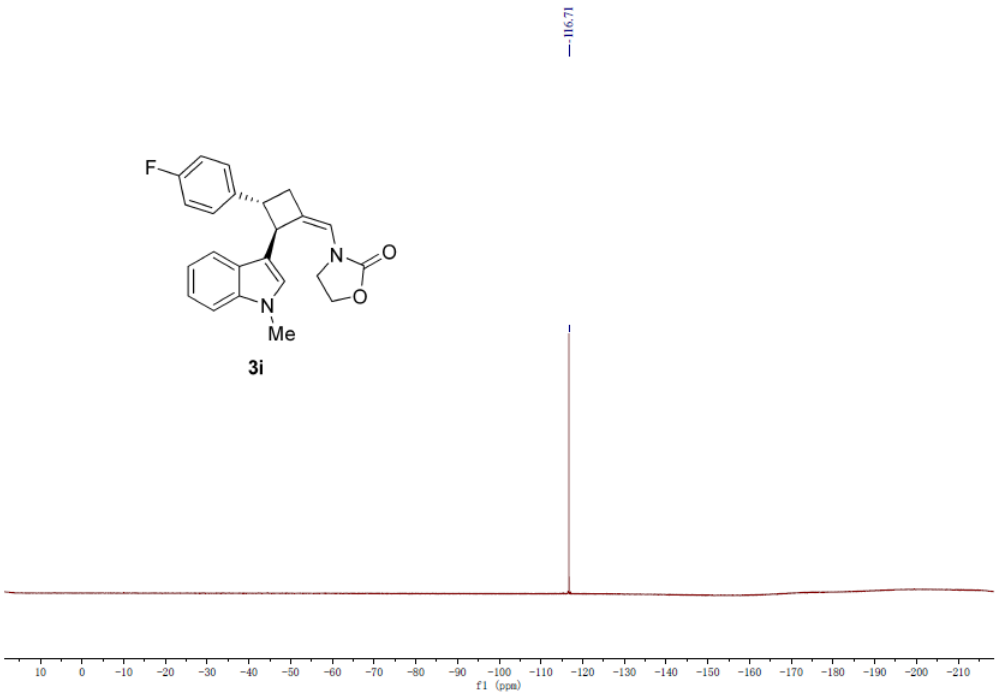
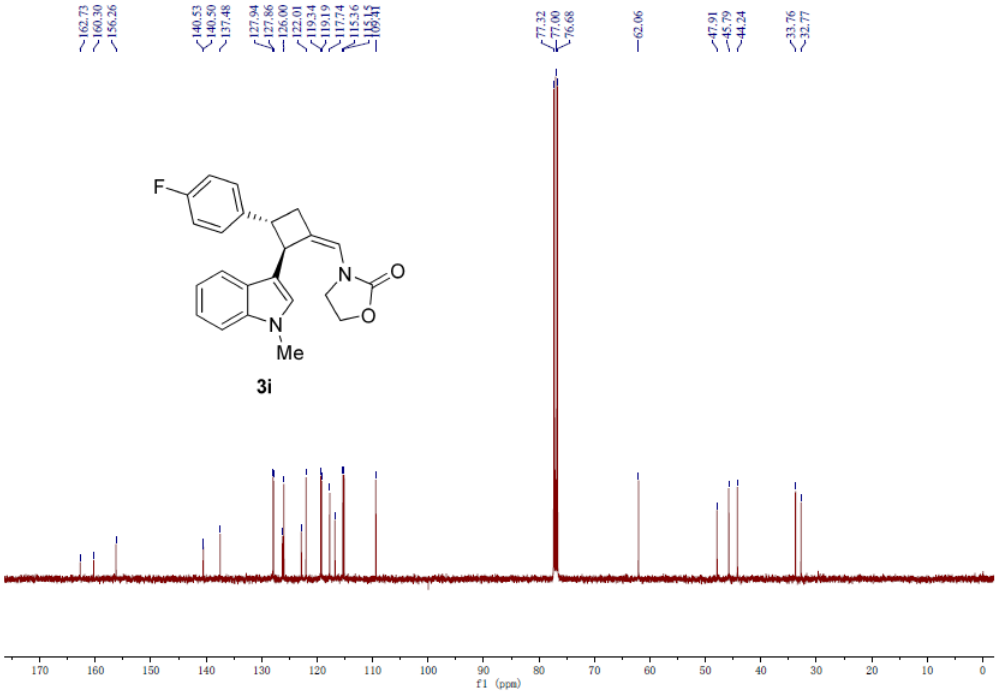
33.46
32.76
Cl
N
O
N
Me
3h
f1 (ppm)


F
N
O
N
O
Me
1.08
4.14
4.14
1.00
1.01
0.93
1.00
2.99
4.21
0.94
f1 (ppm)

