Supporting Information

Domino Reaction between Nitrosoarenes and Ynenones for Catalyst-Free Preparation of Indanone-Fused Tetrahydroisoxazoles

Shaotong Qiu,† Renxiao Liang,† Yongdong Wang,‡ and Shifa Zhu*†,‡
†Key Laboratory of Functional Molecular Engineering of Guangdong Province and Guangdong Engineering Research Center for Green Fine Chemicals, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China
zhusf@scut.edu.cn
‡Singfar Laboratories, Guangzhou, 510670, China

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1. Optimization of reaction conditions

| entry | cat. (mol %) | solv. | Temp. (°C) | add. (100 mg) | Yield (%) |
|-------|--------------|-------|------------|---------------|-----------|
| 1     | IPrAuCl/AgNTf₂ (5) | DCE   | 80         | -             | 15        |
| 2     | PPh₃AuCl/AgNTf₂ (5) | DCE   | 80         | -             | 16        |
| 3     | AgNTf₂ (5)     | DCE   | 80         | -             | nd        |
| 4     | Pd(OAc)₂ (5)   | DCE   | 80         | -             | nd        |
| 5     | PtCl₂ (5)      | DCE   | 80         | -             | 20        |
| 6     | Rh₂(OAc)₄ (5)  | DCE   | 80         | -             | 30        |
| 7     | CuCl₂ (5)      | DCE   | 80         | -             | 32        |
| 8     | -              | DCE   | 80         | -             | 36        |
| 9     | -              | MeCN  | 80         | -             | 62        |
| 10    | -              | DCM   | 80         | -             | 50        |
| 11    | -              | THF   | 80         | -             | 51        |
| 12    | -              | CHCl₃ | 80         | -             | 66        |
| 13    | -              | EA    | 80         | -             | 52        |
| 14    | -              | MePh  | 80         | -             | 49        |
| 15    | -              | CHCl₃ | 80         | 4 Å MS        | 69        |
| 16    | -              | CHCl₃ | 60         | 4 Å MS        | 56        |
| 17    | -              | CHCl₃ | 100        | 4 Å MS        | 40        |

* Unless otherwise noted, the reaction was performed with 1a (0.25 mmol) and 2a (1.0 mmol), 24 h, under N₂ atmosphere. *isolated yield. *40% 1a was recovered.

2. Experimental procedures and spectroscopic data

2.1 General information

All reactions were carried out under an inert atmosphere of dry N₂ in Schlenk tube, solvents were purified by standard method. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F). ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra
2.2 Typical procedure for the synthesis of 3

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 4 Å MS (100 mg) was activated by heat gun. After cooling the tube to room temperature, CHCl₃ (2.0 ml), the substrate of 1,6-ynenone 1a (77 mg, 0.25 mmol) and nitrosobenzene 2a (107 mg, 1.0 mmol) were added. The mixture was stirred at 80 °C until the substrate 1a was completely consumed. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 3a (90 mg, 0.17 mmol).

The procedures of other substrates 1 and nitrosobenzenes 2 were similar with that mentioned above.

**(E)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,I,I'-diphenylmethanimine oxide**

![Diagram](image)

Yield 69% (90 mg, 0.17 mmol), yellow solid, m. p. 70-71 °C, Rₜ = 0.45 (EtOAc/petroleum ether = 1/3); ¹H NMR (400 MHz, CDCl₃) δ 9.33 (d, J = 8.0 Hz, 1H), 8.32 (dd, J = 7.9, 1.0 Hz, 1H), 7.87 (td, J = 8.0, 1.4 Hz, 1H), 7.70 (td, J = 7.9, 1.1 Hz, 1H), 7.43 – 7.28 (m, 6H), 7.28 – 7.22 (m, 2H), 7.20 – 7.06 (m, 5H), 7.00 – 6.76 (m, 5H), 5.94 (br, 2H), 4.99 (d, J = 8.6 Hz, 1H), 4.19 (d, J = 8.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 194.5, 146.7, 145.2, 138.6, 136.3, 136.2, 134.8, 132.7, 131.6, 131.3, 129.13, 129.05, 128.93, 128.90, 128.84, 128.83, 128.81, 128.6, 128.2, 126.8, 122.9, 122.3, 116.8, 81.6, 78.8, 68.5; ¹⁵N NMR (100 MHz, CDCl₃) δ 194.6, 147.0, 145.4, 138.7, 136.4, 135.5, 134.8, 132.7, 131.5, 131.4, 129.2, 129.09, 128.96, 128.90, 128.87, 128.3, 128.2, 127.9, 126.5, 122.9, 122.2, 117.0, 81.7, 78.9, 68.5; IR (KBr, cm⁻¹) 3062, 2920, 1689, 1591, 1525, 1490, 1239, 755, 695, 536; HRMS (ESI) Calcd for C₃₇H₂₆N₂O₃ (M+H)⁺ 523.2016, found 523.2014.

