Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iridium(III)-Catalyzed Two-Fold C-H Alkylation of BINOLs with Allyl Alcohols

Hao Liu, Wei Chi, Meng-Ling Lin and Lin Dong*

[§]Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry, Sichuan Research Center for Drug Precision Industrial Technology, West China School of Pharmacy, Sichuan University, Chengdu 610041, China
dongl@scu.edu.cn

Table of Contents

1. General Information
2. General Procedure for Synthesis of BINOL Units
3. Optimization of the Reaction Conditions
4. Screening of Directing Group
5. General Procedure for the Model Reaction
6. The Scope of Alkenes
7. Synthetic Transformations of Product 3aa
8. Mechanistic Studies
9. The Large-Scale Experiments
10. The HPLC Data of Compound 3af and 4af
11. Exploration of Methyl Acrylate and But-3-en-2-ol as the Coupling Partners
12. Characterization Data and NMR Spectra
13. HPLC Data

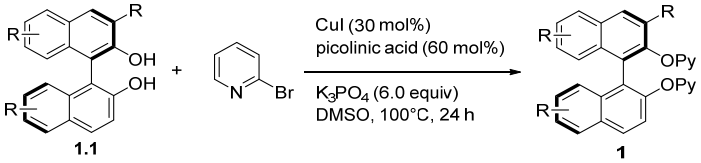
1. General Information

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, sep: septet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. Infrared (IR) spectra were recorded by FTIR spectrometer and reported in terms of wave number (cm-1). UV detection was monitored at 254 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. Enantiomeric excesses were determined on a Thermo Fisher Chiral HPLC or Agilent Chiral HPLC using AD-H column.

Unless otherwise noted, all starting materials were purchased from commercial sources and used without any further purification. Anhydrous THF should be obtained by distillation before use. But-3-en-2-ol **2a** was commercially available, and (R)-BINOL compounds were prepared according to the literature procedures [1]

2. General Procedure for Synthesis of BINOL Units

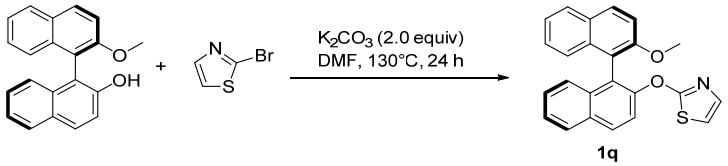
Procedure A:



A 100 mL oven-dried round bottomed flask was charged with a magnetic stirring bar, CuI (285 mg, 1.5 mmol, 30 mol%), picolinic acid (369 mg, 3.0 mmol, 60 mol%), (R)-BINOL (5 mmol), and K_3PO_4 (6360 mg, 30 mmol). The tube was then evacuated and back-filled with Ar. The procedure of evacuation/backfill was sequentially repeated two additional times. It was then added with 2-bromopyridine (24 mmol) and dimethylsulfoxide (25 mL) by syringe under an Ar atmosphere. The tube was placed in a pre-heated oil bath at 100 ºC and the reaction mixture was stirred for 24 h. The reaction mixture was cooled to room temperature and quenched with water (20 mL). Ethyl acetate (30 mL) was added and the organic layer was separated and the aqueous layer was extracted twice more with ethyl acetate. Combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified via silica gel column using ethyl acetate and petroleum ether (1: 12). The product **1a** were obtained with 92 % yield (2.0 g. 4.6 mmol).

1b-**1p** were also prepared according to the procedure A. The corresponding precursor compounds **1.1b**-**1.1p** were prepared according to the literature procedures [1].

Procedure B:



A 100 mL oven-dried round bottomed flask was charged with a magnetic stirring bar, (R)-BINOL (1 mmol), K_2CO_3 (276 mg, 2 mmol) and DMF (2 mL). It was then added with 2-bromothiazole (328 mg, 2 mmol) dropwise. The tube was placed in a pre-heated oil bath at 130 ºC and the reaction mixture was

stirred for 24 h. The reaction mixture was cooled to room temperature and quenched with water. Ethyl acetate was added and the organic layer was separated and the aqueous layer was extracted twice more with ethyl acetate. Combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified via silica gel column using ethyl acetate and petroleum ether (1: 10). The product **1q** were obtained with 88 % yield (337 mg. 0.9 mmol).

References:

[1] Liu, H.; Lin, M. L.; Chen, Y. J.; Huang, Y. H.; Dong, L. Rh(III)-catalyzed one-pot three-component cyclization reaction: rapid selective synthesis of monohydroxy polycyclic BINOL derivatives. *Org. Chem. Front.* **2021**, *8*, 4967–4973.

2. Optimization of the Reaction Conditions

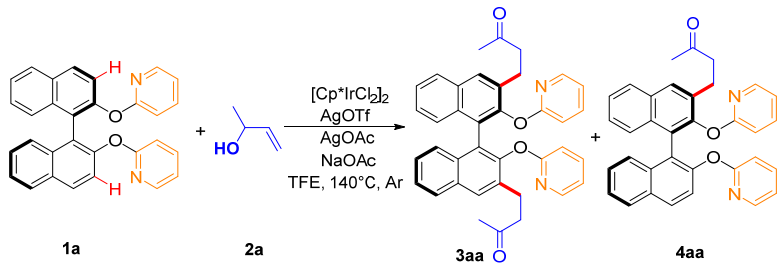


Table S1. The effect of the amount of additives on the reaction.[a]

entry	additives (equiv)	**3aa** yield / %[b]	**4aa** yield/ %[b]
1	AgOTf (0.3)+NaOAc (1)	88	trace
2	AgOTf (0.1)+NaOAc (1)	44	15
3	AgOTf (0.2)+NaOAc (0.5)	82	trace
4	AgOTf (0.2)+NaOAc (1.5)	64	24

[a] Reaction conditions unless otherwise specified: 0.05 mmol of **1a**, 5 equiv of **2a**, 5 mol % of $[Cp^*IrCl_2]_2$, 2 equiv of AgOAc, 0.5 mL of TFE, 140 °C, 24 h, Ar atmosphere. [b] Isolated yield.

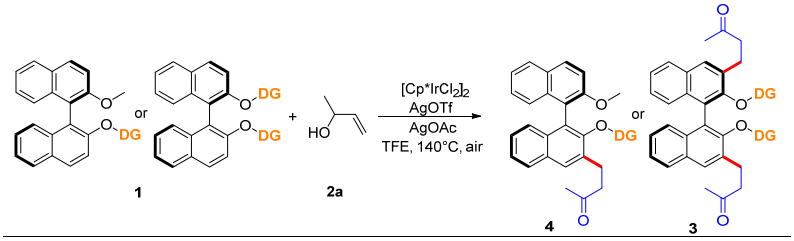
Table S2. The effect of the amount of AgOAc on the reaction.[a]

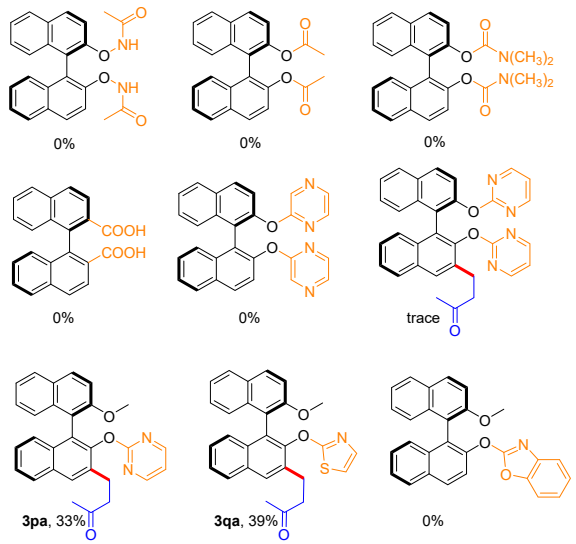
entry	oxidant (equiv)	**3aa** yield / %[b]	**4aa** yield/ %[b]
1	AgOAc (2)	89	trace
2	AgOAc (2.2)	77	11
3	AgOAc (1.8)	74	12

[a] Reaction conditions unless otherwise specified: 0.05 mmol of **1a**, 5 equiv of **2a**, 5 mol % of $[Cp^*IrCl_2]_2$, 0.2 equiv AgOTf, 1 equiv of NaOAc, 0.5 mL of TFE, 140 °C, 24 h, air atmosphere. [b] Isolated yield.

4. Screening of Directing Group

Table S3. Screening of Directing Group[a]





[a] Reaction conditions unless specified otherwise: 0.1 mmol of **1**, 6 equiv of **2a**, 5 mol % of $[Cp^*IrCl_2]_2$, 2 equiv of AgOAc, 0.2 equiv of AgOTf, 1 equiv of NaOAc, 1 mL of TFE, 140 °C, 24 h, air atmosphere. Isolated yield.

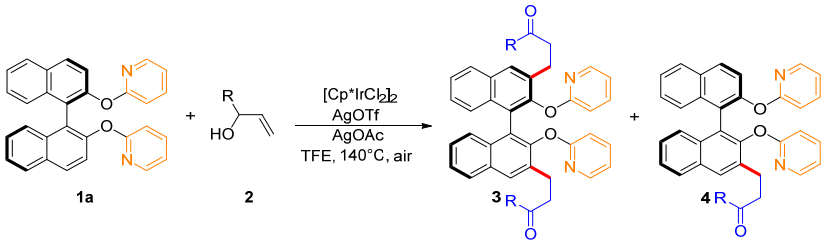
Encouraged by this attractive result, further investigation on the feasibility of different directing group was commenced (Table S3). BINOLs with oxyacetamide, acyloxy, dimethylcarbamate, even elaborate carboxyl group under the indicated conditions, no desired product was observed. Nevertheless, switching to the heteroatom substituted BINOL compounds, **3pa** and **3qa** were obtained in slightly low yield respectively. Thus, compared with other directing groups, the 2-pyridyloxy had exhibited a powerful potential in two-fold C−H alkylation of BINOLs.

5. General Procedure for the Model Reaction

To a flame dried screw-cap tube equipped with magnetic stir bar were introduced (R)-(+)-2,2'-bis(pyridin-2-yloxy)-1,1'-binaphthalene **1a** (22.0 mg, 0.05 mmol), and but-3-en-2-ol **2a** (26.0 μL, 6.0 equiv), $[Cp^*IrCl_2]_2$ (2.0 mg, 5 mol %), AgOAc (16.8 mg, 2.0 equiv), AgOTf (2.6 mg, 0.2 equiv), NaOAc (4.1 mg, 1.0 equiv) and TFE (0.5 mL). The reaction mixture was stirred in preheated oil bath at 140 °C under air atmosphere for 24 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:4) to give the product **3aa** as a colorless oil (27.0 mg, 93%).

6. The Scope of Alkenes [a]

The but-3-en-2-ol **2a** was replaced by other substituents as below, but all gave inferior results.



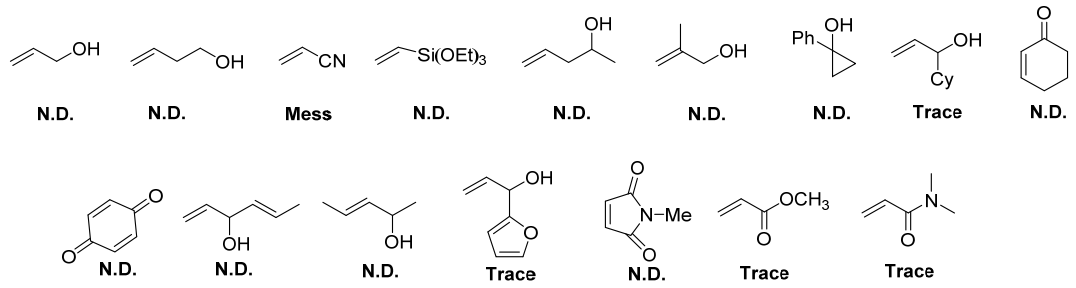
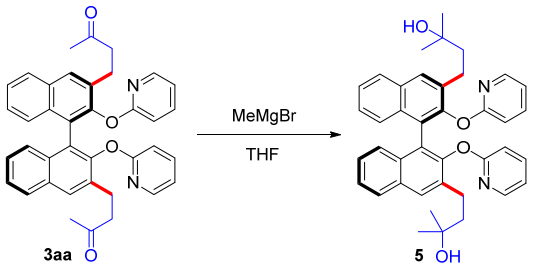


Table S4: [a] Reaction conditions unless otherwise specified: 0.1 mmol of **1**, 6 equiv of **2a**, 5 mol % of $[Cp^*IrCl_2]_2$, 2 equiv of AgOAc, 0.2 equiv of AgOTf, 1 equiv of NaOAc, 1 mL of TFE, 140 ℃, 24 h, air atmosphere. Isolated yield.

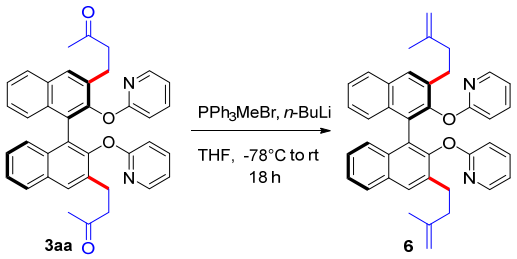
7. Synthetic Transformations of Product 3aa

Procedure for synthesis of **5**:



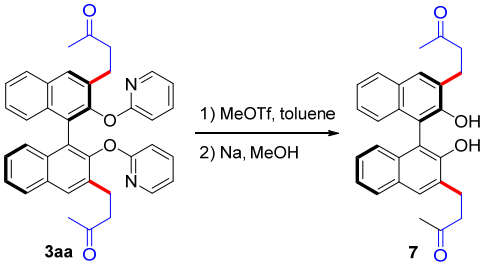
To a solution of compound **3aa** (29 mg, 0.05 mmol) in THF (1 mL) was added 3.0 M THF solution of MeMgBr (0.05 mL, 0.15 mmol) at 0 °C under nitrogen. After stirring at 25 °C temperature for 60 min, the mixture was quenched with saturated aqueous solution of NH_4Cl, and extracted with EtOAc. The collected organic layers were dried with anhydrous Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1:2) as an eluent to obtain product **5** as a yellow oil (25.1 mg, 82%).

Procedure for synthesis of **6**:



To an oven dried round bottom flask equipped with a stir bar under a N_2 atmosphere was added PPh_3MeBr (3.50 eq.). The flask was evacuated and back filled with N_2 and dry THF (0.1 M) was added. The resultant mixture was cooled to -78 ℃ to which a solution of *n*-BuLi in hexanes (1.6M, 3.50 eq.) was added. The solution was allowed to warm to rt and stirred for 30 mins before ketone substrate was added (0.05 mmol). The reaction was allowed to stir at rt for 18 h before being diluted with ethyl acetate and quenched with H_2O. The collected organic layers were dried with anhydrous Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1:10) as an eluent to obtain product **6** as a colorless oil (23.3 mg, 81%).

Procedure for synthesis of **7**:

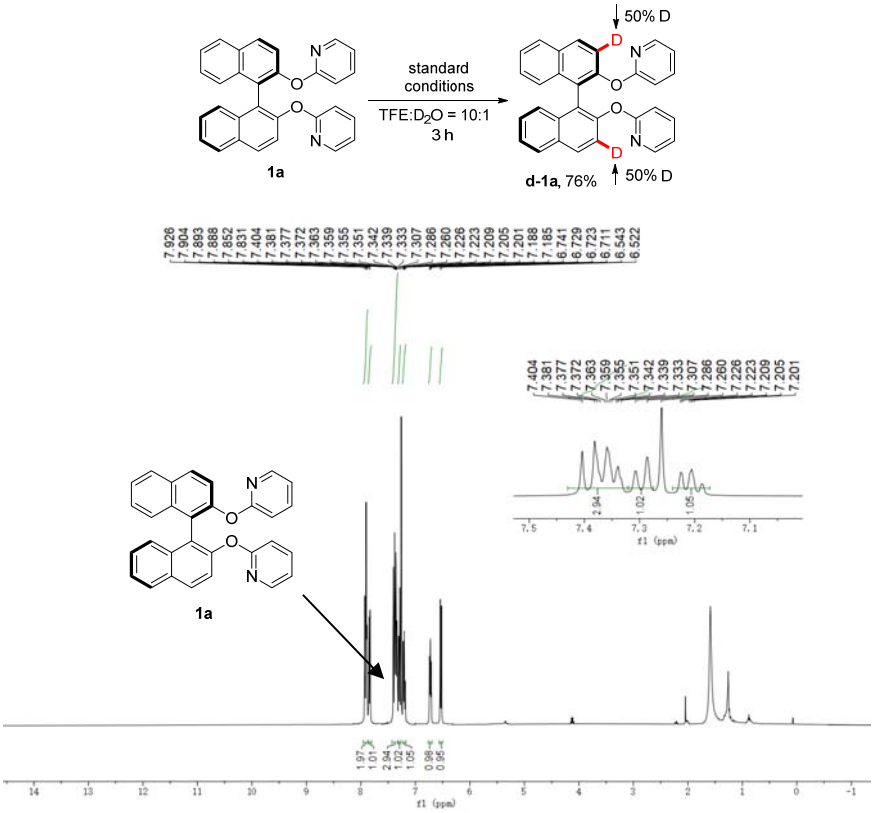


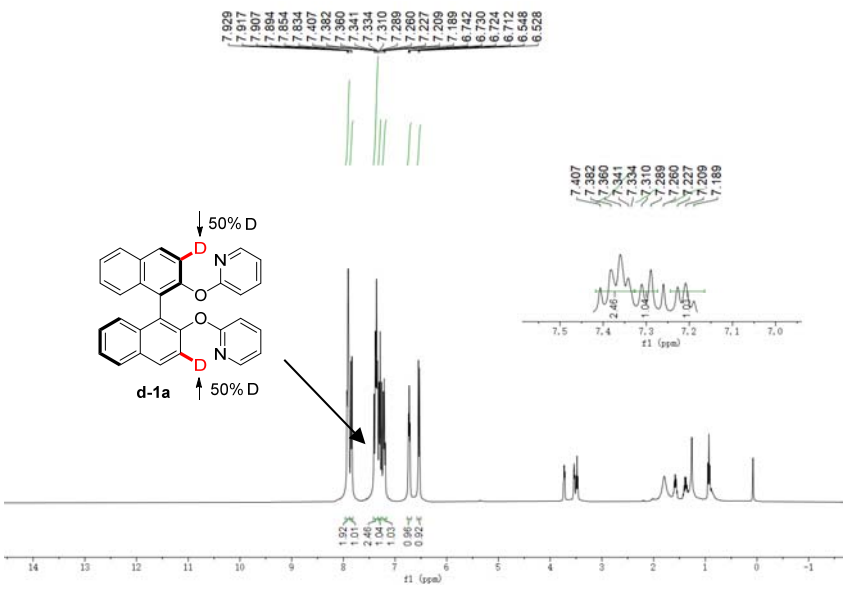
To a solution of **3aa** (29 mg, 0.05 mmol) in PhMe (1 mL) under N_2 was added MeOTf (50 μL, 0.45 mmol). The reaction mixture was stirred under N_2 at 100 °C for 2 h. The reaction mixture was allowed to cool to ambient temperature. Evaporation of the solvent *in vacuo* yielded a yellow solid. The solid was dissolved in dry methanol (1.0 mL) and was added under N_2 to a solution of Na (69 mg, 3 mmol) in dry methanol (1 mL). The reaction mixture was heated at 80 °C for 15 min. The reaction mixture was allowed to cool to ambient temperature and the solvent was evaporated *in vacuo*. H_2O was added, and the resulting mixture was extracted with EtOAc. The collected organic layers were dried with anhydrous Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography using ethyl acetate/petroleum ether (1:8) as an eluent to obtain product **7** as a colorless oil (15.5 mg, 73%).

8. Mechanistic Studies

(1) Deuterium Exchange Experiments of 1a

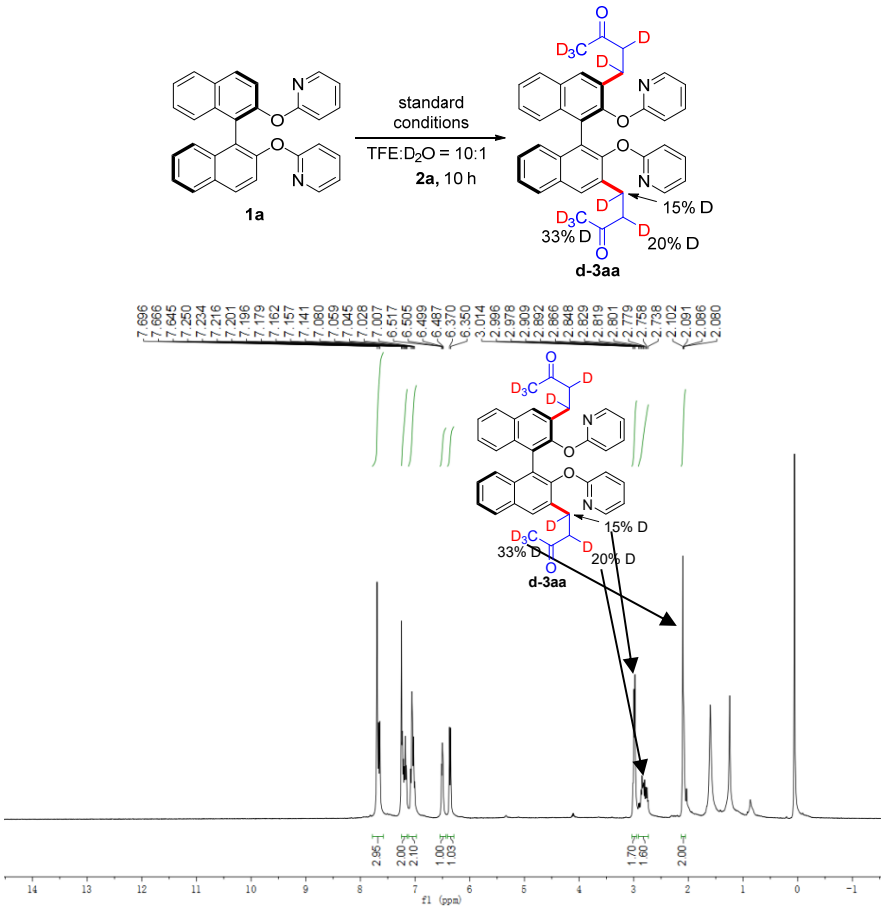
To a test tube equipped with magnetic stir bar were added **1a** (22.0 mg, 0.05 mmol, 1.0 equiv), $[Cp^*IrCl_2]_2$ (5 mol %), AgOAc (2.0 equiv), AgOTf (0.2 equiv), NaOAc (1.0 equiv) and D_2O (0.05 mL) were stirred in TFE (0.5 mL) under air atmosphere at 140 °C in preheated oil bath for 3 h. The solution was concentrated and the residue was separated on a flash column with PE/EA (5:1) as the eluent.





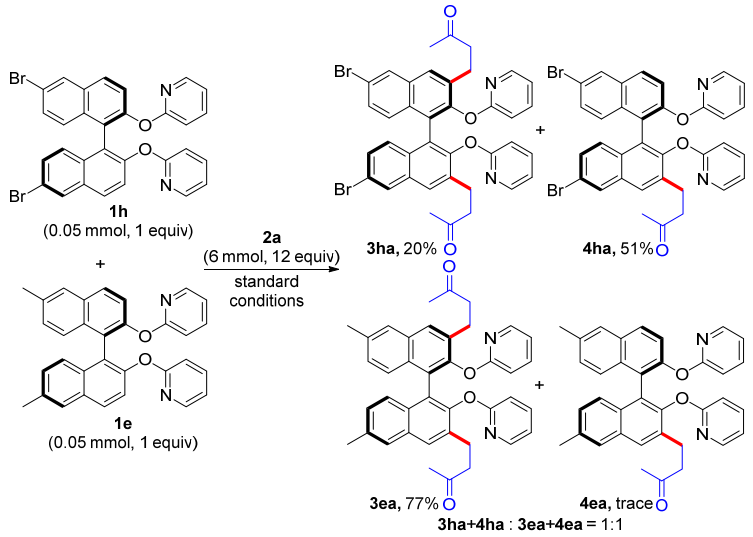
(2) Deuterium Exchange Experiments of 1a and 2a

To a test tube equipped with magnetic stir bar were added **1a** (22.0 mg, 0.05 mmol, 1.0 equiv), but-3-en-2-ol **2a** (26.0 μL, 6.0 equiv), $[Cp^*IrCl_2]_2$ (5 mol %), AgOAc (2.0 equiv), AgOTf (0.2 equiv), NaOAc (1.0 equiv) and D_2O (0.05 mL) were stirred in TFE (0.5 mL) under air atmosphere at 140 °C in preheated oil bath for 10 h. The solution was concentrated and the residue was separated on a flash column with PE/EA (3:1) as the eluent.



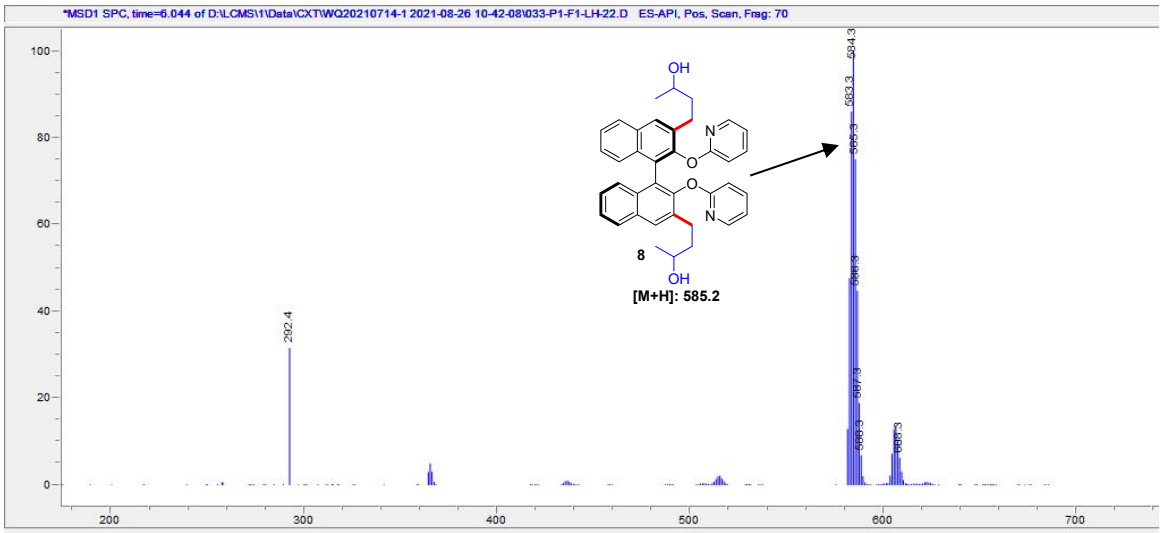
(3) Procedure for Competition Experiments

Representative procedure for competition between **1e** and **1h**: To a flame dried screwcap tube equipped with magnetic stir bar was introduced **1e** (0.05 mmol, 1.0 equiv), **1h** (0.05 mmol, 1.0 equiv), but-3-en-2-ol **2a** (52.0 μL, 12.0 equiv), $[Cp^*IrCl_2]_2$ (10 mol %), AgOAc (4.0 equiv), AgOTf (0.4 equiv), and NaOAc (2.0 equiv) were stirred in TFE (1.0 mL) under air atmosphere at 140 °C in preheated oil bath for 24 h. The solution was concentrated and the residue was separated on a flash column with PE/EA (6:1) as the eluent to give the product **3ea** (23.4 mg, 77%), **3ha** (7.4 mg, 20%) and **4ha** (17.0 mg, 51%).



(4) Detection of Intermediate 8 by LCMS Data

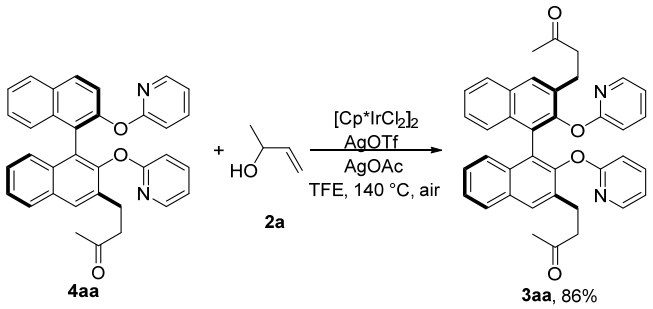
To a flame dried screw-cap tube equipped with magnetic stir bar were introduced (R)-(+)-2,2'-bis(pyridin-2-yloxy)-1,1'-binaphthalene **1a** (22.0 mg, 0.05 mmol), and but-3-en-2-ol **2a** (26.0 μL, 6.0 equiv), $[Cp^*IrCl_2]_2$ (2.0 mg, 5 mol %), AgOAc (16.8 mg, 2.0 equiv), AgOTf (2.6 mg, 0.2 equiv), NaOAc (4.1 mg, 1.0 equiv) and TFE (0.5 mL). The reaction mixture was stirred in preheated oil bath at 140 °C under argon atmosphere for 10 h. After completion, the reaction mixture was then tested by LCMS. Intermediate **8** was detected by LCMS.



(5) Transformation Experiment:

To a flame dried screw-cap tube equipped with magnetic stir bar were introduced **4aa** (51.0 mg, 0.1

mmol), and but-3-en-2-ol **2a** (26.0 μL, 3.0 equiv), $[Cp^*IrCl_2]_2$ (2.0 mg, 2.5 mol %), AgOAc (16.8 mg, 1.0 equiv), AgOTf (2.6 mg, 0.1 equiv), NaOAc (4.1 mg, 0.5 equiv) and TFE (1.0 mL). The reaction mixture was stirred in preheated oil bath at 140 °C under air atmosphere for 24 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:4) to give the product **3aa** as a colorless oil (50.2 mg, 86%) and trace **4aa**. This proved that **4aa** can be transformed into **3aa**, and the reaction is a step-by-step process.



(6) Proposed Reaction Mechanism

Based on these results and previous reports, we propose the reaction mechanism shown in S5. In the initial stage, active iridium coordinates to the nitrogen followed by C−H bond activation to generate the Ir^{III} complex intermediate **I**. Subsequent insertion of the olefin into the C-Ir bond forms intermediate **II**, which undergoes β-H elimination and keto-enol tautomerism pathway to deliver the alkylation product **4aa** along with Ir^{I} specie which is oxidized by Ag^{I} to regenerate the Ir^{III} active catalyst. Then, the second C−H activation process occurs to furnish intermediate **IV**. Finally, the same process occurs to produce the target product **3aa**.

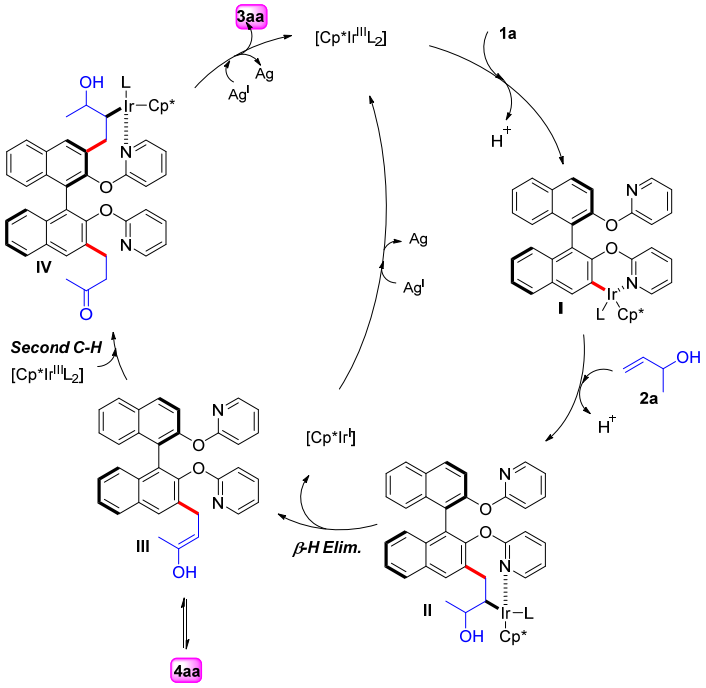


Table S5: Proposed Reaction Mechanism

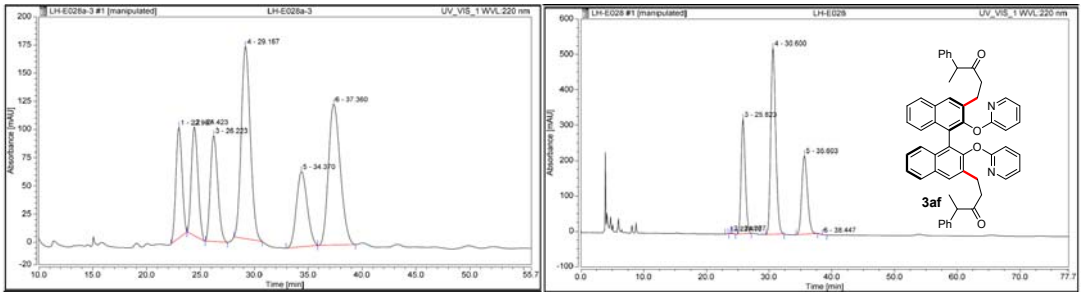
9. The Large-Scale Experiments

The 1a large-scale experiments: To a flame dried screw-cap tube equipped with magnetic stir bar were introduced (R)-(+)-2,2'-bis(pyridin-2-yloxy)-1,1'-binaphthalene **1a** (440.0 mg, 1 mmol), and but-3-en-2-ol **2a** (520.0 μL, 6.0 equiv), $[Cp^*IrCl_2]_2$ (40.0 mg, 5 mol %), AgOAc (336 mg, 2.0 equiv), AgOTf (52.0 mg, 0.2 equiv), NaOAc (82.0 mg, 1.0 equiv) and TFE (10 mL). The reaction mixture was stirred in preheated oil bath at 140 °C under argon atmosphere for 40 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:4) to give the product **3aa** as a colorless oil (348.0 mg, 60%) and **4aa** as a colorless oil (117.3 mg, 23%).

10. The HPLC Data of Compound 3af and 4af

The product **3af** was analyzed by HPLC (AD-H, hexane/i-PrOH = 19/1, detector: 220 nm, flow rate: 0.8 mL/min), d.r. = 1:2:1, t1(minor) = 23.5 min, t2(minor) = 24.1 min, t3(major) = 25.8 min, t4(major) = 30.6 min, t5(major) = 35.6 min, t6(minor) = 38.4 min.

Rac-**3af** Asy-**3af**

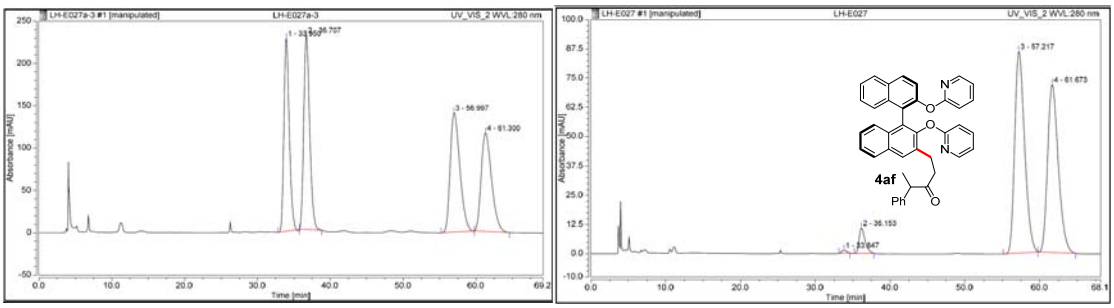


No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	22.987	64.936	98.058	10.63
2	24.423	68.218	96.375	11.17
3	26.223	74.555	93.945	12.21
4	29.167	166.291	170.815	27.23
5	34.370	77.184	67.082	12.64
6	37.360	159.546	125.002	26.12

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	23.470	0.203	0.510	0.02
2	24.077	0.562	1.339	0.06
3	25.823	247.863	323.864	25.71
4	30.600	482.415	526.307	50.03
5	35.603	233.026	222.561	24.17
6	38.447	0.127	0.000	0.01

The product **4af** was analyzed by HPLC (AD-H, hexane/i-PrOH = 35/1, detector: 280 nm, flow rate: 0.8 mL/min), d.r. = 1:1, t1(minor) = 33.8 min, t2(minor) = 36.2 min, t3(major) = 57.2 min, t4(major) = 61.7 min.

Rac-**4af** Asy-**4af**



No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	33.950	192.977	227.821	23.67
2	36.707	215.664	229.810	26.45
3	56.997	215.206	141.019	26.39
4	61.300	191.499	116.403	23.49

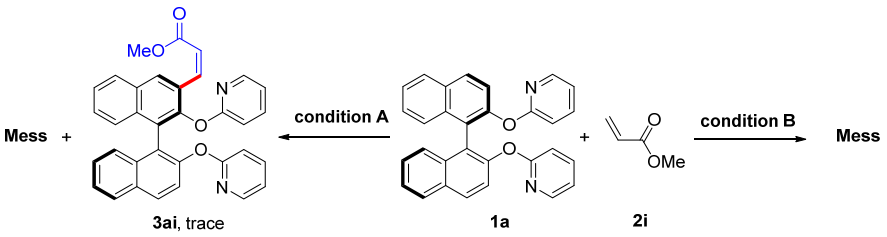
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	33.847	0.955	1.313	0.36
2	36.153	10.264	10.926	3.91
3	57.217	132.169	86.237	50.40
4	61.673	118.851	71.703	45.32

11. Exploration of methyl acrylate and but-3-en-2-ol as the coupling partners

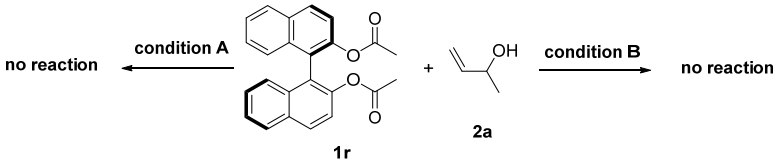
Standard conditions of this manuscript --- **Condition A:** $[Cp^*IrCl_2]_2$ (2.0 mg, 5 mol %), AgOAc (16.8 mg, 2.0 equiv), AgOTf (2.6 mg, 0.2 equiv), NaOAc (4.1 mg, 1.0 equiv) and TFE (0.5 mL). The reaction mixture was stirred in preheated oil bath at 140 °C under argon atmosphere for 24 h.

versus Standard conditions of our previous work (*Org. Lett.* **2020**, *22*, 4648-4652.) --- **Condition B:** $[Cp^*RhCl_2]_2$ (2.1 mg, 7 mol %), $Cu(OAc)_2{\cdot}H_2O$ (30.0 mg, 3.0 equiv), $AgSbF_6$ (5.1 mg, 0.3 equiv) and DCE (0.5 mL). The reaction mixture was stirred in preheated oil bath at 160 °C under argon atmosphere for 22 h.

When **1a** reacted with **2i** under two conditions, the reaction results were as follows: under condition A, **1a** was destroyed and a very small amount of monoalkenylation product **3ai** was generated. The reaction system was messy by TLC. Under condition B, **1a** was decomposed and no product was generated. The reaction system was messy by TLC.



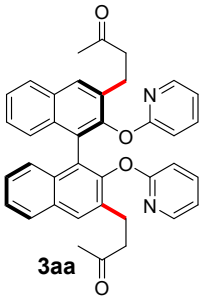
When **1r** reacted with **2a** under two conditions, the reaction results were as follows: under two conditions A and B, **1r** was decomposed and no product was generated.



Thus, we could see the unique interaction between **1a** and **2a**.

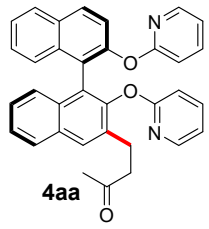
12. Characterization Data and NMR Spectra

4,4'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3aa)



51.6 mg, 89% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 4.5 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.13 (dddd, *J* = 22.1, 8.7, 6.9, 1.8 Hz, 2H), 7.03 – 6.93 (m, 2H), 6.43 (dd, *J* = 7.1, 4.9 Hz, 1H), 6.30 (d, *J* = 8.2 Hz, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.78 (tt, *J* = 19.5, 7.4 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 163.2, 149.6, 147.0, 138.4, 133.8, 132.4, 131.2, 129.0, 127.1, 126.6, 125.1, 125.0, 117.5, 110.5, 43.8, 30.0, 25.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{33}N_2O_4$ 581.2435; Found 581.2440. $[\alpha]^{26}_D$= -88.8(c = 0.51, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 80/20, detector: 254 nm, flow rate: 0.8 mL/min), t1(major) = 8.2 min, t2(minor) = 12.1 min.

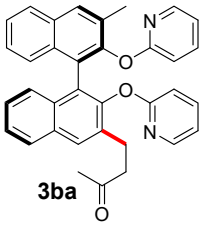
4-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (4aa)



7.7 mg, 30% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.74 – 7.55 (m, 5H), 7.31 – 7.26 (m, 1H), 7.26 – 7.17 (m, 2H), 7.17 – 7.13 (m, 1H), 7.12 – 6.98 (m, 5H), 6.67 – 6.60 (m, 1H), 6.45 – 6.37 (m, 2H), 6.25 (d, *J* = 8.3 Hz, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.71 (dd, *J* = 8.2, 6.0 Hz, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 163.4, 163.3, 150.0, 149.6, 147.1, 147.0, 138.7, 138.4, 133.8, 133.5, 132.8, 131.5, 130.8, 129.3, 129.1, 127.6, 127.4, 126.7, 126.2, 125.8, 125.5, 125.2, 125.1, 124.8, 123.5, 121.6, 117.9, 117.5, 111.6, 110.6, 43.7, 30.0, 25.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{27}N_2O_3$ 511.2016; Found 511.2020. $[\alpha]^{26}_D$= 3.6 (c = 0.11, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 80/20, detector: 254 nm, flow rate: 0.8 mL/min), t1(minor) = 8.3 min, t2(major) = 8.8 min.