3i


116.71
F
N
O
N
O
Me
f1 (ppm)

3i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137.48
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127.86
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122.01
119.34
119.19
117.74
115.36
115.15
109.41
77.32
77.00
76.68
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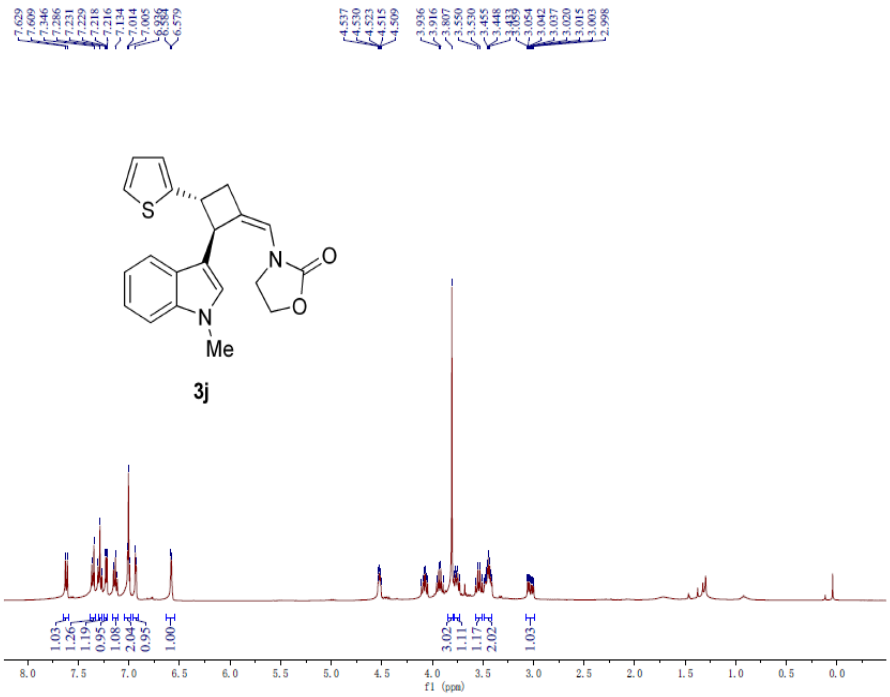
45.79
44.24
33.76
32.77
F
N
O
O
N
Me
3i
f1 (ppm)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7.216
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7.014
7.005
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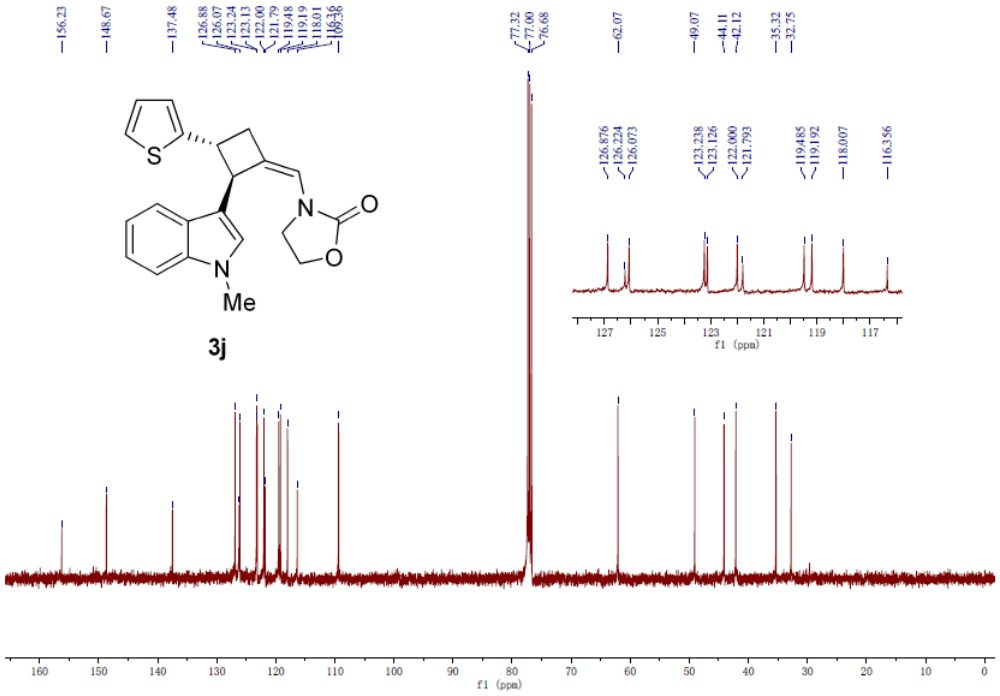
4.537
4.530
4.523
4.515
4.509
3.936
3.916
3.807
3.550
3.530
3.455
3.448
3.054
3.042
3.037
3.020
3.015
3.003
2.998
S
N
O
O
N
Me
3j
1.03
1.26
1.19
0.95
1.08
2.04
0.95
1.00
3.02
1.11
1.17
2.02
1.03
f1 (ppm)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126.07
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123.13
122.00
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119.48
119.19
118.01
116.36
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77.32
77.00
76.68
62.07
49.07
44.11
42.12
35.32
32.75
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126.224
126.073
123.238
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116.356
S
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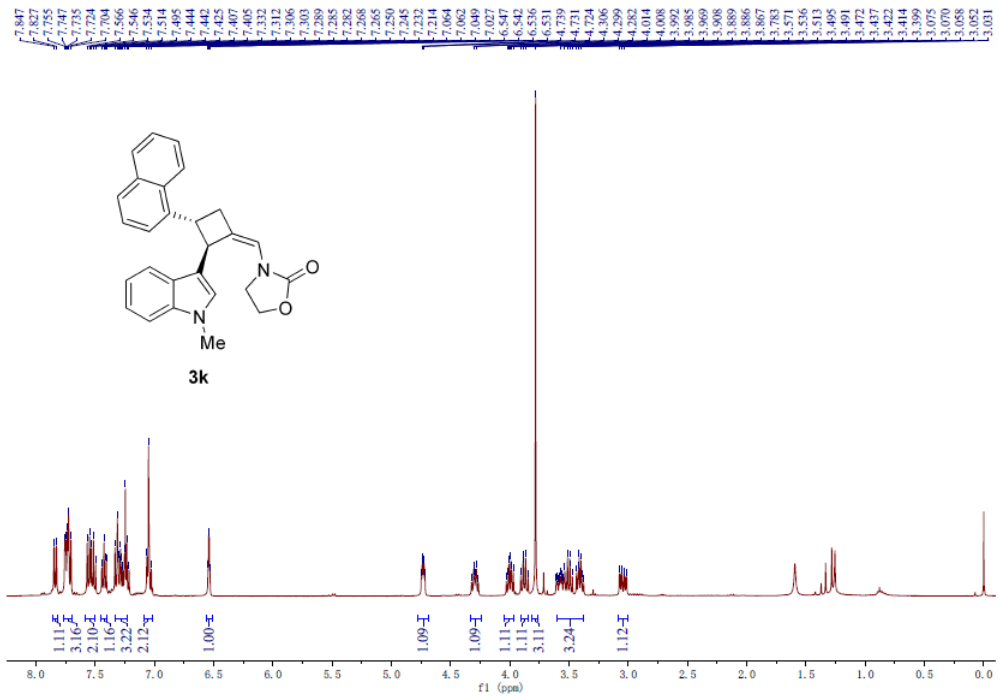
N
Me
3j
f1 (ppm)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7.442
7.425
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7.332
7.312
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7.303
7.289
7.285
7.282
7.268
7.265
7.250
7.245
7.232
7.214
7.064
7.063
7.049
7.027
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6.542
6.536
6.531
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4.731
4.724
4.306
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4.282
4.014
4.008
3.992
3.985
3.969
3.908
3.889
3.886
3.867
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3.571
3.536
3.513
3.495
3.491
3.472
3.437
3.422
3.414
3.399
3.075
3.070
3.058
3.052
3.031
