

Kinetic Resolution of 2,3-Epoxy 3-Aryl Ketones via Catalytic Asymmetric Ring-Opening with Pyrazole Derivatives†

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1. General information

^1H 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 (CDCl_3 , $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}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 (CDCl_3 , $\delta = 77.0$). Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 23 °C. Optical rotations were reported as follows: $[\alpha]_{\text{D}}^{28}$ (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All catalytic reactions were run in dried glassware. THF, toluene and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled over CaH_2 . The *N,N'*-dioxides (**L1-L6**) were prepared according to the previous reports.^[1] Starting material epoxides were prepared according to reported procedure.^[2]

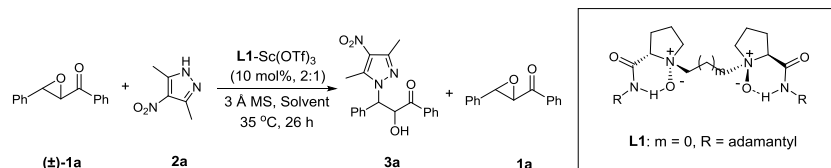
2. Optimization of the reaction conditions

Table 1. Screening of the metals

Entry ^[a]	Metal	Yield [%] ^[b]		<i>ee</i> [%] ^[c]		d.r. ^[d]
		3a	1a	3a	1a	
1	Sc(OTf) ₃	55	40	53	77	> 19:1
2	La(OTf) ₃	81	12	race	25	> 19:1
3	Fe(OTf) ₃	16	75	37	4	> 19:1
4	Y(OTf) ₃	52	40	race	43	> 19:1
5	Gd(OTf) ₃	62	30	8	53	> 19:1
6	Ni(OTf) ₂	N.R.				
7	Zn(OTf) ₂	N.R.				
8	Mg(OTf) ₂	N.R.				

[a] Unless otherwise noted, the reactions were performed with **L1**-metal (10 mol%, 1:1), 3 Å MS 30 mg in CH_2Cl_2 (0.5 mL) at 35 °C for 30 min, (±)-**1a** (0.10 mmol, 1.0 equiv) and **2a** (0.10 mmol, 1.0 equiv) were added in one-portion. The mixture was reacted at 35 °C for 26 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel IC and IE). [d] Determined by ^1H NMR analysis of the product **3a**.

Table 2. Screening of the solvents

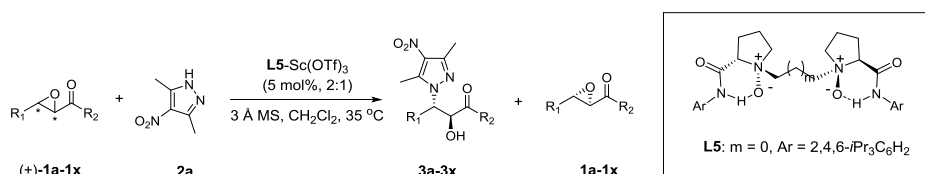


Entry ^[a]	Solvent	Yield [%] ^[b]		<i>ee</i> [%] ^[c]		d.r. ^[d]
		3a	1a	3a	1a	
1	THF	N.R.				> 19:1
2	Et ₂ O	7	90	85	race	> 19:1
3	CH ₂ Cl ₂	19	70	95	26	> 19:1
4	CHCl ₃	13	77	95	10	> 19:1
5	CHCl ₂ CH ₂ Cl	13	80	84	15	> 19:1
6	CHCl ₃ CH ₃	11	75	82	21	> 19:1

[a] Unless otherwise noted, the reactions were performed with **L1**-metal (10 mol%, 1:1), 3 Å MS 30 mg in CH₂Cl₂ (0.5 mL) at 35 °C for 30 min, ($\pm$)-**1a** (0.10 mmol, 1.0 equiv) and **2a** (0.10 mmol, 1.0 equiv) were added in one-portion. The mixture was reacted at 35 °C for 26 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel IC and IE). [d] Determined by ¹H NMR analysis of the product **3a**.

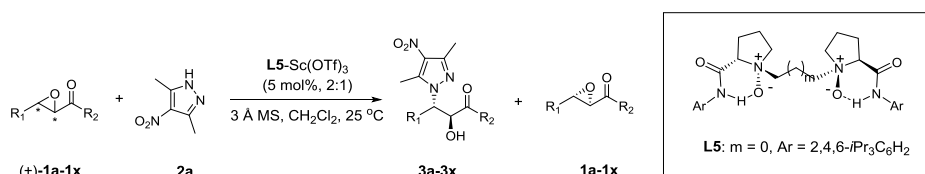
3. General procedure for the Ring-Opening reaction of different epoxides (**1a-1x**)

General procedure A for the reaction of epoxides ($\pm$)-**1**:



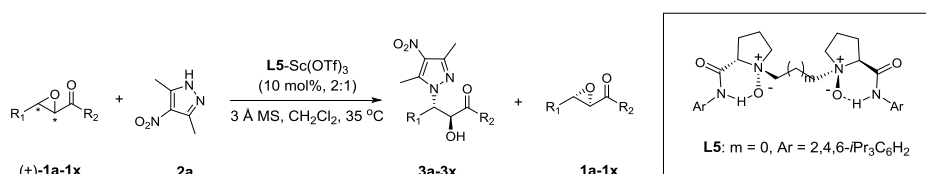
In a test tube with a magnetic stirring bar, *N,N*-dioxide **L5** (0.01 mmol, 6.6 mg), Sc(OTf)₃ (0.005 mmol, 2.5 mg), and the 3 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 35 °C for 30 min. Then, epoxide ($\pm$)-**1** (0.1 mmol) and pyrazole **2** were added to the reaction mixture at 35 °C. The reaction was stirred at 35 °C for 12-72 h. After 50% consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3** and **1**. The product was determined by HPLC and NMR analysis.

General procedure B for the reaction of epoxides ($\pm$)-**1**:



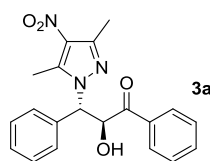
In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.01 mmol, 6.6 mg), Sc(OTf)₃ (0.005 mmol, 2.5 mg), and the 3 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 25 °C for 30 min. Then, epoxide (**±**)-**1** (0.1 mmol) and pyrazole **2** were added to the reaction mixture at 25 °C. The reaction was stirred at 25 °C for 12-24 h. After 50% consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3** and **1**. The product was determined by HPLC and NMR analysis.

General procedure C for the reaction of epoxides (**±**)-**1**:



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.02 mmol, 13.2 mg), Sc(OTf)₃ (0.01 mmol, 4.9 mg), and the 3 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 35 °C for 30 min. Then, epoxide (**±**)-**1** (0.1 mmol) and pyrazole **2** were added to the reaction mixture at 35 °C. The reaction was stirred at 35 °C for 12-72 h. After 50% consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3** and **1**. The product was determined by HPLC and NMR analysis.

4. The analytical and spectral characterization data of the products (3a-3x)



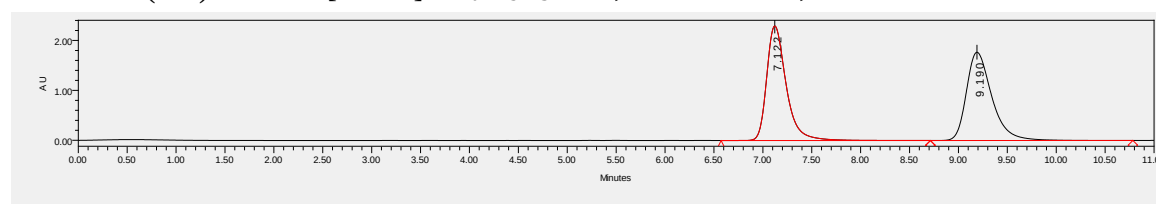
(2*S*,3*S*)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1,3-diphenylpropan-1-one (**3a**)

General procedure A; White solid; 47% yield, 95% *ee*, > 19:1 d.r.; [α]_D²⁴ = -54 (c 0.28, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (minor) = 6.97 min, *t* (major) = 9.03 min];

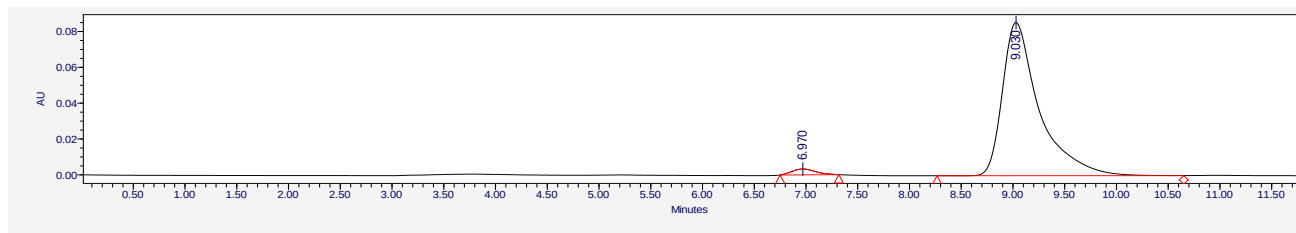
¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.28 (m, 5H), 5.92 (t, *J* = 5.6 Hz, 1H), 5.64 (d, *J* = 5.6 Hz, 1H), 3.82 (d, *J* = 5.6 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.94, 146.10, 140.78, 134.89, 134.88, 133.83, 128.98, 128.95, 128.83, 128.44, 128.25, 74.57, 64.46, 14.23, 11.35.

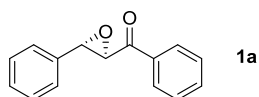
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₉N₃NaO₄, *m/z*: 388.1268, observed: 388.1269.



Retention Time	Area	% Area
7.122	31673831	49.80
9.190	31924377	50.20



Retention Time	Area	% Area
6.970	51658	2.38
9.030	2114907	97.62

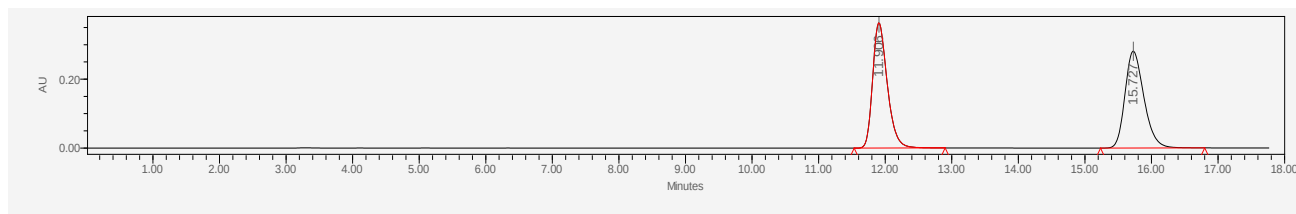


(2R,3S)-phenyl(3-phenyloxiran-2-yl)methanone (**1a**)

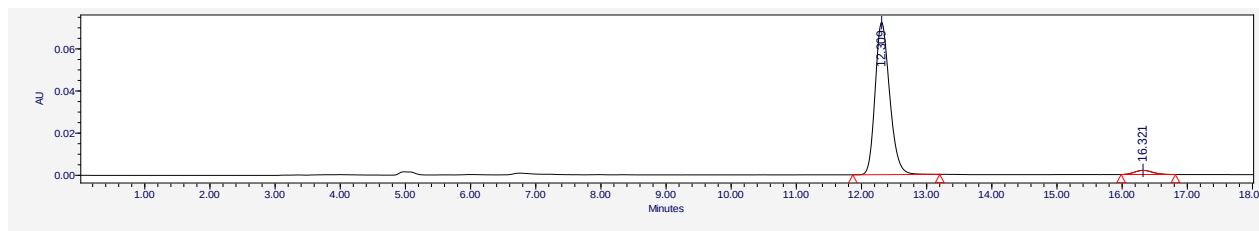
General procedure A; White solid; 49% yield, 94% *ee*, > 99:1 d.r.; $[\alpha]_D^{24} = -225$ (c 0.15, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 12.31 min, t (minor) = 16.32 min];

¹H NMR (400 MHz, CDCl₃) δ 8.08 – 7.96 (m, 2H), 7.62 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.31 (m, 5H), 4.30 (d, *J* = 2.0 Hz, 1H), 4.08 (d, *J* = 1.6 Hz, 1H).

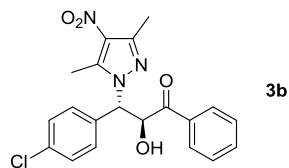
HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₂NaO₂, *m/z*: 247.0730, observed: 247.0732.



Retention Time	Area	% Area
11.906	5532042	49.94
15.727	5544341	50.06



Retention Time	Area	% Area
12.309	1127016	97.04
16.321	34345	2.96



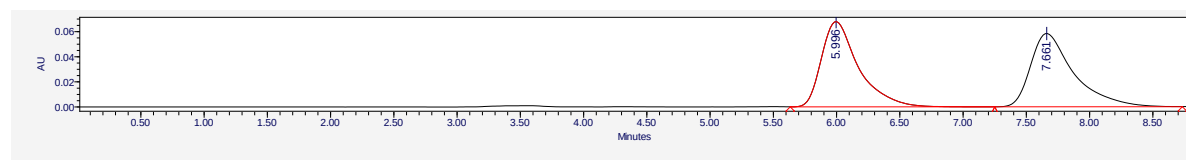
(2*S*,3*S*)-3-(4-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3b**)

General procedure C; White solid; 50% yield, 94% *ee*, > 19:1 d.r.; $[\alpha]_D^{30} = -39$ (c 0.21, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, *t* (minor) = 6.48 min, *t* (major) = 8.05 min];

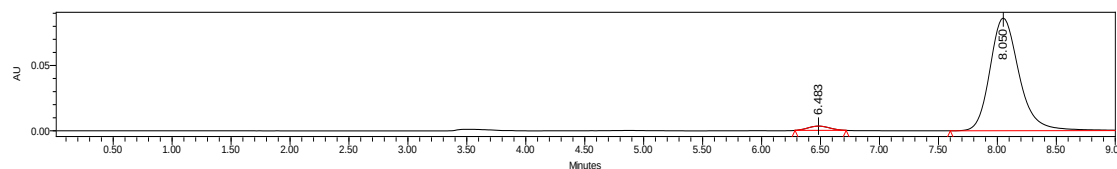
¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.79 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.22 (m, 3H), 5.88 (t, *J* = 6.0 Hz, 1H), 5.61 (d, *J* = 6.0 Hz, 1H), 4.08 (d, *J* = 6.8 Hz, 1H), 3.93 (d, *J* = 6.4 Hz, 1H), 2.51 (d, *J* = 2.4 Hz, 1H), 2.46 (d, *J* = 3.6 Hz, 5H).

¹³C NMR (100 MHz, CDCl₃) δ 198.83, 146.35, 140.74, 135.00, 134.64, 134.04, 133.37, 129.74, 128.99, 128.51, 74.55, 63.70, 14.24, 11.35.

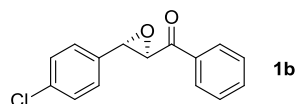
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₈³⁵ClN₃NaO₄, *m/z*: 422.0879, observed: 422.0885; C₂₀H₁₈³⁷ClN₃NaO₄, *m/z*: 424.0849, observed: 422.0868.



Retention Time	Area	% Area
5.996	1384563	50.06
7.661	1380992	49.94



Retention Time	Area	% Area
6.483	41604	2.72
8.050	1485456	97.28

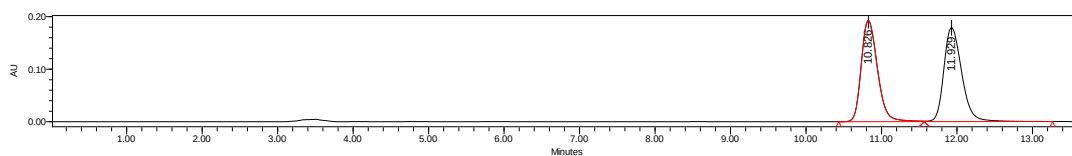


(2*R*,3*S*)-3-(4-chlorophenyl)oxiran-2-yl(phenyl)methanone (**1b**)

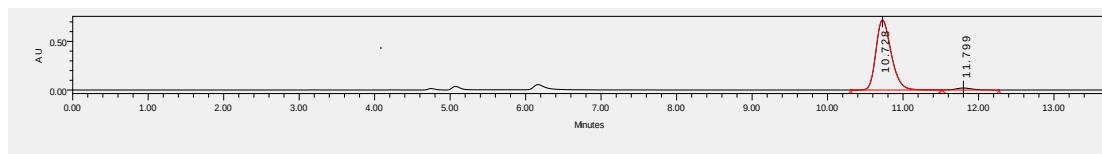
General procedure C; White solid; 49% yield, 95% *ee*, > 99:1 d.r.; $[\alpha]_D^{31} = -204$ (c 0.16, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, *t* (major) = 10.73 min, *t* (minor) = 11.79 min];

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.25 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.6 Hz, 1H).

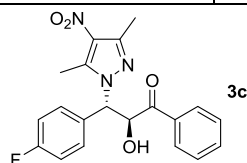
HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₁³⁵ClNaO₂, *m/z*: 281.0340, observed: 281.0348; [M+Na]⁺ C₁₅H₁₁³⁷ClNaO₂, *m/z*: 283.0311, observed: 283.0335.



Retention Time	Area	% Area
10.826	2869652	49.42
11.929	2937552	50.58



Retention Time	Area	% Area
10.728	10138422	97.62
11.799	247009	2.38



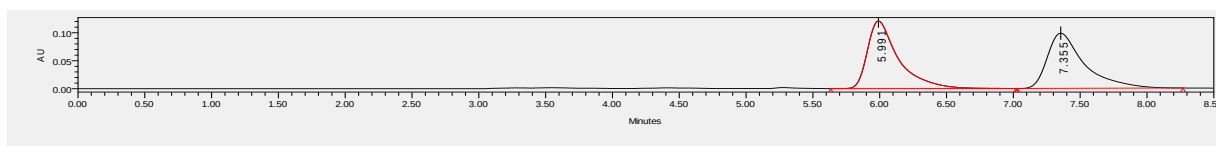
(2S,3S)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-3-(4-fluorophenyl)-2-hydroxy-1-phenylpropan-1-one (**3c**)

General procedure A; White solid; 48% yield, 96% *ee*, > 19:1 d.r.; [α]_D³⁰ = -66 (c 0.20, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 6.57 min, t (major) = 8.06 min];

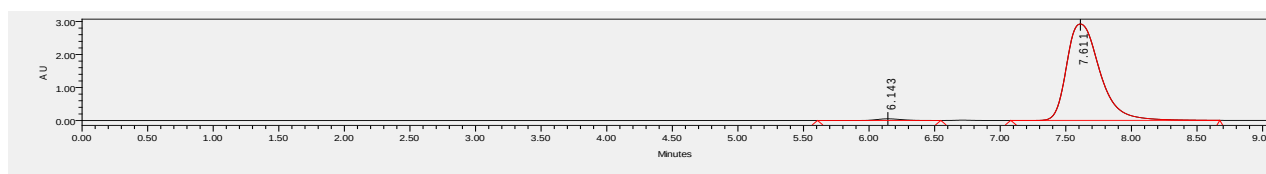
¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.77 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.03 (m, 2H), 5.87 (t, *J* = 6.0 Hz, 1H), 5.62 (d, *J* = 5.6 Hz, 1H), 3.92 (d, *J* = 6.4 Hz, 1H), 2.46 (d, *J* = 6.0 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.94, 164.12, 161.65, 146.29, 140.69, 134.70, 133.99, 131.43, 130.71, 130.68, 130.24, 130.16, 128.97, 128.48, 115.91, 115.69, 74.65, 63.68, 14.24, 11.33.

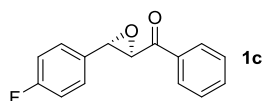
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₈¹⁸FN₃NaO₄, m/z: 406.1174, observed: 406.1176; [M+Na]⁺ C₂₀H₁₈¹⁹FN₃NaO₄, m/z: 407.1208, observed: 407.1188.



Retention Time	Area	% Area
5.991	1946314	50.63
7.355	1897781	49.37



Retention Time	Area	% Area
6.143	671693	1.29
7.611	51365534	98.71

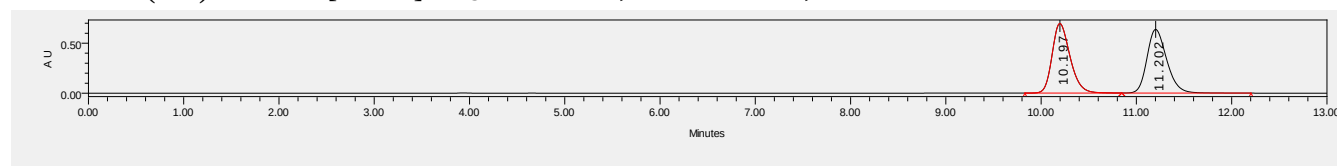


(2R,3S)-3-(4-fluorophenyl)oxiran-2-yl(phenyl)methanone (**1c**)

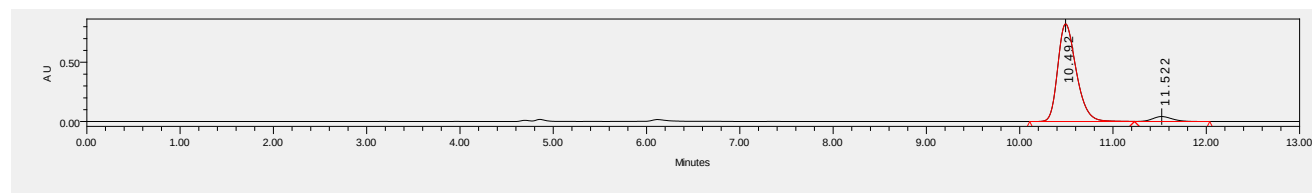
General procedure A; White solid; 51% yield, 91% *ee*, > 99:1 d.r.; $[\alpha]_D^{30} = -167$ (c 0.21, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 10.49 min, t (minor) = 11.52 min];

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.35 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 4.26 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.6 Hz, 1H).

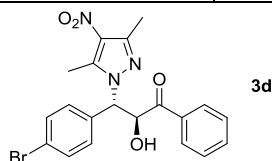
HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₁¹⁸FNaO₂, m/z: 265.0635, observed: 265.0640.



Retention Time	Area	% Area
10.197	9136381	49.92
11.202	9164885	50.08



Retention Time	Area	% Area
10.492	11348345	95.87
11.522	488776	4.13



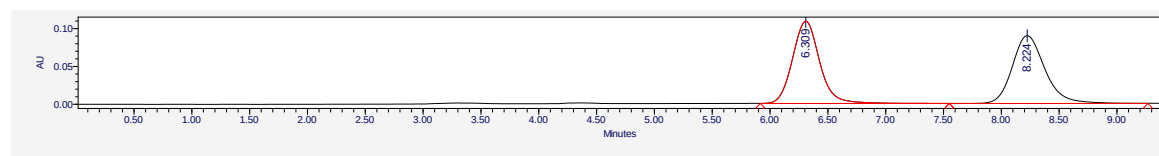
(2S,3S)-3-(4-bromophenyl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3d**)

General procedure C; colorless oil; 48% yield, 93% *ee*, d.r. = 17:1; $[\alpha]_D^{31} = -28$ (c 0.16, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 6.80 min, t (major) = 8.89 min];

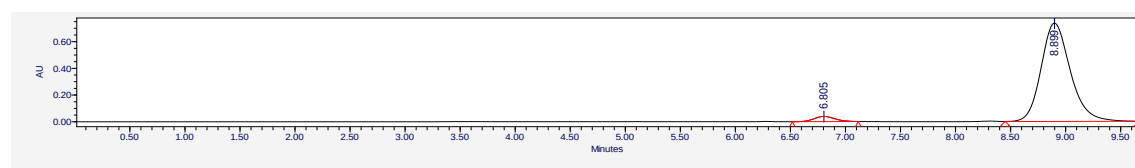
¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.87 (d, *J* = 5.6 Hz, 1H), 5.60 (d, *J* = 5.6 Hz, 1H), 4.12 – 3.61 (m, 1H), 2.46 (d, *J* = 4.0 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 198.81, 146.34, 140.72, 134.65, 134.02, 133.91, 131.94, 130.03, 128.98, 128.50, 123.21, 74.50, 63.78, 14.21, 11.33.

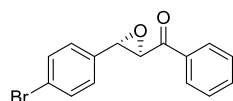
HRMS (ESI) calcd for $[\text{M}+\text{H}]^+ \text{C}_{20}\text{H}_{18}^{79}\text{BrN}_3\text{O}_4$, m/z : 444.0554, observed: 444.0553;
 $[\text{M}+\text{H}]^+ \text{C}_{20}\text{H}_{18}^{81}\text{BrN}_3\text{O}_4$, m/z : 446.0533, observed: 444.0542.



Retention Time	Area	% Area
6.309	1765827	50.06
8.224	1761612	49.94



Retention Time	Area	% Area
6.805	511650	3.63
8.899	13600580	96.37



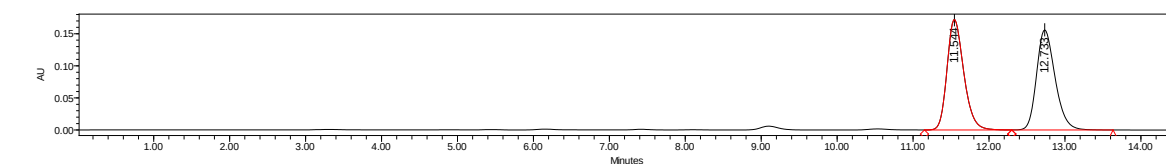
1d

(2*R*,3*S*)-(3-(4-bromophenyl)oxiran-2-yl)(phenyl)methanone (**1d**)

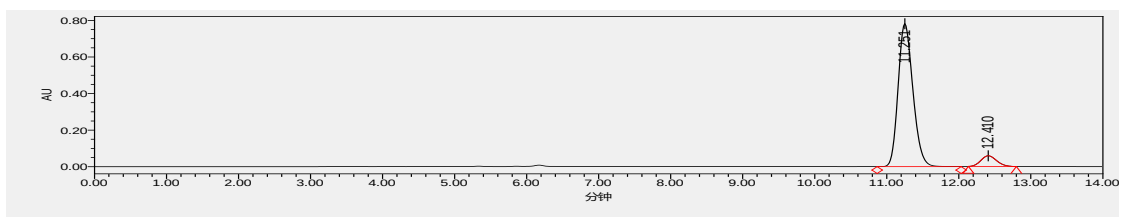
General procedure C; White solid; 52% yield, 85% *ee*, > 99:1 d.r.; $[\alpha]_{\text{D}}^{32} = -154$ (c 0.29, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 11.25 min, t (minor) = 12.41 min];

^1H NMR (400 MHz, CDCl_3) δ 8.06 – 7.94 (m, 2H), 7.67 – 7.60 (m, 1H), 7.57 – 7.45 (m, 4H), 7.26 – 7.21 (m, 2H), 4.24 (d, $J = 1.6$ Hz, 1H), 4.05 (d, $J = 1.6$ Hz, 1H).

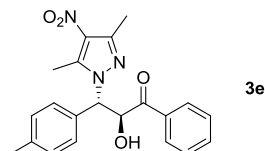
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{15}\text{H}_{11}^{79}\text{BrNaO}_2$, m/z : 324.9835, observed: 324.9836;
 $[\text{M}+\text{Na}]^+ \text{C}_{15}\text{H}_{11}^{81}\text{BrNaO}_2$, m/z : 326.9815, observed: 326.9820.



Retention Time	Area	% Area
11.544	2639531	50.01
12.733	2638257	49.99



Retention Time	Area	% Area
11.251	11155295	92.67
12.410	882343	7.33



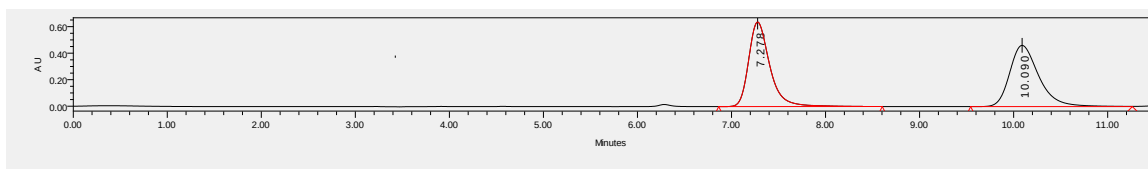
(2S,3S)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-1-phenyl-3-(p-tolyl)propan-1-one (**3e**)

General procedure B; White solid; 50% yield, 91% *ee*, > 19:1 d.r.; $[\alpha]_D^{31} = -58$ (c 0.17, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 7.02 min, t (major) = 9.62 min];

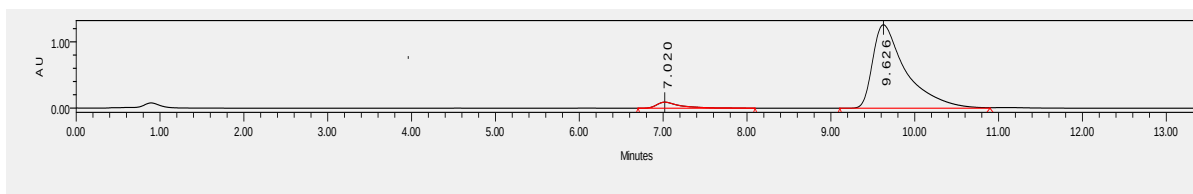
¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.17 (m, 4H), 5.91 (t, *J* = 6.0 Hz, 1H), 5.59 (d, *J* = 6.0 Hz, 1H), 3.76 (d, *J* = 6.0 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 6H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 199.02, 146.06, 140.68, 138.92, 134.84, 133.85, 131.82, 131.37, 129.53, 128.96, 128.45, 128.16, 74.39, 64.26, 21.17, 14.26, 11.36.

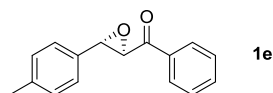
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₂₁N₃NaO₄, *m/z*: 402.1424, observed: 402.1424.



Retention Time	Area	% Area
7.278	9952884	50.01
10.090	9949981	49.99



Retention Time	Area	% Area
7.020	1554652	4.27
9.626	34852371	95.73



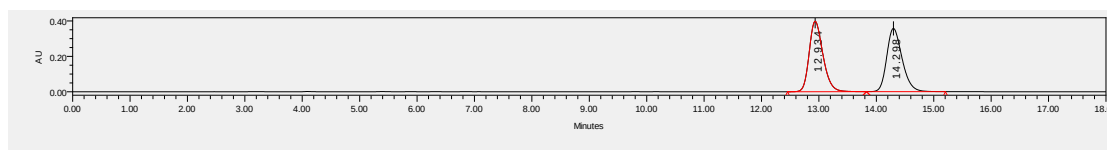
1e

(2R,3S)-phenyl(3-(p-tolyl)oxiran-2-yl)methanone (**1e**)

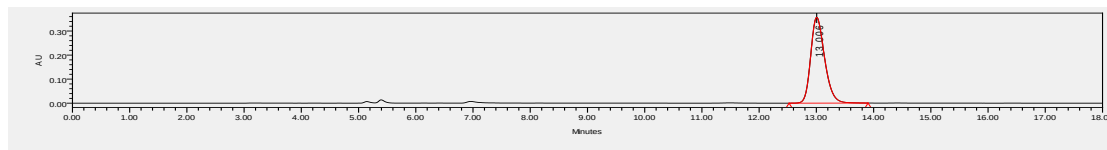
General procedure B; White solid; 43% yield, > 99% *ee*, > 99:1 d.r.; $[\alpha]_D^{31} = -206$ (c 0.16, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 13.06 min];

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.29 (d, *J* = 1.6 Hz, 1H), 4.04 (d, *J* = 1.6 Hz, 1H), 2.38 (s, 3H).

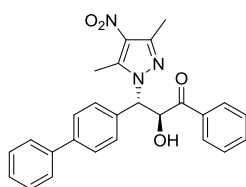
HRMS (ESI) calcd for [M+Na]⁺ C₁₆H₁₄NaO₂, m/z: 261.0886, observed: 261.0893.



Retention Time	Area	% Area
12.934	6653296	50.08
14.298	6630912	49.92



Retention Time	Area	% Area
13.006	6022414	100.00



3f

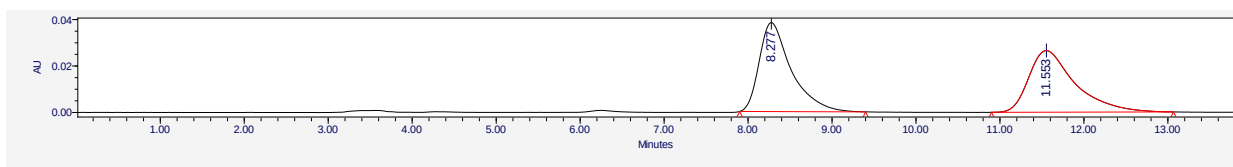
(2S,3S)-3-([1,1'-biphenyl]-4-yl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3f**)

General procedure A; White solid; 49% yield, 95% *ee*, > 19:1 d.r.; $[\alpha]_D^{17} = 6$ (c 0.19, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 8.91 min, t (major) = 12.51 min];

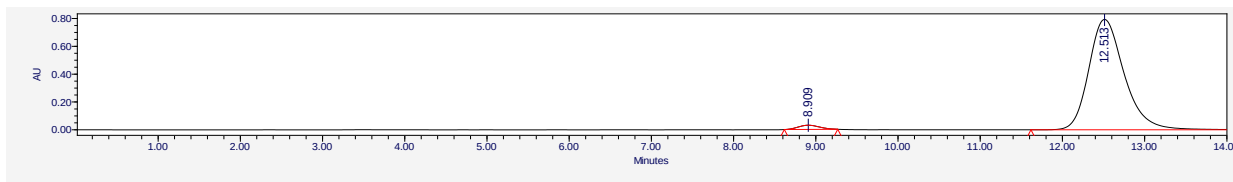
¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.54 (m, 5H), 7.45 – 7.31 (m, 7H), 5.93 (d, *J* = 6.0 Hz, 1H), 5.68 (d, *J* = 6.0 Hz, 1H), 3.91 (d, *J* = 6.0 Hz, 1H), 2.47 (d, *J* = 18.0 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.97, 146.18, 141.86, 140.81, 140.24, 134.88, 133.87, 131.44, 129.00, 128.87, 128.72, 128.46, 127.69, 127.51, 127.11, 74.51, 64.17, 14.25, 11.38.

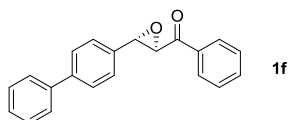
HRMS (ESI) calcd for [M+Na]⁺ C₂₆H₂₃N₃NaO₄, m/z: 464.1581, observed: 464.1585.



Retention Time	Area	% Area
8.277	1013796	50.10
11.553	1009787	49.90



Retention Time	Area	% Area
8.909	550999	2.26
12.513	23883011	97.74

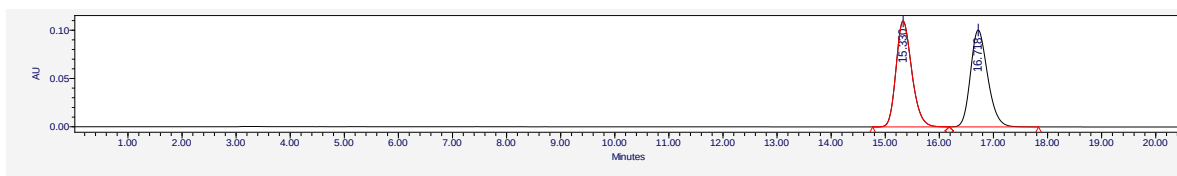


(2R,3S)-(3-([1,1'-biphenyl]-4-yl)oxiran-2-yl)(phenyl)methanone (**1f**)

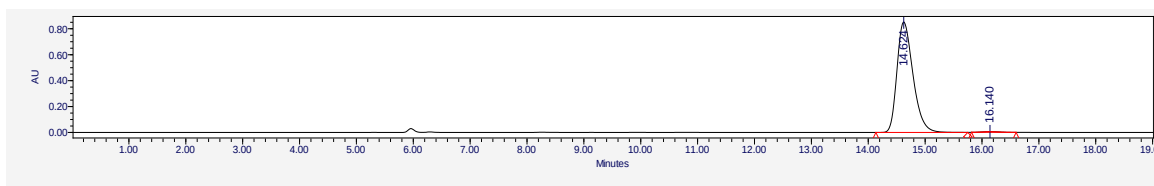
General procedure A; White solid; 48% yield, 98% *ee*, > 99:1 d.r.; [α]_D³² = -248 (c 0.21, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 14.62 min, t (minor) = 16.14 min];

¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.62 (m, 5H), 7.54 – 7.43 (m, 6H), 7.38 (t, *J* = 7.2 Hz, 1H), 4.35 (d, *J* = 1.6 Hz, 1H), 4.13 (d, *J* = 1.2 Hz, 1H).

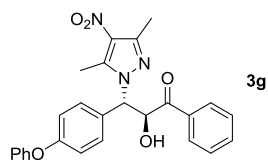
HRMS (ESI) calcd for [M+H]⁺ C₂₁H₁₆O₂, m/z: 301.1223, observed: 301.1233.



Retention Time	Area	% Area
15.330	2212822	50.02
16.718	2211067	49.98



Retention Time	Area	% Area
14.624	16693482	99.29
16.140	119198	0.71



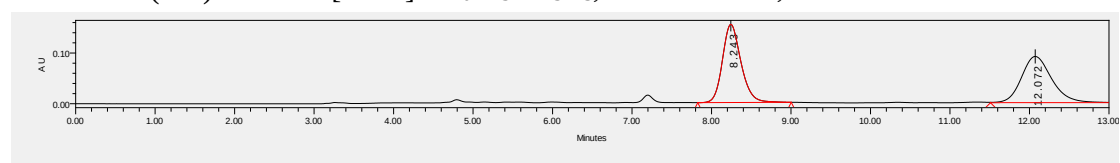
(2*S*,3*S*)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-(4-phenoxyphenyl)-1-phenylpropan-1-one (**3g**)

General procedure B; colorless oil; 50% yield, 91% *ee*, d.r. = 16:1; $[\alpha]_D^{31} = -33$ (c 0.22, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, *t* (minor) = 8.30 min, *t* (major) = 12.75 min];

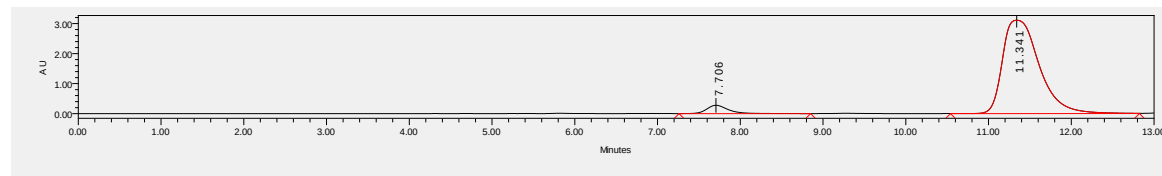
¹H NMR (400 MHz, CDCl₃) δ 7.88 (t, *J* = 11.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.93 (t, *J* = 10 Hz, 2H), 5.88 (d, *J* = 4.8 Hz, 1H), 5.61 (d, *J* = 6.0 Hz, 1H), 3.89 (d, *J* = 5.2 Hz, 1H), 2.50 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 199.03, 158.08, 156.33, 146.16, 140.67, 134.86, 133.87, 129.87, 129.82, 129.18, 129.00, 128.44, 123.91, 119.49, 118.45, 74.70, 63.90, 14.22, 11.36.

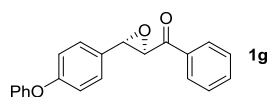
HRMS (ESI) calcd for [M+K]⁺ C₂₆H₂₃KN₃O₅, *m/z*: 496.1269, observed: 496.1276.



Retention Time	Area	% Area
8.243	2485991	50.79
12.072	2408978	49.21



Retention Time	Area	% Area
7.706	4446021	4.47
11.341	94957345	95.53

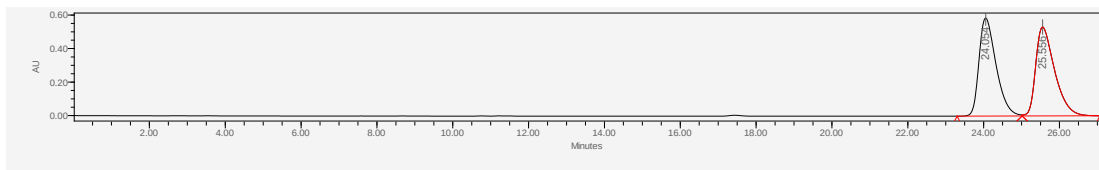


(2*R*,3*S*)-3-(4-phenoxyphenyl)oxiran-2-yl(phenyl)methanone (**1g**)

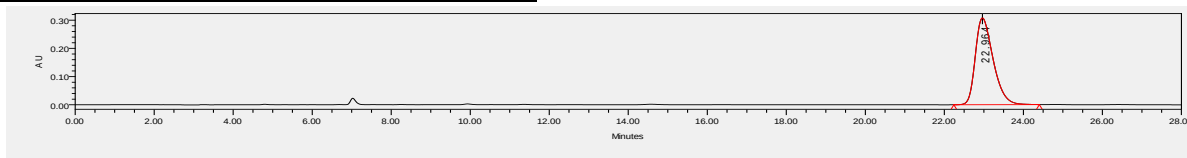
General procedure B; White solid; 46% yield, > 99% *ee*, > 99:1 d.r.; $[\alpha]_D^{32} = -213$ (c 0.19, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, *t* (major) = 22.96 min];

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.35 (m, 4H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.03 (m, 4H), 4.30 (d, *J* = 1.6 Hz, 1H), 4.06 (d, *J* = 1.2 Hz, 1H).

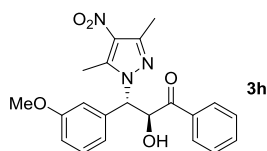
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₁₆NaO₃, *m/z*: 339.0992, observed: 339.0990.



Retention Time	Area	% Area
24.054	18266081	49.95
25.556	18302963	50.05



Retention Time	Area	% Area
22.964	9616968	100.00



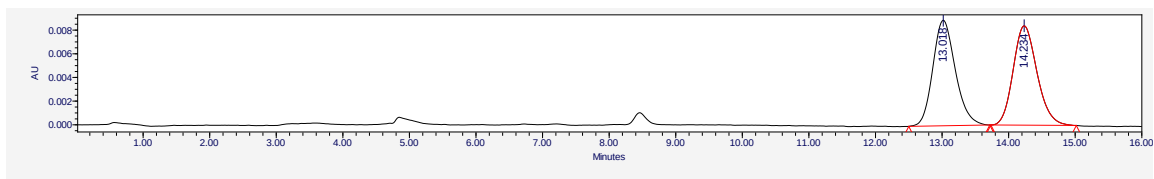
(2S,3S)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-(3-methoxyphenyl)-1-phenylpropan-1-one (**3h**)

General procedure C; colorless oil; 48% yield, 91% *ee*, > 19:1 d.r.; $[\alpha]_D^{31} = -54$ (c 0.10, CH₂Cl₂) Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 10.79 min, t (major) = 12.14 min];

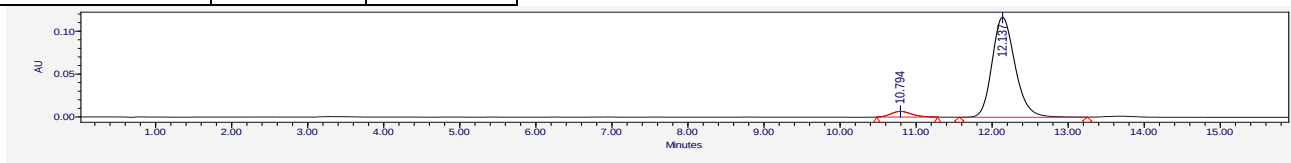
¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.27 (s, 1H), 7.24 (s, 1H), 6.92 – 6.77 (m, 3H), 5.90 (t, *J* = 6.0 Hz, 1H), 5.61 (d, *J* = 6.0 Hz, 1H), 3.76 (s, 3H), 2.46 (d, *J* = 14.8 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.80, 159.82, 146.06, 140.86, 136.38, 134.94, 133.80, 129.89, 128.99, 128.44, 120.47, 114.30, 113.93, 74.55, 64.34, 55.28, 14.23, 11.35.

HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₂₁N₃NaO₅, *m/z*: 418.1373, observed: 418.1381.

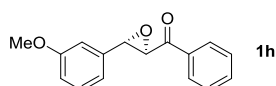


Retention Time	Area	% Area
13.018	209689	50.15
14.234	208413	49.85



Retention Time	Area	% Area
10.794	124868	4.86

12.137	2442466	95.14
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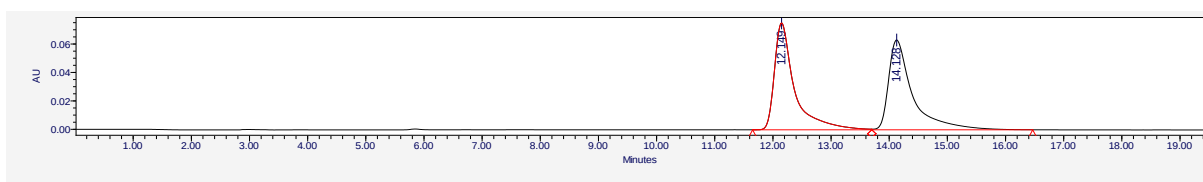


(2R,3S)-3-(3-methoxyphenyl)oxiran-2-yl(phenyl)methanone (**1h**)

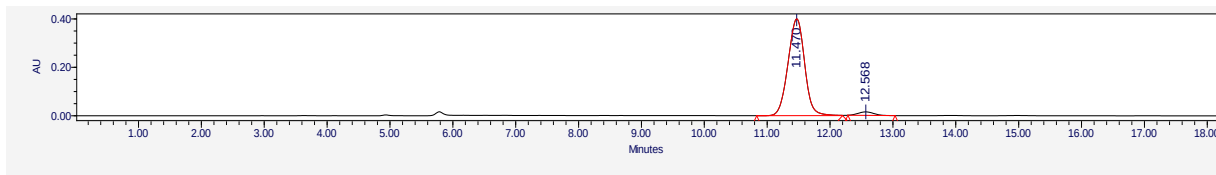
General procedure C; White solid; 48% yield, 93% *ee*, > 99:1 d.r.; $[\alpha]_D^{32} = -225$ (c 0.19, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IA, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 11.47 min, t (minor) = 12.57 min];

¹H NMR (400 MHz, CDCl₃) δ 8.01 (m, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.03 – 6.85 (m, 3H), 4.28 (d, *J* = 1.6 Hz, 1H), 4.06 (d, *J* = 1.6 Hz, 1H), 3.83 (s, 3H).

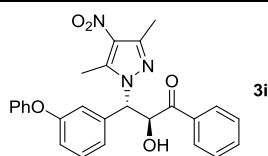
HRMS (ESI) calcd for [M+Na]⁺ C₁₆H₁₄NaO₃, m/z: 277.0835, observed: 277.0840.



Retention Time	Area	% Area
12.149	1801348	49.90
14.128	1808915	50.10



Retention Time	Area	% Area
11.470	7312077	96.68
12.568	250723	3.32



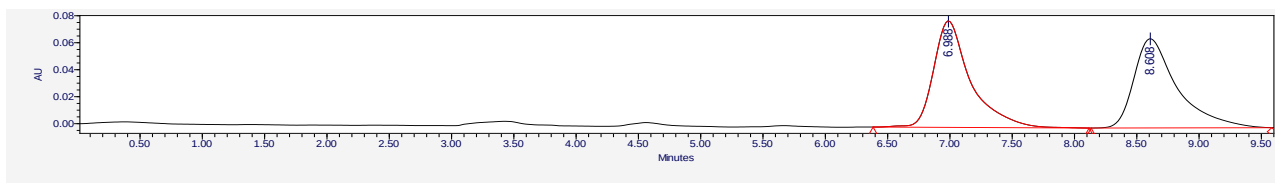
(2S,3S)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-(3-phenoxyphenyl)-1-phenylpropan-1-one (**3i**)

General procedure C; colorless oil; 42% yield, 93% *ee*, d.r. = 10:1; $[\alpha]_D^{30} = -71$ (c 0.11, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 7.37 min, t (major) = 9.18 min];

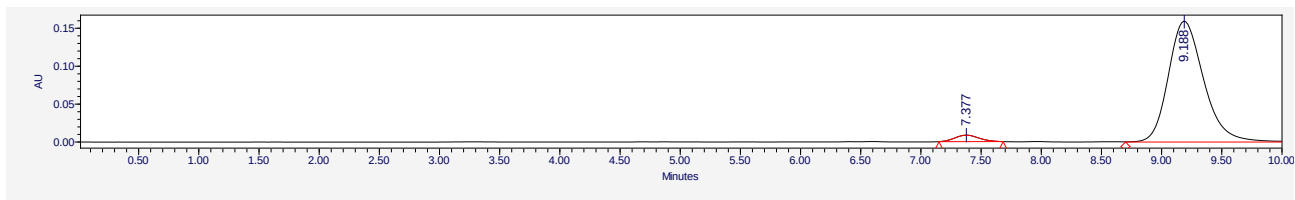
¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (m, 3H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.94 (m, 4H), 5.87 (s, 1H), 5.60 (d, *J* = 5.6 Hz, 1H), 3.90 (s, 1H), 2.45 (d, *J* = 20.2 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.81, 157.75, 156.43, 146.16, 140.84, 136.79, 134.85, 133.87, 130.10, 129.85, 129.03, 128.44, 123.78, 122.75, 119.21, 118.70, 118.35, 74.72, 64.17, 14.19, 11.35.

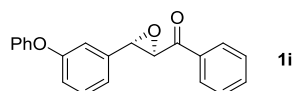
HRMS (ESI) calcd for [M+Na]⁺ C₂₆H₂₃N₃NaO₅, m/z: 480.1530, observed: 480.1536.



Retention Time	Area	% Area
6.988	1629393	50.43
8.608	1601548	49.57



Retention Time	Area	% Area
7.377	118591	3.50
9.188	3272449	96.50

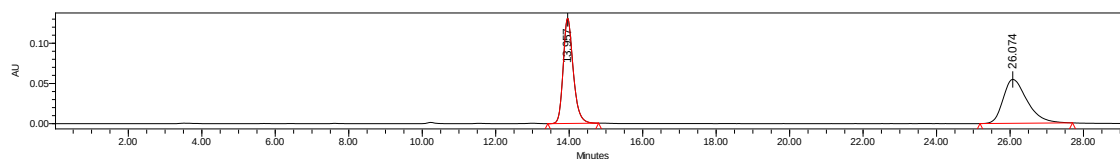


(2*R*,3*S*)-(3-(3-phenoxyphenyl)oxiran-2-yl)(phenyl)methanone (**3i**)

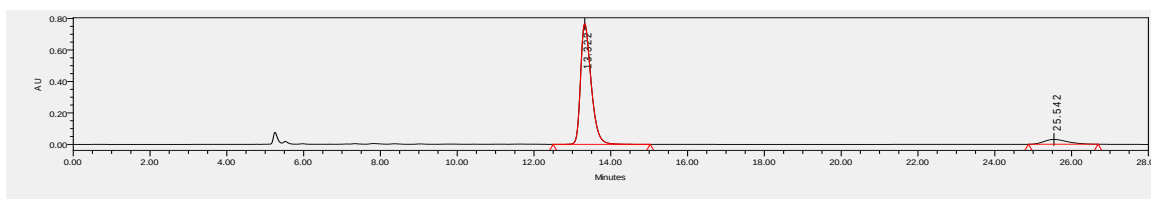
General procedure C; White solid; 52% yield, 83% *ee*, > 99:1 d.r.; [α]_D³¹ = -130 (c 0.30, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 13.32 min, t (major) = 25.54 min];

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.36 (m, 3H), 7.12 (m, 2H), 7.02 (m, 4H), 4.25 (d, *J* = 1.6 Hz, 1H), 4.05 (d, *J* = 1.6 Hz, 1H).

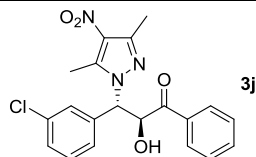
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₁₆NaO₃, m/z: 339.0992, observed: 339.0996.



Retention Time	Area	% Area
13.957	2465878	49.83
26.074	2482718	50.17



Retention Time	Area	% Area
13.322	14599620	91.76
25.542	1311397	8.24



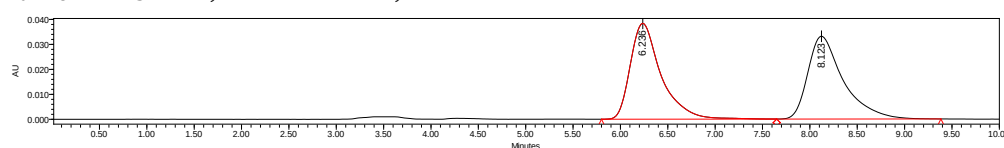
(2S,3S)-3-(3-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3j**)

General procedure C; colorless oil; 32% yield, 97% *ee*, > 19:1 d.r.; $[\alpha]_D^{31} = -44$ (c 0.10, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 6.35 min, t (major) = 8.19 min];

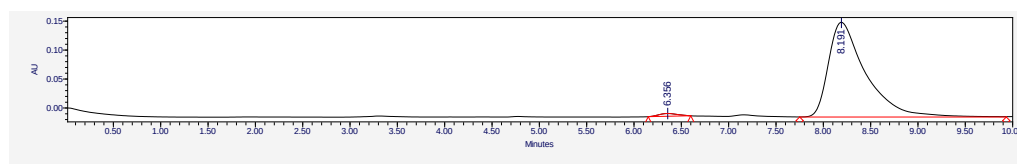
¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.82 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 1H), 5.88 (t, *J* = 6.0 Hz, 1H), 5.60 (d, *J* = 6.0 Hz, 1H), 3.85 (d, *J* = 6.4 Hz, 1H), 2.47 (d, *J* = 11.2 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.76, 146.40, 140.79, 136.91, 134.76, 134.67, 134.03, 130.00, 129.17, 128.99, 128.49, 126.59, 74.45, 63.76, 14.23, 11.34.

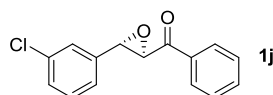
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₈³⁵ClN₃NaO₄, m/z: 422.0879, observed: 422.0883; C₂₀H₁₈³⁷ClN₃NaO₄, m/z: 424.0849, observed: 424.0868



Retention Time	Area	% Area
6.236	866195	50.13
8.123	861676	49.87



Retention Time	Area	% Area
6.356	66749	1.46
8.191	4492145	98.54

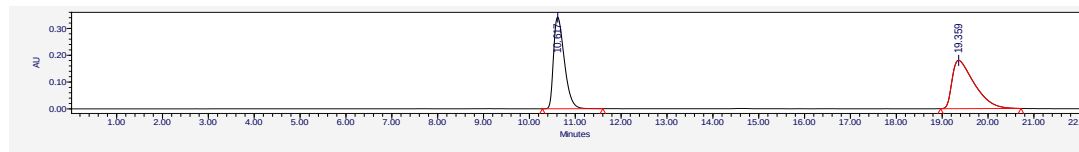


(2R,3S)-3-(3-chlorophenyl)oxiran-2-yl(phenyl)methanone (**1j**)

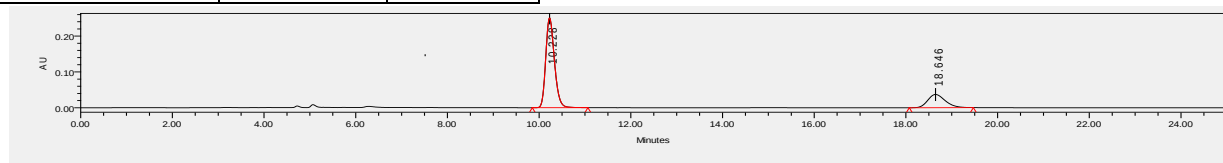
General procedure C; White solid; 63% yield, 54% *ee*, > 99:1 d.r.; $[\alpha]_D^{28} = -100$ (c 0.29, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 10.22 min, t (minor) = 18.65 min];

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 7.6$ Hz, 2H), 7.63 (t, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.39 – 7.30 (m, 3H), 7.29 – 7.23 (m, 1H), 4.26 (d, $J = 1.6$ Hz, 1H), 4.06 (d, $J = 1.2$ Hz, 1H).

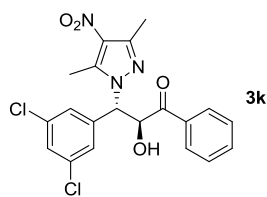
HRMS (ESI) calcd for $[\text{M}+\text{K}]^+ \text{C}_{15}\text{H}_{11}^{35}\text{ClKO}_2$, m/z : 297.0080, observed: 297.0087; $[\text{M}+\text{K}]^+ \text{C}_{15}\text{H}_{11}^{37}\text{ClKO}_2$, m/z : 299.0050, observed: 299.0053.



Retention Time	Area	% Area
10.617	5580943	48.05
19.359	6033762	51.95



Retention Time	Area	% Area
10.228	3295080	77.07
18.646	980253	22.93



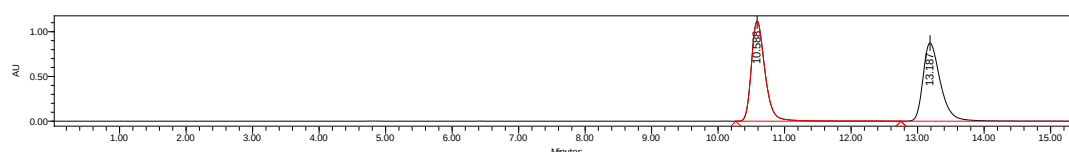
(2S,3S)-3-(3,5-dichlorophenyl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3k**)

General procedure C; colorless oil; 28% yield, 98% *ee*, > 19:1 d.r.; $[\alpha]_{\text{D}}^{31} = -17$ (c 0.11, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.14 min, t (major) = 12.94 min];

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.2$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.50 – 7.37 (m, 4H), 7.21 (m, 1H), 5.85 (t, $J = 6.0$ Hz, 1H), 5.58 (d, $J = 6.0$ Hz, 1H), 3.92 (d, $J = 6.4$ Hz, 1H), 2.47 (d, $J = 10.1$ Hz, 6H).

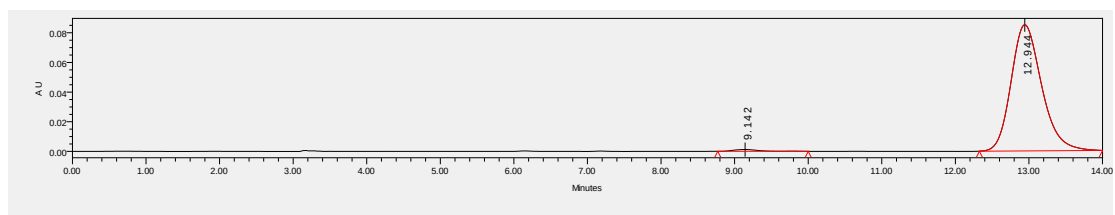
^{13}C NMR (100 MHz, CDCl_3) δ 198.69, 146.60, 140.75, 135.06, 134.49, 134.19, 133.34, 133.01, 130.65, 130.43, 129.00, 128.52, 127.80, 74.40, 63.14, 14.22, 11.33.