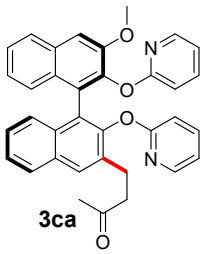
The crude material **1a** of **3aa** and **4aa** was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 10.3 min, t2(major) = 14.5 min. So the process of C-H functionalization didn't affect the ee of the compounds.

4-(3'-methyl-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (3ba)



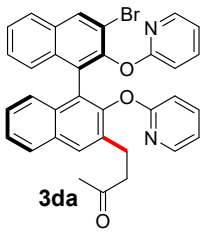
49.3 mg, 94% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.65 – 7.52 (m, 5H), 7.14 (qd, *J* = 7.8, 3.9 Hz, 3H), 7.09 – 6.99 (m, 3H), 6.98 – 6.87 (m, 2H), 6.47 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.40 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.32 (d, *J* = 8.3 Hz, 1H), 6.27 (d, *J* = 8.2 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.73 (tq, *J* = 17.3, 9.0, 8.1 Hz, 2H), 2.27 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 163.3, 163.3, 149.7, 149.7, 147.1, 147.0, 138.4, 133.9, 132.6, 132.2, 131.3, 131.3, 131.2, 129.6, 129.0, 127.2, 126.8, 126.7, 126.6, 125.3, 125.2, 125.0, 124.9, 124.8, 124.7, 117.5, 117.3, 110.7, 110.4, 43.8, 30.0, 26.0, 17.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{35}H_{29}N_2O_3$ 525.2173; Found 525.2178. $[\alpha]^{26}_D$= -75.0 (c = 1.59, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 80/20, detector: 254 nm, flow rate: 0.8 mL/min), t1(major) = 5.5 min, t2(minor) = 6.3 min.

4-(3'-methoxy-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (3ca)



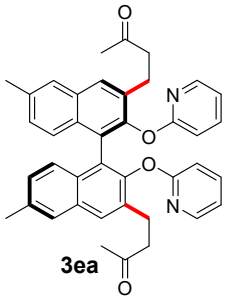
45.9 mg, 85% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.71 – 7.63 (m, 3H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.11 (m, 6H), 7.06 – 6.98 (m, 2H), 6.90 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.59 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.51 – 6.42 (m, 2H), 6.36 (d, *J* = 8.3 Hz, 1H), 3.79 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.72 (td, *J* = 8.0, 7.5, 4.4 Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 163.3, 151.3, 149.4, 147.0, 146.9, 141.6, 138.5, 138.3, 133.8, 132.6, 131.8, 131.4, 129.2, 128.4, 127.2, 126.8, 126.5, 126.3, 126.3, 125.4, 125.3, 125.2, 124.9, 123.4, 117.5, 117.4, 110.6, 110.3, 107.6, 55.8, 43.7, 30.0, 26.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{29}N_2O_4$ 541.2122; Found 541.2125. $[\alpha]^{26}_D$= -49.5 (c = 0.44, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 254 nm, flow rate: 0.8 mL/min), t1(major) = 16.7 min, t2(minor) = 20.8 min.

4-(3'-bromo-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (3da)



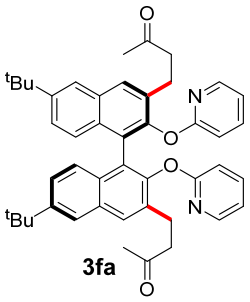
43.5 mg, 74% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.77 – 7.67 (m, 2H), 7.67 – 7.56 (m, 3H), 7.25 – 7.19 (m, 3H), 7.19 – 7.13 (m, 1H), 7.11 – 6.99 (m, 4H), 6.56 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.45 (dd, *J* = 11.4, 7.5 Hz, 2H), 6.36 (d, *J* = 8.3 Hz, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.77 (tq, *J* = 17.2, 8.9, 8.0 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.1, 163.2, 162.7, 149.7, 147.0, 146.9, 146.8, 138.5, 133.8, 132.5, 132.4, 132.2, 131.7, 131.2, 129.4, 127.3, 127.2, 127.2, 127.1, 126.6, 126.4, 125.9, 125.8, 125.3, 125.1, 124.4, 117.7, 117.6, 116.9, 110.8, 110.5, 43.7, 30.0, 25.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{26}BrN_2O_3$ 589.1121; Found 589.1125. $[\alpha]^{26}_D$= -10.2 (c = 2.39, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(major) = 6.8 min, t2(minor) = 9.8 min.

4,4'-(6,6'-dimethyl-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one)



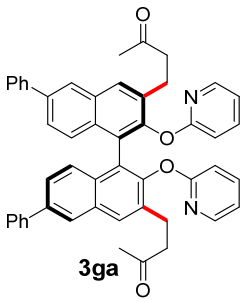
(3ea) 55.9 mg, 92% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.53 (s, 1H), 7.36 (s, 1H), 7.12 (ddd, *J* = 8.9, 7.3, 1.9 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.79 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.45 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.30 (d, *J* = 8.3 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.74 (tt, *J* = 19.2, 7.3 Hz, 2H), 2.28 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 163.3, 148.8, 147.0, 138.4, 134.5, 133.6, 131.5, 130.7, 128.3, 127.4, 126.5, 126.1, 125.1, 117.4, 110.5, 43.9, 30.0, 25.9, 21.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{37}N_2O_4$ 609.2748; Found 609.2753. $[\alpha]^{25}_D$= -67.1 (c = 0.38, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(major) = 16.4 min, t2(minor) = 25.7 min.

4,4'-(6,6'-di-tert-butyl-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3fa) 64.4 mg, 93% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 4.9, 2.0 Hz, 1H), 7.68 (s, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.21 – 7.08 (m, 2H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.50 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.81 (dt, *J* = 11.8, 7.8 Hz, 2H), 2.10 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.3, 163.4, 149.0, 147.5, 147.0, 138.2, 133.5, 131.1, 130.6, 128.9, 126.3, 124.8, 123.9, 122.0, 117.3, 110.5, 43.9, 34.5, 31.1, 29.9, 25.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{46}H_{49}N_2O_4$ 693.3687; Found 693.3688. $[\alpha]^{26}_D$= -36.7 (c = 0.32, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >95% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 7.9 min, t2(major) = 9.3 min.

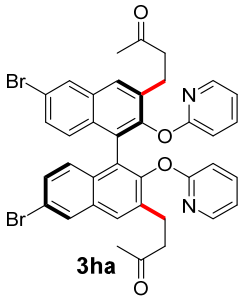


The crude material **1f** of **3fa** was analyzed by HPLC to determine the enantiomeric excess: >95% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 9.8 min, t2(major) = 11.3 min. So the process of C-H functionalization didn't affect the ee of the compounds.

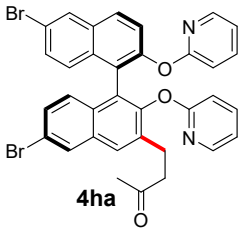
4,4'-(6,6'-diphenyl-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3ga) 65.1 mg, 89% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.9 Hz, 1H), 7.58 (s, 1H), 7.53 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.16 – 7.08 (m, 2H), 7.04 – 6.97 (m, 2H), 6.31 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.21 (d, *J* = 8.3 Hz, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.66 (qd, *J* = 17.1, 7.8 Hz, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 163.3, 149.8, 147.1, 141.0, 138.5, 137.6, 134.3, 131.7, 131.5, 129.4, 128.8, 127.3, 127.2, 125.0, 125.0, 124.8, 117.6, 110.6, 43.8, 30.0, 25.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{50}H_{41}N_2O_4$ 733.3061; Found 733.3064. $[\alpha]^{25}_D$= -1.2 (c = 1.07, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 80/20, detector: 220 nm, flow rate: 0.8 mL/min), t1(major) = 10.0 min, t2(minor) = 11.7 min.



4,4'-(6,6'-dibromo-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3ha) 16.2 mg, 22% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 5.1, 2.0 Hz, 1H), 7.50 (s, 1H), 7.16 – 7.06 (m, 1H), 6.99 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 1H), 6.44 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.27 (d, *J* = 8.3 Hz, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.79 – 2.61 (m, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 162.0, 149.0, 145.9, 137.6, 134.3, 131.2, 129.7, 128.1, 127.4, 127.2, 123.8, 118.1, 116.8, 109.5, 42.5, 28.9, 24.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{31}Br_2N_2O_4$ 737.0645; Found 737.0649. $[\alpha]^{26}_D$= -47.4 (c = 1.68, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 65/35, detector: 280 nm, flow rate: 0.6 mL/min), t1(major) = 7.7 min, t2(minor) = 37.6 min.

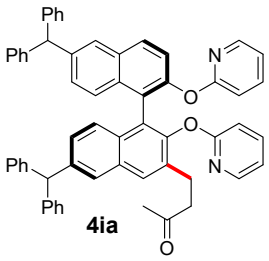


4-(6,6'-dibromo-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (4ha)



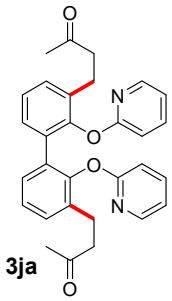
46.0 mg, 69% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 19.0, 2.2 Hz, 3H), 7.74 – 7.66 (m, 3H), 7.45 – 7.36 (m, 2H), 7.26 – 7.17 (m, 3H), 7.04 (t, *J* = 8.3 Hz, 2H), 6.79 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.60 – 6.51 (m, 2H), 6.37 (d, *J* = 8.2 Hz, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.80 (dd, *J* = 9.3, 6.9 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 163.1, 163.0, 150.3, 150.0, 147.1, 147.0, 138.9, 138.7, 135.4, 132.5, 131.9, 131.8, 131.1, 129.6, 129.4, 129.2, 128.9, 128.5, 128.4, 128.3, 127.8, 124.8, 123.3, 122.9, 119.4, 118.9, 118.3, 117.8, 111.6, 110.6, 43.4, 30.0, 25.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{25}Br_2N_2O_3$ 667.0226; Found 667.0230. $[\alpha]^{24}_D$= 1.9 (c = 0.68, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >94% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(major) = 10.8 min, t2(minor) = 12.7 min.

4-(6,6'-dibenzhydryl-2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (4ia)

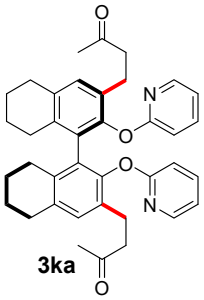


21.1 mg, 25% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.69 – 7.57 (m, 3H), 7.36 – 7.22 (m, 14H), 7.20 (dq, *J* = 8.1, 3.7, 2.8 Hz, 4H), 7.15 – 7.12 (m, 1H), 7.11 – 7.01 (m, 8H), 6.92 (ddd, *J* = 8.8, 4.7, 1.9 Hz, 2H), 6.69 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.48 (dd, *J* = 7.8, 4.0 Hz, 2H), 6.32 (d, *J* = 8.3 Hz, 1H), 5.56 (d, *J* = 5.6 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.76 (dd, *J* = 9.0, 7.1 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.2, 163.5, 163.3, 149.9, 149.4, 147.1, 147.0, 143.7, 143.7, 143.6, 140.7, 140.2, 138.5, 138.3, 133.9, 132.1, 131.3, 130.7, 129.5, 129.5, 129.2, 128.9, 128.2, 128.2, 128.2, 127.9, 127.7, 127.4, 127.3, 126.8, 126.3, 126.3, 124.8, 123.5, 121.7, 117.7, 117.3, 111.4, 110.6, 56.7, 56.6, 43.7, 29.9, 25.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{60}H_{47}N_2O_3$ 843.3581; Found 843.3543. $[\alpha]^{26}_D$= 28.5 (c = 0.11, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 80/20, detector: 220 nm, flow rate: 0.8 mL/min), t1(minor) = 7.0 min, t2(major) = 7.6 min.

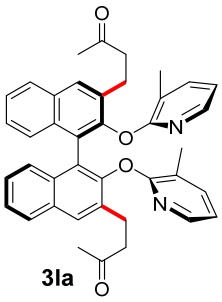
4,4'-(2,2'-bis(pyridin-2-yloxy)-5,6-dihydro-[1,1'-biphenyl]-3,3'-diyl)bis(butan-2-one) (3ja)



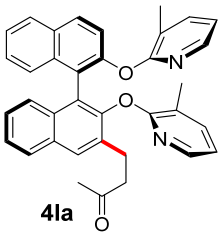
39.0 mg, 81% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 4.9 Hz, 1H), 7.44 (td, *J* = 7.9, 7.4, 1.9 Hz, 1H), 7.11 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.04 – 6.91 (m, 2H), 6.84 – 6.74 (m, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.65 (dd, *J* = 11.2, 4.9 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 163.5, 149.4, 147.3, 138.9, 134.0, 131.9, 129.7, 129.7, 125.0, 117.7, 110.5, 43.7, 29.9, 25.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{28}N_2NaO_4$ 503.1941; Found 503.1964.

4,4'-(2,2'-bis(pyridin-2-yloxy)-5,5',6,6',7,7',8,8'-octahydro-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3ka) 

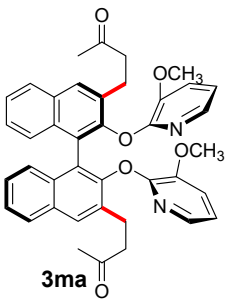
50.0 mg, 85% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.41 (td, *J* = 7.8, 1.9 Hz, 1H), 6.85 (s, 1H), 6.79 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.45 (d, *J* = 8.3 Hz, 1H), 2.70 (tdd, *J* = 16.9, 12.8, 7.7 Hz, 5H), 2.49 (dt, *J* = 16.0, 7.0 Hz, 1H), 2.23 – 2.11 (m, 2H), 2.07 (s, 3H), 1.52 (dh, *J* = 13.9, 6.7, 4.3 Hz, 3H), 1.16 (tdd, *J* = 11.6, 9.3, 8.3, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 163.4, 147.5, 147.1, 138.6, 135.7, 134.0, 131.1, 130.0, 129.7, 117.5, 110.8, 44.1, 29.9, 29.4, 26.8, 25.1, 22.9, 22.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{38}H_{41}N_2O_4$ 589.3061; Found 589.3062. $[\alpha]^{26}_D$= -191.1(c = 0.21, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(major) = 5.2 min, t2(minor) = 8.2 min.

4,4'-(2,2'-bis((3-methylpyridin-2-yl)oxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3la) 

32.2 mg, 53% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 24.0 Hz, 2H), 7.40 – 6.71 (m, 5H), 6.22 (s, 1H), 2.93 (d, *J* = 68.9 Hz, 4H), 1.99 (d, *J* = 27.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 161.6, 150.0, 144.1, 138.4, 132.2, 131.0, 128.5, 126.9, 124.7, 120.4, 117.4, 43.8, 29.9, 25.5, 15.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{40}H_{37}N_2O_4$ 609.2748; Found 609.2753. $[\alpha]^{26}_D$= -31.5 (c = 1.19, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(major) = 9.5 min, t2(minor) = 10.4 min.

4-(2,2'-bis((3-methylpyridin-2-yl)oxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (4la) 

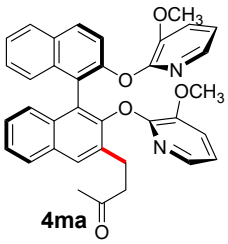
13.5 mg, 25% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.59 (m, 5H), 7.58 – 6.87 (m, 10H), 6.48 (d, *J* = 83.6 Hz, 2H), 3.08 (td, *J* = 7.5, 3.6 Hz, 2H), 2.90 (td, *J* = 21.5, 19.0, 10.6 Hz, 2H), 2.12 (s, 3H), 2.03 – 1.45 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 161.6, 144.1, 138.7, 138.5, 132.7, 131.3, 130.7, 128.6, 127.2, 126.5, 125.2, 125.0, 124.6, 122.2, 117.7, 117.4, 43.9, 30.0, 25.7, 15.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{36}H_{31}N_2O_3$ 539.2329; Found 539.2333. $[\alpha]^{26}_D$= -12.3 (c = 0.45, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 80/20, detector: 220 nm, flow rate: 0.8 mL/min), t1(minor) = 5.7 min, t2(major) = 7.0 min.

4,4'-(2,2'-bis((3-methoxypyridin-2-yl)oxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) 

(3ma) 37.8 mg, 59% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.58 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.39 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.50 (s, 3H), 3.12 – 2.92 (m, 3H), 2.82 (ddd, *J* = 16.4, 9.0, 6.3 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 153.9, 150.6, 143.7, 137.5, 134.1, 132.3, 131.0, 128.4, 126.8, 124.8, 124.7, 124.7, 119.2, 117.9, 55.8, 43.8, 29.9, 25.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{40}H_{37}N_2O_6$ 641.2646; Found 641.2646. $[\alpha]^{25}_D$= -81.8 (c = 1.15,

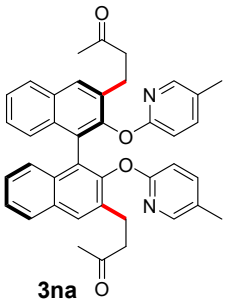
chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(major) = 9.1 min, t2(minor) = 15.0 min.

4-(2,2'-bis((3-methoxypyridin-2-yl)oxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (4ma)



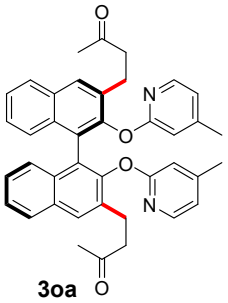
13.7 mg, 24% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.70 – 7.61 (m, 3H), 7.36 – 7.27 (m, 2H), 7.23 – 7.11 (m, 5H), 7.05 – 6.96 (m, 2H), 6.70 (dd, *J* = 5.6, 4.0 Hz, 1H), 6.52 (td, *J* = 8.3, 7.4, 4.5 Hz, 2H), 6.37 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.39 (s, 3H), 3.31 (s, 3H), 3.03 – 2.75 (m, 4H), 2.03 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 154.0, 154.0, 150.7, 150.6, 144.3, 143.9, 137.8, 137.5, 134.1, 133.6, 132.7, 131.3, 130.7, 128.8, 128.7, 127.3, 127.1, 126.9, 126.6, 125.5, 125.1, 124.9, 124.9, 124.6, 123.5, 121.9, 120.4, 119.1, 118.3, 118.0, 56.3, 55.8, 43.8, 30.0, 25.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{31}N_2O_5$ 571.2227; Found 571.2230. $[\alpha]^{26}_D$= -6.7 (c = 0.14, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 80/20, detector: 254 nm, flow rate: 0.8 mL/min), t1(minor) = 8.6 min, t2(major) = 13.5 min.

4,4'-(2,2'-bis((5-methylpyridin-2-yl)oxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3na)



59.6 mg, 98% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 2.5 Hz, 1H), 7.13 (ddd, *J* = 8.1, 6.4, 1.5 Hz, 1H), 7.00 – 6.90 (m, 2H), 6.86 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.15 (d, *J* = 8.3 Hz, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.78 (qd, *J* = 17.1, 7.7 Hz, 2H), 2.02 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 161.6, 150.1, 146.6, 139.1, 133.8, 132.4, 131.1, 129.0, 127.1, 126.7, 126.5, 125.0, 125.0, 124.8, 110.0, 43.8, 30.0, 26.0, 17.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{37}N_2O_4$ 609.2748; Found 609.2750. $[\alpha]^{25}_D$= -33.3 (c = 0.54, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >97% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(major) = 25.9 min, t2(minor) = 30.0 min.

4,4'-(2,2'-bis((4-methylpyridin-2-yl)oxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (3oa)

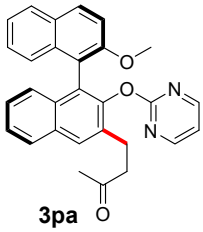


52.3 mg, 86% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.47 (d, *J* = 5.2 Hz, 1H), 7.19 – 7.12 (m, 1H), 7.05 – 6.92 (m, 2H), 6.22 (d, *J* = 5.2 Hz, 1H), 6.08 (s, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.87 – 2.68 (m, 2H), 2.03 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 162.5, 148.8, 148.6, 145.5, 132.7, 131.4, 130.1, 128.0, 126.0, 125.5, 124.0, 123.9, 123.9, 117.9, 109.8, 42.8, 29.0, 24.9, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{37}N_2O_4$ 609.2748; Found 609.2749. $[\alpha]^{25}_D$= -12.7 (c = 0.86, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >95% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 6.0 min, t2(major) = 7.6 min.

The crude material of **3ab** was analyzed by HPLC to determine the enantiomeric excess: >96% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 7.1 min, t2(major) =

14.4 min. So the process of C-H functionalization didn't affect the ee of the compounds.

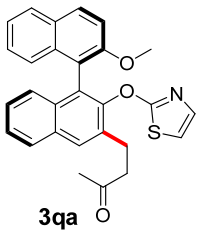
4-(2'-methoxy-2-(pyrimidin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)butan-2-one (3pa)



3pa

14.8 mg, 33% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 4.8 Hz, 2H), 7.81 (d, *J* = 6.9 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 9.5 Hz, 1H), 7.16 – 7.01 (m, 5H), 6.50 (t, *J* = 4.8 Hz, 1H), 3.66 (s, 3H), 2.99 (dd, *J* = 11.5, 4.9 Hz, 2H), 2.89 (dd, *J* = 11.0, 6.7 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 164.8, 158.9, 155.0, 148.7, 133.3, 133.3, 132.9, 131.9, 129.9, 129.0, 128.7, 127.8, 127.5, 126.0, 126.0, 125.9, 125.9, 125.8, 125.5, 123.3, 117.7, 115.2, 113.4, 43.7, 30.1, 25.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{25}N_2O_3$ 449.1860; Found 449.1863. $[\alpha]^{26}_D$= 7.0 (c = 0.33, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 65/35, detector: 254 nm, flow rate: 0.6 mL/min), t1(major) = 7.9 min, t2(minor) = 8.8 min.

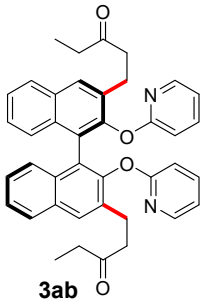
4-(2'-methoxy-2-(thiazol-2-yloxy)-[1,1'-binaphthalen]-3-yl)butan-2-one (3qa)



3qa

17.7 mg, 39% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (q, *J* = 5.8, 4.8 Hz, 3H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.23 – 7.10 (m, 5H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 6.34 (d, *J* = 3.7 Hz, 1H), 3.62 (s, 3H), 3.10 (t, *J* = 7.7 Hz, 2H), 2.96 – 2.87 (m, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 173.5, 154.9, 150.8, 136.8, 133.4, 132.9, 132.8, 132.1, 130.2, 129.4, 128.8, 127.7, 127.7, 126.3, 126.1, 126.1, 126.0, 125.9, 125.4, 123.4, 117.3, 113.1, 112.2, 56.3, 43.8, 30.1, 25.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{24}NO_3S$ 454.1471; Found 454.1477. $[\alpha]^{25}_D$= 3.1 (c = 1.87, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >93% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 7.5 min, t2(major) = 8.2 min.

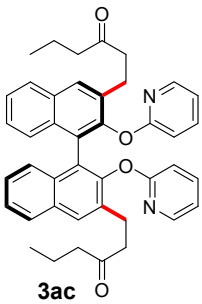
1,1'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(pentan-3-one) (3ab)



3ab

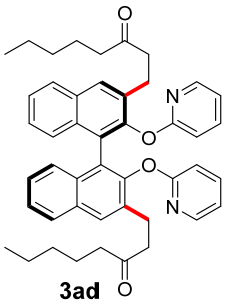
49.9 mg, 82% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 3H), 7.20 – 7.07 (m, 2H), 6.97 (dt, *J* = 15.1, 8.2 Hz, 2H), 6.42 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.30 (d, *J* = 8.3 Hz, 1H), 2.93 (t, *J* = 7.7 Hz, 2H), 2.73 (dtd, *J* = 24.8, 16.7, 7.2 Hz, 2H), 2.30 (qd, *J* = 7.4, 3.9 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 162.2, 148.6, 145.9, 137.3, 132.9, 131.3, 130.2, 128.0, 126.1, 125.6, 124.0, 124.0, 123.9, 116.4, 109.5, 41.4, 34.9, 24.9, 6.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{37}N_2O_4$ 609.2748; Found 609.2761. $[\alpha]^{26}_D$= -76.0 (c = 0.33, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 80/20, detector: 254 nm, flow rate: 0.8 mL/min), t1(major) = 7.1 min, t2(minor) = 8.8 min.

1,1'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(hexan-3-one) (3ac)



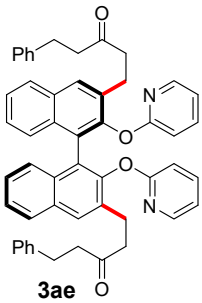
51.5 mg, 81% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 3.6 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.06 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.41 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.29 (d, *J* = 8.3 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.82 – 2.61 (m, 2H), 2.25 (td, *J* = 7.3, 3.4 Hz, 2H), 1.47 (h, *J* = 7.4 Hz, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 163.3, 149.6, 147.0, 138.4, 133.9, 132.4, 131.2, 129.0, 127.1, 126.7, 125.1, 125.0, 125.0, 117.5, 110.6, 44.8, 42.9, 25.9, 17.3, 13.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{42}H_{41}N_2O_4$ 637.3066; Found 637.3078. $[\alpha]^{25}_D$= -95.0 (c = 1.81, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 90/10, detector: 254 nm, flow rate: 0.8 mL/min), t1(major) = 12.5 min, t2(minor) = 14.9 min.

1,1'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(octan-3-one) (3ad)



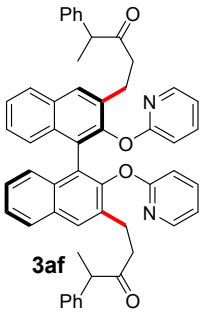
51.9 mg, 75% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 4.0 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.19 – 7.08 (m, 2H), 6.98 (dt, *J* = 15.0, 8.4 Hz, 2H), 6.43 (dd, *J* = 7.1, 4.9 Hz, 1H), 6.30 (d, *J* = 8.2 Hz, 1H), 2.93 (t, *J* = 7.7 Hz, 2H), 2.83 – 2.64 (m, 2H), 2.27 (td, *J* = 7.4, 3.9 Hz, 2H), 1.45 (p, *J* = 7.4 Hz, 2H), 1.16 (dp, *J* = 15.2, 6.4, 5.2 Hz, 4H), 0.77 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 162.2, 148.6, 145.9, 137.3, 132.9, 131.3, 130.2, 128.0, 126.1, 125.6, 124.0, 124.0, 123.9, 116.4, 109.5, 41.8, 41.8, 30.4, 24.8, 22.5, 21.4, 12.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{46}H_{49}N_2O_4$ 693.3687; Found 693.3692. $[\alpha]^{26}_D$= -28.6 (c = 0.21, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 220 nm, flow rate: 0.8 mL/min), t1(major) = 10.6 min, t2(minor) = 20.7 min.

5,5'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(1-phenylpentan-3-one) (3ae)



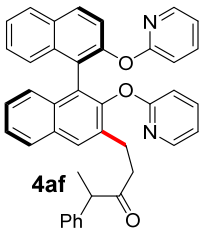
70.7 mg, 93% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 3H), 7.07 – 6.99 (m, 3H), 6.99 – 6.88 (m, 4H), 6.88 – 6.78 (m, 2H), 6.27 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.13 (d, *J* = 8.3 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.63 (dt, *J* = 14.4, 7.7 Hz, 3H), 2.58 – 2.51 (m, 1H), 2.47 (td, *J* = 8.4, 7.7, 5.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 163.3, 149.6, 147.0, 141.1, 138.4, 133.8, 132.4, 131.2, 129.1, 128.5, 128.3, 127.1, 126.7, 126.1, 125.1, 125.1, 125.0, 117.5, 110.6, 44.4, 43.0, 29.7, 25.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{52}H_{45}N_2O_4$ 761.3374; Found 761.3375. $[\alpha]^{26}_D$= -75.4 (c = 0.27, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 220 nm, flow rate: 0.8 mL/min), t1(major) = 9.6 min, t2(minor) = 11.5 min.

5,5'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(2-methylpentan-3-one) (3af)



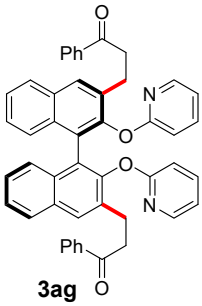
10.6 mg, 14% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 3H), 7.23 – 7.10 (m, 4H), 7.07 (d, *J* = 7.3 Hz, 2H), 7.03 – 6.96 (m, 1H), 6.93 (d, *J* = 5.9 Hz, 2H), 6.41 – 6.32 (m, 1H), 6.14 (dt, *J* = 12.0, 7.7 Hz, 1H), 3.65 (p, *J* = 6.9 Hz, 1H), 2.96 – 2.56 (m, 4H), 1.28 (dd, *J* = 7.0, 4.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 210.1, 163.2, 149.6, 149.6, 146.8, 140.6, 140.6, 138.2, 138.2, 138.2, 133.8, 133.7, 132.3, 131.1, 128.9, 128.8, 128.8, 127.9, 127.8, 127.1, 127.1, 127.0, 127.0, 126.6, 124.9, 124.8, 117.3, 110.6, 52.9, 41.4, 41.3, 25.9, 25.8, 17.5, 17.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{52}H_{45}N_2O_4$ 761.3374; Found 761.3375.

1-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)-4-methylpentan-3-one (4af)



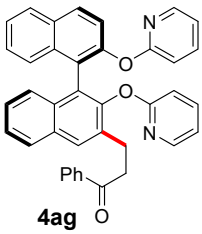
40.2 mg, 67% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (td, *J* = 4.9, 1.9 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.46 – 7.38 (m, 2H), 7.17 – 6.86 (m, 14H), 6.51 (q, *J* = 5.8 Hz, 1H), 6.35 – 6.22 (m, 2H), 6.07 (dd, *J* = 11.4, 8.3 Hz, 1H), 3.48 (p, *J* = 7.0 Hz, 1H), 2.82 – 2.45 (m, 4H), 1.12 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 210.1, 163.4, 163.2, 163.2, 150.0, 145.0, 149.5, 147.1, 146.9, 140.5, 138.7, 138.7, 138.4, 138.4, 133.9, 133.8, 133.5, 133.5, 132.7, 131.4, 130.7, 129.3, 129.3, 129.0, 128.9, 128.9, 127.9, 127.9, 127.5, 127.4, 127.3, 127.1, 126.7, 126.2, 125.7, 125.7, 125.4, 125.1, 125.0, 124.7, 123.5, 121.5, 121.5, 118.0, 117.9, 117.4, 111.6, 111.6, 110.6, 110.6, 53.0, 52.9, 41.2, 41.2, 26.0, 25.9, 17.5, 17.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{33}N_2O_3$ 601.2486; Found 601.2491.

3,3'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(1-phenylpropan-1-one) (3ag)



14.8 mg, 21% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 2H), 7.76 (s, 1H), 7.65 (t, *J* = 5.8 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 4.2 Hz, 2H), 7.11 – 6.98 (m, 2H), 6.43 (dd, *J* = 7.1, 4.7 Hz, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 3.46 – 3.25 (m, 2H), 3.15 (dq, *J* = 14.4, 7.3, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 163.3, 149.8, 147.0, 138.3, 136.9, 134.0, 133.0, 132.4, 131.2, 129.3, 128.6, 128.1, 127.1, 126.7, 125.0, 124.9, 117.4, 110.6, 39.2, 26.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{48}H_{37}N_2O_4$ 705.2748; Found 705.2750. $[\alpha]^{26}_D$= -3.0 (c = 0.76, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 220 nm, flow rate: 0.8 mL/min), t1(major) = 13.6 min, t2(minor) = 14.9 min.

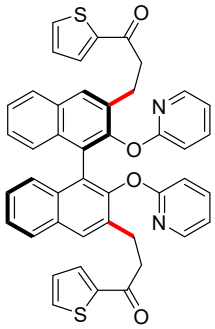
3-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)-1-phenylpropan-1-onee (4ag)



22.9 mg, 40% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 4H), 7.81 – 7.62 (m, 4H), 7.51 – 7.44 (m, 1H), 7.39 – 7.22 (m, 6H), 7.20 – 7.03 (m, 5H), 6.68 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.52 – 6.43 (m, 2H), 6.33 (d, *J* = 8.3 Hz, 1H), 3.42 – 3.23 (m, 2H), 3.11 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 163.3, 150.0, 149.7, 138.9, 138.6, 136.8, 134.1, 133.5, 133.0, 132.8, 131.5, 130.8, 129.5, 128.5, 128.2, 127.6, 127.5, 126.8, 126.2, 125.8, 125.6, 125.2, 124.8, 123.5, 121.7, 118.0, 117.6, 111.7, 110.7, 39.1, 26.5. HRMS

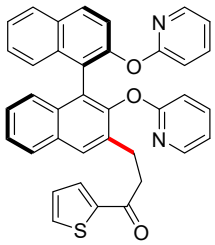
(ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{29}N_2O_3$ 573.2173; Found 573.2178. $[\alpha]^{26}_D$= 2.0 (c = 0.15, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 16.8 min, t2(major) = 24.7 min.

3,3'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(thiophen-2-yl)propan-1-one) (3ah) 10.7 mg, 15% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.67 (dd, *J* = 6.2, 3.2 Hz, 3H), 7.60 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 – 7.00 (m, 4H), 6.47 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 1H), 3.41 – 3.27 (m, 2H), 3.27 – 3.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 163.2, 149.8, 146.8, 144.3, 138.6, 133.6, 133.5, 132.4, 132.1, 131.2, 129.5, 128.1, 127.2, 126.7, 125.1, 125.0, 117.5, 110.8, 39.7, 26.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{33}N_2O_4S_2$ 717.1876; Found 717.1880. $[\alpha]^{26}_D$= -5.9 (c = 0.57, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >98% ee (AD-H, hexane/i-PrOH = 80/20, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 15.4 min, t2(major) = 16.9 min.



3ah

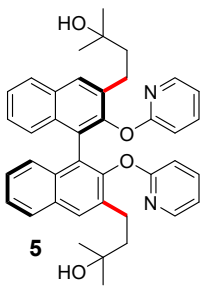
3-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalen]-3-yl)-1-(thiophen-2-yl)propan-1-one (4ah)



4ah

23.1 mg, 40% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 1H), 7.84 – 7.59 (m, 5H), 7.53 (dd, *J* = 12.4, 4.3 Hz, 2H), 7.30 (dd, *J* = 11.5, 5.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.03 (m, 6H), 6.98 (t, *J* = 4.3 Hz, 1H), 6.67 (t, *J* = 5.6 Hz, 1H), 6.46 (t, *J* = 7.3 Hz, 2H), 6.32 (d, *J* = 8.2 Hz, 1H), 3.23 (q, *J* = 8.0 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 163.4, 163.3, 150.0, 149.7, 147.1, 147.0, 144.3, 138.8, 138.6, 133.8, 133.5, 133.5, 132.8, 132.0, 131.5, 130.8, 129.5, 129.4, 128.0, 127.6, 127.5, 126.8, 126.3, 125.8, 125.6, 125.2, 125.1, 124.8, 123.5, 121.6, 118.0, 117.5, 111.7, 110.7, 39.7, 26.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{37}H_{27}N_2O_3S$ 579.1737; Found 579.1740. $[\alpha]^{26}_D$= -0.6 (c = 0.33, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 280 nm, flow rate: 0.8 mL/min), t1(minor) = 19.8 min, t2(major) = 26.3 min.

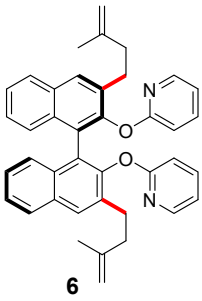
4,4'-(2,2'-bis(pyridin-2-yloxy)-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(2-methylbutan-2-ol) (5)



5

25.1 mg, 82% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 5.9 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.10 (ddd, *J* = 10.2, 5.8, 1.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.93 (ddd, *J* = 8.3, 6.7, 1.2 Hz, 1H), 6.42 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.29 (d, *J* = 8.3 Hz, 1H), 2.69 (t, *J* = 8.4 Hz, 2H), 1.83 (dt, *J* = 13.6, 7.9 Hz, 1H), 1.72 (dt, *J* = 13.6, 8.2 Hz, 1H), 1.08 (d, *J* = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 149.6, 146.9, 138.4, 135.3, 132.2, 131.3, 128.7, 127.0, 126.7, 125.1, 124.9, 117.4, 110.6, 70.9, 44.0, 29.2, 29.1, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{41}N_2O_4$ 613.3061; Found 613.3066. $[\alpha]^{26}_D$= -35.4 (c = 0.26, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 220 nm, flow rate: 0.8 mL/min), t1(minor) = 24.5 min, t2(major) = 27.4 min.

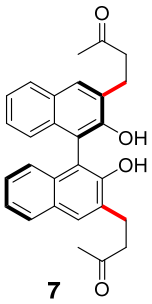
2,2'-((3,3'-bis(3-methylbut-3-en-1-yl)-(R)-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy))dipyridine (6)



6

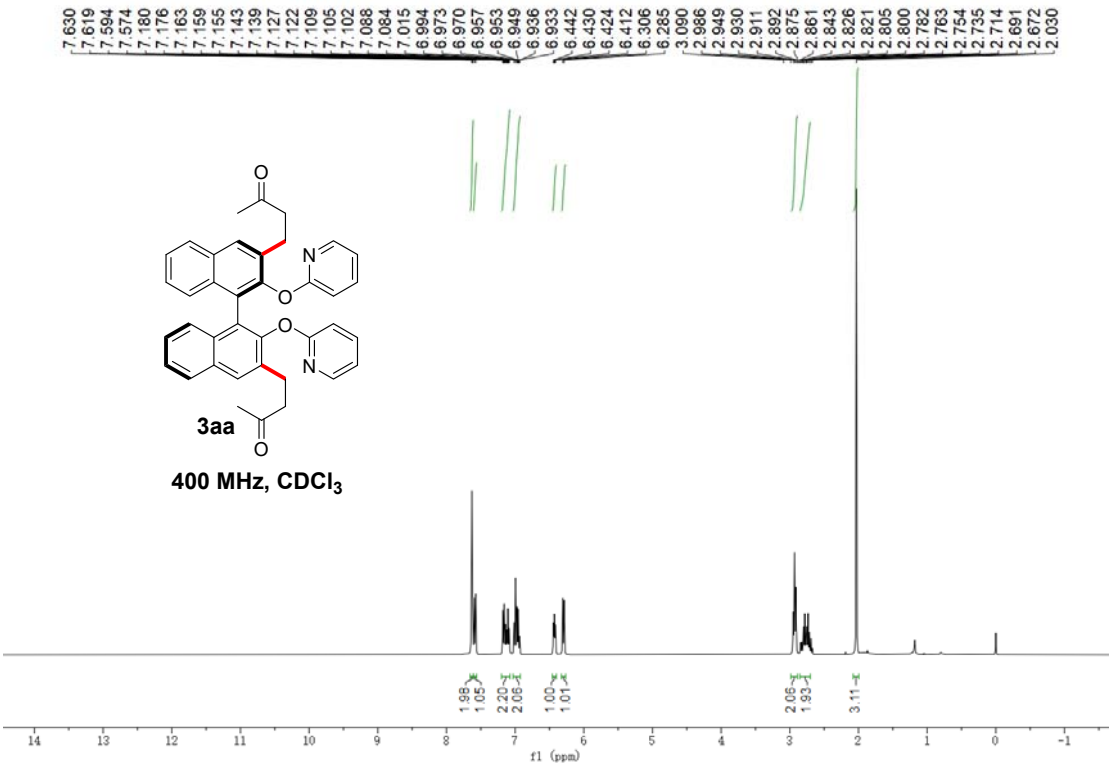
23.3 mg, 81% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 5.1 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.11 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.97 (ddd, *J* = 8.2, 6.6, 1.2 Hz, 1H), 6.45 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 4.62 (d, *J* = 5.8 Hz, 2H), 2.77 (tt, *J* = 14.2, 7.2 Hz, 2H), 2.34 (dddd, *J* = 41.5, 14.9, 9.8, 6.2 Hz, 2H), 1.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4, 149.6, 146.9, 145.6, 138.2, 134.9, 132.3, 131.3, 128.5, 127.0, 126.7, 125.1, 124.8, 117.2, 110.6, 110.1, 38.0, 29.9, 22.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{37}N_2O_2$ 577.2850; Found 577.2850. $[\alpha]^{26}_D$= -65.4 (c = 0.57, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 35/1, detector: 220 nm, flow rate: 0.8 mL/min), t1(major) = 8.1 min, t2(minor) = 8.7 min.