N
O
N
Me
3k
1.11
3.16
2.10
1.16
3.22
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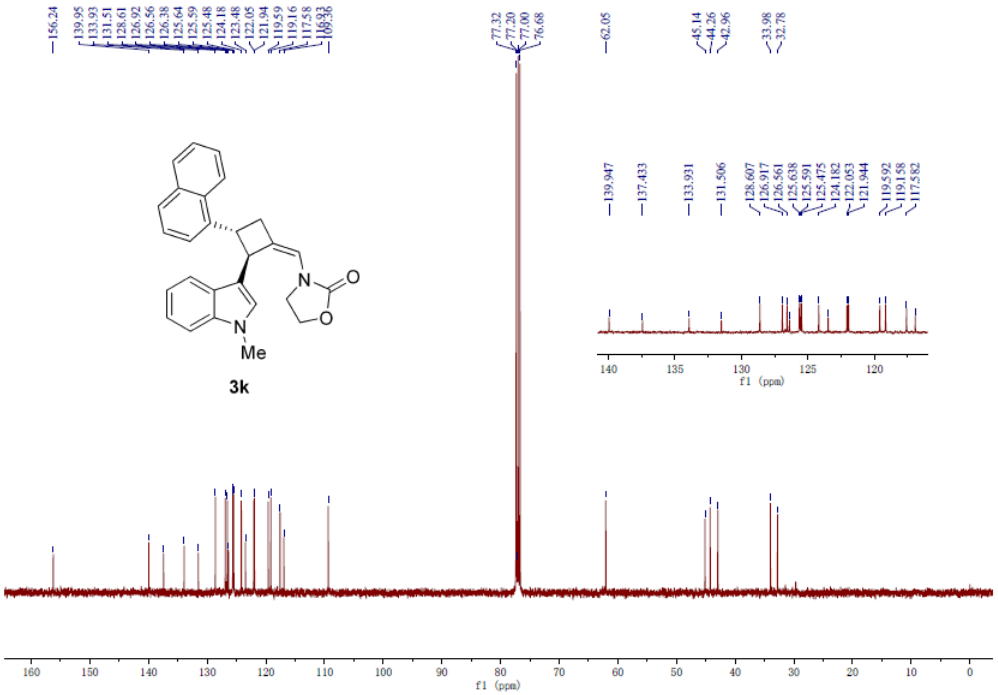
1.00
1.09
1.09
1.11
1.11
3.11
3.24
1.12
f1 (ppm)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128.61
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126.38
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125.59
125.48
124.18
123.48
122.05
121.94
119.59
119.16
117.58
110.33
77.32
77.20
77.00
76.68
62.05
45.14
44.26
42.96
33.98
32.78
139.947
137.433
133.931
131.506
128.607
126.917
126.561
125.638
125.591
125.475
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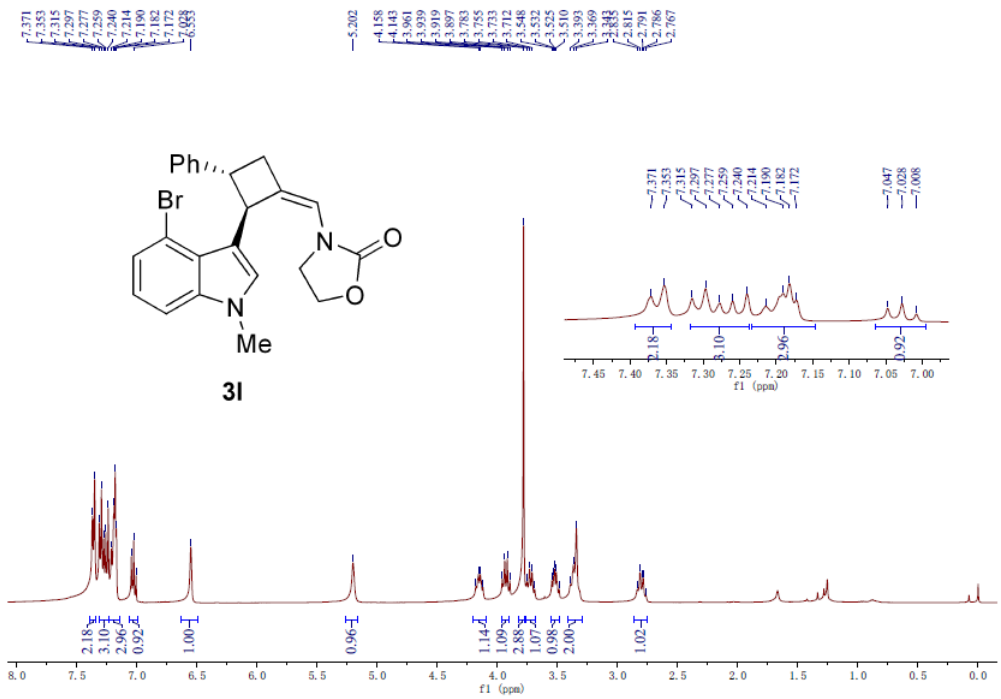
122.053
121.944
119.592
119.158
117.582
N
O
N
Me
3k
f1 (ppm)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7.277
7.259
7.240
7.214
7.190
7.182
7.172
5.202
4.158
4.143
3.961
3.939
3.919
3.897
3.783
3.755
3.733
3.712
3.548
3.532
3.525
3.510
3.393
3.369
2.815
2.791
2.786
2.767
Ph
Br
N
O
N
Me
3l
7.047
7.028
7.008
2.18
3.10
2.96
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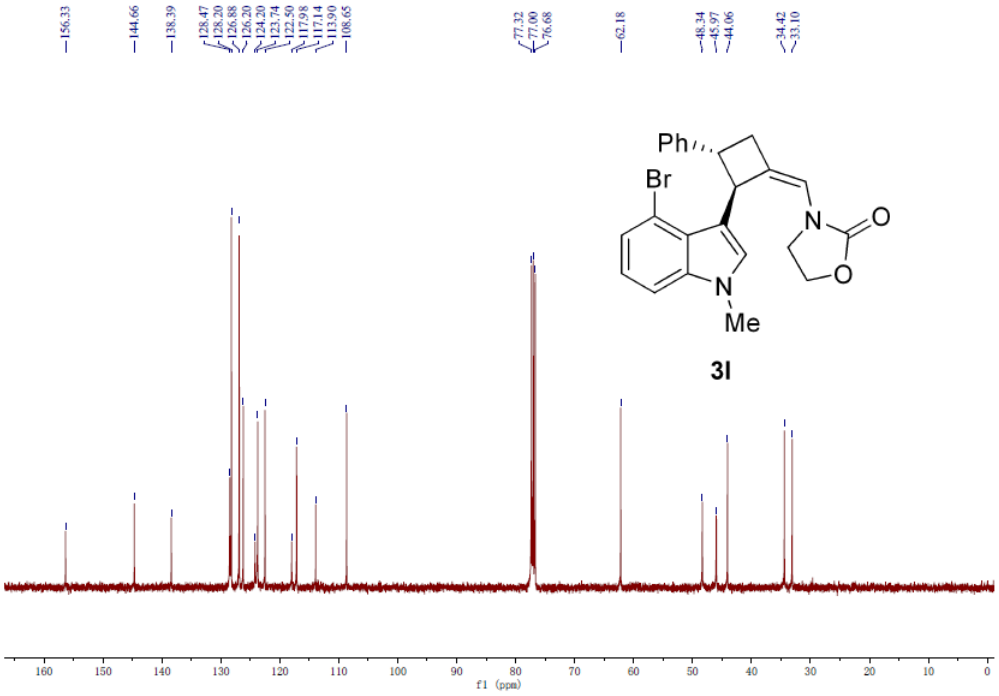
0.96
1.14
1.09
2.88
1.07
0.98
2.00
1.02
f1 (ppm)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128.47
128.20
126.88
126.20
124.20
123.74
122.59
117.98
117.14
113.90
108.65
77.32
77.00
76.68
62.18
48.34
45.97
44.06
34.42
33.10
Ph
Br
N
O
N
Me
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150
140
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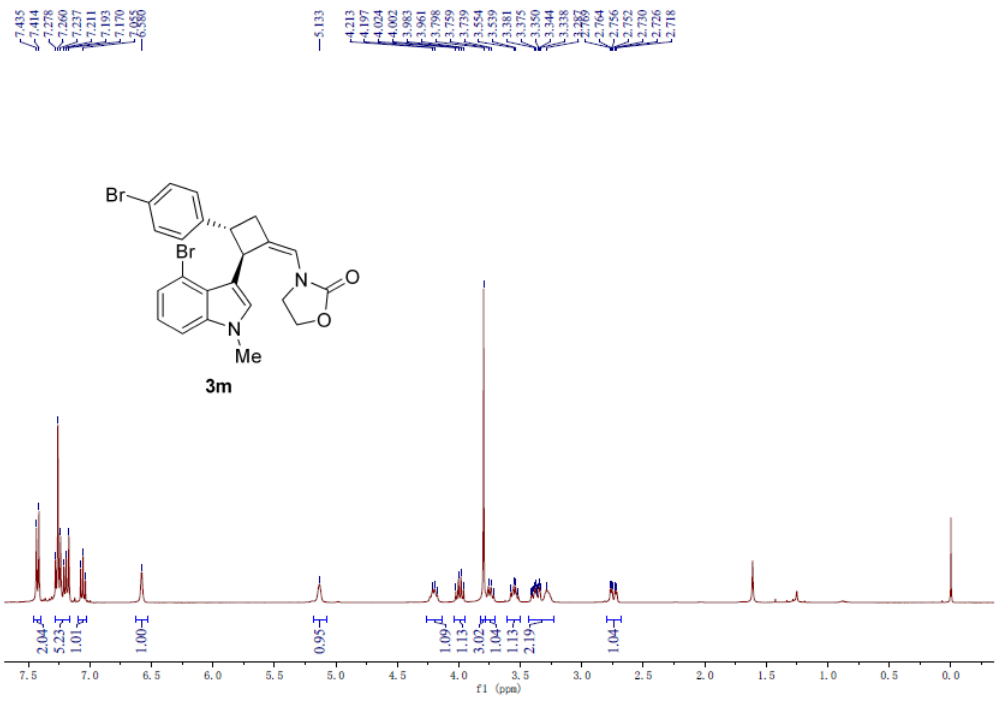
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3l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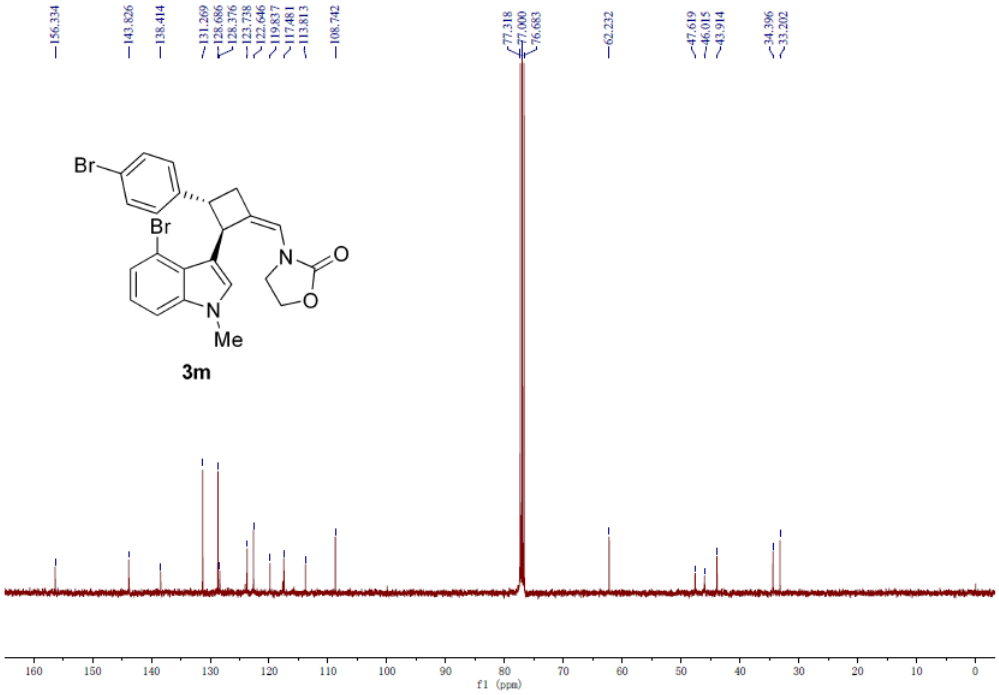
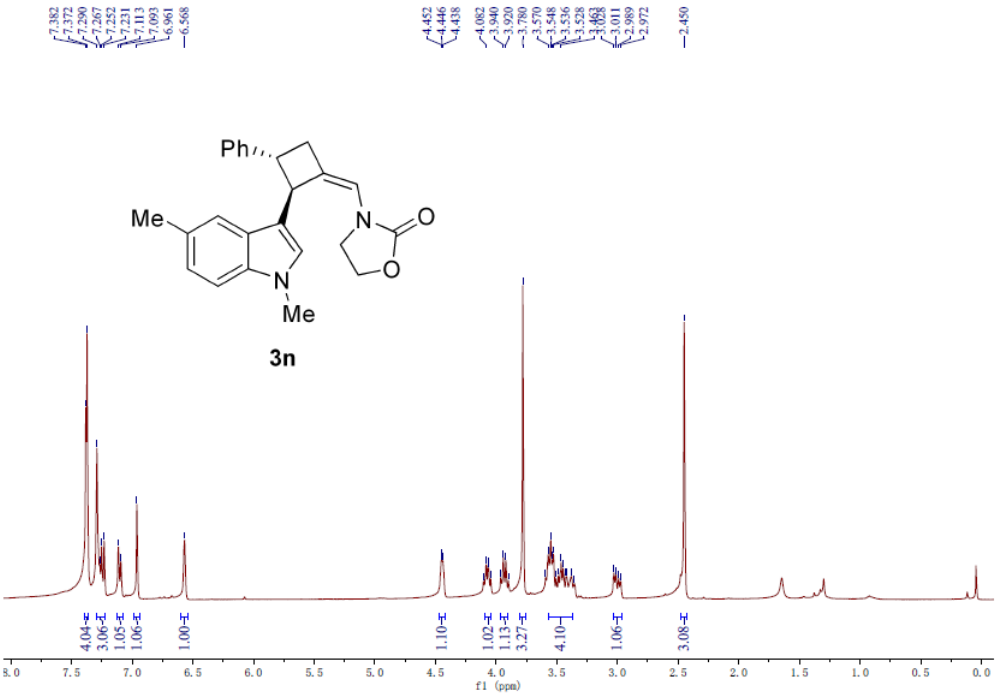
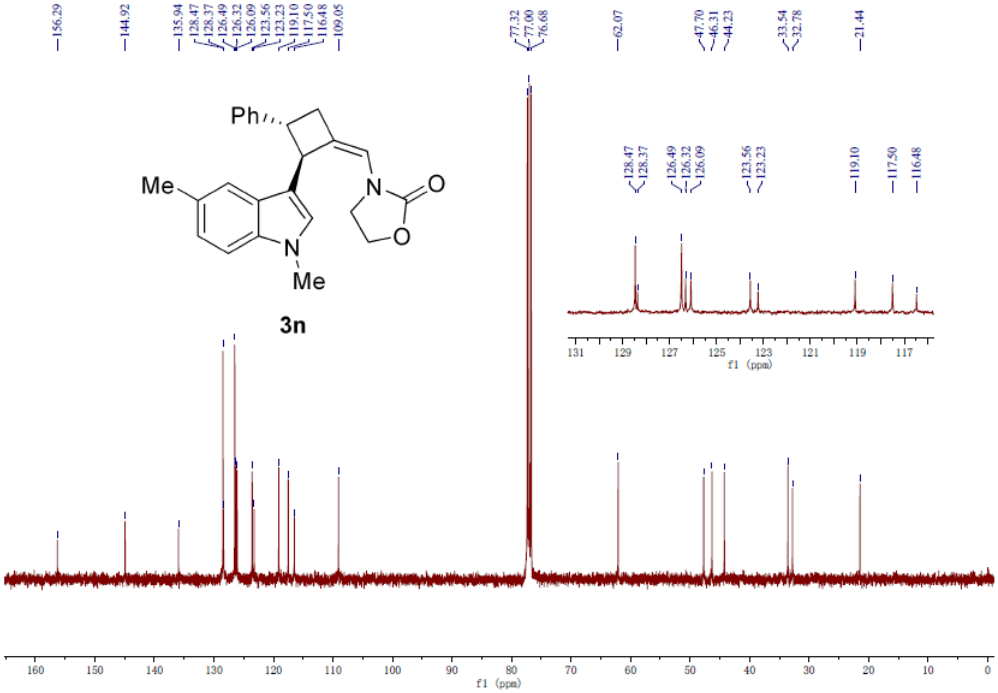
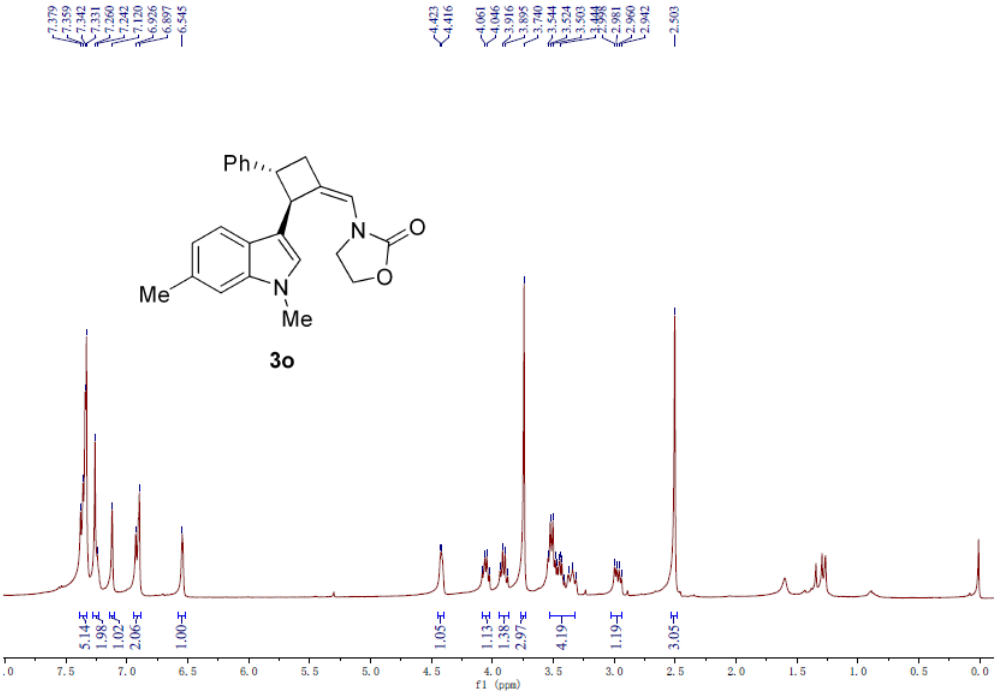
7.260
7.237
7.211
7.193
7.170
7.055
6.980
5.133
4.213
4.197
4.024
4.002
3.983
3.961
3.798
3.759
3.739
3.554
3.539
3.381
3.375
3.350
3.344
3.338
2.769
2.764
2.756
2.752
2.730
2.726
2.718
Br
Br
N
O
N
Me
2.04
5.23
1.01
1.00
0.95
1.09
1.13
3.02
1.04
1.13
2.19
1.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