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{20}\text{H}_{17}^{35}\text{Cl}_2\text{N}_3\text{NaO}_4$, m/z : 456.0489, observed: 456.0488; $[\text{M}+\text{Na}]^+ \text{C}_{20}\text{H}_{17}^{37}\text{Cl}_2\text{N}_3\text{NaO}_4$, m/z : 458.0459, observed: 456.046.

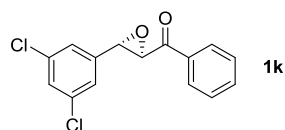


Retention Time	Area	% Area
10.588	15894585	50.09

13.187	15834355	49.91
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Retention Time	Area	% Area
9.142	20387	0.83
12.944	2448445	99.17

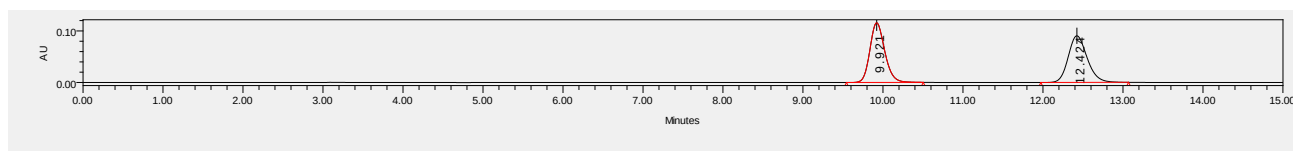


(2R,3S)-3-(3,5-dichlorophenyl)oxiran-2-yl(phenyl)methanone (**1k**)

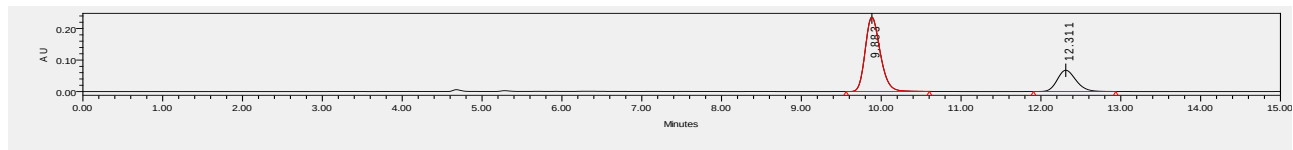
General procedure C; White solid; 66% yield, 49% *ee*, > 99:1 d.r.; $[\alpha]_D^{23} = -99$ (c 0.35, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.89 min, t (minor) = 12.31 min];

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.22 (m, 1H), 4.24 (d, *J* = 1.6 Hz, 1H), 4.06 (s, 1H).

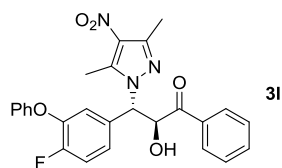
HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₀³⁵Cl₂NaO₂, m/z: 314.9951, observed: 314.9961; [M+Na]⁺ C₁₅H₁₀³⁷Cl₂NaO₂, m/z: 316.9921, observed: 314.9935;



Retention Time	Area	% Area
9.921	1487109	50.09
12.424	1482037	49.91



Retention Time	Area	% Area
9.883	3085170	74.87
12.311	1035790	25.13



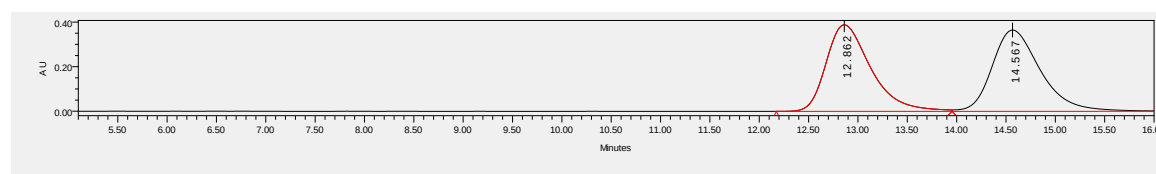
(2S,3S)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-3-(4-fluoro-3-phenoxyphenyl)-2-hydroxy-1-phenylpropan-1-one (**3l**)

General procedure C; colorless oil; 43% yield, 92% *ee*, > 19:1 d.r.; [α]_D³³ = -43 (c 0.33, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 12.96 min, t (major) = 14.54 min];

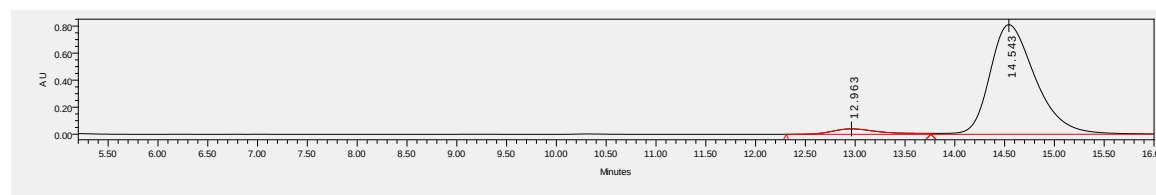
¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.17 – 7.09 (m, 2H), 7.08 – 7.00 (m, 2H), 6.89 (d, *J* = 7.6 Hz, 2H), 5.80 (t, *J* = 5.6 Hz, 1H), 5.55 (d, *J* = 5.6 Hz, 1H), 3.97 (d, *J* = 6.0 Hz, 1H), 2.43 (d, *J* = 18.0 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.84, 156.73, 155.45, 152.95, 146.33, 144.04, 143.93, 140.74, 134.67, 134.03, 131.65, 131.61, 131.44, 129.80, 129.01, 128.47, 124.50, 124.43, 123.57, 121.56, 117.50, 117.43, 117.24, 74.81, 63.59, 14.16, 11.33.

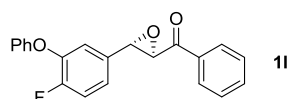
HRMS (ESI) calcd for [M+Na]⁺ C₂₆H₂₂¹⁸FN₃NaO₅, m/z: 498.1436, observed: 498.1442; [M+Na]⁺ C₂₆H₂₂¹⁹FN₃NaO₅, m/z: 499.1470, observed: 499.1475.



Retention Time	Area	% Area
12.862	12230774	49.57
14.567	12442833	50.43



Retention Time	Area	% Area
12.963	1031087	3.84
14.543	25792195	96.16

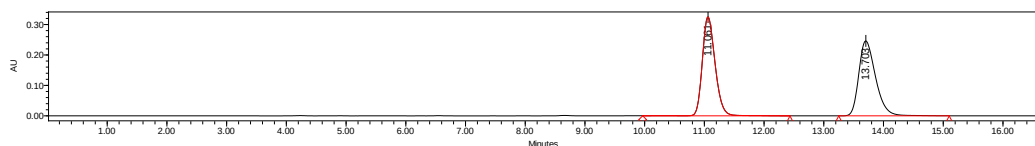


(2*R*,3*S*)-3-(4-fluoro-3-phenoxyphenyl)oxiran-2-yl(phenyl)methanone (**1l**)

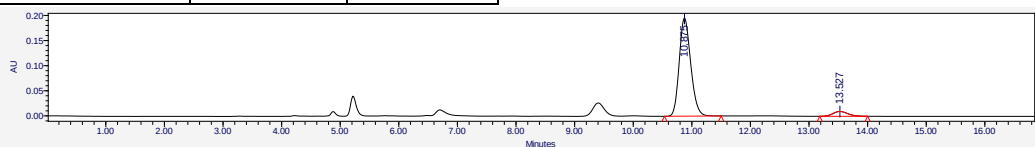
General procedure C; White solid; 47% yield, 88% *ee*, > 99:1 d.r.; [α]_D³¹ = -122 (c 0.32, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 10.88 min, t (minor) = 13.53 min];

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.22 (m, 1H), 7.17 – 7.08 (m, 2H), 7.06 – 6.95 (m, 3H), 4.19 (d, *J* = 1.6 Hz, 1H), 4.01 (s, 1H).

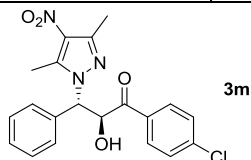
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₁₅¹⁸FNaO₃, m/z: 357.0897, observed: 357.0902; [M+Na]⁺ C₂₁H₁₅¹⁹FNaO₃, m/z: 358.0931, observed: 357.0938;



Retention Time	Area	% Area
11.061	4827979	50.19
13.703	4790596	49.81



Retention Time	Area	% Area
10.875	2660315	94.02
13.527	169117	5.98



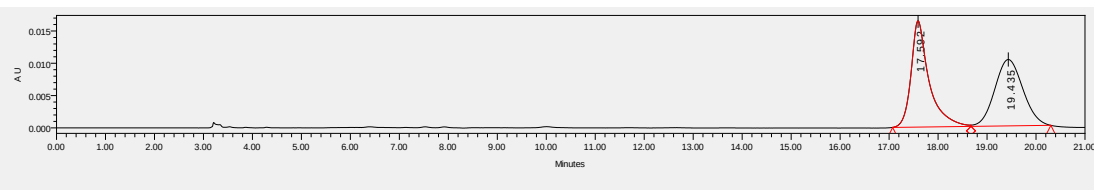
(2S,3S)-1-(4-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3m**)

General procedure C; White solid; 50% yield, 95% *ee*, > 19:1 d.r.; $[\alpha]_D^{33} = -119$ (c 0.21, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 16.73 min, t (major) = 18.11 min];

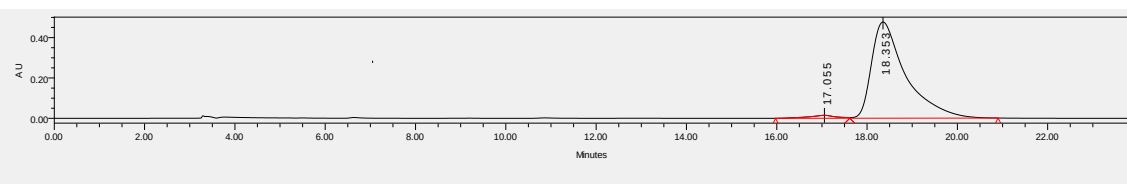
¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.27 (m, 6H), 7.25 (s, 1H), 5.80 (t, *J* = 5.6 Hz, 1H), 5.71 (d, *J* = 5.6 Hz, 1H), 4.00 (d, *J* = 5.6 Hz, 1H), 2.49 (d, *J* = 8.0 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 197.52, 146.05, 140.94, 140.21, 134.78, 133.46, 130.63, 129.02, 128.90, 128.69, 128.13, 75.47, 64.23, 14.25, 11.36.

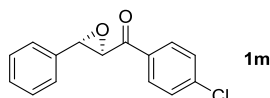
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₈³⁵ClN₃NaO₄, m/z: 422.0879, observed: 422.0884; [M+Na]⁺ C₂₀H₁₈³⁷ClN₃NaO₄, m/z: 424.0849, observed: 424.0869.



Retention Time	Area	% Area
17.592	419618	50.58
19.435	410035	49.42



Retention Time	Area	% Area
17.055	601801	2.35
18.353	25011278	97.65

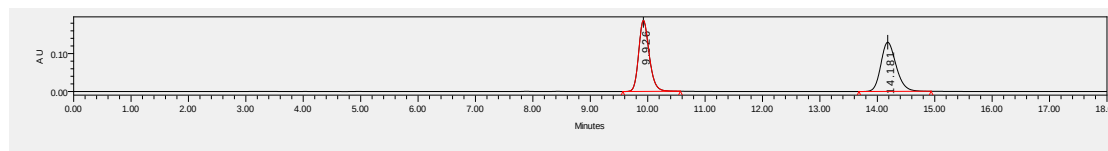


(2R,3S)- (4-chlorophenyl)(3-phenyloxiran-2-yl)methanone (**1m**)

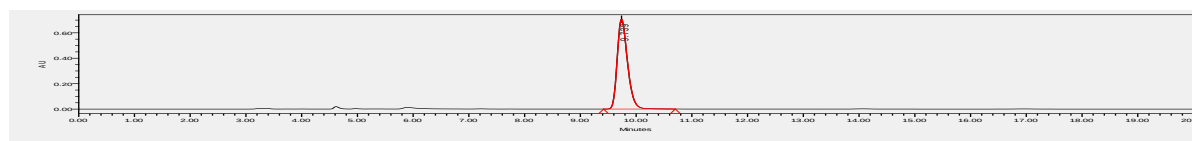
General procedure C; White solid; 49% yield, > 99% *ee*, > 99:1 d.r.; $[\alpha]_D^{32} = -214$ (c 0.16, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 95/5, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.93 min];

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.38 (m, 5H), 4.23 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.2 Hz, 1H);

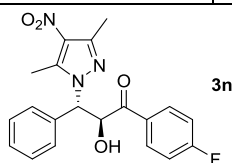
HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₁³⁵ClNaO₂, m/z: 281.0340, observed: 281.0346; [M+Na]⁺ C₁₅H₁₁³⁷ClNaO₂, m/z: 283.0311, observed: 281.0329.



Retention Time	Area	% Area
9.926	2393439	50.00
14.181	2393114	50.00



Retention Time	Area	% Area
9.739	9094943	100.00



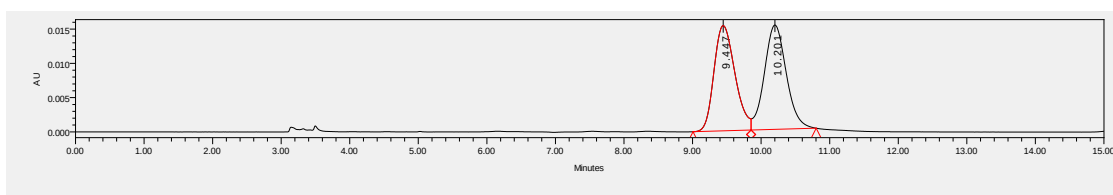
(2S,3S)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-1-(4-fluorophenyl)-2-hydroxy-3-phenylpropan-1-one (**3n**)

General procedure C; White solid; 51% yield, 95% *ee*, > 19:1 d.r.; $[\alpha]_D^{30} = -61$ (c 0.10, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.16 min, t (major) = 9.87 min];

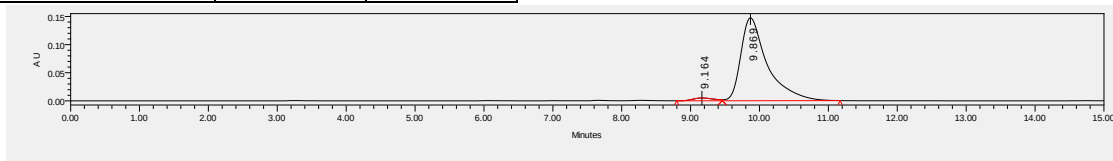
¹H NMR (400 MHz, CDCl₃) δ 7.91 (m, 2H), 7.46 – 7.20 (m, 5H), 7.06 (t, *J* = 8.4 Hz, 2H), 5.82 (t, *J* = 5.6 Hz, 1H), 5.70 (d, *J* = 5.6 Hz, 1H), 3.96 (d, *J* = 5.6 Hz, 1H), 2.48 (d, *J* = 10.0 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 197.08, 167.29, 164.74, 146.04, 140.90, 134.85, 132.07, 131.97, 131.50, 128.99, 128.88, 128.17, 115.68, 115.46, 75.27, 64.28, 14.22, 11.33.

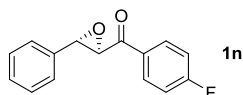
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₈¹⁸FN₃NaO₄, m/z: 406.1174, observed: 406.1176; [M+Na]⁺ C₂₀H₁₈¹⁹FN₃NaO₄, m/z: 407.1208, observed: 407.1216.



Retention Time	Area	% Area
9.447	326445	49.09
10.201	338608	50.91



Retention Time	Area	% Area
9.164	98148	2.45
9.869	3913950	97.55

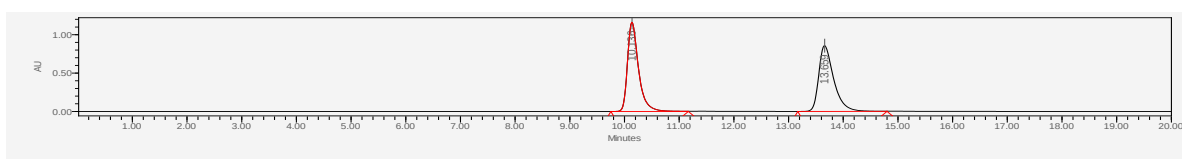


(2R,3S)- (4-fluorophenyl)(3-phenyloxiran-2-yl)methanone (**1n**)

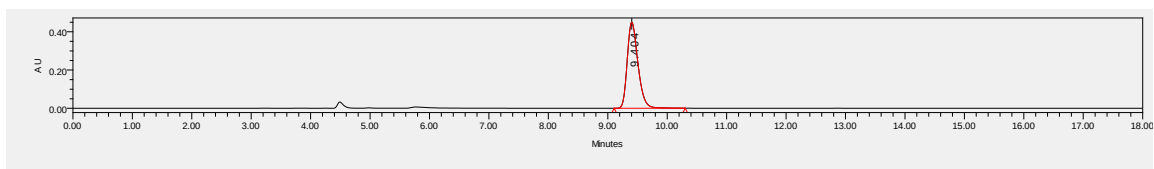
General procedure C; White solid; 49% yield, > 99% *ee*, > 99:1 d.r.; $[\alpha]_D^{30} = -187$ (c 0.23, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, *t* (major) = 9.40 min];

¹H NMR (400 MHz, CDCl₃) δ 8.13 – 7.98 (m, 2H), 7.48 – 7.29 (m, 5H), 7.17 (t, *J* = 8.4 Hz, 2H), 4.24 (d, *J* = 1.6 Hz, 1H), 4.08 (d, *J* = 1.6 Hz, 1H);

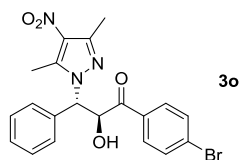
HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₁¹⁸FNaO₂, *m/z*: 265.0635, observed: 265.0639; [M+Na]⁺ C₁₅H₁₁¹⁹FNaO₂, *m/z*: 266.0669, observed: 265.0678.



Retention Time	Area	% Area
10.136	16305463	50.06
13.659	16269563	49.94



Retention Time	Area	% Area
9.404	5634983	100.00



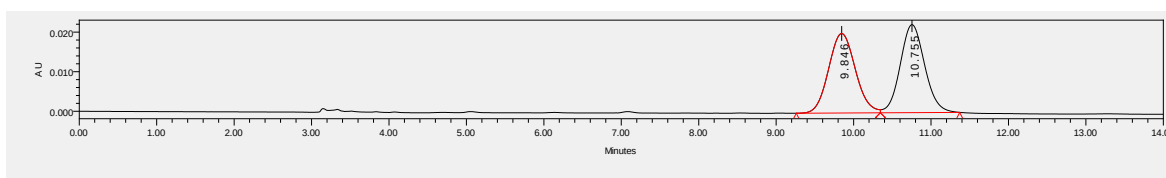
(2*S*,3*S*)-1-(4-bromophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3o**)

General procedure C; White solid; 51% yield, 96% *ee*, > 19:1 d.r.; [α]_D³⁰ = -83 (c 0.05, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, *t* (minor) = 9.96 min, *t* (major) = 10.84 min];

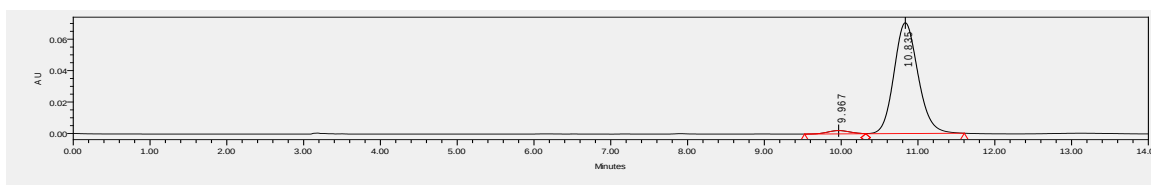
¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.26 (t, *J* = 2.8 Hz, 2H), 5.99 – 5.55 (m, 2H), 4.01 (d, *J* = 5.6 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 197.74, 146.05, 140.94, 134.76, 133.89, 131.68, 130.68, 129.03, 128.98, 128.91, 128.12, 75.50, 64.22, 14.25, 11.36.

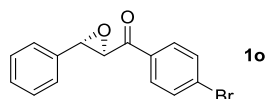
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₈⁷⁹BrN₃NaO₄, *m/z*: 466.0373, observed: 466.0382; [M+Na]⁺ C₂₀H₁₈⁸¹BrN₃NaO₄, *m/z*: 468.0353, observed: 466.0375.



Retention Time	Area	% Area
9.846	481747	49.73
10.755	487032	50.27



Retention Time	Area	% Area
9.960	29615	1.89
10.835	1533332	98.11

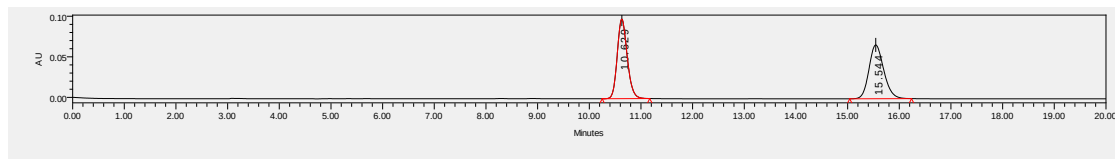


(2*R*,3*S*)-(4-bromophenyl)(3-phenyloxiran-2-yl)methanone (**1o**)

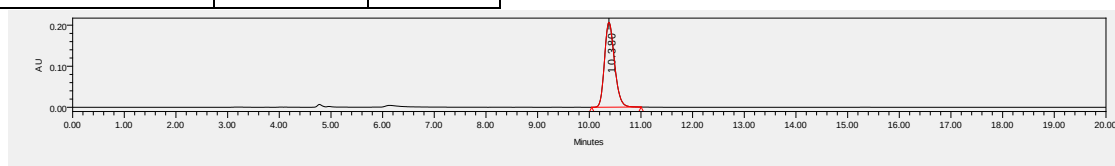
General procedure C; White solid; 47% yield, > 99% *ee*, > 99:1 d.r.; [α]_D³¹ = -126 (c 0.29, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 10.38 min];

¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.38 (m, 5H), 4.22 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.2 Hz, 1H);

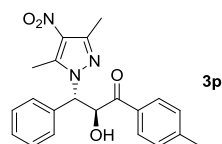
HRMS (ESI) calcd for $[M+Na]^+$ C₁₅H₁₁⁷⁹BrNaO₂, m/z: 324.9835, observed: 324.9838;
 $[M+Na]^+$ C₁₅H₁₁⁸¹BrNaO₂, m/z: 326.9815, observed: 324.9824.



Retention Time	Area	% Area
10.629	1317442	50.01
15.544	1316953	49.99



Retention Time	Area	% Area
10.380	2779639	100.00



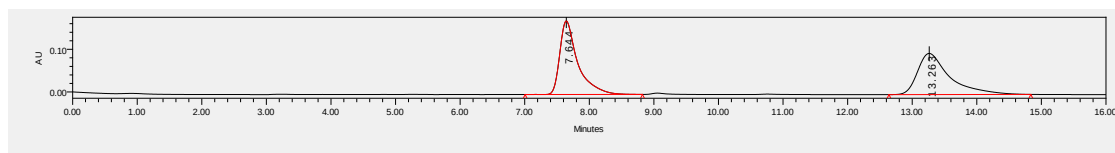
(2S,3S)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(p-tolyl)propan-1-one (3p)

General procedure C; colorless oil; 48% yield, 82% ee, > 19:1 d.r.; $[\alpha]_D^{30} = -63$ (c 0.11, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 8.04 min, t (major) = 14.31 min];

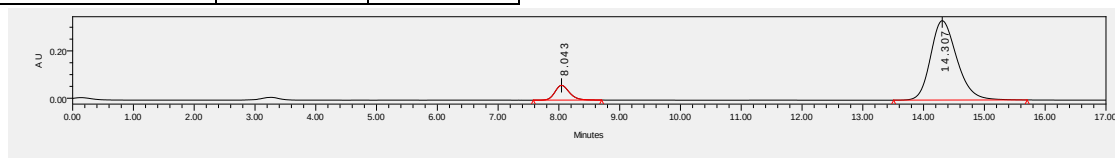
¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.27 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.91 (t, *J* = 6.0 Hz, 1H), 5.60 (d, *J* = 6.0 Hz, 1H), 3.75 (d, *J* = 6.4 Hz, 1H), 2.43 (d, *J* = 24.4 Hz, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 198.46, 146.13, 145.13, 140.74, 134.89, 132.14, 129.19, 129.11, 128.92, 128.79, 128.31, 74.25, 64.57, 21.76, 14.27, 11.36.

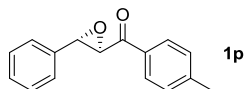
HRMS (ESI) calcd for $[M+Na]^+$ C₂₁H₂₁N₃NaO₄, m/z: 402.1424, observed: 402.1428.



Retention Time	Area	% Area
7.644	3329482	50.07
13.263	3319873	49.93



Retention Time	Area	% Area
8.043	1005501	9.00
14.307	10171377	91.00

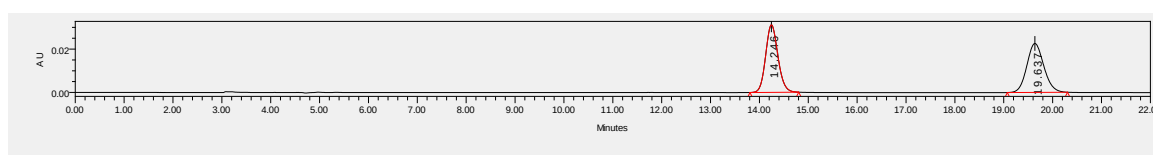


(2R,3S)-(3-phenyloxiran-2-yl)(p-tolyl)methanone (**1p**)

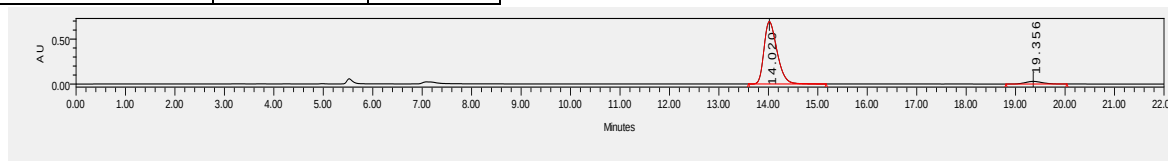
General procedure C; White solid; 42% yield, 90% *ee*, > 99:1 d.r.; $[\alpha]_D^{31} = -153$ (c 0.24, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 14.25 min, t (minor) = 19.64 min];

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.33 (m, 5H), 7.32 – 7.23 (m, 2H), 4.28 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.2 Hz, 1H), 2.42 (s, 3H);

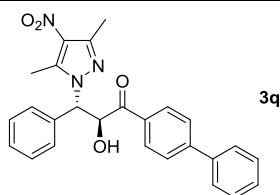
HRMS (ESI) calcd for [M+Na]⁺ C₁₆H₁₄NaO₂, m/z: 261.0886, observed: 261.0887.



Retention Time	Area	% Area
14.246	544206	50.09
19.637	542206	49.91



Retention Time	Area	% Area
14.020	12675657	95.12
19.356	650792	4.88



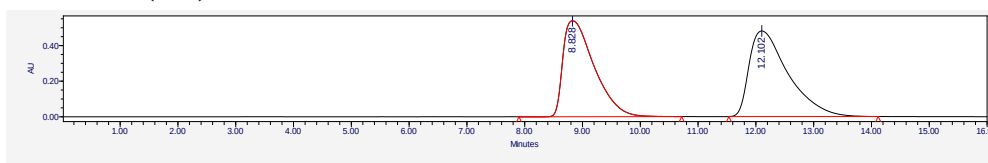
(2S,3S)-1-([1,1'-biphenyl]-4-yl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3q**)

General procedure A; White solid; 46% yield, 95% *ee*, > 19:1 d.r.; $[\alpha]_D^{29} = -131$ (c 0.12, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.02 min, t (major) = 11.99 min];

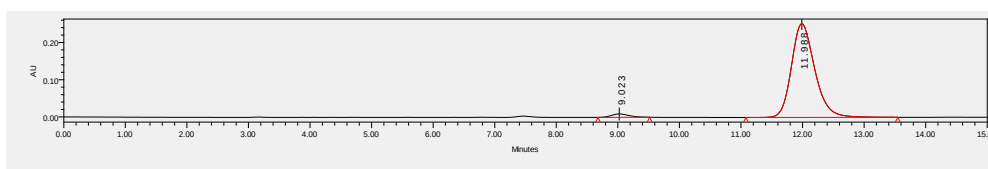
¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.61 (m, 4H), 7.52 – 7.28 (m, 8H), 5.94 (t, *J* = 6.0 Hz, 1H), 5.68 (d, *J* = 5.6 Hz, 1H), 3.88 (d, *J* = 6.0 Hz, 1H), 2.48 (d, *J* = 10.0 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.42, 146.61, 146.12, 140.85, 139.61, 134.88, 133.52, 129.64, 129.03, 128.96, 128.85, 128.48, 128.27, 127.31, 127.08, 74.79, 64.50, 14.30, 11.40.

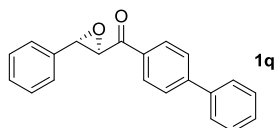
HRMS (ESI) calcd for $[M+Na]^+$ $C_{26}H_{23}N_3NaO_4$, m/z : 464.1581, observed: 464.1590.



Retention Time	Area	% Area
8.828	20177562	47.21
12.102	22562437	52.79



Retention Time	Area	% Area
9.023	180506	2.66
11.988	6605163	97.34

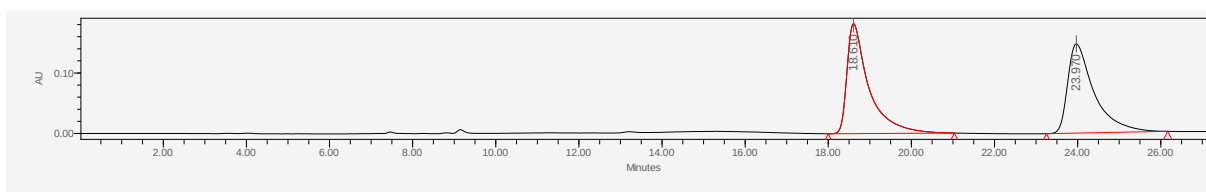


(2R,3S)-[1,1'-biphenyl]-4-yl(3-phenyloxiran-2-yl)methanone (**1q**)

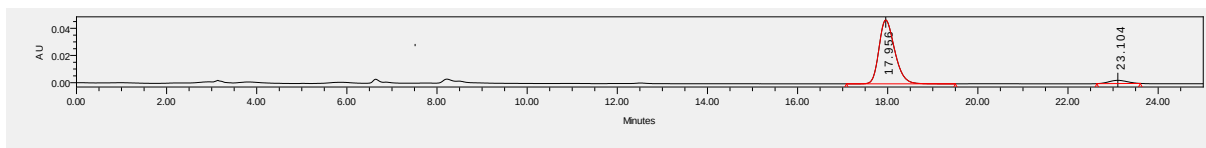
General procedure A; White solid; 50% yield, 89% *ee*, > 99:1 d.r.; $[\alpha]_D^{29} = -151$ (c 0.23, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 17.96 min, t (minor) = 23.10 min];

1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 7.2$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.45 – 7.36 (m, 6H), 4.33 (d, $J = 1.6$ Hz, 1H), 4.11 (d, $J = 1.2$ Hz, 1H).

HRMS (ESI) calcd for $[M+Na]^+$ $C_{21}H_{16}NaO_2$, m/z : 323.1043, observed: 323.1047.

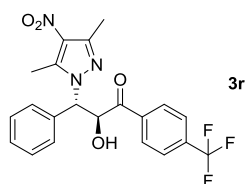


Retention Time	Area	% Area
18.610	6645429	50.52
23.970	6509203	49.48



Retention Time	Area	% Area
17.956	1133399	94.53

23.104	65572	5.47
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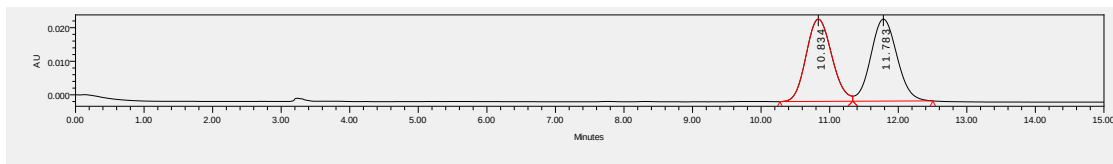
(2*S*,3*S*)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3r**)

General procedure B; colorless oil; 50% yield, 97% *ee*, > 19:1 d.r.; [α]_D³² = -93 (c 0.20, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 10.94 min, t (major) = 12.02 min];

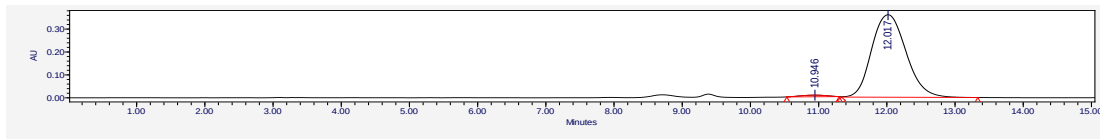
¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.24 (m, 2H), 5.77 (d, *J* = 5.2 Hz, 2H), 4.16 (s, 1H), 2.50 (d, *J* = 10.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 198.09, 146.01, 141.02, 138.26, 134.67, 134.35, 131.57, 129.47, 129.07, 128.95, 128.02, 125.24, 125.20, 124.81, 122.10, 76.20, 64.19, 14.20, 11.34.

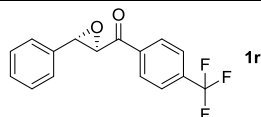
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₁₈¹⁸F₃N₃NaO₄, *m/z*: 456.1142, observed: 456.1150; [M+Na]⁺ C₂₁H₁₈¹⁹F₃N₃NaO₄, *m/z*: 457.1176, observed: 456.1170.



Retention Time	Area	% Area
10.834	638608	49.56
11.783	649828	50.44



Retention Time	Area	% Area
10.946	191652	1.49
12.017	12643015	98.51

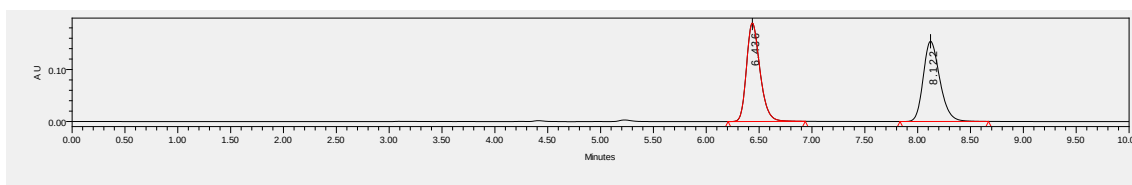


(2*R*,3*S*)-(3-phenyloxiran-2-yl)(4-(trifluoromethyl)phenyl)methanone (**1r**)

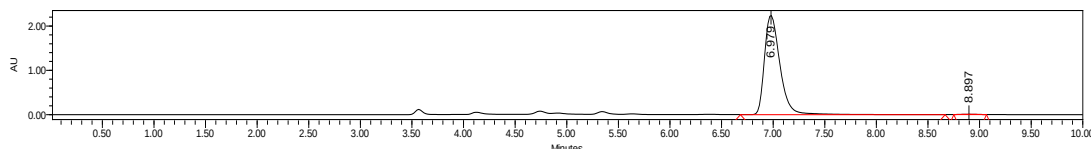
General procedure B; White solid; 49% yield, > 99% *ee*, > 99:1 d.r.; [α]_D¹⁸ = -128 (c 0.23, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.97 min, t (minor) = 8.88 min];

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.38 (m, 5H), 4.26 (d, *J* = 1.6 Hz, 1H), 4.09 (d, *J* = 1.2 Hz, 1H).

HRMS (ESI) calcd for [M+Na]⁺ C₁₆H₁₁¹⁸F₃NaO₂, *m/z*: 315.0603, observed: 315.0609; [M+K]⁺ C₁₆H₁₁¹⁹F₃NaO₂, *m/z*: 332.0377, observed: 332.0379.

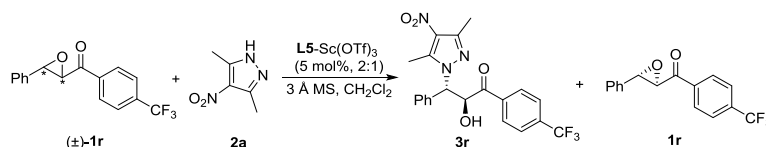


Retention Time	Area	% Area
6.436	1679737	49.97
8.122	1682041	50.03

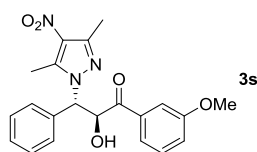


Retention Time	Area	% Area
6.979	23414261	99.74
8.897	61195	0.26

we did three parallel tests by using substrate **1r** to confirm the *s* value.



entry	Yield [%]		ee [%]		<i>s</i>
	1r	3r	1r	3r	
1	50	50	97.3	97.4	329
2	50	50	96.5	98.0	404
3	49	50	99.1	97.1	367



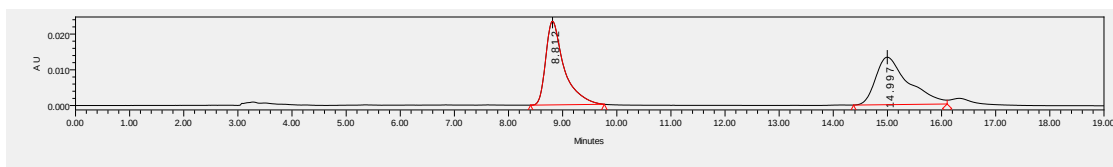
(2*S*,3*S*)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-(3-methoxyphenyl)-3-phenylpropan-1-one (**3s**)

General procedure C; colorless oil; 49% yield, 91% *ee*, > 19:1 d.r.; $[\alpha]_{\text{D}}^{32} = -33$ (c 0.07, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (minor) = 9.36 min, *t* (major) = 16.28 min];

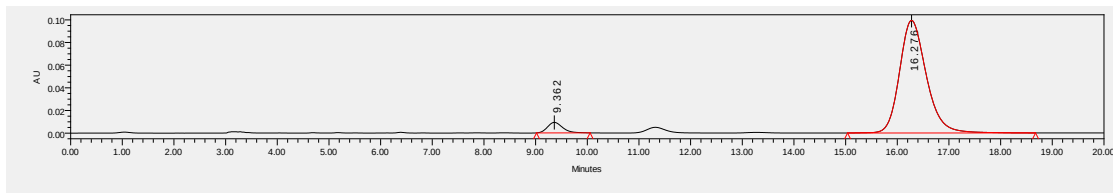
¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.27 (m, 7H), 7.10 (m, 1H), 5.89 (d, *J* = 4.8 Hz, 1H), 5.63 (d, *J* = 6.0 Hz, 1H), 3.81 (s, 4H), 2.47 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 193.08, 159.38, 146.14, 146.12, 140.79, 136.11, 134.86, 129.49, 128.97, 128.83, 128.27, 121.47, 120.16, 113.45, 74.66, 64.51, 55.47, 14.25, 11.37.

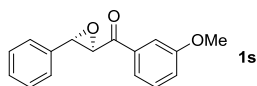
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₂₁N₃NaO₅, *m/z*: 418.1373, observed: 418.1378.



Retention Time	Area	% Area
8.812	549040	49.54
14.997	559244	50.46



Retention Time	Area	% Area
9.362	187574	4.99
16.276	3571343	95.01

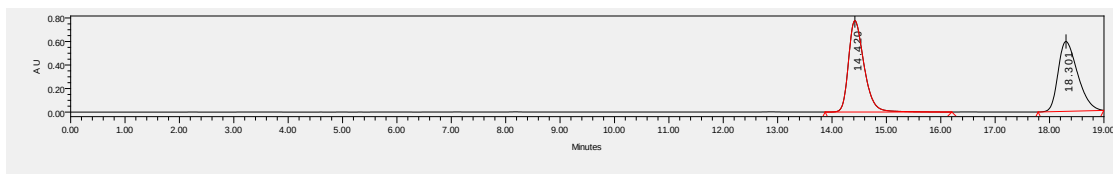


(2R,3S)-(3-methoxyphenyl)(3-phenyloxiran-2-yl)methanone (**1s**)

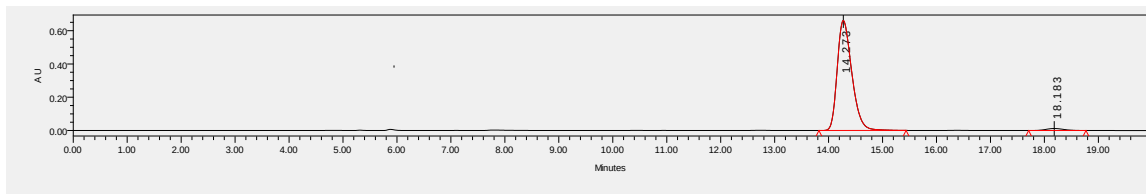
General procedure C; colorless oil; 47% yield, 95% *ee*, > 99:1 d.r.; $[\alpha]_D^{29} = -180$ (c 0.11, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 14.27 min, t (minor) = 18.18min];

^1H NMR (400 MHz, CDCl_3) δ 7.57 (m, 1H), 7.52 (d, $J = 1.6$ Hz, 1H), 7.42 – 7.33 (m, 6H), 7.18 – 7.12 (m, 1H), 4.27 (d, $J = 1.6$ Hz, 1H), 4.06 (d, $J = 1.6$ Hz, 1H), 3.84 (d, $J = 1.2$ Hz, 3H).

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{16}\text{H}_{14}\text{NaO}_3$, m/z: 277.0835, observed: 277.0844.

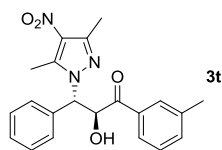


Retention Time	Area	% Area
14.420	15505719	51.25
18.301	14751523	48.75



Retention Time	Area	% Area
14.273	12411419	97.83
18.183	12411419	2.17

18.183	275528	2.17
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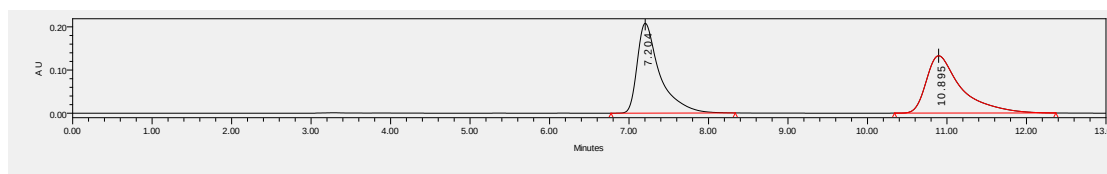
(2*S*,3*S*)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(*m*-tolyl)propan-1-one (**3t**)

General procedure C; White solid; 46% yield, 90% *ee*, > 99:1 d.r.; [α]_D³² = -41 (c 0.20, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (minor) = 7.28 min, *t* (major) = 10.61 min];

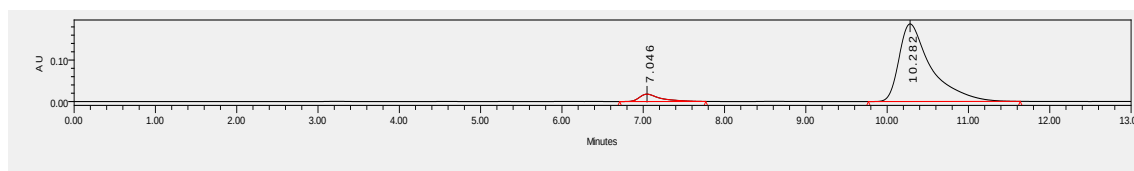
¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.52 (m, 2H), 7.42 – 7.27 (m, 7H), 5.91 (t, *J* = 6.0 Hz, 1H), 5.61 (d, *J* = 6.0 Hz, 1H), 3.78 (d, *J* = 6.4 Hz, 1H), 2.77 – 2.18 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 199.17, 146.11, 140.78, 138.40, 134.91, 134.82, 134.68, 129.39, 128.93, 128.80, 128.35, 128.29, 126.17, 74.40, 64.53, 21.30, 14.28, 11.36.

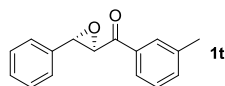
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₂₁N₃NaO₄, *m/z*: 402.1424, observed: 402.1424.



Retention Time	Area	% Area
7.204	4093715	50.23
10.895	4056049	49.77



Retention Time	Area	% Area
7.046	263480	4.91
10.282	5103290	95.09

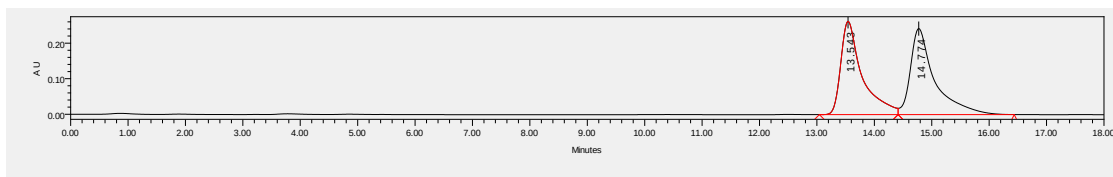


(2*R*,3*S*)-(3-phenyloxiran-2-yl)(*m*-tolyl)methanone (**1t**)

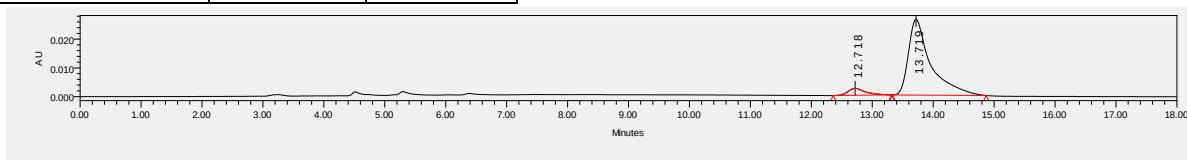
General procedure C; White solid; 47% yield, 89% *ee*, > 99:1 d.r.; [α]_D²⁹ = -138 (c 0.25, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (minor) = 12.72 min, *t* (major) = 13.72 min];

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.68 (m, 2H), 7.48 – 7.31 (m, 7H), 4.29 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.2 Hz, 1H), 2.40 (s, 3H).

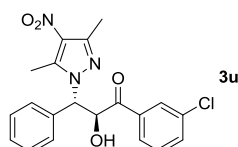
HRMS (ESI) calcd for [M+Na]⁺ C₁₆H₁₄NaO₂, *m/z*: 261.0886, observed: 261.0896.



Retention Time	Area	% Area
13.543	6770077	48.81
14.774	7100673	51.19



Retention Time	Area	% Area
12.718	37679	5.34
13.719	668186	94.66



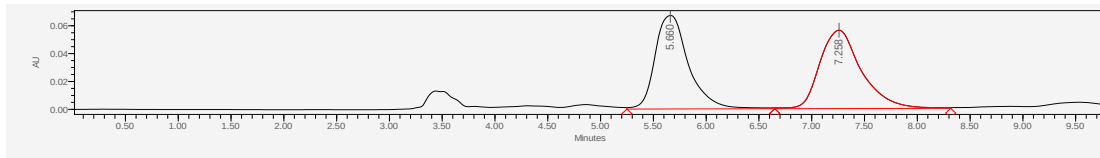
(2S,3S)-1-(3-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3u**)

General procedure C; colorless oil; 46% yield, 85% *ee*, > 19:1 d.r.; $[\alpha]_D^{27} = -47$ (c 0.15, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.43 min, t (minor) = 8.57 min];

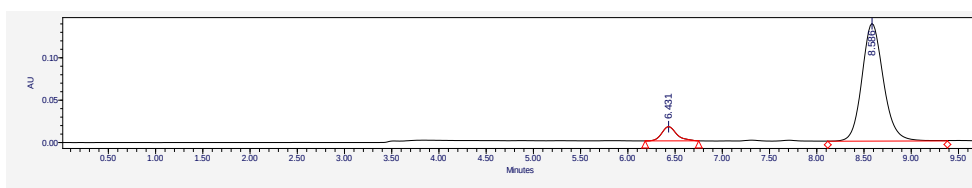
¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.50 (m, 1H), 7.34 (m, 4H), 7.31 – 7.27 (m, 2H), 5.79 (t, *J* = 5.2 Hz, 1H), 5.69 (d, *J* = 5.6 Hz, 1H), 3.98 (d, *J* = 5.2 Hz, 1H), 2.50 (t, *J* = 4.8 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 197.65, 146.12, 140.91, 136.69, 134.73, 134.62, 133.50, 129.65, 129.29, 129.08, 128.92, 128.14, 127.17, 75.49, 64.23, 14.24, 11.34.

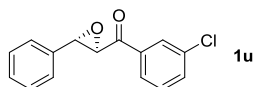
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₈³⁵ClN₃NaO₄, *m/z*: 422.0879, observed: 422.0885; [M+Na]⁺ C₂₀H₁₈³⁷ClN₃NaO₄, *m/z*: 424.0849, observed: 424.0869.



Retention Time	Area	% Area
5.660	1483352	49.00
7.258	1543825	51.00



Retention Time	Area	% Area
6.431	181837	7.66
8.586	2190765	92.34

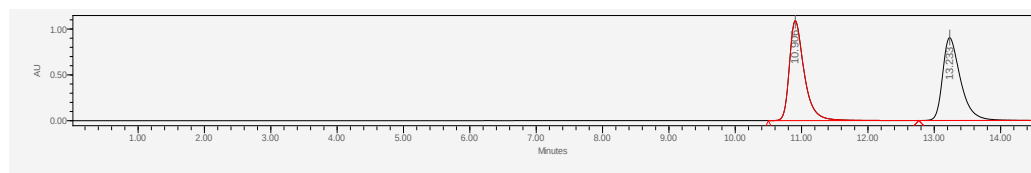


(2R,3S)-3-(3-chlorophenyl)-3-(3-phenyloxiran-2-yl)propan-1-one (**1u**)

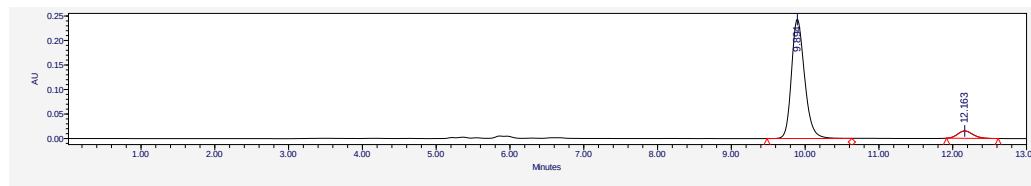
General procedure C; White solid; 49% yield, 87% *ee*, > 99:1 d.r.; $[\alpha]_D^{29} = -157$ (c 0.14, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.89 min, t (minor) = 12.16 min];

¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.32 (m, 6H), 4.24 (d, *J* = 1.6 Hz, 1H), 4.08 (s, 1H).

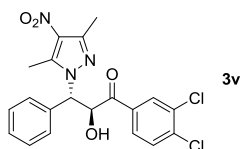
HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₁³⁵ClNaO₂, *m/z*: 281.0340, observed: 281.0347; [M+Na]⁺ C₁₅H₁₁³⁷ClNaO₂, *m/z*: 283.0311, observed: 283.0325.



Retention Time	Area	% Area
10.906	16940061	50.08
13.233	16885253	49.92



Retention Time	Area	% Area
9.894	3009377	93.30
12.163	216145	6.70



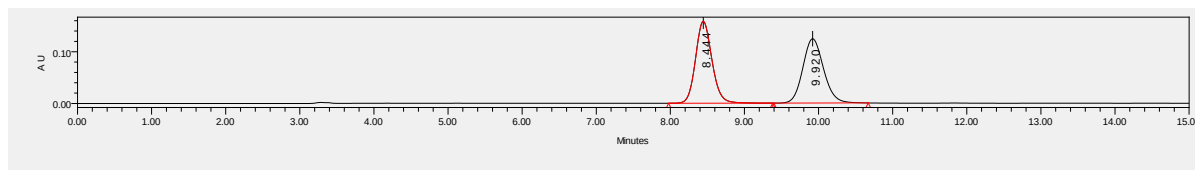
(2S,3S)-1-(3,4-dichlorophenyl)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3v**)

General procedure B; White solid; 48% yield, 95% *ee*, > 99:1 d.r.; $[\alpha]_D^{32} = -116$ (c 0.30, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 8.05 min, t (major) = 9.61 min];

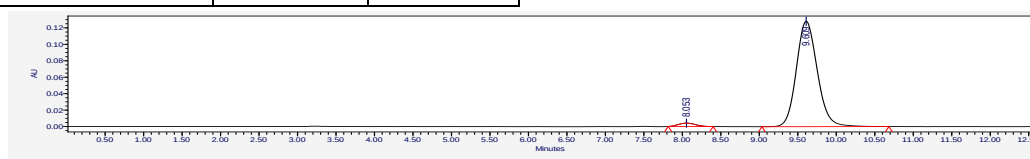
¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 1.6 Hz, 1H), 7.68 (m, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.25 (m, 2H), 5.73 (s, 2H), 4.20 (s, 1H), 2.51 (d, *J* = 2.4 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 196.57, 146.08, 141.01, 138.16, 134.84, 134.62, 132.92, 131.37, 130.39, 129.14, 128.97, 128.32, 128.06, 76.16, 64.12, 14.23, 11.34.

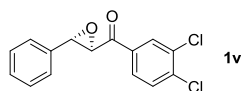
HRMS (ESI) calcd for $[M+Na]^+ C_{20}H_{17}^{35}Cl_2N_3NaO_4$, m/z : 456.0489, observed: 456.0496;
 $[M+Na]^+ C_{20}H_{17}^{37}Cl_2N_3NaO_4$, m/z : 458.0459, observed: 458.0470.



Retention Time	Area	% Area
8.444	2437261	50.25
9.920	2412968	49.75



Retention Time	Area	% Area
8.053	63205	2.54
9.609	2426362	97.46

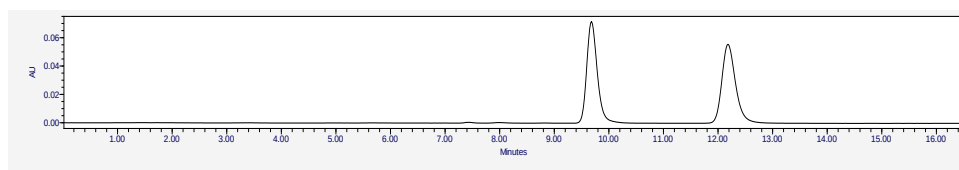


(2R,3S)-(3,4-dichlorophenyl)(3-phenyloxiran-2-yl)methanone (**1v**)

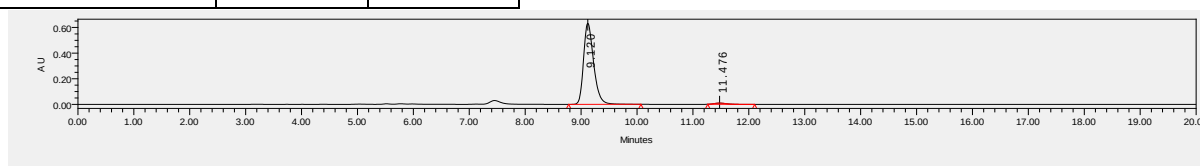
General procedure B; White solid; 49% yield, 96% *ee*, > 99:1 d.r.; $[\alpha]_D^{32} = -137$ (c 0.19, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.12 min, t (minor) = 11.48 min];

1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 2.0$ Hz, 1H), 7.86 (m, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.48 – 7.31 (m, 5H), 4.19 (d, $J = 1.6$ Hz, 1H), 4.08 (d, $J = 1.6$ Hz, 1H);

HRMS (ESI) calcd for $[M+Na]^+ C_{15}H_{10}^{35}Cl_2NaO_2$, m/z : 314.9951, observed: 314.9951;
 $[M+Na]^+ C_{15}H_{10}^{37}Cl_2NaO_2$, m/z : 316.9921, observed: 316.9932

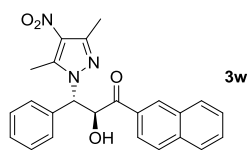


Retention Time	Area	% Area
9.681	961711	49.97
12.182	962741	50.03



Retention Time	Area	% Area
9.120	7903751	98.27

11.476	139299	1.73
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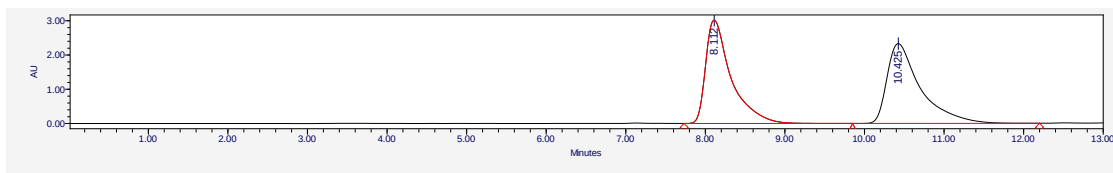
(2*S*,3*S*)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-(naphthalen-2-yl)-3-phenylpropan-1-one (**3w**)

General procedure C; White solid; 48% yield, 83% *ee*, > 19:1 d.r.; [α]_D³² = -117 (c 0.25, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (minor) = 8.61 min, *t* (major) = 11.25 min];

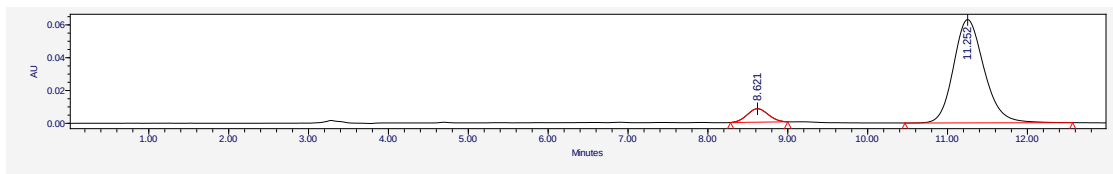
¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 8.06 – 7.77 (m, 4H), 7.58 (m, 2H), 7.34 (s, 5H), 6.05 (t, *J* = 6.0 Hz, 1H), 5.68 (d, *J* = 6.0 Hz, 1H), 3.90 (d, *J* = 6.0 Hz, 1H), 2.43 (d, *J* = 38.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 190.78, 146.12, 141.03, 140.64, 135.84, 135.35, 134.42, 128.82, 128.68, 128.20, 127.92, 77.65, 64.32.

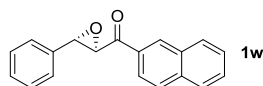
HRMS (ESI) calcd for [M+Na]⁺ C₂₄H₂₁N₃NaO₄, *m/z*: 438.1424, observed: 438.1432.