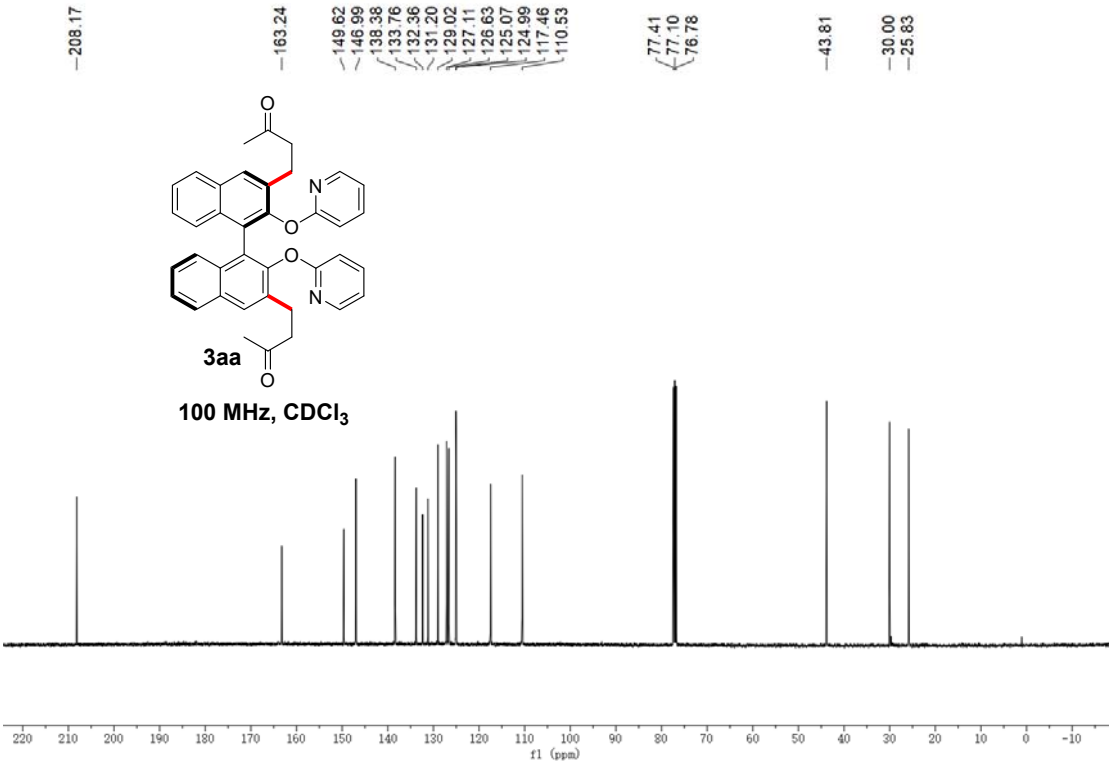
4,4'-(2,2'-dihydroxy-(R)-[1,1'-binaphthalene]-3,3'-diyl)bis(butan-2-one) (7)

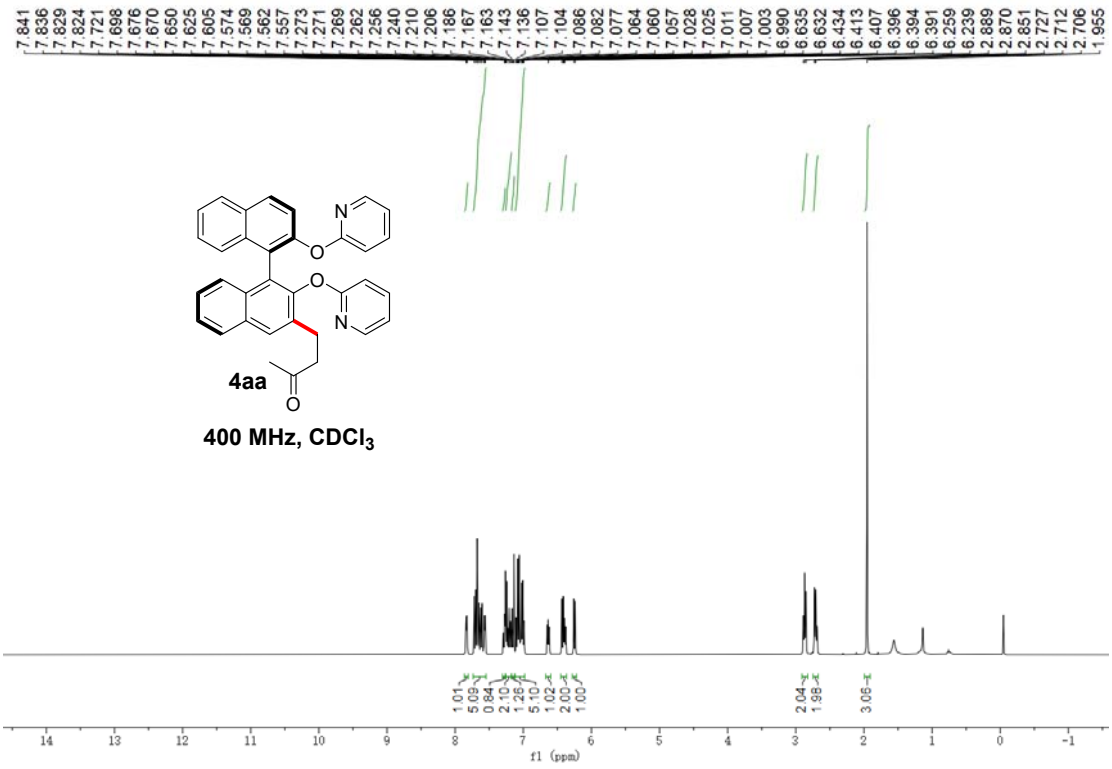


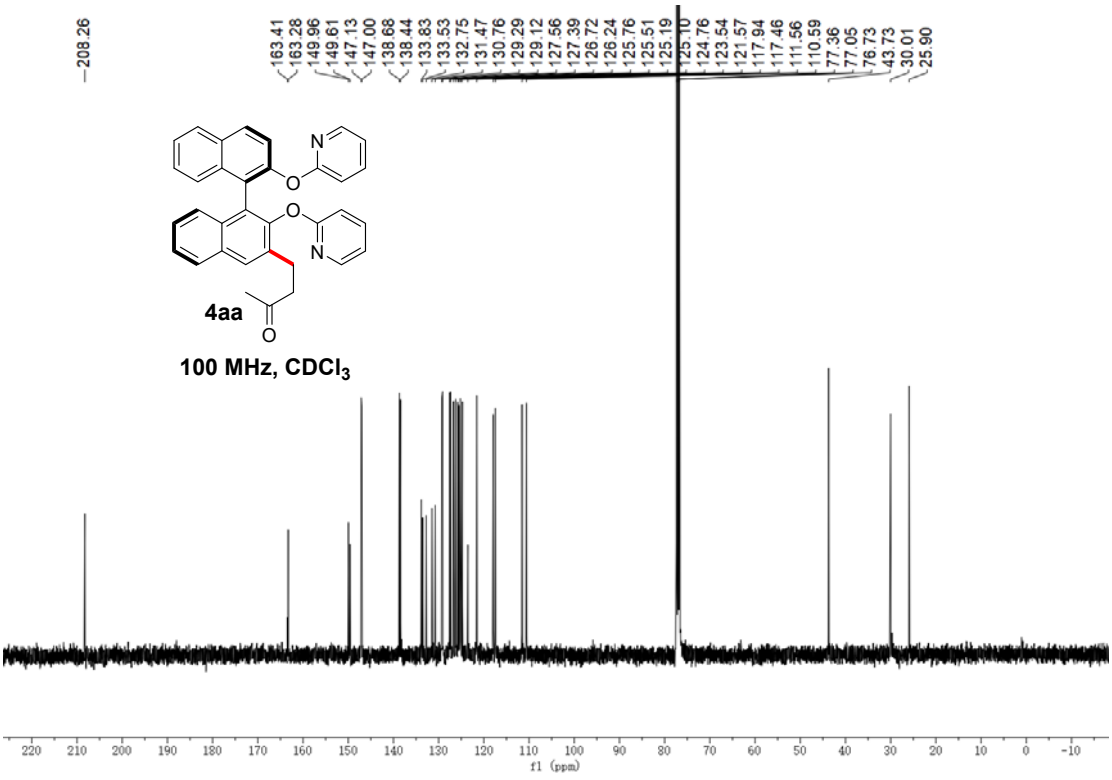
7

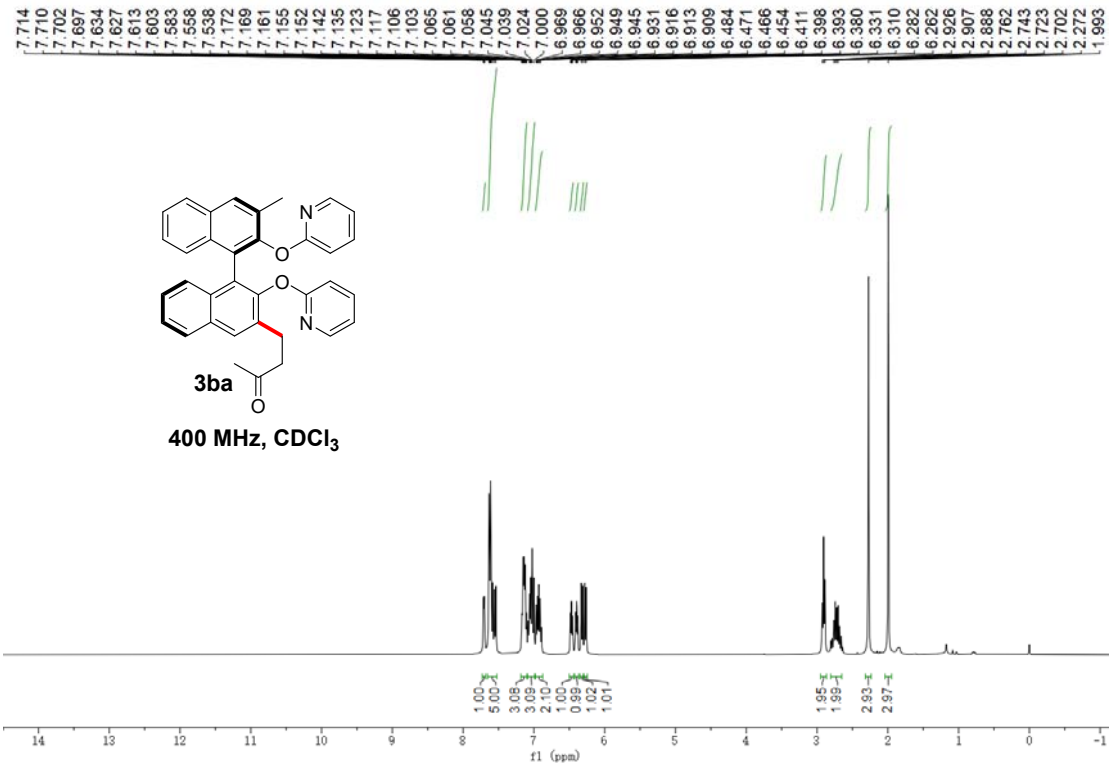
15.5 mg, 73% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.34 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 5.52 (s, 1H), 3.16 (t, *J* = 7.4 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 151.5, 132.4, 130.4, 129.7, 129.4, 127.8, 126.7, 124.1, 124.1, 111.7, 43.7, 30.0, 25.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{26}NaO_4$ 449.1723; Found 449.1729. $[\alpha]^{24}_D$= 21.5 (c = 0.22, chloroform). The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (AD-H, hexane/i-PrOH = 90/10, detector: 220 nm, flow rate: 0.8 mL/min), t1(minor) = 19.2 min, t2(major) = 32.5 min.

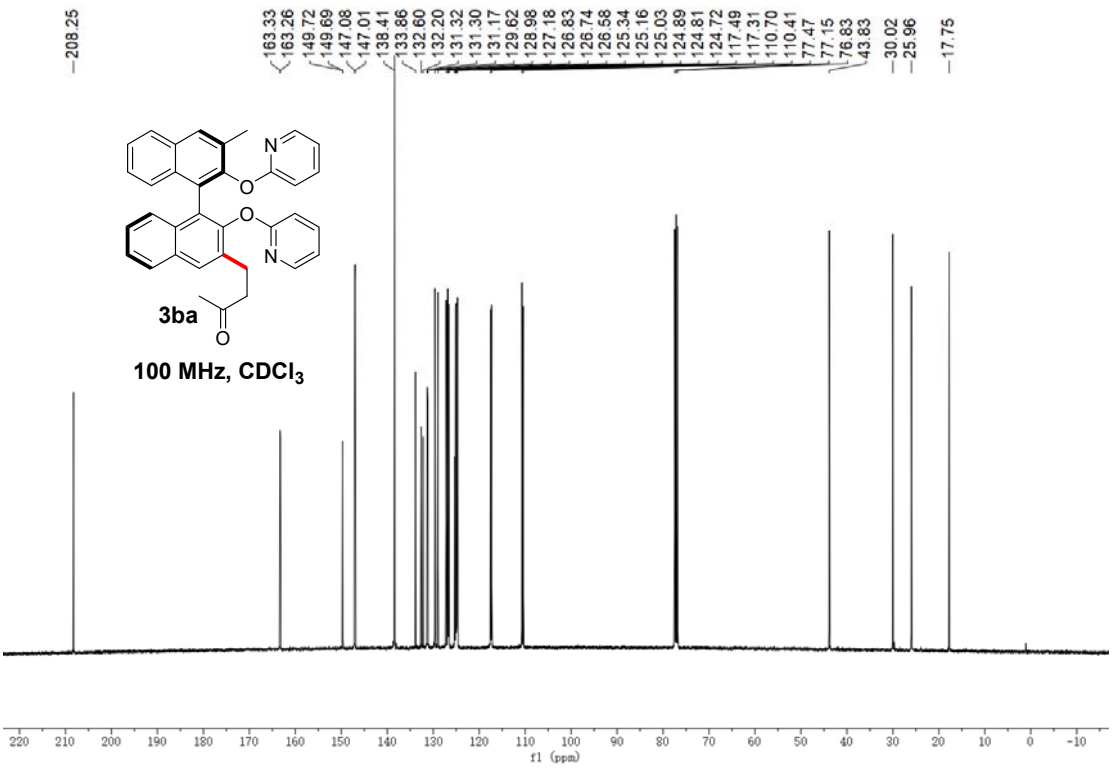

7.630
7.619
7.594
7.574
7.180
7.176
7.163
7.159
7.155
7.143
7.139
7.127
7.122
7.109
7.105
7.102
7.088
7.084
7.015
6.994
6.973
6.970
6.957
6.953
6.949
6.936
6.933
6.442
6.430
6.424
6.412
6.306
6.285
3.090
2.986
2.949
2.930
2.911
2.892
2.875
2.861
2.843
2.826
2.821
2.805
2.800
2.782
2.763
2.754
2.735
2.714
2.691
2.672
2.030
O
N
O
O
N
O
3aa
400 MHz, CDCl3
1.98
1.05
2.20
2.06
1.00
1.01
2.06
1.93
3.11
f1 (ppm)

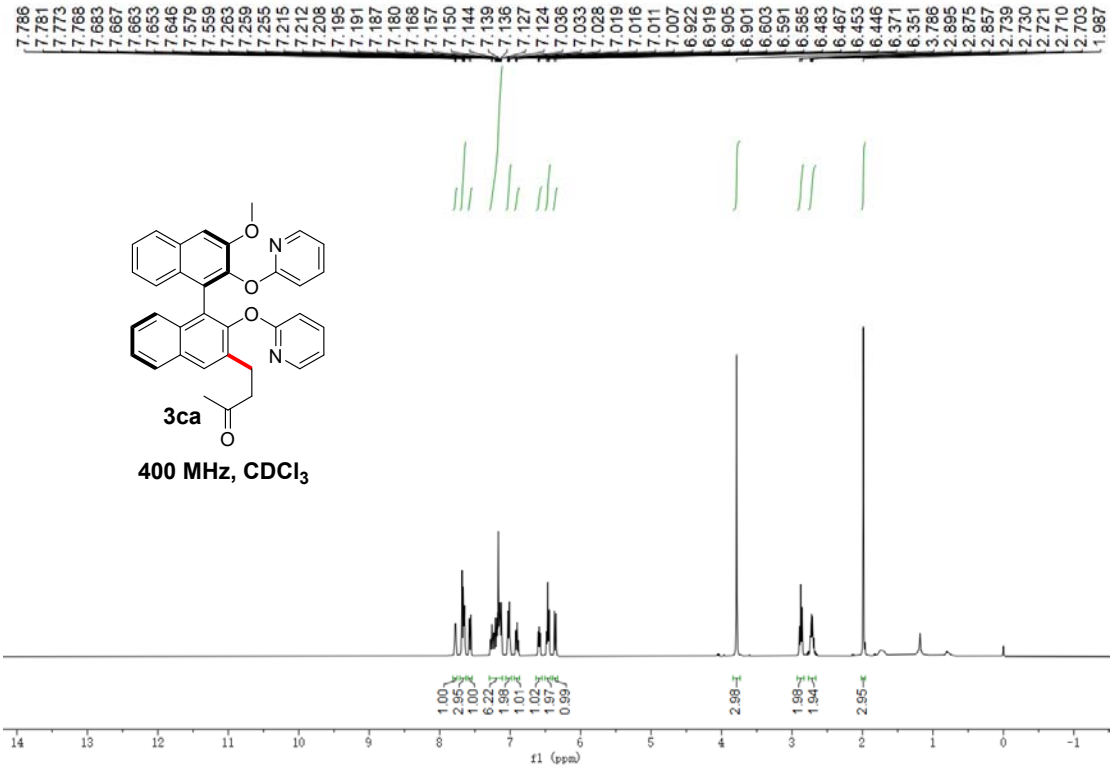

208.17
163.24
149.62
146.99
138.38
133.76
132.36
131.20
129.02
127.11
126.63
125.07
124.99
117.46
110.53
77.41
77.10
76.78
43.81
30.00
25.83
O
N
O
O
N
O
3aa
100 MHz, CDCl3
f1 (ppm)

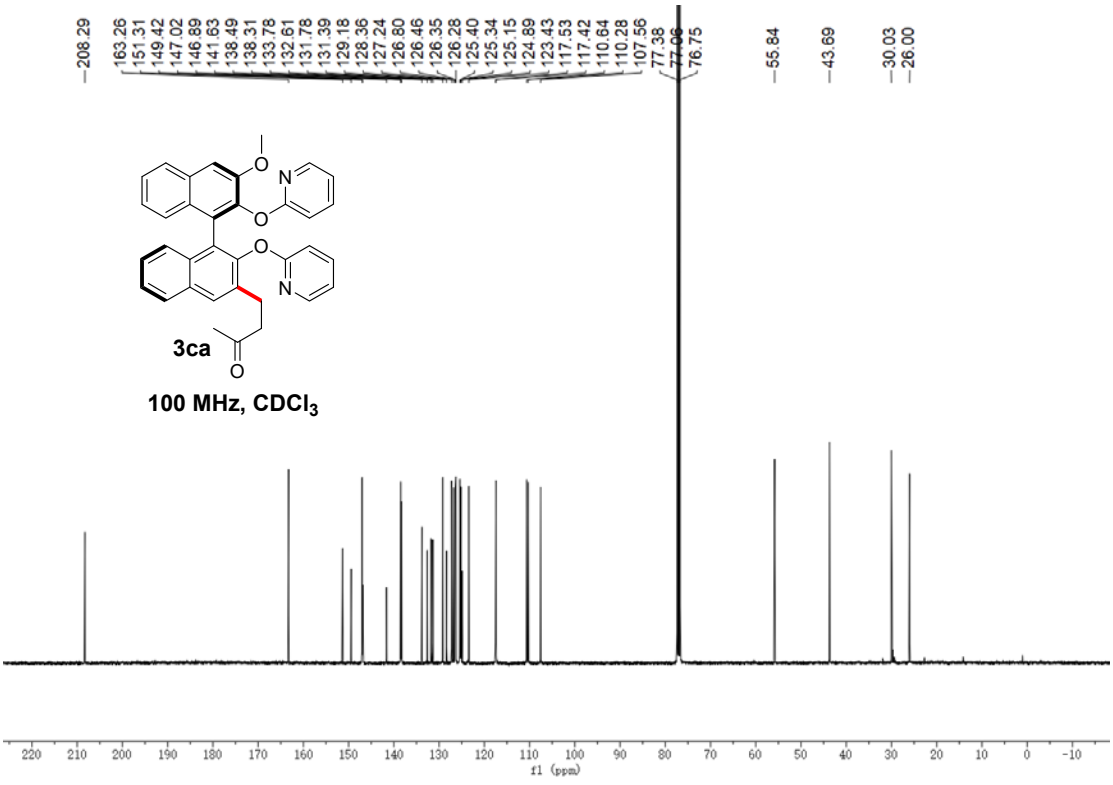

4aa
400 MHz, CDCl3
f1 (ppm)

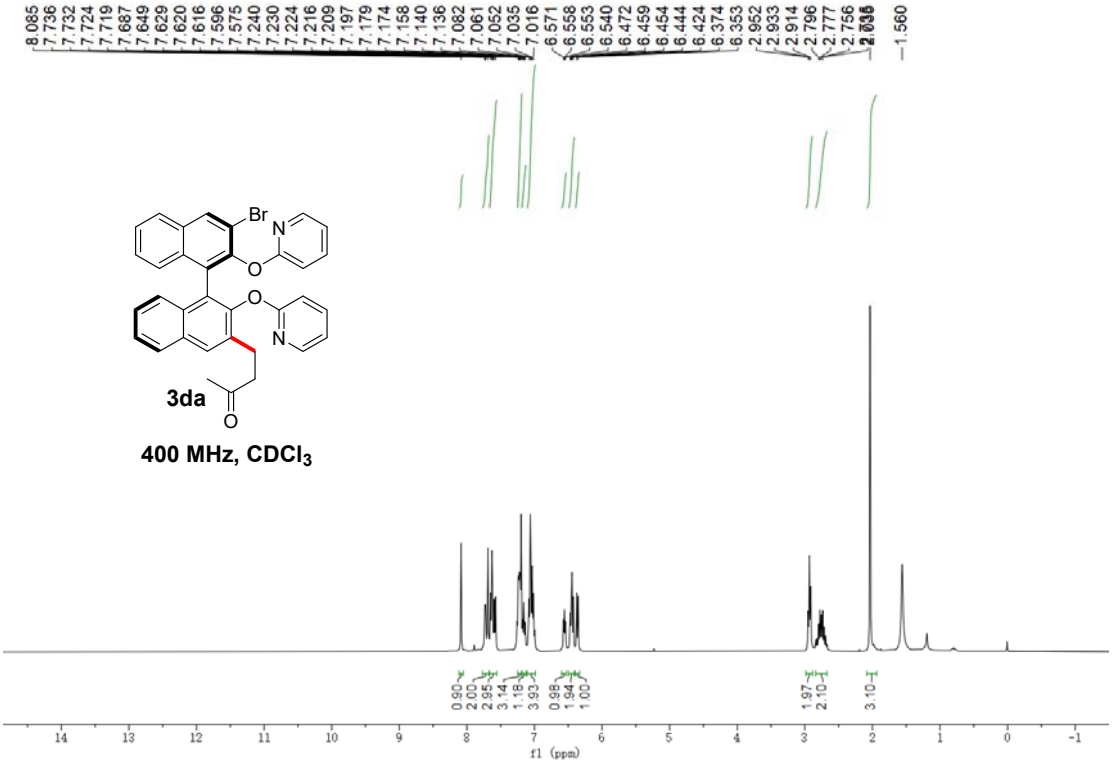

4aa
100 MHz, CDCl3
f1 (ppm)

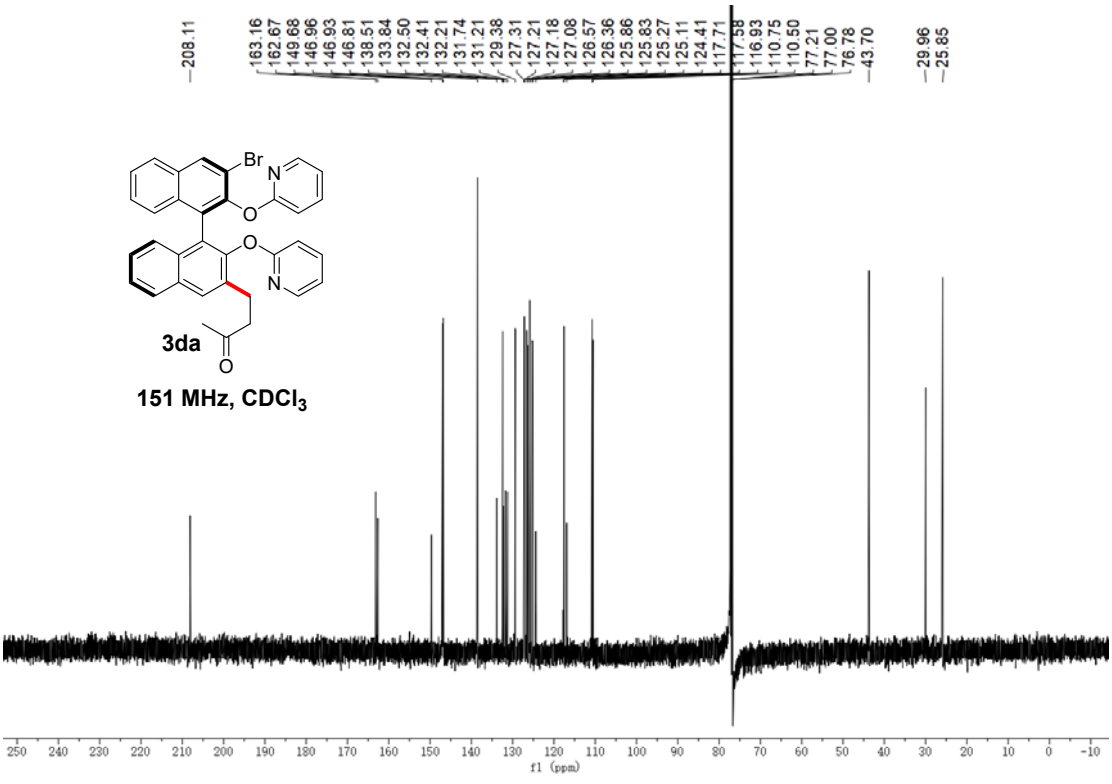

3ba
400 MHz, CDCl3
f1 (ppm)

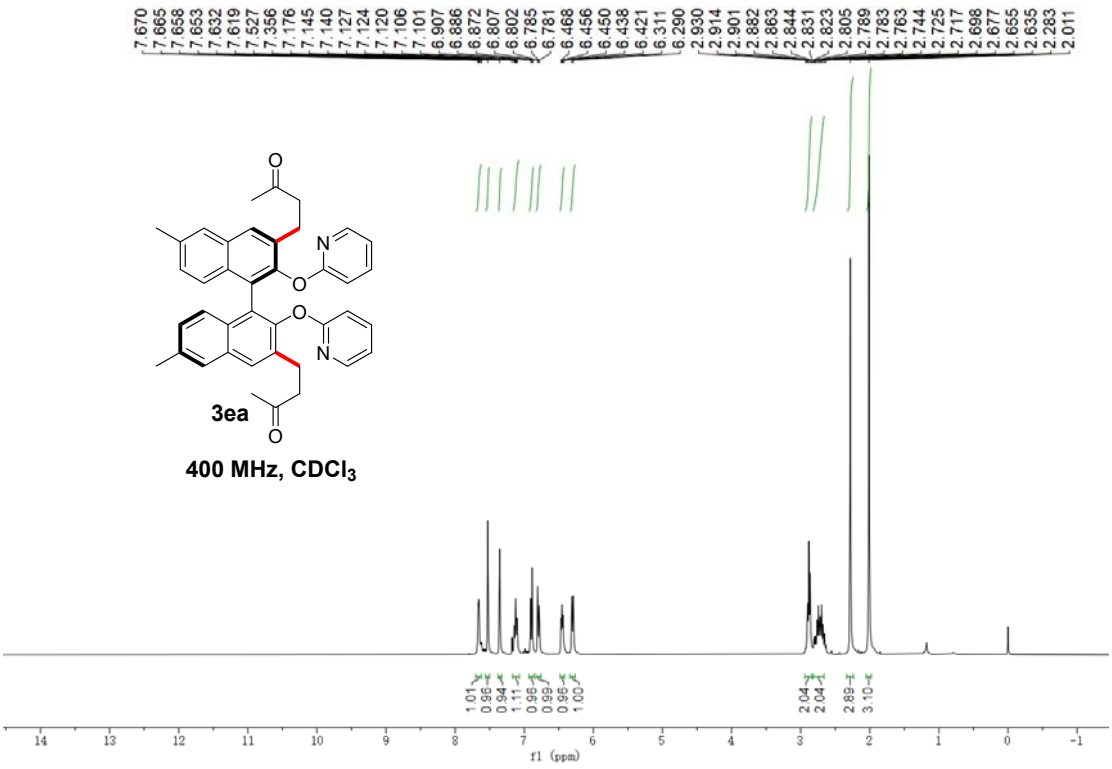

3ba
100 MHz, CDCl3
f1 (ppm)

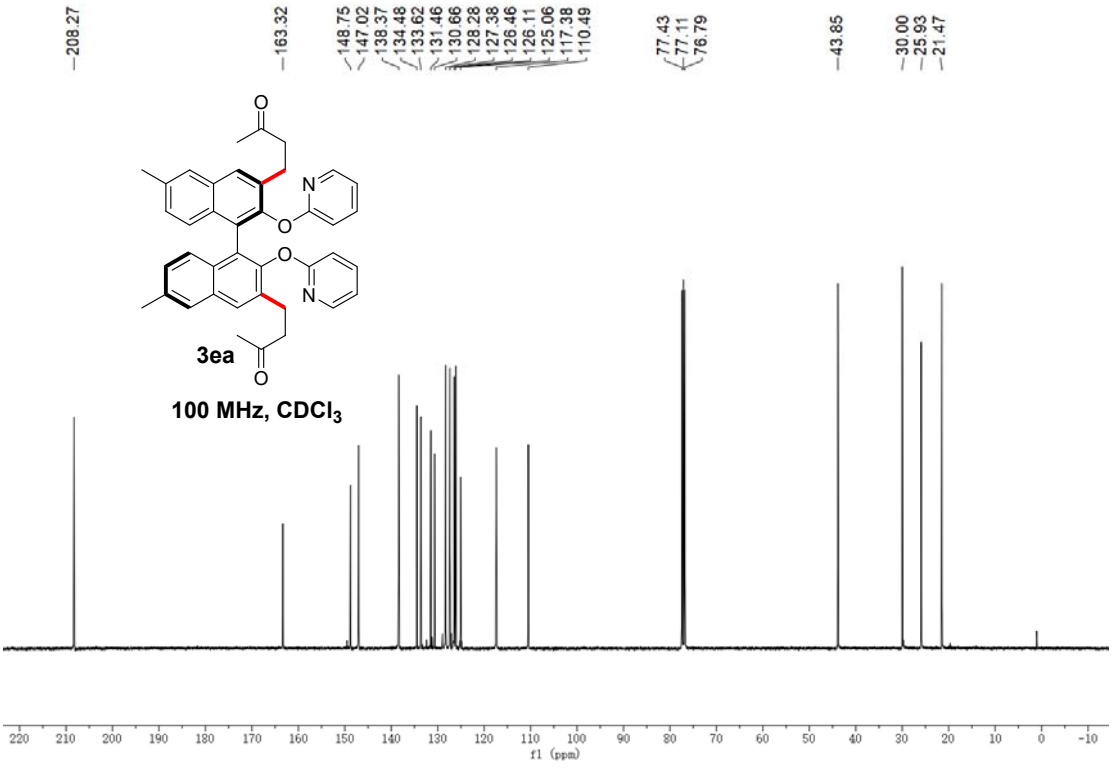

7.786
7.781
7.773
7.768
7.683
7.667
7.663
7.653
7.646
7.579
7.559
7.263
7.259
7.255
7.215
7.212
7.208
7.195
7.191
7.187
7.180
7.168
7.157
7.150
7.144
7.139
7.136
7.127
7.124
7.036
7.033
7.028
7.019
7.016
7.011
7.007
6.922
6.919
6.905
6.901
6.603
6.591
6.585
6.483
6.467
6.453
6.446
6.371
6.351
3.786
2.895
2.875
2.857
2.739
2.730
2.721
2.710
2.703
1.987
O
N
O
O
N
3ca
O
400 MHz, CDCl3
1.00
2.95
1.00
6.22
1.68
1.01
1.02
1.97
0.99
2.98
1.98
1.94
2.95
f1 (ppm)

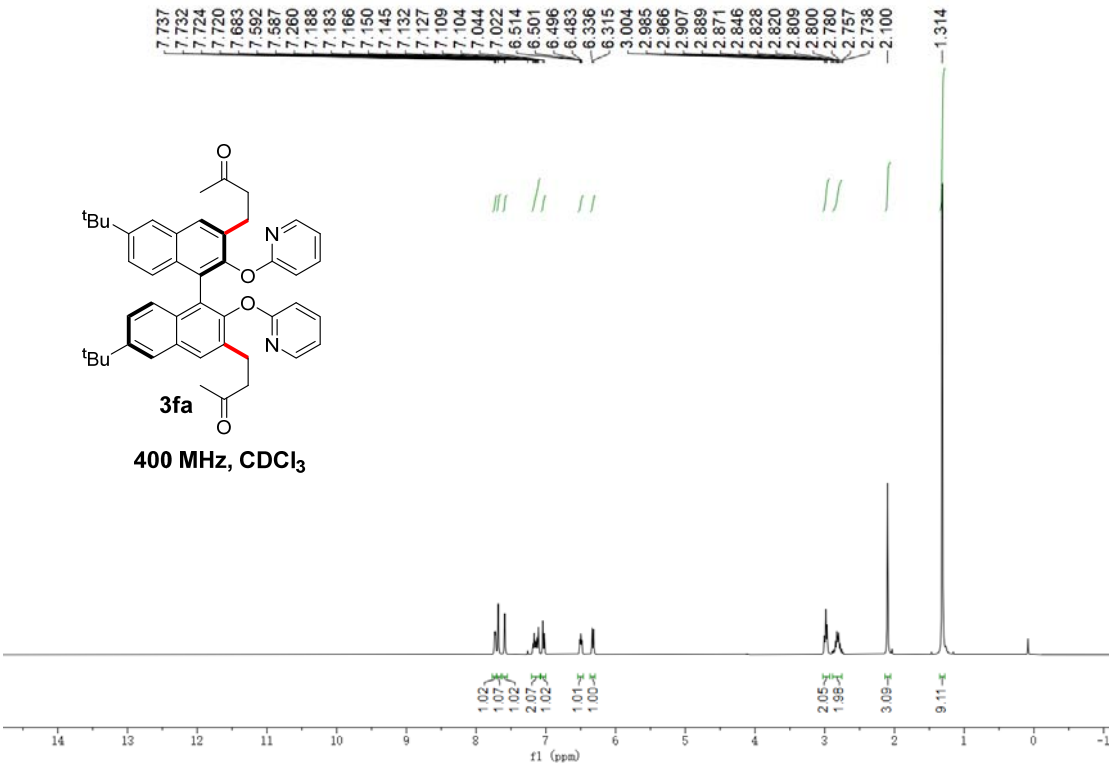

208.29
163.26
151.31
149.42
147.02
146.89
141.63
138.49
138.31
133.78
132.61
131.78
131.39
129.18
128.36
127.24
126.80
126.46
126.35
126.28
125.40
125.34
125.15
124.89
123.43
117.53
117.42
110.64
110.28
107.56
77.38
77.06
76.75
55.84
43.69
30.03
26.00
O
N
O
O
N
3ca
O
100 MHz, CDCl3
f1 (ppm)

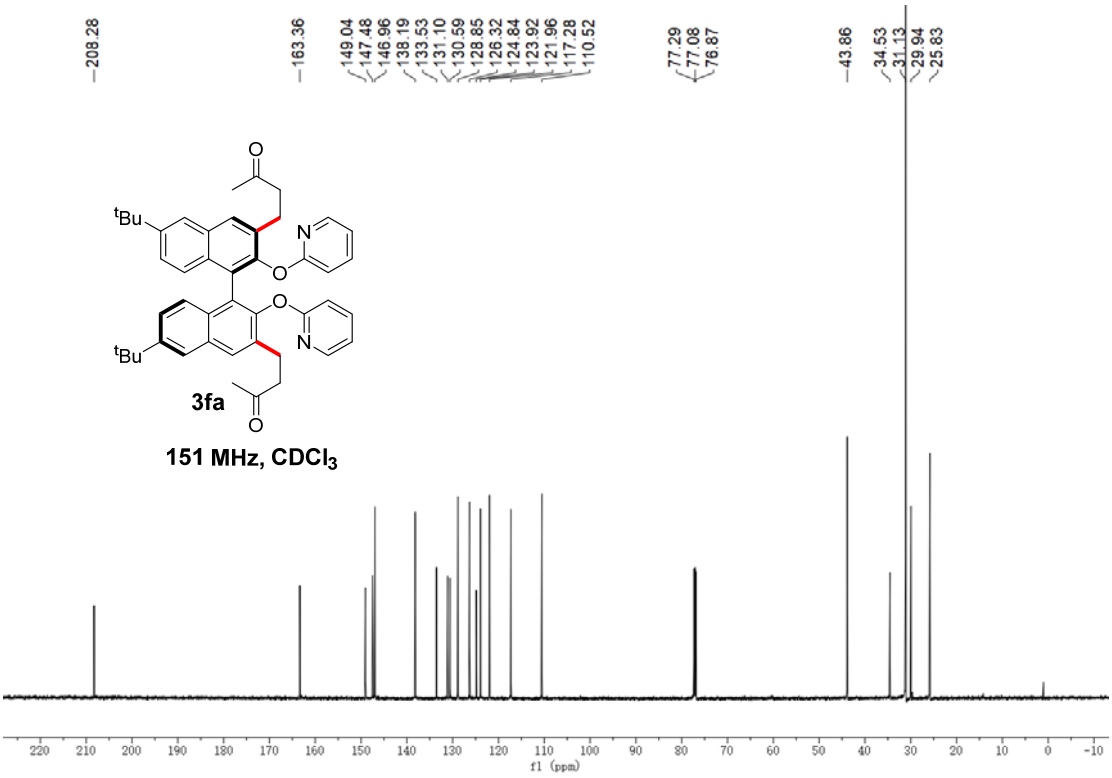

3da
400 MHz, CDCl3
f1 (ppm)

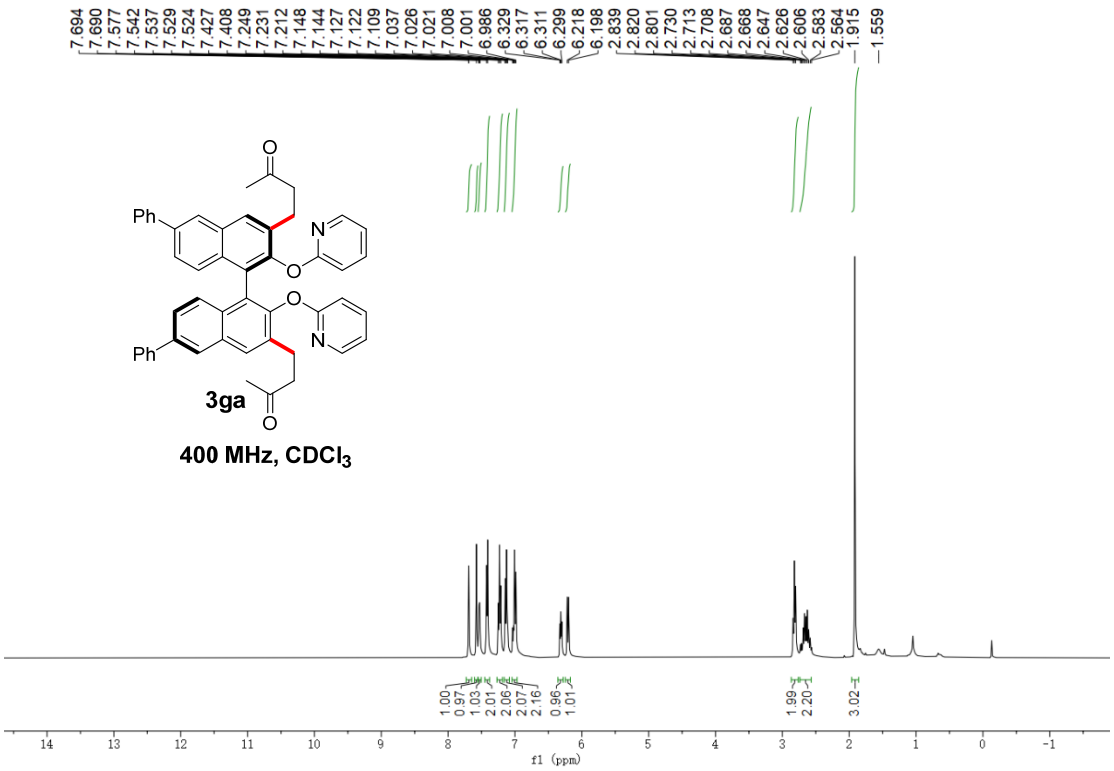

3da
151 MHz, CDCl3
f1 (ppm)