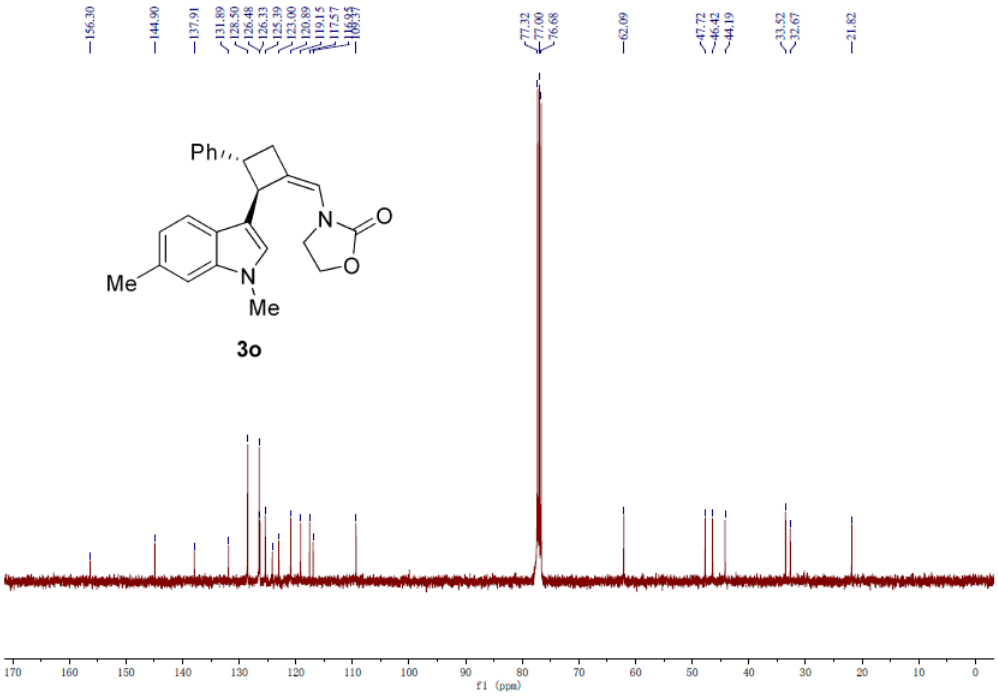
3m


156.334
143.826
138.414
131.269
128.686
128.376
123.738
122.646
119.837
117.481
113.813
108.742
77.318
77.000
76.683
62.232
47.619
46.015
43.914
34.396
33.202
Br
Br
N
O
N
O
Me
3m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

