

**Visible-light driven enantioselective intermolecular photocyclization via bathochromic excitation by  
chiral phosphoric acid**

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Contents	Page
1. General methods	S2
2. Additional data of condition screening	S3
3. Synthetic procedures and characterization of new compounds	
3-1. General procedure of [2+2] cycloaddition	S6
3-2. Synthesis of <b>2</b>	S17
4. Mechanistic studies	
4-1. UV–Vis spectra	S23
4-2. <sup>1</sup> H NMR study	S24
4-3. Correlation between ee of <b>1b</b> and ee of <b>3ab</b> in photocycloaddition	S25
4-4. Correlation between ee of <b>1b</b> and ee of <b>3ag</b> in photocycloaddition	S26
4-5. DFT calculation	S27
5. HPLC data	S32
6. NMR spectra	S52

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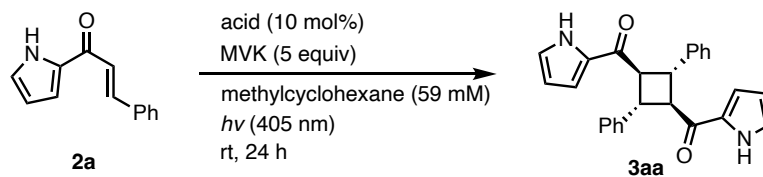
## 1. General methods

All operations were performed under nitrogen unless otherwise noted. NMR spectra for products data ( $^1\text{H}$  and  $^{13}\text{C}$ ) were recorded on a Bruker AVANCE-III (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ , 376 MHz for  $^{19}\text{F}$ ) and JEOL ECZ-400 (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ , 376 MHz for  $^{19}\text{F}$ ) spectrometer using  $\text{CDCl}_3$  [tetramethylsilane (0 ppm) served as an internal standard in  $^1\text{H}$  NMR and  $\text{CDCl}_3$  (77.0 ppm) in  $^{13}\text{C}$  NMR, hexafluorobenzene ( $-163.9$  ppm) or benzotrifluoride ( $-63.7$  ppm) served as an internal or external standard in  $^{19}\text{F}$  NMR]. Chemical shifts are expressed in parts per million (ppm). ESI mass analyses were performed on Bruker micrOTOF mass spectrometer. IR spectra were recorded on a FT/IR-4200 (JASCO Co., Ltd.). UV-Vis spectra were recorded on a V-670 UV-VIS-NIR spectrometer (JASCO Co., Ltd.). Emission spectra were recorded on a FP-6500 (JASCO Co., Ltd.). Visible light irradiation was performed with LED405-100STND (Optcode Co., Ltd.) for 405 nm LED and Twin LED Light (Relyon Co., Ltd.) for 365 nm LED. High performance liquid chromatography (HPLC) was performed on a Chromaster (Hitachi High-Tech Co., Ltd.) with CHIRALPak<sup>®</sup> IF (Daicel Co., Ltd.).

Solvents were distilled according to the usual procedures and stored over molecular sieves unless otherwise noted. All of the substrates were purified by distillation (for liquid) or recrystallization (for solid). Other chemicals were purchased and used as received.

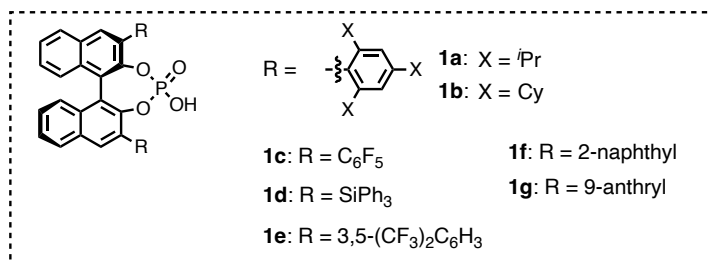
## 2. Additional data of conditions screening

**Table S1. Screening of conditions of [2+2] photocycloaddition**

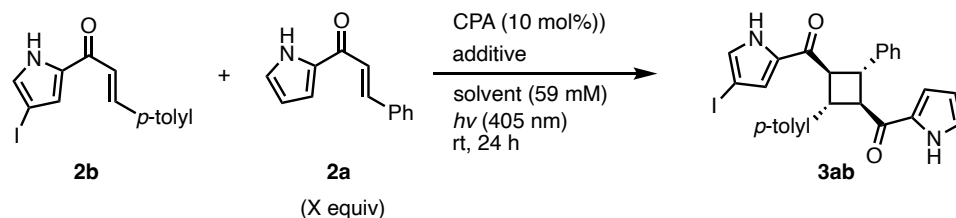


entry	acid	solvent	yield
1	–	toluene	2.1%
2	<b>1a</b>	toluene	21%
3	<b>1c</b>	toluene	3.6%
4	<b>1d</b>	toluene	1.5%
5	<b>1e</b>	toluene	7.5%
6	<b>1f</b>	toluene	8.4%
7	–	CyMe	<1%
8	<b>1a</b>	CyMe	57%
9	<b>1b</b>	CyMe	23%
10	<b>1g</b>	CyMe	0%
11	diphenylphosphoric acid	CyMe	23%
12	benzoic acid	CyMe	1.5%
13	TsOH·H <sub>2</sub> O	CyMe	1.5%
14	TFA	CyMe	33%
15	<b>1a</b>	benzene	3.0%
16	<b>1a</b>	cyclohexane	20%
17	<b>1a</b>	PhCF <sub>3</sub>	1.9%
18	<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	1.1%
19	<b>1a</b>	<i>m</i> -xylene	1.4%
20 <sup>a)</sup>	<b>1a</b>	CyMe	22%

a) 29 mM.

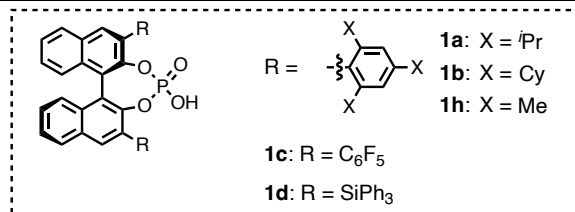


**Table S2. Screening of conditions of enantioselective [2+2] photocycloaddition**

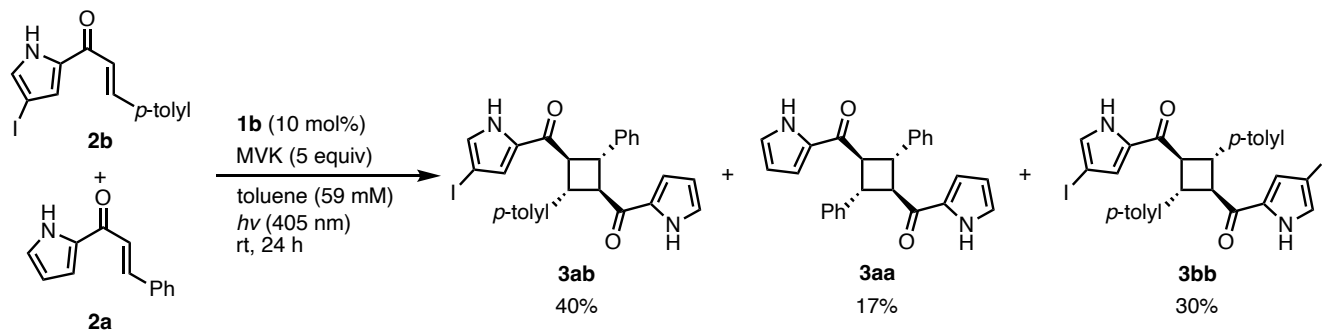


entry	CPA	solvent	additive	X	<b>3ab</b>		<b>3bb</b>
					yield	ee	
1	<b>1a</b>	toluene	MVK (5 equiv)	1	17%	68%	11%
2	<b>1b</b>	toluene	MVK (5 equiv)	1	40%	90%	30%
3	<b>1c</b>	toluene	MVK (5 equiv)	1	< 1.0%	0%	6%
4	<b>1d</b>	toluene	MVK (5 equiv)	1	3.8%	— <sup>a</sup>	6%
5	<b>1b</b>	CyMe	MVK (5 equiv)	1	37%	83%	5.0%
6	<b>1b</b>	DCM	MVK (5 equiv)	1	28%	76%	42%
7	<b>1b</b>	PhCF <sub>3</sub>	MVK (5 equiv)	1	18%	87%	4.0%
8	<b>1b</b>	toluene	none	1	25%	84%	22%
9	<b>1b</b>	toluene	MVK (3 equiv)	1	36%	88%	37%
10	<b>1b</b>	toluene	MVK (10 equiv)	1	44%	87%	38%
11	<b>1b</b>	toluene	MVK (50 equiv)	1	34%	72%	42%
12	<b>1b</b>	toluene	2-butanone (5 equiv)	1	34%	86%	25%
13	<b>1b</b>	toluene	MVK (10 equiv)	1	44%	87%	38%
14	<b>1b</b>	toluene	acetophenone	1	17%	72%	— <sup>e</sup>
15	<b>1b</b>	toluene	MS4A (100 wt%)	1	0%	—	0%
16	<b>1b</b>	toluene	MVK (5 equiv)	3	85%	98%	11%
17 <sup>a)</sup>	—	toluene	MVK (5 equiv)	3	0%	—	0%
18 <sup>b)</sup>	<b>1b</b>	toluene	MVK (5 equiv)	3	0%	—	0%
19 <sup>c)</sup>	<b>1b</b>	toluene	MVK (5 equiv)	3	80%	98%	— <sup>e</sup>
20 <sup>d)</sup>	<b>1b</b>	toluene	MVK (5 equiv)	3	78%	98%	— <sup>e</sup>
21	<b>1h</b>	toluene	MVK (5 equiv)	3	23%	89%	— <sup>e</sup>

a) Without CPA.  
 b) Under dark conditions.  
 c) Under air  
 d) Under oxygen  
 e) Not isolated.

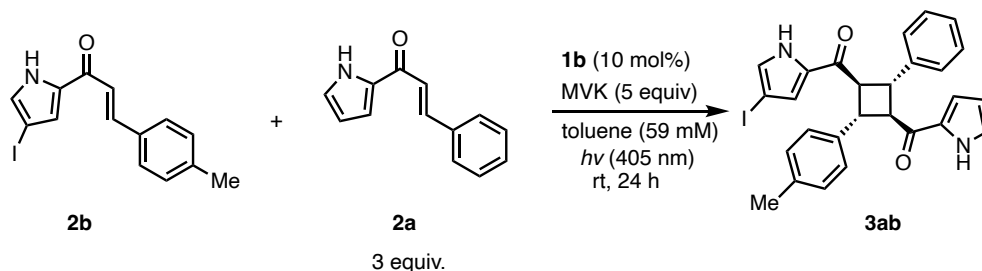


Scheme S1. Selectivity of *homo-* or *hetero-* coupling products



### 3. Synthetic procedures and characterization of new compounds

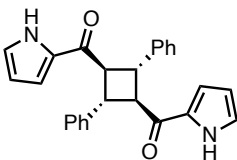
#### 3-1. General procedure of [2+2] cycloaddition (Procedure I)

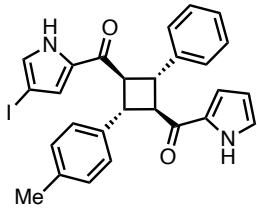


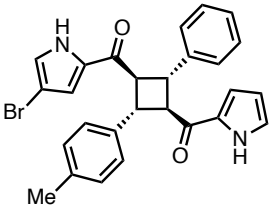
In a dried test tube, **2a** (17.3 mg, 0.088 mmol), **2b** (9.9 mg, 0.029 mmol), **1b** (1.0 mg, 0.0029 mmol), methyl vinyl ketone (12.3  $\mu$ L, 0.145 mmol) and were mixed in toluene (0.5 mL), and degassed three times by the freeze-pump-thaw. The mixture was irradiated with 405 nm violet LED for 24 h. After the irradiation, the solvent was removed. The crude mixture was purified by preparative TLC on SiO<sub>2</sub> (toluene: ethyl acetate = 7 : 3) to give **3ab** (13.3 mg, 24.9  $\mu$ mol) in 85%.

The reactions of other substrates in Figure 2 were performed based on this Procedure I.

#### Data of products

<b>3aa</b>	White powder
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 9.58 (brs, 2H), 7.32 (d, $J$ = 4.0 Hz, 8H), 7.28 – 7.21 (m, 2H), 7.00 (ddd, $J$ = 2.7, 2.7, 1.3 Hz, 2H), 6.37 – 6.31 (m, 2H), 6.11 – 6.04 (m, 2H), 4.24 – 4.14 (m, 2H), 4.04 – 3.97 (m, 2H).
	<sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): $\delta$ 188.0, 141.6, 131.4, 128.7, 127.3, 127.1, 125.2, 117.0, 110.7, 52.4, 42.6.
	LRMS (ESI): $m/z$ = 417 [M+Na].
	HRMS (ESI): Calcd for C <sub>26</sub> H <sub>22</sub> N <sub>2</sub> NaO <sub>2</sub> : 417.1579. Found 417.1573.
	IR (neat, cm <sup>-1</sup> ): 3274, 1624, 1403.

<b>3ab</b>	White powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.51 (brs, 1H), 9.44 (brs, 1H), 7.38 – 7.28 (m, 5H), 7.20 (d, <i>J</i> = 8.1 Hz, 2H), 7.15 (d, <i>J</i> = 8.0 Hz, 2H), 7.02 (dd, <i>J</i> = 2.9, 1.3 Hz, 1H), 7.00 (ddd, <i>J</i> = 2.7, 2.7, 1.2 Hz, 1H), 6.39 – 6.34 (m, 1H), 6.30 (dd, <i>J</i> = 2.5, 1.4 Hz, 1H), 6.09 (dt, <i>J</i> = 3.9, 2.5 Hz, 1H), 4.16 (t, <i>J</i> = 9.3 Hz, 1H), 4.07 (t, <i>J</i> = 9.3 Hz, 1H), 3.99 (t, <i>J</i> = 9.3 Hz, 1H), 3.87 (t, <i>J</i> = 9.3 Hz, 1H), 2.35 (s, 3H).
	<sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 187.9, 187.5, 141.3, 138.1, 136.9, 132.8, 131.4, 129.8, 129.4, 128.8, 127.2, 127.1, 125.3, 123.5, 117.1, 110.8, 62.0, 52.9, 52.2, 42.7, 42.3, 21.1.
	LRMS (ESI): <i>m/z</i> = 557 [M+Na].
	HRMS (ESI): Calcd for C <sub>27</sub> H <sub>23</sub> IN <sub>2</sub> NaO <sub>2</sub> , 557.0702: Found 557.0696.
	IR (neat, cm <sup>-1</sup> ): 3293, 1625, 1395.
	[α] <sub>D</sub> <sup>24</sup> -14.5 (c 0.3, CHCl <sub>3</sub> ).

<b>3ac</b>	White powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.57 (brs, 1H), 9.49 (brs, 1H), 7.38 – 7.27 (m, 5H), 7.20 (d, <i>J</i> = 8.1 Hz, 2H), 7.15 (d, <i>J</i> = 8.1 Hz, 2H), 7.00 (ddd, <i>J</i> = 2.7, 2.7, 1.3 Hz, 1H), 6.97 (dd, <i>J</i> = 3.0, 1.4 Hz, 1H), 6.38 – 6.33 (m, 1H), 6.25 (dd, <i>J</i> = 2.7, 1.4 Hz, 1H), 6.09 (dt, <i>J</i> = 3.9, 2.5 Hz, 1H), 4.17 (t, <i>J</i> = 9.4 Hz, 1H), 4.09 (t, <i>J</i> = 9.3 Hz, 1H), 3.99 (t, <i>J</i> = 9.4 Hz, 1H), 3.87 (t, <i>J</i> = 9.3 Hz, 1H), 2.34 (s, 3H).
	<sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 187.9, 187.8, 141.3, 138.2, 136.9, 131.4, 131.3, 129.4, 128.8, 127.20, 127.17, 127.1, 125.2, 124.8, 118.3, 117.0, 110.8, 98.0, 52.8, 52.4, 42.6, 42.2, 21.1.
	LRMS (ESI): <i>m/z</i> = 507, 509 [M+Na].
	HRMS (ESI): Calcd for C <sub>27</sub> H <sub>23</sub> BrN <sub>2</sub> NaO <sub>2</sub> , 509.0840: Found 509.0814.
	IR (neat, cm <sup>-1</sup> ): 3279, 1631, 1395.
	[α] <sub>D</sub> <sup>24</sup> +13.0 (c 0.2, CHCl <sub>3</sub> ).

<b>3ad</b>	White powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.69 (brs, 1H), 9.63 (brs, 1H), 7.37 – 7.27 (m, 5H), 7.20 (d, $J$ = 8.1 Hz, 2H), 7.15 (d, $J$ = 8.0 Hz, 2H), 7.01 (ddd, $J$ = 2.7, 2.7, 1.3 Hz, 1H), 6.94 (dd, $J$ = 3.1, 1.5 Hz, 1H), 6.39 – 6.33 (m, 1H), 6.19 (dd, $J$ = 2.7, 1.5 Hz, 1H), 6.09 (dt, $J$ = 3.9, 2.5 Hz, 1H), 4.18 (t, $J$ = 9.4 Hz, 1H), 4.09 (t, $J$ = 9.3 Hz, 1H), 3.99 (t, $J$ = 9.3 Hz, 1H), 3.88 (t, $J$ = 9.3 Hz, 1H), 2.34 (s, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 188.0, 187.9, 141.3, 138.2, 136.9, 131.4, 130.3, 129.4, 128.8, 127.19, 127.16, 127.1, 125.3, 122.6, 117.1, 115.8, 114.2, 110.8, 52.7, 52.4, 42.6, 42.2, 21.1.
	LRMS (ESI): $m/z$ = 463, 465 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{23}\text{ClN}_2\text{NaO}_2$ , 465.1346: Found 465.1346.
	IR (neat, $\text{cm}^{-1}$ ): 3272, 1628, 1396.
	$[\alpha]_{\text{D}}^{24}$ -29.1 (c 0.2, $\text{CHCl}_3$ ).

<b>3ae</b>	Colorless oil.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.47 (brs, 1H), 9.19 (brs, 1H), 7.37 – 7.30 (m, 5H), 7.25 – 7.21 (m, 2H), 7.17 – 7.11 (m, 2H), 6.99 (ddd, $J$ = 2.7, 2.7, 1.3 Hz, 1H), 6.78 (dd, $J$ = 2.8, 1.6 Hz, 1H), 6.41 – 6.36 (m, 1H), 6.08 (dt, $J$ = 3.8, 2.5 Hz, 1H), 5.99 (dd, $J$ = 2.6, 1.6 Hz, 1H), 4.21 – 4.12 (m, 1H), 4.09 – 4.00 (m, 2H), 3.93 – 3.84 (m, 1H), 2.33 (s, 3H), 1.02 (s, 9H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 188.1, 187.5, 141.8, 138.6, 137.5, 136.7, 131.5, 130.7, 129.3, 128.6, 127.4 (2C), 127.0, 124.9, 120.6, 116.8, 114.7, 110.7, 53.5, 52.1, 42.7, 42.0, 31.3, 30.2, 21.1.
	LRMS (ESI): $m/z$ = 487 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{31}\text{H}_{32}\text{N}_2\text{NaO}_2$ , 487.2361: Found 487.2356.
	IR (neat, $\text{cm}^{-1}$ ): 3277, 2957, 1625, 1400.
	$[\alpha]_{\text{D}}^{24}$ -1.0 (c 0.2, $\text{CHCl}_3$ ).



<b>3af</b>	White powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ): δ 9.68 (brs, 1H), 9.41 (brs, 1H), 7.35 – 7.28 (m, 4H), 7.25 – 7.18 (m, 3H), 7.13 (d, <i>J</i> = 7.9 Hz, 2H), 7.03 – 6.99 (m, 1H), 6.80 – 6.75 (m, 1H), 6.41 – 6.35 (m, 1H), 6.12 – 6.06 (m, 2H), 4.19 (t, <i>J</i> = 9.4 Hz, 1H), 4.10 (t, <i>J</i> = 9.4 Hz, 1H), 3.99 (t, <i>J</i> = 9.4 Hz, 1H), 3.92 (t, <i>J</i> = 9.4 Hz, 1H), 2.33 (s, 3H), 2.26 (t, <i>J</i> = 7.6 Hz, 2H), 1.39 – 1.13 (m, 8H), 0.88 (t, <i>J</i> = 6.9 Hz, 3H).
	<sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 188.2, 187.7, 141.8, 138.6, 136.6, 131.5, 131.0, 129.3, 128.6, 127.3, 127.2, 126.9, 126.9, 125.2, 123.2, 117.0, 116.9, 110.6, 52.8, 52.4, 42.6, 42.2, 31.6, 30.6, 28.8, 26.4, 22.6, 21.1, 14.1.
	LRMS (ESI): <i>m/z</i> = 515 [M+Na].
	HRMS (ESI): Calcd for C <sub>33</sub> H <sub>36</sub> N <sub>2</sub> NaO <sub>2</sub> , 515.2674: Found 515.2659.
	IR (neat, cm <sup>-1</sup> ): 3274, 2924, 1624, 1402.
	[α] <sub>D</sub> <sup>24</sup> +30.3 (c 0.2, CHCl <sub>3</sub> ).

<b>3ag</b>	White powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.47 (brs, 1H), 9.41 (brs, 1H), 7.35 – 7.22 (m, 5H), 7.19 (d, <i>J</i> = 8.1 Hz, 2H), 7.13 (d, <i>J</i> = 7.8 Hz, 2H), 7.08 (dd, <i>J</i> = 3.0, 1.4 Hz, 1H), 7.00 (ddd, <i>J</i> = 2.7, 2.7, 1.3 Hz, 1H), 6.40 (dd, <i>J</i> = 2.6, 1.4 Hz, 1H), 6.37 – 6.34 (m, 1H), 6.09 (dt, <i>J</i> = 3.9, 2.5 Hz, 1H), 4.18 (t, <i>J</i> = 9.4 Hz, 1H), 4.10 (t, <i>J</i> = 9.3 Hz, 1H), 3.95 (t, <i>J</i> = 9.4 Hz, 1H), 3.92 (t, <i>J</i> = 9.4 Hz, 1H), 2.35 – 2.29 (m, 5H), 1.56 – 1.47 (m, 2H), 1.47 – 1.37 (m, 2H), 0.93 (t, <i>J</i> = 7.3 Hz, 3H).
	<sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 188.3, 188.0, 141.5, 138.3, 136.8, 131.5, 131.0, 129.4, 128.7, 128.0, 127.12, 127.07, 125.1, 119.4, 117.0, 110.7, 107.7, 89.2, 73.5, 52.5, 52.3, 42.7, 42.3, 30.8, 21.9, 21.1, 19.0, 13.6.
	LRMS (ESI): <i>m/z</i> = 511 [M+Na].
	HRMS (ESI): Calcd for C <sub>33</sub> H <sub>32</sub> N <sub>2</sub> NaO <sub>2</sub> , 511.2361: Found 511.2356
	IR (neat, cm <sup>-1</sup> ): 3272, 2927, 1627, 1401.
	[α] <sub>D</sub> <sup>24</sup> +2.9 (c 0.2, CHCl <sub>3</sub> ).

<b>3ah</b>	White powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.55 (brs, 1H), 9.52 (brs, 1H), 7.35 – 7.21 (m, 5H), 7.18 (d, $J$ = 8.1 Hz, 2H), 7.16 – 7.12 (m, 2H), 7.08 (dd, $J$ = 3.0, 1.4 Hz, 1H), 7.01 (ddd, $J$ = 2.7, 2.7, 1.3 Hz, 1H), 6.40 (dd, $J$ = 2.6, 1.4 Hz, 1H), 6.39 – 6.35 (m, 1H), 6.09 (dt, $J$ = 3.9, 2.5 Hz, 1H), 4.20 (t, $J$ = 9.4 Hz, 1H), 4.09 (t, $J$ = 9.4 Hz, 1H), 3.97 (t, $J$ = 9.4 Hz, 1H), 3.92 (t, $J$ = 9.4 Hz, 2H), 2.33 (s, 3H), 1.25 (s, 9H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 188.3, 188.0, 141.5, 138.3, 136.7, 131.5, 131.0, 129.4, 128.7, 128.0, 127.11, 127.10, 127.0, 125.1, 119.7, 117.0, 110.7, 107.6, 97.4, 71.9, 52.4, 52.4, 42.9, 42.3, 31.0, 27.9, 21.1.
	LRMS (ESI): $m/z$ = 511 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2\text{NaO}_2$ , 511.2361: Found 511.2356.
	IR (neat, $\text{cm}^{-1}$ ): 3275, 2317, 1627, 1401.
	$[\alpha]_{\text{D}}^{24}$ +2.9 (c 0.5, $\text{CHCl}_3$ ).

<b>3ai</b>	White powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.59 (brs, 1H), 9.36 (brs, 1H), 7.55 (dd, $J$ = 3.2, 1.4 Hz, 1H), 7.38 – 7.23 (m, 5H), 7.23 – 7.19 (m, 2H), 7.15 (d, $J$ = 7.8 Hz, 2H), 6.99 (ddd, $J$ = 2.7, 2.7, 1.3 Hz, 1H), 6.70 (dd, $J$ = 2.6, 1.4 Hz, 1H), 6.37 – 6.31 (m, 1H), 6.09 (dt, $J$ = 3.8, 2.5 Hz, 1H), 4.21 (q, $J$ = 7.2 Hz, 2H), 4.17 (t, $J$ = 9.3 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.99 (t, $J$ = 9.4 Hz, 1H), 3.98 (t, $J$ = 9.4 Hz, 1H), 2.34 (s, 3H), 1.28 (t, $J$ = 7.1 Hz, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 189.0, 188.0, 163.7, 141.3, 138.1, 136.9, 131.7, 131.4, 129.4, 128.9, 128.8, 127.2, 127.1, 125.4, 118.4, 117.5, 117.3, 110.7, 60.0, 52.5, 42.6, 42.4, 21.1, 14.3.
	LRMS (ESI): $m/z$ = 503 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{NaO}_4$ , 503.1946: Found 503.1936.
	IR (neat, $\text{cm}^{-1}$ ): 3285, 1705, 1633, 1209.
	$[\alpha]_{\text{D}}^{24}$ -22.3 (c 0.1, $\text{CHCl}_3$ ).

<b>3bj</b>	Colorless oil.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.72 (brs, 1H), 9.59 (brs, 1H), 7.23 (d, $J = 8.6$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.03 (dd, $J = 3.0, 1.4$ Hz, 1H), 7.00 (ddd, $J = 2.7, 2.7, 1.3$ Hz, 1H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.40 – 6.35 (m, 1H), 6.31 (dd, $J = 2.5, 1.4$ Hz, 1H), 6.09 (dt, $J = 3.9, 2.5$ Hz, 1H), 4.11 (t, $J = 9.3$ Hz, 1H), 4.03 (t, $J = 9.3$ Hz, 1H), 3.95 (t, $J = 9.3$ Hz, 1H), 3.82 (t, $J = 9.3$ Hz, 1H), 3.81 (s, 3H), 2.34 (s, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 188.0, 187.6, 158.7, 138.3, 136.8, 133.4, 132.8, 131.4, 129.7, 129.4, 128.3, 127.1, 125.2, 123.5, 117.1, 114.1, 110.7, 62.0, 55.3, 53.3, 52.6, 42.4, 41.9, 21.1.
	LRMS (ESI): $m/z = 587$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{28}\text{H}_{25}\text{IN}_2\text{NaO}_3$ , 587.0808: Found 587.0802.
	IR (neat, $\text{cm}^{-1}$ ): 3273, 1629, 1247.
	$[\alpha]_{\text{D}}^{24} +4.5$ (c 0.2, $\text{CHCl}_3$ ).

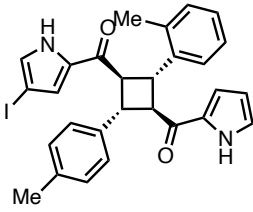
<b>3bk</b>	White powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.47 (brs, 1H), 9.41 (brs, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.20 – 7.13 (m, 6H), 7.04 (dd, $J = 2.9, 1.3$ Hz, 1H), 7.01 (ddd, $J = 2.7, 2.7, 1.3$ Hz, 1H), 6.38 – 6.34 (m, 1H), 6.31 (dd, $J = 2.5, 1.4$ Hz, 1H), 6.11 (dt, $J = 3.9, 2.5$ Hz, 1H), 4.18 (t, $J = 9.3$ Hz, 1H), 4.00 (t, $J = 9.2$ Hz, 1H), 3.93 (t, $J = 9.3$ Hz, 1H), 3.81 (t, $J = 9.3$ Hz, 1H), 2.35 (s, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 187.5, 187.1, 140.4, 137.8, 137.2, 132.7, 131.8, 131.3, 129.7, 129.5, 128.8, 127.1, 125.3, 123.4, 120.9, 117.0, 110.9, 62.1, 52.8, 52.2, 43.3, 41.0, 21.1.
	LRMS (ESI): $m/z = 635$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{22}\text{BrIN}_2\text{NaO}_2$ , 634.9807: Found 634.9802.
	IR (neat, $\text{cm}^{-1}$ ): 3280, 1630, 1392.
	$[\alpha]_{\text{D}}^{24} +34.4$ (c 0.4, $\text{CHCl}_3$ ).

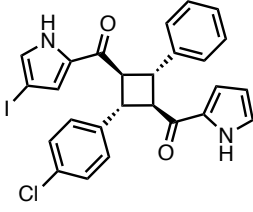
<b>3bl</b>	Colorless oil.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.70 (brs, 1H), 9.58 (brs, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.19 – 7.13 (m, 4H), 7.05 (dd, $J = 2.9, 1.3$ Hz, 1H), 7.02 (ddd, $J = 2.7, 2.7, 1.2$ Hz, 1H), 6.40 – 6.34 (m, 1H), 6.32 (dd, $J = 2.5, 1.3$ Hz, 1H), 6.11 (dt, $J = 4.0, 2.5$ Hz, 1H), 4.19 (t, $J = 9.4$ Hz, 1H), 4.01 (t, $J = 9.2$ Hz, 1H), 3.94 (t, $J = 9.3$ Hz, 1H), 3.82 (t, $J = 9.3$ Hz, 2H), 2.35 (s, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 187.6, 187.2, 139.9, 137.8, 137.1, 132.9, 132.7, 131.3, 129.9, 129.5, 128.9, 128.5, 127.1, 125.4, 123.5, 117.1, 110.9, 62.1, 52.9, 52.2, 43.2, 41.1, 21.1.
	LRMS (ESI): $m/z = 589, 591$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{22}\text{ClIN}_2\text{NaO}_2$ , 591.0312: Found 591.0307.
	IR (neat, $\text{cm}^{-1}$ ): 3274, 2924, 1634, 1394.
	$[\alpha]_{\text{D}}^{24} -31.3$ (c 0.2, $\text{CHCl}_3$ ).

<b>3bm</b>	Colorless oil.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.70 (brs, 1H), 9.59 (brs, 1H), 7.63 – 7.53 (m, 4H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.40 – 7.31 (m, 3H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 7.07 – 6.96 (m, 2H), 6.45 – 6.39 (m, 1H), 6.38 – 6.31 (m, 1H), 6.14 – 6.06 (m, 1H), 4.22 (t, $J = 9.2$ Hz, 1H), 4.12 – 4.00 (m, 2H), 3.90 (t, $J = 9.1$ Hz, 1H), 2.35 (s, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 187.9, 187.5, 140.7, 140.4, 140.1, 138.1, 137.0, 132.8, 131.4, 129.8, 129.5, 128.8, 127.6, 127.5, 127.3, 127.2, 127.1, 125.3, 123.6, 117.2, 110.8, 62.0, 53.0, 52.2, 42.8, 41.9, 21.1.
	LRMS (ESI): $m/z = 633$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{33}\text{H}_{27}\text{IN}_2\text{NaO}_2$ , 633.1015: Found 633.1009.
	IR (neat, $\text{cm}^{-1}$ ): 3273, 2924, 1628, 1395.
	$[\alpha]_{\text{D}}^{24} +7.8$ (c 0.5, $\text{CHCl}_3$ ).

<b>3bn</b>	White powder.
	$^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.56 (brs, 1H), 9.48 (brs, 1H), 7.62 (d, $J$ = 8.4 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.18 (s, 4H), 7.06 (dd, $J$ = 2.9, 1.4 Hz, 1H), 7.03 (dd, $J$ = 2.7, 2.7, 1.2 Hz, 1H), 6.36 – 6.32 (m, 1H), 6.27 (dd, $J$ = 2.5, 1.3 Hz, 1H), 6.11 (dt, $J$ = 3.9, 2.6 Hz, 1H), 4.41 (t, $J$ = 9.3 Hz, 1H), 3.97 (t, $J$ = 9.1 Hz, 1H), 3.90 (t, $J$ = 8.9 Hz, 1H), 3.84 (t, $J$ = 9.1 Hz, 1H), 2.37 (s, 3H).
	$^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ 187.1, 186.7, 147.0, 137.5, 137.3, 132.6, 132.5, 131.1, 130.0, 129.6, 127.8, 127.2, 125.6, 123.6, 118.7, 117.1, 111.0, 110.8, 62.2, 52.6, 51.9, 44.6, 40.2, 21.1.
	LRMS (ESI): $m/z$ = 246 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{28}\text{H}_{22}\text{IN}_3\text{NaO}_2$ , 582.0654: Found 582.0649.
	IR (neat, $\text{cm}^{-1}$ ): 3275, 2227, 1633, 1395, 1371.
	$[\alpha]_{\text{D}}^{24}$ -29.3 (c 0.4, $\text{CHCl}_3$ ).

<b>3bo</b>	White powder.
	$^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.57 (brs, 1H), 9.49 (brs, 1H), 8.01 (d, $J$ = 8.3 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.21 – 7.14 (m, 4H), 7.07 – 7.03 (m, 1H), 7.03 – 7.00 (m, 1H), 6.37 – 6.34 (m, 1H), 6.33 (dd, $J$ = 2.6, 1.3 Hz, 1H), 6.10 (ddd, $J$ = 3.8, 2.5, 2.5 Hz, 1H), 4.37 (q, $J$ = 7.1 Hz, 2H), 4.30 (t, $J$ = 9.0 Hz, 1H), 4.06 – 3.94 (m, 2H), 3.88 (t, $J$ = 9.3 Hz, 1H), 2.36 (s, 3H), 1.39 (t, $J$ = 7.1 Hz, 3H).
	$^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ 187.4, 187.1, 166.3, 146.5, 137.8, 137.2, 132.6, 131.2, 130.0, 129.8, 129.5, 129.3, 127.2, 127.1, 125.3, 123.4, 117.1, 110.9, 62.1, 61.0, 52.6, 52.1, 43.5, 41.3, 21.1, 14.3.
	LRMS (ESI): $m/z$ = 629 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{30}\text{H}_{27}\text{IN}_2\text{NaO}_4$ , 629.0913: Found 629.0908.
	IR (neat, $\text{cm}^{-1}$ ): 3278, 1632, 1278, 1108.
	$[\alpha]_{\text{D}}^{24}$ +7.7 (c 0.5, $\text{CHCl}_3$ ).

