Supporting Information

Diastereoselective Radical Aminoacylation of Olefins through N-Heterocyclic Carbene Catalysis

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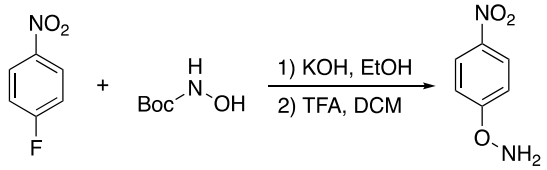
1. General information

All reactions were performed in dry solvents under a N_2 atmosphere and anhydrous conditions. CH_2Cl_2 and CH_3CN were distilled over CaH_2 before use. THF was distilled from sodium benzophenone ketyl before use. DMSO (99.7% extra dry) was purchased from Energy Chemical. All other reagents were used as received from commercial sources. Pd/C was 10% palladium on carbon (wetted with ca. 55% water). Reactions were monitored through thin layer chromatography (TLC) on 0.25-mm silica gel plates and visualized under UV light (254 nm). Flash column chromatography (FCC) was performed using silica gel. NMR spectra were recorded using Bruker Avance II 400 and Vaian DL G400 instruments, calibrated to $CDCl_3$ as the internal reference (7.26 and 77.0 ppm for ^1H and ^{13}C NMR spectra, respectively). ^1H NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data are reported in terms of chemical shift (δ, ppm). The following abbreviations indicate the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra were obtained using Thermo Scientific Q Exactive Plus MS with electrospray ionization (ESI) probe operating in positive ion mode. X-ray crystallographic data were collected using a Bruker Smart APEXII diffractometer. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. The thiazolium salts **N1**–**N5**[1] and triazolium salt **N6**[2] were prepared according to previous reports.

2. Iminoacylation of olefins through N-heterocyclic carbene catalysis

2.1 Synthesis of *O*-(4-nitrophenyl)hydroxylamine

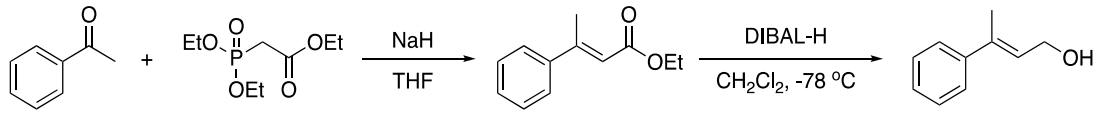


To a freshly prepared solution of KOH (2.62 g, 46.8 mmol) in 100 mL ethanol was added *tert*-butyl-*N*-hydroxy carbamate (6.80 g, 51 mmol) at 23 ℃. 1-Fluoro-4-nitrobenzene (6.00 g, 42.4 mmol) was added to the resulting mixture and the solution was warmed to 60 ℃. After stirring for 48 hours, the reaction mixture was allowed to cool and concentrated in vacuo. The resulting red oil was redissolved in EtOAc (150 mL) and washed with saturated aqueous NH_4Cl (3 × 30 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. Then the crude product was dissolved in CH_2Cl_2 (100 mL) and treated with trifluoroacetic acid (11.0 mL) at 23 ℃. After consumption of the substrate, the reaction mixture was concentrated in vacuo and dissolved in CH_2Cl_2 (150 mL). The solution was washed with saturated aqueous $NaHCO_3$ (3 × 20 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by column chromatography afforded the product as a light-yellow solid (3.60 g, 55%

yield for 2 steps).[3]

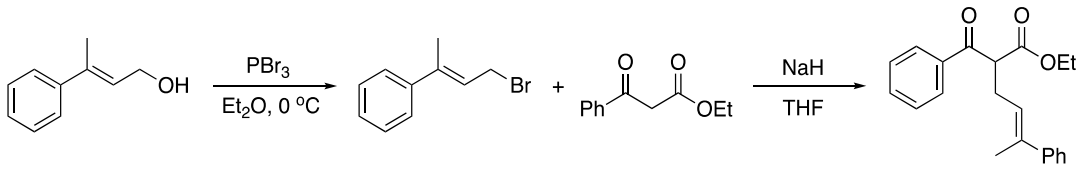
2.2 Synthesis of *O*-aryloximes

2.2.1 General Procedure 1 (GP1)



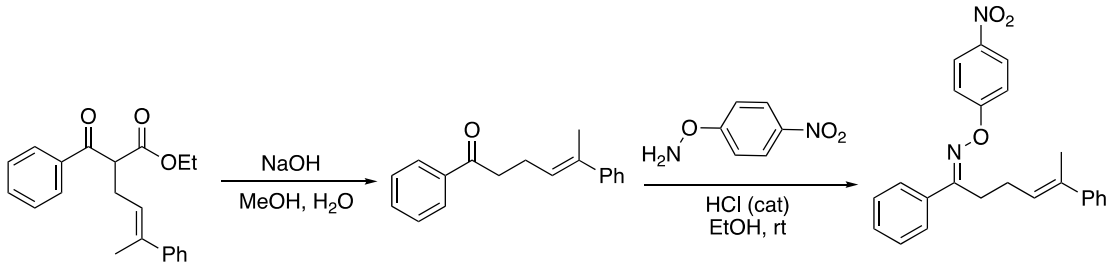
To a solution of NaH (1.5 equiv, 60% in mineral oil) in THF (0.5 M) was added triethyl phosphonoacetate (1.6 equiv) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 30 min, before acetophenone (1 equiv) was added at room temperature. The mixture was stirred for 12 h and saturated aqueous NH_4Cl was added. The resulting slurry was diluted with EtOAc and washed with water and brine. The organic layer was separated and dried over $MgSO_4$. Then, the drying agent was removed by filtration, and the resulting solution was concentrated in vacuo. The residue was purified by flash chromatography on silica gel (0–1% EtOAc in petroleum ether) to afford the alkenoate.[4]

