

## Electronic Supplementary Information

### Chiral *N,N'*-Dioxide-Sc(NTf<sub>2</sub>)<sub>3</sub>-Complex-Catalyzed Asymmetric Bromoamination of Chalones with *N*-Bromosuccinimide as Both Bromine and Amide Sources

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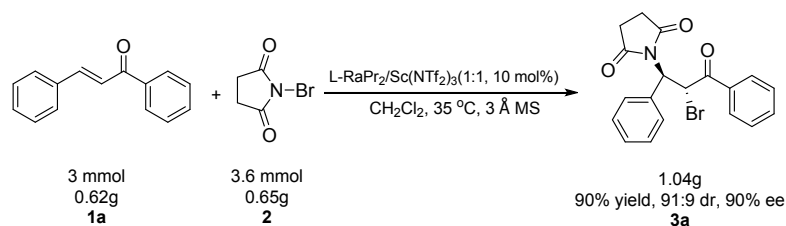
## 1. General method

$^1\text{H}$  NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ( $\text{CDCl}_3$ ,  $\delta = 7.26$ ). Spectra were reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment.  $^{13}\text{C}$  NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ( $\text{CDCl}_3$ ,  $\delta = 77.0$ ). Reactions were carried out using commercial available reagents in over-dried apparatus.  $\text{CH}_2\text{Cl}_2$  was dried over powdered  $\text{CaH}_2$  and distilled under nitrogen just before use. Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 25 °C with UV detector at 254 nm. Diastereoselectivity (*dr*) was determined by  $^1\text{H}$  NMR spectra. HRMS was recorded on a commercial apparatus (ESI Source) and  $^{78,9183}\text{Br}$  and  $^{80,9163}\text{Br}$  were chosen as references to calculate the exact mass. Chiral *N,N'*-dioxide ligand were prepared using literature method<sup>1</sup>. Optical rotations were reported at indicated wavelength as follows:  $[\alpha]_D^{25} = (c \text{ g}/100\text{mL}, \text{ in solvent})$ . NBS and NCS were recrystallized from acetone and petroleum ether.

## 2. General procedure of the catalytic reactions

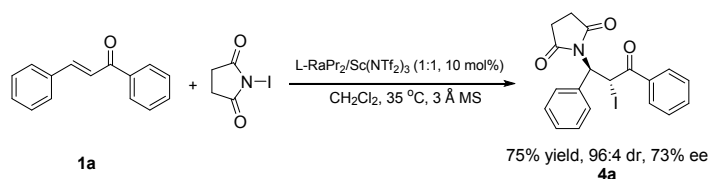
**L-RaPr<sub>2</sub>** (7.0 mg, 0.01 mmol), **Sc(NTf<sub>2</sub>)<sub>3</sub>** (8.8 mg, 0.01 mmol), 3 Å molecular sieve (40 mg) and chalone analogs (0.10 mmol) were added to an over-dried reaction tube under nitrogen atmosphere. 0.3 mL Anhydrous  $\text{CH}_2\text{Cl}_2$  was added and the solution was stirred at 35 °C for 30 minutes. Subsequently, NBS **2** (0.12 mmol) was added and the reaction mixture continued stirring for 36-48 hours. The products were purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1-2:1).

## 3. Gram scale experiment

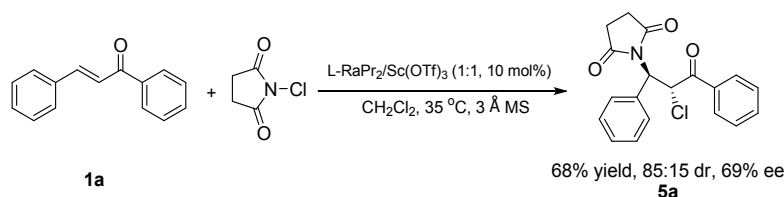


To a dry round-bottom flask, **L-RaPr<sub>2</sub>** (210 mg, 0.30 mmol), Sc(NTf<sub>2</sub>)<sub>3</sub> (264 mg, 0.30 mmol), 3 Å molecular sieve (600 mg) and chalone (624 mg, 3.0 mmol) were added under nitrogen atmosphere. 6.0 mL Anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added and the solution was stirred at 35 °C for 30 minutes. Next, NBS **2** (650 mg, 3.6 mmol) was added and the reaction mixture continued stirring for 40 hours at 35 °C. The residue was purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1-2:1) to afford the product **3a** in 1.04 g with 90% yield, 90% ee, and 91:9 dr.

#### 4. The asymmetric haloamination of chalone with *N*-iodosuccinimide and *N*-chlorosuccinimide as both halogen and amide sources

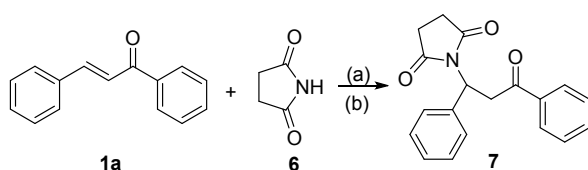


**L-RaPr<sub>2</sub>** (7.0 mg, 0.01 mmol), Sc(NTf<sub>2</sub>)<sub>3</sub> (8.8 mg, 0.01 mmol), 3 Å molecular sieve (40 mg) and chalone **1a** (20.8 mg, 0.10 mmol) were added to an over-dried reaction tube under nitrogen atmosphere. 0.3 mL Anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added and the solution was stirred at 35 °C for 30 minutes. Then, NIS (26.9 mg, 0.12 mmol) was added and the reaction mixture continued stirring for 36 hours at 35 °C. The residue was purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1-2:1) to afford the product **4a** in 32.5 mg with 75% yield, 96:4 dr and 73% ee.



**L-RaPr<sub>2</sub>** (7.0 mg, 0.01 mmol), Sc(OTf)<sub>3</sub> (4.9 mg, 0.01 mmol), 3 Å molecular sieve (40 mg) and chalone **1a** (20.8 mg, 0.10 mmol) were added to an over-dried reaction tube under nitrogen atmosphere. 0.3 mL Anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added and the solution was stirred at 35 °C for 30 minutes. Then, NCS (16.0 mg, 0.12 mmol) was added and the reaction mixture continued stirring for 36 hours at 35 °C. The residue was purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1-2:1) to afford the product **5a** in 23.2 mg with 68% yield, 85:15 dr and 69% ee.

## 5. Control experiments



(a) L-RaPr<sub>2</sub>/Sc(NTf<sub>2</sub>)<sub>3</sub> (1:1, 10 mol%), CH<sub>2</sub>Cl<sub>2</sub>, 35 °C, 3 Å MS

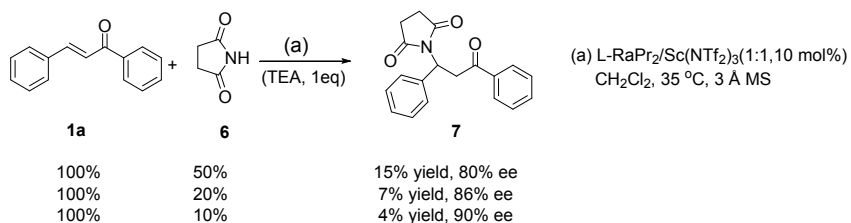
(b) The additional base

(1) without base: trace

(2) base: TEA yield: 21%, ee: 75%

(3) base: DIPA yield: 15%, ee: 33%

**L-RaPr<sub>2</sub>** (7.0 mg, 0.01 mmol), Sc(NTf<sub>2</sub>)<sub>3</sub> (8.8 mg, 0.01 mmol), 3 Å molecular sieve (40 mg) and chalone (20.8 mg, 0.10 mmol) were added to an over-dried reaction tube under nitrogen atmosphere. 0.3 mL Anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added and the solution was stirred at 35 °C for 30 minutes. Then, succinimide **6** (11.9 mg, 0.12 mmol) and the corresponding base (0.10 mmol) were added under these conditions. The reaction mixture continued stirring for 24 hours. The residue was purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1-2:1) to afford the product **7**.

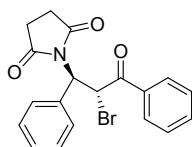


**L-RaPr<sub>2</sub>** (7.0 mg, 0.01 mmol), Sc(NTf<sub>2</sub>)<sub>3</sub> (8.8 mg, 0.01 mmol), 3 Å molecular sieve (40 mg) and chalone (20.8 mg, 0.10 mmol) were added to an over-dried reaction tube under nitrogen atmosphere. 0.3 mL Anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added and the solution was stirred at 35 °C for 30 minutes. Then, succinimide **6** (11.9 mg, 0.12 mmol) and the corresponding base TEA (0.10 mmol) were added under these conditions. The reaction mixture continued stirring for 24 hours. The residue was purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1-2:1) to afford the product **7**.

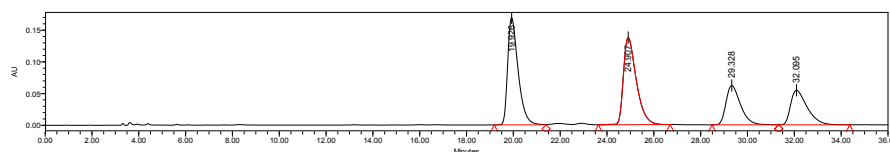
## 6. Product characterization data

### 1-((1*R*,2*R*)-2-Bromo-3-oxo-1,3-diphenylpropyl)pyrrolidine-2,5-dione

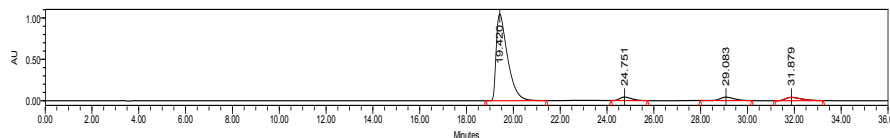
3a



Yield: 33.6 mg (87%), white amorphous solid, 91:9 dr [determined by the ratio of area at  $\delta$  6.02 (d,  $J = 11.6$  Hz, 0.09H) and  $\delta$  5.81 (d,  $J = 11.2$  Hz, 0.91H) in  $^1\text{H}$  NMR]; 91% ee;  $[\alpha]^{24.9}_{\text{D}} = 64.0$  ( $c = 0.73$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/ *i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 19.93$  min,  $t_{\text{R}(\text{minor})} = 24.91$  min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.04$  (d,  $J = 7.2$  Hz, 1.82H), 7.94 (d,  $J = 7.6$  Hz, 0.18H), 7.67 – 7.48 (m, 5H), 7.39 (d, 2.74H), 7.24 (d, 0.26H), 6.83 (d,  $J = 11.2$  Hz, 0.09H), 6.63 (d,  $J = 11.2$  Hz, 0.91H), 6.02 (d,  $J = 11.6$  Hz, 0.09H), 5.81 (d,  $J = 11.2$  Hz, 0.91H), 2.73 – 2.49 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 192.0$ , 176.6, 136.7, 134.0, 133.8, 129.0, 128.9, 57.4, 44.5, 28.0. ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{16}^{78,9183}\text{BrNO}_3 + \text{Na}^+]$  408.0206, found 408.0212; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{16}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  410.0186, found 410.0196.



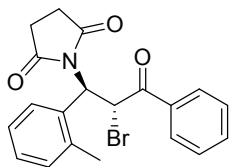
	Retention Time	% Area
1	19.926	33.22
2	24.907	33.06
3	29.328	16.86
4	32.095	16.86



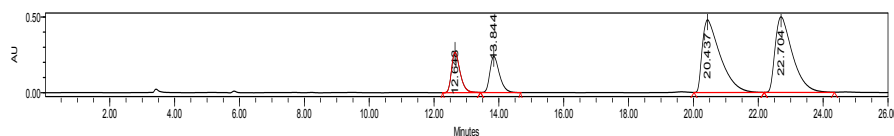
	Retention Time	% Area
1	19.420	87.37
2	24.751	3.75
3	29.083	4.22
4	31.879	4.66

**1-((1R,2R)-2-Bromo-3-oxo-3-phenyl-1-(o-tolyl)propyl)pyrrolidine-2,5-dione**

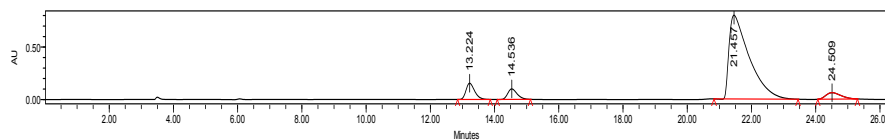
**3b**



Yield: 32.7 mg (82%), white amorphous solid, 89:11 dr [determined by the ratio of area at  $\delta$  6.25 (d,  $J = 11.2$  Hz, 0.11 H) and  $\delta$  6.11 (d,  $J = 11.2$  Hz, 0.89 H) in  $^1\text{H NMR}$ ], 90% ee;  $[\alpha]^{24.9}_{\text{D}} = 99.0$  ( $c = 0.63$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 20.45$  min,  $t_{\text{R}(\text{minor})} = 22.70$  min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.04$  (d,  $J = 7.6$  Hz, 1.78 H),  $\delta 7.91$  (d,  $J = 7.6$  Hz, 0.22 H), 7.82 – 7.80 (m, 1 H), 7.62 – 7.59 (m, 1H), 7.56 – 7.41 (m, 2 H), 7.26 – 7.02 (m, 3H), 6.88 (d,  $J = 11.2$  Hz, 0.11 H), 6.61 (d,  $J = 11.2$  Hz, 0.89 H), 6.25 (d,  $J = 11.2$  Hz, 0.11 H), 6.11 (d,  $J = 11.2$  Hz, 0.89 H), 2.67 (s, 3H), 2.66 – 2.51 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 192.1$ , 177.3, 138.2, 136.4, 134.0, 133.7, 130.8, 128.9, 128.8, 127.5, 126.8, 53.2, 46.7, 28.0, 20.2. ESI-HRMS calcd for  $[\text{C}_{20}\text{H}_{18}^{78,9183}\text{BrNO}_3 + \text{Na}^+]$  422.0363, found 422.0369; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  424.0342, found 424.0346.



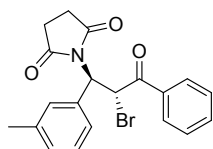
	Retention Time	% Area
1	12.648	10.48
2	13.844	10.41
3	20.437	39.46
4	22.704	39.65



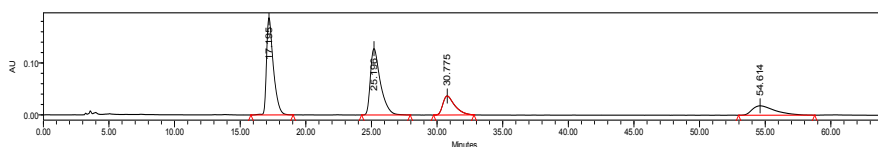
	Retention Time	% Area
1	13.224	6.91
2	14.536	4.88
3	21.457	83.41
4	24.509	4.80

**1-((1R,2R)-2-Bromo-3-oxo-3-phenyl-1-(m-tolyl)propyl)pyrrolidine-2,5-dione**

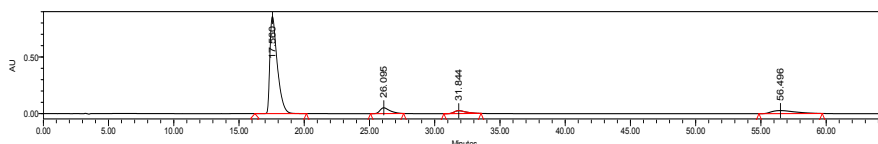
**3c**



Yield: 35.9 mg (90%), white amorphous solid, 88:12 dr [determined by the ratio of area at  $\delta$  5.98 (d,  $J$  = 11.2 Hz , 0.12H) and  $\delta$  5.76 (d,  $J$  = 10.8 Hz, 0.88H) in  $^1\text{H}$  NMR], 86% ee;  $[\alpha]^{24.9}_{\text{D}}$  = 74.9 ( $c$  = 0.85,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel ID,  $n$ -hexane/ $i$ -PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 17.20 min,  $t_{\text{R(minor)}}$  = 25.20 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.06 – 7.94 (m, 2H), 7.63 – 7.58 (m, 1H), 7.53 – 7.27 (m, 5H), 7.19 – 7.03 (m, 1H), 6.81 (d,  $J$  = 11.2 Hz, 0.12H), 6.62 (d,  $J$  = 11.2 Hz , 0.88H), 5.98 (d,  $J$  = 11.2 Hz , 0.12H), 5.76 (d,  $J$  = 10.8 Hz, 0.88H), 2.74 – 2.52 (m, 4H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.0, 176.7, 138.6, 136.6, 134.0, 133.9, 129.8, 129.6, 128.9, 128.7, 126.0, 57.4, 28.0, 21.5. ESI-HRMS calcd for  $[\text{C}_{20}\text{H}_{18}^{78,9183}\text{BrNO}_3+\text{Na}^+]$  422.0363, found 422.0374; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{80,9163}\text{BrNO}_3+\text{Na}^+]$  424.0342, found 424.0359.



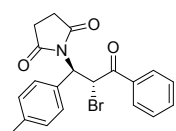
	Retention Time	% Area
1	17.195	37.59
2	25.196	37.44
3	30.775	12.81
4	54.614	12.15



	Retention Time	% Area
1	17.560	81.52
2	26.095	6.46
3	31.844	3.88
4	56.496	8.14

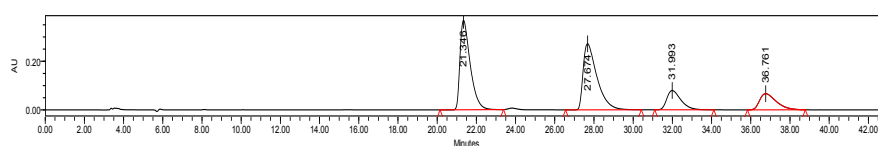
**1-((1R,2R)-2-Bromo-3-oxo-3-phenyl-1-(p-tolyl)propyl)pyrrolidine-2,5-dione**

**3d**

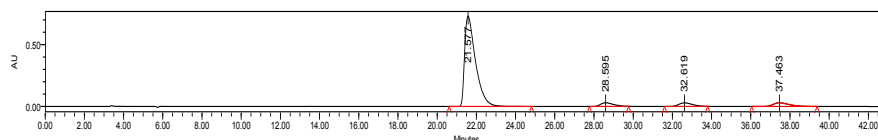


Yield: 35.5 mg (89%), white amorphous solid, 90:10 dr [determined by the ratio of area at  $\delta$  6.00 (d,  $J$  = 11.6 Hz, 0.10H) and  $\delta$  5.79 (d,  $J$  = 11.2 Hz, 0.90H) in

$^1\text{H}$  NMR], 91% ee;  $[\alpha]^{28.0}_{\text{D}} = 83.7$  ( $c = 0.10$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 21.35$  min,  $t_{\text{R}(\text{minor})} = 27.67$  min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.04$  (d,  $J = 7.6$  Hz, 1.80H), 8.04 (d,  $J = 7.6$  Hz, 0.20H), 7.63 – 7.43 (m, 5H), 7.21 (d,  $J = 7.6$  Hz, 1.80H), 7.21 (d,  $J = 7.6$  Hz, 0.20H), 6.80 (d,  $J = 11.6$  Hz, 0.10H), 6.62 (d,  $J = 10.8$  Hz, 0.90H), 6.00 (d,  $J = 11.6$  Hz, 0.10H), 5.79 (d,  $J = 11.2$  Hz, 0.90H), 2.74 – 2.54 (m, 4H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 192.1, 176.1, 138.9, 133.8, 129.5, 128.9, 57.1, 44.6, 28.0, 21.3$ . ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{78,9183}\text{BrNO}_3 + \text{Na}^+]$  422.0363, found 422.0362; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  424.0342, found 424.0344.

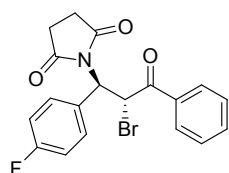


	Retention Time	% Area
1	21.346	38.67
2	27.674	38.57
3	31.993	11.44
4	36.761	11.33



	Retention Time	% Area
1	21.577	86.61
2	28.595	4.06
3	32.619	4.19
4	37.463	5.14

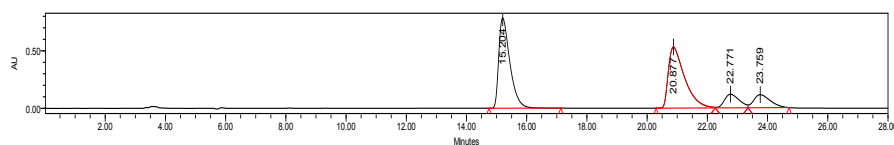
**1-((1*R*,2*R*)-2-Bromo-1-(4-fluorophenyl)-3-oxo-3-phenylpropyl)pyrrolidine-2,5-dione 3e**



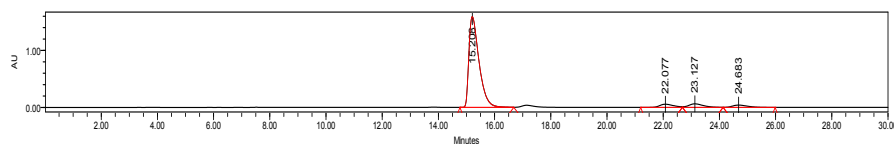
Yield: 33.8 mg (84%), white amorphous solid, 90:10 dr [determined by the ratio of area at  $\delta 6.00$  (d,  $J = 11.6$  Hz, 0.10H) and  $\delta 5.81$  (d,  $J = 11.2$  Hz, 0.90H) in  $^1\text{H}$  NMR], 91% ee;  $[\alpha]^{28.0}_{\text{D}} = 129.2$  ( $c = 0.13$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 15.20$  min,  $t_{\text{R}(\text{minor})} =$



20.88 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.03 (d,  $J$  = 8.0 Hz, 1.80H), 7.94 (d,  $J$  = 8.0 Hz, 0.20H), 7.65 – 7.49 (m, 5H), 7.08 (t,  $J$  = 8.8 Hz, 1.80H), 6.92 (t,  $J$  = 8.4 Hz, 0.20H), 6.76 (d,  $J$  = 11.2 Hz, 0.10H), 6.58 (d,  $J$  = 10.8 Hz, 0.90H), 6.00 (d,  $J$  = 11.6 Hz, 0.10H), 5.81 (d,  $J$  = 11.2 Hz, 0.90H), 2.76 – 2.51 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.8, 176.7, 164.1, 161.7, 134.1, 132.6, 130.9, 130.8, 128.9, 128.9, 115.9, 115.7, 56.7, 44.4, 28.0. ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78,9183}\text{BrFNO}_3+\text{Na}^+]$  426.0112, found 426.0121; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80,9163}\text{BrClNO}_3+\text{Na}^+]$  428.0092, found 428.0103.

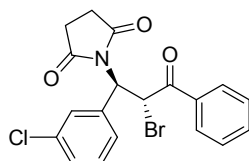


	Retention Time	% Area
1	15.204	41.58
2	20.877	41.05
3	22.771	8.38
4	23.759	9.00



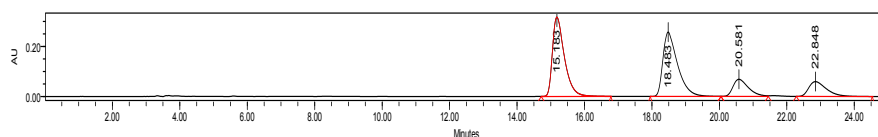
	Retention Time	% Area
1	15.208	87.67
2	22.077	4.19
3	23.127	4.91
4	24.683	3.24

### 1-((1*R*,2*R*)-2-Bromo-1-(3-chlorophenyl)-3-oxo-3-phenylpropyl)pyrrolidine-2,5-dione **3f**

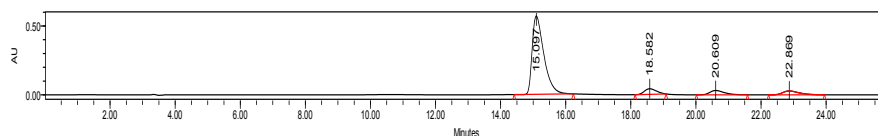


Yield: 38.4 mg (92%), white amorphous solid, 89:11 dr [determined by the ratio of area of  $\delta$  5.98 (d,  $J$  = 10.8 Hz, 0.11H) and 5.78 (d,  $J$  = 11.2 Hz, 0.89H) in  $^1\text{H}$  NMR], 86% ee;  $[\alpha]^{24.9}_{\text{D}}$  = 123.4 ( $c$  = 0.09,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE,  $n$ -hexane/ $i$ -PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})}$  = 15.18 min,  $t_{\text{R}(\text{minor})}$  = 18.48 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.04 (d,  $J$  = 7.6 Hz, 1.78H), 7.96 (d,  $J$  = 7.6

Hz, 0.22H), 7.67 – 6.47 (m, 5H), 7.35 – 7.31 (m, 1.78H), 7.21 – 7.15 (m, 0.22H), 6.76 (d,  $J = 11.2$  Hz 0.11H), 6.57 (d,  $J = 11.2$  Hz 0.89H), 5.98 (d,  $J = 10.8$  Hz, 0.11H), 5.78 (d,  $J = 11.2$  Hz, 0.89H), 2.17 – 2.58 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 191.7, 176.6, 138.6, 134.7, 134.1, 133.6, 130.1, 129.3, 128.9, 127.5, 56.9, 44.1, 28.0$ . ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78,9183}\text{BrClNO}_3+\text{Na}^+]$  441.9817, found 441.9825; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80,9163}\text{BrClNO}_3+\text{Na}^+]$  443.9796, found 443.9799.

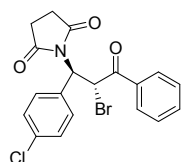


	Retention Time	% Area
1	15.183	39.20
2	18.483	38.93
3	20.581	10.97
4	22.848	10.89



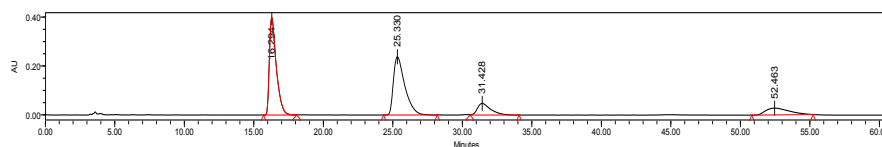
	Retention Time	% Area
1	15.097	82.55
2	18.582	6.10
3	20.609	5.57
4	22.869	5.78

### 1-((1*R*,2*R*)-2-Bromo-1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)pyrrolidine-2,5-dione **3g**

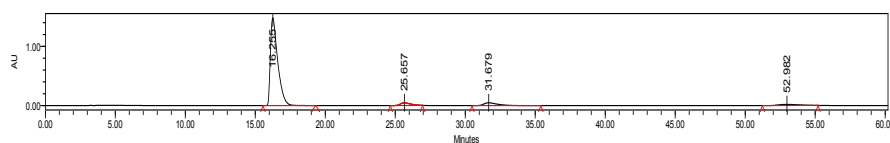


Yield: 35.5 mg (85%), white amorphous solid, 91:9 dr [determined by the ratio of area at  $\delta$  5.99 (d,  $J = 11.2$  Hz, 0.09H) and  $\delta$  5.78 (d,  $J = 10.8$  Hz, 0.91H) in  $^1\text{H}$  NMR], 92% ee;  $[\alpha]^{24.9}_{\text{D}} = 54.8$  ( $c = 0.75$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 16.29$  min,  $t_{\text{R}(\text{minor})} = 25.33$  min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.03$  (d,  $J = 7.2$  Hz, 1.82H), 7.94 (d,  $J = 7.6$  Hz, 0.18H), 7.64 – 7.44 (m, 5H), 7.37 (d,  $J = 8.4$  Hz, 1.82H), 7.20 (d,  $J = 8.4$  Hz, 0.18H), 6.75 (d,  $J = 11.6$  Hz,

0.09H), 6.58 (d,  $J = 10.8$  Hz, 0.91H), 5.99 (d,  $J = 11.2$  Hz, 0.09H), 5.78 (d,  $J = 10.8$  Hz, 0.91H), 2.76 – 2.50 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 191.7, 176.6, 135.2, 134.9, 134.1, 133.7, 130.4, 129.1, 129.0, 128.9, 56.7, 44.1, 28.0$ . ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78.9183}\text{BrClNO}_3 + \text{Na}^+]$  441.9817, found 441.9824; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80.9163}\text{BrClNO}_3 + \text{Na}^+]$  443.9796, found 443.9795.

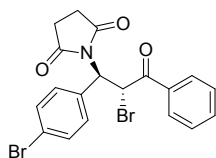


	Retention Time	% Area
1	16.294	40.76
2	25.330	40.21
3	31.428	9.32
4	52.463	9.71



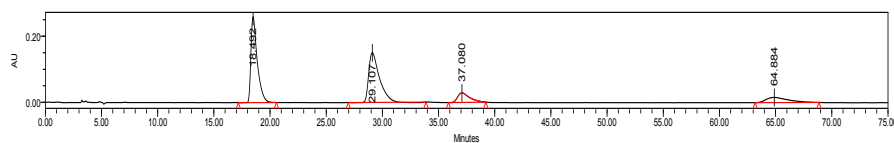
	Retention Time	% Area
1	16.255	87.67
2	25.657	4.09
3	31.679	4.71
4	52.982	3.53

### 1-((1*R*,2*R*)-2-Bromo-1-(4-bromophenyl)-3-oxo-3-phenylpropyl)pyrrolidine-2,5-dione **3h**

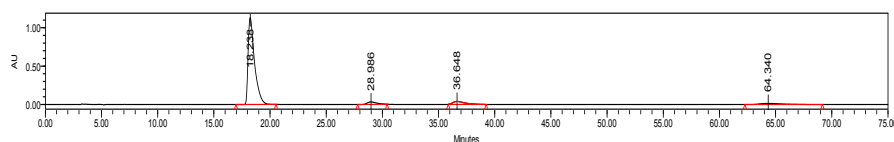


Yield: 38.8 mg (84%), white amorphous solid, 90:10 dr [determined by the ratio of area at  $\delta$  5.97 (d,  $J = 11.2$  Hz, 0.10H) and  $\delta$  5.78 (d,  $J = 11.6$  Hz, 0.90H) in  $^1\text{H}$  NMR], 92% ee;  $[\alpha]^{28.0}_{\text{D}} = 59.6$  ( $c = 0.10, \text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel ID, *n*-hexane/ *i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 18.49$  min,  $t_{\text{R}(\text{minor})} = 29.11$  min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.03$  (d,  $J = 7.6$  Hz, 1.80H), 7.94(d,  $J = 7.6$  Hz, 0.20H), 7.64 – 7.35 (m, 7H), 6.75 (d,  $J = 11.6$  Hz, 0.10H), 6.58 (d,  $J = 10.8$  Hz, 0.90H), 5.97 (d,  $J = 11.2$  Hz, 0.10H), 5.78 (d,  $J = 11.6$  Hz, 0.90H), 2.76 – 2.51 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

$\delta = 191.7, 176.6, 135.7, 134.1, 133.7, 132.1, 130.7, 129.0, 128.9, 123.2, 56.8, 44.0, 28.0$ . ESI-HRMS calcd for  $[\text{C}_{19}\text{H}_{15}^{78,9183}\text{Br}_2\text{NO}_3+\text{Na}^+]$  485.9311, found 485.9317; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78,9183}\text{Br}^{80,9163}\text{BrNO}_3+\text{Na}^+]$  487.9291, found 487.9288; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80,9163}\text{Br}_2\text{NO}_3+\text{Na}^+]$  489.9270, found 489.9274.

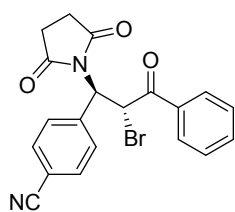


	Retention Time	% Area
1	18.492	41.36
2	29.107	41.16
3	37.080	8.77
4	64.884	8.71



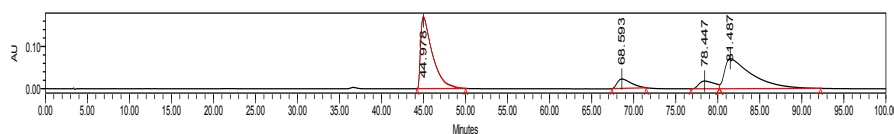
	Retention Time	% Area
1	18.238	87.01
2	28.986	3.61
3	36.648	5.59
4	64.340	3.79

#### 4-((1*R*,2*R*)-2-Bromo-1-(2,5-dioxopyrrolidin-1-yl)-3-oxo-3-phenylpropyl)benzonitrile 3i

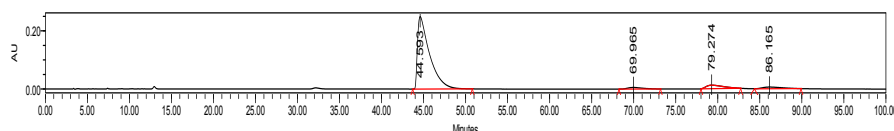


Yield: 29.9 mg (73%), white amorphous solid, 91:9 dr [determined by the ratio of area at  $\delta$  6.04 (d,  $J = 11.6$  Hz, 0.09H) and  $\delta$  5.86 (d,  $J = 10.8$  Hz, 0.91H) in  $^1\text{H}$  NMR], 94% ee;  $[\alpha]^{24.9}_{\text{D}} = 50.4$  ( $c = 0.71$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 44.98$  min,  $t_{\text{R}(\text{minor})} = 81.49$  min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.03$  (d,  $J = 7.2$  Hz, 1.82H), 7.95 (d,  $J = 7.6$  Hz, 0.18H), 7.79 (d, 2H), 7.71 – 7.62 (m, 3H), 7.54 – 7.46 (m, 2H), 6.77 (d,  $J = 11.6$  Hz, 0.09H), 6.60 (d,  $J = 10.8$  Hz, 0.91H), 6.04 (d,  $J = 11.6$  Hz, 0.09H), 5.86 (d,  $J = 10.8$  Hz, 0.91H), 2.79 – 2.55 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 191.4, 176.6, 141.6, 133.5, 129.9,$

128.9, 118.3, 113.0, 55.9, 43.3, 28.0. ESI-HRMS: calcd for  $[C_{20}H_{15}^{78,9183}BrN_2O_3+Na^+]$  433.0159, found 433.0165; ESI-HRMS: calcd for  $[C_{20}H_{15}^{80,9163}BrN_2O_3+Na^+]$  435.0138, found 435.0147.

