

Electronic Supplementary Information

Catalytic asymmetric amination of azlactones with azobenzenes

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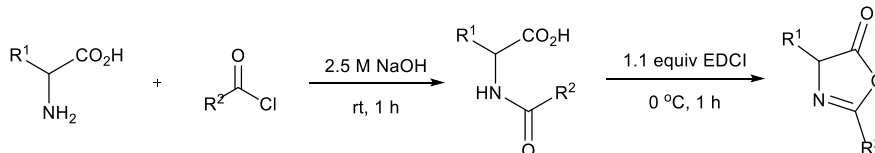
1. General Information

NMR characterization data were collected on Bruker ASCEND™ operating at 400 or 600 MHz for ^1H NMR, 101 or 151 MHz for ^{13}C NMR (with complete proton decoupling), and 377 or 565 MHz for $^{19}\text{F}\{^1\text{H}\}$ NMR (with complete proton decoupling). ^1H NMR and ^{13}C NMR: chemical shifts δ were recorded in ppm relative to tetramethylsilane and internally referenced to the residual solvent signal (for ^1H NMR: $\text{CDCl}_3 = 7.26$ ppm; for ^{13}C NMR: $\text{CDCl}_3 = 77.16$ ppm). $^{19}\text{F}\{^1\text{H}\}$ NMR: chemical shifts are reported in ppm with relative to CFCl_3 (external reference, $\delta(^{19}\text{F}(\text{CFCl}_3)) = 0$). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constants (Hz), integration. Enantiomeric excesses (ee) were determined by Ultra Performance Convergence Chromatography (UPCC) on systems on Daicel Chiralcel in the experimental procedures at 35 °C. High resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima (ν , cm^{-1}). Circular dichroism spectrum (CD) were recorded on Applied Photophysics Chirascan. Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows: $[\alpha]_D^{25}$ (c: g/100 mL, in CH_2Cl_2). Melting point ranges were determined on OptiMelt. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II.

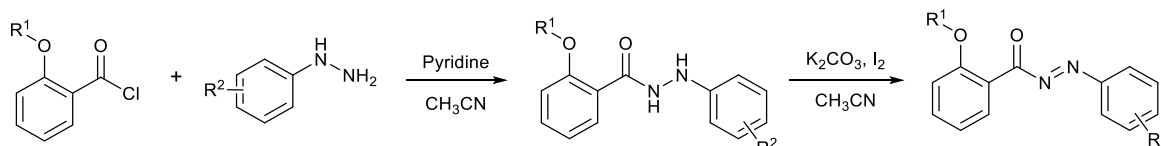
All catalytic reactions were run in dried glassware. THF, toluene and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl before use. Ethyl acetate, CH_2Cl_2 was distilled over CaH_2 before use. The experimental substrates azlactones¹, *N*-acyldiazene², and chiral *N,N'*-dioxide ligands³ were synthesized according to known procedures. The starting materials were purchased from Accela, 3A chemicals, Aladdin, Adamas, Acros, Aldrich or Ark, and used without further purification. Reactions were monitored using thin-layer chromatography (TLC) on GF254 silica gel. Visualization of the developed plates was performed under UV light (254 nm) or using iodine, cobalt thiocyanate or KMnO_4 . The products were purified by flash column chromatography with Silicycle 300–400 mesh silica gel.

2. General procedures for the preparation of the substrates

2.1 General procedure for the synthesis of azlactones according to the literature procedure.¹



2.2 General procedure for the synthesis of oxodiazene².

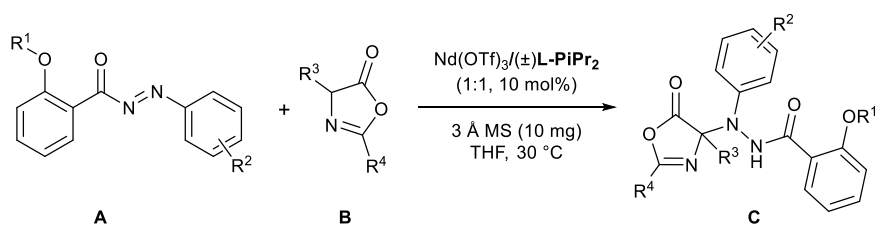


Step 1: A solution of the hydrazine (10 mmol) in MeCN (20 mL) was treated with pyridine (11 mmol), then acyl chloride (11 mmol) was added slowly at 0 °C and stirred at r.t. for 1 h. The reaction was subsequently quenched with 4M aq. HCl, and the solid hydrazide product was filtered and used in next step directly without further purified.

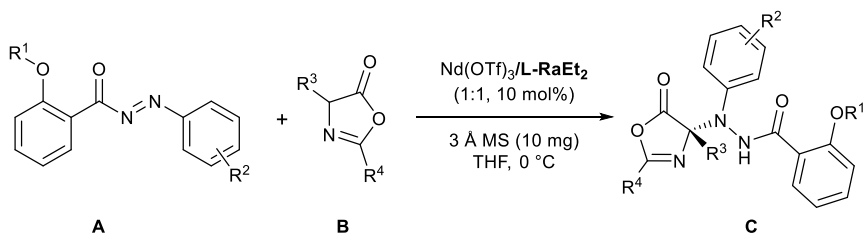
Step 2: A solution of the hydrazide (10 mmol) in MeCN (20 mL) was treated sequentially with I_2 (12 mmol) and K_2CO_3 (30 mmol), and then stirred at room temperature (25 °C) for 2 h until TLC indicated the disappearance of hydrazide. The reaction was subsequently quenched with sat. $\text{Na}_2\text{S}_2\text{O}_3$ (80 mL), diluted with H_2O (100 mL), and extracted with EtOAc (20 mL $\times$ 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the crude oxodiazene and purified by column chromatography. Then the residue was further recrystallized by petroleum ether /dichloromethane to give the desired oxodiazene.

3. General procedures for the preparation of the products

General procedure for the synthesis of racemic product: In a dry tube was charged with the $\text{Nd}(\text{OTf})_3/(\pm)\text{-L-PiPr}_2$ (1:1, 10 mol%), 3 Å MS (10 mg), oxodiazene **A** (0.10 mmol), and azlactone **B** (0.11 mmol) in THF (0.5 mL). The reaction was stirred at 30 °C and monitored by TLC. After the complete conversion of starting material, the solvent was removed under reduced pressure, and then the mixture was purified by column chromatography (petroleum ether/ethyl acetate = 2/1, v/v) to afford the product **C**.



Typical procedure for the asymmetric catalytic reaction: In a dry tube was charged with the $\text{Nd}(\text{OTf})_3/\text{L-RaEt}_2$ (1:1, 10 mol%), 3 Å MS (10 mg), oxodiazenes **A** (0.10 mmol), and azlactone **B** (0.11 mmol). Under N_2 atmosphere, the mixture was stirred at 0 °C for 10 min, and THF (0.5 mL) was added. Next the mixture was stirred at 0 °C and monitored by TLC until completion of the reaction. The mixture was purified by column chromatography (petroleum ether/ethyl acetate = 2/1, v/v) to afford the product **C**.



4. Optimization of the reaction conditions

Table S1. Screening of the reaction conditions ^[a]

	A0	B1	D0
entry	Metal salt	yield (%)	ee (%)
1	$\text{Mg}(\text{OTf})_2$	28	0
2	$\text{Al}(\text{OTf})_3$	24	0
3	$\text{Fe}(\text{OTf})_3$	trace	--
4	$\text{Co}(\text{OTf})_2$	13	0
5	$\text{Ni}(\text{OTf})_2$	18	0
6	$\text{Cu}(\text{OTf})_2$	20	0
7	$\text{Zn}(\text{OTf})_2$	15	0
8	$\text{Sc}(\text{OTf})_3$	trace	--
9	$\text{Y}(\text{OTf})_3$	22	4
10	$\text{Yb}(\text{OTf})_3$	21	5
11	$\text{La}(\text{OTf})_3$	43	11
12	$\text{Ce}(\text{OTf})_3$	41	10
13	$\text{Pr}(\text{OTf})_3$	37	7
14	$\text{Nd}(\text{OTf})_3$	37	11
15	$\text{Sm}(\text{OTf})_3$	30	4
16	$\text{Eu}(\text{OTf})_3$	24	2
17	$\text{Gd}(\text{OTf})_3$	29	0
18	$\text{Tb}(\text{OTf})_3$	30	3
19	$\text{Dy}(\text{OTf})_3$	25	-2
20	$\text{Ho}(\text{OTf})_3$	20	-2
21	$\text{Er}(\text{OTf})_3$	21	-2

22	Tm(OTf) ₃	21	-5
23	Lu(OTf) ₃	21	-2
24 ^[b]	La(OTf) ₃	57	34
25 ^[b,c]	La(OTf) ₃	72	43
26 ^[b,c,d]	La(OTf) ₃	68	55

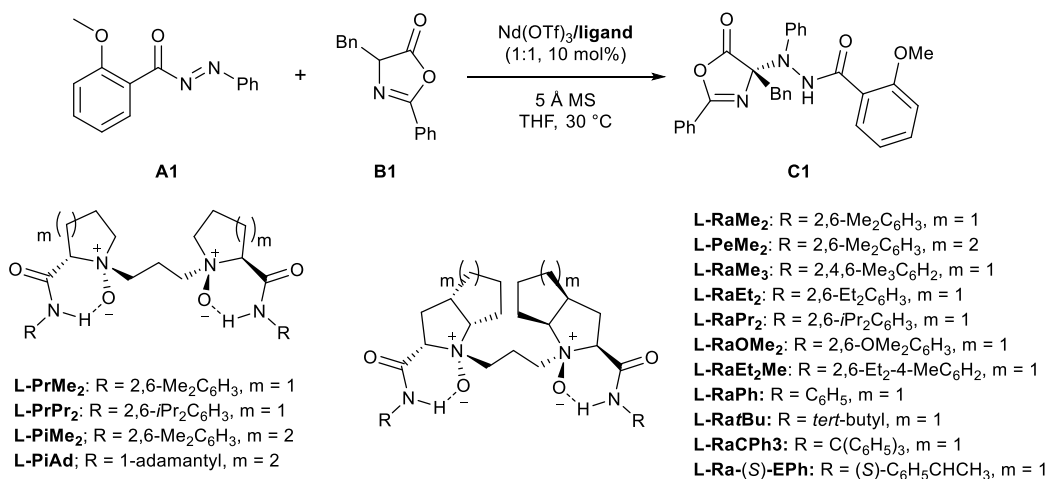
[a] Reaction condition: **A0** (0.1 mmol), **B1** (0.1 mmol), **M/L-PrPr₂** (1:1, 10 mol%) in THF (0.5 mL) at 30 °C for 24 h. Isolated yield, ee values were determined by UPCC analysis. [b] La(OTf)₃/**L-PiAd** (1:1, 10 mol%). [c] -10 °C for 4d. [d] 5 Å MS (10 mg).

Table S2. Screening of the metal salts ^[a]

entry	Metal salt	yield (%)	ee (%)
1	Mg(OTf) ₂	8	0
2	Al(OTf) ₃	9	0
3	Fe(OTf) ₃	5	0
7	Zn(OTf) ₂	22	6
8	Sc(OTf) ₃	13	10
9	Y(OTf) ₃	7	28
10	Yb(OTf) ₃	14	21
11	La(OTf) ₃	10	49
12	Ce(OTf) ₃	24	60
13	Pr(OTf) ₃	20	61
14	Nd(OTf) ₃	18	64
15	Sm(OTf) ₃	9	56
16	Eu(OTf) ₃	18	52
17	Gd(OTf) ₃	13	48
18	Tb(OTf) ₃	15	51
19	Dy(OTf) ₃	16	46

[a] Reaction condition: **A1** (0.1 mmol), **B1** (0.1 mmol), **M/L-PiAd** (1:1, 10 mol%) and 5 Å MS (10 mg) in THF (0.5 mL) at -10 °C for 48 h. Isolated yield, ee values were determined by UPCC analysis.

Table S3. Screening of the ligands ^[a]



entry	ligand	yield (%)	ee (%)
1	L-PrMe₂	29	49
2	L-PiMe₂	32	66
3	L-RaMe₂	70	85
4	L-PeMe₂	49	69
5	L-RaMe₃	66	80
6	L-RaEt₂	81	89
7	L-RaPr₂	40	23
8	L-RaOMe₂	44	52
9	L-RaEt₂Me	66	87
10	L-RaPh	40	32
11	L-RaⁱBu	56	71
12	L-RaCPh₃	37	4
13	L-Ra-(S)-Eph	55	48
14	w/o	n.r.	—

[a] Reaction condition: **A1** (0.1 mmol), **B1** (0.1mmol), Nd(OTf)₃/L (1:1, 10 mol%) and 5 Å MS (10 mg) in THF (0.5 mL) at 30 °C for 48 h. Isolated yield, ee values were determined by UPCC analysis.

Table S4. Screening of the metal salts ^[a]

A1 **B1** **C1**

entry	Metal salt	yield (%)	ee (%)
1	La(OTf) ₃	57	74
2	Ce(OTf) ₃	68	86
3	Pr(OTf) ₃	71	86
4	Nd(OTf) ₃	81	89
5	Sm(OTf) ₃	71	89
6	Eu(OTf) ₃	72	88
7	Gd(OTf) ₃	73	88

[a] Reaction condition: **A1** (0.1 mmol), **B1** (0.1 mmol), M/L-RaEt₂ (1:1, 10 mol%) and 5 Å MS (10 mg) in THF (0.5 mL) at 30 °C for 48 h. Isolated yield, ee values were determined by UPCC analysis.

Table S5. Screening of the solvents ^[a]

A1 **B1** **C1**

entry	solvent	yield (%)	ee (%)
1	CH ₂ Cl ₂	37	12
2	Et ₂ O	30	7
3	Toluene	32	8
4	AcOEt	50	61
5	THF	81	89

[a] Reaction condition: **A1** (0.1 mmol), **B1** (0.1 mmol), Nd(OTf)₃/**L-RaEt**₂ (1:1, 10 mol%) and 5 Å MS (10 mg) in solvent (0.5 mL) at 30 °C for 48 h. Isolated yield, ee values were determined by UPCC analysis.

Table S6. Screening of the additives ^[a]

A1 + **B1** $\xrightarrow[\text{additive, THF, 30 } ^\circ\text{C}]{\text{Nd(OTf)}_3/\text{L-RaEt}_2 \text{ (1:1, 10 mol\%)}}$ **C1**

entry	additive	yield (%)	ee (%)
1	3 Å MS (10 mg)	84	90
2	4 Å MS (10 mg)	81	89
3	5 Å MS (10 mg)	79	88
4	Na ₂ SO ₄ (1.0 equiv)	61	82
5	MgSO ₄ (1.0 equiv)	63	83
6	No additives	55	81

[a] Reaction condition: **A1** (0.1 mmol), **B1** (0.1 mmol), Nd(OTf)₃/**L-RaEt**₂ (1:1, 10 mol%) and additive in THF (0.5 mL) at 30 °C for 48 h. Isolated yield, ee values were determined by UPCC analysis.

Table S7. Screening of the ratio of metal salt and ligand ^[a]

A1 + **B1** $\xrightarrow[\text{3 Å MS, THF, 30 } ^\circ\text{C}]{\text{Nd(OTf)}_3/\text{L-RaEt}_2 \text{ (m:n, 10 mol\%)}}$ **C1**

entry	m:n (10 mol%)	yield (%)	ee (%)
1	1.2:1	77	85
2	1.1:1	84	88
3	1:1	84	90
4	1:1.1	87	90
5	1:1.2	82	90

[a] Reaction condition: **A1** (0.1 mmol), **B1** (0.1 mmol), Nd(OTf)₃/**L-RaEt**₂ (m:n, 10 mol%), and 3 Å MS (10 mg) in THF (0.5 mL) at 30 °C for 48 h. Isolated yield, ee values were determined by UPCC analysis.

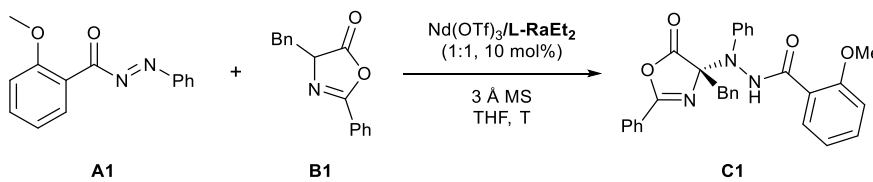
Table S8. Screening of the ratio of **1a** and **2a** ^[a]

A1 + **B1** $\xrightarrow[\text{3 Å MS, THF, 30 } ^\circ\text{C}]{\text{Nd(OTf)}_3/\text{L-RaEt}_2 \text{ (1:1, 10 mol\%)}}$ **C1**

entry	A1 : B1	yield (%)	ee (%)
1	1.5:1	84	89
2	1.2:1	79	90
3	1.1:1	84	90
4	1:1.1	86	90
5	1:1.2	80	90
6	1:1.5	80	89

[a] Reaction condition : **A1** or **B1** at 0.1 mmol scale, Nd(OTf)₃/**L-RaEt**₂ (1:1, 10 mol%) and 3 Å MS (10 mg) in THF (0.5 mL) at 30 °C for 48 h. Isolated yield, ee values were determined by UPCC analysis.

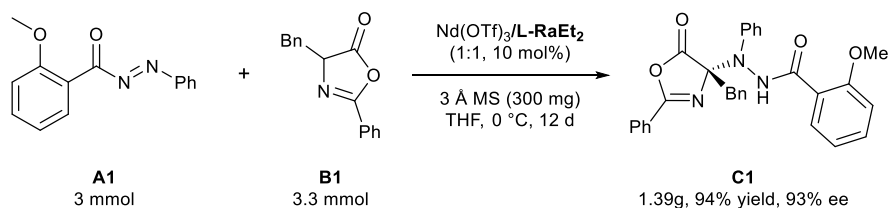
Table S9. Screening of the temperature ^[a]



entry	T (°C)	yield (%)	ee (%)
1	20	91	92
2	10	93	92
3	0	90	94
4	-10	75	94

[a] **A1** (0.1 mmol), **B1** (0.11 mmol), Nd(OTf)₃/**L-RaEt**₂ (1:1, 10 mol%) and 3 Å MS (10 mg) in THF (0.5 mL) for 3 d. Isolated yield, ee values were determined by UPCC analysis.

5. Gram-scale synthesis



To a 50 mL oven-dried round-bottom flask was charged with the Nd(OTf)₃/**L-RaEt**₂ (1:1, 10 mol%), 3 Å MS (300 mg). Under N₂ atmosphere, the mixture was stirred in THF (15 mL) at 30 °C for 4 h and then cooled to 0 °C for 30 min. Next **A1** and **B1** was added, and the mixture was stirred at 0 °C and monitored by TLC until completion of the reaction. The solvent was removed under reduced pressure, and the mixture was purified by column chromatography to afford the product **C1**.

6. X-ray diffraction analysis of the compound C2 and the catalyst

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **C2** in DCM and petroleum ether at r.t.. The colourless crystal in block-shape, with approximate dimensions of 0.558 × 0.315 × 0.256 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (K_{α} = 0.71073Å). The colourless crystal in block-shape, with approximate dimensions of 0.050 × 0.092 × 0.368 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_{α} = 1.54178Å).

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **L-RaEt**₂/Nd(OTf)₃ in MeOH and ether at r.t.. The colourless crystal in block-shape, with approximate dimensions of 0.418 × 0.226 × 0.156 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 170(2)K equipped with micro-focus Mo radiation source (K_{α} = 0.71073Å).

Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^{a, b, c, d}. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.

References:

- ^a Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.
- ^b Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3–8.
- ^c Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3–8.
- ^d Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **2009**, 42, 339-341.
- ^e Spek, A. L. *J. Appl. Cryst.* **2003**, 36, 7–13.

The crystal data and further details are listed in **Table S8**. CCDC **2158047**, and **2158159** which contain the crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ,

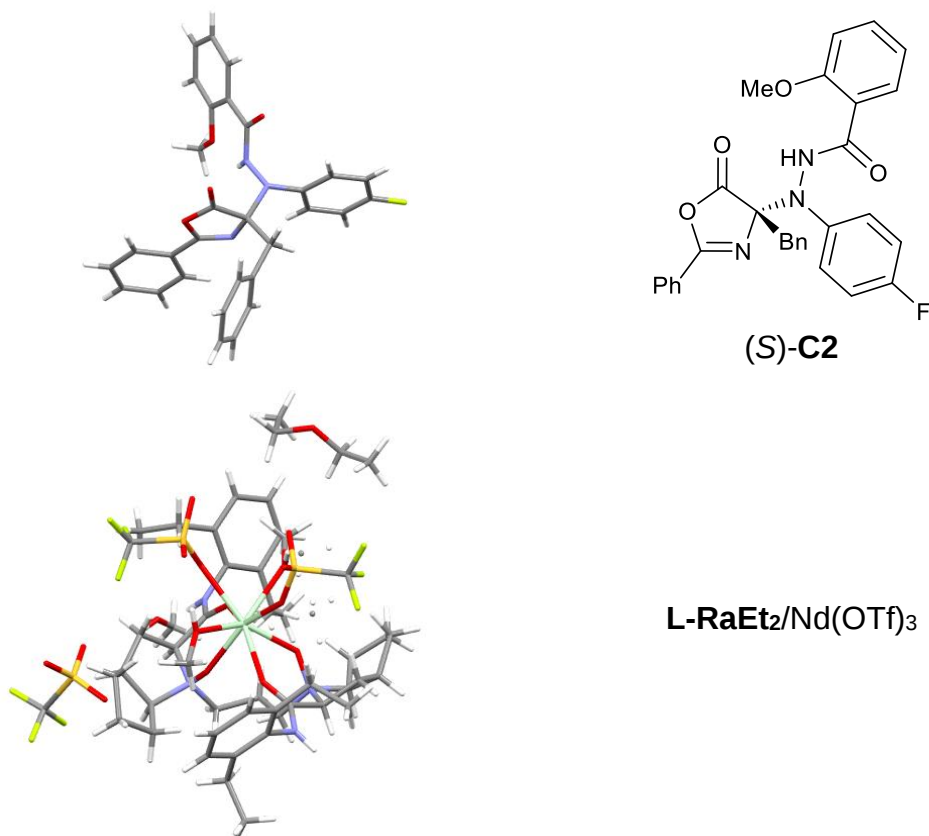


Table S10. The crystal data and further details.

compound	C2	L-RaEt₂/Nd(OTf)₃
Formula	C ₃₀ H ₂₄ FN ₃ O ₄	C ₄₉ H ₇₈ F ₉ N ₄ NdO ₁₇ S ₃
Formula mass (amu)	509.52	1406.57
Space group	P 21 21 2	P 21
<i>a</i> (Å)	10.3838(3)	11.9119(5)
<i>b</i> (Å)	37.4871(10)	20.9804(9)
<i>c</i> (Å)	6.6582(2)	13.0380(5)
α (deg)	90	90
β (deg)	90	105.863(1)
γ (deg)	90	90
<i>V</i> (Å ³)	2591.76(13)	3134.3(2)
<i>Z</i>	4	2
λ (Å)	1.54178	0.71073
<i>T</i> (K)	173 K	140 K
ρ_{calcd} (g cm ⁻³)	1.306	1.490
μ (mm ⁻¹)	0.763	1.021
Transmission factors	0.692–1.000	0.931–1.000
$2\theta_{\text{max}}$ (deg)	80.727	27.545
No. of unique data, including $F_o^2 < 0$	5304	14436
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	5013	14154
No. of variables	348	787
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0407	0.0216

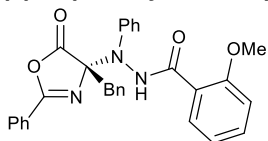
$R_w(F_o^2)^b$	0.1068	0.0500
Goodness of fit	1.066	1.113

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

7. Characterization of the products

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C1)



White solid; m.p. 77–82 °C; 44.0 mg, 90% yield, 94% ee; $[\alpha]_D^{21} = -109.67$ ($c = 4.15$ in CH_2Cl_2).

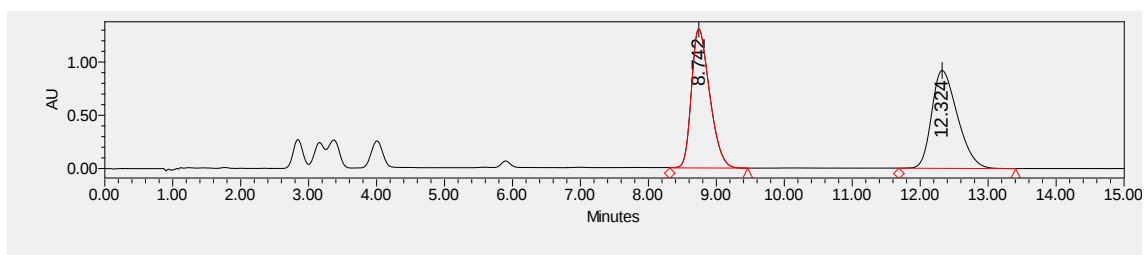
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 8.66 min, t_R (minor) = 12.20 min.

IR (neat): 3322, 3062, 1652, 1598, 1482, 1289, 1234 and 698 cm^{-1} .

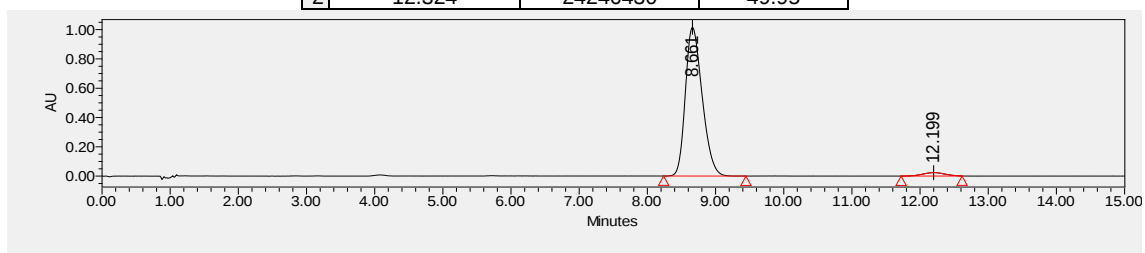
^1H NMR (600 MHz, CDCl_3) δ = 9.80 (s, 1H), 8.24 – 8.24 (m, 1H), 7.93 – 7.86 (m, 2H), 7.73 – 7.67 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.37 – 7.33 (m, 2H), 7.24 – 7.22 (m, 1H), 7.18 – 7.14 (m, 2H), 7.14 – 7.07 (m, 3H), 7.05 – 7.01 (m, 1H), 6.90 – 6.84 (m, 1H), 3.65 (s, 3H), 3.58 (d, $J = 13.2$ Hz, 1H), 3.34 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.5, 163.8, 161.8, 157.3, 146.0, 133.3, 133.3, 133.0, 133.0, 130.7, 129.1, 128.92, 128.3, 128.2, 127.5, 127.3, 126.9, 125.3, 121.6, 120.4, 111.3, 91.0, 55.8, 41.9.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{26}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 492.1918, Found 429.1918.

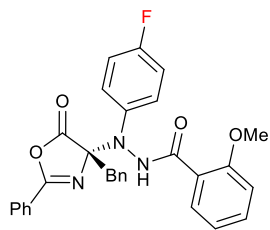


	Retention Time	Area	% Area
1	8.742	24291684	50.05
2	12.324	24246430	49.95



	Retention Time	Area	% Area
1	8.661	17360076	97.03
2	12.199	532089	2.97

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N'-(4-fluorophenyl)-2-methoxybenzohydrazide (C2)



White solid; m.p. 140–145 °C; 33.3 mg, 65% yield, 90% ee; $[\alpha]_D^{21} = -109.31$ ($c = 0.75$ in CH_2Cl_2).

UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 6.30 min, t_R (minor) = 7.72 min.

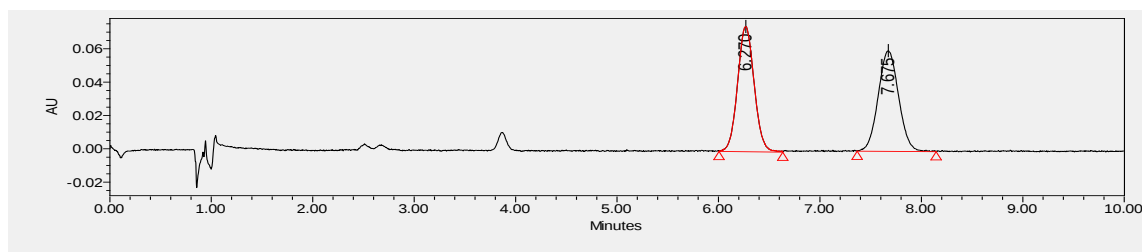
IR (neat): 3322, 3066, 2361, 1829, 1654, 1600, 1503, 1291, 1238 and 701 cm^{-1} .

^1H NMR (600 MHz, CDCl_3) δ = 9.78 (s, 1H), 8.25 – 8.12 (m, 1H), 7.94 – 7.84 (m, 2H), 7.76 – 7.68 (m, 2H), 7.60 – 7.55 (m, 1H), 7.48 – 7.43 (m, 2H), 7.43 – 7.38 (m, 1H), 7.16 – 7.08 (m, 5H), 7.06 – 6.99 (m, 3H), 6.90 – 6.84 (m, 1H), 3.64 (s, 3H), 3.53 (d, $J = 13.2$ Hz, 1H), 3.29 (d, $J = 13.2$ Hz, 1H).

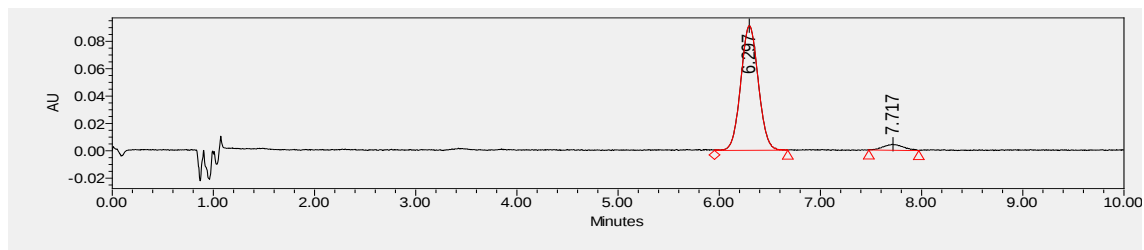
^{13}C NMR (151 MHz, CDCl_3) δ = 174.4, 163.8, 162.0, 161.6 (d, $J = 246.4$ Hz), 157.3, 142.0 (d, $J = 3.2$ Hz), 133.5, 133.4, 132.9, 132.8, 130.7, 129.1 (d, $J = 8.7$ Hz), 129.0, 128.3, 128.1, 127.5, 125.1, 121.6, 120.3, 115.9 (d, $J = 22.8$ Hz), 111.3, 91.0, 77.4, 77.2, 76.9, 55.8, 41.9.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ = -114.1.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}\text{FN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 510.1824, Found 510.1826.

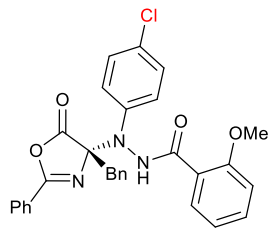


	Retention Time	Area	% Area
1	6.270	854431	50.32
2	7.675	843603	49.68



	Retention Time	Area	% Area
1	6.297	1095209	94.83
2	7.717	59766	5.17

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N'-(4-chlorophenyl)-2-methoxybenzohydrazide (C3)



Colorless oil; 34.2 mg, 65% yield, 85% ee; $[\alpha]_D^{21} = -89.36$ ($c = 0.72$ in CH_2Cl_2).

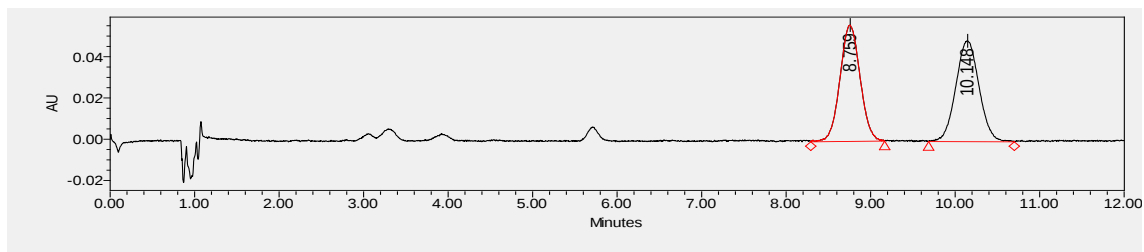
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 8.77 min, t_R (minor) = 10.20 min.

IR (neat): 3320, 3065, 2361, 1829, 1654, 1600, 1484, 1292, 1239 and 700 cm^{-1} .

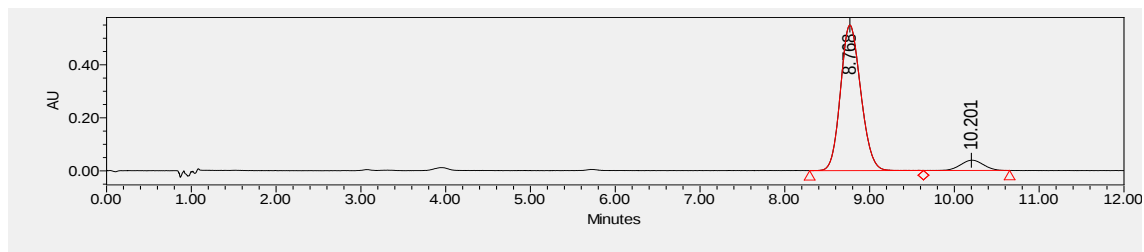
^1H NMR (600 MHz, CDCl_3) δ = 9.81 (s, 1H), 8.23 – 8.14 (m, 1H), 7.91 – 7.85 (m, 2H), 7.68 – 7.61 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 – 7.44 (m, 2H), 7.43 – 7.40 (m, 1H), 7.33 – 7.29 (m, 2H), 7.16 – 7.09 (m, 5H), 7.06 – 7.02 (m, 1H), 6.90 – 6.86 (m, 1H), 3.67 (s, 3H), 3.55 (d, $J = 13.2$ Hz, 1H), 3.34 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.3, 163.8, 162.0, 157.3, 144.6, 133.5, 133.5, 133.0, 132.8, 132.7, 130.7, 129.3, 129.0, 128.3, 128.2, 127.6, 125.1, 121.6, 120.2, 111.3, 90.8, 77.4, 77.2, 76.9, 55.8, 41.9.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}^{35}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 526.1528, Found 526.1534, $\text{C}_{30}\text{H}_{25}^{37}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 527.1562, Found 527.1566.

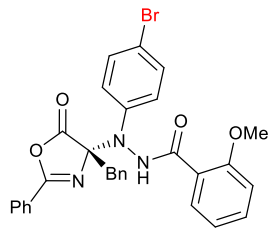


	Retention Time	Area	% Area
1	8.759	931753	49.91
2	10.148	934992	50.09



	Retention Time	Area	% Area
1	8.768	9102945	92.54
2	10.201	733848	7.46

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N'-(4-bromophenyl)-2-methoxybenzohydrazide (C4)



Colorless oil; 33.4 mg, 59% yield, 83% ee; $[\alpha]^{21}_D = -69.43$ ($c = 0.57$ in CH_2Cl_2).

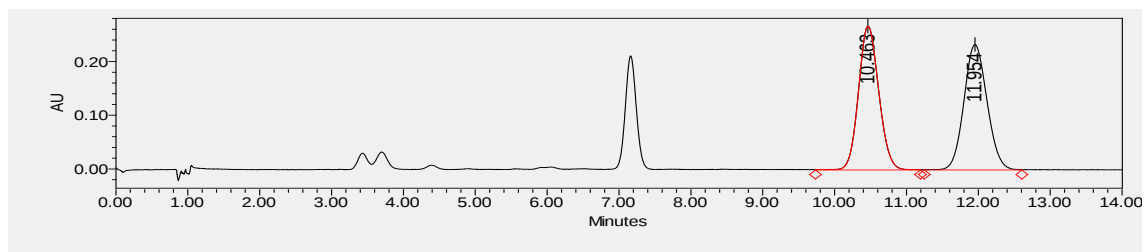
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 10.59 min, t_R (minor) = 12.20 min.

IR (neat): 3321, 3064, 2361, 1828, 1654, 1600, 1483, 1292, 1239 and 700 cm^{-1} .

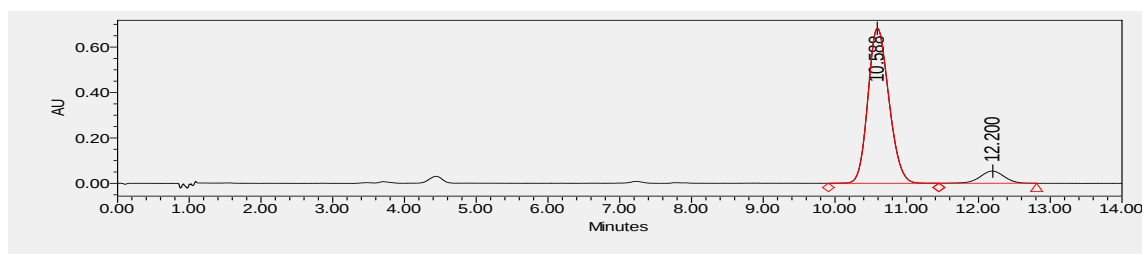
^1H NMR (600 MHz, CDCl_3) $\delta = 9.81$ (s, 1H), 8.22 – 8.12 (m, 1H), 7.94 – 7.82 (m, 2H), 7.60 – 7.55 (m, 3H), 7.48 – 7.40 (m, 5H), 7.16 – 7.08 (m, 5H), 7.06 – 7.02 (m, 1H), 6.90 – 6.86 (m, 1H), 3.68 (s, 3H), 3.55 (d, $J = 13.2$ Hz, 1H), 3.35 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) $\delta = 174.3, 163.9, 162.0, 157.3, 145.1, 133.5, 132.9, 132.6, 132.2, 130.7, 129.0, 128.4, 128.3, 128.2, 127.6, 125.0, 121.6, 120.8, 120.2, 111.3, 90.8, 77.4, 77.2, 76.9, 55.8, 41.9$.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}^{79}\text{BrN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 570.1023, Found 570.1027, $\text{C}_{30}\text{H}_{25}^{81}\text{BrN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 572.1002, Found 572.1008.

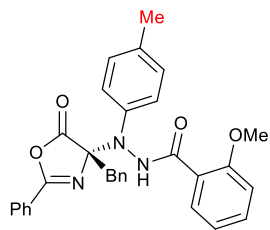


	Retention Time	Area	% Area
1	10.463	5245565	50.12
2	11.954	5220635	49.88



	Retention Time	Area	% Area
1	10.588	13860068	91.65
2	12.200	1262245	8.35

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-(p-tolyl)benzohydrazide (C5)



Colorless oil; 40.0 mg, 80% yield, 94% ee; $[\alpha]^{21}_D = -68.26$ ($c = 1.42$ in CH_2Cl_2).

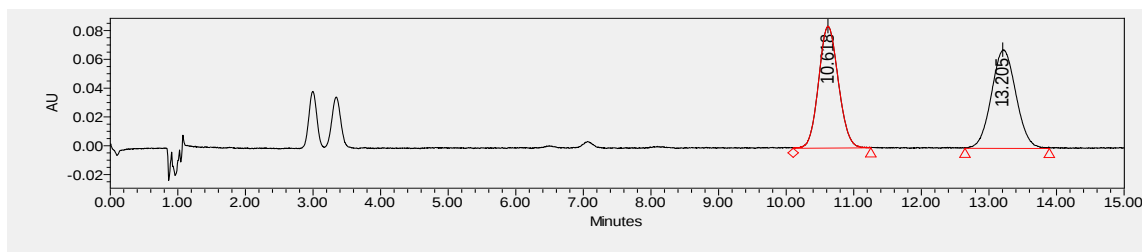
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 10.88 min, t_R (minor) = 13.86 min.

IR (neat): 3324, 3031, 2361, 1828, 1653, 1601, 1511, 1480, 1292, 1239 and 700 cm^{-1} .

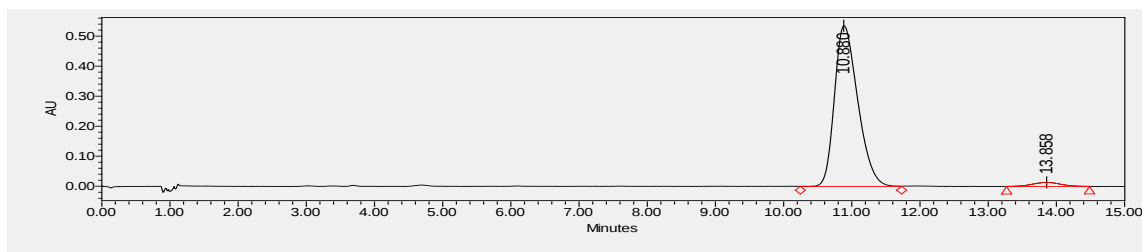
^1H NMR (600 MHz, CDCl_3) δ = 9.75 (s, 1H), 8.23 – 8.15 (m, 1H), 7.96 – 7.84 (m, 2H), 7.62 – 7.54 (m, 3H), 7.47 – 7.43 (m, 2H), 7.41 – 7.36 (m, 1H), 7.18 – 7.13 (m, 4H), 7.13 – 7.08 (m, 3H), 7.04 – 7.00 (m, 1H), 6.88 – 6.80 (m, 1H), 3.62 (s, 3H), 3.56 (d, $J = 13.2$ Hz, 1H), 3.32 (d, $J = 13.2$ Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.5, 163.7, 161.7, 157.3, 143.5, 137.3, 133.3, 133.2, 133.0, 132.9, 130.7, 129.7, 128.9, 128.2, 128.1, 127.4, 127.0, 125.3, 121.5, 120.5, 111.2, 91.2, 77.4, 77.2, 76.9, 55.7, 42.0, 21.2.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 506.2074, Found 506.2074.

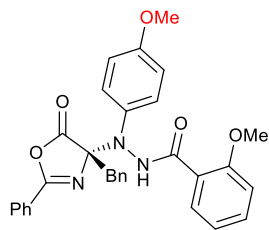


	Retention Time	Area	% Area
1	10.618	1715808	49.85
2	13.205	1726280	50.15



	Retention Time	Area	% Area
1	10.880	12706413	97.01
2	13.858	391066	2.99

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-(4-methoxyphenyl)benzohydrazide (C6)



Colorless oil; 48.7 mg, 93% yield, 94% ee; $[\alpha]^{22}_D = -63.62$ ($c = 0.84$ in CH_2Cl_2).

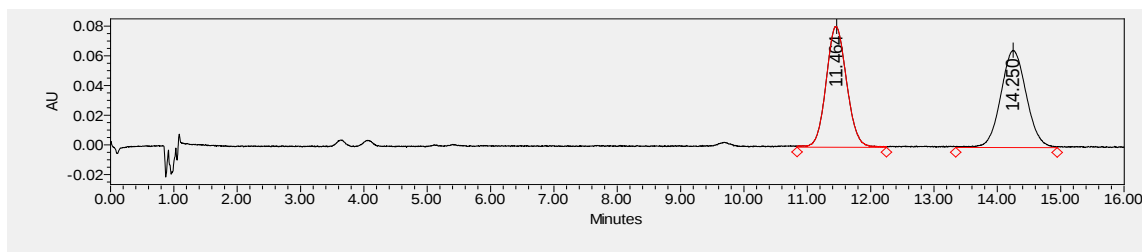
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 11.43 min, t_R (minor) = 14.37 min.

IR (neat): 3322, 2938, 2360, 1828, 1652, 1600, 1506, 1292, 1244 and 699 cm^{-1} .

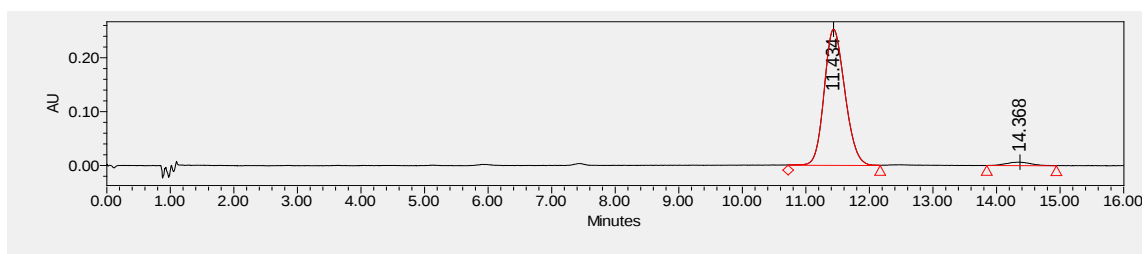
^1H NMR (600 MHz, CDCl_3) δ = 9.70 (s, 1H), 8.23 – 8.14 (m, 1H), 7.94 – 7.86 (m, 2H), 7.72 – 7.65 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.40 – 7.35 (m, 1H), 7.17 – 7.14 (m, 2H), 7.13 – 7.07 (m, 3H), 7.03 – 6.99 (m, 1H), 6.88 – 6.85 (m, 2H), 6.85 – 6.82 (m, 1H), 3.76 (s, 3H), 3.60 (s, 3H), 3.53 (d, $J = 13.2$ Hz, 1H), 3.27 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.4, 163.6, 161.8, 158.7, 157.3, 138.9, 133.3, 133.2, 133.1, 132.9, 130.6, 128.9, 128.8, 128.2, 128.1, 127.4, 125.3, 121.5, 120.5, 114.2, 111.2, 91.3, 77.4, 77.2, 76.9, 55.7, 55.5, 42.0.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_5^+$ ($[\text{M}+\text{H}^+]$) = 522.2023, Found 522.2023.

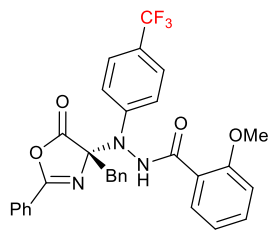


	Retention Time	Area	% Area
1	11.464	1831904	50.05
2	14.250	1828374	49.95



	Retention Time	Area	% Area
1	11.434	5715216	96.94
2	14.368	180491	3.06

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-(4-(trifluoromethyl)phenyl)benzohydrazide (C7)



White solid; m.p. 60–65 °C; 25.5 mg, 45% yield, 83% ee; $[\alpha]^{22}_D = -80.49$ ($c = 0.41$ in CH_2Cl_2).

UPCC (chiral IB-3 column), $\text{CO}_2/\text{MeOH} = 90/10$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 6.57 min, t_R (minor) = 7.35 min.

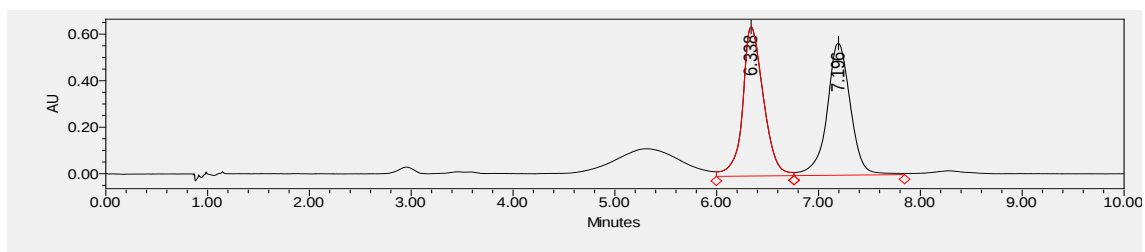
IR (neat): 3319, 2361, 1829, 1654, 1600, 1481, 1324, 1118 and 700 cm^{-1} .

^1H NMR (400 MHz, CDCl_3) $\delta = 9.91$ (s, 1H), 8.22 – 8.15 (m, 1H), 7.90 – 7.84 (m, 2H), 7.75 – 7.68 (m, 2H), 7.61 – 7.55 (m, 3H), 7.48 – 7.42 (m, 3H), 7.18 – 7.11 (m, 5H), 7.09 – 7.04 (m, 1H), 6.96 – 6.90 (m, 1H), 3.76 (s, 3H), 3.60 (d, $J = 13.2$ Hz, 1H), 3.46 (d, $J = 13.2$ Hz, 1H).

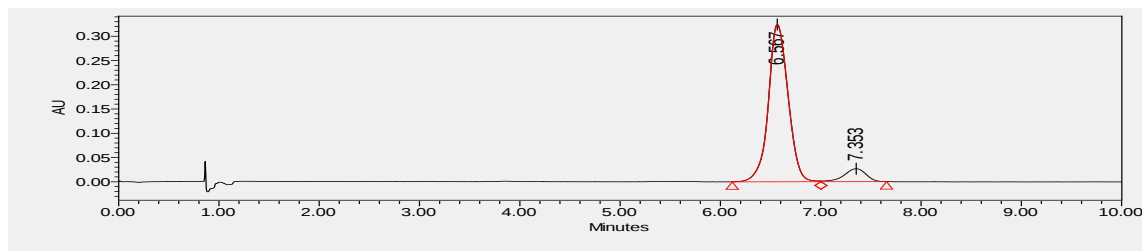
^{13}C NMR (101 MHz, CDCl_3) $\delta = 174.3, 164.2, 162.1, 157.4, 149.1, 133.7, 133.6, 133.0, 132.5, 130.8, 129.0, 128.4, 128.2, 127.7, 126.3$ (q, $J = 3.6$ Hz), 125.2, 125.0, 121.8, 120.0, 111.4, 90.4, 77.5, 77.2, 76.8, 55.9, 42.0.

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3) $\delta = -62.3$.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{25}\text{F}_3\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 560.1792, Found 560.1791.

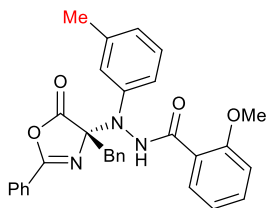


	Retention Time	Area	% Area
1	6.338	9130461	50.07
2	7.196	9104536	49.93



	Retention Time	Area	% Area
1	6.567	4431076	91.64
2	7.353	404151	8.36

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-(m-tolyl)benzohydrazide (C8)



Colorless oil; 40.5 mg, 80% yield, 94% ee; $[\alpha]_D^{21} = -85.70$ ($c = 0.79$ in CH_2Cl_2).

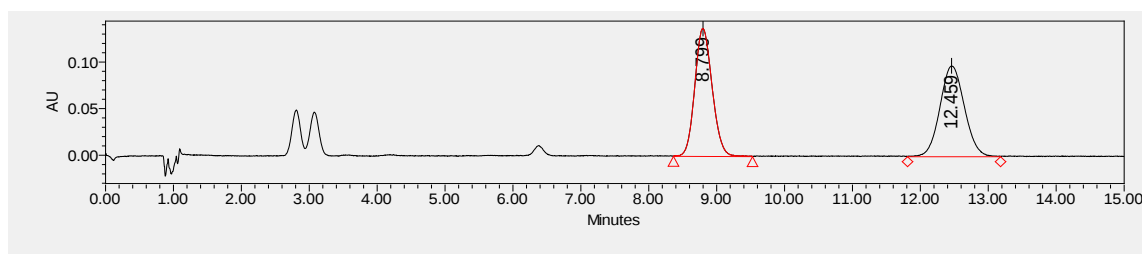
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 8.72 min, t_R (minor) = 12.33 min.

IR (neat): 3323, 3032, 2360, 1829, 1653, 1601, 1482, 1291, 1239 and 702 cm^{-1} .

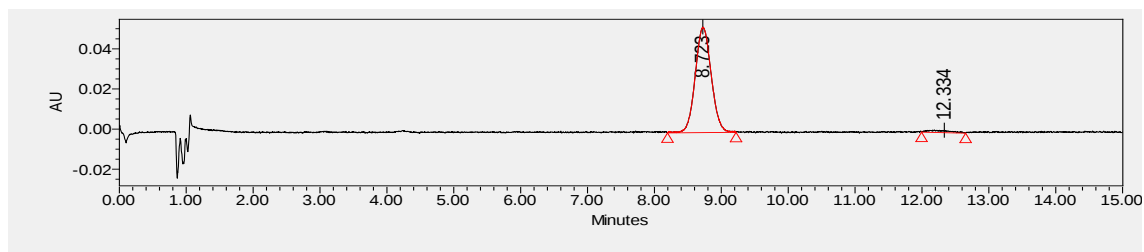
^1H NMR (600 MHz, CDCl_3) δ = 9.77 (s, 1H), 8.23 – 8.15 (m, 1H), 7.93 – 7.84 (m, 2H), 7.58 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 7.47 – 7.43 (m, 2H), 7.41 – 7.38 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 7.13 – 7.08 (m, 3H), 7.05 – 7.00 (m, 2H), 6.89 – 6.82 (m, 1H), 3.64 (s, 3H), 3.57 (d, $J = 13.2$ Hz, 1H), 3.34 (d, $J = 13.2$ Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.5, 163.8, 161.8, 157.3, 145.9, 138.9, 133.3, 133.3, 133.0, 133.0, 130.7, 128.9, 128.8, 128.2, 128.1, 128.0, 127.4, 125.3, 123.4, 121.5, 120.5, 111.3, 91.0, 77.4, 77.2, 76.9, 55.7, 41.9, 21.6.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) = 506.2074, Found 506.2077.