To a solution of the alkenoate (1.0 equiv) in CH_2Cl_2 was added DIBAL-H (1.02 M in hexane, 2.2 equiv) at –78 °C. After stirring for 2 h, saturated aqueous NH_4Cl was added and the mixture was vigorously stirred for 10 min. The reaction mixture was then filtered through celite and the filtrate was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (10–50% EtOAc in petroleum ether) to give the allylic alcohol.[4]



To a stirred solution of the allylic alcohol (1.0 equiv) in Et_2O (1 M) was added phosphorus tribromide (0.5 equiv) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. After saturated aqueous NH_4Cl was added, the organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried with $MgSO_4$. Then, the drying agent was removed by filtration, and the resulting solution was concentrated in vacuo. The resulting yellow residue was used in the next step without further purification.[5]

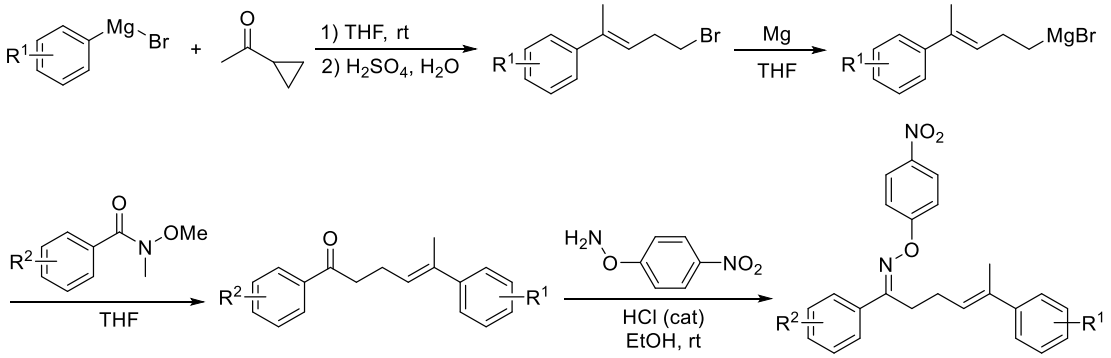
A solution of ethyl 3-oxo-3-phenylpropanoate (1.0 equiv) in THF (0.17 M) was treated with NaH (1.0 equiv, 60% in mineral oil). After stirring for 1 h, the allylic bromide (1.1 equiv) was added. The mixture was stirred at 40 °C overnight. Then the mixture was cooled to room temperature and MeOH was added. The crude product was purified by column chromatography on silica gel to give the β-ketoester.[6]



A mixture of the β-ketoester (1.0 equiv) and NaOH (4.0 equiv) was refluxed in MeOH/H_2O (0.01 M, v/v = 2:1) for 2 h. Then the mixture was cooled to room temperature and MeOH was removed in vacuo. EtOAc was added and the organic layer was separated. The aqueous layer was then washed with EtOAc and the combined organic fractions were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to give the ketone.[6]

A solution of the ketone (1.0 equiv) in EtOH (0.1 M) was treated with *O*-(4-nitrophenyl)hydroxylamine (1.0 equiv) and stirred at room temperature overnight. H_2O was added and EtOH was removed in vacuo. The mixture was diluted with EtOAc and the organic layer was separated. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to give the *O*-aryloxime.[6]

2.2.2 General Procedure 2 (GP2)



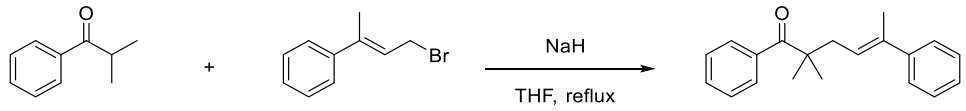
To an oven-dried round-bottomed flask was added Grignard reagent (24 mmol, 1.2 equiv) under nitrogen atmosphere. After addition of THF (20 mL), the reaction was cooled to 0 ℃. Then a solution of 1-cyclopropylethanone (1.68 g, 20 mmol, 1.0 equiv) in THF (10 mL) was added. The resulting solution was warmed up to room temperature and stirred for 6 h. Then a mixture of H_2SO_4 (4 mL) and H_2O (8 mL) was added at 0 ℃. The resulting mixture was stirred for 60 min at room temperature and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether) to afford the desired product.[7]

The reaction was carried out with Mg turnings (1.2 equiv) and catalytic amount of I_2 in a round-bottomed flask under nitrogen atmosphere. After addition of alkyl bromide

(1.2 equiv), the mixture was refluxed for 40 min. Then a solution of Weinreb amide in THF was added dropwise into the solution at 0 ℃. The resulting mixture was stirred at room temperature overnight. The reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 19/1) to give the ketone.[6,7]

