Supporting Information

Lithium tert-Butoxide-Mediated Efficient Transesterification of *N*-Hydroxyphthalimide Esters toward Oxime Functionalization

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(A). General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

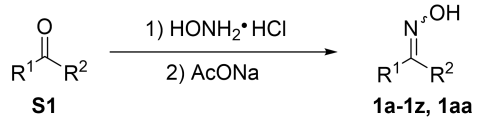
NMR spectrum: All ^{1}H, ^{13}C and ^{19}F spectra are recorded on the Bruker AVANCE spectrometer, operating at 300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR and 564 MHz for ^{19}F NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from $CDCl_3$ (δ: 7.26 ppm) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), m (multiple), dd (doublet of doublet). Coupling constants are reported in Hertz (Hz).

Mass spectroscopy: High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry.

Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

Melting point: Melting point was recorded on Hanon MP100 Apparatus.

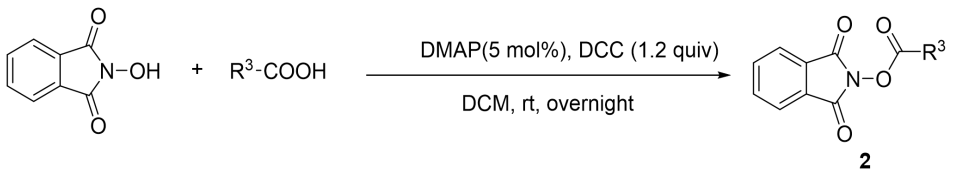
(a) General Procedure for the preparation of Oximes 1



S1 **1a-1z, 1aa**

To a solution of ketone (5 mmol) in 20 mL methol was added sodium acetate (25 mmol) and hydroxylamine hydrochloride (15 mmol) at room temperature. The mixture was heated to reflux for overnight. Then, the mixture was concentrated in vacuo, extracted with ethyl acetate and the combined organic layers were washed with water and brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford the oxime.[1]

(b) General Procedure for the preparation of NHPI esters



The corresponding carboxylic acids (12 mmol, 1.2 equiv), *N*-hydroxyphthalimide (1.63 g, 10 mmol, 1.0 equiv), and 4-dimethylaminopyridine (61 mg, 0.5 mmol, 5 mol %) were mixed in a flask with a magnetic stirring bar, 30 mL CH_2Cl_2 was added. Then a solution of *N*, *N′*-dicyclohexylcarbodiimide (2.06 g, 12mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) was added slowly at room temperature. The reaction mixture was maintained at room temperature with stirring for overnight. When the *N*-hydroxyphthalimide was completely converted, the white precipitate was filtered off and the solution was concentrated on a rotary evaporator. The residue was purified by flash column chromatography to give corresponding redox active esters. [2]

(c) General Procedure and Date for Compounds 3 or 4

The oximes **1** (0.2 mmol), NHPI esters **2** (0.3 mmol), *t*-BuOLi (1.5 equiv) and acetonitrile (3.0 mL) were orderly added to a 10 mL Schlenk tube. Then, the mixture was stirring at room temperature for 3 h. After completion of the reaction (monitored by TLC), the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product **3** or **4**.

(d) Gram-Scale Preparation of 4b.

The oximes **1a** (0.68g, 5 mmol), NHPI esters **2b** (1.55g, 7.5 mmol), *t*-BuOLi (1.5 equiv) and acetonitrile (20 mL) were orderly added to a 50 mL round-bottom flak. Then, the mixture was stirring at room temperature for 6 h. After completion of the reaction (monitored by TLC), the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product **4b** (1.11g, 93%).

(e) Derivatization of 4b.

The oxime ester **4b** (0.2 mmol), PhCHO (0.24 mmol, 1.2 equiv), Cs_2CO_3 (2.0 equiv), and DMSO (2 mL) were sequentially added to a 10 mL Schlenk tube. The

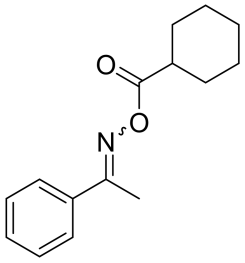
mixture was then stirred at room temperature for 0.5 hours. Upon completion of the reaction, as monitored by TLC, the solvent was diluted with EtOAc, washed with water, and the residue was subjected to silica gel column chromatography using petroleum ether/ethyl acetate as the eluent, affording product **5** in a 72% yield.

The oxime ester **4b** (0.2 mmol), $Et_2O \cdot BF_3$ (1.0 mmol, 5 equiv), DCE (2 mL) were sequentially added to a 10 mL Schlenk tube. The mixture was then stirred at room temperature for 18 hours. Upon completion of the reaction, as monitored by TLC, the solvent was removed under vocanno and the residue was subjected to silica gel column chromatography using petroleum ether/ethyl acetate as the eluent, affording product **6** in a 64% yield.

The oxime ester **4b** (0.2 mmol), $LiAlH_4$ (1.0 M in THF, 1 mL, 5 equiv), THF (2 mL) were sequentially added to a 10 mL Schlenk tube. The mixture was then stirred at room temperature for 2 hours. Upon completion of the reaction, as monitored by TLC, the solvent was quenched with saturated NH_4Cl solution and extracted three times with ethyl acetate. The combined organic layers were subjected to silica gel column chromatography using petroleum ether/ethyl acetate as the eluent, yielding product **7** in an 83% yield.

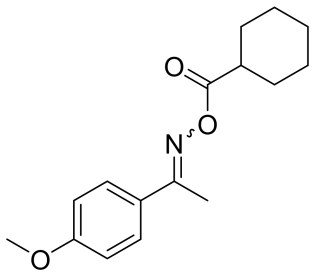
(B) Analytical data for products

1-phenylethan-1-one *O*-cyclohexanecarbonyl oxime (3a):



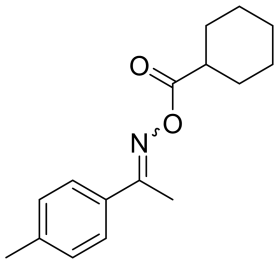
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 98%, 47.8 mg, white solid. mp 94.4-95.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.7 Hz, *J* =1.7 Hz, 2H), 7.51-7.34 (m, 3H), 2.56-2.47 (m, 1H), 2.38 (s, 3H), 2.02 (d, *J* = 13.3 Hz, 1H), 1.84-1.79 (m, 2H), 1.70-1.52 (m, 3H), 1.40-1.24 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 173.1, 162.8, 134.9, 130.5, 128.5, 127.0, 42.3, 29.3, 25.7, 25.4, 14.4. HRMS (ESI) Calcd for $C_{15}H_{20}NO_2$ [M+H$^+$] 246.1489, found 246.1485.

1-(4-methoxyphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3b):



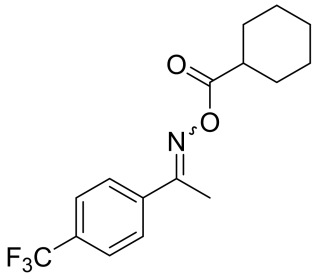
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 89%, 49.0 mg, white solid. mp 52.1-53.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.27 (m, 3H), 7.00 – 6.97 (m, 1H), 3.84 (s, 3H), 2.57-2.49 (m, 1H), 2.37 (s, 3H), 2.05-2.01 (m, 2H), 1.83-1.81 (m, 1H), 1.70 -1.54 (m, 3H), 1.41-1.22 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 173.1, 162.8, 159.5, 136.3, 134.7, 129.5, 123.8, 119.5, 116.5, 112.0, 55.3, 42.3, 29.0, 25.6, 25.4, 14.5. HRMS (ESI) Calcd for $C_{16}H_{22}NO_3$ [M+H$^+$] 276.1594, found 276.1588.

1-(*p*-tolyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3c):



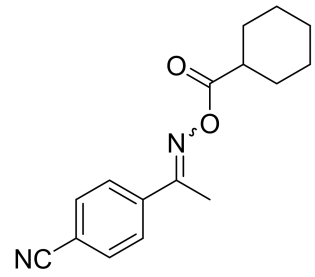
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 99%, 51.5 mg, off-white solid. mp 71.3-72.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.55-2.46 (m, 1H), 2.36 (s, 6H), 1.99-1.98 (m, 1H), 1.83-1.78 (m, 2H), 1.71-1.51 (m, 3H), 1.39-1.22 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 173.2, 162.7, 140.8, 131.9, 129.2, 126.9, 42.3, 29.0, 25.6, 25.4, 21.3, 21.0, 14.3, 14.1. HRMS (ESI) Calcd for $C_{16}H_{22}NO_2$ [M+H$^+$] 260.1645, found 260.1645.

1-(4-(trifluoromethyl)phenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3d):



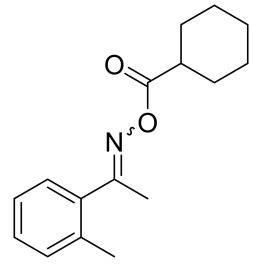
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 65%, 40.7 mg, white solid. mp 78.8-79.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 6.9 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 2.53 (tt, *J* = 11.1Hz, *J* = 3.6 Hz, 1H), 2.42 (s, 3H), 2.02 (d, *J* = 13.2 Hz, 2H), 1.84-1.79 (m, 2H), 1.71-1.52 (m, 4H), 1.41-1.28 (m, 2H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 172.9, 161.5, 159.8, 135.8, 130.8, 130.2, 129.1, 127.1, 127.1, 125.6, 123.8 ($J_{C\text{-}F}$ = 6.25 Hz), 42.3, 29.0, 25.6, 25.4, 14.4. ^{19}F NMR (564 MHz, $CDCl_3$): -62.7. HRMS (ESI) Calcd for $C_{16}H_{29}F_3NO_2$ [M+H$^+$] 314.1362, found 314.1358.

4-(1-(((cyclohexanecarbonyl)oxy)imino)ethyl)benzonitrile (3e):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 93%, 50.2 mg, white solid. mp 121.7-122.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 2.52 (tt, *J* = 11.3 Hz, *J* = 3.6 Hz, 1H), 2.39 (S, 3H), 2.04-1.98 (m, 2H), 1.83-1.78 (m, 2H), 1.72-1.51 (m, 3H), 1.40-1.23 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 172.7, 170.0, 139.2, 132.3, 127.6, 118.2, 113.9, 42.2, 29.0, 25.6, 25.3, 14.2. HRMS (ESI) Calcd for $C_{16}H_{19}N_2O_2$ [M+H$^+$] 271.1441, found 271.1436.

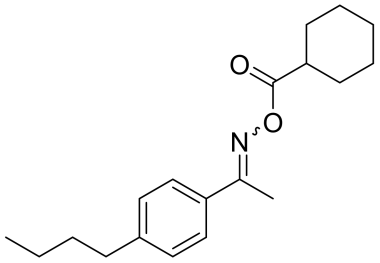
1-(*o*-tolyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3f):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:12. Yield = 79%, 40.8 mg, yellow solid. mp 99.6-100.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.18 (m, 4H), 2.52 (tt, *J* = 11.4 Hz, *J* = 3.6 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H), 2.05-2.01 (m, 2H), 1.85-1.79 (m, 2H), 1.70-1.52 (m, 4H), 1.40-1.36 (m, 2H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.1, 165.5, 135.8, 135.7, 130.7,

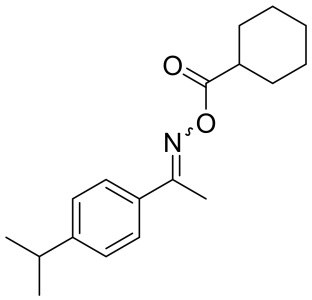
129.2, 128.2, 125.8, 42.3, 29.0, 25.7, 25.4, 20.1, 18.0. HRMS (ESI) Calcd for $C_{16}H_{22}NO_2$ [M+H$^+$] 260.1645, found 260.1643.1

1-(4-butylphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3g):



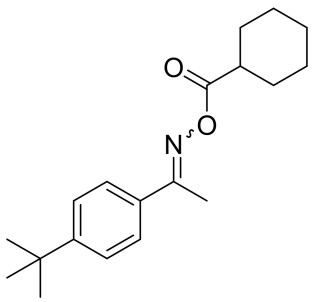
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:12. Yield = 99%, 59.6 mg, yellow solid. mp 79.1-80.4 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.51 (tt, *J* = 11.4 *Hz, J* = 3.6 Hz, 1H), 2.36 (s, 3H), 2.05-1.98 (m, 2H), 1.83-1.78 (m, 2H), 1.69-1.51 (m, 5H), 1.40-1.23 (m, 5H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.2, 162.8, 145.7, 132.1, 128.5, 126.9, 42.3, 35.4, 33.3, 29.0, 25.6, 25.4, 22.2, 14.3, 13.9. HRMS (ESI) Calcd for $C_{19}H_{28}NO_2$ [M+H$^+$] 302.2115, found 302.2111.

1-(4-isopropylphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3h):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 99%, 57.0 mg, white solid. mp 64.7-65.2 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 2.93 (dt, *J* = 13.8 Hz, *J* = 6.9 Hz, 1H), 2.53 (tt, *J* = 11.3 Hz, *J* =3.6 Hz, 1H), 2.37 (s, 3H), 2.09-1.95 (m, 2H), 1.81 (dd, *J* = 9.6, *J* = 2.8 Hz, 2H), 1.73-1.48 (m, 3H), 1.43-1.28 (m, 3H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.2, 162.8, 151.6, 132.4, 127.0, 126.6, 42.3, 33.9, 29.0, 25.6, 25.4, 23.7, 14.3. HRMS (ESI) Calcd for $C_{18}H_{26}NO_2$ [M+H$^+$] 288.1958, found 288.1956.

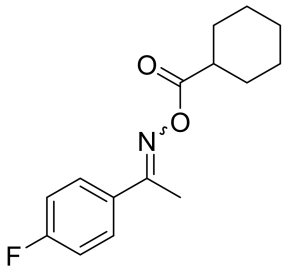
1-(4-(tert-butyl)phenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3i):



Column chromatography was eluted with ethyl acetate:

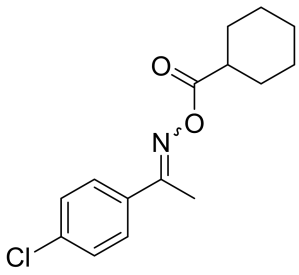
petroleum ether = 1:15. Yield = 90%, 54.1 mg, white solid. mp 71.2-71.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 2.53 (tt, J = 11.3, 3.6 Hz, 1H), 2.37 (s, 3H), 2.02 (d, J = 12.9 Hz, 2H), 1.81 (dd, J = 9.6, 2.8 Hz, 2H), 1.72-1.50 (m, 4H), 1.43-1.33 (m, 2H), 1.32 (s, 9H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.2, 162.7, 153.9, 132.0, 126.7, 125.5, 42.4, 34.8, 31.1, 29.0, 25.7, 25.4, 14.3. HRMS (ESI) Calcd for $C_{19}H_{28}NO_2$ [M+H$^+$] 302.2115, found 302.2108.

1-(4-fluorophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3j):



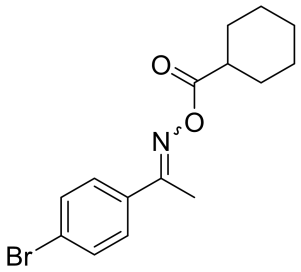
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 98%, 51.4 mg, off-white solid. mp 57.8-58.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 8.7 Hz, *J* = 5.4 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 2.52 (tt, *J* = 11.3, *J* = 3.5 Hz, 1H), 2.37 (s, 3H), 2.01 (d, *J* = 13.2 Hz, 2H), 1.81 (dd, *J* = 9.6 Hz, *J* = 2.8 Hz, 2H), 1.75 -1.61 (m, 2H), 1.59-1.50 (m, 1H), 1.40-1.24 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.1, 165.8, 162.5, 161.7, 131.0, 131.0, 129.1, 129.0, 115.7, 115.4, 42.3, 29.0, 25.6, 25.4, 14.4. ^{19}F NMR (564 MHz, $CDCl_3$): -109.9. HRMS (ESI) Calcd for $C_{15}H_{19}FNO_2$ [M+H$^+$] 264.1394, found 264.1388.

1-(4-chlorophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3k):



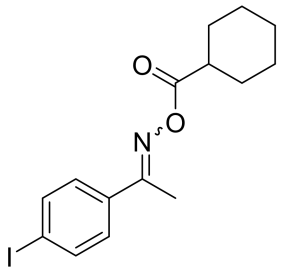
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 95%, 52.9 mg, off-white solid. mp 67.0-68.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 2.51 (tt, *J* = 11.3, *J* = 3.6 Hz, 1H), 2.36 (s, 3H), 2.00 (d, *J* = 13.2 Hz, 2H), 1.83-1.78 (m, 2H), 1.70-1.50 (m, 3H), 1.40-1.23 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.0, 161.6, 136.6, 133.3, 128.7, 128.3, 42.23, 29.0, 25.6, 25.4, 14.2. HRMS (ESI) Calcd for $C_{15}H_{19}ClNO_2$ [M+H$^+$] 280.1099, found 280.1093.

1-(4-bromophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3l):



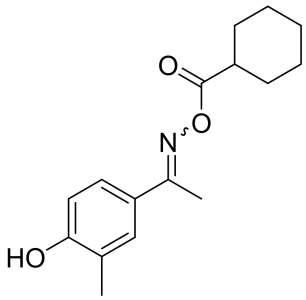
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 99%, 64.4 mg, off-white solid. mp 85.8-86.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 2.52 (tt, *J* = 11.4 Hz, *J* = 3.6 Hz, 1H), 2.36 (s, 3H), 2.01 (d, *J* = 13.2 Hz, 2H), 1.83-1.78 (m, 2H), 1.70-1.51 (m, 4H), 1.40-1.24 (m, 2H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.0, 161.7, 133.8, 131.7, 128.5, 125.1, 42.3, 29.0, 25.6, 25.4, 14.2. HRMS (ESI) Calcd for $C_{15}H_{19}BrNO_2$ [M+H$^+$] 324.0594, found 324.0591.

1-(4-iodophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3m):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:20. Yield = 85%, 62.9 mg, off-white solid. mp 90.1-91.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 2.51 (tt, *J* = 11.4 Hz, *J* = 3.6 Hz, 1H), 2.35 (s, 3H), 2.00 (d, *J* = 13.1 Hz, 2H), 1.83-1.78 (m, 2H), 1.69-1.50 (m, 3H), 1.39-1.25 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.0, 161.9, 137.7, 134.3, 128.5, 97.2, 42.3, 29.0, 25.6, 25.4, 14.1. HRMS (ESI) Calcd for $C_{15}H_{19}INO_2$ [M+H$^+$] 372.0455, found 372.0451.

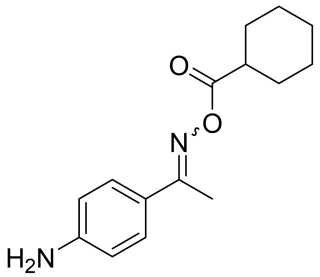
1-(4-hydroxy-3-methylphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3n):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:6. Yield = 54%, 29.7 mg, white solid. mp 70.4-71.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (s, 0.6 H), 7.49 (s, 1H), 7.45 (dd, *J* = 8.4 Hz, *J* = 2.1 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 2.60 (tt, *J* = 11.3 Hz, *J* = 3.6 Hz, 1H), 2.27 (s, 3H), 2.19 (s, 3H), 2.09 (d, *J* = 13.2 Hz, 2H), 1.86-1.81 (m, 2H), 1.73-1.55 (m, 3H), 1.45-1.25 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 174.1, 155.5, 150.2, 134.1, 130.3, 128.8, 124.7, 122.0, 43.2, 29.0, 25.7, 25.4, 16.3,

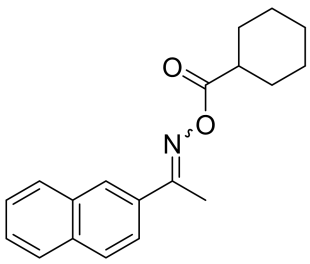
12.2. HRMS (ESI) Calcd for $C_{16}H_{22}NO_3$ [M+H$^+$] 276.1594, found 276.1592.

1-(4-aminophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3o):



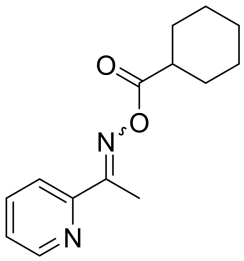
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:4. Yield = 66%, 34.3 mg, yellow solid. mp 77.4-79.2 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 3.84 (brs, 2H), 2.50 (t, *J* = 11.3 Hz, 1H), 2.31 (s, 3H), 2.00 (d, *J* = 12.3 Hz, 2H), 1.81-1.78 (m, 2H), 1.69 -1.50 (m, 3H), 1.39-1.23 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.4, 162.5, 148.8, 129.9, 128.4, 124.4, 114.4, 42.4, 29.0, 25.7, 25.4, 13.9. HRMS (ESI) Calcd for $C_{15}H_{21}N_2O_2$ [M+H$^+$] 261.1598, found 261.1595.

1-(naphthalen-2-yl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3p):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:12. Yield = 69%, 40.7 mg, yellow solid. mp 90.2-90.8 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.5 Hz, 1H), 7.91-7.86 (m, 2H), 7.57-7.44 (m, 4H), 2.57 (tt, *J* = 11.4 Hz, *J* = 3.6 Hz, 1H), 2.50 (s, 3H), 2.07 (d, *J* = 13.4 Hz, 2H), 1.84 (d, *J* = 12.3 Hz, 2H), 1.72-1.56 (m, 3H), 1.43-1.25 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.1, 165.1, 133.7, 133.6, 130.45, 130.0, 128.5, 126.9, 126.4, 126.1, 125.1, 125.0, 42.3, 29.1, 25.7, 25.4, 18.8. HRMS (ESI) Calcd for $C_{19}H_{22}NO_2$ [M+H$^+$] 296.1645, found 296.1646.

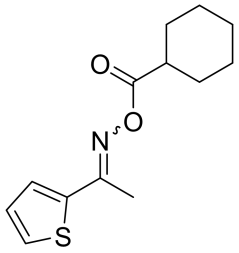
1-(pyridin-2-yl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3q):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:8. Yield = 99%, 48.6 mg, (E/Z = 16:9), yellow solid. mp 63.9-64.5 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (d, *J* = 3.1 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 0.64H), 7.78-7.66 (m, 1.36H), 7.36-7.27 (m, 1H), 2.59-2.50 (m, 0.66H), 2.49 (s,

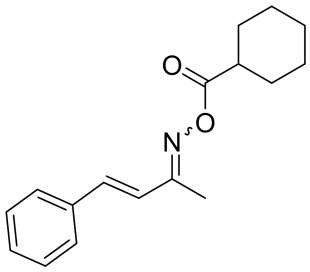
2H), 2.40 (s, 1H), 2.38-2.26 (m, 0.35H), 2.05-1.91 (m, 2H), 1.83-1.73 (m, 2H), 1.69-1.56 (m, 2H), 1.52-1.39 (m, 1H), 1.37-1.29 (m, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 181.1, 173.0, 163.5, 152.7, 149.0, 136.5, 136.4, 124.9, 123.8, 122.0, 120.5, 42.8, 42.3, 29.0, 28.9, 25.7, 25.6, 25.4, 12.8, 11.0. HRMS (ESI) Calcd for $C_{14}H_{19}N_2O_2$ [M+H$^+$] 247.1441, found 247.1439.

1-(thiophen-2-yl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3r):



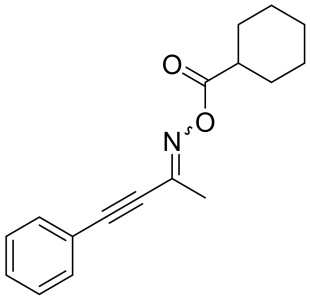
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:10. Yield = 98%, 49.2 mg, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 5.1 Hz, 1H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.13 (t, *J* = 4.2 Hz, 1H), 2.57 (tt, J = 11.5 Hz, 3.5 Hz, 1H), 2.48 (s, 3H), 2.04 (d, *J* = 13.2 Hz, 2H), 1.84-1.79 (m, 2H), 1.69-1.55 (m, 3H), 1.42-1.23 (m, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 172.9, 153.0, 134.6, 132.6, 132.0, 131.6, 126.2, 123.8, 42.4, 28.9, 25.6, 25.3, 20.1. HRMS (ESI) Calcd for $C_{13}H_{18}NO_2S$ [M+H$^+$] 252.1053, found 252.1048.

(3*E*)-4-phenylbut-3-en-2-one *O*-cyclohexanecarbonyl oxime (3s):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 87%, 47.1 mg, off-white solid. mp 50.7-51.2 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 6.9 Hz, 2H), 7.36 (dd, *J* = 14.7 Hz, *J* = 7.2 Hz, 3H), 7.06 (s, 2H), 2.49 (tt, *J* = 11.4 Hz, *J* = 3.6 Hz, 1H), 2.23 (s, 3H), 2.01 (*d*, *J* = 11.0 Hz, 2H), 1.84-1.78 (m, 2H), 1.70-1.51 (m, 3H), 1.40-1.23 (m, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 173.0, 162.6, 137.1, 135.5, 129.1, 128.8, 127.1, 124.4, 42.3, 28.9, 25.6, 25.3, 11.6. HRMS (ESI) Calcd for $C_{17}H_{22}NO_2$ [M+H$^+$] 272.1645, found 272.1645.

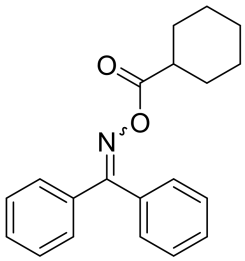
4-phenylbut-3-yn-2-one *O*-cyclohexanecarbonyl oxime (3t):



Column chromatography was eluted with ethyl acetate:

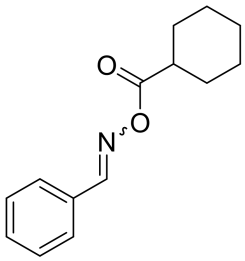
petroleum ether = 1:15. Yield = 98%, 52.7 mg, white solid. mp 71.9-72.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 7.7 Hz, *J* = 1.5 Hz, 2H), 7.42 -7.29 (m, 3H), 2.48 (tt, *J* = 11.3 Hz, *J* = 3.6 Hz, 1H), 2.24 (s, 3H), 1.98 (d, *J* = 13.1 Hz, 2H), 1.81-1.76 (m, 2H), 1.68-1.49 (m, 3H), 1.38 -1.22 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 172.2, 150.4, 132.1, 129.7, 128.4, 121.1, 93.8, 84.0, 42.1, 28.9, 25.5, 25.3, 18.3. HRMS (ESI) Calcd for $C_{17}H_{20}NO_2$ [M+H$^+$] 270.1489, found 270.1487.

diphenylmethanone *O*-cyclohexanecarbonyl oxime (3u):



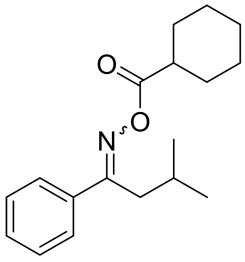
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:20. Yield = 97%, 59.6 mg, white solid. mp 103.4-104.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.50 -7.41 (m, 4H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.33-7.28 (m, 2H), 2.30 (tt, *J* = 11.1 Hz, *J* = 3.5 Hz, 1H), 1.80 (d, *J* = 12.9 Hz, 2H), 1.71-1.59 (m, 3H), 1.42-1.33 (m, 2H), 1.28-1.17 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.1, 165.2, 134.7, 132.6, 130.8, 129.5, 129.0, 128.7, 128.3, 128.1, 42.0, 28.6, 25.6, 25.2. HRMS (ESI) Calcd for $C_{20}H_{22}NO_2$ [M+H$^+$] 308.1645, found 308.1642.

benzaldehyde *O*-cyclohexanecarbonyl oxime (3v)[3]:



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 93%, 43.0 mg, off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.75-7.23 (m, 2H), 7.50 – 7.38 (m, 3H), 2.47 (tt, *J* = 11.4 Hz, *J* = 3.6 Hz, 1H), 1.99 (d, *J* = 13.2 Hz, 2H), 1.83-1.78 (m, 2H), 1.73-1.50 (m, 3H), 1.39-1.23 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.3, 156.0, 131.6, 130.2, 128.8, 128.3, 42.0, 28.9, 25.6, 25.3.

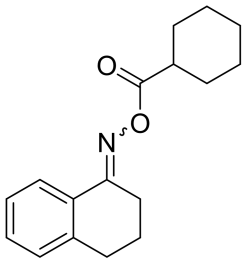
3-methyl-1-phenylbutan-1-one *O*-cyclohexanecarbonyl oxime (3w):



Column chromatography was eluted with ethyl acetate:

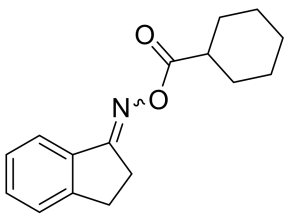
petroleum ether = 1:15. Yield = 67%, 38.5 mg, (E/Z = 53:47), yellow solid. mp 101.2-101.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.36 (m, 4H), 7.14 (dd, *J* = 6.5 Hz, *J* = 3.0 Hz, 1H), 3.57-3.46 (m, 0.52 H), 3.06 -2.96 (m, 0.41H), 2.50 (tt, *J* = 11.4, *J* = 3.6 Hz, 0.53H), 2.16 (tt, *J* = 10.8 Hz, *J* = 3.5 Hz, 0.47H), 2.02 (d, *J* = 13.2 Hz, 1H), 1.81 (dd, *J* = 9.6 Hz, *J* = 2.8 Hz, 1H), 1.70-1.52 (m, 5H), 1.41-1.27 (m, 4H), 1.23 (d, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.14-1.10 (m, 1H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.3, 173.0, 172.6, 172.2, 134.1, 133.0, 129.4, 128.7, 128.2, 128.0, 126.7, 42.4, 42.0, 35.0, 30.0, 29.0, 28.5, 25.6, 25.6, 25.4, 25.2, 19.8, 19.6. HRMS (ESI) Calcd for $C_{18}H_{26}NO_2$ [M+H$^+$] 288.1958, found 288.1953.

3,4-dihydronaphthalen-1(2H)-one *O*-cyclohexanecarbonyl oxime (3x):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:12. Yield = 97%, 52.4 mg, white solid. mp 111.7-111.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.27-7.20 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 2.87 (t, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.52 (tt, *J* = 11.3 Hz, *J* = 3.4 Hz, 1H), 2.05-1.99 (m, 2H), 1.88 (dd, *J* = 12.7 Hz, *J* = 6.6 Hz, 2H), 1.88-1.79 (m, 2H), 1.70 -1.51 (m, 3H), 1.40-1.28 (m, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 173.2, 161.7, 140.8, 130.6, 128.9, 128.6, 126.5, 125.7, 42.4, 29.5, 29.0, 25.6, 25.6, 25.4, 21.2. HRMS (ESI) Calcd for $C_{17}H_{22}NO_2$ [M+H$^+$] 272.1645, found 272.1643.

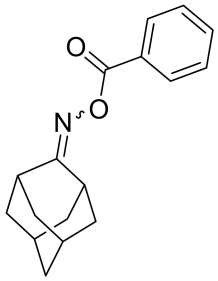
2,3-dihydro-1H-inden-1-one *O*-cyclohexanecarbonyl oxime (3y):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:12. Yield = 99%, 50.8 mg, off-white solid. mp 92.8-94.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.37-7.27 (m, 2H), 3.08-3.00 (m, 4H), 2.51 (tt, *J* = 11.1Hz, *J* =3.6 Hz, 1H), 2.05-1.98 (m, 2H), 1.81 (dd, *J* = 9.3 Hz, *J* = 3.0 Hz, 2H), 1.70-1.64 (m, 1H), 1.61-1.52 (m, 2H), 1.40-1.28

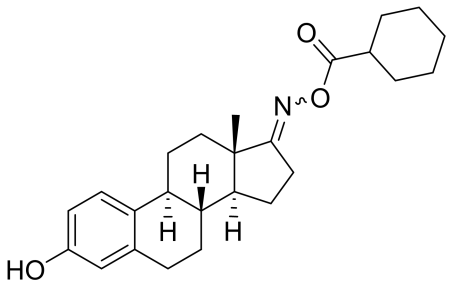
(m, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 173.4, 170.7, 149.7, 134.3, 132.0, 127.2, 125.5, 123.2, 42.3, 29.1, 28.4, 27.6, 25.6, 25.4. HRMS (ESI) Calcd for $C_{16}H_{20}NO_2$ [M+H$^+$] 258.1489, found 258.1485.

adamantan-2-one *O*-benzoyl oxime (3z):



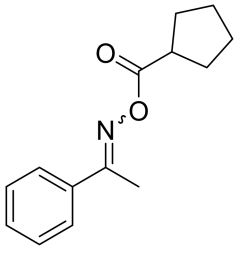
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15. Yield = 84%, 45.3 mg, white solid. mp 78.3-79.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 3.62 (s, 1H), 2.92 (s, 1H), 2.10-1.89 (m, 12H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 175.6, 164.5, 133.0, 129.5, 128.4, 38.8, 37.8, 36.1, 31.4, 27.4. HRMS (ESI) Calcd for $C_{17}H_{20}NO_2$ [M+H$^+$] 270.1489, found 270.1486.

(8R,9S,13S,14S)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one *O*-cyclohexanecarbonyl oxime (3aa):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:10. Yield = 68%, 53.8 mg, white solid. mp 198.3-199.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 0.64H), 7.27 (d, *J* = 8.7 Hz, 1H), 6.83-6.77 (m, 2H), 2.89-2.86 (m, 2H), 2.59-2.48 (m, 3H), 2.40-2.26 (m, 2H), 2.12-2.02(m, 3H), 1.97-1.93 (m, 2H), 1.83-1.79 (m, 2H), 1.71-1.24 (m, 12H), 0.95 (s, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 174.9, 171.1, 148.6, 137.9, 137.3, 126.3, 121.5, 118.6, 52.8, 44.2, 44.1, 43.1, 37.7, 33.9, 29.4, 28.9, 27.0, 25.9, 25.7, 25.3, 25.1, 22.9, 17.1. HRMS (ESI) Calcd for $C_{25}H_{34}NO_3$ [M+H$^+$] 396.2533, found 396.2524.

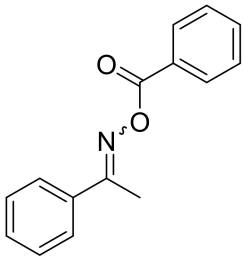
1-phenylethan-1-one *O*-cyclopentanecarbonyl oxime (4a):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15 Yield = 85%, 39.2 mg, white solid. mp

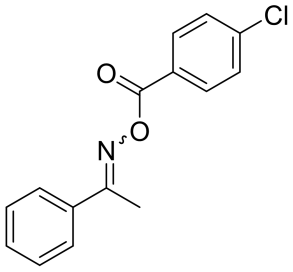
54.9-55.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 7.7 Hz, *J* = 1.6 Hz, 2H), 7.47 -7.36 (m, 3H), 3.01-2.89 (m, 1H), 2.39 (s, 3H), 2.02-1.90 (m, 4H), 1.80-1.72 (m, 2H), 1.70-1.59 (m, 2H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 174.1, 162.6, 135.0, 130.5, 128.5, 127.0, 42.6, 30.1, 25.9, 14.4. HRMS (ESI) Calcd for $C_{14}H_{18}NO_2$ [M+H$^+$] 232.1332, found 232.1330.

1-phenylethan-1-one *O*-benzoyl oxime (4b) [4]:



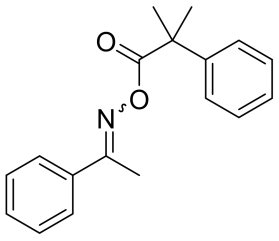
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15 Yield = 98%, 47.1 mg, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16-8.12 (m, 2H), 7.83 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.53-7.40 (m, 5H), 2.53 (s, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 163.8, 163.6, 134.8, 133.3, 130.7, 129.6, 129.1, 128.6, 127.1,

1-phenylethan-1-one *O*-(4-chlorobenzoyl) oxime (4c) [5]:



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15 Yield = 72%, 39.5 mg, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.82 (dd, *J* = 7.5Hz, *J* = 1.2 Hz, 2H), 7.49-7.40 (m, 5H), 2.52 (s, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 163.8, 163.0, 139.8, 134.6, 131.0, 130.8, 129.0, 128.6, 127.5, 127.1, 14.8.