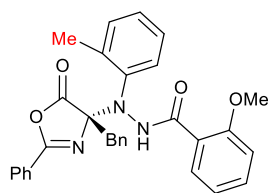


	Retention Time	Area	% Area
1	8.799	2440373	50.00
2	12.459	2440077	50.00



	Retention Time	Area	% Area
1	8.723	872956	97.00
2	12.334	27037	3.00

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-(o-tolyl)benzohydrazide (C9)



Colorless oil; 46.8 mg, 93% yield, 94% ee; $[\alpha]^{22}_D = -62.04$ ($c = 0.92$ in CH_2Cl_2).

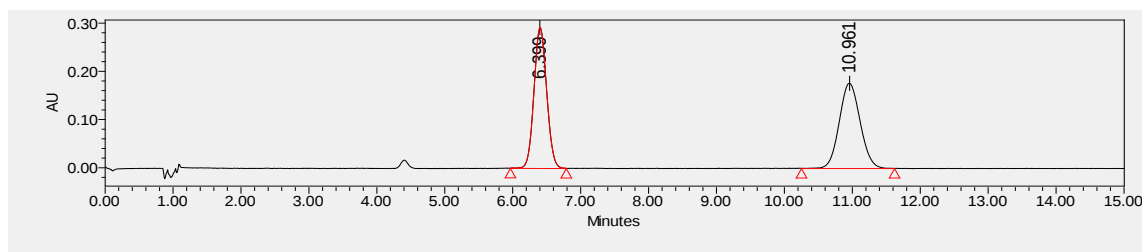
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 6.65 min, t_R (minor) = 11.46 min.

IR (neat): 3327, 3063, 2361, 1827, 1653, 1600, 1482, 1290, 1236 and 700 cm^{-1} .

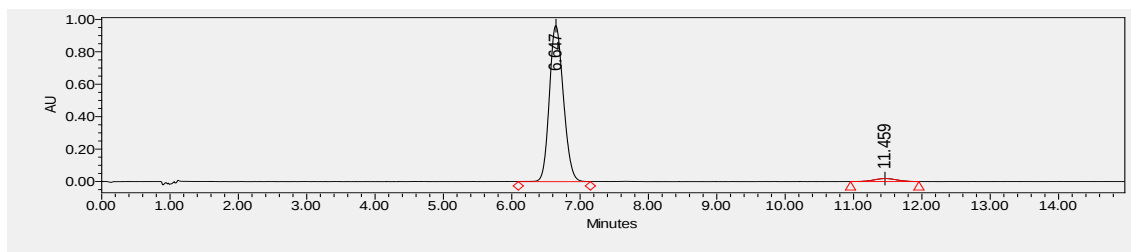
^1H NMR (600 MHz, CDCl_3) δ = 9.89 (s, 1H), 8.22 – 8.13 (m, 1H), 7.91 – 7.84 (m, 2H), 7.66 – 7.58 (m, 1H), 7.57 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 7.41 – 7.37 (m, 1H), 7.26 – 7.23 (m, 1H), 7.18 – 7.08 (m, 7H), 7.04 – 7.00 (m, 1H), 6.92 – 6.82 (m, 1H), 3.70 (s, 3H), 3.52 (d, $J = 13.2$ Hz, 1H), 3.27 (d, $J = 13.2$ Hz, 1H), 2.89 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ = 163.7, 161.5, 157.3, 144.6, 139.3, 133.2, 133.2, 133.0, 132.8, 131.3, 130.7, 128.9, 128.2, 128.1, 127.9, 127.4, 126.6, 125.4, 121.5, 120.6, 111.3, 91.3, 77.4, 77.4, 77.2, 76.9, 55.8, 41.3, 18.9.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 506.2074, Found 506.2074.

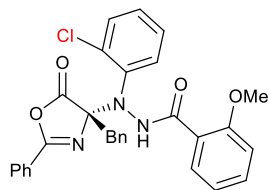


	Retention Time	Area	% Area
1	6.399	3792819	50.04
2	10.961	3786464	49.96



	Retention Time	Area	% Area
1	6.647	13692200	96.96
2	11.459	429572	3.04

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N'-(2-chlorophenyl)-2-methoxybenzohydrazide (C10)



Colorless oil; 40.9 mg, 78% yield, 85% ee; $[\alpha]^{22}_D = -40.05$ ($c = 0.86$ in CH_2Cl_2).

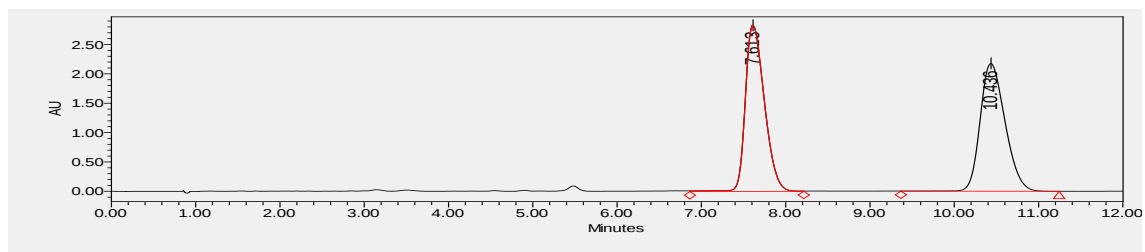
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 7.74 min, t_R (minor) = 10.74 min.

IR (neat): 3330, 3064, 2361, 1827, 1655, 1600, 1477, 1291, 1238 and 699 cm^{-1} .

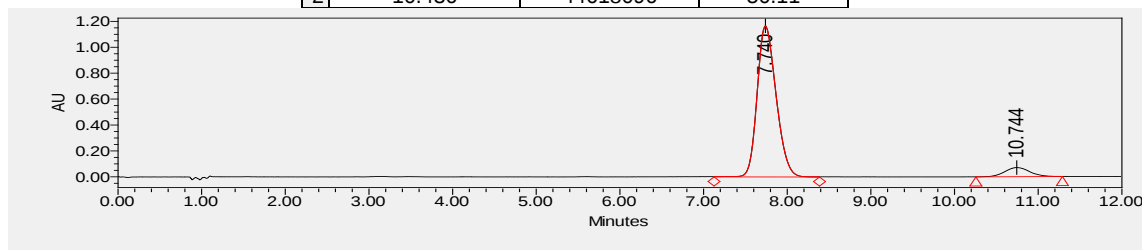
^1H NMR (600 MHz, CDCl_3) δ = 9.98 (s, 1H), 8.14 – 8.03 (m, 2H), 7.92 – 7.83 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.40 (m, 3H), 7.39 – 7.35 (m, 1H), 7.35 – 7.31 (m, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.14 (m, 2H), 7.14 – 7.08 (m, 3H), 7.00 – 6.95 (m, 1H), 6.87 – 6.83 (m, 1H), 3.70 (s, 3H), 3.53 (d, $J = 13.2$ Hz, 1H), 3.25 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.6, 164.4, 161.3, 157.4, 141.5, 133.7, 133.3, 133.1, 132.8, 132.7, 130.8, 130.6, 128.8, 128.7, 128.2, 127.4, 127.4, 125.4, 121.4, 120.3, 111.3, 90.9, 77.4, 77.2, 76.9, 55.8, 41.4.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}^{35}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 526.1528, Found 526.1530, $\text{C}_{30}\text{H}_{25}^{37}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 527.1562, Found 527.1560.

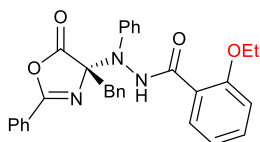


	Retention Time	Area	% Area
1	7.613	44417718	49.89
2	10.436	44618096	50.11



	Retention Time	Area	% Area
1	7.740	18322125	92.59
2	10.744	1465762	7.41

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-ethoxy-N'-phenylbenzohydrazide (C11)



Colorless oil; 28.6 mg, 56% yield, 88% ee; $[\alpha]^{22}_D = -125.157$ ($c = 0.64$ in CH_2Cl_2).

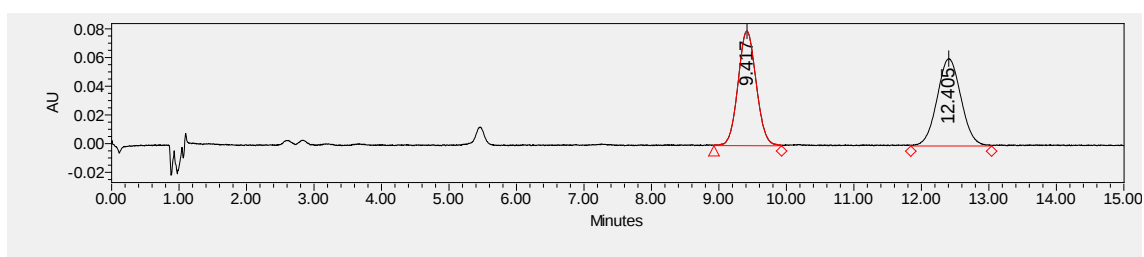
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 9.33 min, t_R (minor) = 12.20 min.

IR (neat): 3322, 3063, 2361, 1828, 1654, 1599, 1487, 1292, 1232 and 700 cm^{-1} .

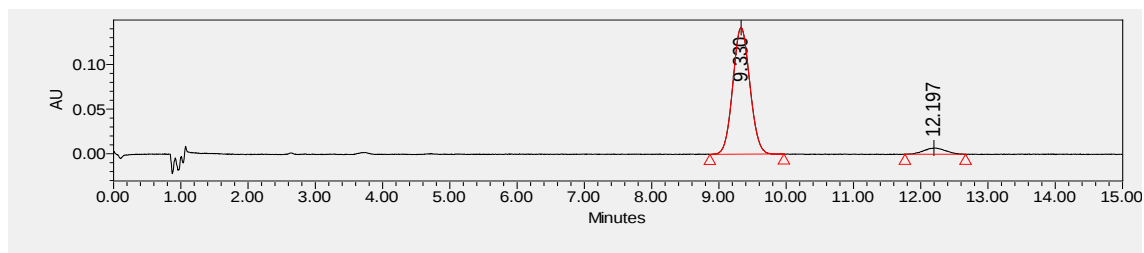
^1H NMR (600 MHz, CDCl_3) δ = 9.97 (s, 1H), 8.28 – 8.18 (m, 1H), 7.86 – 7.80 (m, 2H), 7.73 – 7.64 (m, 2H), 7.57 – 7.52 (m, 1H), 7.44 – 7.37 (m, 3H), 7.35 – 7.30 (m, 2H), 7.23 – 7.19 (m, 1H), 7.17 – 7.14 (m, 2H), 7.13 – 7.07 (m, 3H), 7.05 – 7.01 (m, 1H), 6.91 – 6.85 (m, 1H), 4.15 – 4.03 (m, 2H), 3.59 (d, $J = 13.2$ Hz, 1H), 3.40 (d, $J = 13.2$ Hz, 1H), 1.45 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.2, 164.3, 161.5, 156.7, 146.1, 133.3, 133.2, 133.1, 133.0, 130.7, 129.2, 128.8, 128.2, 128.2, 127.4, 127.1, 125.3, 121.4, 120.5, 112.1, 91.2, 77.4, 77.2, 76.9, 64.8, 42.2, 14.9.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) = 506.2074, Found 506.2075.

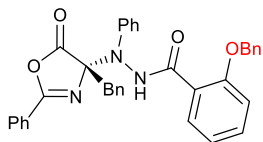


	Retention Time	Area	% Area
1	9.417	1488877	49.76
2	12.405	1503312	50.24



	Retention Time	Area	% Area
1	9.330	2494401	94.07
2	12.197	157226	5.93

(S)-N'-(4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-(benzyloxy)-N'-phenylbenzohydrazide (C12)



Colorless oil; 28.0 mg, 49% yield, 87% ee; $[\alpha]^{22}_D = -73.90$ ($c = 0.64$ in CH_2Cl_2).

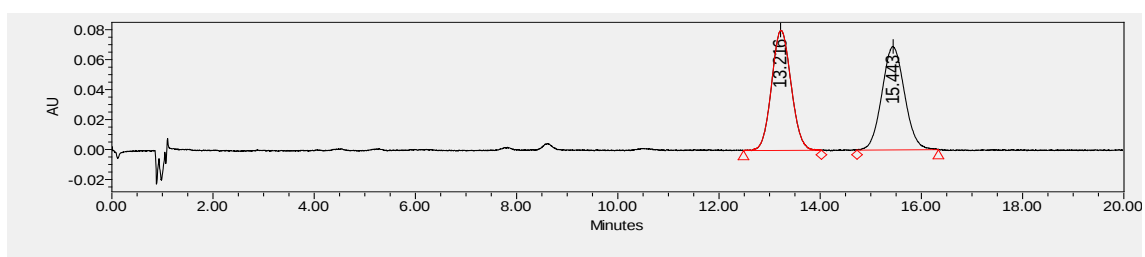
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 12.12 min, t_R (minor) = 15.27 min.

IR (neat): 3325, 3063, 2361, 1827, 1654, 1599, 1489, 1292, 1228 and 699 cm^{-1} .

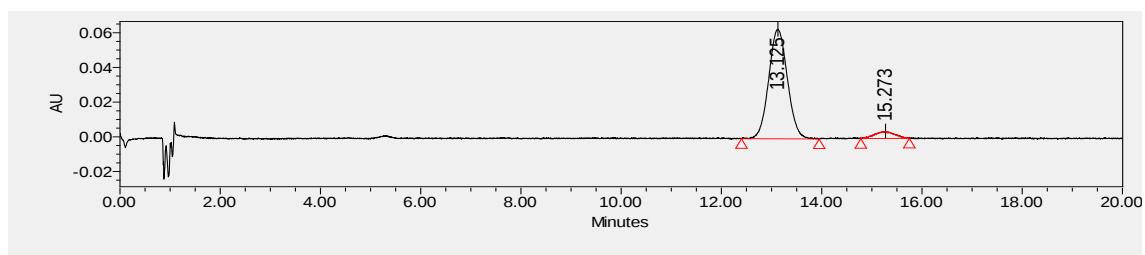
^1H NMR (600 MHz, CDCl_3) $\delta = 9.73$ (s, 1H), 8.28 – 8.19 (m, 1H), 7.75 – 7.69 (m, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.35 (m, 8H), 7.32 – 7.26 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 7.12 – 7.03 (m, 6H), 6.96 – 6.91 (m, 1H), 5.11 – 4.99 (m, 2H), 3.52 (d, $J = 13.2$ Hz, 1H), 3.27 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) $\delta = 174.2, 164.4, 161.4, 156.4, 145.9, 135.4, 133.2, 133.2, 133.1, 133.0, 130.7, 129.1, 129.0, 128.8, 128.7, 128.2, 128.1, 127.4, 127.4, 127.2, 125.2, 121.8, 120.8, 112.5, 91.1, 77.4, 77.2, 76.9, 71.1, 42.1$.

HRMS (ESI-FT) calcd for $\text{C}_{36}\text{H}_{30}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) = 568.2231, Found 568.2233.

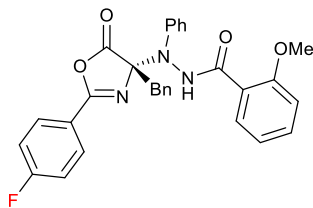


	Retention Time	Area	% Area
1	13.216	2147500	50.03
2	15.443	2145002	49.97



	Retention Time	Area	% Area
1	13.125	1634613	93.67
2	15.273	110410	6.33

(S)-N'-(4-benzyl-2-(4-fluorophenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C13)



Colorless oil; 28.8 mg, 56% yield, 92% ee; $[\alpha]^{22}_D = -84.46$ ($c = 0.92$ in CH_2Cl_2).

UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 6.98 min, t_R (minor) = 9.51 min.

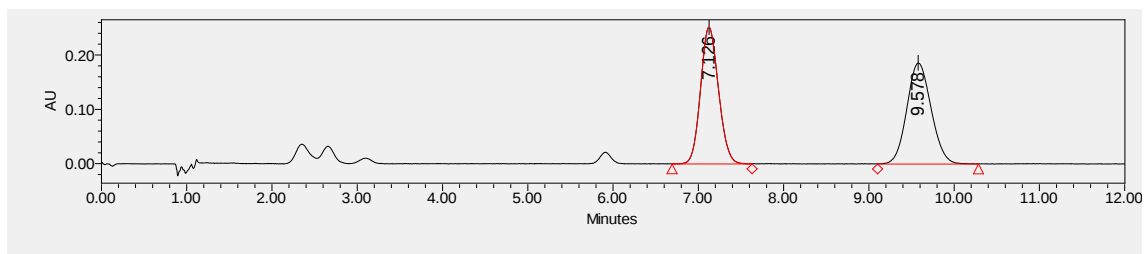
IR (neat): 3324, 3064, 2361, 1829, 1654, 1600, 1508k, 1483, 1293, 1235, 755 and 700 cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ = 9.80 (s, 1H), 8.26 – 8.14 (m, 1H), 7.93 – 7.84 (m, 2H), 7.70 – 7.63 (m, 2H), 7.46 – 7.39 (m, 1H), 7.36 – 7.30 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.09 (m, 7H), 7.07 – 7.02 (m, 1H), 6.92 – 6.87 (m, 1H), 3.73 (s, 3H), 3.58 (d, $J = 13.2$ Hz, 1H), 3.36 (d, $J = 13.2$ Hz, 1H).

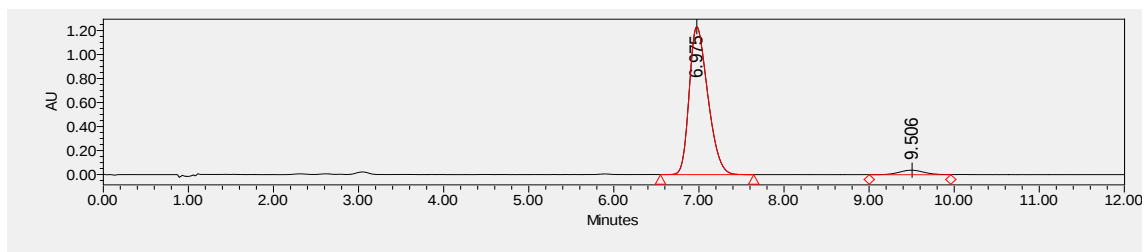
^{13}C NMR (101 MHz, CDCl_3) δ = 174.4, 165.8 (d, $J = 255.3$ Hz), 163.9, 160.8, 157.3, 145.9, 133.4, 133.0, 132.9, 130.7, 130.6 (d, $J = 9.2$ Hz), 129.1, 128.3, 127.52, 127.3, 126.7, 121.7, 121.5 (d, $J = 3.5$ Hz), 120.5, 116.3 (d, $J = 22.1$ Hz), 111.3, 91.0, 55.9, 42.0.

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3) δ = -104.2.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}\text{FN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 510.1824, Found 510.1822.

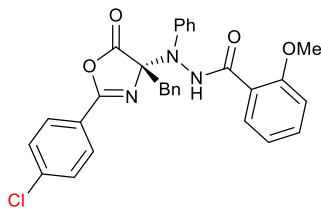


	Retention Time	Area	% Area
1	7.126	3676231	49.96
2	9.578	3682308	50.04



	Retention Time	Area	% Area
1	6.975	18675413	96.09
2	9.506	759699	3.91

(S)-N'-(4-benzyl-2-(4-chlorophenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C14)



Colorless oil; 26.4 mg, 50% yield, 93% ee; $[\alpha]^{22}_D = -84.44$ ($c = 0.51$ in CH_2Cl_2).

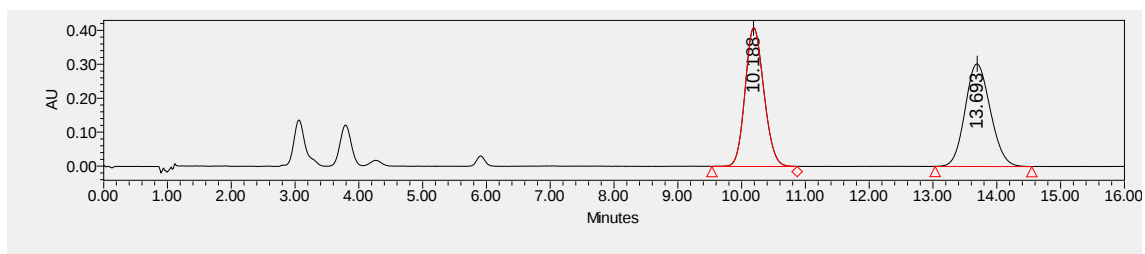
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 10.06 min, t_R (minor) = 13.61 min.

IR (neat): 3325, 3063, 2361, 1829, 1653, 1598, 1484, 1293, 1239, 755 and 699 cm^{-1} .

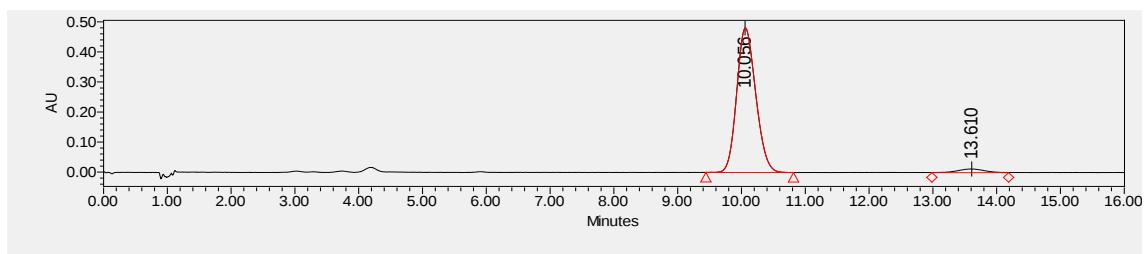
^1H NMR (400 MHz, CDCl_3) δ = 9.80 (s, 1H), 8.22 – 8.15 (m, 1H), 7.84 – 7.76 (m, 2H), 7.69 – 7.63 (m, 2H), 7.45 – 7.39 (m, 3H), 7.37 – 7.30 (m, 2H), 7.24 – 7.18 (m, 1H), 7.16 – 7.09 (m, 5H), 7.07 – 7.02 (m, 1H), 6.92 – 6.87 (m, 1H), 3.74 (s, 3H), 3.58 (d, $J = 13.2$ Hz, 1H), 3.37 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 174.3, 164.0, 160.9, 157.3, 145.9, 139.8, 133.4, 133.0, 132.9, 130.7, 129.4, 129.4, 129.2, 128.3, 127.6, 127.3, 126.7, 123.7, 121.7, 120.5, 111.4, 91.1, 77.5, 77.2, 76.8, 55.9, 42.0.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}^{35}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 526.1528, Found 526.1527, $\text{C}_{30}\text{H}_{25}^{37}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 527.1562, Found 527.1558.

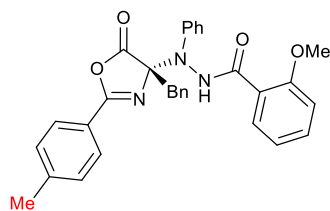


	Retention Time	Area	% Area
1	10.188	8354220	50.09
2	13.693	8325376	49.91



	Retention Time	Area	% Area
1	10.056	9956214	96.56
2	13.610	355219	3.44

(S)-N'-(4-benzyl-5-oxo-2-(p-tolyl)-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C15)



Colorless oil; 37.6 mg, 74% yield, 93% ee; $[\alpha]^{22}_D = -40.20$ ($c = 2.39$ in CH_2Cl_2).

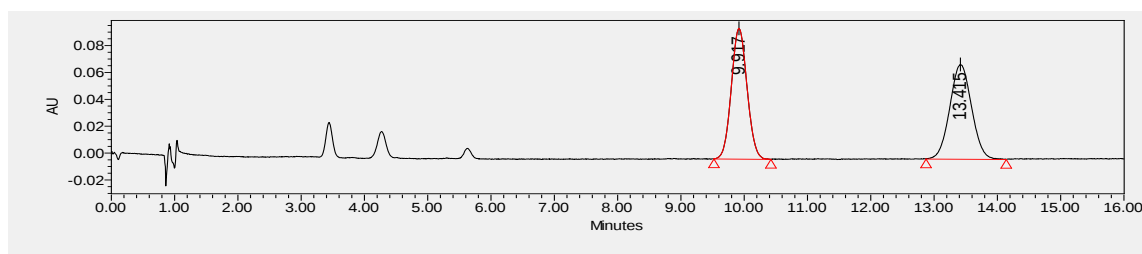
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 10.04 min, t_R (minor) = 13.94 min.

IR (neat): 3324, 3033, 2361, 1827, 1651, 1599, 1483, 1292, 1238, 758 and 700 cm^{-1} .

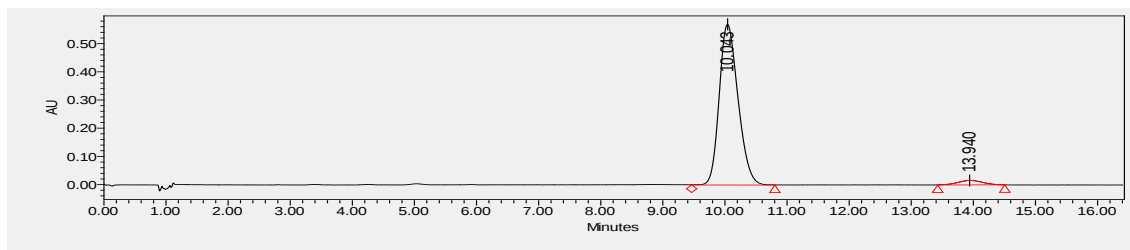
^1H NMR (400 MHz, CDCl_3) δ = 9.82 (s, 1H), 8.26 – 8.14 (m, 1H), 7.81 – 7.74 (m, 2H), 7.73 – 7.67 (m, 2H), 7.43 – 7.37 (m, 1H), 7.37 – 7.31 (m, 2H), 7.26 – 7.18 (m, 3H), 7.18 – 7.08 (m, 5H), 7.06 – 7.00 (m, 1H), 6.89 – 6.84 (m, 1H), 3.67 (s, 3H), 3.57 (d, $J = 13.0$ Hz, 1H), 3.34 (d, $J = 13.1$ Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ = 174.6, 163.8, 161.8, 157.3, 146.1, 144.2, 133.3, 133.0, 133.0, 130.7, 129.6, 129.1, 128.2, 128.2, 127.4, 127.3, 126.9, 122.5, 121.5, 120.5, 111.3, 90.9, 77.5, 77.2, 76.8, 55.8, 42.0, 21.9.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 506.2074, Found 506.2073.

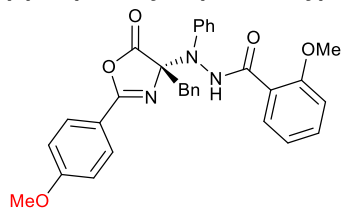


	Retention Time	Area	% Area
1	9.917	1678928	49.88
2	13.415	1687073	50.12



	Retention Time	Area	% Area
1	10.043	11993274	96.50
2	13.940	435238	3.50

(S)-N'-(4-benzyl-2-(4-methoxyphenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C16)



Colorless oil; 35.8 mg, 69% yield, 80% ee; $[\alpha]^{22}_D = -77.46$ ($c = 0.73$ in CH_2Cl_2).

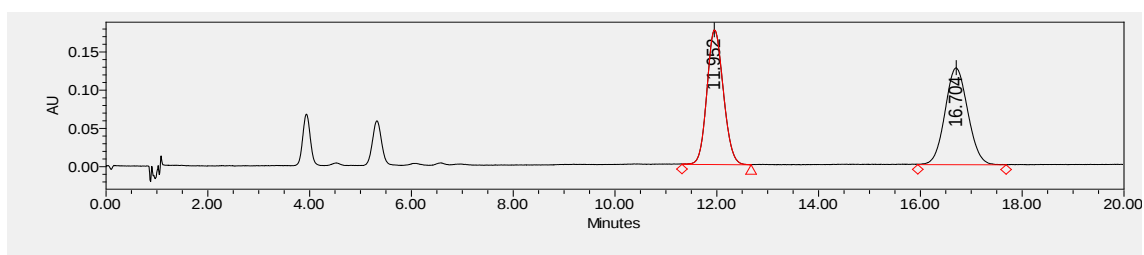
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 11.94 min, t_R (minor) = 16.87 min.

IR (neat): 3322, 2938, 2361, 1826, 1649, 1603, 1511, 1295, 1259 and 700 cm^{-1} .

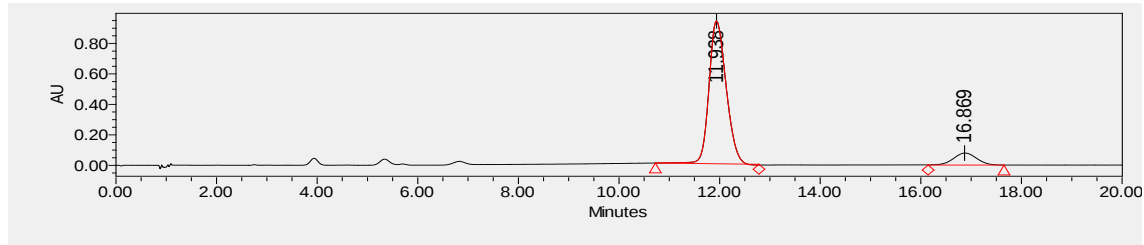
^1H NMR (600 MHz, CDCl_3) δ = 9.82 (s, 1H), 8.21 – 8.16 (m, 1H), 7.86 – 7.80 (m, 2H), 7.73 – 7.66 (m, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 7.23 – 7.19 (m, 1H), 7.17 – 7.14 (m, 2H), 7.13 – 7.08 (m, 3H), 7.05 – 7.01 (m, 1H), 6.94 – 6.90 (m, 2H), 6.88 – 6.84 (m, 1H), 3.85 (s, 3H), 3.67 (s, 3H), 3.56 (d, $J = 13.2$ Hz, 1H), 3.31 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.7, 163.8, 163.6, 161.5, 157.3, 146.1, 133.3, 133.1, 133.0, 130.7, 130.1, 129.1, 128.2, 127.4, 127.2, 126.9, 121.5, 120.5, 117.4, 114.3, 111.3, 90.9, 77.4, 77.2, 76.9, 55.8, 55.6, 42.0.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_5^+$ ($[\text{M}+\text{H}]^+$) = 522.2023, Found 522.2028.

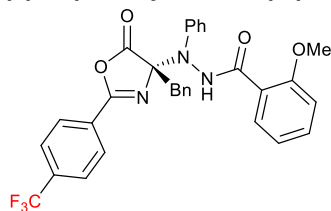


	Retention Time	Area	% Area
1	11.952	3940567	50.04
2	16.704	3934933	49.96



	Retention Time	Area	% Area
1	11.938	22188498	89.70
2	16.869	2548286	10.30

(S)-N'-(4-benzyl-5-oxo-2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C17)



Colorless oil; 27.8 mg, 50% yield, 95% ee; $[\alpha]_D^{22} = -89.03$ ($c = 0.47$ in CH_2Cl_2).

UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 3.80 min, t_R (minor) = 4.98 min.

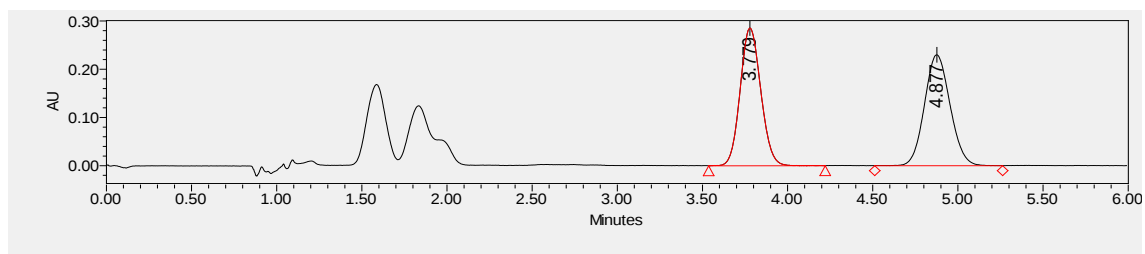
IR (neat): 3327, 3064, 2361, 1831, 1655, 1599, 1484, 1322, 1130 and 701 cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ = 9.82 (s, 1H), 8.21 – 8.16 (m, 1H), 8.01 – 7.94 (m, 2H), 7.73 – 7.68 (m, 2H), 7.67 – 7.62 (m, 2H), 7.46 – 7.40 (m, 1H), 7.37 – 7.31 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.09 (m, 5H), 7.08 – 7.02 (m, 1H), 6.93 – 6.89 (m, 1H), 3.77 (s, 3H), 3.61 (d, $J = 13.2$ Hz, 1H), 3.42 (d, $J = 13.2$ Hz, 1H).

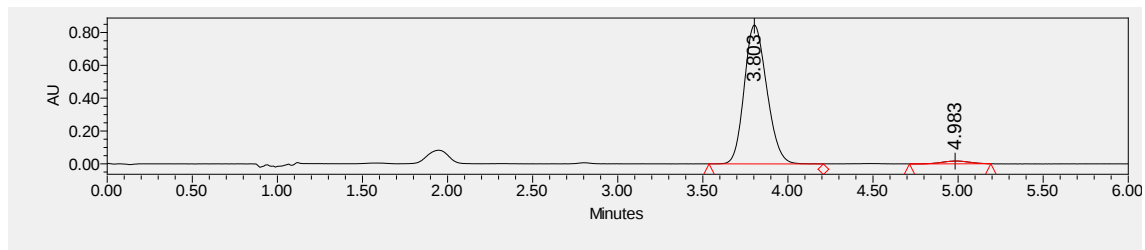
^{13}C NMR (101 MHz, CDCl_3) δ = 174.1, 164.1, 160.6, 157.3, 145.8, 134.9, 134.6, 133.5, 133.0, 132.7, 130.7, 129.2, 128.6, 128.5, 128.4, 127.7, 127.4, 126.6, 125.9 (q, $J = 3.7$ Hz), 124.9, 122.2, 121.7, 120.5, 111.4, 91.2, 77.5, 77.2, 76.8, 56.0, 42.0.

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3) δ = -63.2.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{25}\text{F}_3\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 560.1792, Found 560.1793.

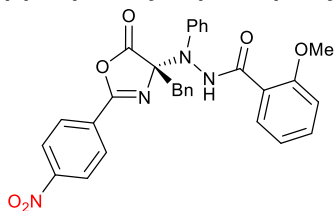


	Retention Time	Area	% Area
1	3.779	2404956	49.98
2	4.877	2407126	50.02



	Retention Time	Area	% Area
1	3.803	7778310	97.57
2	4.983	193393	2.43

(S)-N'-(4-benzyl-2-(4-nitrophenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C18)



Colorless oil; 27.3 mg, 51% yield, 91% ee; $[\alpha]^{22}_D = -82.21$ ($c = 0.42$ in CH_2Cl_2).

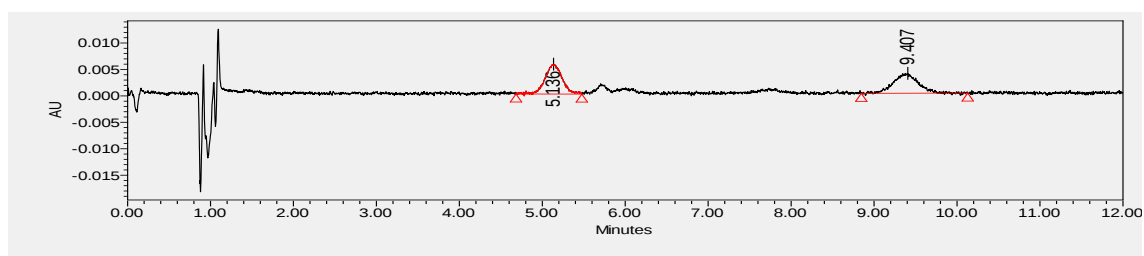
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (minor) = 5.39 min, t_R (major) = 9.55 min.

IR (neat): 3327, 2938, 2361, 1831, 1655, 1599, 1525, 1481, 1347, 1294, 1241, 755 and 703 cm^{-1} .

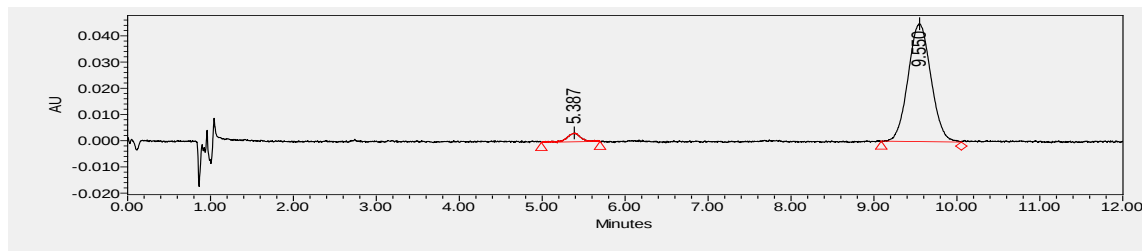
^1H NMR (400 MHz, CDCl_3) $\delta = 9.82$ (s, 1H), 8.33 – 8.24 (m, 2H), 8.20 – 8.14 (m, 1H), 8.05 – 7.99 (m, 2H), 7.67 – 7.60 (m, 2H), 7.48 – 7.40 (m, 1H), 7.37 – 7.30 (m, 2H), 7.24 – 7.19 (m, 1H), 7.16 – 7.10 (m, 5H), 7.08 – 7.03 (m, 1H), 6.95 – 6.90 (m, 1H), 3.82 (s, 3H), 3.61 (d, $J = 13.2$ Hz, 1H), 3.45 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) $\delta = 173.9, 164.2, 160.0, 157.3, 150.6, 145.7, 133.5, 133.0, 132.6, 130.8, 130.7, 129.2, 129.2, 128.4, 127.7, 127.4, 126.4, 124.1, 121.8, 120.4, 111.5, 91.3, 77.5, 77.2, 76.8, 56.1, 42.1$.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}\text{N}_4\text{O}_6^+$ ($[\text{M}+\text{H}]^+$) = 537.1769, Found 537.1768.

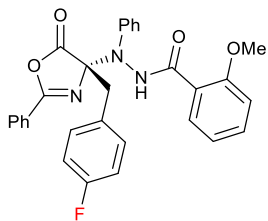


	Retention Time	Area	% Area
1	5.136	81006	50.57
2	9.407	79166	49.43



	Retention Time	Area	% Area
1	5.387	39101	4.36
2	9.550	857384	95.64

(S)-N'-(4-(4-fluorobenzyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C19)



White solid; m.p. 66–70 °C; 25.4 mg, 50% yield, 92% ee; $[\alpha]_D^{22} = -90.84$ ($c = 0.57$ in CH_2Cl_2).

UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 6.71 min, t_R (minor) = 10.09 min.

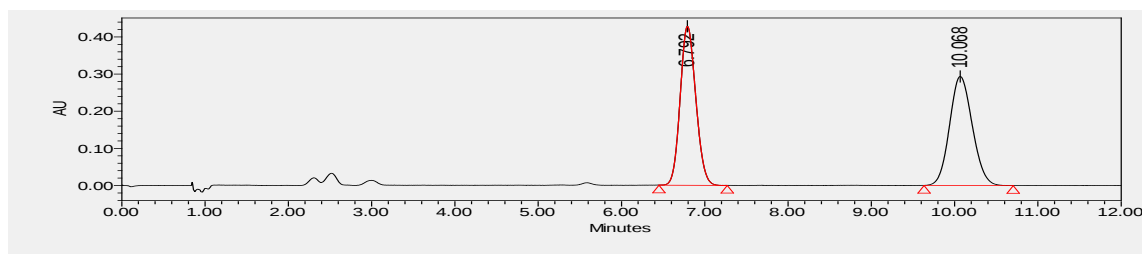
IR (neat): 3324, 3066, 2361, 1828, 1653, 1600, 1509, 1292, 1227 and 701 cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ = 9.78 (s, 1H), 8.25 – 8.13 (m, 1H), 7.94 – 7.87 (m, 2H), 7.73 – 7.65 (m, 2H), 7.62 – 7.55 (m, 1H), 7.49 – 7.44 (m, 2H), 7.43 – 7.37 (m, 1H), 7.37 – 7.31 (m, 2H), 7.25 – 7.19 (m, 1H), 7.16 – 7.09 (m, 2H), 7.07 – 7.00 (m, 1H), 6.89 – 6.84 (m, 1H), 6.84 – 6.77 (m, 2H), 3.65 (s, 3H), 3.55 (d, $J = 13.2$ Hz, 1H), 3.30 (d, $J = 13.2$ Hz, 1H).

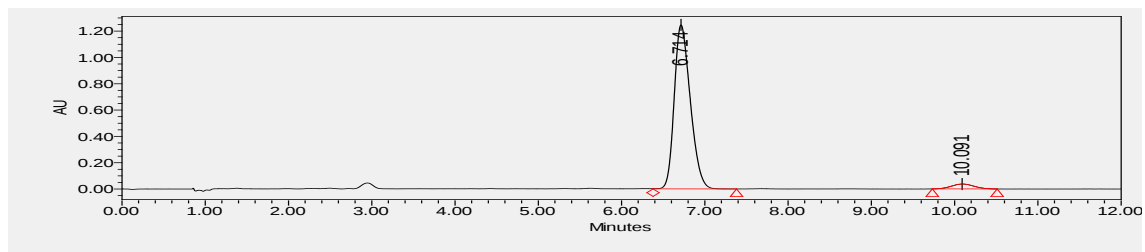
^{13}C NMR (101 MHz, CDCl_3) δ = 174.4, 163.9, 162.2 (d, $J = 245.7$ Hz), 161.9, 157.3, 145.9, 133.5, 133.4, 133.0, 132.3 (d, $J = 8.0$ Hz), 129.2, 129.0, 128.8 (d, $J = 3.1$ Hz), 128.12, 127.4, 126.9, 125.1, 121.6, 120.4, 115.2 (d, $J = 21.5$ Hz), 111.3, 90.9, 55.8, 41.1.

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3) δ = –115.0.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}\text{FN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 510.1824, Found 510.1825.

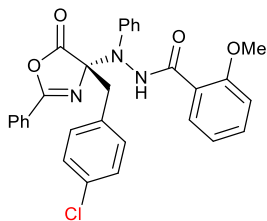


	Retention Time	Area	% Area
1	6.792	5588983	50.05
2	10.068	5577411	49.95



	Retention Time	Area	% Area
1	6.714	16697561	95.97
2	10.091	701778	4.03

(S)-N'-(4-(4-chlorobenzyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C20)



Colorless oil; 39.9 mg, 76% yield, 94% ee; $[\alpha]_D^{22} = -65.92$ ($c = 0.76$ in CH_2Cl_2).

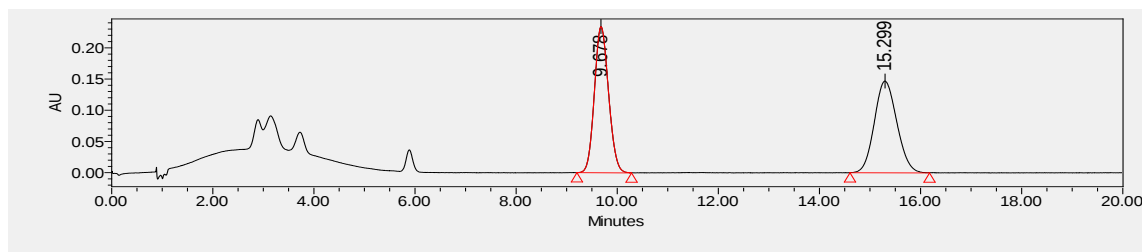
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 9.40 min, t_R (minor) = 14.93 min.

IR (neat): 3327, 3064, 2361, 1829, 1654, 1599, 1484, 1293, 1240, 756 and 699 cm^{-1} .

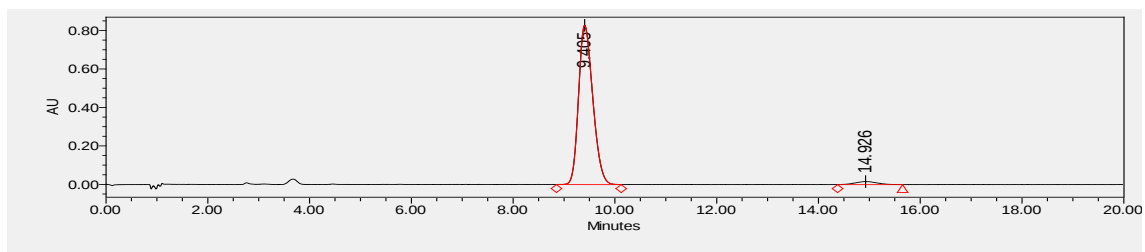
^1H NMR (600 MHz, CDCl_3) δ = 9.78 (s, 1H), 8.25 – 8.13 (m, 1H), 7.95 – 7.89 (m, 2H), 7.72 – 7.64 (m, 2H), 7.62 – 7.56 (m, 1H), 7.50 – 7.45 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.25 – 7.20 (m, 1H), 7.13 – 7.07 (m, 4H), 7.05 – 7.01 (m, 1H), 6.88 – 6.83 (m, 1H), 3.63 (s, 3H), 3.54 (d, $J = 13.2$ Hz, 1H), 3.30 (d, $J = 13.2$ Hz, 1H)

^{13}C NMR (151 MHz, CDCl_3) δ = 174.3, 163.8, 162.0, 157.3, 145.8, 133.6, 133.5, 133.4, 133.0, 132.0, 131.6, 129.2, 129.0, 128.5, 128.2, 127.5, 126.9, 125.0, 121.6, 120.3, 111.3, 90.8, 77.4, 77.2, 76.9, 55.8, 41.2.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}^{35}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 526.1528, Found 526.1537, $\text{C}_{30}\text{H}_{25}^{37}\text{ClN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 527.1562, Found 527.1567.

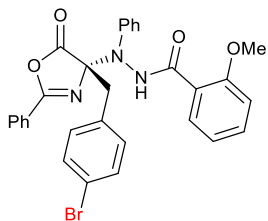


	Retention Time	Area	% Area
1	9.678	4557446	50.07
2	15.299	4545177	49.93



	Retention Time	Area	% Area
1	9.405	16111393	97.06
2	14.926	487799	2.94

(S)-N'-(4-(4-bromobenzyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C21)



Colorless oil; 51.4 mg, 90% yield, 94% ee; $[\alpha]^{22}_D = -94.61$ ($c = 0.98$ in CH_2Cl_2).

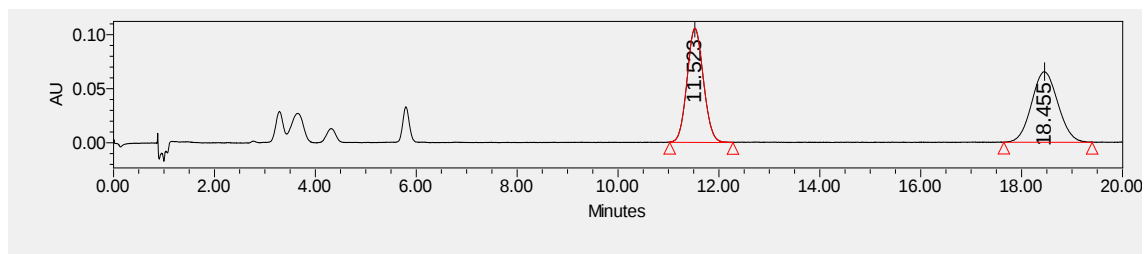
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 11.43 min, t_R (minor) = 18.49 min.

IR (neat): 3323, 3064, 2361, 1828, 1653, 1598, 1484, 1292, 1238, 757 and 701 cm^{-1} .

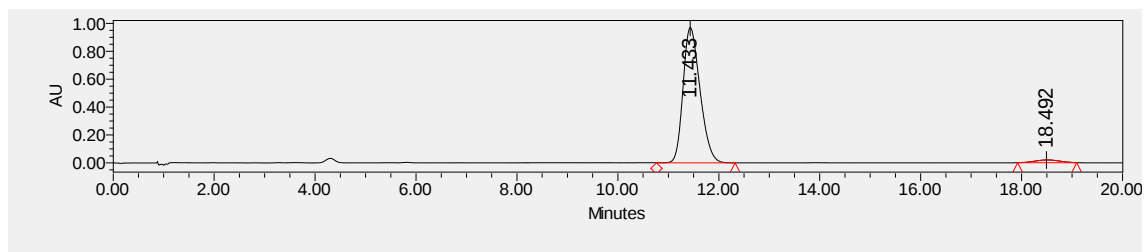
^1H NMR (400 MHz, CDCl_3) δ = 9.78 (s, 1H), 8.22 – 8.15 (m, 1H), 7.96 – 7.88 (m, 2H), 7.71 – 7.65 (m, 2H), 7.62 – 7.56 (m, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 7.27 – 7.19 (m, 3H), 7.06 – 7.00 (m, 3H), 6.89 – 6.82 (m, 1H), 3.63 (s, 3H), 3.53 (d, $J = 13.2$ Hz, 1H), 3.29 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 174.2, 163.8, 162.1, 157.3, 145.8, 133.6, 133.4, 132.9, 132.4, 132.1, 131.4, 129.2, 129.0, 128.2, 127.5, 126.9, 125.0, 121.7, 121.6, 120.3, 111.3, 90.7, 77.5, 77.2, 76.8, 55.7, 41.2.

HRMS (ESI-FT) calcd for $\text{C}_{30}\text{H}_{25}^{79}\text{BrN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 570.1023, Found 570.1024, $\text{C}_{30}\text{H}_{25}^{81}\text{BrN}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 572.1002, Found 572.1006.

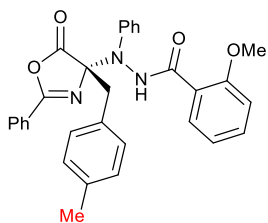


	Retention Time	Area	% Area
1	11.523	2379816	50.09
2	18.455	2370893	49.91



	Retention Time	Area	% Area
1	11.433	22638566	97.12
2	18.492	670509	2.88

(S)-2-methoxy-N'-(4-(4-methylbenzyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N'-phenylbenzohydrazide (C22)



Colorless oil; 36.6 mg, 72% yield, 92% ee; $[\alpha]_D^{22} = -85.06$ ($c = 0.68$ in CH_2Cl_2).

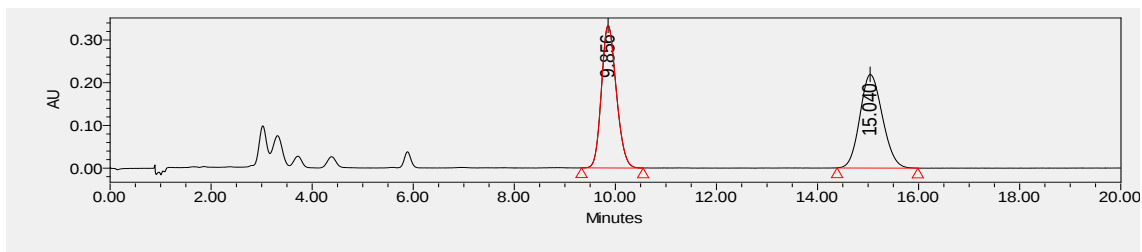
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 9.52 min, t_R (minor) = 14.41 min.

IR (neat): 3324, 2943, 2361, 1828, 1654, 1599, 1482, 1292, 1239, 756 and 701 cm^{-1} .

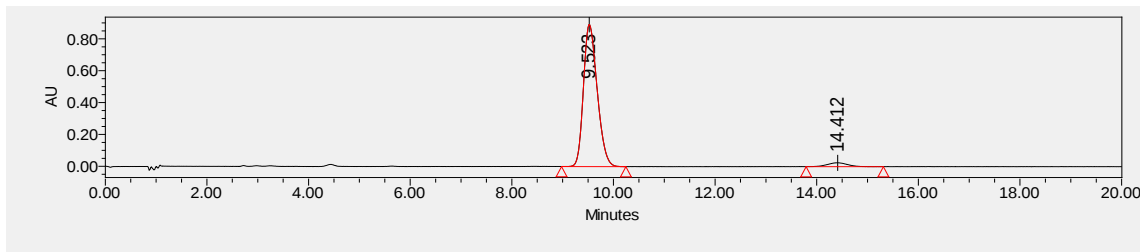
^1H NMR (600 MHz, CDCl_3) δ = 9.78 (s, 1H), 8.25 – 8.13 (m, 1H), 7.95 – 7.89 (m, 2H), 7.72 – 7.64 (m, 2H), 7.62 – 7.56 (m, 1H), 7.50 – 7.45 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.25 – 7.20 (m, 1H), 7.13 – 7.07 (m, 4H), 7.05 – 7.01 (m, 1H), 6.88 – 6.83 (m, 1H), 3.63 (s, 3H), 3.54 (d, $J = 13.2$ Hz, 1H), 3.30 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.3, 163.8, 162.0, 157.3, 145.8, 133.6, 133.5, 133.4, 133.0, 132.0, 131.6, 129.2, 129.0, 128.5, 128.2, 127.5, 126.9, 125.0, 121.6, 120.3, 111.3, 90.8, 77.4, 77.2, 76.9, 55.8, 41.2.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 506.2074, Found 506.2076.