A solution of the ketone (1.0 equiv) in EtOH (0.1 M) was treated with *O*-(4-nitrophenyl)hydroxylamine (1.0 equiv) and stirred at room temperature overnight. H_2O was added and EtOH was removed in vacuo. The mixture was diluted with EtOAc and the organic layer was separated. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to give the *O*-aryloxime.[6]

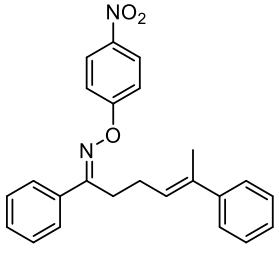
2.2.3 General Procedure 3 (GP3)



The reaction was carried out with isobutyrophenone (580 mg, 3.88 mmol) in a 2-neck round-bottomed flask under nitrogen atmosphere. After addition of dry THF (15 mL), NaH (240 mg, 5.82 mmol) was added slowly. Then the mixture was stirred at room temperature for 30 min. A solution of (*E*)-(4-bromobut-2-en-2-yl)benzene (980 mg, 4.66 mmol) in THF (5.0 mL) was added dropwise and the solution was stirred at 66 ℃ for 8 h. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) at room temperature, and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to give (*E*)-2,2-dimethyl-1,5-diphenylhex-4-en-1-one.[8]

2.3 Characterization data for *O*-aryloximes

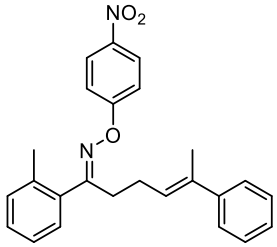
(4*E*)-1,5-diphenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



1a

Synthesized according to General Procedure **1**. White solid, m.p. 91 – 93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.20 (m, 2H), 7.79 – 7.77 (m, 2H), 7.50 – 7.43 (m, 3H), 7.38 – 7.35 (m, 2H), 7.26 – 7.19 (m, 5H), 5.79 (t, *J* = 8.0 Hz, 1H), 3.12 (t, *J* = 8.0 Hz, 2H), 2.55 (q, *J* = 8.0 Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.6, 143.3, 142.3, 136.5, 134.1, 130.4, 128.8, 128.1, 126.9, 126.8, 125.8, 125.7, 125.5, 114.4, 27.4, 26.0, 15.8. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}N_2O_3^+$ ([M+H$^+$]), 387.17032, found: 387.17096.

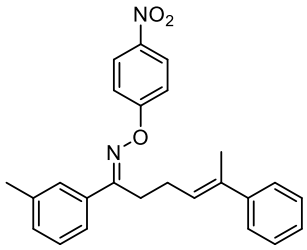
(4*E*)-5-phenyl-1-(*o*-tolyl)hex-4-en-1-one *O*-(4-nitrophenyl) oxime



38a

Synthesized according to General Procedure **2**. Orange oil, *E:Z* 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.12 (m, 2H), 7.36 – 7.16 (m, 11H), 5.80 (td, *J* = 8.0, 4.0 Hz, 0.33H), 5.72 (td, *J* = 8.0, 4.0 Hz, 0.66H), 3.06 (t, *J* = 8.0, 1.33H), 2.81 – 2.79 (m, 0.66H), 2.59 – 2.49 (m, 2H), 2.42 (s, 2H), 2.23 (s, 1H), 2.01 (d, *J* = 1.2 Hz, 1H), 1.95 (d, *J* = 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 164.3, 164.0, 164.0, 143.4, 143.2, 142.2, 142.1, 136.4, 136.1, 134.8, 134.5, 133.8, 130.9, 130.1, 129.3, 128.9, 128.7, 128.5, 128.2, 128.1, 126.8, 126.2, 125.9, 125.9, 125.7, 125.5, 125.5, 125.5, 114.4, 114.3, 35.9, 30.5, 25.1, 25.0, 20.3, 19.6, 15.9, 15.7. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_3^+$ ([M+H$^+$]), 401.18597, found: 401.18572.

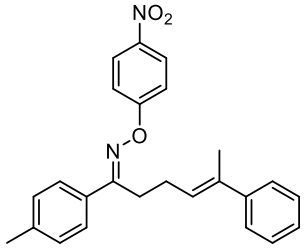
(4*E*)-5-phenyl-1-(*m*-tolyl)hex-4-en-1-one *O*-(4-nitrophenyl) oxime



39a

Synthesized according to General Procedure **2**. White solid, m.p. 60 – 62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.38 – 7.33 (m, 3H), 7.30 – 7.19 (m, 6H), 5.80 (t, *J* = 8.0 Hz, 1H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.55 (q, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.9, 143.3, 142.3, 138.5, 136.4, 134.1, 131.2, 128.6, 128.1, 127.5, 126.8, 125.9, 125.7, 125.5, 124.1, 114.5, 27.6, 26.0, 21.5, 15.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_3^+$ ([M+H$^+$]), 401.18597, found: 401.18489.