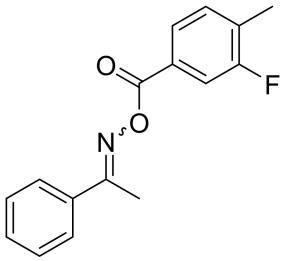
1-phenylethan-1-one *O*-(2-methyl-2-phenylpropanoyl) oxime (4d):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15 Yield = 90%, 50.6 mg, white solid. mp 65.7-67.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 2H), 7.46-7.32 (m, 7H), 7.29-7.23 (m, 1H), 2.13 (s, 3H), 1.72 (s, 6H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 163.5, 144.2, 134.8, 130.5, 128.5, 128.4, 127.0, 126.8, 125.7, 46.5, 26.6, 14.2. HRMS

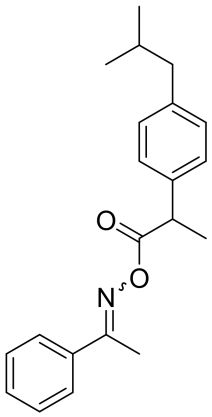
(ESI) Calcd for $C_{18}H_{20}NO_2$ [M+H$^+$] 282.1489, found 282.1482.

1-phenylethan-1-one *O*-(3-fluoro-4-methylbenzoyl) oxime (4e):



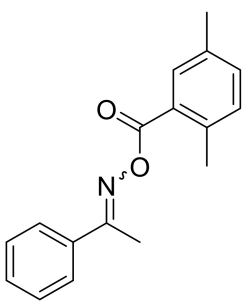
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15 Yield = 64%, 38.0 mg, (Z/E = 1:1), off-white solid. mp 62.9-64.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84-7.81 (m, 2H), 7.78-7.70 (m, 1H), 7.49-7.42 (m, 3H), 7.35-7.21 (m, 2H), 2.57 (s, 1.5H), 2.54 (s, 1.5H), 2.49 (s, 1.5H), 2.37 (s, 1.5H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 163.8, 134.6, 131.7, 131.6, 130.8, 128.6, 127.1, 127.1, 126.7, 126.6, 125.7, 125.2, 119.1, 118.8, 116.2, 115.9, 14.9, 14.8, 12.0, 11.9. ^{19}F NMR (564 MHz, $CDCl_3$): -114.8, -116.2. HRMS (ESI) Calcd for $C_{16}H_{15}FNO_2$ [M+H$^+$] 272.1081, found 272.1077.

1-phenylethan-1-one *O*-(2-(4-isobutylphenyl)propanoyl) oxime (4f):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15 Yield = 83%, 53.6 mg, white solid. mp 77.6-79.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.8Hz, *J* = 1.8 Hz, 2H), 7.46-7.34 (m, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 3.91 (q, *J* = 7.2 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.91-1.77 (m, 1H), 1.61 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 171.8, 163.3, 140.7, 137.2, 134.7, 130.5, 129.4, 128.5, 127.3, 127.0, 45.0, 44.1, 30.2, 22.3, 18.4, 14.3. HRMS (ESI) Calcd for $C_{21}H_{26}NO_2$ [M+H$^+$] 324.1958, found 324.1953.

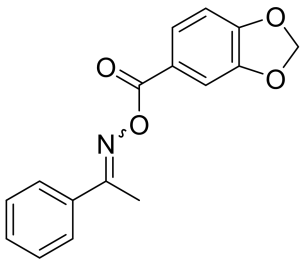
1-phenylethan-1-one *O*-(2,5-dimethylbenzoyl) oxime (4g):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:15 Yield = 82%, 43.8 mg, white solid. mp 74.5-75.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 7.8Hz, *J* = 1.5 Hz, 2H), 7.76 (s, 1H), 7.47 – 7.39 (m, 3H), 7.27

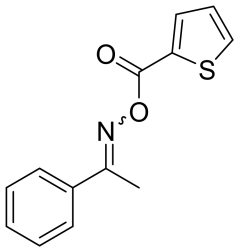
(d, *J* = 6.6 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 2.62 (s, 3H), 2.49 (s, 3H), 2.38 (s, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 165.0, 163.2, 137.2, 135.3, 134.8, 133.0, 131.7, 130.6, 130.6, 128.5, 128.3, 127.1, 21.1, 20.9, 14.9. HRMS (ESI) Calcd for $C_{17}H_{18}NO_2$ $[M+H^+]$ 268.1332, found 268.1328.

1-phenylethan-1-one *O*-(benzo[*d*][1,3]dioxole-5-carbonyl) oxime (4h):



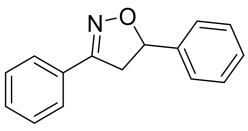
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:10 Yield = 52%, 29.2 mg, off-white solid. mp 127.4-129.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 2H), 7.75 (dd, *J* = 8.1Hz, *J* = 1.5 Hz, 1H), 7.55 (d, *J* = 1.5 Hz, 1H), 7.47-7.42 (m, 3H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.08 (s, 2H), 2.51 (s, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 163.3, 163.2, 151.9, 147.8, 134.8, 130.6, 128.6, 127.1, 125.5, 122.8, 109.4, 108.2, 101.9, 14.7. HRMS (ESI) Calcd for $C_{16}H_{14}NO_4$ $[M+H^+]$ 284.0917, found 284.0912.

1-phenylethan-1-one *O*-thiophene-2-carbonyl oxime (4i):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:10. Yield = 83%, 40.6 mg, off-white solid. mp 57.7-58.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, *J* = 2.1 Hz, 1H), 7.81 (dd, *J* = 7.7 Hz, *J* =1.7 Hz, 2H), 7.66-7.61 (m, 1H), 7.48-7.35 (m, 4H), 2.51 (s, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 163.4, 159.9, 134.8, 133.1, 131.9, 130.6, 128.6, 128.4, 127.7, 127.1, 126.3, 14.7. HRMS (ESI) Calcd for $C_{13}H_{12}NO_2S$ $[M+H^+]$ 246.0583, found 246.0581.

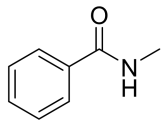
3,5-diphenyl-4,5-dihydroisoxazole (5):



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:40. Yield = 72%, 32.1 mg, pale-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72-7.68 (m, 2H), 7.43-7.30 (m, 8H), 5.75 (dd, *J* = 10.8 Hz, *J* = 8.1 Hz, 1H), 3.79 (dd, *J* = 16.8 Hz, *J* =

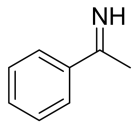
11.1 Hz, 1H), 3.35 (dd, *J* = 16.5 Hz, *J* = 8.2 Hz, 1H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$):δ 156.1, 140.9, 130.1, 129.4, 128.7, 128.2, 126.7, 125.9, 82.5, 43.2, 29.7.

***N*-methylbenzamide (6):**



Column chromatography was eluted with ethyl acetate: petroleum ether = 1:5. Yield = 64%, 17.3 mg, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$):δ 7.76 (bs, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.33-7.26 (m, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 2.16 (s, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 168.7, 137.9, 128.9, 124.3, 120.0, 24.5.

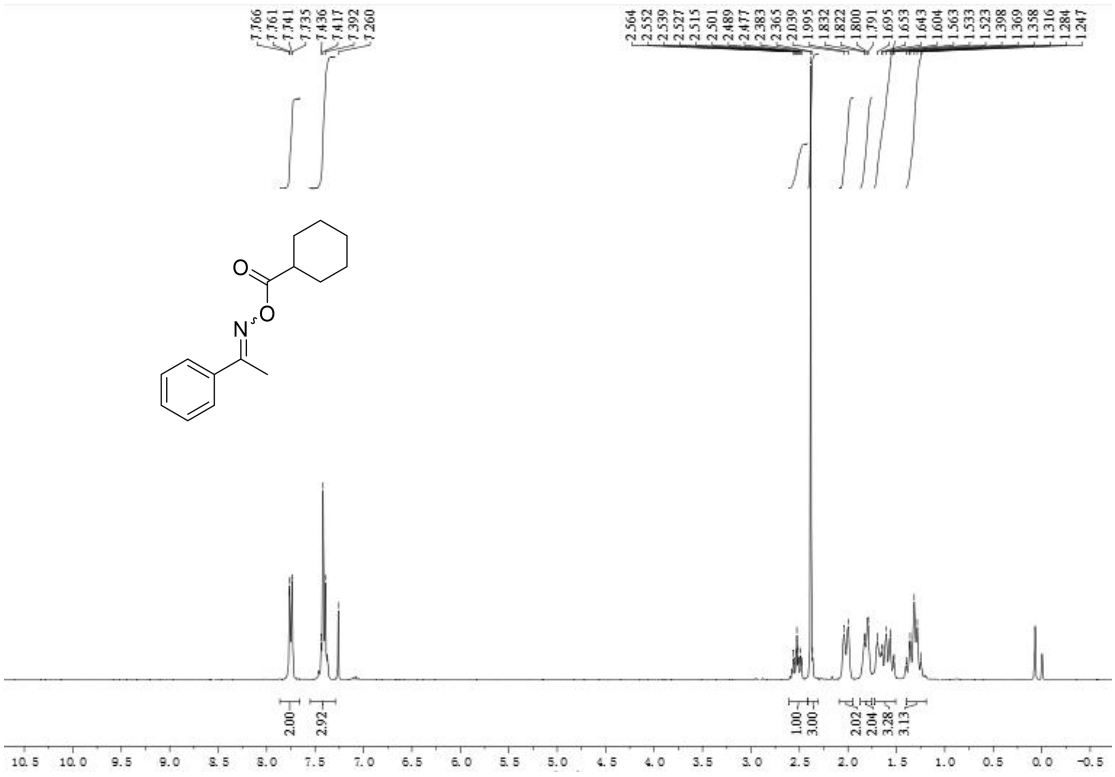
1-phenylethan-1-imine (7):



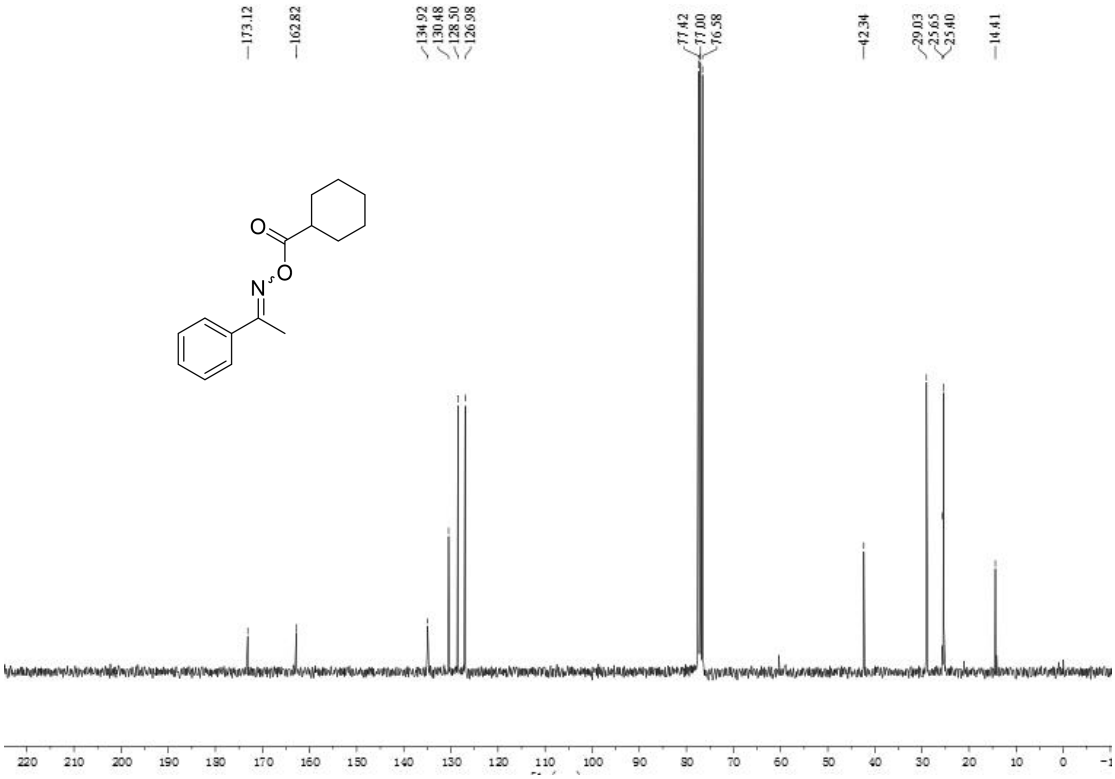
Column chromatography was eluted with ethyl acetate: petroleum ether = 1:20. Yield = 83%, 19.8 mg, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$):δ 7.65-7.61 (m, 2H), 7.41-7.35 (m, 3H), 7.33-7.26 (m, 2H), 4.70 (s, 1H), 2.31 (s, 3H). $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ 156.0, 136.5, 129.2, 128.5, 127.0, 126.0, 12.3.

(C) NMR Spectra

1-oxide1-phenylethan-1-one *O*-cyclohexanecarbonyl oxime (3a):

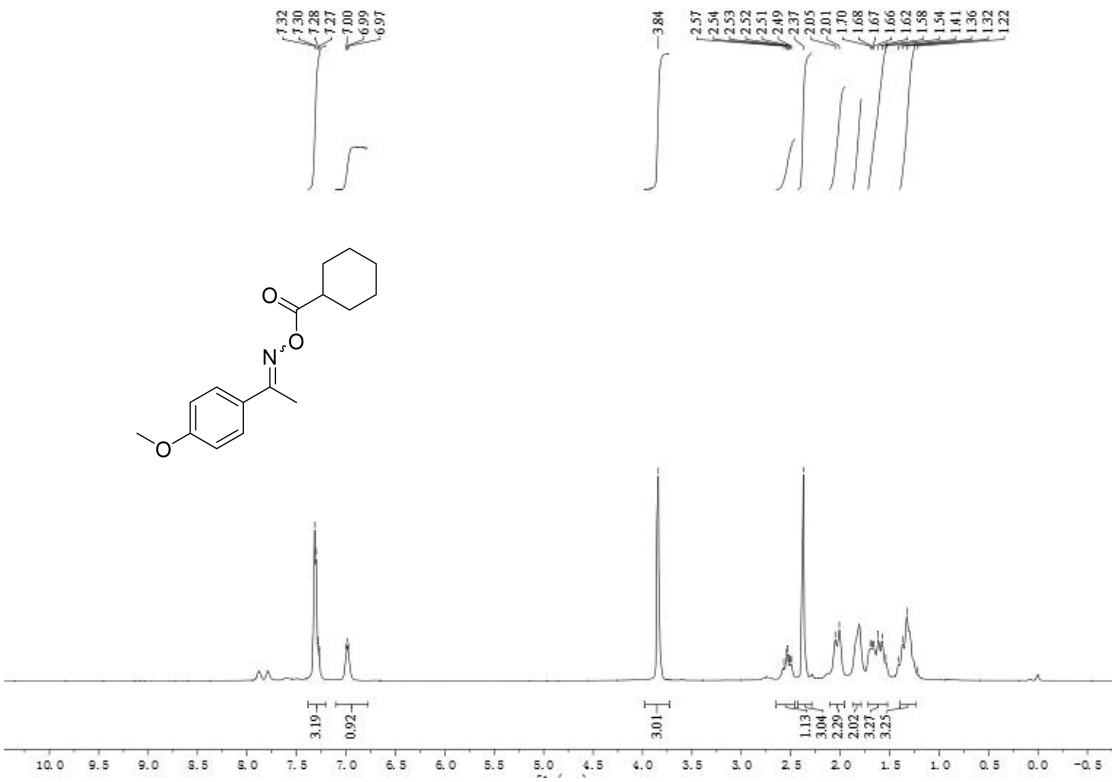


^{1}H NMR (300 MHz, $CDCl_3$)

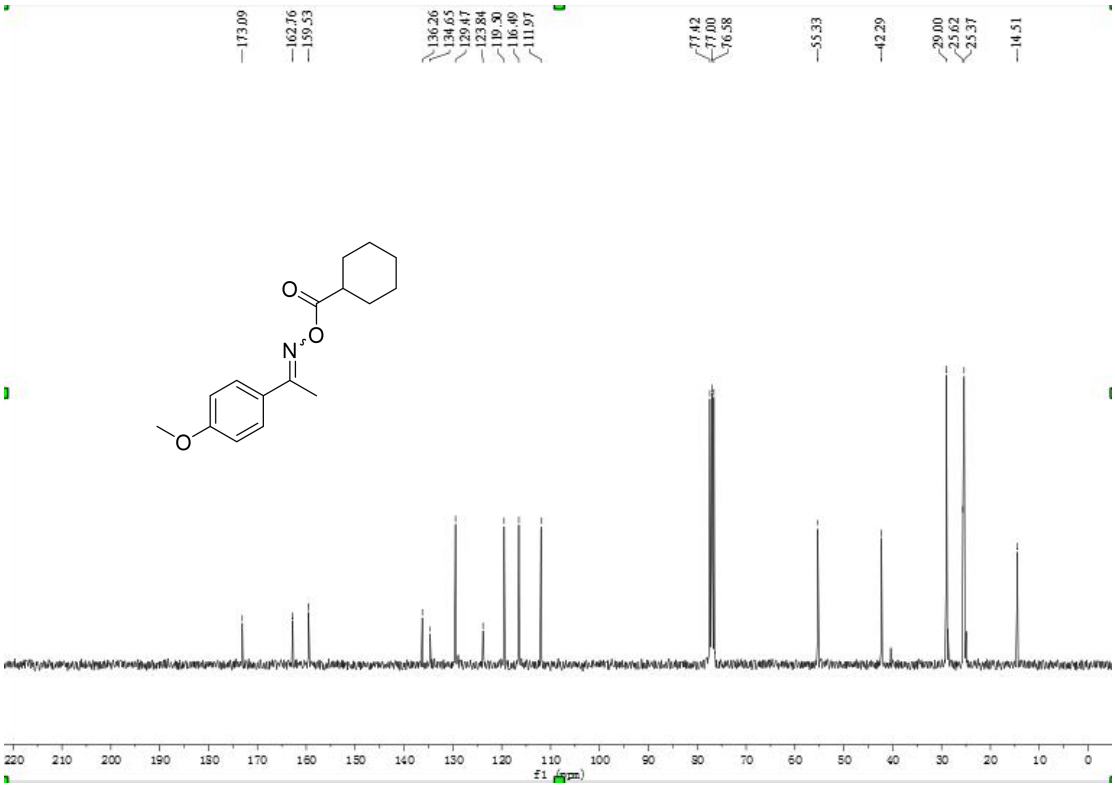


^{13}C NMR (125 MHz, $CDCl_3$)

1-(4-methoxyphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3b):

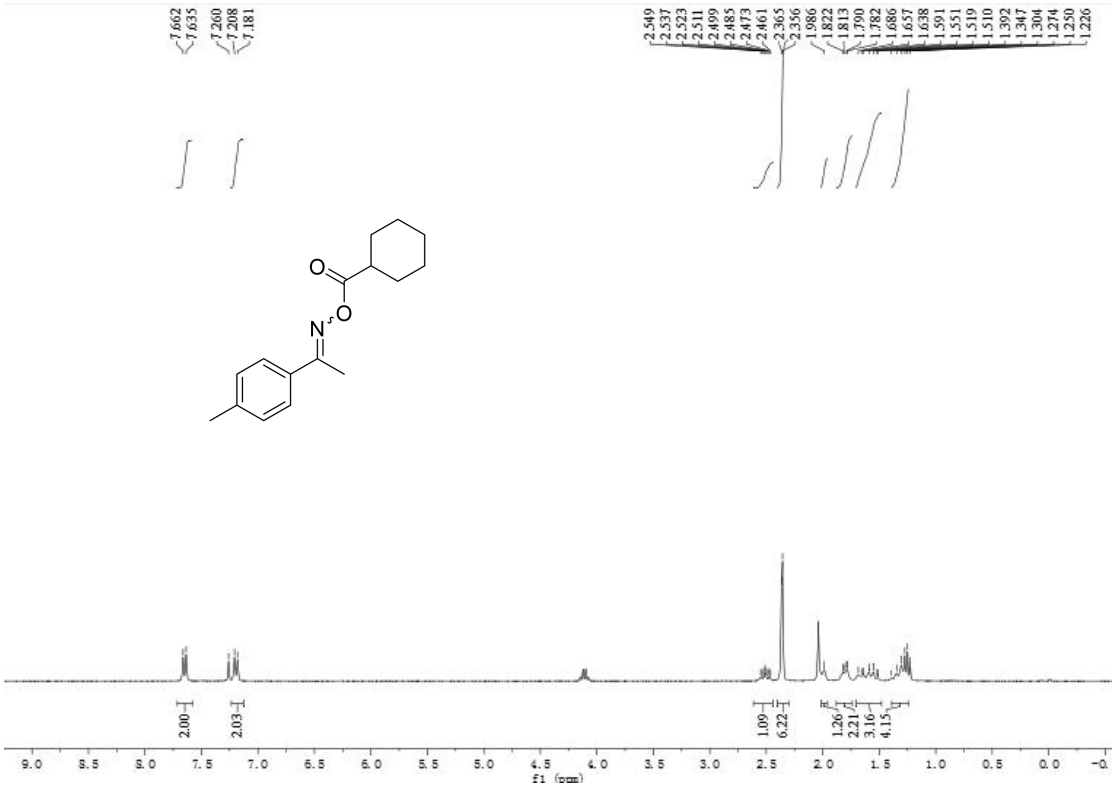


^{1}H NMR (300 MHz, $CDCl_3$)

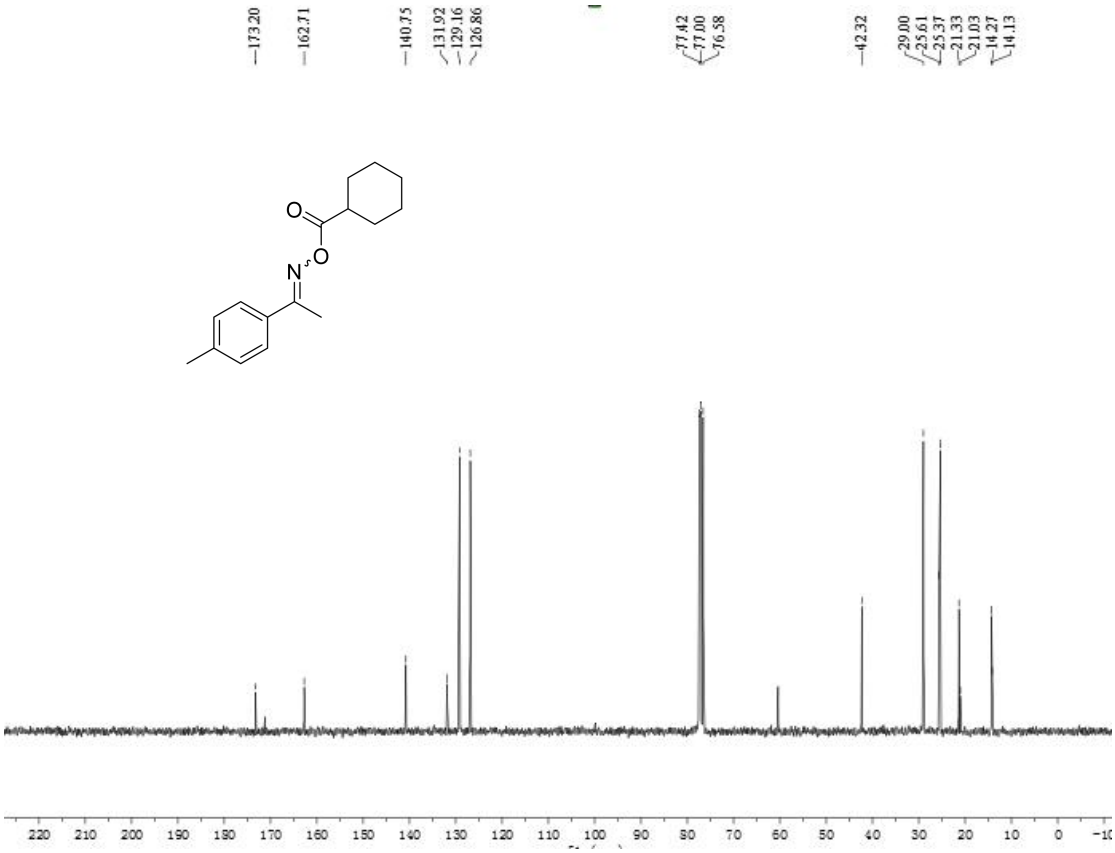


^{13}C NMR (125 MHz, $CDCl_3$)

1-(*p*-tolyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3c):

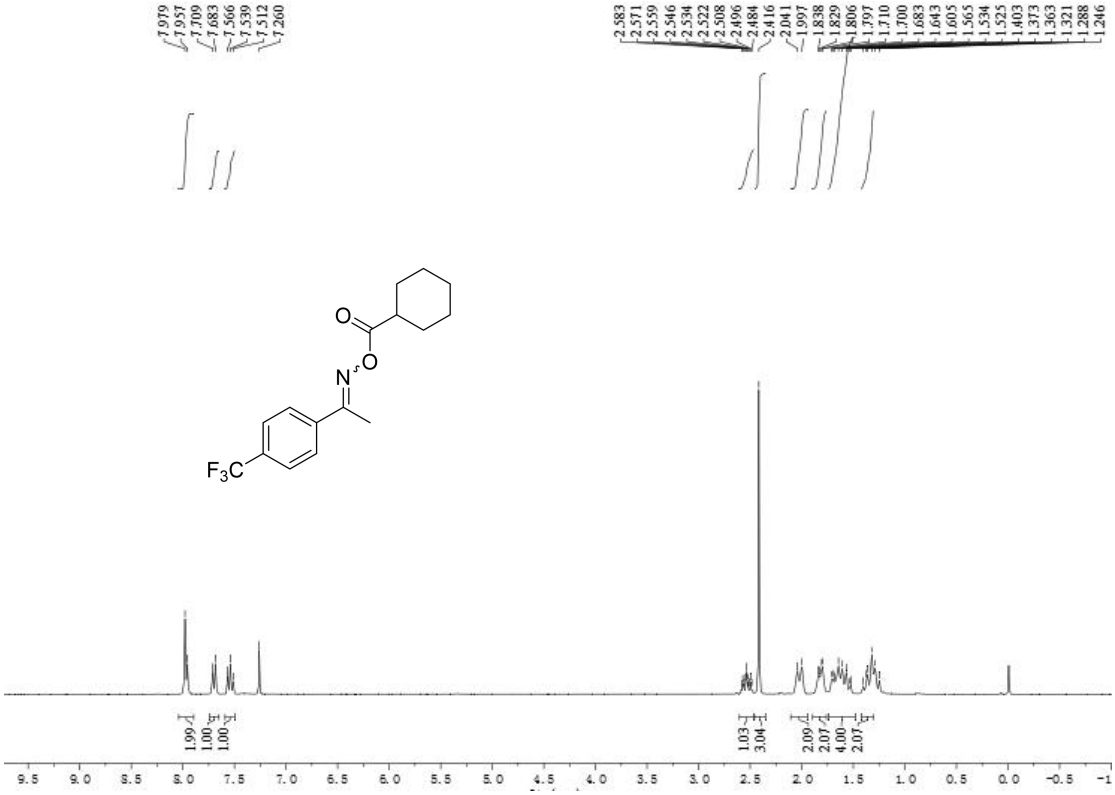


^{1}H NMR (300 MHz, $CDCl_3$)

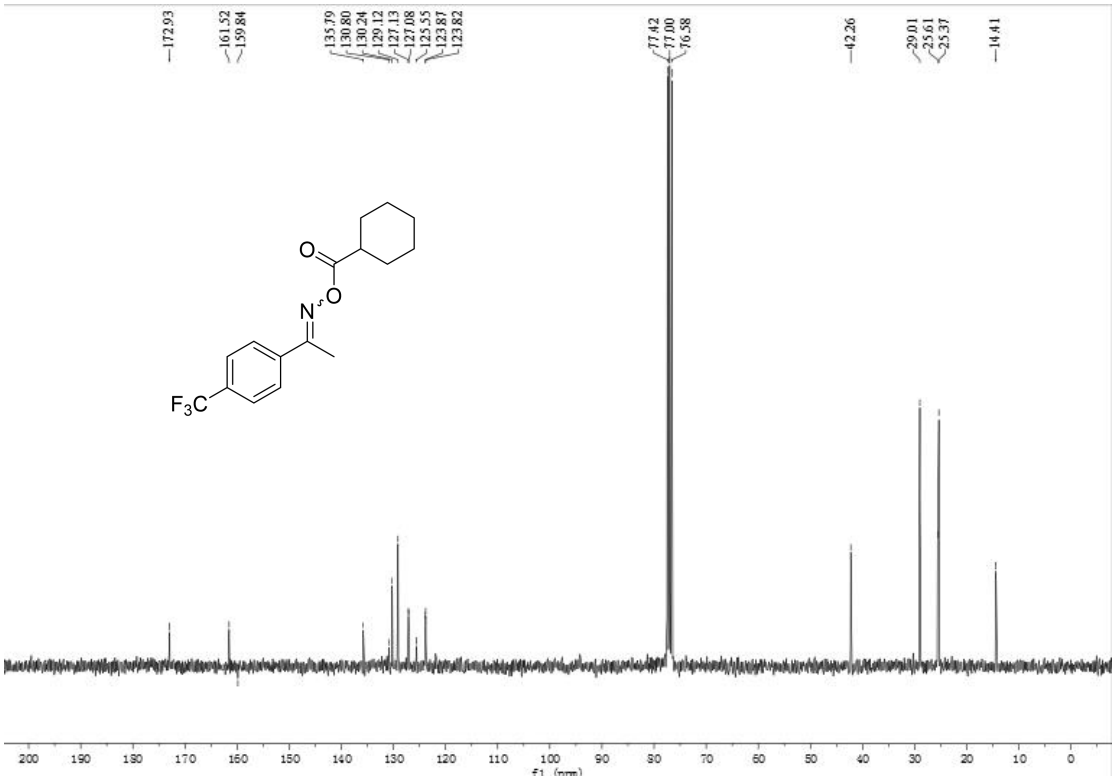


^{13}C NMR (125 MHz, $CDCl_3$)

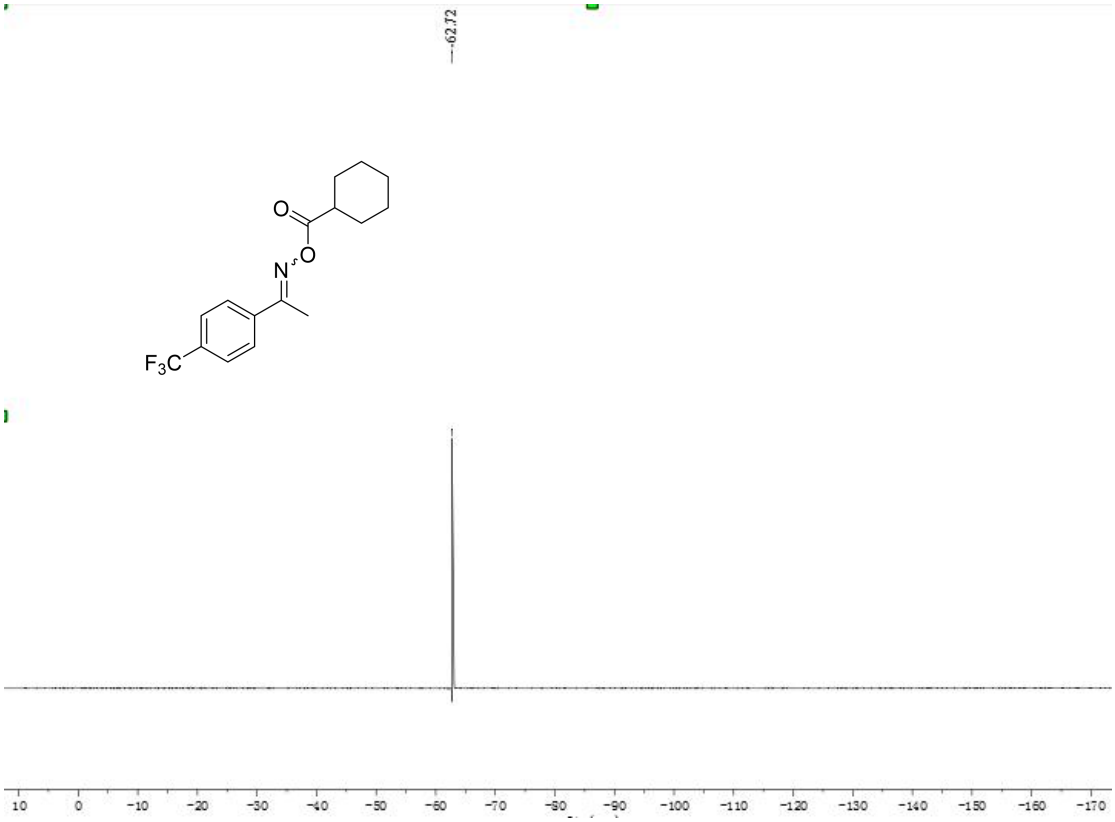
1-(4-(trifluoromethyl)phenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3d):



^{1}H NMR (300 MHz, $CDCl_3$)

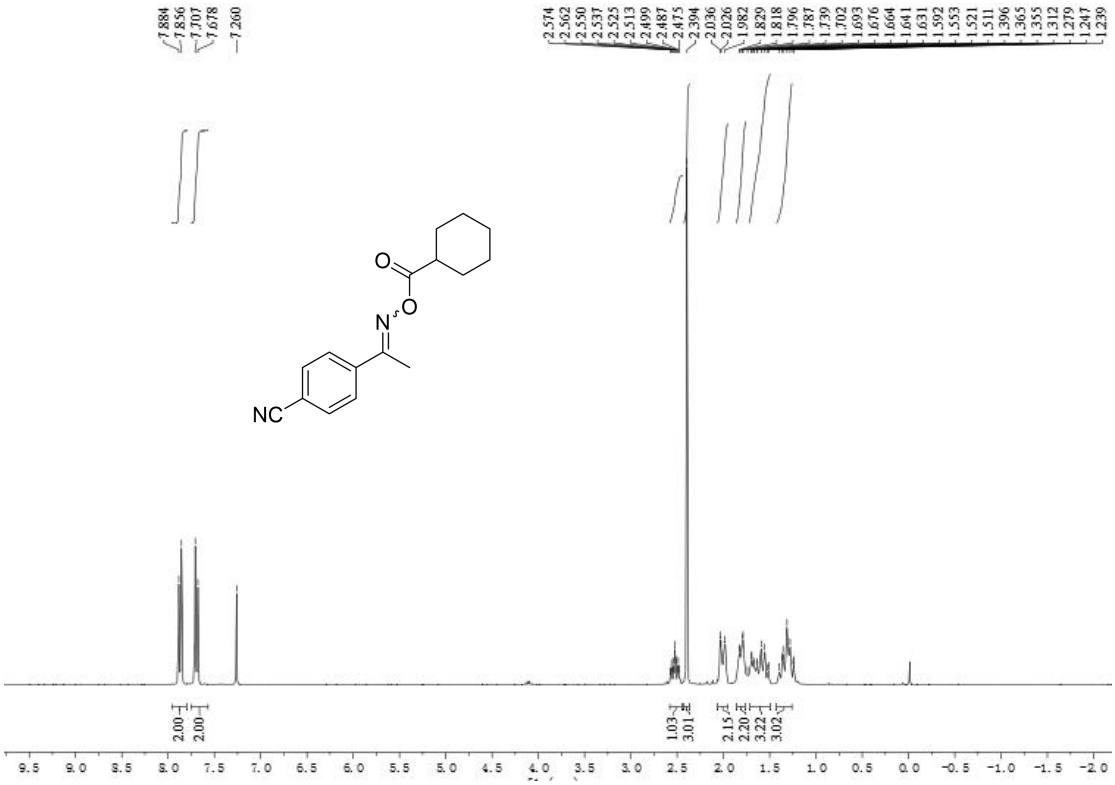


^{13}C NMR (75 MHz, $CDCl_3$)

