



## Supporting Information

for

### **Enantioselective Diels–Alder reaction of anthracene by chiral tritylium catalysis**

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**Experimental procedures and characterization data of all products, copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, HRMS, and HPLC spectra of all compounds**

## Table of contents

1. General information and materials.....	S2
2. Experimental section.....	S3
3. Characterization .....	S7
3. <sup>1</sup> H NMR and <sup>13</sup> C NMR spectra.....	S19
4. HPLC spectra .....	S35

## General information and materials

Commercial reagents were used as received, unless other indicated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a NMR instrument (400 and 500 MHz for  $^1\text{H}$  NMR, 100 and 125 MHz for  $^{13}\text{C}$  NMR). Tetramethylsilane (TMS) served as the internal standard for  $^1\text{H}$  NMR, and  $\text{CDCl}_3$  served as the internal standard for  $^{13}\text{C}$  NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. Silica gel (200–300 mesh) was used for column chromatography. The enantioselective excesses (ee) were determined by HPLC analysis on Chiral Daicel Chiralcel AD-H, OD-H, AS-H and OJ-H columns. Optical rotation were measured on a commercial polarimeter and are reported as follows:  $[\alpha]_{\text{D}}^{25}$  ( $c = \text{g}/100 \text{ mL}$ , solvent). HRMS were recorded on a commercial apparatus (ESI Source).

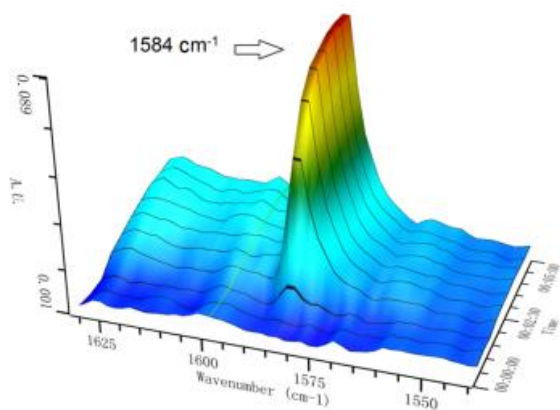
## Experimental section

### Dissociation of latent carbocation by using Lewis acids

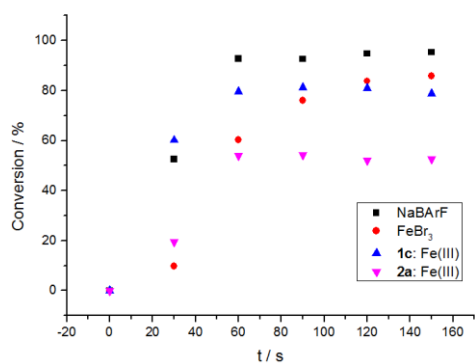
**General procedure I:** TP (0.005 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The corresponding Lewis acid (0.005 mmol), such as InCl<sub>3</sub>, InBr<sub>3</sub>, InI<sub>3</sub>, In(OTf)<sub>3</sub>, Sc(OTf)<sub>3</sub>, Hf(OTf)<sub>4</sub>, and GaCl<sub>3</sub>, was added, respectively. After each addition, the solution was stirred for 10 min before UV–vis testing was performed (see Figure 1a).

**General procedure II:** Ph<sub>3</sub>CBr (0.005 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and the corresponding chiral Lewis acid (0.005 mmol) was added. After each addition, the solution was stirred for 30 min before UV–vis testing was performed (see Figure 1b).

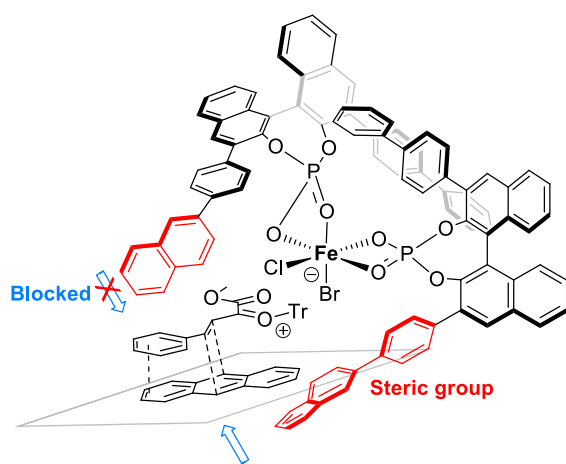
**General procedure III:** To an oven-dried reaction tube was added the corresponding Lewis acid (0.05 mmol), and distilled anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.8 mL) was added. Then, a solution of trityl bromide in CH<sub>2</sub>Cl<sub>2</sub> (0.2 mL) was added and the reaction mixture stirred at room temperature. In situ IR spectroscopy was used to monitor the reaction progress (at 1584 cm<sup>-1</sup>, Figure S1) as well as for monitoring of the conversion of the free carbocation (Figure S2).



**Figure S1:** Representative 3D stacking plots of in situ IR spectra of trityl cation generation.



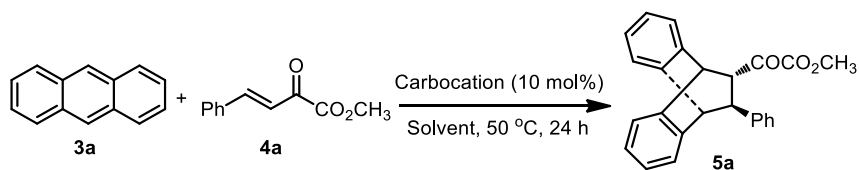
**Figure S2:** Dissociation progress of  $\text{Ph}_3\text{CBr}$  (0.05 mmol) in the presence of NaBARf,  $\text{FeBr}_3$ , **1c**, or **2a** (0.05 mmol), monitored by in situ IR at  $1584\text{ cm}^{-1}$ .



**Figure S3:** Proposed transition-state mode.

**General procedure for chiral carbocation catalyzed asymmetric Diels–Alder reactions between anthracene and  $\beta,\gamma$ -unsaturated- $\alpha$ -keto esters:** To dichloromethane was added  $\text{FeBr}_3$  (0.02 mmol, 10 mol %) and silver salt of chiral phosphoric acid (0.04 mmol, 20 mol %). After stirring for 3 h,  $\text{Ph}_3\text{CCl}$  (0.02 mmol, 10 mol %) was added and the reaction mixture was stirred for additional 3 h at rt. Then,  $\beta,\gamma$ -unsaturated- $\alpha$ -keto esters **4** (0.2 mmol) and anthracene (**3**, 0.4 mmol) were added and the reaction mixture was stirred for up to 3 d at rt. Purification by column chromatography on silica gel with petroleum ether/dichloromethane 2:1 afforded the desired products **5**.

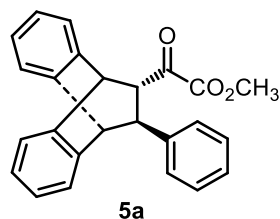
**Table S1:** Optimization studies for asymmetric catalyzed Diels–Alder reaction of anthracene by **TP** and different Lewis acids.



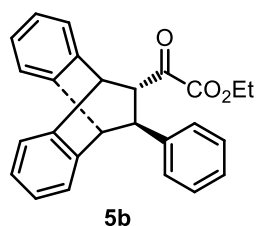
entry <sup>a</sup>	carbocation		solvent	yield (%) <sup>b</sup>	ee <sup>c</sup>
	TrX	Lewis acid			
1	<b>TP</b>	None	DCE	9	97
2	<b>TP</b>	InCl <sub>3</sub>	DCE	62	9
3	<b>TP</b>	InBr <sub>3</sub>	DCE	94	Rac.
4	<b>TP</b>	InI <sub>3</sub>	DCE	42	36
5	<b>TP</b>	In(OTf) <sub>3</sub>	DCE	89	Rac.
6	<b>TP</b>	Hf(OTf) <sub>4</sub>	DCE	90	Rac.
7	<b>TP</b>	Sc(OTf) <sub>3</sub>	DCE	86	Rac.
8	<b>TP</b>	GaCl <sub>3</sub>	DCE	81	-21

<sup>a</sup> General condition: **3a** (0.4 mmol), **4a** (0.2 mmol), **TP** (10 mol%), and Lewis acid (10 mol%) in the reaction solvent (2 mL) at 50 °C.

## Characterization



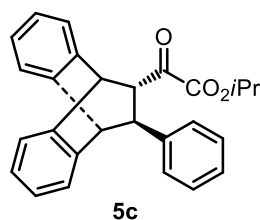
**5a:** Colorless solid; 70% yield, 91% *ee*;  $[\alpha]_{\text{D}}^{22} = +25.5$  ( $c = 1.04$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.5$  Hz, 1H), 7.33 (d,  $J = 7.5$  Hz, 1H), 7.25-7.09 (m, 8H), 7.03 (d,  $J = 7.0$  Hz, 1H), 6.57 (d,  $J = 5.5$  Hz, 2H), 4.80 (s, 1H), 4.25 (s, 1H), 3.80 (s, 3H), 3.73 (dd,  $J = 6.0$  Hz, 2.0 Hz, 1H), 3.63 (dd,  $J = 6.0$  Hz, 2.0 Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6, 162.1, 144.1, 142.5, 142.5, 140.9, 138.5, 128.3, 128.1, 126.9, 126.9, 126.6, 126.5, 126.4, 126.3, 125.1, 123.5, 123.4, 56.8, 53.0, 51.9, 46.9, 46.8 ppm; HPLC analysis: Daicel Chiralpak AS-H, hexane/iso-propanol = 97:3, flow rate = 1.0 mL/min,  $\lambda = 206$  nm, retention time: 9.5 min (major) and 13.1 min (minor); IR (KBr,  $\text{cm}^{-1}$ ): 3025, 2952, 1732, 1601, 1493, 1467, 1458, 1259, 1205, 1152, 1073, 760, 702, 640, 587, 567; HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{24}\text{O}_3\text{Na}^+$ : 391.1305, found: 391.1304.



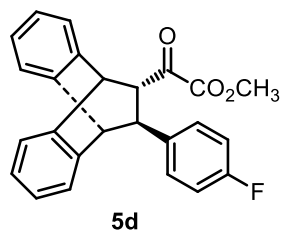
**5b:** Colorless solid; 82% yield, 74% *ee*;  $[\alpha]_{\text{D}}^{22} = +22.0$  ( $c = 1.06$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.2$  Hz, 1H), 7.30 (d,  $J = 6.8$  Hz, 1H), 7.23-7.06 (m, 8H), 7.00 (d,  $J = 7.2$  Hz, 1H), 6.57 (dd,  $J = 5.2$  Hz, 1.6 Hz, 2H), 4.81 (d,  $J = 2.0$  Hz, 1H), 4.24-4.15 (m, 3H), 3.71 (dd,  $J = 6.0$  Hz, 2.0 Hz, 1H), 3.62 (dd,  $J = 6.0$  Hz, 2.0 Hz, 1H), 1.21 (t,  $J$



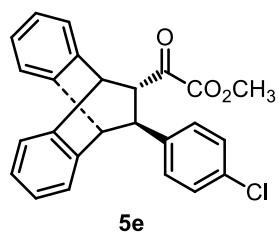
= 7.2 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.0, 161.7, 144.0, 142.5, 140.9, 138.6, 128.3, 128.0, 126.8, 126.7, 126.5, 126.5, 126.3, 126.2, 125.1, 123.4, 123.3, 62.5, 56.7, 51.9, 46.7, 46.7, 13.9 ppm; HPLC analysis: Daicel Chiralpak AS-H, hexane/iso-propanol = 97:3, flow rate = 1.0 mL/min,  $\lambda$  = 206 nm, retention time: 8.1 min (major) and 13.2 min (minor); IR (KBr,  $\text{cm}^{-1}$ ): 3067, 3025, 2982, 2949, 1726, 1467, 1458, 1298, 1256, 1072, 1033, 1019, 760, 702; HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{22}\text{O}_3\text{Na}^+$ : 405.1461, found: 405.1459.



**5c:** Colorless solid; 46% yield, 55% *ee*;  $[\alpha]_{\text{D}}^{22} = +11.3$  ( $c = 0.98$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.2$  Hz, 1H), 7.30 (d,  $J = 6.8$  Hz, 1H), 7.23-7.06 (m, 8H), 7.00 (d,  $J = 7.2$  Hz, 1H), 6.59-6.57 (m, 2H), 5.10-5.04 (m, 1H), 4.79 (s, 1H), 4.23 (d,  $J = 1.6$  Hz, 1H), 3.68 (dd,  $J = 6.0, 2.0$  Hz, 1H), 3.62 (dd,  $J = 6.0, 2.0$  Hz, 1H), 1.24 (d,  $J = 6.4$  Hz, 3H), 1.21 (d,  $J = 6.4$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.4, 161.5, 144.0, 142.6, 142.5, 140.9, 138.7, 128.3, 128.0, 126.8, 126.7, 126.5, 126.5, 126.3, 126.2, 125.2, 123.4, 123.3, 70.8, 56.6, 52.0, 46.7, 46.7, 21.6, 21.6 ppm; HPLC analysis: Daicel Chiralpak AS-H, hexane/iso-propanol = 97:3, flow rate = 1.0 mL/min,  $\lambda$  = 206 nm, retention time: 7.2 min (major) and 11.8 min (minor); IR (KBr,  $\text{cm}^{-1}$ ): 3067, 3025, 2982, 2939, 1722, 1467, 1458, 1259, 1082, 1071, 761, 702; HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{25}\text{O}_3^+$ : 397.1798, found: 397.1794.

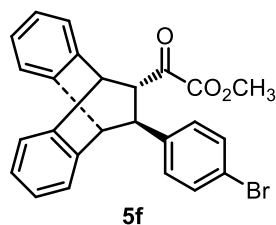


**5d:** Colorless solid; 74% yield, 80% *ee*;  $[\alpha]_{\text{D}}^{22} = +24.7$  ( $c = 1.16$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.0$  Hz, 1H), 7.20 (d,  $J = 7.0$  Hz, 1H), 7.24–7.08 (m, 5H), 7.02 (d,  $J = 7.0$  Hz, 1H), 6.80 (t,  $J = 8.5$  Hz, 2H), 6.51 (dd,  $J = 8.5, 5.5$  Hz, 2H), 4.80 (s, 1H), 4.21 (s, 1H), 3.80 (s, 3H), 3.67–3.62 (m, 2H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3, 161.9, 161.7 (d,  $J = 243.8$  Hz), 143.7, 142.2, 140.6, 138.3, 138.1, 129.3 (d,  $J = 6.6$  Hz), 126.8, 126.5, 126.4, 126.4, 126.2, 125.0, 123.5, 123.3, 115.0 (d,  $J = 21.0$  Hz), 56.8, 53.0, 51.8, 46.7, 45.8 ppm; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/isopropanol = 97:3, flow rate = 0.6 mL/min,  $\lambda = 230$  nm, retention time: 31.7 min (minor) and 36.0 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3069, 3044, 3024, 2953, 1733, 1603, 1511, 1458, 1259, 1226, 1170, 1078, 837, 801. 759, 703; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{19}\text{O}_3\text{FNa}^+$ : 409.1210, found: 409.1210.

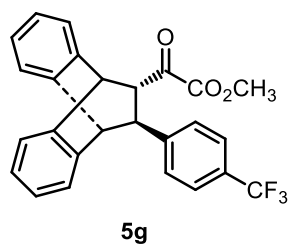


**5e:** Colorless solid; 68% yield, 75% *ee*;  $[\alpha]_{\text{D}}^{22} = +36.2$  ( $c = 1.01$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.2$  Hz, 1H), 7.30 (d,  $J = 7.2$  Hz, 1H), 7.20–7.04 (m, 7H), 6.99 (d,  $J = 7.2$  Hz, 1H), 6.46 (d,  $J = 8.4$  Hz, 2H), 4.81 (d,  $J = 1.6$  Hz, 1H), 4.20 (d,  $J = 1.6$  Hz,

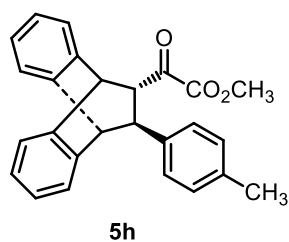
1H), 3.73 (s, 3H), 3.66 (dd,  $J = 5.6, 2.0$  Hz, 1H), 6.62 (dd,  $J = 5.6, 2.0$  Hz, 1H) ppm;  
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3, 161.9, 143.6, 142.2, 140.9, 140.5, 138.3, 132.6,  
129.3, 128.3, 126.8, 126.6, 126.4, 126.4, 126.3, 125.0, 123.5, 123.4, 56.7, 52.9, 51.6,  
46.6, 46.0; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/iso-propanol = 97:3,  
flow rate = 0.6 mL/min,  $\lambda = 210$  nm, retention time: 36.0 min (minor) and 40.5 min  
(major); IR (KBr,  $\text{cm}^{-1}$ ): 3069, 3043, 3024, 2952, 1732, 1492, 1458, 1265, 1078, 1013,  
830, 759, 721; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{19}\text{O}_3\text{ClNa}^+$ : 425.0915, found: 425.0915.



**5f**: Colorless solid; 66% yield, 81% *ee*;  $[\alpha]_{\text{D}}^{22} = +46.8$  ( $c = 1.02$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.5$  Hz, 1H), 7.32 (d,  $J = 7.0$  Hz, 1H), 7.24 (d,  $J = 9.0$  Hz, 3H), 7.22-7.09 (m, 4H), 7.02 (d,  $J = 7.0$  Hz, 1H), 6.42 (d,  $J = 8.5$  Hz, 2H), 4.80 (s, 1H), 4.20 (s, 1H), 3.83 (s, 3H), 3.65 (dd,  $J = 6.0, 2.0$  Hz, 1H), 3.60 (dd,  $J = 5.5, 1.5$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3, 161.9, 143.6, 142.3, 141.5, 140.5, 138.4, 131.4, 129.7, 128.0, 126.9, 126.7, 126.5, 126.5, 126.4, 125.1, 123.6, 123.4, 120.8, 56.8, 53.1, 51.6, 46.7, 46.2; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/iso-propanol = 97:3, flow rate = 0.6 mL/min,  $\lambda = 254$  nm, retention time: 39.0 min (minor) and 42.1 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3032, 3023, 2951, 1729, 1489, 1458, 1264, 1076, 1009, 816, 759; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{19}\text{O}_3\text{BrNa}^+$ : 469.0410, found: 469.0409.

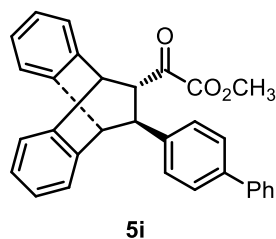


**5g:** Colorless solid; 77% yield, 76% *ee*;  $[\alpha]_{\text{D}}^{22} = +25.6$  ( $c = 1.14$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 7.5$  Hz, 1H), 7.38 (d,  $J = 8.0$  Hz, 2H), 7.34 (d,  $J = 7.0$  Hz, 1H), 7.27–7.11 (m, 5H), 7.02 (d,  $J = 7.5$  Hz, 1H), 6.67 (d,  $J = 8.0$  Hz, 2H), 4.83 (s, 1H), 4.24 (d, 1H), 3.84 (s, 3H), 3.71 (s, 2H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.1, 161.9, 146.6, 143.5, 142.3, 140.4, 138.4, 129.2 (q,  $J = 32.3$  Hz), 128.4, 127.0, 126.8, 126.6, 126.6, 126.5, 125.3 (q,  $J = 3.9$  Hz), 125.2, 124.2 (q,  $J = 270.5$  Hz), 123.7, 123.5, 56.7, 53.1, 51.5, 46.8, 46.5 ppm; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/isopropanol = 97:3, flow rate = 0.6 mL/min,  $\lambda = 206$  nm, retention time: 31.2 min (minor) and 35.1 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3071, 3044, 3025, 2954, 1732, 1618, 1458, 1326, 1259, 1166, 1114, 1069, 1017, 842, 759, 660; HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_3\text{F}_3^-$ : 435.1214, found: 435.1213.

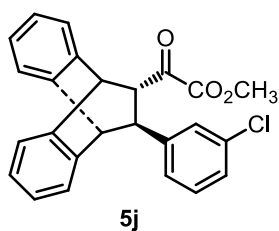


**5h:** Colorless solid; 48% yield, 80% *ee*;  $[\alpha]_{\text{D}}^{22} = +46.8$  ( $c = 0.92$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 7.0$  Hz, 1H), 7.32 (d,  $J = 7.5$  Hz, 1H), 7.25–7.08 (m, 5H), 7.04 (d,  $J = 7.0$  Hz, 1H), 6.93 (d,  $J = 8.0$  Hz, 2H), 6.46 (d,  $J = 8.0$  Hz, 2H), 4.79 (d,  $J = 1.0$  Hz, 1H), 4.22 (d,  $J = 1.5$  Hz, 1H), 3.80 (s, 3H), 3.70 (dd,  $J = 6.0, 1.5$  Hz, 1H), 3.59 (dd,  $J =$

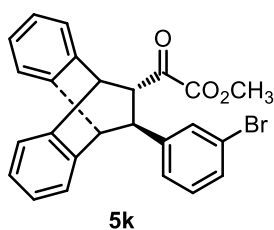
5.5, 1.5 Hz, 1H), 2.25 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6, 162.0, 144.1, 142.4, 140.9, 139.4, 138.5, 136.3, 128.9, 127.8, 126.7, 126.5, 126.4, 126.3, 126.1, 125.0, 123.4, 123.3, 56.8, 52.8, 51.9, 46.8, 46.3, 21.0 ppm; HPLC analysis: Daicel Chiralpak AS-H, hexane/iso-propanol = 97:3, flow rate = 1.0 mL/min,  $\lambda$  = 206 nm, retention time: 8.6 min (minor) and 12.3 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3023, 2951, 1733, 1514, 1467, 1078, 813, 758, 722; HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{22}\text{O}_3\text{Na}^+$ : 405.1460, found: 405.1461.



