

Supporting Information

Catalytic asymmetric transformation of nitrones and allenes to dihydropyridoindoles via chiral *N,N'*-dioxide/cobalt(II) catalysis

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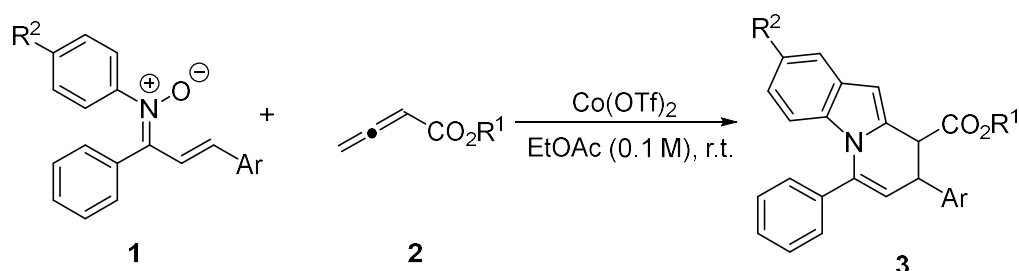
1. General information

¹H NMR spectra were recorded on commercial instruments (400 MHz or 600 MHz). Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl₃, δ = 77.0). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration. ¹³C{¹H} NMR data were collected on commercial instruments (101 MHz, 600MHz) with complete proton decoupling. ¹⁹F{¹H} NMR spectra were collected on commercial instruments (376 MHz) with complete proton decoupling. Melting points (M.p.) were determined using OptiMelt automated melting point system. High resolution mass spectra (HRMS) analyses were recorded on Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (ESI Source) and methanol were used to dissolve the sample. Enantiomeric excesses (ee) were determined by UPC² analysis by using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C with UV detector at 254 nm. Optical rotations were measured on a Rudolph Autopol V automatic polarimeter and are reported as follows: $[\alpha]_D^{25} = (c = \text{g}/100 \text{ mL, in solvent})$. IR spectra were recorded on Bruker TENSOR II IR spectrophotometer. Circular dichroism spectrum (CD) were recorded on Applied Photophysics Chirascan.

Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. Solvents were dried and distilled prior to use according to the standard methods. Metal salts obtained from commercial sources were used without further purification. The chiral *N,N'*-dioxide ligands were synthesized by the same procedure in the literature.^[1] The nitrones were prepared according to literature procedure.^[2] The allenes were synthesized by following the literature procedure.^[3]

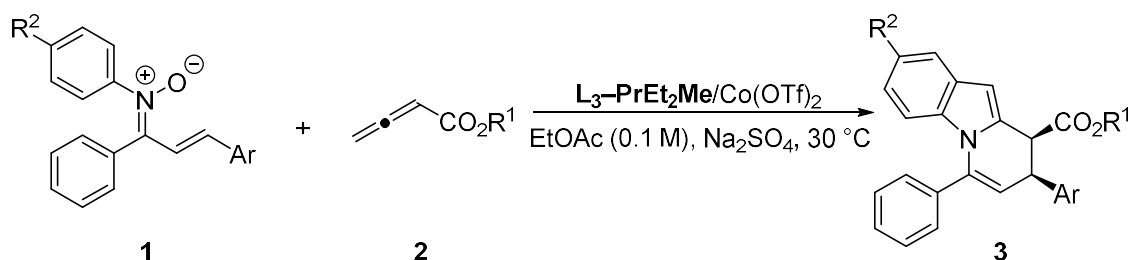
2. Procedures for the catalytic reaction

2.1 General procedure for the preparation of the racemic products



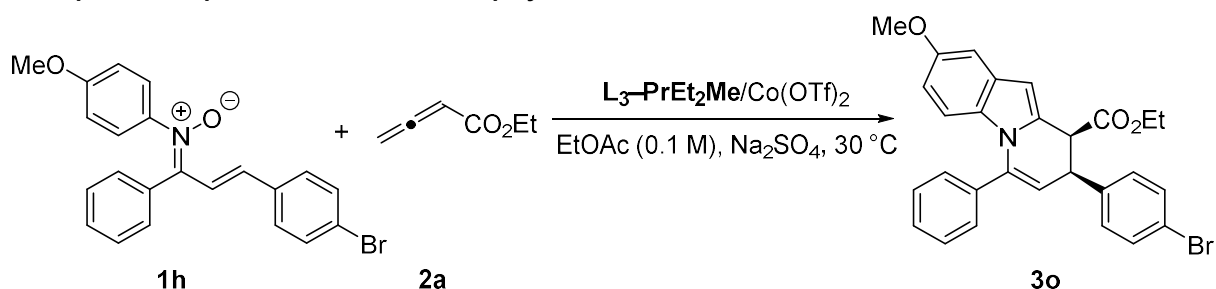
A dry reaction tube was charged with *N*-aryl nitron **1** (0.10 mmol), Co(OTf)₂ (3.6 mg, 0.01 mmol, 10 mol%), allene **2** (0.10 mmol) in EtOAc (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 30 °C for 24 h. The desired product was purified directly by silica gel column chromatograph (ethyl acetate/petroleum ether, 50:1) to afford the corresponding product **3**.

2.2 General procedure for the catalytic asymmetric reaction



A dry reaction tube was charged with *N*-aryl nitron **1** (0.10 mmol), Co(OTf)₂/L₃-PrEt₂Me (10 mol%, 1.2:1), allene **2** (0.10 mmol), Na₂SO₄ (20 mg) in EtOAc (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 30 °C for 24 h. The desired product was purified directly by silica gel column chromatograph (ethyl acetate/petroleum ether, 50:1) to afford the corresponding product **3**.

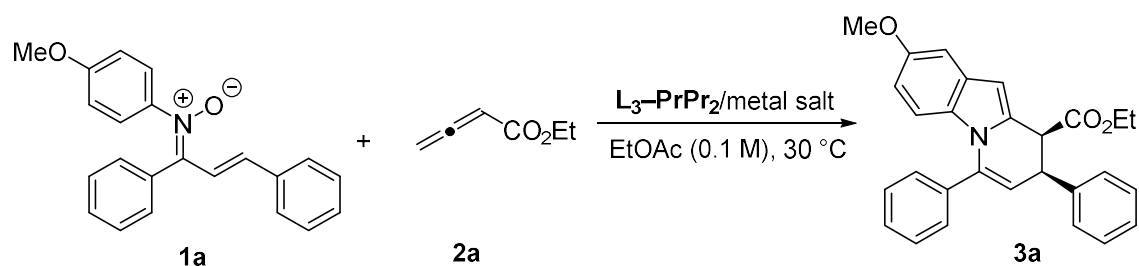
2.3 Experimental procedure for the scale-up synthesis of **3o**



A dry reaction tube was charged with *N*-aryl nitron **1h** (3.5 mmol, 1.42 g), Co(OTf)₂/L₃-PrEt₂Me (10 mol%, 1.2:1), allene **2a** (3.5 mmol, 0.39 mL), Na₂SO₄ (0.70 g) in EtOAc (35.0 mL) under argon atmosphere. The reaction mixture was stirred at 30 °C for 24 h. The desired product was purified directly by silica gel column chromatograph (ethyl acetate/petroleum ether, 50:1) to afford the corresponding product **3o** (1.15 g, 65% yield, 98:2 dr, 98% ee).

3. Optimization of reaction conditions

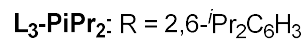
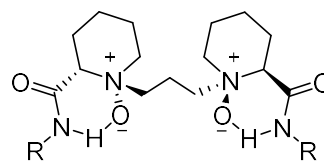
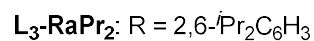
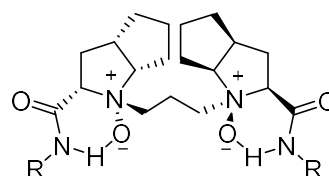
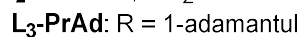
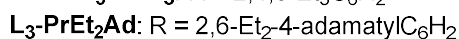
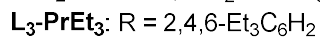
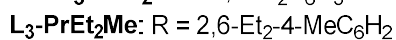
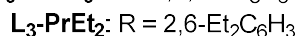
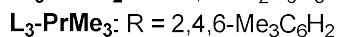
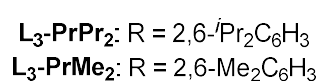
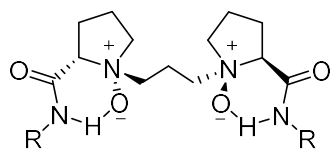
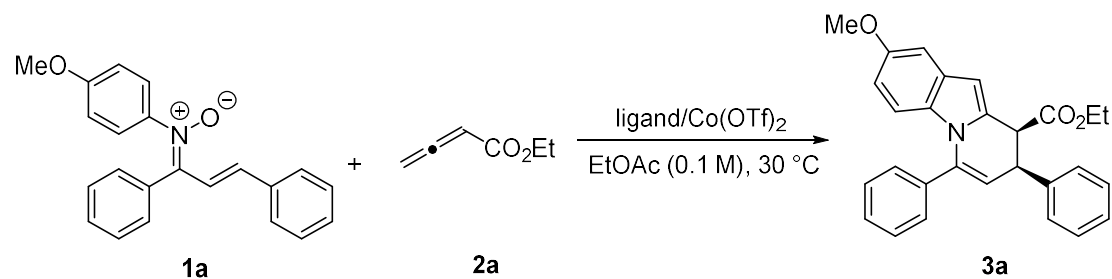
3.1 Screening of metal salts



entry ^[a]	metal salt	yield (%) ^[b]	dr ^[c]	ee (%) ^[c]
1	Sc(OTf) ₃	24	95:5	race
2	Mg(OTf) ₂	51	92:8	76/9
3	Co(OTf) ₂	61	90:10	87/33
4	Ni(OTf) ₂	50	86:14	90/50
5	Cu(OTf) ₂	25	74:26	37/12
6	Zn(OTf) ₂	31	94:6	86/35
7	Fe(OTf) ₂	28	90:10	2/3
8	La(OTf) ₃	60	95:5	-30
9	Co(NTf ₂) ₂	51	88:12	89/47
10	Co(ClO ₄) ₂ ·6H ₂ O	58	86:14	61/53
11	Co(BF ₄) ₂ ·6H ₂ O	56	89:11	81/37

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), and metal salt/ $L_3\text{-PrPr}_2$ (1:1, 10 mol%) in EtOAc (1.0 mL) under argon atmosphere at 30 °C for 24 h. [b] Isolated yield of **3a**. [c] Determined by UPC² analysis on a chiral stationary.

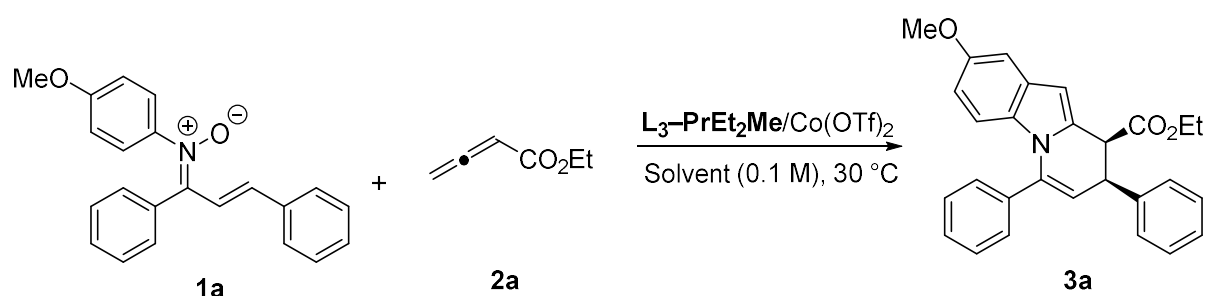
3.2 Screening of ligands



entry ^[a]	ligand	yield (%) ^[b]	dr ^[c]	ee (%) ^[c]
1	L₃-PiPr₂	59	83:17	92/83
2	L₃-RaPr₂	53	84:16	91/56
3	L₃-PrPr₂	61	90:10	87/41
4	L₃-PrMe₂	59	93:7	90/77
5	L₃-PrMe₃	61	92:8	98/89
6	L₃-PrEt₂	55	95:5	99
7	L₃-PrEt₂Me	67	95:5	97
8	L₃-PrEt₃	60	97:3	99
9	L₃-PrEt₂Ad	61	96:4	99
10	L₃-PrAd	58	95:5	30/40

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), and Co(OTf)₂/ligand (1:1, 10 mol%) in EtOAc (1.0 mL) under argon atmosphere at 30 °C for 24 h. [b] Isolated yield of **3a**. [c] Determined by UPC² analysis on a chiral stationary.

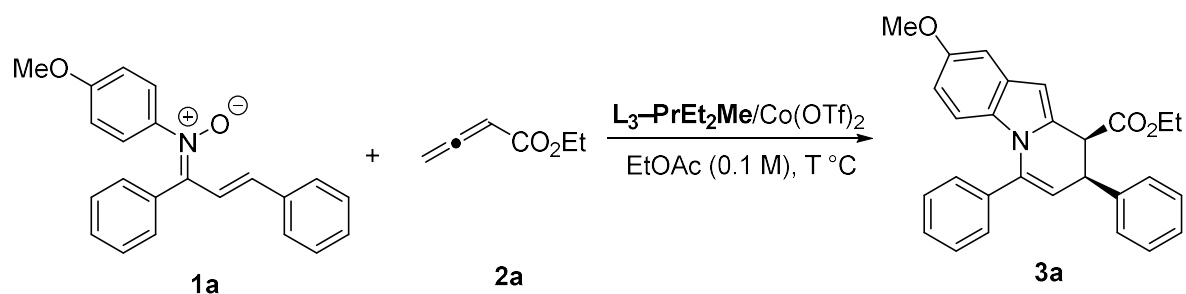
3.3 Screening of solvents



entry ^[a]	solvent	yield (%) ^[b]	dr ^[c]	ee (%) ^[c]
1	Et ₂ O	62	88:12	91/79
2	CH ₂ Cl ₂	65	85:15	96/49
3	THF	70	96:4	83
4	PhCH ₃	57	88:12	92/77
5	HCOOCH ₂ CH ₃	52	95:5	45/31
6	CH ₃ COOCH ₃	53	94:6	97/69
7	EtOAc	67	95:5	97
8	HCOOCH ₃	62	91:9	89/53

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), and Co(OTf)₂/**L₃-PrEt₂Me** (1:1, 10 mol%) in solvent (1.0 mL) under argon atmosphere at 30 °C for 24 h. [b] Isolated yield of **3a**. [c] Determined by UPC² analysis on a chiral stationary.

3.4 Screening of temperature

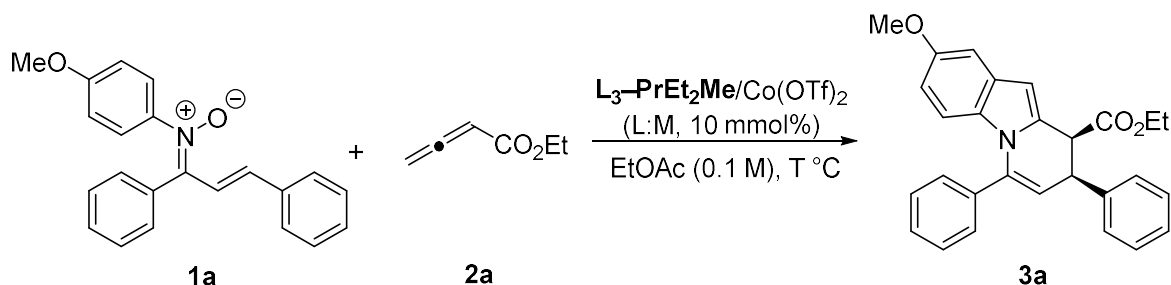


entry ^[a]	T (°C)	yield (%) ^[b]	dr ^[c]	ee (%) ^[c]
1	0	27	97	95:5

2	20	53	98	95:5
3	30	67	97	95:5
4	40	69	97/70	93:7
5	60	67	96/79	91:9

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), and $\text{Co}(\text{OTf})_2/\text{L}_3\text{-PrEt}_2\text{Me}$ (1:1, 10 mol%) in EtOAc (1.0 mL) under argon atmosphere at T °C for 24 h. [b] Isolated yield of **3a**. [c] Determined by UPC² analysis on a chiral stationary.

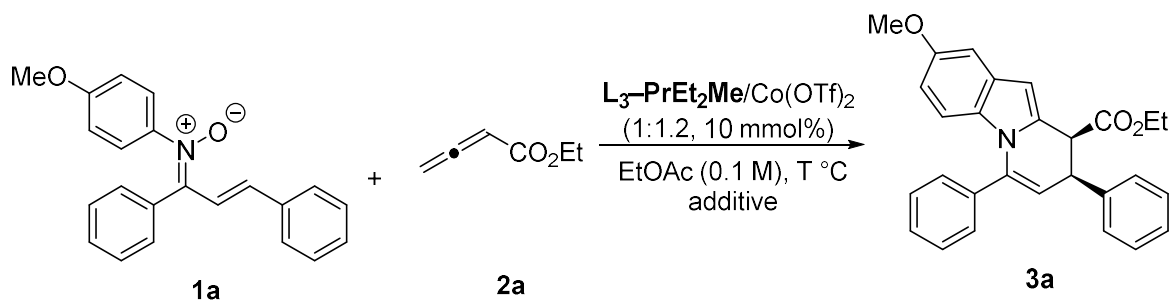
3.5 Screening of the ratio of metal to ligand



entry ^[a]	L:M	yield (%) ^[b]	dr ^[c]	ee (%) ^[c]
1	1:1	67	95:5	97
2	1.2:1	47	97:3	99
3	1.5:1	44	98:2	99
4	1:1.2	72	95:5	97
5	1:1.5	74	90:10	67/30
6	1:2	74	86:14	35/12

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and $\text{L}_3\text{-PrEt}_2\text{Me}/\text{Co}(\text{OTf})_2$ (L:M, 10 mol%) in EtOAc (1 mL) under argon atmosphere at 30 °C for 24 h. [b] Isolated yield **3a**. [c] Determined by UPC² analysis on a chiral stationary.

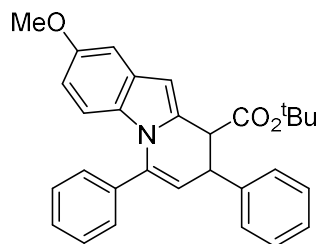
3.6 Screening of additives



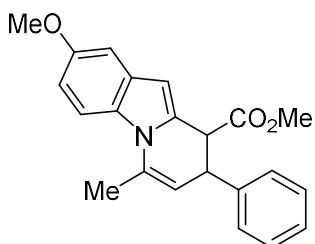
entry ^[a]	Additive	yield (%) ^[b]	dr ^[c]	ee (%) ^[c]
1	3 Å MS (20 mg)	31	95:5	97
2	4 Å MS (20 mg)	31	95:5	97
3	5 Å MS (20 mg)	32	95:5	97
4	Na_2SO_4 (20 mg)	79	95:5	97
5	Na_2SO_4 (40 mg)	79	95:5	97
6	Na_2SO_4 (60 mg)	79	95:5	97

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), $\text{Co}(\text{OTf})_2/\text{L}_3\text{-PrEt}_2\text{Me}$ (1.2:1, 10 mol%) and additive in EtOAc (1 mL) under argon atmosphere at 30 °C for 24 h. [b] Isolated yield **3a**. [c] Determined by UPC² analysis on a chiral stationary.

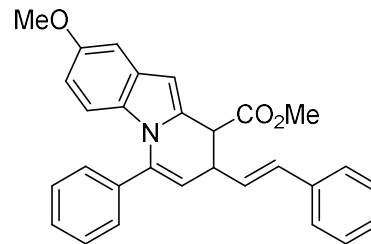
4. Limited substrates



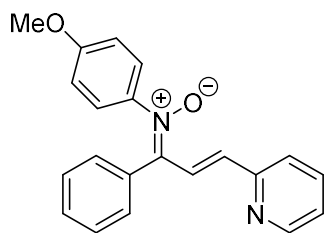
yield = 51%
ee = 57%/93%, dr = 60:40



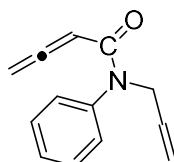
yield = 19%,
race, dr = 88:12



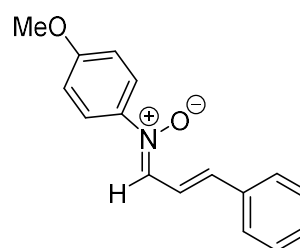
yield = 54%
ee = 90%/63%, dr = 78:22



complex

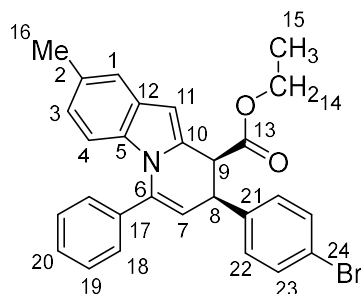


complex



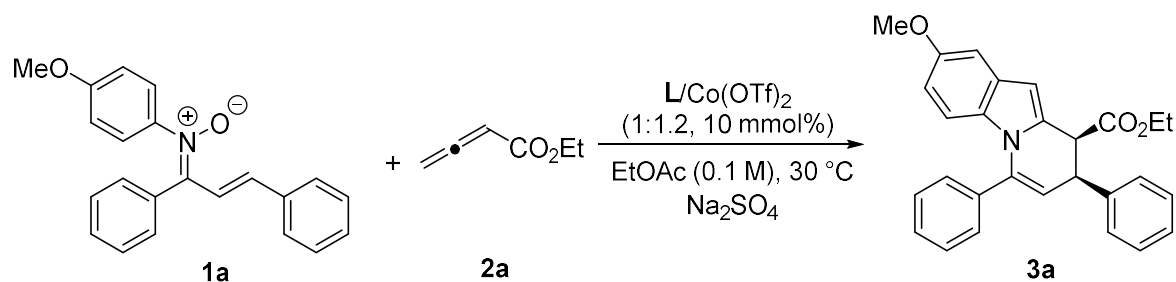
N.D.

5. Analysis of 2D NMR spectra of the product 3z



Number of Atom	H	C	Number of Atom	H	C
1	6.71	123.3	13	-	169.4
2	-	129.7	14	4.05	60.8
3	7.33	120.5	15	1.14	14.0
4	6.69	104.2	16	2.38	21.3
5	-	-	17	-	135.9
6	-	139.4	18-20	7.42-7.50	128.1
7	5.58	112.3			128.5
8	4.18	41.7			128.8
9	4.37	46.6	21	-	138.7
10	-	-	22	6.88-6.96	129.9
11	6.13	112.7	23	7.31-7.38	131.5
12	-	-	24	-	-

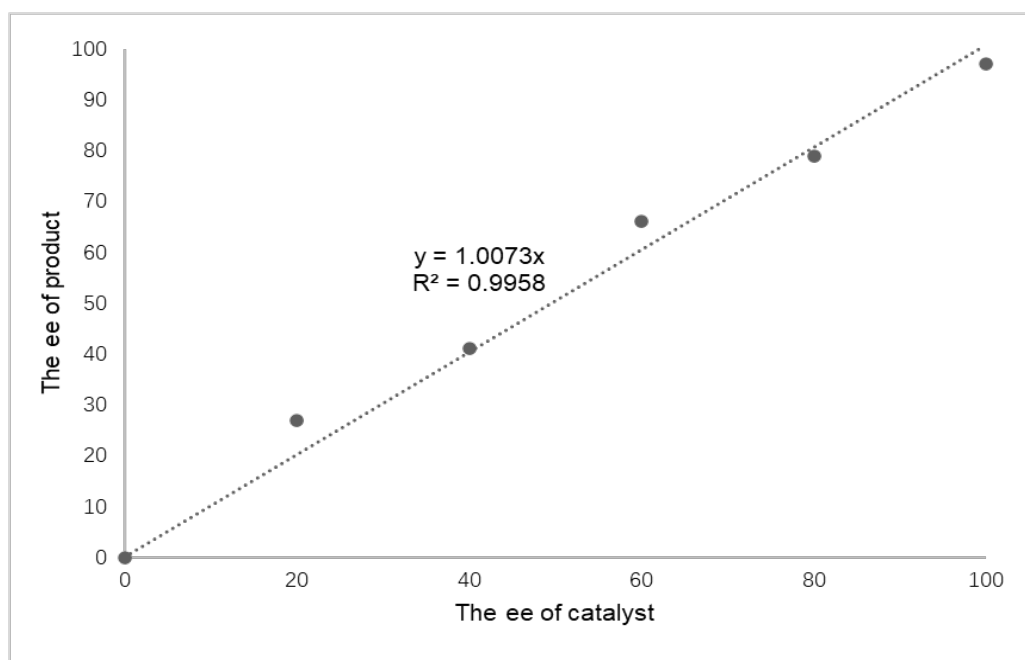
6. Nonlinear effect



A dry reaction tube was charged with *N*-aryl nitron **1a** (0.10 mmol), $Co(OTf)_2/L$ (10 mol%, 1.2:1), allene **2a** (0.10 mmol), Na_2SO_4 (20 mg) in EtOAc (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 30 °C for 24 h. The desired product was purified directly by silica gel column chromatograph (ethyl acetate/petroleum ether, 50:1) to afford the corresponding product **3a**.

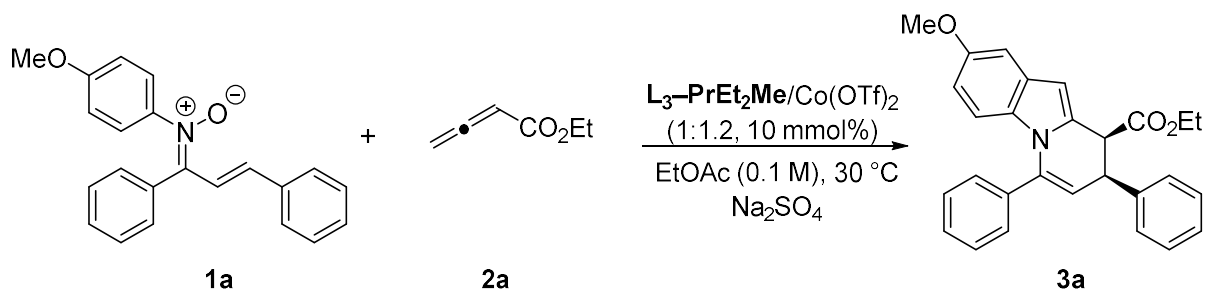
Entry ^[a]	ee of catalyst L (%)	ee of product ^[b]
1	0	0
2	20	27
3	40	41
4	60	66
5	80	79
6	100	97

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), $Co(OTf)_2/L$ (1.2:1, 10 mol%) and Na_2SO_4 (20 mg) in EtOAc (1 mL) under argon atmosphere at 30 °C for 24 h. [b] Determined by UPC² analysis on a chiral stationary.



7. Mechanism study

7.1 Trace the reaction by ¹H NMR analysis

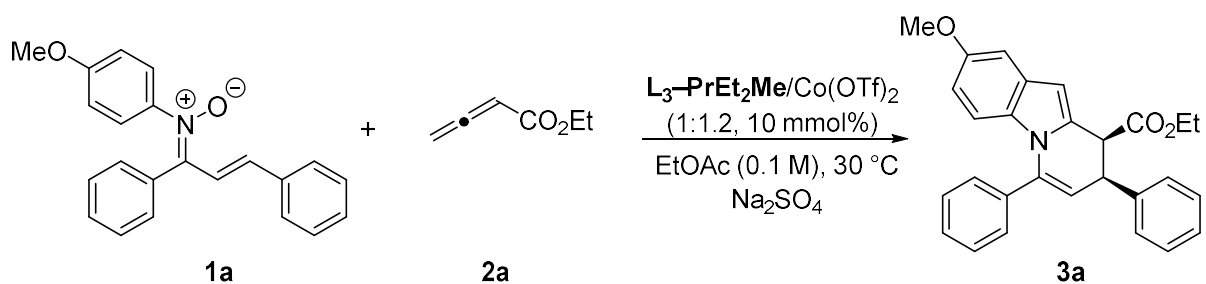


A dry reaction tube was charged with *N*-aryl nitronium **1a** (0.10 mmol), Co(OTf)₂/L (10 mol%, 1.2:1), allene **2a** (0.10 mmol), Na₂SO₄ (20 mg) in EtOAc (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 30 °C for x h, and filtered with suction. The yield was determined by ¹H NMR. (¹H NMR see SI control experiment ¹H NMR, CH₂Br₂ as the internal standard solvent)

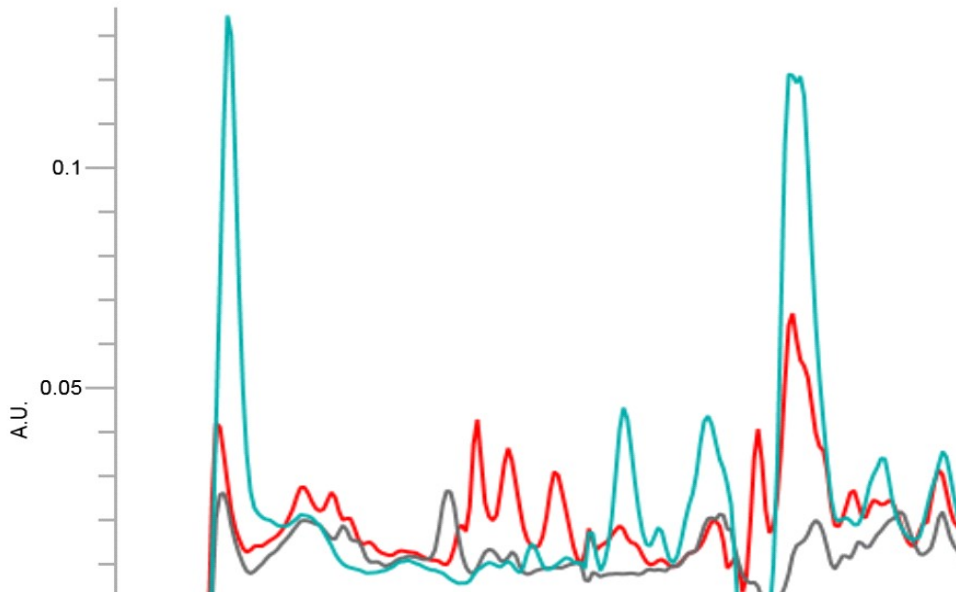
Entry ^[a]	T/h	Yield ^[b]
1	0	0
2	1	1
3	2	1
4	3	1
5	4	9
6	5	14

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), Co(OTf)₂/L (1.2:1, 10 mol%) and Na₂SO₄ (20 mg) in EtOAc (1 mL) under argon atmosphere at 30 °C for T h. [b] Determined by ¹H NMR.

7.2 Operando IR experiments

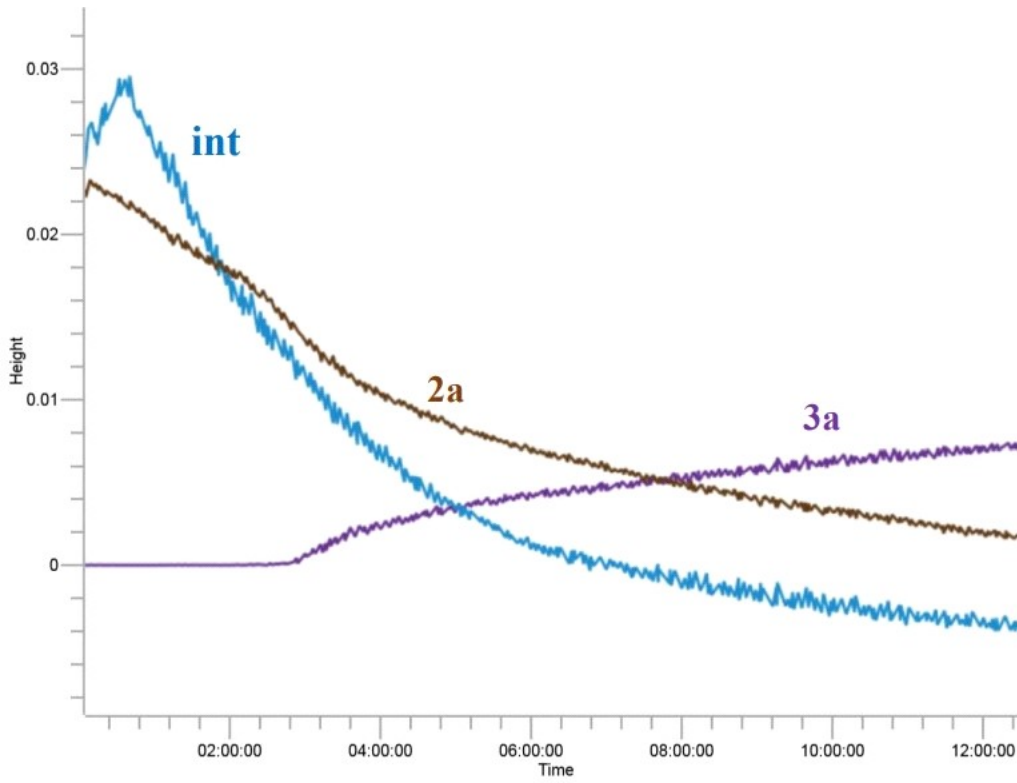


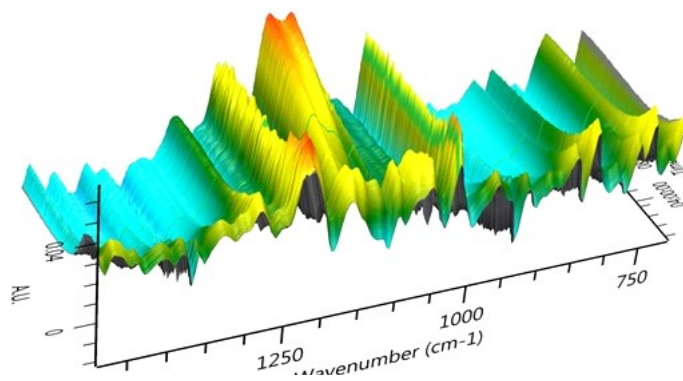
Initially, the infrared absorption spectra of each reactant (**1a**, **2a**) and product **3a** in EtOAc were collected. The following figure shows the absorption of each participant minus the absorption of solvent.



Spectrum Name	Color	Units
3a minus EA	—	A.U.
1a-2 minus 1a EA	—	A.U.
2a-2 minus 1a EA	—	A.U.

Figure1. The IR spectra of each component.








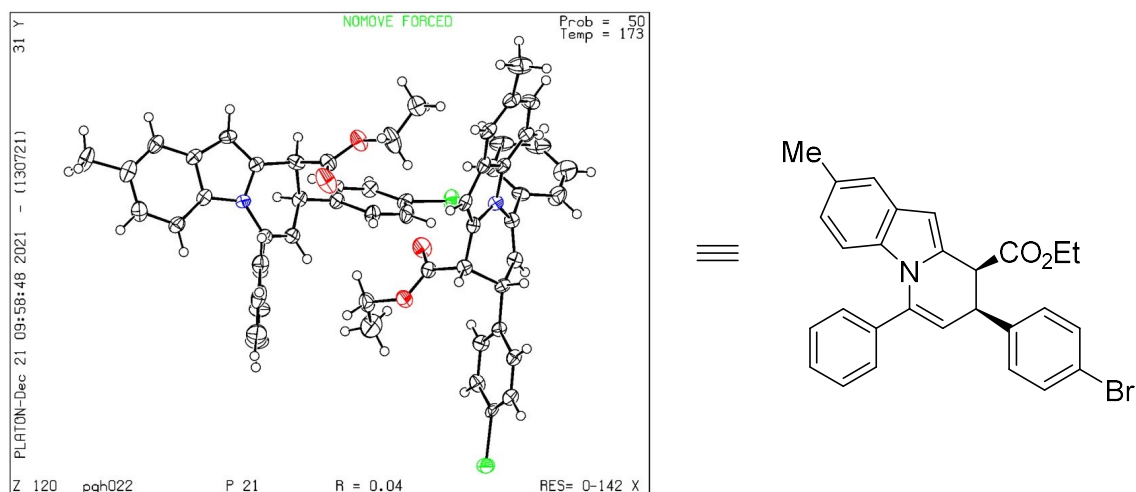
Trend	Color	Units
Peak at 1446 cm-1		Height
Peak at 1413 cm-1		Height
Peak at 1504 cm-1		Height

Figure 2. 3D ATR-FTIR profile of the catalytic asymmetric cascade reaction of each component.

The Operando IR experiments is consistent with the ^1H NMR experiment. There is basically no product formed in 3 hours. A newly absorption peak increased first and then decreased before and after adding the substrate **1a**. These implied that this newly generated species could be the intermediate.

8. X-ray crystallography of 3z

The colourless crystal in block-shape, with approximate dimensions of $0.136 \times 0.165 \times 0.511 \text{ mm}^3$, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source ($K_{\alpha} = 0.71073\text{\AA}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^{a, b, c, d}. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.



Crystallographic Data for $\text{C}_{56}\text{H}_{48}\text{Br}_2\text{N}_2\text{O}_4$.

Formula	$\text{C}_{56}\text{H}_{48}\text{Br}_2\text{N}_2\text{O}_4$
Formula mass (amu)	972.78
Space group	P 21
<i>a</i> (Å)	11.505(3)
<i>b</i> (Å)	8.2528(15)
<i>c</i> (Å)	24.175(5)
α (deg)	90
β (deg)	92.468(6)
γ (deg)	90
<i>V</i> (Å ³)	2293.3(8)
<i>Z</i>	2
λ (Å)	0.71073
<i>T</i> (K)	173 K
ρ_{calcd} (g cm ⁻³)	1.409
μ (mm ⁻¹)	1.818
Transmission factors	0.605, 0.985
θ_{max} (deg)	26.414
No. of unique data, including $F_o^2 < 0$	9150
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	7256
No. of variables	581

$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0428
$R_w(F_o^2)$ ^b	0.1093
Goodness of fit	1.006

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w(F_o^2) = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}}{w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]}, \text{ where } p = [\max(F_o^2, 0) + 2F_c^2] / 3.$$

References:

^a Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

^b Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8.

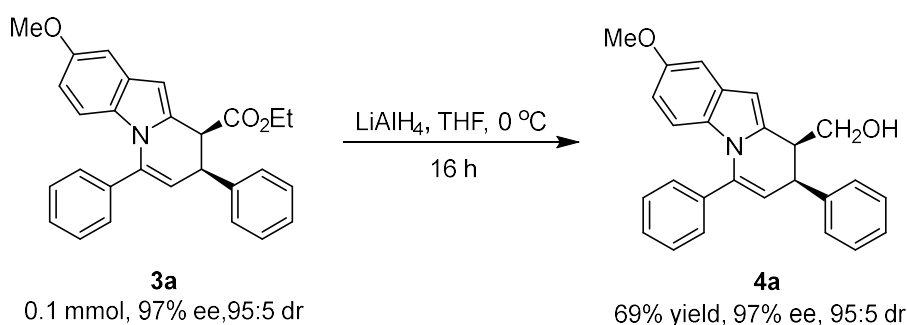
^c Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3–8.

^d Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.

^e Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7–13.

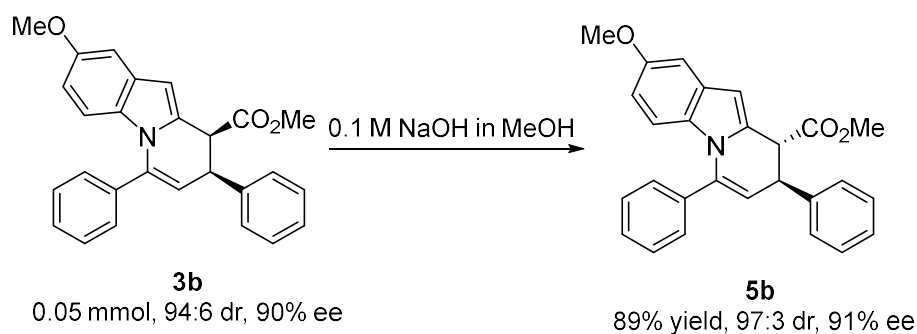
9. Transformation of products

9.1 Reduction of 3a



Synthesis of **4a**: A dry reaction tube was charged with **3a** (42.3 mg, 0.1 mmol, 97% ee, 95:5 dr) in anhydrous THF (1.0 mL). The mixture was stirred at 0 °C for 10 min. Then LiAlH₄ (8.4 mg, 0.22 mmol, 2.2 equiv) was added at 0 °C and stirred at 0 °C for 12 hours. After the reaction was completed, the mixture was extracted with ethyl acetate. The combined organics were dried and concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1 and 2/1, v/v) to afford the product **4a** (2.63 mg, 69% yield, 97% ee, 95:5 dr).

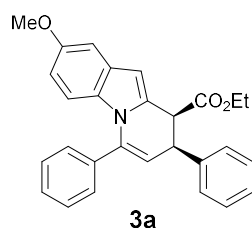
9.2 Epimerization of 3b



A dry reaction tube was charged with *syn*-dihydropyridoindole **3b** (0.05 mmol, 0.204 g), and then a 0.1 M solution of NaOH in MeOH (0.11 mL, 0.010 mmol) was added to the reaction tube. The reaction mixture was stirred at 25 °C for 1 h. The reaction mixture was then diluted with CH₂Cl₂ (10.0 mL), washed with brine (3 x 5.0 mL), and dried with Na₂SO₄. The CH₂Cl₂ solution was then concentrated under vacuum and purified directly by silica gel column chromatograph (ethyl acetate/petroleum ether, 50:1) to afford the corresponding product **5b** (0.0182 g, 89% yield, 97:3 dr, 91% ee).

10. Characterization of Typical Products

Ethyl (8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3a**



Yellow oil; *R*_f = 0.6 (petroleum ether/ethyl acetate = 6/1), 79% yield, 97% ee, 95:5 dr. [α]_D²⁵ = +32.6 (c = 0.60, in CH₂Cl₂, λ = 589 nm).

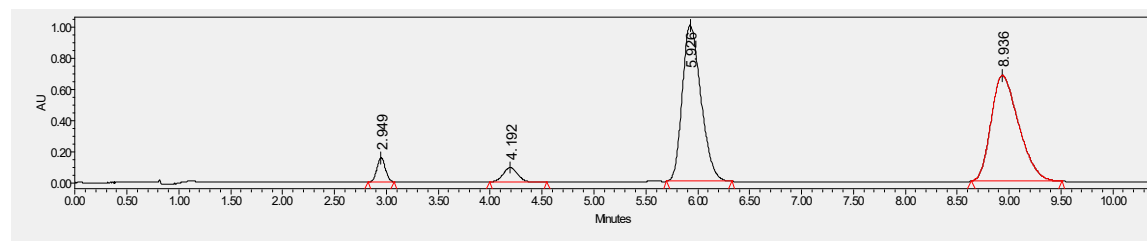
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, CO₂/CH₃OH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm) retention time: *t*₁ = 2.94 min, *t*₂ = 4.18 min, *t*₃ = 5.93 min, *t*₄ = 9.02 min. dr = 95:5 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.50 – 7.42 (m, 5H), 7.31 – 7.19 (m, 3H), 7.10 – 7.06 (m, 2H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.65 (s, 1H), 6.52 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.14 (d, *J* = 9.1 Hz, 1H), 5.62 (d, *J* = 4.8 Hz, 1H), 4.35 (d, *J* = 6.0 Hz, 1H), 4.27 – 4.18 (m, 1H), 4.04 – 3.95 (m, 2H), 3.79 (s, 3H), 1.07 (t, *J* = 7.2 Hz, 3H) ppm.

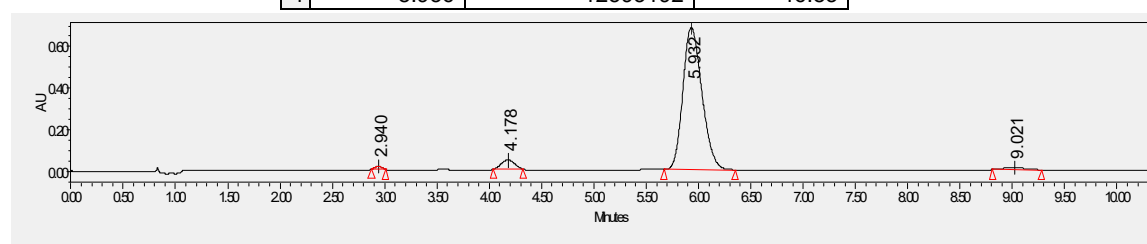
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ = 169.5, 154.3, 139.6, 139.0, 136.1, 133.6, 129.9, 129.6, 128.7, 128.5, 128.5, 128.2, 128.1, 127.3, 113.7, 112.7, 111.2, 103.9, 102.7, 60.7, 55.7, 47.0, 42.3, 14.0 ppm.

IR (neat): 3066, 3034, 2983, 2933, 2838, 1730, 1646, 1615, 1476, 1446, 1399, 1265, 1171, 1032, 843, 735 *ν* (cm⁻¹)

HRMS (ESI-FT) calcd for C₂₈H₂₆NO₃⁺ ([M]+H⁺) = 424.1907, found 424.1902.



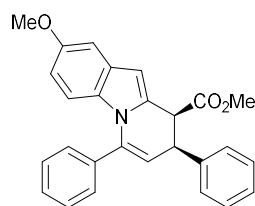
	Retention Time	Area	% Area
1	2.949	879453	3.27
2	4.192	880199	3.27
3	5.926	12540832	46.63
4	8.936	12593192	46.83



	Retention Time	Area	% Area
1	2.940	61386	0.66
2	4.178	386882	4.18
3	5.932	8657185	93.62

4	9.021	141881	1.53
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Methyl (8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3b**



3b

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 74% yield, 90% ee, 95:5 dr. $[\alpha]_D^{25} = +34.5$ ($c = 0.56$, in CH_2Cl_2 , $\lambda = 589$ nm).

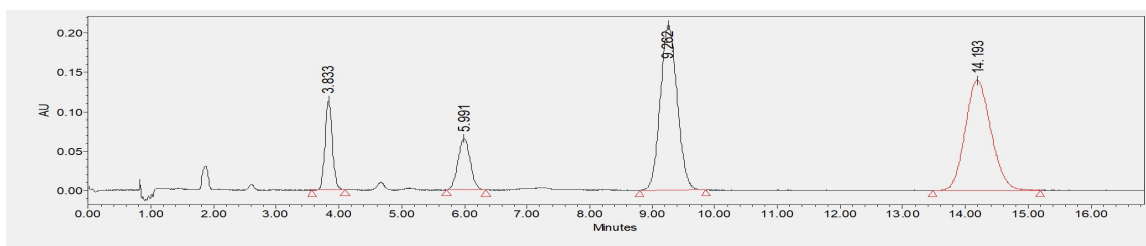
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.81$ min, $t_2 = 5.92$ min, $t_3 = 9.14$ min, $t_4 = 14.07$ min. dr = 95:5 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.53 - 7.37$ (m, 5H), 7.27 - 7.19 (m, 3H), 7.09 - 7.04 (m, 2H), 7.01 (d, $J = 2.6$ Hz, 1H), 6.65 (s, 1H), 6.52 (dd, $J = 9.0, 2.6$ Hz, 1H), 6.14 (d, $J = 9.0$ Hz, 1H), 5.61 (d, $J = 4.9$ Hz, 1H), 4.37 (d, $J = 6.0$ Hz, 1H), 4.25 - 4.18 (m, 1H), 3.79 (s, 3H), 3.54 (s, 3H) ppm.

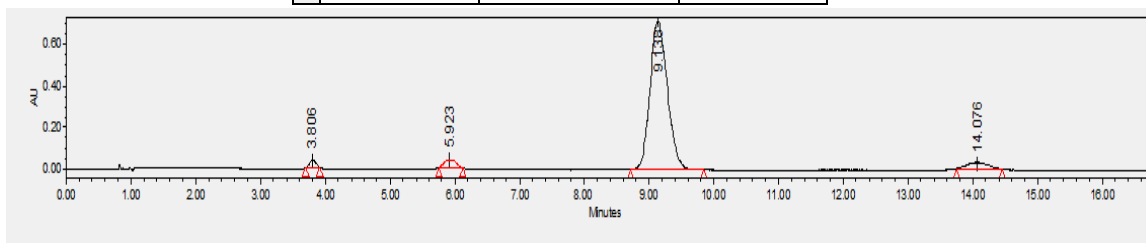
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.9, 154.3, 139.5, 139.1, 136.0, 133.4, 129.9, 129.6, 128.8, 128.5, 128.2, 128.1, 127.4, 113.7, 112.7, 111.3, 103.9, 102.7, 55.6, 51.6, 46.9, 42.4$ ppm.

IR (neat): 3060, 3028, 3002, 2946, 2835, 1736, 1647, 1612, 1476, 1443, 1398, 1341, 1247, 1165, 1032, 842, 737 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_3^+ ([\text{M}+\text{H}]^+) = 410.1751$, found 410.1749.

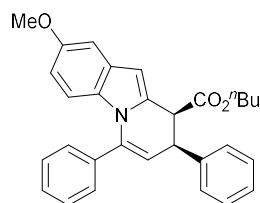


	Retention Time	Area	% Area
1	3.833	917915	9.44
2	5.991	884089	9.09
3	9.262	3941590	40.53
4	14.193	3981201	40.94



	Retention Time	Area	% Area
1	3.806	242230	1.67
2	5.923	456128	3.14
3	9.138	13177685	90.86
4	14.076	627871	4.33

Butyl (8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3c**



3c

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 63% yield, 95% ee, 95:5 dr. $[\alpha]_D^{24} = +25.2$ ($c = 0.58$, in CH_2Cl_2 , $\lambda = 589$ nm).

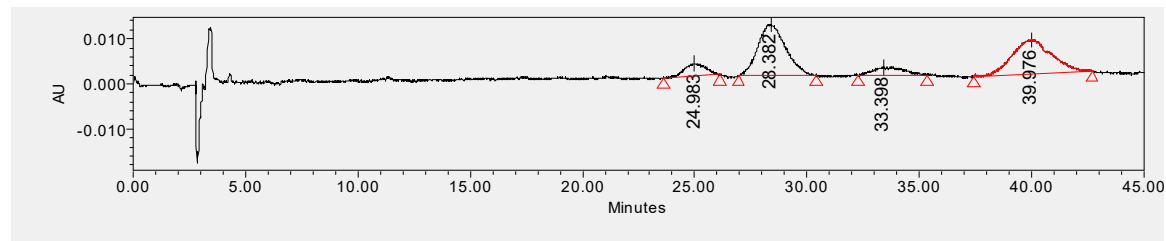
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK AYH, $\text{CO}_2/\text{CH}_3\text{OH} = 90/10$, flow rate = 1.0 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 24.32$ min, $t_2 = 27.56$ min, $t_3 = 32.75$ min, $t_4 = 38.48$ min. dr = 95:5 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.48 – 7.40 (m, 5H), 7.24 – 7.20 (m, 3H), 7.12 – 7.06 (m, 2H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.64 (s, 1H), 6.52 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.14 (d, *J* = 9.0 Hz, 1H), 5.62 (d, *J* = 4.7 Hz, 1H), 4.36 (d, *J* = 5.2 Hz, 1H), 4.26 – 4.18 (m, 1H), 4.00 – 3.87 (m, 2H), 3.79 (s, 3H), 1.47 – 1.37 (m, 2H), 1.23 – 1.13 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H) ppm.

