Rapid Access to Cyclopentadienes Derivatives through Gold-Catalyzed Cycloisomerization of Ynamides with Cyclopropenes by Preferential Activation of Alkene over Alkyne

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1. General information Section

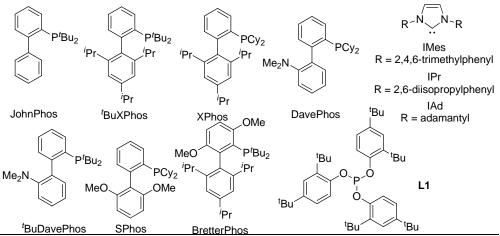
Unless otherwise noted, all reactions were carried out with standard Schlenk techniques under argon. And all reagents were purchased from commercial suppliers without further purification. All solvents were distilled from appropriate drying agents prior to use. Reaction progress was monitored by thin layer chromatography (TLC) and components were visualized by observation under UV light at 254nm. Flash column chromatography was performed using silica gel 60 (200-300 mesh).

All ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were given on Bruker AV-III 400 in CDCl₃. Chemical shifts were reported in parts per million (ppm, δ), referenced to the peak of tetramethylsilane, defined at $\delta = 0.00$ (¹H NMR), or the solvent peak of CDCl₃, defined at $\delta = 77.0$ (¹³C NMR); Data are reported as follows: chemical shift, multiplicity ((s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants were quoted in Hz (*J*). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). Pressed KBr disks for infrared spectra were recorded using a Bruker-VERTEX 70 FT-IR spectrometer. Wavelengths (v) are reported in cm⁻¹. Melting points were recorded using a SGW Melting Point thermometer (X-4). High-resolution mass spectra were obtained using a Thermo Fisher Scientific LTQ FT Ultra.

2. Representative Optimization Studies

Table S1. Optimization of the reaction conditions

 $^{^{\}rm b}$ Yield of the isolated product. $^{\rm c}$ CH $_{\rm 3}$ CN replaced CH $_{\rm 2}$ Cl $_{\rm 2}$ as solvent.



^aConditions: ynamide **1a** (0.2 mmol, 1 equiv), cyclopropane **2a** (1 mmol, 5 equiv).

entry	2 a (n equiv)	Au (x mol%)	T (°C)	solvent	time (h)	yield of 3a (%) ^b	recovered 1a (%) ^b
1	5	5	25	CH ₂ Cl ₂	16	15	84
2	5	5	40	CH ₂ Cl ₂	16	32	68
3	5	5	60	CH ₂ Cl ₂	16	37	58
4	5	5	80	CH ₂ Cl ₂	16	70	25
5	5	5	100	CH ₂ Cl ₂	2.5	92 (97 ^c)	
6	2	5	100	CH ₂ Cl ₂	1.5	74	20
7	3	5	100	CH ₂ CI ₂	2	90	
8	5	1	100	CH ₂ Cl ₂	3	23	75
9	5	3	100	CH_2CI_2	3	92	
10	5	5	100	DCE	1	95 ^c	
11	5	5	25	DCE	22	26	78
12	5	5	40	DCE	5	33	64
13	5	5	60	DCE	5	64	26
14	5	5	80	DCE	1.5	92 ^c	
15	5	3	100	DCE	1	90	
16	5	5	100	PhMe	27	63	25
17	5	5	100	CHCl ₃	1	84	
18	5	5	100	trifluorotoluene	1.5	97	
19	5	5	100	CH ₃ NO ₂	1	98	
20	5	5	100	MeCN	1	98(98 ^c)	
21	3	5	100	DCE	1.5	86	8
22	3	5	100	trifluorotoluene	3	80	11
23	3	5	100	CH_3NO_2	2	64	32
24	3	5	100	CHCl ₃	2	87	10
25	3	5	100	MeCN	2	95	3
26	3	5	80	MeCN	5	95	5

^a Conditions: ynamide 1a (0.2 mmol, 1 equiv). ^b Yield determined by 1 H NMR of the crude product using PhCHO as the internal standard. ^c Yield of the isolated product.

General procedure: Ynamide **1a** (0.20 mmol, 1.0 equiv), catalyst (x mol%) and solvent (0.7 mL) were added to an oven-dried 10 mL pressure tube equipped with a stirrer bar under argon. Cyclopropene **2a** (n equiv) in 0.3 mL of solvent was added in dropwise and the resulting mixture stirred at indicated temperature. After completion of the reaction as indicated by TLC, removing the solvent under reduced pressure. The residual was purified by column chromatography (petroleum ether/ethyl acetate) on silica gel to give cyclopentadienes.

3. Procedures for the Preparation of Cyclopropenes

Preparations of 1,1-disubstituted alkenes

Under an atmosphere of argon, potassium *tert*-butoxide (36 mmol, 1.2 eq) was added to a stirred mixture of methyltriphenylphosphonium bromide (36 mmol, 1.2 eq, pre-dried in a vacuum oven for 5 hr) in anhydrous Et₂O. The resulting canary yellow mixture was allowed to stir for 1 h, after which a solution of the ketone (30 mmol, 1 eq) in anhydrous Et₂O was added dropwise. The reaction was monitored by TLC for complete consumption of the starting material. The crude mixture was then passed through a pad of celite and washed with Et₂O. All volatiles were removed under reduced pressure. The crude reaction mixture was then diluted with hexanes, and passed through a pad of silica gel by eluting with hexanes. The combined hexanes eluent was collected and concentrated under reduced pressure. The alkene product was isolated by flash column chromatography with hexanes as the eluent.

Preparation of 2,2-dibromocyclopropanes

According to a modified procedure of Rubin.¹ To a vigorously stirred mixture of α-methylstyrene (27.3 mL, 0.21 mol), bromoform (40.5 mL) and cetrimide (1 g), 50% aqueous solution of NaOH (45 mL) was added dropwise. A cooling bath was used occasionally to keep the temperature of the reaction mixture in the interval of 35-40

¹ Sherrill, W. M.; Kim, R.; Rubin, M. Tetrahedron, 2008, 64, 8610.

°C. The reaction mixture was vigorously stirred for 30 hrs, then water was added. The organic phase was separated and the aqueous phase was extracted with chloroform. Combined organic phases were washed (water, 2% HCl, brine), dried (CaCl₂), filtered, and concentrated under reduced pressure. Flash column chromatography of the resulting residue on silica gel (eluent – hexanes) gave the dibromocyclopropane products.

Synthesis of bromocyclopropanes

Bromocyclopropanes (0.1 mol) were prepared by partial reduction of the corresponding dibromocyclopropanes with EtMgBr (0.13 mol, 1.3 eq) in the presence of Ti(OⁱPr)₄ (10 mmol, 0.1 eq) according to the reported protocol. Ethylmagnesium bromide was added dropwise to a cooled (0 °C ice bath) stirring solution of the dibromocyclopropane and Ti(OⁱPr)₄ in Et₂O under argon. The mixture turned dark orange instantly with generation of heat (fast addition of the Grignard reagent should be avoided to prevent evaporation of solvent). The reaction mixture was stirred at rt for 4 h, then quenched with 10% aq. HCl. The organic phase was separated and the aqueous layer was extracted twice with Et₂O. The combined ethereal layers were washed consecutively with sat. NaHCO₃ and brine, then dried with Na₂SO₄, filtered and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel (eluent – petroleum ether) to afford the bromocyclopropane as a mixture of diastereomers.

Synthesis of cyclopropenes

Cyclopropenes were prepared according to the literature protocol.¹ A solution of bromocyclopropane (76.3 mmol) in DMSO was added to a stirring solution of

potassium t-butoxide (92 mmol, 1.2 eq) in DMSO. The mixture turned dark brown instantly and was stirred at rt overnight. It was then quenched with H₂O and extracted with ether. The ethereal layers were combined, washed with brine, dried with Na₂SO₄, filtered, and concentrated in vacuo. Flash column chromatography of the residue on silica gel (eluent – petroleum ether) afforded the cyclopropene products.

(1-methylcycloprop-2-en-1-yl)benzene 2a¹



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.28 (t, J = 7.6 Hz, 2H), 7.24 (s, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 1.62 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 149.9, 127.8, 126.0, 125.0, 115.5, 25.4, 21.8.

1-methyl-4-(1-methylcycloprop-2-en-1-yl)benzene 2q¹



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.23 (s, 2H), 7.09 (s, 4H), 2.30 (s, 3H), 1.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 134.4, 128.5, 125.9, 115.7, 25.5, 21.5, 20.8.

1-chloro-4-(1-methylcycloprop-2-en-1-vl)benzene 2r¹



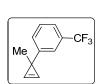
¹H NMR (400 MHz, CDCl₃, TMS) δ 7.23-7.21 (m, 4H), 7.10 (d, J = 8.8Hz, 2H), 1.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 130.7, 127.8, 127.4, 115.4, 25.3, 21.5.

1-bromo-4-(1-methylcycloprop-2-en-1-yl)benzene 2s²



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.36 (d, J = 8.4 Hz, 2H), 7.21 (s, 2H), 7.05 (d, J = 8.4 Hz, 2H), 1.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 130.7, 127.8, 118.8, 115.3, 25.2, 21.5.

1-(1-methylcycloprop-2-en-1-yl)-3-(trifluoromethyl)benzene 2t³



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.43-7.37 (m, 4H), 7.25 (s, 2H), 1.63 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 151.0, 130.2 (q, $J_{\text{C-F}}$ =

Phan, D. T.; Dong, V. M. Tetrahedron, 2013, 69, 5726.

³ Phan, D. H.; Kou, K. G.; Dong, V. M. J. Am. Chem. Soc., **2010**, 132, 16354.

31.4 Hz), 129.4 (d, $J_{\text{C-F}}$ = 1.2 Hz), 128.2, 124.5 (q, $J_{\text{C-F}}$ = 270.4 Hz), 122.7 (q, $J_{\text{C-F}}$ = 3.8 Hz), 121.7 (q, $J_{\text{C-F}}$ = 3.8 Hz), 115.1, 25.1, 21.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.5.

1-chloro-3-(1-methylcycloprop-2-en-1-yl)benzene 2u⁴



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.20 (s, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.11-7.09 (m, 1H), 7.08-7.06 (m,1H), 1.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 133.9, 129.0, 126.3, 125.0, 124.2, 115.1, 25.1,

21.6.

1-chloro-2-(1-methylcycloprop-2-en-1-yl)benzene 2v¹



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.61 (s, 2H), 7.26 (dd, J = 8.0, 1.6 Hz, 1H), 7.21 (dd, J = 7.6, 2.0 Hz, 1H), 7.13 (td, J = 7.2, 1.2 Hz, 1H), 7.05 (td, J = 7.6, 1.6 Hz, 1H), 1.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃)

δ 146.6, 133.6, 129.6, 129.3, 127.2, 127.1, 120.6, 27.3, 23.7.

2-(1-methylcycloprop-2-en-1-yl)naphthalene 2w³



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.78 (d, J = 8.0 Hz, 2H), 7.74(d, J = 8.4 Hz, 1H), 7.68 (s, 1H), 7.45-7.37 (m, 2H), 7.33-7.29 (m, 3H), 1.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 133.3, 131.4, 127.5,

127.4, 127.2, 125.8, 124.9, 124.7, 124.5, 115.7, 25.6, 22.1.

(2-(1-methylcycloprop-2-en-1-yl)ethyl)benzene $2x^5$



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.30 (J =0.4 Hz, 2H), 7.26 -7.22 (m, 2H), 7.15-7.12 (m, 3H), 2.45-2.41 (m, 2H), 1.81-1.77 (m, 2H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 128.4, 128.1, 125.4, 121.8,

41.9, 33.5, 27.1, 20.0.

⁴ Li, Z.; Peng, G.; Zhao, J.; Zhang, Q. Org. Lett. 2016, 18, 4840.

⁵ Young, P. C.; Hadfield, M. S.; Arrowsmith, L.; Macleod, K. M.; Mudd, R. J.; Jordan-Hore, J. A.; Lee, A.-L. *Org. Lett.*, **2012**, 14, 898.

4. Procedure and Spectral Data of Products

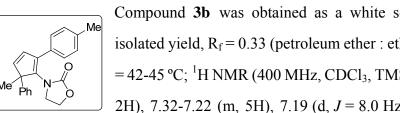
General procedure: Ynamide 1 (0.20 mmol, 1.0 eq), IPrAuNCPhSbF₆ (5 mol%) and CH₃CN (0.7 mL) were added to an oven-dried 10 mL pressure tube equipped with a stirrer bar under argon. The cyclopropene 2 (1 mmol, 5 eq) in 0.3 mL of CH₃CN was added in dropwise and the resulting mixture stirred at 100 °C. After completion of the reaction as indicated by TLC, removing the solvent under reduced pressure, the residual was purified by column chromatography (petroleum ether /ethyl acetate) on silica gel to give cyclopentadiene 3.

3-(5-methyl-2,5-diphenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3a

Compound 3a was obtained as a pale yellow solid in 98% (62 mg) isolated yield, $R_f = 0.34$ (petroleum ether : ethyl acetate = 5 : 1); mp = 154-157 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.48-7.46 (m, 2H),

7.40-7.36 (m, 2H), 7.32-7.26 (m, 5H), 7.24-7.20 (m, 1H), 6.67 (d, J = 5.6 Hz, 1H), 6.52 (d, J = 5.6 Hz, 1H), 4.13-4.01 (m, 2H), 3.15-3.08 (m, 1H), 2.75-2.69 (m, 1H), 1.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 146.0, 143.5, 139.0, 137.6, 134.0, 130.3, 128.64, 128.60, 127.9, 127.05, 126.98, 125.8, 62.4, 60.6, 46.0, 18.3; IR (KBr) 1755, 1492, 1407, 1215, 1115, 748, 701 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₁H₂₀NO₂, 318.1494; found 318.1488.

3-(5-methyl-5-phenyl-2-(p-tolyl)cyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3b

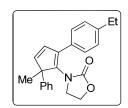


Compound 3b was obtained as a white solid in 97% (64 mg) isolated yield, $R_f = 0.33$ (petroleum ether : ethyl acetate = 5 : 1); mp = 42-45 °C; 1 H NMR (400 MHz, CDCl₃, TMS) δ 7.36 (d, J = 8.0 Hz, 2H), 7.32-7.22 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 5.6

Hz, 1H), 6.51 (d, J = 5.6 Hz, 1H), 4.15-4.02 (m, 2H), 3.17-3.10 (m, 1H), 2.73-2.67 (m,

1H), 2.35 (s, 3H), 1.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.4, 145.9, 142.9, 139.2, 137.8, 137.6, 131.1, 130.4, 129.4, 128.6, 127.0, 125.8, 62.4, 60.6, 46.0, 21.2, 18.4; IR (KBr) 1757, 1407, 1214, 1117, 1037, 823, 763, 703 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₂H₂₂NO₂, 332.1651; found 332.1644.