**5i:** Colorless solid; 68% yield, 93% *ee*;  $[\alpha]_{\text{D}}^{22} = +60.5$  ( $c = 1.02$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-6.98 (m, 15H), 6.62 (d,  $J = 8.4$  Hz, 2H), 4.83 (d,  $J = 1.6$  Hz, 1H), 4.26 (d,  $J = 1.6$  Hz, 1H), 3.77 (dd,  $J = 6.0$  Hz, 2.0 Hz, 1H), 3.71 (dd,  $J = 5.6$  Hz, 1.6 Hz, 1H), 3.61 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.4, 161.9, 143.9, 142.3, 141.4, 140.7, 140.4, 139.5, 138.4, 128.7, 128.3, 127.2, 126.8, 126.7, 126.4, 126.4, 126.3, 126.1, 125.0, 123.4, 123.3, 56.7, 52.7, 51.7, 46.7, 46.3 ppm; HPLC analysis: Daicel Chiralpak AS-H, hexane/iso-propanol = 97:3, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm, retention time: 13.4 min (major) and 28.8 min (minor); IR (KBr,  $\text{cm}^{-1}$ ): 3026, 2951, 1733, 1486, 1458, 1265, 1216, 1078, 1007, 840, 764, 698, 634; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{24}\text{O}_3\text{Na}^+$ : 467.1618, found: 467.1618.

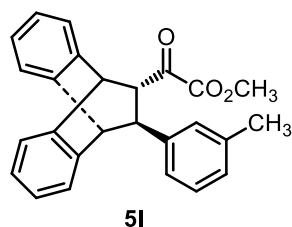


**5j:** Colorless solid; 92% yield, 91% *ee*;  $[\alpha]_{\text{D}}^{22} = +31.9$  ( $c = 1.11$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.0$  Hz, 1H), 7.32 (d,  $J = 7.00$  Hz, 1H), 7.24–7.00 (m, 8H), 6.54 (s, 1H), 6.41 (d,  $J = 7.5$  Hz, 1H), 4.81 (d,  $J = 1.5$  Hz, 1H), 4.23 (d,  $J = 1.5$  Hz, 1H), 3.80 (s, 3H), 3.66 (dd,  $J = 5.5, 1.5$  Hz, 1H), 3.62 (dd,  $J = 5.5, 2.0$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 161.9, 144.6, 143.6, 142.2, 140.5, 138.4, 134.1, 129.5, 128.3, 127.0, 126.9, 126.7, 126.5, 126.5, 126.4, 126.1, 125.1, 123.7, 123.5, 56.7, 53.1, 51.6, 46.7, 46.3 ppm; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/isopropanol = 97:3, flow rate = 0.6 mL/min,  $\lambda = 230$  nm, retention time: 30.4 min (minor) and 34.9 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3069, 3043, 3024, 2952, 1732, 1595, 1467, 1264, 1077, 783, 760, 701; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{18}\text{O}_3\text{Cl}$ : 401.0950, found: 401.0948.

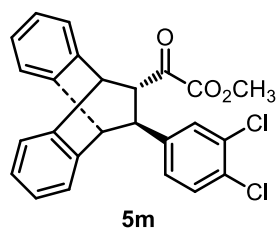


**5k:** Colorless solid; 86% yield, 87% *ee*;  $[\alpha]_{\text{D}}^{22} = +26.7$  ( $c = 1.04$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.2$  Hz, 1H), 7.31 (d,  $J = 7.2$  Hz, 1H), 7.26–7.07 (m, 6H), 7.02 (d,  $J = 7.2$  Hz, 1H), 6.95 (t,  $J = 7.6$  Hz, 1H), 6.70 (s, 1H), 6.43 (d,  $J = 7.6$  Hz, 1H), 4.81 (d,  $J = 1.6$  Hz, 1H), 4.23 (d,  $J = 2.0$  Hz, 1H), 3.79 (s, 3H), 3.66 (dd,  $J = 6.0, 2.0$  Hz, 1H), 3.61 (dd,  $J = 6.0, 2.0$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 161.9, 144.8,

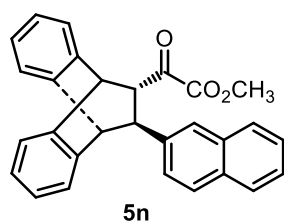
143.5, 142.2, 140.4, 138.3, 131.3, 129.9, 129.8, 126.9, 126.7, 126.5, 126.5, 126.4, 125.1, 123.6, 123.5, 122.3, 56.7, 53.1, 51.5, 46.7, 46.3 ppm; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/iso-propanol = 97:3, flow rate = 0.6 mL/min,  $\lambda$  = 230 nm, retention time: 30.6 min (minor) and 38.4 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3068, 3043, 3023, 2952, 1732, 1592, 1566, 1467, 1458, 1432, 1264, 1076, 782, 759, 698; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{19}\text{O}_3\text{BrNa}^+$ : 469.0410, found: 469.0411.



**51:** Colorless solid; 76% yield, 89% *ee*;  $[\alpha]_{\text{D}}^{22} = +25.0$  ( $c = 1.15$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.0$  Hz, 1H), 7.32 (d,  $J = 7.5$  Hz, 1H), 7.25-6.94 (m, 8H), 6.39 (s, 1H), 6.32 (d,  $J = 7.5$  Hz, 1H), 4.80 (s, 1H), 4.24 (s, 1H), 3.81 (s, 3H), 3.72 (dd,  $J = 6.0, 2.0$  Hz, 1H), 3.59 (dd,  $J = 6.0, 2.0$  Hz, 1H), 2.18 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6, 162.1, 144.1, 142.4, 141.0, 138.5, 137.8, 129.1, 128.2, 128.0, 127.5, 126.8, 126.6, 126.5, 126.3, 126.2, 125.1, 124.9, 123.5, 123.4, 56.8, 53.0, 51.9, 46.9, 46.6, 21.5 ppm; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/iso-propanol = 97:3, flow rate = 0.6 mL/min,  $\lambda$  = 206 nm, retention time: 25.9 min (minor) and 30.5 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3042, 3023, 2951, 1729, 1467, 1458, 1262, 1078, 785, 758, 707; HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{21}\text{O}_3^-$ : 381.1496, found: 381.1495.



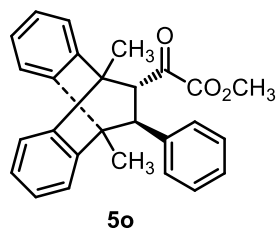
**5m:** Colorless solid; 85% yield, 73% *ee*;  $[\alpha]_{\text{D}}^{22} = +46.8$  ( $c = 1.05$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 7.5$  Hz, 1H), 7.32 (d,  $J = 7.0$  Hz, 1H), 7.25–7.09 (m, 6H), 7.02 (d,  $J = 7.0$  Hz, 1H), 6.63 (d,  $J = 2.0$  Hz, 1H), 6.33 (dd,  $J = 8.0$  Hz, 1.5 Hz, 1H), 4.82 (s, 1H), 4.21 (s, 1H), 3.83 (s, 3H), 3.62 (s, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.0, 161.9, 143.3, 142.8, 142.1, 140.2, 138.3, 132.2, 130.9, 130.2, 130.2, 127.3, 127.0, 126.9, 126.6, 126.6, 126.5, 125.1, 123.7, 123.5, 56.8, 53.2, 51.5, 46.7, 45.8; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/iso-propanol = 97:3, flow rate = 0.6 mL/min,  $\lambda = 230$  nm, retention time: 33.0 min (minor) and 41.0 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3069, 3043, 3024, 2952, 1729, 1468, 1264, 1080, 1029, 758, 709; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{17}\text{O}_3\text{Cl}_2^-$ : 435.0560, found: 435.0564.



**5n:** Colorless solid; 42% yield, 83% *ee*;  $[\alpha]_{\text{D}}^{22} = +47.4$  ( $c = 0.97$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72–7.71 (m, 1H), 7.59–7.57 (m, 2H), 7.51 (d,  $J = 7.5$  Hz, 1H), 7.39–7.34 (m, 3H), 7.27–7.07 (m, 7H), 6.98 (d,  $J = 7.5$  Hz, 1H), 6.61 (dd,  $J = 8.5$  Hz, 1.5 Hz, 1H), 4.86 (d,  $J = 1.5$  Hz, 1H), 4.32 (d,  $J = 1.5$  Hz, 1H), 3.85 (dd,  $J = 6.0$  Hz, 2.0 Hz, 1H), 3.81 (dd,  $J = 6.0$  Hz, 2.0 Hz, 1H), 3.75 (s, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6,



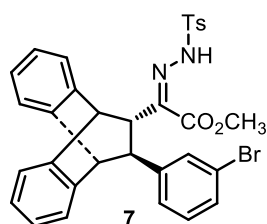
162.1, 144.0, 142.4, 141.0, 139.9, 138.6, 133.3, 132.4, 128.0, 127.9, 127.8, 127.6, 126.9, 126.9, 126.6, 126.6, 126.5, 126.3, 126.2, 126.1, 125.8, 125.2, 123.6, 123.5, 56.8, 53.0, 52.0, 46.9, 46.9; HPLC analysis: Daicel Chiralpak AD-H, hexane/iso-propanol = 97:3, flow rate = 1.0 mL/min,  $\lambda$  = 267 nm, retention time: 16.1 min (minor) and 23.1 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3053, 3023, 2951, 1729, 1466, 1458, 1262, 1079, 818, 746; HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{21}\text{O}_3^-$ : 417.1496, found: 417.1494.



**5o**: Colorless solid; 93% yield, 23% *ee*;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J$  = 7.2 Hz, 1H), 7.35 (d,  $J$  = 6.4 Hz, 1H), 7.28–7.04 (m, 9H), 6.38 (br, 2H), 3.80 (d,  $J$  = 6.8 Hz, 1H), 3.56 (s, 3H), 3.11 (d,  $J$  = 6.4 Hz, 1H), 2.01 (s, 3H), 1.55 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.3, 162.4, 146.9, 145.7, 143.2, 141.4, 141.1, 128.1, 127.5, 127.1, 126.3, 126.2, 126.1, 125.7, 123.6, 122.8, 120.4, 120.4, 120.4, 61.3, 56.4, 52.9, 46.1, 45.4, 16.5, 16.2; HPLC analysis: Daicel Chiralpak AD-H (2x), hexane/iso-propanol = 97:3, flow rate = 0.5 mL/min,  $\lambda$  = 206 nm, retention time: 32.6 min (major) and 34.1 min (minor); IR (KBr,  $\text{cm}^{-1}$ ): 3063, 3028, 1969, 2881, 1733, 1493, 1453, 1381, 1271, 1096, 1068, 765, 750, 702; HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{24}\text{O}_3\text{Na}^+$ : 419.1618, found: 419.1618.

**Procedure for gram-scale reaction of 3a and 4k, and transformation to cycloadduct 5k:** To dichloromethane was added  $\text{FeBr}_3$  (0.5 mmol, 10 mol %) and silver

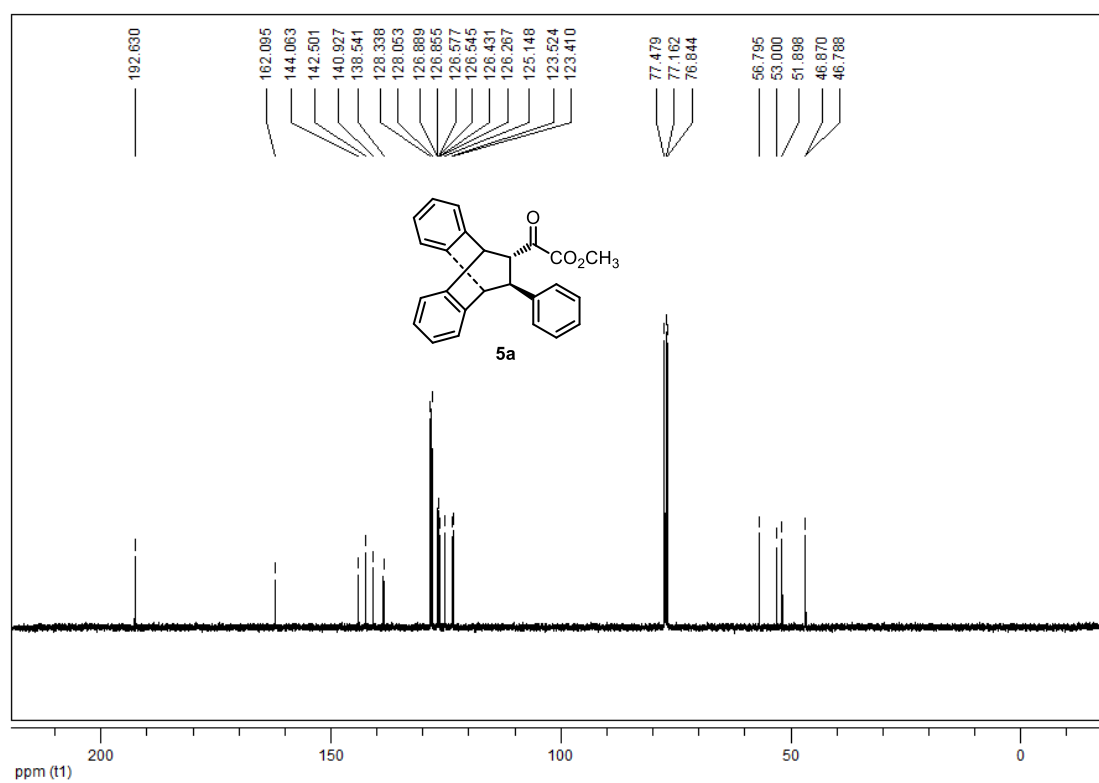
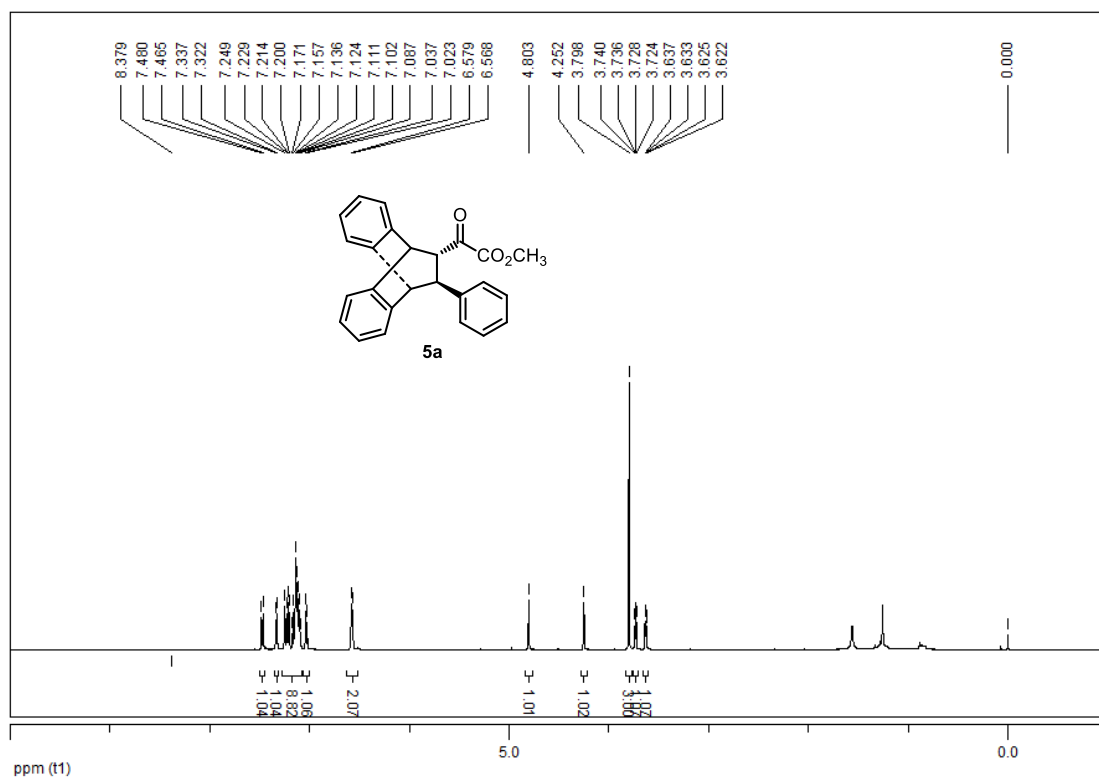
salt of chiral phosphoric acid (1 mmol, 20 mol %). After stirring for 3 h,  $\text{Ph}_3\text{CCl}$  (0.5 mmol, 10 mol %) was added and the reaction mixture was stirred for 3 h at rt. After the addition of the  $\beta,\gamma$ -unsaturated- $\alpha$ -ketoester **4k** (5 mmol) and anthracene (**3a**, 10 mmol), the reaction mixture was stirred for 3 d at rt. The reaction mixture was purified by column chromatography on silica gel with petroleum ether/dichloromethane 2:1 to afford the desired product **5k** in 88% yield and 87% ee. To an oven-dried reaction tube was added cycloadduct **5k** (4.4 mmol), sulfonyl hydrazide **6** (5.3 mmol), and  $\text{MgSO}_4$  (22.0 mmol) and distilled anhydrous  $\text{CH}_2\text{Cl}_2$  was added. The mixture was stirred for 12 h at rt. Purification of the mixture by column chromatography on silica gel gave product **7**.

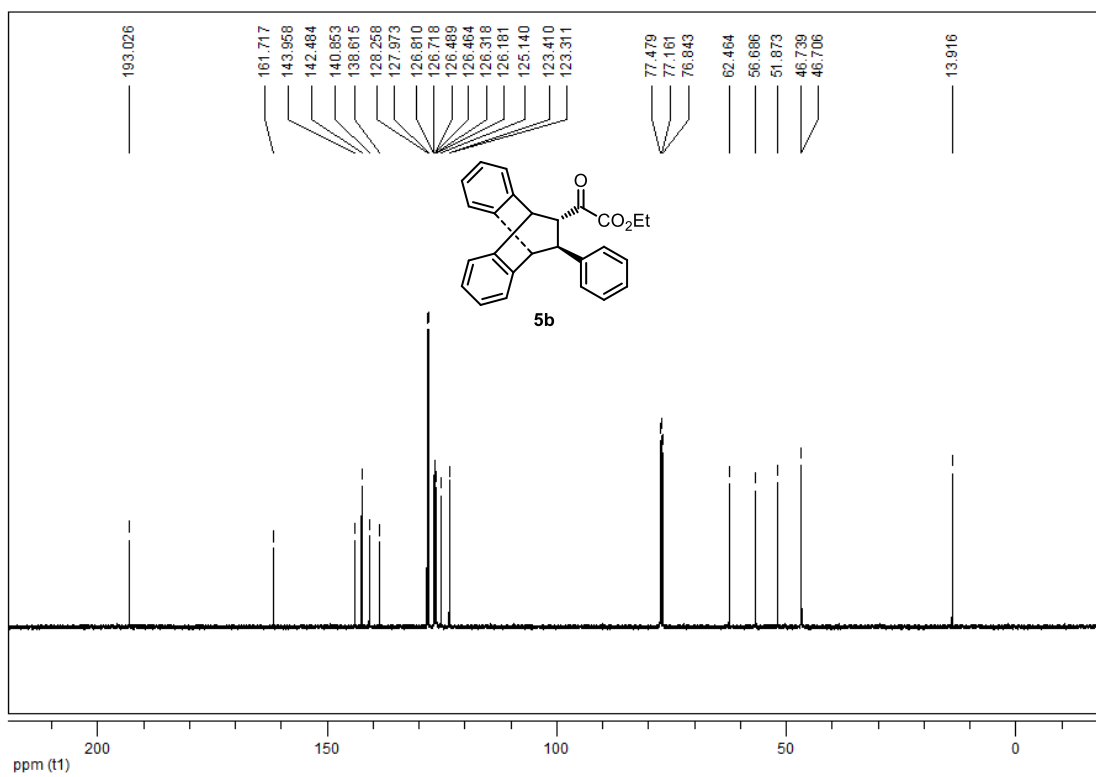
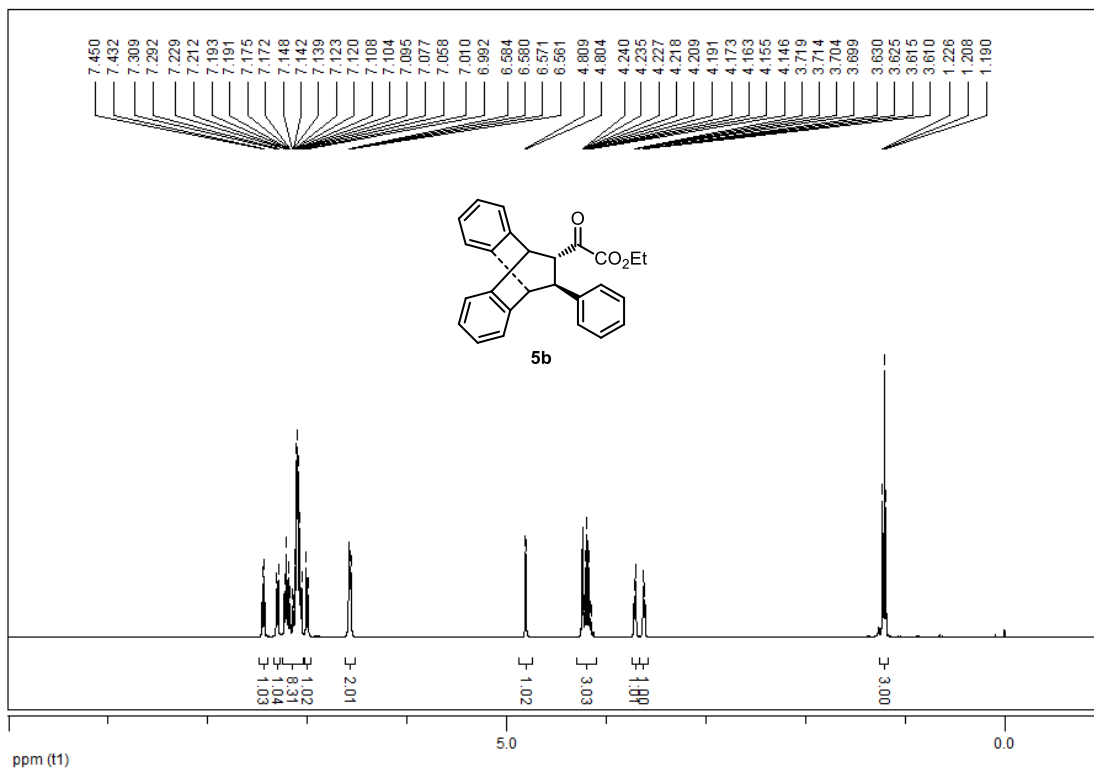