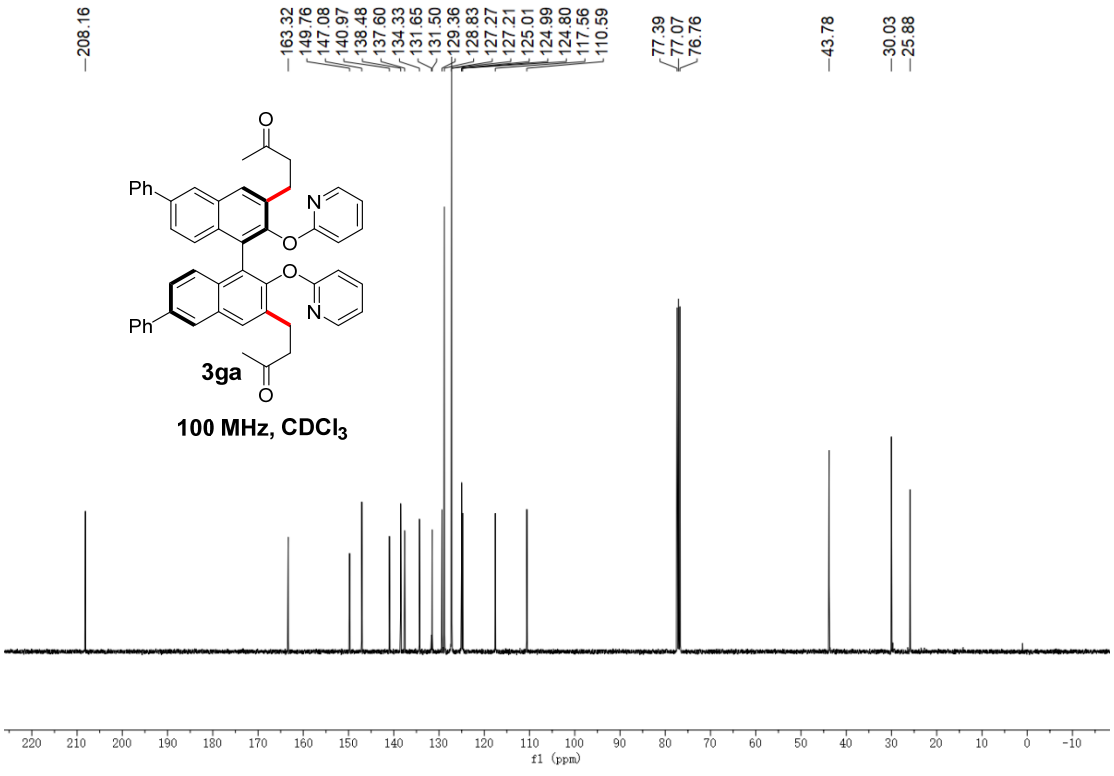

7.670
7.665
7.658
7.653
7.632
7.619
7.527
7.356
7.176
7.145
7.140
7.127
7.124
7.120
7.106
7.101
6.907
6.886
6.872
6.807
6.802
6.785
6.781
6.468
6.456
6.450
6.438
6.421
6.311
6.290
2.930
2.914
2.901
2.882
2.863
2.844
2.831
2.823
2.805
2.789
2.783
2.763
2.744
2.725
2.717
2.698
2.677
2.655
2.635
2.283
2.011
3ea
400 MHz, CDCl3
1.01
0.96
0.94
1.11
0.96
0.99
0.96
1.00
2.04
2.04
2.89
3.10
f1 (ppm)

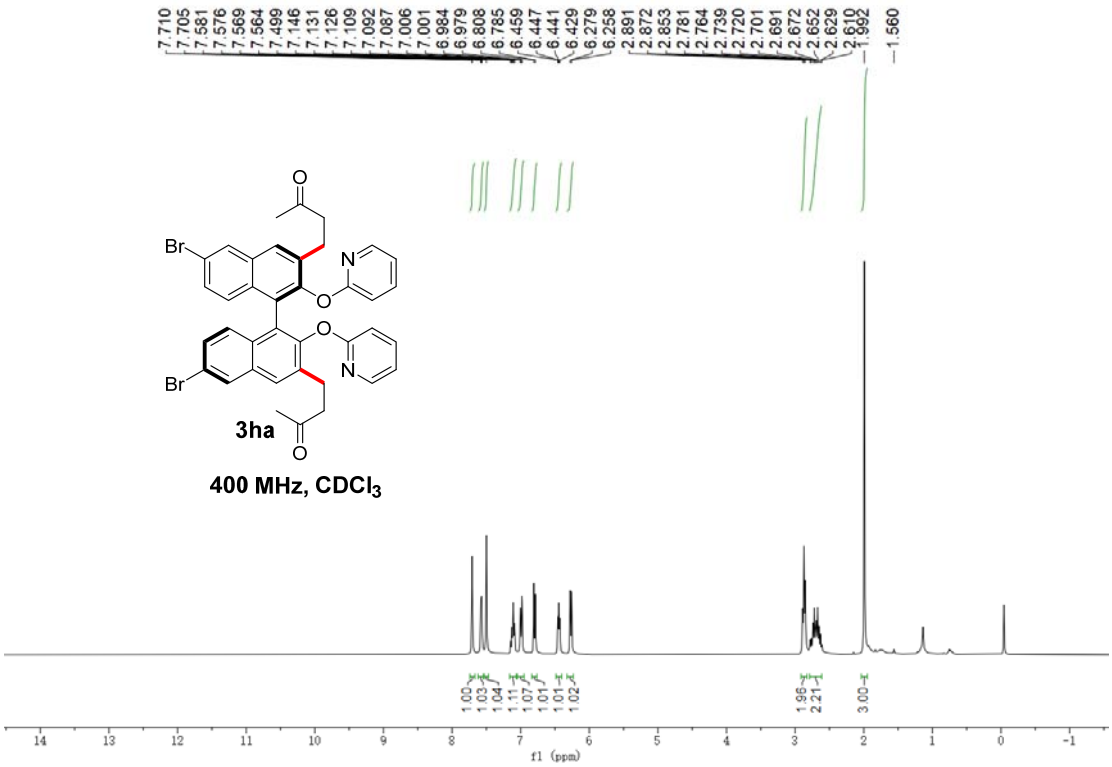

208.27
163.32
148.75
147.02
138.37
134.48
133.62
131.46
130.66
128.28
127.38
126.46
126.11
125.06
117.38
110.49
77.43
77.11
76.79
43.85
30.00
25.93
21.47
3ea
100 MHz, CDCl3
f1 (ppm)

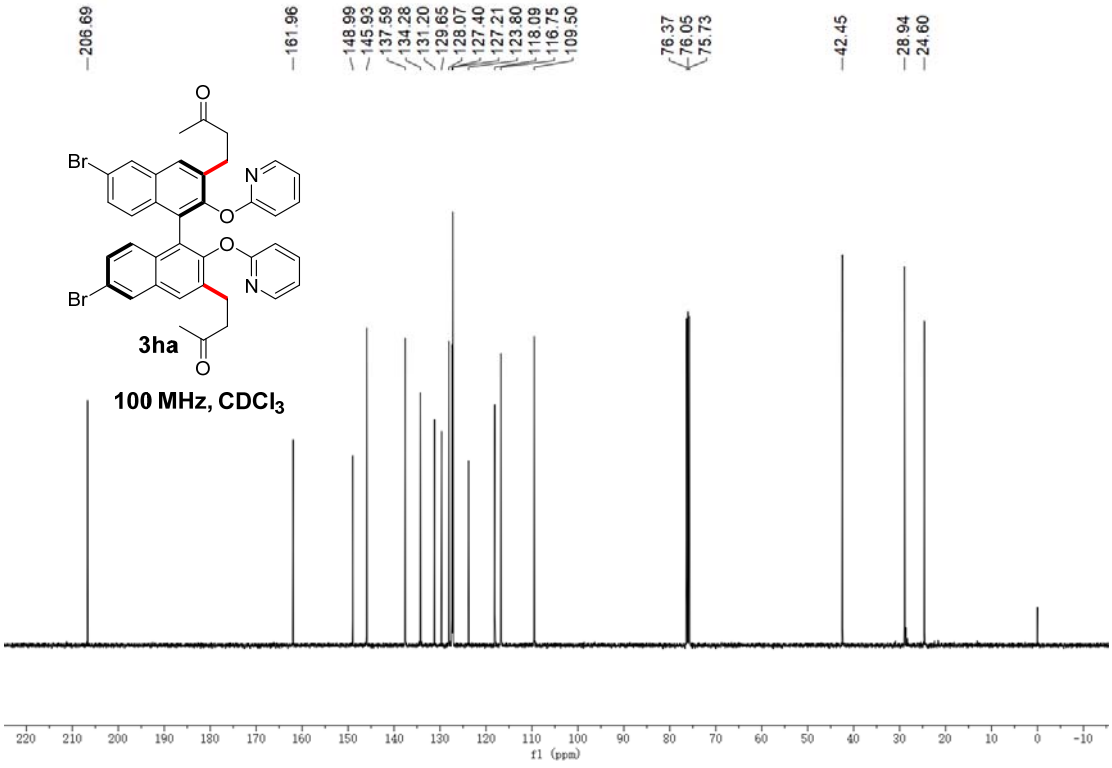

7.737
7.732
7.724
7.720
7.683
7.592
7.587
7.260
7.188
7.183
7.166
7.150
7.145
7.132
7.127
7.109
7.104
7.044
7.022
6.514
6.501
6.496
6.483
6.336
6.315
3.004
2.985
2.966
2.907
2.889
2.871
2.846
2.828
2.820
2.809
2.800
2.780
2.757
2.738
2.100
1.314
tBu
tBu
N
N
O
O
O
O
3fa
400 MHz, CDCl3
1.02
1.07
1.02
2.07
1.02
1.01
1.00
2.05
1.98
3.09
9.11
f1 (ppm)

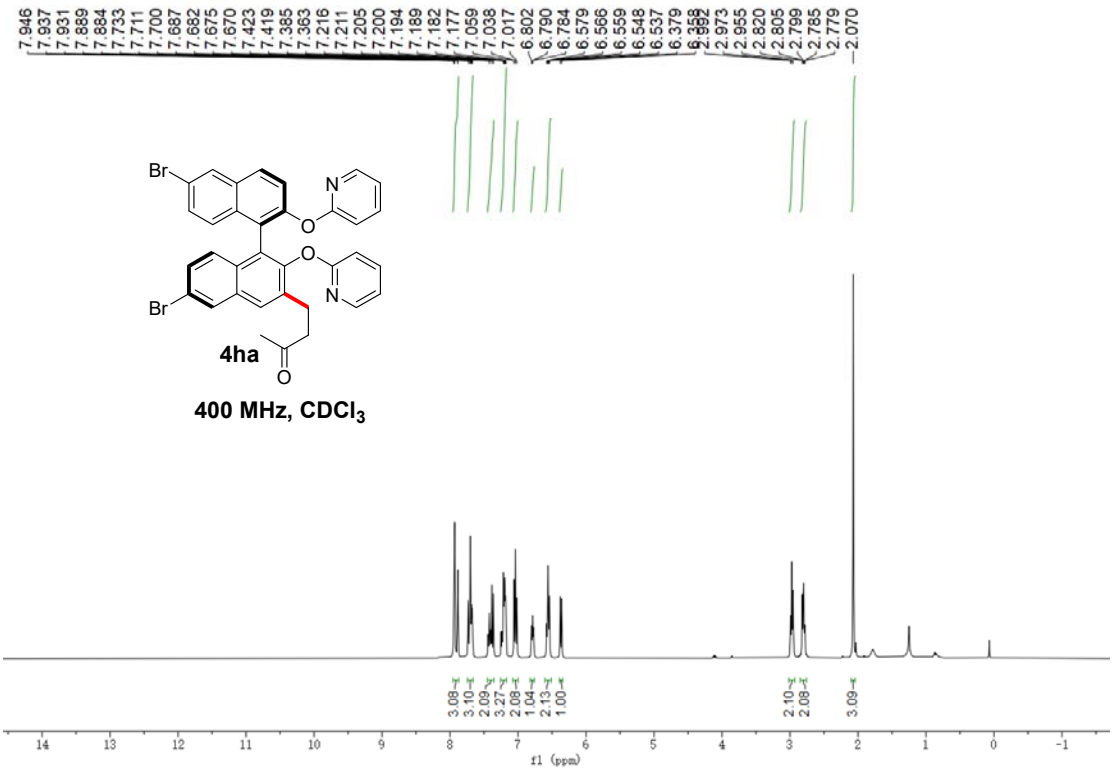

208.28
163.36
149.04
147.48
146.96
138.19
133.53
131.10
130.59
128.85
126.32
124.84
123.92
121.96
117.28
110.52
77.29
77.08
76.87
43.86
34.53
31.13
29.94
25.83
tBu
tBu
N
N
O
O
O
O
3fa
151 MHz, CDCl3
f1 (ppm)

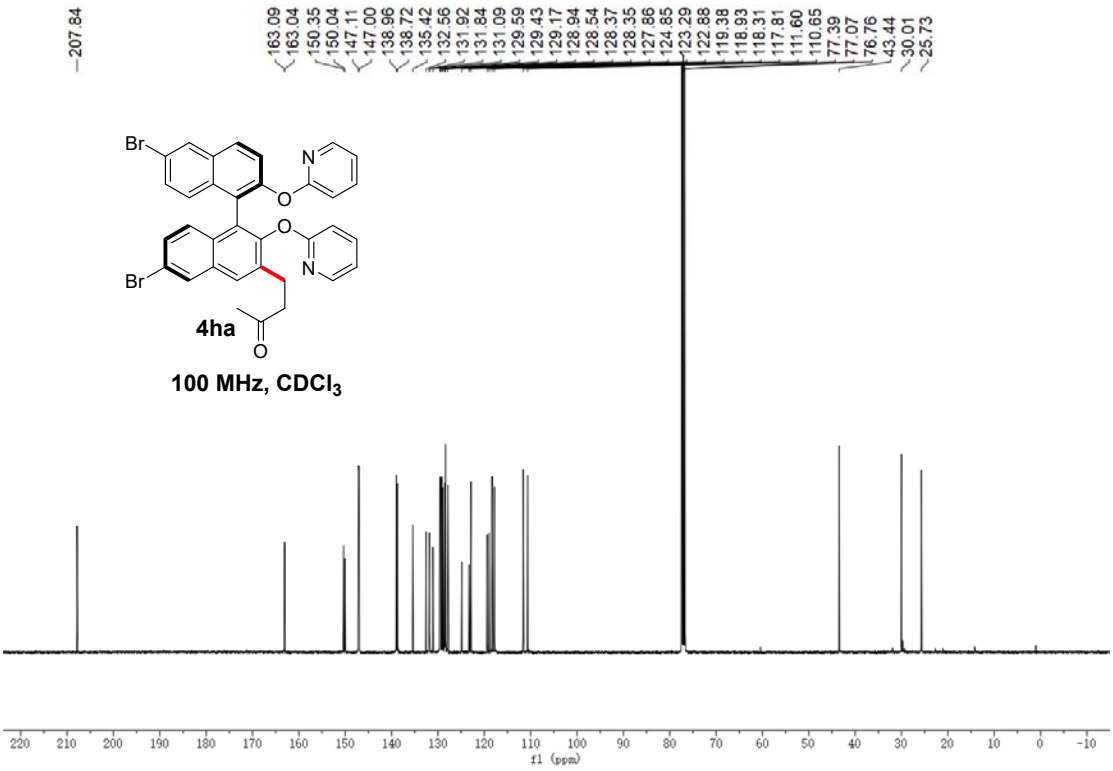

7.694
7.690
7.577
7.542
7.537
7.529
7.524
7.427
7.408
7.249
7.231
7.212
7.148
7.144
7.127
7.122
7.109
7.037
7.026
7.021
7.008
7.001
6.986
6.329
6.317
6.311
6.299
6.218
6.198
2.839
2.820
2.801
2.730
2.713
2.708
2.687
2.668
2.647
2.626
2.606
2.583
2.564
1.915
1.559
Ph
N
O
O
N
Ph
O
3ga
400 MHz, CDCl3
1.00
0.97
1.03
2.01
2.06
2.07
2.16
0.96
1.01
1.99
2.20
3.02
f1 (ppm)

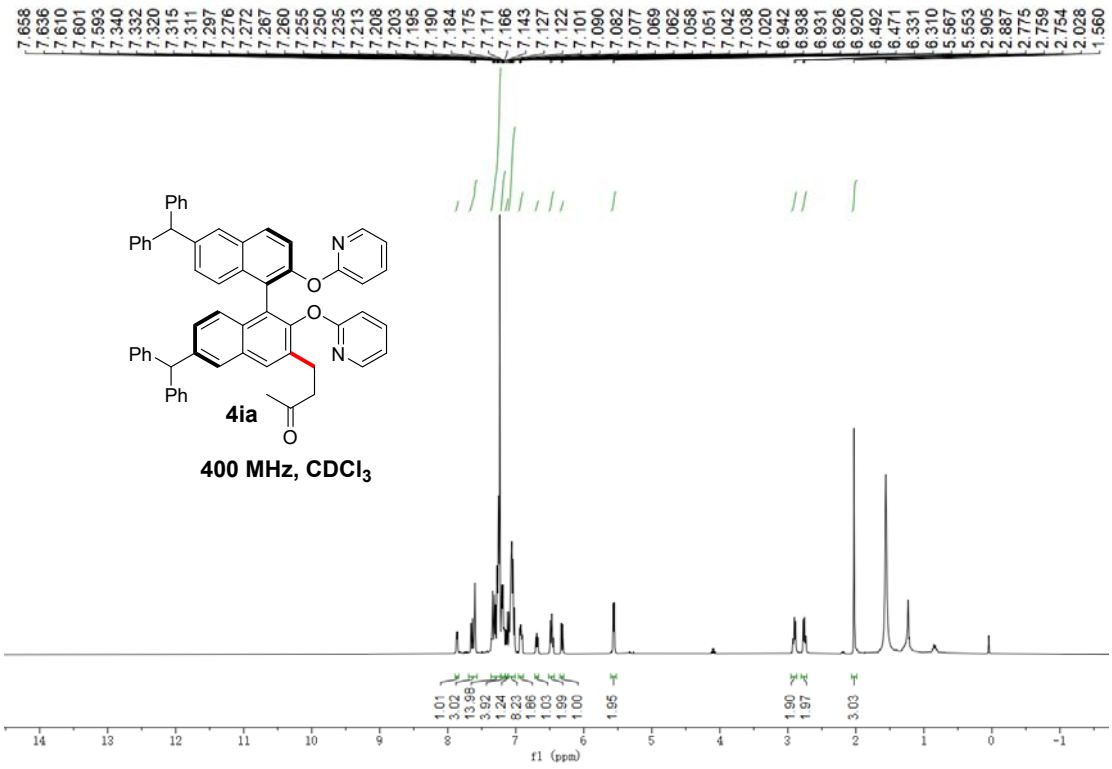

208.16
163.32
149.76
147.08
140.97
138.48
137.60
134.33
131.65
131.50
129.36
128.83
127.27
127.21
125.01
124.99
124.80
117.56
110.59
77.39
77.07
76.76
43.78
30.03
25.88
Ph
N
O
O
N
Ph
O
3ga
100 MHz, CDCl3
f1 (ppm)

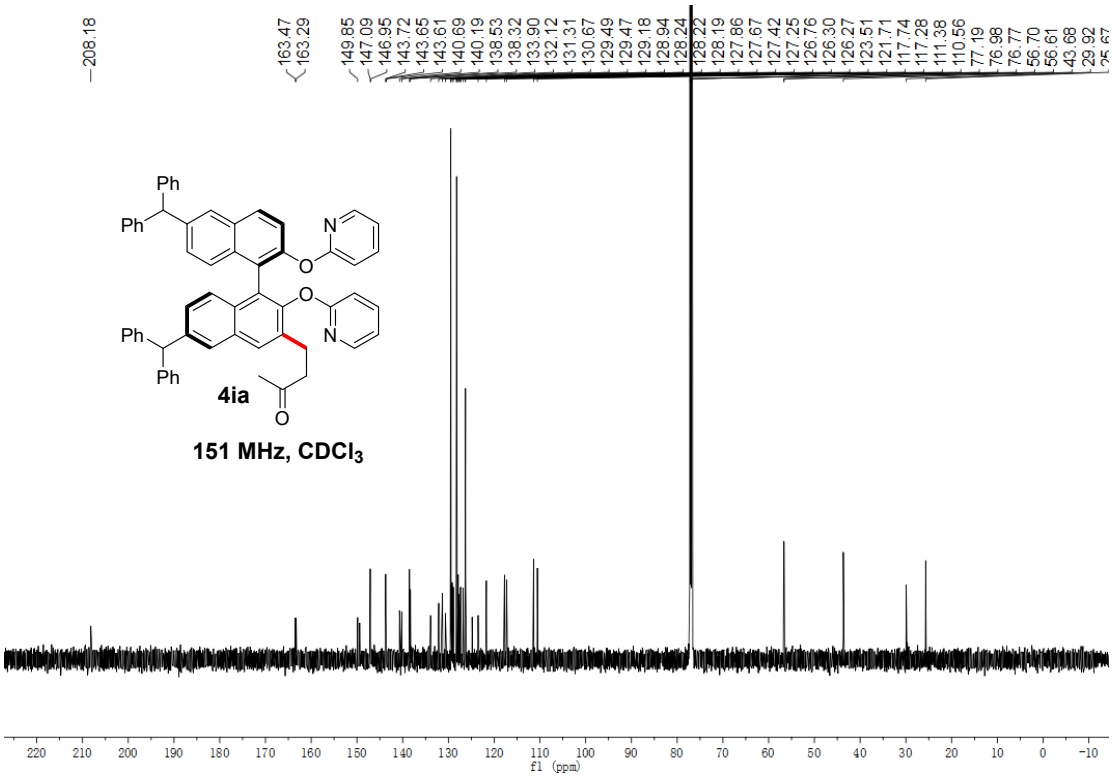

7.710
7.705
7.581
7.576
7.569
7.564
7.499
7.146
7.131
7.126
7.109
7.092
7.087
7.006
7.001
6.984
6.979
6.808
6.785
6.459
6.447
6.441
6.429
6.279
6.258
2.891
2.872
2.853
2.781
2.764
2.739
2.720
2.701
2.691
2.672
2.652
2.629
2.610
1.992
1.560
Br
N
O
Br
3ha
400 MHz, CDCl3
1.00
1.03
1.04
1.11
1.07
1.01
1.01
1.02
1.96
2.21
3.00
f1 (ppm)

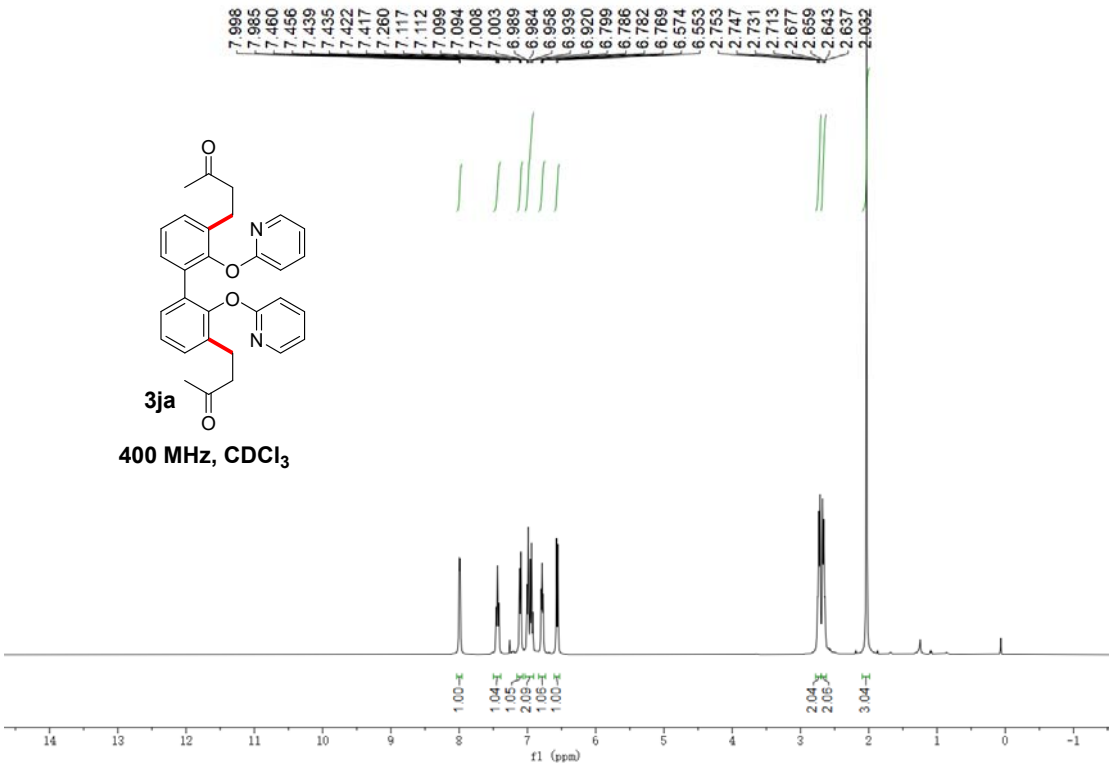

206.69
161.96
148.99
145.93
137.59
134.28
131.20
129.65
128.07
127.40
127.21
123.80
118.09
116.75
109.50
76.37
76.05
75.73
42.45
28.94
24.60
Br
N
O
Br
3ha
100 MHz, CDCl3
f1 (ppm)

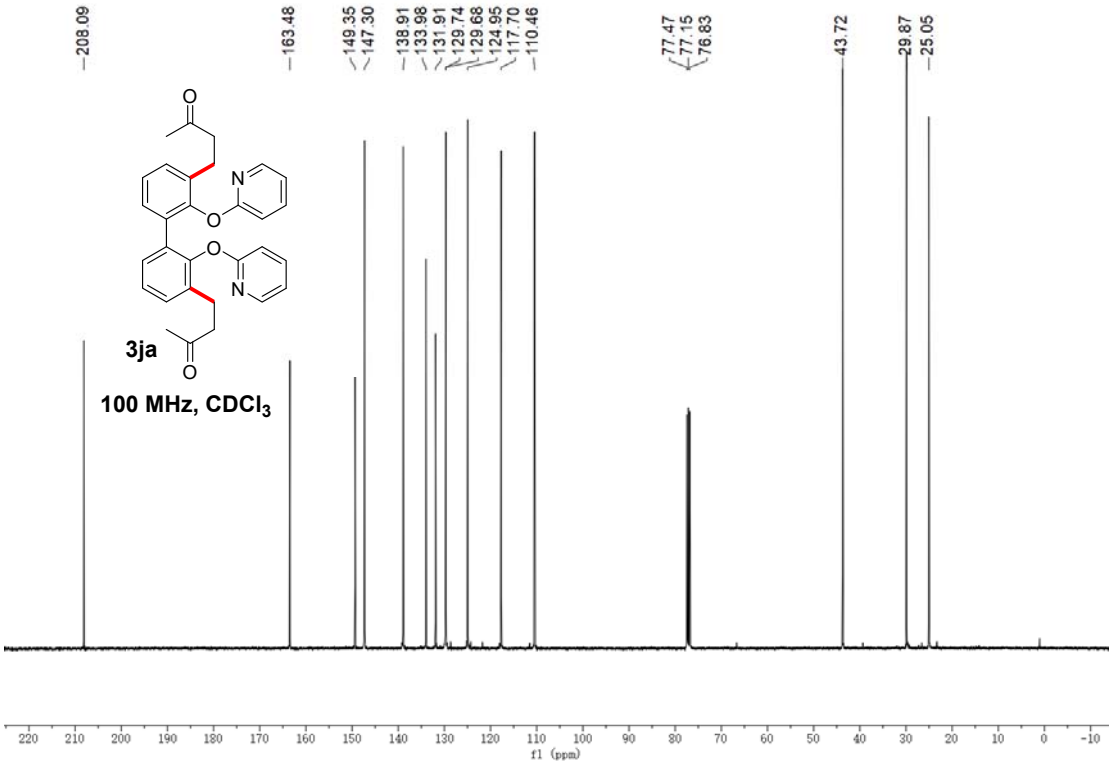

Br
N
O
O
N
Br
4ha
O
400 MHz, CDCl3
f1 (ppm)

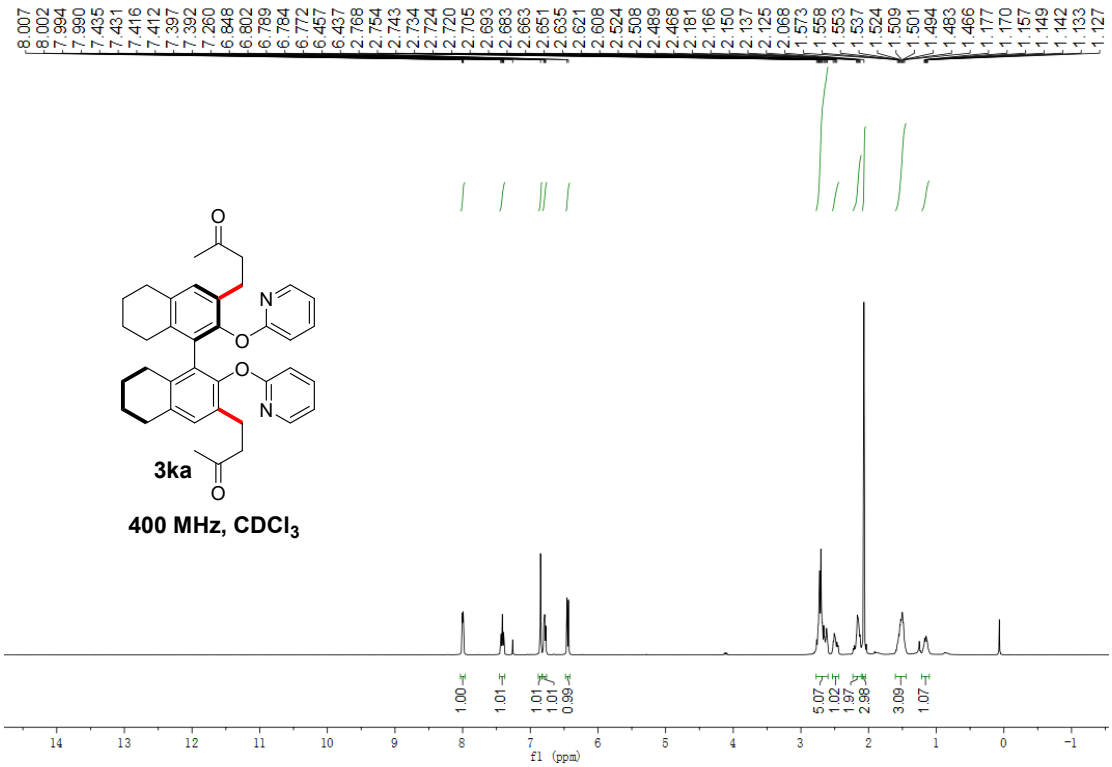

Br
N
O
O
N
Br
4ha
O
100 MHz, CDCl3
f1 (ppm)

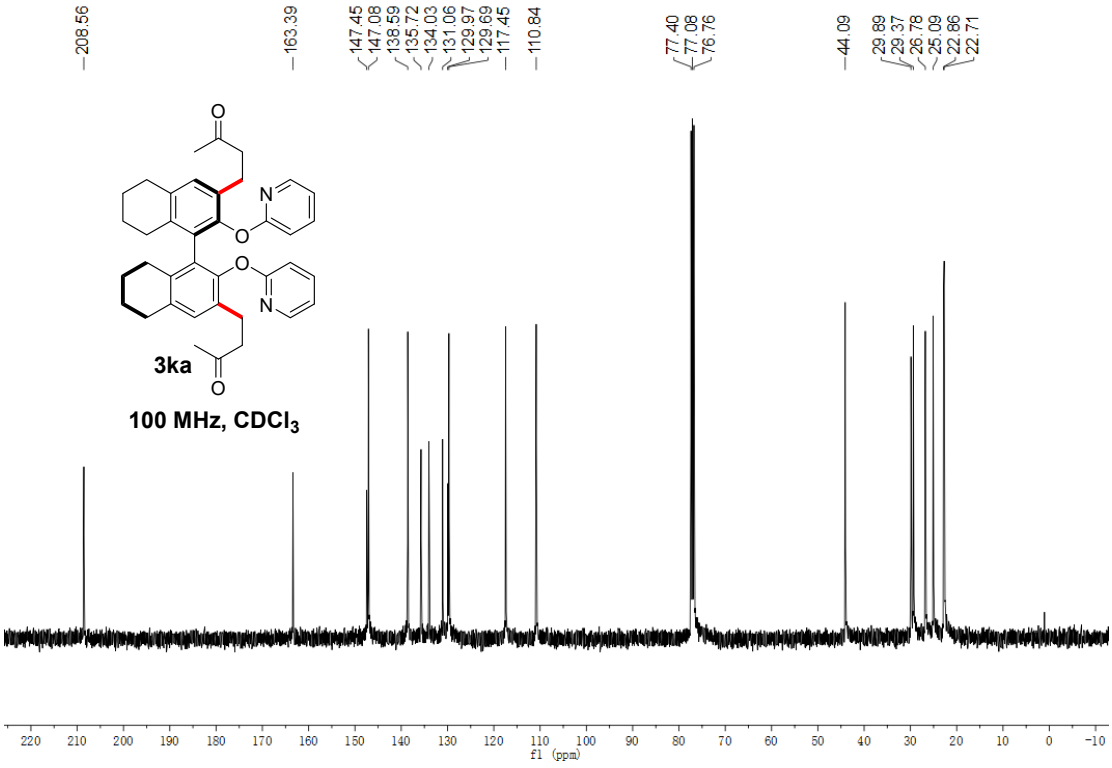

4ia
400 MHz, CDCl3
f1 (ppm)

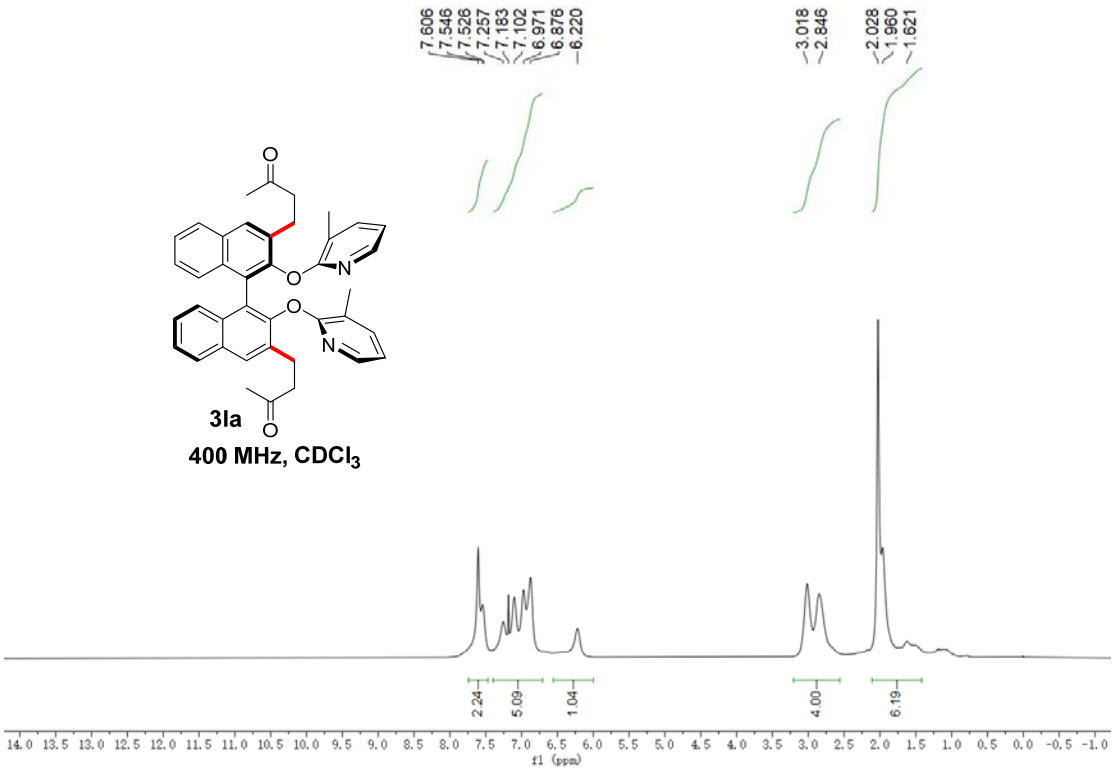

4ia
151 MHz, CDCl3
f1 (ppm)

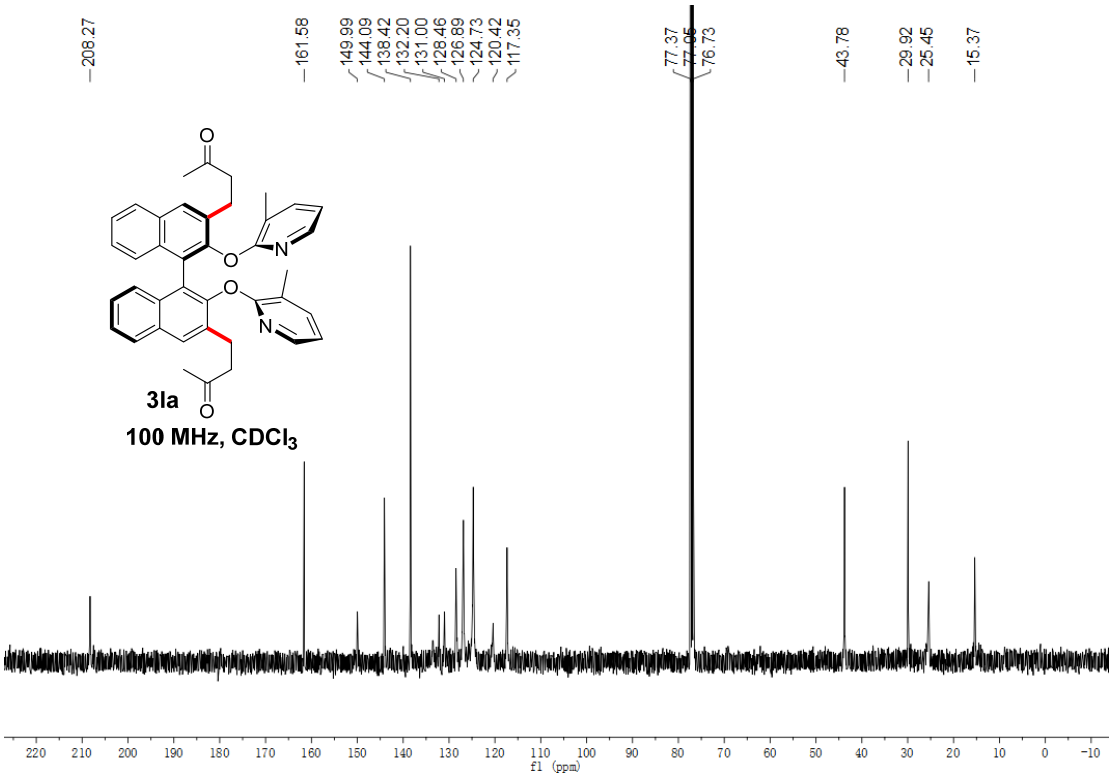

7.998
7.985
7.460
7.456
7.439
7.435
7.422
7.417
7.260
7.117
7.112
7.099
7.094
7.008
7.003
6.989
6.984
6.958
6.939
6.920
6.799
6.786
6.782
6.769
6.574
6.553
2.753
2.747
2.731
2.713
2.677
2.659
2.643
2.637
2.032
3ja
400 MHz, CDCl3
1.00
1.04
1.05
2.09
1.06
1.00
2.04
2.05
3.04
f1 (ppm)

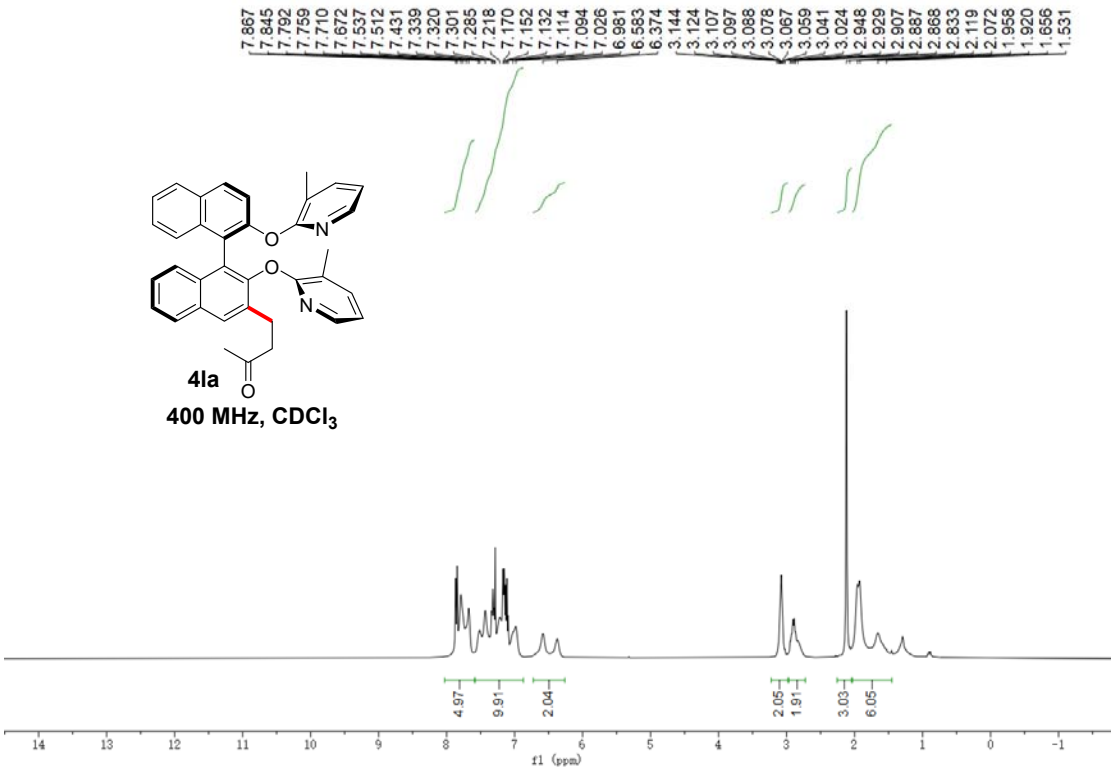

208.09
163.48
149.35
147.30
138.91
133.98
131.91
129.74
129.68
124.95
117.70
110.46
77.47
77.15
76.83
43.72
29.87
25.05
3ja
100 MHz, CDCl3
f1 (ppm)