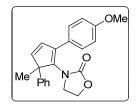
$3\hbox{-}(2\hbox{-}(4\hbox{-}ethylphenyl)\hbox{-}5\hbox{-}methyl\hbox{-}5\hbox{-}phenylcyclopenta\hbox{-}1,}3\hbox{-}dien\hbox{-}1\hbox{-}yl)oxazolidin\hbox{-}2\hbox{-}one\\ 3c$



Compound **3c** was obtained as a white solid in 99% (68.5 mg) isolated yield, $R_f = 0.39$ (petroleum ether : ethyl acetate = 5 : 1); mp = 79-80 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.39 (d, J = 8.0 Hz, 2H), 7.31-7.25 (m, 4H), 7.22 (d, J = 8.0 Hz, 3H), 6.67 (d, J = 5.6

Hz, 1H), 6.50 (d, J = 5.6 Hz, 1H), 4.15-4.01 (m, 2H), 3.17-3.11 (m, 1H), 2.73-2.62 (m, 3H), 1.75 (s, 3H), 1.24 (t, J = 7.6 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 156.4, 145.9, 144.1, 142.9, 139.2, 137.5, 131.3, 130.4, 128.6, 128.2, 127.0, 126.9, 125.8, 62.4, 60.6, 46.0, 28.5, 18.4, 15.3; IR (KBr) 2968, 1762, 1407, 1214, 1109, 1037, 838, 765, 703 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₃H₂₄NO₂, 346.1807; found 346.1801.

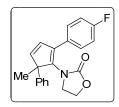
3-(2-(4-methoxyphenyl)-5-methyl-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3d



Compound **3d** was obtained as a pale yellow solid in 99% (69 mg) isolated yield, R_f = 0.19 (petroleum ether : ethyl acetate = 5 : 1); mp = 117-119 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.41 (d, J

= 8.8 Hz, 2H), 7.31-7.20 (m, 5H), 6.92 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 5.6 Hz, 1H), 6.50 (d, J = 5.6 Hz, 1H), 4.15-4.02 (m, 2H), 3.81 (s, 3H), 3.14 (dd, J = 9.2, 16.4 Hz, 1H), 2.69 (dd, J = 9.2, 15.6 Hz, 1H), 1.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 156.4, 145.9, 142.1, 139.3, 137.1, 130.3, 128.6, 128.4, 126.9, 126.4, 125.8, 114.1, 62.4, 60.5, 55.1, 45.9, 18.4; IR (KBr) 2836, 1755, 1607, 1512, 1407, 1118, 1029, 836, 765, 703 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for $C_{22}H_{22}NO_3$, 348.1600; found 348.1593.

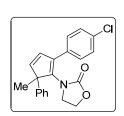
3-(2-(4-fluorophenyl)-5-methyl-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-on e 3e



Compound **3e** was obtained as a white solid in 95% (63.7 mg) isolated yield, $R_f = 0.29$ (petroleum ether : ethyl acetate = 5 : 1); mp = 141-142 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.45 (dd, J = 5.6, 8.8 Hz, 2H), 7.30-7.22 (m, 5H), 7.07 (t, J = 8.8 Hz, 2H), 6.63 (d, J =

6.0 Hz, 1H), 6.52 (d, J = 6.0 Hz, 1H), 4.16-4.05 (m, 2H), 3.14-3.08 (m, 1H), 2.80-2.74 (m, 1H), 1.75 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 162.2 (d, $J_{C-F} = 246.4$ Hz), 156.2, 146.2, 143.3, 138.9, 136.7, 130.19 (d, $J_{C-F} = 3.4$ Hz), 130.1, 128.88 (d, $J_{C-F} = 8.0$ Hz), 128.7, 127.1, 125.8, 115.7 (d, $J_{C-F} = 21.3$ Hz), 62.4, 60.5, 46.0, 18.3; 19 F NMR (376 MHz, CDCl₃) δ -113.1; IR (KBr) 1756, 1602, 1510, 1407, 1115, 841, 765, 703, 526 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₁H₁₉FNO₂, 336.1400; found 336.1393.

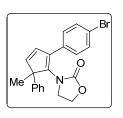
$3\hbox{-}(2\hbox{-}(4\hbox{-}chlorophenyl)\hbox{-}5\hbox{-}methyl\hbox{-}5\hbox{-}phenylcyclopenta\hbox{-}1,}3\hbox{-}dien\hbox{-}1\hbox{-}yl)oxazolidin\hbox{-}2\hbox{-}on$ e 3f



Compound **3f** was obtained as a pale yellow solid in 99% (69.6 mg) isolated yield, $R_f = 0.36$ (petroleum ether : ethyl acetate = 5 : 1); mp = 119-121°C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.40 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.29-7.22 (m, 5H), 6.62 (d, J =

5.6 Hz, 1H), 6.51 (d, J = 5.6 Hz, 1H), 4.16-4.04 (m, 2H), 3.14-3.08 (m 1H), 2.82-2.76 (m, 1H), 1.74 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 156.1, 146.3, 143.9, 138.8, 136.6, 133.7, 132.6, 129.9, 128.9, 128.7, 128.5, 127.1, 125.8, 62.4, 60.6, 46.0, 18.3; IR (KBr) 1756, 1492, 1406, 1212, 1118, 834, 764, 702 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for $C_{21}H_{19}$ ClNO₂, 352.1104; found 352.1098.

3-(2-(4-bromophenyl)-5-methyl-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-on

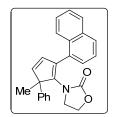


e 3g

Compound **3g** was obtained as a pale yellow solid in 93% (73.6 mg) isolated yield, $R_f = 0.35$ (petroleum ether : ethyl acetate = 5 : 1); mp = 97-99°C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.50 (d, J = 8.4 Hz,

2H), 7.33 (d, J = 8.4 Hz, 2H), 7.29-7.22 (m, 5H), 6.62 (d, J = 5.6 Hz, 1H), 6.52 (d, J = 5.6 Hz, 1H), 4.16-4.05 (m, 2H), 3.11 (dd, J = 8.8, 16.4 Hz, 1H), 2.82-2.76 (m, 1H), 1.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.1, 146.3, 143.9, 138.7, 136.5, 133.0, 131.8, 129.8, 128.7, 127.1, 125.7, 121.9, 62.4, 60.6, 46.0, 18.2; IR (KBr) 1754, 1488, 1406, 1213, 1117, 830, 761, 702 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for $C_{21}H_{19}BrNO_{2}$, 396.0599; found 396.0589.

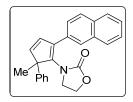
3-(5-methyl-2-(naphthalen-1-yl)-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-o ne 3h



Compound **3h** was obtained as a white solid in 93% (68 mg) isolated yield, $R_f = 0.31$ (petroleum ether : ethyl acetate = 5 : 1); mp = 69-71°C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.96 (d, J = 7.6 Hz, 1H), 7.88-7.86 (m, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.54-7.43 (m, 6H), 7.34

(t, J = 7.2 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 5.6 Hz, 1H), 6.58 (d, J = 5.6 Hz, 1H), 3.89-3.74 (m, 2H), 2.88-2.68 (m, 2H), 1.88 (s, 3H); 13 C NMR (100 MHz, CDCl₃) 8 146.4, 145.5, 139.3, 133.7, 132.2, 130.9, 128.7, 128.6, 128.4, 127.0, 126.2, 125.9, 125.6, 125.2, 62.3, 60.5, 46.5, 18.9; IR (KBr) 1756, 1412, 1215, 1106, 979, 805, 780, 703 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for $C_{25}H_{22}NO_2$, 368.1651; found 368.1644.

3-(5-methyl-2-(naphthalen-2-yl)-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-o ne 3i

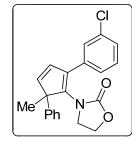


Compound **3i** was obtained as a pale yellow solid in 95% (70 mg) isolated yield, $R_f = 0.29$ (petroleum ether : ethyl acetate = 5 : 1); mp = 58-60°C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.94 (s, 1H),

7.85-7.80 (m, 3H), 7.57 (dd, J = 1.6, 8.4 Hz, 1H), 7.48-7.44 (m, 2H), 7.35-7.21 (m, 5H), 6.78 (d, J = 6.0 Hz, 1H), 6.56 (d, J = 6.0 Hz, 1H), 4.12-4.00 (m, 2H), 3.16-3.09 (m, 1H), 2.75-2.69 (m, 1H), 1.80 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 156.4, 146.1, 143.9, 139.1, 137.7, 133.3, 132.8, 131.5, 130.4, 128.7, 128.4, 128.1, 127.6, 127.0, 126.4, 126.3, 126.2, 125.9, 124.8, 62.5, 60.8, 46.1, 18.5; IR (KBr) 1757, 1596, 1407, 1214, 1109, 1037, 861, 763, 705, 477 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for

C₂₅H₂₂NO₂, 368.1651; found 368.1645.

3-(2-(3-chlorophenyl)-5-methyl-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-on e 3j



Compound **3j** was obtained as a white solid in 85% (59.7 mg) isolated yield, $R_f = 0.30$ (petroleum ether : ethyl acetate = 5 : 1); mp = 155-157°C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.44 (s, 1H), 7.36-7.22 (m, 8H), 6.62 (d, J = 5.6 Hz, 1H), 6.52 (d, J = 5.6 Hz, 1H), 4.18-4.06 (m, 2H), 3.16-3.10 (m, 1H), 2.86-2.80 (m,

1H), 1.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 146.3, 144.4, 138.6, 136.3, 136.0, 134.5, 130.0, 129.8, 128.8, 128.0, 127.2, 125.8, 125.3, 62.5, 60.6, 46.1, 18.2; IR (KBr) 1758, 1594, 1562, 1405, 1211, 1119, 1038, 761, 705 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₁H₁₉ClNO₂, 352.1104; found 352.1099.

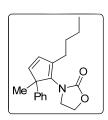
$3\hbox{-}(2\hbox{-}(2\hbox{-}chlorophenyl)\hbox{-}5\hbox{-}methyl\hbox{-}5\hbox{-}phenylcyclopenta\hbox{-}1,}3\hbox{-}dien\hbox{-}1\hbox{-}yl)oxazolidin\hbox{-}2\hbox{-}on$ e3k



Compound **3k** was obtained as a white solid in 84% (59.2 mg) isolated yield, R_f = 0.27 (petroleum ether : ethyl acetate = 5 : 1); mp = 118-119°C; 1 H NMR (400 MHz, CDCl₃, TMS) δ 7.45-7.40 (m, 2H),

7.37 (d, J = 7.2 Hz, 2H), 7.32-7.21 (m, 5H), 6.49 (d, J = 5.6 Hz, 1H), 6.43 (d, J = 5.6 Hz, 1H), 4.04-4.00 (m, 2H), 3.11-3.04 (m, 1H), 2.96-2.90 (m, 1H), 1.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.7, 145.8, 144.9, 138.6, 135.2, 133.9, 132.2, 131.1, 130.5, 129.5, 129.0, 128.7, 127.0, 126.97, 125.8, 62.4, 59.7, 45.7, 18.1; IR (KBr) 1758, 1407, 1214, 1116, 752, 703 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for $C_{21}H_{19}CINO_2$, 352.1104; found 352.1098.

3-(2-butyl-5-methyl-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3l

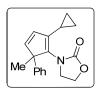


Compound **31** was obtained as a white solid in 94% (55.7 mg) isolated yield, $R_f = 0.41$ (petroleum ether : ethyl acetate = 5 : 1); mp = 43-44°C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.28-7.24 (m, 2H), 7.21-7.17 (m, 3H), 6.34-6.32 (m, 2H), 4.23-4.12 (m, 2H), 3.13-3.07

(m, 1H), 3.00-2.94 (m, 1H), 2.25 (t, J = 7.2 Hz, 2H), 1.60-1.49 (m, 5H), 1.43-1.32 (m,

2H), 0.94 (t, J=7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 145.6, 142.9, 139.3, 139.1, 130.1, 128.5, 126.7, 125.6, 62.2, 58.5, 46.4, 30.0, 26.8, 22.6, 18.0, 13.9; IR (KBr) 1760, 1640, 1408, 1301, 1217, 1113, 757, 702 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₁₉H₂₄NO₂, 298.1807; found 298.1802.

3-(2-cyclopropyl-5-methyl-5-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3m



Compound **3m** was obtained as a white solid in 70% (39 mg) isolated yield, $R_f = 0.24$ (petroleum ether : ethyl acetate = 5 : 1); mp = 87-89°C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.28-7.24 (m, 2H),

7.21-7.18 (m, 3H), 6.31 (d, J = 5.6 Hz, 1H), 6.96 (d, J = 5.6 Hz, 1H), 4.25-4.14 (m, 2H), 3.25-3.19 (m, 1H), 3.02-2.96 (m, 1H), 1.62-1.57 (m, 4H), 0.97-0.83 (m, 2H), 0.75-0.64 (m, 2H); 13 C NMR (100 MHz, CDCl₃) δ 156.3, 145.90, 142.5, 140.2, 139.4, 128.5, 126.7, 126.3, 125.7, 62.3, 58.9, 46.4, 18.1, 8.7, 6.1, 6.0; IR (KBr) 1758, 1412, 1215, 1112, 757, 703 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₁₈H₂₀NO₂, 282.1494; found 282.1487.

3-(5-methyl-5-phenyl-2-(thiophen-2-yl)cyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3n

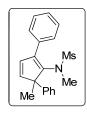


Compound **3n** was obtained as a yellow solid in 48% (26.3 mg) isolated yield, $R_f = 0.24$ (petroleum ether : ethyl acetate = 5 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.33 (d, J = 5.2 Hz, 1H), 7.28-7.21

(m, 6H), 7.07 (dd, J = 3.6, 4.8 Hz, 1H), 6.79 (d, J = 5.6 Hz, 1H), 6.53 (d, J = 5.6 Hz, 1H), 4.34 (dd, J = 8.8, 16.8 Hz, 1H), 4.24-4.18 (m, 1H), 3.35-3.29 (m, 1H), 2.80 (dd, J = 8.8, 16.8 Hz, 1H), 1.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 146.3, 141.0, 138.9, 135.3, 132.0, 128.70, 128.67, 127.12, 126.99, 126.53, 126.45, 125.9, 62.8, 60.2, 45.3, 18.2; IR (KBr) 1756, 1404, 1213, 1112, 764, 702 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₁₉H₁₈NO₂S, 324.1058; found 324.1052.

$N\text{-methyl-N-}(5\text{-methyl-2,}5\text{-diphenylcyclopenta-1,}3\text{-dien-1-yl}) methan esulfon a mide \\ 3o$

Compound **30** was obtained as a oil in 56% (38 mg) isolated yield, $R_f = 0.42$ (petroleum ether : ethyl acetate = 5 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.49 (d, J



= 7.2 Hz, 2H, 7.41 (t, J = 7.2 Hz, 2H), 7.31-7.23 (m, 6H), 6.57 (d, J = 7.2 Hz, 2Hz)5.6 Hz, 1H), 6.47 (d, J = 5.6 Hz, 1H), 2.61 (s, 3H), 2.25 (s, 3H), 1.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.6, 146.8, 140.3, 138.8, 135.0, 130.6, 128.59, 128.56, 128.1, 127.9, 127.0, 126.3, 59.9, 39.4, 37.6, 18.3;

IR (KBr) 1599, 1493, 1445, 1336, 1139, 1026, 963, 894, 854, 697, 572, 517 cm⁻¹; HRMS-(DART) (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}NO_2S$, 340.1371; found 340.1365.