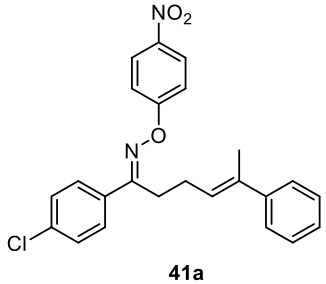
(4*E*)-5-phenyl-1-(*p*-tolyl)hex-4-en-1-one *O*-(4-nitrophenyl) oxime



40a

Synthesized according to General Procedure **2**. White solid, m.p. 84 – 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.18 (m, 7H), 5.81 – 5.77 (m, 1H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.54 (q, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.5, 143.4, 142.3, 140.8, 136.4, 131.2, 129.5, 128.1, 126.8, 126.8, 126.0, 125.7, 125.6, 114.5, 27.4, 26.1, 21.3, 15.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_3^+$ ([M+H$^+$]), 401.18597, found: 401.18600.

(4*E*)-1-(4-chlorophenyl)-5-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime

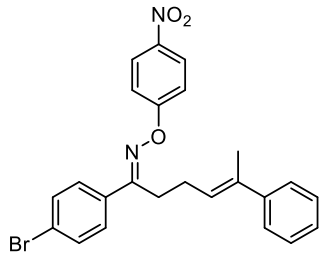


41a

Synthesized according to General Procedure **2**. White solid, m.p. 97 – 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2H), 7.73 – 7.71 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 5H), 5.77 (t, *J* = 8.0 Hz, 1H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.54 (q, *J* = 8.0 Hz, 2H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 162.5, 143.2, 142.5, 136.7, 137.6, 132.6, 129.0, 128.2, 128.1, 126.9, 125.7, 125.6, 125.5, 114.5, 27.3, 25.9,

15.8. HRMS (ESI) *m/z* calcd for $C_{24}H_{22}ClN_2O_3^+$ ([M+H$^+$]), 421.13135, found: 421.12987.

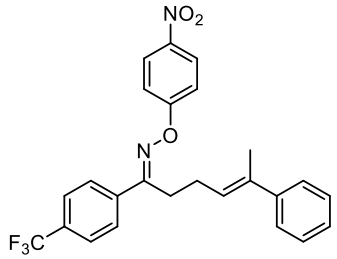
(4*E*)-1-(4-bromophenyl)-5-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



42a

Synthesized according to General Procedure **2**. White solid, m.p. 94 – 95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 5H), 5.77 (t, *J* = 8.0 Hz, 1H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.54 (q, *J* = 8.0 Hz, 2H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 162.6, 143.2, 142.5, 136.7, 133.0, 132.0, 128.4, 128.1, 126.9, 125.7, 126.6, 126.5, 124.9, 114.5, 27.2, 25.9, 15.8. HRMS (ESI) *m/z* calcd for $C_{24}H_{22}BrN_2O_3^+$ ([M+H$^+$]), 465.08083, found: 465.08101.

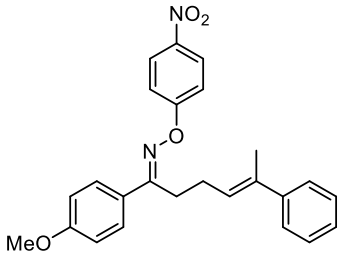
(4*E*)-5-phenyl-1-(4-(trifluoromethyl)phenyl)hex-4-en-1-one *O*-(4-nitrophenyl) oxime



43a

Synthesized according to General Procedure **2**. White solid, m.p. 92 – 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.19 (m, 5H), 5.77 (t, *J* = 8.0 Hz, 1H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.57 (q, *J* = 8.0 Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 162.5, 143.2, 142.7, 137.7, 136.8, 132.1 (q, *J* = 32.5 Hz), 128.2, 127.3, 126.9, 125.7 (q, *J* = 3.6 Hz), 125.5, 125.4, 123.8 (q, *J* = 270.7 Hz), 114.5, 27.4, 25.8, 15.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{22}F_3N_2O_3^+$ ([M+H$^+$]), 455.15770, found: 455.15659.

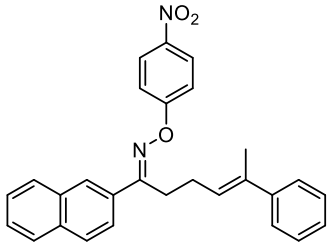
(4*E*)-1-(4-methoxyphenyl)-5-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



44a

Synthesized according to General Procedure **2**. White solid, m.p. 60 – 64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.20 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.35 (m, 2H), 7.27 – 7.19m, 5H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.82 – 5.78 (m, 1H), 3.86 (s, 3H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.54 (q, *J* = 8.0 Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.1, 161.4, 143.4, 142.2, 136.4, 128.4, 128.1, 126.8, 126.3, 126.0, 125.7, 125.6, 114.4, 114.2, 55.4, 27.2, 26.1, 15.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_4^+$ ([M+H$^+$]), 417.18088, found: 417.18005.