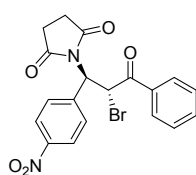


	Retention Time	% Area
1	44.978	44.37
2	68.593	6.83
3	78.447	6.22
4	81.487	42.58

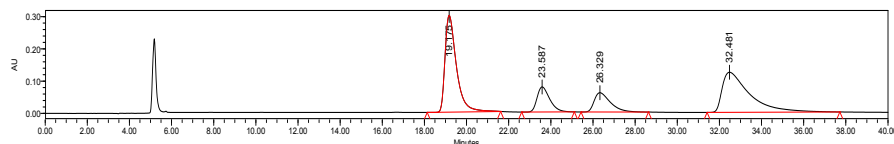


	Retention Time	% Area
1	44.593	88.33
2	69.965	2.26
3	79.274	6.08
4	86.165	3.34

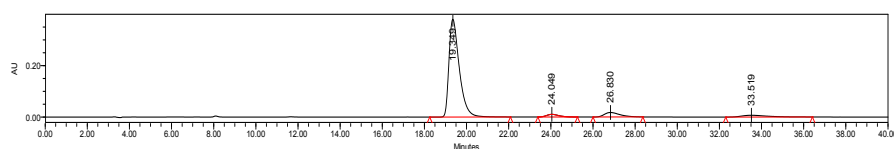
### 1-((1R,2R)-2-Bromo-1-(4-nitrophenyl)-3-oxo-3-phenylpropyl)pyrrolidine-2,5-dione 3j



Yield: 32.3 mg (75%), white amorphous solid, 91:9 dr [determined by the ratio of area at  $\delta = 6.10$  (d,  $J = 11.2$  Hz, 0.09H) and  $\delta 5.93$  (d,  $J = 10.8$  Hz, 0.91H) in  $^1H$  NMR ], 92% ee;  $[\alpha]^{28.0}_D = 58.4$  ( $c = 0.65$ ,  $CH_2Cl_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, 254 nm)  $t_{R(major)} = 19.18$  min,  $t_{R(minor)} = 32.48$  min;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.23 (d, 2H), 8.04 (d,  $J = 7.6$  Hz, 1.82H), 7.95 (d,  $J = 7.6$  Hz, 0.18H), 7.85 (d,  $J = 8.4$  Hz, 1.82H), 7.75 (d,  $J = 8.8$  Hz, 0.18H), 7.66 – 7.45 (m, 3H), 6.80 (d,  $J = 11.6$  Hz, 0.09H), 6.63 (d,  $J = 10.8$  Hz, 0.91H), 6.10 (d,  $J = 11.2$  Hz, 0.09H), 5.93 (d,  $J = 10.8$  Hz, 0.91H), 2.81 – 2.58 (m, 4H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta = 191.3, 176.6, 148.1, 143.4, 130.2, 129.0, 129.0, 124.1, 56.6, 43.3, 28.0$ . ESI-HRMS: calcd for  $[C_{19}H_{15}^{78,9183}BrN_2O_5+Na^+]$  453.0057, found 453.0060; ESI-HRMS: calcd for  $[C_{19}H_{15}^{80,9163}BrN_2O_5+Na^+]$  455.0037, found 455.0052.

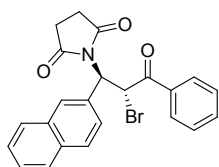


	Retention Time	% Area
1	19.175	38.87
2	23.587	11.19
3	26.329	11.05
4	32.481	38.89

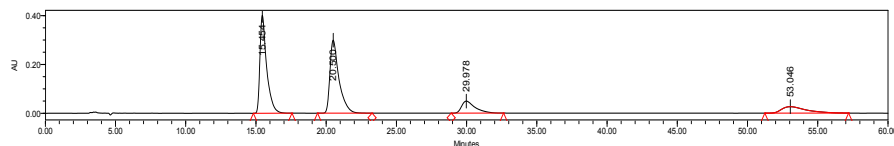


	Retention Time	% Area
1	19.349	87.22
2	24.049	2.78
3	26.830	6.09
4	33.519	3.90

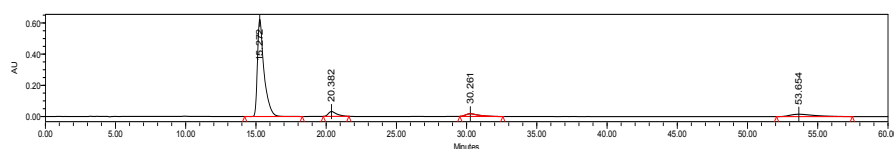
### 1-((1*R*,2*R*)-2-Bromo-1-(naphthalen-2-yl)-3-oxo-3-phenylpropyl)pyrrolidine-2,5-dione **3k**



Yield: 34.4 mg (79%), white amorphous solid, 88:12 dr [determined by the ratio of area at  $\delta$  6.20 (d,  $J = 11.6$  Hz, 0.12H) and  $\delta$  5.99 (d,  $J = 11.2$  Hz, 0.88H) in  $^1\text{H}$  NMR], 88% ee; HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 15.45 min,  $t_{\text{R(minor)}}$  = 20.50 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.12 – 7.94 (m, 3H), 7.90 – 7.60 (m, 5H), 7.54 – 7.40 (m, 4H), 6.95 (d,  $J = 11.6$  Hz, 0.12 H), 6.76 (d,  $J = 11.2$  Hz, 0.88 H), 6.20 (d,  $J = 11.6$  Hz, 0.12H), 5.99 (d,  $J = 11.2$  Hz, 0.88H), 2.73 – 2.48 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.0, 176.8, 134.1, 134.0, 133.8, 133.4, 133.1, 128.9, 128.8, 128.5, 128.3, 127.7, 128.5, 128.3, 127.7, 127.5, 126.7, 126.5, 125.9, 57.6, 44.4, 28.0. ESI-HRMS: calcd for  $[\text{C}_{23}\text{H}_{18}^{78,9183}\text{BrNO}_3 + \text{Na}^+]$  458.0363, found 458.0365; ESI-HRMS: calcd for  $[\text{C}_{23}\text{H}_{18}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  460.0342, found 460.0348.

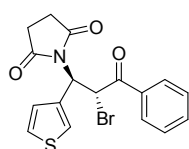


	Retention Time	% Area
1	15.454	40.30
2	20.500	40.09
3	29.978	9.85
4	53.046	9.76

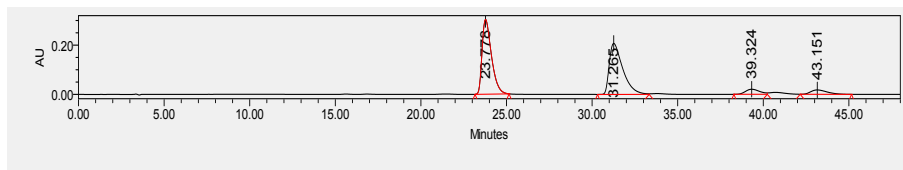


	Retention Time	% Area
1	15.272	82.74
2	20.382	5.34
3	30.261	4.46
4	53.654	7.45

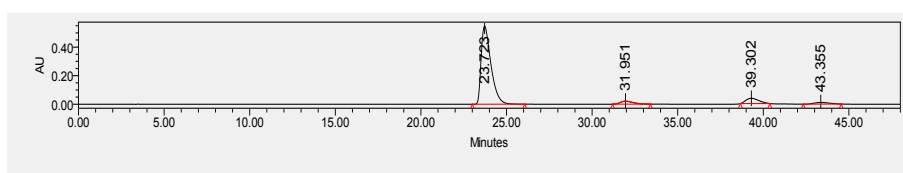
### 1-((1*R*,2*R*)-2-Bromo-3-oxo-3-phenyl-1-(thiophen-3-yl)propyl)pyrrolidine-2,5-dione 3l



Yield: 34.1 mg (87%), white amorphous solid, 90:10 dr [determined by the ratio of area at  $\delta$  6.15 (d,  $J$  = 11.2 Hz, 0.10H) and  $\delta$  5.96 (d,  $J$  = 11.2 Hz, 0.90H) in  $^1\text{H}$  NMR], 92% ee; HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 23.05 min,  $t_{\text{R(minor)}}$  = 30.24 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.03 – 7.93 (m, 2H), 7.64 – 7.46 (m, 4H), 7.37 – 7.33 (m, 1.76H), 7.21 – 7.16 (m, 0.23H), 6.65 (d,  $J$  = 11.2 Hz, 0.10 H), 6.57 (d,  $J$  = 11.2 Hz, 0.90 H), 6.15 (d,  $J$  = 11.2 Hz, 0.10H), 5.96 (d,  $J$  = 11.2 Hz, 0.90H), 2.77 – 2.53 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.0, 176.4, 136.7, 134.1, 133.8, 128.9, 128.8, 127.5, 126.4, 125.8, 52.2, 44.4, 27.9. ESI-HRMS: calcd for  $[\text{C}_{17}\text{H}_{14}^{78,9183}\text{BrNO}_3\text{S}+\text{Na}^+]$  413.9770, found 413.9771; ESI-HRMS: calcd for  $[\text{C}_{17}\text{H}_{148}^{80,9163}\text{BrNO}_3\text{S}+\text{Na}^+]$  415.9750, found 415.9752.



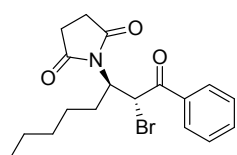
	Retention Time	% Area
1	23.778	45.61
2	31.265	44.90
3	39.324	4.75
4	43.151	4.73



	Retention Time	% Area
1	23.723	85.44
2	31.951	4.21
3	39.302	7.56
4	43.355	2.79

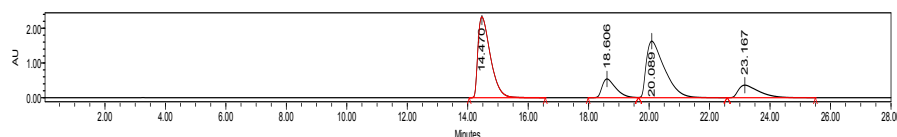
**1-((2*R*,3*R*)-2-Bromo-1-oxo-1-phenyloctan-3-yl)pyrrolidine-2,5-dione**

**3m**

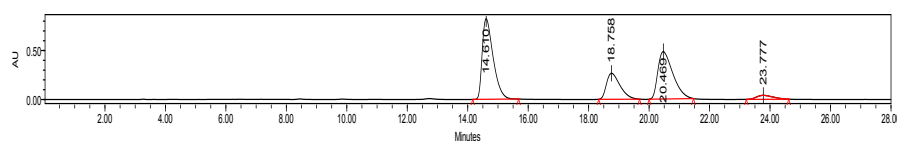


Yield: 34.2 mg (90%), white amorphous solid, 80:20 dr [determined by the ratio of area at  $\delta$  4.95 (td,  $J = 3.2$  Hz, 10.8 Hz, 0.2H) and  $\delta$  4.79 (td,  $J = 3.2$  Hz, 10.8 Hz, 0.8H) in  $^1\text{H}$  NMR], 11% ee; HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 14.47 min,  $t_{\text{R(minor)}}$  = 20.09 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.05 – 7.92 (m, 2H), 7.63 – 7.45 (m, 3H), 6.02 (d, 1H), 4.95 (td,  $J = 3.2$  Hz, 10.8 Hz, 0.2H), 4.79 (td,  $J = 3.2$  Hz, 10.8 Hz, 0.8H), 2.80 – 2.58 (m, 4H), 2.24 – 2.04 (m, 2H), 1.36 – 1.20 (m, 6H), 0.90 – 0.81 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.3, 176.8, 133.9, 128.9, 128.9, 53.2, 45.2, 31.3, 29.1, 27.9, 25.6, 22.5, 14.0. ESI-HRMS: calcd for  $[\text{C}_{18}\text{H}_{22}^{78.9183}\text{BrNO}_3+\text{Na}^+]$  402.0676, found 402.0677; ESI-HRMS: calcd for  $[\text{C}_{18}\text{H}_{22}^{80.9163}\text{BrNO}_3+\text{Na}^+]$  404.0655, found 404.0663.



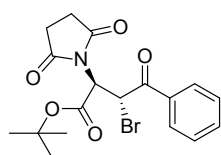


	Retention Time	% Area
1	14.470	39.50
2	18.606	10.07
3	20.089	40.39
4	23.167	10.04

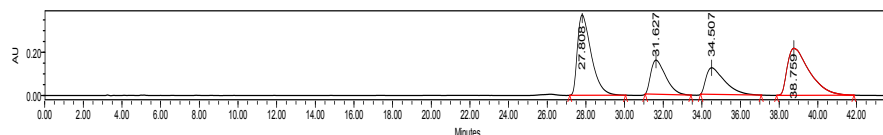


	Retention Time	% Area
1	14.610	43.86
2	18.758	17.46
3	20.469	35.42
4	23.777	3.26

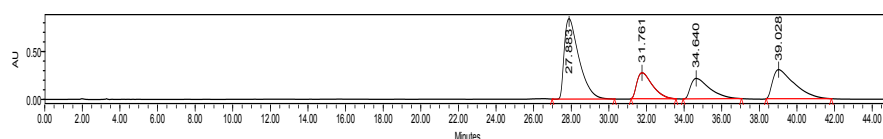
**(2*R*,3*R*)-Tert-butyl 3-bromo-2-(2,5-dioxopyrrolidin-1-yl)-4-oxo-4-phenylbutanoate 3n**



Yield: 26.2 mg (64%), white amorphous solid, 70:30 dr [determined by the ratio of area at  $\delta$  5.72 (d,  $J$  = 10.8 Hz, 0.3H) and  $\delta$  5.32 (d,  $J$  = 10.4 Hz, 0.7H) in  $^1\text{H}$  NMR], 30% ee; HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 27.81 min,  $t_{\text{R(minor)}}$  = 38.76 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.07 – 7.96 (m, 2H), 7.63 – 7.47 (m, 3H), 6.30 (d,  $J$  = 10.0 Hz, 0.7H), 5.99 (d,  $J$  = 10.8 Hz, 0.3H), 5.72 (d,  $J$  = 10.8 Hz, 0.3H), 5.32 (d,  $J$  = 10.4 Hz, 0.7H), 2.86 – 2.61 (m, 4H), 1.51 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.0, 190.7, 175.8, 165.8, 164.6, 134.1, 134.0, 133.6, 129.0, 128.9, 84.7, 84.0, 55.7, 53.8, 41.5, 40.4, 28.0, 27.9, 27.6. ESI-HRMS: calcd for  $[\text{C}_{18}\text{H}_{20}^{78,9183}\text{BrNO}_5 + \text{Na}^+]$  432.0418, found 432.0418; ESI-HRMS: calcd for  $[\text{C}_{18}\text{H}_{22}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  434.0397, found 434.0394.

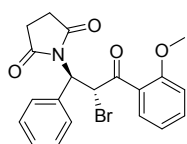


	Retention Time	% Area
1	27.808	35.18
2	31.627	16.13
3	34.507	15.71
4	38.759	32.98

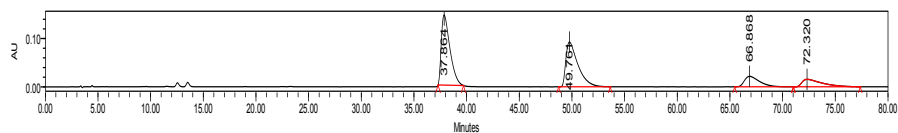


	Retention Time	% Area
1	27.883	45.39
2	31.761	15.44
3	34.640	15.03
4	39.028	24.14

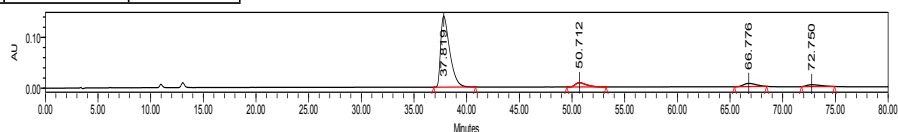
**1-((1*R*,2*R*)-2-Bromo-3-(2-methoxyphenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione **3o****



Yield: 30.3 mg (72%), white amorphous solid, 90:10 dr [determined by the ratio of area at  $\delta$  5.97 (d,  $J = 11.6$  Hz, 0.10H) and  $\delta$  5.82 (d,  $J = 11.2$  Hz, 0.90H) in  $^1\text{H NMR}$ ], 88% ee;  $[\alpha]^{28.0}_{\text{D}} = 125.7$  ( $c = 0.35$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}} = 37.86$  min,  $t_{\text{R(minor)}} = 49.76$  min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.84 - 7.81$  (m, 1H), 7.66 - 7.58 (m, 2H), 7.54 - 7.49 (m, 1H), 7.41 - 7.33 (m, 2.8H), 7.19 - 7.16 (m, 0.20H), 7.05 - 6.96 (m, 2H), 6.94 - 6.84 (m, 1H),  $\delta$  5.97 (d,  $J = 11.6$  Hz, 0.10H),  $\delta$  5.82 (d,  $J = 11.2$  Hz, 0.90H), 4.01 (s, 3H), 2.56 - 2.52 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 193.0, 176.5, 158.9, 136.9, 134.8, 131.5, 129.3, 128.7, 128.6, 124.7, 120.9, 112.2, 57.2, 56.0, 49.4, 27.9$ . ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{78,9183}\text{BrNO}_4 + \text{Na}^+]$  438.0312, found 438.0321; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{80,9163}\text{BrNO}_4 + \text{Na}^+]$  440.0291, found 440.0301.

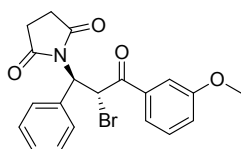


	Retention Time	% Area
1	37.864	41.72
2	49.761	37.14
3	66.868	10.90
4	72.320	10.24



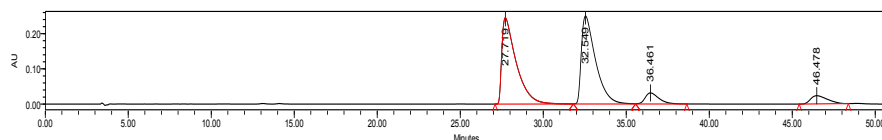
	Retention Time	% Area
1	37.819	84.98
2	50.712	6.18
3	66.776	5.33
4	72.750	3.51

**1-((1*R*,2*R*)-2-Bromo-3-(3-methoxyphenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione 3p**

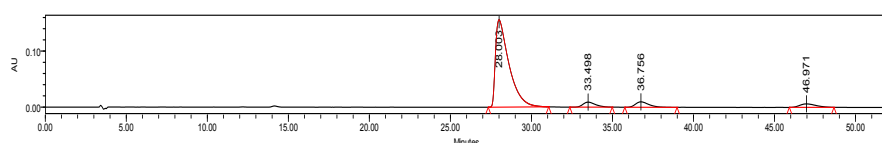


Yield: 34.5 mg (83%), white amorphous solid, 91:9 dr [determined by the ratio of area at  $\delta$  6.01 (d,  $J$  = 11.6 Hz, 0.09H) and  $\delta$  5.80 (d,  $J$  = 11.2 Hz, 0.91H) in  $^1\text{H NMR}$  ], 90% ee;  $[\alpha]^{28.0}_{\text{D}} = 73.0$  ( $c$  = 0.53,  $\text{CH}_2\text{Cl}_2$ );

HPLC (Daicel chiralcel IE,  $n$ -hexane/  $i$ -PrOH 80/20, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 27.72$  min,  $t_{\text{R}(\text{minor})} = 32.55$  min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.80 – 7.57 (m, 4H), 7.44 – 7.35 (m, 4H), 7.17 – 7.13 (m, 1H), 6.80 (d,  $J$  = 11.2 Hz, 0.09H), 6.60 (d,  $J$  = 11.2 Hz, 0.91H), 6.01 (d,  $J$  = 11.6 Hz, 0.09H), 5.80 (d,  $J$  = 11.2 Hz, 0.91H), 3.87 (s, 3H), 2.75 – 2.51 (m, 4H),  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.9, 160.0, 136.7, 135.1, 128.9, 120.6, 113.2, 57.4, 55.5, 44.6, 28.0. ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{78,9183}\text{BrNO}_4 + \text{Na}^+]$  38.0312, found 438.0316; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{80,9163}\text{BrNO}_4 + \text{Na}^+]$  440.0291, found 440.0294.

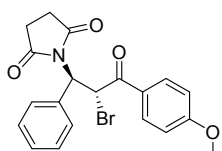


	Retention Time	% Area
1	27.719	44.61
2	32.549	44.99
3	36.461	5.49
4	46.478	4.92

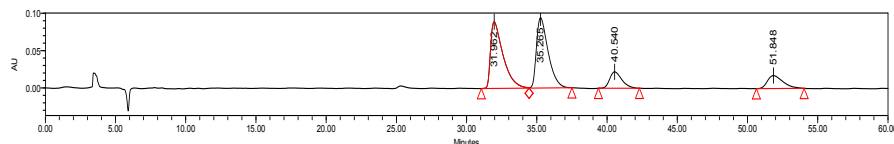


	Retention Time	% Area
1	28.003	86.09
2	33.498	4.50
3	36.756	5.29
4	46.971	4.12

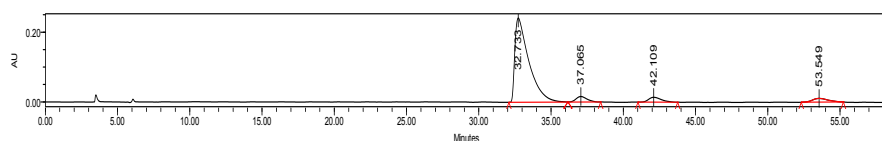
### 1-((1*R*,2*R*)-2-Bromo-3-(4-methoxyphenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione **3q**



Yield: 36.1 mg (87%), white amorphous solid, 92:8 dr [determined by the ratio of area at  $\delta$  6.02 (d,  $J$  = 11.2 Hz, 0.08H) and  $\delta$  5.82 (d,  $J$  = 11.2 Hz, 0.92H) in  $^1\text{H}$  NMR], 91% ee;  $[\alpha]^{24.9}_{\text{D}} = 40.6$  ( $c$  = 0.66,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/ *i*-PrOH 80/20, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 31.96 min,  $t_{\text{R(minor)}}$  = 35.27 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J$  = 8.8 Hz 1.84H), 7.94 (d,  $J$  = 8.8 Hz 0.16H), 7.67 – 7.53 (m, 2H), 7.42 – 7.35 (m, 2.76H), 7.23 – 7.21 (m, 0.24H), 6.97 (d,  $J$  = 9.2 Hz, 1.84H), 6.92 (d,  $J$  = 8.8 Hz, 0.16H), 6.79 (d,  $J$  = 13.2 Hz, 0.08H), 6.61 (d,  $J$  = 11.2 Hz, 0.92H), 6.02 (d,  $J$  = 11.2 Hz, 0.08H), 5.82 (d,  $J$  = 11.2 Hz, 0.92H), 3.89 (s, 3H), 2.74-2.45 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.5, 176.7, 164.3, 136.8, 131.4, 129.1, 128.9, 128.8, 126.6, 114.2, 57.5, 55.6, 44.3, 28.0. ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{78,9183}\text{BrNO}_4 + \text{Na}^+]$  438.0312, found 438.0304 ; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{80,9163}\text{BrNO}_4 + \text{Na}^+]$  440.0291, found 440.0284.



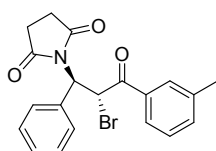
	Retention Time	% Area
1	31.962	40.49
2	35.265	39.98
3	40.540	9.70
4	51.848	9.83



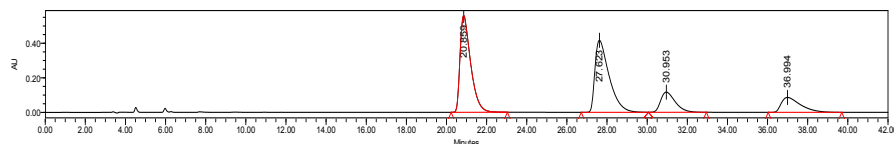
	Retention Time	% Area
1	32.733	86.71
2	37.065	4.49
3	42.109	4.50
4	53.549	4.30

### 1-((1*R*,2*R*)-2-Bromo-3-oxo-1-phenyl-3-(*m*-tolyl)propyl)pyrrolidine-2,5-dione

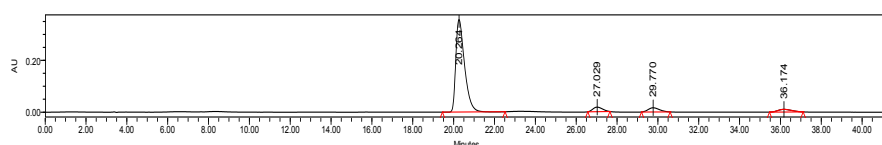
**3r**



Yield: 33.9 mg (85%), white amorphous solid, 90/10 dr [determined by ratio of area at  $\delta$  6.02 (d,  $J = 11.6$  Hz, 0.10H) and  $\delta$  5.81 (d,  $J = 11.2$  Hz, 0.90H) in  $^1\text{H NMR}$ ], 91% ee;  $[\alpha]^{28.0}_{\text{D}} = 187.5$  ( $c = 0.10$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}} = 20.86$  min,  $t_{\text{R(minor)}} = 27.62$  min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.85 - 7.74$  (m, 2H), 7.67 - 7.54 (m, 2H), 7.43 - 7.35 (m, 4.70H), 7.24 - 7.21 (m, 0.30H), 6.81 (d,  $J = 11.2$  Hz, 0.10H), 6.61 (d,  $J = 10.8$  Hz, 0.90H), 6.02 (d,  $J = 11.6$  Hz, 0.10H), 5.81 (d,  $J = 11.2$  Hz, 0.90H), 2.74 - 2.49 (m, 4H), 2.43(s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 192.2, 138.8, 136.7, 134.9, 133.8, 129.0, 128.8, 1126.2, 100.0, 57.4, 44.6, 28.0, 21.2$ . ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{78,9183}\text{BrNO}_3 + \text{Na}^+]$  422.0363, found 422.0368; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{118}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  424.0342, found 424.0358.



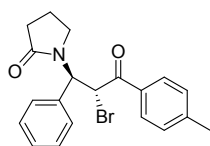
	Retention Time	% Area
1	20.859	38.97
2	27.623	38.88
3	30.953	11.23
4	36.994	10.92



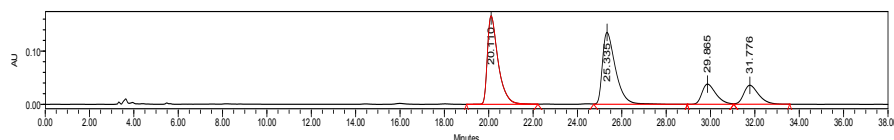
	Retention Time	% Area
1	20.264	86.45
2	27.029	4.66
3	29.770	5.00
4	36.174	3.89

**1-((1*R*,2*R*)-2-Bromo-3-oxo-1-phenyl-3-(*p*-tolyl)propyl)pyrrolidine-2,5-dione**

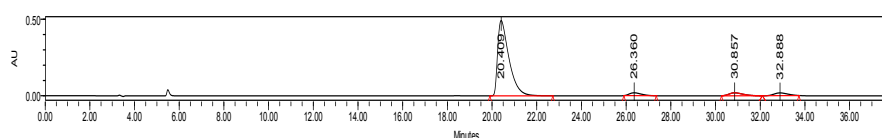
**3s**



Yield: 34.2 mg (86%), white amorphous solid, 90:10 dr [determined by ratio of area at  $\delta$  6.01 (d,  $J$  = 11.6 Hz, 0.10H) and  $\delta$  5.81 (d,  $J$  = 11.2 Hz, 0.90H) in  $^1\text{H}$  NMR ], 91% ee;  $[\alpha]^{24.9}_{\text{D}}$  = 53.8 ( $c$  = 0.60,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 20.11 min,  $t_{\text{R(minor)}}$  = 25.34 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.94 (d,  $J$  = 8.0 Hz, 1.80H), 7.84 (d,  $J$  = 8.4 Hz, 0.20H), 7.67 – 7.65 (m, 2H), 7.39 – 7.29 (m, 4.6H), 7.23 – 7.20 (t, 0.4H), 6.80 (d,  $J$  = 11.2 Hz, 0.10H), 6.61 (d,  $J$  = 11.2 Hz, 0.90H), 6.01 (d,  $J$  = 11.6 Hz, 0.10H), 5.81 (d,  $J$  = 11.2 Hz, 0.90H), 2.58 – 2.49 (m, 4H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.6, 176.7, 145.1, 136.8, 131.3, 129.6, 129.1, 128.9, 128.8, 57.4, 44.5, 28.0, 21.8. ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{78,91}\text{BrNO}_3 + \text{Na}^+]$  422.0363, found 422.0371; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{18}^{80,91}\text{BrNO}_3 + \text{Na}^+]$  424.0342, found 424.0352.

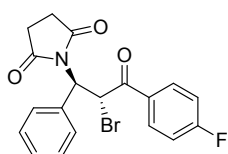


	Retention Time	% Area
1	20.110	38.57
2	25.335	38.34
3	29.865	11.55
4	31.776	11.54

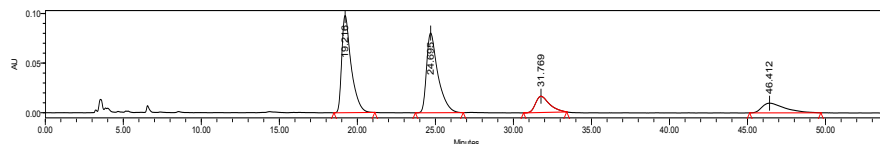


	Retention Time	% Area
1	20.409	88.42
2	26.360	3.60
3	30.857	4.18
4	32.888	3.80

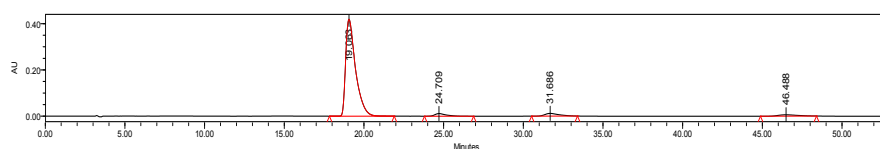
**1-((1*R*,2*R*)-2-Bromo-3-(4-fluorophenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione 3t**



Yield: 32.6 mg (81%), white amorphous solid, 92:8 dr [determined by the ratio of area of  $\delta$  6.00 (d,  $J = 11.6$  Hz, 0.08H) and  $\delta$  5.79 (d,  $J = 11.2$  Hz, 0.92H) in  $^1\text{H NMR}$ ], 93% ee;  $[\alpha]^{24.9}_{\text{D}} = 43.8$  ( $c = 0.27$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 19.22 min,  $t_{\text{R(minor)}}$  = 24.71 min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.09 – 7.96(m, 2H), 7.65 – 7.39 (m, 5H), 7.23 – 7.10 (m, 2H), 6.78 (d,  $J = 11.6$  Hz, 0.08H), 6.58 (d,  $J = 10.8$  Hz, 0.92H), 6.00 (d,  $J = 11.6$  Hz, 0.08H), 5.79 (d,  $J = 11.2$  Hz, 0.92H), 2.75 – 2.49 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.5, 167.5, 165.0, 136.7, 131.8, 128.9, 116.3, 116.0, 57.5, 44.5, 28.0. ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78,9183}\text{BrFNO}_3+\text{Na}^+]$  426.0112, found 426.0116; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80,9163}\text{BrClNO}_3+\text{Na}^+]$  428.0092, found 428.0096.

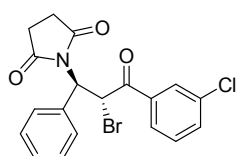


	Retention Time	% Area
1	19.216	40.36
2	24.695	39.88
3	31.769	9.99
4	46.412	9.78



	Retention Time	% Area
1	19.063	91.09
2	24.709	2.87
3	31.686	3.61
4	46.488	2.43

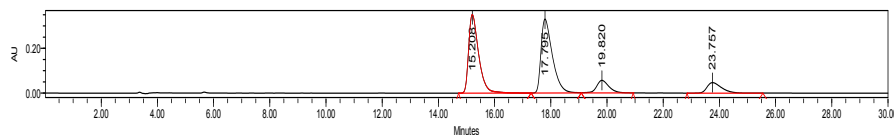
**1-((1R,2R)-2-Bromo-3-(3-chlorophenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione **3u****



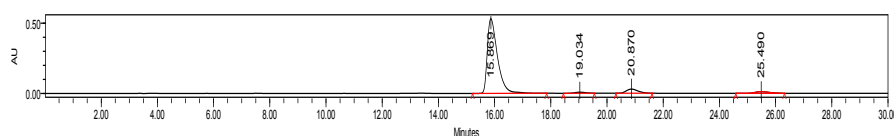
Yield: 33.4 mg (80%), white amorphous solid, 92:8 dr [determined by the ratio of area at  $\delta$  6.00 (d,  $J$  = 11.2 Hz, 0.08H) and  $\delta$  5.77 (d,  $J$  = 11.2 Hz, 0.92H) in  $^1\text{H}$  NMR], 97% ee;  $[\alpha]^{24.9}_{\text{D}} = 80.7$  ( $c$  = 0.27,  $\text{CH}_2\text{Cl}_2$ );

HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 15.21$  min,  $t_{\text{R}(\text{minor})} = 17.80$  min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.00 (s, 1H), 7.93 – 7.08 (m, 4H), 7.48 – 7.24 (m, 4H), 6.75 (d,  $J$  = 11.6 Hz, 0.08H), 6.55 (d,  $J$  = 10.8 Hz, 0.92H), 6.00 (d,  $J$  = 11.2 Hz, 0.08H), 5.77 (d,  $J$  = 11.2 Hz, 0.92H), 2.76 – 2.56 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.7, 176.7, 136.5, 135.4, 135.3, 133.9, 130.2, 129.1, 128.9, 127.0, 57.5, 44.7, 28.0. ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78,9183}\text{BrClNO}_3+\text{Na}^+]$  441.9817, found 441.9818; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80,9163}\text{BrClNO}_3+\text{Na}^+]$  443.9796, found 443.9792.