**(E)-1-(4-oxo-1-phenyl-3-(p-tolyl)-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,I,I'-diphenylmethanimine oxide**

Yield 73% (98 mg, 0.18 mmol), yellow solid, m. p. 139-140 °C, Rₜ = 0.4 (EtOAc/petroleum ether = 1/3); ¹H NMR (400 MHz, CDCl₃) δ 9.33 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.5 Hz, 1H), 7.84 (t, J = 7.8 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.24 (d, J = 2.4 Hz, 2H), 7.16 – 7.07 (m, 5H), 7.03 (d, J = 8.2 Hz, 2H), 6.97 – 6.82 (m, 5H), 6.00 (br, 2H), 4.98 (d, J = 8.6 Hz, 1H), 4.19 (d, J = 8.6 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.5, 146.8, 145.3, 138.8, 136.37, 136.34, 135.4, 134.8, 132.7, 131.5, 131.3, 129.6, 129.1, 128.9, 128.83, 128.76, 128.5, 128.2, 127.9, 126.5, 123.0, 122.2, 116.8, 81.6, 78.7, 68.4, 21.3; IR (KBr, cm⁻¹) 3064, 2938, 1690, 1506, 1300, 1239, 758, 692; HRMS (ESI) Calcd for C₃₈H₃₂N₂O₃ (M+H)⁺ 537.2173, found 537.2172.
(E)-1-(3-(4-fluorophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,N-diphenylmethanimine oxide

Yield 80% (108 mg, 0.20 mmol), yellow solid, m. p. 140-141 °C, R_t = 0.4 (EtOAc/petroleum ether = 1/3); ^1H NMR (400 MHz, CDCl_3) δ 9.37 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 7.9 Hz, 1H), 7.90 (t, J = 7.8 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.38 – 7.35 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 (t, J = 6.5 Hz, 3H), 7.16 – 7.10 (m, 2H), 7.06 (t, J = 8.6 Hz, 2H), 7.02 – 6.89 (m, 5H), 6.06 (br, 2H), 5.00 (d, J = 8.4 Hz, 1H), 4.23 (d, J = 8.4 Hz, 1H); ^13C NMR (100 MHz, CDCl_3) δ 194.4, 163.1 (d, J = 246.6 Hz), 146.7, 145.3, 136.11, 136.07, 134.9, 134.8 (d, J = 3.3 Hz), 132.7, 131.6, 131.1, 129.2, 129.0, 128.93, 128.87, 128.5, 128.4, 128.2 (d, J = 8.3 Hz), 128.0, 122.9, 122.5, 116.9, 115.9 (d, J = 21.5 Hz), 112.7, 78.8, 68.4; ^19F NMR (376 MHz, CDCl_3) δ -112.47; IR (KBr, cm^-1) 3066, 2929, 1689, 1590, 1503, 1349, 1302, 1230, 1161, 907, 841, 741, 697; HRMS (ESI) Calcd for C_{35}H_{33}FN_{2}O_{5} (M+H)^+ 541.1922, found 541.1917.

(3)-1-(3-(4-chlorophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,N-diphenylmethanimine oxide

Yield 69% (96 mg, 0.17 mmol), yellow solid, m. p. 132-133 °C, R_t = 0.4 (EtOAc/petroleum ether = 1/3); ^1H NMR (400 MHz, CDCl_3) δ 9.34 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.38 – 7.28 (m, 4H), 7.19 (t, J = 8.4 Hz, 5H), 7.10 (t, J = 7.9 Hz, 2H), 6.92 (t, J = 7.2 Hz, 5H), 6.04 (br, 2H), 4.95 (d, J = 8.3 Hz, 1H), 4.19 (d, J = 8.3 Hz, 1H); ^13C NMR (100 MHz, CDCl_3) δ 194.4, 146.6, 145.2, 137.6, 136.1, 136.0, 134.9, 134.8, 132.7, 131.6, 131.1, 129.22, 129.15, 129.08, 128.96, 128.93, 128.88, 128.5, 128.1, 128.0, 127.8, 122.9, 122.5, 116.9, 80.9, 78.8, 68.4; IR (KBr, cm^-1) 3063, 2925, 1689, 1590, 1503, 1491, 1456, 1351, 1239, 1163, 1001, 831, 765, 695; HRMS (ESI) Calcd for C_{35}H_{32}ClN_{2}O_{5} (M+H)^+ 557.1626, found 557.1629.

(E)-1-(3-(4-bromophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,N-diphenylmethanimine oxide

Yield 63% (95 mg, 0.16 mmol), yellow solid, m. p. 164-165 °C, R_t = 0.4 (EtOAc/petroleum ether = 1/3); ^1H NMR (400 MHz, CDCl_3) δ 9.34 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.86 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.23 – 7.07 (m, 7H), 6.93 (dd, J = 12.7, 6.5 Hz, 5H), 6.05 (br, 2H), 4.93 (d, J = 8.3 Hz, 1H), 4.19 (d, J = 8.3 Hz, 1H); ^13C NMR (100 MHz, CDCl_3) δ 194.3, 146.6, 145.2, 138.2, 136.1, 136.0, 134.9, 132.7, 132.1, 131.1, 130.2, 129.0, 128.91, 128.5, 128.1, 128.0, 122.9, 122.5, 116.9, 80.9, 78.8, 68.4; IR (KBr, cm^-1) 3064, 2927, 1689, 1589, 1525, 1488, 1238, 1162, 1000, 911, 831, 764, 694; HRMS (ESI) Calcd for C_{36}H_{35}BrN_{2}O_{5} (M+H)^+ 601.1121, found 601.1122.