(4R)-3-(5-methyl-2,5-diphenylcyclopenta-1,3-dien-1-yl)-4-phenyloxazolidin-2-one **3p**



Compound 3p was obtained as a pale yellow oil in 85% (100.5 mg) isolated yield, $R_f = 0.34$ (petroleum ether : ethyl acetate = 5 : 1); ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3, \text{TMS}) \delta 7.41-7.40 \text{ (m, 4H)}, 7.16-7.11 \text{ (m, 7H)}, 6.96 \text{ (d, } J = 8.0 \text{ Hz},$ 2H), 6.54 (d, J = 7.2 Hz, 2H), 6.42 (d, J = 5.6 Hz, 1H), 6.32 (d, J = 5.6 Hz, 1H), 4.81 (t, J = 8.0 Hz, 1H), 4.37 (t, J = 8.0 Hz, 1H), 3.95 (dd, $J_1 = 8.4 \text{ Hz}$, $J_2 = 8.0 \text{ Hz}$, 1H), 1.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.4, 146.3, 142.4, 138.5, 138.3, 136.8, 135.0, 130.0, 128.5, 128.42, 128.40, 128.1, 127.9, 127.8, 126.9, 126.7, 126.4, 70.2, 61.1, 61.0, 21.0; IR (KBr) 2961, 1741, 1394, 1251, 1037, 745, 700 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for C₂₇H₂₃NNaO₂, 416.1626; found 416.1620.

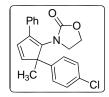
3-(5-methyl-2-phenyl-5-(p-tolyl)cyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3q



Compound **3q** was obtained as a pale yellow solid in 71% (47.2 mg) isolated yield, $R_f = 0.34$ (petroleum ether : ethyl acetate = 5 : 1); mp = 82-83 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.47-7.45 (m, 2H),

7.39-7.35 (m, 2H), 7.30-7.26 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 5.6 Hz, 1H), 6.48 (d, J = 5.6 Hz, 1H), 4.13-4.02 (m, 2H), 3.15-3.09 (m, 1H), 2.81-2.75 (m, 1H), 2.30 (s, 3H), 1.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 146.1, 143.4, 137.4, 136.5, 135.8, 134.0, 130.0, 129.3, 128.6, 127.8, 127.0, 125.6, 62.4, 60.2, 46.0, 20.9, 18.3; IR (KBr) 1758, 1511, 1407, 1212, 818, 746, 698, 522 cm⁻¹; HRMS-(DART) (m/z): $[M+H]^+$ calcd for $C_{22}H_{22}NO_2$, 332.1651; found 332.1645.

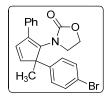
3-(5-(4-chlorophenyl)-5-methyl-2-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-on e 3r



Compound **3r** was obtained as a pale yellow solid in 99% (71 mg) isolated yield, $R_f = 0.32$ (petroleum ether : ethyl acetate = 5 : 1); mp = 145-146 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.46 (d, J = 7.2 Hz,

2H), 7.40 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.27-7.22 (m, 4H), 6.68 (d, J = 5.6 Hz, 1H), 6.48 (d, J = 5.6 Hz, 1H), 4.18-4.07 (m, 2H), 3.20-3.14 (m, 1H), 2.84-2.78 (m, 1H), 1.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 145.7, 143.2, 137.9, 137.7, 133.8, 132.7, 130.6, 128.7, 128.1, 127.4, 127.1, 62.4, 60.1, 46.1, 18.4; IR (KBr) 1753, 1490, 1406, 1211, 1012, 827, 750, 697 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₁H₁₉ClNO₂, 352.1104; found 352.1099.

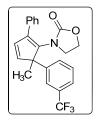
3-(5-(4-bromophenyl)-5-methyl-2-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-on e 3s



Compound **3s** was obtained as a pale yellow solid in 98% (77.8 mg) isolated yield, $R_f = 0.30$ (petroleum ether : ethyl acetate = 5 : 1); mp = 149-150 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.47-7.45 (m, 2H),

7.41-7.37 (m, 4H), 7.33-7.29 (m, 1H), 7.18 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 5.6 Hz, 1H), 6.48 (d, J = 5.6 Hz, 1H), 4.18-4.07 (m, 2H), 3.21-3.14 (m, 1H), 2.85-2.79 (m, 1H), 1.74 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 156.3, 145.6, 143.2, 138.3, 138.0, 133.8, 131.7, 130.7, 128.7, 128.1, 127.8, 127.1, 120.8, 62.4, 60.2, 46.1, 18.4; IR (KBr) 1763, 1487, 1407, 1117, 1009, 825, 749, 522 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for $C_{21}H_{19}BrNO_2$, 396.0599; found 396.0594.

$3\hbox{-}(5\hbox{-}methyl\hbox{-}2\hbox{-}phenyl\hbox{-}5\hbox{-}(3\hbox{-}(trifluoromethyl)phenyl)cyclopenta\hbox{-}1,}3\hbox{-}dien\hbox{-}1\hbox{-}yl)oxaz$ olidin-2-one 3t

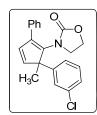


Compound **3t** was obtained as a white solid in 88% (68.1 mg) isolated yield, $R_f = 0.33$ (petroleum ether : ethyl acetate = 5 : 1); mp = 112-114 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.55 (s, 1H), 7.52-7.45 (m, 4H), 7.43-7.38 (m, 3H), 7.34-7.30 (m, 1H), 6.71 (d, J = 5.6 Hz, 1H),

6.52 (d, J = 5.6 Hz, 1H), 4.17-4.04 (m, 2H), 3.20-3.14 (m, 1H), 2.75-2.69 (m, 1H),

1.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 145.4, 143.1, 140.5, 138.4, 133.7, 131.0, 130.9 (q, $J_{C-F} = 31.8 \text{ Hz}$), 129.48 (d, $J_{C-F} = 1.0 \text{ Hz}$), 129.1, 128.8, 128.2, 127.1, 124.0 (q, J_{C-F} = 270.9 Hz), 123.9 (q, J_{C-F} = 3.8 Hz), 122.6 (q, J_{C-F} = 3.8 Hz), 62.4, 60.4, 46.1, 18.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.5; IR (KBr) 1758, 1493, 1404, 1331, 1036, 979, 807, 747, 700 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₂H₁₉F₃NO₂, 386.1368; found 386.1362.

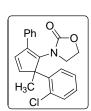
3-(5-(3-chlorophenyl)-5-methyl-2-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-on e 3u



Compound 3u was obtained as a yellow solid in 96% (67.8 mg) isolated yield, $R_f = 0.29$ (petroleum ether : ethyl acetate = 5 : 1); mp = 132-134 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.48-7.45 (m, 2H), 7.41-7.38 (m, 2H), 7.34-7.28 (m, 2H), 7.25-7.18 (m, 3H), 6.68 (d, J =

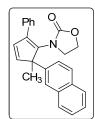
6.0 Hz, 1H), 6.48 (d, J = 6.0 Hz, 1H), 4.18 - 4.07 (m, 2H), 3.22 - 3.15 (m, 1H), 2.83 - 2.77 (m, 2H)(m, 1H), 1.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 145.4, 143.0, 141.4, 138.1, 134.4, 133.7, 130.8, 129.9, 128.7, 128.2, 127.2, 127.1, 126.1, 124.1, 62.4, 60.3, 46.1, 18.3; IR (KBr) 1756, 1593, 1479, 1408, 1213, 1116, 1038, 754, 699 cm⁻¹; HRMS-(DART) (m/z): $[M+H]^+$ calcd for $C_{21}H_{19}CINO_2$, 352.1104; found 352.1099.

3-(5-(2-chlorophenyl)-5-methyl-2-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-on e 3v



Compound 3v was obtained as a white solid in 90% (63.1 mg) isolated yield, $R_f = 0.22$ (petroleum ether : ethyl acetate = 5 : 1); mp = 161-162 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.62 (dd, J = 1.2, 7.6 Hz, 1H), 7.47-7.45 (m, 2H), 7.41-7.37 (m, 1H), 7.33-7.19 (m, 4H), 6.69 (d, J =5.6 Hz, 1H), 6.34 (d, J = 5.6 Hz, 1H), 4.20-4.13 (m, 1H), 4.09-4.03 (m, 1H), 3.45-3.39 (m, 1H), 3.08-3.01 (m, 1H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.8, 142.5, 140.0, 138.5, 137.3, 134.7, 134.1, 131.5, 131.0, 129.2, 128.6, 128.5, 127.7, 127.3, 127.0, 62.4, 60.1, 44.9, 22.7; IR (KBr) 1755, 1405, 1211, 1115, 1041, 748, 699 cm⁻¹; HRMS-(DART) (m/z): $[M+H]^+$ calcd for $C_{21}H_{19}CINO_2$, 352.1104; found 352.1099.

3-(5-methyl-5-(naphthalen-2-yl)-2-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-o ne 3w



Compound **3w** was obtained as a pale yellow solid in 80% (59 mg) isolated yield, $R_f = 0.29$ (petroleum ether : ethyl acetate = 5 : 1); mp = 64-67 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.87 (s, 1H), 7.83 (d, J = 7.2 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H),

7.52-7.45 (m, 4H), 7.43-7.39 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.21 (dd, J = 1.6, 8.4 Hz, 1H), 6.74 (d, J = 5.6 Hz, 1H), 6.55 (d, J = 5.6 Hz, 1H), 4.09-3.94 (m, 2H), 3.13-3.07 (m, 1H), 2.79-2.73 (m, 1H), 1.88 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 156.3, 146.1, 143.6, 138.3, 136.8, 134.1, 133.8, 132.5, 130.7, 128.8, 128.1, 128.0, 127.8, 127.4, 127.2, 126.2, 125.9, 124.6, 124.3, 62.4, 60.7, 46.0, 18.2; IR (KBr) 1759, 1407, 1210, 1113, 1038, 745, 698, 478 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₅H₂₂NO₂, 368.1652; found 368.1645.

3-(5-methyl-5-phenethyl-2-phenylcyclopenta-1,3-dien-1-yl)oxazolidin-2-one 3x



Compound 3x was obtained as a colourless oil in 81% (55.7 mg) isolated yield, $R_f = 0.38$ (petroleum ether : ethyl acetate = 5 : 1); 1 H NMR (400 MHz, CDCl₃, TMS) δ 7.45-7.43 (m, 2H), 7.41-7.37 (m, 2H), 7.32-7.28 (m,

1H), 7.23 (d, J = 7.2 Hz, 2H), 7.19-7.12 (m, 3H), 6.56 (d, J = 5.6 Hz, 1H), 6.34 (d, J = 5.6 Hz, 1H), 4.31-4.27 (m, 2H), 3.53 (t, J = 8.0 Hz, 2H), 2.72-2.64 (m, 1H), 2.56-2.48 (m, 1H), 2.08-1.94 (m, 2H), 1.34 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 156.9, 143.8, 142.7, 141.3, 138.7, 134.3, 130.0, 128.7, 128.4, 128.2, 127.9, 127.2, 125.6, 62.5, 58.3, 46.3, 38.4, 31.2, 21.1; IR (KBr) 1755, 1409, 1212, 1115, 1039, 753, 700 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₃H₂₄NO₂, 346.1807; found 346.1802.

3-(4-(1-phenylvinyl)-3,4-dihydronaphthalen-2-yl)oxazolidin-2-one 4a



Compound **4a** was obtained as a colourless oil in 35% (22 mg) isolated yield, $R_f = 0.48$ (petroleum ether : ethyl acetate = 3 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.52-7.50 (m, 1H), 7.40-7.32 (m, 4H), 7.28-7.23

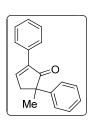
(m, 4H), 6.98 (s, 1H), 5.62 (d, J = 3.2 Hz, 1H), 5.16 (d, J = 2.4 Hz, 1H), 4.51 (dd, J = 6.0, 8.8 Hz, 1H), 4.25-4.13 (m, 2H), 3.65-3.52 (m, 2H), 3.23-3.08 (m, 2H); ¹³C NMR

(100 MHz, CDCl₃) δ 157.1, 151.3, 144.3, 139.5, 136.2, 135.4, 129.1, 128.8, 128.44, 128.38, 127.4, 126.9, 125.5, 121.0, 104.0, 61.6, 47.5, 43.7, 35.0; IR (KBr) 2922, 1749, 1557, 1398, 1243, 1039, 753, 698 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for $C_{21}H_{19}NNaO_2$, 340.1313; found 340.1309.

5. Representative synthetic application

Ynamide 1 (0.50 mmol, 1.0 eq), IPrAuNCPhSbF6 (5 mol%) and CH₃CN (1 mL) were added to an oven-dried 10 mL pressure tube equipped with a stirrer bar under argon, the cyclopropene 2 (1.5 mmol, 3 eq) was added in dropwise and the resulting mixture stirred at 100 °C. After completion of the reaction as indicated by TLC, 12 M HCl (340 μl, 8 equiv) was added, the reaction mixture was stirred at 100 °C for 3 h. Removing the solvent under reduced pressure, the residual was purified by column chromatography (petroleum ether/ethyl acetate 40:1) on silica gel to give cyclopent-2-enone 6.

5-methyl-2,5-diphenylcyclopent-2-enone 6a⁶



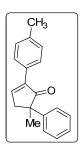
Compound **6a** was obtained as a yellow solid in 80% (99.6 mg) isolated yield, $R_f = 0.55$ (petroleum ether : ethyl acetate =15 : 1); mp = 79-80 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.89 (t, J = 2.8 Hz, 1H), 7.77-7.75 (m, 2H), 7.41-7.28 (m, 7H), 7.23-7.19 (m, 1H), 3.14 (dd, J = 2.8, 19.6

Hz, 1H), 2.88 (dd, J = 2.8, 19.6 Hz, 1H), 1.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.2, 156.4, 143.7, 141.3, 131.7, 128.55, 128.47, 128.4, 127.1, 126.6, 125.9, 51.9, 45.2, 24.4.

⁶ P. Prempree, T. Siwapinyoyos, C. Thebtaranonth, Y. Thebtaranonth, *Tetrehedron Lett.* **1980**, *21*, 1169.

5-methyl-5-phenyl-2-(p-tolyl)cyclopent-2-enone 6b

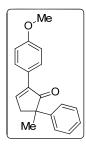
Compound 6b was obtained as a pale yellow solid in 73% (95.4 mg) isolated yield, R_f



= 0.58 (petroleum ether : ethyl acetate =15 : 1); mp = 104-105 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.85 (t, J = 2.8 Hz, 1H), 7.67(d, J = 8.4 Hz, 2H), 7.32-7.28 (m, 4H), 7.25-7.19 (m, 3H), 3.13 (dd, J = 2.8, 19.6 Hz, 1H), 2.87 (dd, J = 2.8, 19.6 Hz, 1H), 2.36 (s, 3H), 1.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.3, 155.5, 143.8, 141.2, 138.4, 129.1, 128.8,

128.5, 127.0, 126.5, 125.9, 51.9, 45.2, 24.4, 21.3; IR (KBr) 1698, 1303, 824, 748, 700 cm⁻¹; HRMS-(DART) (m/z): $[M+Na]^+$ calcd for $C_{19}H_{18}NaO$, 285.1255; found 285.1250.

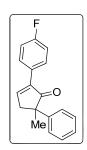
2-(4-methoxyphenyl)-5-methyl-5-phenylcyclopent-2-enone 6c



Compound **6c** was obtained as a white solid in 78% (108.4 mg) isolated yield, $R_f = 0.32$ (petroleum ether : ethyl acetate =15 : 1); mp = 98-99 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.78 (t, J = 2.8 Hz, 1H), 7.75-7.73 (m, 2H), 7.30-7.29 (m, 4H), 7.22-7.18 (m, 1H), 6.93-6.89 (m, 2H), 3.79 (s, 3H), 3.09 (dd, J = 2.8, 19.6 Hz, 1H), 2.83 (dd, J = 2.8, 19.6 Hz, 1H),

1.59 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 209.4, 159.8, 154.5, 143.8, 140.5, 128.5, 128.3, 126.5, 125.8, 124.3, 113.8, 55.2, 51.8, 45.1, 24.3; IR (KBr) 1699, 1510, 1260, 749, 698 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for $C_{19}H_{19}O_2$, 279.1385; found 279.1380.