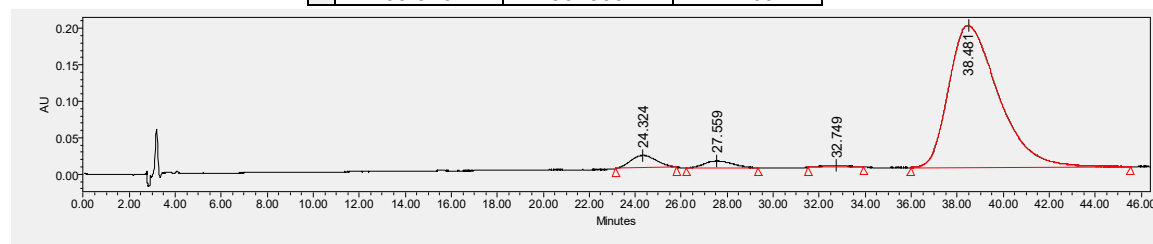
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ = 169.7, 154.3, 139.6, 139.0, 136.0, 133.6, 129.9, 129.6, 128.7, 128.5, 128.5, 128.1, 127.3, 113.7, 112.8, 111.2, 103.9, 102.7, 64.6, 55.7, 47.1, 42.3, 30.4, 19.0, 13.6 ppm.

IR (neat): 3063, 3034, 2956, 2931, 2874, 2835, 1730, 1646, 1615, 1475, 1446, 1399, 1339, 1279, 1169, 1035, 843, 761 ν (cm⁻¹)

HRMS (ESI-FT) calcd for C₃₀H₃₀NO₃⁺ ([M]+H⁺) = 452.2220, found 452.2211.

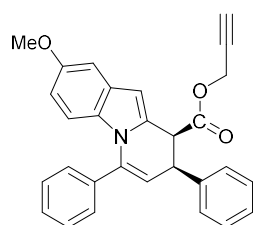


	Retention Time	Area	% Area
1	24.983	182261	8.16
2	28.382	965980	43.25
3	33.398	154147	6.90
4	39.976	931305	41.69



	Retention Time	Area	% Area
1	24.324	1344648	4.30
2	27.559	789171	2.52
3	32.749	156290	0.50
4	38.481	29011987	92.68

Prop-2-yn-1-yl (8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3d**



3d

Yellow oil; *R*_f = 0.6 (petroleum ether/ethyl acetate = 6/1), 59% yield, 99% ee, 98:2 dr. [α]_D²⁵ = +42.3 (c = 0.35, in CH₂Cl₂, λ = 589 nm).

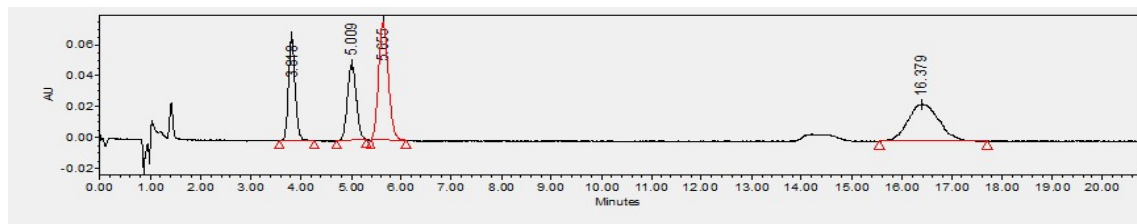
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK AD-3, CO₂/CH₃OH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm) retention time: *t*₁ = 3.85 min, *t*₂ = 5.04 min, *t*₃ = 5.71 min, *t*₄ = 15.97 min. dr = 98:2 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.52 – 7.39 (m, 5H), 7.24 – 7.20 (m, 3H), 7.10 – 7.05 (m, 2H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.68 (s, 1H), 6.53 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.14 (d, *J* = 9.0 Hz, 1H), 5.62 (d, *J* = 5.0 Hz, 1H), 4.63 – 4.46 (m, 2H), 4.41 (d, *J* = 6.0 Hz, 1H), 4.25 (t, *J* = 5.5 Hz, 1H), 3.79 (s, 3H), 2.41 (t, *J* = 2.5 Hz, 1H) ppm.

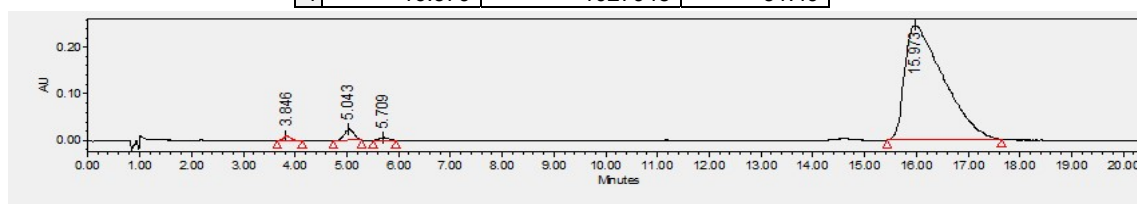
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ = 168.6, 154.3, 139.2, 139.2, 136.0, 132.8, 129.9, 129.6, 128.8, 128.6, 128.5, 128.2, 128.2, 127.5, 113.7, 112.6, 111.4, 104.3, 104.2, 102.8, 75.2, 75.1, 55.6, 52.1, 46.7, 42.3 ppm.

IR (neat): 3265, 3059, 3028, 3002, 2930, 2832, 1740, 1644, 1612, 1475, 1446, 1400, 1273, 1146, 1033, 844, 762 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{29}\text{H}_{24}\text{NO}_3^+$ ($[\text{M}+\text{H}^+]$) = 434.1751, found 434.1745.

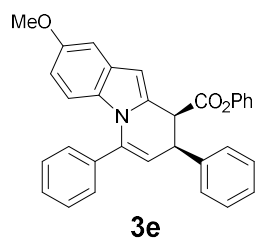


	Retention Time	Area	% Area
1	3.818	617697	18.92
2	5.009	601000	18.41
3	5.655	1017614	31.17
4	16.379	1027948	31.49



	Retention Time	Area	% Area
1	3.846	86911	0.66
2	5.043	284934	2.16
3	5.709	58141	0.44
4	15.973	12733391	96.73

Phenyl (8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3e**



Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate = 6/1), 66% yield, 97% ee/82% ee, 93:7 dr. $[\alpha]_D^{26} = +33.2$ ($c = 0.59$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK AD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 7.01$ min, $t_2 = 8.43$ min, $t_3 = 11.30$ min, $t_4 = 25.64$ min. dr = 93:7 determined by ¹H NMR.

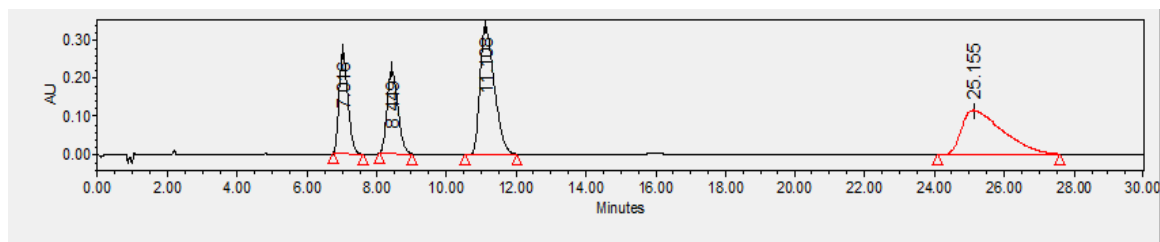
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.50 - 7.38$ (m, 5H), 7.31 - 7.25 (m, 5H), 7.22 - 7.12 (m, 3H), 7.04 (d, $J = 2.6$ Hz, 1H), 6.81 - 6.75 (m, 3H), 6.54 (dd, $J = 9.1$,

2.6 Hz, 1H), 6.15 (d, $J = 9.0$ Hz, 1H), 5.67 (d, $J = 4.9$ Hz, 1H), 4.62 (d, $J = 6.1$ Hz, 1H), 4.41 - 4.34 (m, 1H), 3.80 (s, 3H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 168.0$, 154.4, 150.3, 139.4, 139.1, 135.9, 132.8, 130.0, 129.6, 129.3, 128.8, 128.7, 128.5, 128.4, 128.2, 127.6, 125.8, 121.4, 113.8, 112.4, 111.5, 104.4, 102.8, 55.6, 46.8, 42.4 ppm.

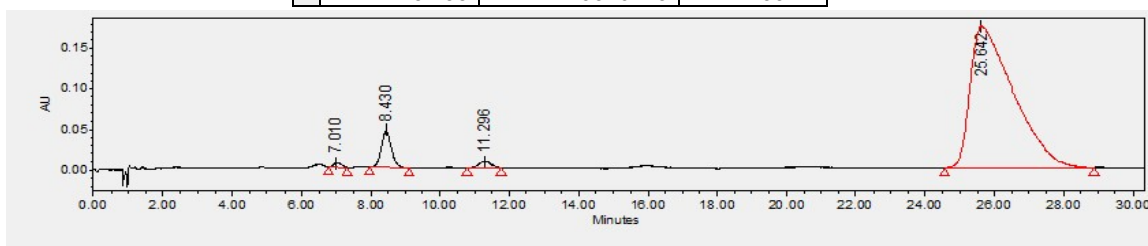
IR (neat): 3060, 3031, 2999, 2929, 2832, 1757, 1646, 1594, 1478, 1446, 1401, 1167, 1034, 834, 739 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{32}\text{H}_{26}\text{NO}_3^+$ ($[\text{M}+\text{H}^+]$) = 472.1907, found 472.1899.



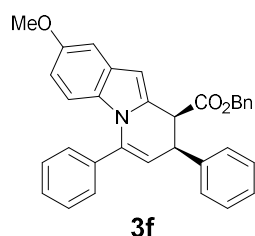
	Retention	Area	% Area
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	Time		
1	7.016	4663551	16.58
2	8.449	4656015	16.55
3	11.108	9465537	33.65
4	25.155	9340223	33.21



	Retention Time	Area	% Area
1	7.010	77065	0.47
2	8.430	938276	5.77
3	11.296	199383	1.23
4	25.642	15055054	92.53

Benzyl (8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3f**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 62% yield, 98% ee, 95:5 dr. $[\alpha]_D^{25} = +18.5$ ($c = 0.55$, in CH_2Cl_2 , $\lambda = 589$ nm).

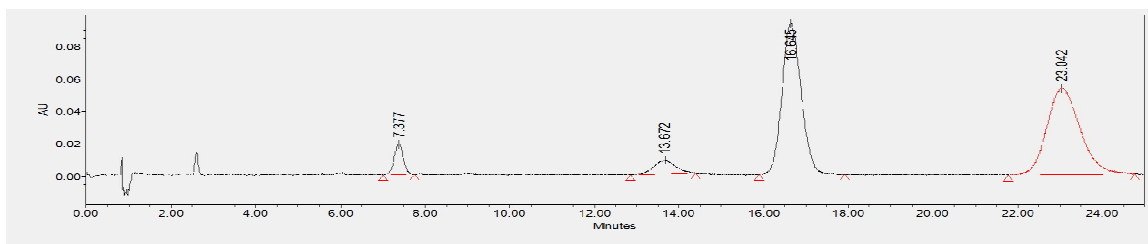
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 7.44$ min, $t_2 = 13.84$ min, $t_3 = 16.89$ min, $t_4 = 22.71$ min. dr = 95:5 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.47 - 7.38$ (m, 5H), 7.31 - 7.25 (m, 3H), 7.21 - 7.18 (m, 3H), 7.13 - 7.08 (m, 2H), 7.05 - 6.98 (m, 3H), 6.65 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.13 (d, $J = 9.1$ Hz, 1H), 5.59 (d, $J = 4.8$ Hz, 1H), 4.96 (q, $J = 12.3$ Hz, 2H), 4.41 (d, $J = 6.1$ Hz, 1H), 4.27 - 4.19 (m, 1H), 3.79 (s, 3H) ppm.

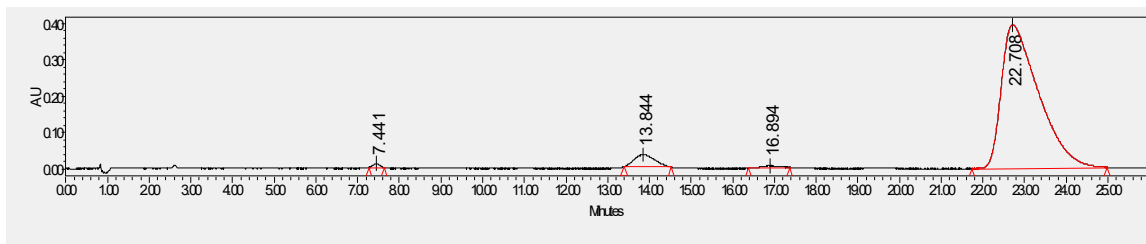
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.3, 154.3, 139.5, 139.1, 136.0, 135.3, 133.4, 129.9, 129.6, 128.7, 128.6, 128.5, 128.4, 128.4, 128.2, 128.2, 127.3, 113.7, 112.6, 111.3, 104.0, 102.7, 66.6, 55.7, 47.1, 42.4$ ppm.

IR (neat): 3056, 3031, 2999, 2930, 2838, 1732, 1645, 1612, 1475, 1446, 1400, 1268, 1158, 1035, 843, 737 cm^{-1}

HRMS (ESI-FT) calcd for $\text{C}_{32}\text{H}_{26}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) = 472.1907, found 472.1899.

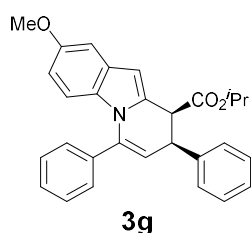


	Retention Time	Area	% Area
1	7.377	275336	4.32
2	13.672	283294	4.44
3	16.645	2908860	45.61
4	23.042	2909604	45.63



	Retention Time	Area	% Area
1	7.441	126195	0.49
2	13.844	1153321	4.48
3	16.894	159046	0.62
4	22.708	24318927	94.41

Isopropyl (8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3g**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 61% yield, 91% ee/94% ee, 80:20 dr. $[\alpha]_D^{24} = +18.9$ ($c = 0.62$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 90/10$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 5.79$ min, $t_2 = 7.24$ min, $t_3 = 8.28$ min, $t_4 = 8.88$ min. dr = 80:20 determined by ¹H NMR.

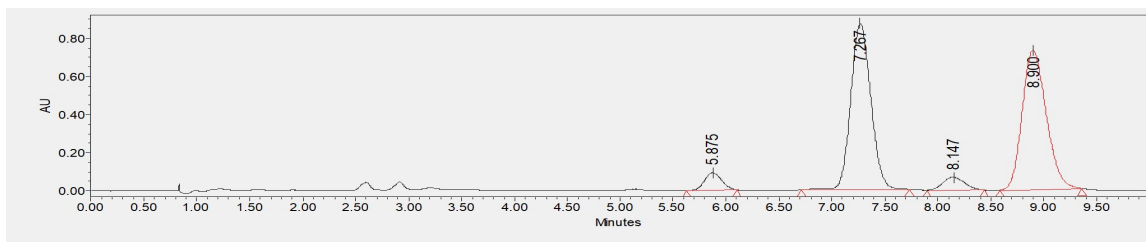
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.50 - 7.35$ (m, 5H), 7.24 – 7.17 (m, 3H), 7.14 – 7.06 (m, 2H), 7.02 (d, $J = 2.6$ Hz, 1H), 6.66 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz,

1H), 6.14 (d, $J = 9.1$ Hz, 1H), 5.63 (d, $J = 4.9$ Hz, 1H), 4.86 (p, $J = 6.3$ Hz, 1H), 4.32 (d, $J = 6.1$ Hz, 1H), 4.24 – 4.16 (m, 1H), 3.80 (s, 3H), 1.10 (d, $J = 6.4$ Hz, 3H), 1.01 (d, $J = 6.2$ Hz, 3H) ppm.

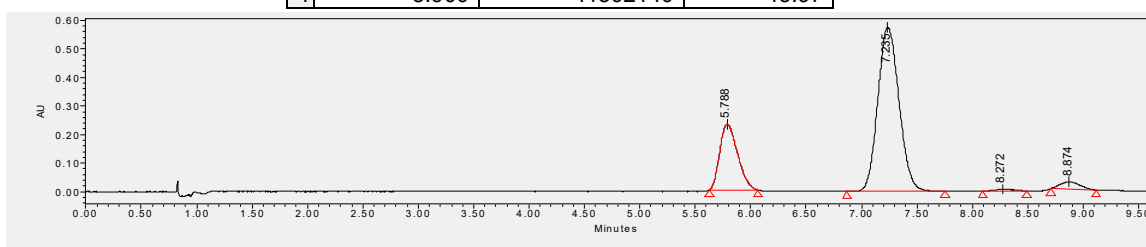
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.1, 154.3, 139.6, 138.9, 136.1, 133.8, 129.9, 129.6, 128.7, 128.5, 128.4, 128.3, 128.2, 127.3, 113.7, 112.9, 111.1, 103.9, 102.7, 68.3, 55.7, 47.0, 42.2, 21.7, 21.6$ ppm.

IR (neat): 3066, 3034, 2980, 2935, 1727, 1645, 1615, 1475, 1460, 1400, 1275, 1171, 1036, 843, 760 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{29}\text{H}_{28}\text{NO}_3^+$ ($[\text{M}] + \text{H}^+$) = 438.2064, found 438.2057.



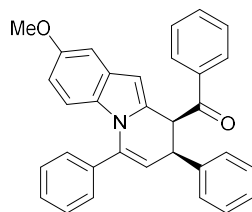
	Retention Time	Area	% Area
1	5.875	1043375	4.17
2	7.267	11506402	45.99
3	8.147	968116	3.87
4	8.900	11502140	45.97



	Retention Time	Area	% Area
1	5.788	2563691	24.22
2	7.235	7611775	71.91
3	8.272	78007	0.74

4	8.874	332196	3.14
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(8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indol-9-yl)(phenyl)methanone **3h**



3h

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 71% yield, 96% ee/57% ee, 67:33 dr. $[\alpha]_D^{25} = +39.8$ ($c = 0.64$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 7.25$ min, $t_2 = 12.55$ min, $t_3 = 15.17$ min, $t_4 = 41.58$ min. dr = 95:5 determined by ¹H NMR.

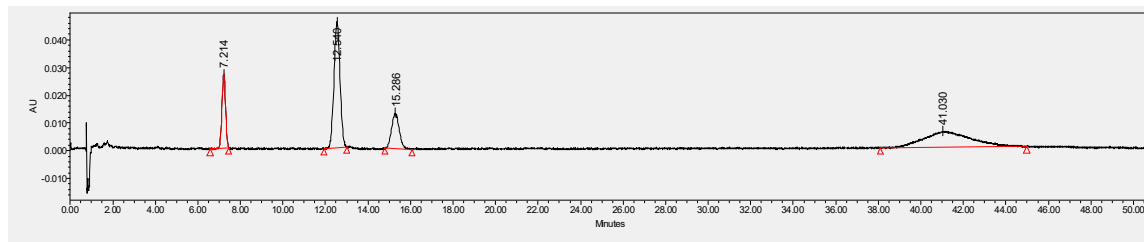
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.74$ (d, $J = 7.7$ Hz, 2H), 7.61 – 7.40 (m, 7H), 7.34 (m, 2H), 7.27 – 7.20 (m, 2H), 7.12 – 7.05 (m, 2H), 7.00 – 6.91 (m, 2H),

6.55 – 6.52 (m, 1H), 6.23 – 6.12 (m, 1H), 5.64 (d, $J = 4.8$ Hz, 1H), 5.38 (d, $J = 5.8$ Hz, 1H), 4.30 (d, $J = 5.5$ Hz, 1H), 3.76 (s, 3H) ppm.

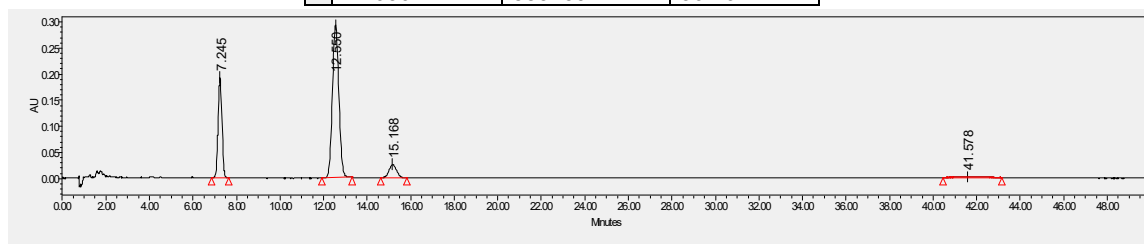
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 196.2$, 154.3, 139.3, 139.2, 137.4, 136.1, 134.8, 132.8, 129.9, 129.6, 128.8, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 127.2, 113.7, 113.0, 111.1, 103.8, 102.7, 55.7, 47.2, 43.6 ppm.

IR (neat): 3060, 3037, 3002, 2941, 2835, 1683, 1646, 1606, 1476, 1442, 1399, 1206, 1169, 837, 760 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{32}\text{H}_{26}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) = 456.1959, found 456.1953.

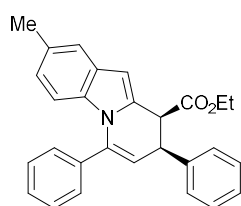


	Retention Time	Area	% Area
1	7.214	314336	12.98
2	12.540	908893	37.52
3	15.286	316101	13.05
4	41.030	883259	36.46



	Retention Time	Area	% Area
1	7.245	2393980	26.09
2	12.550	6015096	65.55
3	15.168	645594	7.04
4	41.578	121761	1.33

Ethyl (8*S*,9*S*)-2-methyl-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3i**



3i

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 51% yield, 96% ee, 95:5 dr. $[\alpha]_D^{26} = +29.5$ ($c = 0.26$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 2.18$ min, $t_2 = 3.44$ min, $t_3 = 3.97$ min, $t_4 = 7.18$ min. dr = 95:5 determined by ¹H NMR.

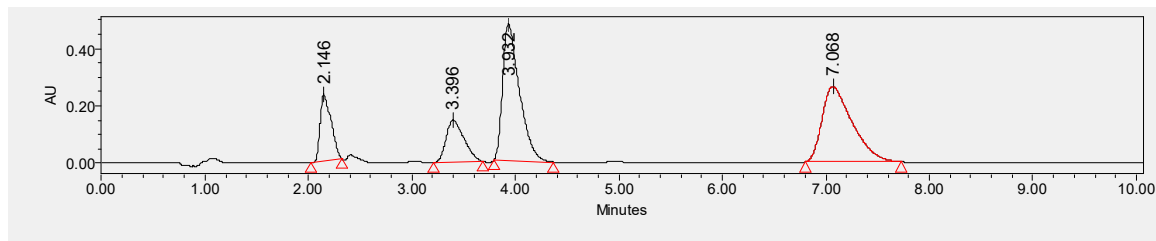
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.50$ – 7.39 (m, 5H), 7.33 (s, 1H), 7.24 –

7.20 (m, 3H), 7.16 – 7.03 (m, 2H), 6.69 (dd, $J = 8.6, 1.7$ Hz, 1H), 6.64 (s, 1H), 6.14 (d, $J = 8.5$ Hz, 1H), 5.62 (d, $J = 4.8$ Hz, 1H), 4.35 (d, $J = 6.0$ Hz, 1H), 4.26 – 4.18 (m, 1H), 3.99 (m, 2H), 2.36 (s, 3H), 1.07 (t, $J = 7.1$ Hz, 3H) ppm.

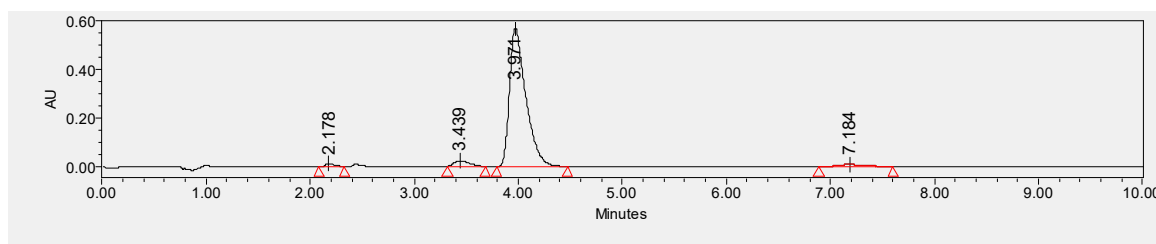
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) $\delta = 169.6, 139.7, 139.1, 136.2, 133.1, 129.6, 129.3, 128.7, 128.5, 128.2, 128.2, 127.3, 123.2, 120.4, 112.9, 112.7, 103.8, 60.7, 47.0, 42.4, 21.2, 14.0$ ppm.

IR (neat): 3063, 3028, 2983, 2928, 2854, 1734, 1647, 1600, 1493, 1449, 1254, 1176, 1072, 872, 759 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{26}\text{NO}_2^+$ ($[\text{M}+\text{H}^+]$) = 408.1958, found 408.1950.

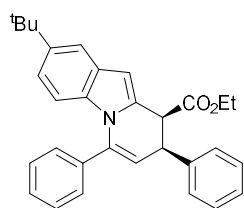


	Retention Time	Area	% Area
1	2.146	1723619	12.13
2	3.396	1762165	12.40
3	3.932	5383442	37.88
4	7.068	5343918	37.60



	Retention Time	Area	% Area
1	2.178	80906	1.21
2	3.439	238162	3.56
3	3.971	6197125	92.62
4	7.184	174446	2.61

Ethyl (8*S*,9*S*)-2-(*tert*-butyl)-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3j**



3j

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 63% yield, 95% ee, 96:4 dr. $[\alpha]_D^{26} = +39.6$ ($c = 0.48$, in CH_2Cl_2 , $\lambda = 589$ nm).

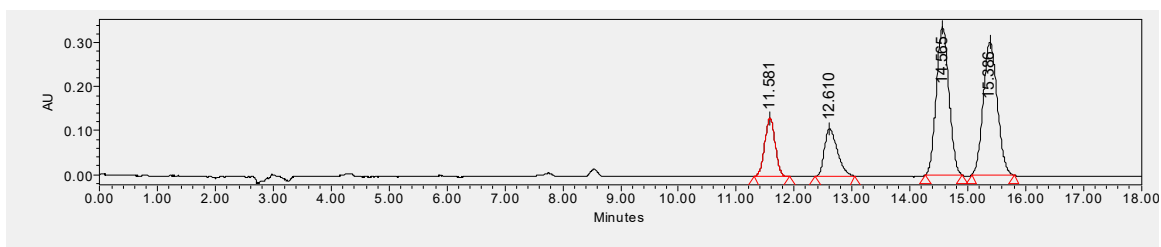
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK ODH, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 11.68$ min, $t_2 = 12.76$ min, $t_3 = 14.72$ min, $t_4 = 15.51$ min. dr = 96:4 determined by ^1H NMR.

^1H NMR (400 MHz, Chloroform- d) $\delta = 7.54$ (d, $J = 2.0$ Hz, 1H), 7.52 – 7.40 (m, 5H), 7.23 (d, $J = 4.1$ Hz, 3H), 7.14 – 7.08 (m, 2H), 6.95 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.67 (s, 1H), 6.17 (d, $J = 8.8$ Hz, 1H), 5.59 (d, $J = 4.6$ Hz, 1H), 4.35 (d, $J = 6.1$ Hz, 1H), 4.24 – 4.17 (m, 1H), 3.98 (m, 2H), 1.32 (s, 9H), 1.06 (t, $J = 7.1$ Hz, 3H) ppm.

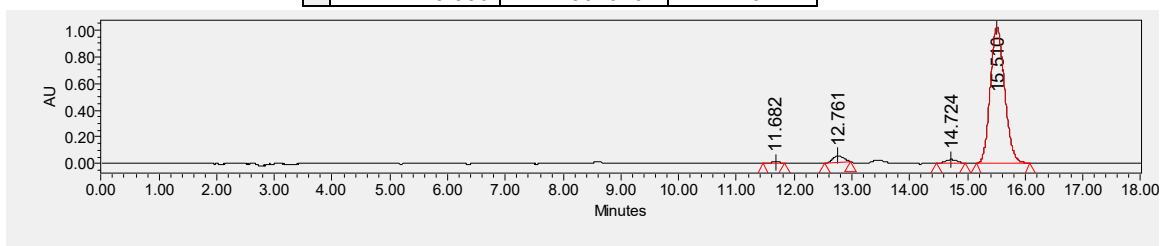
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) $\delta = 169.6, 143.2, 139.8, 139.2, 136.3, 133.0, 128.8, 128.7, 128.5, 128.3, 128.2, 127.3, 119.9, 116.6, 112.5, 112.5, 104.3, 60.7, 47.0, 42.5, 34.4, 31.8, 14.0$ ppm.

IR (neat): 3066, 3031, 2958, 2933, 2832, 1730, 1646, 1602, 1474, 1450, 1397, 1290, 1174, 1030, 878, 759 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{32}\text{NO}_2^+$ ($[\text{M}+\text{H}^+]$) = 450.2428, found 450.2422.

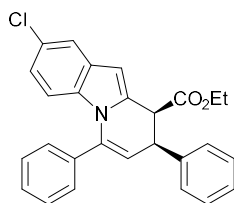


	Retention Time	Area	% Area
1	11.581	1660795	12.25
2	12.610	1672297	12.34
3	14.565	5143436	37.94
4	15.386	5079707	37.47



	Retention Time	Area	% Area
1	11.682	120216	0.64
2	12.761	664646	3.54
3	14.724	415491	2.21
4	15.510	17589562	93.61

Ethyl (8*S*,9*S*)-2-chloro-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3k**



3k

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 63% yield, 99% ee, 95:5 dr. $[\alpha]_D^{26} = +37.3$ ($c = 0.43$, in CH_2Cl_2 , $\lambda = 589$ nm).

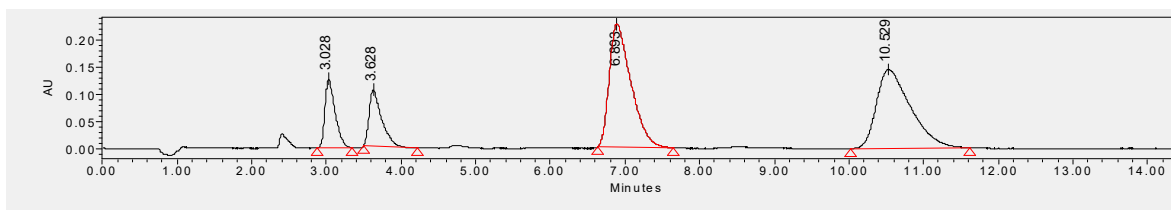
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.05$ min, $t_2 = 3.65$ min, $t_3 = 6.93$ min, $t_4 = 10.65$ min. dr = 95:5 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.50$ (d, $J = 2.1$ Hz, 1H), 7.49 – 7.40 (m, 5H), 7.23 (d, $J = 2.2$ Hz, 3H), 7.10 – 7.02 (m, 2H), 6.81 (dd, $J = 8.9, 2.2$ Hz, 1H), 6.68 (s, 1H), 6.15 (d, $J = 8.9$ Hz, 1H), 5.69 (d, $J = 4.9$ Hz, 1H), 4.35 (d, $J = 6.0$ Hz, 1H), 4.28 – 4.19 (m, 1H), 4.00 (m, 2H), 1.08 (t, $J = 7.2$ Hz, 3H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.3, 139.2, 138.8, 135.7, 134.5, 133.0, 130.1, 129.0, 128.6, 128.5, 128.1, 128.1, 127.4, 126.0, 121.9, 120.0, 113.9, 113.8, 103.7, 60.8, 46.8, 42.2, 14.0$ ppm.

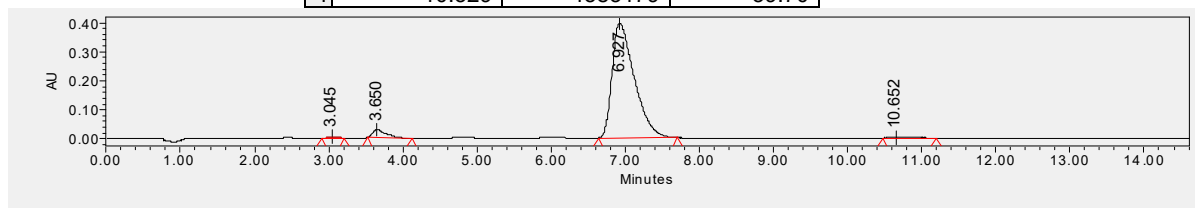
IR (neat): 3063, 3031, 2983, 2928, 2854, 1734, 1647, 1600, 1493, 1449, 1397, 1254, 1176, 1072, 868, 760 cm^{-1}

HRMS (ESI-FT) calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_2\text{Cl}^+ ([\text{M}+\text{H}]^+) = 428.1412$, found 428.1418.



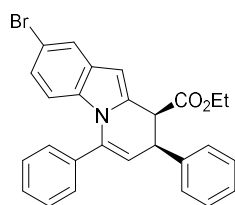
	Retention	Area	% Area
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	Time		
1	3.028	1193743	10.34
2	3.628	1215513	10.53
3	6.893	4552915	39.44
4	10.529	4583179	39.70



	Retention Time	Area	% Area
1	3.045	45945	0.53
2	3.650	355228	4.11
3	6.927	8217266	95.02
4	10.652	29106	0.34

Ethyl (8S,9S)-2-bromo-6,8-diphenyl-8,9-dihydropyrido[1,2-a]indole-9-carboxylate **3I**



3I

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 70% yield, 93% ee/ 50% ee, 93:7 dr. $[\alpha]_D^{25} = +35.2$ ($c = 0.47$, in CH_2Cl_2 , $\lambda = 589$ nm).

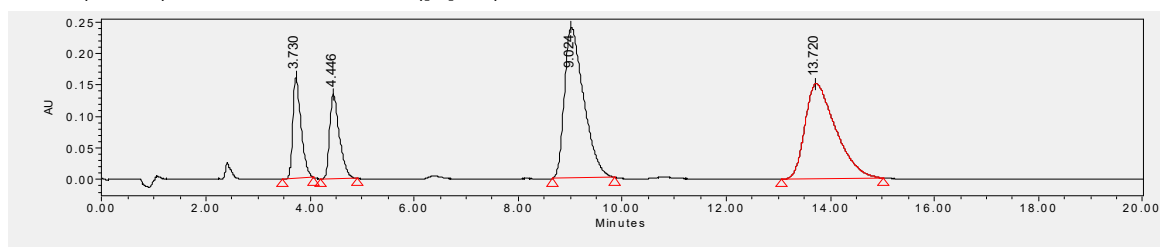
Dissolved in iPrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.77$ min, $t_2 = 4.50$ min, $t_3 = 9.12$ min, $t_4 = 14.00$ min. dr = 93:7 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.66$ (d, $J = 2.0$ Hz, 1H), 7.48 – 7.40 (m, 5H), 7.23 (dd, $J = 5.1, 1.8$ Hz, 3H), 7.06 (dd, $J = 6.7, 2.9$ Hz, 2H), 6.94 (dd, $J = 8.9, 2.1$ Hz, 1H), 6.68 (s, 1H), 6.11 (d, $J = 8.9$ Hz, 1H), 5.70 (d, $J = 4.9$ Hz, 1H), 4.35 (d, $J = 6.1$ Hz, 1H), 4.28 – 4.19 (m, 1H), 4.00 (m, 2H), 1.08 (t, $J = 7.1$ Hz, 3H) ppm.

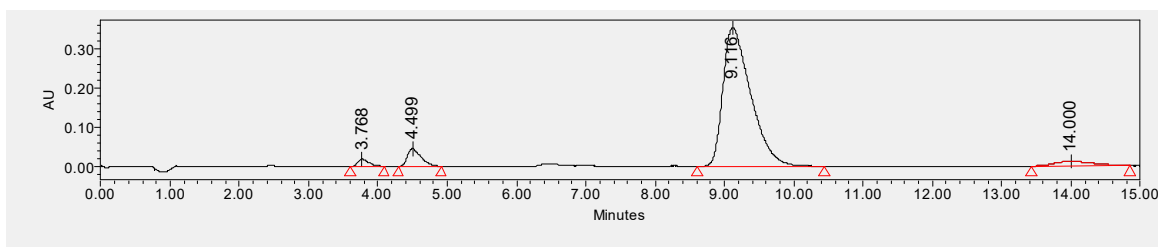
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.2, 139.2, 138.7, 135.7, 134.3, 133.3, 130.7, 129.0, 128.6, 128.5, 128.1, 128.1, 127.4, 124.5, 123.1, 114.4, 113.9, 113.7, 103.6, 60.8, 46.8, 42.2, 14.0$ ppm.

IR (neat): 3060, 3031, 2986, 2826, 2851, 1733, 1647, 1599, 1493, 1450, 1396, 1256, 1176, 1029, 868, 759 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_2\text{Br}^+$ ($[\text{M}+\text{H}]^+$) = 472.0907, found 472.0909.

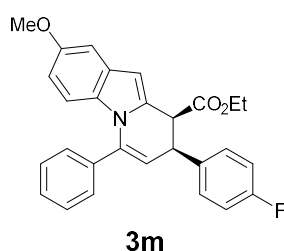


	Retention Time	Area	% Area
1	3.730	1753267	11.08
2	4.446	1737505	10.98
3	9.024	6153464	38.89
4	13.720	6178646	39.05



	Retention Time	Area	% Area
1	3.768	190471	1.73
2	4.499	608459	5.53
3	9.116	9749106	88.53
4	14.000	464148	4.21

Ethyl (8*S*,9*S*)-8-(4-fluorophenyl)-2-methoxy-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3m**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 66% yield, 97% ee, 97:3 dr. $[\alpha]_D^{26} = +40.0$ ($c = 0.57$, in CH_2Cl_2 , $\lambda = 589$ nm).

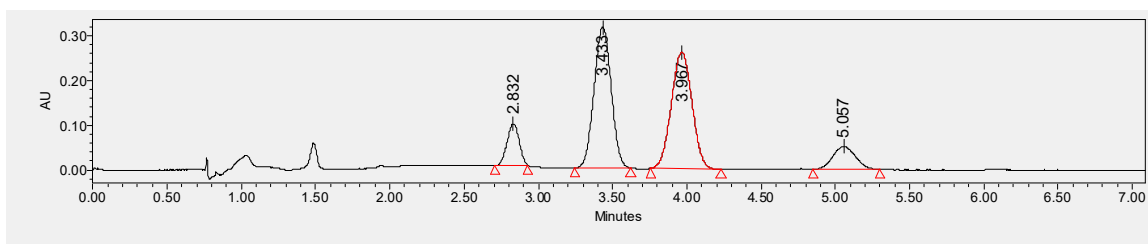
Dissolved in iPrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.16$ min, $t_2 = 3.78$ min, $t_3 = 4.62$ min, $t_4 = 5.34$ min. dr = 97:3 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.48 - 7.41$ (m, 5H), 7.05 – 6.98 (m, 3H), 6.95 – 6.88 (m, 2H), 6.67 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.13 (d, $J = 9.1$ Hz, 1H), 5.58 (d, $J = 5.1$ Hz, 1H), 4.34 (d, $J = 6.0$ Hz, 1H), 4.20 (t, $J = 5.6$ Hz, 1H), 4.08 – 3.98 (m, 2H), 3.79 (s, 3H), 1.12 (t, $J = 7.1$ Hz, 3H) ppm.

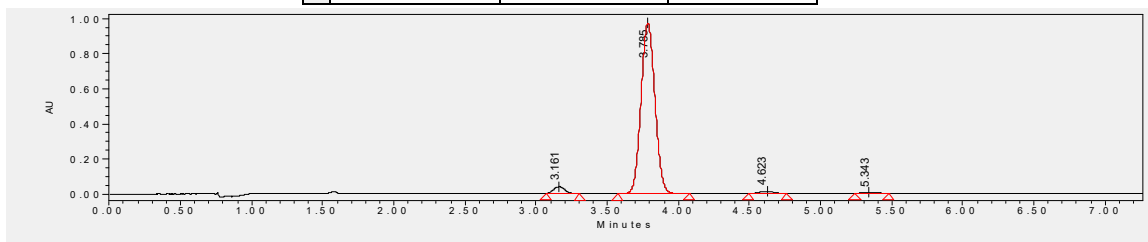
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.4, 162.0$ ($J = 246.6$ Hz), 154.4, 139.2, 135.9, 135.3 ($J = 2.9$ Hz), 133.2, 129.8 ($J = 4.0$ Hz), 129.7, 129.7, 128.9, 128.5, 128.2, 115.4, 115.2, 113.7, 112.6, 111.3, 104.3, 102.8, 60.8, 55.7, 46.9, 41.5, 14.0 ppm.

IR (neat): 3063, 2989, 2933, 2832, 1730, 1646, 1606, 1507, 1475, 1444, 1398, 1206, 1163, 1032, 841, 761 cm^{-1}

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_3\text{F}^+$ ($[\text{M}+\text{H}]^+$) = 442.1813, found 442.1811.

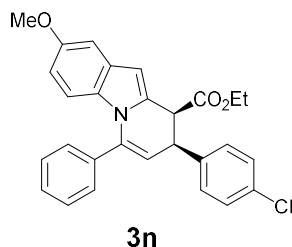


	Retention Time	Area	% Area
1	2.832	527432	8.60
2	3.433	2546717	41.52
3	3.967	2523072	41.14
4	5.057	536259	8.74



	Retention Time	Area	% Area
1	3.161	216289	3.12
2	3.785	6576564	94.85
3	4.623	94282	1.36
4	5.343	46871	0.68

Ethyl (8*S*,9*S*)-8-(4-chlorophenyl)-2-methoxy-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3n**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 65% yield, 97% ee, 96:4 dr. $[\alpha]_D^{24} = +44.1$ ($c = 0.53$, in CH_2Cl_2 , $\lambda = 589$ nm).

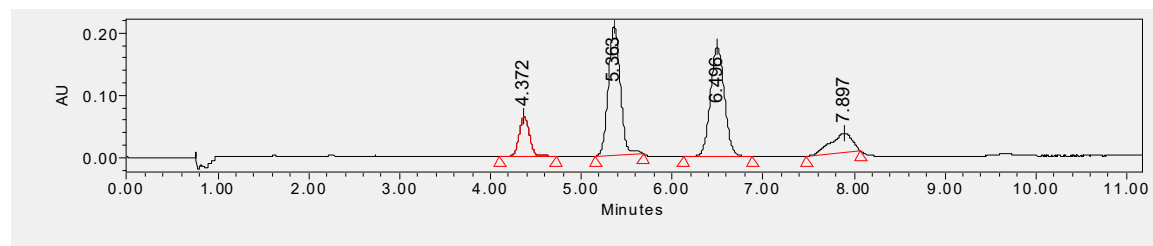
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 4.36$ min, $t_2 = 5.34$ min, $t_3 = 6.52$ min, $t_4 = 8.16$ min. dr = 96:4 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.49 - 7.42$ (m, 5H), 7.22 – 7.15 (m, 2H), 7.01 (d, $J = 2.6$ Hz, 1H), 7.00 – 6.93 (m, 2H), 6.68 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.13 (d, $J = 9.1$ Hz, 1H), 5.57 (d, $J = 5.1$ Hz, 1H), 4.35 (d, $J = 6.0$ Hz, 1H), 4.18 (t, $J = 5.6$ Hz, 1H), 4.07 – 3.99 (m, 2H), 3.79 (s, 3H), 1.13 (t, $J = 7.1$ Hz, 3H) ppm.

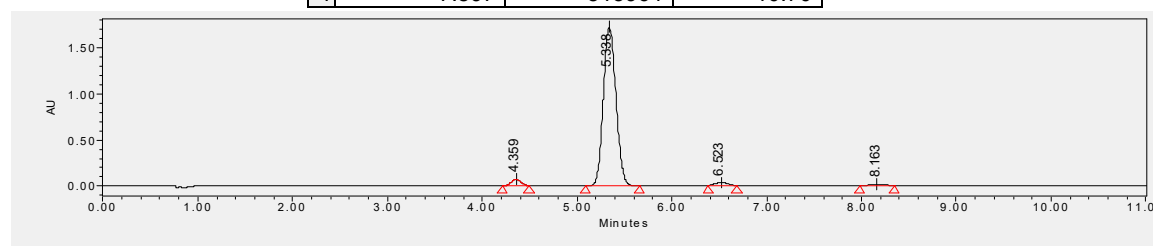
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.3, 154.4, 139.3, 138.1, 135.8, 133.1, 129.8, 129.6, 129.6, 128.9, 128.6, 128.5, 128.1, 113.7, 112.2, 111.3, 104.3, 102.7, 60.8, 55.7, 46.7, 41.6, 14.0$ ppm.

IR (neat): 3056, 2983, 2934, 2835, 1731, 1646, 1616, 1477, 1444, 1400, 1205, 1171, 1094, 760 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_3\text{Cl}^+$ ($[\text{M}]^+\text{H}^+$) = 458.1517, found 458.1517.

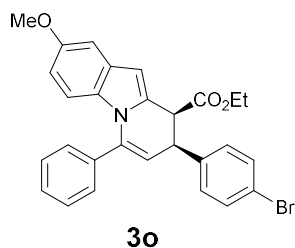


	Retention Time	Area	% Area
1	4.372	509252	10.61
2	5.363	1892515	39.42
3	6.496	1885588	39.27
4	7.897	513964	10.70



	Retention Time	Area	% Area
1	4.359	499610	2.94
2	5.338	16007058	94.26
3	6.523	315663	1.86
4	8.163	160009	0.94

Ethyl (8*S*,9*S*)-8-(4-bromophenyl)-2-methoxy-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3o**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 69% yield, 99% ee, 97:3 dr. $[\alpha]_D^{26} = +47.0$ ($c = 0.47$, in CH_2Cl_2 , $\lambda = 589$ nm).

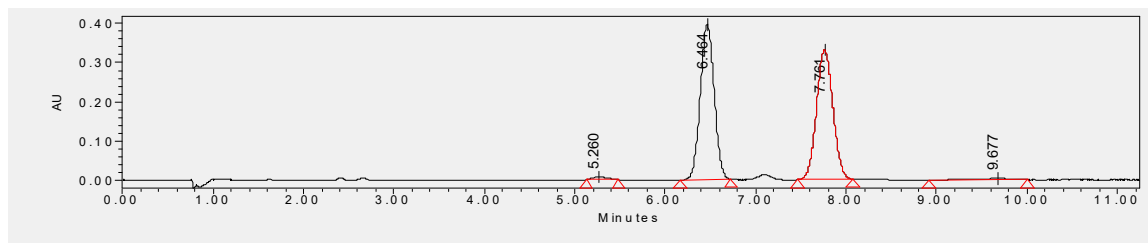
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 5.26$ min, $t_2 = 6.44$ min, $t_3 = 7.78$ min, $t_4 = 9.55$ min. dr = 95:5 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.49 - 7.41$ (m, 5H), 7.37 - 7.30 (m, 2H), 7.01 (d, $J = 2.6$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 6.68 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.12 (d, $J = 9.1$ Hz, 1H), 5.56 (d, $J = 5.2$ Hz, 1H), 4.35 (d, $J = 4.9$ Hz, 1H), 4.17 (t, $J = 5.6$ Hz, 1H), 4.09 - 3.99 (m, 2H), 3.80 (s, 3H), 1.13 (t, $J = 7.1$ Hz, 3H) ppm.

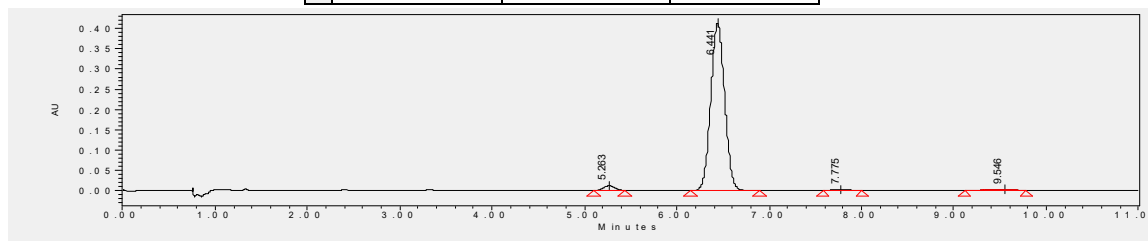
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.3, 154.4, 139.3, 138.6, 135.8, 133.1, 131.5, 130.0, 129.8, 129.7, 128.9, 128.5, 128.1, 121.2, 113.7, 112.2, 111.4, 104.4, 102.8, 60.9, 55.7, 46.6, 41.7, 14.1$ ppm.

IR (neat): 3063, 2986, 2931, 2854, 2832, 1731, 1647, 1617, 1479, 1447, 1400, 1205, 1172, 1074, 841, 759 cm^{-1}

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_3\text{Br}^+$ ($[\text{M}] + \text{H}^+$) = 502.1012, found 502.1009.

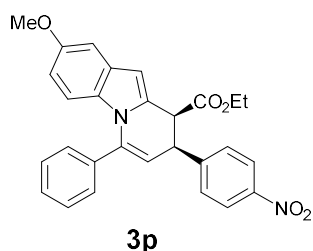


	Retention Time	Area	% Area
1	5.260	75499	0.88
2	6.464	4212517	49.32
3	7.761	4180452	48.94
4	9.677	73103	0.86



	Retention Time	Area	% Area
1	5.263	105436	2.35
2	6.441	4320725	96.41
3	7.775	21722	0.48
4	9.546	33729	0.75

Ethyl (8*S*,9*S*)-2-methoxy-8-(4-nitrophenyl)-6-phenyl-8,9-dihydroindolo[1,2-*a*]pyridine-9-carboxylate **3p**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 70% yield, 97% ee, 98:2 dr. $[\alpha]_D^{26} = +86.5$ ($c = 0.51$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 6.43$ min, $t_2 = 7.07$ min, $t_3 = 10.34$ min, $t_4 = 13.64$ min. dr = 98:2 determined by ¹H NMR.

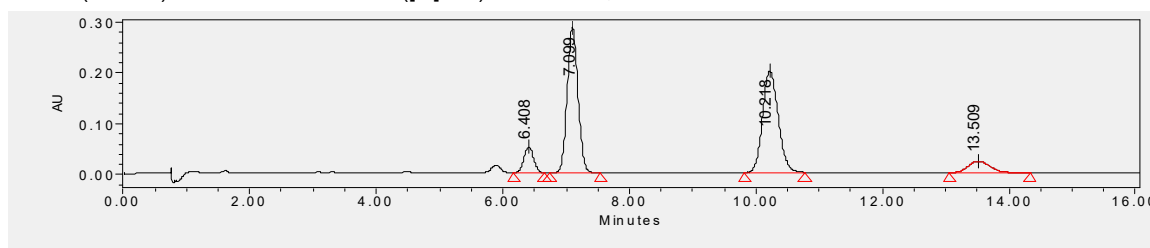
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 8.10 - 8.02$ (m, 2H), 7.51 - 7.43 (m,

5H), 7.20 – 7.13 (m, 2H), 7.02 (d, $J = 2.6$ Hz, 1H), 6.72 (s, 1H), 6.54 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.13 (d, $J = 9.1$ Hz, 1H), 5.59 (d, $J = 5.5$ Hz, 1H), 4.43 (d, $J = 4.6$ Hz, 1H), 4.30 (t, $J = 5.7$ Hz, 1H), 4.11 – 4.02 (m, 2H), 3.80 (s, 3H), 1.15 (t, $J = 7.1$ Hz, 3H) ppm.