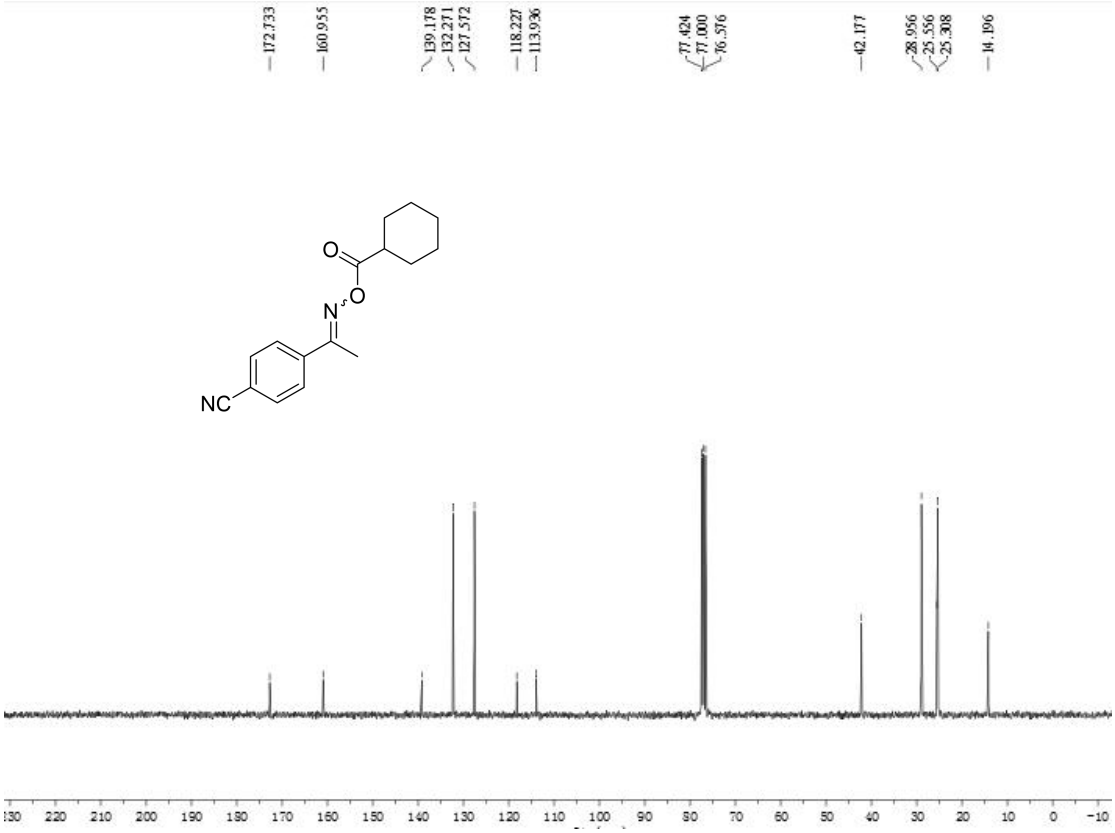


^{19}F NMR (564 MHz, $CDCl_3$)

4-(1-(((cyclohexanecarbonyl)oxy)imino)ethyl)benzonitrile (3e):

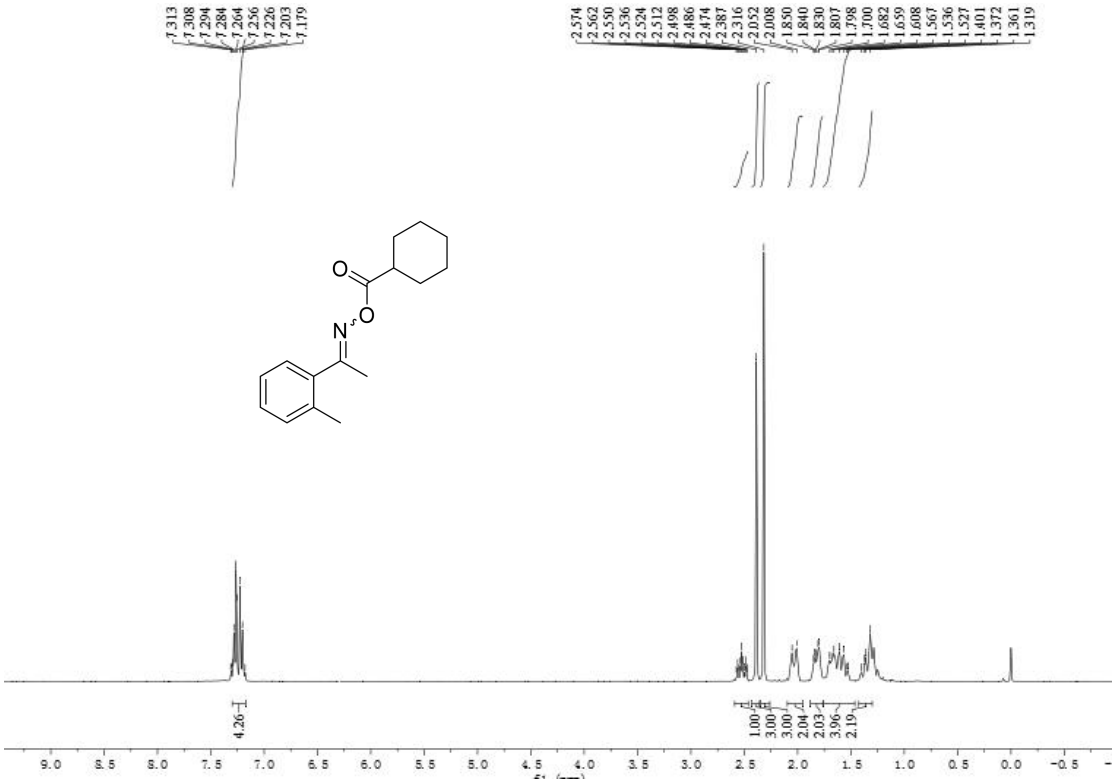


^{1}H NMR (300 MHz, $CDCl_3$)

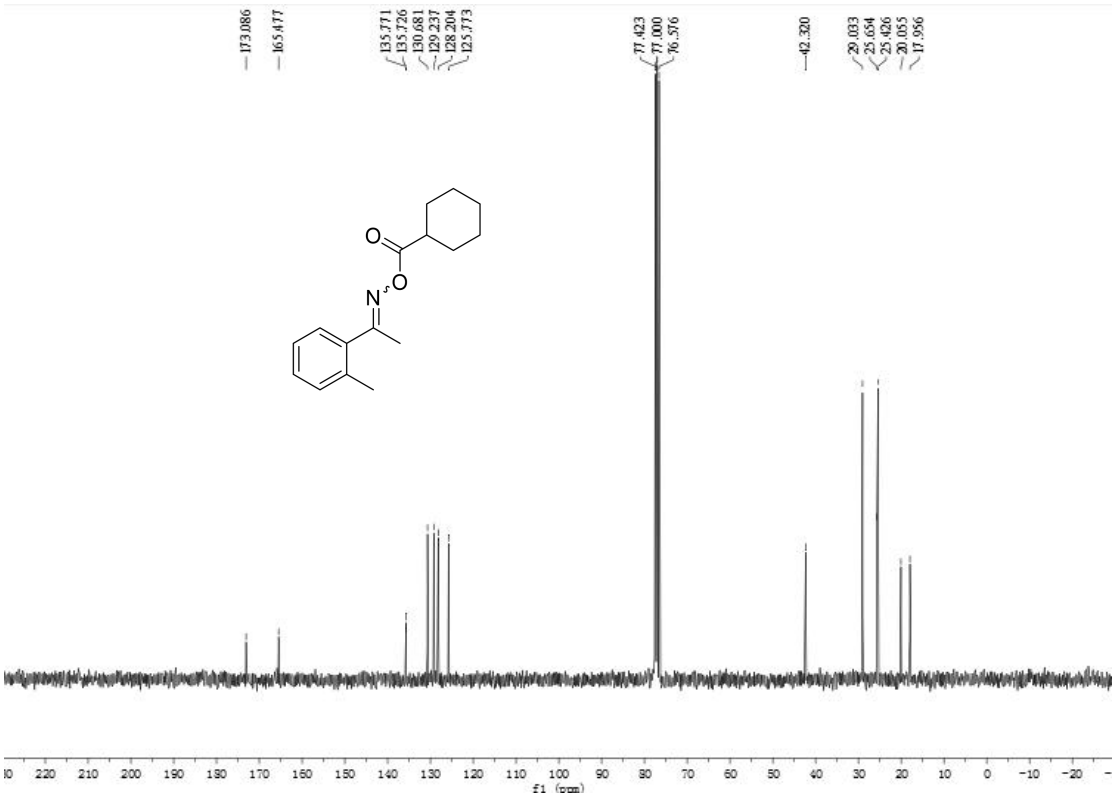


^{13}C NMR (75 MHz, $CDCl_3$)

1-(*o*-tolyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3f):

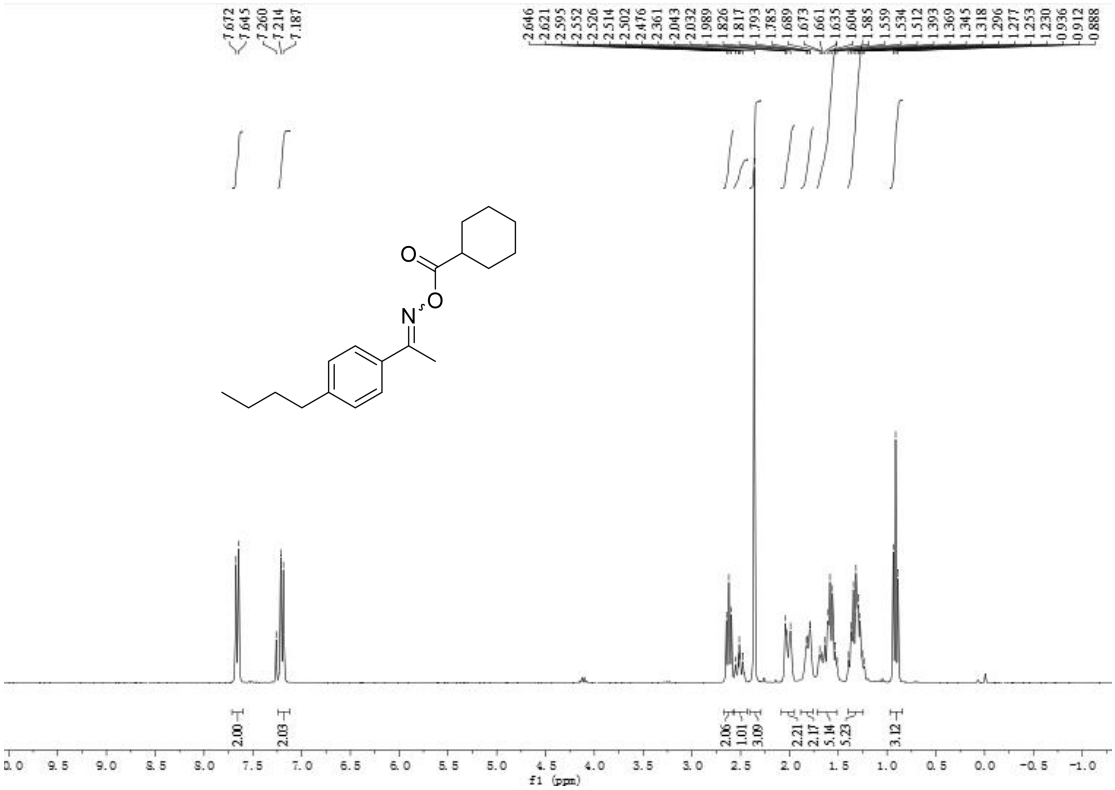


^{1}H NMR (300 MHz, $CDCl_3$)

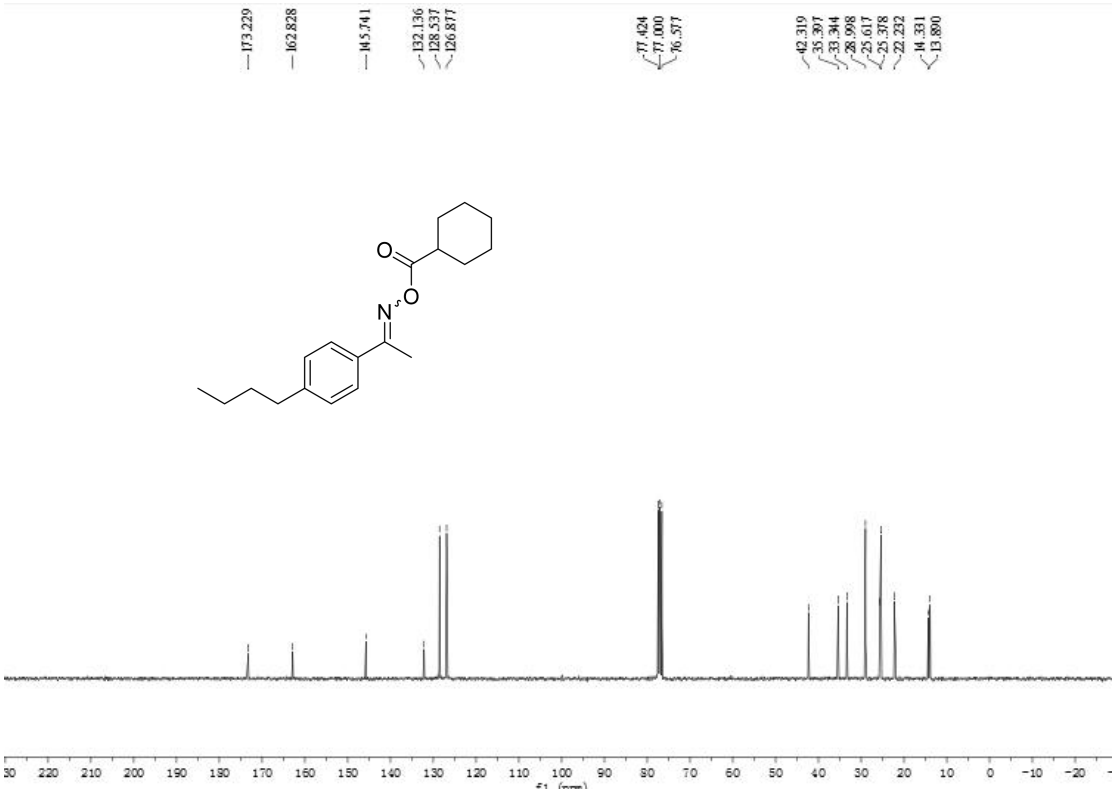


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-butylphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3g):

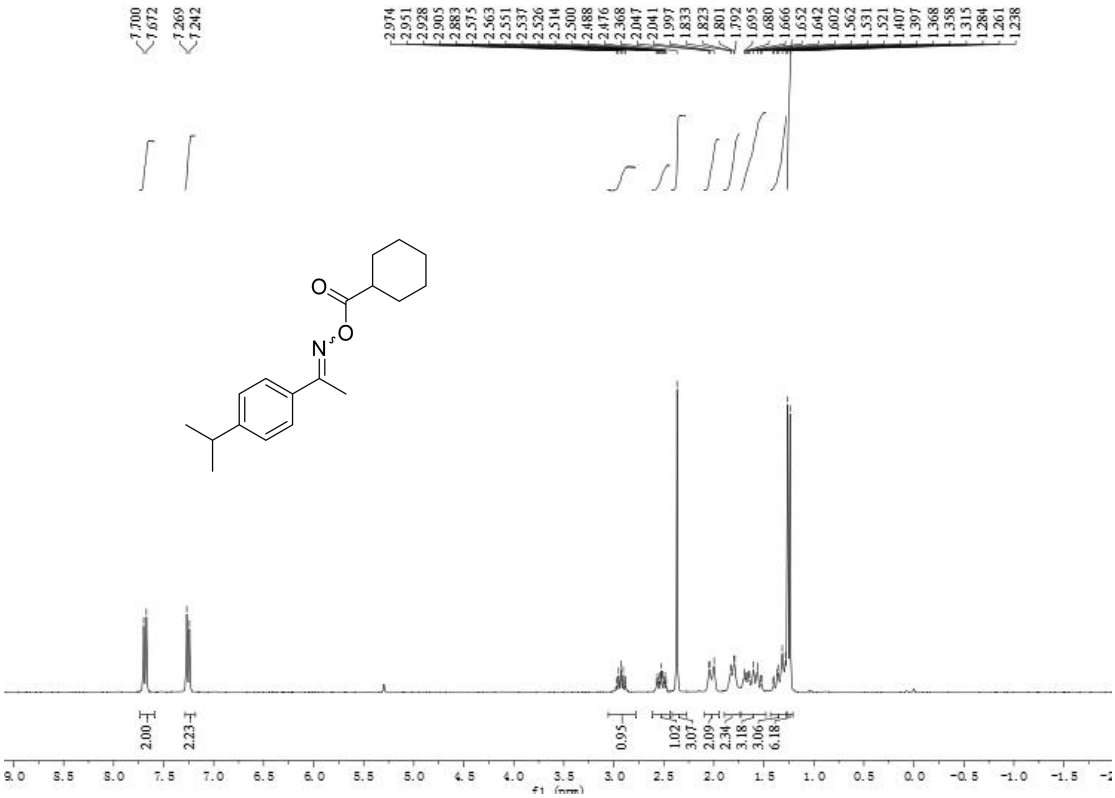


^{1}H NMR (300 MHz, $CDCl_3$)

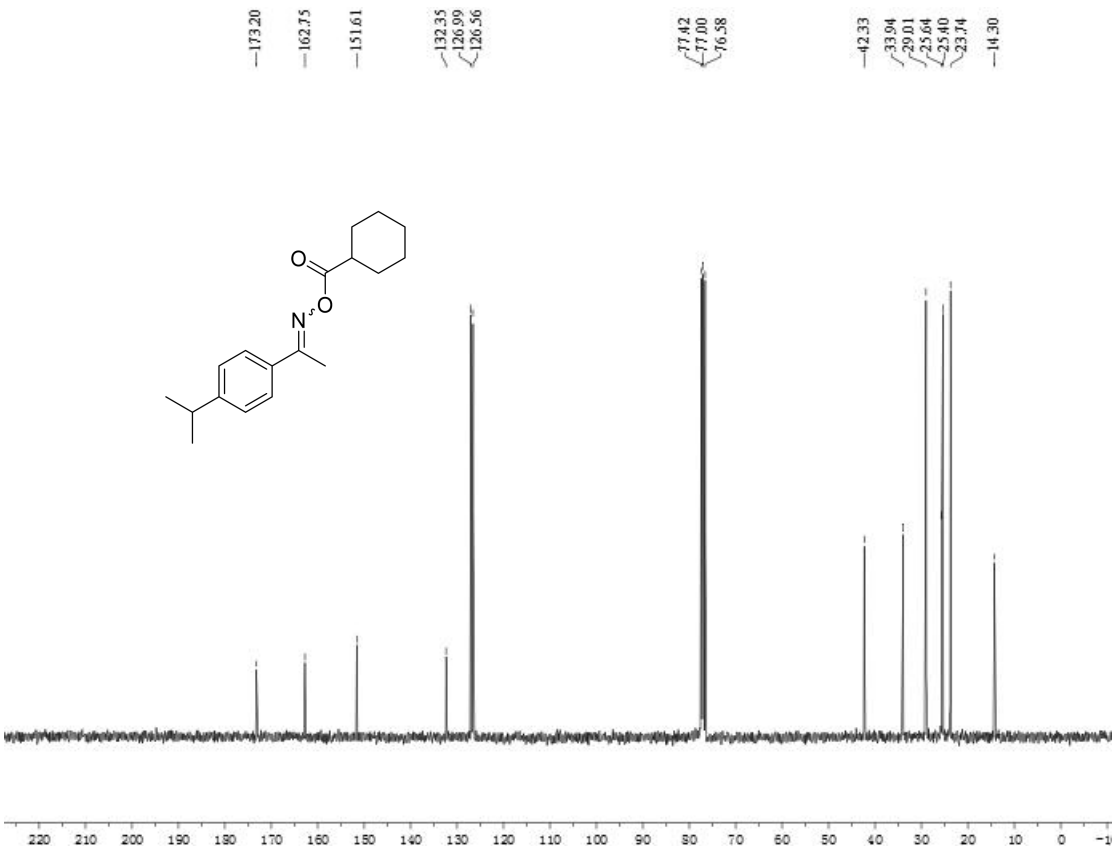


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-isopropylphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3h)：

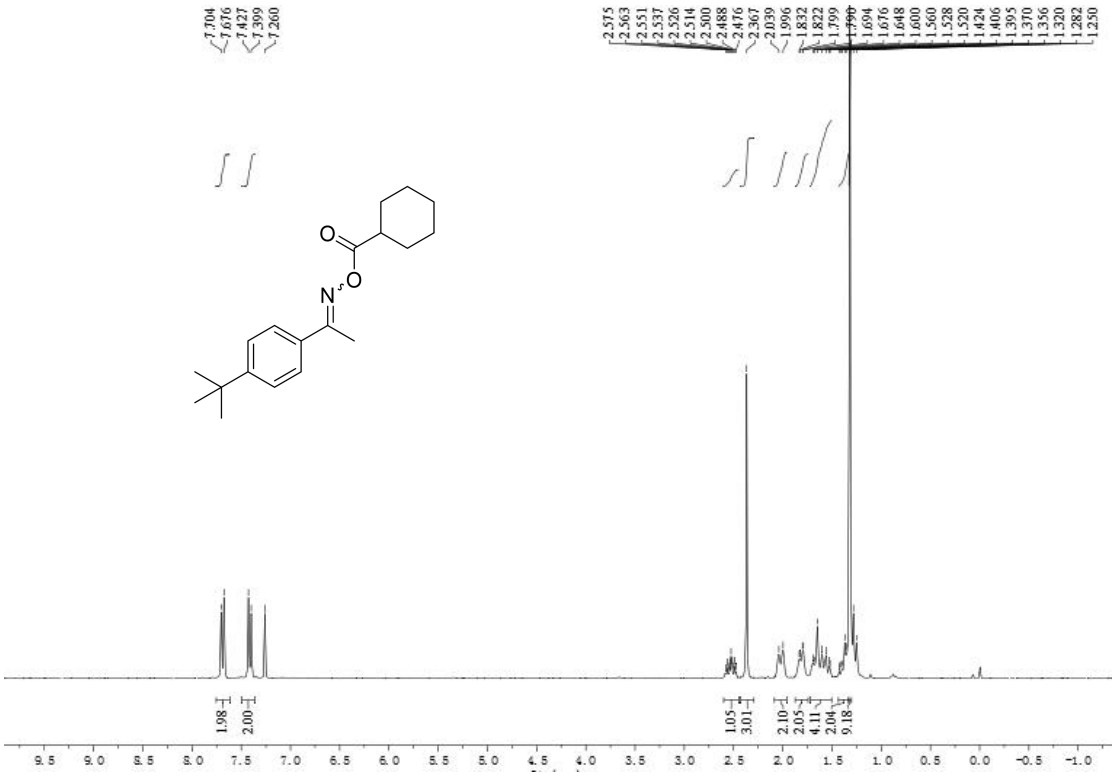


^{1}H NMR (300 MHz, $CDCl_3$)

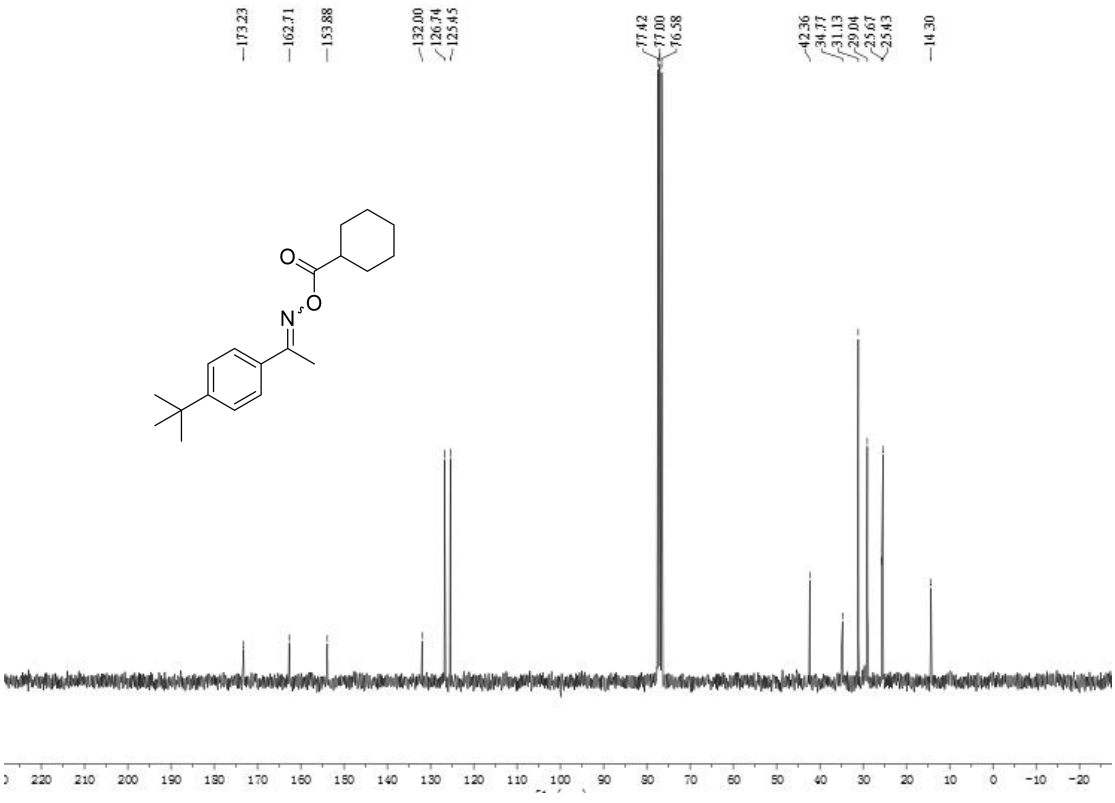


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-(tert-butyl)phenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3i):

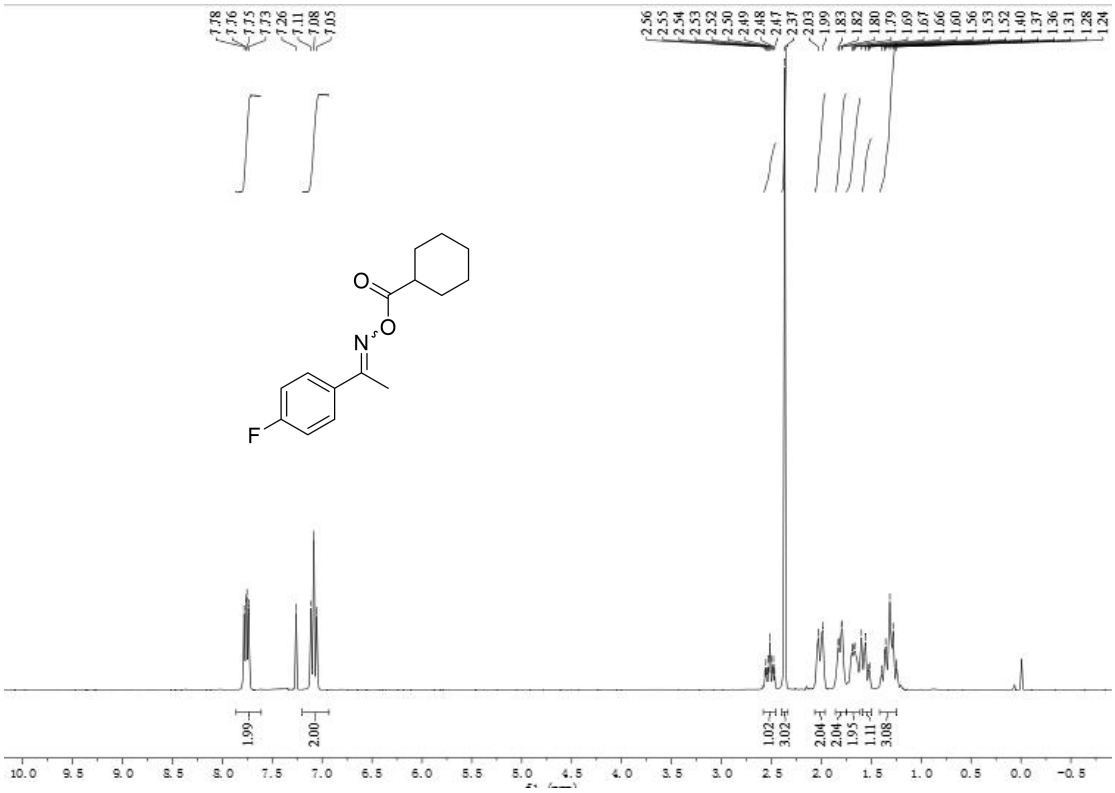


^{1}H NMR (300 MHz, $CDCl_3$)

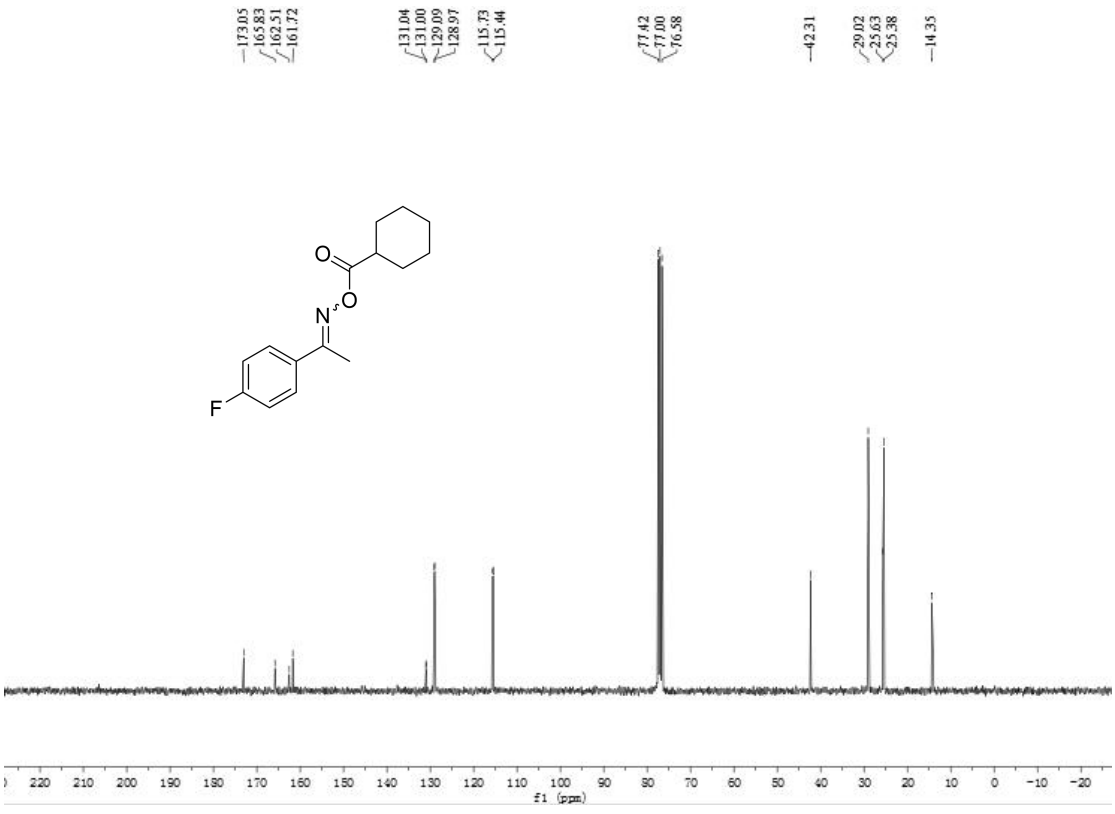


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-fluorophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3j):



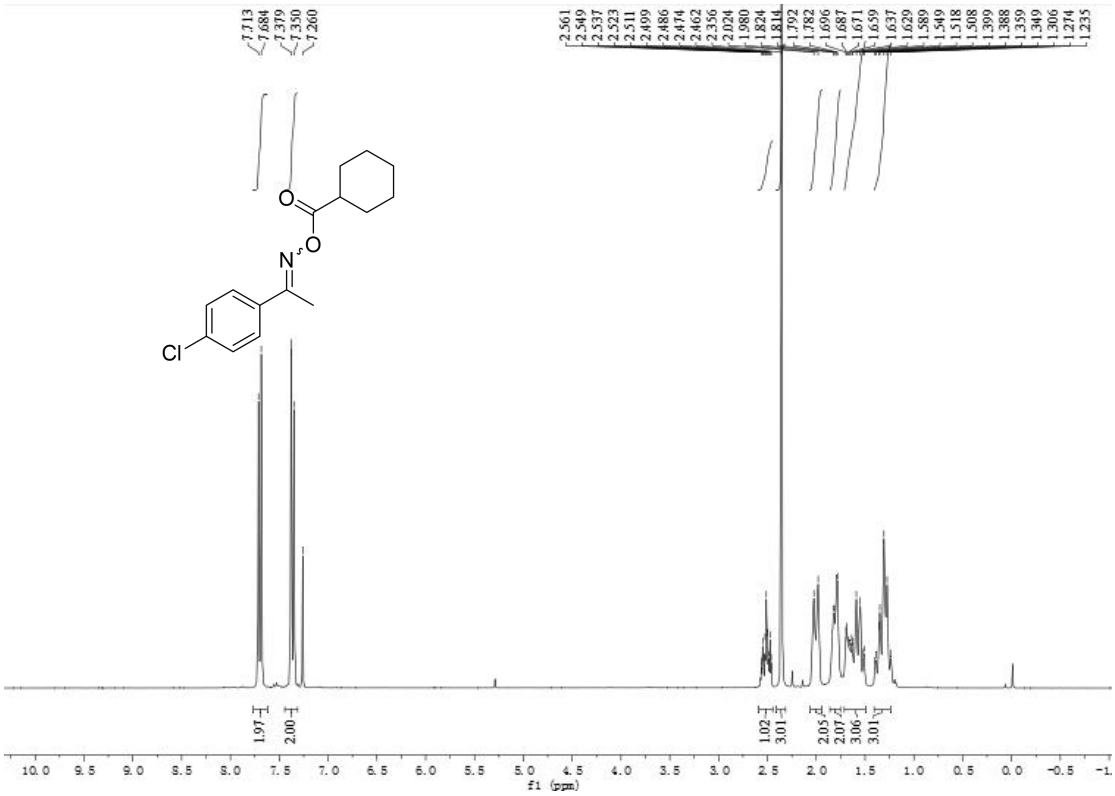
^{1}H NMR (300 MHz, $CDCl_3$)



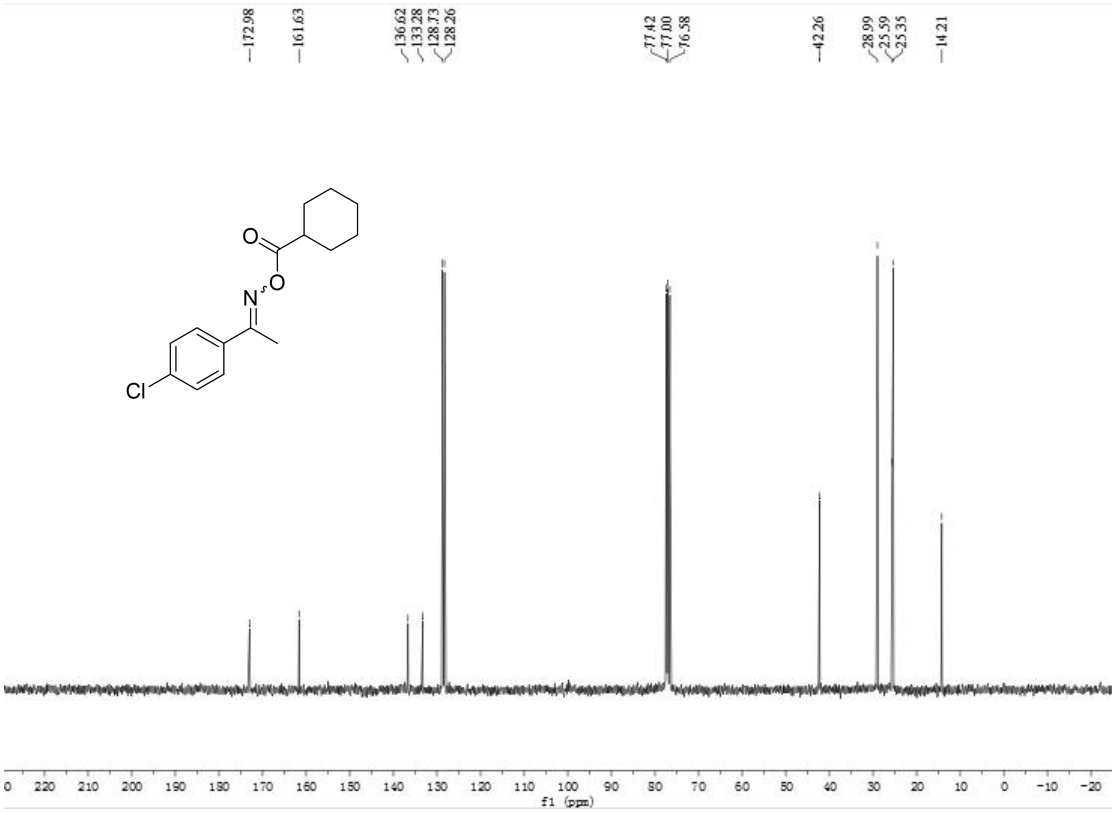
^{13}C NMR (75 MHz, $CDCl_3$)

^{19}F NMR (564 MHz, $CDCl_3$)

1-(4-chlorophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3k):