<b>3bp</b>	White powder.
	$^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.40 (brs, 1H), 9.36 (brs, 1H), 7.66 – 7.58 (m, 1H), 7.37 – 7.30 (m, 1H), 7.22 (d, $J$ = 8.1 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.09 (d, $J$ = 7.5 Hz, 1H), 7.00 (dd, $J$ = 2.9, 1.4 Hz, 1H), 6.98 (ddd, $J$ = 2.7, 2.7, 1.3 Hz, 1H), 6.35 – 6.30 (m, 1H), 6.28 (dd, $J$ = 2.5, 1.4 Hz, 1H), 6.07 (dt, $J$ = 3.9, 2.5 Hz, 1H), 4.33 (t, $J$ = 9.4 Hz, 1H), 4.12 (t, $J$ = 9.4 Hz, 1H), 4.01 (t, $J$ = 9.4 Hz, 1H), 3.89 (t, $J$ = 9.4 Hz, 1H), 2.35 (s, 3H), 2.11 (s, 3H).
	$^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ 188.0, 187.5, 139.3, 138.4, 137.0, 136.8, 132.7, 131.4, 130.5, 129.42, 129.41, 127.12 (2C), 127.07, 126.6, 126.0, 124.9, 123.1, 116.7, 110.8, 62.0, 53.3, 52.7, 41.8, 38.8, 21.1, 19.9.
	LRMS (ESI): $m/z$ = 571 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{28}\text{H}_{25}\text{N}_2\text{NaO}_2$ , 571.0858: Found 571.0853.
	IR (neat, $\text{cm}^{-1}$ ): 3274, 2922, 2852, 1626, 1394.
	$[\alpha]_{\text{D}}^{24}$ -25.2 (c 0.2, $\text{CHCl}_3$ ).

<b>3aq</b>	White powder.
	$^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ). $\delta$ 9.90 (s, 1H), 9.72 (s, 1H), 7.45 – 7.16 (m, 9H), 7.12 – 6.97 (m, 2H), 6.40 – 6.35 (m, 1H), 6.35 – 6.30 (m, 1H), 6.13 – 6.07 (m, 1H), 4.18 (t, $J$ = 9.4 Hz, 1H), 4.09 (t, $J$ = 8.6 Hz, 1H), 3.97 (t, $J$ = 9.4 Hz, 1H), 3.86 (t, $J$ = 9.4 Hz, 1H).
	$^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ 187.6, 187.2, 140.9, 139.8, 133.0, 132.7, 131.3, 130.3, 129.0, 128.9, 128.5, 127.5, 127.2, 125.7, 123.7, 117.3, 110.9, 62.1, 52.7, 52.2, 43.2, 41.5.
	LRMS (ESI): $m/z$ = 575, 577 [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{20}\text{ClIN}_2\text{NaO}_2$ , 577.0156: Found 577.0123.
	IR (neat, $\text{cm}^{-1}$ ): 3279, 2918, 1633, 1135.
	$[\alpha]_{\text{D}}^{24}$ -25.2 (c 0.2, $\text{CHCl}_3$ ).

<b>3jr</b>	White powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 7.33 – 7.21 (m, 6H), 7.22 – 7.13 (m, 5H), 7.01 – 6.95 (m, 2H), 6.90 (d, <i>J</i> = 8.6 Hz, 2H), 6.43 – 6.38 (m, 1H), 6.38 – 6.32 (m, 1H), 6.13 – 6.05 (m, 1H), 4.13 (t, <i>J</i> = 9.3 Hz, 1H), 4.08 (t, <i>J</i> = 9.3 Hz, 1H), 4.01 (t, <i>J</i> = 9.2 Hz, 1H), 3.91 (t, <i>J</i> = 9.3 Hz, 1H), 3.80 (s, 3H), 2.36 (s, 3H).
	<sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 188.13, 188.08, 158.7, 138.7, 136.8, 134.1, 133.8, 131.8, 131.5, 129.4, 128.64, 128.55, 127.3, 126.7, 126.2, 125.0(2C), 121.5, 117.0, 114.2, 114.1, 110.7, 55.3, 53.9, 52.5, 42.2, 42.0, 21.1.
	LRMS (ESI): <i>m/z</i> = 537 [M+Na].
	HRMS (ESI): Calcd for C <sub>34</sub> H <sub>30</sub> N <sub>2</sub> NaO <sub>3</sub> , 537.2154: Found 537.2125.
	IR (neat, cm <sup>-1</sup> ): 3274, 1625, 1513, 1399.
	[α] <sub>D</sub> <sup>24</sup> +4.5 (c 0.1, CHCl <sub>3</sub> ).

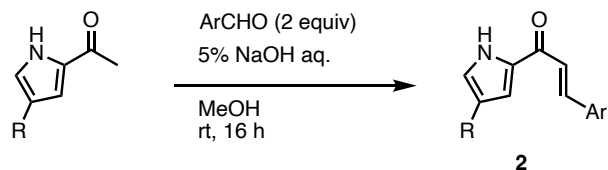
<b>3cj</b>	White powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.60 (brs, 1H), 9.51 (brs, 1H), 7.25 – 7.21 (m, 2H), 7.19 (d, <i>J</i> = 8.1 Hz, 2H), 7.14 (d, <i>J</i> = 7.9 Hz, 2H), 7.01 – 6.98 (m, 1H), 6.98 – 6.95 (m, 1H), 6.91 – 6.85 (m, 2H), 6.38 – 6.33 (m, 1H), 6.28 – 6.24 (m, 1H), 6.12 – 6.05 (m, 1H), 4.12 (t, <i>J</i> = 9.3, 9.3 Hz, 1H), 4.03 (t, <i>J</i> = 9.3, 9.3 Hz, 1H), 3.94 (t, <i>J</i> = 9.3, 9.3 Hz, 1H), 3.87 – 3.77 (m, 4H), 2.34 (s, 3H).
	<sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 188.0, 187.9, 158.7, 138.3, 136.8, 133.4, 131.4, 131.3, 129.4, 128.3, 127.1, 125.2, 124.8, 118.3, 117.1, 114.2, 110.8, 98.0, 55.3, 53.1, 52.7, 42.4, 41.9, 21.1.
	LRMS (ESI): <i>m/z</i> = 537, 539 [M+Na].
	HRMS (ESI): Calcd for C <sub>28</sub> H <sub>25</sub> BrN <sub>2</sub> NaO <sub>3</sub> , 539.0946: Found 539.0941.
	IR (neat, cm <sup>-1</sup> ): 3274, 1632, 1514, 1396.
	[α] <sub>D</sub> <sup>24</sup> +24.9(c 0.2, CHCl <sub>3</sub> ).

<b>3cl</b>	White powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ). $\delta$ 9.63 (s, 1H), 9.54 (s, 1H), 7.30 (d, $J = 8.5$ Hz, 2H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.20 – 7.13 (m, 4H), 7.03 – 7.00 (m, 1H), 7.00 – 6.97 (m, 1H), 6.38 – 6.33 (m, 1H), 6.28 – 6.24 (m, 1H), 6.13 – 6.07 (m, 1H), 4.19 (t, $J = 9.4$ Hz, 1H), 4.02 (t, $J = 9.3$ Hz, 1H), 3.93 (t, $J = 9.3$ Hz, 1H), 3.82 (t, $J = 9.4$ Hz, 1H), 2.35 (s, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ) $\delta$ 187.53, 187.48, 139.9, 137.8, 137.2, 132.9, 131.3, 131.2, 129.5, 128.9, 128.5, 127.1, 125.4, 125.0, 118.3, 117.1, 110.9, 98.1, 52.7, 52.4, 43.2, 41.1, 21.1.
	LRMS (ESI): $m/z = 539, 541, 543$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{22}\text{BrClN}_2\text{NaO}_2$ , 543.0451: Found 543.0445.
	IR (neat, $\text{cm}^{-1}$ ): 3271, 1629, 1385.
	$[\alpha]_{\text{D}}^{24} -10.3$ (c 0.5, $\text{CHCl}_3$ ).

<b>3cm</b>	White powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.37 (brs, 2H), 7.63 – 7.54 (m, 4H), 7.48 – 7.41 (m, 2H), 7.41 – 7.31 (m, 3H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 7.00 (ddd, $J = 2.8, 2.8, 1.2$ Hz, 1H), 6.97 (dd, $J = 3.0, 1.4$ Hz, 1H), 6.42 – 6.37 (m, 1H), 6.28 (dd, $J = 2.6, 1.4$ Hz, 1H), 6.10 (dt, $J = 3.9, 2.5$ Hz, 1H), 4.23 (t, $J = 9.3$ Hz, 1H), 4.09 (t, $J = 9.3$ Hz, 1H), 4.02 (t, $J = 9.3$ Hz, 1H), 3.90 (t, $J = 9.3$ Hz, 1H), 2.35 (s, 3H).
	$^{13}\text{C NMR}$ (100 MHz, $\text{CDCl}_3$ ): $\delta$ 187.93, 187.85, 140.7, 140.4, 140.1, 138.1, 137.0, 131.4, 131.3, 129.5, 128.8, 127.6, 127.5, 127.3, 127.1, 127.0, 125.4, 125.1, 118.5, 117.2, 110.8, 98.1, 52.8, 52.3, 42.9, 41.9, 21.1.
	LRMS (ESI): $m/z = 583, 585$ [M+Na].
	HRMS (ESI): Calcd for $\text{C}_{33}\text{H}_{27}\text{BrN}_2\text{NaO}_2$ , 585.1154: Found 585.1148.
	IR (neat, $\text{cm}^{-1}$ ): 3275, 1627, 1395.
	$[\alpha]_{\text{D}}^{24} -1.3$ (c 0.2, $\text{CHCl}_3$ ).



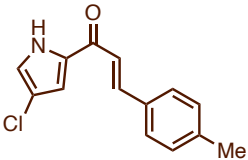
### 3-2. Synthesis of 2

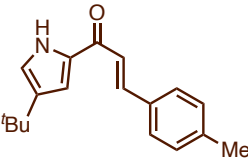


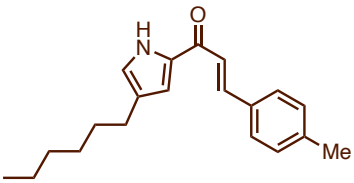
In round bottom flask, 2-acetylpyrrole (500 mg, 4.58 mmol) and aldehyde (9.16 mmol) were mixed in methanol (20 mL). 5% NaOH aq. was added to the solution and the mixture was stirred overnight at room temperature. Then, the precipitate was filtered and washed with water. The solid was recrystallized from ethanol to give **2**.

Data of new products.

<b>2b</b>	Pale yellow powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.45 (brs, 1H), 7.81 (d, $J = 15.6$ Hz, 1H), 7.53 (d, $J = 8.3$ Hz, 2H), 7.25 – 7.18 (m, 3H), 7.15 – 7.13 (m, 1H), 7.13 – 7.11 (m, 1H), 2.40 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, $\text{CDCl}_3$ ) $\delta$ 178.2, 143.4, 141.1, 134.5, 131.9, 129.7, 129.5, 128.5, 122.2, 120.1, 62.3, 21.5. LRMS (ESI): $m/z = 360$ [M+Na]. HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_{12}\text{INNaO}$ , 359.9861; Found 359.9856. IR (neat, $\text{cm}^{-1}$ ): 3216, 1649, 1579.
<b>2c</b>	Pale yellow powder.
	$^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ 9.43 (brs, 1H), 7.82 (d, $J = 15.7$ Hz, 1H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.25 – 7.18 (m, 4H), 7.08 – 7.06 (m, 1H), 7.05 – 7.03 (m, 1H), 2.40 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, $\text{CDCl}_3$ ) $\delta$ 178.5, 143.5, 141.2, 133.0, 131.9, 129.7, 128.5, 124.6, 120.1, 117.3, 98.3, 21.5. LRMS (ESI): $m/z = 312, 314$ [M+Na]. HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_{12}\text{BrNNaO}$ , 312.0000; Found 311.9994. IR (neat, $\text{cm}^{-1}$ ): 3224, 1649, 1579.

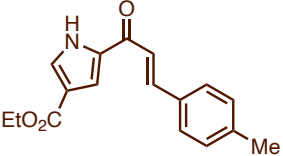
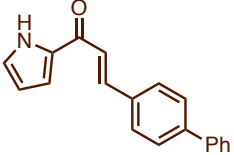
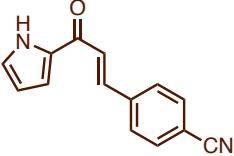
<b>2d</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.59 (brs, 1H), 7.82 (d, <i>J</i> = 15.7 Hz, 1H), 7.53 (d, <i>J</i> = 8.2 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.06 – 7.01 (m, 1H), 6.99 – 6.95 (m, 1H), 2.40 (s, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 178.6, 143.5, 141.1, 132.1, 131.9, 129.7, 128.5, 122.1, 120.0, 114.7, 114.5, 21.5.
	LRMS (ESI): <i>m/z</i> = 268, 270 [M+Na].
	HRMS (ESI): Calcd for C <sub>14</sub> H <sub>12</sub> ClNNaO, 268.0505; Found 268.0500.
	IR (neat, cm <sup>-1</sup> ): 3244, 1649, 1574.

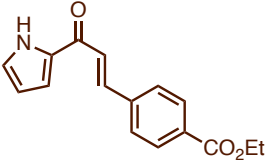
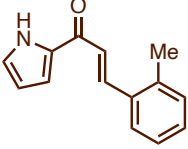
<b>2e</b>	Colorless oil.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.23 (brs, 1H), 7.78 (d, <i>J</i> = 15.7 Hz, 1H), 7.55 (d, <i>J</i> = 8.1 Hz, 2H), 7.31 (d, <i>J</i> = 15.7 Hz, 1H), 7.22 (d, <i>J</i> = 7.9 Hz, 2H), 6.99 – 6.95 (m, 1H), 6.95 – 6.91 (m, 1H), 2.39 (s, 3H), 1.30 (s, 9H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 178.7, 142.0, 140.5, 138.1, 132.8, 132.4, 129.6, 128.3, 121.04, 120.97, 113.4, 31.7, 30.6, 21.5.
	LRMS (ESI): <i>m/z</i> = 290 [M+Na].
	HRMS (ESI): Calcd for C <sub>18</sub> H <sub>21</sub> NO, 290.1521; Found 290.1515.
	IR (neat, cm <sup>-1</sup> ): 3441, 1645, 1579.

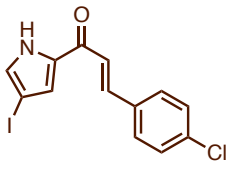
<b>2f</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.34 (brs, 1H), 7.78 (d, <i>J</i> = 15.7 Hz, 1H), 7.54 (d, <i>J</i> = 8.2 Hz, 2H), 7.29 (d, <i>J</i> = 15.7 Hz, 1H), 7.22 (d, <i>J</i> = 7.9 Hz, 2H), 6.93 – 6.85 (m, 2H), 2.50 (t, <i>J</i> = 7.7 Hz, 2H), 2.39 (s, 3H), 1.67 – 1.53 (m, 2H), 1.42 – 1.22 (m, 6H), 0.95 – 0.85 (m, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 178.6, 141.9, 140.5, 132.9, 132.4, 129.6, 128.3, 127.4, 123.1, 121.0, 115.8, 31.7, 31.0, 29.0, 26.7, 22.6, 21.5, 14.1.
	LRMS (ESI): <i>m/z</i> = 318 [M+Na].
	HRMS (ESI): Calcd for C <sub>20</sub> H <sub>25</sub> NNaO, 318.1834; Found 318.1828.
	IR (neat, cm <sup>-1</sup> ): 3242, 1649, 1580.

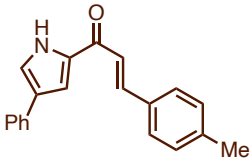
<b>2g</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.47 (brs, 1H), 7.80 (d, <i>J</i> = 15.7 Hz, 1H), 7.52 (d, <i>J</i> = 8.2 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.19 – 7.14 (m, 1H), 7.10 – 7.04 (m, 1H), 2.44 – 2.35 (m, 5H), 1.64 – 1.53 (m, 2H), 1.53 – 1.41 (m, 2H), 0.95 (t, <i>J</i> = 7.2 Hz, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 178.8, 142.9, 140.9, 132.5, 132.1, 129.7, 128.4, 127.6, 120.5, 118.3, 108.0, 89.5, 73.6, 30.9, 22.0, 21.5, 19.1, 13.7.
	LRMS (ESI): <i>m/z</i> = 314 [M+Na].
	HRMS (ESI): Calcd for C <sub>20</sub> H <sub>21</sub> NNaO, 314.1521; Found 314.1515.
	IR (neat, cm <sup>-1</sup> ): 3250, 2344, 1647, 1577.

<b>2h</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.45 (brs, 1H), 7.79 (d, <i>J</i> = 15.7 Hz, 1H), 7.52 (d, <i>J</i> = 8.3 Hz, 2H), 7.28 – 7.19 (m, 3H), 7.19 – 7.13 (m, 1H), 7.12 – 7.06 (m, 1H), 2.39 (s, 3H), 1.31 (s, 9H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 178.8, 142.8, 140.9, 132.5, 132.1, 129.7, 128.4, 127.5, 120.5, 118.5, 107.9, 97.6, 72.1, 31.1, 28.0, 21.5.
	LRMS (ESI): <i>m/z</i> = 314 [M+Na].
	HRMS (ESI): Calcd for C <sub>20</sub> H <sub>21</sub> NNaO, 314.1521; Found 314.1515.
	IR (neat, cm <sup>-1</sup> ): 3249, 2358, 1645, 1575.

<b>2i</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.88 (s, 1H), 7.84 (d, <i>J</i> = 15.6 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.55 (d, <i>J</i> = 8.2 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.32 (d, <i>J</i> = 15.7 Hz, 1H), 7.24 (d, <i>J</i> = 7.9 Hz, 2H), 4.34 (q, <i>J</i> = 7.1 Hz, 2H), 2.40 (s, 3H), 1.38 (t, <i>J</i> = 7.1 Hz, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 179.4, 163.9, 143.6, 141.2, 133.5, 131.9, 129.7, 128.5, 128.4, 120.0, 118.7, 116.1, 60.3, 21.6, 14.4.
	LRMS (ESI): <i>m/z</i> = 306 [M+Na].
	HRMS (ESI): Calcd for C <sub>17</sub> H <sub>17</sub> NNaO <sub>3</sub> , 306.1106; Found 306.1101.
	IR (neat, cm <sup>-1</sup> ): 3237, 1709, 1648, 1207.
<b>2m</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.72 (brs, 1H), 7.87 (d, <i>J</i> = 15.7 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.68 – 7.60 (m, 4H), 7.50 – 7.43 (m, 2H), 7.43 – 7.35 (m, 2H), 7.16 – 7.07 (m, 2H), 6.37 (dt, <i>J</i> = 3.8, 2.5 Hz, 1H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 178.8, 143.0, 141.8, 140.2, 134.0, 133.2, 128.9, 128.8, 127.8, 127.5, 127.0, 125.2, 121.7, 116.2, 111.0.
	LRMS (ESI): <i>m/z</i> = 296 [M+Na].
	HRMS (ESI): Calcd for C <sub>19</sub> H <sub>15</sub> NNaO, 296.1051; Found 296.1046.
	IR (neat, cm <sup>-1</sup> ): 3260, 1649, 1585.
<b>2n</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.81 (brs, 1H), 7.79 (d, <i>J</i> = 15.7 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.41 (d, <i>J</i> = 15.7 Hz, 1H), 7.17 (td, <i>J</i> = 2.7, 1.3 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.39 (dt, <i>J</i> = 4.0, 2.5 Hz, 1H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 177.8, 139.7, 139.3, 132.9, 132.6, 128.6, 126.1, 125.1, 118.5, 116.9, 113.1, 111.3.
	LRMS (ESI): <i>m/z</i> = 245 [M+Na].
	HRMS (ESI): Calcd for C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> NaO, 245.0691; Found 245.0685.
	IR (neat, cm <sup>-1</sup> ): 3244, 2223, 1645, 1590.

<b>2o</b>	Pale yellow powder.
	<p><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 9.86 (brs, 1H), 8.08 (d, <math>J = 8.4</math> Hz, 2H), 7.84 (d, <math>J = 15.7</math> Hz, 1H), 7.69 (d, <math>J = 8.4</math> Hz, 2H), 7.42 (d, <math>J = 15.7</math> Hz, 1H), 7.15 (td, <math>J = 2.7, 1.3</math> Hz, 1H), 7.14 – 7.08 (m, 1H), 6.38 (dt, <math>J = 3.9, 2.5</math> Hz, 1H), 4.40 (q, <math>J = 7.1</math> Hz, 2H), 1.42 (t, <math>J = 7.1</math> Hz, 3H).</p> <p><math>^{13}\text{C}</math> NMR (101 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 178.3, 166.0, 140.8, 139.1, 133.0, 131.6, 130.0, 128.1, 125.8, 124.0, 116.7, 111.2, 61.2, 14.3.</p> <p>LRMS (ESI): <math>m/z = 292</math> [M+Na].</p> <p>HRMS (ESI): Calcd for <math>\text{C}_{16}\text{H}_{15}\text{NNaO}</math>, 292.0950; Found 292.0944.</p> <p>IR (neat, <math>\text{cm}^{-1}</math>): 3253, 1707, 1645, 1587, 1284.</p>
<b>2p</b>	Pale yellow powder.
	<p><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 9.56 (brs, 1H), 8.11 (d, <math>J = 15.6</math> Hz, 1H), 7.73 – 7.66 (m, 1H), 7.33 – 7.20 (m, 4H), 7.13 – 7.09 (m, 1H), 7.09 – 7.04 (m, 1H), 6.39 – 6.32 (m, 1H), 2.49 (s, 3H).</p> <p><math>^{13}\text{C}</math> NMR (101 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 178.9, 139.9, 138.2, 134.0, 133.2, 130.8, 130.0, 126.3, 126.3, 125.0, 123.0, 116.1, 111.0, 19.9.</p> <p>LRMS (ESI): <math>m/z = 234</math> [M+Na].</p> <p>HRMS (ESI): Calcd for <math>\text{C}_{14}\text{H}_{13}\text{NNaO}</math>, 234.0895; Found 234.0889.</p> <p>IR (neat, <math>\text{cm}^{-1}</math>): 3410, 1643, 1586, 1403.</p>

<b>2q</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.53 (s, 1H), 7.77 (d, <i>J</i> = 15.7 Hz, 1H), 7.56 (d, <i>J</i> = 8.5 Hz, 2H), 7.40 (d, <i>J</i> = 8.5 Hz, 2H), 7.23 (d, <i>J</i> = 15.7 Hz, 1H), 7.17 – 7.11 (m, 2H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 177.7, 141.9, 136.5, 134.4, 133.2, 129.6, 129.6, 129.3, 122.4, 121.6, 62.4.
	LRMS (ESI): <i>m/z</i> = 354, 356 [M+Na].
	HRMS (ESI): Calcd for C <sub>13</sub> H <sub>9</sub> ClINNaO, 379.9315; Found 379.9310.
	IR (neat, cm <sup>-1</sup> ): 3224, 1649, 1581.

<b>2r</b>	Pale yellow powder.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 9.60 (brs, 1H), 7.84 (d, <i>J</i> = 15.6 Hz, 1H), 7.57 (dd, <i>J</i> = 7.8, 1.2 Hz, 1H), 7.44 – 7.31 (m, 4H), 7.28 – 7.21 (m, 2H), 2.40 (s, 3H).
	<sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 179.0, 142.7, 140.9, 134.3, 133.8, 132.2, 129.7, 128.8, 128.4, 127.4, 126.5, 125.3, 121.7, 120.6, 112.8, 21.5.
	LRMS (ESI): <i>m/z</i> = 310 [M+Na].
	HRMS (ESI): Calcd for C <sub>20</sub> H <sub>17</sub> NNaO, 310.1208; Found 310.1202.
	IR (neat, cm <sup>-1</sup> ): 3224, 1647, 1583.

## 4. Mechanistic study

### 4-1. UV-Vis spectra

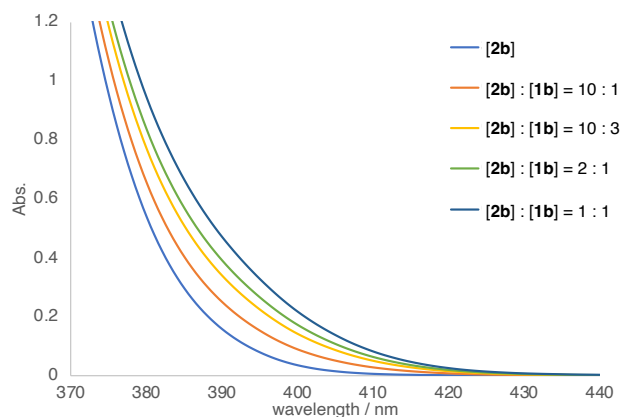


Figure S1. UV-Vis spectra

Solution (A) was prepared by dissolving **2b** (1.0 mg, 2.9  $\mu\text{mol}$ ) in toluene (12 mL).

Solution (B) was prepared by dissolving **1b** (2.9 mg, 2.9  $\mu\text{mol}$ ) in 4 mL of solution (A).

In quartz cell ( $l = 1 \text{ cm}$ ), 2.0 mL of solution (A) and various volume (0, 0.1, 0.3, 0.5, 1.0 mL) of solution (B) were mixed. Then UV-Vis spectra were measured by V-670 UV-VIS-NIR spectrometer (JASCO Co., Ltd.).

### Addition of MVK

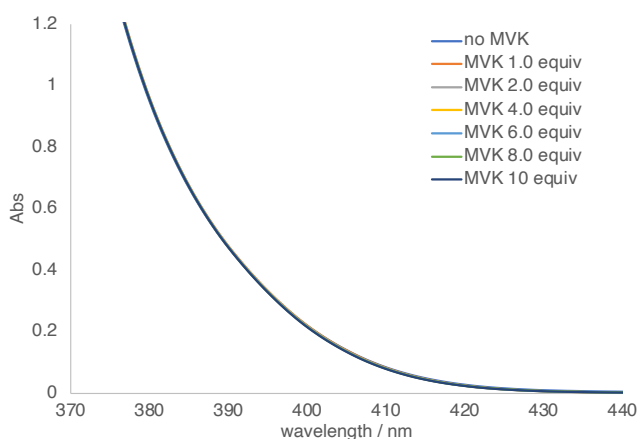


Figure S2. UV-Vis spectra of addition of MVK.

To a toluene solution of 1:1 ratio **2b** and **1b**, various amount of MVK was added and UV-Vis spectra were measured. However, no change was observed.

#### 4-2. $^1\text{H}$ NMR study

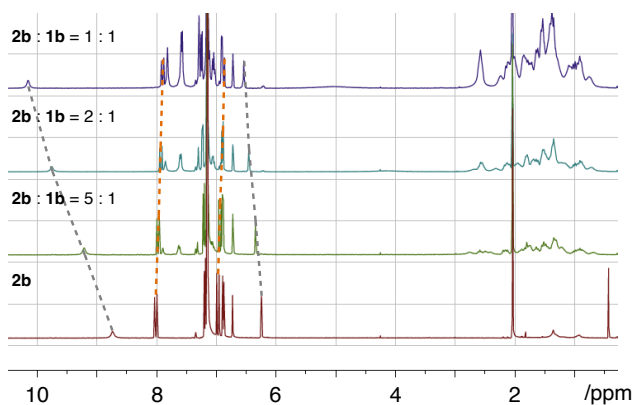


Figure S3.  $^1\text{H}$  NMR spectra of **2b** and **1b** in benzene- $d_6$ .

In a NMR tube, several ratio of **2b** and **1b** was mixed in benzene- $d_6$ . Interaction of **2b** and **1b** was observed in  $^1\text{H}$  NMR.

#### Addition of MVK

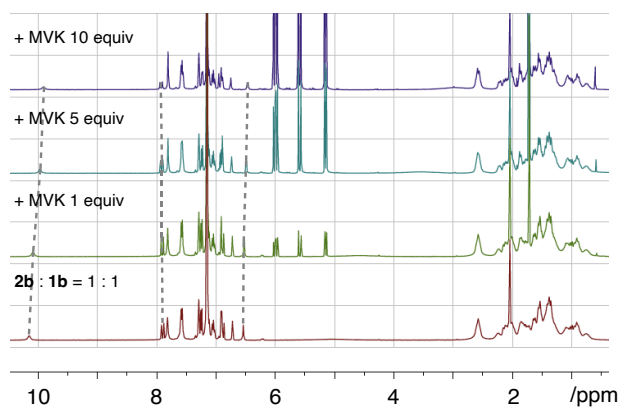
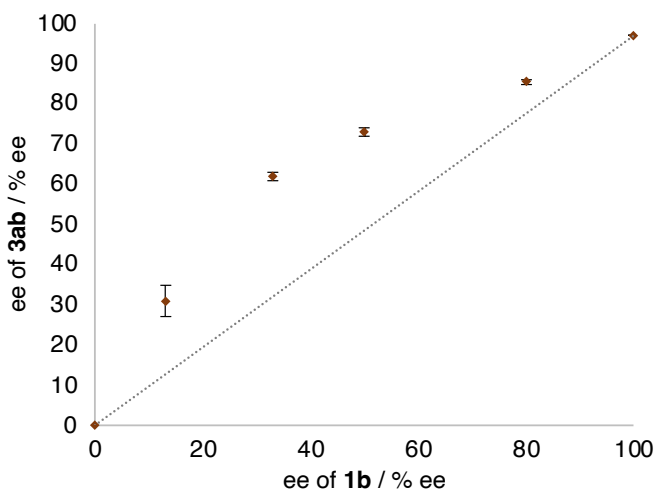
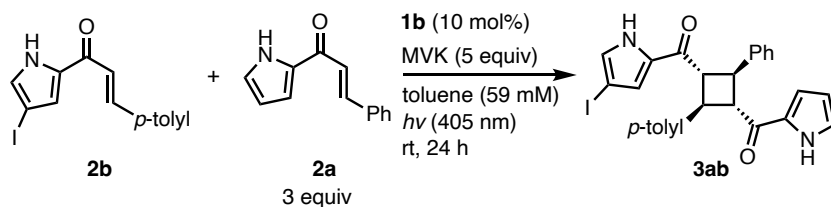


Figure S4.  $^1\text{H}$  NMR spectra of **2b** and **1b** with MVK in benzene- $d_6$ .

To the benzene- $d_6$  solution of 1:1 ratio **2b** and **1b**, various amount of MVK was added and  $^1\text{H}$  NMR were measured. However, remarkable change was not observed.



#### 4-3. Correlation between ee of **1b** and ee of **3ab** in photocycloaddition



**Figure S5. Correlation of ee of **1b** and **3ab** in photocycloaddition.**

In a dried test tube, **2a** (17.3 mg, 0.088 mmol), **2b** (9.9 mg, 0.029 mmol), methyl vinyl ketone (12.3  $\mu$ L, 0.145 mmol) and various ratio (shown in Table S3) of (*R*)-**1b** and (*S*)-**1b** were mixed in toluene (0.5 mL), and degassed three times by the freeze-pump-thaw. The mixture was irradiated with 405 nm violet LED for 24 h. After the irradiation, the solvent was removed. The crude mixture was purified by preparative TLC on SiO<sub>2</sub> (toluene: ethyl acetate = 7 : 3 / v:v) to give **3ab**.

**Table S3. Results of the correlation of ee**

ee of <b>1b</b>	ee of <b>3ab</b>
13% ee	27% ee
13% ee	35% ee
33% ee	61% ee
33% ee	63% ee
50% ee	72% ee
50% ee	74% ee
80% ee	86% ee
80% ee	86% ee
100% ee	97% ee

#### 4-4. Correlation between ee of 1b and ee of 3ag in photocycloaddition

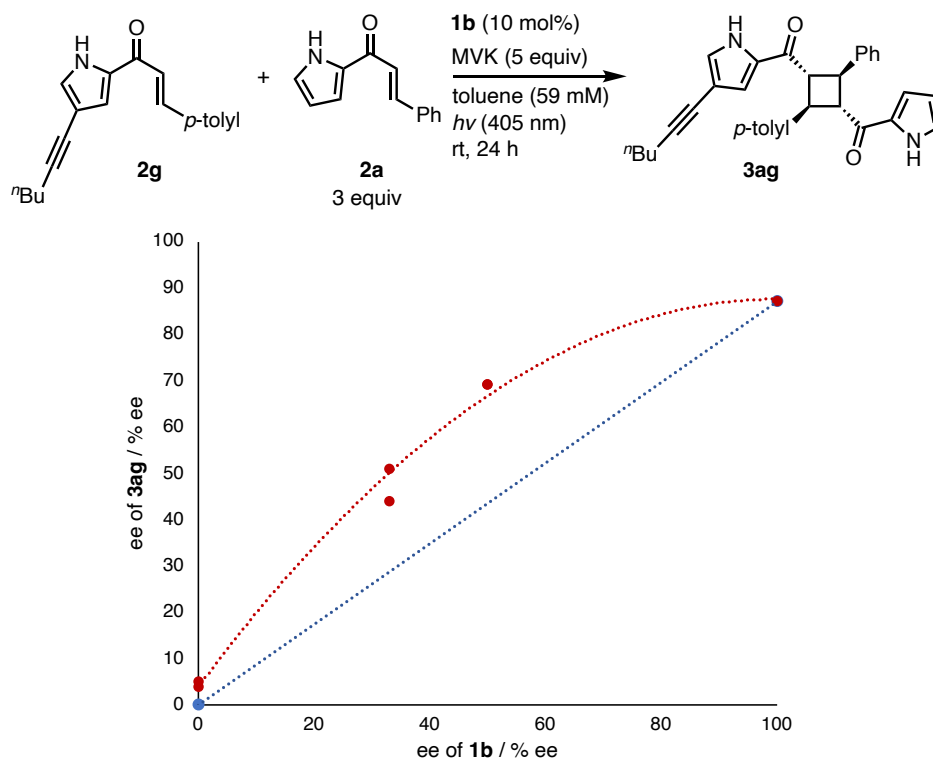


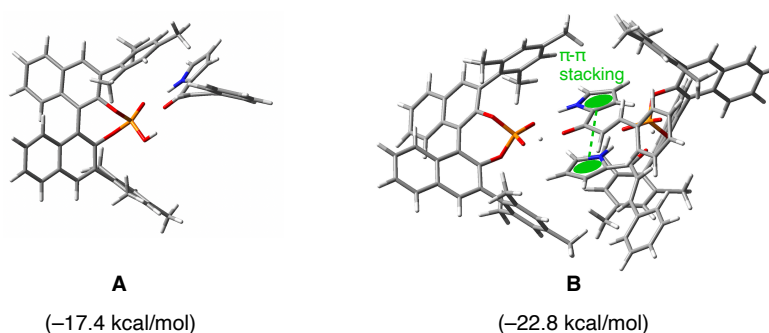
Figure S6. Correlation of ee of **1b** and **3ag** in photocycloaddition.