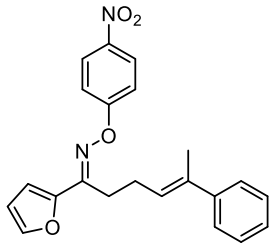
(4*E*)-1-(naphthalen-2-yl)-5-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



45a

Synthesized according to General Procedure **2**. Yellow solid, m.p. 96 – 97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 12.0 Hz, 2H), 8.17 (s, 1H), 7.99 – 7.97 (m, 1H), 7.90 – 7.86 (m, 3H), 7.56 – 7.53 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.17 (m, 5H), 5.86 – 5.83 (m, 1H), 3.22 (t, *J* = 8.0 Hz, 2H), 2.61 (q, *J* = 8.0 Hz, 2H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.4, 143.3, 142.4, 136.5, 134.2, 133.0, 131.4, 128.6, 128.5, 128.1, 127.7, 127.3, 127.2, 126.8, 126.7, 125.9, 125.7, 125.5, 123.7, 114.5, 27.2, 26.2, 15.8. HRMS (ESI) *m/z* calcd for $C_{28}H_{25}N_2O_3^+$ ([M+H$^+$]), 437.18597, found: 437.18653.

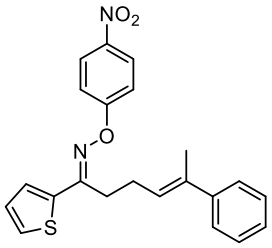
(4*E*)-1-(furan-2-yl)-5-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



46a

Synthesized according to General Procedure **2**. Yellow solid, *E:Z* 1:1, m.p. 58 – 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 12.0 Hz, 2H), 7.58 (s, 1H), 7.50 (d, *J* = 4.0 Hz, 0.5H), 7.38 – 7.35 (m, 3H), 7.31 – 7.20 (m, 4H), 6.92 (d, *J* = 4.0 Hz, 0.5H), 6.63 – 6.62 (m, 0.5H), 6.54 – 6.53 (m, 0.5H), 5.84 (dt, *J* = 24.0, 8.0 Hz, 1H), 3.02 – 2.95 (m, 2H), 2.68 – 2.57 (m, 2H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 163.9, 155.4, 151.0, 148.3, 144.9, 144.6, 143.8, 143.6, 143.3, 142.5, 136.6, 136.1, 128.2, 128.1, 126.8, 126.7, 126.4, 125.7, 125.7, 125.6, 125.6, 120.0, 114.5, 114.4, 112.6, 112.5, 111.9, 31.4, 27.0, 26.6, 26.2, 15.8, 15.7. HRMS (ESI) *m/z* calcd for $C_{22}H_{21}N_2O_4^+$ ([M+H$^+$]), 377.14958, found: 377.14933.

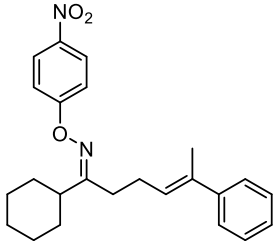
(4*E*)-5-phenyl-1-(thiophen-2-yl)hex-4-en-1-one *O*-(4-nitrophenyl) oxime



47a

Synthesized according to General Procedure **1**. Yellow solid, *E:Z* 1:1, m.p. 70 – 74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.19 (m, 2H), 7.67 – 7.65 (m, 1H), 7.46 – 7.09 (m, 9H), 5.84 (dt, *J* = 20.0, 8.0 Hz, 1H), 3.09 – 3.00 (m, 2H), 2.70 (q, *J* = 8.0 Hz, 1H), 2.62 (q, *J* = 8.0 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 163.4, 159.1, 153.9, 143.4, 143.3, 142.45, 142.4, 137.6, 136.7, 136.2, 132.3, 131.3, 131.0, 128.9, 128.5, 128.2, 128.1, 127.4, 126.8, 126.3, 126.2, 125.7, 125.6, 125.6, 125.5, 114.4, 114.4, 33.6, 28.0, 26.9, 26.3, 15.9, 15.8. HRMS (ESI) *m/z* calcd for $C_{22}H_{21}N_2O_3S^+$ ([M+H$^+$]), 393.12674, found: 393.12613.

(4*E*)-1-cyclohexyl-5-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime

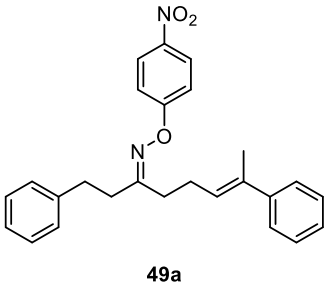


48a

Synthesized according to General Procedure **2**. Yellow solid, *E:Z* 4:1, m.p. 51 – 54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 2H), 7.39 – 7.19 (m, 7H), 5.84 – 5.77 (m, 1H), 2.60 – 2.54 (m, 2H), 2.52 – 2.46 (m, 2H), 2.37 – 2.30 (m, 1H), 2.08 (s, 0.6H), 2.06 (s, 2.4H), 1.94 – 1.72 (m, 5H), 1.46 – 1.23 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.3,

164.4, 143.5, 143.3, 141.9, 136.1, 135.6, 128.1, 128.1, 127.0, 126.7, 126.7, 126.2, 125.6, 125.6, 125.5, 114.2, 114.2, 44.1, 38.6, 30.8, 30.2, 29.6, 29.0, 28.2, 26.0, 25.9, 25.9, 25.7, 25.0, 15.9, 15.7. HRMS (ESI) *m/z* calcd for $C_{24}H_{29}N_2O_3^+$ ([M+H$^+$]), 393.21727, found: 393.21652.