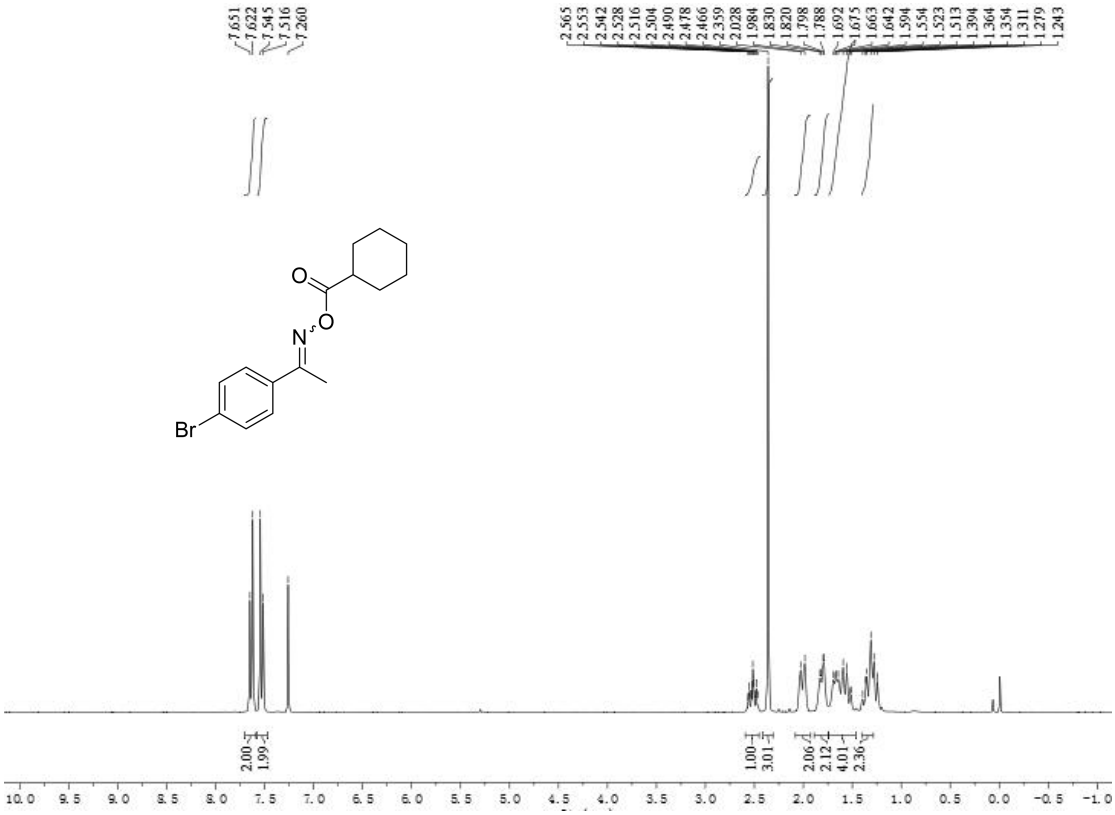


^{1}H NMR (300 MHz, $CDCl_3$)

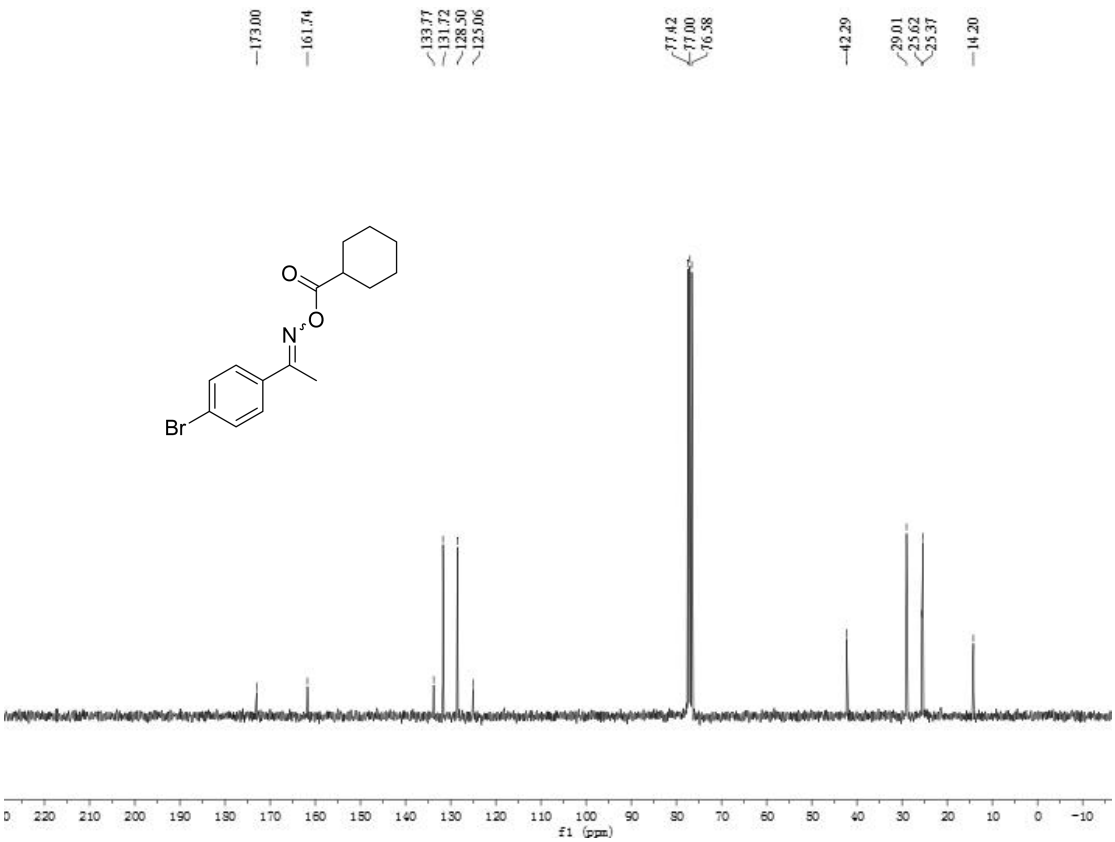


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-bromophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3l):

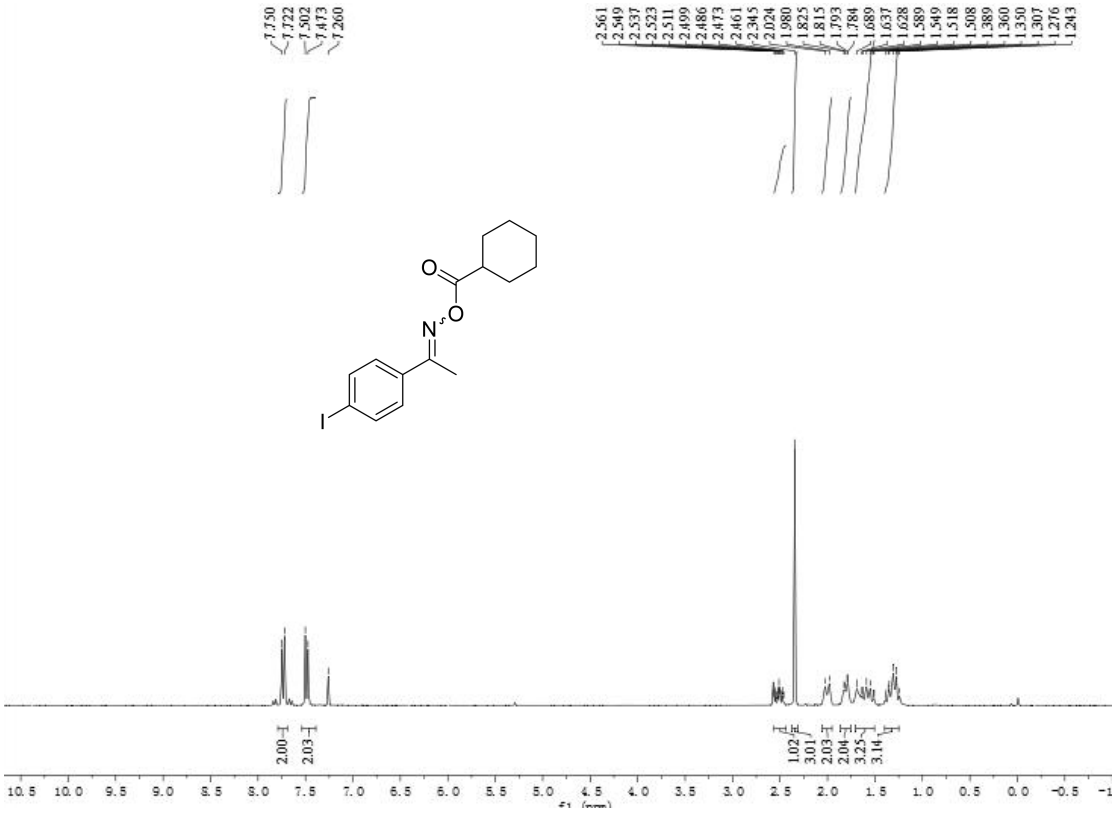


^{1}H NMR (300 MHz, $CDCl_3$)

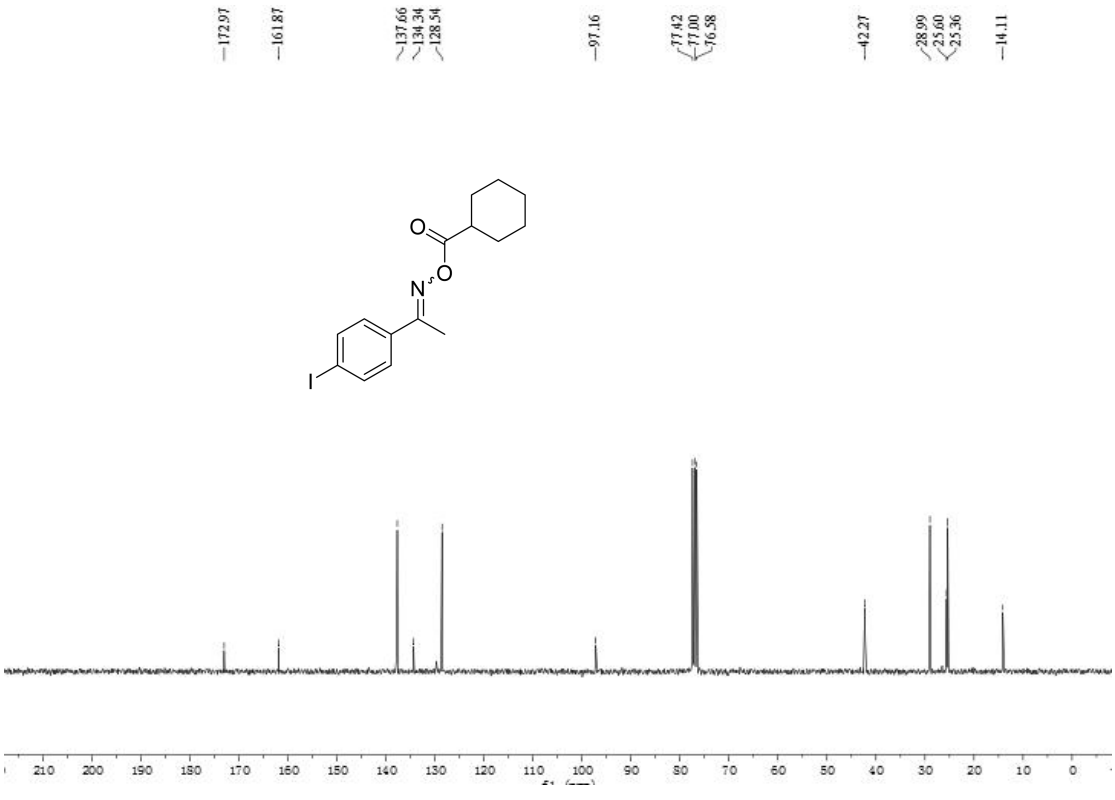


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-iodophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3m):

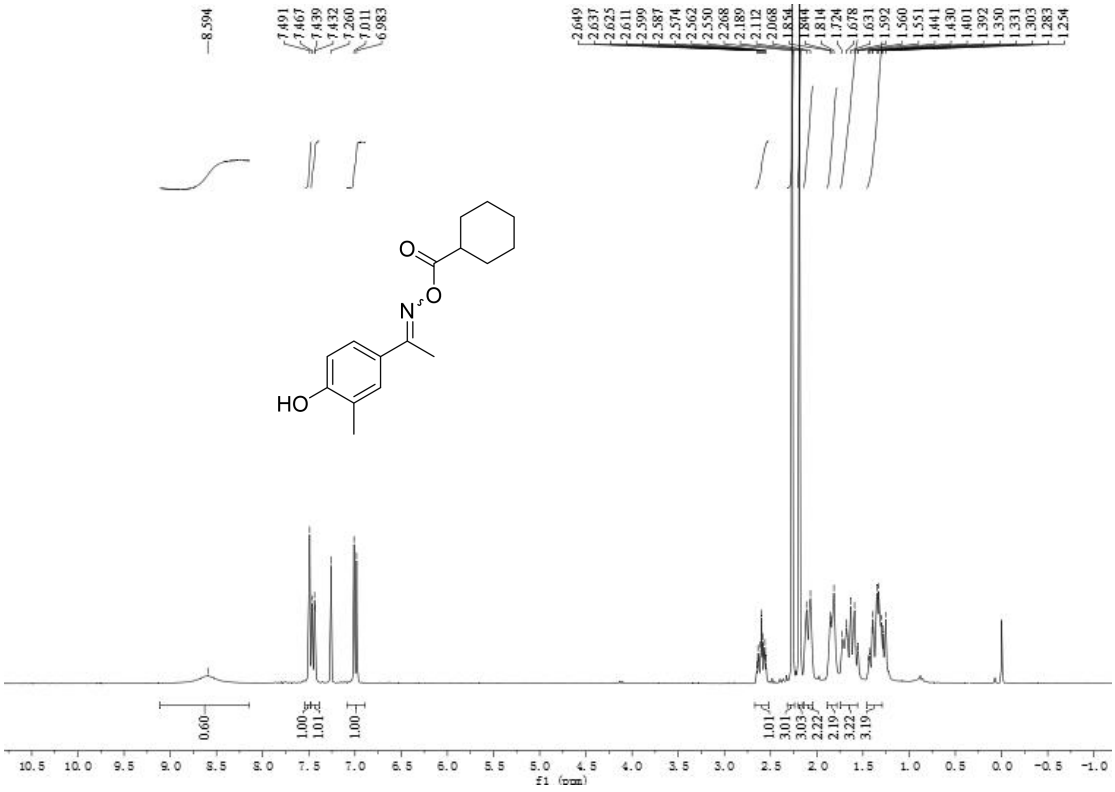


^{1}H NMR (300 MHz, $CDCl_3$)

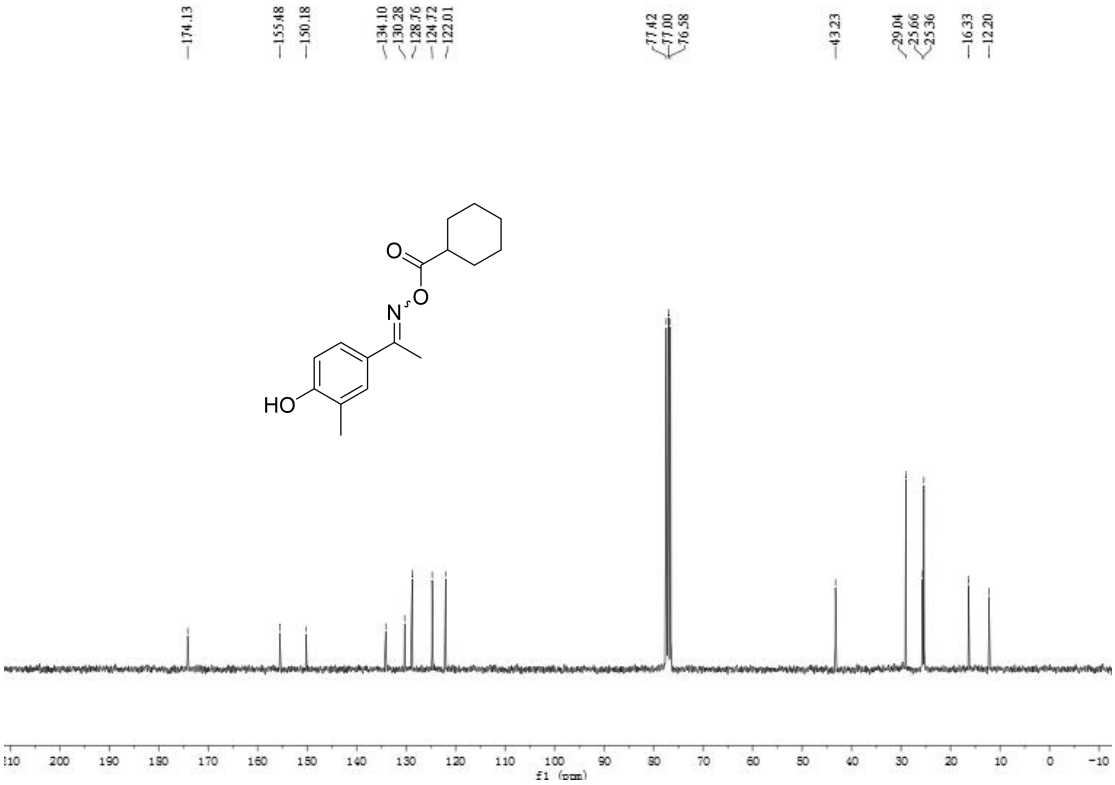


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-hydroxy-3-methylphenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3n):

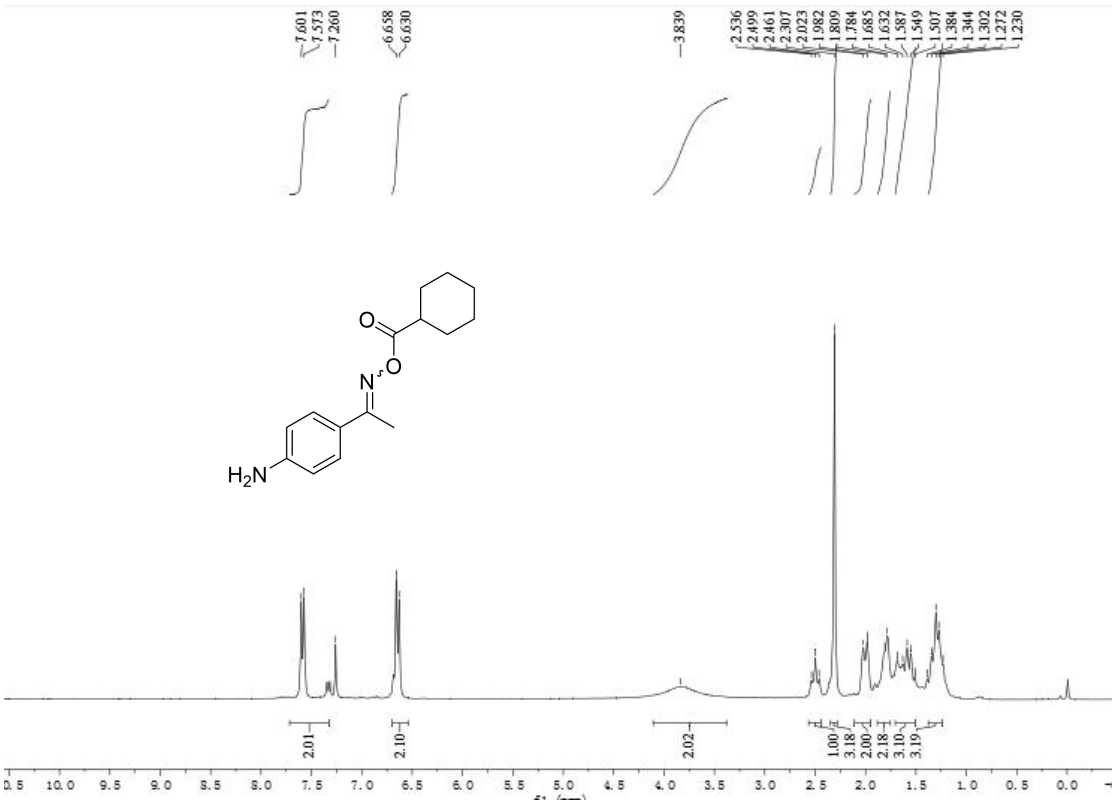


^{1}H NMR (300 MHz, $CDCl_3$)

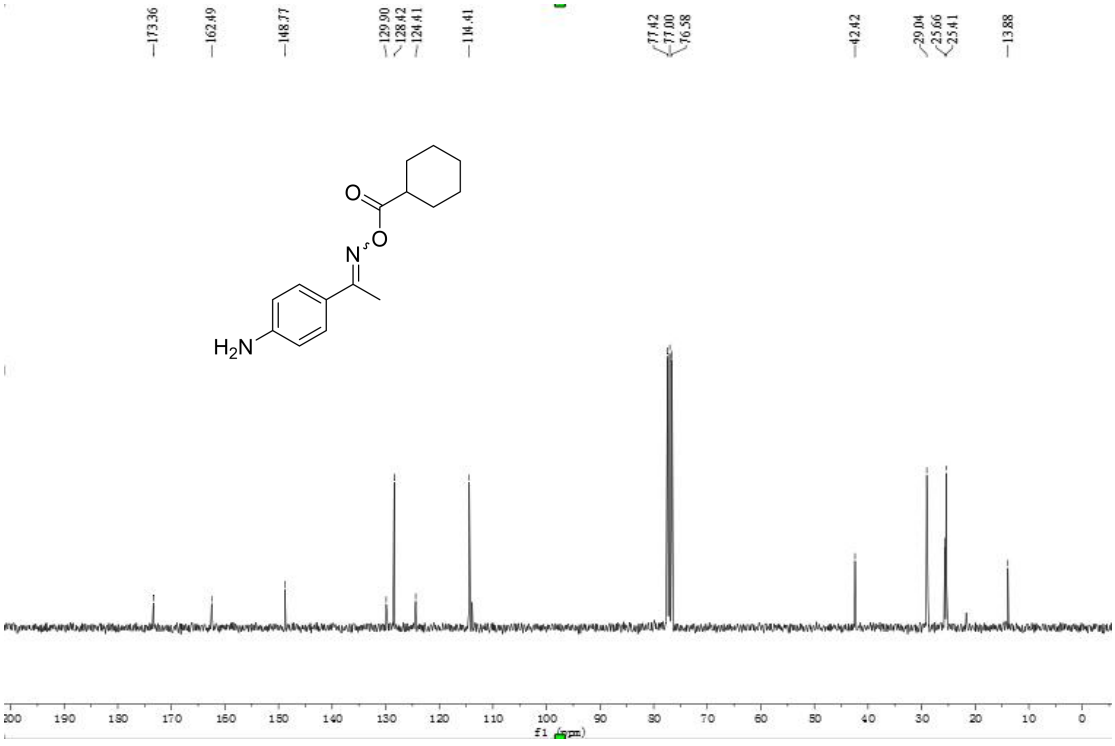


^{13}C NMR (75 MHz, $CDCl_3$)

1-(4-aminophenyl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3o):

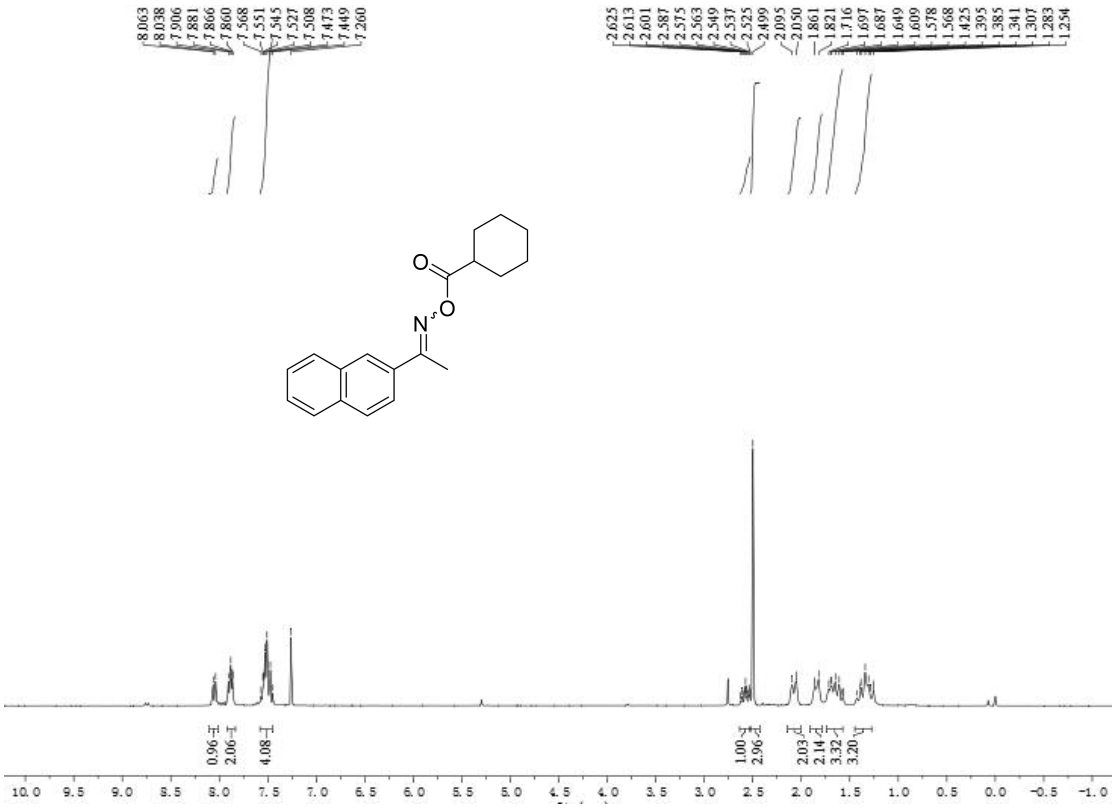


^{1}H NMR (300 MHz, $CDCl_3$)

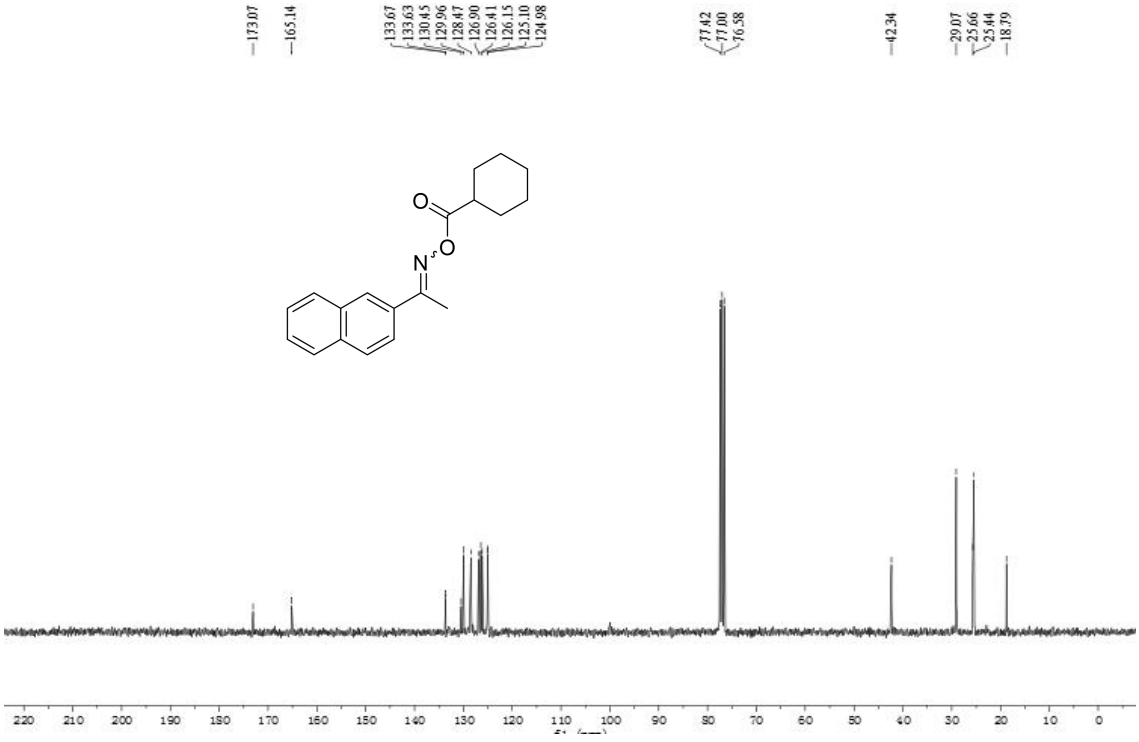


^{13}C NMR (75 MHz, $CDCl_3$)

1-(naphthalen-2-yl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3p):

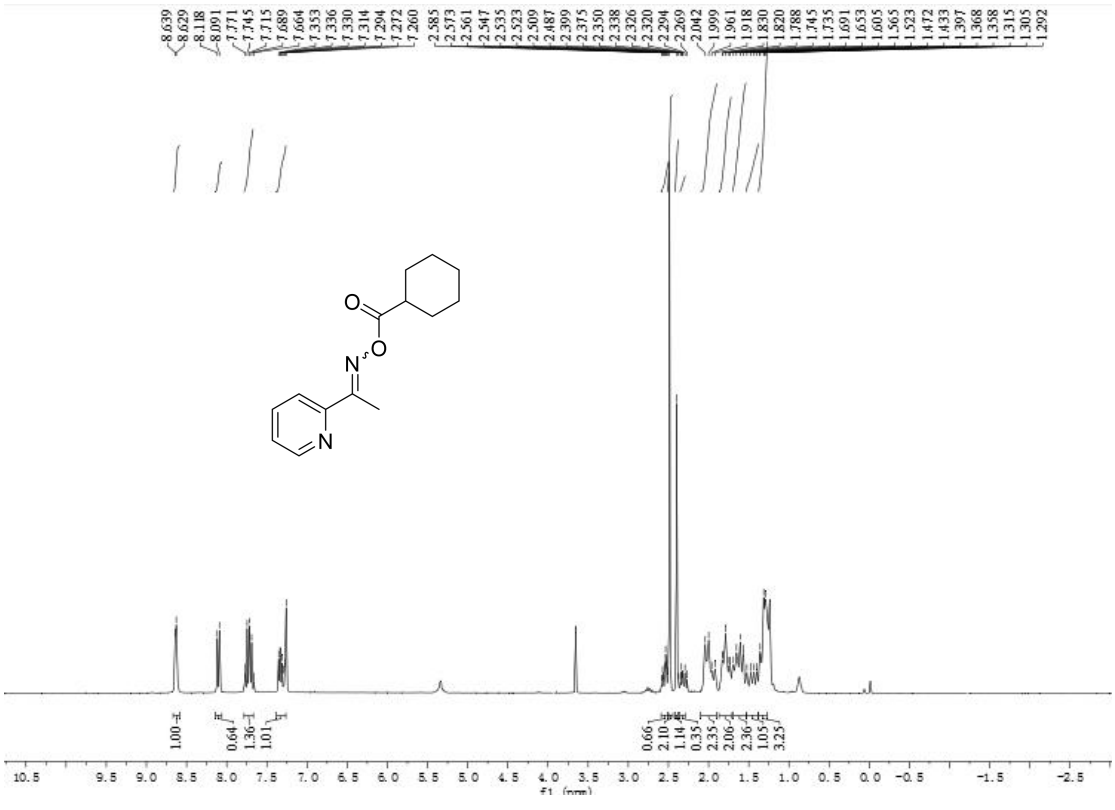


^{1}H NMR (300 MHz, $CDCl_3$)

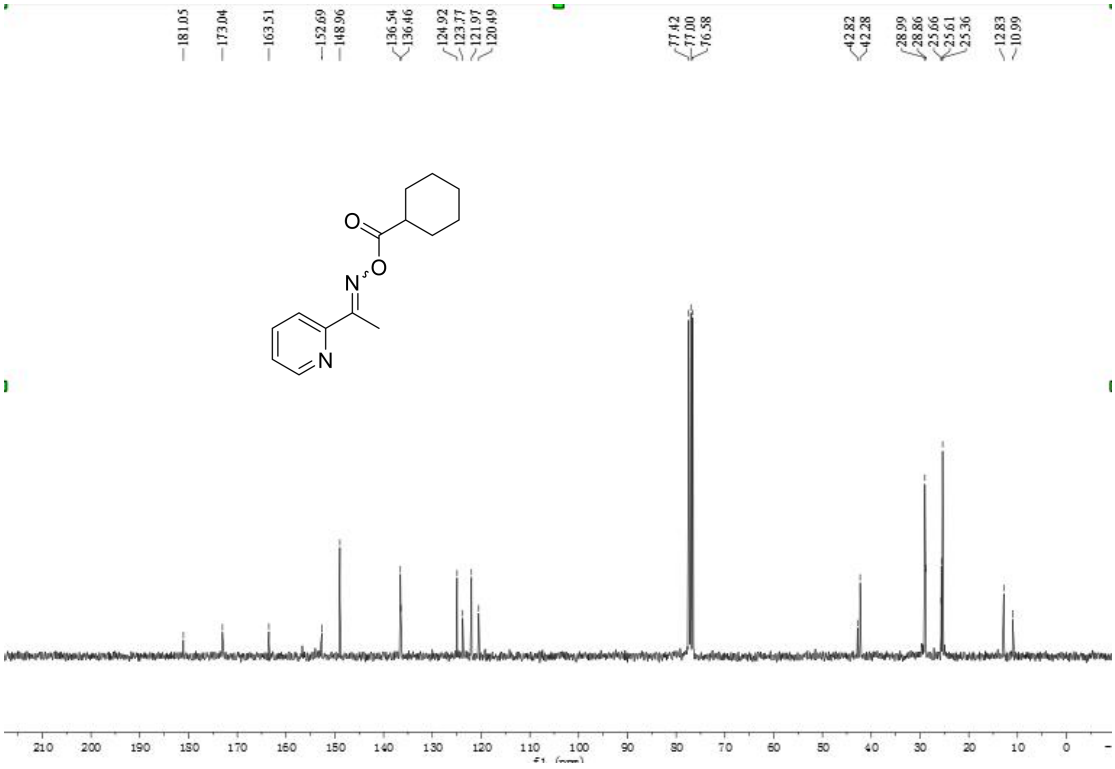


^{13}C NMR (75 MHz, $CDCl_3$)

1-(pyridin-2-yl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3q):

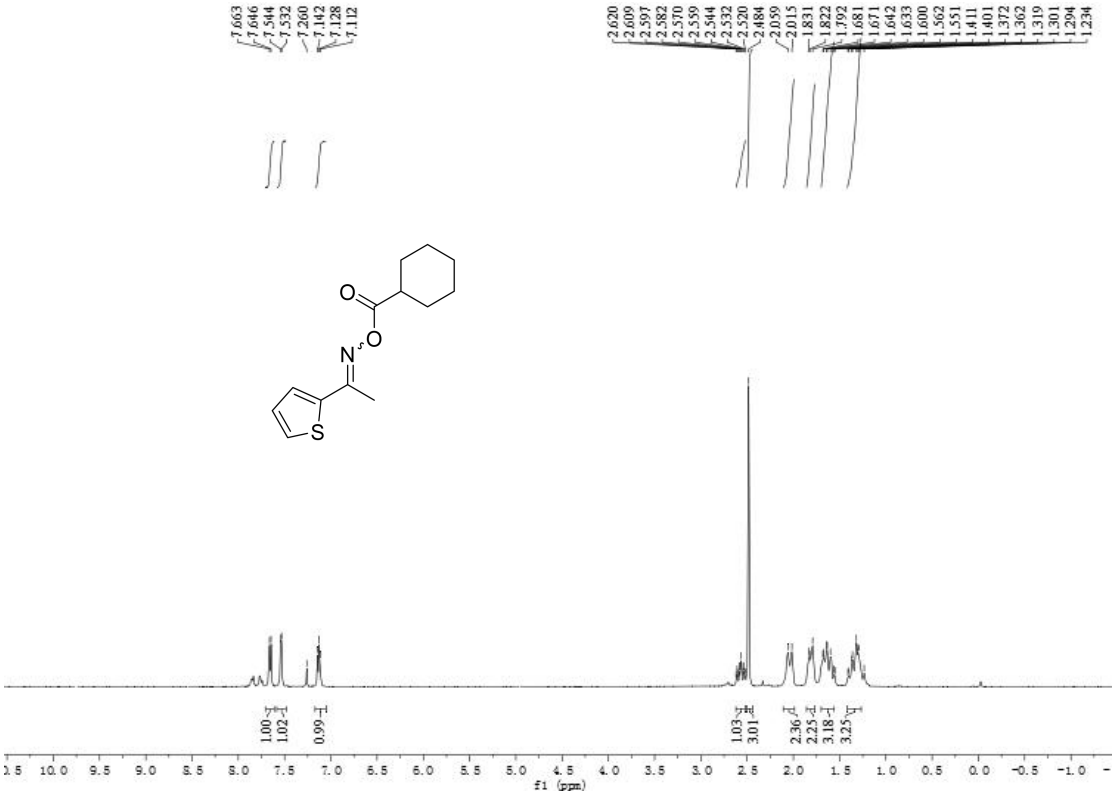


^{1}H NMR (300 MHz, $CDCl_3$)