Table S4. Results of the correlation of ee

ee of <b>1b</b>	ee of <b>3ab</b>
33% ee	44% ee
33% ee	51% ee
50% ee	69% ee
50% ee	69% ee
100% ee	87% ee

#### 4-5. DFT calculation

All calculations were performed with Gaussian 16 program by using M06-2X method with basis set of 6-31G (d,p) for other atoms.<sup>S1</sup> In order to elucidate the origin of the non-linear effect, we calculated and compared the monomer complex and dimer complex of **1f** as CPA and **2a** as substrate.



**Table S4. Sum of thermal free energies**

	G(hartree)	G(kcal/mol)
<b>1f</b>	-2109.068224	-1323461.401
<b>2a</b>	-631.540993	-396298.289
<b>A</b>	-2740.623118	-1719768.413
<b>B</b>	-5481.254729	-3439542.155

#### Cartesian Coordinates

**1f**

**Charge = 0 Multiplicity = 1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)									
			X	Y	Z							
1	6	0	2.256462	4.548883	-2.593184	12	1	0	-0.709546	3.490520	-1.296558	
2	6	0	3.069304	3.526038	-2.182882	13	1	0	0.232834	5.324510	-2.619315	
3	6	0	2.548433	2.441583	-1.427763	14	6	0	1.496880	0.271391	-0.049923	
4	6	0	1.170885	2.434717	-1.070696	15	6	0	2.872854	0.259714	-0.387964	
5	6	0	0.349676	3.501040	-1.528227	16	6	0	-0.722868	1.353547	0.250094	
6	6	0	0.878916	4.525677	-2.270235	17	6	0	-1.204740	2.441624	1.054152	
7	1	0	4.433743	1.389470	-1.281863	18	6	0	-1.581483	0.307504	-0.005240	
8	1	0	2.660569	5.370160	-3.175654	19	6	0	-0.357616	3.480992	1.526263	
9	1	0	4.125558	3.518695	-2.437031	20	6	0	-2.578185	2.468884	1.422758	
10	6	0	3.374279	1.359151	-1.038360	21	6	0	-2.958603	0.313389	0.342816	
11	6	0	0.662746	1.343747	-0.290149	22	6	0	-0.860027	4.503950	2.289311	
						23	1	0	0.700232	3.449449	1.289430	
						24	6	0	-3.070893	3.550252	2.199345	
						25	6	0	-3.430001	1.404643	1.027991	
						26	6	0	-2.234530	4.550087	2.620240	
						27	1	0	-0.195271	5.282680	2.648475	
						28	1	0	-4.124747	3.559344	2.463062	
						29	1	0	-4.483576	1.448664	1.291935	
						30	1	0	-2.618452	5.369577	3.218715	
						31	8	0	1.006727	-0.821839	0.644321	
						32	15	0	-0.105331	-1.787786	-0.007156	

33	8	0	0.520200	-2.487115	-1.262469	8	1	0	3.885068	-2.833417	-0.758815
34	1	0	0.988355	-3.311190	-0.968656	9	1	0	1.470992	-1.632281	-0.978476
35	8	0	-0.650220	-2.652630	1.058385	10	6	0	1.626229	1.265943	0.074897
36	8	0	-1.115744	-0.778807	-0.738757	11	6	0	0.161213	1.162163	-0.100499
37	6	0	-3.849777	-0.823968	-0.044243	12	1	0	-0.301378	2.111116	-0.358579
38	6	0	-4.040095	-1.882784	0.869401	13	6	0	-0.580981	0.068386	0.161248
39	6	0	-4.497685	-0.833937	-1.292462	14	1	0	-0.067409	-0.827926	0.501106
40	6	0	-4.880662	-2.935708	0.513237	15	6	0	-2.039851	-0.052778	0.079100
41	6	0	-5.324714	-1.919394	-1.599181	16	6	0	-2.641060	-1.253607	0.497496
42	6	0	-5.529282	-2.976016	-0.719963	17	6	0	-2.873823	0.973575	-0.404806
43	1	0	-5.028867	-3.751055	1.216184	18	6	0	-4.022542	-1.425478	0.442379
44	1	0	-5.827622	-1.933556	-2.564605	19	1	0	-2.011804	-2.056875	0.872125
45	6	0	3.770984	-0.862968	0.019626	20	6	0	-4.252665	0.802265	-0.460365
46	6	0	4.272899	-1.792814	-0.913108	21	1	0	-2.439712	1.908761	-0.743552
47	6	0	4.206084	-0.896622	1.373841	22	6	0	-4.834131	-0.396988	-0.036691
48	6	0	5.238521	-2.715601	-0.465607	23	1	0	-4.464248	-2.360983	0.772590
49	6	0	5.116210	-1.875822	1.753547	24	1	0	-4.878993	1.605423	-0.837363
50	6	0	5.670994	-2.781390	0.847345	25	1	0	-5.911291	-0.526605	-0.082395
51	1	0	5.680766	-3.386154	-1.195462	26	8	0	2.133136	2.364054	0.336573
52	1	0	5.442095	-1.913017	2.791545						
53	6	0	-4.454446	0.290798	-2.325357						
54	1	0	-4.813299	-0.169218	-3.254018						
55	6	0	-3.411008	-1.859977	2.256095						
56	1	0	-2.476507	-1.293918	2.194051						
57	6	0	-6.427184	-4.140354	-1.091650						
58	1	0	-6.823681	-3.939286	-2.094924						
59	6	0	3.970845	-1.904185	-2.424507						
60	1	0	4.940849	-1.731931	-2.913298						
61	6	0	3.867482	0.139031	2.457639						
62	1	0	4.500194	-0.166907	3.298232						
63	6	0	6.764623	-3.722591	1.322100						
64	1	0	6.394704	-4.205943	2.237281						
65	1	0	-7.256077	-4.224458	-0.420261						
66	1	0	-5.876225	-5.056744	-1.131339						
67	1	0	-5.155474	1.056815	-2.067138						
68	1	0	-3.502074	0.721412	-2.554395						
69	1	0	-4.061182	-1.364552	2.946549						
70	1	0	-3.165229	-2.833328	2.626338						
71	1	0	4.168272	1.138235	2.220957						
72	1	0	2.869195	0.138067	2.842765						
73	1	0	7.640339	-3.166128	1.583580						
74	1	0	7.015388	-4.489228	0.619047						
75	1	0	3.272145	-1.237421	-2.885098						
76	1	0	3.673167	-2.898735	-2.683655						

2a

Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.506204	-0.899751	0.092387
2	6	0	3.631896	-1.826785	-0.458085
3	6	0	2.367380	-1.203577	-0.556383
4	6	0	2.496115	0.092612	-0.056115
5	7	0	3.811647	0.245104	0.323956
6	1	0	4.151095	1.128755	0.677137
7	1	0	5.557152	-0.980004	0.328569

A

Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.414174	-1.069157	4.292416
2	6	0	5.425690	0.075650	3.541515
3	6	0	4.639289	0.181202	2.363376
4	6	0	3.853907	-0.928762	1.944127
5	6	0	3.841783	-2.092923	2.760929
6	6	0	4.600991	-2.159093	3.900737
7	1	0	5.199969	2.229422	1.952510
8	1	0	6.013968	-1.139554	5.193753
9	1	0	6.027774	0.929597	3.838976
10	6	0	4.599123	1.386359	1.620037
11	6	0	3.082133	-0.815770	0.741712
12	1	0	3.214595	-2.930852	2.478852
13	1	0	4.573252	-3.054576	4.512916
14	6	0	3.054803	0.401871	0.092755
15	6	0	3.802613	1.531920	0.510000
16	6	0	2.262873	-1.944147	0.221092
17	6	0	2.823491	-3.224322	-0.097416
18	6	0	0.915329	-1.753564	0.003144
19	6	0	4.219701	-3.485400	-0.040834
20	6	0	1.955311	-4.268882	-0.522628
21	6	0	0.029947	-2.773032	-0.431924
22	6	0	4.715169	-4.725305	-0.353095
23	1	0	4.894888	-2.686215	0.244134
24	6	0	2.498907	-5.545578	-0.825222
25	6	0	0.566789	-4.015828	-0.660816
26	6	0	3.846511	-5.773618	-0.738655
27	1	0	5.784660	-4.903366	-0.309590
28	1	0	1.820931	-6.334935	-1.137369
29	1	0	-0.087448	-4.824869	-0.976355
30	1	0	4.252855	-6.751098	-0.976568
31	8	0	2.281463	0.538094	-1.051115
32	15	0	0.673622	0.600705	-0.898349

33	8	0	0.313394	1.902690	-0.090610
34	1	0	-0.706021	2.378774	-0.314697
35	8	0	0.057117	0.368019	-2.218184
36	8	0	0.373054	-0.492674	0.241352
37	6	0	-1.424044	-2.495886	-0.615034
38	6	0	-1.970374	-2.441884	-1.906999
39	6	0	-2.239750	-2.310936	0.513000
40	6	0	-3.338706	-2.209847	-2.045468
41	6	0	-3.602370	-2.085623	0.329854
42	6	0	-4.169611	-2.028399	-0.942211
43	1	0	-3.764513	-2.163477	-3.045330
44	1	0	-4.236565	-1.951350	1.203582
45	6	0	3.740236	2.843273	-0.201273
46	6	0	3.148443	3.942832	0.442843
47	6	0	4.349149	3.001112	-1.458563
48	6	0	3.221586	5.199084	-0.162343
49	6	0	4.419592	4.276834	-2.015712
50	6	0	3.880915	5.392152	-1.373670
51	1	0	2.767027	6.050959	0.339427
52	1	0	4.906637	4.400188	-2.981081
53	6	0	-1.656595	-2.357458	1.902487
54	1	0	-2.447763	-2.351092	2.655066
55	6	0	-1.103790	-2.603688	-3.130896
56	1	0	-0.296216	-1.866277	-3.119623
57	6	0	-5.639274	-1.744627	-1.119087
58	1	0	-6.223390	-2.146857	-0.287578
59	6	0	2.444805	3.791940	1.770512
60	1	0	3.156706	3.665113	2.592214
61	6	0	4.914517	1.822263	-2.205917
62	1	0	5.513158	2.152899	-3.057120
63	6	0	4.022074	6.766336	-1.976740
64	1	0	3.808952	6.754781	-3.050300
65	6	0	-3.276827	0.000935	-3.754127
66	6	0	-4.640936	-0.079002	-3.515079
67	6	0	-4.872882	0.522410	-2.263616
68	6	0	-3.641255	0.957623	-1.779901
69	7	0	-2.692070	0.634693	-2.714272
70	1	0	-1.691142	0.826743	-2.606294
71	1	0	-2.689840	-0.352605	-4.588575
72	1	0	-5.375324	-0.517789	-4.173531
73	1	0	-5.826225	0.672106	-1.777275
74	6	0	-3.259388	1.729359	-0.602847
75	6	0	-4.117310	1.737753	0.599208
76	1	0	-3.561678	1.867810	1.524097
77	6	0	-5.436543	1.495603	0.582759
78	1	0	-5.913785	1.311712	-0.377691
79	6	0	-6.326133	1.432885	1.749614
80	6	0	-7.683864	1.159859	1.542726
81	6	0	-5.878028	1.641904	3.062268
82	6	0	-8.572217	1.097928	2.610761
83	1	0	-8.040890	0.994593	0.529799
84	6	0	-6.763811	1.580471	4.128854
85	1	0	-4.829642	1.851344	3.249213
86	6	0	-8.114095	1.308997	3.907534
87	1	0	-9.620594	0.884432	2.430215
88	1	0	-6.401754	1.743556	5.138712
89	1	0	-8.803434	1.261380	4.744149
90	8	0	-2.207352	2.371187	-0.594109
91	1	0	-6.018223	-2.180121	-2.046797
92	1	0	-5.824214	-0.666159	-1.160765

93	1	0	-1.048299	-3.255034	2.049385
94	1	0	-1.011345	-1.491140	2.080877
95	1	0	-0.651900	-3.598707	-3.181934
96	1	0	-1.693962	-2.452796	-4.037234
97	1	0	5.537980	1.198456	-1.558076
98	1	0	4.103092	1.195505	-2.592117
99	1	0	5.040923	7.145444	-1.846549
100	1	0	3.342678	7.479551	-1.501372
101	1	0	1.786719	2.919004	1.772503
102	1	0	1.843894	4.678584	1.984780

## B

### Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-7.081342	-6.024785	-3.799154
2	6	0	-6.229423	-5.106527	-4.352904
3	6	0	-5.906644	-3.904836	-3.669389
4	6	0	-6.504715	-3.641555	-2.404088
5	6	0	-7.360146	-4.627980	-1.842071
6	6	0	-7.640672	-5.785419	-2.522106
7	1	0	-4.485901	-3.233623	-5.157947
8	1	0	-7.316815	-6.942010	-4.328629
9	1	0	-5.773317	-5.287132	-5.322187
10	6	0	-4.958530	-2.996325	-4.208096
11	6	0	-6.189459	-2.414187	-1.734273
12	1	0	-7.785984	-4.459125	-0.859329
13	1	0	-8.292868	-6.527939	-2.073948
14	6	0	-5.251149	-1.587223	-2.312050
15	6	0	-4.587883	-1.857728	-3.538269
16	6	0	-6.773100	-2.027514	-0.419594
17	6	0	-8.187354	-1.924955	-0.205452
18	6	0	-5.935580	-1.692261	0.625181
19	6	0	-9.133416	-2.104228	-1.251271
20	6	0	-8.669894	-1.590836	1.091203
21	6	0	-6.393418	-1.329681	1.920307
22	6	0	-10.478835	-2.002544	-1.007882
23	1	0	-8.778152	-2.313794	-2.253867
24	6	0	-10.069884	-1.506970	1.313890
25	6	0	-7.748613	-1.312015	2.133054
26	6	0	-10.957695	-1.714033	0.291807
27	1	0	-11.183477	-2.137933	-1.821837
28	1	0	-10.420100	-1.262611	2.312855
29	1	0	-8.128920	-1.051991	3.117811
30	1	0	-12.025469	-1.642987	0.470555
31	8	0	-4.916954	-0.415212	-1.649761
32	15	0	-3.850794	-0.590283	-0.449089
33	8	0	-4.557377	-1.734339	0.443679
34	6	0	-5.412757	-0.966574	2.986061
35	6	0	-5.233674	0.383072	3.333917
36	6	0	-4.666991	-1.970739	3.624153
37	6	0	-4.280414	0.703588	4.300234
38	6	0	-3.736416	-1.607973	4.598820
39	6	0	-3.513840	-0.273442	4.933385
40	1	0	-4.123705	1.750520	4.555551
41	1	0	-3.151714	-2.385050	5.087147

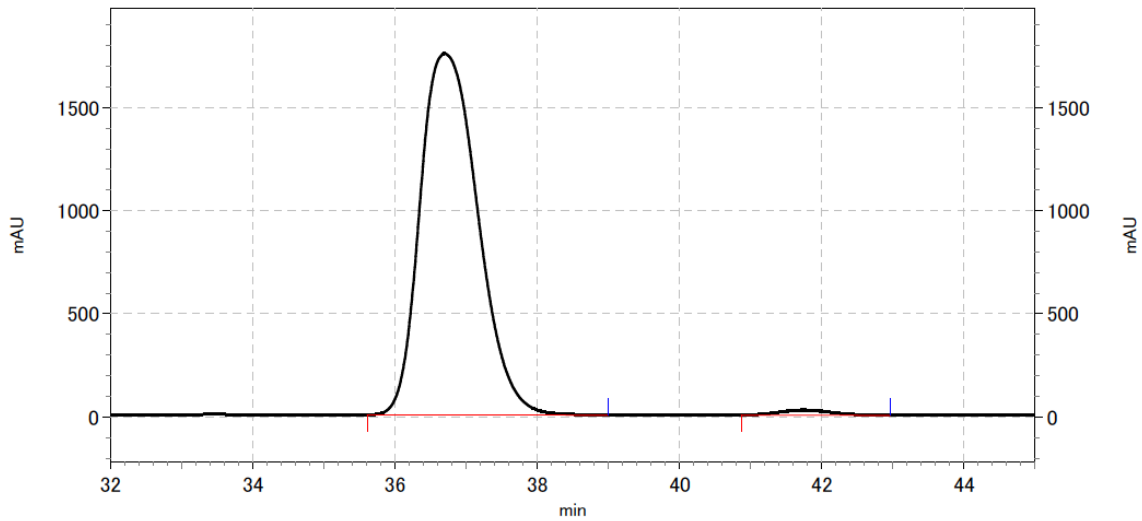
42	6	0	-3.475934	-0.964981	-3.978126	102	1	0	-3.295340	1.445323	0.147534
43	6	0	-2.153864	-1.433695	-3.876249	103	6	0	7.925299	-6.610230	-0.363631
44	6	0	-3.731341	0.355571	-4.378324	104	6	0	7.011349	-6.362730	0.626105
45	6	0	-1.110665	-0.559218	-4.157581	105	6	0	6.535874	-5.046352	0.867136
46	6	0	-2.652250	1.203508	-4.646064	106	6	0	7.042976	-3.968196	0.086927
47	6	0	-1.335405	0.767328	-4.524231	107	6	0	7.966792	-4.262302	-0.952404
48	1	0	-0.085773	-0.911270	-4.057522	108	6	0	8.395678	-5.546612	-1.169140
49	1	0	-2.850843	2.231072	-4.942747	109	1	0	5.127940	-5.644524	2.398674
50	6	0	-4.846026	-3.417265	3.240846	110	1	0	8.278606	-7.620269	-0.542906
51	1	0	-4.292420	-4.070800	3.918160	111	1	0	6.622791	-7.172258	1.237688
52	6	0	-6.045998	1.473671	2.681736	112	6	0	5.527630	-4.804410	1.836003
53	1	0	-6.034868	1.374065	1.594096	113	6	0	6.575010	-2.640159	0.356948
54	6	0	-2.422036	0.118279	5.893130	114	1	0	8.326628	-3.456545	-1.582311
55	1	0	-2.156908	-0.706959	6.559081	115	1	0	9.098059	-5.750449	-1.970740
56	6	0	-1.848504	-2.830948	-3.398800	116	6	0	5.583872	-2.483571	1.301514
57	1	0	-2.219785	-3.592977	-4.090049	117	6	0	5.011167	-3.549955	2.044259
58	6	0	-5.143839	0.870246	-4.496946	118	6	0	7.061351	-1.440444	-0.380118
59	1	0	-5.168094	1.808921	-5.054773	119	6	0	8.448501	-1.079534	-0.432184
60	6	0	-0.156483	1.676891	-4.768018	120	6	0	6.150500	-0.603573	-0.992991
61	1	0	-0.473465	2.718543	-4.867634	121	6	0	9.451586	-1.786878	0.285583
62	6	0	0.756547	0.297032	-1.357241	122	6	0	8.840583	0.055112	-1.197041
63	6	0	1.742355	1.281759	-1.417706	123	6	0	6.515541	0.546001	-1.741062
64	6	0	1.104858	2.502463	-1.166478	124	6	0	10.768332	-1.412444	0.207813
65	6	0	-0.259064	2.235742	-0.963743	125	1	0	9.162646	-2.625291	0.909085
66	7	0	-0.424726	0.876068	-1.089034	126	6	0	10.214504	0.408134	-1.268831
67	1	0	-1.295826	0.349257	-0.975939	127	6	0	7.853283	0.835488	-1.849452
68	1	0	0.838440	-0.775717	-1.456665	128	6	0	11.160616	-0.310604	-0.588425
69	1	0	2.796002	1.122803	-1.602200	129	1	0	11.516935	-1.962591	0.768407
70	1	0	1.589282	3.464050	-1.073822	130	1	0	10.495721	1.270149	-1.867247
71	6	0	-1.344315	3.079754	-0.529507	131	1	0	8.164297	1.699730	-2.431398
72	6	0	-1.181588	4.550417	-0.495095	132	1	0	12.207284	-0.030552	-0.644826
73	1	0	-1.772528	5.034777	0.279366	133	8	0	5.109169	-1.202539	1.548200
74	6	0	-0.471608	5.249001	-1.388239	134	15	0	4.033037	-0.634677	0.486738
75	1	0	0.061142	4.704227	-2.165492	135	8	0	4.793396	-0.893037	-0.914980
76	6	0	-0.324850	6.711797	-1.432481	136	6	0	5.475770	1.402972	-2.381461
77	6	0	0.667557	7.262205	-2.253366	137	6	0	5.208192	2.682410	-1.862443
78	6	0	-1.131655	7.578898	-0.681426	138	6	0	4.790381	0.936239	-3.514133
79	6	0	0.865848	8.637586	-2.311076	139	6	0	4.254287	3.474976	-2.499081
80	1	0	1.291053	6.596797	-2.845577	140	6	0	3.848339	1.764060	-4.123815
81	6	0	-0.936033	8.952942	-0.742695	141	6	0	3.566631	3.033872	-3.628887
82	1	0	-1.924006	7.178024	-0.056593	142	1	0	4.041986	4.465472	-2.099162
83	6	0	0.064830	9.487301	-1.553908	143	1	0	3.316457	1.403424	-5.001800
84	1	0	1.642952	9.045449	-2.949020	144	6	0	3.841257	-3.288326	2.932571
85	1	0	-1.575560	9.611976	-0.163460	145	6	0	2.569454	-3.738296	2.532231
86	1	0	0.212121	10.561284	-1.600790	146	6	0	3.990981	-2.542584	4.110314
87	8	0	-2.434198	2.634134	-0.131493	147	6	0	1.469430	-3.424858	3.325682
88	1	0	-2.715133	0.975883	6.504929	148	6	0	2.856867	-2.229194	4.862932
89	1	0	-1.520232	0.396808	5.333370	149	6	0	1.586306	-2.650437	4.480343
90	1	0	-5.900448	-3.707915	3.263685	150	1	0	0.485005	-3.776732	3.023581
91	1	0	-4.481072	-3.592329	2.223150	151	1	0	2.972728	-1.633739	5.765858
92	1	0	-7.090022	1.440617	3.009661	152	6	0	5.060720	-0.440628	-4.063250
93	1	0	-5.642866	2.455552	2.939518	153	1	0	4.562301	-0.579647	-5.024632
94	1	0	-5.787878	0.149136	-5.008119	154	6	0	5.925987	3.199805	-0.641089
95	1	0	-5.574193	1.052154	-3.506914	155	1	0	5.906500	2.460750	0.163368
96	1	0	0.377494	1.399806	-5.684310	156	6	0	2.514580	3.894528	-4.265510
97	1	0	0.559041	1.613826	-3.934720	157	1	0	2.262706	3.543349	-5.268278
98	1	0	-2.310982	-3.005942	-2.423497	158	6	0	2.367954	-4.478803	1.233610
99	1	0	-0.769907	-2.968001	-3.293542	159	1	0	2.899630	-5.433751	1.211555
100	8	0	-2.496967	-1.007974	-0.866562	160	6	0	5.349997	-2.063110	4.552978
101	8	0	-4.011218	0.742879	0.333904	161	1	0	5.319892	-1.714190	5.587344

162	6	0	0.355496	-2.276487	5.265296	186	1	0	-2.997848	6.930055	5.582579
163	1	0	0.590206	-1.558437	6.054684	187	1	0	-0.842489	8.441227	2.185270
164	6	0	-0.542672	-1.091659	1.830324	188	1	0	-2.346659	8.833892	4.128709
165	6	0	-1.709942	-0.392775	2.123775	189	8	0	2.139930	2.060930	1.768325
166	6	0	-1.349933	0.951713	2.268296	190	1	0	2.839201	4.938018	-4.338077
167	6	0	0.038545	1.038860	2.090924	191	1	0	1.592329	3.867289	-3.672152
168	7	0	0.492111	-0.234267	1.831273	192	1	0	6.132775	-0.608926	-4.201598
169	1	0	1.436411	-0.497630	1.540687	193	1	0	4.694959	-1.208593	-3.373843
170	1	0	-0.390924	-2.133415	1.590711	194	1	0	6.973893	3.428259	-0.859190
171	1	0	-2.706345	-0.805065	2.194393	195	1	0	5.450734	4.114142	-0.279464
172	1	0	-2.031163	1.773798	2.429122	196	1	0	6.094365	-2.861238	4.480050
173	6	0	0.933056	2.165464	2.039228	197	1	0	5.692489	-1.235514	3.923976
174	6	0	0.424640	3.539034	2.259603	198	1	0	-0.099688	-3.156276	5.732757
175	1	0	0.966468	4.284933	1.683049	199	1	0	-0.397062	-1.827155	4.606170
176	6	0	-0.517173	3.892742	3.144813	200	1	0	2.731609	-3.871734	0.398797
177	1	0	-0.962399	3.122783	3.771917	201	1	0	1.306355	-4.679586	1.071434
178	6	0	-0.998531	5.260262	3.384286	202	8	0	2.716884	-1.307313	0.495936
179	6	0	-1.855632	5.492910	4.466873	203	8	0	4.083851	0.894027	0.750615
180	6	0	-0.646918	6.343156	2.563948	204	1	0	3.231633	1.308617	1.141821
181	6	0	-2.337345	6.769355	4.736824						
182	1	0	-2.140640	4.659037	5.103333						
183	6	0	-1.128031	7.617773	2.832953						
184	1	0	-0.002203	6.190192	1.702328						
185	6	0	-1.972591	7.836598	3.921301						

## 5. HPLC data

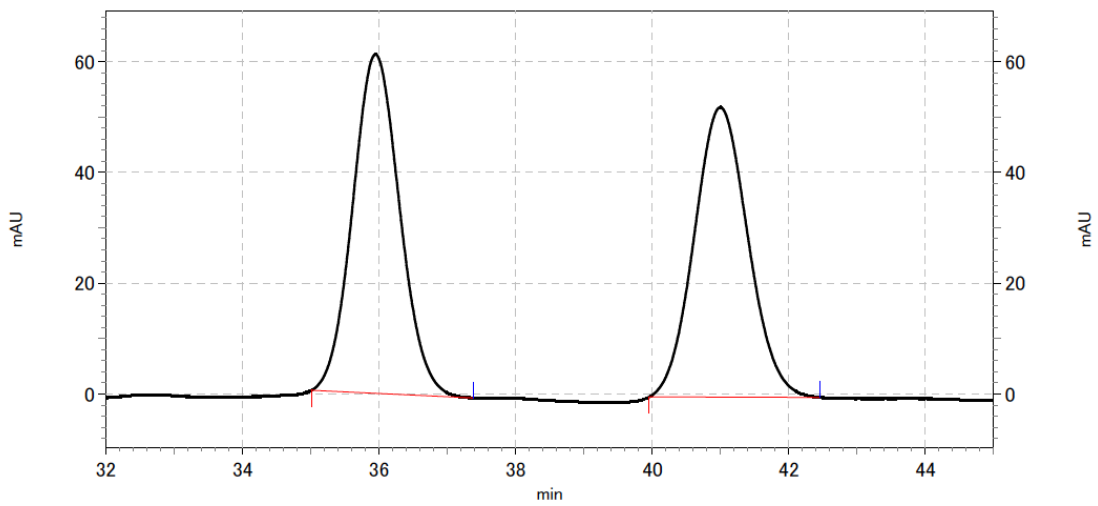
### 3ab

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 36.70$  min,  $t_{\text{minor}} = 41.70$  min.



Peak #	Retention time	Area	Area %
1	36.700	394544953	98.670
2	41.740	5318253	1.330

### Racemate

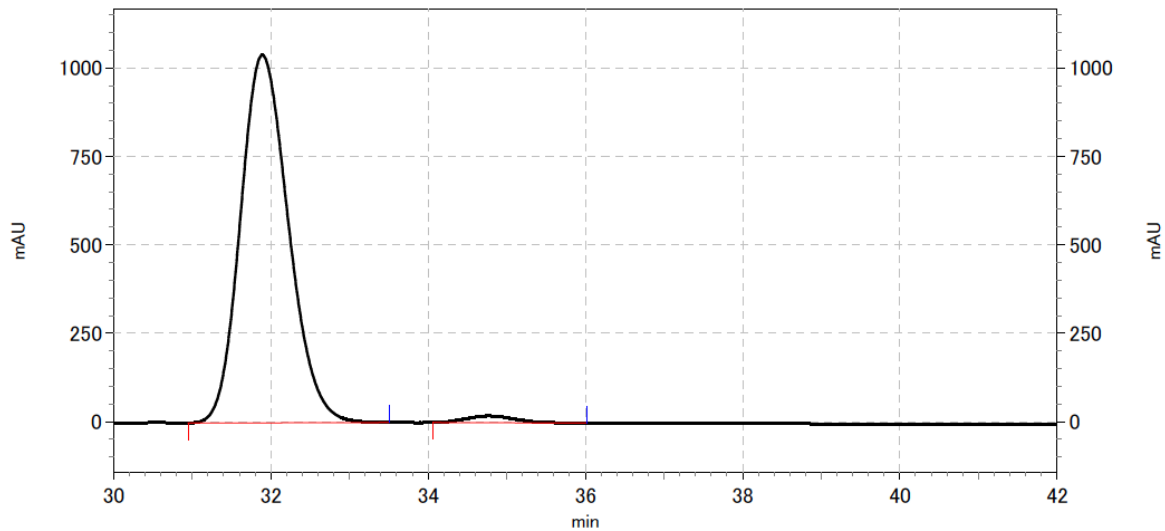


Peak #	Retention time	Area	Area %
1	35.953	11712105	50.590
2	41.000	11438835	49.410



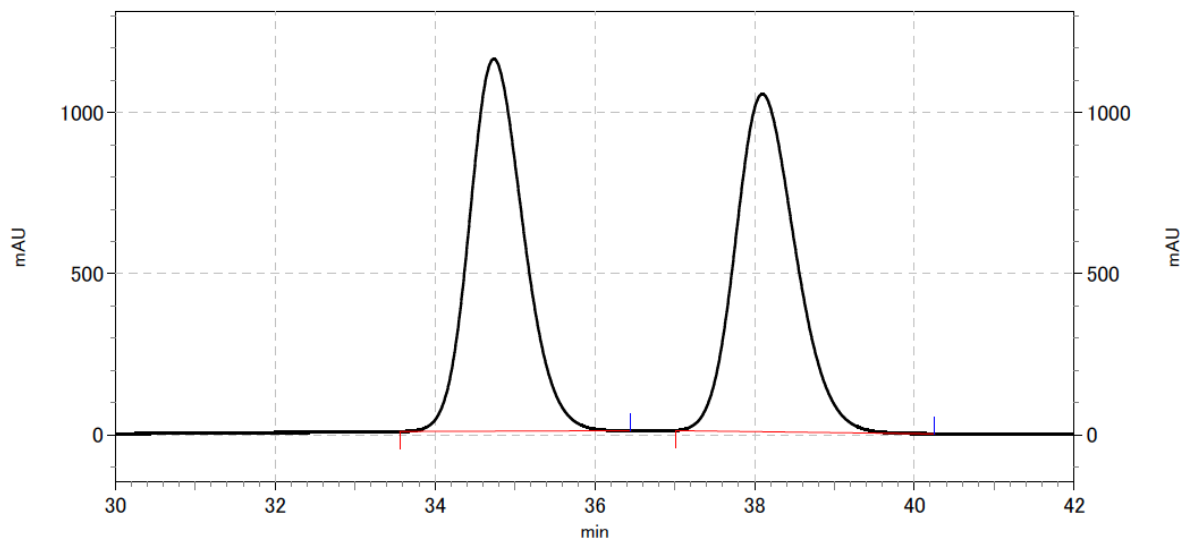
### 3ac

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 31.89$  min,  $t_{\text{minor}} = 34.76$  min.



Peak #	Retention time	Area	Area %
1	31.893	176162551	98.156
2	34.767	3310208	1.844

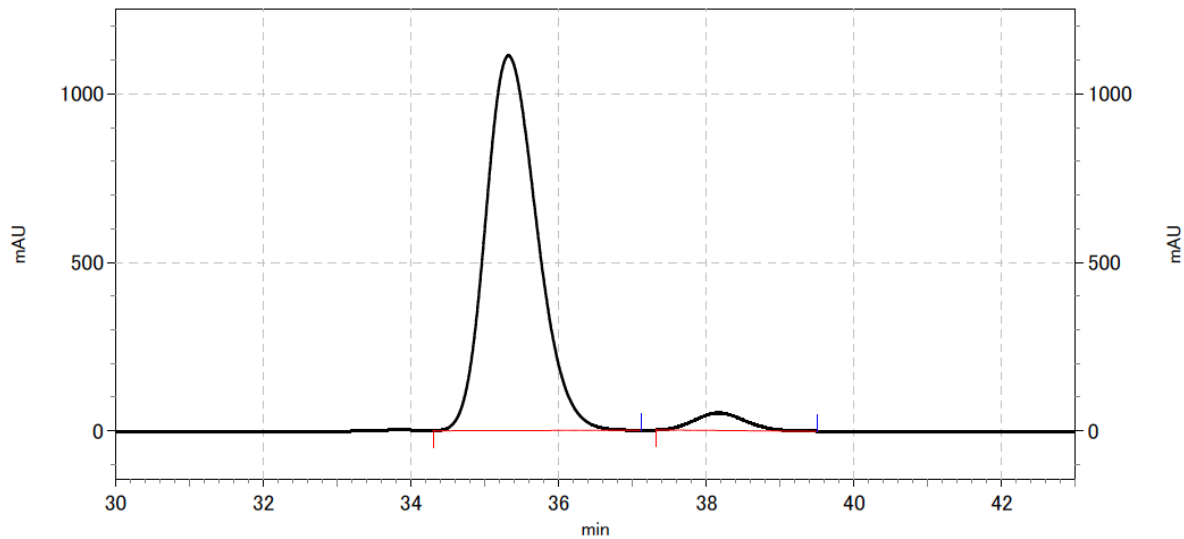
### Racemate



Peak #	Retention time	Area	Area %
1	34.740	218428161	49.911
2	38.100	219208512	50.089

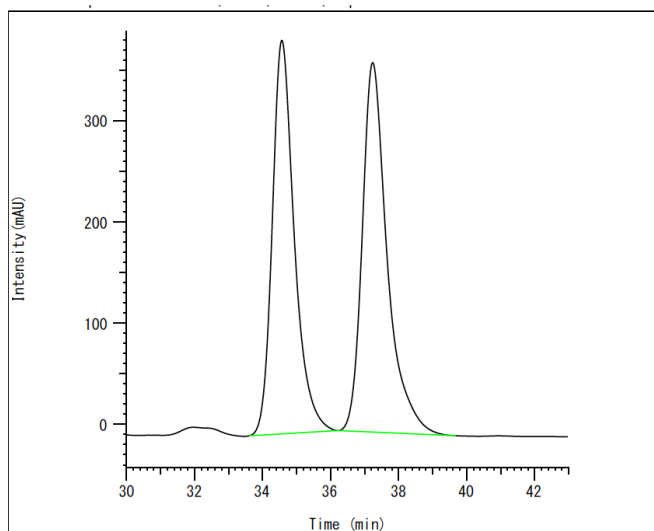
**3ad**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{major} = 35.32$  min,  $t_{minor} = 38.16$  min.