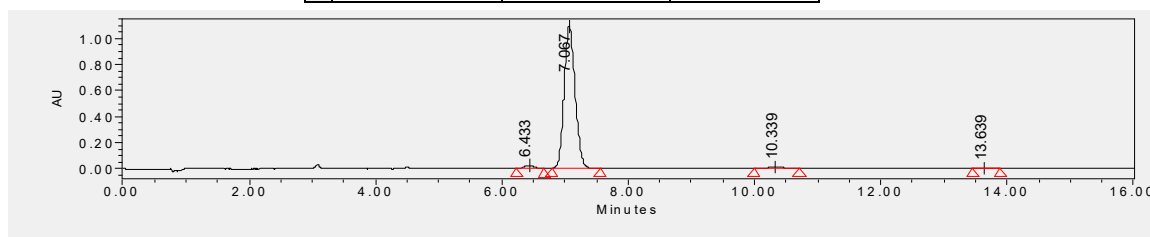
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) $\delta = 169.0, 154.6, 147.3, 147.1, 140.0, 135.5, 132.4, 129.8, 129.7, 129.2, 129.2, 128.6, 128.1, 123.6, 113.7, 111.6, 111.1, 104.9, 102.9, 61.1, 55.7, 46.4, 41.8, 14.1$ ppm.

IR (neat): 3066, 2986, 2932, 2854, 2835, 1731, 1646, 1601, 1519, 1476, 1445, 1399, 1205, 1173, 1032, 855, 760 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{25}\text{N}_2\text{O}_5^+$ ($[\text{M}+\text{H}^+]$) = 469.1758, found 469.1757.

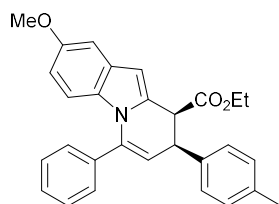


	Retention Time	Area	% Area
1	6.408	544572	6.86
2	7.099	3407337	42.92
3	10.218	3446546	43.41
4	13.509	540310	6.81



	Retention Time	Area	% Area
1	6.433	257767	1.87
2	7.067	13335283	96.52
3	10.339	201310	1.46
4	13.639	21632	0.16

Ethyl (8*S*,9*S*)-2-methoxy-6-phenyl-8-(*p*-tolyl)-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3q**



3q

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 75% yield, 96% ee/62% ee, 94:6 dr. $[\alpha]_D^{26} = +36.9$ ($c = 0.54$, in CH_2Cl_2 , $\lambda = 589$ nm).

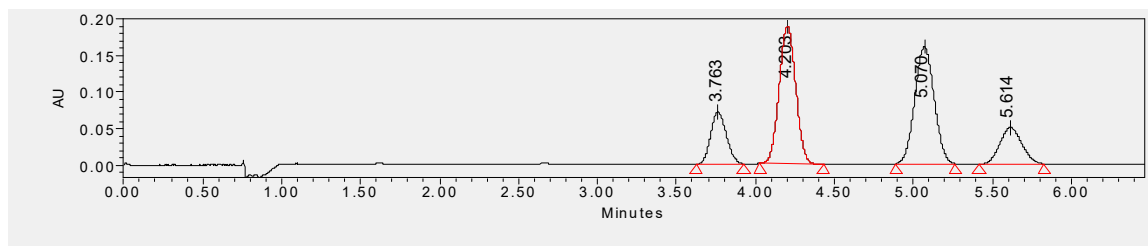
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.81$ min, $t_2 = 4.25$ min, $t_3 = 5.14$ min, $t_4 = 5.71$ min. dr = 94:6 determined by ^1H NMR.

^1H NMR (400 MHz, Chloroform- d) $\delta = 7.51 - 7.39$ (m, 5H), 7.10 – 6.99 (m, 3H), 6.97 – 6.85 (m, 2H), 6.65 (s, 1H), 6.51 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.14 (d, $J = 9.0$ Hz, 1H), 5.61 (d, $J = 5.0$ Hz, 1H), 4.33 (d, $J = 6.1$ Hz, 1H), 4.18 (t, $J = 5.5$ Hz, 1H), 4.06 – 3.97 (m, 2H), 3.79 (s, 3H), 2.28 (s, 3H), 1.10 (t, $J = 7.1$ Hz, 3H) ppm.

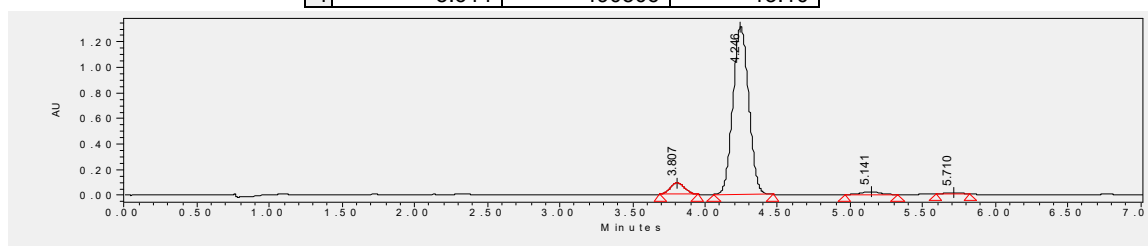
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) $\delta = 169.6, 154.3, 138.9, 136.9, 136.4, 136.1, 133.7, 129.9, 129.6, 129.2, 128.7, 128.5, 128.2, 128.0, 113.7, 113.1, 111.1, 103.9, 102.8, 60.7, 55.7, 47.0, 42.0, 21.0, 14.0$ ppm.

IR (neat): 3056, 2979, 2924, 2854, 2835, 1730, 1644, 1615, 1475, 1444, 1398, 1206, 1169, 1031, 841, 734 ν (cm^{-1})

HRMS (ESI-FT) calcd for $C_{29}H_{28}NO_3^+$ ($[M]+H^+$) = 438.2064, found 438.2059.

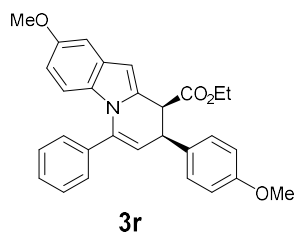


	Retention Time	Area	% Area
1	3.763	494680	13.21
2	4.203	1384496	36.97
3	5.070	1375122	36.72
4	5.614	490506	13.10



	Retention Time	Area	% Area
1	3.807	612304	5.60
2	4.246	10025184	91.77
3	5.141	192471	1.76
4	5.710	94724	0.87

Ethyl (8*S*,9*S*)-2-methoxy-8-(4-methoxyphenyl)-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3r**



Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate = 6/1), 74% yield, 94% ee/49% ee, 88:12 dr. $[\alpha]_D^{26} = +34.7$ ($c = 0.44$, in CH_2Cl_2 , $\lambda = 589$ nm).

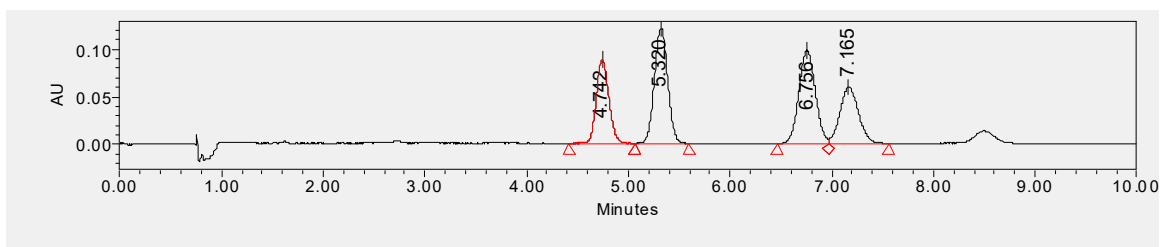
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $CO_2/CH_3OH=80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 4.81$ min, $t_2 = 5.42$ min, $t_3 = 6.87$ min, $t_4 = 7.28$ min. dr = 88:12 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.52 – 7.39 (m, 5H), 7.01 (d, $J = 2.6$ Hz, 1H), 7.00 – 6.92 (m, 2H), 6.80 – 6.71 (m, 2H), 6.67 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.14 (d, $J = 9.0$ Hz, 1H), 5.60 (d, $J = 5.1$ Hz, 1H), 4.32 (d, $J = 5.0$ Hz, 1H), 4.17 (t, $J = 5.6$ Hz, 1H), 4.03 (qd, $J = 7.1, 3.7$ Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 1.12 (t, $J = 7.1$ Hz, 3H) ppm.

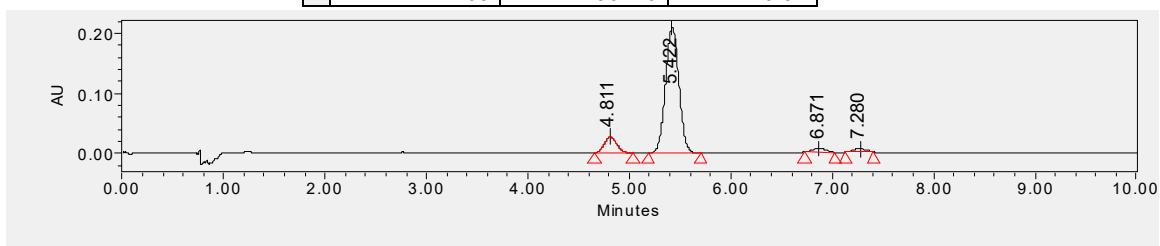
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ = 169.6, 158.8, 154.3, 138.8, 136.1, 133.6, 131.5, 129.9, 129.7, 129.2, 128.7, 128.5, 128.2, 113.8, 113.7, 113.3, 111.1, 104.0, 102.7, 60.7, 55.7, 55.2, 47.0, 41.5, 14.1 ppm.

IR (neat): 3066, 2995, 2932, 2835, 1732, 1646, 1612, 1583, 1511, 1476, 1446, 1399, 1250, 1175, 1034, 762 cm^{-1}

HRMS (ESI-FT) calcd for $C_{29}H_{28}NO_4^+$ ($[M]+H^+$) = 454.2013, found 454.2009.

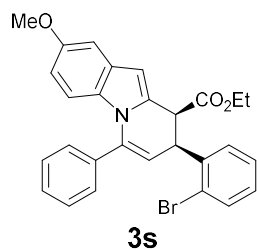


	Retention Time	Area	% Area
1	4.742	756955	20.35
2	5.320	1103021	29.66
3	6.756	1103091	29.66
4	7.165	756416	20.34



	Retention Time	Area	% Area
1	4.811	230733	10.15
2	5.422	1937645	85.25
3	6.871	56240	2.47
4	7.280	48232	2.12

Ethyl (8*S*,9*S*)-8-(2-bromophenyl)-2-methoxy-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3s**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 61% yield, 97% ee, 98:2 dr. $[\alpha]_D^{24} = +40.2$ ($c = 0.47$, in CH_2Cl_2 , $\lambda = 589$ nm).

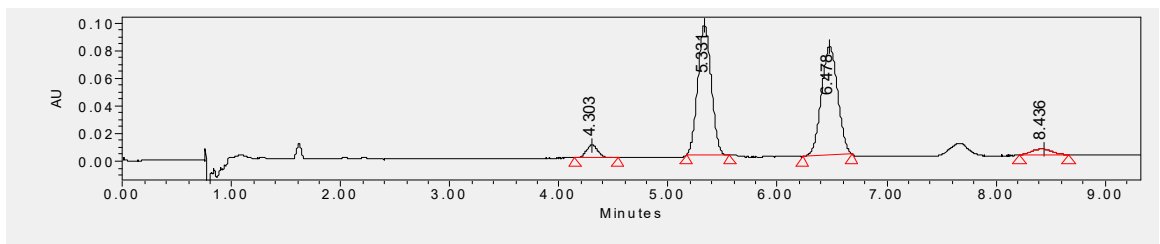
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 4.30$ min, $t_2 = 5.32$ min, $t_3 = 6.50$ min, $t_4 = 8.52$ min. dr = 98:2 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.49 - 7.42$ (m, 5H), $7.21 - 7.16$ (m, 2H), 7.01 (d, $J = 2.6$ Hz, 1H), $7.00 - 6.93$ (m, 2H), 6.68 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.13 (d, $J = 9.1$ Hz, 1H), 5.57 (d, $J = 5.2$ Hz, 1H), 4.34 (d, $J = 7.1$ Hz, 1H), 4.18 (t, $J = 5.6$ Hz, 1H), $4.08 - 3.96$ (m, 2H), 3.80 (s, 3H), 1.13 (t, $J = 7.1$ Hz, 3H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.3, 154.4, 139.3, 138.1, 135.8, 133.1, 129.8, 129.6, 129.6, 128.9, 128.6, 128.5, 128.1, 113.7, 112.2, 111.3, 104.3, 102.7, 60.8, 55.7, 46.7, 41.6, 14.1$ ppm.

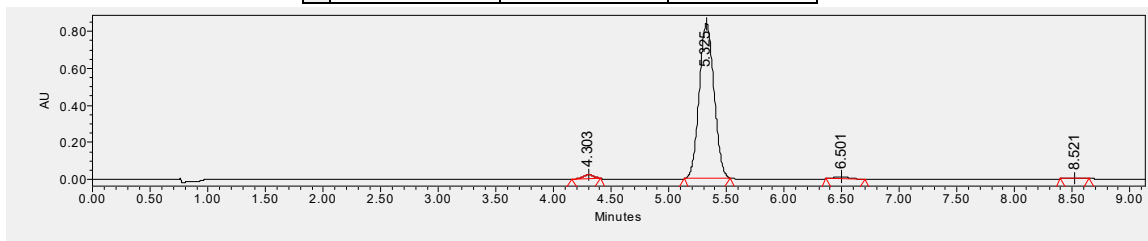
IR (neat): 3060, 2983, 2935, 2832, 1730, 1647, 1616, 1477, 1444, 1399, 1205, 1171, 1033, 760 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_3\text{Br}^+$ ($[\text{M}] + \text{H}^+$) = 502.1012, found 502.1012.



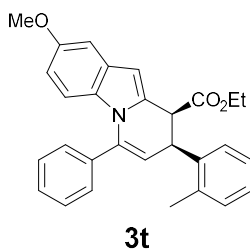
	Retention Time	Area	% Area
1	4.303	65502	3.74

2	5.331	809553	46.22
3	6.478	819534	46.79
4	8.436	56787	3.24



	Retention Time	Area	% Area
1	4.303	142777	1.84
2	5.325	7506504	96.62
3	6.501	99073	1.28
4	8.521	20397	0.26

Ethyl (8*S*,9*S*)-2-methoxy-6-phenyl-8-(*o*-tolyl)-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3t**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 70% yield, 95% ee, 99:1 dr. $[\alpha]^{24}_D = -16.5$ ($c = 0.58$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.31$ min, $t_2 = 4.09$ min, $t_3 = 4.61$ min, $t_4 = 5.50$ min. dr = 99:1 determined by ¹H NMR.

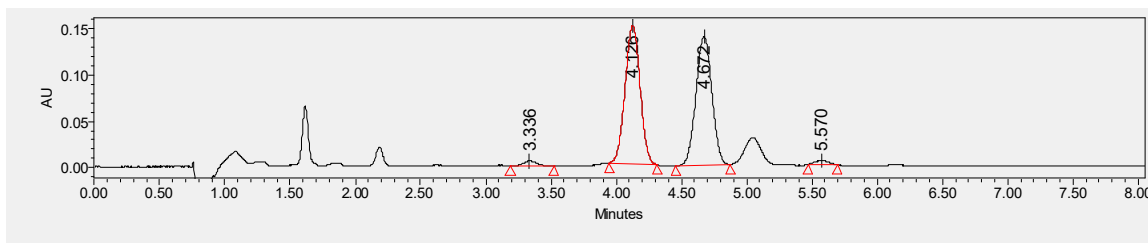
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.49 - 7.42$ (m, 5H), 7.21 - 7.12 (m, 2H), 7.10 - 7.07 (m, 2H), 7.02 (d, $J = 2.6$ Hz, 1H), 6.56 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$

Hz, 1H), 6.14 (d, $J = 9.1$ Hz, 1H), 5.56 (d, $J = 3.8$ Hz, 1H), 4.50 (dd, $J = 6.3, 3.7$ Hz, 1H), 4.30 (dt, $J = 6.3, 0.9$ Hz, 1H), 4.00 - 3.83 (m, 2H), 3.80 (s, 3H), 2.43 (s, 3H), 0.98 (t, $J = 7.1$ Hz, 3H) ppm.

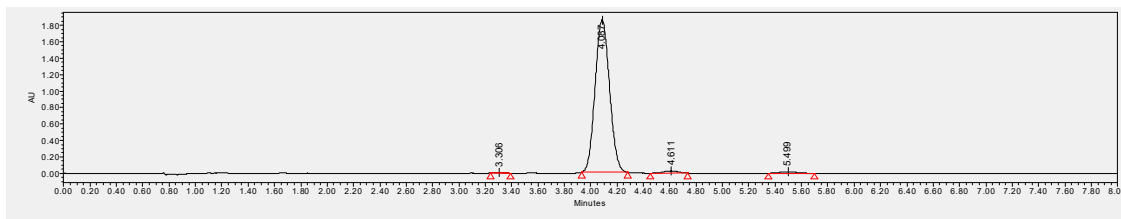
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.6, 154.3, 138.9, 138.3, 136.2, 135.8, 134.0, 130.4, 130.0, 129.4, 128.6, 128.5, 127.7, 127.2, 126.3, 113.7, 113.0, 111.3, 103.1, 102.6, 60.6, 55.7, 45.3, 38.1, 19.4, 13.8$ ppm.

IR (neat): 3060, 3031, 2983, 2935, 2835, 1732, 1646, 1616, 1477, 1445, 1400, 1207, 1172, 1033, 843, 759 cm^{-1}

HRMS (ESI-FT) calcd for $\text{C}_{29}\text{H}_{28}\text{NO}_3^+$ ($[\text{M}+\text{H}^+]$) = 438.2064, found 438.2064.

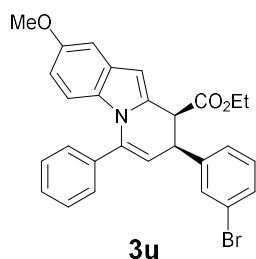


	Retention Time	Area	% Area
1	3.336	35734	1.46
2	4.126	1199409	48.99
3	4.672	1180552	48.22
4	5.570	32727	1.34



	Retention Time	Area	% Area
1	3.306	36981	0.25
2	4.087	14110550	97.21
3	4.611	208243	1.43
4	5.499	159890	1.10

Ethyl (8S,9S)-8-(3-bromophenyl)-2-methoxy-6-phenyl-8,9-dihydropyrido[1,2-a]indole-9-carboxylate **3u**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 63% yield, 97% ee, 95:5 dr. $[\alpha]^{25}_D = +20.2$ ($c = 0.51$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in $i\text{PrOH}$ for UPC²; UPC² (Daicel CHIRALPAK OJH, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 10.99$ min, $t_2 = 20.63$ min, $t_3 = 23.85$ min, $t_4 = 28.59$ min. dr = 95:5 determined by ^1H NMR.

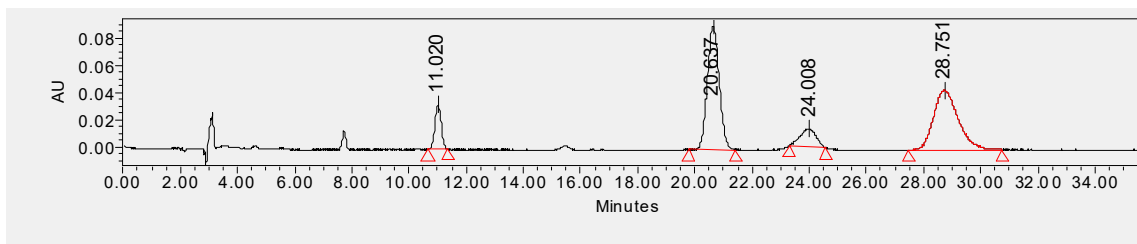
^1H NMR (400 MHz, Chloroform- d) $\delta = 7.49 - 7.43$ (m, 5H), 7.39 – 7.28 (m, 2H), 7.10 (t, $J = 7.8$ Hz, 1H), 7.01 (d, $J = 2.6$ Hz, 1H), 6.98 – 6.92 (m, 1H), 6.64 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.13 (d, $J = 9.1$ Hz, 1H), 5.54 (d, $J = 4.6$ Hz, 1H),

4.32 (d, $J = 6.4$ Hz, 1H), 4.22 – 4.15 (m, 1H), 4.03 (q, $J = 7.1$ Hz, 2H), 3.79 (s, 3H), 1.11 (t, $J = 7.1$ Hz, 3H) ppm.

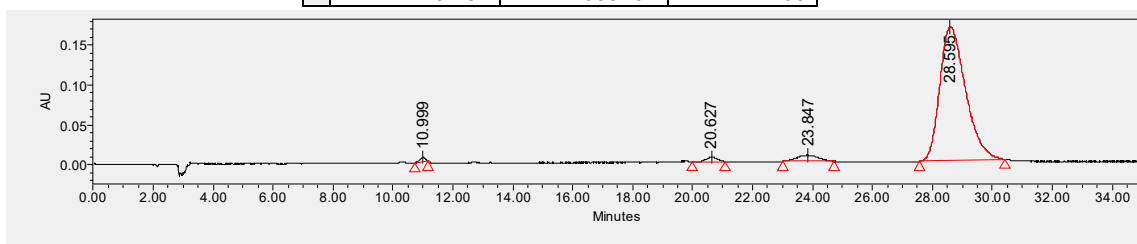
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) $\delta = 169.3, 154.4, 142.1, 139.5, 135.8, 133.2, 131.4, 130.4, 130.1, 129.9, 129.5, 128.9, 128.5, 128.1, 126.7, 122.4, 113.7, 111.6, 111.4, 104.1, 102.7, 60.9, 55.7, 46.9, 41.9, 14.0$ ppm.

IR (neat): 3060, 2986, 2934, 2829, 1732, 1644, 1616, 1476, 1445, 1399, 1266, 1172, 1033, 843, 763 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_3\text{Br}^+$ ($[\text{M}+\text{H}]^+$) = 502.1012, found 502.1017.

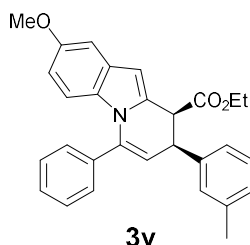


	Retention Time	Area	% Area
1	11.020	505317	8.05
2	20.637	2627806	41.87
3	24.008	503678	8.03
4	28.751	2639161	42.05



	Retention Time	Area	% Area
1	10.999	76556	0.72
2	20.627	154421	1.45
3	23.847	394539	3.71
4	28.595	10018259	94.12

Ethyl (8*S*,9*S*)-2-methoxy-6-phenyl-8-(*m*-tolyl)-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3v**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 68% yield, 92% ee/57% ee, 94:6 dr. $[\alpha]_D^{24} = +13.2$ ($c = 0.56$, in CH_2Cl_2 , $\lambda = 589$ nm).

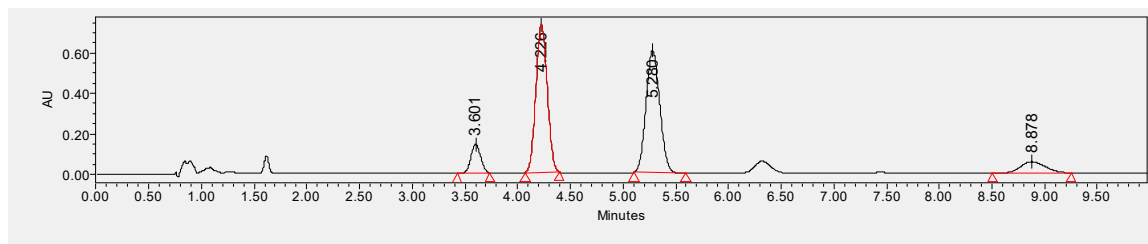
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.57$ min, $t_2 = 4.19$ min, $t_3 = 5.25$ min, $t_4 = 8.95$ min. dr = 94:6 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.55 - 7.37$ (m, 5H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.06 - 7.00 (m, 2H), 6.97 (s, 1H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.61 (s, 1H), 6.52 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.14 (d, $J = 9.0$ Hz, 1H), 5.60 (d, $J = 4.4$ Hz, 1H), 4.31 (d, $J = 6.1$ Hz, 1H), 4.23 - 4.16 (m, 1H), 4.04 - 3.94 (m, 2H), 3.79 (s, 3H), 2.27 (s, 3H), 1.06 (t, $J = 7.1$ Hz, 3H) ppm.

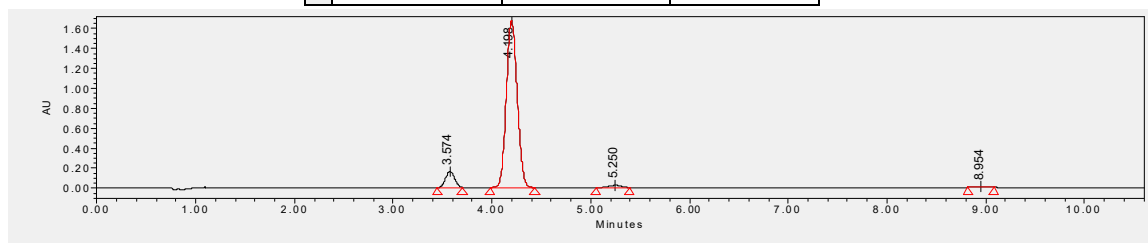
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.6, 154.3, 139.6, 139.0, 137.9, 136.1, 133.8, 129.9, 129.5, 129.0, 128.7, 128.5, 128.4, 128.1, 128.0, 125.1, 113.7, 112.8, 111.2, 103.6, 102.7, 60.6, 55.7, 47.2, 42.3, 21.4, 14.0$ ppm.

IR (neat): 3053, 3028, 2983, 2930, 2835, 1730, 1646, 1611, 1475, 1444, 1396, 1205, 1169, 1032, 842, 763 cm^{-1}

HRMS (ESI-FT) calcd for $\text{C}_{29}\text{H}_{28}\text{NO}_3^+ ([\text{M}]+\text{H}^+) = 438.2064$, found 438.2057.

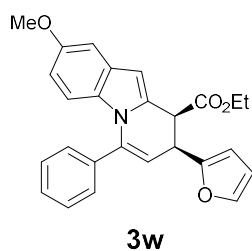


	Retention Time	Area	% Area
1	3.601	914596	7.18
2	4.226	5443032	42.74
3	5.280	5472098	42.97
4	8.878	904782	7.10



	Retention Time	Area	% Area
1	3.574	1032790	7.27
2	4.198	12903719	90.85
3	5.250	209092	1.47
4	8.954	58122	0.41

Ethyl (8*S*,9*S*)-8-(furan-2-yl)-2-methoxy-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3w**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 60% yield, 90% ee/70% ee, 80:20 dr. $[\alpha]^{26}_D = +15.7$ ($c = 0.41$, in CH_2Cl_2 , $\lambda = 589$ nm).

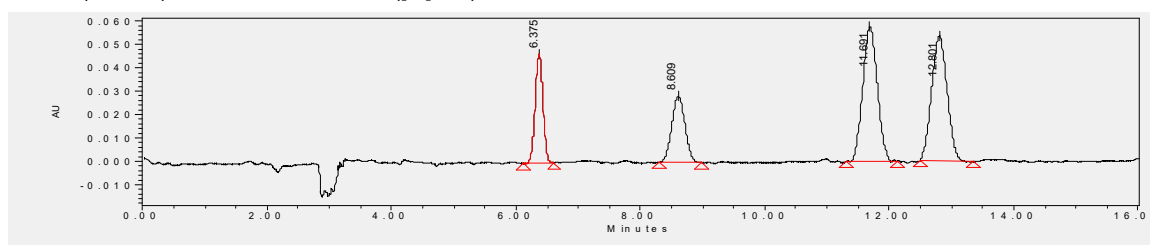
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 6.39$ min, $t_2 = 8.63$ min, $t_3 = 11.69$ min, $t_4 = 12.84$ min. dr = 80:20 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.46 - 7.40$ (m, 5H), 7.36 – 7.34 (m, 1H), 7.01 (d, $J = 2.6$ Hz, 1H), 6.62 (s, 1H), 6.51 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.28 (dd, $J = 3.3, 1.8$ Hz, 1H), 6.12 (d, $J = 9.1$ Hz, 1H), 6.06 (d, $J = 3.9$ Hz, 1H), 5.55 (d, $J = 4.3$ Hz, 1H), 4.41 (d, $J = 5.8$ Hz, 1H), 4.35 – 4.31 (m, 1H), 4.03 (q, $J = 7.2$ Hz, 2H), 3.79 (s, 3H), 1.11 (t, $J = 7.1$ Hz, 3H) ppm.

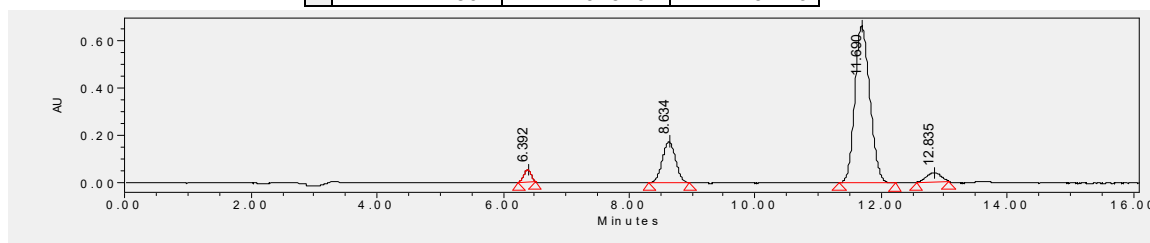
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) $\delta = 169.4, 154.3, 153.3, 141.8, 139.4, 135.8, 133.7, 129.9, 129.4, 128.9, 128.5, 128.2, 113.6, 111.3, 110.4, 109.4, 106.5, 103.6, 102.7, 60.9, 55.7, 45.1, 36.2, 14.0$ ppm.

IR (neat): 3117, 3063, 2983, 2832, 2832, 1733, 1651, 1616, 1477, 1446, 1400, 1207, 1172, 1033, 843, 737 cm^{-1}

HRMS (ESI-FT) calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_4^+$ ($[\text{M}+\text{H}]^+$) = 414.1700, found 414.1703.

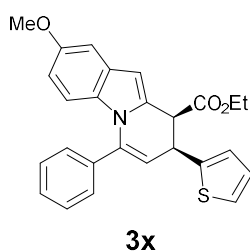


	Retention Time	Area	% Area
1	6.375	405547	15.11
2	8.609	417544	15.55
3	11.691	936160	34.87
4	12.801	925107	34.46



	Retention Time	Area	% Area
1	6.392	421147	2.87
2	8.634	2557167	17.44
3	11.690	11095438	75.65
4	12.835	592898	4.04

Ethyl (8*S*,9*S*)-2-methoxy-6-phenyl-8-(thiophen-2-yl)-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3x**



Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 41% yield, 97% ee/64% ee, 78:22 dr. $[\alpha]^{26}_D = +47.8$ ($c = 0.31$, in CH_2Cl_2 , $\lambda = 589$ nm).

Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OD-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.91$ min, $t_2 = 5.05$ min, $t_3 = 5.58$ min, $t_4 = 6.19$ min. dr = 95:5 determined by ¹H NMR.

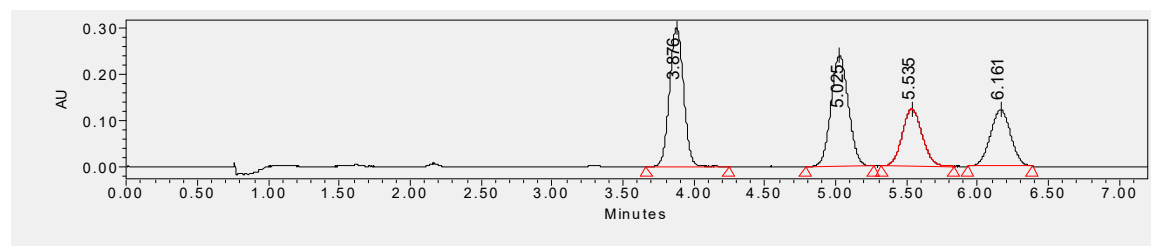
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.48 - 7.41$ (m, 5H), 7.11 – 7.07 (m, 1H),

7.02 (d, $J = 2.6$ Hz, 1H), 6.87 – 6.84 (m, 1H), 6.78 (s, 1H), 6.75 (d, $J = 3.5$ Hz, 1H), 6.51 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.12 (d, $J = 9.1$ Hz, 1H), 5.68 (d, $J = 5.5$ Hz, 1H), 4.51 (t, $J = 5.5$ Hz, 1H), 4.37 (d, $J = 4.4$ Hz, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.79 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 3H) ppm.

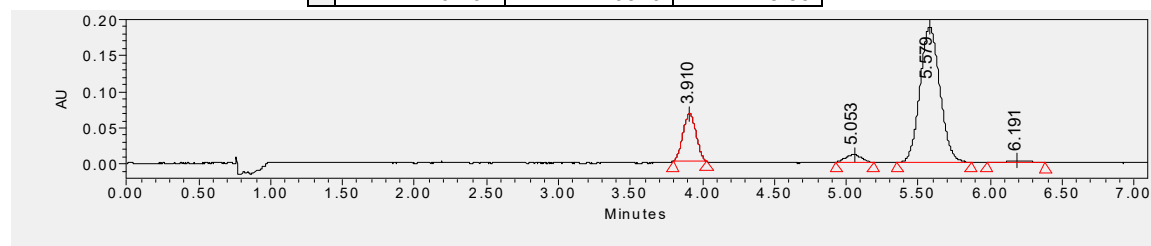
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) $\delta = 169.2, 154.3, 142.1, 138.9, 135.8, 133.0, 129.8, 129.7, 128.9, 128.5, 128.2, 126.6, 125.5, 124.5, 113.6, 112.9, 111.3, 104.8, 102.7, 60.9, 55.6, 47.1, 37.3, 14.1$ ppm.

IR (neat): 3072, 2886, 2929, 2857, 2835, 1734, 1644, 1616, 1476, 1446, 1400, 1206, 1173, 1034, 846, 762 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_3\text{S}^+$ ($[\text{M}+\text{H}^+$) = 430.1471, found 430.1474.

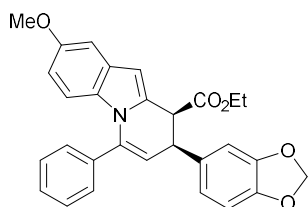


	Retention Time	Area	% Area
1	3.876	2067484	31.61
2	5.025	2049593	31.33
3	5.535	1207992	18.47
4	6.161	1216310	18.59



	Retention Time	Area	% Area
1	3.910	422920	18.04
2	5.053	80032	3.41
3	5.579	1811104	77.26
4	6.191	30185	1.29

Ethyl (8*S*,9*S*)-8-(benzo[d][1,3]dioxol-5-yl)-2-methoxy-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3y**



3y

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 52% yield, 90% ee/70% ee, 80:20 dr. $[\alpha]_D^{27} = +40.0$ ($c = 0.45$, in CH_2Cl_2 , $\lambda = 589$ nm).

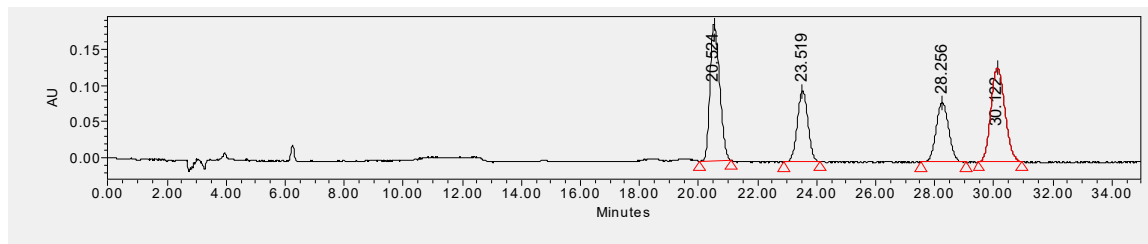
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK ODH, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 20.44$ min, $t_2 = 23.49$ min, $t_3 = 28.28$ min, $t_4 = 30.46$ min. dr = 80:20 determined by ^1H NMR.

^1H NMR (400 MHz, Chloroform- d) $\delta = 7.47 - 7.43$ (m, 5H), 7.01 (d, $J = 2.5$ Hz, 1H), 6.69 – 6.65 (m, 2H), 6.58 (d, $J = 1.8$ Hz, 1H), 6.54 – 6.48 (m, 2H), 6.12 (d, $J = 9.0$ Hz, 1H), 5.89 – 5.85 (m, 2H), 5.56 (d, $J = 5.0$ Hz, 1H), 4.31 (d, $J = 5.0$ Hz, 1H), 4.14 (t, $J = 5.6$ Hz, 1H), 4.09 – 4.03 (m, 2H), 3.79 (s, 3H), 1.15 (t, $J = 7.1$ Hz, 3H) ppm.

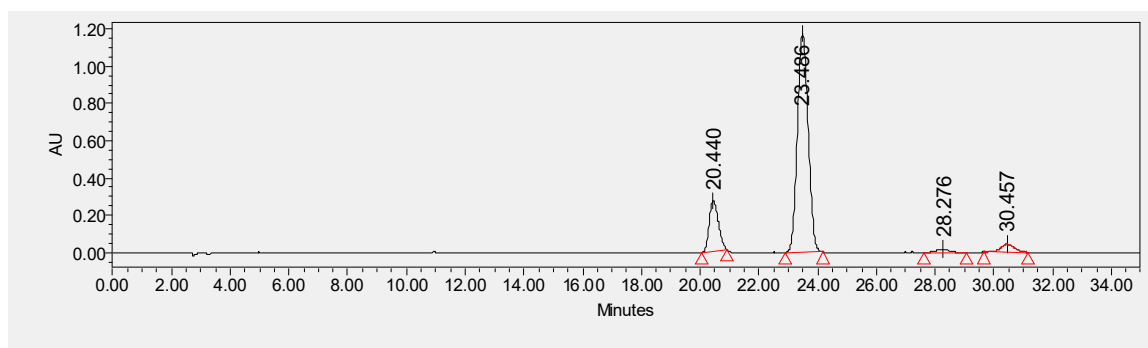
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) $\delta = 169.6, 154.3, 147.6, 146.7, 139.0, 136.0, 133.4, 133.3, 129.8, 129.6, 128.8, 128.5, 128.2, 121.4, 113.7, 112.9, 111.2, 108.6, 108.1, 104.1, 102.8, 100.9, 60.8, 55.7, 47.1, 42.0, 14.1$ ppm.

IR (neat): 3066, 2989, 2927, 2861, 2835, 1733, 1646, 1615, 1482, 1444, 1400, 1247, 1172, 1037, 805, 763 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{29}\text{H}_{26}\text{NO}_5^+$ ($[\text{M}+\text{H}^+]$) = 468.1805, found 468.1798.

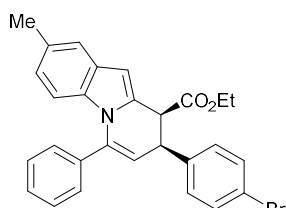


	Retention Time	Area	% Area
1	20.524	4239051	31.87
2	23.519	2399582	18.04
3	28.256	2417954	18.18
4	30.122	4246235	31.92



	Retention Time	Area	% Area
1	20.440	5961412	15.95
2	23.486	29529948	78.99
3	28.276	493001	1.32
4	30.457	1398476	3.74

ethyl (8*S*,9*S*)-8-(4-bromophenyl)-2-methyl-6-phenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate **3z**



3z

Yellow solid, m.p.: 145-149 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 6/1), 61% yield, 97% ee, 98:2 dr. $[\alpha]_D^{25} = +40.8$ ($c = 1.05$, in CH_2Cl_2 , $\lambda = 589$ nm).

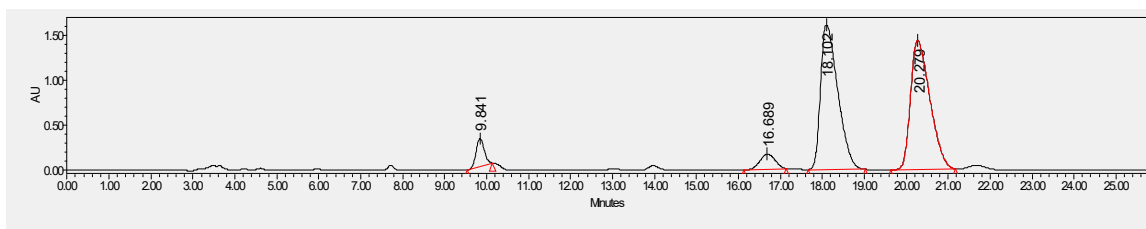
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJH, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 9.78$ min, $t_2 = 16.48$ min, $t_3 = 17.80$ min, $t_4 = 20.25$ min. dr = 98:2 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.50 - 7.42$ (m, 5H), 7.38 - 7.31 (m, 3H), 6.96 - 6.88 (m, 2H), 6.71 (dd, $J = 8.6, 1.8$ Hz, 1H), 6.69 (s, 1H), 6.14 (d, $J = 8.5$ Hz, 1H), 5.58 (d, $J = 5.2$ Hz, 1H), 4.37 (d, $J = 5.9$ Hz, 1H), 4.18 (t, $J = 5.6$ Hz, 1H), 4.05 (m, 2H), 2.38 (s, 3H), 1.14 (t, $J = 7.1$ Hz, 3H) ppm.

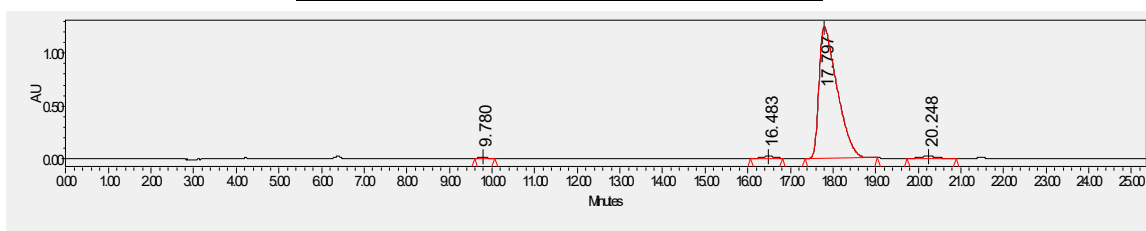
¹³C NMR (101 MHz, Chloroform-*d*) $\delta = 169.4, 139.4, 138.7, 135.9, 132.5, 131.5, 129.9, 129.7, 129.3, 128.8, 128.5, 128.1, 123.3, 121.2, 120.5, 112.7, 112.3, 104.2, 60.8, 46.6, 41.7, 21.1, 14.0$ ppm.

IR (neat): 3056, 3024, 2979, 2925, 2861, 1731, 1645, 1595, 1480, 1449, 1398, 1262, 1074, 871, 736 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{24}\text{NO}_2\text{Br}^+$ ($[\text{M}+\text{H}^+]$) = 486.1064, found 486.1069.

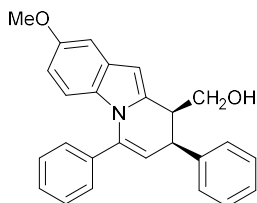


	Retention Time	Area	% Area
1	9.841	4195701	4.17
2	16.689	4234284	4.21
3	18.102	46057114	45.79
4	20.279	46094081	45.83



	Retention Time	Area	% Area
1	9.780	202592	0.54
2	16.483	432811	1.14
3	17.797	36616380	96.74
4	20.248	600454	1.59

((8*S*,9*S*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indol-9-yl)methanol **4a**



4a

Yellow oil; $R_f = 0.2$ (petroleum ether/ethyl acetate = 6/1), 69% yield, 97% ee, 95:5 dr. $[\alpha]_D^{20} = +25.9$ ($c = 0.17$, in CH_2Cl_2 , $\lambda = 589$ nm).

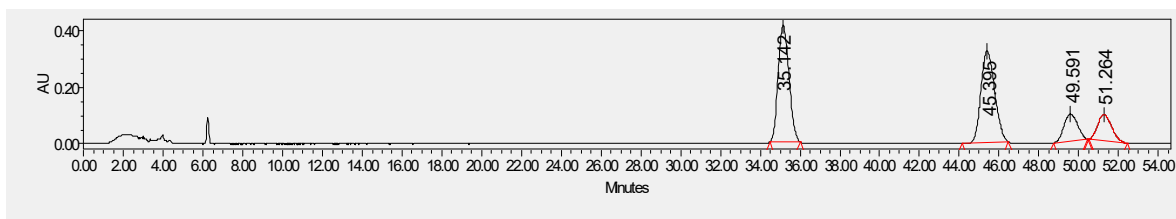
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK ODH, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 35.13$ min, $t_2 = 45.54$ min, $t_3 = 49.57$ min, $t_4 = 51.24$ min. dr = 95:5 determined by ¹H NMR.

¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.58 - 7.40$ (m, 5H), 7.24 – 7.17 (m, 3H), 7.00 (d, $J = 2.5$ Hz, 1H), 6.98 – 6.90 (m, 2H), 6.53 (dd, $J = 9.0, 2.6$ Hz, 1H), 6.34 (s, 1H), 6.19 (d, $J = 9.1$ Hz, 1H), 5.71 (d, $J = 6.0$ Hz, 1H), 4.08 – 4.01 (m, 1H), 3.98 (dd, $J = 9.9, 6.3$ Hz, 1H), 3.81 (s, 3H) 3.67 – 3.49 (m, 2H), 1.55 (s, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) $\delta = 154.2, 139.2, 139.0, 137.3, 136.0, 129.9, 128.8, 128.5, 128.1, 127.0, 114.5, 113.6, 110.7, 102.5, 101.9, 61.2, 55.7, 42.1, 40.5$ ppm.

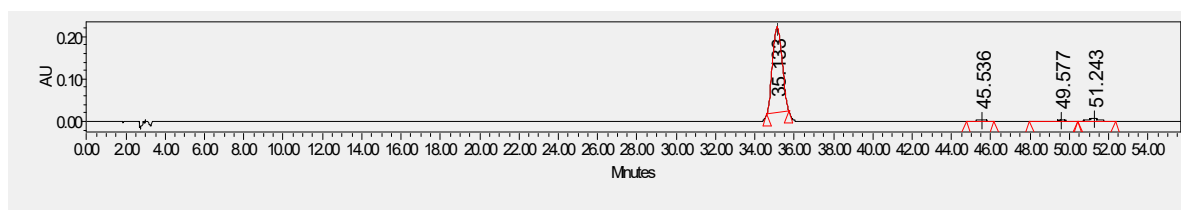
IR (neat): 3061, 3026, 2958, 2925, 2854, 1733, 1647, 1600, 1565, 1513, 1476, 1447, 1400, 1329, 1246, 1114, 1032, 844, 761 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) = 382.1802, found 382.1800.



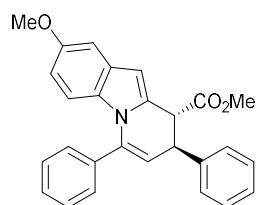
	Retention Time	Area	% Area
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1	35.142	15719915	38.58
2	45.395	15710113	38.55
3	49.591	4657463	11.43
4	51.264	4659985	11.44



	Retention Time	Area	% Area
1	35.133	6938560	93.97
2	45.536	97778	1.32
3	49.577	80505	1.09
4	51.243	267337	3.62

Methyl (8*S*,9*R*)-2-methoxy-6,8-diphenyl-8,9-dihydropyrido[1,2-*a*]indole-9-carboxylate 5b



5b

Yellow oil; $R_f = 0.6$ (petroleum ether/ethyl acetate = 6/1), 89% yield, 91% ee, 97:3 dr. $[\alpha]_D^{15} = +46.7$ ($c = 0.80$, in CH_2Cl_2 , $\lambda = 436$ nm).

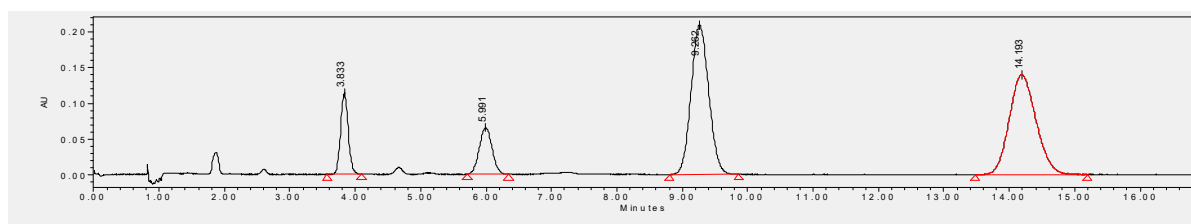
Dissolved in *i*PrOH for UPC²; UPC² (Daicel CHIRALPAK OJ-3, $\text{CO}_2/\text{CH}_3\text{OH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm) retention time: $t_1 = 3.74$ min, $t_2 = 5.80$ min, $t_3 = 9.00$ min, $t_4 = 13.72$ min. dr = 97:3 determined by ¹H NMR.

¹H NMR (600 MHz, Chloroform-*d*) $\delta = 7.41 - 7.47$ (m, 5H), 7.26 - 7.21 (m, 3H), 7.16 (d, $J = 7.7$ Hz, 2H), 6.98 (d, $J = 2.4$ Hz, 1H), 6.52 (dd, $J = 9.2, 2.4$ Hz, 1H), 6.33 (s, 1H), 6.17 (d, $J = 9.1$ Hz, 1H), 5.50 (d, $J = 4.8$ Hz, 1H), 4.24 - 4.18 (m, 1H), 4.14 (d, $J = 7.0$ Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H) ppm.

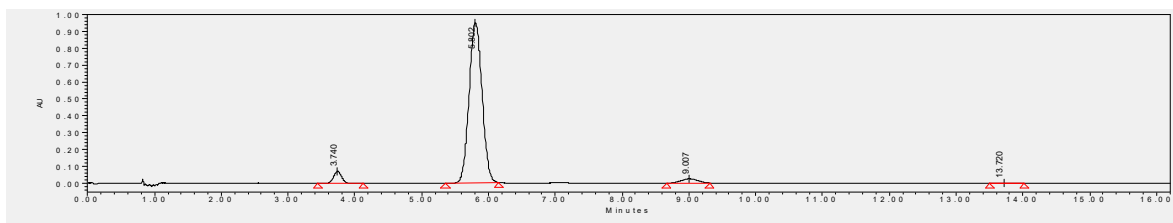
¹³C{¹H} NMR (151 MHz, Chloroform-*d*) $\delta = 171.8, 154.4, 141.4, 139.2, 135.8, 133.7, 129.5, 129.0, 128.8, 128.8, 128.6, 128.2, 127.9, 127.3, 113.7, 113.3, 111.2, 103.4, 102.7, 55.7, 52.5, 49.0, 42.3$ ppm.