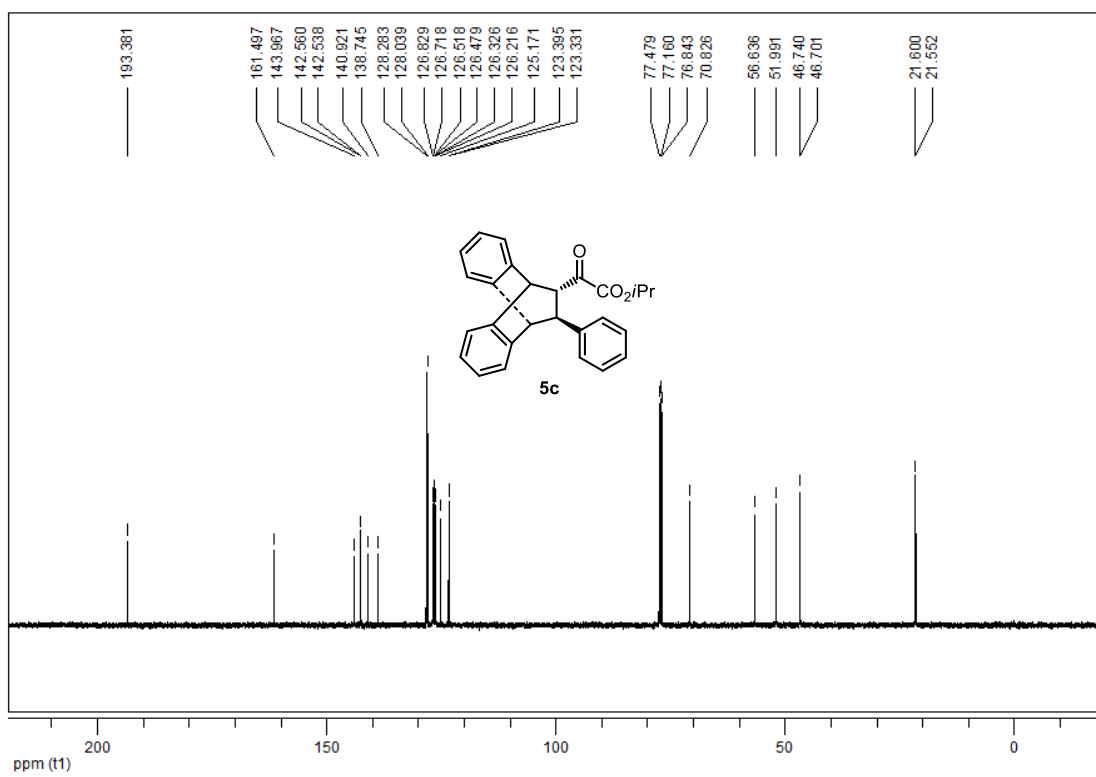
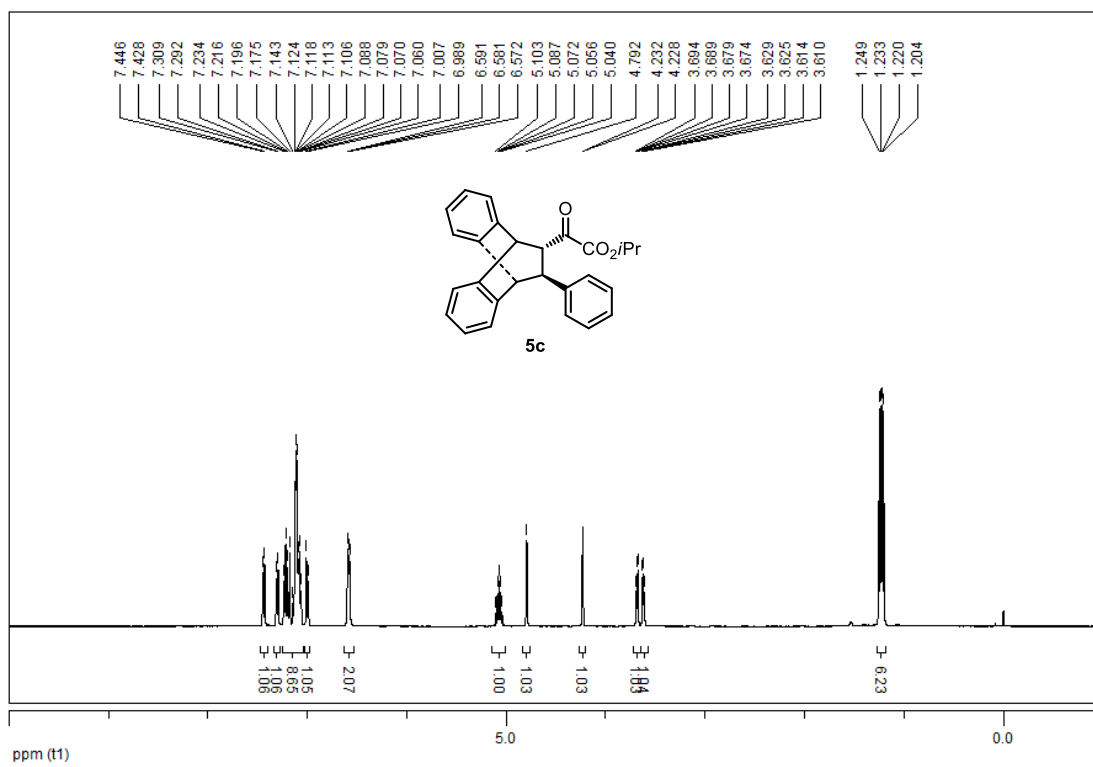
**7**: colorless solid; 83% yield, 82% ee;  $[\alpha]_{\text{D}}^{25} = +226.7$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  11.52 (s, 1H), 7.51 (d,  $J = 7.5$  Hz, 2H), 7.37 (d,  $J = 7.0$  Hz, 1H), 7.27–7.17 (m, 5H), 7.11–7.04 (m, 4H), 6.97–6.90 (m, 2H), 6.65 (s, 1H), 6.35 (d,  $J = 7.45$  Hz, 1H), 4.42 (s, 1H), 4.12 (s, 1H), 3.65 (s, 3H), 3.39 (d,  $J = 5.5$  Hz, 1H), 3.20 (d,  $J = 5.5$  Hz, 1H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2, 146.1, 144.1, 144.0, 143.8, 140.3, 138.8, 136.7, 135.4, 131.2, 129.7, 129.7, 129.5, 127.8, 126.4, 126.4, 126.2, 126.1, 126.0, 125.9, 123.3, 122.6, 122.1, 52.6, 51.5, 50.6, 48.6, 48.1, 21.8; HPLC analysis: Daicel Chiralpak AD-H, hexane/iso-propanol = 90:10, flow rate = 1.0 mL/min,  $\lambda = 206$  nm, retention time: 8.7 min (minor) and 14.9 min (major); IR (KBr,  $\text{cm}^{-1}$ ): 3212, 3068, 3023, 2954,

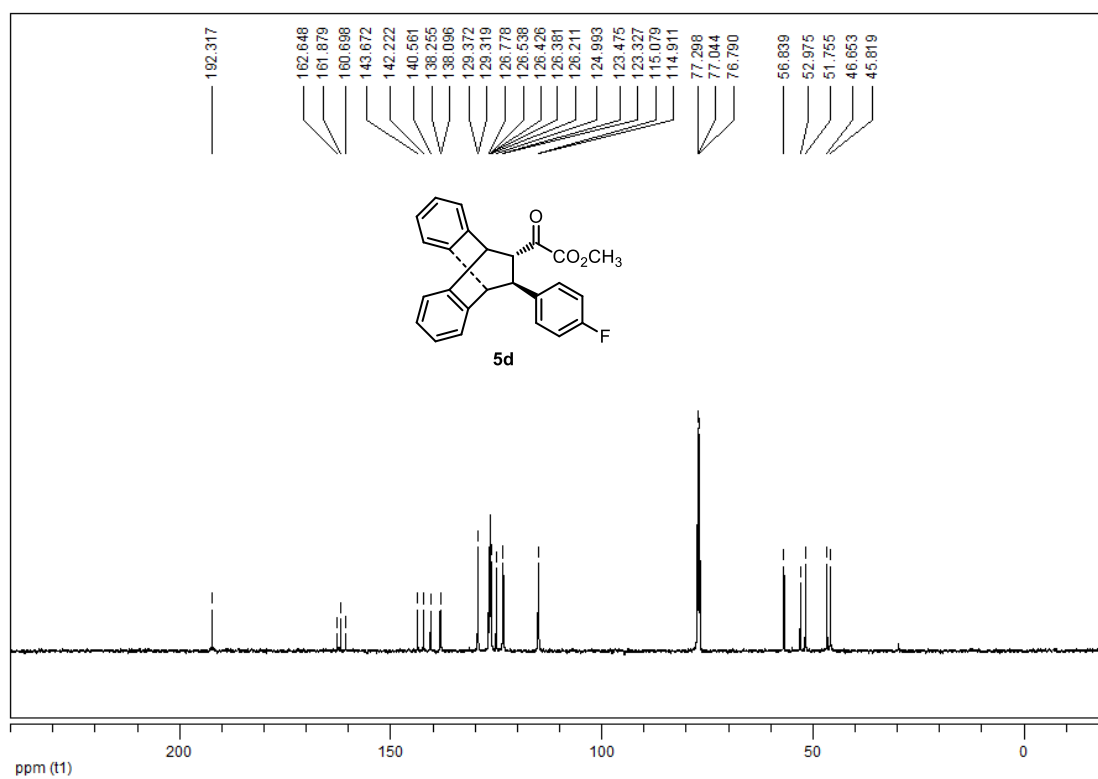
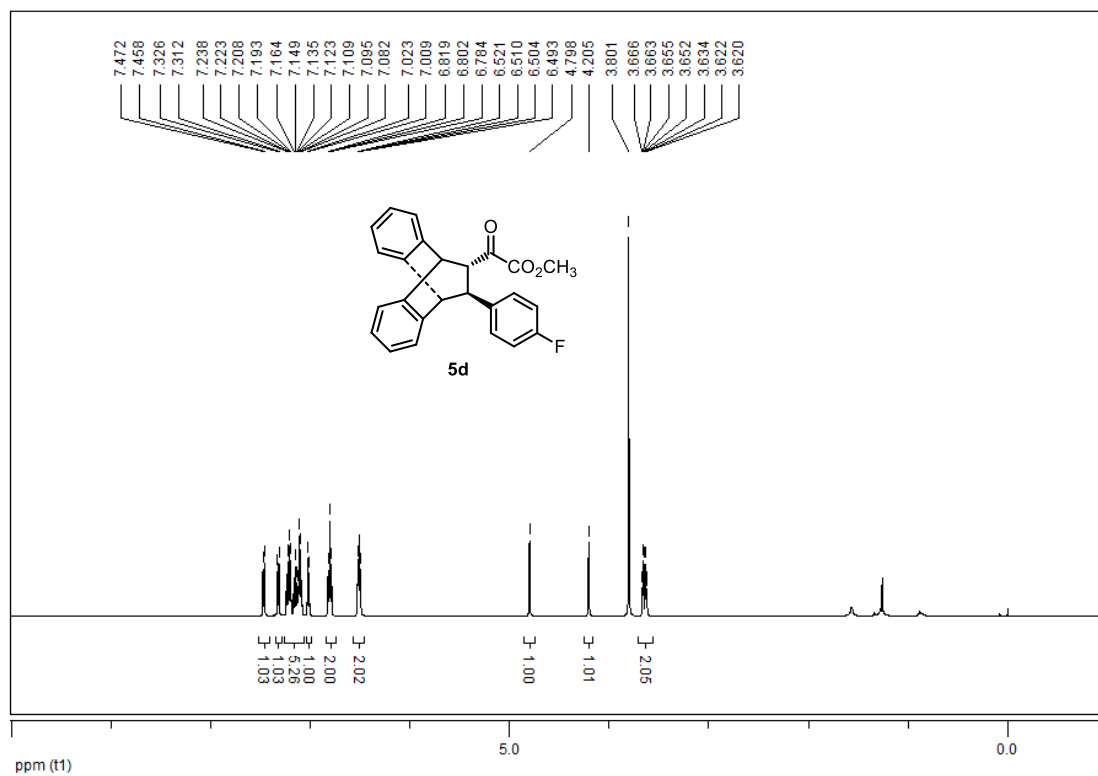
1699, 1592, 1565, 1458, 1377, 1169, 1085, 761, 698, 665; HRMS (ESI) calcd for  $C_{32}H_{27}O_4N_2BrNa^+$ : 637.0767, found: 637.0764.

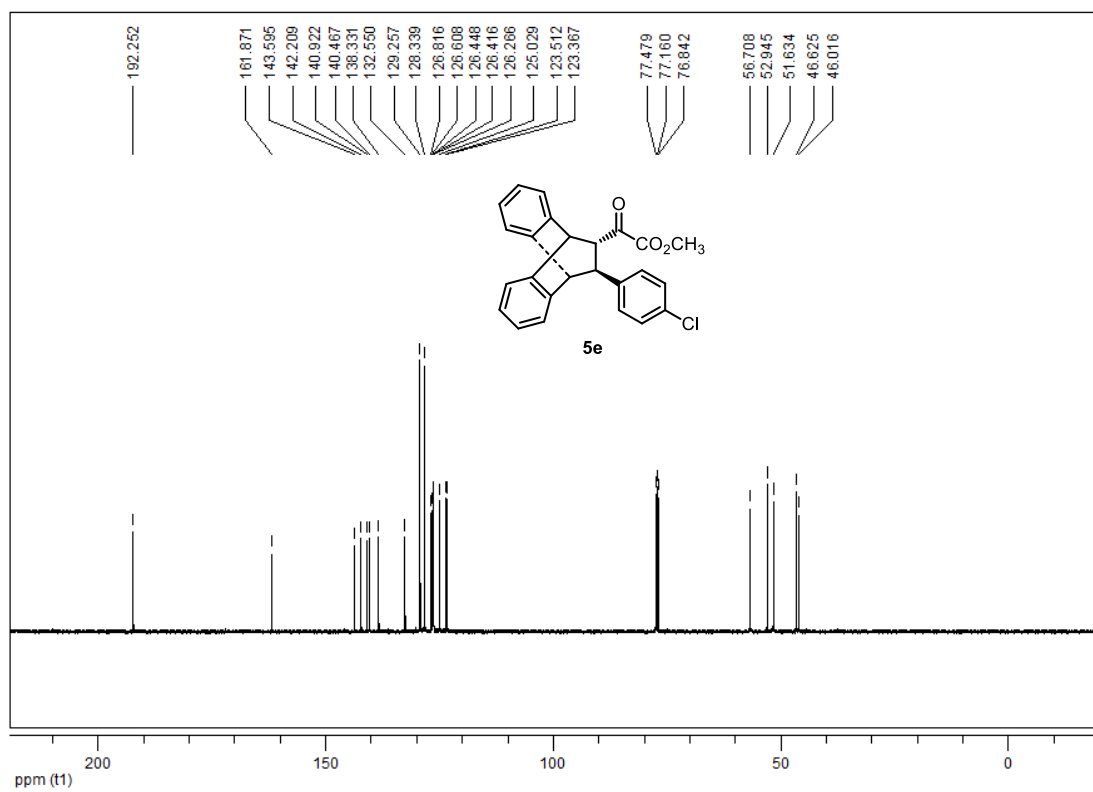
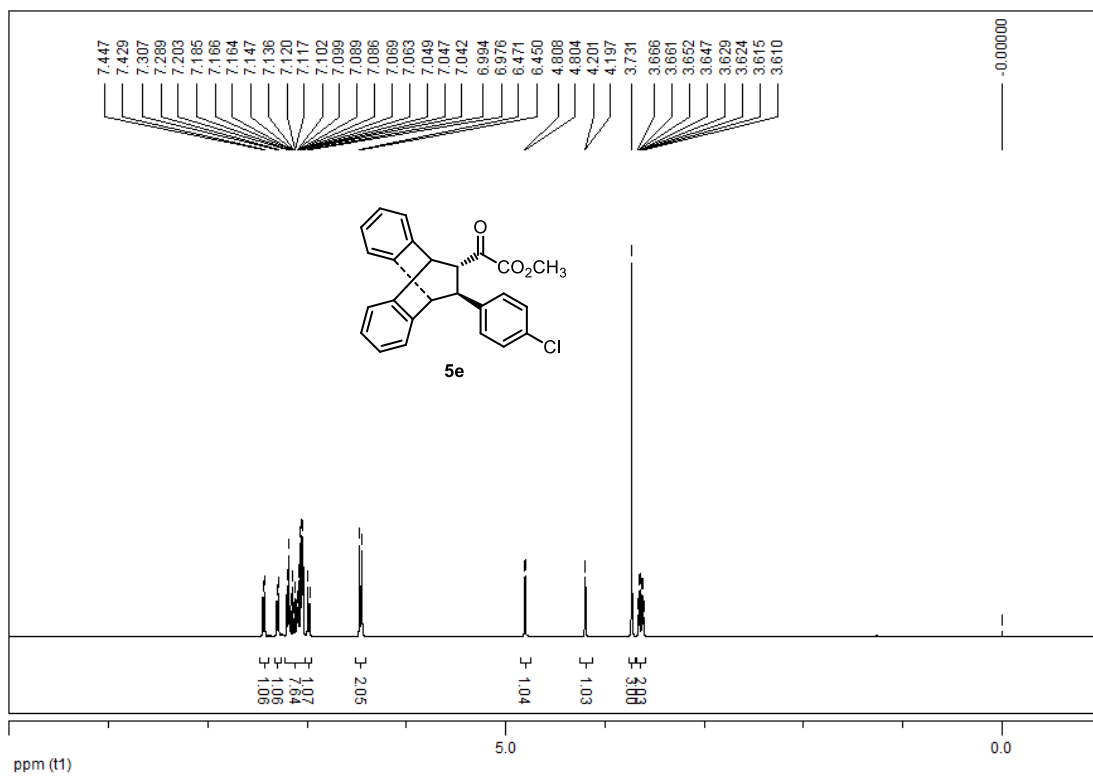
# NMR Spectra



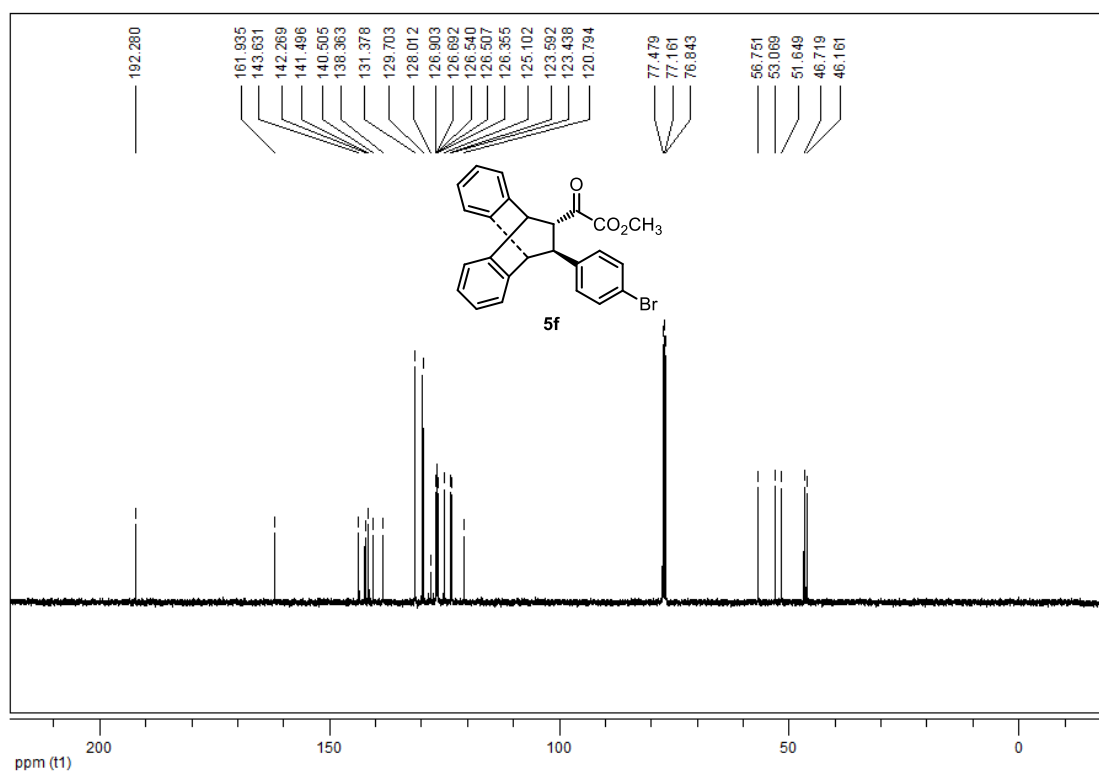
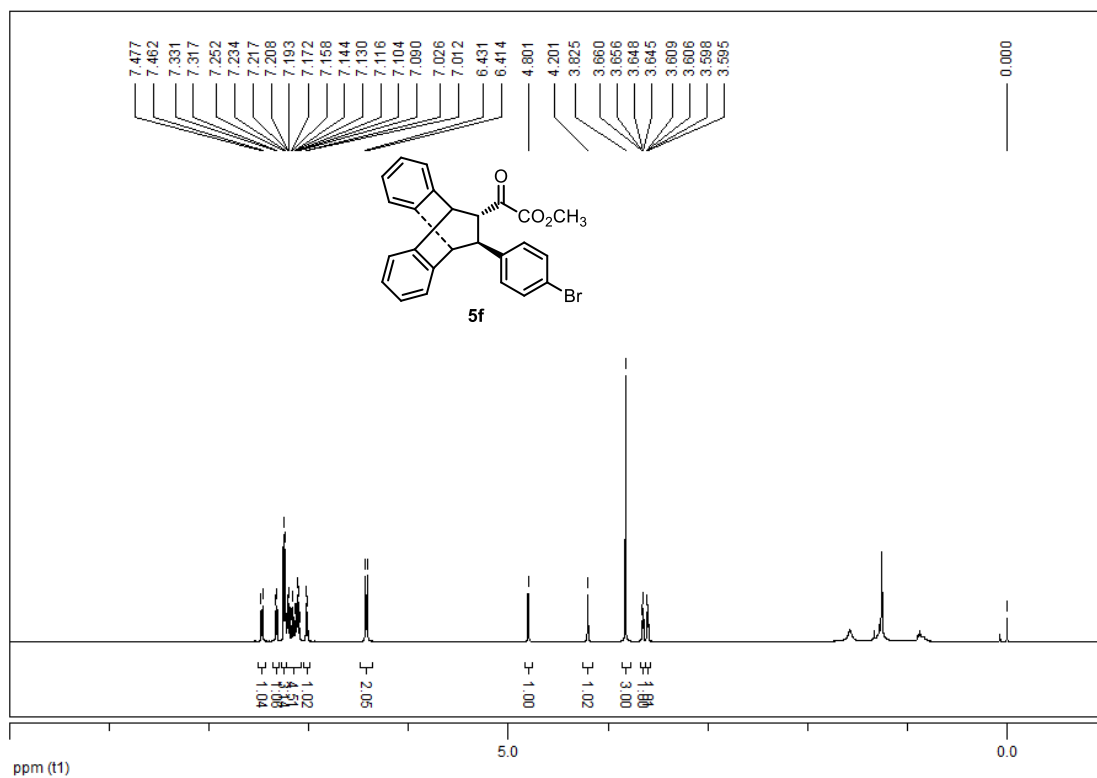