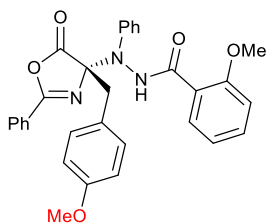


	Retention Time	Area	% Area
1	9.856	6801475	50.05
2	15.040	6788902	49.95



	Retention Time	Area	% Area
1	9.523	16739753	95.98
2	14.412	700284	4.02

(S)-2-methoxy-N'-(4-(4-methoxybenzyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N'-phenylbenzohydrazide (C23)



Colorless oil; 31.8 mg, 61% yield, 90% ee; $[\alpha]^{22}_D = -92.14$ ($c = 0.70$ in CH_2Cl_2).

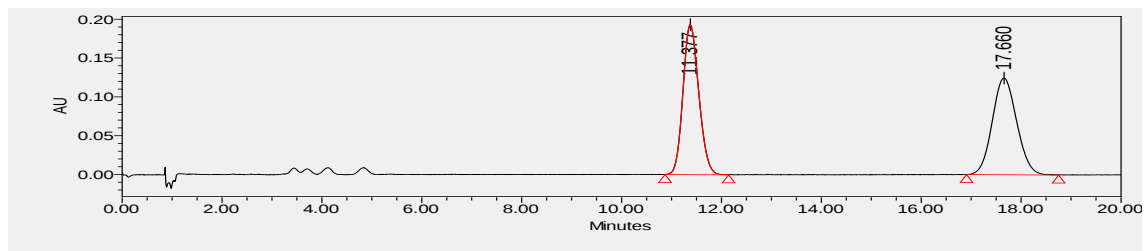
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 11.24 min, t_R (minor) = 17.77 min.

IR (neat): 3323, 2937, 2361, 1828, 1653, 1600, 1511, 1292, 1248, 756 and 701 cm^{-1} .

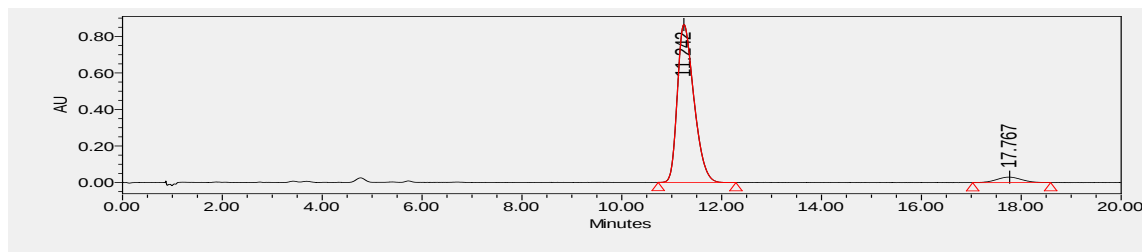
^1H NMR (600 MHz, CDCl_3) δ = 9.79 (s, 1H), 8.22 – 8.15 (m, 1H), 7.94 – 7.87 (m, 3H), 7.73 – 7.65 (m, 3H), 7.60 – 7.54 (m, 2H), 7.48 – 7.42 (m, 3H), 7.39 (m, 1H), 7.37 – 7.31 (m, 3H), 7.24 – 7.18 (m, 1H), 7.10 – 7.05 (m, 2H), 7.05 – 7.00 (m, 1H), 6.88 – 6.83 (m, 1H), 6.68 – 6.61 (m, 2H), 3.65 (s, 3H), 3.63 (s, 3H), 3.52 (d, $J = 13.2$ Hz, 1H), 3.27 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.6, 163.8, 161.8, 158.8, 157.3, 146.0, 133.3, 133.3, 133.0, 131.8, 129.1, 128.9, 128.2, 127.3, 126.9, 125.3, 124.8, 121.6, 120.4, 113.7, 111.3, 91.2, 77.4, 77.2, 76.9, 55.7, 55.1, 41.1.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_5^+$ ($[\text{M}+\text{H}]^+$) = 522.2023, Found 522.2025.

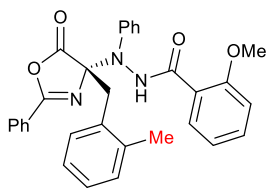


	Retention Time	Area	% Area
1	11.377	4254248	50.10
2	17.660	4237725	49.90



	Retention Time	Area	% Area
1	11.242	19915391	95.02
2	17.767	1044406	4.98

(S)-2-methoxy-N'-(4-(2-methylbenzyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N'-phenylbenzohydrazide (C24)



Colorless oil; 33.9 mg, 67% yield, 90% ee; $[\alpha]^{22}_D = -75.71$ ($c = 0.63$ in CH_2Cl_2).

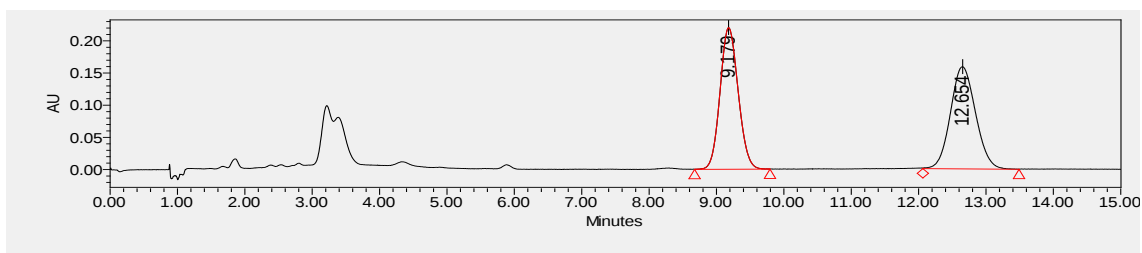
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 8.88 min, t_R (minor) = 12.20 min.

IR (neat): 3322, 3063, 2361, 1828, 1654, 1598, 1483, 1292, 1239, 753 and 701 cm^{-1} .

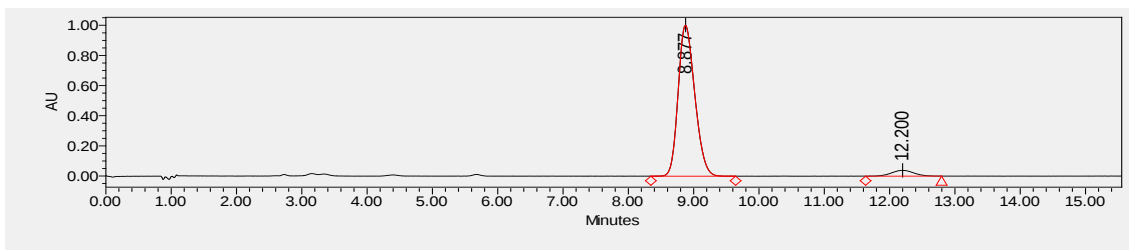
^1H NMR (600 MHz, CDCl_3) δ = 9.86 (s, 1H), 8.23 – 8.18 (m, 1H), 7.88 – 7.83 (m, 2H), 7.76 – 7.69 (m, 2H), 7.57 – 7.53 (m, 1H), 7.46 – 7.42 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.24 – 7.21 (m, 1H), 7.17 – 7.14 (m, 1H), 7.06 – 7.02 (m, 1H), 7.01 – 6.94 (m, 3H), 6.88 – 6.85 (m, 1H), 3.64 (s, 3H), 3.60 (d, $J = 13.2$ Hz, 1H), 3.46 (d, $J = 13.2$ Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ = 175.1, 163.8, 161.5, 157.3, 146.1, 138.1, 133.3, 133.3, 133.0, 131.5, 131.0, 130.5, 129.1, 128.9, 128.1, 127.6, 127.4, 127.0, 125.9, 125.3, 121.6, 120.4, 111.2, 91.7, 77.4, 77.2, 76.9, 55.7, 38.5, 20.1.

HRMS (ESI-FT) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 506.2074, Found 506.2074.

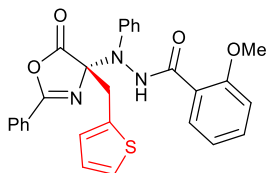


	Retention Time	Area	% Area
1	9.179	4101785	49.95
2	12.654	4109973	50.05



	Retention Time	Area	% Area
1	8.877	17722640	95.00
2	12.200	932442	5.00

(S)-2-methoxy-N'-(5-oxo-2-phenyl-4-(thiophen-2-ylmethyl)-4,5-dihydrooxazol-4-yl)-N'-phenylbenzohydrazide (C25)



Colorless oil; 42.3 mg, 85% yield, 95% ee; $[\alpha]^{22}_D = -89.70$ ($c = 0.95$ in CH_2Cl_2).

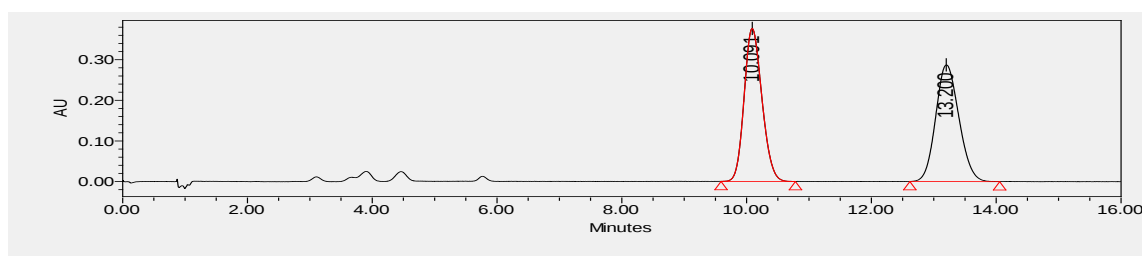
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 10.06 min, t_R (minor) = 13.31 min.

IR (neat): 3322, 3067, 2361, 1828, 1652, 1598, 1483, 1292, 1236, 757 and 699 cm^{-1} .

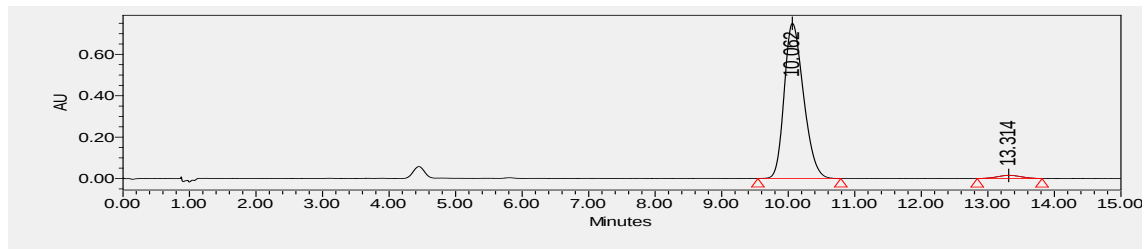
^1H NMR (600 MHz, CDCl_3) δ = 9.81 (s, 1H), 8.22 – 8.15 (m, 1H), 8.02 – 7.94 (m, 2H), 7.70 – 7.64 (m, 2H), 7.62 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 – 7.31 (m, 2H), 7.24 – 7.19 (m, 1H), 7.06 – 7.00 (m, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 6.82 – 6.78 (m, 1H), 3.90 (d, $J = 14.4$ Hz, 1H), 3.67 (s, 3H), 3.52 (d, $J = 14.4$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.1, 163.9, 162.8, 157.3, 145.8, 134.1, 133.5, 133.4, 132.9, 129.2, 129.0, 128.5, 128.4, 127.4, 126.9, 126.8, 125.9, 125.3, 121.5, 120.4, 111.3, 90.6, 77.4, 77.2, 76.9, 55.8, 36.2.

HRMS (ESI-FT) calcd for $\text{C}_{28}\text{H}_{24}\text{N}_3\text{O}_4\text{S}^+$ ($[\text{M}+\text{H}^+]$) = 498.1482, Found 498.1477.

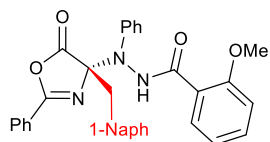


	Retention Time	Area	% Area
1	10.091	7451849	50.09
2	13.200	7426099	49.91



	Retention Time	Area	% Area
1	10.062	15087731	97.49
2	13.314	388001	2.51

(S)-2-methoxy-*N'*-(4-(naphthalen-1-ylmethyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-*N'*-phenylbenzohydrazide (C26)



Colorless oil; 43.2 mg, 80% yield, 94% ee; $[\alpha]^{22}_{\text{D}} = -58.05$ ($c = 0.87$ in CH_2Cl_2).

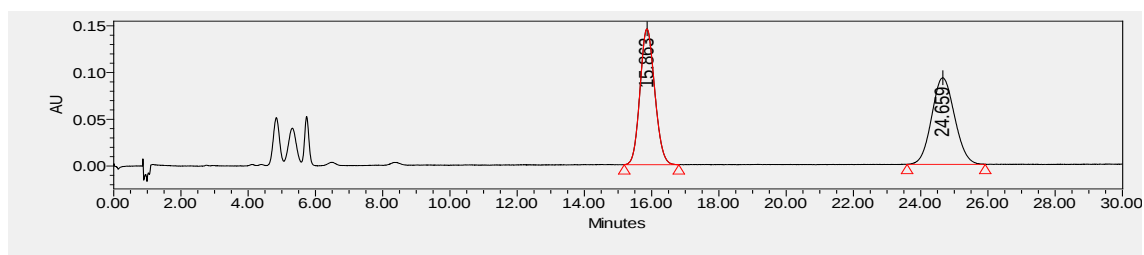
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 15.81 min, t_R (minor) = 24.97 min.

IR (neat): 3322, 3062, 2361, 1828, 1654, 1598, 1483, 1292, 1237 and 701 cm^{-1} .

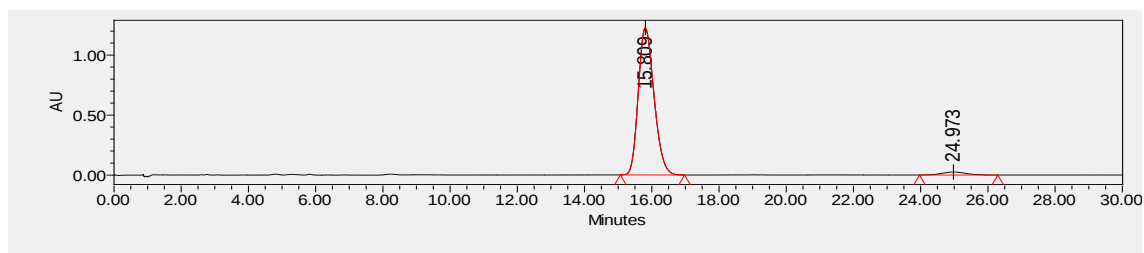
^1H NMR (400 MHz, CDCl_3) δ = 9.94 (s, 1H), 8.24 – 8.20 (m, 1H), 8.19 – 8.15 (m, 1H), 7.82 – 7.74 (m, 2H), 7.65 – 7.54 (m, 4H), 7.52 – 7.47 (m, 1H), 7.44 – 7.32 (m, 6H), 7.29 – 7.22 (m, 4H), 7.06 – 7.01 (m, 1H), 6.89 – 6.83 (m, 1H), 3.97 (s, 2H), 3.66 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ = 174.8, 163.8, 161.5, 157.3, 146.1, 133.7, 133.3, 133.1, 133.0, 132.7, 129.5, 129.3, 129.2, 128.6, 128.5, 128.3, 128.0, 127.5, 127.0, 125.5, 125.4, 125.3, 125.2, 125.0, 121.6, 120.4, 111.3, 91.7, 77.5, 77.2, 76.8, 55.7, 38.2.

HRMS (ESI-FT) calcd for $\text{C}_{34}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) = 542.2074, Found 542.2075.

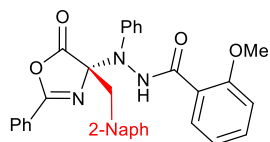


	Retention Time	Area	% Area
1	15.863	4409501	50.12
2	24.659	4388099	49.88



	Retention Time	Area	% Area
1	15.809	39808523	96.97
2	24.973	1242242	3.03

(S)-2-methoxy-*N'*-(4-(naphthalen-2-ylmethyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-*N'*-phenylbenzohydrazide (C27)



Colorless oil; 46.7 mg, 86% yield, 94% ee; $[\alpha]_D^{22} = -112.68$ ($c = 0.98$ in CH_2Cl_2).

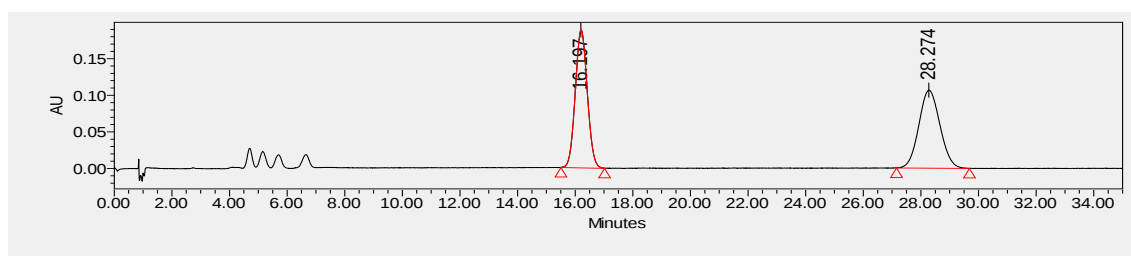
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 16.11 min, t_R (minor) = 28.43 min.

IR (neat): 3323, 3058, 2361, 1829, 1653, 1599, 1483, 1292, 1238, 754 and 702 cm^{-1} .

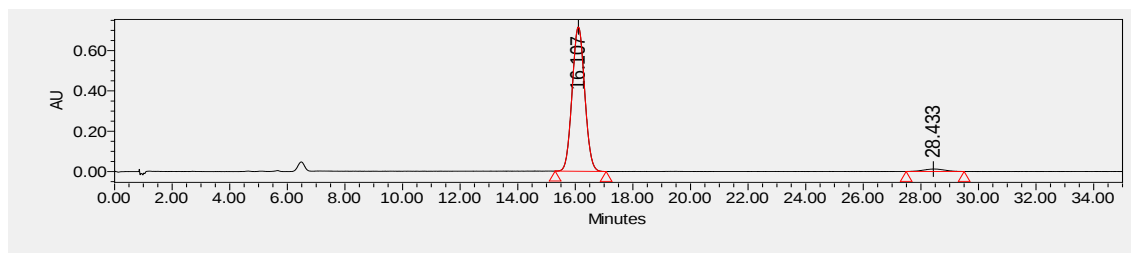
^1H NMR (400 MHz, CDCl_3) δ = 9.85 (s, 1H), 8.24 – 8.18 (m, 1H), 7.89 – 7.84 (m, 2H), 7.78 – 7.72 (m, 2H), 7.70 – 7.64 (m, 3H), 7.61 – 7.57 (m, 1H), 7.55 – 7.49 (m, 1H), 7.43 – 7.34 (m, 7H), 7.32 – 7.28 (m, 1H), 7.26 – 7.21 (m, 1H), 7.06 – 7.00 (m, 1H), 6.88 – 6.82 (m, 1H), 3.76 (d, $J = 13.2$ Hz, 1H), 3.64 (s, 3H), 3.53 (d, $J = 13.2$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 174.4, 163.8, 162.0, 157.3, 146.0, 133.3, 133.2, 133.0, 132.5, 130.6, 129.8, 129.2, 128.9, 128.6, 128.2, 127.9, 127.7, 127.5, 127.4, 127.0, 125.9, 125.9, 125.1, 121.5, 120.4, 111.3, 91.1, 77.5, 77.2, 76.8, 55.7, 42.0.

HRMS (ESI-FT) calcd for $\text{C}_{34}\text{H}_{28}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 542.2074, Found 542.2075.

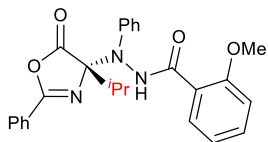


	Retention Time	Area	% Area
1	16.197	5449163	50.12
2	28.274	5422132	49.88



	Retention Time	Area	% Area
1	16.107	21712013	97.14
2	28.433	639580	2.86

(S)-N'-(4-isopropyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C28)



Colorless oil; 27.8 mg, 63% yield, 90% ee; $[\alpha]^{22}_D = +17.08$ ($c = 0.57$ in CH_2Cl_2).

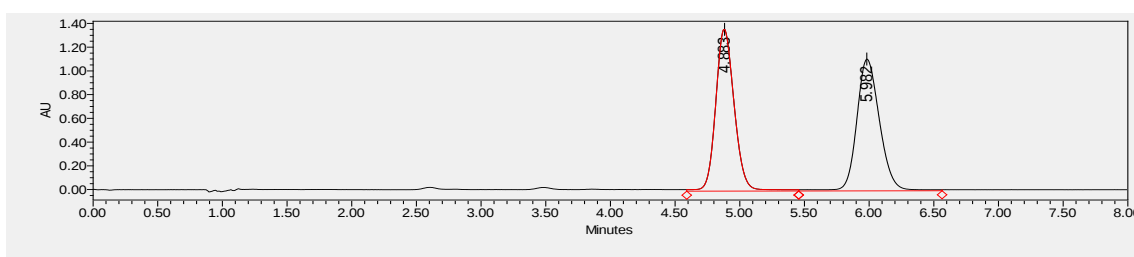
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 4.75 min, t_R (minor) = 5.60 min.

IR (neat): 3323, 2972, 2361, 1834, 1654, 1599, 1484, 1292, 1238, 756 and 700 cm^{-1} .

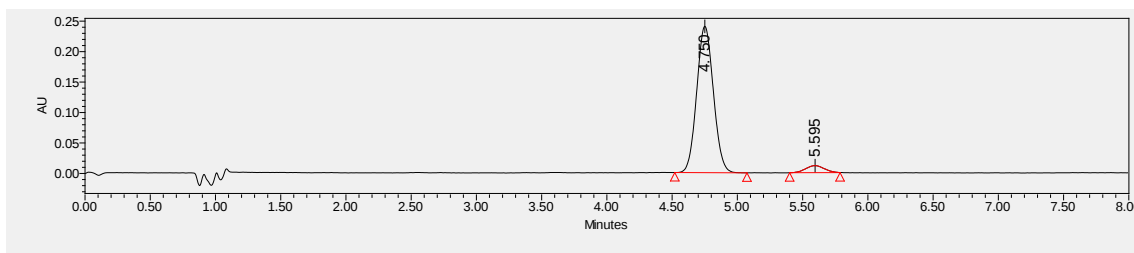
^1H NMR (600 MHz, CDCl_3) $\delta = 10.11$ (s, 1H), 8.23 – 8.16 (m, 1H), 8.03 – 7.95 (m, 2H), 7.61 – 7.57 (m, 1H), 7.56 – 7.52 (m, 2H), 7.51 – 7.47 (m, 2H), 7.46 – 7.42 (m, 1H), 7.24 – 7.20 (m, 2H), 7.12 – 7.08 (m, 1H), 7.07 – 7.03 (m, 1H), 6.97 – 6.92 (m, 1H), 3.90 (s, 3H), 2.68 – 2.60 (m, 1H), 1.20 – 1.07 (m, 6H).

^{13}C NMR (151 MHz, CDCl_3) $\delta = 163.4, 161.7, 157.5, 146.3, 133.4, 133.3, 132.9, 129.0, 128.8, 128.3, 126.8, 126.2, 125.3, 121.5, 120.6, 111.3, 92.5, 77.4, 77.2, 76.9, 56.0, 33.0, 16.7, 15.9$.

HRMS (ESI-FT) calcd for $\text{C}_{26}\text{H}_{26}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 444.1918, Found 444.1919.

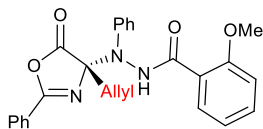


	Retention Time	Area	% Area
1	4.883	13679714	49.96
2	5.982	13699382	50.04



	Retention Time	Area	% Area
1	4.750	2137243	94.92
2	5.595	114334	5.08

(S)-N'-(4-allyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-methoxy-N'-phenylbenzohydrazide (C29)



Colorless oil; 23.0 mg, 52% yield, 90% ee; $[\alpha]^{22}_D = -53.94$ ($c = 0.48$ in CH_2Cl_2).

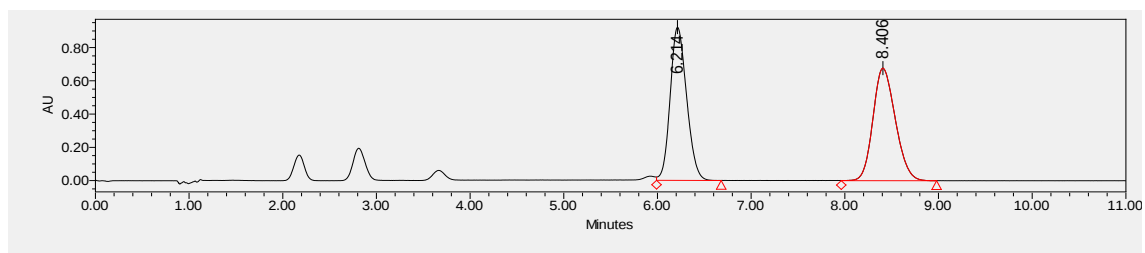
UPCC (chiral IC-3 column), $\text{CO}_2/\text{MeOH} = 80/20$, flow rate = 1.5 mL/min, $\lambda = 254$ nm, t_R (major) = 6.04 min, t_R (minor) = 8.00 min.

IR (neat): 3322, 3068, 2361, 1828, 1652, 1599, 1483, 1292, 1240, 756 and 703 cm^{-1} .

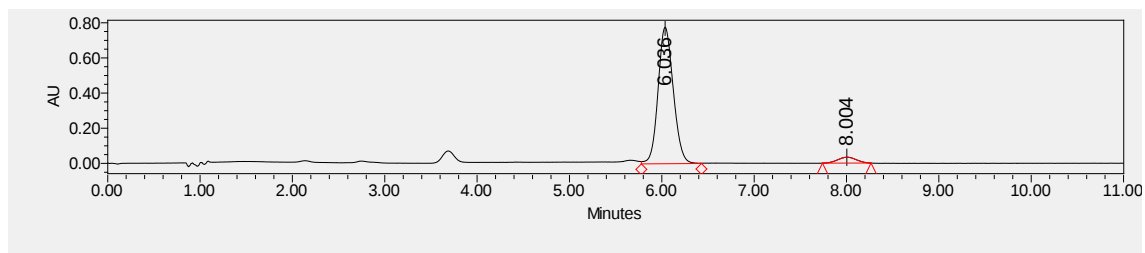
^1H NMR (600 MHz, CDCl_3) δ = 9.74 (s, 1H), 8.19 – 8.15 (m, 1H), 8.11 – 8.06 (m, 2H), 7.66 – 7.60 (m, 3H), 7.56 – 7.51 (m, 2H), 7.43 – 7.38 (m, 1H), 7.34 – 7.30 (m, 2H), 7.22 – 7.18 (m, 1H), 7.06 – 7.00 (m, 1H), 6.89 – 6.85 (m, 1H), 5.63 – 5.54 (m, 1H), 5.18 (d, $J = 16.8$ Hz, 1H), 5.10 (d, $J = 10.2$ Hz, 1H), 3.65 (s, 3H), 3.03 – 2.97 (m, 1H), 2.82 – 2.76 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 174.5, 163.8, 161.9, 157.3, 145.8, 133.6, 133.3, 133.0, 129.4, 129.1, 129.1, 128.4, 127.3, 126.8, 125.4, 121.9, 121.6, 120.4, 111.3, 90.1, 77.4, 77.2, 76.9, 55.8, 40.0.

HRMS (ESI-FT) calcd for $\text{C}_{26}\text{H}_{24}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}^+]$) = 442.1761, Found 442.1763.