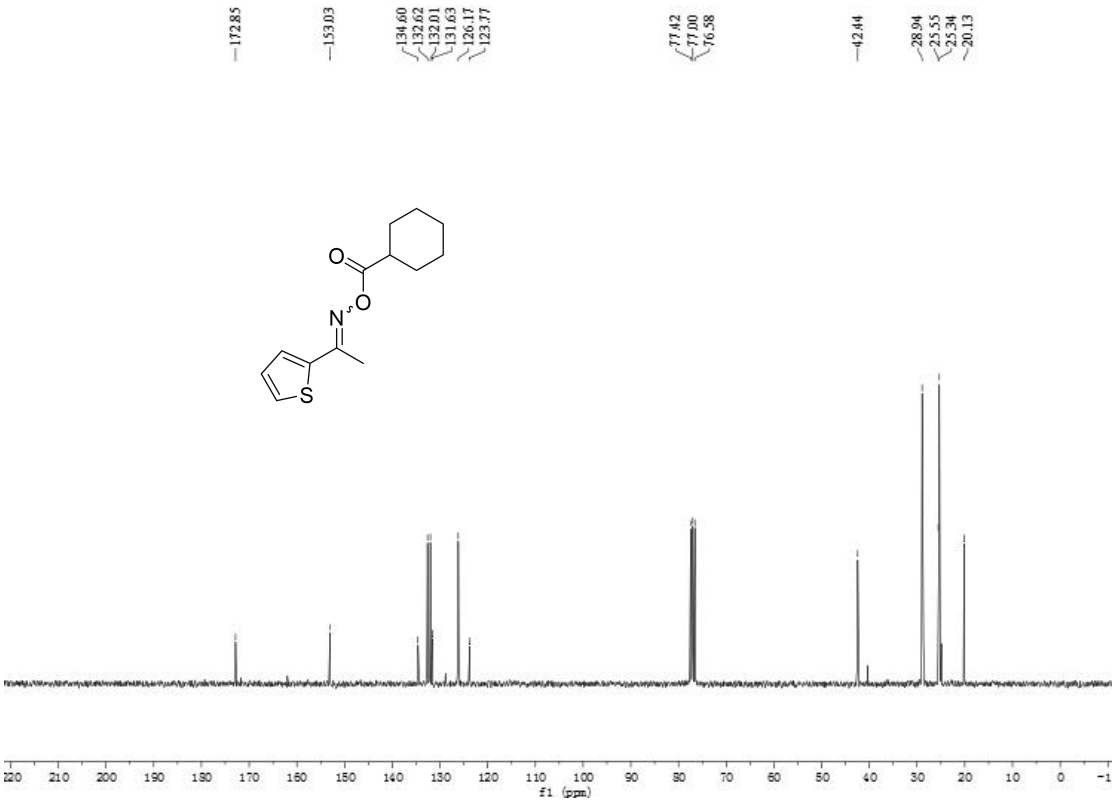


^{13}C NMR (75 MHz, $CDCl_3$)

1-(thiophen-2-yl)ethan-1-one *O*-cyclohexanecarbonyl oxime (3r):

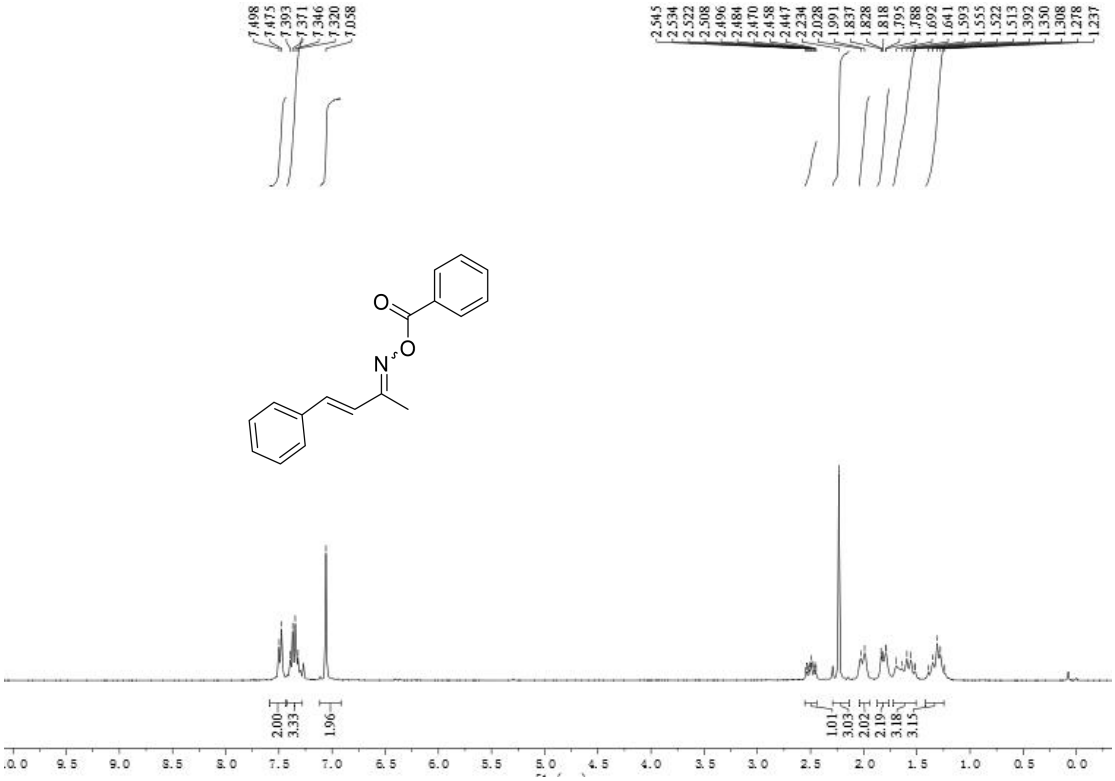


^{1}H NMR (300 MHz, $CDCl_3$)

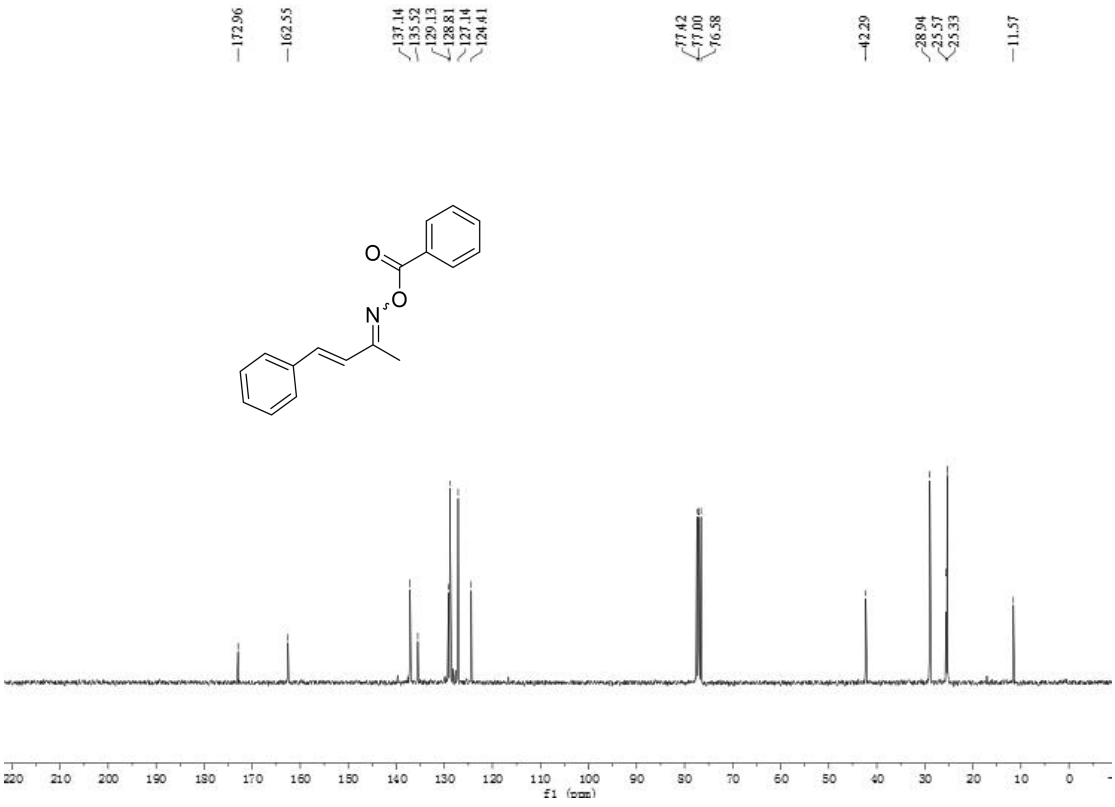


^{13}C NMR (75 MHz, $CDCl_3$)

(3*E*)-4-phenylbut-3-en-2-one *O*-benzoyl oxime (3s):

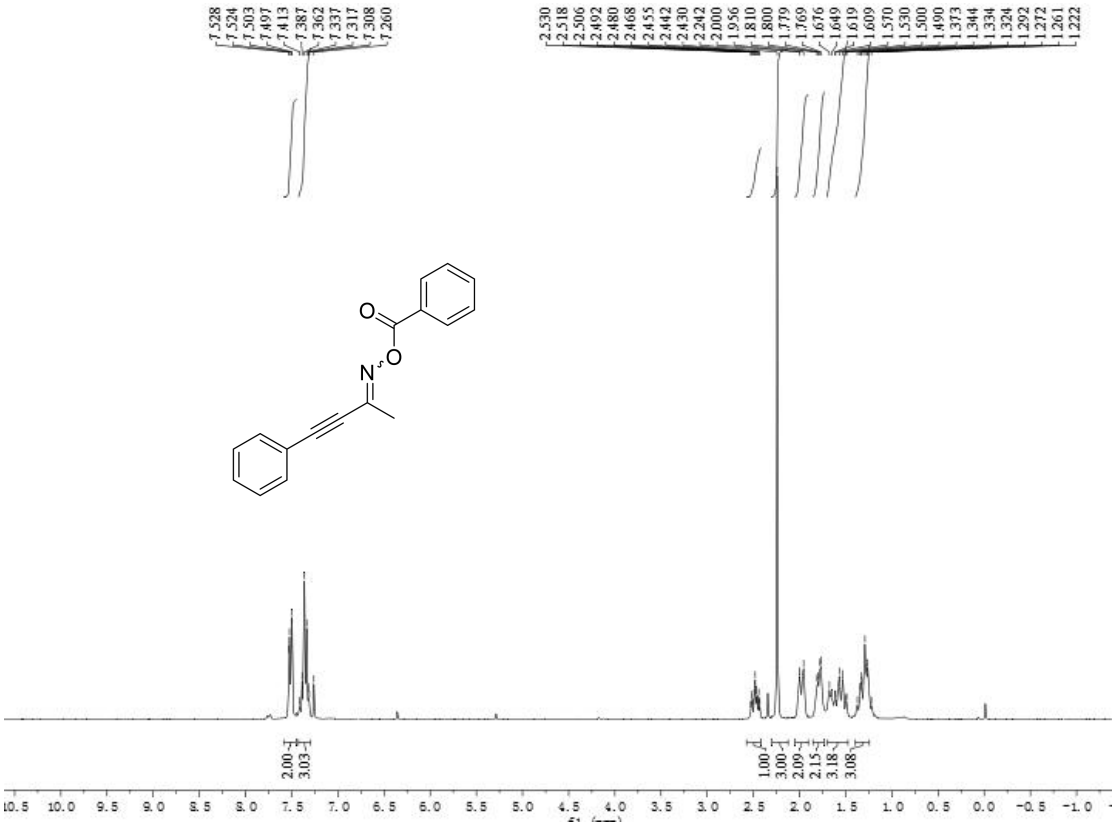


^{1}H NMR (300 MHz, $CDCl_3$)

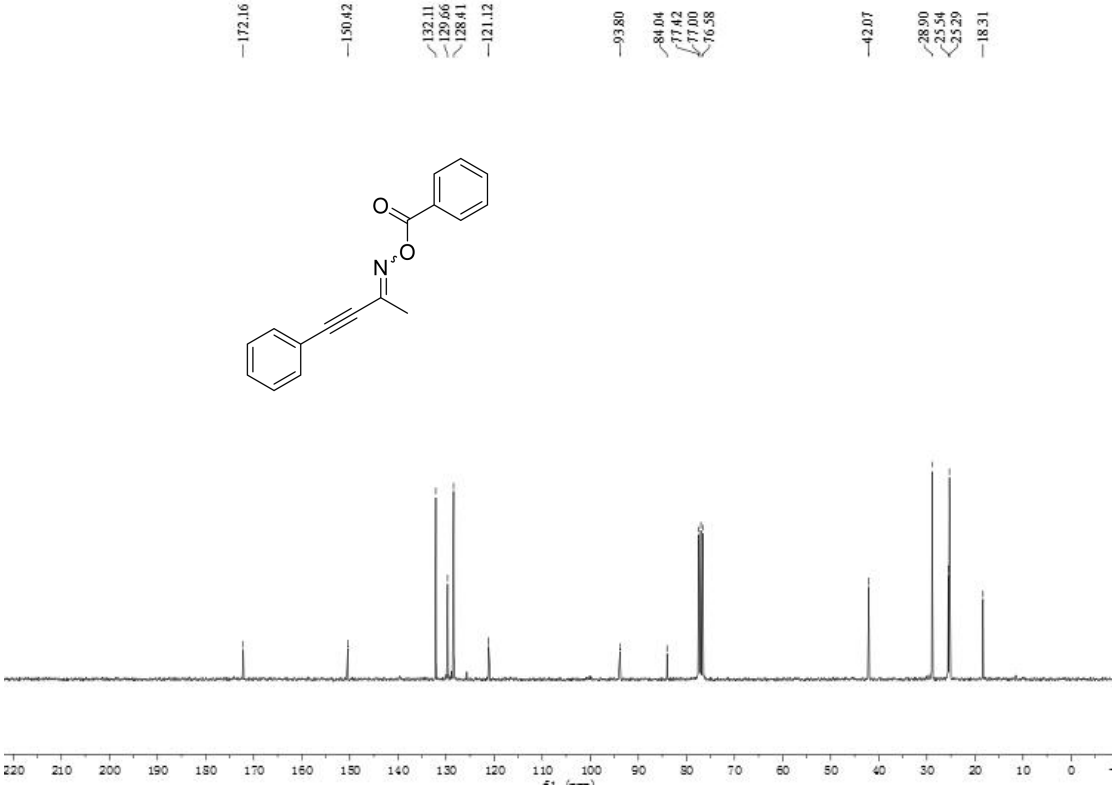


^{13}C NMR (75 MHz, $CDCl_3$)

4-phenylbut-3-yn-2-one *O*-benzoyl oxime (3t):

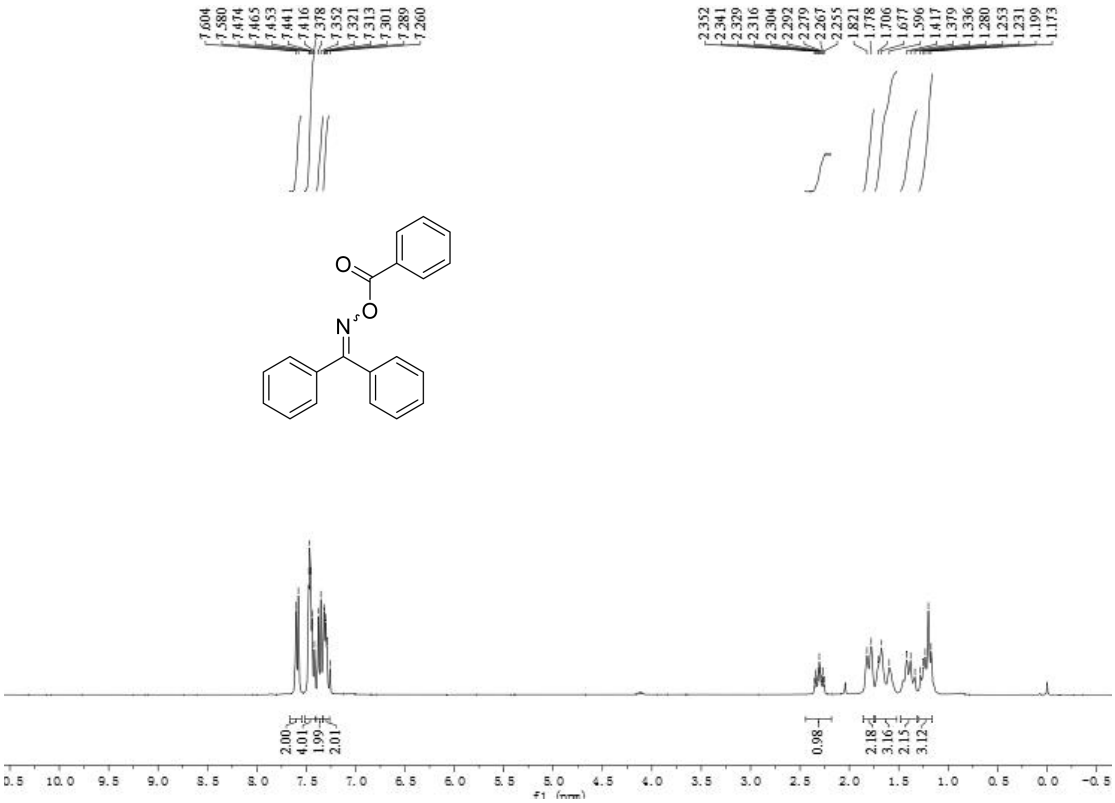


^{1}H NMR (300 MHz, $CDCl_3$)

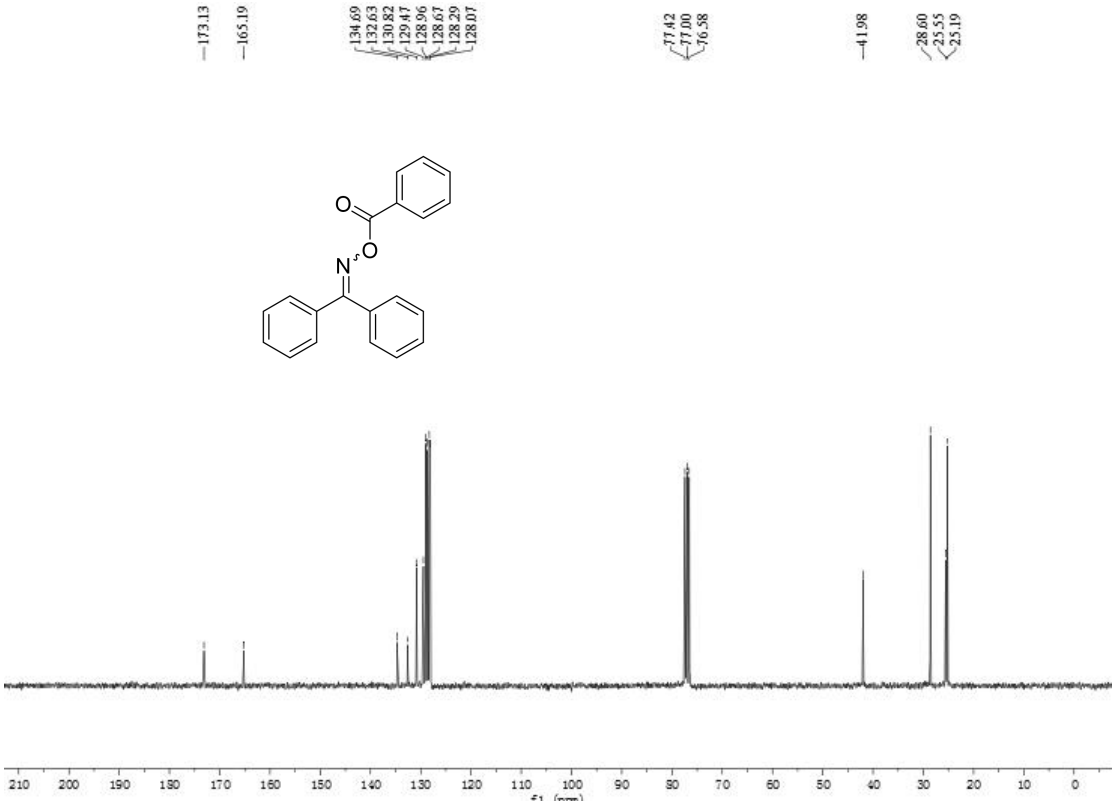


^{13}C NMR (75 MHz, $CDCl_3$)

diphenylmethanone *O*-cyclohexanecarbonyl oxime (3u):

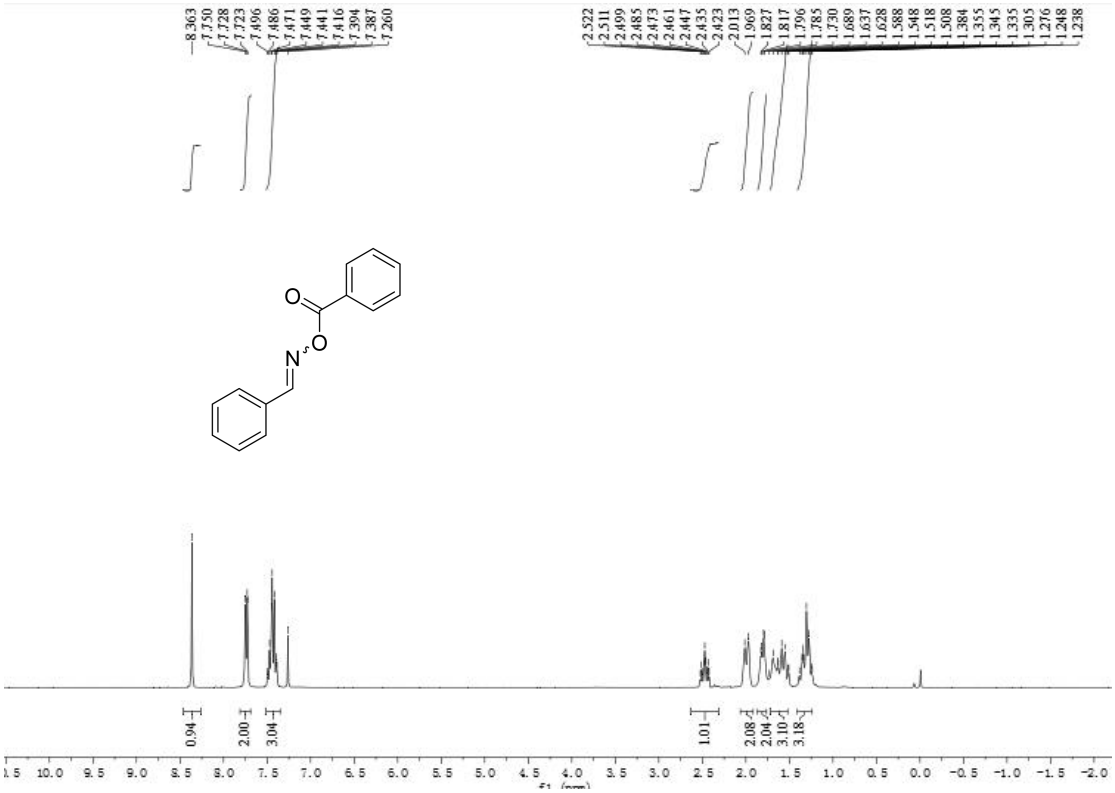


^{1}H NMR (300 MHz, $CDCl_3$)

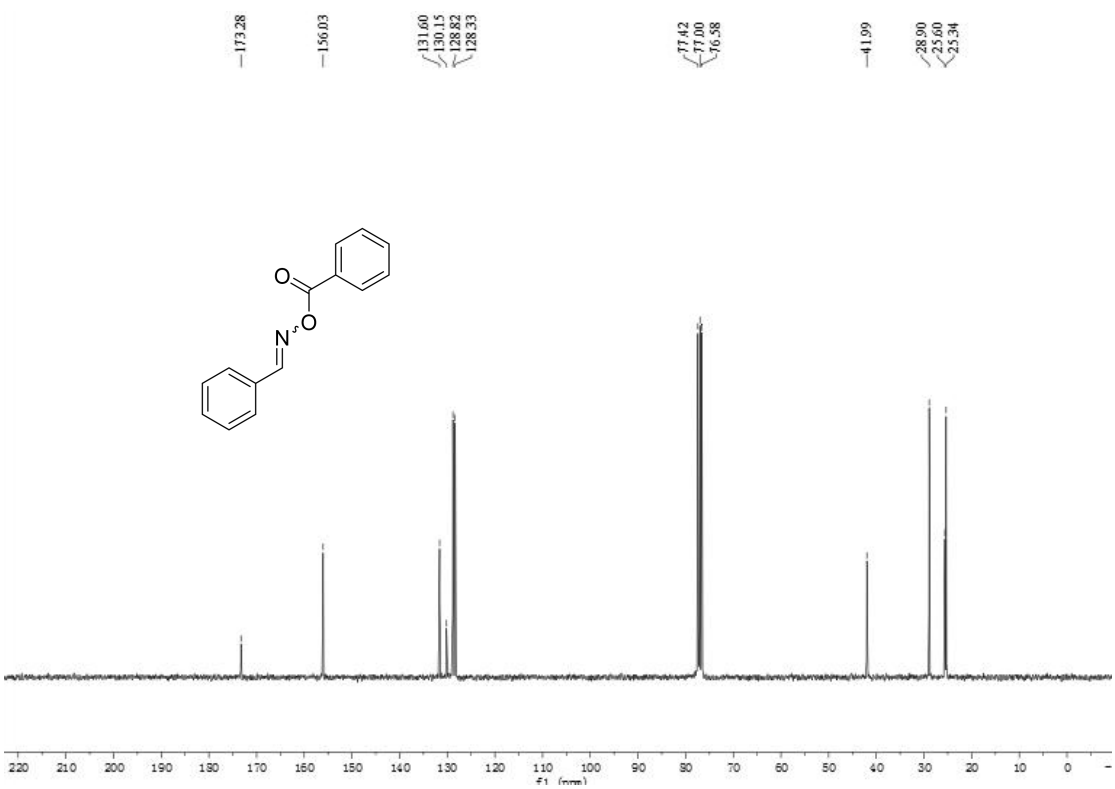


^{13}C NMR (75 MHz, $CDCl_3$)

benzaldehyde *O*-cyclohexanecarbonyl oxime (3v):

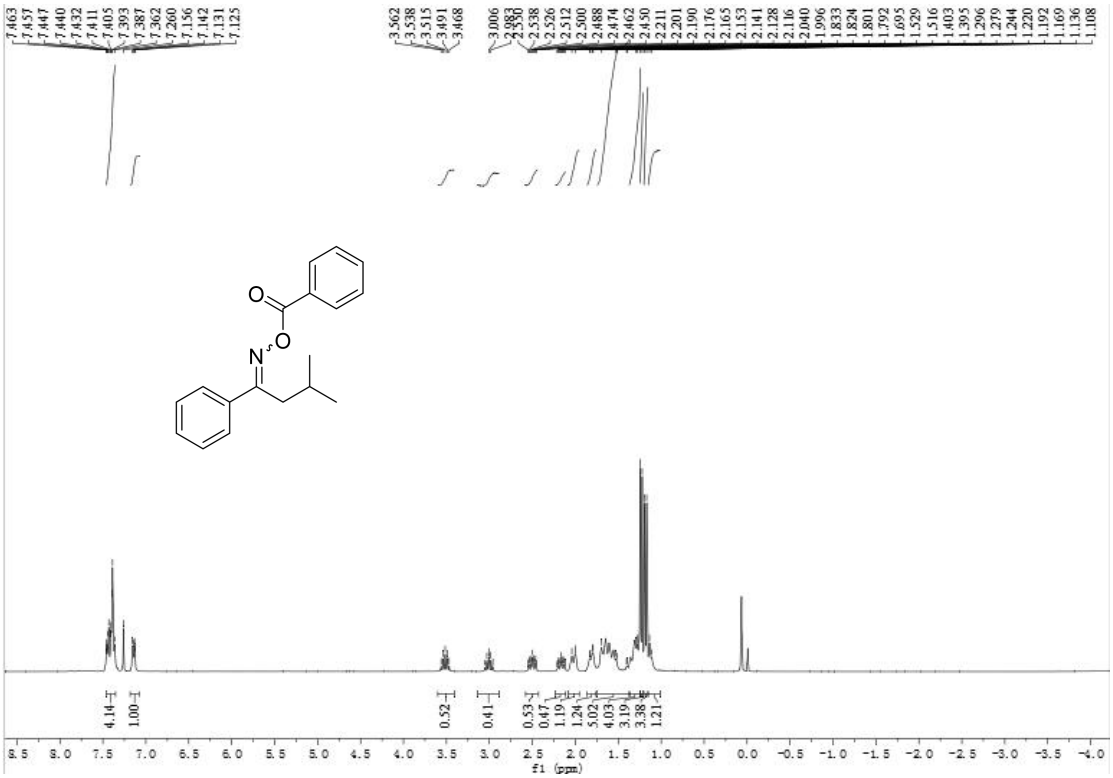


^{1}H NMR (300 MHz, $CDCl_3$)

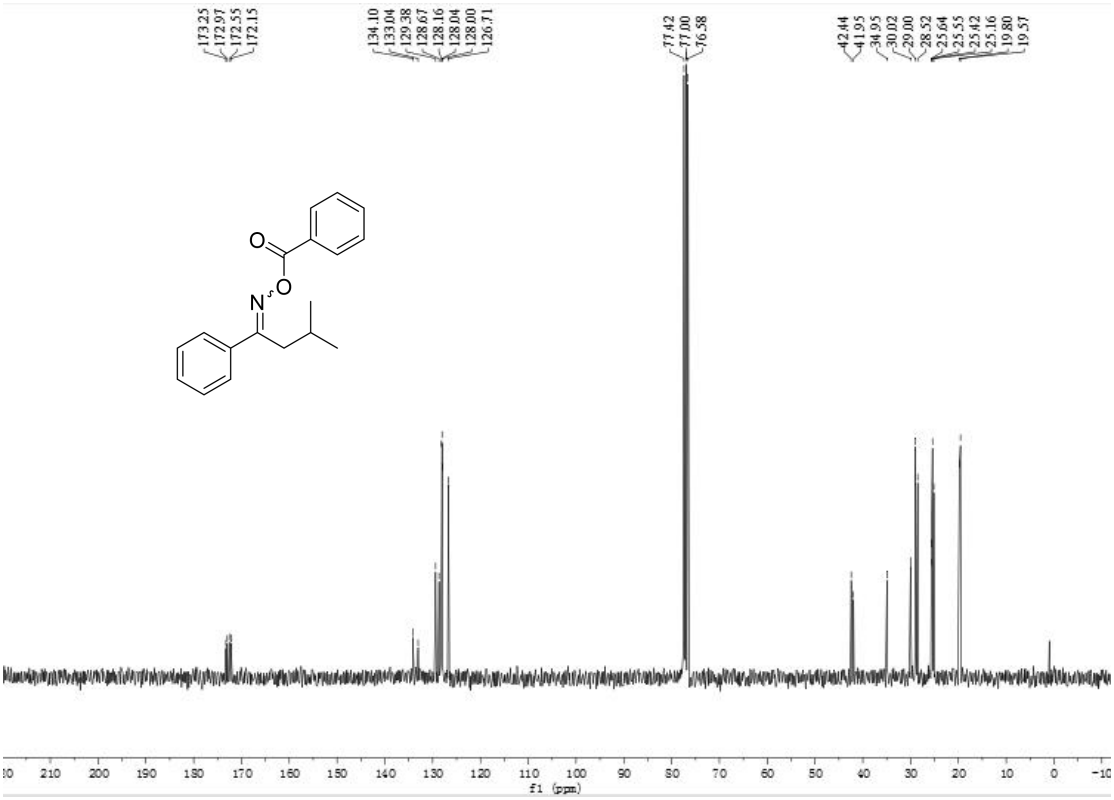


^{13}C NMR (75 MHz, $CDCl_3$)

3-methyl-1-phenylbutan-1-one *O*-cyclohexanecarbonyl oxime (3w):

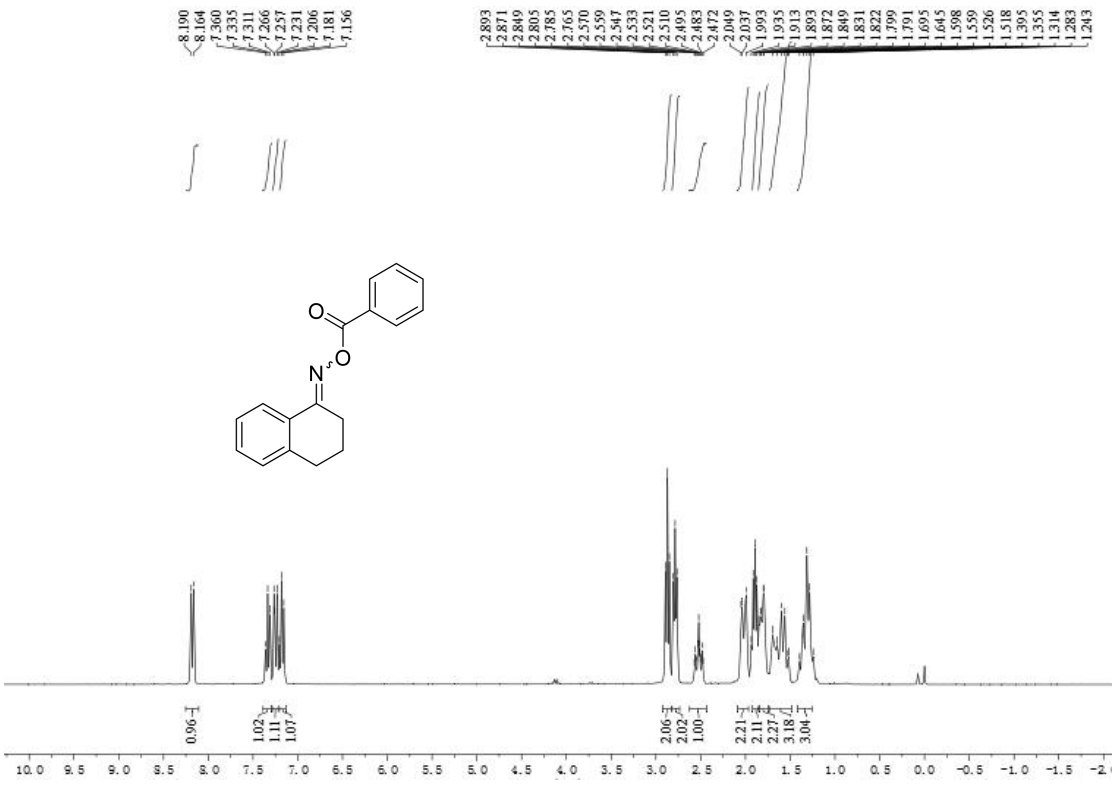


^{1}H NMR (300 MHz, $CDCl_3$)