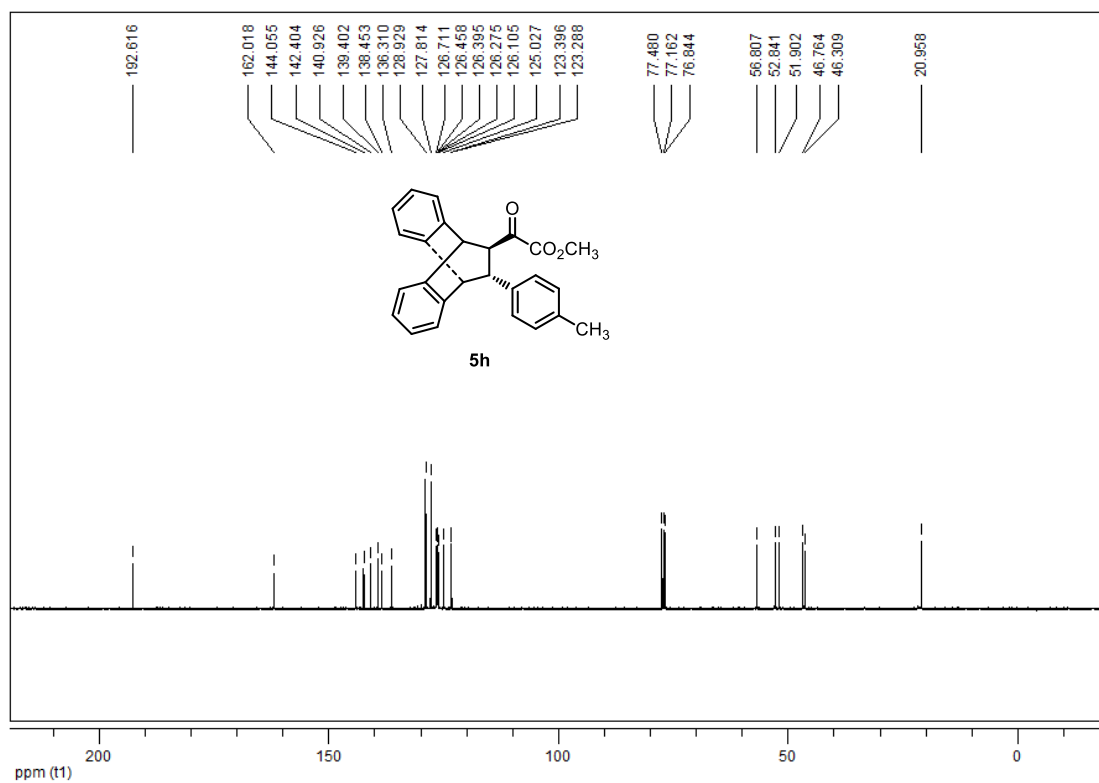
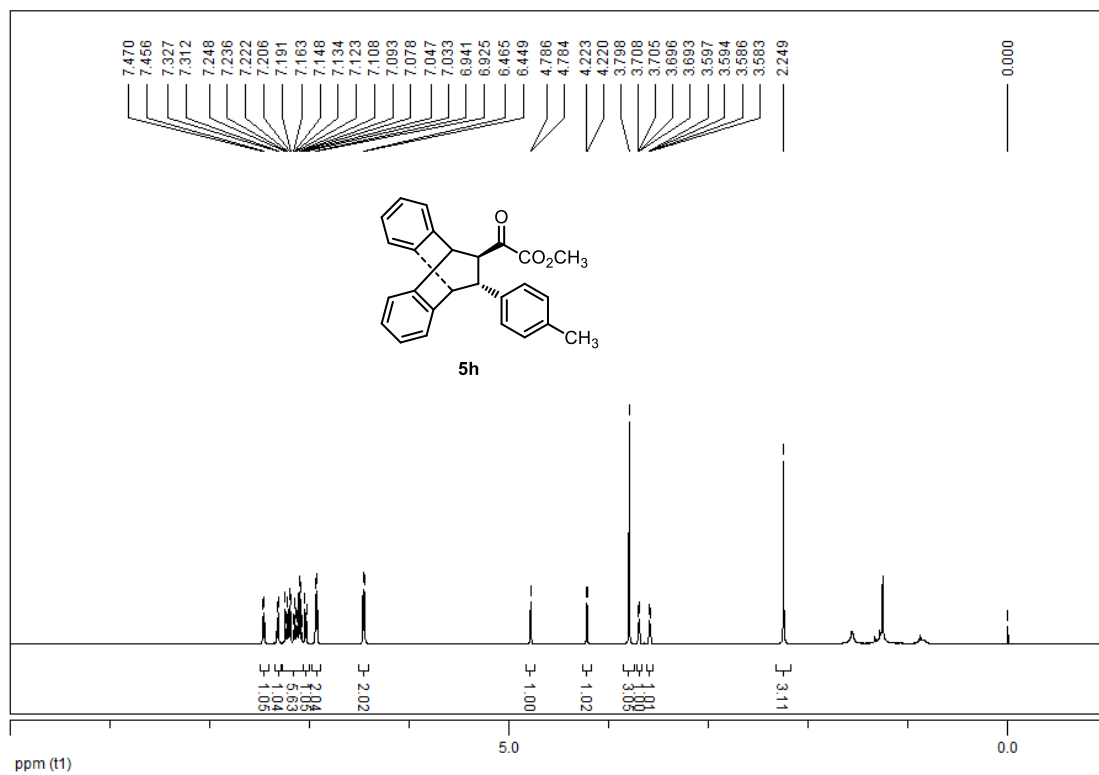


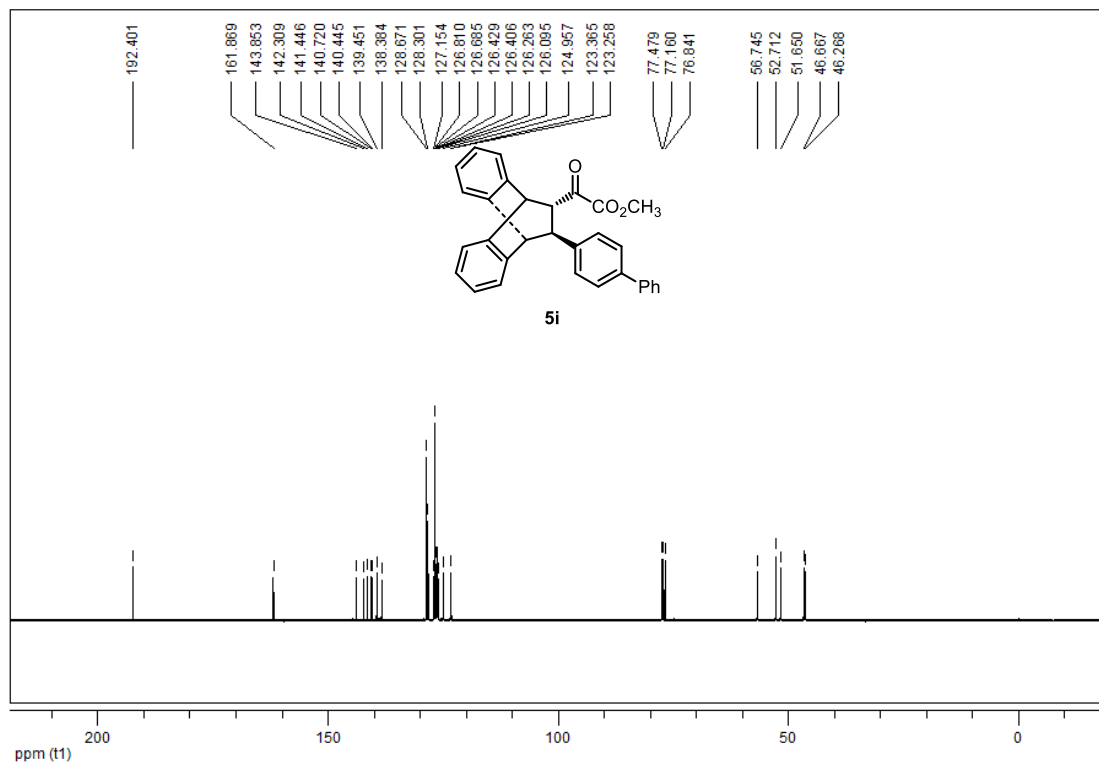
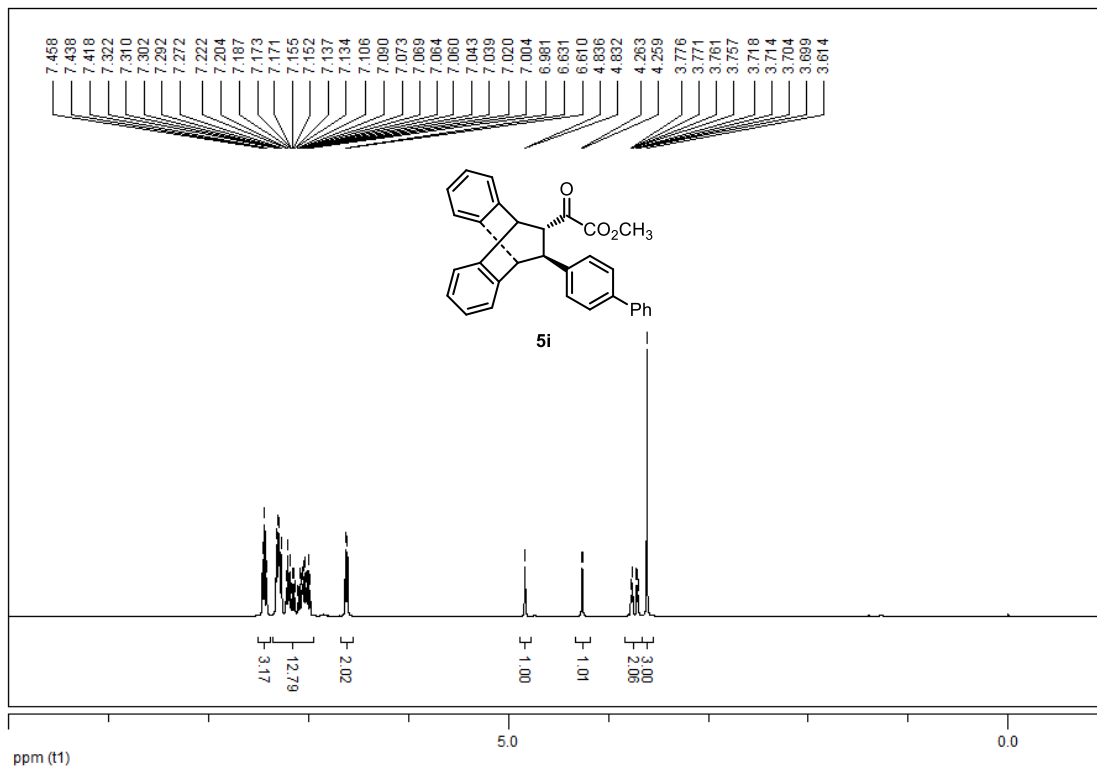


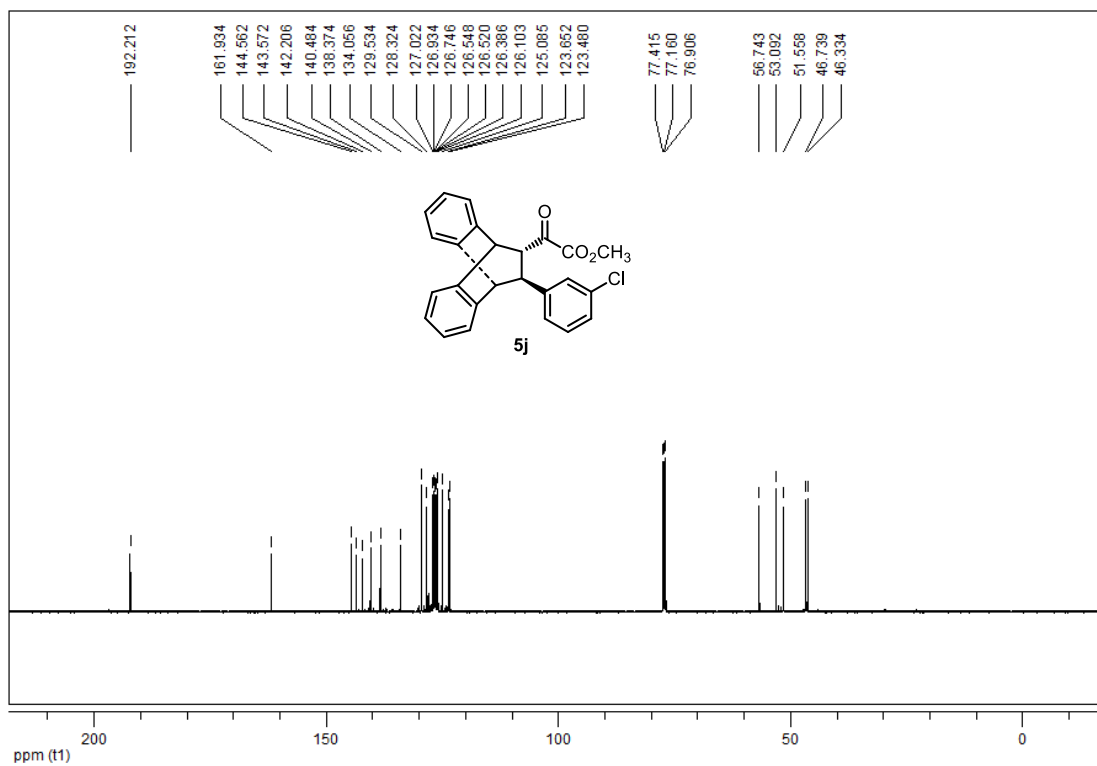
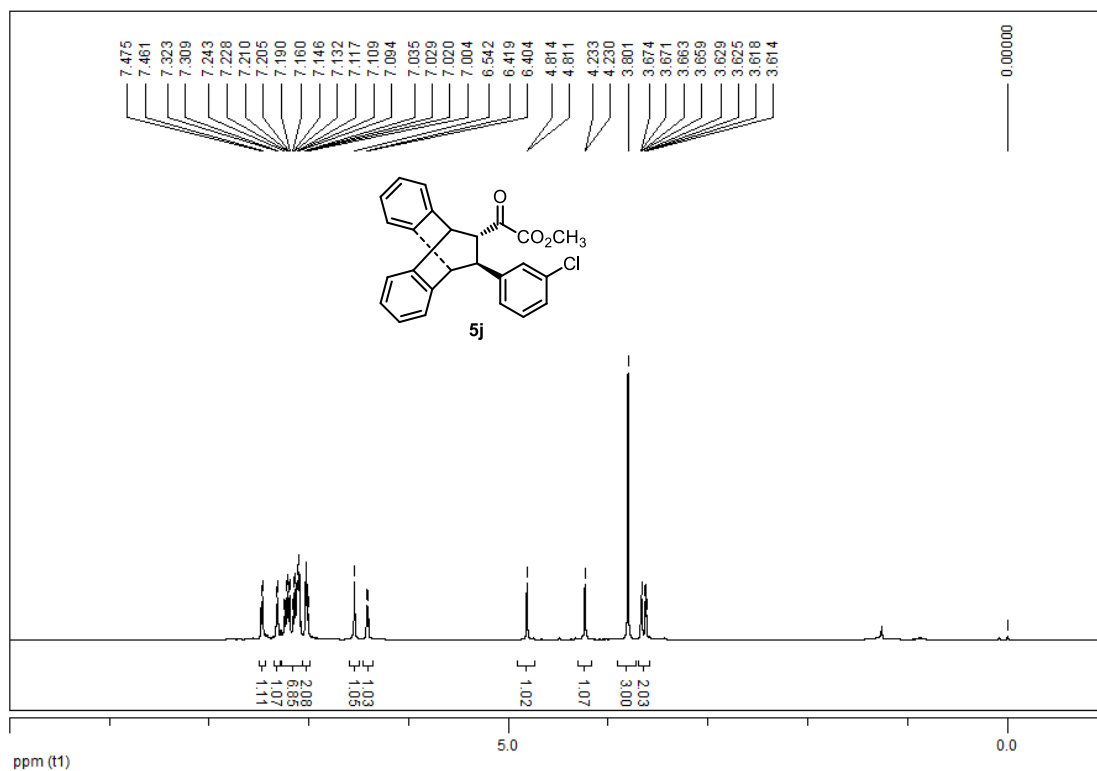


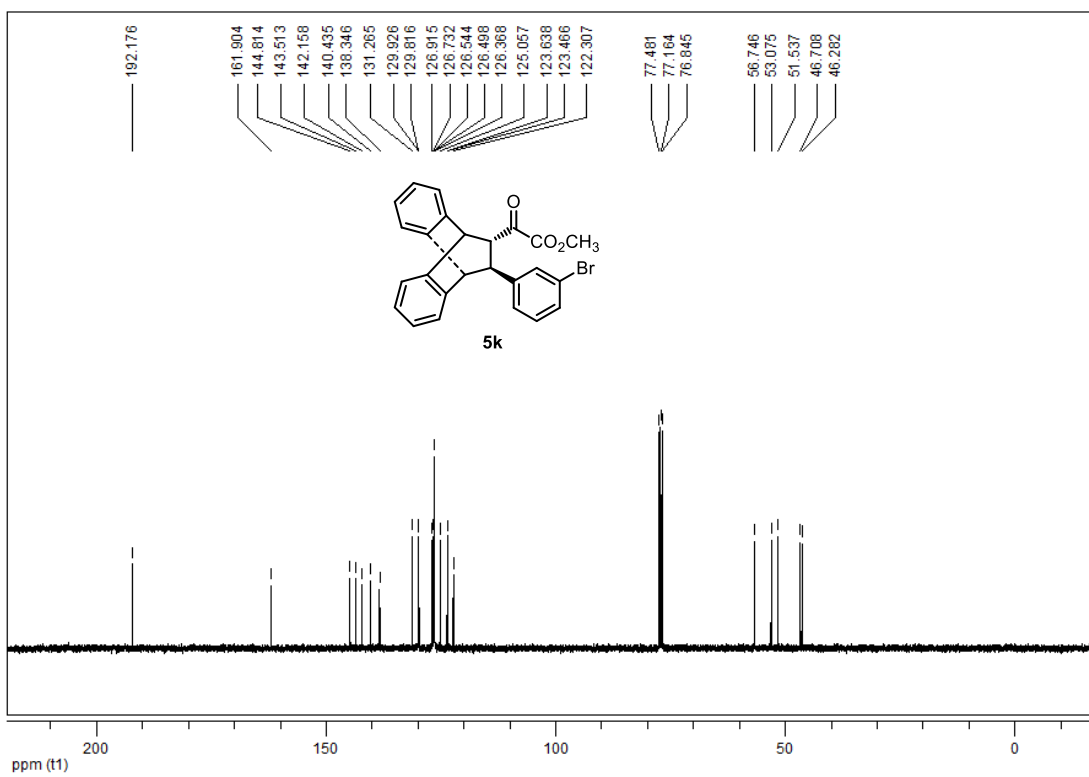
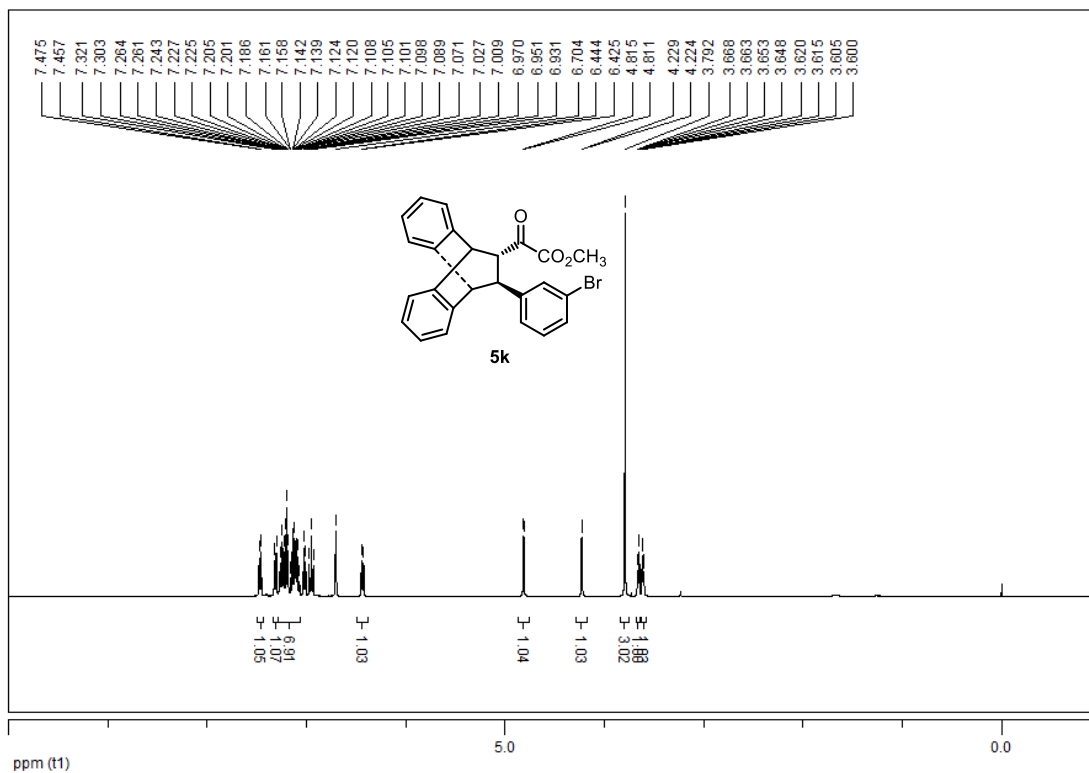