Retention Time	Area	% Area
8.112	6688594	49.58
10.425	6800882	50.42



Retention Time	Area	% Area
8.621	148996	8.17
11.252	1675602	91.83

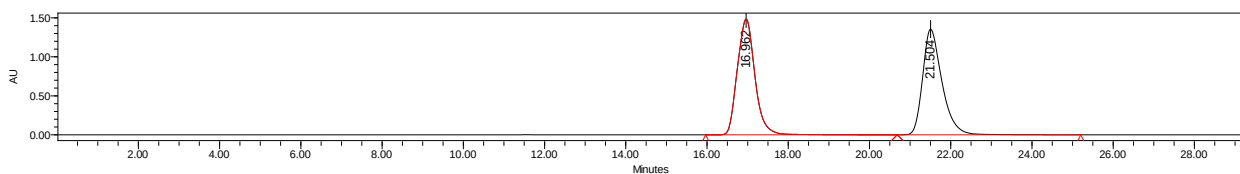


(2*R*,3*S*)-naphthalen-2-yl(3-phenyloxiran-2-yl)methanone (**1w**)

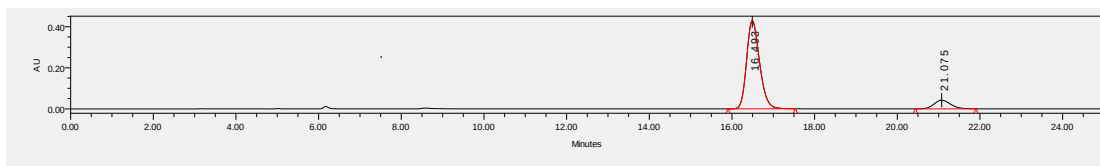
General procedure C; White solid; 47% yield, 79% *ee*, > 99:1 d.r.; [α]_D³² = -110 (c 0.23, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 16.49 min, *t* (minor) = 21.01 min,];

¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.96 – 7.80 (m, 3H), 7.57 (m, 2H), 7.41 (s, 5H), 4.42 (d, *J* = 1.6 Hz, 1H), 4.14 (d, *J* = 12 Hz, 1H).

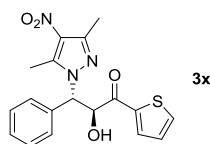
HRMS (ESI) calcd for [M+Na]⁺ C₁₉H₁₄NaO₂, *m/z*: 297.0886, observed: 297.0886.



Retention Time	Area	% Area
16.962	44515793	49.87
21.504	44742642	50.13



Retention Time	Area	% Area
16.493	9347917	89.71
21.075	1072442	10.29



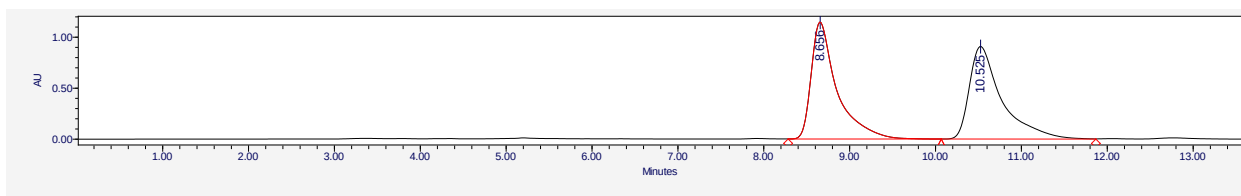
(2S,3S)-3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(thiophen-2-yl)propan-1-one (**3x**)

General procedure C; colorless oil; 35% yield, 82% *ee*, > 19:1 d.r.; $[\alpha]_D^{32} = -117$ (c 0.25, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 10.18 min, t (major) = 12.43 min];

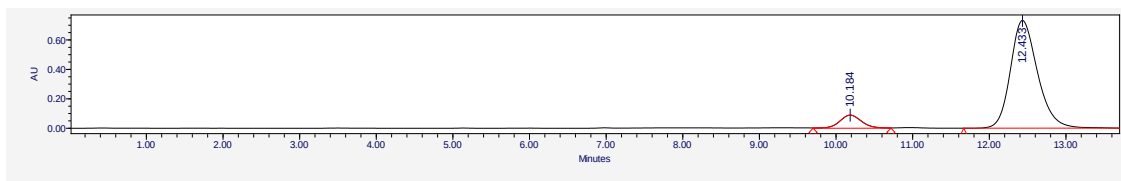
¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 3.6 Hz, 1H), 7.65 (d, *J* = 4.8 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 3H), 7.23 (d, *J* = 3.2 Hz, 2H), 7.04 (t, *J* = 4.4 Hz, 1H), 5.80 (d, *J* = 4.0 Hz, 1H), 5.60 (t, *J* = 4.0 Hz, 1H), 4.63 (d, *J* = 4.4 Hz, 1H), 2.52 (d, *J* = 22.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.83, 146.14, 140.80, 135.80, 135.00, 132.13, 132.02, 131.44, 129.70, 129.08, 128.99, 128.85, 128.41, 128.31, 127.81, 126.98, 124.09, 74.67, 64.64, 14.23, 11.35.

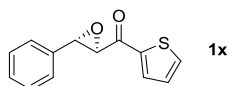
HRMS (ESI) calcd for [M+Na]⁺ C₁₈H₁₇N₃NaO₄S, m/z: 394.0832, observed: 394.0833.



Retention Time	Area	% Area
8.656	23867507	50.05
10.525	23820314	49.95



Retention Time	Area	% Area
10.184	1784240	9.01
12.433	18022249	90.99

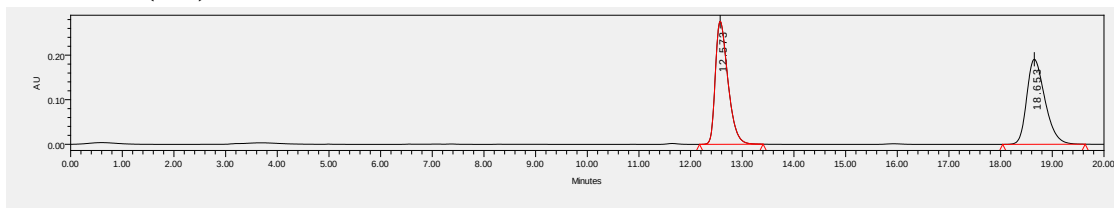


(2R,3S)-(3-phenyloxiran-2-yl)(thiophen-2-yl)methanone (**1x**)

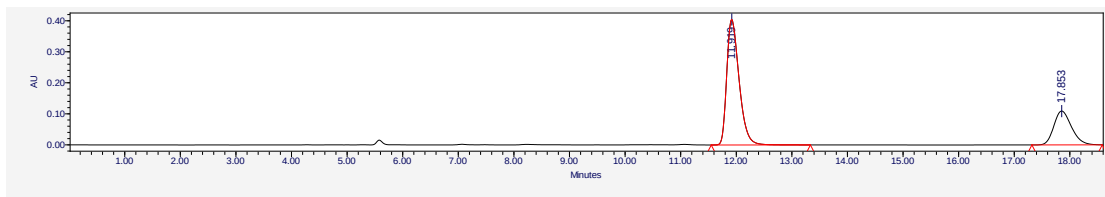
General procedure C; White solid; 65% yield, 44% *ee*, > 99:1 d.r.; $[\alpha]_D^{32} = -110$ (c 0.24, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 11.92 min, t (minor) = 17.85 min,];

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 3.6 Hz, 1H), 7.74 (d, *J* = 4.8 Hz, 1H), 7.36 (m, 5H), 7.18 (t, *J* = 4.4 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.6 Hz, 1H);

HRMS (ESI) calcd for [M+Na]⁺ C₁₃H₁₀NaO₂S, m/z: 253.0294, observed: 253.0296.



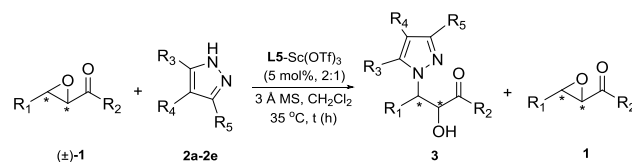
Retention Time	Area	% Area
12.573	4663239	50.01
18.653	4660842	49.99



Retention Time	Area	% Area
11.919	6218685	72.06
17.853	2411023	27.94

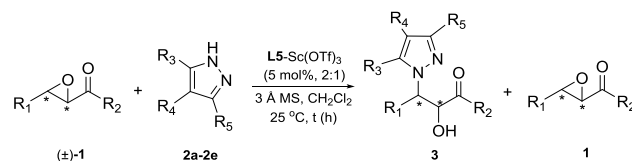
5. General procedure for the Ring-Opening reaction of different pyrazoles (2)

General procedure D for the reaction of pyrazoles **2**:



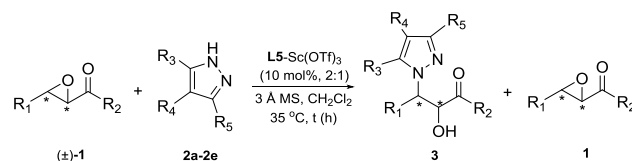
In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.01 mmol, 6.6 mg), $\text{Sc}(\text{OTf})_3$ (0.005 mmol, 2.5 mg), and the 3 Å MS (30 mg) in CH_2Cl_2 (0.5 mL) were stirred at 35 °C for 30 min. Then, epoxide ($\pm$)-**1** (0.1 mmol) and pyrazole **2** (0.2 mmol) were added to the reaction mixture at 35 °C. The reaction was stirred at 35 °C for 22-26 h. After 50% consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3** and **1**. The product was determined by HPLC and NMR analysis.

General procedure E for the reaction of pyrazoles **2**:



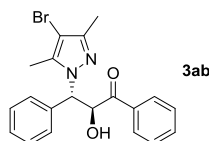
In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.01 mmol, 6.6 mg), $\text{Sc}(\text{OTf})_3$ (0.005 mmol, 2.5 mg), and the 3 Å MS (30 mg) in CH_2Cl_2 (0.5 mL) were stirred at 25 °C for 30 min. Then, epoxide ($\pm$)-**1** (0.1 mmol) and pyrazole **2** (0.2 mmol) were added to the reaction mixture at 25 °C. The reaction was stirred at 25 °C for 25 h. After 50% consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3** and **1**. The product was determined by HPLC and NMR analysis.

General procedure F for the reaction of pyrazoles **2**:



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.02 mmol, 13.2 mg), $\text{Sc}(\text{OTf})_3$ (0.01 mmol, 4.9 mg), and the 3 Å MS (30 mg) in CH_2Cl_2 (0.5 mL) were stirred at 35 °C for 30 min. Then, epoxide ($\pm$)-**1** (0.1 mmol) and pyrazole **2** (0.2 mmol) were added to the reaction mixture at 35 °C. The reaction was stirred at 35 °C for 22-26 h. After 50% consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3** and **1**. The product was determined by HPLC and NMR analysis.

6. The analytical and spectral characterization data of the products (**3**)



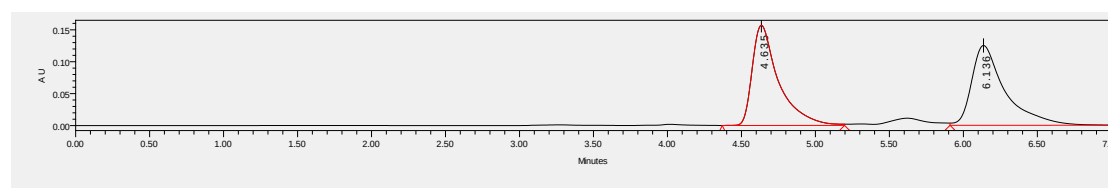
(2*S*,3*S*)-3-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)-2-hydroxy-1,3-diphenylpropan-1-one (**3ab**)

General procedure E; White solid; 49% yield, 90% *ee*, > 19:1 d.r.; $[\alpha]_D^{32} = -49$ (c 0.16, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 4.63 min, t (major) = 6.14 min];

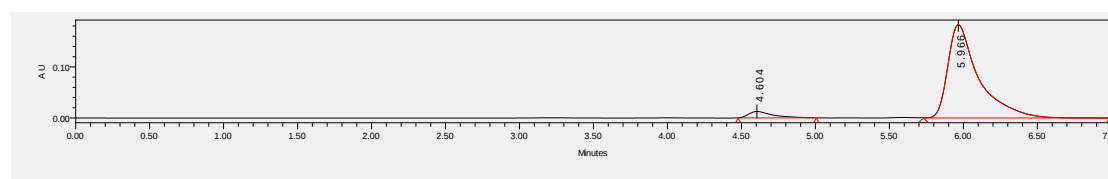
¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.20 (m, 2H), 5.86 (d, *J* = 4.0 Hz, 1H), 5.62 (d, *J* = 4.4 Hz, 1H), 4.61 (s, 1H), 2.18 (s, 3H), 2.04 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 199.67, 146.19, 137.81, 135.88, 135.27, 133.40, 129.05, 128.47, 128.33, 128.24, 128.23, 95.04, 76.23, 64.54, 12.41, 10.29.

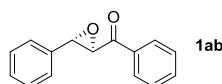
HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₁₉⁷⁹BrN₂NaO₂, m/z: 421.0523, observed: 421.0523; [M+Na]⁺ C₂₀H₁₉⁸¹BrN₂NaO₂, m/z: 423.0502, observed: 423.0511.



Retention Time	Area	% Area
4.635	1941989	49.65
6.136	1969559	50.35



Retention Time	Area	% Area
4.604	137530	4.95
5.966	2642595	95.05

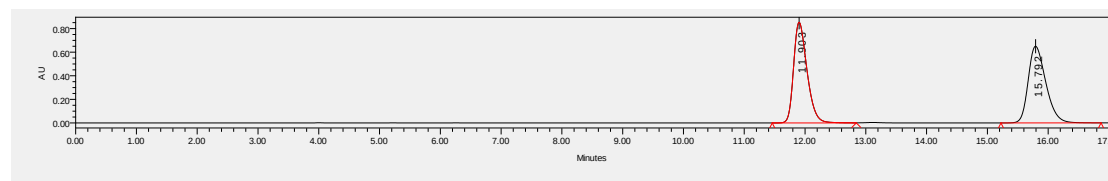


(2*R*,3*S*)-phenyl(3-phenyloxiran-2-yl)methanone (**1ab**)

General procedure E; White solid; 50% yield, 91% *ee*, > 99:1 d.r.; $[\alpha]_D^{32} = -183$ (c 0.23, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 11.90 min, t (minor) = 15.79 min];

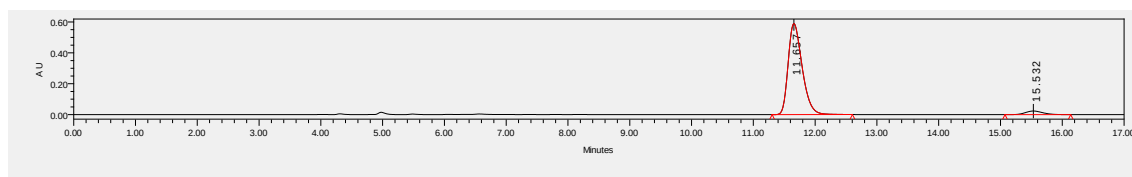
¹H NMR (400 MHz, CDCl₃) δ 8.01 (m, 2H), 7.68 – 7.58 (m, 1H), 7.49 (m, 2H), 7.45 – 7.33 (m, 5H), 4.30 (d, *J* = 2.0 Hz, 1H), 4.08 (d, *J* = 1.6 Hz, 1H).

HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₂NaO₂, m/z: 247.0730, observed: 247.0732.

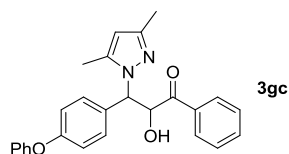


Retention Time	Area	% Area
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11.903	13059530	50.00
15.792	13059754	50.00



Retention Time	Area	% Area
11.657	9259680	95.51
15.532	435470	4.49



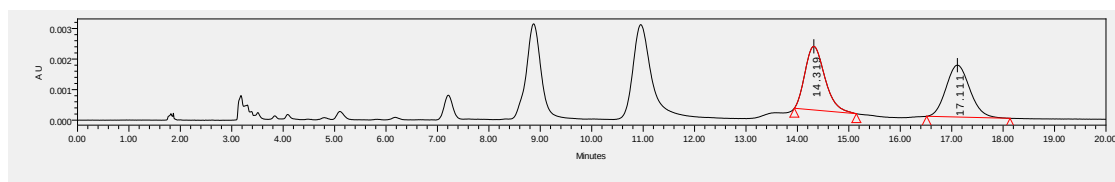
3-(3,5-dimethyl-1H-pyrazol-1-yl)-2-hydroxy-3-(4-phenoxyphenyl)-1-phenylpropan-1-one (3gc)

General procedure D; colorless oil; 40% yield, 88% *ee*, d.r. = 12:1; $[\alpha]_D^{27} = -62$ (c 0.28, CH₂Cl₂) Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 14.20 min, t (major) = 16.66 min];

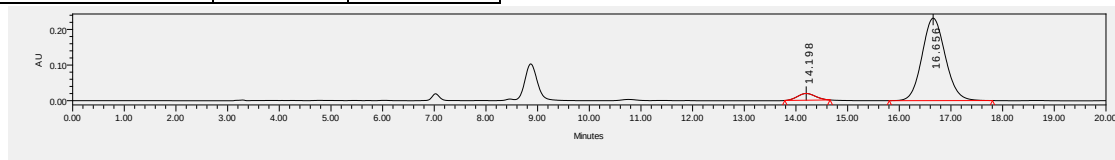
¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.52 (s, 1H), 7.43 – 7.23 (m, 5H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.81 – 5.73 (m, 2H), 5.63 (d, *J* = 3.6 Hz, 1H), 2.21 (s, 3H), 2.07 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 199.86, 157.10, 156.85, 147.52, 139.61, 135.70, 133.17, 131.12, 129.73, 129.71, 129.27, 128.17, 123.42, 119.10, 118.40, 105.48, 77.72, 62.68, 13.57, 11.01.

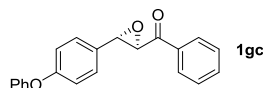
HRMS (ESI) calcd for [M+Na]⁺ C₂₆H₂₄N₂NaO₃, m/z: 435.1679, observed: 435.1684.



Retention Time	Area	% Area
14.319	55899	50.59
17.111	54586	49.41



Retention Time	Area	% Area
14.198	456823	5.93
16.656	7244320	94.07

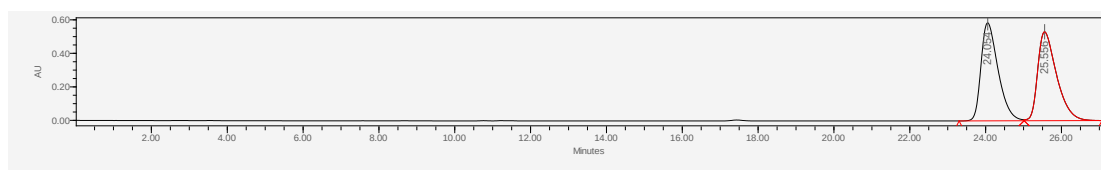


(3-(4-phenoxyphenyl)oxiran-2-yl)(phenyl)methanone (1gc)

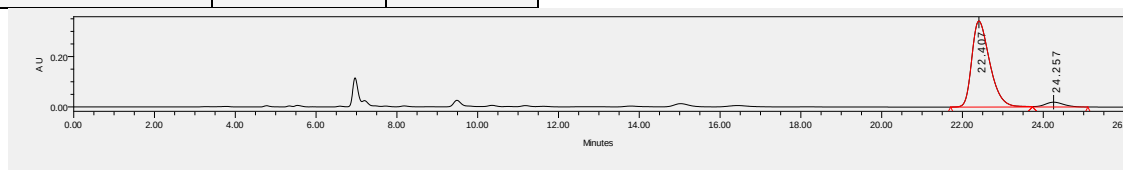
General procedure D; White solid; 49% yield, 90% *ee*, > 99:1 d.r.; $[\alpha]_D^{18} = -86$ (c 0.24, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 24.05 min, t (minor) = 25.55 min];

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.35 (m, 4H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.03 (m, 4H), 4.30 (d, *J* = 1.6 Hz, 1H), 4.06 (d, *J* = 1.2 Hz, 1H).

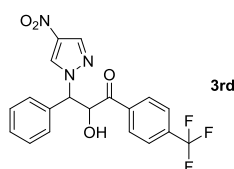
HRMS (ESI) calcd for [M+Na]⁺ C₂₁H₁₆NaO₃, m/z: 339.0992, observed: 339.0990.



Retention Time	Area	% Area
24.054	18266081	49.95
25.556	18302963	50.05



Retention Time	Area	% Area
22.407	10544776	95.32
24.257	517230	4.68



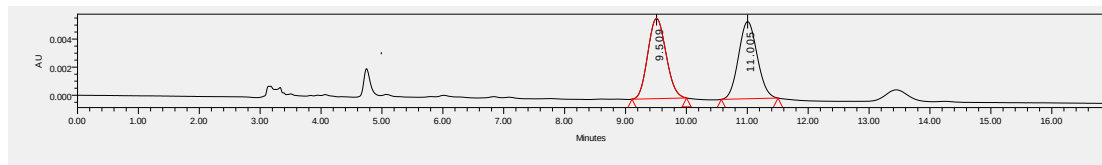
2-hydroxy-3-(4-nitro-1H-pyrazol-1-yl)-3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3rd)

General procedure F; White solid; 44% yield, 95% *ee*, > 19:1 d.r.; $[\alpha]_D^{27} = -33$ (c 0.25, CH₂Cl₂) Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.52 min, t (major) = 11.19 min];

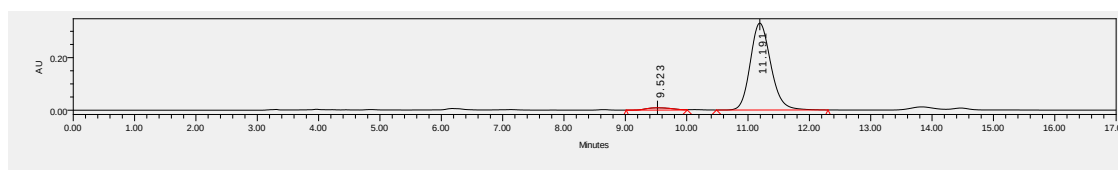
¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 8.13 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.35 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.05 (d, *J* = 2.0 Hz, 1H), 5.79 (d, *J* = 3.2 Hz, 1H), 3.94 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 196.82, 136.61, 135.93, 131.83, 129.97, 129.31, 129.14, 129.07, 128.52, 126.26, 126.22, 124.60, 77.34, 77.02, 76.70, 75.15, 68.73, 31.93, 29.70, 29.37, 22.70, 14.12.

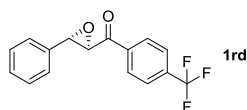
HRMS (ESI) calcd for $[M+Na]^+$ C₁₉H₁₄¹⁸F₃N₃NaO₄, m/z: 428.0829, observed: 428.0833;
 $[M+Na]^+$ C₁₉H₁₄¹⁹F₃N₃NaO₄, m/z: 429.0863, observed: 429.0872.



Retention Time	Area	% Area
9.509	118598	50.30
11.005	117198	49.70



Retention Time	Area	% Area
9.523	183148	2.34
11.191	7636978	97.66

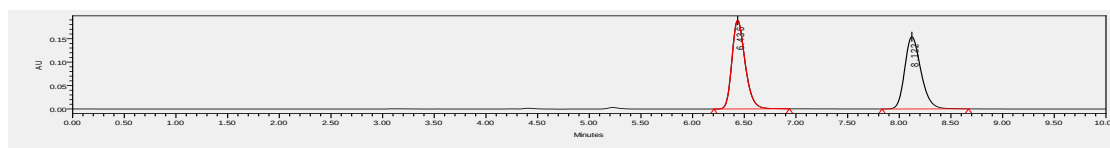


(3-phenyloxiran-2-yl)(4-(trifluoromethyl)phenyl)methanone (**1rd**)

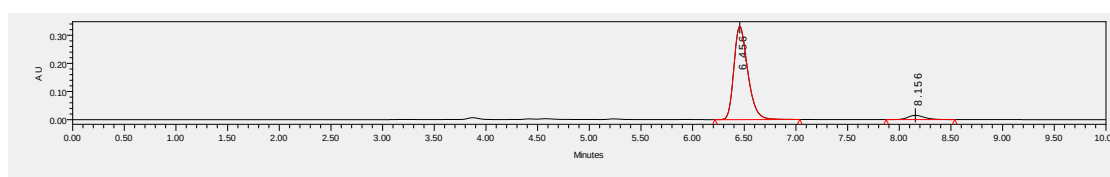
General procedure D; White solid; 50% yield, 90% *ee*, > 99:1 d.r.; $[\alpha]_D^{18} = -120$ (c 0.15, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.43 min, t (minor) = 8.12 min,];

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.38 (m, 5H), 4.26 (d, *J* = 1.6 Hz, 1H), 4.09 (d, *J* = 1.2 Hz, 1H).

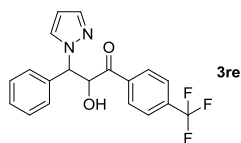
HRMS (ESI) calcd for $[M+Na]^+$ C₁₆H₁₁¹⁸F₃NaO₂, m/z: 315.0603, observed: 315.0609;
 $[M+K]^+$ C₁₆H₁₁¹⁹F₃NaO₂, m/z: 332.0377, observed: 332.0379.



Retention Time	Area	% Area
6.436	1679737	49.97
8.122	1682041	50.03



Retention Time	Area	% Area
6.456	3087726	95.00
8.156	162664	5.00



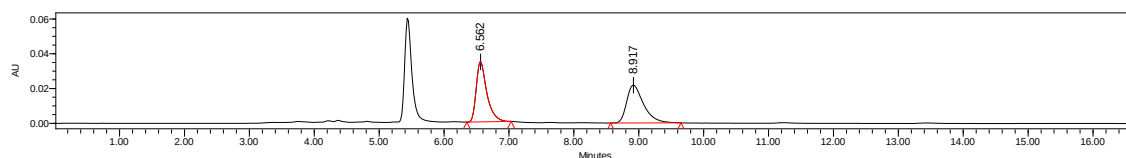
2-hydroxy-3-phenyl-3-(1*H*-pyrazol-1-yl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3re**)

General procedure D; colorless oil; 40% yield, 57% *ee*, > 19:1 d.r.; [α]_D²⁷ = -19 (c 0.21, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak Id, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 6.60 min, *t* (minor) = 9.04 min];

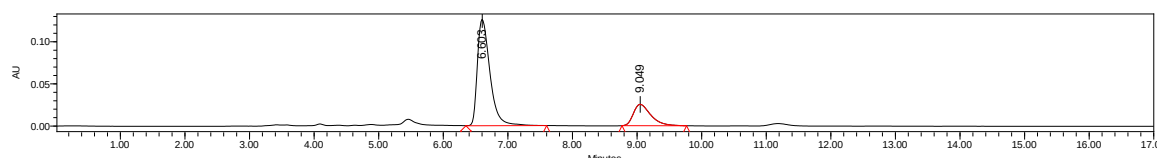
¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.56 (m, 2H), 7.36 – 7.23 (m, 4H), 7.16 (m, 2H), 6.27 (t, *J* = 2.0 Hz, 1H), 5.94 (d, *J* = 3.6 Hz, 1H), 5.83 (d, *J* = 3.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 198.53, 139.51, 137.59, 134.86, 129.94, 129.28, 128.82, 128.56, 128.31, 125.67, 125.64, 106.08, 67.32.

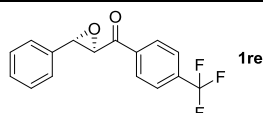
HRMS (ESI) calcd for [M+Na]⁺ C₁₉H₁₅¹⁸F₃N₂NaO₂, *m/z*: 383.0978, observed: 383.0984; [M+Na]⁺ C₁₉H₁₅¹⁹F₃N₂NaO₂, *m/z*: 384.1012, observed: 384.1034.



Retention Time	Area	% Area
6.562	394272	50.05
8.917	393517	49.95



Retention Time	Area	% Area
6.603	1709366	78.32
9.049	473270	21.68

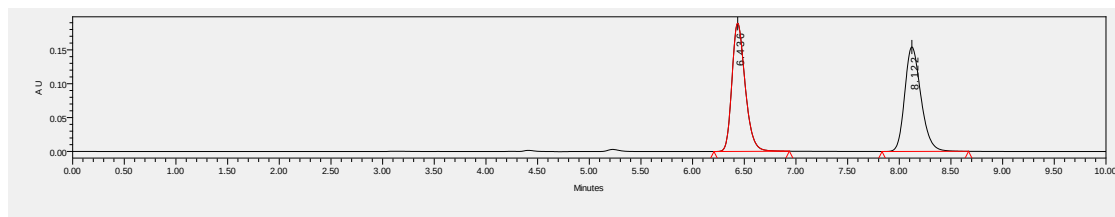


(3-phenyloxiran-2-yl)(4-(trifluoromethyl)phenyl)methanone (**1re**)

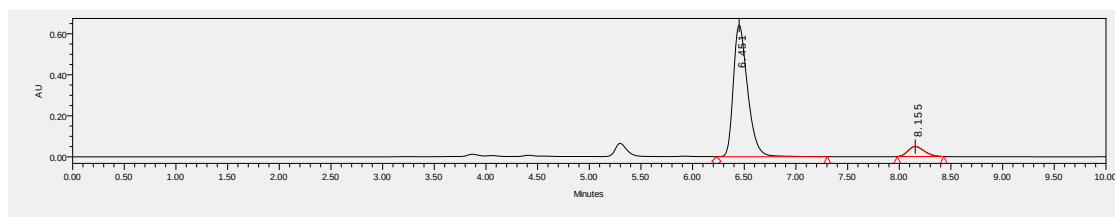
General procedure D; White solid; 50% yield, 84% *ee*, > 99:1 d.r.; [α]_D¹⁸ = -107 (c 0.16, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 6.43 min, *t* (minor) = 8.12 min,];

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.38 (m, 5H), 4.26 (d, *J* = 1.6 Hz, 1H), 4.09 (d, *J* = 1.2 Hz, 1H);

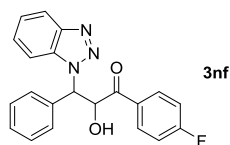
HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{11}^{18}F_3NaO_2$, m/z : 315.0603, observed: 315.0609;
 $[M+Na]^+$ $C_{16}H_{11}^{19}F_3NaO_2$, m/z : 316.0637, observed: 316.0638.



Retention Time	Area	% Area
6.436	1679737	49.97
8.122	1682041	50.03



Retention Time	Area	% Area
6.451	6172741	91.98
8.155	538005	8.02

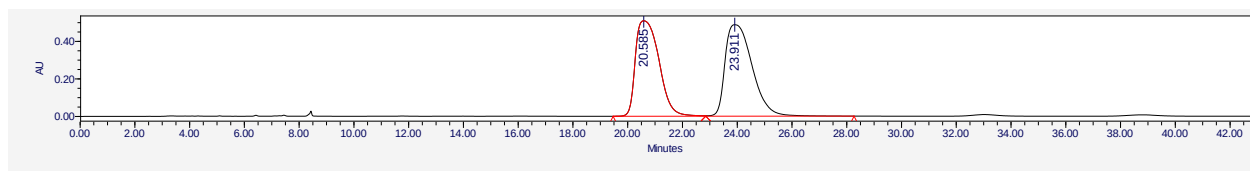


3-(1*H*-benzo[d][1,2,3]triazol-1-yl)-1-(4-fluorophenyl)-2-hydroxy-3-phenylpropan-1-one (**3nf**)
General procedure D; colorless oil; 22% yield, 35% *ee*, > 19:1 d.r., *s* factor of 3. $[\alpha]_D^{26} = -7$ (c 0.15, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak Ic, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, *t* (minor) = 20.58 min, *t* (major) = 23.91 min];

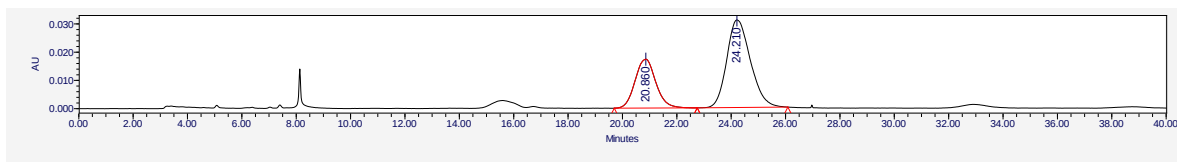
1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J = 8.4$ Hz, 1H), 7.94 – 7.87 (m, 2H), 7.38 – 7.27 (m, 8H), 7.06 (m, 2H), 6.29 – 6.18 (m, 2H), 3.82 (d, $J = 6.4$ Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.97, 134.09, 131.76, 131.66, 129.14, 128.82, 128.43, 127.72, 124.28, 120.01, 116.07, 115.85, 110.20, 74.56, 65.33.

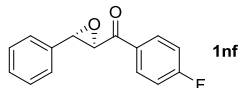
HRMS (ESI) calcd for $[M+Na]^+$ $C_{21}H_{16}^{18}FN_3NaO_2$, m/z : 384.1119, observed: 384.1122;
 $[M+Na]^+$ $C_{21}H_{16}^{19}FN_3NaO_2$, m/z : 385.1153, observed: 385.1214.



Retention Time	Area	% Area
20.585	30387160	47.66
23.911	33370033	52.34



Retention Time	Area	% Area
20.860	915917	32.83
24.210	1874209	67.17

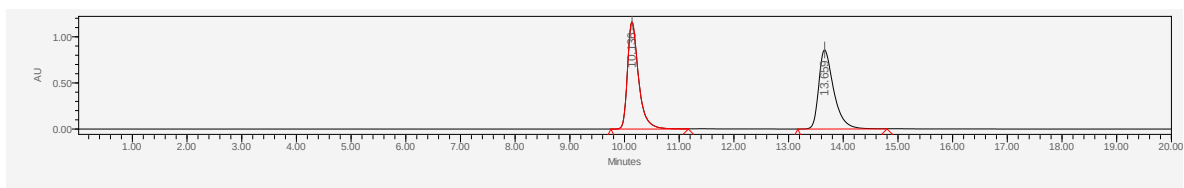


(4-fluorophenyl)(3-phenyloxiran-2-yl)methanone (**1nf**)

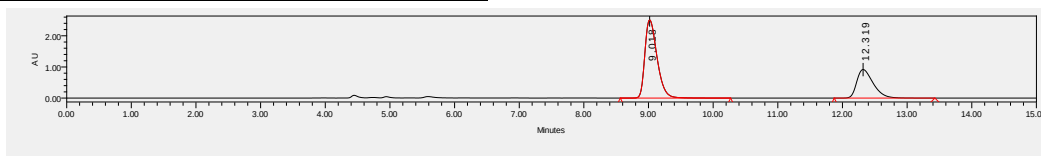
General procedure D; White solid; 50% yield, 34% *ee*, > 99:1 d.r.; $[\alpha]_{\text{D}}^{26} = -78$ (c 0.24, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.02 min, t (minor) = 12.32 min];

^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.00 (m, 2H), 7.38 (m, 5H), 7.17 (m, 2H), 4.24 (d, $J = 1.6$ Hz, 1H), 4.08 (d, $J = 1.6$ Hz, 1H).

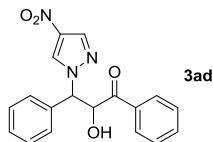
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{15}\text{H}_{11}^{18}\text{FNaO}_2$, m/z : 265.0636, observed: 265.0641; $[\text{M}+\text{Na}]^+ \text{C}_{15}\text{H}_{11}^{19}\text{FNaO}_2$, m/z : 266.0669, observed: 266.0682.



Retention Time	Area	% Area
10.136	16305463	50.06
13.659	16269563	49.94



Retention Time	Area	% Area
9.018	32753780	66.95
12.319	16167391	33.05



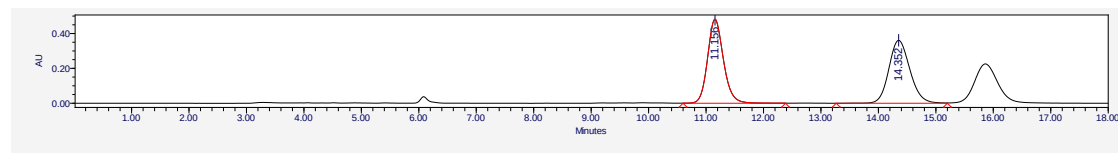
2-hydroxy-3-(4-nitro-1H-pyrazol-1-yl)-1,3-diphenylpropan-1-one (**3ad**)

General procedure D; colorless oil; 28% yield, 90% *ee*; $[\alpha]_{\text{D}}^{26} = -21$ (c 0.26, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 11.16 min, t (major) = 14.35 min];

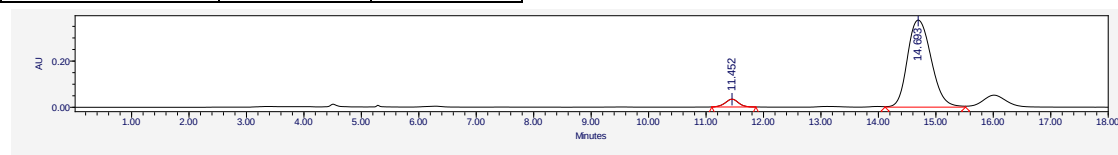
^1H NMR (400 MHz, CDCl_3) δ 8.52 (s, 1H), 8.13 (s, 1H), 7.94 – 7.87 (m, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.39 – 7.27 (m, 3H), 7.09 (d, J = 7.2 Hz, 2H), 6.06 (m, 1H), 5.82 (d, J = 3.2 Hz, 1H), 4.04 (d, J = 6.4 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 197.19, 135.92, 134.81, 133.41, 131.72, 129.78, 129.39, 129.28, 128.95, 128.64, 128.53, 74.58, 69.23.

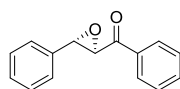
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{18}\text{H}_{15}\text{N}_3\text{NaO}_4$, m/z : 360.0955, observed: 360.0962.



Retention Time	Area	% Area
11.156	9246197	50.16
14.352	9186262	49.84



Retention Time	Area	% Area
11.452	538627	4.74
14.693	10814272	95.26



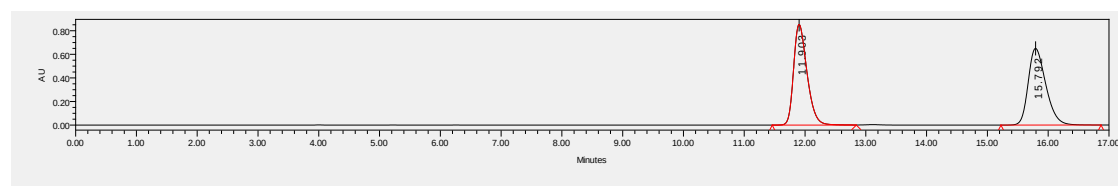
1ad

phenyl(3-phenyloxiran-2-yl)methanone (**1ad**)

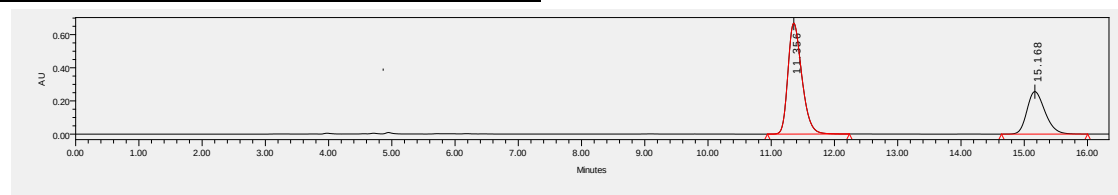
General procedure D; White solid; 65% yield, 33% *ee*, > 99:1 d.r.; $[\alpha]_{\text{D}}^{26}$ = -65 (c 0.32, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 11.36 min, t (minor) = 15.17 min];

^1H NMR (400 MHz, CDCl_3) δ 8.09 – 7.95 (m, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 4.8 Hz, 5H), 4.30 (d, J = 1.6 Hz, 1H), 4.08 (d, J = 1.6 Hz, 1H).

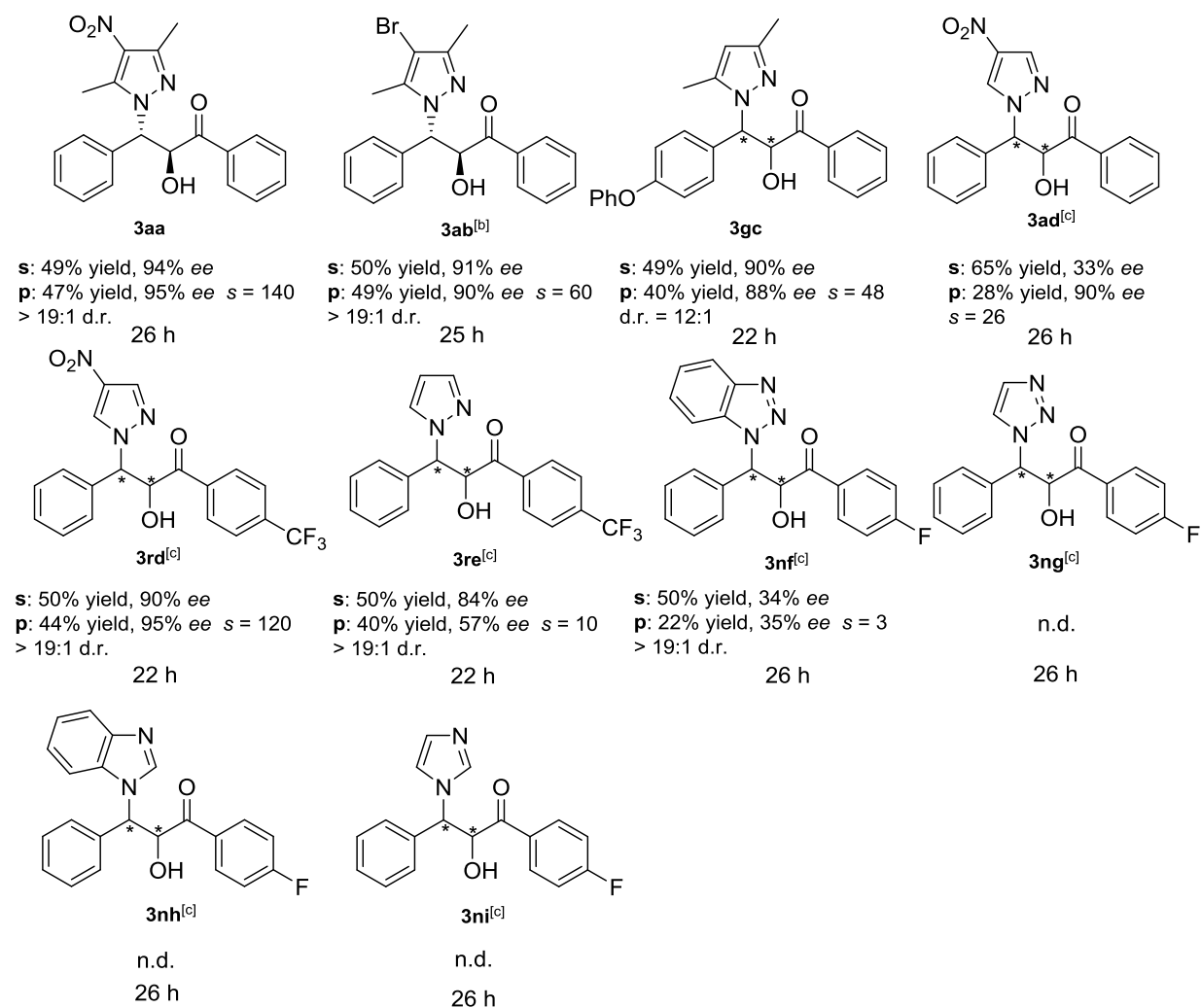
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{15}\text{H}_{12}\text{NaO}_2$, m/z : 247.0730, observed: 247.0732.



Retention Time	Area	% Area
11.903	13059530	50.00
15.792	13059754	50.00



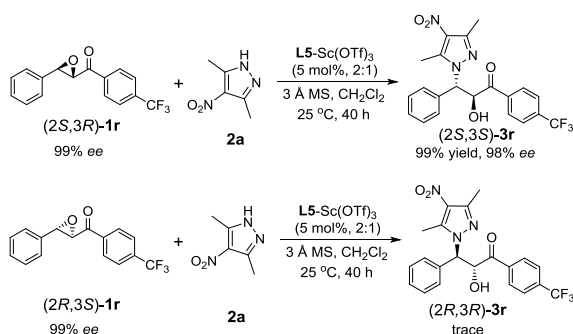
Retention Time	Area	% Area
11.356	10188503	66.77
15.168	5070589	33.23



[a] Unless otherwise noted, the reactions were performed with **L5**-Sc(OTf)₃ (5 mol%), 30 mg 3 Å MS and **2** (0.2 mmol) with (±)-**1** (0.1 mmol) under nitrogen in CH₂Cl₂ (0.5 mL) at 35 °C; The diastereoselectivities were determined by ¹H NMR analysis of the product **3**; The enantioselectivities were determined by HPLC analysis; Isolated yield; *s* = ln[(1 - Conv.)(1 - *ee*¹)]/ln[(1 - Conv.)(1 + *ee*¹)]; Conv = *ee*¹/(*ee*¹ + *ee*³); *s* = starting material; **p** = product; n.d. = not detected. [b] At 25 °C. [c] 10 mol% catalyst loading.

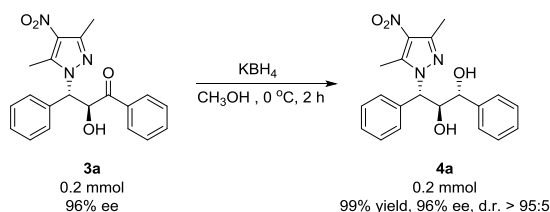
7.

a. Control experiments



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.01 mmol, 6.6 mg), Sc(OTf)₃ (0.005 mmol, 2.5 mg), and the 3 Å MS (30 mg) in CH₂Cl₂ (0.5 mL) were stirred at 25 °C for 30 min, corresponding optical epoxides **1r** (0.1 mmol) and pyrazole **2a** (28.3 mg, 0.2 mmol) were added to the reaction mixture at 25 °C. Then the reaction was stirred at 25 °C for 40 h. The mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3r** as a white solid. The product was determined by HPLC and NMR analysis.

b. Experimental procedure for the reduction of **3a**.



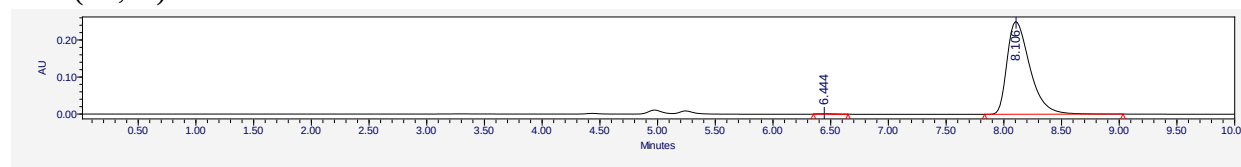
To a solution of the adduct **3a** (73.0 mg, 0.2 mmol) in CH₃OH (1.0 mL) was added KBH₄ (29.0 mg) at 0 °C. The mixture was allowed to stir for 2 h. Then saturated NH₄Cl aqueous solution (2.0 mL) was added to the mixture. The mixture was extracted with CH₂Cl₂, drying over Na₂SO₄. After evaporation of the solvent, the adduct **4a** was purified on silica gel chromatography (EtOAc : Pet = 1 : 5). The results were 99% yield, > 95:5 d.r. and 96% *ee*.

8. The analytical and spectral characterization data of the products

a. Control experiments

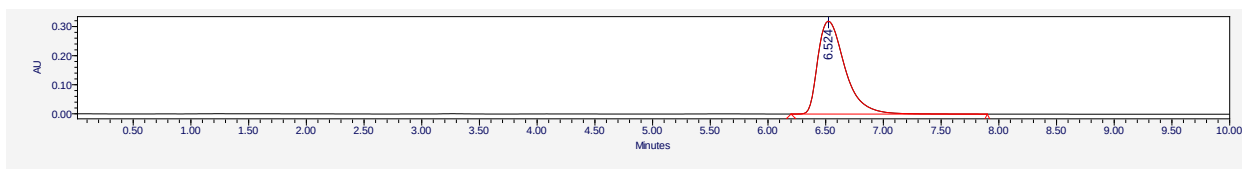
Before reaction

(2R,3S) – **1r**



Retention Time	Area	% Area
6.444	9035	0.26
8.106	3438999	99.74

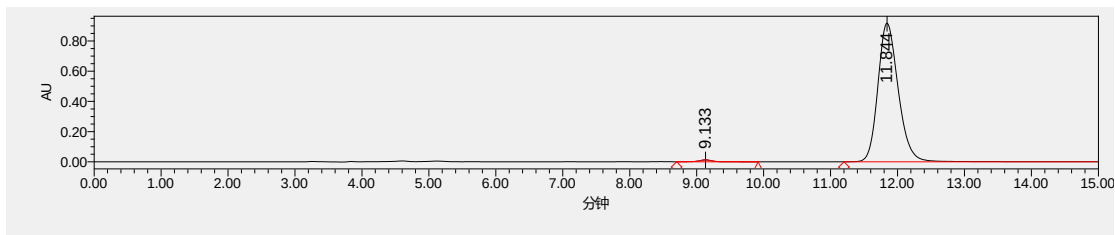
(2S,3R) – **1r**



Retention Time	Area	% Area
6.524	5219999	100.00

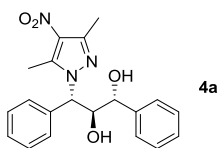
After reaction

(2S,3S) – 3r



Retention Time	Area	% Area
9.133	176887	0.90
11.844	19440593	99.10

b. Experimental procedure for the reduction of 3a.



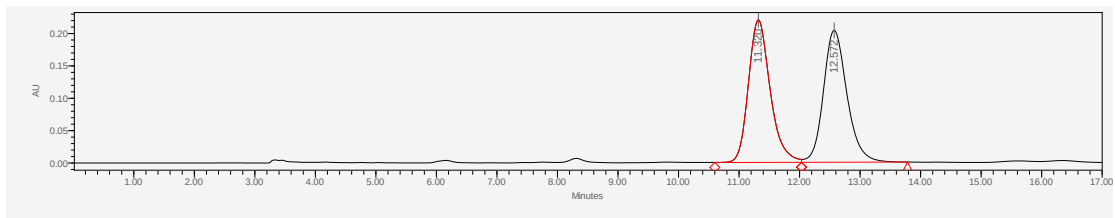
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-1,3-diphenylpropane-1,2-diol (**4a**)

White solid; 99% yield, 96% *ee*, > 19:1 d.r.; Determined by HPLC analysis [Daicel chiralpak IE, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, *t* (major) = 11.27 min, *t* (minor) = 12.56 min];

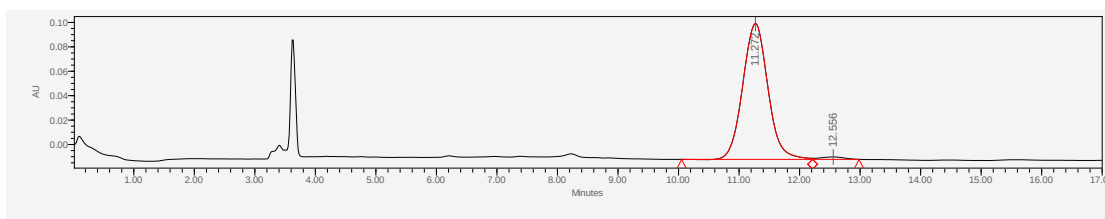
¹H NMR (400 MHz, CDCl₃) δ 7.31 (m, 10H), 5.63 (d, *J* = 2.4 Hz, 1H), 4.78 – 4.61 (m, 2H), 4.30 (d, *J* = 8.4 Hz, 1H), 2.46 (d, *J* = 38.6 Hz, 6H), 2.36 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 145.80, 141.10, 141.03, 134.78, 128.67, 128.57, 128.48, 128.47, 128.43, 127.11, 76.16, 73.47, 62.78, 14.32, 11.41.

HRMS (ESI) calcd for [M+Na]⁺ C₂₀H₂₁N₃NaO₄, *m/z*: 390.1424, observed: 390.1434.

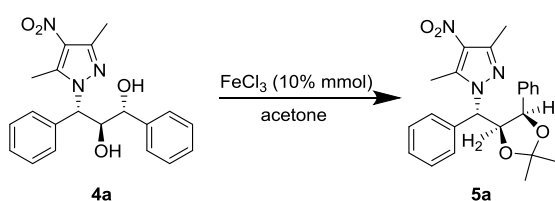


Retention Time	Area	% Area
11.320	5493283	49.97
12.572	5500366	50.03



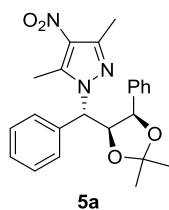
Retention Time	Area	% Area
11.272	3218916	98.34
12.556	54404	1.66

c. Determination of the absolute configuration of **4a**



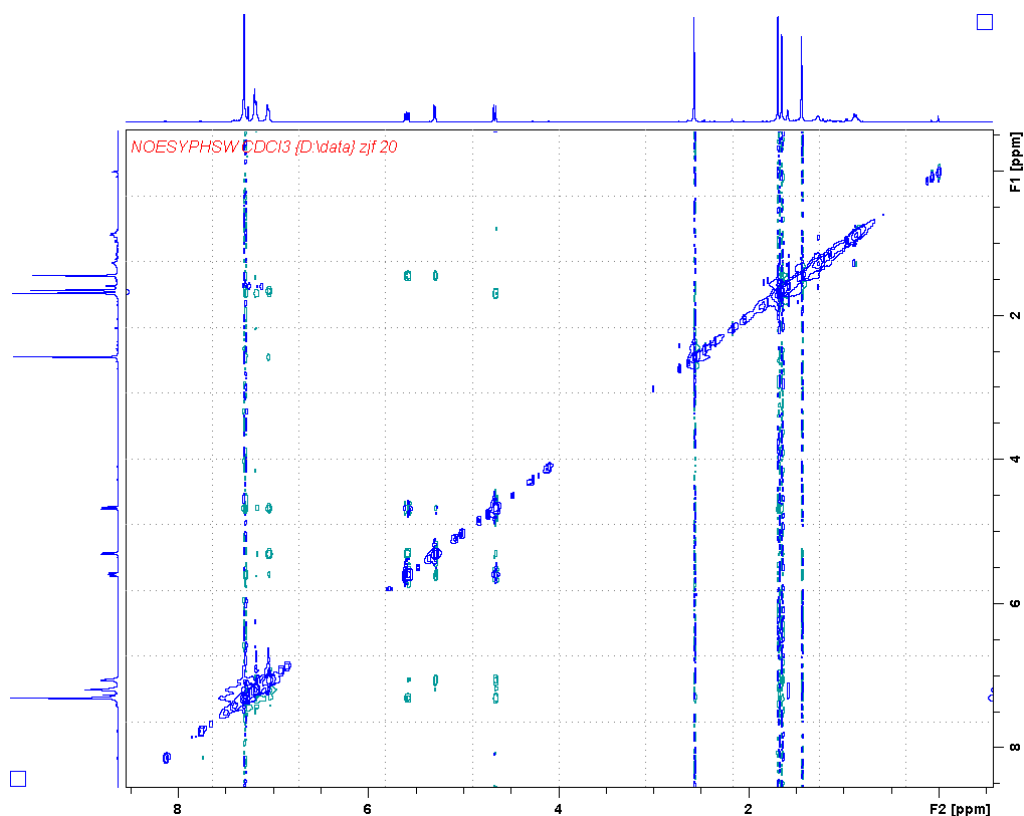
In a test tube with a magnetic stirring bar, **4a** (0.2 mmol, 73.4 mg), FeCl_3 (0.02 mmol, 3.2 mg), in acetone (1 mL) were stirred at 15 °C for 8 h, then, the mixture was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **5a** (16.4 mg, 20% yield) as a colorless oil. The product was determined by NMR analysis.

To determine the absolute configuration of **4a**, we convert **4a** to **5a**. We could easily found the signal between H_1 and H_2 from the NOESY spectra, so the absolute configuration of **5a** was determined to be (1*R*,2*S*,3*S*). Based on these information, we deduce the absolute configuration of **4a** is (1*R*,2*S*,3*S*).



1-((*S*)-((4*S*,5*R*)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl)(phenyl)methyl)-3,5-dimethyl-4-nitro-1*H*-pyrazole (**5a**)

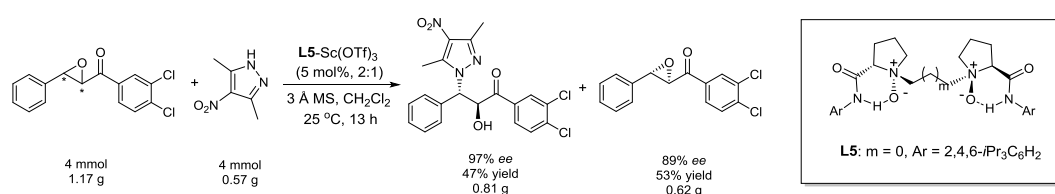
Colorless oil; 20% yield.



^1H NMR (400 MHz, CDCl_3) δ 7.30 (s, 5H, Ar-H), 7.18 (d, $J = 5.6$ Hz, 3H, Ar-H), 7.05 (d, $J = 5.6$ Hz, 2H, Ar-H), 5.59 (dd, $J = 9.8, 6.7$ Hz, 1H, Chiral center: N-CH), 5.29 (d, $J = 6.4$ Hz, 1H, Chiral center: O-CH), 4.66 (d, $J = 9.6$ Hz, 1H, Chiral center: O-CH), 2.57 (s, 3H, C-H), 1.69 (s, 3H, C-H), 1.65 (s, 3H, C-H), 1.44 (s, 3H, C-H).

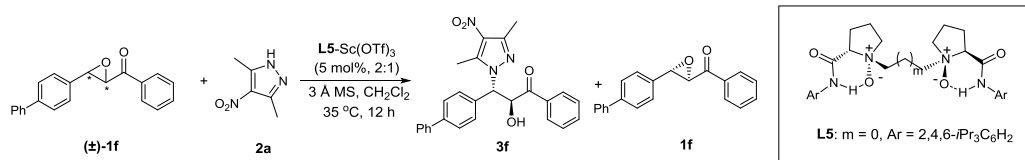
^{13}C NMR (100 MHz, CDCl_3) δ 145.72, 140.67, 137.26, 137.03, 128.71, 128.52, 128.24, 127.91, 127.55, 126.62, 109.02, 79.47, 78.69, 62.07, 26.91, 24.27, 14.25, 10.15.

9. Gram scale experiment

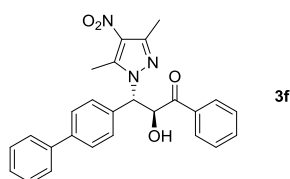


In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.4 mmol, 268 mg), Sc(OTf)₃ (0.20 mmol, 100 mg), and the 3 Å MS (1.20 g) in CH₂Cl₂ (20 mL) were stirred at 25 °C for 2 h, epoxide ($\pm$)-**1v** (1.17 g, 4 mmol) and pyrazole **2a** (0.57 g, 4 mmol) were added to the reaction mixture at 25 °C. Then the reaction was stirred at 25 °C for 13 h. After 50% consumption of the starting materials, the mixture was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3v** (0.81 g, 47% yield) as a white solid, and **1v** (0.62 g, 53% yield) as a white solid. The product was determined by HPLC and NMR analysis.