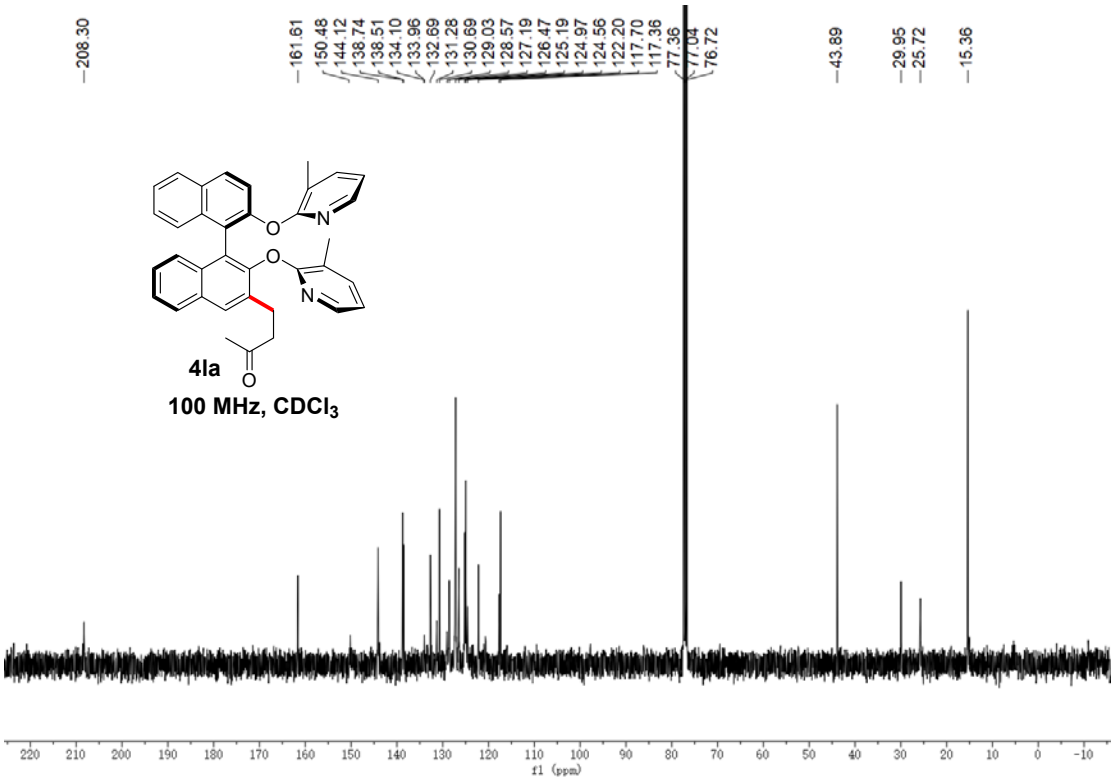

8.007
8.002
7.994
7.990
7.435
7.431
7.416
7.412
7.397
7.392
7.260
6.848
6.802
6.789
6.784
6.772
6.457
6.437
2.768
2.754
2.743
2.734
2.724
2.720
2.705
2.693
2.683
2.663
2.651
2.635
2.621
2.608
2.524
2.508
2.489
2.468
2.181
2.166
2.150
2.137
2.125
2.068
1.573
1.558
1.553
1.537
1.524
1.509
1.501
1.494
1.483
1.466
1.177
1.170
1.157
1.149
1.142
1.133
1.127
3ka
400 MHz, CDCl3
1.00
1.01
1.01
1.01
0.99
5.07
1.02
1.97
2.98
3.09
1.07
f1 (ppm)

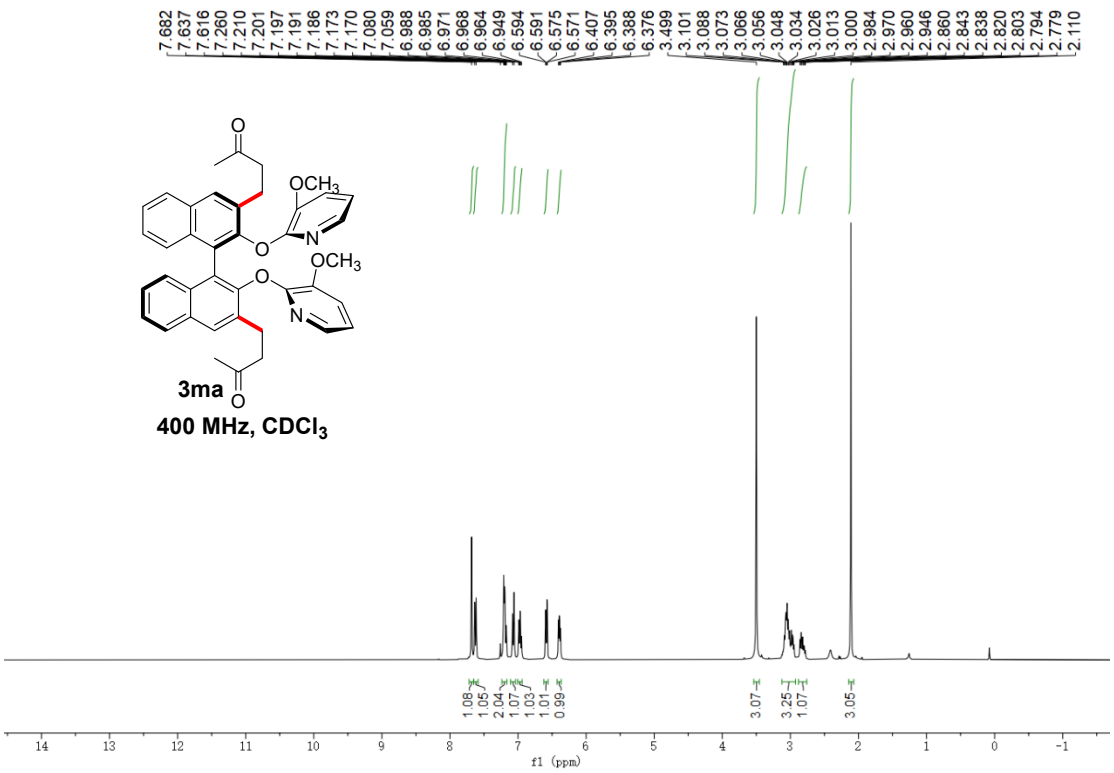

208.56
163.39
147.45
147.08
138.59
135.72
134.03
131.06
129.97
129.69
117.45
110.84
77.40
77.08
76.76
44.09
29.89
29.37
26.78
25.09
22.86
22.71
3ka
100 MHz, CDCl3
f1 (ppm)

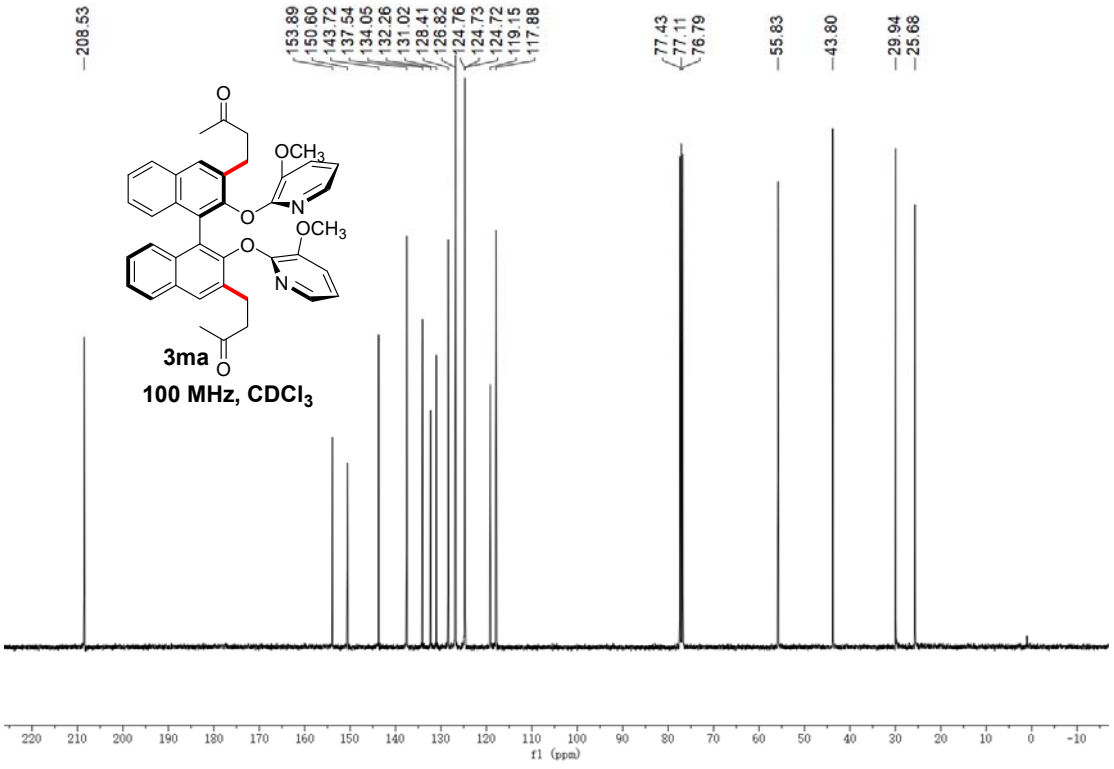

7.606
7.546
7.526
7.257
7.183
7.102
6.971
6.876
6.220
3.018
2.846
2.028
1.960
1.821
3Ia
400 MHz, CDCl3
2.24
5.09
1.04
4.00
6.19
f1 (ppm)

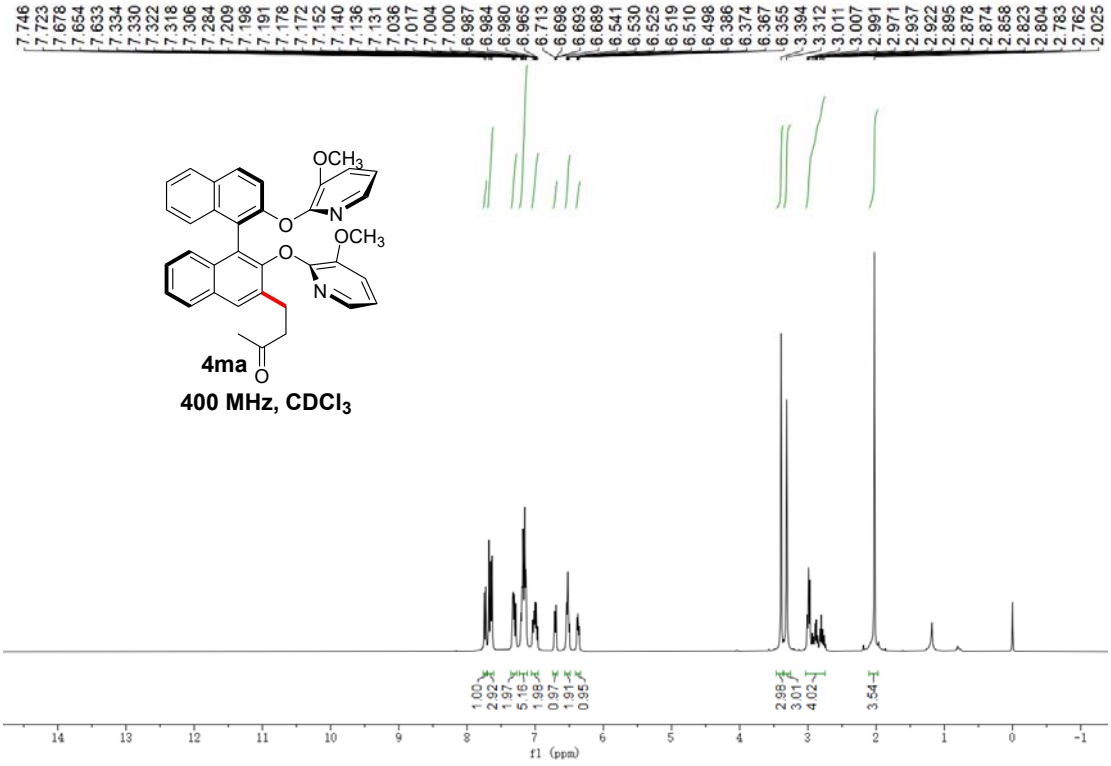

208.27
161.58
149.99
144.09
138.42
132.20
131.00
128.46
126.89
124.73
120.42
117.35
77.37
77.05
76.73
43.78
29.92
25.45
15.37
3Ia
100 MHz, CDCl3
f1 (ppm)

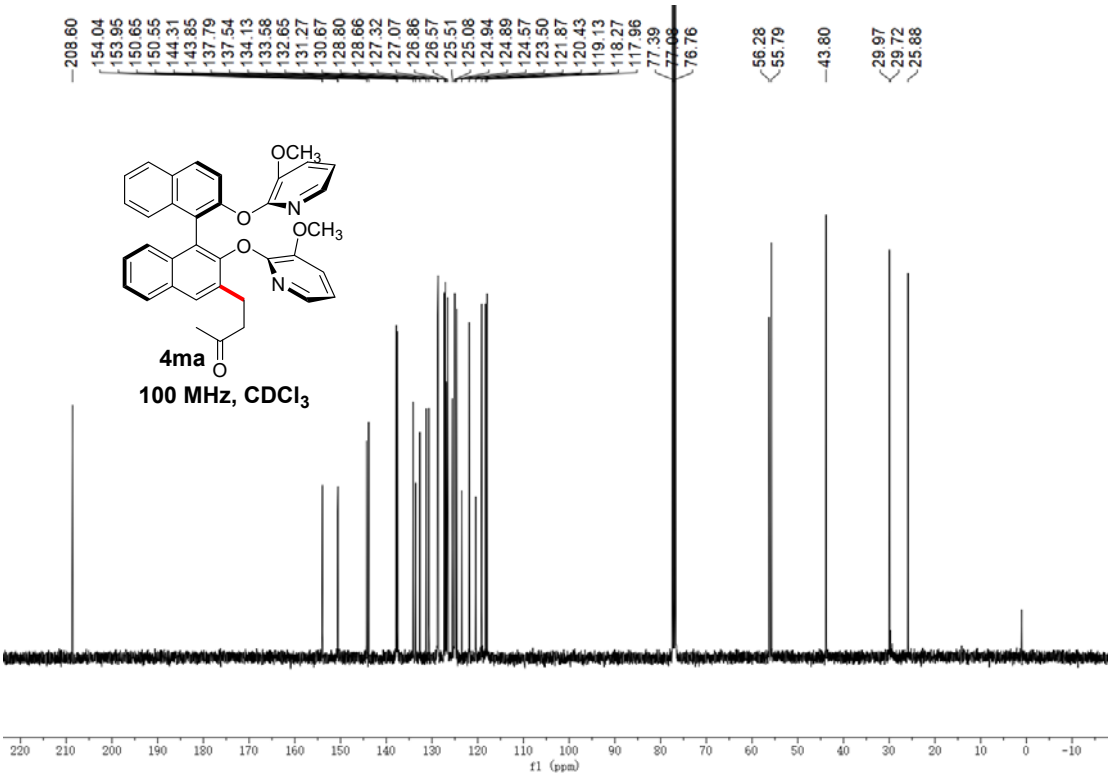

4la
400 MHz, CDCl3
f1 (ppm)

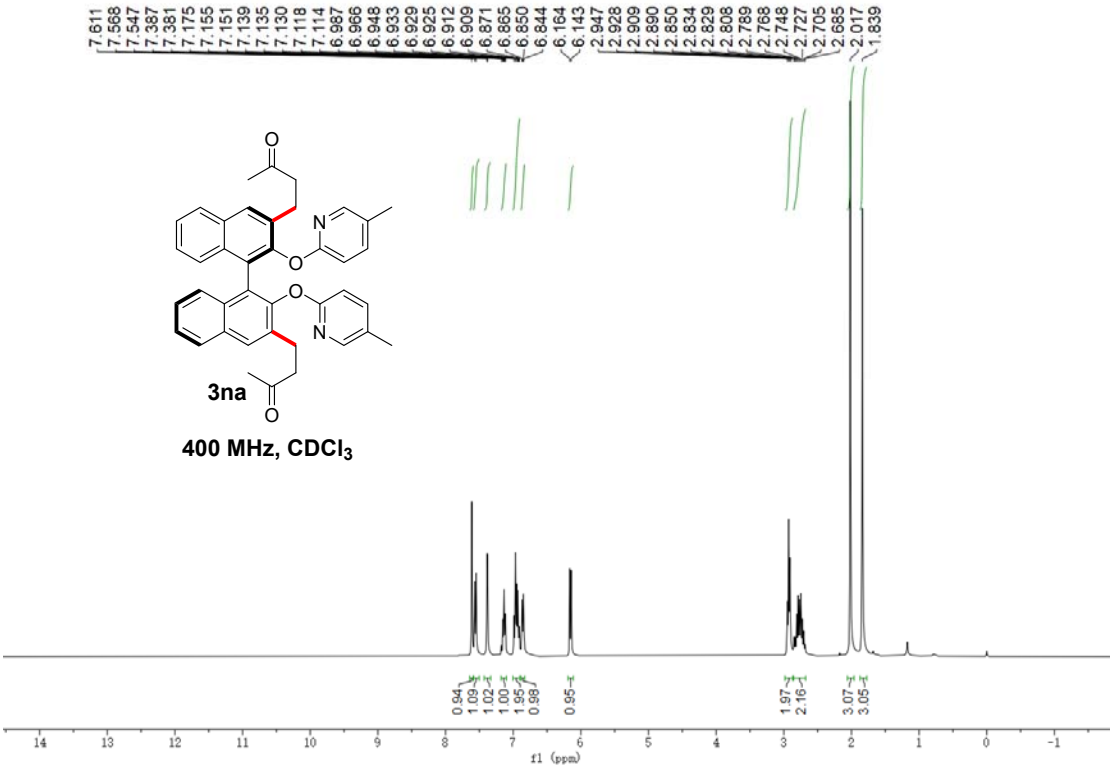

4la
100 MHz, CDCl3
f1 (ppm)

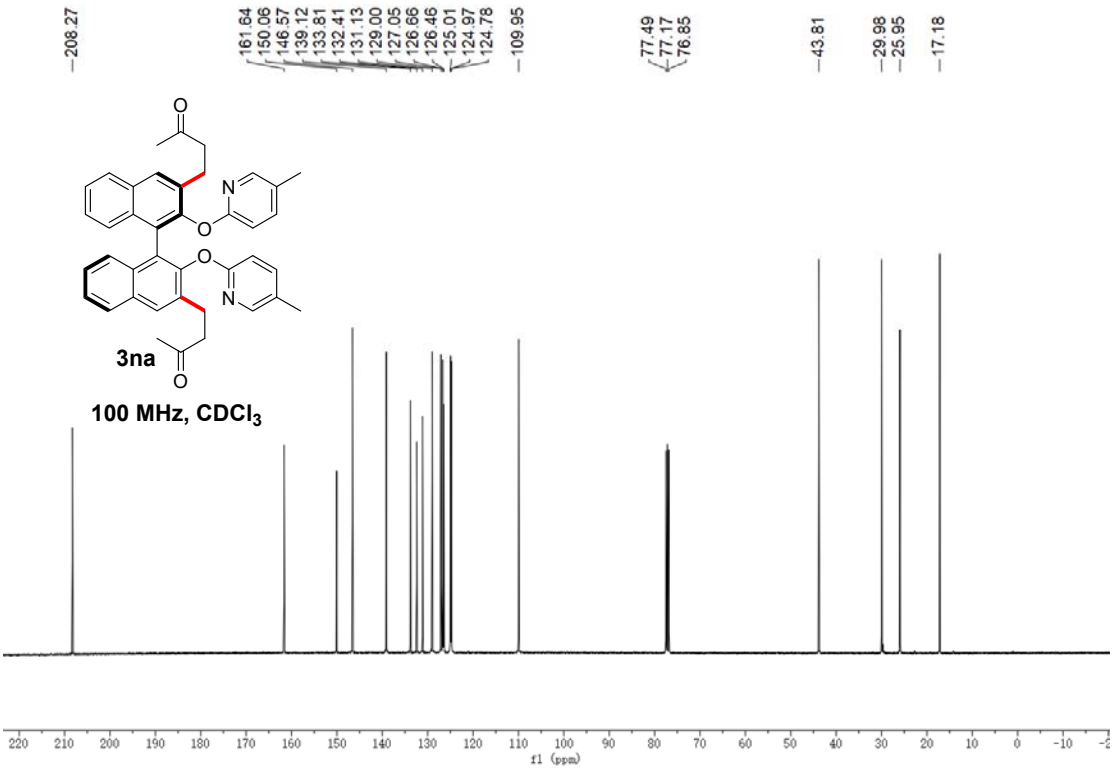

7.682
7.637
7.616
7.260
7.210
7.201
7.197
7.191
7.186
7.173
7.170
7.080
7.059
6.988
6.985
6.971
6.968
6.964
6.949
6.594
6.591
6.575
6.571
6.407
6.395
6.388
6.376
3.499
3.101
3.088
3.073
3.066
3.056
3.048
3.034
3.026
3.013
3.000
2.984
2.970
2.960
2.946
2.860
2.843
2.838
2.820
2.803
2.794
2.779
2.110
OCH3
OCH3
3ma
400 MHz, CDCl3
1.08
1.05
2.04
1.07
1.03
1.01
0.99
3.07
3.25
1.07
3.05
f1 (ppm)

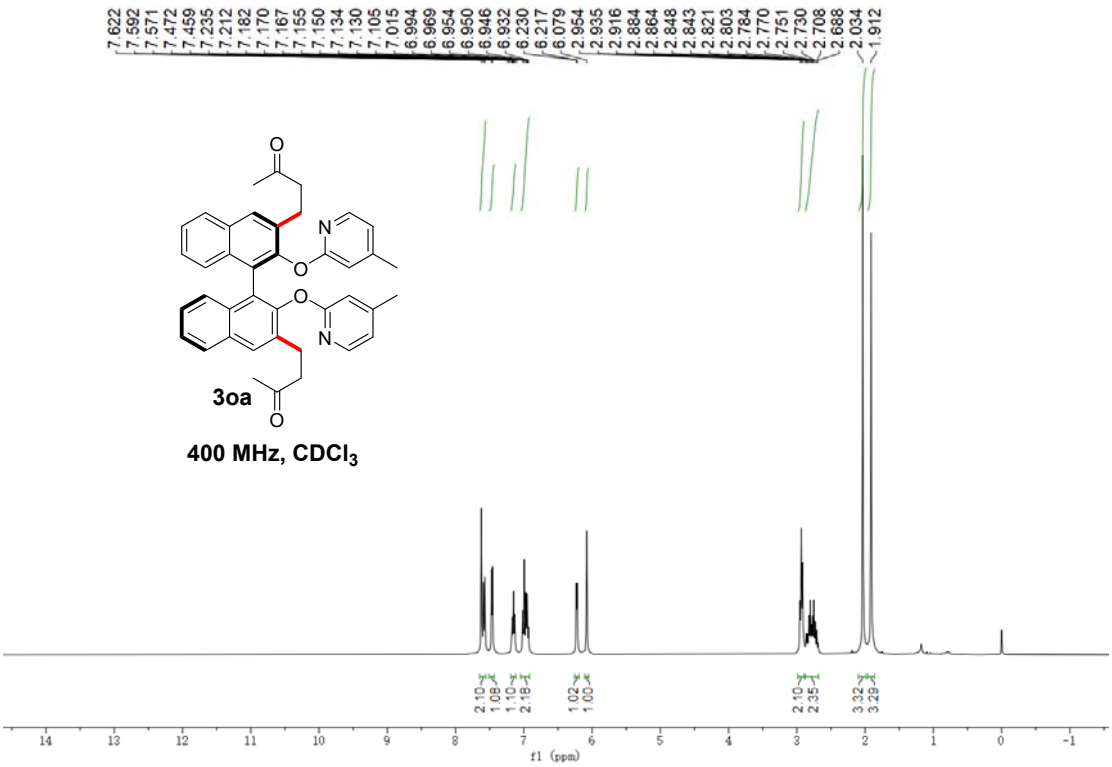

208.53
153.89
150.60
143.72
137.54
134.05
132.26
131.02
128.41
126.82
124.76
124.73
124.72
119.15
117.88
77.43
77.11
76.79
55.83
43.80
29.94
25.68
OCH3
OCH3
3ma
100 MHz, CDCl3
f1 (ppm)

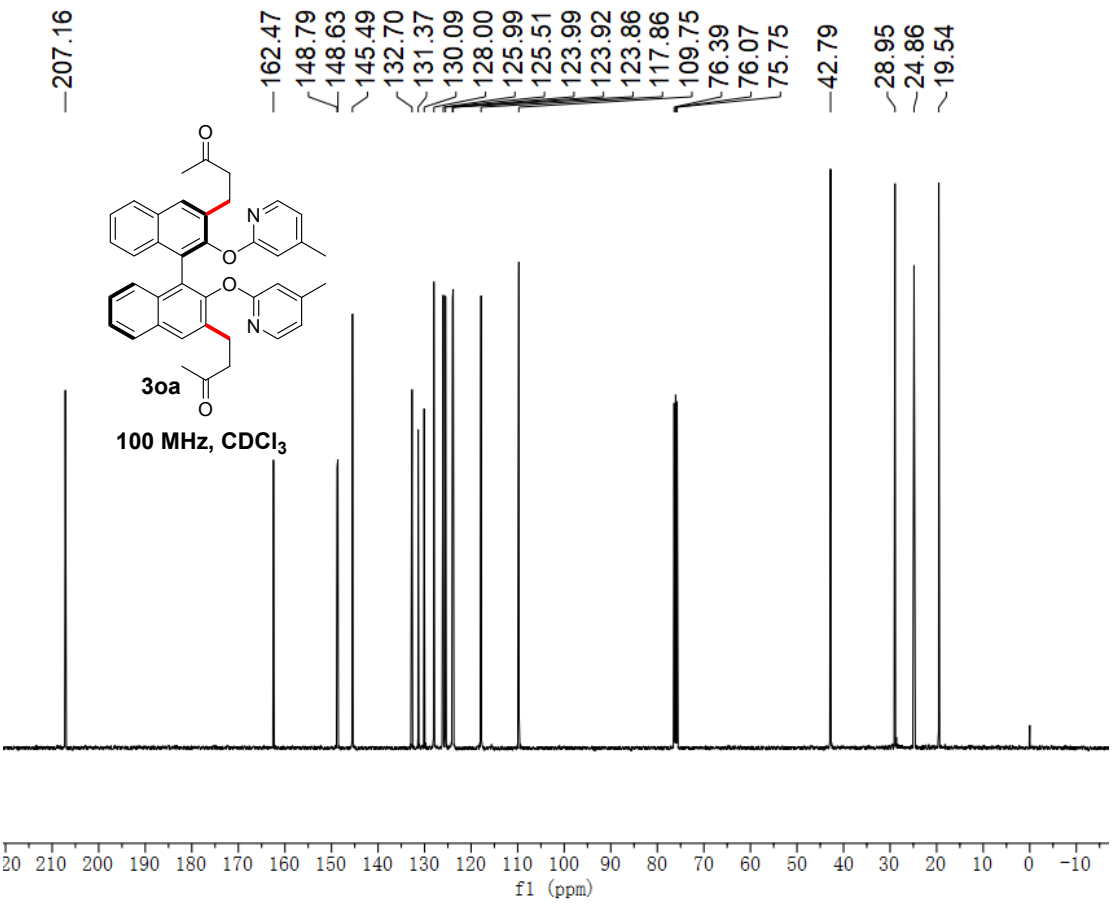

4ma
400 MHz, CDCl3
f1 (ppm)

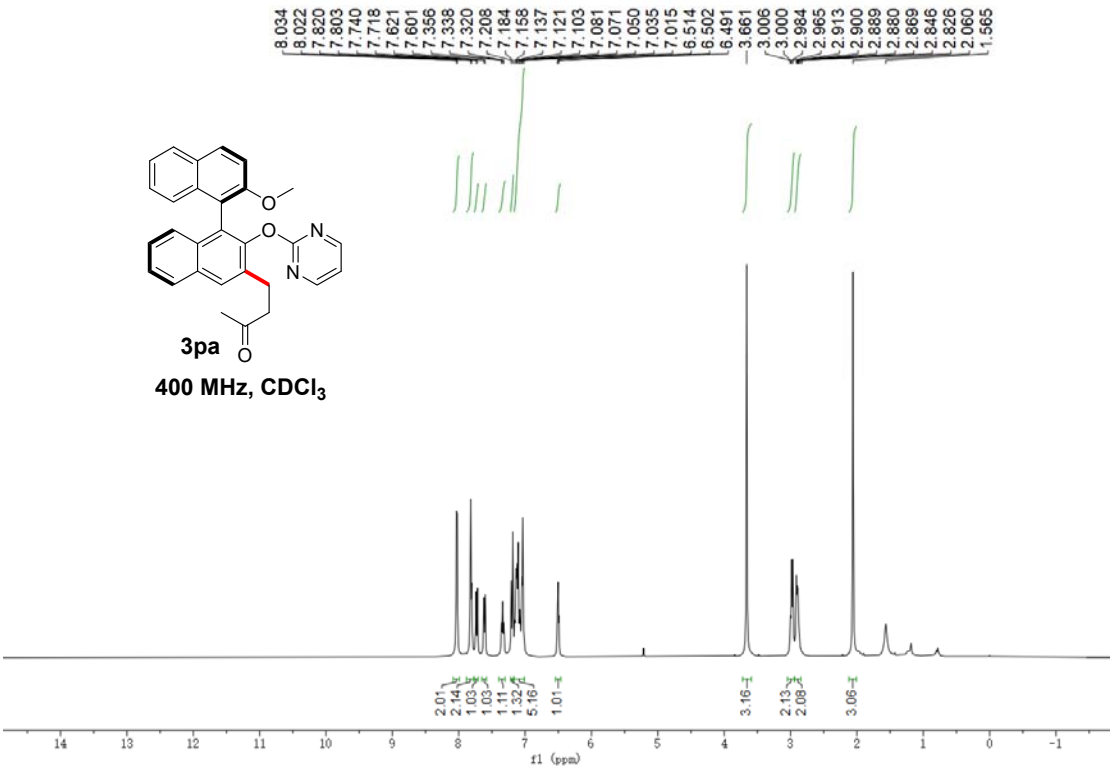

4ma
100 MHz, CDCl3
f1 (ppm)

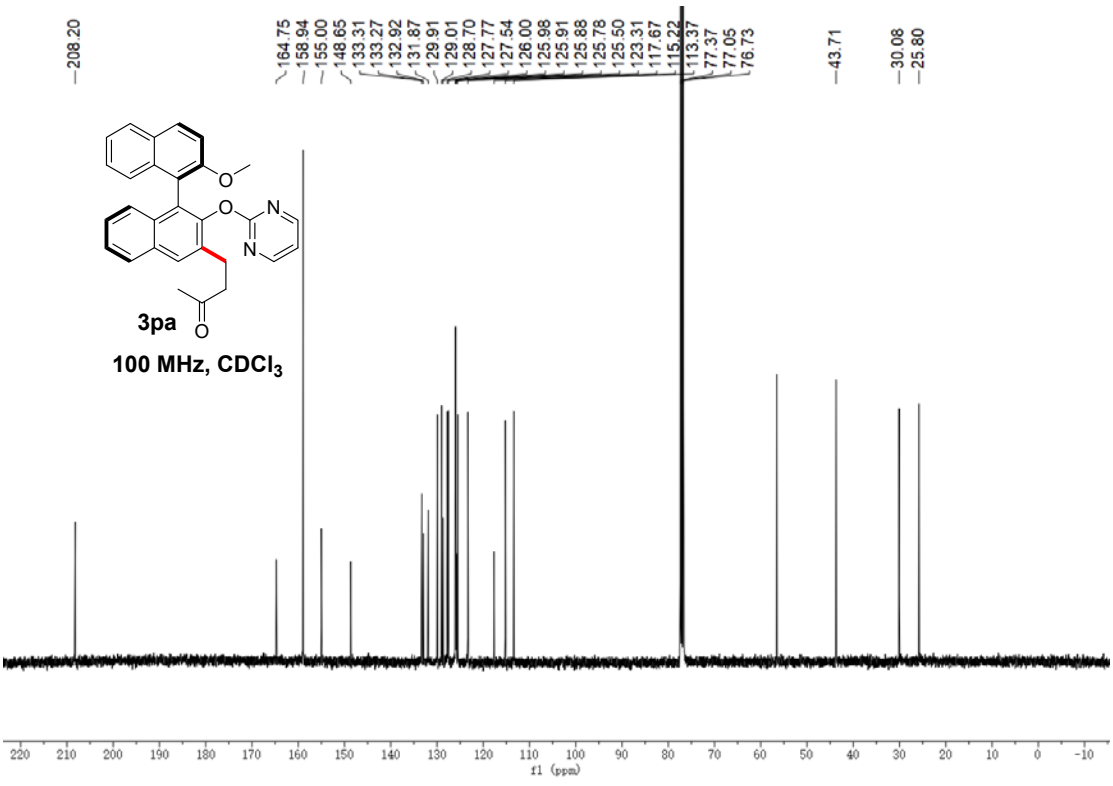

7.611
7.568
7.547
7.387
7.381
7.175
7.155
7.151
7.139
7.135
7.130
7.118
7.114
6.987
6.966
6.948
6.933
6.929
6.925
6.912
6.909
6.871
6.865
6.850
6.844
6.164
6.143
2.947
2.928
2.909
2.890
2.850
2.834
2.829
2.808
2.789
2.768
2.748
2.727
2.705
2.685
2.017
1.839
3na
400 MHz, CDCl3
f1 (ppm)

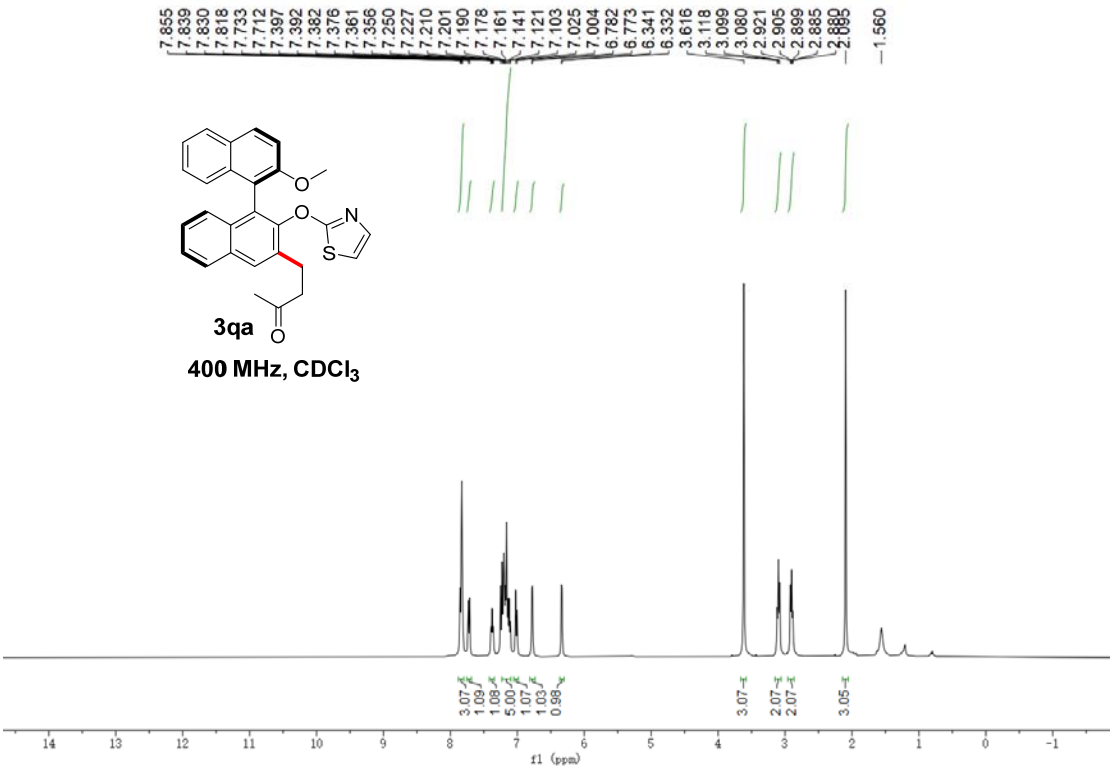

208.27
161.64
150.06
146.57
139.12
133.81
132.41
131.13
129.00
127.05
126.66
126.46
125.01
124.97
124.78
109.95
77.49
77.17
76.85
43.81
29.98
25.95
17.18
3na
100 MHz, CDCl3
f1 (ppm)

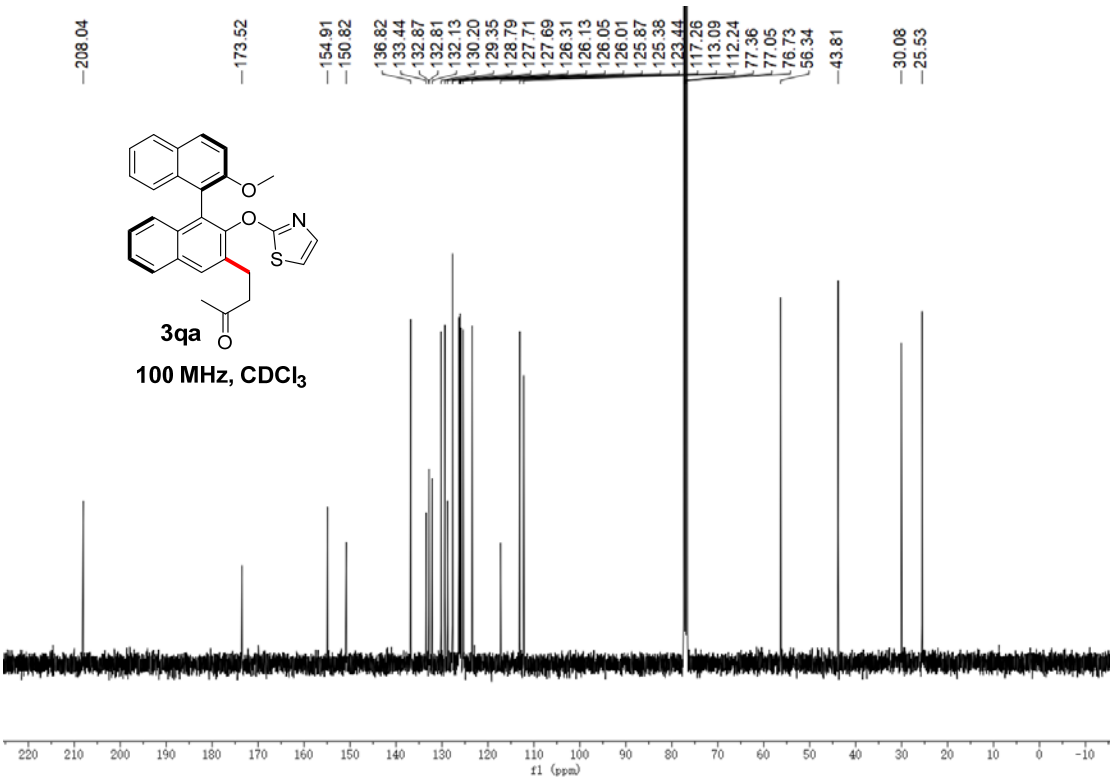

7.622
7.592
7.571
7.472
7.459
7.235
7.212
7.182
7.170
7.167
7.155
7.150
7.134
7.130
7.105
7.015
6.994
6.969
6.954
6.950
6.946
6.932
6.230
6.217
6.079
2.954
2.935
2.916
2.884
2.864
2.848
2.843
2.821
2.803
2.784
2.770
2.751
2.730
2.708
2.688
2.034
1.912
O
N
O
O
N
O
3oa
400 MHz, CDCl3
2.10
1.08
1.10
2.18
1.02
1.00
2.10
2.35
3.32
3.29
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