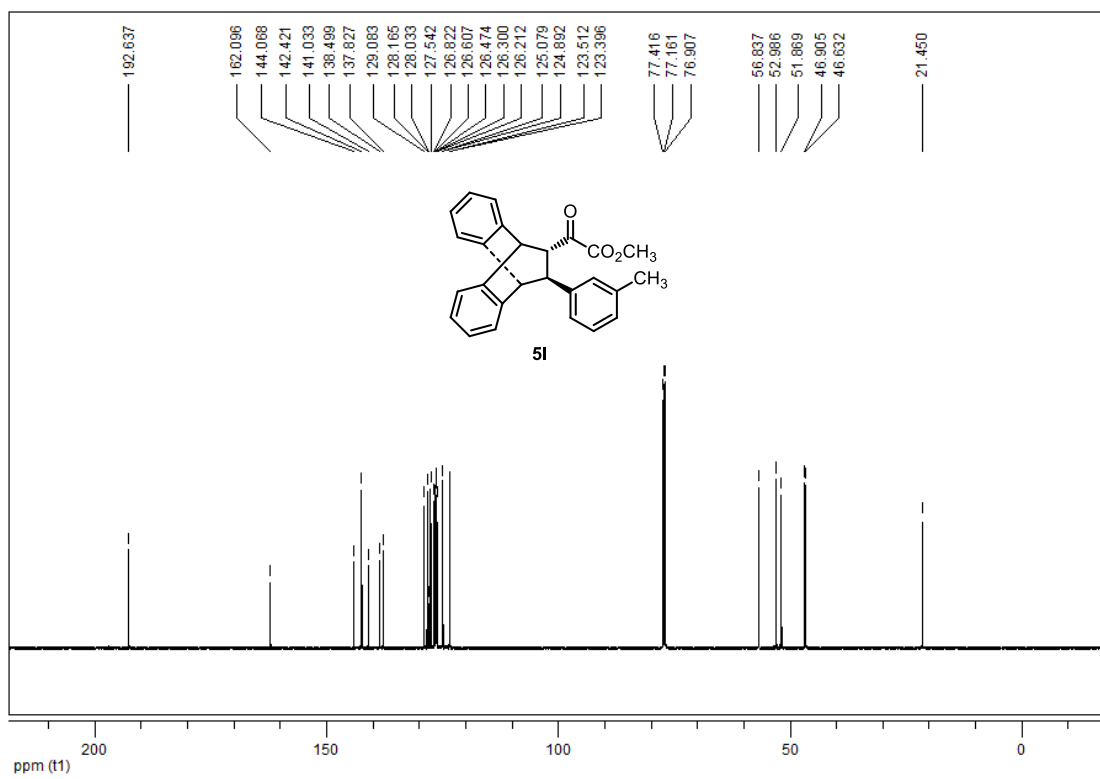
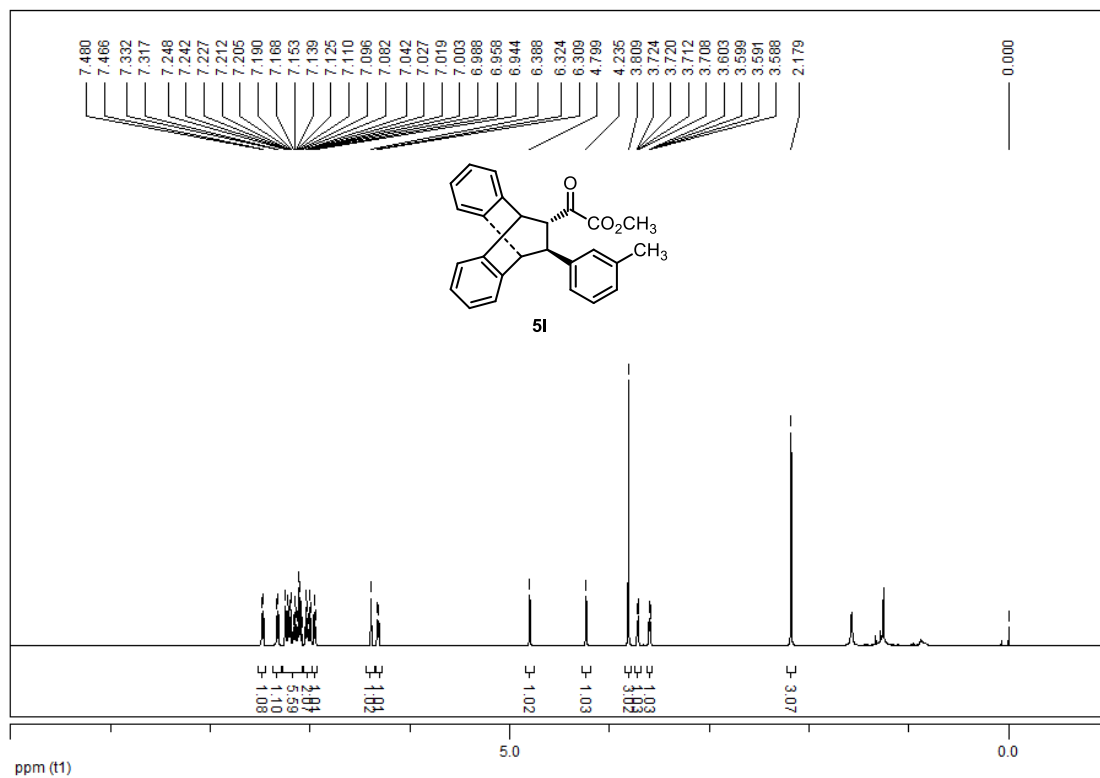


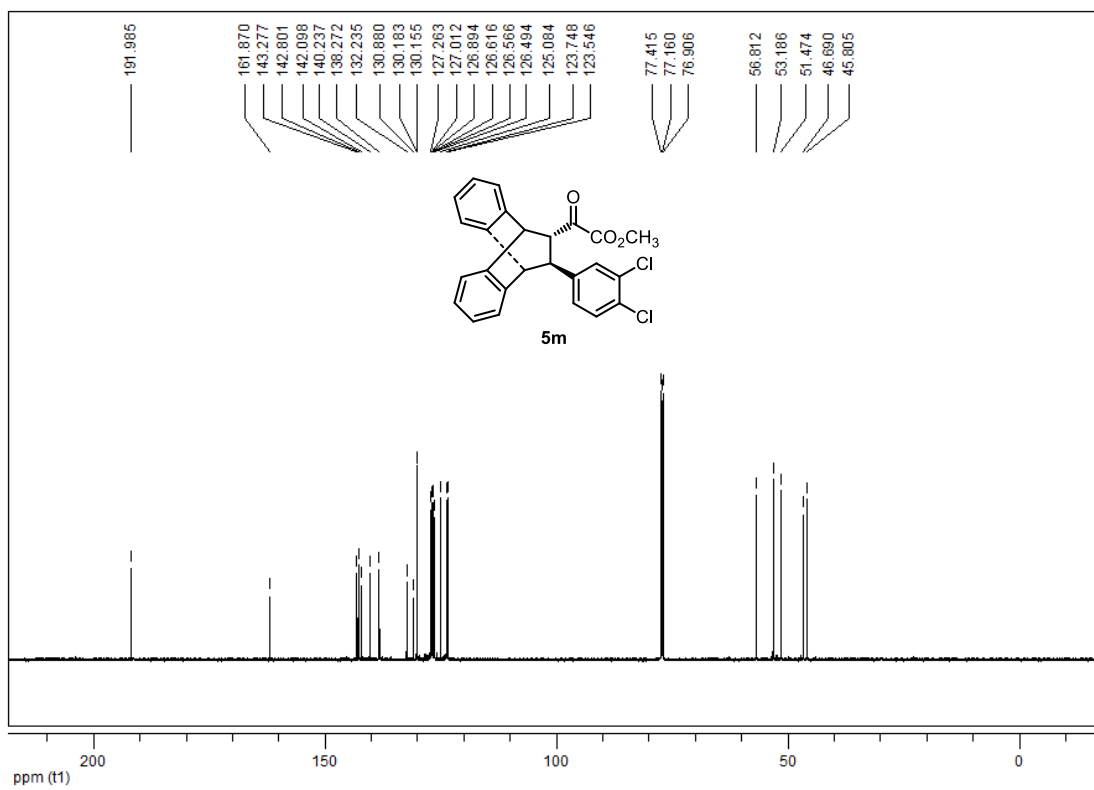
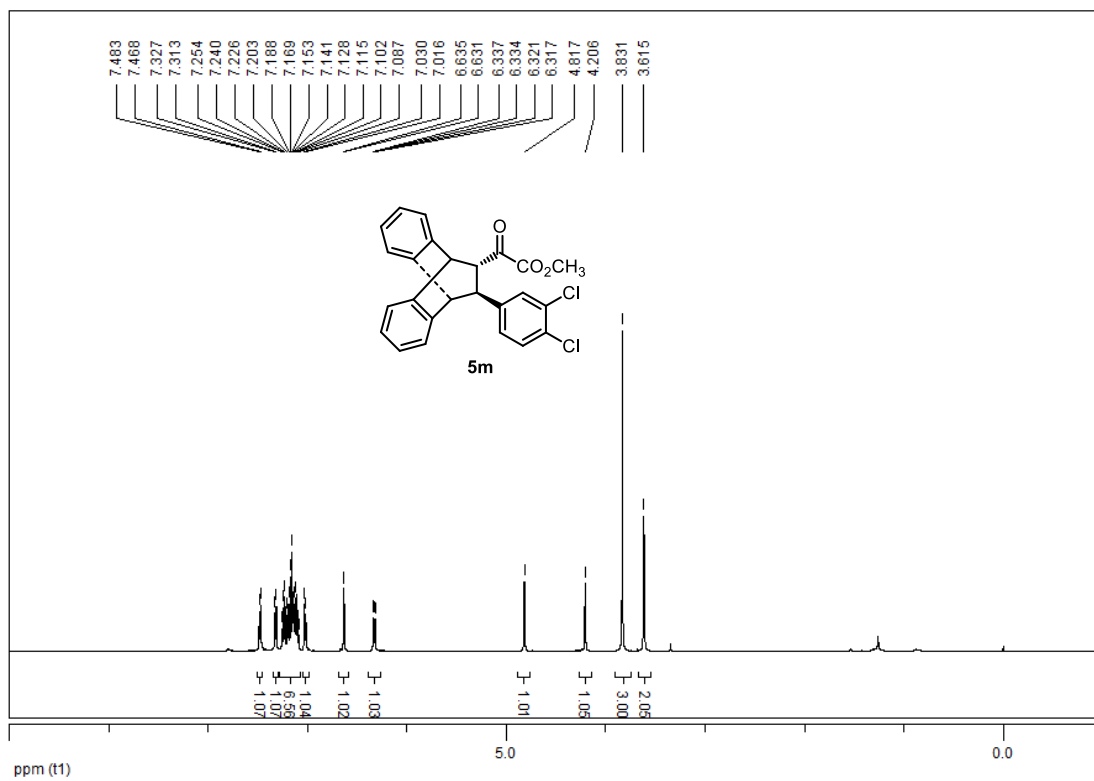






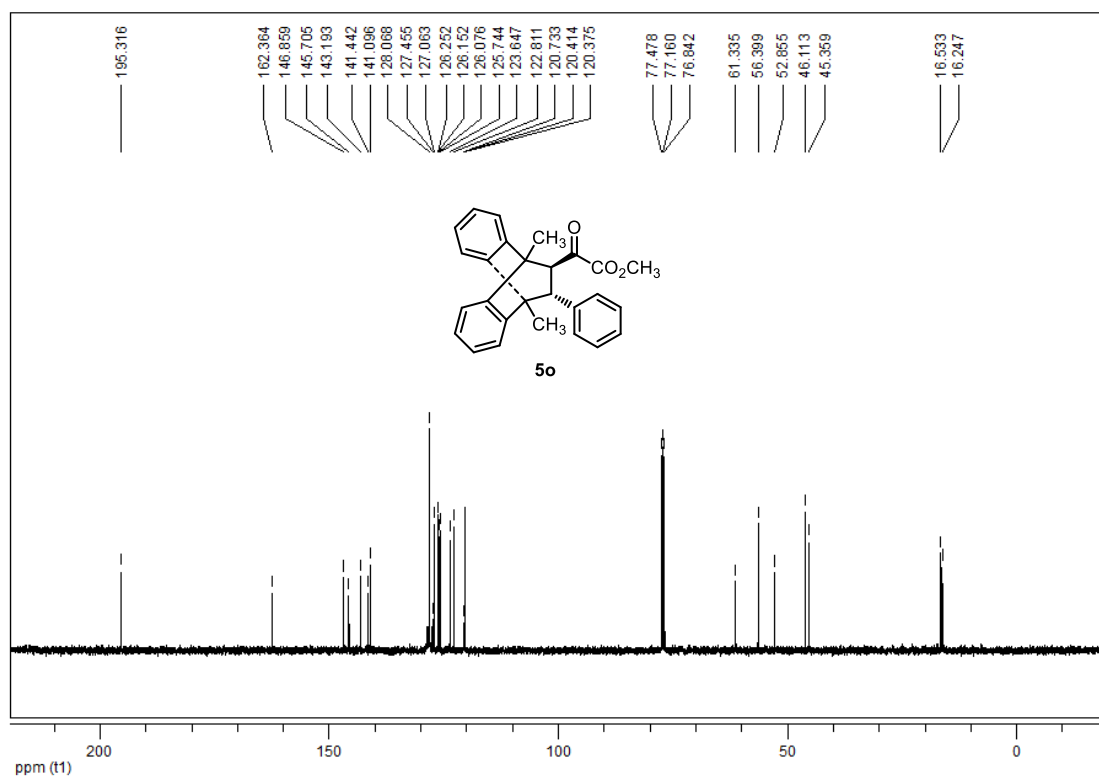
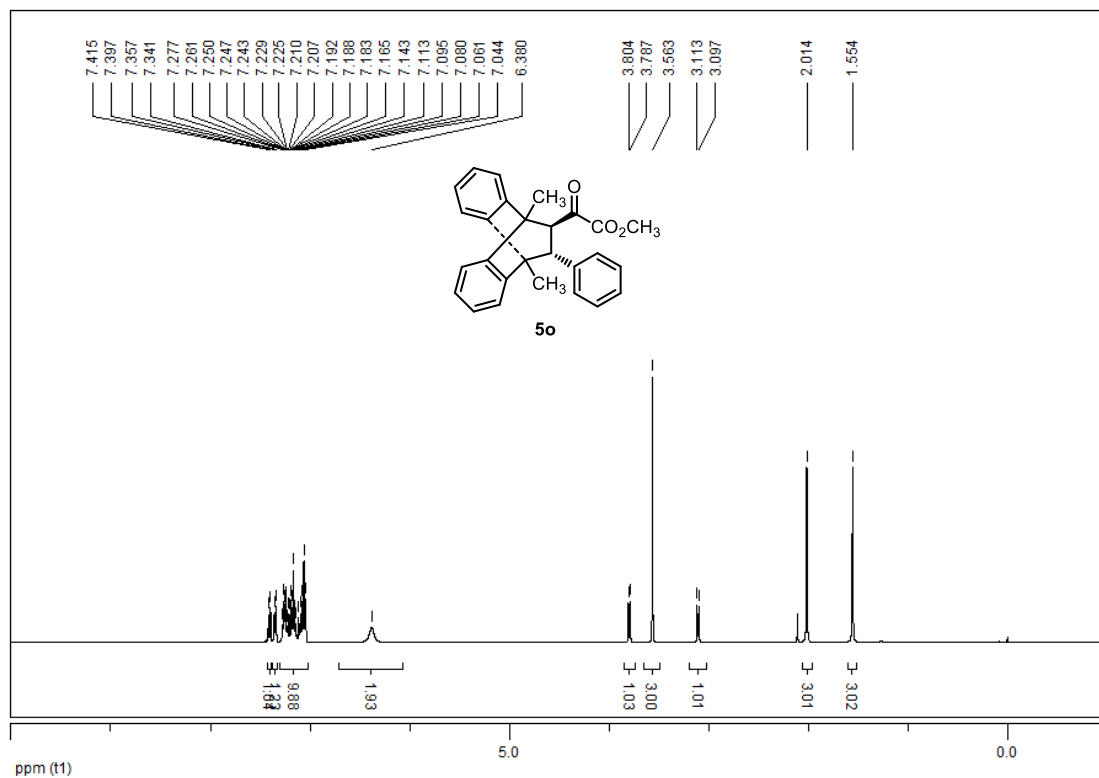


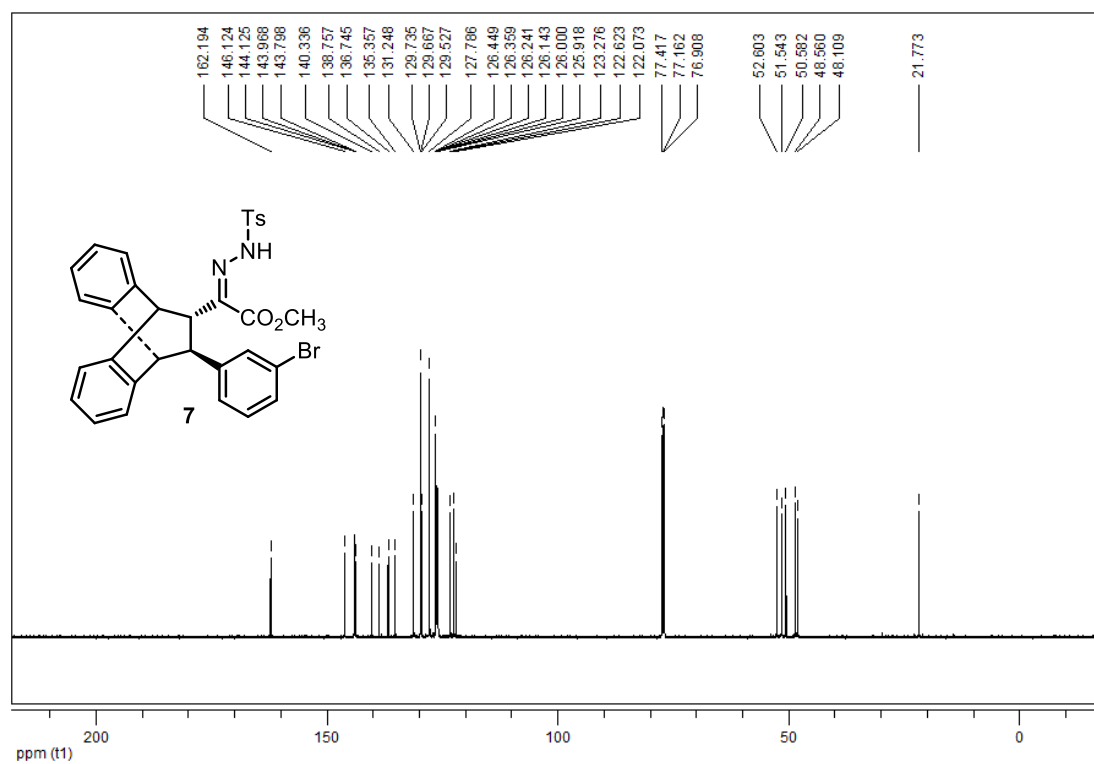
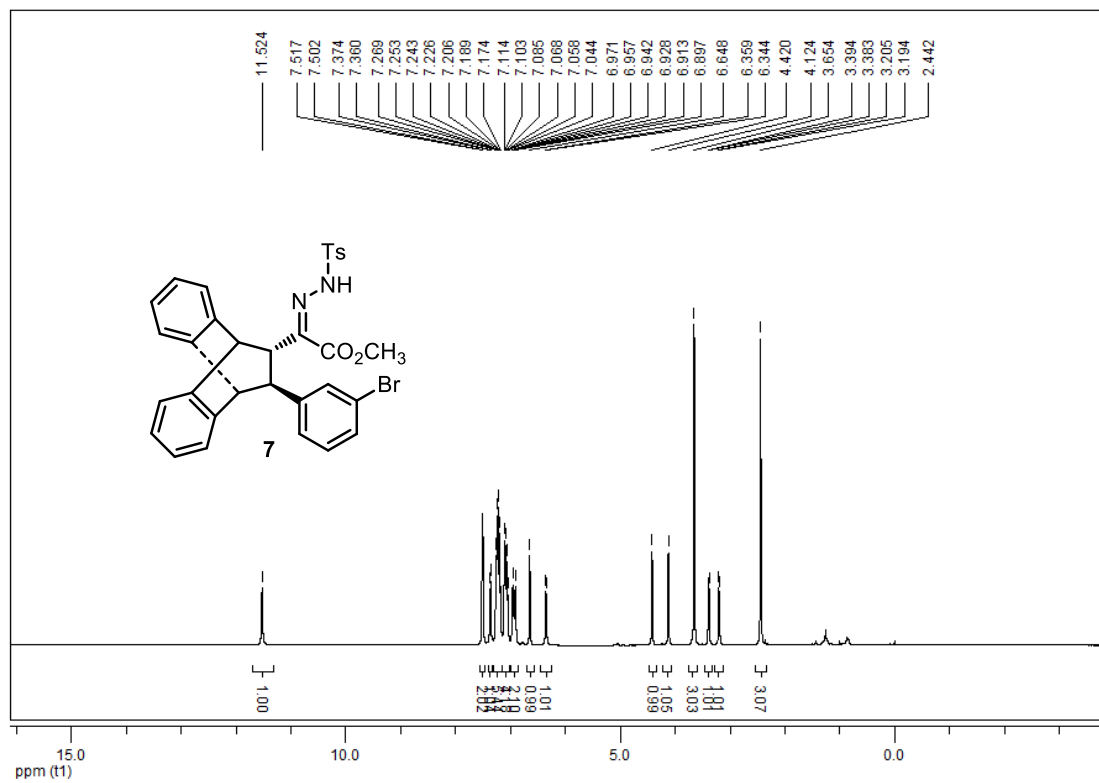