10. Determination of the absolute configuration of **3f** by the x-ray crystal structure.

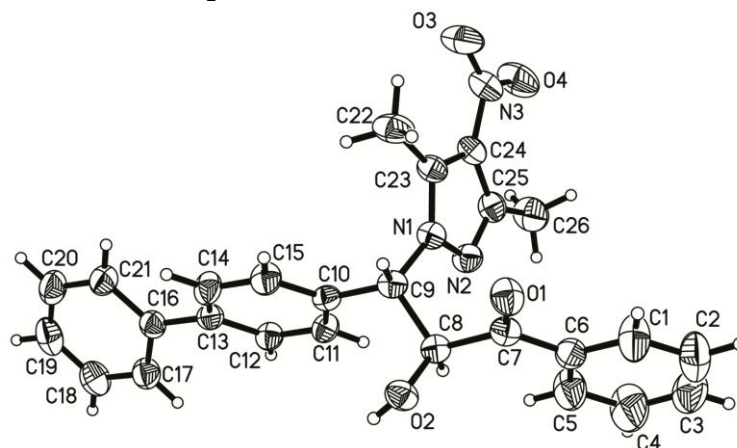


In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L5** (0.01 mmol, 6.6 mg), $\text{Sc}(\text{OTf})_3$ (0.005 mmol, 2.5 mg), and the 3 Å MS (30 mg) in CH_2Cl_2 (0.5 mL) were stirred at 35 °C for 30 min, epoxides **(±)-1f** (30 mg, 0.1 mmol) and pyrazole **2a** (28.3 mg, 0.2 mmol) were added to the reaction mixture at 35 °C. Then the reaction was stirred at 35 °C for 12 h. After 50% consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **3f** (0.05 mmol, 50% yield) as a white solid, and **1f** (0.05 mmol, 50% yield) as a white solid. The product was determined by HPLC and NMR analysis.



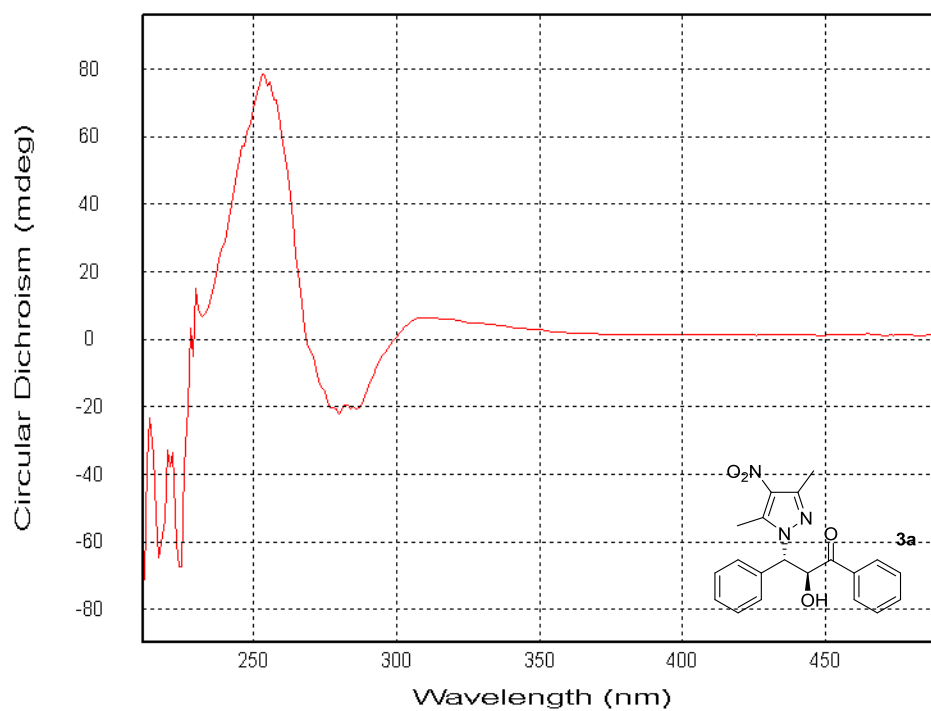
3-([1,1'-biphenyl]-4-yl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3f**)

X-ray crystal structure of product **3f**:

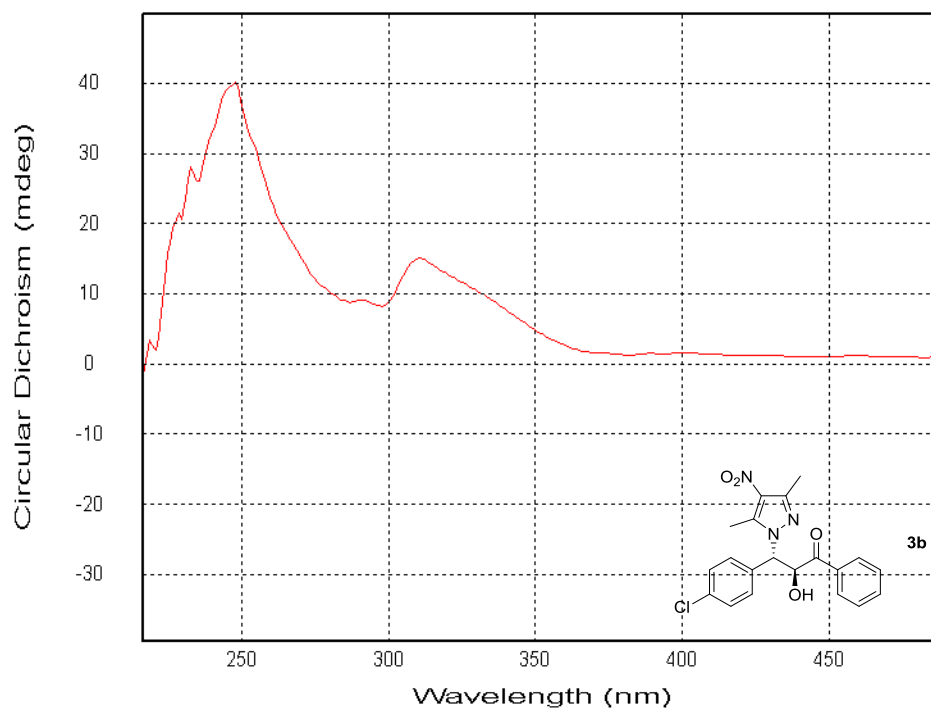


11. CD information of the products

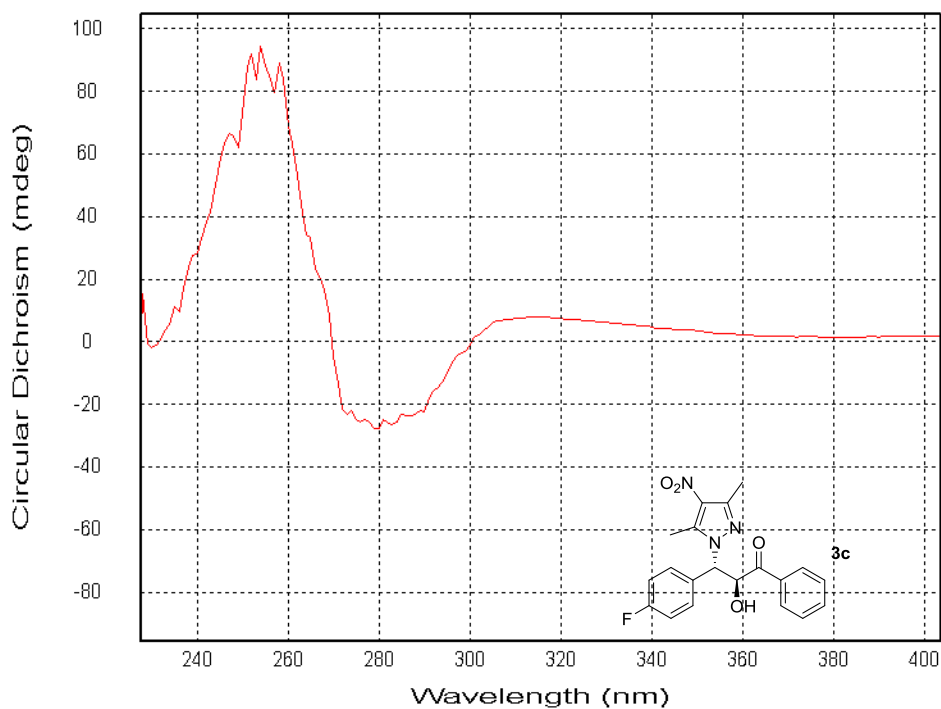
(2S,3S) - 3-(3,5-dimethyl-4-nitro-1H-pyrazol-1-yl)-2-hydroxy-1,3-diphenylpropan-1-one (3a)



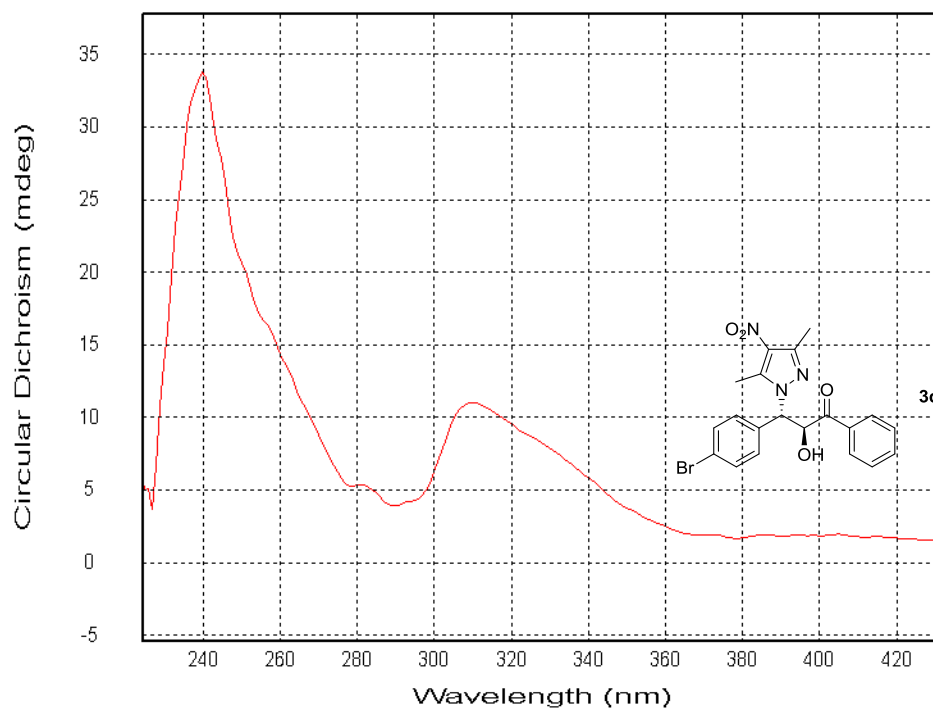
3-(4-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3b**)



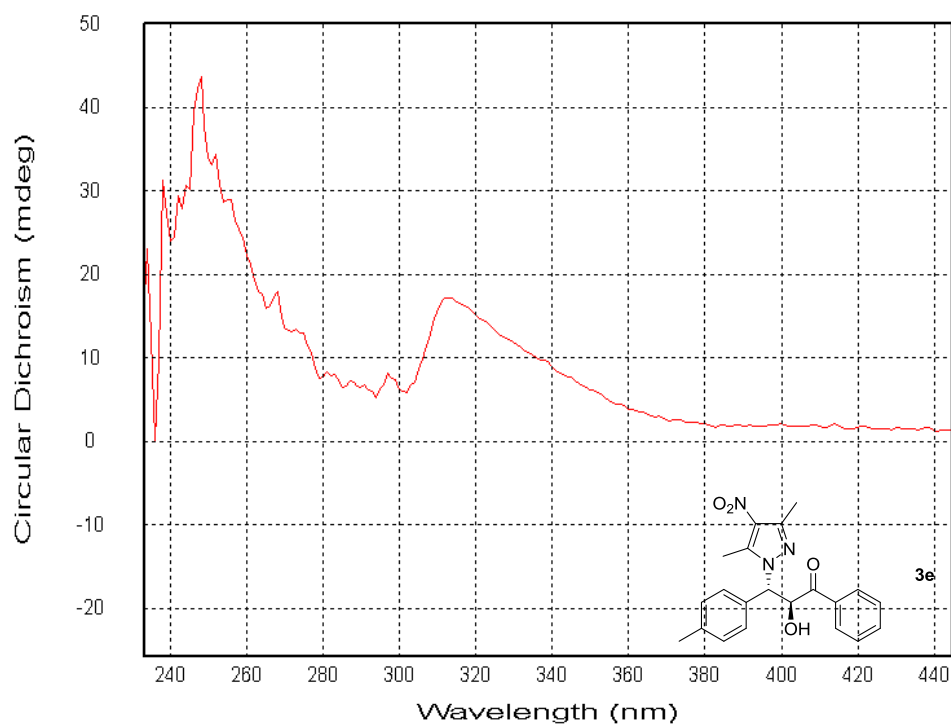
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-3-(4-fluorophenyl)-2-hydroxy-1-phenylpropan-1-one (3c)



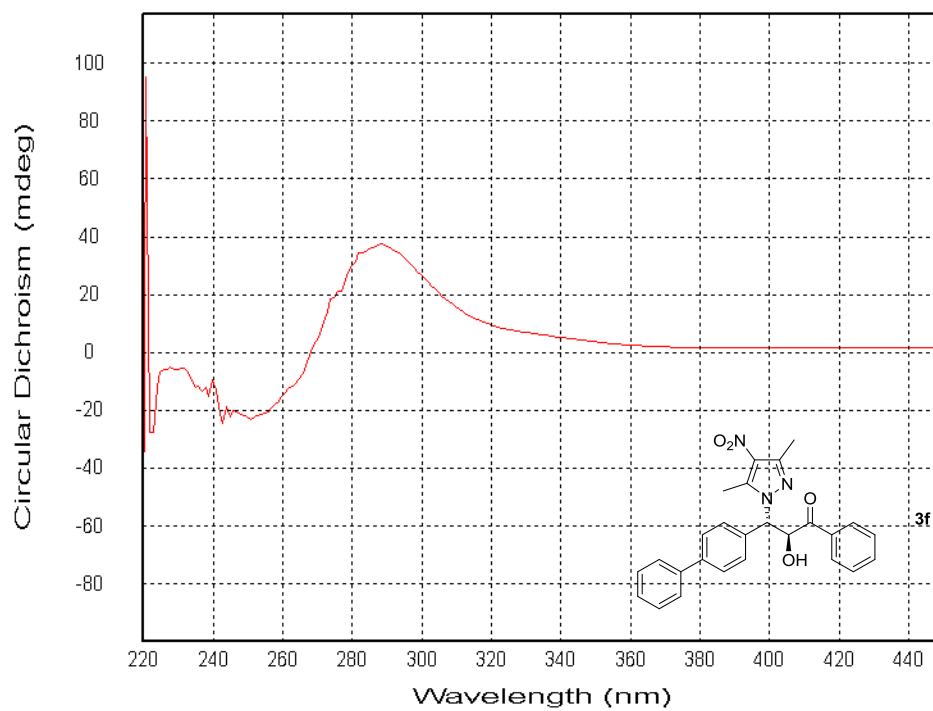
3-(4-bromophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (3d)



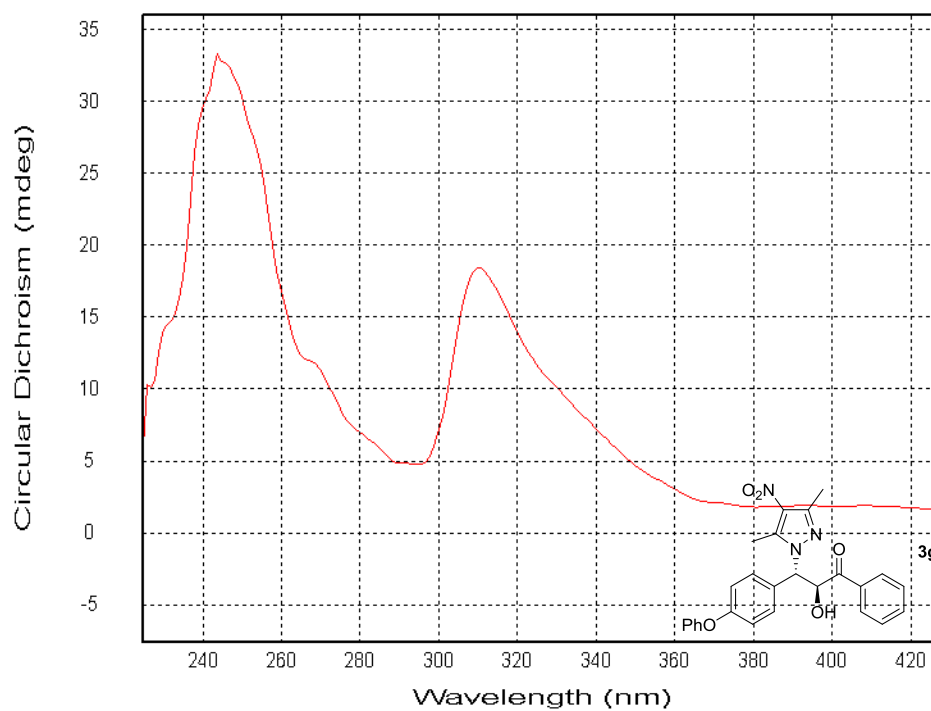
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenyl-3-(*p*-tolyl)propan-1-one (**3e**)



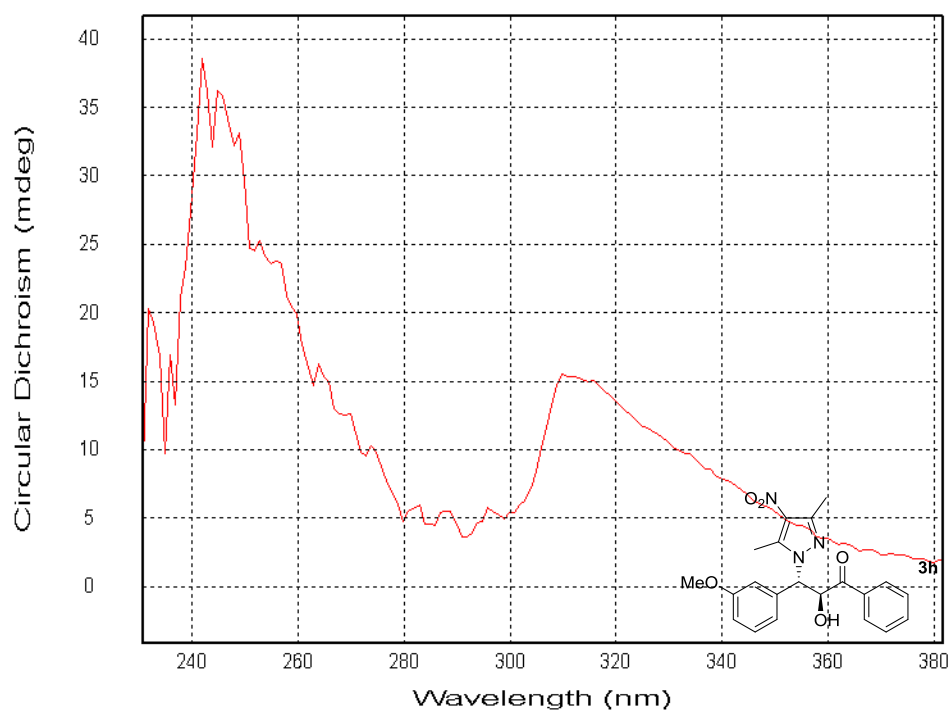
3-([1,1'-biphenyl]-4-yl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3f**)



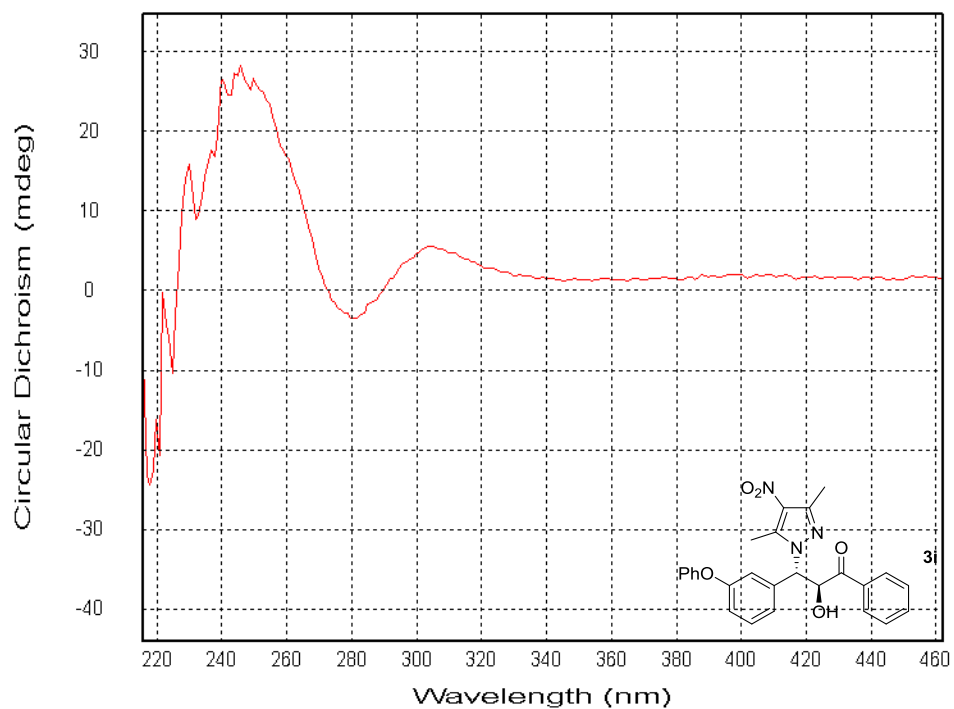
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-(4-phenoxyphenyl)-1-phenylpropan-1-one (**3g**)



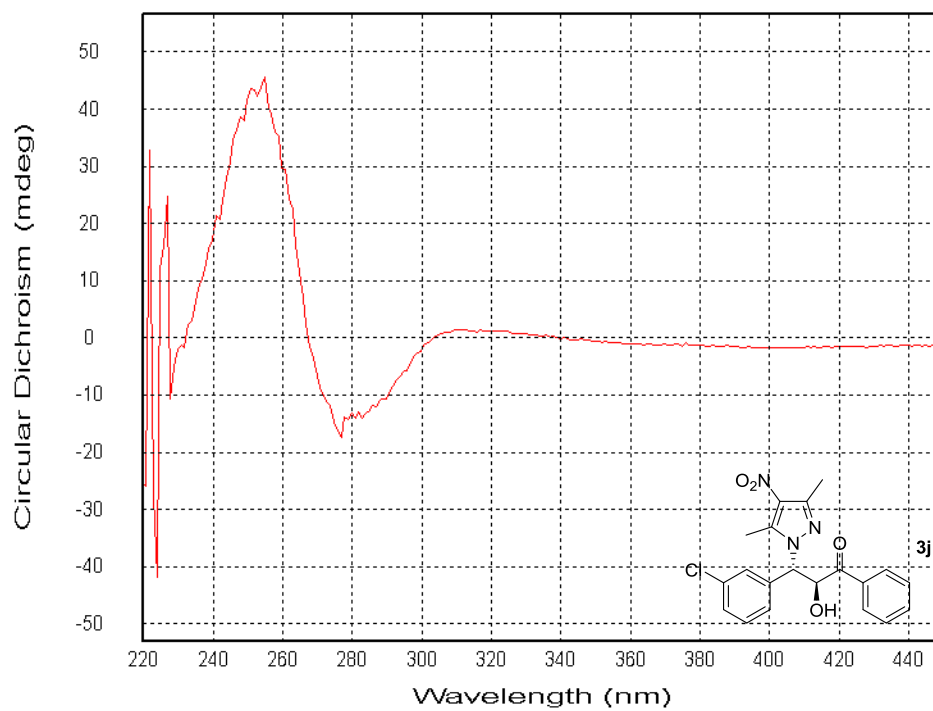
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-(3-methoxyphenyl)-1-phenylpropan-1-one (**3h**)



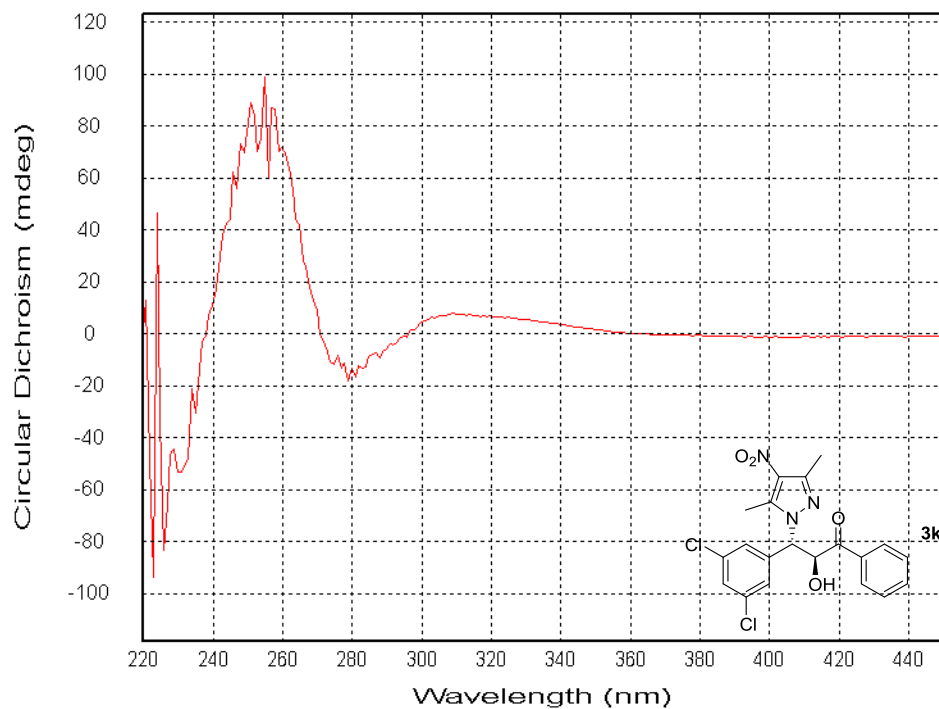
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-(3-phenoxyphenyl)-1-phenylpropan-1-one (3i)



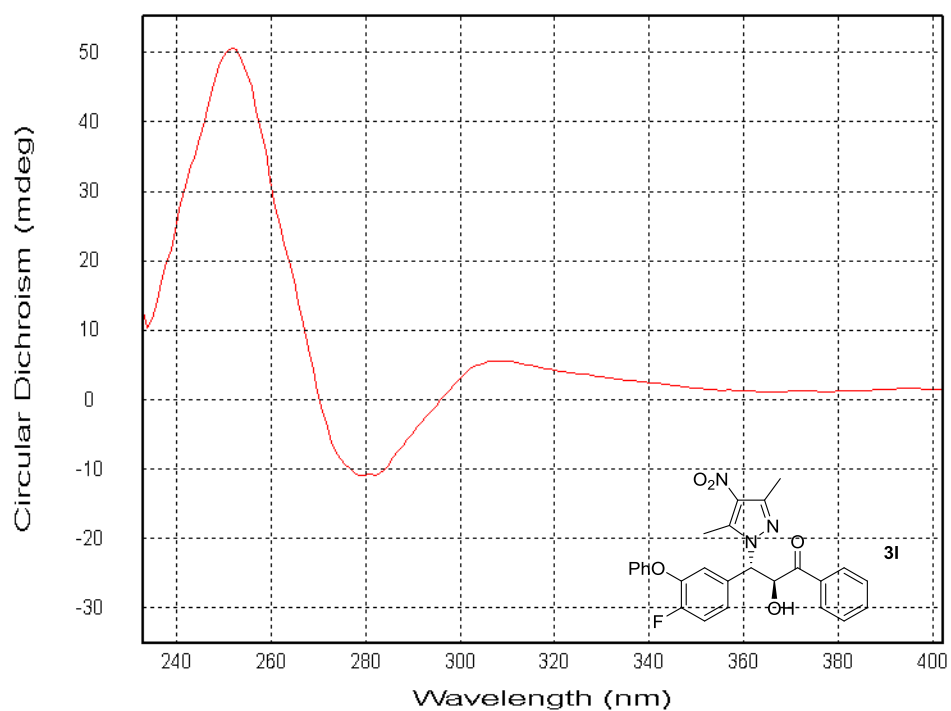
3-(3-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (3j)



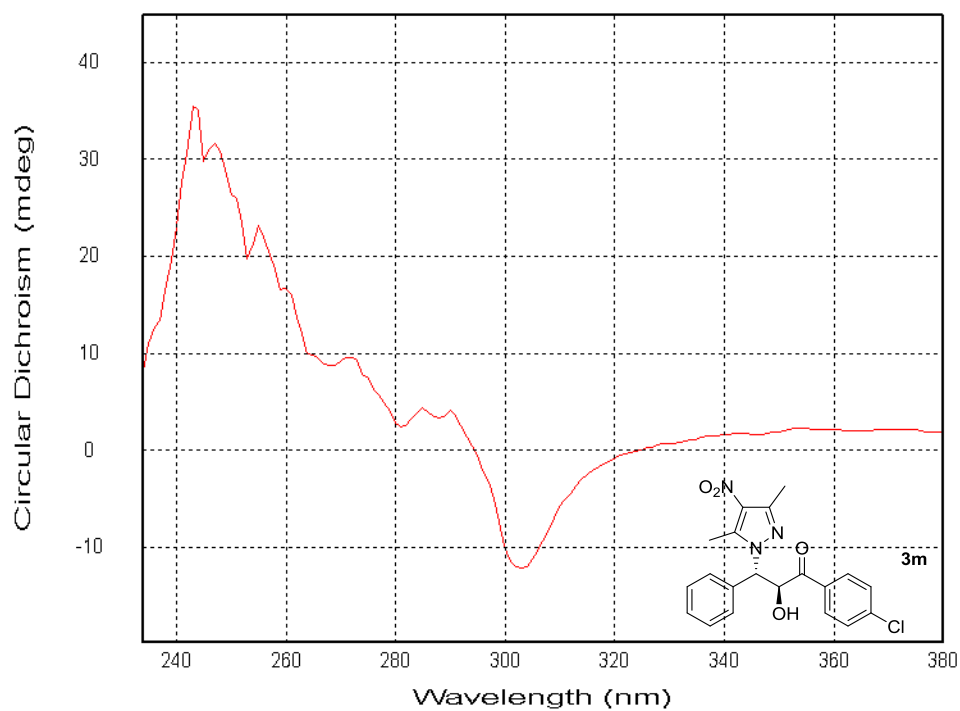
3-(3,5-dichlorophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-phenylpropan-1-one (**3k**)



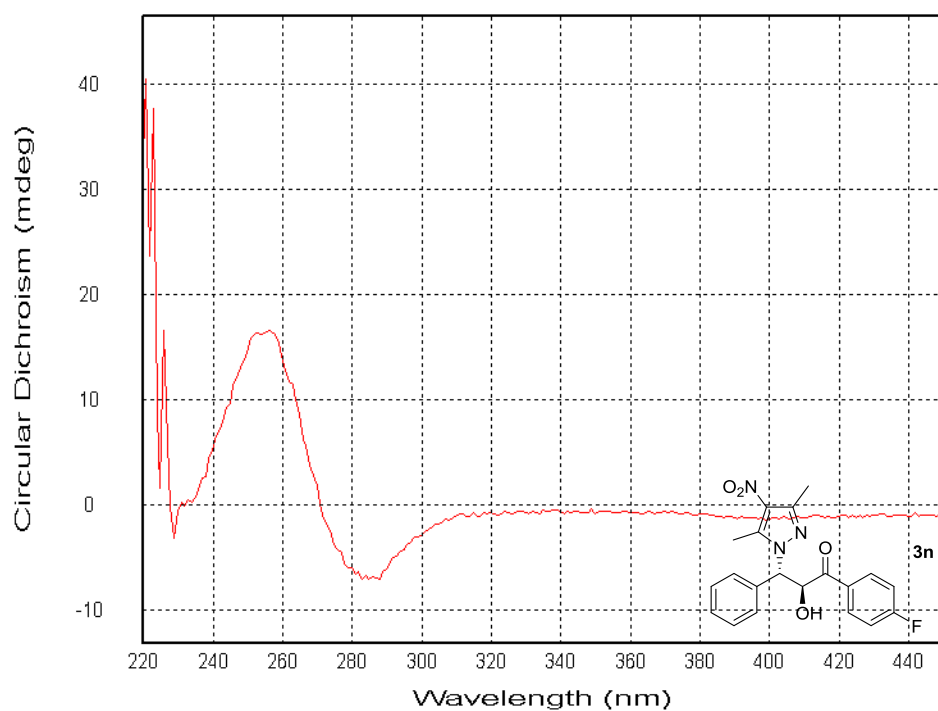
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-3-(4-fluoro-3-phenoxyphenyl)-2-hydroxy-1-phenylpropan-1-one (**3l**)



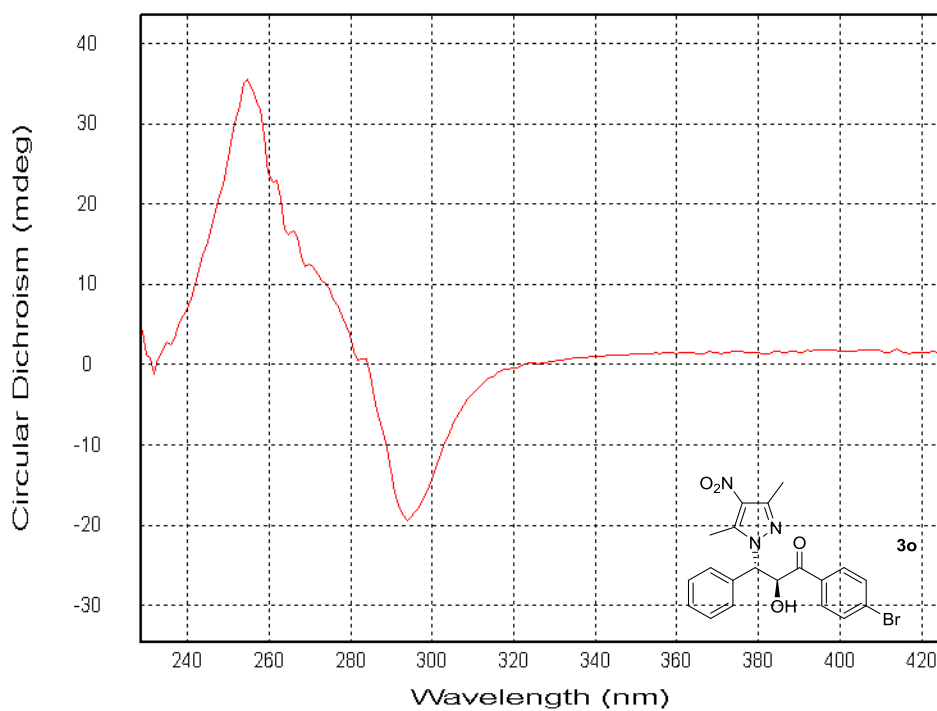
1-(4-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (3m)



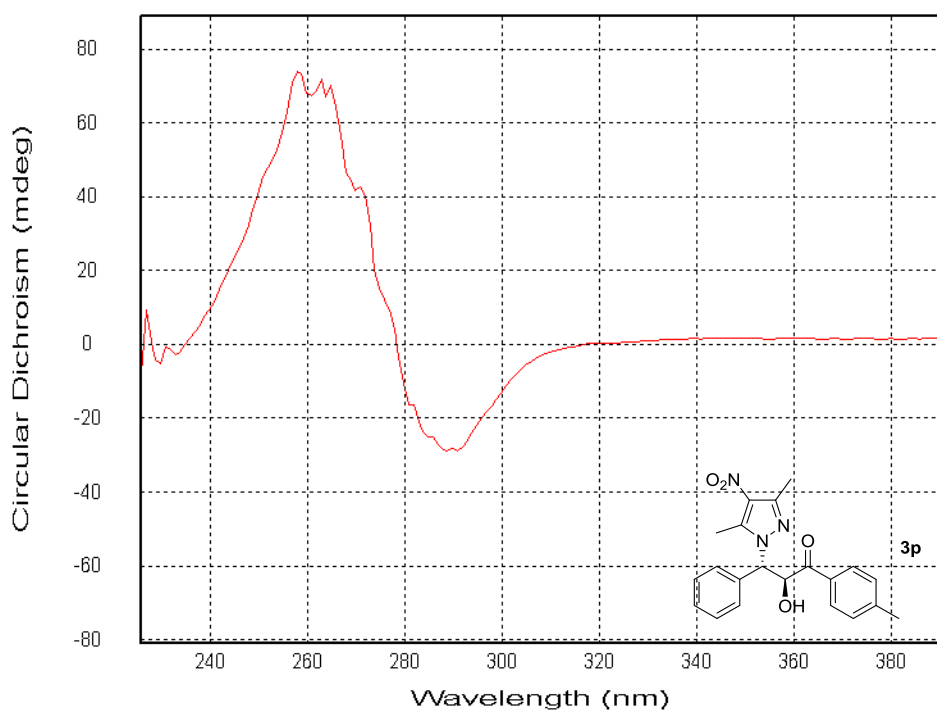
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-1-(4-fluorophenyl)-2-hydroxy-3-phenylpropan-1-one (3n)



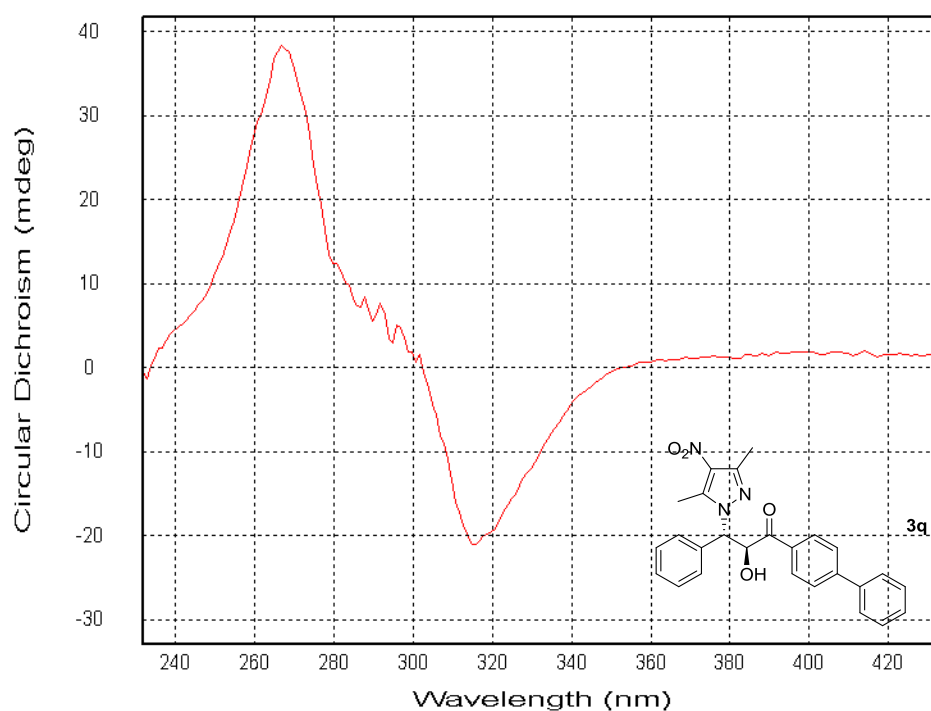
1-(4-bromophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (3o)



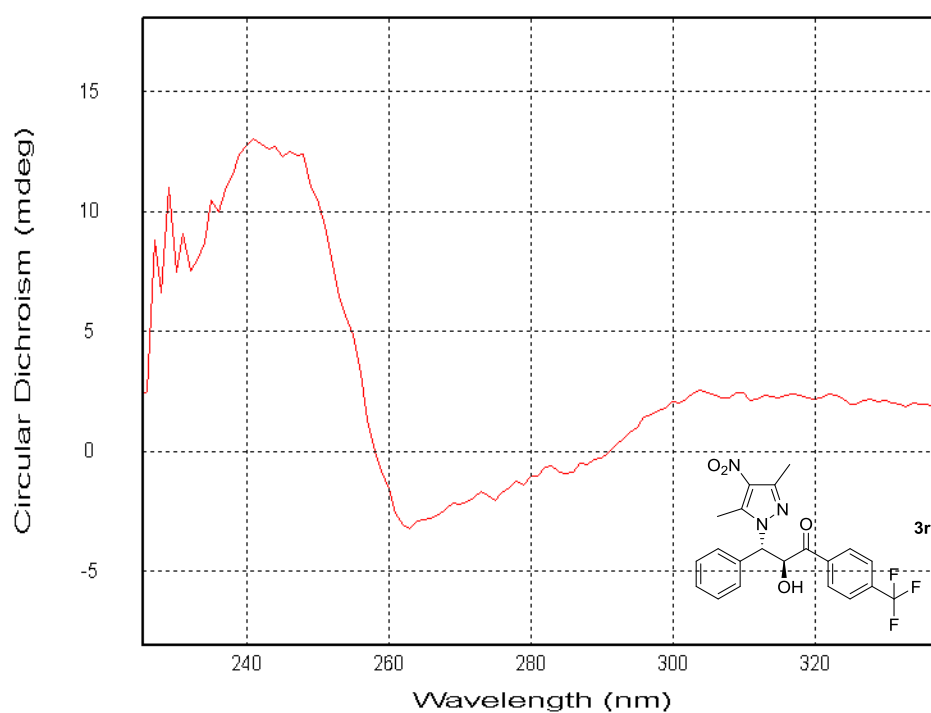
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(*p*-tolyl)propan-1-one (3p)



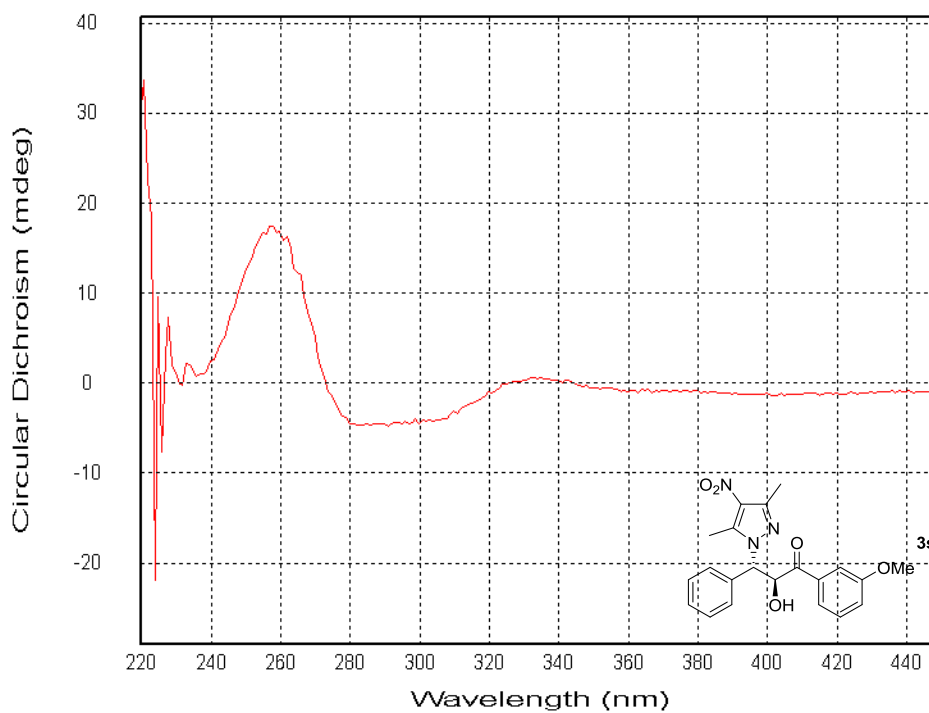
1-([1,1'-biphenyl]-4-yl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3q**)



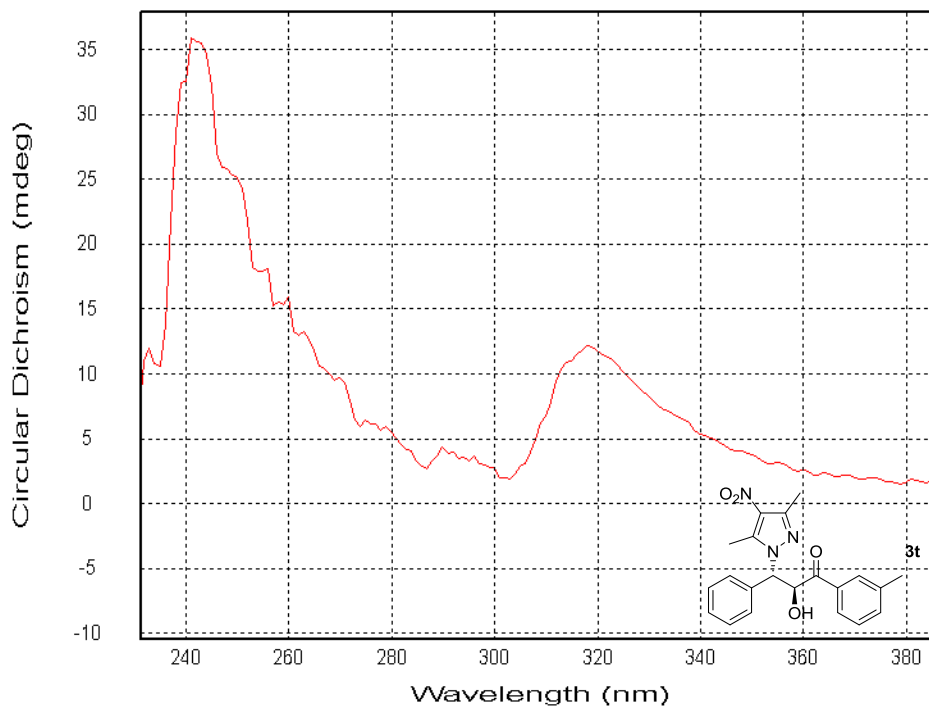
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3r**)



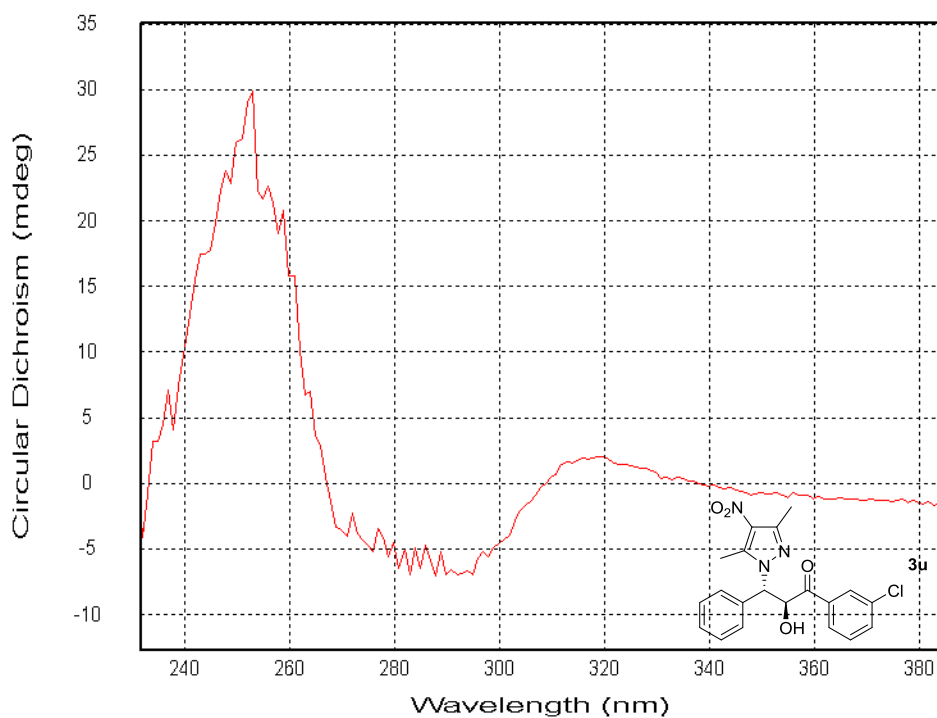
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-(3-methoxyphenyl)-3-phenylpropan-1-one (**3s**)



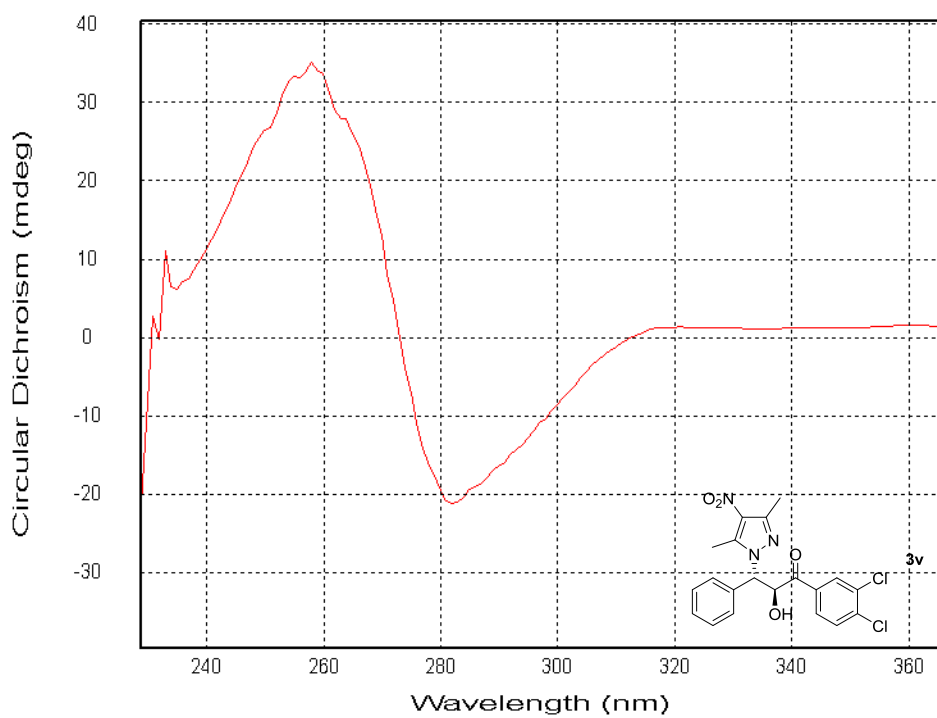
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(*m*-tolyl)propan-1-one (**3t**)



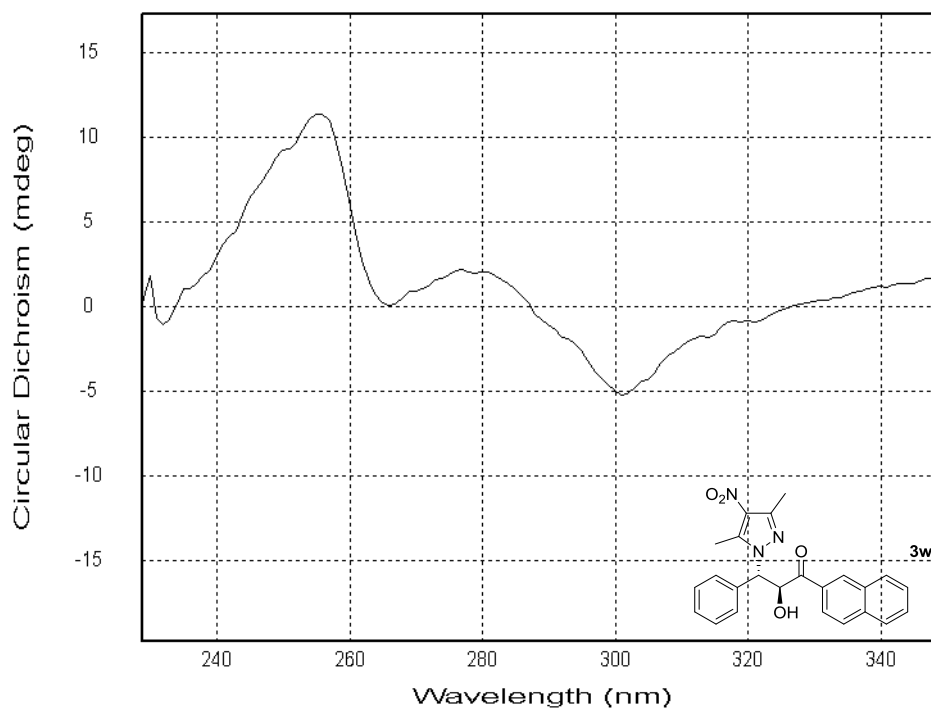
1-(3-chlorophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3u**)



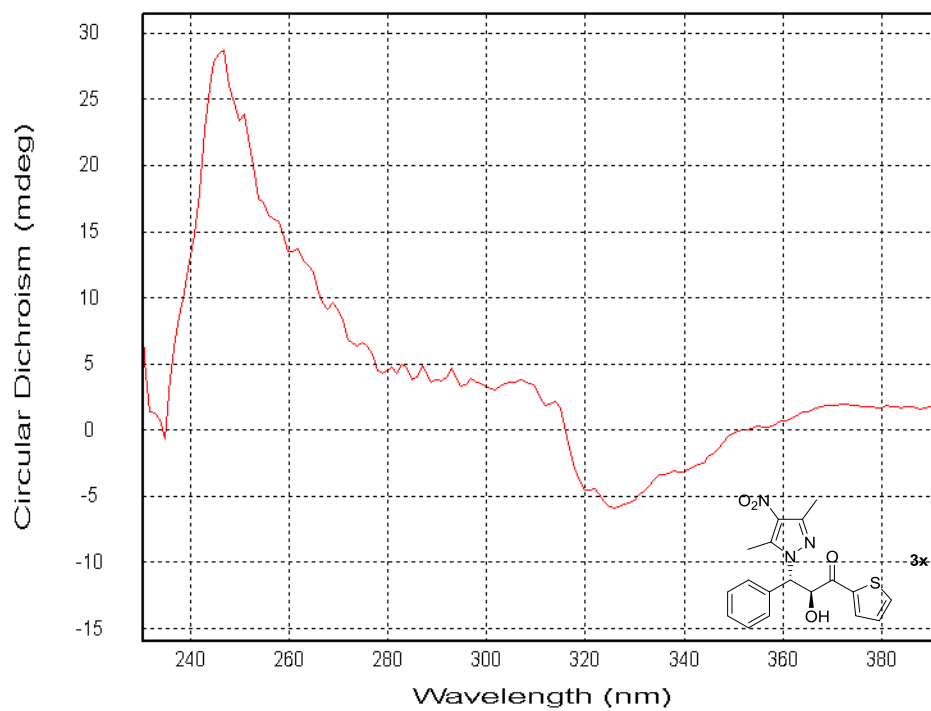
1-(3,4-dichlorophenyl)-3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (**3v**)



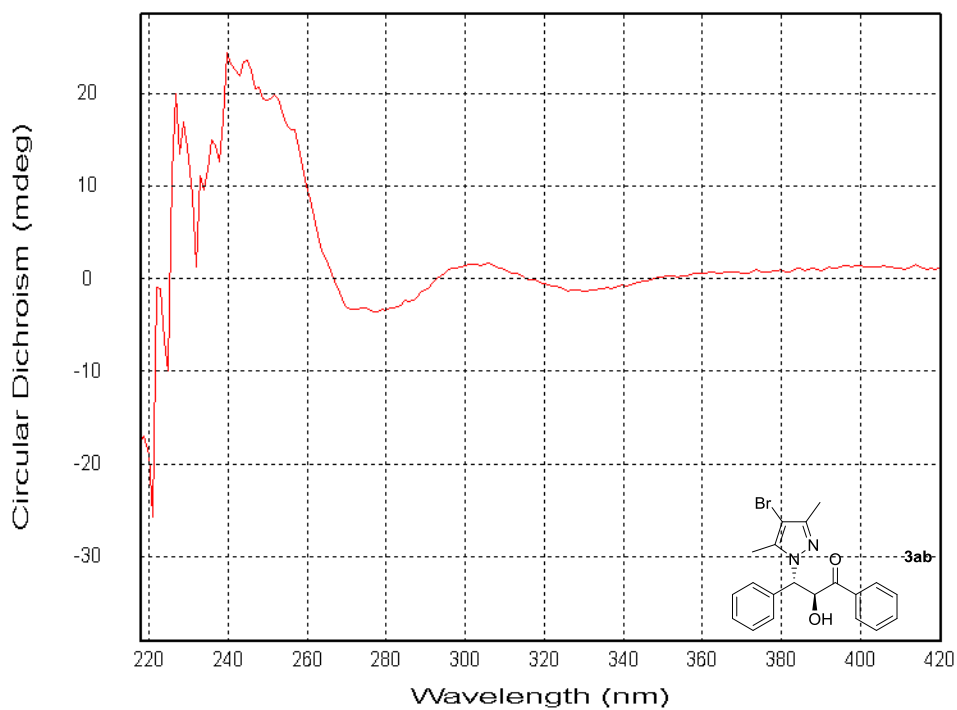
3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-1-(naphthalen-2-yl)-3-phenylpropan-1-one
ne (**3w**)



3-(3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)-2-hydroxy-3-phenyl-1-(thiophen-2-yl)propan-1-one
(**3x**)