IR (neat): 3056, 3036, 2998, 2954, 2835, 1736, 1641, 1617, 1602, 1585, 1477, 1445, 1400, 1246, 1167, 1034, 915, 844, 732 ν (cm^{-1})

HRMS (ESI-FT) calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) = 410.1751, found 410.1750.

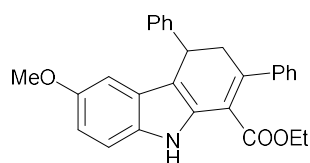


	Retention Time	Area	% Area
1	3.833	917915	9.44
2	5.991	884089	9.09
3	9.262	3941590	40.53
4	14.193	3981201	40.94



	Retention Time	Area	% Area
1	3.740	574638	4.16
2	5.802	12799467	92.64
3	9.007	432248	3.13
4	13.720	10225	0.07

Ethyl 6-methoxy-2,4-diphenyl-4,9-dihydro-3H-carbazole-1-carboxylate **6a**



6a

¹H NMR (400 MHz, Chloroform-*d*) δ = 9.22 (s, 1H), 7.40 – 7.21 (m, 9H), 7.19 – 7.01 (m, 2H), 6.76 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.30 (d, *J* = 2.5 Hz, 1H), 4.54 – 4.37 (m, 1H), 4.01 (dd, *J* = 7.2, 4.0 Hz, 2H), 3.60 (s, 3H), 3.23 (dd, *J* = 17.8, 8.0 Hz, 1H), 3.05 (dd, *J* = 17.8, 9.7 Hz, 1H), 0.84 (t, *J* = 7.1 Hz, 3H) ppm.

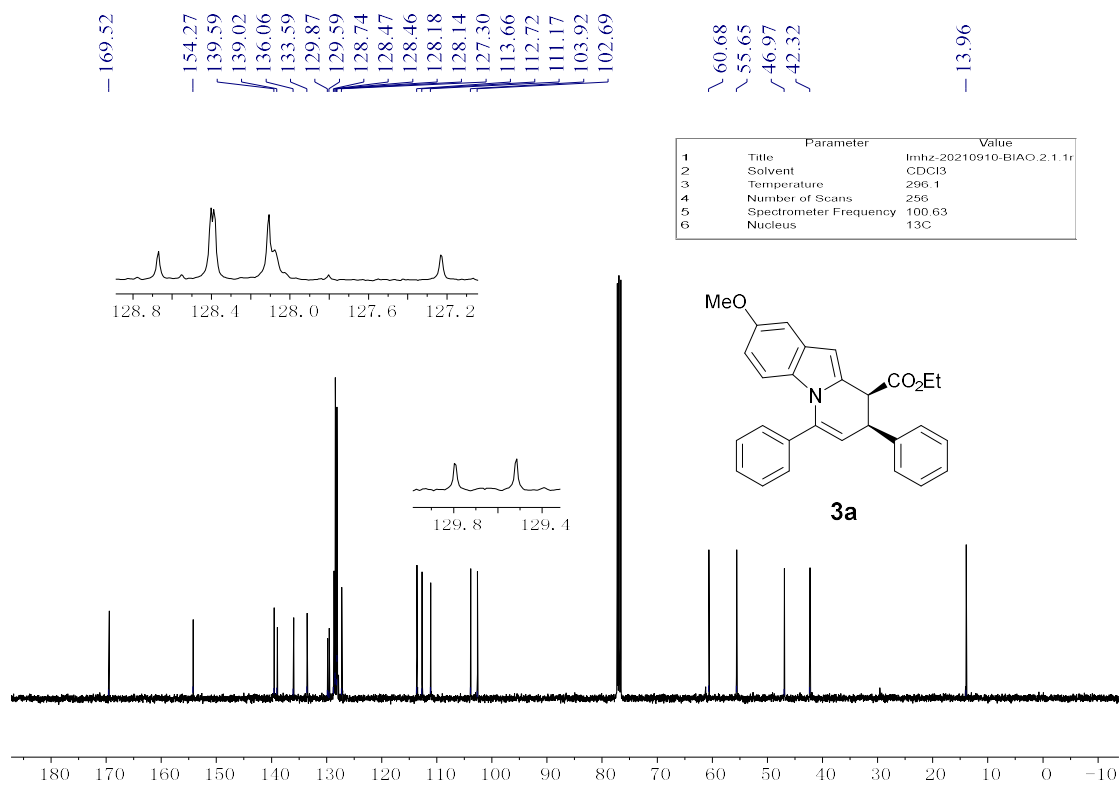
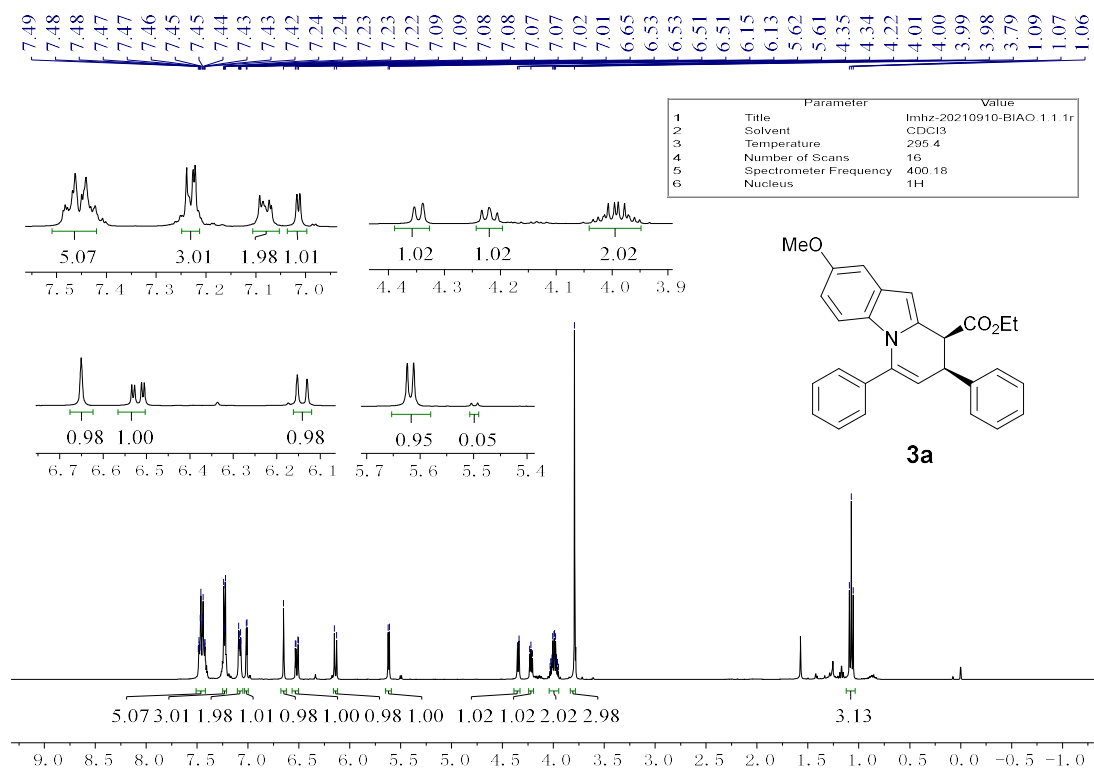
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ = 167.2, 153.9, 146.5, 144.1, 141.8, 132.3, 131.7, 128.5, 127.9, 127.9, 127.5, 127.5, 126.6, 126.3, 112.3, 111.9,

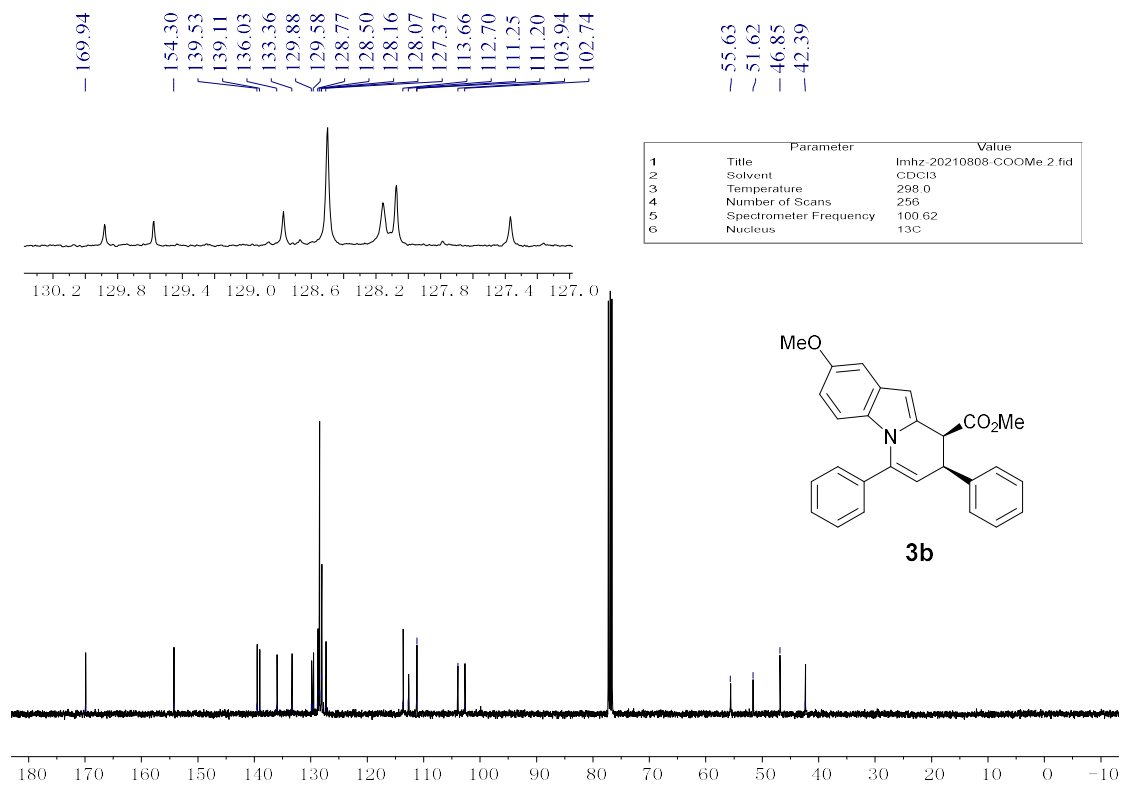
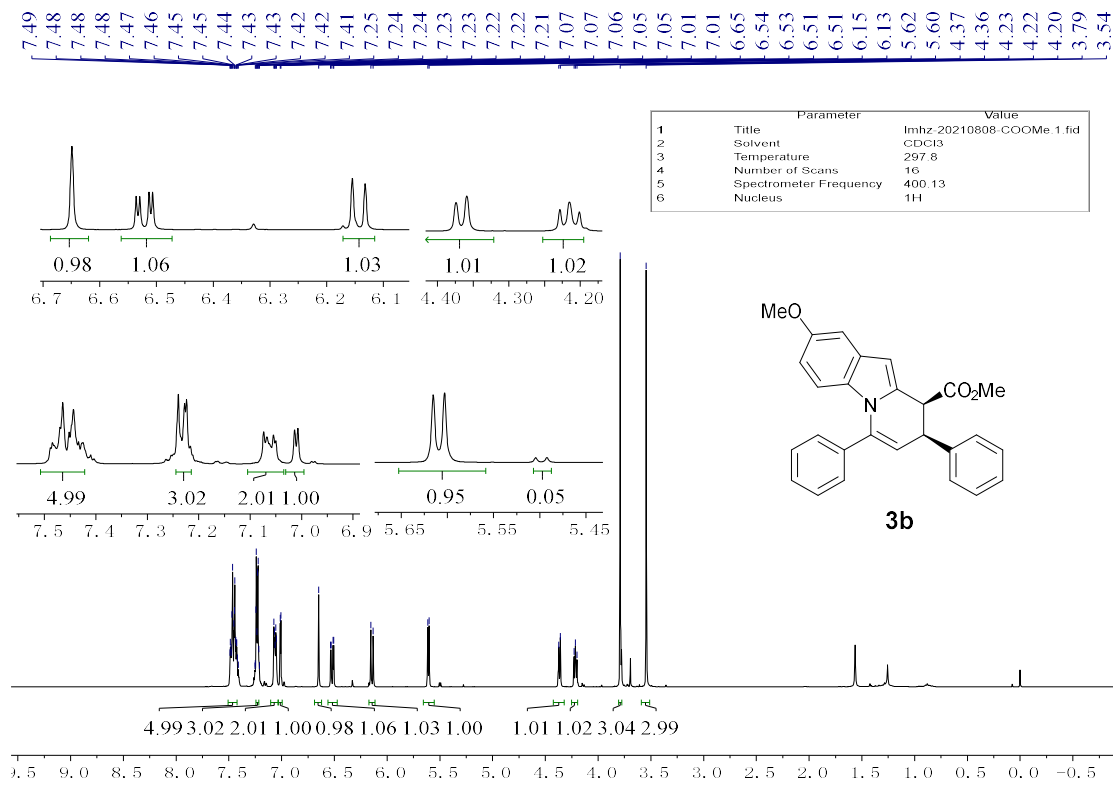
111.4, 100.8, 60.7, 55.4, 43.3, 38.5, 13.3 ppm.

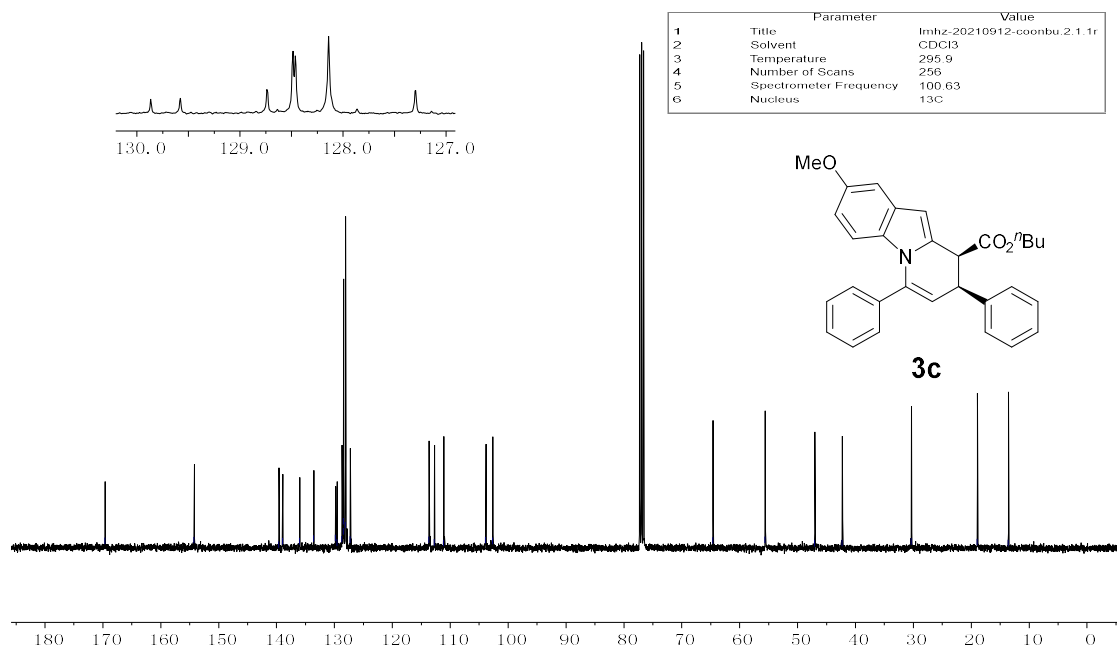
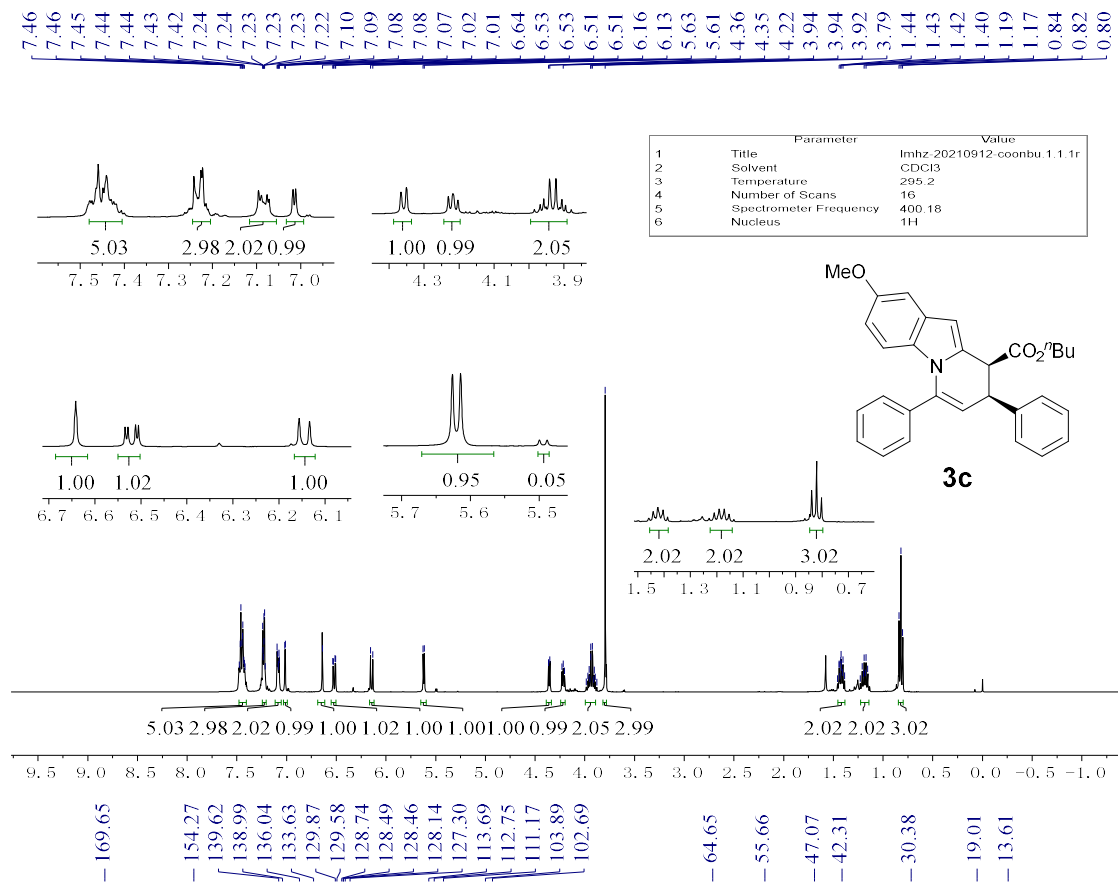
11. References

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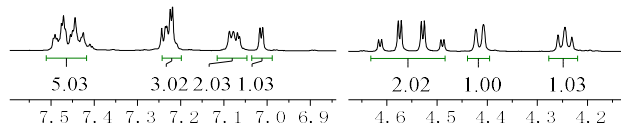
12. Copies of NMR spectra for products



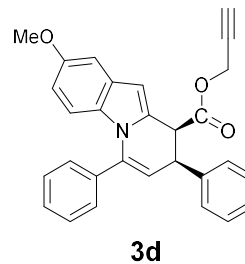
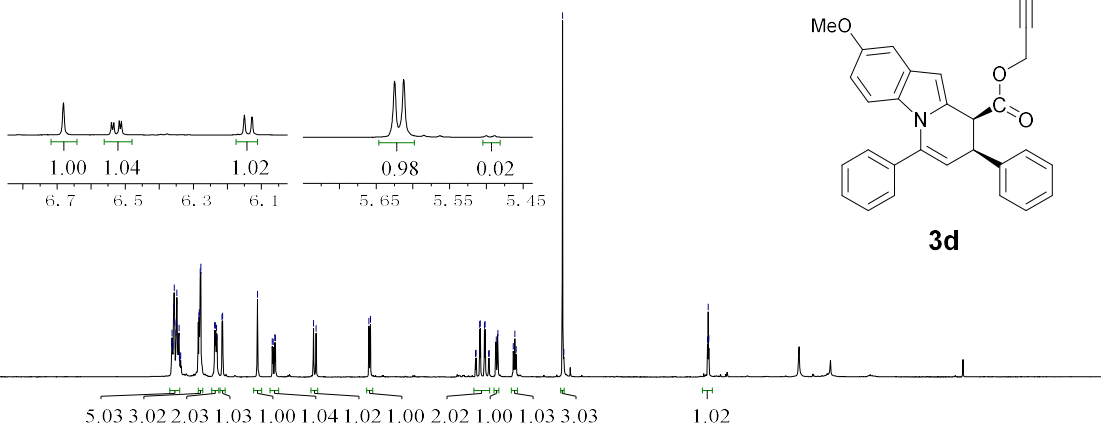




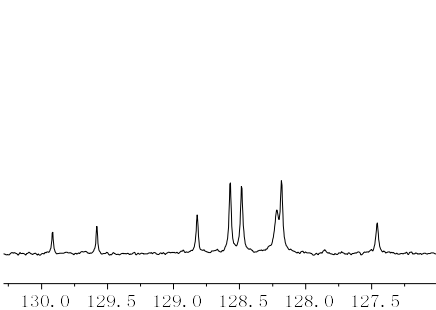
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2.41



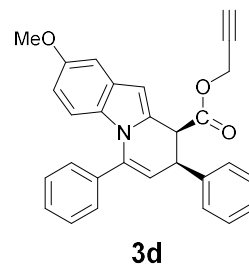
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4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H



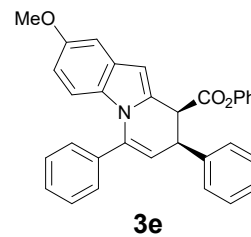
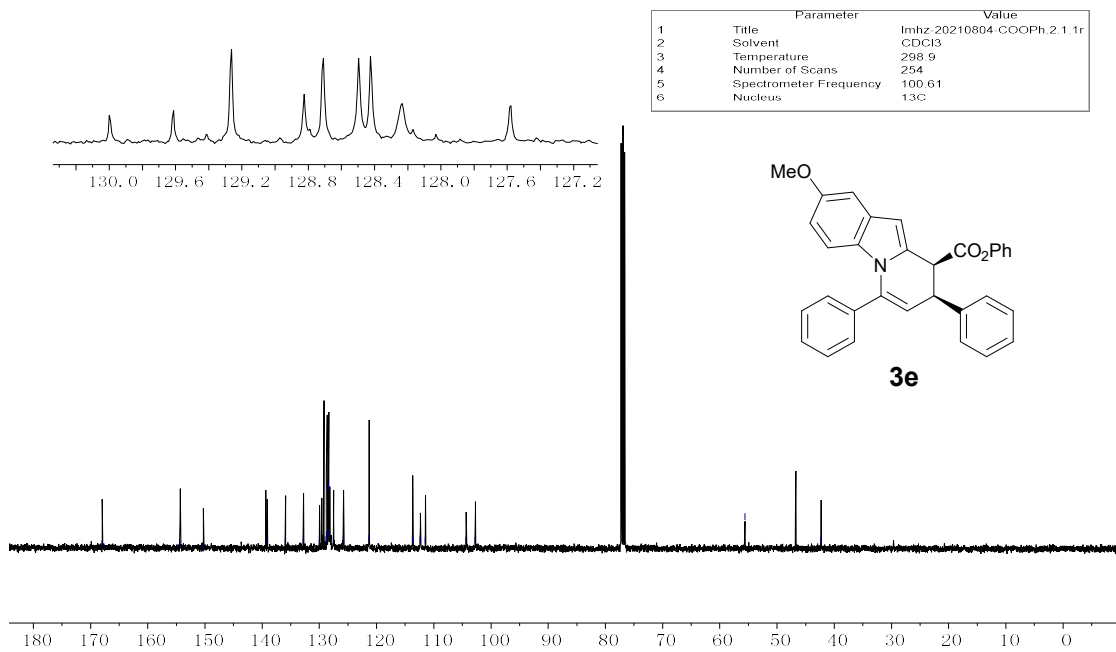
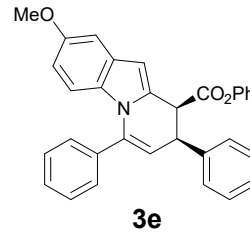
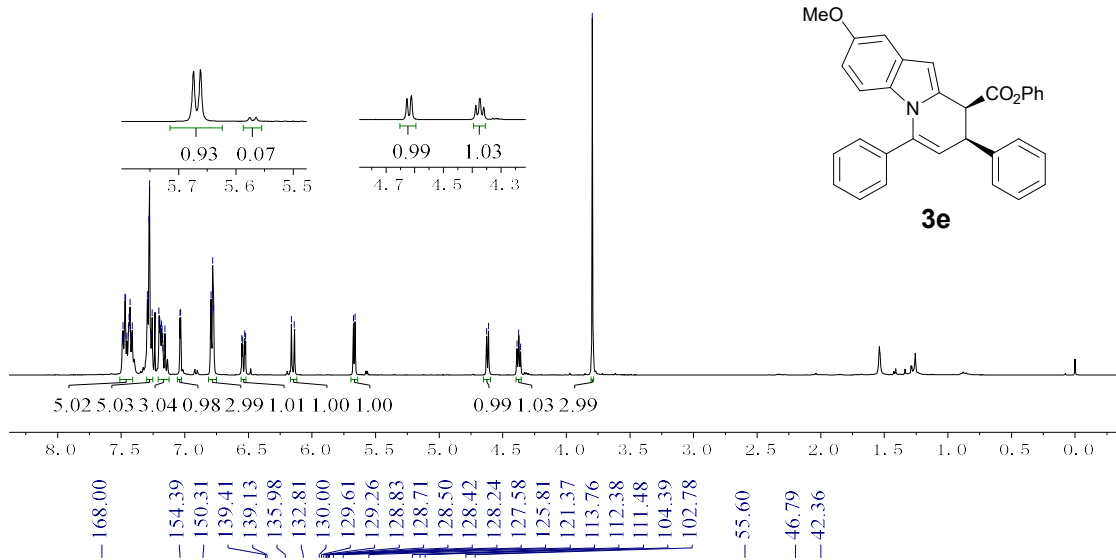
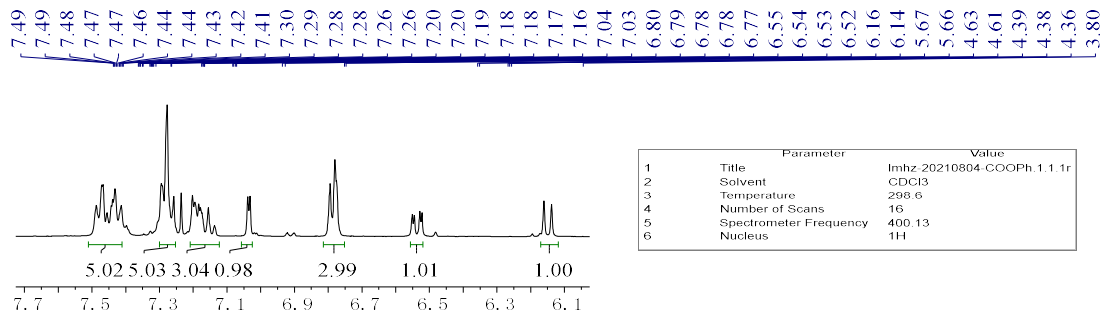
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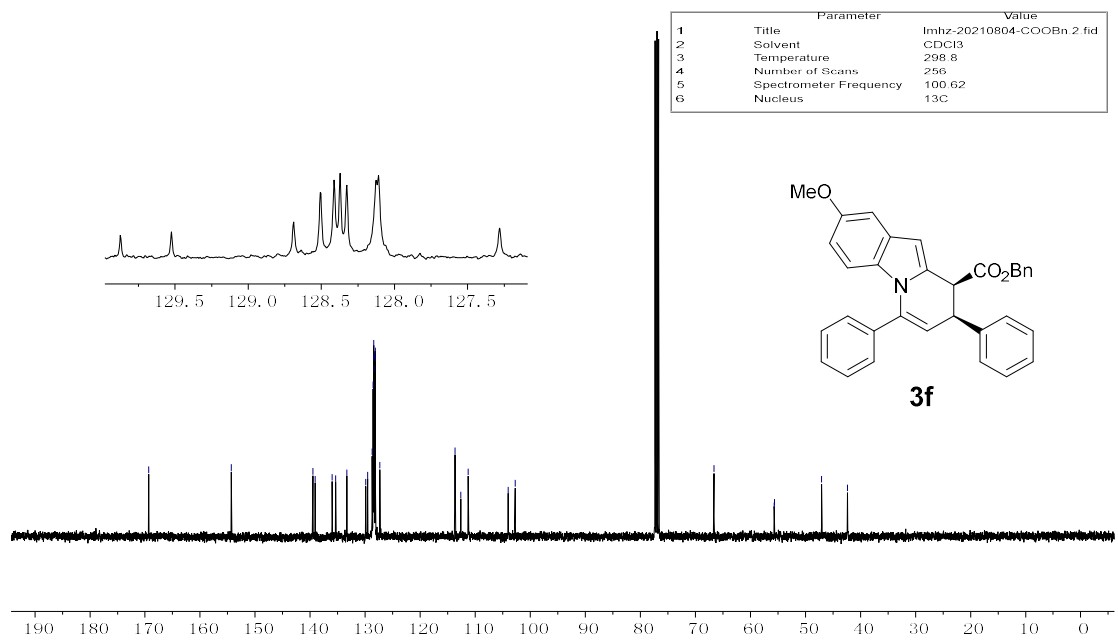
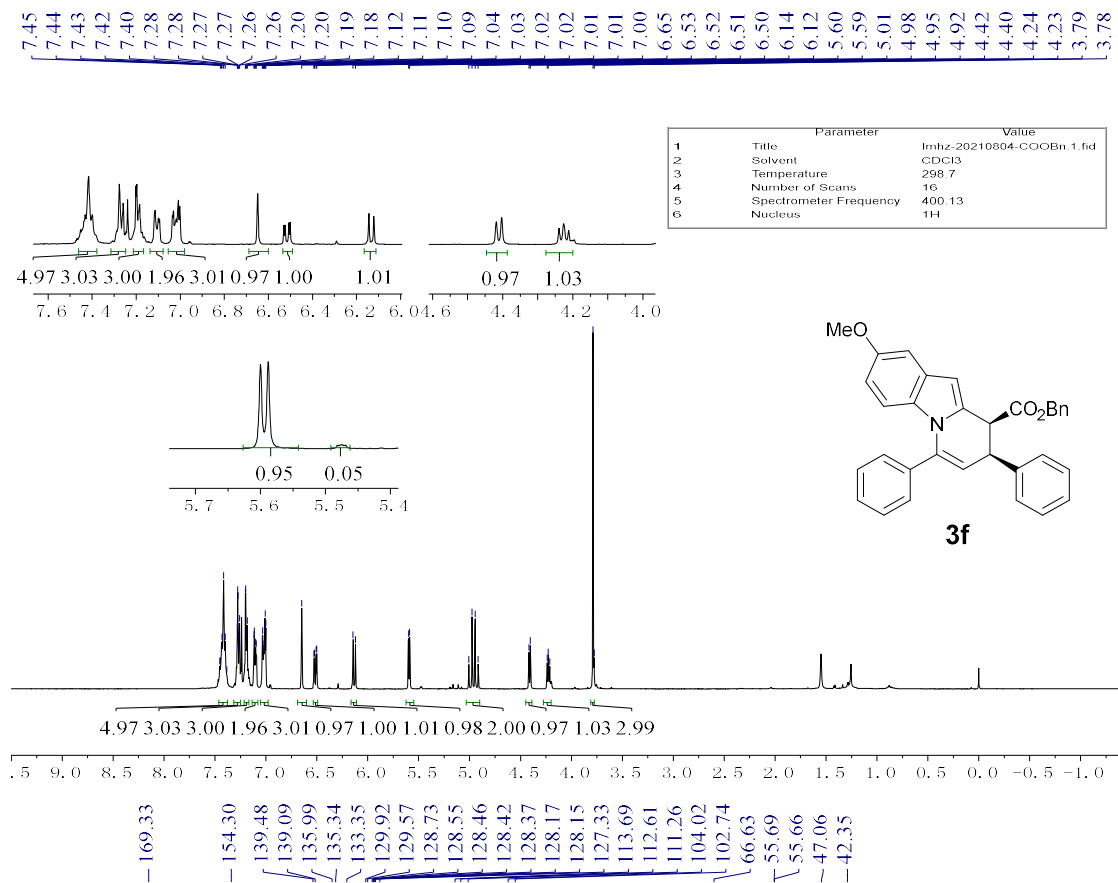


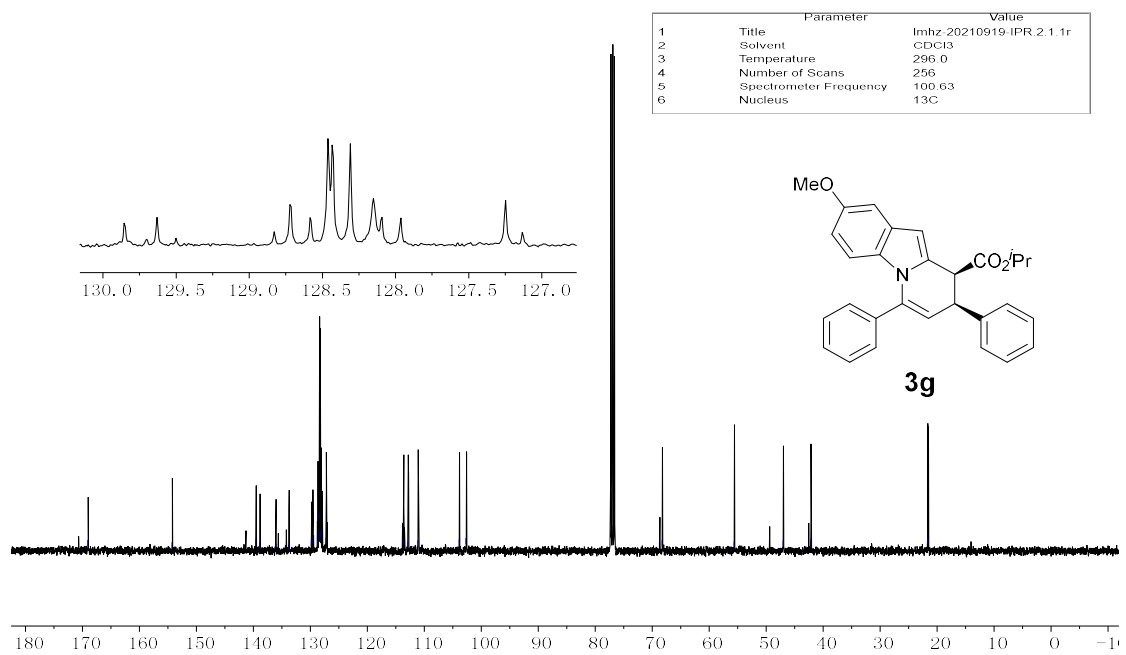
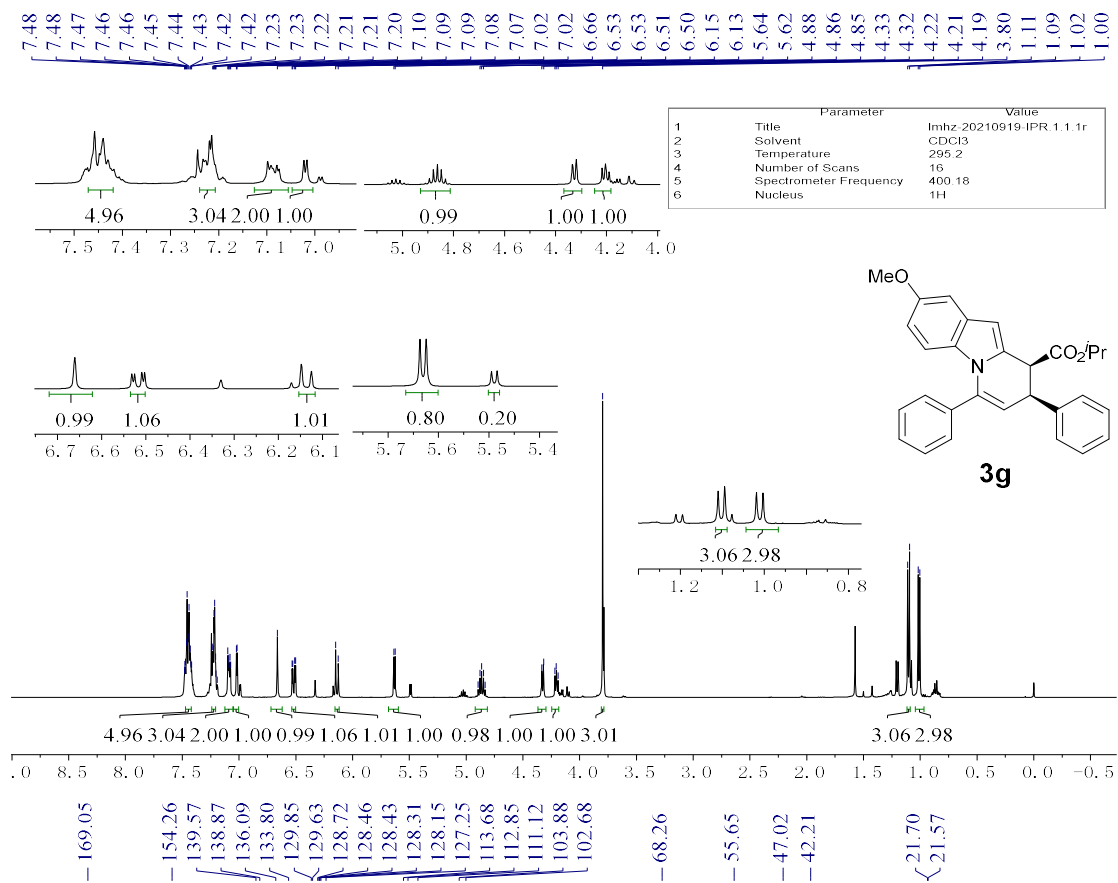
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6 Nucleus	13C

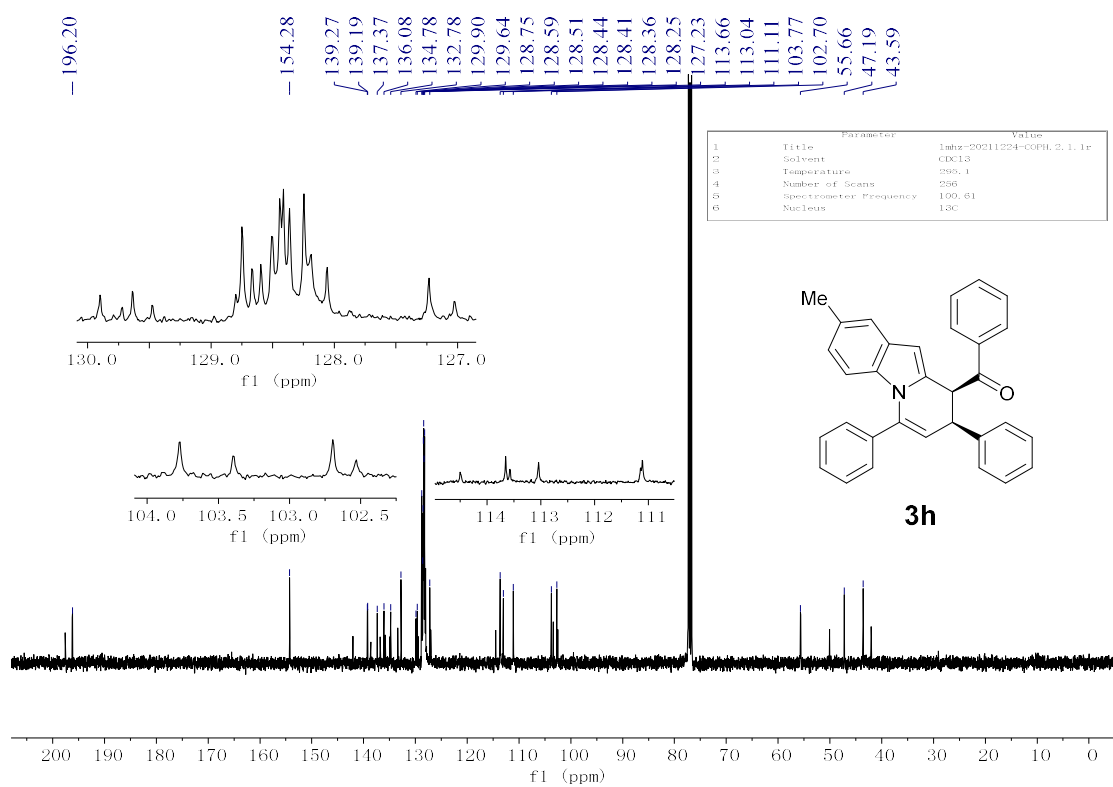
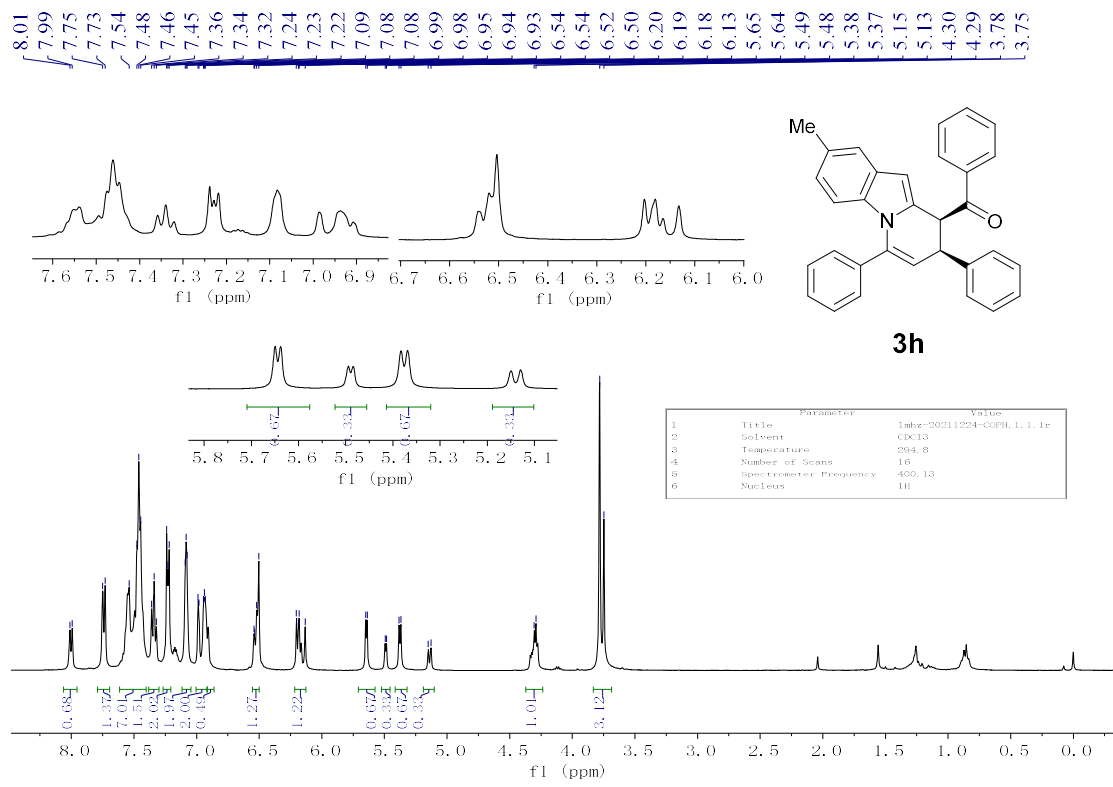


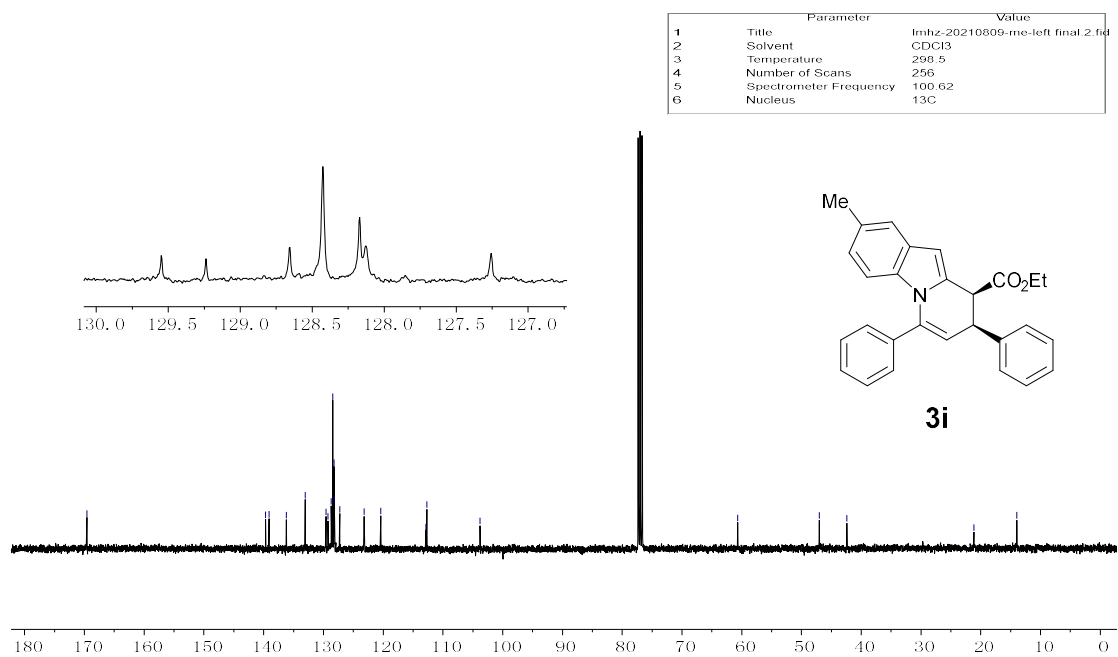
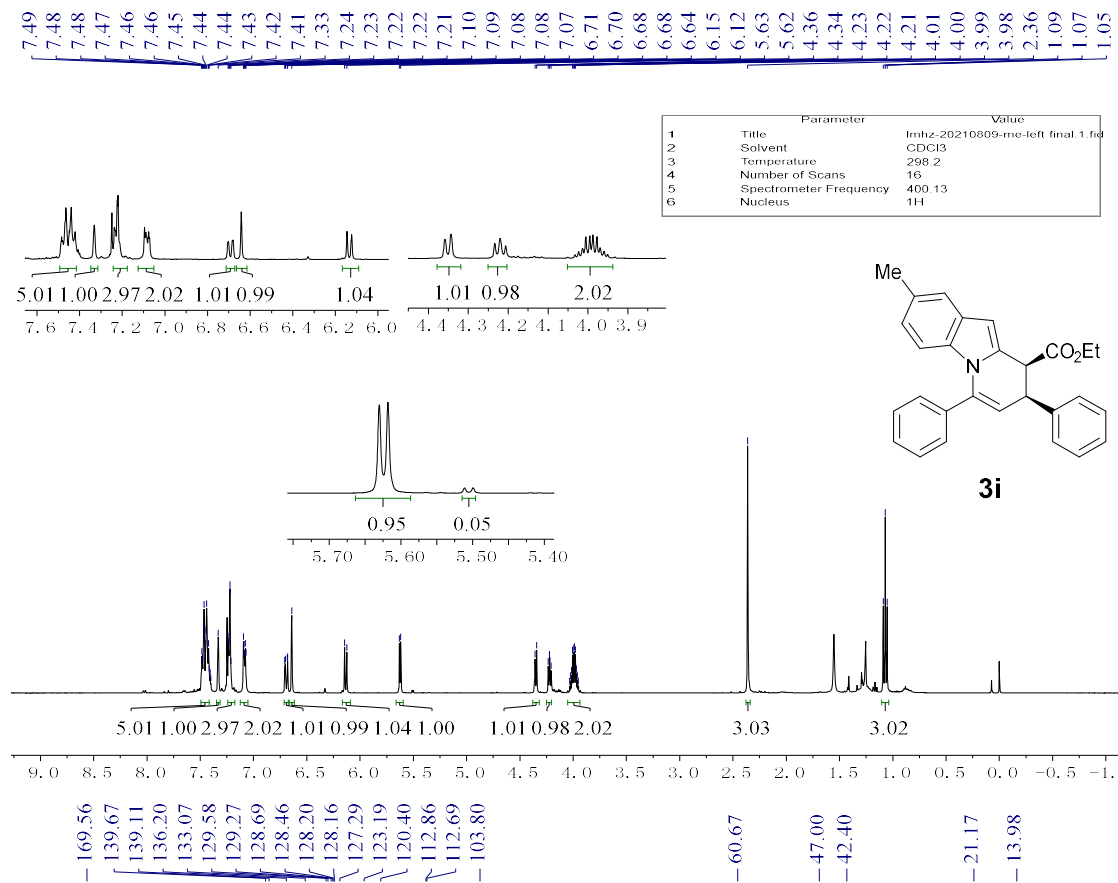
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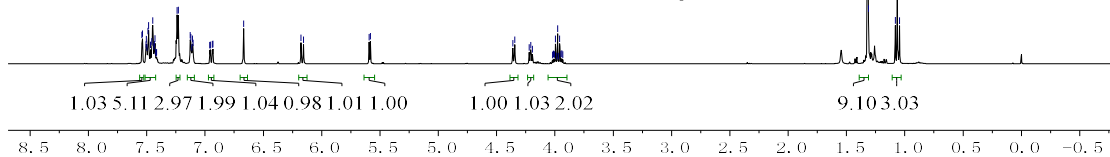
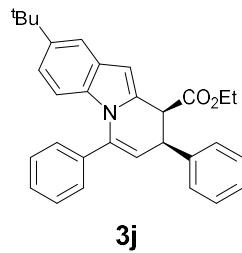
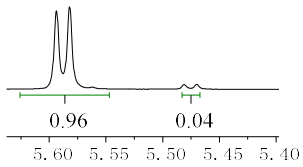
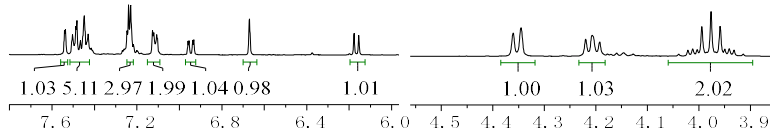