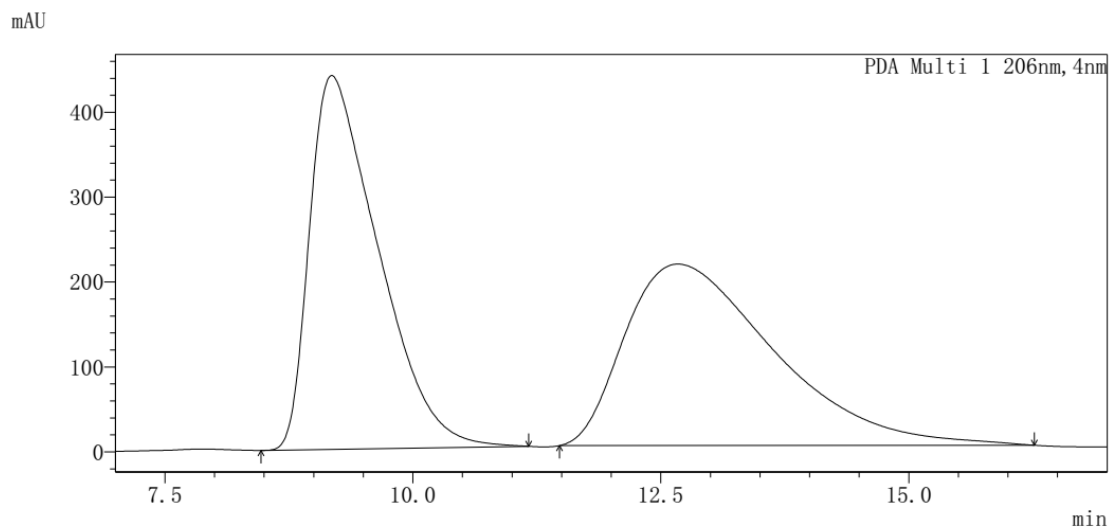
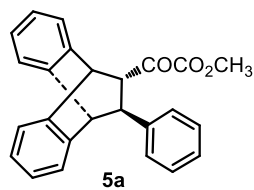








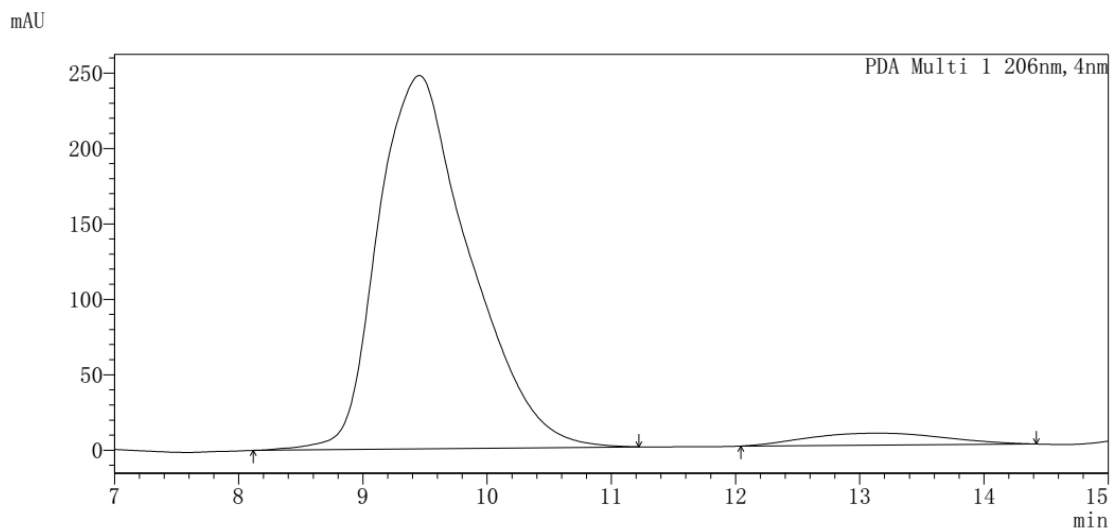
## HPLC Spectra



### <Peak Results>

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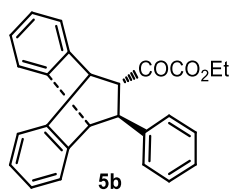
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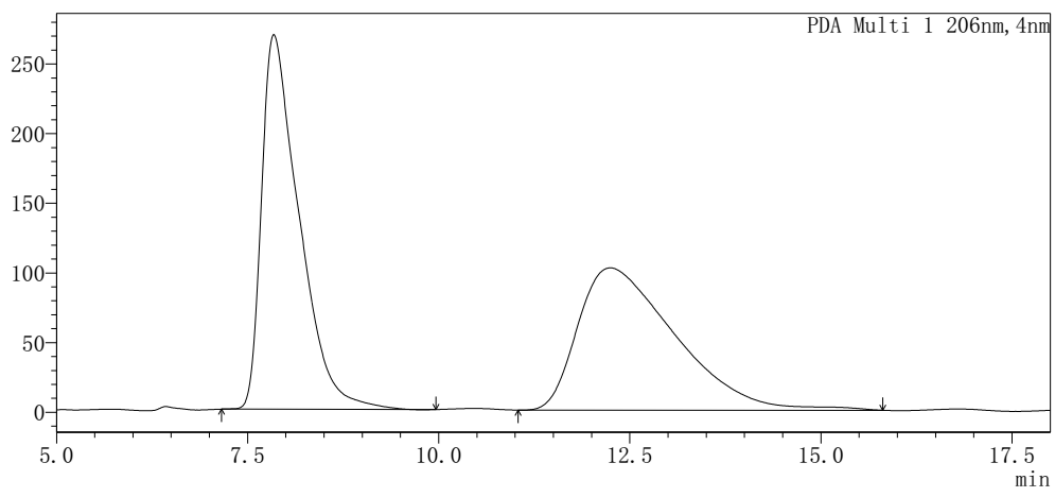
### <Peak Results>

PDA Ch1 206nm

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mAU

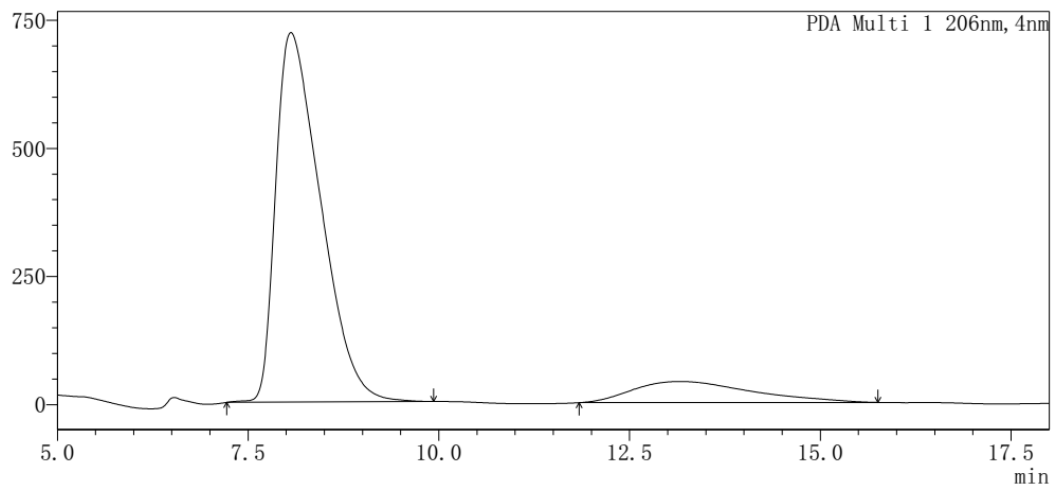


<Peak Results>

PDA Ch1 206nm

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1	7.843	268981	9186776	50.418
2	12.242	102174	9034453	49.582

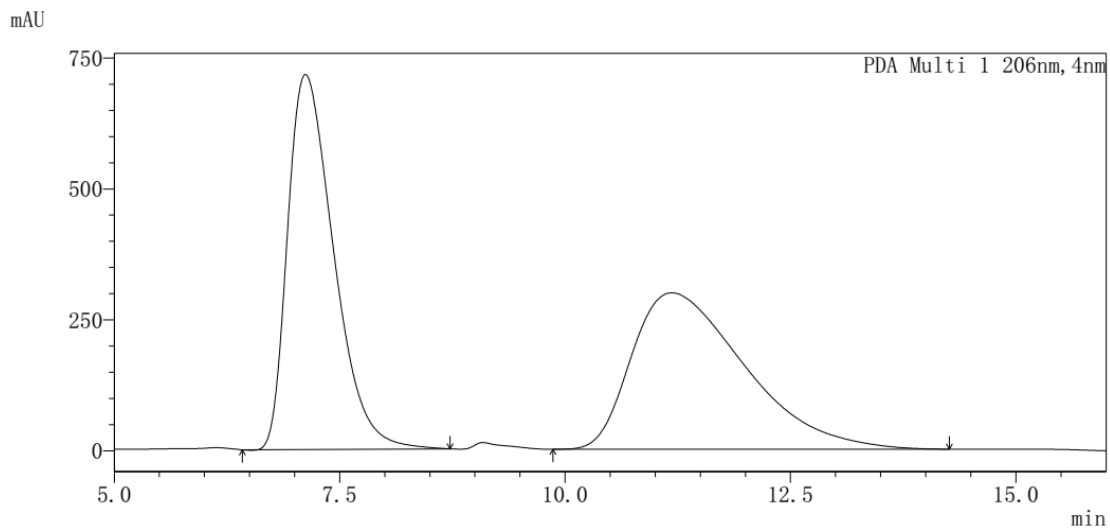
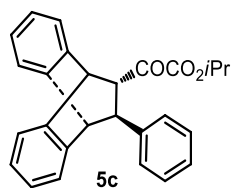
mAU



<Peak Results>

PDA Ch1 206nm

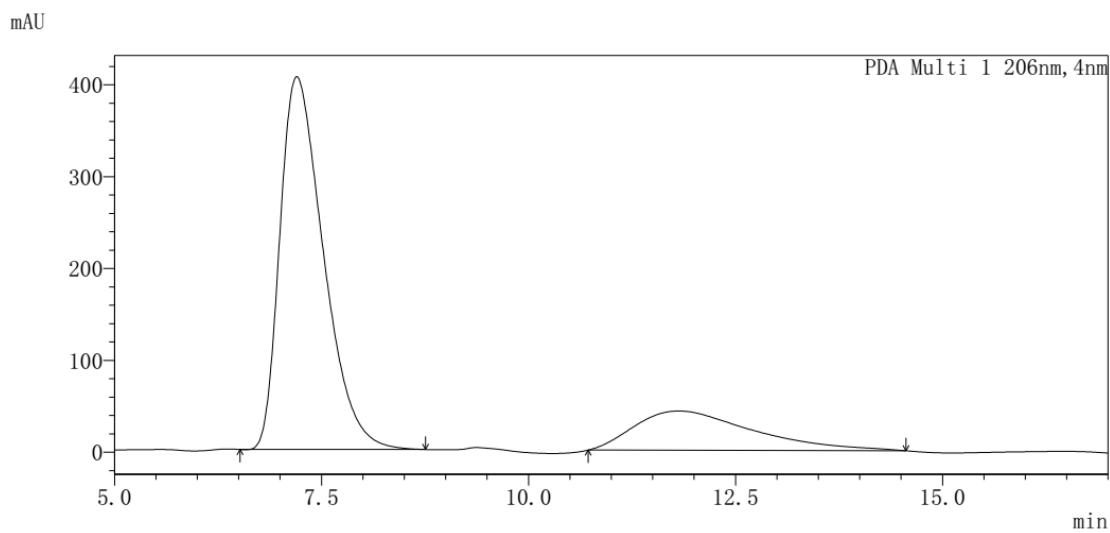
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.061	720599	29467553	86.829
2	13.166	41188	4469754	13.171



<Peak Results>

PDA Ch1 206nm

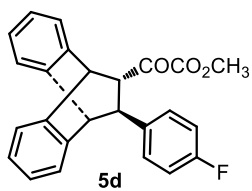
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.119	716402	25480269	49.411
2	11.182	298863	26087405	50.589



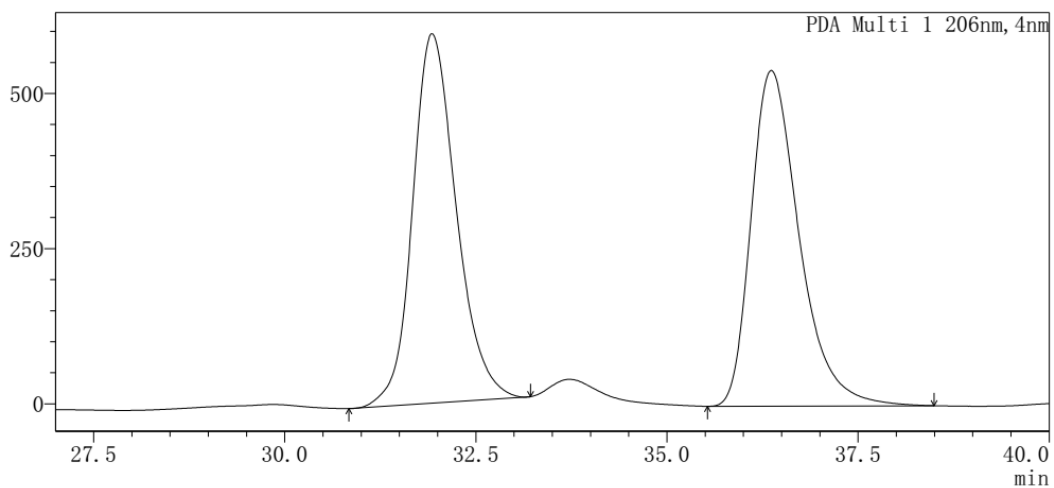
<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.201	406002	14844113	77.688
2	11.822	42816	4263235	22.312



mAU

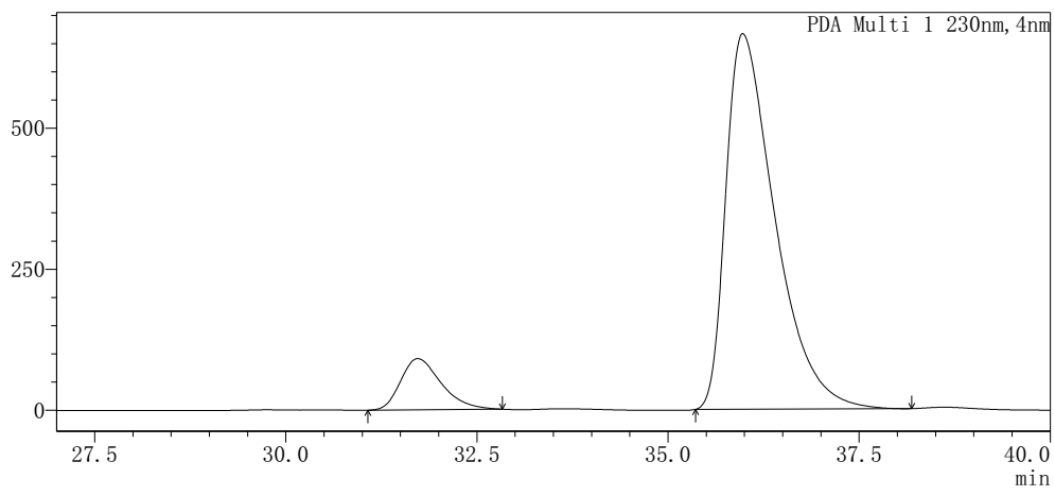


<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/ %
1	31.925	595421	23645482	49.952
2	36.364	540898	23690963	50.048

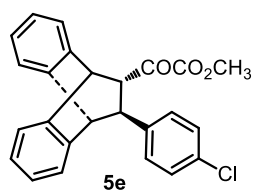
mAU



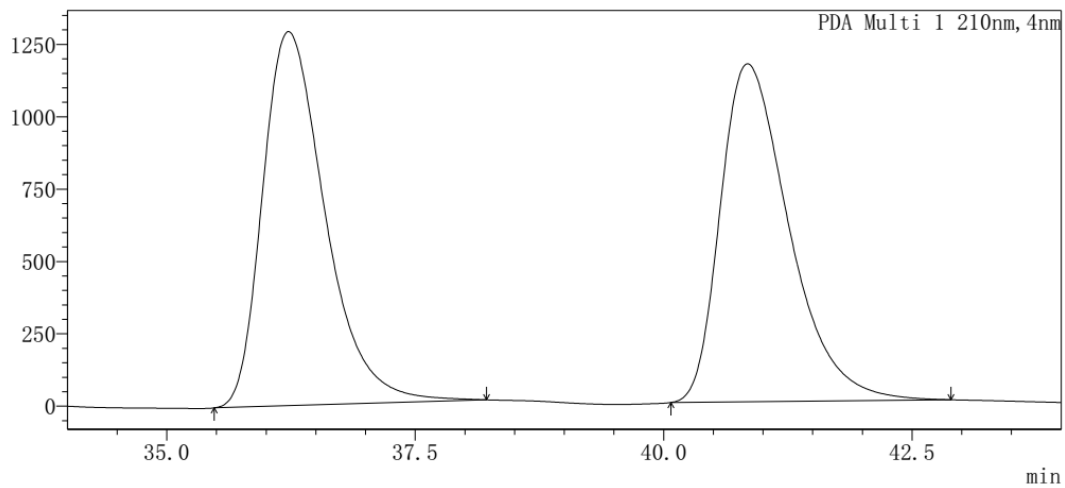
<Peak Results>

PDA Ch1 230nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/ %
1	31.727	90762	3346172	10.114
2	35.978	665705	29736945	89.886



mAU

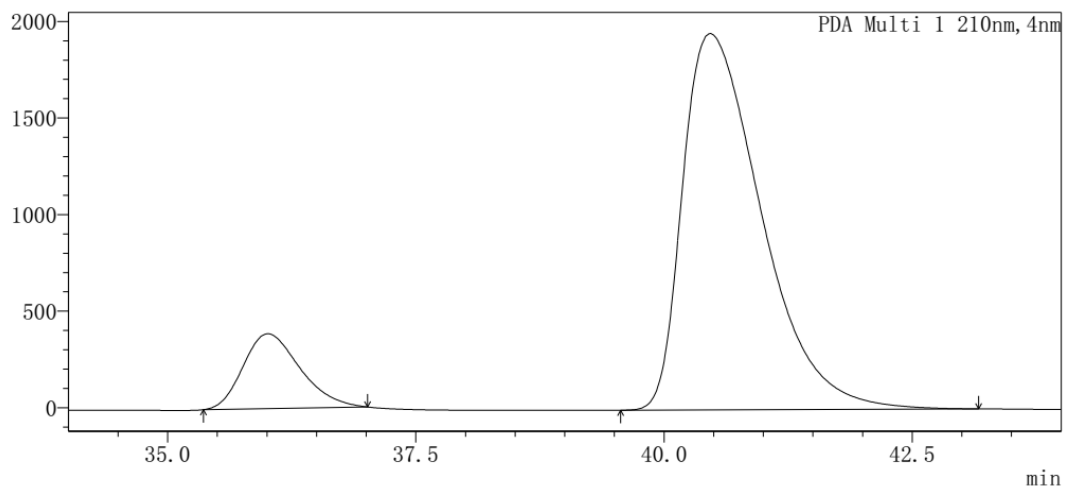


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	36.224	1292603	56691467	50.213
2	40.844	1167899	56209909	49.787

