

Supporting Information for

**Asymmetric Ruthenium-Catalyzed Hydrogenation of Terpyridine-type  
N-Heteroarenes: Direct Access to Chiral Tridentate Nitrogen Ligands**

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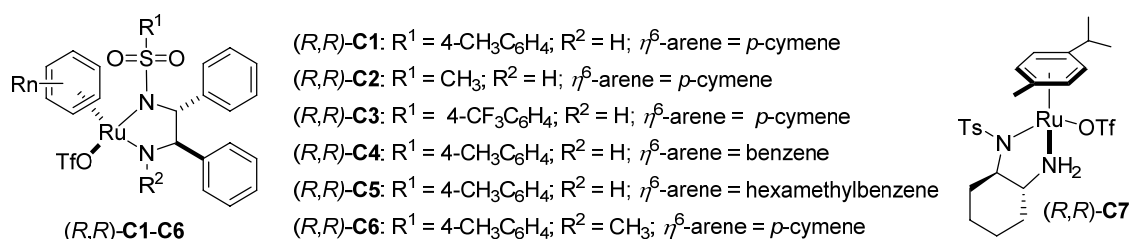
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## 1. General information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Model Avance DMX 300 Spectrometer ( $^1\text{H}$  300 MHz and  $^{13}\text{C}$  75 MHz, respectively), Bruker Model Avance DMX 400 Spectrometer ( $^1\text{H}$  400 MHz and  $^{13}\text{C}$  100 MHz, respectively), Bruker Model Avance DMX 500 Spectrometer ( $^1\text{H}$  500 MHz and  $^{13}\text{C}$  125 MHz, respectively) and Bruker Model Avance DMX 600 Spectrometer ( $^1\text{H}$  600 MHz and  $^{13}\text{C}$  150 MHz, respectively). Chemical shifts ( $\delta$ ) were given in ppm and were referenced to residual solvent or TMS peaks. Optical rotations were measured with Rudolph Autopl VI polarimeter. High resolution ESI mass spectra (P-ESI HRMS) were obtained on Thermo Fisher Q Exactive Mass Spectrometer. HPLC analyses were performed on a Varian Prostar 210 liquid chromatography. All organic solvents were dried using standard, published methods and were distilled before use. All other chemicals were used as received from Aldrich or Acros without further purification. The catalysts<sup>[1]</sup> and substrates<sup>[2]</sup> were synthesized according to the modified literature methods.

## 2. Optimization of conditions for asymmetric hydrogenation reactions

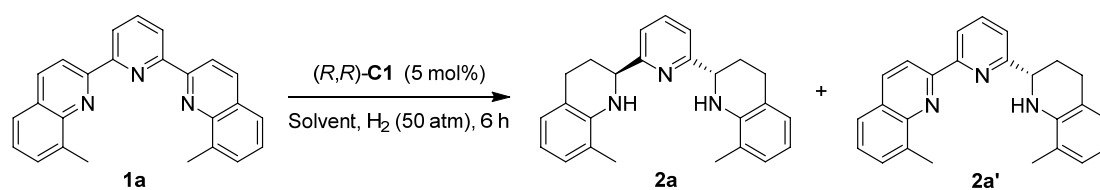
For this study, we chose the chiral diamines DPEN and CYDN as the ligand skeletons and prepared a series of Ru-complexes bearing chloride as anion according to the previous method.<sup>[1]</sup> Then, the anion  $\text{Cl}^-$  was exchanged to the weakly coordinating counteranions, giving the corresponding cationic ruthenium catalysts in quantitative yields, which did not require further purification. Their structures are shown in Scheme S1.



**Scheme S1.** Chiral ruthenium diamine catalysts used in this study

Optimization of conditions for asymmetric hydrogenation reactions are shown in Table S1-S5.

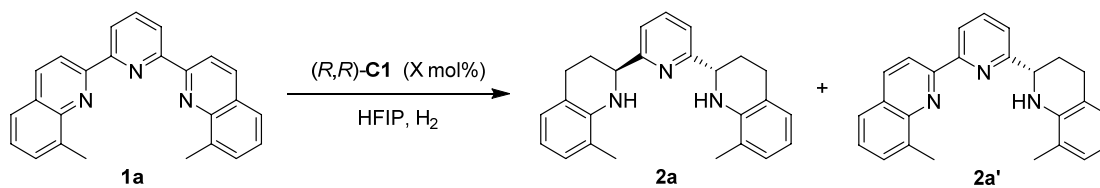
**Table S1.** Screening of the solvents<sup>[a]</sup>



Entry	Solvent	Conv. (%) <sup>[b]</sup>	<b>2a:2a'</b> <sup>[b]</sup>	ee of <b>2a</b>	<i>dl/meso</i> <sup>[c]</sup>
1	MeOH	< 5	-	-	-
2	IPA	20	>20:1	>99	88:12
3	TFE	36	>20:1	>99	86:14
4	<b>HFIP</b>	<b>&gt;99</b>	<b>&gt;20:1</b>	<b>&gt;99</b>	<b>88:12</b>
5	THF	54	1:2	95	79:21
6	1,4-dioxane	97	12:1	92	75:25
7	DCM	>99	>20:1	96	82:18
8	toluene	99	11:1	84	69:31
9	ethyl acetate	50	4:1	95	77:23

[a] Reaction conditions: substrate **1a** (0.05 mmol) in solvent (0.5 mL), (*R,R*)-**C1** (5.0 mol%), H<sub>2</sub> (50 atm), stirred at 25 °C for 6 h. [b] Determined by <sup>1</sup>H NMR analysis of crude product. [c] Determined by HPLC analysis with chiral AS-H column. IPA = isopropanol, TFE = 2,2,2-trifluoroethanol, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, THF = tetrahydrofuran, DCM = dichloromethane.

**Table S2.** Optimization of other reaction conditions<sup>[a]</sup>



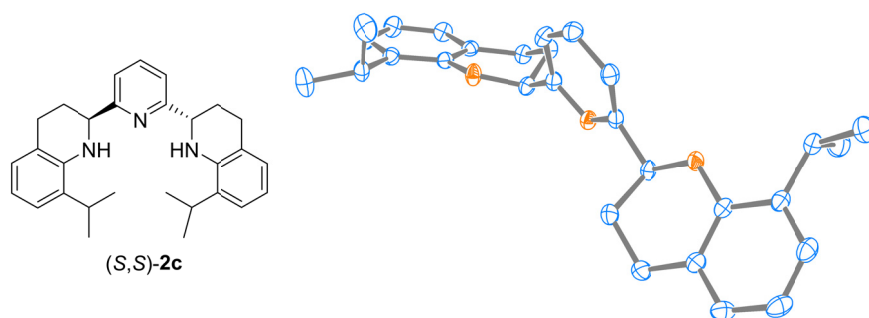
Entry	S/C	Temp. (°C)	H <sub>2</sub> (atm)	Time (h)	Conv. (%) <sup>[b]</sup>	<b>2a:2a'</b> <sup>[b]</sup>	ee of <b>2a'</b> (%) <sup>[c]</sup>	<i>dl/meso</i> <sup>[c]</sup>
1	20	0	50	6	98	3:1	>99	92:8
2	20	0	50	12	>99	14:1	>99	92:8
3	20	0	50	24	>99	>20:1	>99	92:8
<b>4</b>	<b>10</b>	<b>0</b>	<b>50</b>	<b>24</b>	<b>&gt;99</b>	<b>&gt;20:1</b>	<b>&gt;99</b>	<b>94:6</b>
5	20	25	50	6	>99	>20:1	>99	89:11
6	20	50	50	6	>99	>20:1	>99	84:16
7	20	25	70	6	>99	>20:1	>99	89:11
8	20	25	30	6	>99	>20:1	>99	87:13
9	50	25	50	24	>99	>20:1	>99	87:13
10	100	25	50	24	88	1:1	>99	86:14

[a] Reaction conditions: **1a** (0.05 mmol) in 0.5 mL HFIP. [b] Determined by <sup>1</sup>H NMR analysis of crude product. [c] Determined by HPLC analysis with chiral column.

### 3. Determination of absolute configuration

#### 3.1 X-Ray crystal structure of **2c**

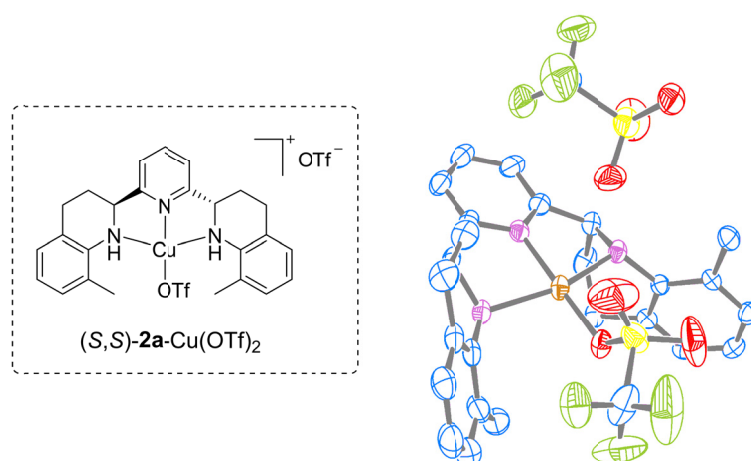
A crystal of **2c** (> 99% ee) suitable for X-ray diffraction was obtained by slow evaporation from the saturated solution of chloroform/acetonitrile at room temperature. The absolute configuration of **2c** was determined to be (*S,S*) based on the single-crystal X-ray analysis. CCDC 1995240 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



**Figure S1.** Single crystal structure of (*S,S*)-**2c**. The ORTEP view with displacement ellipsoids drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

#### 3.2 X-Ray crystal structure of (*S,S*)-**2a**-Cu(OTf)<sub>2</sub>

A crystal suitable for X-ray diffraction was obtained by diffusion of diethyl ether into a dichloromethane solution of (*S,S*)-**2a**-Cu(OTf)<sub>2</sub> at room temperature in glovebox. CCDC 1995242 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



**Figure S2.** Single crystal structure of (*S,S*)-**2a**-Cu(OTf)<sub>2</sub>. The ORTEP view with displacement ellipsoids drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

**Table S3.** Crystal data and structure refinement for **2c**.

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Identification code	<b>2c</b>
Empirical formula	C <sub>29</sub> H <sub>35</sub> N <sub>3</sub>
Formula weight	425.60
Temperature/K	170.00(14)
Crystal system	monoclinic
Space group	C2
a/Å	17.66374(8)
b/Å	8.92292(5)
c/Å	15.18432(6)
α/°	90
β/°	99.5320(4)
γ/°	90
Volume/Å <sup>3</sup>	2360.191(19)
Z	4
ρ calc g/cm <sup>3</sup>	1.198
μ /mm l	0.534
F(000)	920.0
Crystal size/mm <sup>3</sup>	0.23 × 0.15 × 0.03
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	5.902 to 150.996
Index ranges	-21 ≤ h ≤ 21, -10 ≤ k ≤ 10, -18 ≤ l ≤ 18
Reflections collected	22028
Independent reflections	534 [R <sub>int</sub> = 0.0173, R <sub>sigma</sub> = 0.0105]
Data/restraints/parameters	4534/1/293
Goodness-of-fit on F <sup>2</sup>	1.080
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0288, wR <sub>2</sub> = 0.0752
Final R indexes [all data]	R <sub>1</sub> = 0.0289, wR <sub>2</sub> = 0.0753
Largest diff. peak/hole / e Å <sup>-3</sup>	0.15/-0.17
Flack parameter	0.10(7)

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**Table S4.** Crystal data and structure refinement for (*S,S*)-**2a**-Cu(OTf)<sub>2</sub>.

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Identification code	( <i>S,S</i> )- <b>2a</b> -Cu(OTf) <sub>2</sub>
Empirical formula	C <sub>27</sub> H <sub>27</sub> CuF <sub>6</sub> N <sub>3</sub> O <sub>6</sub> S <sub>2</sub>
Formula weight	731.17
Temperature	170.00(10) K
Crystal system	trigonal
Space group	P32
a/Å	17.3237(2)
b/Å	17.3237(2)
c/Å	8.4613(2)
α/°	90
β/°	90
γ/°	120
Volume/Å <sup>3</sup>	2199.12(7)
Z	3
ρ calc g/cm <sup>3</sup>	1.656
μ /mm <sup>-1</sup>	0.973
F(000)	1119.0
Crystal size/mm <sup>3</sup>	0.525 × 0.112 × 0.086
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	7.186 to 61.38
Index ranges	-24 ≤ h ≤ 20, -24 ≤ k ≤ 24, -11 ≤ l ≤ 12
Reflections collected	37133
Independent reflections	8014 [R <sub>int</sub> = 0.0246, R <sub>sigma</sub> = 0.0241]
Data/restraints/parameters	8014/1/408
Goodness-of-fit on F <sup>2</sup>	1.020
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0524, wR <sub>2</sub> = 0.1387
Final R indexes [all data]	R <sub>1</sub> = 0.0587, wR <sub>2</sub> = 0.1432
Largest diff. peak/hole / e Å <sup>-3</sup>	1.62/-0.61
Flack parameter	0.000(5)

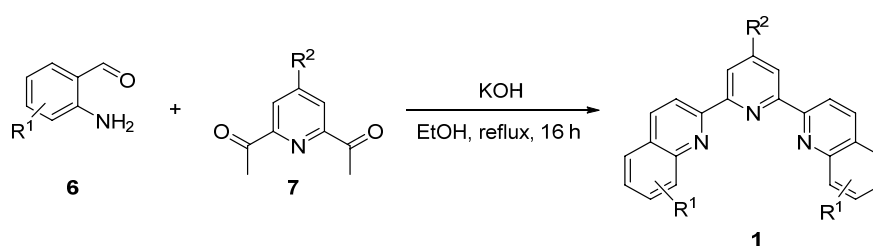
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## 4. General procedure for the synthesis of substrates

### 4.1 Synthesis of terpyridine-type substrate PyBQs (1)

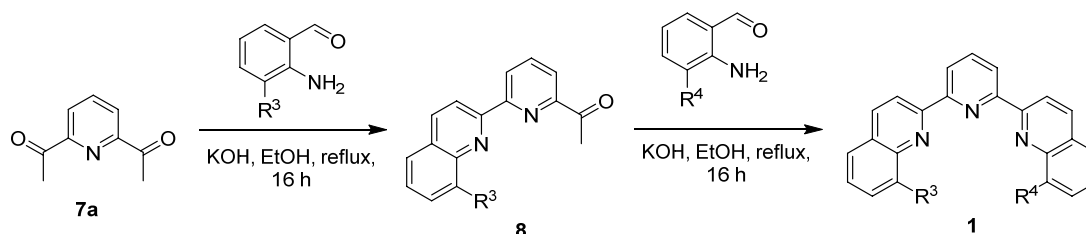
The corresponding 2,6-di(quinolin-2-yl)pyridine derivatives **1** were synthesized according to the previously reported procedures.<sup>[2a,2b]</sup> The corresponding 2-aminobenzaldehydes (**8**)<sup>[2c]</sup> and 2,6-diacetylpyridine derivatives (**9**)<sup>[2d-2g]</sup> were synthesized according to the previously reported procedures.

#### Method A:



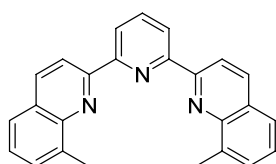
**Typical procedure:** In a 250 mL flask, 2-amino-3-methylbenzaldehyde **6** (270 mg, 2.000 mmol) was dissolved in ethyl alcohol (100 mL). Then, 2,6-diacetylpyridine **7** (163 mg, 1.000 mmol), potassium hydroxide (22 mg, 0.400 mmol) were added, and the reaction mixture was stirred at 95 °C oil bath for 16 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: dichloromethane/petroleum ether) to afford 2,6-bis(8-methylquinolin-2-yl)pyridine (**1a**) as white solid. The analytical data of the products are summarized below.

#### Method B:

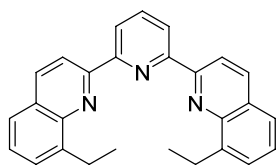


**Typical procedure:** In a 250 mL flask, o-aminobenzaldehyde (121 mg, 1.0 mmol) was dissolved in ethyl alcohol (100 mL). Then, 2,6-diacetylpyridine **7a** (163 mg, 1.0 mmol),

potassium hydroxide (11 mg, 0.2 mmol) were added, and the reaction mixture was stirred at 95 °C for 16 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduce pressure, and the crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether) to afford 1-(6-(quinolin-2-yl)pyridin-2-yl)ethan-1-one **8**. Then, **8** (248 mg, 1.000 mmol), 2-amino-3-isopropylbenzaldehyde (163 mg, 1.0 mmol), potassium hydroxide (11 mg, 0.2 mmol) and 100 mL ethanol were added in 250 mL flask, and the reaction mixture was stirred at 95 °C oil bath for 16 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduce pressure. The residue was purified by column chromatography on silica gel (eluent: dichloromethane/petroleum ether) to yield the desired 8-isopropyl-2-(6-(naphthalen-2-yl)pyridin-2-yl) quinoline (**1o**). The analytical data of the products are summarized below.

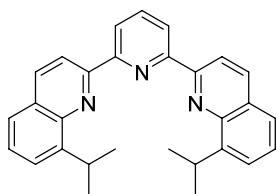


**2,6-bis(8-methylquinolin-2-yl)pyridine (1a):** (Following the method A, new compound). White solid, m.p. 229-232 °C, 0.177 g, isolated yield 49%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 8.85 (t, *J* = 7.4 Hz, 4H), 8.30 (d, *J* = 8.7 Hz, 2H), 8.06 (t, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 6.9 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 2.96 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 155.8, 154.9, 147.0, 146.6, 137.9, 137.9, 137.1, 129.8, 128.4, 126.7, 125.7, 122.1, 118.7, 18.1. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>20</sub>N<sub>3</sub> 362.16517; Found 362.16528 .

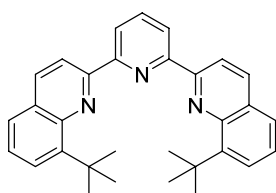


**2,6-bis(8-ethylquinolin-2-yl)pyridine (1b):** (Following the method A, new compound). White solid, m.p. 155-157 °C, 0.218 g, isolated yield 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.85 (dd, *J* = 16.8, 8.3 Hz, 4H), 8.32 (d, *J* = 9.0 Hz, 2H), 8.08 (t, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 3.47 (q, *J* = 7.5 Hz, 4H), 1.50 (t, *J* = 7.5 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 155.8, 154.6, 146.2, 143.6, 138.1, 137.3, 128.5, 128.2, 126.9, 125.7, 122.1, 118.7, 24.9, 15.4. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>24</sub>N<sub>3</sub>

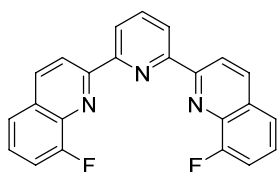
390.19647; Found 390.19629.



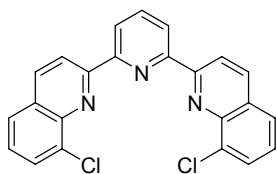
**2,6-bis(8-isopropylquinolin-2-yl)pyridine (1c):** (Following the method A, new compound). White solid, m.p. 181-183 °C, 0.280 g, isolated yield 67%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.85 (dd, *J* = 14.9, 8.3 Hz, 4H), 8.32 (d, *J* = 8.4 Hz, 2H), 8.08 (t, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 4.61-4.47 (m, 2H), 1.50 (d, *J* = 6.9 Hz, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 156.0, 154.7, 147.8, 145.7, 137.9, 137.3, 128.6, 126.9, 125.5, 125.5, 122.0, 118.6, 28.0, 23.7. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>28</sub>N<sub>3</sub> 418.22777; Found 418.22760.



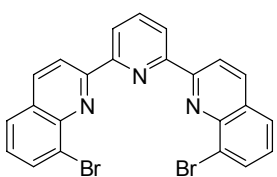
**2,6-bis(8-(tert-butyl)quinolin-2-yl)pyridine (1d):** (Following the method A, new compound). White solid, m.p. 231-233 °C, 0.328 g, isolated yield 72%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.88 (d, *J* = 8.5 Hz, 2H), 8.76 (d, *J* = 7.5 Hz, 2H), 8.34 (d, *J* = 9.0 Hz, 2H), 8.11 (t, *J* = 8.0 Hz, 1H), 7.74 (dd, *J* = 13.0, 7.5 Hz, 4H), 7.50 (t, *J* = 7.5 Hz, 2H), 1.82 (s, 18H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 155.9, 153.3, 148.3, 146.6, 138.2, 137.9, 129.5, 126.8, 126.6, 122.1, 118.1, 36.8, 31.5. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>32</sub>N<sub>3</sub> 446.25852; Found 446.25839.



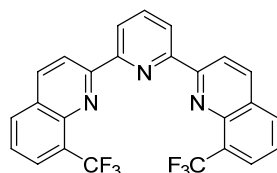
**2,6-bis(8-fluoroquinolin-2-yl)pyridine (1e):** (Following the method A, new compound). White solid, m.p. 283-285 °C, 0.181 g, isolated yield 49%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.93-8.88 (m, 4H), 8.38 (d, *J* = 8.7 Hz, 2H), 8.16 (t, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.56-7.43 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 158.5 (d, *J*<sub>C-F</sub> = 257.8 Hz), 156.2, 155.1, 138.5, 138.3 (d, *J*<sub>C-F</sub> = 12.6 Hz), 136.7 (d, *J*<sub>C-F</sub> = 2.5 Hz), 130.1 (d, *J*<sub>C-F</sub> = 1.3 Hz), 126.8 (d, *J*<sub>C-F</sub> = 7.5 Hz), 123.4 (d, *J*<sub>C-F</sub> = 5.0 Hz), 123.0, 120.1, 113.9 (d, *J*<sub>C-F</sub> = 18.9 Hz). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>14</sub>F<sub>2</sub>N<sub>3</sub> 370.11503; Found 370.11447.



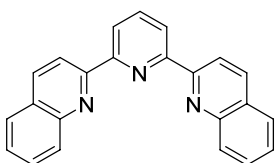
**2,6-bis(8-chloroquinolin-2-yl)pyridine (1f):** (Following the method A, new compound). Yellow solid, m.p. 282-285 °C, 0.172 g, isolated yield 43%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.96 (t, *J* = 9.0 Hz, 4H), 8.37 (d, *J* = 8.7 Hz, 2H), 8.16 (t, *J* = 7.8 Hz, 1H), 7.85 (dd, *J* = 19.5, 7.8 Hz, 4H), 7.50 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 156.5, 155.2, 144.2, 138.5, 137.4, 134.3, 129.9, 129.8, 126.9, 123.2, 119.9. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>3</sub> 402.05593; Found 402.05554.



**2,6-bis(8-bromoquinolin-2-yl)pyridine (1g):** (Following the method A, new compound). White solid, m.p. 293-295 °C, 0.200 g, isolated yield 41%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) 8.98 (d, *J* = 7.8 Hz, 2H), 8.93 (d, *J* = 9.0 Hz, 2H), 8.34 (d, *J* = 8.4 Hz, 2H), 8.13 (t, *J* = 7.8 Hz, 1H), 8.10 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.86 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ (ppm) 156.8, 155.2, 145.0, 138.4, 137.4, 133.4, 129.8, 127.7, 127.4, 125.8, 123.2, 119.8. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>14</sub>Br<sub>2</sub>N<sub>3</sub> 489.95490; Found 489.95477.

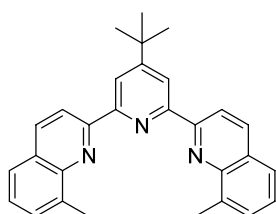


**2,6-bis(8-(trifluoromethyl)quinolin-2-yl)pyridine (1h):** (Following the method A, new compound). White solid, m.p. 308-310 °C, 0.244 g, isolated yield 52%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.97 (d, *J* = 8.0 Hz, 2H), 8.89 (d, *J* = 7.5 Hz, 2H), 8.39 (d, *J* = 8.5 Hz, 2H), 8.12-8.06 (m, 5H), 7.61 (t, *J* = 7.3 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 155.6, 155.0, 144.5, 138.5, 137.0, 132.2, 128.8, 128.3 (q, *J*<sub>C-F</sub> = 30.2 Hz), 128.2 (q, *J*<sub>C-F</sub> = 6.3 Hz), 125.5, 123.3, 124.4 (q, *J*<sub>C-F</sub> = 272.9 Hz), 119.7. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>14</sub>F<sub>6</sub>N<sub>3</sub> 470.10864; Found 470.10849.



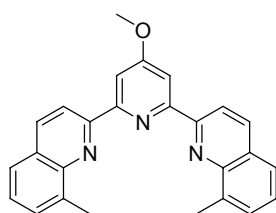
**2,6-di(quinolin-2-yl)pyridine (1i):** (Following the method A, Known compound, see: Teulade-Fichou, M.-P. *et al. Org. Biomol. Chem.* **2009**, *7*, 2864-2871). White solid, m.p. 236-239 °C, 0.213 g, isolated yield 64%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.85 (d, *J* = 8.5 Hz, 2H),

8.79 (d,  $J = 8.0$  Hz, 2H), 8.34 (d,  $J = 8.5$  Hz, 2H), 8.23 (d,  $J = 8.5$  Hz, 2H), 8.07 (t,  $J = 7.8$  Hz, 1H), 7.89 (d,  $J = 8.0$  Hz, 2H), 7.76 (t,  $J = 7.5$  Hz, 2H), 7.58 (t,  $J = 7.3$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 156.3, 155.6, 148.0, 138.1, 136.9, 130.0, 129.8, 128.5, 127.8, 126.9, 122.3, 119.3. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{16}\text{N}_3$  334.13332; Found 334.13358.



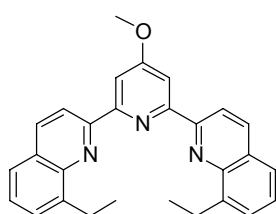
**2,2'-(4-(tert-butyl)pyridine-2,6-diyl)bis(8-methylquinoline) (1j):**

(Following the method A, new compound). White solid, m.p. 246-248 °C, 0.217 g, isolated yield 52%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.92 (s, 2H), 8.88 (d,  $J = 8.7$  Hz, 2H), 8.31 (d,  $J = 8.7$  Hz, 2H), 7.73 (d,  $J = 8.1$  Hz, 2H), 7.61 (d,  $J = 6.9$  Hz, 2H), 7.46 (t,  $J = 7.5$  Hz, 2H), 2.98 (s, 6H), 1.57 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.2, 155.7, 155.1, 146.9, 137.7, 137.1, 129.8, 128.4, 126.6, 125.7, 119.3, 119.0, 35.5, 30.9, 18.0. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{29}\text{H}_{28}\text{N}_3$  418.22777; Found 418.22739.



**2,2'-(4-methoxypyridine-2,6-diyl)bis(8-methylquinoline) (1k):**

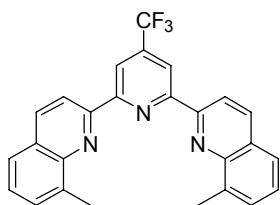
(Following the method A, new compound). White solid, m.p. 207-210 °C, 0.156 g, isolated yield 40%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.83 (d,  $J = 8.5$  Hz, 2H), 8.39 (s, 2H), 8.27 (d,  $J = 8.5$  Hz, 2H), 7.70 (d,  $J = 8.0$  Hz, 2H), 7.58 (d,  $J = 6.5$  Hz, 2H), 7.45 (t,  $J = 7.5$  Hz, 2H), 4.12 (s, 3H), 2.94 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 167.7, 157.6, 154.6, 146.9, 137.8, 137.0, 129.7, 128.5, 126.7, 125.7, 118.9, 107.8, 55.6, 18.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{22}\text{ON}_3$  392.17574; Found 392.17545.



**2,2'-(4-methoxypyridine-2,6-diyl)bis(8-ethylquinoline) (1l):**

(Following the method A, new compound). White solid, m.p. 151-154 °C, 0.143 g, isolated yield 34%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.84 (d,  $J = 8.8$  Hz, 2H), 8.39 (s, 2H), 8.29 (d,  $J = 8.4$  Hz, 2H), 7.72 (d,  $J = 8.0$  Hz, 2H), 7.60 (d,  $J = 6.8$  Hz, 2H), 7.49 (t,  $J = 7.4$  Hz, 2H), 4.12 (s, 3H), 3.46 (q,  $J = 7.5$  Hz, 4H), 1.50 (t,  $J = 7.4$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 167.6, 157.9,

154.7, 146.3, 143.6, 137.0, 128.6, 128.1, 126.8, 125.7, 118.9, 107.7, 55.4, 24.9, 15.4. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{28}H_{26}ON_3$  420.20704; Found 420.20755.



**2,2'-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(8-methylquinoline)**

**(1m):** (Following the method A, new compound). White solid, m.p.

230-232 °C, 0.193 g, isolated yield 45%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):

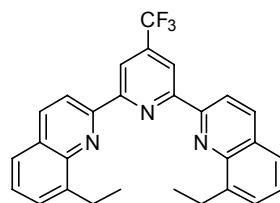
$\delta$  (ppm) 8.96 (s, 2H), 8.77 (d,  $J = 8.4$  Hz, 2H), 8.28 (d,  $J = 8.4$  Hz, 2H),

7.70 (d,  $J = 8.1$  Hz, 2H), 7.59 (d,  $J = 6.9$  Hz, 2H), 7.46 (t,  $J = 7.5$  Hz, 2H), 2.92 (s, 6H);  $^{13}C$

NMR (150 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.3, 153.5, 147.0, 140.3 (q,  $J_{C-F} = 33.5$  Hz), 138.1, 137.3,

130.0, 128.7, 127.2, 125.7, 123.5 (q,  $J_{C-F} = 272.0$ Hz), 118.5, 117.5, 18.0. HRMS (ESI)  $m/z$ :

$[M + H]^+$  Calcd for  $C_{26}H_{19}F_3N_3$  430.15256; Found 430.15283.



**2,2'-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(8-ethylquinoline)**

**(1n):** (Following the method A, new compound). White solid, m.p.

221-224 °C, 0.178 g, isolated yield 39%.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):

$\delta$  (ppm) 8.98 (s, 2H), 8.81 (d,  $J = 8.5$  Hz, 2H), 8.32 (d,  $J = 9.0$  Hz,

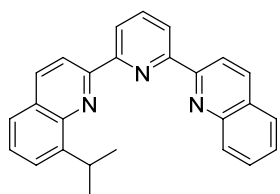
2H), 7.72 (d,  $J = 8.0$  Hz, 2H), 7.62 (d,  $J = 7.0$  Hz, 2H), 7.52 (t,  $J = 7.5$  Hz, 2H), 3.46 (q,  $J =$

7.5 Hz, 4H), 1.50 (t,  $J = 7.5$  Hz, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.4, 153.4,

146.3, 143.8, 140.3 (q,  $J_{C-F} = 33.8$  Hz), 137.4, 128.8, 128.4, 127.3, 125.7, 123.5 (q,  $J_{C-F} =$

271.7 Hz), 118.5, 117.4 (q,  $J_{C-F} = 3.8$  Hz), 24.8, 15.3. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for

$C_{28}H_{23}F_3N_3$  458.18386; Found 458.18442.



**8-isopropyl-2-(6-(quinolin-2-yl)pyridin-2-yl)quinoline** **(1o):**

(Following the method B, new compound). White solid, m.p. 129-131

°C, 0.188 g, isolated yield 50%.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  (ppm)

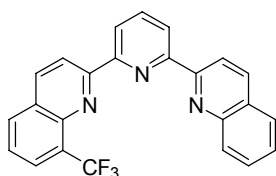
8.89-8.83 (m, 3H), 8.78 (d,  $J = 7.2$  Hz, 1H), 8.35 (d,  $J = 8.4$  Hz, 1H),

8.32 (d,  $J = 8.4$  Hz, 1H), 8.23 (d,  $J = 7.2$  Hz, 1H), 8.08 (t,  $J = 7.8$  Hz, 1H), 7.90 (d,  $J = 7.8$  Hz,

1H), 7.77 (t,  $J = 7.5$  Hz, 1H), 7.72 (d,  $J = 7.8$  Hz, 1H), 7.64 (d,  $J = 6.6$  Hz, 1H), 7.58 (t,  $J =$

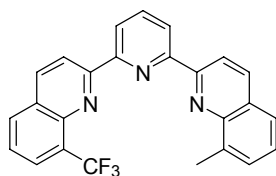
7.5 Hz, 1H), 7.53 (t,  $J = 7.5$  Hz, 1H), 4.57-4.50 (m, 1H), 1.50 (d,  $J = 7.2$  Hz, 6H);  $^{13}C$  NMR

(150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 156.5, 156.2, 154.6, 147.9, 145.8, 138.0, 137.2, 136.9, 130.0, 129.7, 128.6, 128.5, 127.8, 126.9, 125.5, 125.5, 122.2, 122.1, 119.3, 118.5, 28.0, 23.7. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>26</sub>H<sub>22</sub>N<sub>3</sub> 376.18082; Found 376.18121.



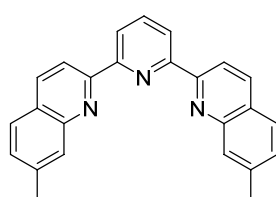
**2-(6-(quinolin-2-yl)pyridin-2-yl)-8-(trifluoromethyl)quinoline (1p):**

(Following the method B, new compound). White solid, m.p. 207-209 °C, 0.160 g, isolated yield 40%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.98 (d,  $J = 9.0$  Hz, 1H), 8.88 (d,  $J = 7.5$  Hz, 1H), 8.84 (d,  $J = 8.5$  Hz, 1H), 8.81 (d,  $J = 7.5$  Hz, 1H), 8.39 (d,  $J = 8.5$  Hz, 1H), 8.35 (d,  $J = 8.5$  Hz, 1H), 8.24 (d,  $J = 7.0$  Hz, 1H), 8.12-8.06 (m, 3H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.77 (t,  $J = 7.5$  Hz, 1H), 7.63-7.57 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 156.6, 156.2, 155.5, 155.1, 148.0, 144.5, 138.3, 137.0, 132.2, 129.9, 129.8, 128.8, 128.5, 128.3 (q,  $J_{C-F} = 28.9$  Hz), 128.2 (q,  $J_{C-F} = 5.0$  Hz), 127.8, 127.0, 125.4, 124.4 (q,  $J_{C-F} = 272.9$  Hz), 122.9, 122.8, 119.8, 119.2. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>24</sub>H<sub>15</sub>F<sub>3</sub>N<sub>3</sub> 402.12126; Found 402.12173.



**8-methyl-2-(6-(8-(trifluoromethyl)quinolin-2-yl)pyridin-2-yl)quinoline (1q):**

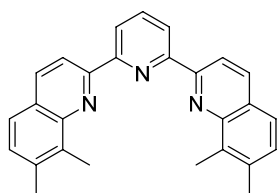
(Following the method B, new compound). White solid, m.p. 250-253 °C, 0.232 g, isolated yield 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.98 (d,  $J = 8.5$  Hz, 1H), 8.87-8.83 (m, 3H), 8.37 (d,  $J = 8.5$  Hz, 1H), 8.30 (d,  $J = 9.0$  Hz, 1H), 8.11-8.05 (m, 3H), 7.72 (d,  $J = 8.0$  Hz, 1H), 7.60 (t,  $J = 7.3$  Hz, 2H), 7.46 (t,  $J = 7.5$  Hz, 1H), 2.95 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 156.7, 155.9, 154.9, 154.7, 146.9, 144.4, 138.2, 137.9, 137.1, 136.9, 132.2, 129.8, 128.8, 128.4, 128.3 (q,  $J_{C-F} = 28.9$  Hz), 128.2 (t,  $J_{C-F} = 6.3$  Hz), 126.7, 125.7, 125.4, 124.4 (q,  $J_{C-F} = 273.7$  Hz), 122.7, 119.8, 118.6, 18.1. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>25</sub>H<sub>17</sub>F<sub>3</sub>N<sub>3</sub> 416.13691; Found 416.13754.



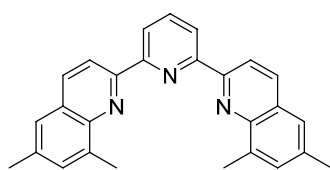
**2,6-bis(7-methylquinolin-2-yl)pyridine (1r):**

(Following the method A, new compound) White solid, m.p. 231-233 °C, 0.112 g, isolated yield 31%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.77 (dd,  $J = 13.5$ ,

8.5 Hz, 4H), 8.29 (d,  $J = 8.5$  Hz, 2H), 8.08-8.01 (m, 3H), 7.78 (d,  $J = 8.0$  Hz, 2H), 7.41 (d,  $J = 8.0$  Hz, 2H), 2.61 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 156.3, 155.8, 148.3, 140.0, 138.1, 136.6, 129.2, 129.0, 127.4, 126.6, 122.1, 118.5, 22.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_3$  362.16517; Found 362.16476.



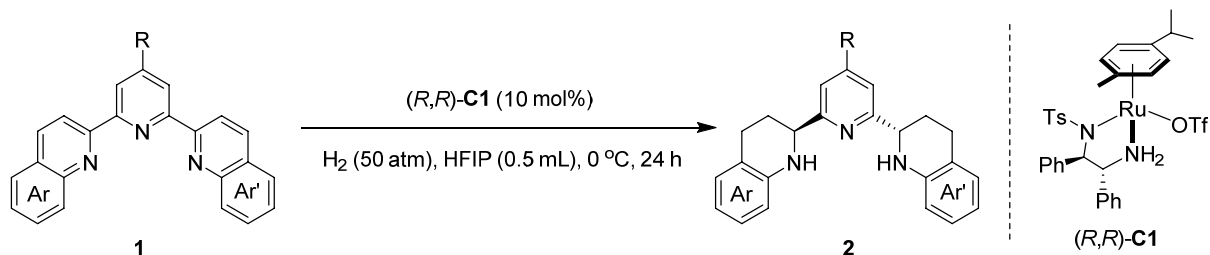
**2,6-bis(7,8-dimethylquinolin-2-yl)pyridine (1s):** (Following the method A, new compound). White solid, m.p. 249-251 °C, 0.253 g, isolated yield 65%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.82 (dd,  $J = 11.3, 8.3$  Hz, 4H), 8.25 (d,  $J = 8.4$  Hz, 2H), 8.05 (t,  $J = 7.8$  Hz, 1H), 7.63 (d,  $J = 8.4$  Hz, 2H), 7.38 (d,  $J = 8.1$  Hz, 2H), 2.91 (s, 6H), 2.55 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 156.1, 154.9, 146.9, 137.8, 137.3, 136.9, 135.0, 129.8, 126.8, 124.7, 121.9, 117.7, 20.8, 13.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{27}\text{H}_{24}\text{N}_3$  390.19647; Found 390.19595.



**2,6-bis(6,8-dimethylquinolin-2-yl)pyridine (1t):** (Following the method A, new compound). White solid, m.p. 255-258 °C, 0.280 g, isolated yield 72%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.82 (d,  $J = 3.3$  Hz, 2H), 8.79 (d,  $J = 2.1$  Hz, 2H), 8.19 (d,  $J = 8.7$  Hz, 2H), 8.04 (t,  $J = 7.8$  Hz, 1H), 7.45 (d,  $J = 10.8$  Hz, 4H), 2.91 (s, 6H), 2.52 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 155.8, 154.0, 145.5, 137.9, 137.4, 136.5, 136.3, 132.1, 128.5, 124.6, 121.7, 118.7, 21.8, 17.9. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{27}\text{H}_{24}\text{N}_3$  390.19647; Found 390.19595.

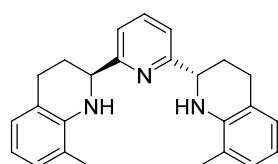
## 5. General procedure for asymmetric hydrogenation

### 5.1 Asymmetric hydrogenation of substrate PyBQs (1)



**Typical procedure:** A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate **1** (0.05 mmol), Ru-catalyst  $(R,R)$ -C1 (0.005 mmol) in 0.5 mL of solvent under N<sub>2</sub> atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 0 °C for 24 h. Then the hydrogen gas was carefully released and the conversion was determined by <sup>1</sup>H NMR spectroscopy. The reaction mixture was filtered through a short pad of silica eluted with ethyl acetate and petroleum ether to give the chiral product 2,6-bis(tetrahydroquinolin-2-yl)pyridines (PyBTHQs, **2**). The diastereomeric ratio and the enantiomeric excess of the product was determined by HPLC with a chiral column.

The pure main isomer of **2** (PyBTHQs) for NMR characterization and as ligand in asymmetric catalysis were isolated by flash column chromatography or recrystallization.

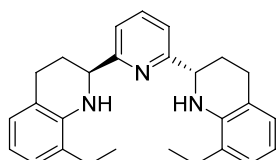


#### 2,6-bis((*S*)-8-methyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridine

**((*S,S*)-2a):** (New compound). White solid, m.p. 93-94 °C, isolated yield 88%, 94:6 *dl/meso*, > 99% ee.  $[\alpha]_D^{20} = -51.2$  ( $c = 1.0$ , CHCl<sub>3</sub>, > 99% ee); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.70 (t,  $J = 7.8$  Hz, 1H), 7.36 (d,  $J = 7.5$  Hz, 2H), 6.94 (dd,  $J = 23.0, 7.5$  Hz, 4H), 6.63 (t,  $J = 7.3$  Hz, 2H), 4.69 (d,  $J = 4.5$  Hz, 2H), 4.51 (br, 2H), 3.00-2.94 (m, 2H), 2.77-2.72 (m, 2H), 2.34-2.29 (m, 2H), 2.20 (s, 6H), 2.07-2.00 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 162.6, 142.2, 137.7, 128.2, 127.2, 121.6, 120.7,

119.1, 116.8, 57.0, 28.8, 26.4, 17.4. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{25}H_{28}N_3$  370.22777; Found 370.22757.

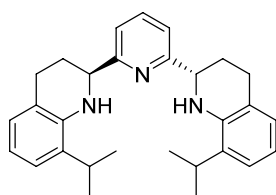
The enantiomeric excess was determined by HPLC on the connection of Chiralcel AS-H column and Chiralcel AS-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 35.0$  min (major),  $t_{R2} = 41.0$  min (minor).



**2,6-bis((S)-8-ethyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridine**

**((S,S)-2b)**: (New compound). White solid, m.p. 89-91 °C, isolated yield 85%, 91:9 *dl/meso*, > 99% ee.  $[\alpha]_D^{20} = -74.8$  ( $c = 1.0$ ,  $CHCl_3$ , > 99% ee);  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.69 (t,  $J = 7.8$  Hz, 1H), 7.35 (d,  $J = 7.6$  Hz, 2H), 6.99 (d,  $J = 7.6$  Hz, 2H), 6.93 (d,  $J = 7.2$  Hz, 2H), 6.68 (t,  $J = 7.4$  Hz, 2H), 4.67 (dd,  $J = 9.0, 3.4$  Hz, 2H), 4.61 (br, 2H), 3.01-2.93 (m, 2H), 2.78-2.72 (m, 2H), 2.55 (q,  $J = 7.5$  Hz, 4H), 2.34-2.27 (m, 2H), 2.06-1.97 (m, 2H), 1.31 (t,  $J = 7.4$  Hz, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 162.8, 141.6, 137.6, 127.2, 127.2, 126.0, 120.8, 119.0, 116.9, 57.1, 28.8, 26.6, 23.9, 13.0. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{27}H_{32}N_3$  398.25907; Found 398.25870.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel IA-H column and Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 1.0 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 17.6$  min (major),  $t_{R2} = 21.3$  min (minor).

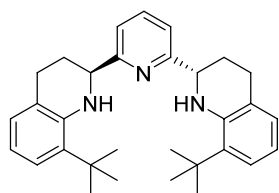


**2,6-bis((S)-8-isopropyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridine**

**((S,S)-2c)**: (New compound). White solid, m.p. 129-131 °C, isolated yield 81%, 90:10 *dl/meso*, > 99% ee.  $[\alpha]_D^{20} = -97.2$  ( $c = 1.0$ ,  $CHCl_3$ , > 99% ee);  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.74 (t,  $J = 7.8$  Hz, 1H), 7.40 (d,  $J = 7.5$  Hz, 2H), 7.12 (d,  $J = 7.5$  Hz, 2H), 6.96 (d,  $J = 7.5$  Hz, 2H), 6.76 (t,  $J = 7.5$  Hz, 2H), 4.77-4.73 (m, 4H), 3.06-2.96 (m, 4H), 2.84-2.78 (m, 2H), 2.38-2.32 (m, 2H), 2.10-2.03 (m, 2H), 1.37 (d,  $J = 7.0$  Hz, 12H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 162.8, 140.9, 137.7, 131.8, 127.1, 123.2, 121.1, 119.1, 117.1, 57.1, 28.7, 27.4, 26.8, 22.5, 22.4. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{29}H_{36}N_3$  426.29037; Found 426.29013.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel IA-H

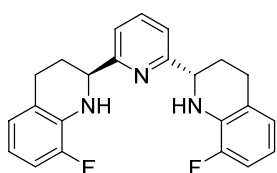
column and Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 1.0 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 14.0$  min (major),  $t_{R2} = 14.8$  min (minor).



**2,6-bis((*S*)-8-(tert-butyl)-1,2,3,4-tetrahydroquinolin-2-yl)pyridine**

**((*S,S*)-2d):** (New compound). White solid, m.p. 135-137 °C, total yield 88%, 68:32 *dl/meso*, 92% ee.  $[\alpha]_D^{20} = -53.1$  ( $c = 1.0$ , CHCl<sub>3</sub>, 92% ee, 68:32 *dl/meso*). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.71 (t,  $J = 7.8$  Hz, 1H), 7.37-7.34 (m, 2H), 7.18 (d,  $J = 7.6$  Hz, 2H), 6.94 (d,  $J = 7.6$  Hz, 2H), 6.66 (t,  $J = 7.6$  Hz, 2H), 5.10 (br, 2H), 4.73-4.71 (m, 2H), 3.06-2.97 (m, 2H), 2.82-2.76 (m, 2H), 2.35-2.29 (m, 2H), 2.08-1.99 (m, 2H), 1.51 (s, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 162.6, 142.3, 137.6, 132.8, 127.8, 124.5, 121.6, 118.8, 116.4, 57.2, 34.4, 30.1, 28.3, 27.3. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>31</sub>H<sub>40</sub>N<sub>3</sub> 454.32167; Found 454.32153.

The enantiomeric excess was determined by HPLC on the Chiralcel IG-H column (10 mmol/L Ammonium phosphate dibasic (PH = 8.0) : Acetonitrile = 30 : 70, flowing rate = 0.8 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 24.4$  min (minor),  $t_{R2} = 26.9$  min (minor),  $t_{R3} = 30.3$  min (major).

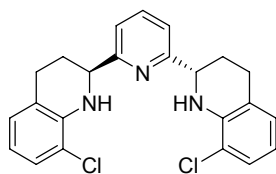


**2,6-bis((*S*)-8-fluoro-1,2,3,4-tetrahydroquinolin-2-yl)pyridine**

**((*S,S*)-2e):** (New compound). Pale yellow viscous solid, total yield 88%, 80:20 *dl/meso*, > 99% ee.  $[\alpha]_D^{20} = -65.2$  ( $c = 1.0$ , CHCl<sub>3</sub>, > 99% ee, 80:20 *dl/meso*); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.69 (t,  $J = 7.8$  Hz, 1H), 7.35 (d,  $J = 7.5$  Hz, 2H), 6.90-6.86 (m, 2H), 6.81 (d,  $J = 7.5$  Hz, 2H), 6.60-6.56 (m, 2H), 4.73 (br, 2H), 4.64 (d,  $J = 8.0$  Hz, 2H), 2.98-2.90 (m, 2H), 2.76-2.69 (m, 2H), 2.33-2.28 (m, 2H), 2.11-2.04 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 162.3, 151.1 (d,  $J_{C-F} = 238.5$  Hz), 137.7, 132.7 (d,  $J_{C-F} = 12.1$  Hz), 124.4 (d,  $J_{C-F} = 3.0$  Hz), 123.5 (d,  $J_{C-F} = 3.0$  Hz), 119.0, 116.1 (d,  $J_{C-F} = 7.5$  Hz), 112.5 (d,  $J_{C-F} = 18.1$  Hz), 56.2, 28.5, 25.6. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>23</sub>H<sub>22</sub>F<sub>2</sub>N<sub>3</sub> 378.17763; Found 378.17737.

The enantiomeric excess was determined by HPLC on Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 1.0 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} =$

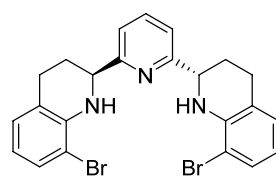
24.6 min (minor),  $t_{R2}$  = 37.3 min (major).



**2,6-bis((S)-8-chloro-1,2,3,4-tetrahydroquinolin-2-yl)pyridine**

**((S,S)-2f):** (New compound). Pale yellow solid, m.p. 102-103 °C, total yield 81%, 88:12 *dl/meso*, > 99% ee.  $[\alpha]_D^{20}$  = -89.2 ( $c$  = 1.0, CHCl<sub>3</sub>, > 99% ee, 88:12 *dl/meso*); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.69 (t,  $J$  = 7.8 Hz, 1H), 7.33 (d,  $J$  = 7.8 Hz, 2H), 7.16 (d,  $J$  = 7.8 Hz, 2H), 6.92 (d,  $J$  = 7.2 Hz, 2H), 6.59 (t,  $J$  = 7.7 Hz, 2H), 5.21 (br, 2H), 4.71 (dd,  $J$  = 4.5, 2.7 Hz, 2H), 2.97-2.87 (m, 2H), 2.75-2.66 (m, 2H), 2.36-2.27 (m, 2H), 2.15-2.03 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 162.2, 140.2, 137.9, 127.6, 127.2, 122.6, 119.1, 118.5, 116.9, 56.5, 28.1, 26.0. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>23</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>3</sub> 410.11853; Found 410.11838.

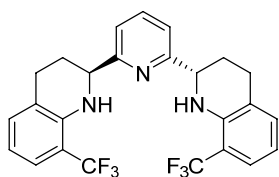
The enantiomeric excess was determined by HPLC on the connection of Chiralcel AD-H column and Chiralcel AD-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda$  = 254 nm),  $t_{R1}$  = 33.8 min (major),  $t_{R2}$  = 43.7 min (minor).



**2,6-bis((S)-8-bromo-1,2,3,4-tetrahydroquinolin-2-yl)pyridine**

**((S,S)-2g):** (New compound). Pale yellow solid, m.p. 105-107 °C, isolated yield 93%, 87:13 *dl/meso*, > 99% ee.  $[\alpha]_D^{20}$  = -106.1 ( $c$  = 1.0, CHCl<sub>3</sub>, > 99% ee, 87:13 *dl/meso*); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.72-7.71 (m, 1H), 7.33-7.30 (m, 4H), 6.94 (d,  $J$  = 7.5 Hz, 2H), 6.52 (t,  $J$  = 7.8 Hz, 2H), 5.23 (br, 2H), 4.74 (br, 2H), 2.93-2.87 (m, 2H), 2.70-2.65 (m, 2H), 2.33-2.28 (m, 2H), 2.12-2.05 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 162.1, 141.2, 138.0, 130.4, 128.3, 122.8, 119.1, 117.5, 109.1, 56.7, 28.1, 26.1. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>23</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>3</sub> 498.01750; Found 498.01776.

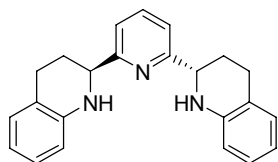
The enantiomeric excess was determined by HPLC on the connection of Chiralcel AD-H column and Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda$  = 254 nm),  $t_{R1}$  = 27.5 min (major),  $t_{R2}$  = 35.3 min (minor).



**2,6-bis((S)-8-(trifluoromethyl)-1,2,3,4-tetrahydroquinolin-2-yl)pyridine ((S,S)-2h):** (New compound). Pale yellow viscous solid, total

yield 92%, 86:14 *dl/meso*, 98% ee.  $[\alpha]_D^{20} = -98.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 98% ee, 86:14 *dl/meso*);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.69 (t,  $J = 7.8$  Hz, 1H), 7.34 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 7.5$  Hz, 2H), 7.13 (d,  $J = 7.5$  Hz, 2H), 6.66 (t,  $J = 7.8$  Hz, 2H), 5.43 (br, 2H), 4.72-4.71 (m, 2H), 2.94-2.88 (m, 2H), 2.73-2.67 (m, 2H), 2.35-2.29 (m, 2H), 2.11-2.07 (m, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 161.8, 141.9, 137.9, 132.9, 125.5 (q,  $J_{\text{C-F}} = 272.5$  Hz), 124.8 (q,  $J_{\text{C-F}} = 5.4$  Hz), 122.6, 118.9, 115.6, 112.7 (q,  $J_{\text{C-F}} = 29.0$  Hz), 56.3, 27.3, 26.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{22}\text{N}_3\text{F}_6$  478.17124; Found 478.17160.

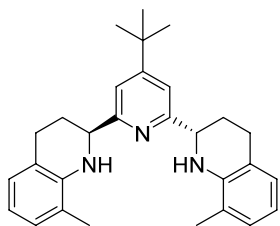
The enantiomeric excess was determined by HPLC on the connection of Chiralcel IA-H column and Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{\text{R}1} = 19.7$  min (minor),  $t_{\text{R}2} = 20.4$  min (major),  $t_{\text{R}3} = 23.0$  min (minor).



**2,6-bis((S)-1,2,3,4-tetrahydroquinolin-2-yl)pyridine ((S,S)-2i):**

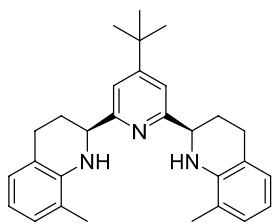
(New compound). White solid, m.p. 98-100 °C, total yield 90%, 75:25 *dl/meso*, 96% ee.  $[\alpha]_D^{20} = -41.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 96% ee, 75:25 *dl/meso*);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.67 (t,  $J = 7.6$  Hz, 1H), 7.32 (d,  $J = 7.6$  Hz, 2H), 7.06-7.00 (m, 4H), 6.69-6.62 (m, 4H), 4.59 (dd,  $J = 8.6, 3.4$  Hz, 2H), 2.96-2.88 (m, 2H), 2.74-2.67 (m, 2H), 2.32-2.25 (m, 2H), 2.07-1.98 (m, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.5, 144.3, 137.5, 129.4, 127.1, 121.3, 119.1, 117.4, 114.6, 56.8, 28.9, 26.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{24}\text{N}$  342.19702; Found 342.19728.

The enantiomeric excess was determined by HPLC on the Chiralcel AS-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{\text{R}1} = 18.6$  min (minor),  $t_{\text{R}2} = 22.6$  min (major),  $t_{\text{R}3} = 30.2$  min (minor).

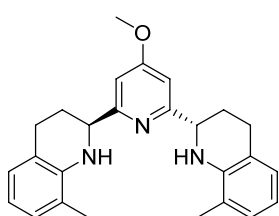


**(2*S*,2'*S*)-2,2'-(4-(tert-butyl)pyridine-2,6-diyl)bis(8-methyl-1,2,3,4-tetrahydroquinoline) ((*S,S*)-2j):** (New compound). Pale yellow viscous solid, isolated yield 86%, 93:7 *dl/meso*, > 99% ee.  $[\alpha]_{\text{D}}^{20} = -57.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.41 (s, 2H), 6.95 (dd,  $J = 12.6, 7.4$  Hz, 4H), 6.64 (t,  $J = 7.4$  Hz, 2H), 4.64 (d,  $J = 7.2$  Hz, 2H), 4.50 (br, 2H), 3.08-2.99 (m, 2H), 2.84-2.78 (m, 2H), 2.36-2.32 (m, 2H), 2.19 (s, 6H), 2.03-1.94 (m, 2H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.3, 162.0, 142.4, 128.2, 127.2, 121.7, 120.8, 116.9, 116.1, 57.5, 35.2, 30.8, 29.4, 27.0, 17.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{29}\text{H}_{36}\text{N}_3$  426.29037; Found 426.29044.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel IA-H column and Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 1.0 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{\text{R}1} = 23.4$  min (major),  $t_{\text{R}2} = 31.0$  min (minor).



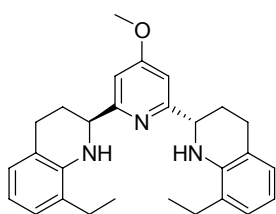
**(*S*)-2-(4-(tert-butyl)-6-((*R*)-8-methyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridin-2-yl)-8-methyl-1,2,3,4-tetrahydroquinoline (*meso*-2j):** (New compound). Pale yellow viscous solid, isolated yield 5%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.39 (s, 2H), 6.94 (dd,  $J = 10.6, 7.8$  Hz, 4H), 6.62 (t,  $J = 7.4$  Hz, 2H), 4.63 (dd,  $J = 9.8, 3.0$  Hz, 2H), 4.51 (br, 2H), 3.07-2.99 (m, 2H), 2.84-2.78 (m, 2H), 2.37-2.30 (m, 2H), 2.18 (s, 6H), 2.05-1.95 (m, 2H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.2, 161.9, 142.4, 128.1, 127.1, 121.7, 120.7, 116.8, 116.1, 57.4, 35.1, 30.8, 29.3, 27.0, 17.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{29}\text{H}_{36}\text{N}_3$  426.29037; Found 426.29001.



**(2*S*,2'*S*)-2,2'-(4-methoxypyridine-2,6-diyl)bis(8-methyl-1,2,3,4-tetrahydroquinoline) ((*S,S*)-2k):** (New compound). Pale yellow viscous solid, isolated yield 86%, 92:8 *dl/meso*, > 99% ee.  $[\alpha]_{\text{D}}^{20} = -106.3$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 6.97-6.91 (m, 6H), 6.63 (t,  $J = 7.3$  Hz, 2H), 4.62 (d,  $J = 6.5$  Hz, 2H), 4.42 (br, 2H), 3.84 (s, 3H), 3.01-2.95 (m, 2H), 2.78-2.73 (m, 2H), 2.33-2.27 (m, 2H), 2.19 (s, 6H), 2.06-1.98 (m,

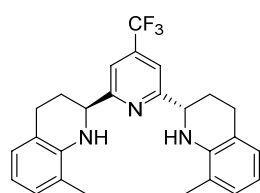
2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 167.5, 164.8, 142.2, 128.2, 127.2, 121.6, 120.8, 116.9, 105.1, 57.3, 55.3, 29.0, 26.6, 17.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{30}\text{ON}_3$  400.23834; Found 400.23813.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel IA-H column and Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{\text{R1}} = 43.7$  min (major),  $t_{\text{R2}} = 70.2$  min (minor).



**(2*S*,2'*S*)-2,2'-(4-methoxypyridine-2,6-diyl)bis(8-ethyl-1,2,3,4-tetrahydroquinoline) ((*S,S*)-2I):** (New compound). Pale yellow viscous solid, isolated yield 85%, 91 : 9 *dl/meso*, > 99% ee.  $[\alpha]_{\text{D}}^{20} = -68.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 6.98 (d,  $J = 7.5$  Hz, 2H), 6.93-6.92 (m, 4H), 6.68 (t,  $J = 7.5$  Hz, 2H), 4.62 (dd,  $J = 8.8, 2.8$  Hz, 2H), 4.53 (br, 2H), 3.83 (s, 3H), 3.01-2.95 (m, 2H), 2.79-2.74 (m, 2H), 2.55 (q,  $J = 7.5$  Hz, 4H), 2.32-2.27 (m, 2H), 2.07-1.97 (m, 2H), 1.31 (t,  $J = 7.5$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 167.5, 164.9, 141.6, 127.2, 127.2, 126.0, 120.9, 117.0, 105.1, 57.2, 55.3, 29.0, 26.7, 23.9, 13.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{34}\text{ON}_3$  428.26964; Found 428.26947.