Peak #	Retention time	Area	Area %
1	35.327	214433451	95.472
2	38.167	10169716	4.528

**Racemate**

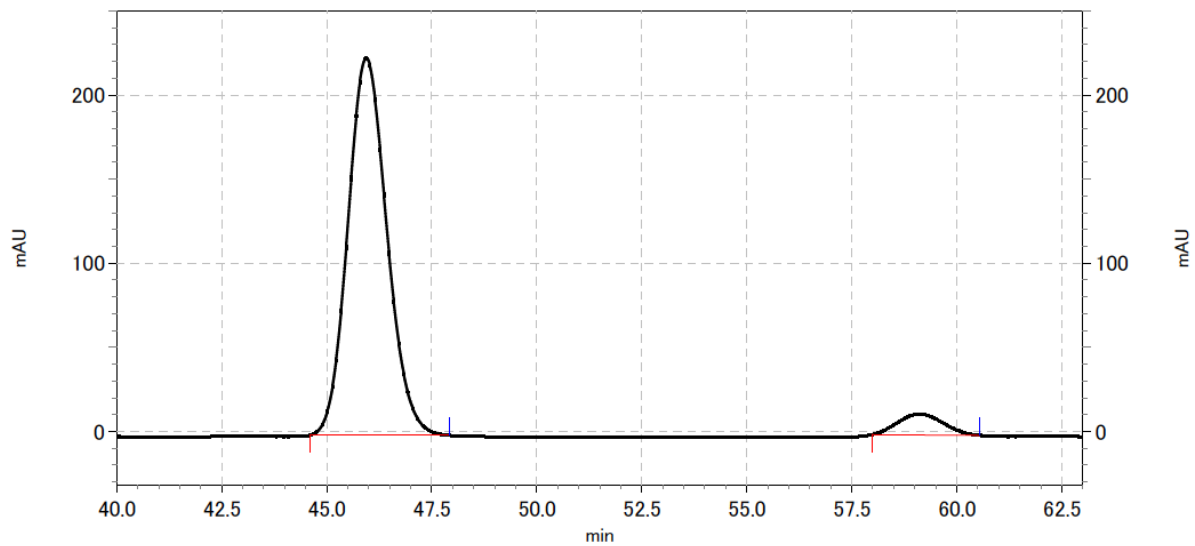


5430 Diode Array Detector SampleID:1 kt-349-rac (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	34.487	17478901	48.478
2 Peak 2	37.240	18576281	51.522
		36055182	100.000

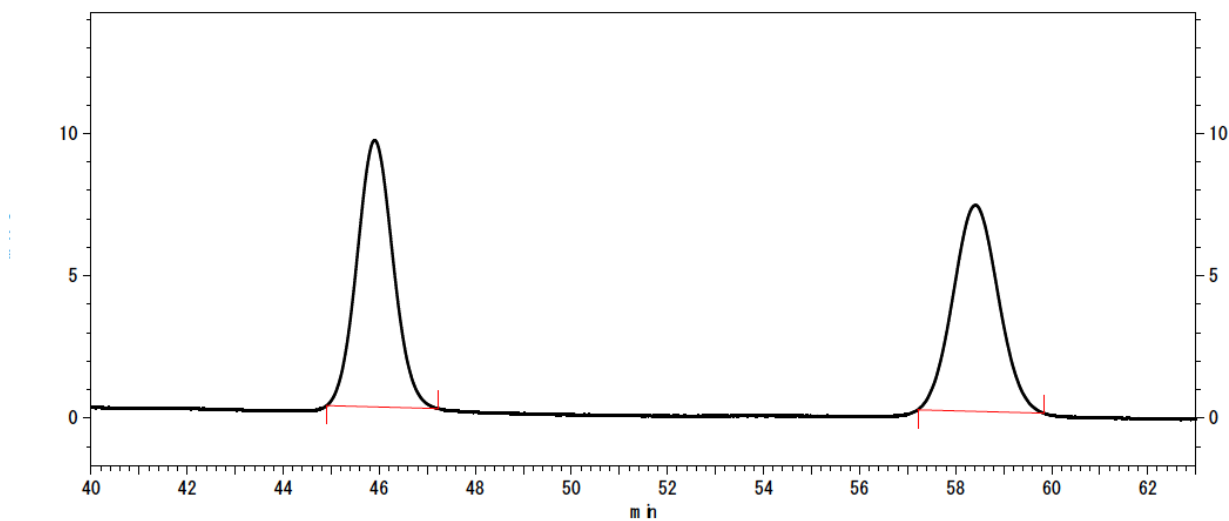
**3ae**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 45.94$  min,  $t_{\text{minor}} = 59.10$  min.



Peak #	Retention time	Area	Area %
1	45.940	58170513	93.977
2	59.107	3728442	6.023

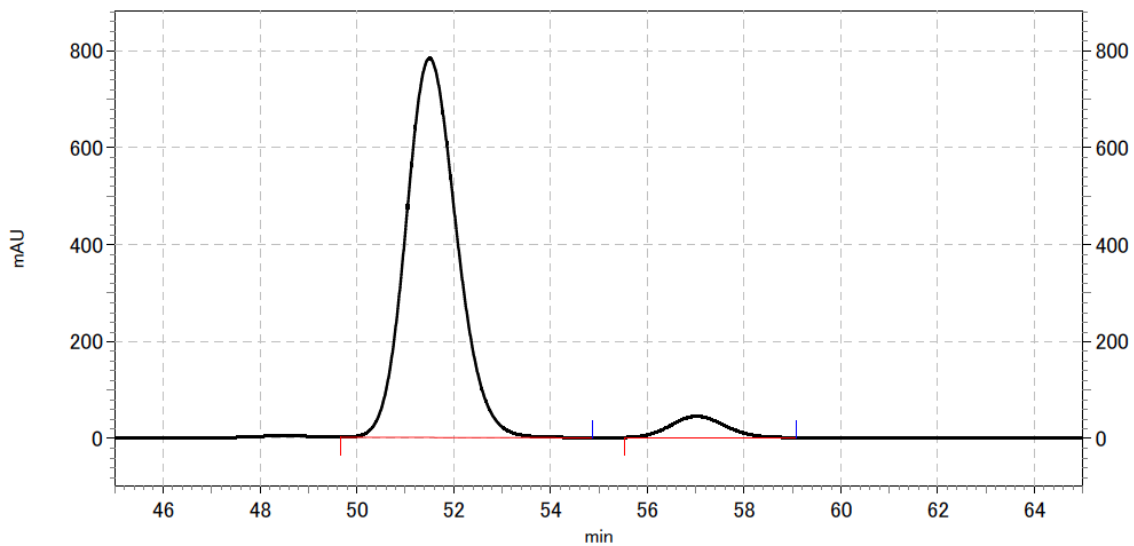
**Racemate**



Peak #	Retention time	Area	Area %
1	45.900	1959874	50.754
2	58.413	1901657	49.246

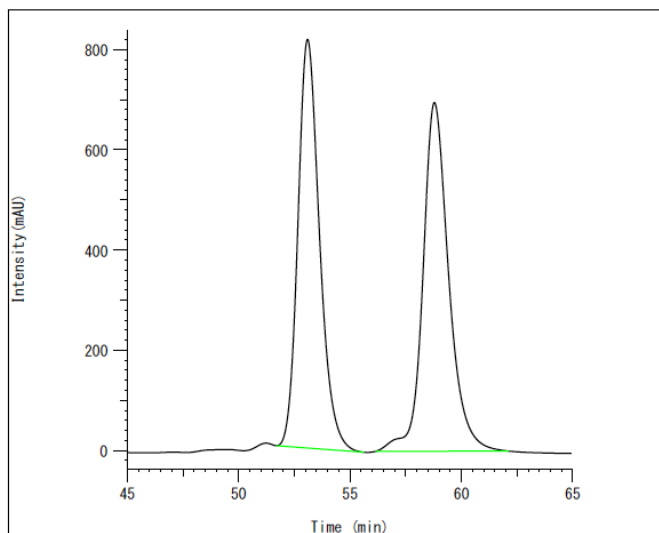
### 3af

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 51.50$  min,  $t_{\text{minor}} = 57.02$  min.



Peak #	Retention time	Area	Area %
1	51.500	228338153	94.233
2	57.020	13973153	5.767

### Racemate

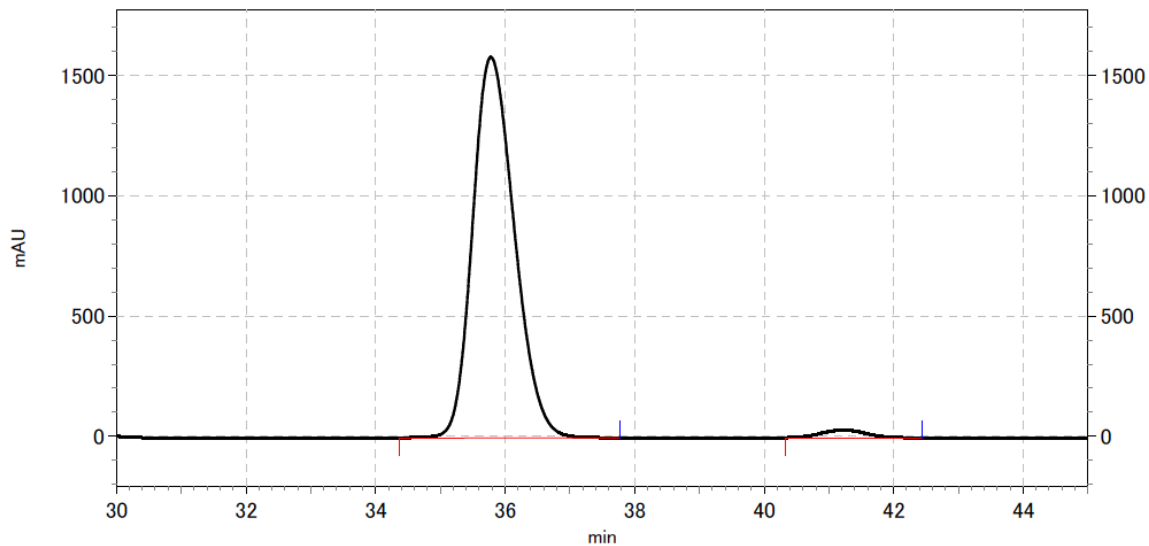


5430 Diode Array Detector SampleID:1 kt-385-rac (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	53.093	54981235	49.457
2 Peak 2	58.793	56188199	50.543
		111169434	100.000

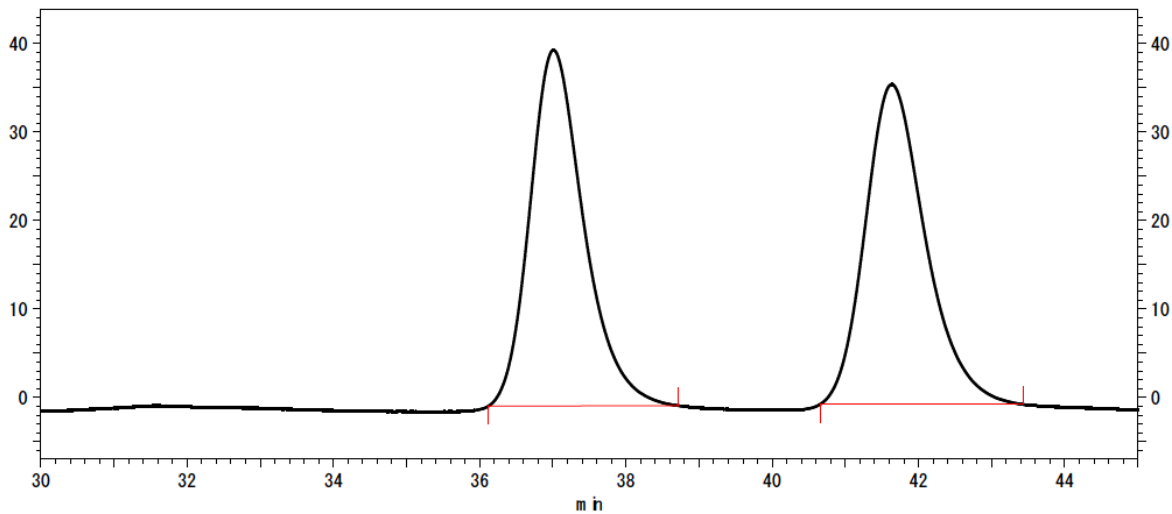
**3ag**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{major} = 35.78$  min,  $t_{minor} = 41.22$  min.



Peak #	Retention time	Area	Area %
1	35.780	284280000	97.797
2	41.227	6403619	2.203

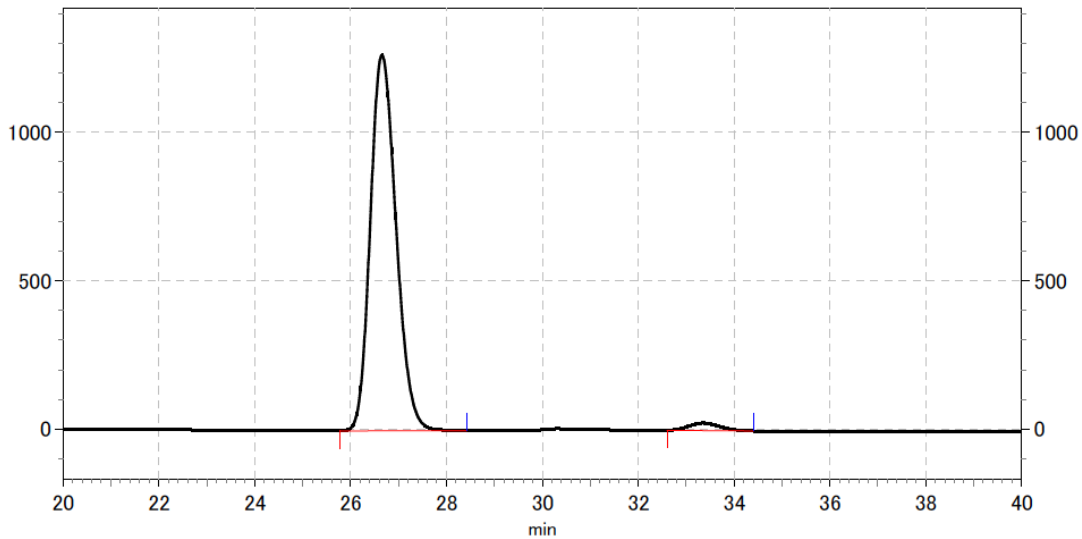
**Racemate**



Peak #	Retention time	Area	Area %
1	37.007	8273810	49.894
2	41.640	8308941	50.106

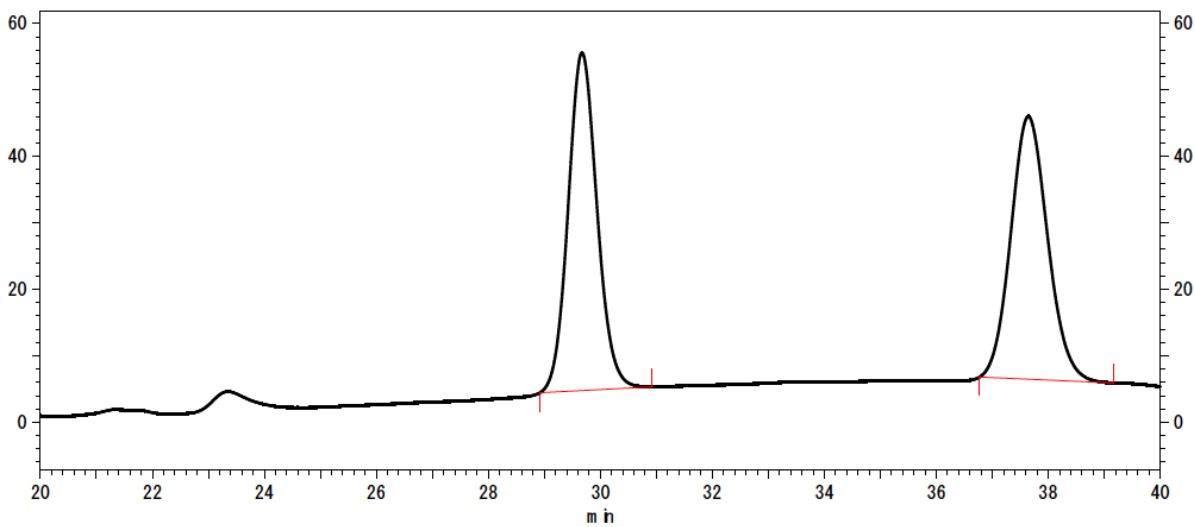
### 3ah

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 26.65$  min,  $t_{\text{minor}} = 33.35$  min.



Peak #	Retention time	Area	Area %
1	26.653	188900469	97.548
2	33.353	4747361	2.452

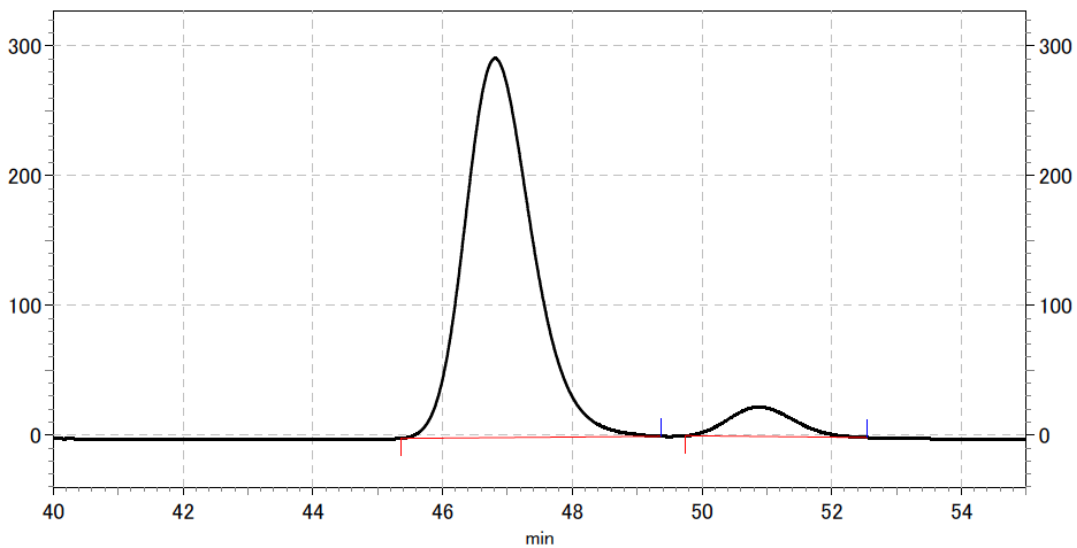
### Racemate



Peak #	Retention time	Area	Area %
1	29.673	7285650	50.151
2	37.640	7241802	49.849

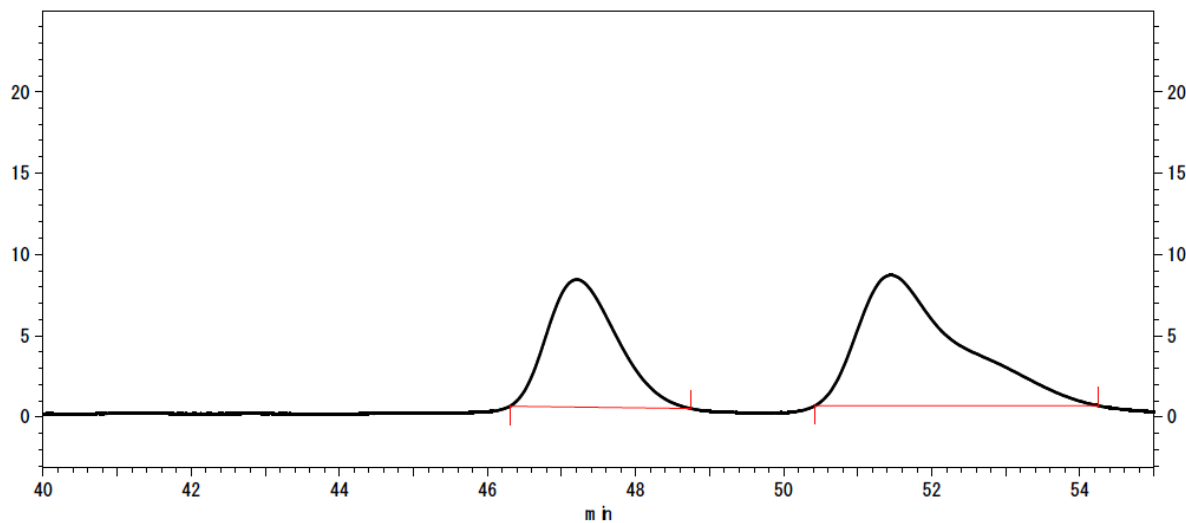
**3ai**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 46.81$  min,  $t_{\text{minor}} = 50.88$  min.



Peak #	Retention time	Area	Area %
1	46.813	84596180	92.926
2	50.887	6439471	7.074

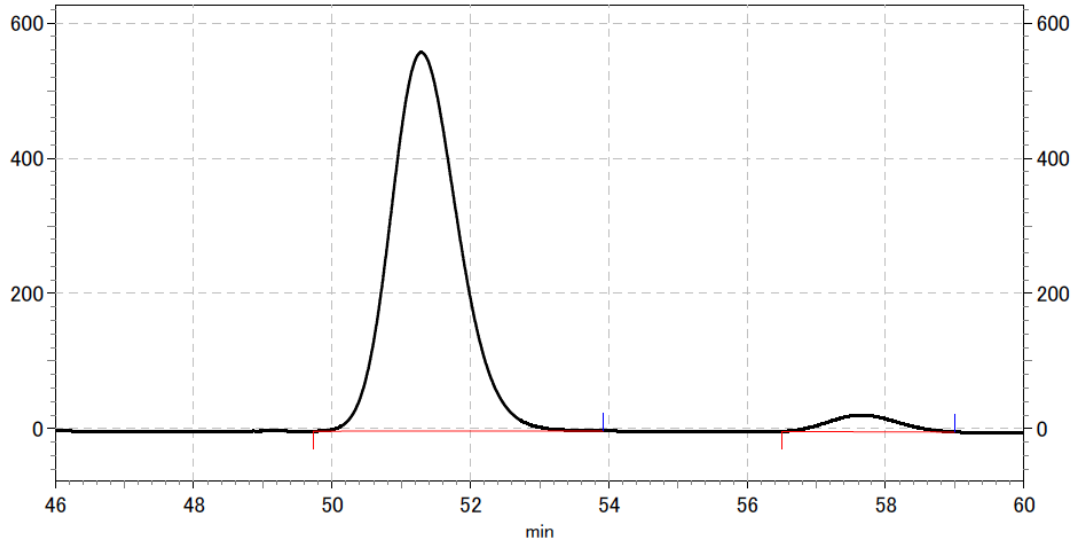
**Racemate**



Peak #	Retention time	Area	Area %
1	47.207	2037797	40.009
2	51.447	3055582	59.991

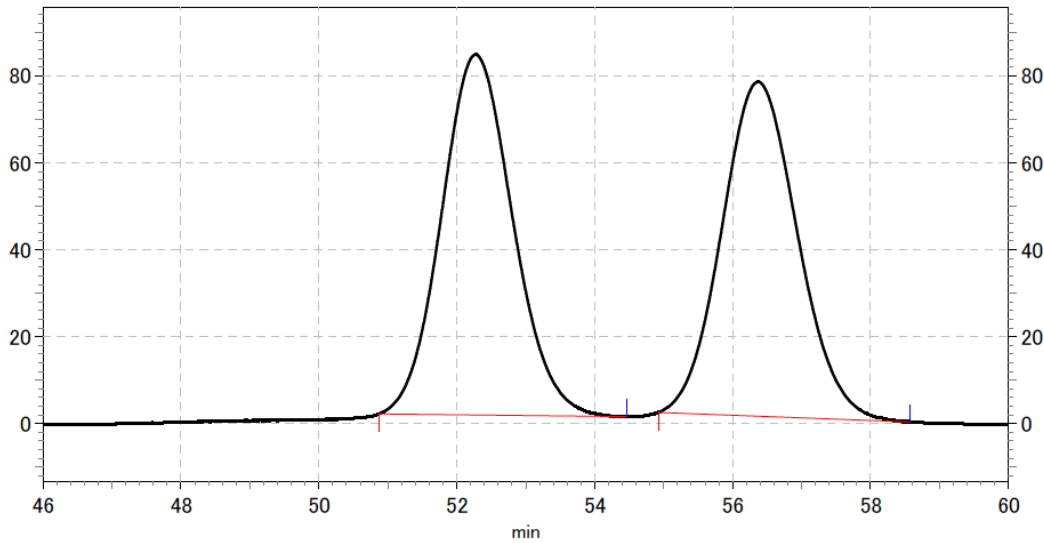
**3bj**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 51.28$  min,  $t_{\text{minor}} = 57.66$  min.



Peak #	Retention time	Area	Area %
1	51.287	152842046	95.678
2	57.660	6904746	4.322

**Racemate**

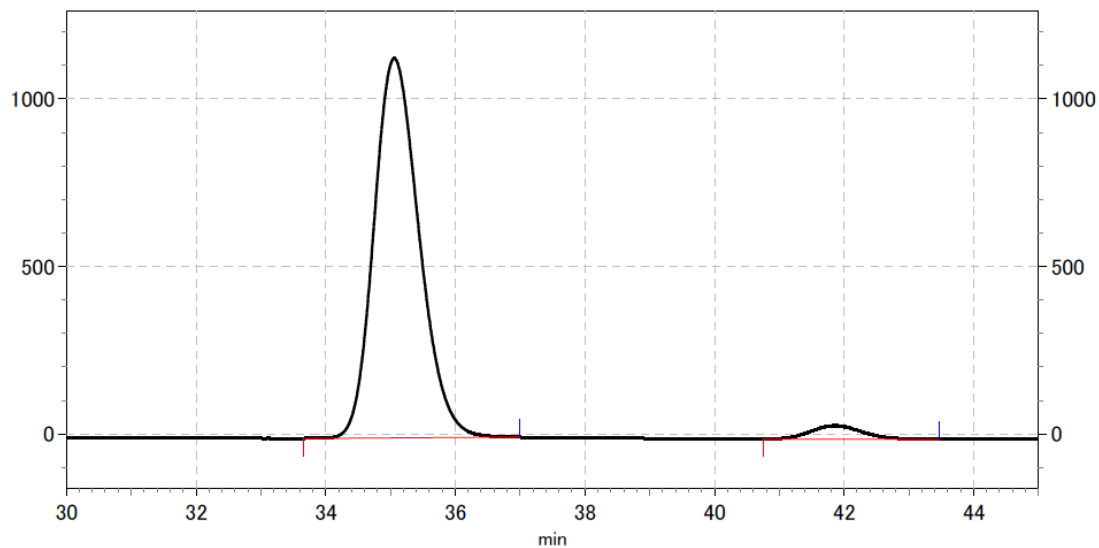


Peak #	Retention time	Area	Area %
1	52.273	23852462	50.383
2	56.373	23489518	49.617



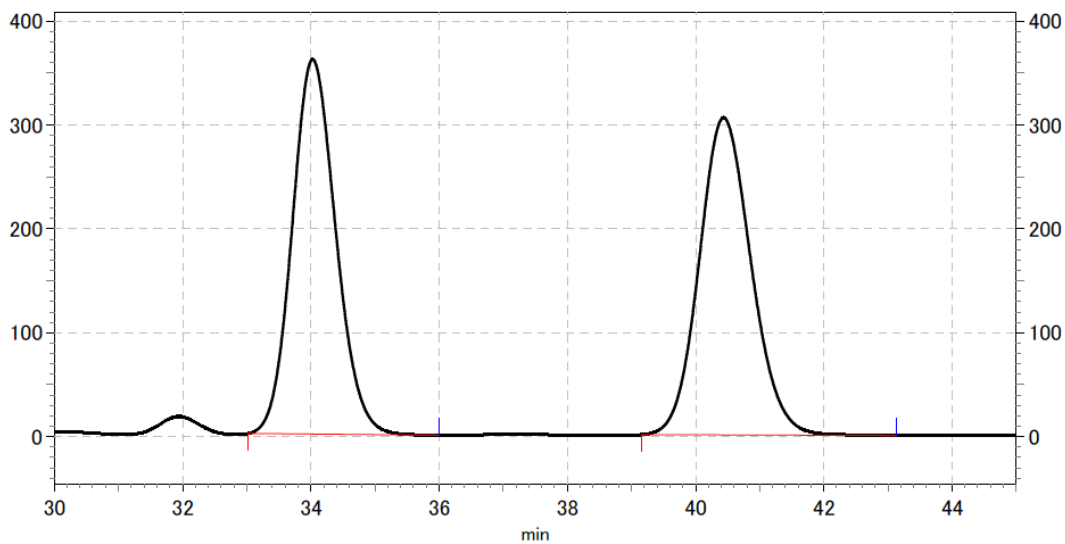
**3bk**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 35.06$  min,  $t_{\text{minor}} = 41.86$  min.



Peak #	Retention time	Area	Area %
1	35.060	219025585	96.067
2	41.860	8967755	3.933

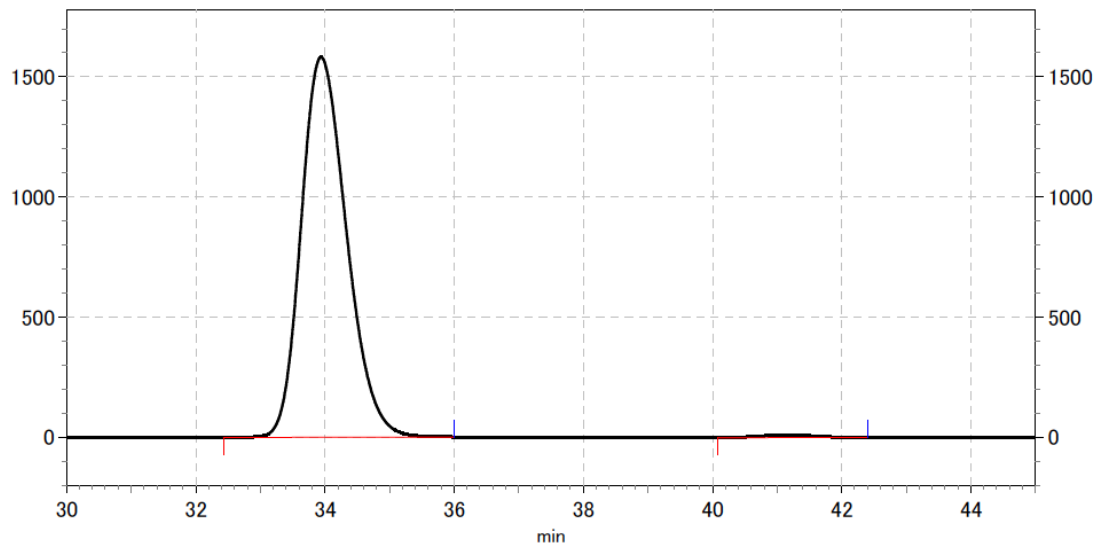
**Racemate**



Peak #	Retention time	Area	Area %
1	34.027	68324317	49.820
2	40.440	68817597	50.180

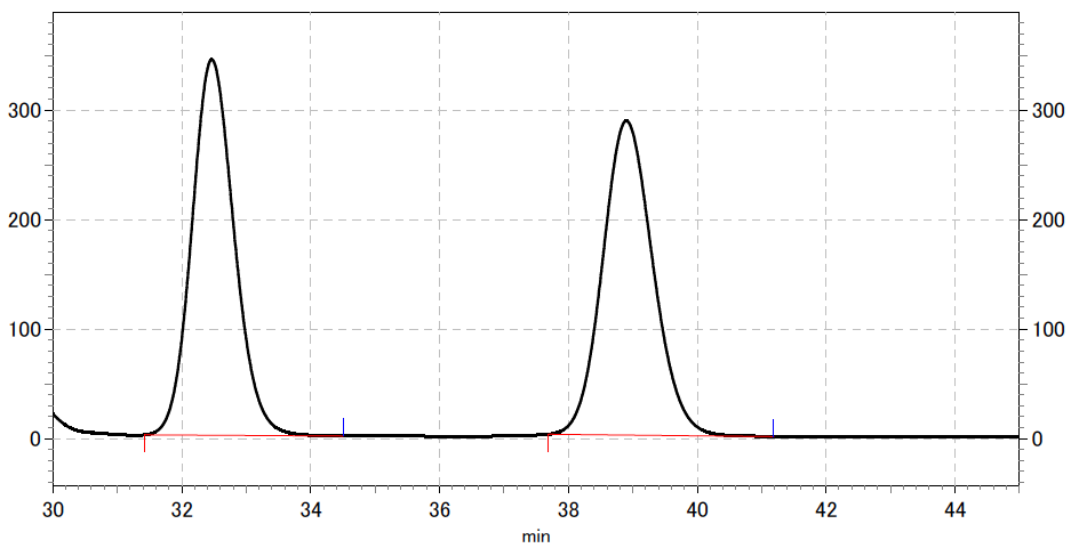
**3bl**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 33.94$  min,  $t_{\text{minor}} = 41.16$  min.



Peak #	Retention time	Area	Area %
1	33.940	309416343	99.171
2	41.160	2585252	0.829

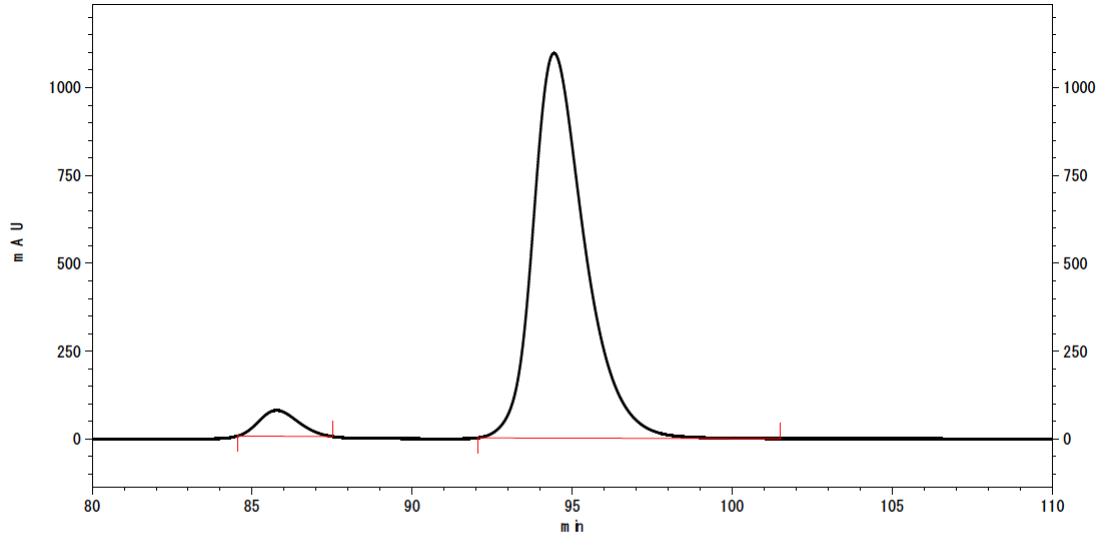
**Racemate**



Peak #	Retention time	Area	Area %
1	32.467	62900764	50.138
2	38.900	62555295	49.862

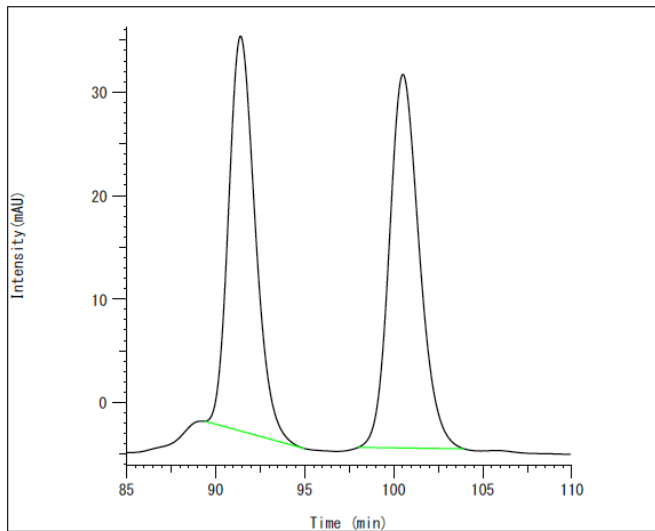
### 3bm

CHIRALPAK® IA-3 column, *n*-hexane/*i*-PrOH = 85/15, flow rate = 0.5 mL/min,  $t_{\text{major}} = 96.10$  min,  $t_{\text{minor}} = 88.00$  min.