	Retention Time	Area	% Area
1	6.214	11244231	50.06
2	8.406	11215569	49.94



	Retention Time	Area	% Area
1	6.036	8891684	95.06
2	8.004	462551	4.94

8. Copies of NMR spectra for products

Figure S1. ^1H NMR of C1

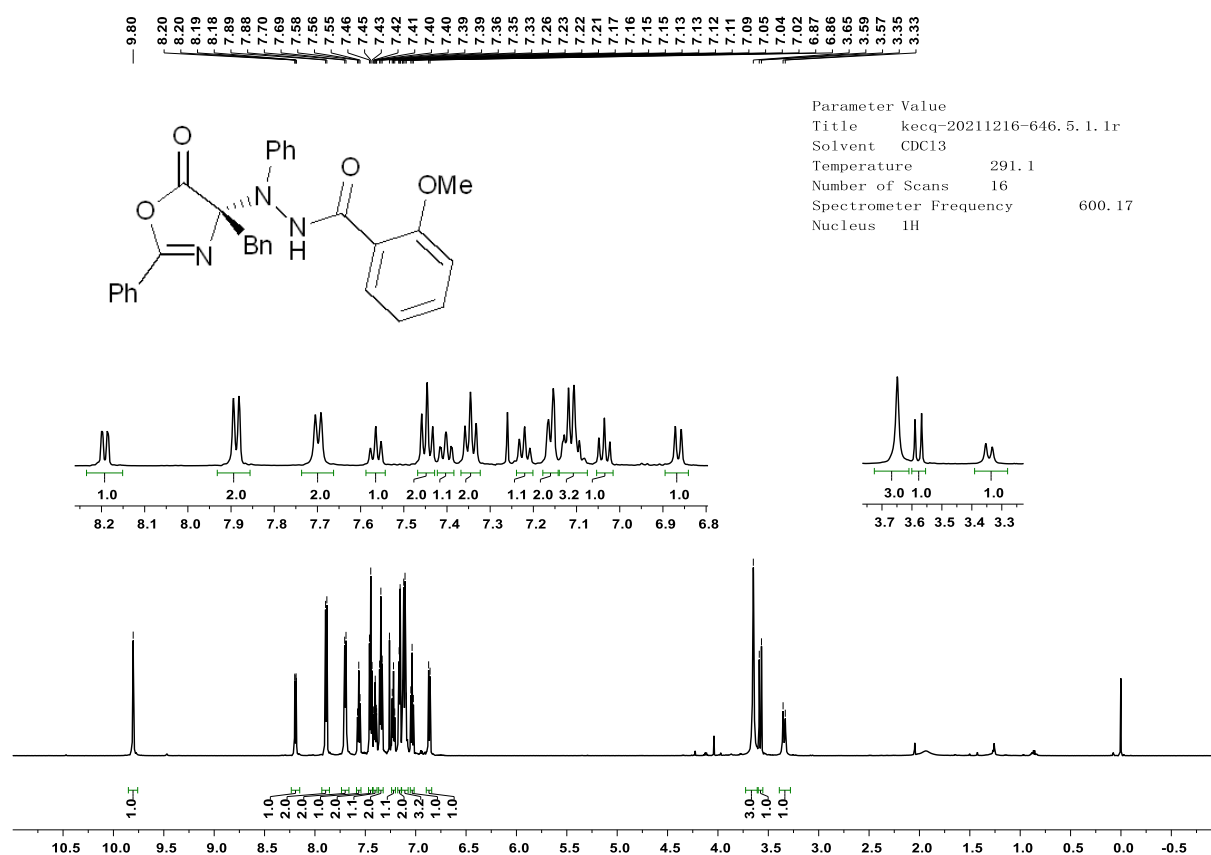


Figure S2. ^{13}C NMR of C1

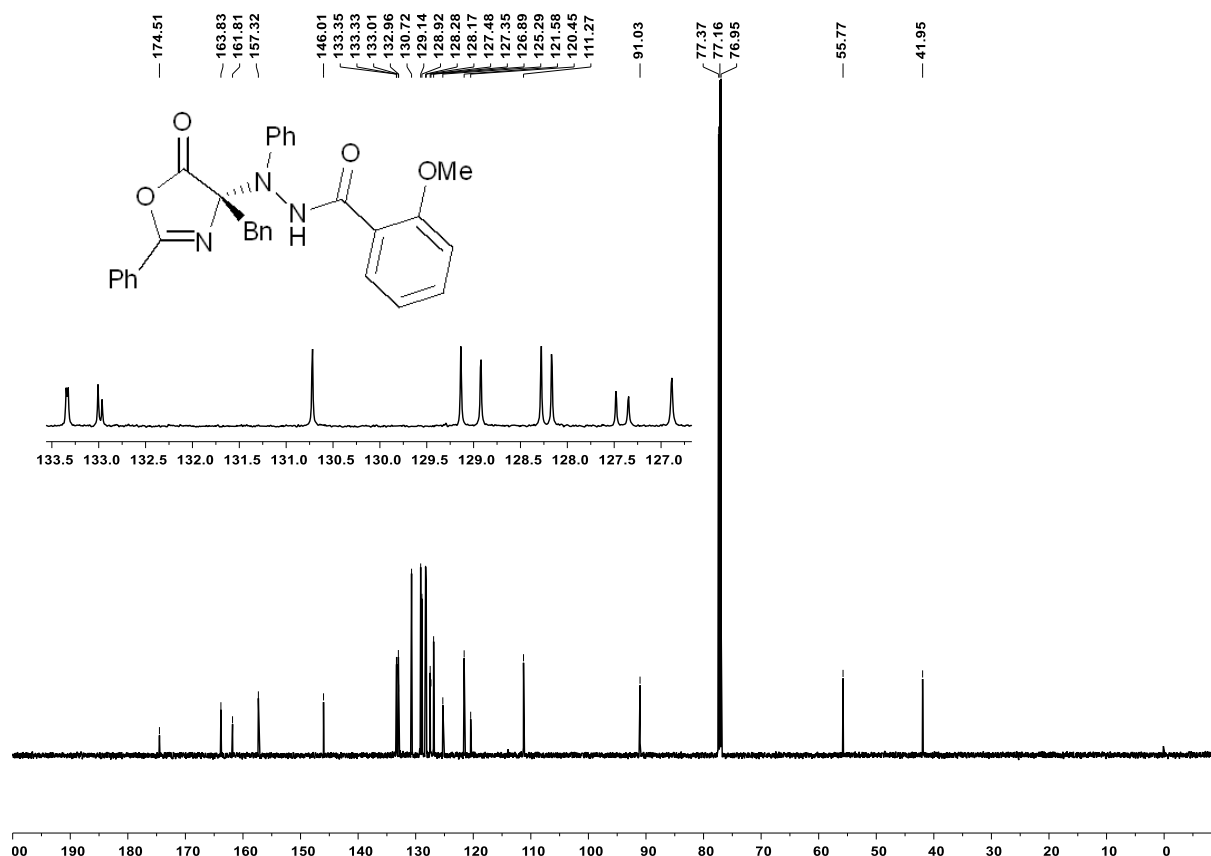


Figure S3. ^1H NMR of C2

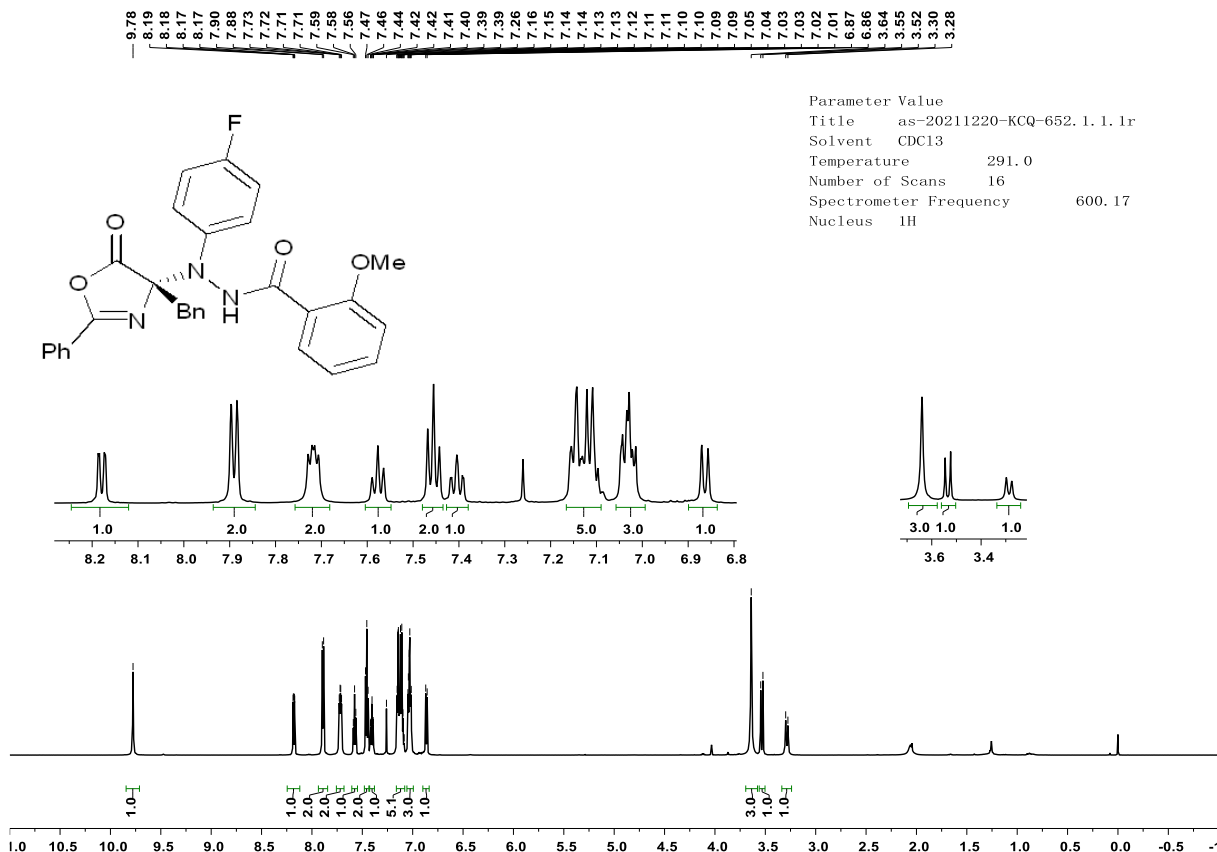


Figure S4. ^{13}C NMR of C2

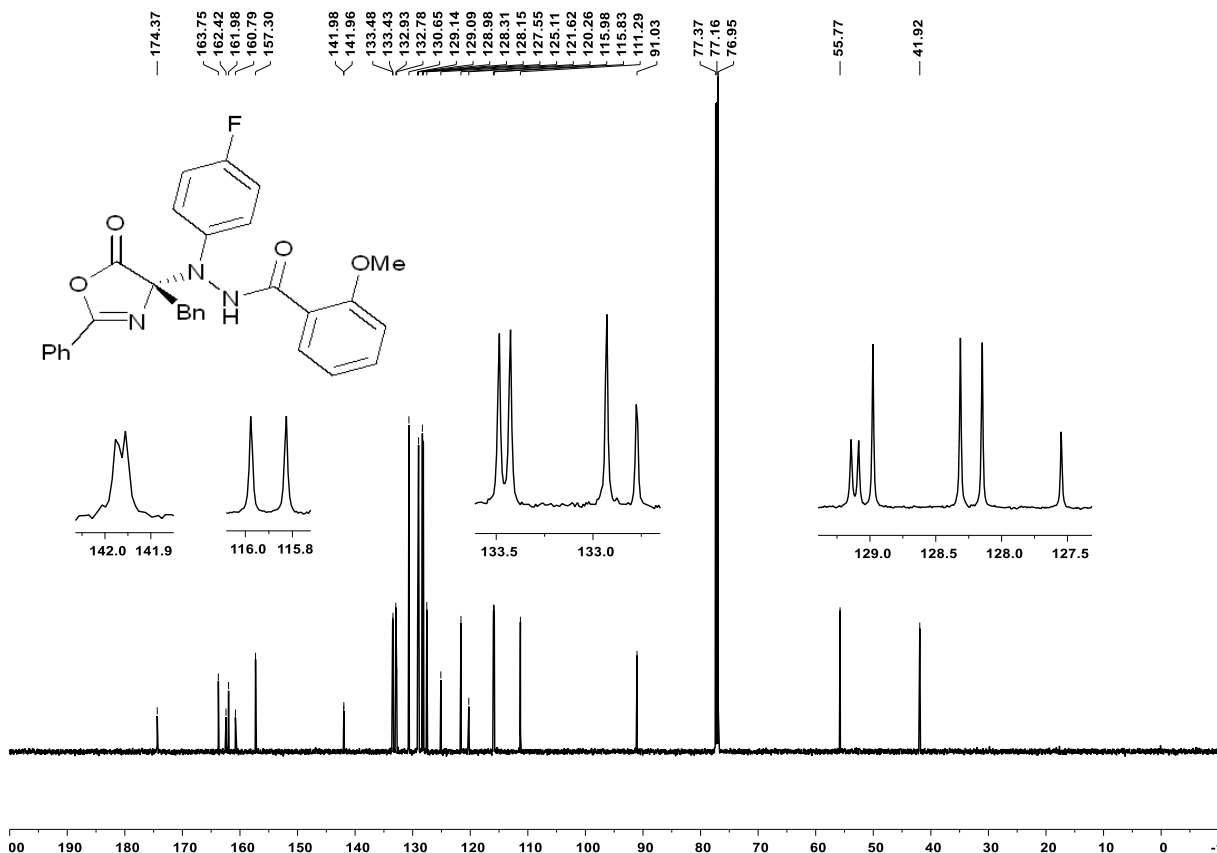


Figure S5. $^{19}\text{F}\{^1\text{H}\}$ NMR of C2

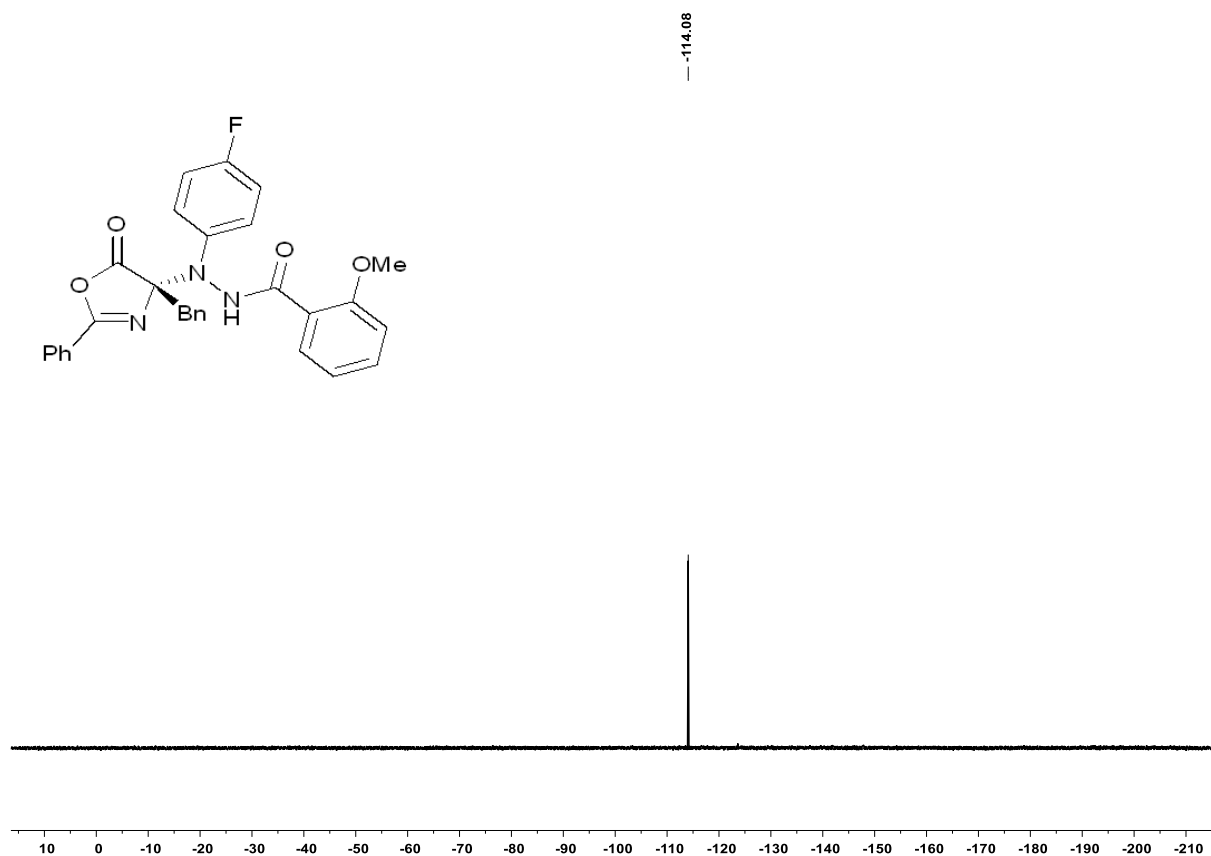


Figure S6. ^1H NMR of C3

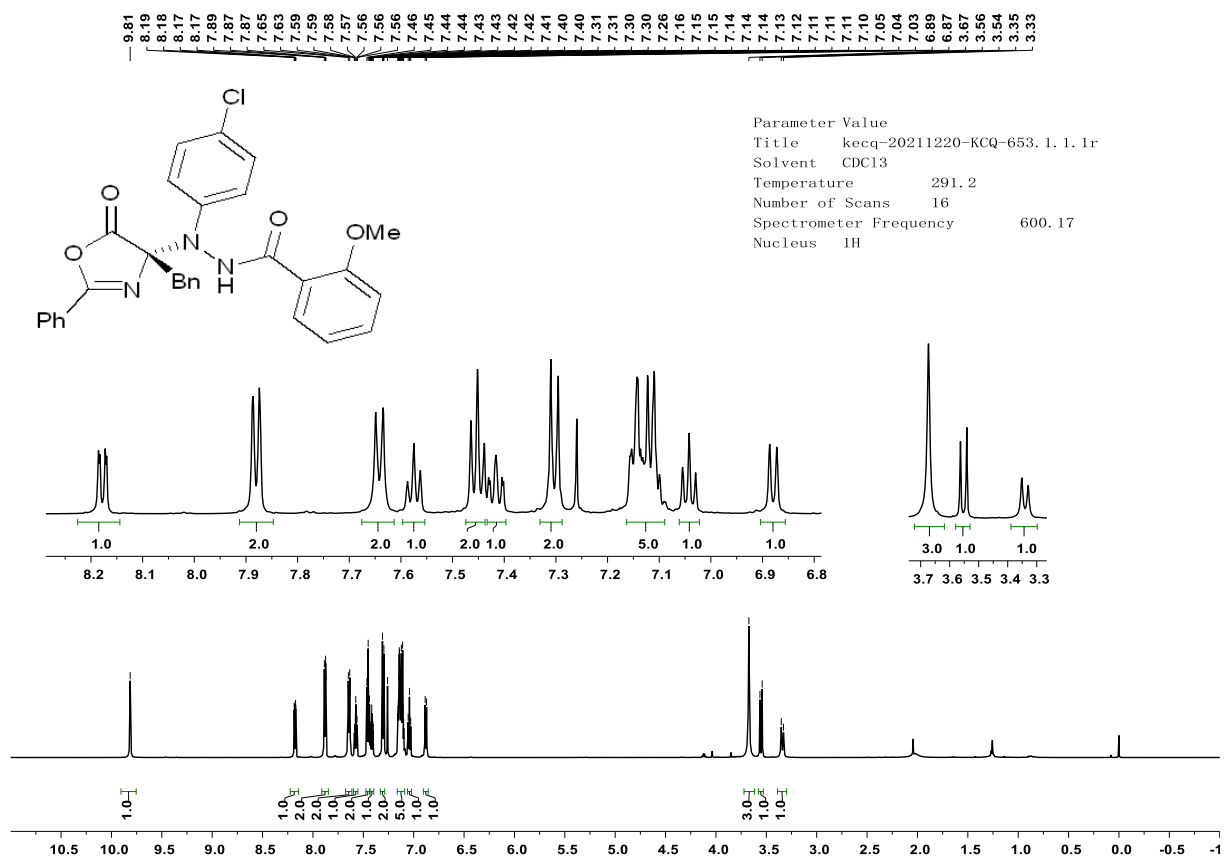


Figure S7. ^{13}C NMR of C3

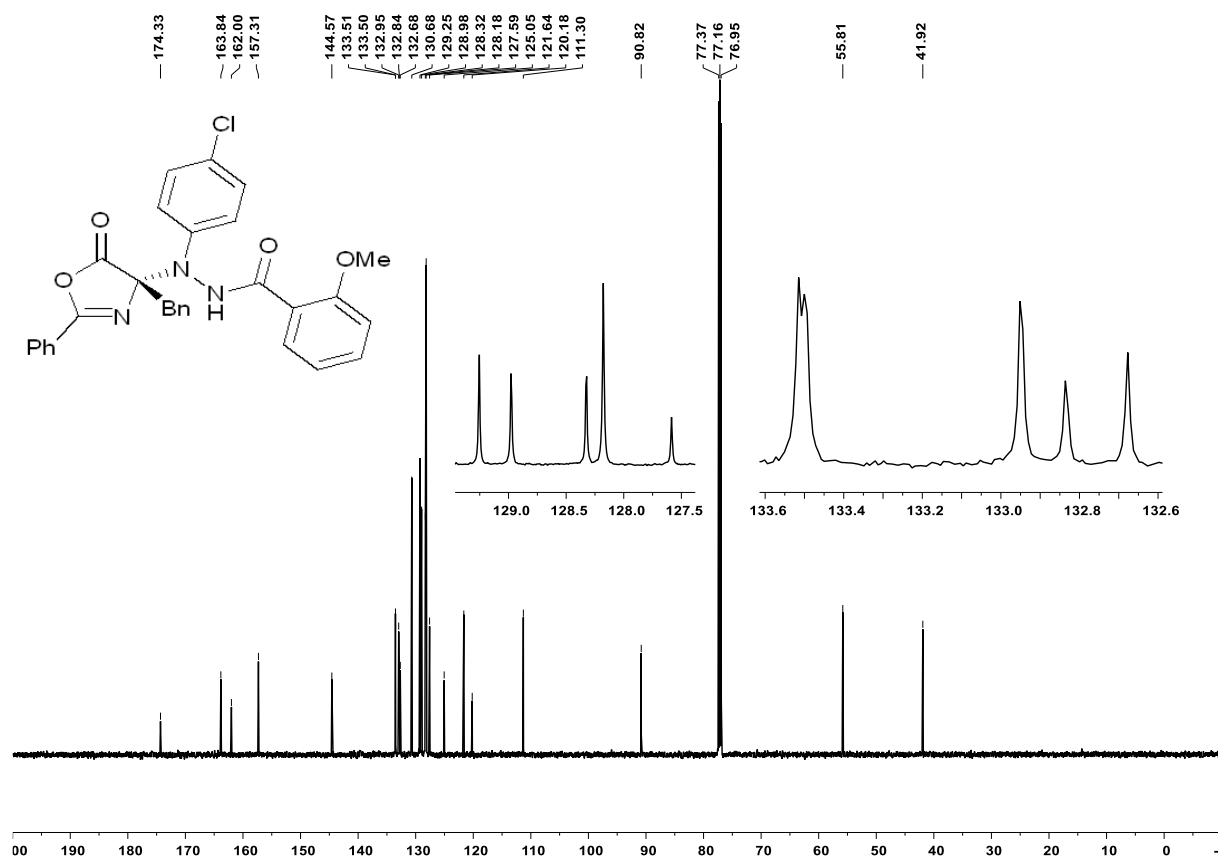


Figure S8. ^1H NMR of C4

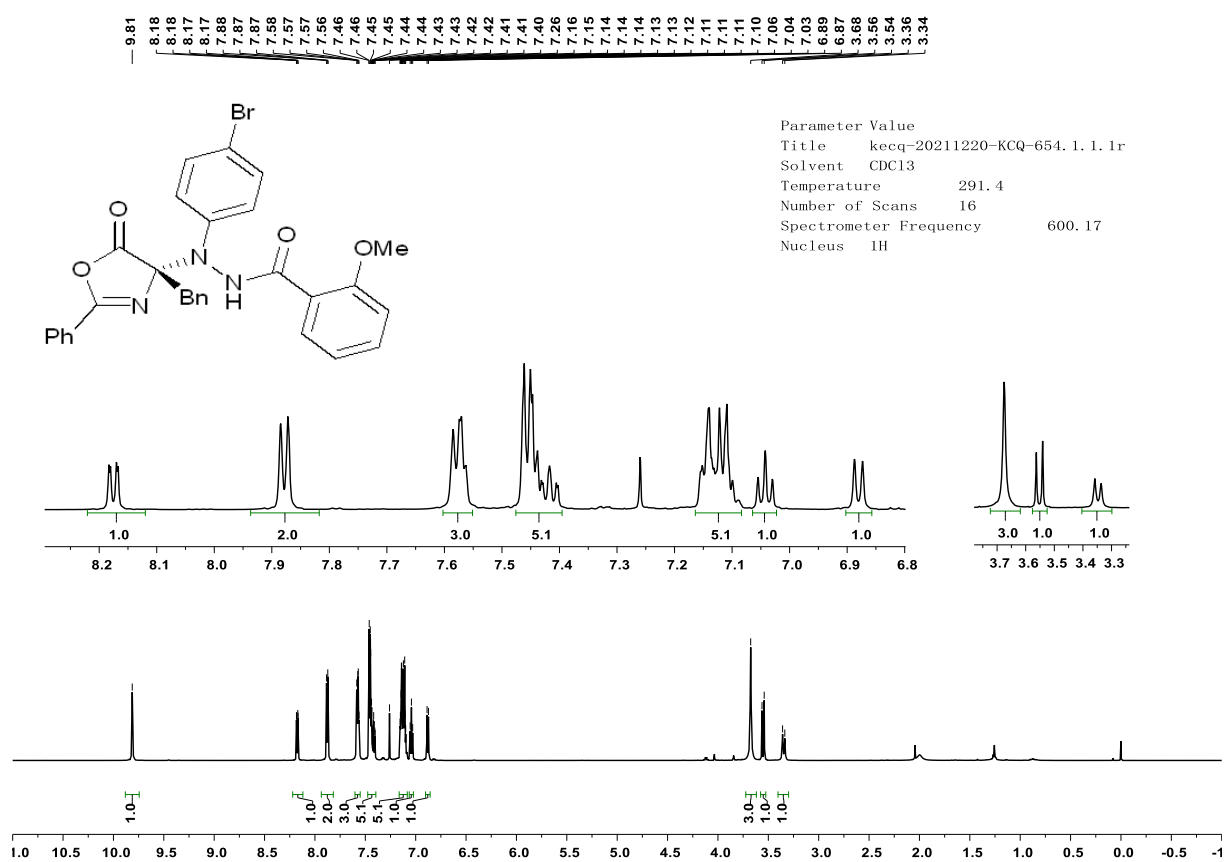


Figure S9. ^{13}C NMR of C4

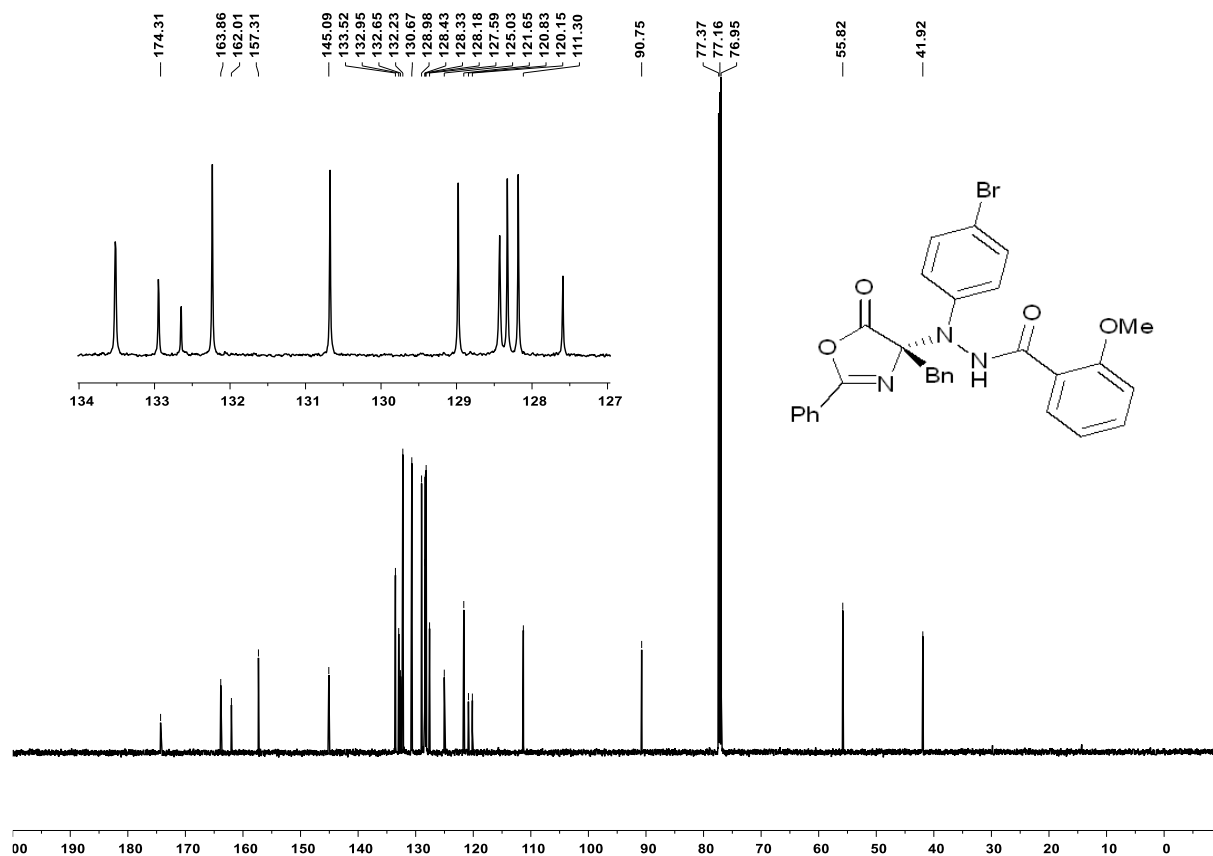


Figure S10. ^1H NMR of C5

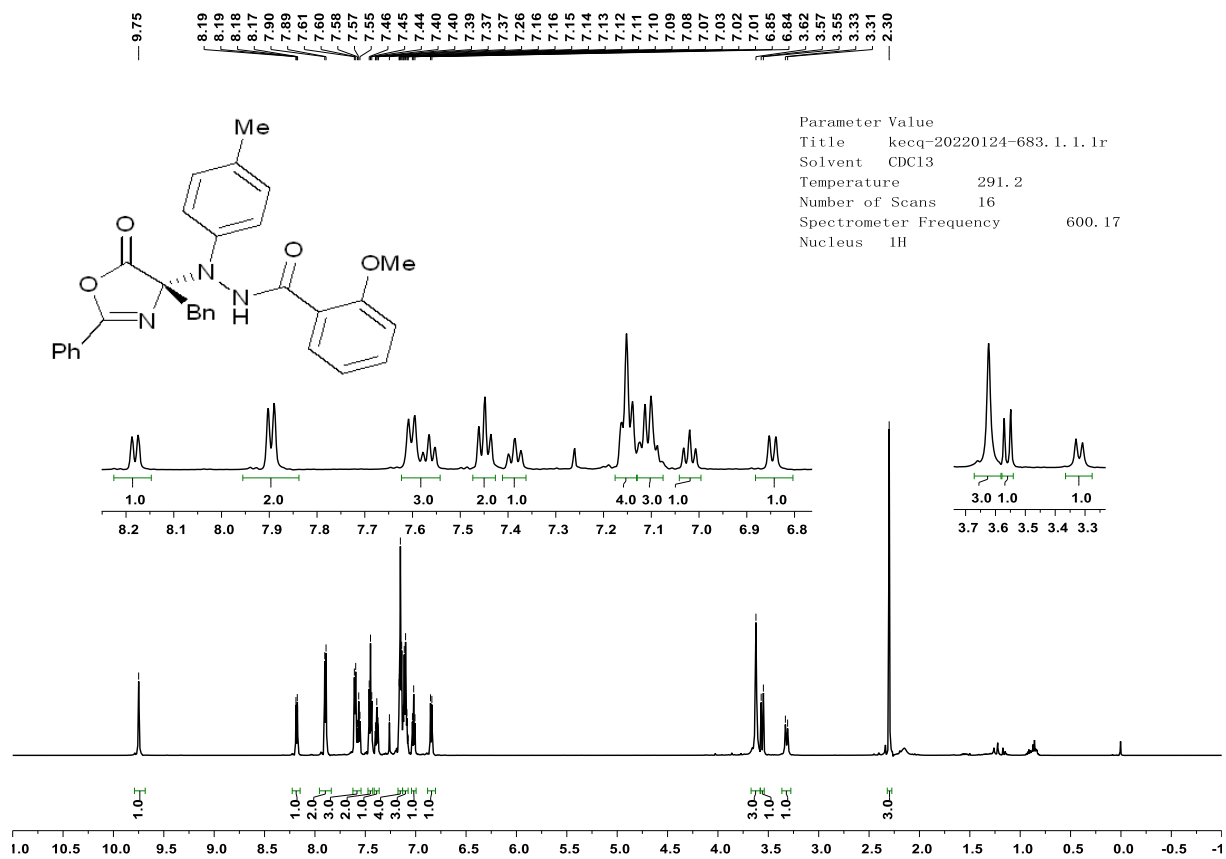


Figure S11. ^{13}C NMR of C5

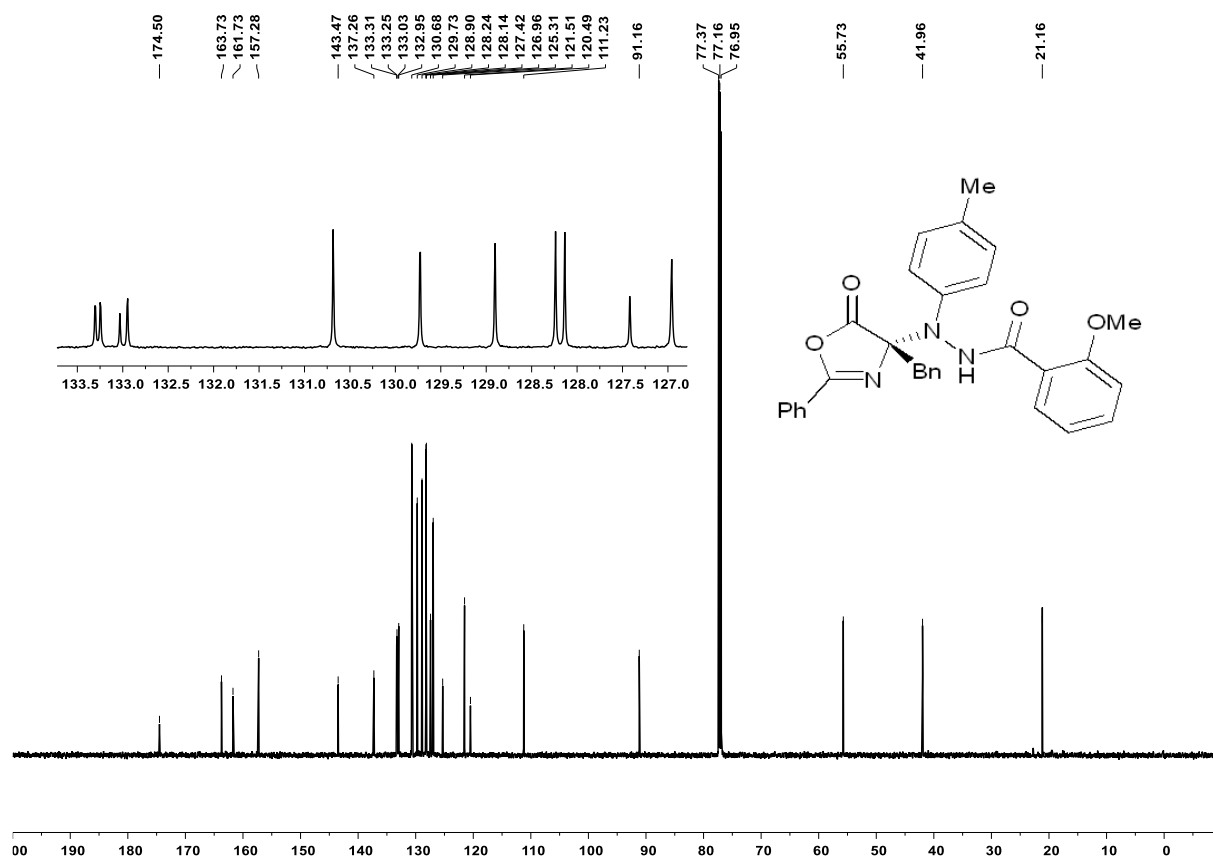


Figure S12. ^1H NMR of C6

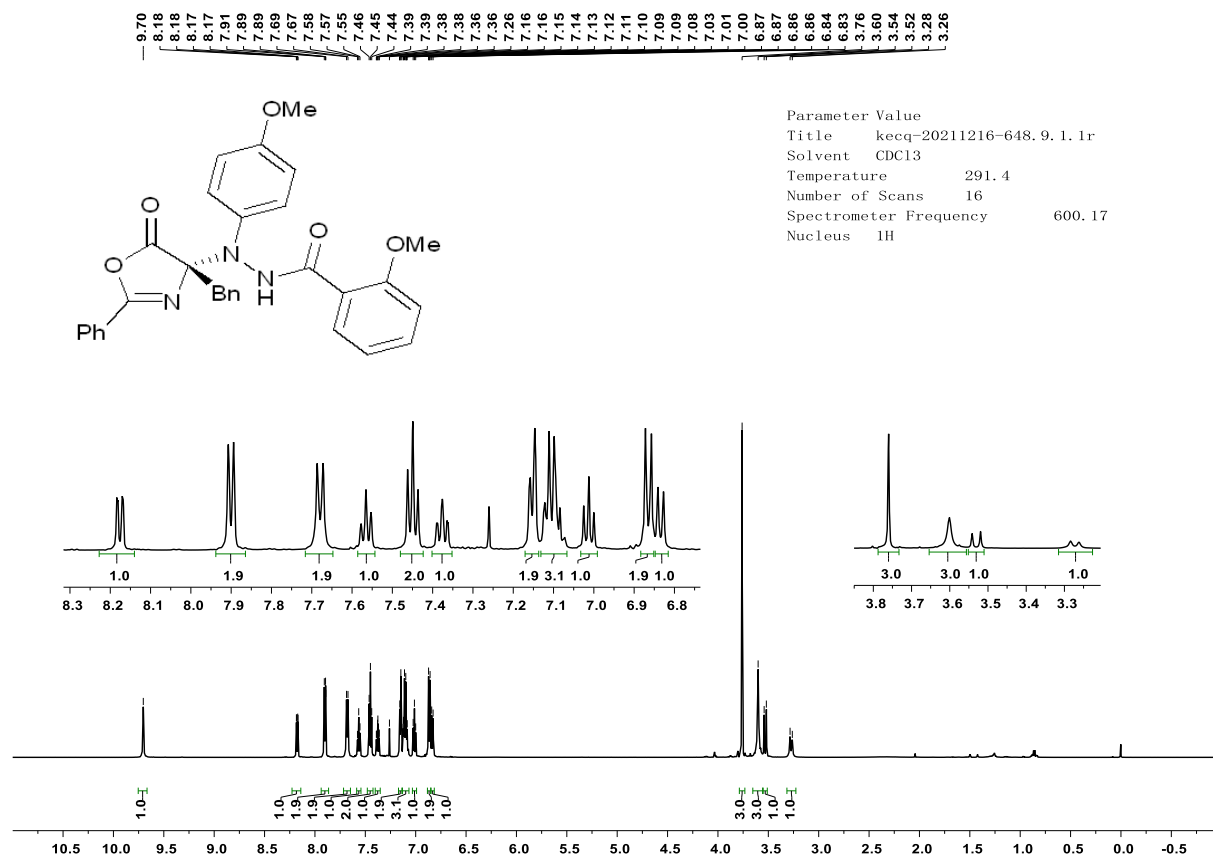


Figure S13. ^{13}C NMR of C6

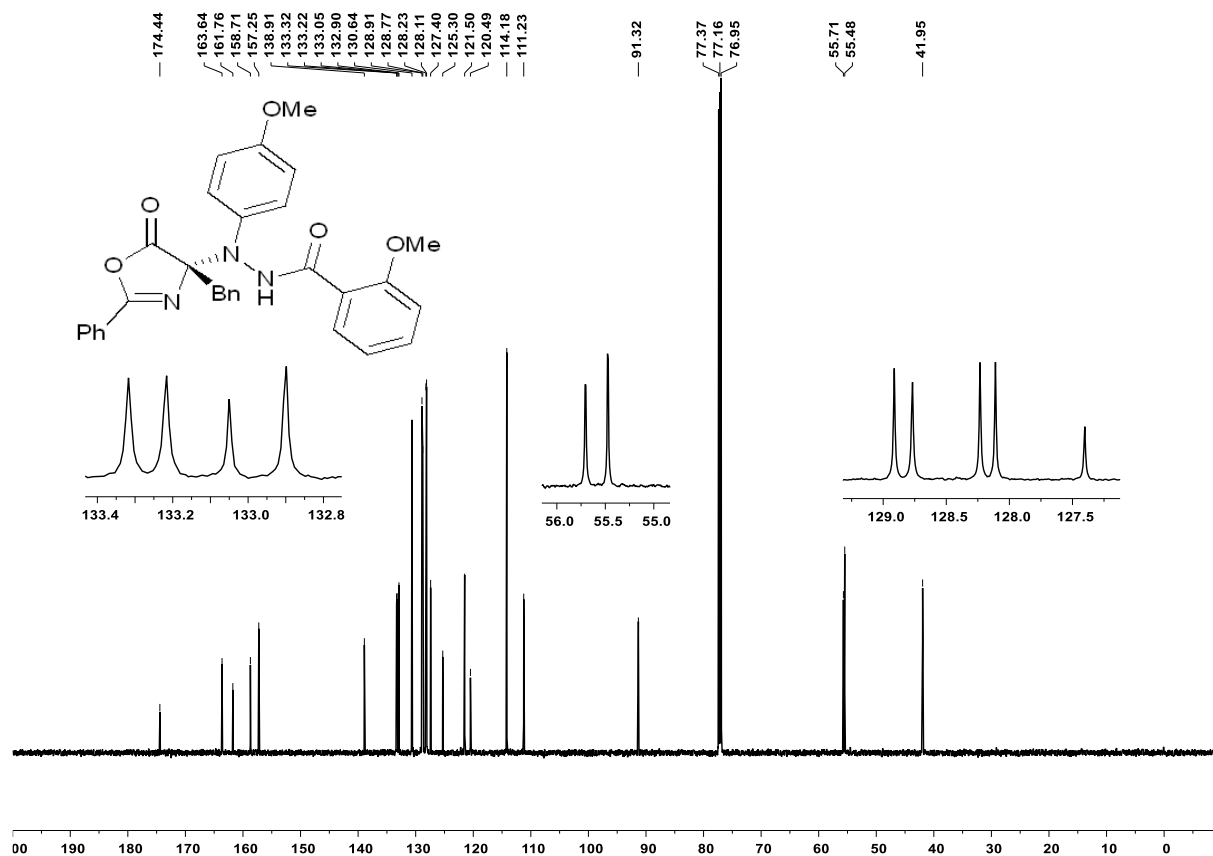


Figure S14. ^1H NMR of C7

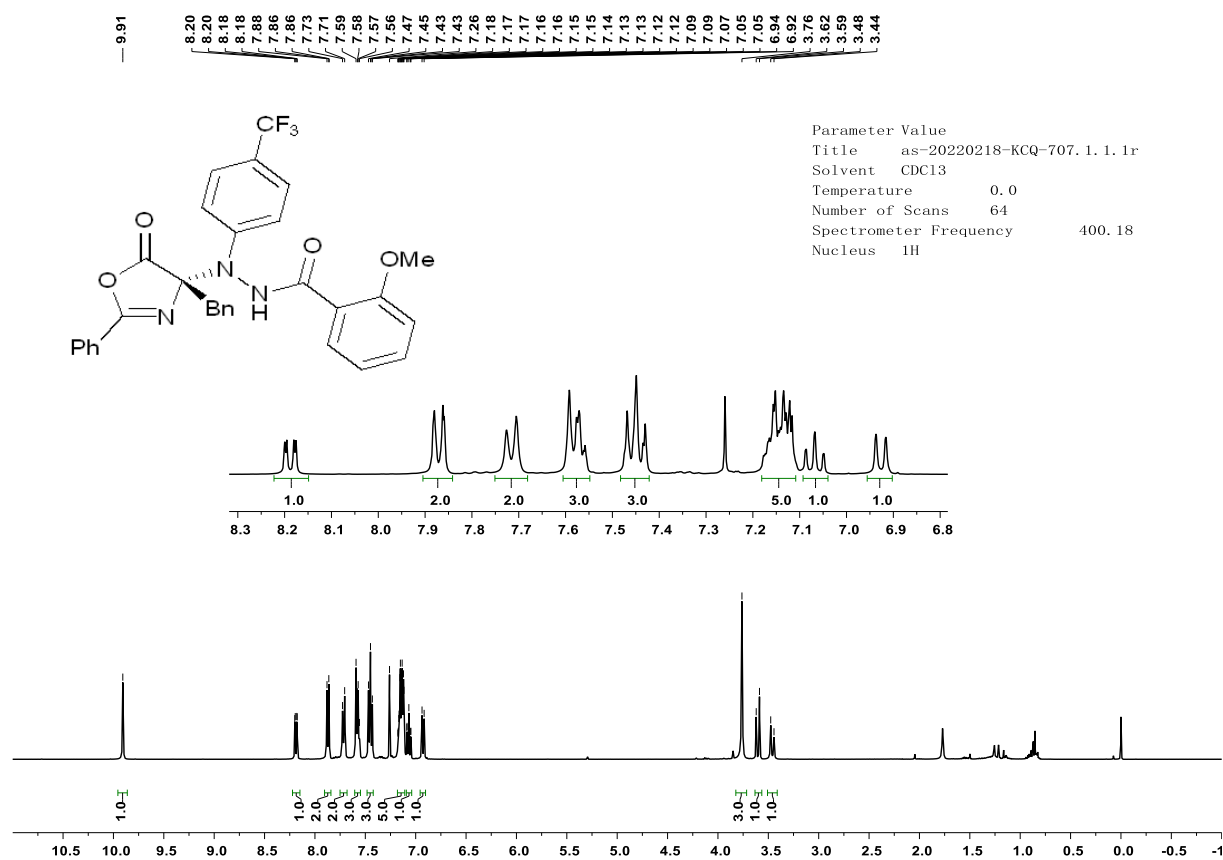


Figure S15. ^{13}C NMR of C7

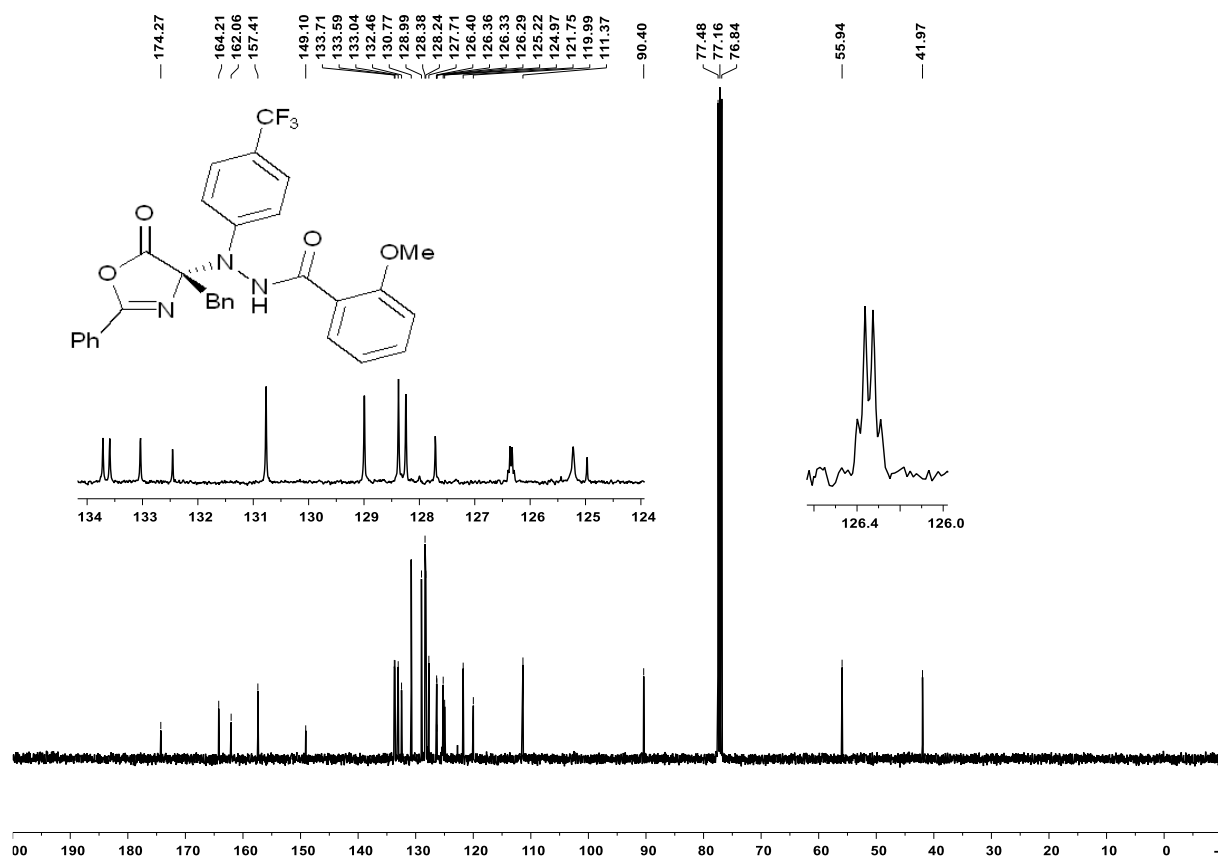


Figure S16. $^{19}\text{F}\{^1\text{H}\}$ NMR of C7