2-(4-fluorophenyl)-5-methyl-5-phenylcyclopent-2-enone 6d

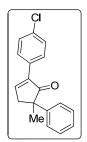


Compound **6d** was obtained as a yellow solid in 74% (94.5 mg) isolated yield, $R_f = 0.51$ (petroleum ether : ethyl acetate = 15 : 1); mp = 50-51 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.86 (t, J = 3.2 Hz, 1H), 7.79-7.75 (m, 2H), 7.34-7.30 (m, 4H), 7.25-7.20 (m, 1H), 7.11-7.06 (m, 2H), 3.15 (dd, J = 3.2, 20.0 Hz, 1H), 2.89 (dd, J = 3.2, 20.0 Hz, 1H), 1.62 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 209.2, 162.9 (d, J_{C-F} = 246.6 Hz), 156.0, 143.6, 140.3, 128.9 (d, J = 8.0 Hz), 128.6, 127.8 (d, J = 3.2 Hz), 126.7, 125.9, 115.4 (d, J_{C-F} = 21.3 Hz), 51.9, 45.2, 24.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -112.8; IR (KBr) 1704, 1508, 833,

699, 572 cm⁻¹; HRMS-(DART) (m/z): $[M+Na]^+$ calcd for $C_{18}H_{15}FNaO$, 289.1005; found 289.0999.

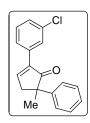
2-(4-chlorophenyl)-5-methyl-5-phenylcyclopent-2-enone 6e



Compound **6e** was obtained as a yellow solid in 76% (106.3 mg) isolated yield, $R_f = 0.51$ (petroleum ether : ethyl acetate =15 : 1); mp = 78-79 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.90 (t, J = 3.2 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.37-7.31 (m, 6H), 7.25-7.20 (m, 1H), 3.15 (dd, J = 3.2, 20.0 Hz, 1H), 2.89 (dd, J = 3.2, 20.0 Hz, 1H), 1.61 (s, 3H); ¹³C NMR

 $(100 \text{ MHz}, \text{CDCl}_3) \ \delta \ 209.0, \ 156.6, \ 143.5, \ 140.1, \ 134.4, \ 130.1, \ 128.65, \ 128.61, \ 128.4, \\ 126.7, \ 125.9, \ 51.9, \ 45.2, \ 24.5; \ \text{IR} \ (\text{KBr}) \ 1703, \ 1492, \ 1092, \ 829, \ 699 \ \text{cm}^{-1}; \\ \text{HRMS-(DART) (m/z): [M+Na]}^+ \ \text{calcd for C}_{18}\text{H}_{15}\text{ClNaO}, \ 305.0709; \ \text{found } 305.0704.$

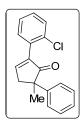
2-(3-chlorophenyl)-5-methyl-5-phenylcyclopent-2-enone 6f



Compound **6f** was obtained as a yellow solid in 74% (104 mg) isolated yield, $R_f = 0.45$ (petroleum ether : ethyl acetate =15 : 1); mp = 71-72 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.86 (t, J = 2.8 Hz, 1H), 7.78 (s, 1H), 7.65-7.62 (m, 1H), 7.29-7.27 (m, 6H), 7.22-7.17 (m, 1H), 3.10 (dd,

 $J = 2.8, 20.0 \text{ Hz}, 1\text{H}), 2.84 \text{ (dd, } J = 2.8, 20.0 \text{ Hz}, 1\text{H}), 1.58 \text{ (s, 3H);} ^{13}\text{C NMR (100 MHz, CDCl₃)} & 208.7, 157.5, 143.4, 139.8, 134.2, 133.3, 129.6, 128.5, 128.4, 127.0, 126.6, 125.8, 125.1, 51.8, 45.1, 24.3; IR (KBr) 1702, 1561, 734, 698 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for <math>C_{18}H_{15}CINaO$, 305.0709; found 305.0704.

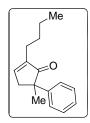
2-(2-chlorophenyl)-5-methyl-5-phenylcyclopent-2-enone 6g



Compound **6g** was obtained as a yellow oil in 64% (90.2 mg) isolated yield, $R_f = 0.43$ (petroleum ether : ethyl acetate =15 : 1); 1H NMR (400 MHz, CDCl₃, TMS) δ 7.87 (t, J = 2.8 Hz, 1H), 7.42-7.40 (m, 1H), 7.36-7.29 (m, 5H), 7.26-7.19 (m, 3H), 3.17 (dd, J = 2.8, 19.6 Hz, 1H),

2.93 (dd, J = 2.8, 19.6 Hz, 1H), 1.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.2, 160.4, 143.5, 140.9, 133.1, 131.0, 130.8, 129.7, 129.3, 128.5, 126.55, 126.48, 125.9, 50.9, 45.8, 24.4; IR (KBr) 1702, 1044, 752, 698 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for C₁₈H₁₅ClNaO, 305.0709; found 305.0704.

2-butyl-5-methyl-5-phenylcyclopent-2-enone 6h



Compound 6h was obtained as a yellow oil in 84% (95.5 mg) isolated yield, $R_f = 0.66$ (petroleum ether : ethyl acetate = 15 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.34-7.32 (m, 1H), 7.31-7.24 (m, 4H), 7.21-7.17 (m, 1H), 3.01-2.94 (m, 1H), 2.76-2.69 (m, 1H), 2.26-2.22 (m, 2H),

1.55-1.47 (m, 5H), 1.40-1.31 (m, 2H), 0.92 (t, J = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 211.4, 154.9, 144.5, 144.0, 128.4, 126.4, 125.8, 50.7, 45.7, 29.8, 24.8, 24.4, 22.4, 13.8; IR (KBr) 1705, 1496, 1445, 762, 699 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for C₁₆H₂₀NaO, 251.1412; found 251.1406.

5-(4-chlorophenyl)-5-methyl-2-phenylcyclopent-2-enone 6i



Compound 6i was obtained as a pale yellow solid in 78% (110 mg) isolated yield, $R_f = 0.43$ (petroleum ether : ethyl acetate =15 : 1); mp = 83.5-84.5 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.85 (t, J = 2.8 Hz,

1H), 7.75-7.73 (m, 2H), 7.39-7.30 (m, 3H), 7.26-7.20 (m, 4H), 3.04 (dd, J = 2.8, 19.6Hz, 1H), 2.83 (dd, J = 2.8, 19.6 Hz, 1H), 1.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.6, 156.3, 142.2, 141.0, 132.3, 131.4, 128.53, 128.51, 128.4, 127.4, 127.0, 51.4, 44.9, 24.5; IR (KBr) 1702, 1493, 1095, 823, 695 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for C₁₈H₁₅ClNaO, 305.0709; found 305.0704.

5-(4-bromophenyl)-5-methyl-2-phenylcyclopent-2-enone 6j



Compound 6j was obtained as a yellow oil in 83% (135.1 mg) isolated yield, $R_f = 0.38$ (petroleum ether : ethyl acetate =15 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.83 (t, J = 2.8 Hz, 1H), 7.75-7.73 (m, 2H), 7.41-7.29 (m, 5H), 7.18-7.15 (m, 2H), 3.02 (dd, J=2.8, 20.0 Hz, 1H), 2.81 (dd, J=2.8, 20.0 Hz, 1H), 1.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.5, 156.4, 142.7, 140.9, 131.44, 131.36, 128.5, 128.3, 127.7, 127.0, 120.4, 51.4, 44.8, 24.4; IR (KBr) 1700, 1490, 1008, 745, 694 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for C₁₈H₁₅BrNaO, 349.0204; found 349.0198.

5-(3-chlorophenyl)-5-methyl-2-phenylcyclopent-2-enone 6k

Compound **6k** was obtained as a yellow oil in 80% (112.8 mg) isolated yield, $R_f = 0.45$ (petroleum ether : ethyl acetate =15 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.85 (t, J = 2.8 Hz, 1H), 7.76-7.74 (m, 2H), 7.39-7.31 (m, 4H), 7.23-7.15 (m, 3H), 3.05 (dd, J = 2.8, 19.6 Hz, 1H), 2.83 (dd, J = 2.8, 19.6 Hz, 1H), 1.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.4, 156.4, 145.7, 141.1, 134.3, 131.4, 129.7, 128.5, 128.4, 127.0, 126.7, 126.3, 124.2, 51.6, 44.9, 24.4; IR (KBr) 1704, 1595, 750, 695 cm⁻¹; HRMS-(DART) (m/z): [M+Na]⁺ calcd for $C_{18}H_{15}CINaO$, 305.0709; found 305.0704.

Ynamide **1a** (0.30 mmol, 1.0 eq), IPrAuNCPhSbF6 (5 mol%) and CH₃CN (1.0 mL) were added to an oven-dried 10 mL pressure tube equipped with a stirrer bar under argon, the cyclopropene **2a** (0.9 mmol, 3.0 eq) and styrene (0.9 mmol, 3.0 equiv) was added dropwise and the resulting mixture stirred at 100 °C. After completion of the reaction as indicated by TLC, removing the solvent under reduced pressure, the residual was purified by column chromatography on silica gel.

((E)-1-((1S, 2S)-2-Phenylcyclopropyl)prop-1-en-2-yl)benzene 5⁷

Compound **5** was obtained as a colourless oil in 35% (79 mg) isolated yield, $R_f = 0.5$ (petroleum ether); 1H NMR (400 MHz, CDCl₃, cis isomer): 7.28-7.10 (m, 10H), 5.10 (d, J = 9.2 Hz, 1H), 2.43 (dd, J = 8.4, 15.2 Hz, 1H), 2.13 (s, 3H), 2.10-2.02 (m, 1H), 1.41-1.35 (m, 1H), 1.06-1.02 (m, 1H); (trans isomer, only clearly assignable signals are listed): 5.32 (d, J = 9.2 Hz, 1H), 2.01-1.97 (m, 1H), 1.97-1.87 (m, 1H), 1.34-1.29 (m, 1H), 1.15-1.11 (m, 1H). 13 C NMR (100 MHz, CDCl₃, cis isomer): 143.6, 138.9, 135.2, 129.0, 128.01, 127.96, 127.6, 126.3, 125.9, 125.3, 23.6, 18.9, 16.2, 13.0; (trans isomer, only clearly assignable signals are listed): 130.9,

⁷ González, M. J.; González, J.; López, L. A.; Vicente, R. *Angew. Chem. Int. Ed.* **2015**, *54*, 12139.

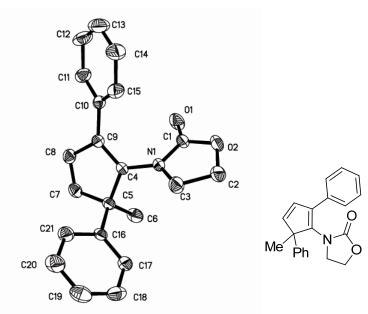
 $128.3,\,128.2,\,126.5,\,125.7,\,125.6,\,25.6,\,24.4,\,17.6,\,16.24.$

6. X-ray crystal structures

General procedure for preparation of the crystal: The product (40 mg) was dissolved in ethyl acetate. The filtered through a pad of filter paper. The filtrate was then transferred into several test-tubes by different volumes. To these solution were added petroleum ether in dropwise. The samples prepared in this way were allowed to evaporate slowly at room temperature, which would eventually give colorless crystals on the surface of the tubes.

Colorless granular-shaped crystals 3a was obtained from mixed solution (PE: EA





X-ray structure of **3a**. Hydrogen atoms have been omitted for clarity. CCDC 1478721.

Bond precision: C-C = 0.0026 A Wavelength=0.71073 Cell: a=8.0521(16) b=10.418(2) c=10.027(2)

alpha=90 beta=96.73(3) gamma=90

Temperature: 293 K

Calculated Reported

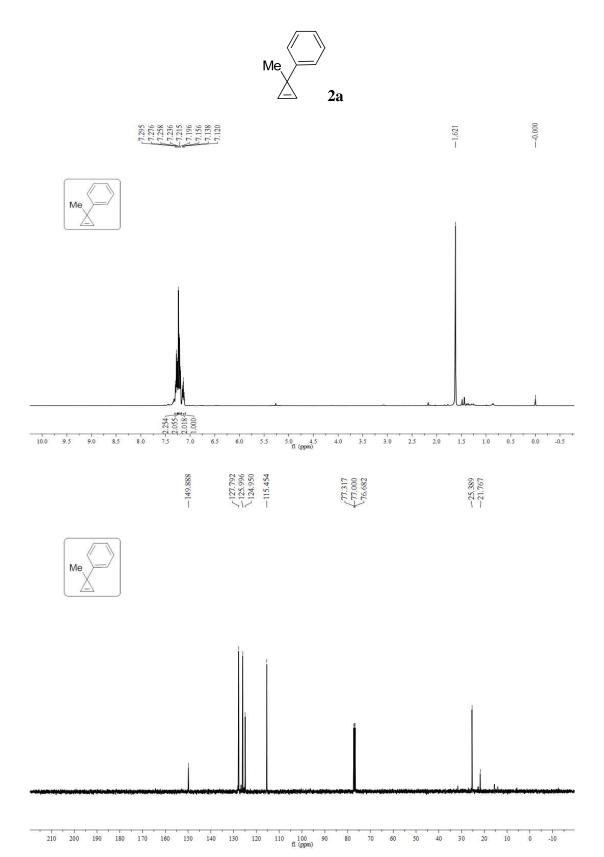
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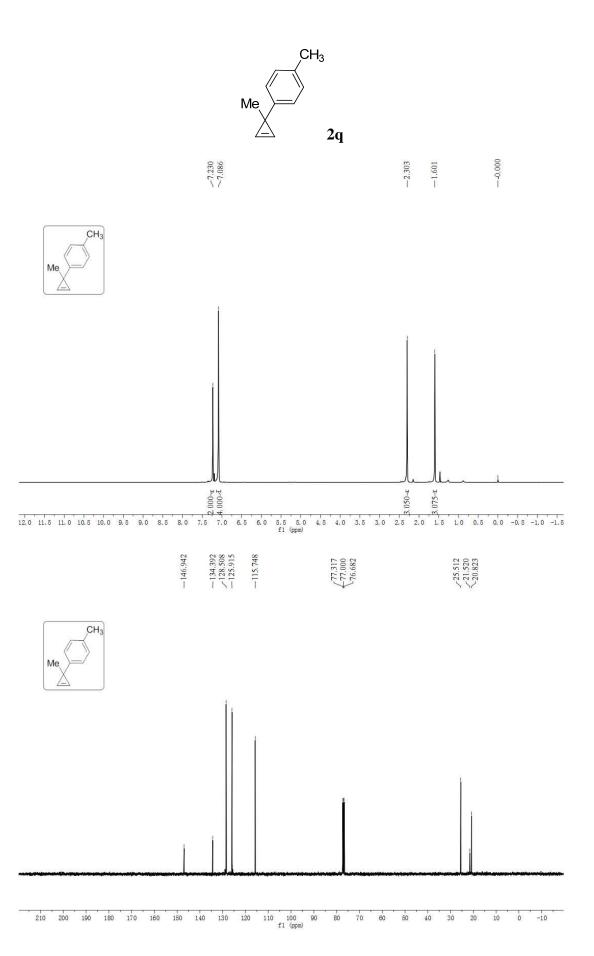
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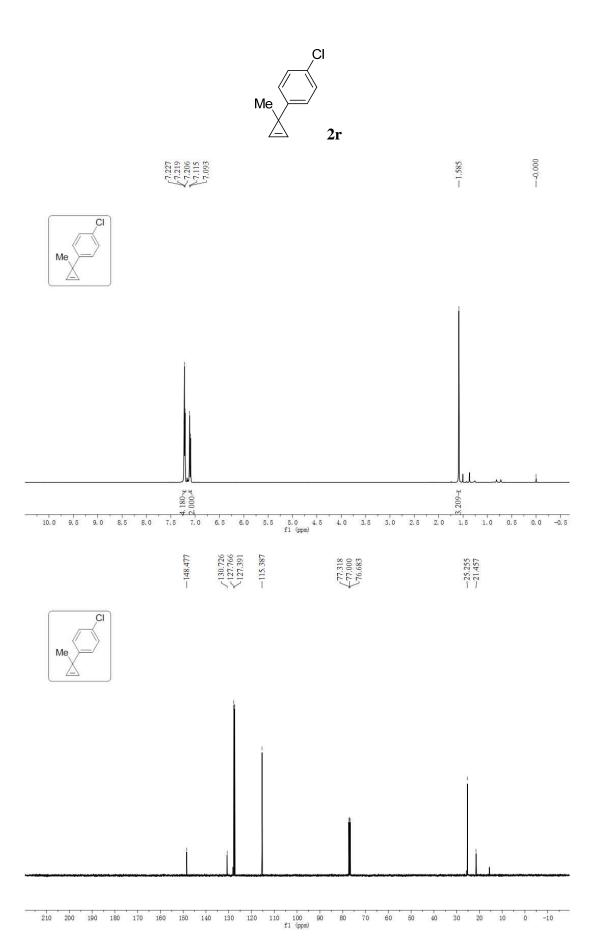
Hall group P 2yb