Peak #	Retention time	Area	Area%
1	85.760	24891460	4.810
2	94.433	492613603	95.190

### Racemate

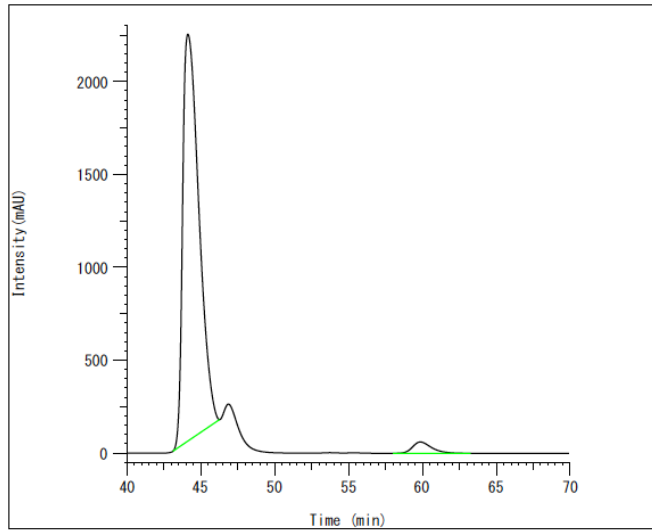


5430 Diode Array Detector SampleID:1 kt-268-rac (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	91.407	3954316	48.343
2 Peak 2	100.520	4225466	51.657
		8179783	100.000

### 3bn

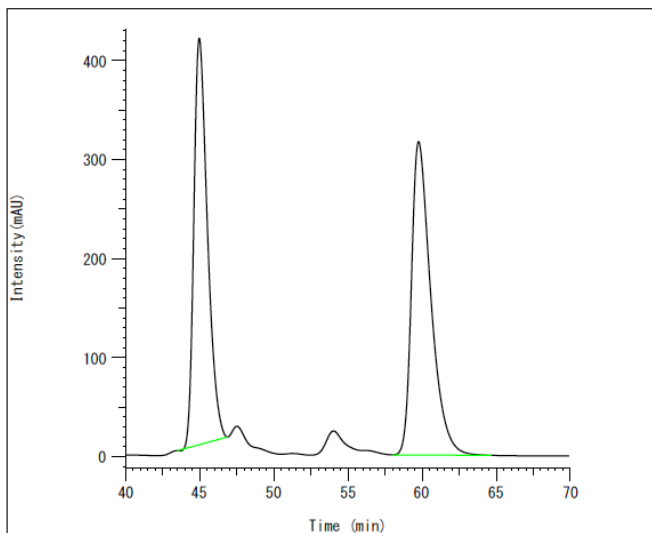
CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 44.12$  min,  $t_{\text{minor}} = 59.86$  min.



5430 Diode Array Detector SampleID:1 UNK001 (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	44.120	167025788	96.796
2 Peak 2	59.860	5528738	3.204
		172554526	100.000

### Racemate

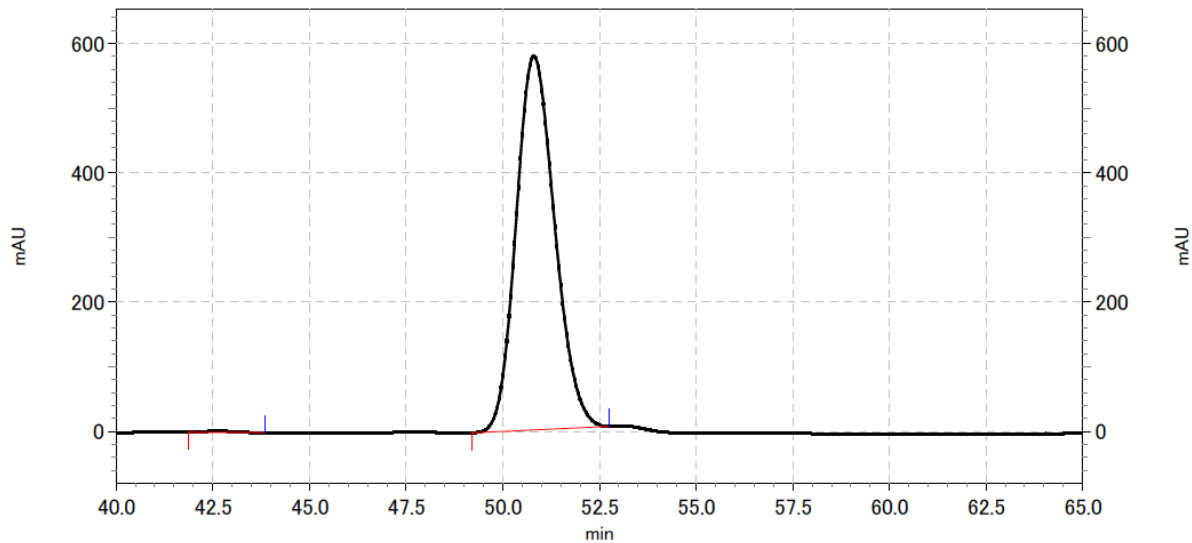


5430 Diode Array Detector SampleID:1 kt-435-rac-2 (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	44.960	26106229	47.597
2 Peak 2	59.760	28742303	52.403
		54848532	100.000

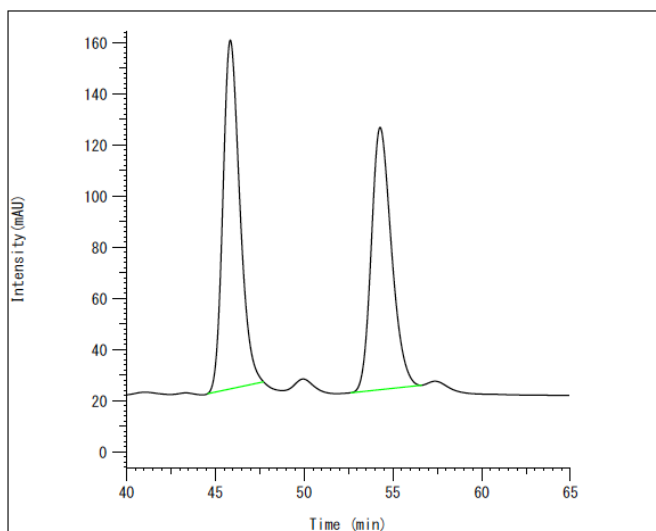
**3bo**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{major} = 44.12$  min,  $t_{minor} = 59.86$  min.



Peak #	Retention time	Area	Area %
1	42.567	507304	0.315
2	50.807	160630543	99.685

**Racemate**

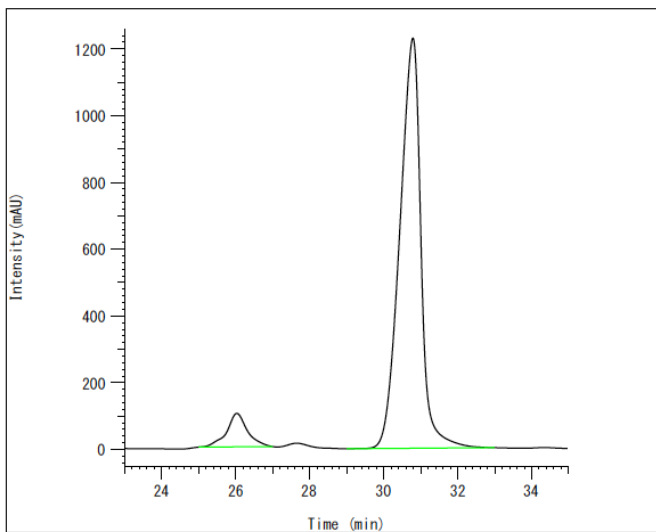


5430 Diode Array Detector SampleID:1 kt-604 rac (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	45.847	9022375	52.688
2 Peak 2	54.287	8101921	47.312
		17124295	100.000

### 3bp

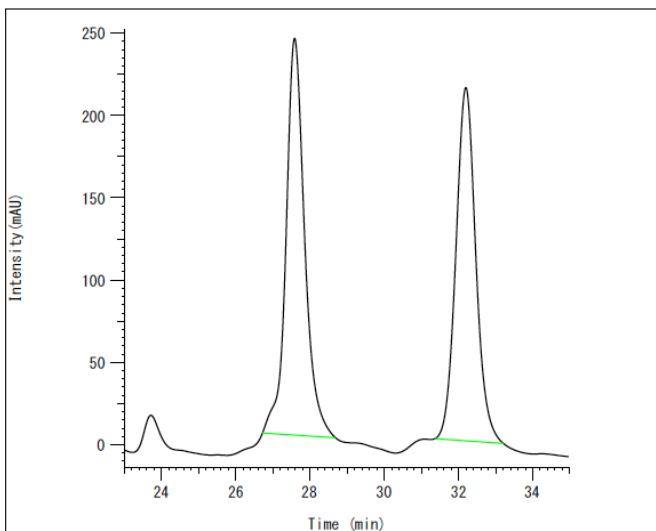
CHIRALPAK® IA-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 30.78$  min,  $t_{\text{minor}} = 26.03$  min.



5430 Diode Array Detector SampleID:1 kt-tu-l-o-Me (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	26.033	3902409	7.416
2 Peak 2	30.787	48722086	92.584
		52624495	100.000

### Racemate

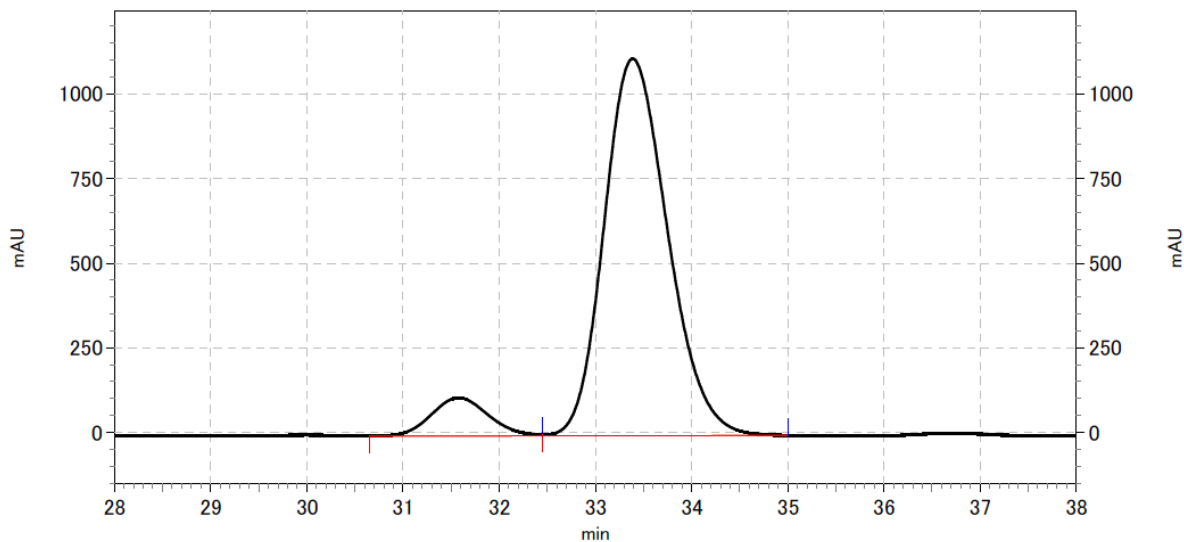


5430 Diode Array Detector SampleID:1 kt-603 rac (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	27.587	8394856	51.298
2 Peak 2	32.200	7969869	48.702
		16364725	100.000

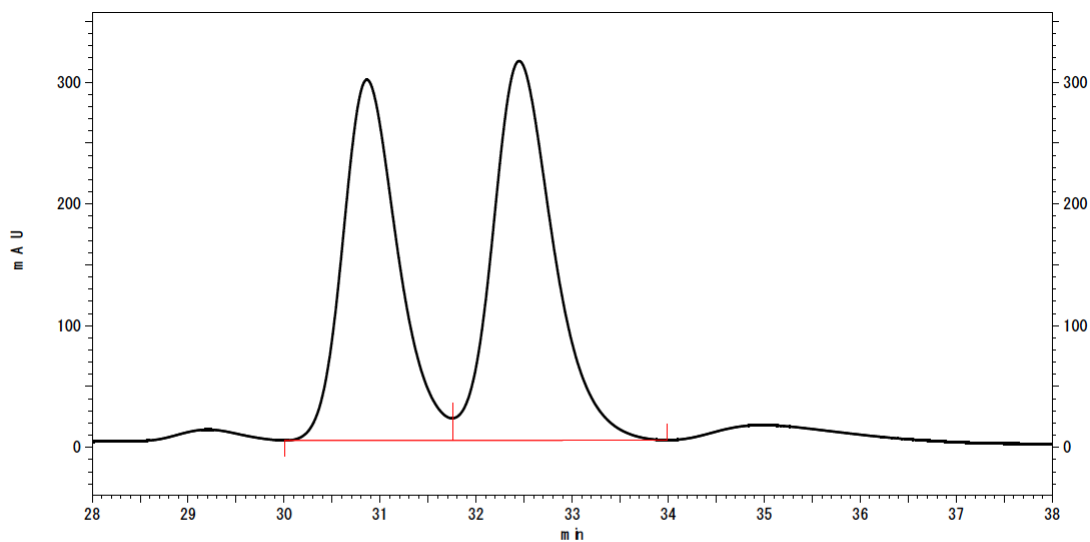
**3aq**

CHIRALPAK® IA-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 34.50$  min,  $t_{\text{minor}} = 39.20$  min.



Peak #	Retention time	Area	Area %
1	31.573	18532309	8.320
2	33.387	204204871	91.680

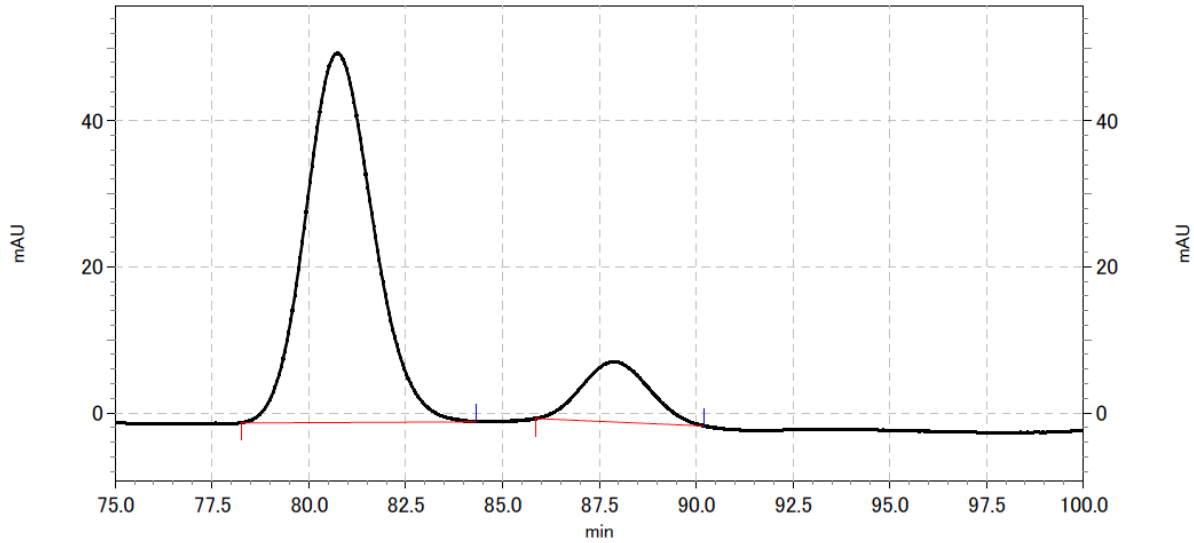
**Racemate**



Peak #	Retention time	Area	Area%
1	30.860	47246484	46.294
2	32.447	54811228	53.706

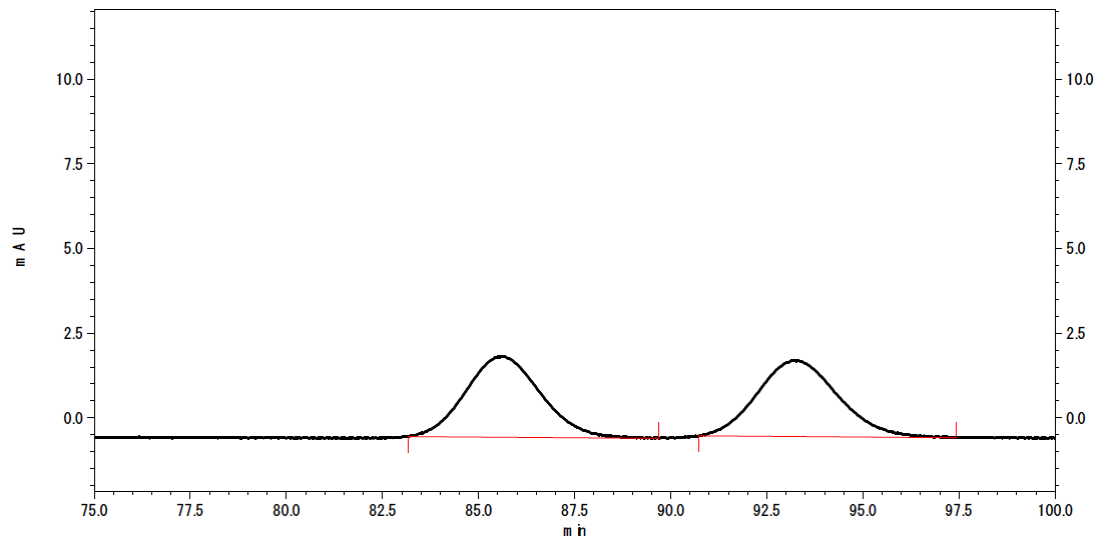
3jr

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 80.74$  min,  $t_{\text{minor}} = 87.88$  min.



Peak #	Retention time	Area	Area %
1	80.740	24509992	86.012
2	87.887	3986024	13.988

Racemate

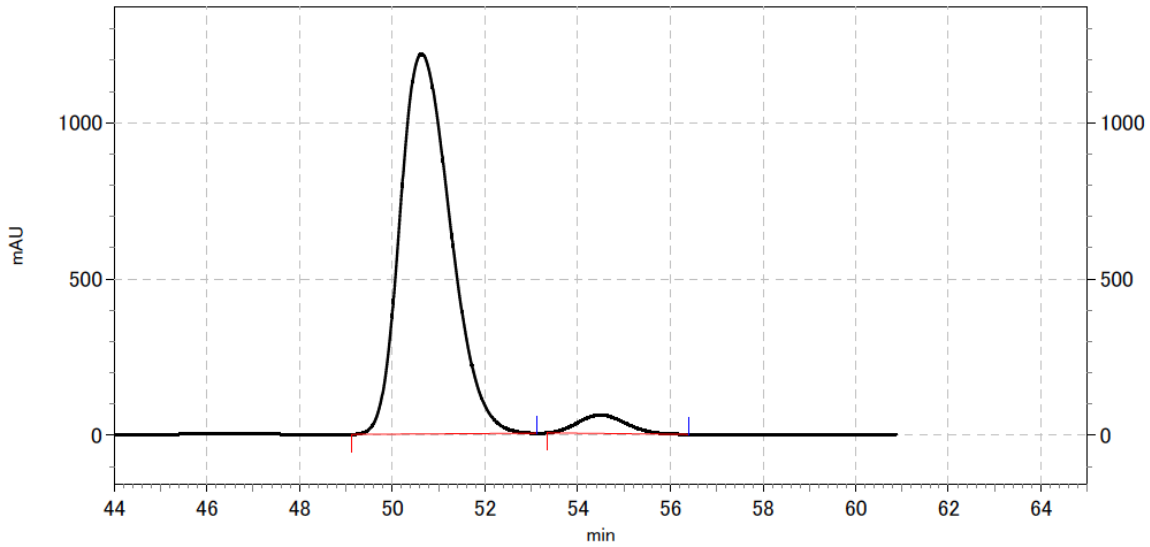


Peak #	Retention time	Area	Area%
1	85.600	1298412	49.727
2	93.207	1312654	50.273



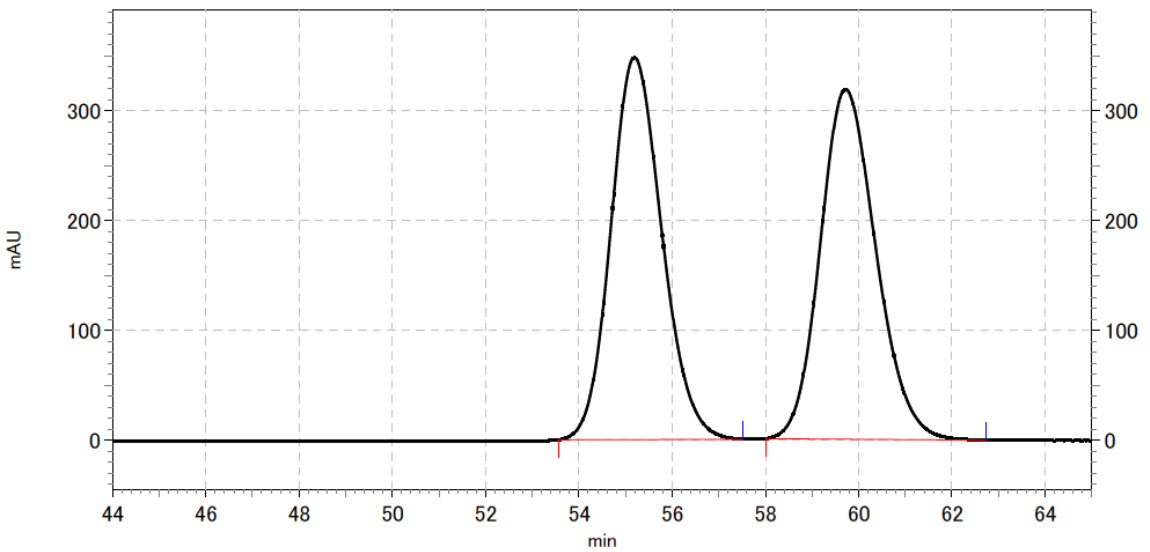
3cj

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 50.62$  min,  $t_{\text{minor}} = 54.48$  min.



Peak #	Retention time	Area	Area %
1	50.620	367245405	95.542
2	54.487	17135685	4.458

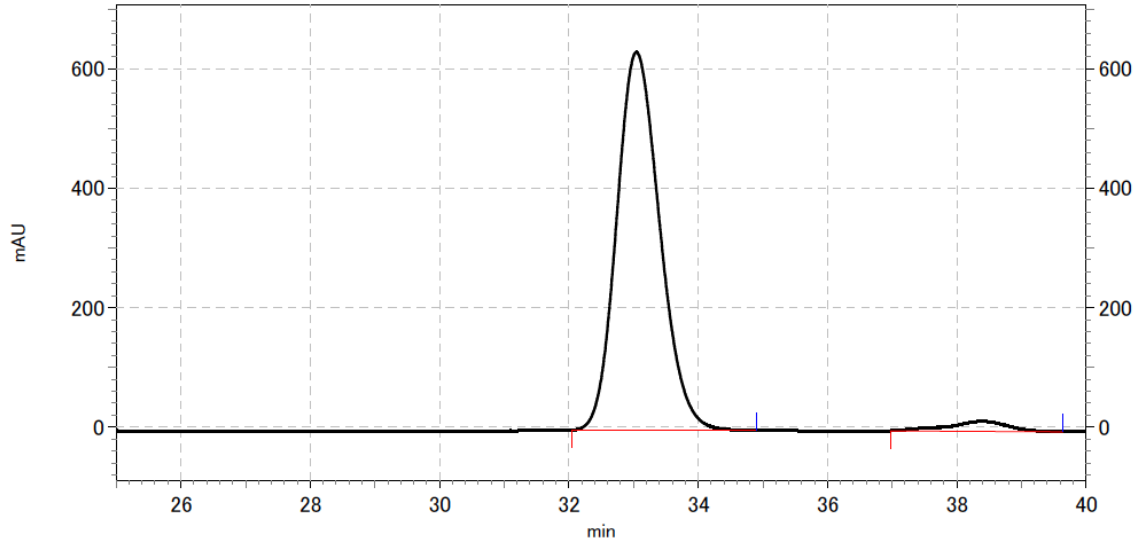
Racemate



Peak #	Retention time	Area	Area %
1	55.193	105806865	49.988
2	59.720	105856990	50.012

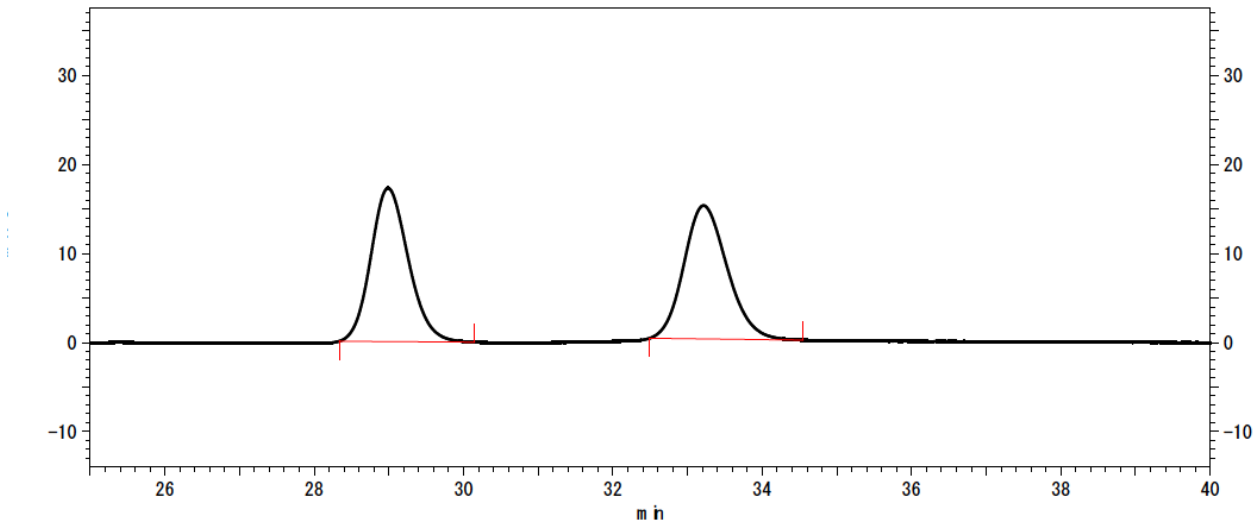
**3cl**

CHIRALPAK® IF-3 column, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.5 mL/min,  $t_{\text{major}} = 33.04$  min,  $t_{\text{minor}} = 38.38$  min.



Peak #	Retention time	Area	Area %
1	33.040	117479643	96.439
2	38.387	4337967	3.561

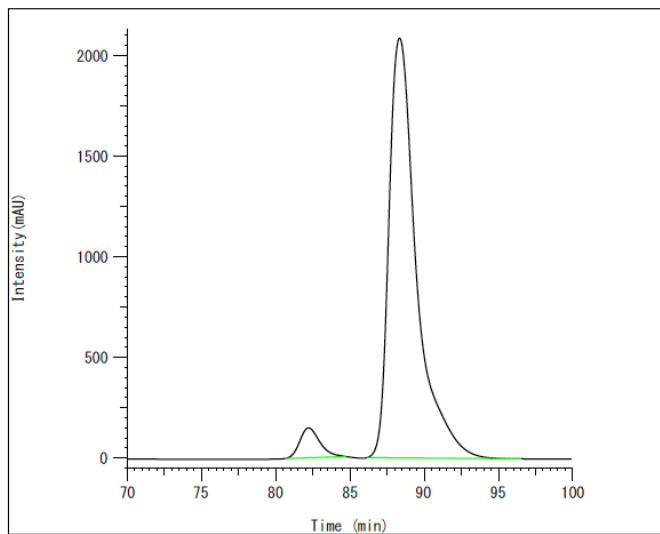
**Racemate**



Peak #	Retention time	Area	Area %
1	28.987	2414092	49.912
2	33.213	2422645	50.088

### 3cm

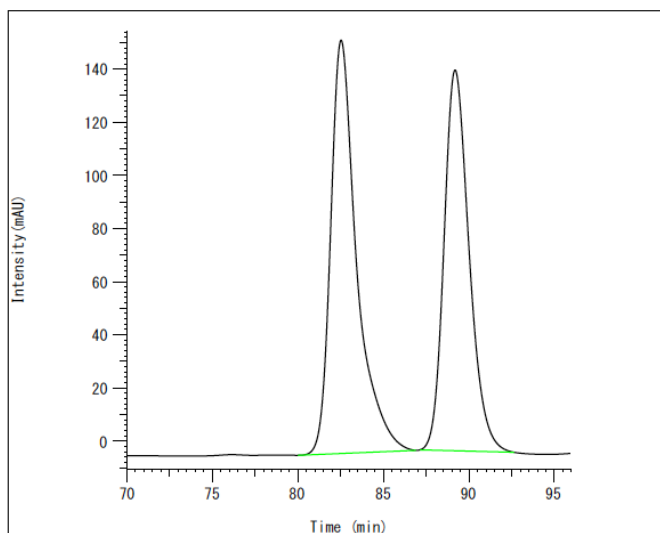
CHIRALPAK® IA-3 column, *n*-hexane/*i*-PrOH = 85/15, flow rate = 0.5 mL/min,  $t_{\text{major}} = 88.33$  min,  $t_{\text{minor}} = 82.20$  min.