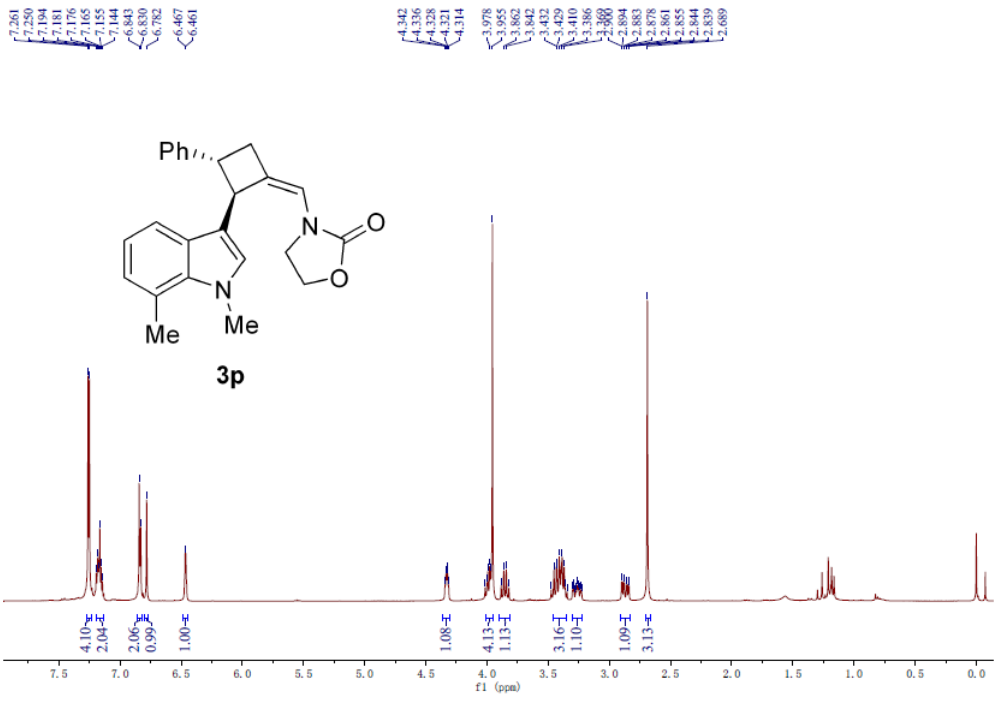

7.382
7.372
7.290
7.267
7.252
7.231
7.113
7.093
6.961
6.568
4.452
4.446
4.438
4.082
3.940
3.920
3.780
3.570
3.548
3.536
3.528
3.463
3.028
3.011
2.989
2.972
2.450
Ph
Me
N
O
N
O
Me
3n
4.04
3.06
1.05
1.06
1.00
1.10
1.02
1.13
3.27
4.10
1.06
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.29
144.92
135.94
128.47
128.37
126.49
126.32
126.09
123.56
123.23
119.10
117.50
116.48
109.05
77.32
77.00
76.68
62.07
47.70
46.31
44.23
33.54
32.78
21.44
Ph
Me
N
O
N
Me
3n
f1 (ppm)

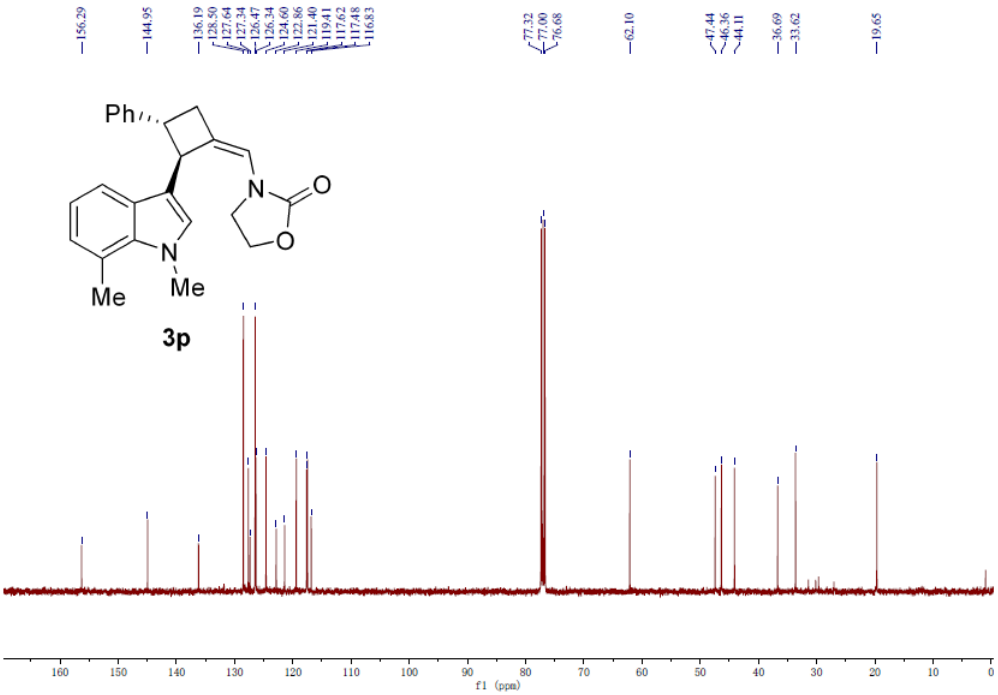

7.379
7.359
7.342
7.331
7.260
7.242
7.120
6.926
6.897
6.545
4.423
4.416
4.061
4.046
3.916
3.895
3.740
3.544
3.524
3.503
2.981
2.960
2.942
2.503
Ph
Me
N
O
N
Me
3o
5.14
1.98
1.02
2.06
1.00
1.05
1.13
1.38
2.97
4.19
1.19
3.05
f1 (ppm)

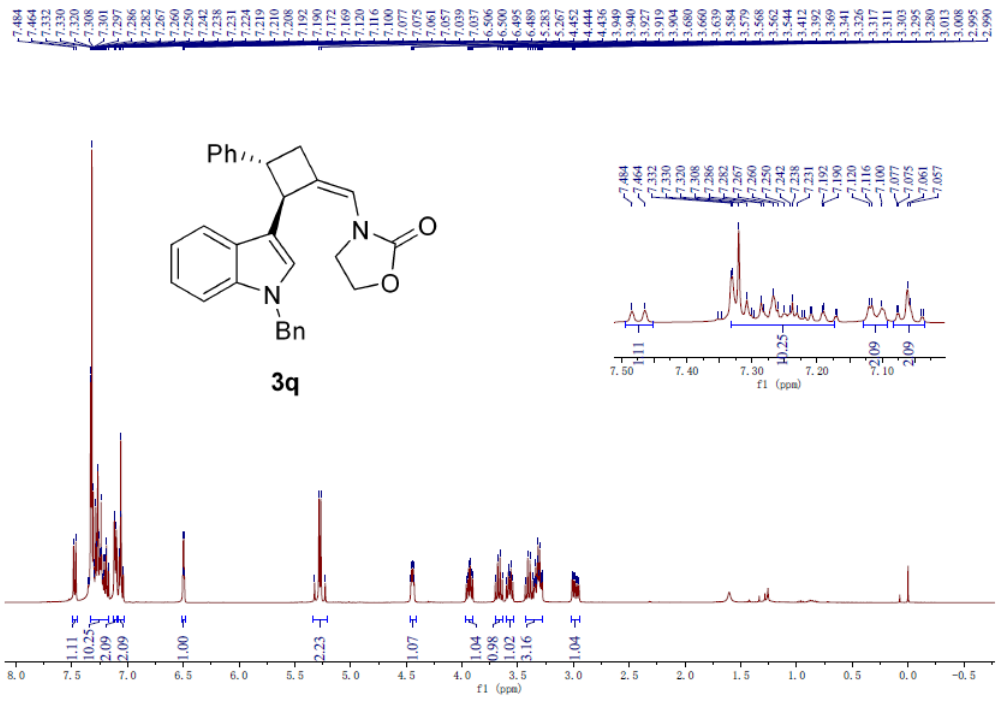

156.30
144.90
137.91
131.89
128.50
126.48
126.33
125.39
123.00
120.89
119.15
117.57
108.34
77.32
77.00
76.68
62.09
47.72
46.42
44.19
33.52
32.67
21.82
Ph
N
O
O
Me
N
Me
f1 (ppm)