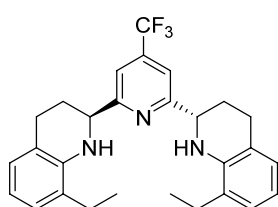
The enantiomeric excess was determined by HPLC on the three Chiralcel IA-H column connected in series (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{\text{R1}} = 46.7$  min (major),  $t_{\text{R2}} = 84.2$  min (minor).



**(2*S*,2'*S*)-2,2'-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(8-methyl-1,2,3,4-tetrahydroquinoline) ((*S,S*)-2m):** (New compound). white solid, m.p. 107-108 °C, isolated yield 81%, 87:13 *dl/meso*, > 99% ee.  $[\alpha]_{\text{D}}^{20} = -132$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.62 (s, 2H), 6.98 (d,  $J = 7.0$  Hz, 2H), 6.93 (d,  $J = 7.5$  Hz, 2H), 6.66 (t,  $J = 7.5$  Hz, 2H), 4.74 (dd,  $J = 9.0, 3.5$  Hz, 2H), 4.50 (br, 2H), 3.01-2.95 (m, 2H), 2.78-2.72 (m, 2H), 2.35-2.30 (m, 2H), 2.20 (s, 6H), 2.09-2.02 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 164.7, 141.7, 140.1 (q,  $J_{\text{C-F}} = 34.0$  Hz), 128.4, 127.2, 123.1 (q,  $J_{\text{C-F}} = 273.7$  Hz), 121.9, 120.8, 117.4, 115.1 (q,  $J_{\text{C-F}} = 3.4$  Hz), 57.2, 28.9, 26.4, 17.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{27}\text{F}_3\text{N}_3$

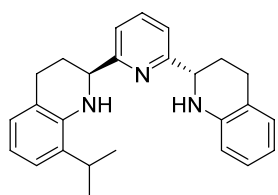
438.21516; Found 438.21567.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel IA-H column and Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 22.7$  min (major),  $t_{R2} = 29.2$  min (minor).



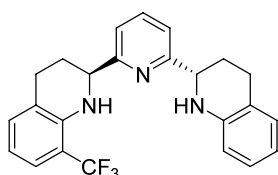
**(2*S*,2'*S*)-2,2'-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(8-ethyl-1,2,3,4-tetrahydroquinoline) ((*S,S*)-2n):** (New compound). white solid, m.p. 103-105 °C, isolated yield 80%, 86:14 *dl/meso*, > 99% ee.  $[\alpha]_D^{20} = -70.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.62 (s, 2H), 7.01 (d,  $J = 7.0$  Hz, 2H), 6.94 (d,  $J = 7.5$  Hz, 2H), 6.71 (t,  $J = 7.5$  Hz, 2H), 4.75 (dd,  $J = 8.8, 3.3$  Hz, 2H), 4.55 (br, 2H), 3.03-2.97 (m, 2H), 2.79-2.74 (m, 2H), 2.57 (q,  $J = 7.7$  Hz, 4H), 2.35-2.30 (m, 2H), 2.10-2.03 (m, 2H), 1.32 (t,  $J = 7.5$  Hz, 6H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 164.8, 141.1, 140.1 (q,  $J_{\text{C-F}} = 34.0$  Hz), 127.5, 127.2, 126.2, 123.1 (q,  $J_{\text{C-F}} = 274.2$  Hz), 120.8, 117.4, 115.0 (q,  $J_{\text{C-F}} = 3.8$  Hz), 57.2, 28.9, 26.5, 23.9, 13.0. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{31}\text{F}_3\text{N}_3$  466.24646; Found 466.24622.

The enantiomeric excess was determined by HPLC on the three Chiralcel IA-H column connected in series (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 28.6$  min (major),  $t_{R2} = 36.4$  min (minor).



**(*S*)-8-isopropyl-2-(6-((*S*)-1,2,3,4-tetrahydroquinolin-2-yl)pyridin-2-yl)-1,2,3,4-tetrahydroquinoline ((*S,S*)-2o):** (New compound). Pale yellow viscous solid, isolated yield 83%, 91 : 9 *dr*, > 99% ee.  $[\alpha]_D^{20} = -43.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.69 (t,  $J = 7.8$  Hz, 1H), 7.35-7.33 (m, 2H), 7.07-7.01 (m, 3H), 6.92 (d,  $J = 7.0$  Hz, 1H), 6.72-6.66 (m, 2H), 6.64 (d,  $J = 8.0$  Hz, 1H), 4.81 (br, 1H), 4.67-4.60 (m, 3H), 3.03-2.90 (m, 3H), 2.80-2.69 (m, 2H), 2.34-2.26 (m, 2H), 2.08-1.93 (m, 2H), 1.33-1.31 (m, 6H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.6, 162.4, 144.2, 140.9, 137.6, 131.8, 129.4, 127.1, 127.0, 123.1, 121.2, 121.0, 119.1, 119.0, 117.4, 117.0, 114.5, 57.0, 56.9, 28.8, 27.4, 26.9, 26.1, 22.6, 22.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{30}\text{N}_3$  384.24342; Found 384.24326.

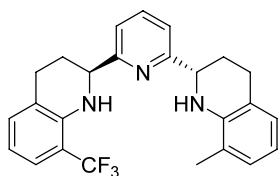
The enantiomeric excess was determined by HPLC on the four Chiralcel OD-H column connected in series (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 172.4$  min (minor),  $t_{R2} = 179.9$  min (minor) ,  $t_{R3} = 189.9$  min (minor) ,  $t_{R4} = 210.2$  min (major).



**(S)-2-(6-((S)-1,2,3,4-tetrahydroquinolin-2-yl)pyridin-2-yl)-8-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline ((S,S)-2p):** (New compound).

Pale yellow viscous solid, total yield 93%, 87:13 dr, 99% ee.  $[\alpha]_D^{20} = -57.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 99% ee, 87:13 dr);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.67 (t,  $J = 7.8$  Hz, 1H), 7.33 (d,  $J = 8.0$  Hz, 2H), 7.26 (t,  $J = 7.0$  Hz, 1H), 7.12 (d,  $J = 7.5$  Hz, 1H), 7.03 (t,  $J = 7.5$  Hz, 1H), 6.99 (d,  $J = 7.5$  Hz, 1H), 6.67-6.62 (m, 3H), 5.56 (br, 1H), 4.68-4.58 (m, 3H), 2.96-2.88 (m, 2H), 2.75-2.67 (m, 2H), 2.36-2.26 (m, 2H), 2.08-1.95 (m, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.5, 161.3, 144.2, 142.0, 137.7, 132.9, 129.4, 127.1, 125.6 (q,  $J_{\text{C-F}} = 272.9$  Hz), 124.8 (q,  $J_{\text{C-F}} = 5.4$  Hz), 122.5, 121.2, 119.2, 118.8, 117.4, 115.5, 114.6, 112.8 (q,  $J_{\text{C-F}} = 29.3$  Hz), 56.7, 56.2, 28.6, 27.6, 26.5, 26.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{23}\text{F}_3\text{N}_3$  410.18386; Found 410.18396.

The enantiomeric excess was determined by HPLC on the four Chiralcel OD-H column connected in series (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 157.3$  min (minor),  $t_{R2} = 178.8$  min (minor) ,  $t_{R3} = 195.8$  min (minor) ,  $t_{R4} = 209.3$  min (major).

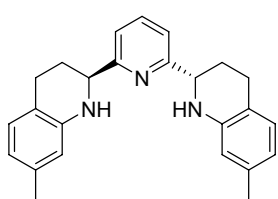


**(S)-8-methyl-2-(6-((S)-8-(trifluoromethyl)-1,2,3,4-tetrahydroquinolin-2-yl)pyridin-2-yl)-1,2,3,4-tetrahydroquinoline ((S,S)-2q):** (New compound).

Pale yellow viscous solid, total yield 90%, 91:9 dr, > 99% ee.  $[\alpha]_D^{20} = -26.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee, 91:9 dr);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.69 (t,  $J = 7.5$  Hz, 1H), 7.36-7.28 (m, 3H), 7.13 (d,  $J = 7.5$  Hz, 1H), 6.95 (d,  $J = 7.5$  Hz, 1H), 6.91 (d,  $J = 7.5$  Hz, 1H), 6.67-6.60 (m, 2H), 5.45 (br, 1H), 4.70-4.66 (m, 2H), 4.46 (br, 1H), 2.98-2.89 (m, 2H), 2.75-2.69 (m, 2H), 2.35-2.27 (m, 2H), 2.18 (s, 3H), 2.08-2.01 (m, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.9, 161.6, 142.1, 141.9, 137.8,

132.9, 128.2, 127.8 (q,  $J_{C-F} = 277.1$  Hz), 127.2, 124.8 (q,  $J_{C-F} = 5.0$  Hz), 122.6, 121.6, 120.7, 119.2, 118.8, 116.9, 115.6, 112.8 (q,  $J_{C-F} = 29.3$  Hz), 57.0, 56.3, 28.6, 27.5, 26.3, 26.3, 17.4. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{25}H_{25}F_3N_3$  424.19951; Found 424.19980.

The enantiomeric excess was determined by HPLC on the four Chiralcel OD-H column connected in series (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 97.2$  min (minor),  $t_{R2} = 107.2$  min (minor) ,  $t_{R3} = 111.6$  min (minor) ,  $t_{R4} = 149.8$  min (major).

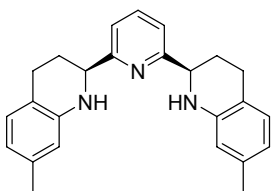


**2,6-bis((S)-7-methyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridine**

**((S,S)-2r)**: (New compound). White solid, m.p. 97-99 °C, isolated yield 68%, 74:26 *dl/meso*, 98% ee.  $[\alpha]_D^{20} = -66.8$  ( $c = 1.0$ ,  $CHCl_3$ , 98% ee);  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.66 (t,  $J = 7.8$  Hz, 1H),

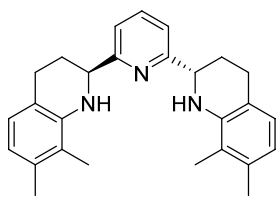
7.31 (d,  $J = 7.6$  Hz, 2H), 6.90 (d,  $J = 7.6$  Hz, 2H), 6.51 (d,  $J = 7.6$  Hz, 2H), 6.47 (s, 2H), 4.59-4.52 (m, 4H), 2.92-2.84 (m, 2H), 2.70-2.63 (m, 2H), 2.31-2.24 (m, 2H), 2.29 (s, 6H), 2.05-1.96 (m, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 162.6, 144.1, 137.5, 136.8, 129.2, 119.0, 118.4, 118.3, 115.1, 56.9, 29.1, 25.7, 21.3. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{25}H_{28}N_3$  370.22777; Found 370.22781.

The enantiomeric excess was determined by HPLC on the Chiralcel IA-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 14.2$  min (minor),  $t_{R2} = 26.3$  min (minor) ,  $t_{R2} = 39.4$  min (major).



**2-((R)-7-methyl-1,2,3,4-tetrahydroquinolin-2-yl)-6-((S)-7-methyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridine (meso-2r)**: (New compound).

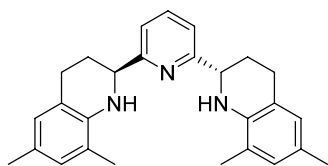
Pale yellow solid, m.p. 102-105 °C, isolated yield 15% ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.68 (t,  $J = 7.8$  Hz, 1H), 7.34 (d,  $J = 7.6$  Hz, 2H), 6.95 (d,  $J = 7.6$  Hz, 2H), 6.55 (d,  $J = 7.6$  Hz, 2H), 6.50 (s, 2H), 4.62-4.44 (m, 4H), 2.96-2.88 (m, 2H), 2.74-2.67 (m, 2H), 2.37-2.29 (m, 8H), 2.10-2.01 (m, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 162.5, 144.1, 137.4, 136.6, 129.2, 118.9, 118.3, 115.1, 56.7, 28.9, 25.6, 21.3. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{25}H_{28}N_3$  370.22777; Found 370.22757.



**2,6-bis((*S*)-7,8-dimethyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridine ((*S,S*)-2s):** (New compound). white solid, m.p. 115-117 °C, isolated

yield 81%, 87:13 *dl/meso*, > 99% ee.  $[\alpha]_D^{20} = -82.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.72 (t,  $J = 7.8$  Hz, 1H), 7.39 (d,  $J = 7.5$  Hz, 2H), 6.86 (d,  $J = 7.5$  Hz, 2H), 6.60 (d,  $J = 7.5$  Hz, 2H), 4.70 (dd,  $J = 9.0, 3.0$  Hz, 2H), 4.58 (br, 2H), 3.02-2.96 (m, 2H), 2.79-2.74 (m, 2H), 2.36-2.30 (m, 8H), 2.15 (s, 6H), 2.08-2.01 (m, 2H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.7, 142.0, 137.7, 134.6, 126.4, 119.9, 119.1, 119.0, 118.7, 57.2, 28.8, 26.4, 20.6, 12.7. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{27}\text{H}_{32}\text{N}_3$  398.25907; Found 398.25928.

The enantiomeric excess was determined by HPLC on Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 15.7$  min (minor),  $t_{R2} = 20.2$  min (major),  $t_{R3} = 22.6$  min (minor).



**2,6-bis((*S*)-6,8-dimethyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridine ((*S,S*)-2t):** (New compound). white solid, m.p. 117-118 °C, isolated

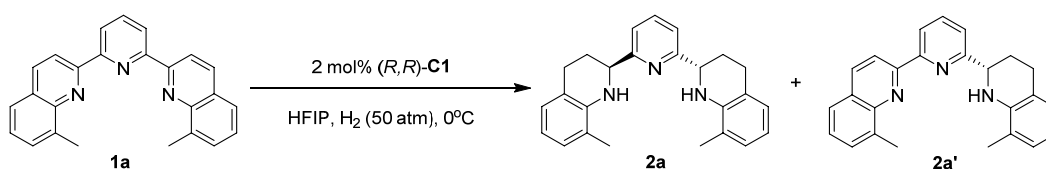
yield 81%, 88:12 *dl/meso*, > 99% ee.  $[\alpha]_D^{20} = -47.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , > 99% ee);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.68 (t,  $J = 7.6$  Hz, 1H), 7.35 (d,  $J = 7.6$  Hz, 2H), 6.79 (s, 2H), 6.74 (s, 2H), 4.63 (dd,  $J = 8.6, 2.6$  Hz, 2H), 4.33 (br, 2H), 2.97-2.89 (m, 2H), 2.72-2.66 (m, 2H), 2.33-2.23 (m, 8H), 2.16 (s, 6H), 2.05-1.96 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.8, 139.8, 137.6, 129.0, 127.7, 126.1, 121.9, 120.9, 119.1, 57.3, 29.0, 26.4, 20.5, 17.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{27}\text{H}_{32}\text{N}_3$  398.25907; Found 398.25903.

The enantiomeric excess was determined by HPLC on Chiralcel IA-H column (*n*-hexane : isopropanol = 99 : 1, flowing rate = 0.5 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 20.6$  min (major),  $t_{R3} = 22.7$  min (minor).

## 6. Study of catalytic pathway and control experiments

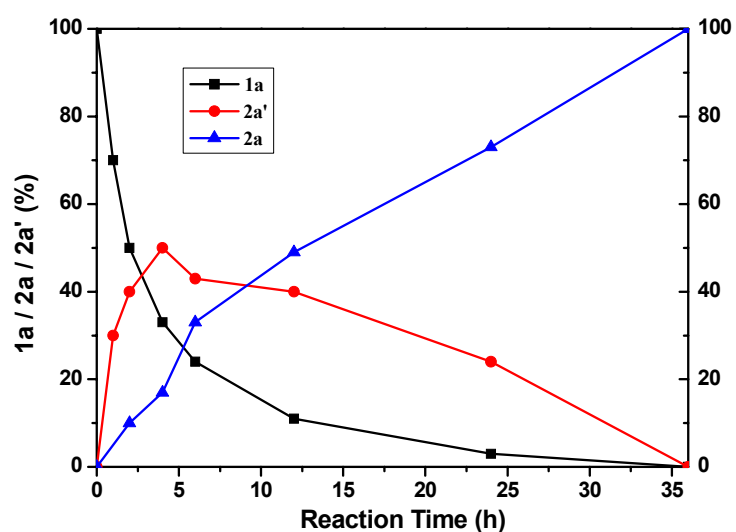
To further understand the hydrogenation behavior, a kinetic study of the reaction was carried out in HFIP at 0 °C by using 2 mol% (*R,R*)-**C1** as the catalyst. Aliquots were taken from an active hydrogenation mixture and immediately analyzed by <sup>1</sup>H NMR spectroscopy. As shown in Table S8 and Figure S4, a clear selectivity for the hydrogenation of only one quinolinyl ring at the beginning (ca. 4 h) was observed, thus providing (*S*)-**2a'** as the main product with 94% ee. Upon prolonged reaction time to 36 h, almost complete conversion was obtained to give (*S,S*)-**2a** with >99% ee and 94:6 *dl/meso*.

**Table S5.** Study of the catalytic pathway with substrate **1a**<sup>a</sup>

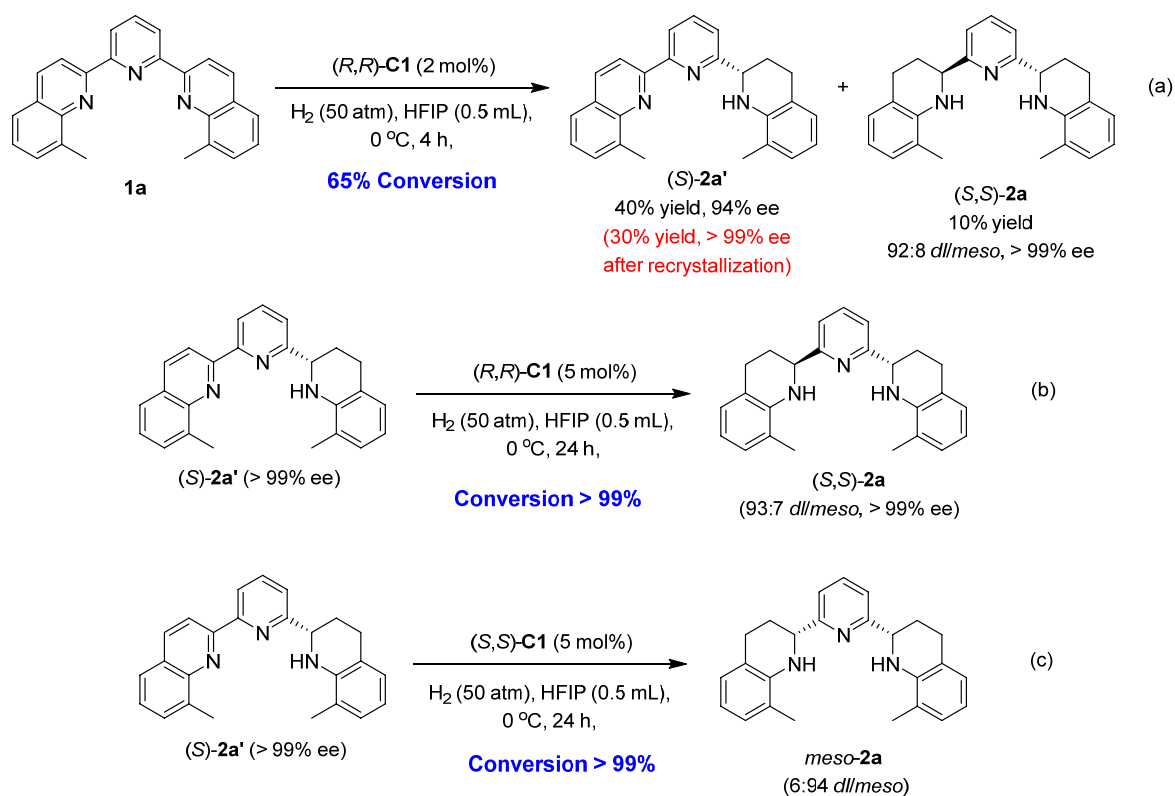


Entry	Time (h)	Conv. (%) <sup>[b]</sup>	<b>1a</b> : <b>2a'</b> : <b>2a</b> <sup>[b]</sup>	<i>ee</i> of <b>2a'</b> (%) <sup>[c]</sup>	<i>ee</i> of <b>2a</b> (%) <sup>[d]</sup>	<i>dl/meso</i> of <b>2a</b> <sup>[d]</sup>
1	0.5	~5	95:~5:0	-	-	-
2	1.0	30	70:30:0	93	-	-
3	2.0	50	50:40:10	94	98	91:9
4	4.0	67	33:50:17	94	99	92:8
5	6.0	76	24:43:33	97	>99	93:7
6	12.0	89	11:40:49	97	>99	93:7
7	24.0	97	3:24:73	97	>99	94:6
8	36.0	100	0:0:100	-	>99	94:6

[a] Reaction conditions: substrate **1a** (1.0 mmol, 360.1 mg) in solvent (10 mL HFIP), (*R,R*)-**C1** (2.0 mol %), H<sub>2</sub> (50 atm), stirred at 0 °C. [b] The conversions were determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by HPLC with chiral IA-H column. [d] Determined by HPLC analysis with chiral AS-H column.

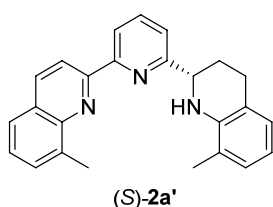


**Figure S3.** Reaction profiles. Reaction conditions: 1 mmol **1a** in 10 mL HFIP, 2.0 mol% (*R,R*)-**C1**, 50 atm H<sub>2</sub>, 0 °C.



**Scheme S1.** Preparation of intermediate **(S)-2a'**, and asymmetric hydrogenation of **(S)-2a'** with (*R,R*)-**C1** and (*S,S*)-**C1**, respectively.

**Synthesis of (*S*)-2a'**: A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate (0.5 mmol) and Ru-catalyst (*R,R*)-C1 (0.01 mmol) in 5.0 mL HFIP under N<sub>2</sub> atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 0 °C for 4 h. Then the hydrogen gas was carefully released and the conversion was determined by <sup>1</sup>H NMR spectroscopy. The reaction mixture was filtered through a short pad of silica eluted with EA and PE. The optically pure product (*S*)-2a' was obtained after recrystallization (> 99% ee, 54.8 mg, 30% yield).



**(*S*)-8-methyl-2-(6-(8-methyl-1,2,3,4-tetrahydroquinolin-2-yl)pyridin-2-yl)quinoline ((*S*)-2a')**. > 99% ee,  $[\alpha]_D^{20} = -41.5$  ( $c = 1.0$ , CHCl<sub>3</sub>, > 99% ee); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.72-8.66 (m, 2H), 8.27 (d,  $J = 8.7$  Hz, 1H), 7.88 (t,  $J = 7.8$  Hz, 1H), 7.72 (d,  $J = 8.1$  Hz, 1H), 7.62 (d,  $J = 6.9$  Hz, 1H), 7.50-7.45 (m, 2H), 7.02 (dd,  $J = 16.1, 7.4$  Hz, 2H), 6.70 (t,  $J = 7.4$  Hz, 1H), 4.82-4.78 (m, 2H), 3.11-3.01 (m, 1H), 2.98 (s, 3H), 2.88-2.80 (m, 1H), 2.46-2.38 (m, 1H), 2.33 (s, 3H), 2.19-2.07 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 162.1, 155.9, 154.8, 146.9, 142.3, 137.8, 137.6, 137.0, 129.7, 128.3, 128.2, 127.2, 126.6, 125.7, 121.6, 120.9, 120.7, 120.2, 118.4, 116.7, 56.9, 28.7, 26.7, 18.0, 17.5. HRMS (ESI)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>25</sub>H<sub>24</sub>N<sub>3</sub> 366.19647; Found 366.19604.

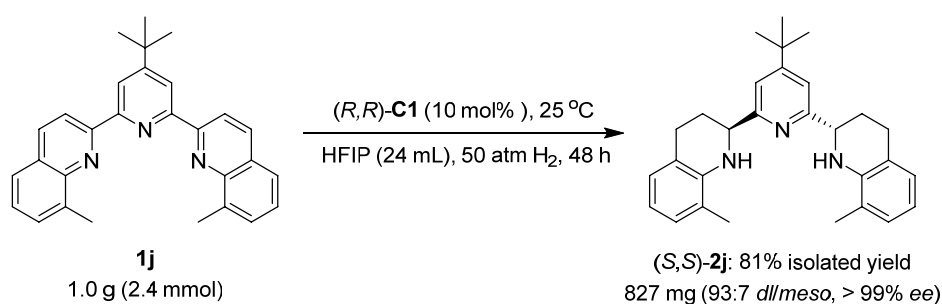
The enantiomeric excess was determined by HPLC on the connection of Chiralcel IA-H column (hexane : isopropanol = 99 : 1, flowing rate = 1.0 mL/min, 10 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 6.9$  min (minor),  $t_{R2} = 7.4$  min (major).

**Typical procedure for 2a**: A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate (*S*)-2a' (0.05 mmol) and Ru-catalyst (*R,R*)-C1 or (*S,S*)-C1 (0.0025 mmol) in 0.5 mL HFIP under N<sub>2</sub> atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 0

°C for 24 h. Then the hydrogen gas was carefully released and the conversion was determined by <sup>1</sup>H NMR spectroscopy. The reaction mixture was filtered through a short pad of silica eluted with EA and PE to give the isolated pure product. The enantiomeric excess of the product was determined by HPLC with a chiral column.

## 7. Scale-up syntheses and synthetic applications

### 7.1 Scale-up synthesis

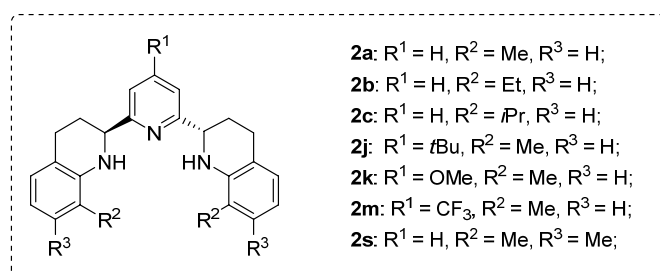
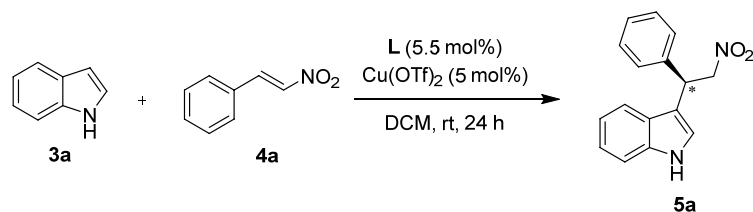


**Scheme S2.** Scale-up synthesis

**Typical procedure:** A 100 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate **1j** (2.4 mmol), Ru-catalyst  $(R,R)$ -**C1** (0.24 mmol) in 24 mL of HFIP under N<sub>2</sub> atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 °C for 48 h. Then the hydrogen gas was carefully released and the conversion was determined by <sup>1</sup>H NMR spectroscopy. The reaction mixture was filtered through a short pad of silica eluted with ethyl acetate and petroleum ether to give the chiral product  $(S,S)$ -**2j**. The diastereomeric ratio and the enantiomeric excess of the product was determined by HPLC with a chiral column.

## 7.2 Asymmetric Friedel–Crafts alkylation of indole

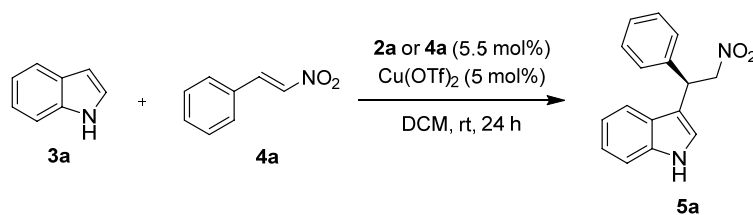
**Table S5.** Screening of chiral tridentate or tetradentate ligand-copper catalysts for catalytic asymmetric Friedel–Crafts alkylation with  $\beta$ -nitrostyrene



Entry	Ligand	Conv. (%) <sup>a</sup>	ee (%) <sup>b</sup>
1	<b>2a</b>	>99	65
2	<b>2b</b>	>99	57
3	<b>2c</b>	>99	29
4	<b>2j</b>	>99	64
5	<b>2k</b>	95%	53
6	<b>2m</b>	80%	55
7	<b>2s</b>	>99	62

[a] The reaction was performed at room temperature with 0.25 mmol of substrate and 5 mol % catalyst (Cu(OTf)<sub>2</sub>/L = 1:1.1) in 1 mL of dichloromethane unless stated otherwise. [b] The conversions were determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. [c] Determined by chiral HPLC analysis of the product using a Daicel Chiralcel OD-H column.

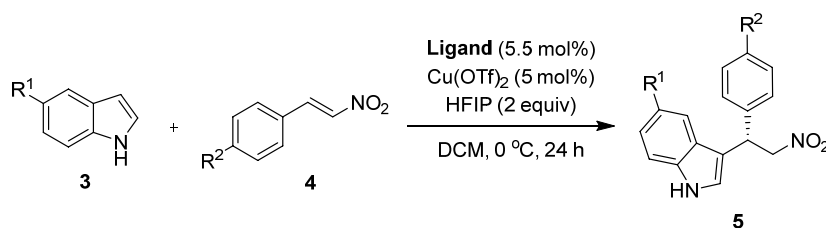
**Table S6.** Optimization of the reaction conditions for copper-catalyzed Friedel–Crafts alkylation with  $\beta$ -nitrostyrene.



Entry	Ligand	Temp ( $^{\circ}\text{C}$ )	additive	Conv. (%) <sup>a</sup>	ee (%) <sup>b</sup>
1	<b>2a</b>	25	-	>99	65
2	<b>2a</b>	25	HFIP <sup>c</sup>	>99	77
3	<b>2a</b>	0	HFIP <sup>c</sup>	>99	89
4	<b>2a</b>	-15	HFIP <sup>c</sup>	87	87

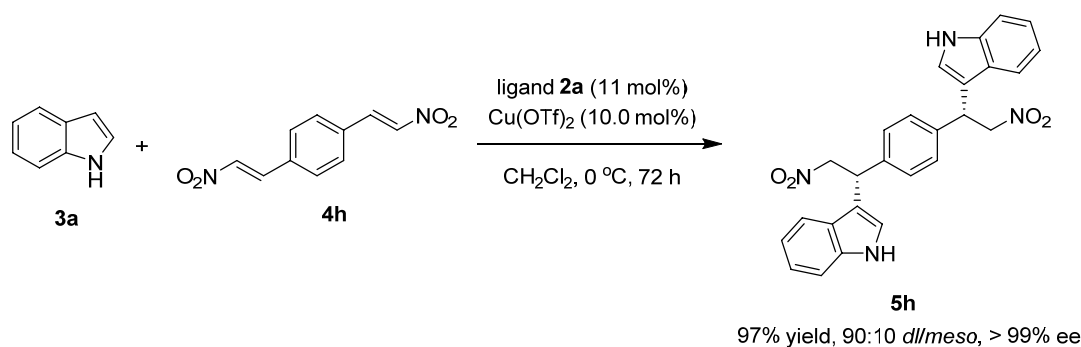
[a] The conversions were determined by  $^1\text{H}$  NMR spectroscopy of the crude reaction mixture. [b] Determined by chiral HPLC analysis of the product using a Daicel Chiralcel OD-H column. [c] Conditions: 2.0 equiv were added.

**Table S7.** Asymmetric Friedel–Crafts reaction of indoles with nitroalkenes: substrate scope.



Entry	Ligand	Substrate	Time (h)	Yield (%) <sup>a</sup>	ee (%) <sup>b</sup>
1	<b>2a</b>	$\text{R}^1 = \text{H}, \text{R}^2 = \text{H}$	24	98	89
2	<b>2a</b>	$\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$	24	99	91
3	<b>2a</b>	$\text{R}^1 = \text{OMe}, \text{R}^2 = \text{H}$	24	98	87
4	<b>2a</b>	$\text{R}^1 = \text{Br}, \text{R}^2 = \text{H}$	72	98	82
5	<b>2a</b>	$\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$	48	99	89
6	<b>2a</b>	$\text{R}^1 = \text{H}, \text{R}^2 = \text{OMe}$	48	98	87
7	<b>2a</b>	$\text{R}^1 = \text{H}, \text{R}^2 = \text{Cl}$	48	97	84

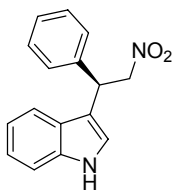
[a] Isolated yield. [b] Determined by chiral HPLC analysis of the product using Daicel Chiralcel OD-H and Chiralpak AD-H columns.



**Scheme S3.** Double asymmetric Friedel–Crafts reaction

**Synthesis of Cu(II) complexes (*S,S*)-2a-Cu(OTf)<sub>2</sub>.**<sup>[3c]</sup> The reduced product (*S,S*)-2a (0.1 mmol), Cu(OTf)<sub>2</sub> (0.1 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (5 mL) were added to a 25 mL round flask. The mixture was stirred for 6 h under nitrogen atmosphere until the starting materials were consumed as indicated by TLC. After the reaction completed, the solvent was removed under reduced pressure to afford (*S,S*)-2a-Cu(OTf)<sub>2</sub> as tan solid (99% yield). Crystals suitable for X-ray analysis were grown by diffusion of diethyl ether into a dichloromethane solution of (*S,S*)-2a-Cu(OTf)<sub>2</sub> at room temperature in glovebox. m.p. 175-177 °C.

**General procedure for the catalytic asymmetric Friedel–Crafts reaction:** Chiral tridentate and tetradentate pyridine-amine-type ligands PyBTHQs **2** (0.01375 mmol) and Cu(OTf)<sub>2</sub> (0.0125 mmol) were added to a round flask containing a stir bar under N<sub>2</sub>. 1 mL CH<sub>2</sub>Cl<sub>2</sub> was added to the flask and the mixture was stirred for 6 h. After cooling to 0 °C, to the mixture was added nitroalkene **4** (0.5 mmol), indole **3** (0.25 mmol) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, 0.5 mmol). After being stirred for appropriate time, the reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 9/1 to 2/1, v/v) to afford Friedel-Crafts adduct **5**. The diastereomeric ratio was determined by crude <sup>1</sup>H NMR. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H and Chiralpak AD-H. The absolute configurations were determined by comparison of the optical rotations and retention times on a chiral HPLC column with reported results.<sup>[3]</sup>



**(R)-3-(2-nitro-1-phenylethyl)-1H-indole ((R)-5a).** (Known compound, see:

Sato, T.; Arai, T. *Synlett* **2014**, 25, 349-354). 98% yield, yellow oil, 89% ee,

$[\alpha]_D^{20} = -21.9$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 89% ee);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)

8.08 (br, 1H), 7.45 (d,  $J = 8.0$  Hz, 1H), 7.37-7.18 (m, 7H), 7.09-7.04 (m, 2H),

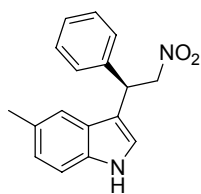
5.19 (t,  $J = 8.0$  Hz, 1H), 5.07 (dd,  $J = 12.8, 7.8$  Hz, 1H), 4.95 (dd,  $J = 12.5, 8.5$  Hz, 1H);  $^{13}\text{C}$

NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) 139.3, 136.6, 129.1, 127.9, 127.7, 126.3, 122.9, 121.7,

120.1, 119.1, 114.7, 111.5, 79.7, 41.7. HRMS (ESI)  $m/z$ :  $[\text{M} - \text{H}]^-$  Calcd for  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}_2$

265.09825; Found 265.09833.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel OD-H column (*n*-hexane : isopropanol = 70 : 30, flowing rate = 0.5 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 29.7$  min (minor),  $t_{R2} = 34.1$  min (major).



**(R)-5-methyl-3-(2-nitro-1-phenylethyl)-1H-indole ((R)-5b).** (Known

compound, see: Sato, T.; Arai, T. *Synlett* **2014**, 25, 349-354). 99% yield,

white solid, m.p. 141-142 °C. 91% ee,  $[\alpha]_D^{20} = +14.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 91%

ee);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.96 (br, 1H), 7.34-7.30 (m, 4H),

7.27-7.22 (m, 3H), 6.98 (dd,  $J = 8.3, 0.8$  Hz, 1H), 6.95 (d, 2.5 Hz, 1H), 5.15 (t,  $J = 8.0$  Hz,

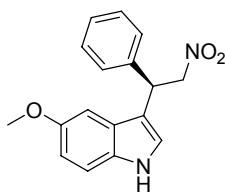
1H), 5.04 (dd,  $J = 12.5, 7.5$  Hz, 1H), 4.92 (dd,  $J = 12.5, 8.5$  Hz, 1H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR

(125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 139.4, 134.9, 129.4, 129.0, 127.9, 127.7, 126.5, 124.5, 121.9,

118.6, 114.0, 111.2, 79.7, 41.7, 21.7. HRMS (ESI)  $m/z$ :  $[\text{M} - \text{H}]^-$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$

279.11390; Found 279.11365.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel OD-H column (*n*-hexane : isopropanol = 70 : 30, flowing rate = 0.5 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 32.8$  min (major),  $t_{R2} = 51.9$  min (minor).



**(R)-5-methoxy-3-(2-nitro-1-phenylethyl)-1H-indole ((R)-5c).** (Known

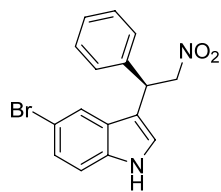
compound, see Sato, T.; Arai, T. *Synlett* **2014**, 25, 349-354). 98% yield,

white solid, m.p. 138-139 °C. 87% ee,  $[\alpha]_D^{20} = +22.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 87%

ee);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.99 (br, 1H), 7.34-7.30 (m,

4H), 7.27-7.23(m, 2H), 7.00 (d,  $J = 2.0$  Hz, 1H), 6.86-6.83 (m, 2H), 5.14 (t,  $J = 8.0$  Hz, 1H), 5.04 (dd,  $J = 12.5, 7.5$  Hz, 1H), 4.93 (dd,  $J = 12.3, 8.3$  Hz, 1H), 3.77 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 154.4, 139.3, 131.7, 129.1, 127.9, 127.7, 126.7, 122.4, 114.3, 112.9, 112.2, 101.0, 79.6, 56.0, 41.7. HRMS (ESI)  $m/z$ :  $[\text{M} - \text{H}]^-$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$  295.10882; Found 295.10861.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel OD-H column (*n*-hexane : isopropanol = 85 : 15, flowing rate = 0.5 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm),  $t_{\text{R}1} = 60.9$  min (major),  $t_{\text{R}2} = 81.8$  min (minor).

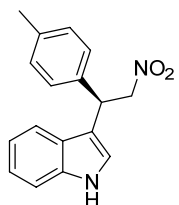


**(*R*)-5-bromo-3-(2-nitro-1-phenylethyl)-1H-indole ((*R*)-5d).** (Known

compound, see: Sato, T.; Arai, T. *Synlett* **2014**, 25, 349-354). 98% yield, white solid, m. p. 119-121 °C. 82% ee,  $[\alpha]_{\text{D}}^{20} = +58.3$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 82% ee);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.00 (br, 1H), 7.33-7.23 (m, 6H),

7.01-6.99 (m, 3H), 5.17 (t,  $J = 8.0$  Hz, 1H), 5.05 (dd,  $J = 12.5, 7.5$  Hz, 1H), 4.93 (dd,  $J = 12.5, 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 139.4, 136.2, 129.0, 127.9, 127.7, 125.8, 123.4, 121.4, 120.7, 120.3, 116.8, 115.1, 79.7, 41.8. HRMS (ESI)  $m/z$ :  $[\text{M} - \text{H}]^-$  Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2\text{Br}$  343.00876; Found 343.00836.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel OD-H column (*n*-hexane : isopropanol = 85 : 15, flowing rate = 0.5 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm),  $t_{\text{R}1} = 25.1$  min (major),  $t_{\text{R}2} = 37.5$  min (minor).



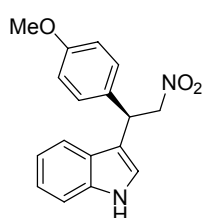
**(*R*)-3-(2-nitro-1-(p-tolyl)ethyl)-1H-indole ((*R*)-5e).** (Known compound, see:

Liu, H.; Du, D.-M. *Eur. J. Org. Chem.* **2010**, 2121-2131). 99% yield, yellow oil, 89% ee,  $[\alpha]_{\text{D}}^{20} = -12.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 89% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.96 (br, 1H), 7.42 (d,  $J = 8.0$  Hz, 1H), 7.26 (d,  $J = 8.0$  Hz,

1H), 7.18-7.13 (m, 3H), 7.09-7.02 (m, 3H), 6.89 (d,  $J = 2.0$  Hz, 1H), 5.11 (t,  $J = 8.0$  Hz, 1H), 4.98 (dd,  $J = 12.0, 7.6$  Hz, 1H), 4.86 (dd,  $J = 12.4, 8.4$  Hz, 1H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 137.3, 136.5, 136.3, 129.7, 127.7, 126.2, 122.7, 121.7, 120.0, 119.0, 114.5, 111.5, 79.7, 41.3, 21.1. HRMS (ESI)  $m/z$ :  $[\text{M} - \text{H}]^-$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$  279.11390;

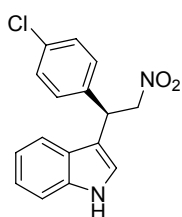
Found 279.11368.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel OD-H column (*n*-hexane : isopropanol = 70 : 30, flowing rate = 0.5 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 36.3$  min (minor),  $t_{R2} = 41.3$  min (major).



**(R)-3-(1-(4-methoxyphenyl)-2-nitroethyl)-1H-indole ((R)-5f).** (Known compound, see: Sato, T.; Arai, T. *Synlett* **2014**, 25, 349-354). 98% yield, white solid, m.p. 149-150 °C. 87% ee,  $[\alpha]_D^{20} = -13.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 87% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.06 (br, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 7.32 (d,  $J = 8.0$  Hz, 1H), 7.24-7.16 (m, 3H), 7.06 (t,  $J = 7.2$  Hz, 1H), 6.97 (s, 1H), 6.83 (d,  $J = 8.0$  Hz, 2H), 5.12 (t,  $J = 7.6$  Hz, 1H), 5.05-5.00 (m, 1H), 4.90-4.85 (m, 1H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 159.0, 136.6, 131.3, 128.9, 126.2, 122.8, 121.6, 120.0, 119.1, 114.9, 114.4, 111.5, 79.9, 55.4, 41.0. HRMS (ESI)  $m/z$ :  $[\text{M} - \text{H}]^-$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$  295.10882; Found 295.10870.

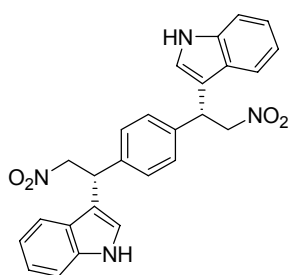
The enantiomeric excess was determined by HPLC on the connection of Chiralcel OD-H column (*n*-hexane : isopropanol = 70 : 30, flowing rate = 0.5 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm),  $t_{R1} = 52.6$  min (minor),  $t_{R2} = 59.3$  min (major).



**(R)-3-(1-(4-chlorophenyl)-2-nitroethyl)-1H-indole ((R)-5g).** (Known compound, see: Liu, H.; Du, D.-M. *Eur. J. Org. Chem.* **2010**, 2121-2131). 97% yield, yellow oil, 84% ee,  $[\alpha]_D^{20} = -6.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 84% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.05 (br, 1H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.26-7.16 (m, 5H), 7.06 (t,  $J = 7.6$  Hz, 1H), 6.92 (d,  $J = 0.8$  Hz, 1H), 5.12 (t,  $J = 7.8$  Hz, 1H), 4.99 (dd,  $J = 12.6, 7.4$  Hz, 1H), 4.85 (dd,  $J = 12.6, 8.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 137.8, 136.6, 133.5, 129.2, 129.2, 126.0, 122.9, 121.6, 120.2, 118.9, 113.9, 111.6, 79.4, 41.0. HRMS (ESI)  $m/z$ :  $[\text{M} - \text{H}]^-$  Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2\text{Cl}$  299.05928; Found 299.05914.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel OD-H column (hexane : isopropanol = 70 : 30, flowing rate = 0.5 mL/min, 25 °C, UV detection at  $\lambda$

= 254 nm),  $t_{R1}$  = 52.3 min (minor),  $t_{R2}$  = 63.9 min (major).



**1,4-bis((*R*)-1-(1H-indol-3-yl)-2-nitroethyl)benzene ((*R,R*)-5h).**

(Known compound, see: Sato, T.; Arai, T. *Synlett* **2014**, 25, 349-354). 97% yield, white solid, m.p. 101-102 °C. 90:10 *dl/meso*, > 99% ee,  $[\alpha]_D^{20}$  = +19.2 ( $c$  = 1.0, CHCl<sub>3</sub>, > 99% ee); <sup>1</sup>H NMR (300 MHz, acetone-*d*<sup>6</sup>):  $\delta$  (ppm) 10.20 (br, 2H), 7.50-7.34 (m, 10H), 7.08 (t,  $J$  = 7.5 Hz, 2H), 6.97-6.92 (m, 2H), 5.28-5.10 (m, 6H); <sup>13</sup>C NMR (75 MHz, acetone-*d*<sup>6</sup>):  $\delta$  (ppm) 140.4, 137.8, 129.2, 127.4, 123.1, 123.1, 122.8, 120.0, 119.6, 114.9, 112.5, 80.2, 42.0. HRMS (ESI)  $m/z$ : [M - H]<sup>-</sup> Calcd for C<sub>26</sub>H<sub>21</sub>O<sub>4</sub>N<sub>4</sub> 453.15683; Found 453.15656.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel AD-H column (hexane : isopropanol = 70 : 30, flowing rate = 0.7 mL/min, 25 °C, UV detection at  $\lambda$  = 254 nm),  $t_{R1}$  = 37.3 min (major).

## 8. References

- [1] (a) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *128*, 8724. (b) Wang, T. L.; Zhuo, L.-G.; Li, Z.; Chen, F.; Ding, Z.; He, Y.-M.; Fan, Q.-H.; Xiang, J.-F.; Yu, Z.-X.; Chan, A. S. C. *J. Am. Chem. Soc.* **2011**, *133*, 9878.
- [2] (a) Bertrand, H.; Bombard, S.; Monchaud, D.; Talbot, E.; Gúedin, A.; Mergny, J.-L.; Grünert, R.; Bednarski, P. -J.; Teulade-Fichou, M.-P. *Org. Biomol. Chem.* **2009**, *7*, 2864. (b) Largy, E.; Hamon, F.; Rosu, F.; Gabelica, V.; Pauw, E.-D.; Gúedin, A.; Mergny, J.-L.; Teulade-Fichou, M.-P. *Chem. Eur. J.* **2011**, 13274. (c) Liu, Y.-R.; Chen, F.; He, Y.-M.; Li, C.-H.; Fan, Q.-H. *Org. Biomol. Chem.* **2019**, *17*, 5099. (d) Seitz, M.; Milius, W.; Alt, H.-G. *J. Mol. Catal. A: Chem.* **2007**, *261*, 246. (e) Darmon, J.-M.; Turner, Z.-R.; Lobkovsky, E.; Chirik, P.-J. *Organometallics*. **2012**, *31*, 2275. (f) Nüchel, S.; Burger, P. *Organometallics* **2001**, *20*, 4345. (g) Gygi, D.; Hwang, S.-J.; Nocera, D.-H. *J. Org. Chem.* **2017**, *82*, 12933.
- [3] (a) Liu, H.; Du, D.-M. *Eur. J. Org. Chem.* **2010**, 2121-2131. (b) Wu, J.; Li, X.; Wu, F.; Wan, B. *Org. Lett.* **2011**, *13*, 4834-4837. (c) Sato, T.; Arai, T. *Synlett* **2014**, *25*, 349-354.

## 9. Copy of NMR spectra for all substrates and products

Figure S4.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **1a** ( $\text{CDCl}_3$ )

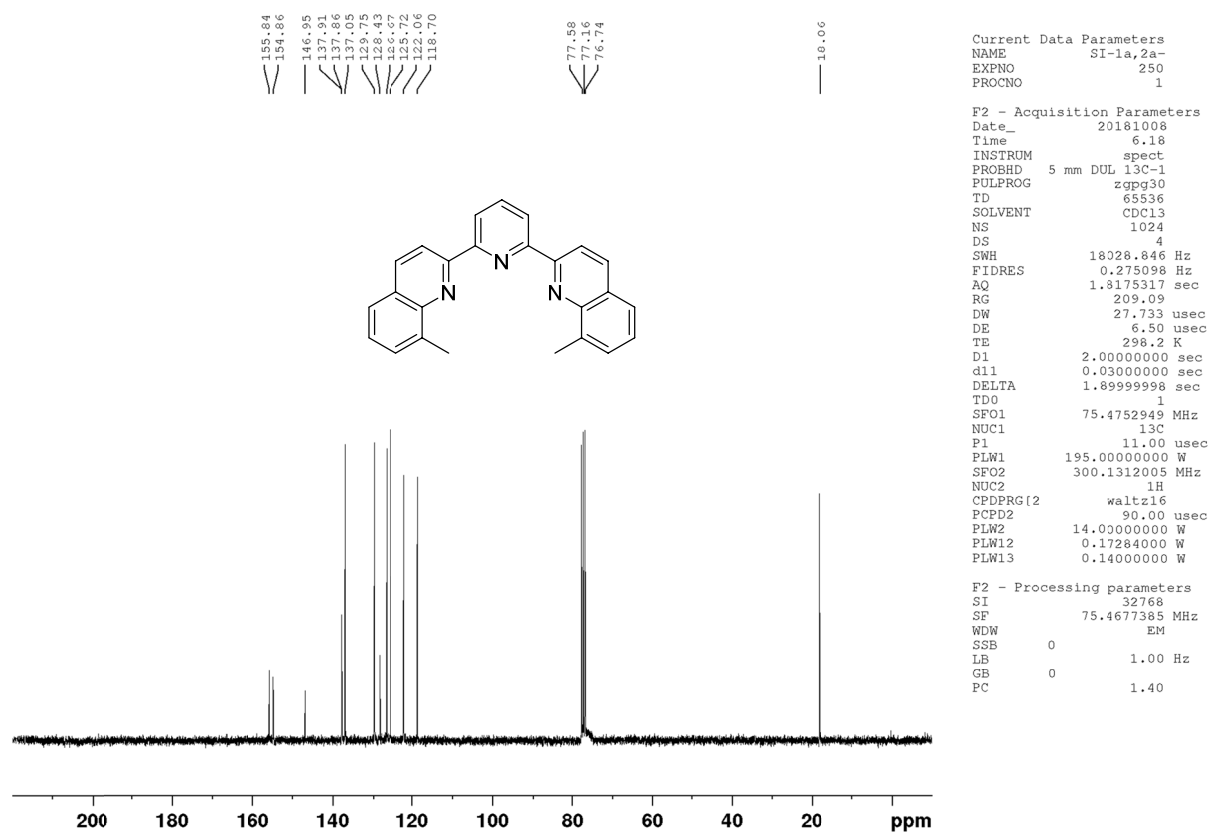
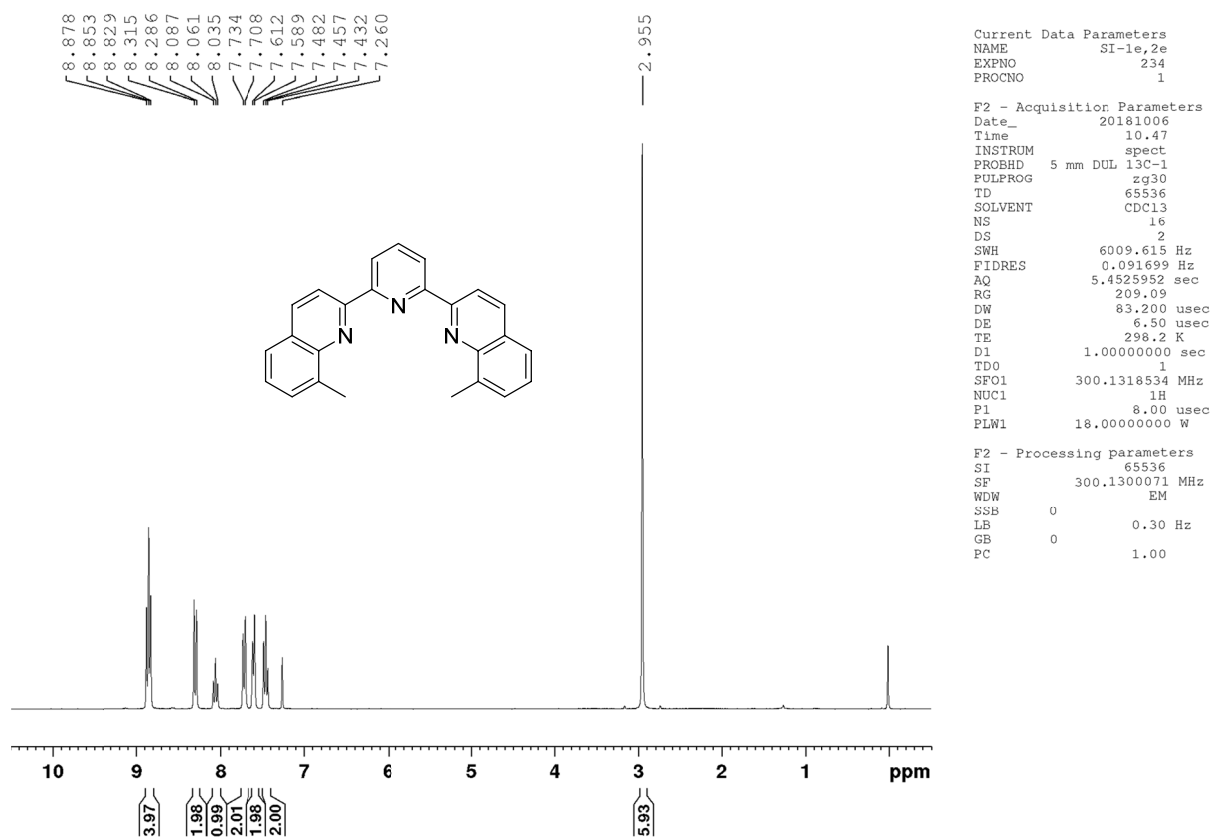


Figure S5. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1b** (CDCl<sub>3</sub>)

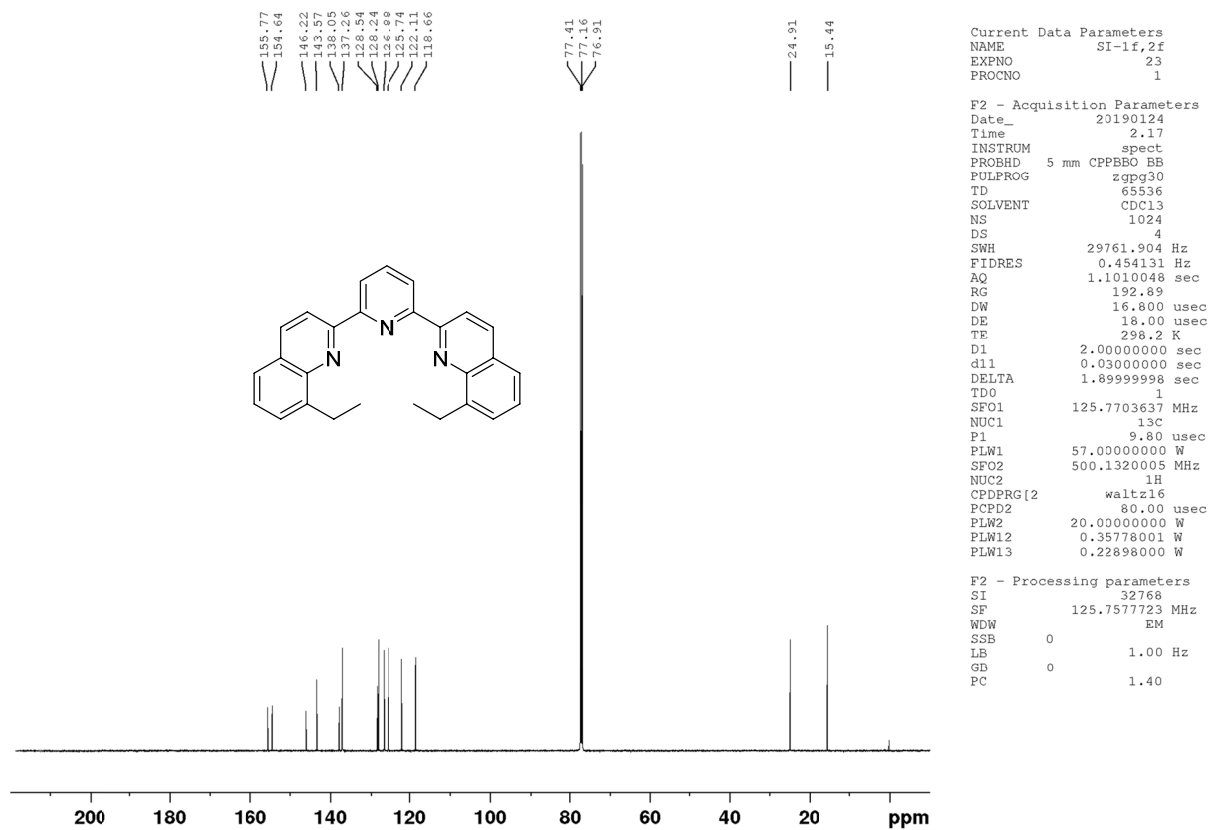
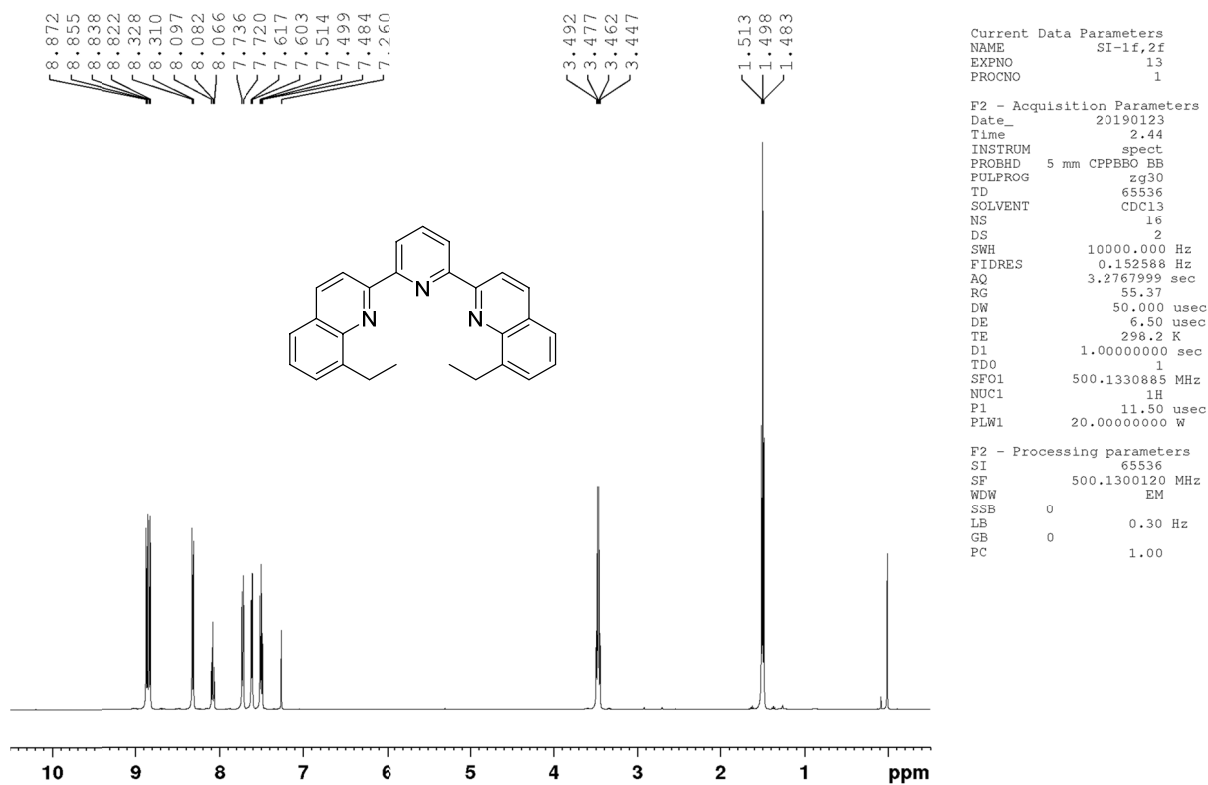