5430 Diode Array Detector SampleID:1 kt-479-Br-Ph pro (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	82.207	13896385	4.929
2 Peak 2	88.333	268011906	95.071
		281908290	100.000

### Racemate



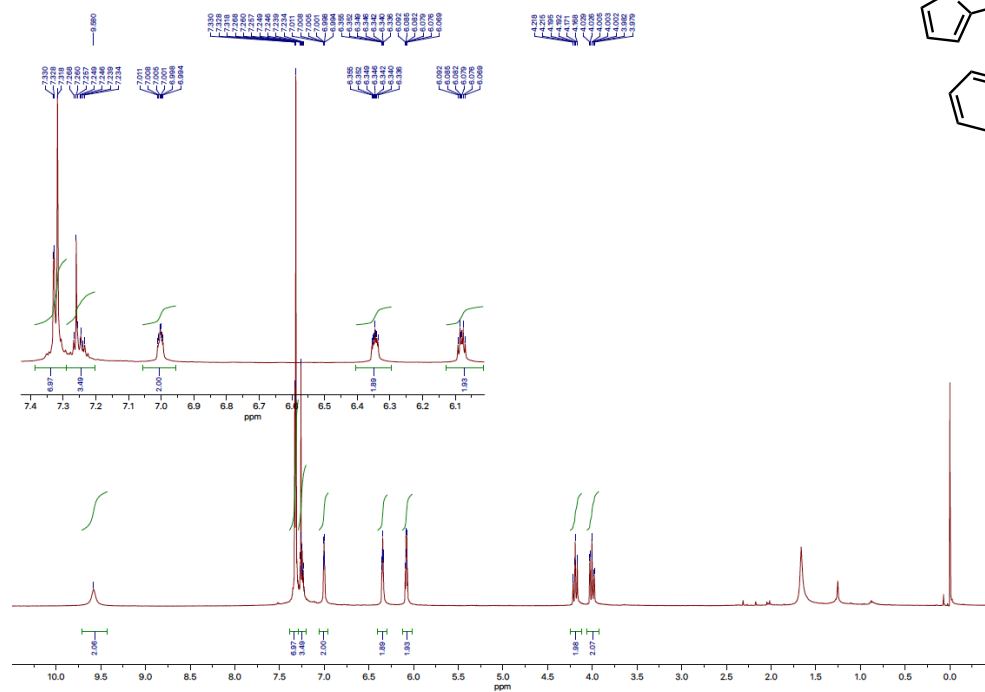
5430 Diode Array Detector SampleID:1 kt-366-rac-2 (Extract, 300nm) Repeat:1

No. Compounds	RT	Area	Area%
1 Peak 1	82.527	16434737	53.006
2 Peak 2	89.193	14570542	46.994
		31005280	100.000

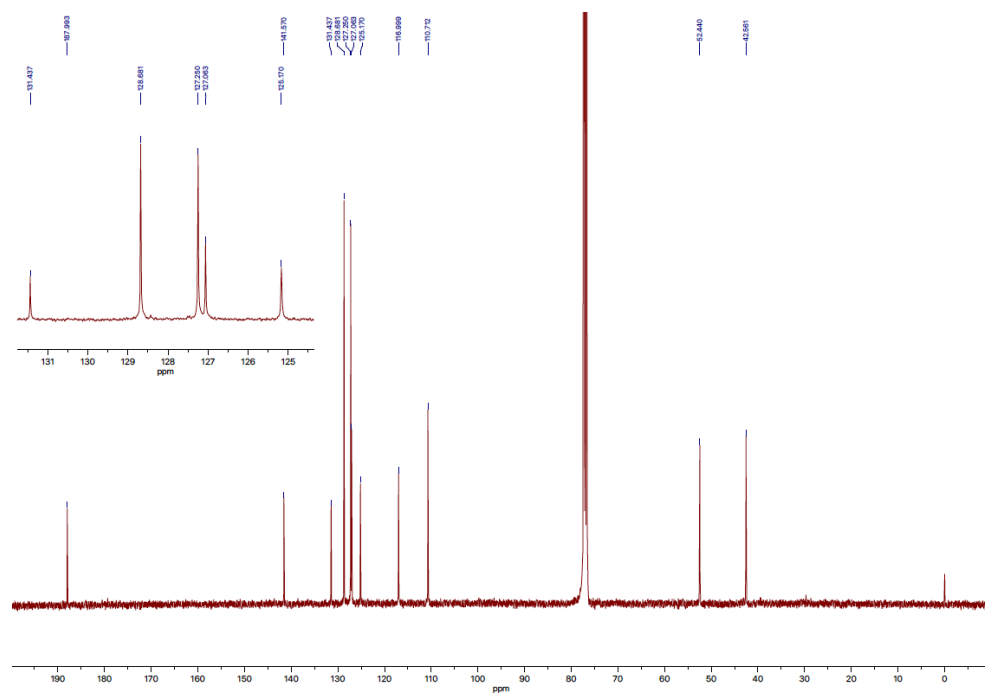
## 6. NMR spectra

3aa

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

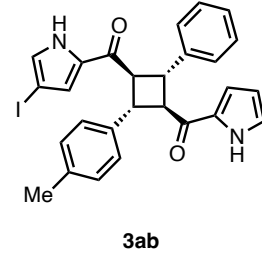
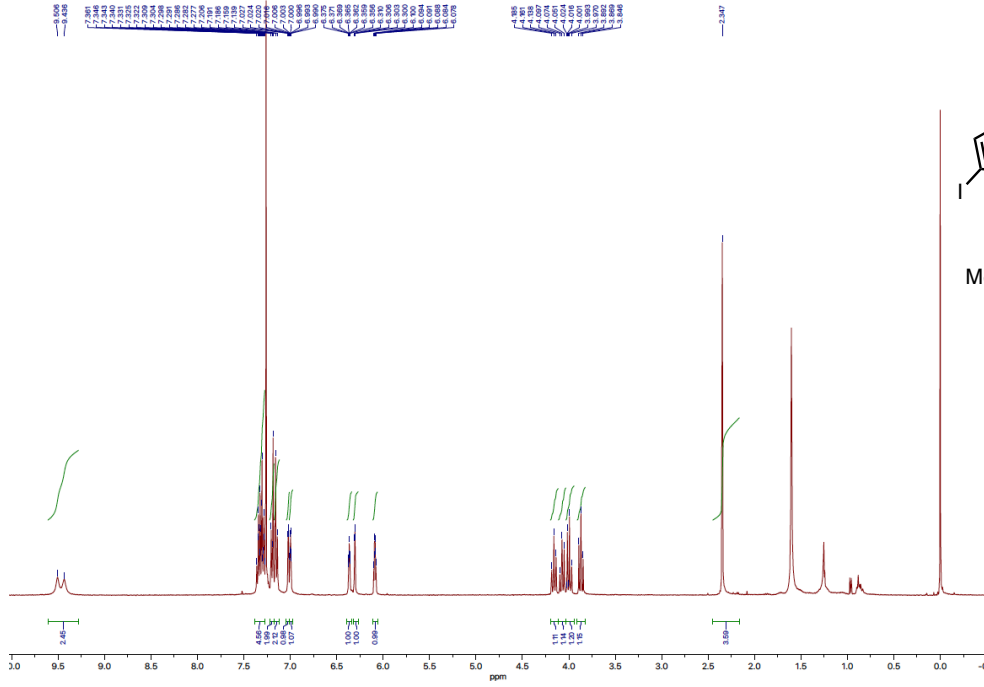


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

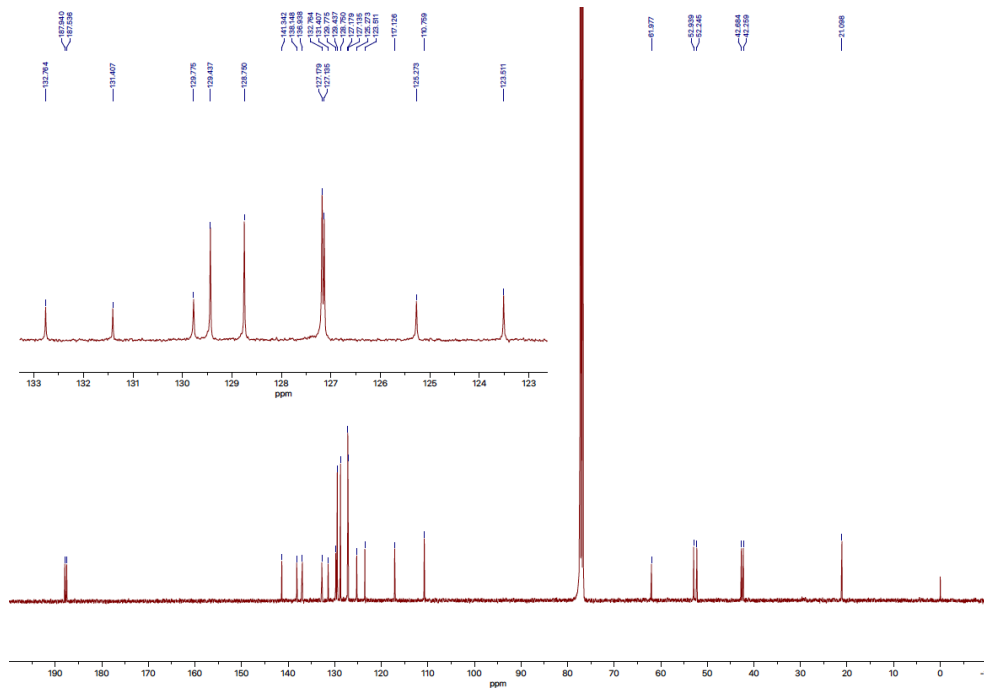


3ab

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

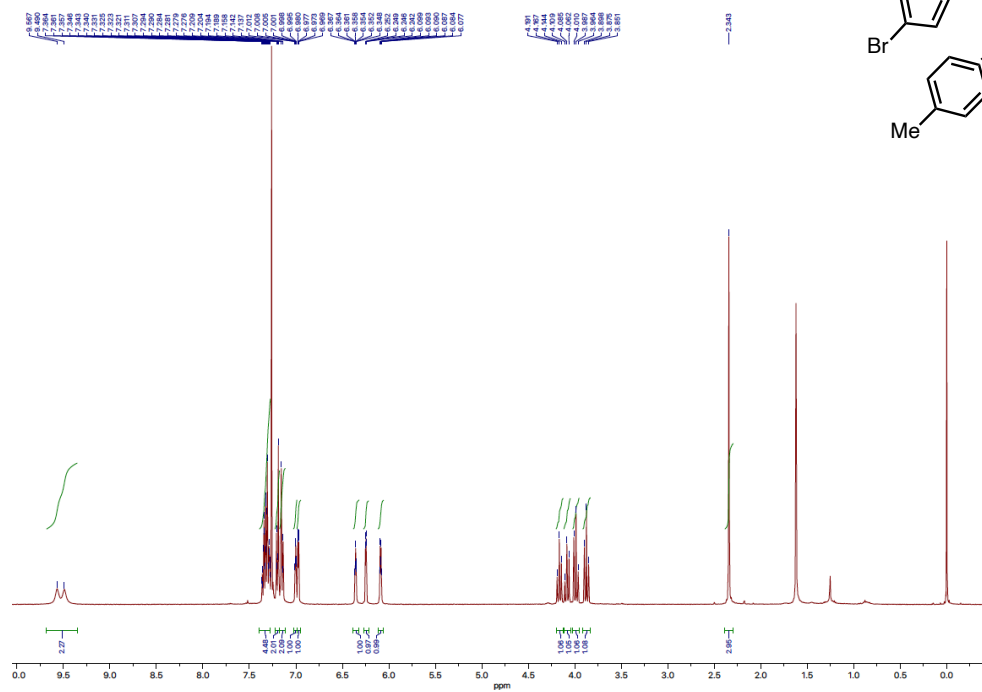


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

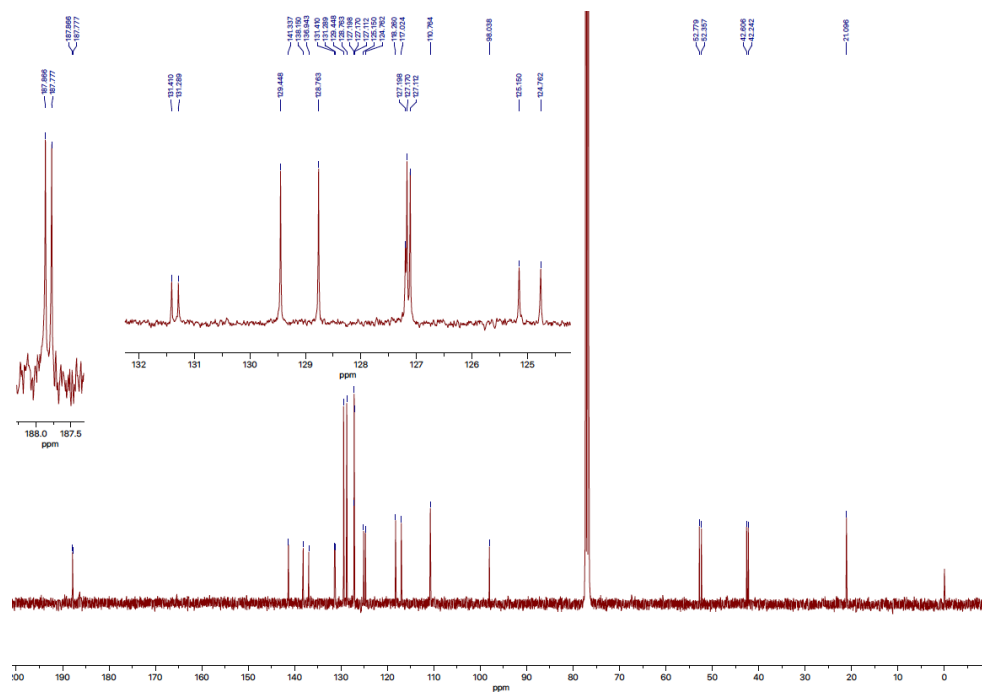


**3ac**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



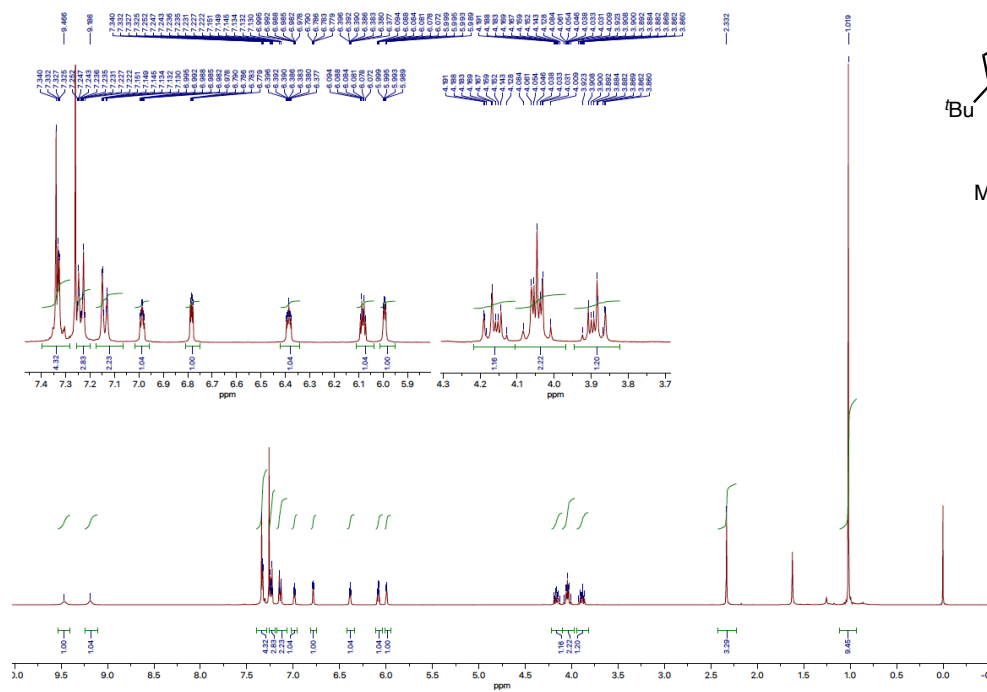
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**



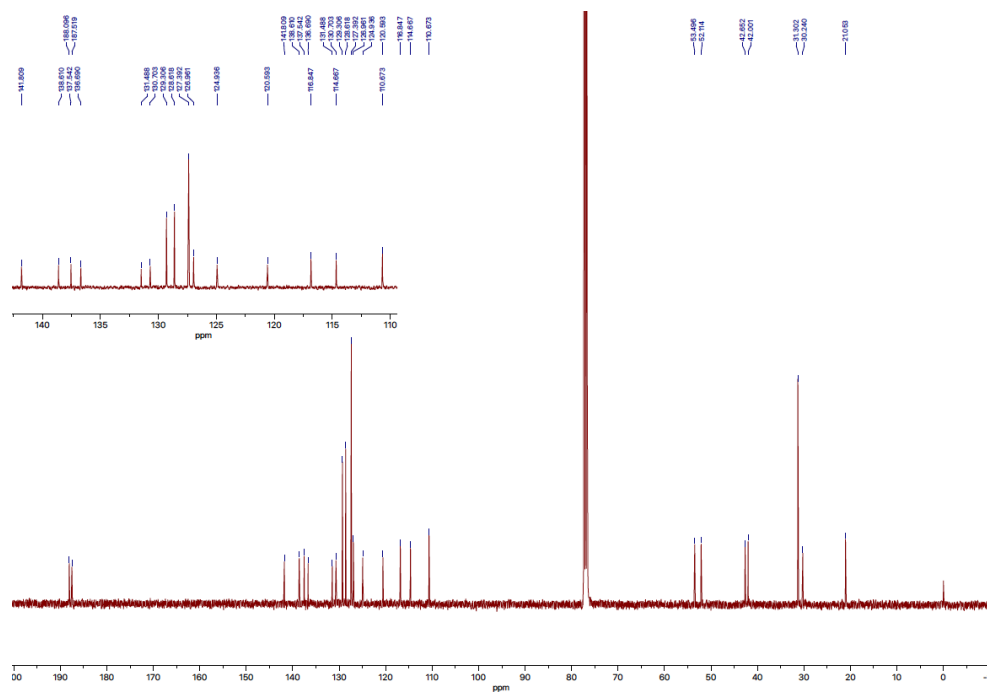


3ae

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

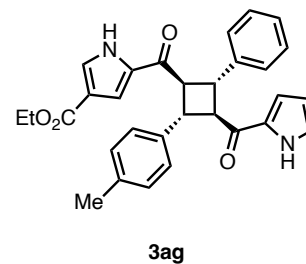
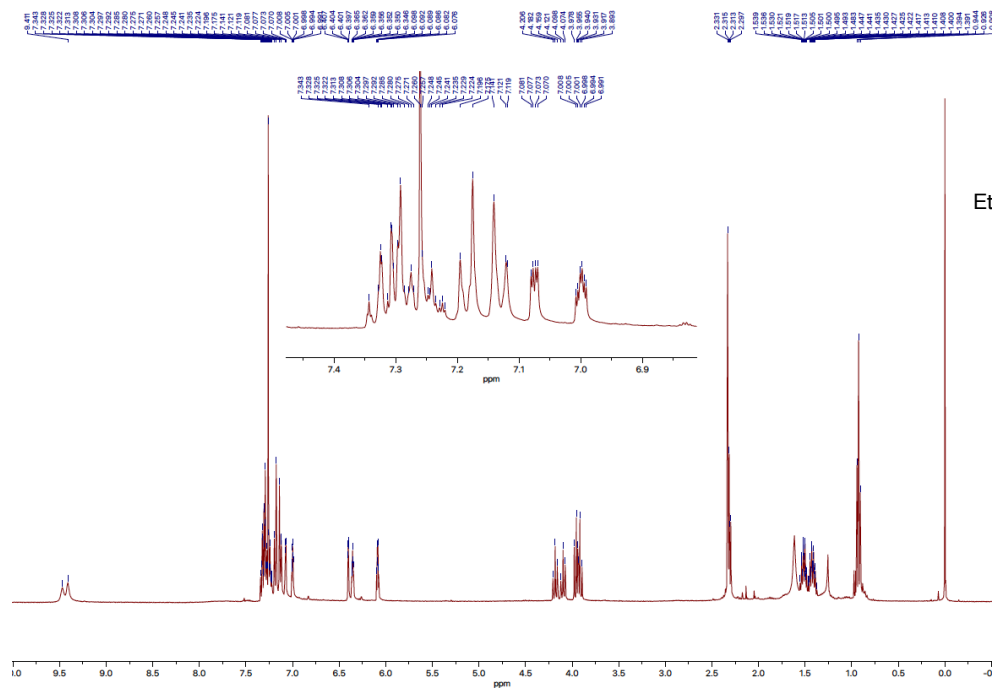




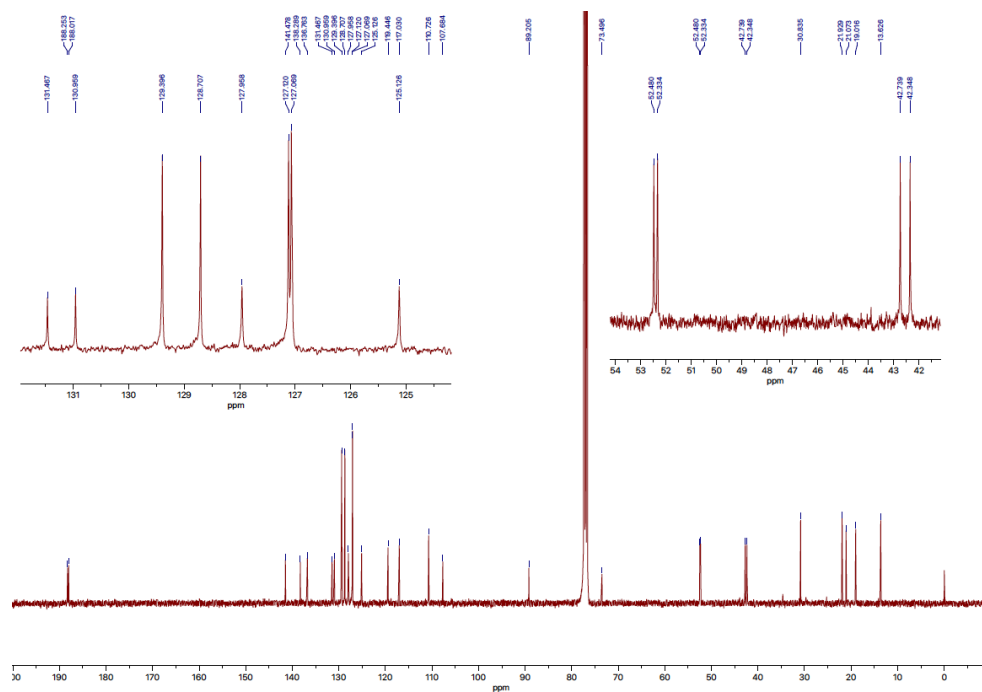


3ag

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

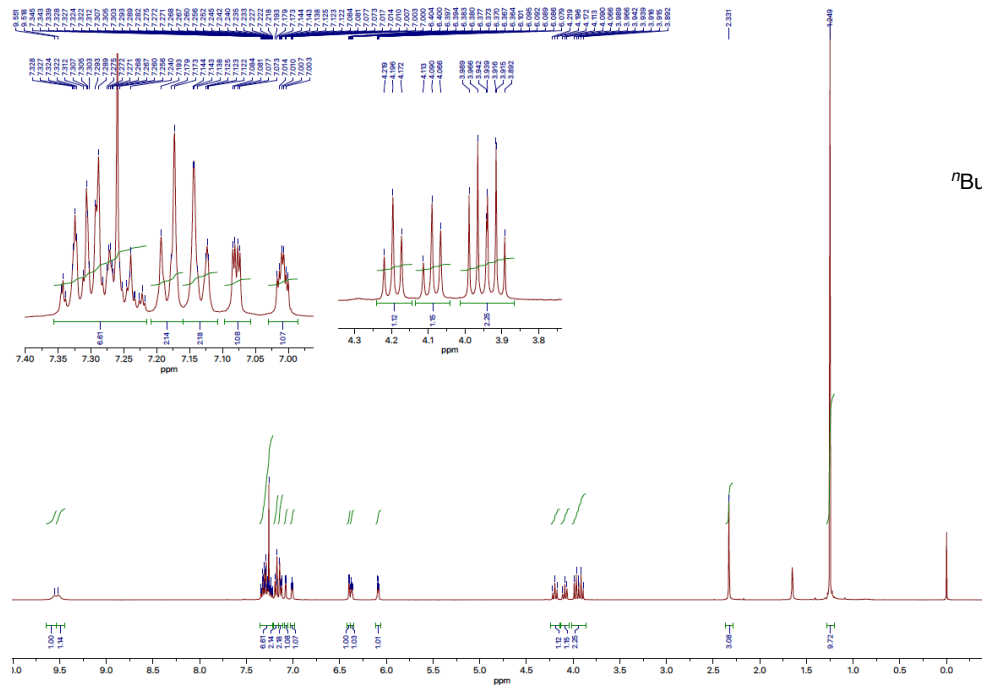


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



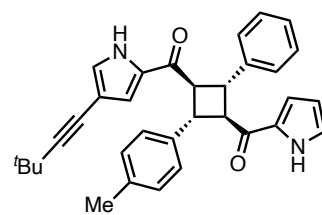
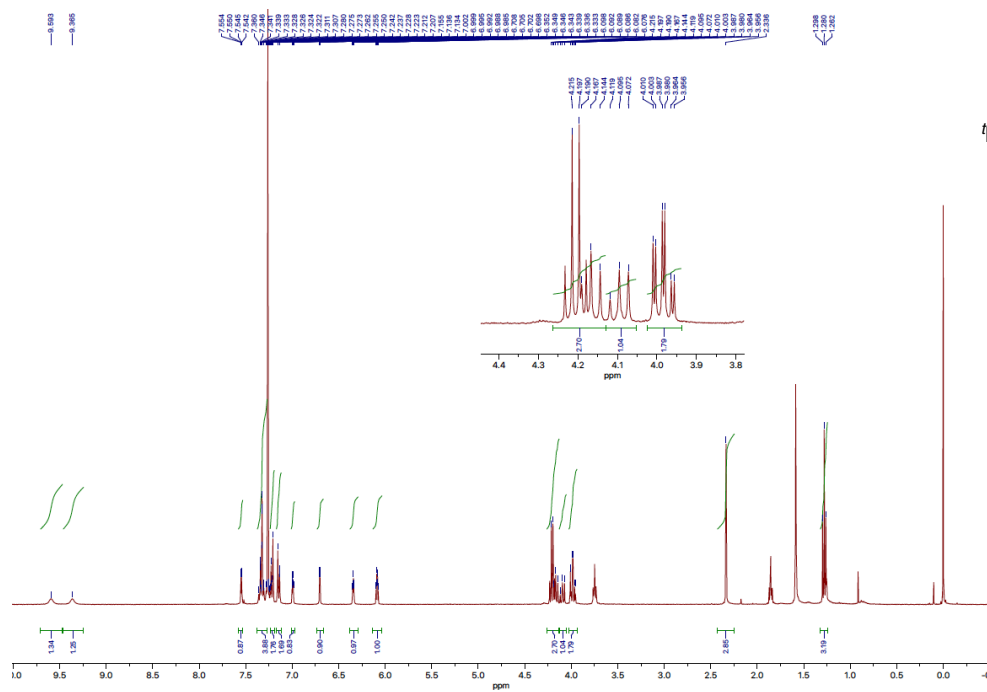
3ah

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



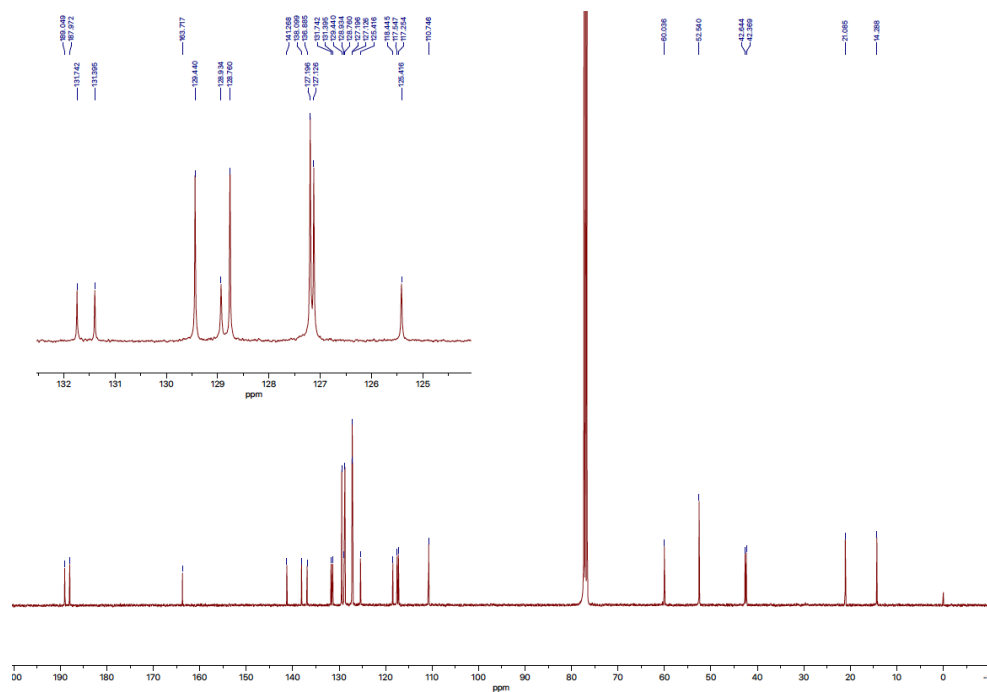
**3ai**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



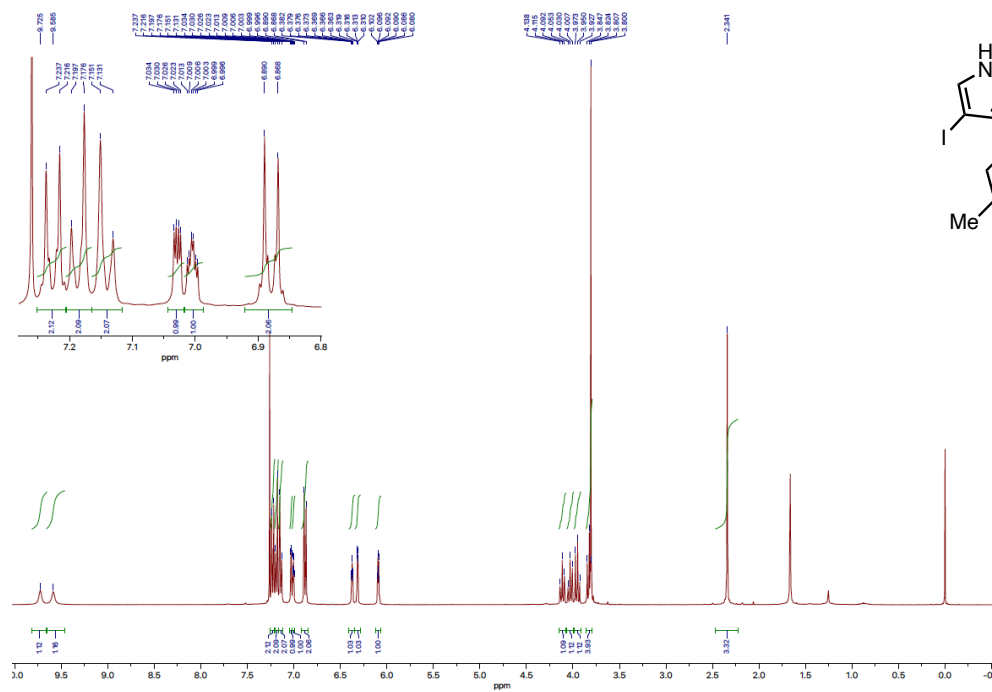
**3ai**

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**

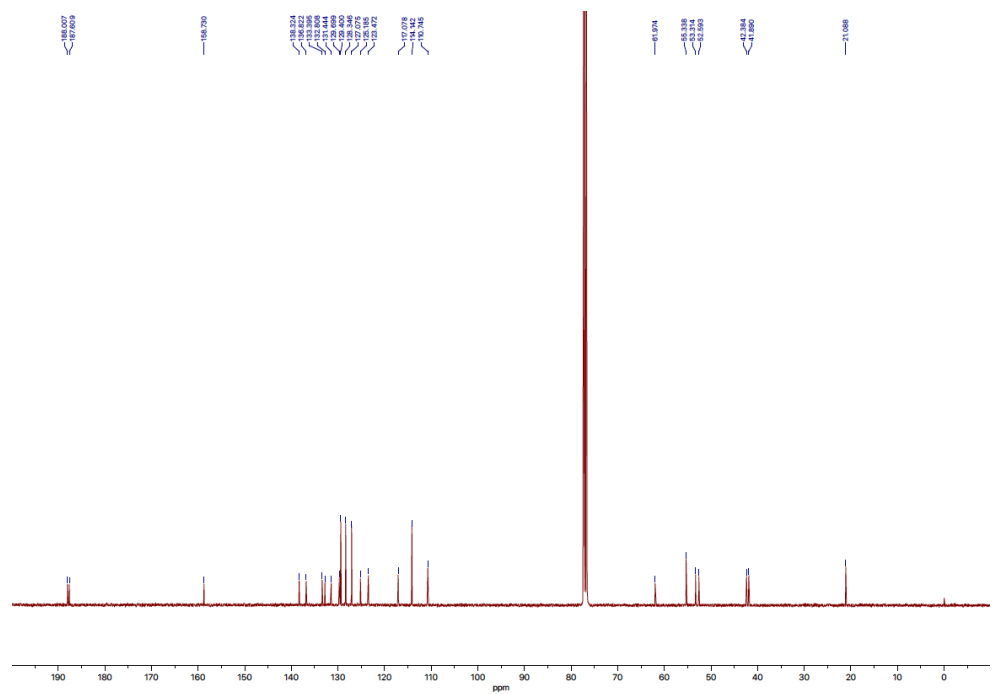


3bj

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

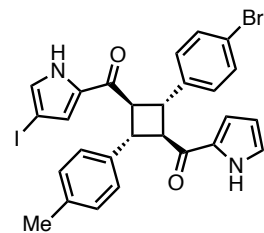
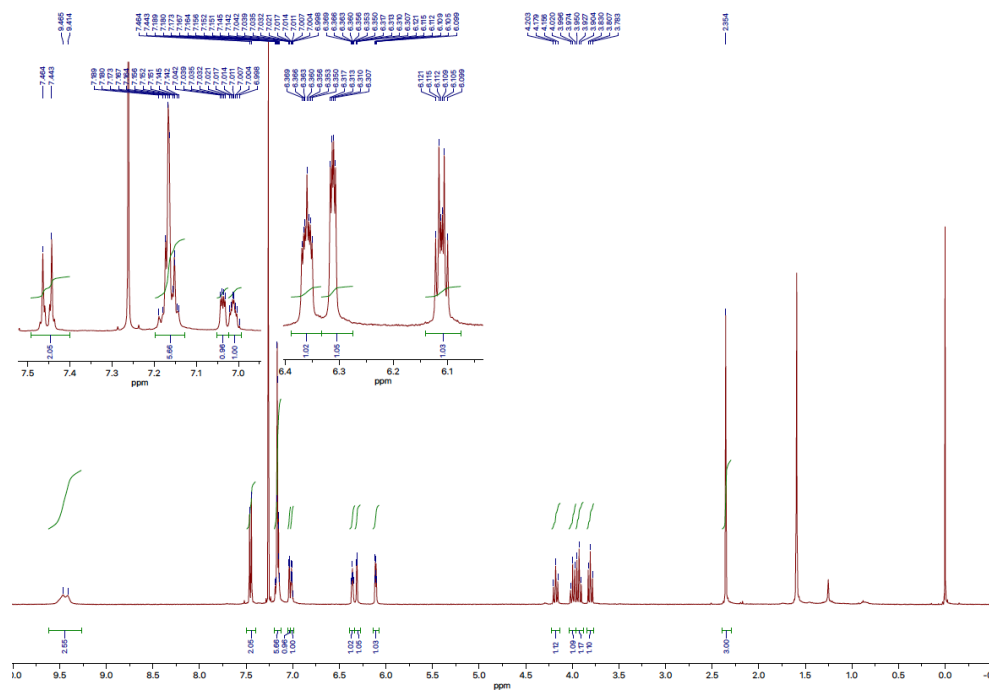


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



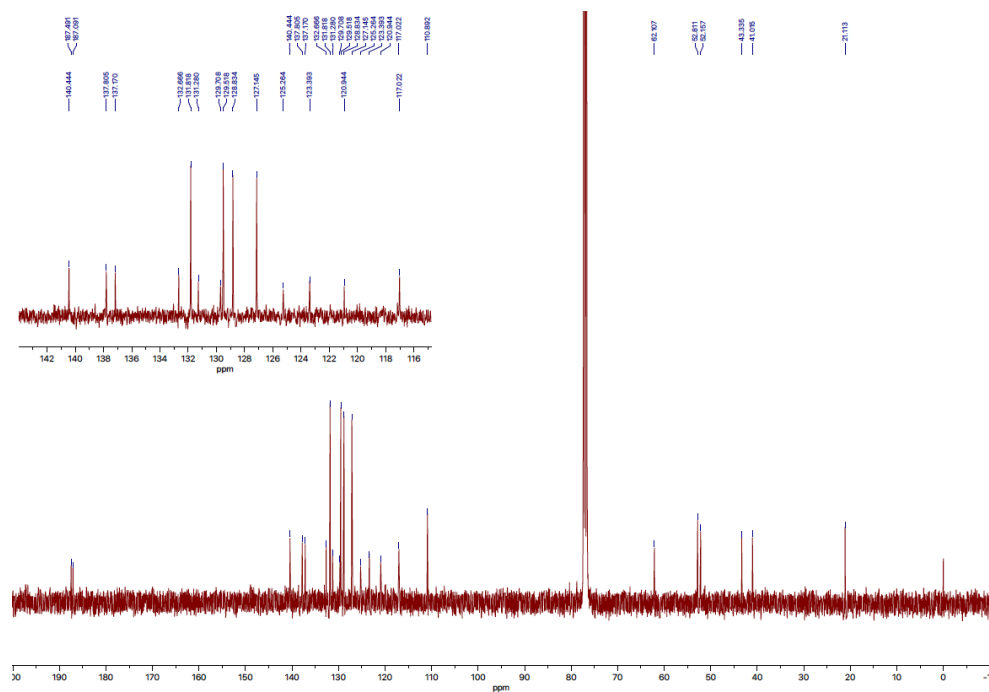
**3bk**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