(E)-1-(3-(4-nitrophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,N-diphenylmethanimine oxide

Yield 60% (85 mg, 0.15 mmol), yellow solid, m. p. 163-164 °C, R_t = 0.5 (EtOAc/petroleum ether = 1/2); ^1H NMR (400 MHz, CDCl_3) δ 9.39 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.6 Hz, 2H), 8.21 (d, J = 8.6 Hz, 2H), 8.01 (t, J = 7.7 Hz, 1H),
7.75 (t, J = 7.6 Hz, 1H), 7.49 (dd, J = 14.8, 7.9 Hz, 3H), 7.40 (t, J = 7.6 Hz, 2H), 7.28 – 7.13 (m, 5H), 7.00 (t, J = 7.3 Hz, 1H), 6.94 (d, J = 8.0 Hz, 4H), 6.16 (br, 2H), 5.08 (d, J = 7.8 Hz, 1H), 4.29 (d, J = 7.8 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 194.1, 148.1, 147.1, 146.4, 145.1, 135.9, 135.6, 135.0, 132.8, 131.8, 131.0, 129.4, 129.2, 129.0, 128.4, 128.2, 128.1, 127.2, 124.1, 123.1, 122.9, 117.2, 80.4, 79.1, 68.2; IR (KBr, cm⁻¹) 3066, 2926, 1689, 1594, 1523, 1490, 1347, 1303, 1240, 761, 695; HRMS (ESI) Calcd for C38H28N2O5 (M+H)⁺ 586.1876, found 586.1870.

(E)-1-(3-(4-isopropylphenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1,N1-diphenylmethanimine oxide

![Structure of (E)-1-(3-(4-isopropylphenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1,N1-diphenylmethanimine oxide](image)

Yield 61% (86 mg, 0.15 mmol), yellow solid, m.p. 200-201 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); ¹H NMR (400 MHz, CDCl3) δ 9.32 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.18 – 7.12 (m, 5H), 7.09 (t, J = 7.9 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.87 (dd, J = 15.3, 7.9 Hz, 3H), 5.93 (br, 2H), 4.98 (d, J = 8.7 Hz, 1H), 4.15 (d, J = 8.7 Hz, 1H), 3.07 – 2.81 (m, 1H), 1.30 (d, J = 6.9, 2.6 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 194.5, 150.1, 146.8, 145.3, 136.4, 136.3, 135.6, 134.8, 132.7, 131.5, 131.3, 129.1, 128.90, 128.88, 128.75, 128.73, 128.6, 128.2, 127.9, 127.1, 126.5, 123.0, 122.1, 116.8, 81.6, 78.7, 68.5, 34.1, 24.21, 24.17; IR (KBr, cm⁻¹) 3306, 3063, 2924, 1688, 1589, 1522, 1239, 888, 837, 760, 697; HRMS (ESI) Calcd for C38H28N2O5 (M+H)⁺ 565.2486, found 565.2485.

(E)-1-(3-(3,5-di-tert-butylphenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1,N1-diphenylmethanimine oxide

![Structure of (E)-1-(3-(3,5-di-tert-butylphenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1,N1-diphenylmethanimine oxide](image)

Yield 60% (95 mg, 0.15 mmol), yellow solid, m.p. 173-174 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); ¹H NMR (400 MHz, CDCl3) δ 9.36 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.88 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.45 (s, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 7.10 (q, J = 5.9 Hz, 5H), 6.96 (d, J = 8.1 Hz, 2H), 6.88 (dd, J = 27.8, 20.4 Hz, 3H), 5.94 (br, 2H), 4.97 (d, J = 8.4 Hz, 1H), 4.16 (d, J = 8.4 Hz, 1H), 1.31 (s, 18H); 13C NMR (100 MHz, CDCl3) δ 194.7, 151.7, 146.9, 145.3, 138.2, 136.54, 136.45, 134.8, 132.8, 131.5, 131.4, 129.2, 128.9, 128.8, 128.74, 128.66, 128.5, 128.0, 127.9, 122.9, 122.8, 122.2, 120.3, 117.0, 82.2, 78.7, 68.9, 34.9, 31.5; IR (KBr, cm⁻¹) 3116, 2943, 1688, 1585, 1523, 1503, 1286, 1237, 889, 740, 702, 517; HRMS (ESI) Calcd for C38H28N2O5 (M+H)⁺ 635.3268, found 635.3269.

(E)-1-(3-(naphthalen-1-yl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1,N1-diphenylmethanimine oxide

![Structure of (E)-1-(3-(naphthalen-1-yl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1,N1-diphenylmethanimine oxide](image)

Yield 61% (87 mg, 0.15 mmol), yellow solid, m.p. 181-182 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/3); ¹H NMR (400 MHz, CDCl3) δ 9.38 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 7.8 Hz, 1H), 7.98 – 7.84 (m, 4H), 7.75 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.0 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.34 (t, J = 7.5 Hz, 2H), 7.26 (s, 1H),

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(E)-1-[(3-furan-2-yl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8(3H)-yl]-N,1-diphenylmethanimine oxide

Yield 36% (46 mg, 0.09 mmol), yellow solid, m. p. 151-152 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.32 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.7 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.13 (t, J = 7.7 Hz, 2H), 7.06 (t, J = 7.8 Hz, 2H), 6.91 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 8.3 Hz, 2H), 6.71 – 5.76 (m, 4H), 4.99 (d, J = 7.6 Hz, 1H), 4.70 (d, J = 7.6 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 194.5, 150.2, 146.7, 145.7, 143.6, 136.9, 135.9, 134.7, 133.0, 131.6, 131.0, 129.2, 129.10, 129.05, 129.0, 128.3, 128.1, 127.9, 122.9, 122.8, 117.3, 110.7, 110.5, 79.0, 74.2, 63.4; IR (KBr, cm⁻¹) 3067, 2920, 2857, 1700, 1588, 1459, 1369, 1236, 753, 695; HRMS (ESI) Calcd for C30H29N3O3 (M+H)⁺ 513.1809, found 513.1808.