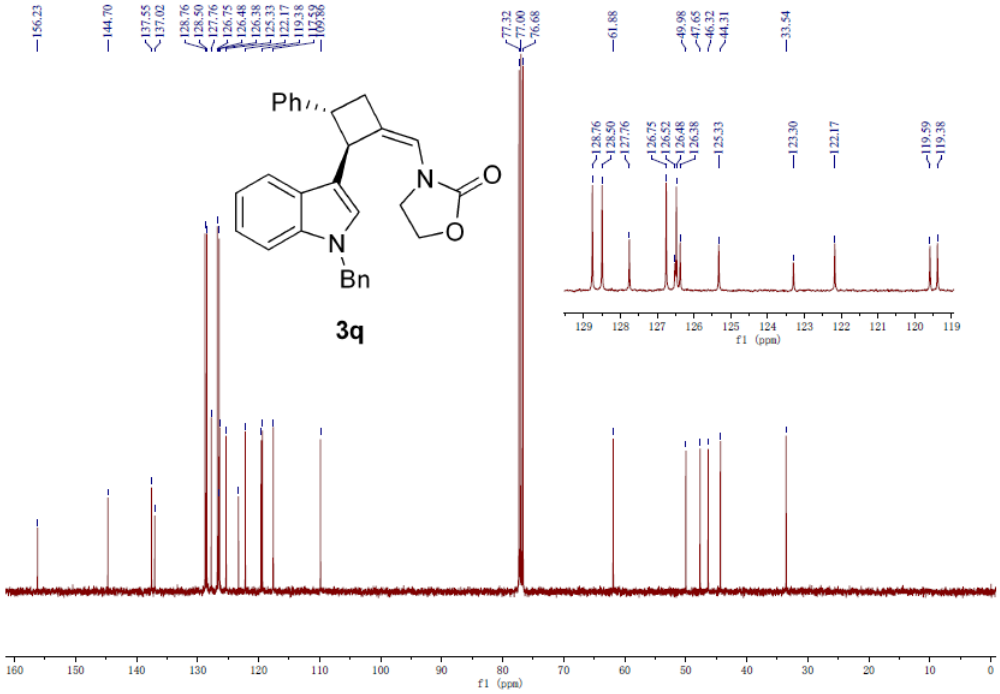
3o

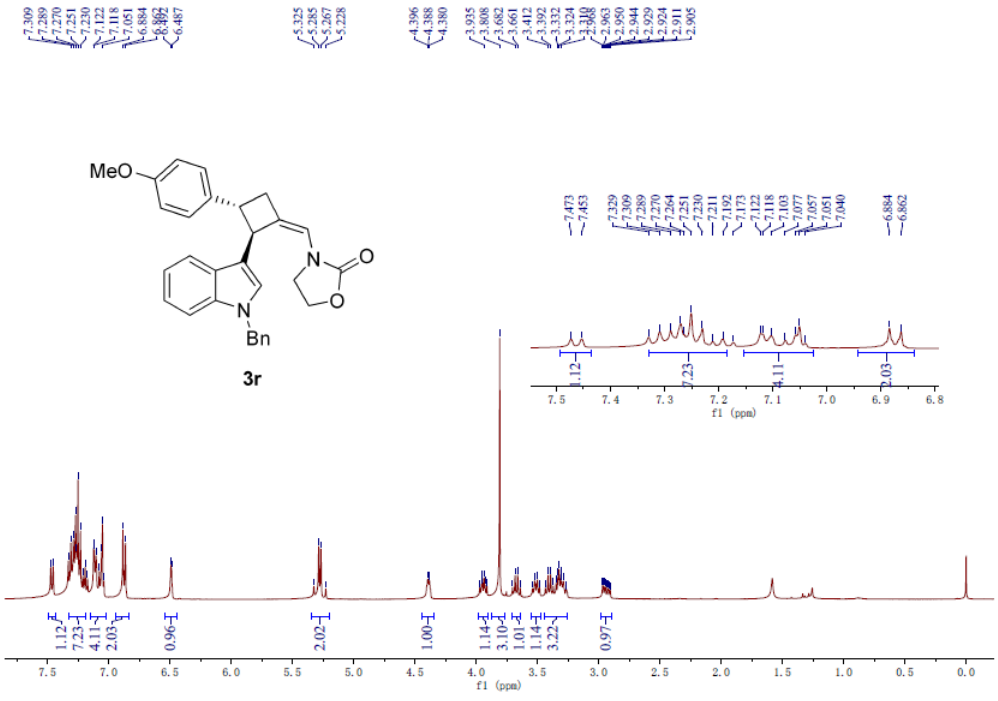

7.261
7.250
7.194
7.181
7.176
7.165
7.155
7.144
6.843
6.830
6.782
6.467
6.461
4.342
4.336
4.328
4.321
4.314
3.978
3.955
3.862
3.842
3.432
3.429
3.410
3.386
2.894
2.883
2.878
2.861
2.855
2.844
2.839
2.689
Ph
N
O
O
Me
N
Me
4.10
2.04
2.06
0.99
1.00
1.08
4.13
1.13
3.16
1.10
1.09
3.13
f1 (ppm)

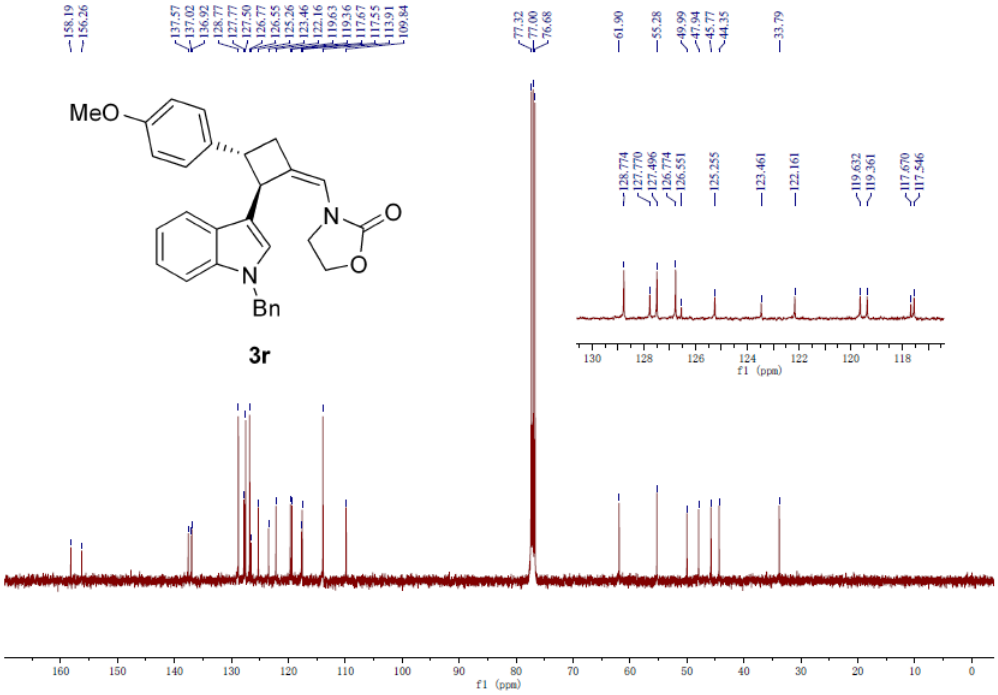
3p

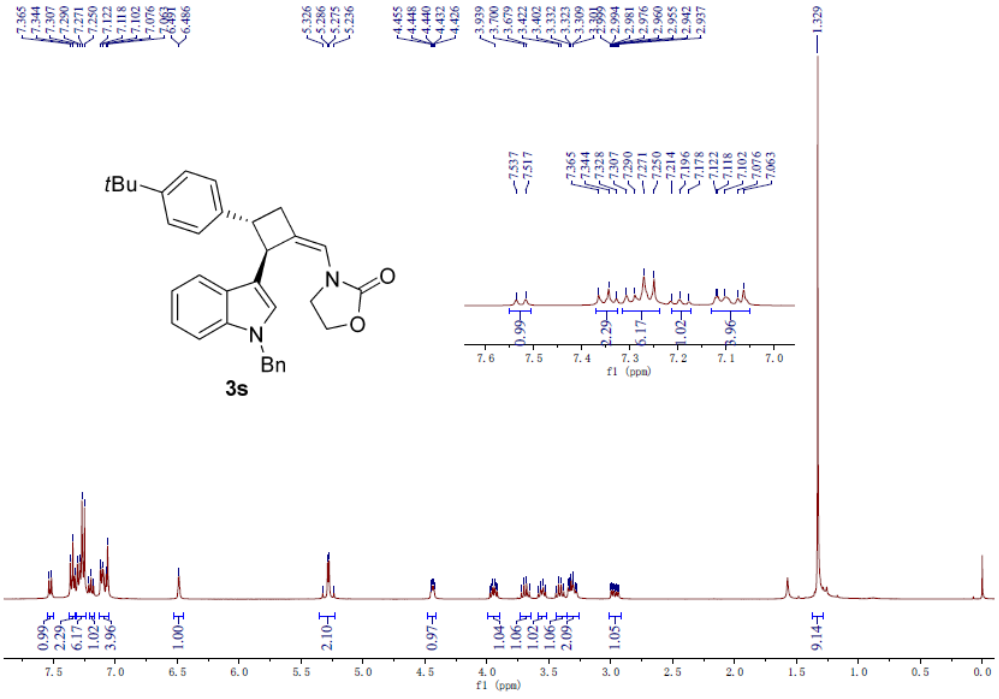

Ph
N
O
N
O
Me
Me
3p
156.29
144.95
136.19
128.50
127.64
127.34
126.47
126.34
124.60
122.86
121.40
119.41
117.62
117.48
116.83
77.32
77.00
76.68
62.10
47.44
46.36
44.11
36.69
33.62
19.65
f1 (ppm)