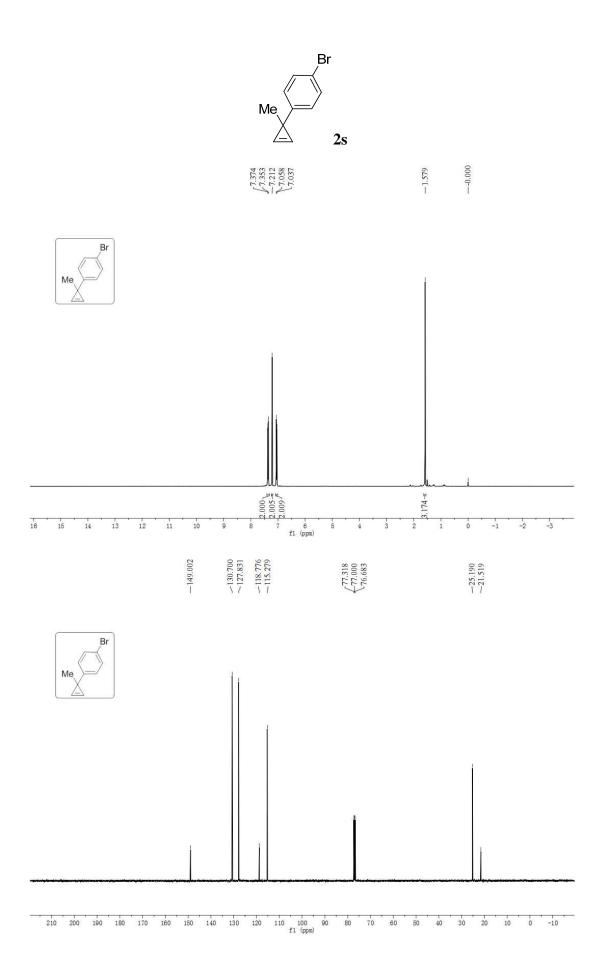
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Sum formula	C21 H19 N O2	C21 H19 N O2
Mr	317.37	317.37
Dx,g cm-3	1.262	1.262
Z	2	2
Mu (mm-1)	0.081	0.081
F000	336.0	336.0
F000'	336.14	
h,k,lmax	10,13,13	10,13,13
Nref	3822[2017]	3594
Tmin,Tmax	0.990,0.992	
Tmin'	0.922	
Correction method=	Not given	
Data completeness= 1.78	3/0.94	Theta(max)= 27.480
R(reflections)= 0.0396(2	2677)	wR2(reflections)= 0.0844(3594)
S = 0.992	Npar= 218	

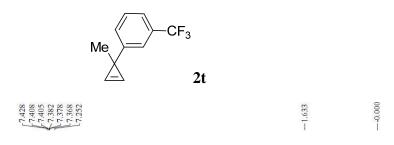
7. 1 H and 13 C NMR spectra of the substrates