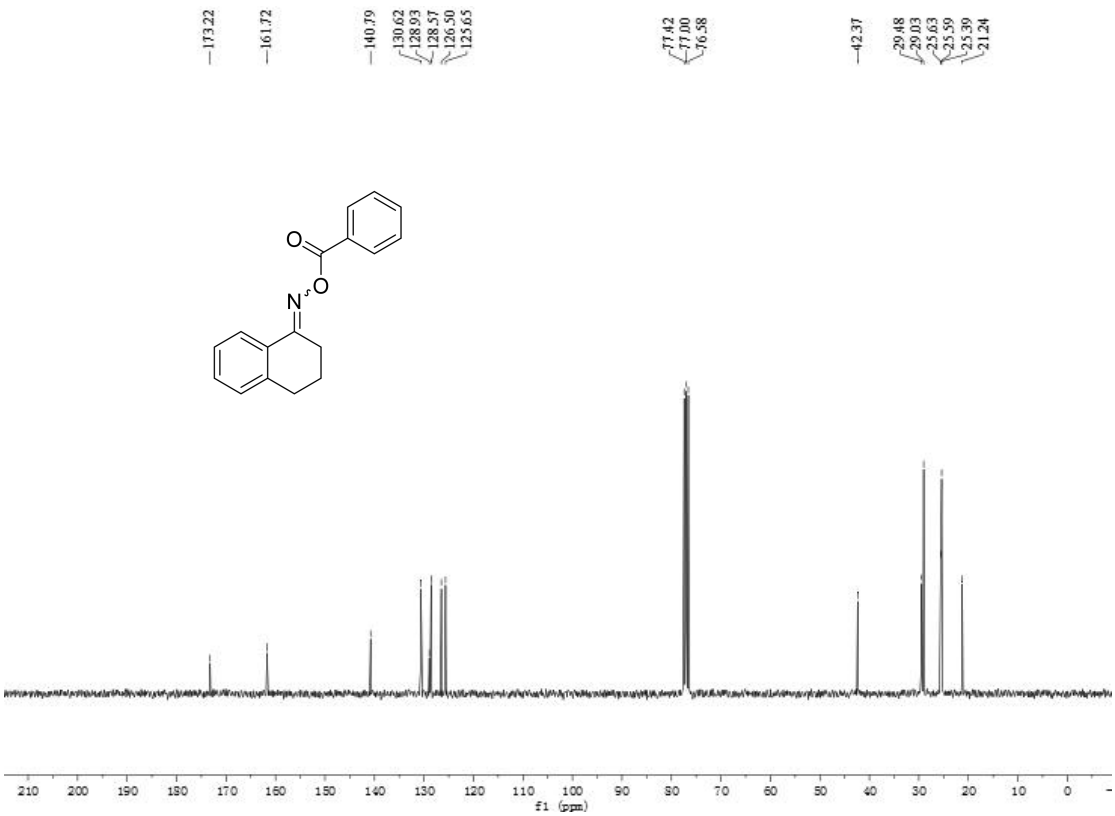


^{13}C NMR (75 MHz, $CDCl_3$)

3,4-dihydronaphthalen-1(2H)-one *O*-cyclohexanecarbonyl oxime (3x):

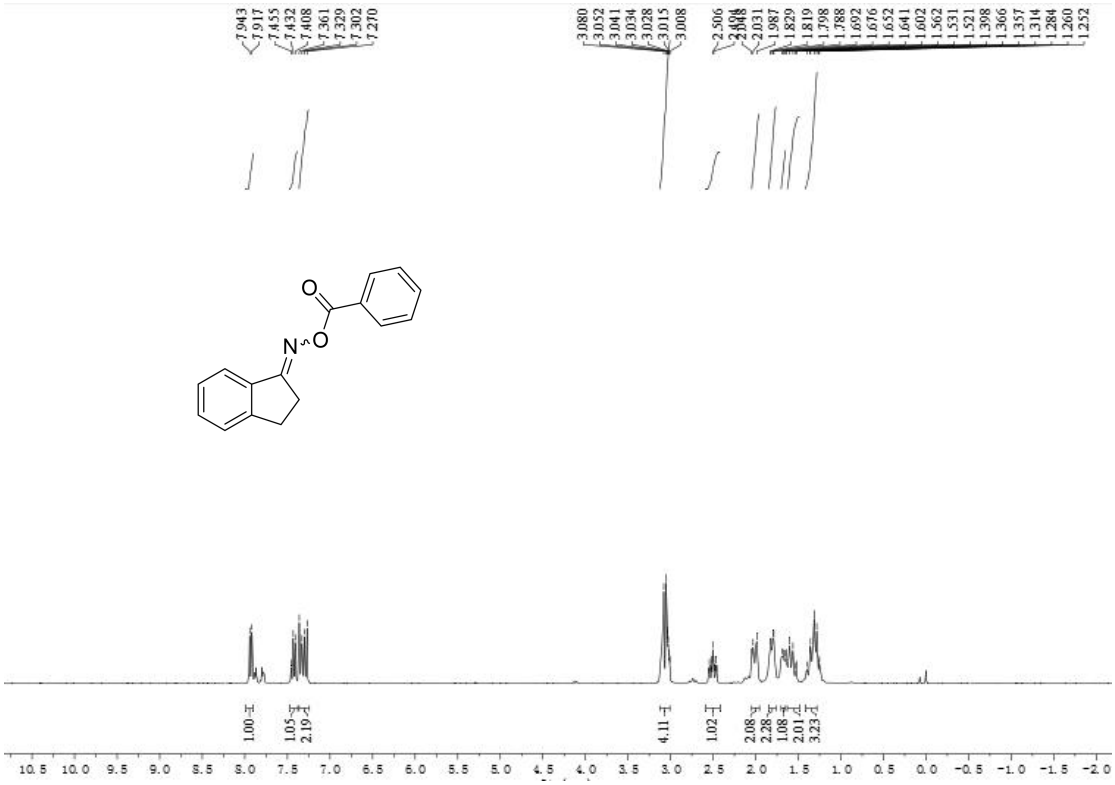


^{1}H NMR (300 MHz, $CDCl_3$)

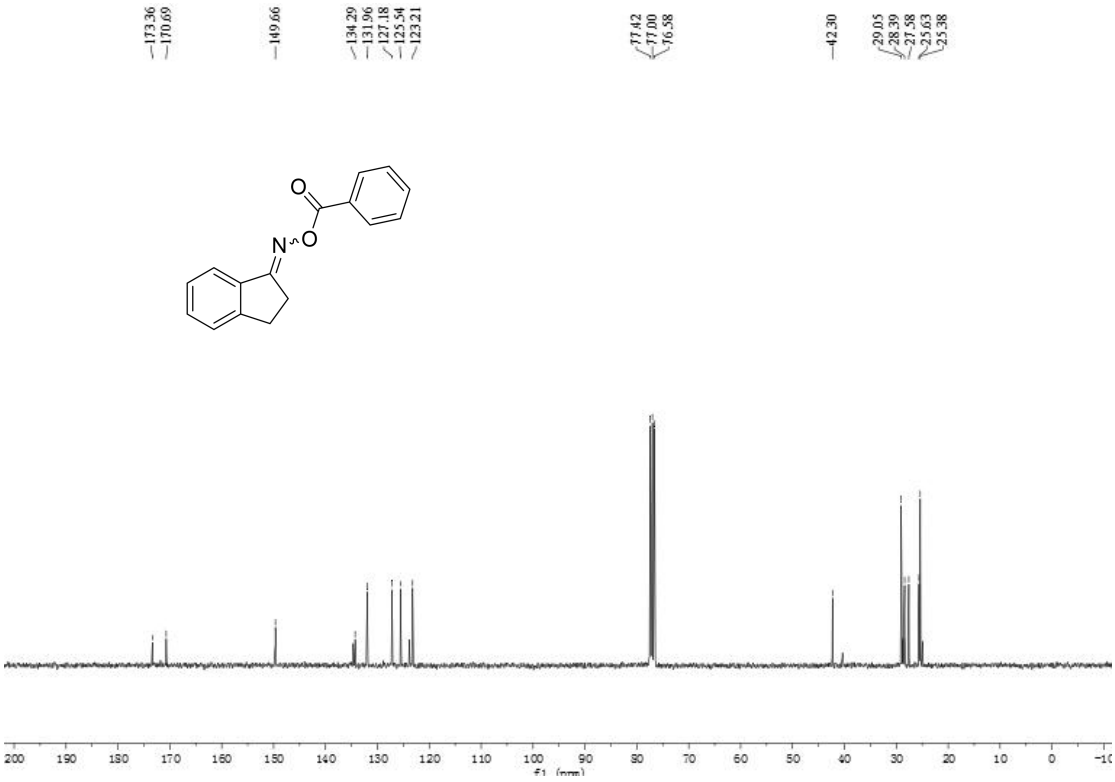


^{13}C NMR (75 MHz, $CDCl_3$)

2,3-dihydro-1H-inden-1-one *O*-cyclohexanecarbonyl oxime (3y):

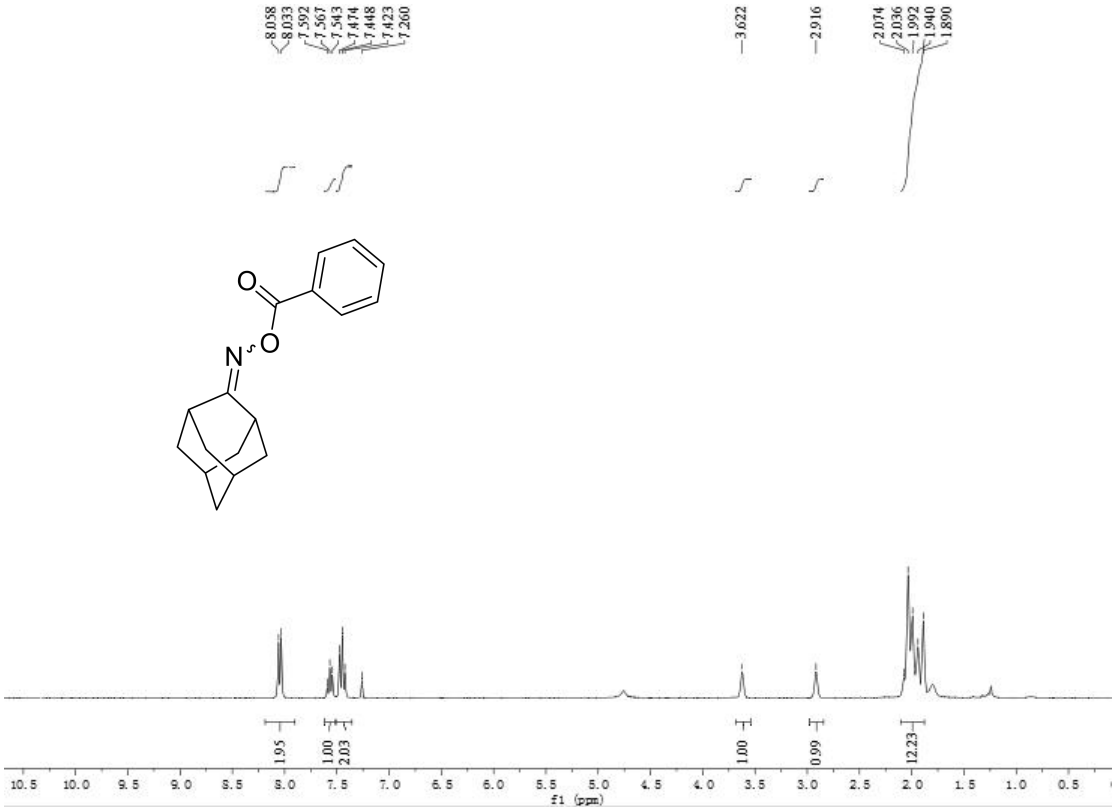


^{1}H NMR (300 MHz, $CDCl_3$)

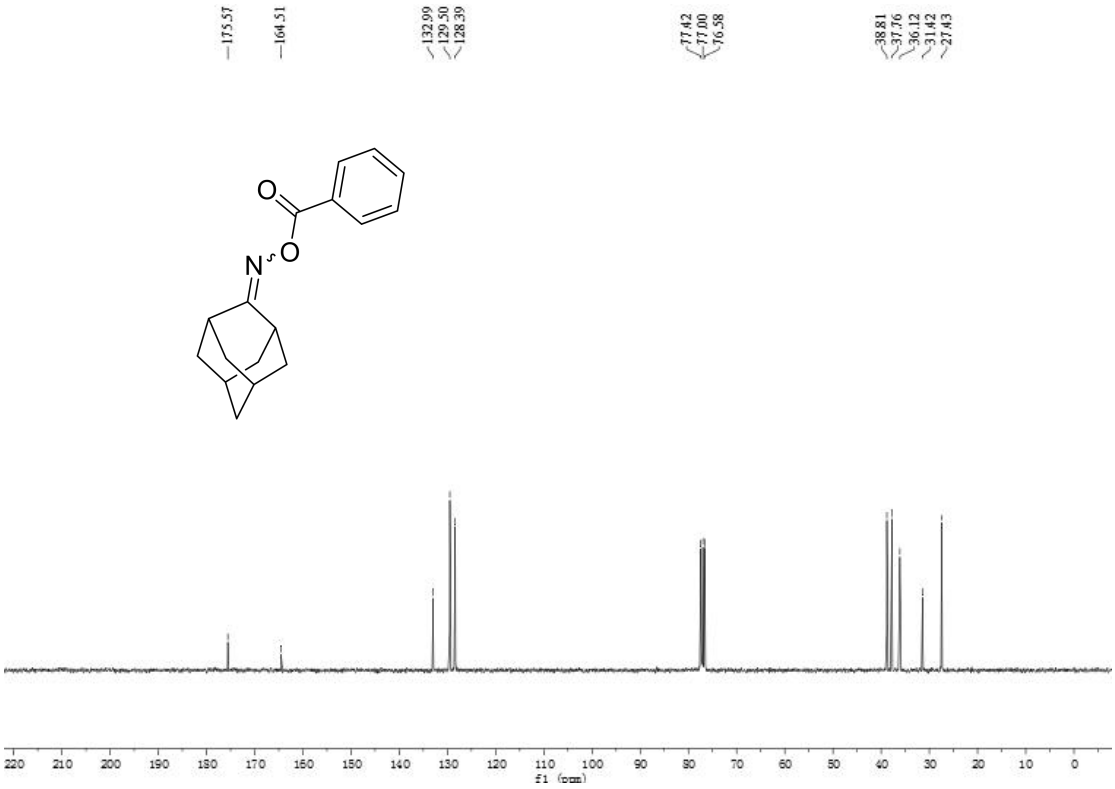


^{13}C NMR (75 MHz, $CDCl_3$)

adamantan-2-one *O*-benzoyl oxime (3z):

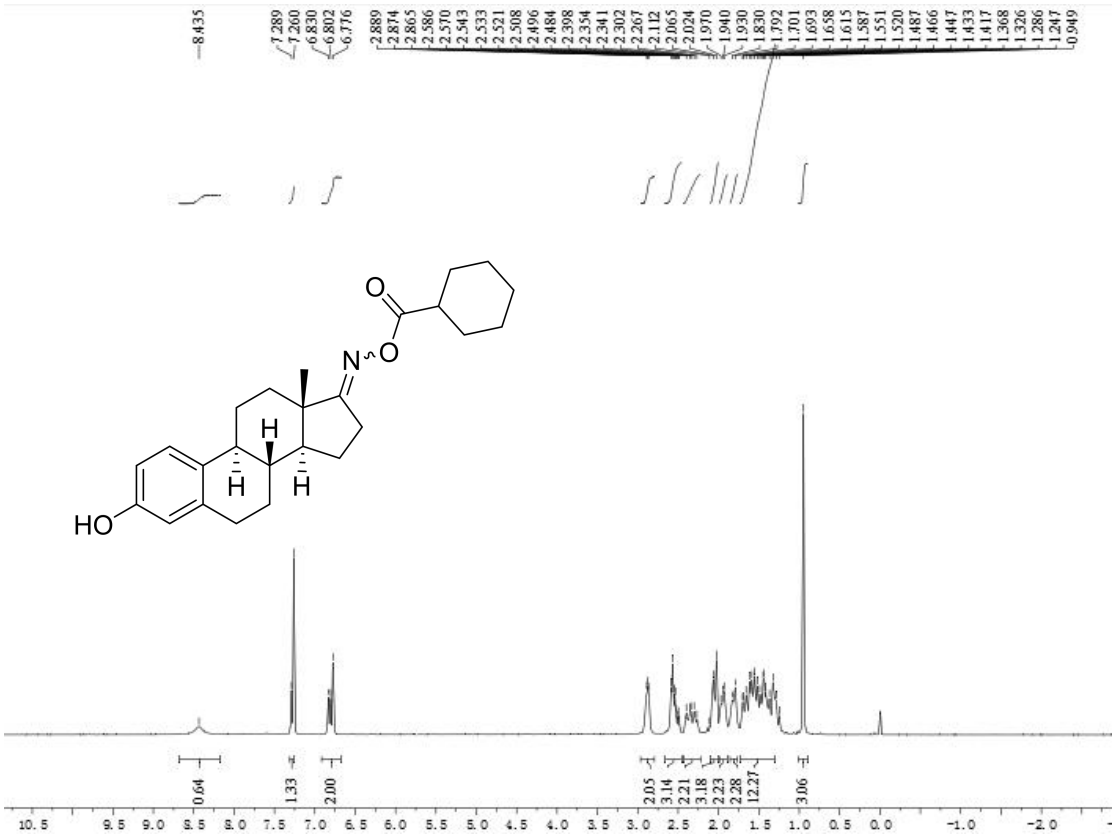


^{1}H NMR (300 MHz, $CDCl_3$)

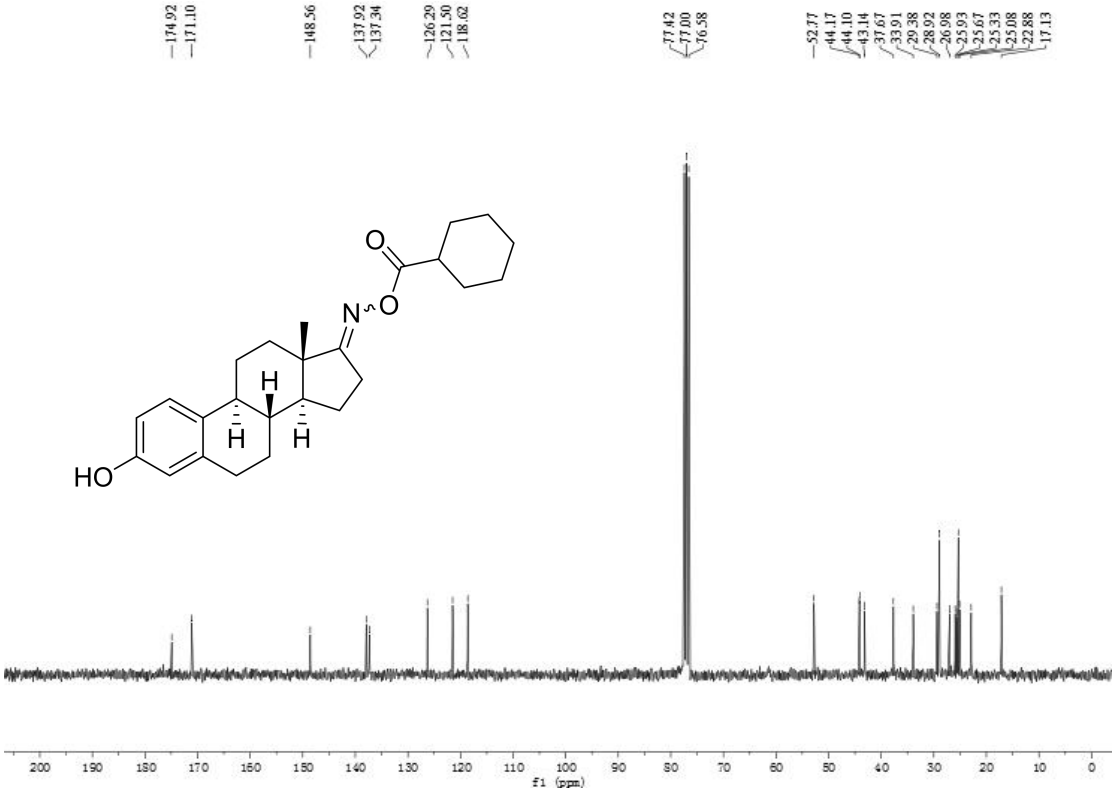


^{13}C NMR (75 MHz, $CDCl_3$)

(8R,9S,13S,14S)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one *O*-cyclohexanecarbonyl oxime (3aa):

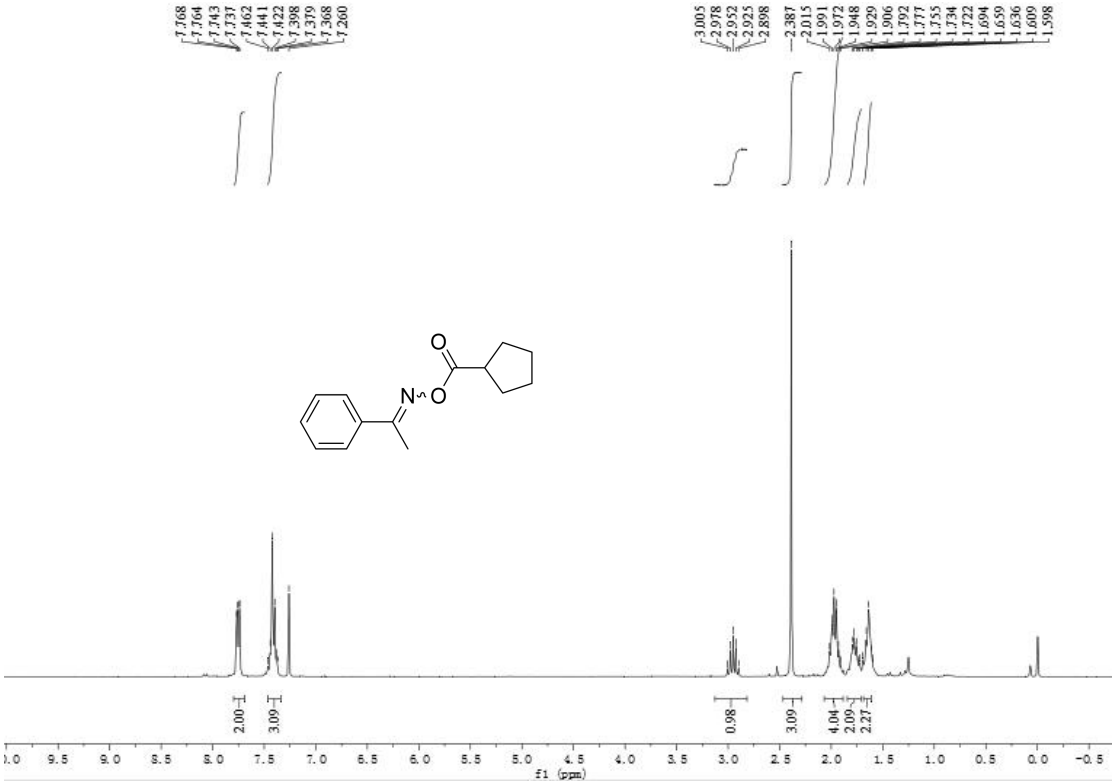


^{1}H NMR (300 MHz, $CDCl_3$)

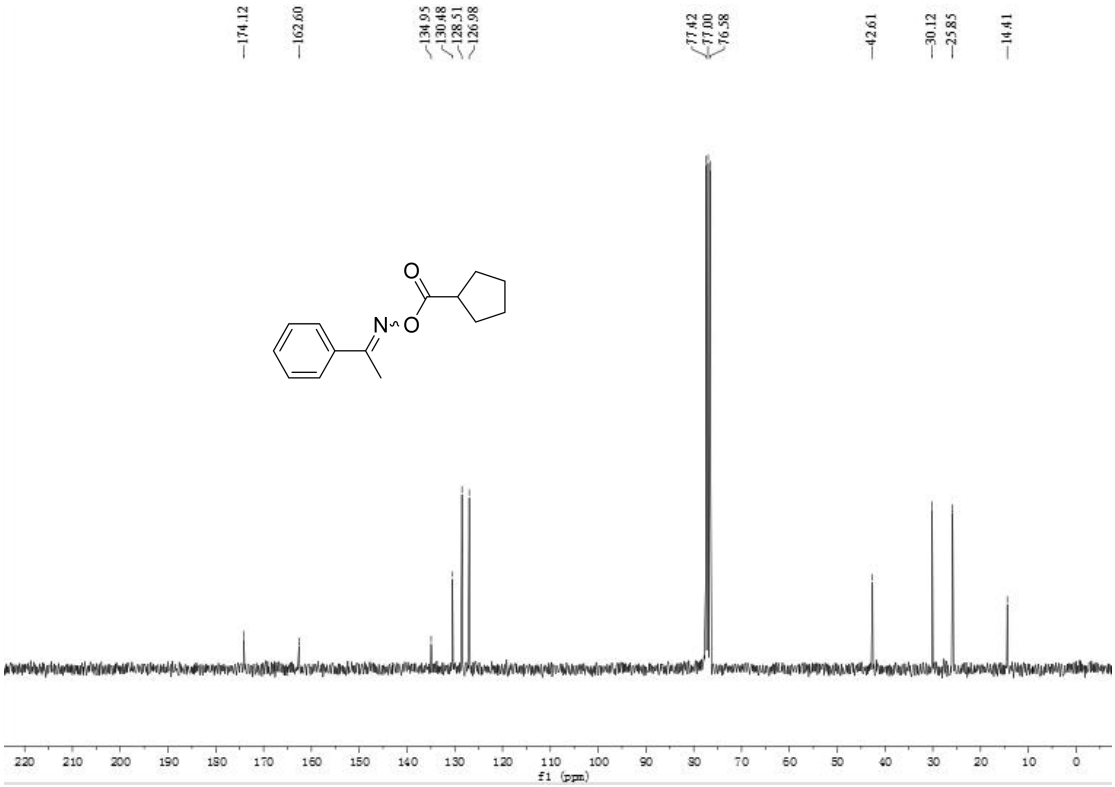


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-cyclopentanecarbonyl oxime (4a):

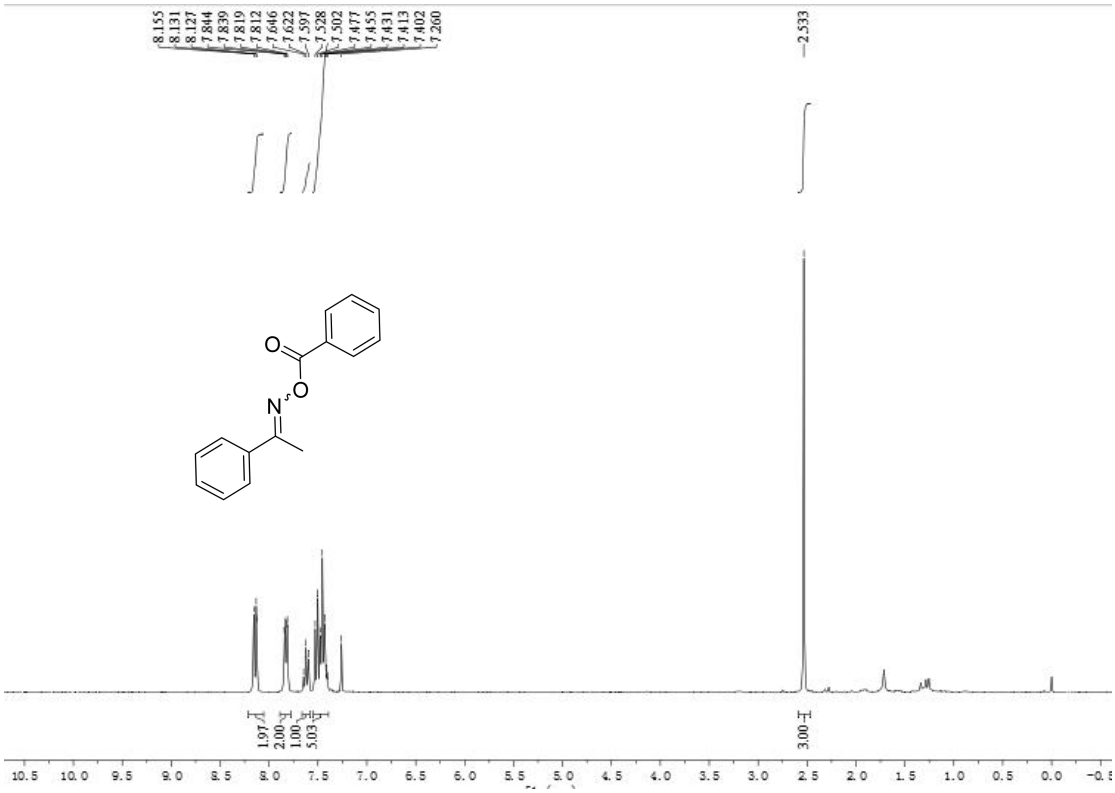


^{1}H NMR (300 MHz, $CDCl_3$)

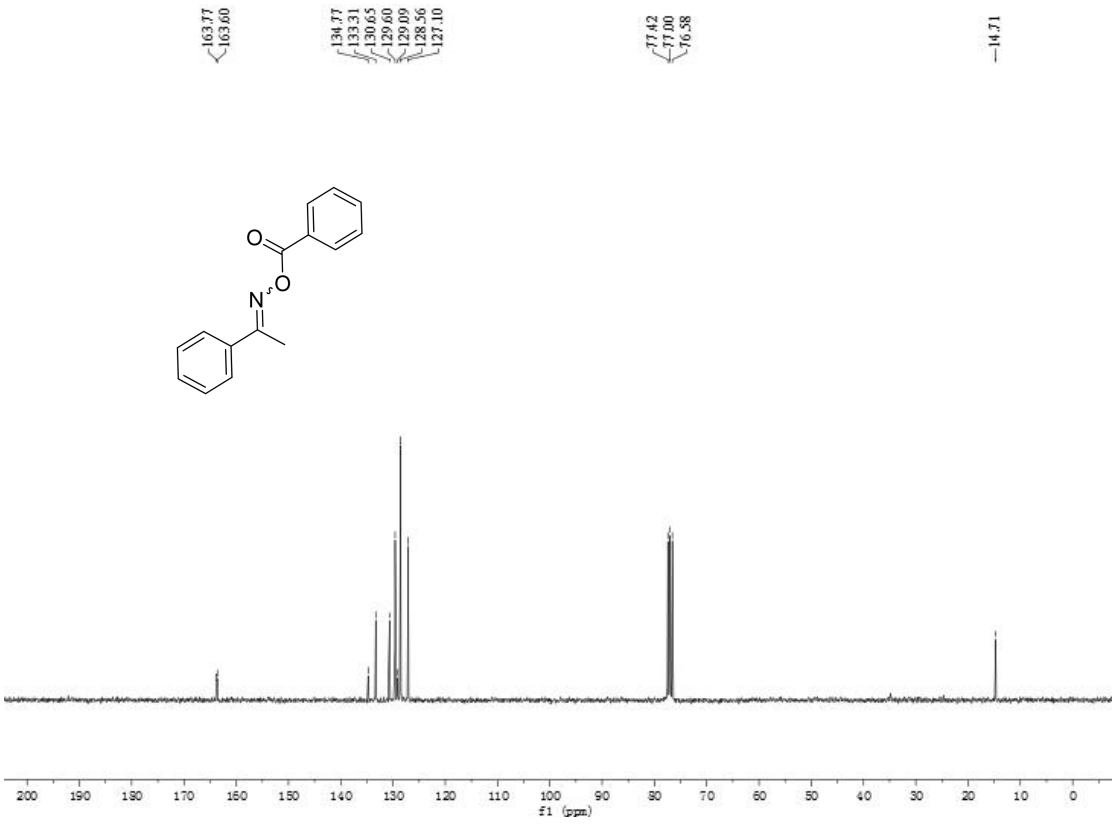


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-benzoyl oxime (4b):

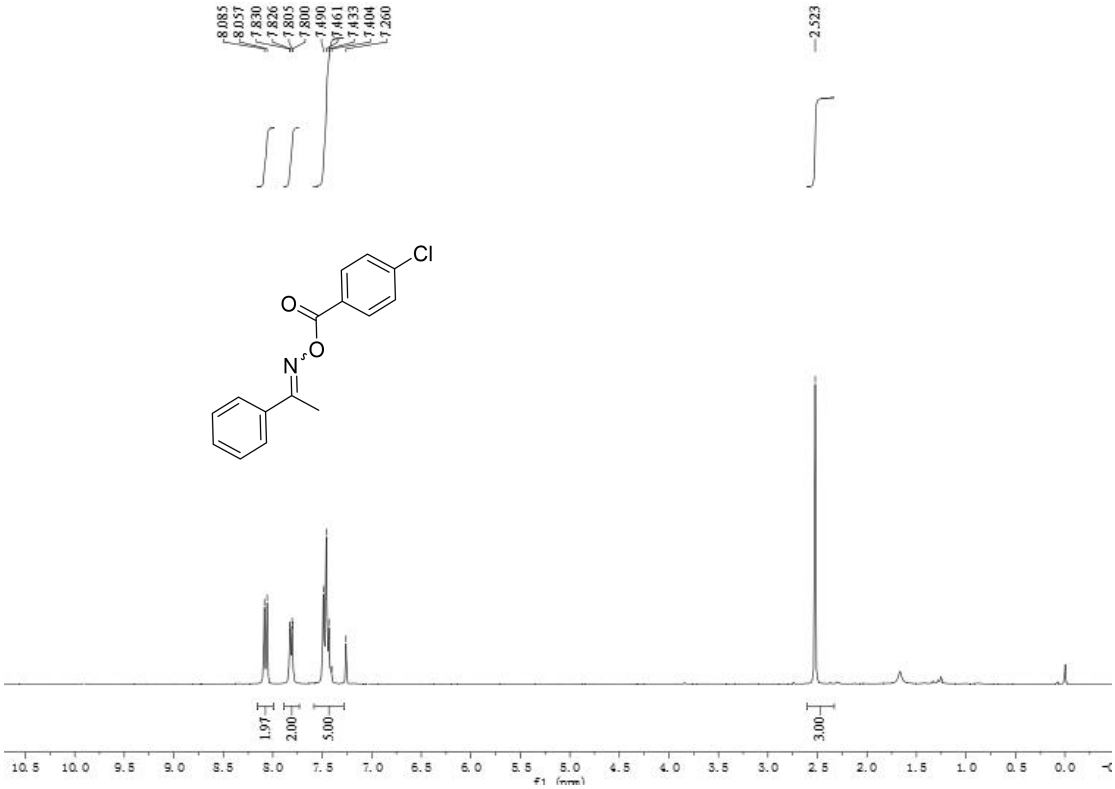


^{1}H NMR (300 MHz, $CDCl_3$)

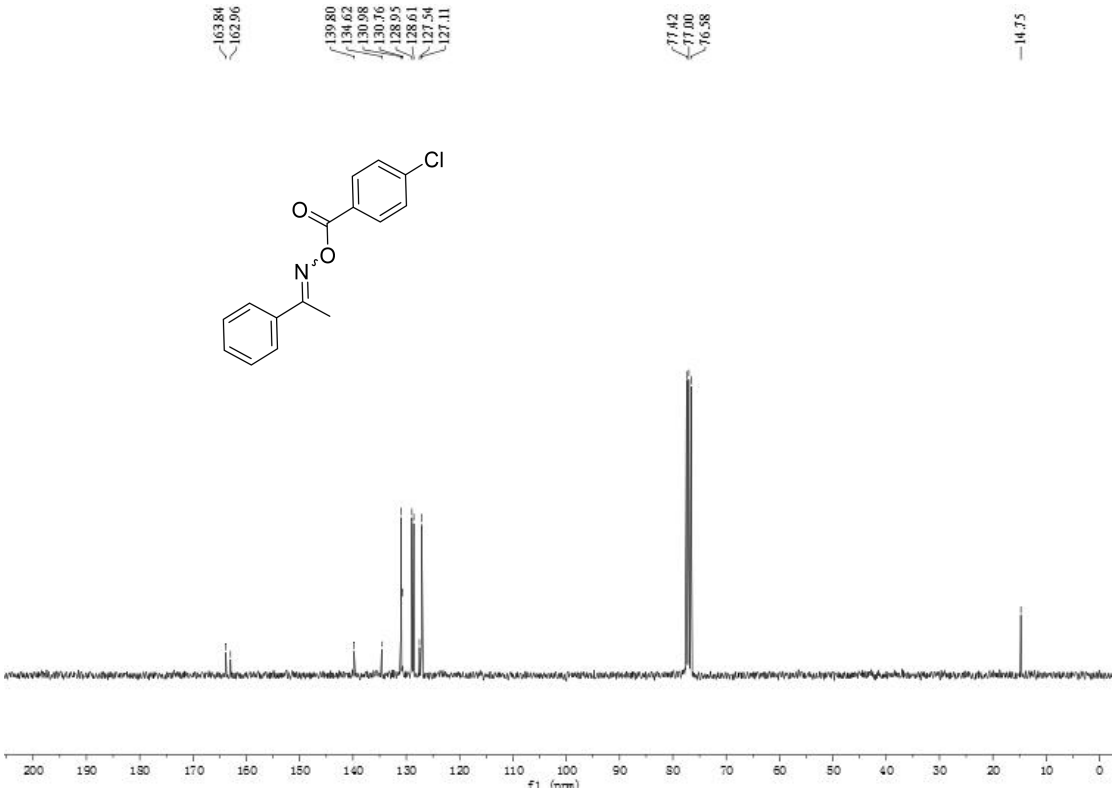


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-(4-chlorobenzoyl) oxime (4c):