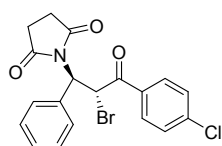


	Retention Time	% Area
1	15.208	40.69
2	17.795	43.42
3	19.820	7.97
4	23.757	7.92

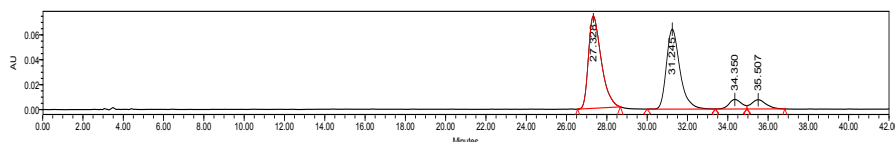


	Retention Time	% Area
1	15.869	90.22
2	19.034	1.22
3	20.870	5.77
4	25.490	2.79

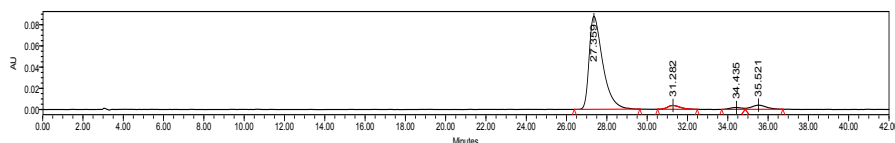
**1-((1*R*,2*R*)-2-Bromo-3-(4-chlorophenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione 3v**



Yield: 34.7 mg (83%), white amorphous solid, 91/9 dr [determined by the ratio of area at  $\delta$  5.99 (d,  $J = 11.2$  Hz, 0.09H) and 5.78 (d,  $J = 11.2$  Hz, 0.91H) in  $^1\text{H NMR}$ ], 92% ee;  $[\alpha]^{24.9}_{\text{D}} = 51.1$  ( $c = 0.57$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 27.33 min,  $t_{\text{R(minor)}}$  = 31.25 min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.98 (d,  $J = 8.4$  Hz, 1.82H), 7.88 (d,  $J = 8.4$  Hz, 0.18H), 7.65 – 7.46 (m, 4H), 7.41 – 7.38 (m, 2.73H), 7.23 (d, 0.27H), 6.76 (d,  $J = 11.6$  Hz, 0.09H), 6.56 (d,  $J = 11.2$  Hz, 0.91H), 5.99 (d,  $J = 11.2$  Hz, 0.09H), 5.78 (d,  $J = 11.2$  Hz, 0.91H), 2.74 – 2.48 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.8, 176.7, 140.5, 136.6, 132.1, 130.3, 129.3, 129.0, 128.9, 57.5, 44.5, 28.0. ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78,9183}\text{BrClNO}_3 + \text{Na}^+]$  441.9817, found 441.9822; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80,9163}\text{BrClNO}_3 + \text{Na}^+]$  443.9796, found 443.9801.

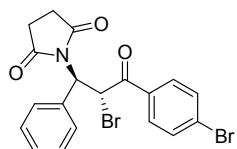


	Retention Time	% Area
1	27.328	46.87
2	31.245	42.87
3	34.350	4.84
4	35.507	5.42

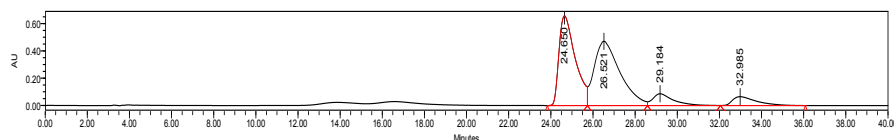


	Retention Time	% Area
1	27.359	90.42
2	31.282	3.49
3	34.435	1.62
4	35.521	4.46

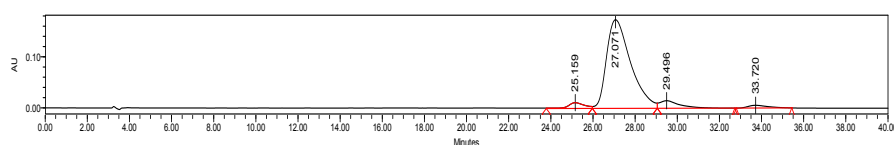
### 1-((1*R*,2*R*)-2-Bromo-3-(4-bromophenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione **3w**



Yield: 36.5 mg (79%), white amorphous solid, 91/9 dr [determined by the ratio of area at  $\delta$  5.99 (d,  $J = 11.6$  Hz, 0.09H) and 5.77 (d,  $J = 11.2$  Hz, 0.91H) in  $^1\text{H NMR}$ ], 90% ee;  $[\alpha]^{24.6}_{\text{D}} = 57.3$  ( $c = 0.45$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}(\text{major})} = 26.52$  min,  $t_{\text{R}(\text{minor})} = 24.65$  min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.90$  (d,  $J = 8.8$  Hz, 1.82H), 7.79 (d,  $J = 8.4$  Hz, 0.18H), 7.65 – 7.52 (m, 4H), 7.41 – 7.38 (m, 2.73H), 7.23 (d, 0.23H), 6.76 (d,  $J = 11.6$  Hz, 0.09H), 6.56 (d,  $J = 11.2$  Hz, 0.91H), 5.99 (d,  $J = 11.6$  Hz, 0.09H), 5.77 (d,  $J = 11.2$  Hz, 0.91H), 2.74 – 2.47 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 191.0, 176.8, 136.6, 132.5, 132.3, 130.4, 129.4, 129.1, 129.0, 128.9, 57.5, 44.6, 28.0$ . ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78.9183}\text{Br}_2\text{NO}_3 + \text{Na}^+]$  485.9311, found 485.9313; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{78.9183}\text{Br}^{80.9163}\text{BrNO}_3 + \text{Na}^+]$  487.9291, found 487.9291; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80.9163}\text{Br}_2\text{NO}_3 + \text{Na}^+]$  489.9270, found 489.9275.

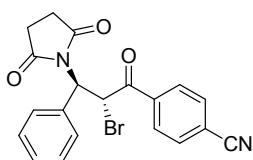


	Retention Time	% Area
1	24.650	40.76
2	26.521	46.43
3	29.184	6.86
4	32.985	5.96



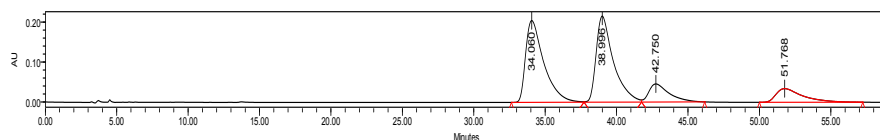
	Retention Time	% Area
1	25.159	3.63
2	27.071	88.23
3	29.496	5.89
4	33.720	2.25

**4-((2R,3R)-2-Bromo-3-(2,5-dioxopyrrolidin-1-yl)-3-phenylpropanoyl)benzotrile 3x**

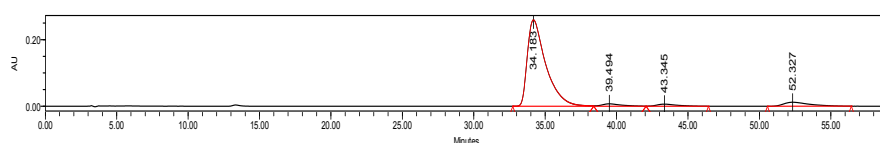


Yield: 29.5 mg (72%), white amorphous solid, 92:8 dr [determined by the ratio of area at  $\delta$  5.98 (d,  $J$  = 11.2 Hz, 0.08H) and  $\delta$  5.76 (d,  $J$  = 11.2 Hz, 0.92H) in  $^1\text{H}$  NMR], 94% ee;  $[\alpha]^{24.9}_{\text{D}}$  = 103.7 ( $c$  = 0.38,  $\text{CH}_2\text{Cl}_2$ );

HPLC (Daicel chiralcel ID, *n*-hexane /*i*-PrOH 85/15, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 34.06 min,  $t_{\text{R(minor)}}$  = 39.00 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.13 (d,  $J$  = 8.4 Hz, 1.84H), 8.02 (d,  $J$  = 8.4 Hz, 0.16H), 7.81 (d,  $J$  = 8.4 Hz, 1.84H), 7.75 (d,  $J$  = 8.4 Hz, 0.16H), 7.63 – 7.61 (m, 2H), 7.42 – 7.38 (m, 2.76H), 7.25 – 7.24 (m, 0.24H), 6.78 (d,  $J$  = 11.6 Hz, 0.08H), 6.57 (d,  $J$  = 10.8 Hz, 0.92H), 5.98 (d,  $J$  = 11.2 Hz, 0.08H), 5.76 (d,  $J$  = 11.2 Hz, 0.92H), 2.76 – 2.53 (m, 4H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.7, 176.9, 137.1, 136.4, 132.7, 129.3, 129.2, 129.0, 128.8, 117.8, 111.7, 57.6, 45.0, 28.0. ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{15}^{78.9183}\text{BrN}_2\text{O}_3+\text{Na}^+]$  433.0159, found 433.0162; ESI-HRMS: calcd for  $[\text{C}_{20}\text{H}_{15}^{80.9163}\text{BrN}_2\text{O}_3+\text{Na}^+]$  435.0138, found 435.0138.

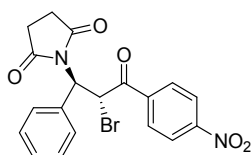


	Retention Time	% Area
1	34.060	40.19
2	38.996	40.13
3	42.750	9.84
4	51.768	9.83

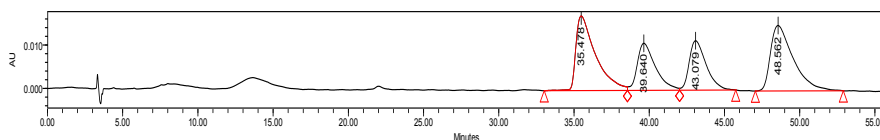


	Retention Time	% Area
1	34.183	89.26
2	39.494	2.61
3	43.345	2.32
4	52.327	5.81

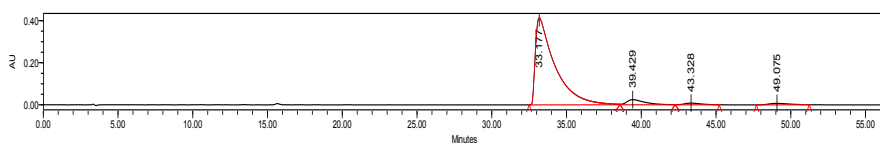
### 1-((1*R*,2*R*)-2-Bromo-3-(4-nitrophenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione **3y**



Yield: 32.2mg (75%), white amorphous solid, 91/9 dr [determined by ratio of area at  $\delta$  5.99 (d,  $J = 11.6$  Hz, 0.09H) and  $\delta$  5.76 (d,  $J = 11.2$  Hz, 0.91H) in  $^1\text{H NMR}$ ], 92% ee;  $[\alpha]^{28.0}_{\text{D}} = 63.2$  ( $c = 0.74$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}} = 35.49$  min,  $t_{\text{R(minor)}} = 48.56$  min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.37 - 8.28$  (m, 2H), 8.22 - 8.08 (m, 2H), 7.64 - 7.54 (m, 2H), 7.44 - 7.37 (m, 2.79H), 7.25 (d, 0.21H), 6.81 (d,  $J = 11.6$  Hz 0.09H), 6.59 (d,  $J = 11.2$  Hz, 0.91H), 5.99 (d,  $J = 11.6$  Hz, 0.09H), 5.76 (d,  $J = 11.2$  Hz, 0.91H), 2.78 - 2.55 (m, 4H),  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 191.3, 176.6, 148.2, 143.4, 133.5, 130.0, 129.0, 124.1, 56.6, 43.3, 28.0$ . ESI-HRMS calcd for  $[\text{C}_{19}\text{H}_{15}^{78.9183}\text{BrN}_2\text{O}_5 + \text{Na}^+]$  453.0057, found 453.0067; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{15}^{80.9163}\text{BrN}_2\text{O}_5 + \text{Na}^+]$  455.0037, found 455.0045.

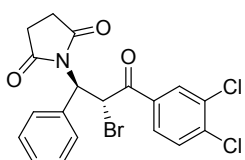


	Retention Time	% Area
1	35.478	31.57
2	39.640	18.41
3	43.079	18.00
4	48.562	32.02

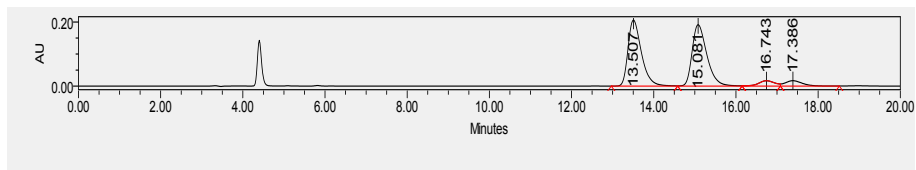


	Retention Time	% Area
1	33.177	91.89
2	39.429	5.11
3	43.328	1.45
4	49.075	1.55

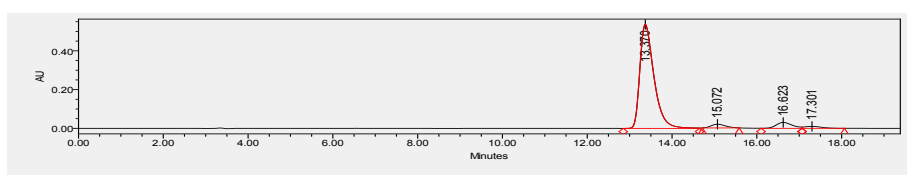
### 1-((1*R*,2*R*)-2-Bromo-3-(3,4-dichlorophenyl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione **3z**



Yield: 34.5 mg (76%), white amorphous solid, 93:7 dr [determined by the ratio of area at  $\delta$  5.98 (d,  $J$  = 11.2 Hz, 0.07H)) and  $\delta$  5.75 (d,  $J$  = 11.2 Hz, 0.93H) in  $^1\text{H}$  NMR], 92% ee;  $[\alpha]^{24.6}_{\text{D}} = 74.0$  ( $c$  = 0.48,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 13.51 min,  $t_{\text{R(minor)}}$  = 15.08 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.11 (d,  $J$  = 2.0 Hz, 0.93H), 8.00 (d,  $J$  = 2.4 Hz, 0.07H), 7.88 – 7.75 (m, 1H), 7.64 – 7.37 (m, 5.79H), 7.25 – 7.24 (t, 0.21H), 6.72 (d,  $J$  = 11.6 Hz, 0.07H), 6.50 (d,  $J$  = 11.2 Hz, 0.93H), 5.98 (d,  $J$  = 11.2 Hz, 0.07H), 5.75 (d,  $J$  = 11.2 Hz, 0.93H) 2.76 – 2.52 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 189.8, 176.8, 138.7, 136.5, 133.7, 133.3, 131.0, 130.8, 129.1, 129.0, 128.9, 127.9, 57.5, 44.7, 28.0. ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{14}^{78.9183}\text{BrCl}_2\text{NO}_3+\text{Na}^+]$  475.9427, found 475.9424; ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{14}^{80.9163}\text{BrCl}_2\text{NO}_3+\text{Na}^+]$  477.9406, found 477.9389.

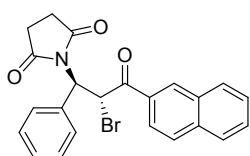


	Retention Time	% Area
1	13.507	45.02
2	15.081	45.87
3	16.743	4.38
4	17.386	4.72

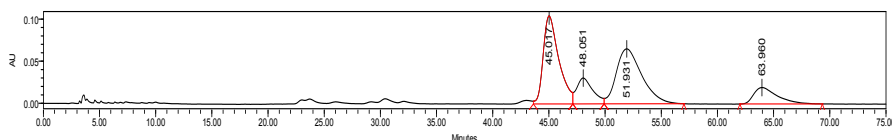


	Retention Time	% Area
1	13.370	89.07
2	15.072	3.16
3	16.623	5.78
4	17.301	1.98

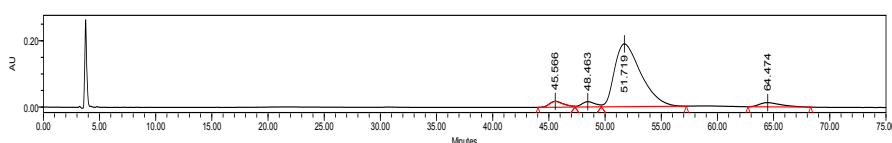
### 1-((1*R*,2*R*)-2-Bromo-3-(naphthalen-2-yl)-3-oxo-1-phenylpropyl)pyrrolidine-2,5-dione **3aa**



Yield: 35.7 mg (82%), white amorphous solid, 91:9 dr [determined by the ratio of area at  $\delta$  6.10 (d,  $J$  = 11.6 Hz, 0.09H) and  $\delta$  5.88 (d,  $J$  = 11.2 Hz, 0.91H) in  $^1\text{H NMR}$ ], 91% ee;  $[\alpha]^{24.9}_{\text{D}} = 9.6$  ( $c = 0.36$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 48.05 min,  $t_{\text{R(minor)}}$  = 45.02 min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.60 (s, 1H), 8.06 – 7.70 (m, 6H), 7.62 – 7.50 (m, 2H), 7.43 – 7.36 (m, 2.73H), 7.24 – 7.19 (m, 0.26H), 7.00 (d,  $J$  = 11.6 Hz, 0.09H), 6.81 (d,  $J$  = 11.2 Hz, 0.91H), 6.10 (d,  $J$  = 11.6 Hz, 0.09H), 5.88 (d,  $J$  = 11.2 Hz, 0.91H), 2.73 – 2.47 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.0, 176.8, 136.8, 136.0, 132.5, 131.1, 130.9, 129.9, 129.0, 128.9, 127.8, 127.0, 124.2, 57.5, 44.6, 28.0. ESI-HRMS: calcd for  $[\text{C}_{23}\text{H}_{18}^{78,9183}\text{BrNO}_3 + \text{Na}^+]$  458.0363, found 458.0371; ESI-HRMS: calcd for  $[\text{C}_{23}\text{H}_{18}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  460.0342, found 460.0343.

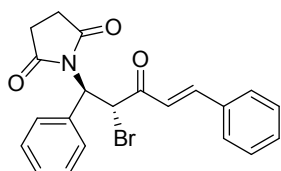


	Retention Time	% Area
1	45.017	38.28
2	48.051	11.69
3	51.931	39.16
4	63.960	10.87

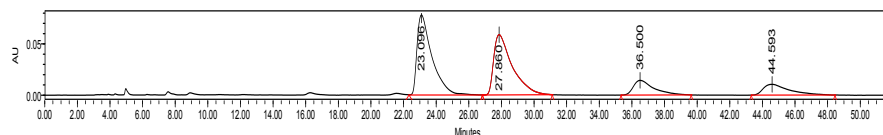


	Retention Time	% Area
1	45.566	4.46
2	48.463	3.82
3	51.719	86.87
4	64.474	4.85

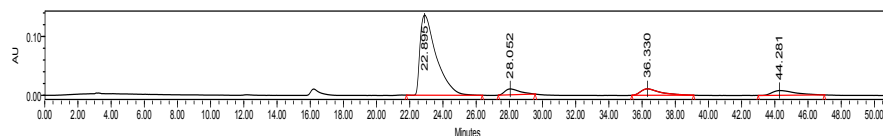
**1-((1R,2R,E)-2-Bromo-3-oxo-1,5-diphenylpent-4-en-1-yl)pyrrolidine-2,5-dione **3ab****



Yield: 34.5 mg (84%), white amorphous solid, 85/15 dr [determined by ratio of area at  $\delta$  5.87 (d,  $J$  = 12.0 Hz, 0.15H) and  $\delta$  5.72 (d,  $J$  = 11.2 Hz, 0.85H) in  $^1\text{H}$  NMR], 86% ee;  $[\alpha]^{24.6}_{\text{D}} = 56.4$  ( $c = 0.57$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel ID,  $n$ -hexane/ $i$ -PrOH 85/15, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 23.10 min,  $t_{\text{R(minor)}}$  = 27.86 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d, 1H), 7.61 – 7.36 (m, 10H), 6.92 (d,  $J$  = 16.0 Hz, 0.85H), 6.82 (d,  $J$  = 16.0 Hz, 0.15H), 6.21 (d,  $J$  = 11.6 Hz, 0.15H), 6.01 (d,  $J$  = 11.6 Hz, 0.85H), 5.87 (d,  $J$  = 12.0 Hz, 0.15H), 5.72 (d,  $J$  = 11.2 Hz, 0.85H), 2.74 – 2.55 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.0, 176.6, 145.5, 131.2, 128.9, 128.8, 122.4, 57.2, 48.4, 28.0. ESI-HRMS: calcd for  $[\text{C}_{21}\text{H}_{18}^{78,9183}\text{BrNO}_3 + \text{Na}^+]$  434.0363, found 434.0371; ESI-HRMS: calcd for  $[\text{C}_{21}\text{H}_{18}^{80,9163}\text{BrNO}_3 + \text{Na}^+]$  436.0342, found 436.0354.



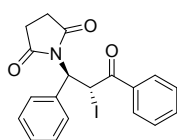
	Retention Time	% Area
1	23.096	41.42
2	27.860	38.53
3	36.500	10.38
4	44.593	9.67



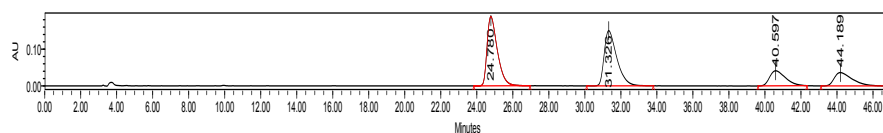
	Retention Time	% Area
1	22.895	80.02
2	28.052	5.40
3	36.330	7.89
4	44.281	6.68

### 1-((1*R*,2*R*)-2-Iodo-3-oxo-1,3-diphenylpropyl)pyrrolidine-2,5-dione

4a



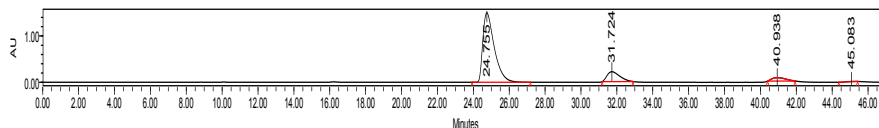
Yield: 32.5 mg (75%), white amorphous solid, 96/4 dr [determined by ratio of area at  $\delta$  6.01 (d,  $J = 11.6$  Hz, 0.04H) and  $\delta$  5.88 (d,  $J = 11.6$  Hz, 0.96H) in  $^1\text{H}$  NMR], 73% ee; HPLC (Daicel chiralcel IE, *n*-hexane/ *i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R(major)}}$  = 24.78 min,  $t_{\text{R(minor)}}$  = 31.33 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 – 7.92 (m, 2H), 7.68 – 7.37 (m, 8H), 7.10 (d,  $J = 11.6$  Hz, 0.04H), 6.85 (d,  $J = 11.6$  Hz, 0.96H), 6.01 (d,  $J = 11.6$  Hz, 0.04H), 5.88 (d,  $J = 11.6$  Hz, 0.96H), 2.76 – 2.49 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.6, 176.6, 137.5, 133.8, 133.6, 129.1, 129.0, 128.9, 128.7, 58.7, 27.9, 25.1. ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{16}\text{INO}_3 + \text{Na}^+]$  456.0068, found 456.0081.



Retention Time	% Area



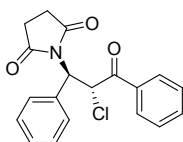
1	24.780	37.81
2	31.326	36.90
3	40.597	12.63
4	44.189	12.67



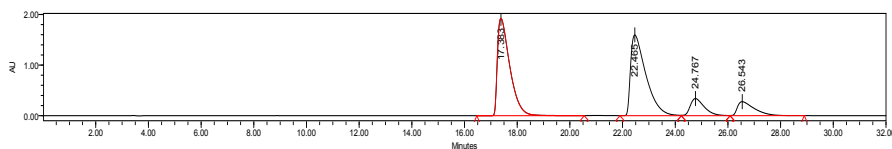
	Retention Time	% Area
1	24.755	82.07
2	31.724	12.87
3	40.938	4.83
4	45.083	0.23

### 1-((1*R*,2*R*)-2-Chloro-3-oxo-1,3-diphenylpropyl)pyrrolidine-2,5-dione

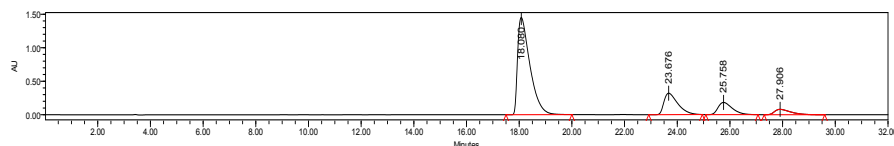
5a



Yield: 23.2 mg (68%), white amorphous solid, 85/15 dr [determined by ratio of area at  $\delta$  5.96 (d,  $J = 11.2$  Hz, 0.15H) and  $\delta$  5.71 (d,  $J = 10.8$  Hz, 0.85H) in  $^1\text{H NMR}$ ], 69% ee;  $[\alpha]^{28.0}_{\text{D}} = 55.1$  ( $c = 0.65$ ,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Daicel chiralcel IE, *n*-hexane/ *i*-PrOH 90/10, 1.0 mL/min, 254 nm)  $t_{\text{R}}(\text{major}) = 17.38$  min,  $t_{\text{R}}(\text{minor}) = 22.47$  min;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 – 8.04 (m, 2H), 7.67 – 7.45 (m, 5H), 7.40 – 7.37 (m, 2.70H), 7.23 – 7.21 (m, 0.30H), 6.72 (d,  $J = 11.6$  Hz, 0.15H), 6.60 (d,  $J = 11.2$  Hz, 0.85H), 5.96 (d,  $J = 11.2$  Hz, 0.15H), 5.71 (d,  $J = 10.8$  Hz, 0.85H), 2.75 – 2.50 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 191.9, 176.8, 136.3, 134.1, 133.8, 129.1, 129.0, 128.8, 122.4, 57.3, 53.7, 28.0$ . ESI-HRMS: calcd for  $[\text{C}_{19}\text{H}_{16}\text{ClNO}_3 + \text{Na}^+]$  364.0711, found 364.0712.



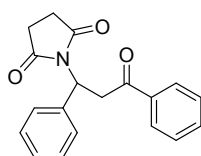
	Retention Time	% Area
1	17.383	41.24
2	22.465	42.40
3	24.767	8.23
4	26.543	8.13



	Retention Time	% Area
1	18.080	68.28
2	23.676	16.96
3	25.758	9.91
4	27.906	4.85

### 1-(3-oxo-1,3-Diphenylpropyl)pyrrolidine-2,5-dione

7



(1) without base, yield: trace; (2) base Et<sub>3</sub>N, yield: 6.45 mg (21%), ee: 75%;

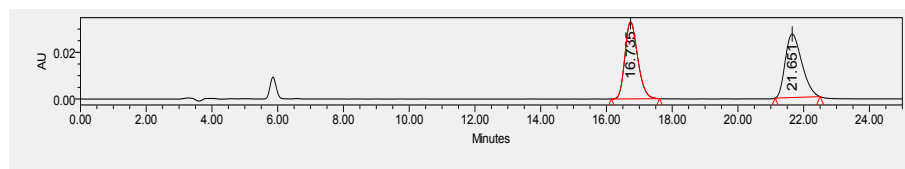
(3) base DIPA, yield: 4.6 mg (15%), ee: 33%, white amorphous solid, <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, 2H), 7.67 – 7.56 (d, 3H), 7.45 (t, 2H),

7.36 – 7.29 (m, 3H), 5.90 – 5.86 (d, 1H), 4.62 – 4.55 (d, 1H), 3.70 – 3.64 (d, 1H), 2.62 (s, 4H).

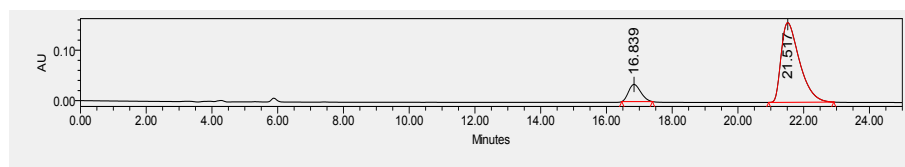
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 197.0, 177.4, 138.8, 136.4, 133.5, 128.8, 128.7, 128.3, 128.1,

128.0, 51.2, 39.2, 28.0. ESI-HRMS: calcd for [C<sub>19</sub>H<sub>16</sub>ClNO<sub>3</sub>+Na<sup>+</sup>] 330.1101, found 330.1108.



	Retention Time	% Area
1	16.735	48.40
2	21.651	51.60

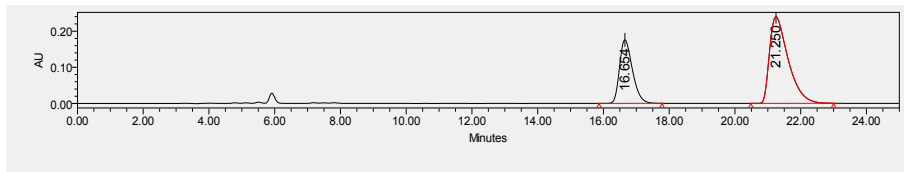
(2) base: TEA



	Retention Time	% Area
1	16.839	12.39

2	21.517	87.61
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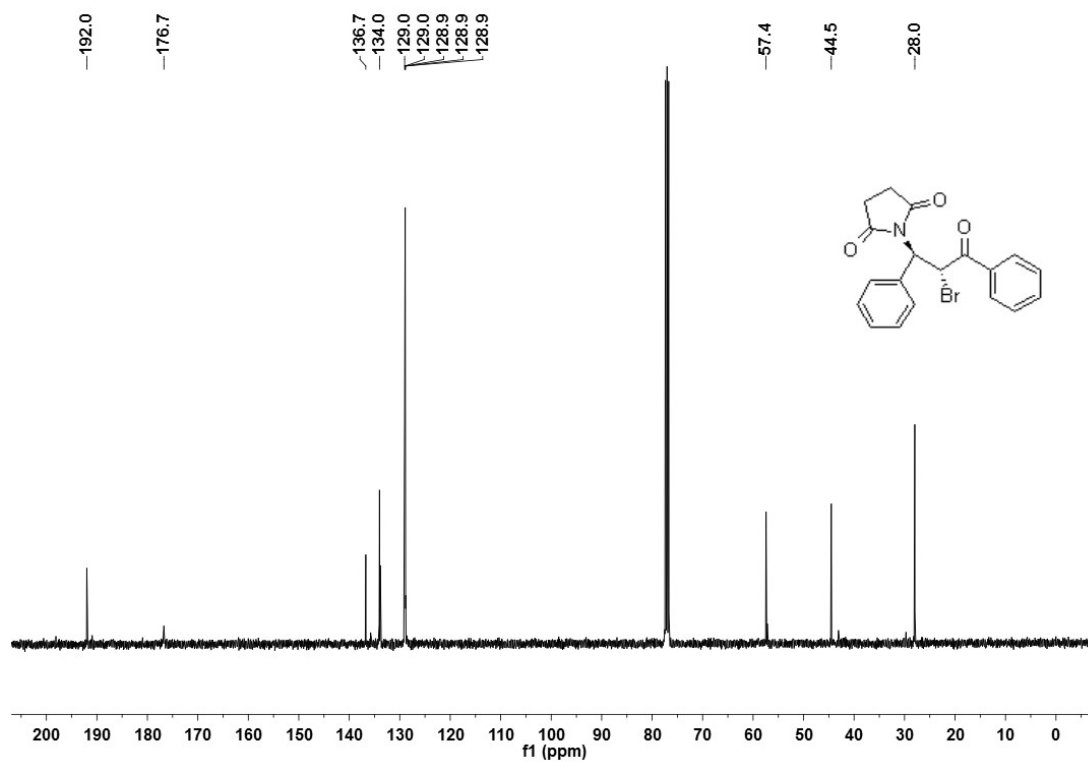
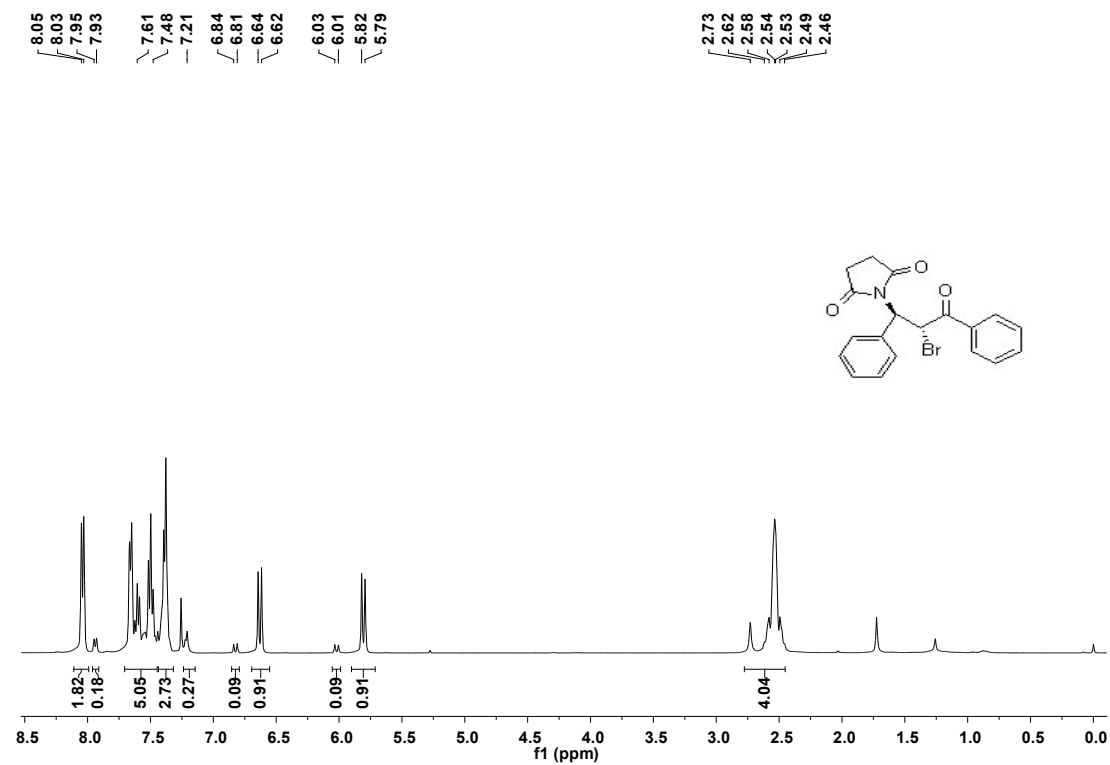
(3) base: DIPA