Figure S6. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1c** (CDCl<sub>3</sub>)

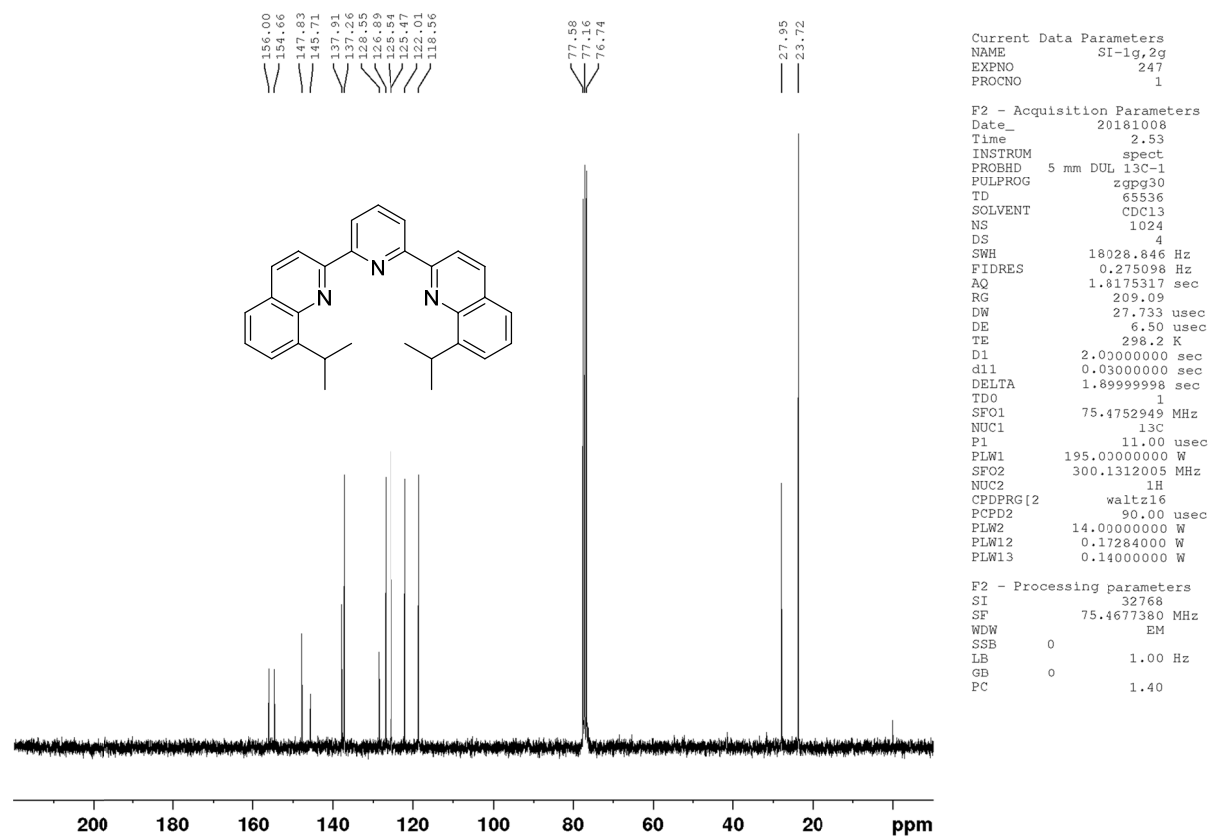
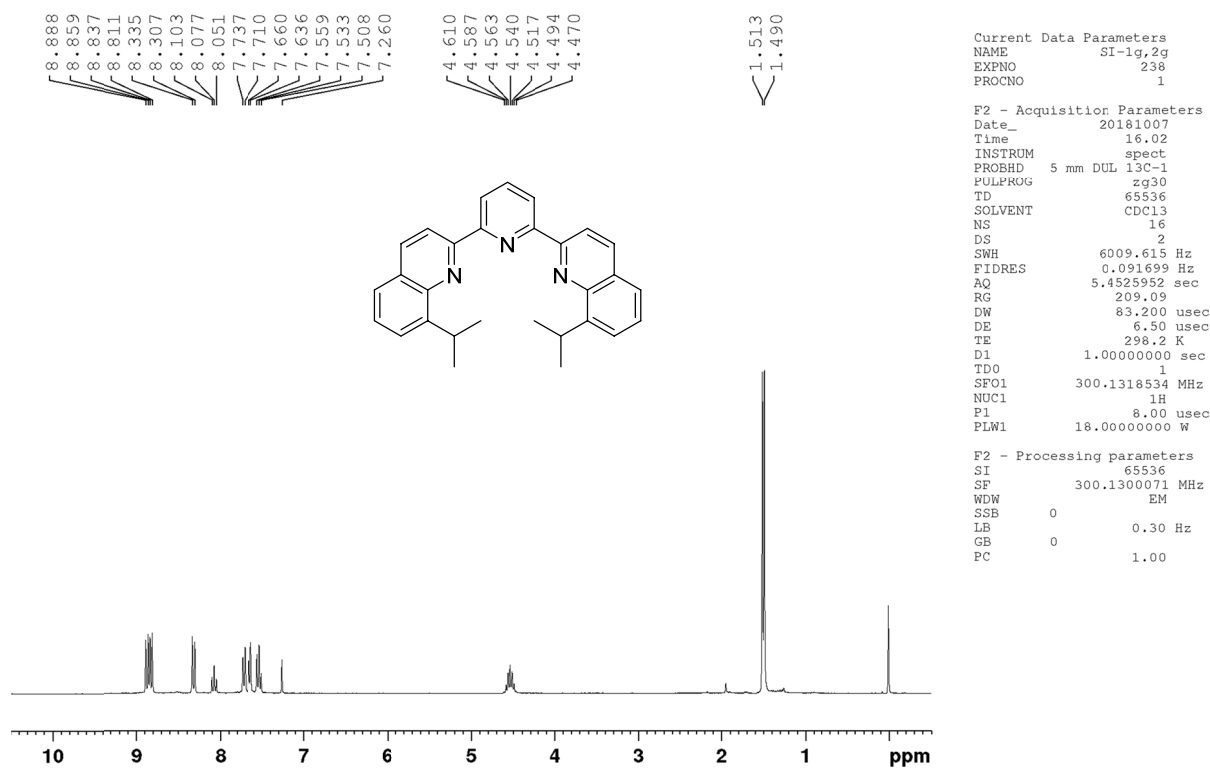
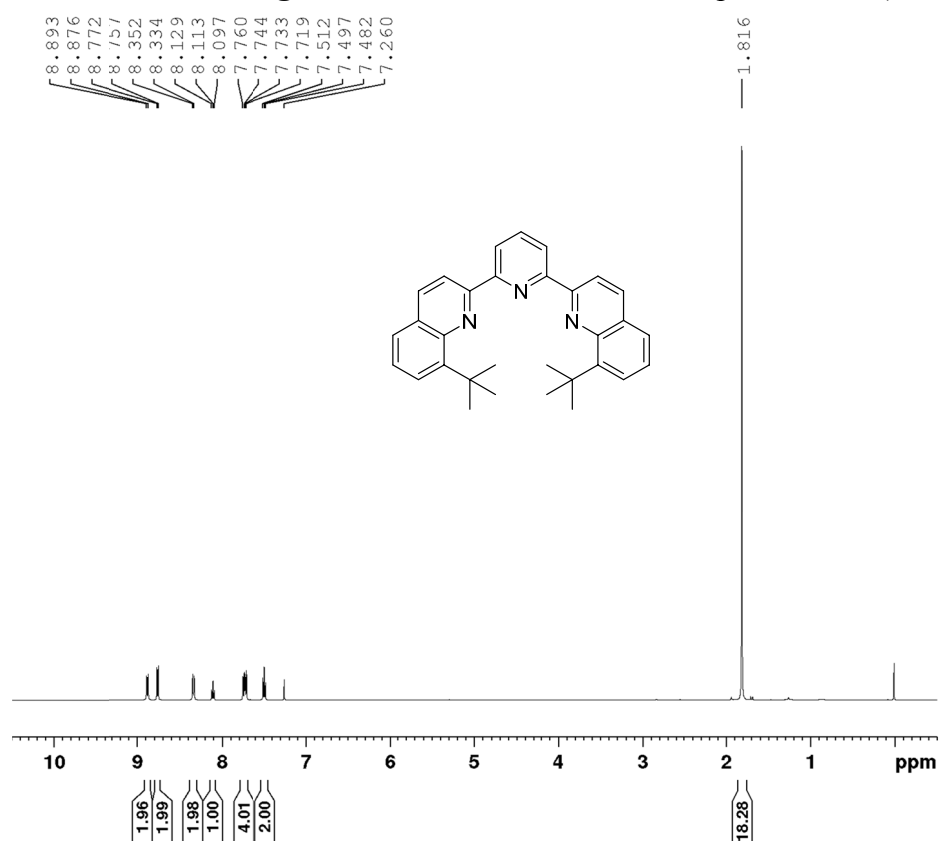


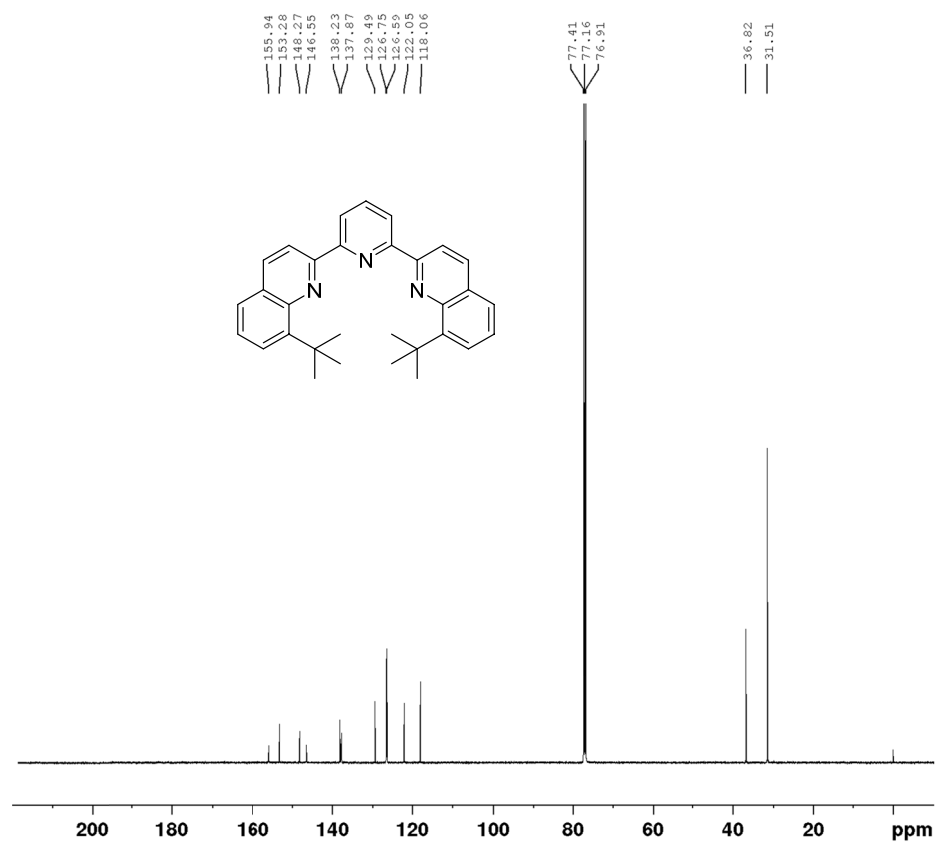
Figure S7. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1d** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-7-Me-8-tBu-2  
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 PROCNO 1

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 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 55.37  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.0000000 sec  
 TD0 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 11.50 usec  
 PLW1 20.0000000 W

F2 - Processing parameters  
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 SF 500.1300119 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

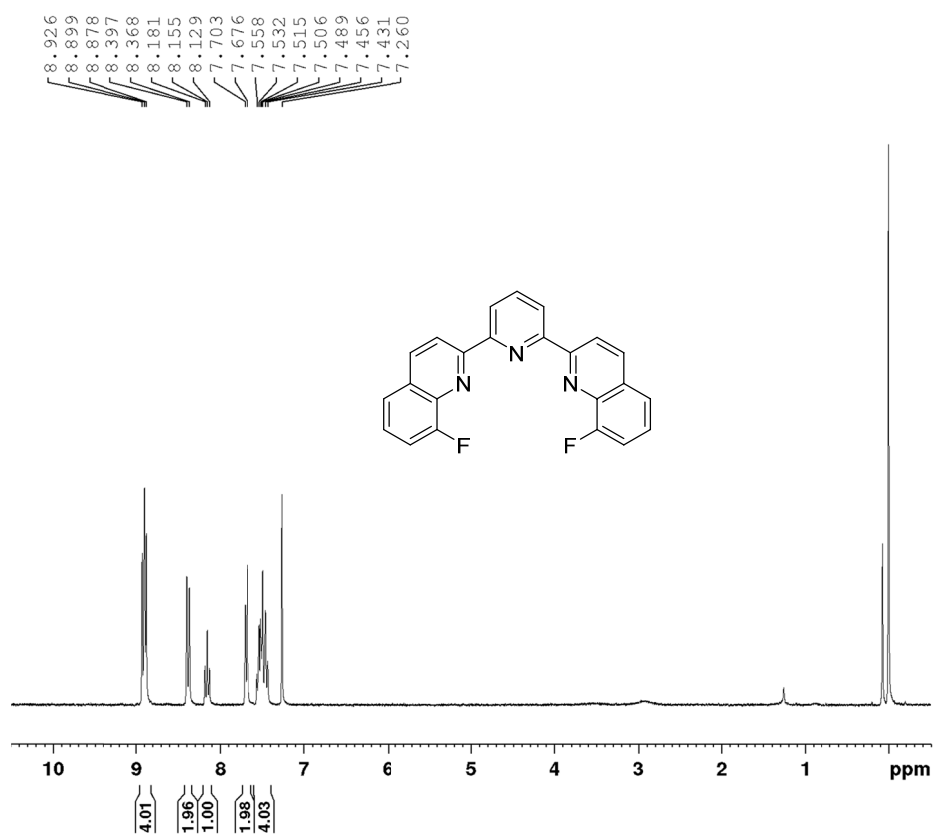


Current Data Parameters  
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 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
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 Time 4.40  
 INSTRUM spect  
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 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.1 K  
 D1 2.0000000 sec  
 d11 0.0300000 sec  
 DELTA 1.89999998 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.0000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.0000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
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 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

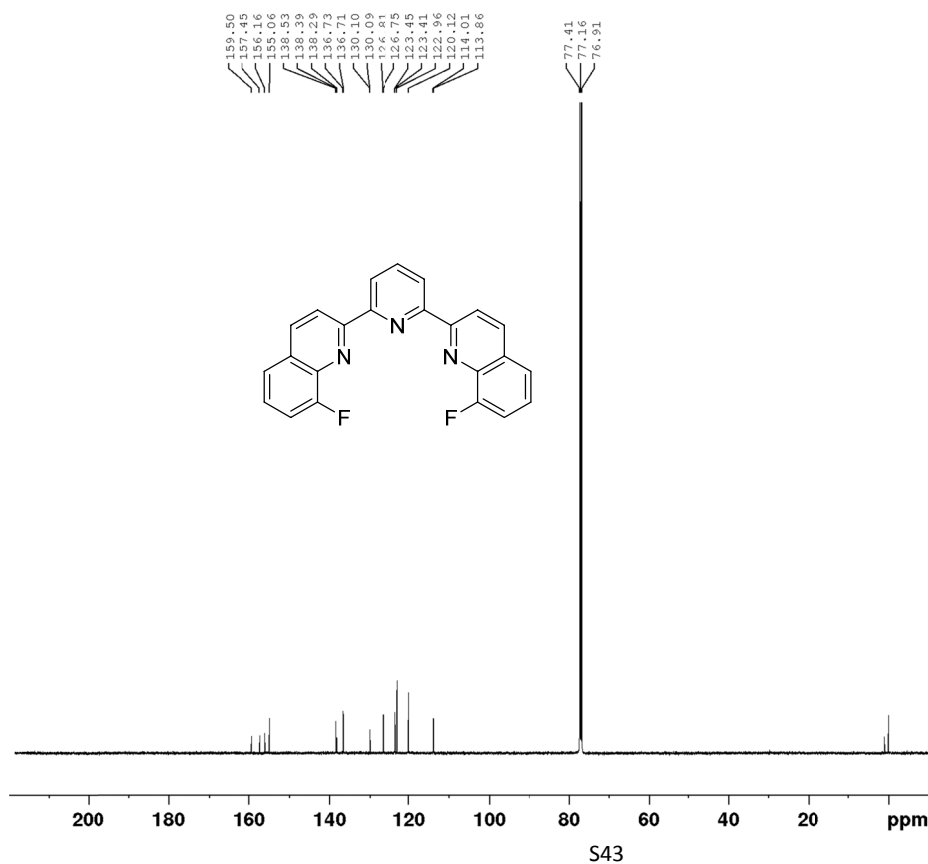
Figure S8. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1e** (CDCl<sub>3</sub>)



Current Data Parameters  
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 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20181007  
 Time 17.08  
 INSTRUM spect  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6009.615 Hz  
 FIDRES 0.091699 Hz  
 AQ 5.4525952 sec  
 RG 209.09  
 DW 83.200 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 TD0 1  
 SFO1 300.1318534 MHz  
 NUC1 1H  
 P1 8.00 usec  
 PLW1 18.00000000 W

F2 - Processing parameters  
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 SF 300.1300072 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

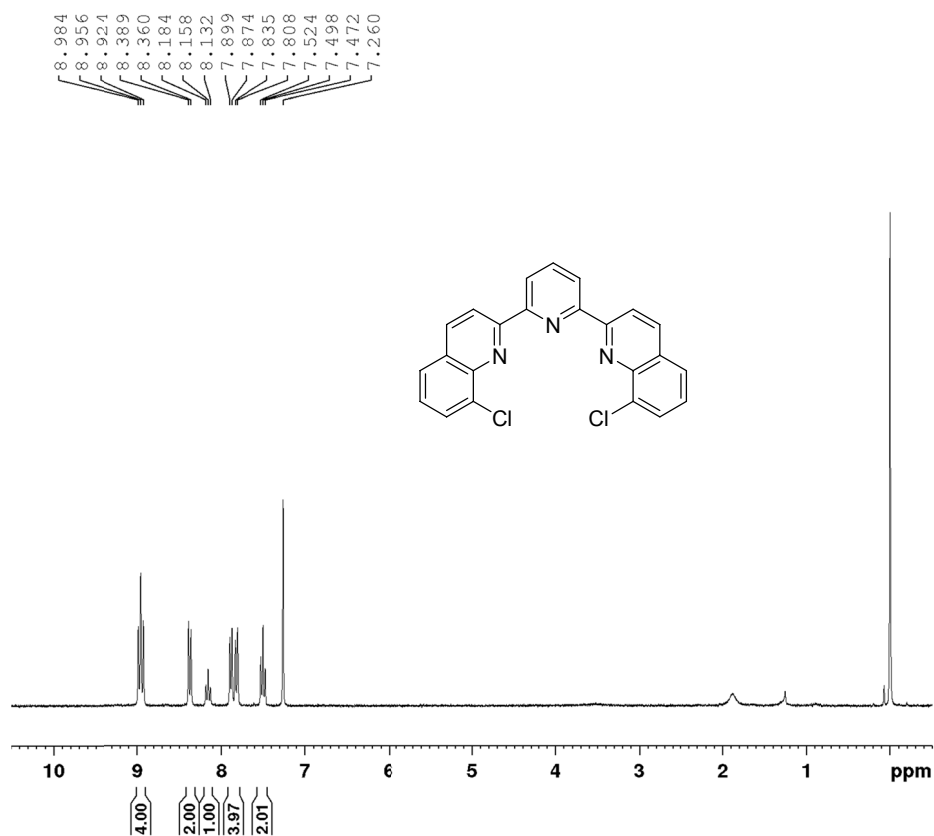


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 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.859999998 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing Parameters  
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 SF 125.7577713 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

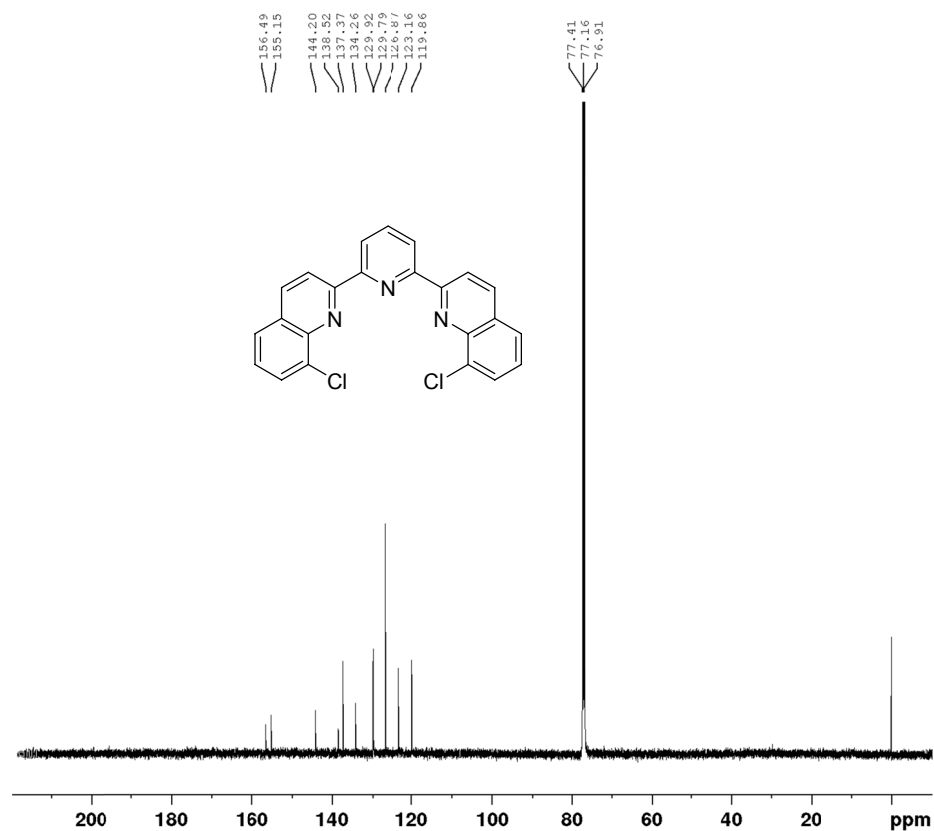
Figure S9. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1f** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1f,2f  
 EXPNO 244  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20181007  
 Time 17.25  
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 PROBHD 5 mm DUL 13C-1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6009.615 Hz  
 FIDRES 0.091699 Hz  
 AQ 5.452592 sec  
 RG 209.09  
 DW 83.200 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.0000000 sec  
 TD0 1  
 SFO1 300.1318534 MHz  
 NUC1 1H  
 P1 8.00 usec  
 PLW1 18.00000000 W

F2 - Processing parameters  
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 LB 0.30 Hz  
 GB 0  
 PC 1.00

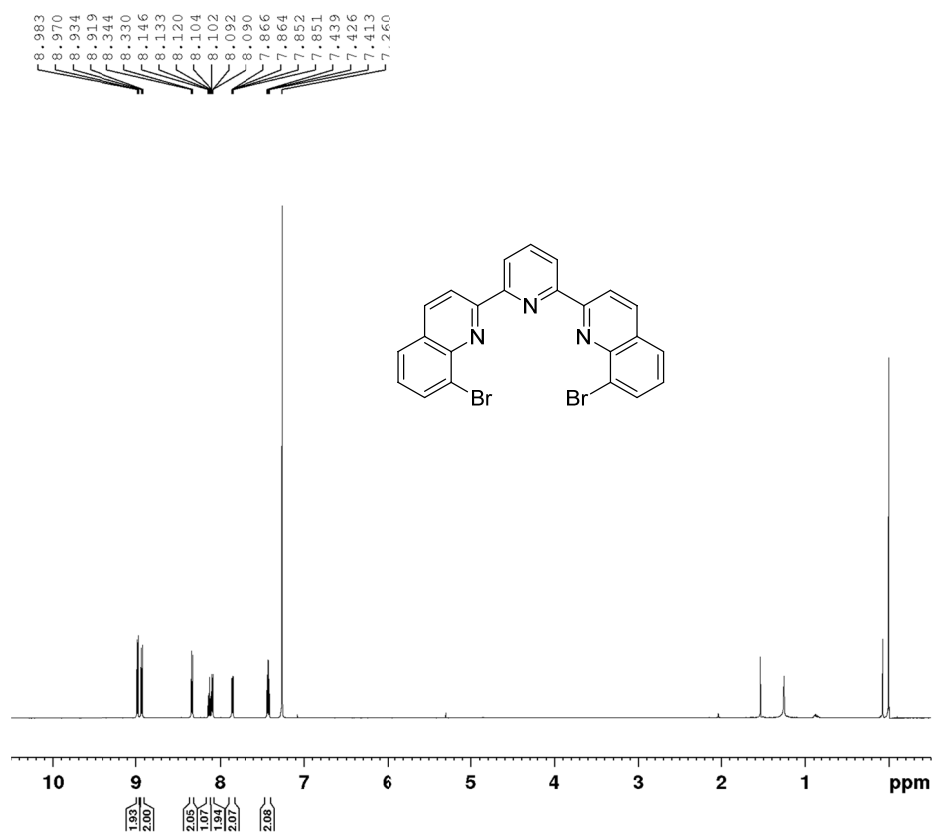


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 Time 9.06  
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 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.1 K  
 D1 2.0000000 sec  
 d11 0.0300000 sec  
 DELTA 1.89999998 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.0000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.0000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
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 WDW RM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

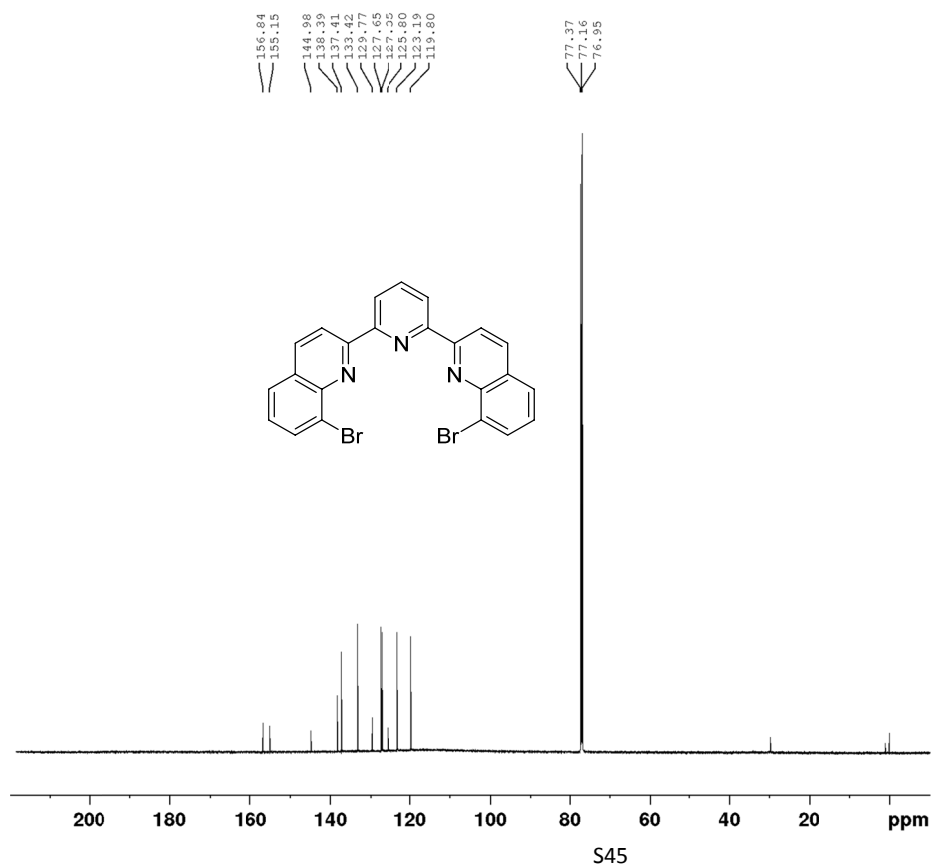
Figure S10. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1g** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1g,2g  
 EXPNO 15  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20191213  
 Time 21.08  
 INSTRUM Avance  
 PROBHD Z124704\_0003 ( )  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 11904.762 Hz  
 FIDRES 0.181652 Hz  
 AQ 2.7525120 sec  
 RG 101  
 DW 42.000 usec  
 DE 11.43 usec  
 TE 297.5 K  
 D1 1.00000000 sec  
 TDO 1  
 SFO1 600.1337058 MHz  
 NUC1 1H  
 P1 15.00 usec  
 PLW1 30.60499954 W

F2 - Processing parameters  
 SI 65536  
 SF 600.1300147 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME SI-1g,2g-  
 EXPNO 16  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20191214  
 Time 11.10  
 INSTRUM Avance  
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 PULPROG zgpg  
 TD 32768  
 SOLVENT CDCl3  
 NS 25000  
 DS 4  
 SWH 35714.285 Hz  
 FIDRES 1.089913 Hz  
 AQ 0.4587520 sec  
 RG 101  
 DW 14.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 1.50000000 sec  
 d11 0.03000000 sec  
 DELTA 1.39999998 sec  
 TDO 1  
 SFO1 150.9178988 MHz  
 NUC1 13C  
 P1 12.00 usec  
 PLW1 51.29700089 W  
 SFO2 600.1324005 MHz  
 NUC2 1H  
 CPDPRG2 waltz65  
 PCPD2 70.00 usec  
 PLW2 30.60499954 W  
 PLW12 1.40530002 W  
 PLW13 0.70686001 W

F2 - Processing parameters  
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 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S11. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1h** (CDCl<sub>3</sub>)

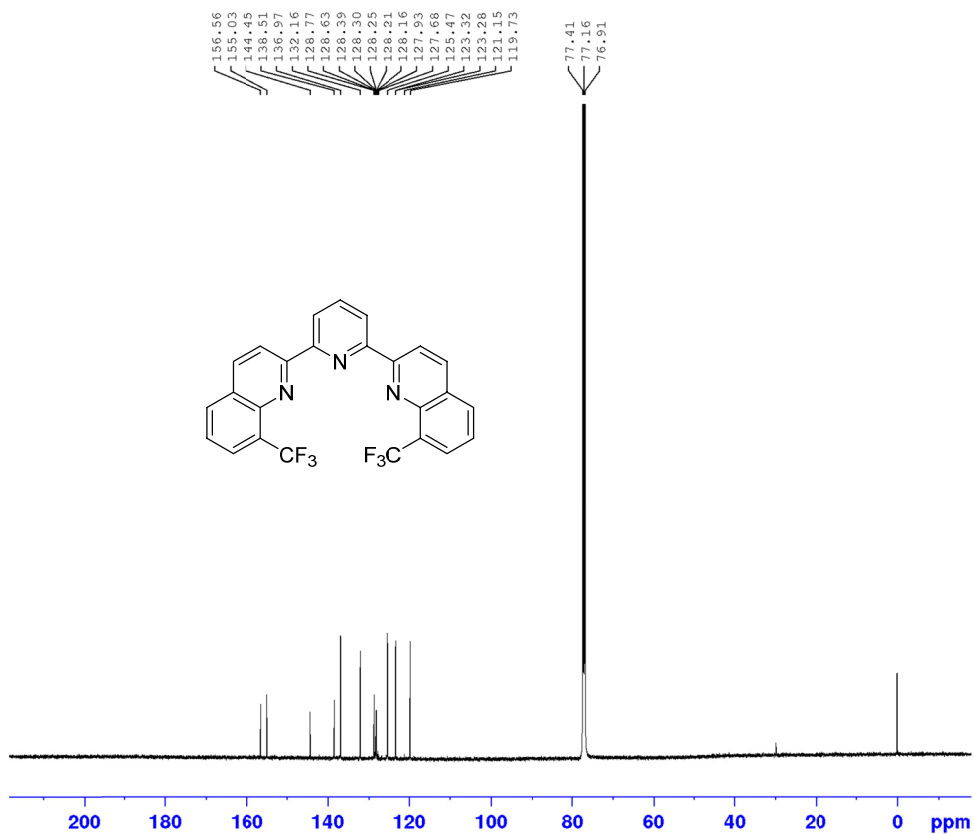
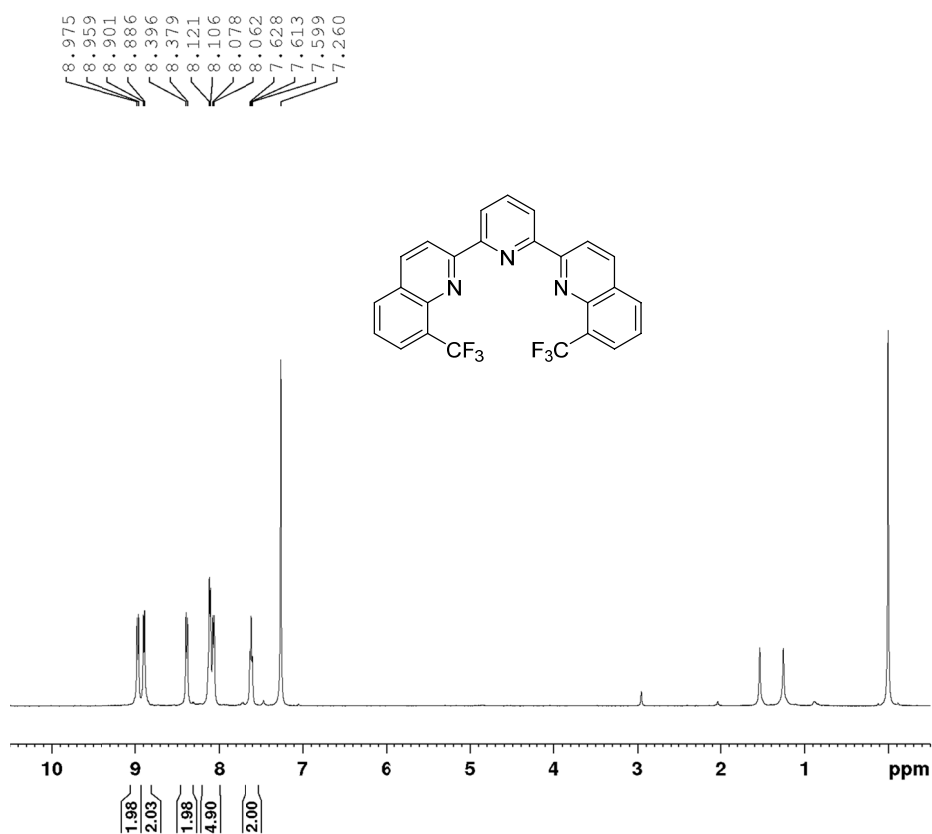


Figure S12. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1i** (CDCl<sub>3</sub>)

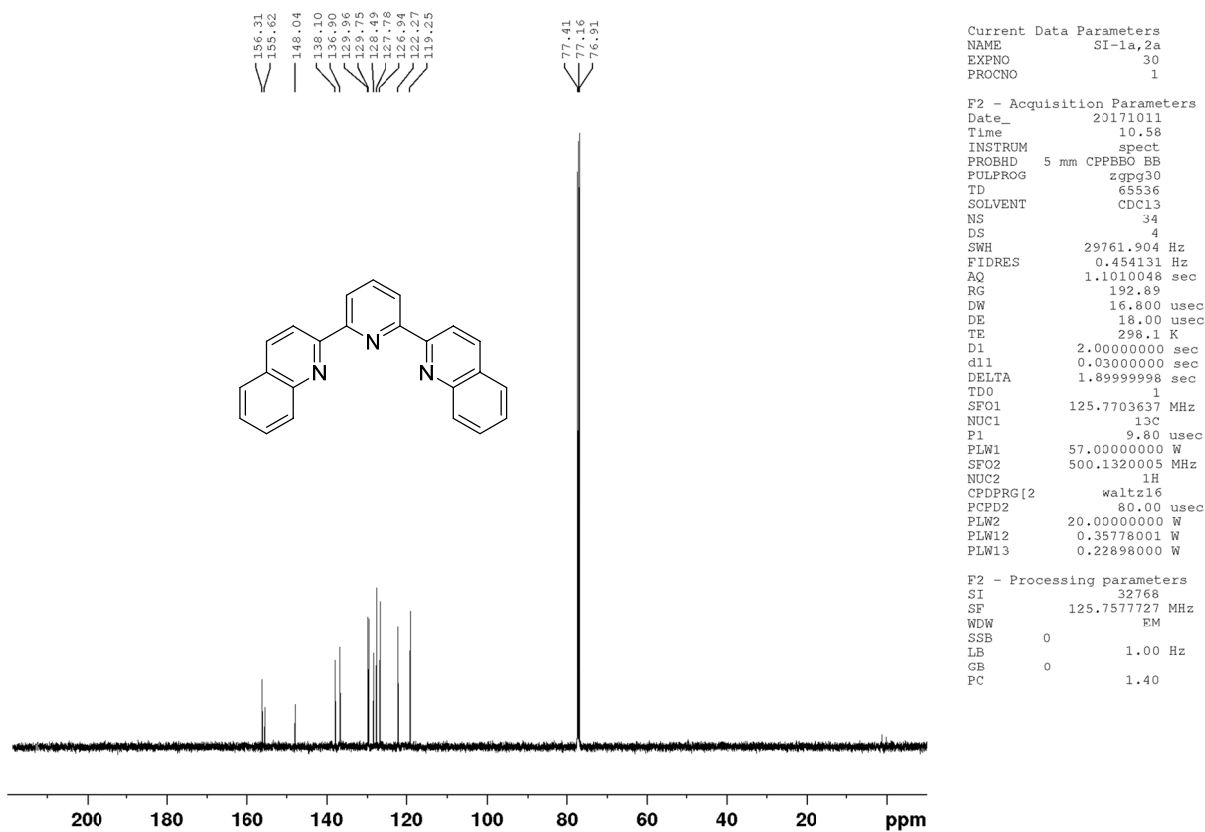
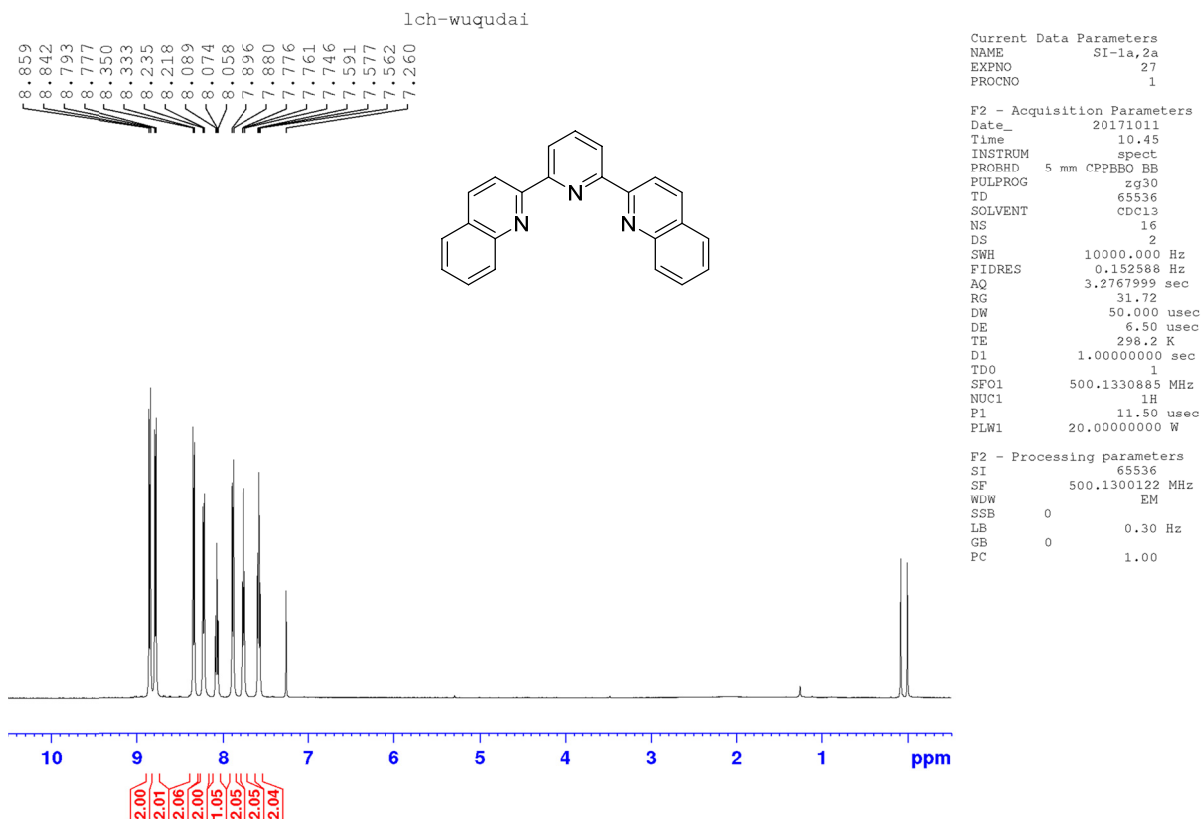


Figure S13. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1j** (CDCl<sub>3</sub>)

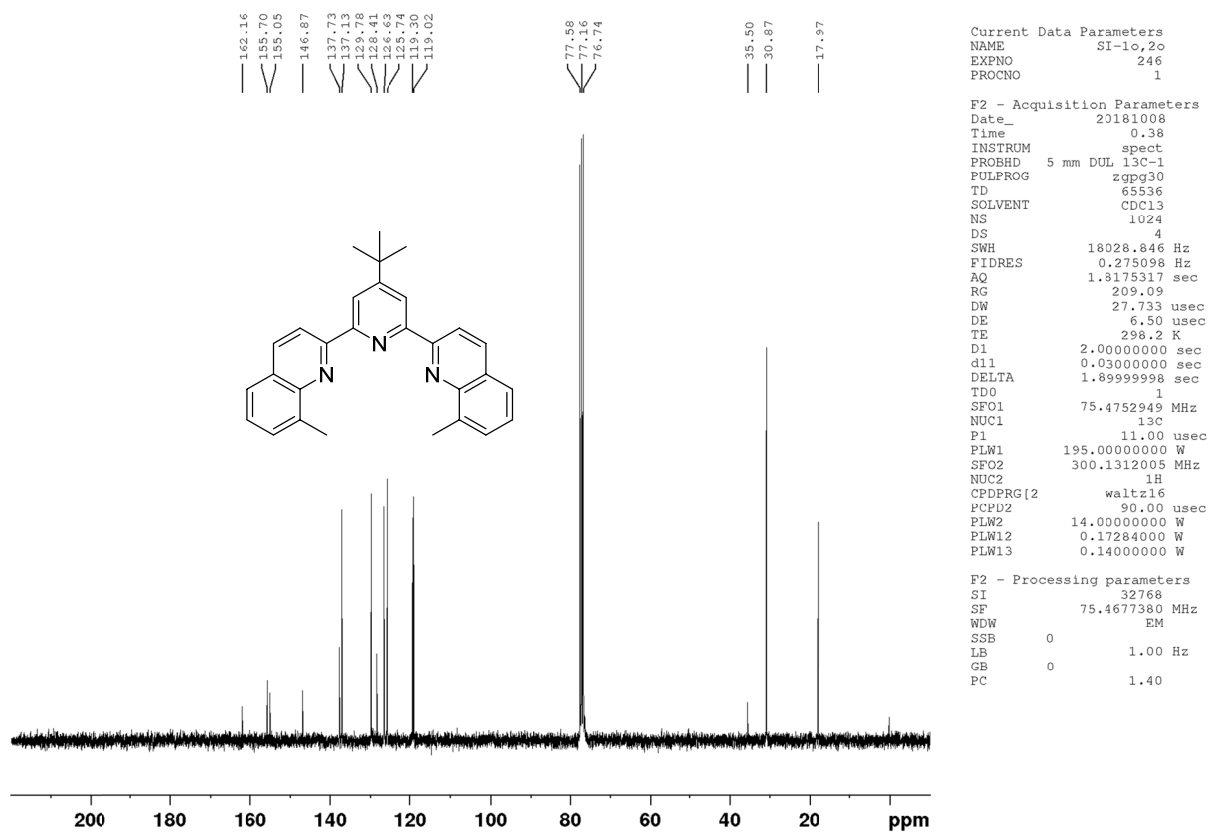
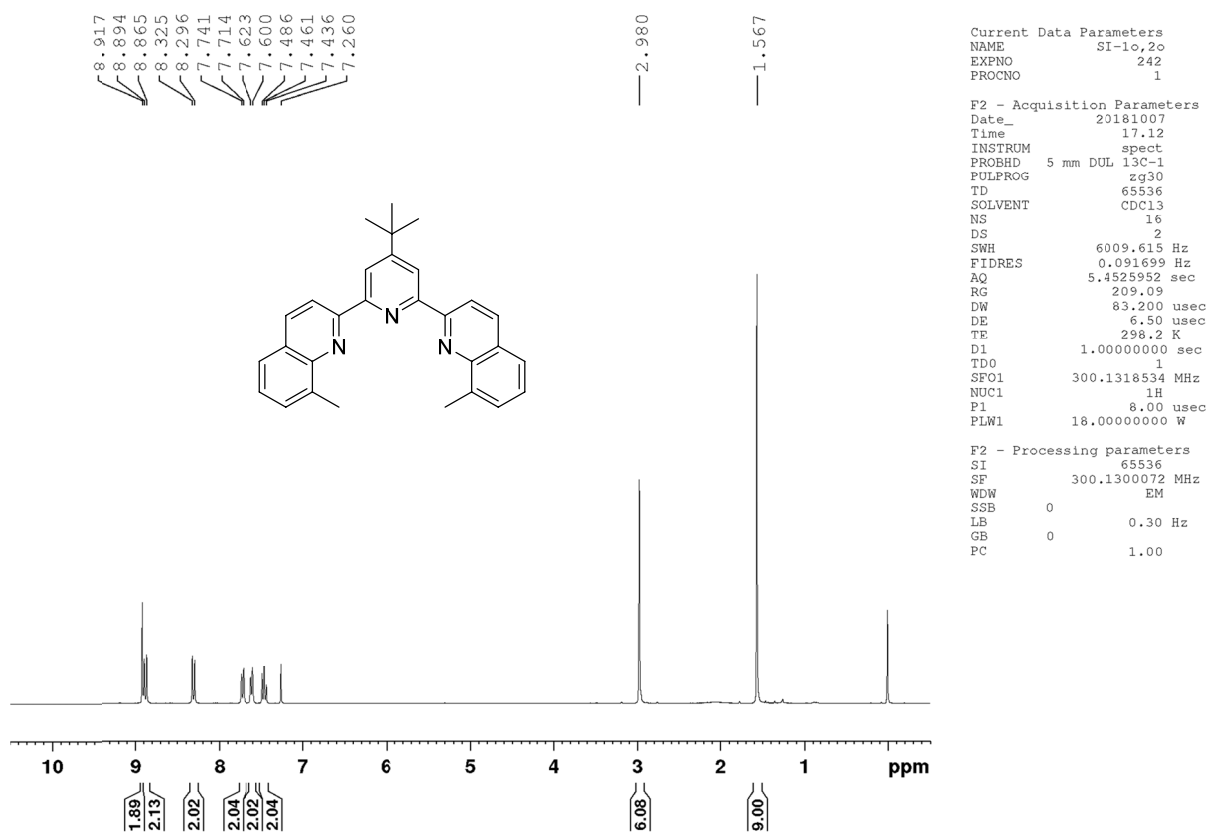
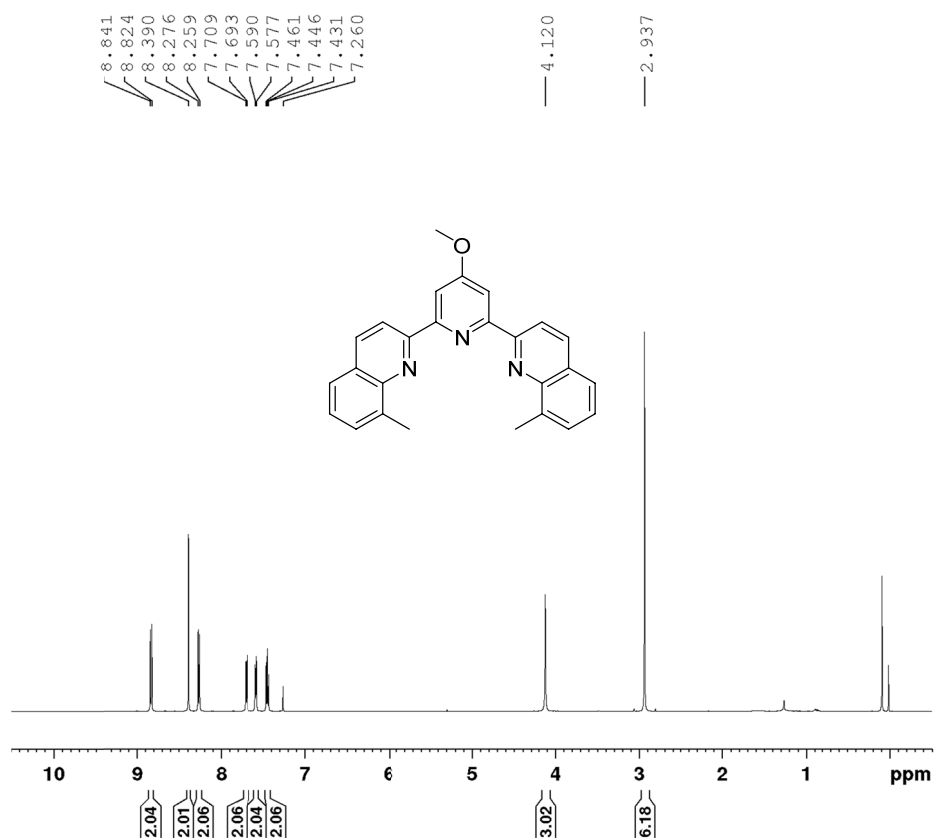


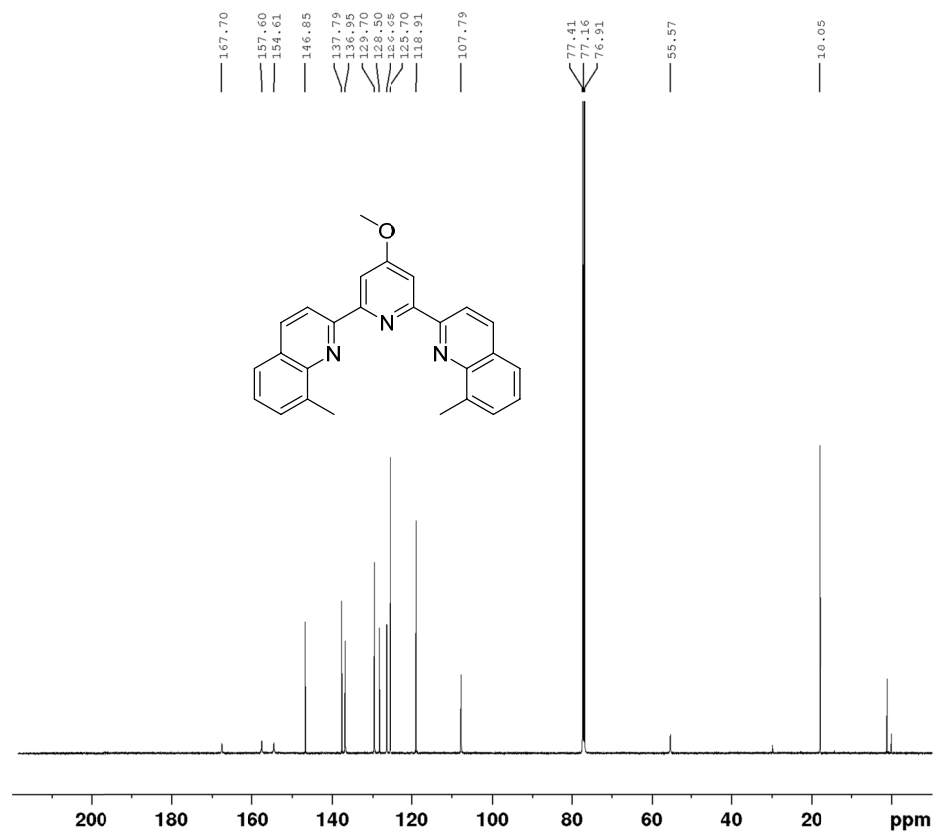
Figure S14. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1k** (CDCl<sub>3</sub>)



Current Data Parameters  
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 PROCNO 1

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 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 49.27  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.00000000 sec  
 TD0 1  
 SFO1 500.1330805 MHz  
 NUC1 1H  
 P1 11.50 usec  
 PLW1 20.0000000 W

F2 - Processing parameters  
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 GB 0  
 PC 1.00

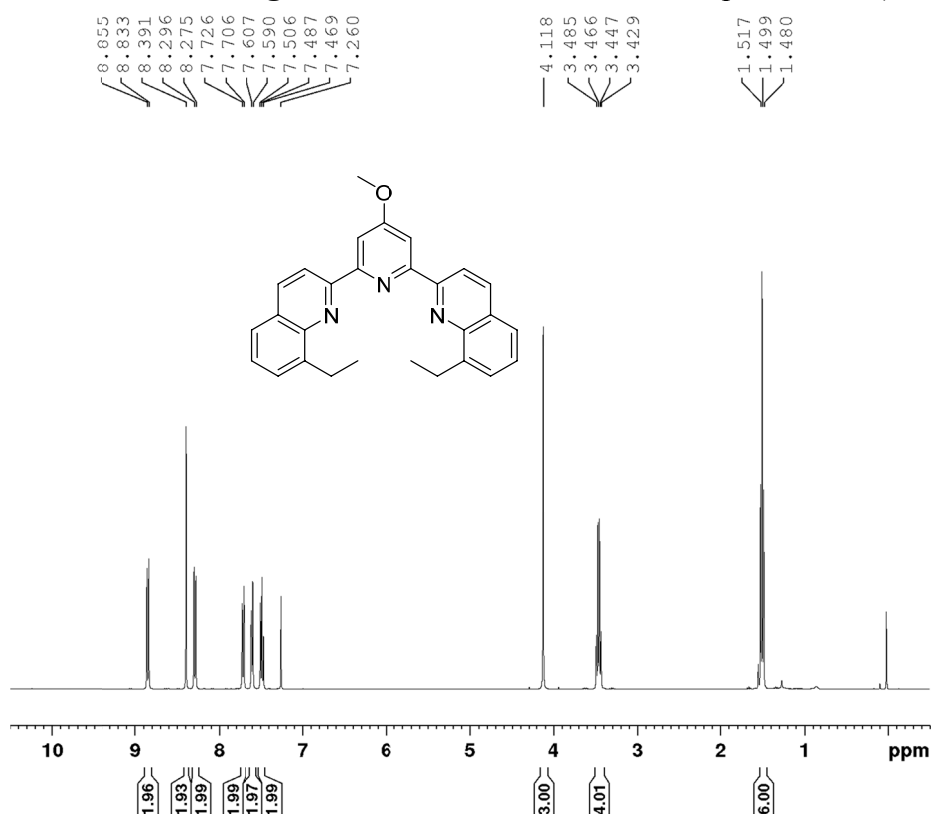


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 PROCNO 1

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 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1646  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.1 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLN1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

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 LB 1.00 Hz  
 GB 0  
 PC 1.40

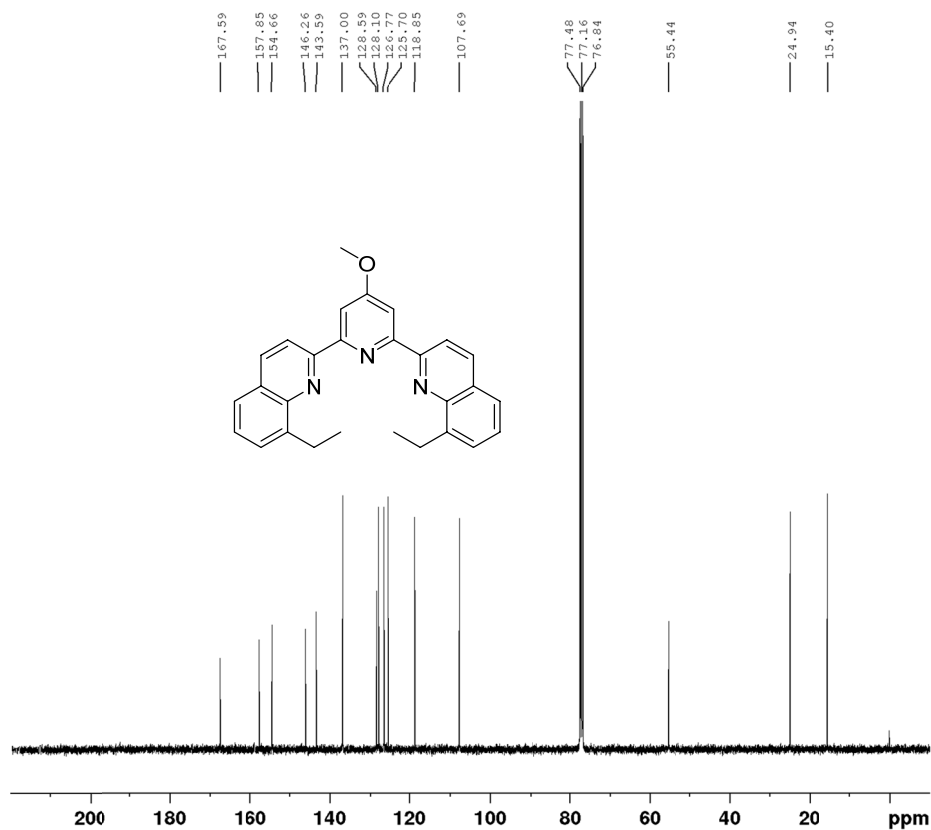
Figure S15. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **11** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-lr,2r  
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 PROCNO 1