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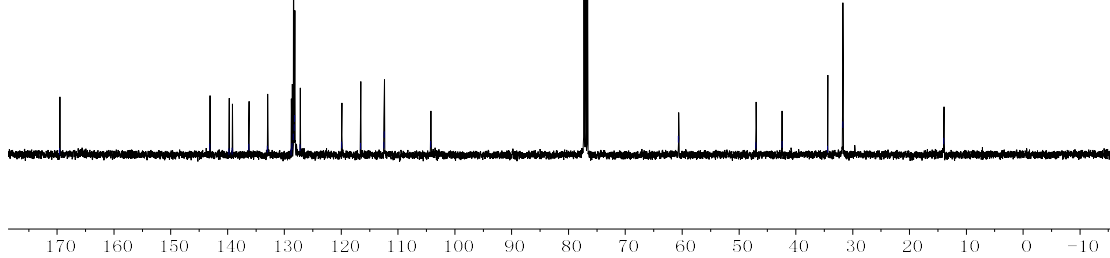
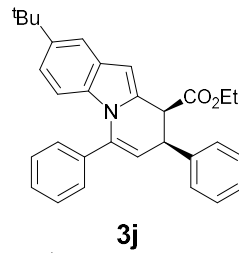
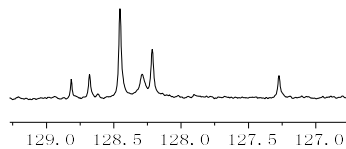
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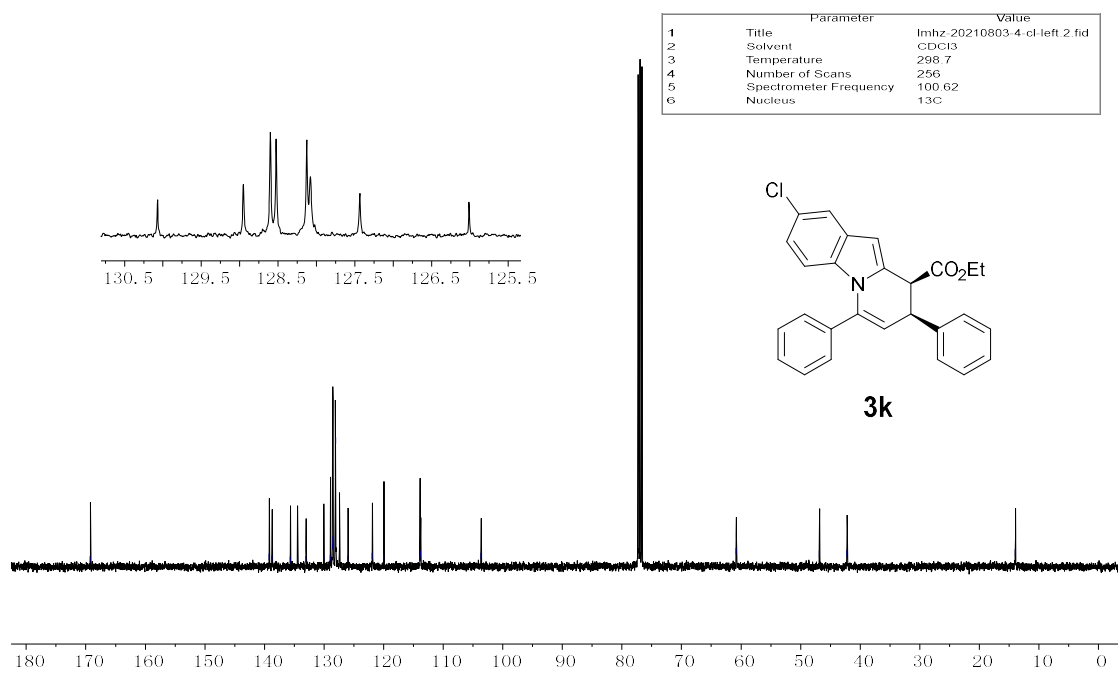
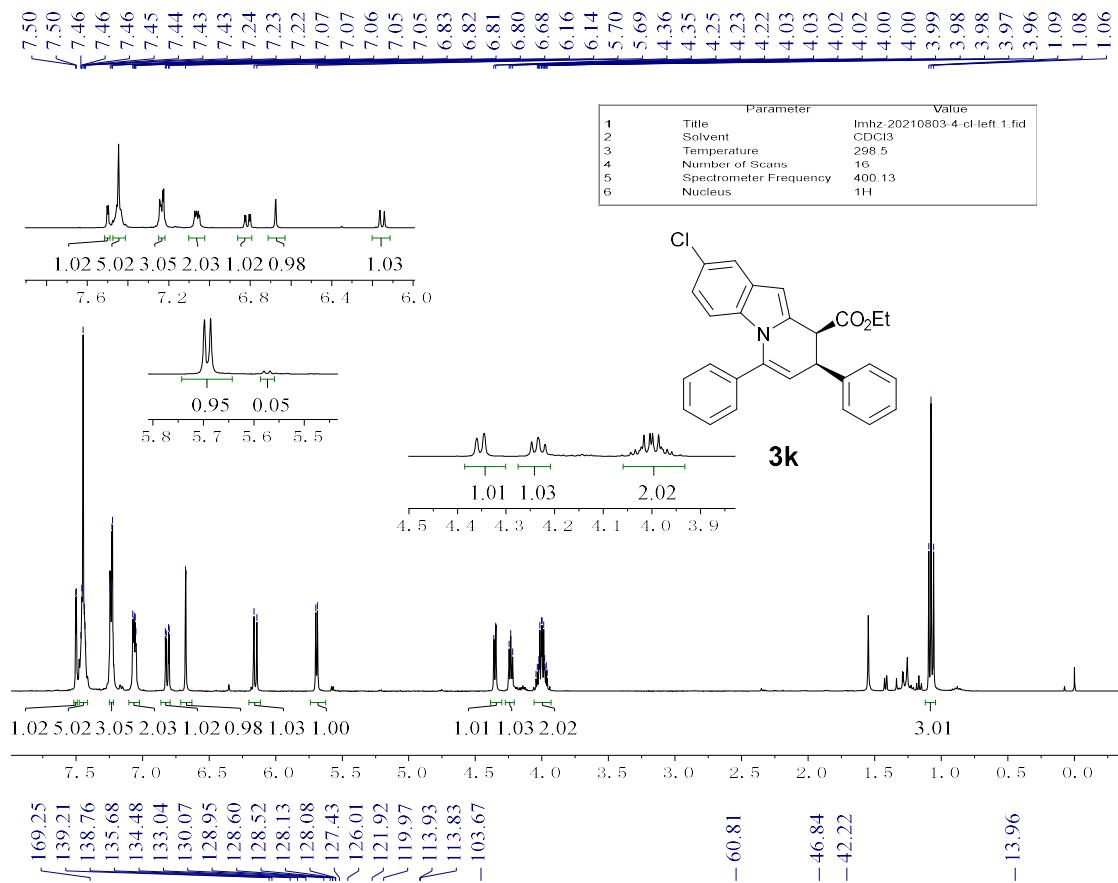


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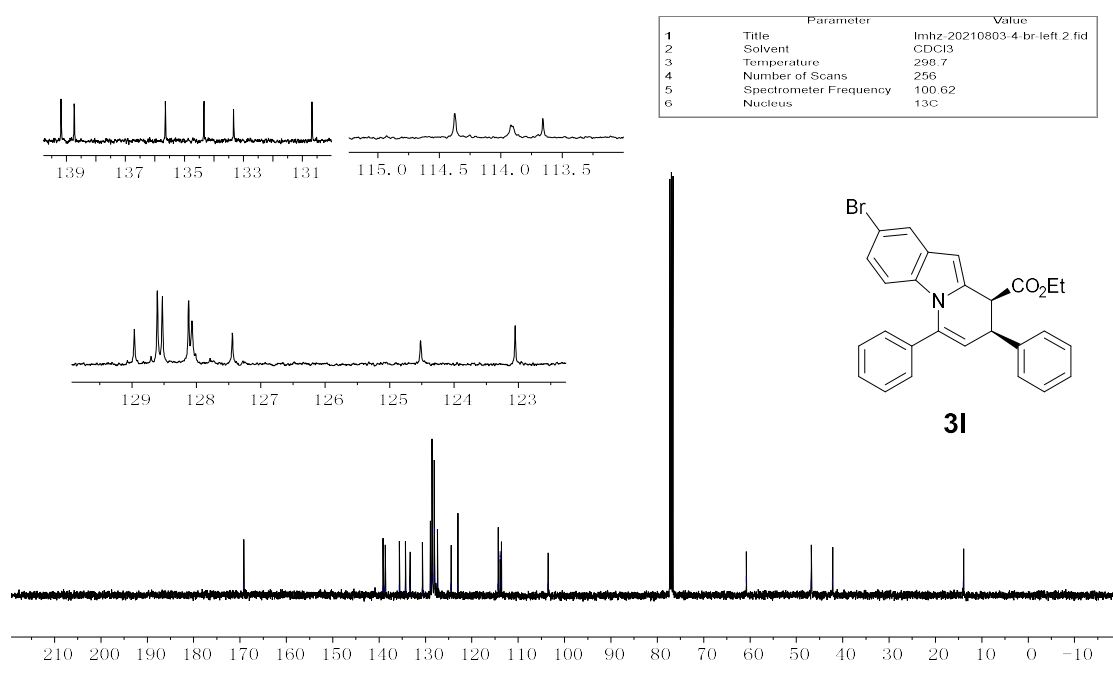
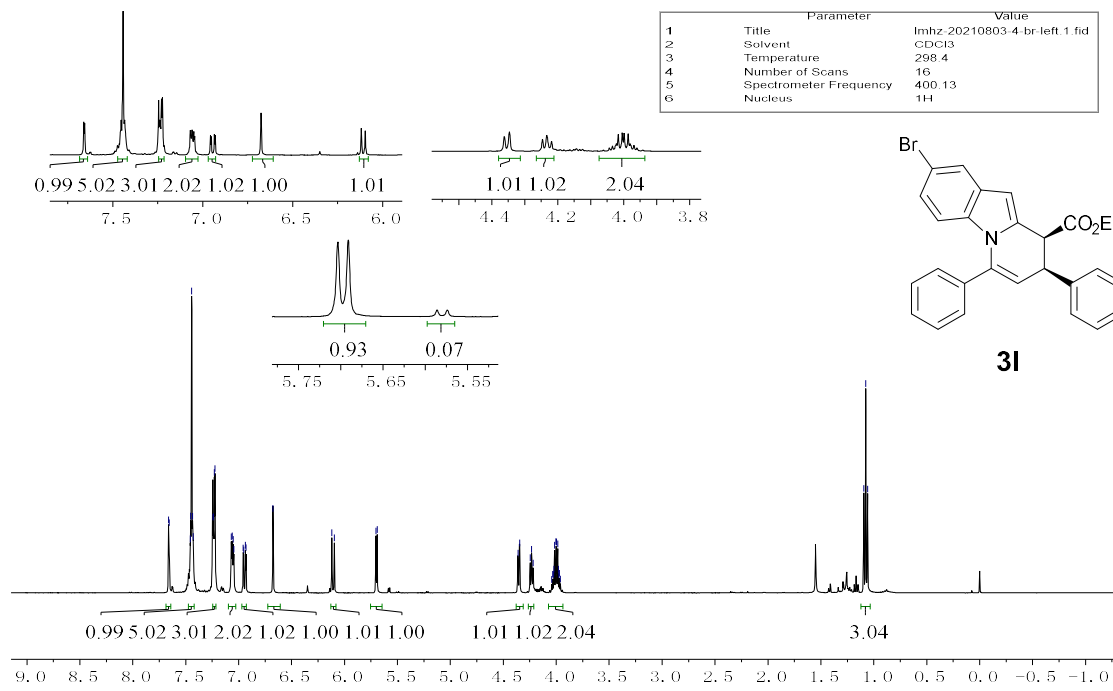
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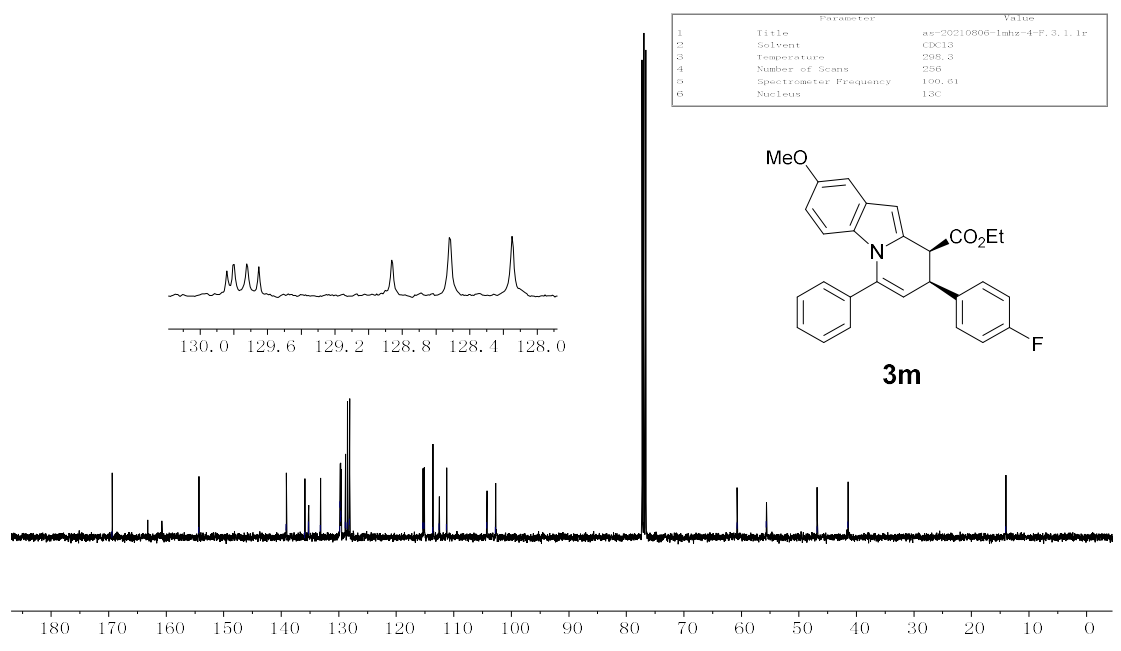
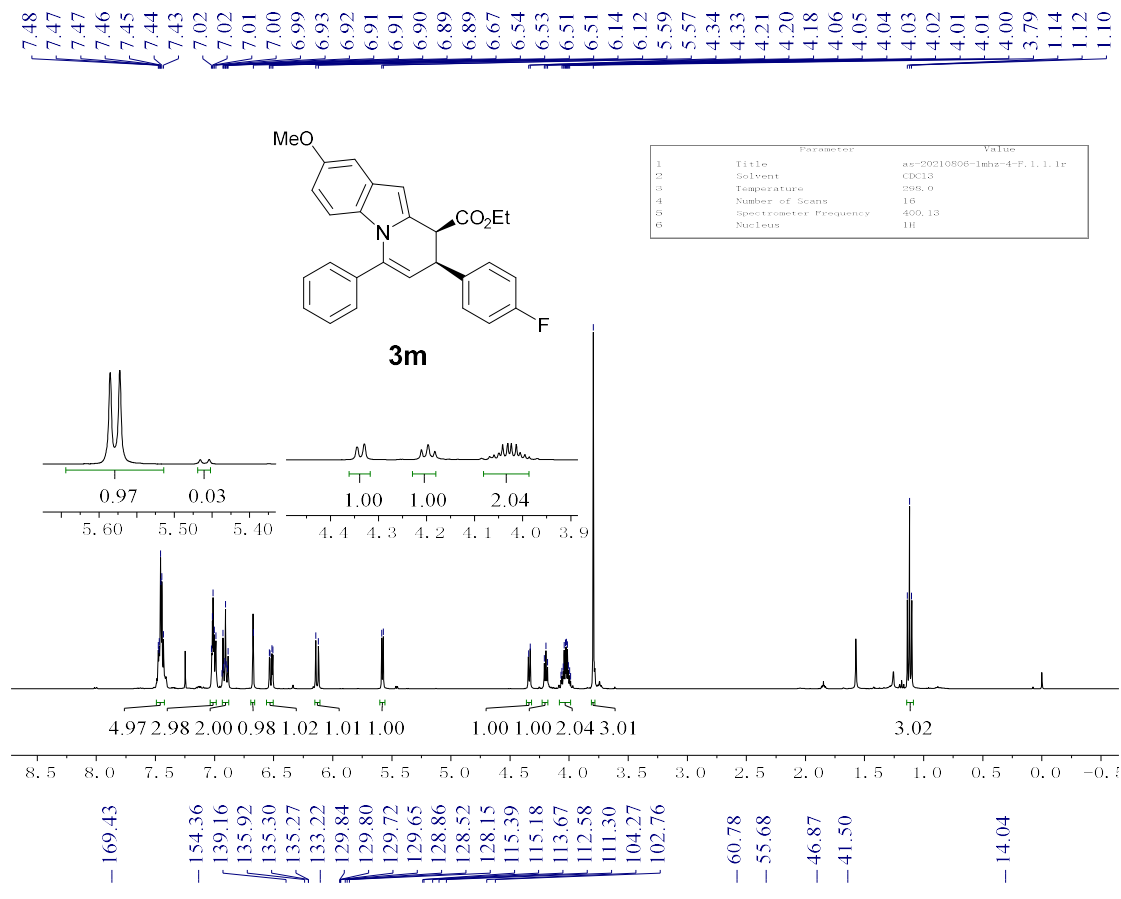
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6	Nucleus	13C

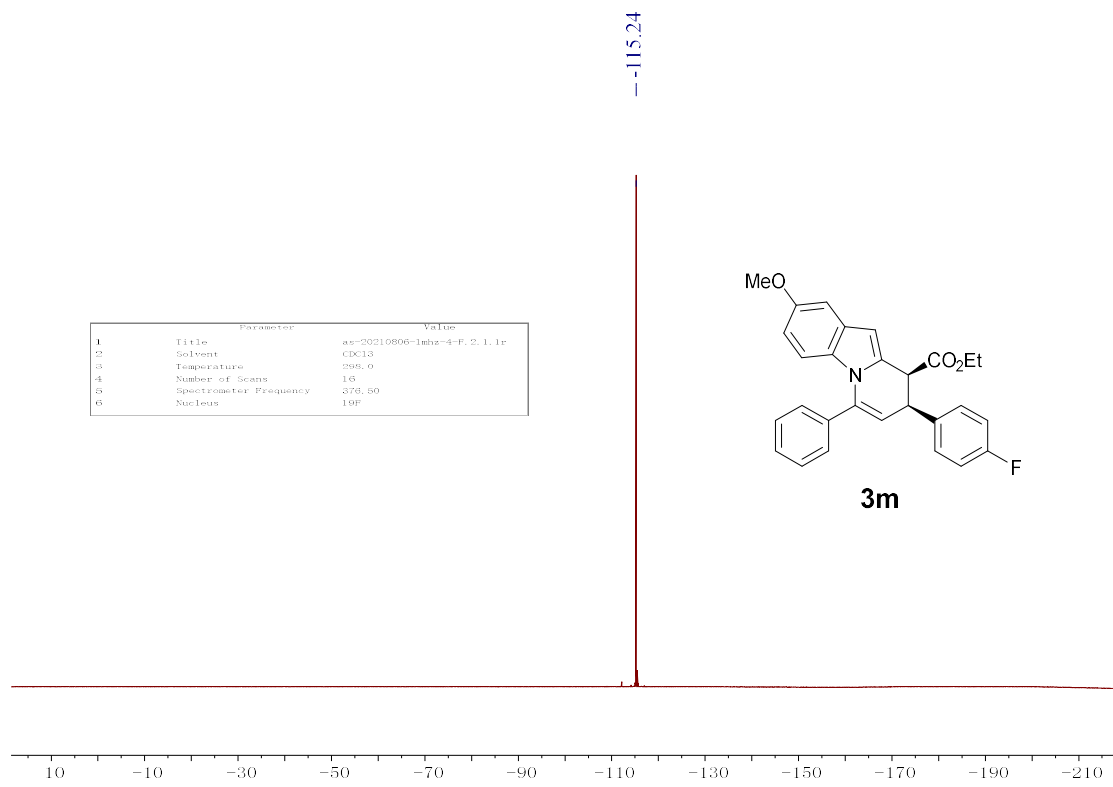




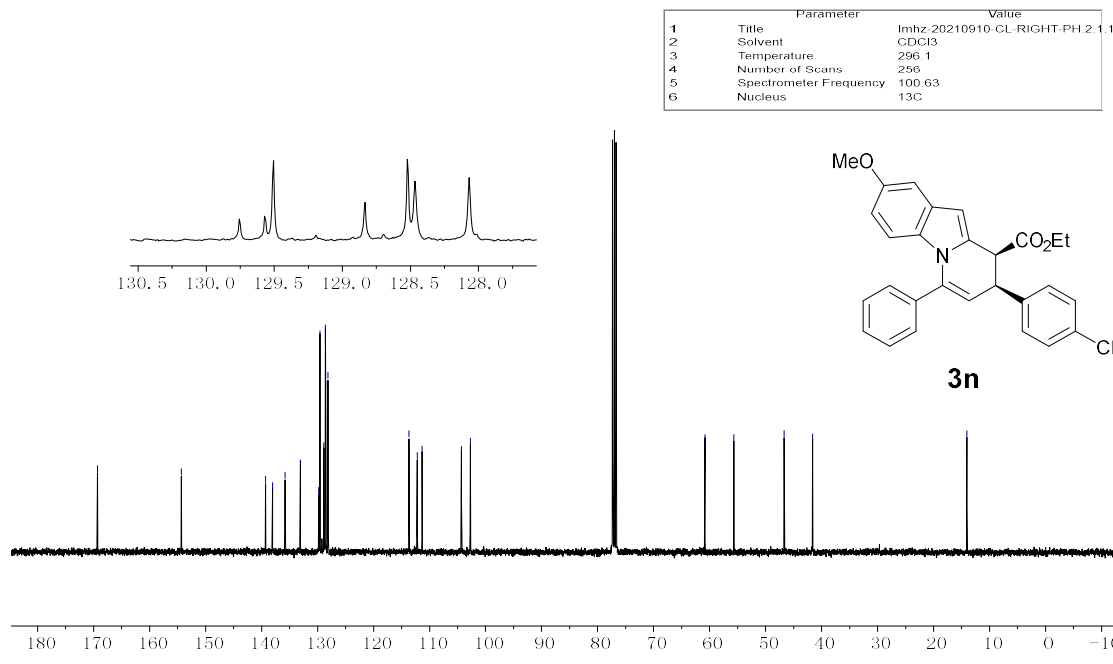
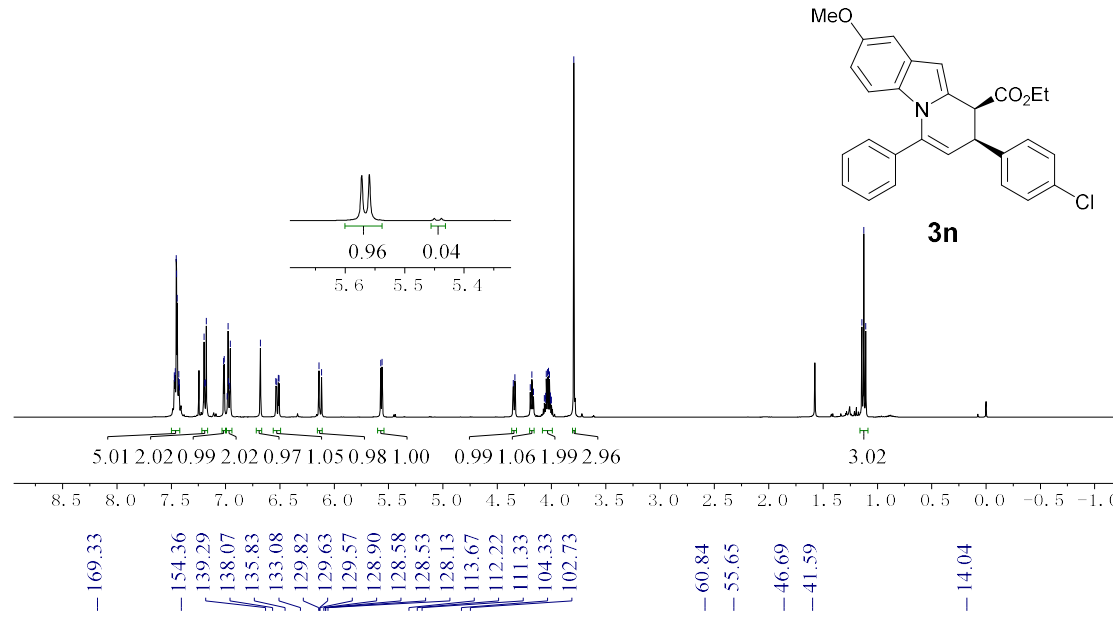
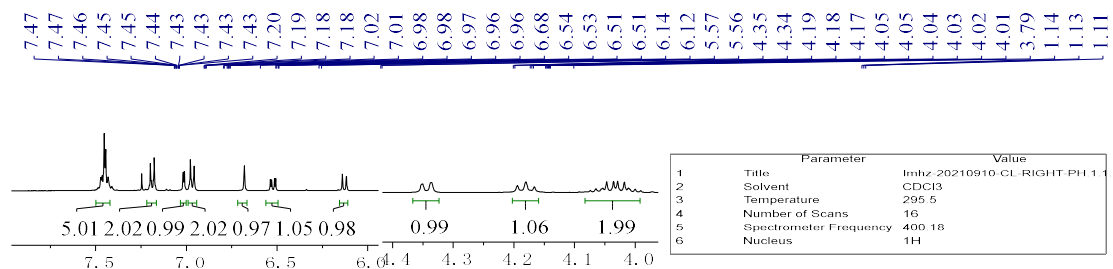
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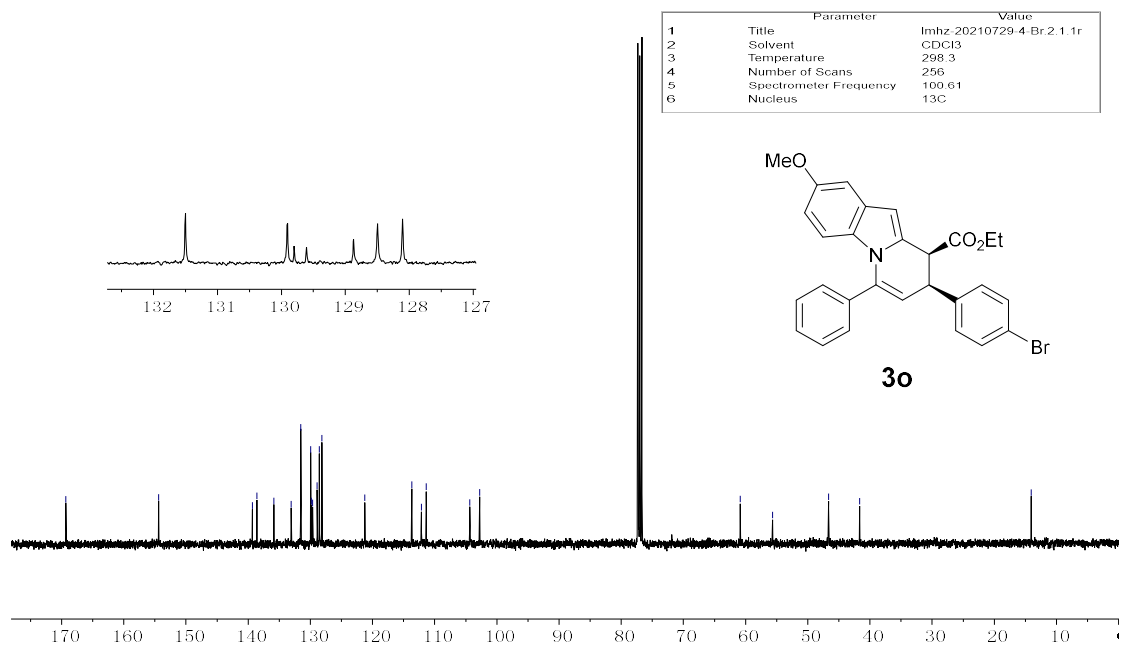
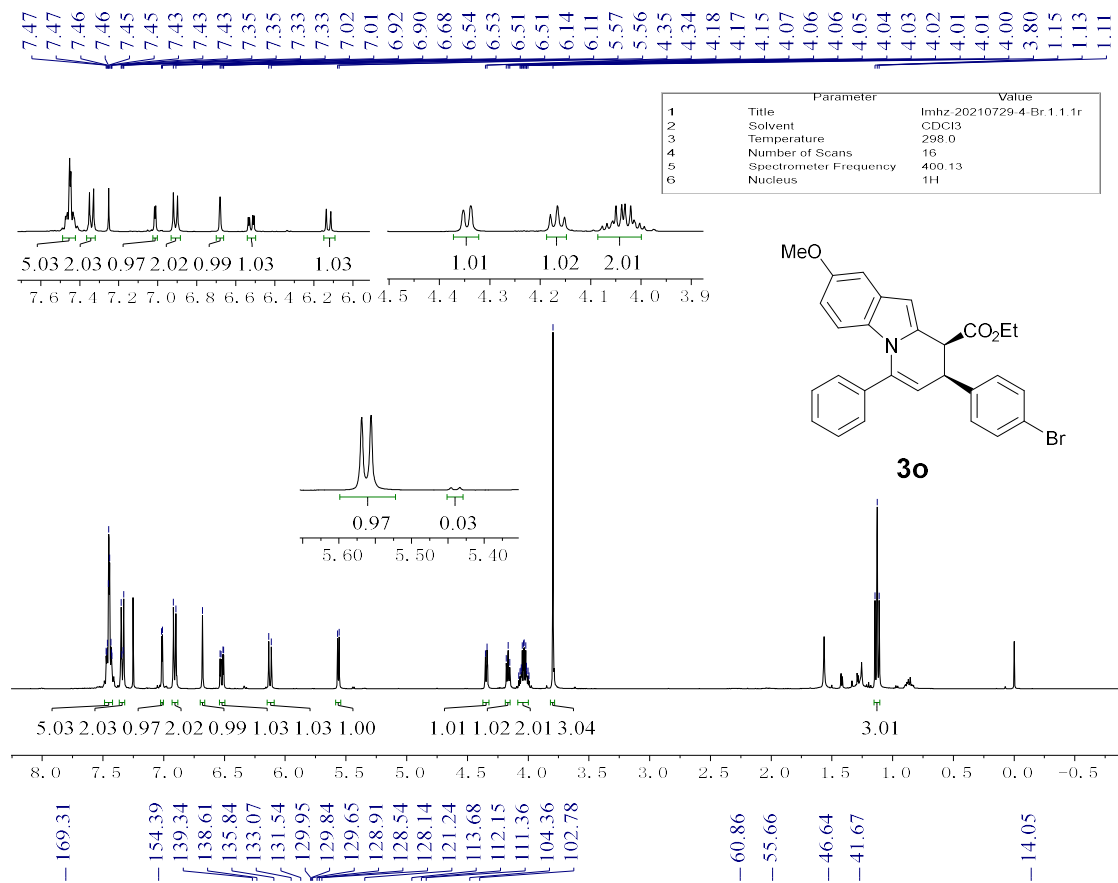


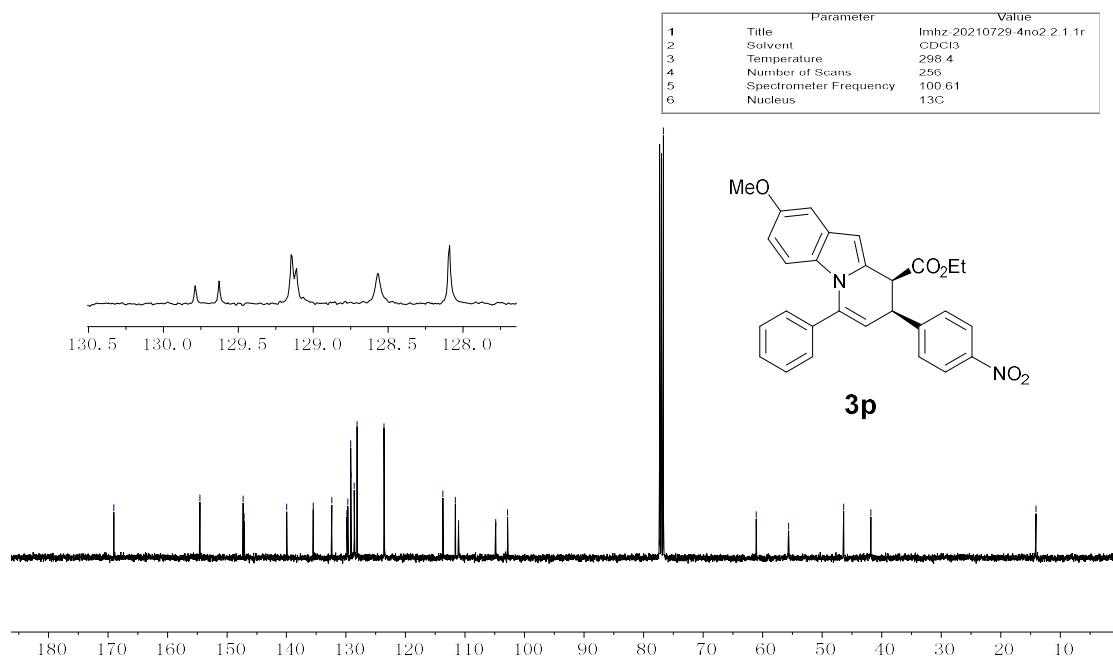
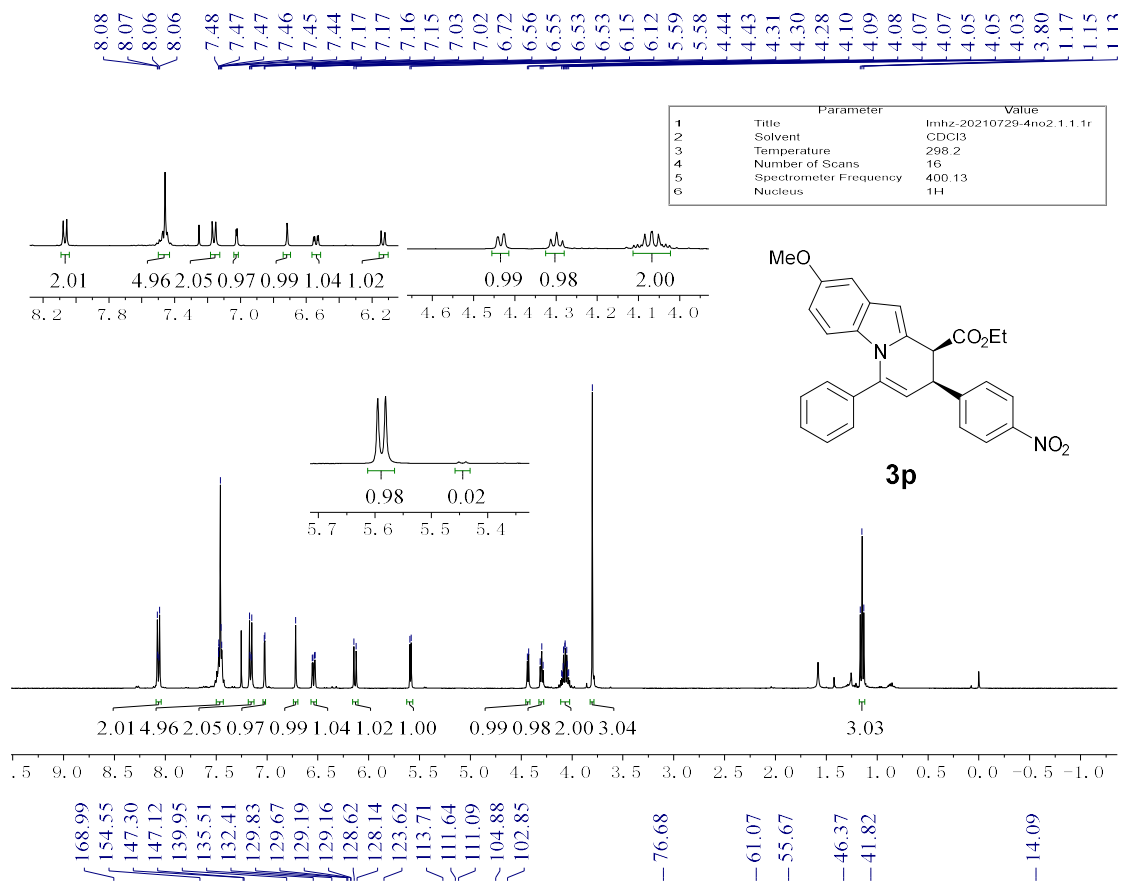


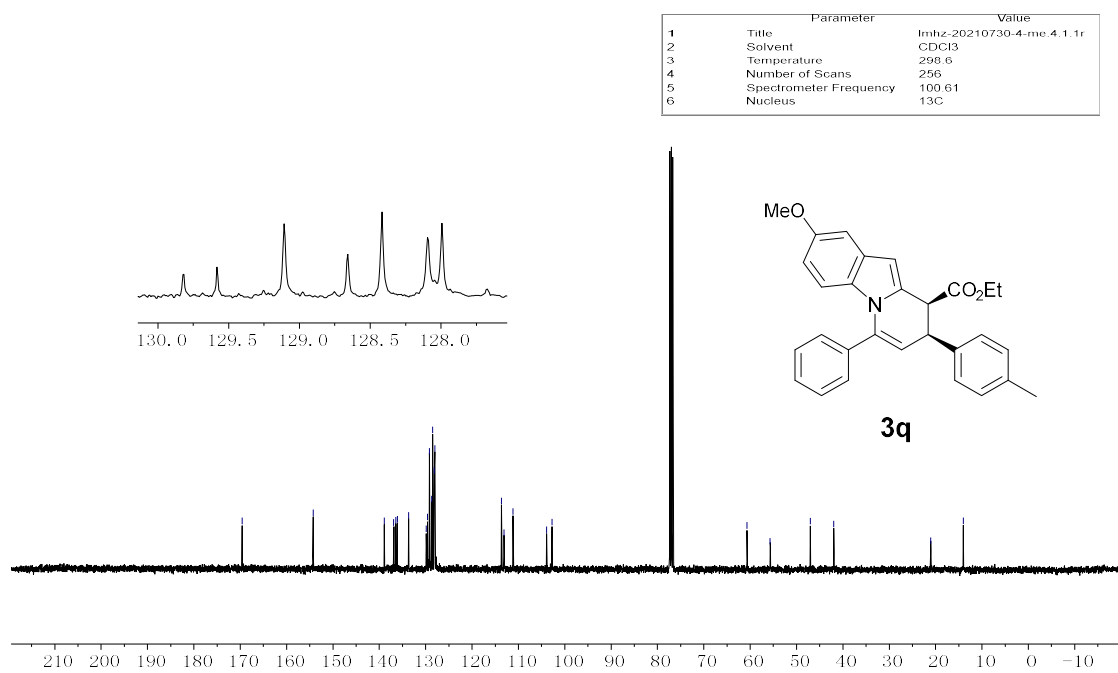
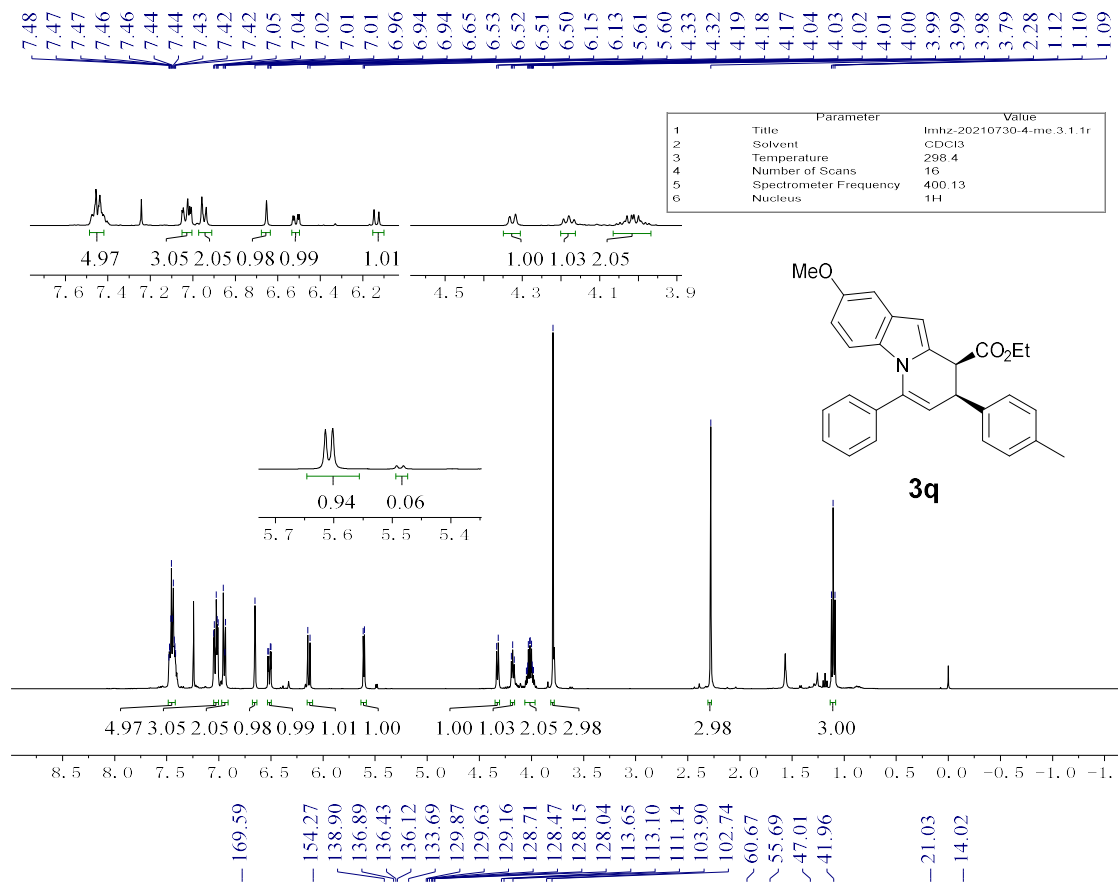


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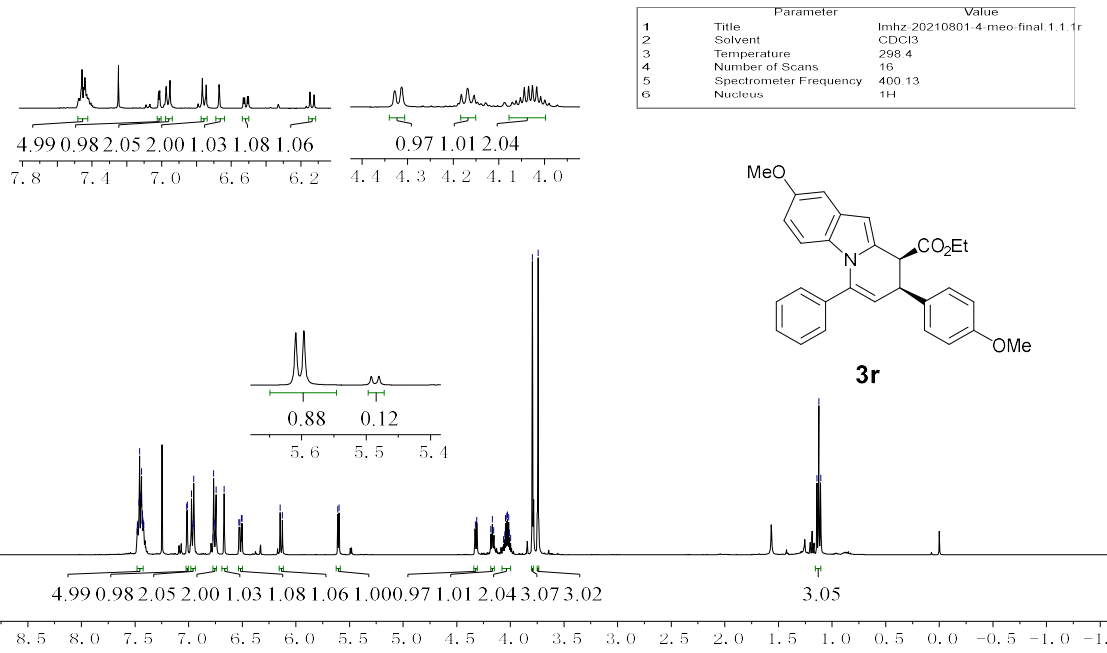




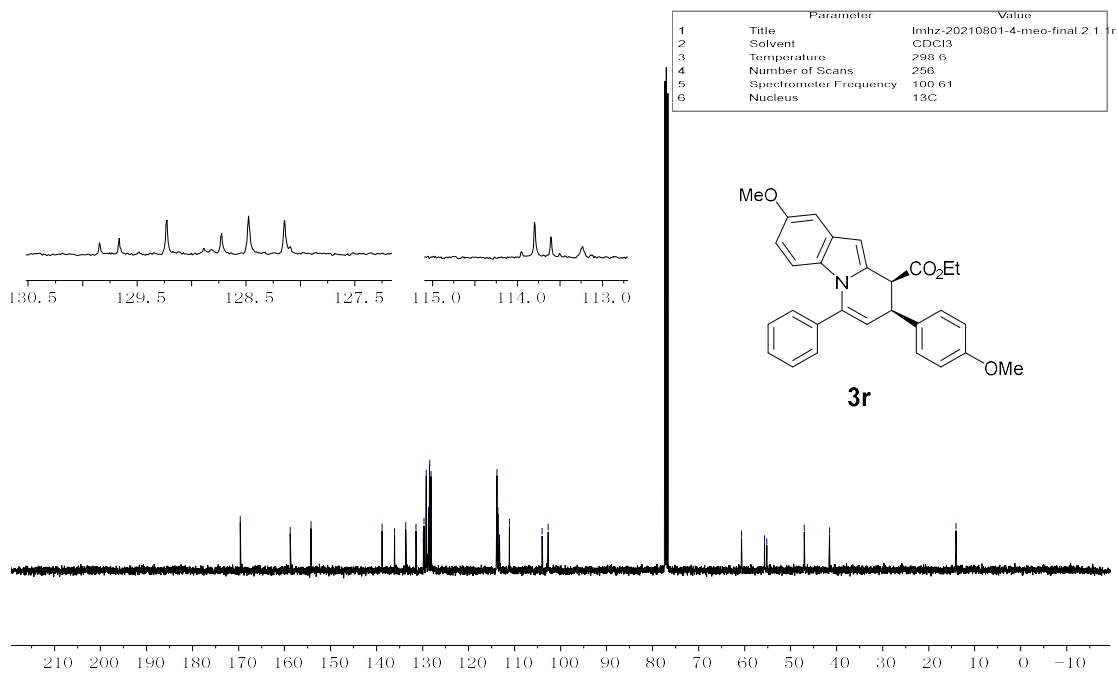


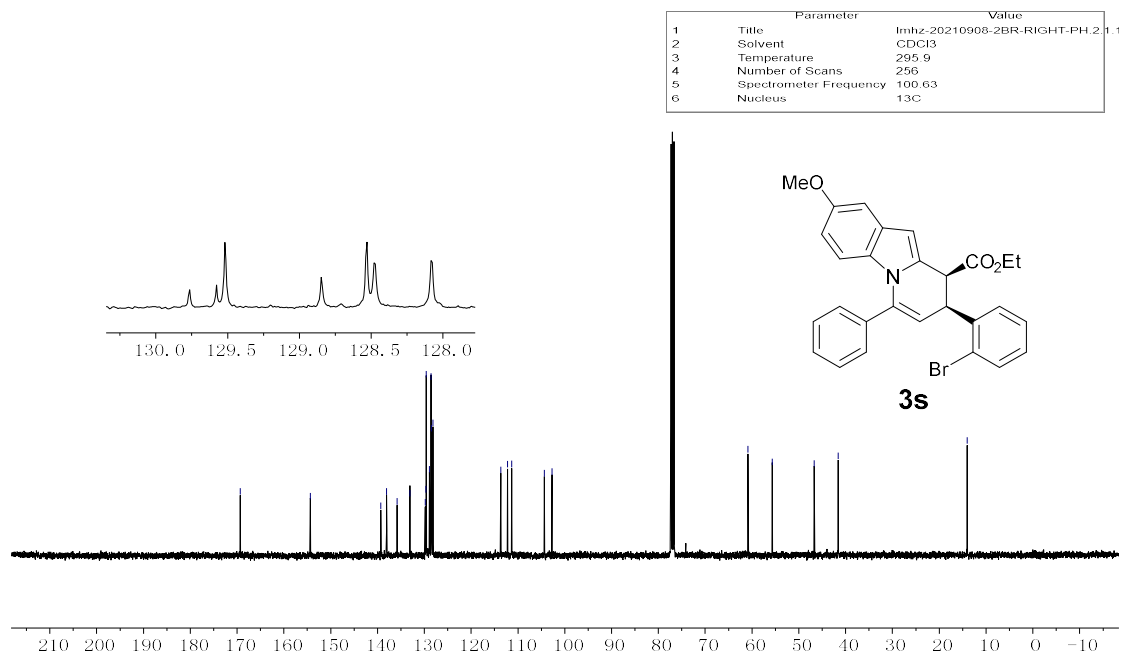
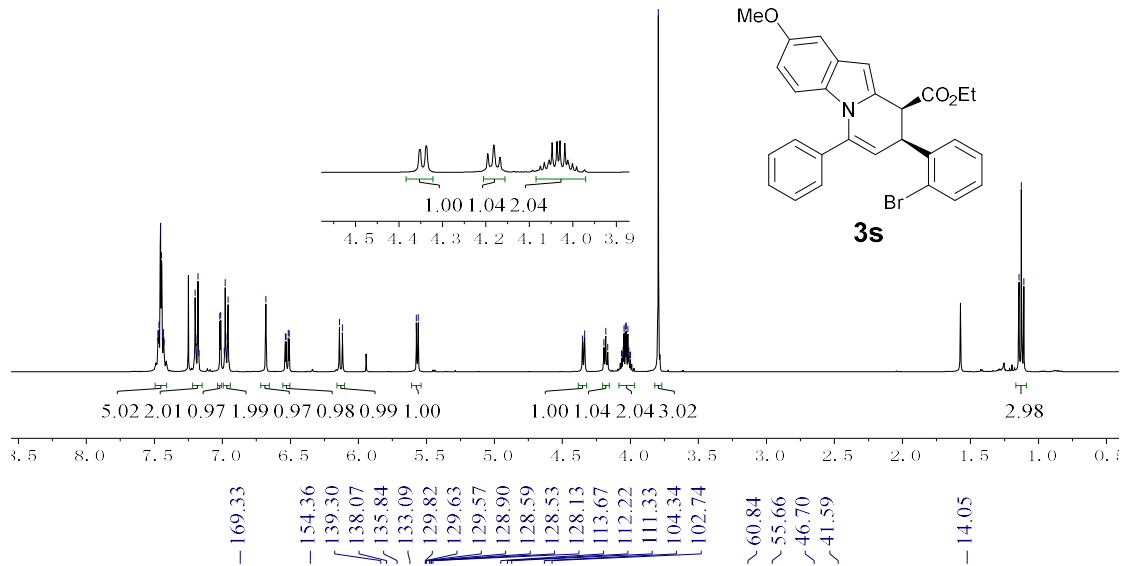
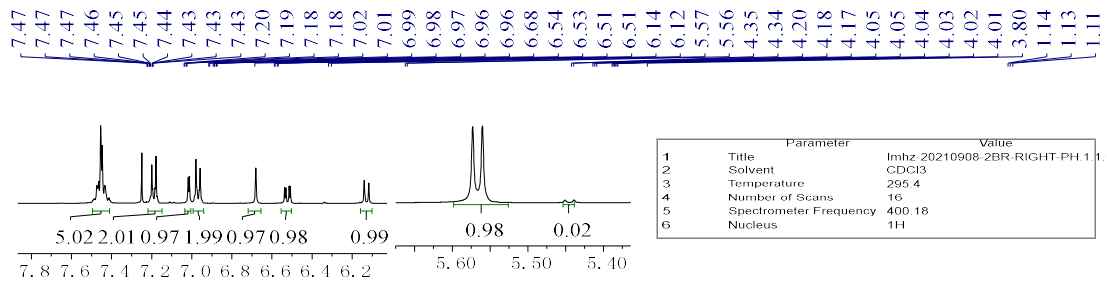