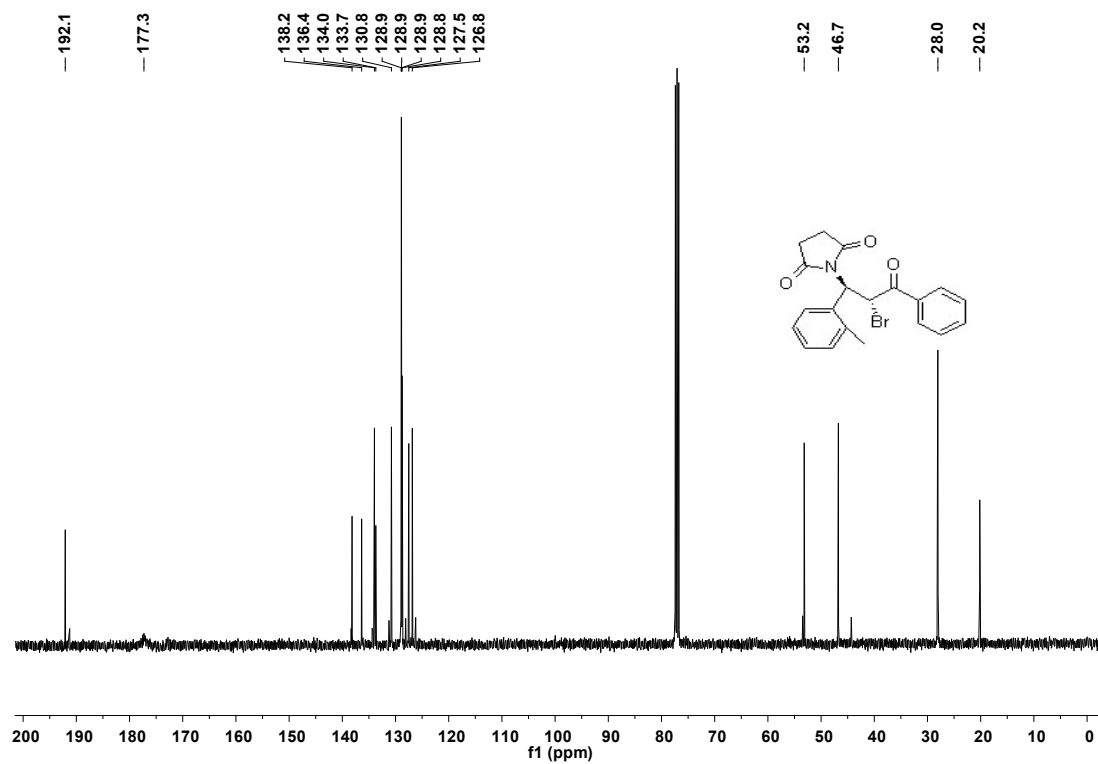
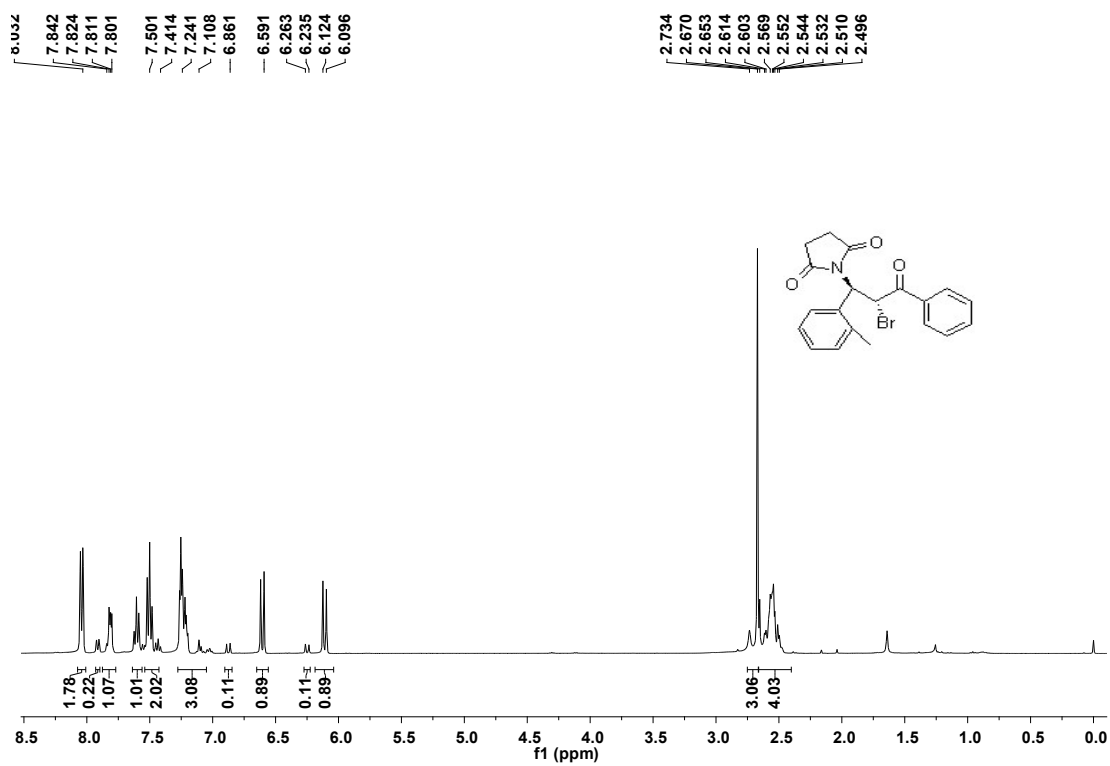
	Retention Time	% Area
1	16.654	33.78
2	21.250	66.22

## 7. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra for Product

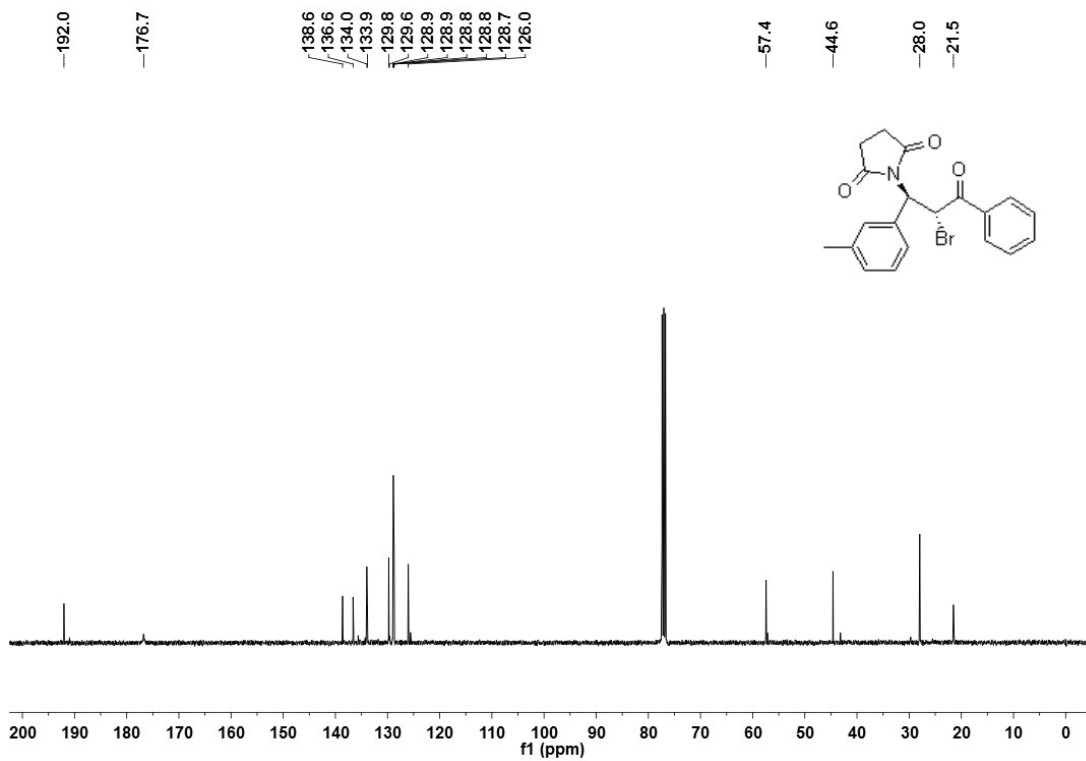
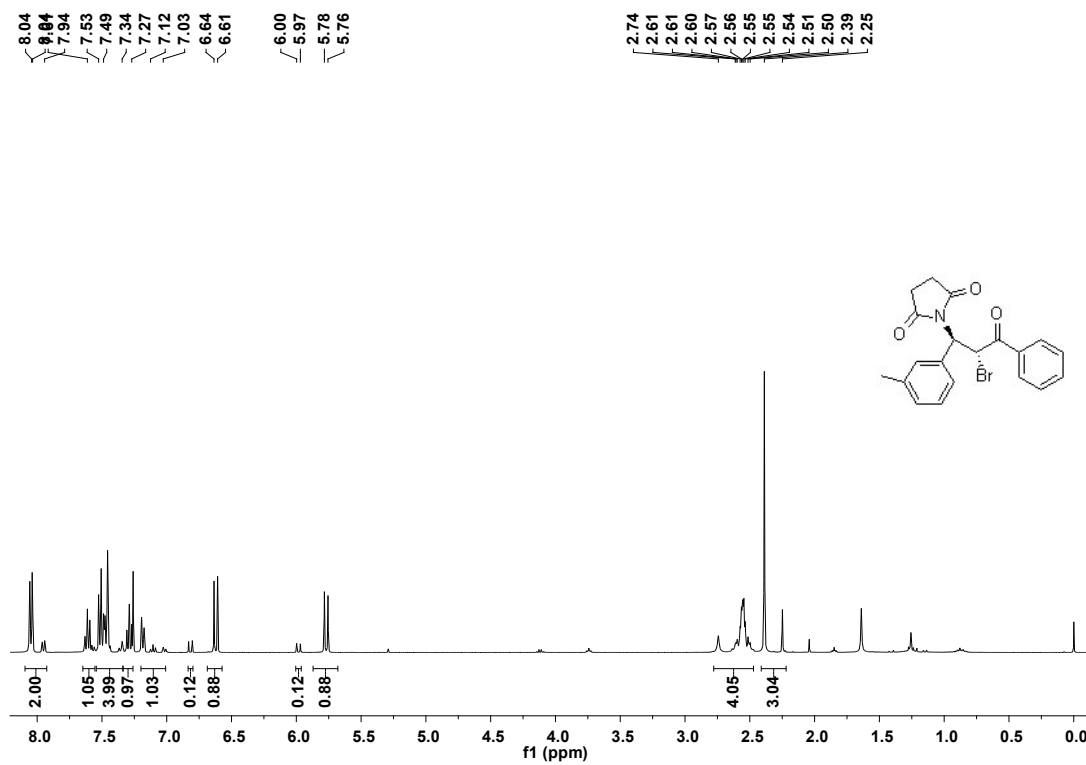
3a



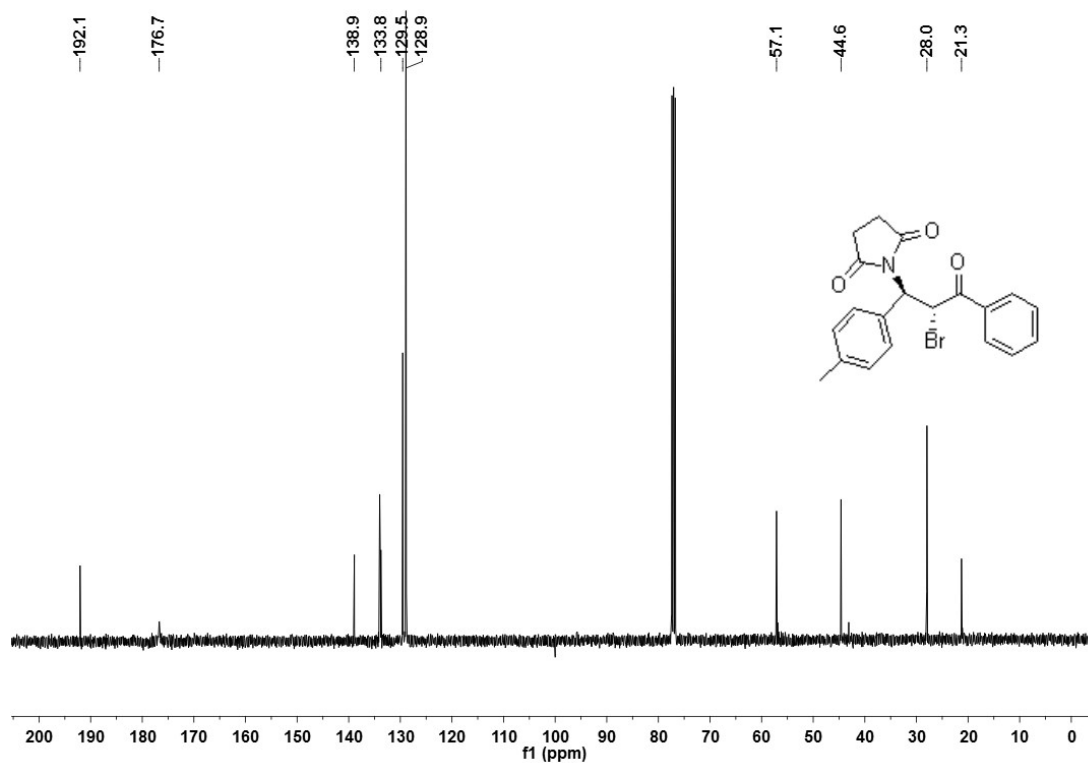
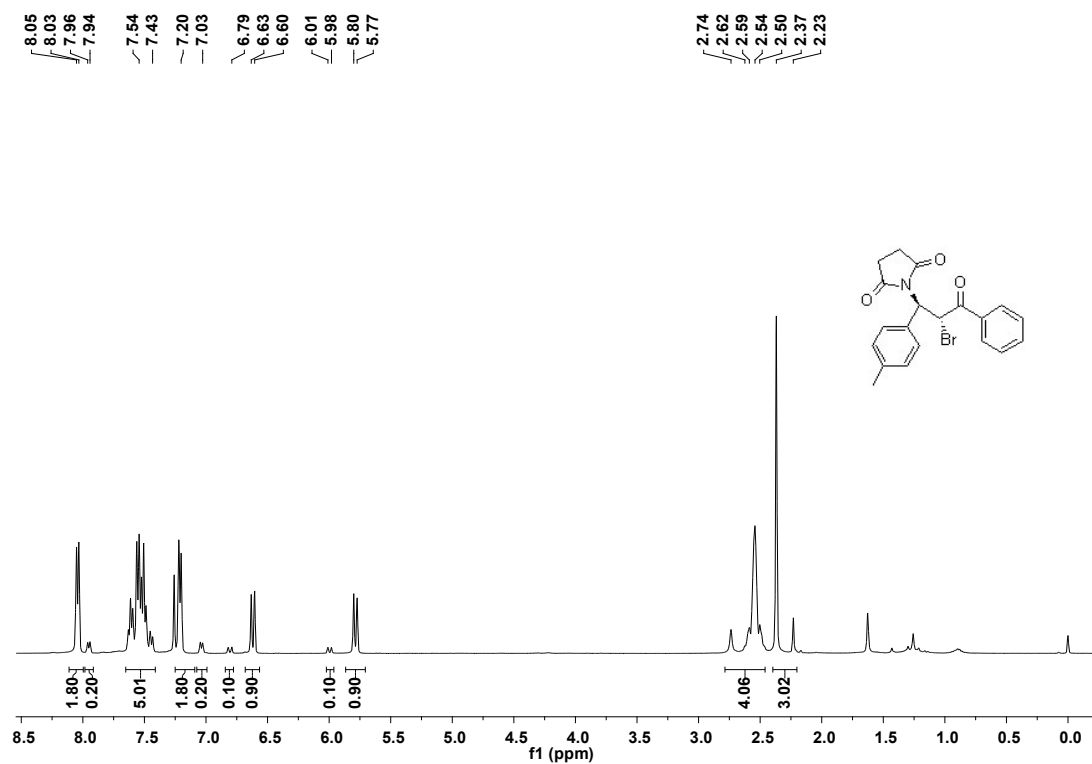
3b



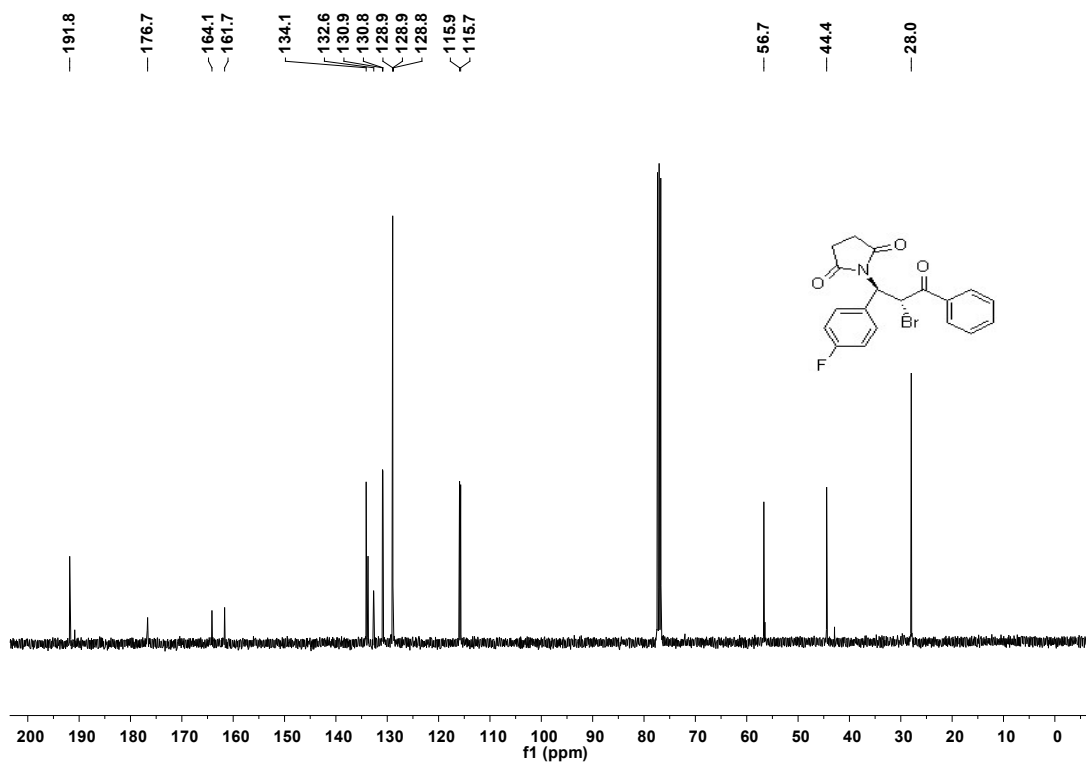
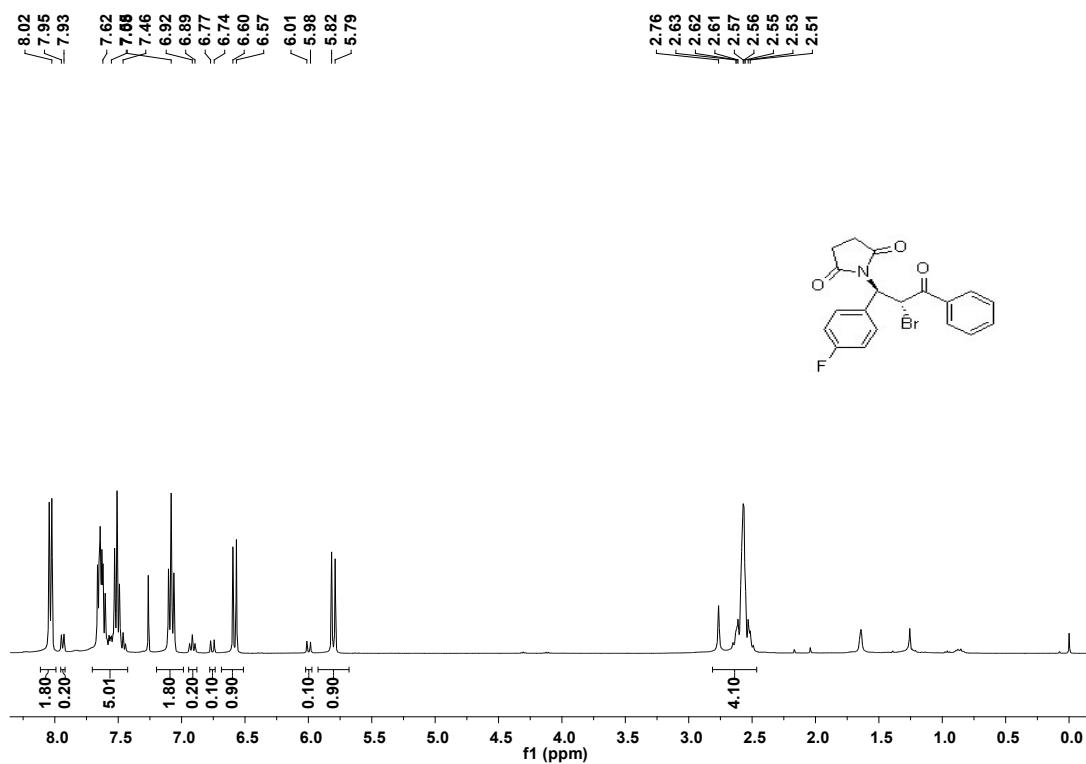
3c



3d

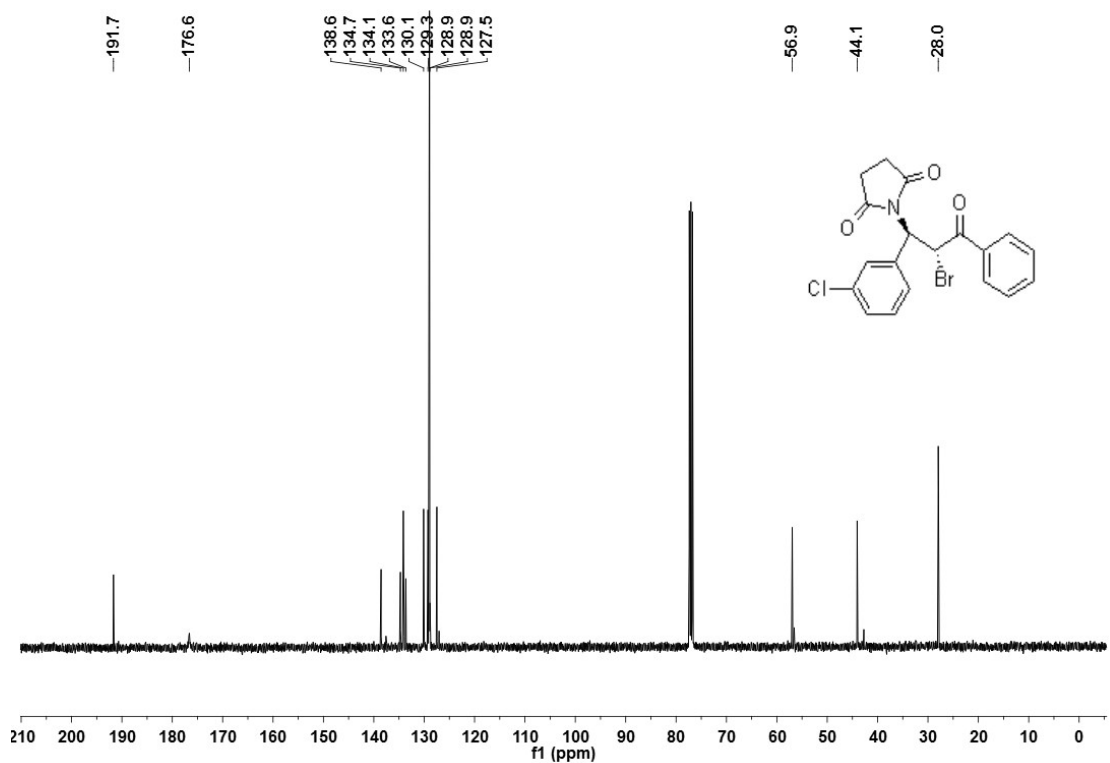
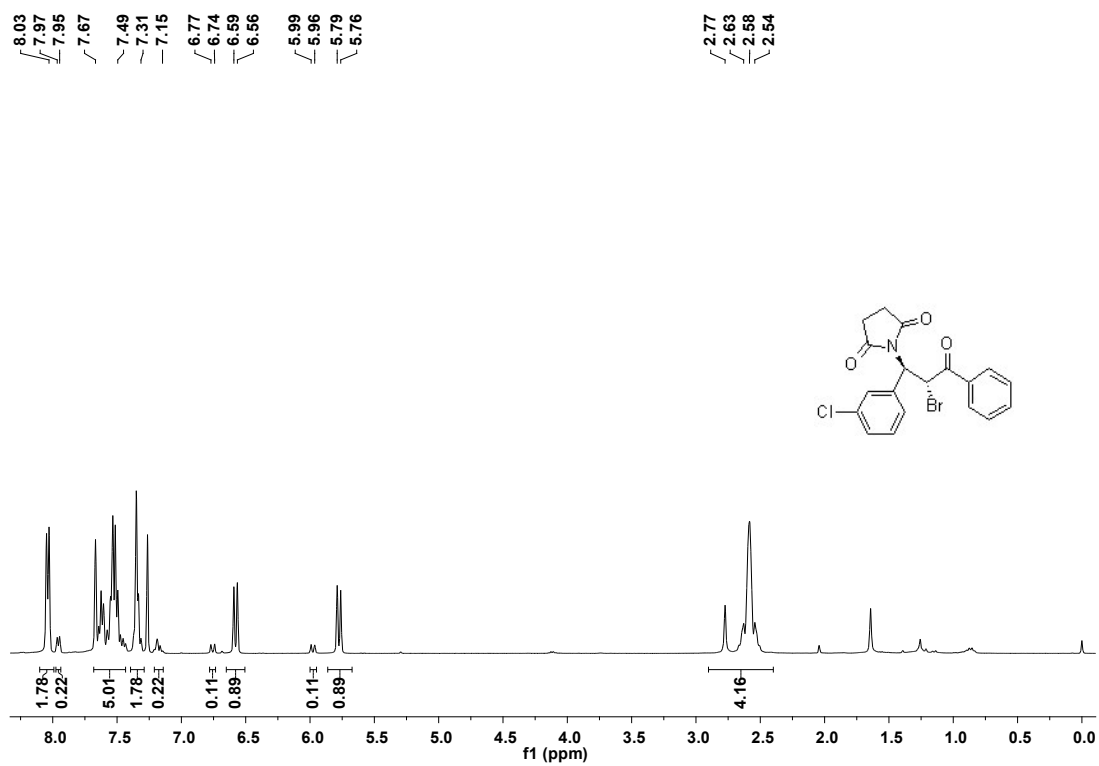


3e

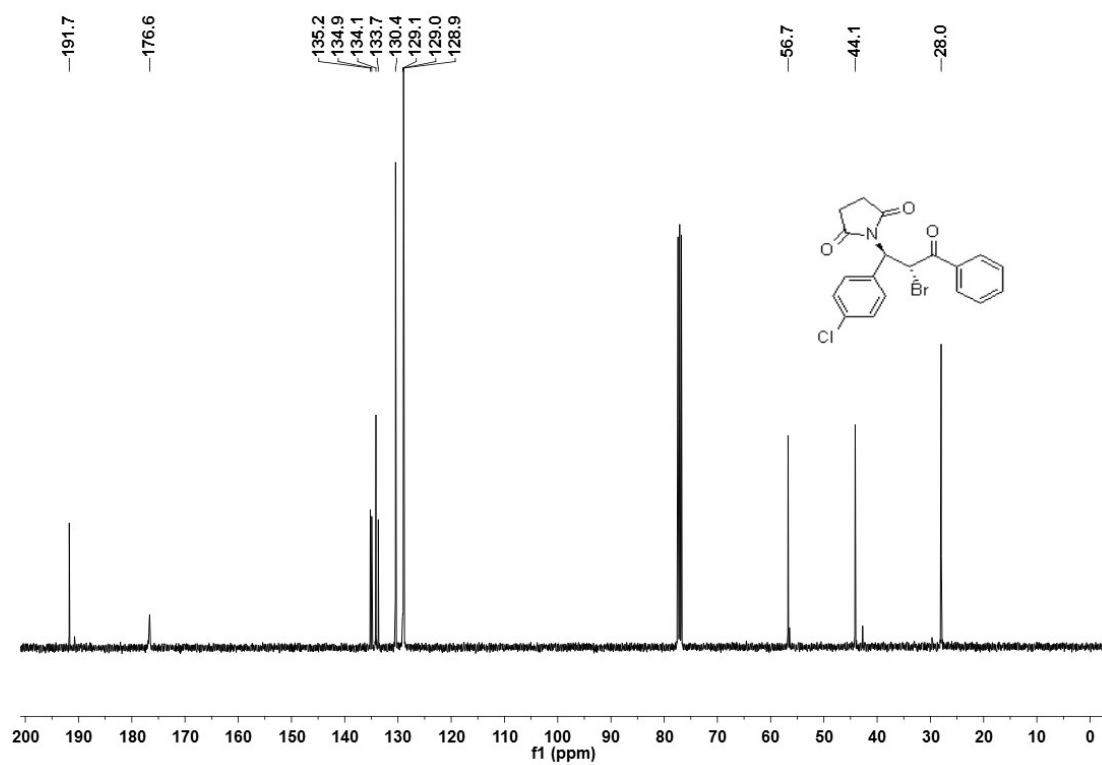
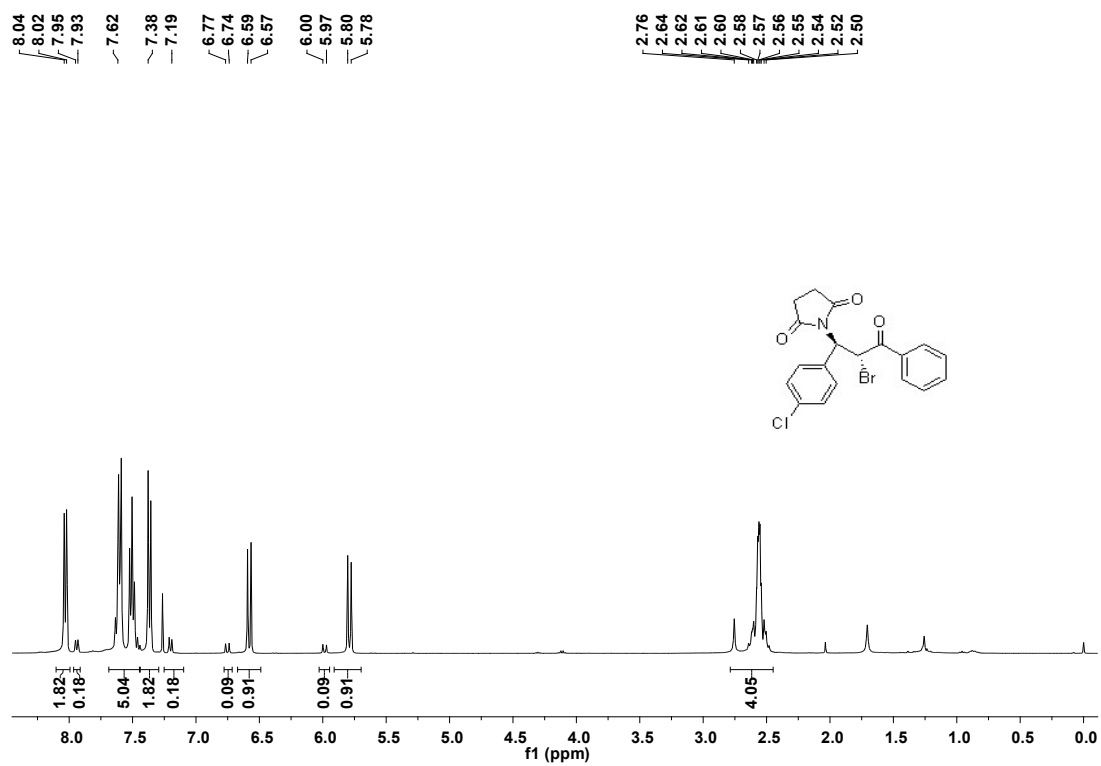