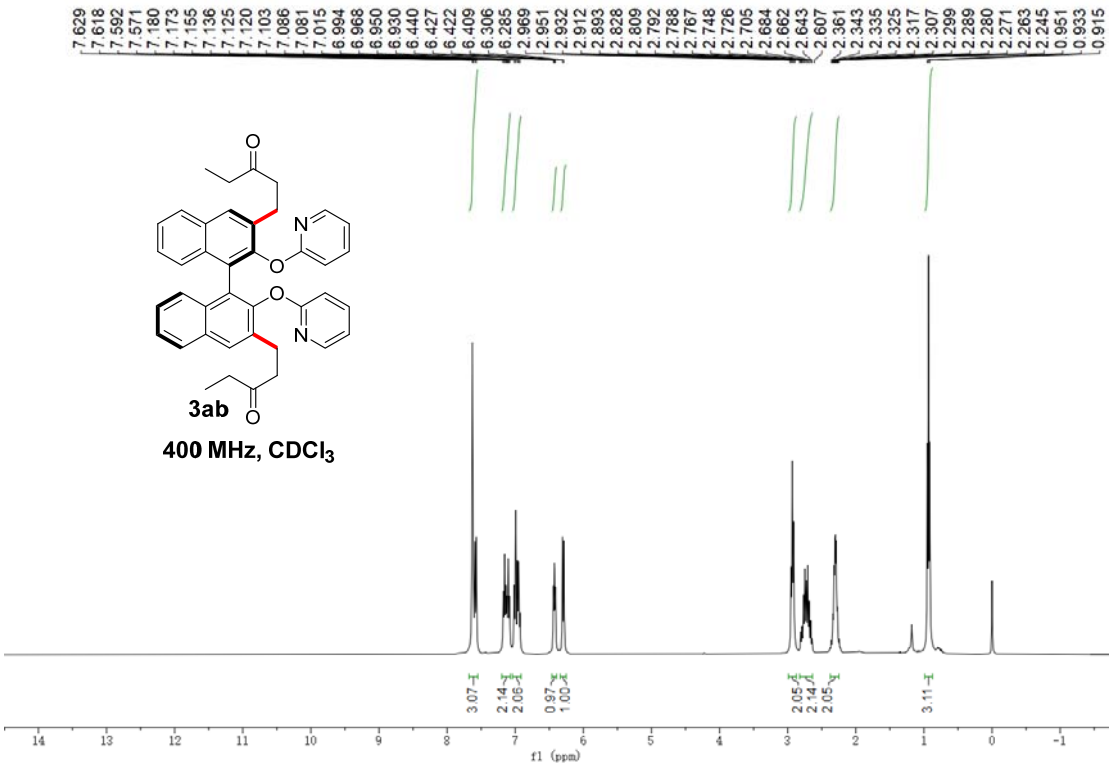

207.16
162.47
148.79
148.63
145.49
132.70
131.37
130.09
128.00
125.99
125.51
123.99
123.92
123.86
117.86
109.75
76.39
76.07
75.75
42.79
28.95
24.86
19.54
O
N
O
O
N
O
3oa
100 MHz, CDCl3
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

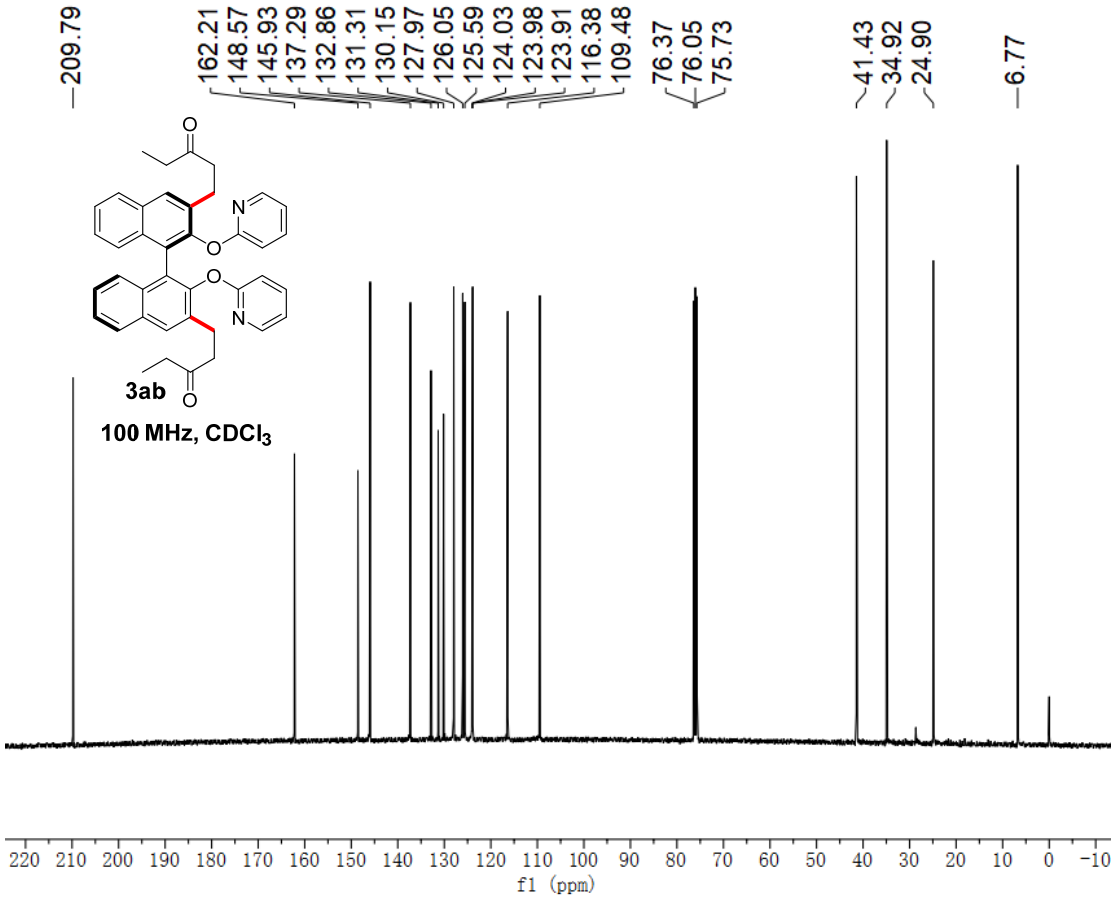

8.034
8.022
7.820
7.803
7.740
7.718
7.621
7.601
7.356
7.338
7.320
7.208
7.184
7.158
7.137
7.121
7.103
7.081
7.071
7.050
7.035
7.015
6.514
6.502
6.491
3.661
3.006
3.000
2.984
2.965
2.913
2.900
2.889
2.880
2.869
2.846
2.826
2.060
1.565
3pa
400 MHz, CDCl3
f1 (ppm)

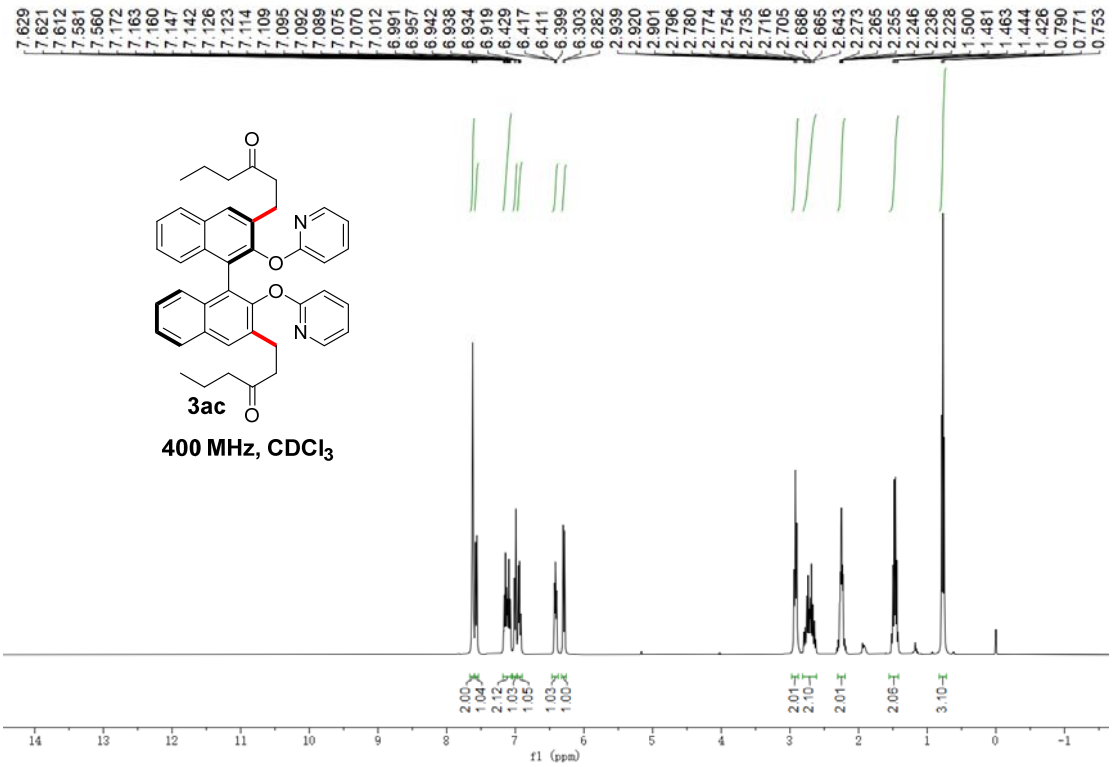

208.20
164.75
158.94
155.00
148.65
133.31
133.27
132.92
131.87
129.91
129.01
128.70
127.77
127.54
126.00
125.98
125.91
125.88
125.78
125.50
123.31
117.67
115.22
113.37
77.37
77.05
76.73
43.71
30.08
25.80
3pa
100 MHz, CDCl3
f1 (ppm)

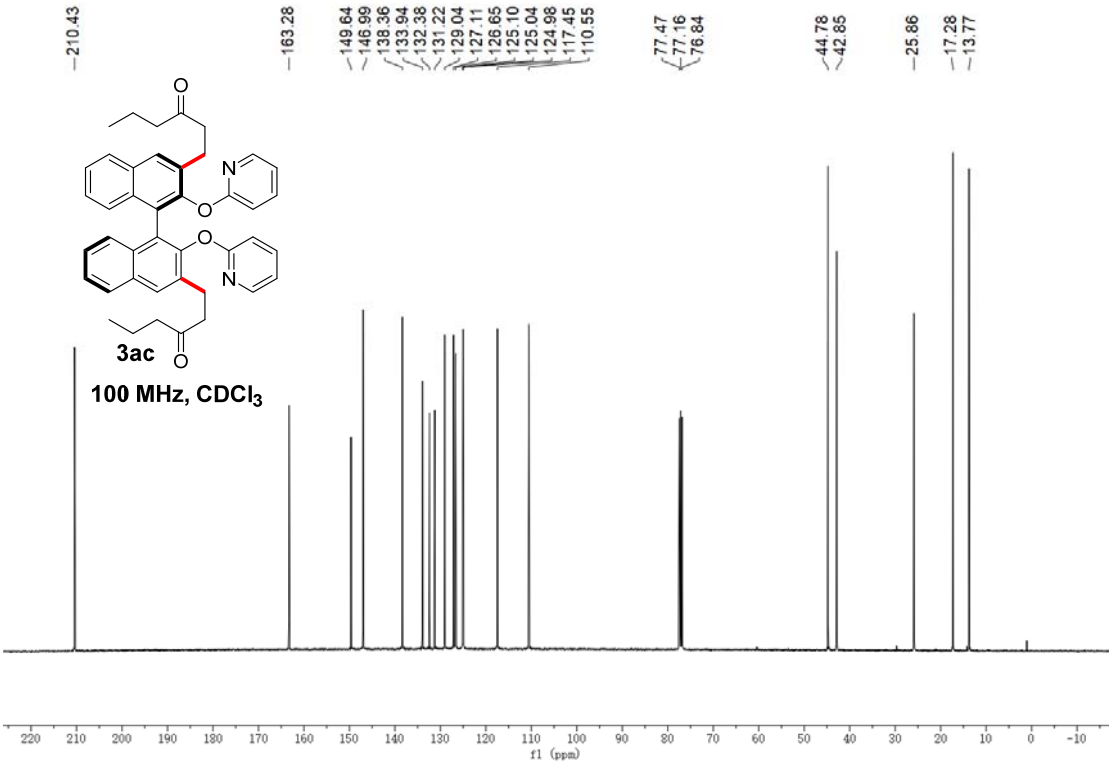

7.855
7.839
7.830
7.818
7.733
7.712
7.397
7.392
7.382
7.376
7.361
7.356
7.250
7.227
7.210
7.201
7.190
7.178
7.161
7.141
7.121
7.103
7.025
7.004
6.782
6.773
6.341
6.332
3.616
3.118
3.099
3.080
2.921
2.905
2.899
2.885
2.880
2.095
1.560
3qa
400 MHz, CDCl3
f1 (ppm)

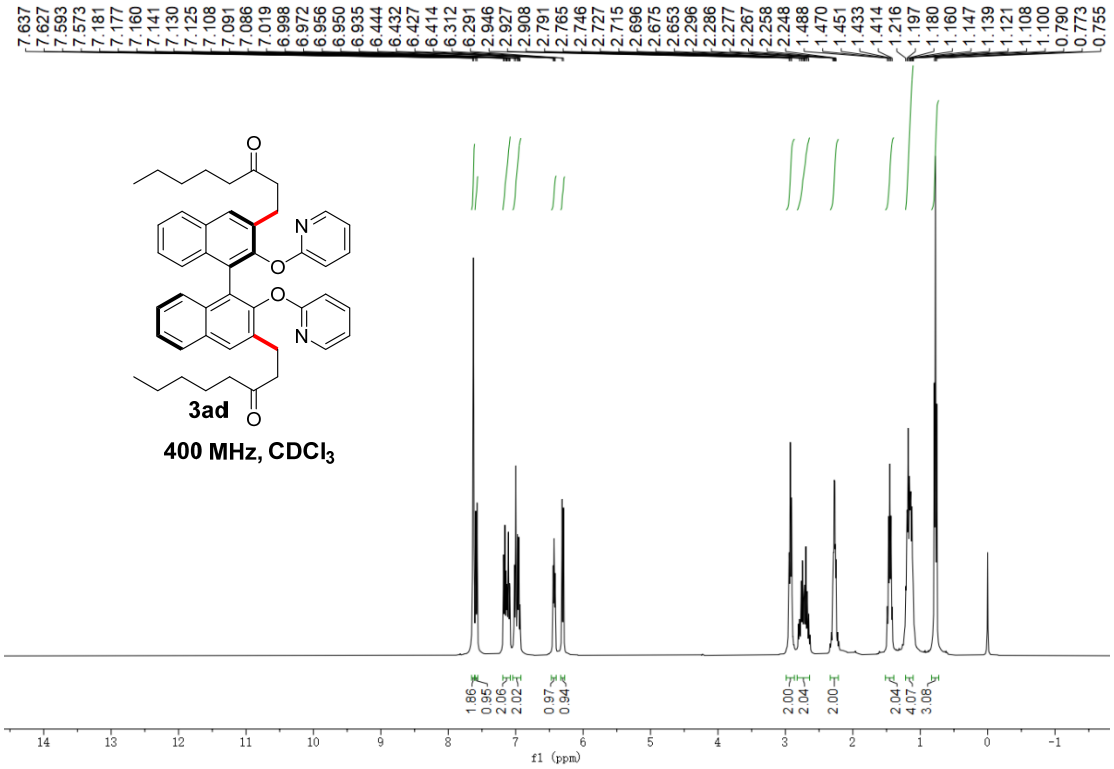

208.04
173.52
154.91
150.82
136.82
133.44
132.87
132.81
132.13
130.20
129.35
128.79
127.71
127.69
126.31
126.13
126.05
126.01
125.87
125.38
123.44
117.26
113.09
112.24
77.36
77.05
76.73
56.34
43.81
30.08
25.53
3qa
100 MHz, CDCl3
f1 (ppm)

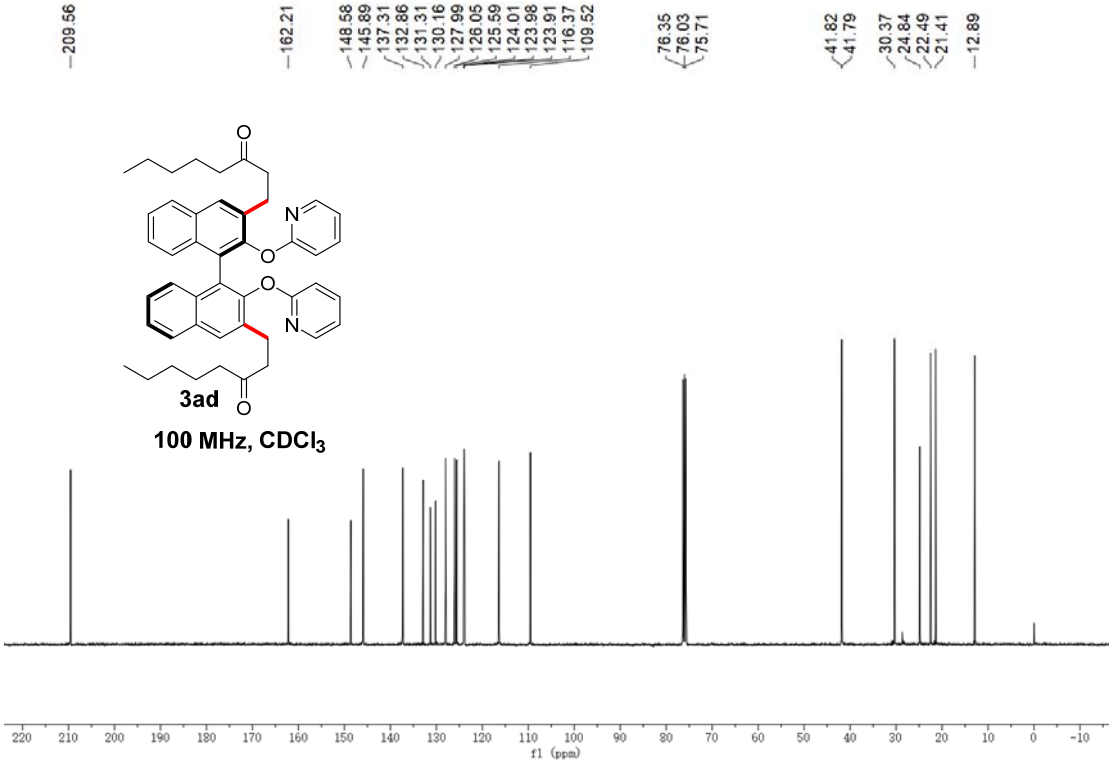

7.629
7.618
7.592
7.571
7.180
7.173
7.155
7.136
7.125
7.120
7.103
7.086
7.081
7.015
6.994
6.968
6.950
6.930
6.440
6.427
6.422
6.409
6.306
6.285
2.969
2.951
2.932
2.912
2.893
2.828
2.809
2.792
2.788
2.767
2.748
2.726
2.705
2.684
2.662
2.643
2.607
2.361
2.343
2.335
2.325
2.317
2.307
2.299
2.289
2.280
2.271
2.263
2.245
0.951
0.933
0.915
3ab
400 MHz, CDCl3
3.07
2.14
2.06
0.97
1.00
2.05
2.14
2.05
3.11
f1 (ppm)

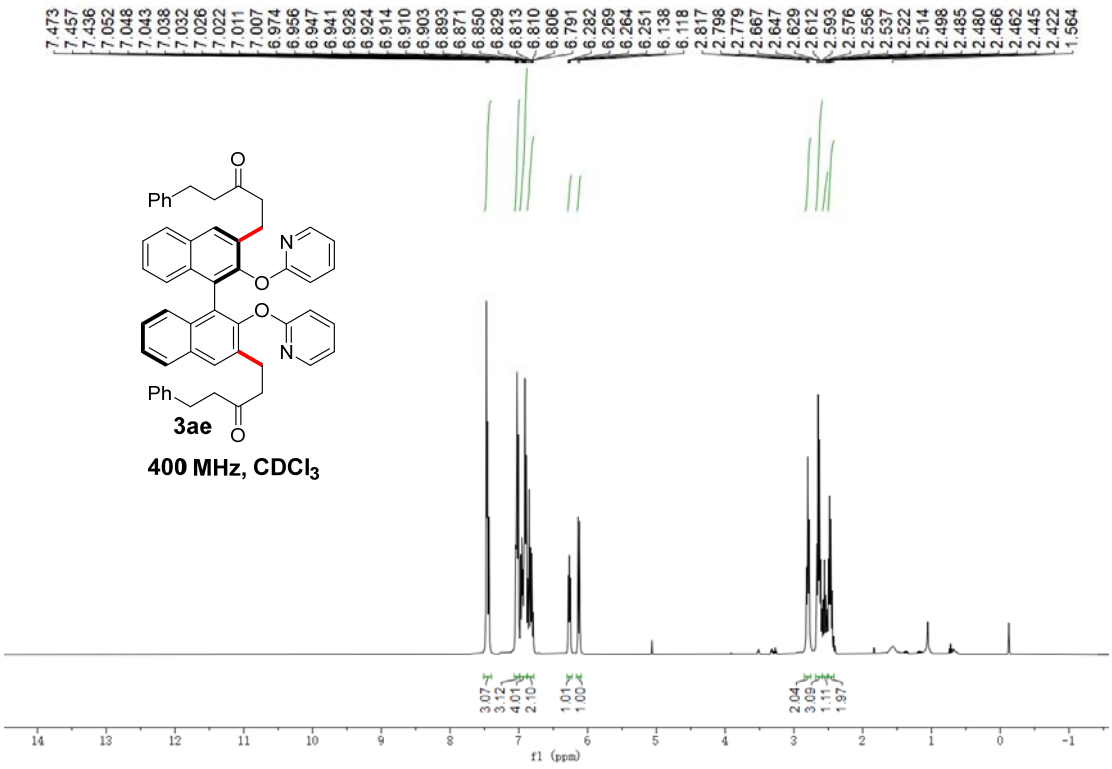

209.79
162.21
148.57
145.93
137.29
132.86
131.31
130.15
127.97
126.05
125.59
124.03
123.98
123.91
116.38
109.48
76.37
76.05
75.73
41.43
34.92
24.90
6.77
3ab
100 MHz, CDCl3
f1 (ppm)

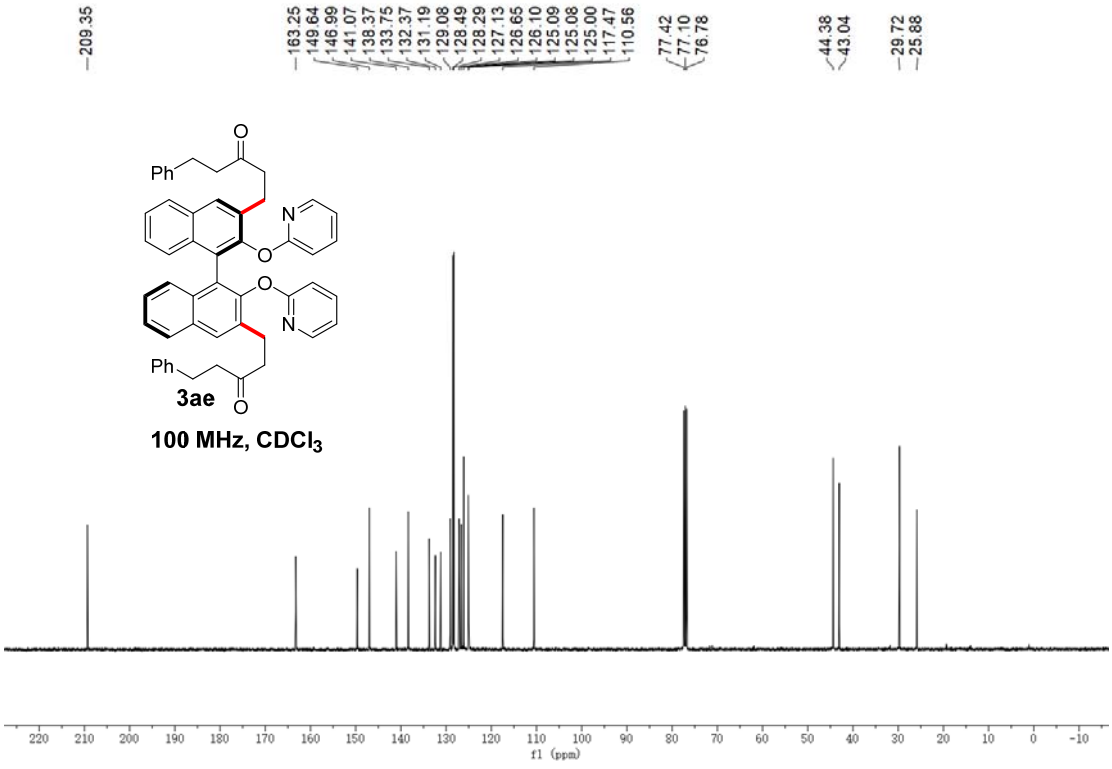

7.629
7.621
7.612
7.581
7.560
7.172
7.163
7.160
7.147
7.142
7.126
7.123
7.114
7.109
7.095
7.092
7.089
7.075
7.070
7.012
6.991
6.957
6.942
6.938
6.934
6.919
6.429
6.417
6.411
6.399
6.303
6.282
2.939
2.920
2.901
2.796
2.780
2.774
2.754
2.735
2.716
2.705
2.686
2.665
2.643
2.273
2.265
2.255
2.246
2.236
2.228
1.500
1.481
1.463
1.444
1.426
0.790
0.771
0.753
3ac
400 MHz, CDCl3
f1 (ppm)

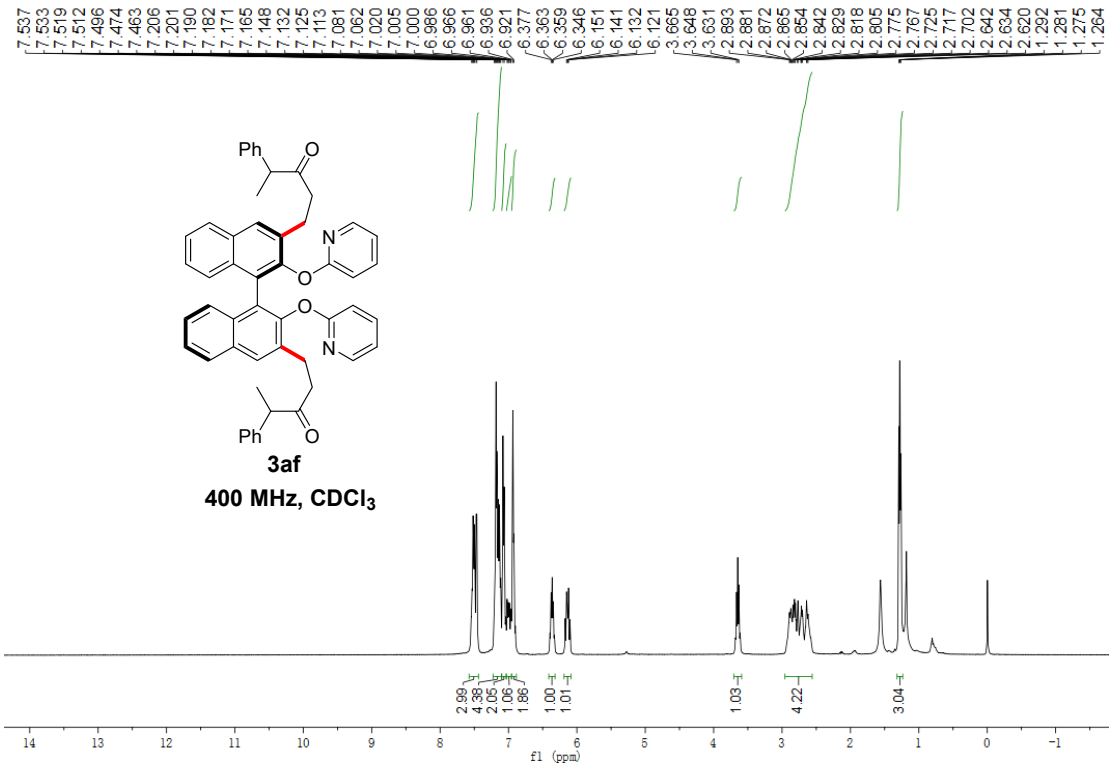

210.43
163.28
149.64
146.99
138.36
133.94
132.38
131.22
129.04
127.11
126.65
125.10
125.04
124.98
117.45
110.55
77.47
77.16
76.84
44.78
42.85
25.86
17.28
13.77
3ac
100 MHz, CDCl3
f1 (ppm)

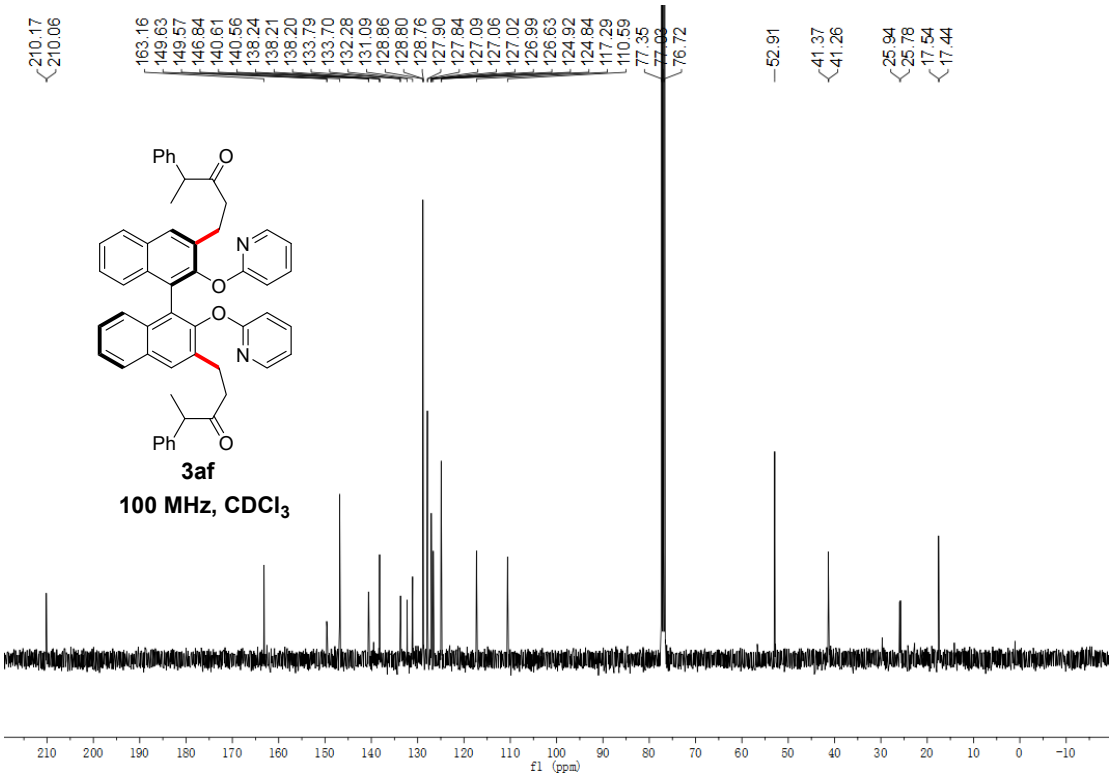

7.637
7.627
7.593
7.573
7.181
7.177
7.160
7.141
7.130
7.125
7.108
7.091
7.086
7.019
6.998
6.972
6.956
6.950
6.935
6.444
6.432
6.427
6.414
6.312
6.291
2.946
2.927
2.908
2.791
2.765
2.746
2.727
2.715
2.696
2.675
2.653
2.296
2.286
2.277
2.267
2.258
2.248
1.488
1.470
1.451
1.433
1.414
1.216
1.197
1.180
1.160
1.147
1.139
1.121
1.108
1.100
0.790
0.773
0.755
3ad
400 MHz, CDCl3
1.86
0.95
2.06
2.02
0.97
0.94
2.00
2.04
2.00
2.04
4.07
3.08
f1 (ppm)

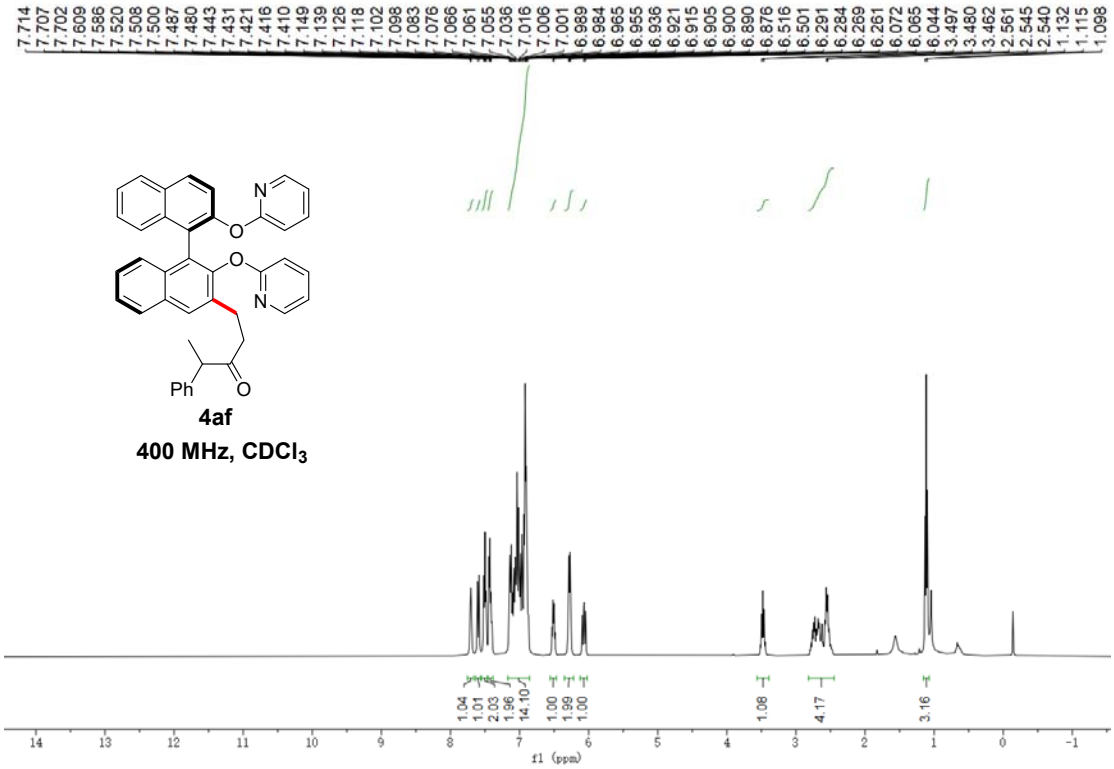

209.56
162.21
148.58
145.89
137.31
132.86
131.31
130.16
127.99
126.05
125.59
124.01
123.98
123.91
116.37
109.52
76.35
76.03
75.71
41.82
41.79
30.37
24.84
22.49
21.41
12.89
3ad
100 MHz, CDCl3
f1 (ppm)


7.473
7.457
7.436
7.052
7.048
7.043
7.038
7.032
7.026
7.022
7.011
7.007
6.974
6.956
6.947
6.941
6.928
6.924
6.914
6.910
6.903
6.893
6.871
6.850
6.829
6.813
6.810
6.806
6.791
6.282
6.269
6.264
6.251
6.138
6.118
2.817
2.798
2.779
2.667
2.647
2.629
2.612
2.593
2.576
2.556
2.537
2.522
2.514
2.498
2.485
2.480
2.466
2.462
2.445
2.422
1.564
Ph
N
O
O
N
Ph
O
3ae
400 MHz, CDCl3
3.07
3.12
4.01
2.10
1.01
1.00
2.04
3.09
1.11
1.97
f1 (ppm)


209.35
163.25
149.64
146.99
141.07
138.37
133.75
132.37
131.19
129.08
128.49
128.29
127.13
126.65
126.10
125.09
125.08
125.00
117.47
110.56
77.42
77.10
76.78
44.38
43.04
29.72
25.88
Ph
N
O
O
N
Ph
O
3ae
100 MHz, CDCl3
f1 (ppm)

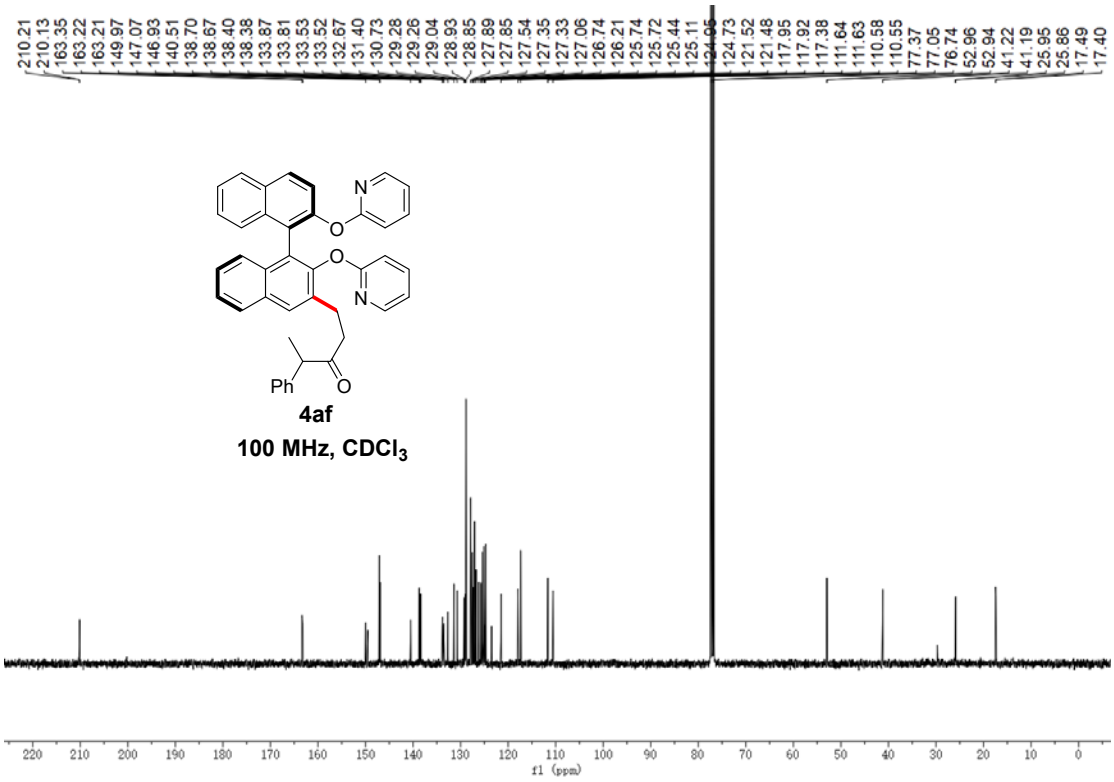

7.537
7.533
7.519
7.512
7.496
7.474
7.463
7.206
7.201
7.190
7.182
7.171
7.165
7.148
7.132
7.125
7.113
7.081
7.062
7.020
7.005
7.000
6.986
6.966
6.961
6.936
6.921
6.377
6.363
6.359
6.346
6.151
6.141
6.132
6.121
3.665
3.648
3.631
2.893
2.881
2.872
2.865
2.854
2.842
2.829
2.818
2.805
2.775
2.767
2.725
2.717
2.702
2.642
2.634
2.620
1.292
1.281
1.275
1.264
Ph
O
N
O
O
N
Ph
O
3af
400 MHz, CDCl3
2.99
4.38
2.05
1.06
1.86
1.00
1.01
1.03
4.22
3.04
f1 (ppm)


210.17
210.06
163.16
149.63
149.57
146.84
140.61
140.56
138.24
138.21
138.20
133.79
133.70
132.28
131.09
128.86
128.80
128.76
127.90
127.84
127.09
127.06
127.02
126.99
126.63
124.92
124.84
117.29
110.59
77.35
77.03
76.72
52.91
41.37
41.26
25.94
25.78
17.54
17.44
Ph
O
N
O
O
N
Ph
O
3af
100 MHz, CDCl3
f1 (ppm)