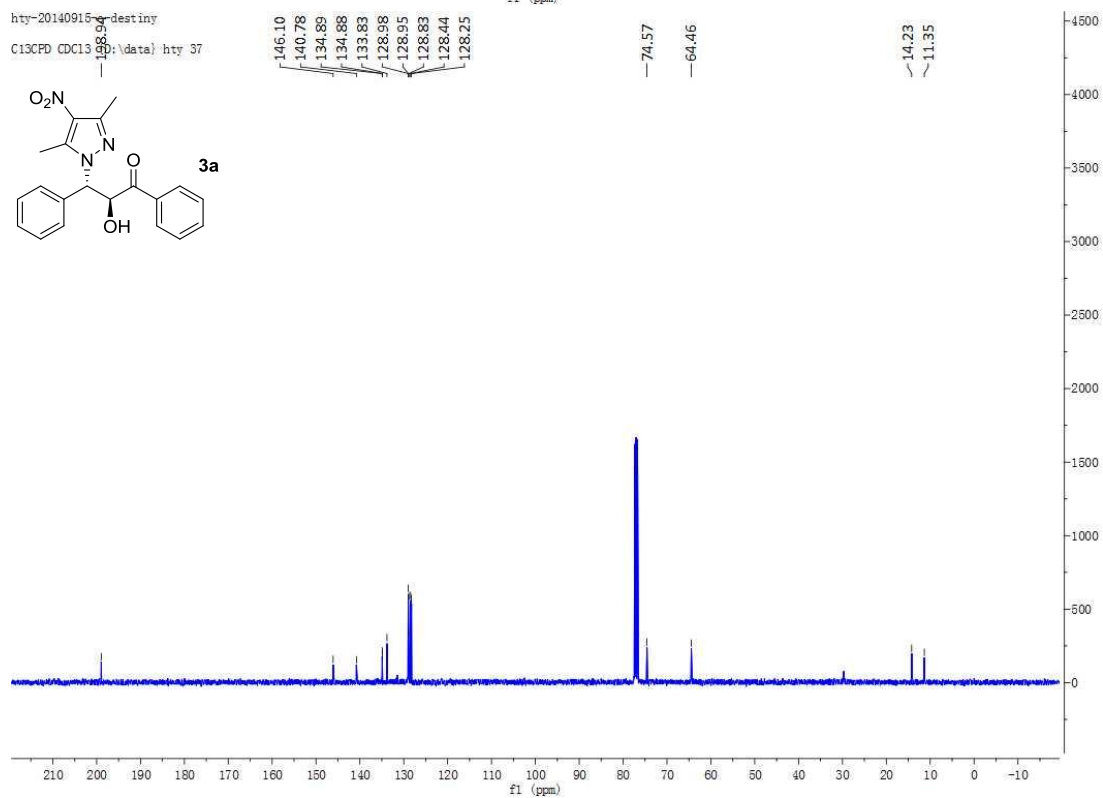
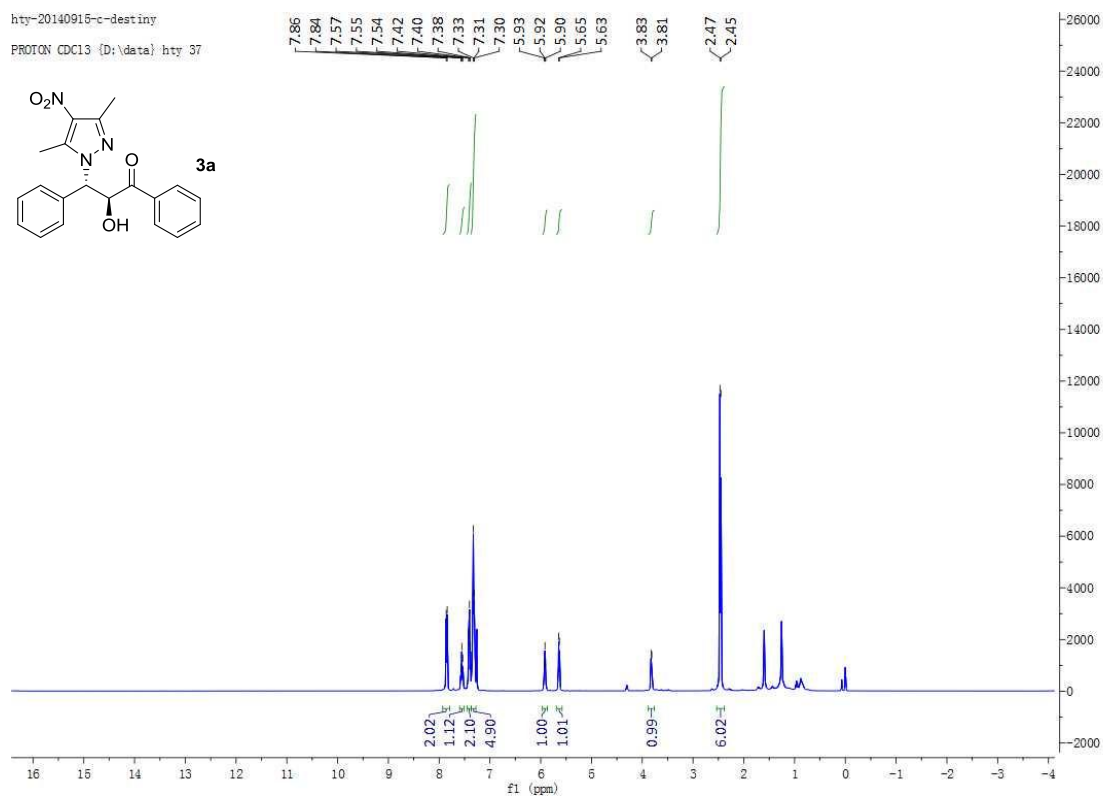
3-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)-2-hydroxy-1,3-diphenylpropan-1-one (**3ab**)

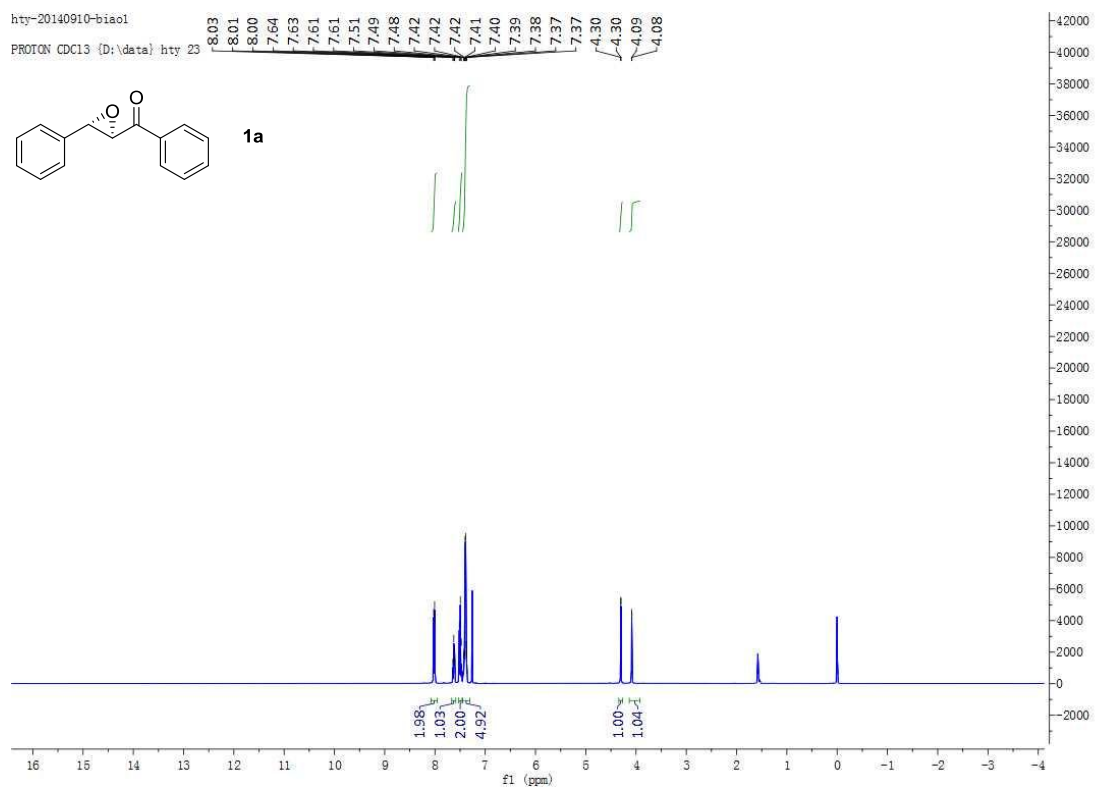


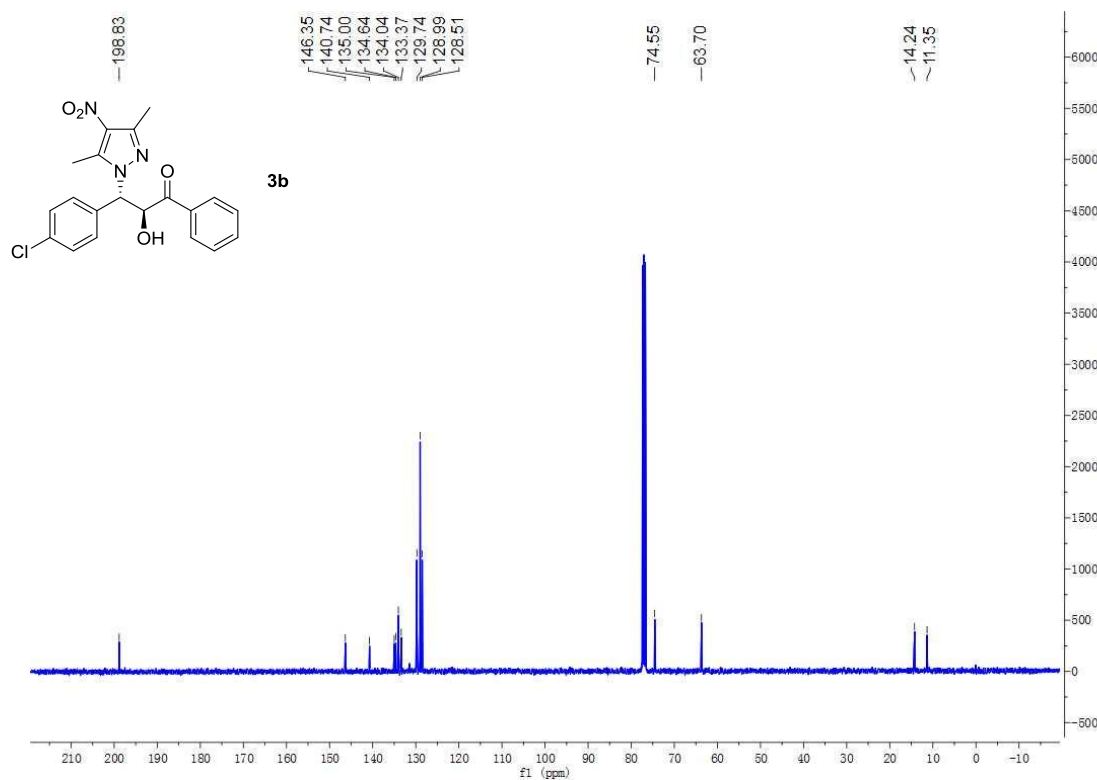
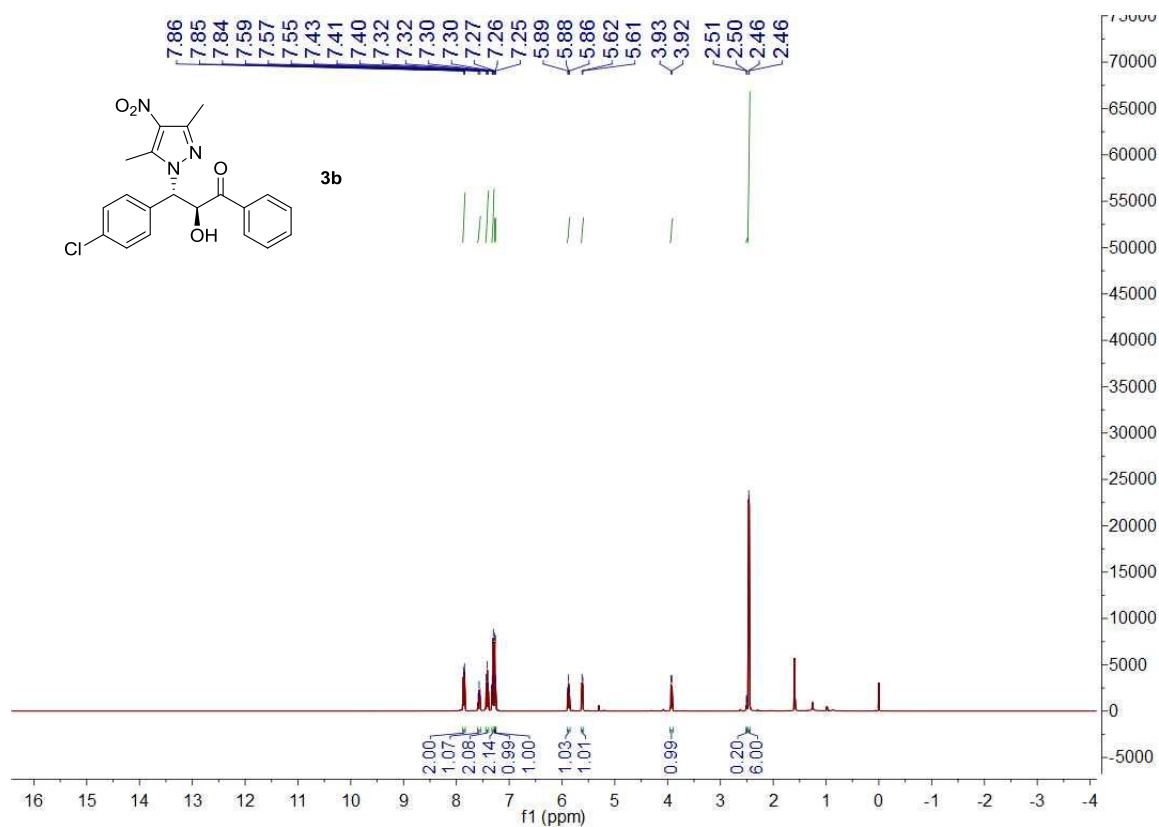
12. References

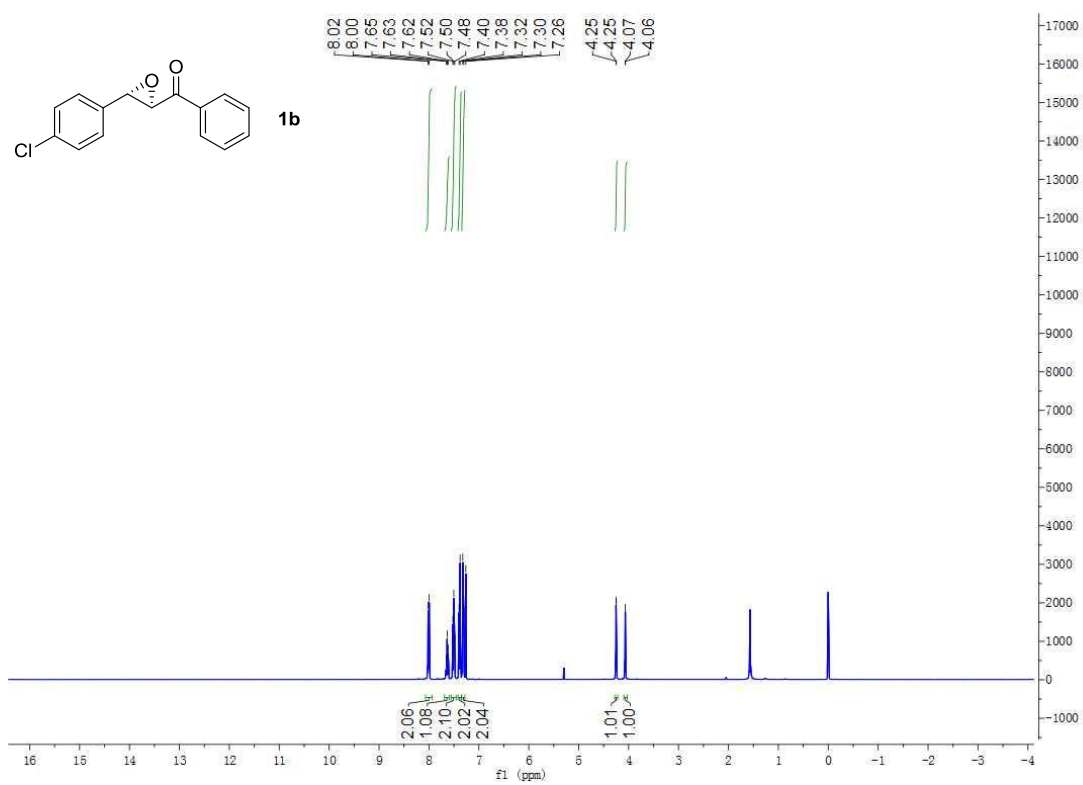
- [1] Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett.* **2005**, 2445.
- [2] Y. Y. Chu, X. H. Liu, W. Li, X. L. Hu, L. L. Lin, X. M. Feng, *Chem. Sci.* **2012**, 3, 1996.

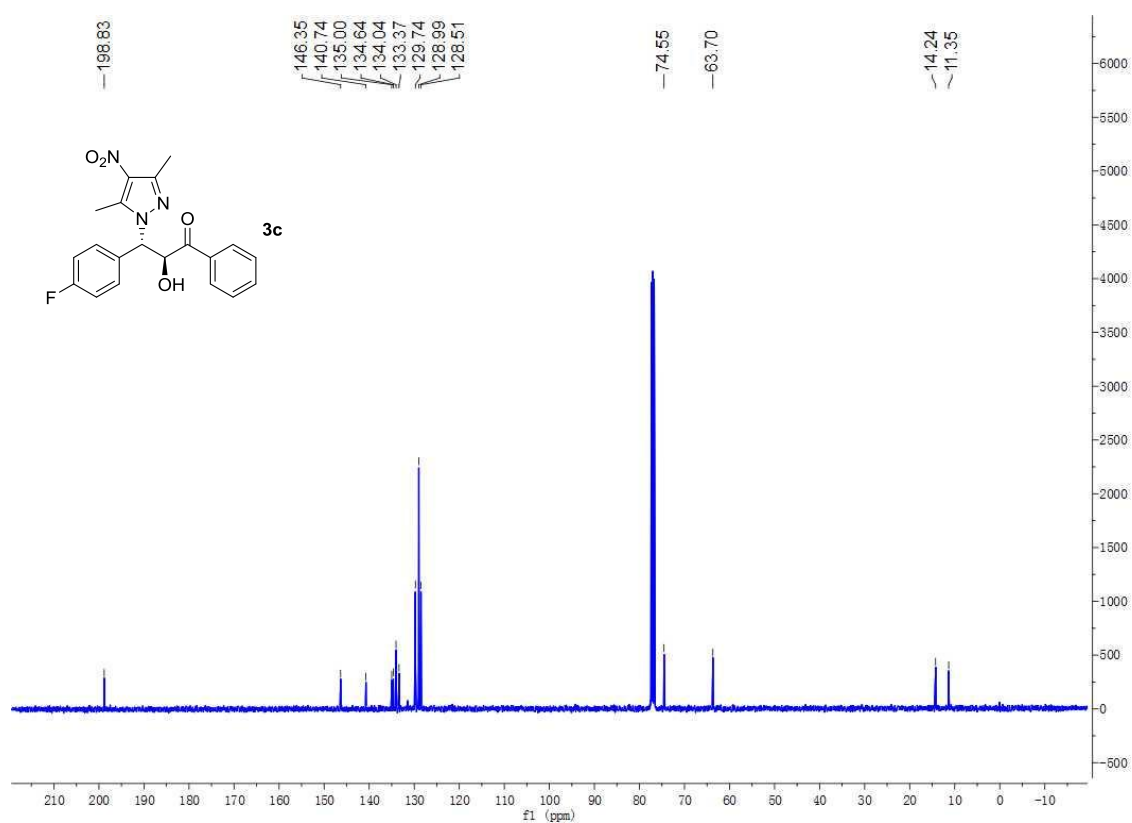
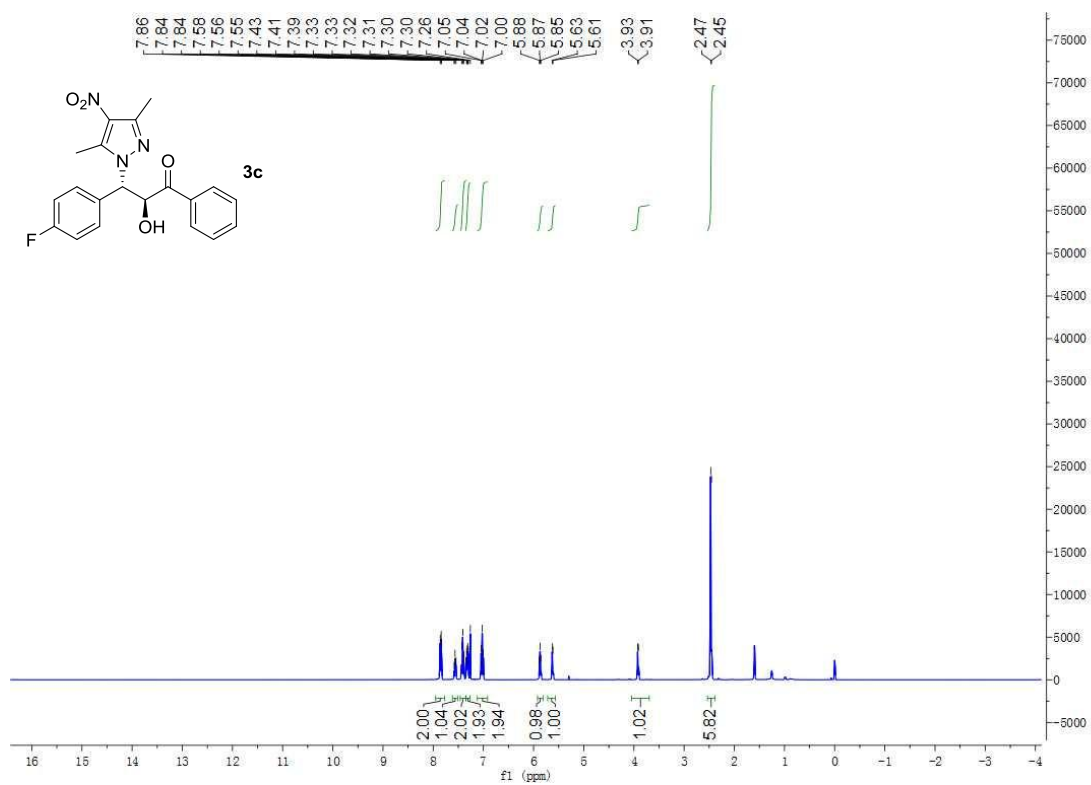
13. NMR spectra

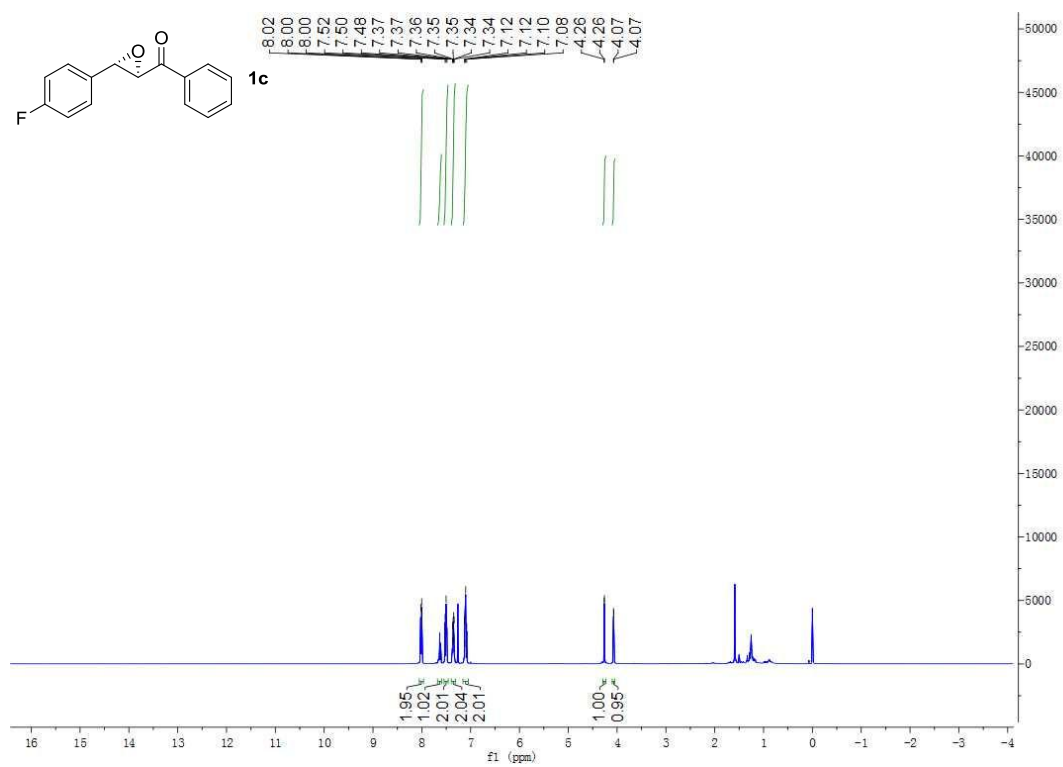


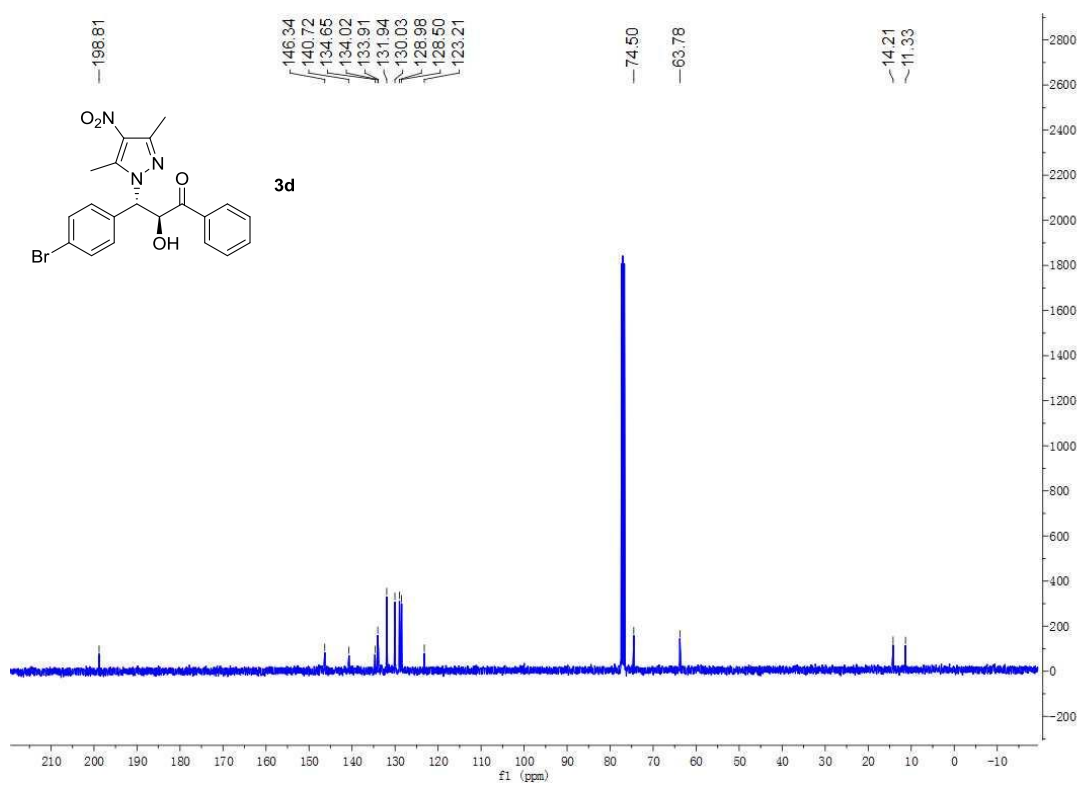
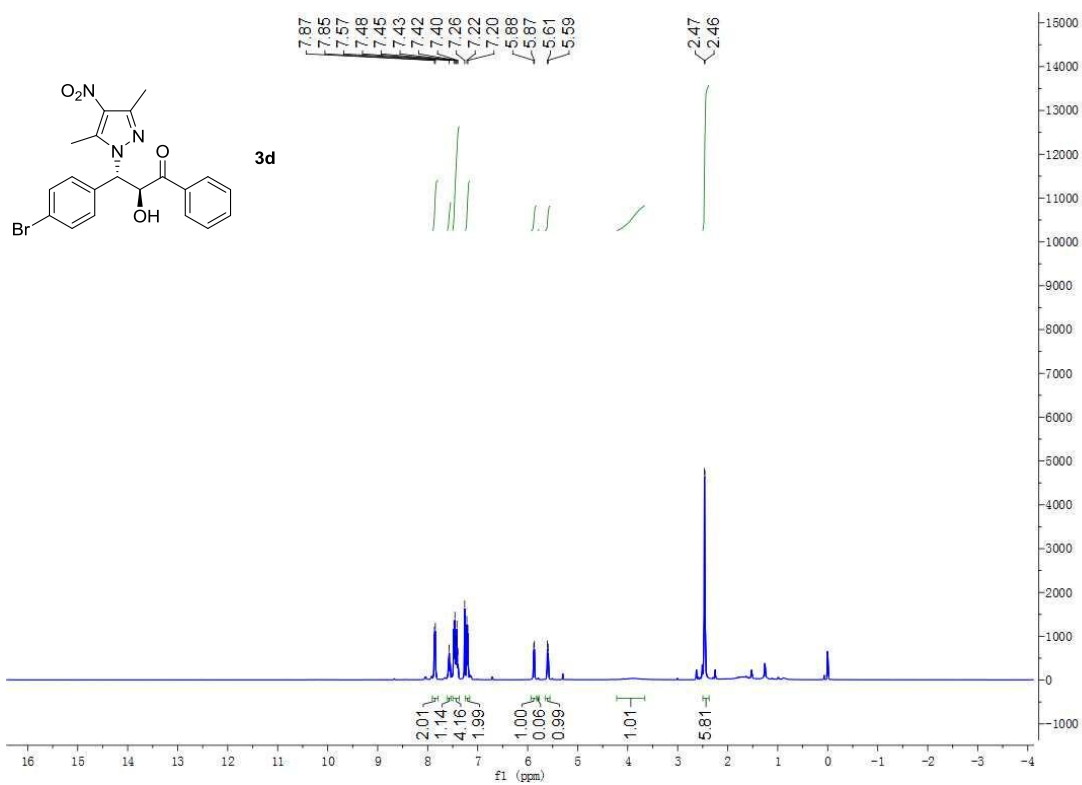




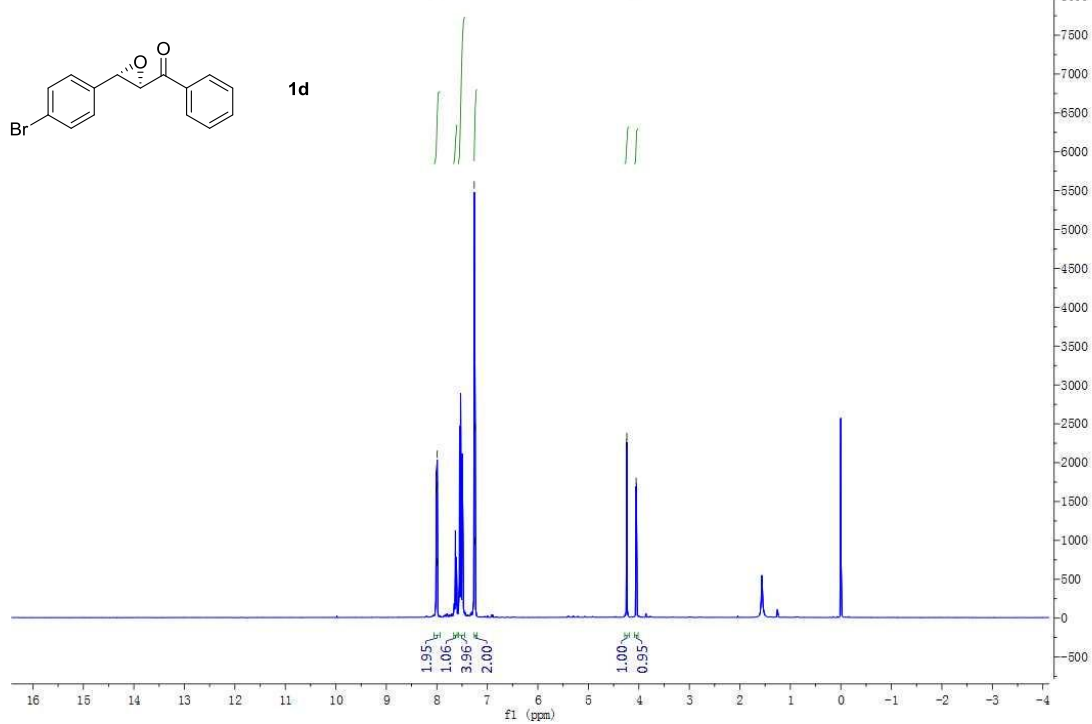
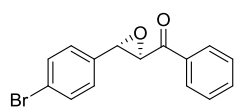


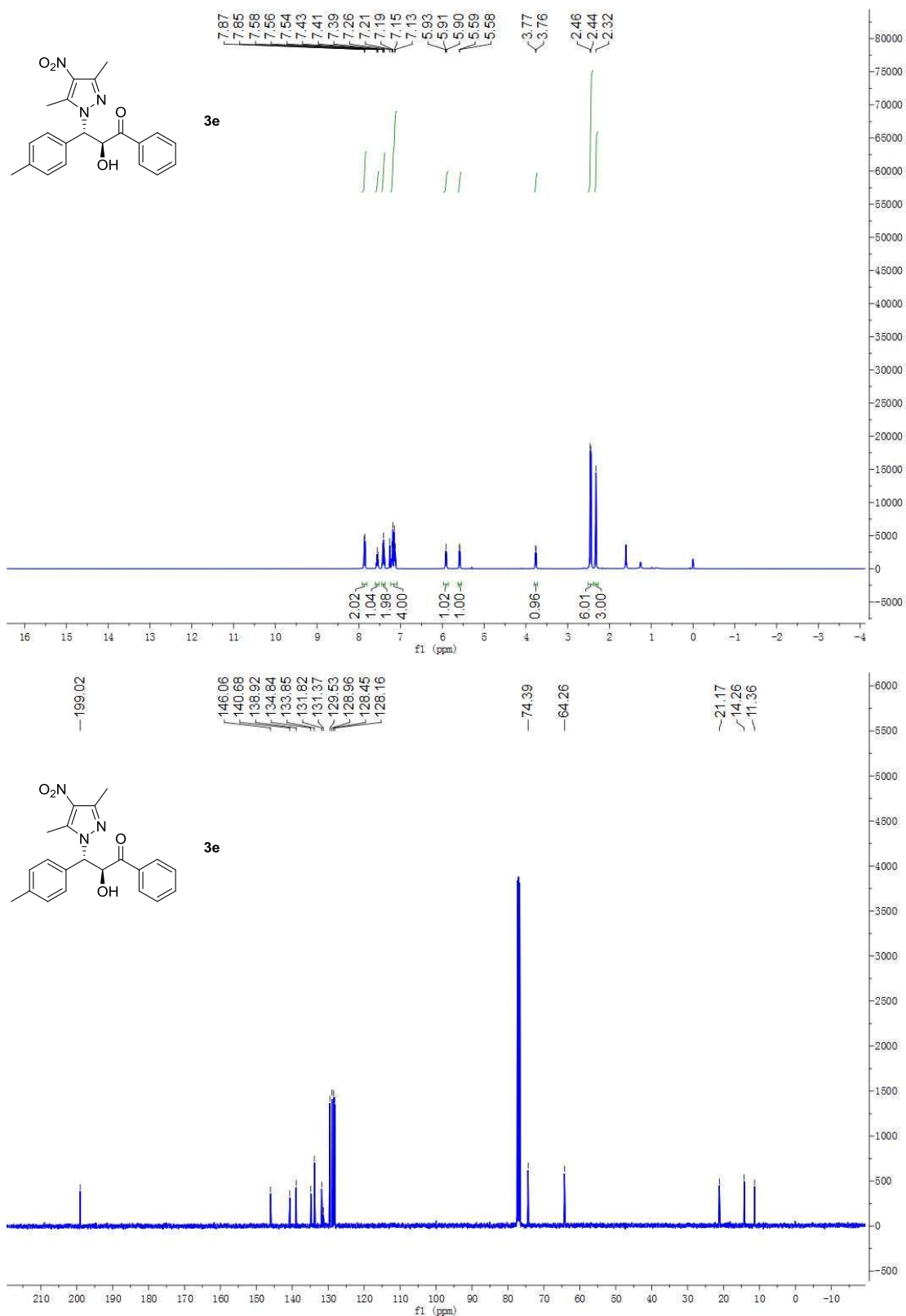


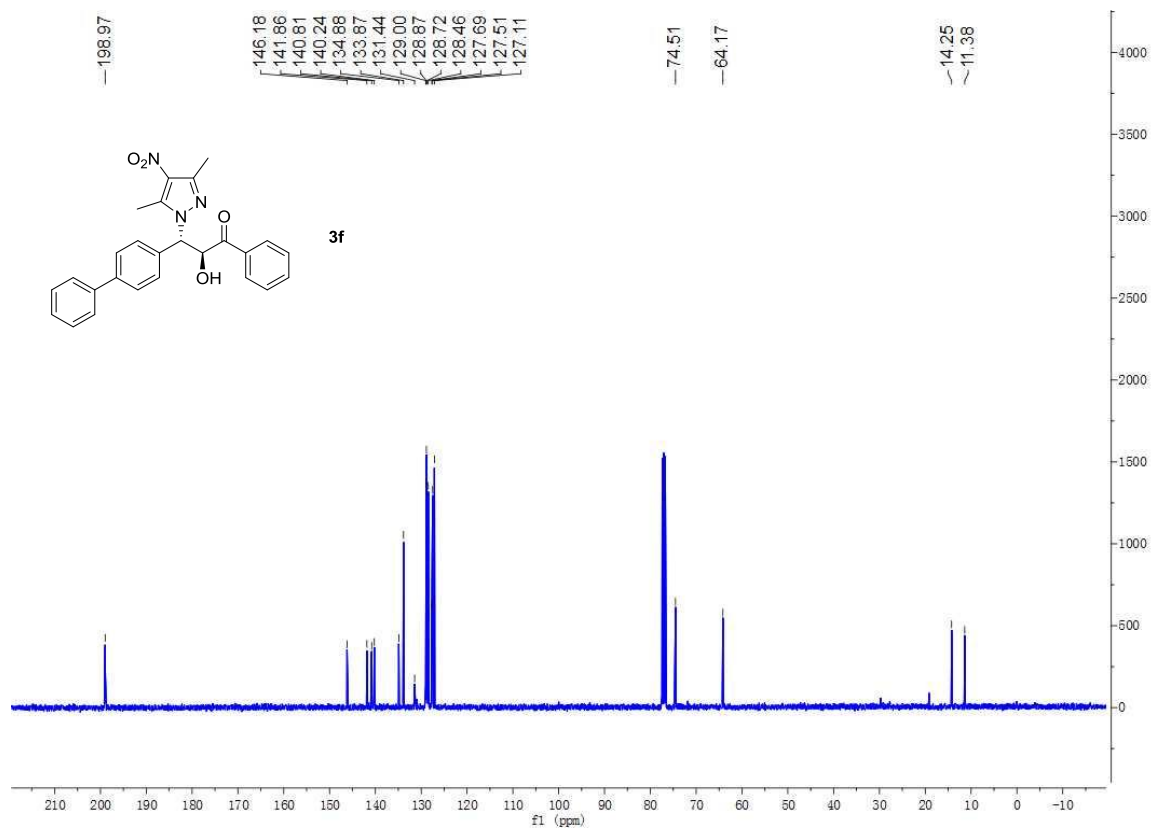
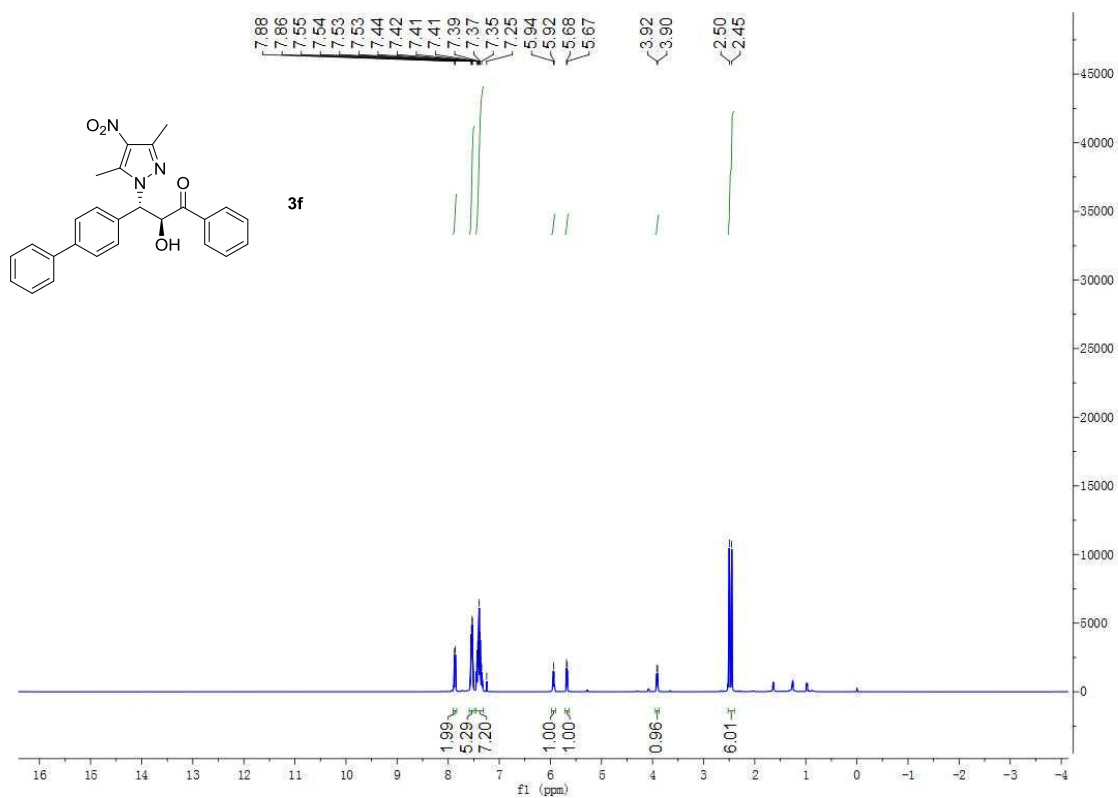


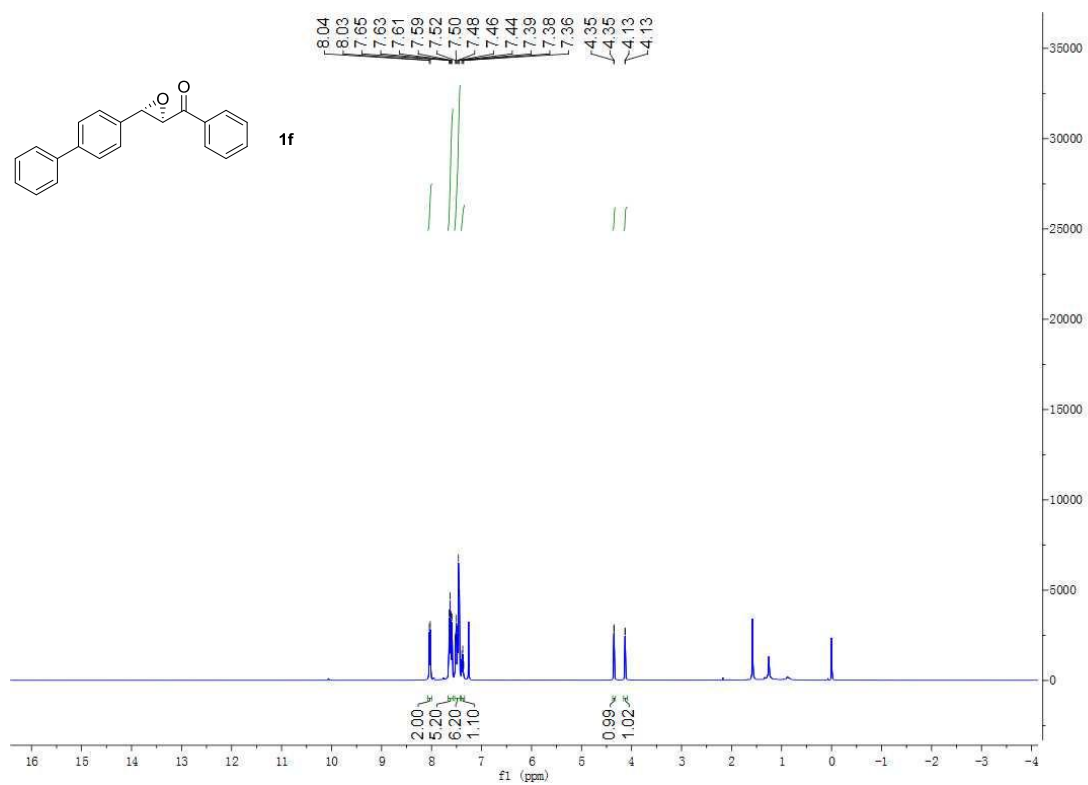


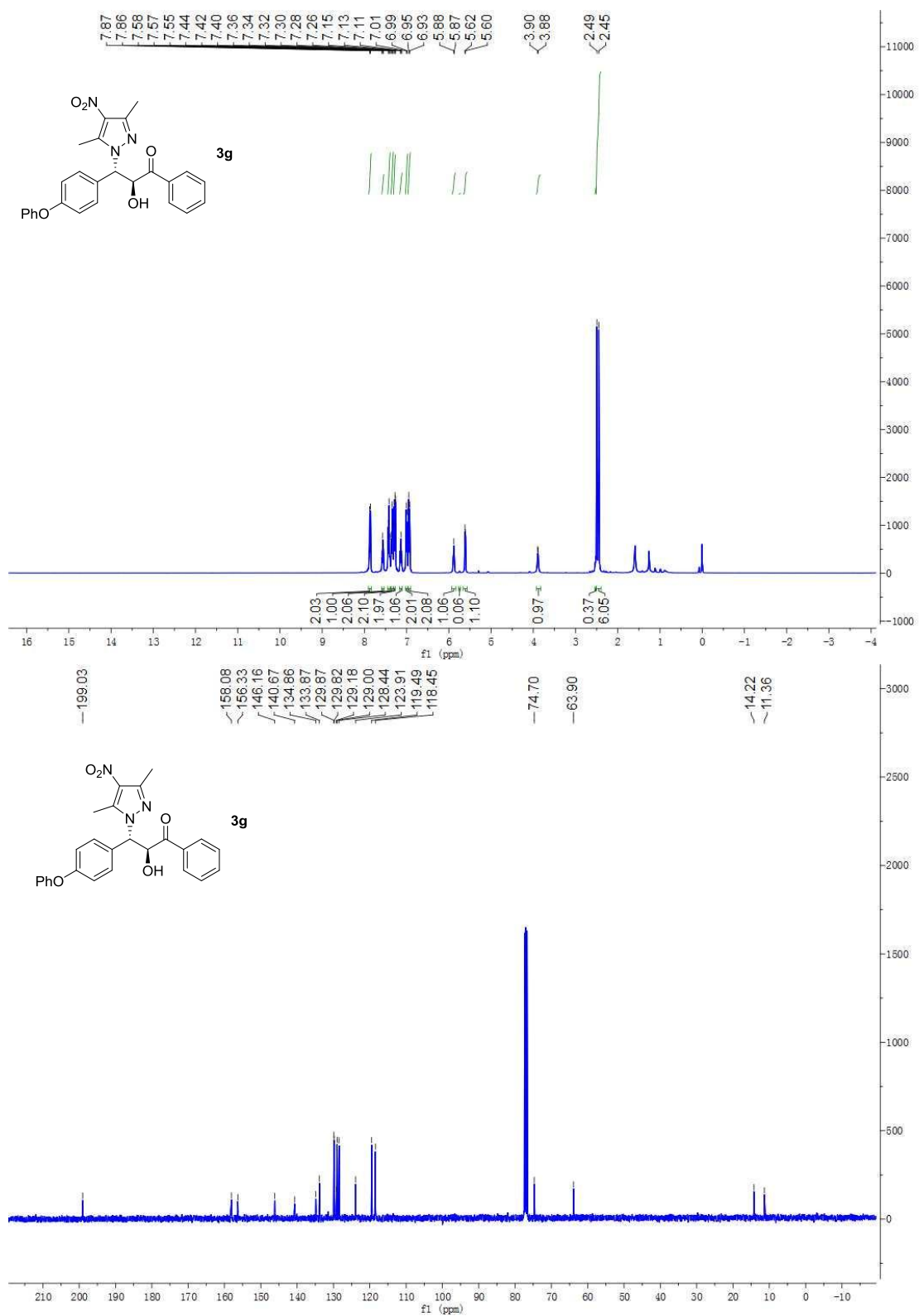
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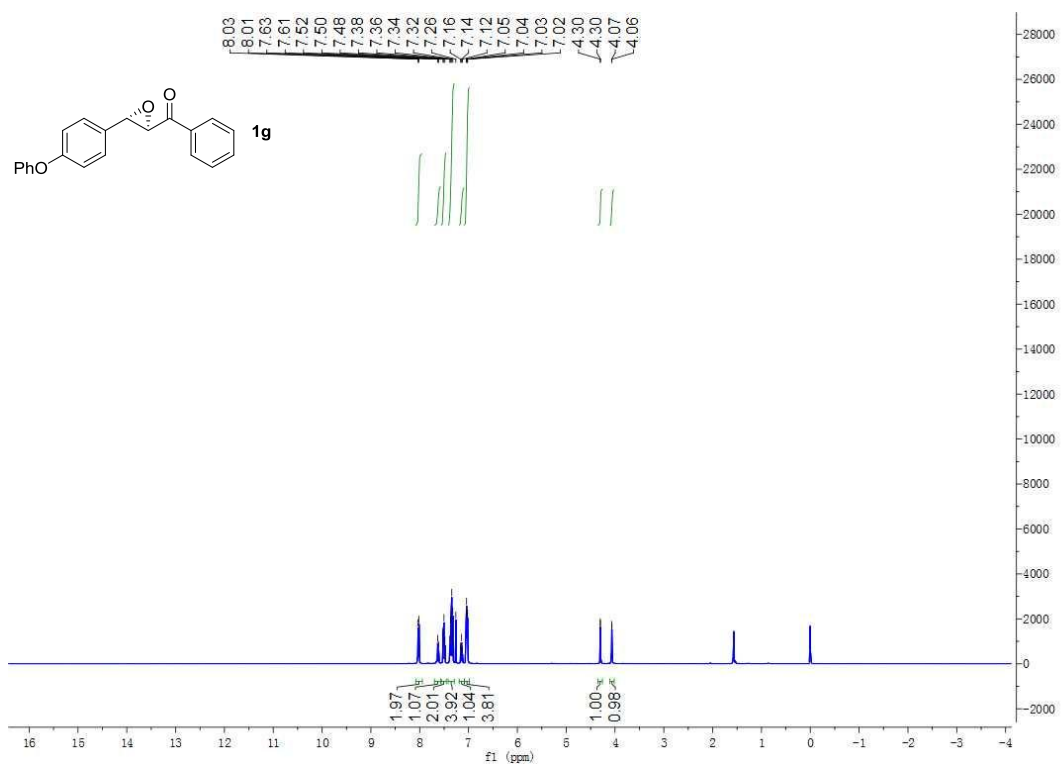


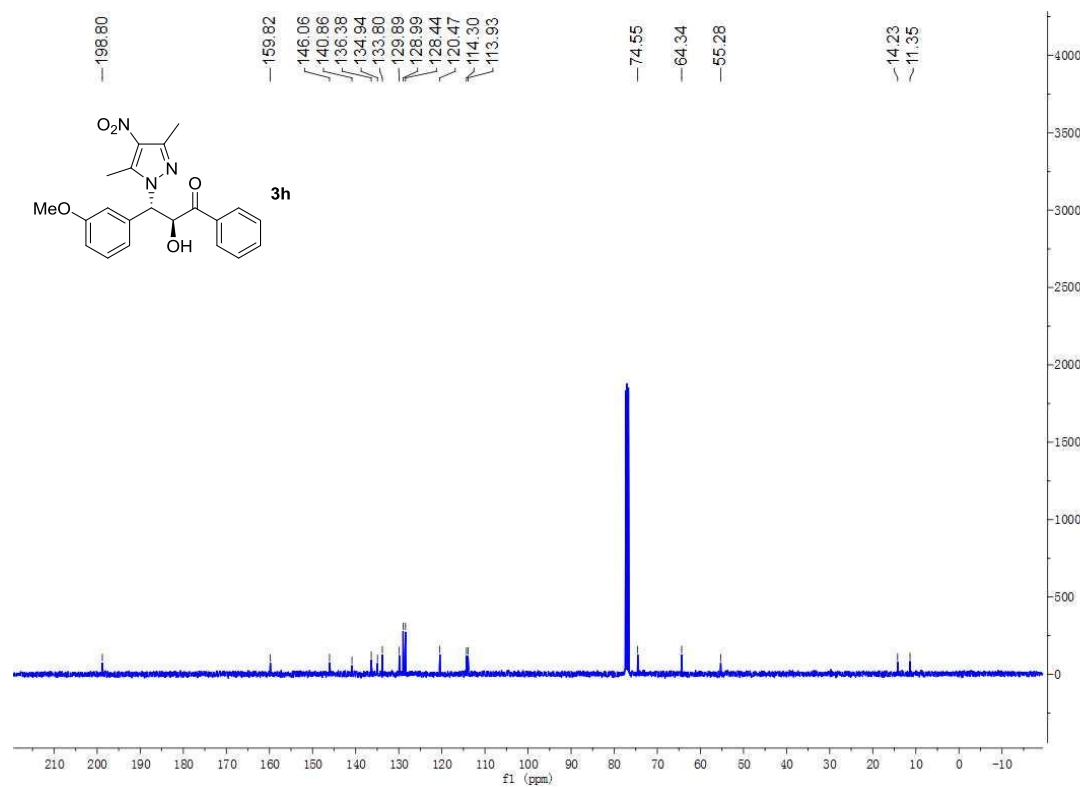
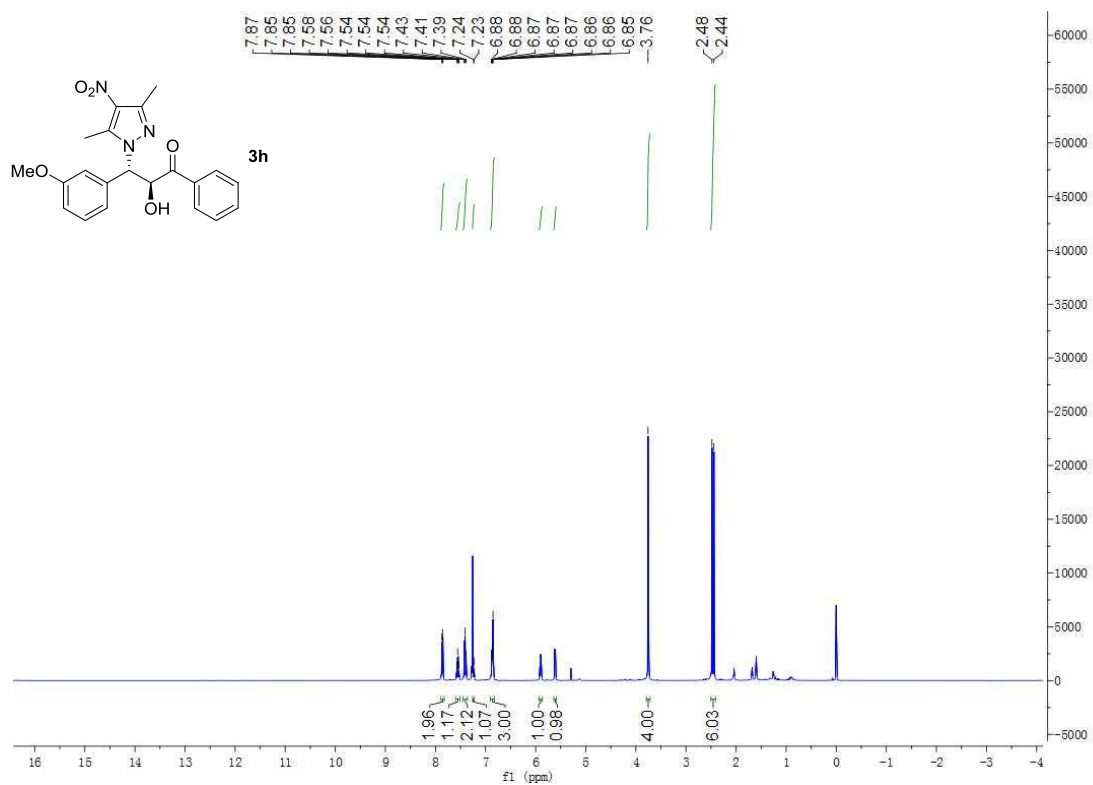