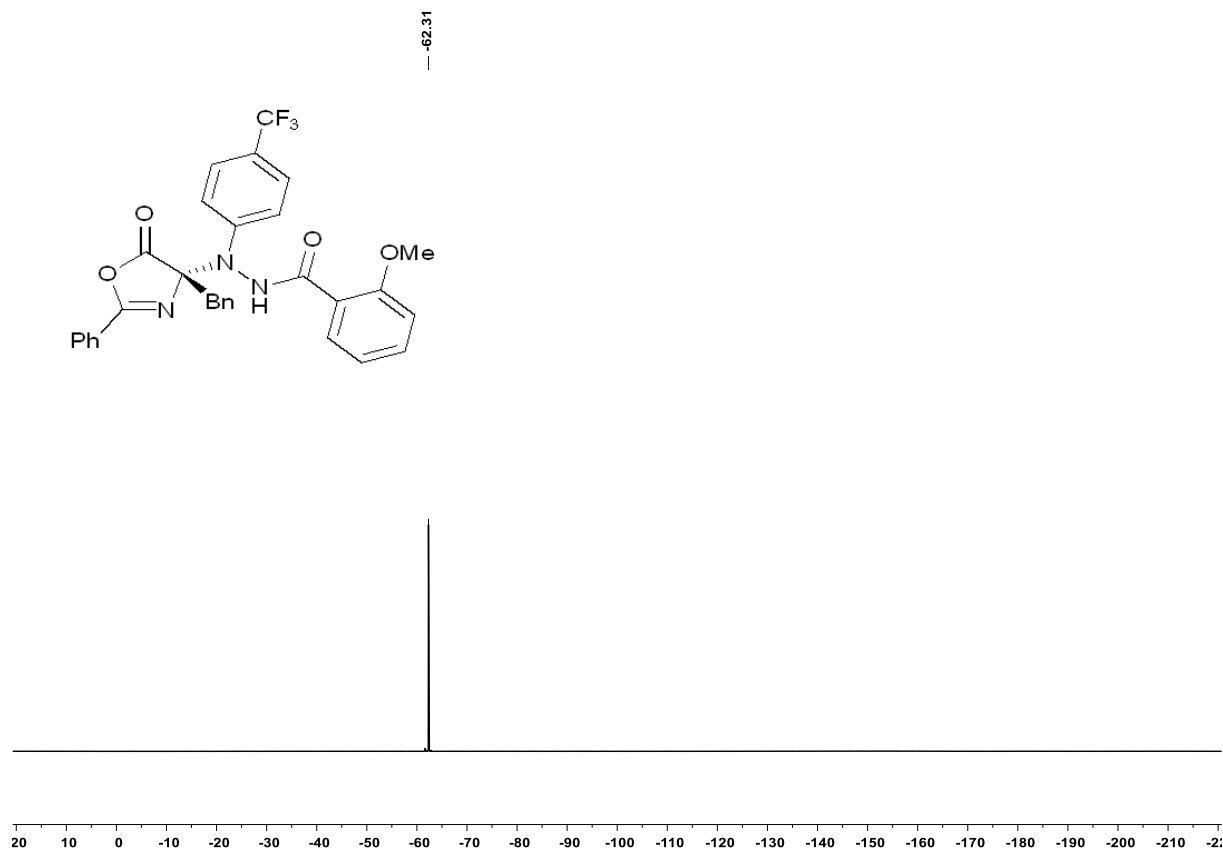


Figure S17. ^1H NMR of C8

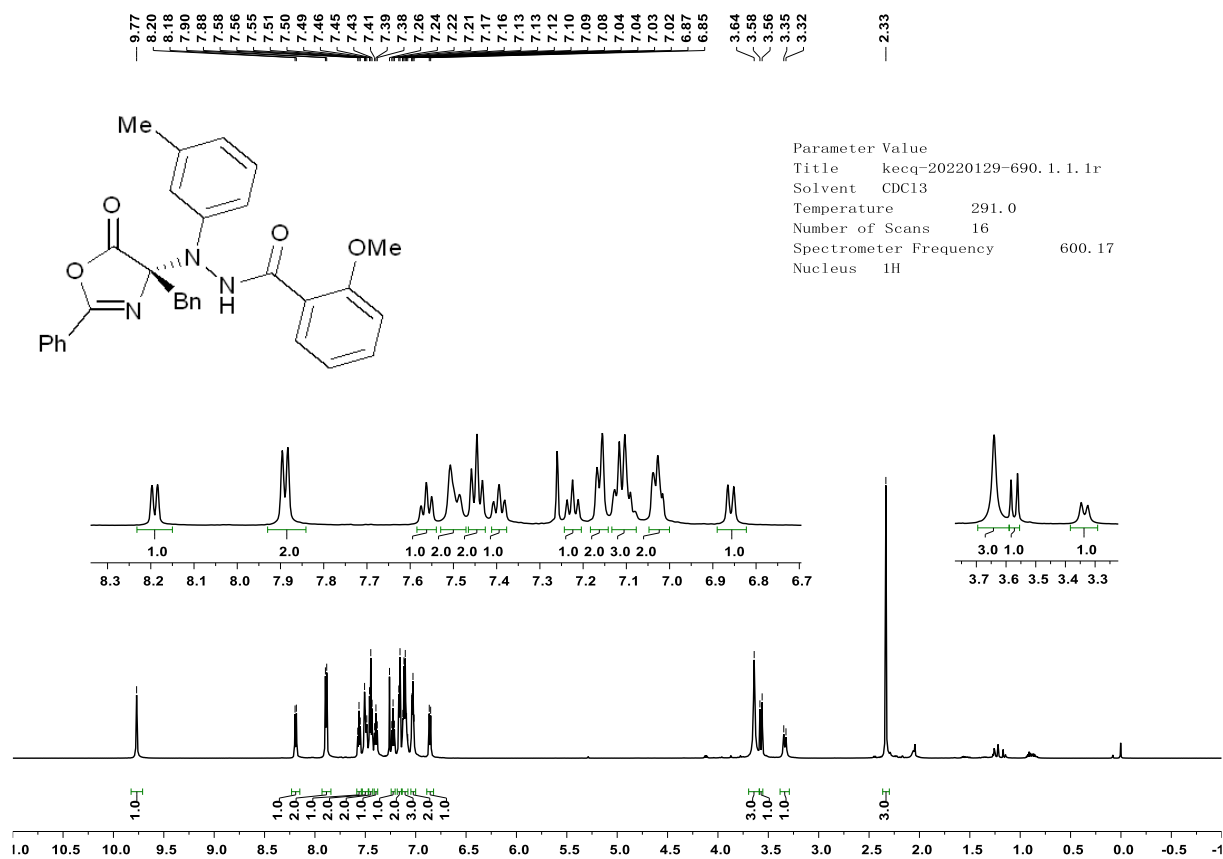


Figure S18. ^{13}C NMR of C8

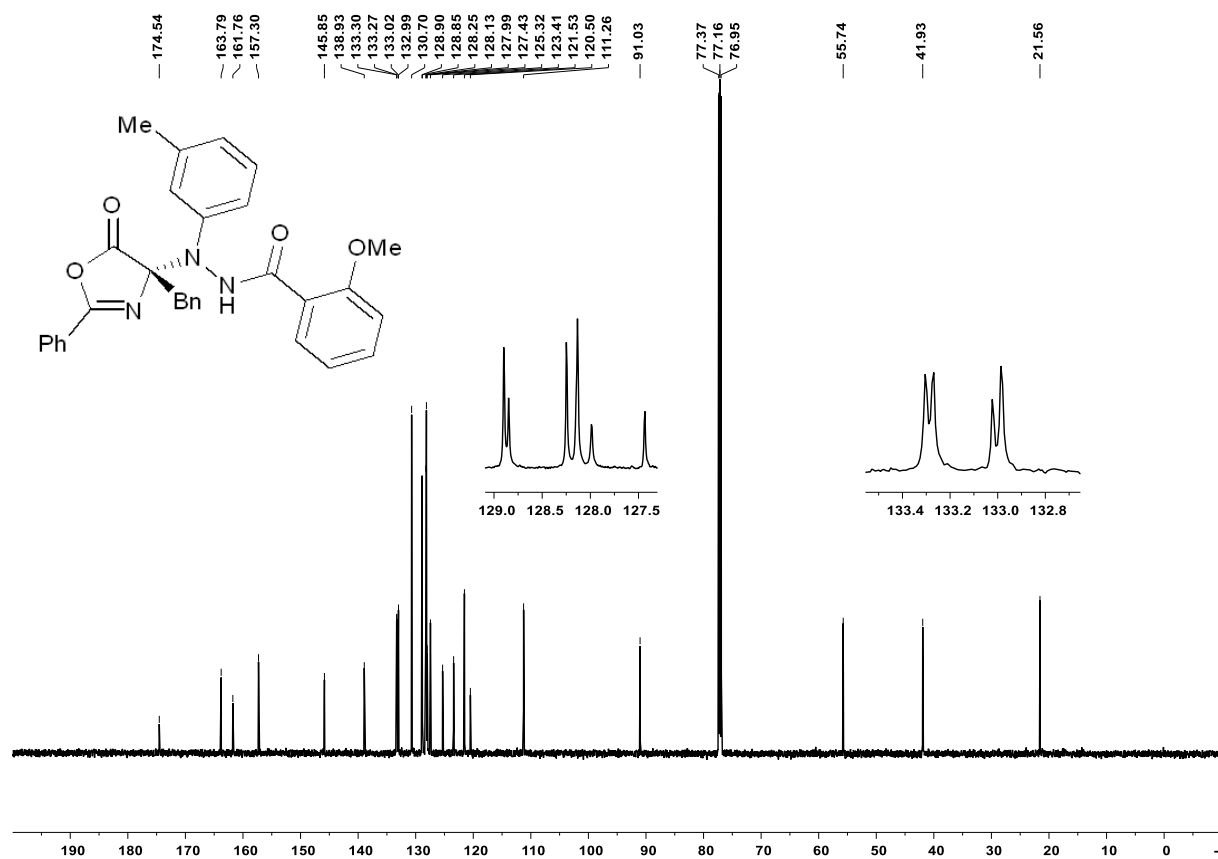


Figure S19. ^1H NMR of C9

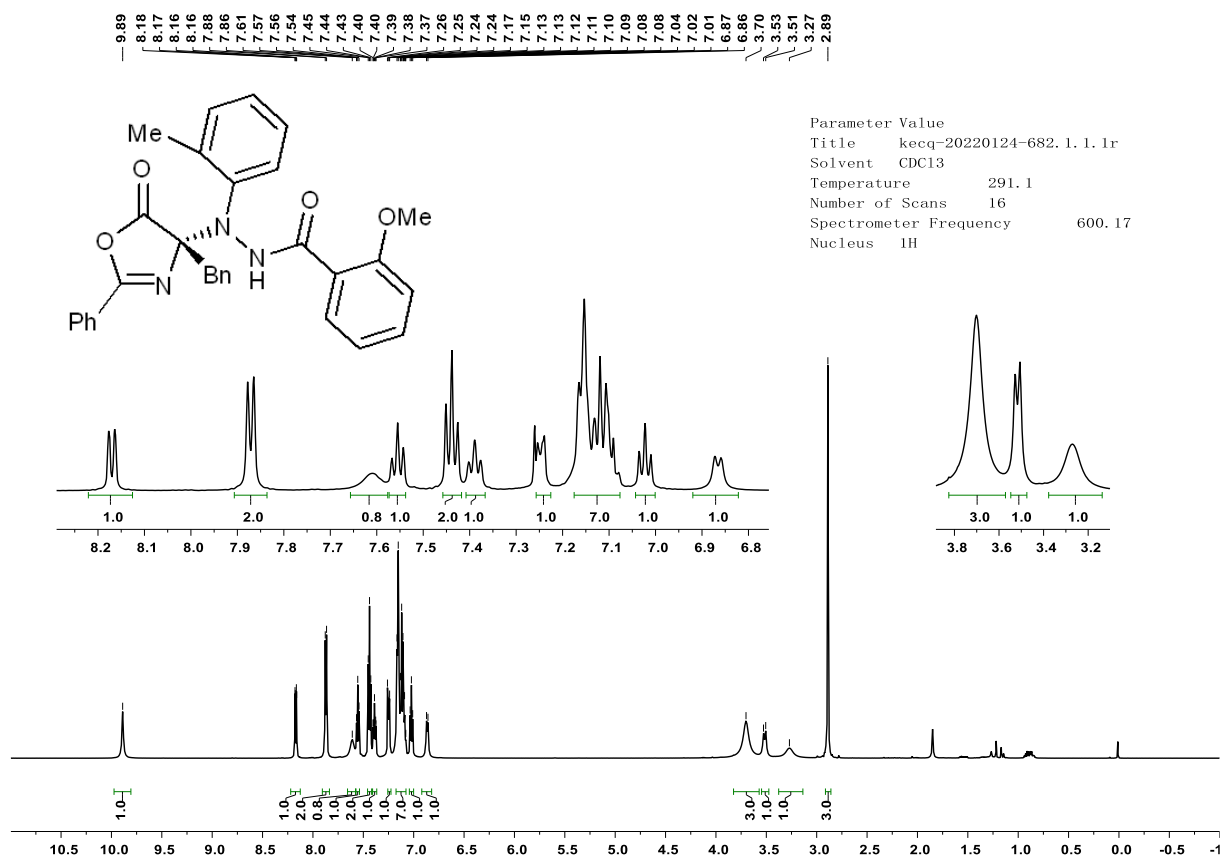


Figure S20. ^{13}C NMR of C9

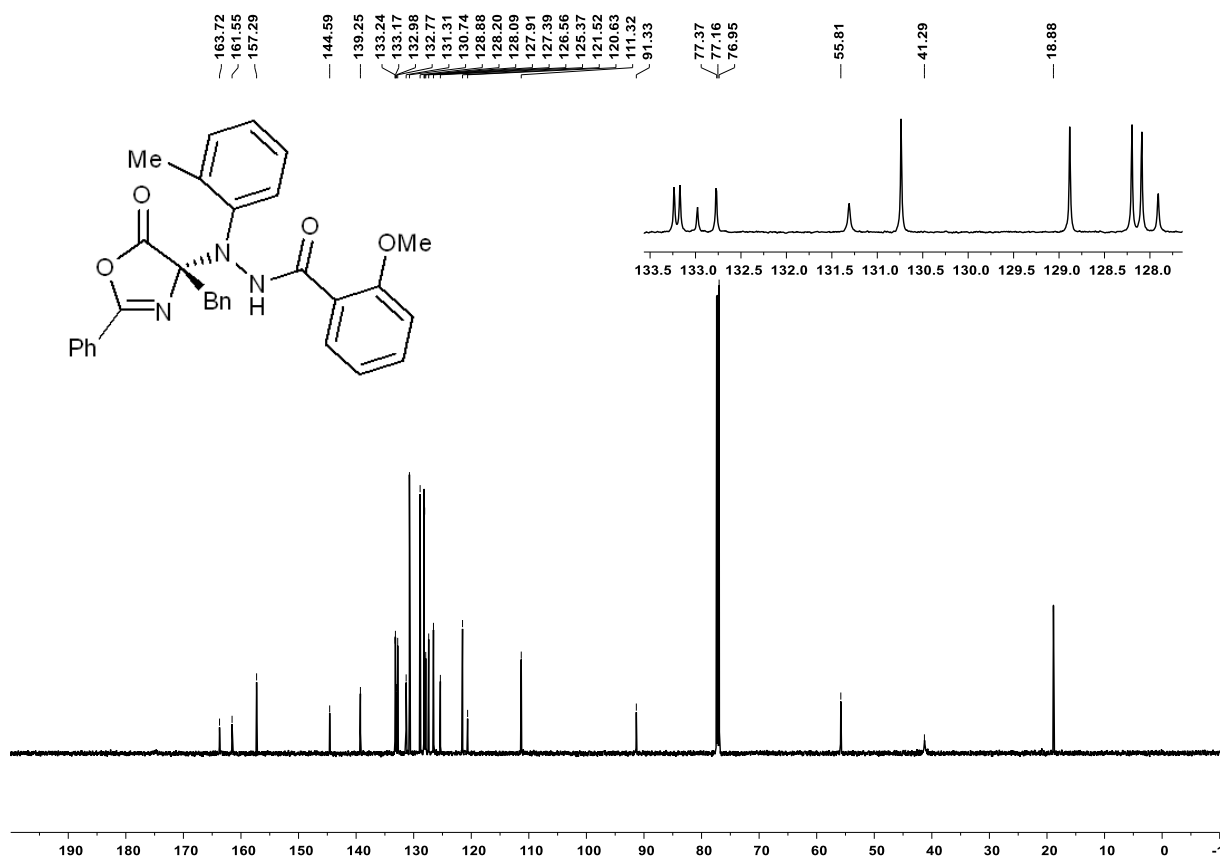


Figure S21. ^1H NMR of C10

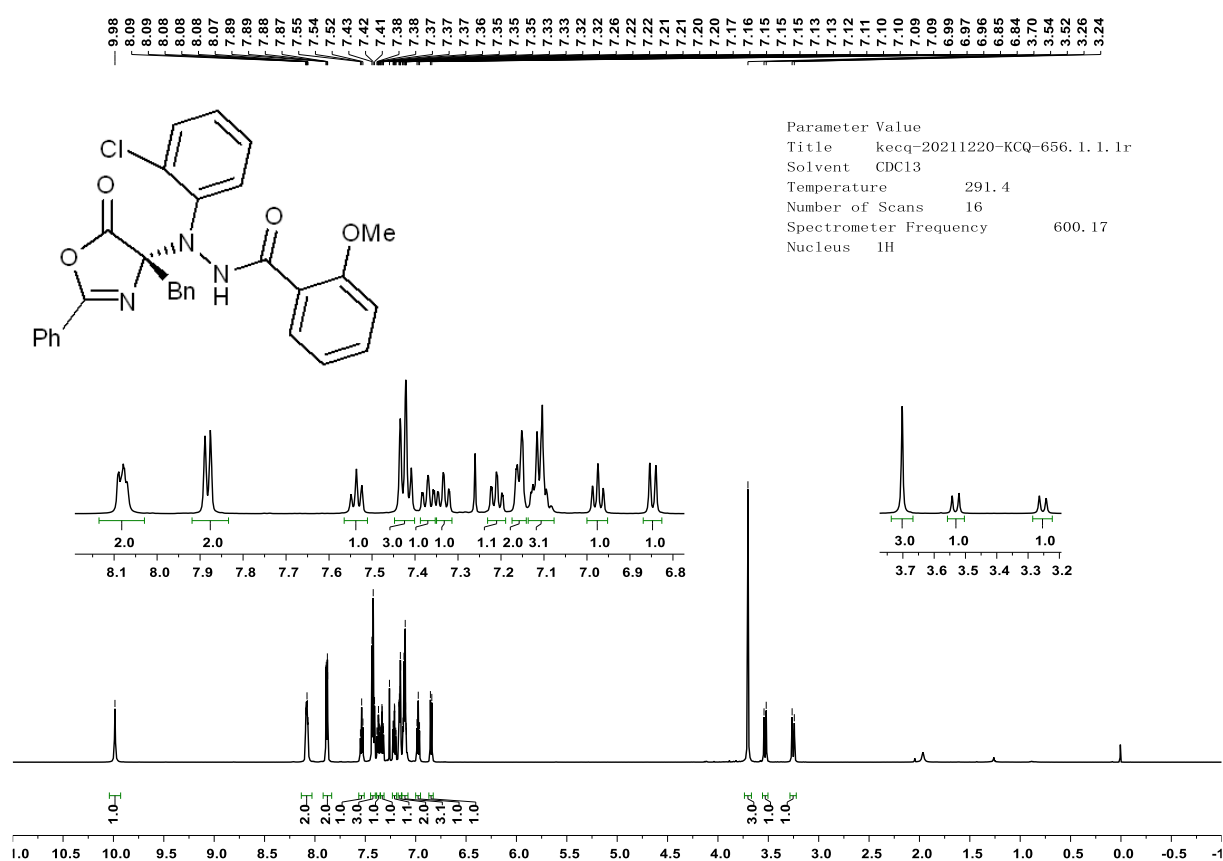


Figure S22. ^{13}C NMR of C10

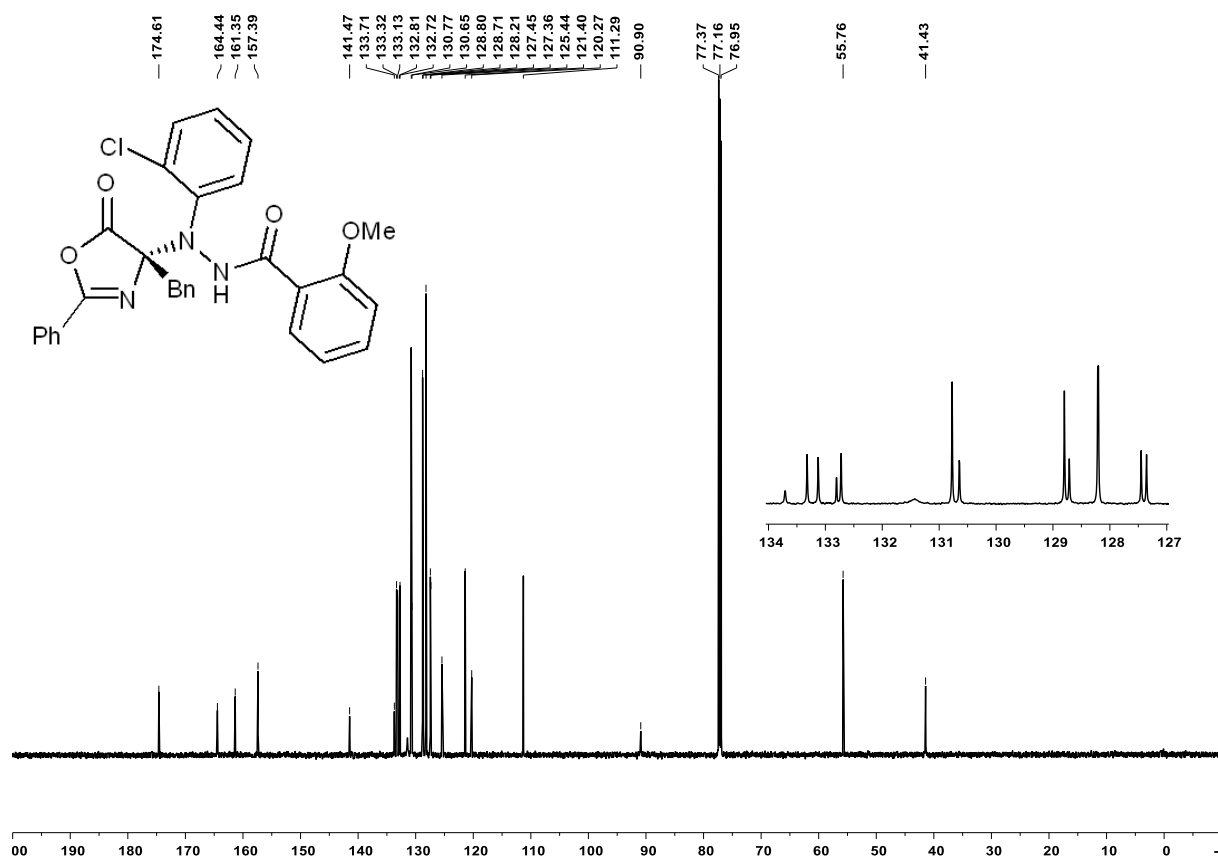


Figure S23. ^1H NMR of C11

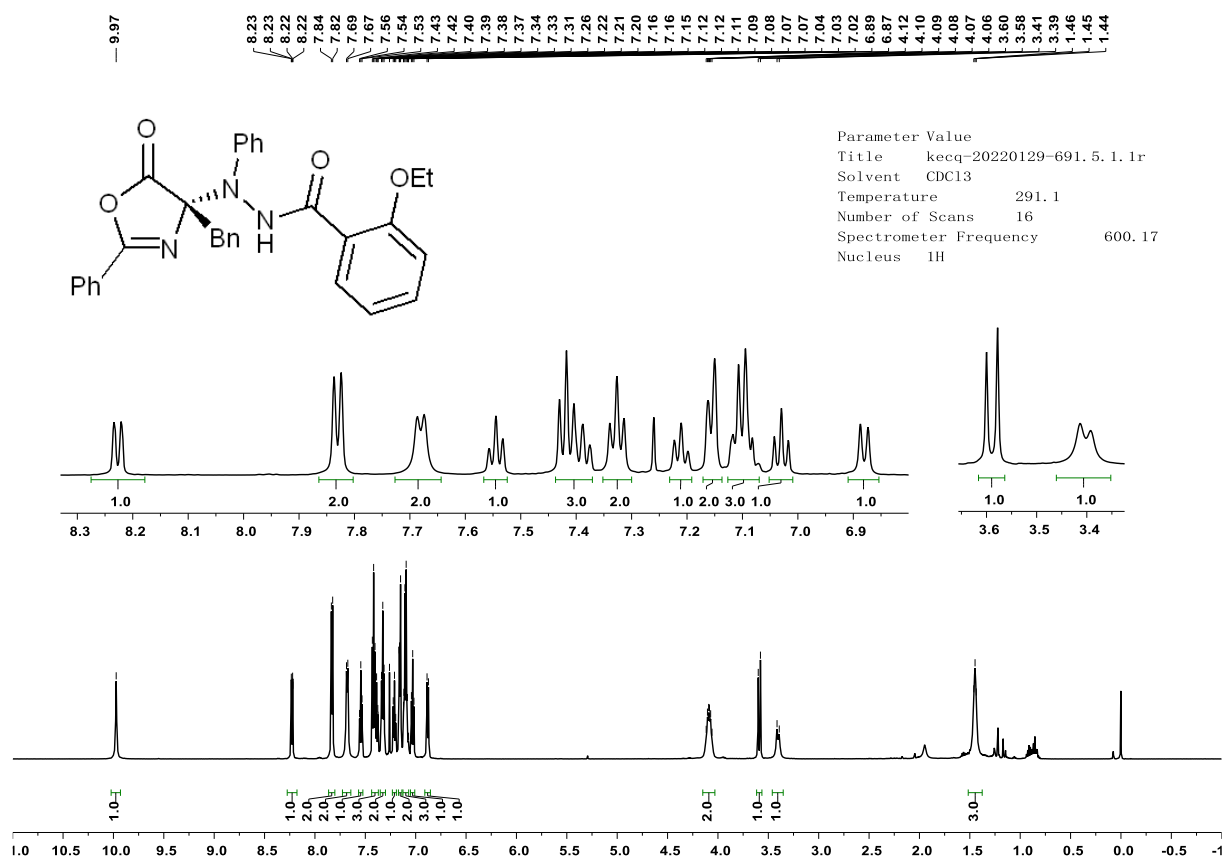


Figure S24. ^{13}C NMR of C11

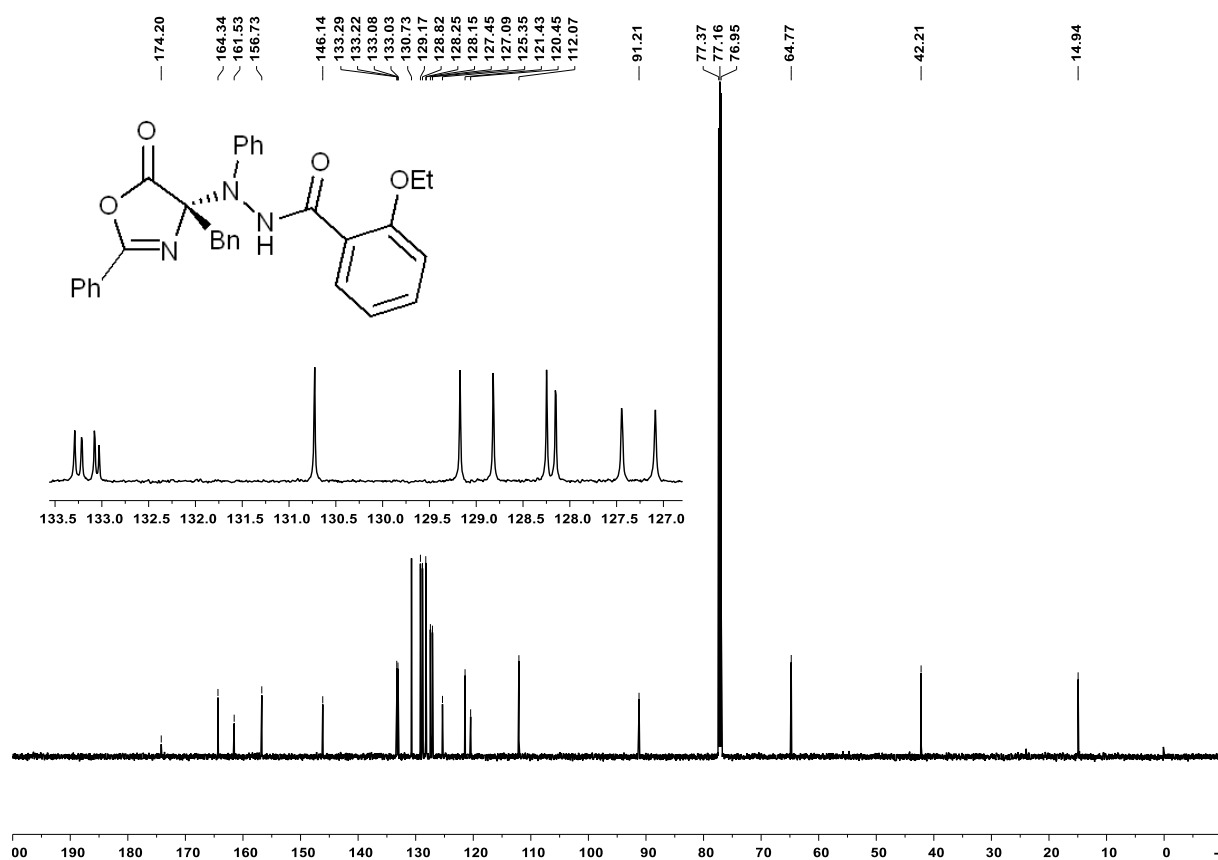


Figure S25. ^1H NMR of C12

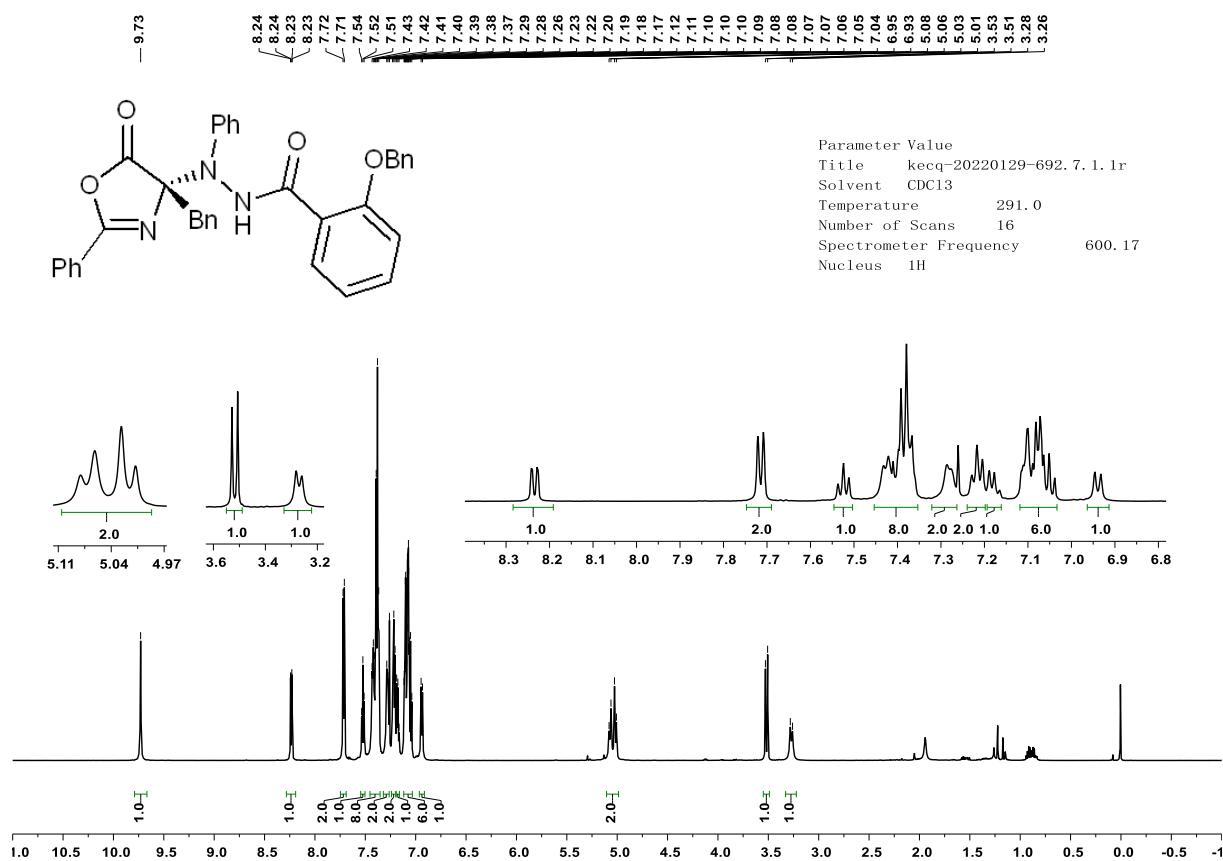


Figure S26. ^{13}C NMR of C12

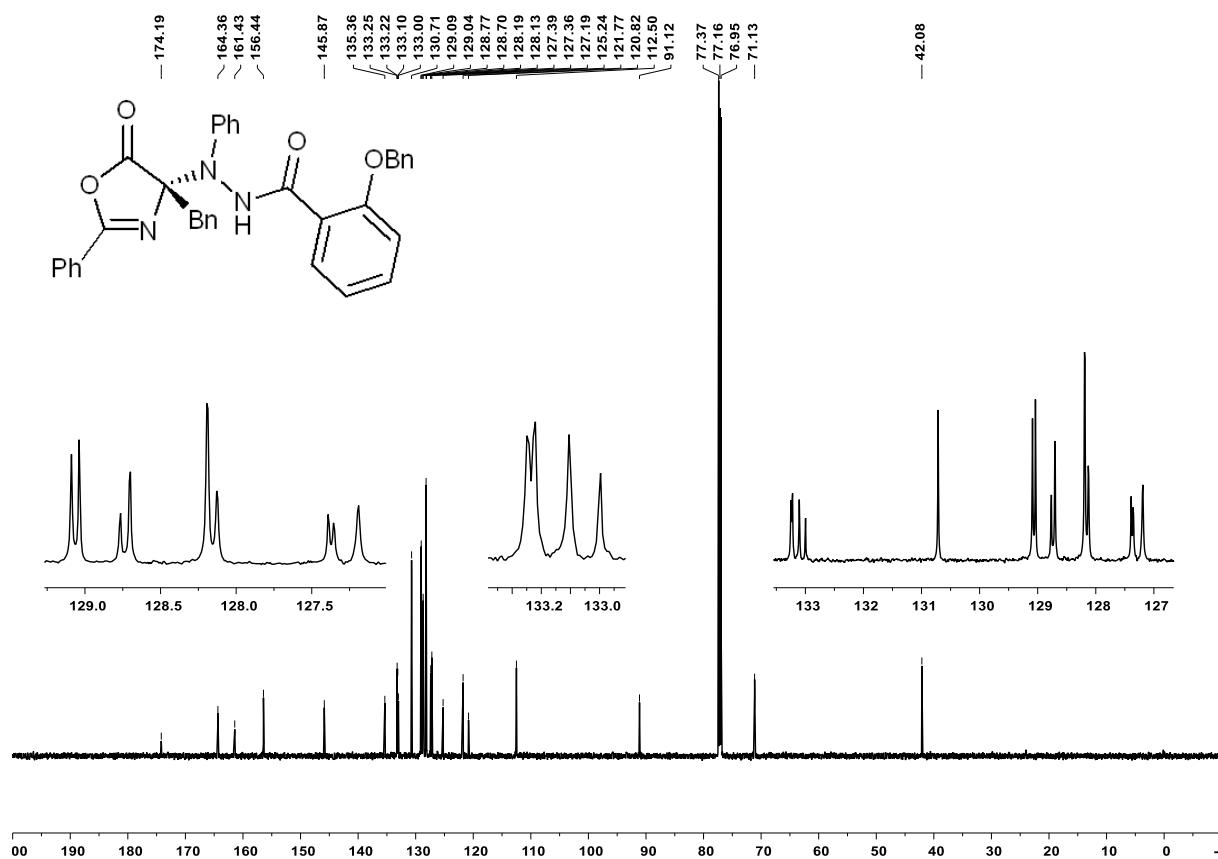


Figure S27. ^1H NMR of C13

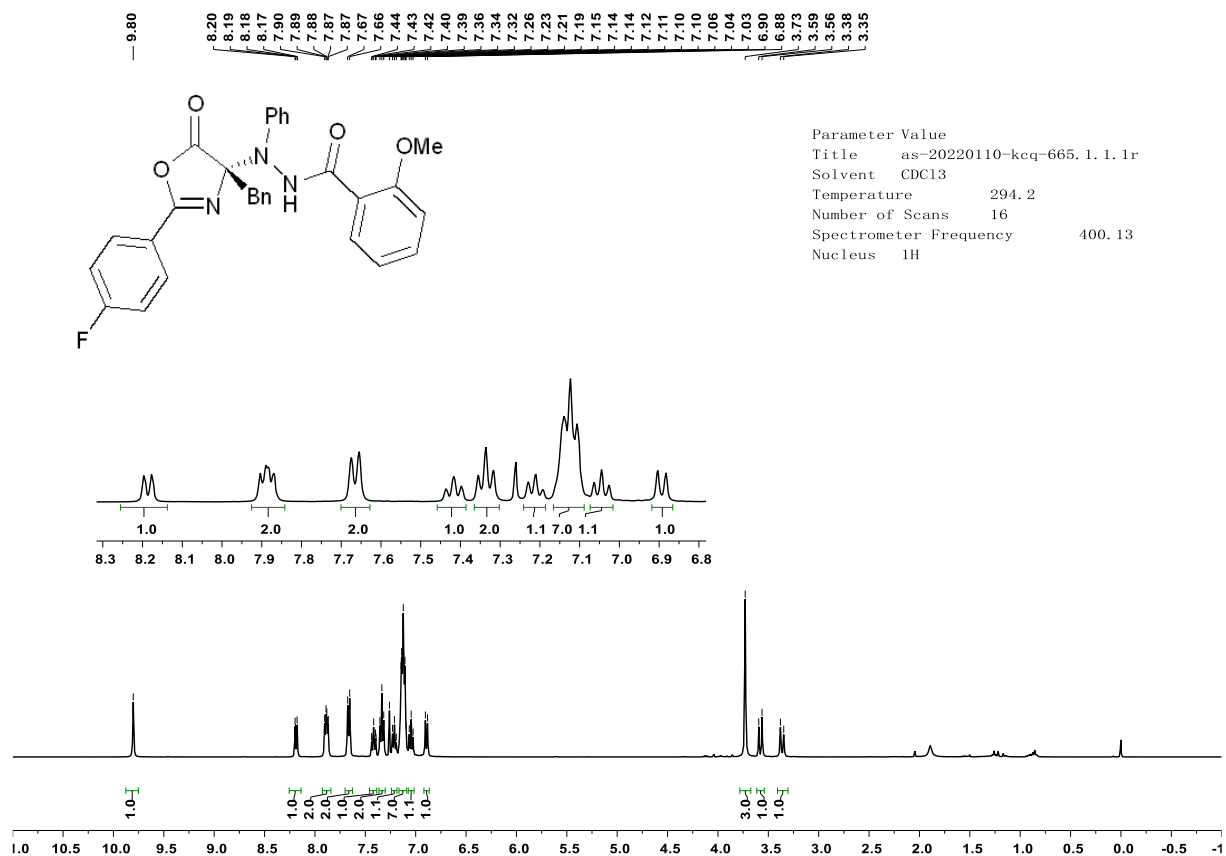


Figure S28. ^{13}C NMR of C13

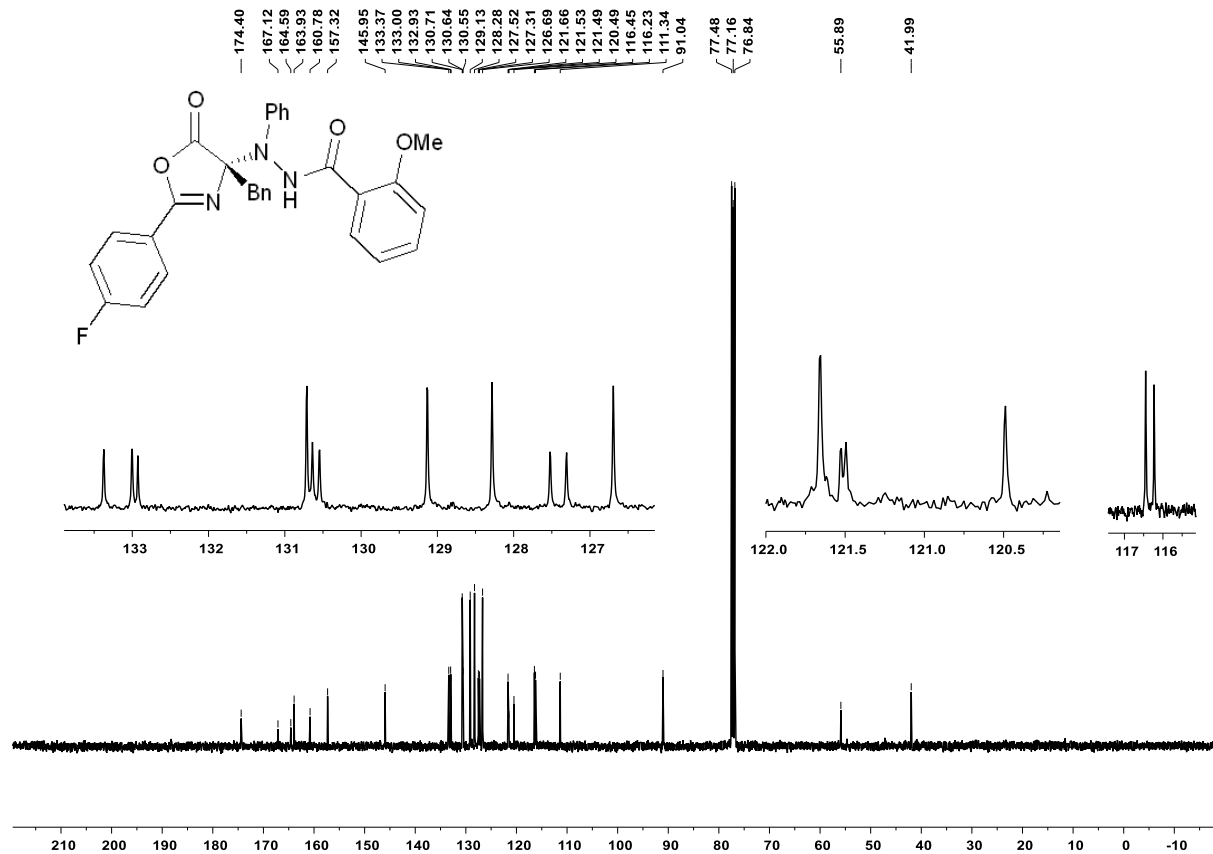


Figure S29. $^{19}\text{F}\{^1\text{H}\}$ NMR of C13

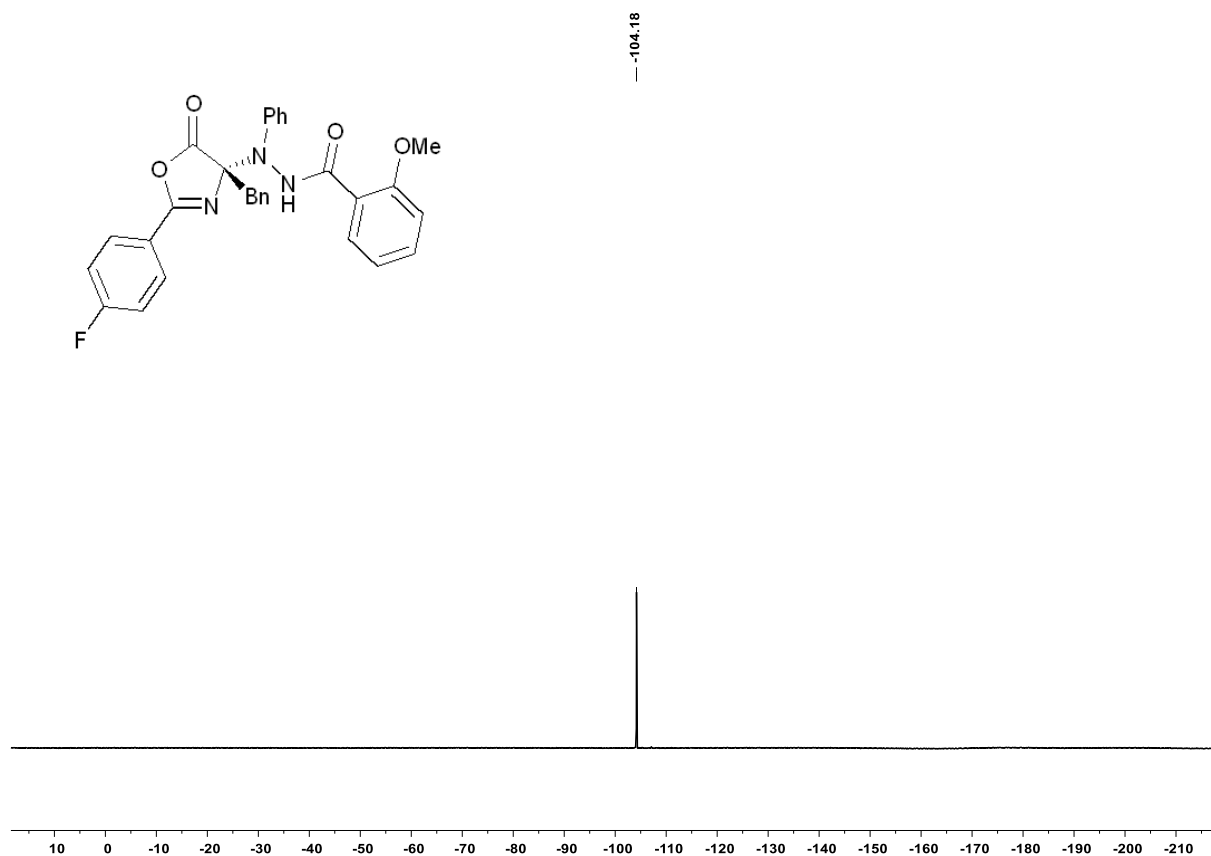


Figure S30. ^1H NMR of C14

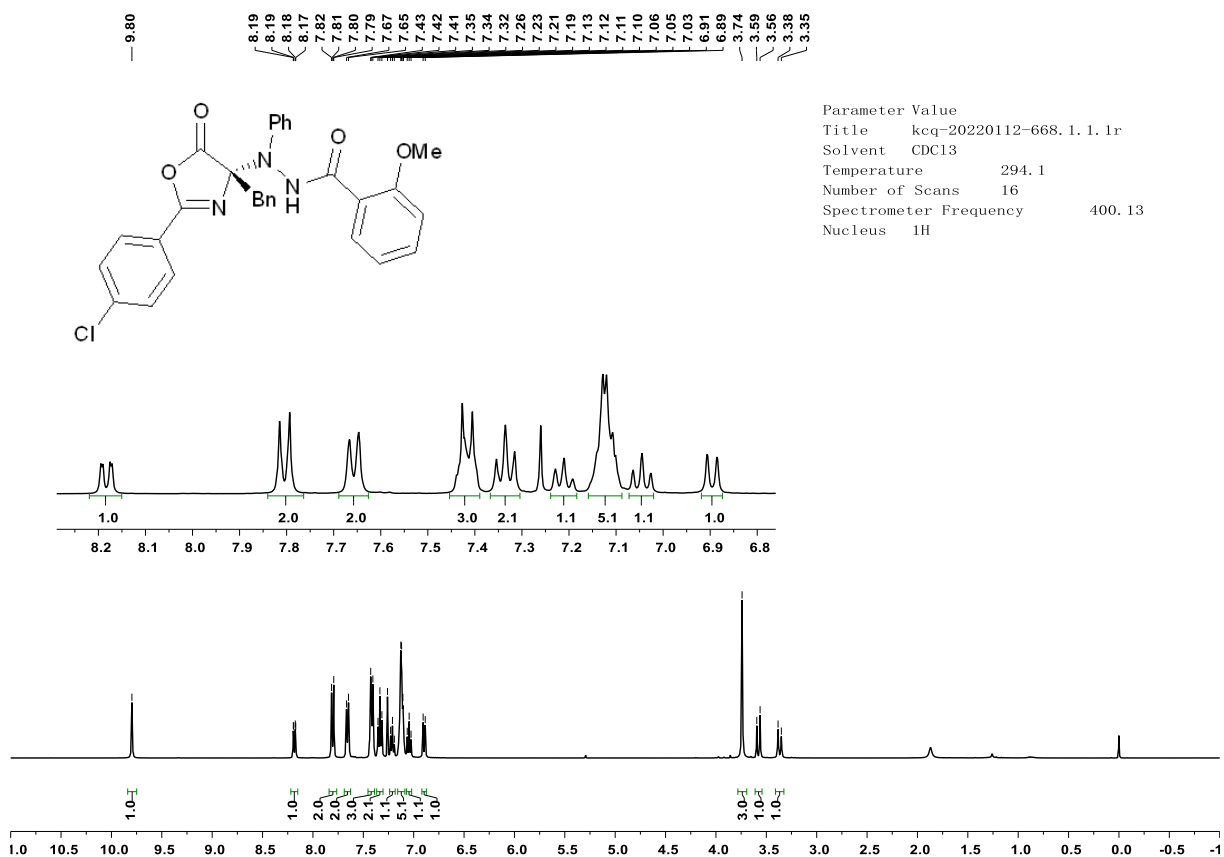


Figure S31. ^{13}C NMR of C14

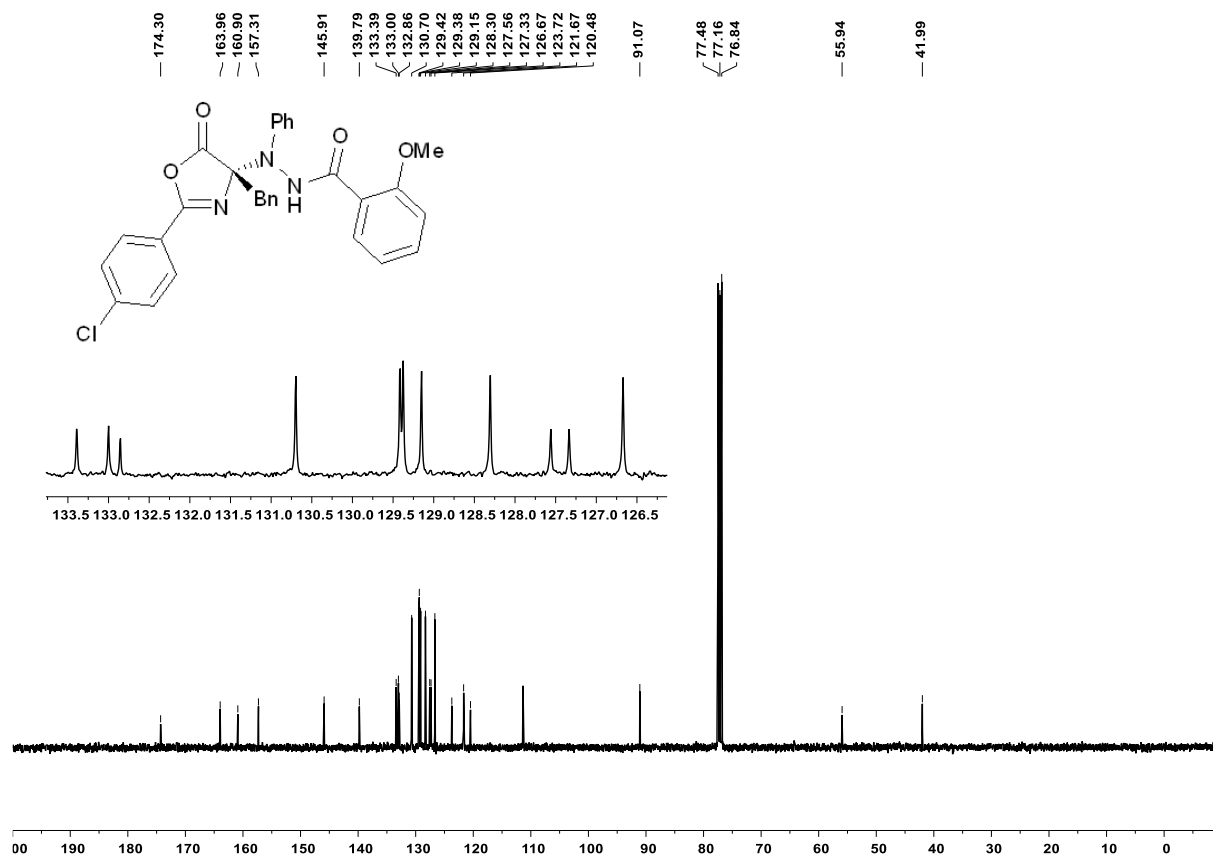


Figure S32. ^1H NMR of C15

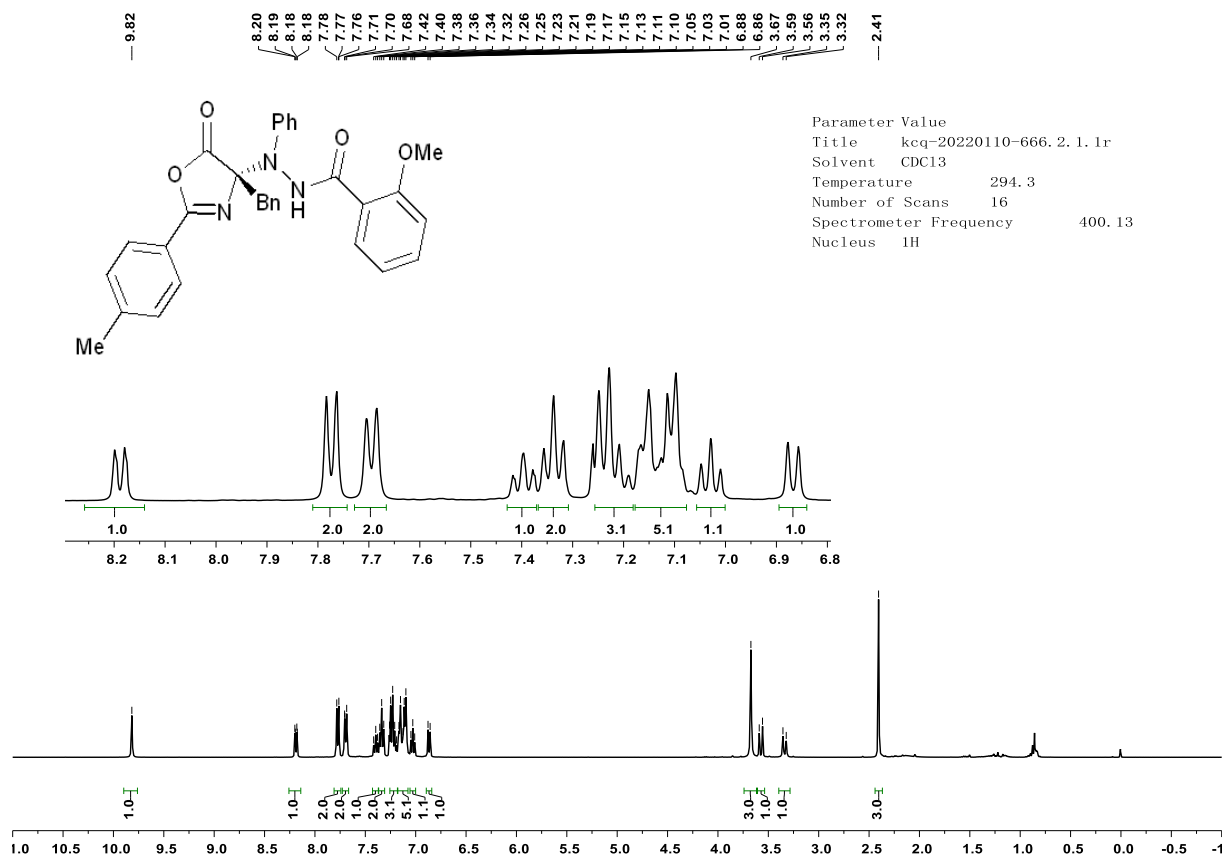


Figure S33. ^{13}C NMR of C15

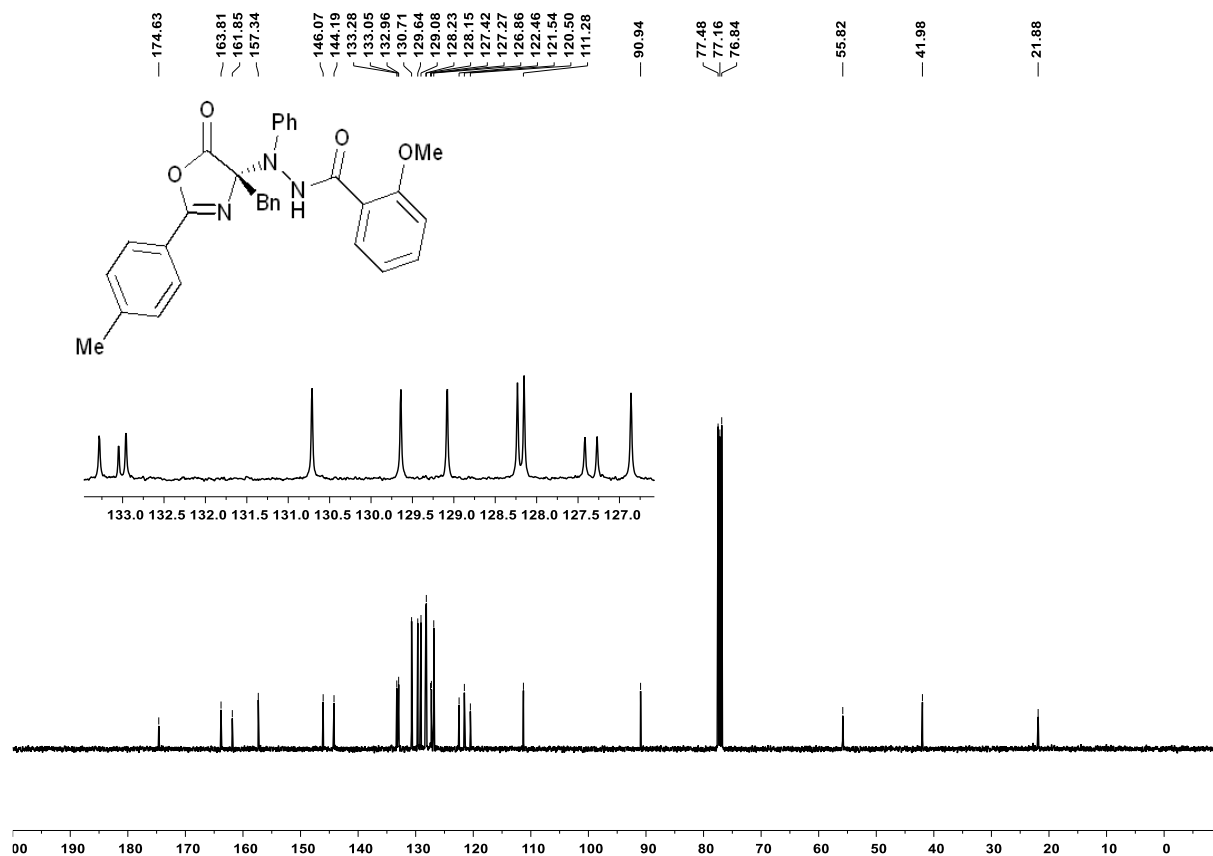


Figure S34. ^1H NMR of C16