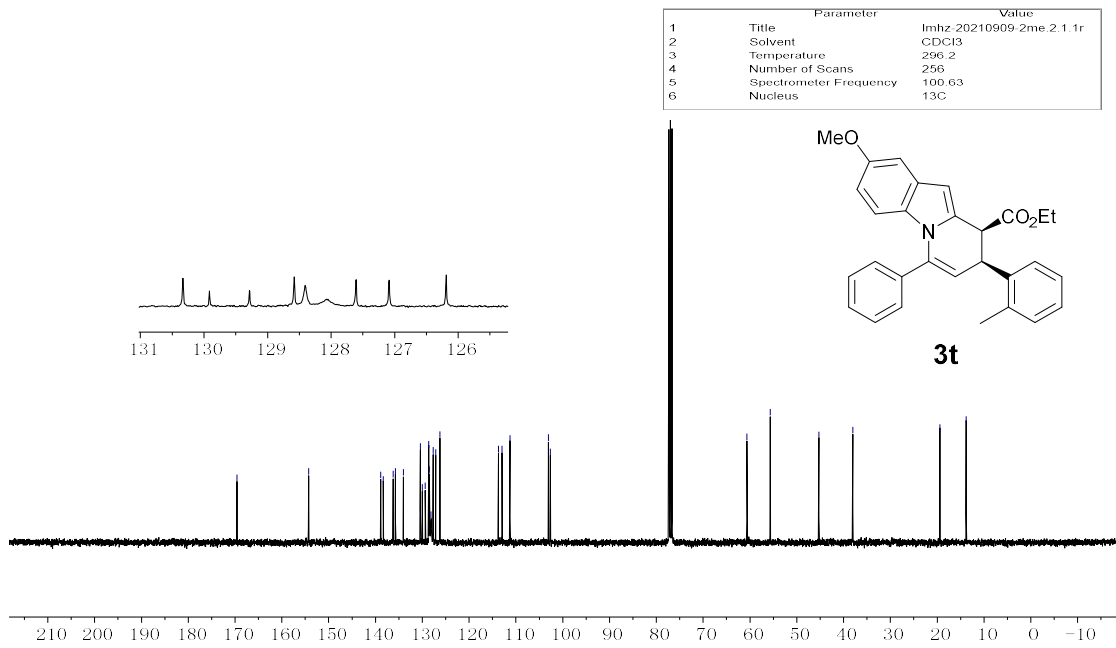
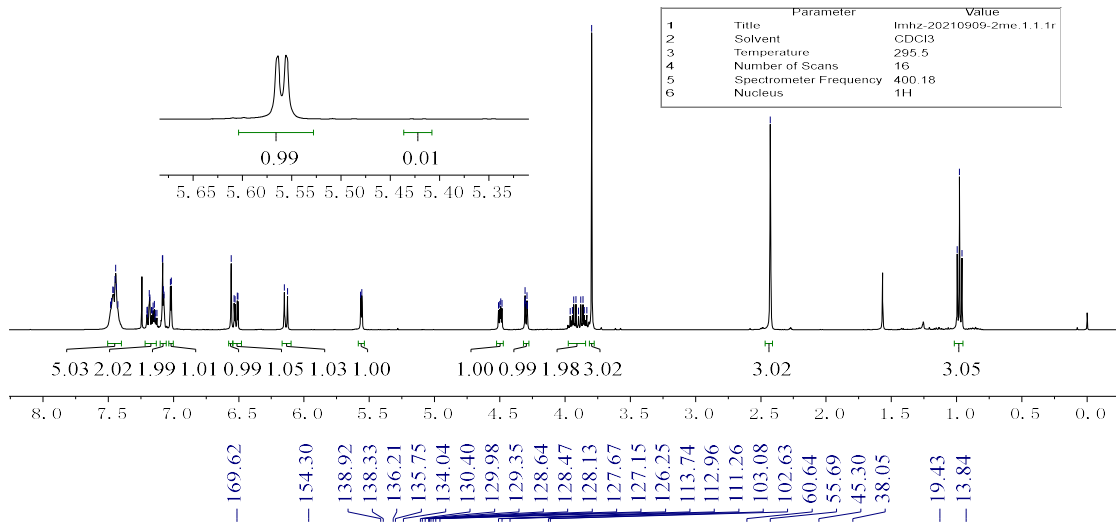
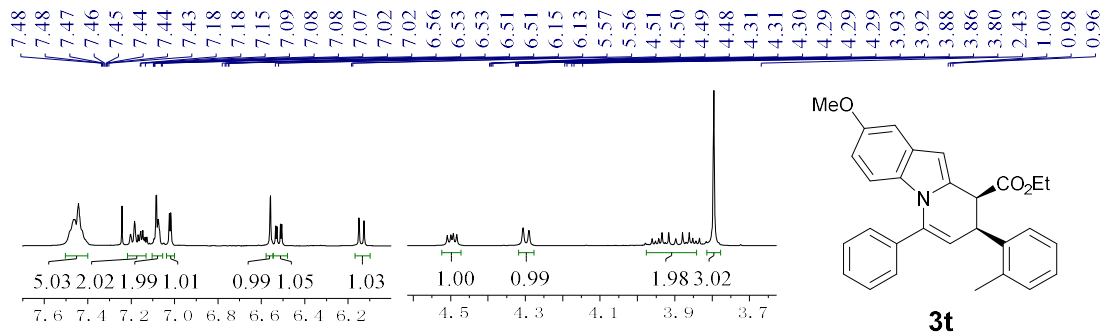
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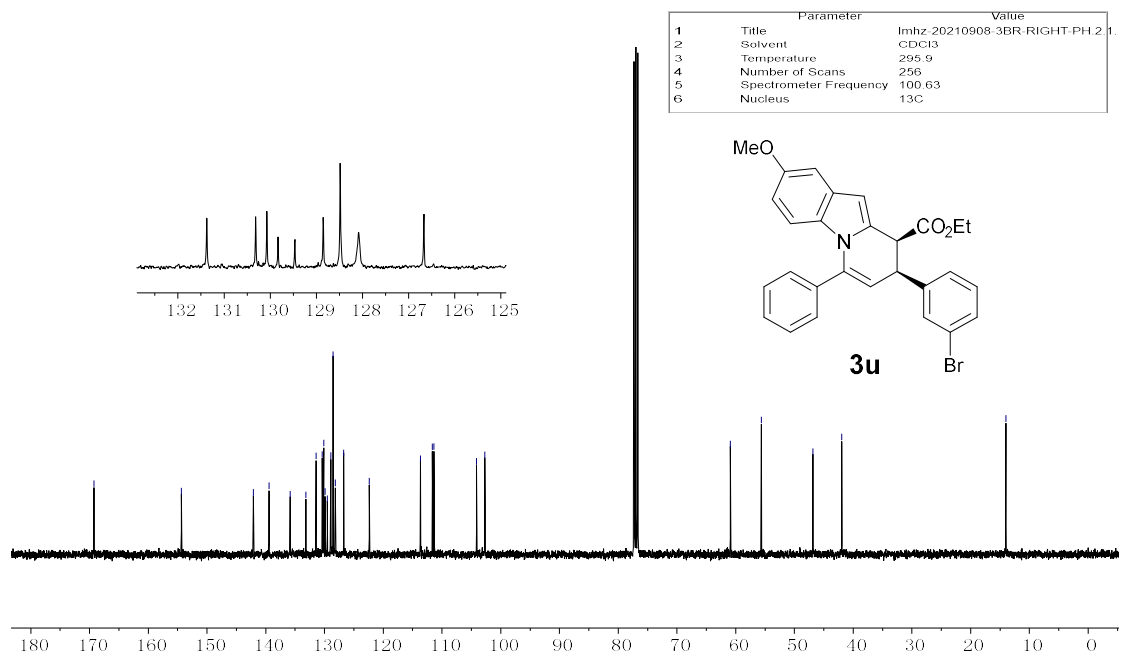
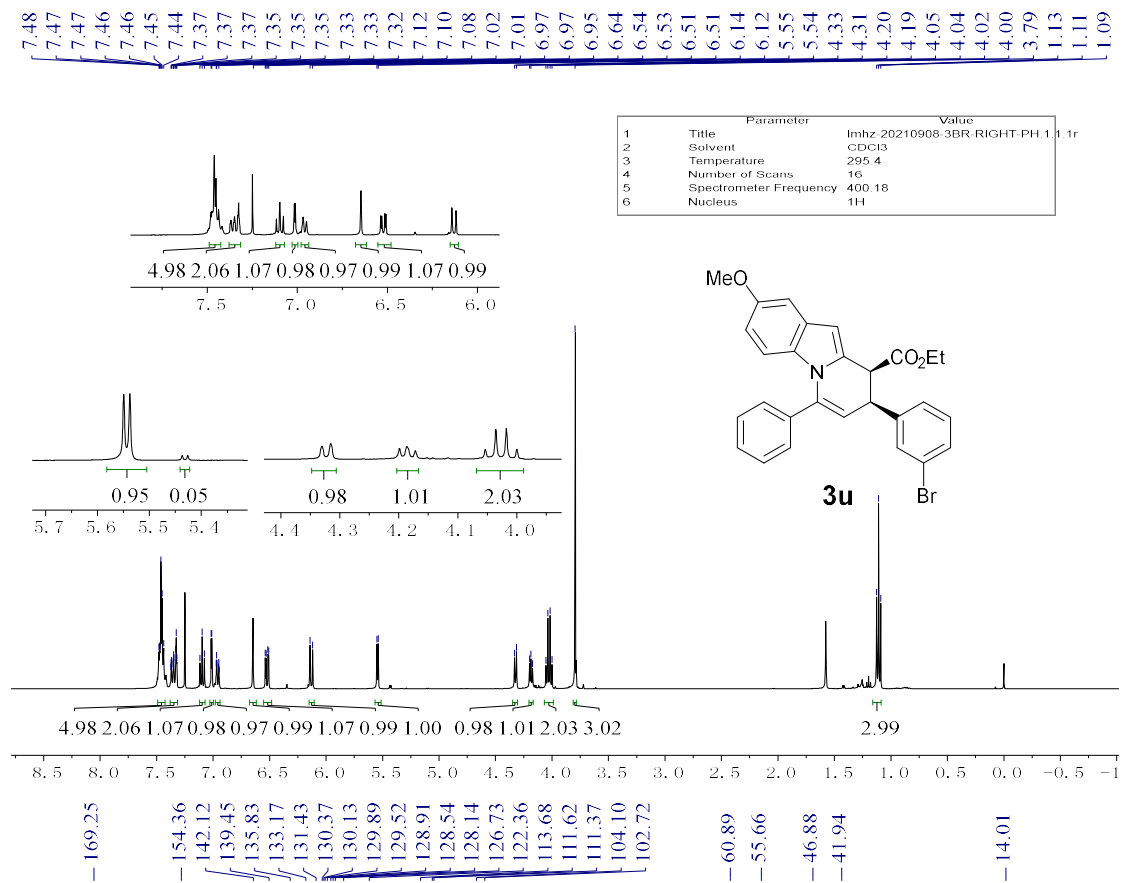


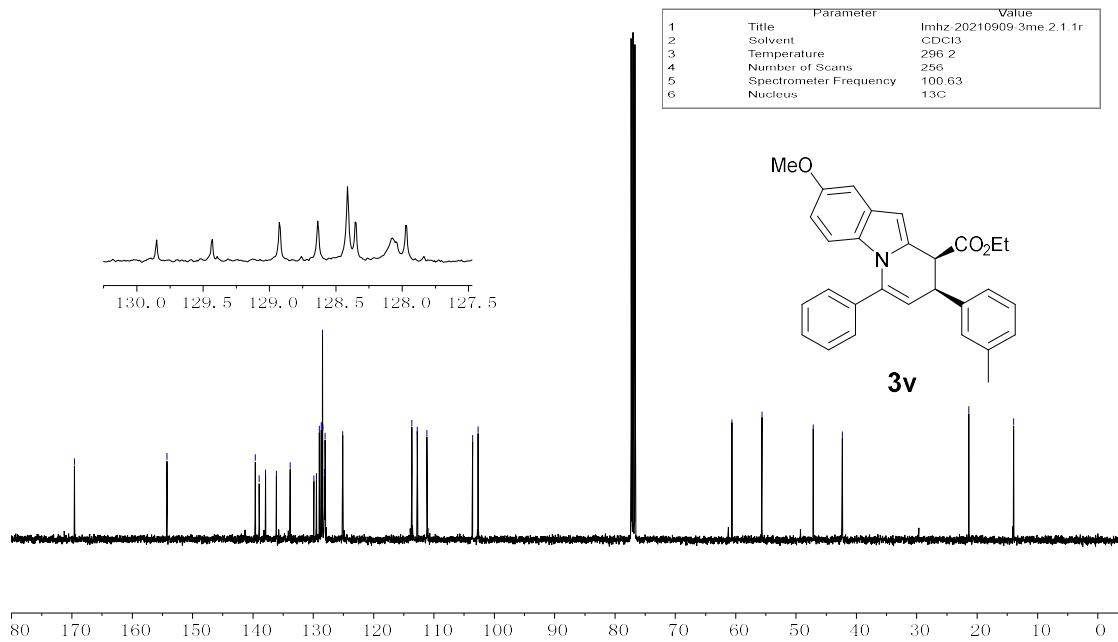
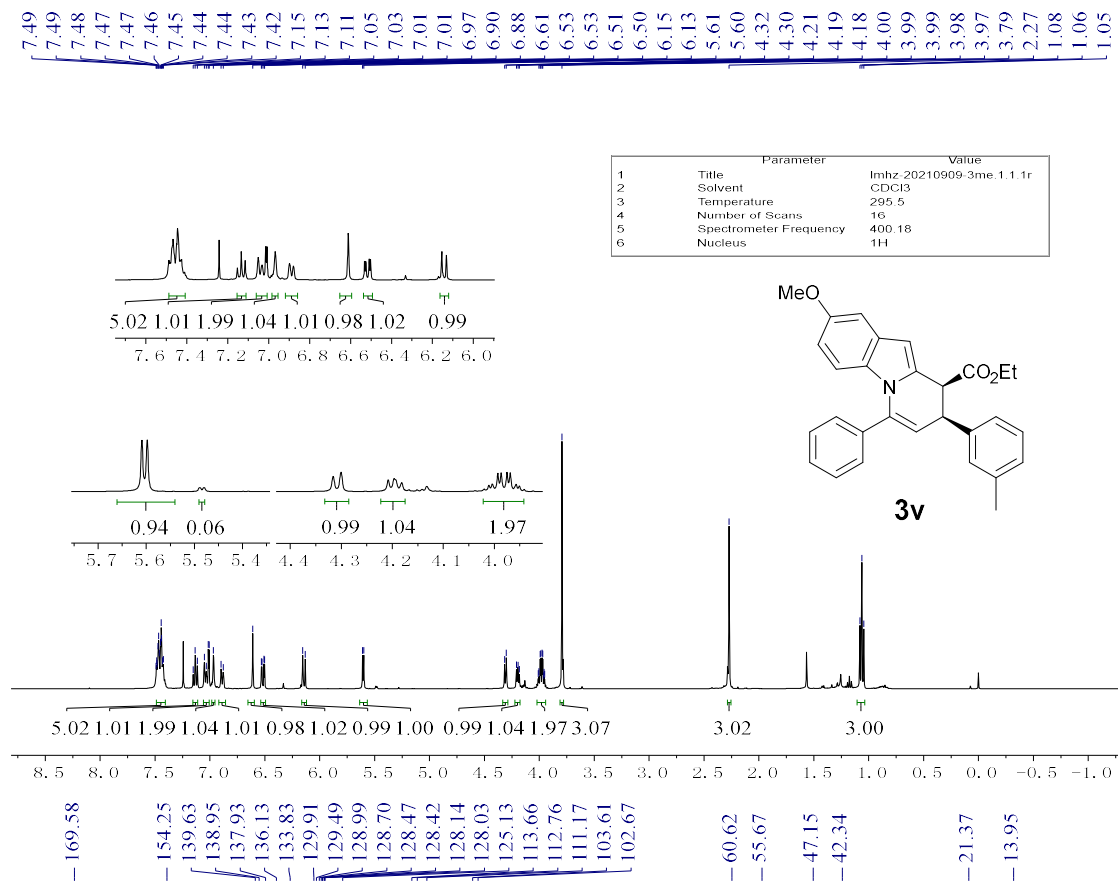
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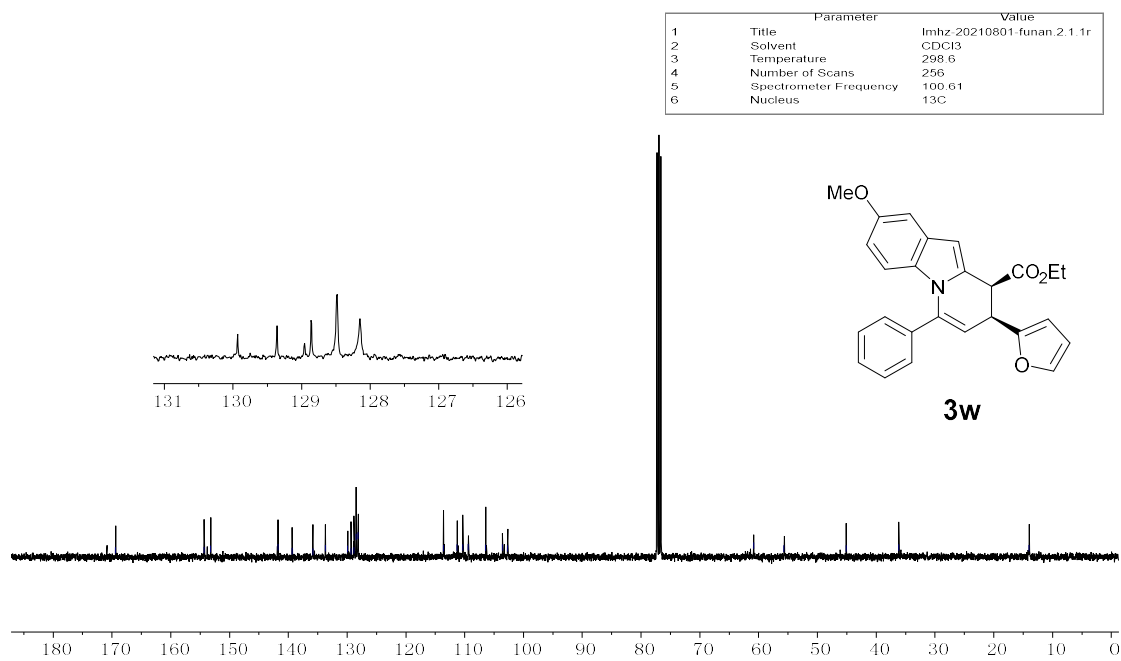
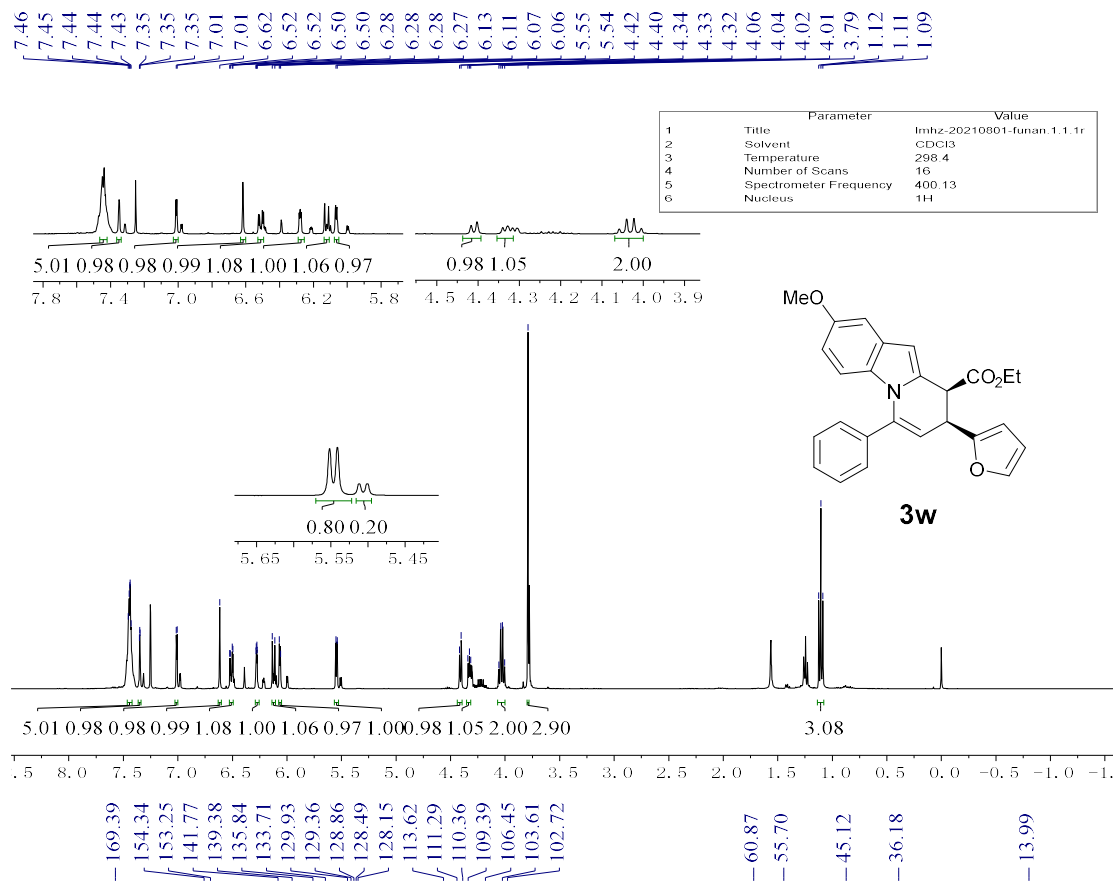




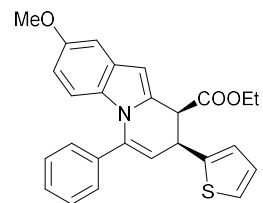
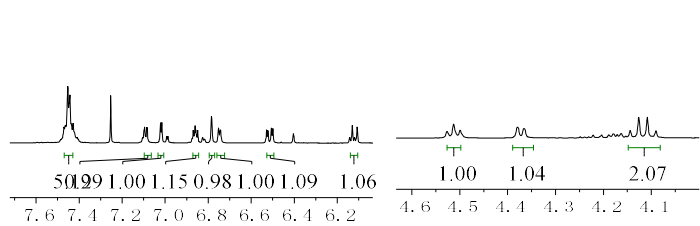






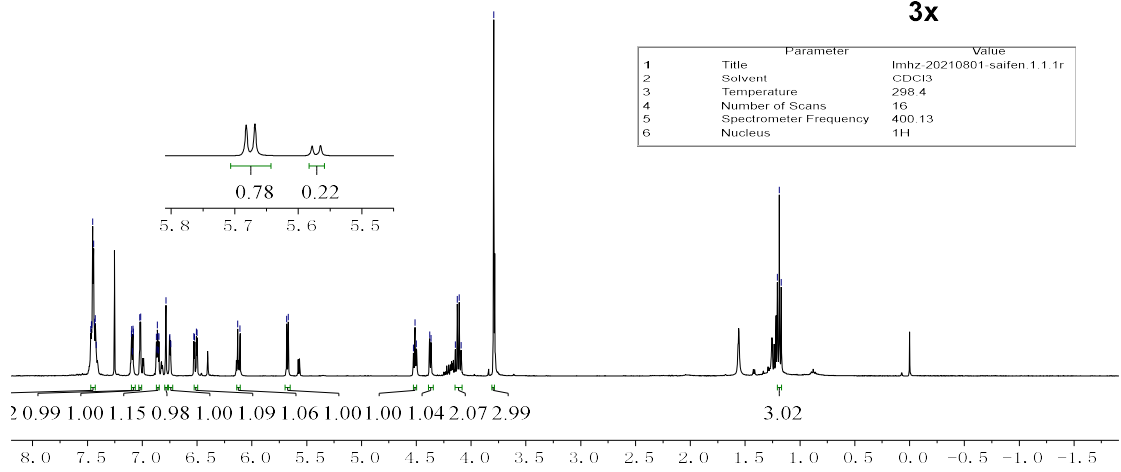


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6.86
6.85
6.85
6.78
6.75
6.74
6.53
6.52
6.51
6.50
6.13
6.11
5.68
5.67
4.53
4.51
4.50
4.38
4.37
4.14
4.13
4.11
4.09
3.79
1.21
1.19
1.17



3x

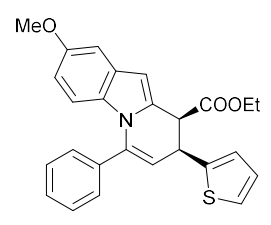
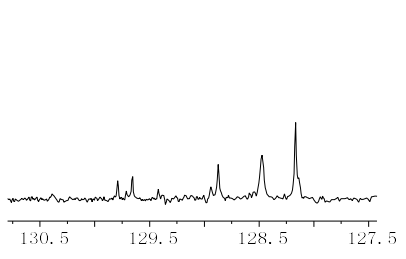
Parameter	Value
1 Title	Imhz 20210801-saifen.1.1.1r
2 Solvent	CDCl3
3 Temperature	298.4
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H



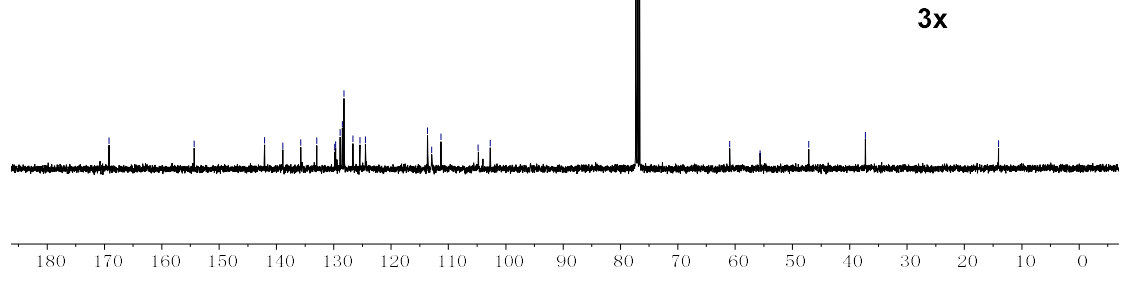
169.19
154.34
142.07
138.88
135.75
132.97
129.83
129.69
128.91
128.51
128.20
126.64
125.45
124.48
113.63
112.93
111.30
104.81
102.73

60.94
55.64
47.14
37.30
14.06

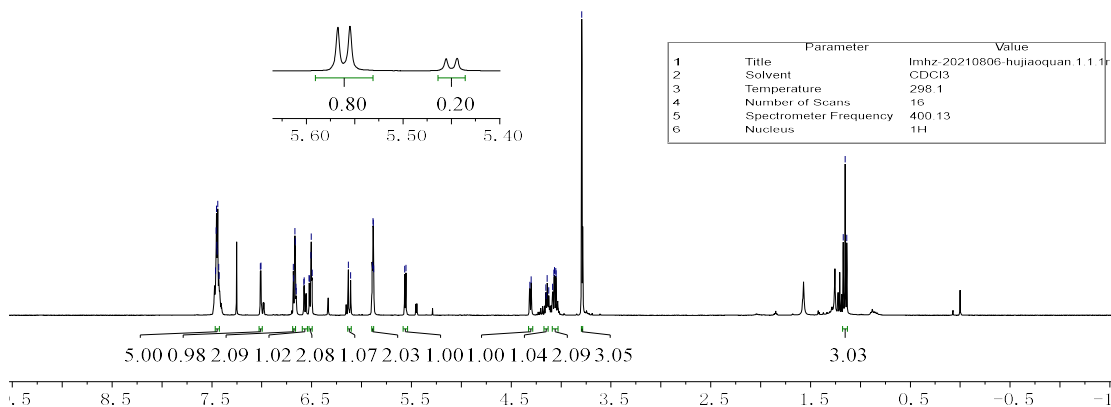
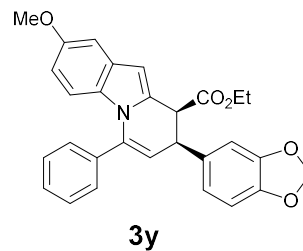
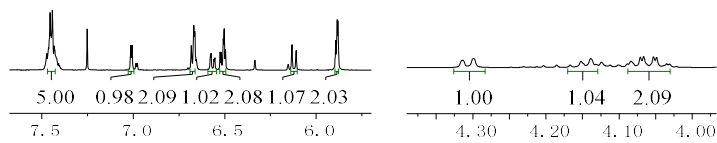
Parameter	Value
1 Title	Imhz 20210801-saifen.2.1.1r
2 Solvent	CDCl3
3 Temperature	298.6
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



3x



7.46
7.45
7.45
7.44
7.43
7.43
7.01
7.01
6.68
6.68
6.67
6.66
6.66
6.65
6.58
6.57
6.53
6.52
6.51
6.50
6.50
6.13
6.11
6.11
5.89
5.89
5.88
5.88
5.57
5.55
5.55
4.31
4.30
4.15
4.14
4.12
4.08
4.07
4.07
4.05
4.05
3.79
1.17
1.15
1.14

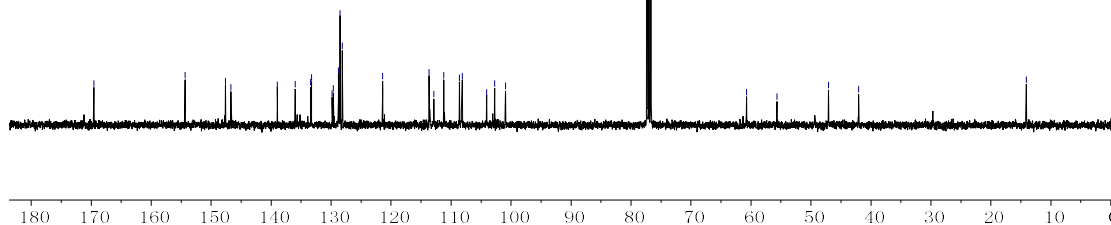
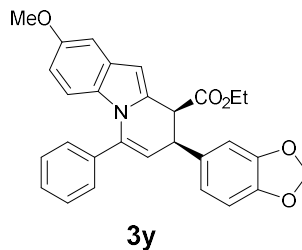
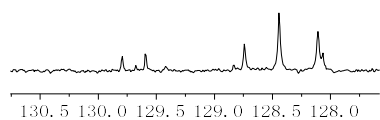


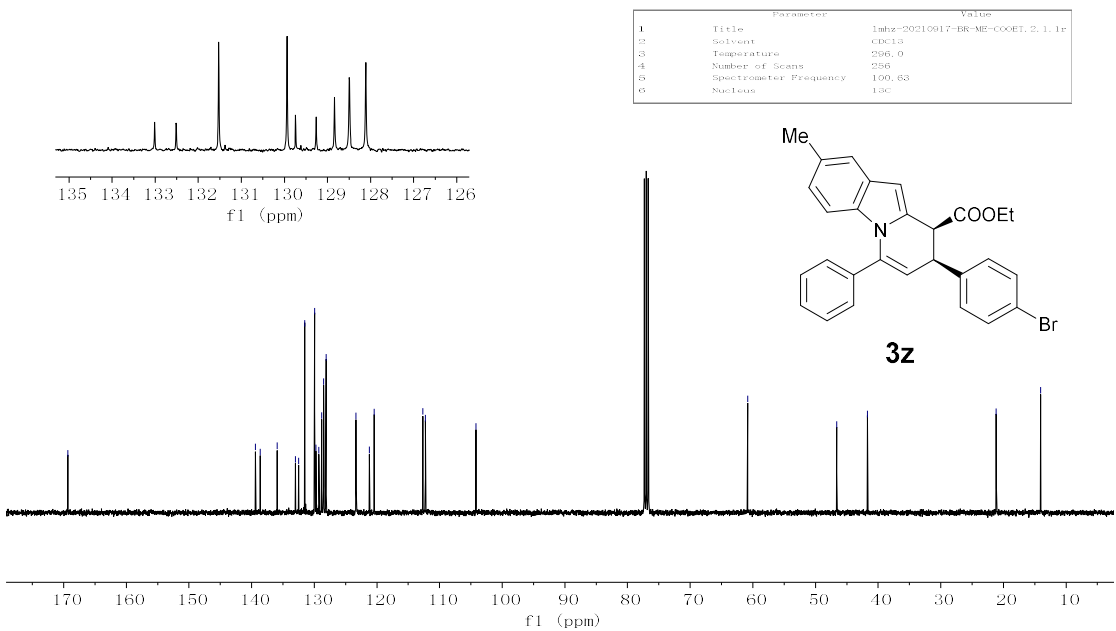
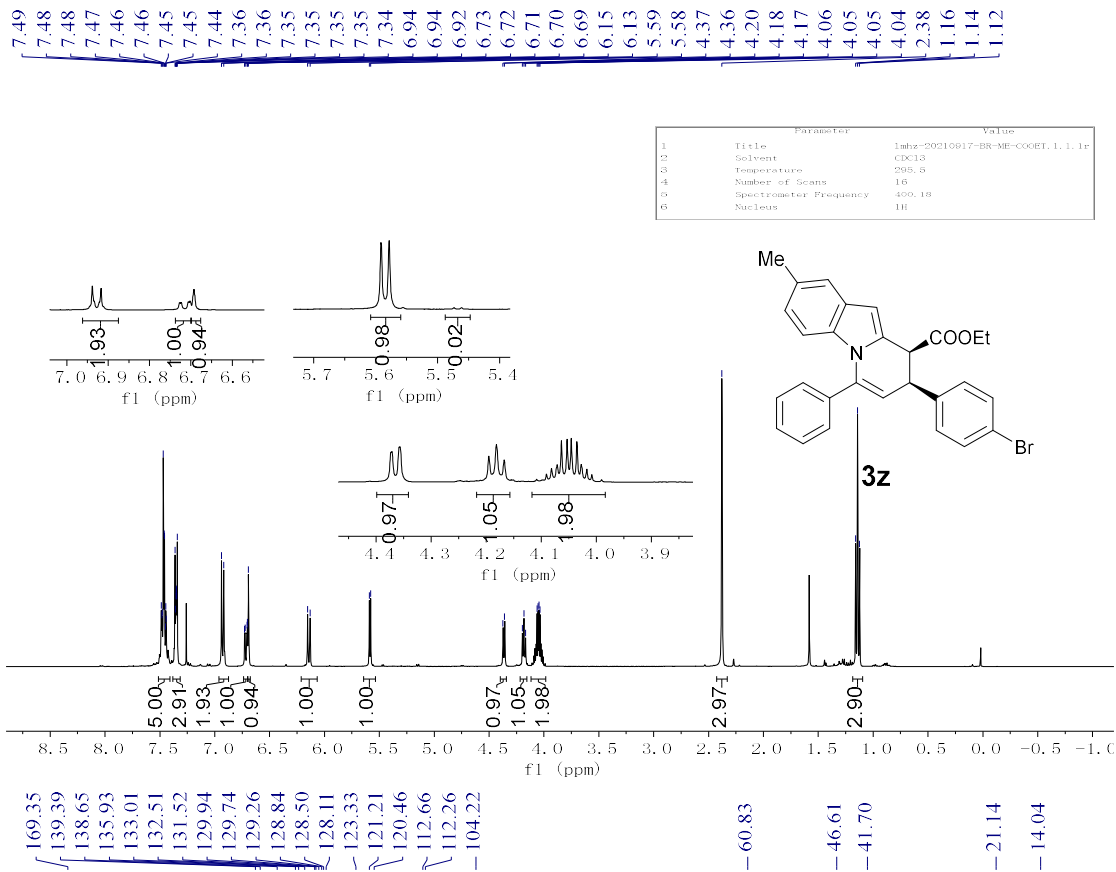
Parameter	Value
1 Title	Imhz-20210806-hujiaoquan 1.1 1
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

169.55
154.31
147.63
146.73
138.96
136.00
133.41
133.28
129.83
129.64
128.78
128.48
128.15
121.43
113.66
112.87
111.23
108.58
108.14
104.09
102.75
100.92

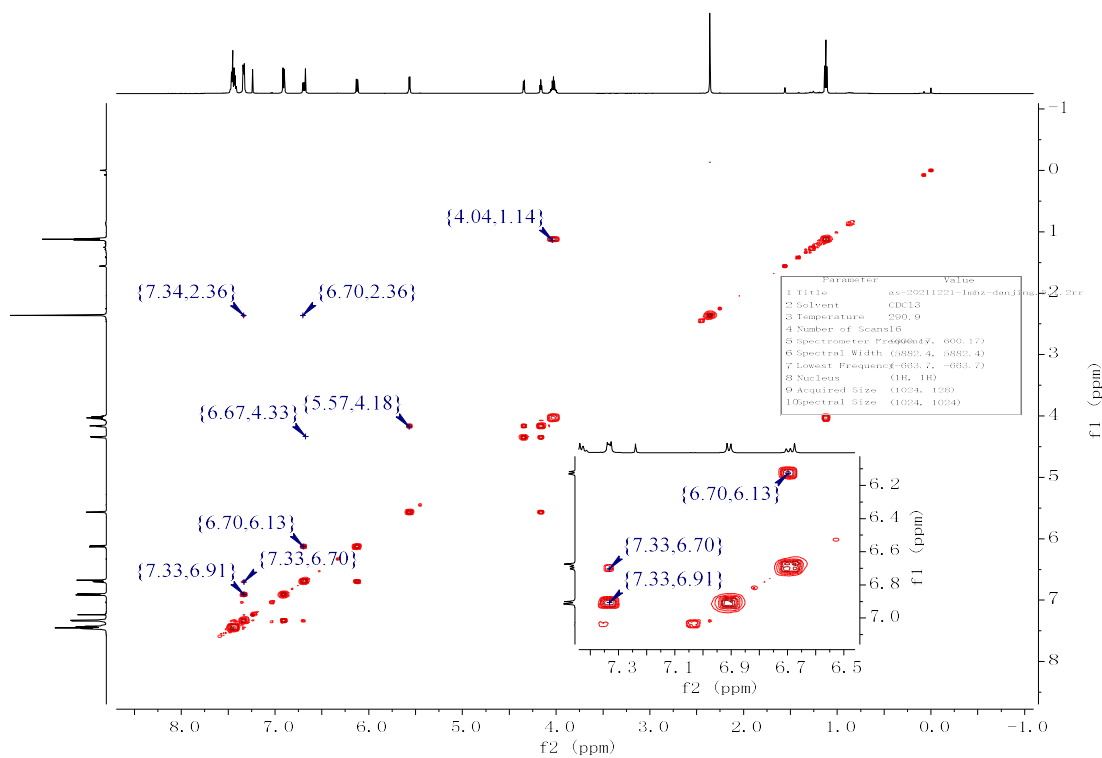
60.76
55.66
47.06
42.03
14.11

Parameter	Value
1 Title	Imhz-20210806-hujiaoquan 2.1 1
2 Solvent	CDCl3
3 Temperature	298.3
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

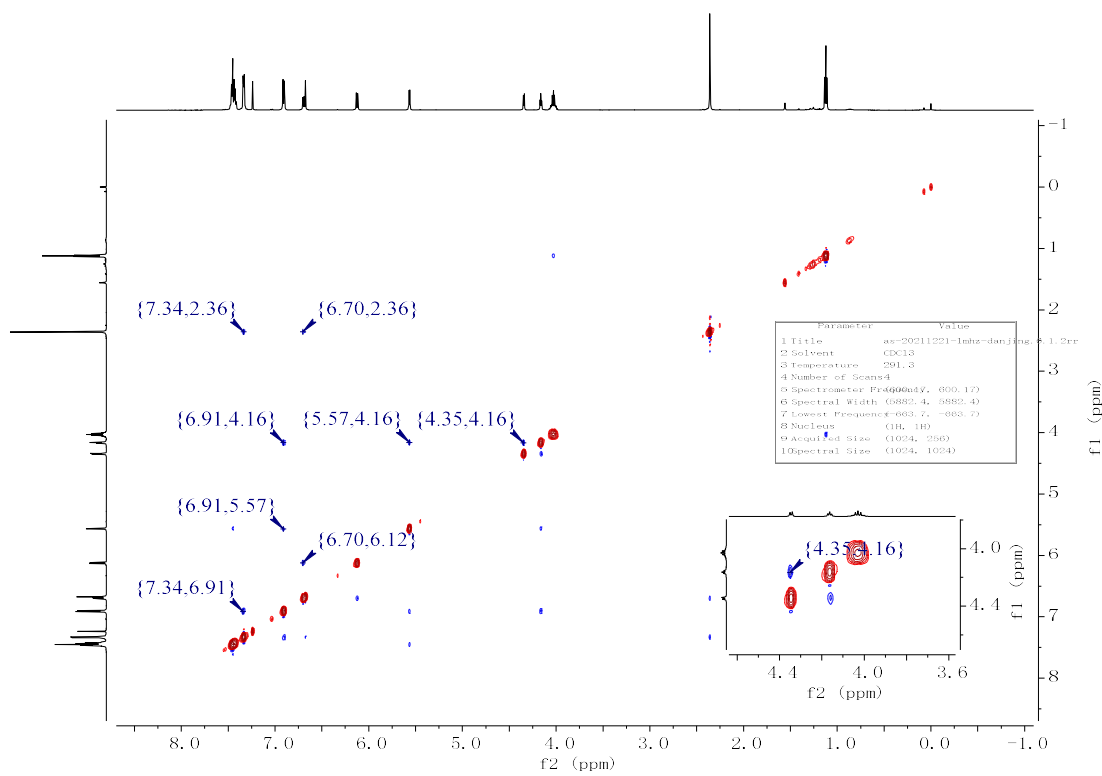




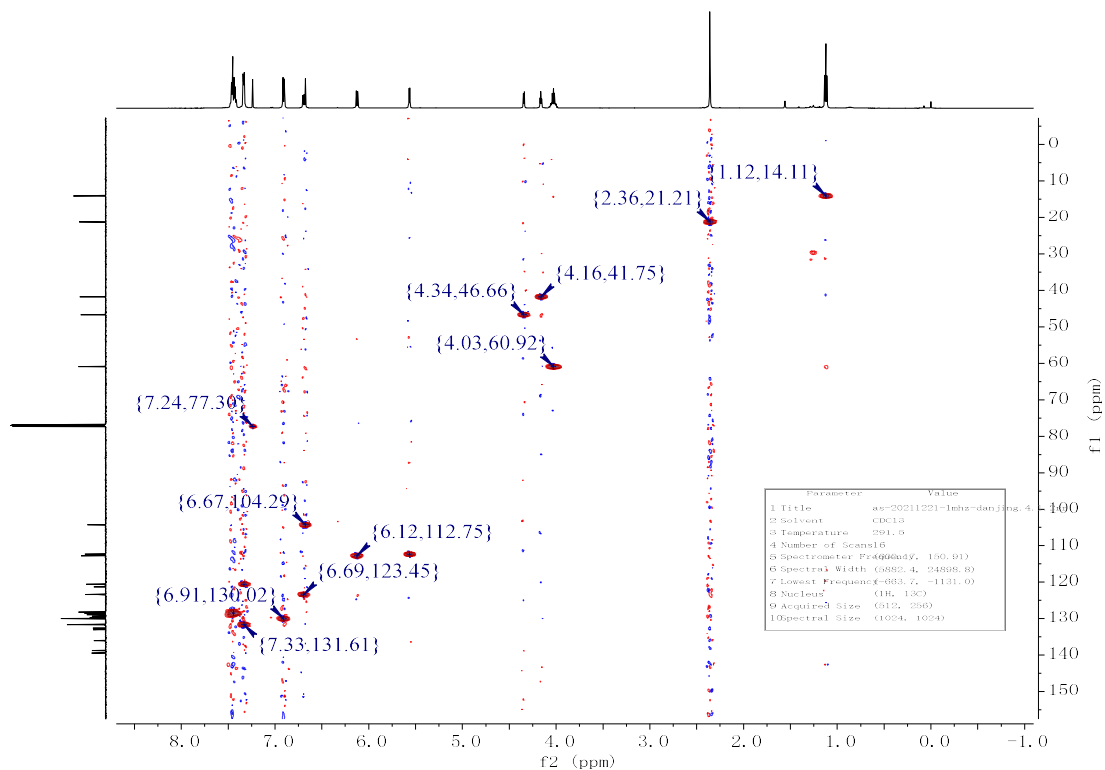
GCOSY:



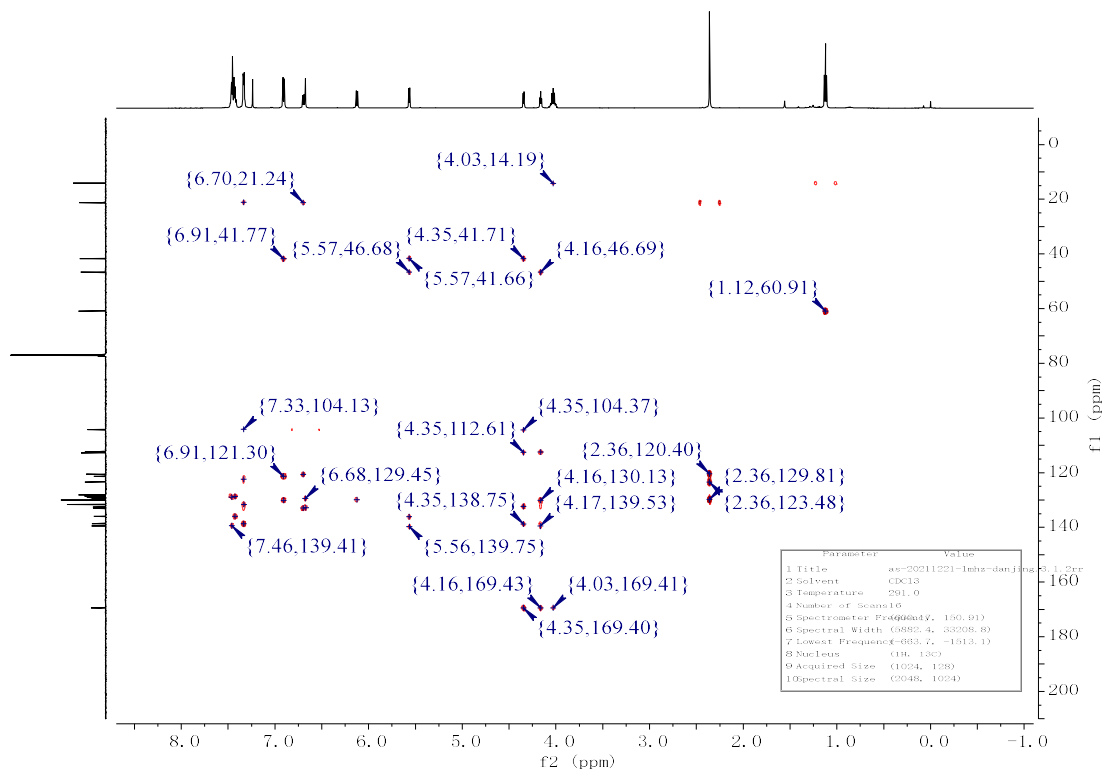
NOESY:



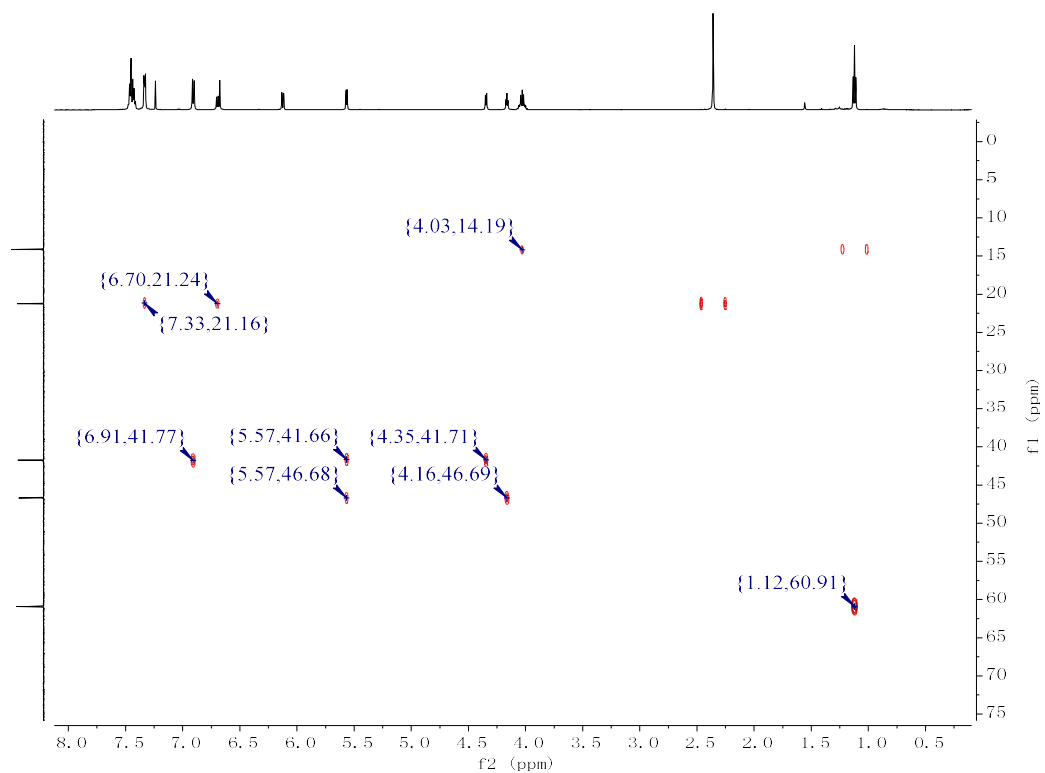
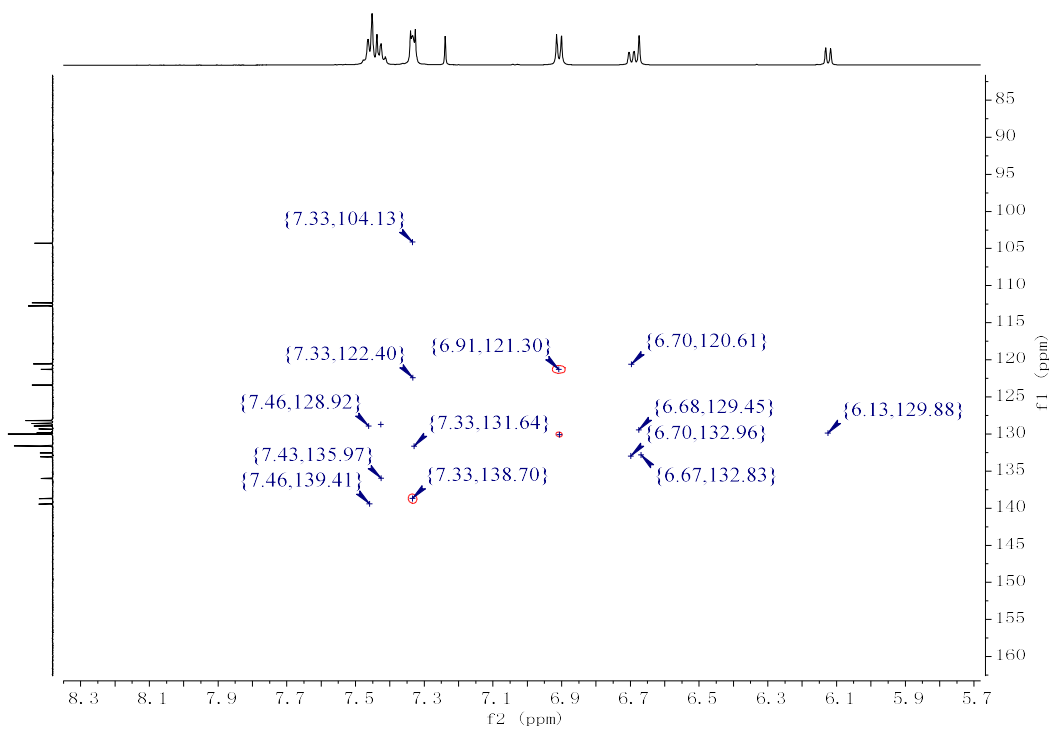
GHSQC