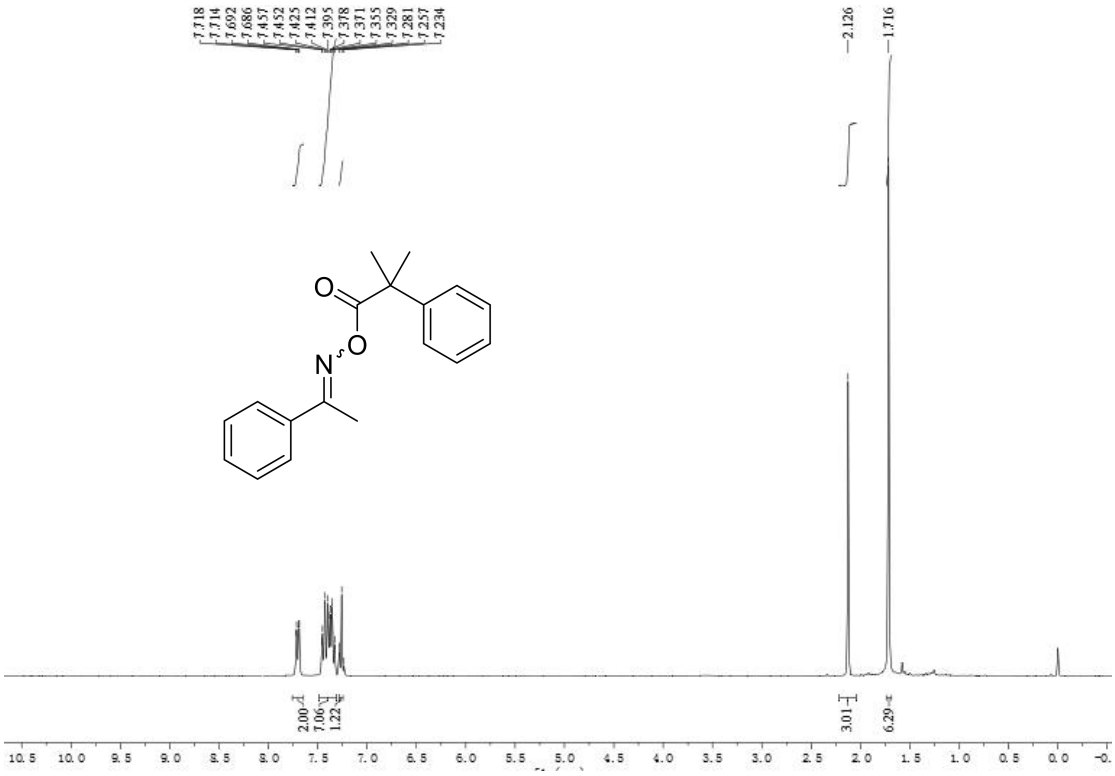


^{1}H NMR (300 MHz, $CDCl_3$)

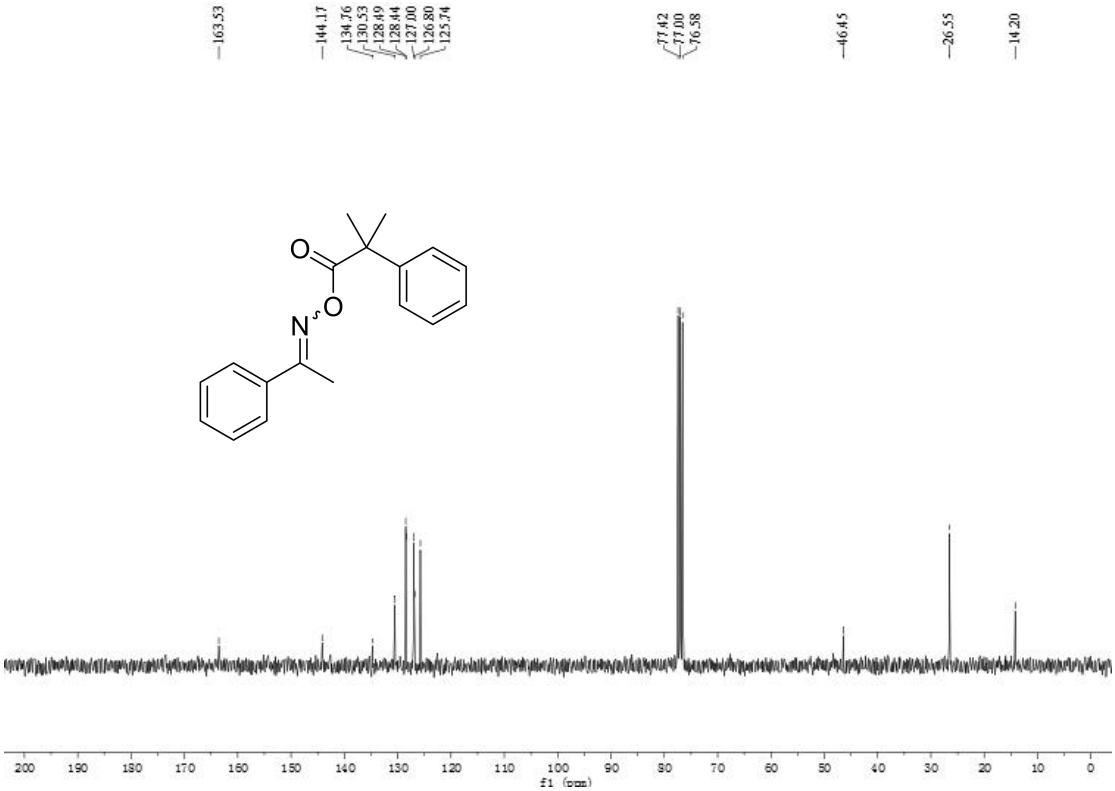


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-(2-methyl-2-phenylpropanoyl) oxime (4d):

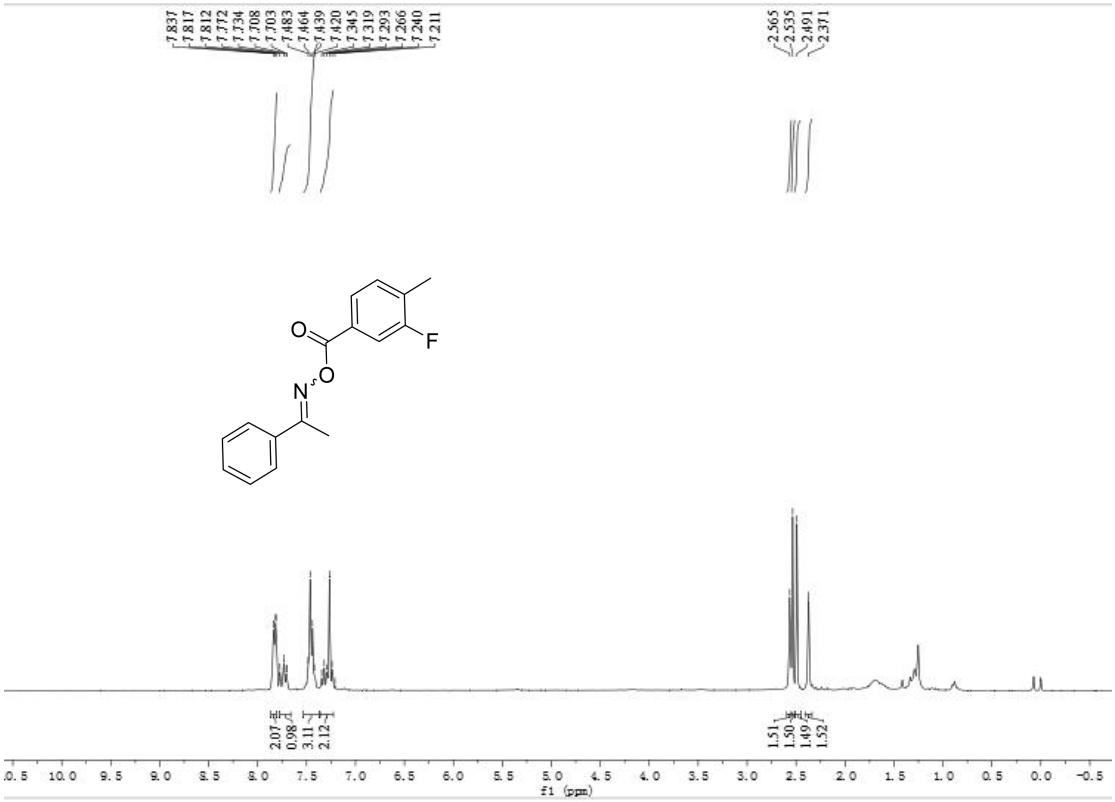


^{1}H NMR (300 MHz, $CDCl_3$)

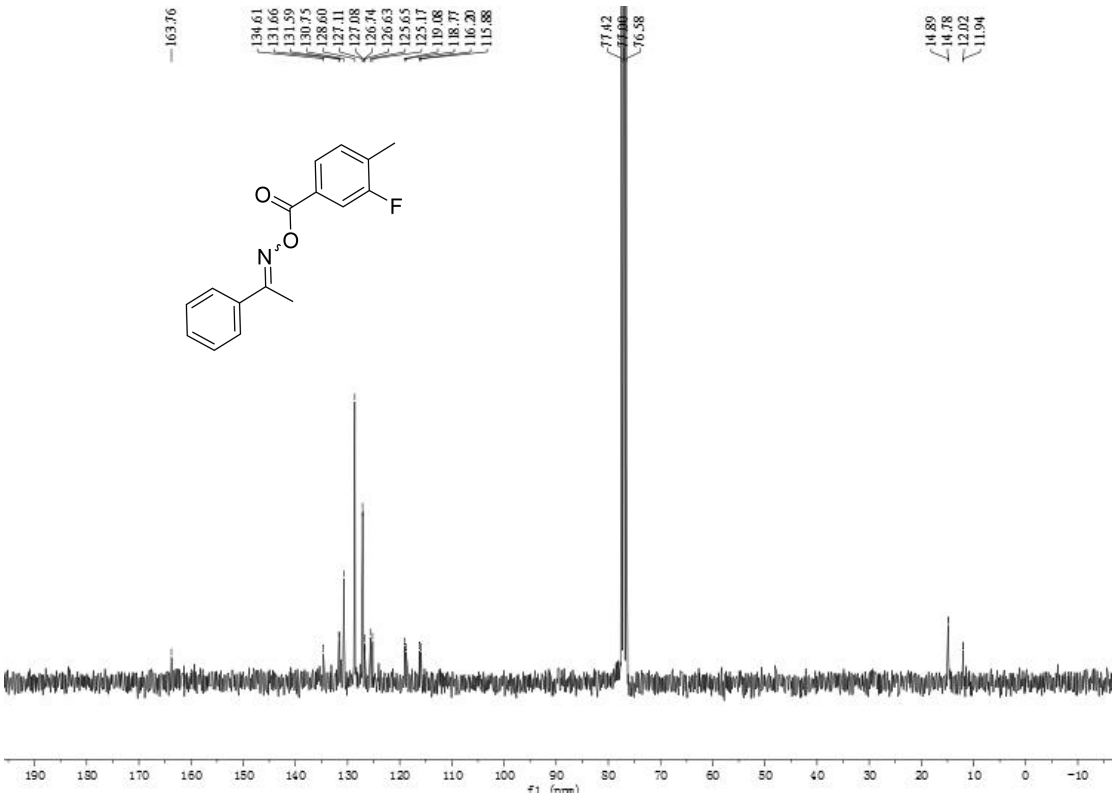


^{13}C NMR (75 MHz, $CDCl_3$)

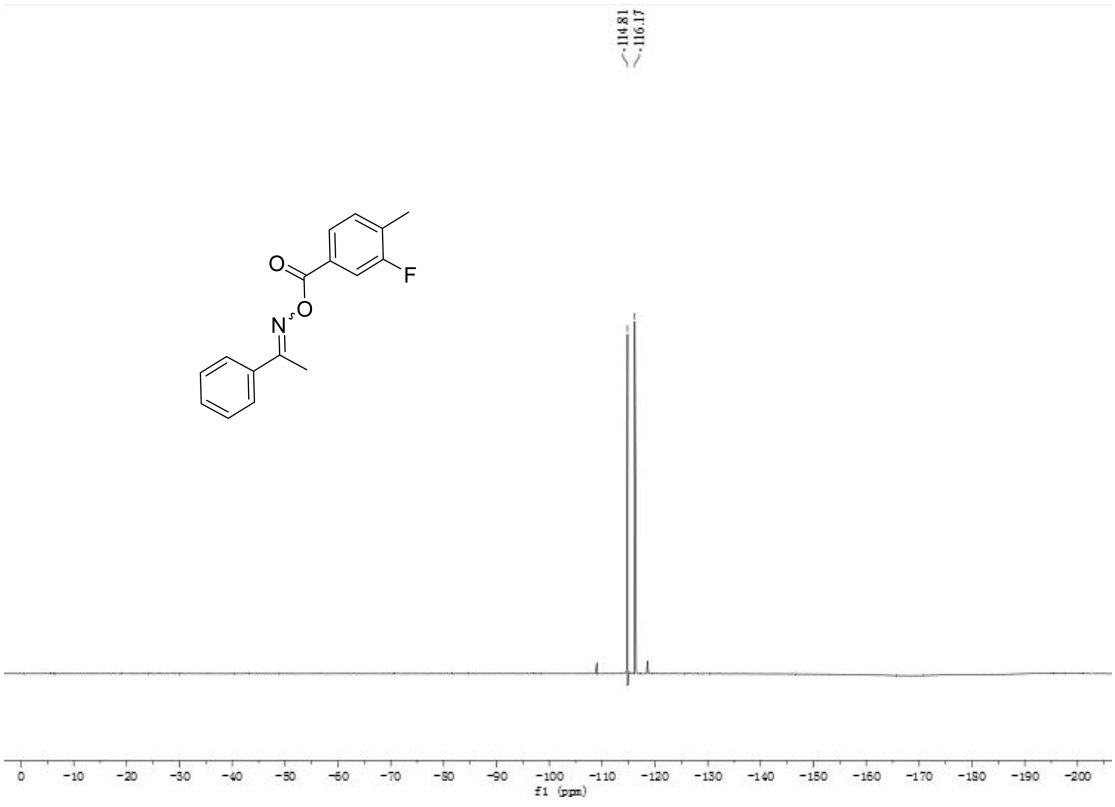
1-phenylethan-1-one *O*-(3-fluoro-4-methylbenzoyl) oximee (4e):



^{1}H NMR (300 MHz, $CDCl_3$)

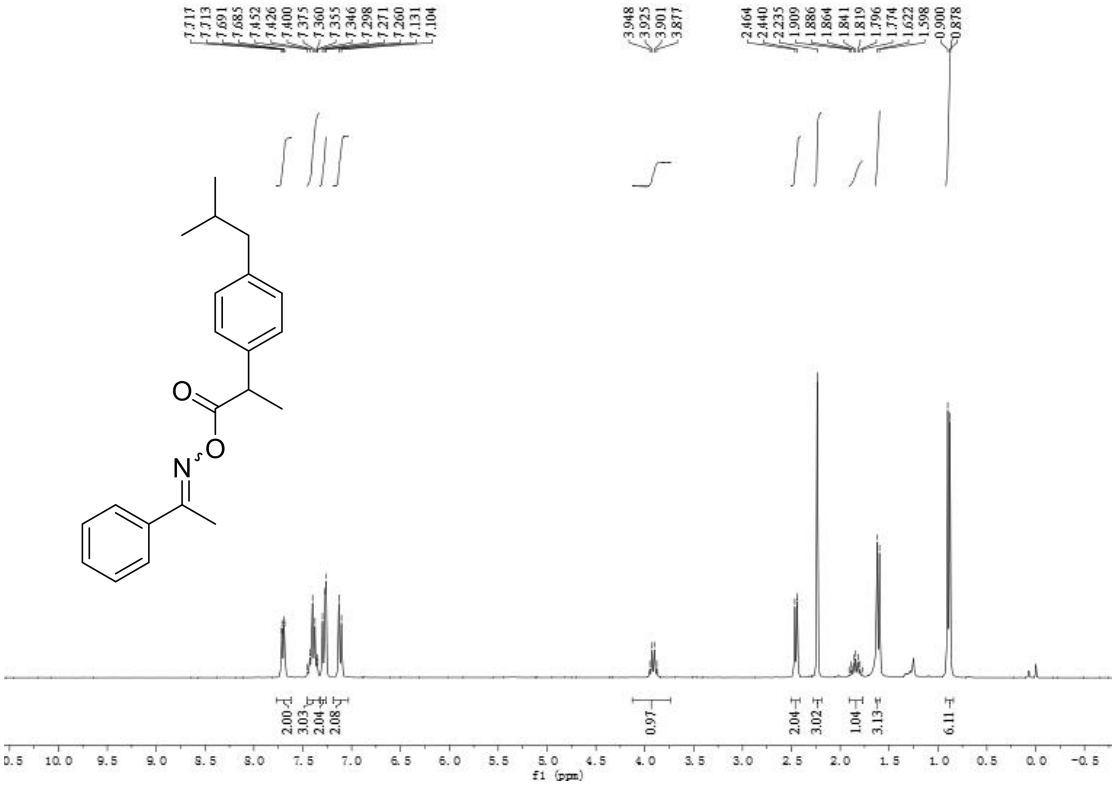


^{13}C NMR (75 MHz, $CDCl_3$)

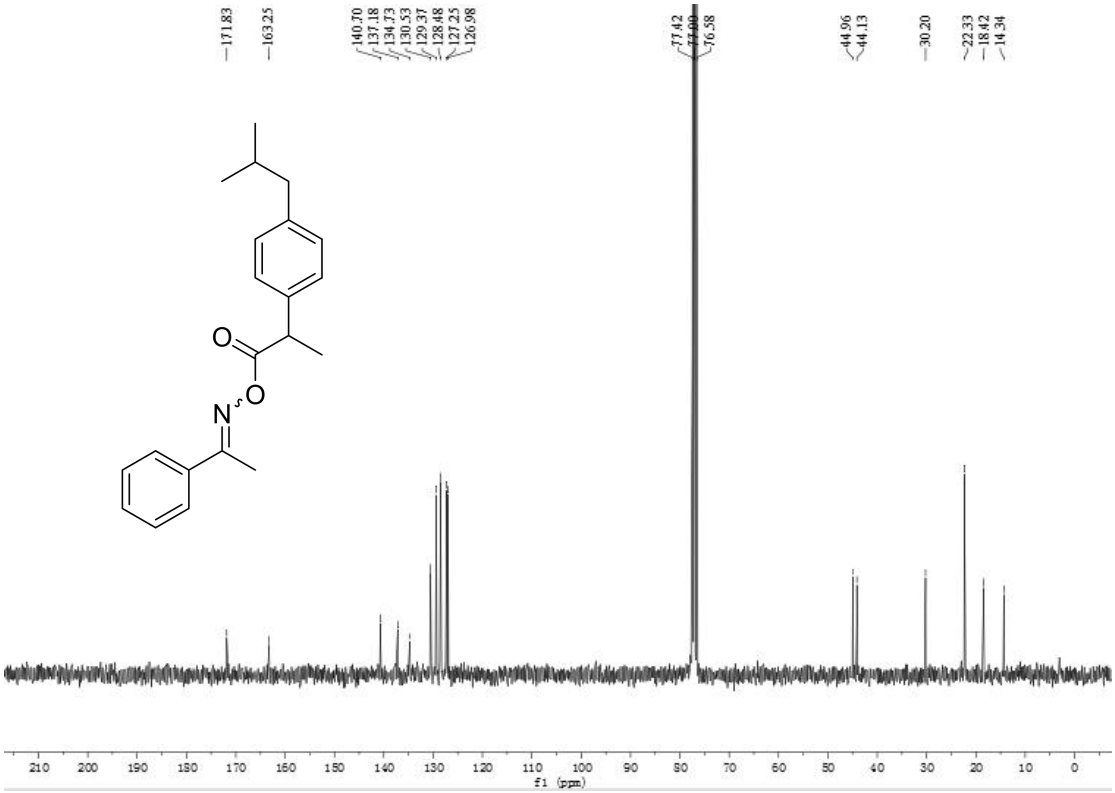


^{19}F NMR (564 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-(2-(4-isobutylphenyl)propanoyl) oxime (4f):

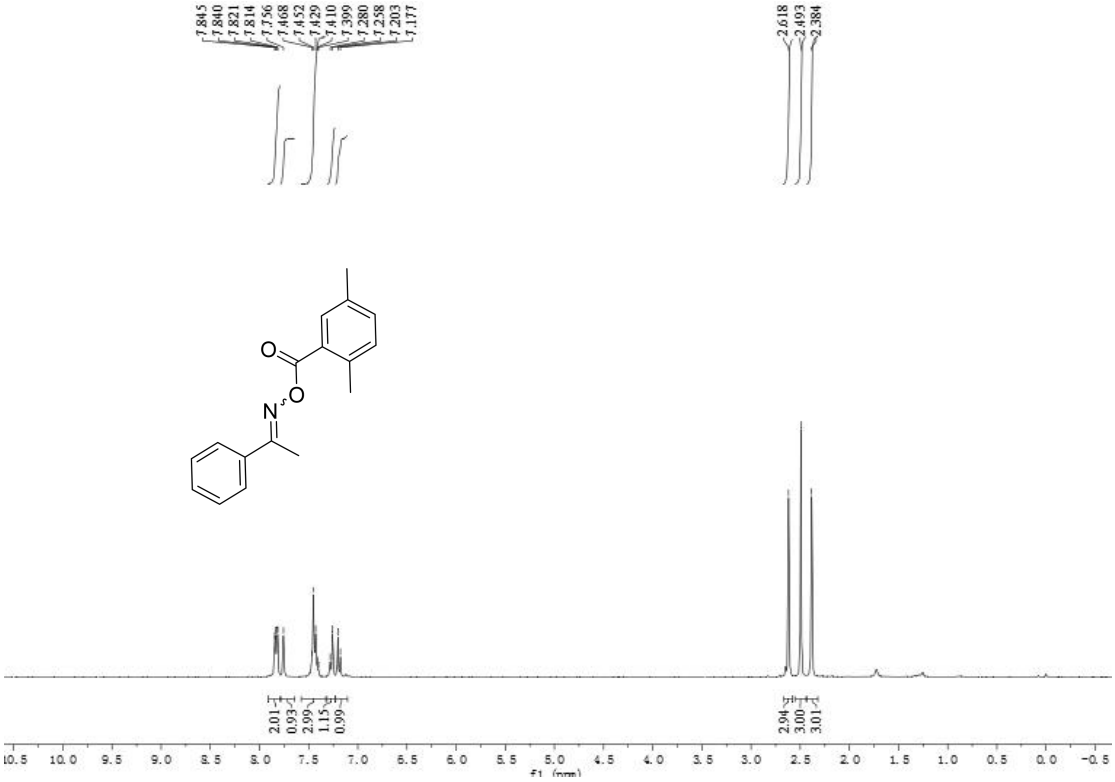


^{1}H NMR (300 MHz, $CDCl_3$)

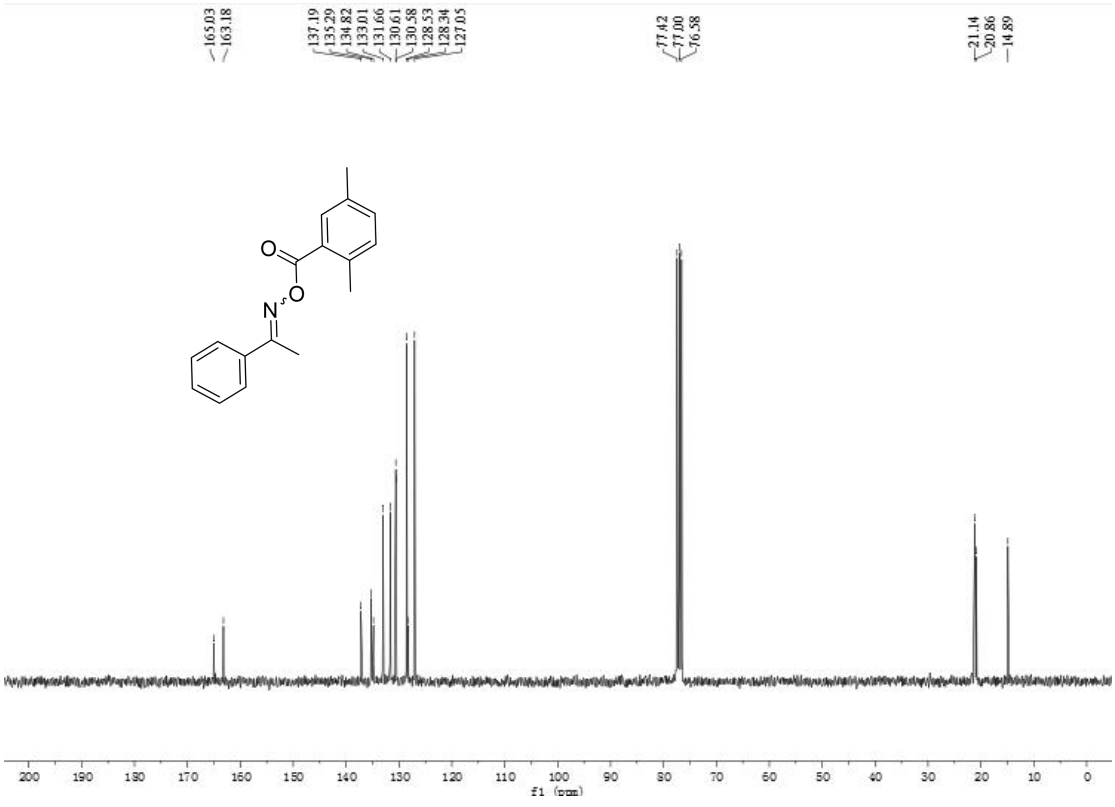


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-(2-(2,5-dimethylphenyl)propanoyl) oxime (4g):

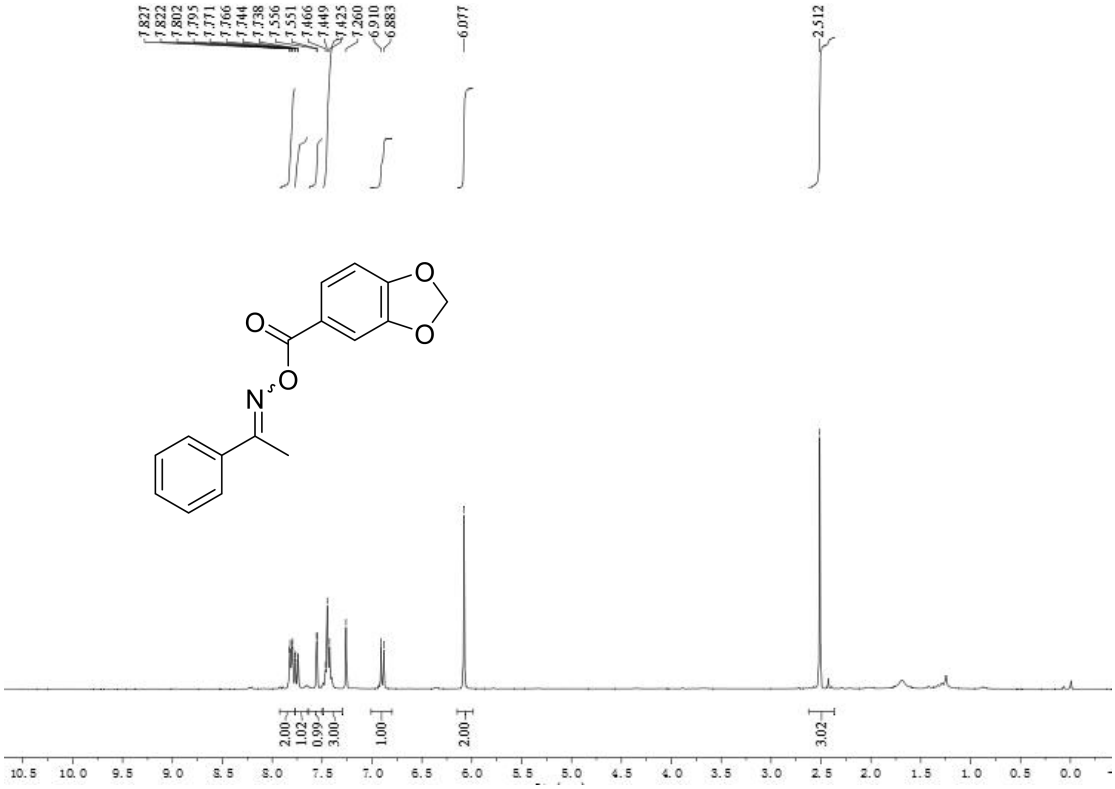


^{1}H NMR (300 MHz, $CDCl_3$)

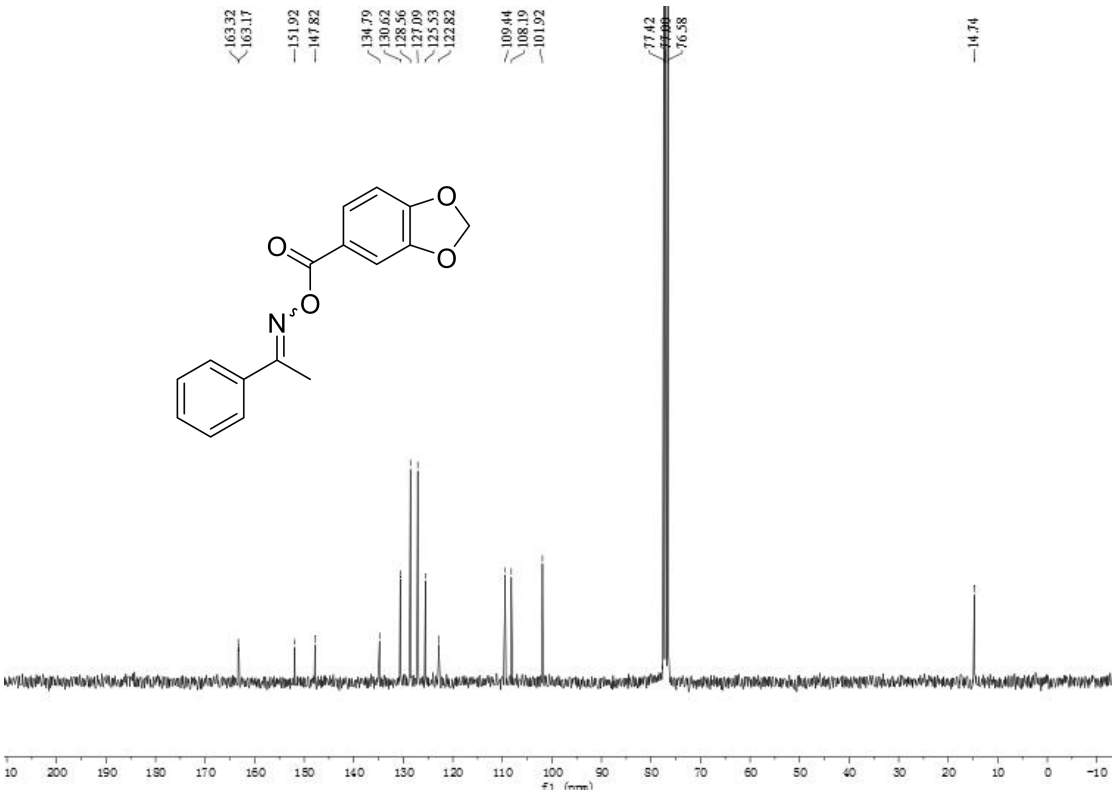


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-(benzo[*d*][1,3]dioxole-5-carbonyl) oxime (4h):

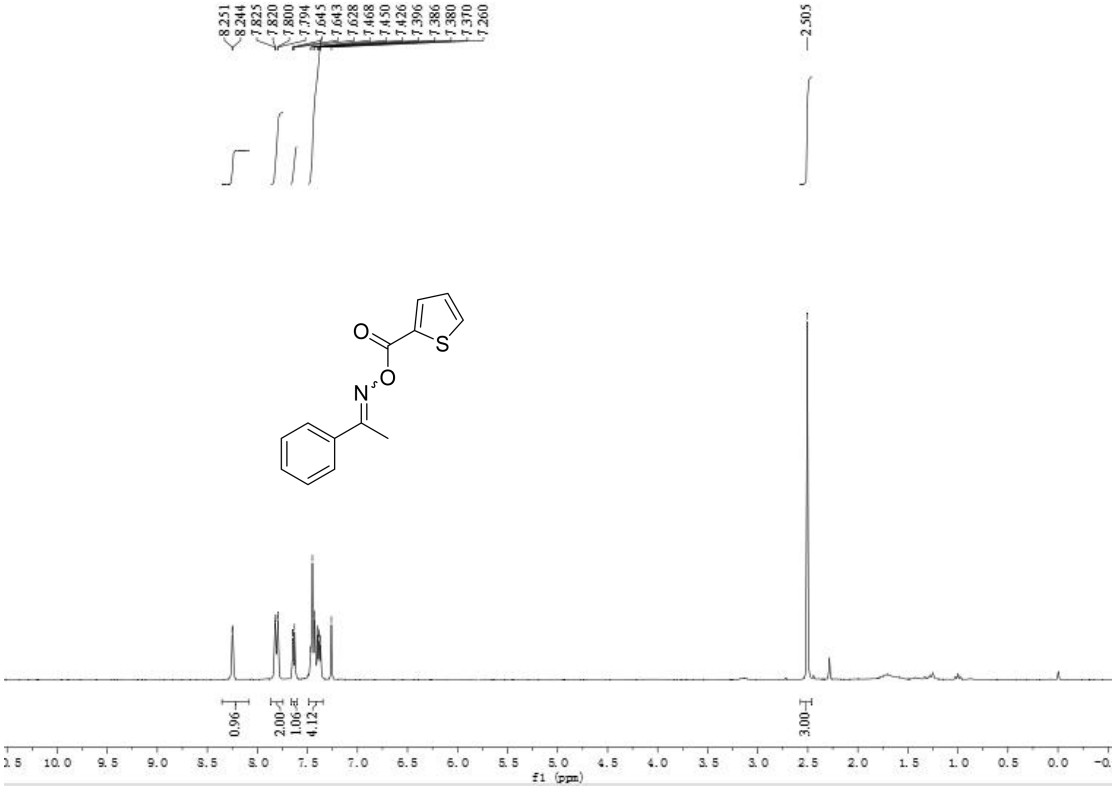


^{1}H NMR (300 MHz, $CDCl_3$)

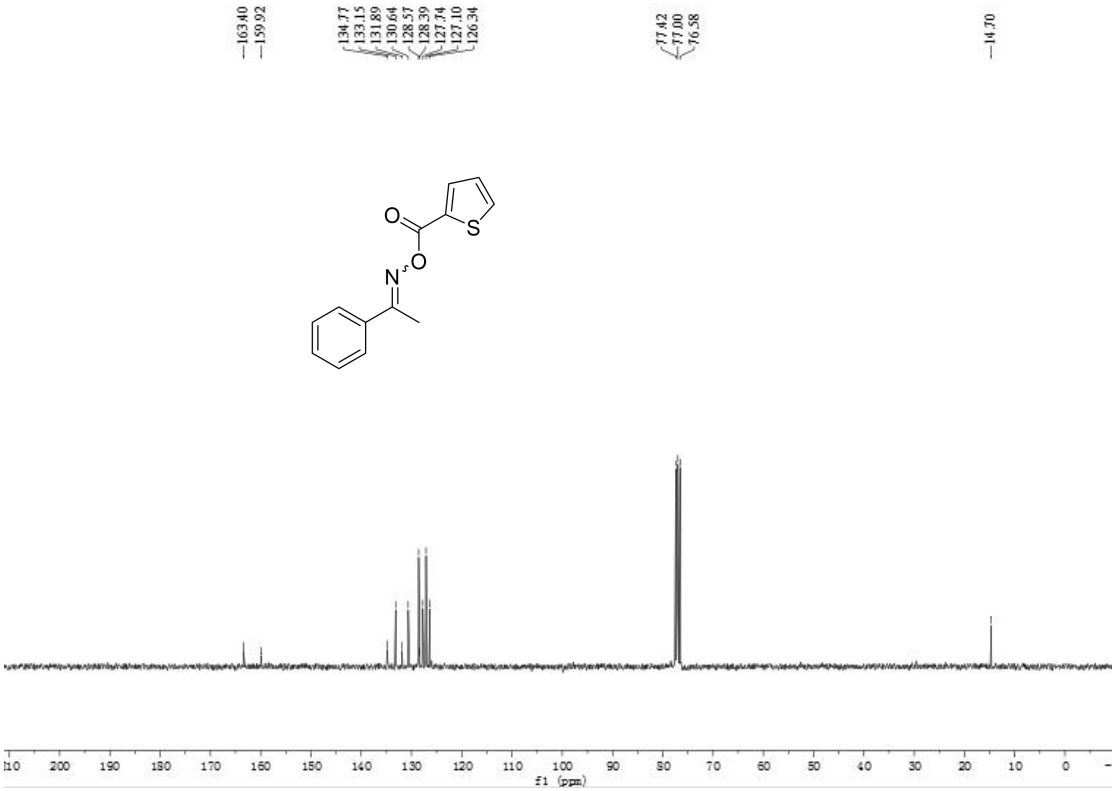


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-one *O*-thiophene-2-carbonyl oxime (4i):