F2 - Acquisition Parameters  
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 Time\_ 0.38  
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 PROBHD 5 mm PABBO BB/  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 16  
 DS 0  
 SWH 8012.820 Hz  
 FIDRES 0.244532 Hz  
 AQ 2.0447233 sec  
 RG 206.33  
 DW 62.400 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 2.0000000 sec  
 TD0 1  
 SFO1 400.2424716 MHz  
 NUC1 1H  
 P1 14.30 usec  
 PLW1 12.00000000 W

F2 - Processing parameters  
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 SF 400.2400097 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

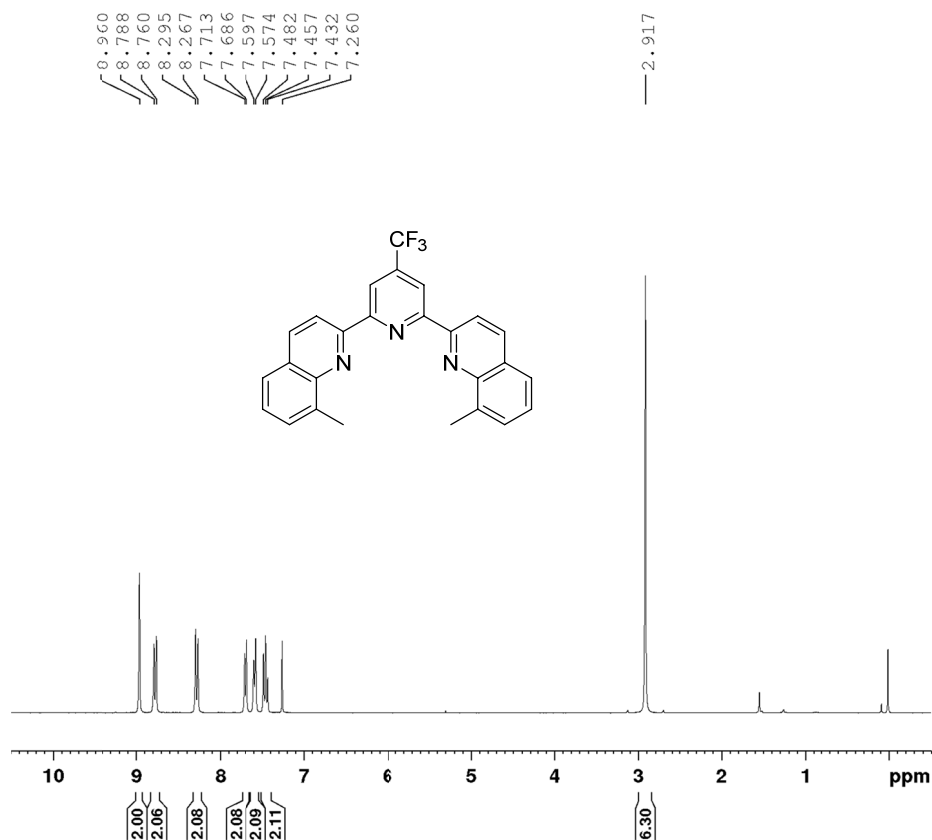


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 PROCNO 1

F2 - Acquisition Parameters  
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 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 24038.461 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 206.33  
 DW 20.800 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 2.0000000 sec  
 d11 0.0300000 sec  
 DELTA 1.89999999 sec  
 TD0 1  
 SFO1 100.6504916 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 54.0000000 W  
 SFO2 400.2416010 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
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 PLW12 0.30294999 W  
 PLW13 0.24539000 W

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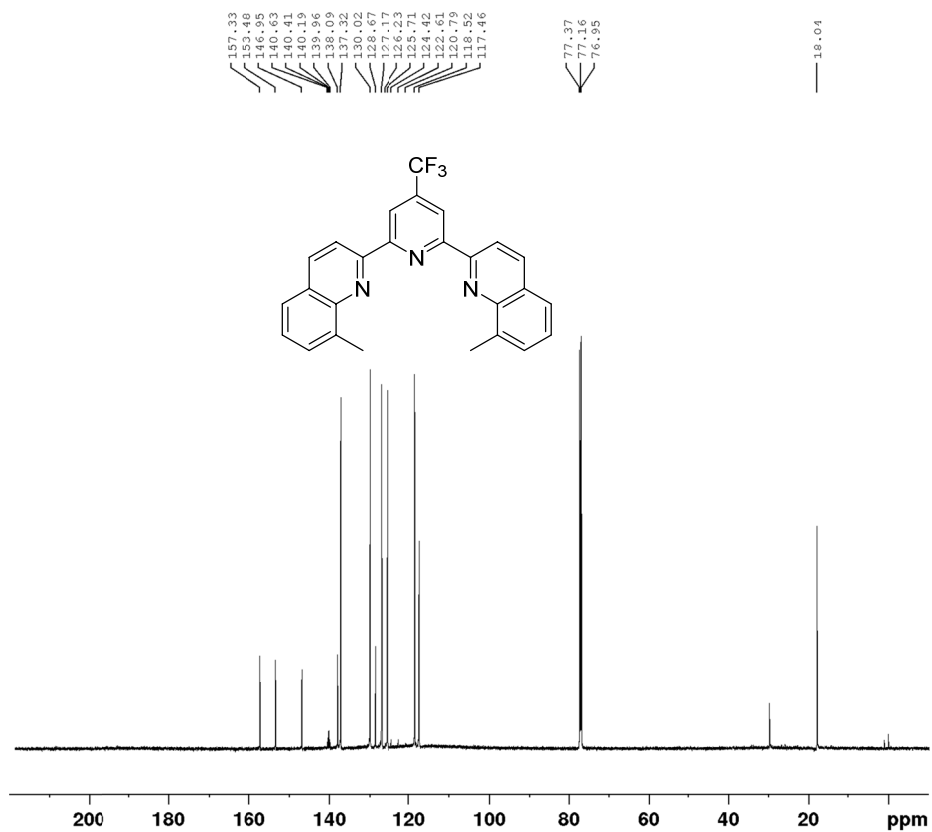
Figure S16. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1m** (CDCl<sub>3</sub>)



Current Data Parameters  
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 PROCNO 1

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 Time 20.18  
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 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6009.615 Hz  
 FIDRES 0.091699 Hz  
 AQ 5.4525952 sec  
 RG 209.09  
 DW 83.200 usec  
 DE 6.50 usec  
 TE 309.5 K  
 D1 1.00000000 sec  
 TD0 1  
 SFO1 300.1318534 MHz  
 NUC1 1H  
 P1 8.00 usec  
 PLW1 18.00000000 W

F2 - Processing parameters  
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 SF 300.1300072 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

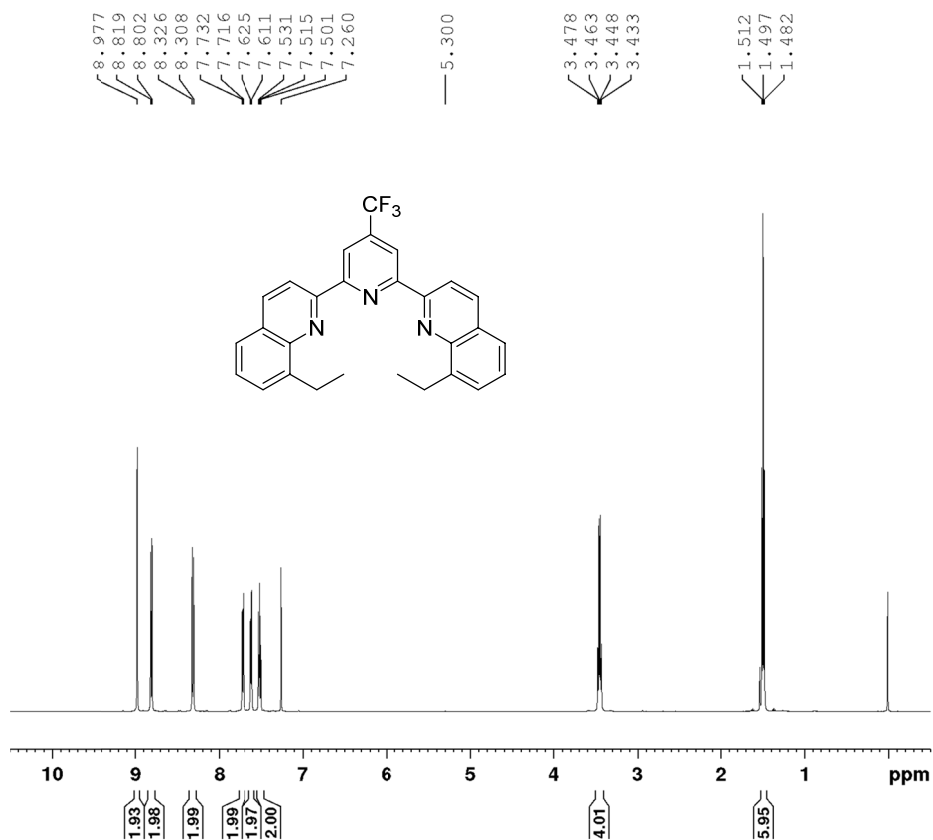


Current Data Parameters  
 NAME SI-11,21  
 EXPNO 18  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20191215  
 Time 1.17  
 INSTRUM Avance  
 PROBHD z124704\_0003 ( )  
 PULPROG zgpg  
 TD 32768  
 SOLVENT CDCl3  
 NS 25000  
 DS 0  
 SWH 35714.285 Hz  
 FIDRES 1.089913 Hz  
 AQ 0.4587520 sec  
 RG 101  
 DW 14.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 1.50000000 sec  
 d11 0.03000000 sec  
 DELTA 1.39999998 sec  
 TD0 1  
 SFO1 150.9178988 MHz  
 NUC1 13C  
 P1 12.00 usec  
 PLW1 51.29700089 W  
 SFO2 600.1324005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 30.60499954 W  
 PLW12 1.40530002 W  
 PLW13 0.70686001 W

F2 - Processing parameters  
 SI 32768  
 SF 150.9027877 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

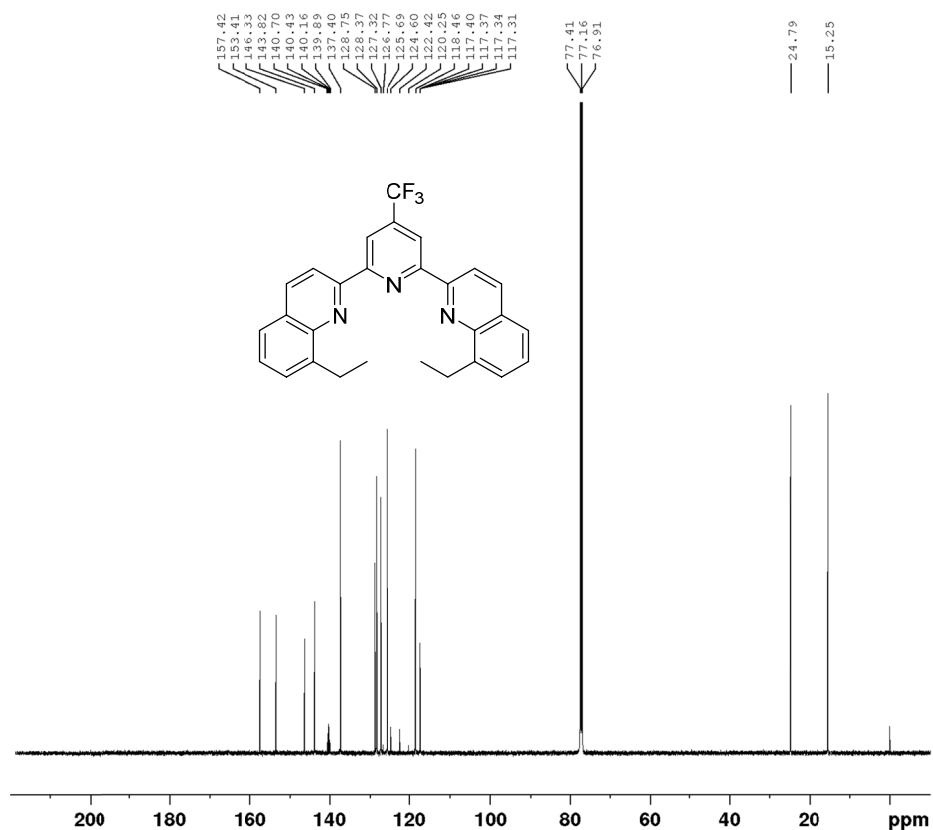
Figure S17. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1n** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1t,2t  
 EXPNO 5  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20191122  
 Time 9.53  
 INSTRUM spect  
 PROBHD 5 mm CP2BBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152568 Hz  
 AQ 3.2767999 sec  
 RG 62.06  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 TDO 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 F1 10.60 usec  
 PLW1 20.03000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300123 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

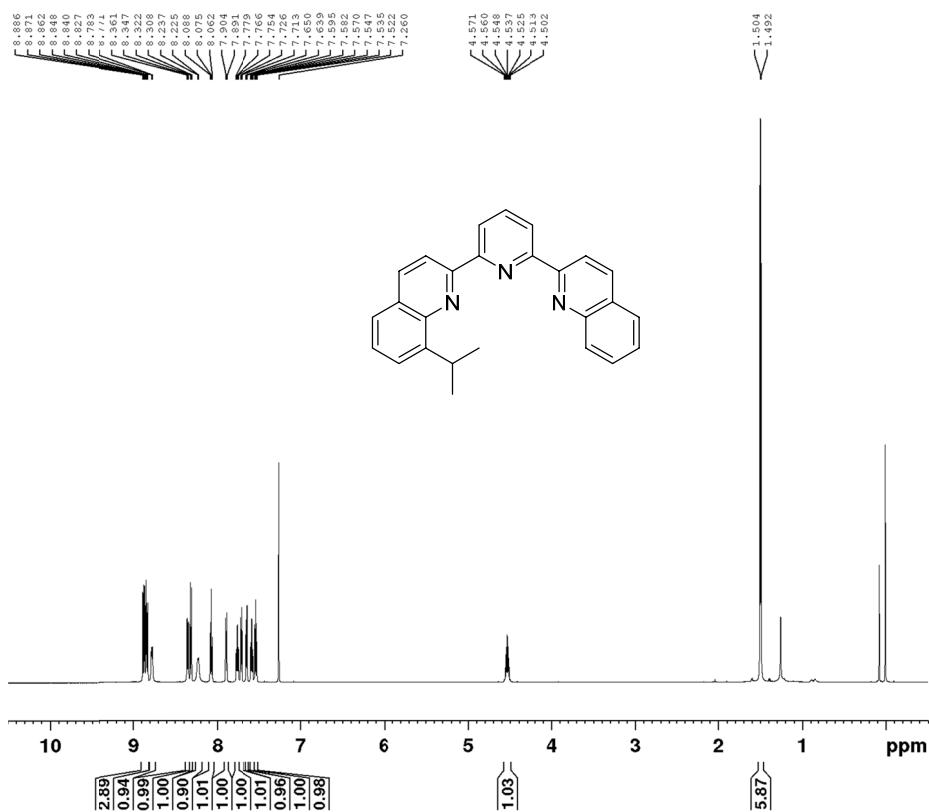


Current Data Parameters  
 NAME SI-1t,2t  
 EXPNO 6  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20191122  
 Time 10.47  
 INSTRUM spect  
 PROBHD 5 mm CP2BBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.899999998 sec  
 TDO 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 F1 9.80 usec  
 PLW1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577714 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.00

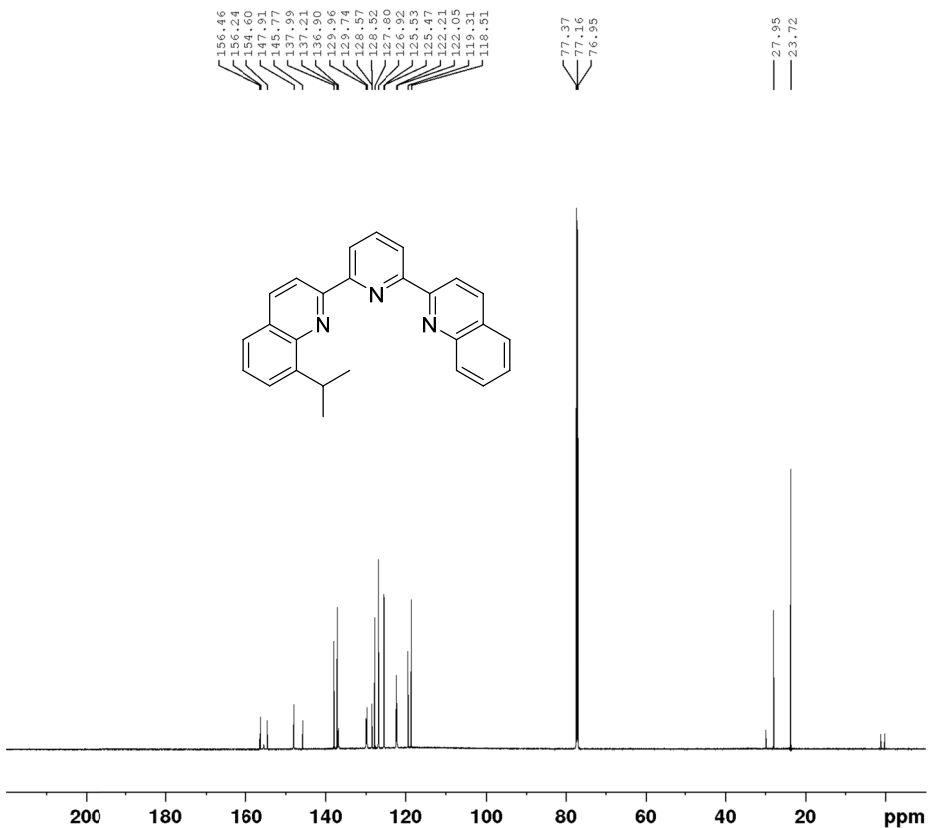
Figure S18. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1o** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-ln,2n  
 EXPNO 14  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200306  
 Time 12.21  
 INSTRUM Avance  
 PROBHD Z124704\_0003 ( )  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 48  
 DS 0  
 SWH 11904.762 Hz  
 FIDRES 0.181652 Hz  
 AQ 2.7525120 sec  
 RG 101  
 DW 42.000 usec  
 DE 11.43 usec  
 TE 297.9 K  
 D1 1.00000000 sec  
 TD0 1  
 SFO1 600.1337058 MHz  
 NUC1 1H  
 P1 15.00 usec  
 PLW1 30.604999954 W

F2 - Processing parameters  
 SI 65536  
 SF 600.1300145 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

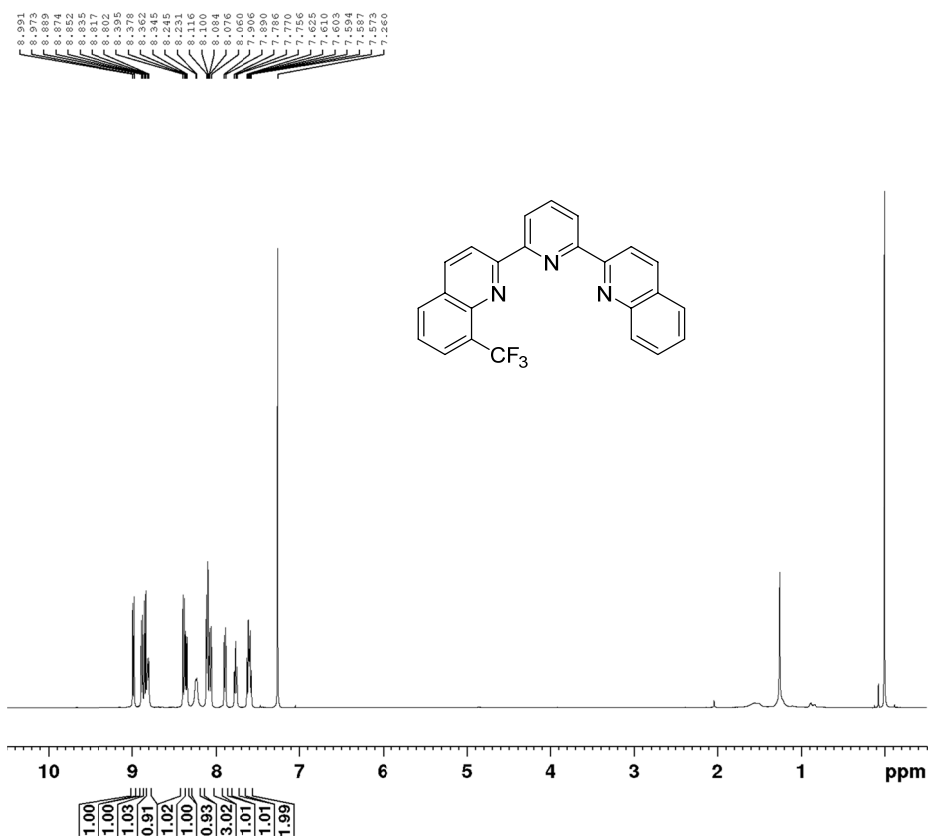


Current Data Parameters  
 NAME SI-ln,2n-  
 EXPNO 15  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200307  
 Time 4.48  
 INSTRUM Avance  
 PROBHD Z124704\_0003 ( )  
 PULPROG zgpg  
 TD 32768  
 SOLVENT CDCl3  
 NS 30000  
 DS 0  
 SWH 39682.539 Hz  
 FIDRES 1.211015 Hz  
 AQ 0.4128768 sec  
 RG 101  
 DW 12.600 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.50000000 sec  
 d11 0.03000000 sec  
 DELTA 1.39999998 sec  
 TD0 1  
 SFO1 150.9178993 MHz  
 NUC1 13C  
 P1 12.00 usec  
 PLW1 51.29700089 W  
 SFO2 600.1324005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 30.60499954 W  
 PLW12 1.40530002 W  
 PLW13 0.70686001 W

F2 - Processing parameters  
 SI 32768  
 SF 150.9027864 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

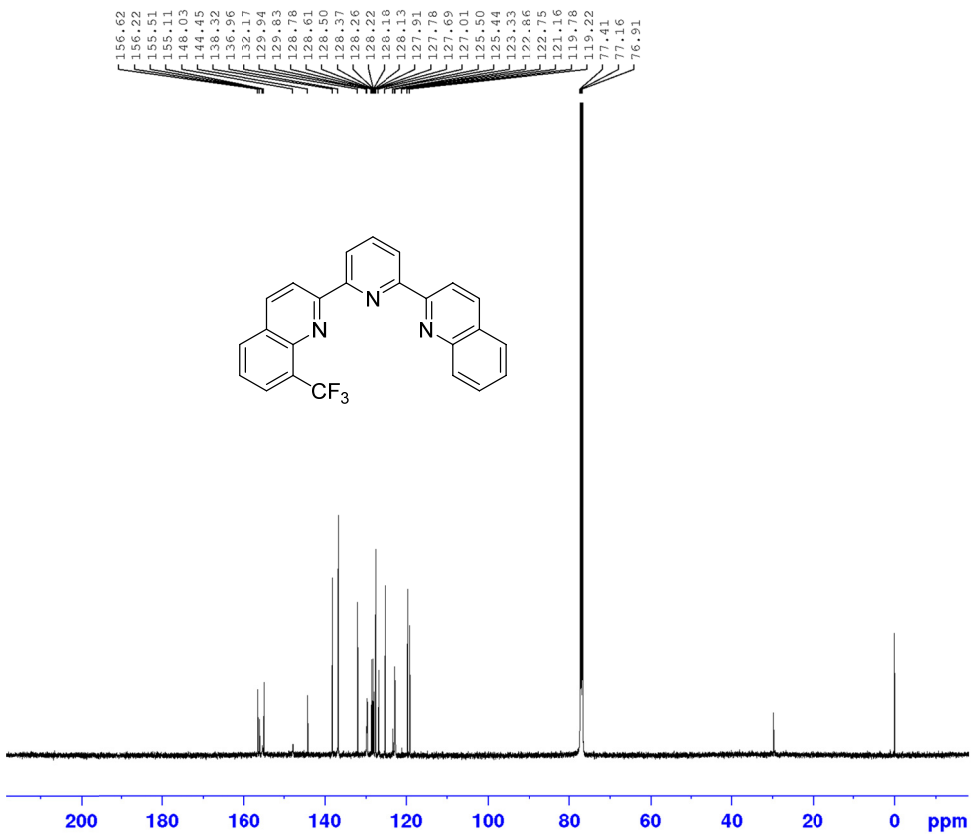
Figure S19. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1p** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1o,2o  
 EXPNO 4  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200307  
 Time 8.42  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 48  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 49.27  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 TDO 1  
 SF01 500.1330885 MHz  
 NUC1 1H  
 P1 10.59 usec  
 PLW1 20.0000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300121 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

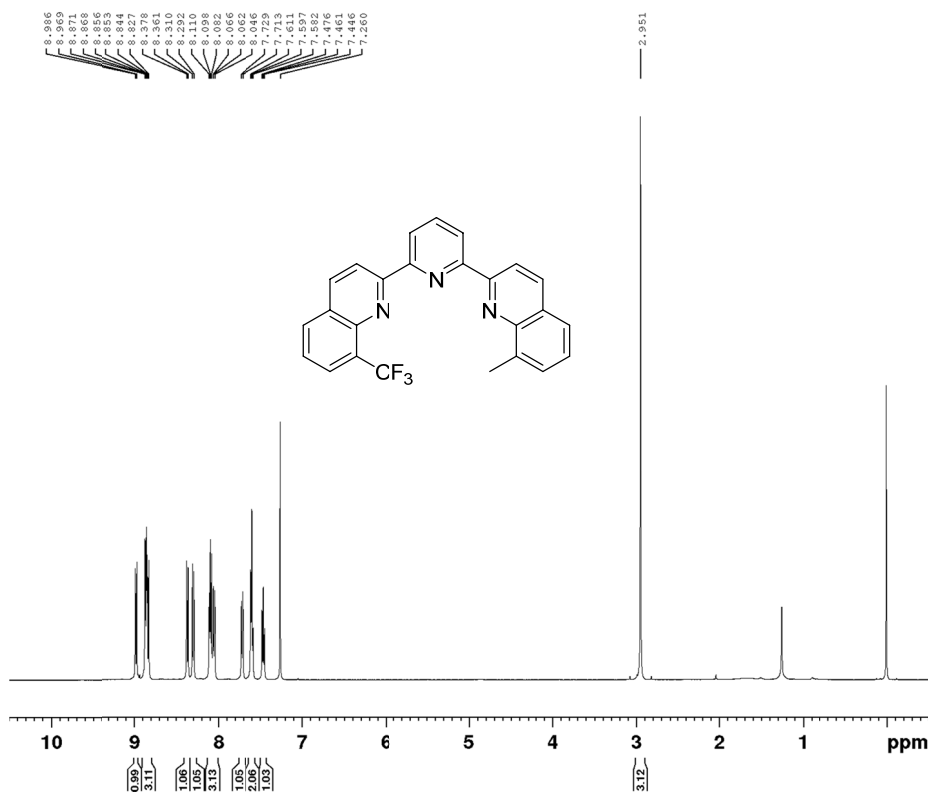


Current Data Parameters  
 NAME SI-1o,2o  
 EXPNO 5  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200307  
 Time 19.39  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 6000  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TDO 1  
 SF01 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.0000000 W  
 SF02 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.0000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577710 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

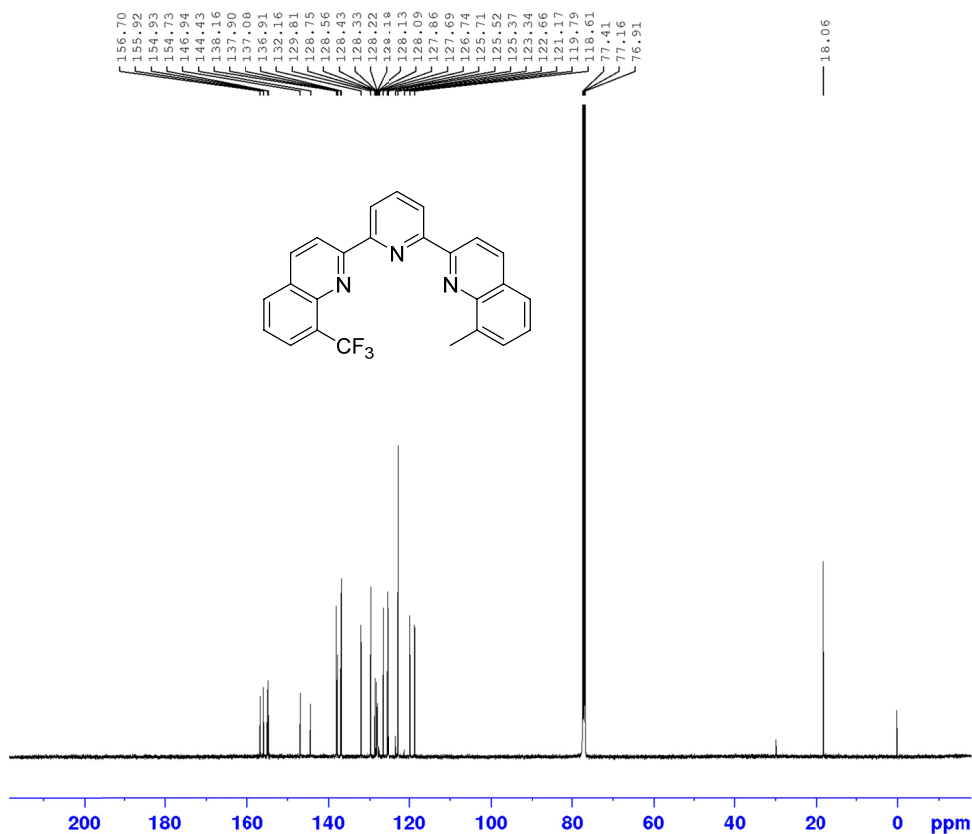
Figure S20. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1q** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-lp,2p  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200307  
 Time 6.01  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 48  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 31.72  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.0000000 sec  
 TD0 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 10.59 usec  
 PLW1 20.0000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300120 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

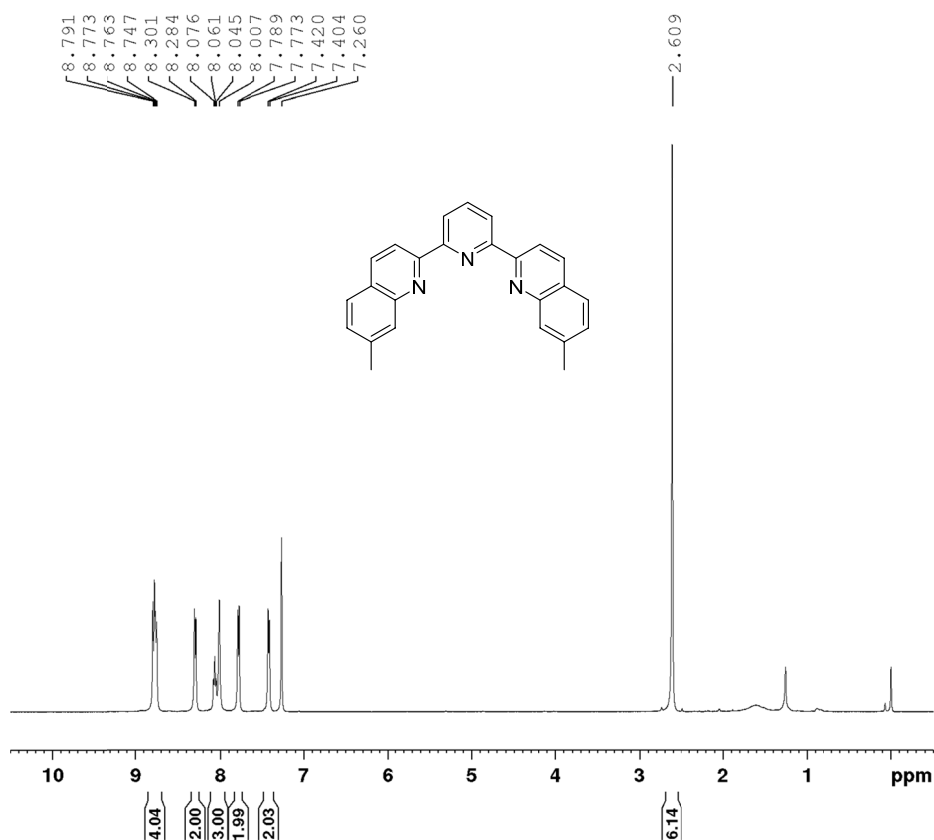


Current Data Parameters  
 NAME SI-lp,2p  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200307  
 Time 8.32  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 2980  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.0000000 sec  
 d11 0.0300000 sec  
 DELTA 1.89999998 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.0000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.0000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577715 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S21. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1r** (CDCl<sub>3</sub>)

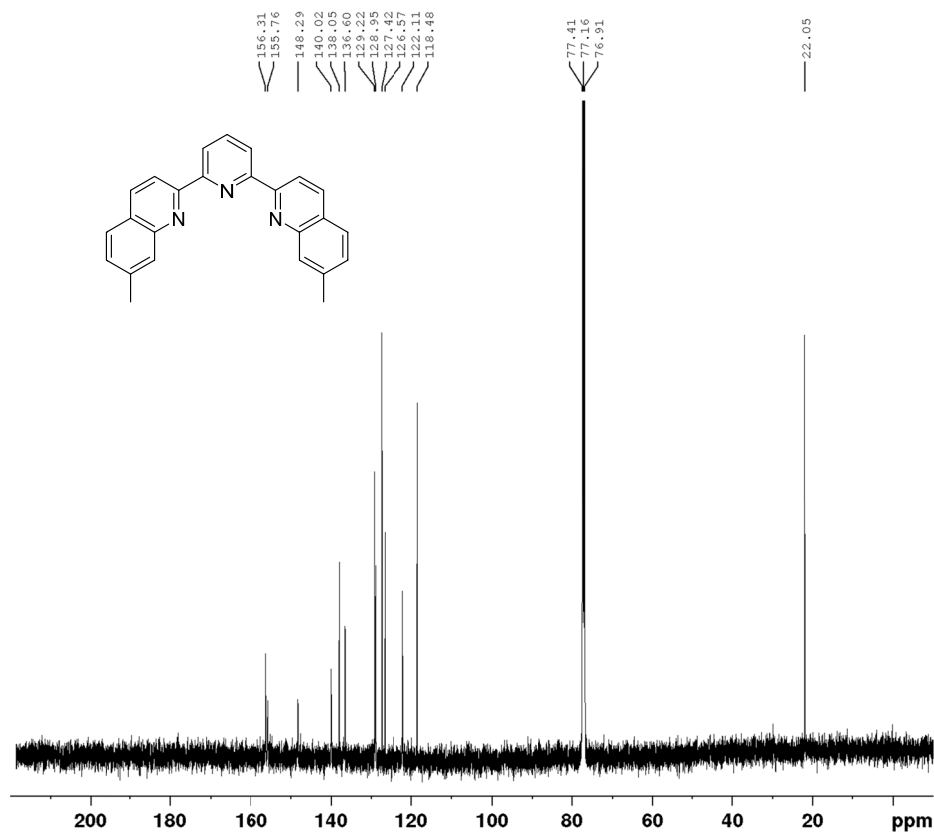


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Current Data Parameters
NAME_ SI-7-Me-8-tBu
EXPNO 129
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200520
Time_ 7.18
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 55.37
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
SFO1 500.1330885 MHz
NUC1 1H
P1 10.59 usec
PLW1 20.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
    