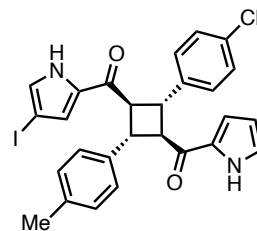
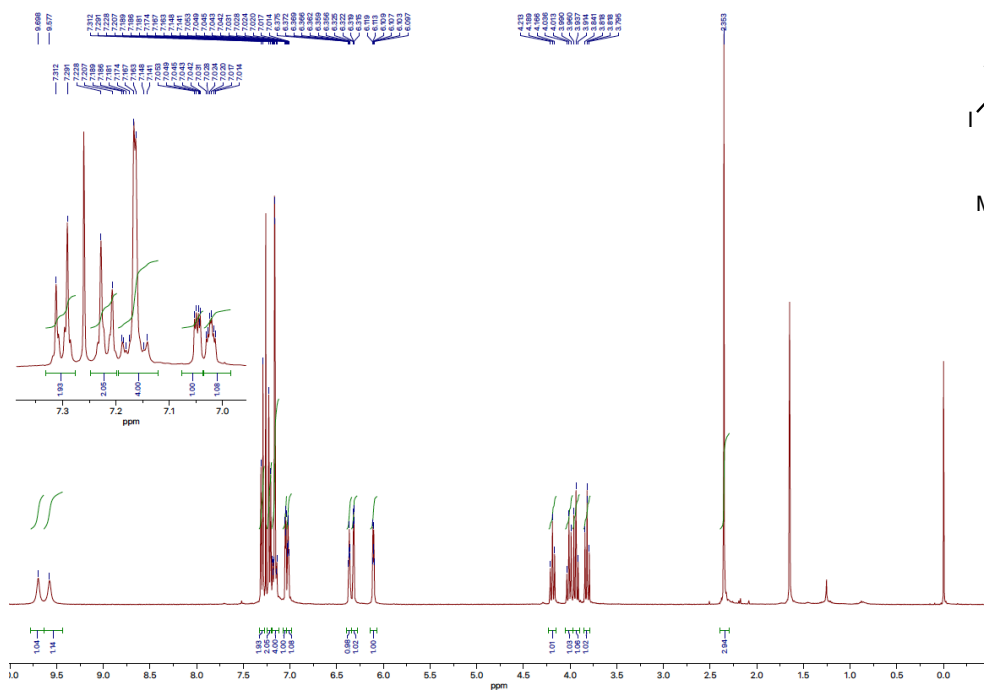
**3bk**

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



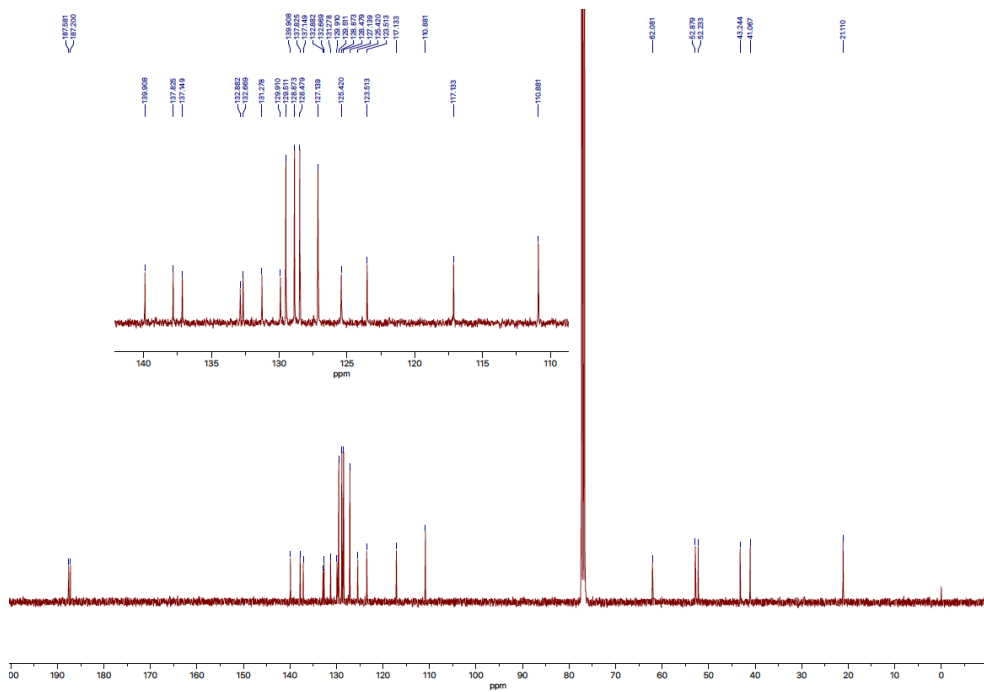
**3bl**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



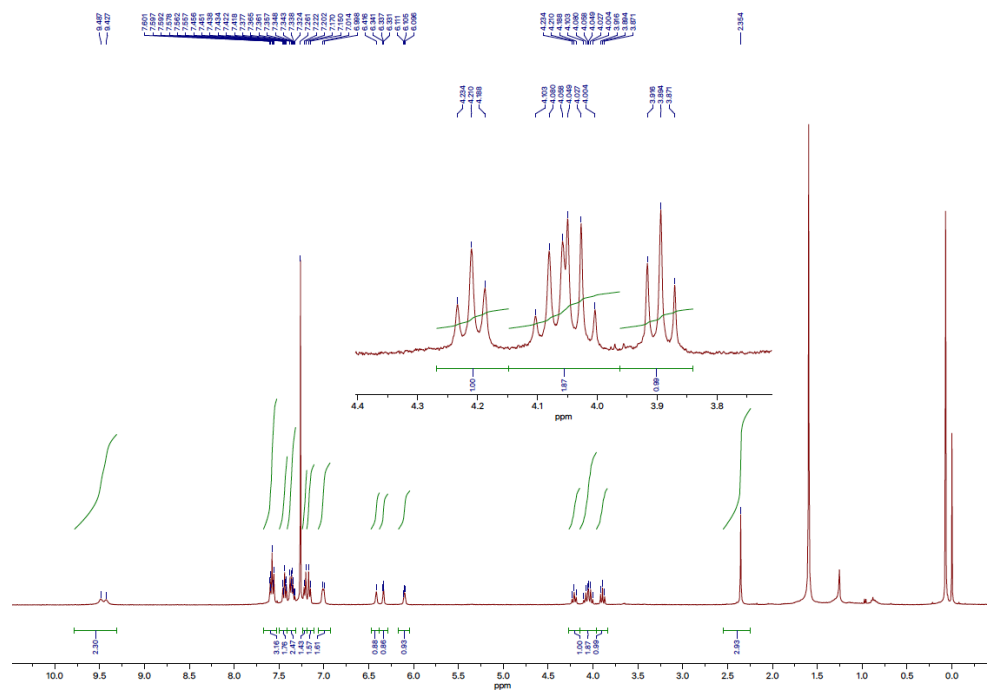
**3bl**

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**

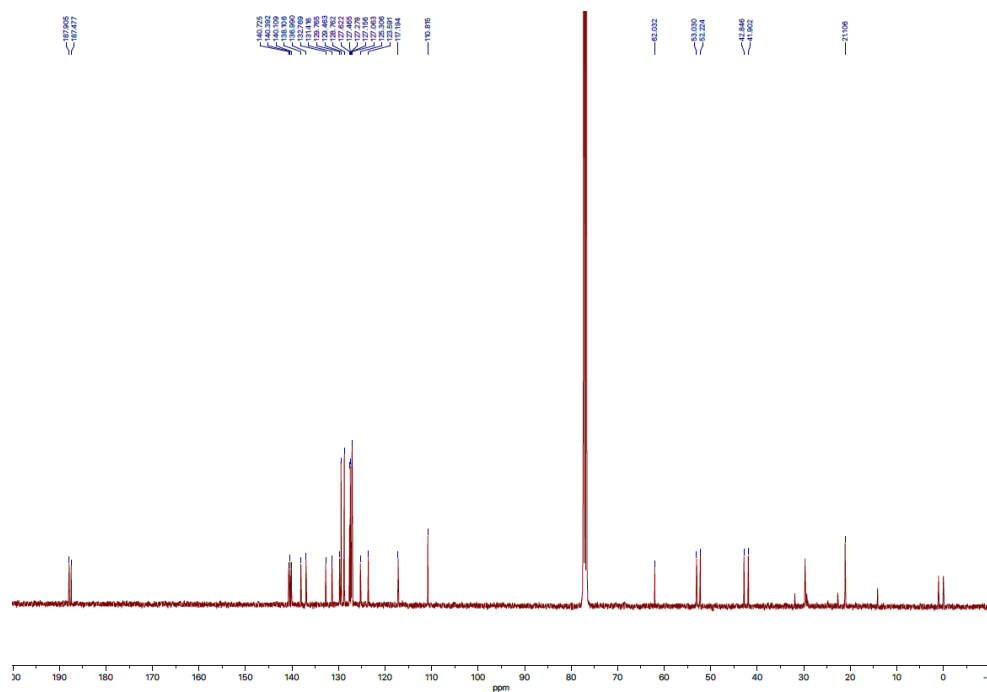


3bm

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )







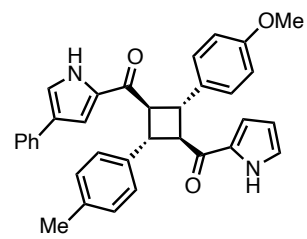
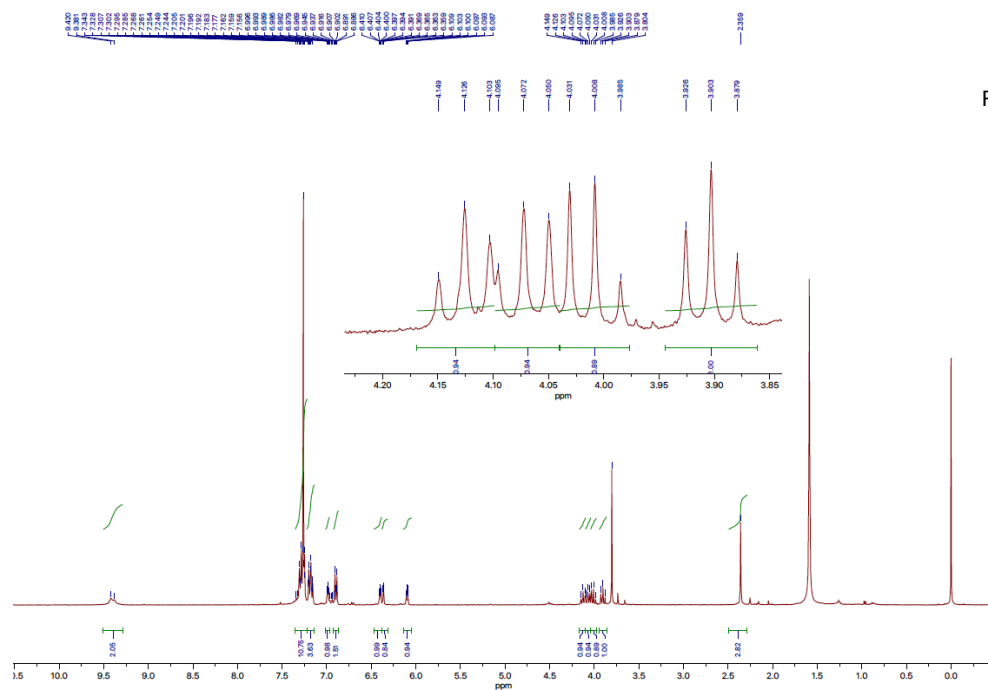






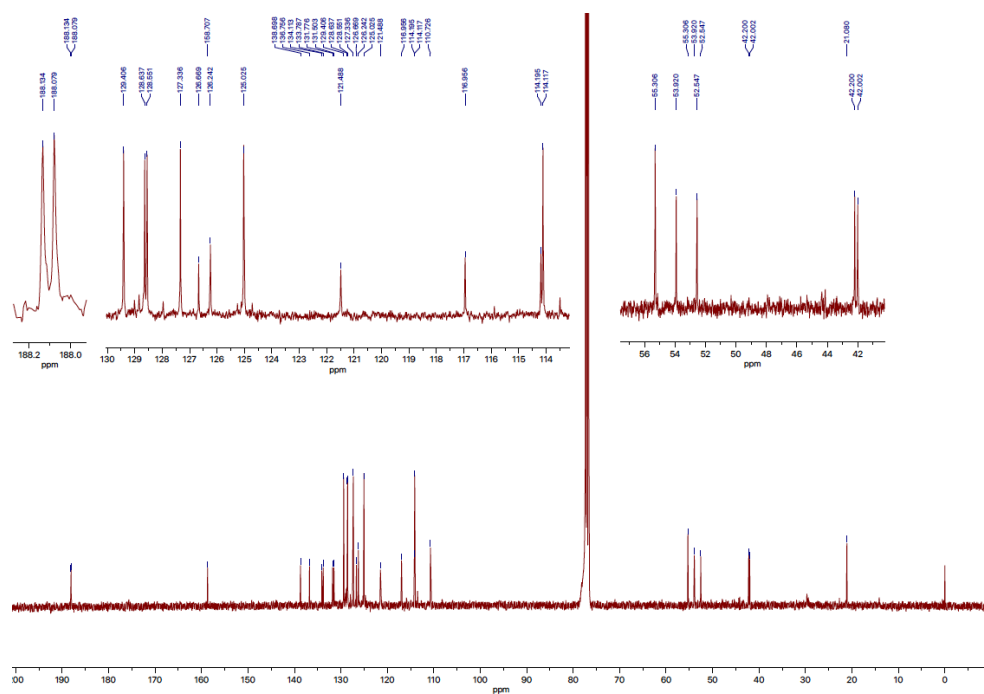
3jr

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



3jr

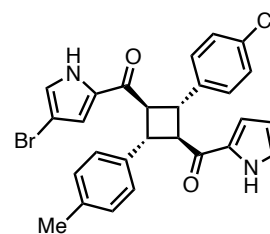
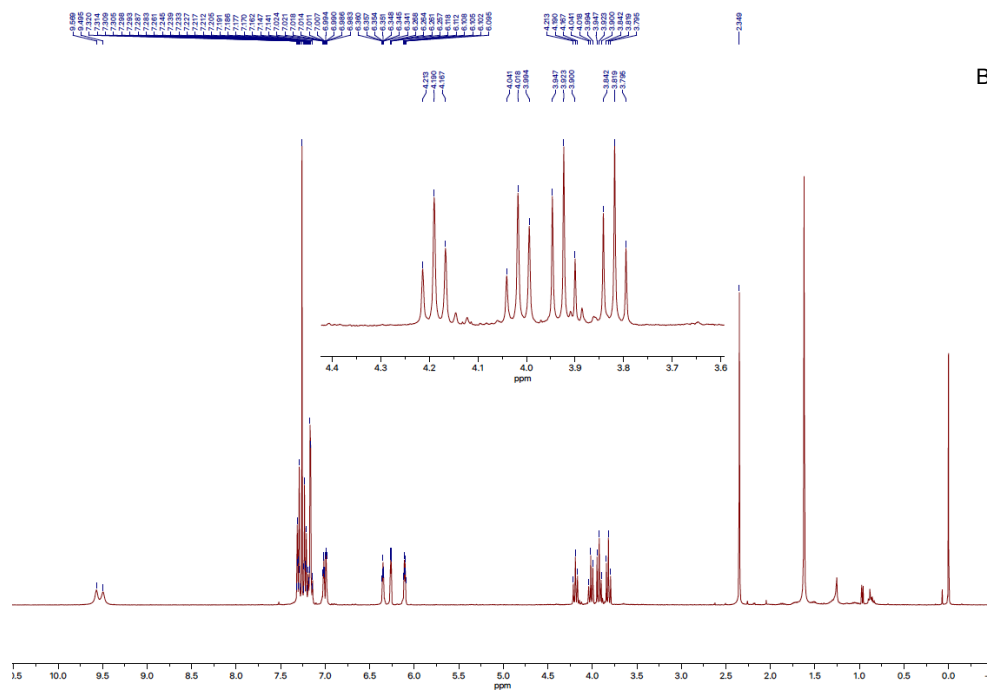
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)





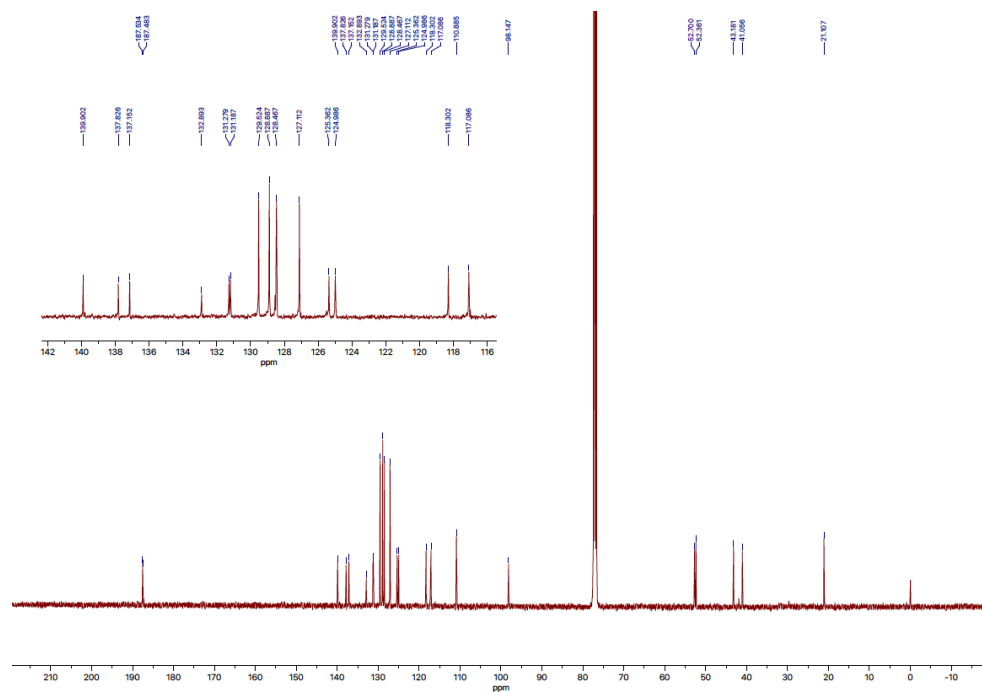
3cl

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )



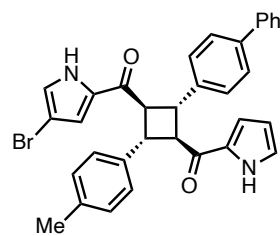
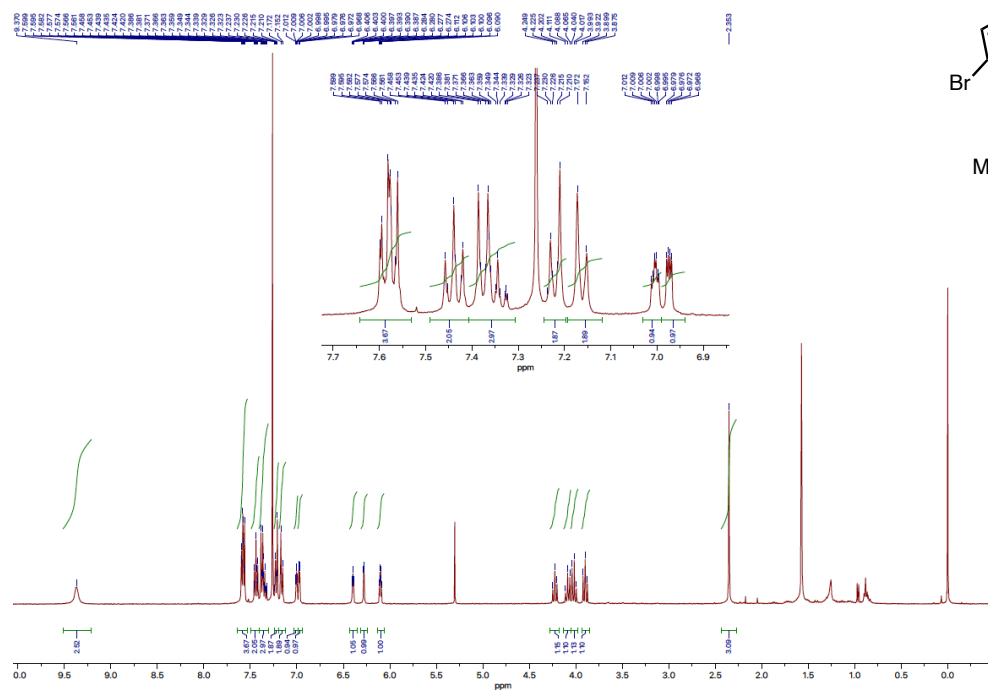
3cl

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )



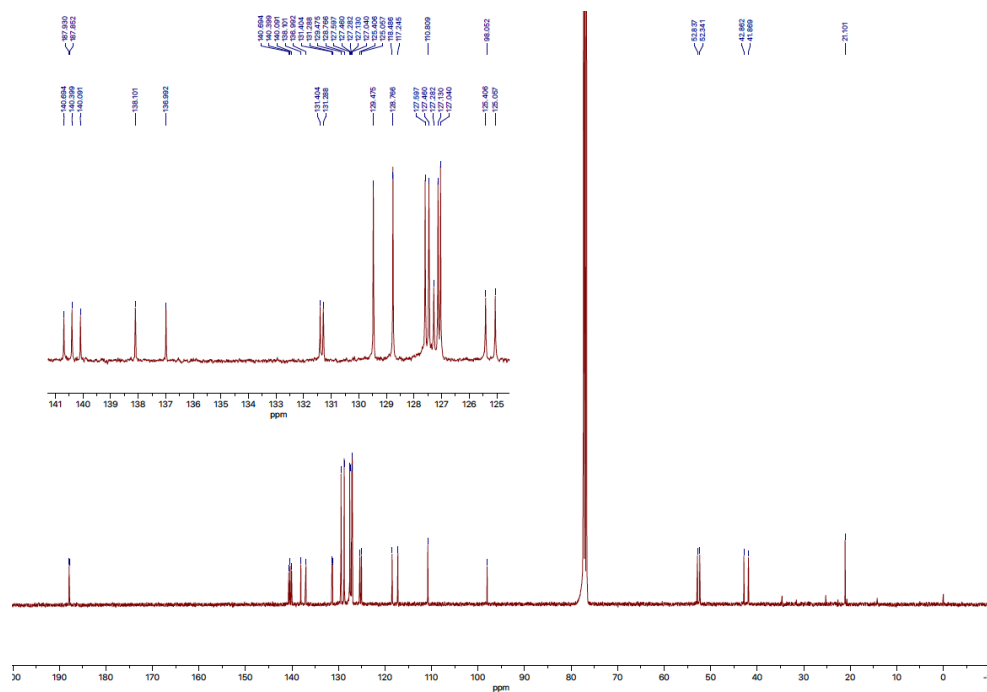
3cm

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



3cm

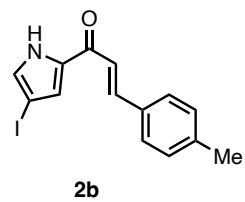
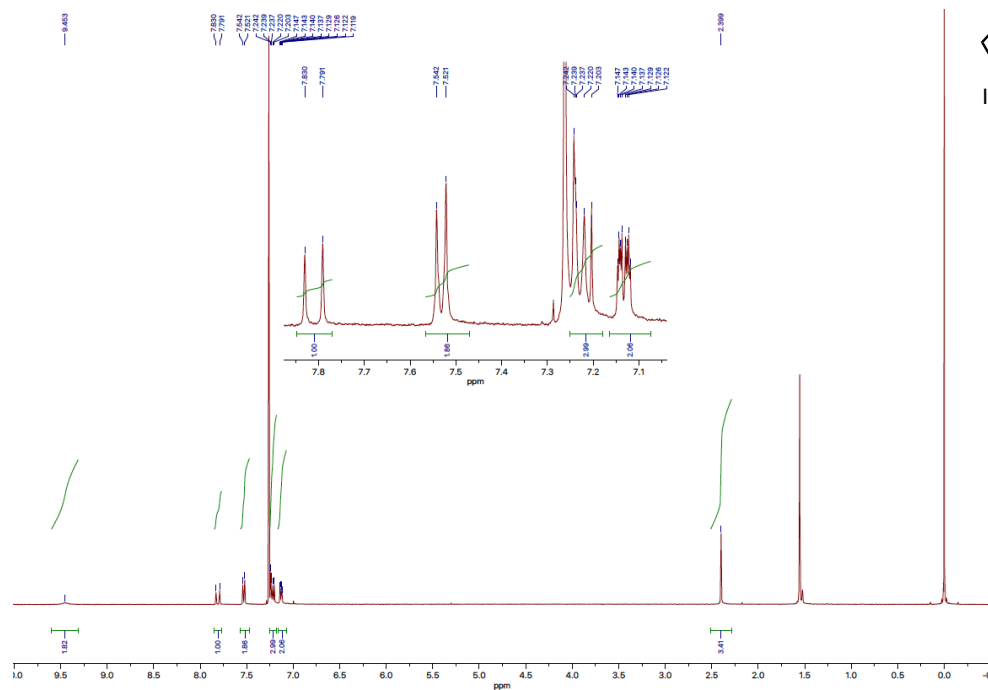
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



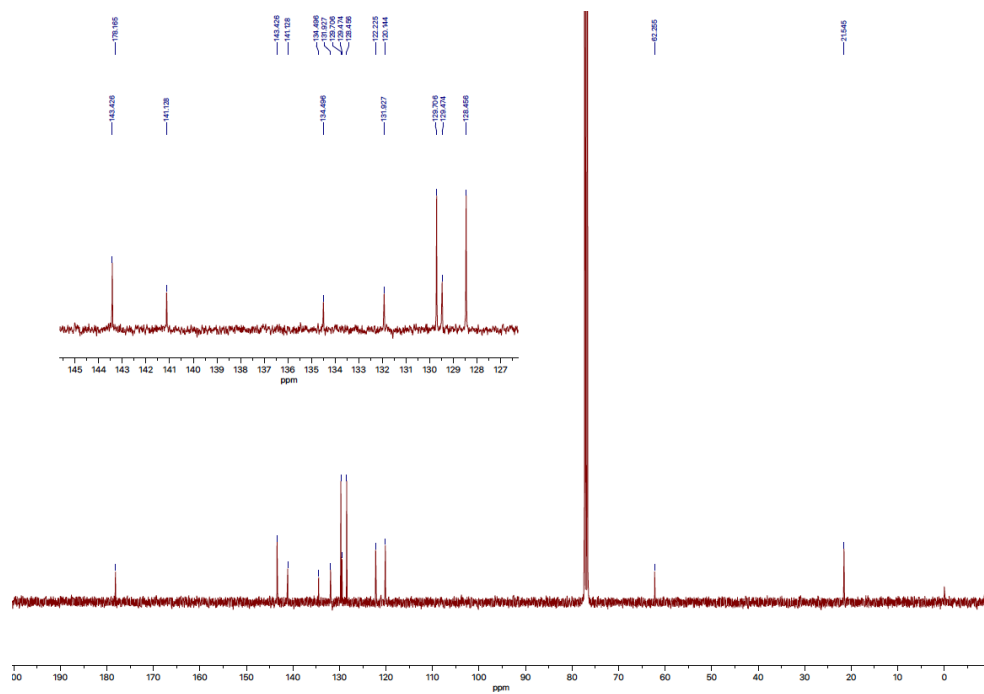


2b

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

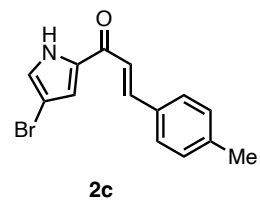
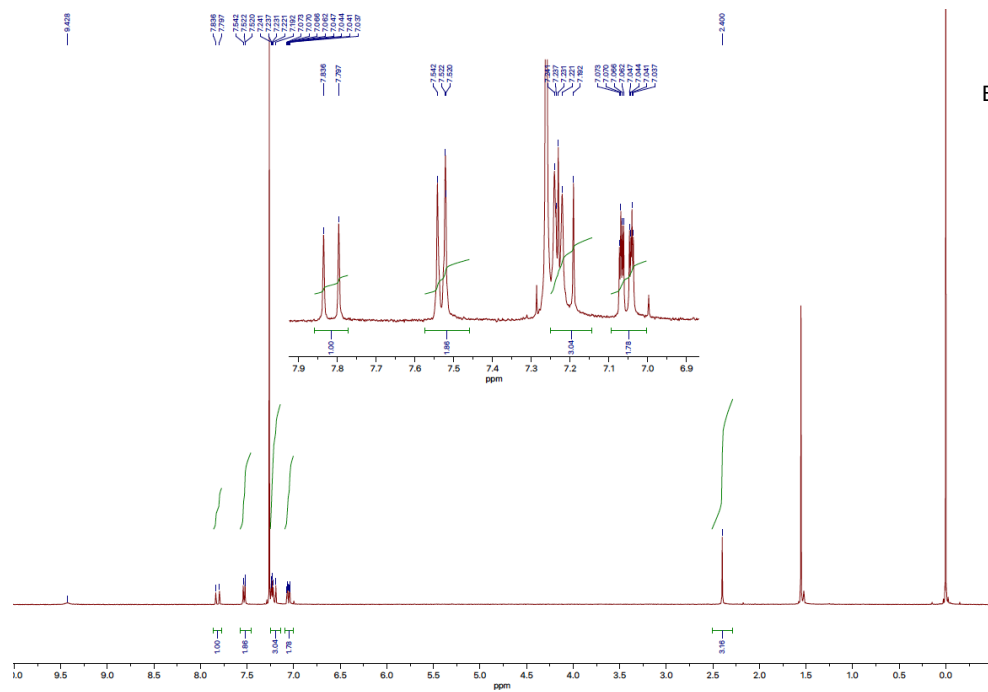


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

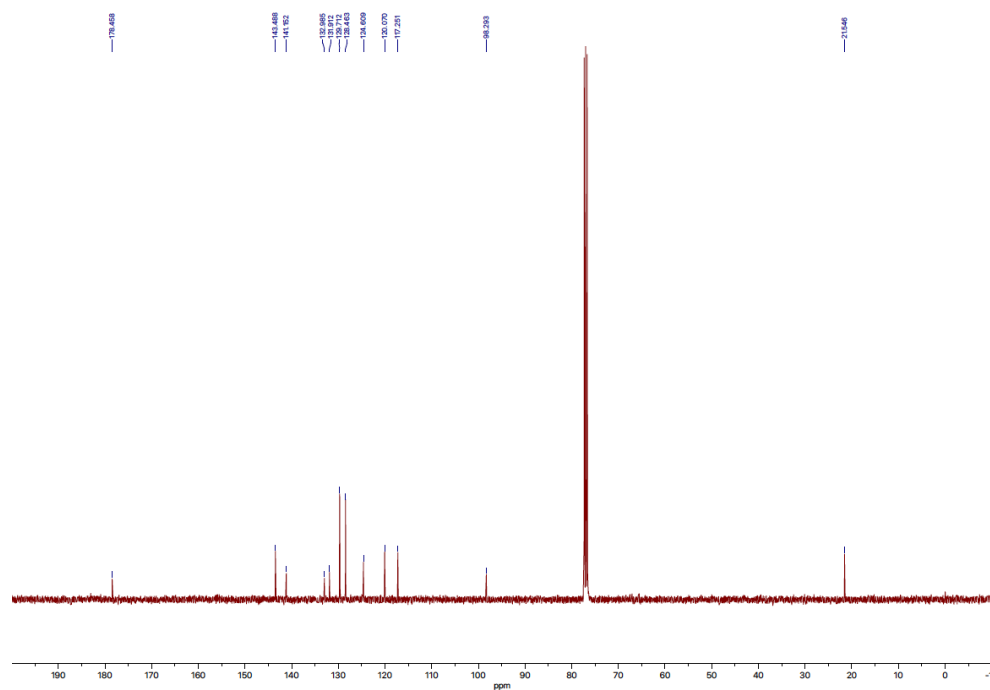


2c

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

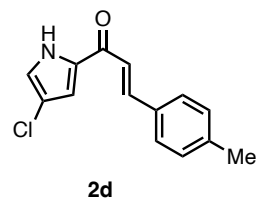
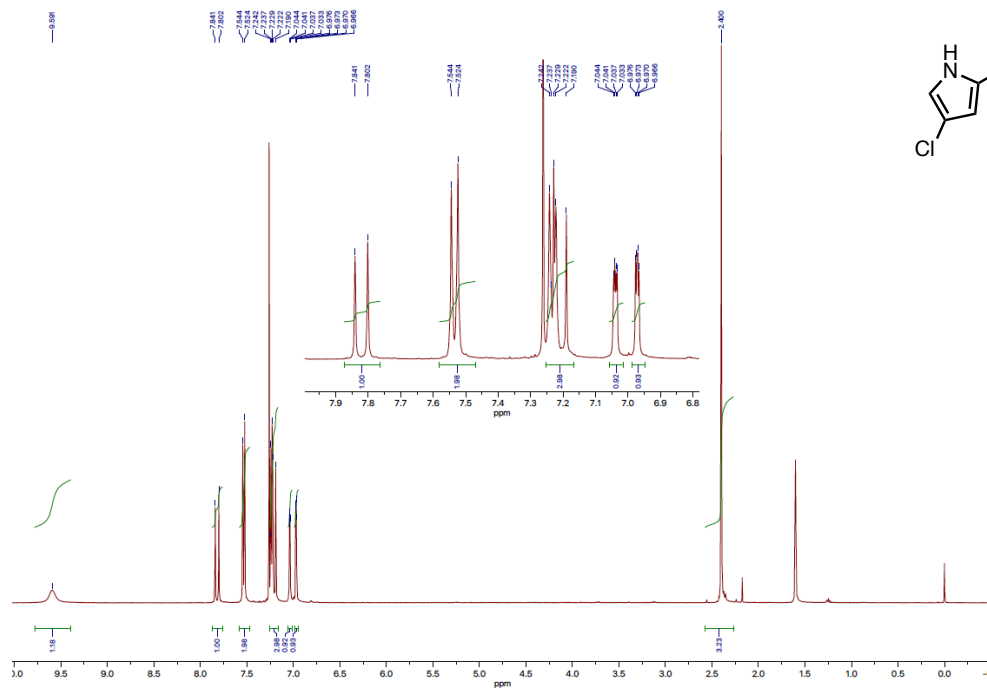