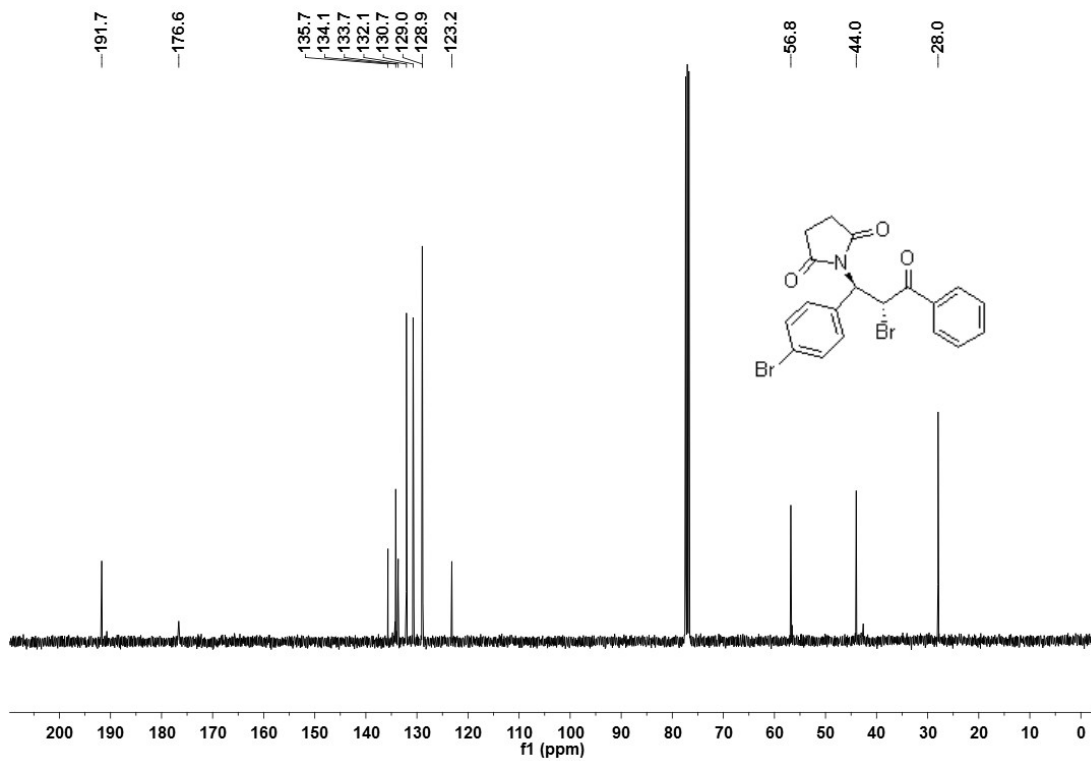
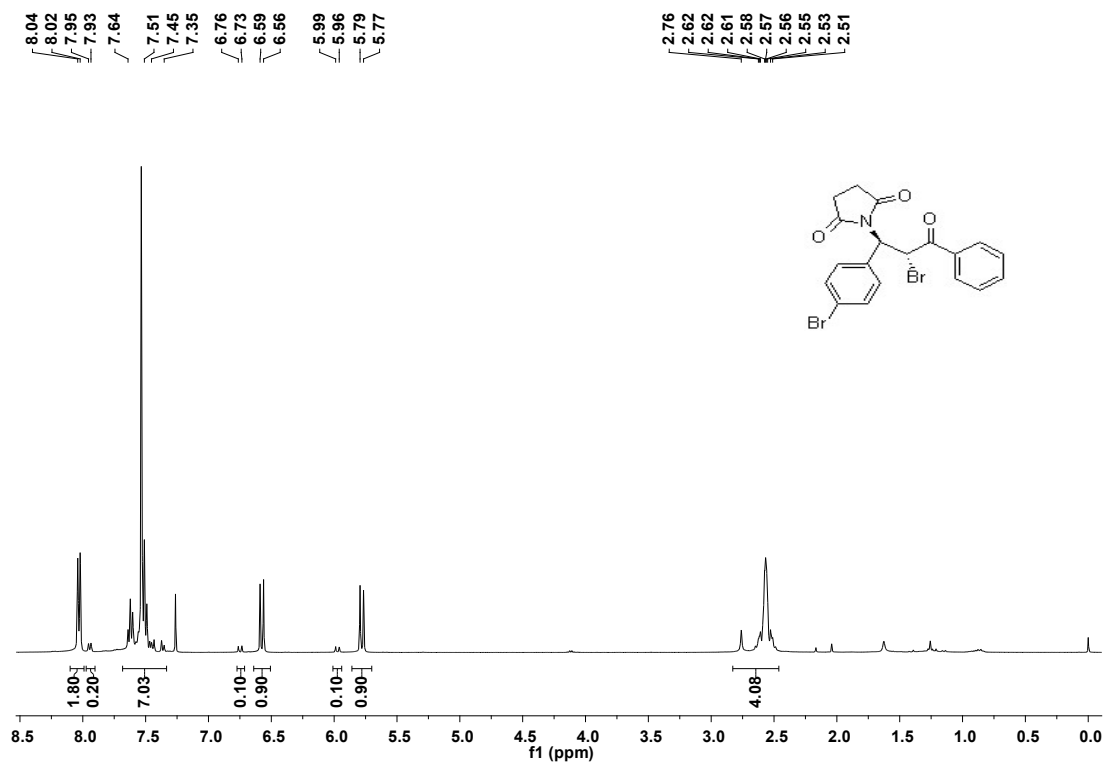
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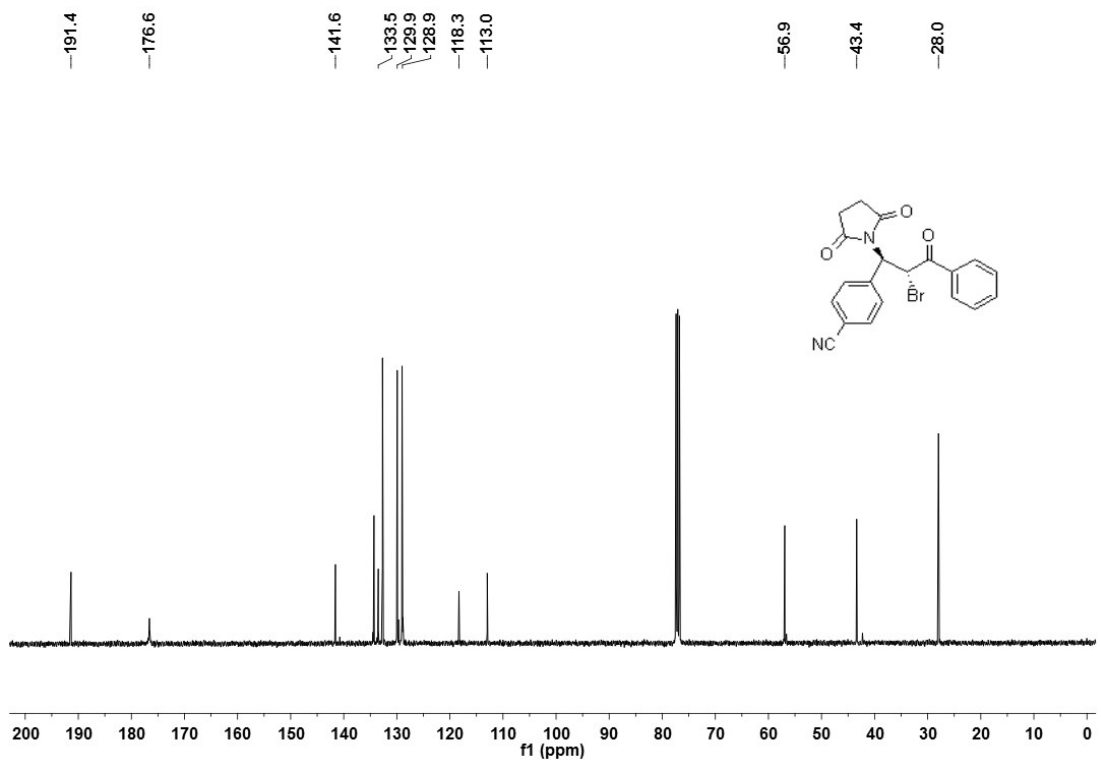
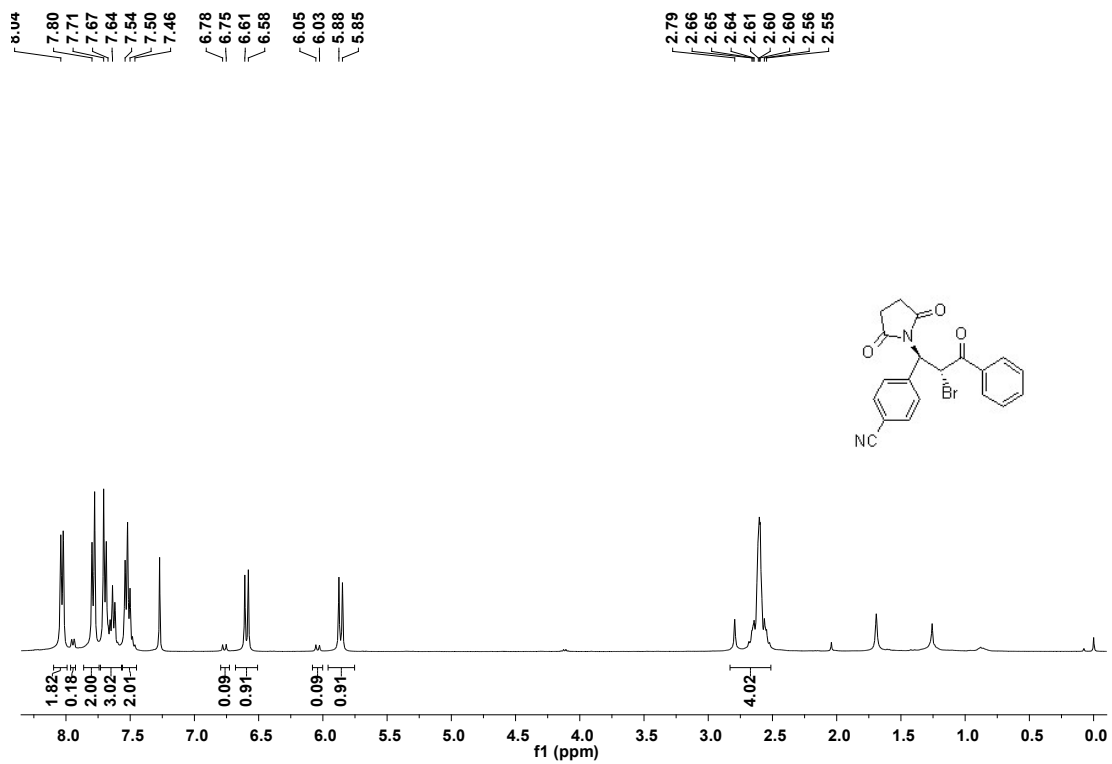
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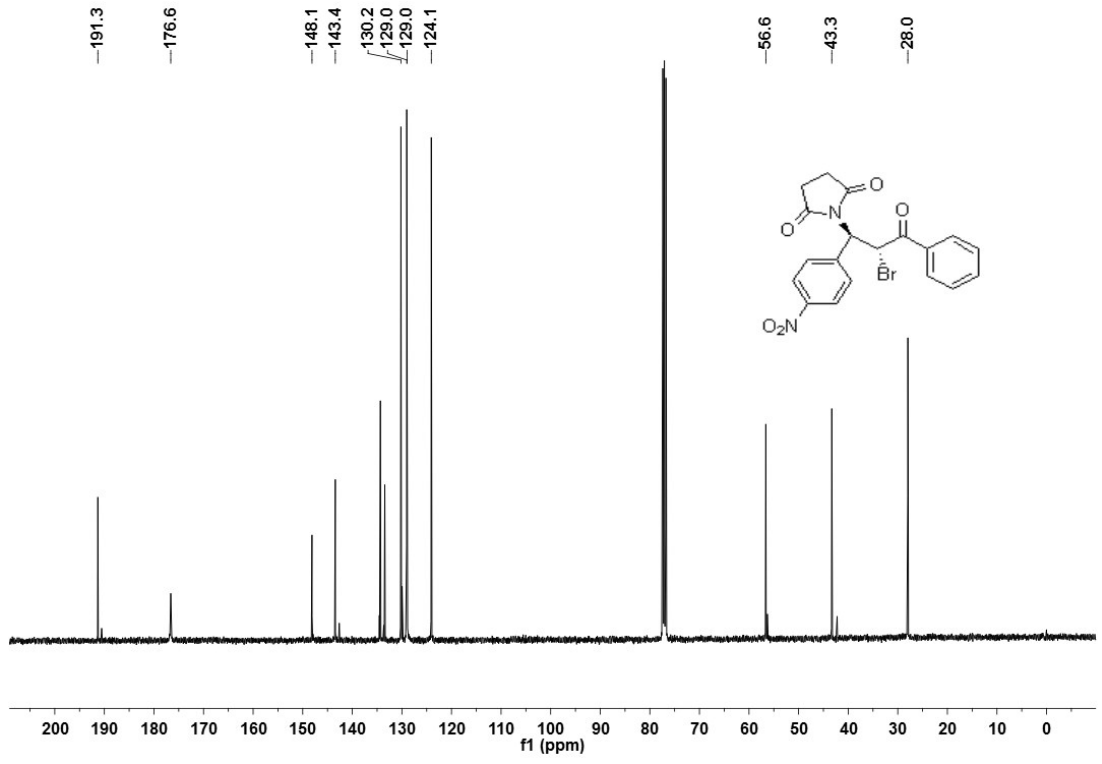
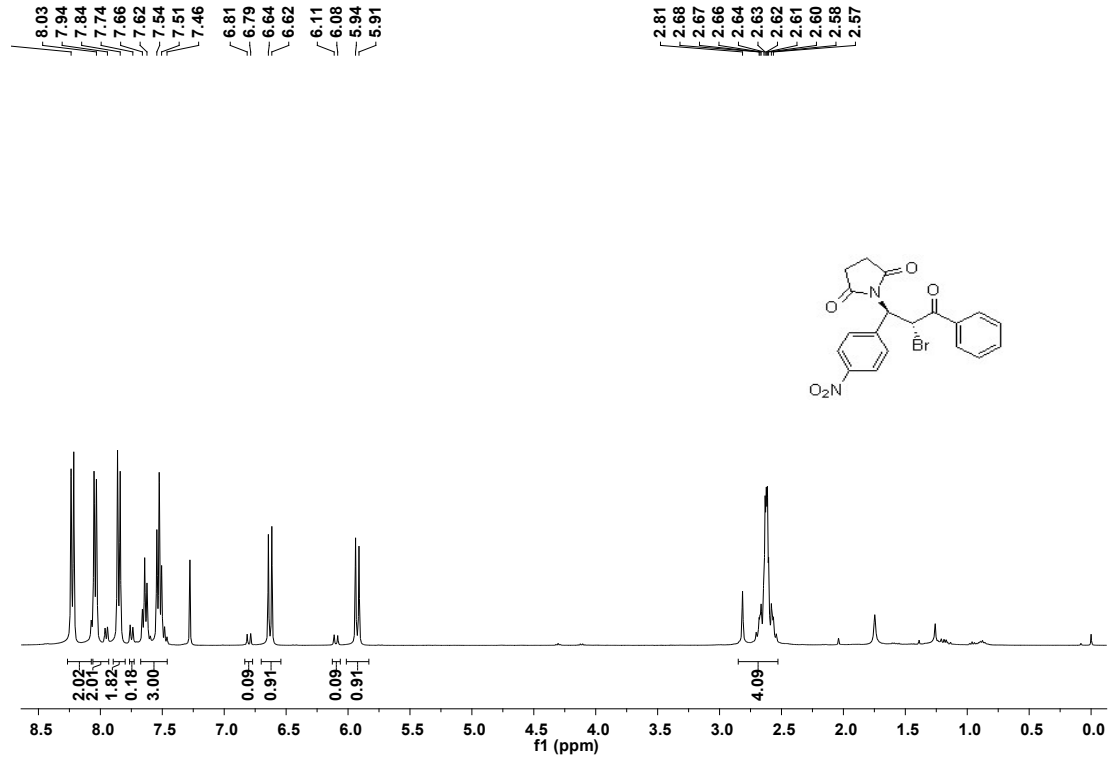
3h



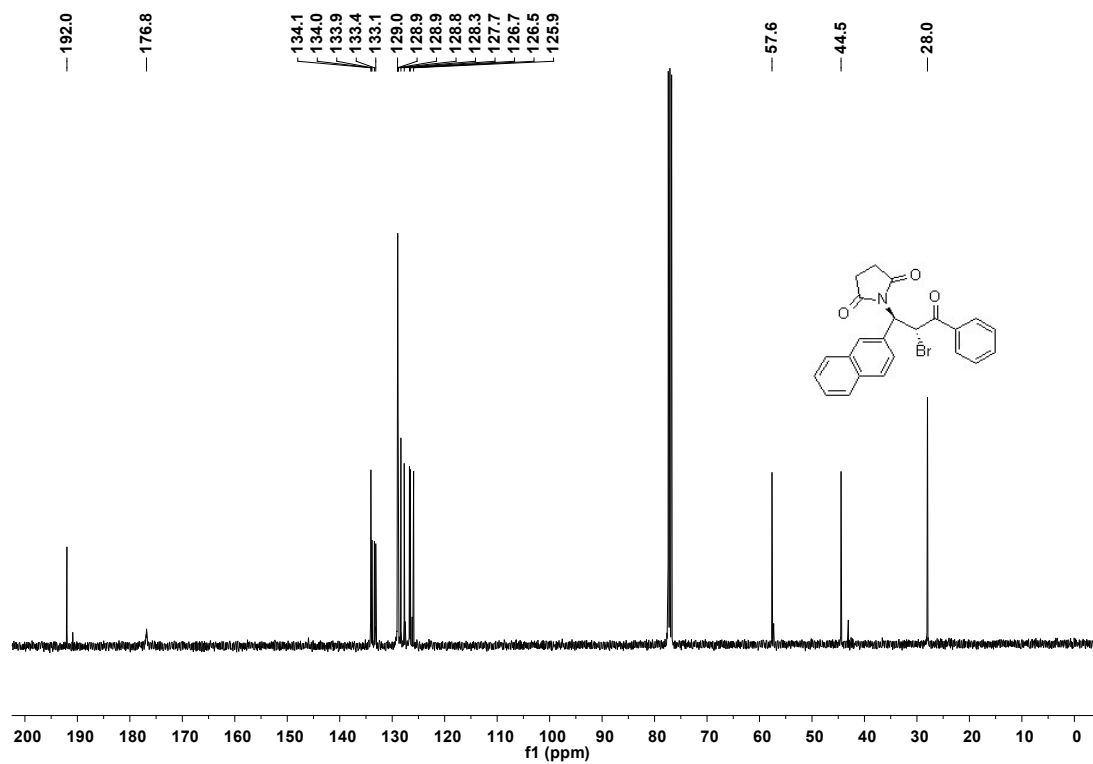
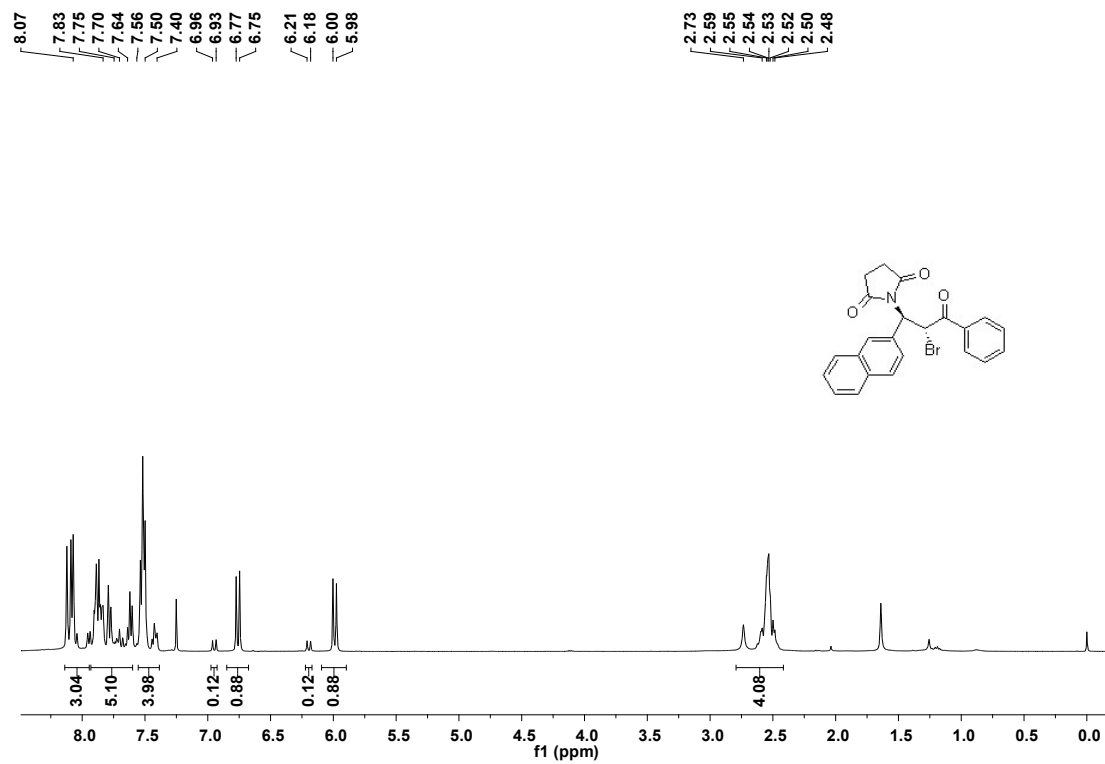
3i



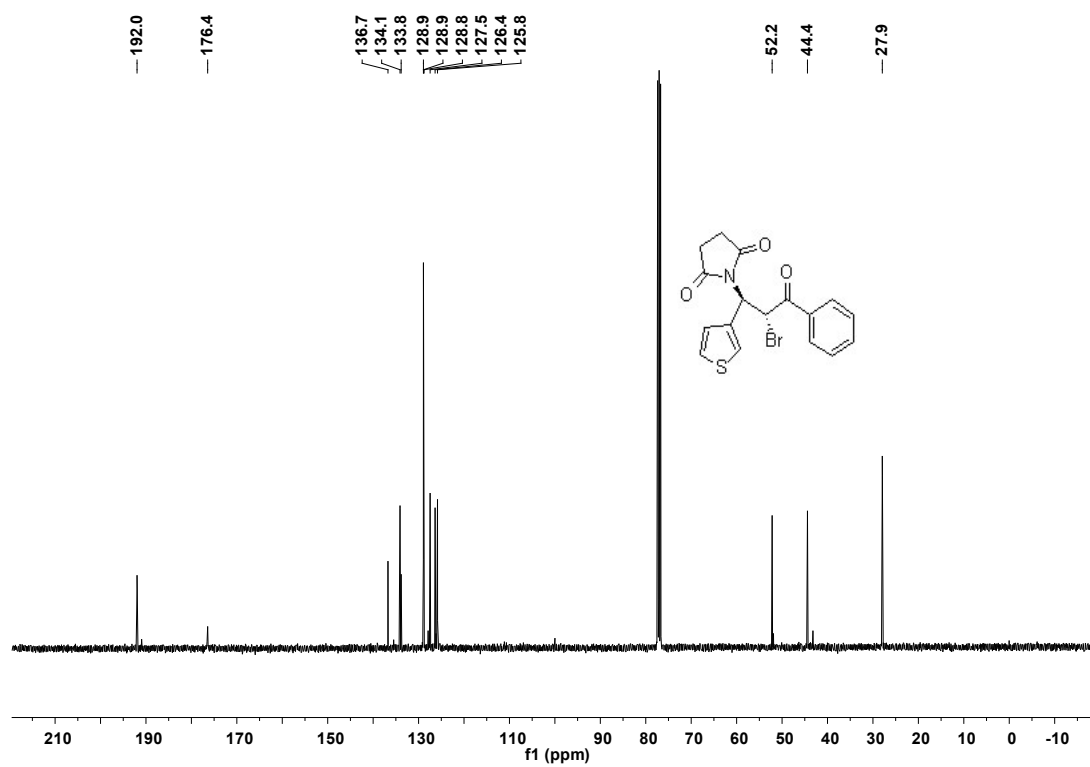
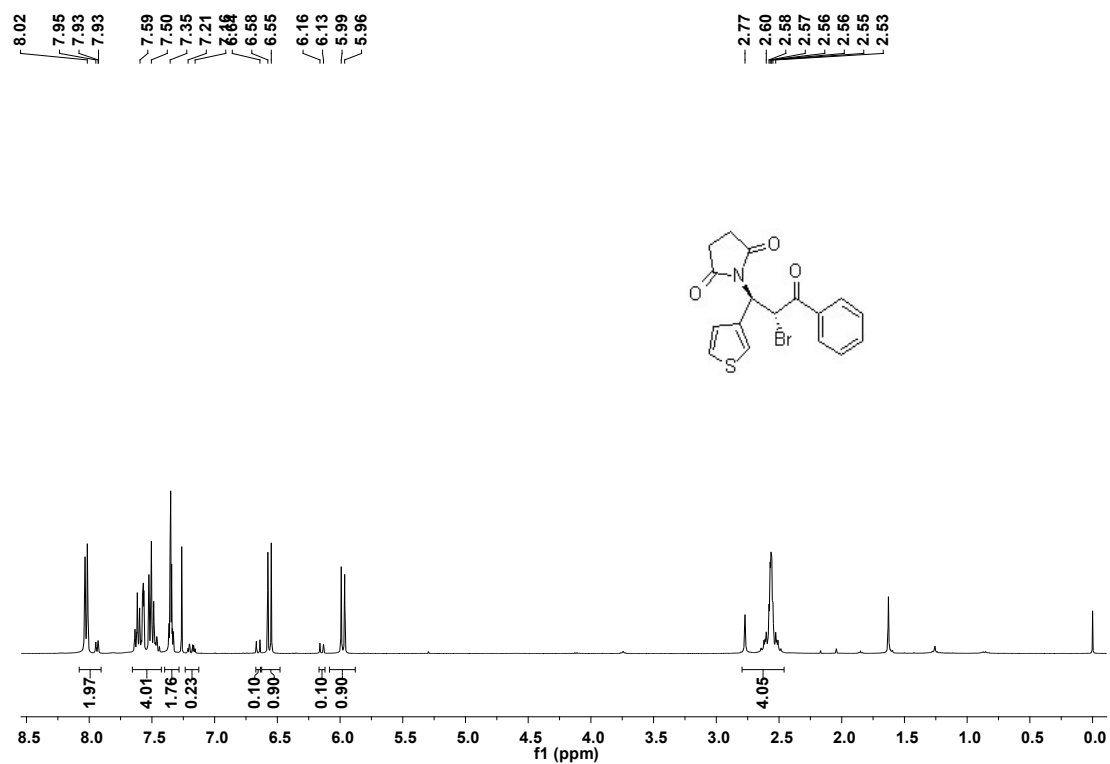
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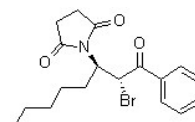
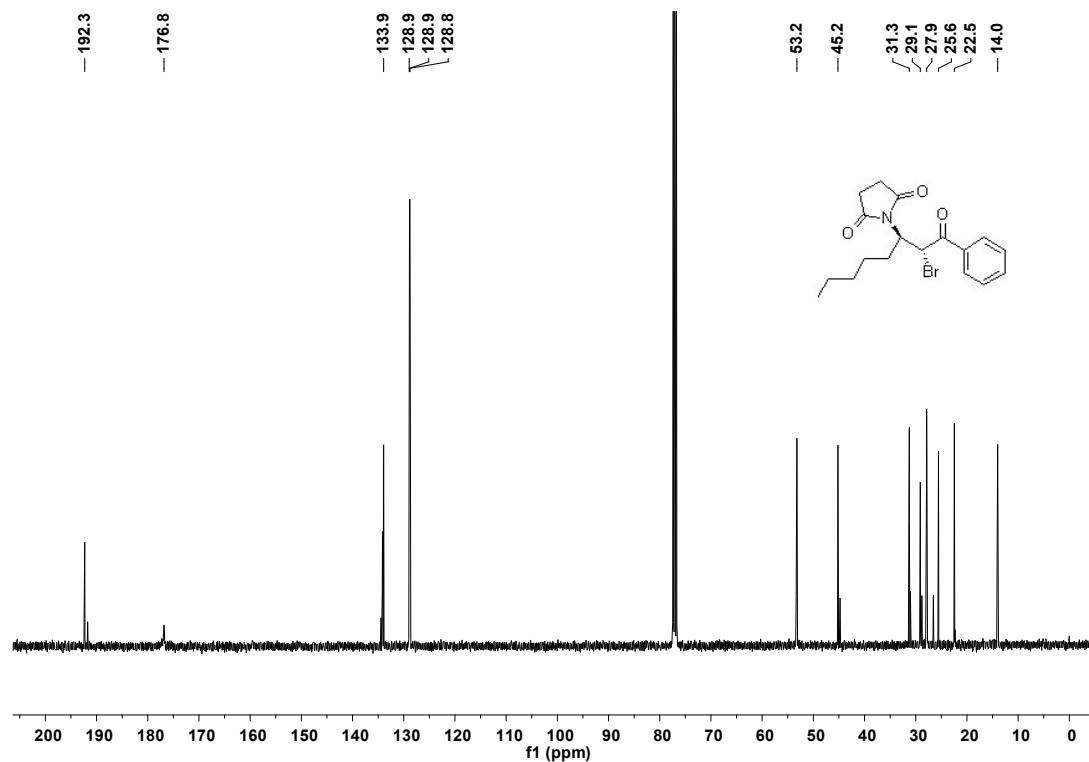
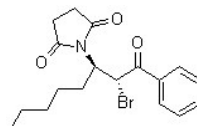
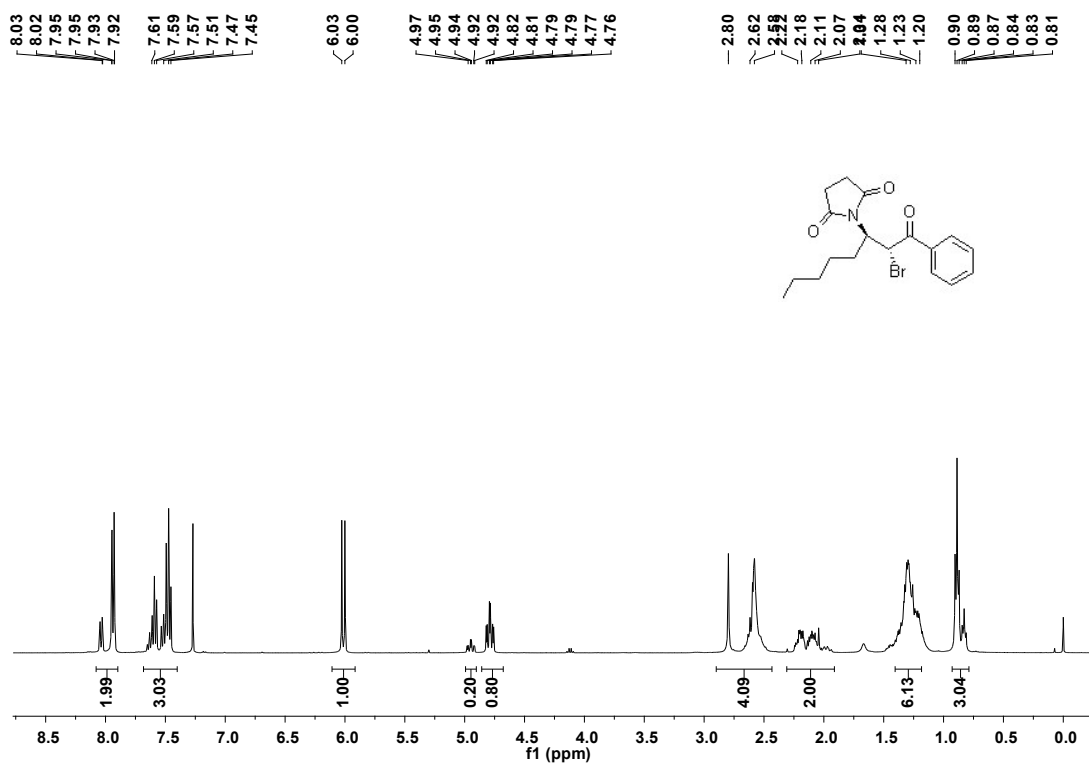
3k



31

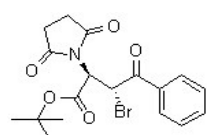
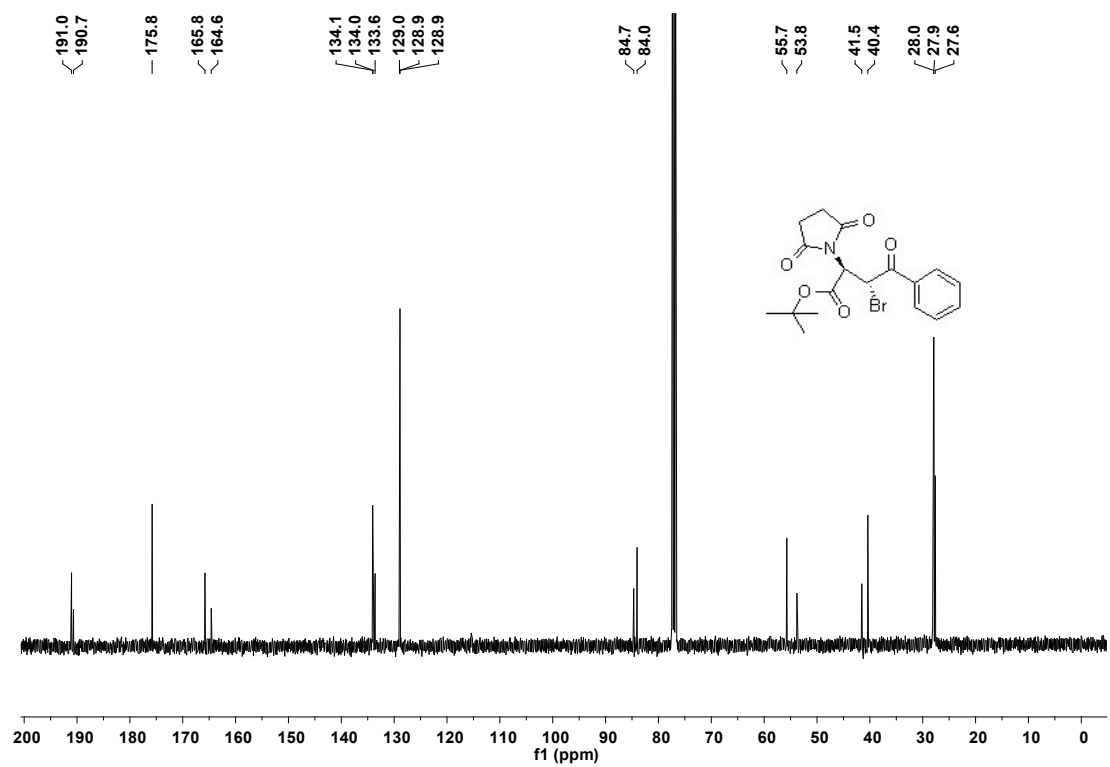
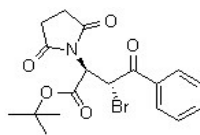
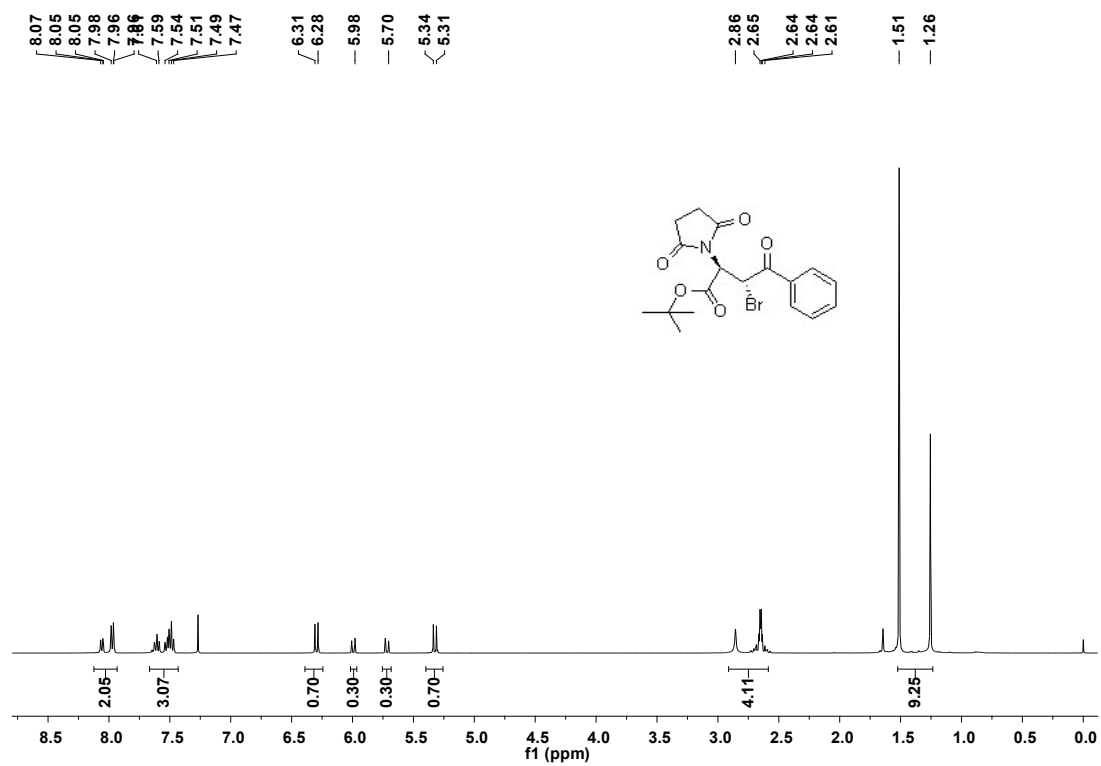