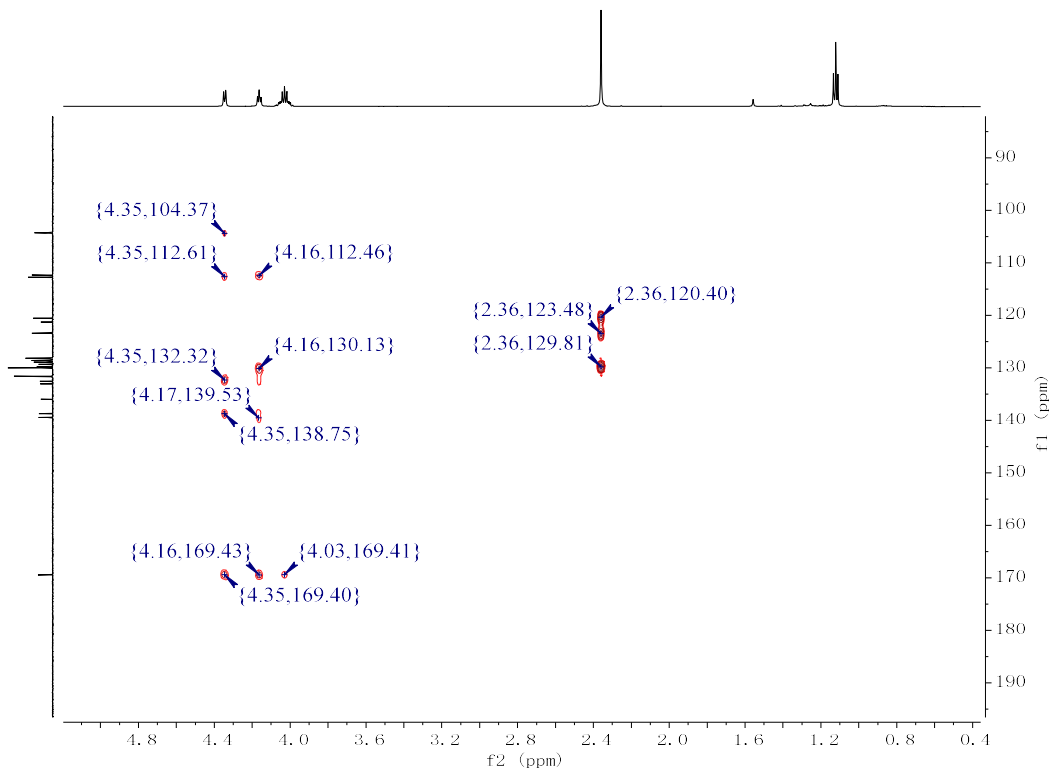


GHMBC



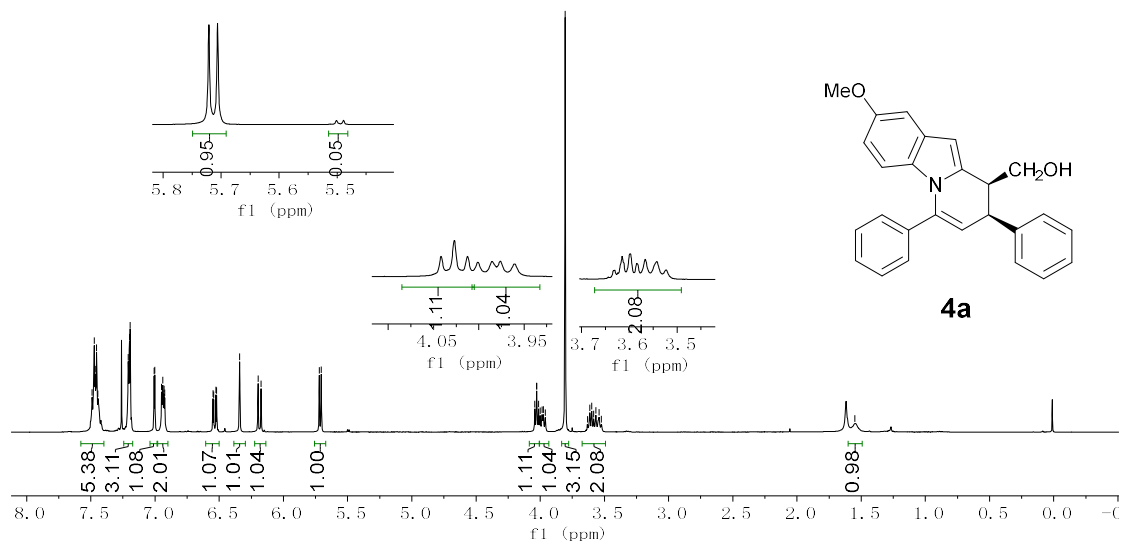
GHMBC(Partial magnification)





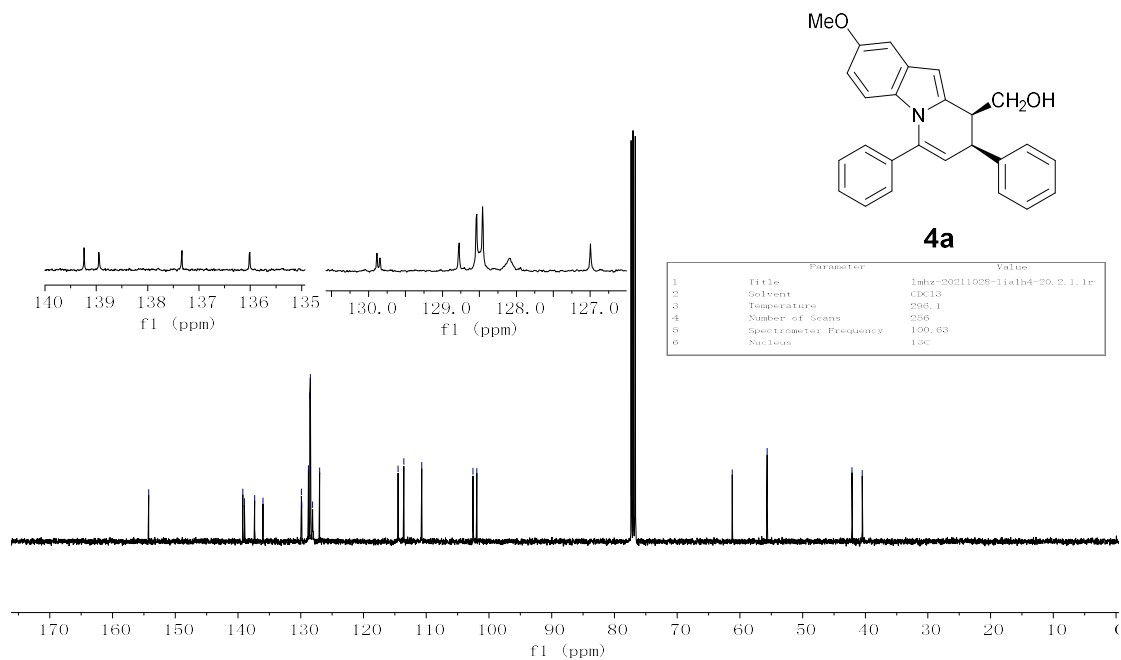
7.49
7.47
7.47
7.46
7.44
7.21
7.20
7.19
7.01
7.00
6.95
6.94
6.94
6.93
6.92
6.55
6.55
6.54
6.53
6.52
6.34
6.20
6.18
5.72
5.71
4.04
4.03
4.03
4.01
4.00
3.99
3.98
3.96
3.81
3.63
3.61
3.60
3.58
3.57
3.54
3.52
1.55

Parameter	Value
1 Title	1mhz-20211028-1ia1h4-20.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.2
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

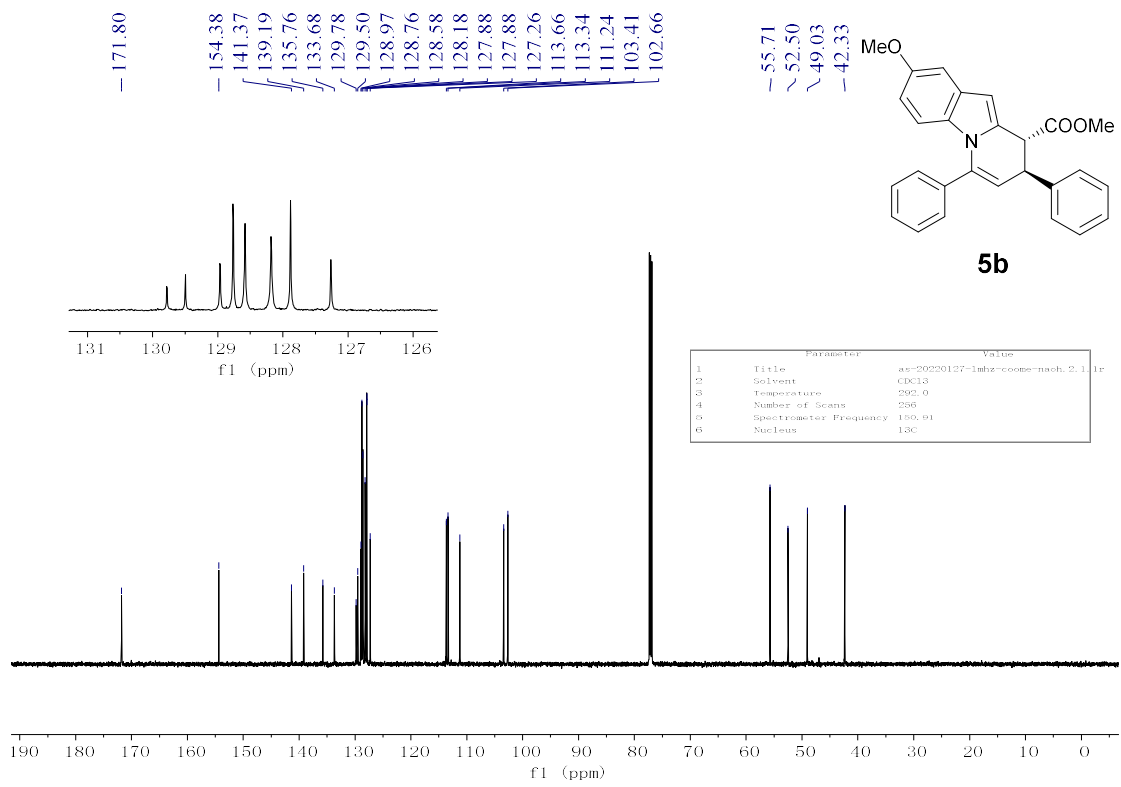
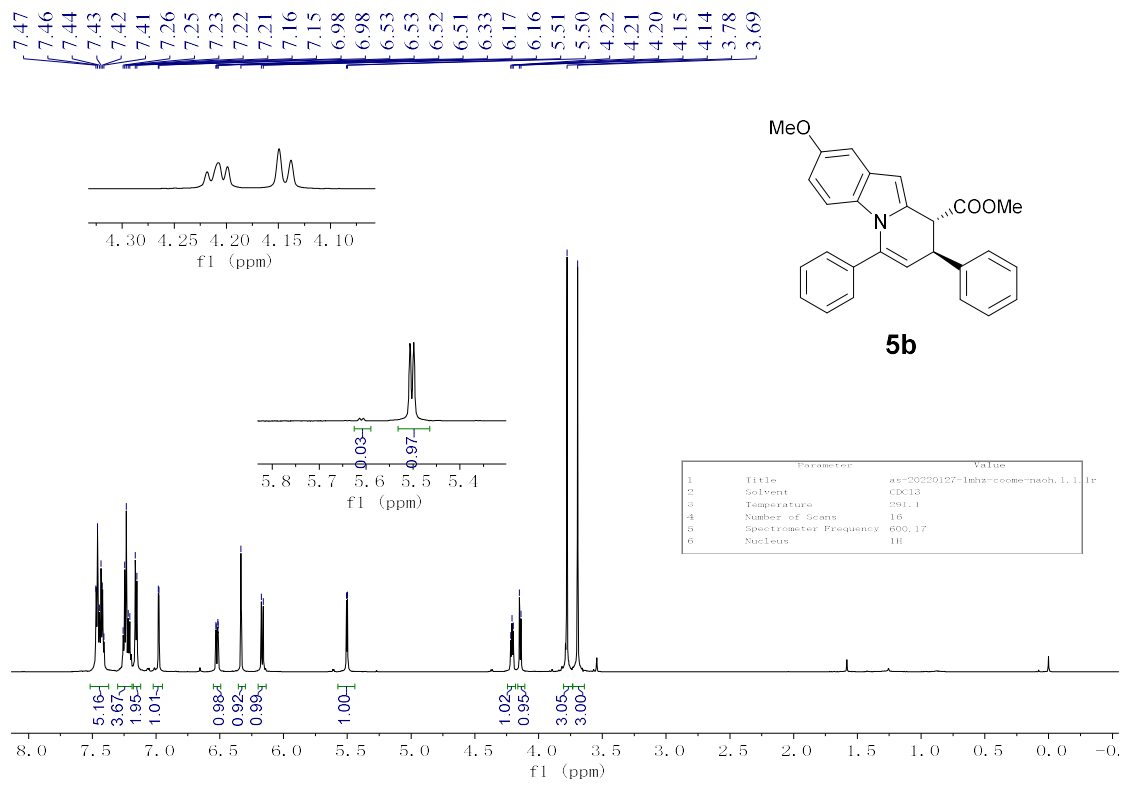


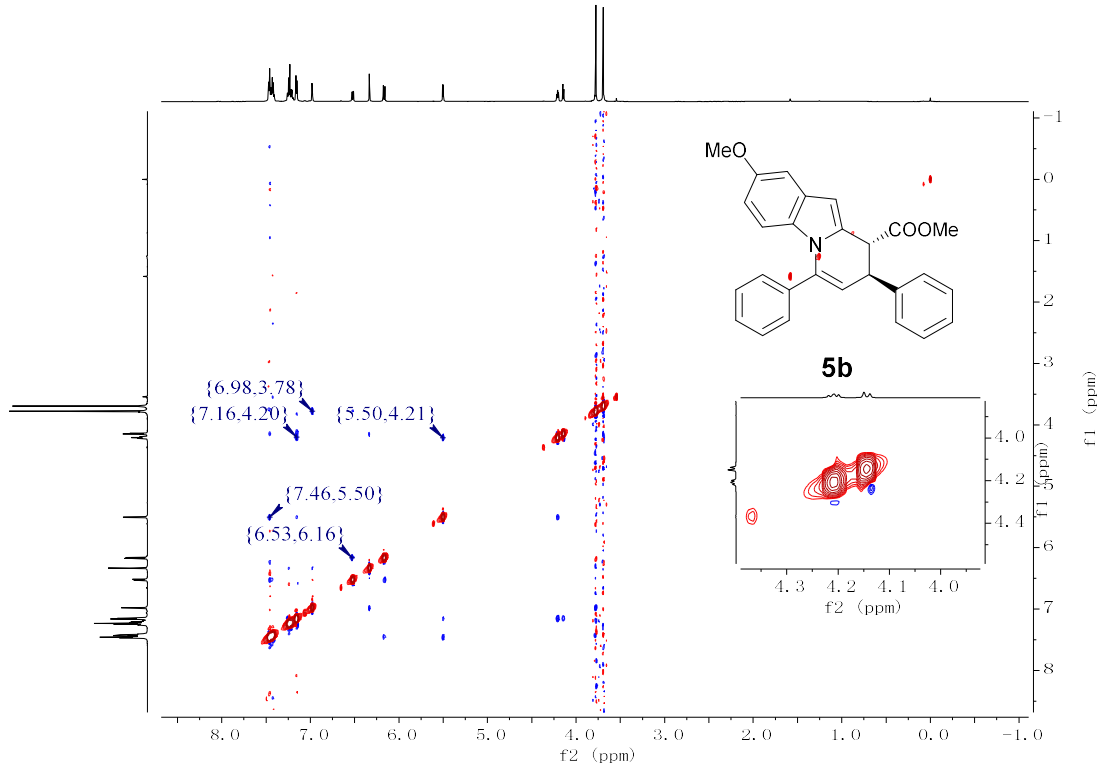
154.23
139.24
138.95
137.33
136.01
129.89
129.85
128.78
128.54
128.46
128.09
127.00
114.48
113.58
110.72
102.51
101.94

61.19
55.66
42.12
40.48

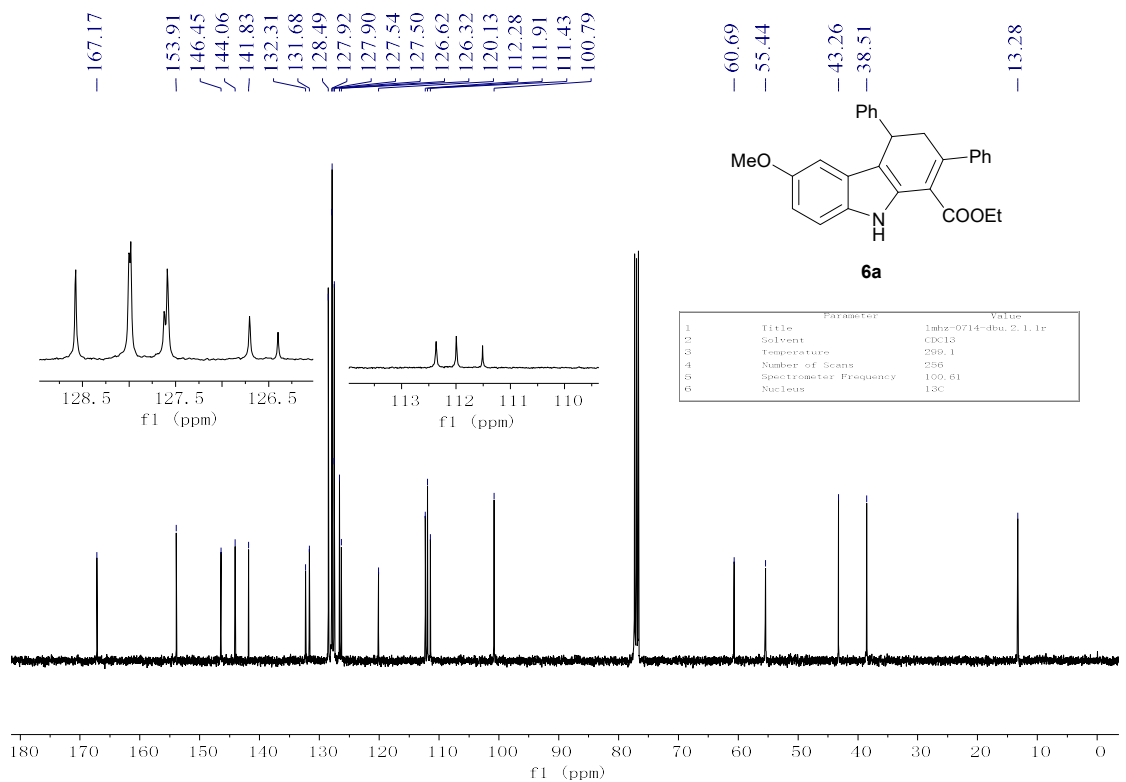
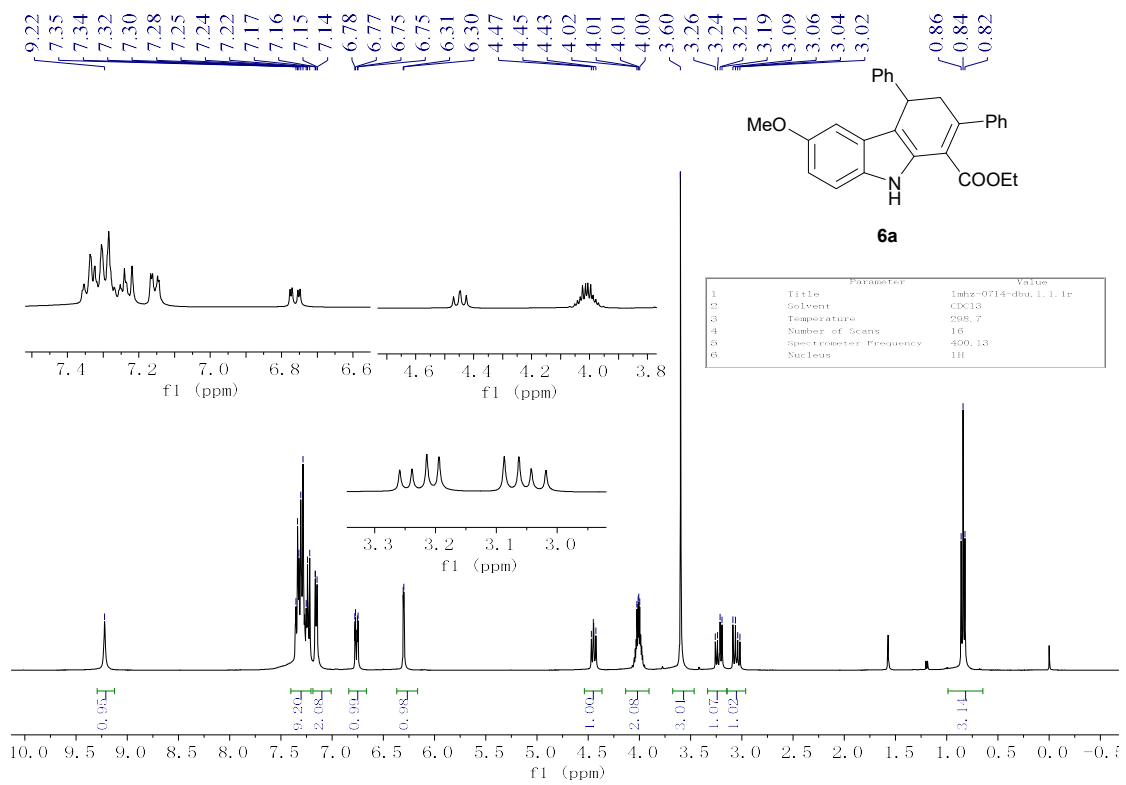


Parameter	Value
1 Title	1mhz-20211028-1ia1h4-20.2.1.1r
2 Solvent	CDCl3
3 Temperature	296.1
4 Number of Scans	236
5 Spectrometer Frequency	100.63
6 Nucleus	13C



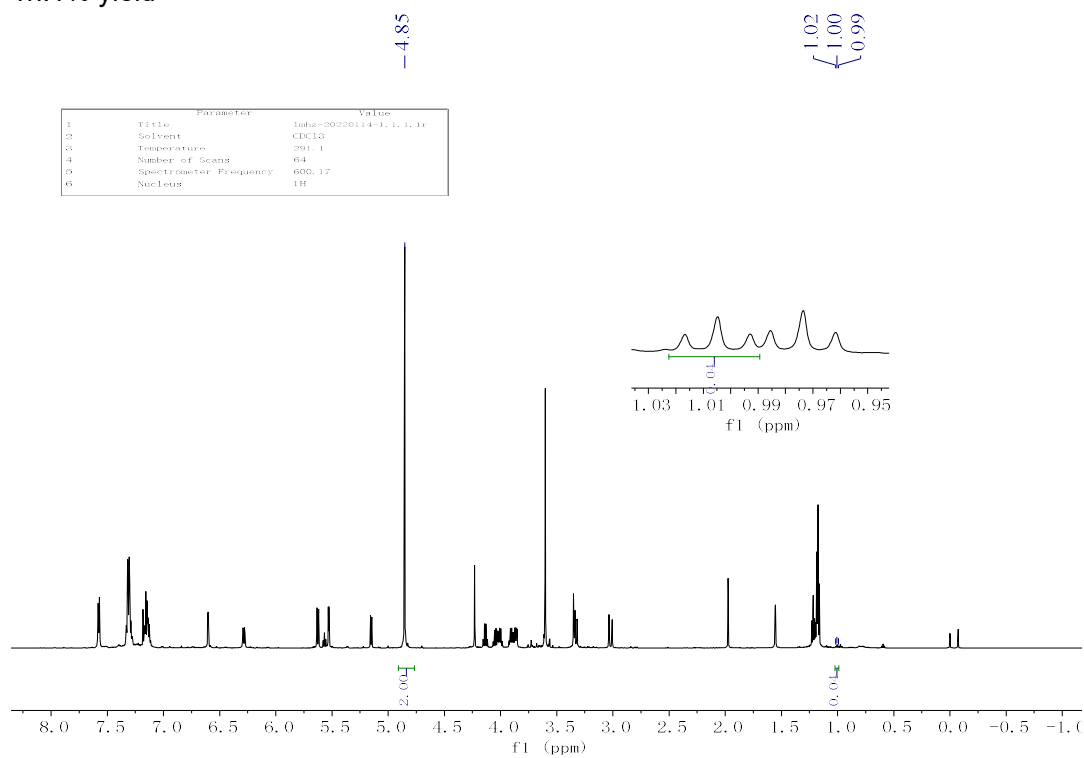


6a

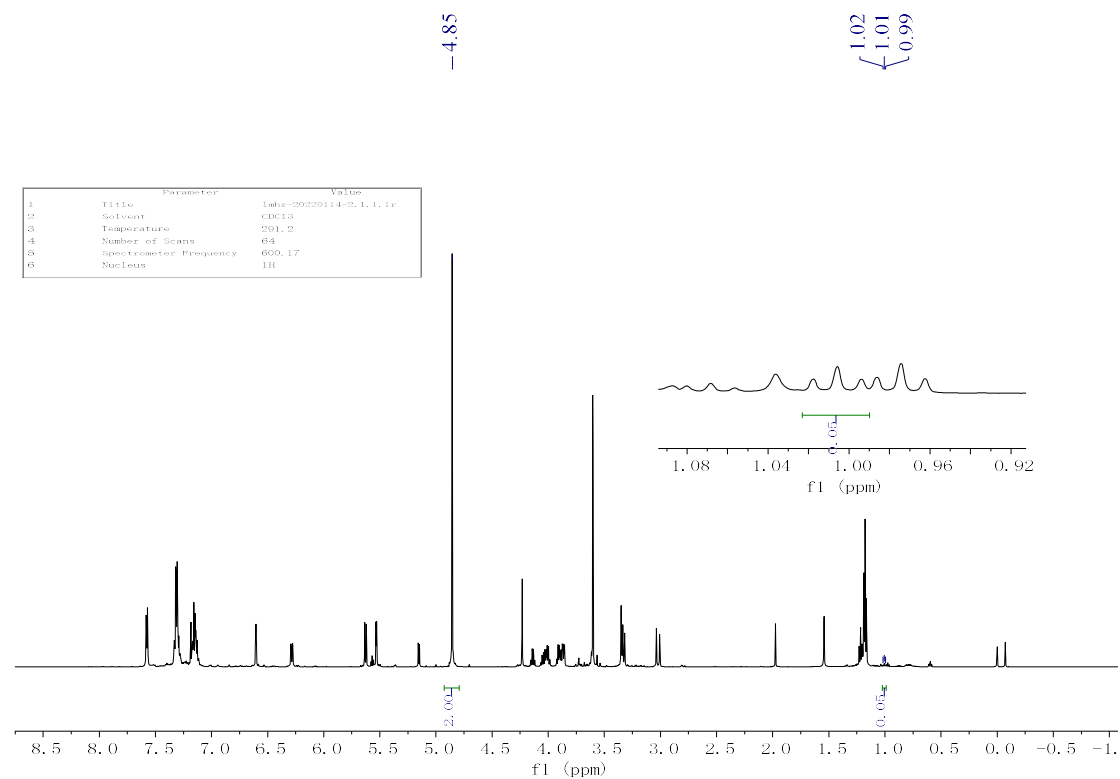


Control experiment NMR:

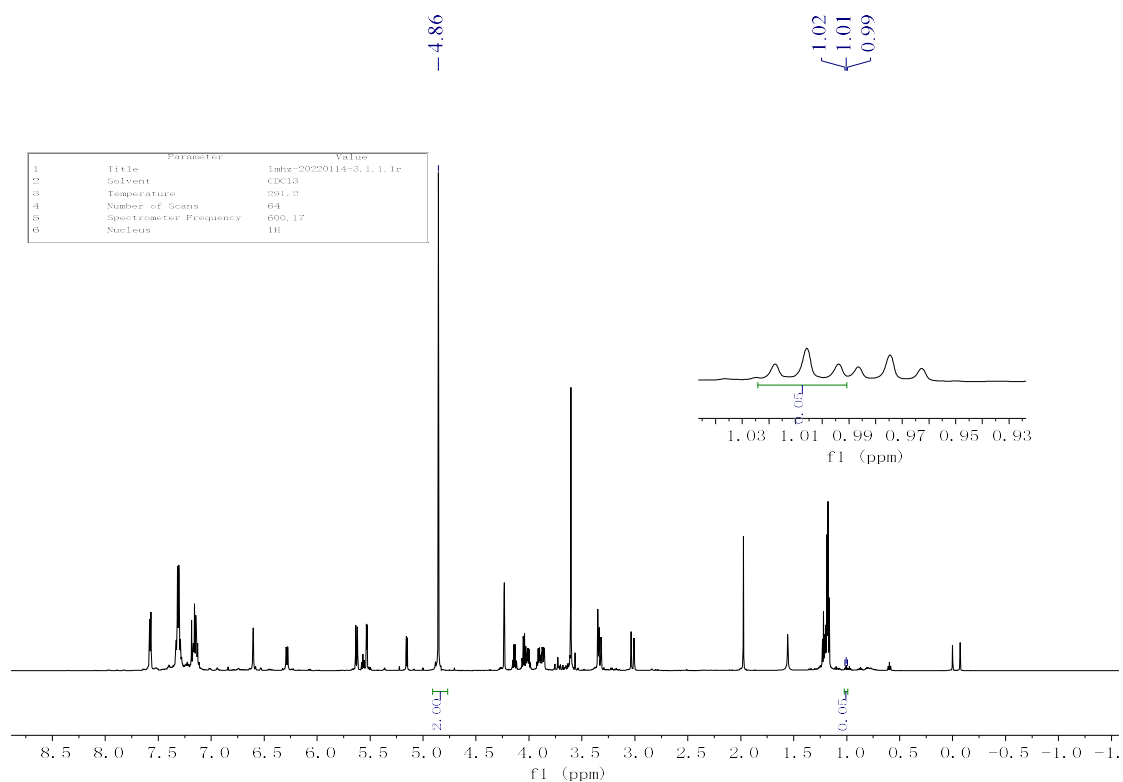
1h:1% yield



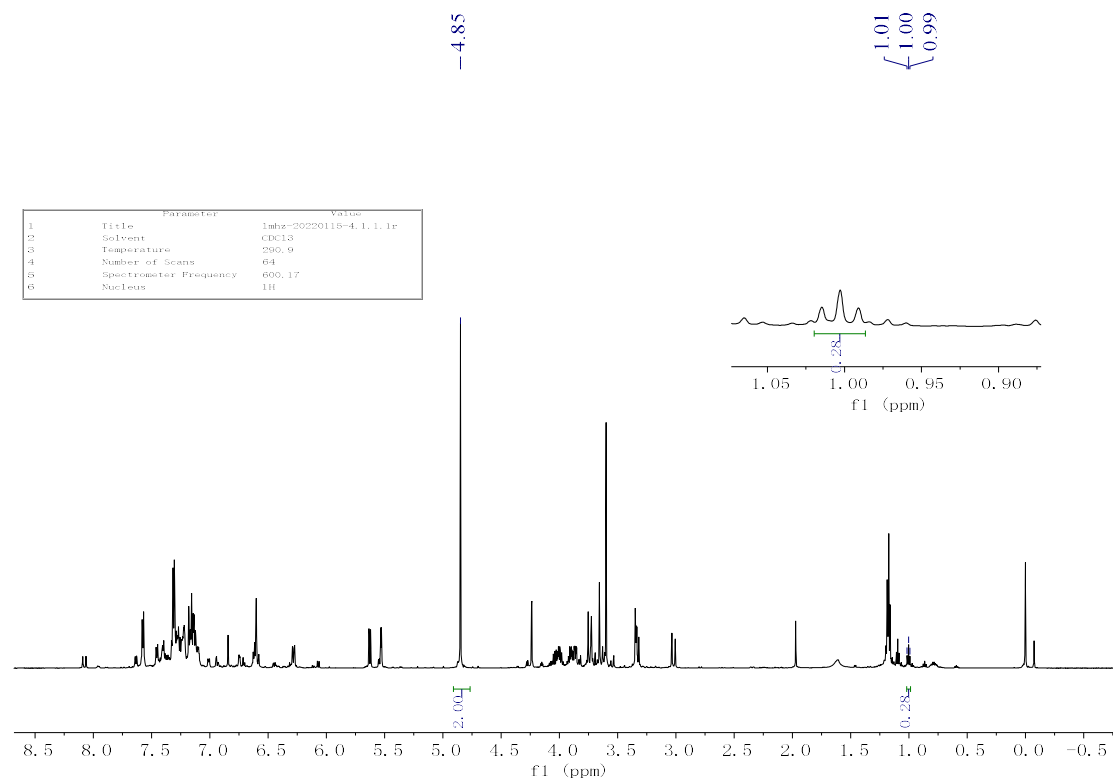
2h:1% yield



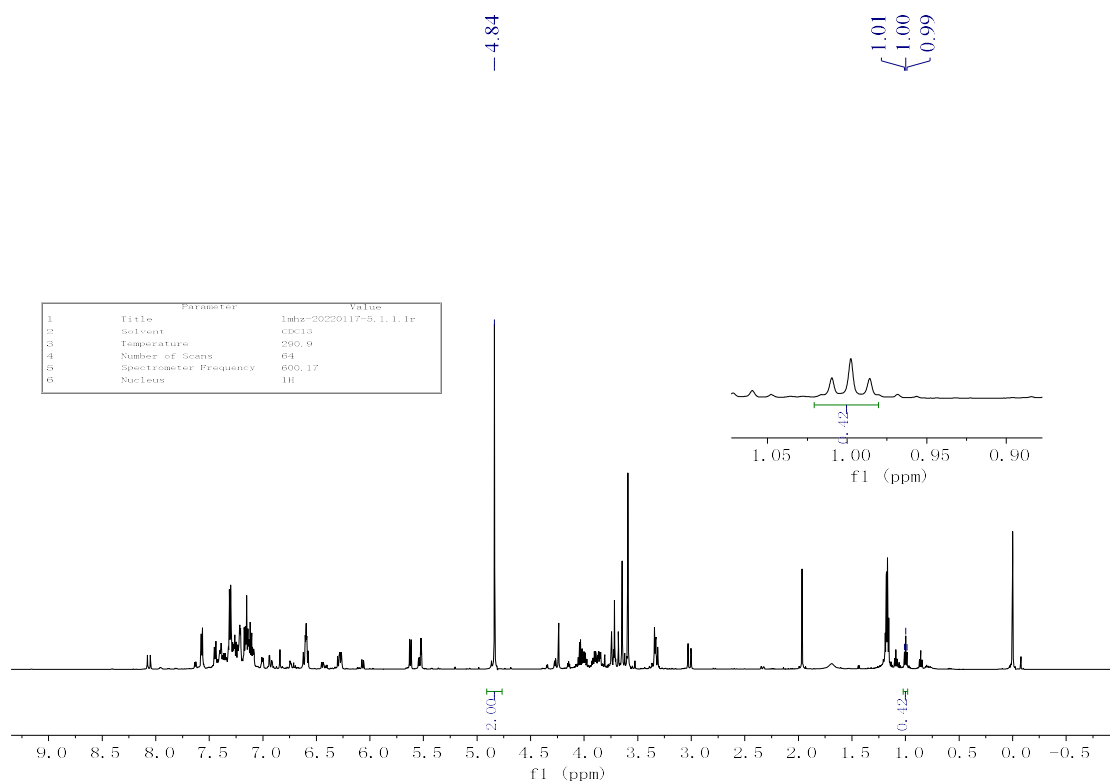
3h:1% yield



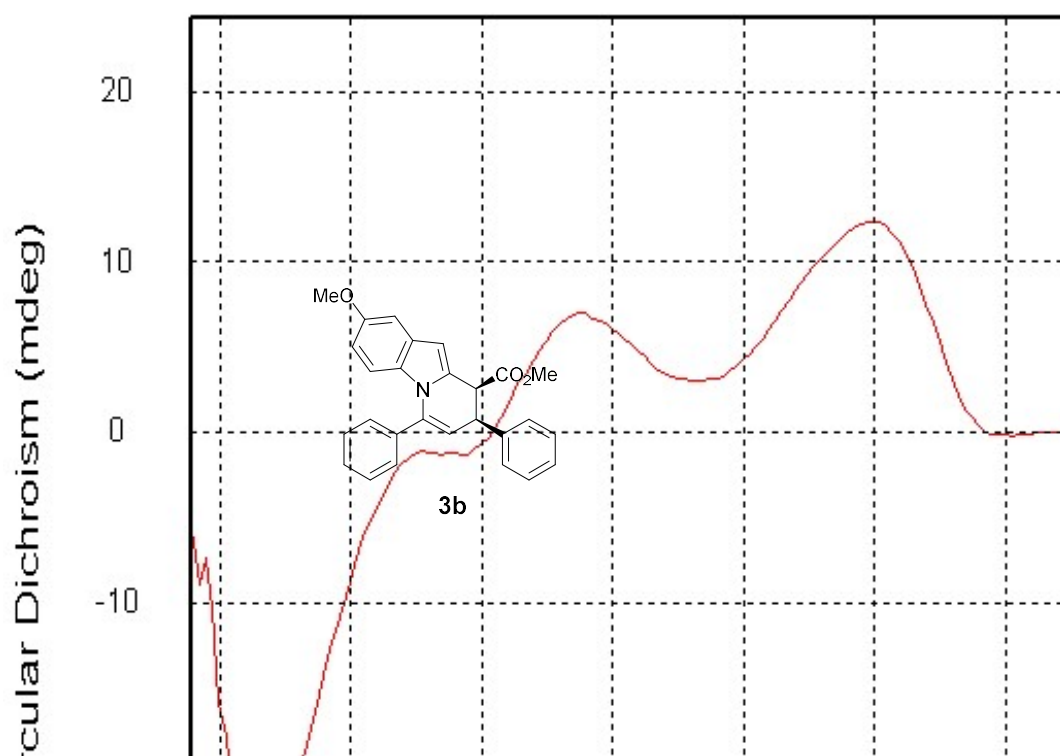
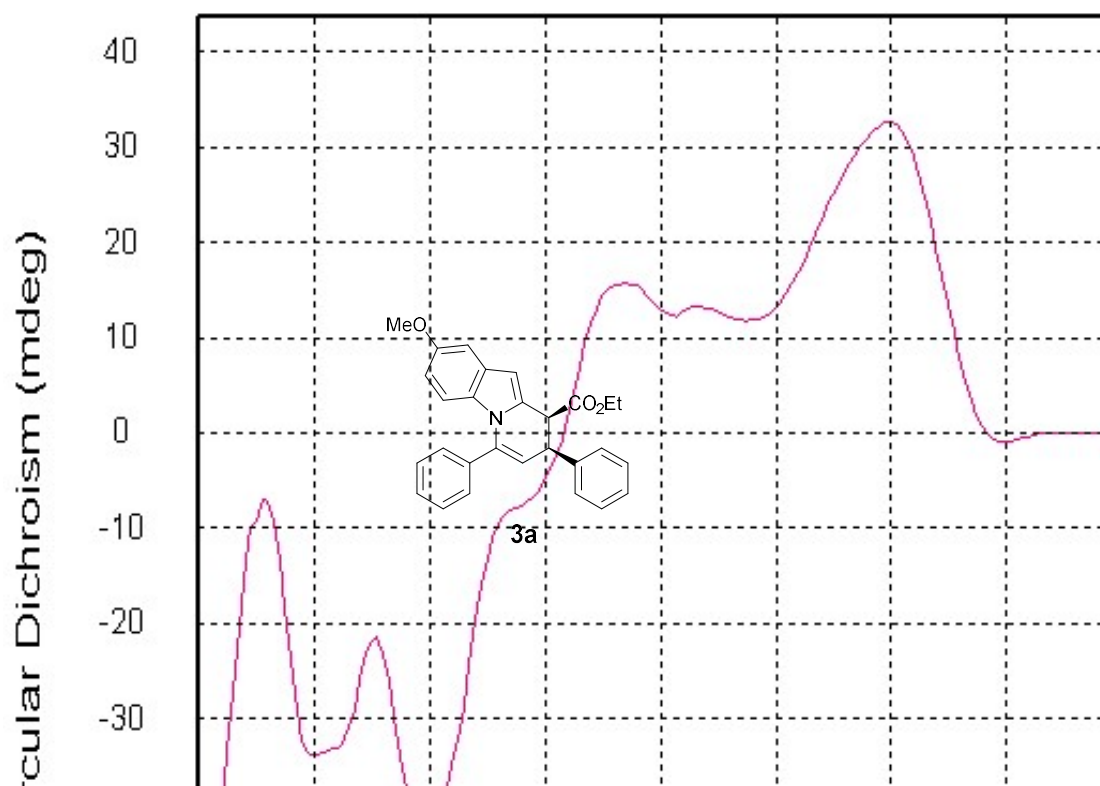
4h:9% yield

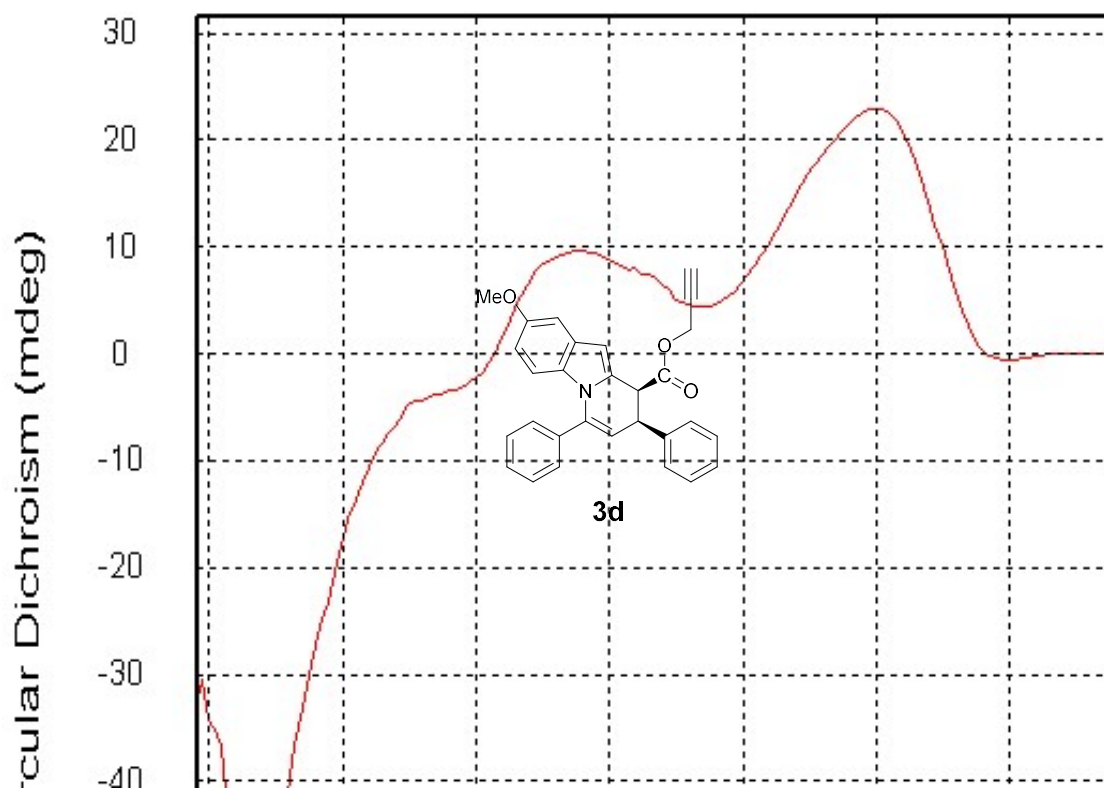
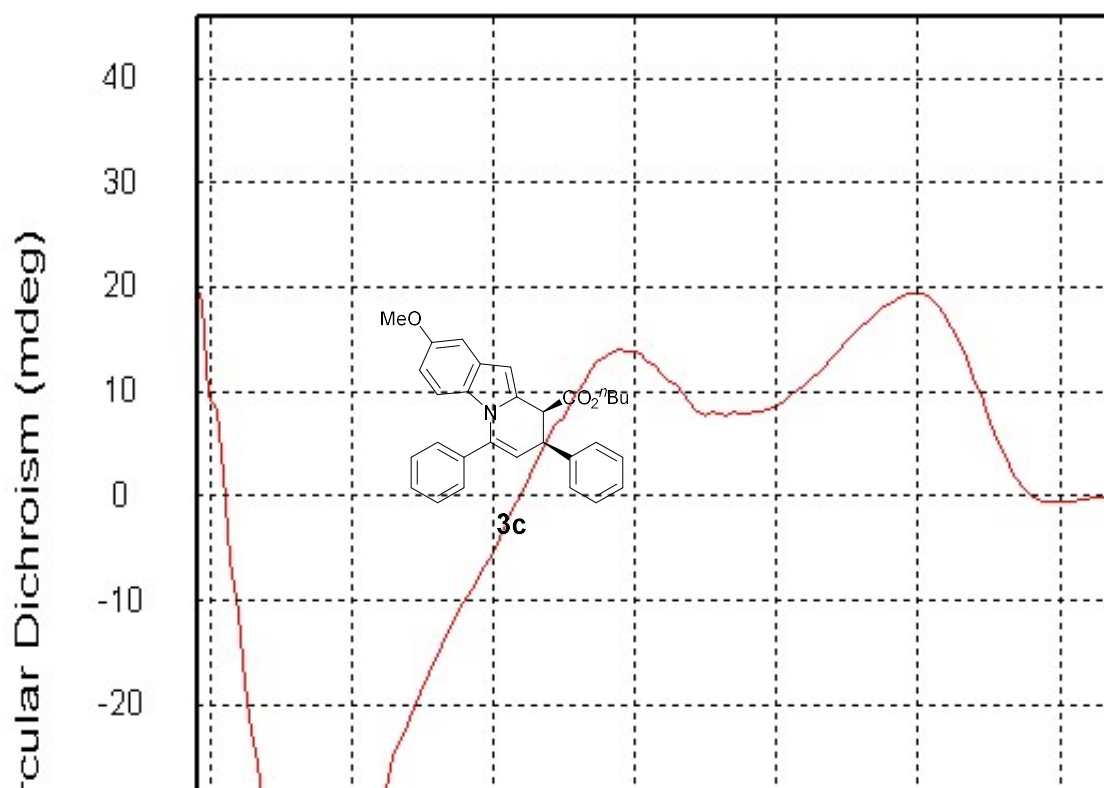