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

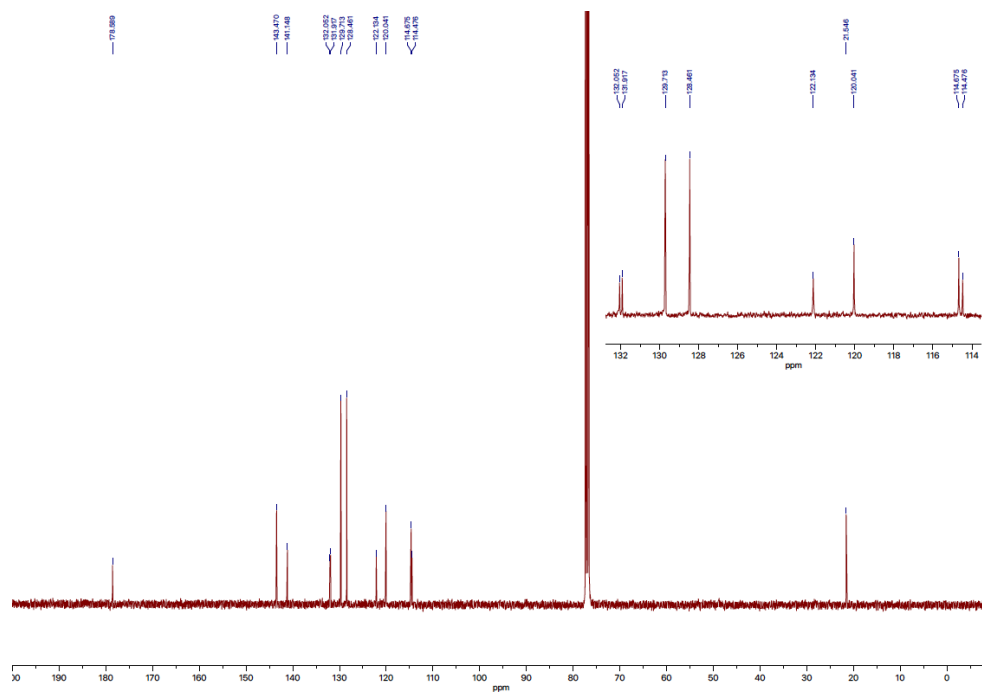


2d

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

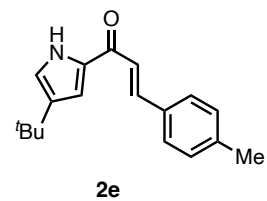
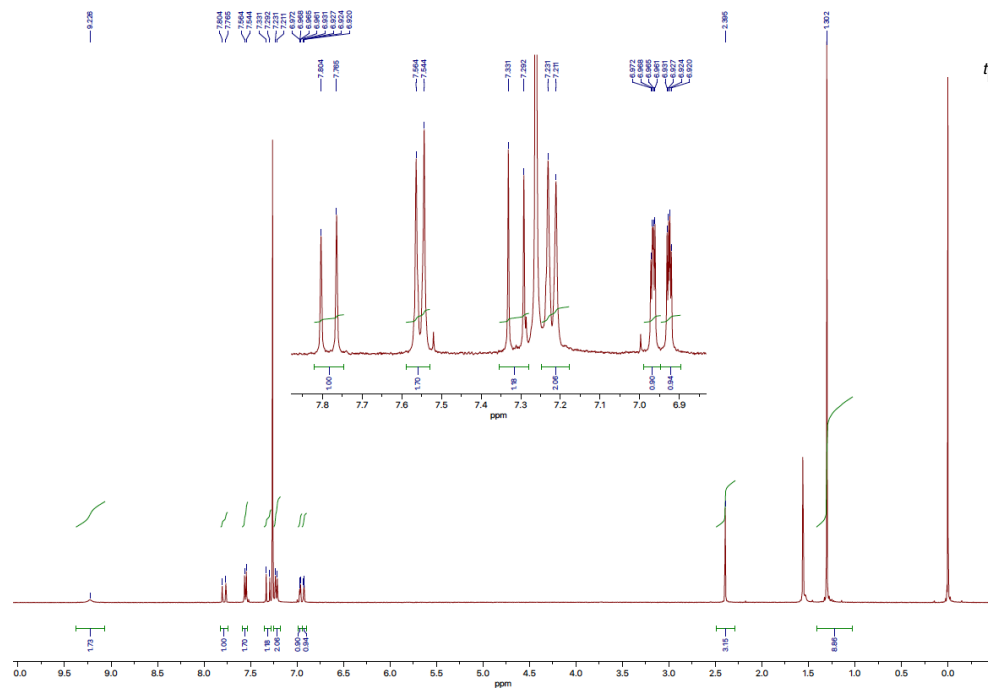


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

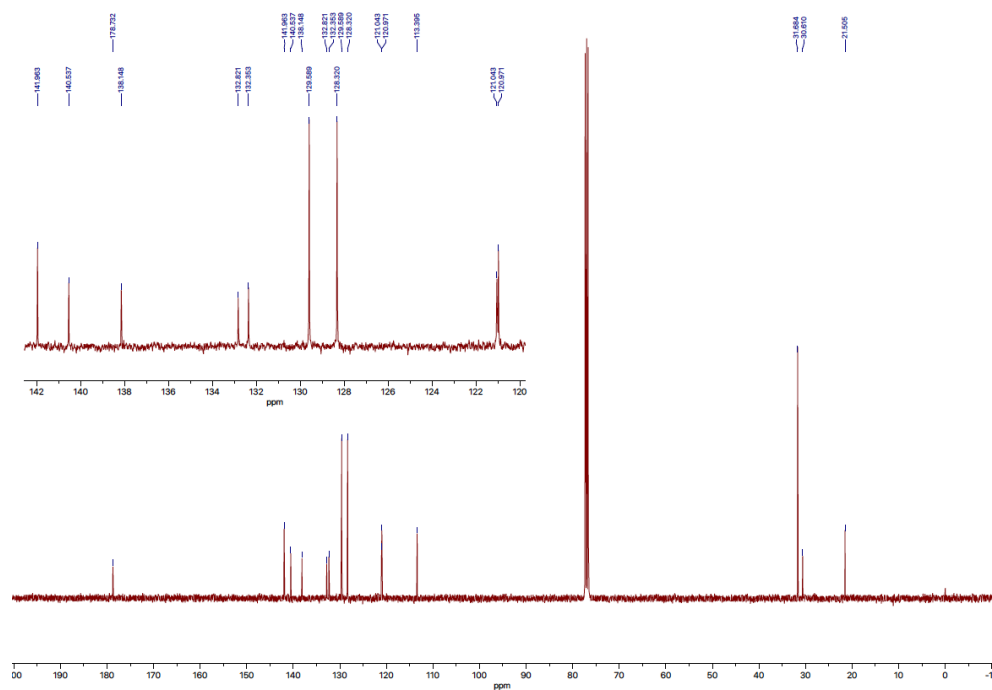


2e

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

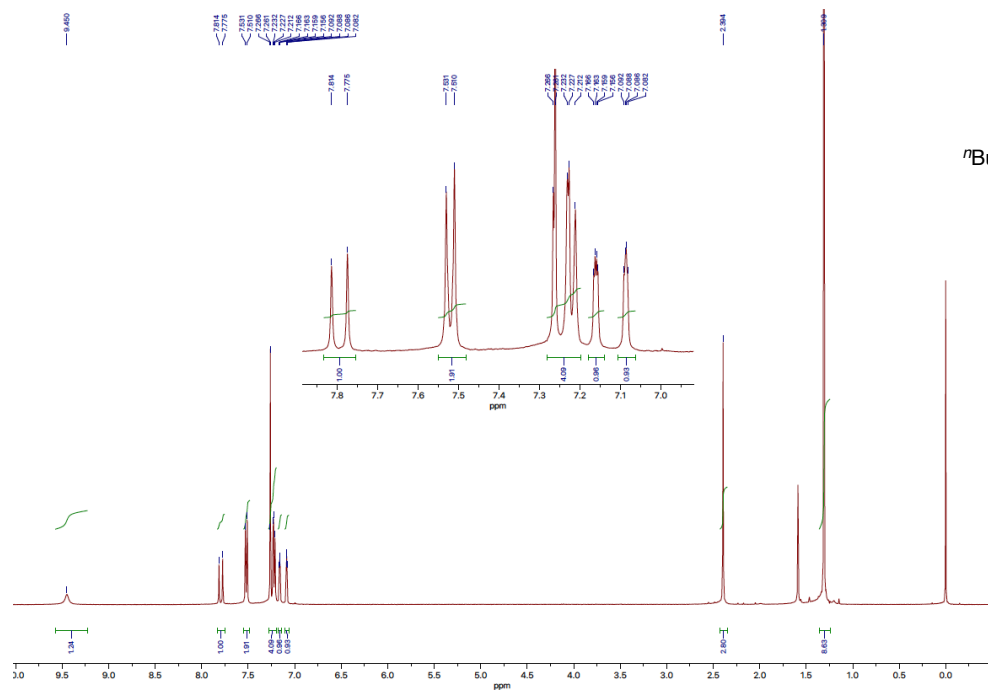




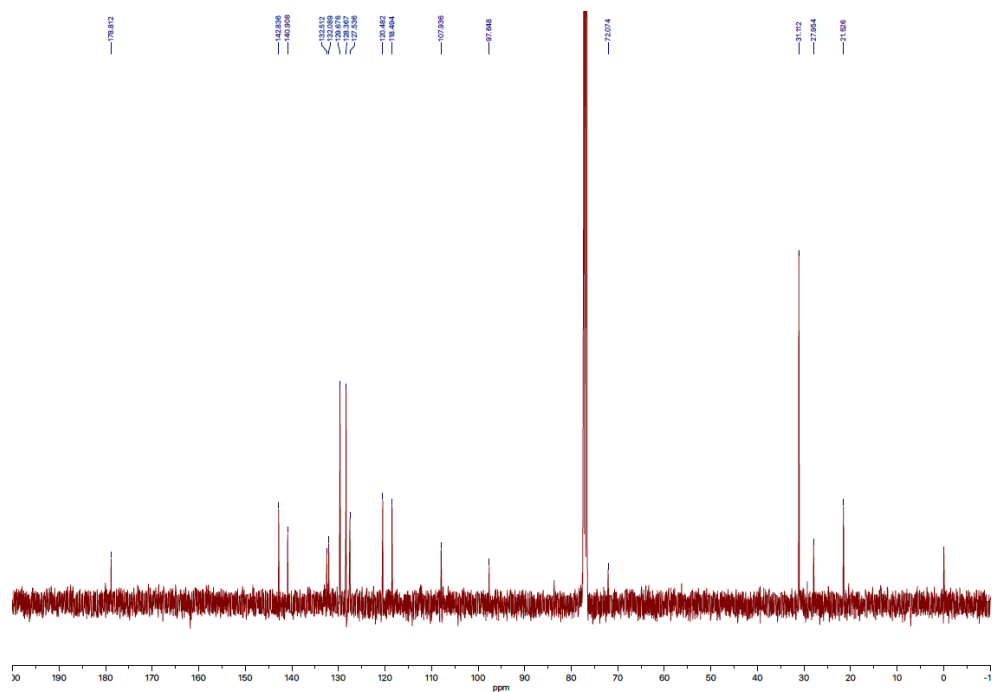


2h

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

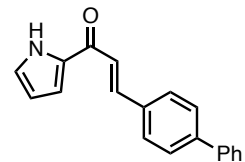
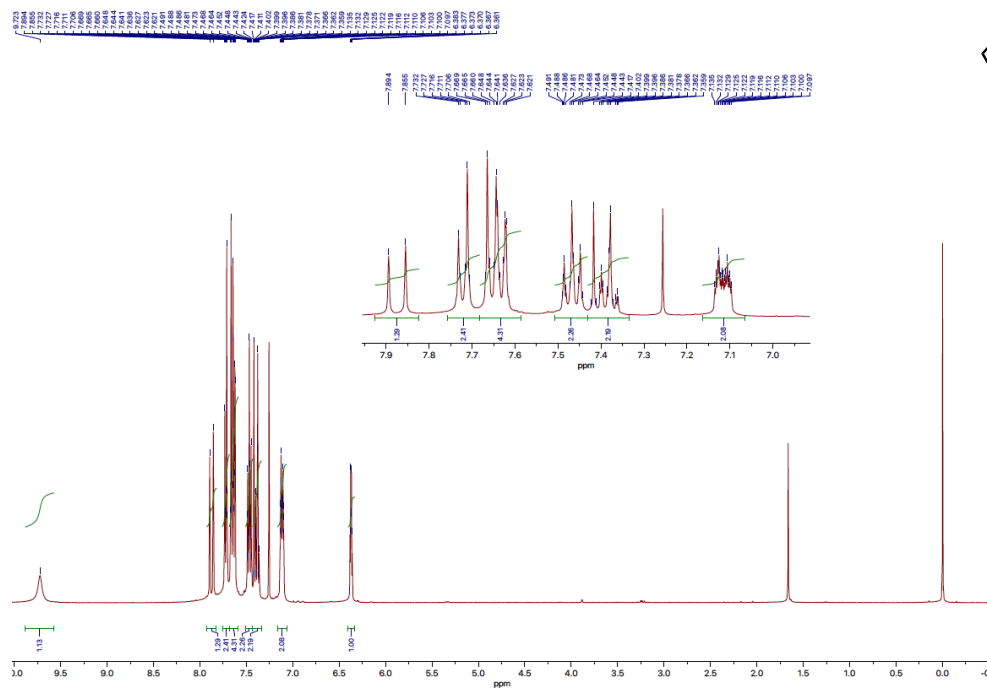






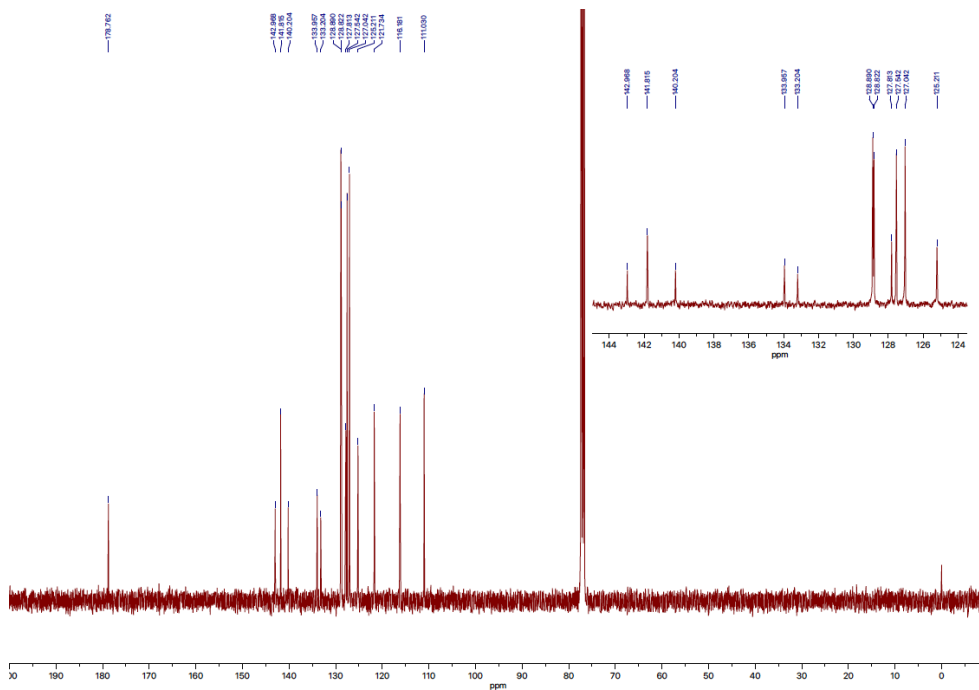
2m

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



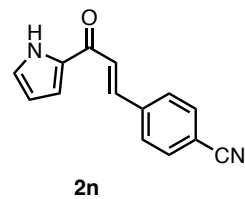
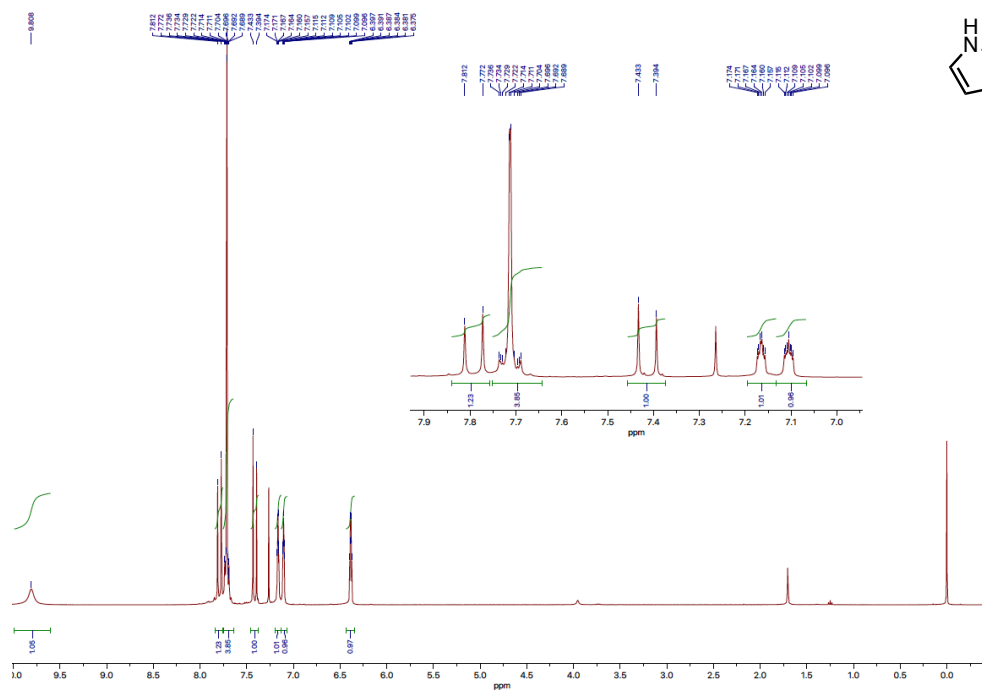
2m

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

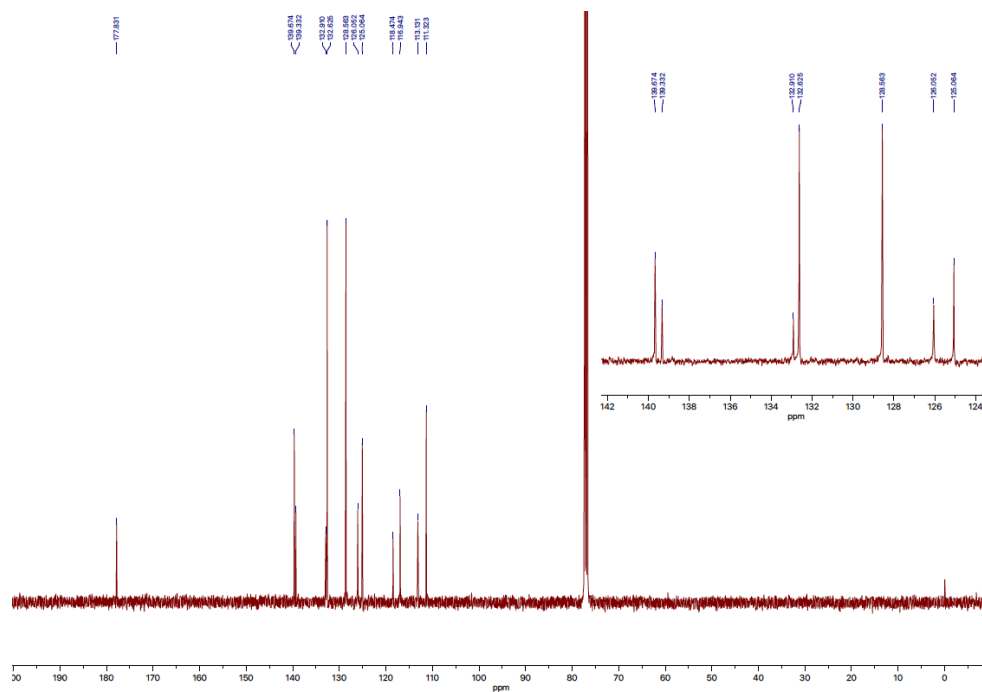


2n

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

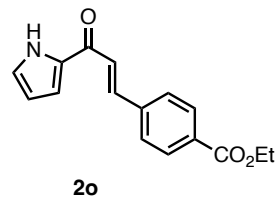
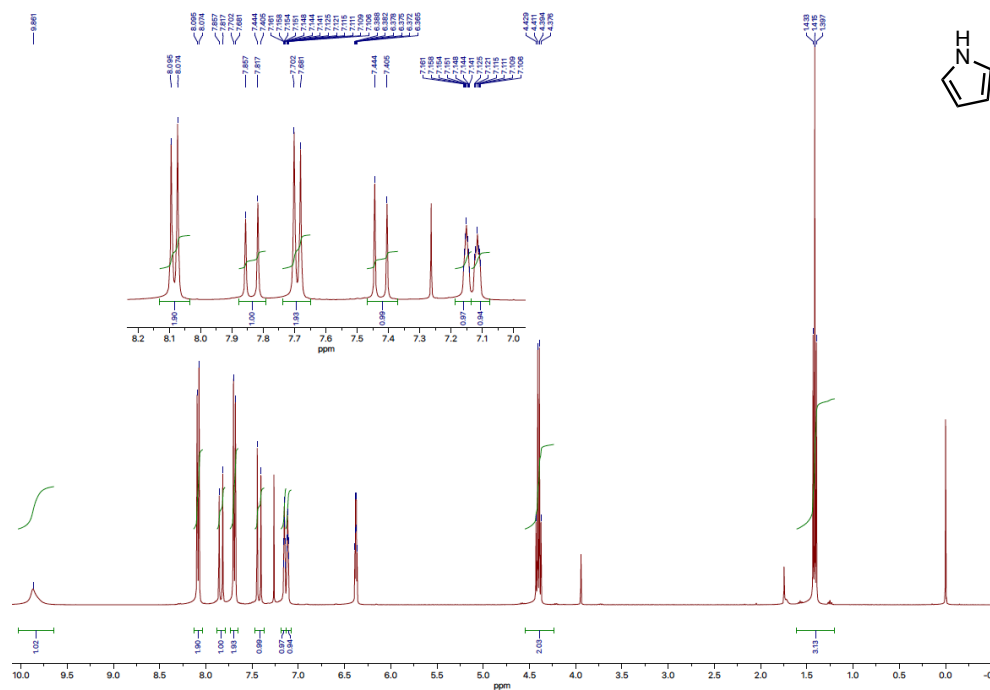


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

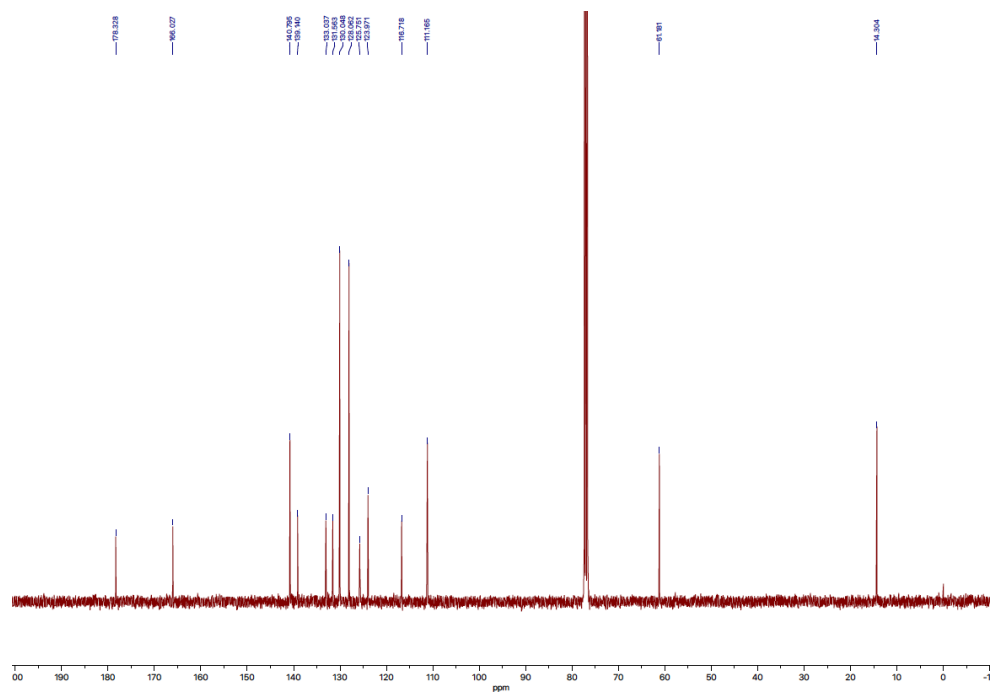


2o

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

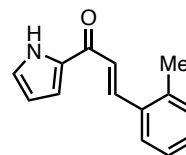
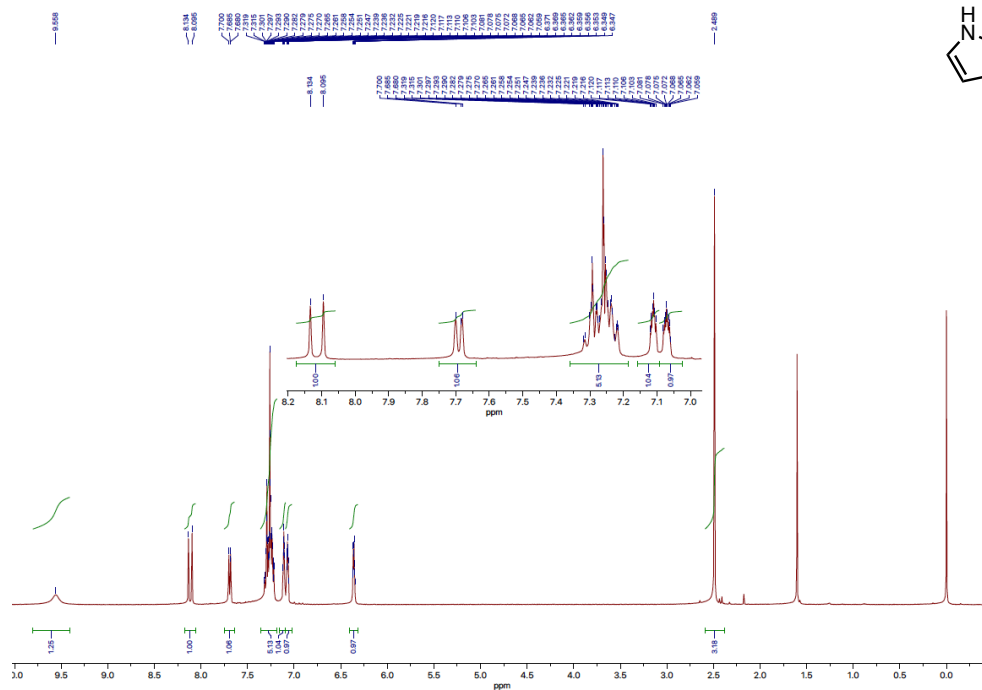


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



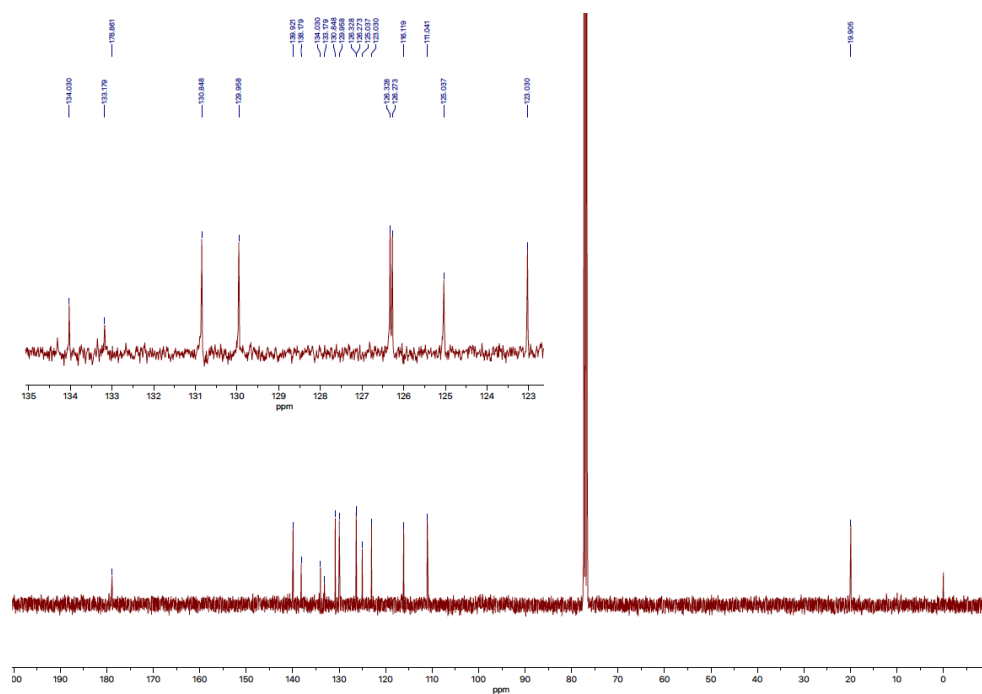
2p

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



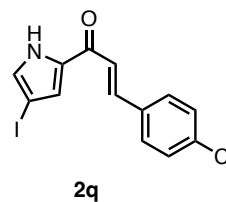
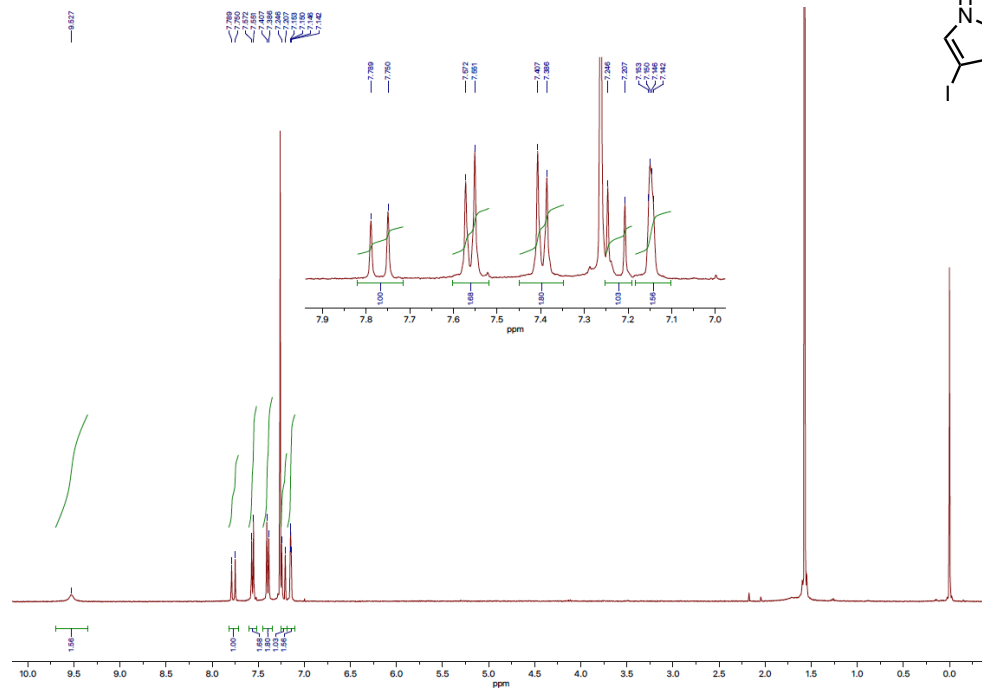
2p

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

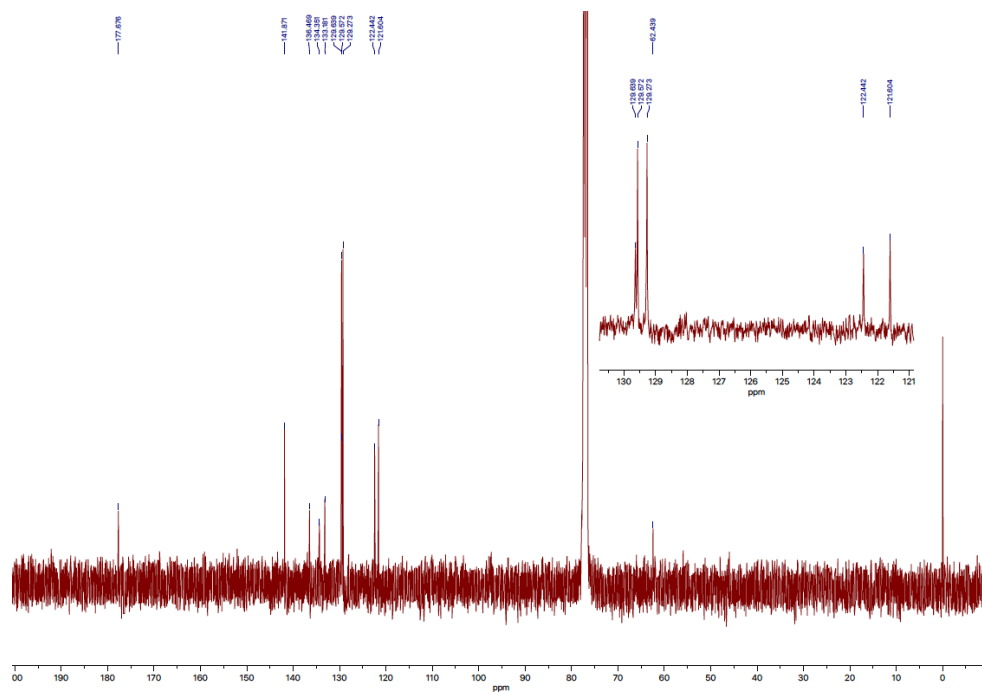


2q

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

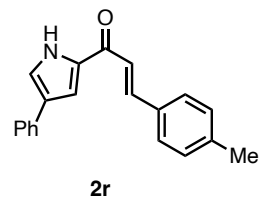
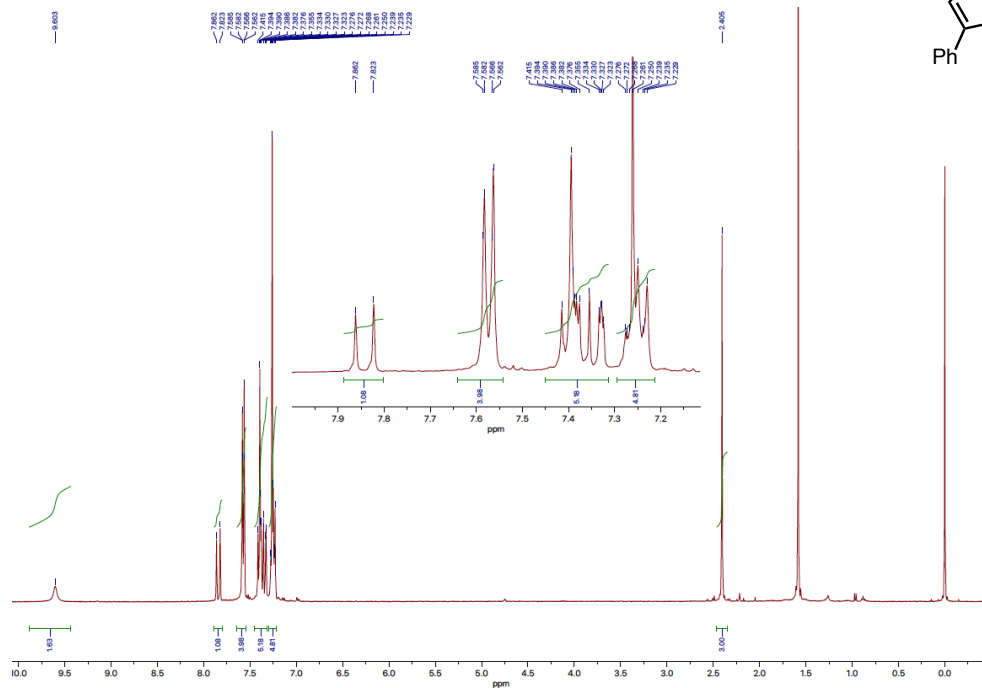


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



2r

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