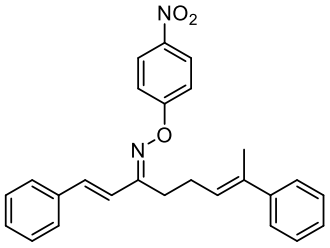
(6*E*)-1,7-diphenyloct-6-en-3-one *O*-(4-nitrophenyl) oxime



49a

Synthesized according to General Procedure **2**. White solid, *E:Z* 1:1, m.p. 57 – 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.37 – 7.16 (m, 12H), 5.76 (t, *J* = 8.0 Hz, 1H), 3.00 – 2.96 (m, 1H), 2.94 – 2.90 (m, 1H), 2.83 – 2.80 (m, 1H), 2.73 – 2.70 (m, 1H), 2.67 – 2.63 (m, 1H), 2.54 – 2.47 (m, 2H), 2.43 – 2.40 (m, 1H), 2.04 (s, 1.5H), 2.04 (s, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.9, 164.1, 164.1, 143.4, 143.2, 142.1, 140.7, 140.3, 136.5, 136.0, 128.6, 128.5, 128.3, 128.2, 128.2, 126.8, 126.8, 126.4, 126.3, 126.2, 125.8, 125.6, 125.5, 125.5, 114.2, 36.2, 34.4, 32.1, 32.0, 31.4, 29.3, 25.2, 25.0, 15.9, 15.8. HRMS (ESI) *m/z* calcd for $C_{26}H_{27}N_2O_3^+$ ([M+H$^+$]), 415.20162, found: 415.20068.

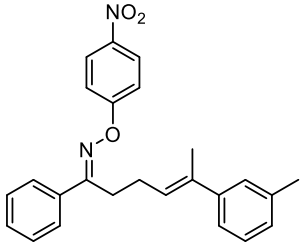
(1*E*,6*E*)-1,7-diphenylocta-1,6-dien-3-one *O*-(4-nitrophenyl) oxime



50a

Synthesized according to General Procedure **2**. Yellow solid, *E:Z* 10:1, m.p. 100 – 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.41 – 7.32 (m, 7H), 7.27 – 7.12 (m, 4H), 6.94 – 6.90 (m, 1H), 5.86 (t, *J* = 8.0 Hz, 1H), 2.94 (t, *J* = 8.0 Hz, 1.8H), 2.83 (t, *J* = 8.0 Hz, 0.18H), 2.67 – 2.55 (m, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 163.7, 143.3, 142.4, 136.4, 136.3, 135.7, 129.2, 128.9, 128.1, 127.2, 126.8, 126.0, 125.7, 125.6, 123.3, 114.5, 26.2, 25.4, 15.8. HRMS (ESI) *m/z* calcd for $C_{26}H_{25}N_2O_3^+$ ([M+H$^+$]), 413.18597, found: 413.18511.

(4*E*)-1-phenyl-5-(*m*-tolyl)hex-4-en-1-one *O*-(4-nitrophenyl) oxime

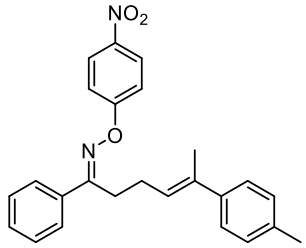


51a

Synthesized according to General Procedure **2**. Orange oil, *E:Z* 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 1.5H), 8.17 – 8.13 (m, 0.5H), 7.79 – 7.77 (m, 1.5H), 7.49 – 7.41 (m, 3.5H), 7.40 – 7.36 (m, 1.5H), 7.23 – 7.20 (m, 0.5H), 7.19 – 7.13 (m, 1.5H), 7.07 – 7.01 (m, 2.5H), 5.79 – 5.75 (m, 1H), 3.12 (t, *J* = 8.0 Hz, 1.5H), 2.87 (t, *J* = 8.0 Hz, 0.5H), 2.55 (q, *J* = 8.0 Hz, 1.5H), 2.48 (q, *J* = 8.0 Hz, 0.5H), 2.33 (s, 0.75H), 2.28 (s, 2.25H), 1.97 (s, 0.75H), 1.94 (s, 2.25H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 164.1, 163.6, 163.5, 143.5, 143,4, 142.4, 142.2, 137.7, 136.6, 136.3, 134.2, 132.7, 130.4, 129.6, 128.8, 128.4, 128.1, 128.0, 127.7, 127.5, 126.9, 126.4, 126.4, 125.8, 125.7, 125.7, 125.6, 122.7, 122.7, 114.5, 114.3, 35.4, 27.4, 26.0, 25.6, 21.5, 21.4, 16.0, 15.8. HRMS (ESI) *m/z* calcd for

$C_{25}H_{25}N_2O_3^+$ ([M+H$^+$]), 401.18597, found: 401.18432.

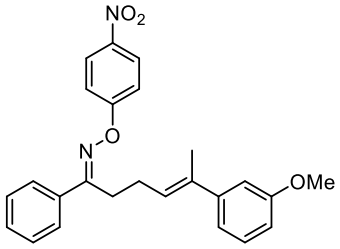
(4*E*)-1-phenyl-5-(*p*-tolyl)hex-4-en-1-one *O*-(4-nitrophenyl) oxime



52a

Synthesized according to General Procedure **2**. White solid, m.p. 85 – 87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.21 (m, 2H), 7.80 – 7.77 (m, 2H), 7.47 – 7.45 (m, 3H), 7.39 – 7.36 (m, 2H), 7.18 – 7.15 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.76 (t, *J* = 8.0 Hz, 1H), 3.11 (t, *J* = 8.0 Hz, 2H), 2.55 (q, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.7, 142.4, 140.5, 136.5, 136.3, 134.2, 130.4, 128.8, 128.8, 126.9, 125.7, 125.4, 125.0, 114.5, 27.5, 26.0, 21.0, 15.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_3^+$ ([M+H$^+$]), 401.18597, found: 401.18497.