mAU

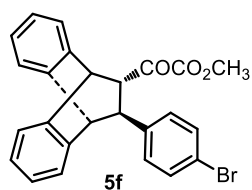


<Peak Results>

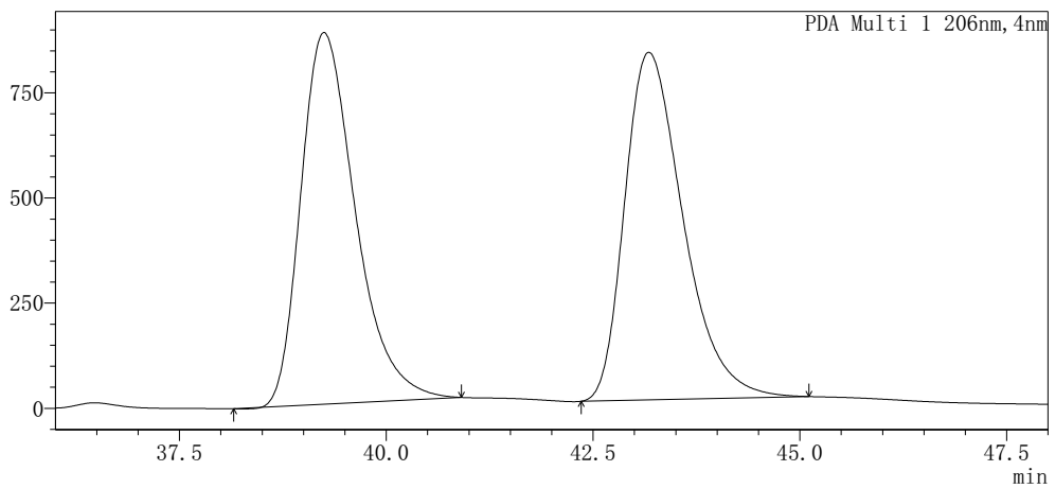
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	36.010	387751	15448626	12.572
2	40.469	1948797	107428429	87.428





mAU

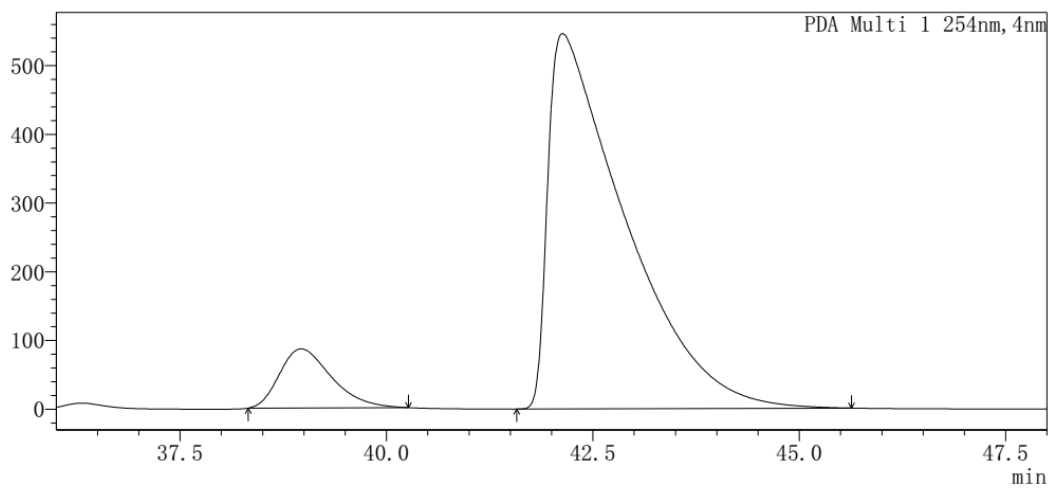


<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/ %
1	39.247	884106	40573007	50.001
2	43.174	826677	40572136	49.999

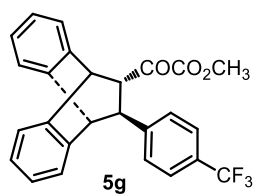
mAU



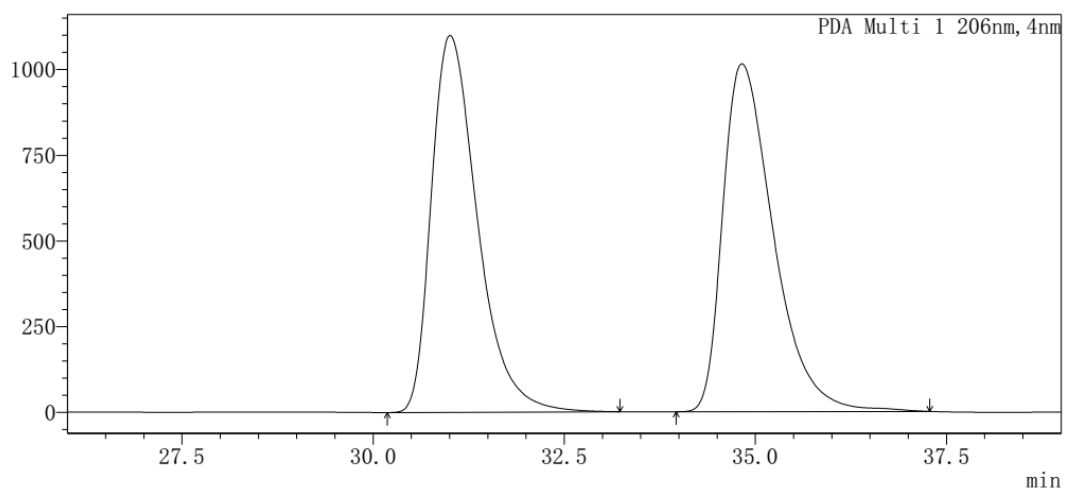
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/ %
1	38.964	86055	3762892	9.556
2	42.131	546441	35612485	90.444



mAU

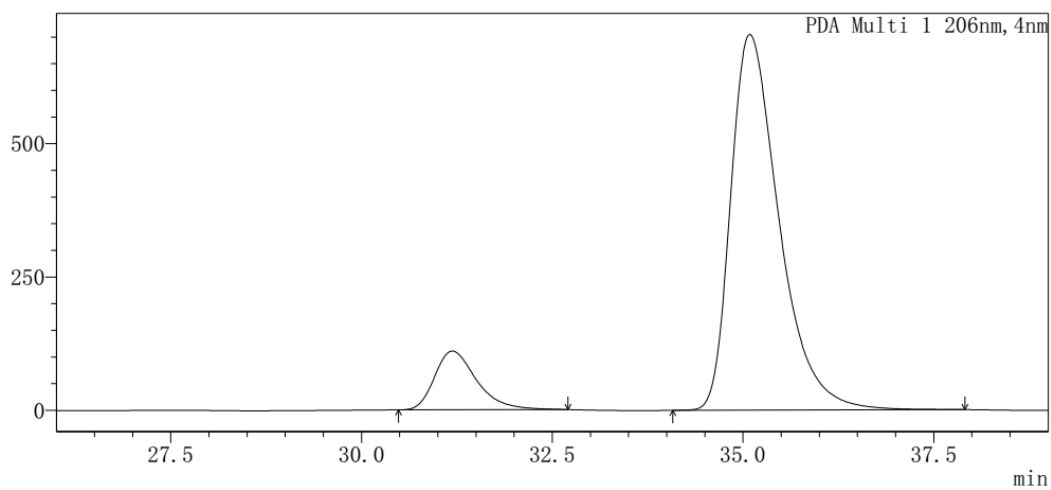


<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	31.007	1099049	46113008	49.621
2	34.824	1014885	46818102	50.379

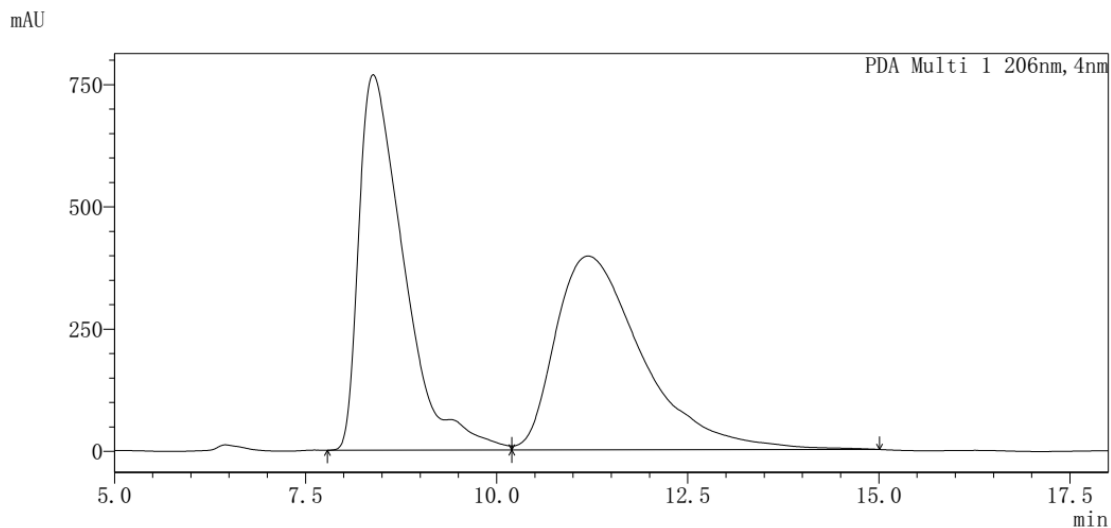
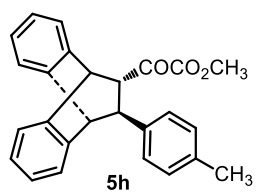
mAU



<Peak Results>

PDA Ch1 206nm

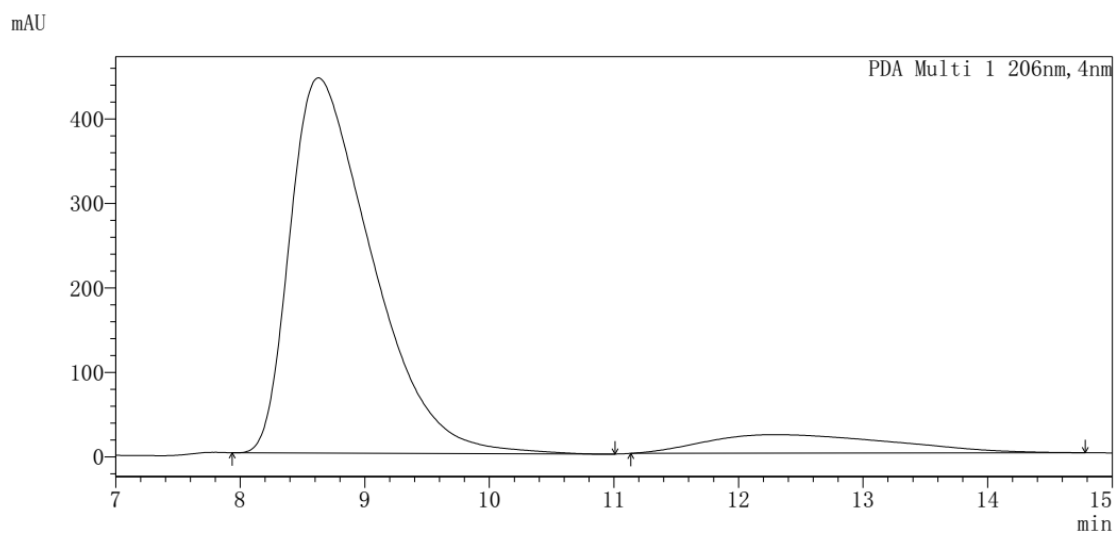
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	31.191	110353	4221185	11.967
2	35.089	704606	31053812	88.033



<Peak Results>

PDA Ch1 206nm

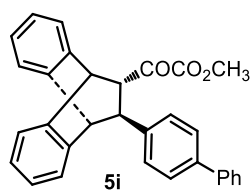
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.383	767827	31416617	49.975
2	11.199	396346	31448599	50.025



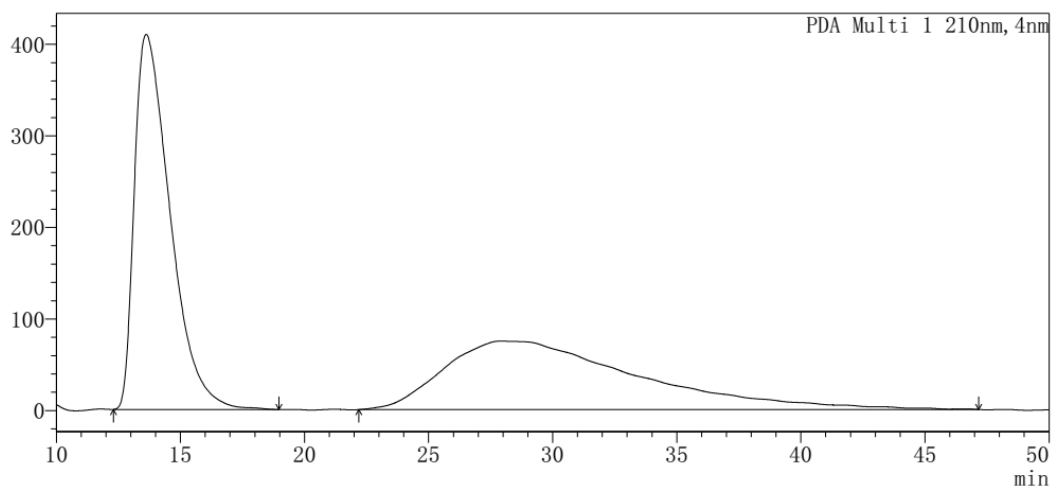
<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.627	444257	20331403	89.811
2	12.280	21930	2306487	10.189



mAU

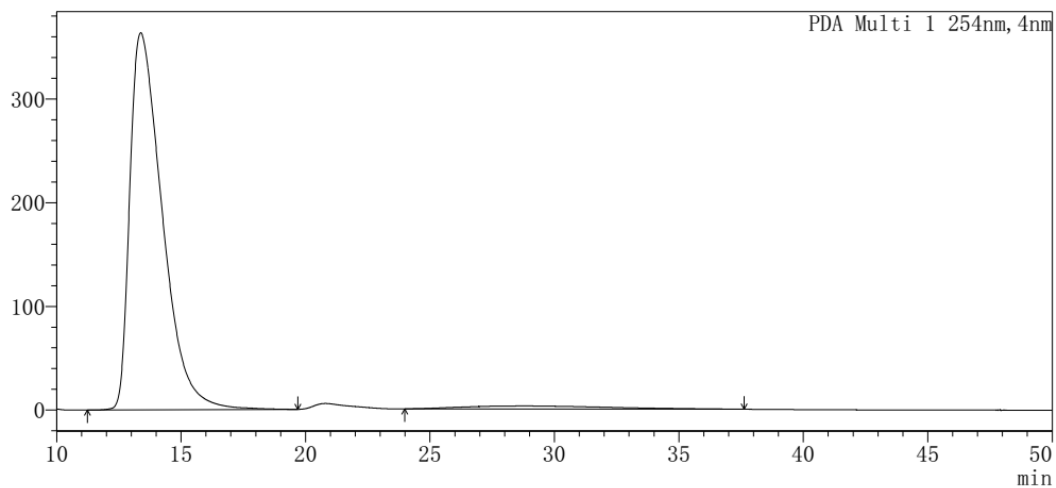


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.617	409603	41067371	50.476
2	27.893	74839	40292421	49.524

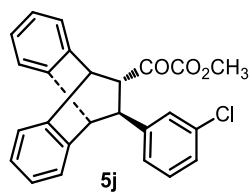
mAU



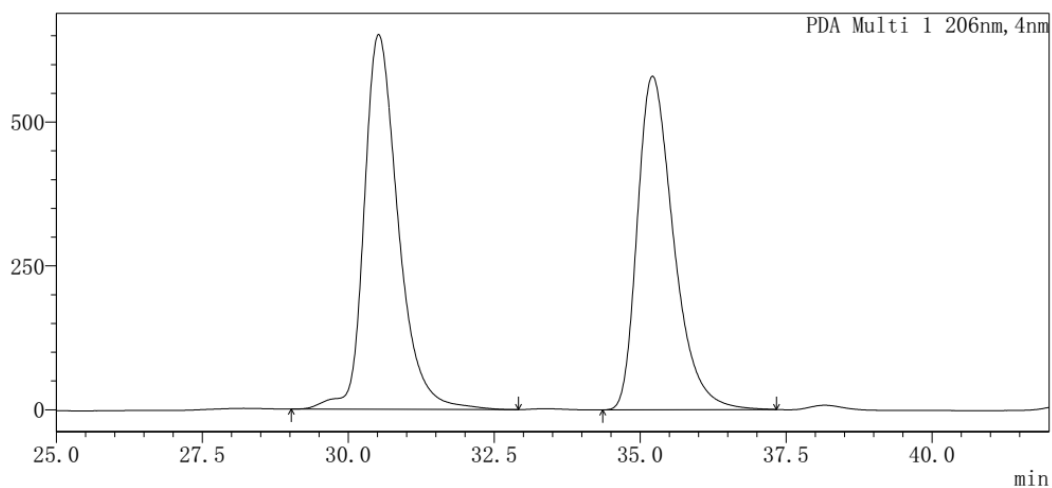
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.378	363706	32931600	96.380
2	28.830	2986	1236955	3.620



mAU

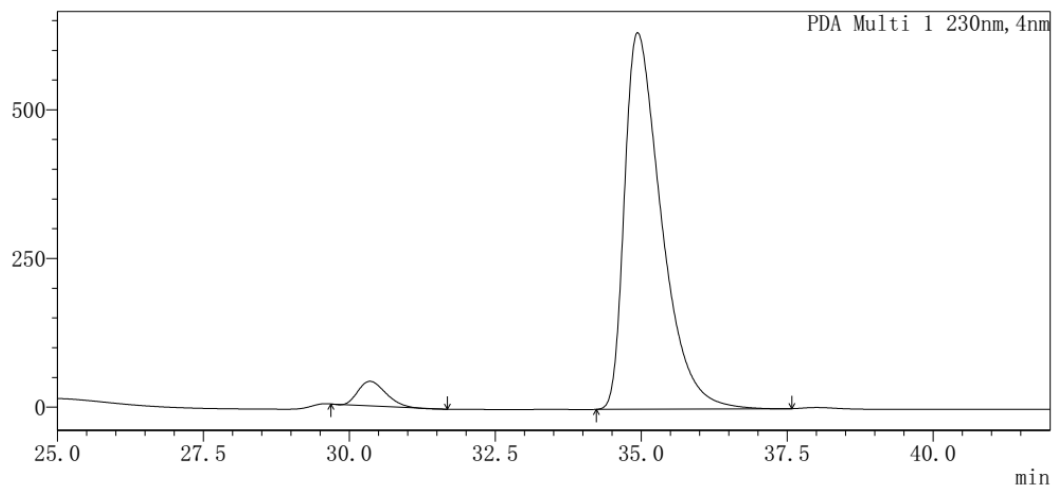


<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	30.519	651739	26535831	51.426
2	35.210	580219	25064688	48.574

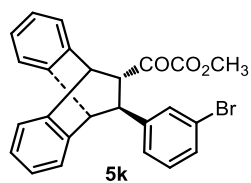
mAU



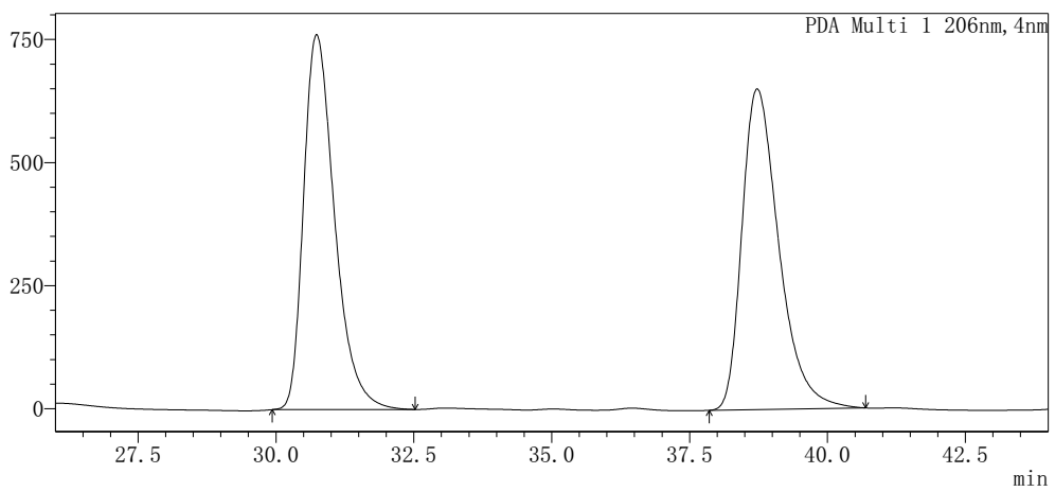
<Peak Results>

PDA Ch1 230nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	30.353	41177	1330066	4.568
2	34.937	633255	27790162	95.432



mAU

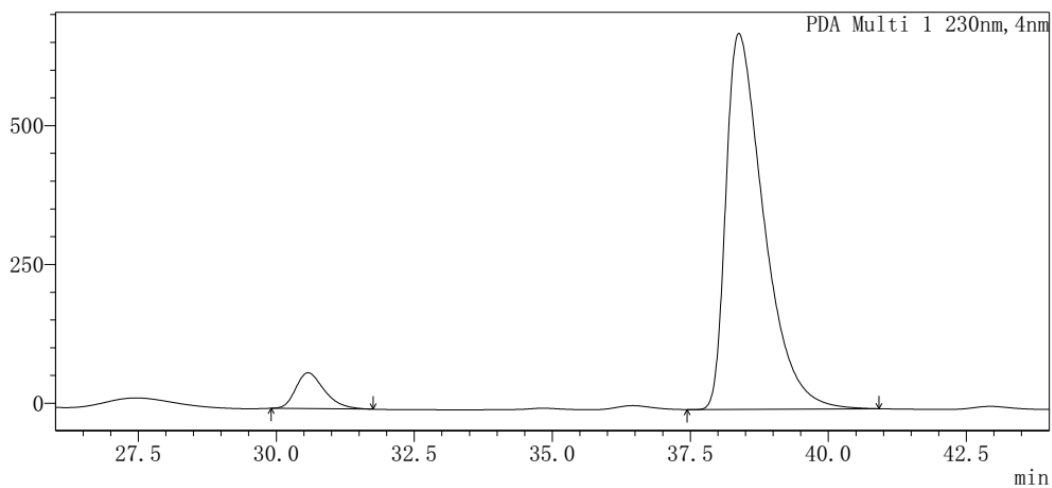


<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	30.735	761910	29784586	49.535
2	38.724	651779	30343271	50.465