```



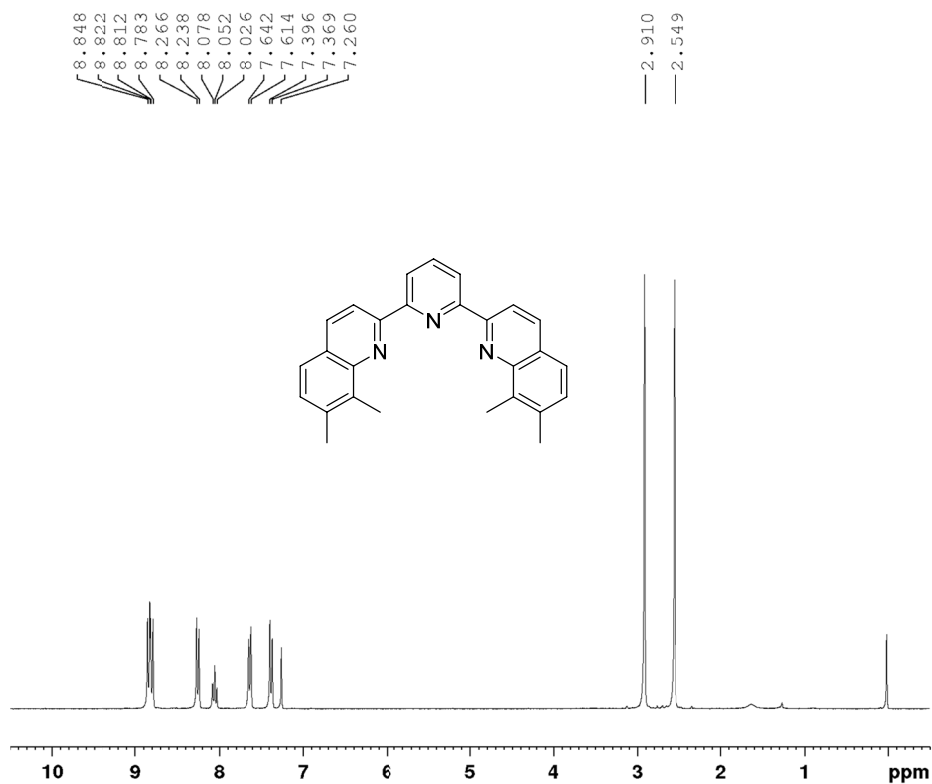
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Current Data Parameters
NAME_ SI-7-Me-8-tBu
EXPNO 131
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200520
Time_ 7.24
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
PLW1 57.00000000 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

F2 - Processing parameters
SI 32768
SF 125.7577703 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

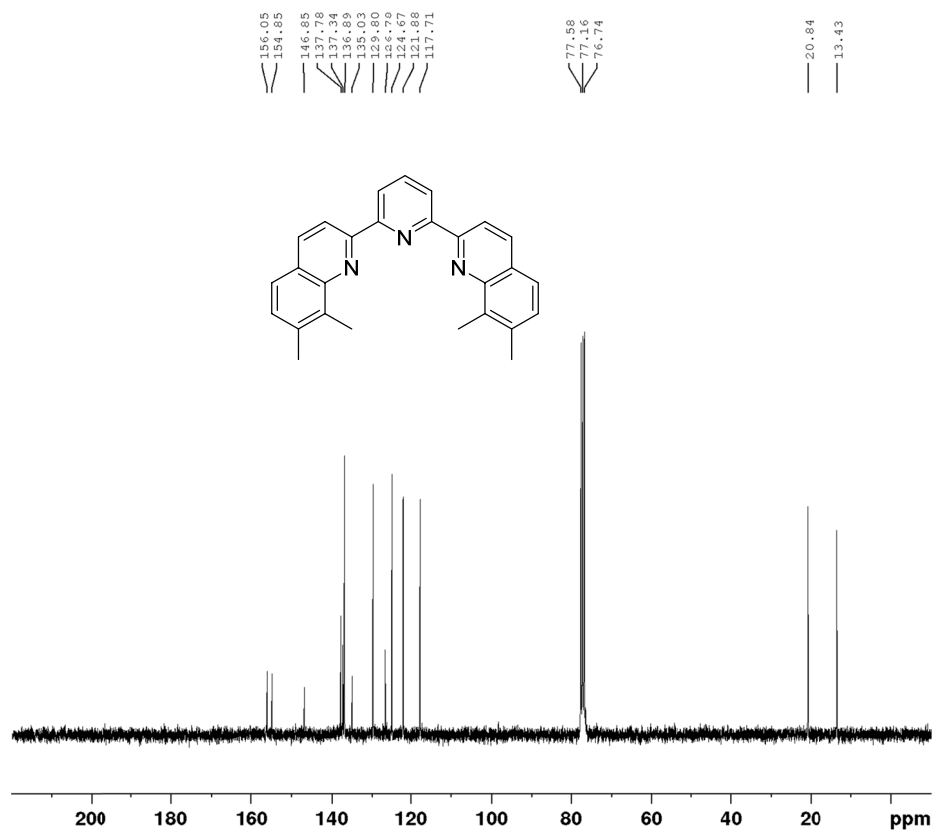
Figure S22. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1s** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-lm,2m  
 EXPNO 240  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20181007  
 Time 16.10  
 INSTRUM spect  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6009.615 Hz  
 FIDRES 0.091699 Hz  
 AQ 5.4525952 sec  
 RG 209.09  
 DW 83.200 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.0000000 sec  
 TDO 1  
 SFO1 300.1318534 MHz  
 NUC1 1H  
 P1 8.00 usec  
 PLW1 18.0000000 W

F2 - Processing parameters  
 SI 65536  
 SF 300.1300073 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME SI-lm,2m  
 EXPNO 248  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20181008  
 Time 4.01  
 INSTRUM spect  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 18028.846 Hz  
 FIDRES 0.275098 Hz  
 AQ 1.8175317 sec  
 RG 209.09  
 DW 27.733 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 2.0000000 sec  
 d11 0.0300000 sec  
 DELTA 1.89999998 sec  
 TDO 1  
 SFO1 75.4752949 MHz  
 NUC1 13C  
 P1 11.00 usec  
 PLW1 195.0300000 W  
 SFO2 300.1312005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 90.00 usec  
 PLW2 14.0000000 W  
 PLW12 0.17284000 W  
 PLW13 0.14000000 W

F2 - Processing parameters  
 SI 32768  
 SF 75.4677387 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

**Figure S23.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **1t** ( $\text{CDCl}_3$ )

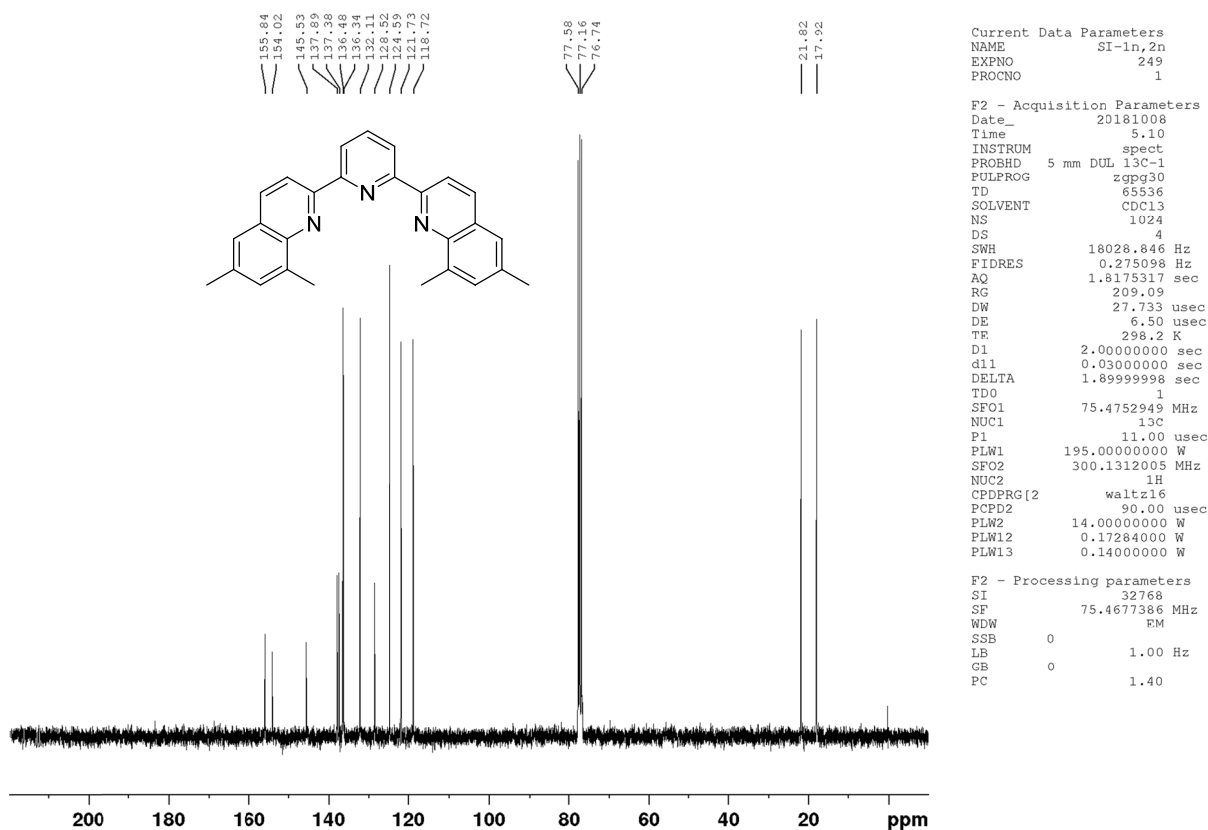
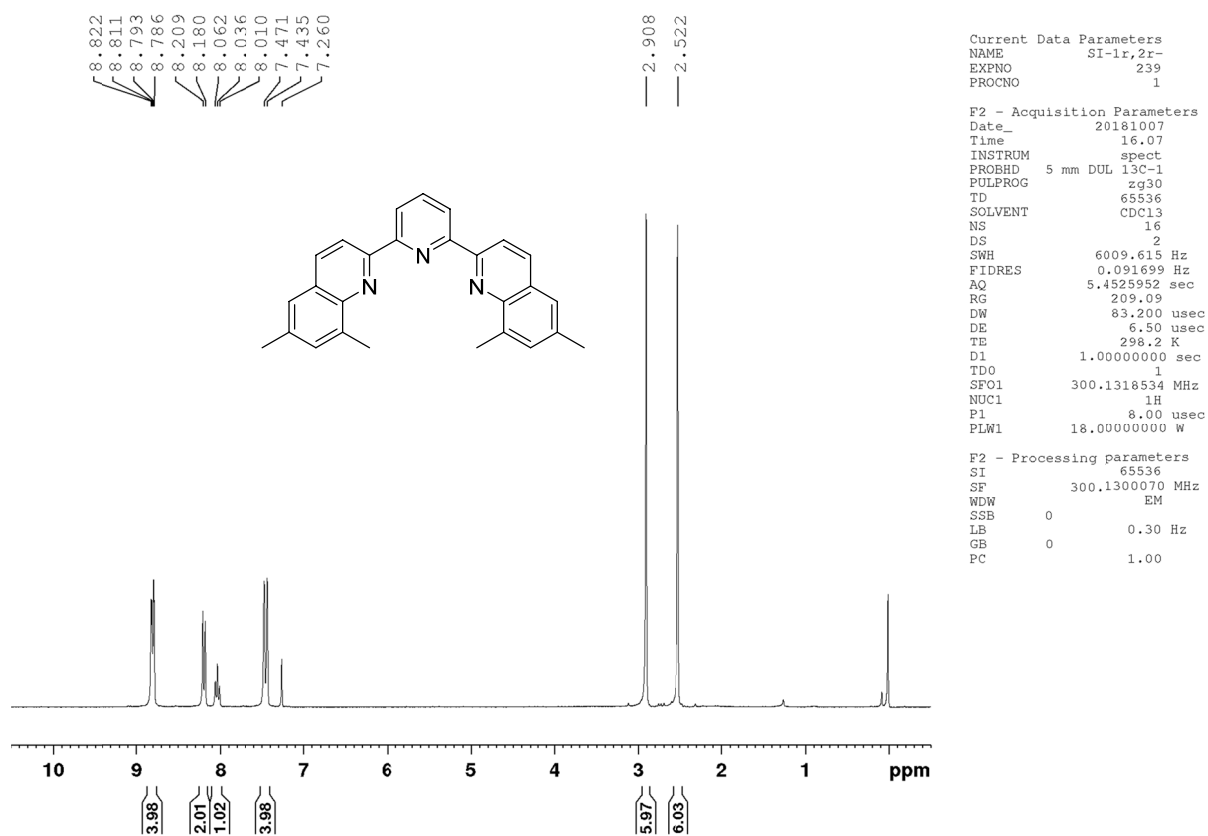
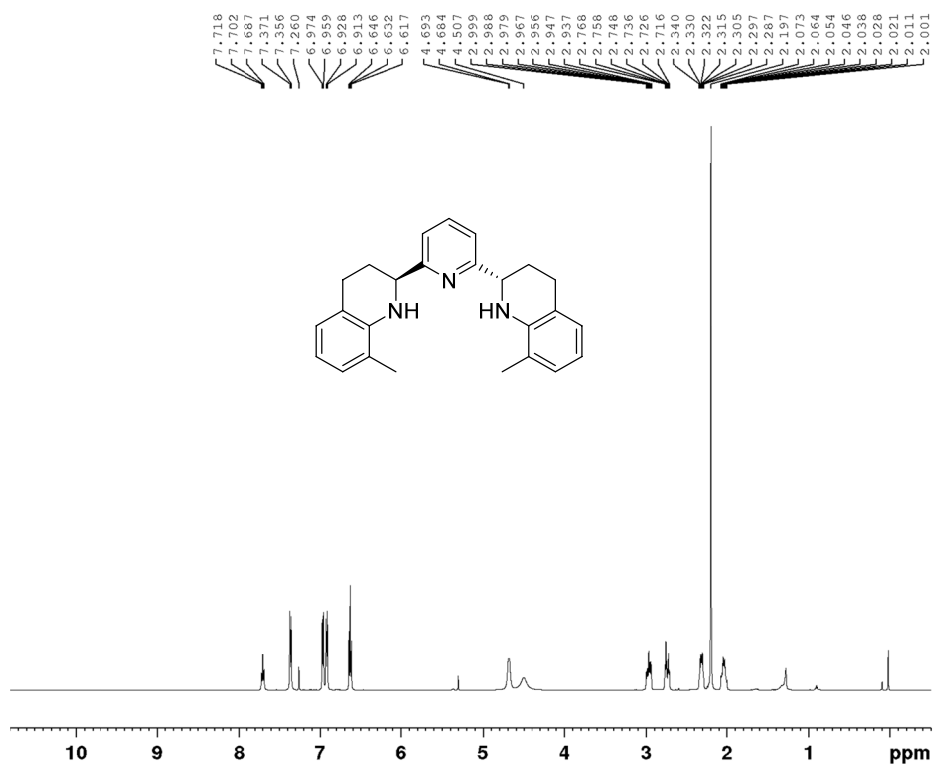


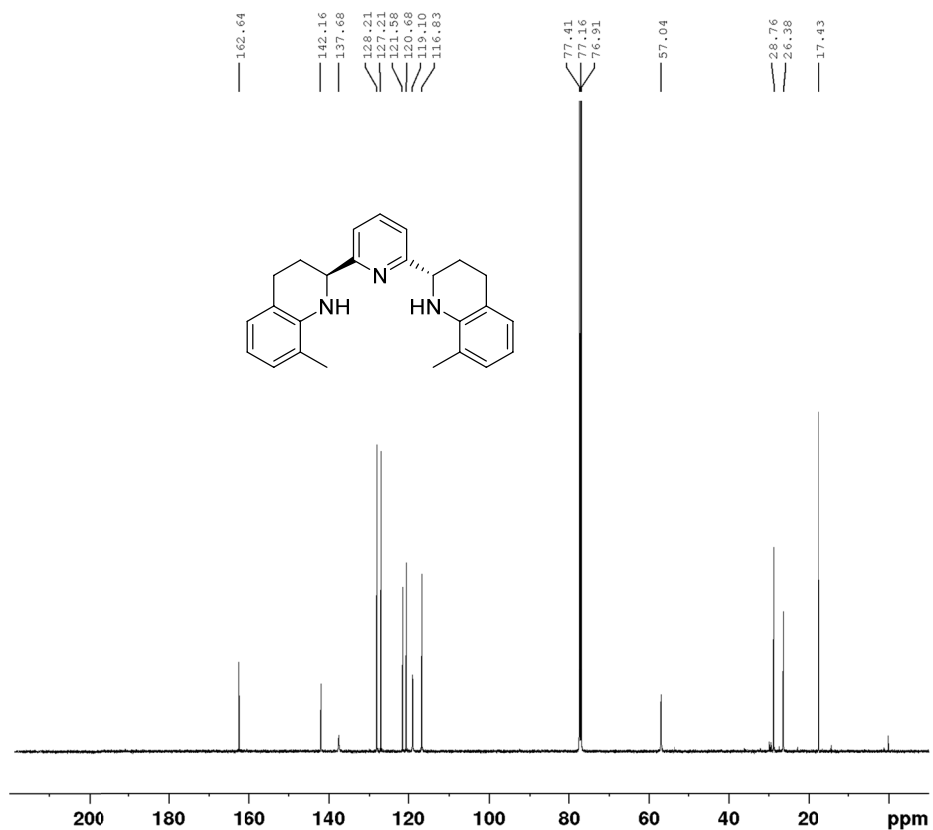
Figure S24. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2a (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1a,2a  
 EXPNO 14  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190123  
 Time 17.45  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152566 Hz  
 AQ 3.2767999 sec  
 RG 31.72  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.03000000 sec  
 TDO 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 11.50 usec  
 PLW1 20.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300119 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME SI-1e,2e  
 EXPNO 19  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190123  
 Time 18.23  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 700  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.1 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TDO 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577755 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S25. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2b** (CDCl<sub>3</sub>)

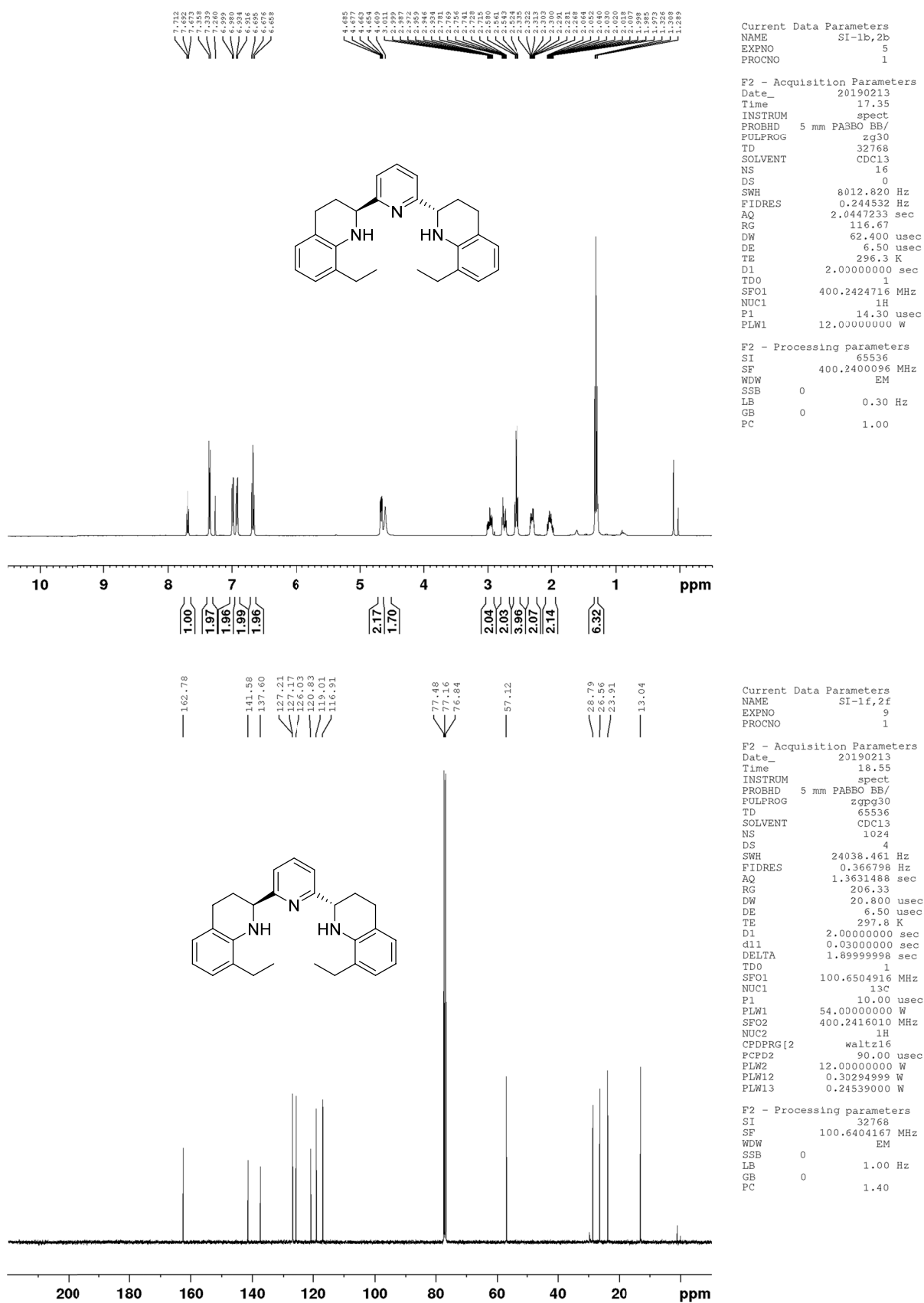
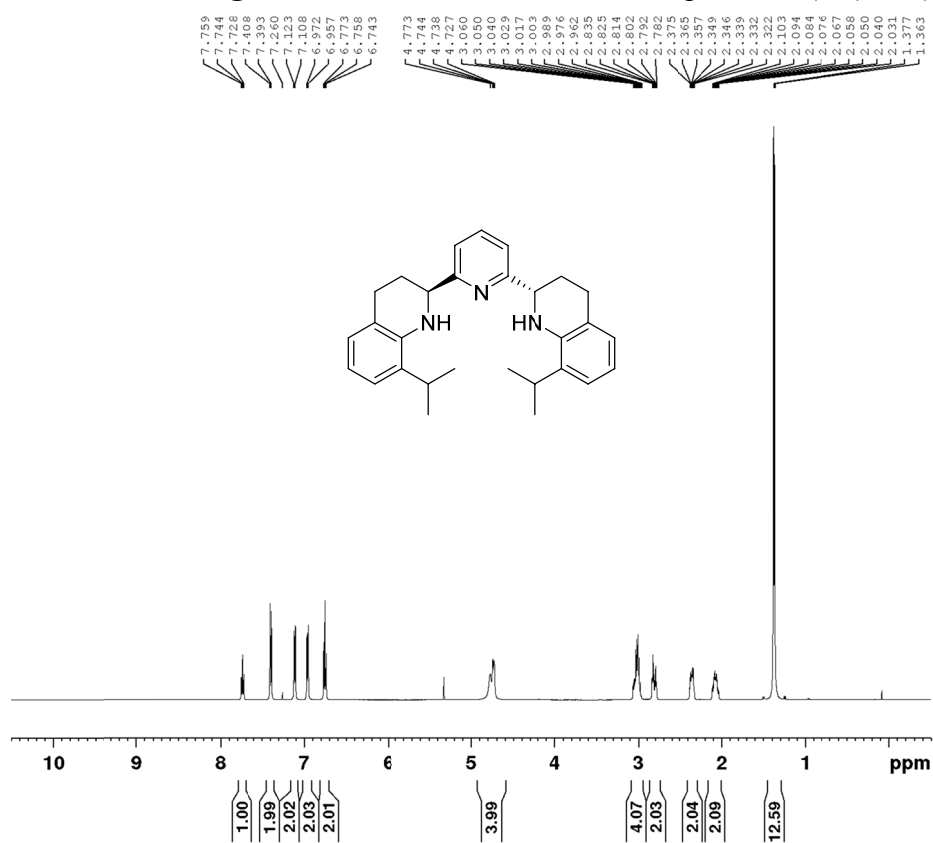


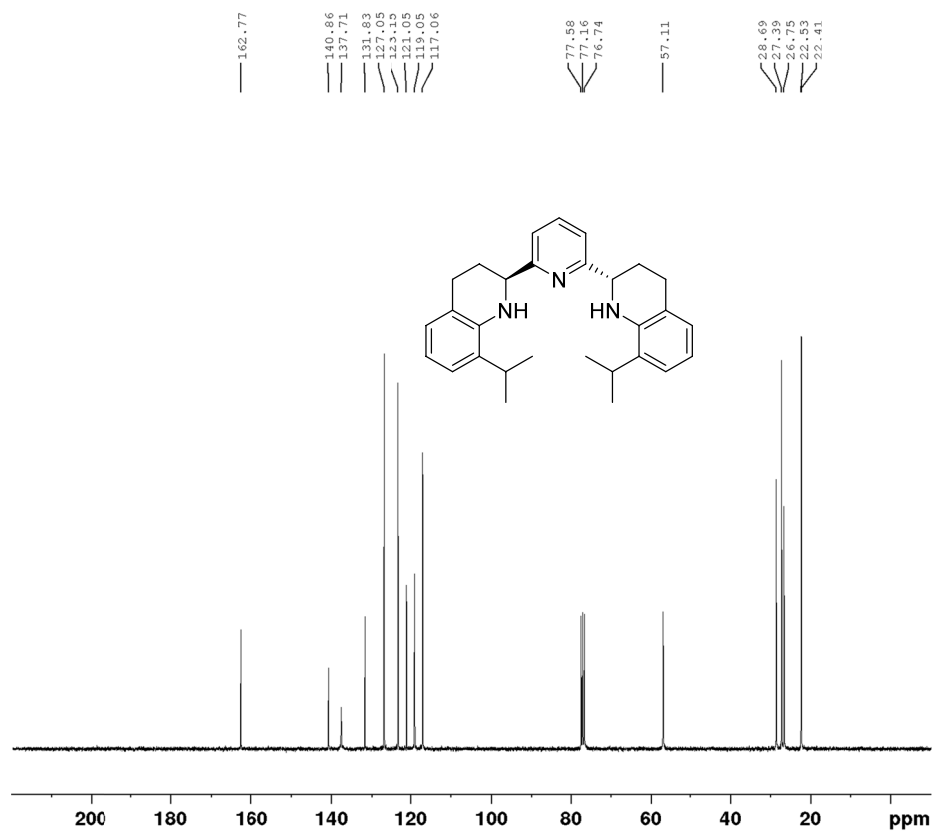
Figure S26. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2c (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1c,2c  
 EXPNO 18  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190123  
 Time 19.06  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 22.1  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.00000000 sec  
 TDO 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 11.50 usec  
 PLW1 20.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300117 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME SI-1c,2c  
 EXPNO 33  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190124  
 Time 2.11  
 INSTRUM spect  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 18028.846 Hz  
 FIDRES 0.275098 Hz  
 AQ 1.8175317 sec  
 RG 209.09  
 DW 27.733 usec  
 DE 6.50 usec  
 TE 0 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.899999998 sec  
 TDO 1  
 SFO1 75.4752949 MHz  
 NUC1 13C  
 P1 11.00 usec  
 PLW1 195.00000000 W  
 SFO2 300.1312005 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 90.00 usec  
 PLW2 14.00000000 W  
 PLW12 0.17284000 W  
 PLW13 0.14000000 W

F2 - Processing parameters  
 SI 32768  
 SF 75.4677421 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S27. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2d (CDCl<sub>3</sub>)

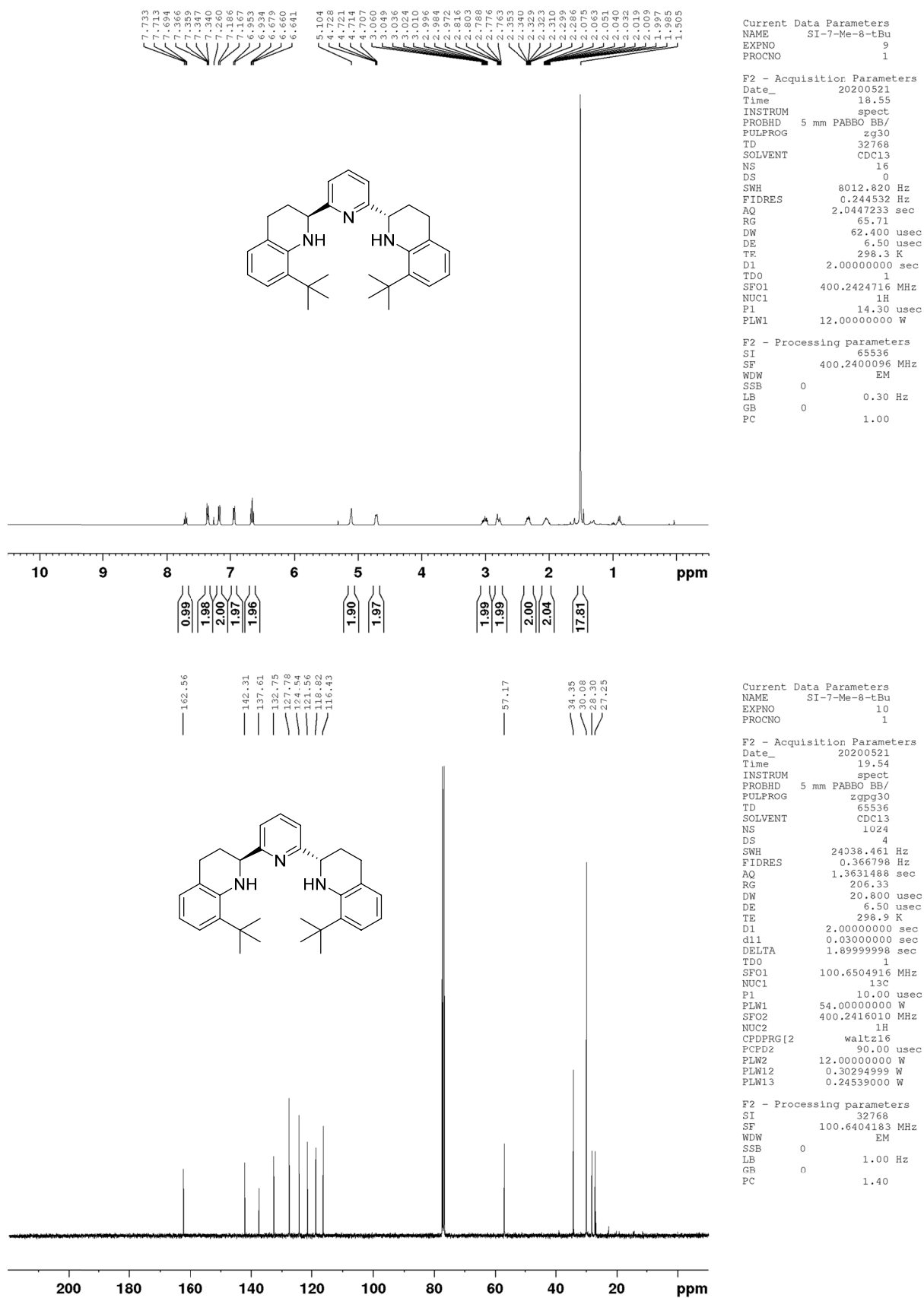


Figure S28. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2e** (CDCl<sub>3</sub>)

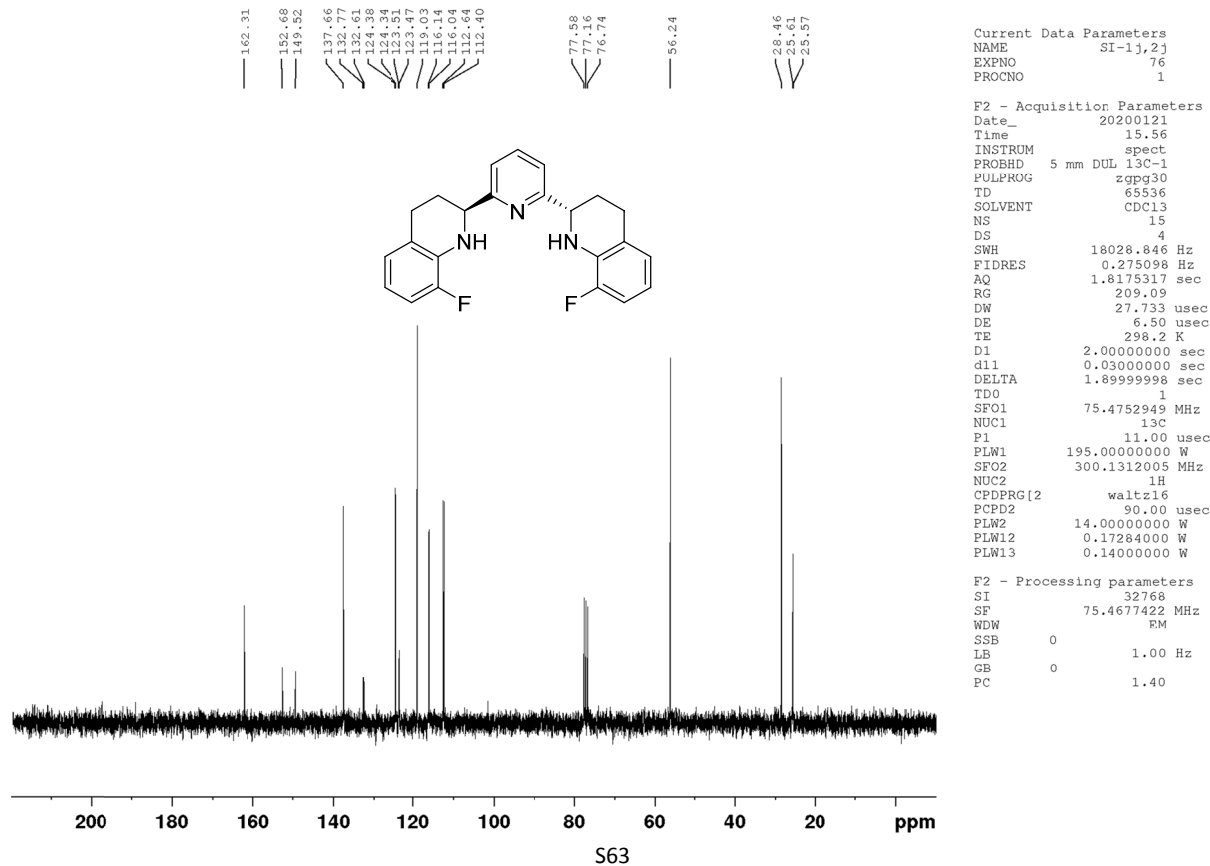
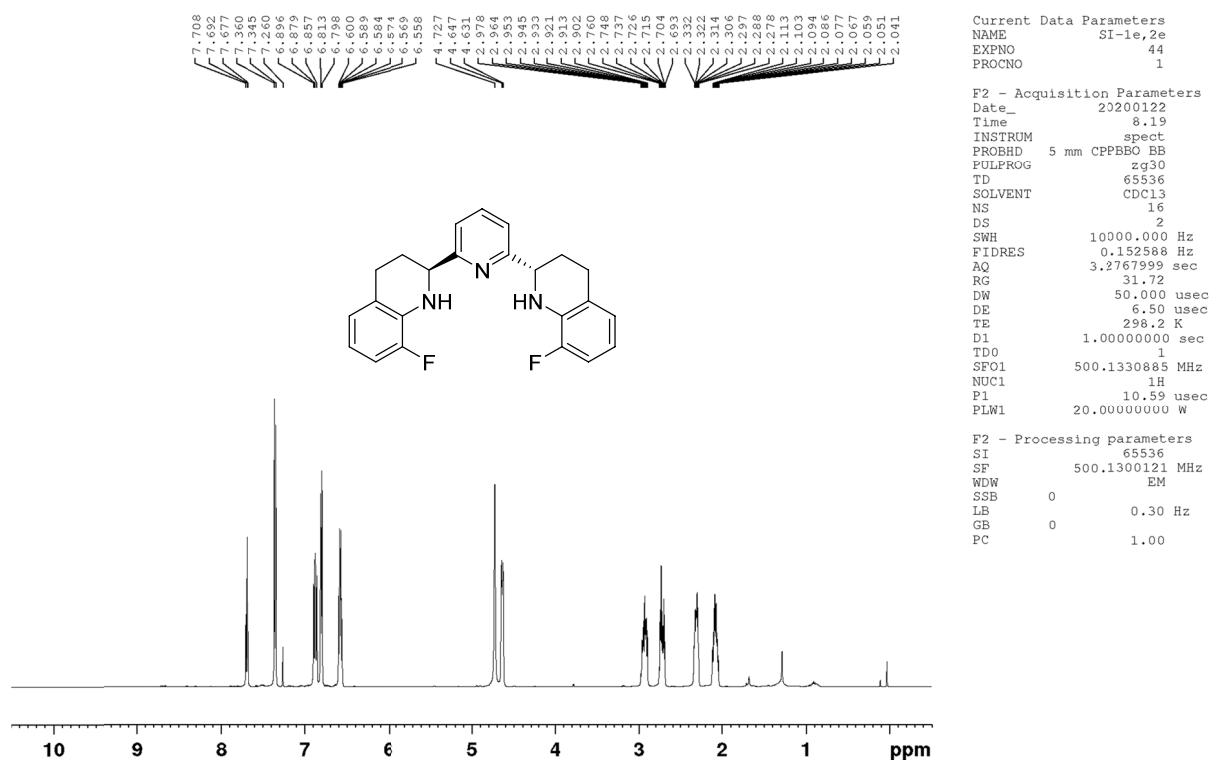
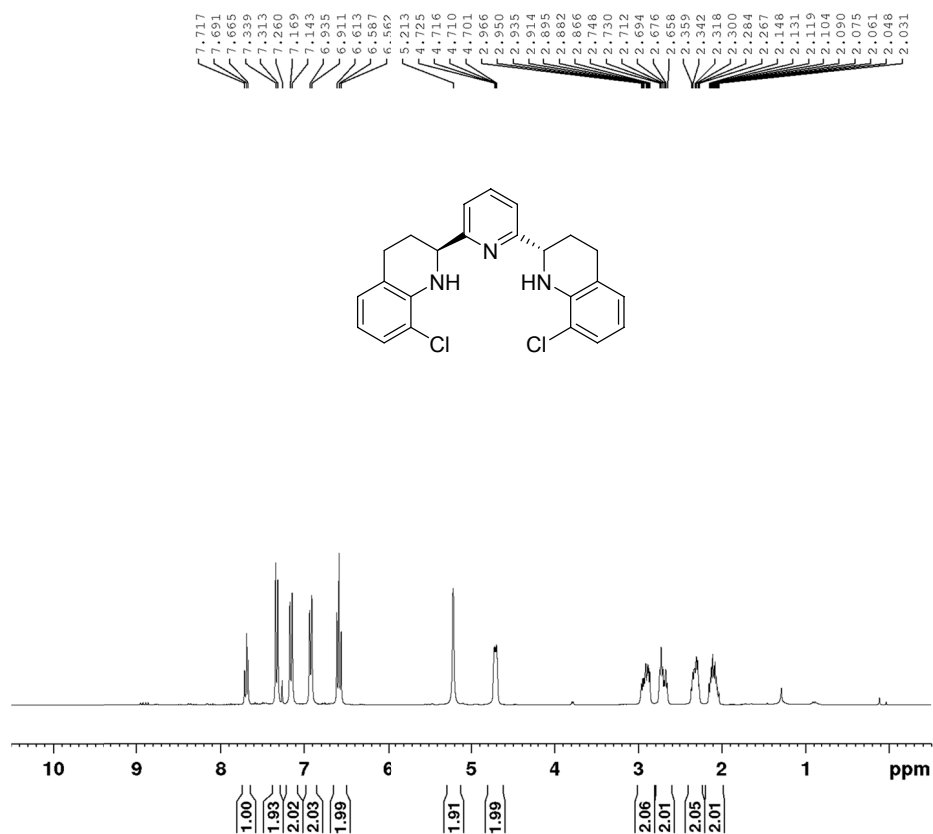


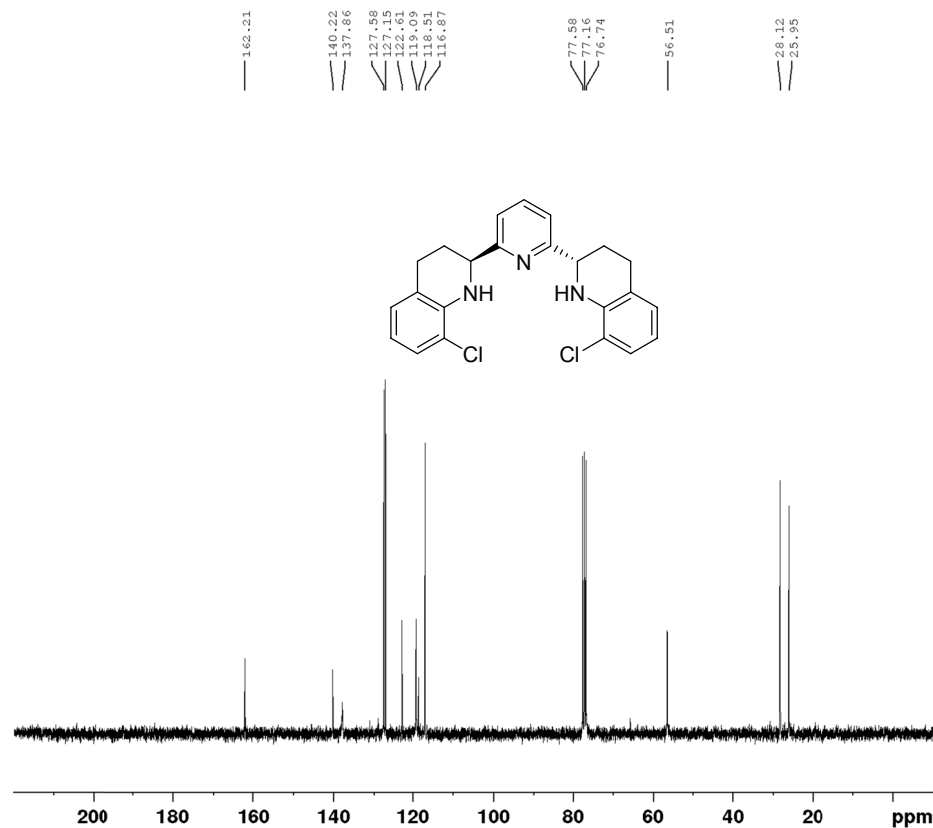
Figure S29. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2f (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1f,2f  
 EXPNO 57  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200119  
 Time 18.41  
 INSTRUM spect  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6009.615 Hz  
 FIDRES 0.091699 Hz  
 AQ 5.4525952 sec  
 RG 186.23  
 DW 83.200 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 TD0 1  
 SFO1 300.1318534 MHz  
 NUC1 1H  
 P1 8.00 usec  
 PLW1 18.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 300.1300071 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

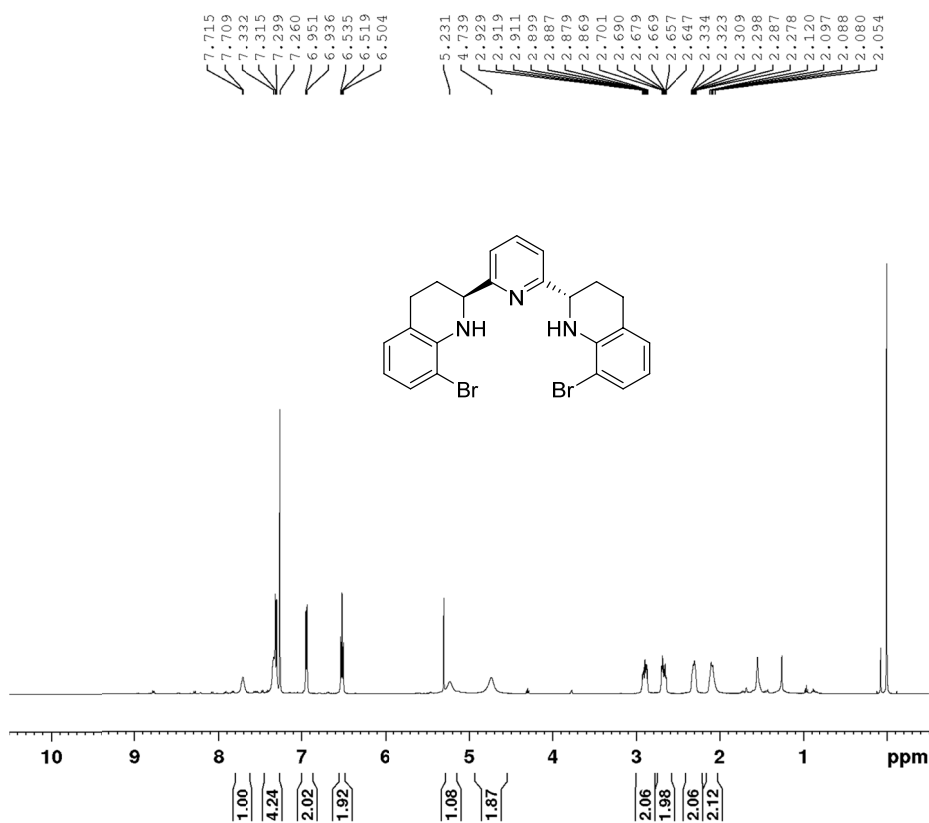


Current Data Parameters  
 NAME SI-1k,2k  
 EXPNO 43  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190124  
 Time 8.00  
 INSTRUM spect  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 311  
 DS 4  
 SWH 18028.846 Hz  
 FIDRES 0.275098 Hz  
 AQ 1.8175317 sec  
 RG 209.09  
 DW 27.733 usec  
 DE 6.50 usec  
 TE 0 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TD0 1  
 SFO1 75.4752949 MHz  
 NUC1 13C  
 P1 11.00 usec  
 PLW1 195.00000000 W  
 SFO2 300.1312005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 90.00 usec  
 PLW2 14.00000000 W  
 PLW12 0.17284000 W  
 PLW13 0.14000000 W

F2 - Processing parameters  
 SI 32768  
 SF 75.4677389 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

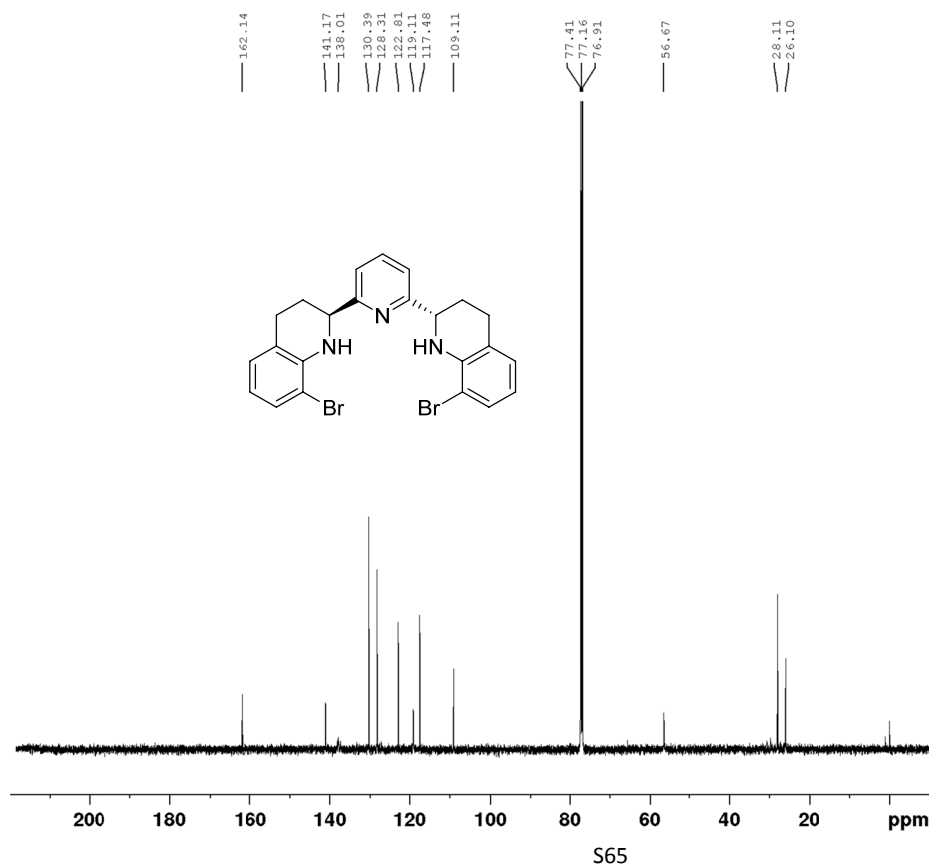
Figure S30. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2g (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1g,2g  
 EXPNO 70  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200312  
 Time 12.02  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 49.27  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.0000000 sec  
 TD0 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 10.59 usec  
 PLW1 20.0000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300121 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 0.50

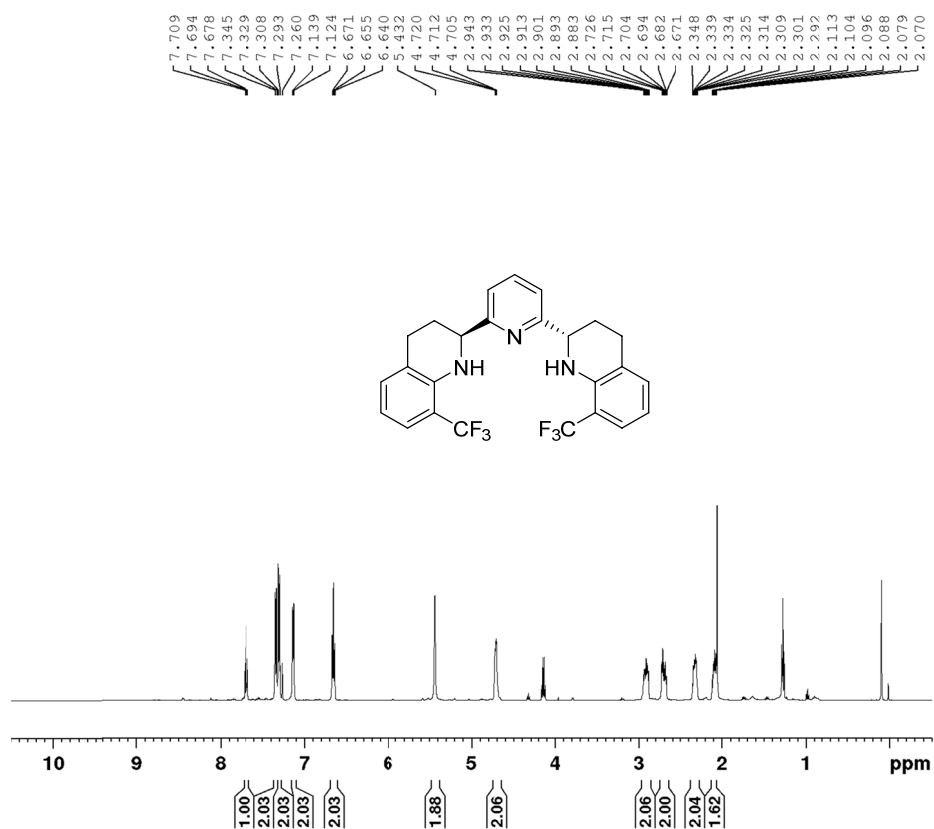


Current Data Parameters  
 NAME SI-1g,2g  
 EXPNO 83  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200314  
 Time 11.21  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 122  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.0000000 sec  
 d11 0.0300000 sec  
 DELTA 1.899999998 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.0000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 80.00 usec  
 PLW2 20.0000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577727 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S31. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2h** (CDCl<sub>3</sub>)

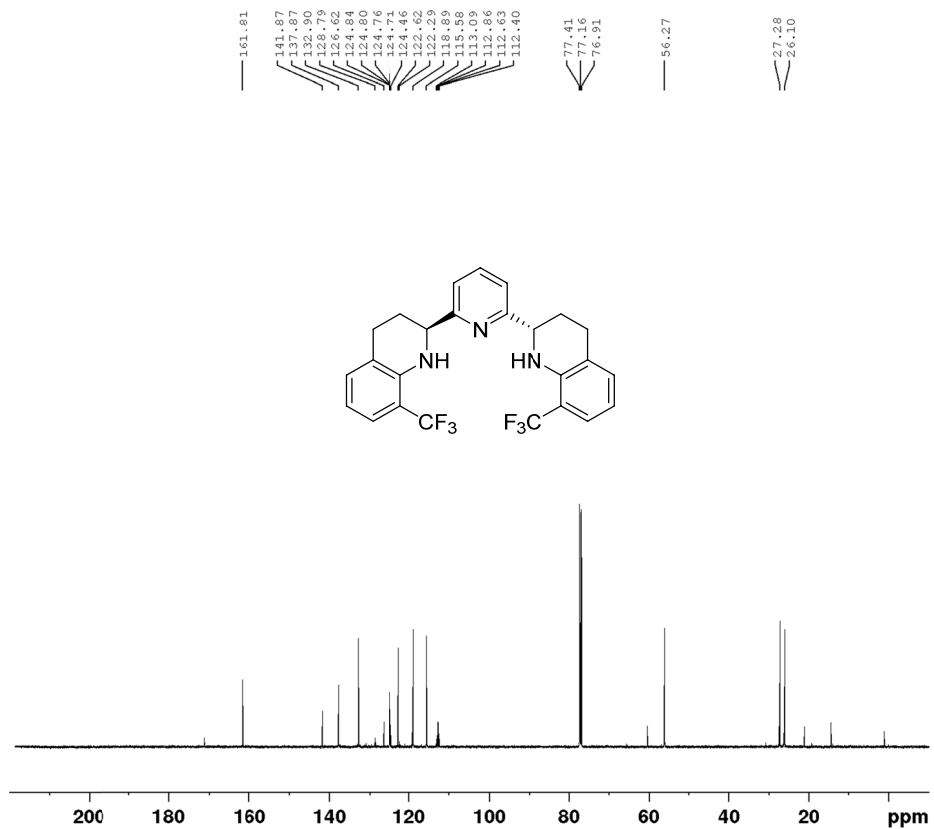


```

Current Data Parameters
NAME          SI-1h-,2h
EXPNO         59
PROCNO        1

F2 - Acquisition Parameters
Date_         20200311
Time          10.05
INSTRUM       spect
PROBHD        5 mm CPPBBO BB
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2767999 sec
RG            31.72
DW            50.000 usec
DE            6.50 usec
TE            298.2 K
D1            1.00000000 sec
TD0           1
SFO1          500.1330885 MHz
NUC1          1H
P1            10.59 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI            65536
SF            500.1300120 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```



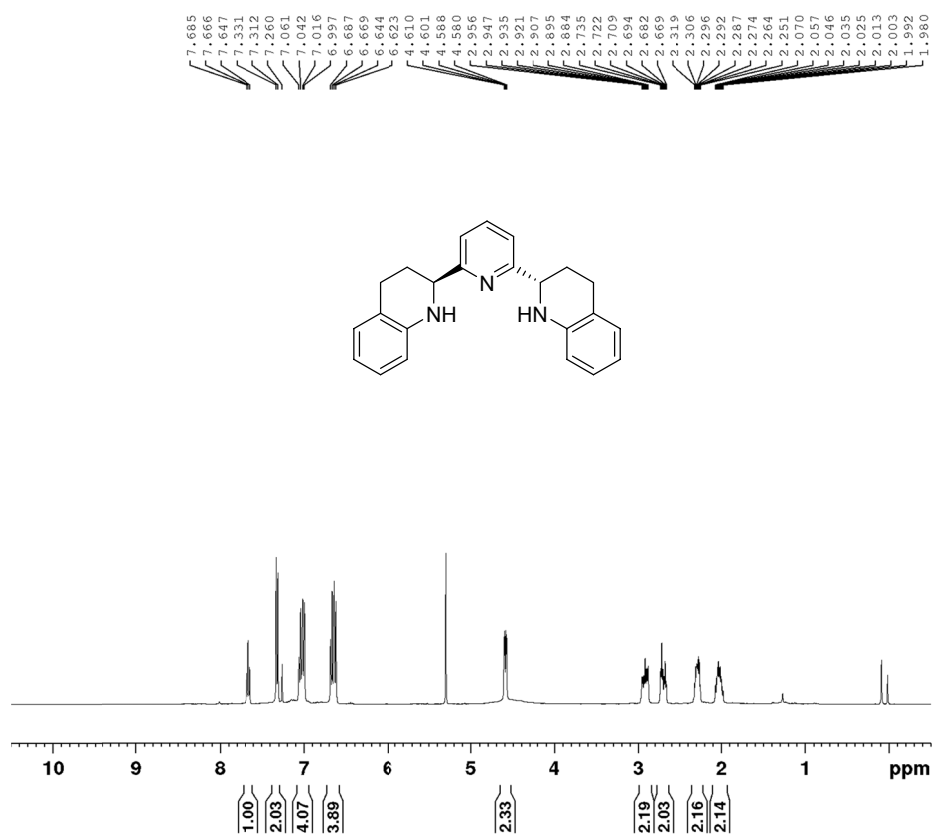
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Current Data Parameters
NAME          SI-1h-,2h-
EXPNO         60
PROCNO        1

F2 - Acquisition Parameters
Date_         20200311
Time          10.09
INSTRUM       spect
PROBHD        5 mm CPPBBO BB
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            74
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010048 sec
RG            192.89
DW            16.800 usec
DE            18.00 usec
TE            298.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999999 sec
TD0           1
SFO1          125.7703637 MHz
NUC1          13C
P1            9.80 usec
PLW1          57.00000000 W
SFO2          500.1320005 MHz
NUC2          1H
CPDPRG[2]    waltz16
PCPD2         80.00 usec
PLW2          20.00000000 W
PLW12         0.35778001 W
PLW13         0.22898000 W

F2 - Processing parameters
SI            32768
SF            125.7577738 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```

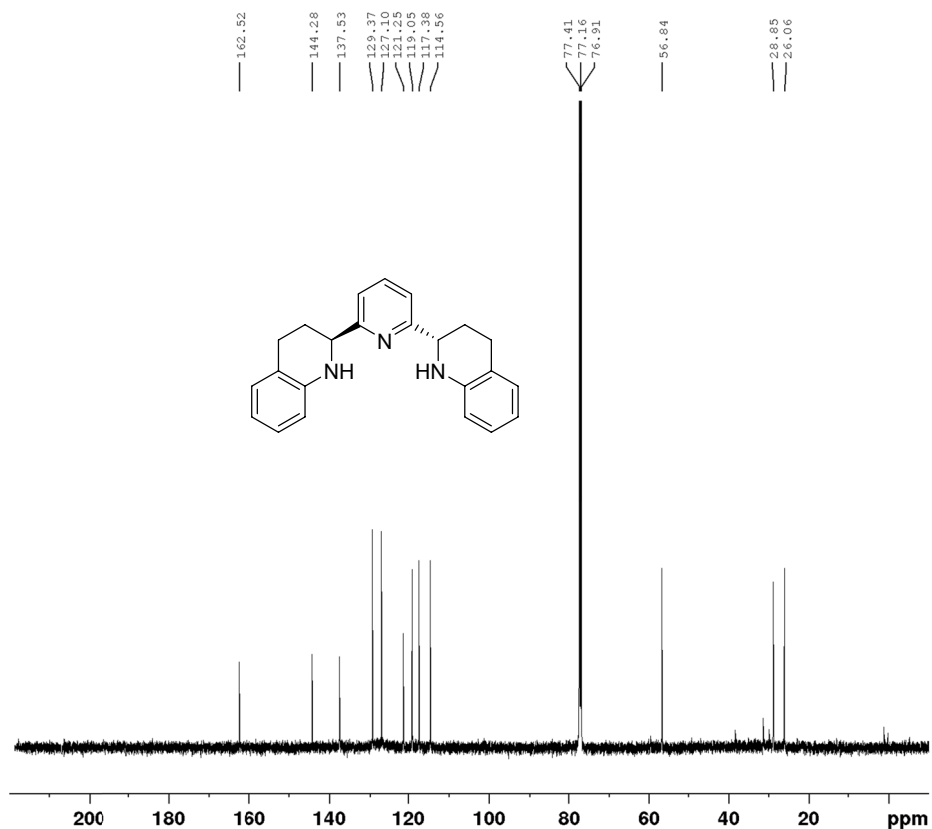
Figure S32. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2i (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1d,2d  
 EXPNO 16  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20170620  
 Time 21.30  
 INSTRUM spect  
 PROBHD 5 mm PA3BO BB/  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 16  
 DS 0  
 SWH 8012.820 Hz  
 FIDRES 0.244532 Hz  
 AQ 2.0447233 sec  
 RG 140.59  
 DW 62.400 usec  
 DE 6.50 usec  
 TE 300.9 K  
 D1 2.00000000 sec  
 TDO 1  
 SFO1 400.2424716 MHz  
 NUC1 1H  
 P1 14.80 usec  
 PLW1 12.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 400.2400096 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME SI-1d,2d  
 EXPNO 33  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20171011  
 Time 12.00  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 105  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TDO 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPMRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577751 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S33. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2j** (CDCl<sub>3</sub>)

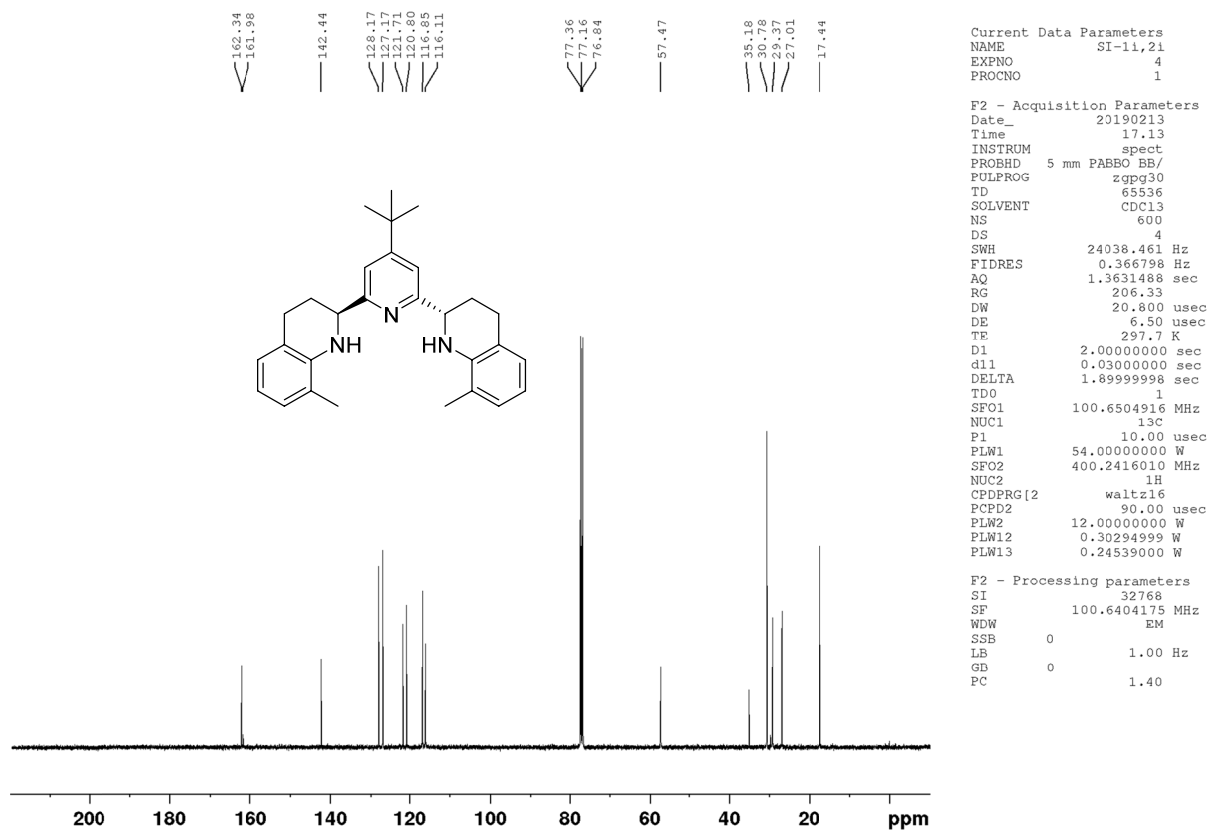
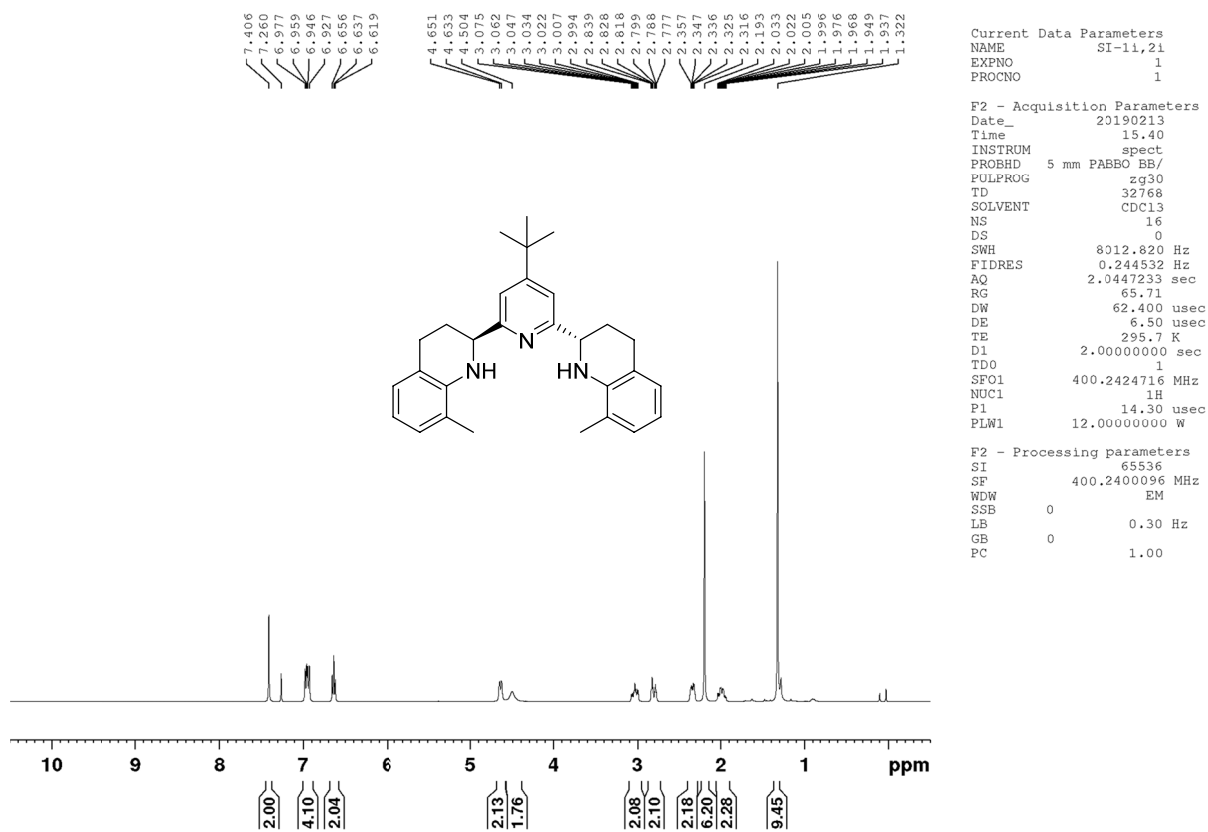


Figure S34. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of *meso*-2j (CDCl<sub>3</sub>)

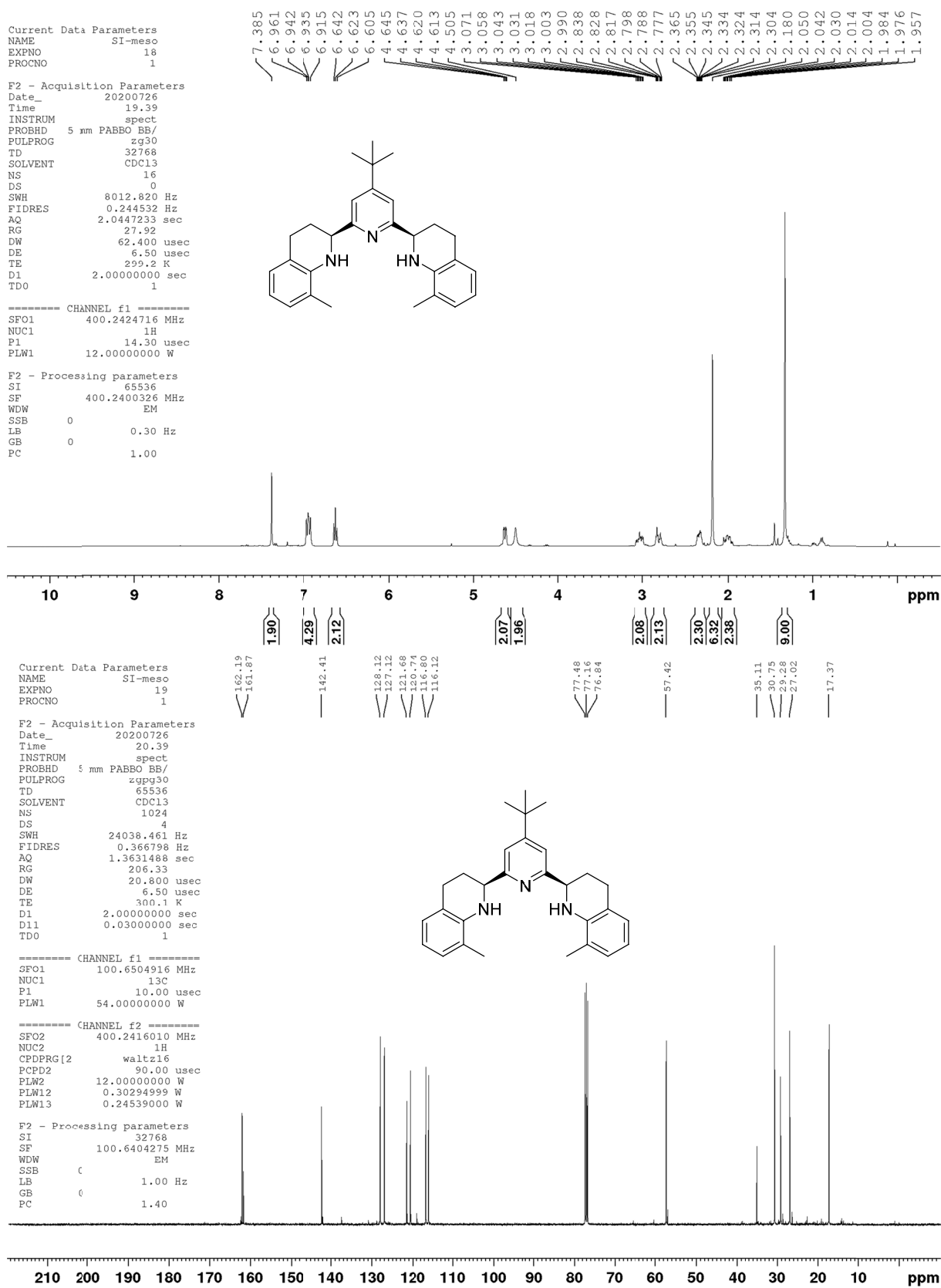
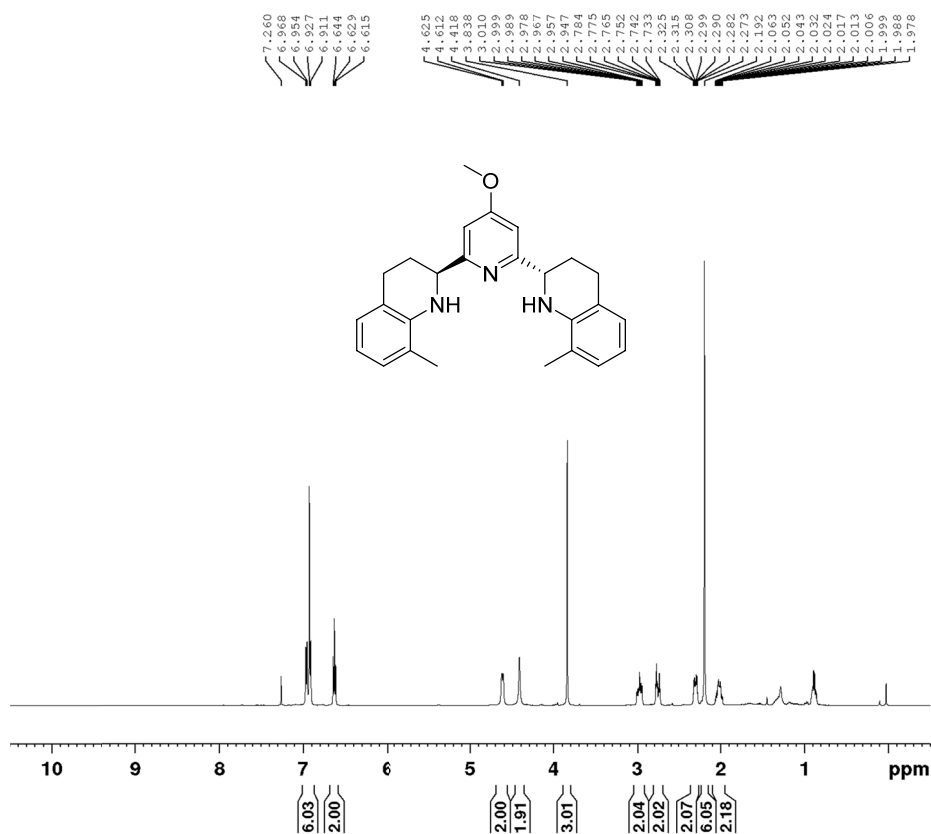


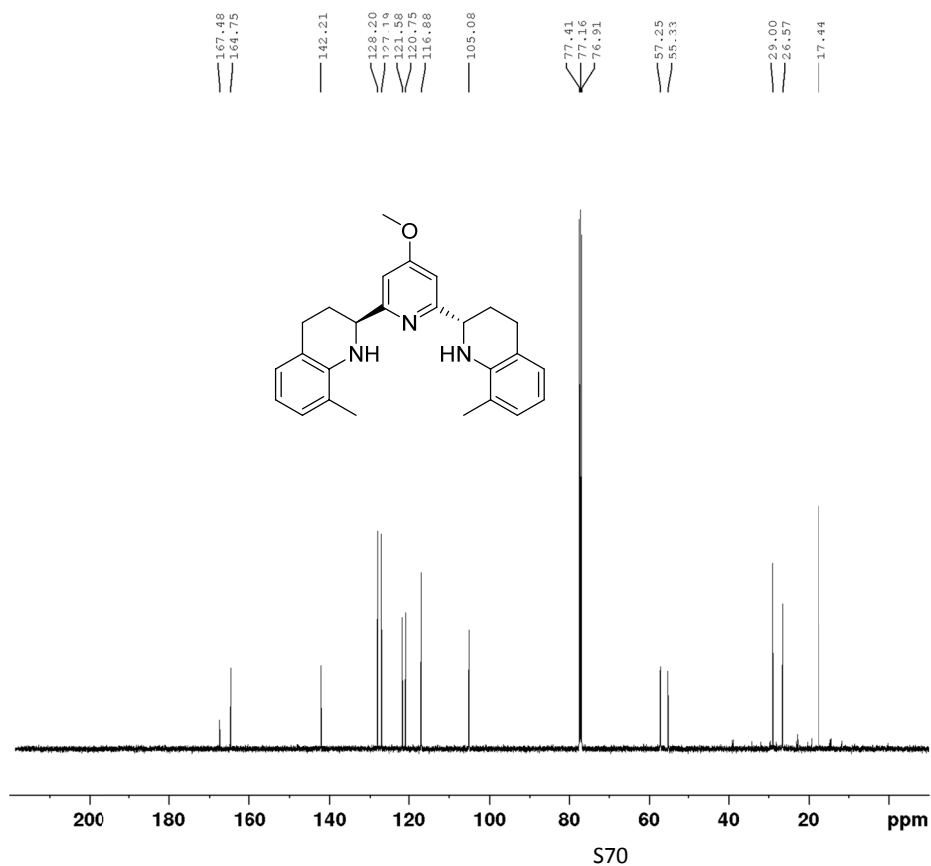
Figure S35. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2k** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1j,2j  
 EXPNO 99  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200324  
 Time 6.31  
 INSTRUM spect  
 PROBHDD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 31.72  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 TD0 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 10.59 usec  
 PLW1 20.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300120 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

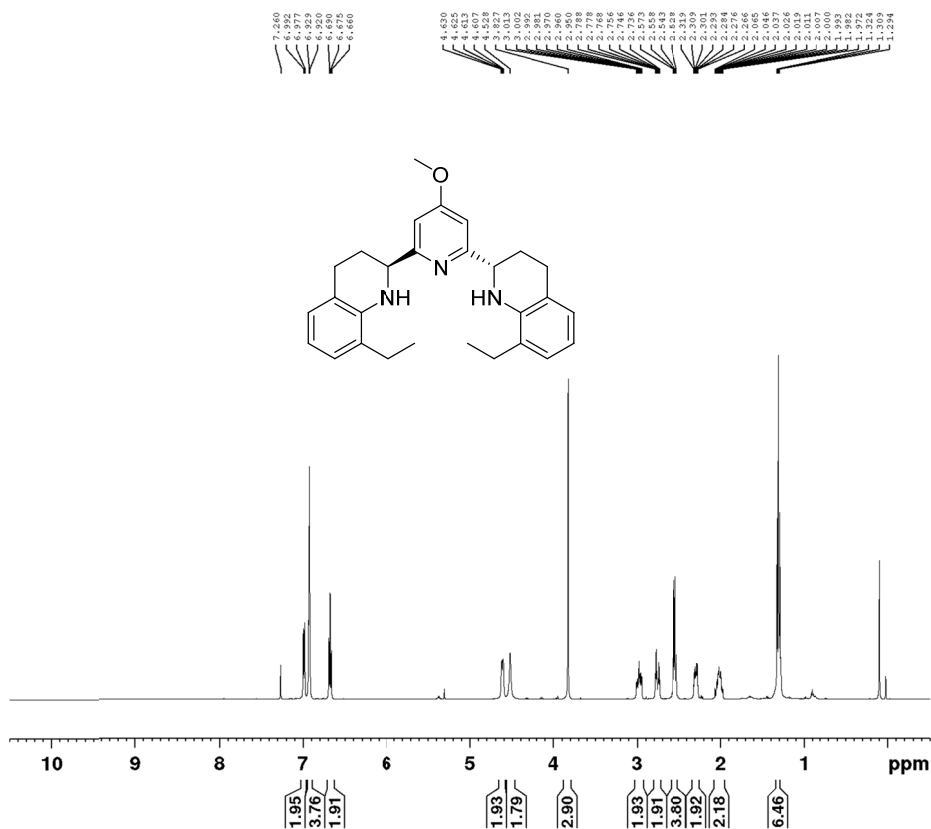


Current Data Parameters  
 NAME SI-1j,2j  
 EXPNO 100  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200324  
 Time 6.33  
 INSTRUM spect  
 PROBHDD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 48  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577760 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

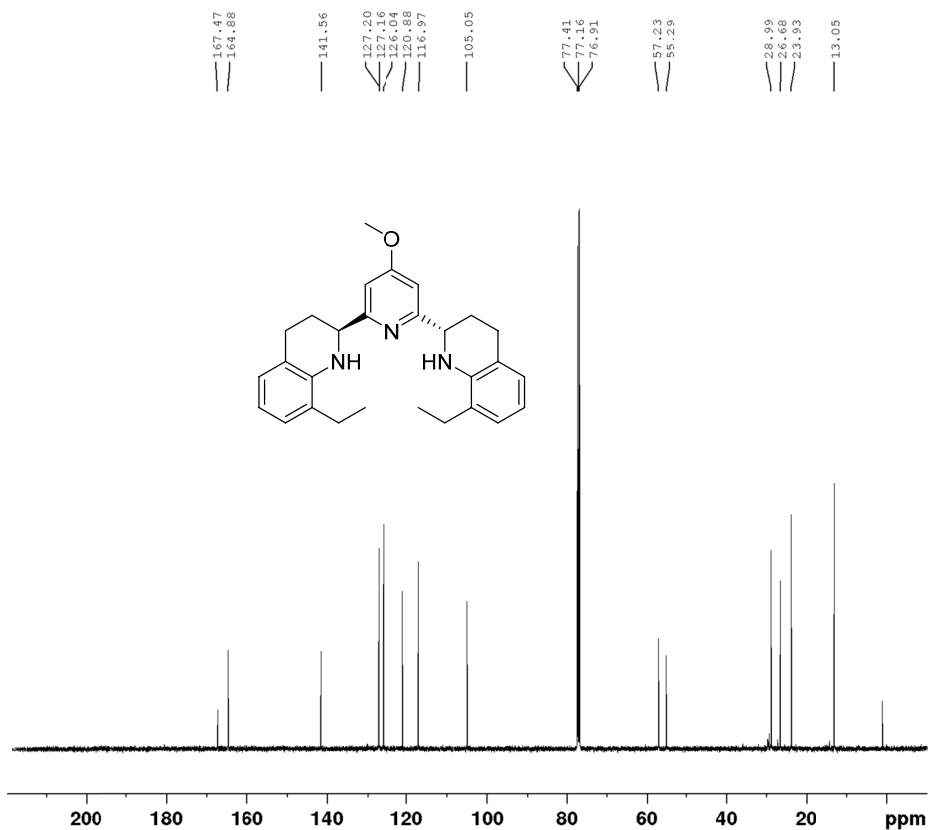
Figure S36. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-21 (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-1k,2k  
 EXPNO 95  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200322  
 Time 7.18  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152588 Hz  
 AQ 3.2767999 sec  
 RG 31.72  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 TD0 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 10.59 usec  
 PLW1 20.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300118 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME SI-1k,2k  
 EXPNO 96  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200322  
 Time 7.21  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 76  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999999 sec  
 TD0 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLN1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577763 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S37. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2m (CDCl<sub>3</sub>)