(E)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8(3H)-yl)-N-phenyl-1-(p-tolyl)methanimine oxide

Yield 70% (94 mg, 0.18 mmol), yellow solid, m. p. 141-142 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.33 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.25 (s, 1H), 7.24 (s, 1H), 7.18 – 7.07 (m, 5H), 7.04 (d, J = 8.1 Hz, 2H), 6.94 – 6.88 (m, 5H), 6.00 (br, 2H), 4.98 (d, J = 8.6 Hz, 1H), 4.19 (d, J = 8.6 Hz, 1H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 194.7, 146.9, 145.3, 138.8, 138.7, 136.5, 134.8, 132.9, 132.7, 131.5, 131.2, 129.8, 129.0, 128.93, 128.86, 128.84, 128.78, 128.5, 128.1, 127.9, 126.5, 123.0, 122.2, 116.8, 81.6, 78.8, 68.2, 21.2; IR (KBr, cm⁻¹) 3062, 2921, 2859, 1689, 1591, 1492, 1457, 1367, 1238, 834, 759, 694; HRMS (ESI) Calcd for C36H33N3O3 (M+H)⁺ 537.2173, found 537.2172.

(E)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8(3H)-yl)-N-phenyl-1-(m-tolyl)methanimine oxide

Yield 71% (95 mg, 0.18 mmol), white solid, 150-151 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.34 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 7.7 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.24 (d, J = 2.8 Hz, 2H), 7.19 (d, J = 4.9 Hz, 2H), 7.15 (d, J = 7.5 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.00 – 6.81 (m, 7H), 5.98 (br, 2H), 4.98 (d, J = 8.6 Hz, 1H), 4.21 (d, J = 8.6 Hz, 1H), 2.27 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 194.7, 147.0, 145.3, 138.9, 138.8, 136.5, 135.9, 134.8, 132.6, 131.6, 131.2, 129.7, 129.1, 128.93, 128.87, 128.82, 128.72, 128.65, 128.5, 127.9, 126.5, 125.3, 123.0, 122.2, 116.8, 81.6, 78.9, 68.3, 21.6; 13C NMR (100 MHz, CDCl3) δ 194.8, 147.2, 145.5, 139.1, 131.0, 136.0, 135.6, 134.7, 132.5, 131.5, 131.3, 129.7, 129.02, 129.00, 128.9, 128.8, 128.73, 128.69, 128.6, 128.2, 127.8, 126.5, 125.2, 122.9, 122.0, 116.9, 81.5, 78.9, 68.2, 21.3; IR (KBr,
cm$^{-1}$) 3116, 2926, 1690, 1525, 1515, 1307, 1236, 920, 768, 697; HRMS (ESI) Calcd for C$_{36}$H$_{29}$N$_{2}$O$_{3}$ (M+H)$^+$ 537.2173, found 537.2173.

(E)-1-(4-methoxyphenyl)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenylmethanimine oxide

Yield 52% (72 mg, 0.13 mmol), yellow solid, m. p. 180-181 °C, R$_f$ = 0.3 (EtOAc/petroleum ether = 1/3); $^1$H NMR (400 MHz, CDCl$_3$) δ 9.34 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.26 (s, 1H), 7.25 (s, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.13 – 7.06 (m, 3H), 7.05 (s, 1H), 6.91 – 6.83 (m, 7H), 6.06 (d, J = 7.9 Hz, 2H), 4.98 (d, J = 8.6 Hz, 1H), 4.21 (d, J = 8.6 Hz, 1H), 3.83 (s, 3H), $^{13}$C NMR (100 MHz, CDCl$_3$) δ 194.7, 160.0, 146.9, 145.3, 138.9, 136.6, 134.8, 132.6, 131.5, 131.2, 129.6, 129.0, 128.9, 128.8, 128.5, 127.9, 127.3, 126.5, 123.0, 122.3, 116.9, 114.4, 81.5, 78.7, 68.0, 55.5; IR (KBr, cm$^{-1}$) 3065, 2921, 2855, 1689, 1592, 1457, 1303, 1241, 1180, 900, 763, 694; HRMS (ESI) Calcd for C$_{36}$H$_{29}$N$_{2}$O$_{3}$ (M+H)$^+$ 553.2122, found 553.2122.

(E)-1-(4-fluorophenyl)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenylmethanimine oxide

Yield 64% (86 mg, 0.16 mmol), yellow solid, 161-162 °C R$_f$ = 0.4 (EtOAc/petroleum ether = 1/3); $^1$H NMR (400 MHz, CDCl$_3$) δ 9.30 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.87 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.24 (d, J = 5.7 Hz, 2H), 7.21 – 7.06 (m, 5H), 7.07 – 6.79 (m, 7H), 6.03 (d, J = 7.7 Hz, 2H), 5.00 (d, J = 8.5 Hz, 1H), 4.15 (d, J = 8.6 Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.82; IR (KBr, cm$^{-1}$) 3066, 2921, 2857, 1689, 1591, 1502, 1458, 1233, 1159, 841, 761, 695; HRMS (ESI) Calcd for C$_{35}$H$_{26}$FN$_{2}$O$_{3}$ (M+H)$^+$ 541.1922, found 541.1917

(E)-1-(4-chlorophenyl)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenylmethanimine oxide