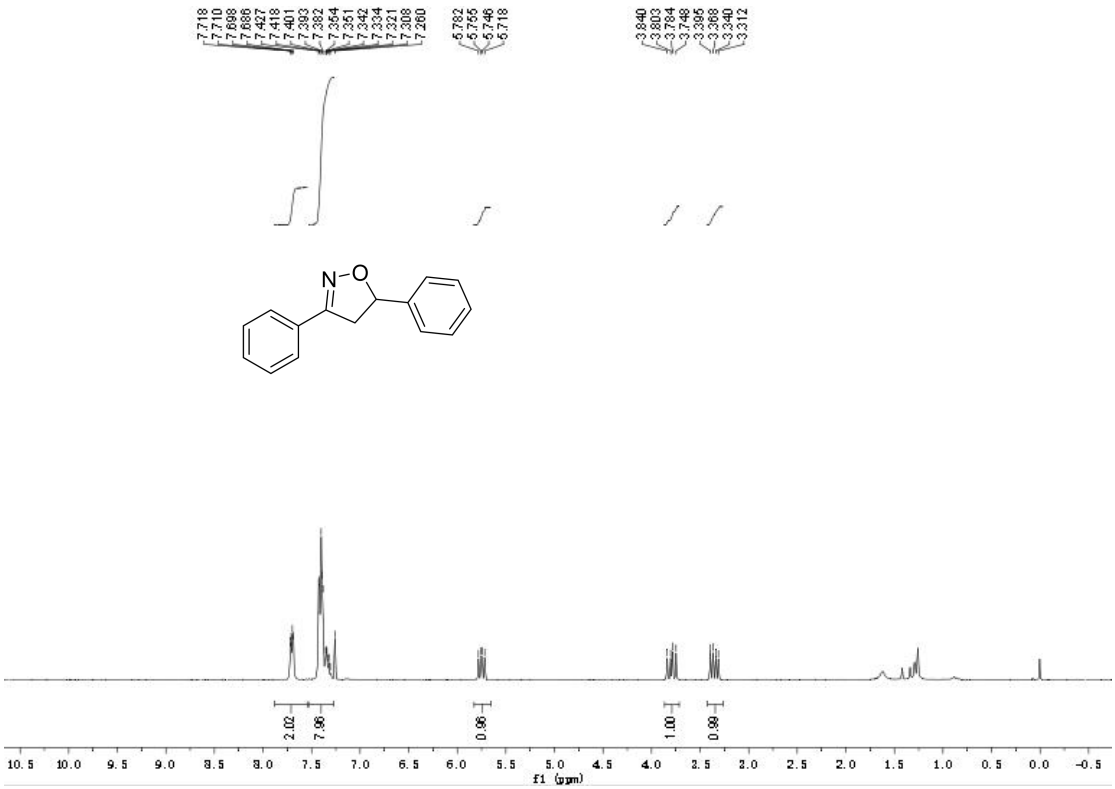


^{1}H NMR (300 MHz, $CDCl_3$)

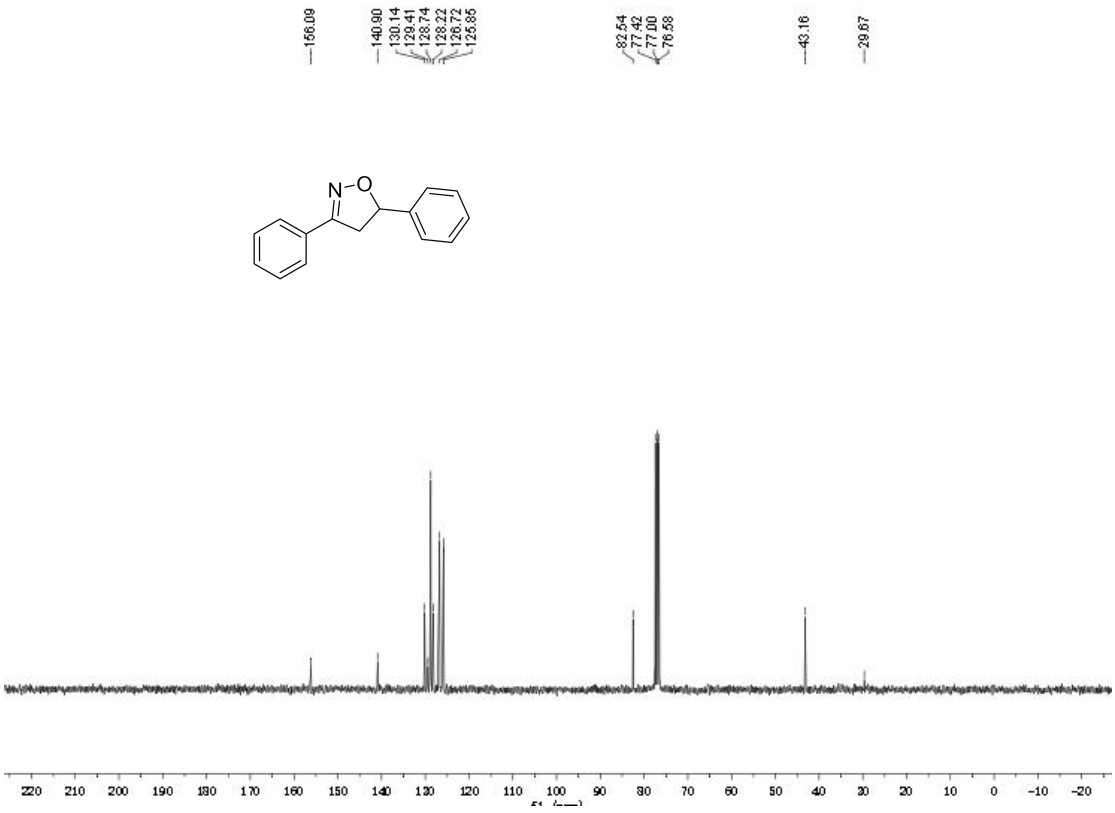


^{13}C NMR (75 MHz, $CDCl_3$)

3,5-diphenyl-4,5-dihydroisoxazole (5):

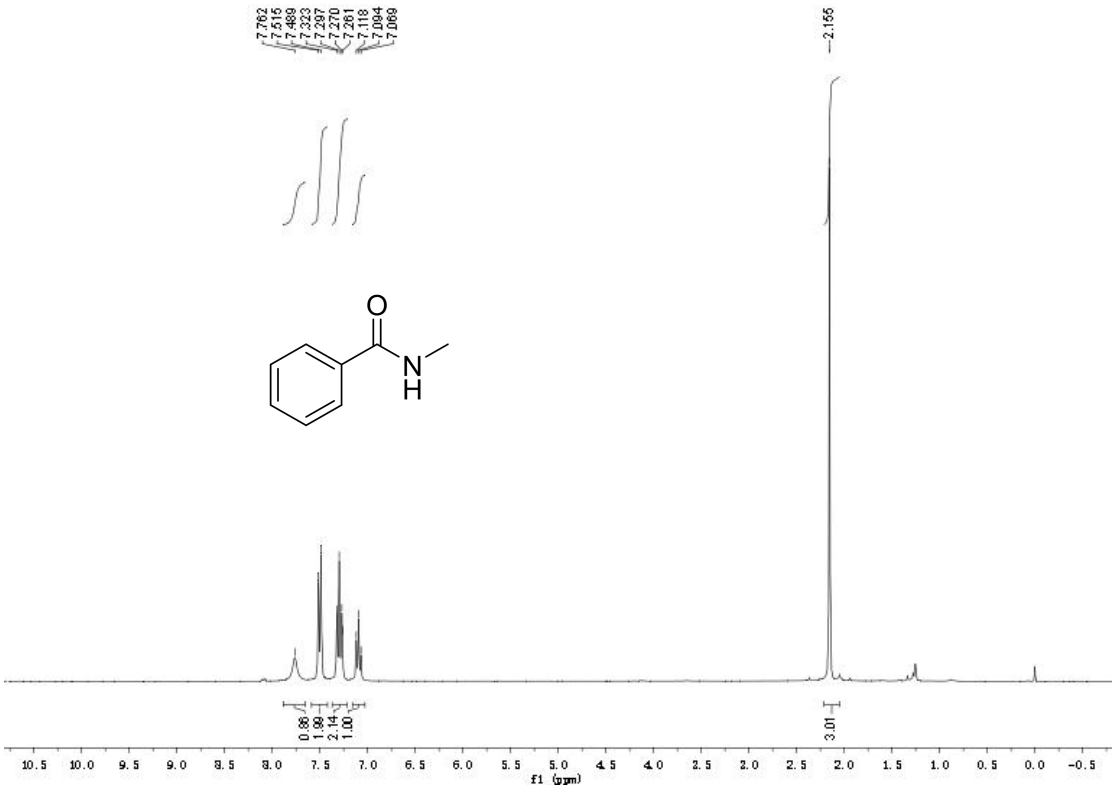


^{1}H NMR (300 MHz, $CDCl_3$)

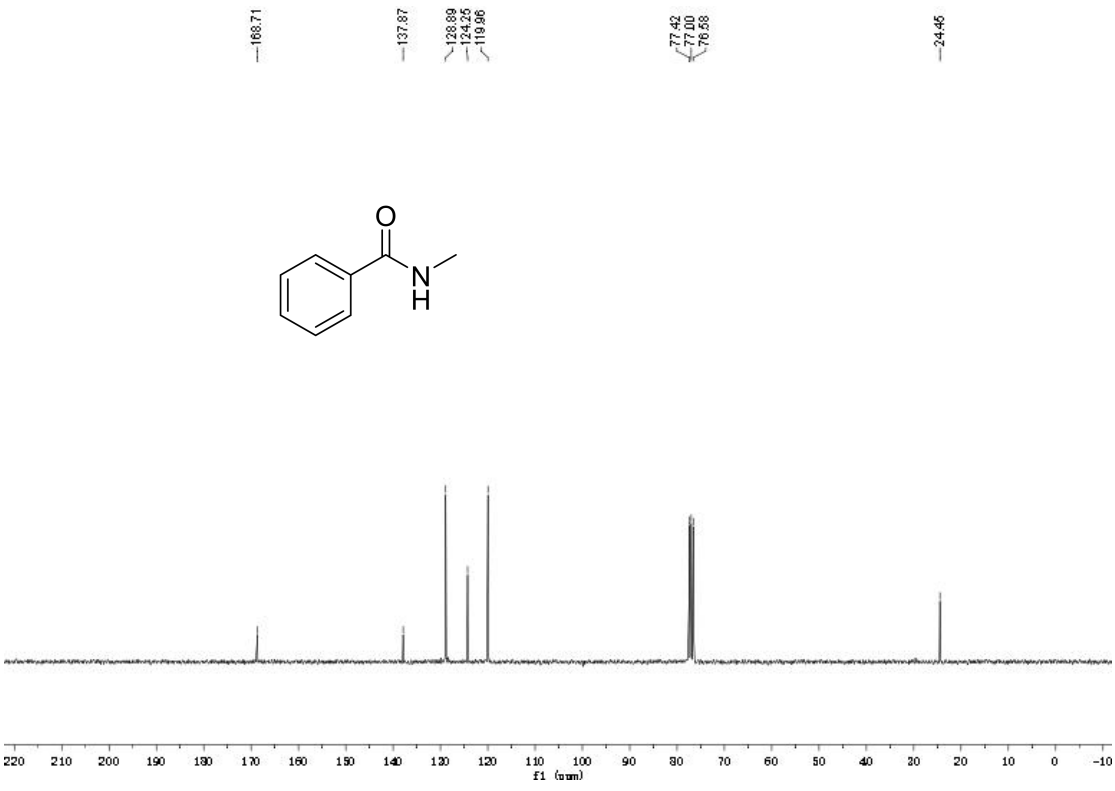


^{13}C NMR (75 MHz, $CDCl_3$)

***N*-methylbenzamide (6):**

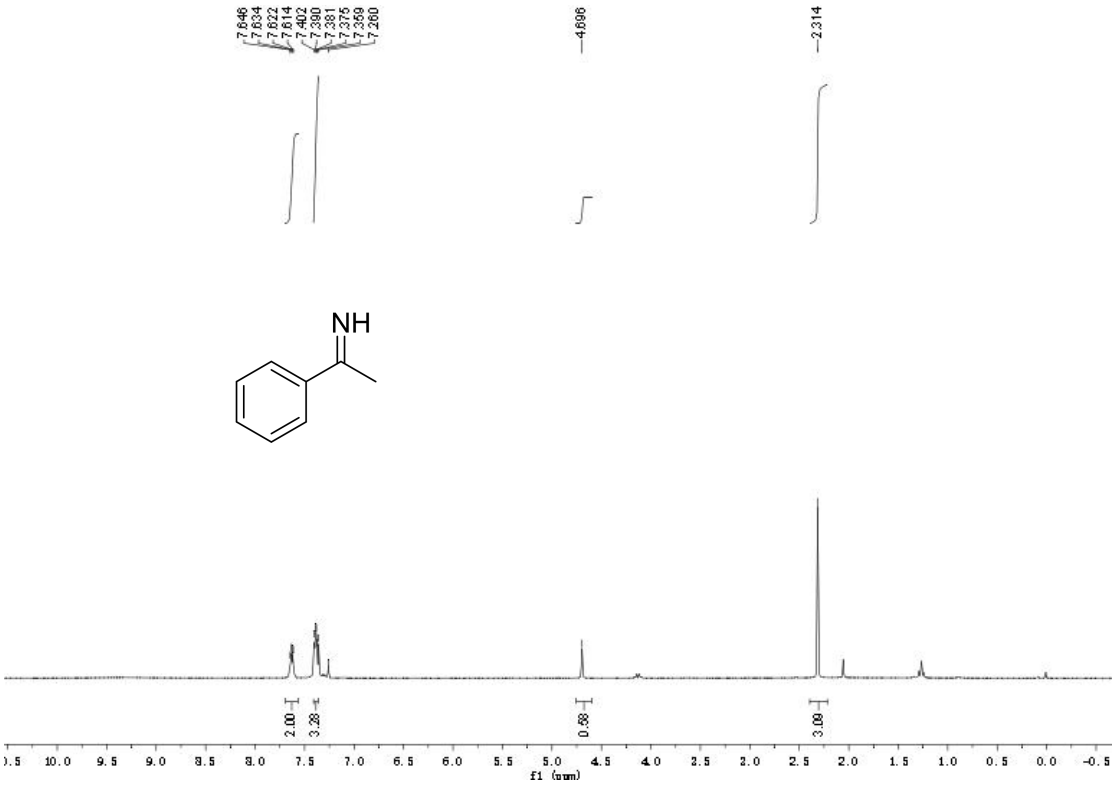


^{1}H NMR (300 MHz, $CDCl_3$)

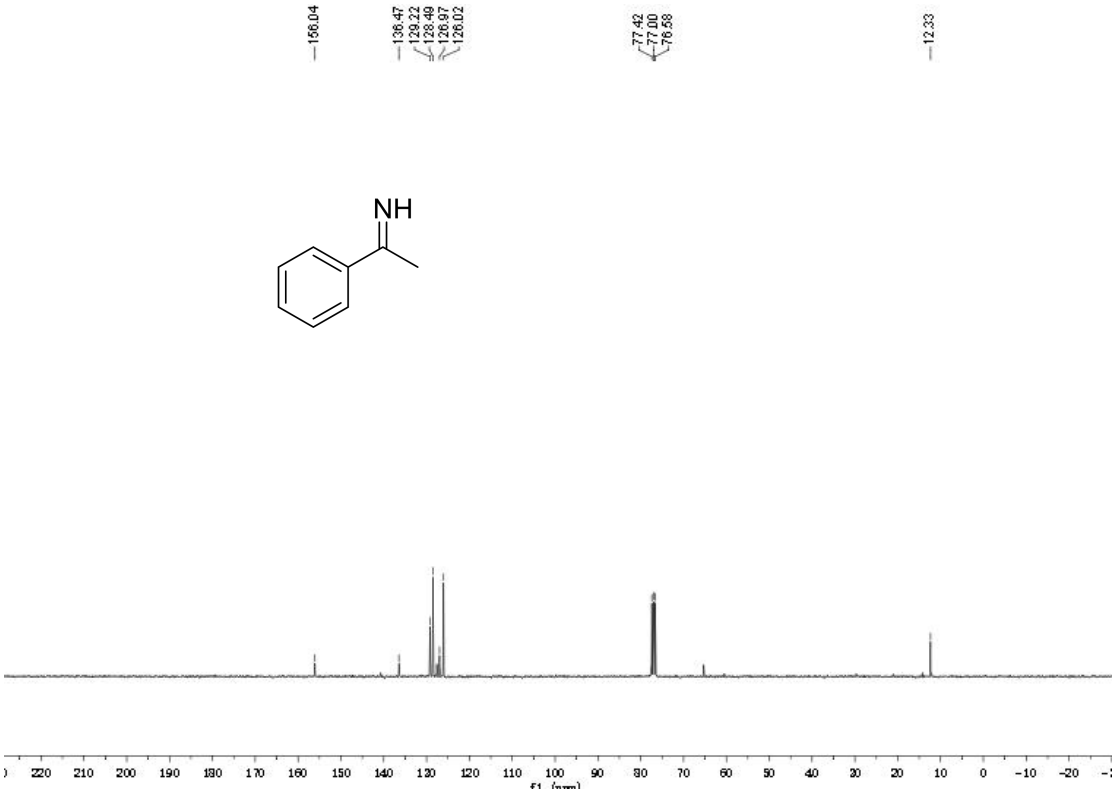


^{13}C NMR (75 MHz, $CDCl_3$)

1-phenylethan-1-imine (7):



^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

(D) HRMS of [8 +Na$^+$]

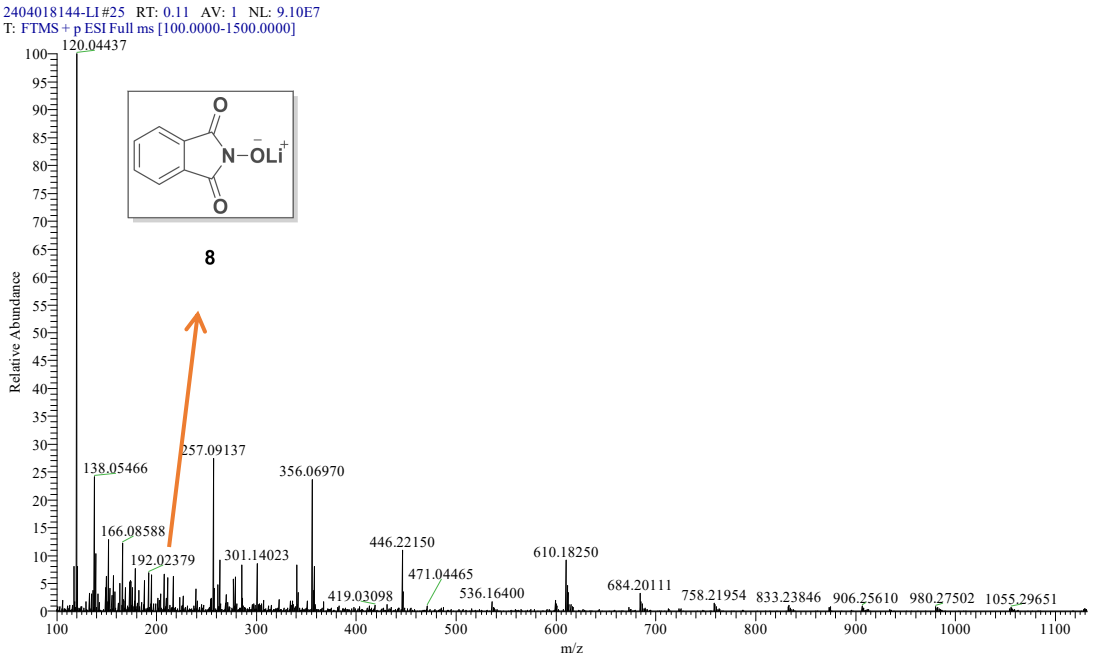


Figure S1 The HRMS spectra of byproduct **8**

(E) DFT calculations

(a) Computational Details

All density functional theory (DFT) calculations were conducted using Gaussian16 software package, Revision C.01[6]. Geometry optimizations and single point calculations of all molecules were performed with the ω-B97xD[7] functional and the def2-SVP[8] basis set. The vibrational frequencies of all species were calculated at the same level and it was ensured that there existed one and only one imaginary frequency in the transition state structures. The integral equation formalism variant of the polarizable continuum model[9] (solvent=acetonitrile) were used in all calculations. The following single point calculations were performed with the same functional and the def2-TZVP[5] basis set. The standard molar Gibbs free energy

$$G_m^{\Theta} = G_{corr}(\omega - \mathrm{B97xD/def2\text{-}SVP}) + E(\omega - \mathrm{B97xD/def2\text{-}TZVP})$$

(b) DFT calculations on mechanism explation

As illustrated in **Figure S2**, the lithium tert-butoxide-mediated transesterification reaction proceeds through a lithium-assisted activation pathway. The reaction is initiated by the

deprotonation of oxime **1a** by *t*-BuOLi, affording the lithium oximate intermediate **INT1** (-11.0 kcal/mol). This transformation significantly enhances the nucleophilicity of the oxime, facilitating its reactivity toward electrophilic species. Subsequently, NHPI ester **2a** is activated via lithium chelation, forming intermediates **INT2** and **INT3**, where the lithium ion coordinates with both the oximate and the carbonyl oxygen of the ester. Among these, **INT3** is thermodynamically more stable than **INT2** (-7.6 kcal/mol vs -5.0 kcal/mol). The chelation effect increases the electrophilicity of the ester moiety and promotes nucleophilic attack. The reaction then proceeds through transition state **TS1** ($\Delta G^{\ddagger}$ = 12.1 kcal/mol), where the oximate attacks the activated ester to form the tetrahedral intermediate **INT4**. In this intermediate, lithium coordinates with both the oxygen and nitrogen atoms, contributing to stabilization. Subsequent bond cleavage occurs via **TS2** with anegative activation energy of -0.9 kcal/mol， during which the NHPI anion begins to dissociate, yielding intermediate **INT5** with a significantly lower energy (-21.2 kcal/mol). Finally, the desired oxime ester **3a** and NHPI lithium salt **8** are generated. The formation of compound **8** was confirmed by high-resolution mass spectrometry (HRMS), providing experimental support for the proposed lithium-mediated reaction mechanism.

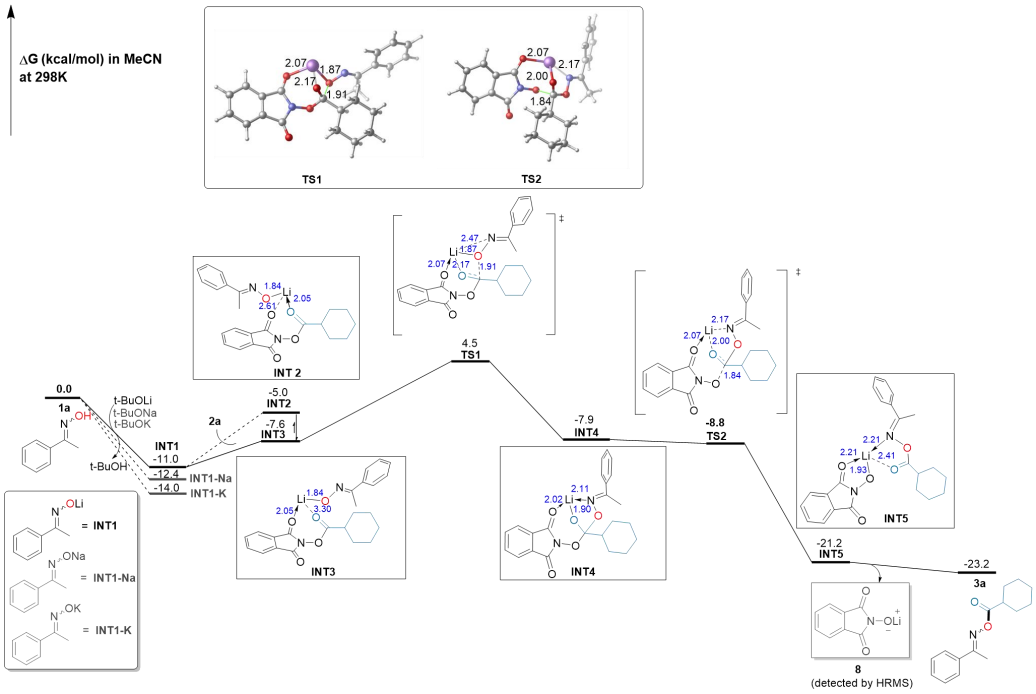
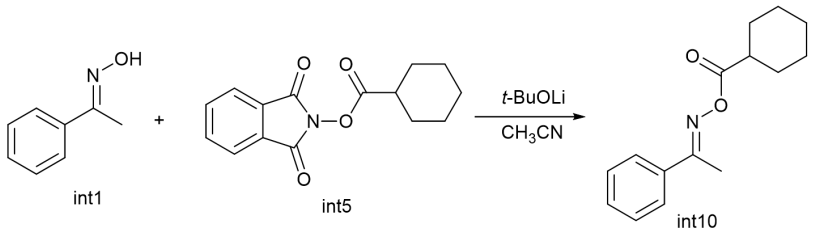
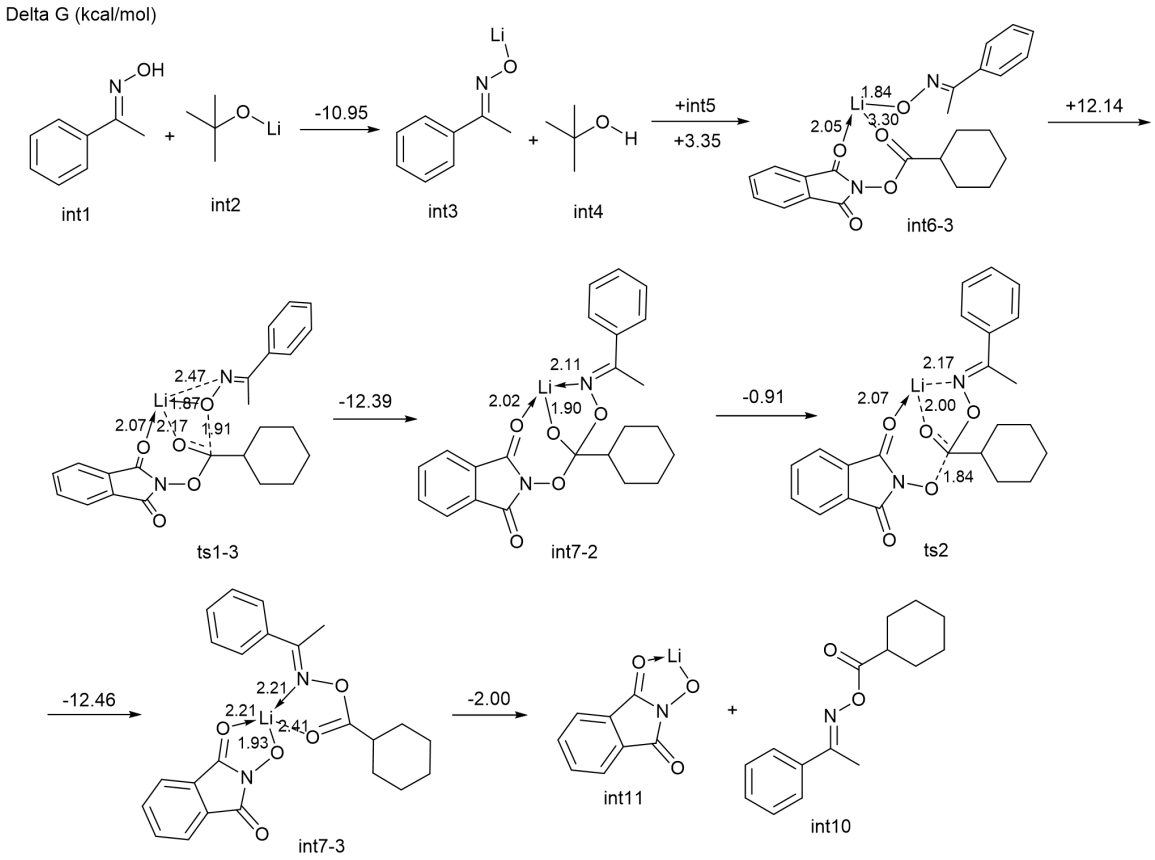


Figure S2 DFT calculations on lithium tert-butoxide (LiO^{t}Bu)-mediated transesterification

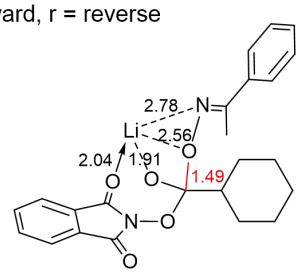
(c) Calculations of ts1 and ts2



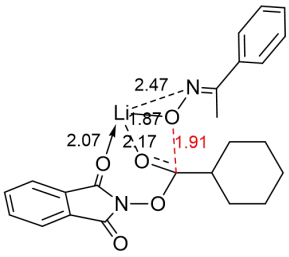


(d) IRC of ts1-3

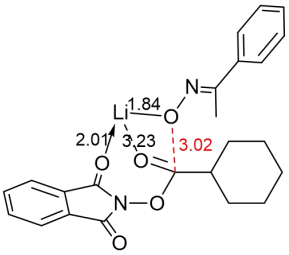
f = forward, r = reverse



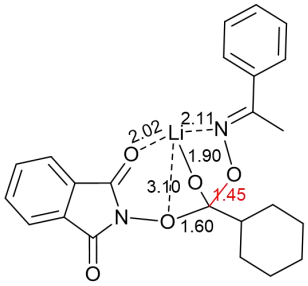
ts1-3-irc-r



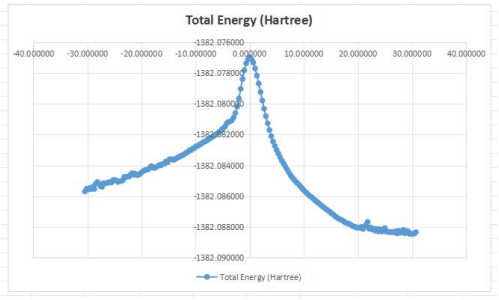
ts1-3

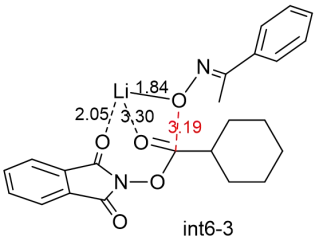


ts1-3-irc-f



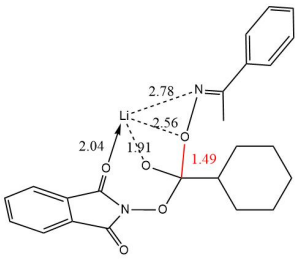
int7-2



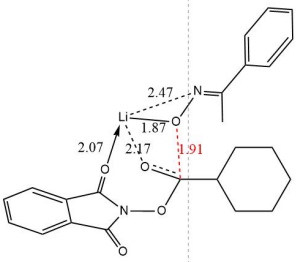


int6-3

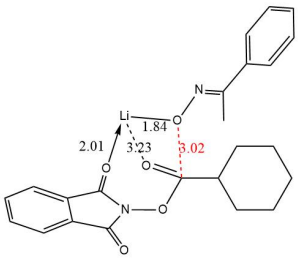
ts1-3-irc



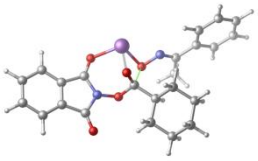
ts1-3-irc-r

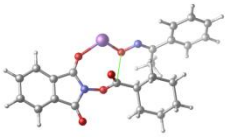


ts1-3

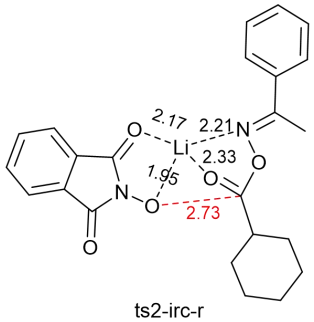


ts1-3-irc-f

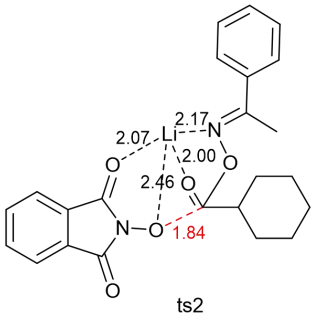




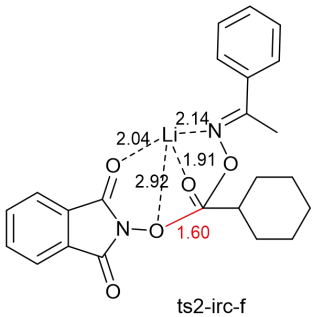
(e) IRC of ts2



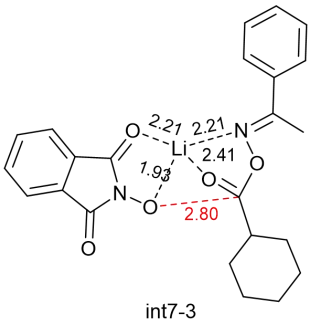
ts2-irc-r



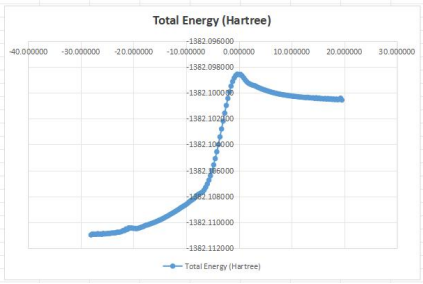
ts2

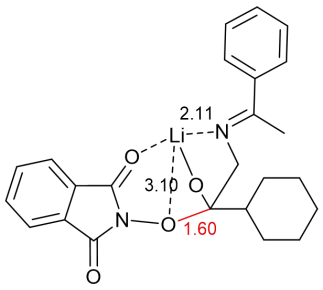


ts2-irc-f

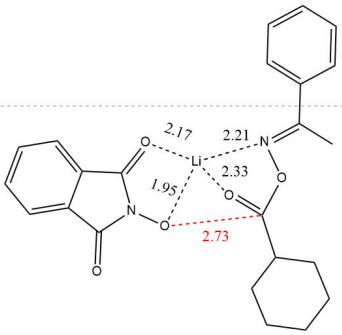


int7-3

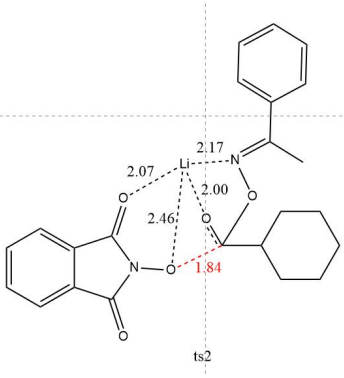




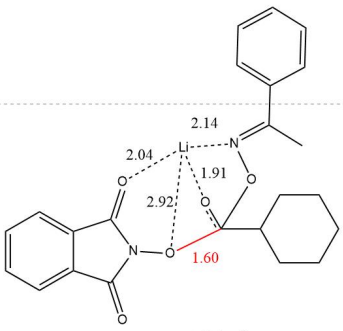
int7-2



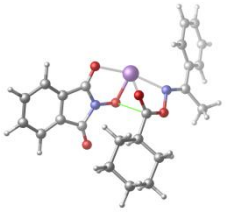
ts2-irc-r

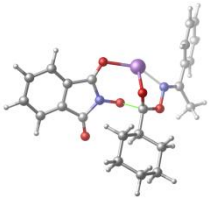


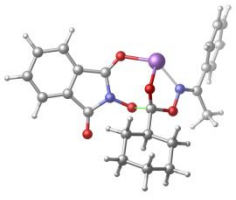
ts2



ts2-irc-f







The energy of **ts2** is slightly lower than that of its adjacent intermediate **int7-2** (-0.91 kcal/mol) because the transition state calculation considers only electronic energy, and the electronic energy of **ts2** is higher than that of **int7-2**. It is only after incorporating free energy correction that a negative value appears.

A reasonable explanation for this scenario is that the process from **int7-2** to **ts2** has a minimal or nearly barrierless energy requirement. The intrinsic reaction coordinate (IRC) of **ts2** also confirms this, as the highest point in the diagram differs from the lowest point on the right side by only about 0.002 a.u. = 1.2 kcal/mol. Further optimizing the structure from the last frame of **ts2-irc-f** during IRC corroborates the accuracy of the structures of both **ts2** and **int7-2**.

(F) References

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