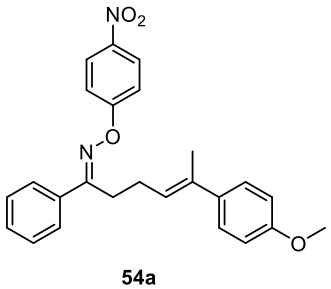
(4*E*)-5-(3-methoxyphenyl)-1-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



53a

Synthesized according to General Procedure **2**. Orange oil, *E:Z* 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 1.5H), 8.17 – 8.13 (m, 0.5H), 7.79 – 7.77 (m, 1.5H), 7.50 – 7.41 (m, 3.5H), 7.39 – 7.35 (m, 1.5H), 7.23 – 7.12 (m, 2H), 7.07 – 7.00 (m, 2.5H), 5.77 (td, *J* = 8.0, 4.0 Hz, 1H), 3.12 (t, *J* = 8.0 Hz, 1.5H), 2.87 (t, *J* = 8.0 Hz, 0.5H), 2.55 (q, *J* = 8.0 Hz, 1.5H), 2.47 (q, *J* = 8.0 Hz, 0.5H), 2.32 (s, 0.75H), 2.28 (s, 2.25H), 1.97 (s, 2.25H), 1.94 (s, 0.75H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 164.0, 163.6, 163.5, 143.5, 143.4, 142.3, 142.1, 137.7, 137.6, 136.6, 136.3, 134.1, 132.7, 130.4, 129.6, 128.7, 128.3, 128.1, 128.0, 127.6, 127.5, 126.9, 126.4, 125.8, 125.7, 125.6, 125.6, 122.7, 122.7, 114.4, 114.3, 35.4, 27.4, 25.9, 25.6, 21.4, 21.4, 15.9, 15.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_4^+$ ([M+H$^+$]), 417.18088, found: 417.17931.

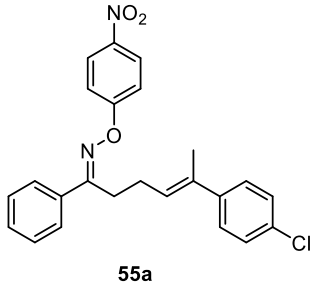
(4*E*)-5-(4-methoxyphenyl)-1-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



54a

Synthesized according to General Procedure **2**. White solid, m.p. 64 – 68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2H), 7.79 – 7.77 (m, 2H), 7.48 – 7.43 (m, 3H), 7.39 – 7.36 (m, 2H), 7.22 – 7.19 (m, 2H), 6.81 – 6.78 (m, 2H), 5.74 – 5.70 (m, 1H), 3.78 (s, 3H), 3.11 (t, *J* = 8.0 Hz, 2H), 2.54 (q, *J* = 8.0 Hz, 2H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.7, 158.6, 142.4, 135.9, 135.8, 134.2, 130.4, 128.8, 126.9, 126.6, 125.7, 124.3, 114.5, 113.5, 55.2, 27.6, 26.0, 15.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_4^+$ ([M+H$^+$]), 417.18088, found: 417.18008.

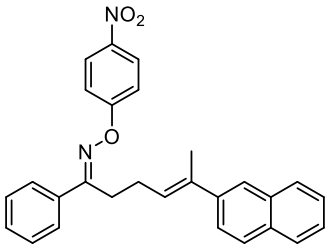
(4*E*)-5-(4-chlorophenyl)-1-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



55a

Synthesized according to General Procedure **2**. White solid, *E:Z* 20:1, m.p. 122 – 123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2 H), 8.17 – 8.15 (m, 0.1H), 7.78 – 7.75 (m, 2H), 7.50 – 7.43 (m, 3H), 7.41 – 7.35 (m, 2H), 7.26 – 7.15 (m, 4H), 5.78 – 5.74 (m, 1H), 3.11 (t, *J* = 8.0 Hz, 2H), 2.86 (t, *J* = 8.0 Hz, 0.1H), 2.57 – 2.47 (m, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.5, 142.4, 141.7, 135.5, 134.1, 132.5, 130.5, 128.8, 128.2, 126.9, 126.8, 126.4, 125.7, 114.5, 27.3, 26.0, 15.7. HRMS (ESI) *m/z* calcd for $C_{24}H_{22}ClN_2O_3^+$ ([M+H$^+$]), 421.13135, found: 421.13146.