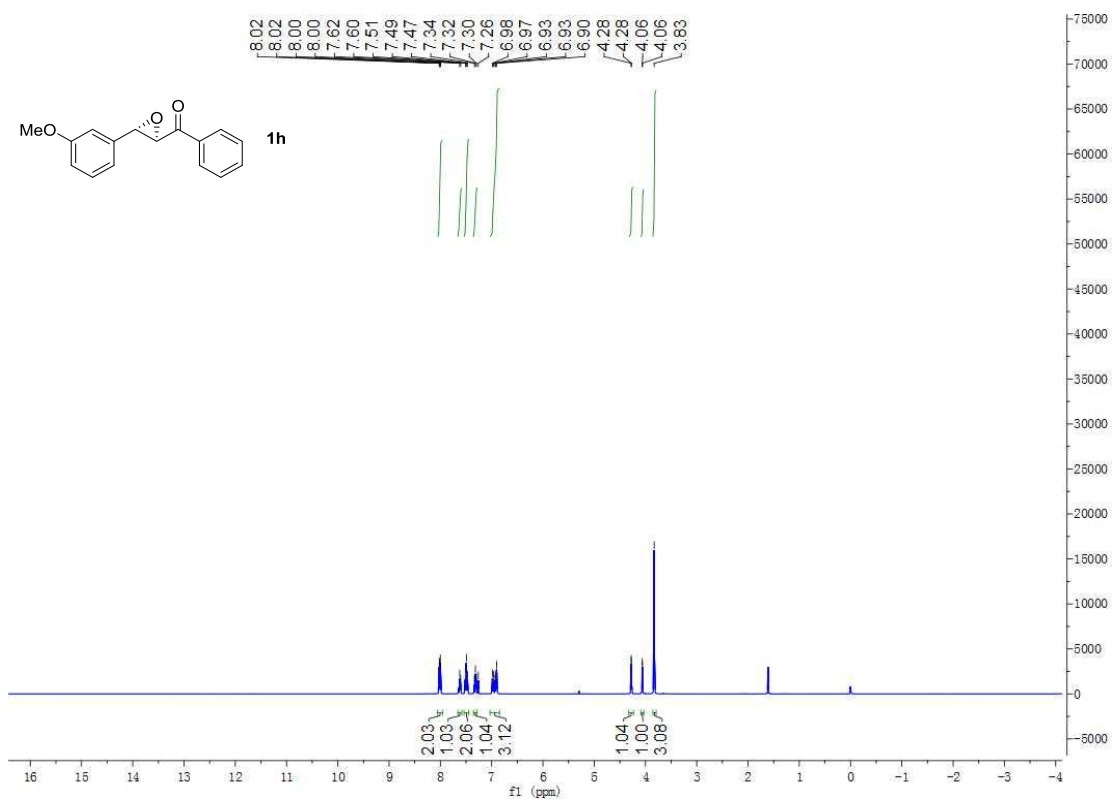


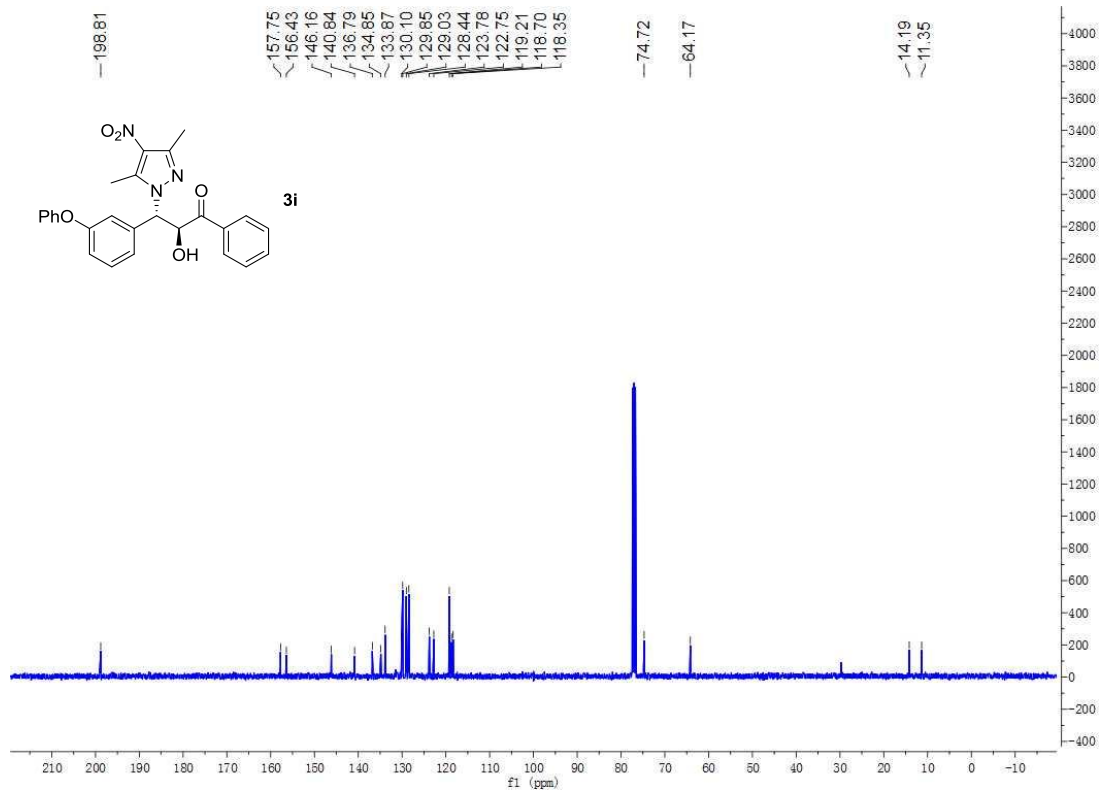
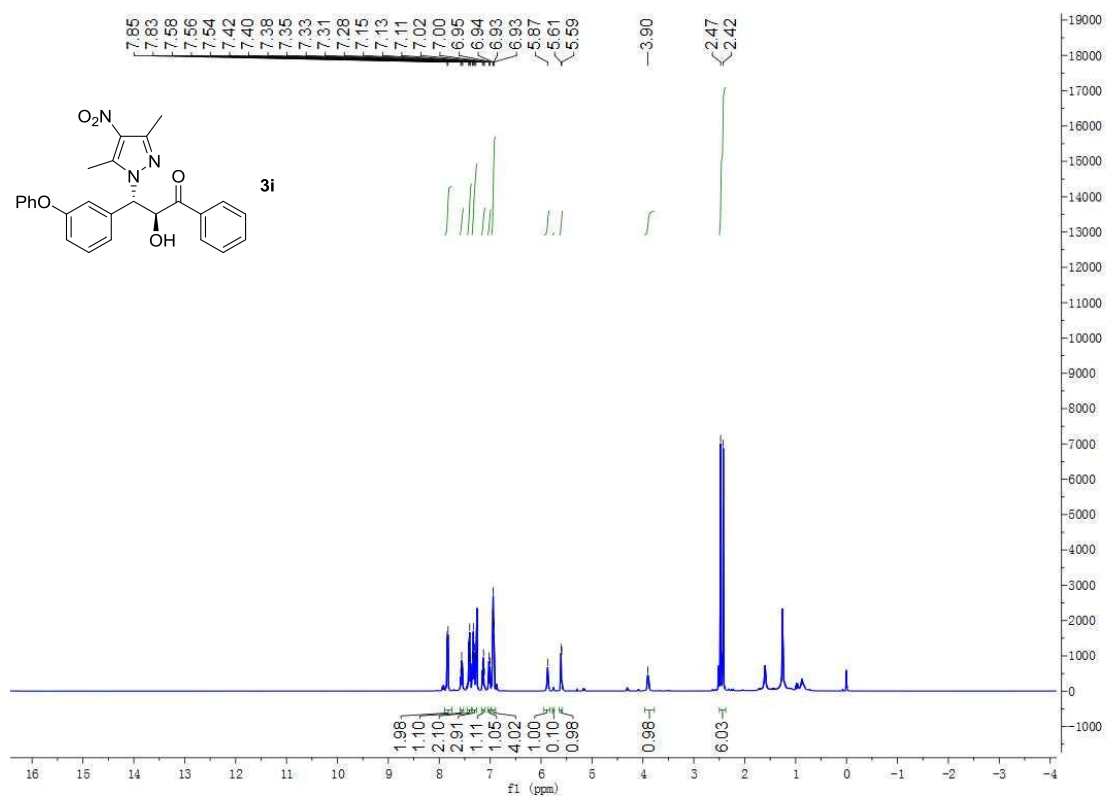


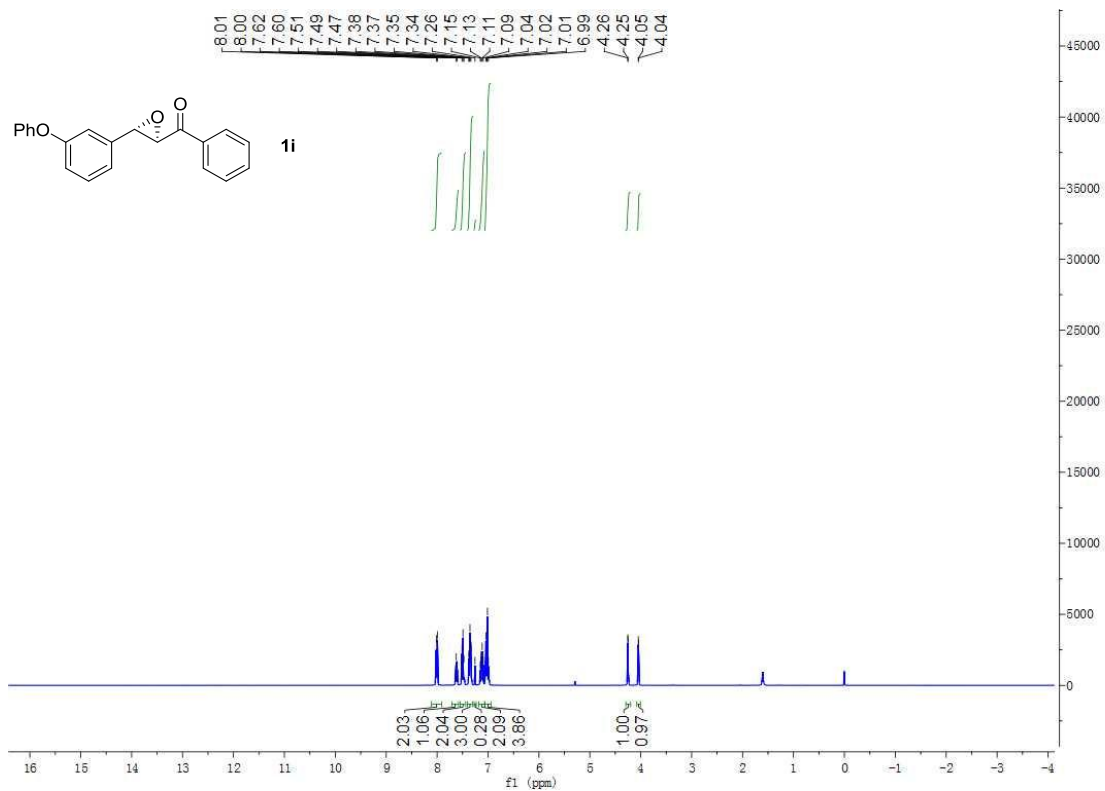


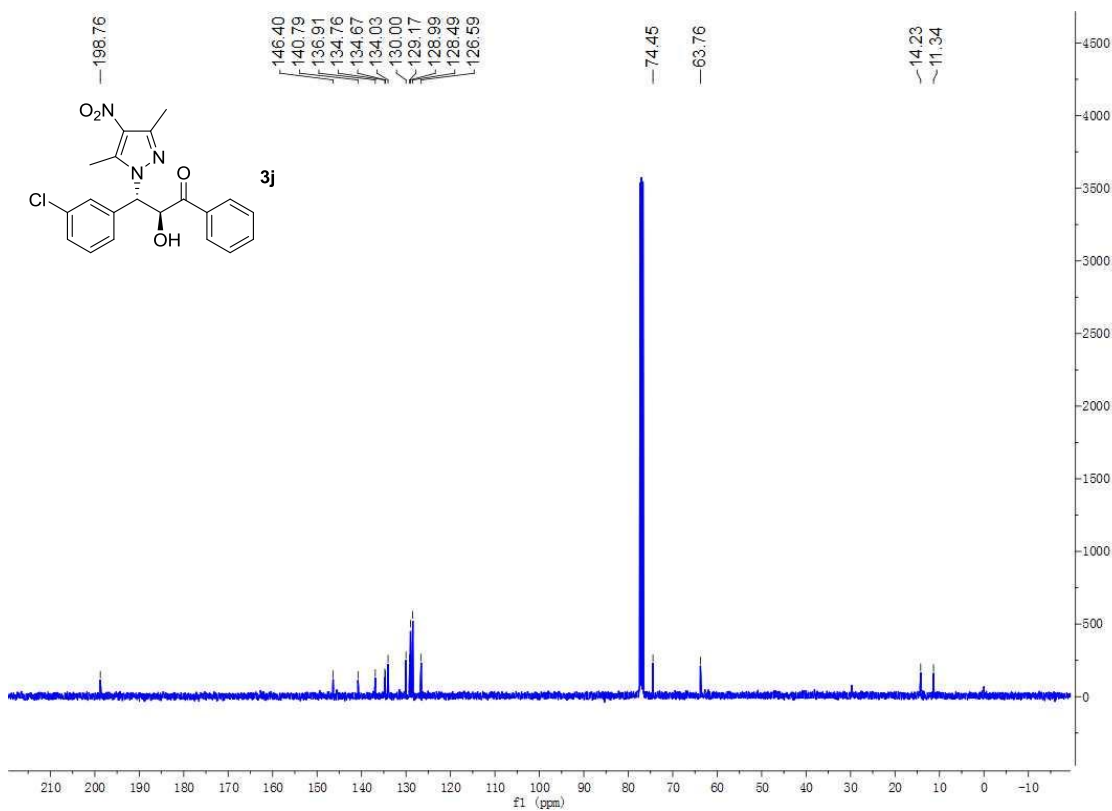
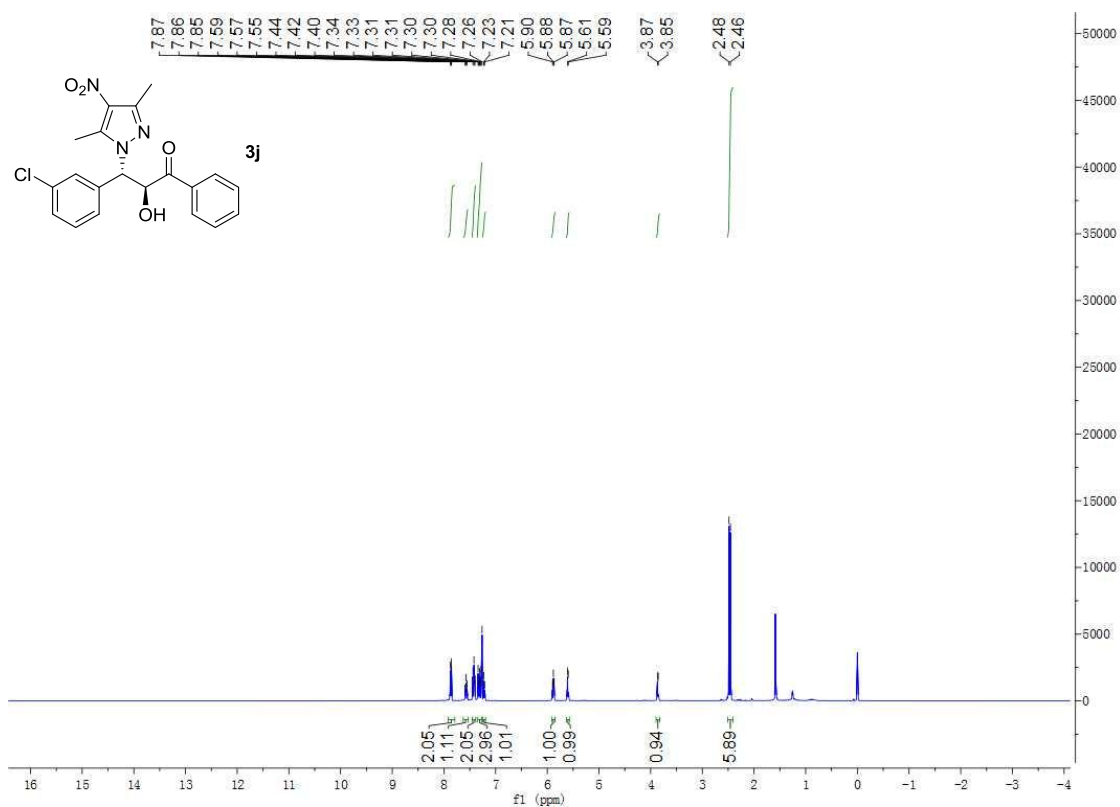


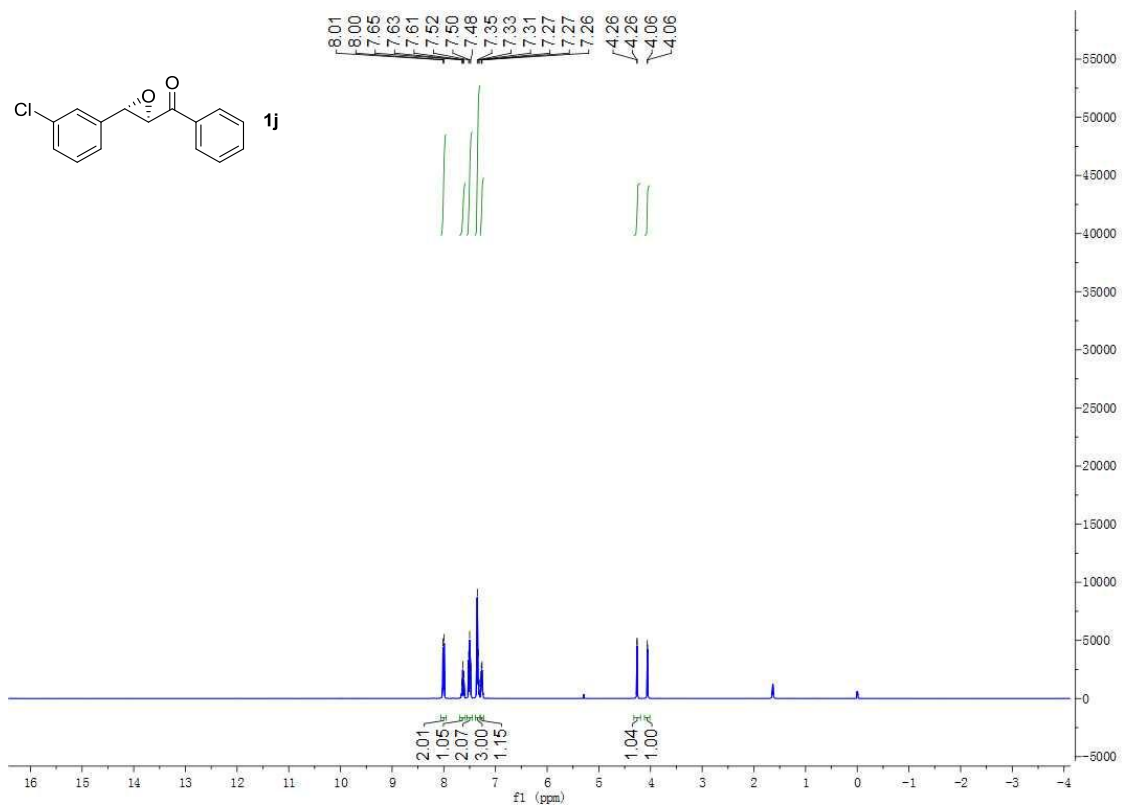


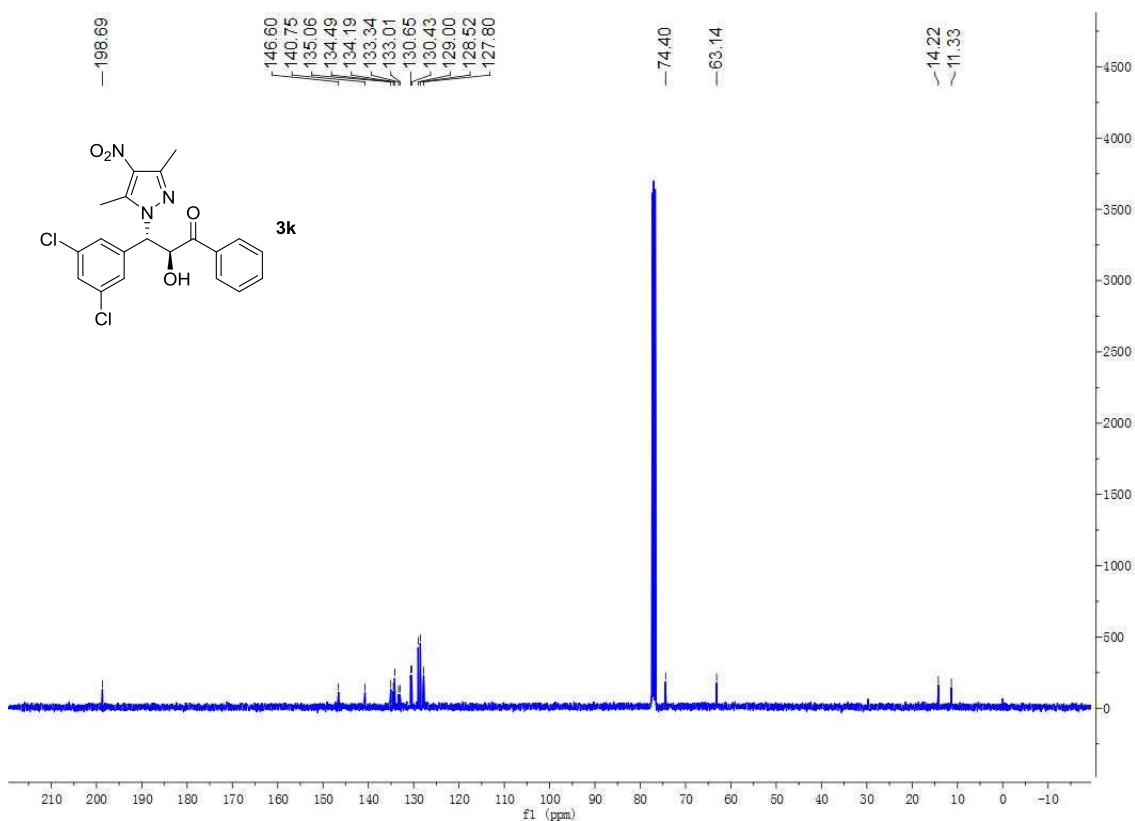
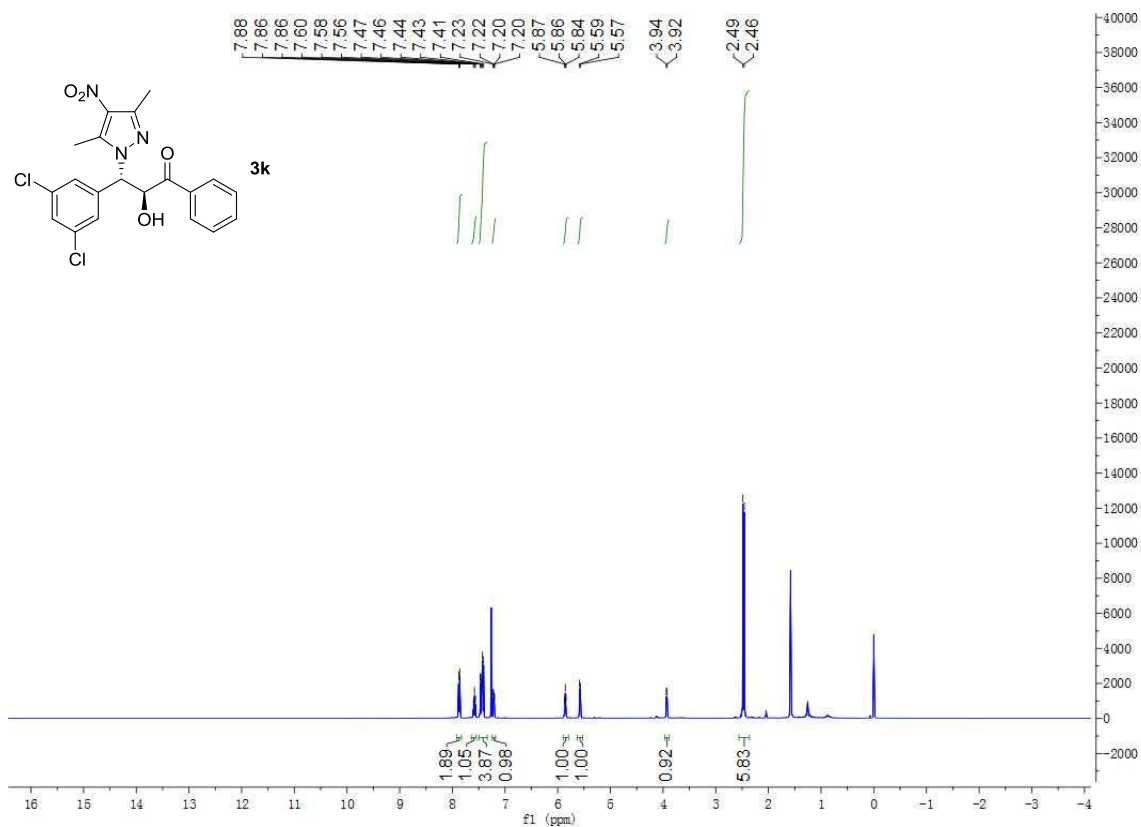


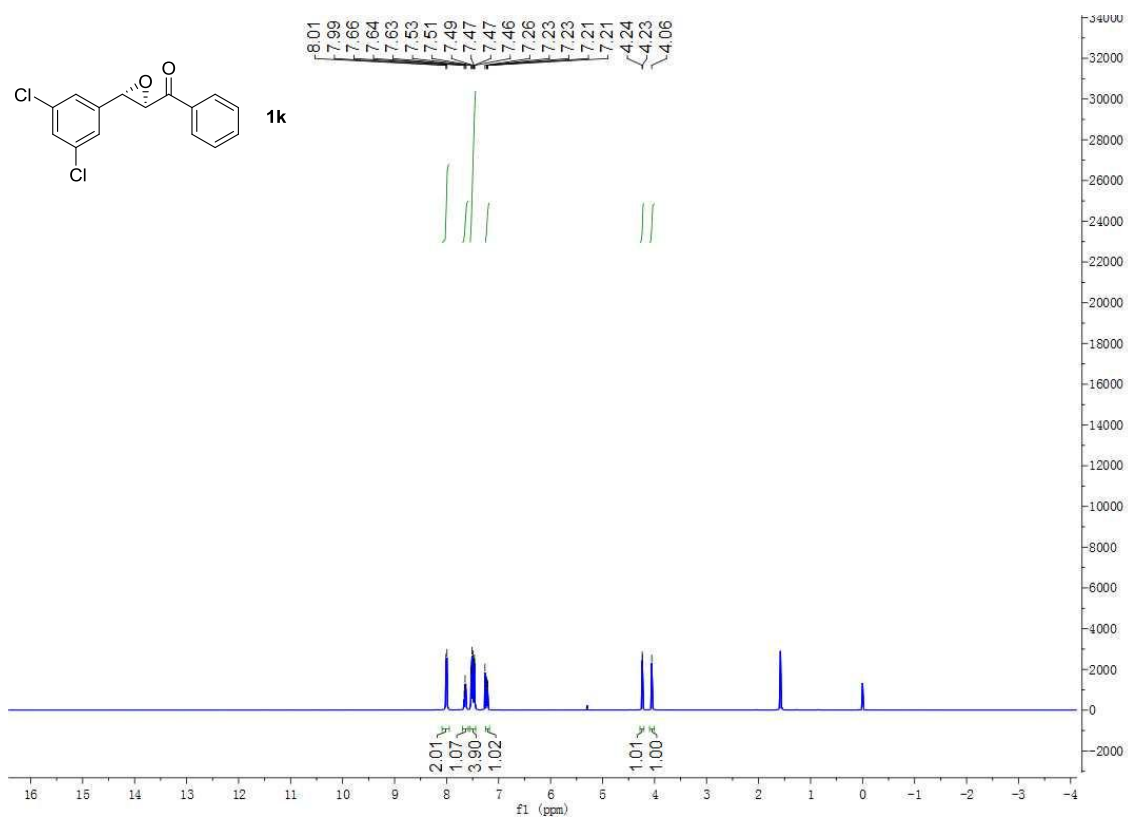


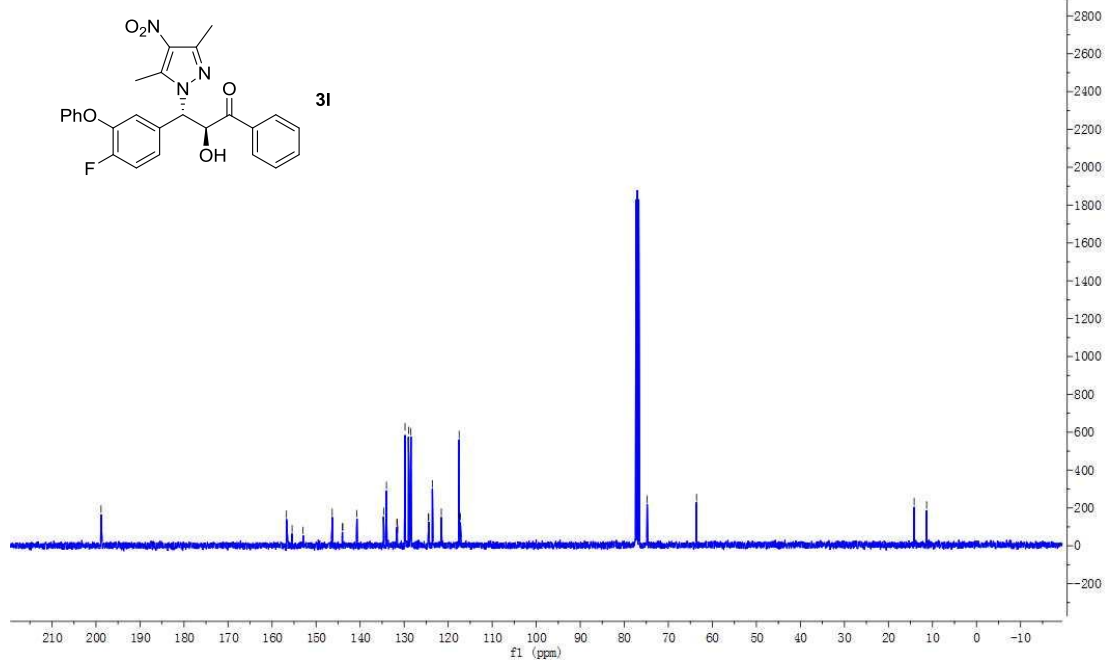
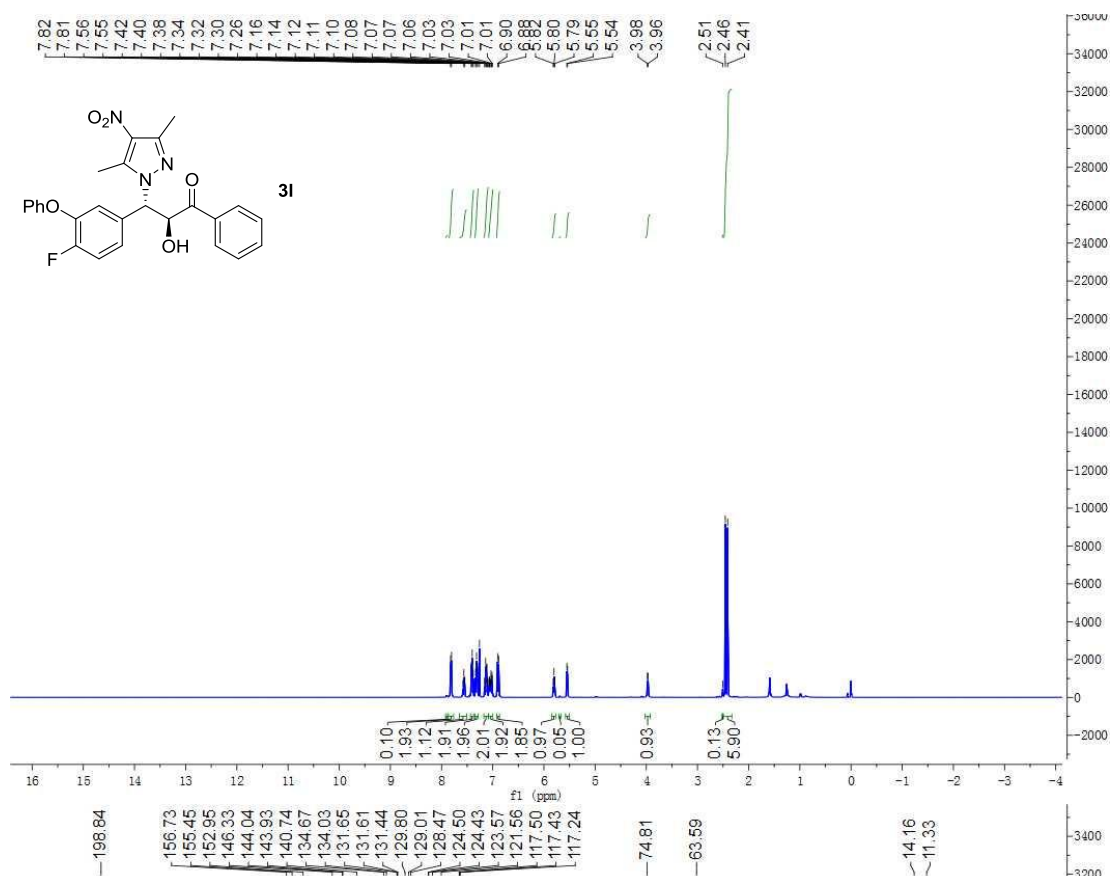


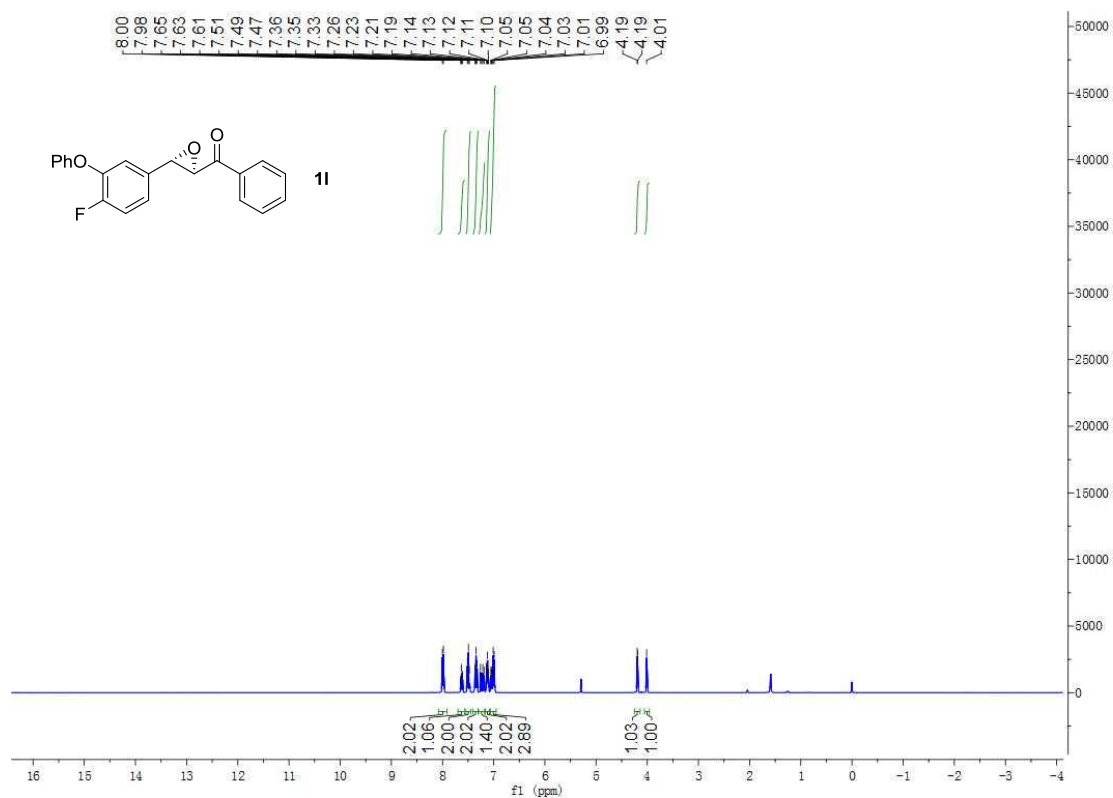


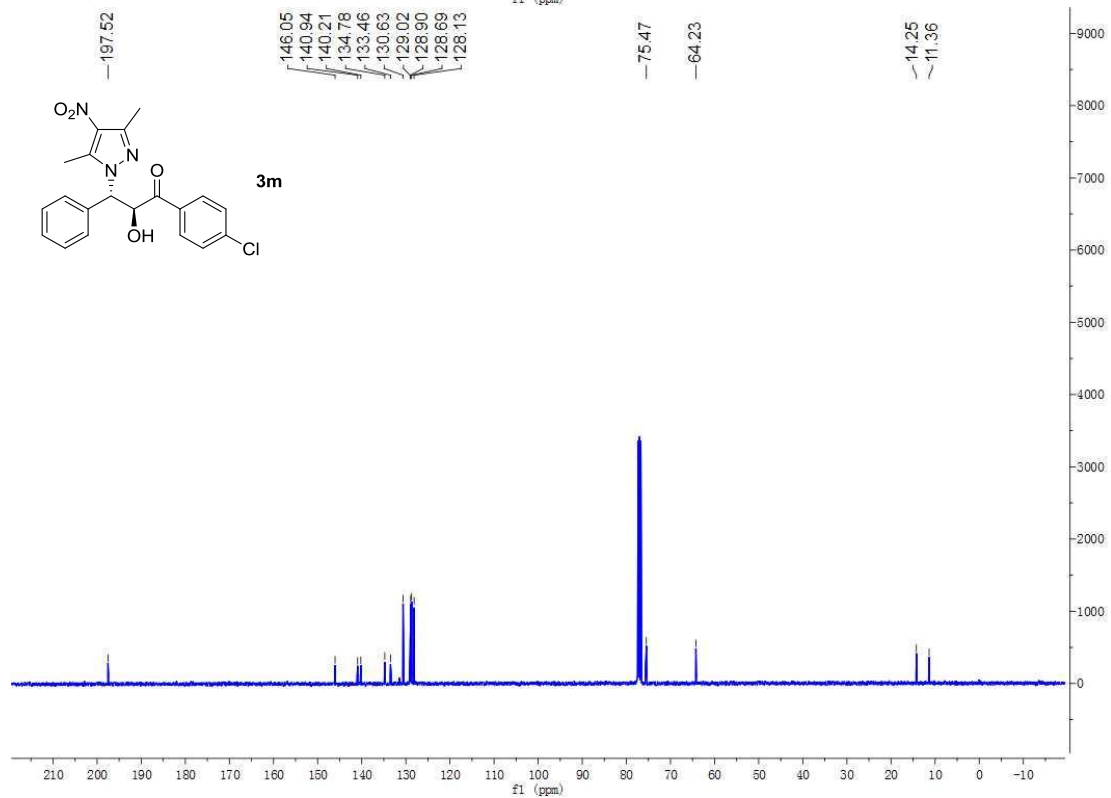
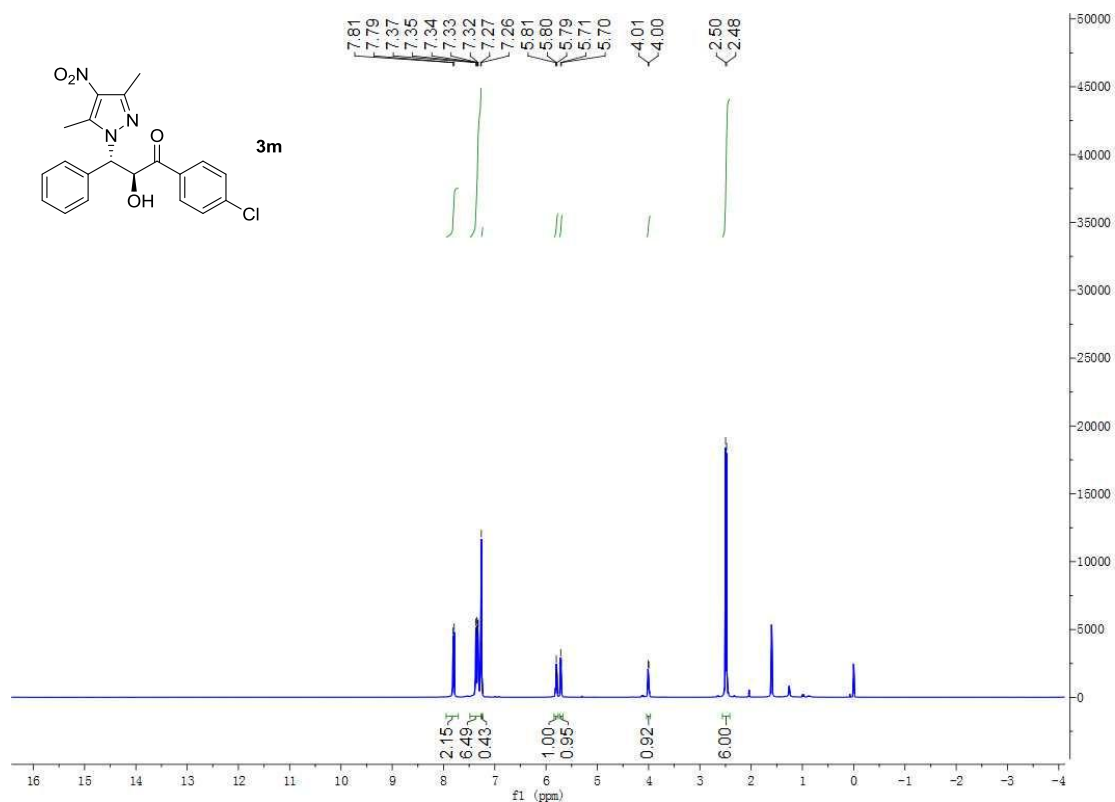


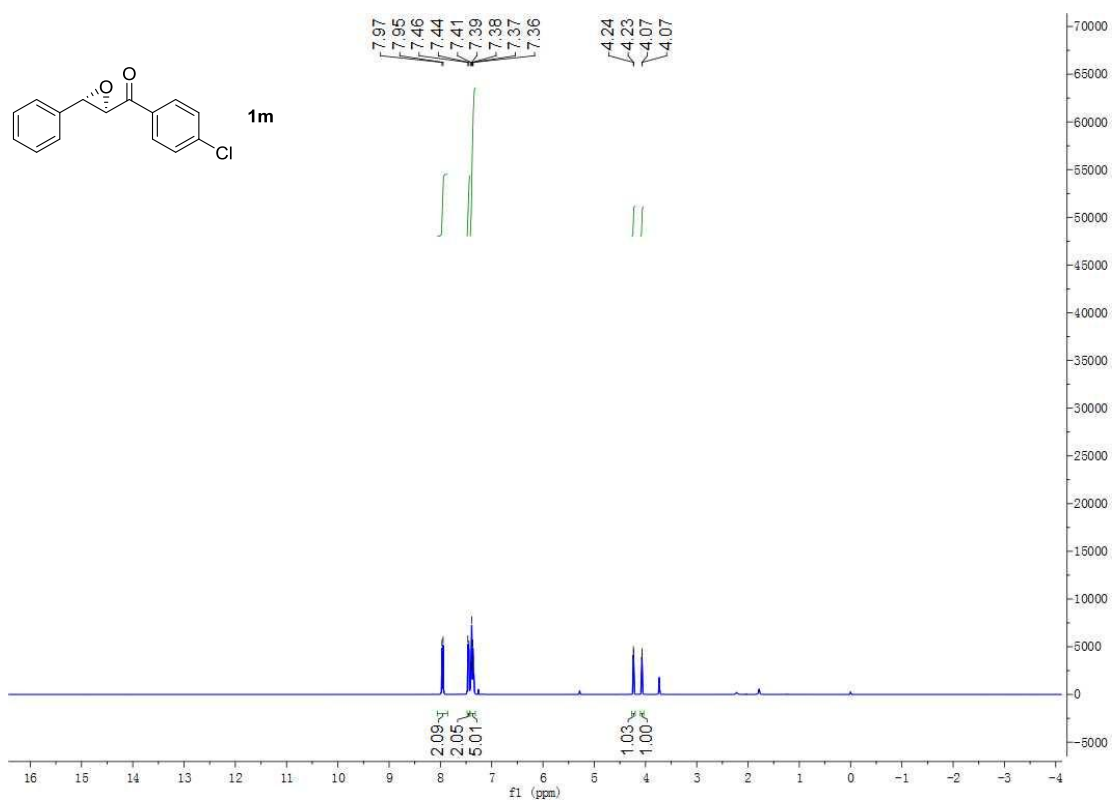


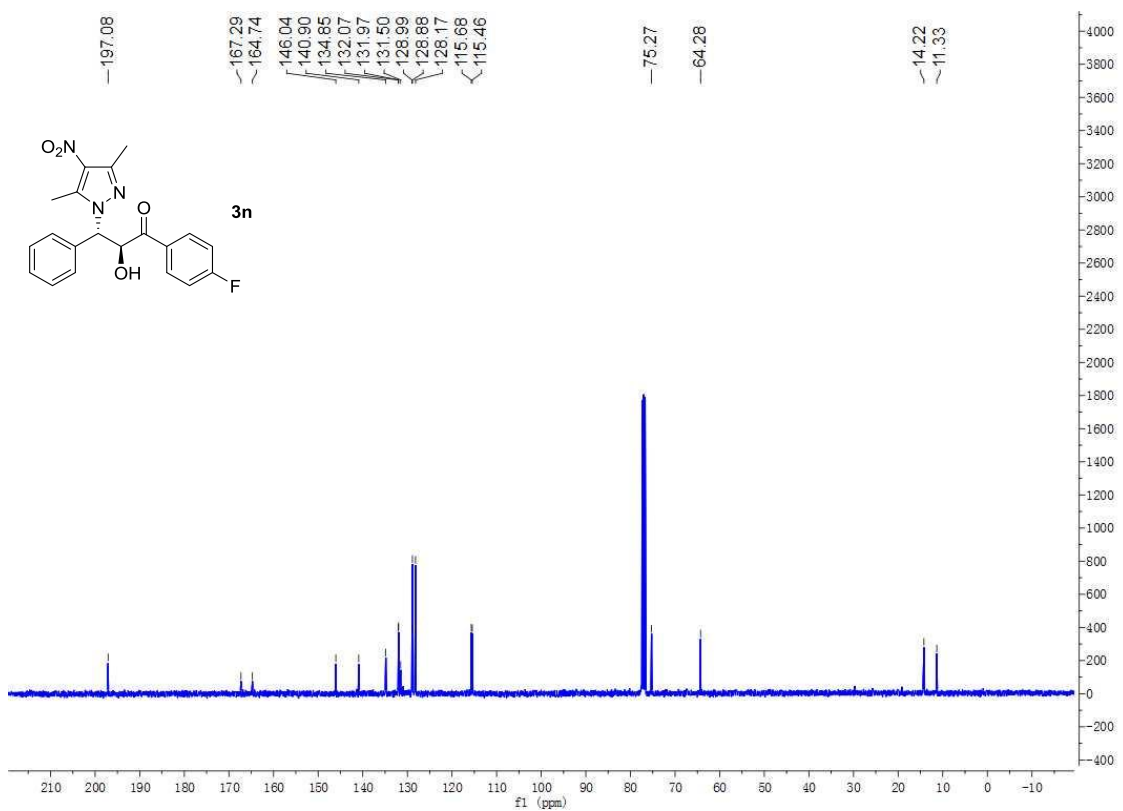
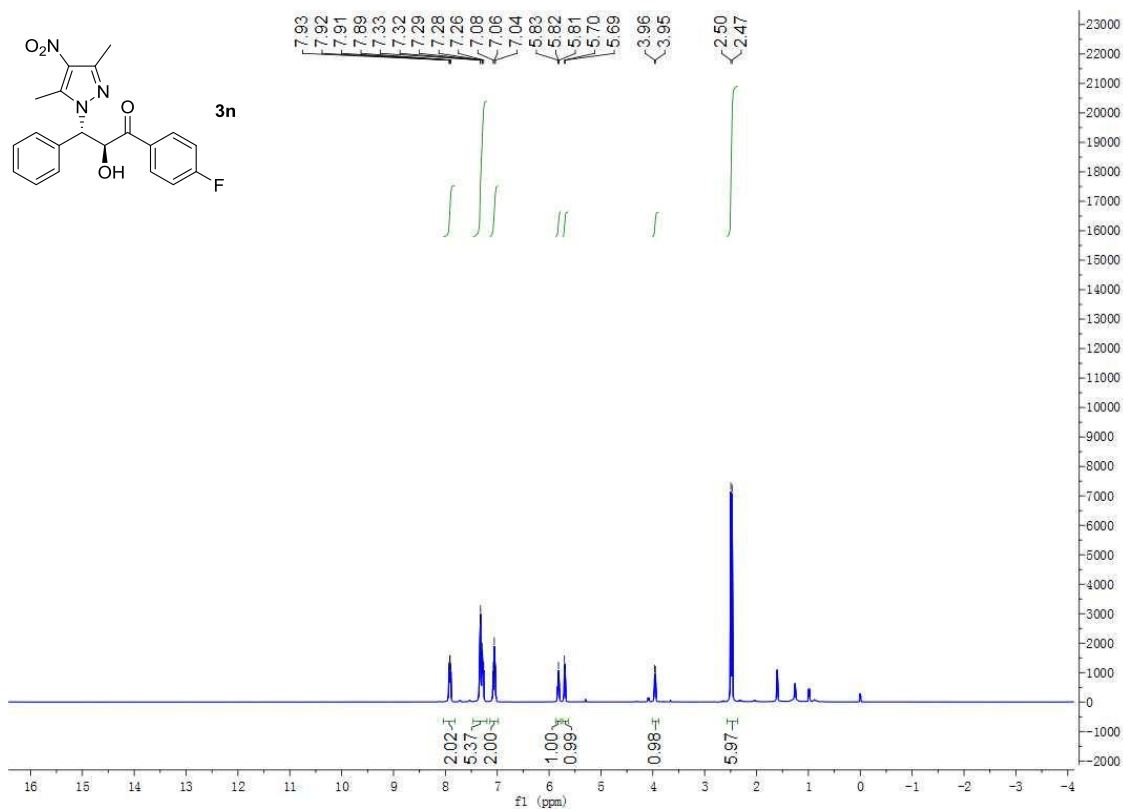


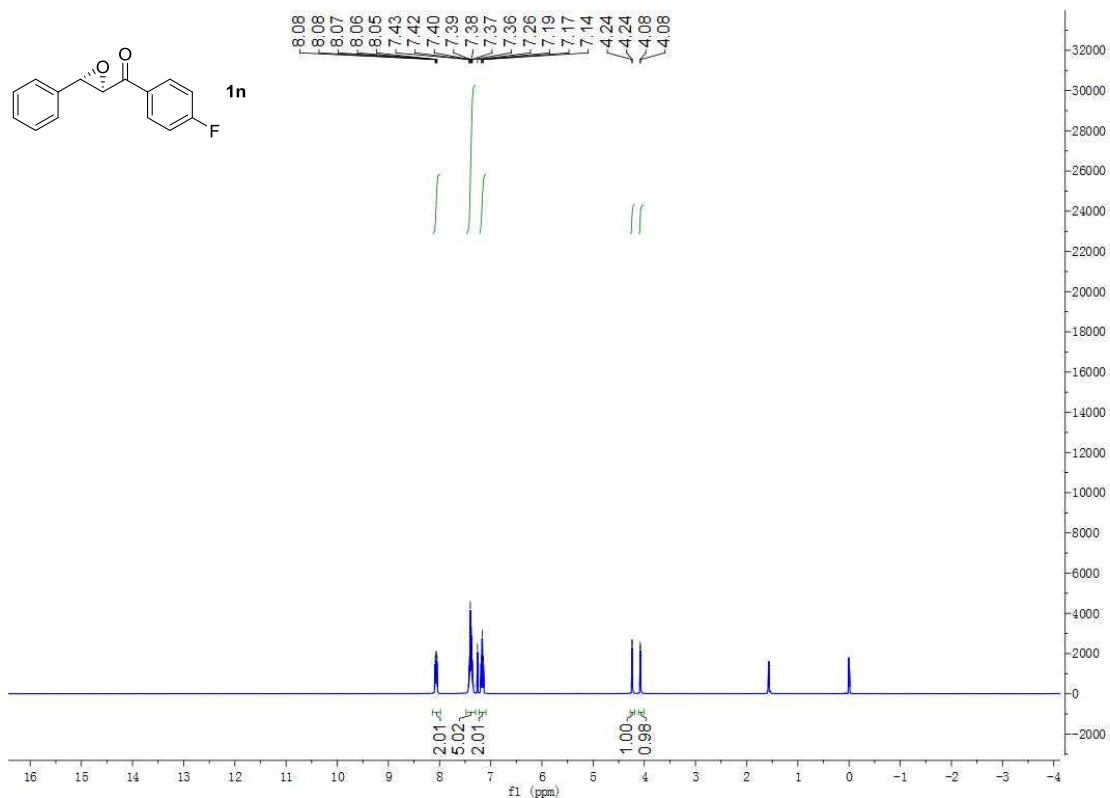


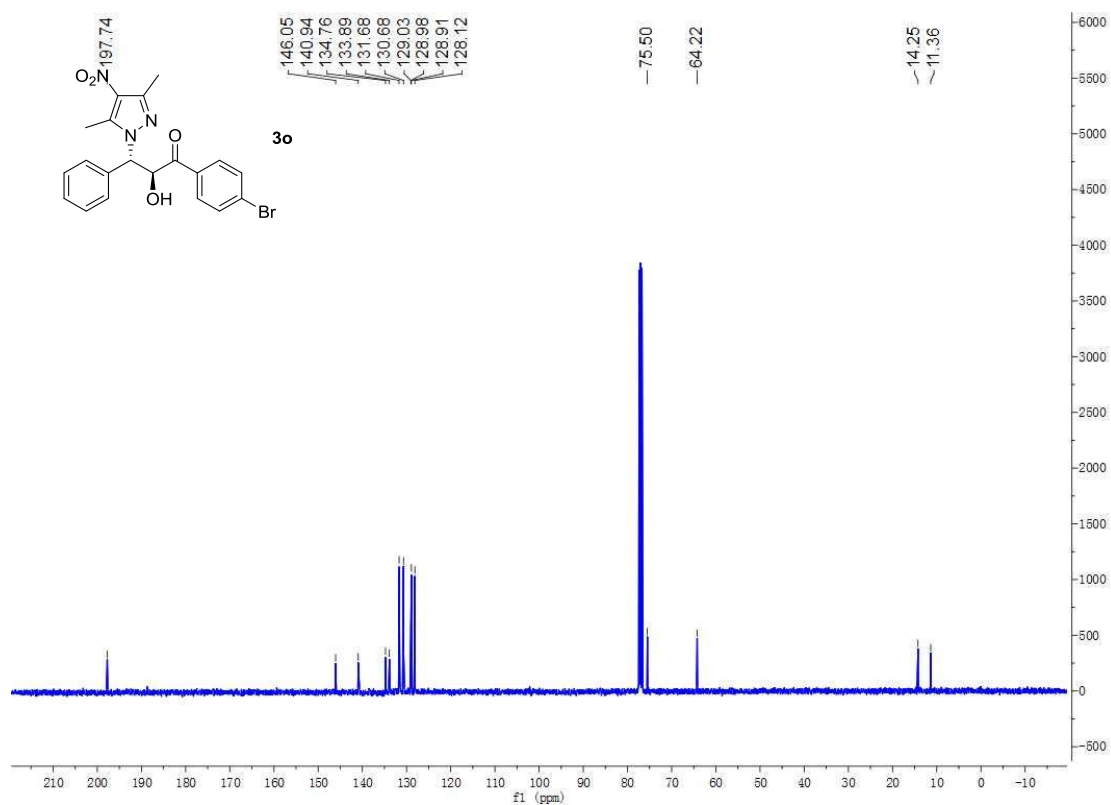
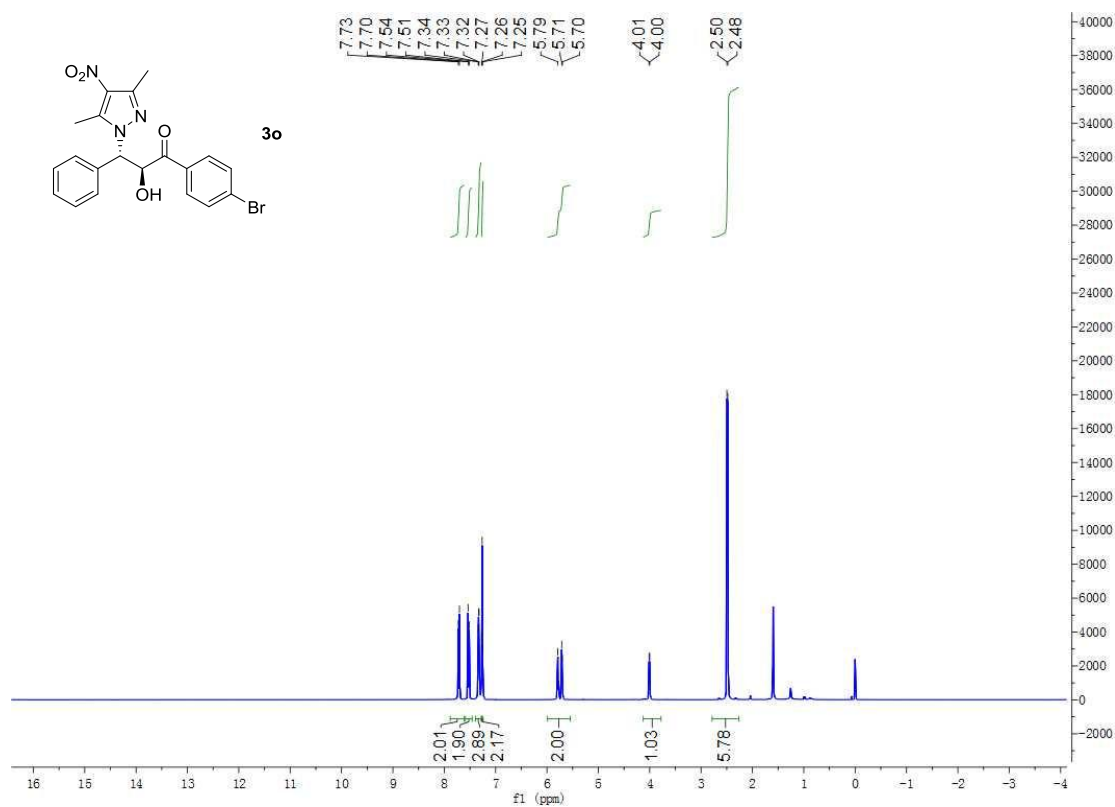