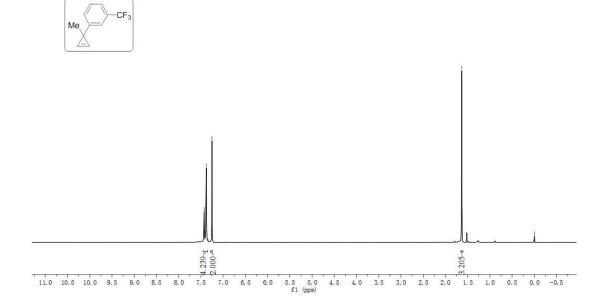


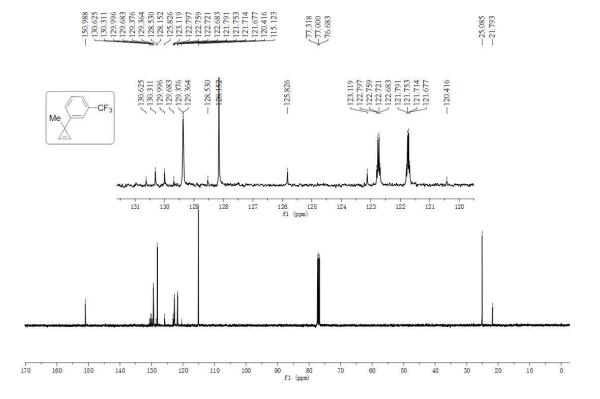


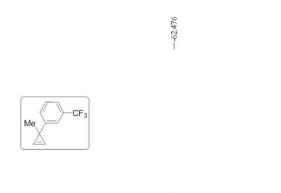


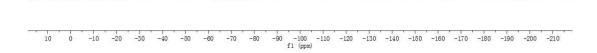


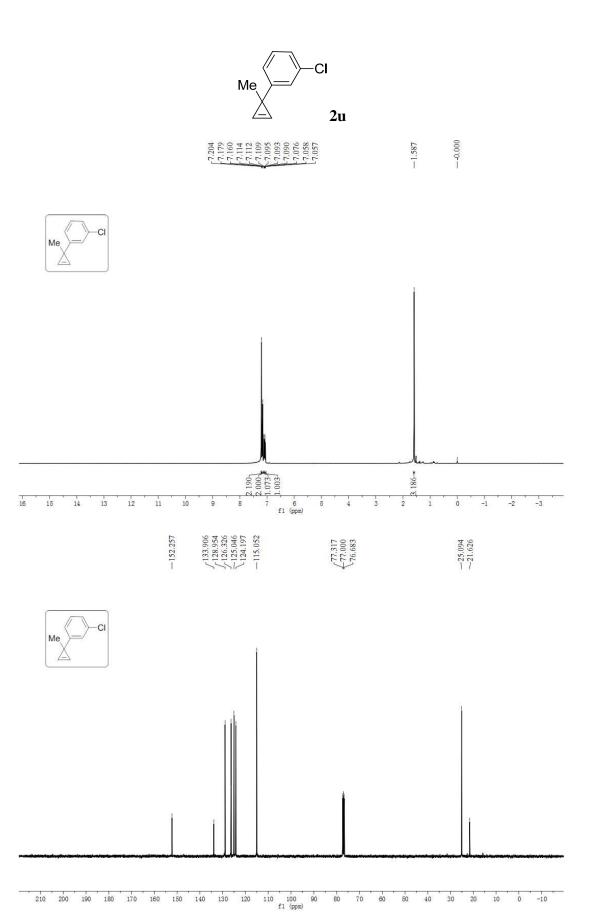


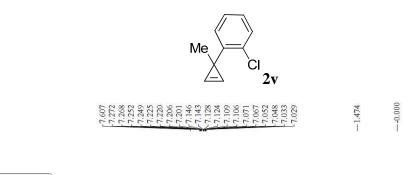


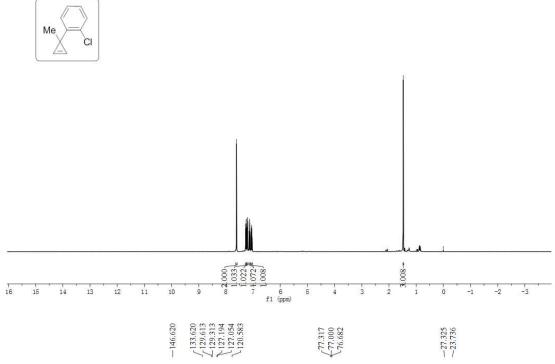


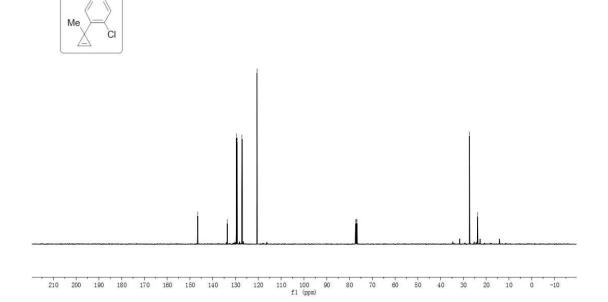


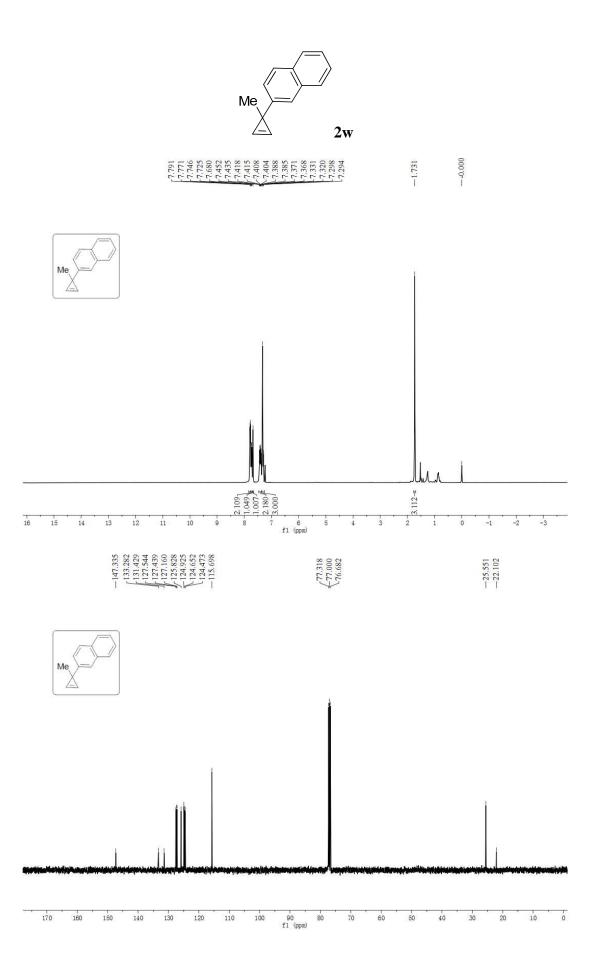


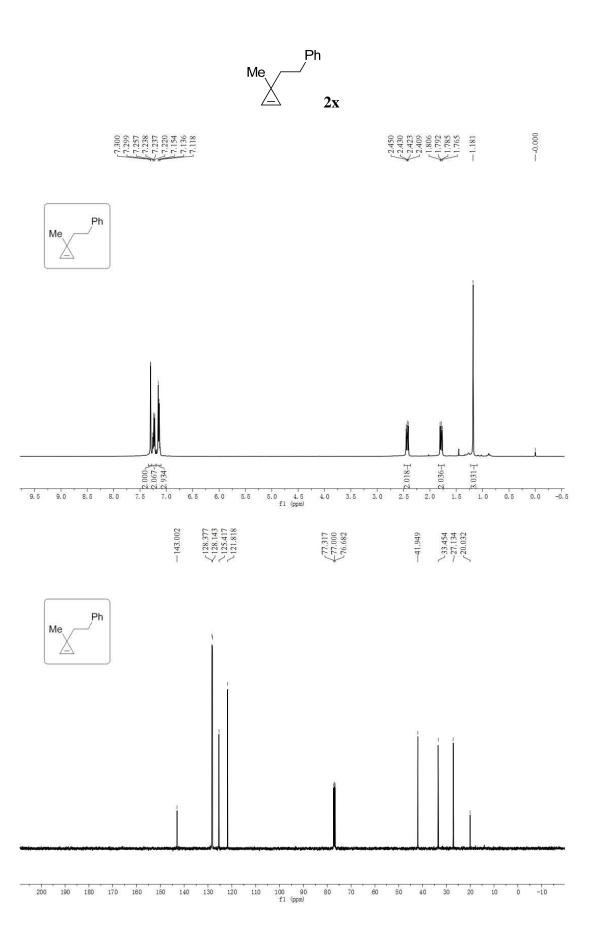




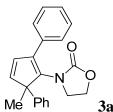


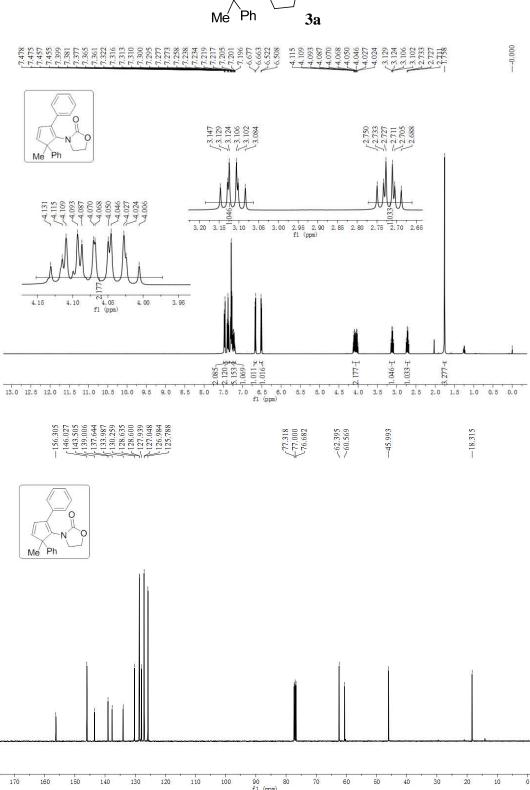


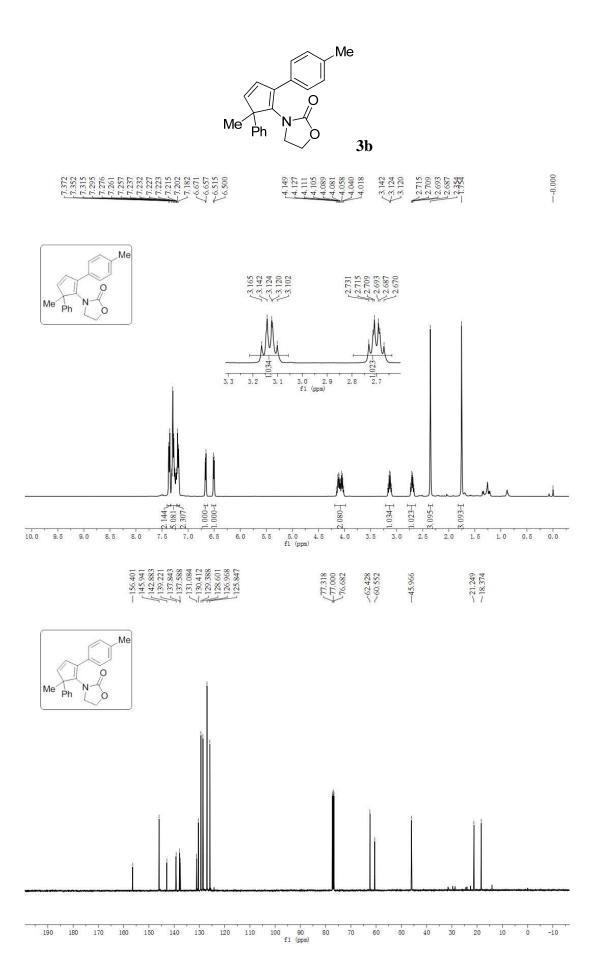


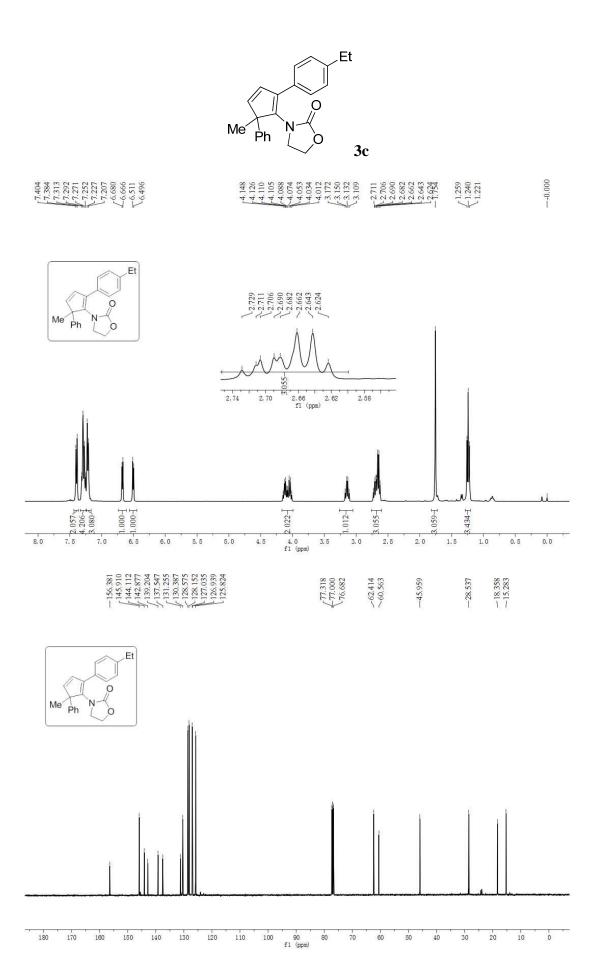


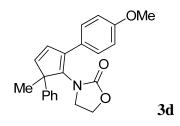
8. ¹H and ¹³C NMR spectra for the products

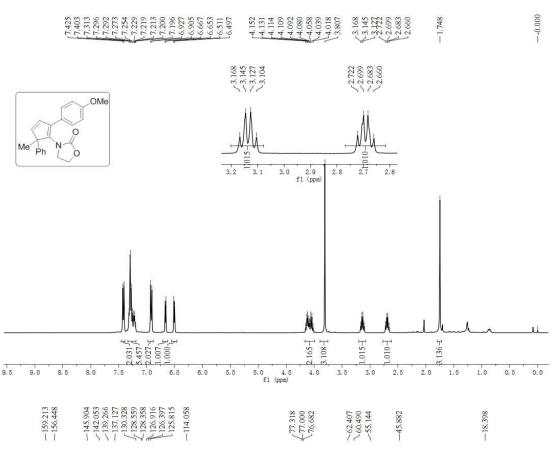


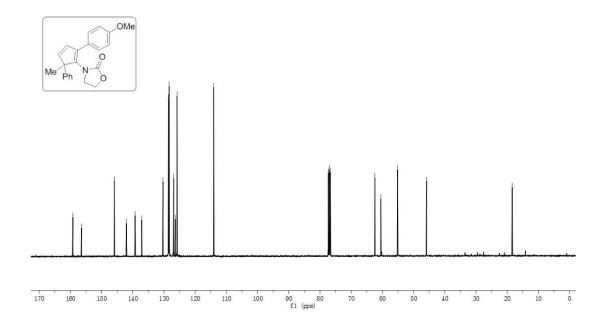


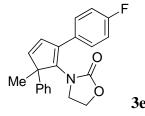


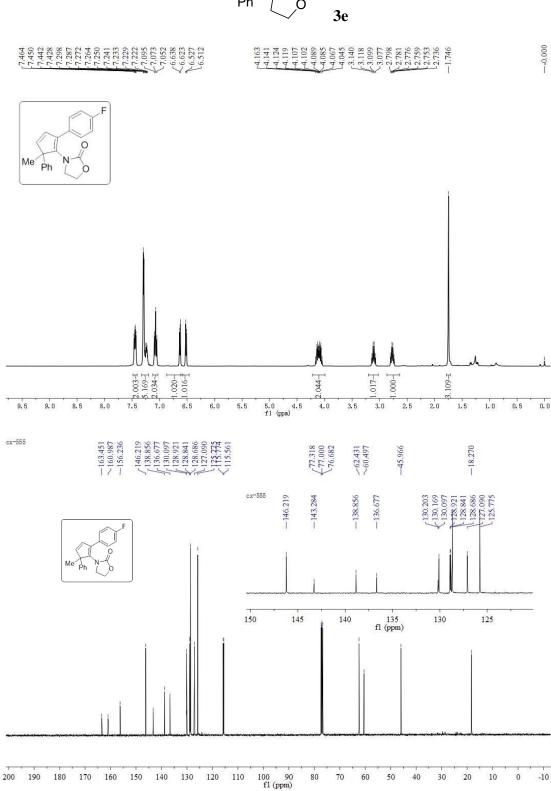




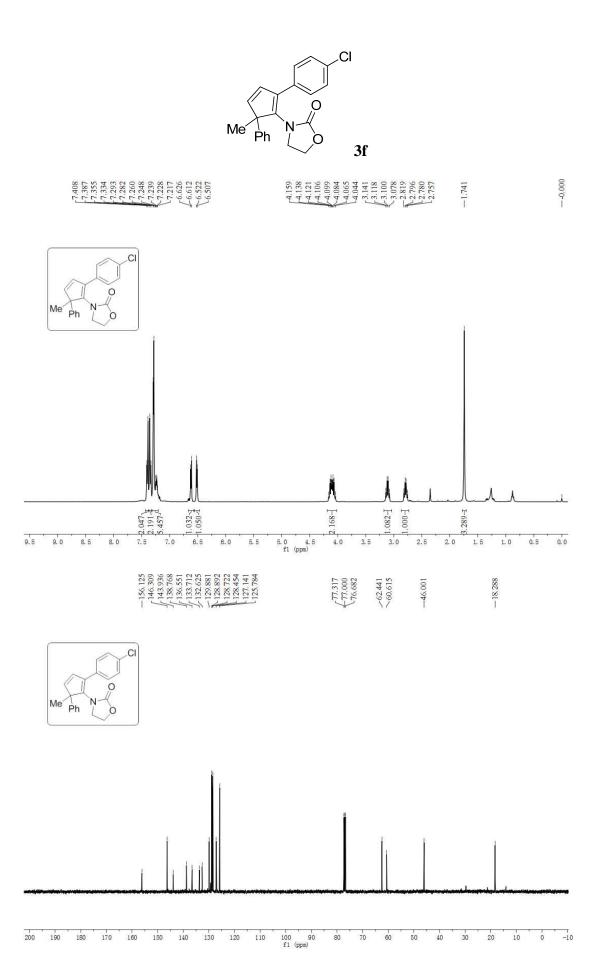


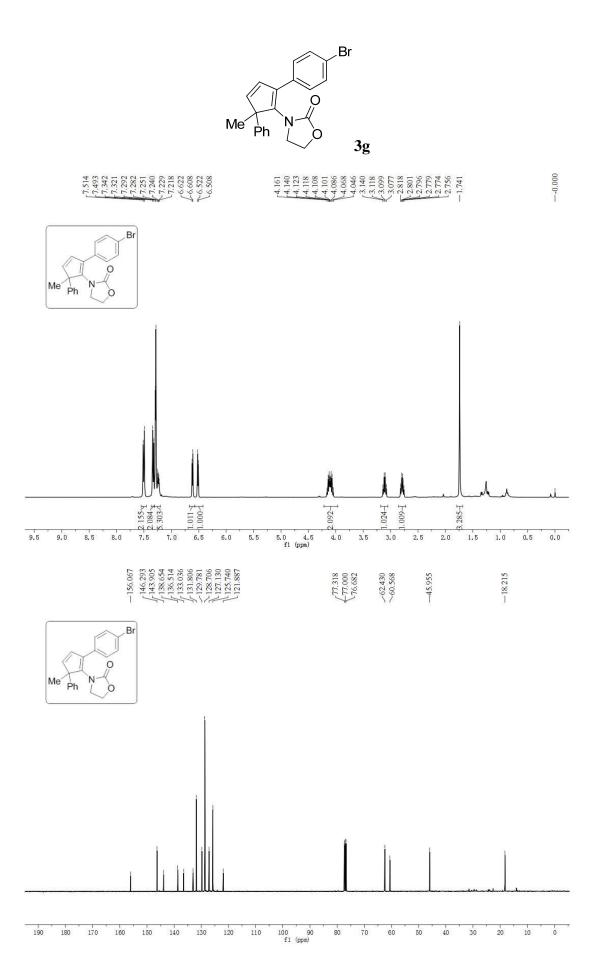


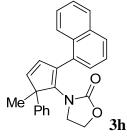


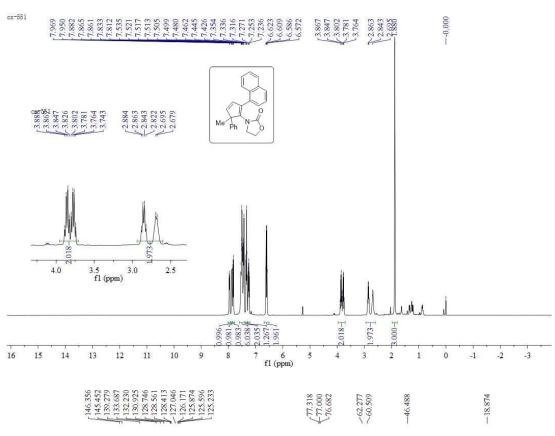


10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

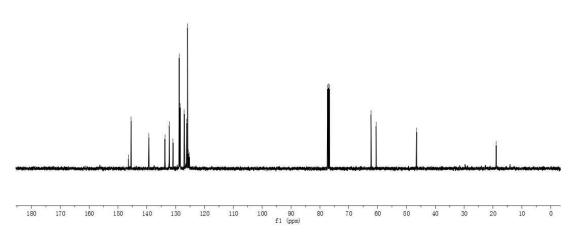


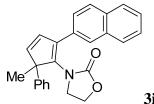


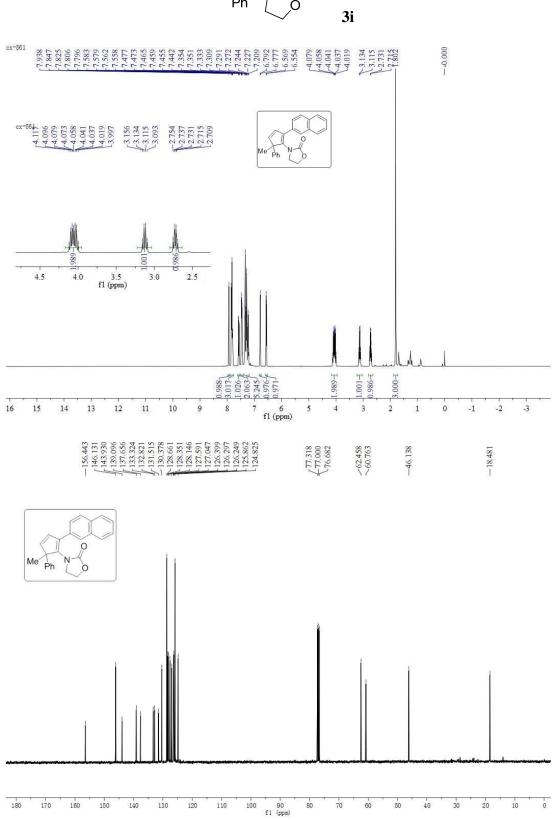


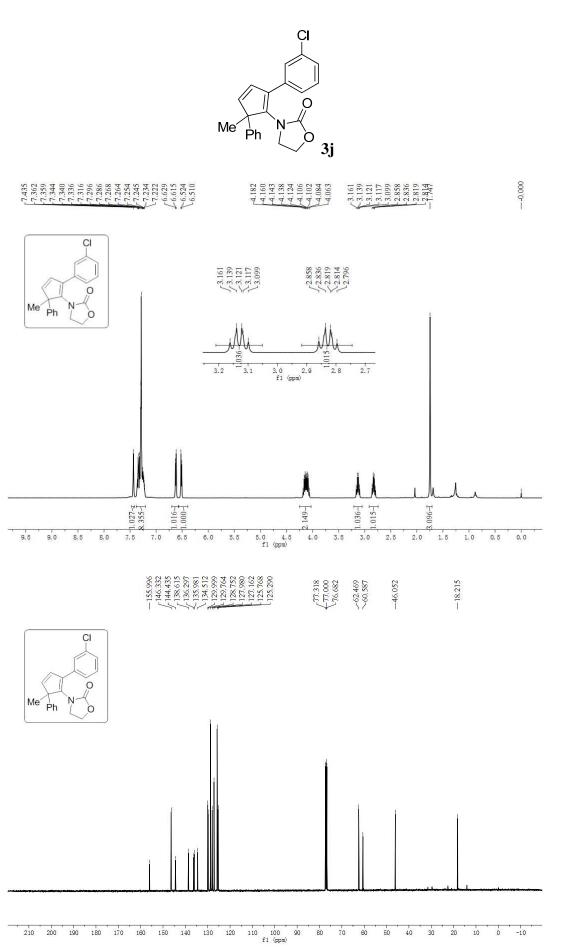








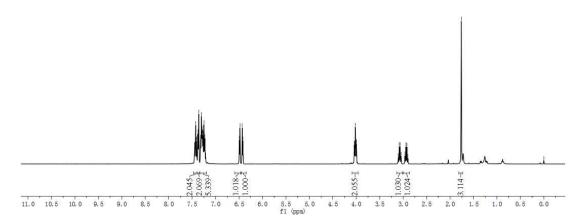




7.448 7.443 7.443 7.443 7.443 7.443 7.443 7.229 4.040 4.0137 4.000 3.997 3.065 3.065 3.043 2.940 2.290 2.290 2.290 2.899