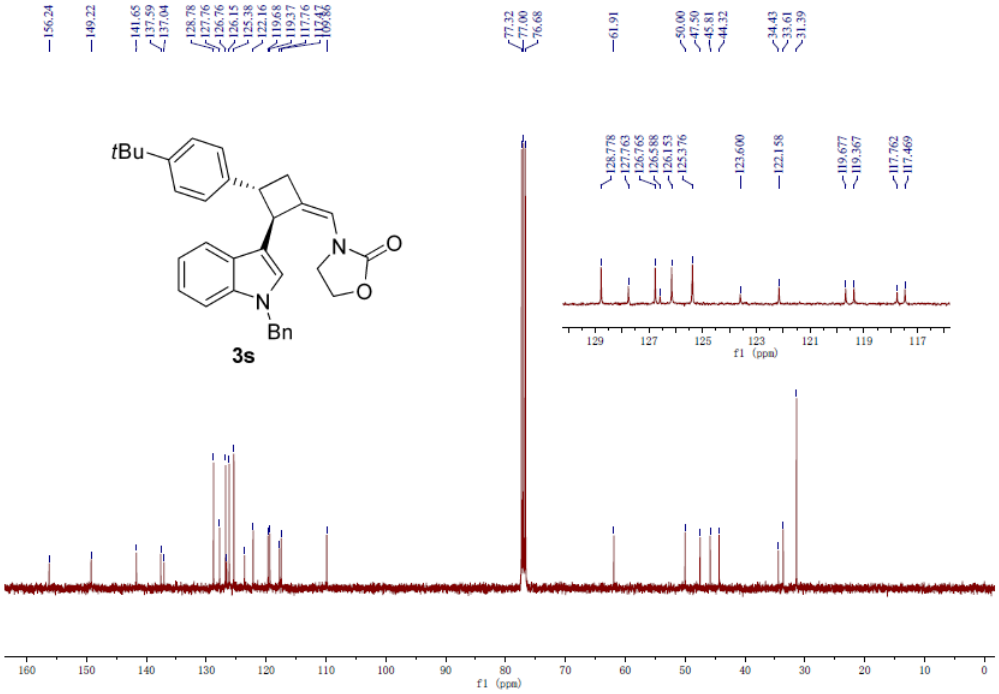

Ph
N
O
N
O
Bn
3q
f1 (ppm)

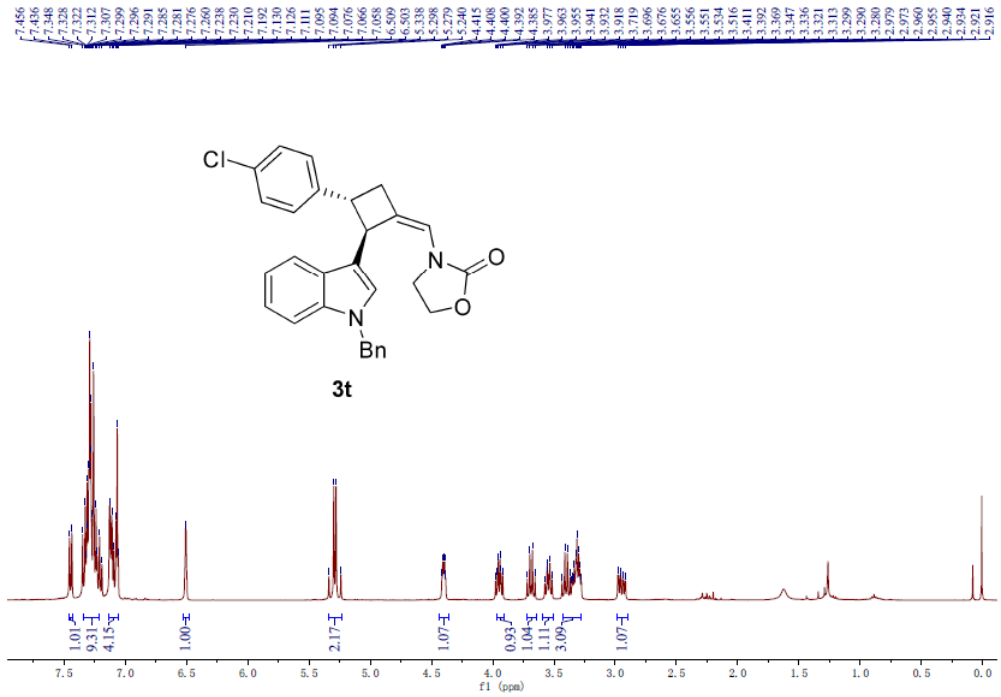

Ph
N
O
N
Bn
3q
f1 (ppm)

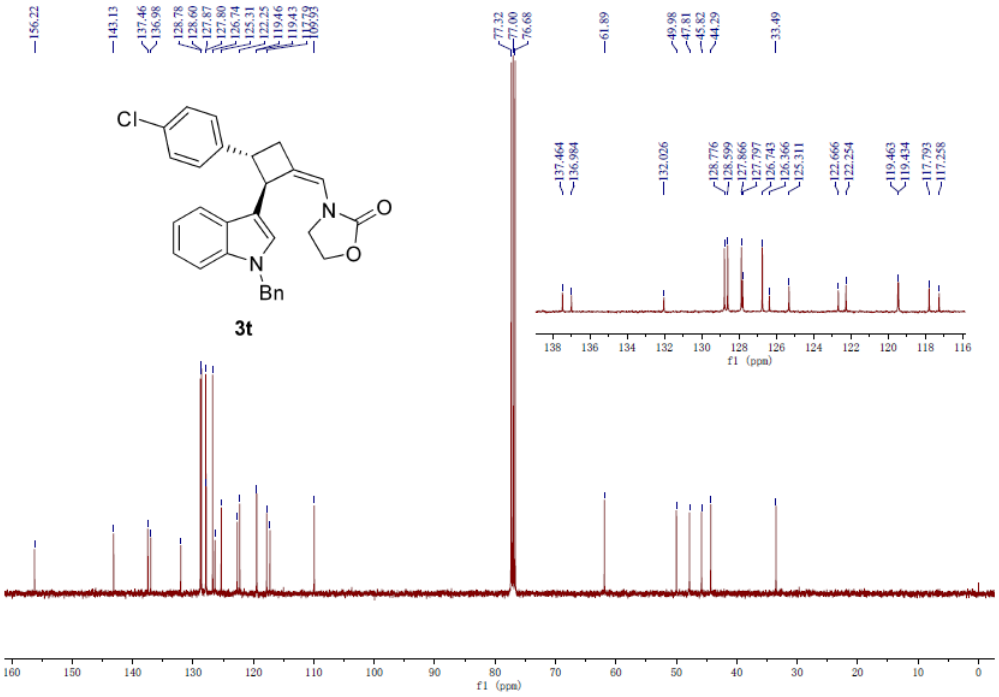

MeO
N
O
N
Bn
3r
f1 (ppm)

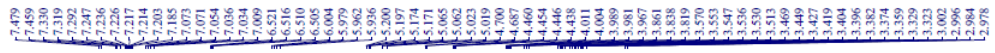

MeO
N
O
N
Bn
3r
f1 (ppm)