Yield 74% (103 mg, 0.19 mmol), yellow solid, m. p. 190-191 °C, R$_f$ = 0.4 (EtOAc/petroleum ether = 1/3); $^1$H NMR (400 MHz, CDCl$_3$) δ 9.28 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.87 (t, J = 7.7 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.29 (d, J = 8.4 Hz, 2H), 7.23 (s, 2H), 7.19 – 7.08 (m, 5H), 7.02 – 6.79 (m, 5H), 6.02 (d, J = 7.9 Hz, 2H), 5.00 (d, J = 8.6 Hz, 1H), 4.11 (d, J = 8.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.8, 146.4, 145.2, 138.1, 134.96, 134.93, 134.86, 132.6, 131.6, 131.3, 129.6, 129.2, 129.1, 129.0, 128.9, 128.7, 128.1, 126.4, 122.8, 122.6, 117.0, 81.8, 78.2, 68.4; $^{19}$F NMR (100 MHz, CDCl$_3$) δ 193.9, 146.6, 145.4, 138.3, 135.1, 135.0, 134.8, 132.5, 131.5, 131.4, 129.7, 129.2, 129.1, 129.02, 128.96, 128.9, 128.8, 128.3, 127.9, 126.4, 122.7, 122.4, 117.0, 81.8, 78.3, 68.2; IR (KBr, cm$^{-1}$) 3124, 2921, 1690, 1515, 1304, 1235, 899, 737, 520; HRMS (ESI) Calcd for C$_{35}$H$_{26}$ClN$_{2}$O$_{3}$ (M+H)$^+$ 557.1626, found 557.1630.
(E)-1-cyclopropyl-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenylmethanimine oxide

Yield 41% (50 mg, 0.10 mmol), yellow solid, m. p. 168-169 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.32 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.7 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.31 – 7.24 (m, 6H), 7.13 – 7.10 (m, 3H), 4.84 (d, J = 8.5 Hz, 1H), 3.94 (d, J = 8.5 Hz, 1H), 1.10 – 0.95 (m, 1H), 0.68 – 0.54 (m, 2H), 0.55 – 0.45 (m, 1H), 0.20 – 0.06 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 191.1, 145.3, 144.1, 136.9, 136.6, 132.9, 130.7, 129.9, 129.4, 127.7, 127.6, 127.5, 127.4, 126.5, 126.4, 125.3, 122.8, 121.5, 118.8, 80.2, 75.4, 61.3, 13.1, 1.0, 0.0; IR (KBr, cm⁻¹) 3064, 2923, 1687, 1590, 1525, 1488, 1457, 1238, 1160, 937, 766, 695, 544; HRMS (ESI) Calcd for C32H27N3O2 (M+H)⁺ 487.2016, found 487.2017.

(E)-1-(7-fluoro-4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1-diphenylmethanimine oxide

Yield 75% (101 mg, 0.19 mmol), yellow solid, m. p. 188-189 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.44 (dd, J = 8.9, 5.4 Hz, 1H), 7.95 (dd, J = 8.7, 2.8 Hz, 1H), 7.60 – 7.48 (m, 1H), 7.44 – 7.36 (m, 2H), 7.36 – 7.31 (m, 4H), 7.28 – 7.22 (m, 2H), 7.16 – 7.13 (m, 3H), 7.10 (t, J = 8.0 Hz, 2H), 6.93 – 6.87 (m, 5H), 5.97 (br, 2H), 4.98 (d, J = 8.5 Hz, 1H), 4.22 (d, J = 8.5 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 193.7, 163.9 (d, J = 254.6 Hz), 146.6, 145.1, 138.6, 135.8, 135.5 (d, J = 2 Hz), 135.4, 135.3, 131.9 (d, J = 7.6 Hz), 129.2, 129.1, 129.01, 129.97, 128.9, 128.1, 128.0, 127.7 (d, J = 3.3 Hz), 126.5, 122.9, 122.5, 122.0, (d, J = 21.9 Hz), 116.9, 114.9 (d, J = 23.1 Hz), 81.6, 79.0, 68.3; 19F NMR (376 MHz, CDCl3) δ -104.65; IR (KBr, cm⁻¹) 3064, 2921, 1692, 1596, 1486, 1259, 1170, 1028, 748, 695; HRMS (ESI) Calcd for C19H17F3N3O2 (M+H)⁺ 541.1922, found 541.1923.

(E)-1-(7-chloro-4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1-diphenylmethanimine oxide

Yield 59% (82 mg, 0.15 mmol), light green solid, m. p. 205-206 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.34 (d, J = 8.6 Hz, 1H), 8.26 (d, J = 2.2 Hz, 1H), 7.79 (dd, J = 8.6, 2.3 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.35 – 7.30 (m, 4H), 7.25 (s, 1H), 7.23 (s, 1H), 7.19 – 7.12 (m, 3H), 7.10 (t, J = 7.9 Hz, 2H), 6.93 – 6.87 (m, 5H), 5.96 (br, 2H), 4.97 (d, J = 8.5 Hz, 1H), 4.22 (d, J = 8.5 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 193.6, 146.6, 145.2, 138.6, 137.8, 135.8, 135.5, 134.7, 134.0, 130.5, 129.6, 129.2, 129.1, 129.02, 128.98, 128.9, 128.4, 128.1, 128.0, 126.5, 122.9, 122.6, 117.0, 81.7, 79.0, 68.2; IR (KBr, cm⁻¹) 3066, 2923, 1690, 1587, 1525, 1492, 1350, 1237, 1202, 910, 842, 754, 696; HRMS (ESI) Calcd for C19H16ClN3O2 (M+H)⁺ 557.1626, found 557.1627.