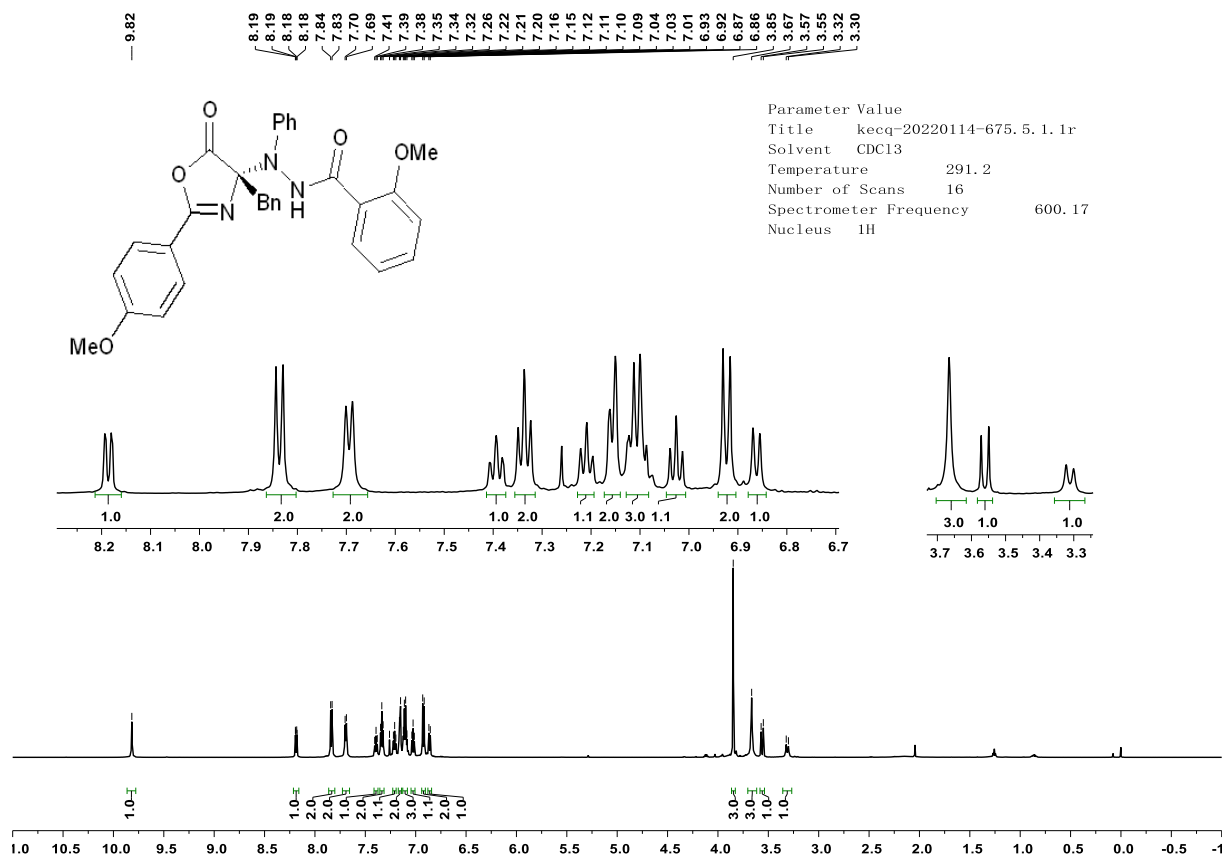


Figure S35. ^{13}C NMR of C16

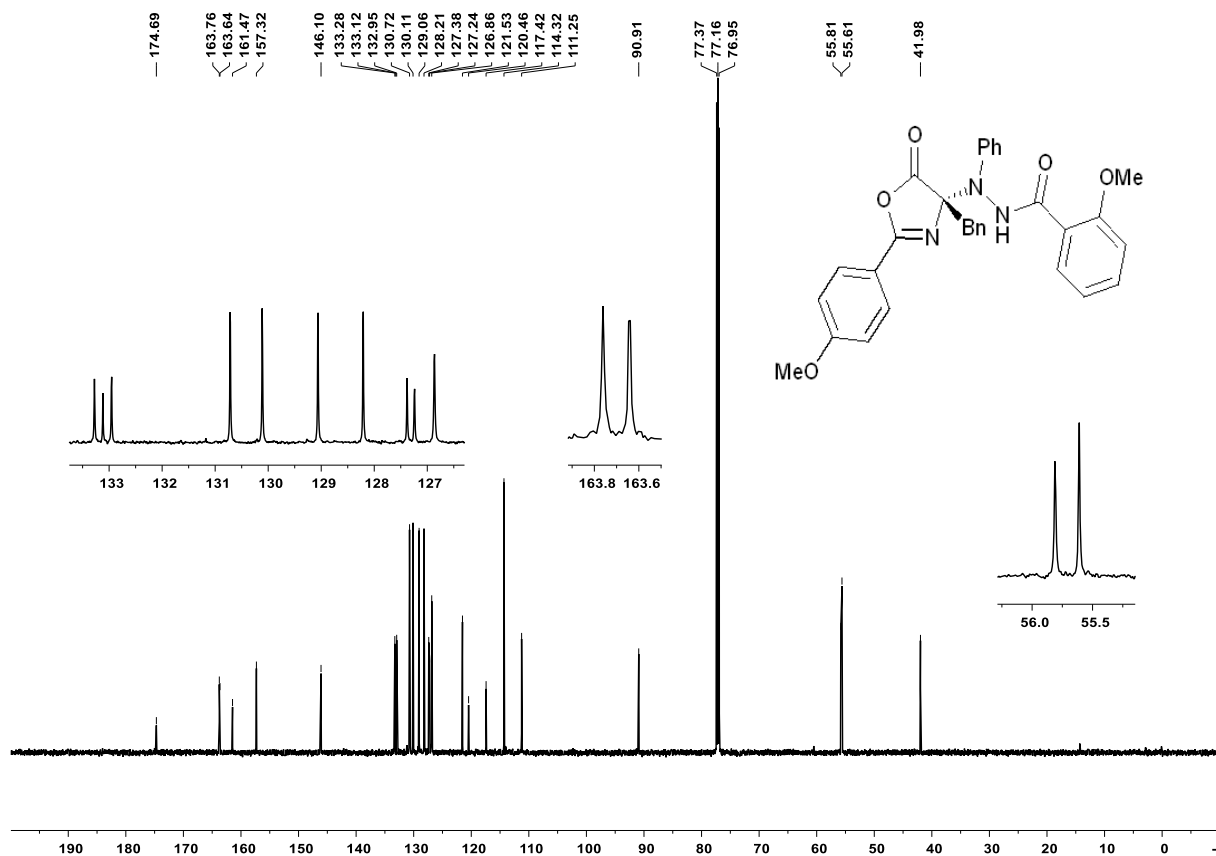


Figure S36. ^1H NMR of C17

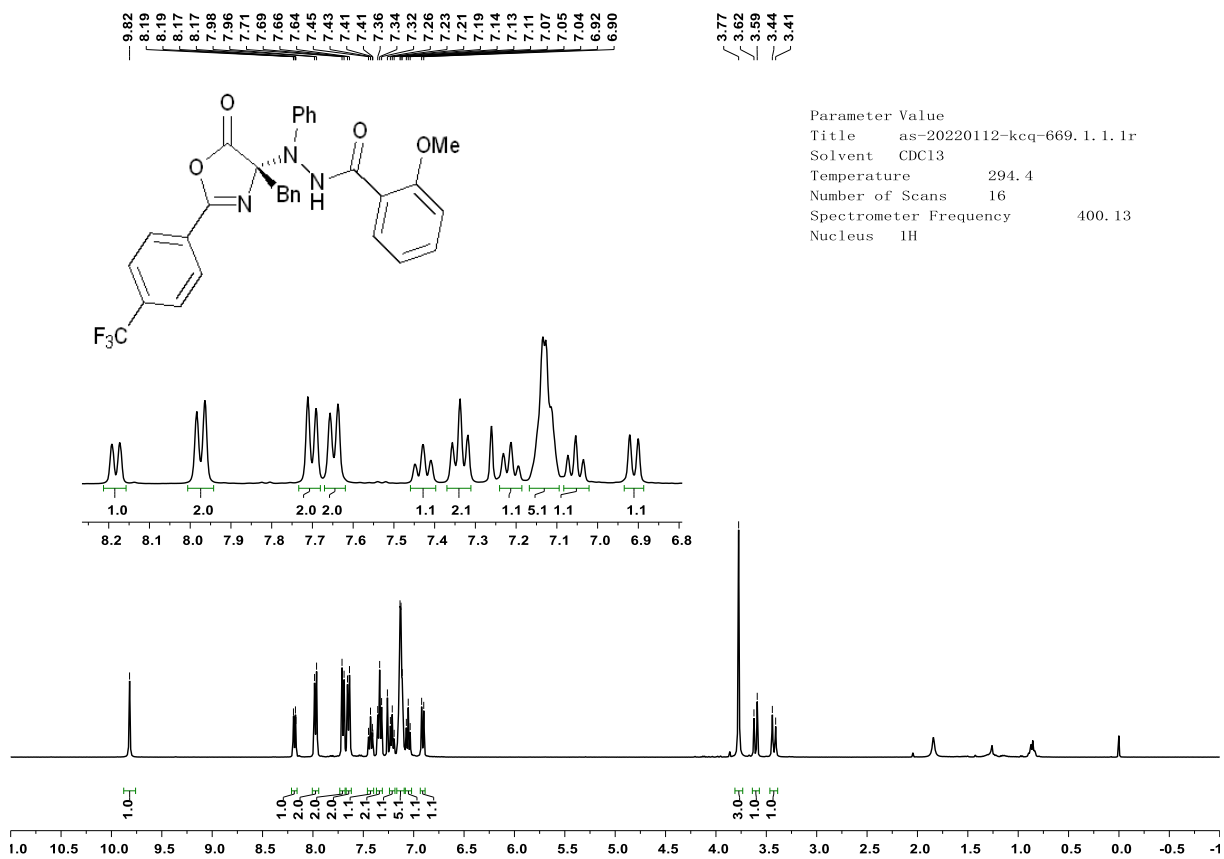


Figure S37. ^{13}C NMR of C17

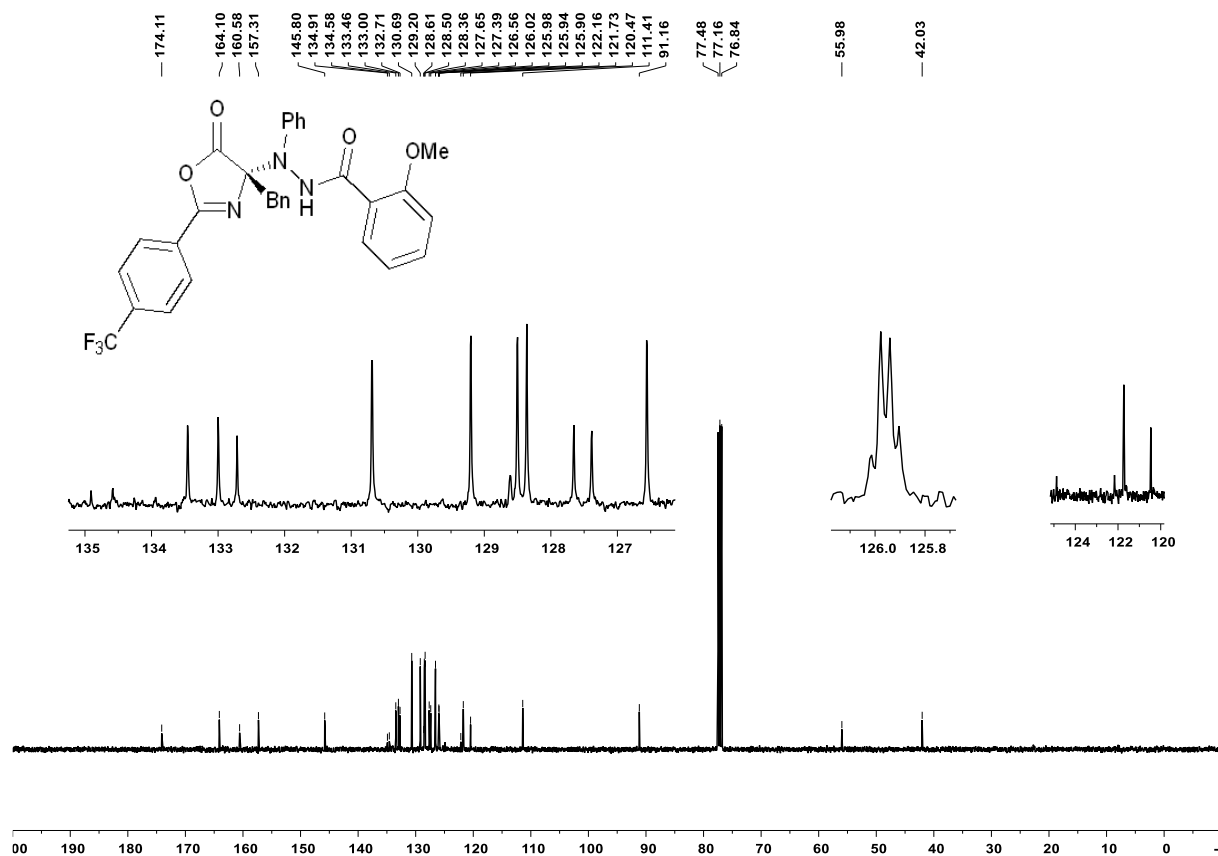


Figure S38. $^{19}\text{F}\{^1\text{H}\}$ NMR of C17

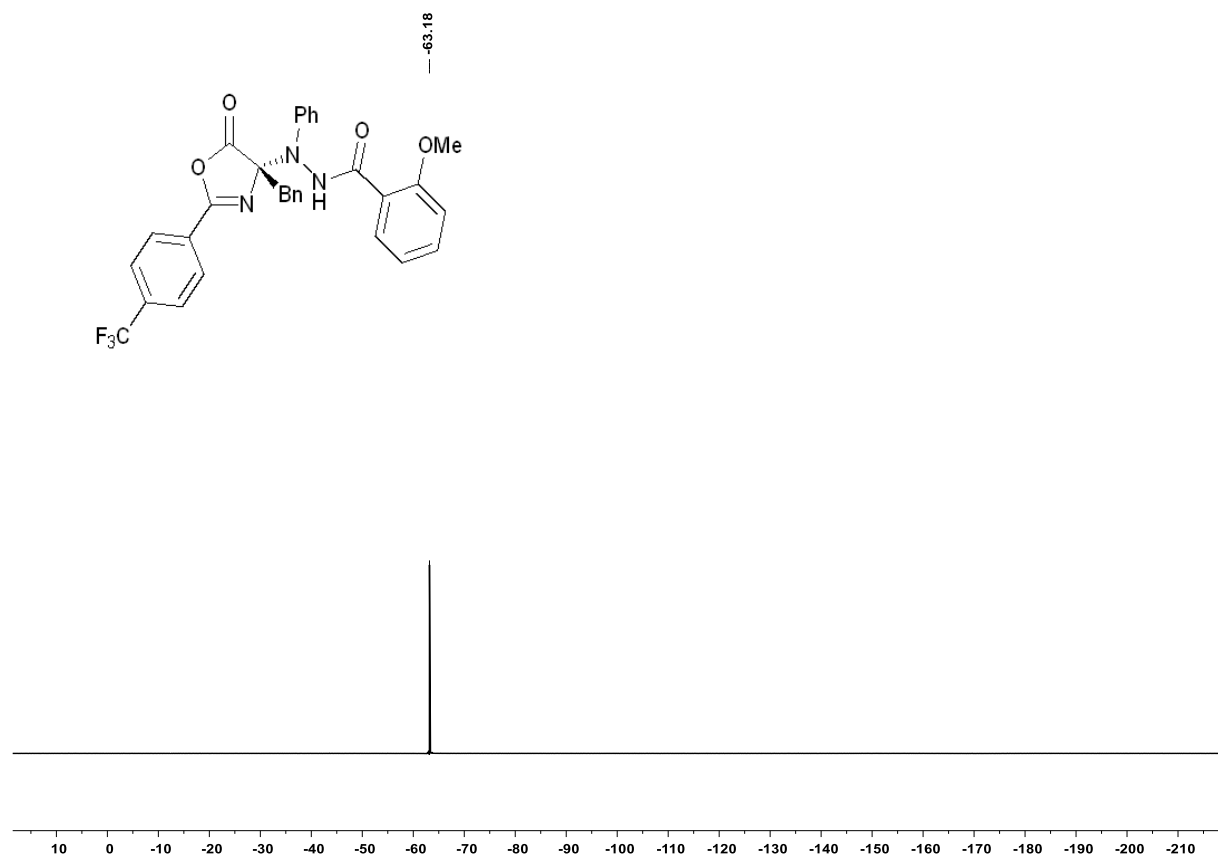


Figure S39. ¹H NMR of C18

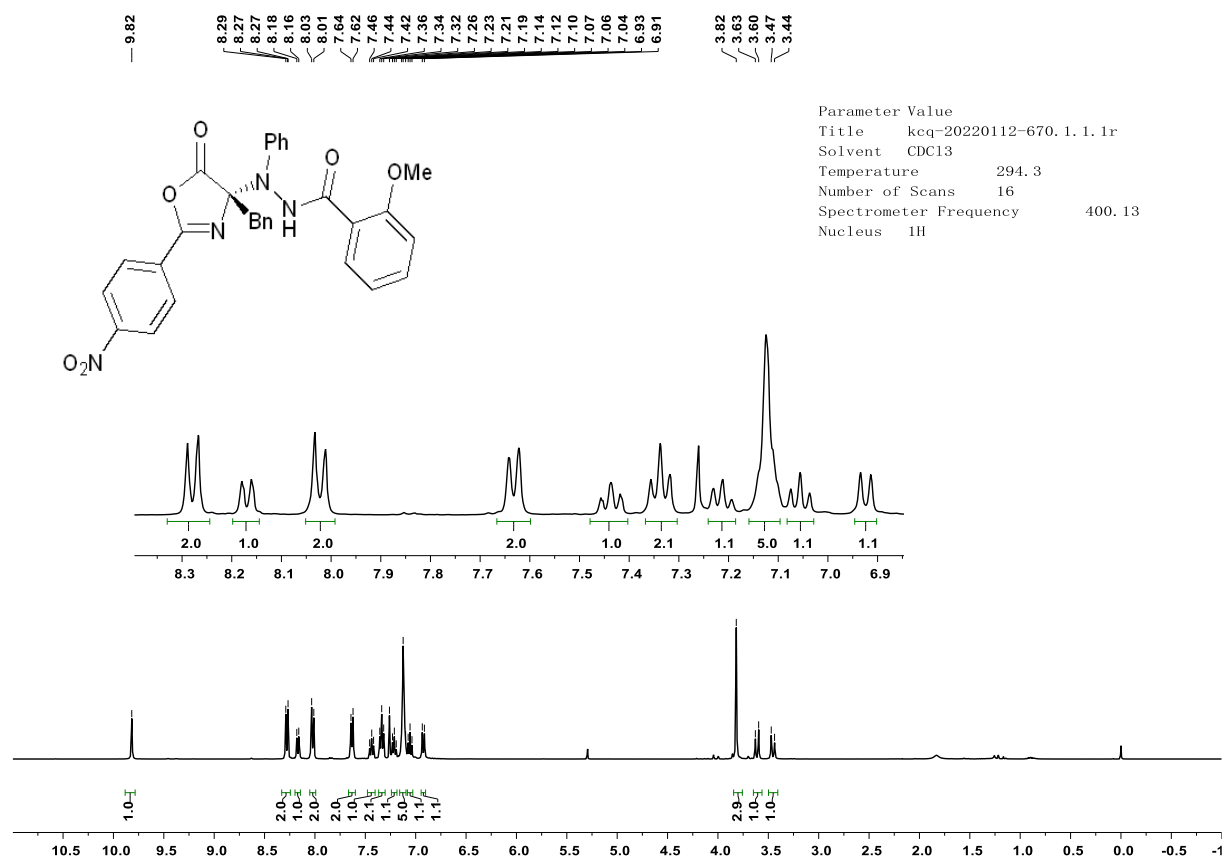


Figure S40. ¹³C NMR of C18

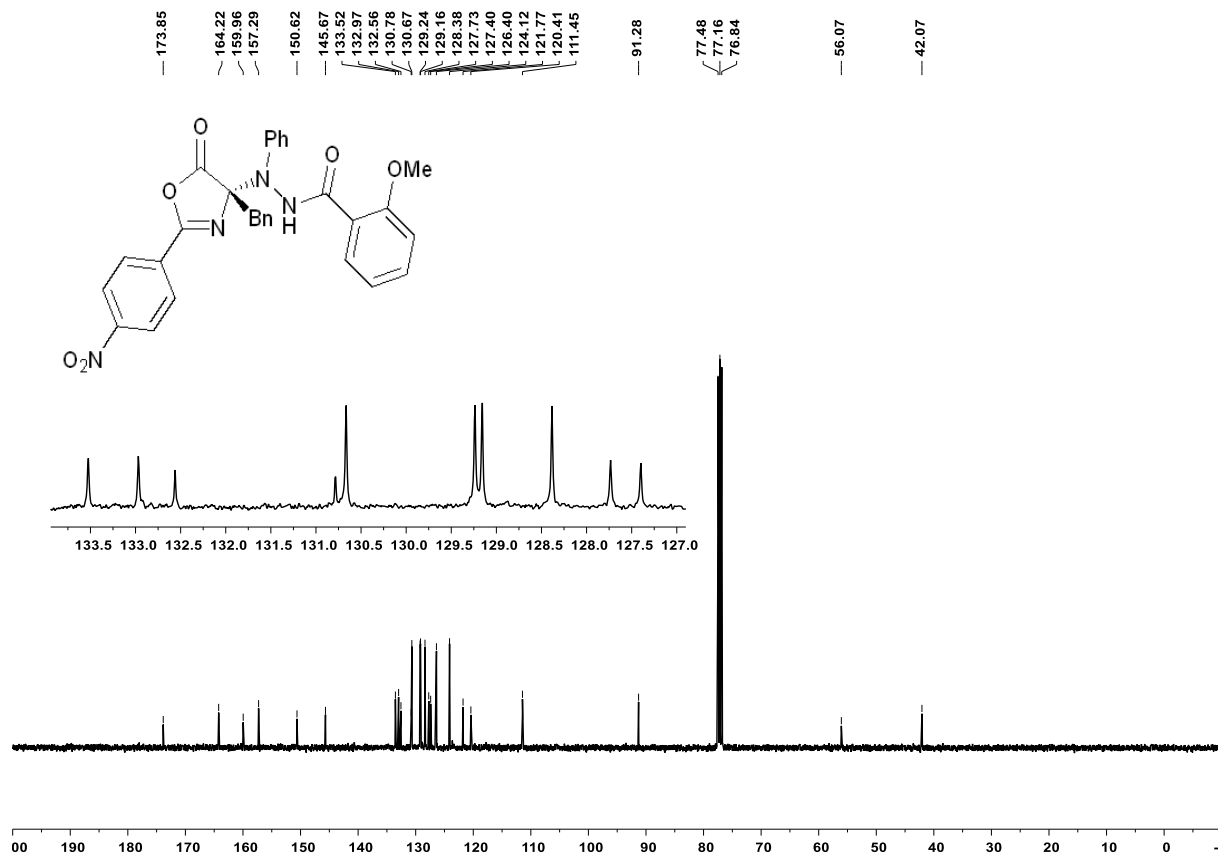


Figure S41. ^1H NMR of C19

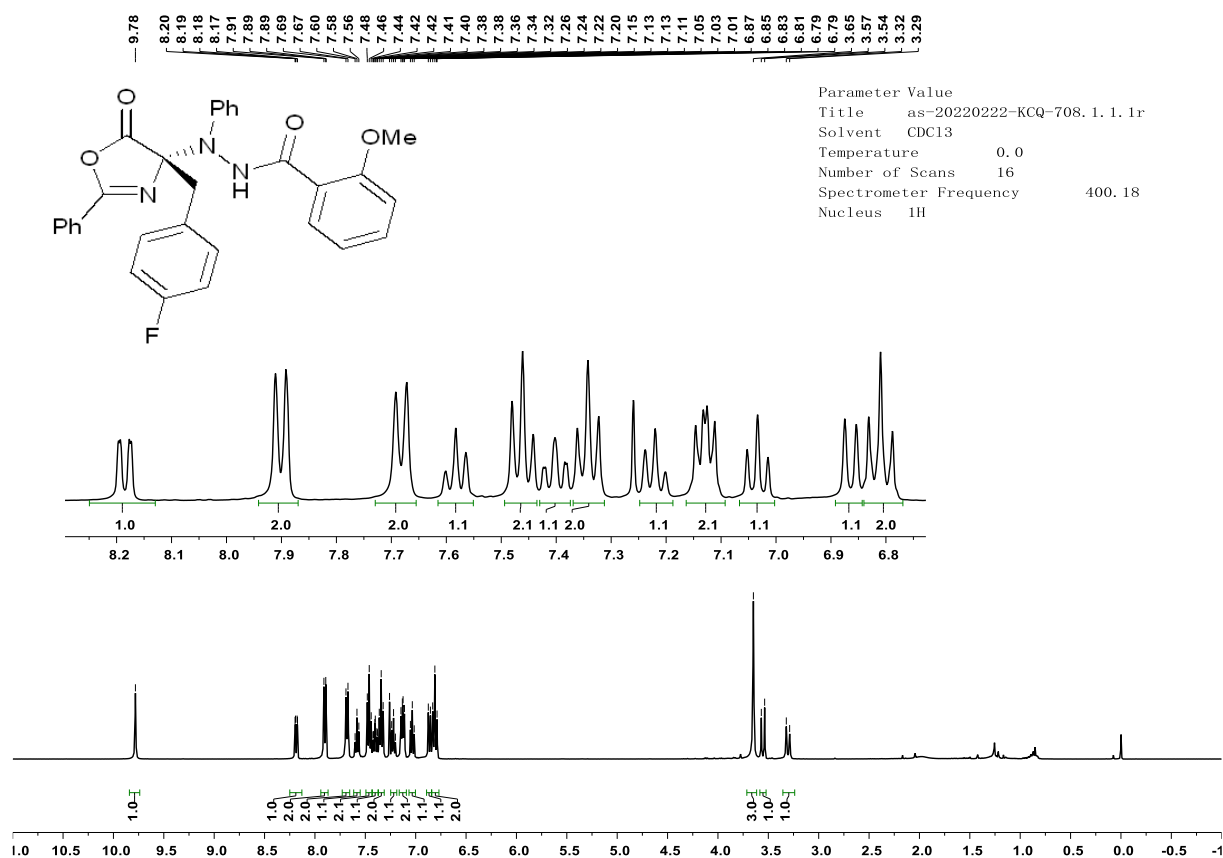


Figure S42. ^{13}C NMR of C19

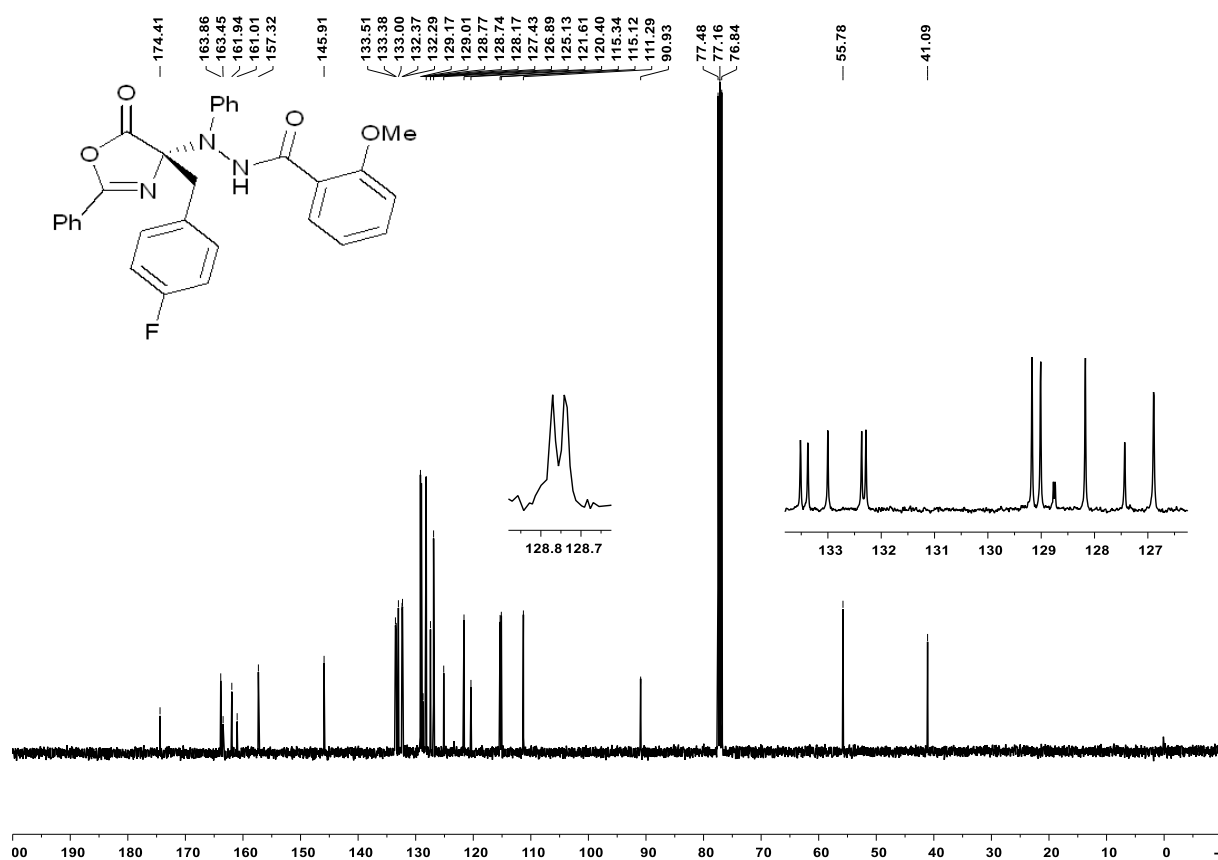


Figure S43. $^{19}\text{F}\{^1\text{H}\}$ NMR of C19

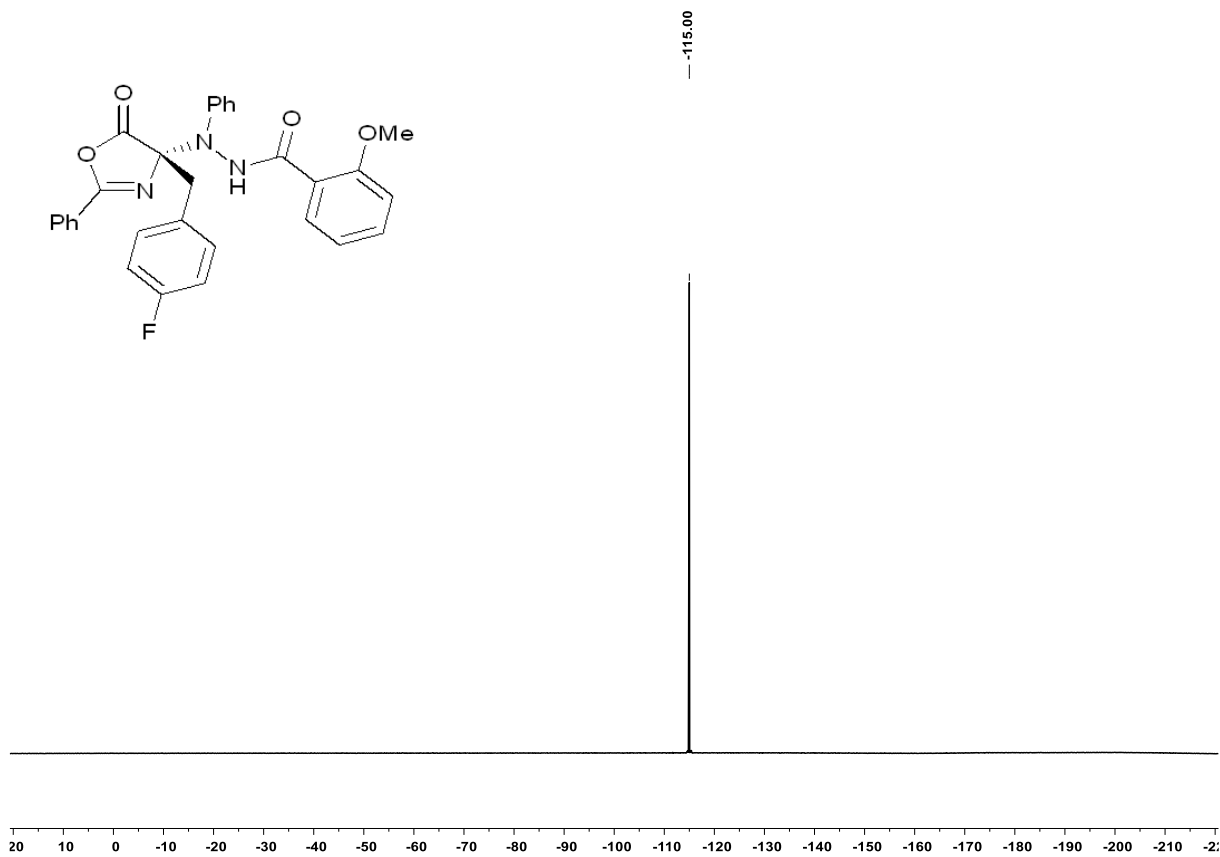


Figure S44. ^1H NMR of C20

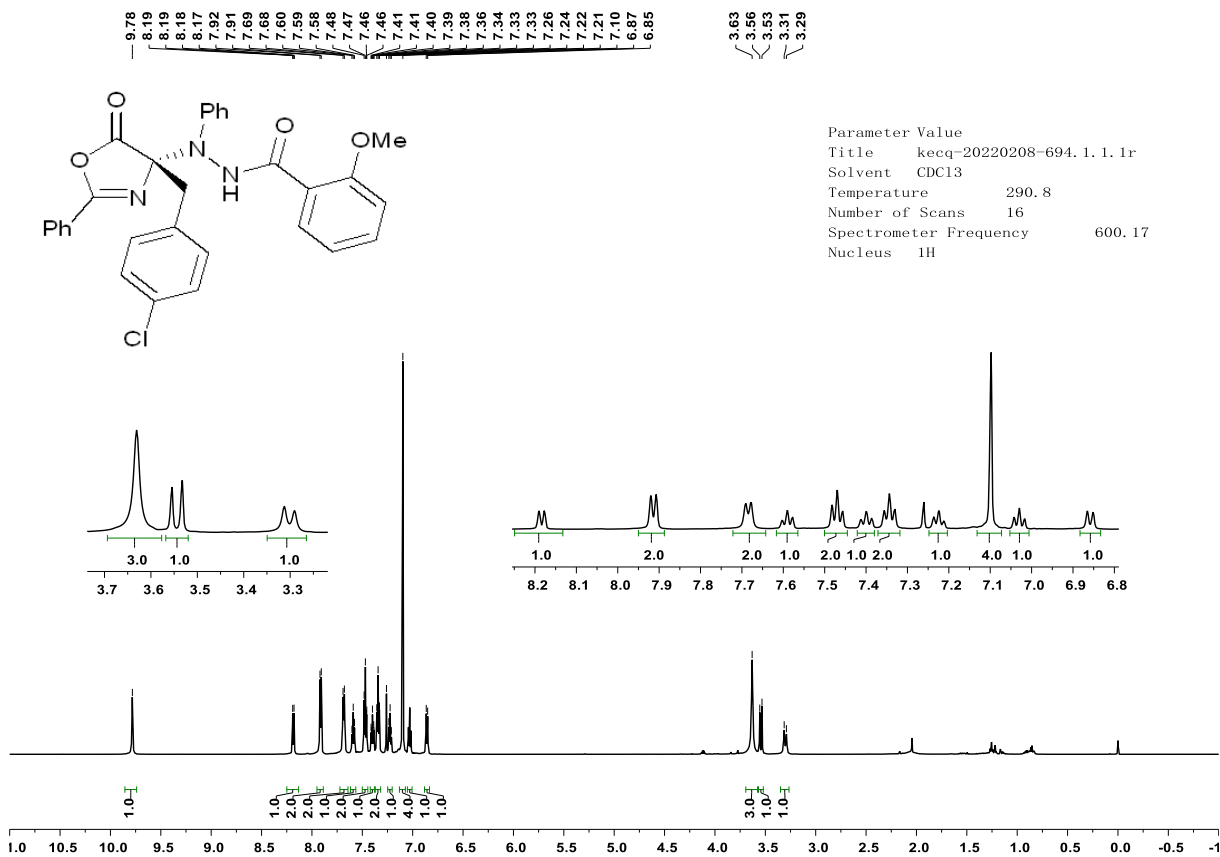


Figure S45. ^{13}C NMR of C20

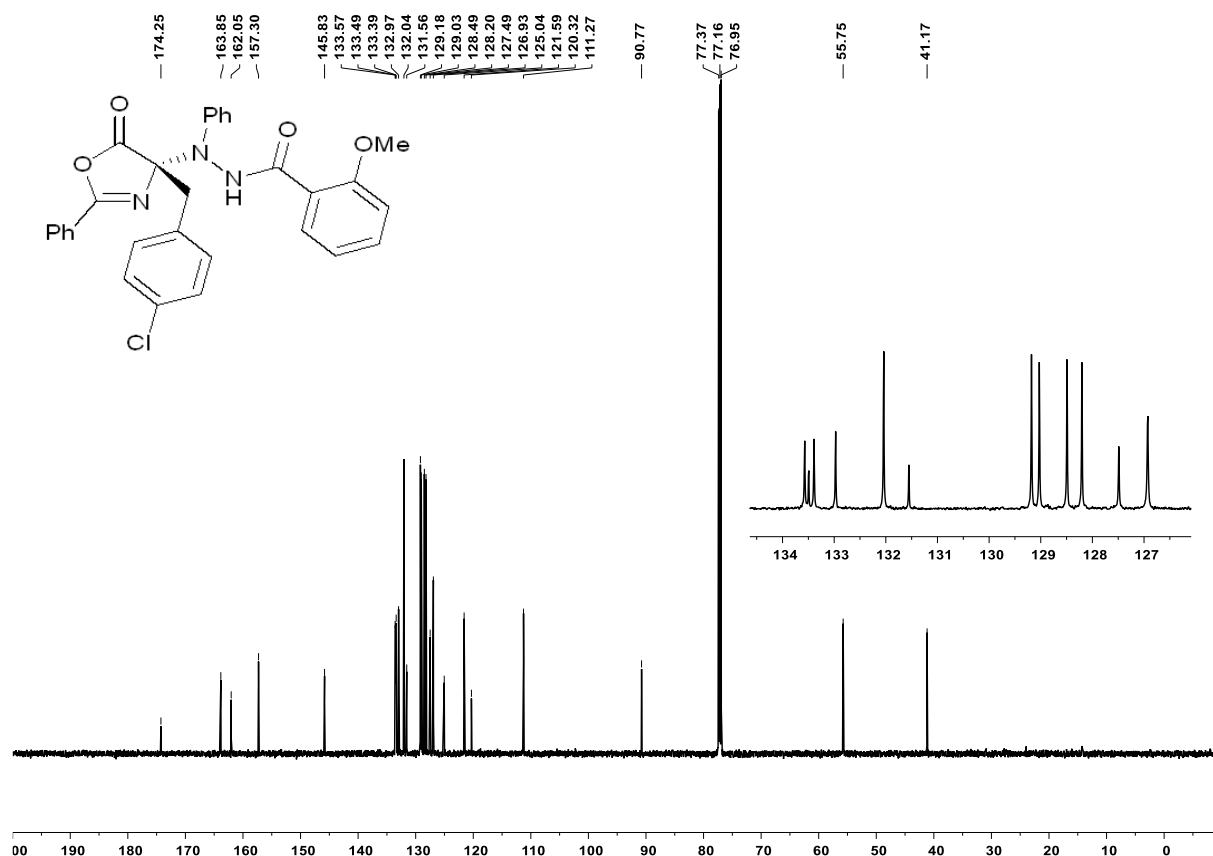


Figure S46. ^1H NMR of C21

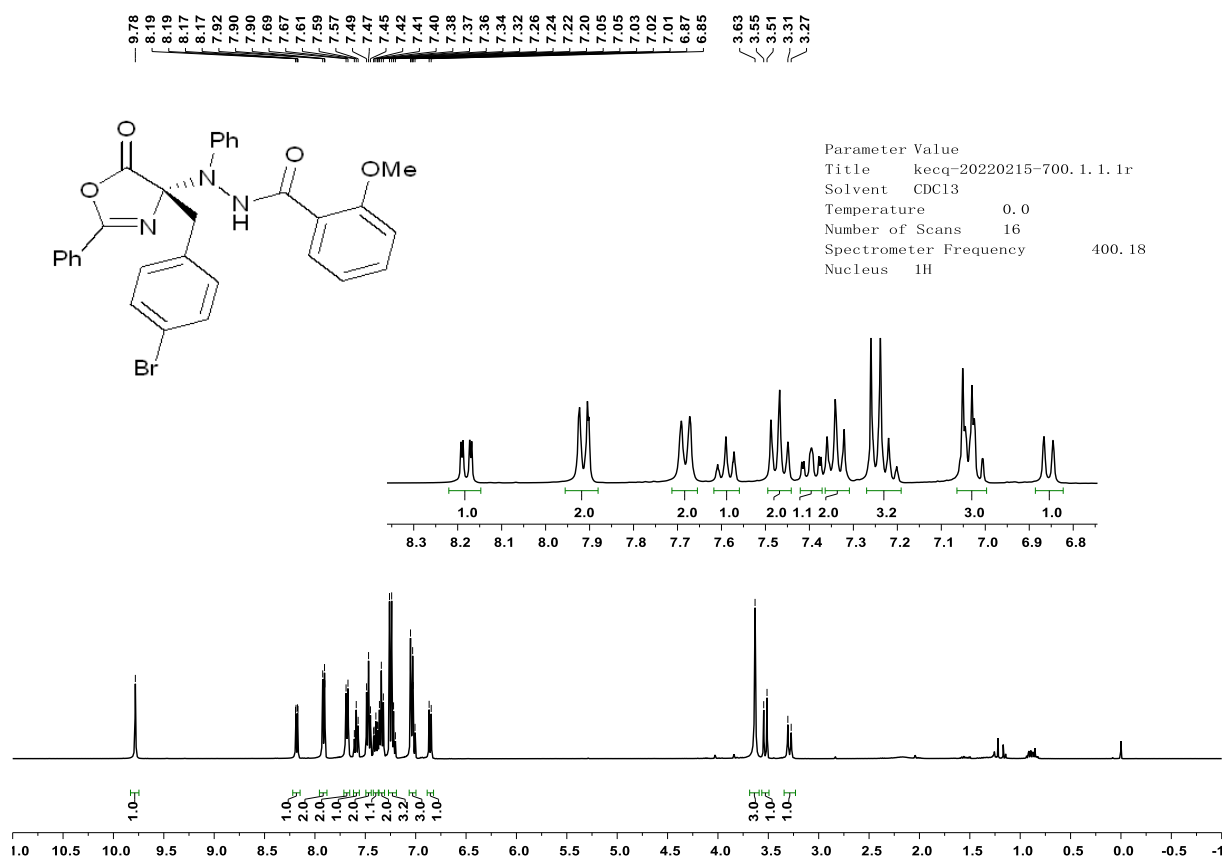


Figure S47. ^{13}C NMR of C21

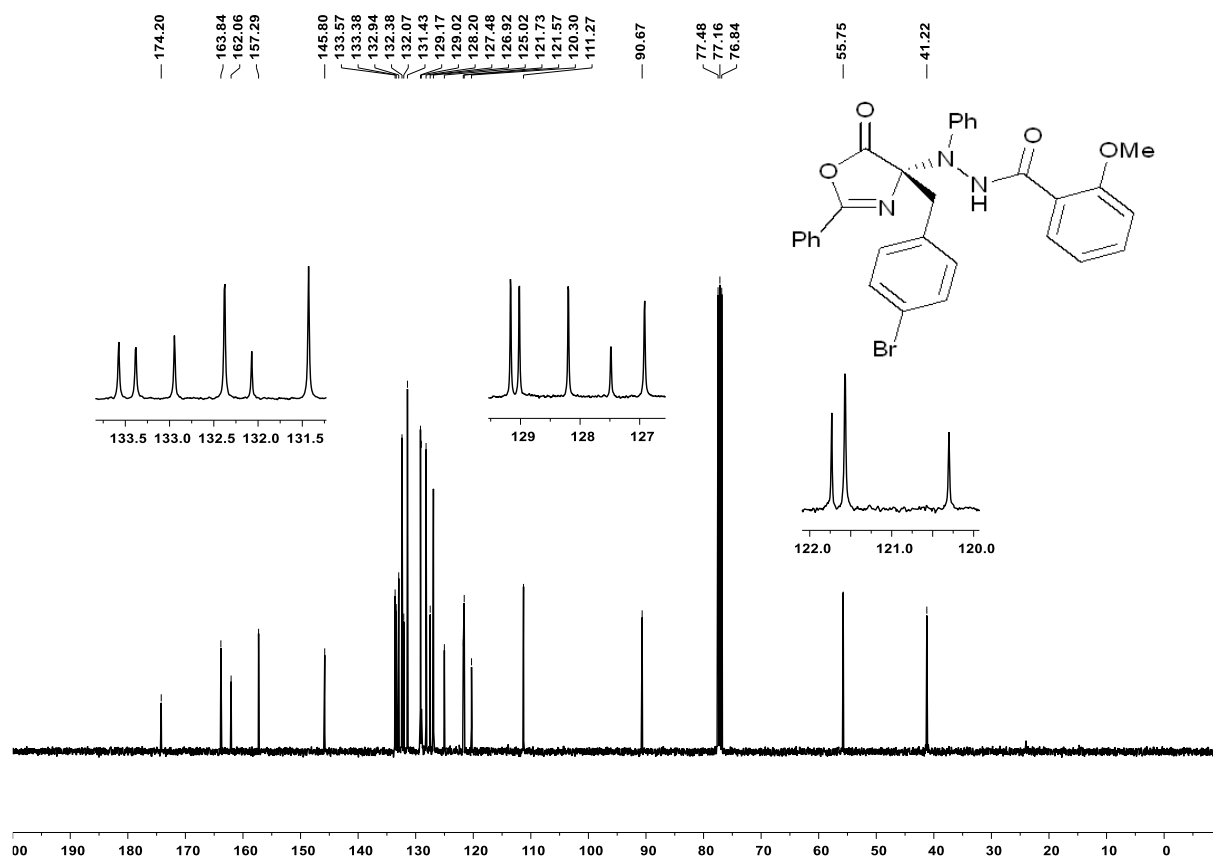


Figure S48. ^1H NMR of C22

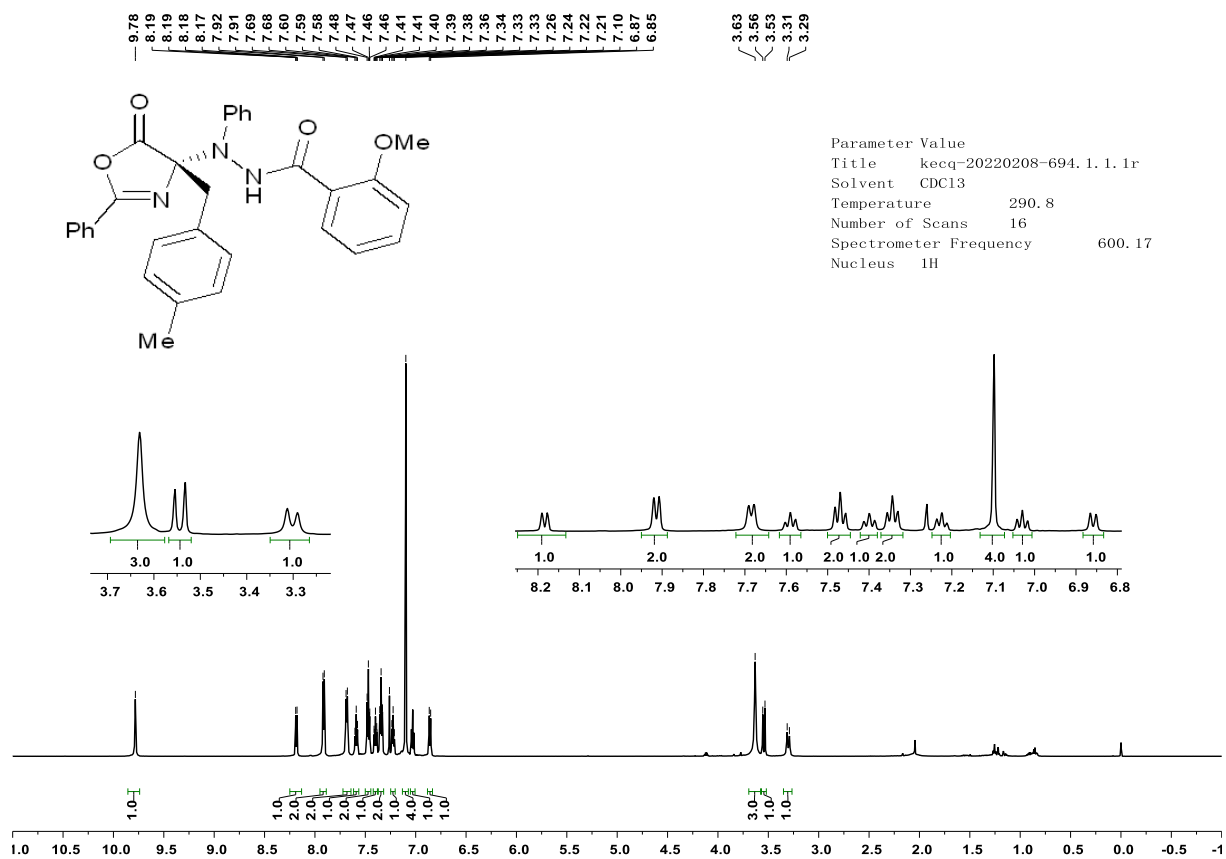


Figure S49. ^{13}C NMR of C22

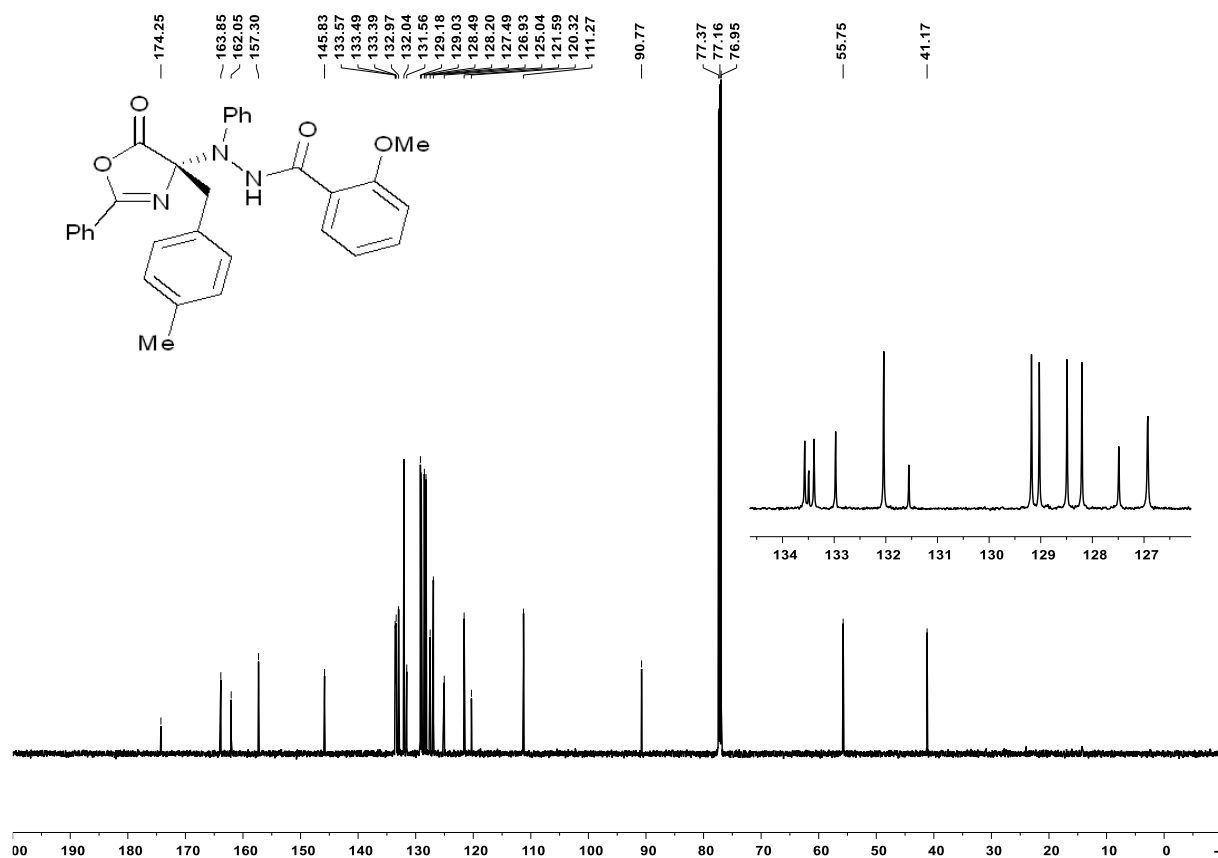


Figure S50. ^1H NMR of C23

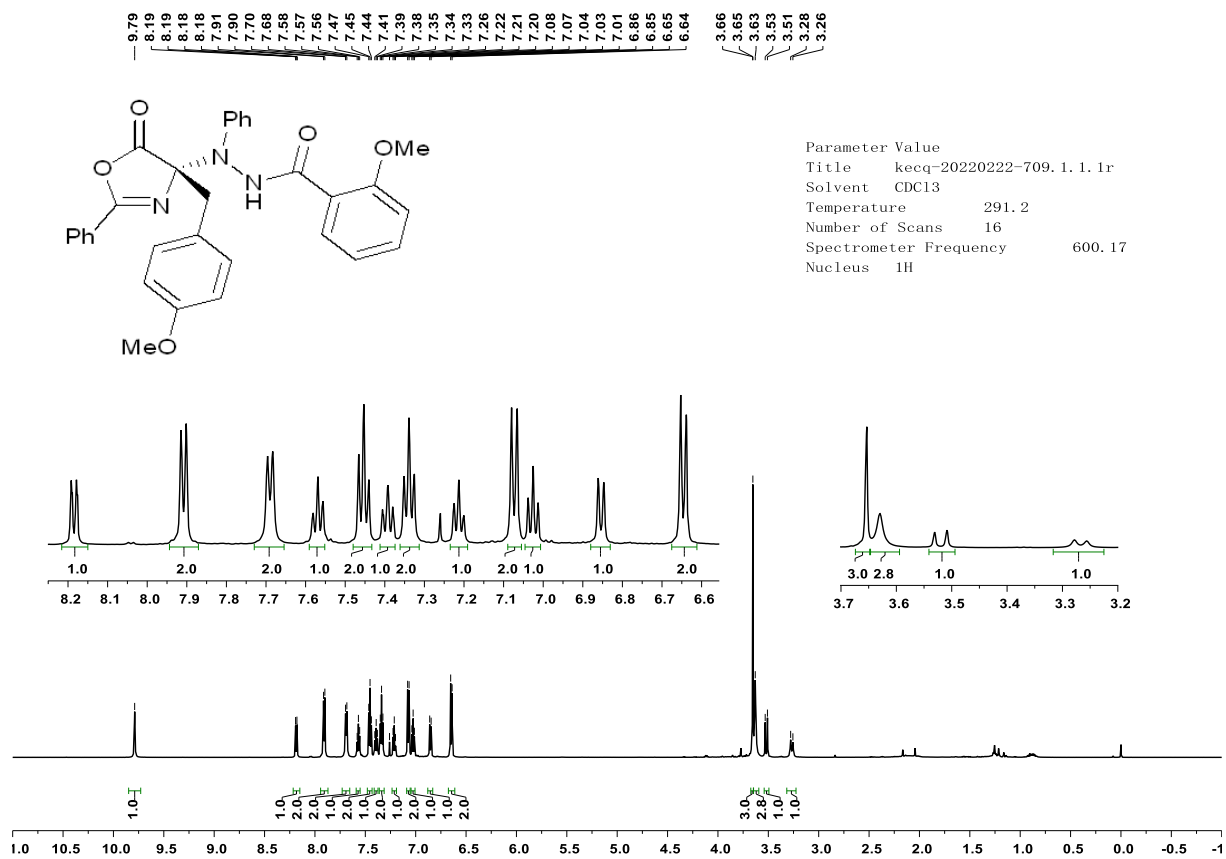


Figure S51. ^{13}C NMR of C23

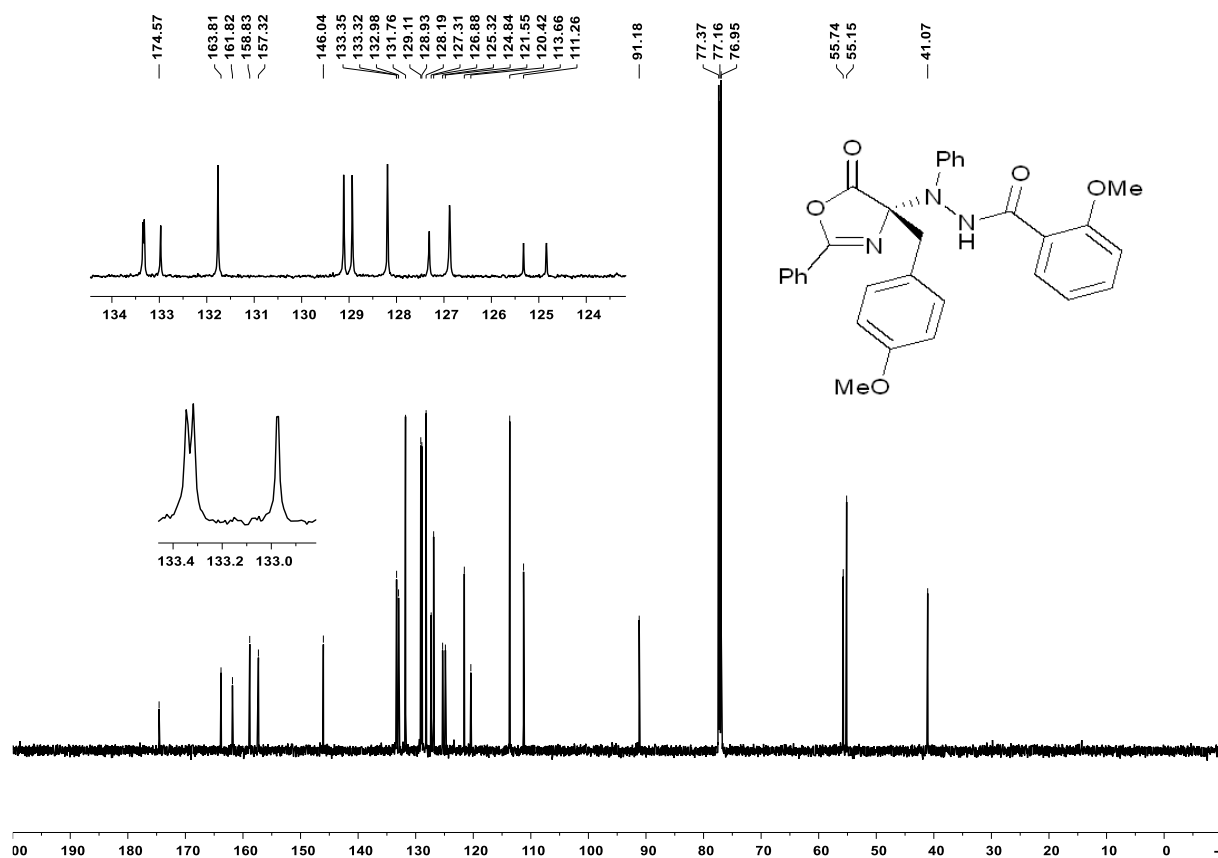


Figure S52. ^1H NMR of C24