3m

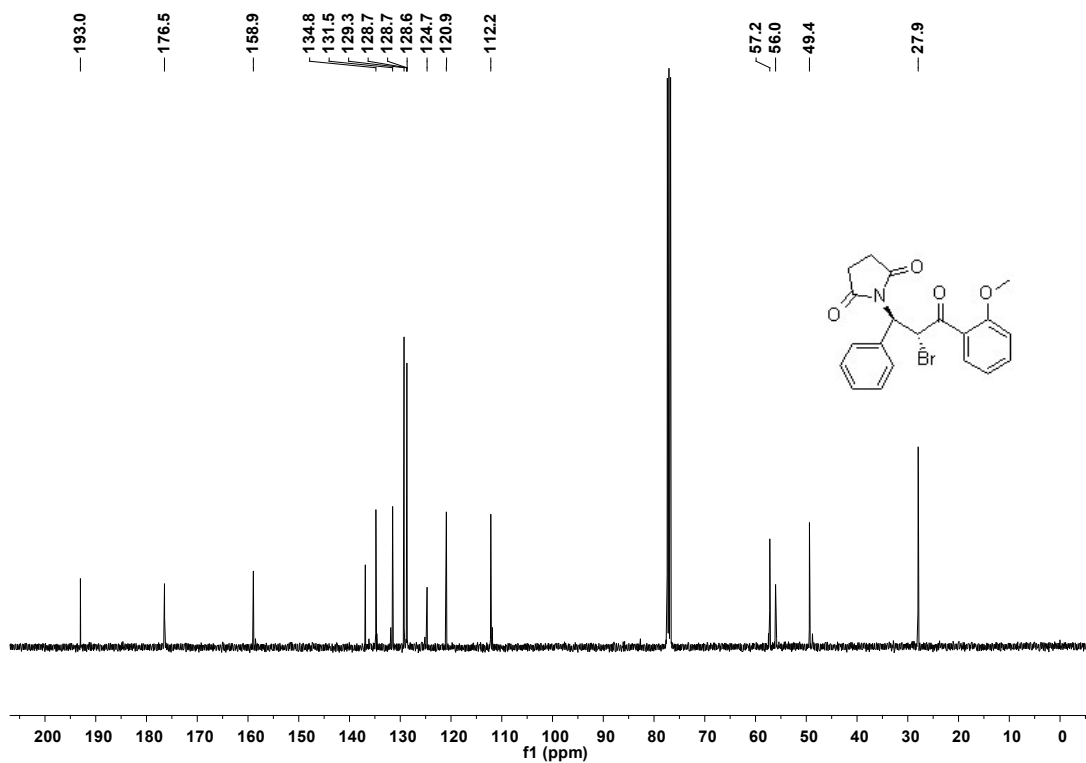
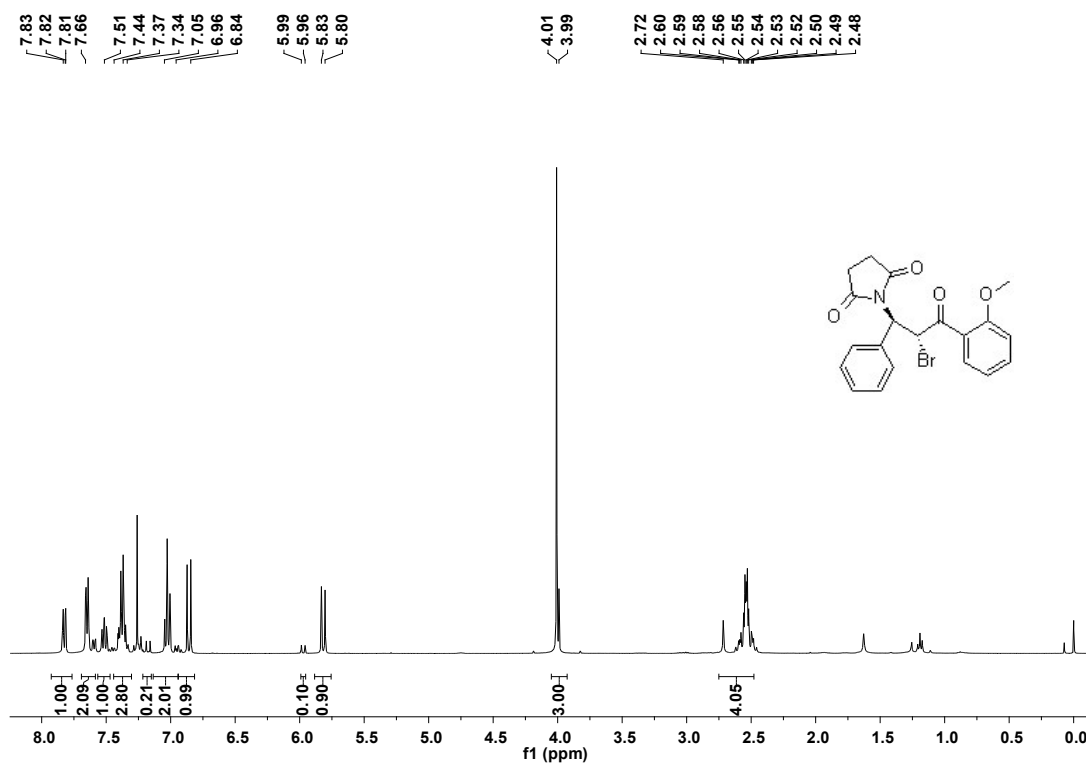




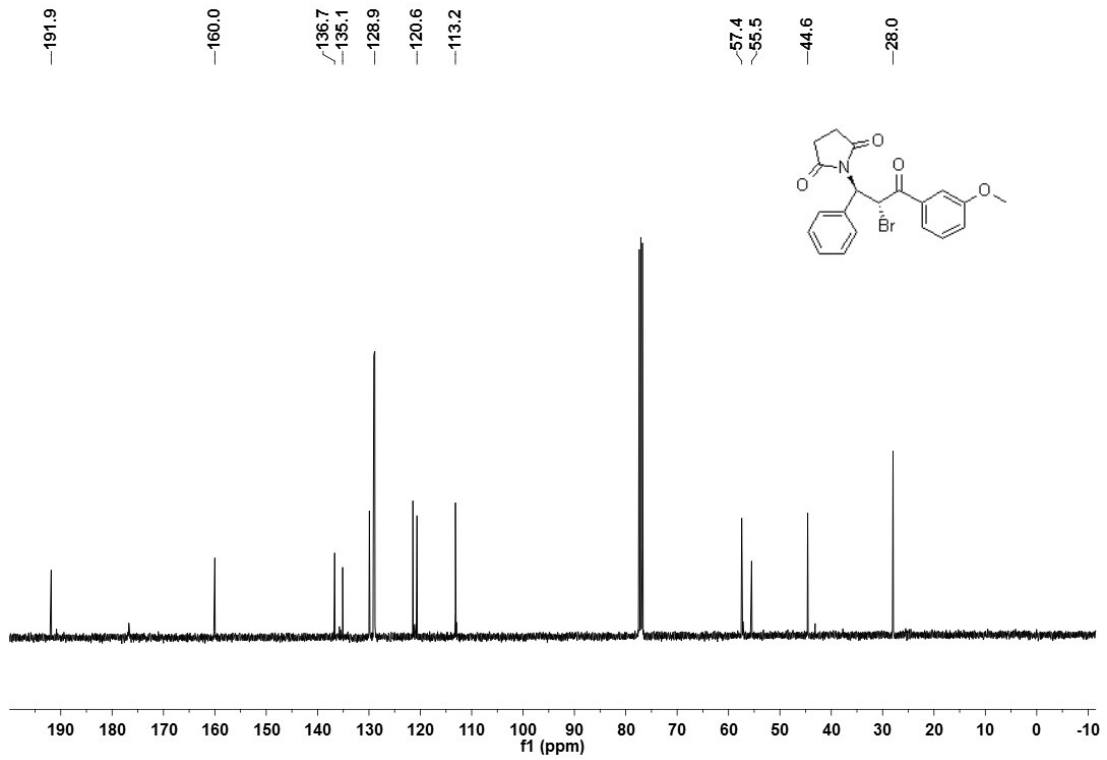
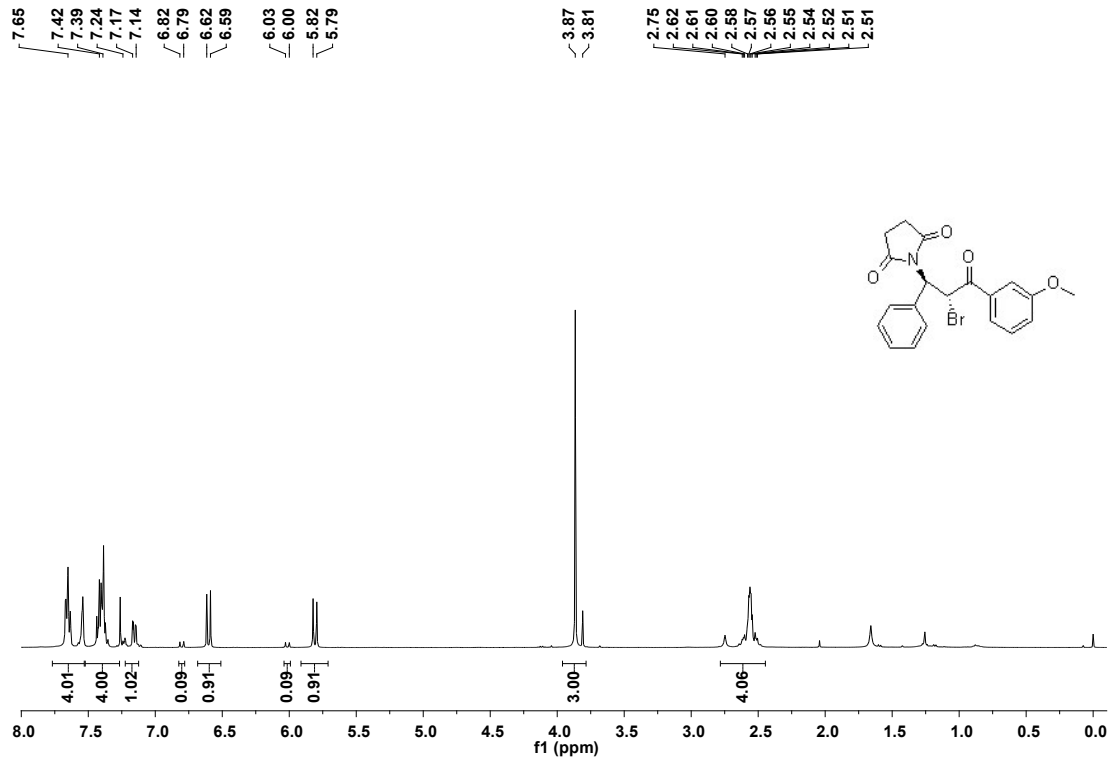
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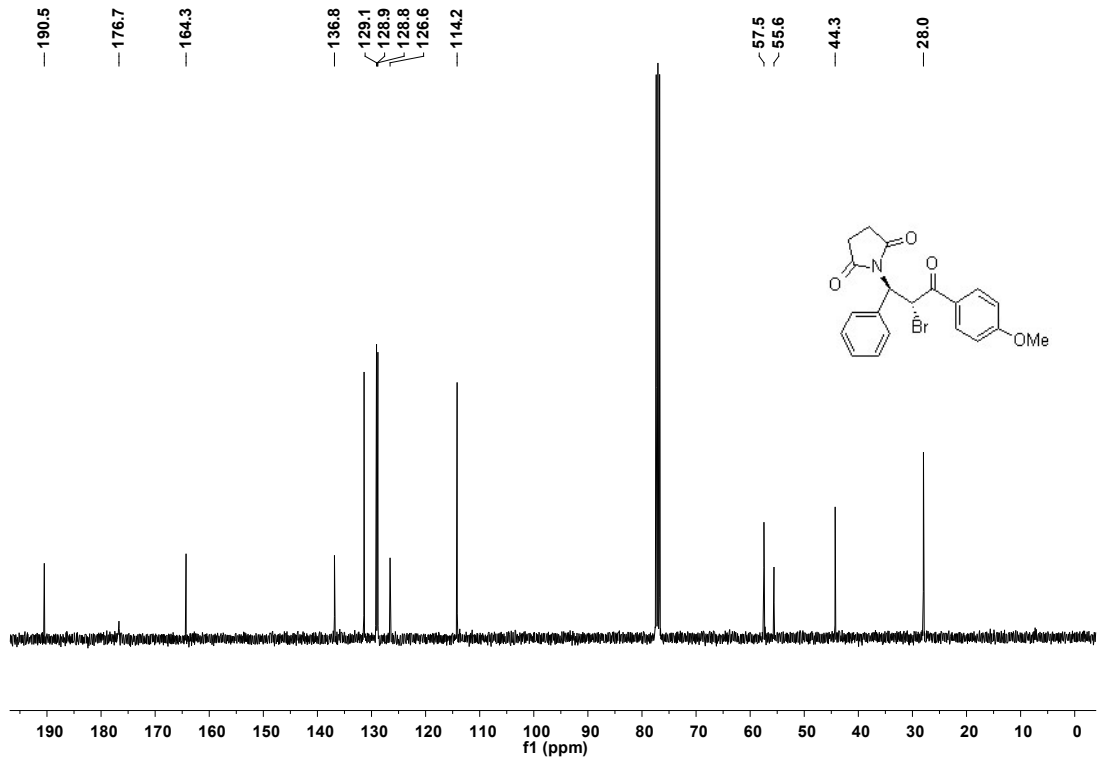
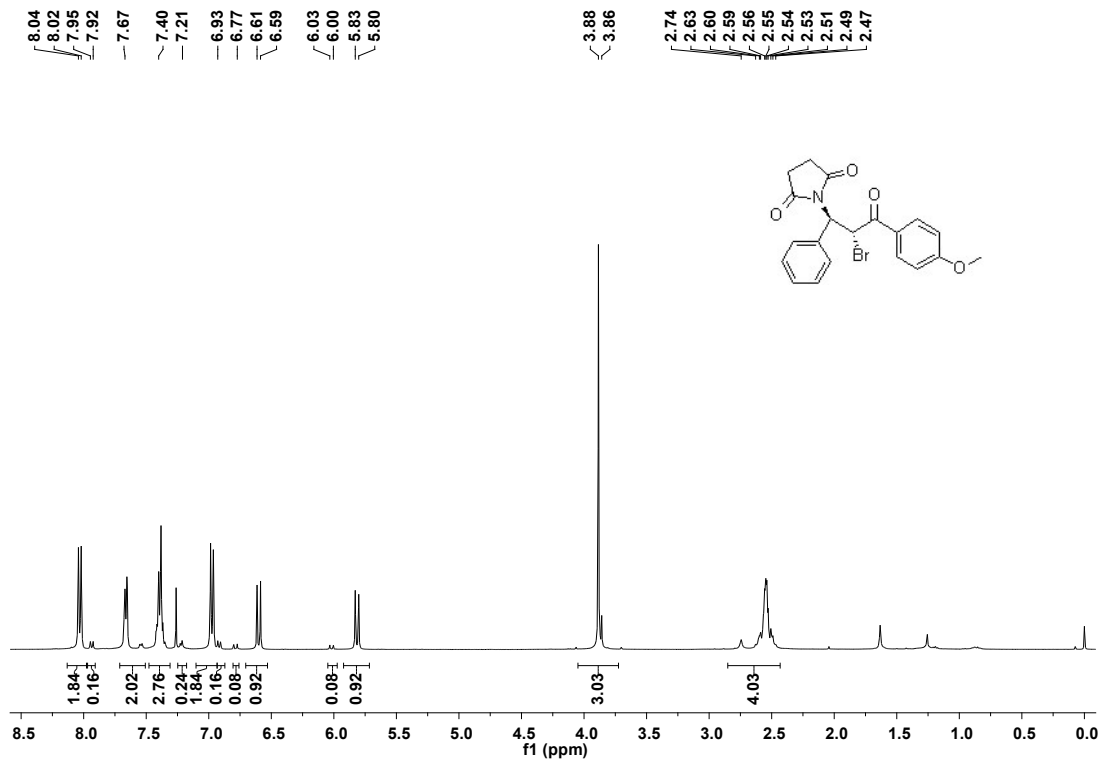
30



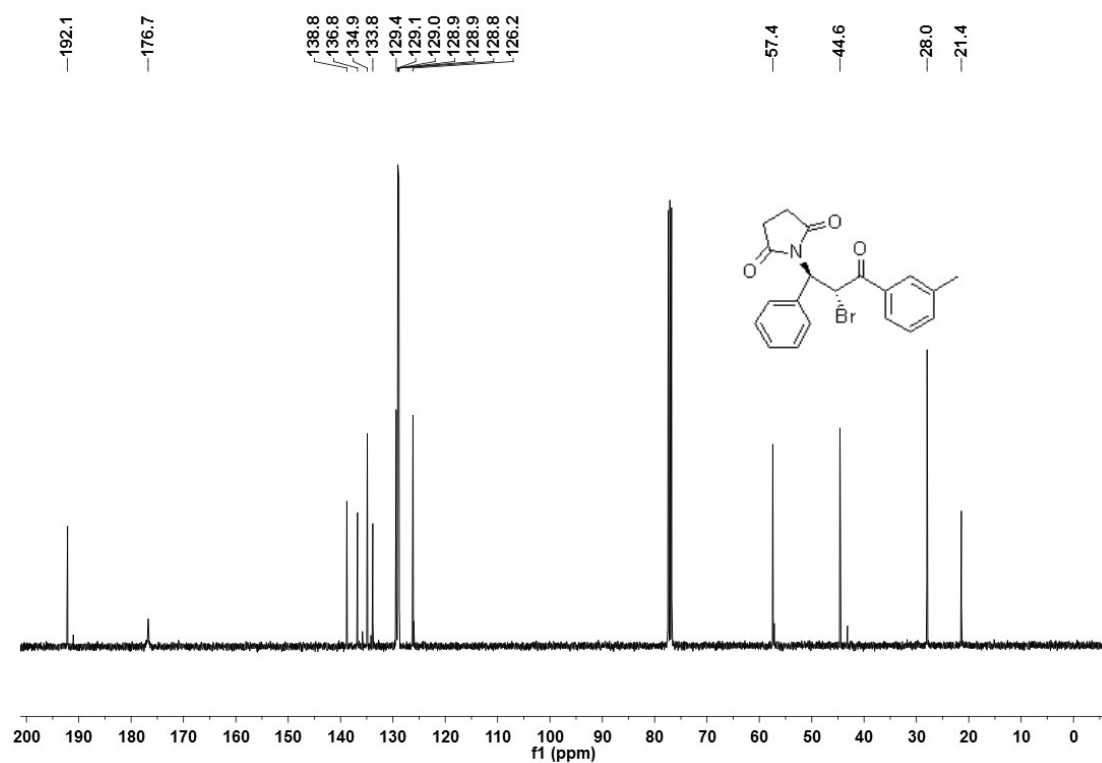
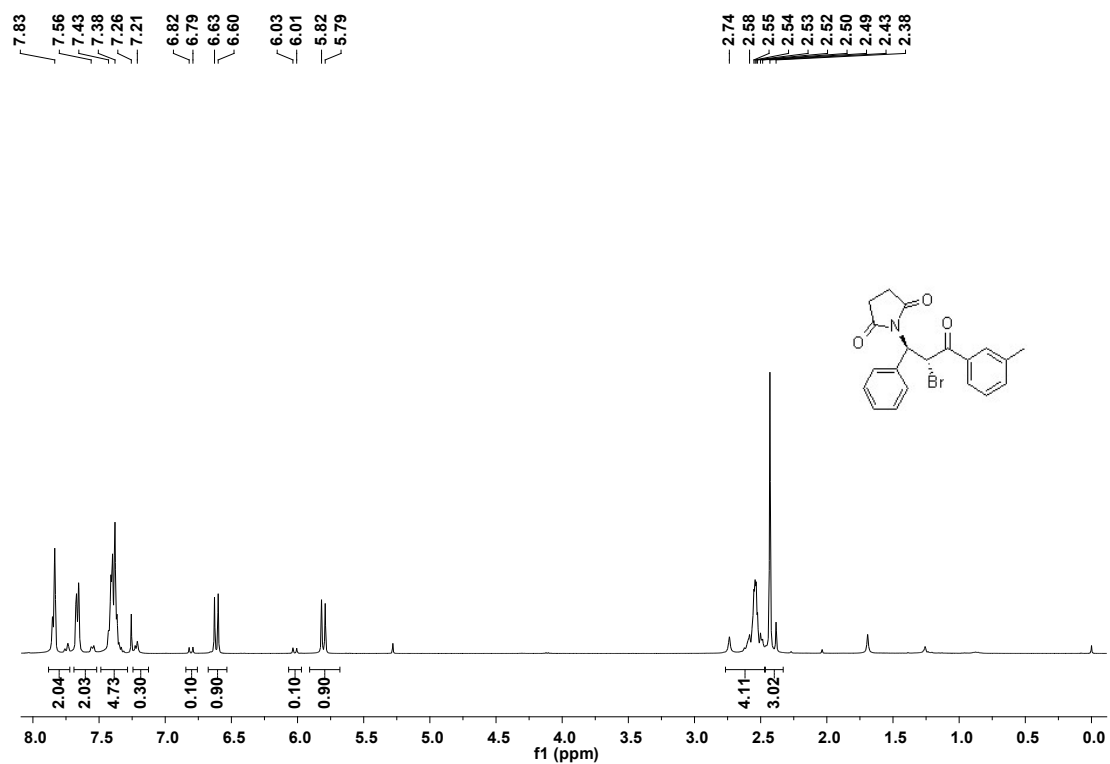
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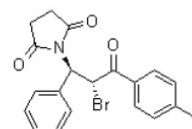
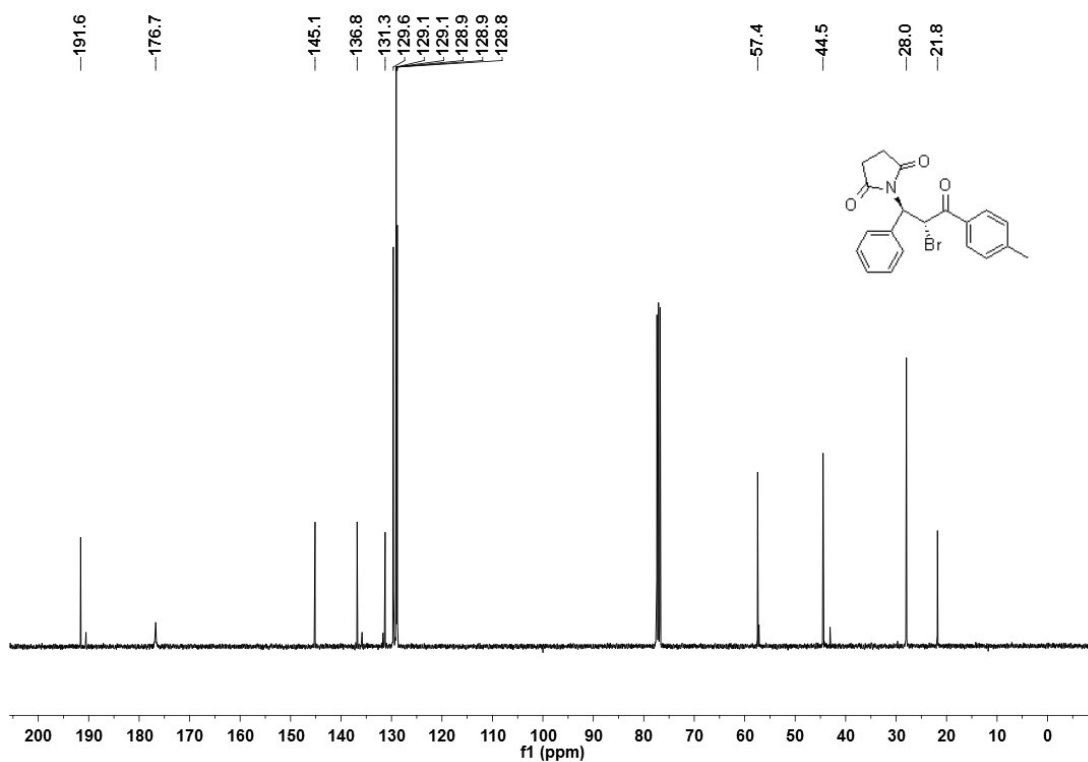
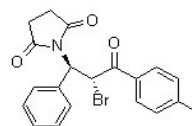
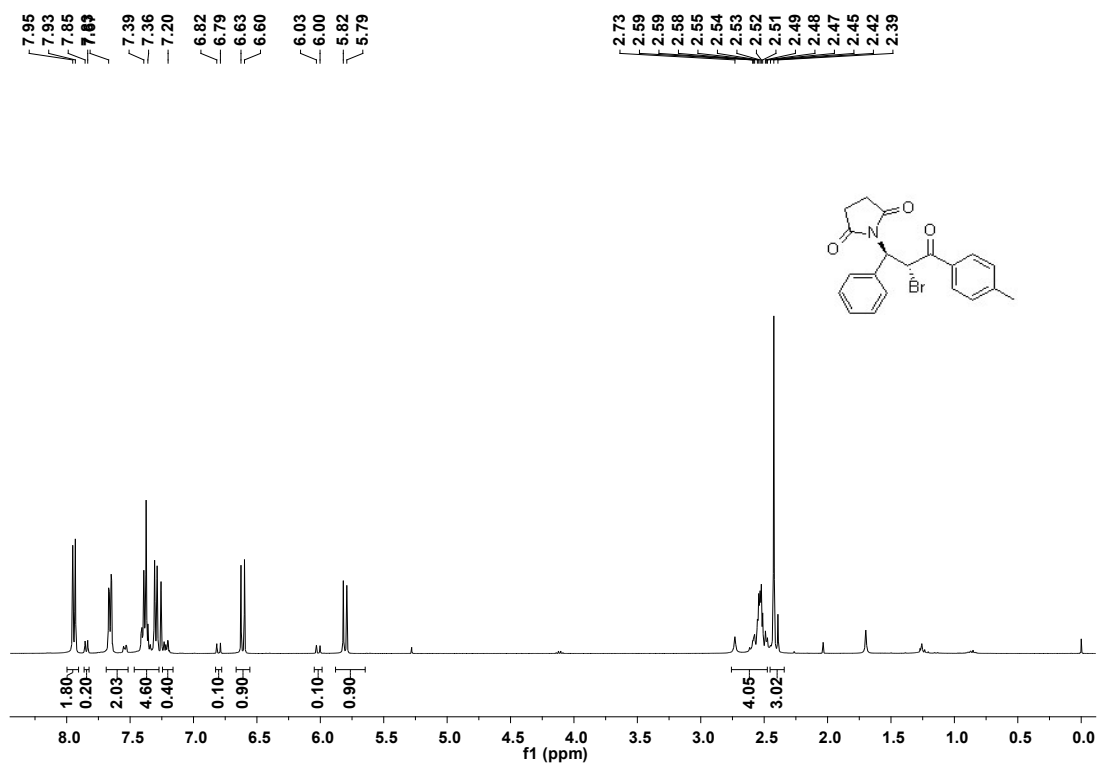
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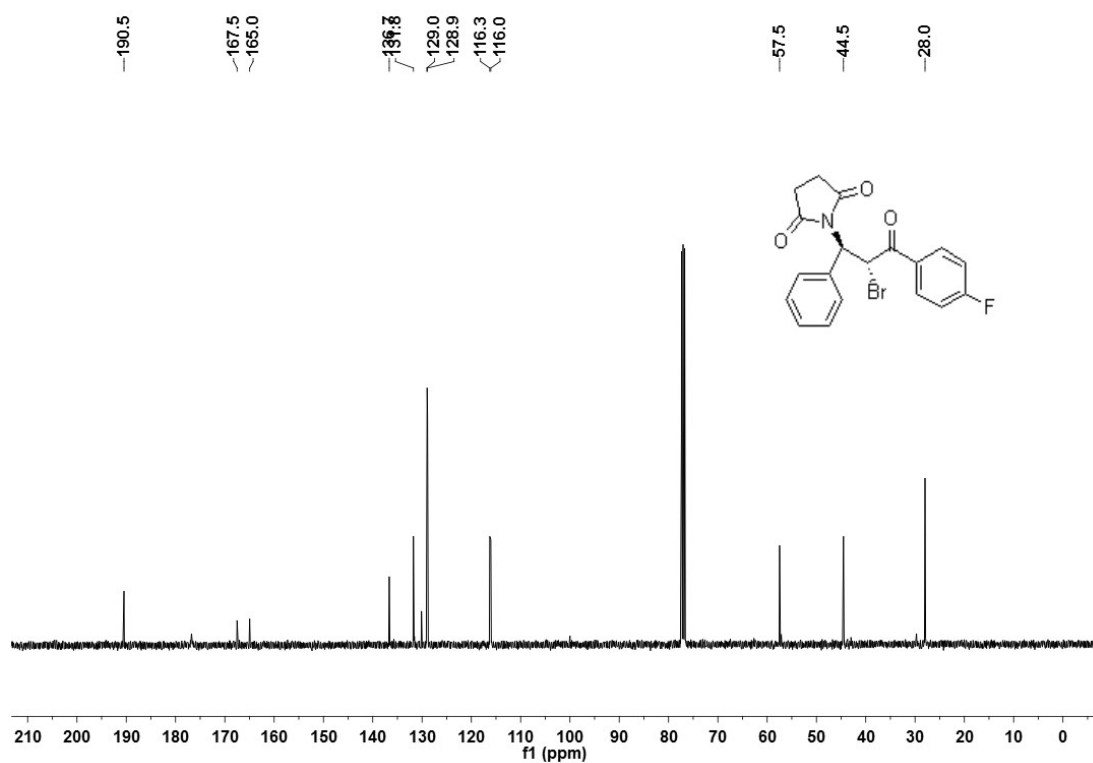
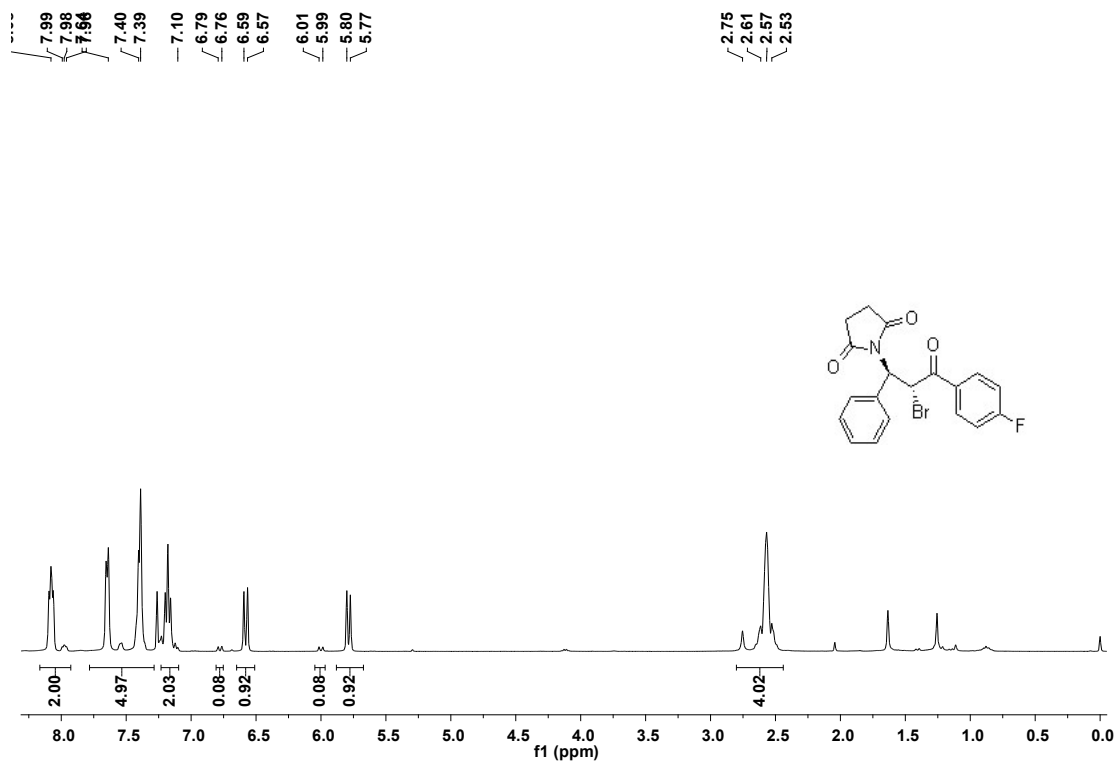
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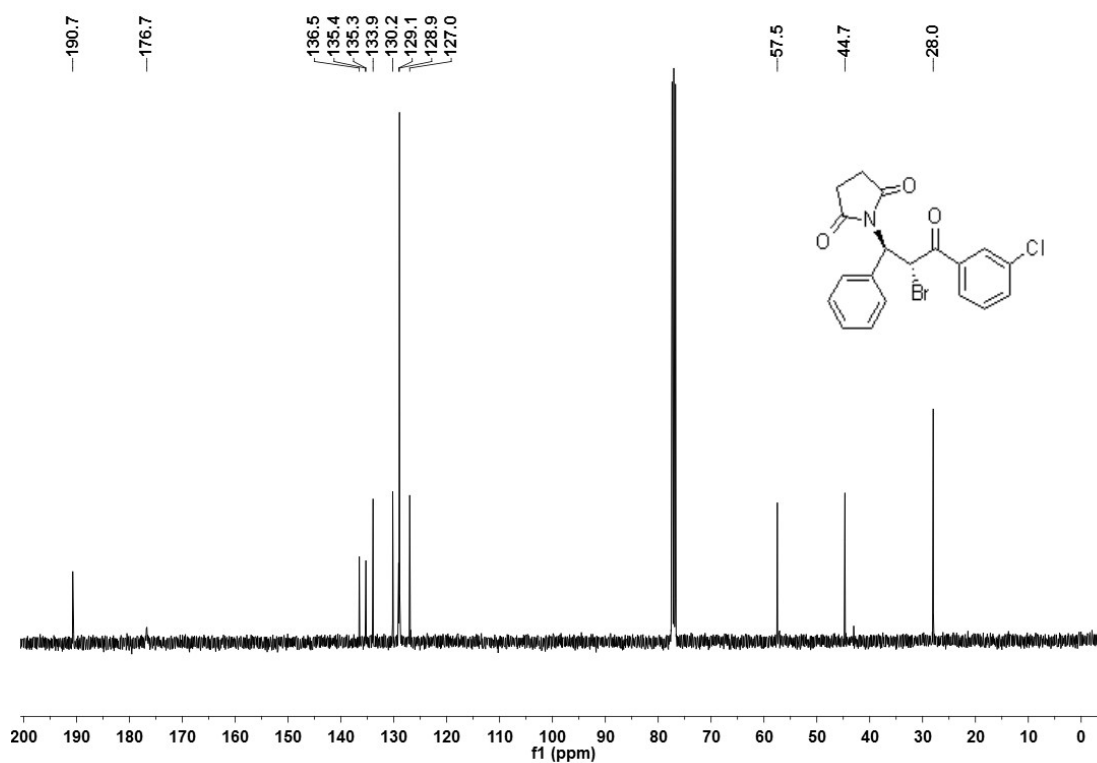
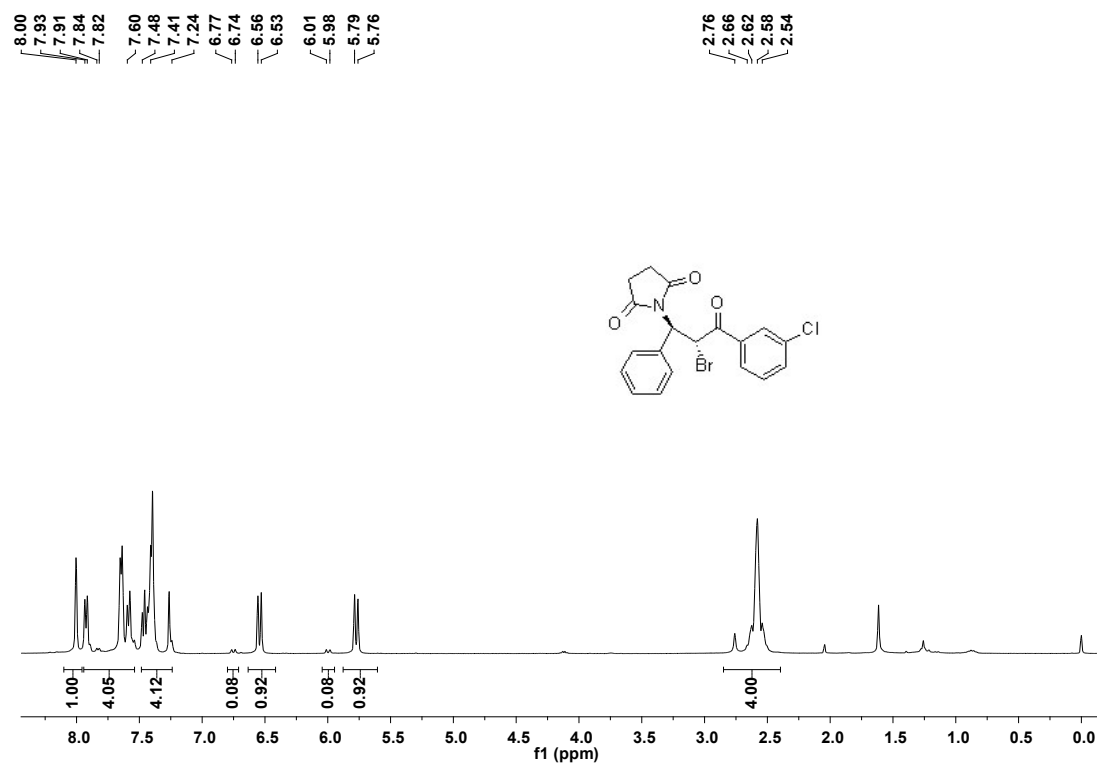
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3t