(E)-1-(7-methoxy-4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N1-diphenylmethanimine oxide

Yield 66% (91 mg, 0.17 mmol), dark yellow solid m. p. 180-182 °C; Rf = 0.3 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.40 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 2.8 Hz, 1H), 7.42 (dt, J = 8.6, 4.9 Hz, 3H), 7.39 – 7.31 (m, 4H), 7.28 (d, J = 5.0 Hz, 2H), 7.24 – 7.08 (m, 5H), 6.94 – 6.89 (m, 5H), 5.99 (br, 2H), 5.03 (d, J = 8.5 Hz, 1H), 4.21 (d, J = 8.6 Hz, 1H), 3.98 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 193.6, 146.6, 145.2, 138.6, 137.8, 135.8, 135.5, 134.7, 134.0, 130.5, 129.6, 129.2, 129.1, 129.02, 128.98, 128.9, 128.4, 128.1, 128.0, 126.5, 122.9, 122.6, 117.0, 81.7, 79.0, 68.2; IR (KBr, cm⁻¹) 3066, 2923, 1690, 1587, 1525, 1492, 1350, 1237, 1202, 910, 842, 754, 696; HRMS (ESI) Calcd for C19H17O3N3O2 (M+H)⁺ 557.1626, found 557.1627.
(E)-1-(4-oxo-3-phenyl-1-(p-tolyl)-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8(3H)-yl)-1-phenyl-N-(p-tolyl)methanimine oxide

Yield 45% (61 mg, 0.11 mmol), yellow solid, m. p. 165-166 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.33 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.0 Hz, 1H), 7.93 – 7.78 (m, 1H), 7.68 (t, J = 7.3 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.30 (d, J = 7.0 Hz, 2H), 7.27 (s, 2H), 7.20 (d, J = 7.6 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.65 (br, 2H), 5.87 (br, 2H), 4.97 (d, J = 8.4 Hz, 1H), 4.25 (d, J = 8.4 Hz, 1H), 2.24 (s, 3H), 2.22 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 194.8, 144.5, 143.1, 139.1, 139.0, 136.5, 136.2, 134.7, 132.8, 131.8, 131.5, 131.4, 129.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 126.5, 122.7, 117.1, 81.6, 78.9, 68.3, 21.1, 20.7; IR (KBr, cm⁻¹) 3065, 2921, 1689, 1592, 1457, 1303, 1241, 1180, 900, 763, 694; HRMS (ESI) Calcd for C38H39N3O4 (M+H)+ 553.2122, found 553.2119.

(E)-N-(4-acetylphenyl)-1-(1-(4-acetylphenyl)-4-oxo-3-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-1-phenylmethanimine oxide

Yield 56% (85 mg, 0.14 mmol), yellow solid, m. p. 195-196 °C, Rf = 0.3 (EtOAc/petroleum ether = 1/2); 1H NMR (400 MHz, CDCl3) δ 9.34 (d, J = 7.9 Hz, 1H), 8.35 (d, J = 6.9 Hz, 1H), 7.96 – 7.87 (m, 1H), 7.78 – 7.71 (m, 3H), 7.53 – 7.32 (m, 8H), 7.22 (d, J = 7.3 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 5.96 (br, 2H), 5.05 (d, J = 9.1 Hz, 1H), 4.08 (d, J = 9.1 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 196.8, 196.3, 193.8, 150.1, 148.0, 137.3, 137.0, 135.72, 135.66, 135.3, 132.1, 132.0, 130.9, 130.4, 129.5, 129.4, 129.31, 129.28, 129.0, 128.92, 128.86, 127.7, 126.4, 122.3, 115.2, 81.6, 78.3, 68.5, 26.7, 26.2; IR (KBr, cm⁻¹) 3120, 2934, 1684, 1592, 1508, 1358, 1238, 953, 904, 842, 704; HRMS (ESI) Calcd for C39H31N2O5 (M+H)+ 607.2227, found 607.2233.

2-cfisoxazol-8b(3H)-yl)-1-phenylmethanimine oxide

Yield 50% (85 mg, 0.13 mmol), yellow solid, m. p. 161-162 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 9.29 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 7.7 Hz, 1H), 7.87 (t, J = 7.4 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.50 – 7.32 (m, 6H), 7.25 – 7.12 (m, 6H), 6.99 (br, 2H), 6.83 (d, J = 8.9 Hz, 2H), 5.78 (br, 2H), 4.98 (d, J = 8.8 Hz, 1H), 4.14 (d, J = 8.8 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 194.2, 145.7, 144.0, 138.0, 135.8, 135.1, 132.4, 132.0, 131.9, 131.0, 130.9, 129.4, 129.22, 129.20, 129.1, 128.9, 128.7, 128.0, 126.4, 124.5, 122.9, 118.4, 114.9, 81.7, 78.6, 68.5; IR (KBr, cm⁻¹) 3064, 2922, 2856, 1689, 1587, 1483, 1246, 1009, 827, 747, 701; HRMS (ESI) Calcd for C35H32Br,N2O5 (M+H)+ 679.0226, found 679.0230.
(E)-9-oxo-N,1,3,9a-tetraphenyl-3,3a,9,9a-tetrahydronaphtho[2,3-c]isoxazol-4(1H)-imine oxide

Yield 9% (12 mg, 0.02 mmol), yellow solid, m. p. 202-203 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/3); 1H NMR (400 MHz, CDCl3) δ 7.70 (d, J = 7.6 Hz, 2H), 7.43 – 7.41 (m, 1H), 7.37 – 7.27 (m, 9H), 7.23 (d, J = 7.2 Hz, 1H), 7.21 – 7.12 (m, 5H), 7.10 – 6.99 (m, 2H), 6.88 (t, J = 7.2 Hz, 1H), 6.75 – 6.59 (m, 3H), 5.55 (d, J = 3.5 Hz, 1H), 5.53 (d, J = 3.5 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 192.8, 146.7, 145.9, 143.3, 139.1, 136.6, 133.9, 132.5, 131.7, 130.3, 129.6, 128.6, 128.3, 128.12, 128.07, 127.94, 127.89, 127.66, 127.65, 125.8, 124.8, 122.4, 116.7, 83.0, 80.7, 61.3; IR (KBr, cm⁻¹) 3061, 2953, 1750, 1716, 1596, 1503, 1431, 1367, 1280, 1227, 744, 688; HRMS (ESI) Calcd for C36H27N3O3 (M+H)+ 523.2016, found 523.2019.