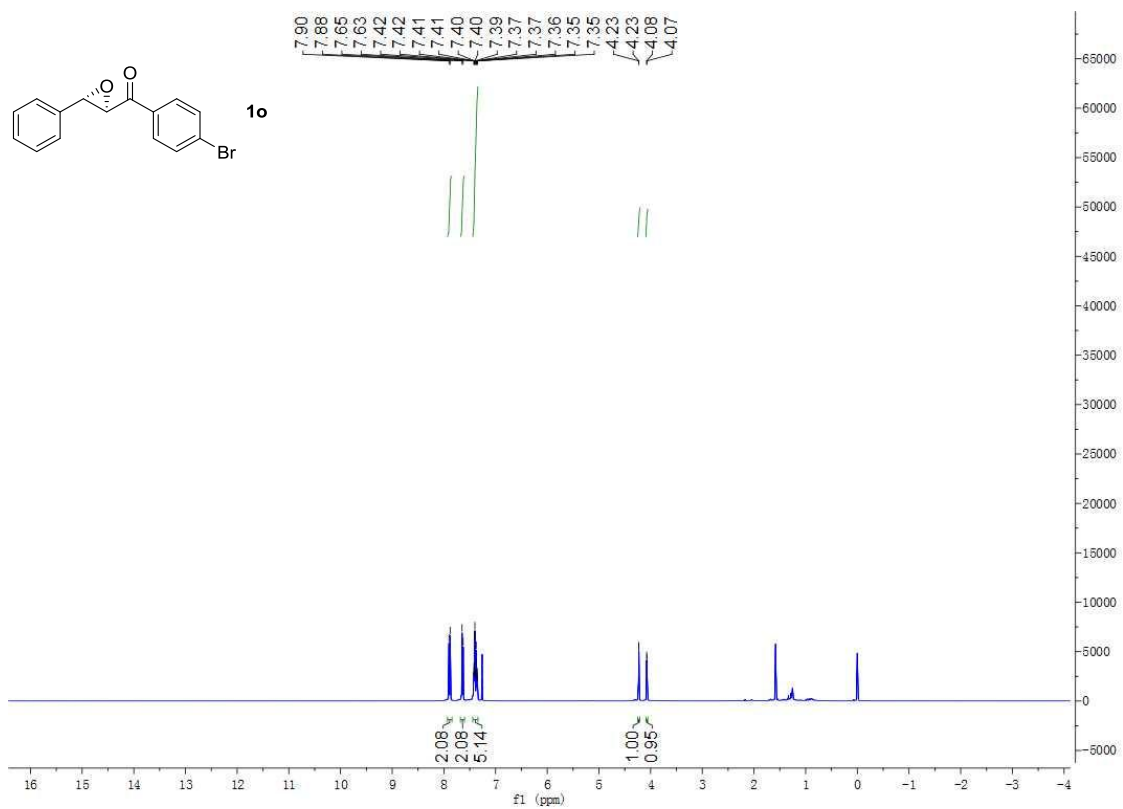


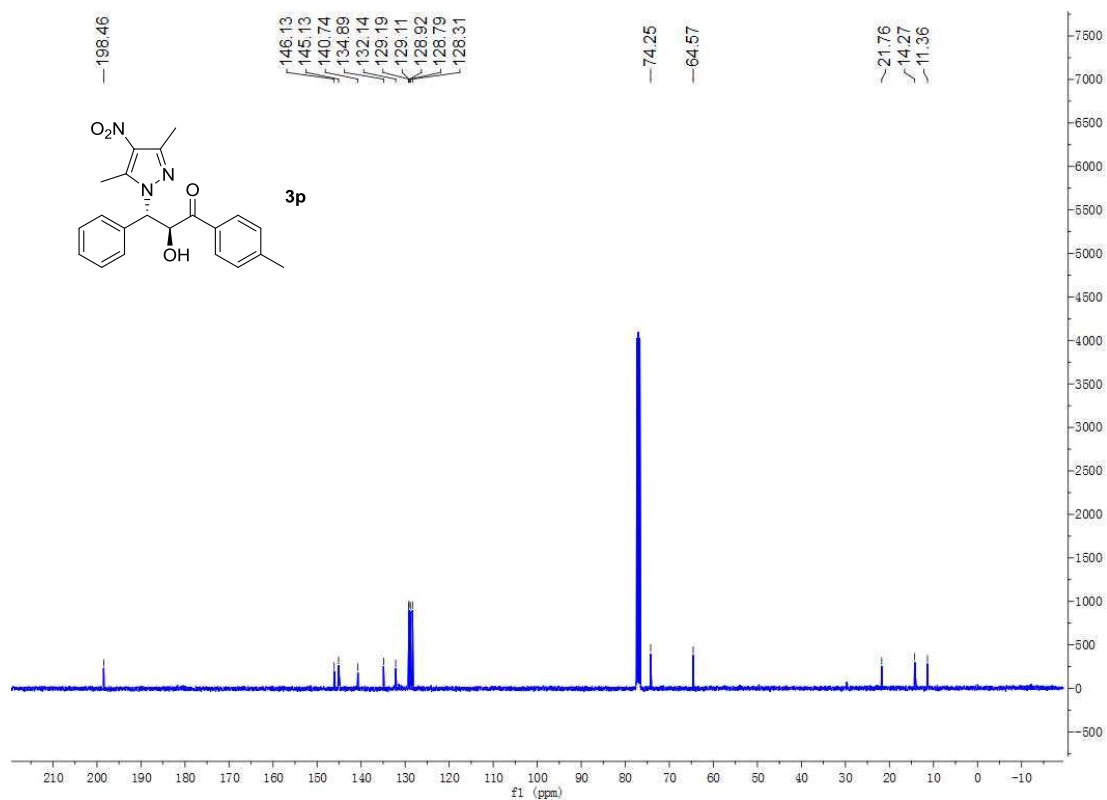
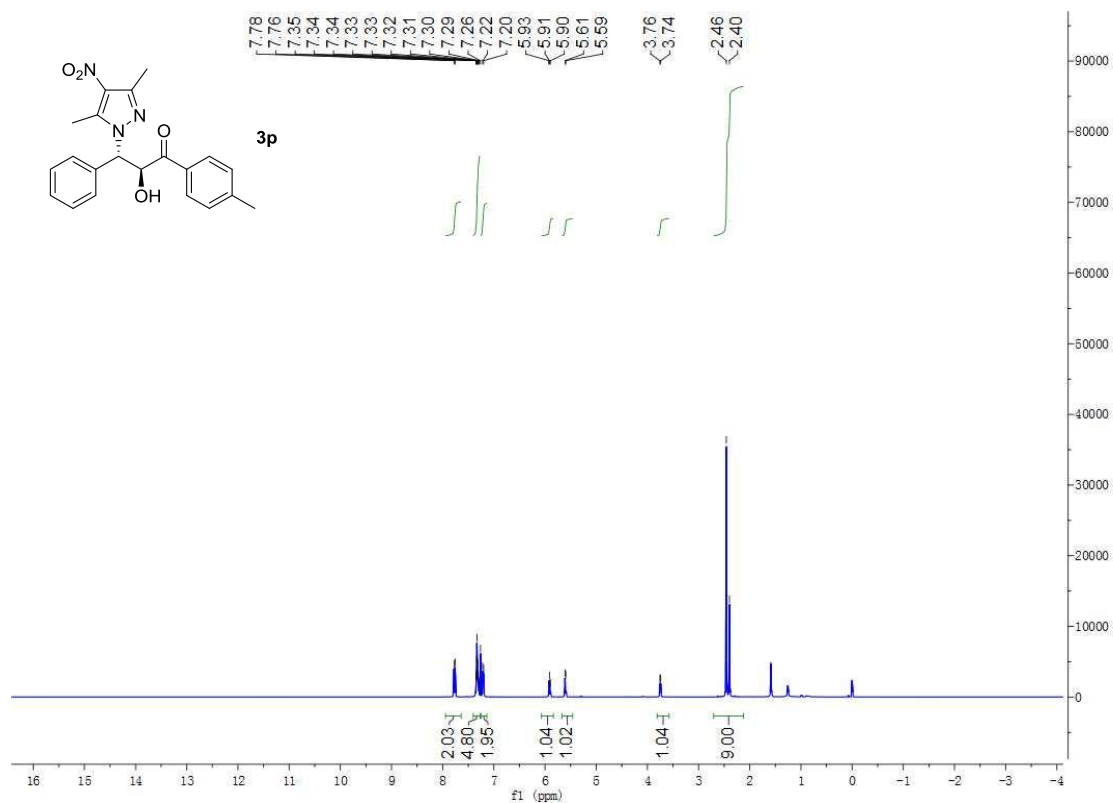


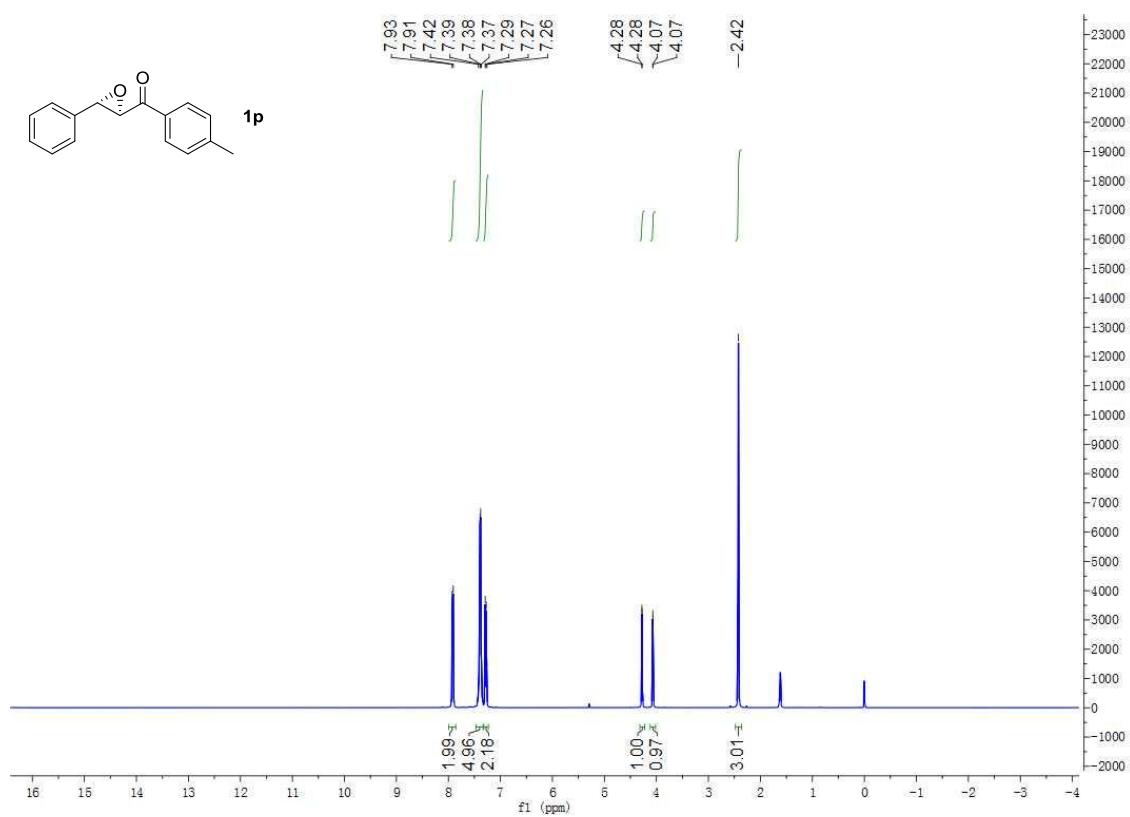


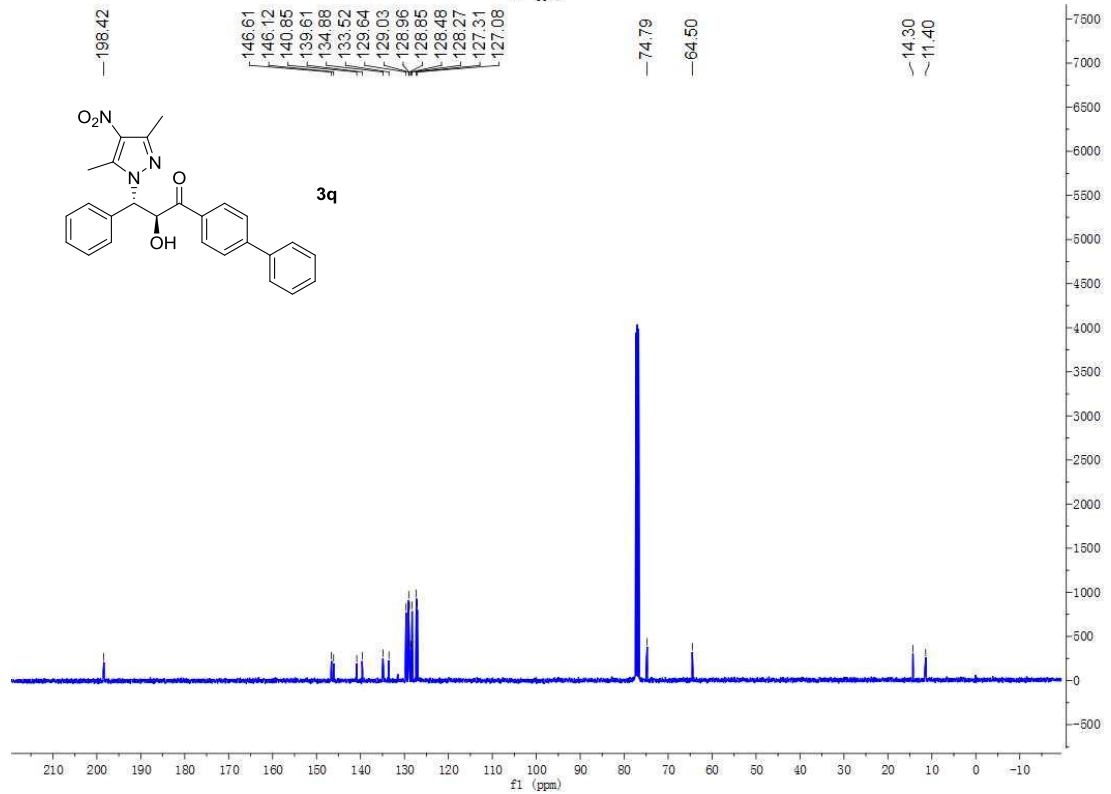
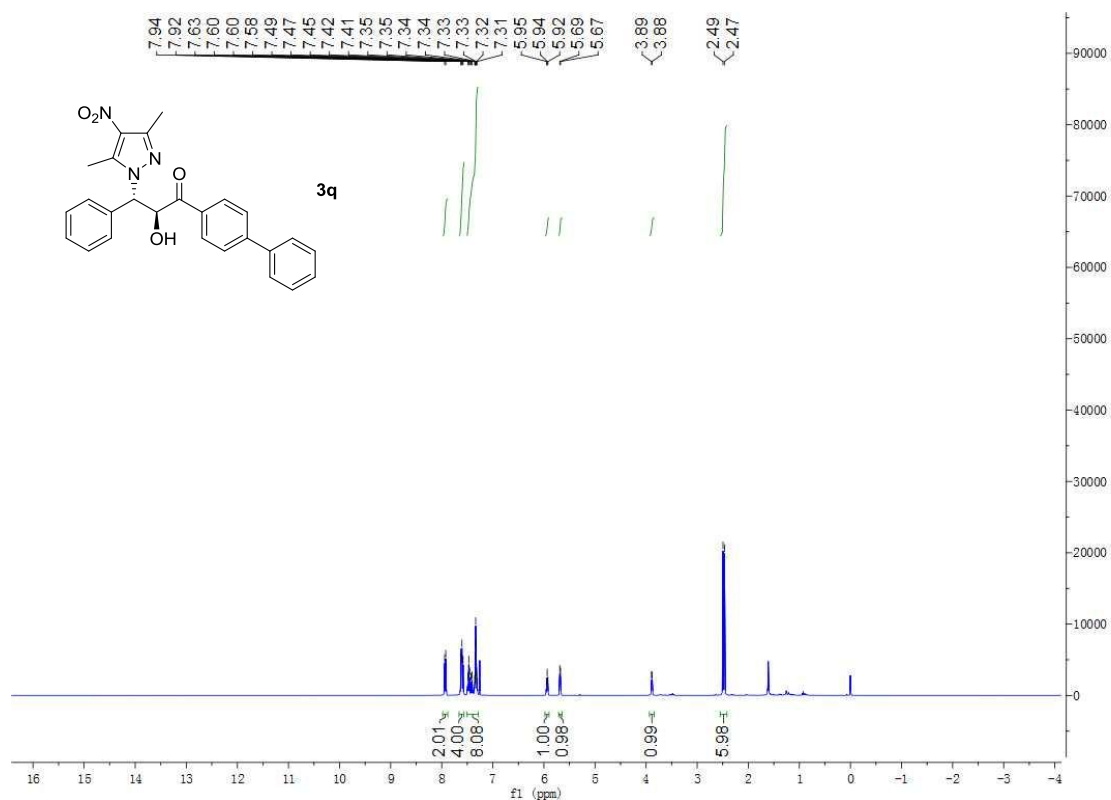


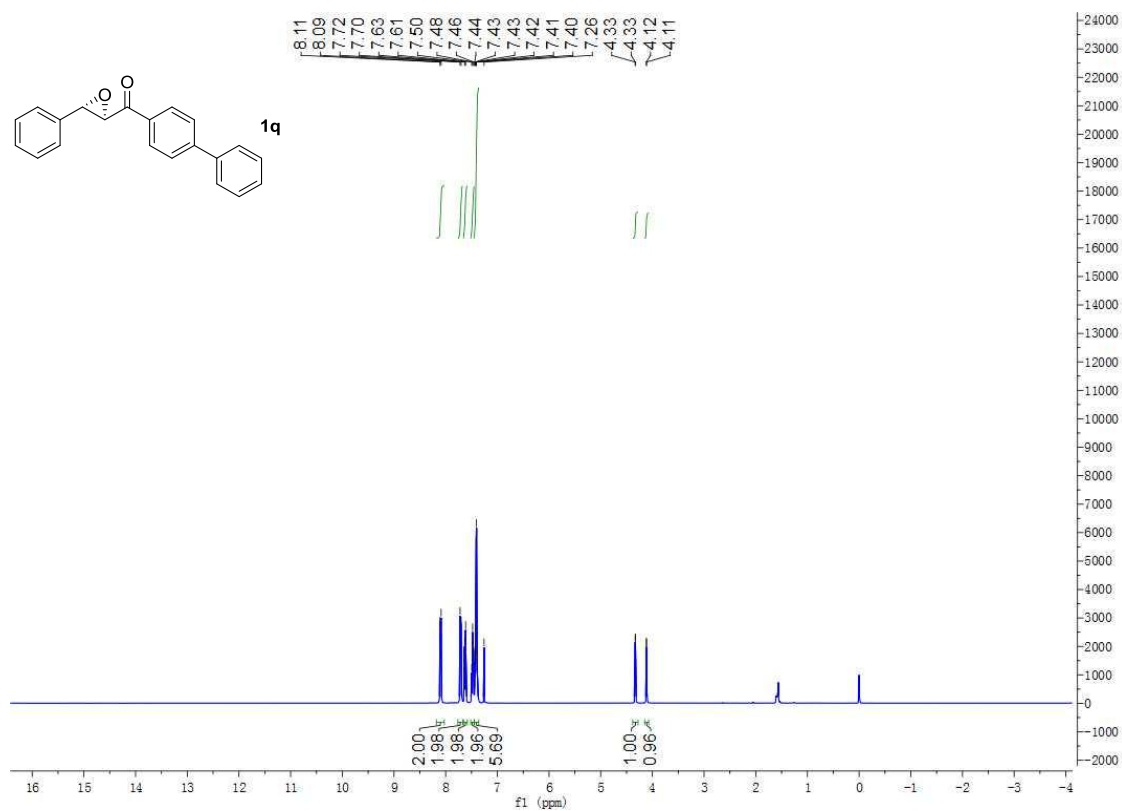


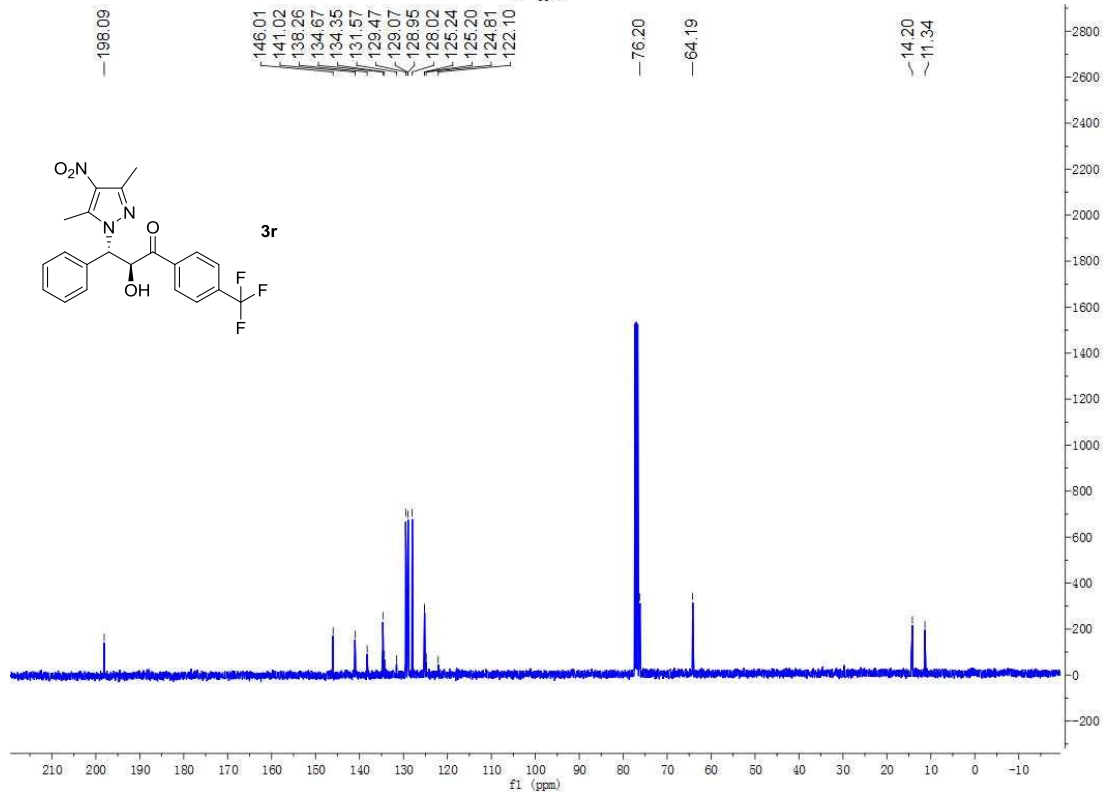
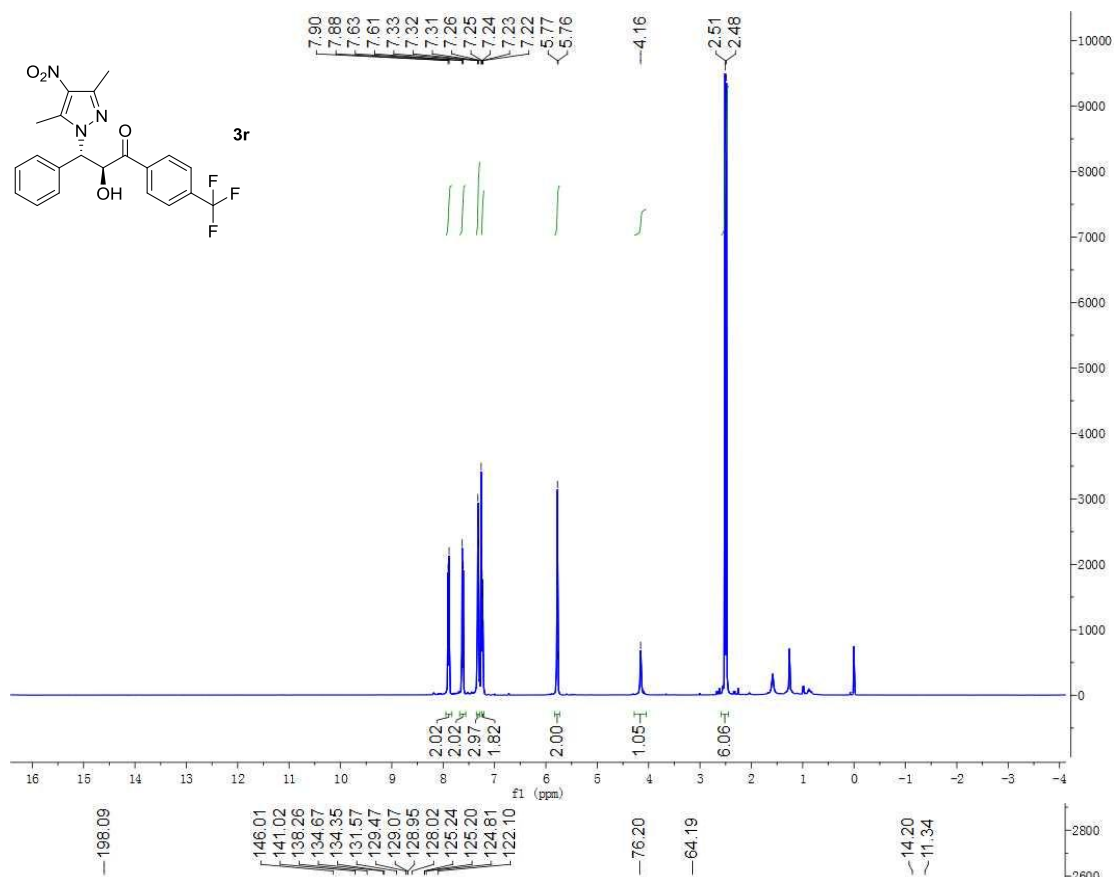


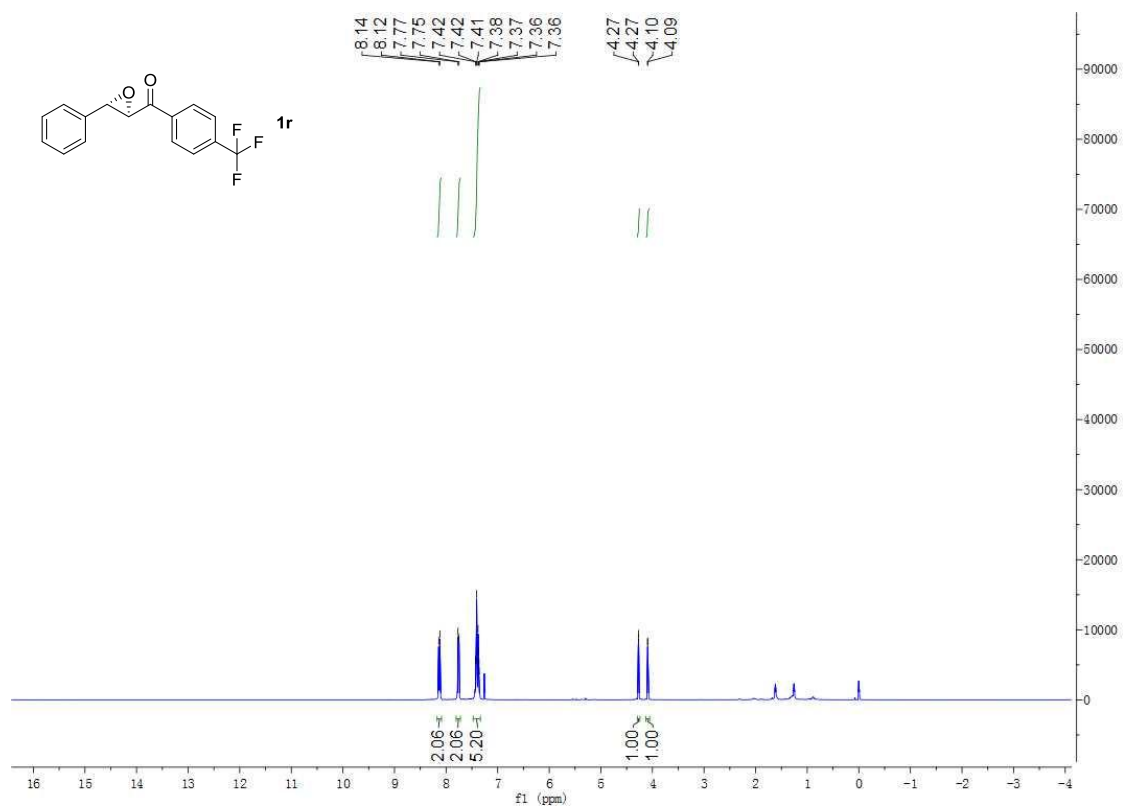


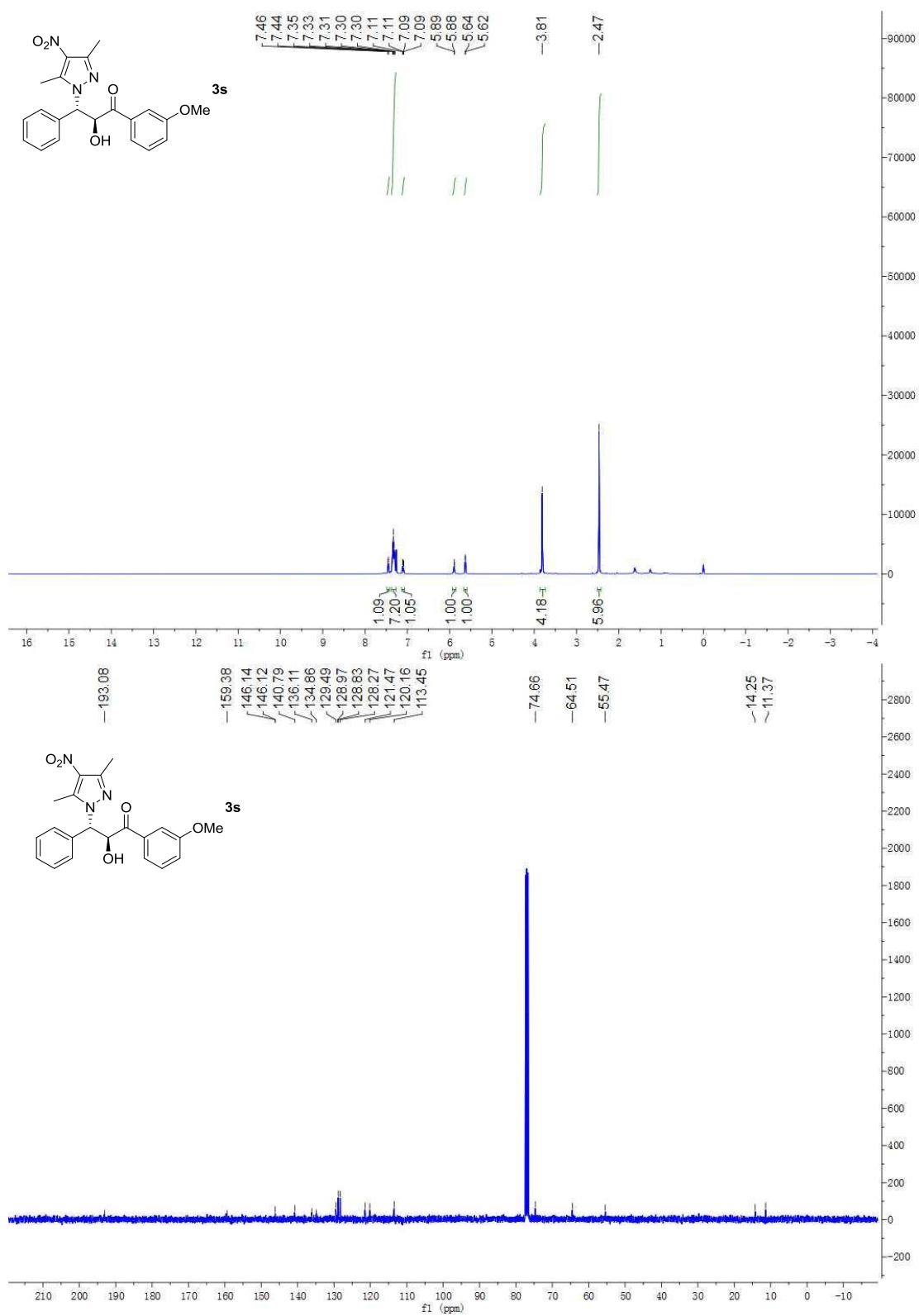


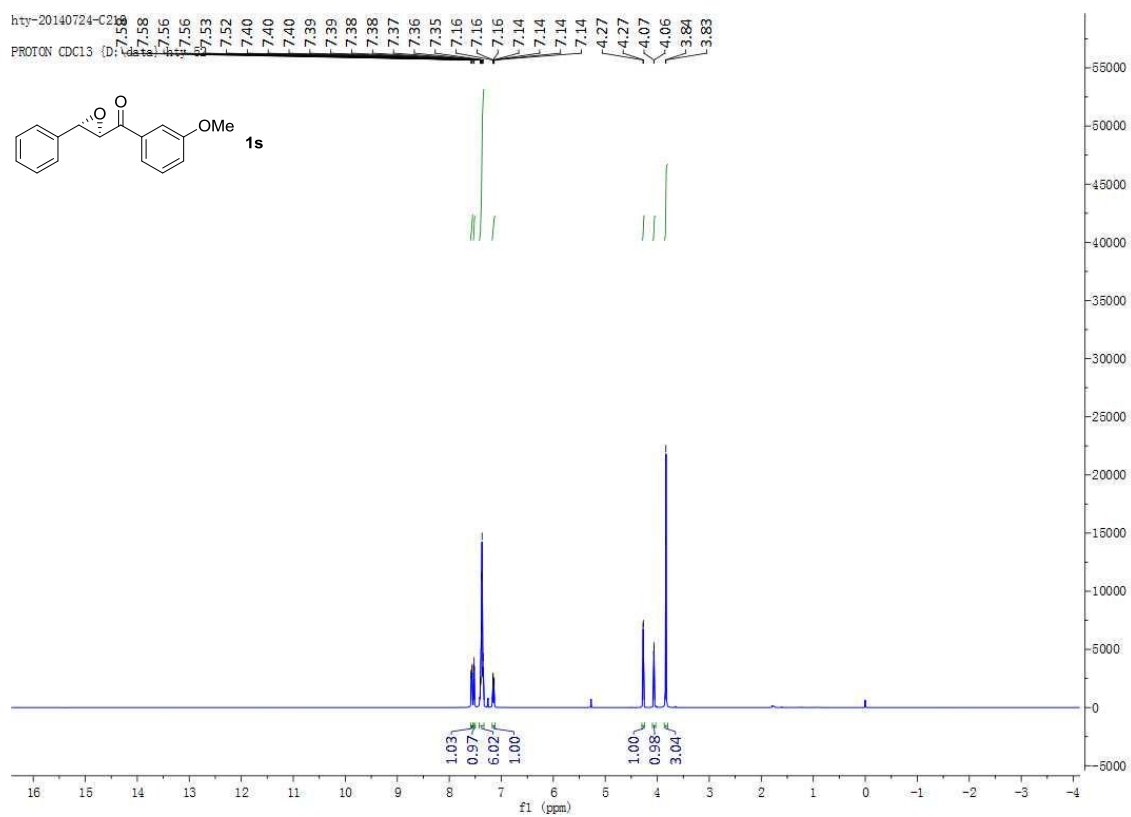


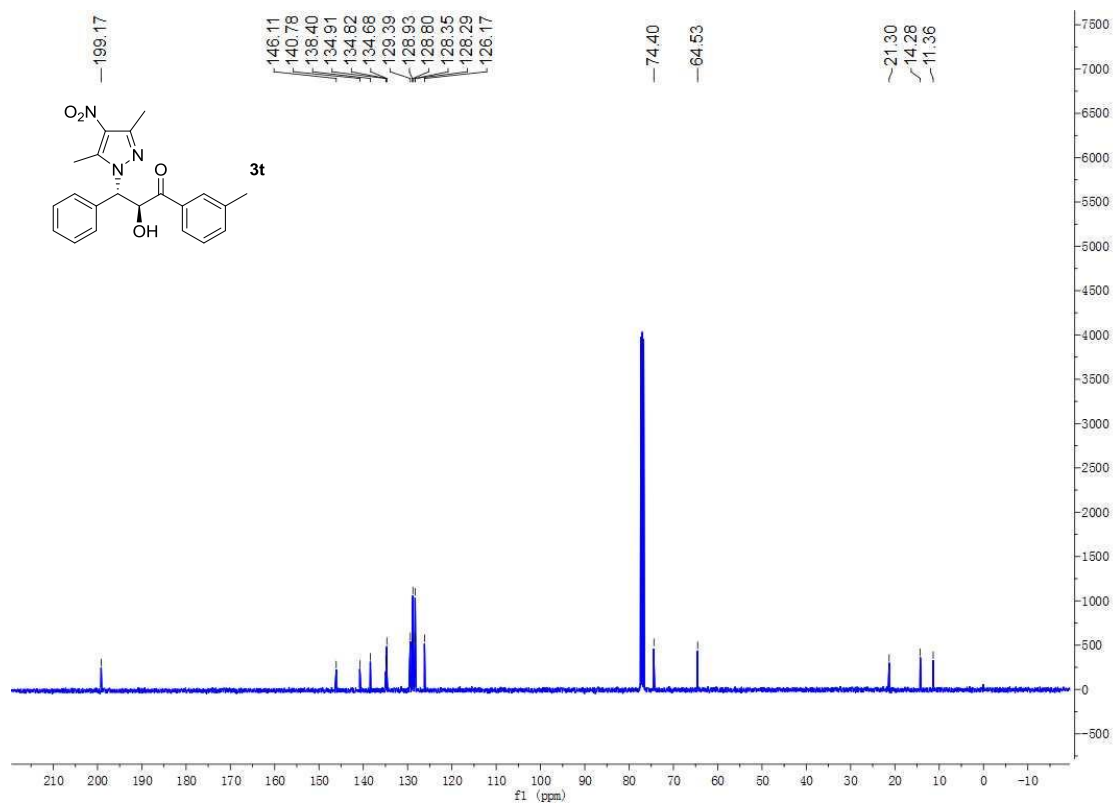
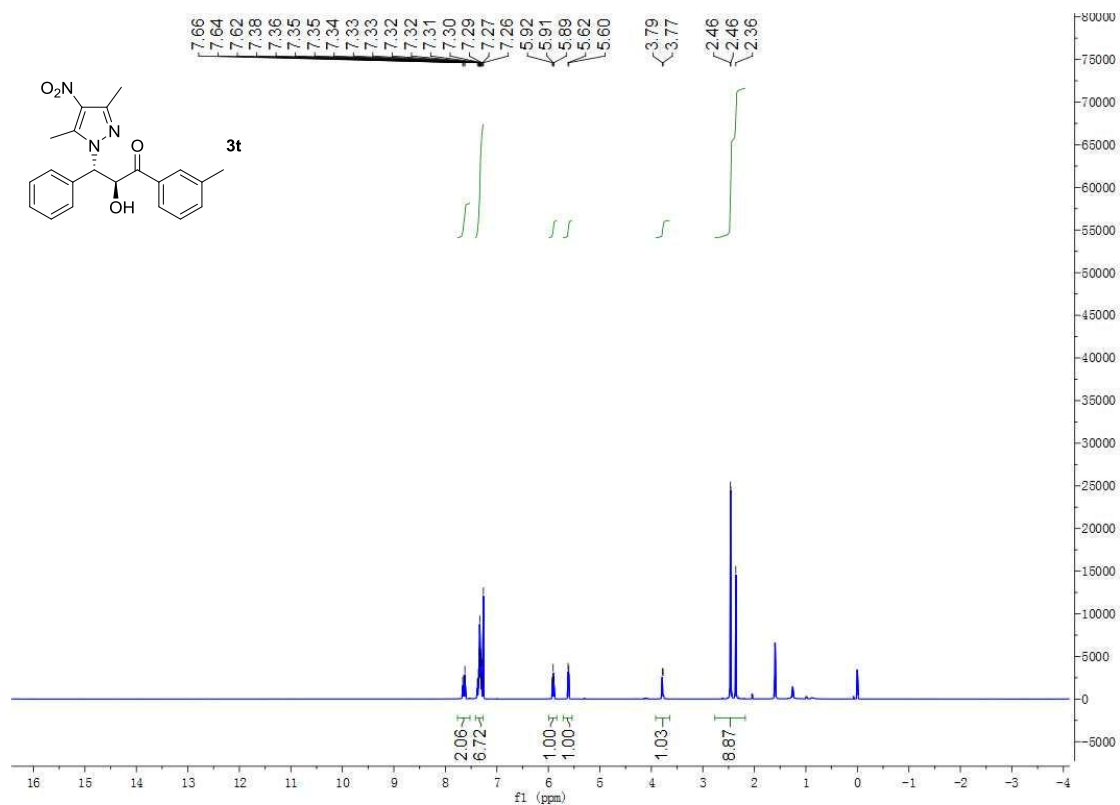


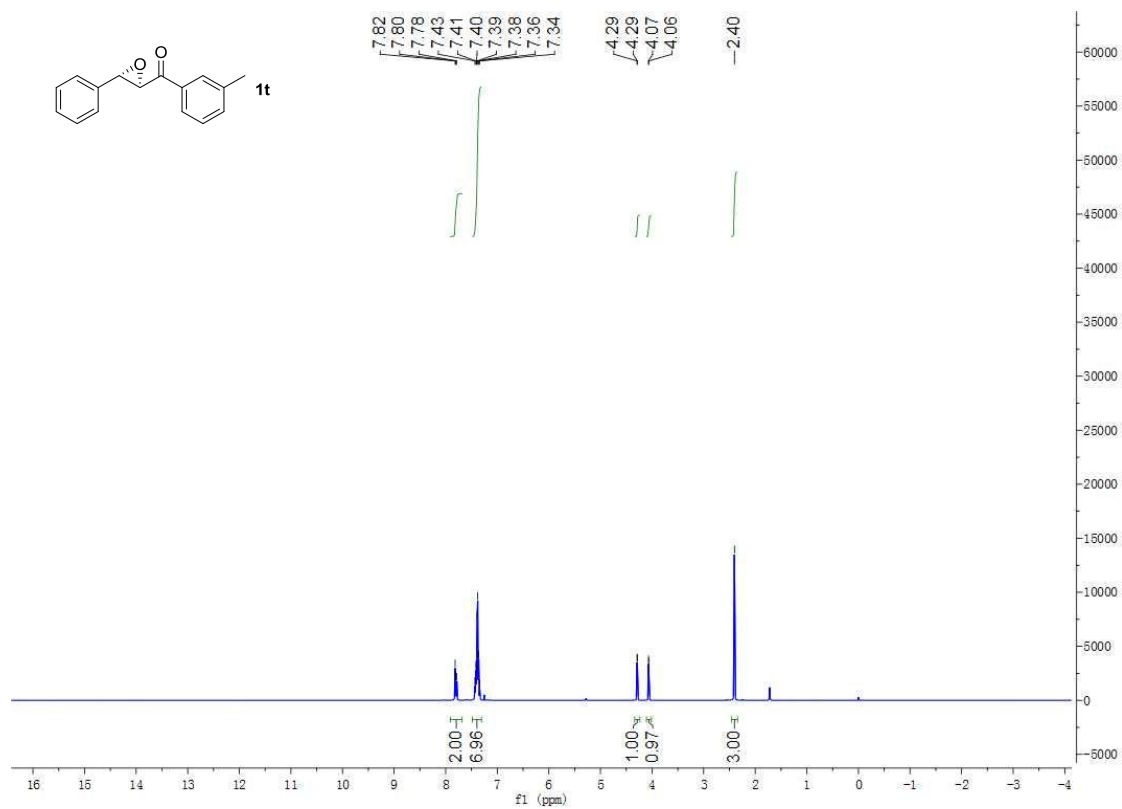


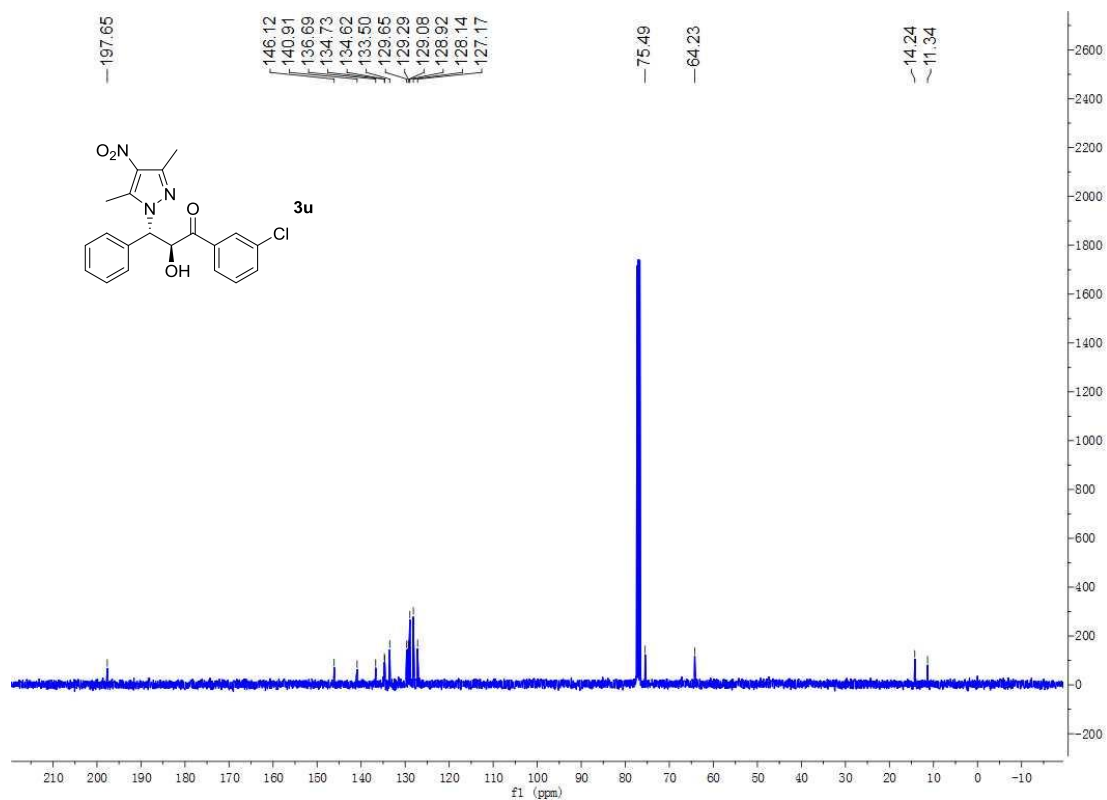
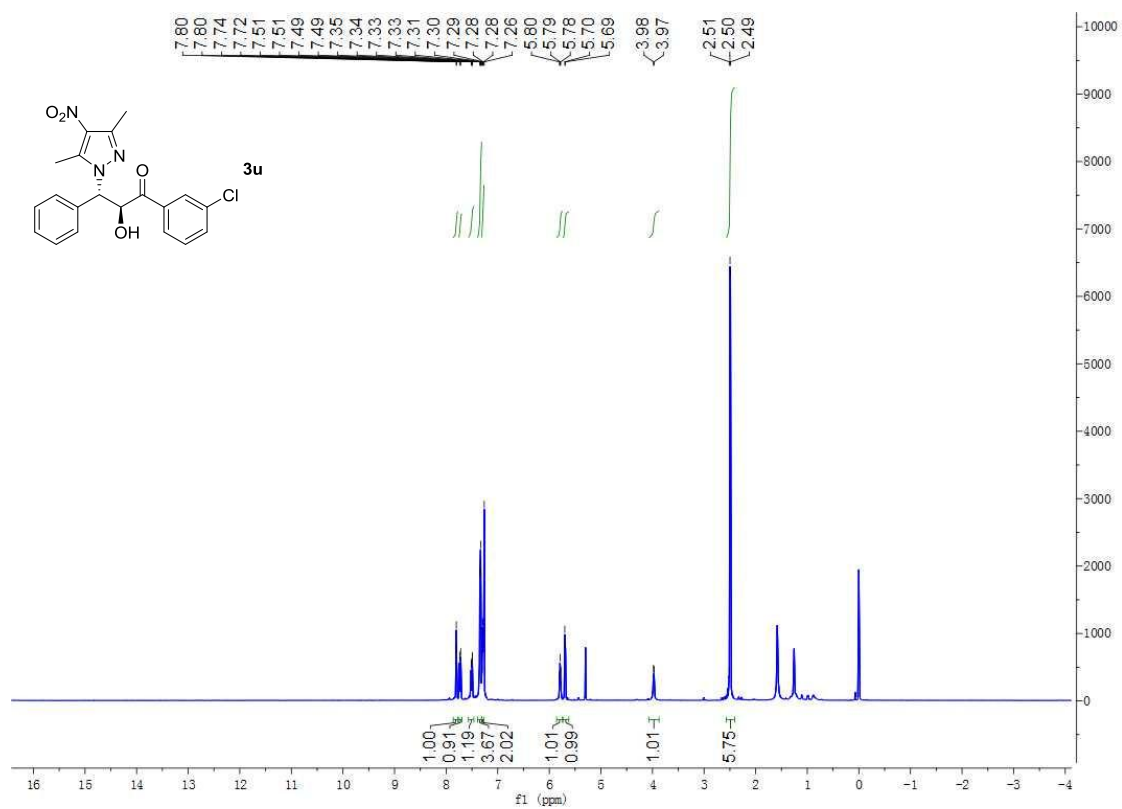


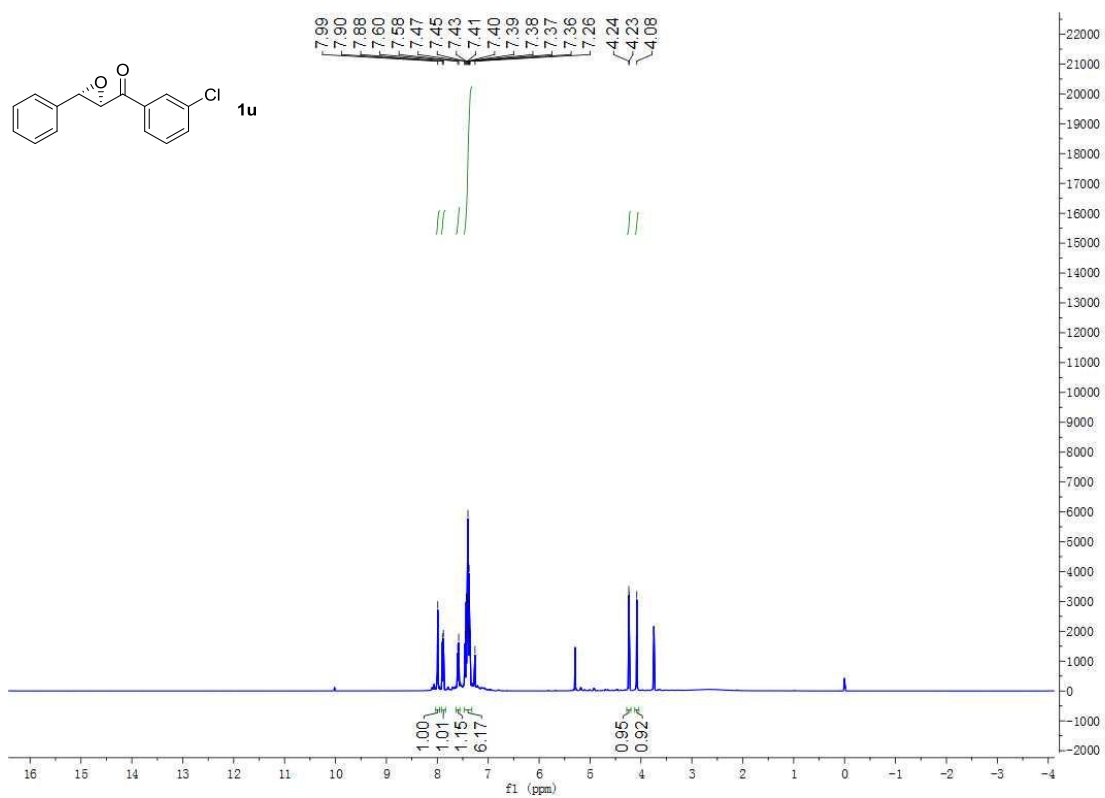


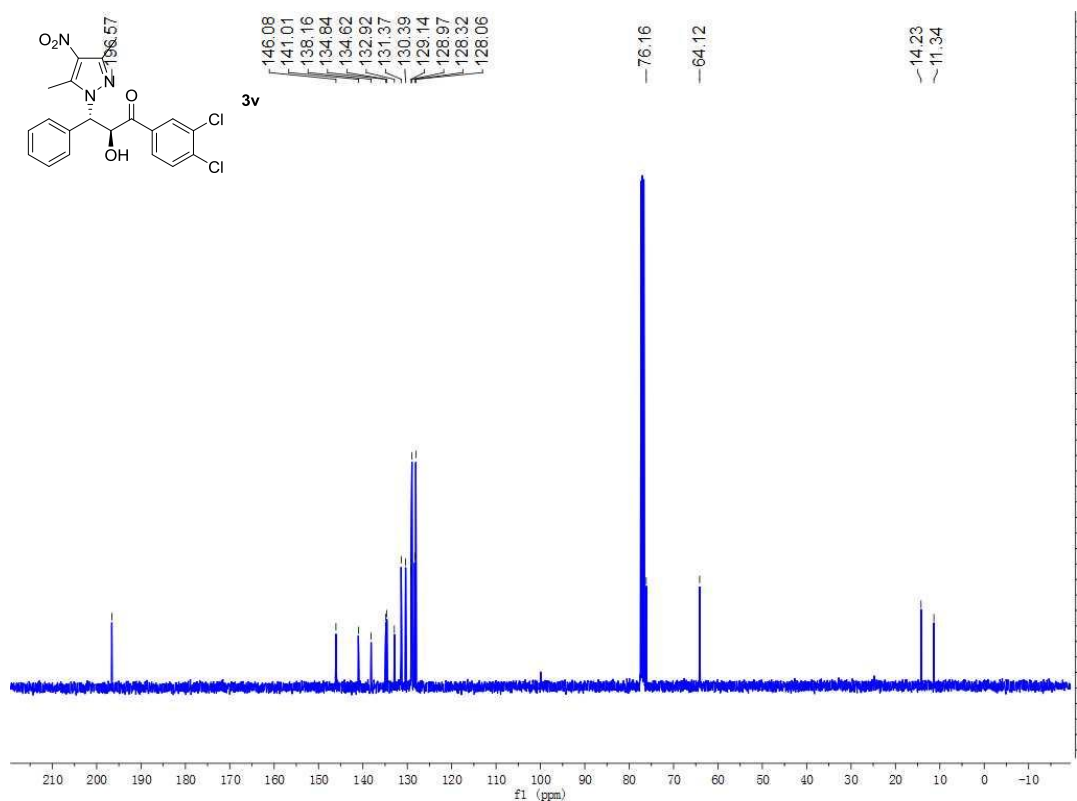
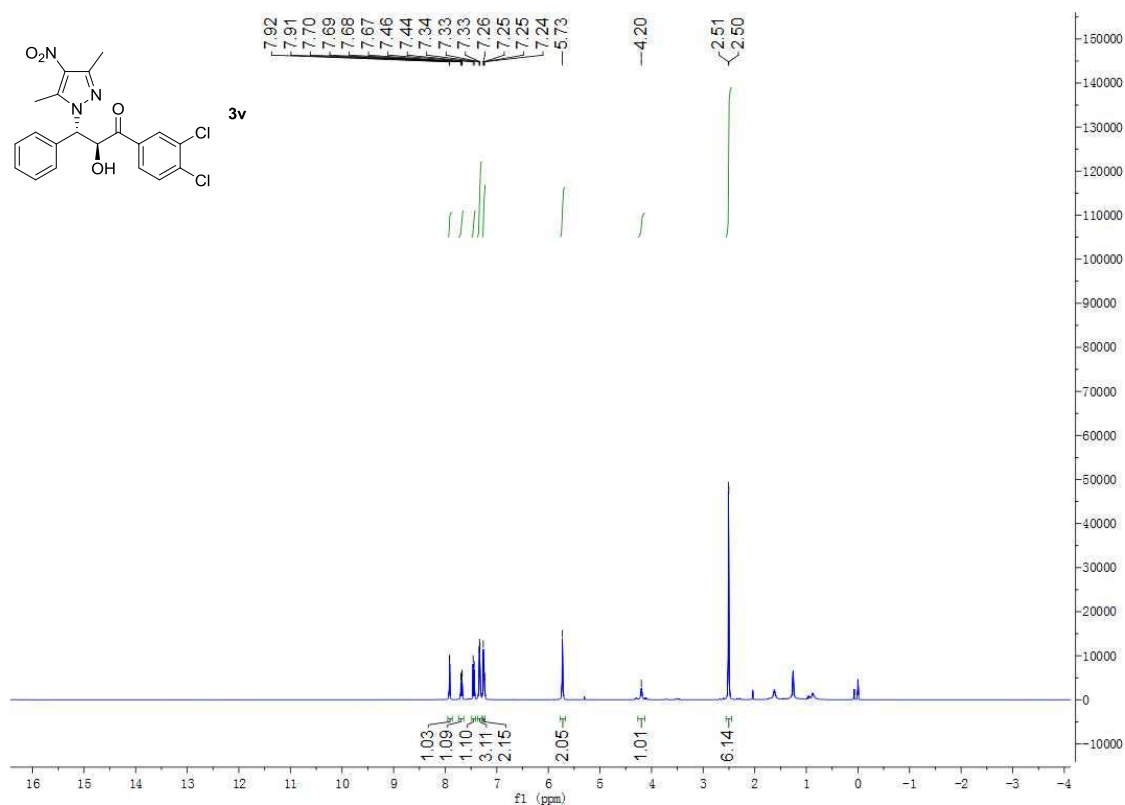


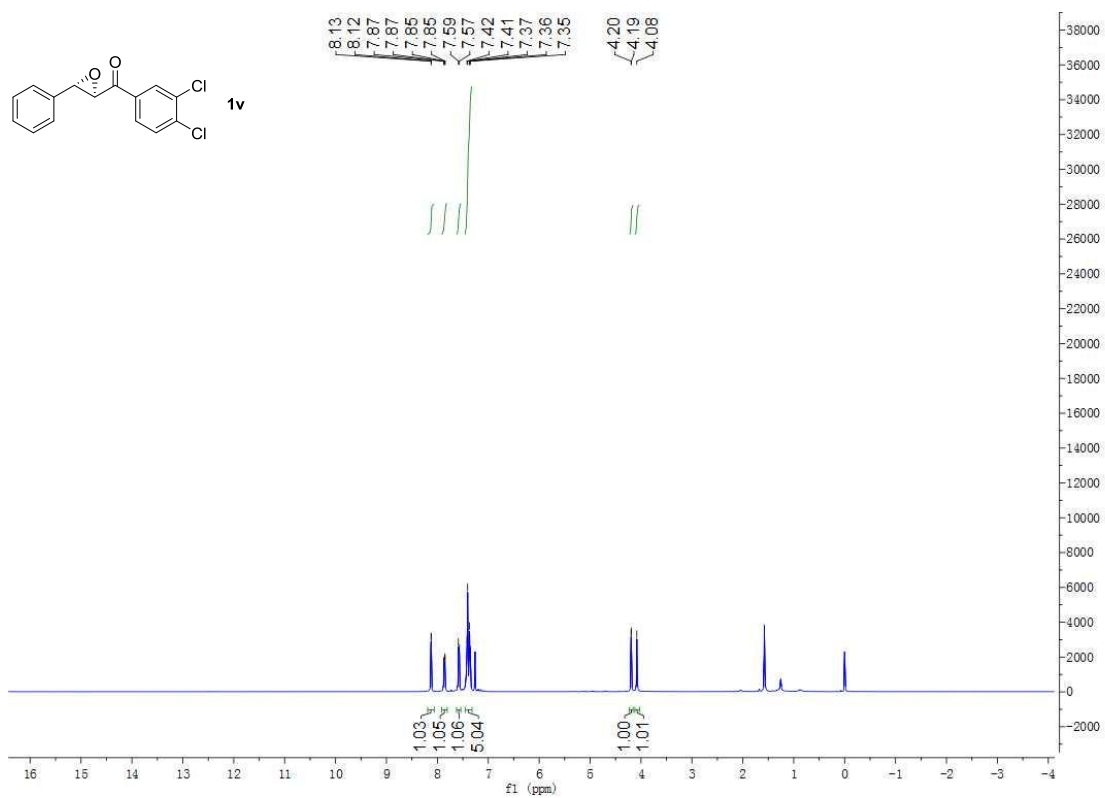


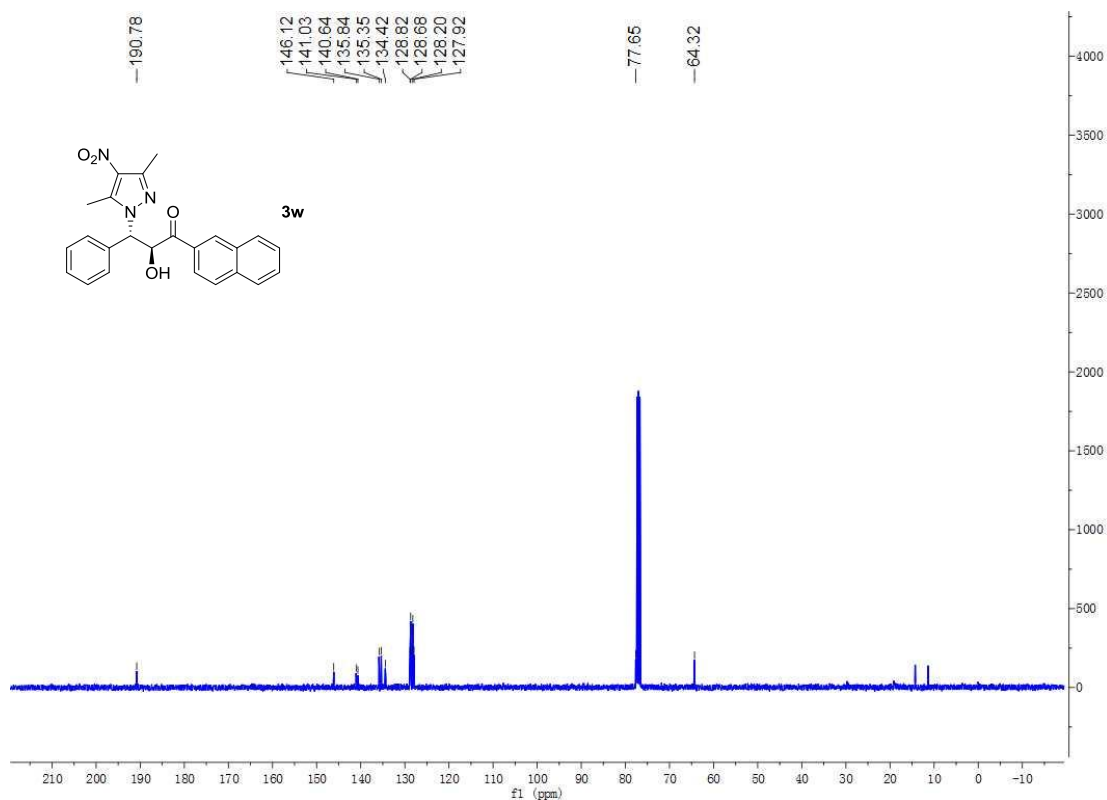
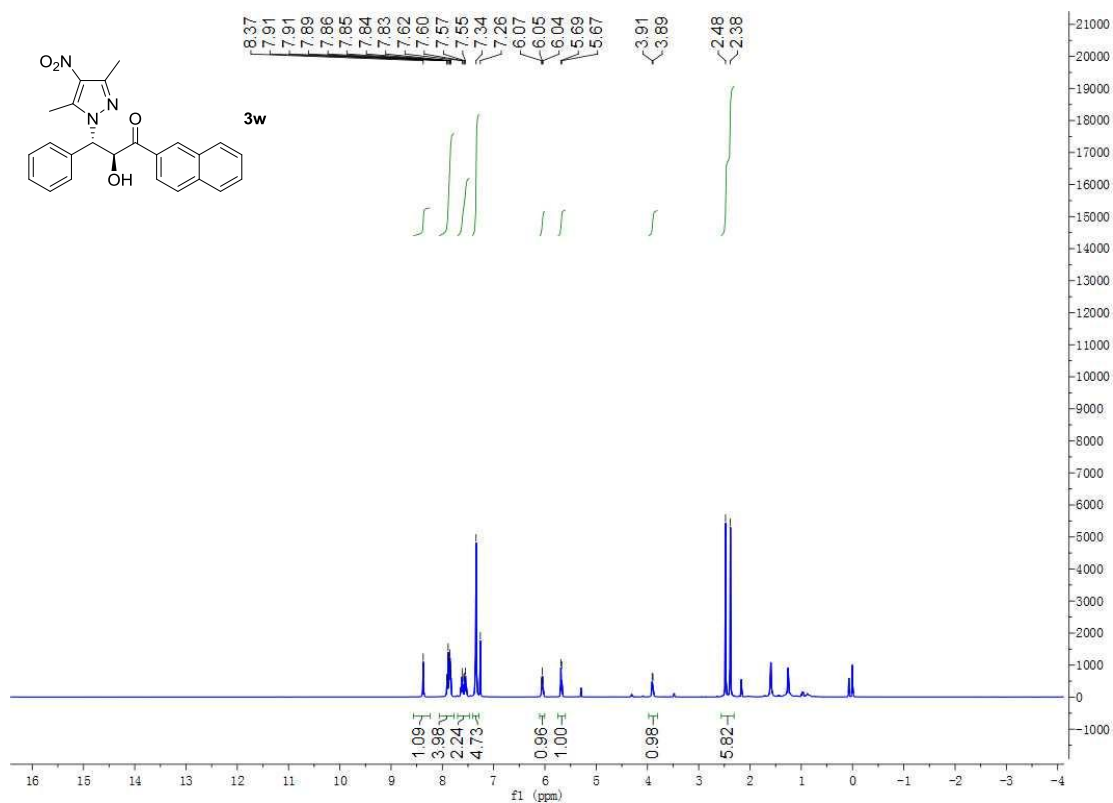