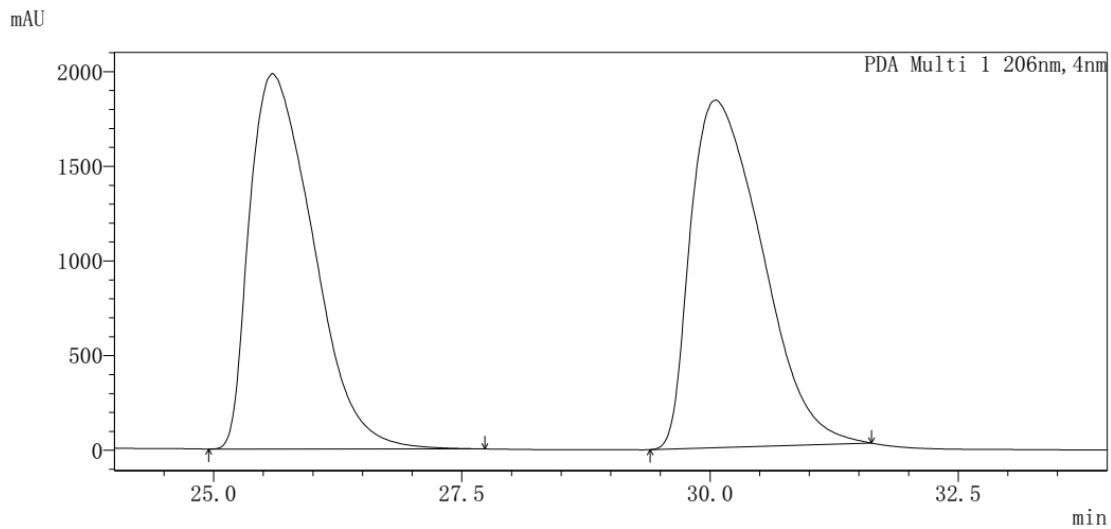
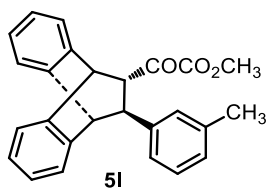
mAU



<Peak Results>

PDA Ch1 230nm

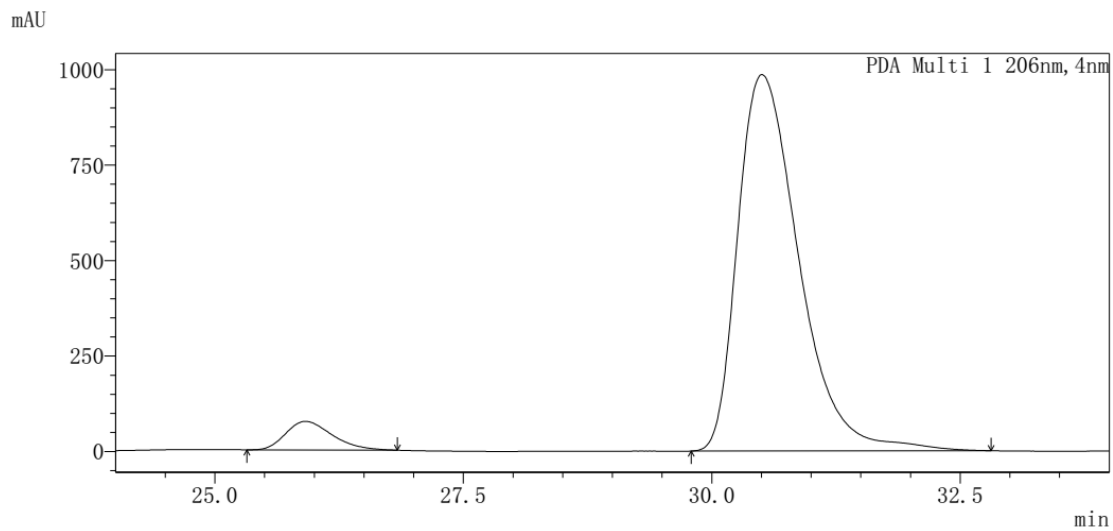
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	30.574	64523	2329933	6.714
2	38.379	677163	32372519	93.286



<Peak Results>

PDA Ch1 206nm

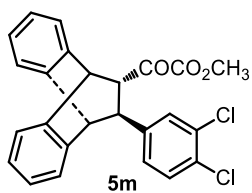
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.593	1983723	88419646	48.983
2	30.061	1836493	92092492	51.017



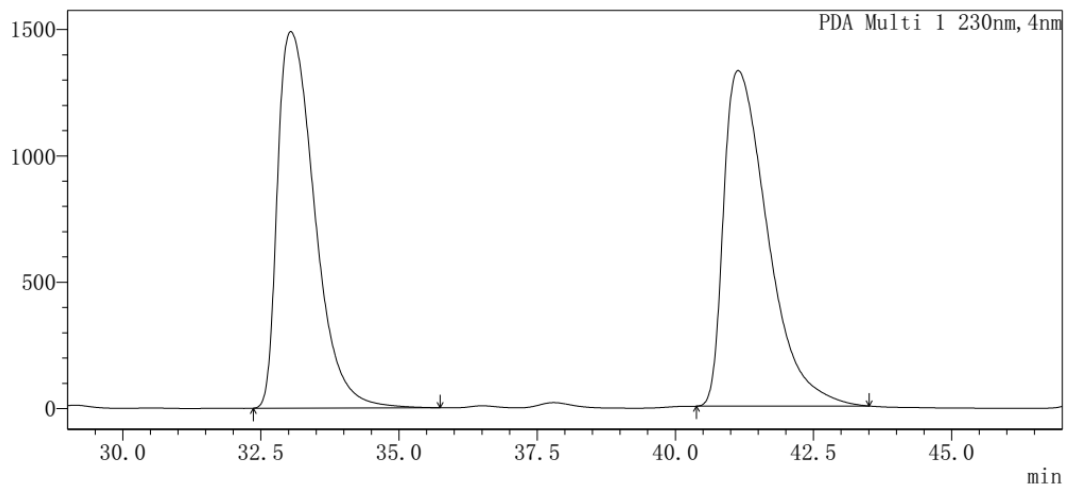
<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.912	74891	2439703	5.471
2	30.505	985695	42156800	94.529



mAU

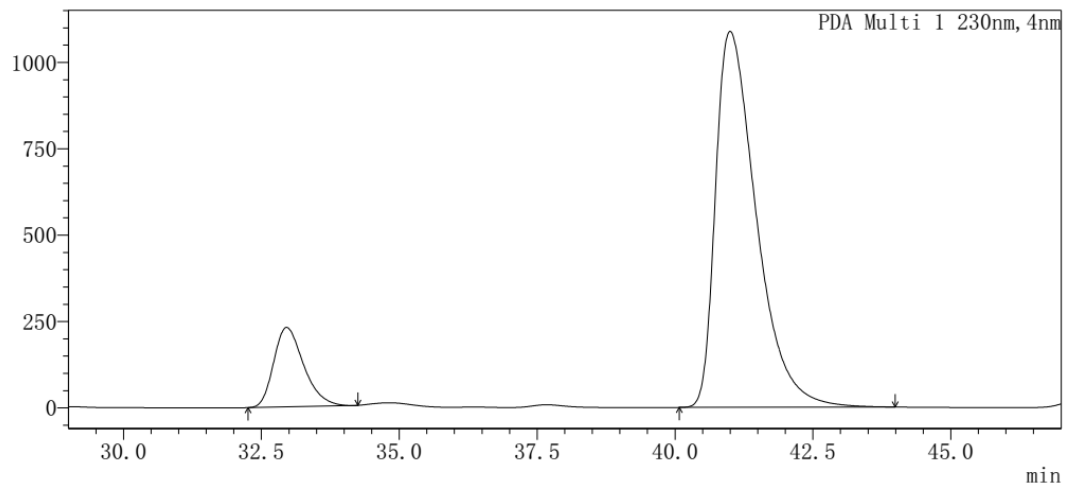


<Peak Results>

PDA Ch1 230nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	33.039	1490359	69674211	48.611
2	41.135	1328321	73655228	51.389

mAU

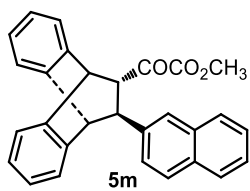


<Peak Results>

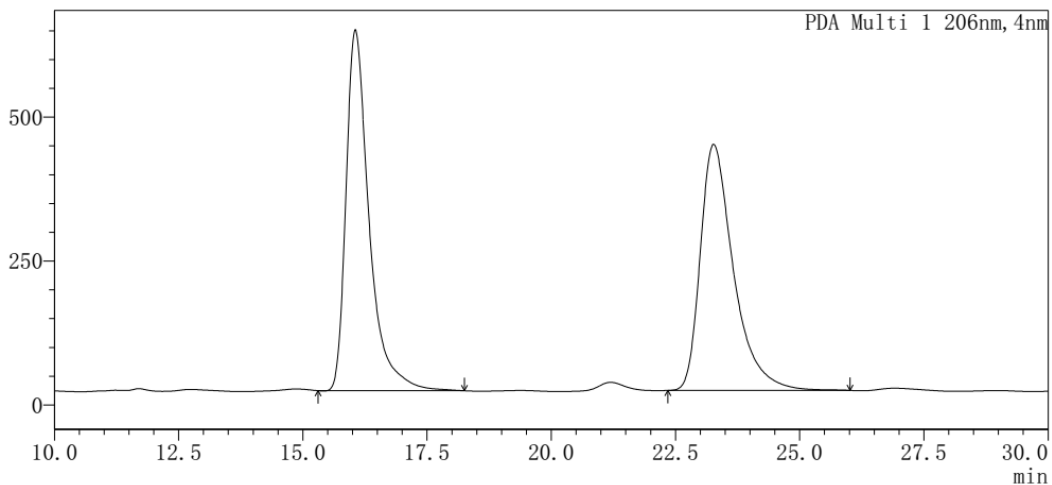
PDA Ch1 230nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	32.956	229901	8694359	13.447
2	40.997	1088312	55961394	86.553





mAU

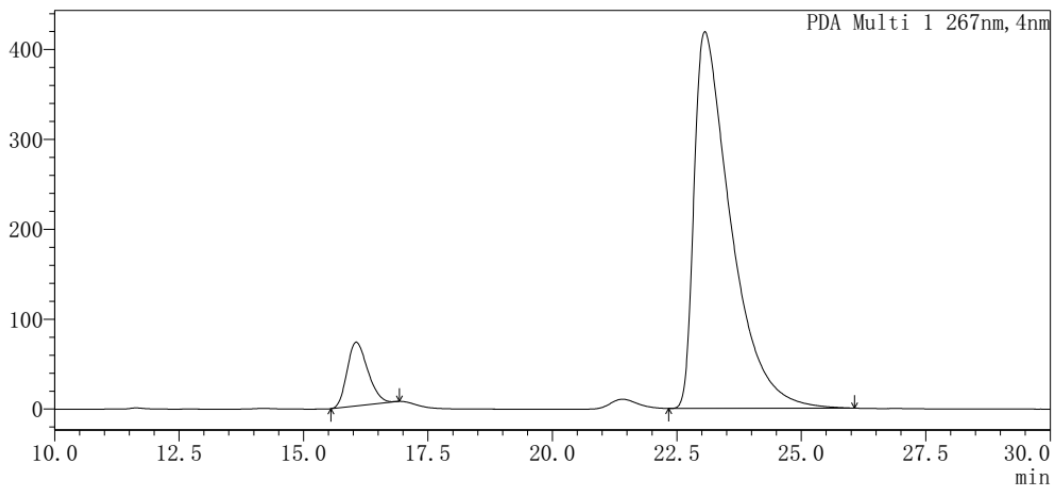


<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.056	627084	20266235	50.445
2	23.266	427529	19908796	49.555

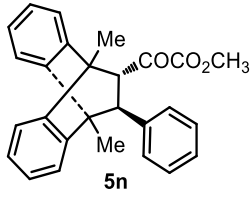
mAU



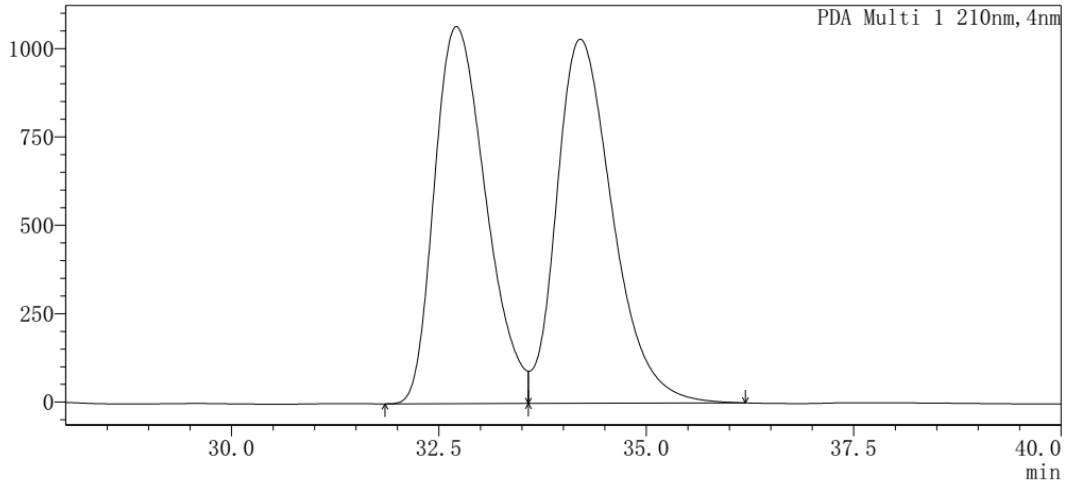
<Peak Results>

PDA Ch1 267nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.059	71061	2051838	8.700
2	23.062	419346	21533171	91.300



mAU

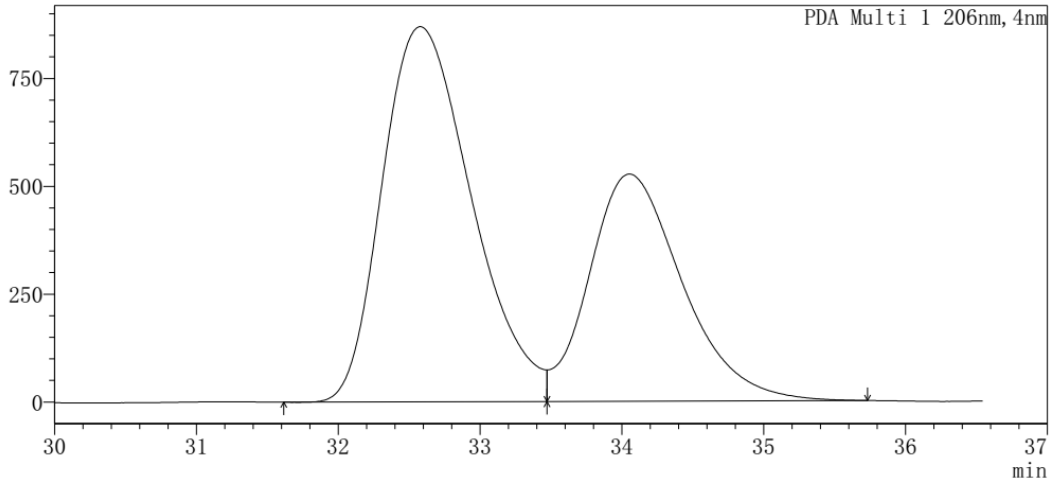


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	32.709	1066540	46063802	48.780
2	34.203	1030215	48367155	51.220

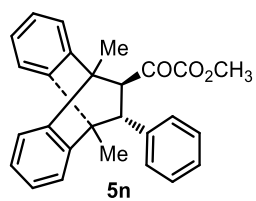
mAU



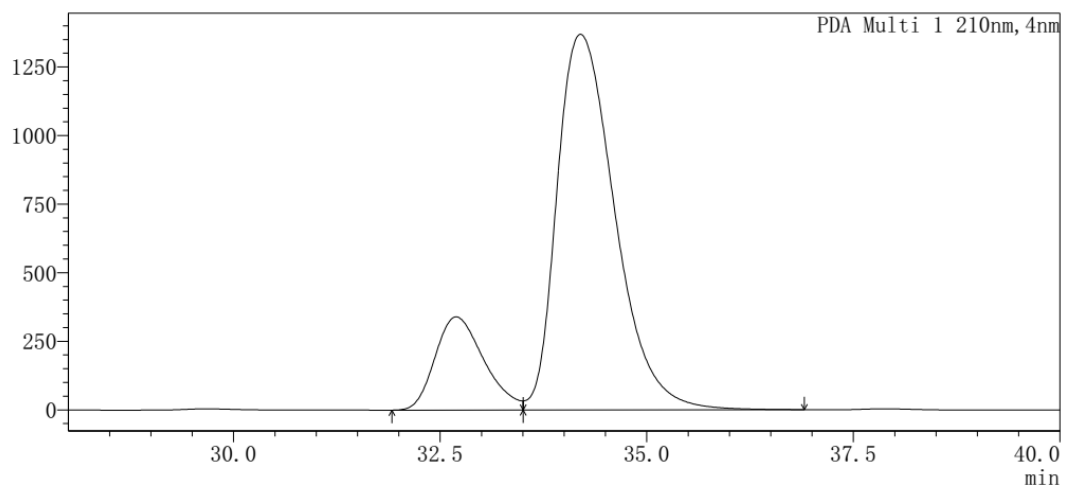
<Peak Results>

PDA Ch1 206nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	32.577	869874	38127719	61.407
2	34.053	526539	23962041	38.593



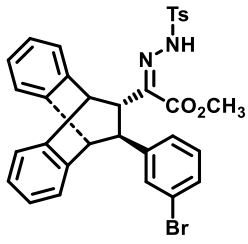
mAU



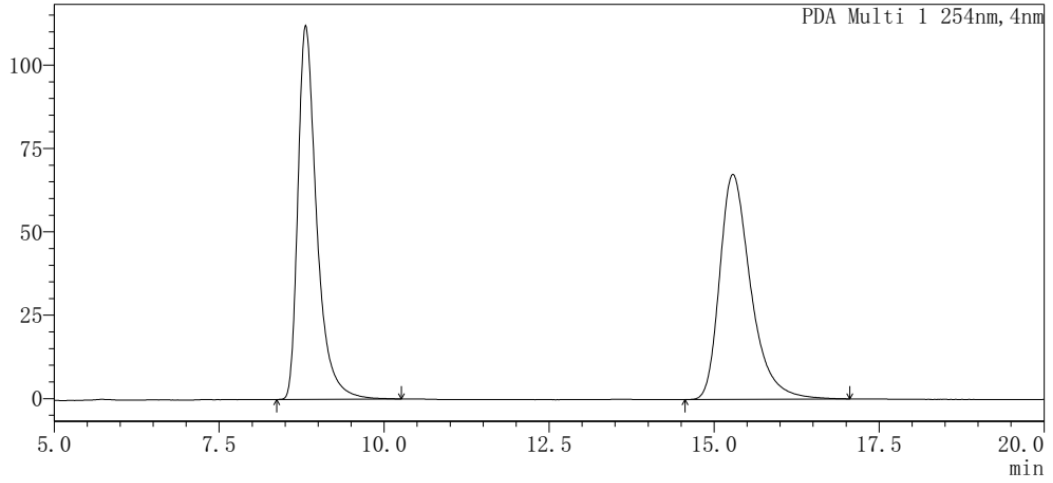
<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	32.693	339816	13941973	17.288
2	34.197	1369764	66703674	82.712



mAU

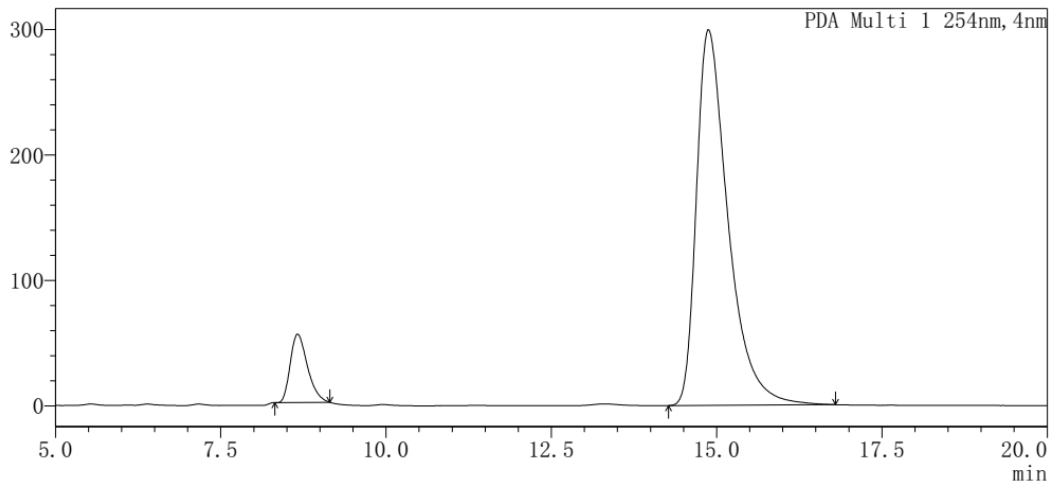


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.809	112158	2218414	50.019
2	15.284	67531	2216685	49.981

mAU



<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.661	54495	988047	9.017
2	14.874	299383	9969296	90.983