8b-(2,3-diphenyl-2,3-dihydrobenzo[d]isoxazol-3-yl)-1,3-diphenyl-1,3,3a,8b-tetrahydro-4H-indeno[1,2-c]isoxazol-4-one

Yield 52% (78 mg, 0.13 mmol), yellow solid, m. p. 190-191 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/10); 1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.43 – 7.40 (m, 5H), 7.28 – 7.13 (m, 6H), 7.10 (t, J = 7.9 Hz, 2H), 6.98 – 6.87 (m, 6H), 6.82 – 6.78 (m, 3H), 6.58 (d, J = 7.6 Hz, 1H), 6.45 (dd, J = 6.6, 2.9 Hz, 2H), 5.56 (d, J = 5.0 Hz, 1H), 4.38 (d, J = 5.0 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 192.6, 149.8, 146.0, 143.1, 140.7, 138.4, 136.3, 135.8, 133.2, 130.1, 128.70, 128.66, 128.4, 128.2, 127.8, 127.52, 127.49, 127.0, 126.4, 126.3, 126.2, 125.4, 123.1, 122.6, 122.2, 117.7, 113.9, 109.3, 101.6, 80.0, 78.7, 68.7, 68.6; IR (KBr, cm⁻¹) 3061, 2922, 1740, 1504, 1363, 1277, 751, 670; HRMS (ESI) Calcd for C43H31N3O3 (M+H)+ 599.2329, found 599.2335.

8b-benzoyl-1,3-diphenyl-1,3,3a,8b-tetrahydro-4H-indeno[1,2-c]isoxazol-4-one

Yield 82% (92 mg, 0.21 mmol), yellow solid, m. p. 190-191 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/10); 1H NMR (400 MHz, CDCl3) δ 8.17 (dd, J = 7.5, 1.5 Hz, 1H), 8.09 (dd, J = 7.3, 1.6 Hz, 1H), 7.87 – 7.72 (m, 2H), 7.52 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.28 (d, J = 4.9 Hz, 2H), 7.25 (d, J = 6.1 Hz, 1H), 7.15 – 7.01 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 6.87 – 6.78 (m, 2H), 5.42 (d, J = 7.4 Hz, 1H), 4.54 (d, J = 7.4 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 194.4, 193.1, 147.0, 139.8, 135.6, 135.4, 134.9, 133.7, 129.10, 129.05, 128.8, 128.32, 128.27, 128.0, 127.8, 127.2, 125.9, 123.1, 118.4, 81.2, 81.2, 71.3; IR (KBr, cm⁻¹) 3070, 2957, 1749, 1715, 1599, 1503, 1427, 1278, 1233, 801, 688; HRMS (ESI) Calcd for C32H26NO3 (M+H)+ 432.1594, found 432.1599.

2.3 Gram-scale reaction of 3a

![Reaction Scheme]

Yield 98% (3.08 g, 10 mmol), yellow solid, m. p. 190-191 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/10); 1H NMR (400 MHz, CDCl3) δ 8.17 (dd, J = 7.5, 1.5 Hz, 1H), 8.09 (dd, J = 7.3, 1.6 Hz, 1H), 7.87 – 7.72 (m, 2H), 7.52 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.28 (d, J = 4.9 Hz, 2H), 7.25 (d, J = 6.1 Hz, 1H), 7.15 – 7.01 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 6.87 – 6.78 (m, 2H), 5.42 (d, J = 7.4 Hz, 1H), 4.54 (d, J = 7.4 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 194.4, 193.1, 147.0, 139.8, 135.6, 135.4, 134.9, 133.7, 129.10, 129.05, 128.8, 128.32, 128.27, 128.0, 127.8, 127.2, 125.9, 123.1, 118.4, 81.2, 81.2, 71.3; IR (KBr, cm⁻¹) 3070, 2957, 1749, 1715, 1599, 1503, 1427, 1278, 1233, 801, 688; HRMS (ESI) Calcd for C32H26NO3 (M+H)+ 432.1594, found 432.1599.
2.4 Intermolecular Trapping

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 4 Å MS (100 mg) was activated by heat gun. After cooling the tube to room temperature, CHCl₃ (2.0 ml), the substrate of tolan 6 (45 mg, 0.25 mmol), nitrosobenzene 2a (107 mg, 1.0 mmol) and Chalcone (104 mg, 0.5 mmol) were added. The mixture was stirred at 80 °C for 24 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 5a (44 mg, 0.22 mmol).

As for dimethyl maleate, 5a (54 mg, 0.27 mmol) was produced in similar method.

2.5 Control Reactions

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 4 Å MS (100 mg) was activated by heat gun. After cooling the tube to room temperature, CHCl₃ (2.0 ml), the substrate of 1,6-ynenone 1a (45 mg, 0.25 mmol), and azoxybenzene 5a (198 mg, 1.0 mmol) were added. The mixture was stirred at 80 °C for 24 h.

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 4 Å MS (100 mg) was activated by heat gun. After cooling the tube to room temperature, CHCl₃ (2.0 ml), the substrate of 1,6-ynenone 1a (45 mg, 0.25 mmol), nitrosobenzene 2a (107 mg, 1.0 mmol) and TEMPO (59 mg, 0.38 mmol) were added. The mixture was stirred at 80 °C for 24 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 3a (22 mg, 0.04 mmol).
2.6 Experimental procedures for the synthesis of compounds 9 and 10

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, MeCN (1.0 ml), 3a (131 mg, 0.25 mmol), benzyn persecutor (149 mg, 0.5 mmol) and CsF (152 mg, 1.0 mmol) were added. The mixture was stirred at 60 °C until 3a was completely consumed. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 9 (78 mg, 0.13 mmol).