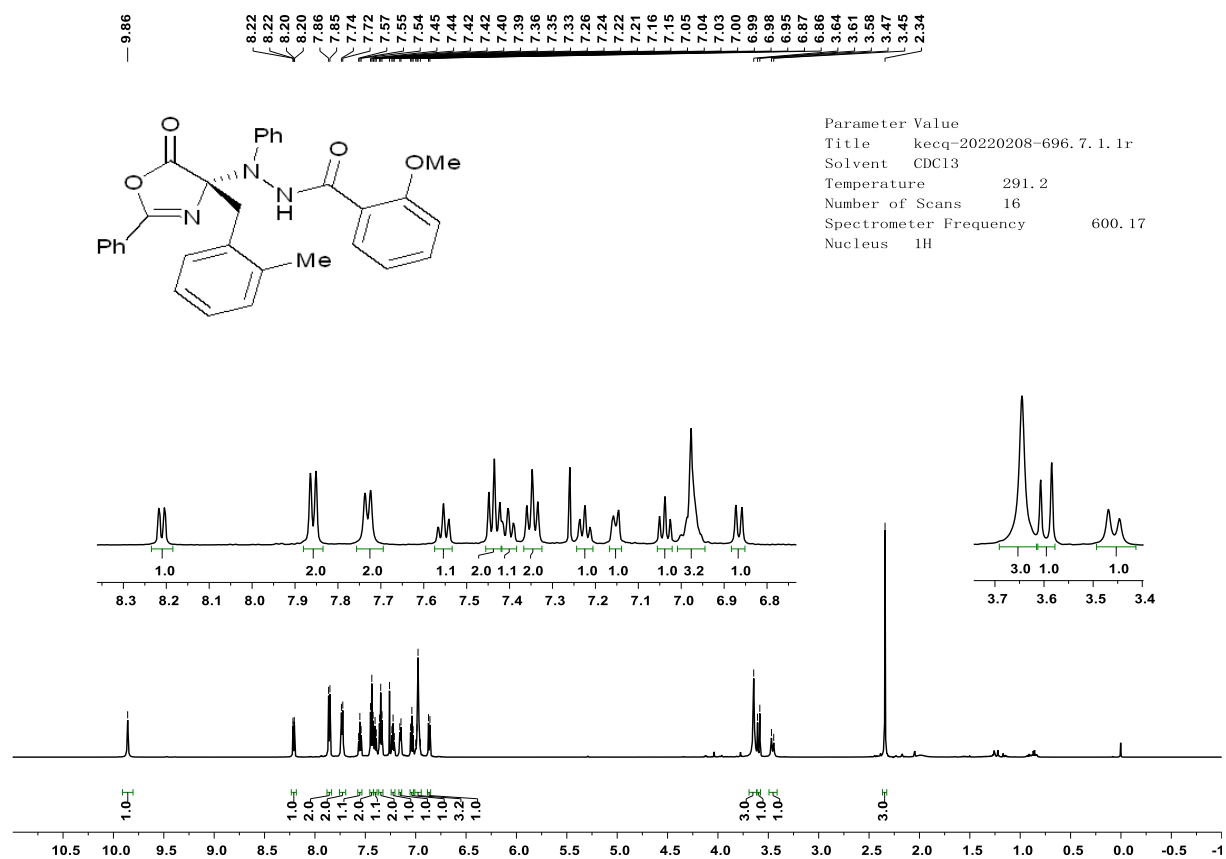


Figure S53. ^{13}C NMR of C24

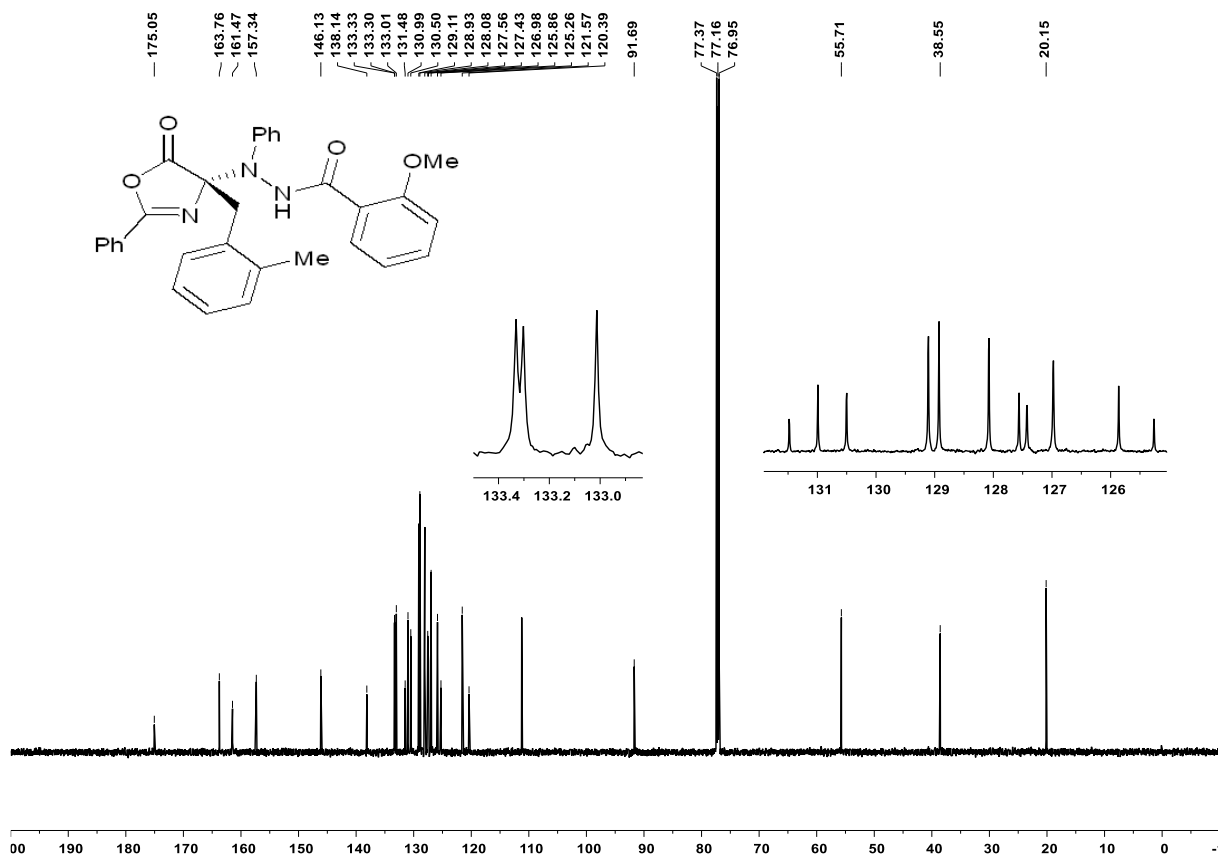


Figure S54. ^1H NMR of C25

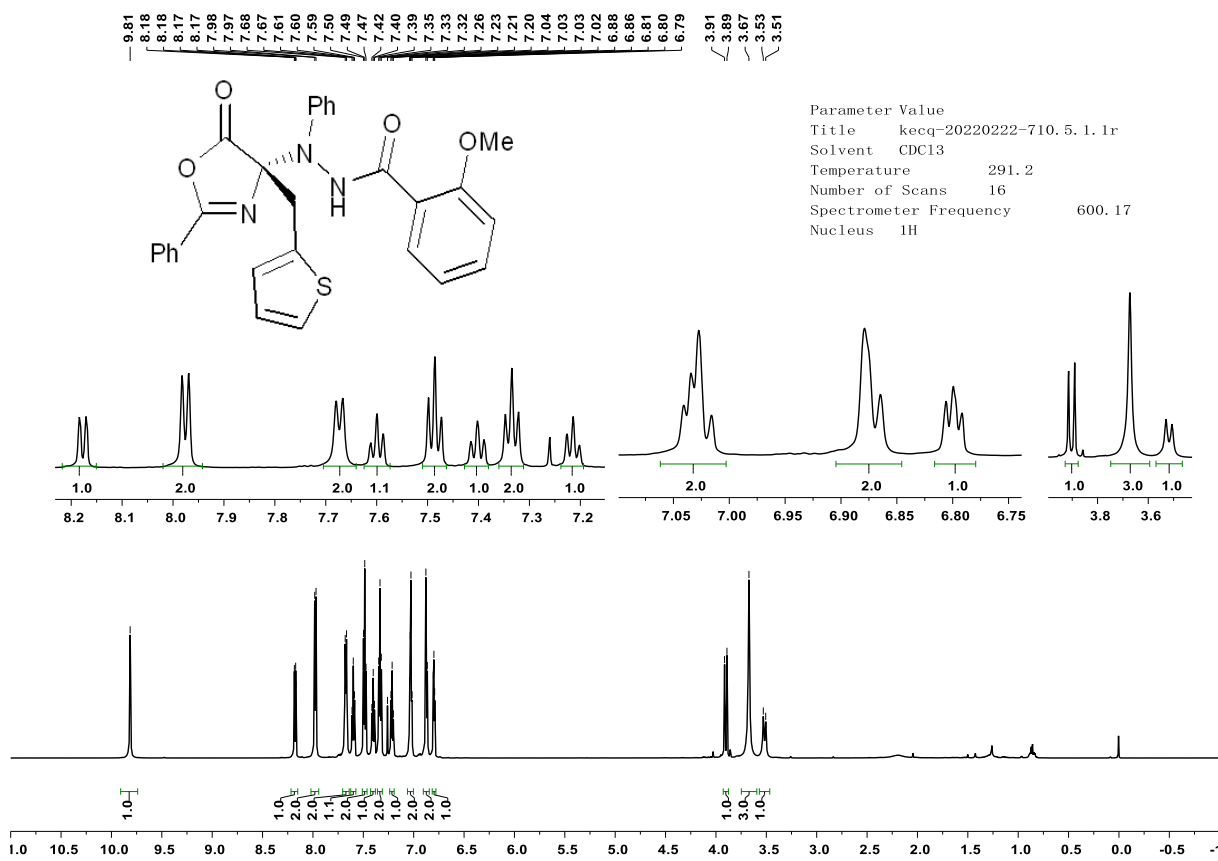


Figure S55. ^{13}C NMR of C25

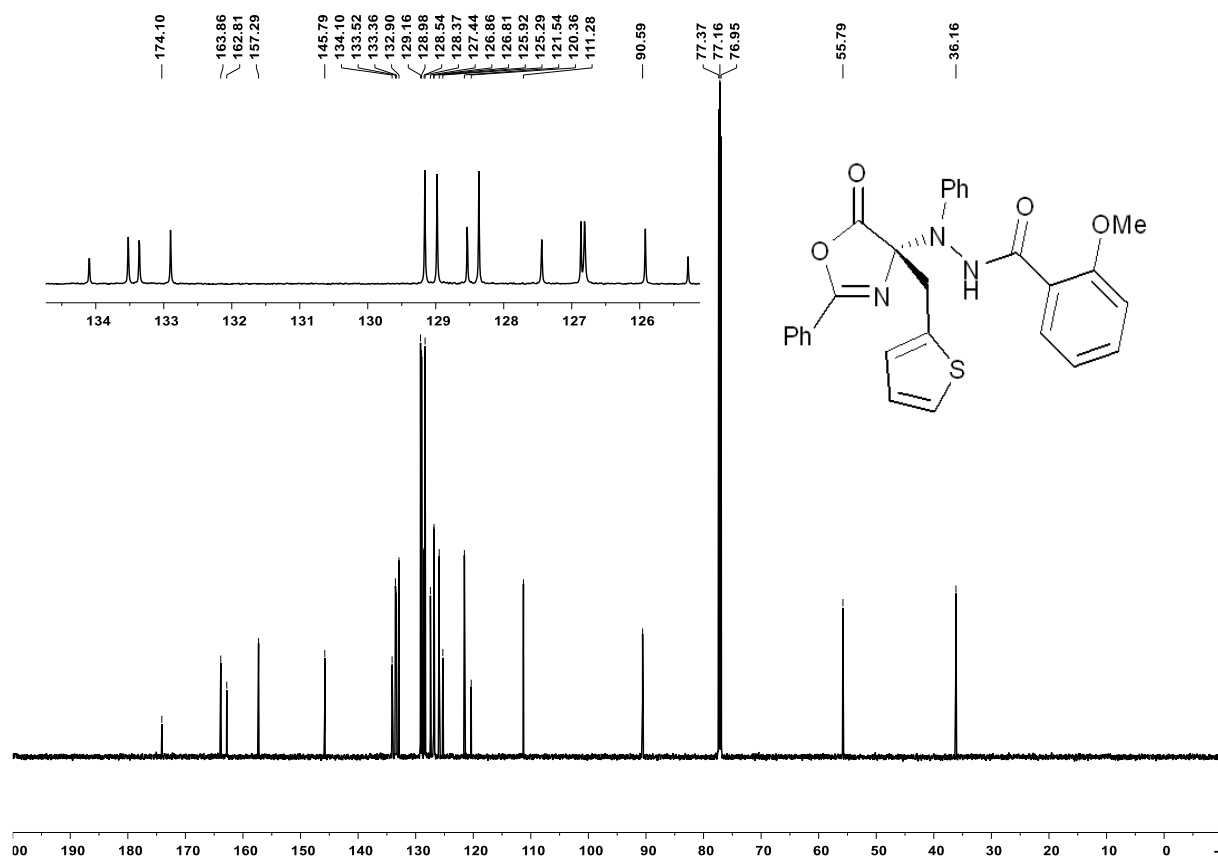


Figure S56. ^1H NMR of C26

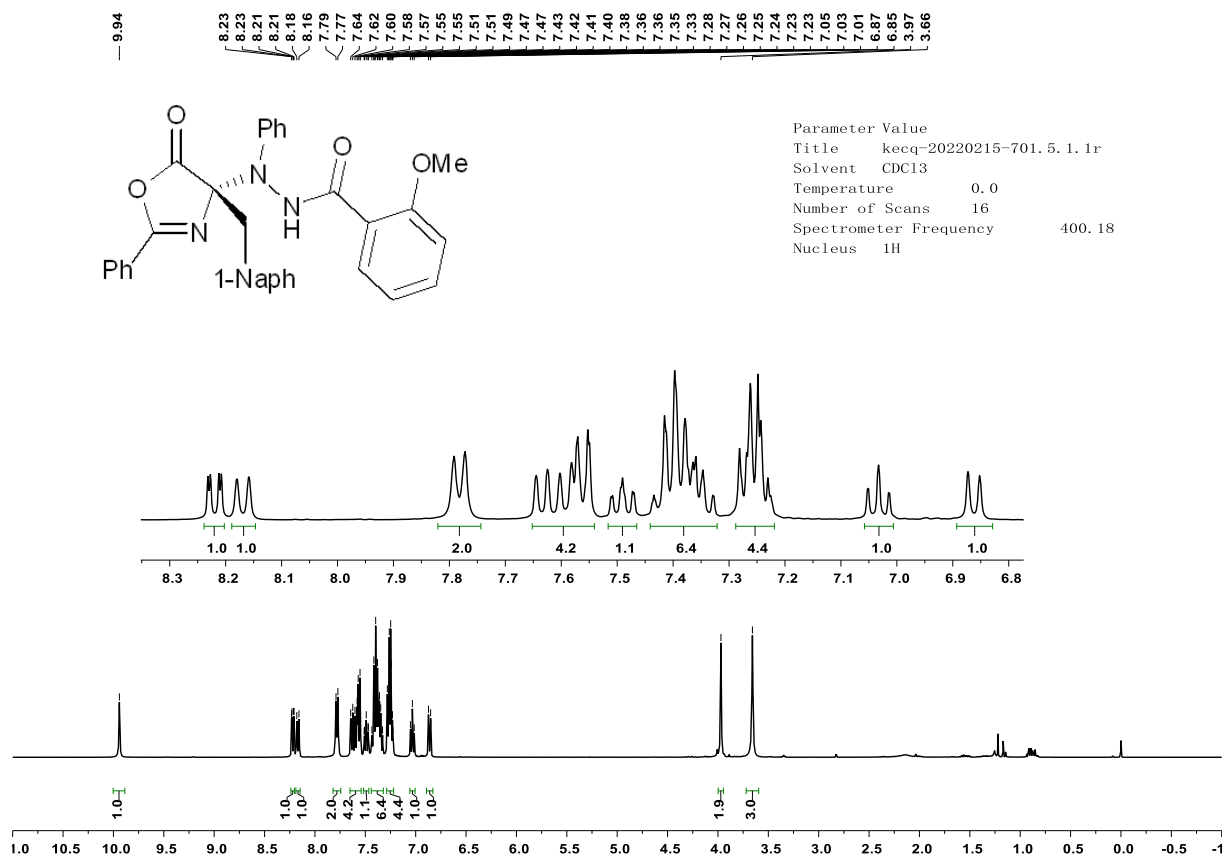


Figure S57. ^{13}C NMR of C26

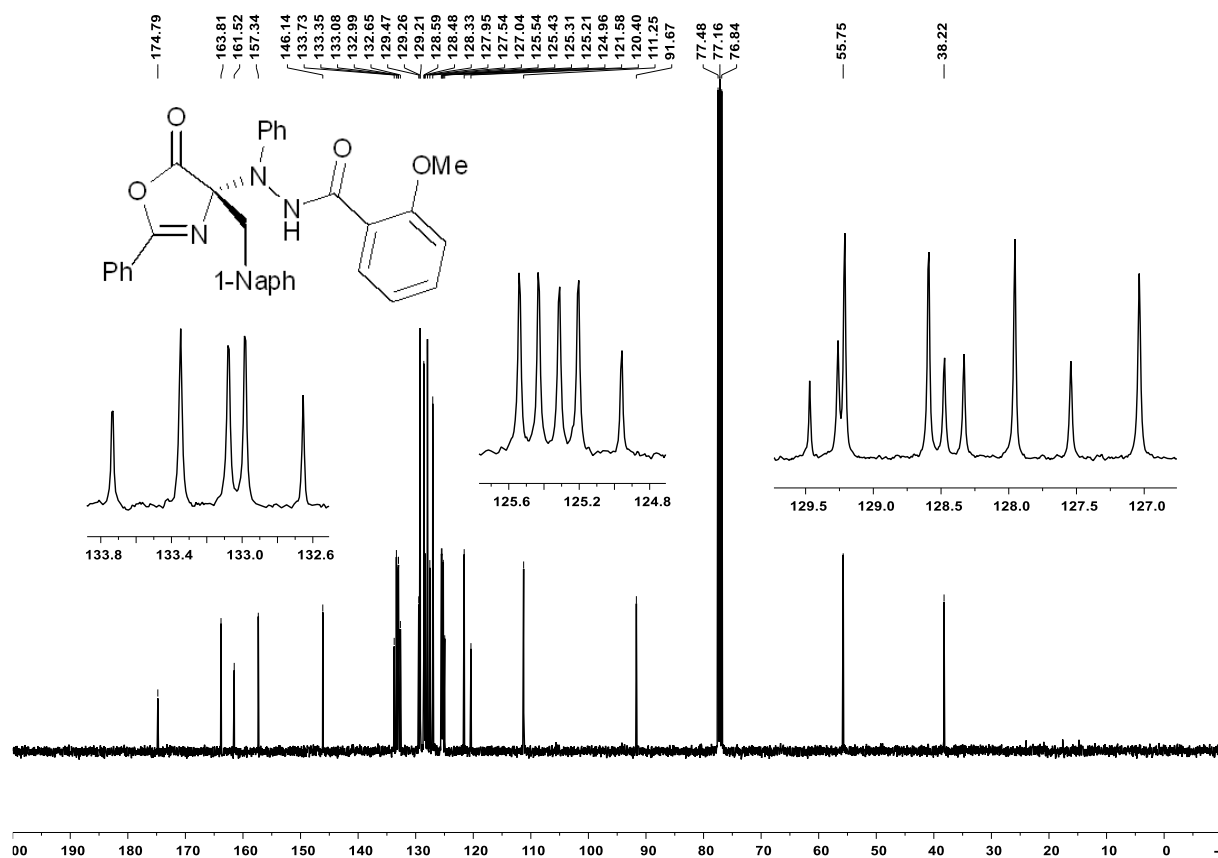


Figure S58. ^1H NMR of C27

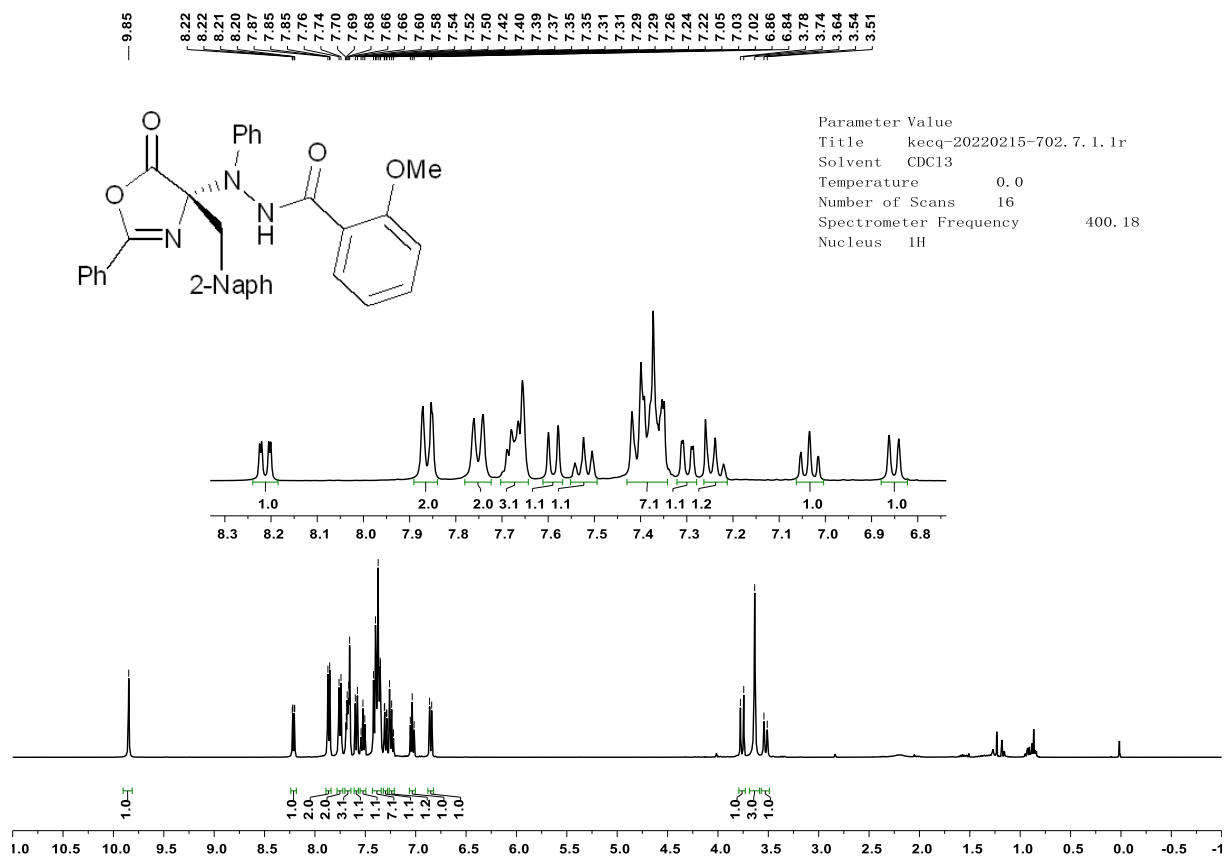


Figure S59. ^{13}C NMR of C27

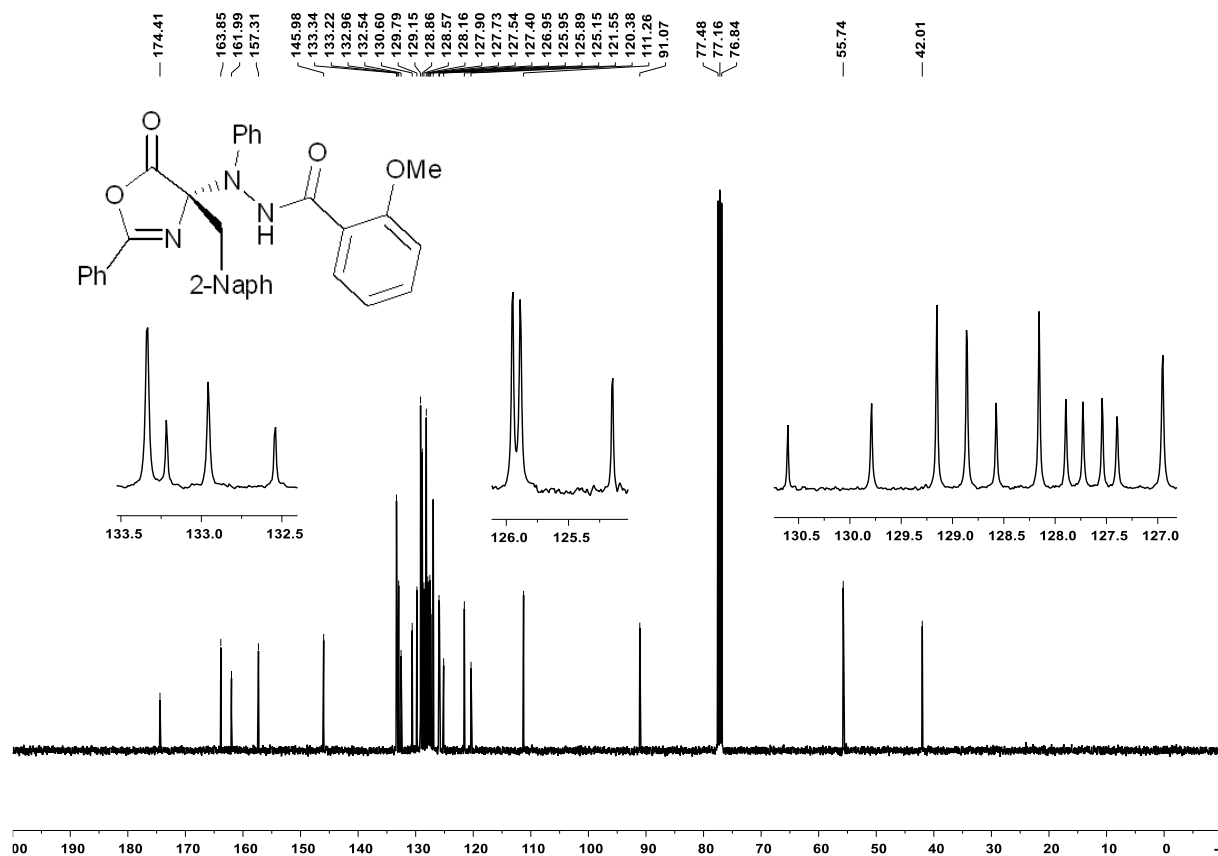


Figure S60. ^1H NMR of C28

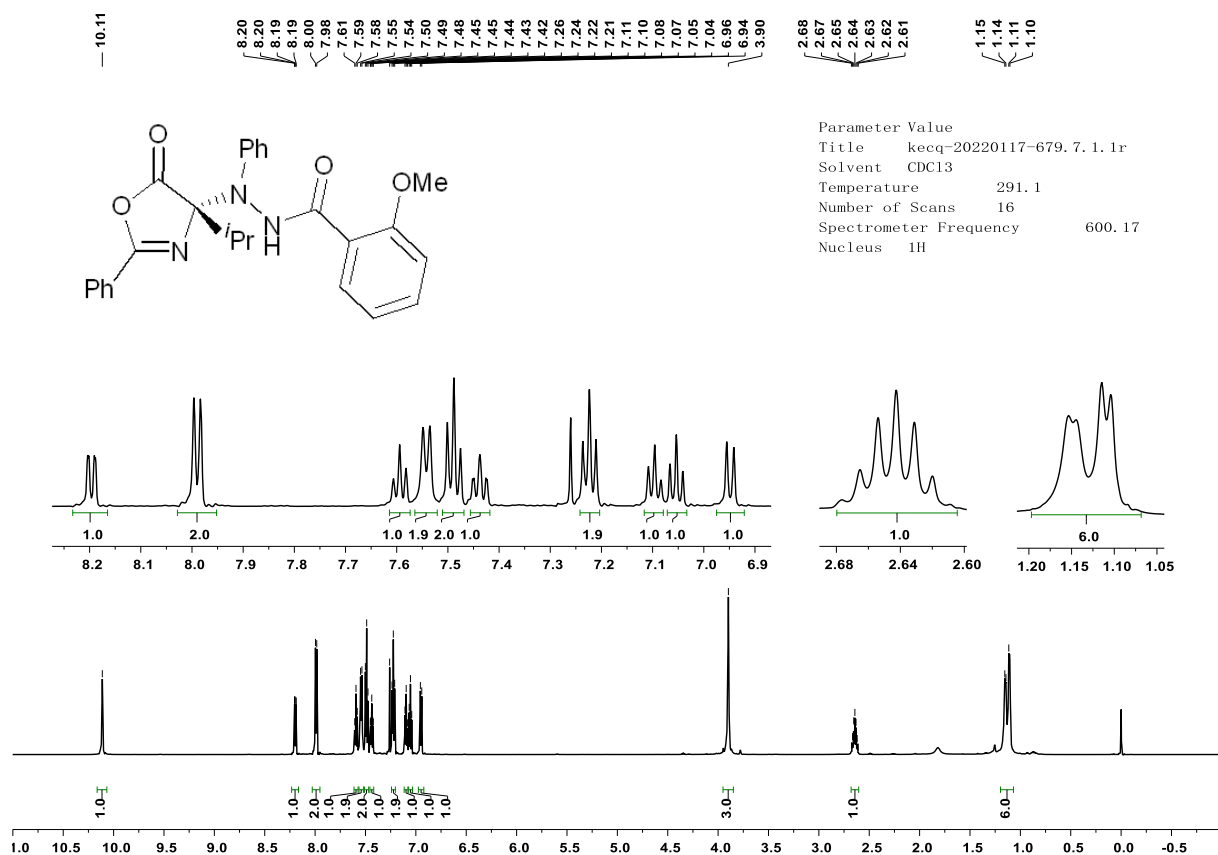


Figure S61. ^{13}C NMR of C28

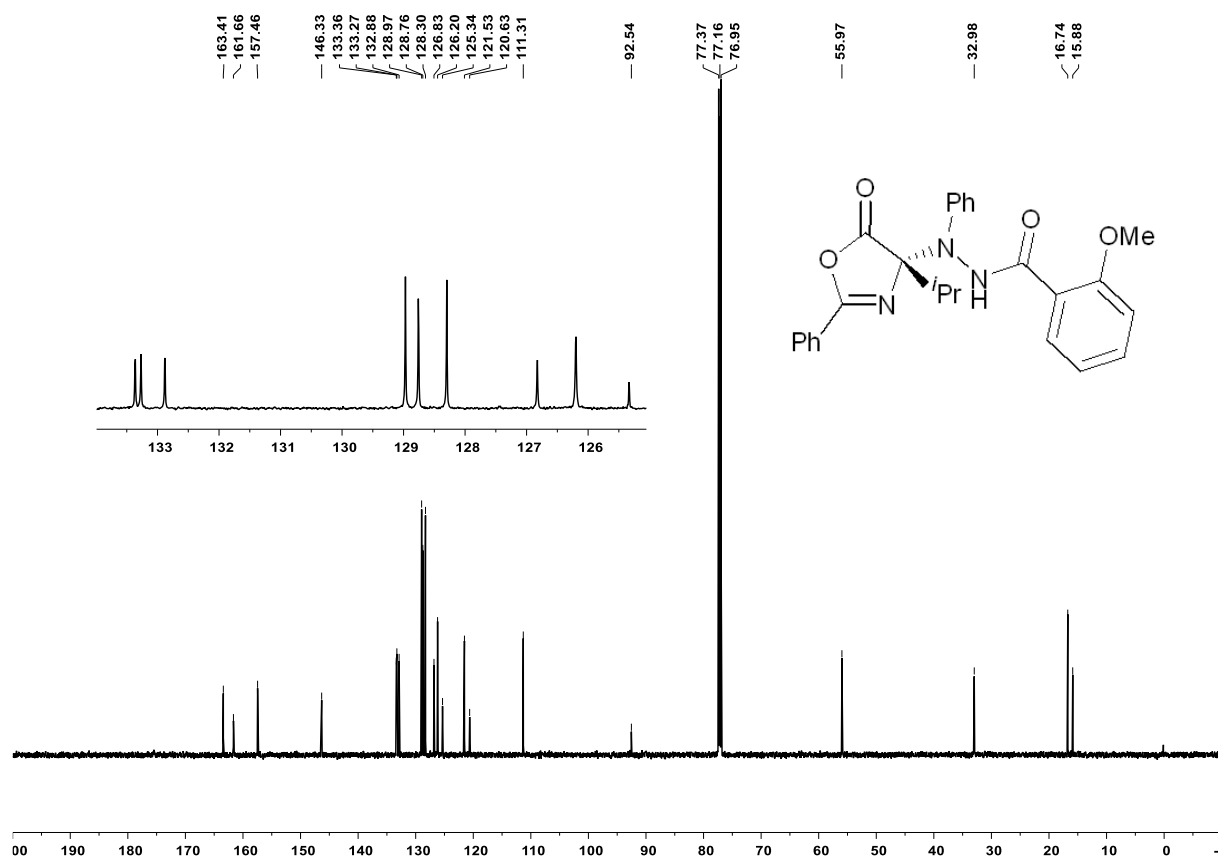


Figure S62. ^1H NMR of C29

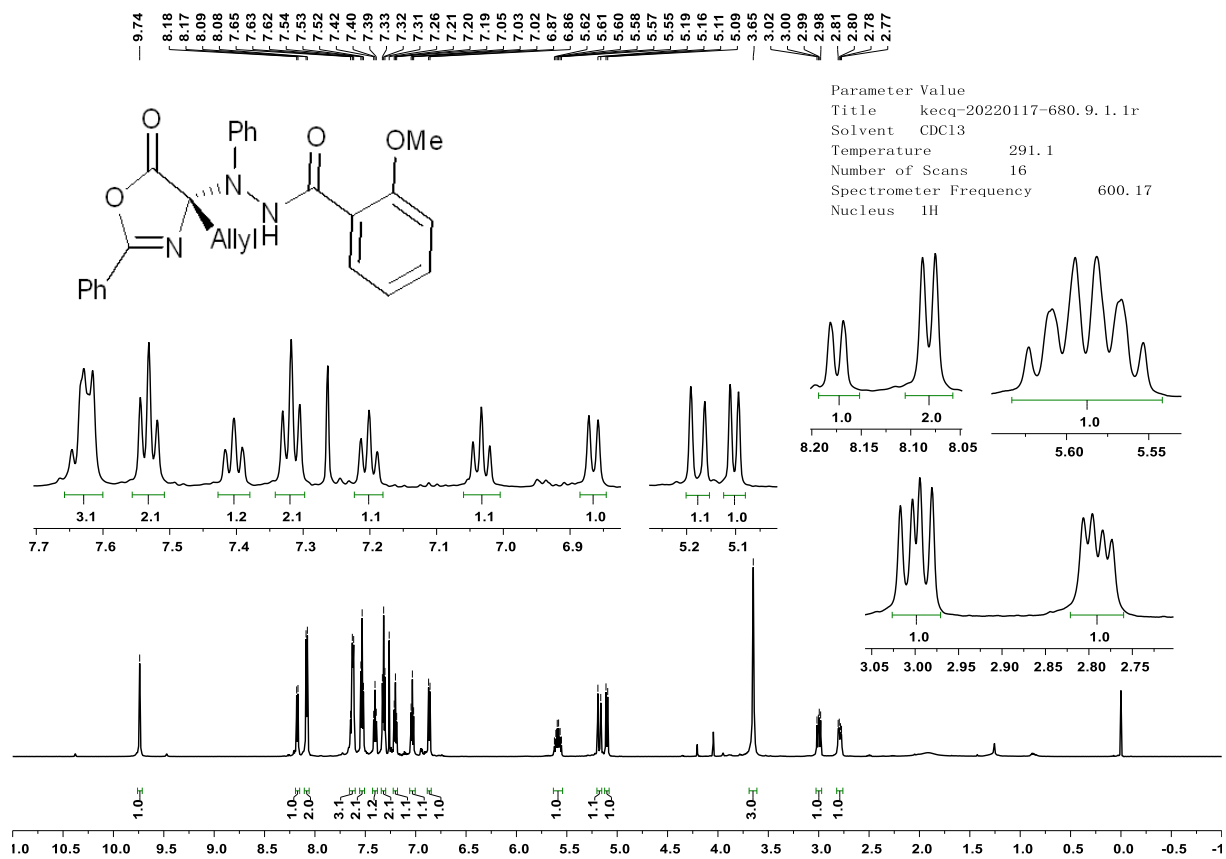
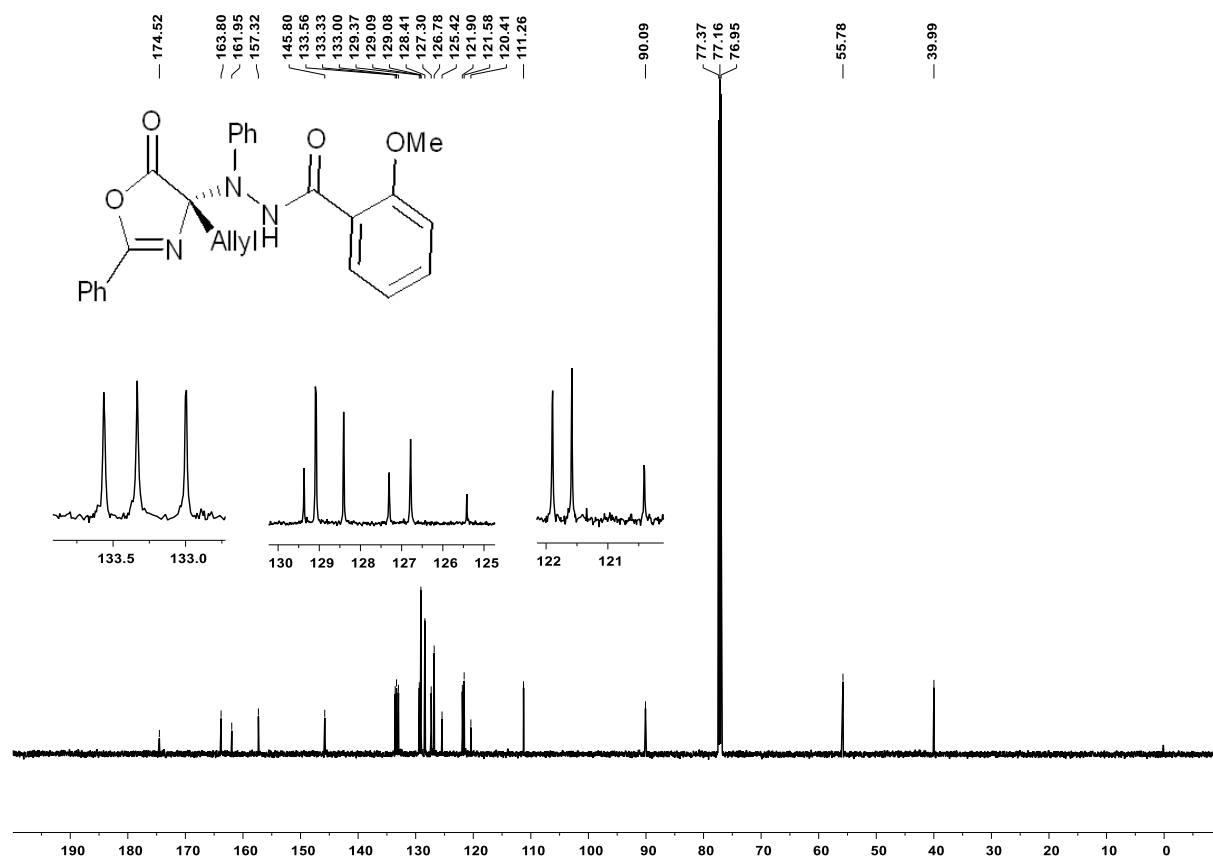
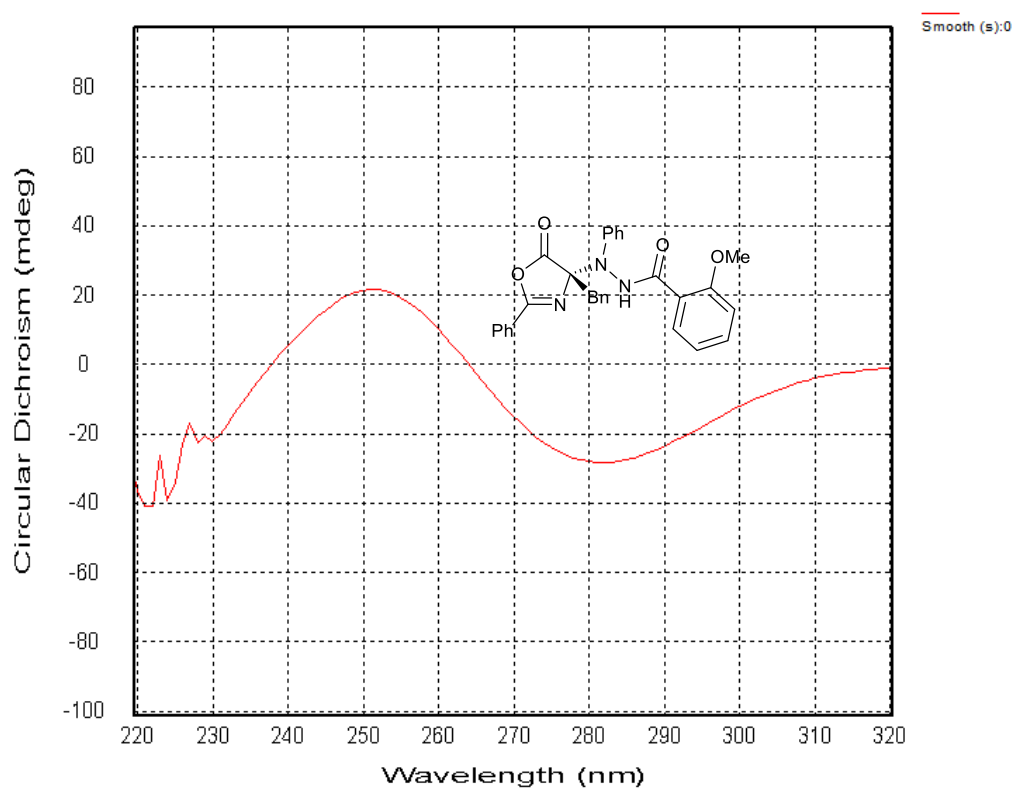


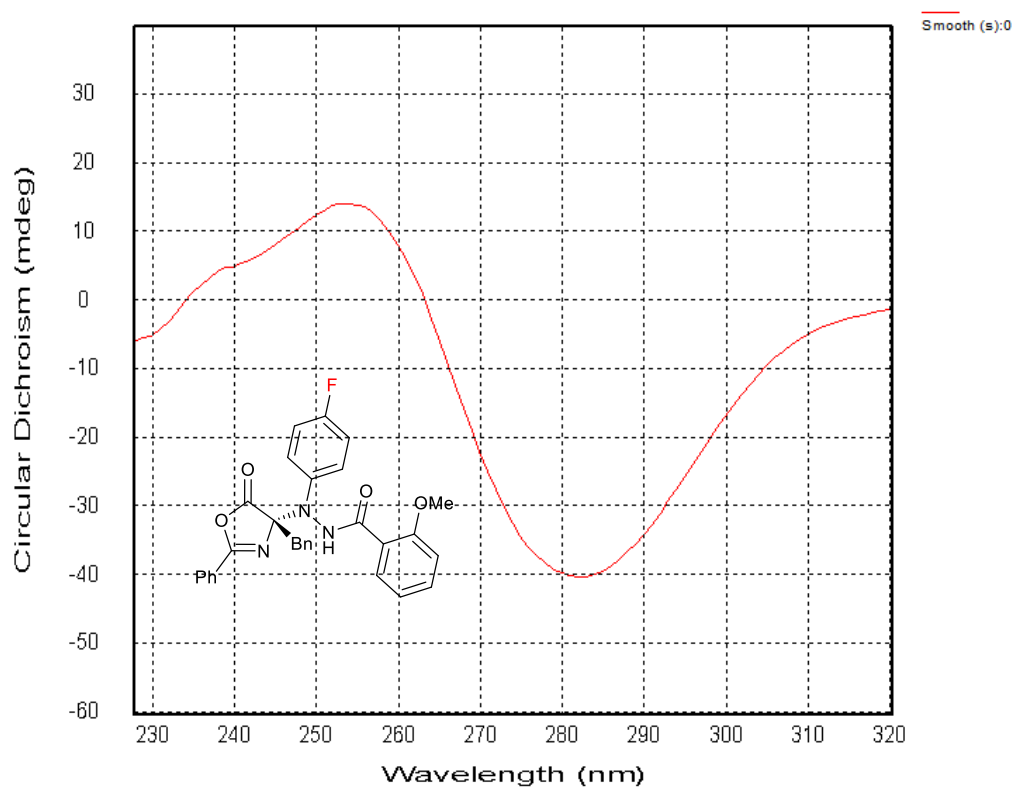
Figure S63. ^{13}C NMR of C29



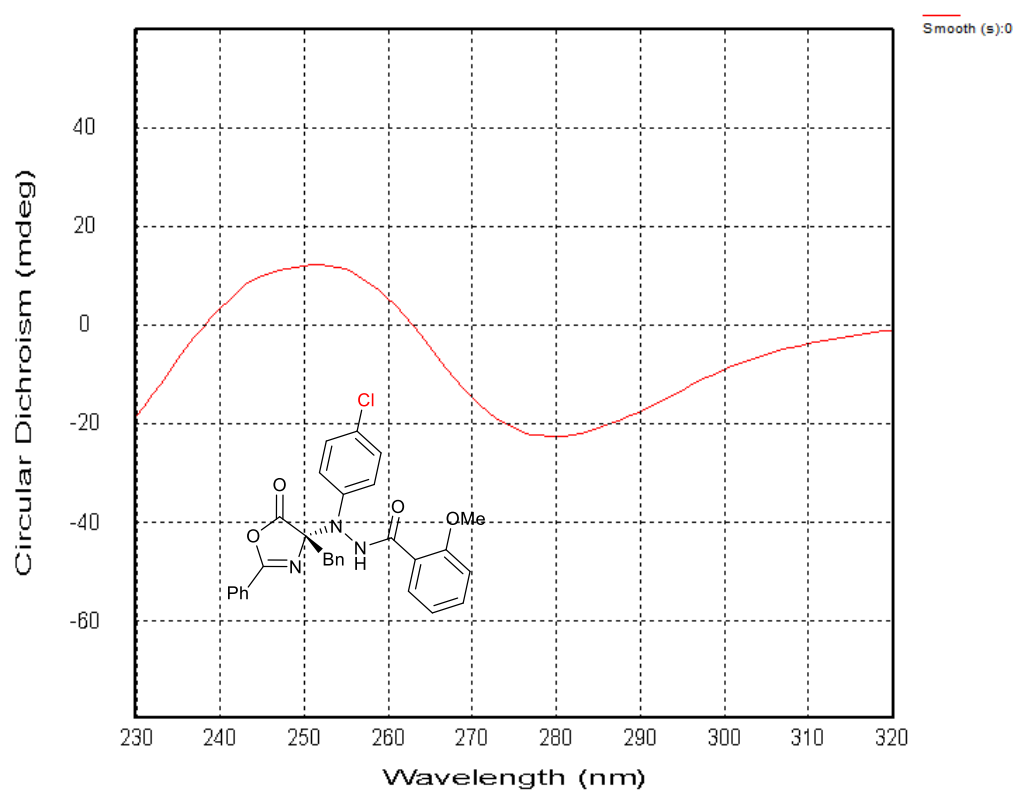
9. Copies of CD spectra for products



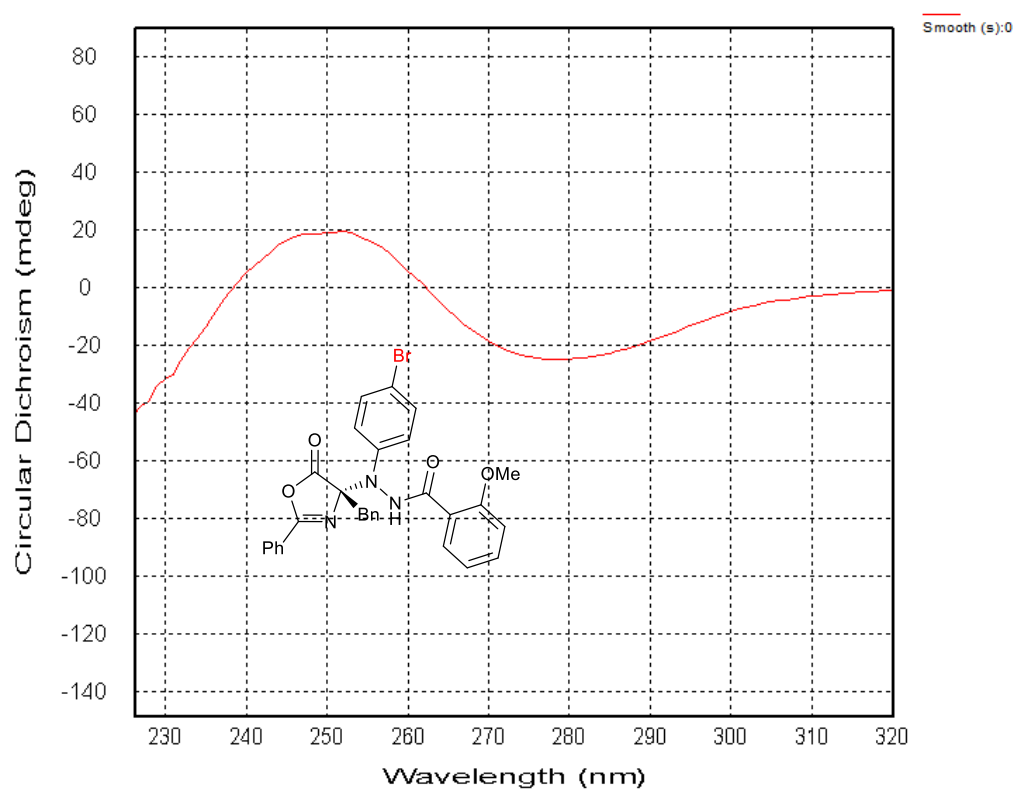
C1



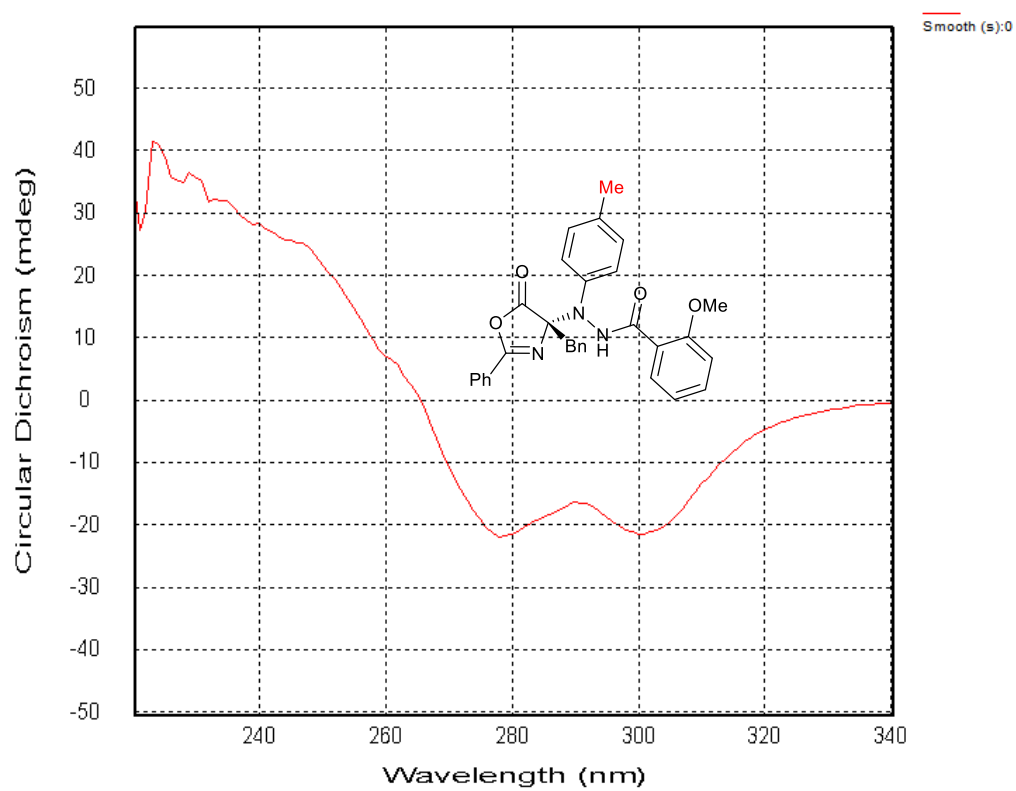
C2



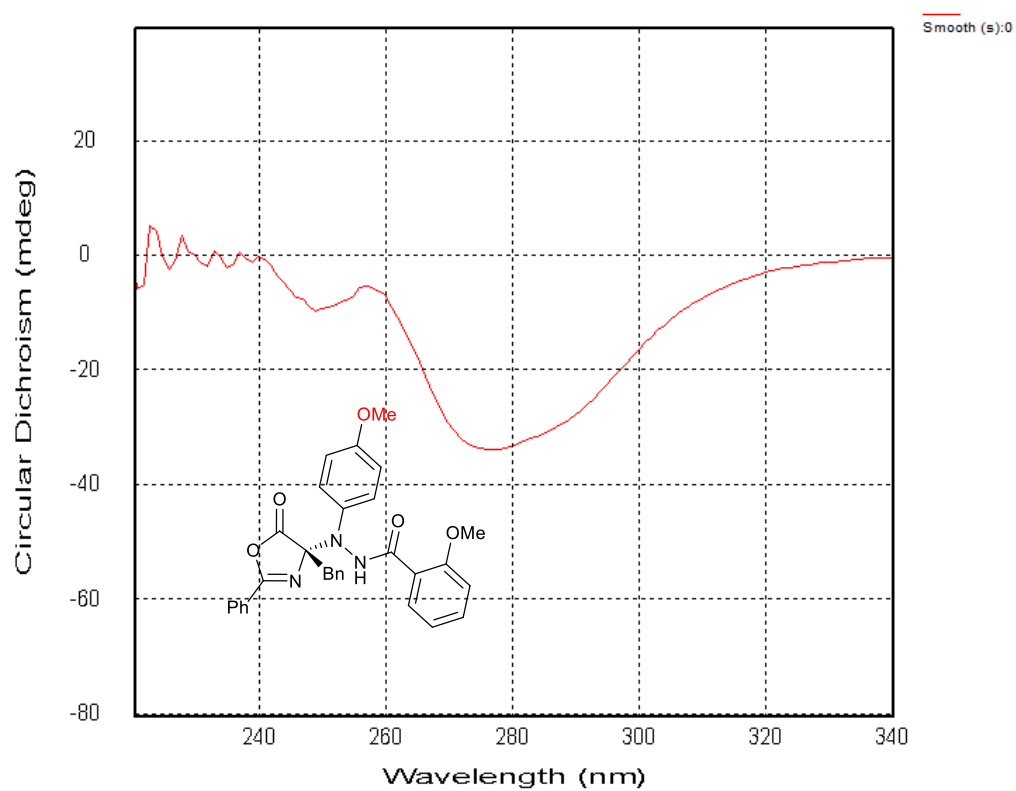
C3



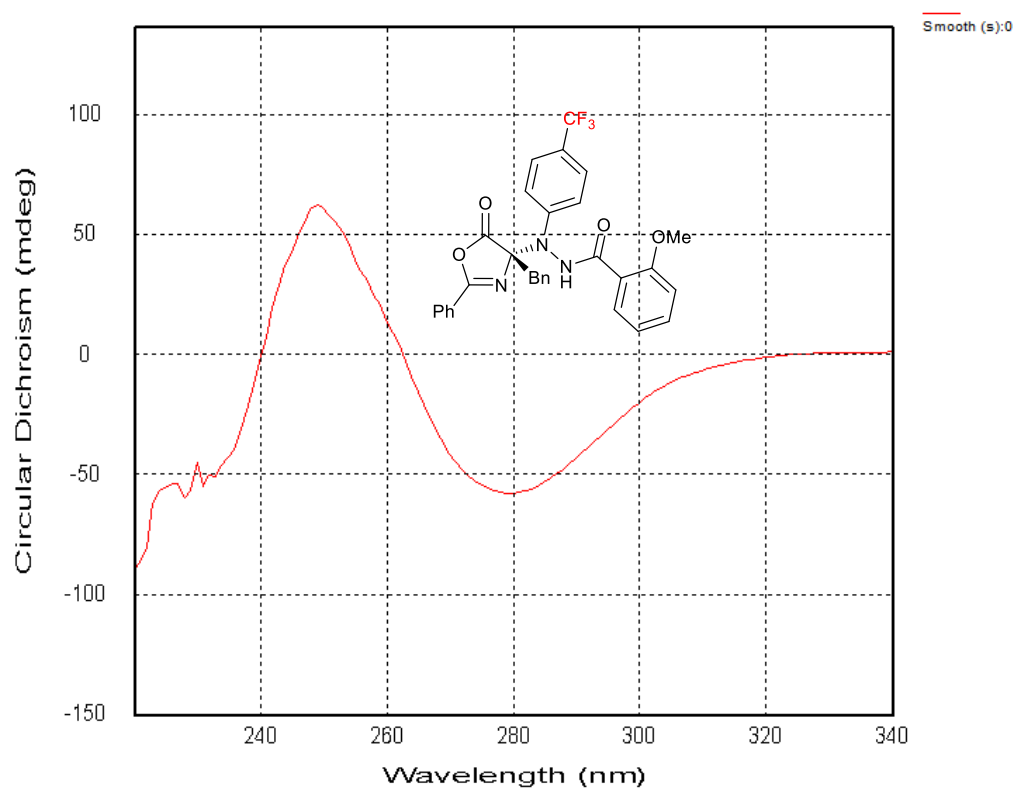
C4



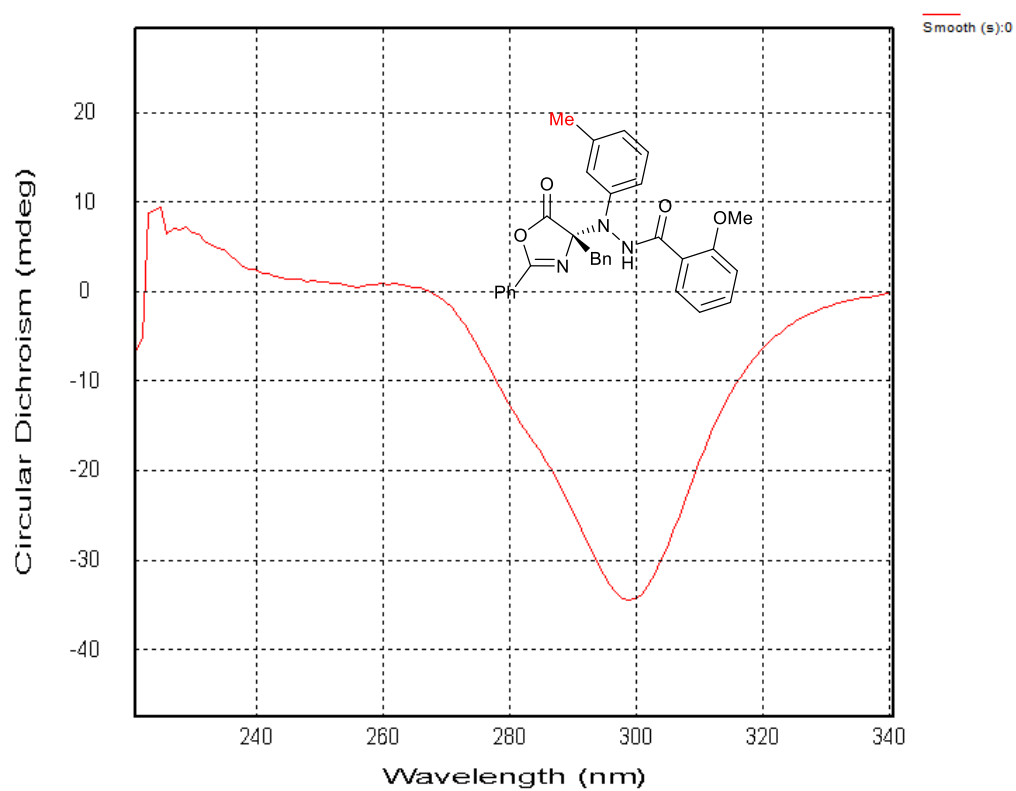
C5



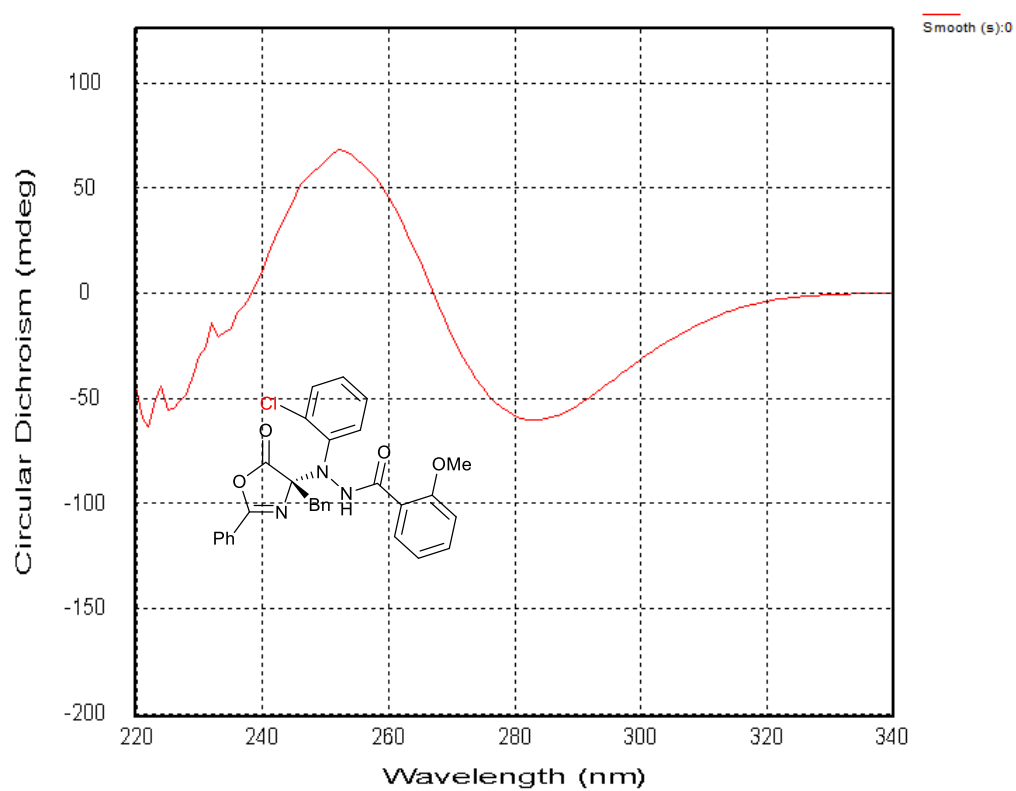
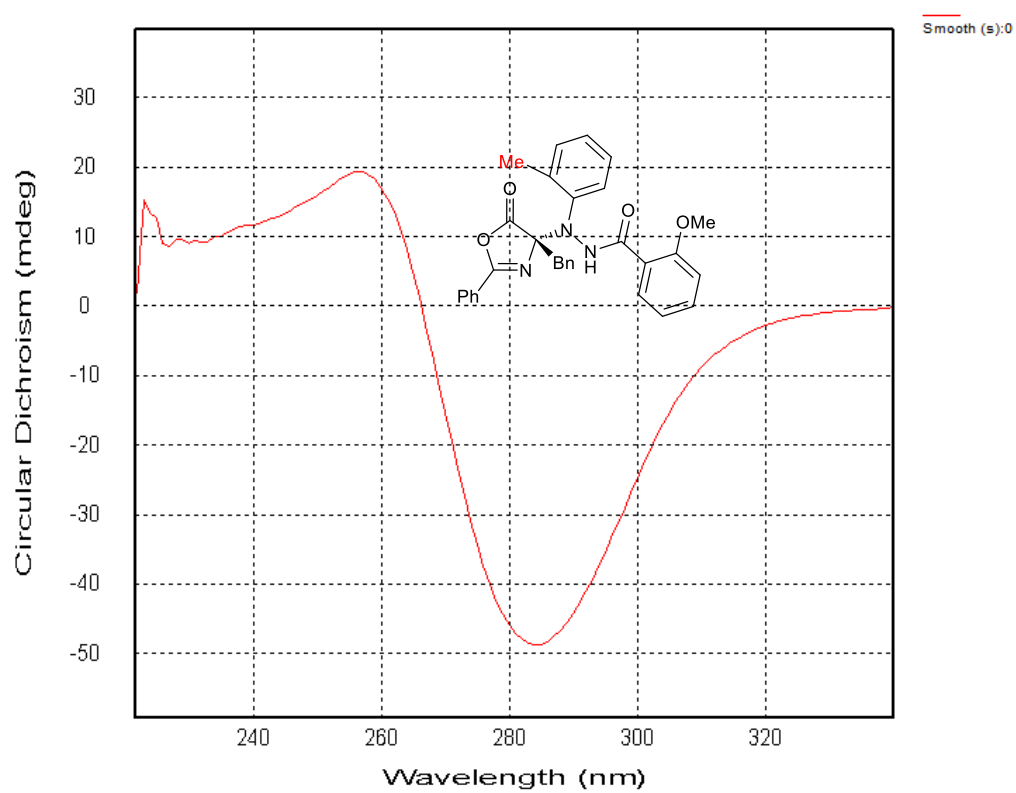
C6