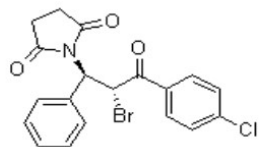
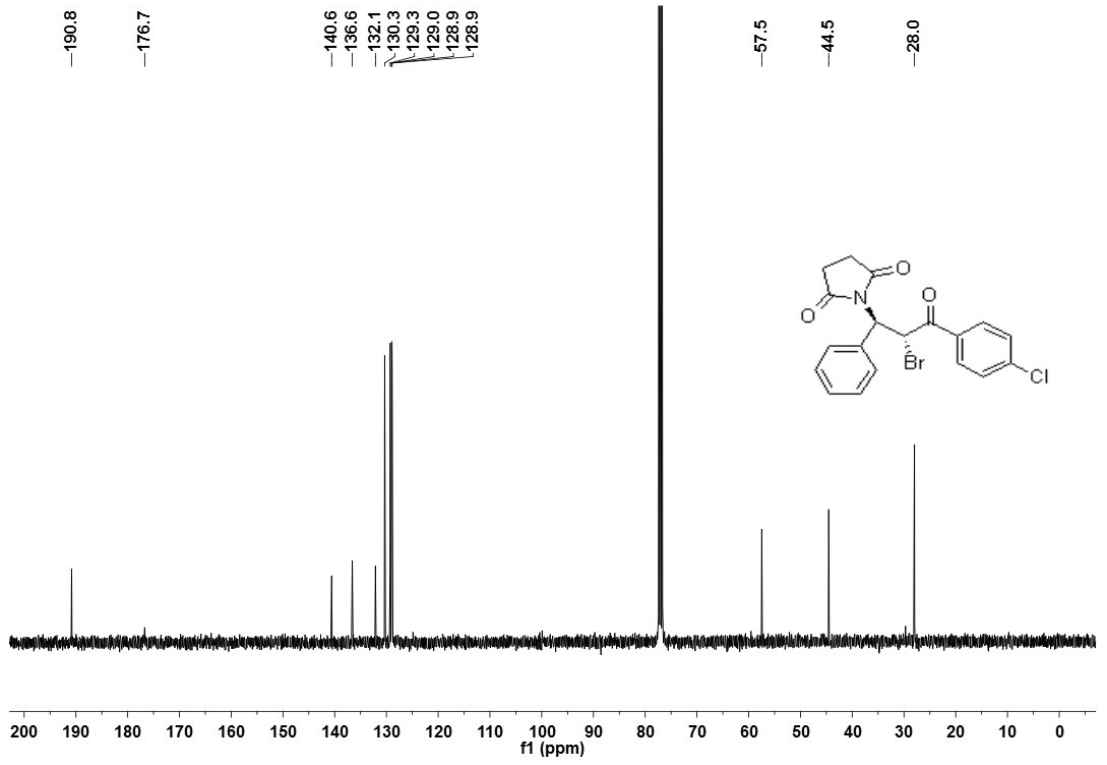
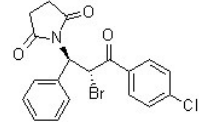
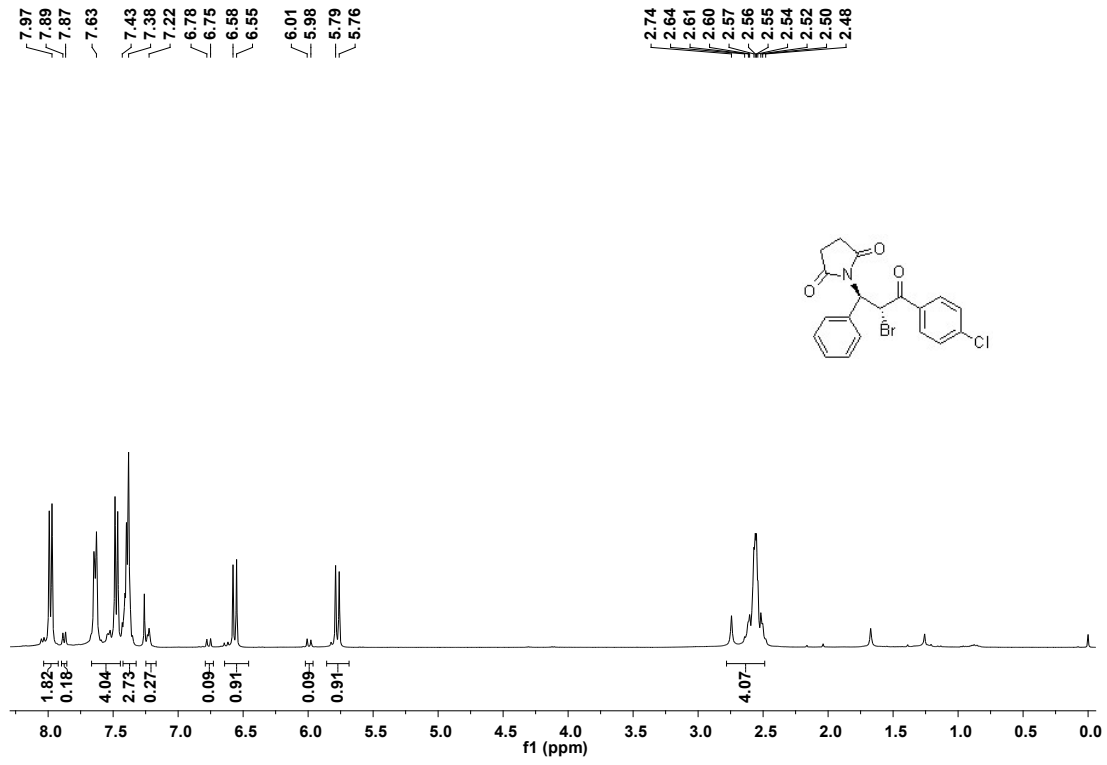


3u





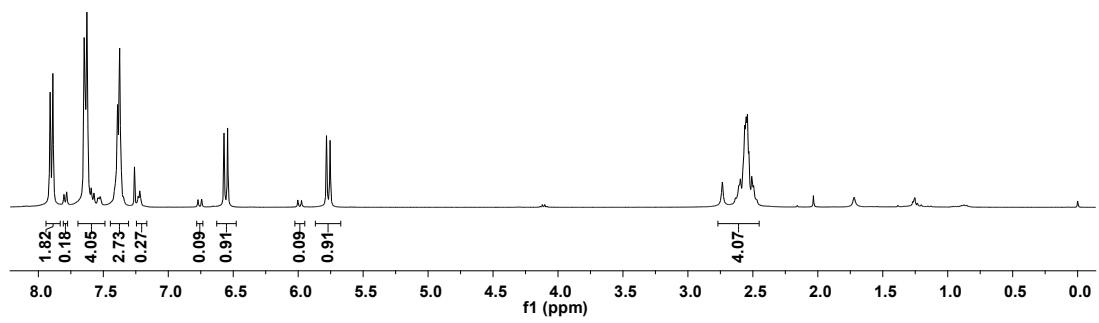
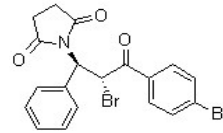
3v



3w

7.91  
7.65  
7.89  
7.54  
7.52  
7.39  
7.35  
7.22  
6.77  
6.74  
6.57  
6.54  
6.00  
5.97  
5.78  
5.75

2.74  
2.63  
2.61  
2.60  
2.56  
2.55  
2.54  
2.53  
2.51  
2.49



191.0

176.8

136.6

132.5

132.3

130.4

129.4

129.1

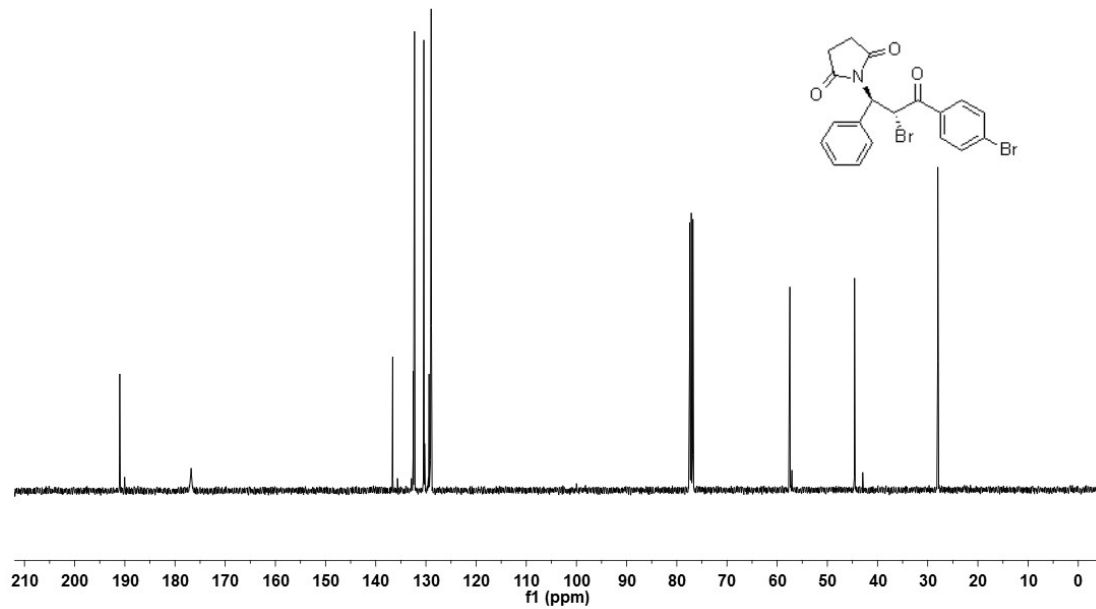
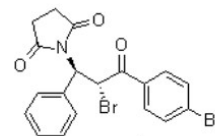
129.0

128.9

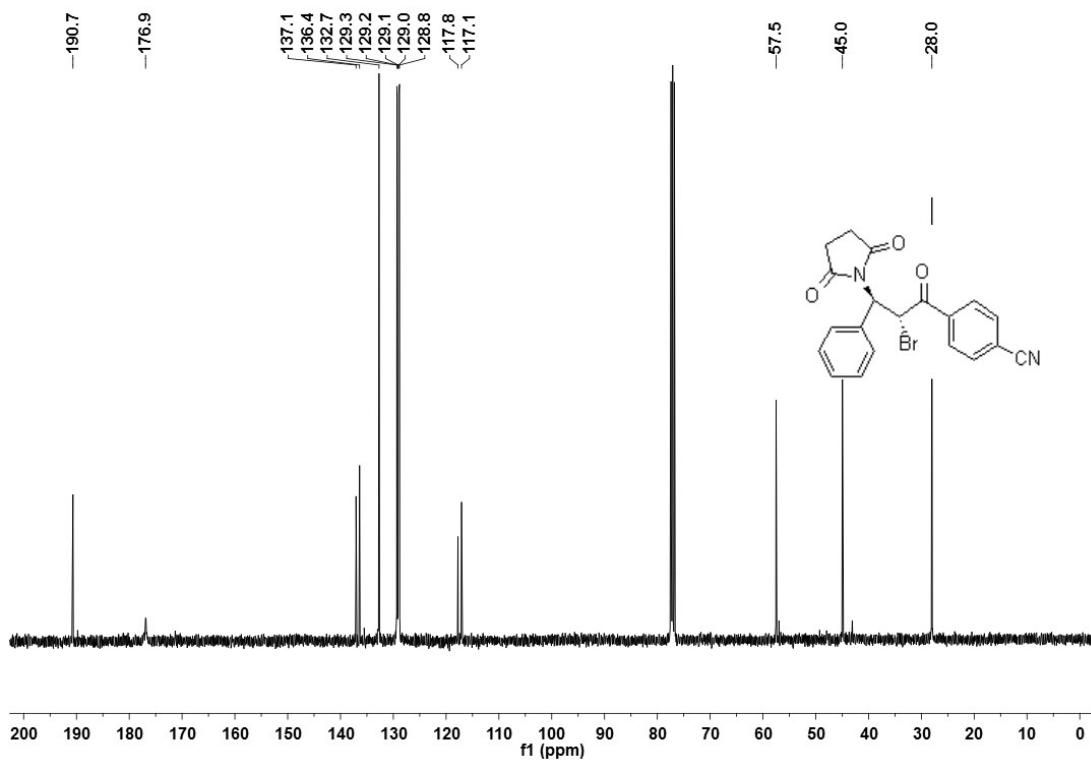
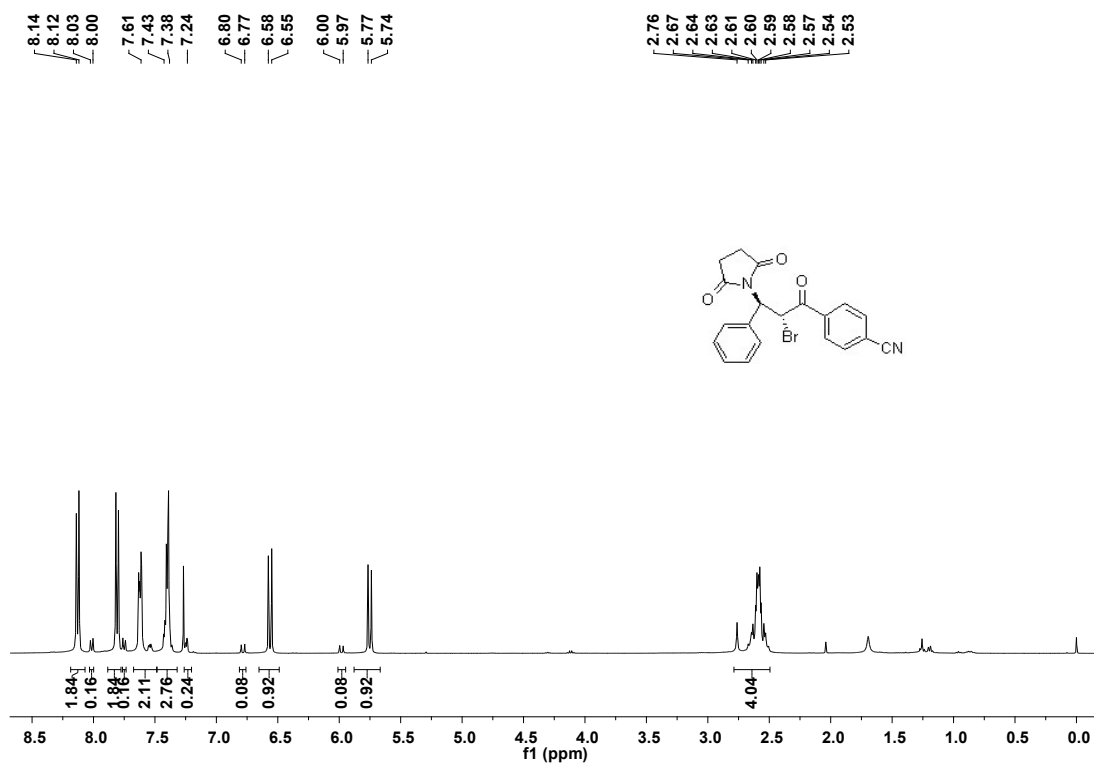
57.5

44.6

28.0



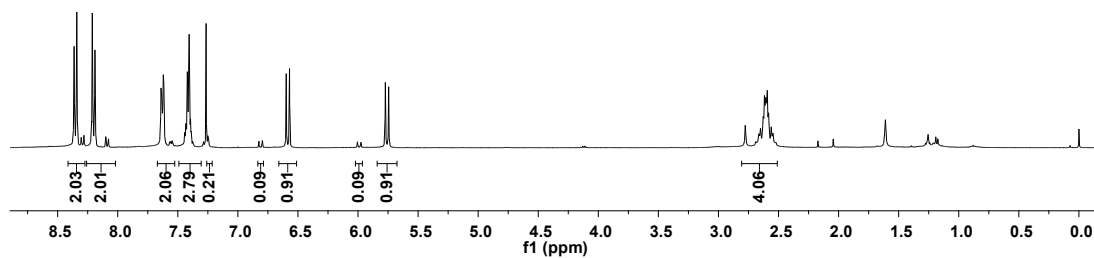
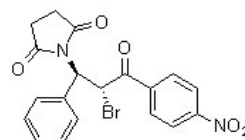
3x



3y

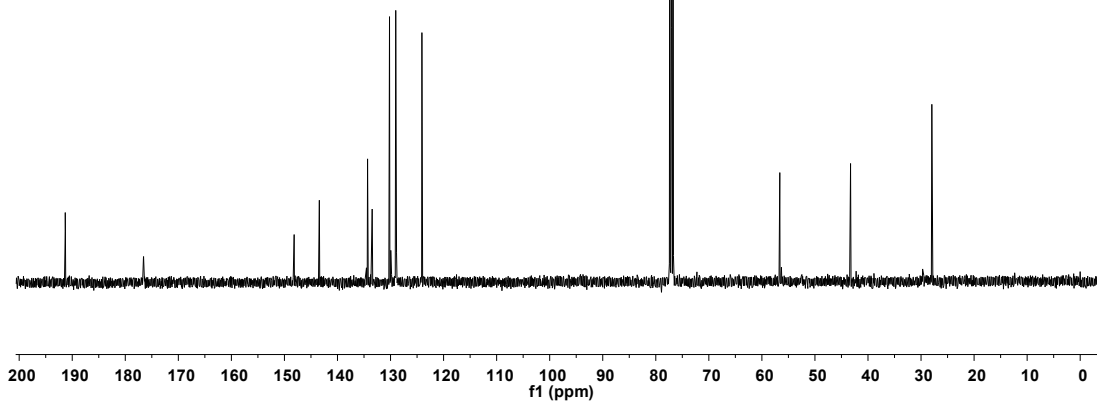
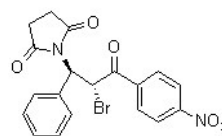
8.34  
8.30  
8.22  
8.19  
8.10  
8.08  
7.64  
7.43  
7.41  
7.25  
6.82  
6.80  
6.60  
6.57  
6.00  
5.98  
5.77  
5.75

2.78  
2.66  
2.65  
2.63  
2.62  
2.60  
2.59  
2.58  
2.56  
2.55

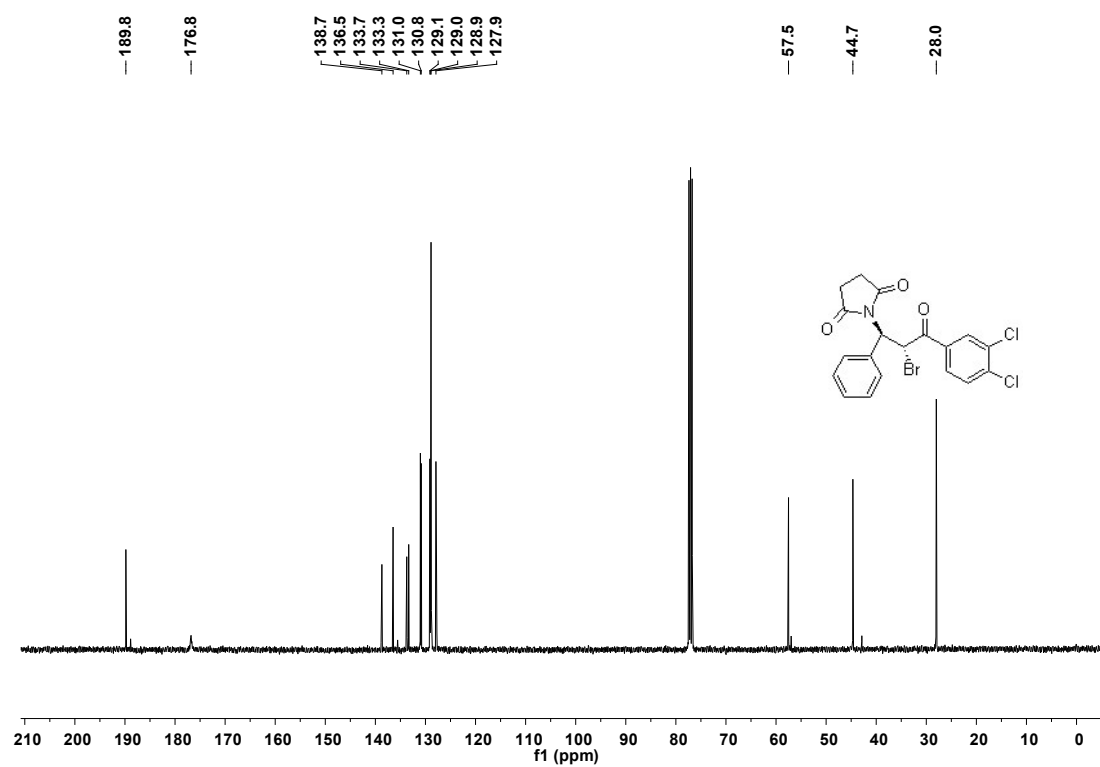
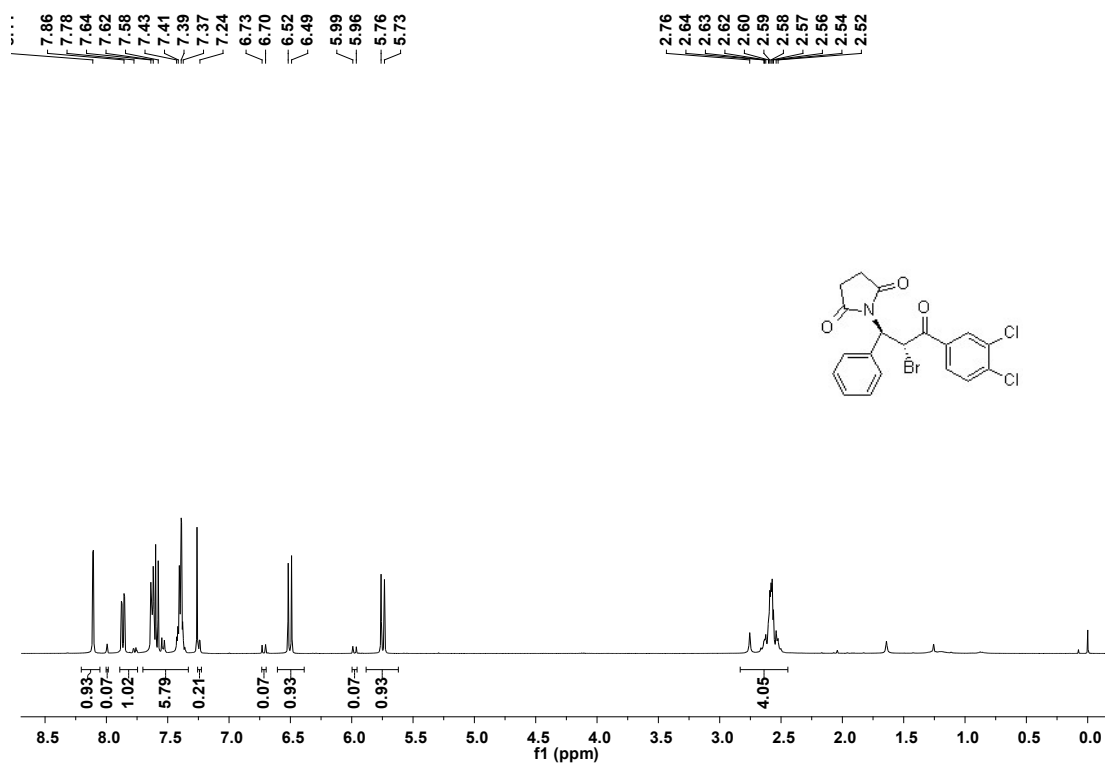


191.3  
176.6  
148.2  
143.4  
133.5  
130.0  
129.0  
124.1

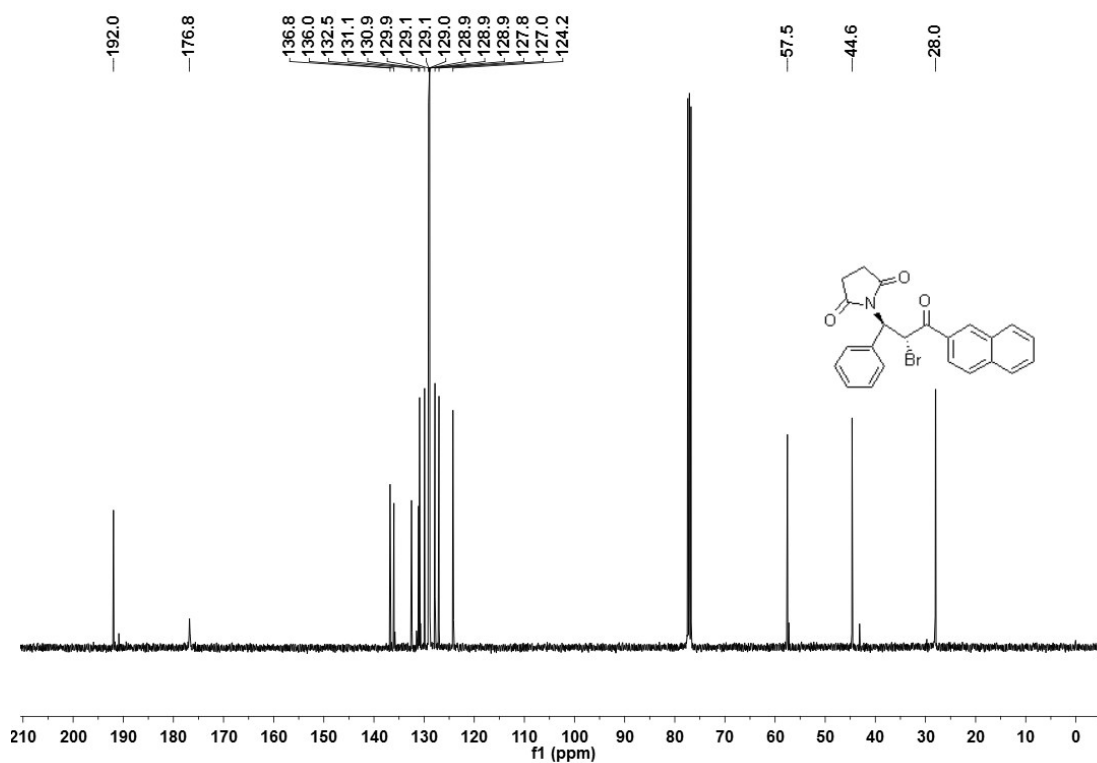
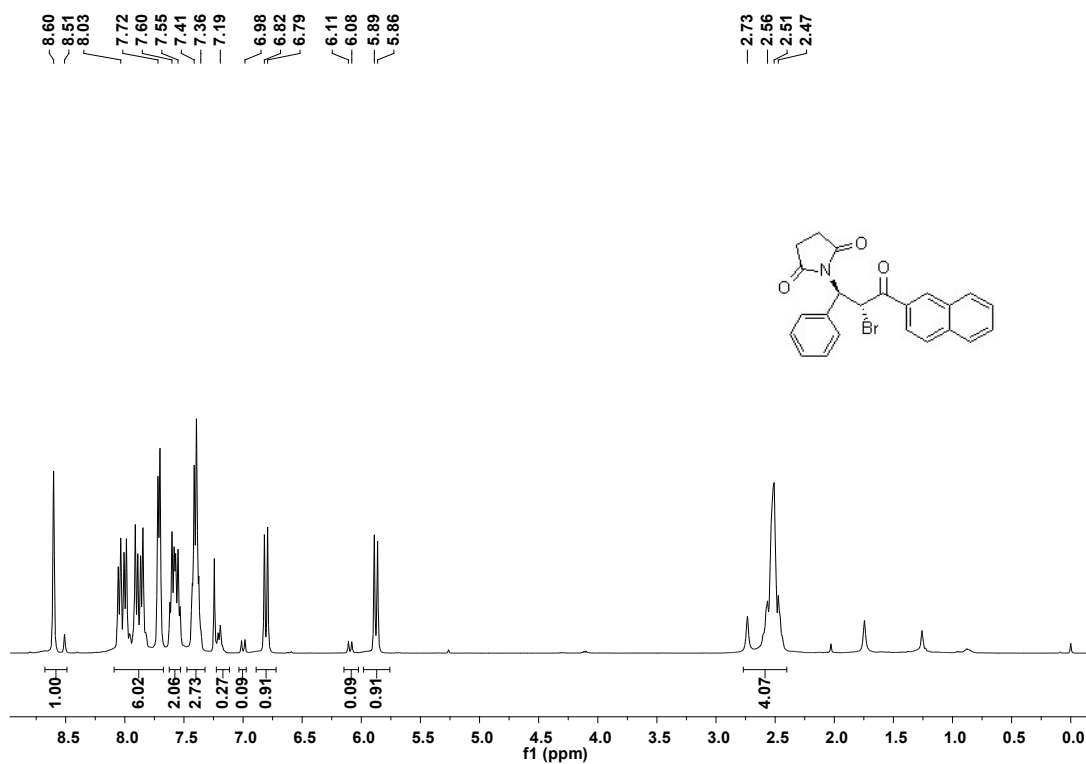
56.6  
43.3  
28.0