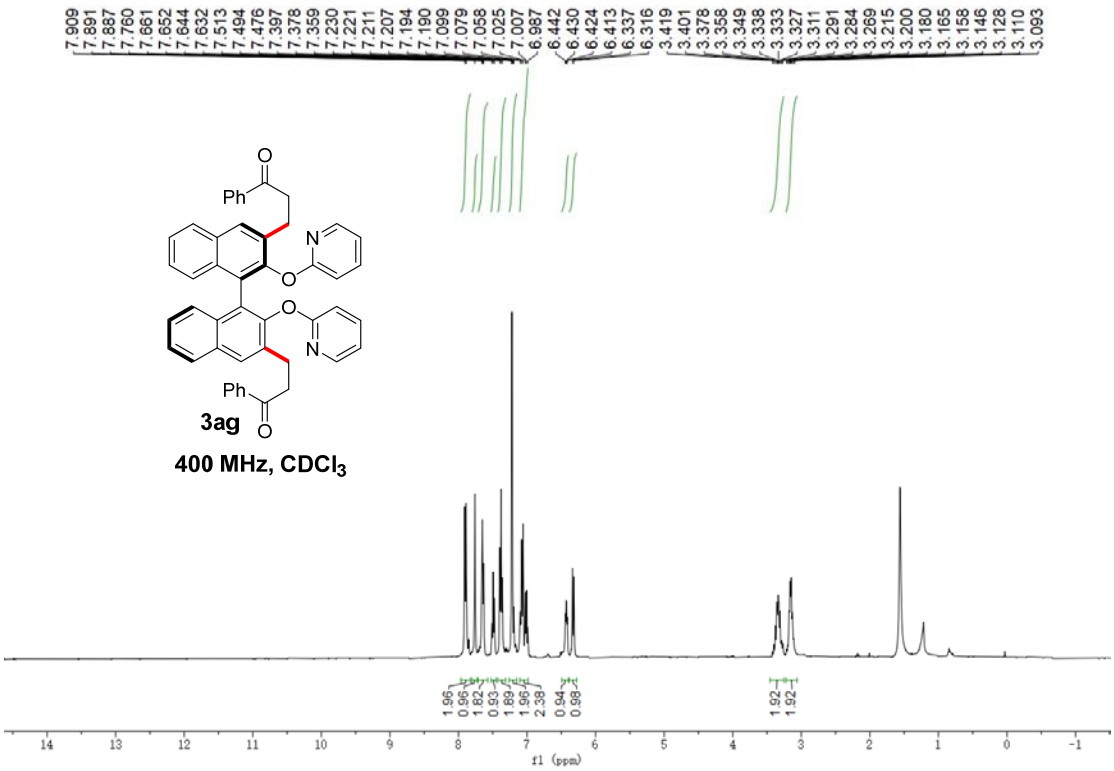
4af

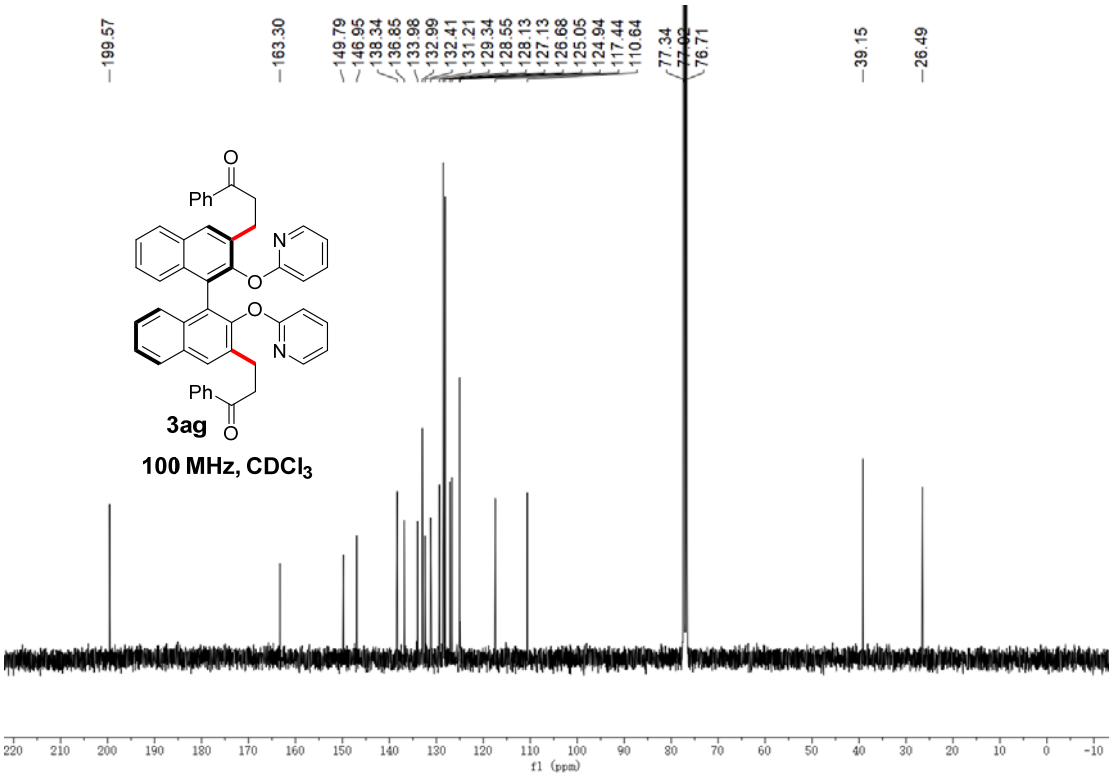
400 MHz, $CDCl_3$

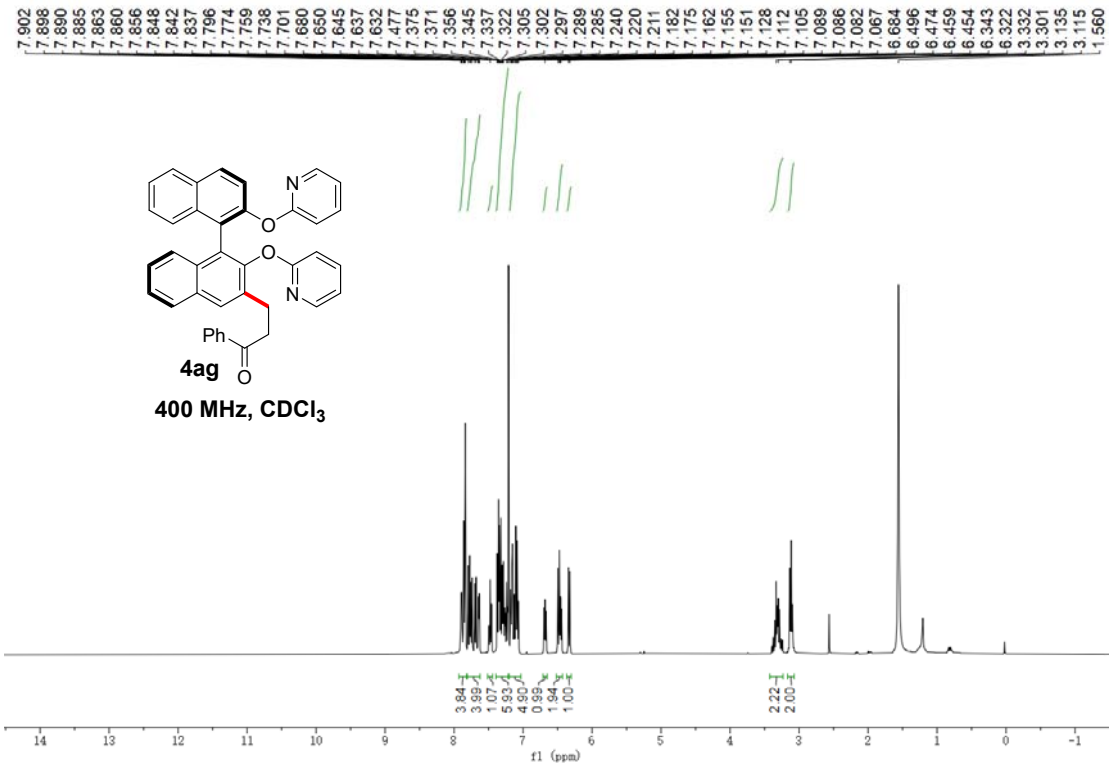


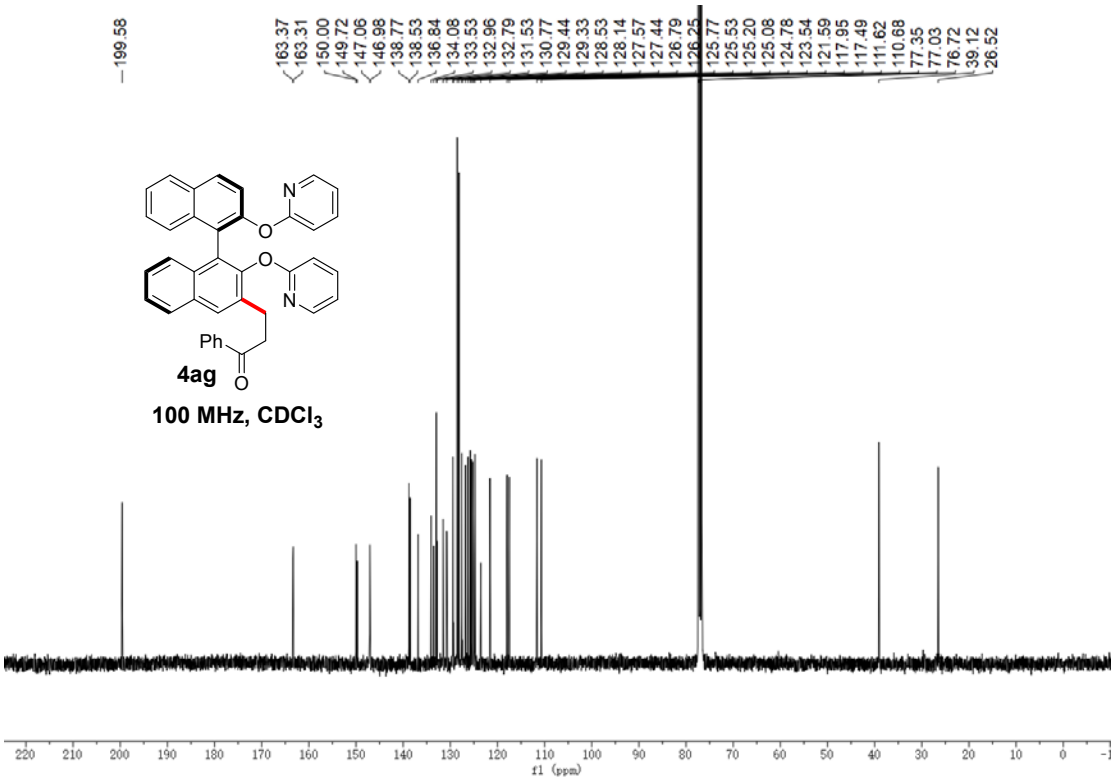
4af

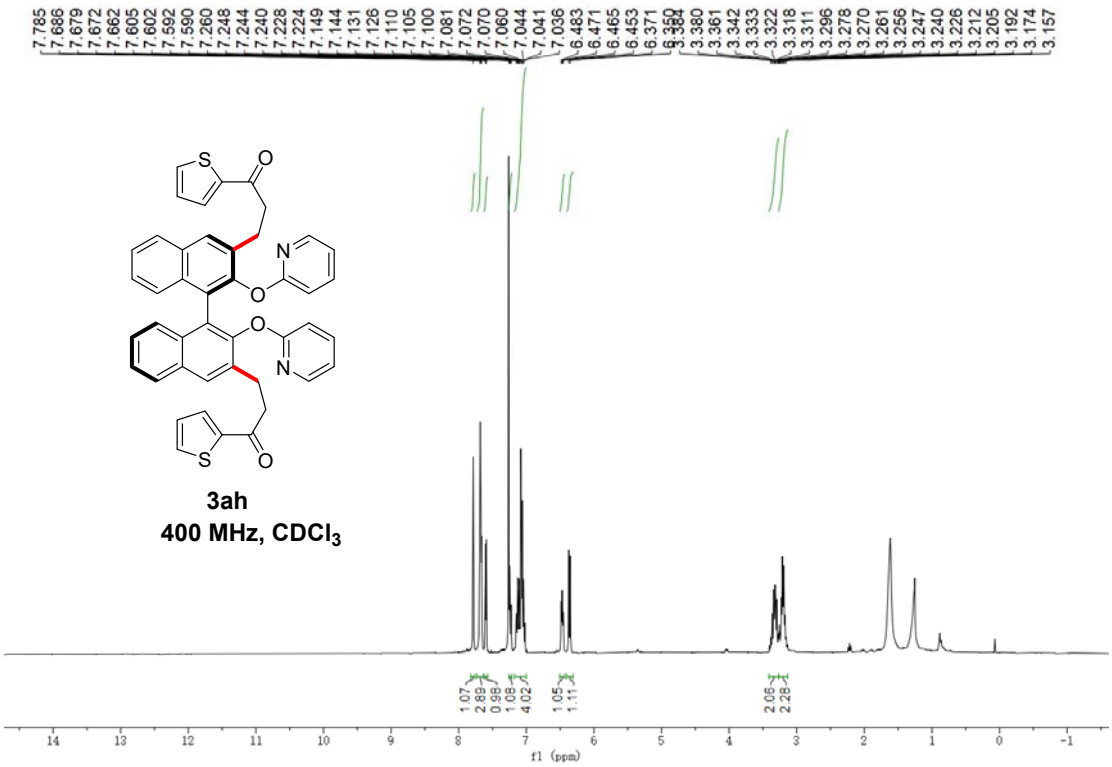
100 MHz, $CDCl_3$


7.909
7.891
7.887
7.760
7.661
7.652
7.644
7.632
7.513
7.494
7.476
7.397
7.378
7.359
7.230
7.221
7.211
7.207
7.194
7.190
7.099
7.079
7.058
7.025
7.007
6.987
6.442
6.430
6.424
6.413
6.337
6.316
3.419
3.401
3.378
3.358
3.349
3.338
3.333
3.327
3.311
3.291
3.284
3.269
3.215
3.200
3.180
3.165
3.158
3.146
3.128
3.110
3.093
Ph
O
N
O
O
N
Ph
O
3ag
400 MHz, CDCl3
1.96
0.96
1.82
0.93
1.89
1.96
2.38
0.94
0.98
1.92
1.92
f1 (ppm)

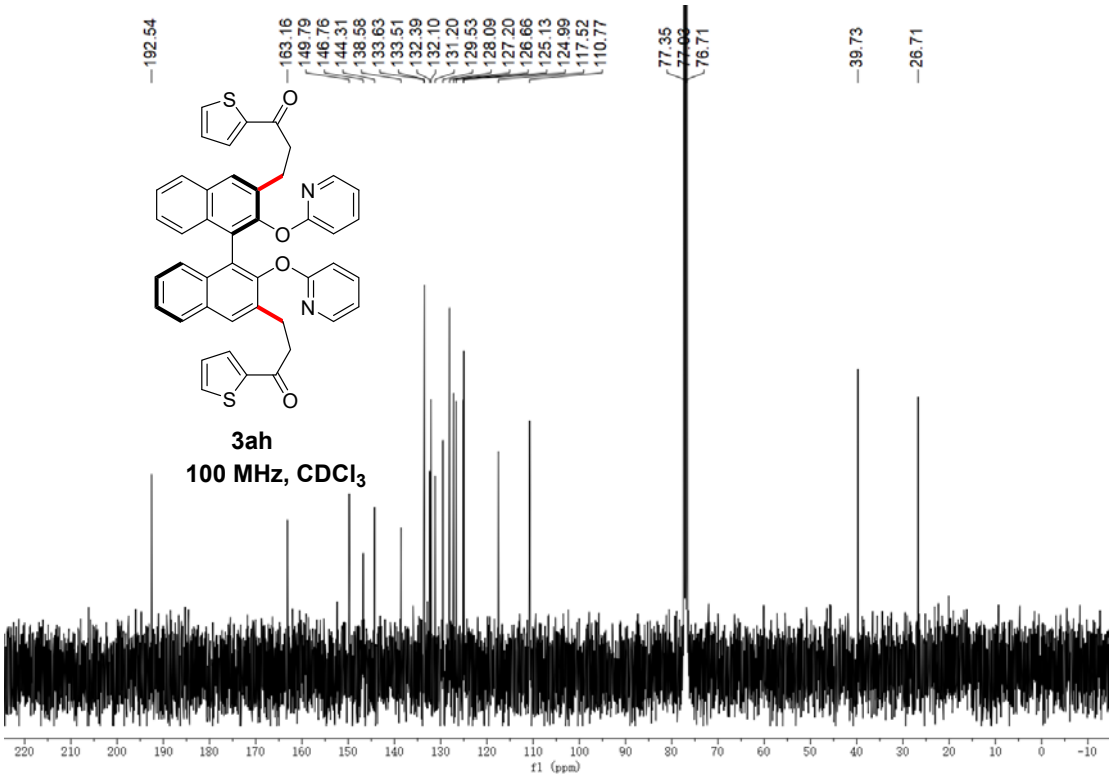

199.57
163.30
149.79
146.95
138.34
136.85
133.98
132.99
132.41
131.21
129.34
128.55
128.13
127.13
126.68
125.05
124.94
117.44
110.64
77.34
77.02
76.71
39.15
26.49
Ph
O
N
O
O
N
Ph
O
3ag
100 MHz, CDCl3
f1 (ppm)


4ag
400 MHz, CDCl3
f1 (ppm)

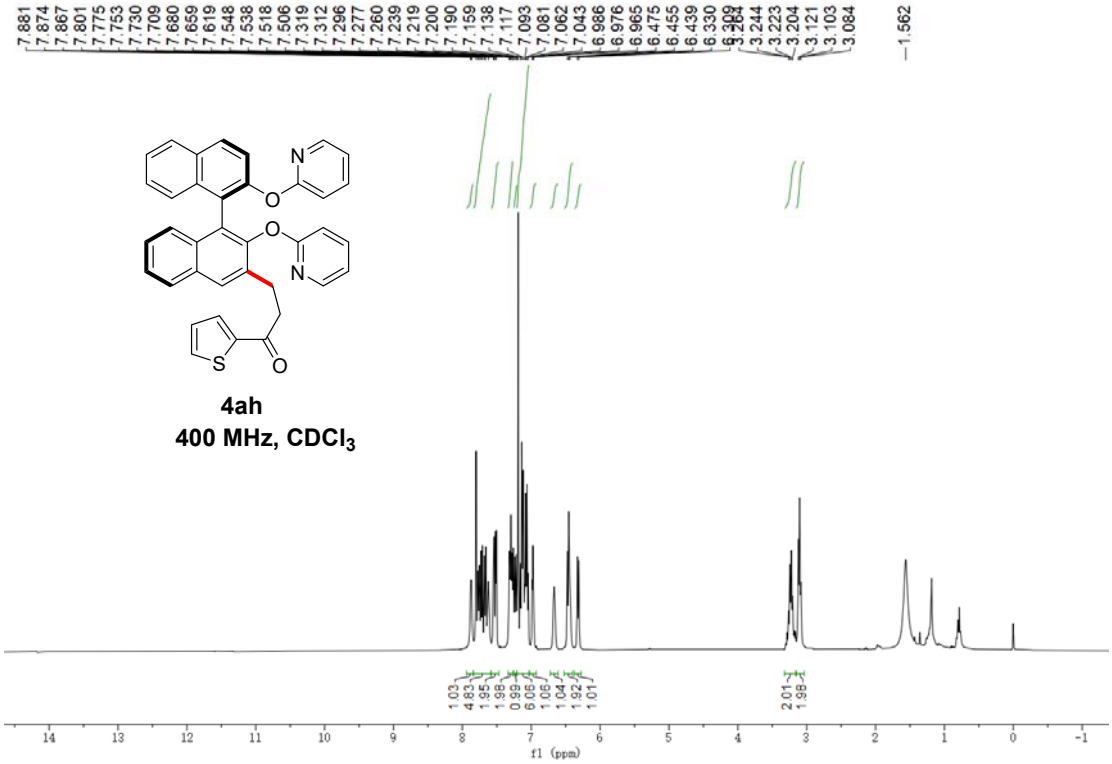

4ag
100 MHz, CDCl3
f1 (ppm)



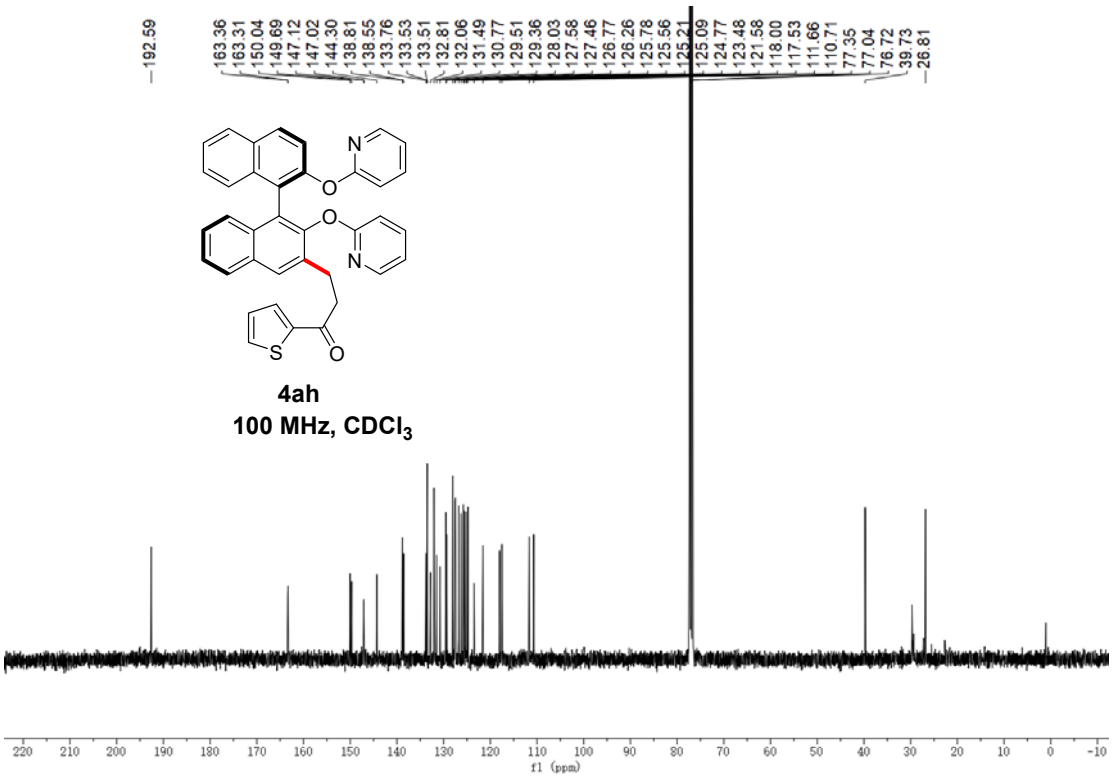
3ah
400 MHz, $CDCl_3$



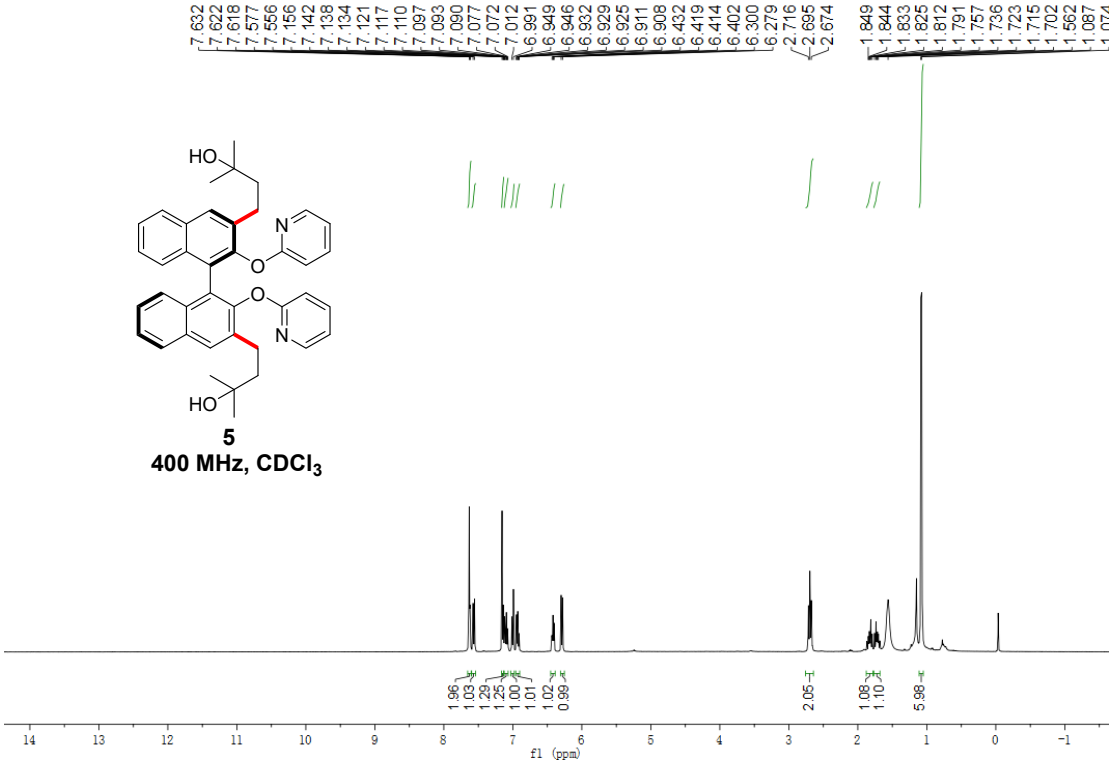
3ah
100 MHz, $CDCl_3$

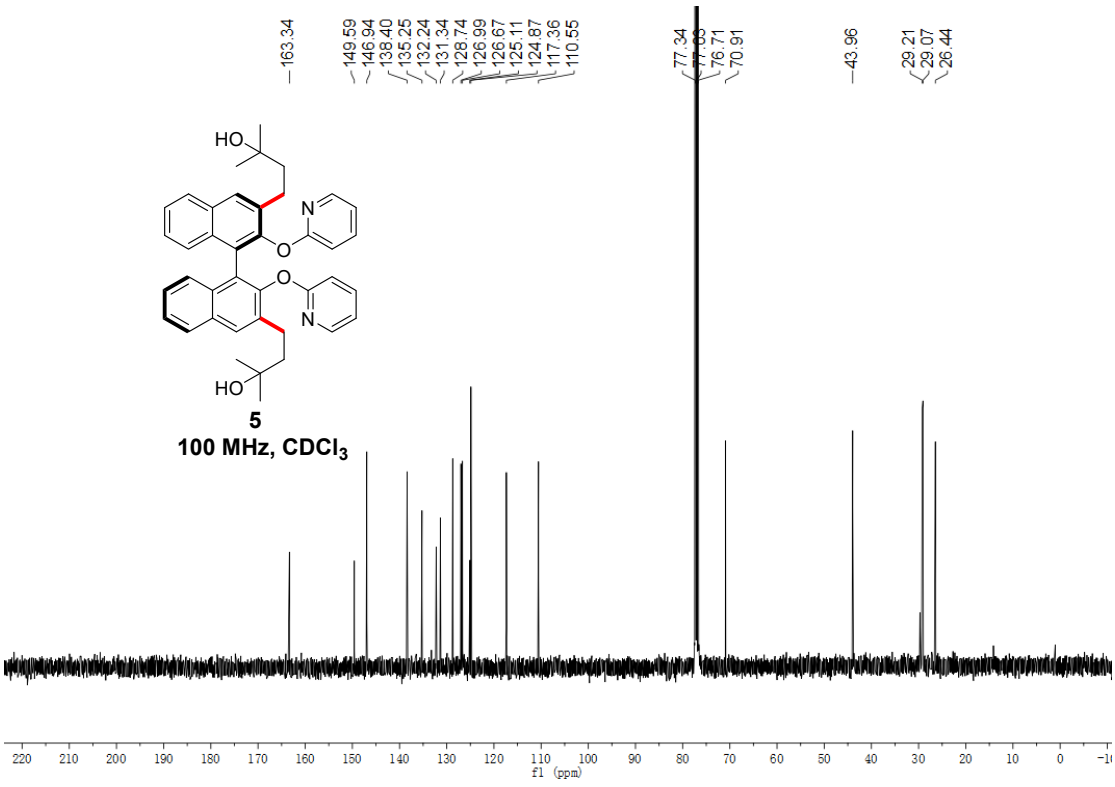


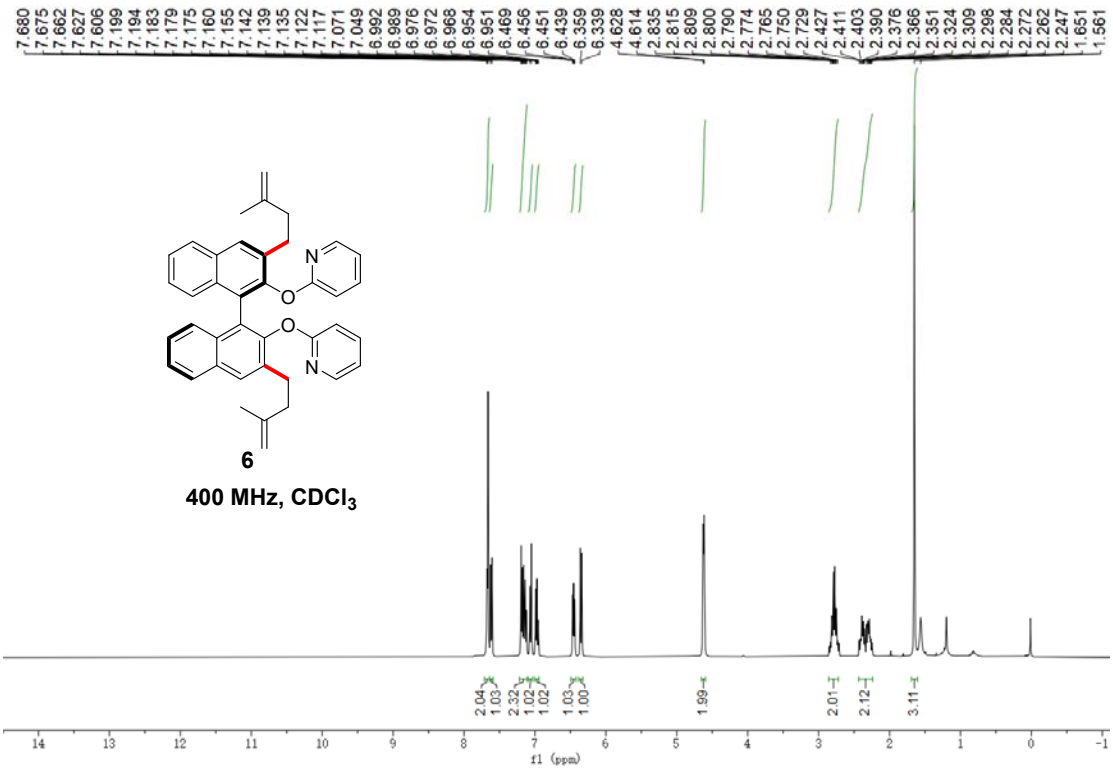
4ah
400 MHz, $CDCl_3$



4ah
100 MHz, $CDCl_3$

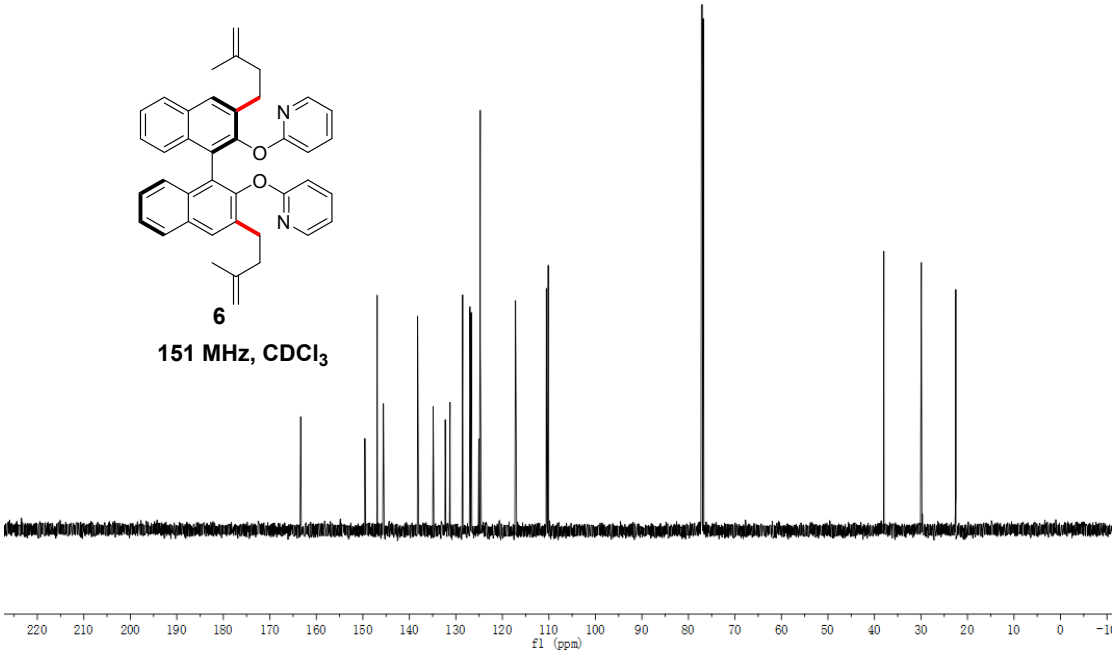

HO
N
O
O
N
HO
5
400 MHz, CDCl3
f1 (ppm)


HO
N
O
O
N
HO
5
100 MHz, CDCl3
f1 (ppm)



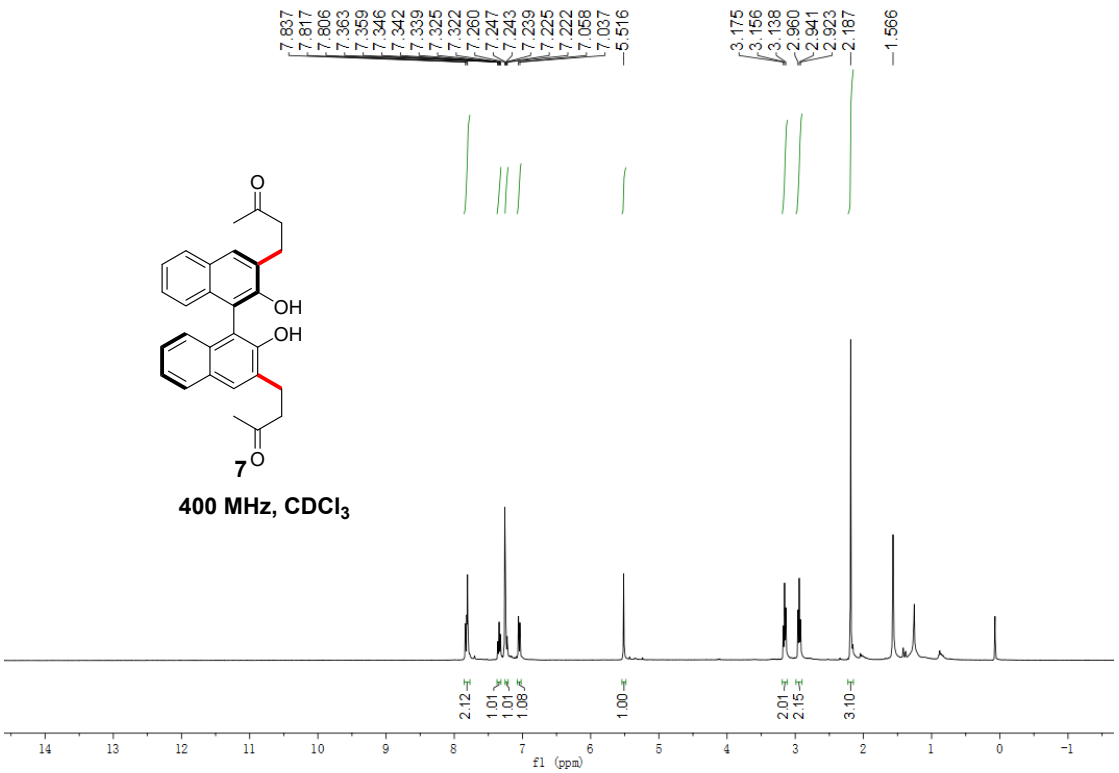
6

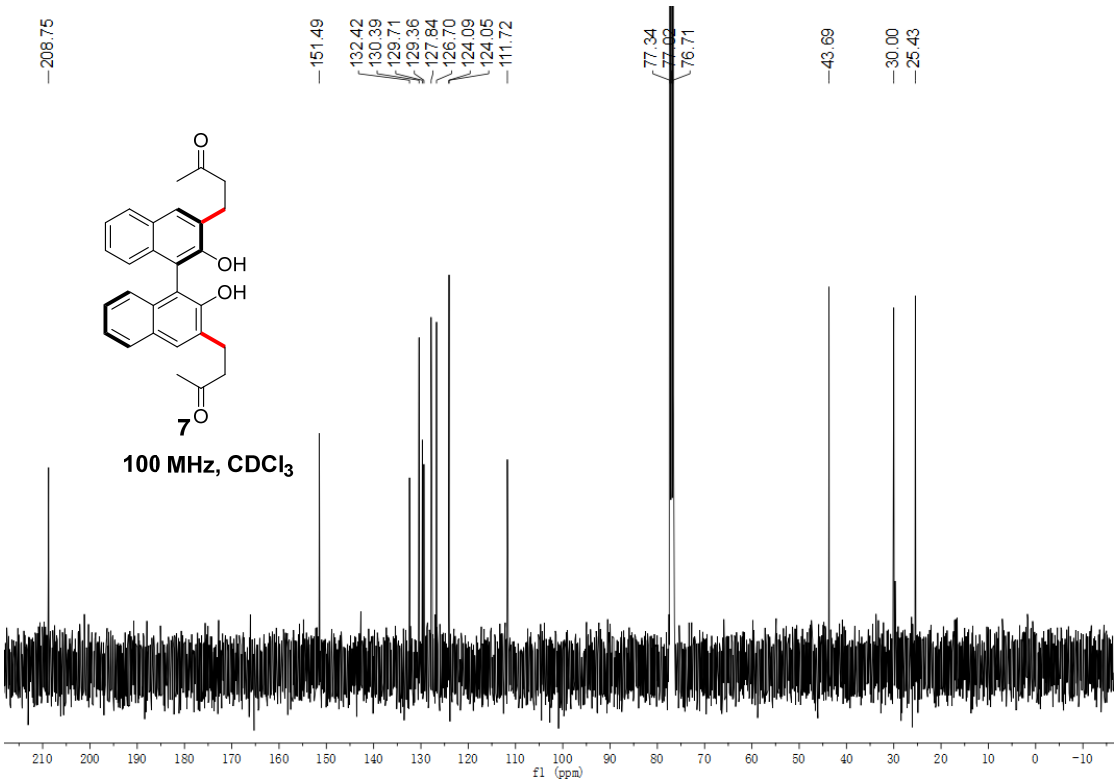
400 MHz, $CDCl_3$



6

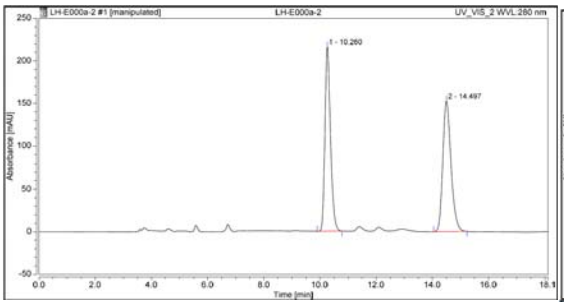
151 MHz, $CDCl_3$


7.837
7.817
7.806
7.363
7.359
7.346
7.342
7.339
7.325
7.322
7.260
7.247
7.243
7.239
7.225
7.222
7.058
7.037
5.516
3.175
3.156
3.138
2.960
2.941
2.923
2.187
1.566
OH
OH
O
O
7
400 MHz, CDCl3
2.12
1.01
1.01
1.08
1.00
2.01
2.15
3.10
f1 (ppm)


208.75
151.49
132.42
130.39
129.71
129.36
127.84
126.70
124.09
124.05
111.72
77.34
77.02
76.71
43.69
30.00
25.43
OH
OH
O
O
7
100 MHz, CDCl3
f1 (ppm)

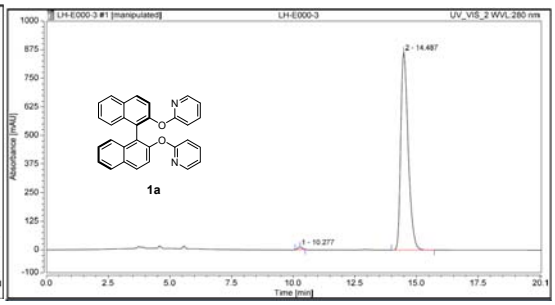
13. HPLC Data

Rac-**1a**



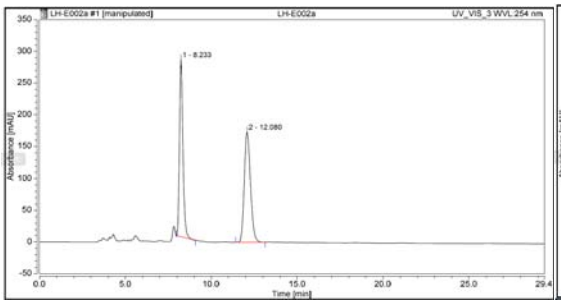
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	10.260	49.347	215.848	48.94
2	14.497	51.489	152.655	51.06

Asy-**1a**



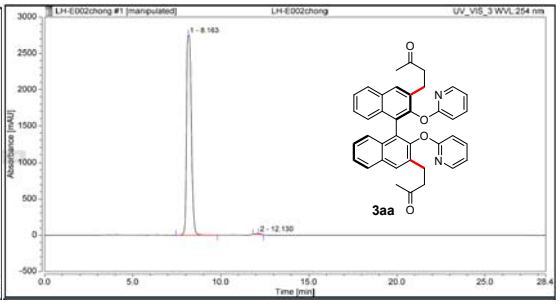
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	10.277	2.366	11.632	0.78
2	14.487	300.943	864.178	99.22

Rac-**3aa**



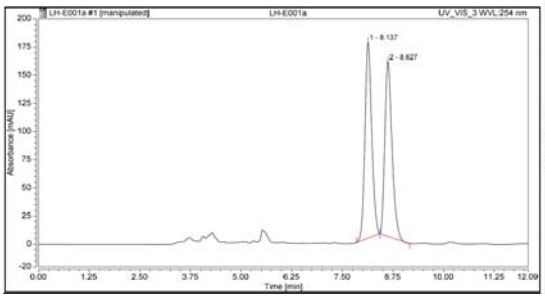
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.233	64.305	278.533	47.02
2	12.080	72.469	173.244	52.98