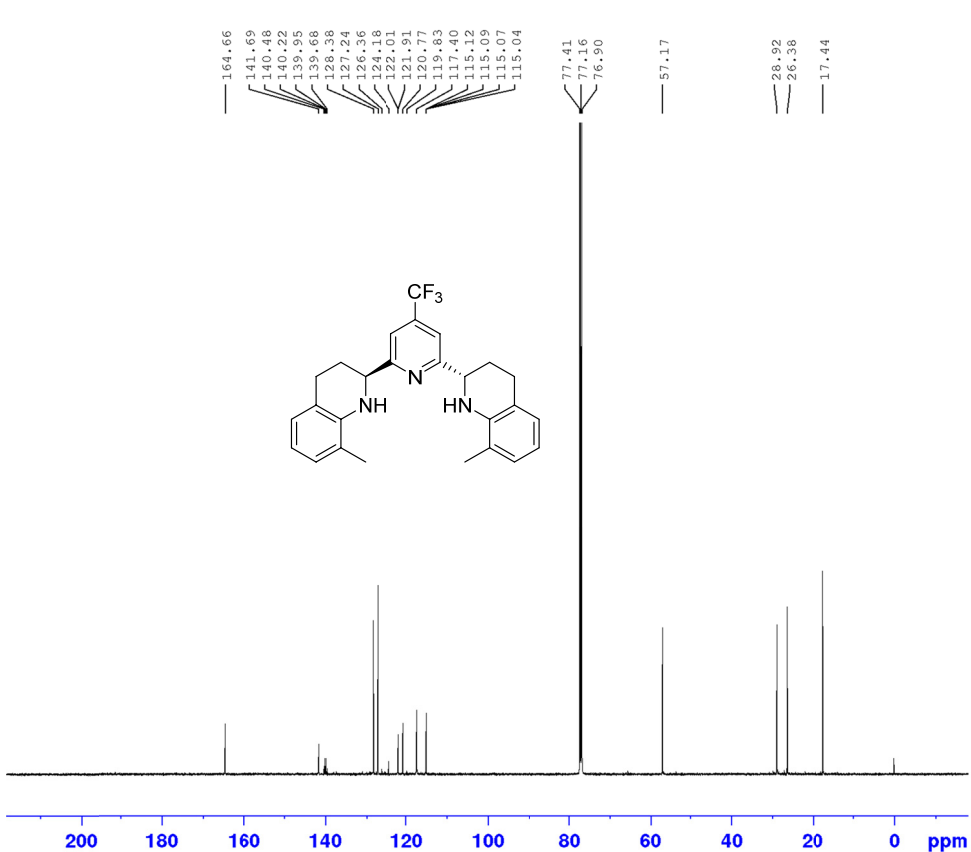
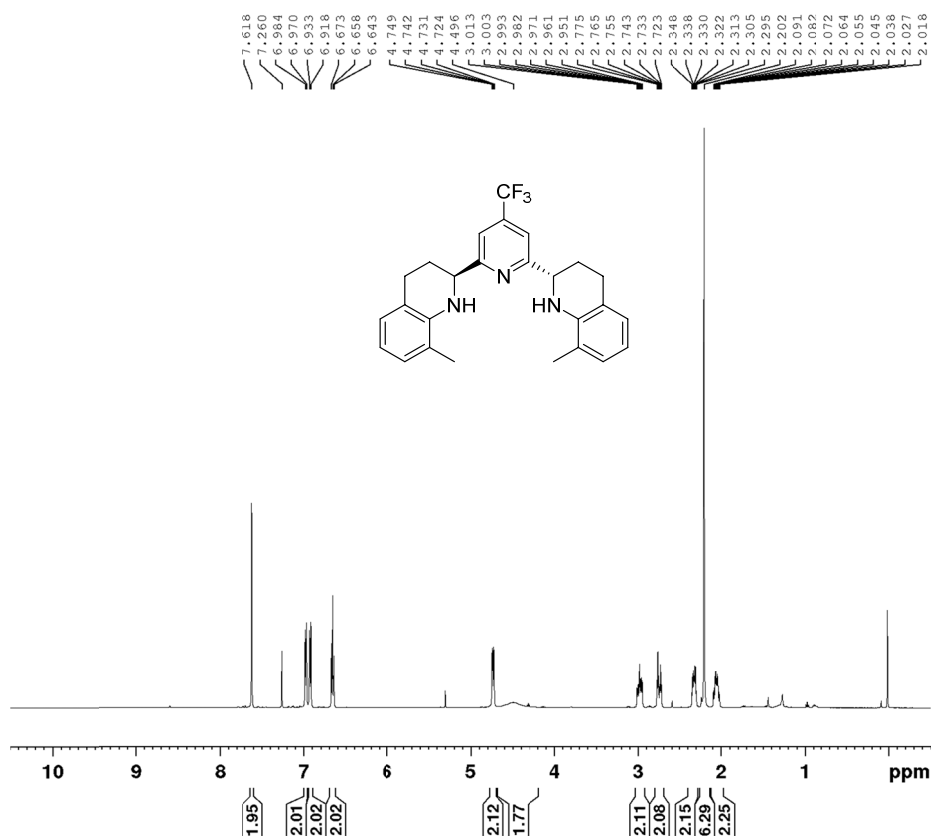


Figure S38. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2n** (CDCl<sub>3</sub>)

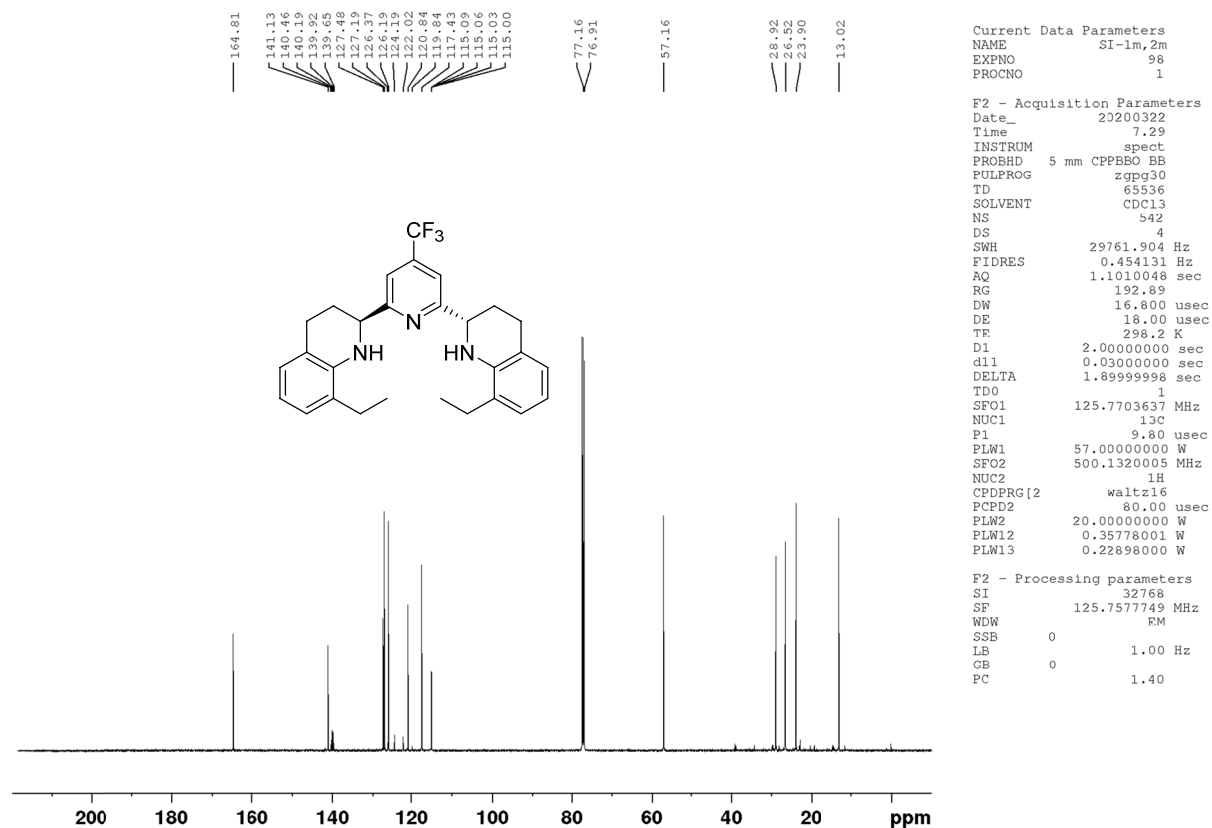
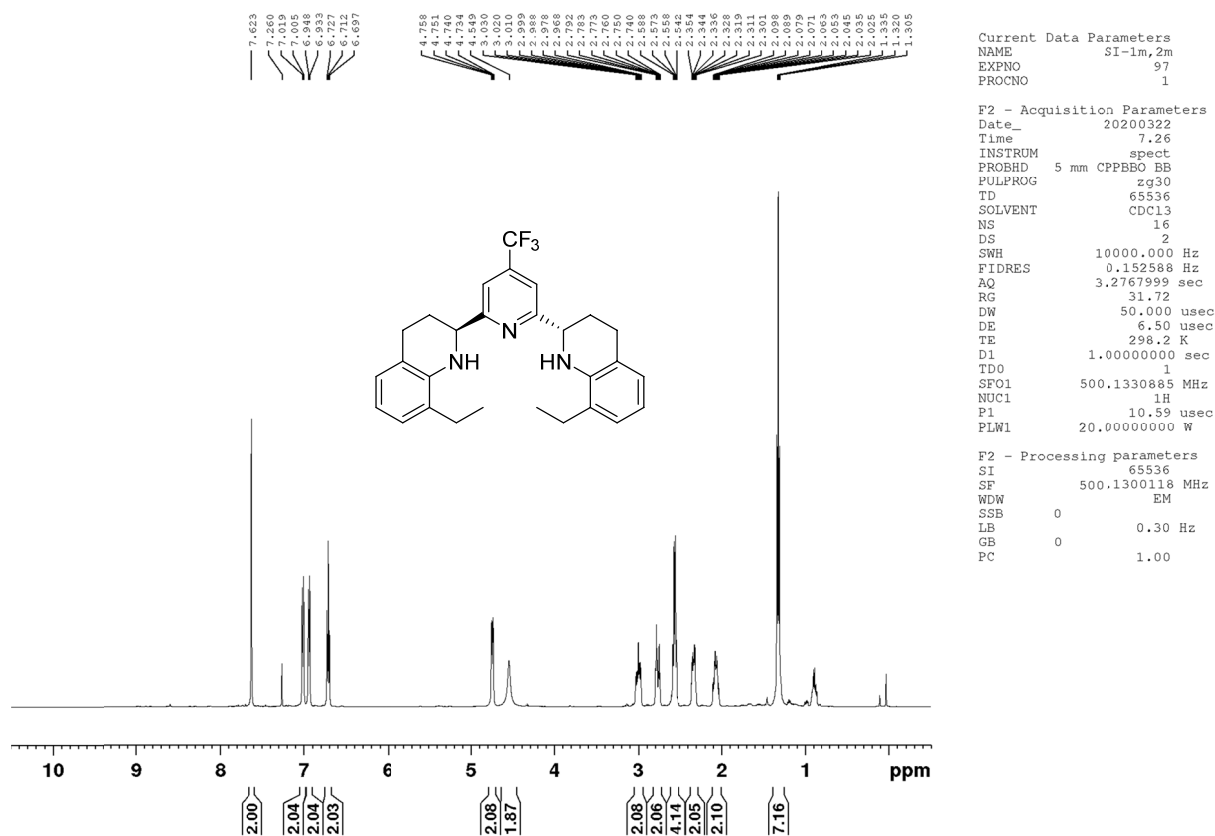


Figure S39. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2o** (CDCl<sub>3</sub>)

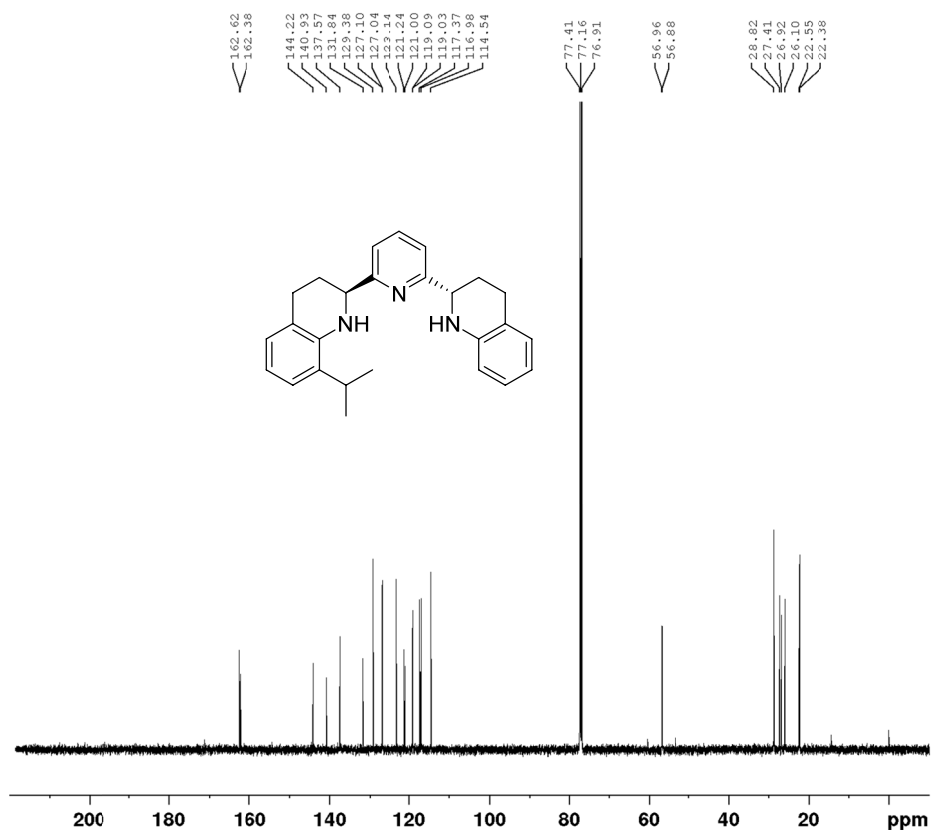
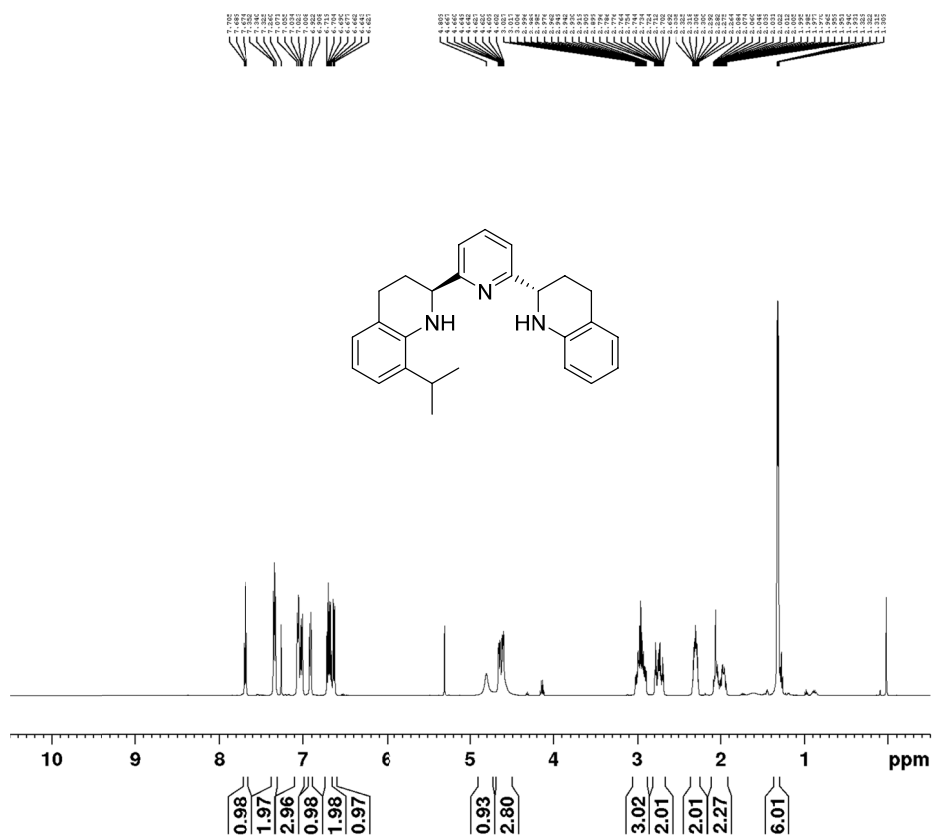
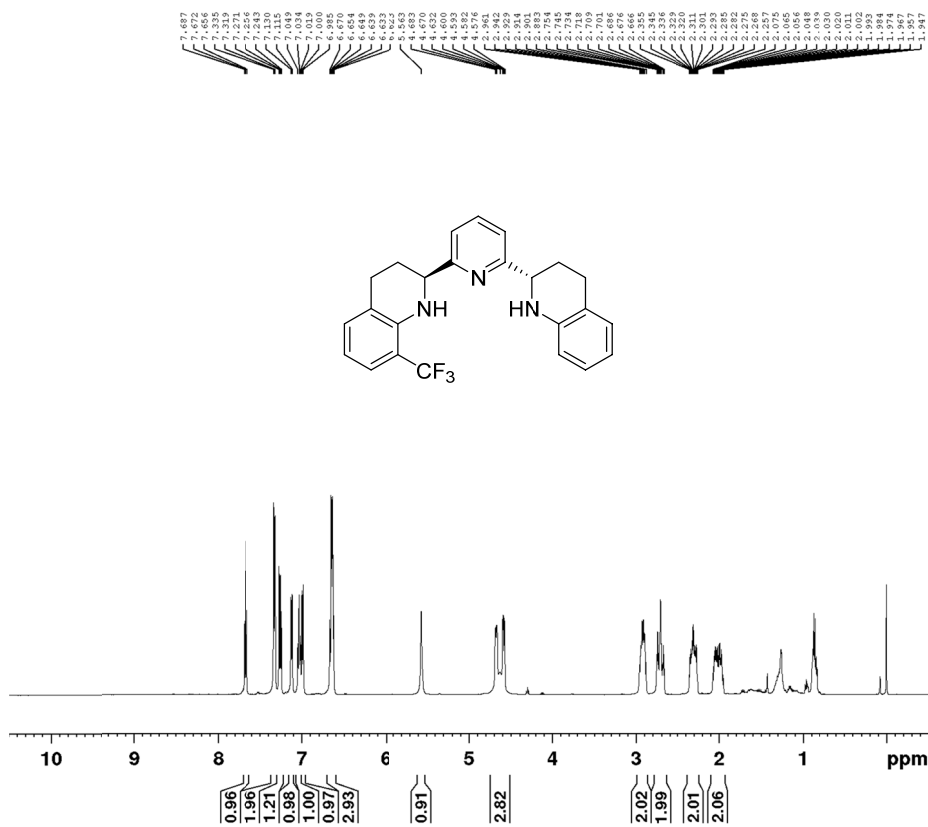


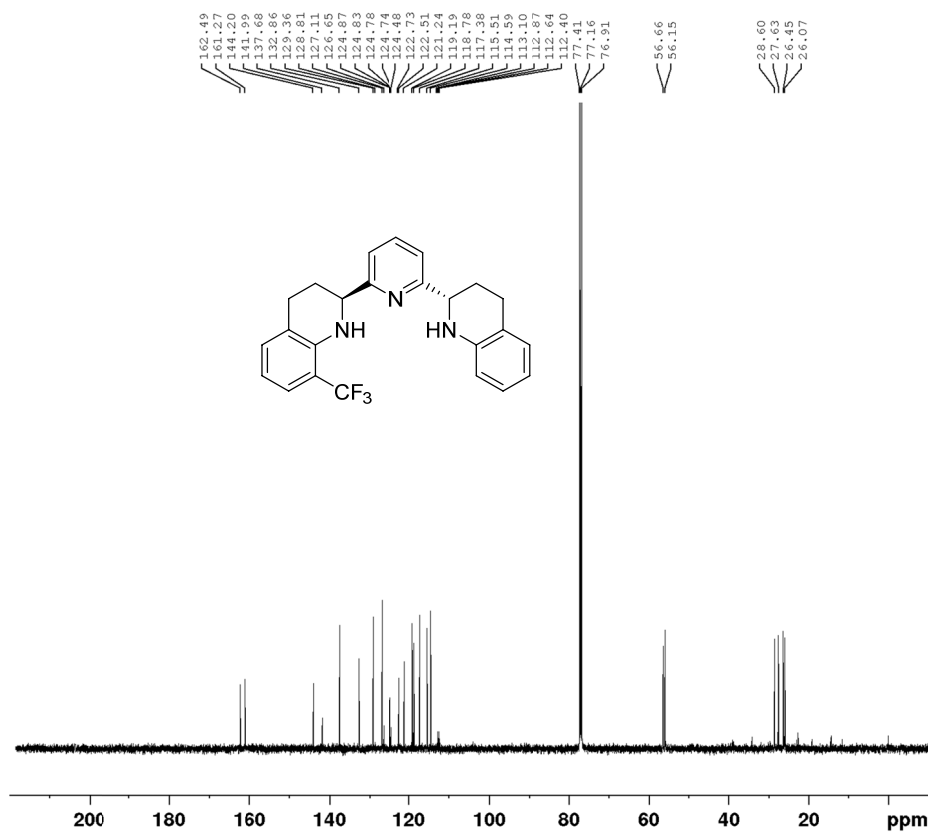
Figure S40. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-**2p** (CDCl<sub>3</sub>)



Current Data Parameters  
 NAME SI-10,2o  
 EXPNO 66  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200312  
 Time 11.46  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.152568 Hz  
 AQ 3.2767999 sec  
 RG 31.72  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 TDO 1  
 SFO1 500.1330885 MHz  
 NUC1 1H  
 P1 10.59 usec  
 PLW1 20.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300205 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME SI-10,2o  
 EXPNO 67  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200312  
 Time 11.47  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 45  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 192.89  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 298.2 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TDO 1  
 SFO1 125.7703637 MHz  
 NUC1 13C  
 P1 9.80 usec  
 PLW1 57.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 80.00 usec  
 PLW2 20.00000000 W  
 PLW12 0.35778001 W  
 PLW13 0.22898000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577743 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 0.80

Figure S41. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2q (CDCl<sub>3</sub>)

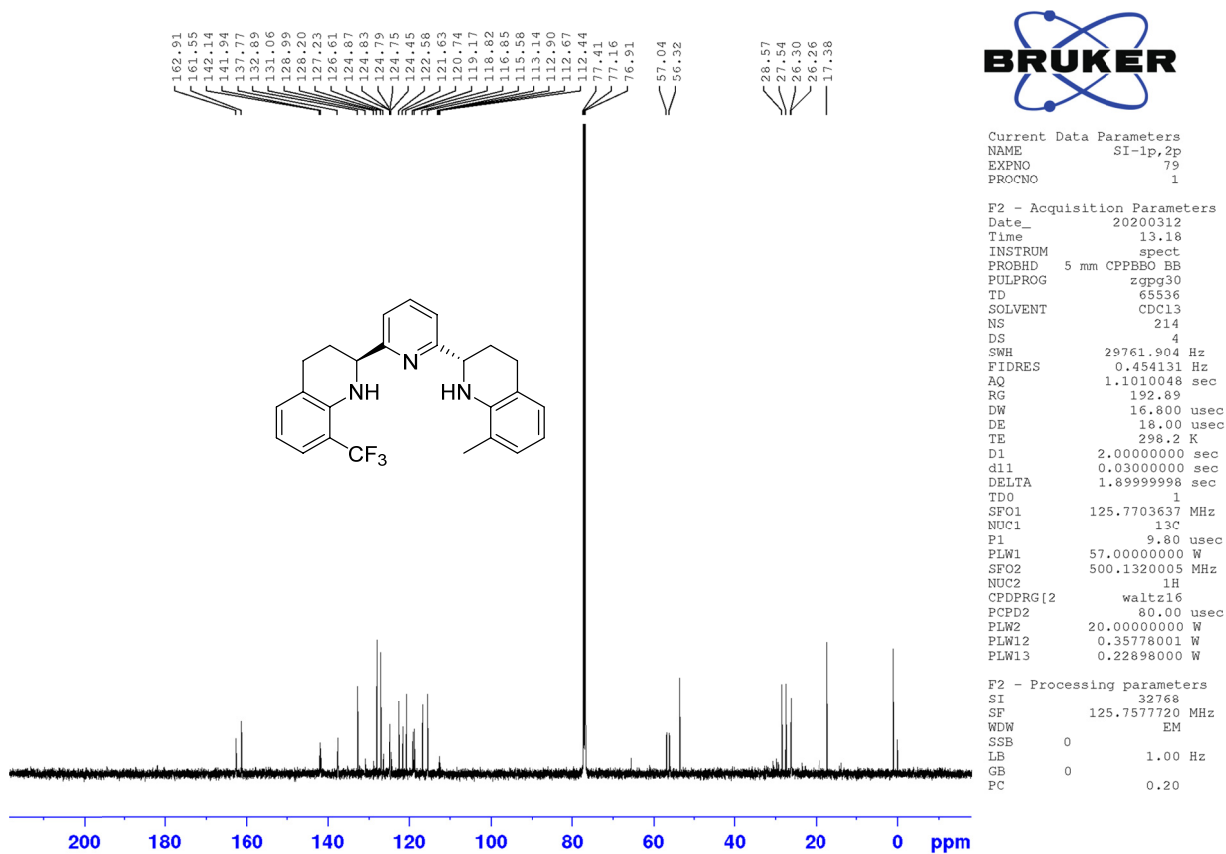
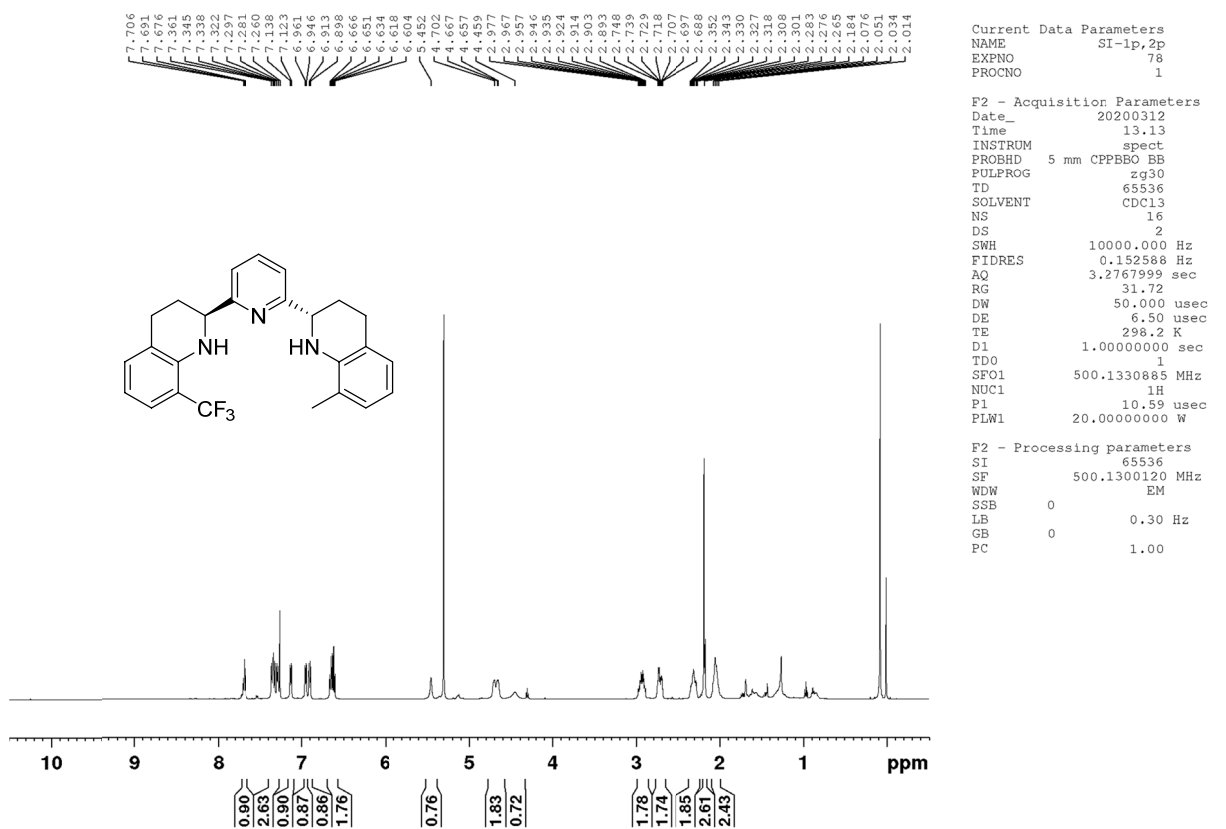


Figure S42. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2r (CDCl<sub>3</sub>)



**Figure S43.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of *meso*-2r ( $\text{CDCl}_3$ )

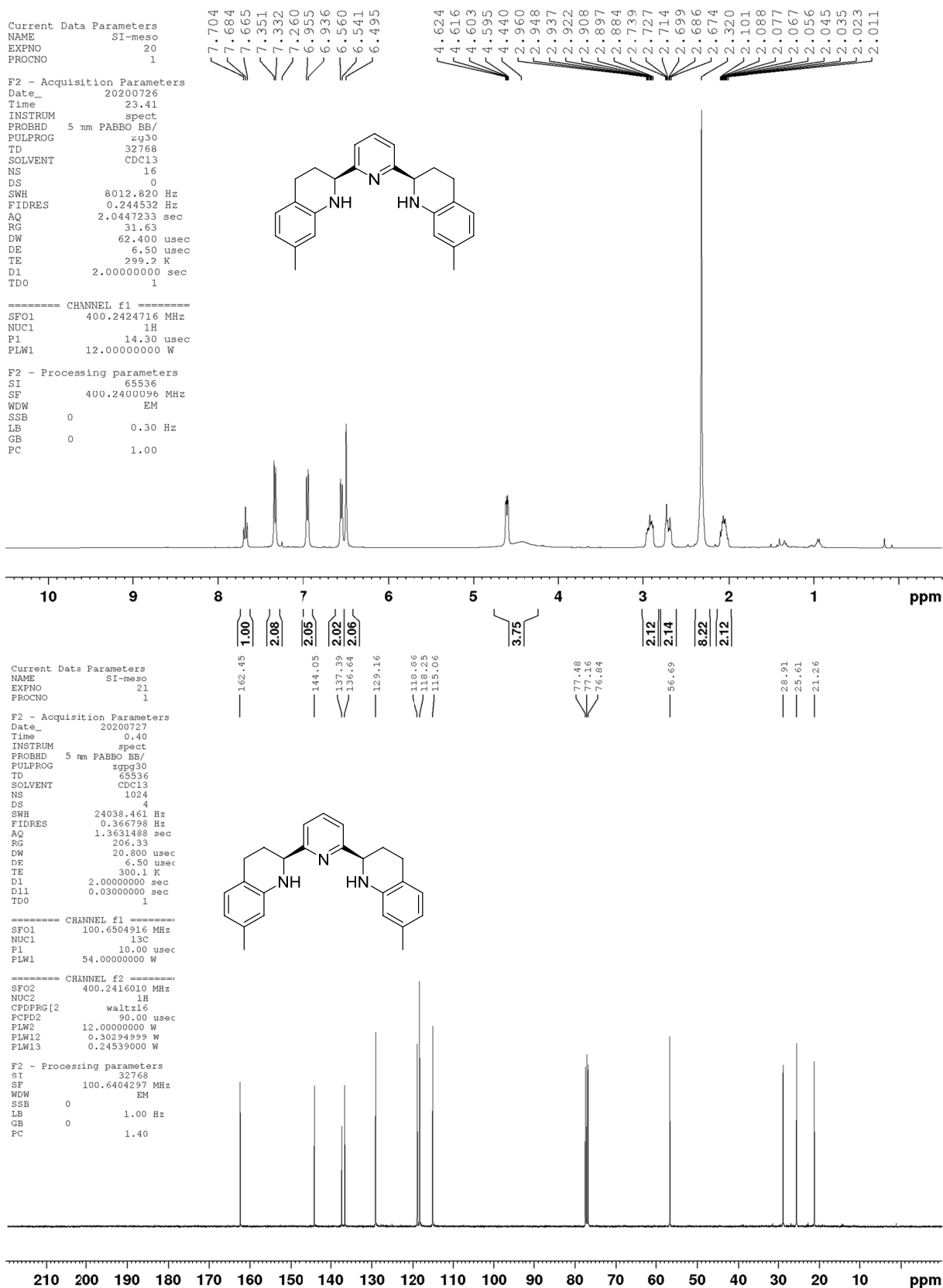


Figure S44. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2s (CDCl<sub>3</sub>)

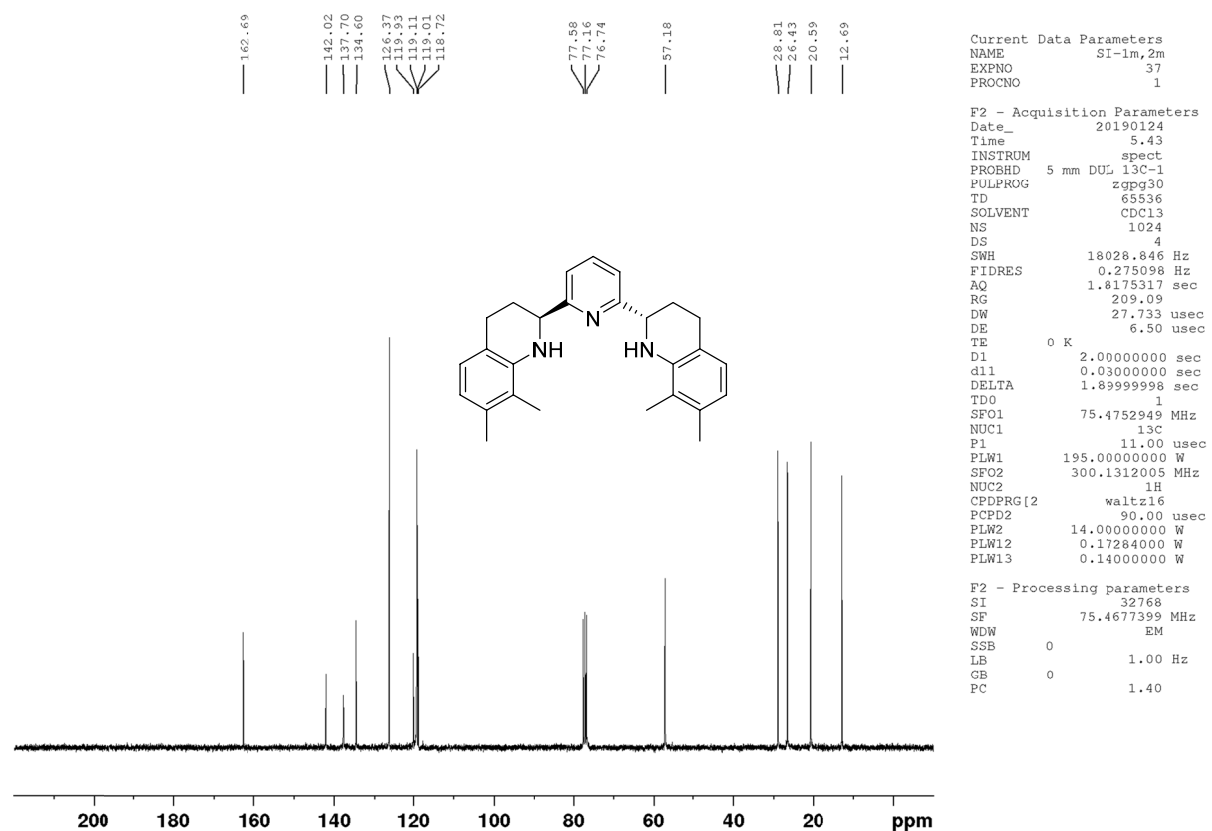
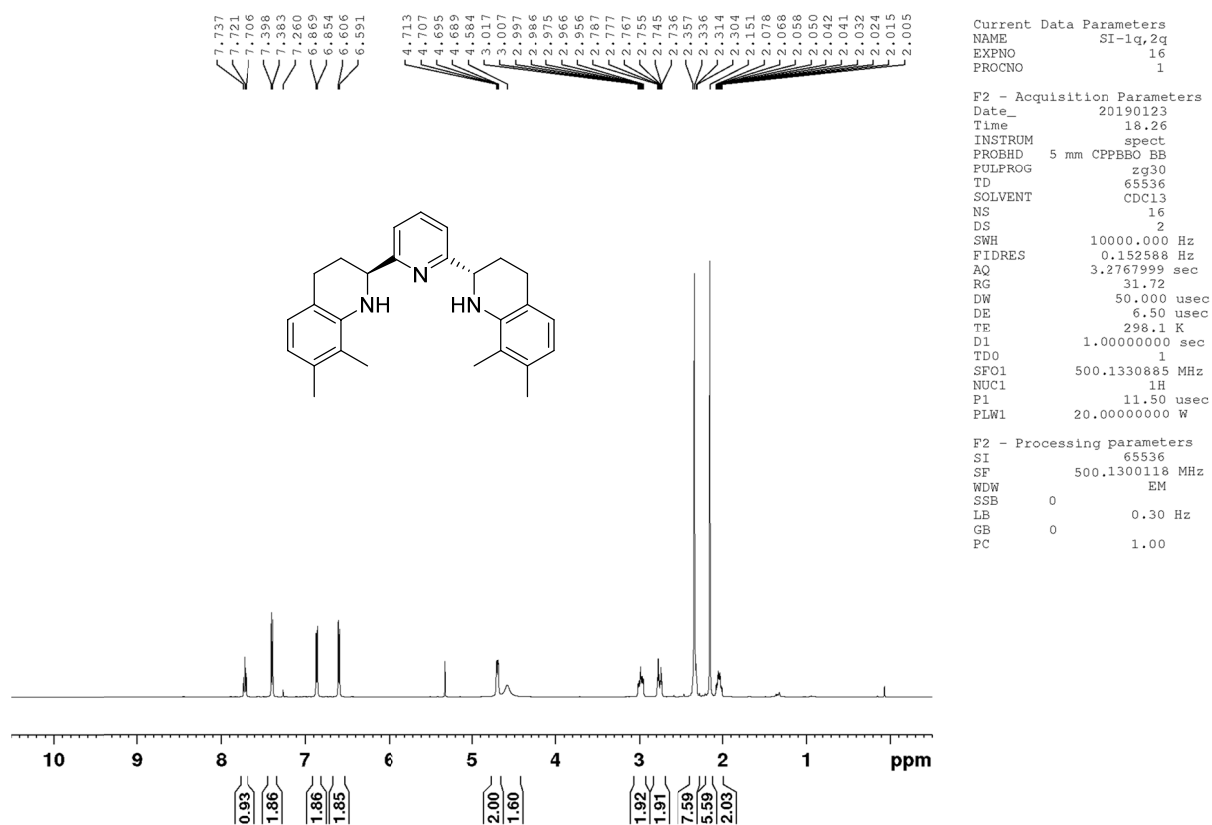


Figure S45. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S,S*)-2t (CDCl<sub>3</sub>)

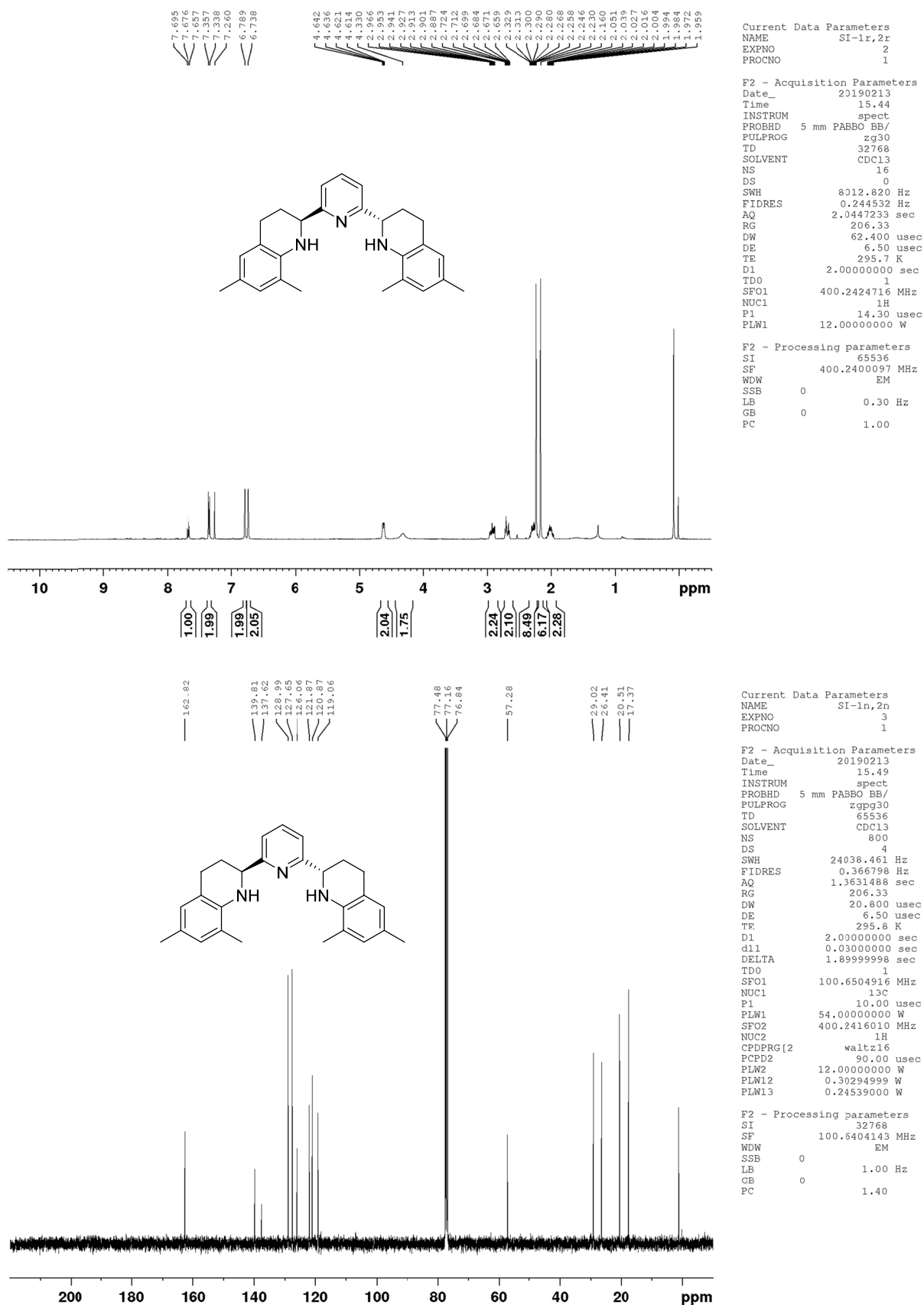
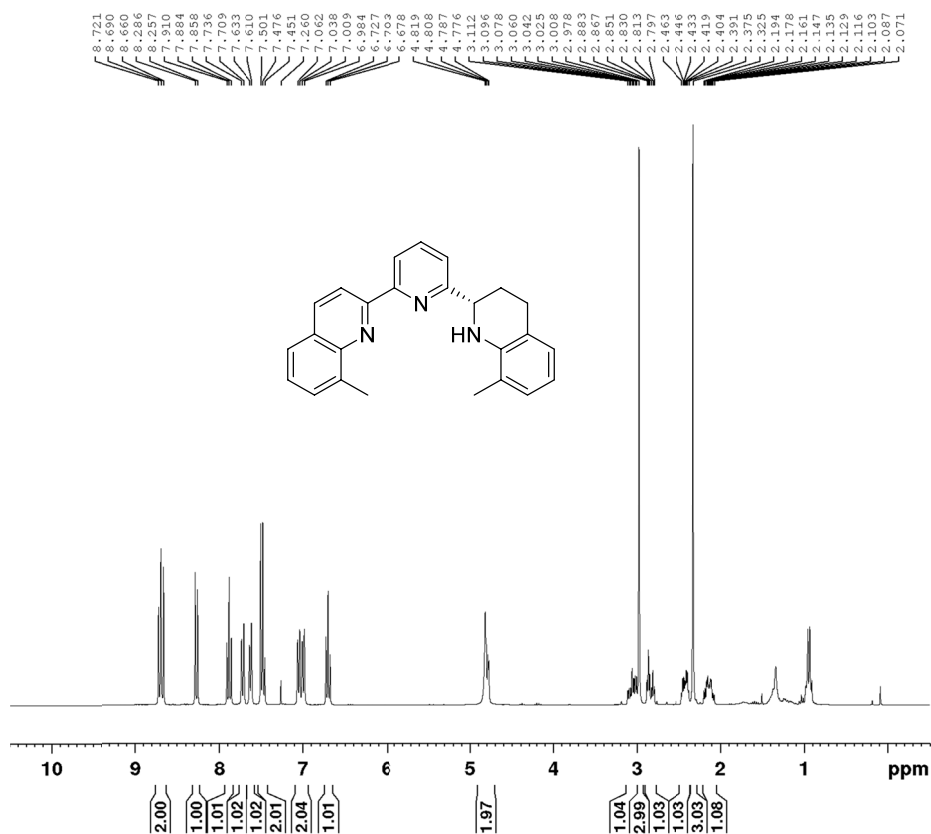


Figure S46. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of (*S*)-2a' (CDCl<sub>3</sub>)

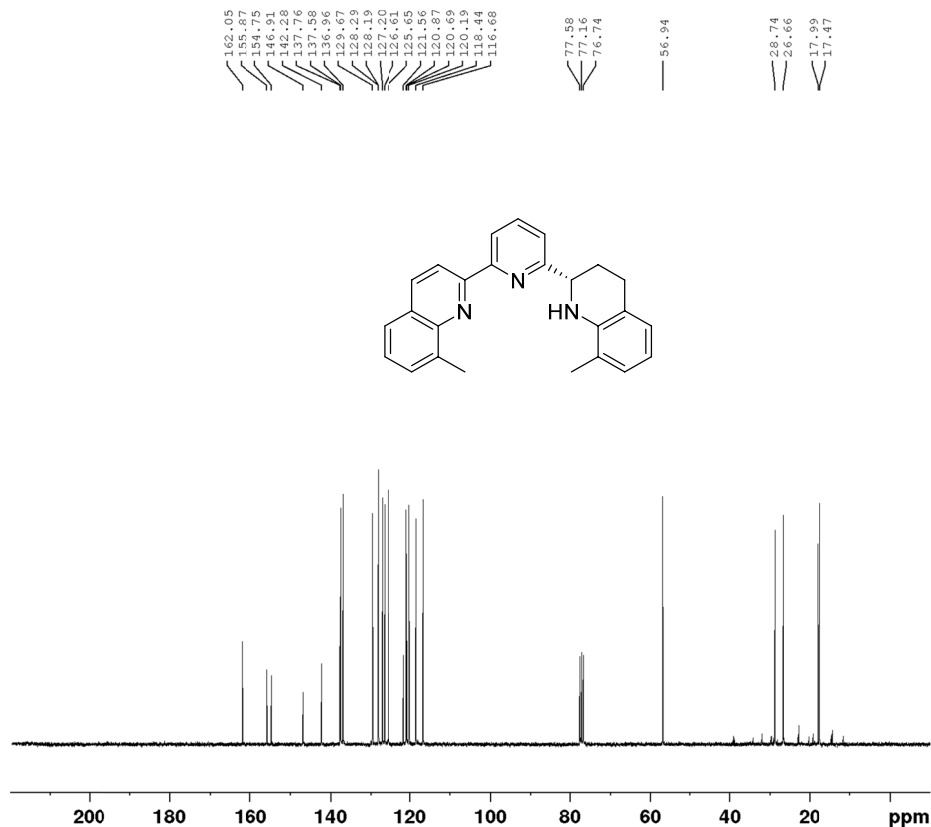


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Current Data Parameters
NAME      SI-2a'
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20200408
Time     19.23
INSTRUM  spect
PROBHD   5 mm DUL 13C-1
PULPROG  zg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       6009.615 Hz
FIDRES    0.091699 Hz
AQ        5.4525952 sec
RG        103.37
DW        83.200 usec
DE        6.50 usec
TE        298.2 K
D1        1.0000000 sec
TD0       1
SFO1     300.1318534 MHz
NUC1      1H
P1        8.00 usec
PLW1     18.0000000 W

F2 - Processing parameters
SI        65536
SF        300.1300069 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
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```

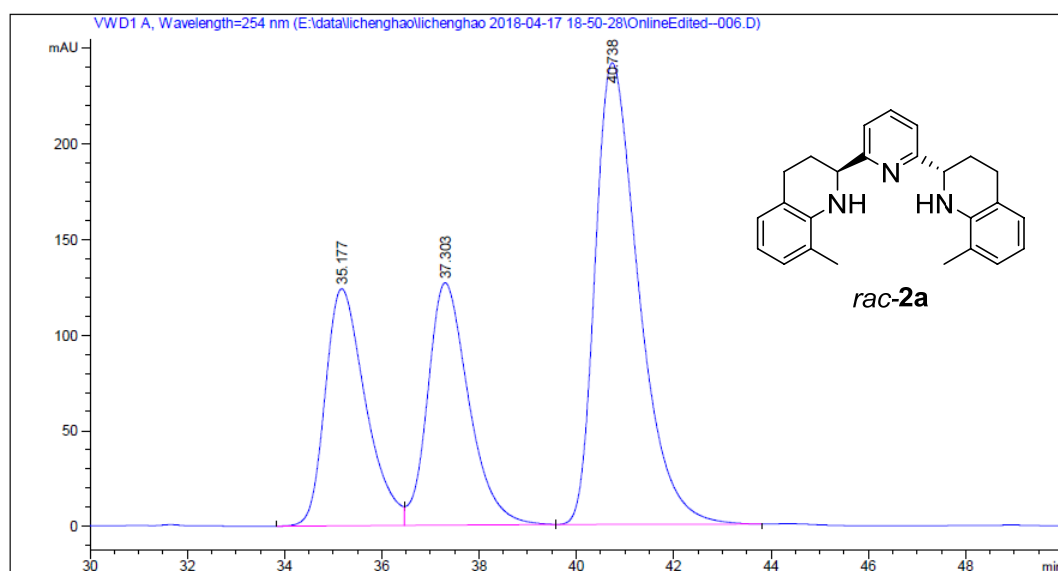
Current Data Parameters
NAME      SI-2a'
EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
Date_    20200408
Time     19.42
INSTRUM  spect
PROBHD   5 mm DUL 13C-1
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        305
DS        4
SWH       18028.846 Hz
FIDRES    0.275098 Hz
AQ        1.8175317 sec
RG        209.09
DW        27.733 usec
DE        6.50 usec
TE        298.2 K
D1        2.0000000 sec
d11       0.0300000 sec
DELTA    1.8999999 sec
TD0       1
SFO1     75.4752949 MHz
NUC1      13C
P1        11.00 usec
PLW1     195.0000000 W
SFO2     300.1312005 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2    90.00 usec
PLW2     14.0000000 W
PLW12    0.17284000 W
PLW13    0.14000000 W

F2 - Processing parameters
SI        32768
SF        75.4677470 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
    
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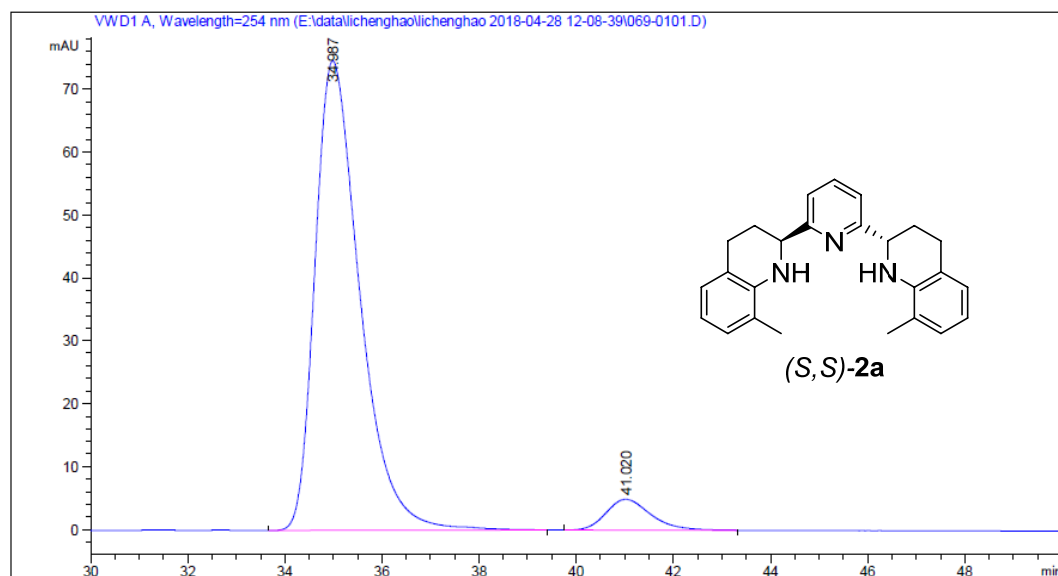
## 10. Copy of HPLC spectra

Figure S45. Copy of HPLC spectra of **2a**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.177	BV	0.8733	7130.60303	123.92323	24.1347
2	37.303	VB	0.8885	7401.84375	126.72173	25.0528
3	40.738	BB	0.9538	1.50125e4	241.32327	50.8125

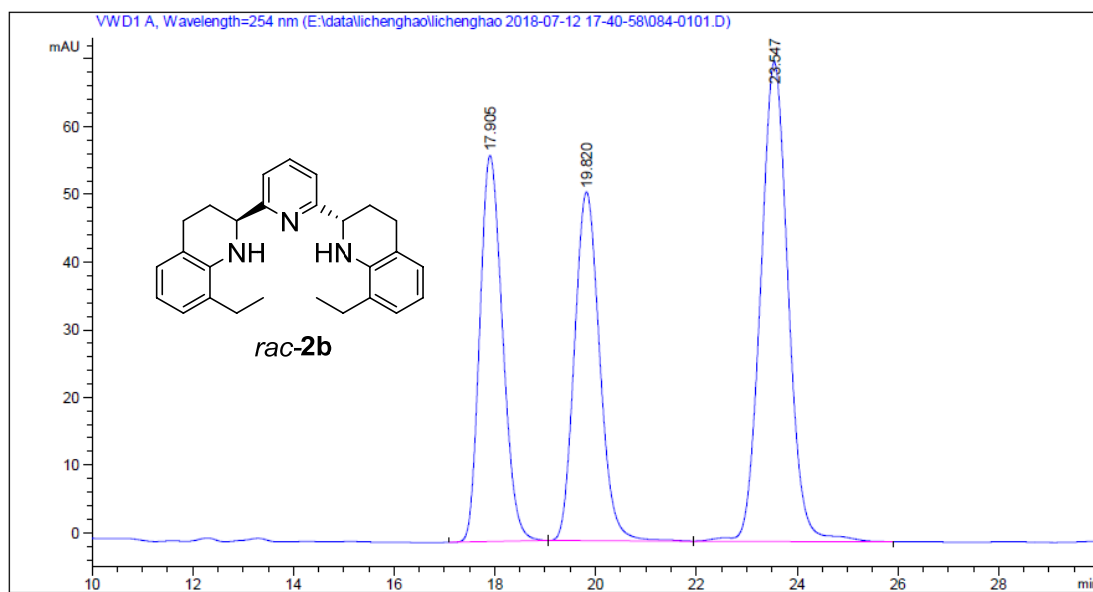
总量 : 2.95450e4 491.96824



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.987	BB	0.9691	4795.30176	74.68375	93.8659
2	41.020	BB	0.9349	313.36942	4.90134	6.1341

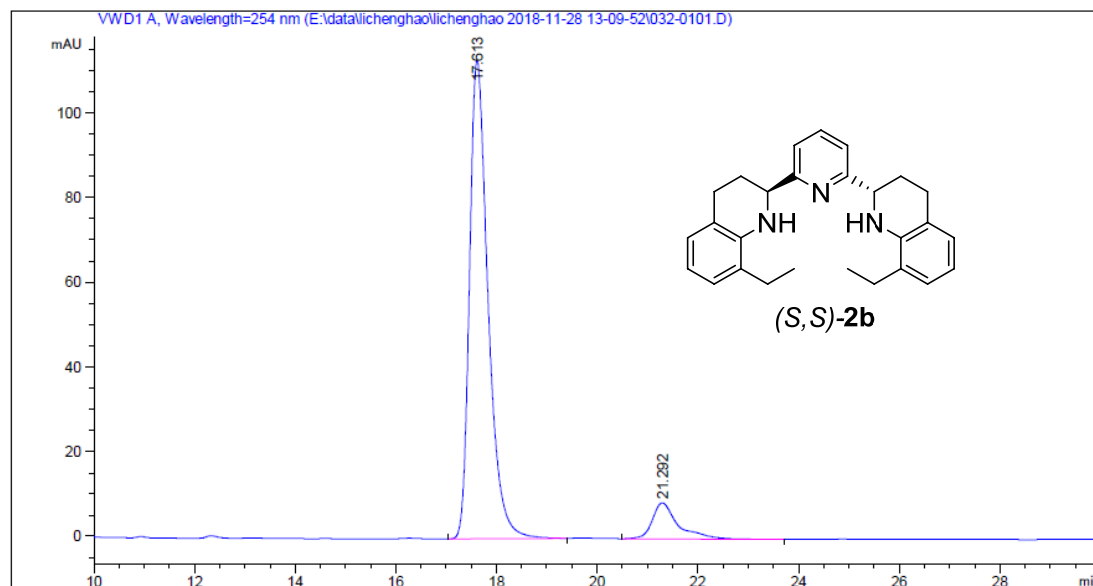
总量 : 5108.67117 79.58510

Figure S46. Copy of HPLC spectra of **2b**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.905	BB	0.4888	1784.65186	57.07648	28.5278
2	19.820	BB	0.5387	1783.13306	51.53272	28.5035
3	23.547	BB	0.5820	2688.05347	70.79456	42.9687

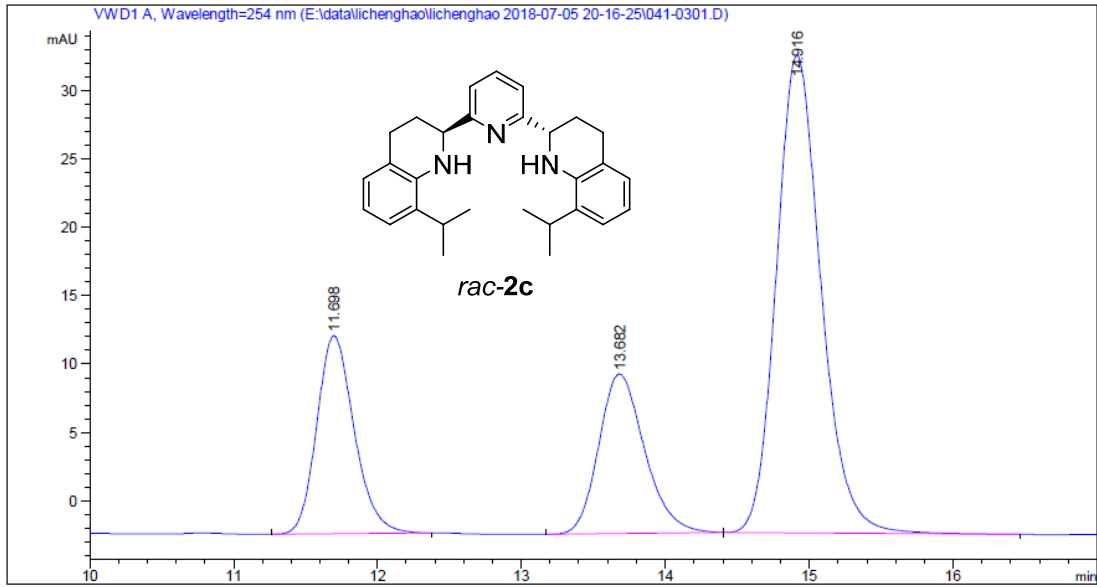
总量 : 6255.83838 179.40377



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.613	BB	0.3881	2886.47510	112.96905	90.5395
2	21.292	BB	0.5157	301.60968	8.50597	9.4605