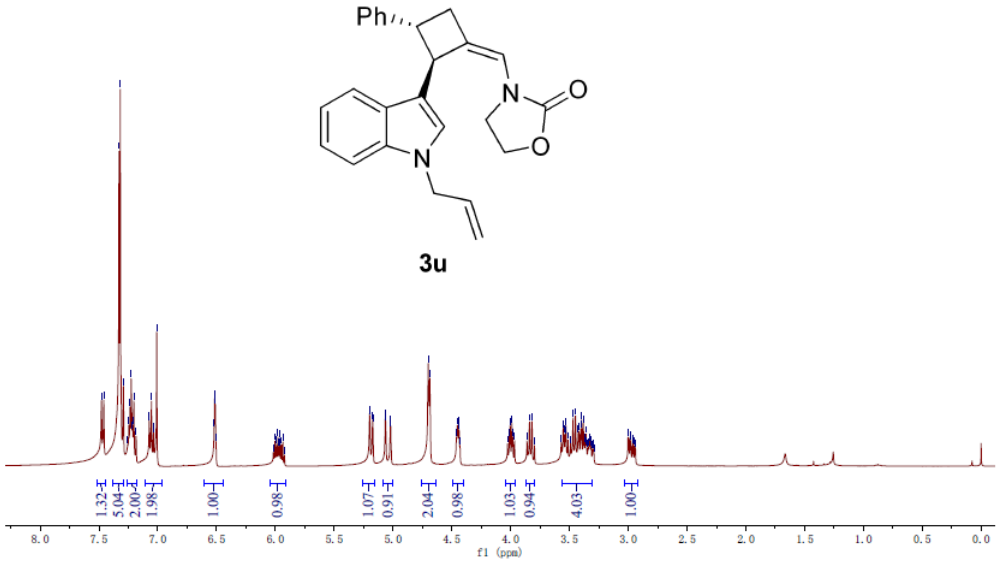

tBu
N
O
N
Bn
3s
f1 (ppm)

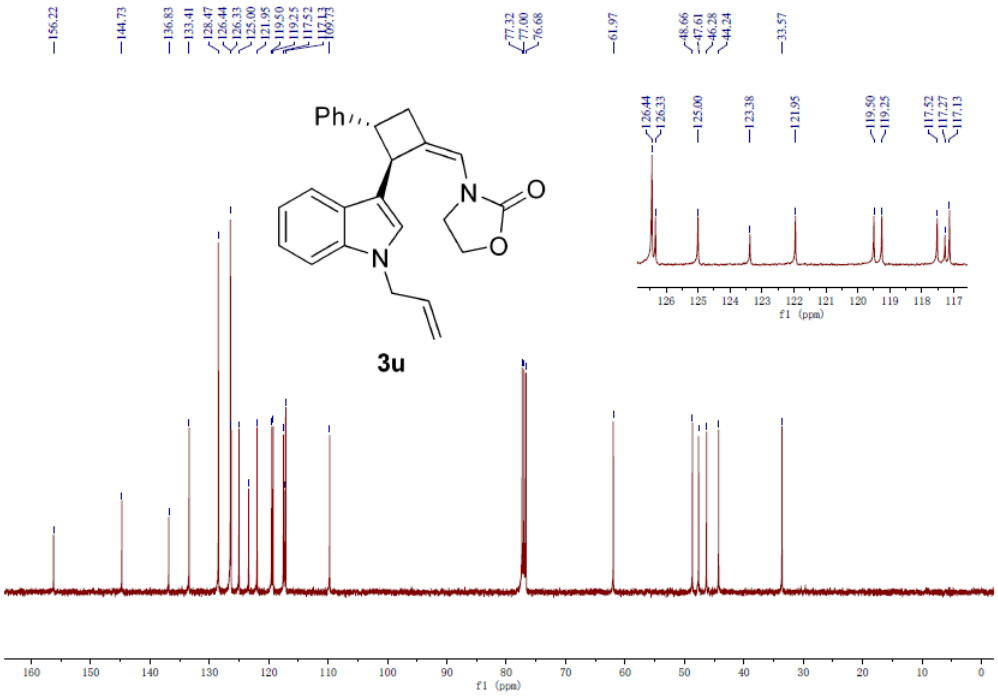

tBu
N
O
N
O
Bn
3s
f1 (ppm)

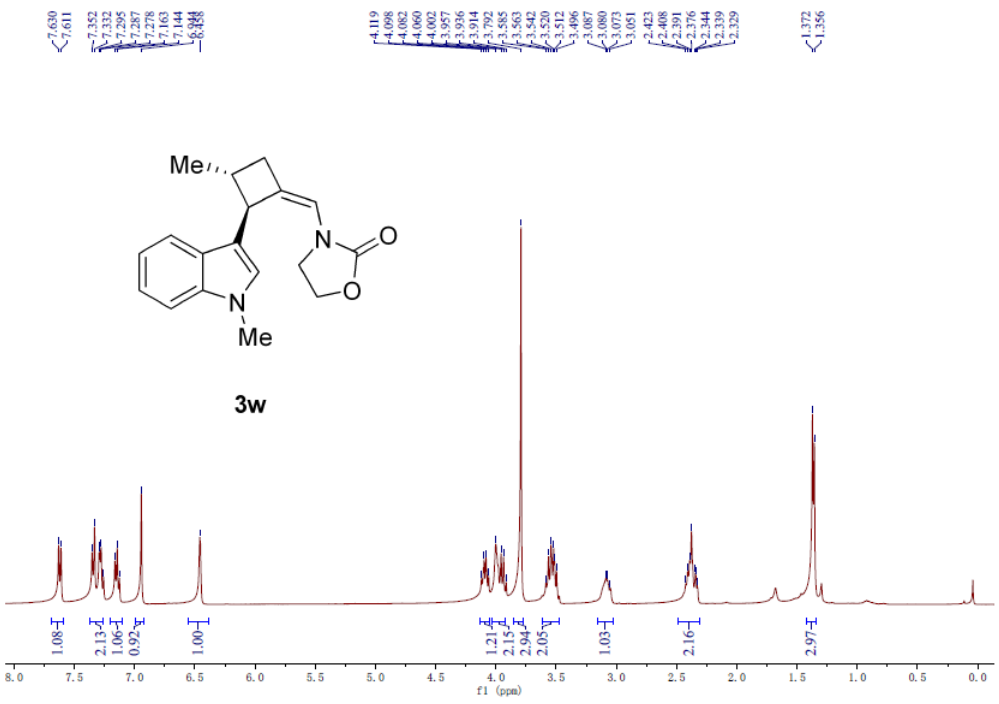

Cl
N
O
N
O
Bn
3t
f1 (ppm)

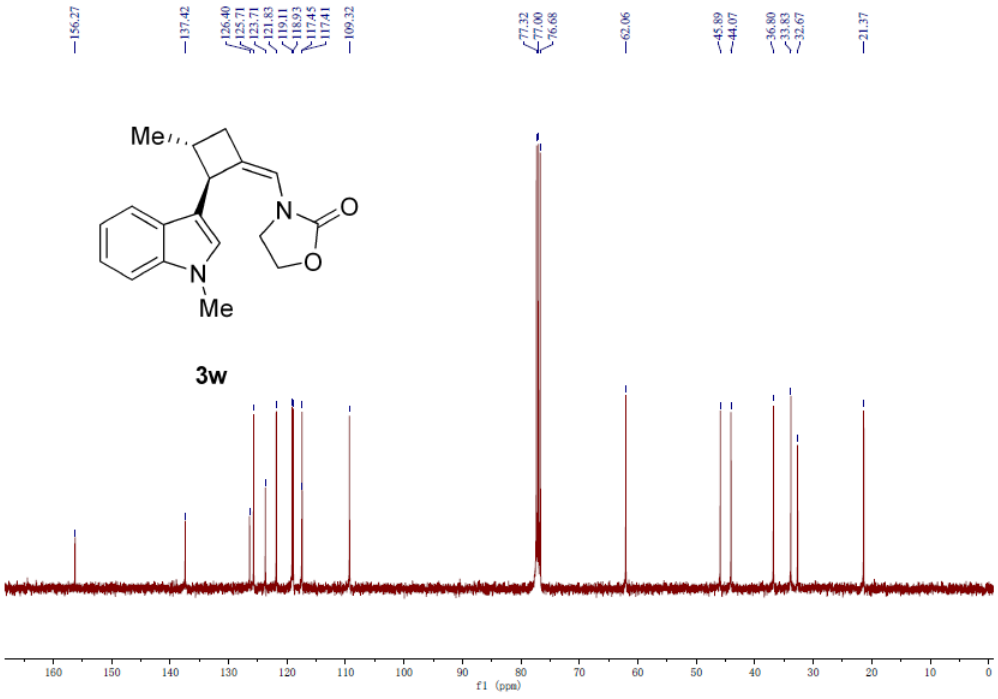

Cl
N
O
N
O
Bn
3t
f1 (ppm)




Ph
N
O
N
O
3u
f1 (ppm)


Ph
N
O
N
O
3u
f1 (ppm)


Me
N
O
N
Me
O
3w
f1 (ppm)


156.27
137.42
126.40
125.71
123.71
121.83
119.11
118.93
117.45
117.41
109.32
77.32
77.00
76.68
62.06
45.89
44.07
36.80
33.83
32.67
21.37
Me
N
O
N
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3w