Asy-**3aa**



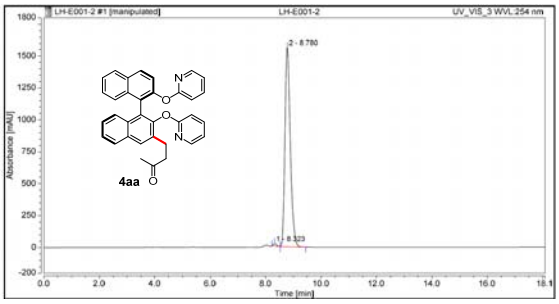
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.163	864.536	2754.466	99.41
2	12.130	5.101	14.648	0.59

Rac-**4aa**



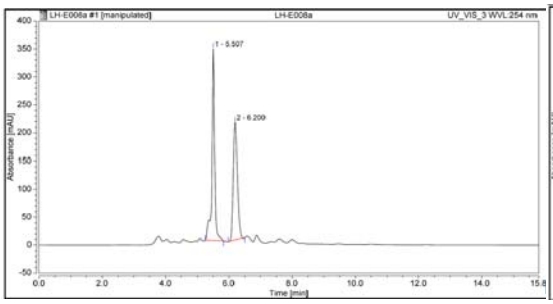
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.137	33.825	173.936	51.45
2	8.627	31.918	155.027	48.55

Asy-**4aa**



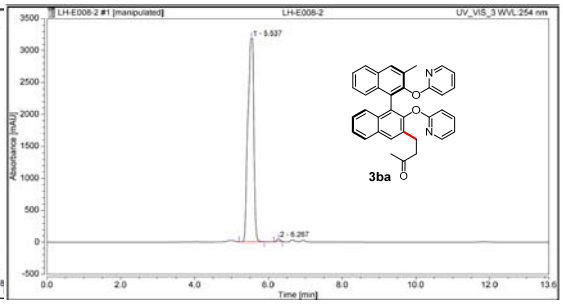
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.323	2.819	19.262	0.80
2	8.780	349.132	1559.241	99.20

Rac-**3ba**



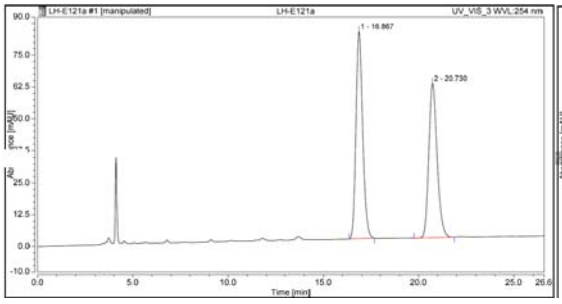
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	5.507	34.270	342.732	52.19
2	6.200	31.397	209.619	47.81

Asy-**3ba**



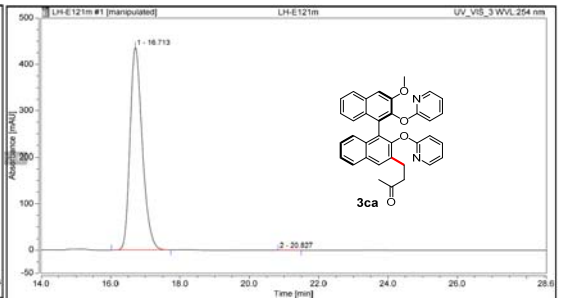
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	5.537	594.152	3186.604	99.28
2	6.267	4.285	37.684	0.72

Rac-**3ca**



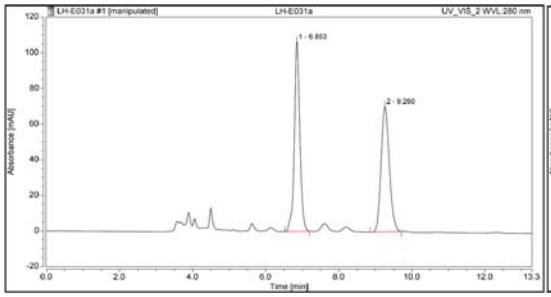
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	16.867	33.211	81.340	52.27
2	20.730	30.320	60.536	47.73

Asy-**3ca**

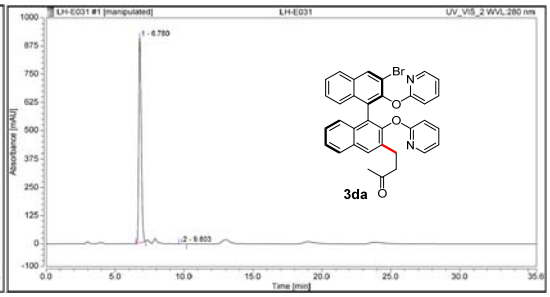


No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	16.713	178.786	437.173	99.99
2	20.827	0.022	0.000	0.01

Rac-**3da**



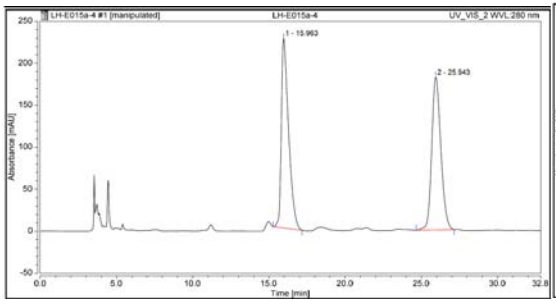
Asy-**3da**



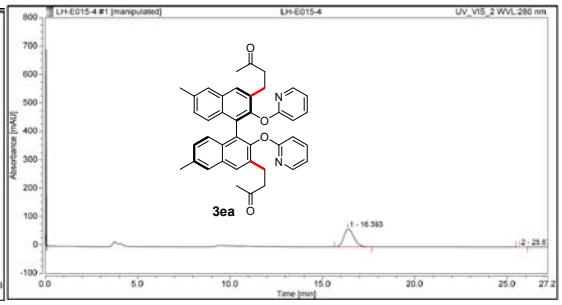
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	6.853	18.441	106.578	50.27
2	9.260	18.242	70.564	49.73

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	6.780	186.688	906.098	99.99
2	9.803	0.012	0.044	0.01

Rac-**3ea**



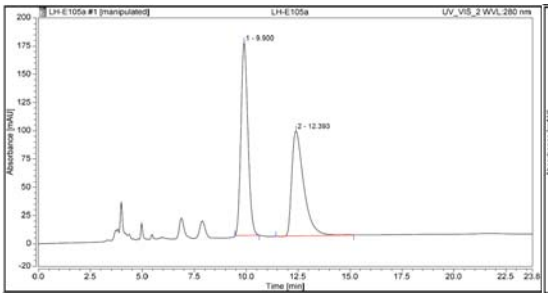
Asy-**3ea**



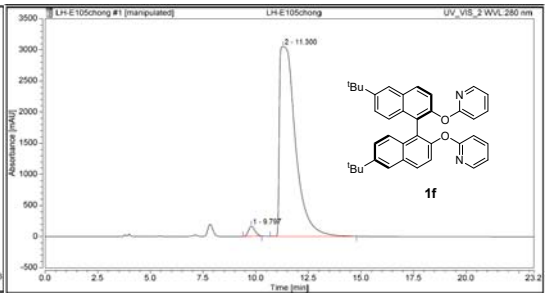
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	15.963	124.121	226.322	49.66
2	25.943	125.844	182.178	50.34

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	16.393	39.670	62.432	99.99
2	25.670	0.003	0.023	0.01

Rac-**1f**



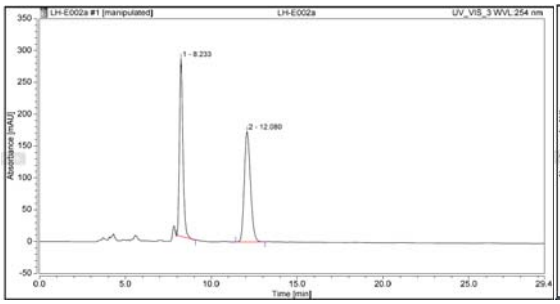
Asy-**1f**



No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.900	66.336	170.694	51.87
2	12.393	61.543	93.012	48.13

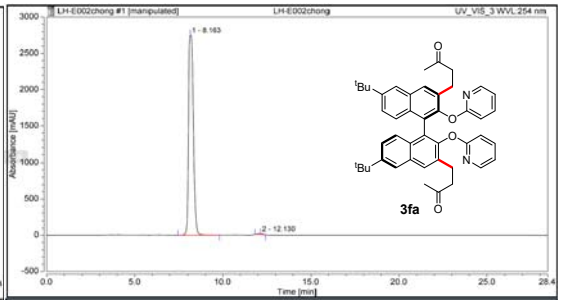
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.797	58.135	162.382	2.13
2	11.300	2670.888	3049.021	97.87

Rac-**3fa**



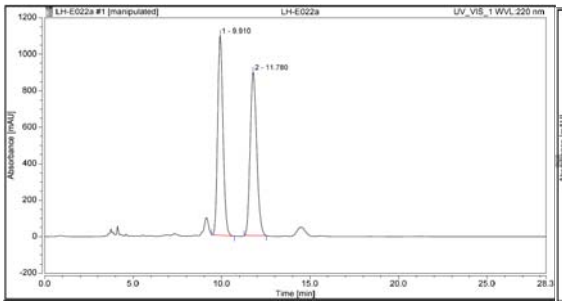
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.483	31.695	119.057	50.06
2	9.743	31.623	94.800	49.94

Asy-**3fa**



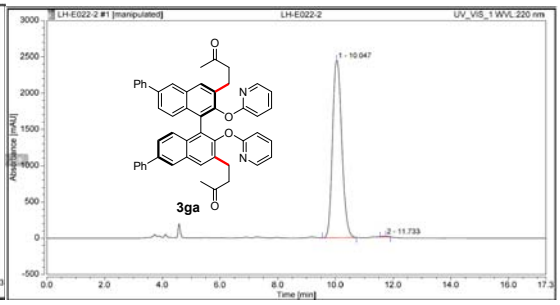
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.873	2.270	11.036	2.23
2	9.347	99.754	364.822	97.77

Rac-**3ga**



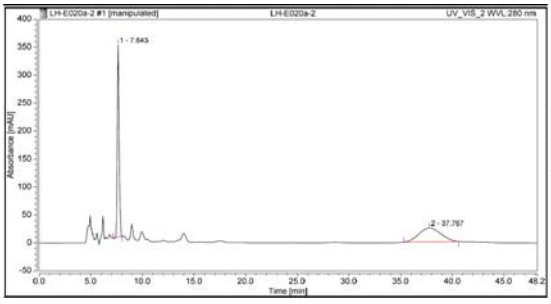
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.910	383.717	1095.335	50.01
2	11.780	383.627	895.634	49.99

Asy-**3ga**



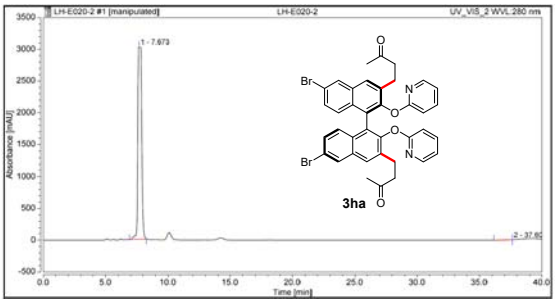
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	10.047	910.223	2447.553	99.78
2	11.733	2.046	9.258	0.22

Rac-**3ha**



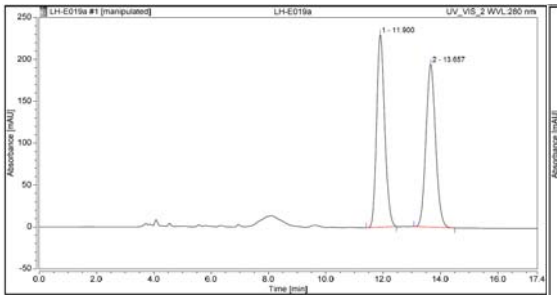
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.643	68.539	343.057	52.98
2	37.767	60.833	24.819	47.02

Asy-**3ha**



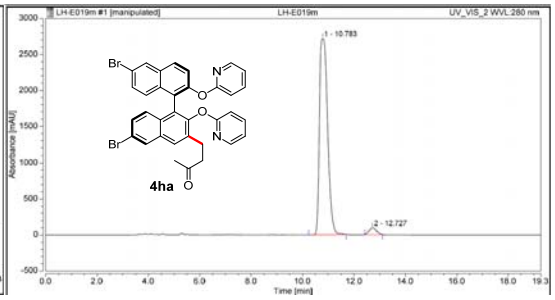
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.673	1079.490	3026.522	99.81
2	37.607	2.066	0.000	0.19

Rac-**4ha**



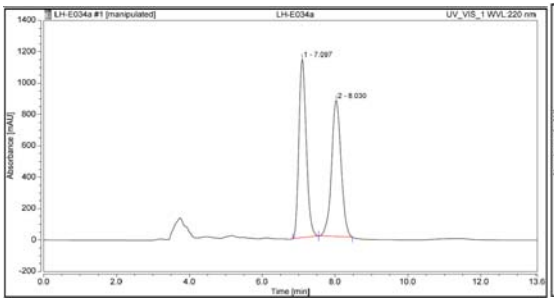
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	11.900	75.123	229.882	49.88
2	13.657	75.478	194.508	50.12

Asy-**4ha**



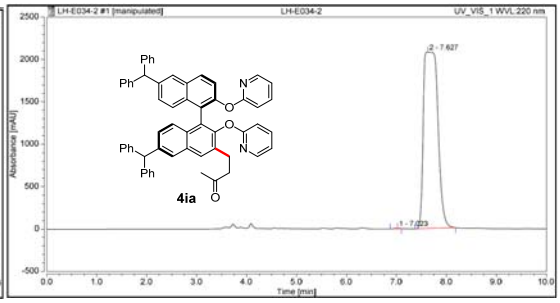
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	10.783	993.084	2717.435	97.10
2	12.727	29.636	91.712	2.90

Rac-**4ia**



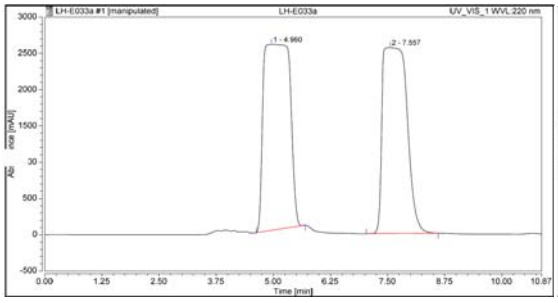
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.097	266.669	1136.483	50.34
2	8.030	263.042	867.487	49.66

Asy-**4ia**



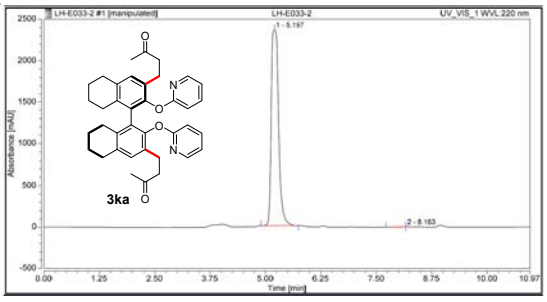
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.023	0.526	4.415	0.08
2	7.627	693.872	2082.389	99.92

Rac-**3ka**



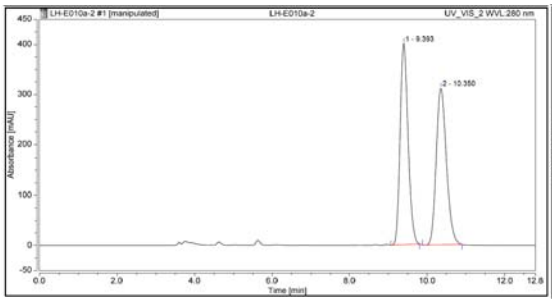
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	4.960	1711.762	2565.564	51.74
2	7.557	1596.436	2566.282	48.26

Asy-**3ka**



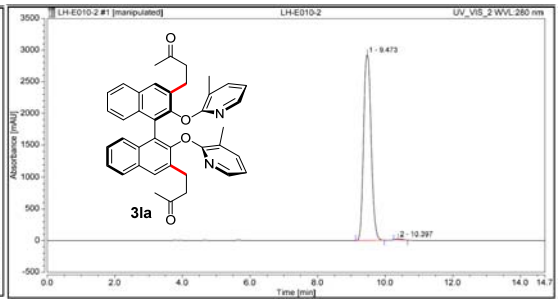
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	5.197	452.671	2358.789	99.89
2	8.163	0.499	0.000	0.11

Rac-**3la**



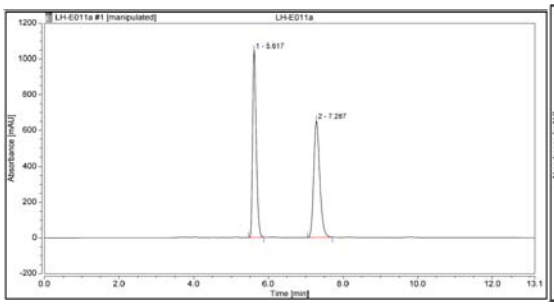
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.393	94.954	400.320	50.02
2	10.350	94.874	311.302	49.98

Asy-**3la**



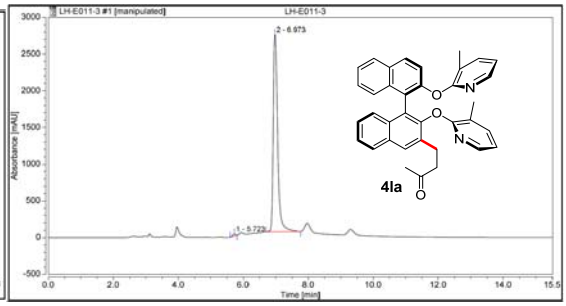
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.473	755.982	2927.992	99.54
2	10.397	3.500	16.141	0.46

Rac-**4la**



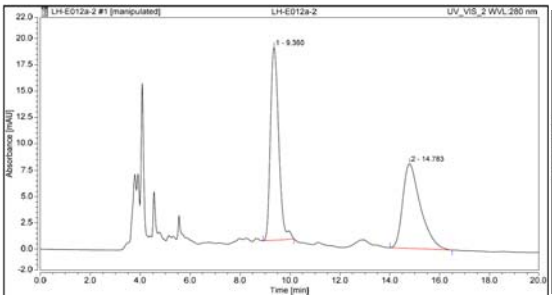
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	5.617	117.316	1044.547	49.17
2	7.287	121.261	650.512	50.83

Asy-**4la**



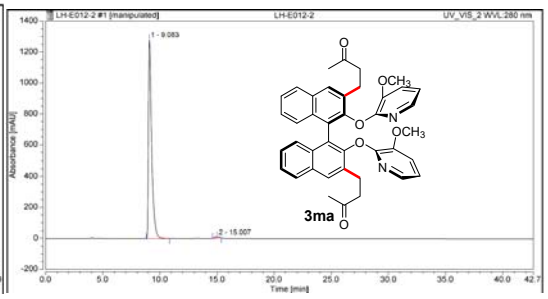
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	5.723	3.037	30.233	0.72
2	6.973	421.185	2687.316	99.28

Rac-**3ma**



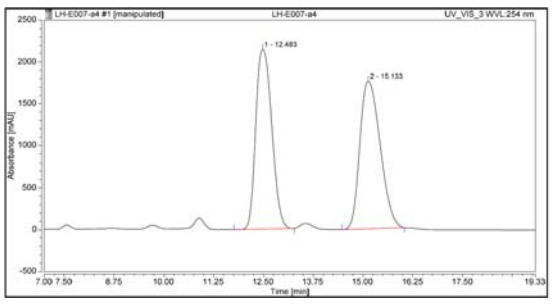
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.360	7.108	18.310	51.77
2	14.783	6.622	8.084	48.23

Asy-**3ma**



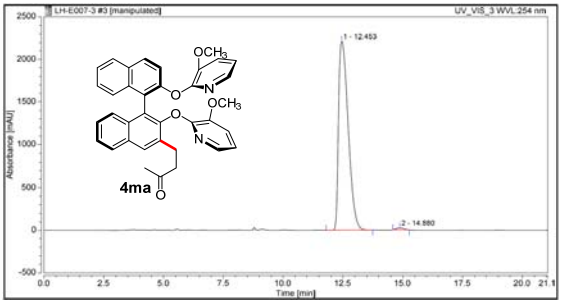
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.083	410.830	1283.698	99.05
2	15.007	3.925	8.682	0.95

Rac-**4ma**



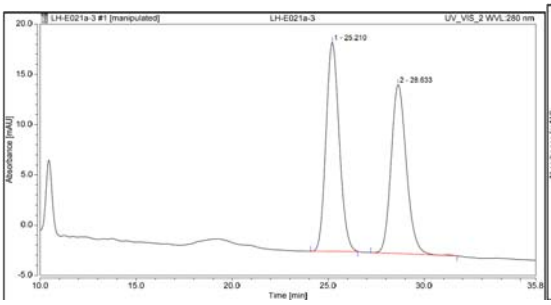
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.780	11.459	49.439	51.93
2	13.270	10.606	31.919	48.07

Asy-**4ma**



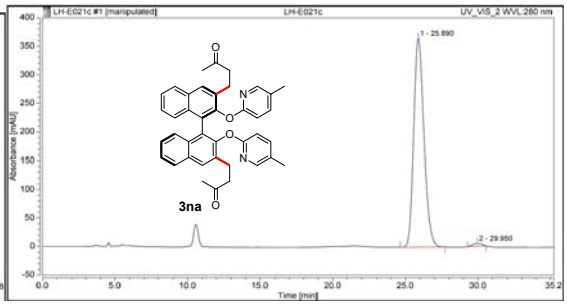
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.643	0.899	4.082	0.42
2	13.457	215.050	595.010	99.58

Rac-**3na**



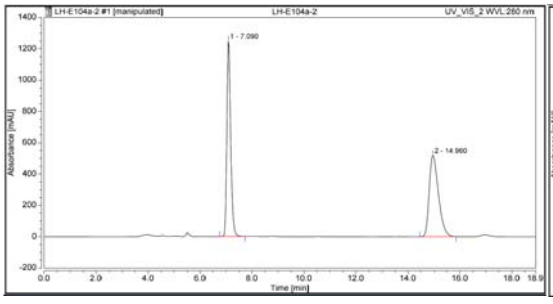
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	25.210	16.648	20.802	51.85
2	28.633	15.458	16.811	48.15

Asy-**3na**



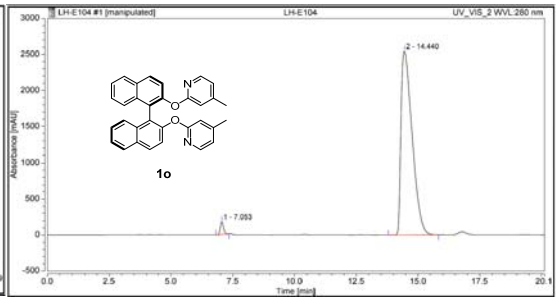
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	25.890	298.101	365.512	98.77
2	29.950	3.724	5.202	1.23

Rac-**1o**



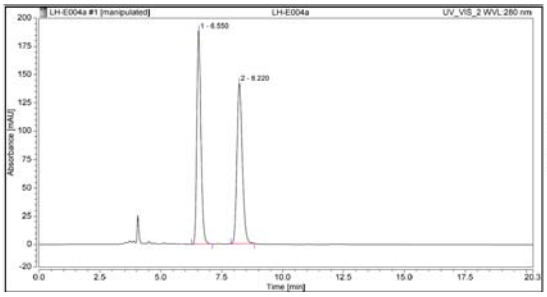
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.090	212.903	1248.124	50.02
2	14.960	212.733	519.510	49.98

Asy-**1o**



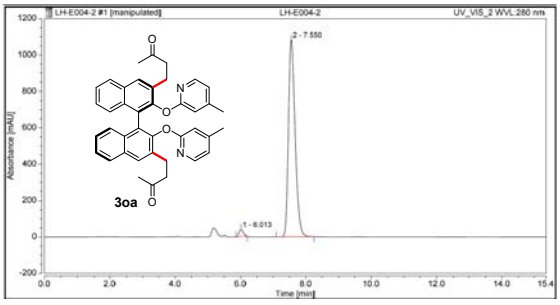
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.053	25.871	176.270	1.91
2	14.440	1326.433	2545.023	98.09

Rac-**3oa**



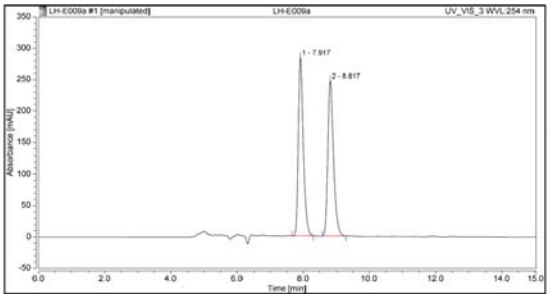
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	6.550	36.346	188.797	49.93
2	8.220	36.450	141.972	50.07

Asy-**3oa**



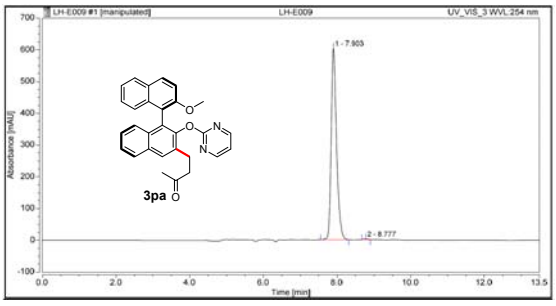
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	6.013	5.901	39.519	2.26
2	7.550	254.648	1082.558	97.74

Rac-**3pa**



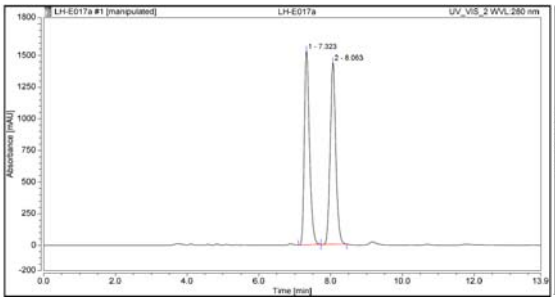
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.917	49.033	283.681	50.16
2	8.817	48.715	246.751	49.84

Asy-**3pa**



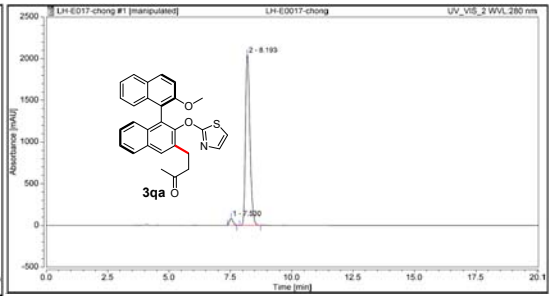
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.903	101.275	603.508	99.71
2	8.777	0.295	2.304	0.29

Rac-**3qa**



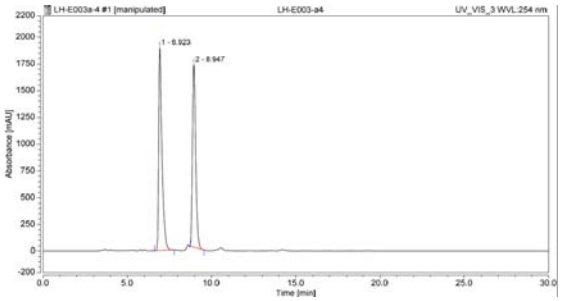
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.323	254.611	1531.746	49.59
2	8.063	258.797	1437.644	50.41

Asy-**3qa**



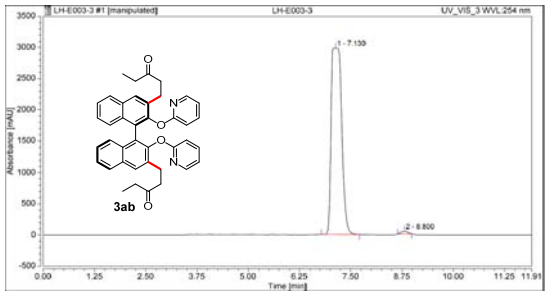
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.530	13.843	84.192	3.12
2	8.193	429.933	2046.831	96.88

Rac-**3ab**



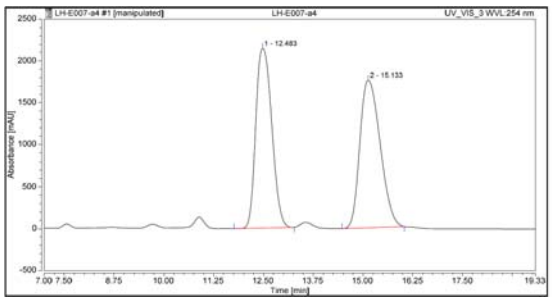
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	6.923	423.186	1903.064	52.77
2	8.947	378.805	1710.434	47.23

Asy-**3ab**



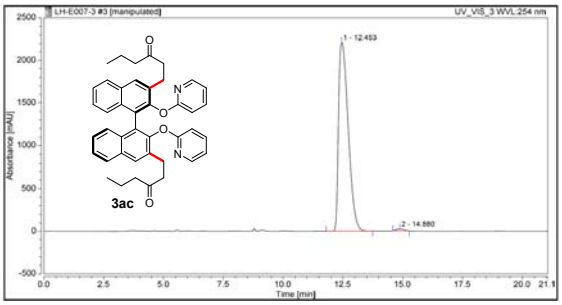
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.130	882.932	2981.227	99.09
2	8.800	8.091	41.530	0.91

Rac-**3ac**



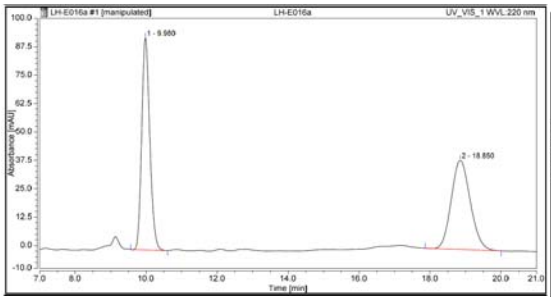
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	12.483	994.542	2144.577	48.95
2	15.133	1037.009	1759.879	51.05

Asy-**3ac**



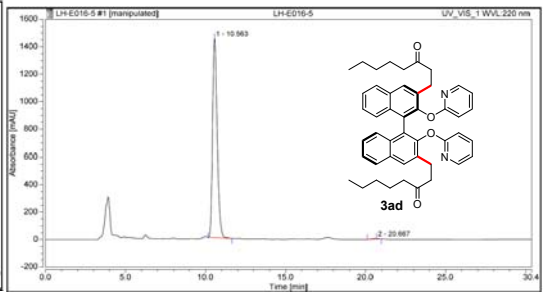
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	12.453	1030.139	2210.899	99.20
2	14.880	8.302	22.580	0.80

Rac-**3ad**



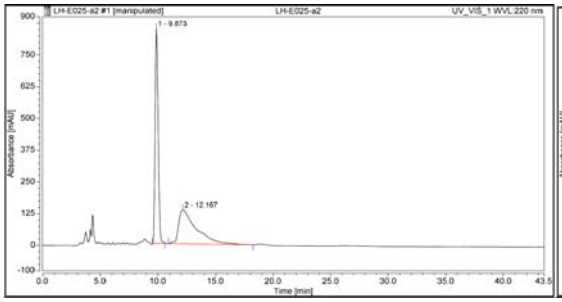
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.980	24.565	93.327	50.23
2	18.850	24.336	39.240	49.77

Asy-**3ad**



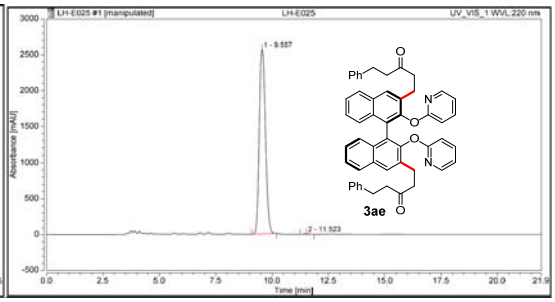
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	10.563	481.105	1447.121	99.57
2	20.667	2.082	4.424	0.43

Rac-**3ae**



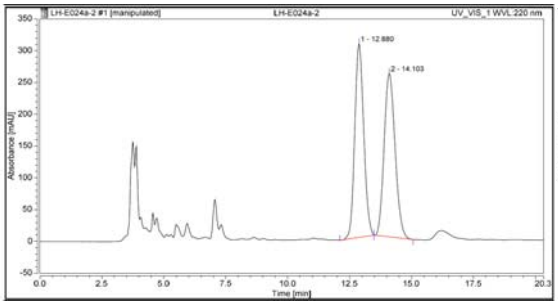
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.873	259.290	847.873	51.98
2	12.167	239.536	134.408	48.02

Asy-**3ae**



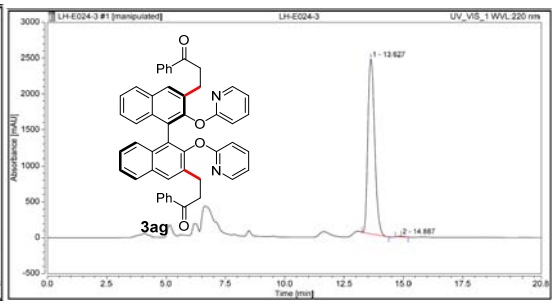
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	9.557	811.434	2563.952	99.68
2	11.523	2.622	8.473	0.32

Rac-**3ag**



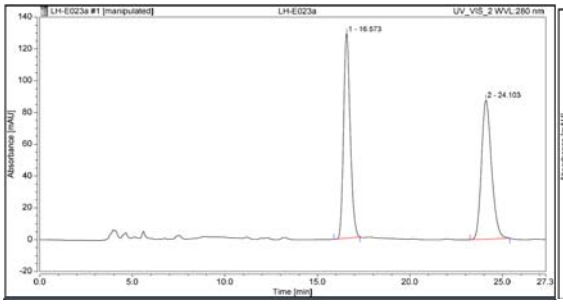
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	12.880	128.083	304.588	49.33
2	14.103	131.564	256.899	50.67

Asy-**3ag**



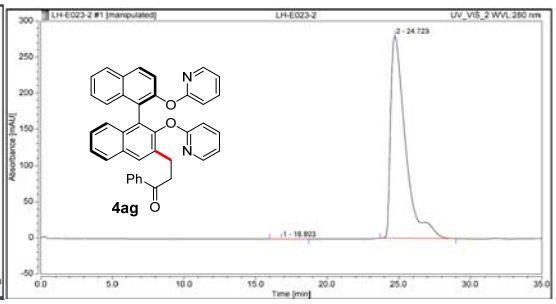
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	13.627	808.592	2434.920	99.56
2	14.887	3.593	10.849	0.44

Rac-**4ag**



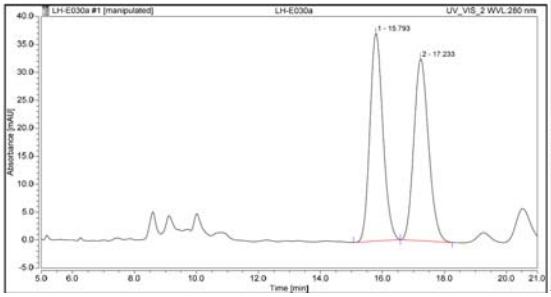
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	16.573	53.516	128.722	49.24
2	24.103	55.172	87.675	50.76

Asy-**4ag**



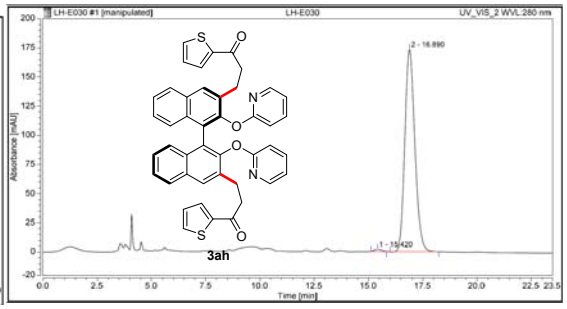
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	16.803	0.027	0.031	0.01
2	24.723	335.326	280.098	99.99

Rac-**3ah**



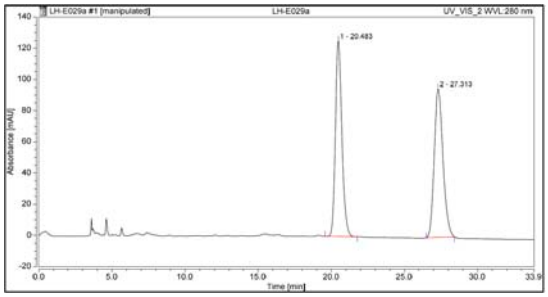
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	15.793	18.082	37.230	50.30
2	17.233	17.869	32.558	49.70

Asy-**3ah**



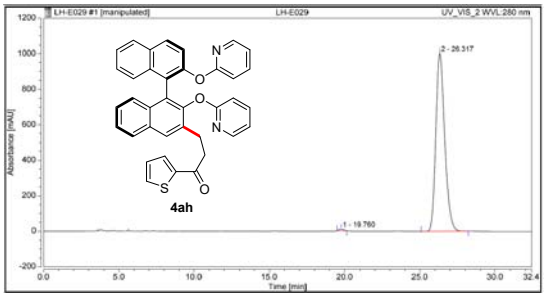
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	15.420	0.708	1.859	0.75
2	16.890	93.051	173.664	99.25

Rac-**4ah**



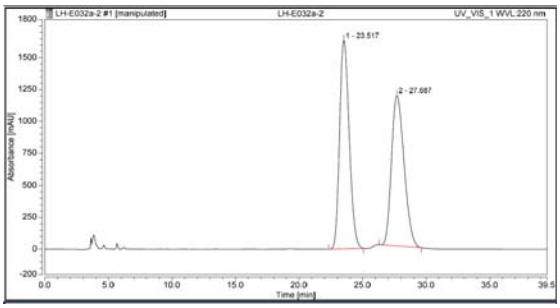
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	20.483	64.487	125.307	49.51
2	27.313	65.765	95.208	50.49

Asy-**4ah**



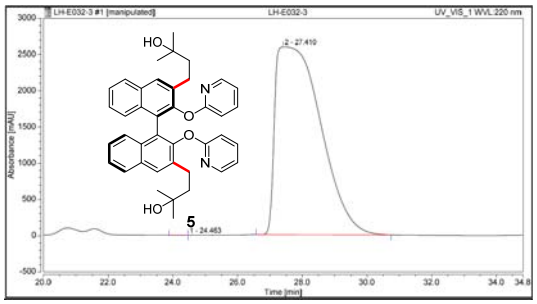
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	19.760	3.282	9.308	0.48
2	26.317	685.717	1002.002	99.52

Rac-**5**



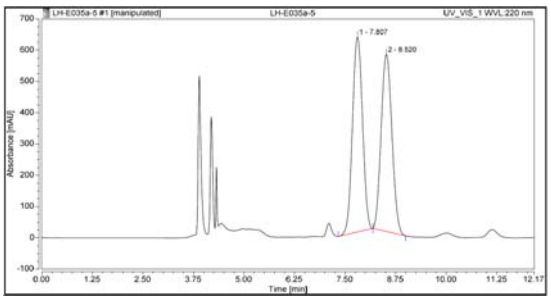
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	23.517	1427.325	1635.293	51.25
2	27.687	1357.620	1179.988	48.75

Asy-**5**



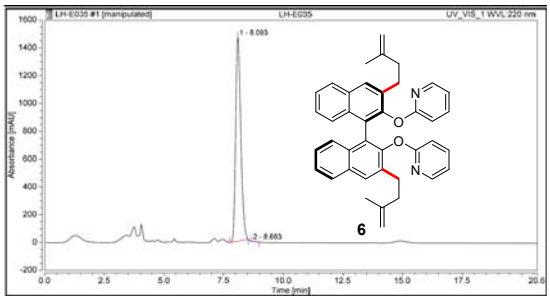
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	24.463	0.268	0.000	0.01
2	27.410	4237.542	2591.211	99.99

Rac-**6**



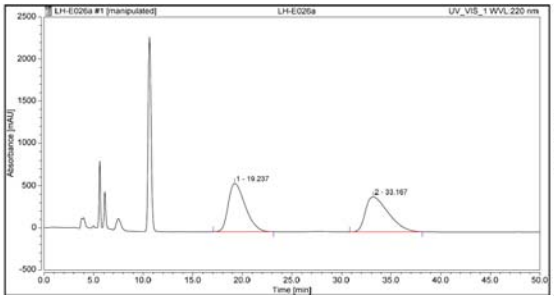
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	7.807	179.176	624.294	50.57
2	8.520	175.168	566.936	49.43

Asy-**6**



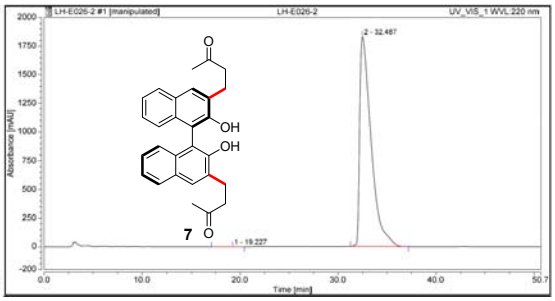
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.093	366.919	1467.986	99.96
2	8.683	0.160	0.000	0.04

Rac-**7**



No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	19.237	1138.845	575.271	50.51
2	33.167	1115.847	418.414	49.49

Asy-**7**



No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	19.227	0.140	0.203	0.01
2	32.487	2465.672	1830.824	99.99