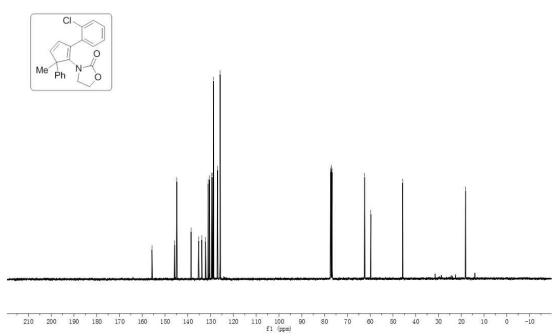
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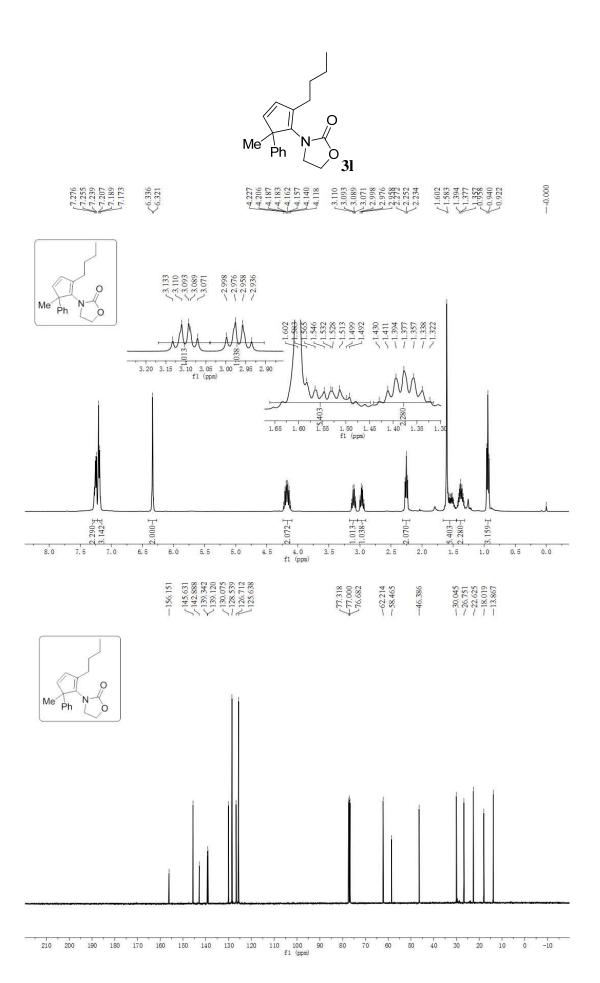


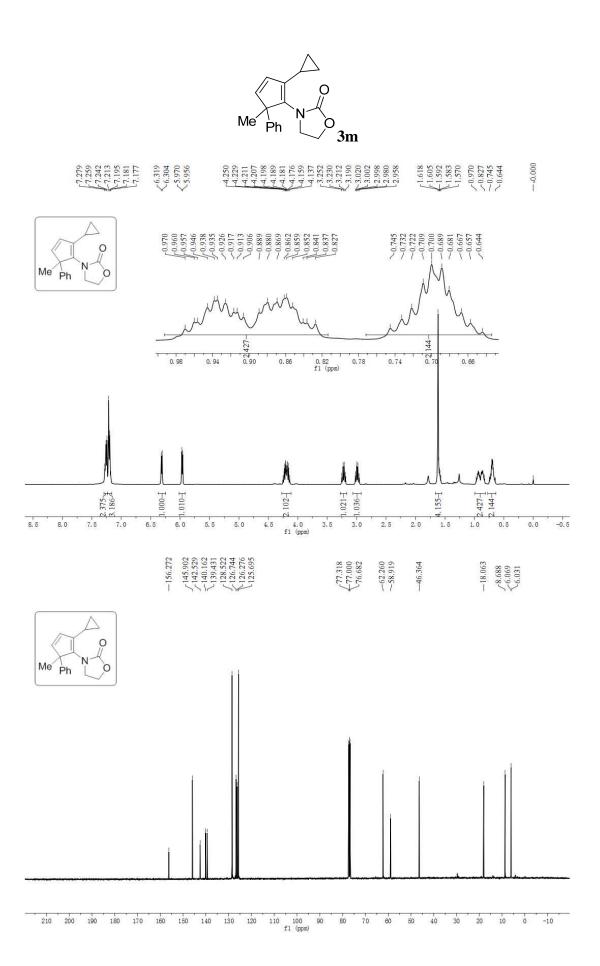


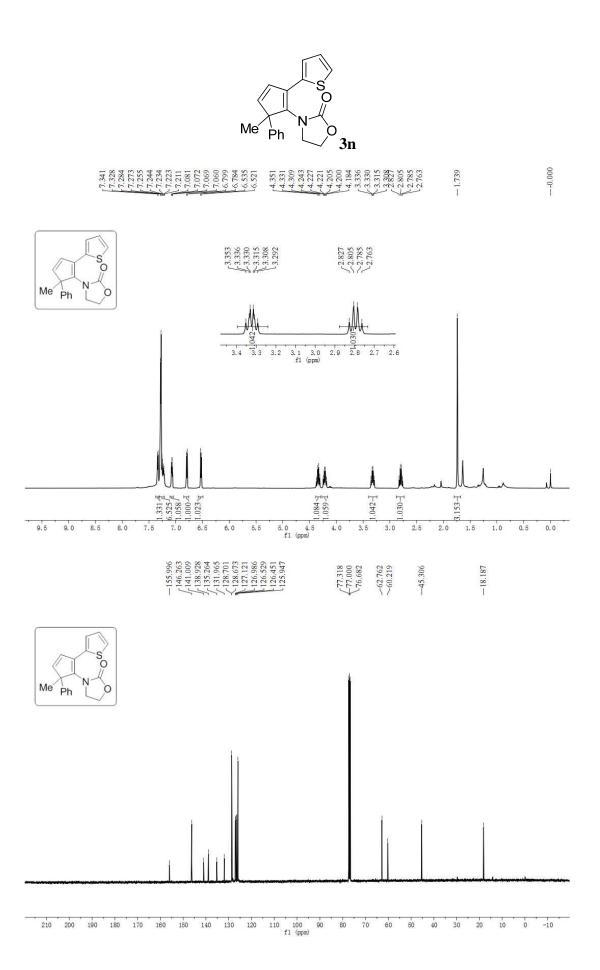
- 155.736 - 145.831 - 138.554 - 135.248 - 132.233 - 132.235 - 130.518 - 129.021 - 128.680 - 129.021 - 128.680 - 129.021 - 128.680 - 126.902 - 126.903 - 126.

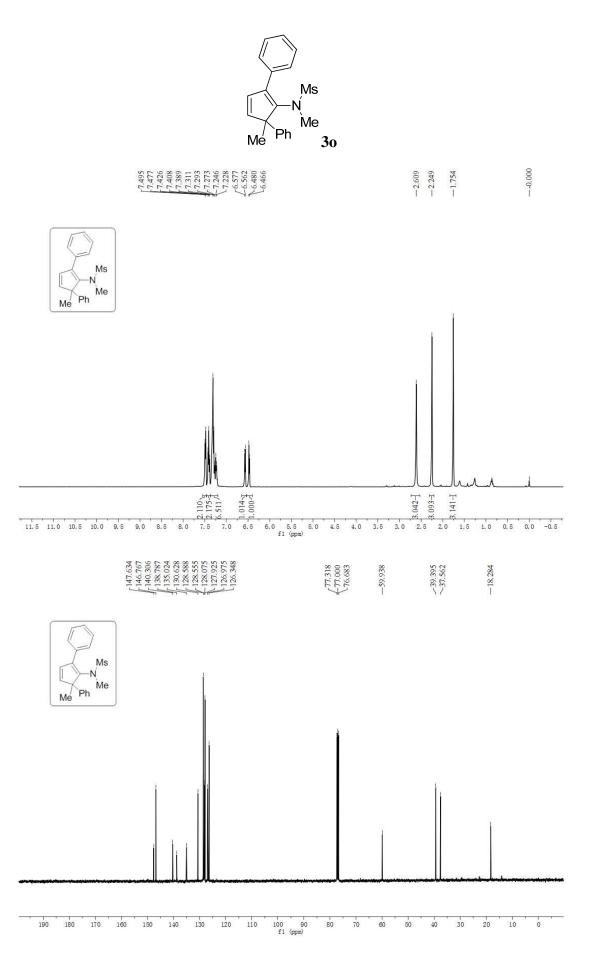
77.318 77.000 76.682 -62.412 -59.681 18.115

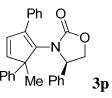


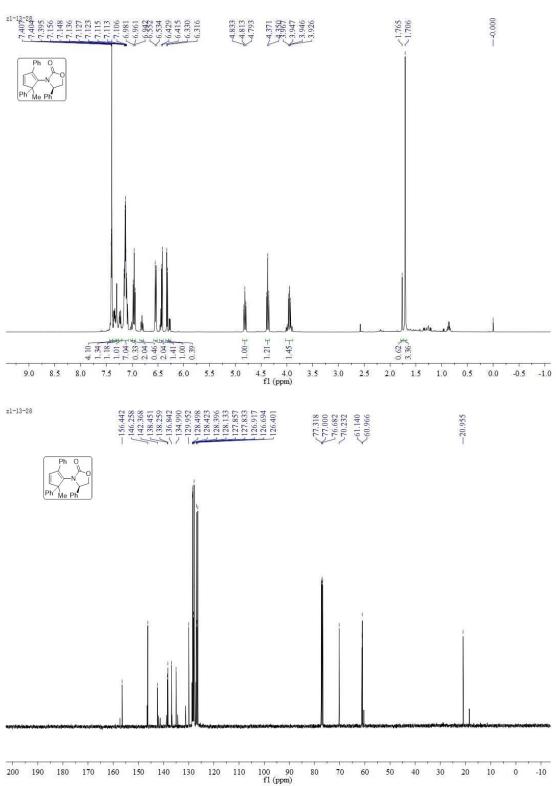


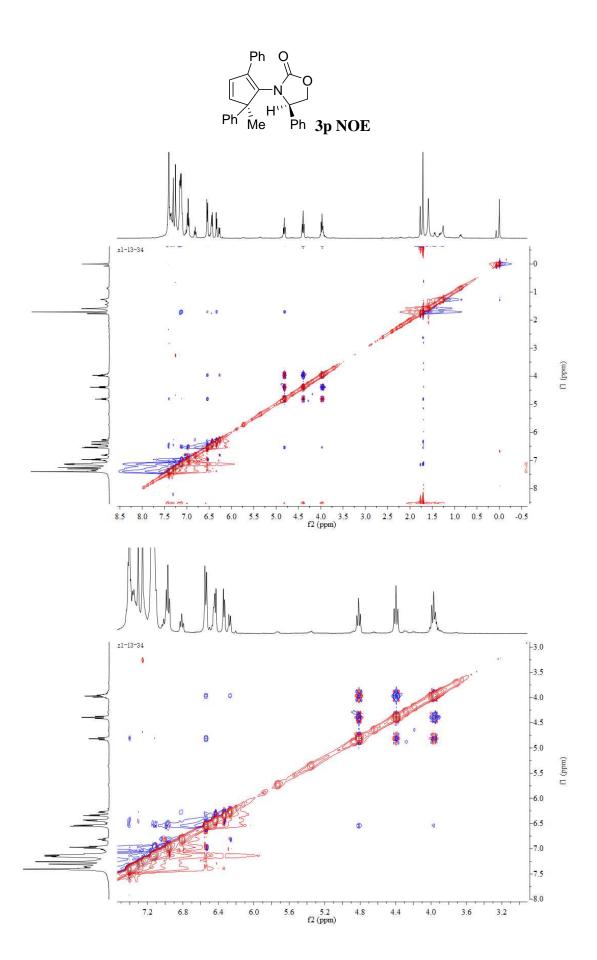


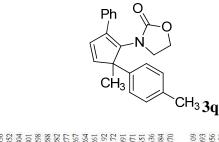




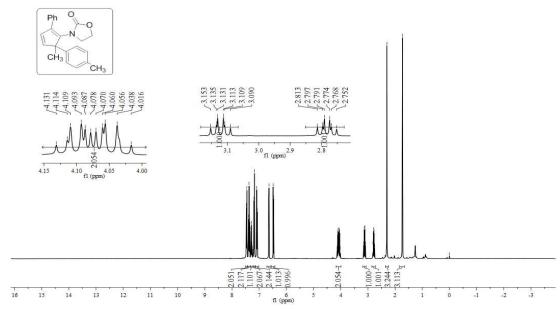






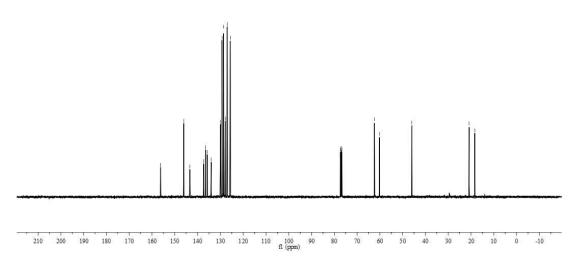


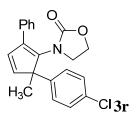
7.4472 7.4679 7.380 7.380 7.381 7.38



7156.254 146.086 7137.387 135.584 135.587 129.393 129.258 129.258 127.836 77.000 77.