5h:14% yield

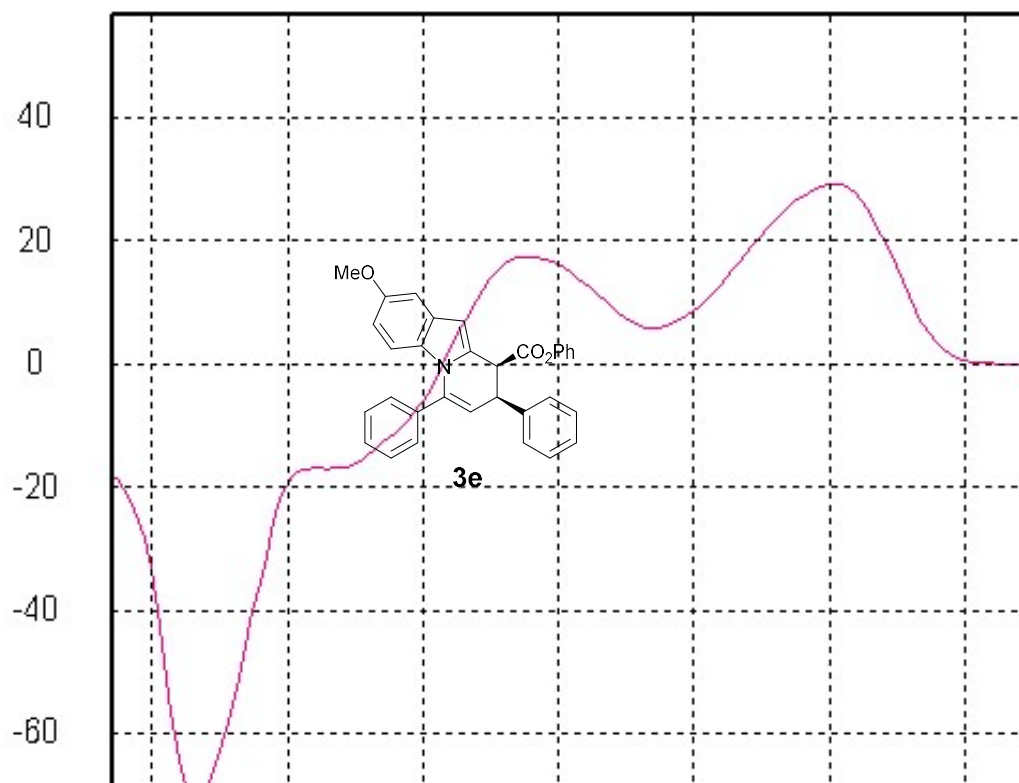


13. Copies of CD spectra for products

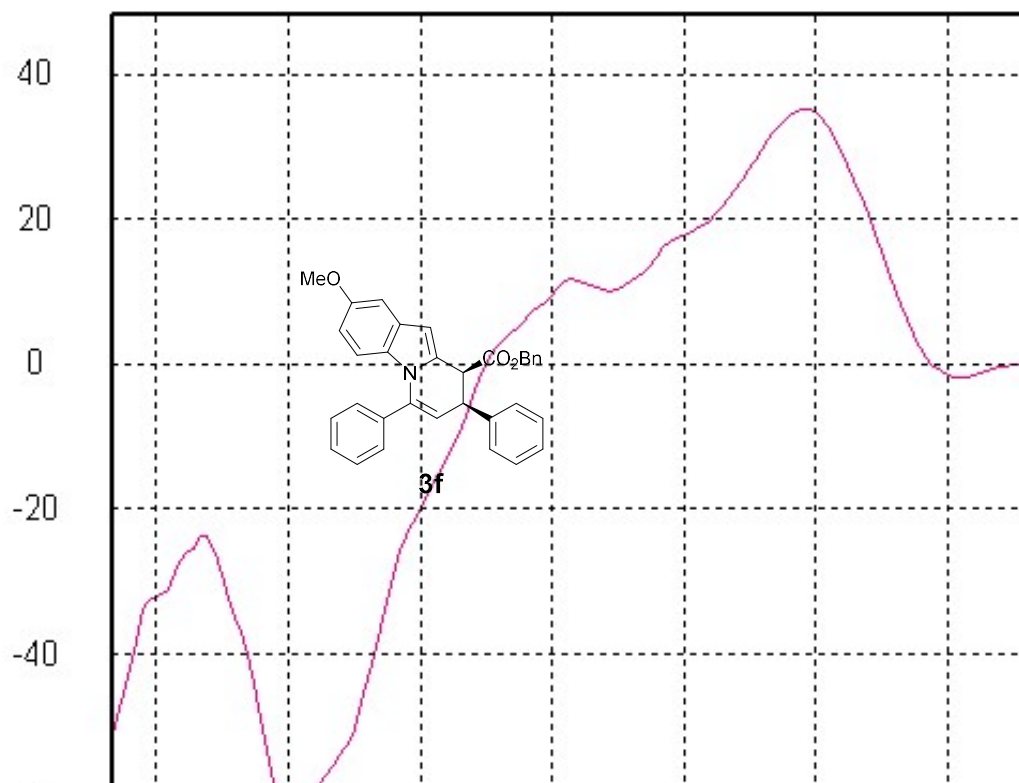


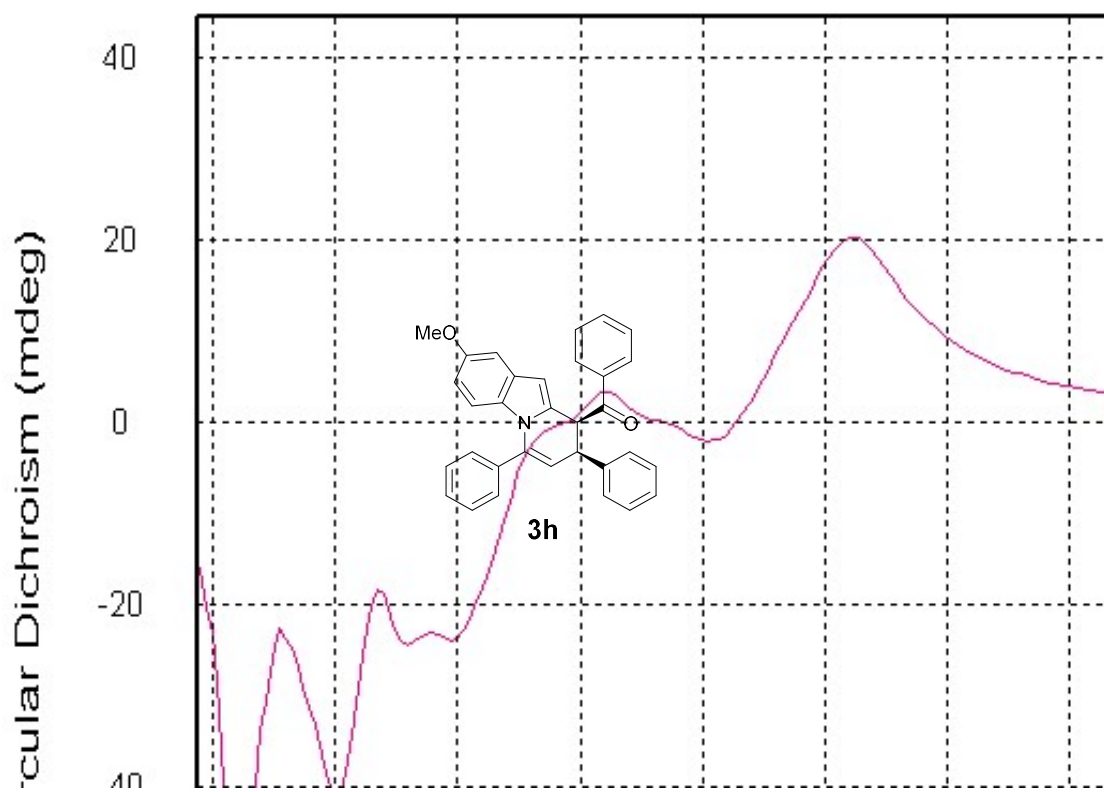
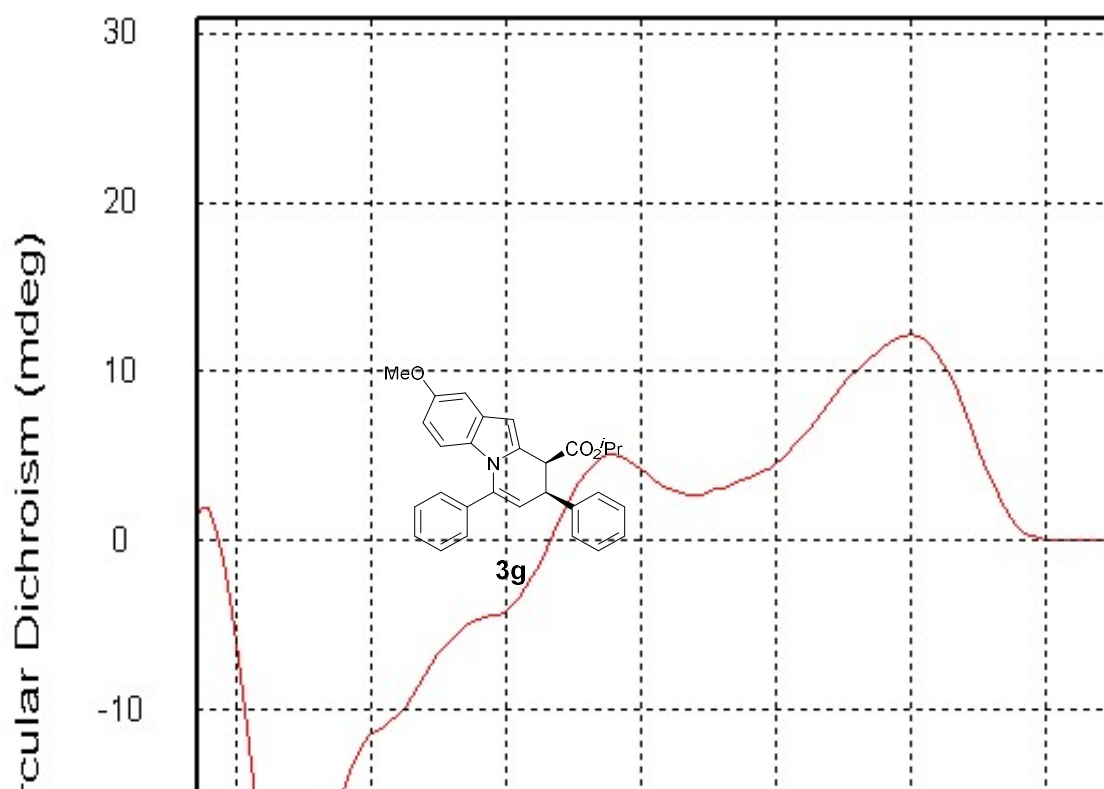


circular Dichroism (mdeg)

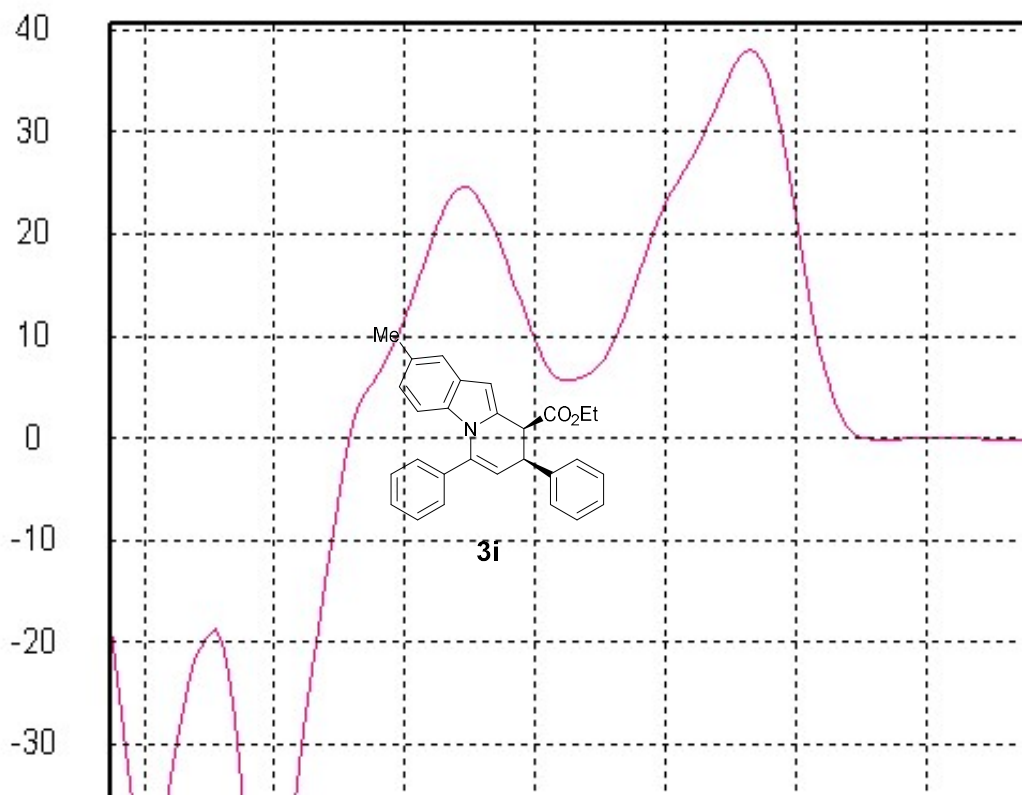


circular Dichroism (mdeg)

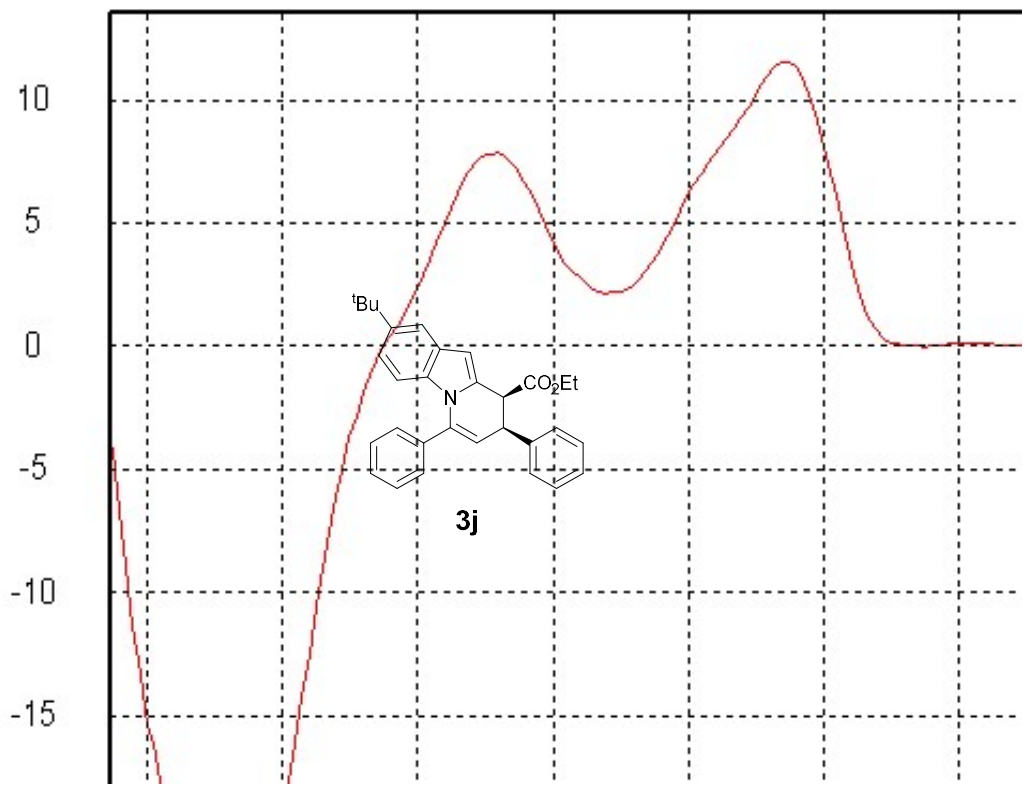




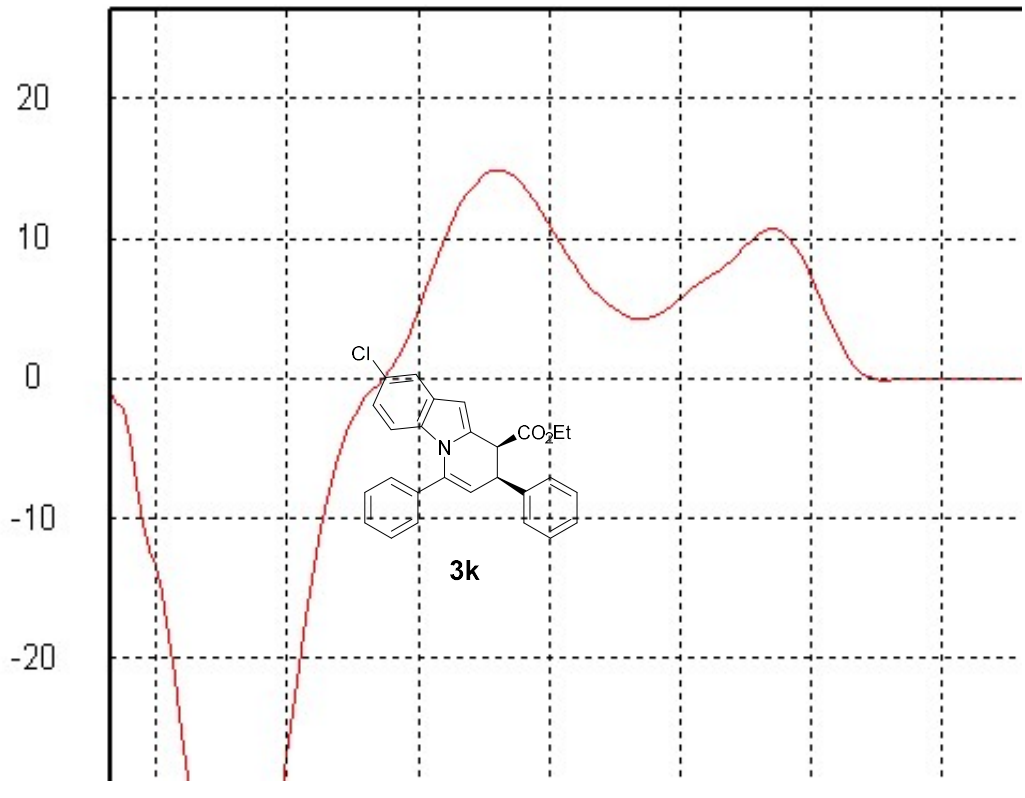
circular Dichroism (mdeg)



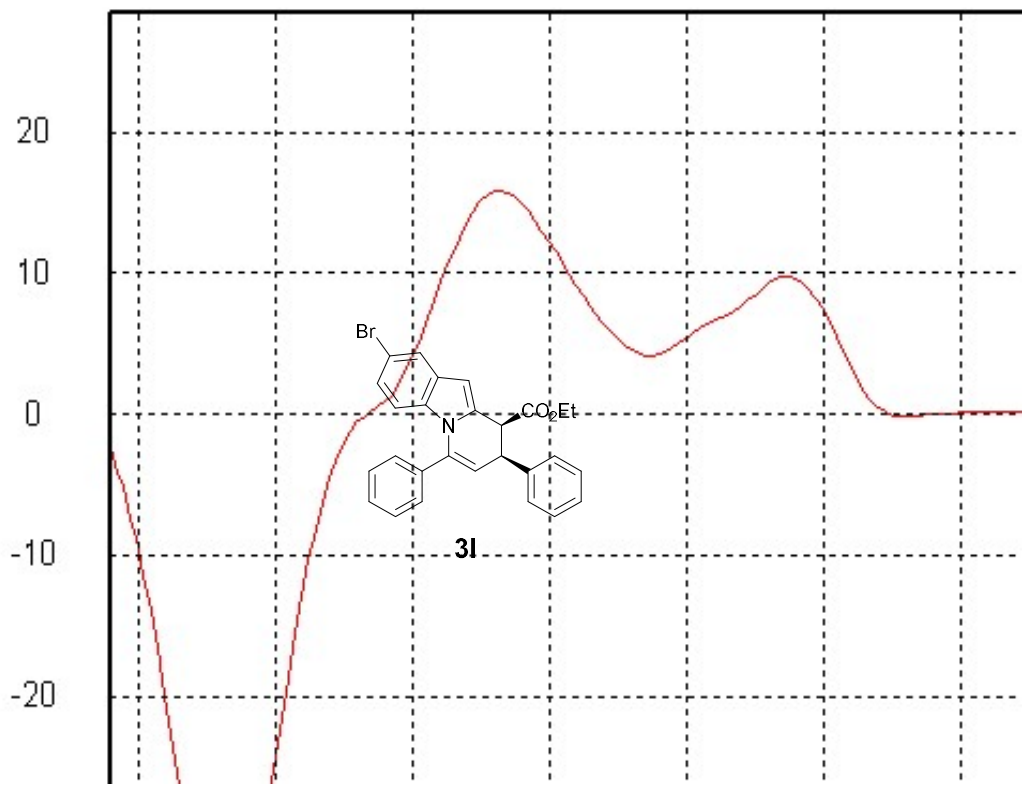
circular Dichroism (mdeg)



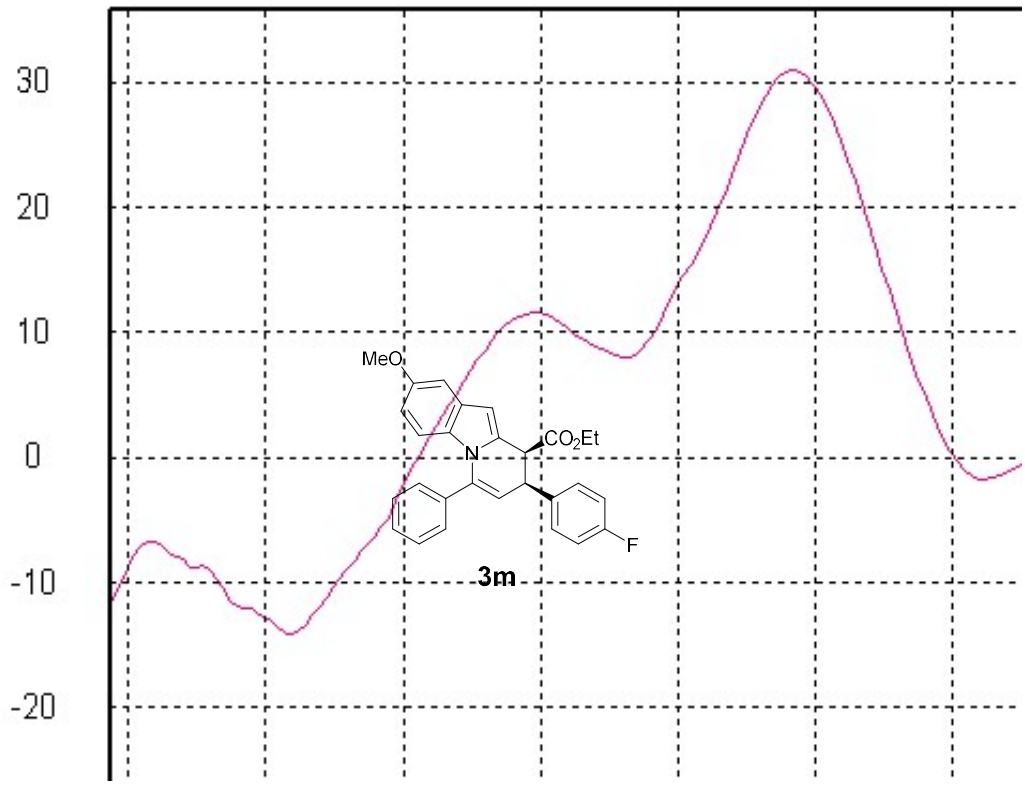
circular Dichroism (mdeg)

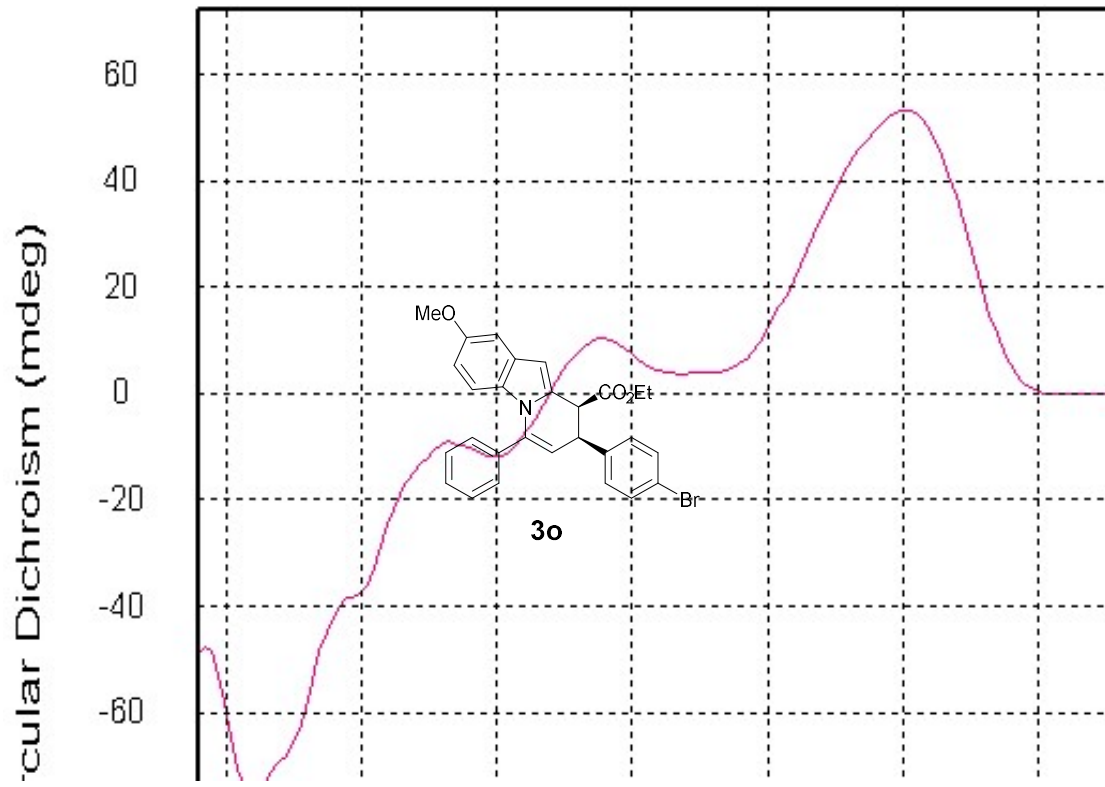
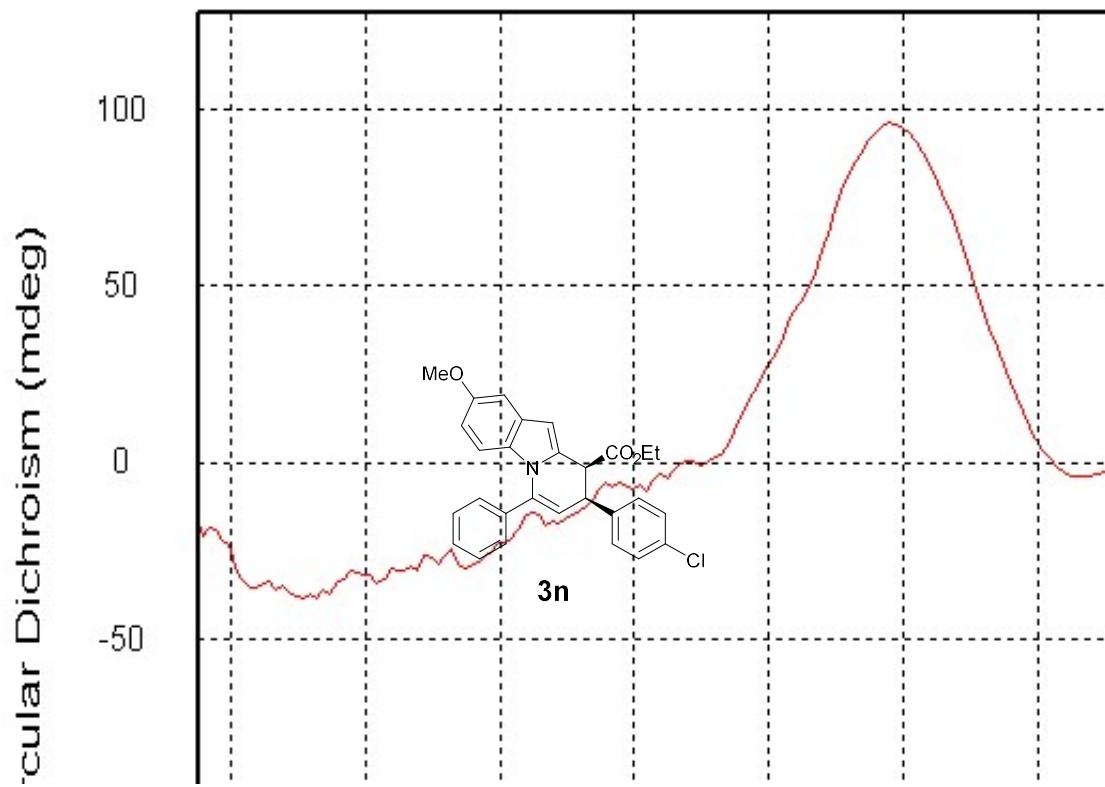


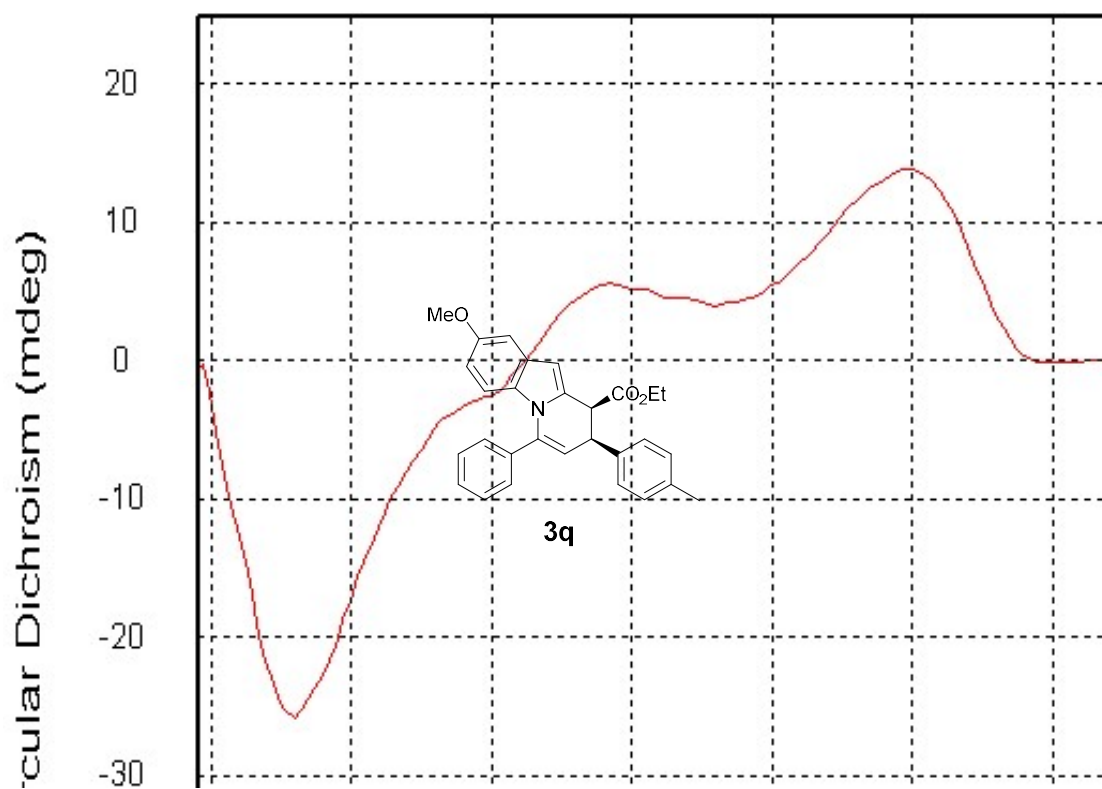
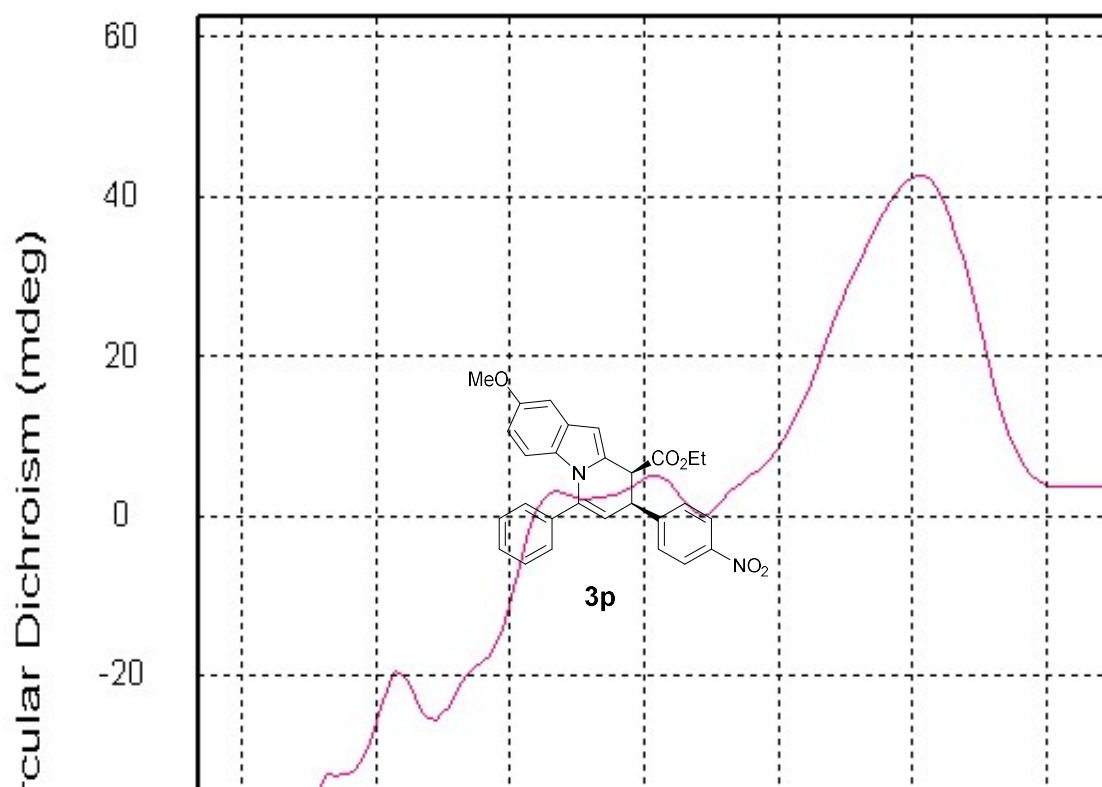
circular Dichroism (mdeg)

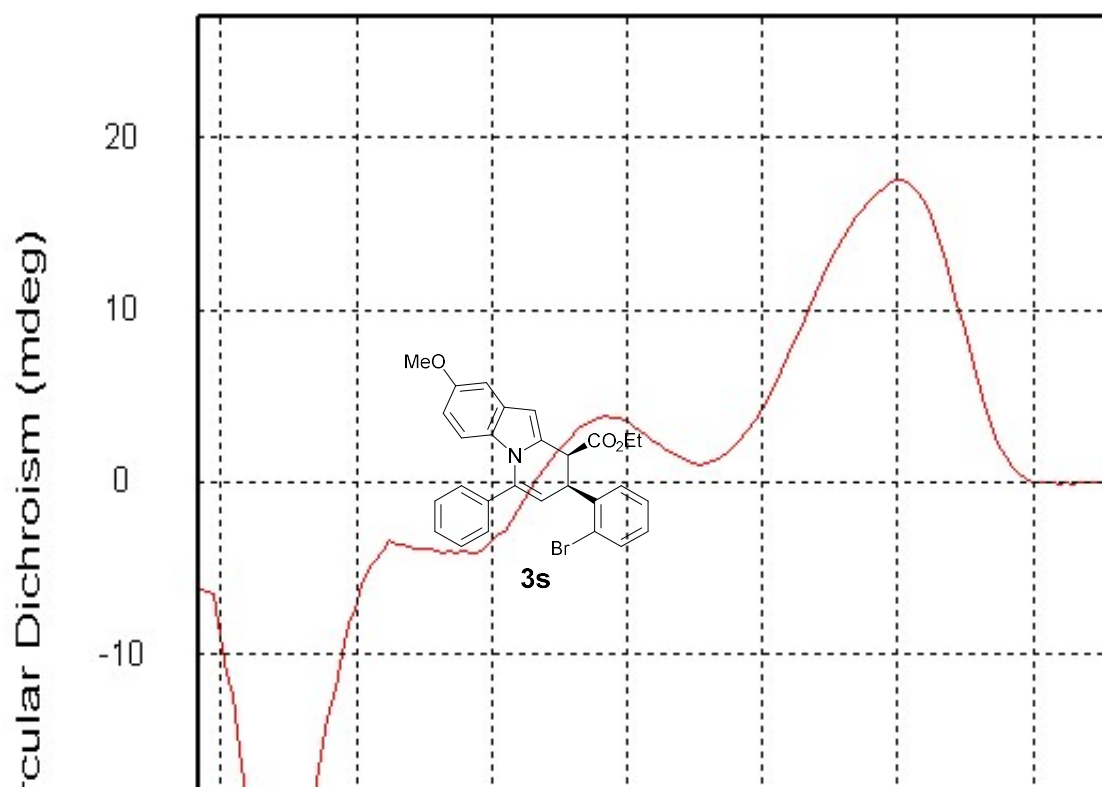
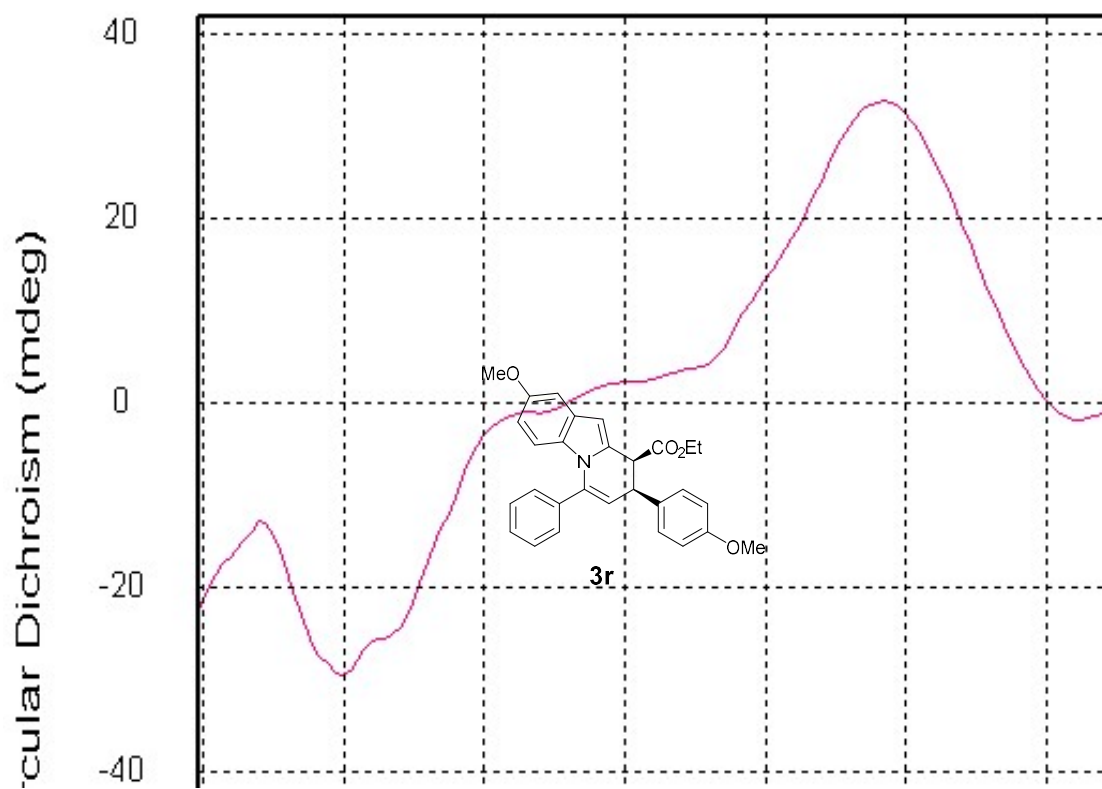


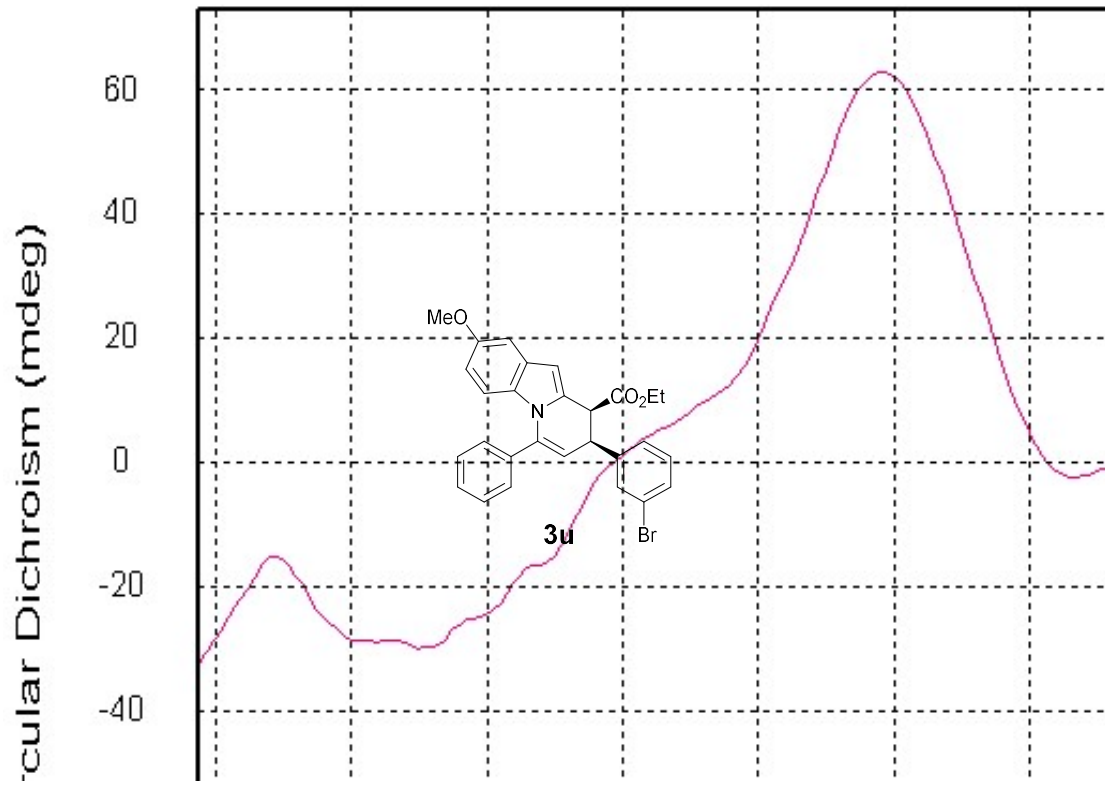
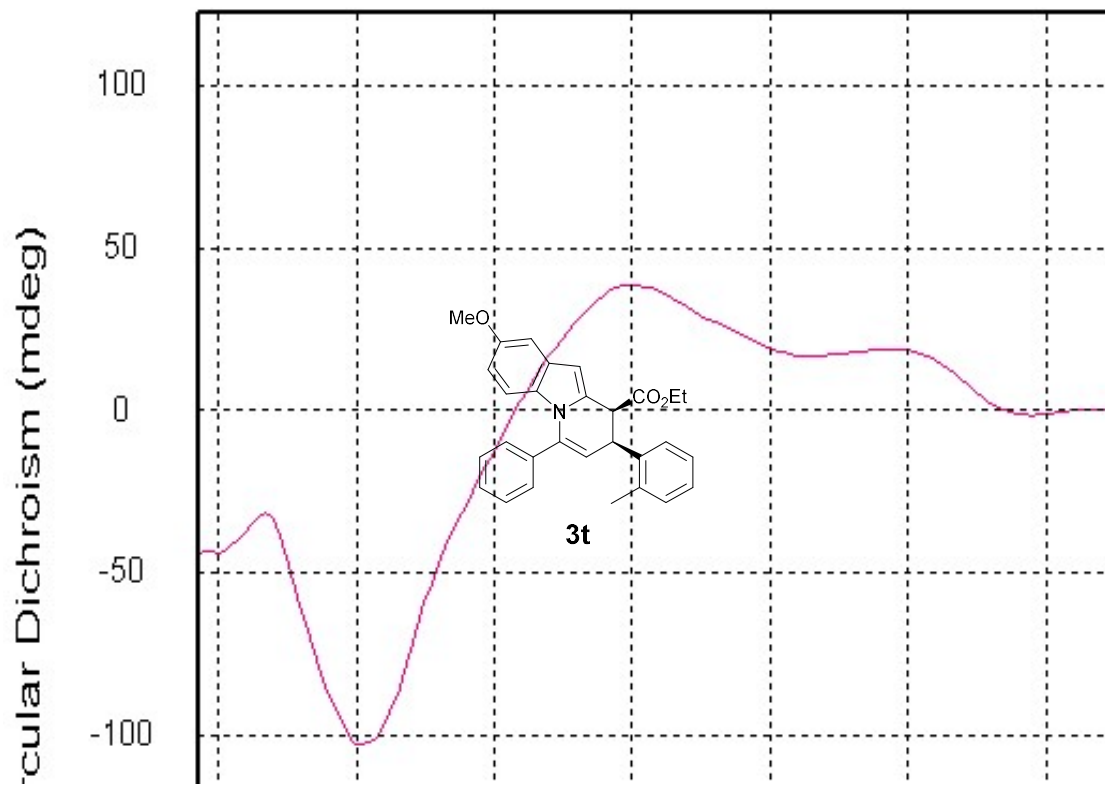
circular Dichroism (mdeg)

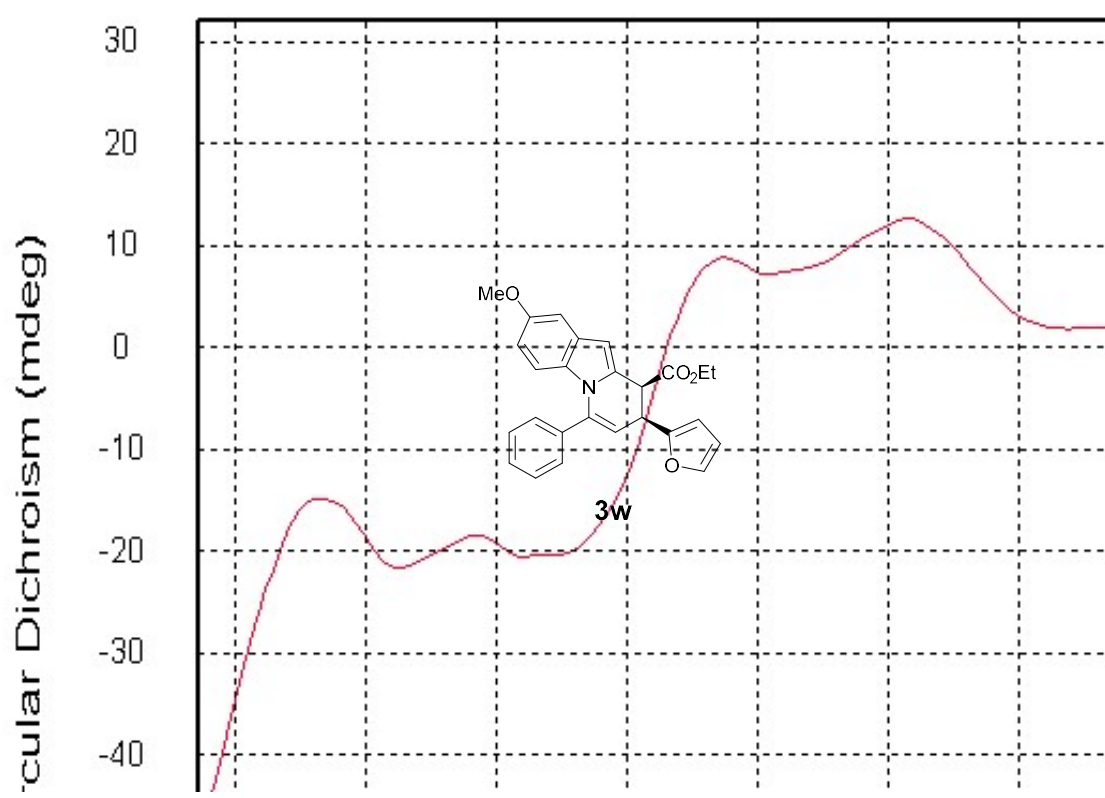
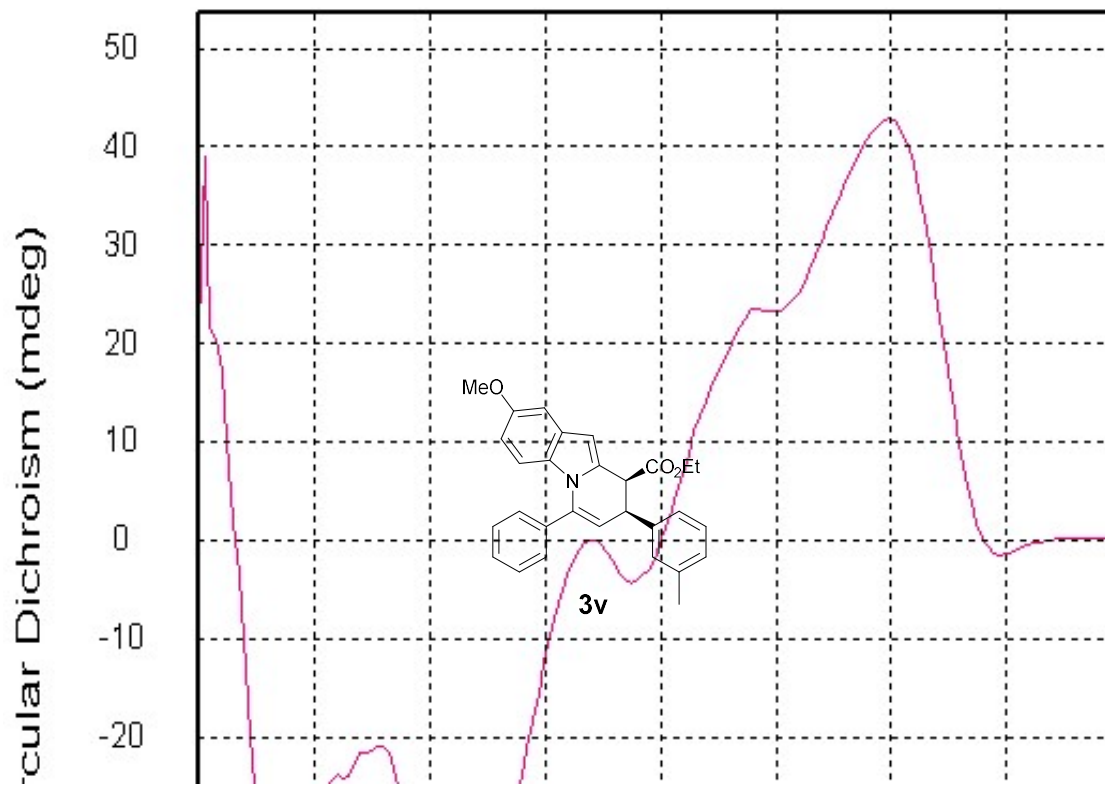




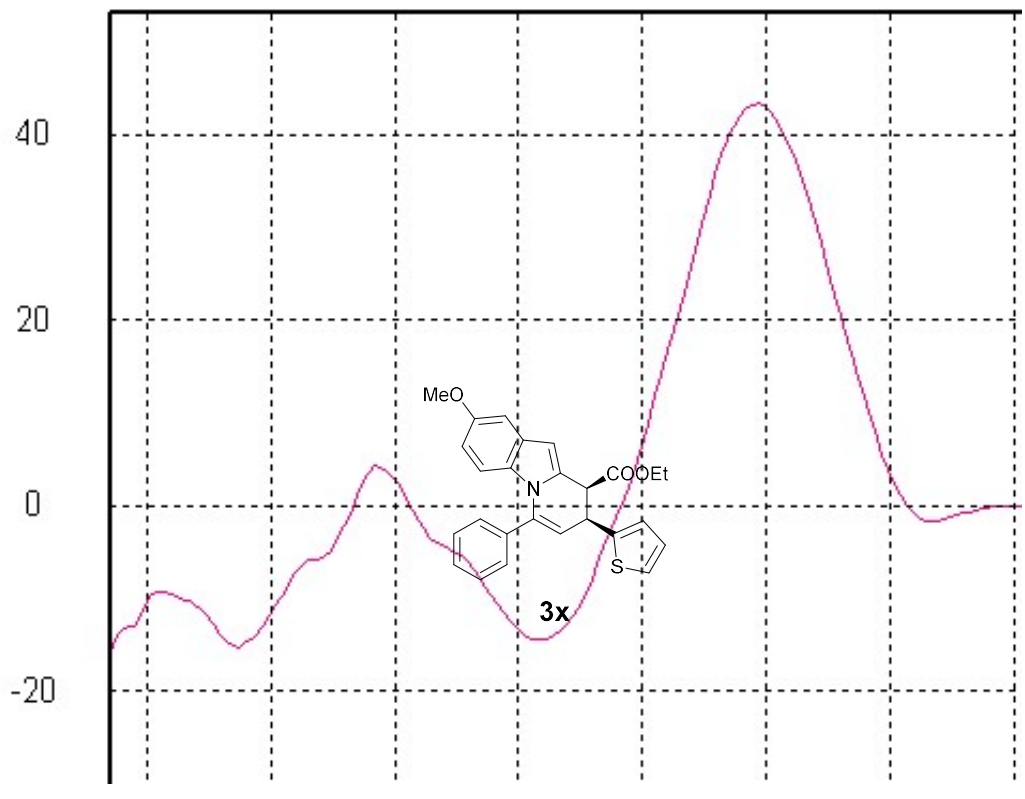








circular Dichroism (mdeg)



circular Dichroism (mdeg)