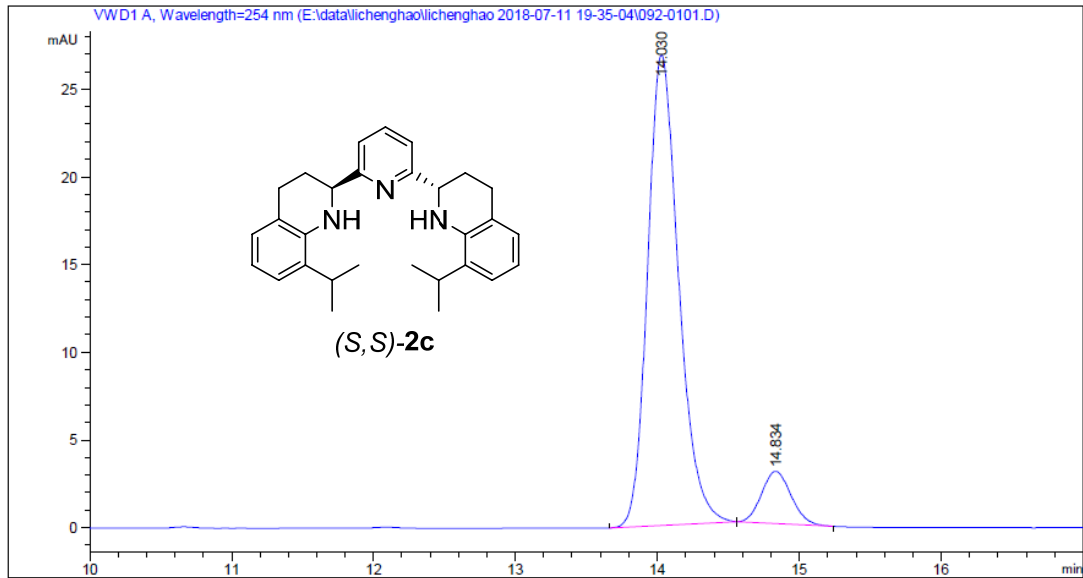
总量 : 3188.08478 121.47502

Figure S47. Copy of HPLC spectra of 2c



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.698	BB	0.2781	261.87531	14.47493	20.5754
2	13.682	BB	0.3414	258.45410	11.66919	20.3066
3	14.916	BB	0.3303	752.42767	34.92674	59.1179

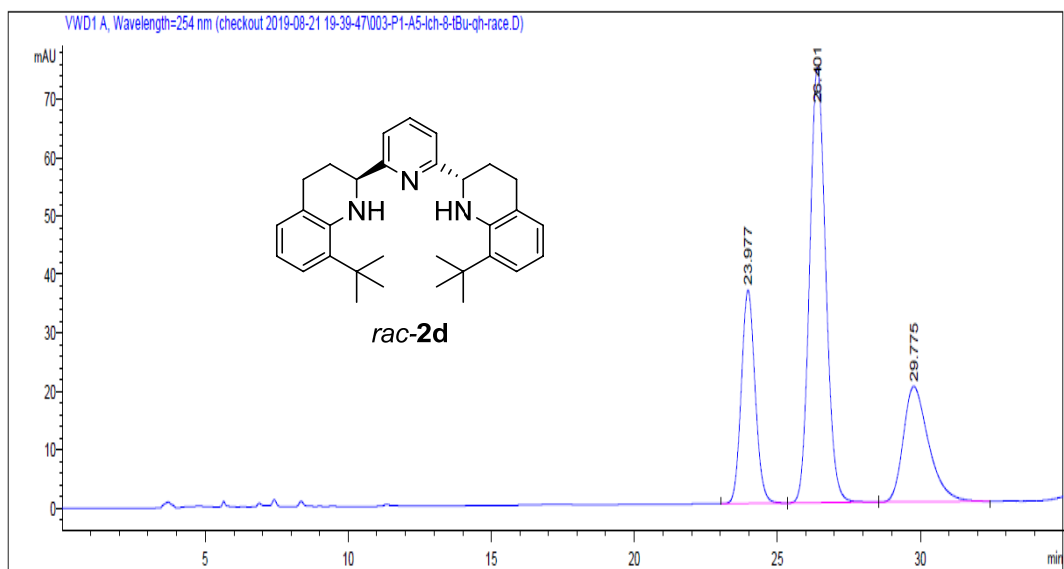
总量 : 1272.75708 61.07086



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.030	BB	0.2321	407.02774	26.81085	90.4294
2	14.834	BB	0.2259	43.07756	2.97482	9.5706

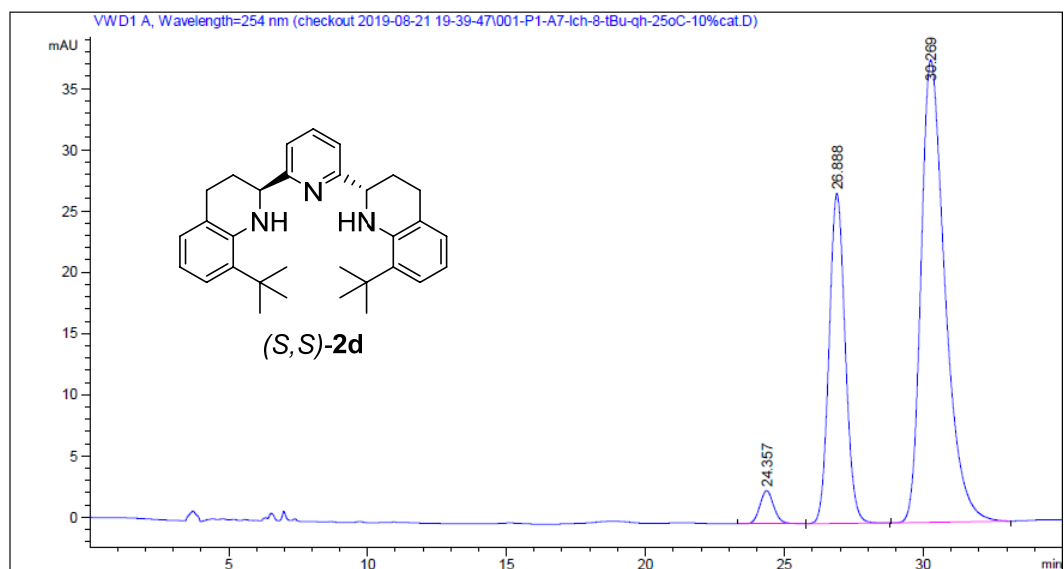
总量 : 450.10530 29.78567

Figure S48. Copy of HPLC spectra of 2d



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.977	BB	0.5201	1225.88635	36.47720	22.8799
2	26.401	BB	0.6015	2915.45068	74.35258	54.4140
3	29.775	BB	0.9357	1216.57190	19.72016	22.7061

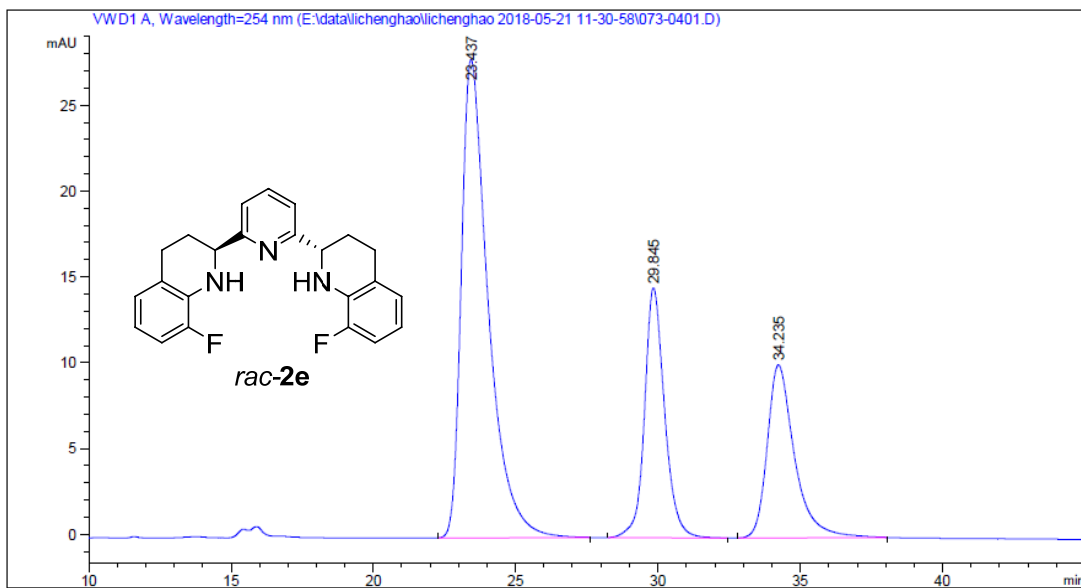
总量 : 5357.90894 130.54994



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.357	BB	0.5425	94.11469	2.70118	2.7305
2	26.888	BB	0.6229	1087.65955	26.94914	31.5553
3	30.269	BB	0.9085	2265.06226	37.72664	65.7142

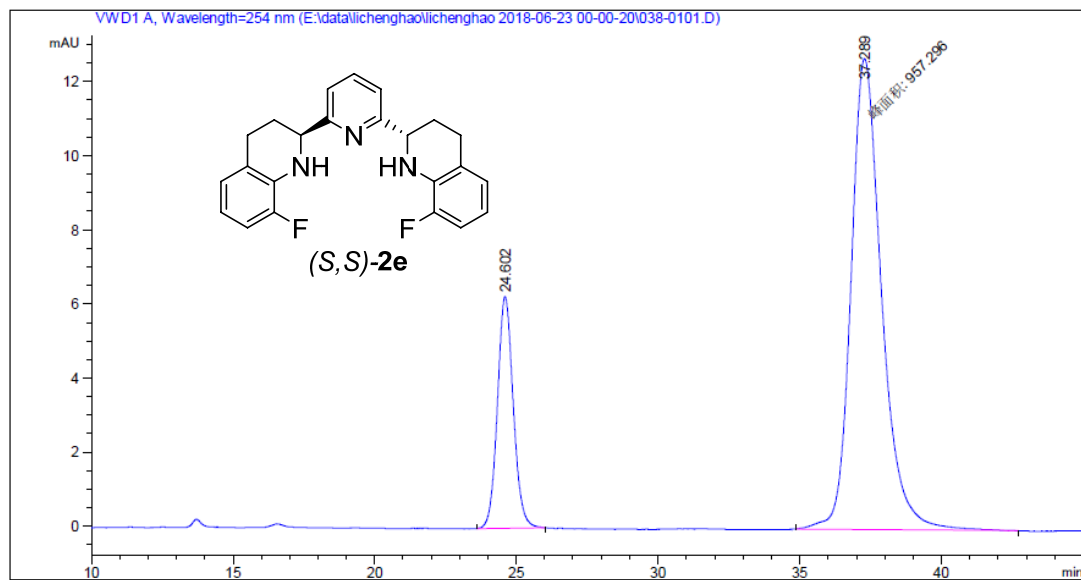
总量 : 3446.83649 67.37696

Figure S49. Copy of HPLC spectra of 2e



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.437	BB	0.9765	1832.71399	27.85980	56.9682
2	29.845	BB	0.7337	713.09552	14.55239	22.1659
3	34.235	BB	0.9779	671.27100	10.06756	20.8658

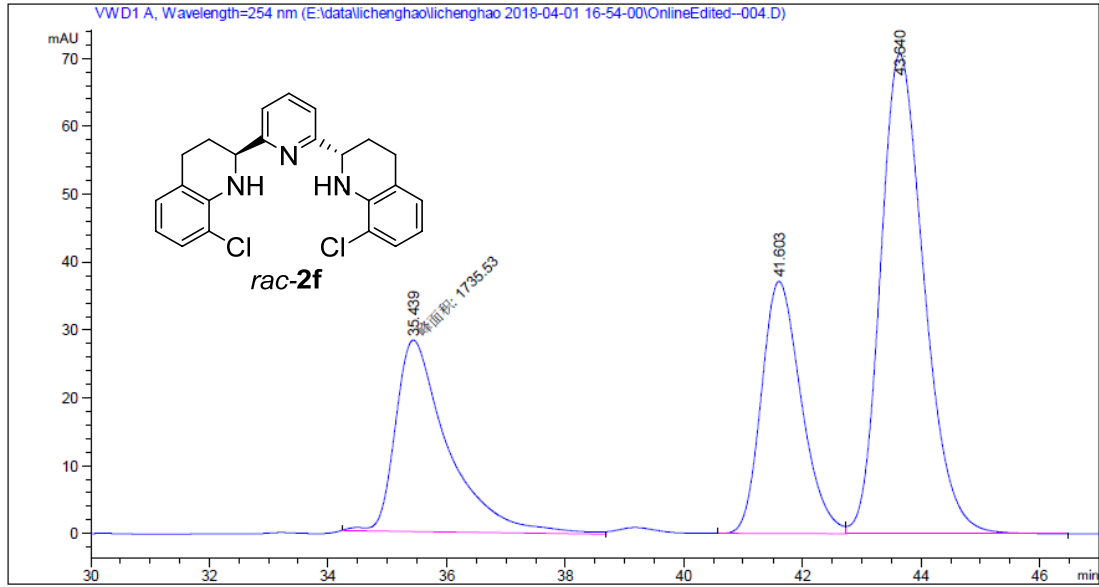
总量 : 3217.08051 52.47975



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.602	BB	0.5965	243.74405	6.25714	20.2944
2	37.289	MM	1.2553	957.29608	12.70966	79.7056

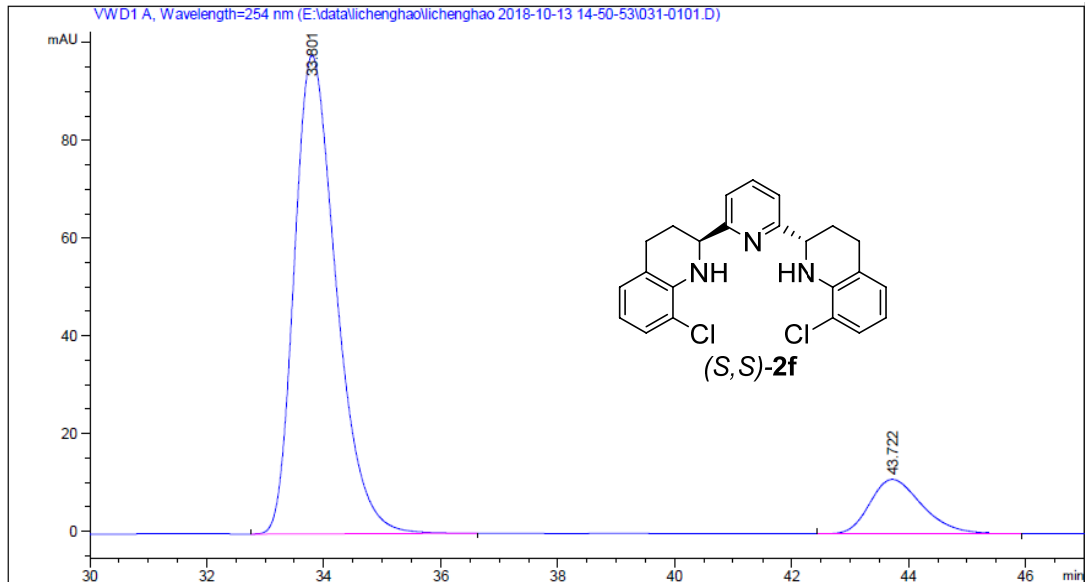
总量 : 1201.04013 18.96681

Figure S50. Copy of HPLC spectra of **2f**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.439	MM	1.0261	1735.52832	28.18846	24.5682
2	41.603	BV	0.7176	1723.20715	37.11708	24.3938
3	43.640	VB	0.7885	3605.39819	70.64001	51.0381

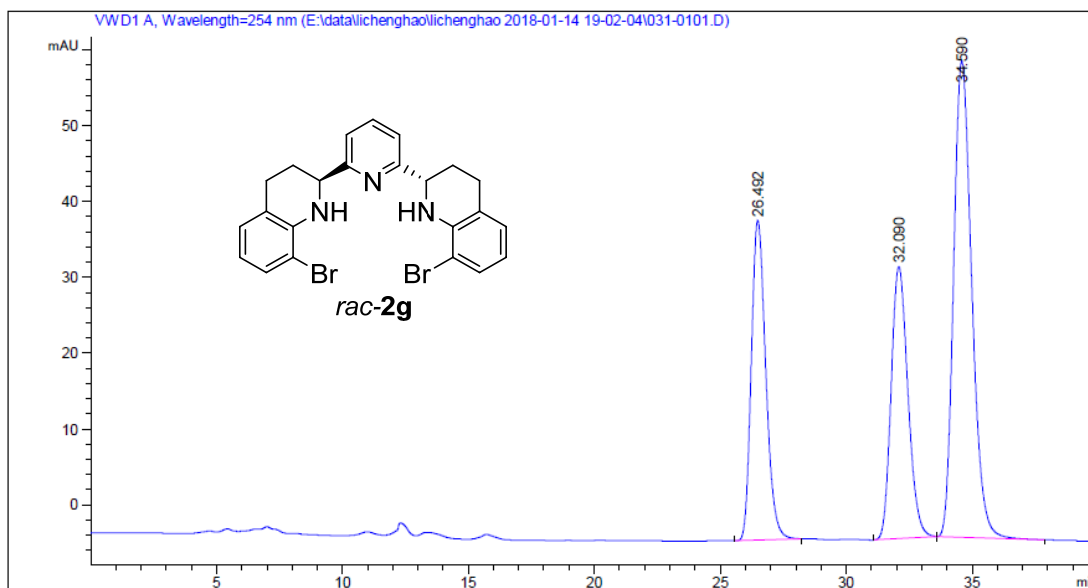
总量 : 7064.13367 135.94555



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.801	BB	0.7616	4873.82813	97.94224	87.5413
2	43.722	BB	0.9330	693.63165	11.14600	12.4587

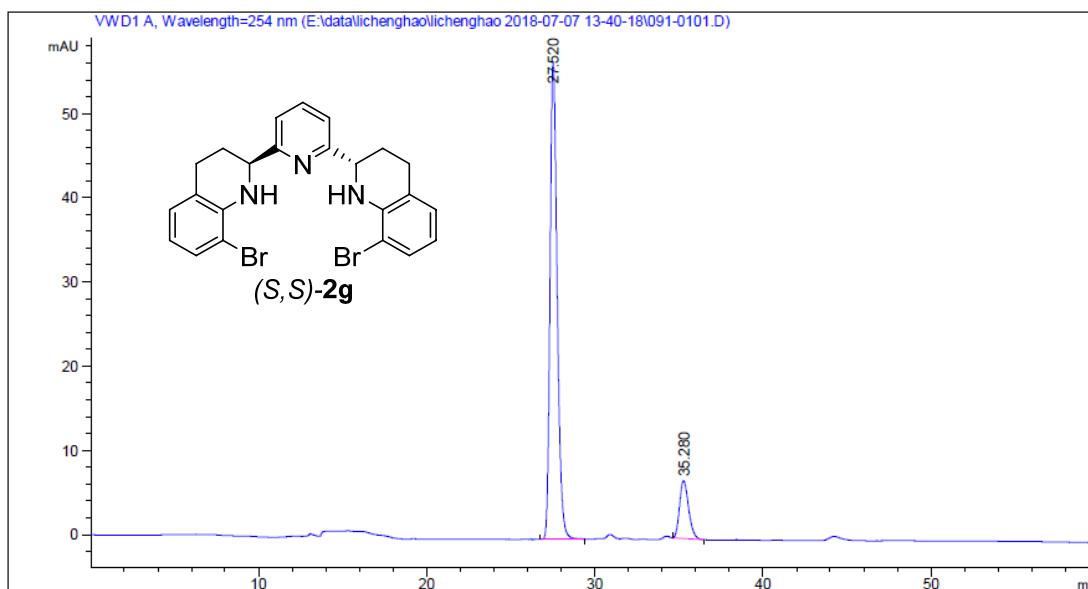
总量 : 5567.45978 109.08824

Figure S51. Copy of HPLC spectra of **2g**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	26.492	BB	0.6185	1681.24158	42.13564	25.9664
2	32.090	BB	0.7143	1655.59009	35.88161	25.5703
3	34.590	BB	0.7751	3137.83838	62.78224	48.4633

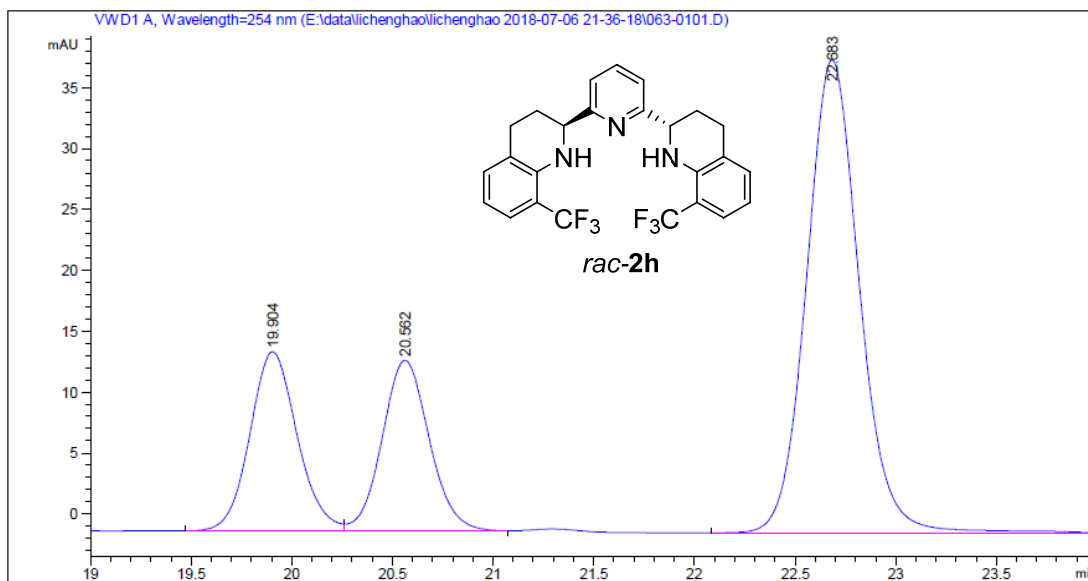
总量 : 6474.67004 140.79949



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	27.520	BB	0.4516	1672.38745	56.62325	86.6789
2	35.280	BB	0.5733	257.01776	6.85750	13.3211

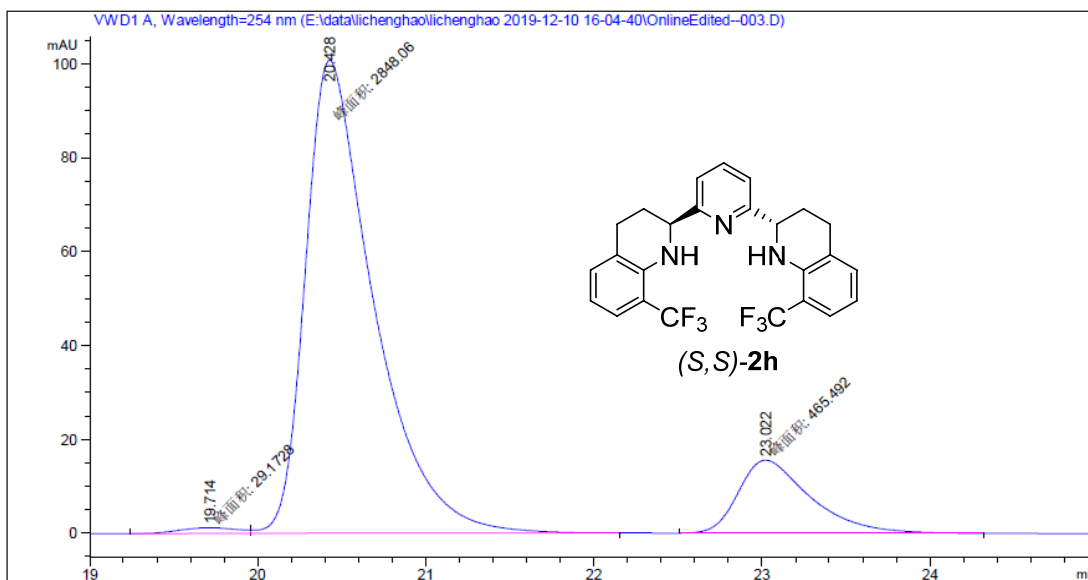
总量 : 1929.40521 63.48076

Figure S52. Copy of HPLC spectra of **2h**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.904	BV	0.2503	239.98854	14.71468	20.3038
2	20.562	VB	0.2518	228.09204	14.02364	19.2973
3	22.683	BB	0.2812	713.90680	38.88718	60.3989

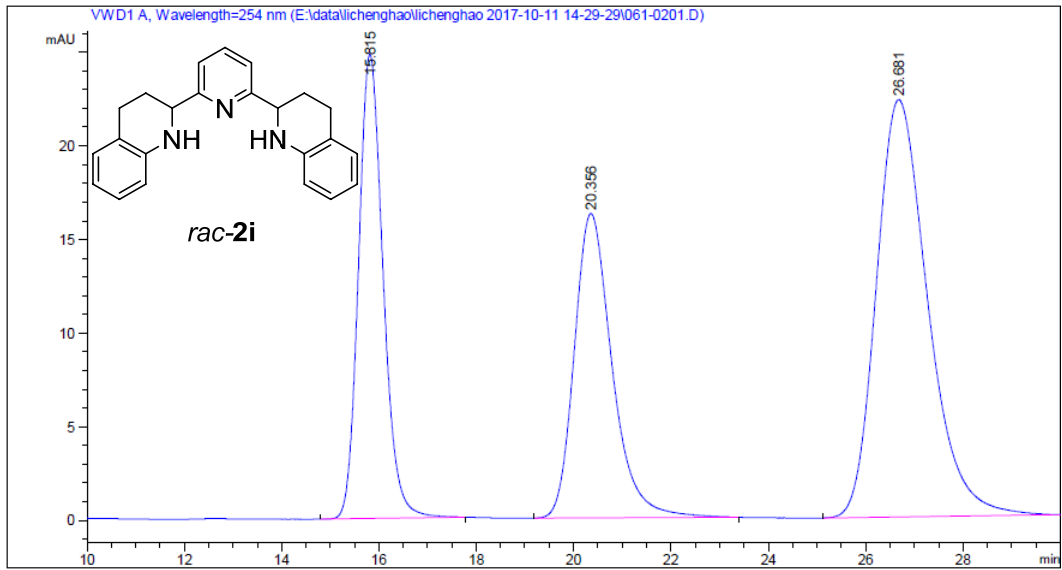
总量 : 1181.98738 67.62550



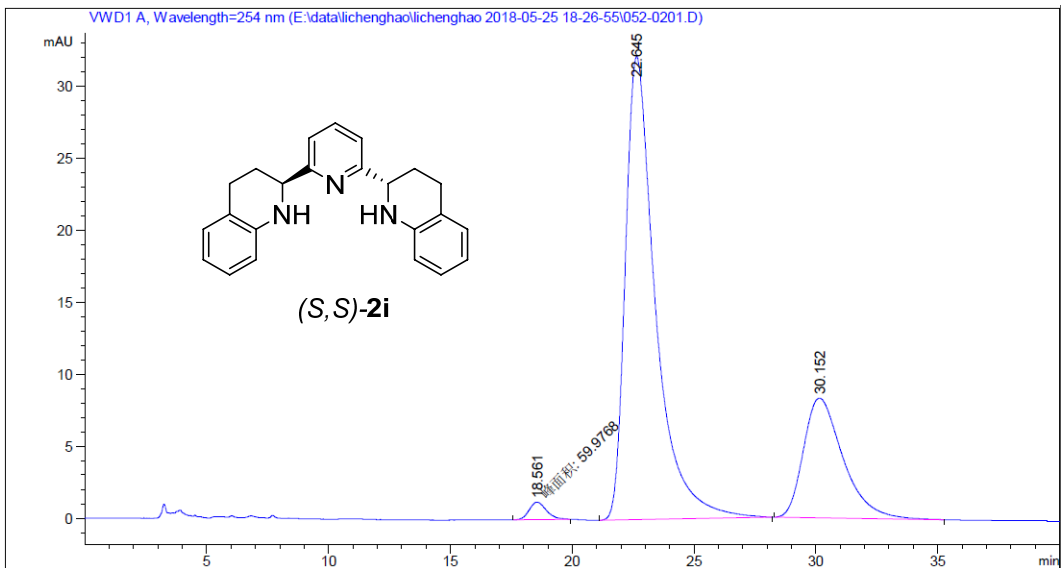
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.714	MF	0.3953	29.17277	1.22987	0.8727
2	20.428	FM	0.4710	2848.05615	100.78342	85.2017
3	23.022	MM	0.4978	465.49179	15.58382	13.9255

总量 : 3342.72071 117.59711

Figure S53. Copy of HPLC spectra of 2i



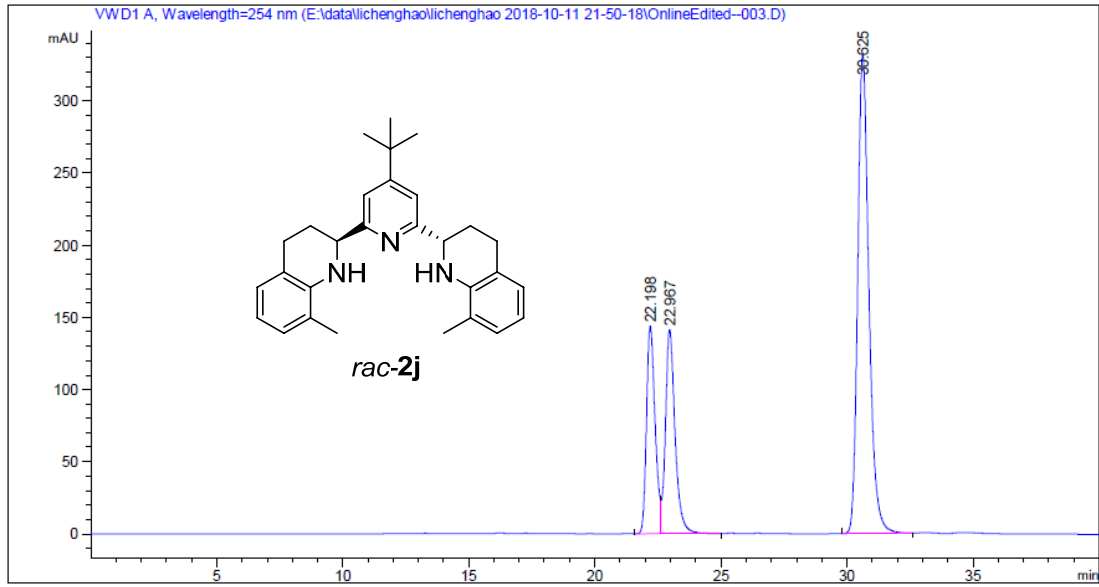
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.815	BB	0.5414	869.97546	24.79234	25.7268
2	20.356	BB	0.8116	877.51331	16.26130	25.9497
3	26.681	BBA	1.1114	1634.10034	22.28723	48.3234



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.561	MM	0.8239	59.97681	1.21321	1.5959
2	22.645	BB	1.2615	2760.49585	32.15820	73.4546
3	30.152	BB	1.5028	937.62604	8.31346	24.9495

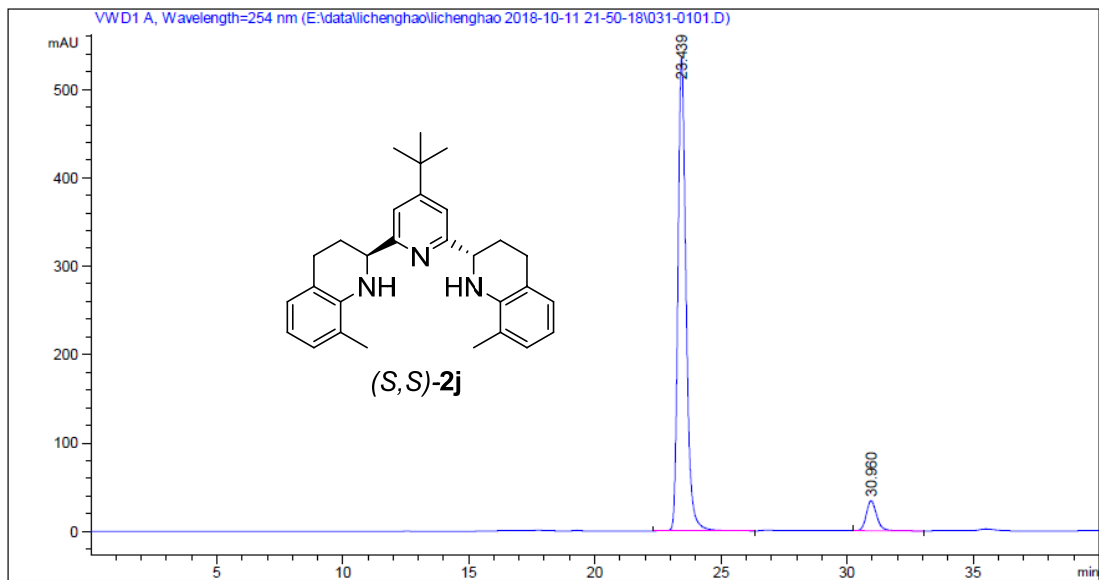
总量 : 3758.09870 41.68487

Figure S54. Copy of HPLC spectra of **2j**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.198	BV	0.3619	3401.12573	143.83495	19.5608
2	22.967	VB	0.3964	3736.81128	141.36555	21.4914
3	30.625	BB	0.4702	1.02496e4	331.94449	58.9479

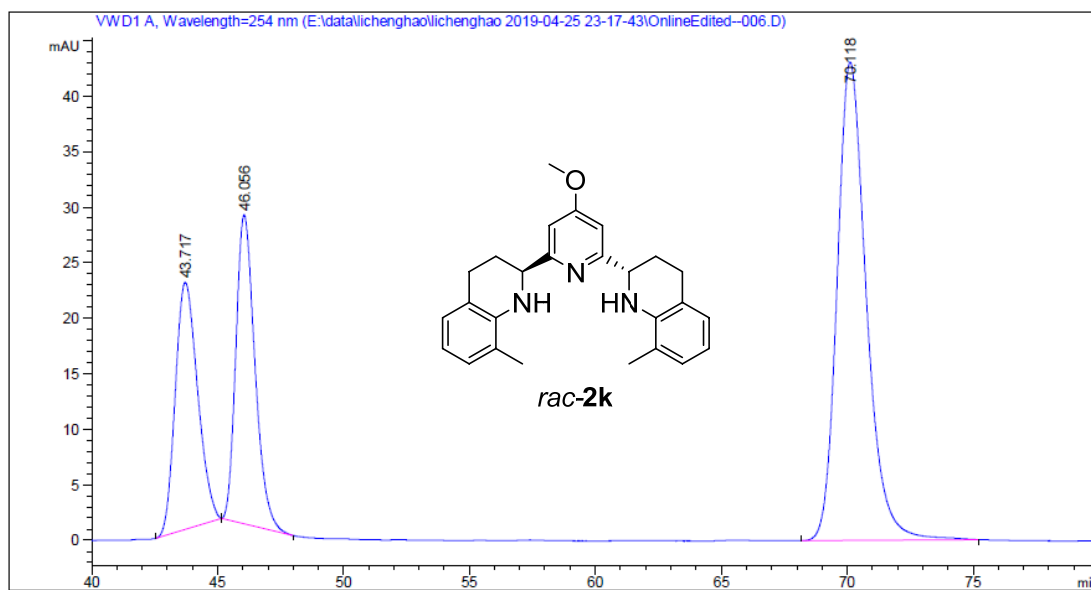
总量 : 1.73875e4 617.14499



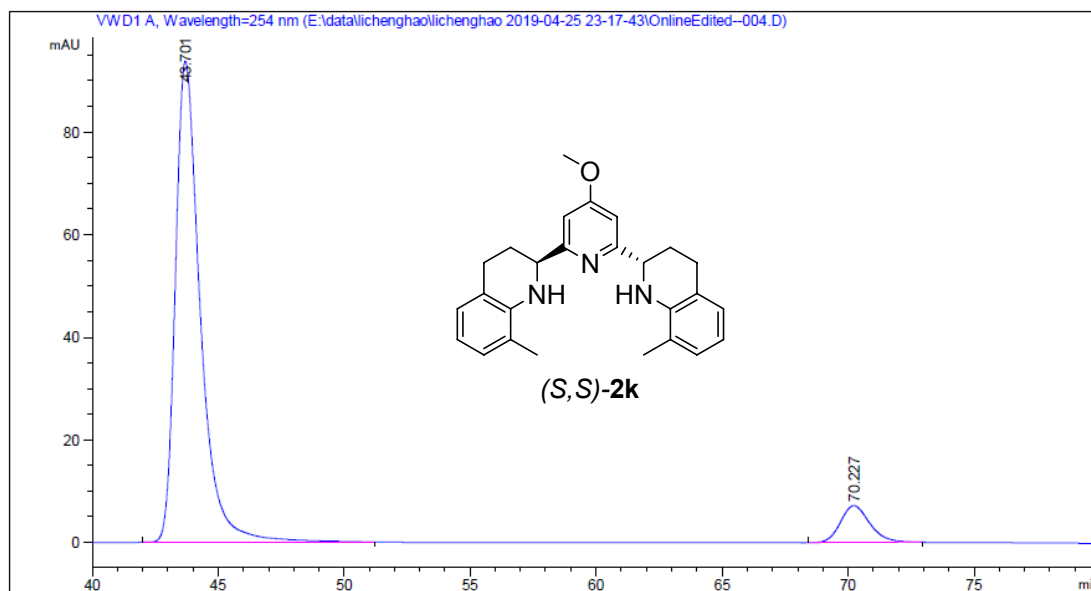
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.439	VB R	0.3441	1.20155e4	534.89716	92.5346
2	30.960	BB	0.4370	969.36975	33.95961	7.4654

总量 : 1.29849e4 568.85676

Figure S55. Copy of HPLC spectra of 2k

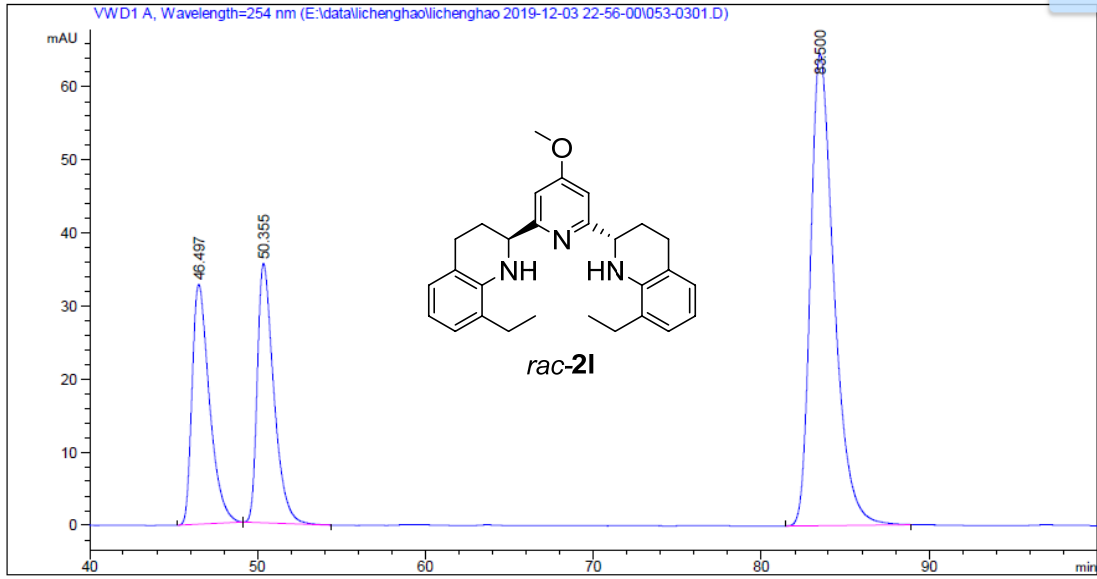


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	43.717	BB	0.9533	1370.96912	22.23532	21.7375
2	46.056	BB	0.8031	1459.37610	27.81779	23.1392
3	70.118	BB	1.2147	3476.59741	43.06954	55.1233
总量 :				6306.94263	93.12264	



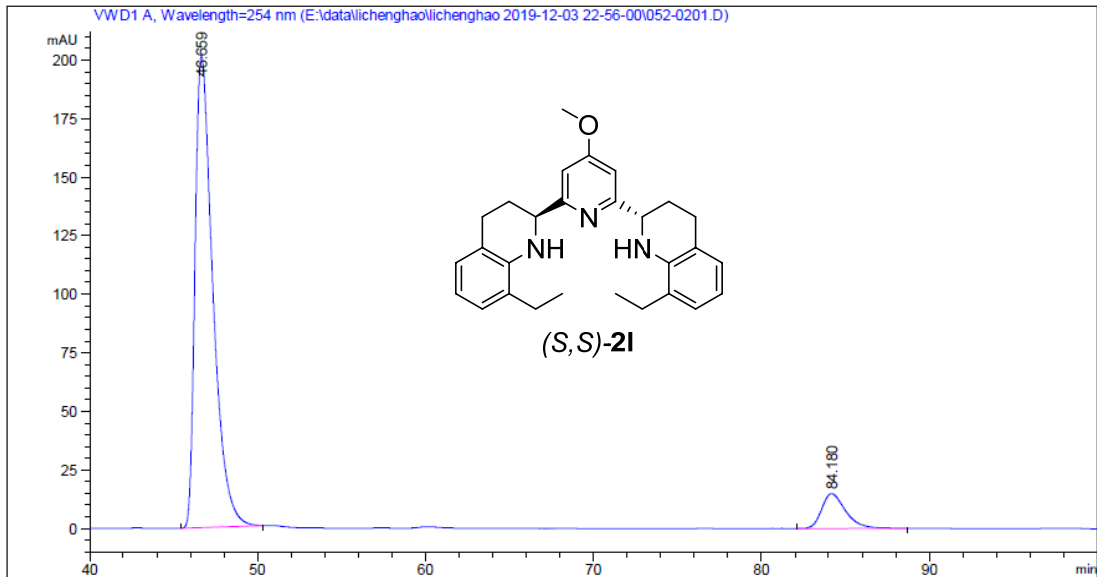
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	43.701	BB	1.0354	6453.58789	93.82890	91.7218
2	70.227	BB	1.1307	582.45905	7.19300	8.2782
总量 :				7036.04694	101.02189	

Figure S56. Copy of HPLC spectra of 21



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	46.497	BB	1.0889	2362.16235	32.80986	21.3351
2	50.355	BB	1.0227	2415.07495	35.49866	21.8130
3	83.500	BB	1.4688	6294.47656	64.54129	56.8519

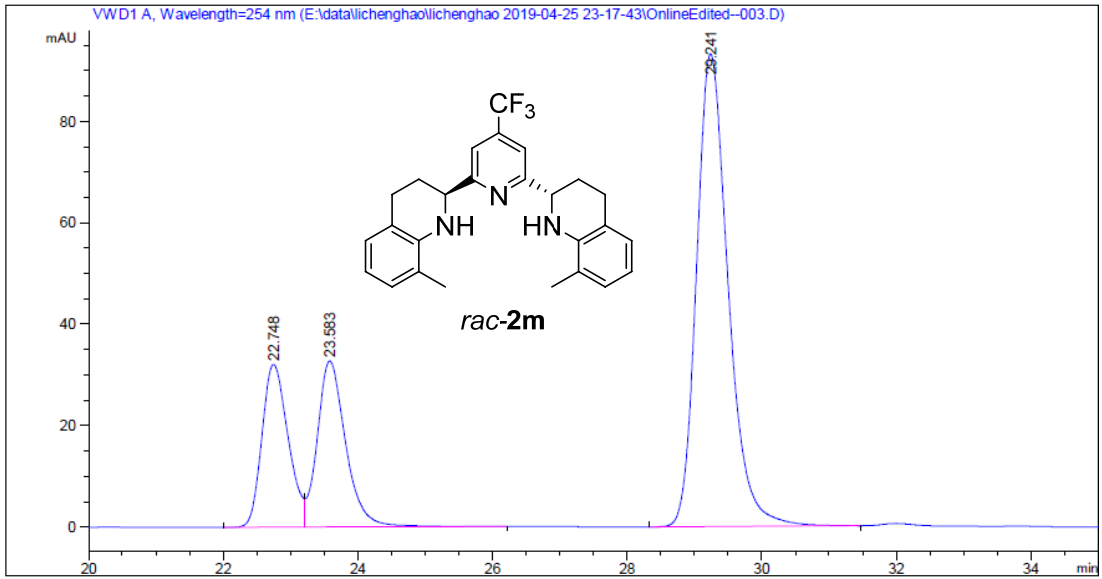
总量 : 1.10717e4 132.84982



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	46.659	BB	1.1101	1.48110e4	201.59511	90.9851
2	84.180	BB	1.4284	1467.49316	14.85624	9.0149

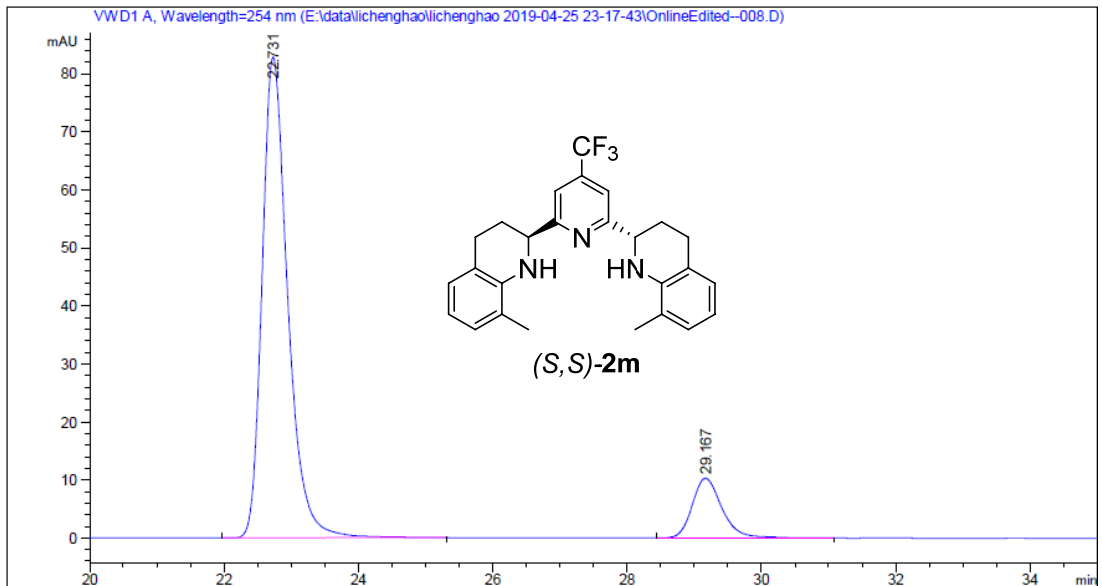
总量 : 1.62785e4 216.45135

Figure S57. Copy of HPLC spectra of **2m**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.748	BV	0.4197	868.27856	32.08829	17.8245
2	23.583	VB	0.4460	962.67157	32.73985	19.7622
3	29.241	BB	0.4997	3040.31494	93.18349	62.4133

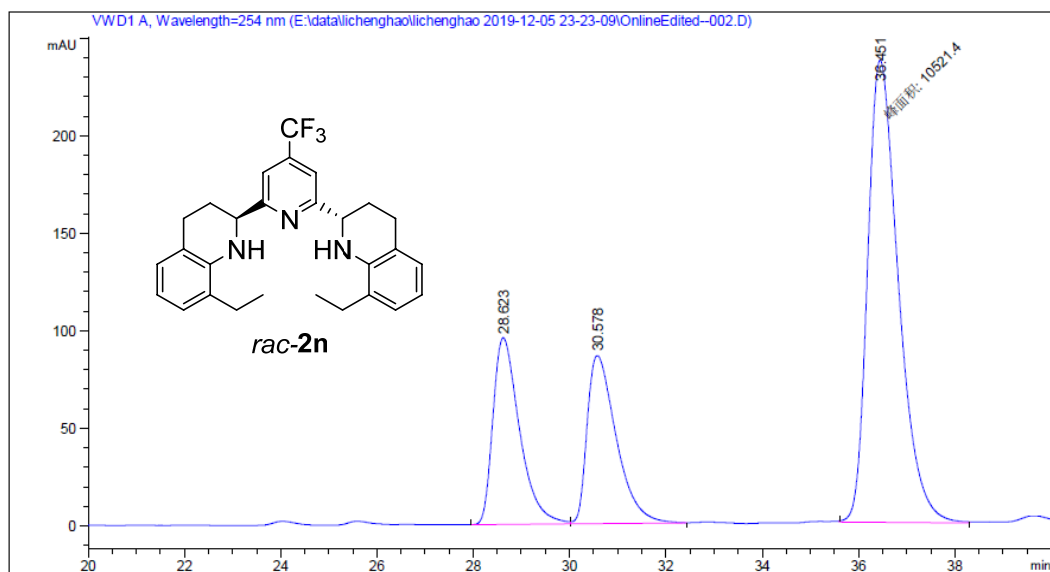
总量 : 4871.26508 158.01163



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.731	BB	0.4020	2193.77539	82.81981	87.3602
2	29.167	BB	0.4669	317.40750	10.31657	12.6398

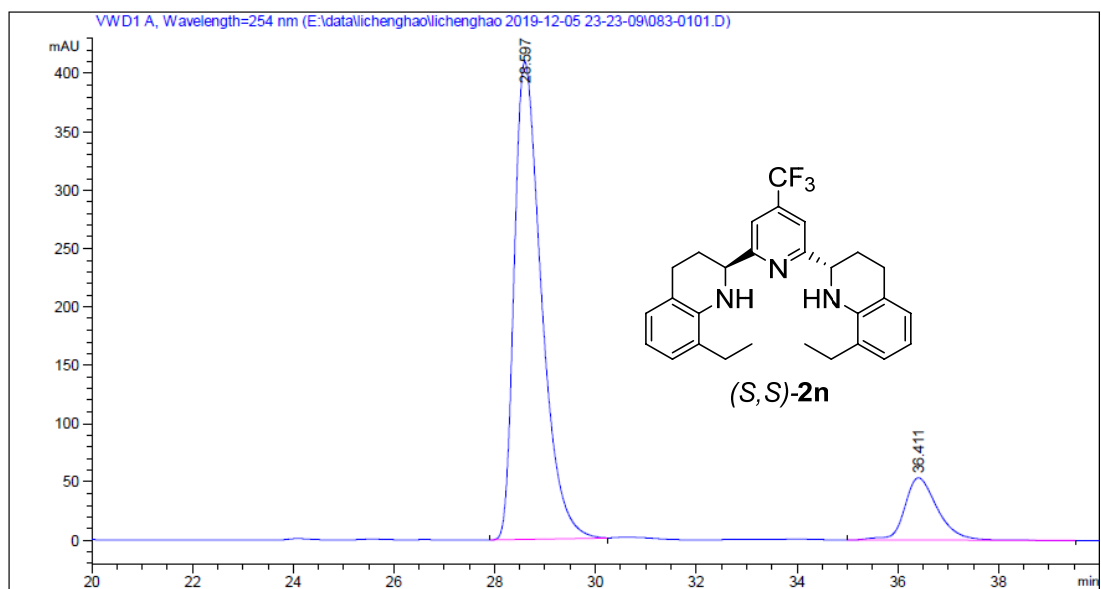
总量 : 2511.18289 93.13638

Figure S58. Copy of HPLC spectra of 2n



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.623	BV	0.5871	3680.95117	95.62511	20.6628
2	30.578	VB	0.6463	3612.03125	86.13173	20.2759
3	36.451	MM	0.7404	1.05214e4	236.84512	59.0614

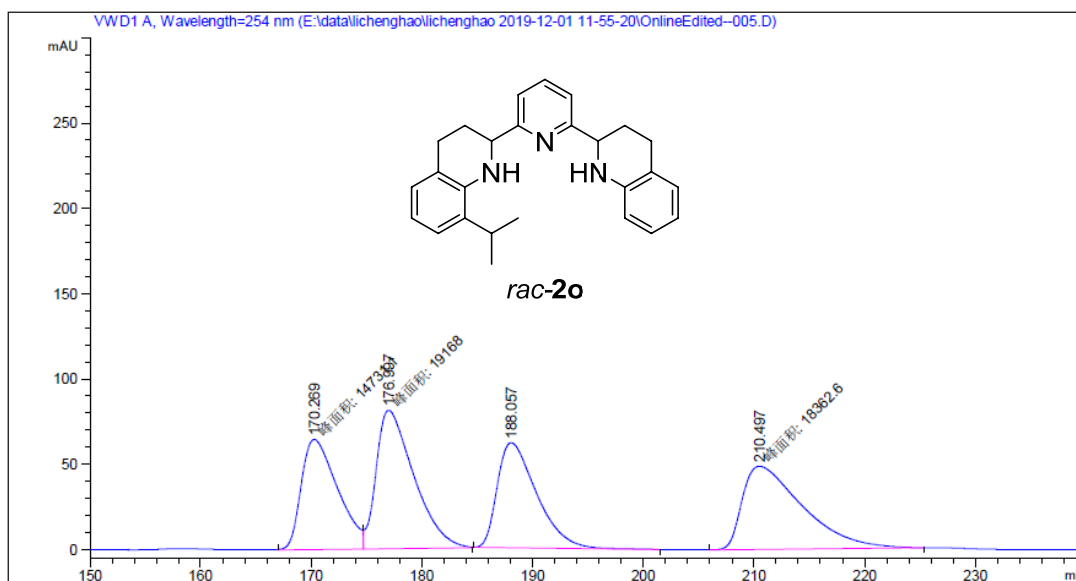
总量 : 1.78144e4 418.60197



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.597	BB	0.5740	1.52957e4	409.25616	86.3850
2	36.411	BB	0.6849	2410.73267	53.37705	13.6150

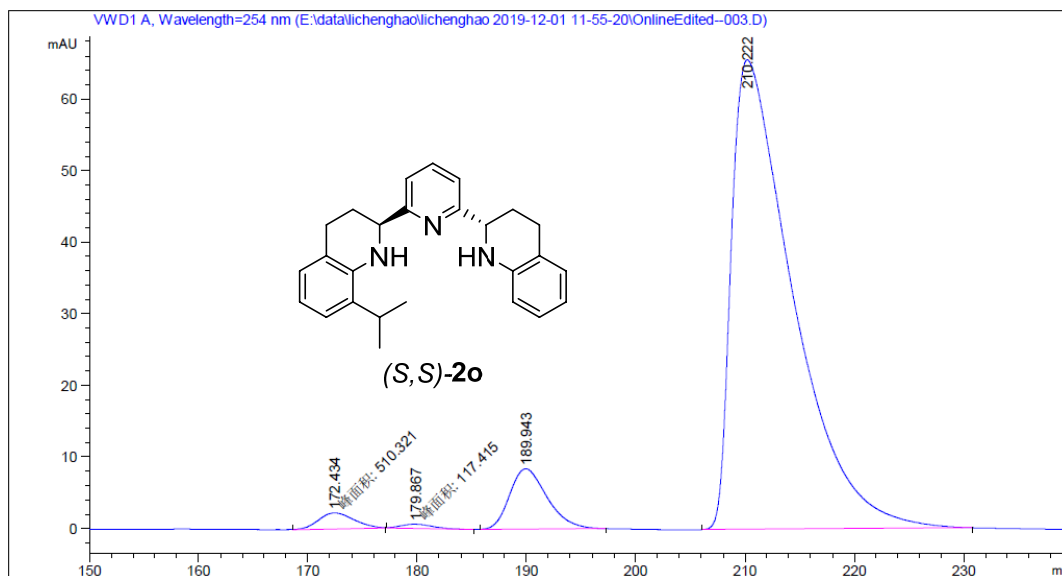
总量 : 1.77064e4 462.63321

Figure S59. Copy of HPLC spectra of **2o**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	170.269	MF	3.8014	1.47311e4	64.58605	21.8497
2	176.997	FM	3.9377	1.91680e4	81.12966	28.4307
3	188.057	BB	3.4814	1.51584e4	61.46043	22.4835
4	210.497	MM	6.2903	1.83626e4	48.65310	27.2361

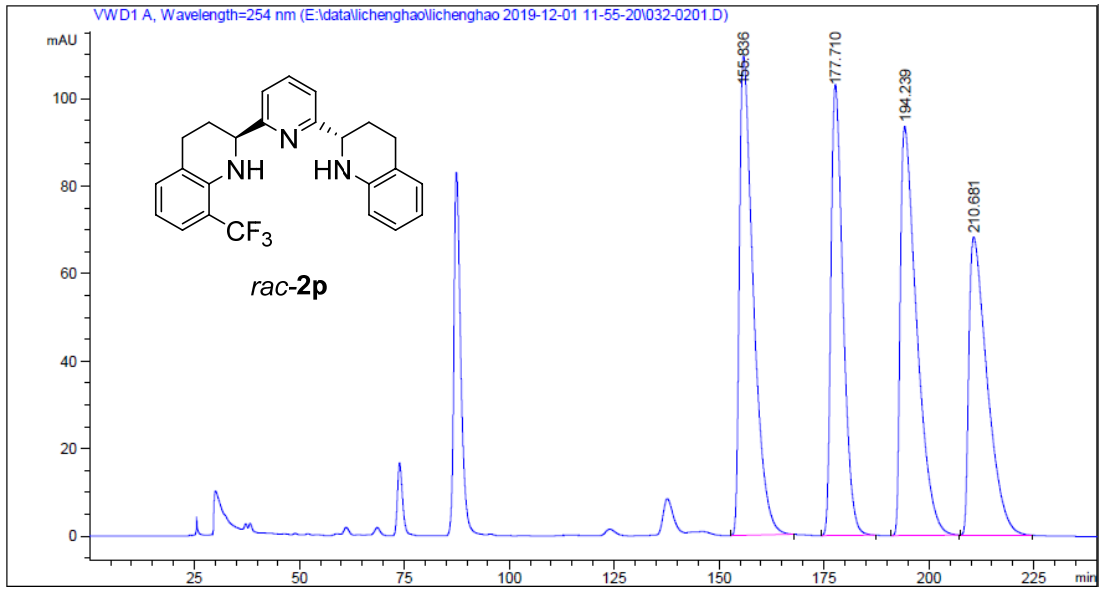
总量 : 6.74201e4 255.82925



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	172.434	MM	3.7645	510.32083	2.25933	1.8053
2	179.867	MM	3.3092	117.41470	5.91358e-1	0.4154
3	189.943	BB	2.7823	2006.11841	8.43929	7.0969
4	210.222	BB	5.0735	2.56337e4	65.57561	90.6824

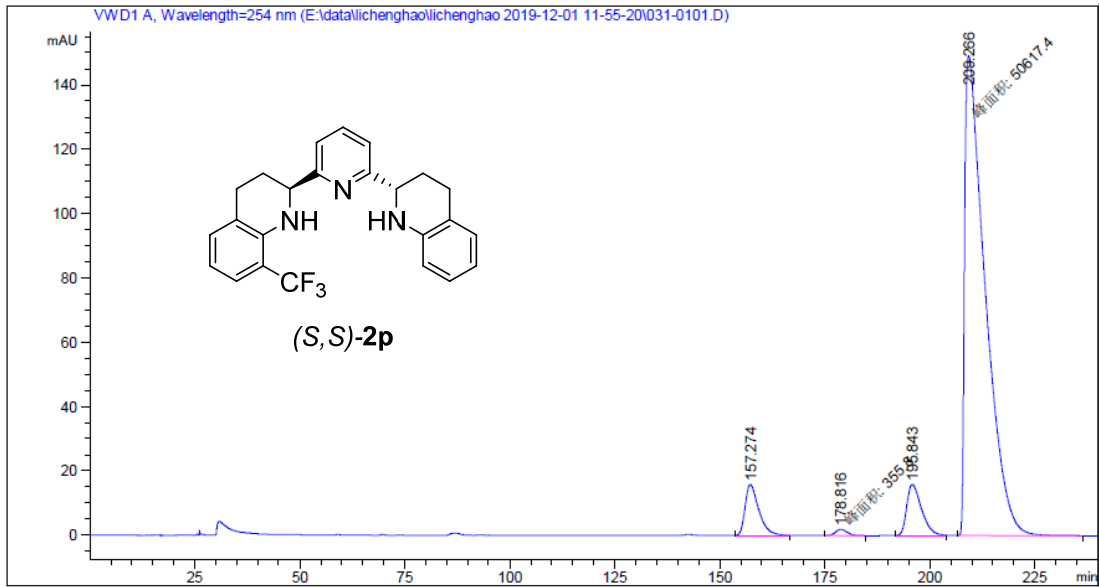
总量 : 2.82676e4 76.86559

Figure S60. Copy of HPLC spectra of 2p



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	155.836	BB	3.2059	2.53684e4	109.62108	27.5238
2	177.710	BB	2.9403	2.06136e4	103.20326	22.3649
3	194.239	BB	3.5384	2.54768e4	93.60341	27.6413
4	210.681	BB	3.8836	2.07104e4	68.14704	22.4700