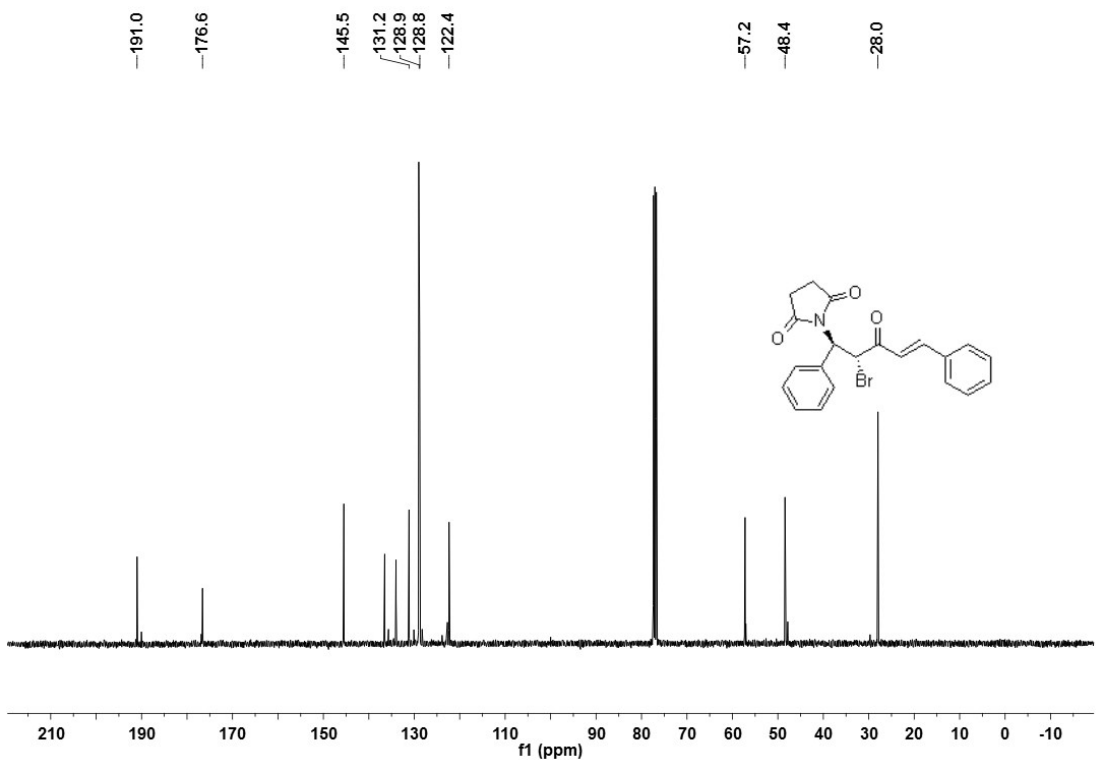
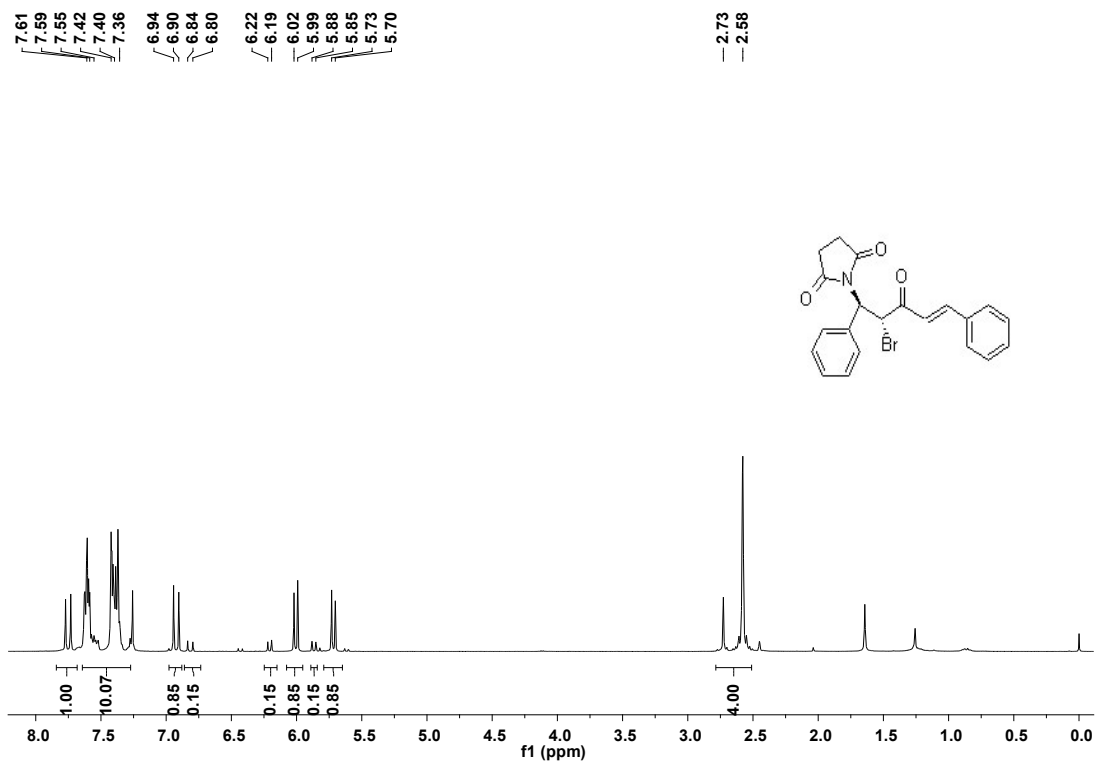
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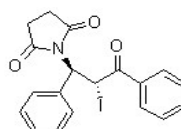
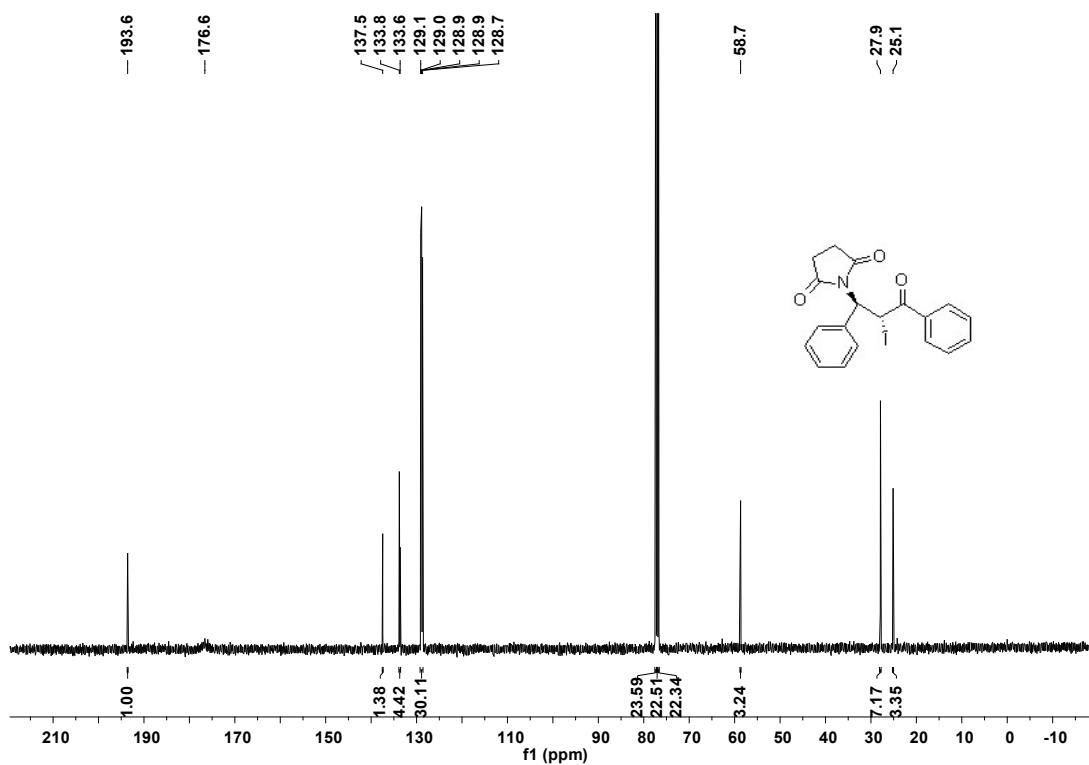
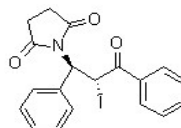
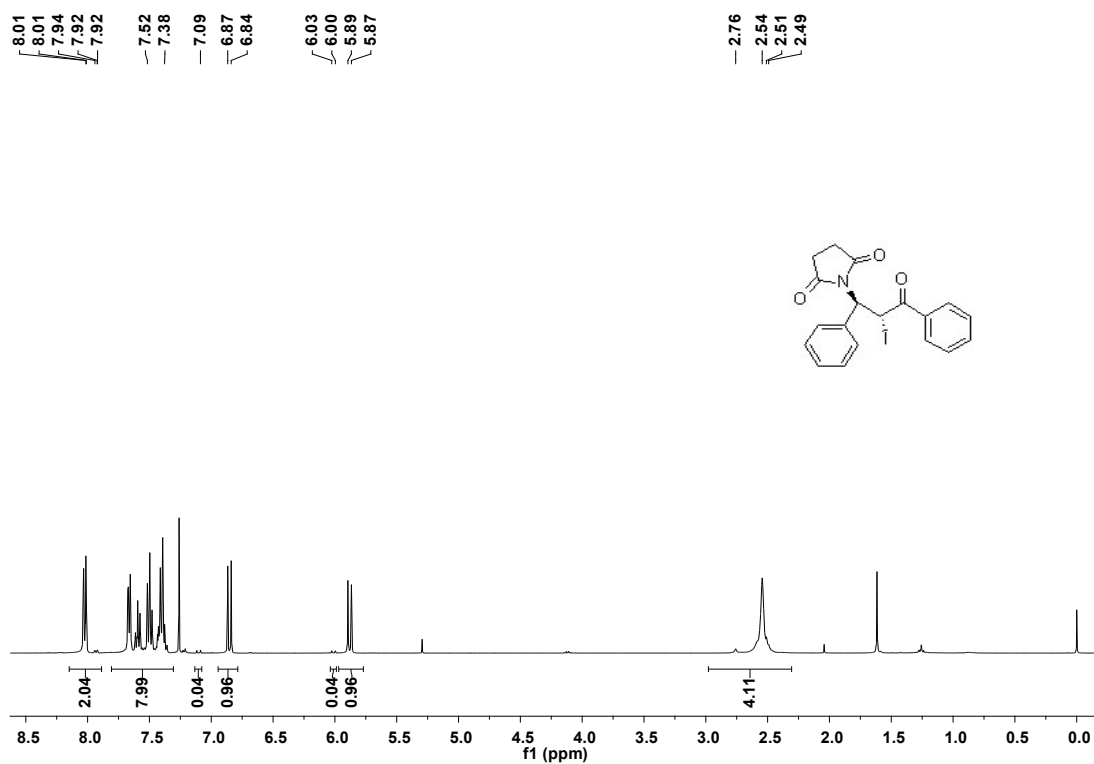
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3ab

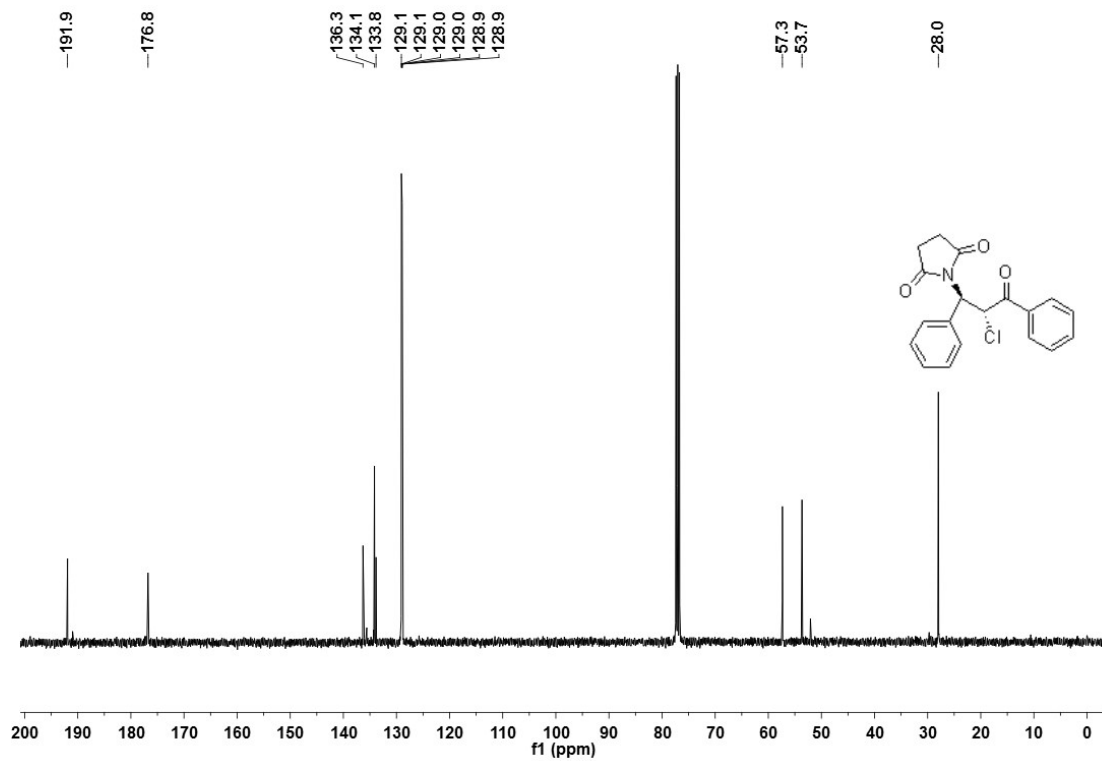
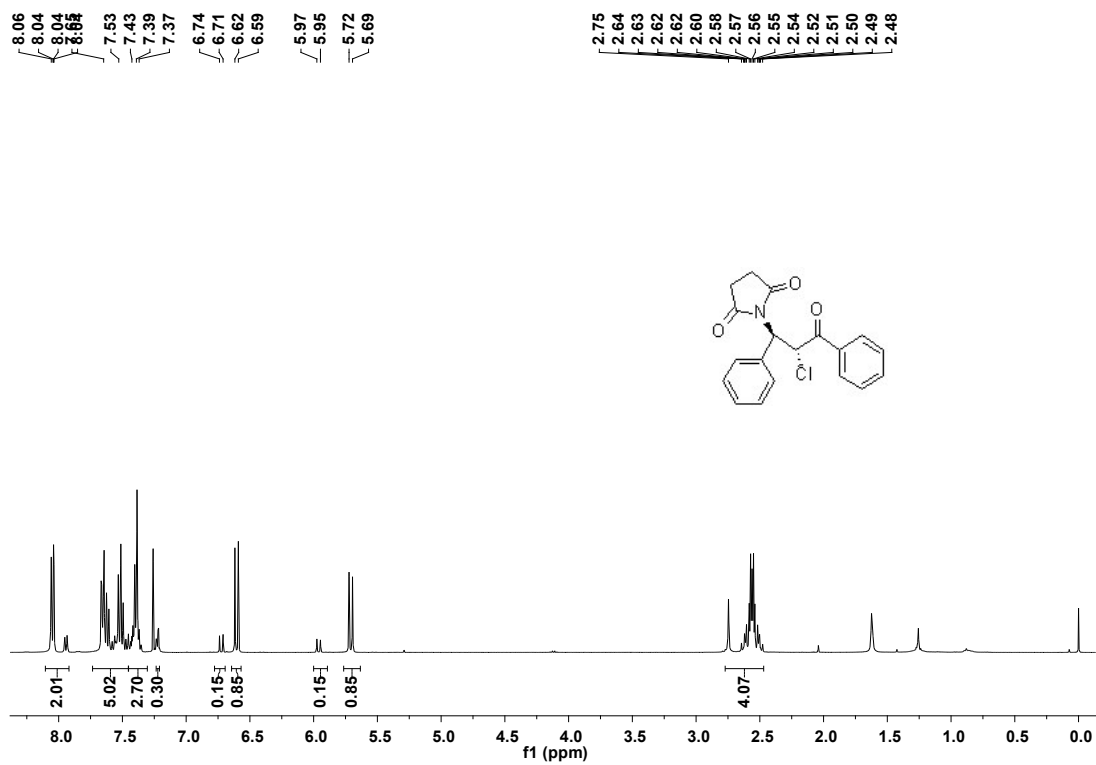


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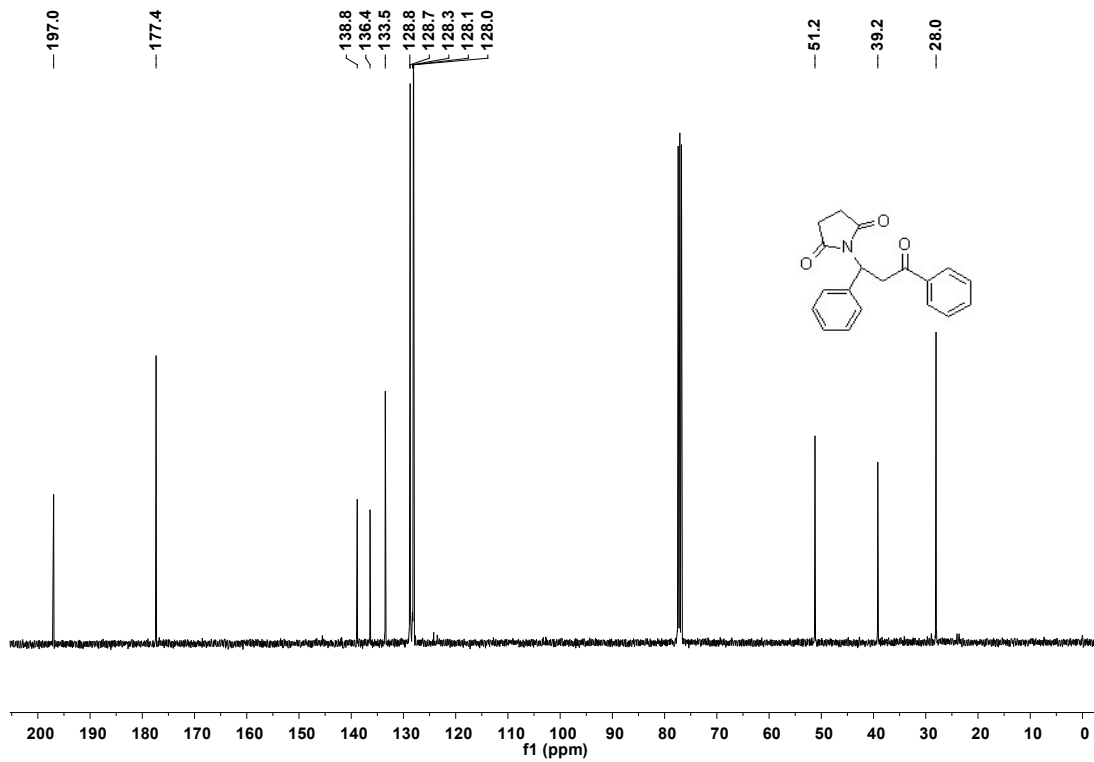
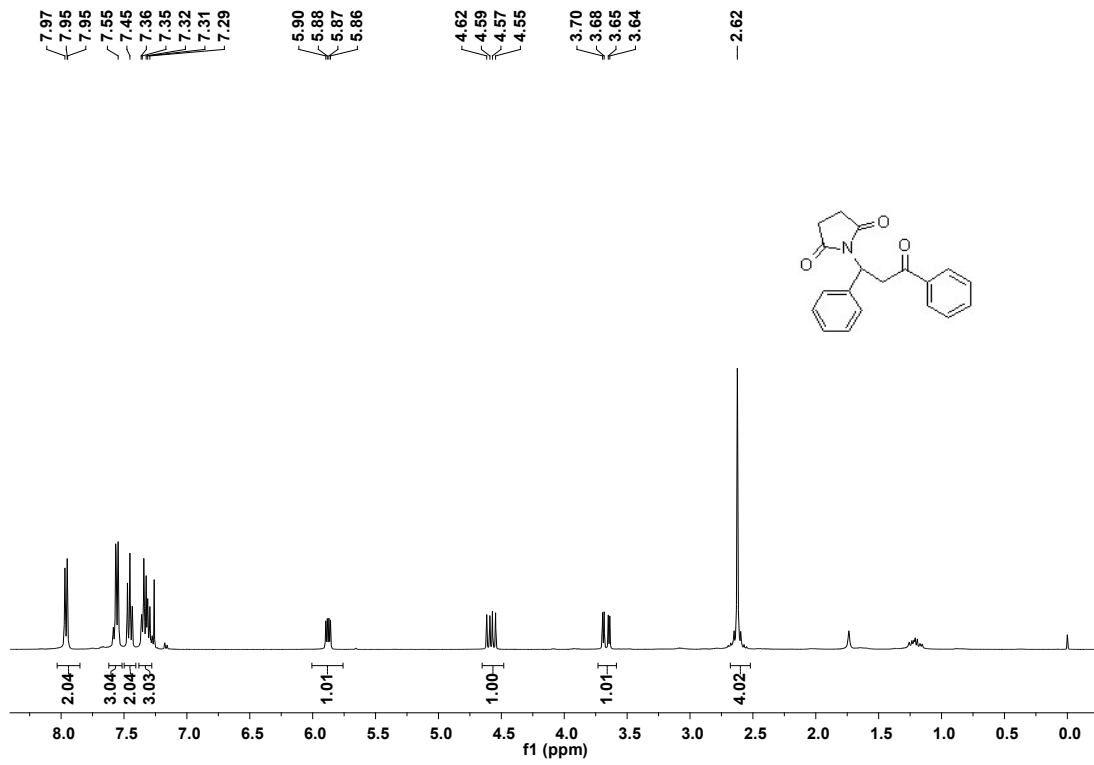




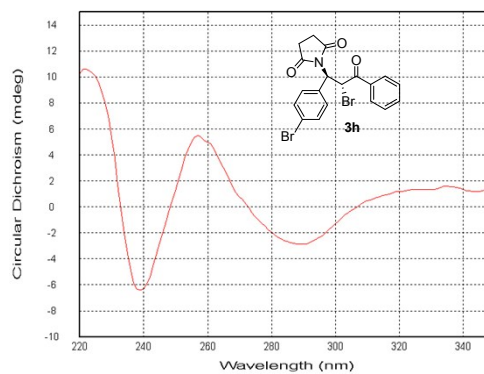
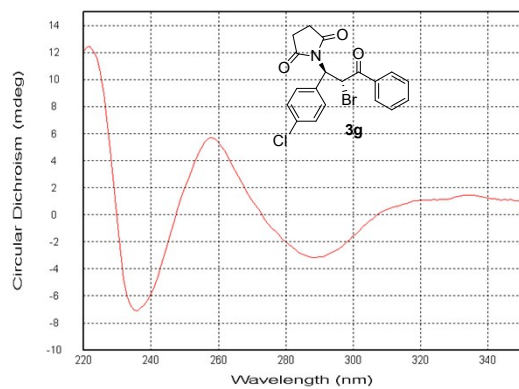
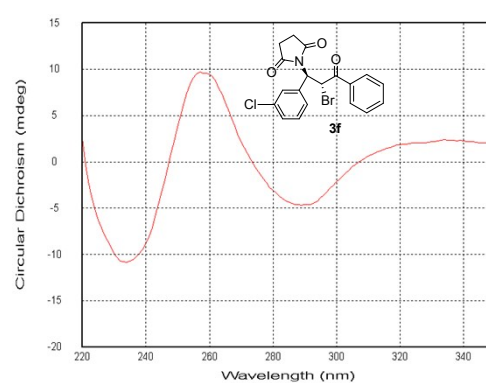
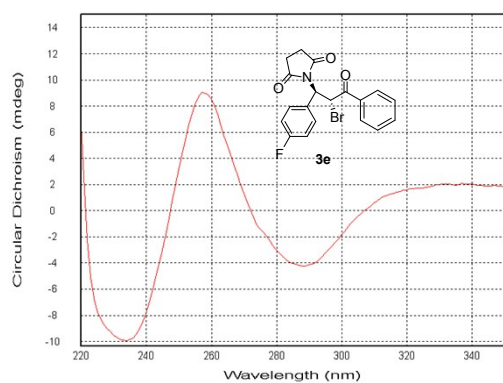
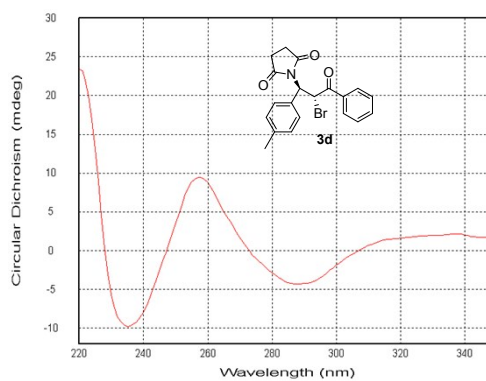
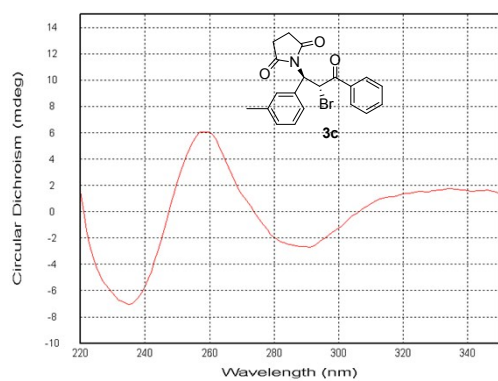
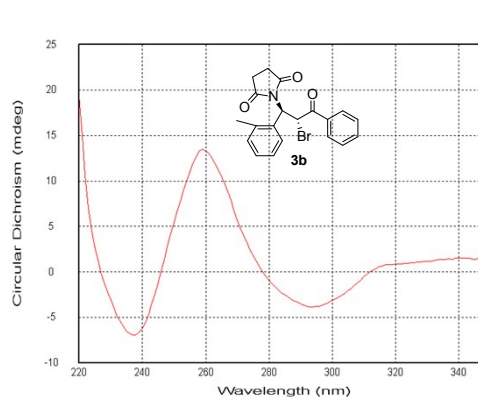
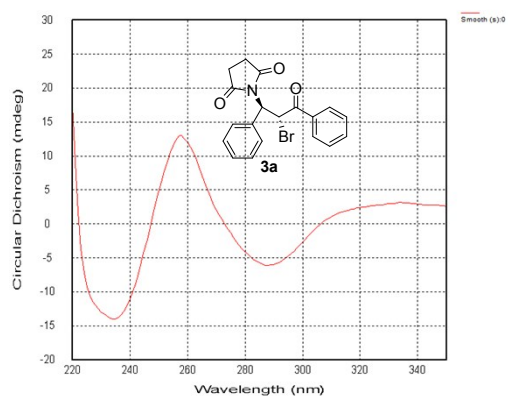
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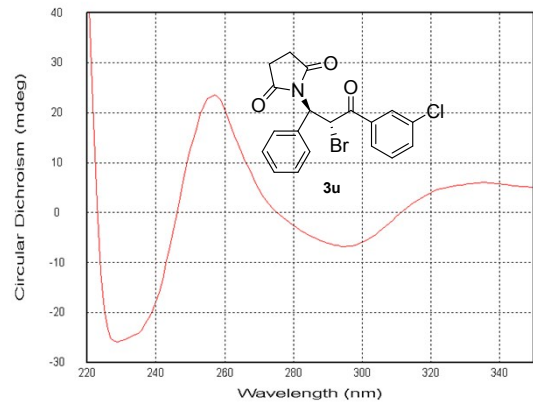
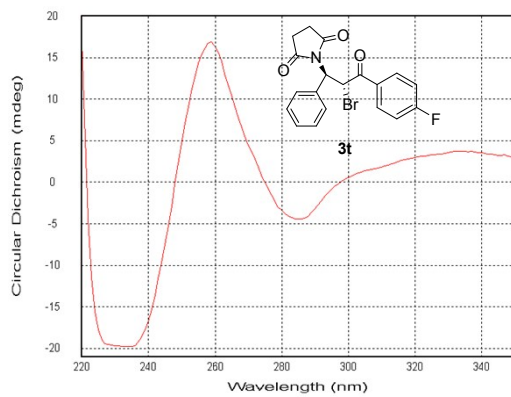
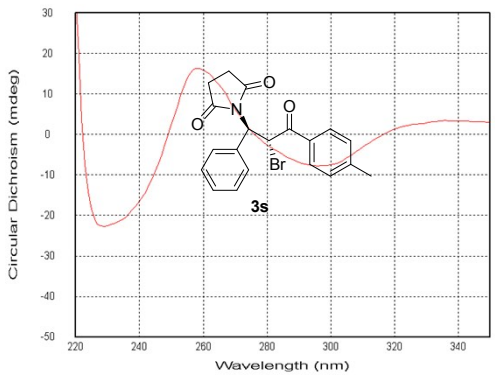
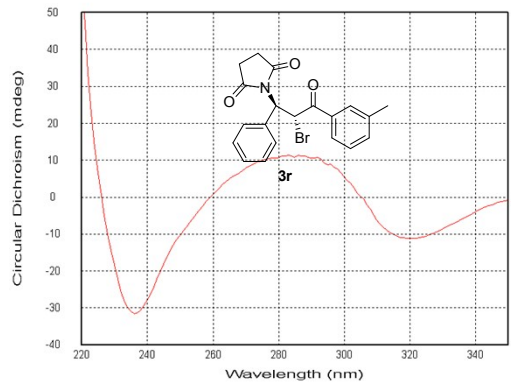
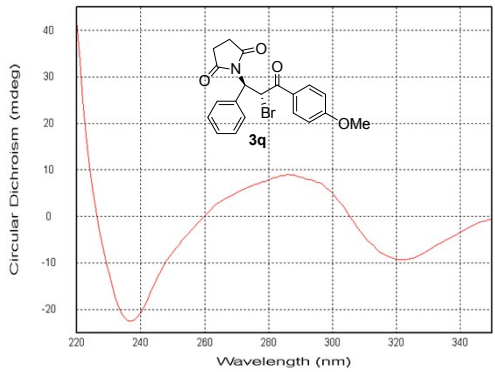
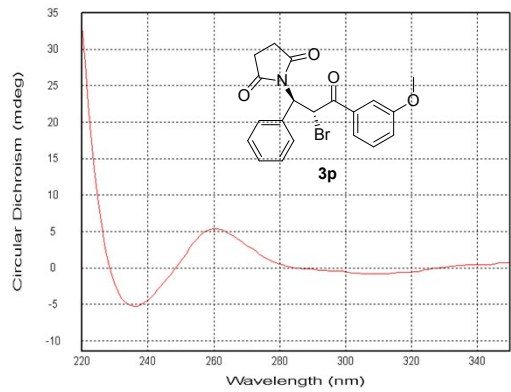
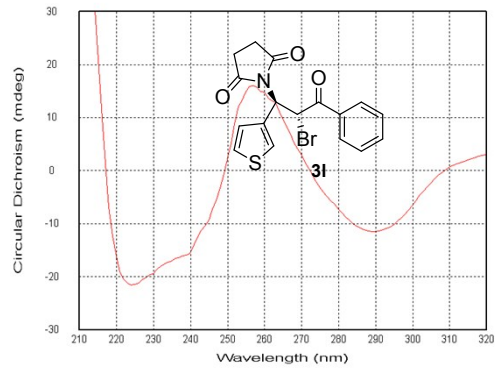
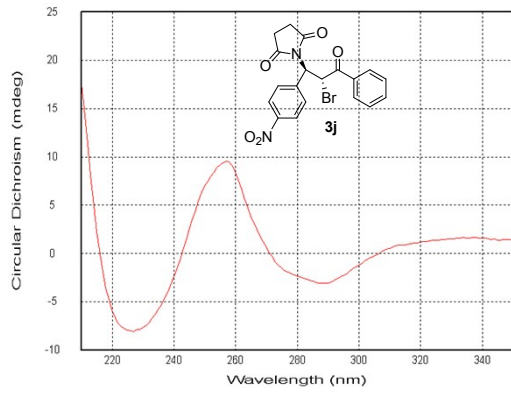


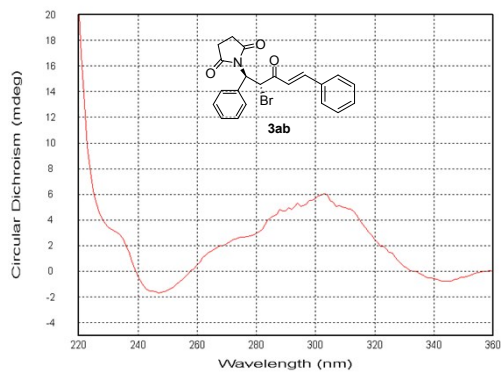
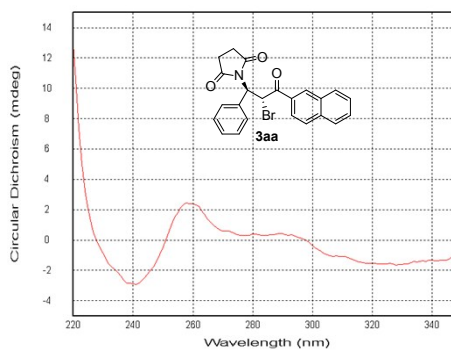
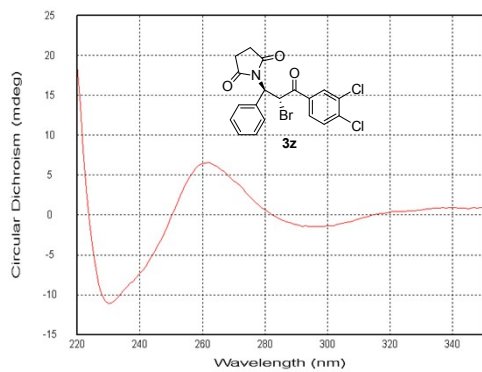
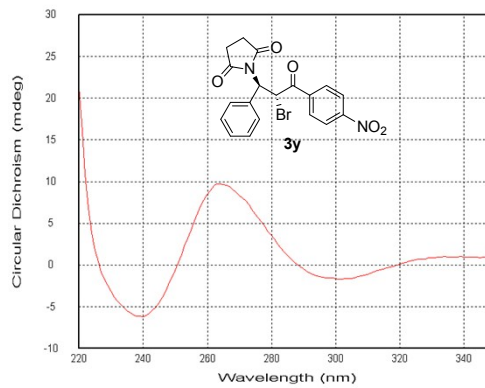
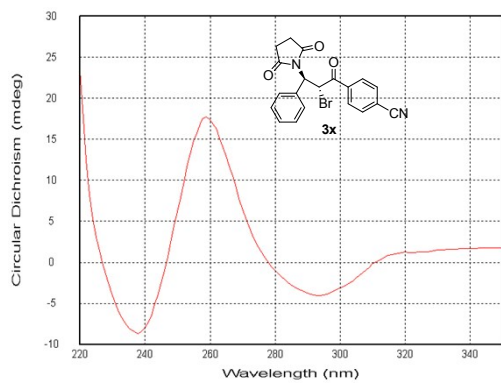
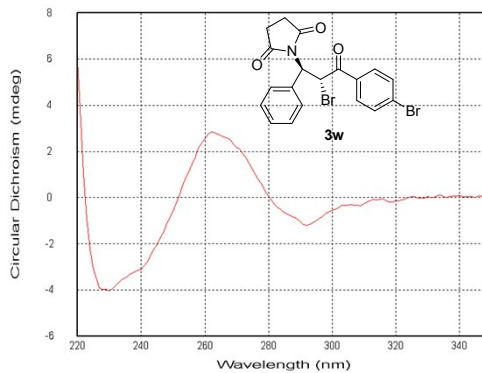
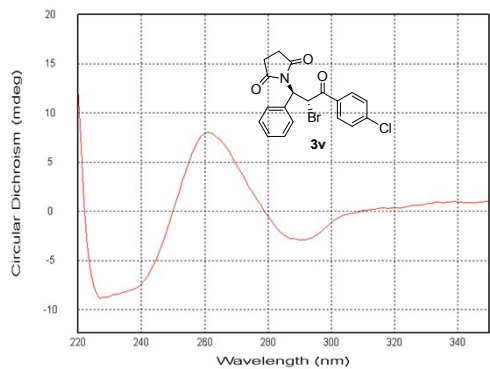
7



## 8. Copies of CD spectra in methanol







## 9. References

1. (a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett*, 2005, 2445; (b) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie and X. M. Feng, *Angew. Chem., Int. Ed.*, 2008, **47**, 1308; (c) K. Zheng, B. Qin, X. H. Liu and X. M. Feng, *J. Org. Chem.*, 2007, **72**, 8478; (d) X. Zhang, D. H. Chen, X. H. Liu and X. M. Feng, *J. Org. Chem.*, 2007, **72**, 5227; (e) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu and X. M. Feng, *Org. Lett.*, 2009, **11**, 1401.