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, EtOH (1.0 ml), 3a (131 mg, 0.25 mmol) and H₂O (18 mg, 1.0 mmol) were added. The mixture was stirred at 60 °C until 3a was completely consumed. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 10 (91 mg, 0.21 mmol).

3. X-Ray diffraction analysis

3.1 Crystal data and structure refinement for 3a
3.2 Crystal data and structure refinement for 4a
| Property                        | Value                      |
|--------------------------------|----------------------------|
| Temperature/K                  | 99.99(10)                  |
| Crystal system                 | triclinic                  |
| Space group                    | P-1                        |
| a/Å                            | 9.7670(4)                  |
| b/Å                            | 13.1585(5)                 |
| c/Å                            | 15.3873(6)                 |
| α/°                            | 114.501(4)                 |
| β/°                            | 94.670(3)                  |
| γ/°                            | 99.144(3)                  |
| Volume/Å³                      | 1752.57(13)                |
| Z                              | 2                          |
| ρ<sub>calc</sub>/cm³           | 1.443                      |
| μ/mm⁻³                         | 0.530                      |
| F(000)                         | 780.0                      |
| Crystal size/mm³               | 0.17 × 0.13 × 0.12         |
| Radiation                      | MoKα (λ = 0.71073)         |
| 2Θ range for data collection/° | 4.282 to 59.008            |
| Index ranges                   | -12 ≤ h ≤ 13, -16 ≤ k ≤ 17, -20 ≤ l ≤ 21 |
| Reflections collected          | 23216                      |
| Independent reflections        | 8346 [R<sub>int</sub> = 0.0398, R<sub>sigma</sub> = 0.0522] |
| Data/restraints/parameters     | 8346/0/433                 |
| Goodness-of-fit on F²          | 1.043                      |
| Final R indexes [I>2σ (I)]     | R₁ = 0.0625, wR₂ = 0.1406  |
| Final R indexes [all data]     | R₁ = 0.0836, wR₂ = 0.1558  |
| Largest diff. peak/hole / e Å³ | 1.17/-1.05                 |
4. Copies of NMR spectrum

Unless otherwise noted, the spectra were performed in CDCl₃.

\((E)\)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-
diphenylmethanimine oxide (3a)
$^{13}$C NMR (100M CD$_2$Cl$_2$) of 3a
(E)-1-(4-oxo-1-phenyl-3-(p-tolyl)-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (3b)
(E)-1-(3-(4-fluorophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (3c)
(E)-1-(3-(4-chlorophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8(3H)-yl)-N,1-diphenylmethanimine oxide (3d)
(E)-1-(3-(4-bromophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (3e)
(E)-1-(3-(4-nitrophenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (3f)
(E)-1-(3-(4-isopropylphenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (3g)
(E)-1-(3-(3,5-di-tert-butylphenyl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl) -N,1-diphenylmethanimine oxide (3h)
(E)-1-(3-(naphthalen-1-yl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (3i)
(E)-1-(3-(furan-2-yl)-4-oxo-1-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-
diphenylmethanimine oxide (3j)
(E)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenyl-1-
(p-tolyl)methanimine oxide (3l)
(E)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenyl-1-(m-tolyl)methanimine oxide (3m)
$^{13}$C NMR (100M CD$_2$Cl$_2$) of 3m
(E)-1-(4-methoxyphenyl)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenylmethanimine oxide (3n)
(E)-1-(4-fluorophenyl)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenylmethanimine oxide (3o)
(E)-1-(4-chlorophenyl)-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N-phenylmethanimine oxide (3p)
$^{13}$C NMR (100M CD$_2$Cl$_2$) of 3p
(E)-1-cyclopropyl-1-(4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]benzo[3,4]dihydroisoxazol-8b(3H)-yl)N-phenylmethanimine oxide (3g)
(E)-1-(7-fluoro-4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (38)
(E)-1-(7-chloro-4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-diphenylmethanimine oxide (3t)
(E)-1-(7-methoxy-4-oxo-1,3-diphenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-N,1-
diphenylmethanimine oxide (3u)
$^{13}$C NMR (100M CD$_2$Cl$_2$) of 3u
(E)-1-(4-oxo-3-phenyl-1-(p-tolyl)-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-1-phenyl-N-(p-tolyl)methanamine oxide (3v)
(E)-N-(4-acetylphenyl)-1-(1-(4-acetylphenyl)-4-oxo-3-phenyl-3a,4-dihydro-1H-indeno[1,2-c]isoxazol-8b(3H)-yl)-1-phenylmethanimine oxide (3w)
(E)-N-(4-bromophenyl)-1-(1-(4-bromophenyl)-4-oxo-3-phenyl-3a,4-dihydro-1H-indeno [1,2-c]isoxazol-8b(3H)-yl)-1-phenylmethanimine oxide (3x)
(E)-9-oxo-N,1,3,9a-tetraphenyl-3,3a,9,9a-tetrahydronaphtho[2,3-c]isoxazol-4(1H)-imine oxide (4a)
8b-(2,3-diphenyl-2,3-dihydrobenzo[d]isoxazol-3-yl)-1,3-diphenyl-1,3,3a,8b-tetrahydro-4H-indeno[1,2-c]isoxazol-4-one (9)
8b-benzoyl-1,3-diphenyl-1,3a,8b-tetrahydro-4H-indeno[1,2-c]isoxazol-4-one (10)