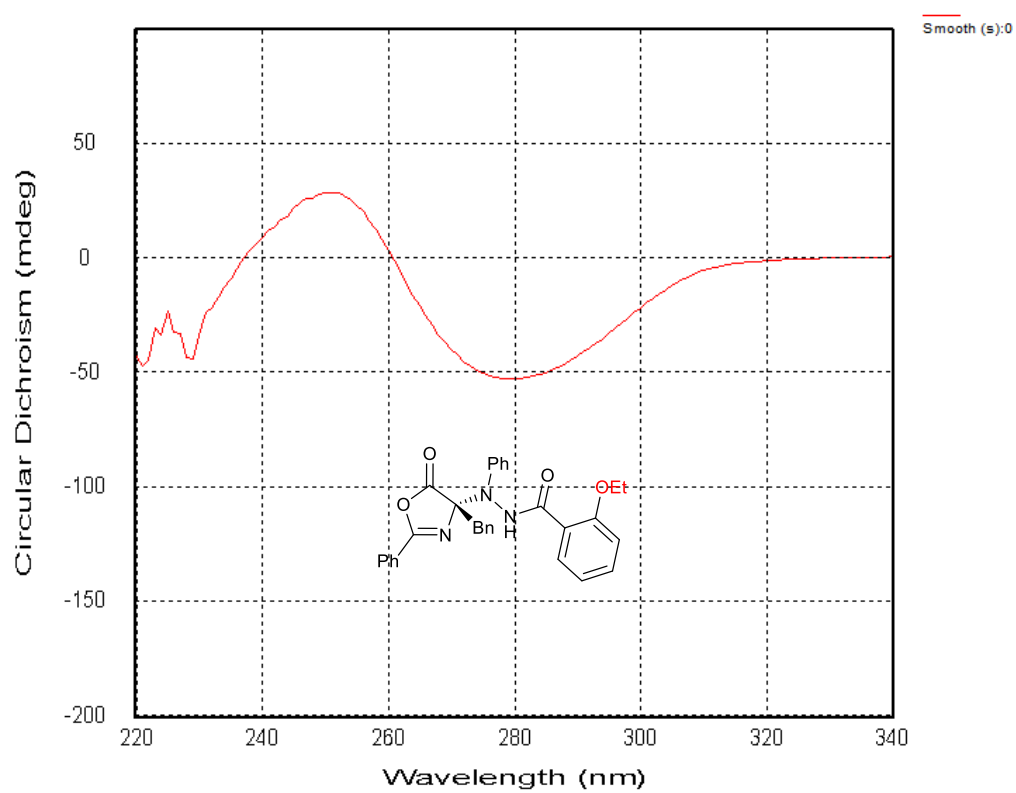


C7

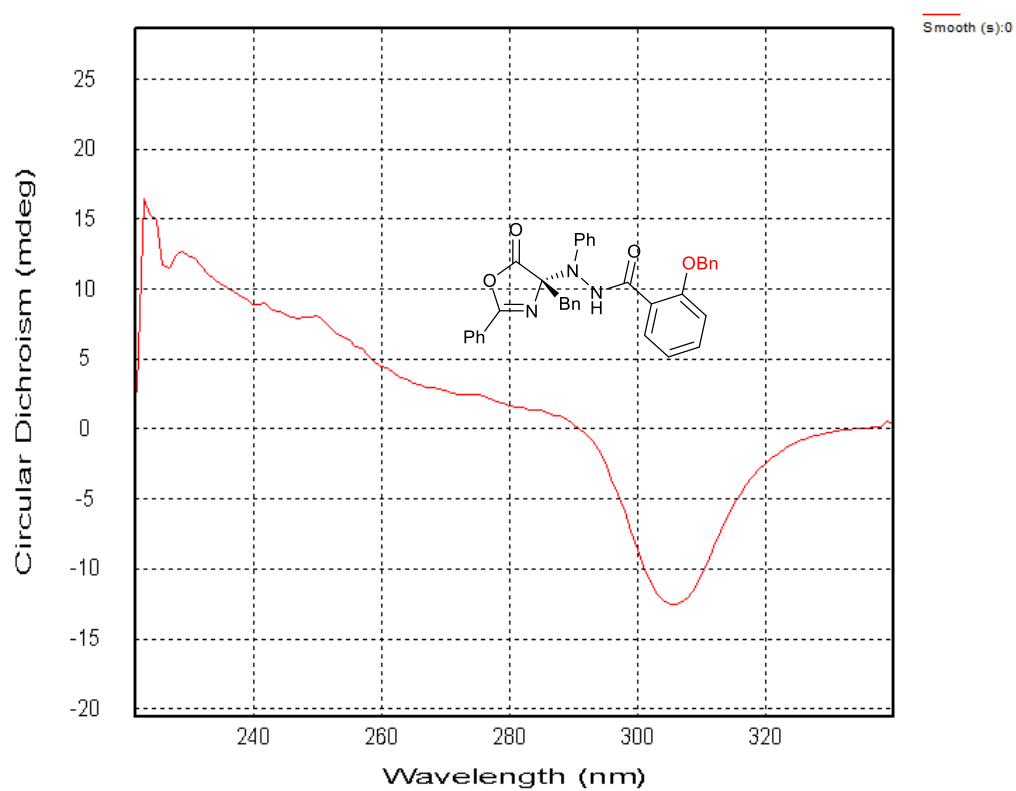


C8

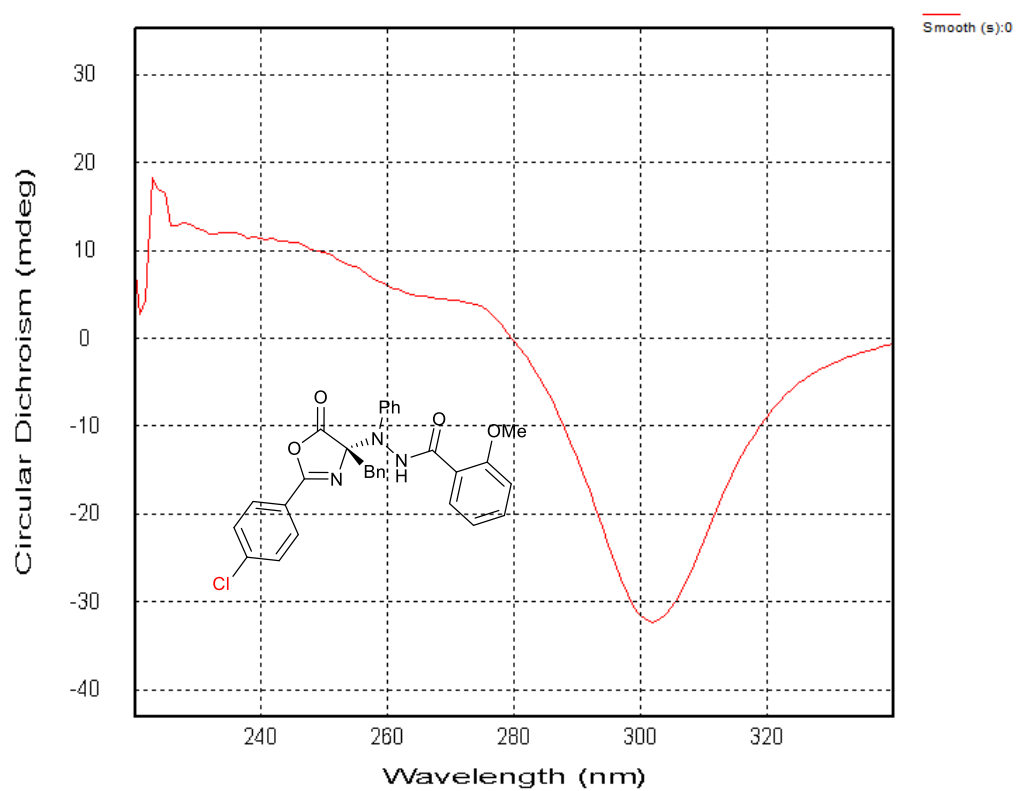
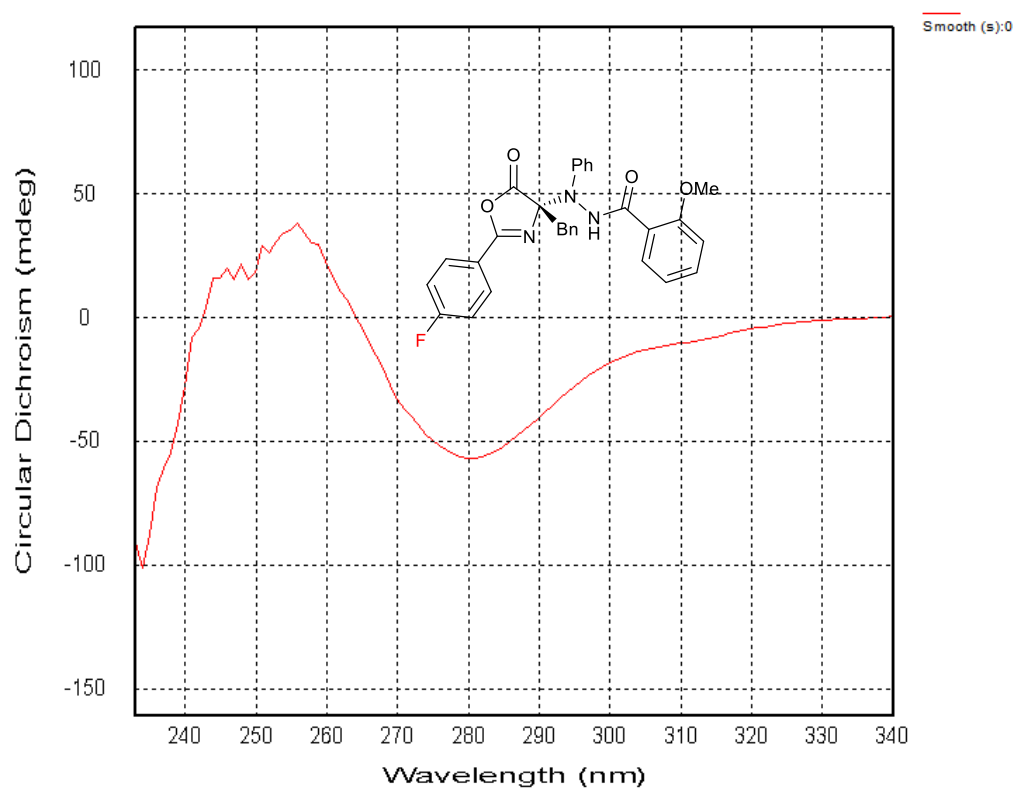


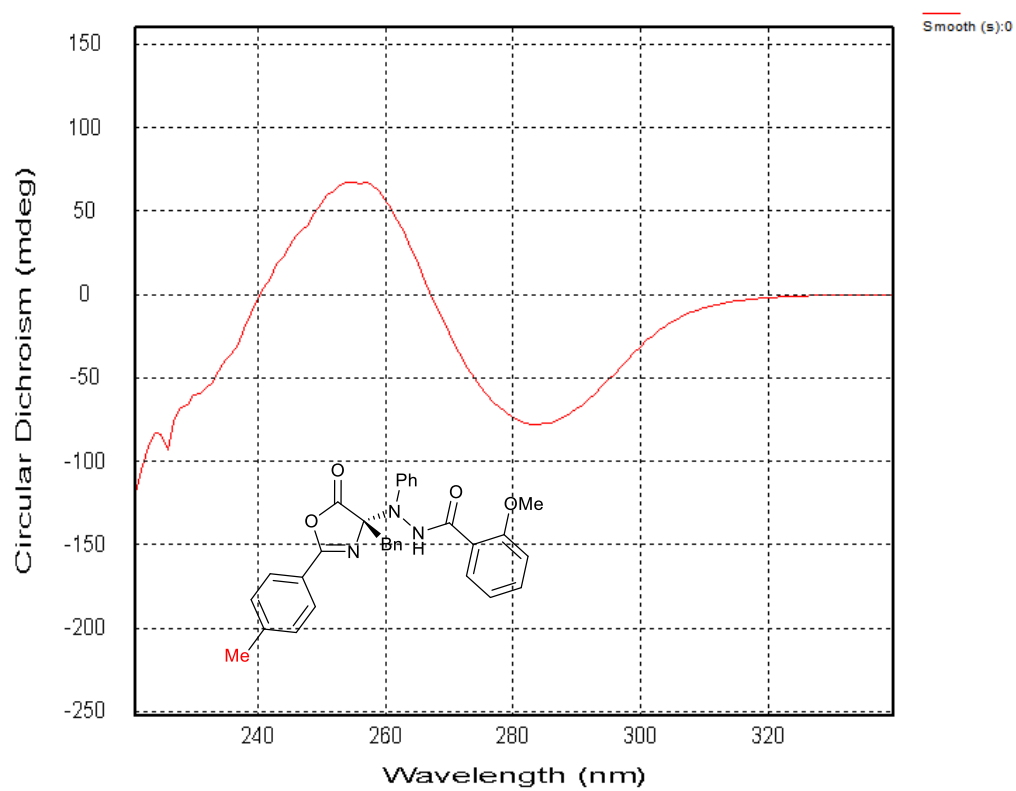


C11

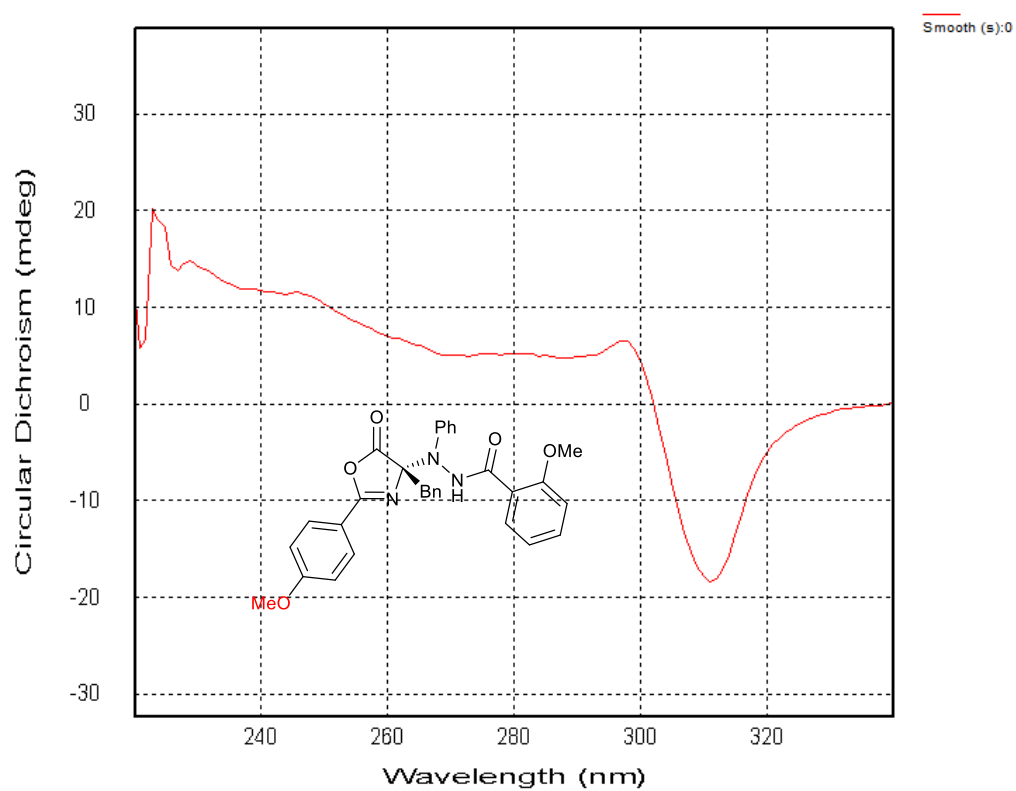


C12

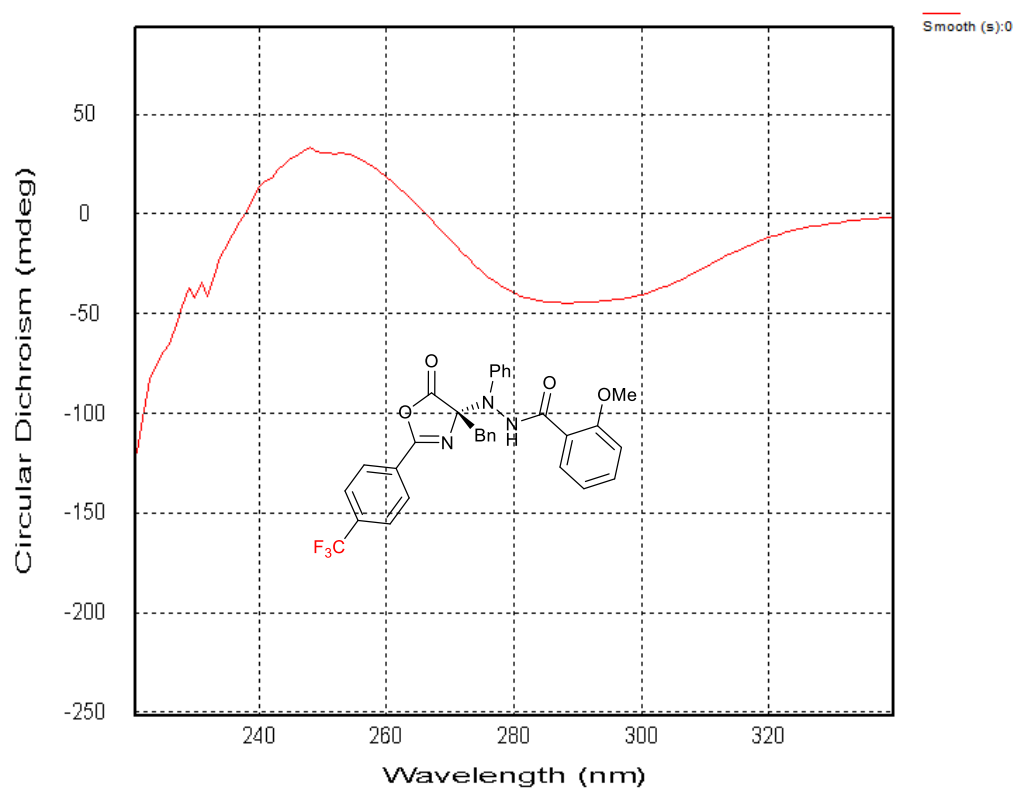




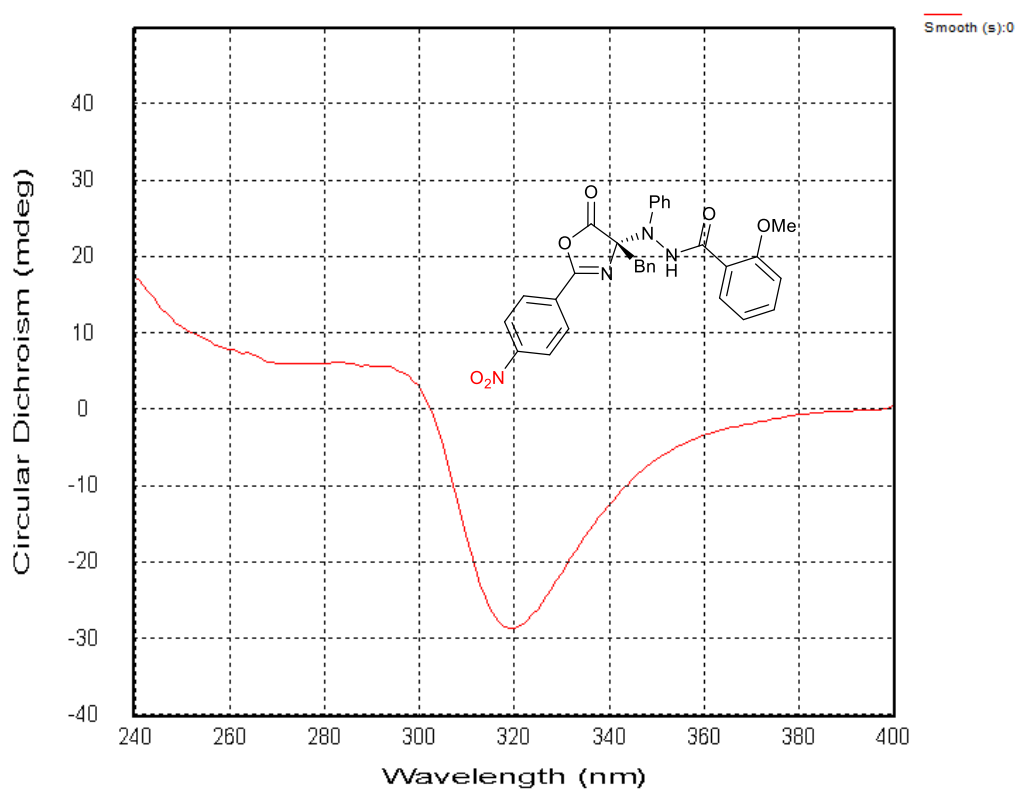
C15



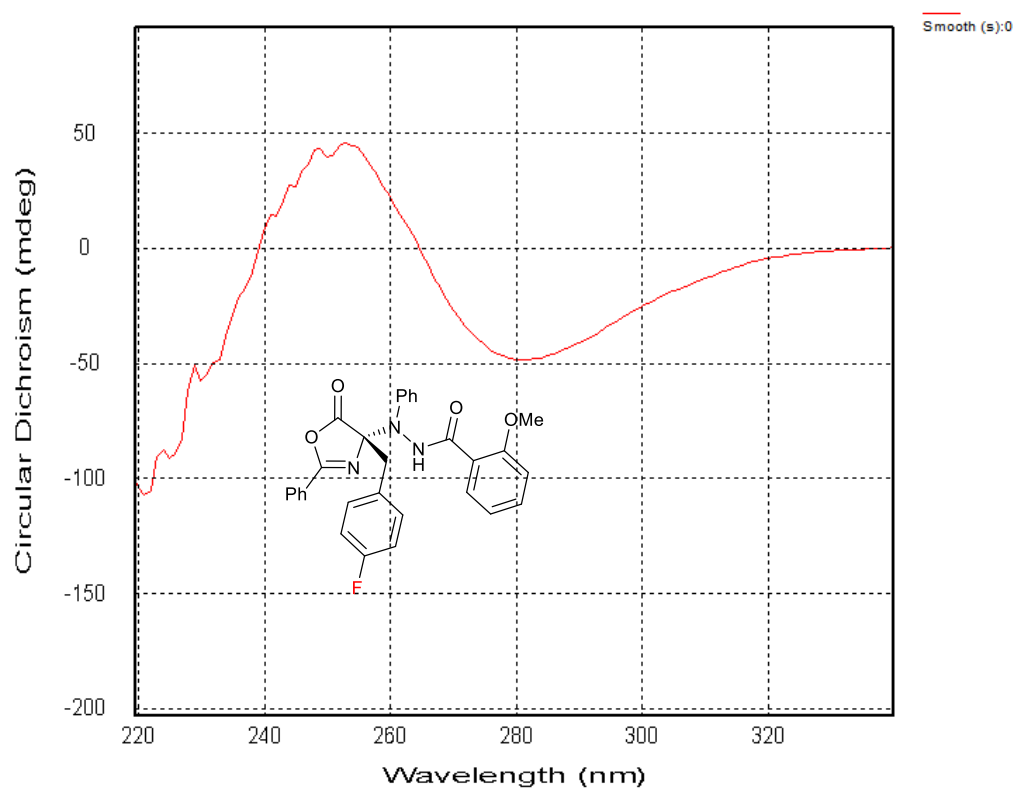
C16



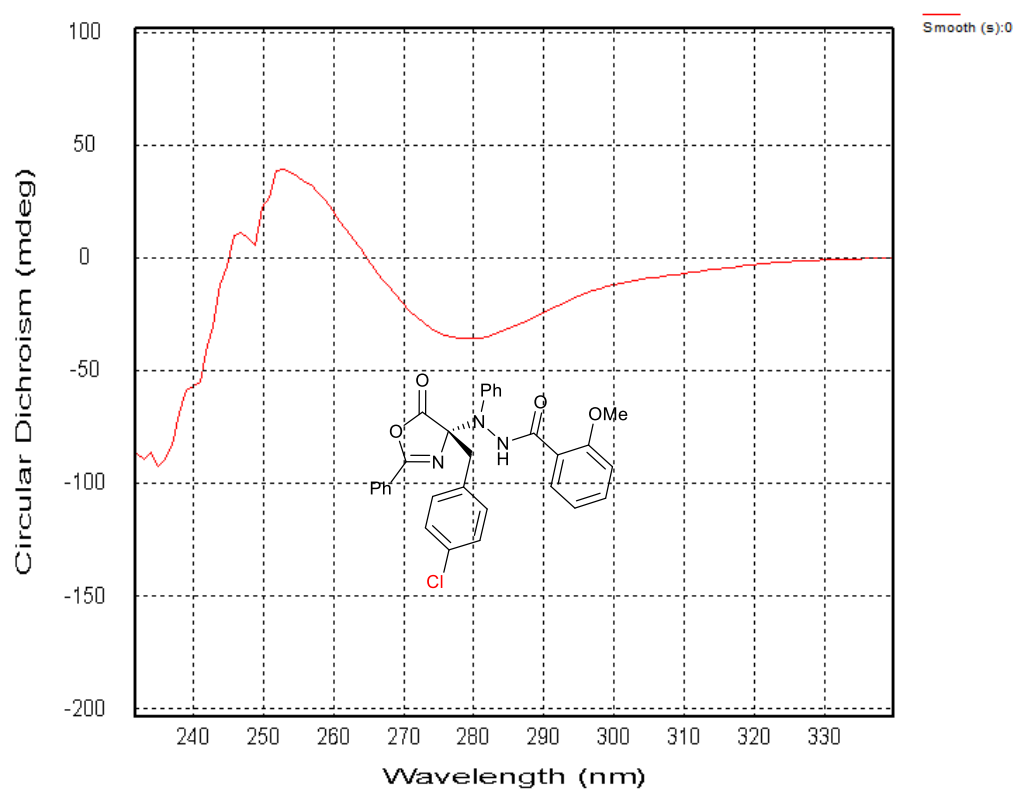
C17



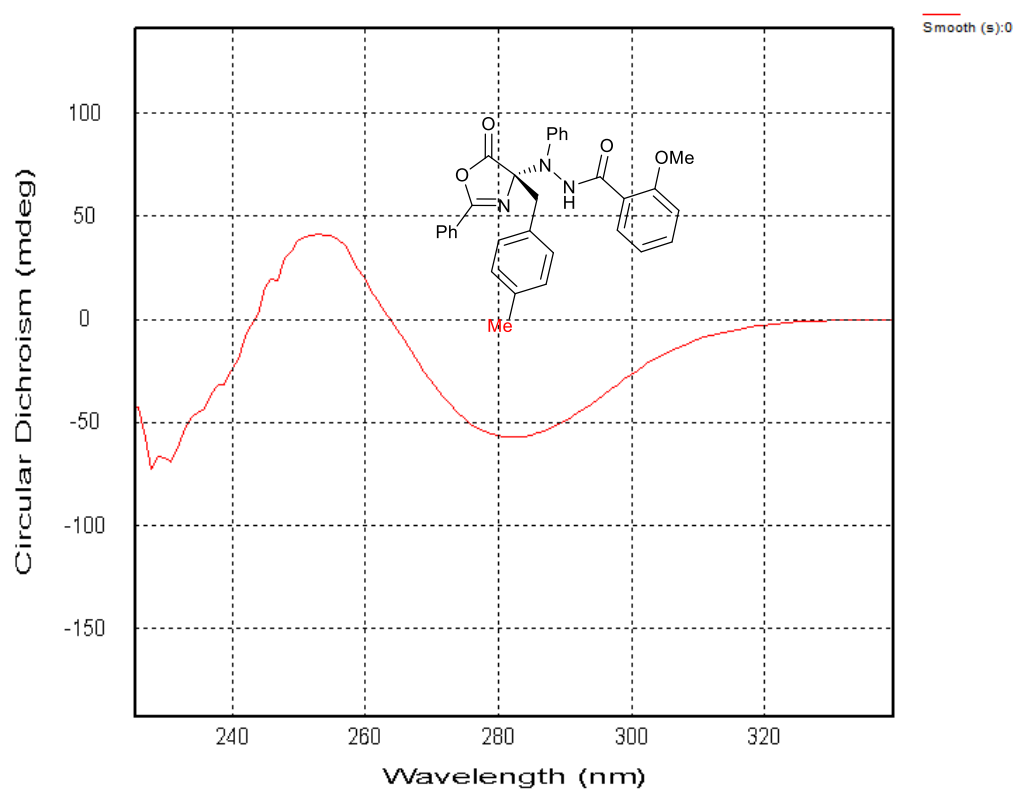
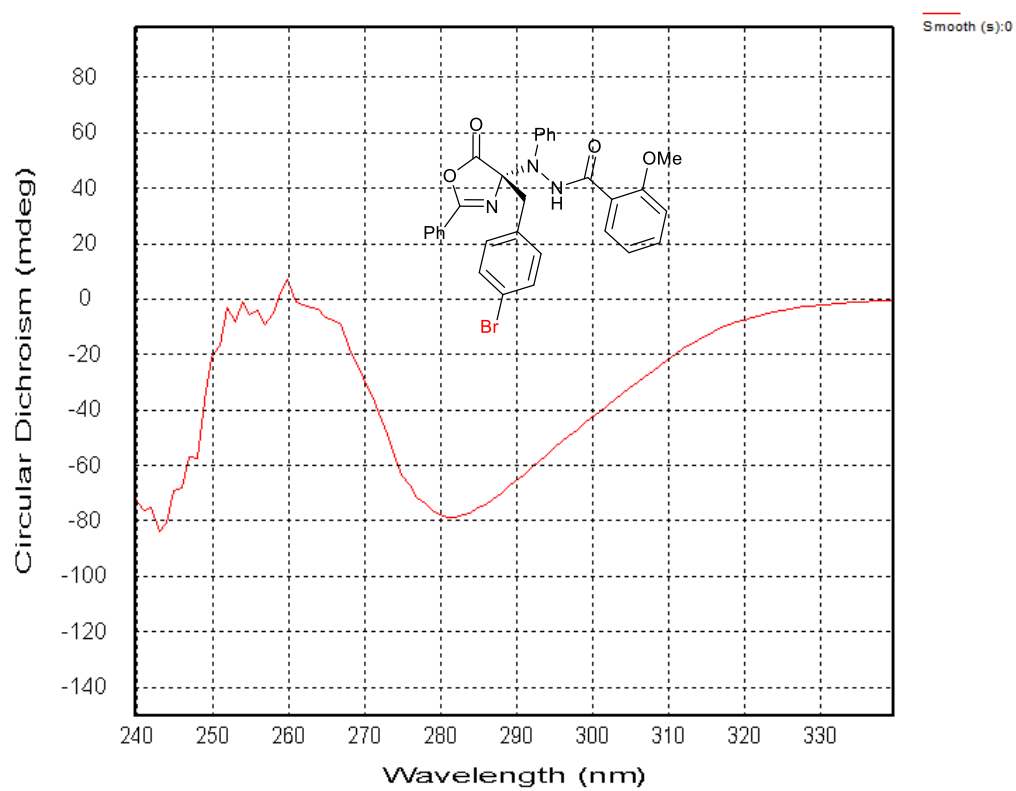
C18

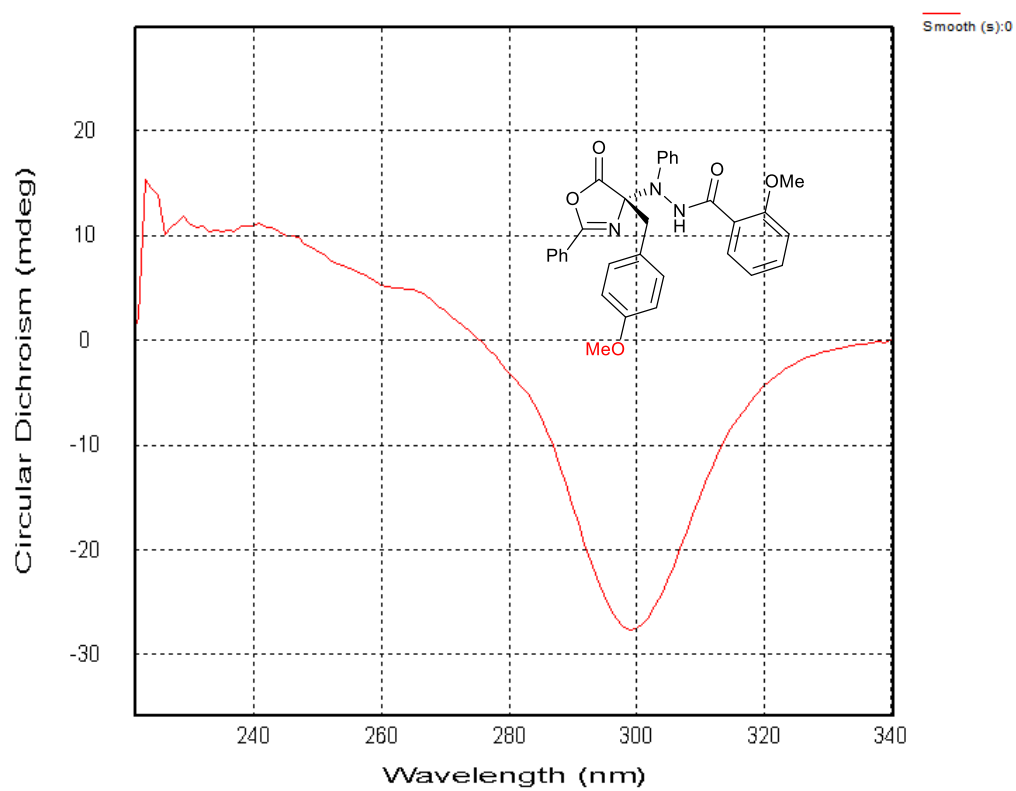


C19

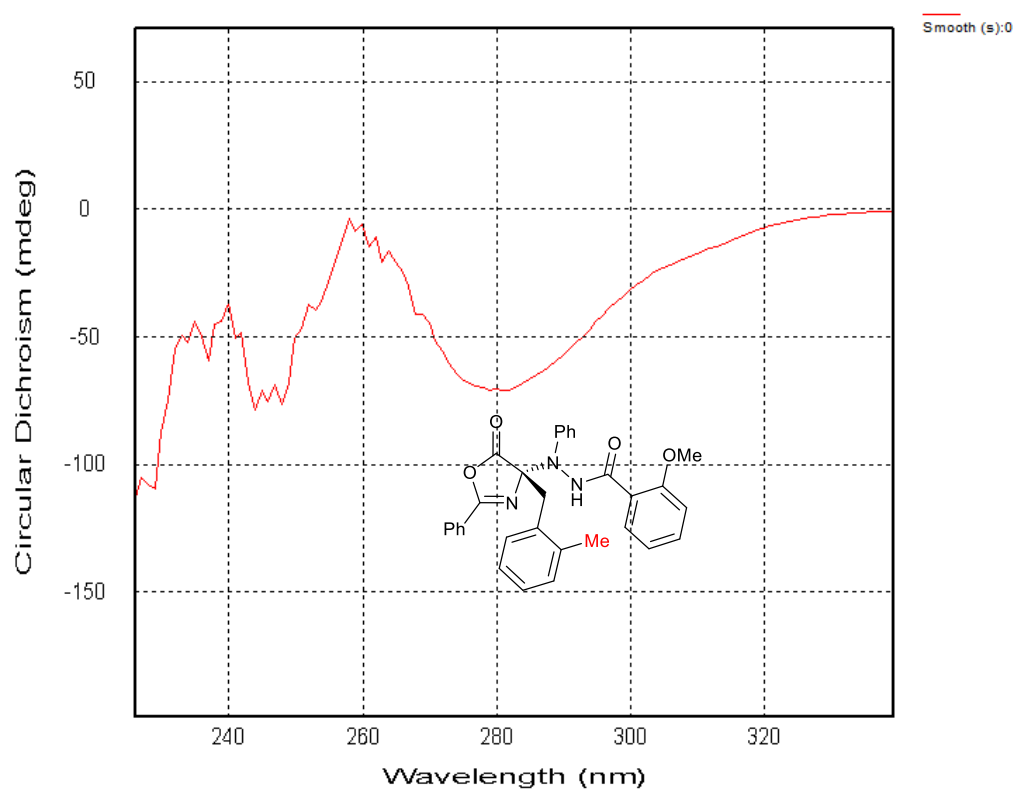


C20

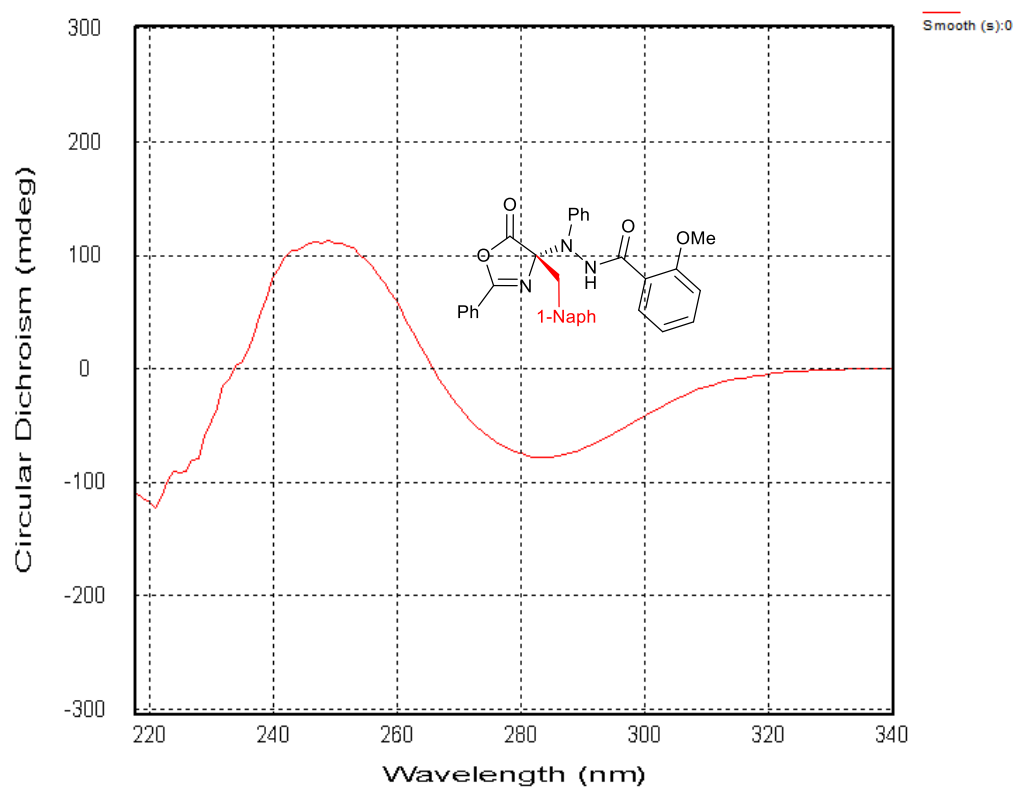
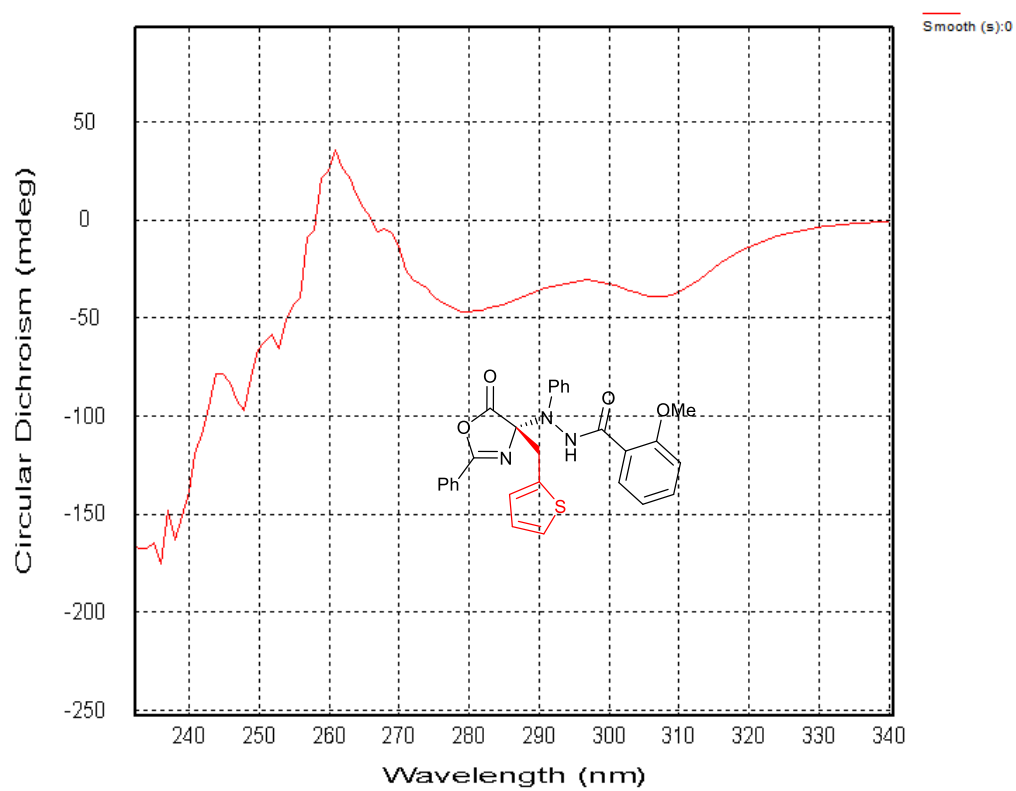


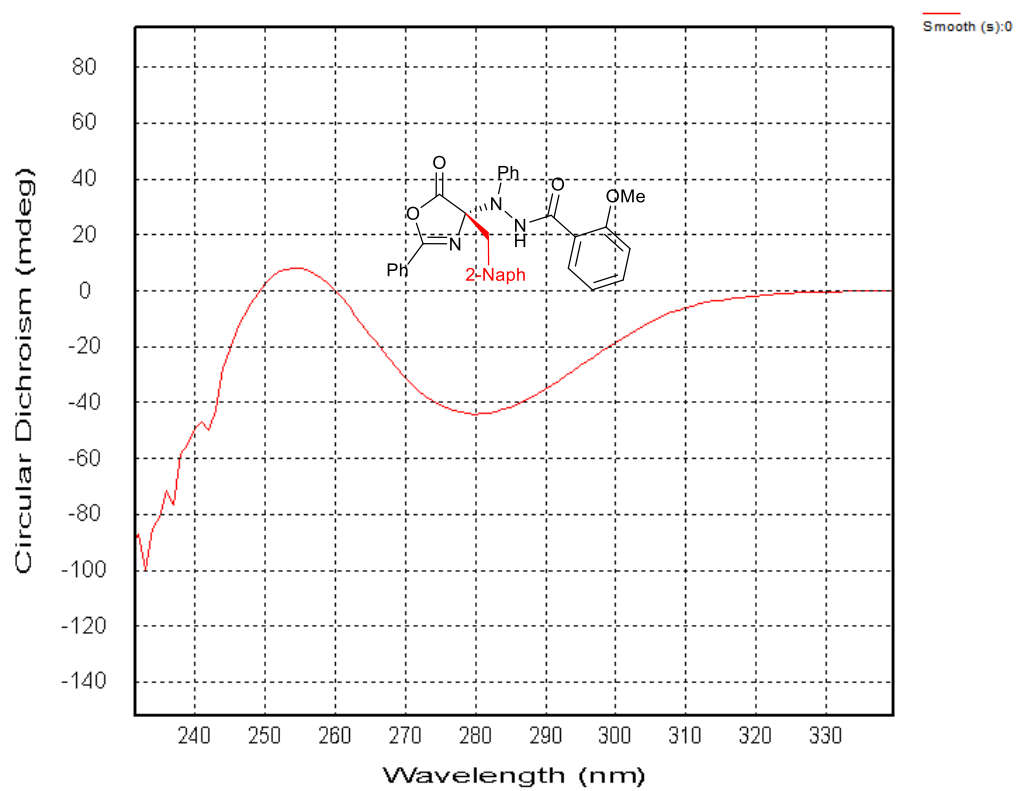


C23

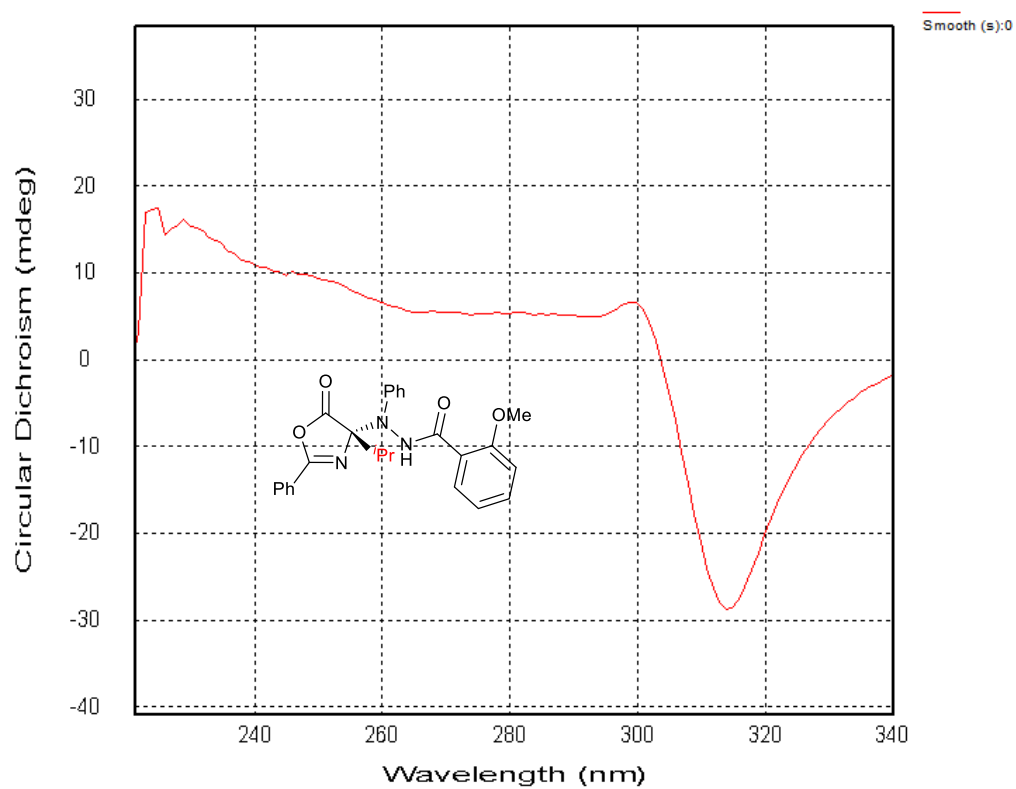


C24

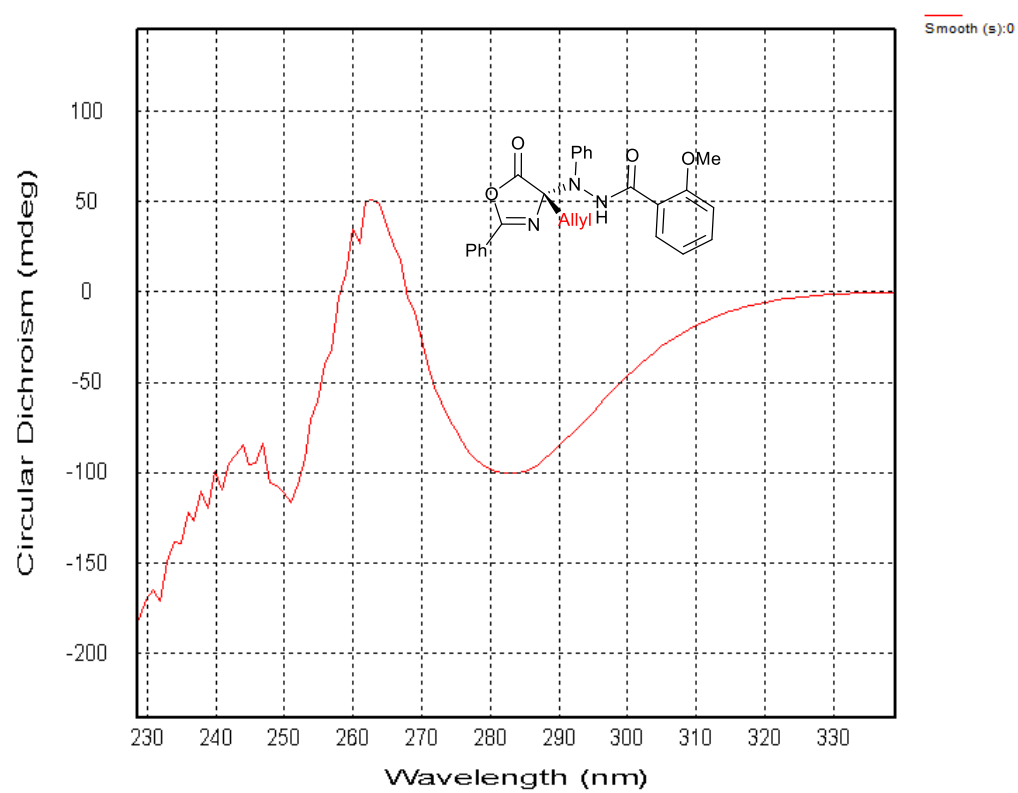




C27

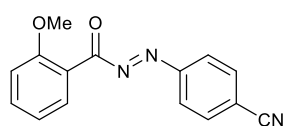


C28

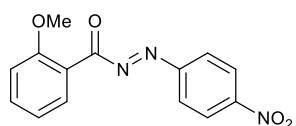


C29

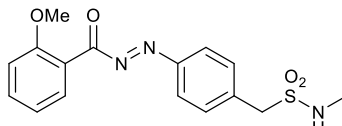
10. Unsuccessful substrate scope



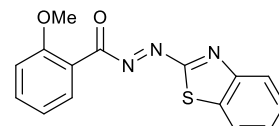
mixture



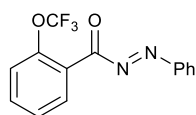
mixture



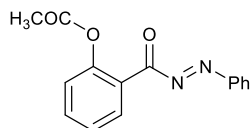
mixture



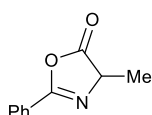
mixture



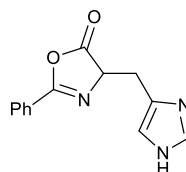
failed



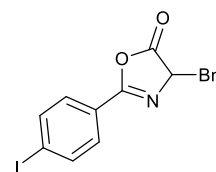
failed



mixture



N.D.



N.D.

11. Reference

- (1) (a) S. X. Dong, X. H. Liu, X. H. Chen, F. Mei, Y. L. Zhang, B. Gao, L. L. Lin and X. M. Feng, *J. Am. Chem. Soc.*, **2010**, 132, 10650–10651; (b) K. A. Teegardina and J. D. Weaver, *Chem. Commun.*, 2017, **53**, 4771–4774.
- (2) Z. Y. Huang, Q. Q. Zhang, Q. L. Zhao, W. Q. Yu and J. B. Chang, *Org. Lett.*, 2020, **22**, 4378–4382.
- (3) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett*, 2005, 2445.