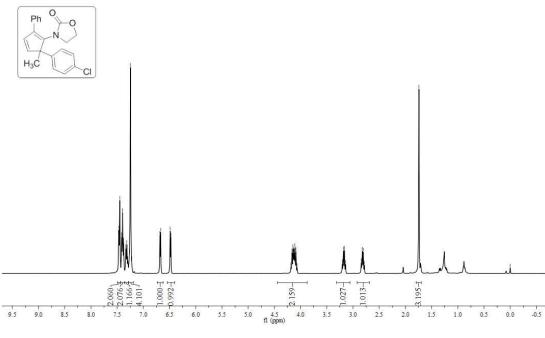






7.467 7.449 7.395 7.335 7.333 7.333 7.257 7.257 7.227 7.227 6.668 6.488 4 184 4 162 4 164 4 164 4 164 4 168 4 168 8 182 3 182 3 183 3 183 3 183 3 183 3 183 3 183 3 183 3 183 5 184

--0.000

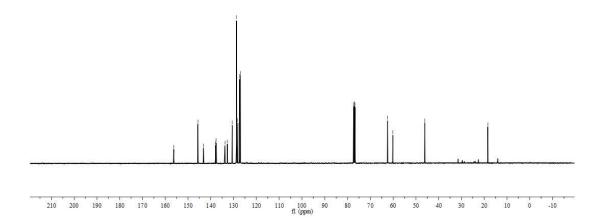


156.269 145.671 143.176 137.908 1137.803 133.781 132.740 128.724 128.724 127.372 127.372

77.318 76.682 62.419 60.109

-18.425

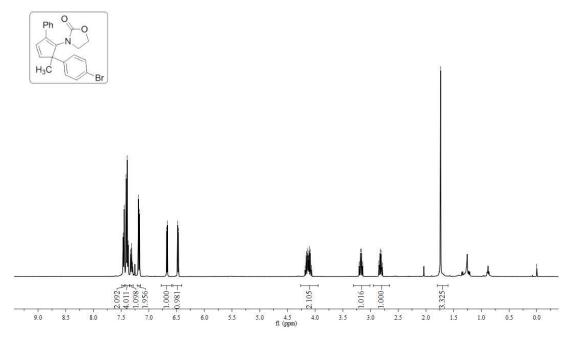




7.466 7.445 7.441 7.331 7.333 7.234 7.234 7.234 7.248 7.2669 7.6669 7.6664

4,180 4,1188 4,1187 4,1137 4,1

-0.00

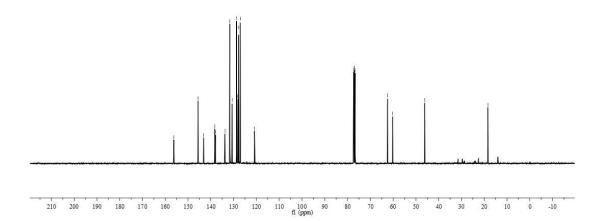


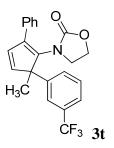
-156.265 -156.265 -137.974 -137.974 -137.974 -137.655 -128.765 -127.769 -127.769

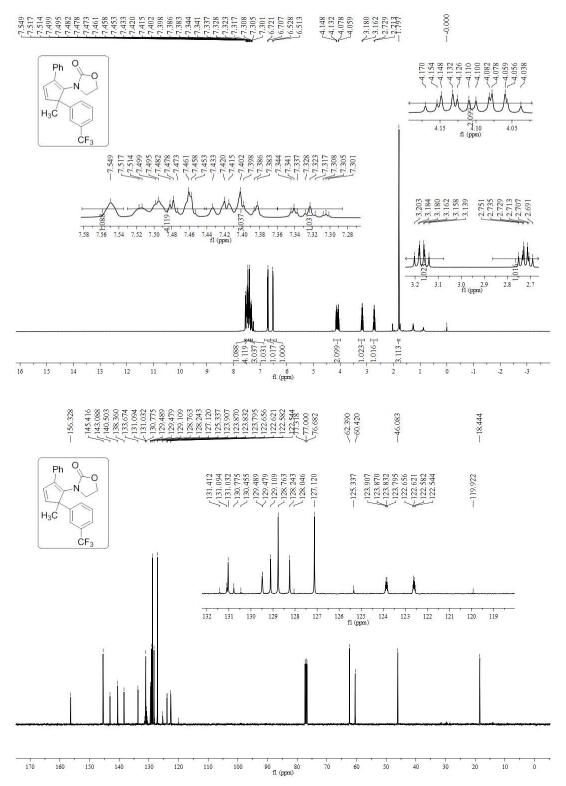
77.318 76.682 62.423 60.187

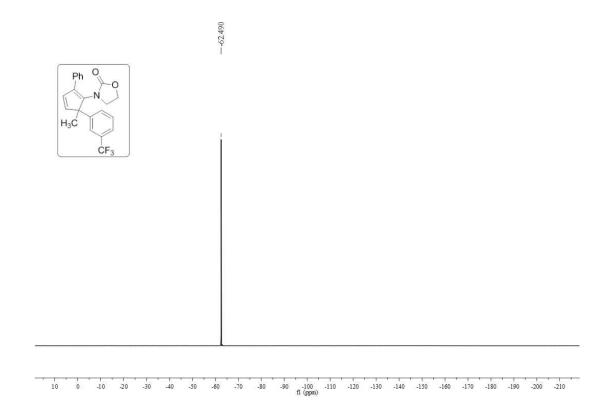
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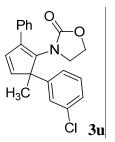


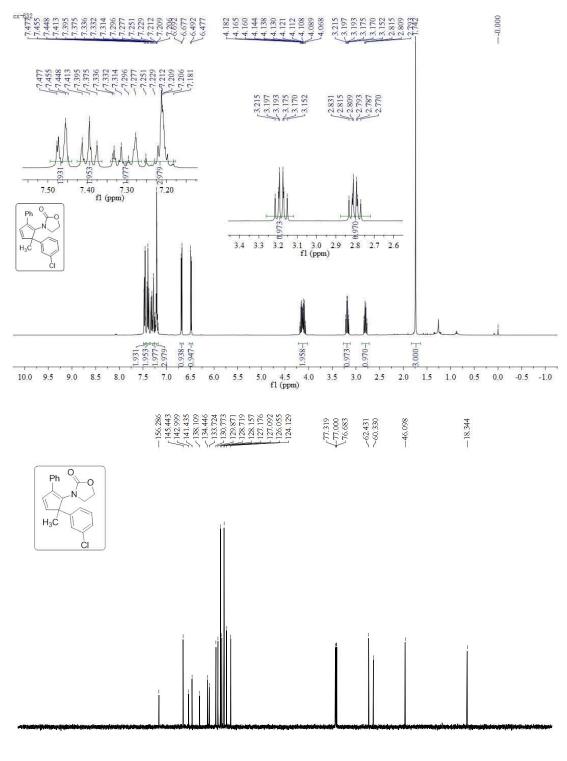












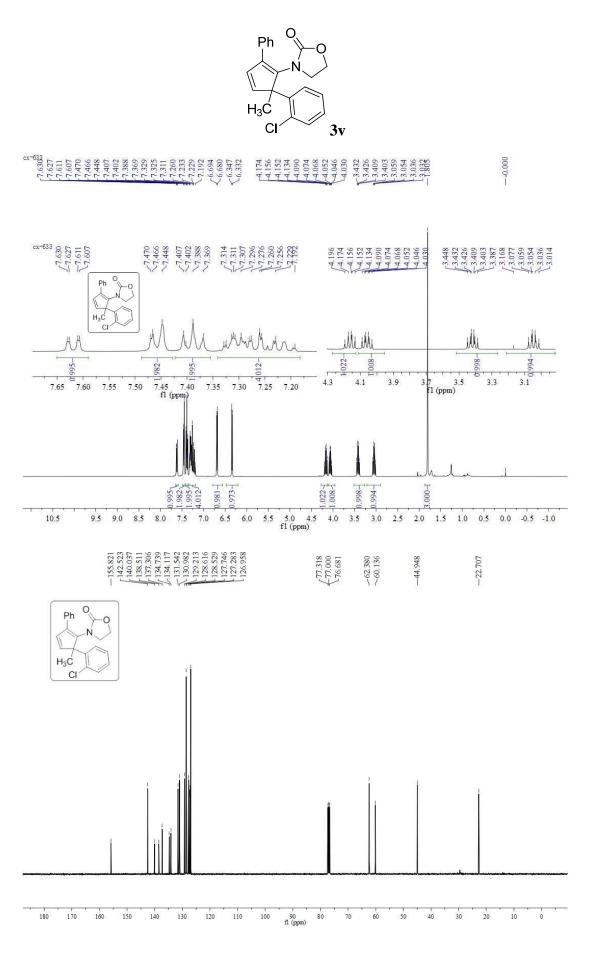
100 90 fl (ppm)

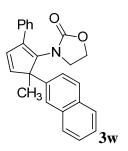
110

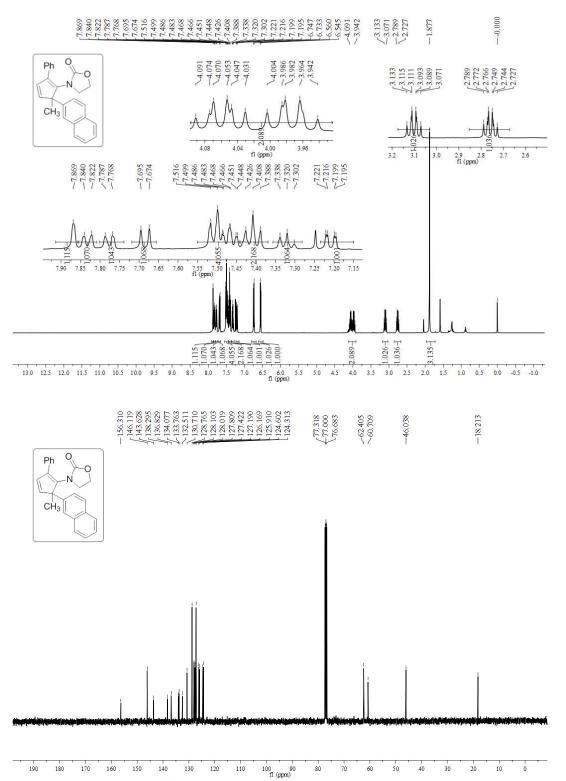
70

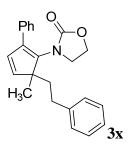
10

210 200 190 180 170 160 150 140 130 120



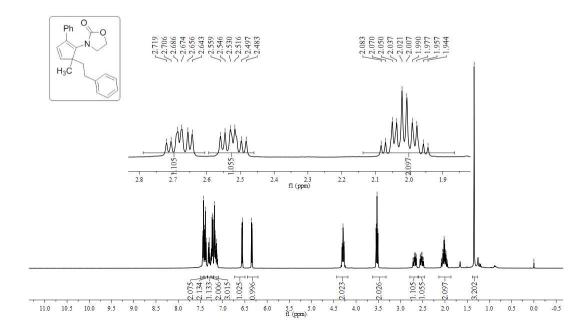






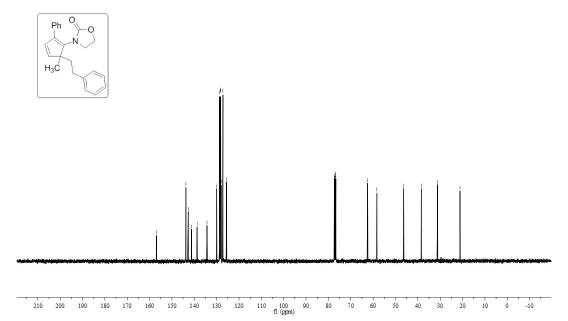
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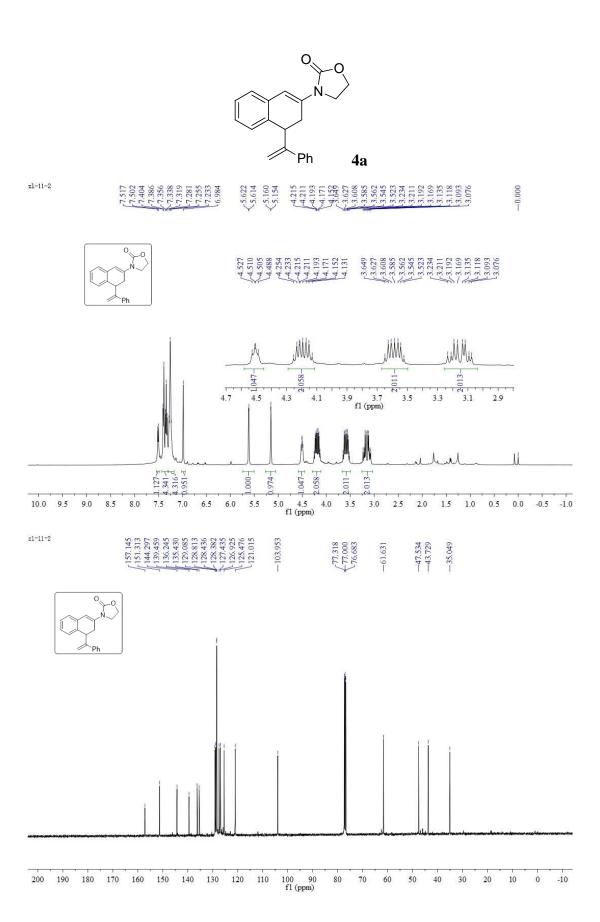
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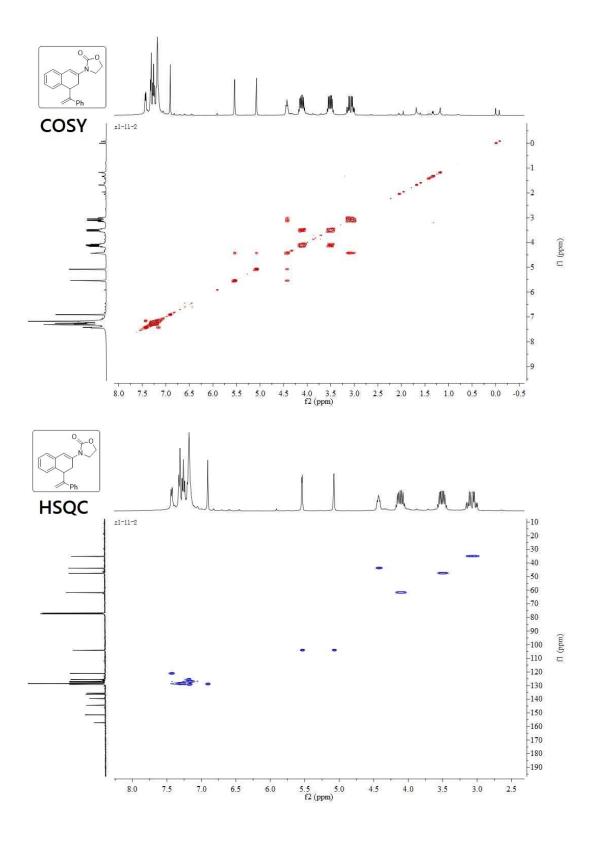


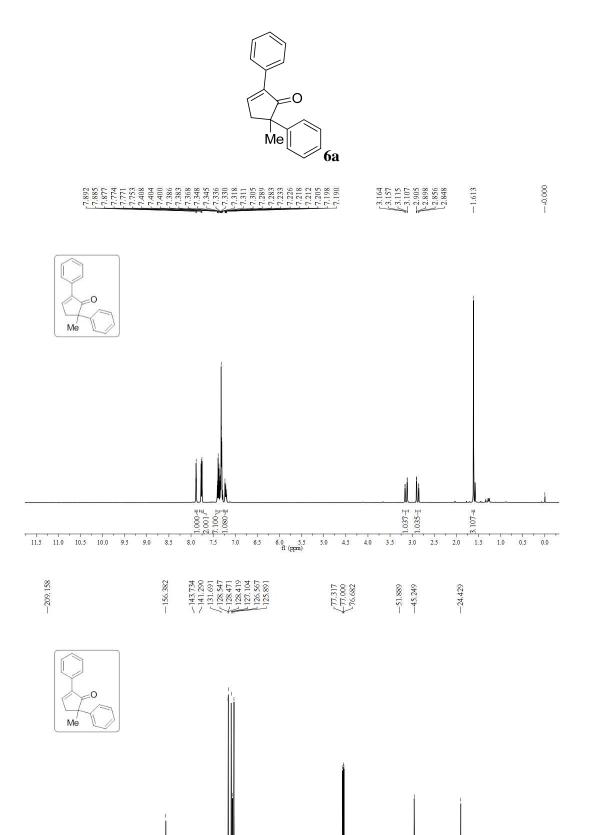
156.872 143.771 142.690 138.729 129.988 129.988 128.716 128.716 128.716 127.201 127.201

77.318 76.682 -62.465 -8.343 -38.449 731.218









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 fl (ppm)