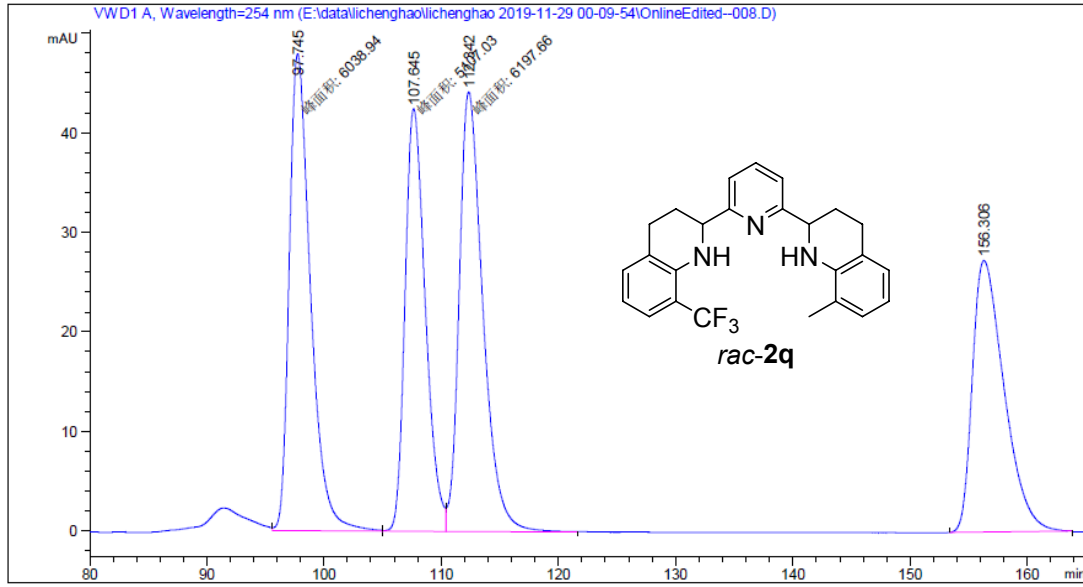
总量 : 9.21693e4 374.57479



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	157.274	BB	2.6375	3562.47388	15.78781	6.1002
2	178.816	MM	3.1309	355.79990	1.89402	0.6093
3	195.843	BB	2.8483	3863.25000	15.92476	6.6153
4	209.266	MM	5.6565	5.06174e4	149.14275	86.6752

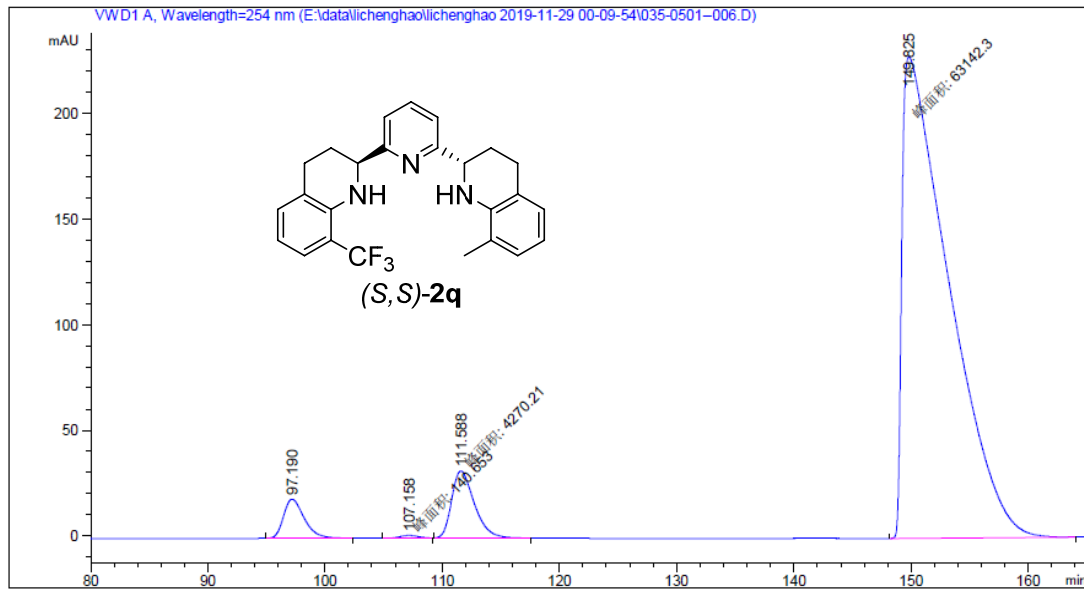
总量 : 5.83989e4 182.74933

Figure S61. Copy of HPLC spectra of 2q



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	97.745	MF	2.1025	6038.94287	47.87217	26.8701
2	107.645	MF	2.0060	5107.03320	42.43071	22.7236
3	112.342	FM	2.3391	6197.65967	44.15909	27.5764
4	156.306	BB	2.4760	5130.90576	27.28340	22.8299

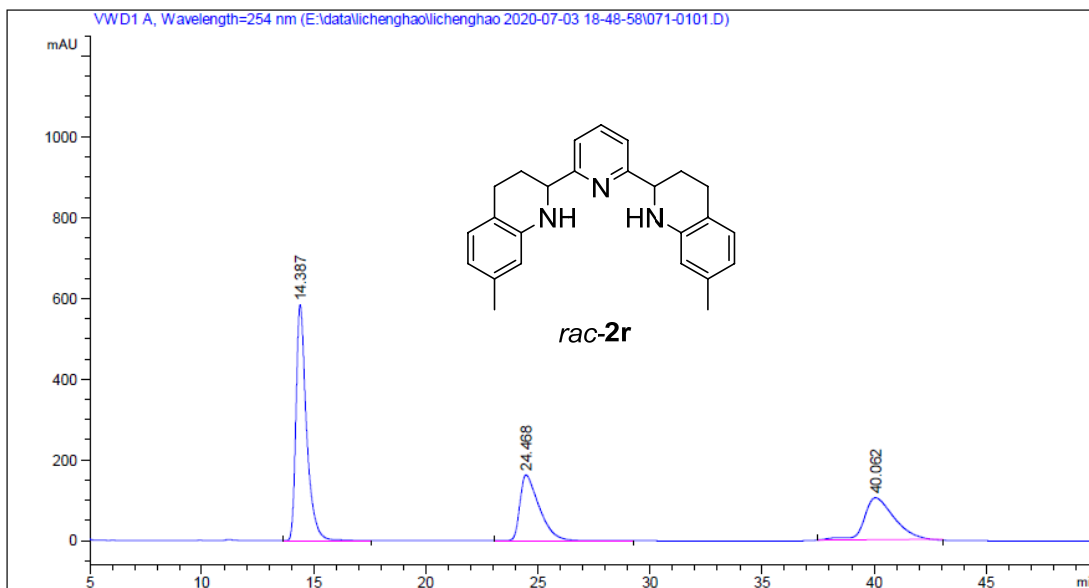
总量 : 2.24745e4 161.74536



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	97.190	BB	1.7616	2260.48926	18.51212	3.2379
2	107.158	MM	1.8329	140.65259	1.27894	0.2015
3	111.588	MM	2.2411	4270.20557	31.75708	6.1166
4	149.825	MM	4.6125	6.31423e4	228.15855	90.4441

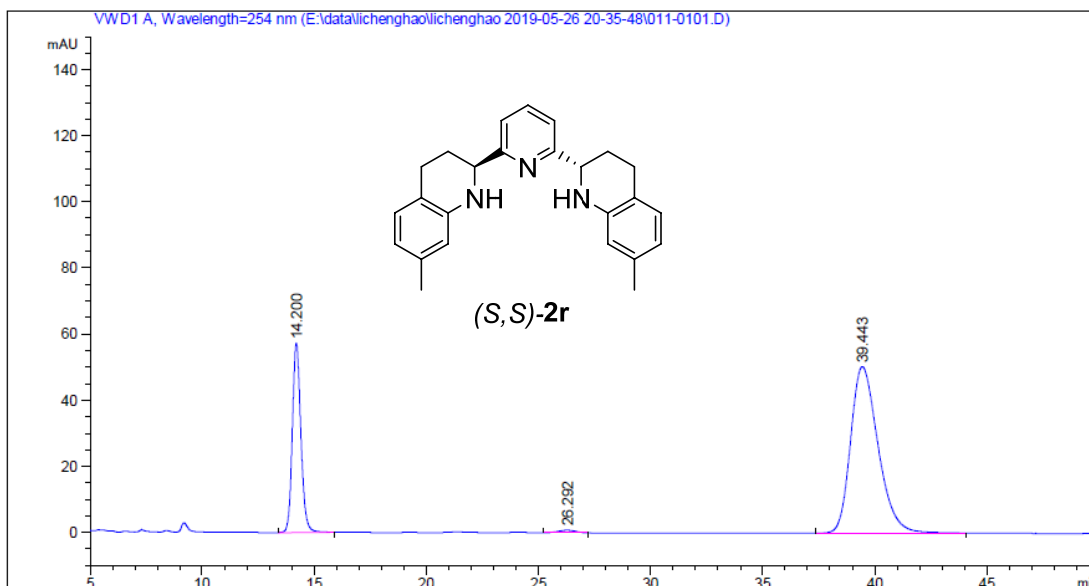
总量 : 6.98136e4 279.70669

Figure S62. Copy of HPLC spectra of 2r



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.387	BB	0.4864	1.90465e4	584.13080	49.3772
2	24.468	BB	0.8843	9748.69727	163.11412	25.2730
3	40.062	MM	1.5642	9778.29492	104.19063	25.3498

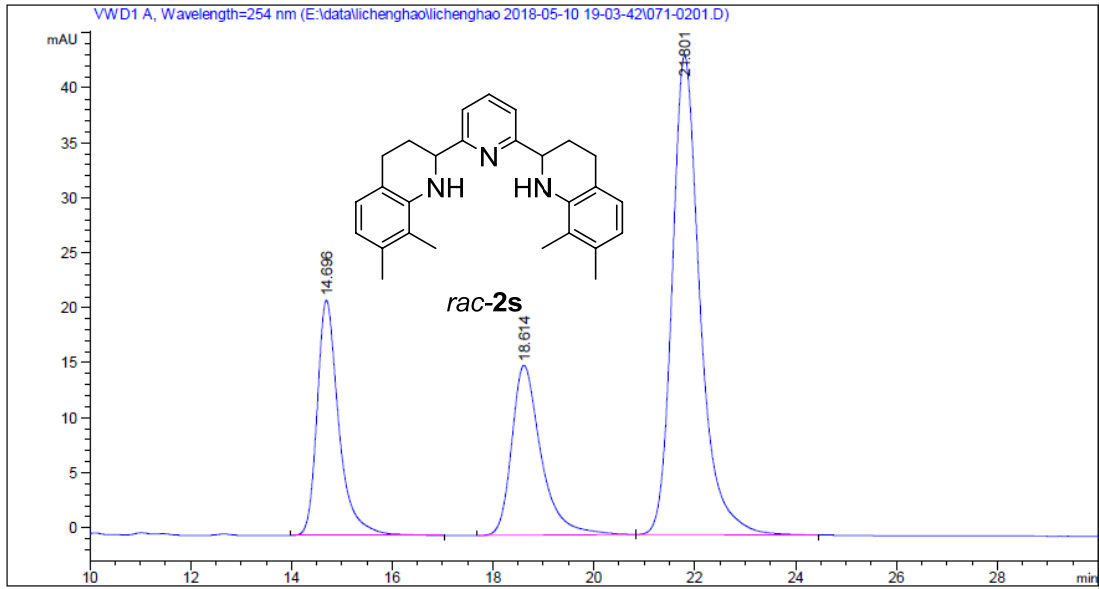
总量 : 3.85735e4 851.43555



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.200	BB	0.4046	1515.58337	57.30341	25.8884
2	26.292	MM	0.8747	43.56870	8.30121e-1	0.7442
3	39.443	BB	1.3054	4295.15381	50.34001	73.3674

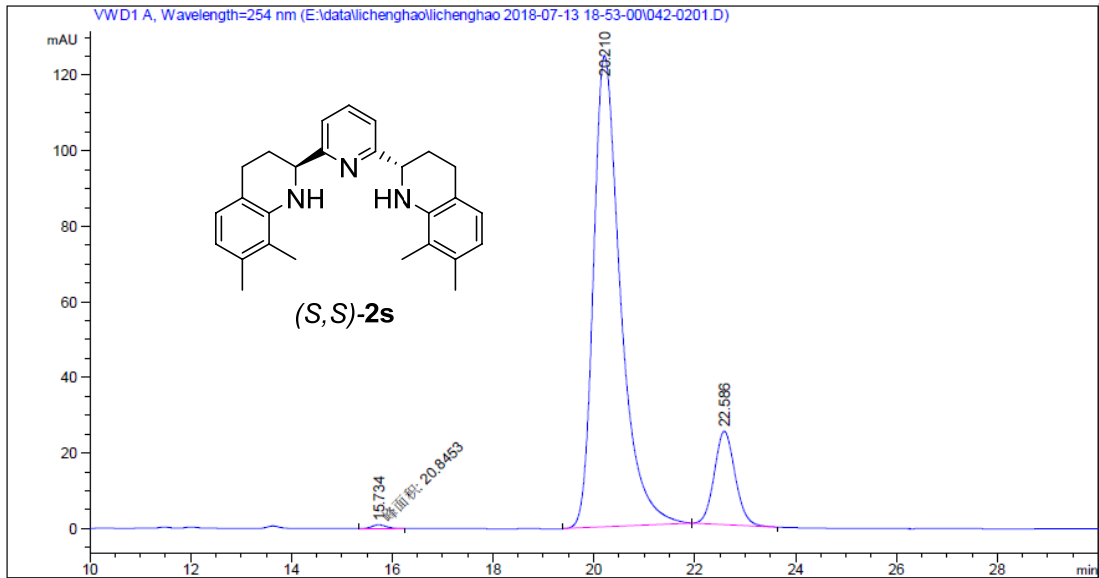
总量 : 5854.30588 108.47354

Figure S63. Copy of HPLC spectra of 2s



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.696	BB	0.4476	639.39703	21.39755	21.7938
2	18.614	BB	0.6037	624.75024	15.45232	21.2946
3	21.801	BB	0.5758	1669.70227	43.59453	56.9117

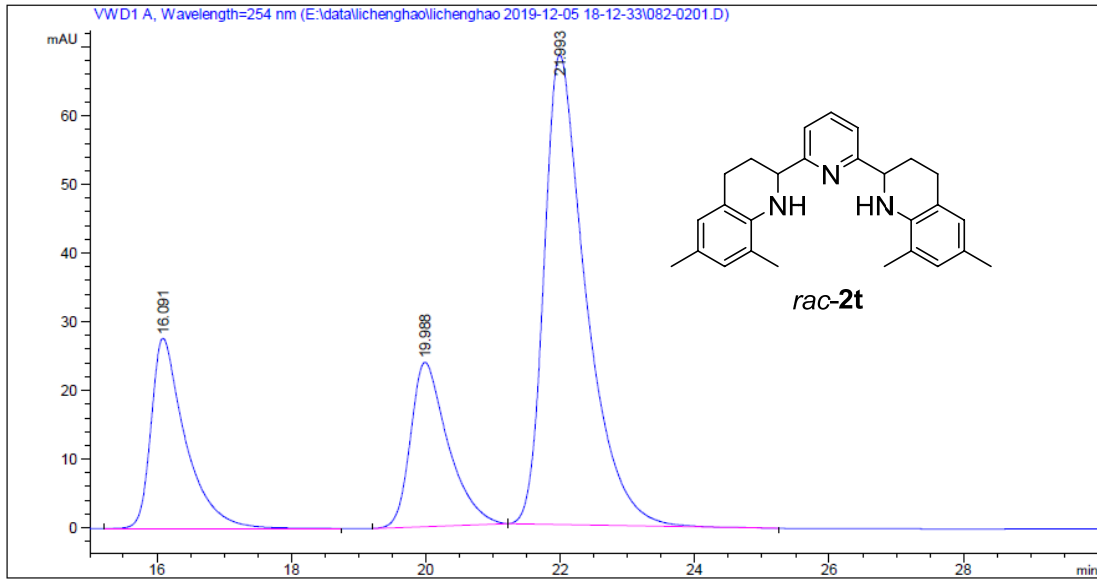
总量 : 2933.84955 80.44440



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.734	MM	0.3483	20.84526	9.97515e-1	0.3878
2	20.210	BB	0.5604	4646.14795	124.77821	86.4458
3	22.586	BB	0.4404	707.64154	24.68790	13.1663

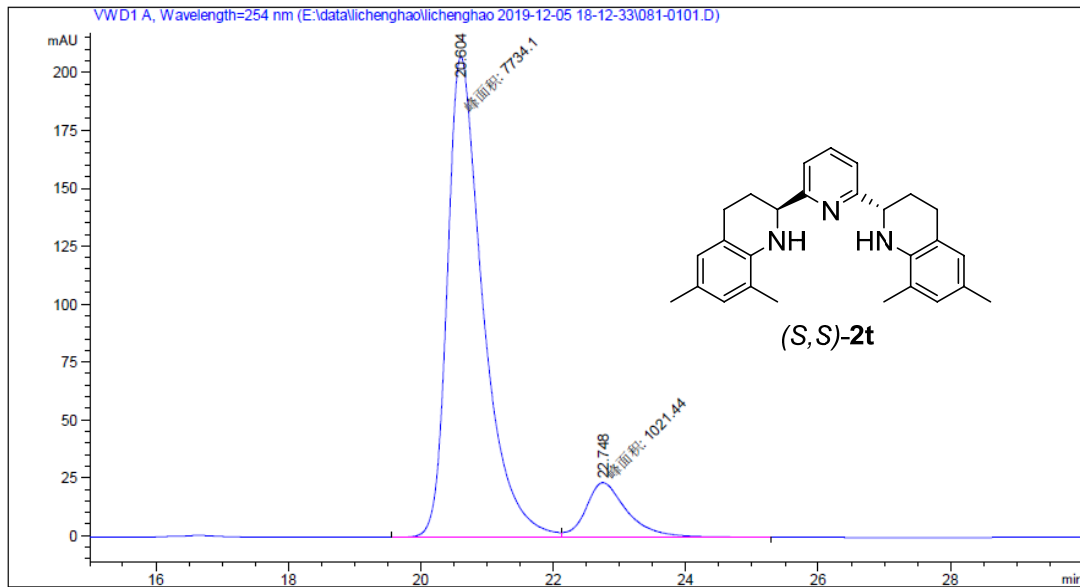
总量 : 5374.63475 150.46362

Figure S64. Copy of HPLC spectra of 2t



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.091	BB	0.5129	980.33539	27.70237	20.1459
2	19.988	BB	0.5731	922.13910	23.90155	18.9499
3	21.993	BB	0.6386	2963.71069	68.38610	60.9042

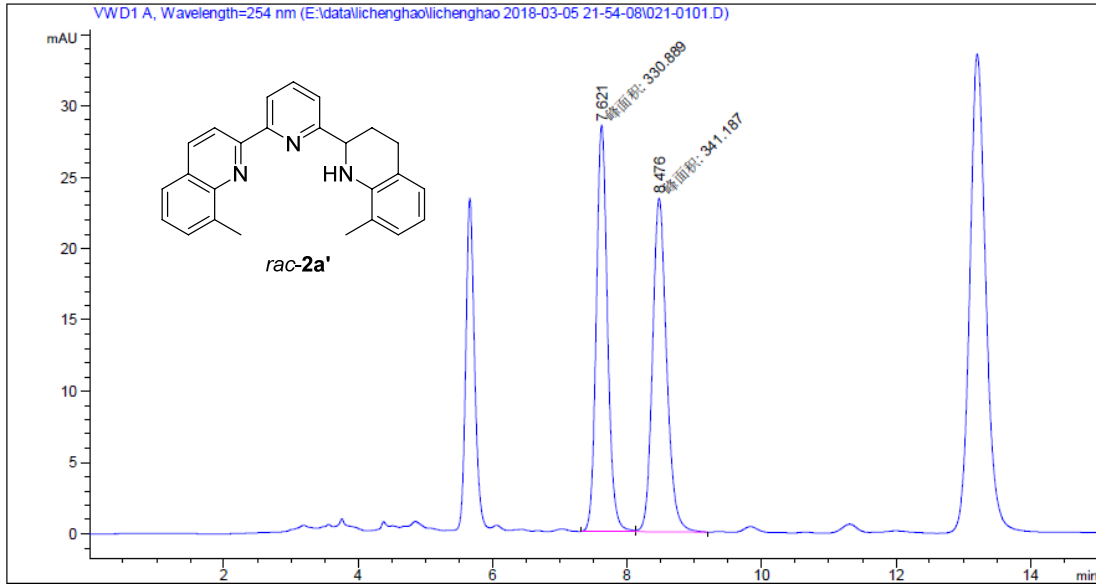
总量 : 4866.18518 119.99001



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.604	MF	0.6215	7734.09717	207.41849	88.3338
2	22.748	FM	0.7230	1021.43768	23.54750	11.6662

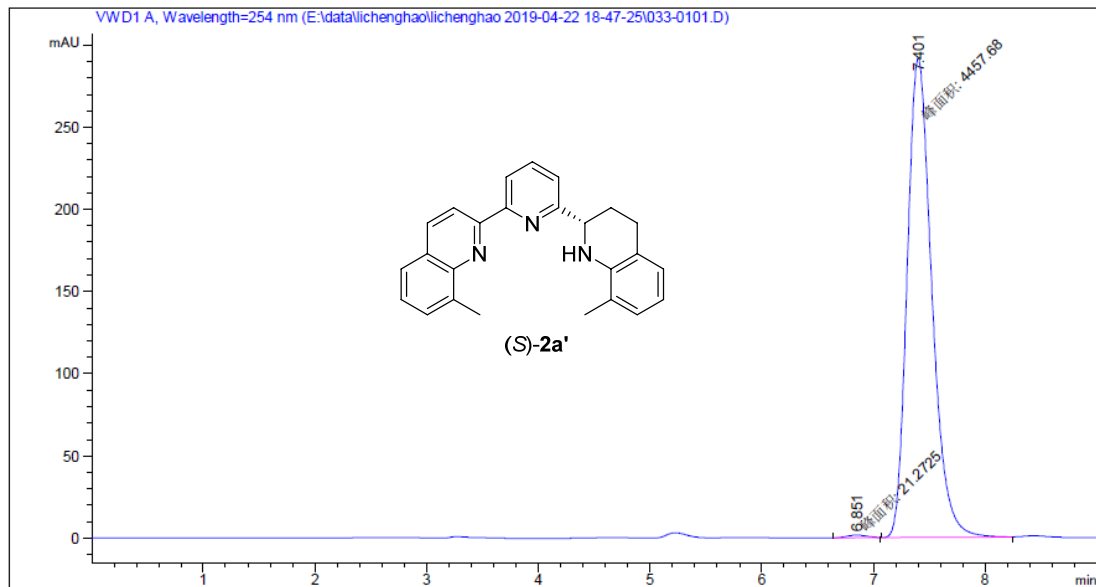
总量 : 8755.53485 230.96598

Figure S65. Copy of HPLC spectra of 2a'



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.621	MF	0.1934	330.88879	28.51781	49.2339
2	8.476	FM	0.2429	341.18674	23.40635	50.7661

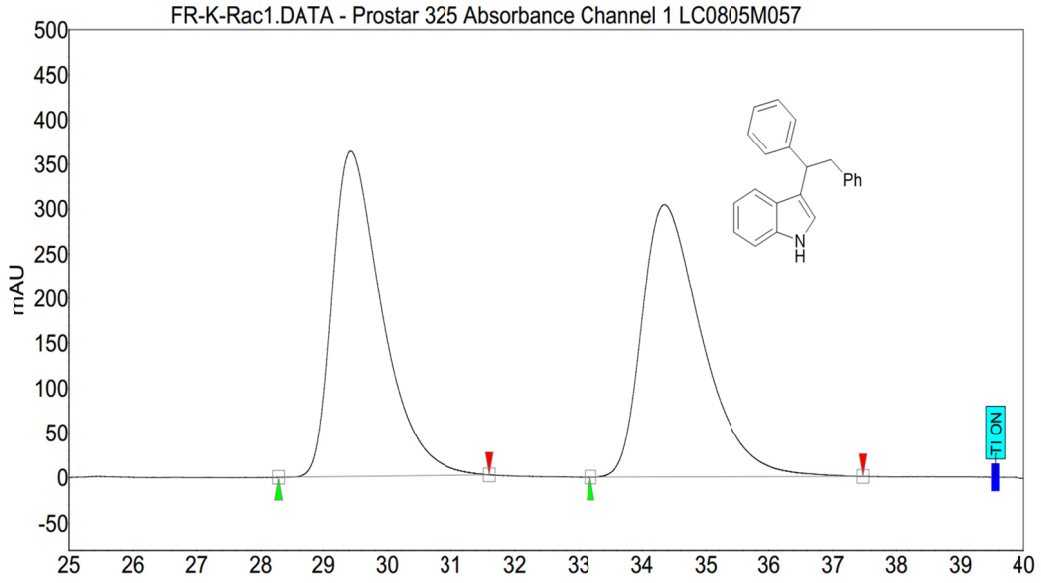
总量 : 672.07553 51.92415



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.851	MM	0.2191	21.27250	1.61843	0.4749
2	7.401	MM	0.2547	4457.68115	291.73544	99.5251

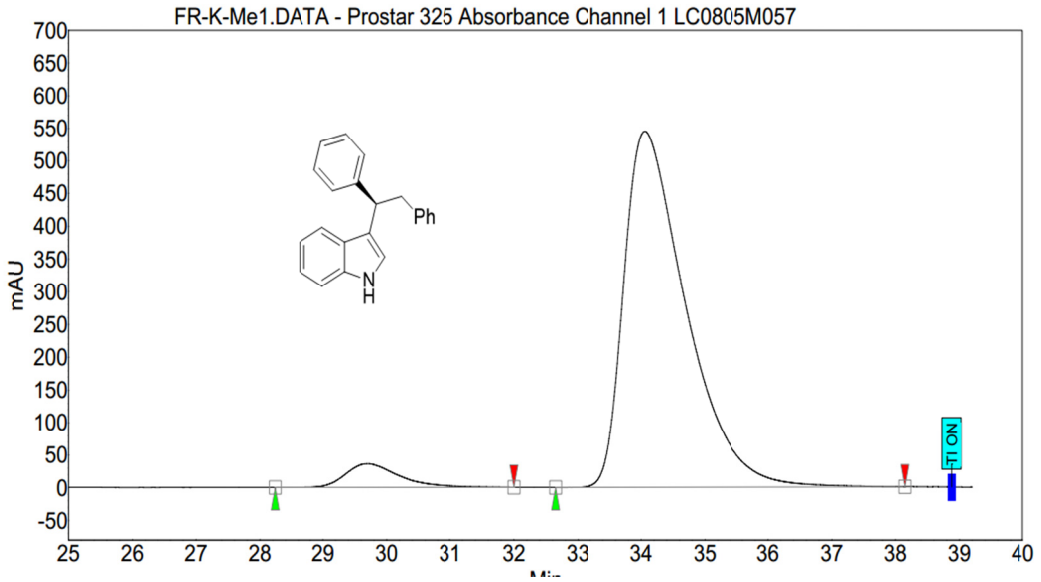
总量 : 4478.95365 293.35387

**Figure S66. Copy of HPLC spectra of 5a**



**Peak results :**

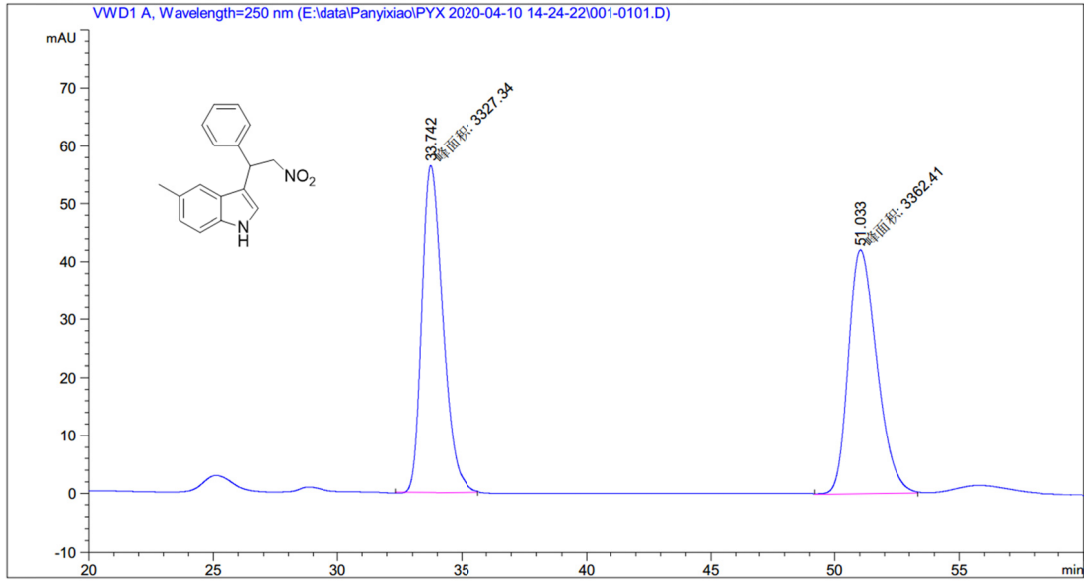
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	29.43	49.58	363.2	326.3	49.581
2	未知	34.35	50.42	303.8	331.9	50.419
Total			100.00	666.9	658.2	100.000



**Peak results :**

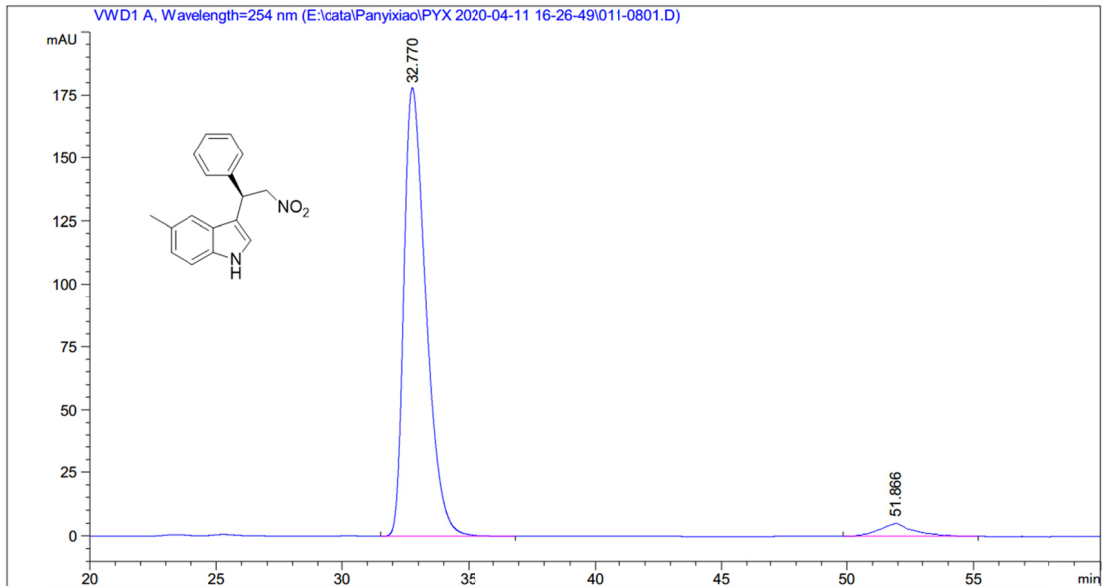
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	29.71	5.42	36.2	35.1	5.422
2	未知	34.06	94.58	544.6	613.1	94.578
Total			100.00	580.8	648.3	100.000

Figure S67. Copy of HPLC spectra of 5b



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.742	MF	0.9827	3327.33765	56.42909	49.7379
2	51.033	MM	1.3291	3362.40527	42.16431	50.2621

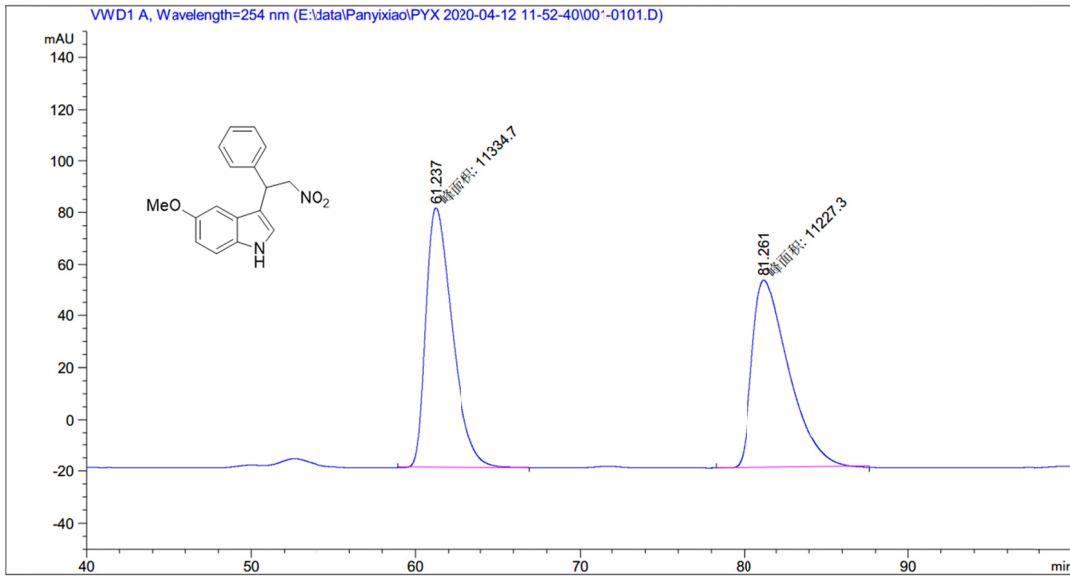
总量 : 6689.74292 98.59340



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	32.770	BB	0.9173	1.06789e4	178.16541	95.4177
2	51.866	BB	1.3229	512.83906	5.48421	4.5823

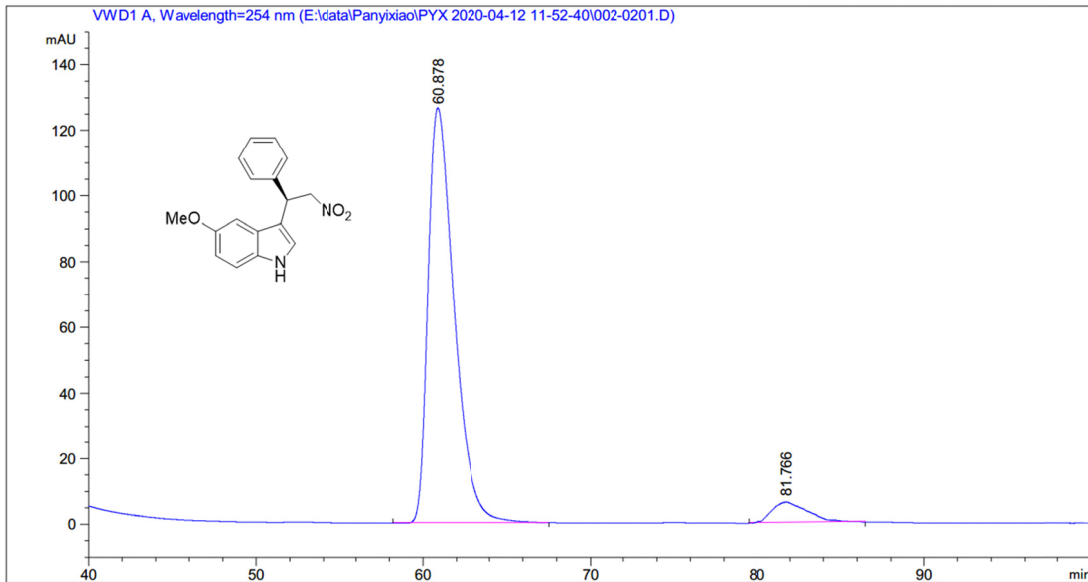
总量 : 1.11917e4 183.64962

Figure S68. Copy of HPLC spectra of 5c



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	61.237	MM	1.8810	1.13347e4	100.42983	50.2380
2	81.261	MM	2.5765	1.12273e4	72.62717	49.7620

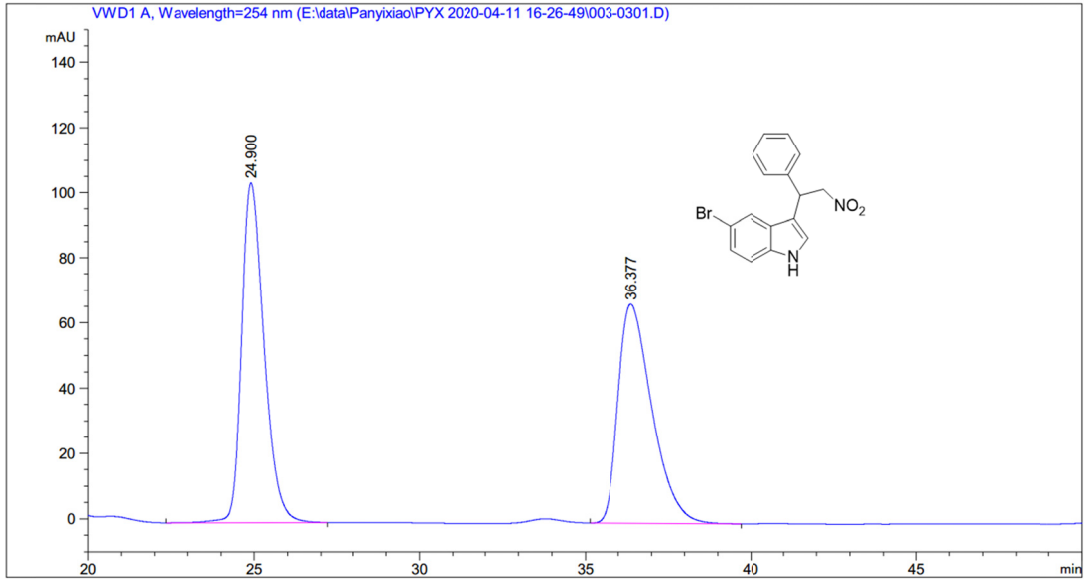
总量 : 2.25621e4 173.05701



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	60.878	MM	1.8039	1.36726e4	126.32443	93.5079
2	81.766	MM	2.3495	949.26617	5.66308	6.4921

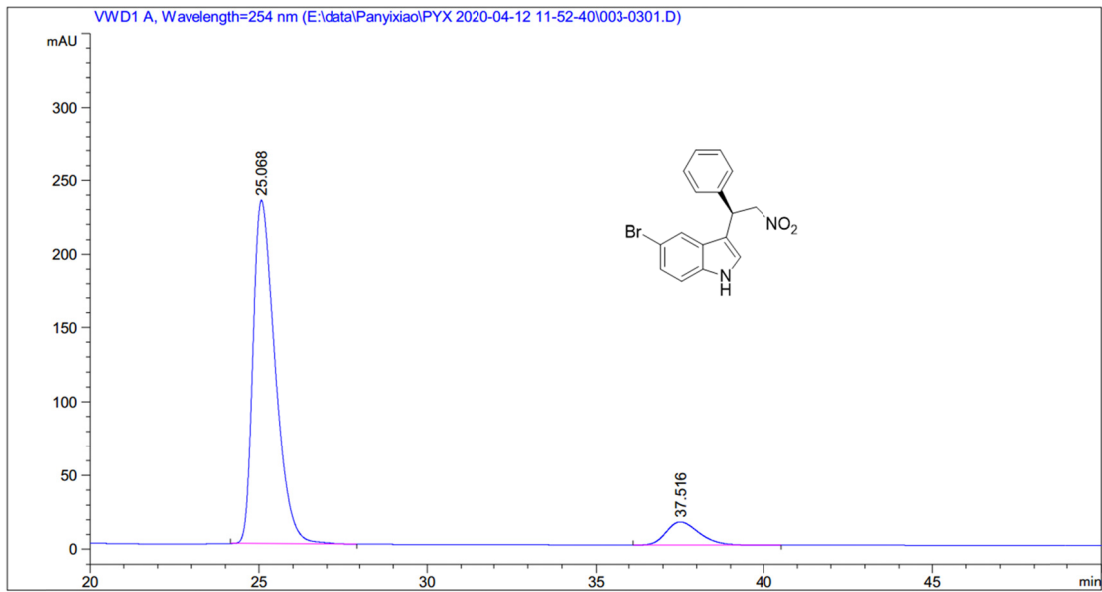
总量 : 1.46219e4 131.98751

Figure S69. Copy of HPLC spectra of 5d



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.900	BB	0.7193	4866.87354	104.12550	50.5697
2	36.377	BB	1.0819	4757.21143	66.95760	49.4303

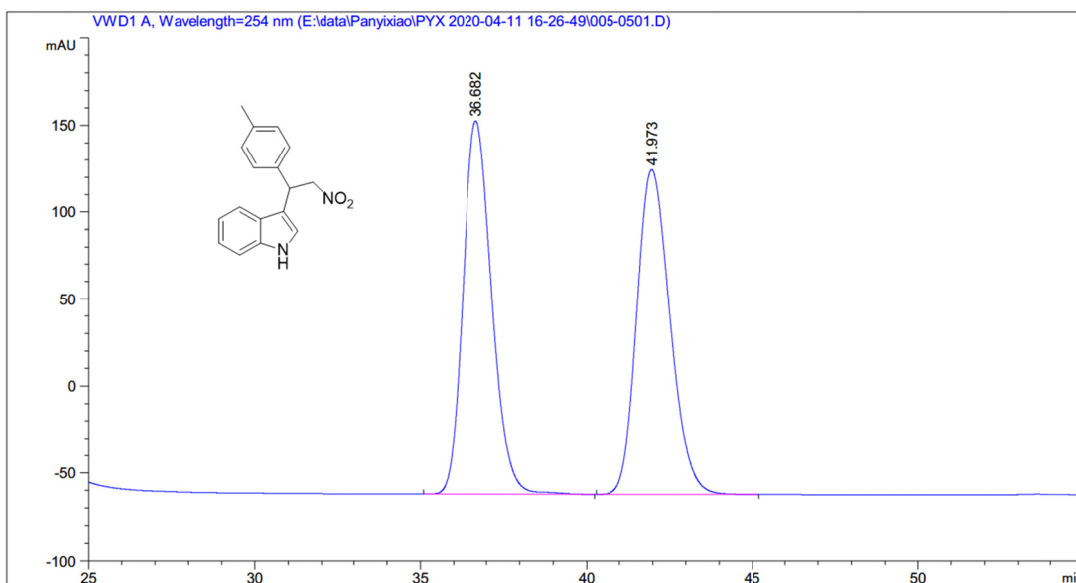
总量 : 9624.08496 171.08309



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.068	BB	0.6872	1.05087e4	232.56877	90.8283
2	37.516	BB	1.0153	1061.14844	15.68455	9.1717

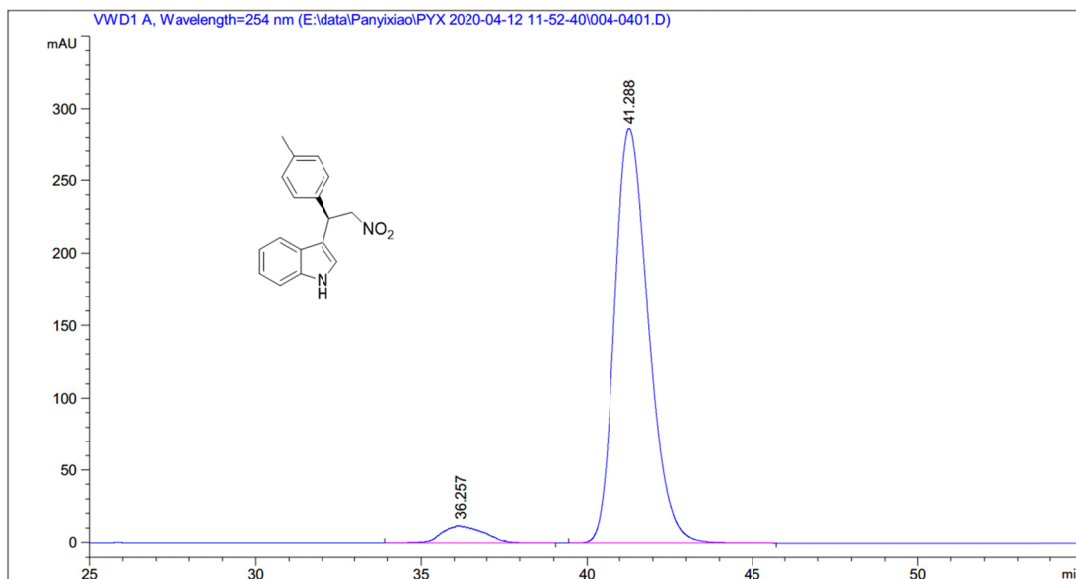
总量 : 1.15698e4 248.25332

Figure S70. Copy of HPLC spectra of 5e



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	36.682	BB	0.9406	1.30336e4	214.90413	50.1107
2	41.973	BB	1.0818	1.29760e4	186.71223	49.8893

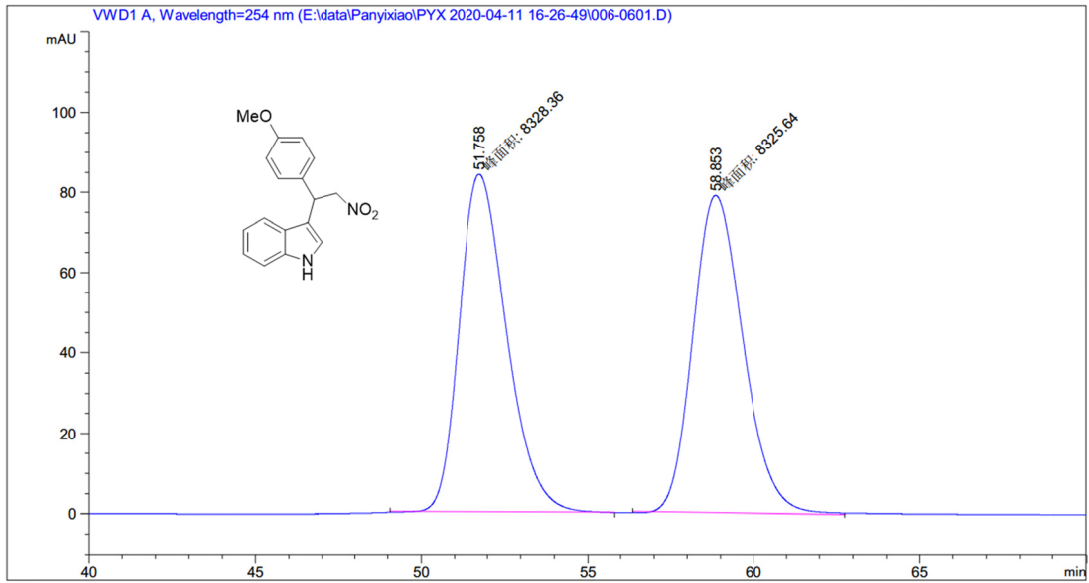
总量 : 2.60096e4 401.61636



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	36.257	BB	0.9470	1166.10312	7.51829	5.4006
2	41.288	BB	1.0893	2.04260e4	286.66364	94.5994

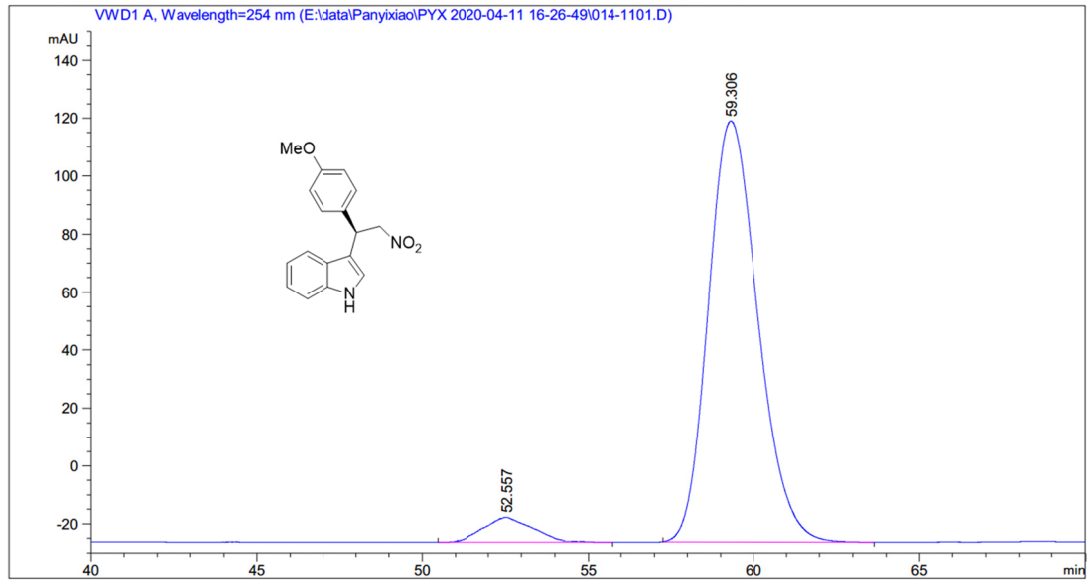
总量 : 2.15921e4 294.18193

Figure S71. Copy of HPLC spectra of 5f



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	51.758	MM	1.6509	8328.35547	84.07790	50.0082
2	58.853	MM	1.7573	8325.63574	78.96339	49.9918

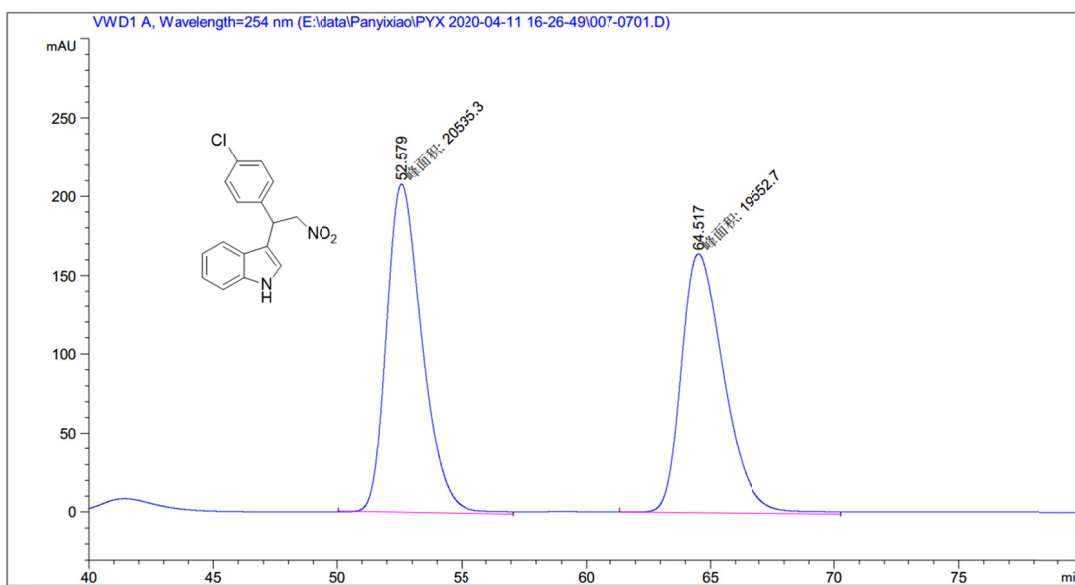
总量 : 1.66540e4 163.04129



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	52.557	BB	1.4141	1059.56984	8.38622	6.5006
2	59.306	BB	1.5280	1.52400e4	145.25894	93.4994

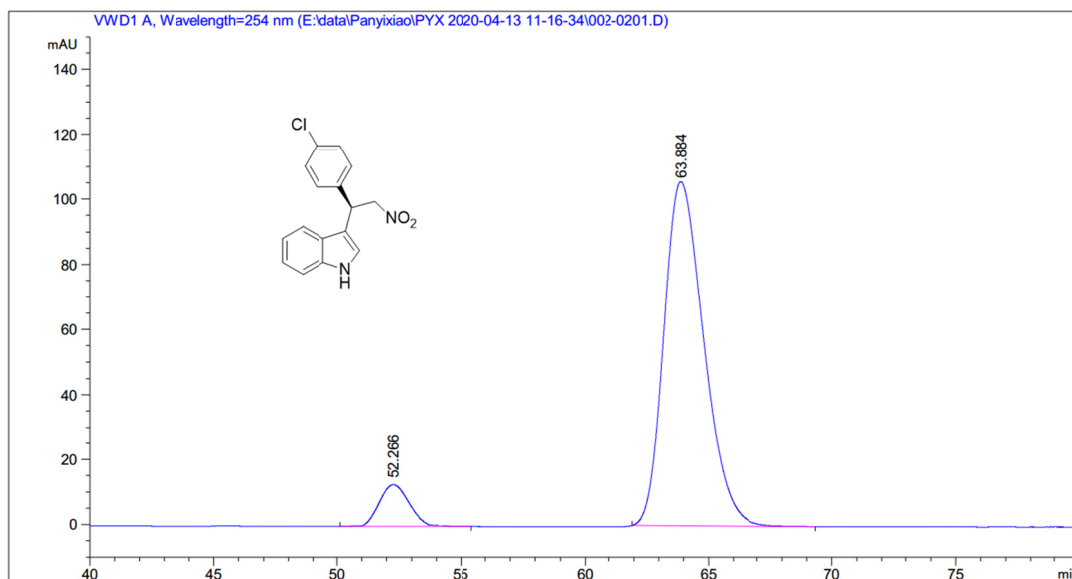
总量 : 1.62996e4 153.64516

Figure S72. Copy of HPLC spectra of 5g



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	52.579	MM	1.6460	2.05353e4	207.93507	51.2256
2	64.517	MM	1.9834	1.95527e4	164.30183	48.7744

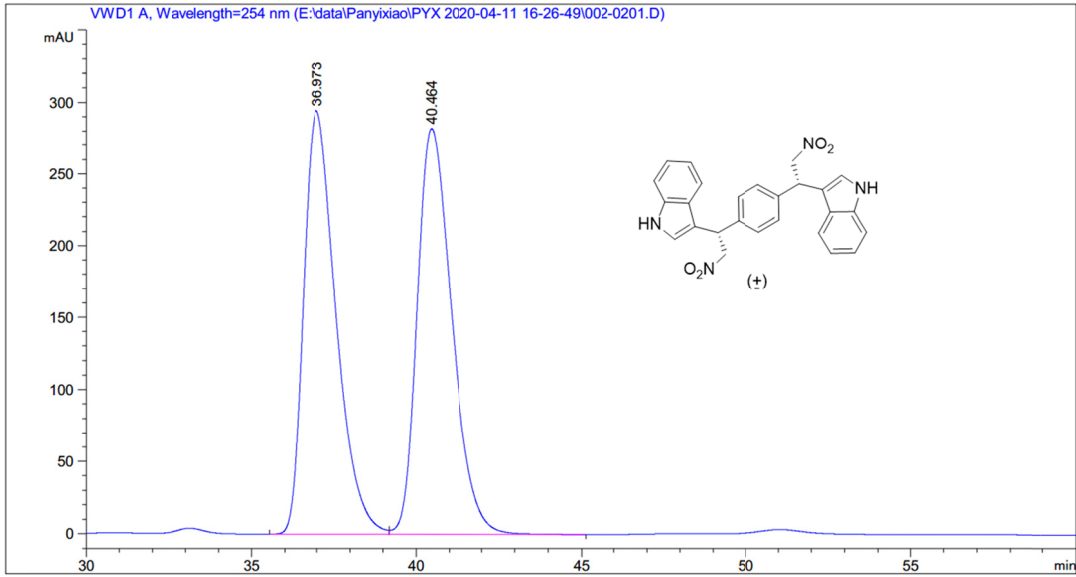
总量 : 4.00881e4 372.23691



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	52.266	BB	1.3155	1033.0584	12.13449	8.0684
2	63.884	BB	1.6032	1.17707e4	105.69833	91.9316

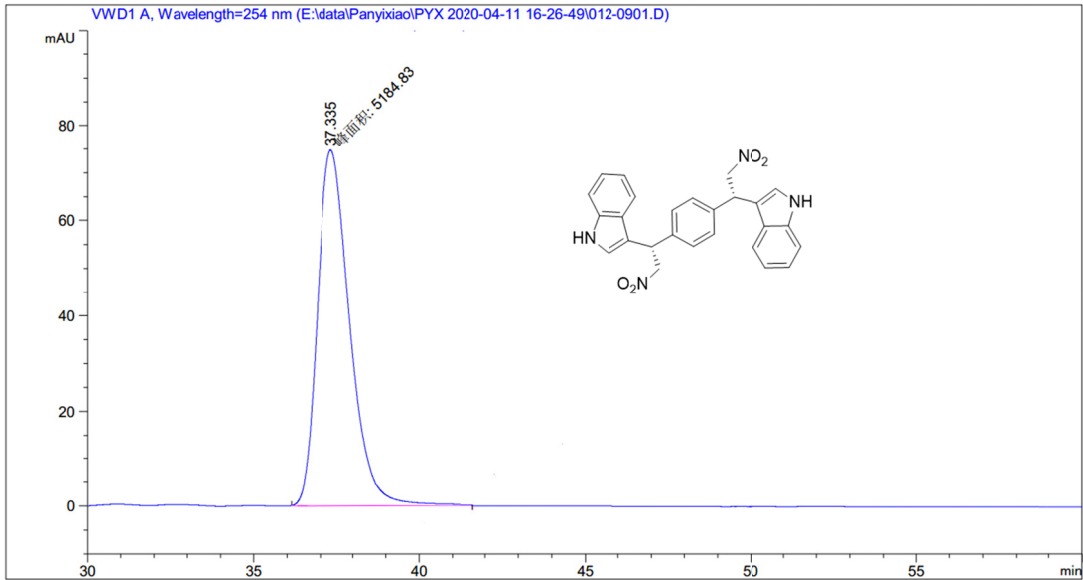
总量 : 1.28038e4 117.83282

Figure S73. Copy of HPLC spectra of 5h



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	36.973	BV	1.0656	2.04655e4	294.55240	49.8451
2	40.464	VB	1.1226	2.05927e4	282.12012	50.1549

总量 : 4.10582e4 576.67252



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	37.335	MM	1.1426	5184.82910	75.62630	100.0000

总量 : 5184.82910 75.62630