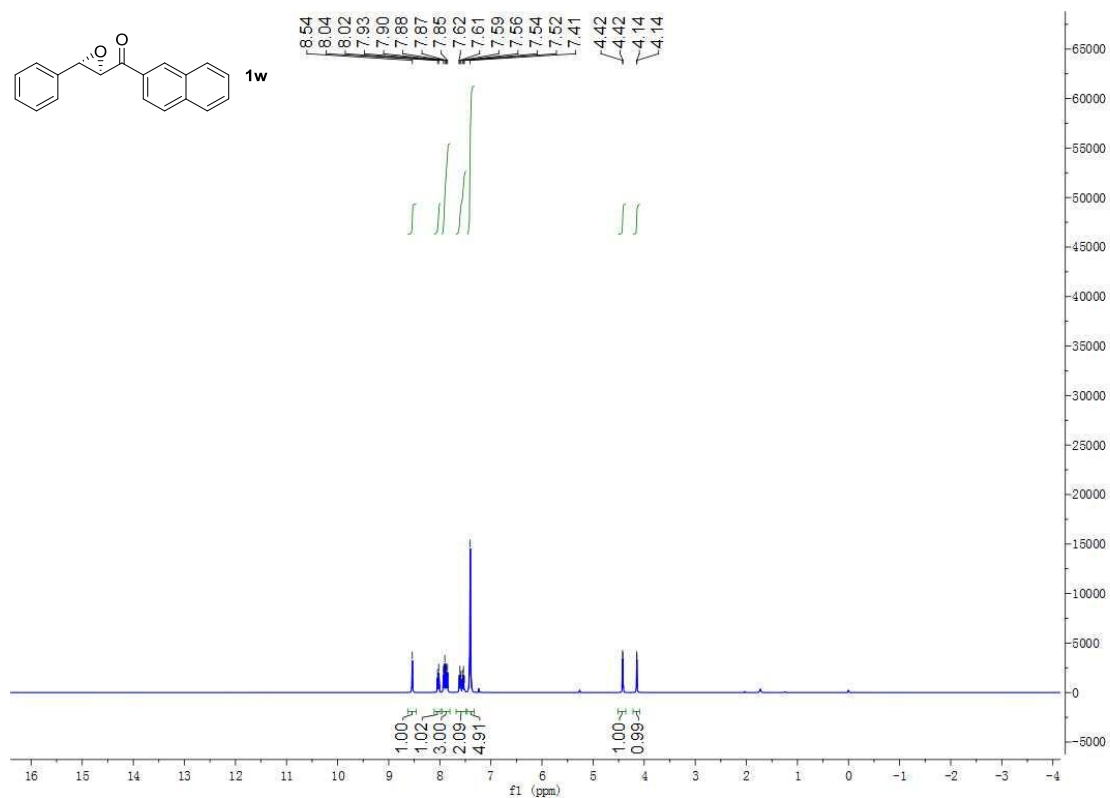


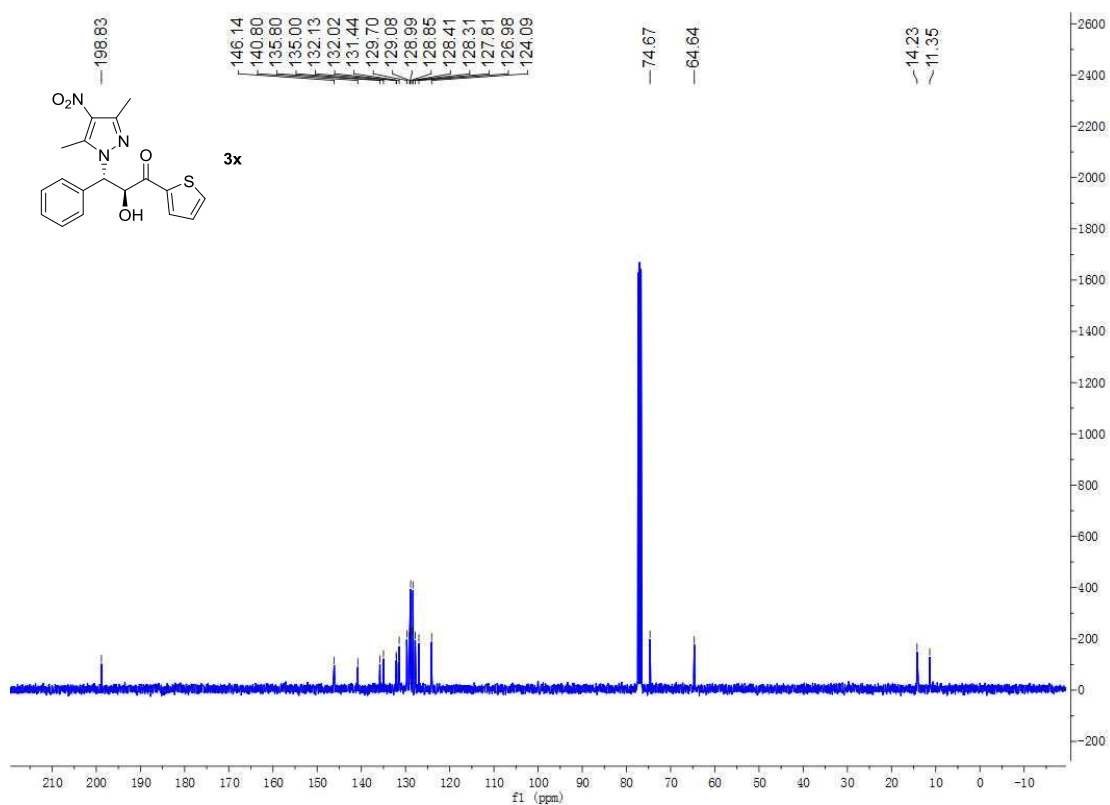
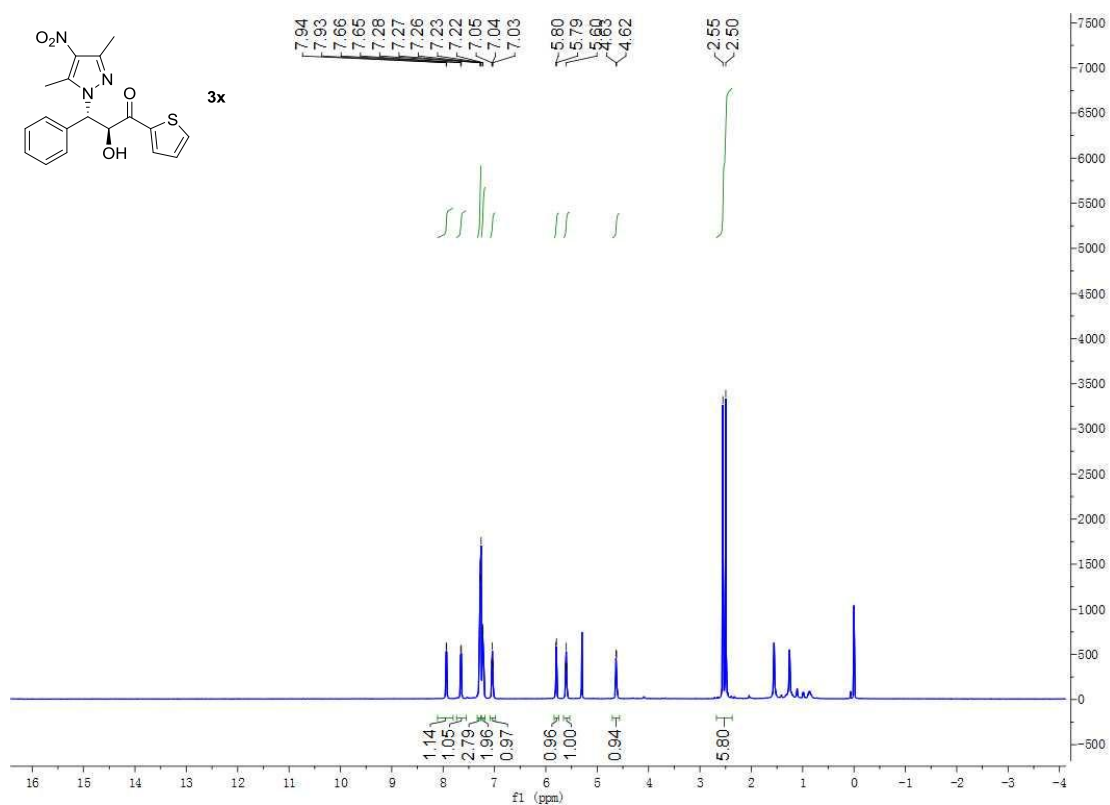


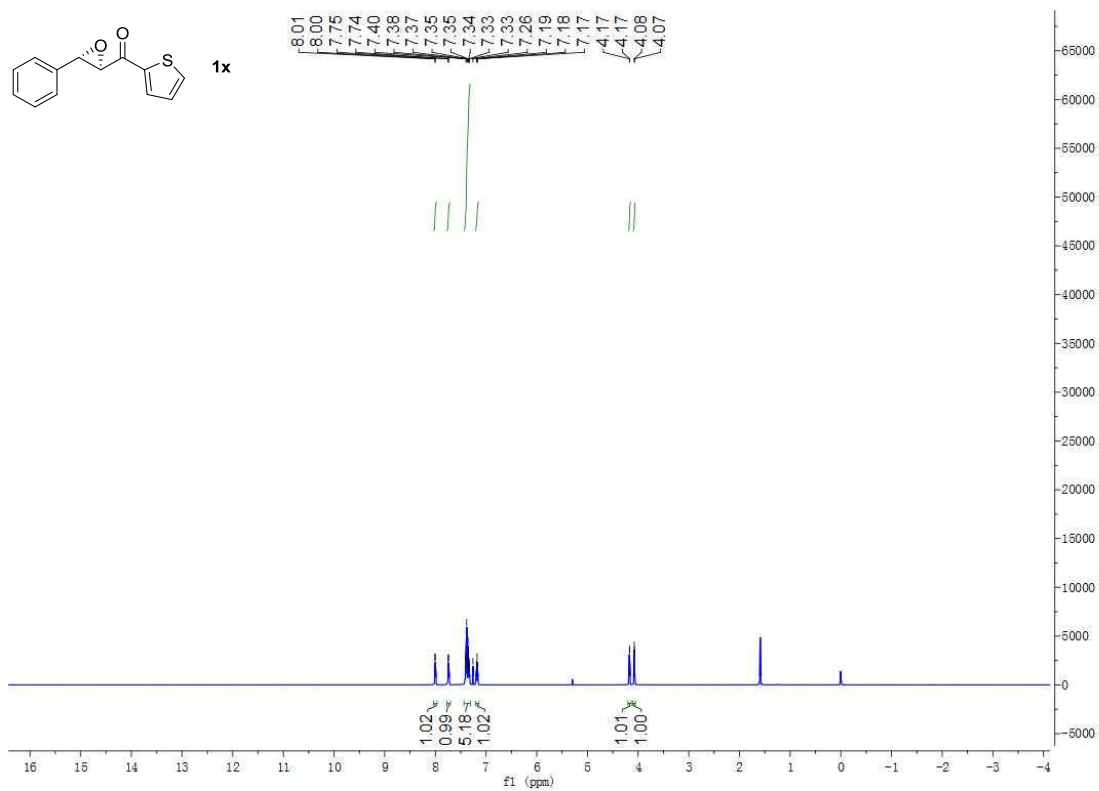


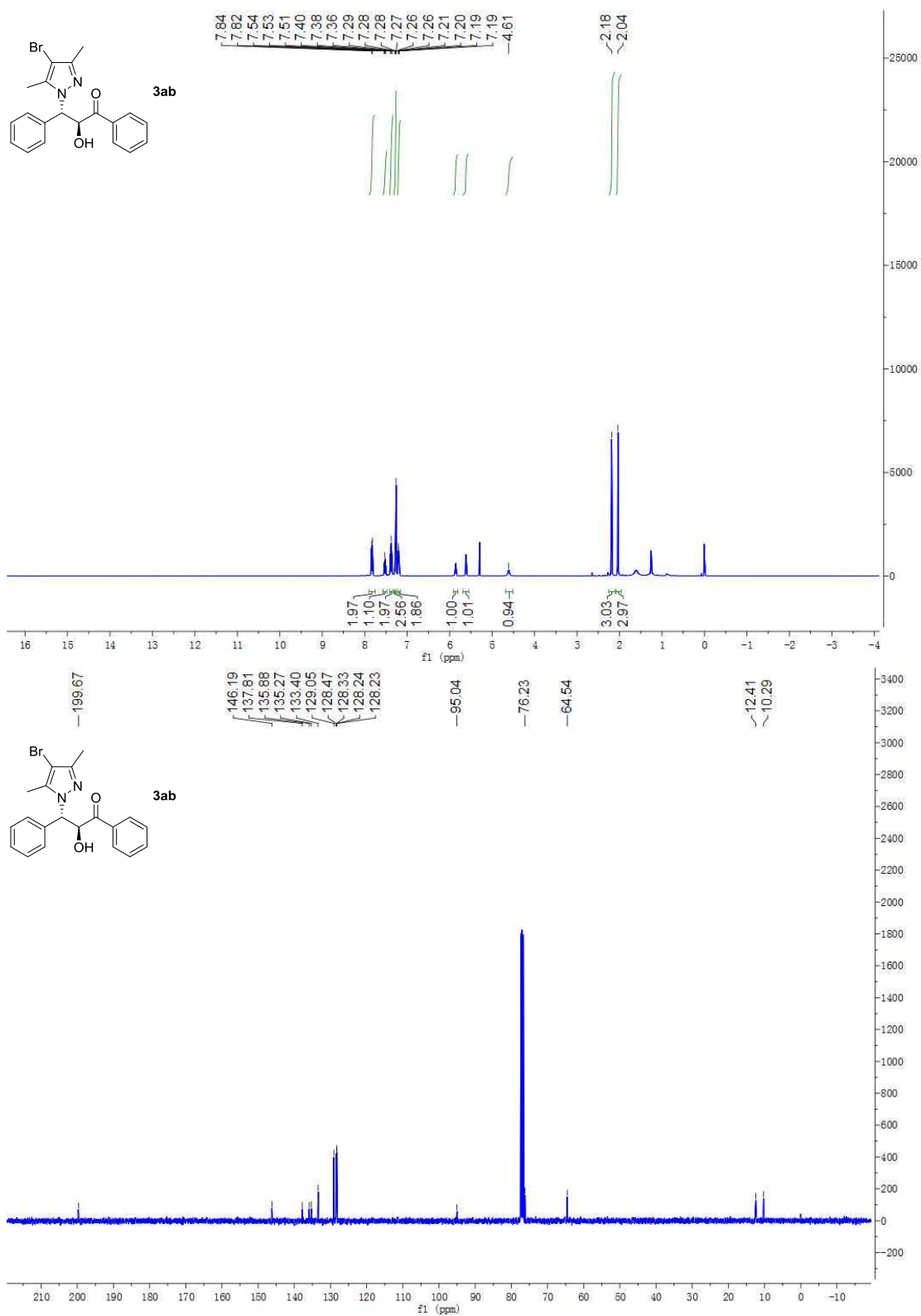


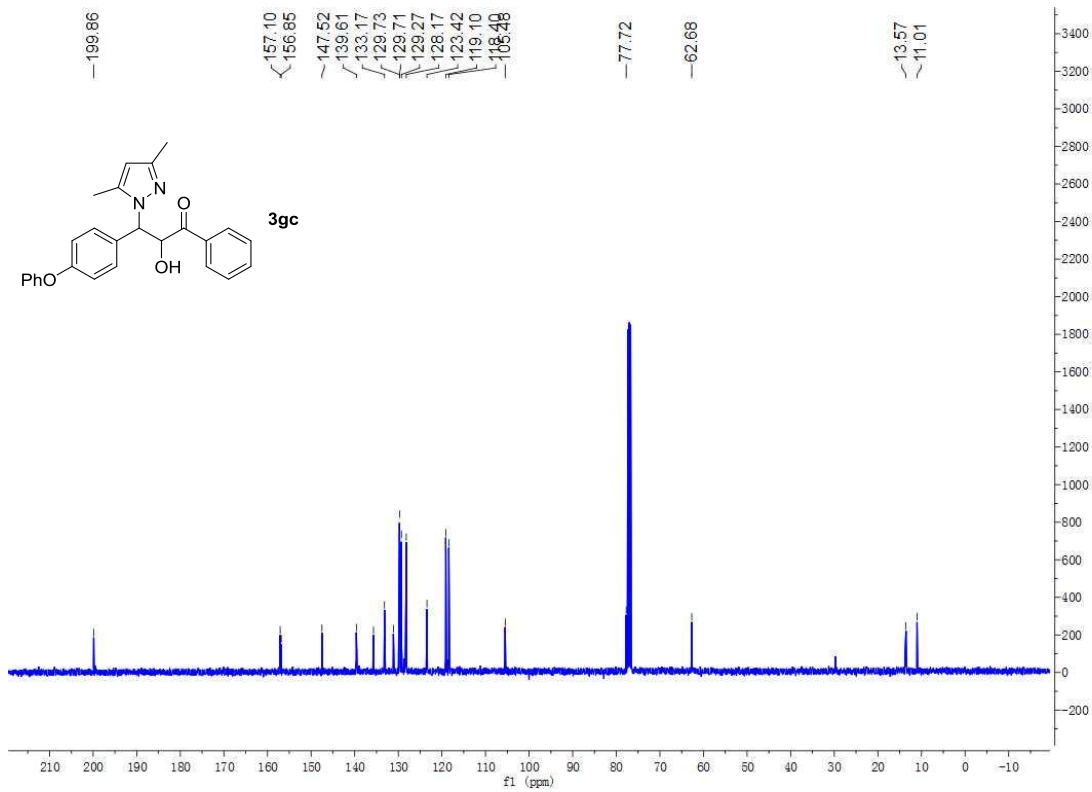
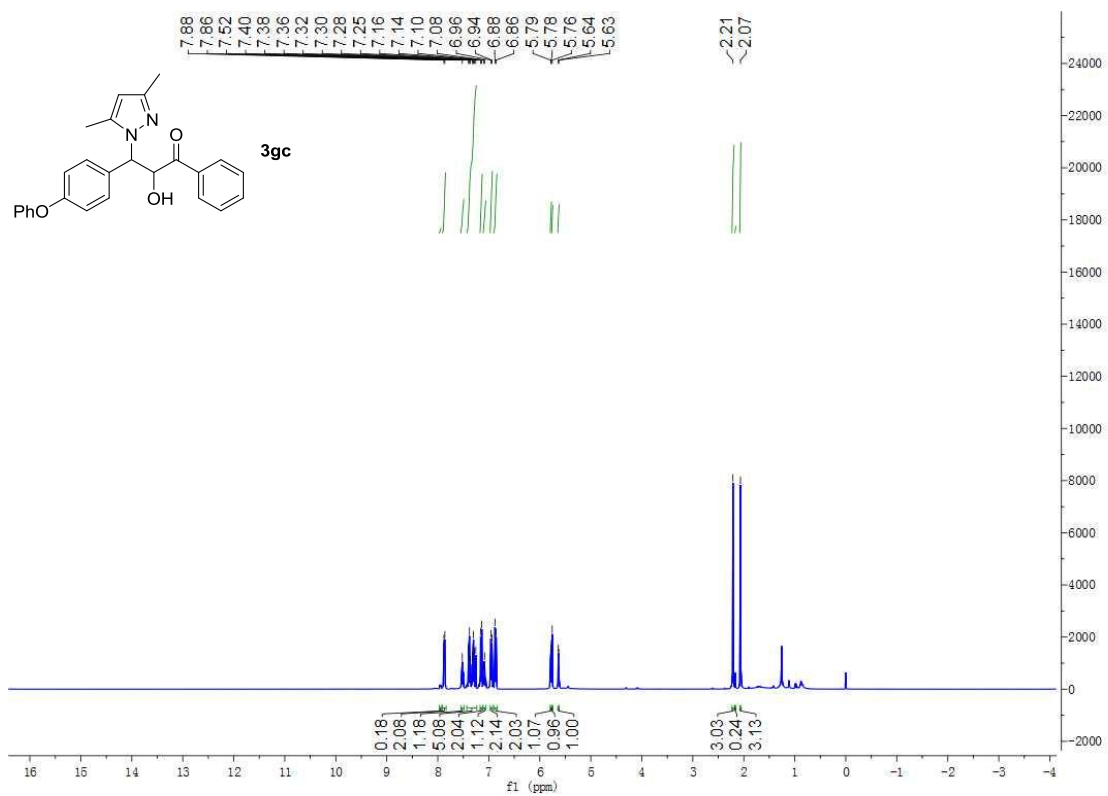


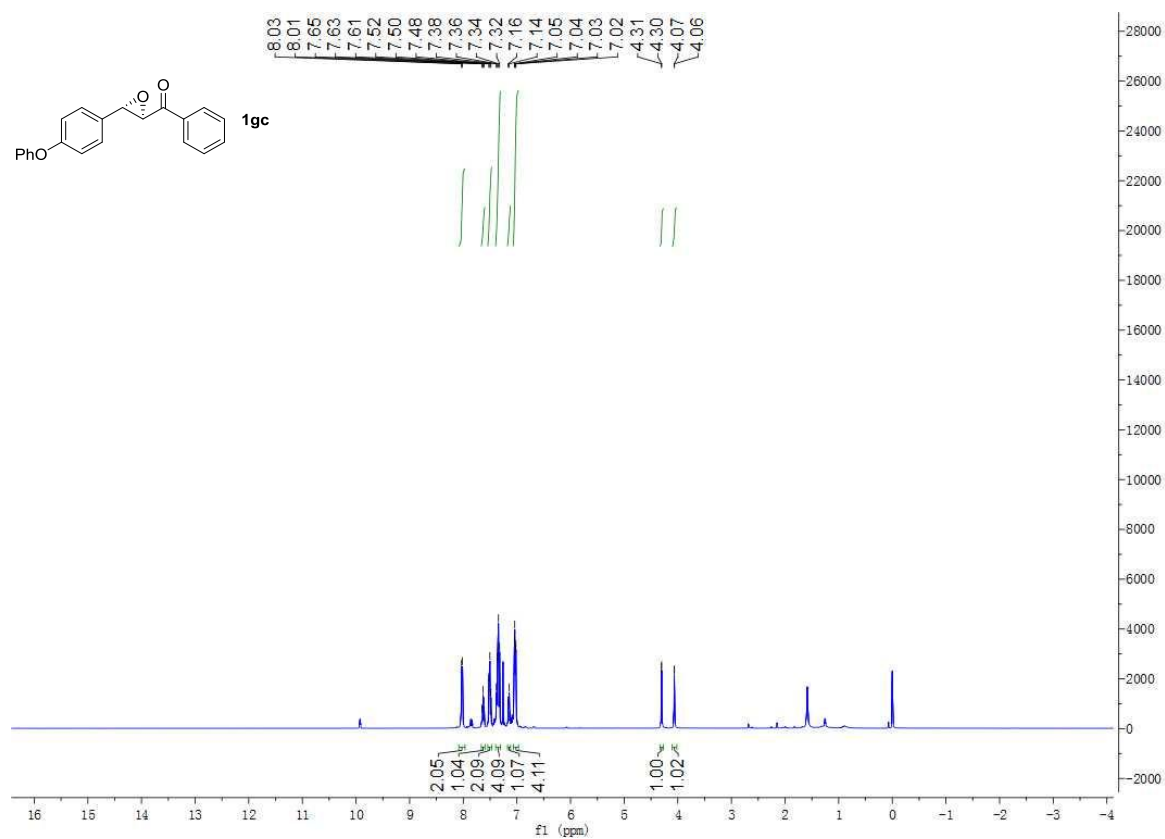


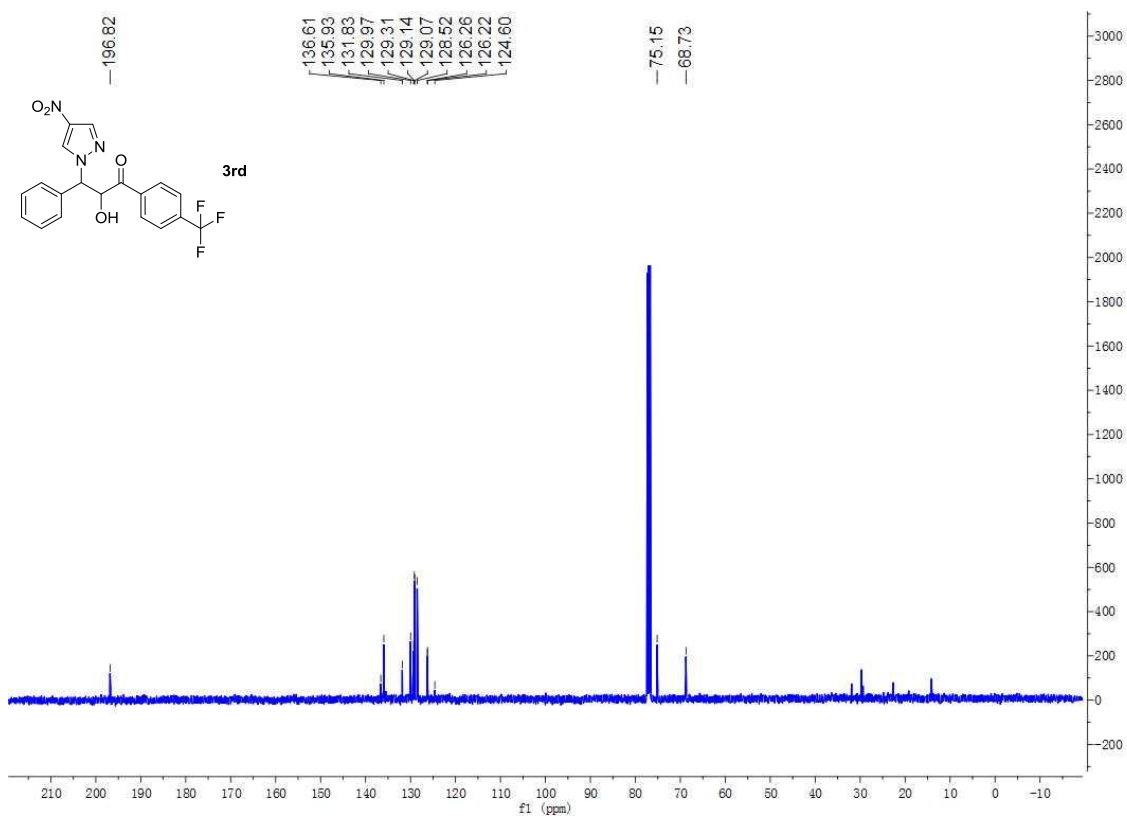
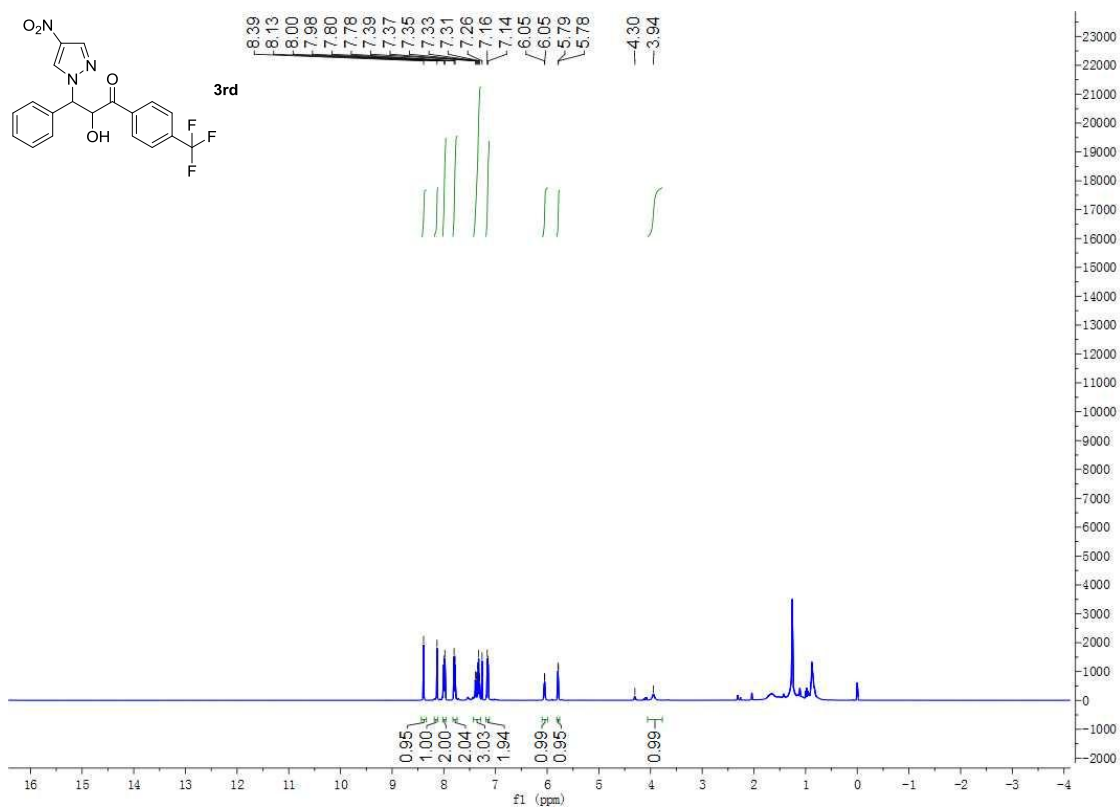


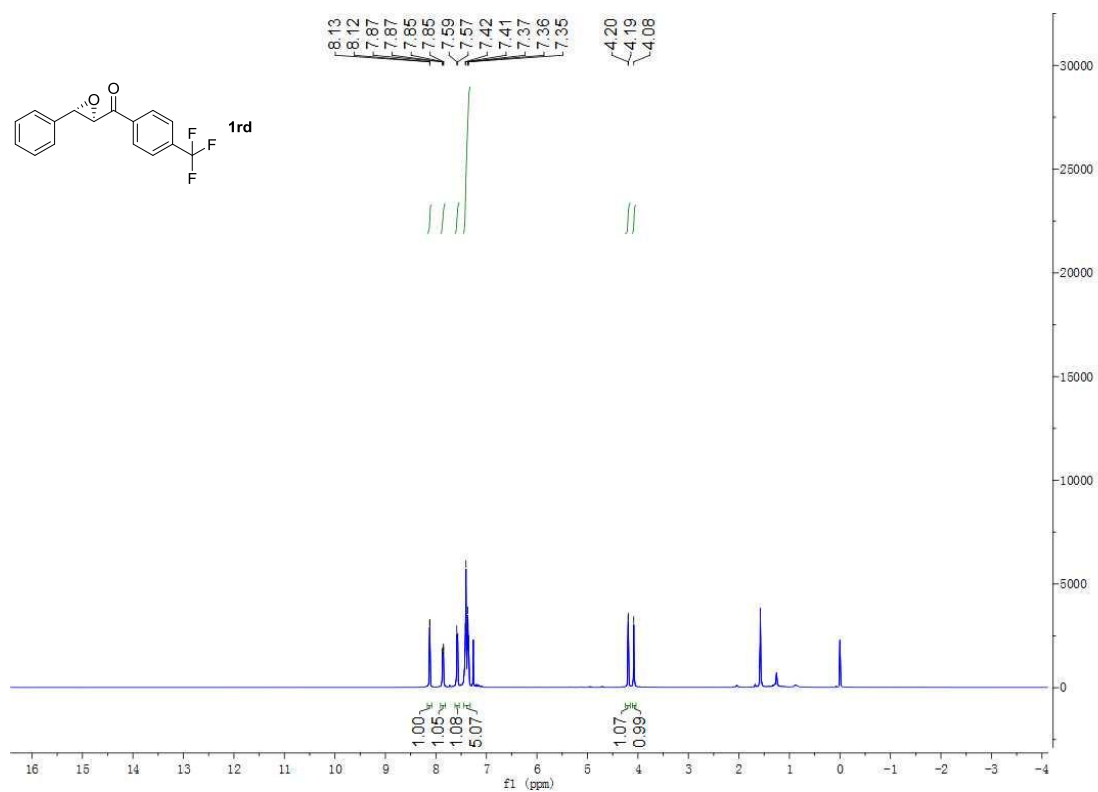


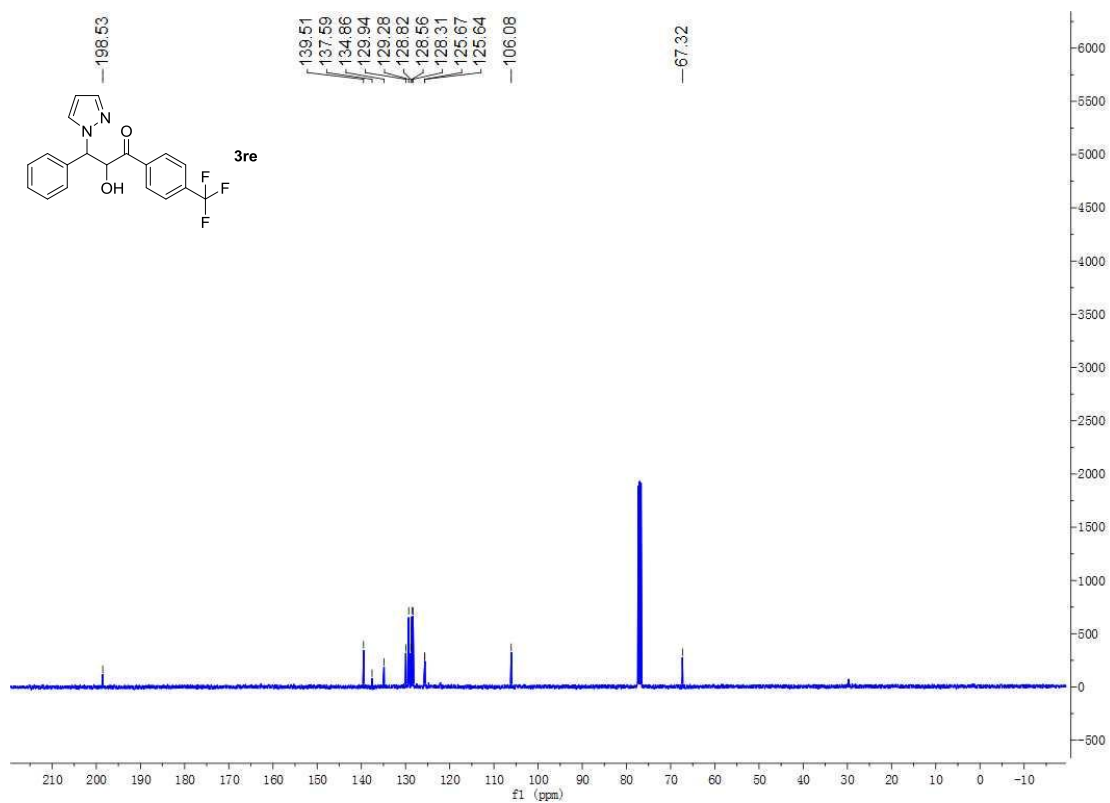
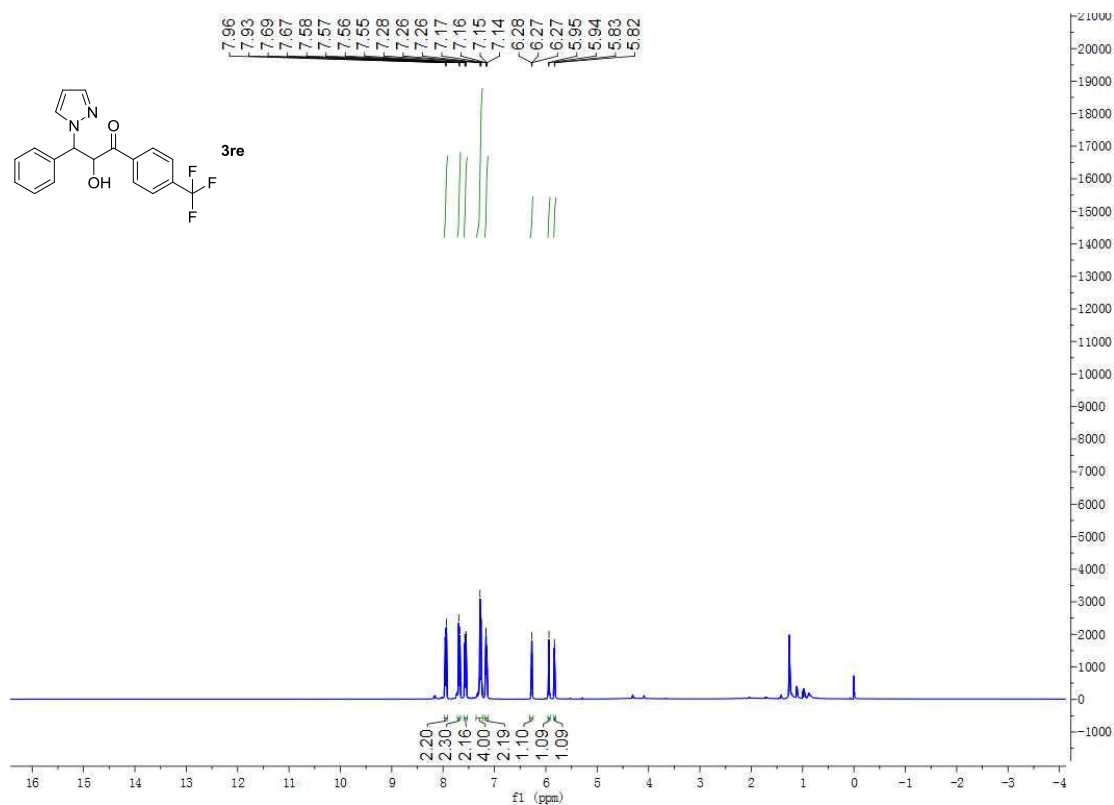


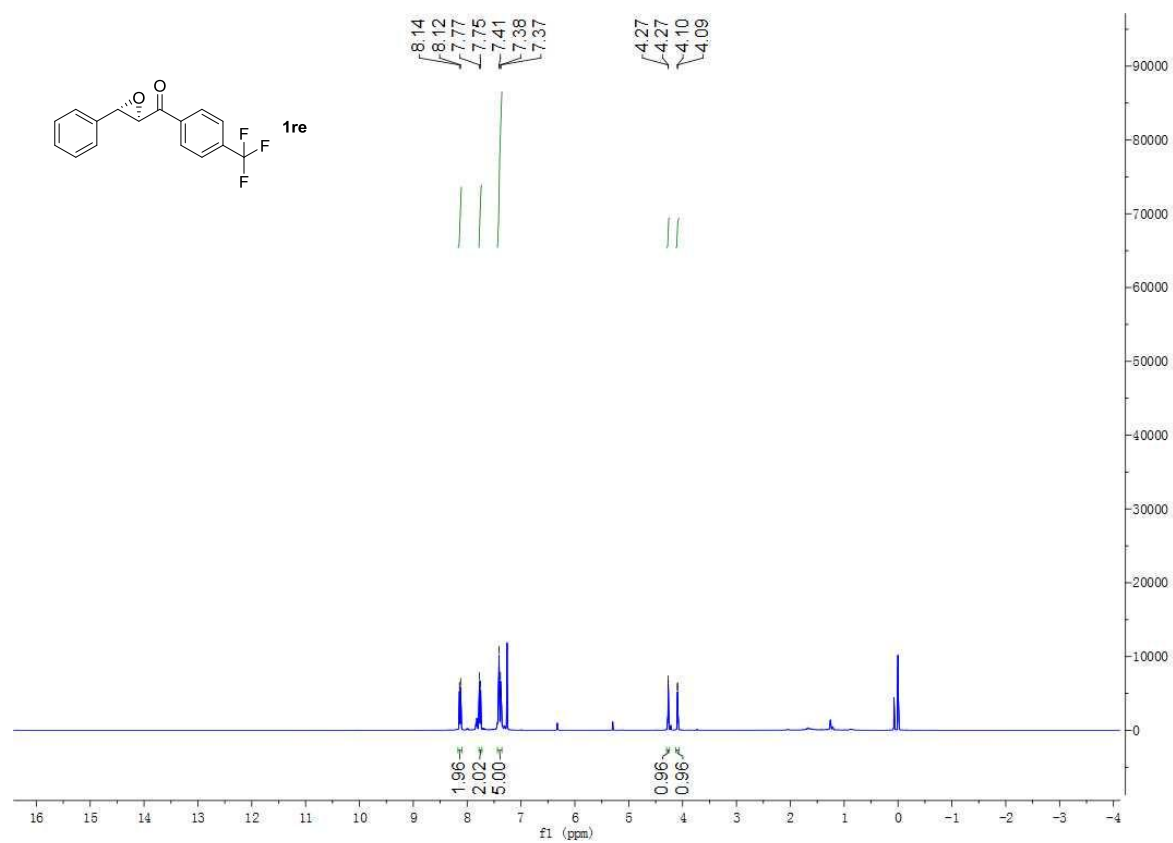


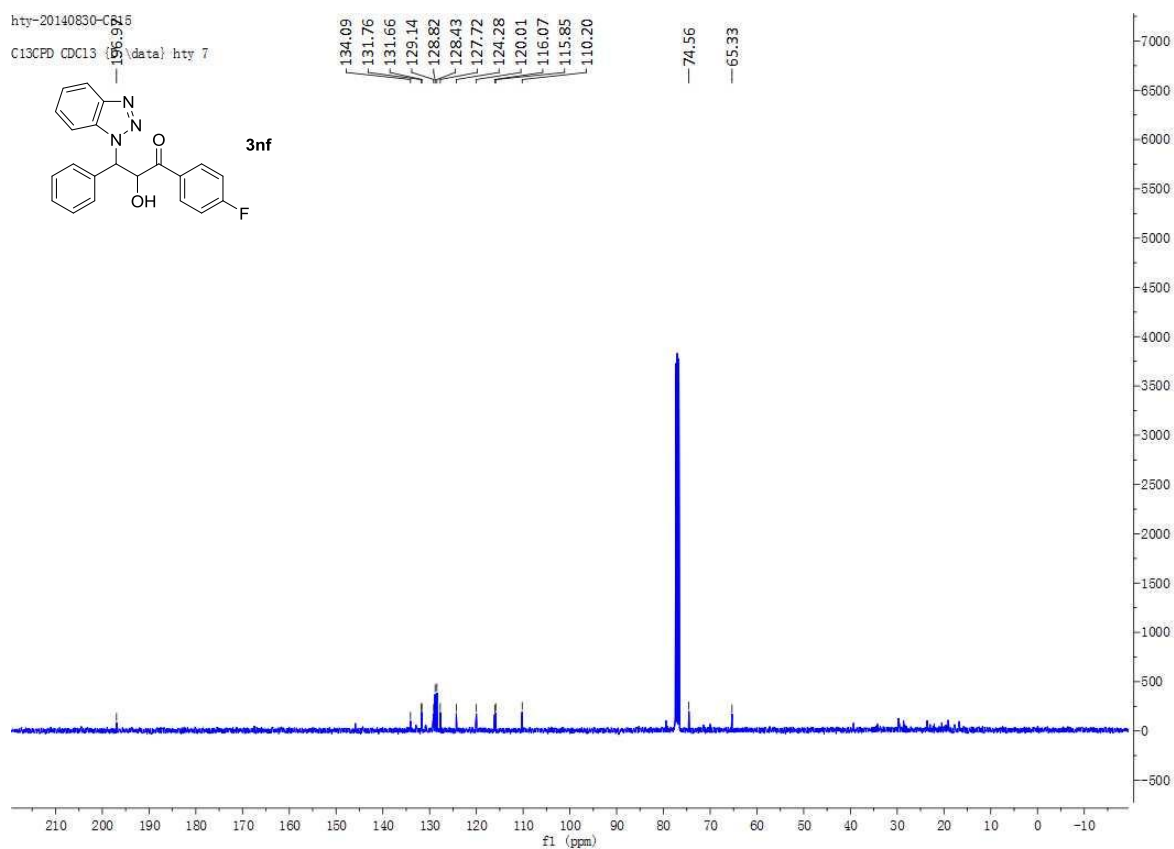
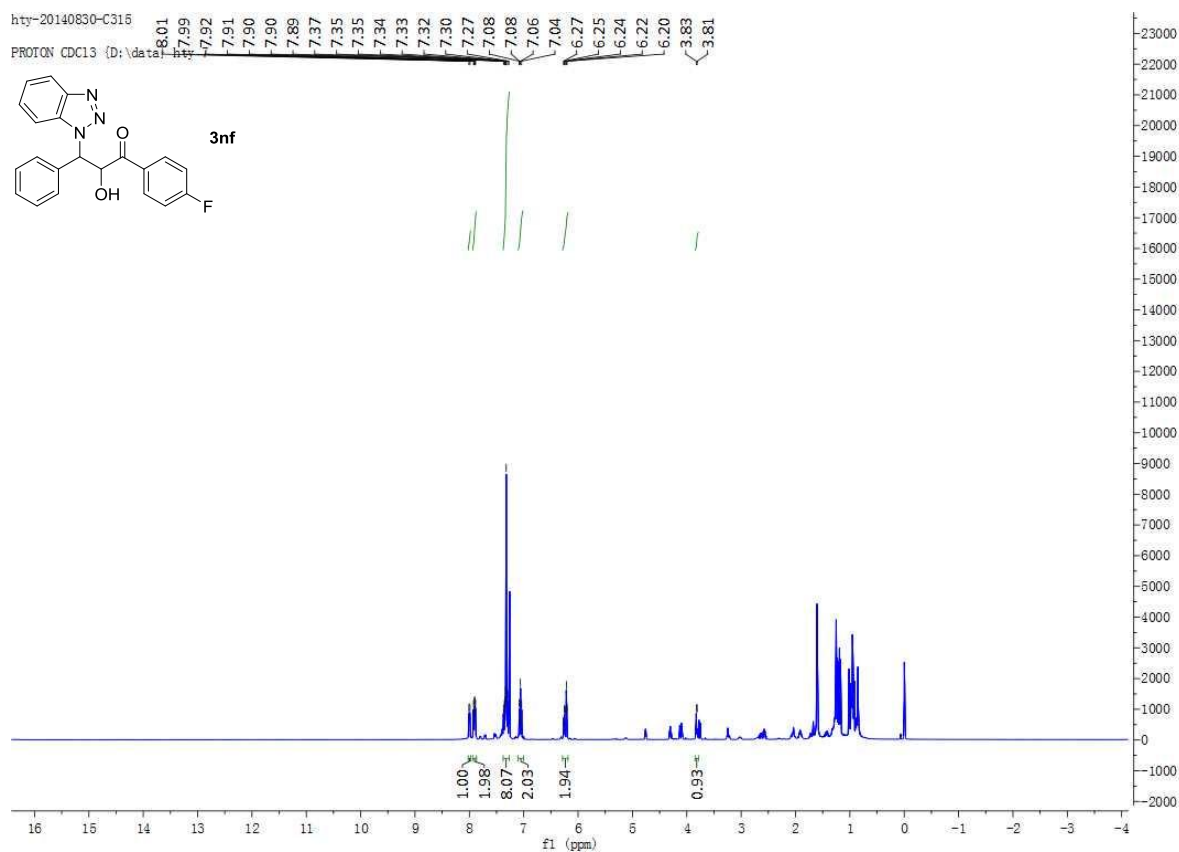






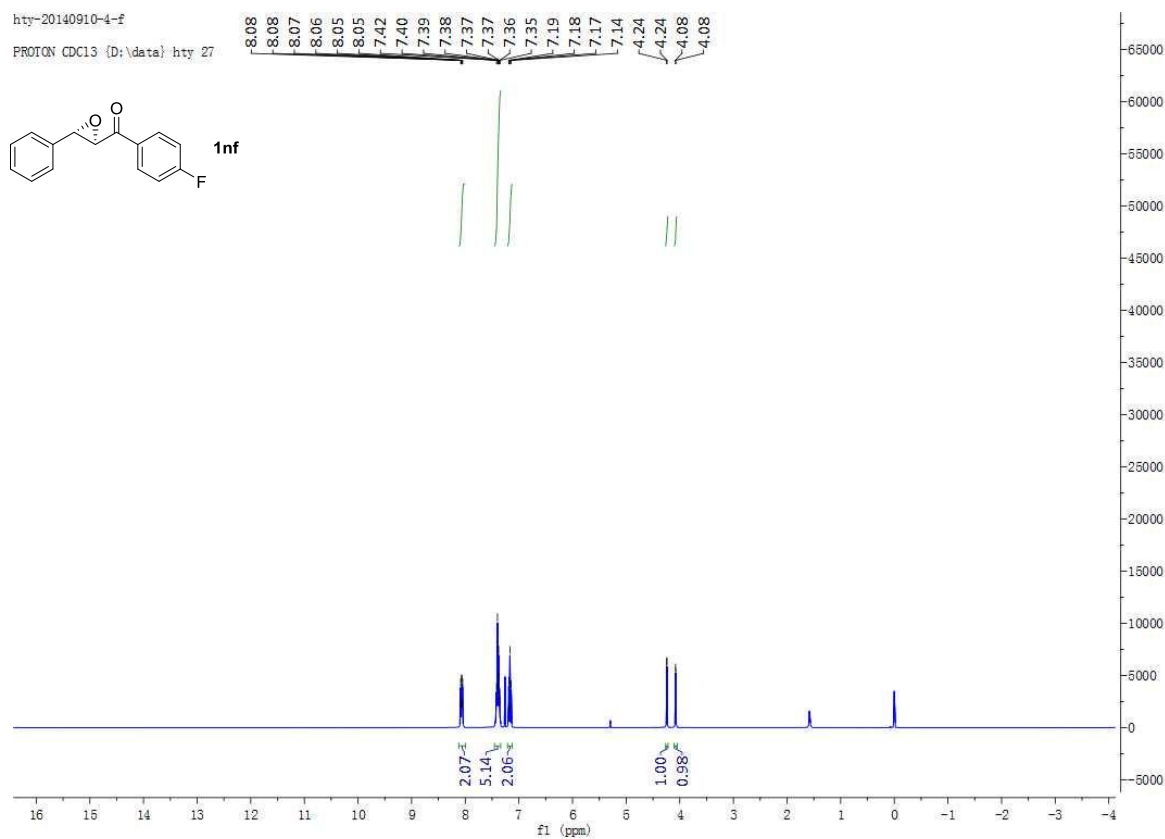
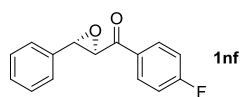




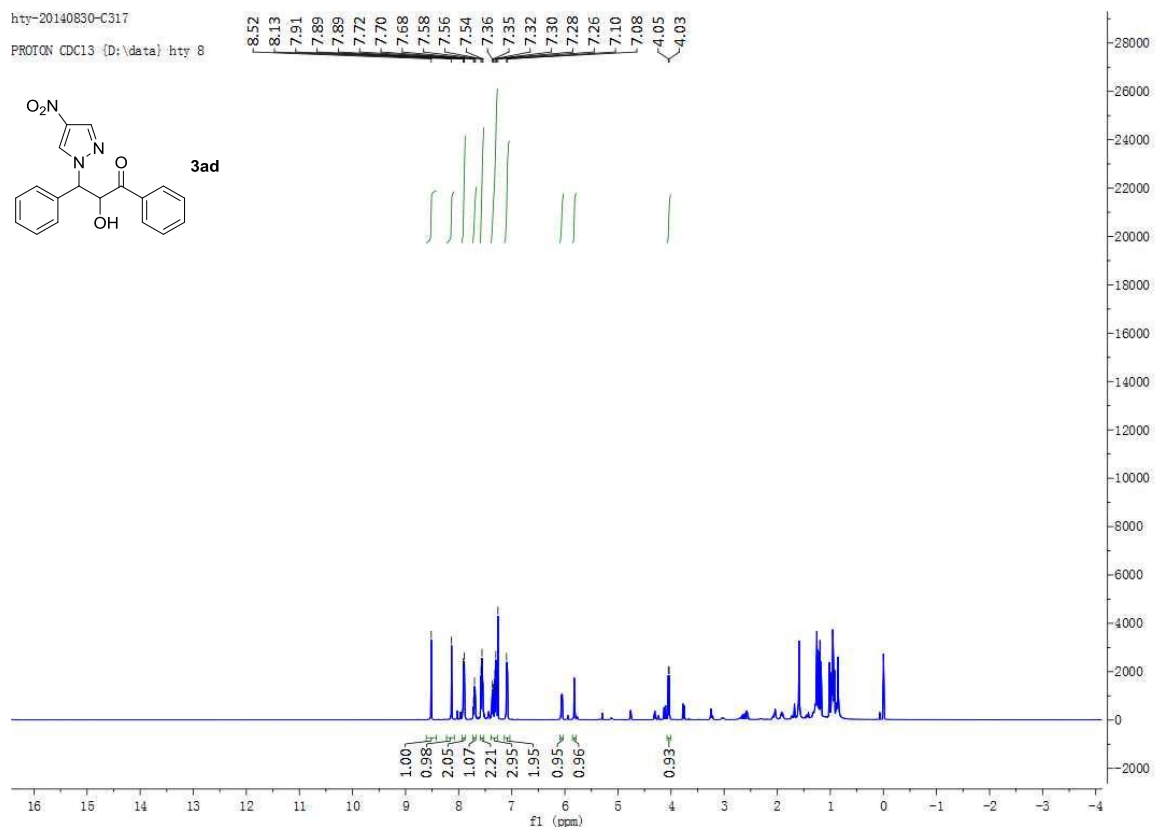
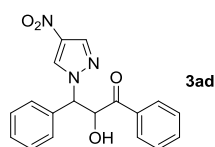


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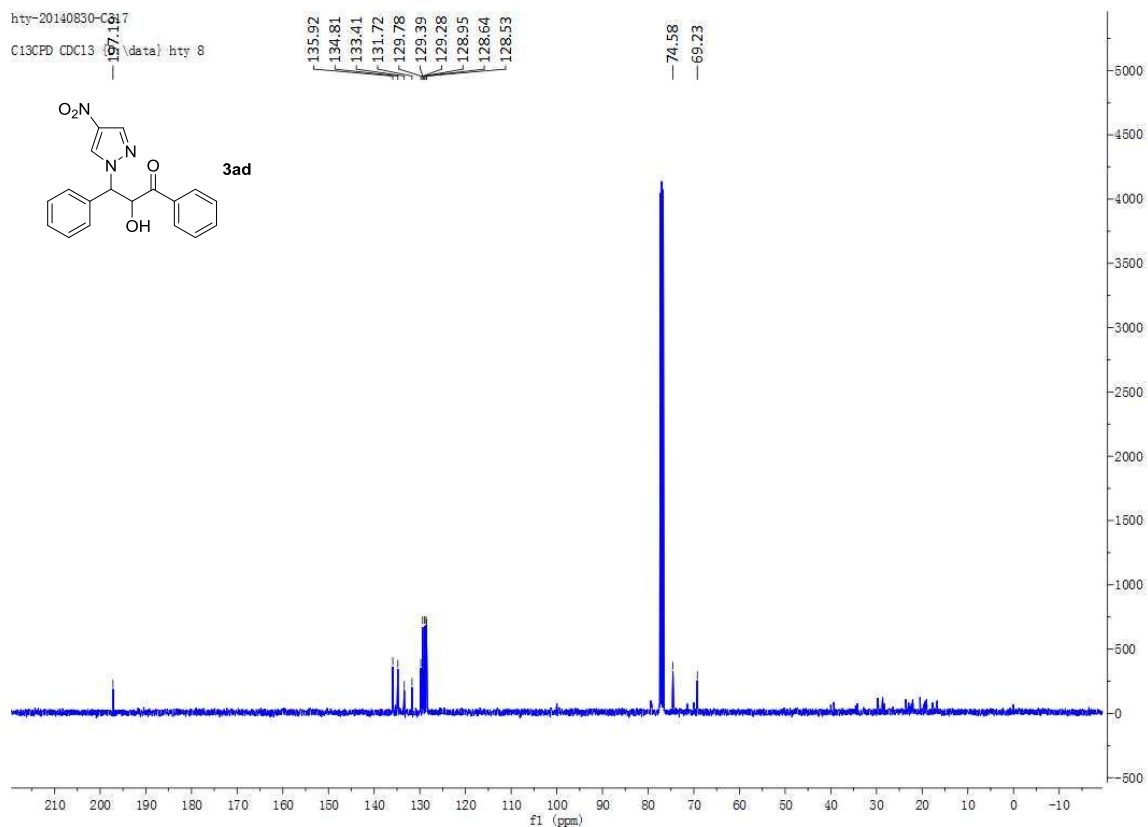
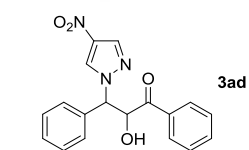
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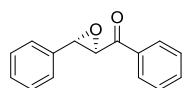


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