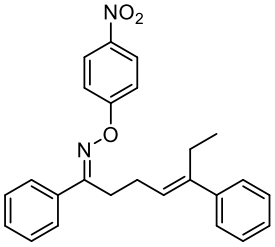
(4*E*)-5-(naphthalen-2-yl)-1-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



56a

Synthesized according to General Procedure **2**. Yellow solid, m.p. 96 – 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 2H), 7.80 – 7.64 (m, 6H), 7.48 – 7.36 (m, 8H), 5.94 (t, *J* = 8.0 Hz, 1H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.61 (q, *J* = 8.0 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.6, 142.4, 140.5, 136.3, 134.2, 133.3, 132.4, 130.4, 128.8, 127.9, 127.6, 127.4, 127.0, 126.5, 126.1, 125.7, 125.6, 124.1, 124.1, 114.5, 27.4, 26.1, 15.8. HRMS (ESI) *m/z* calcd for $C_{28}H_{25}N_2O_3^+$ ([M+H$^+$]), 437.18597, found: 437.18535.

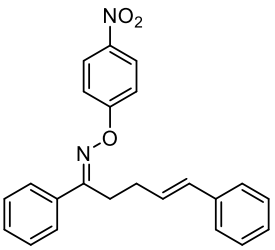
(4*E*)-1,5-diphenylhept-4-en-1-one *O*-(4-nitrophenyl) oxime



57a

Synthesized according to General Procedure **2**. White solid, m.p. 88 – 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.21 (m, 2H), 7.80 – 7.78 (m, 2H), 7.51 – 7.44 (m, 3H), 7.40 – 7.36 (m, 2H), 7.27 – 7.18 (m, 5H), 5.65 (t, *J* = 8.0 Hz, 1H), 3.11 (t, *J* = 8.0 Hz, 2H), 2.55 (q, *J* = 8.0 Hz, 2H), 2.46 (q, *J* = 8.0 Hz, 2H), 0.93 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.5, 143.3, 142.4, 142.4, 134.1, 130.4, 128.8, 128.1, 126.9, 126.7, 126.2, 125.7, 125.6, 114.5, 27.7, 25.7, 22.9, 13.6. HRMS (ESI) *m/z* calcd for $C_{25}H_{25}N_2O_3^+$ ([M+H$^+$]), 401.18597, found: 401.18480.

(4*E*)-1,5-diphenylpent-4-en-1-one *O*-(4-nitrophenyl) oxime

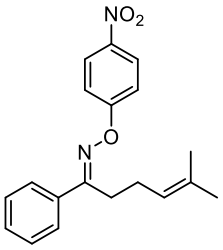


58a

Synthesized according to General Procedure **1** (from cinnamyl alcohol). White solid, m.p. 95 – 96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 2H), 7.78 – 7.75 (m, 2H), 7.50 – 7.43 (m, 3H), 7.37 – 7.33 (m, 2H), 7.25 – 7.16 (m, 5H), 6.40 (d, *J* = 16 Hz, 1H), 6.25 – 6.17 (m, 1H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.54 (q, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 163.4, 142.3, 137.1, 134.0, 131.0, 130.4,

128.8, 128.4, 128.3, 127.2, 126.9, 125.9, 125.6, 114.5, 30.1, 27.4. HRMS (ESI) *m/z* calcd for $C_{23}H_{21}N_2O_3^+$ ([M+H$^+$]), 373.15467, found: 373.15432.

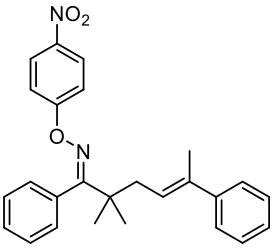
5-methyl-1-phenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



59a

Synthesized according to General Procedure **1** (from 3,3-dimethylallyl bromide). Yellow solid, m.p. 51 – 57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.76 – 7.74 (m, 2H), 7.46 – 7.44 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.19 (t, *J* = 8.0 Hz, 1H), 2.97 (t, *J* = 8.0 Hz, 2H), 2.32 (q, *J* = 8.0 Hz, 2H), 1.65 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.9, 142.4, 134.3, 133.3, 130.3, 128.7, 126.9, 125.7, 122.5, 114.4, 27.8, 25.5, 25.3, 17.6. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}N_2O_3^+$ ([M+H$^+$]), 325.15467, found: 325.15417.

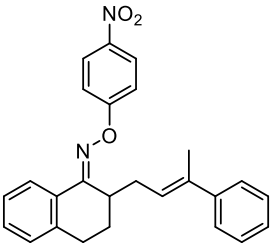
2,2-dimethyl-1,5-diphenylhex-4-en-1-one *O*-(4-nitrophenyl) oxime



61a

Synthesized according to General Procedure **1** and **3**. Orange oil, *E:Z* 15:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H), 7.45 – 7.37 (m, 5H), 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.14 – 7.10 (m, 4H), 5.90 (td, *J* = 8.0, 4.0 Hz, 1H), 2.64 (d, *J* = 8.0 Hz, 0.14H), 2.47 (d, *J* = 8.0 Hz, 2H), 2.03 (s, 3H), 1.96 (s, 0.2H), 1.39 (s, 0.4H), 1.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 164.2, 143.9, 142.1, 137.3, 132.8, 128.3, 128.2, 128.0, 127.0, 126.8, 125.7, 125.5, 123.8, 114.3, 42.1, 39.0, 26.1, 16.4. HRMS (ESI) *m/z* calcd for $C_{26}H_{27}N_2O_3^+$ ([M+H$^+$]), 415.20162, found: 415.20067.

2-((*E*)-3-phenylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one *O*-(4-nitrophenyl) oxime

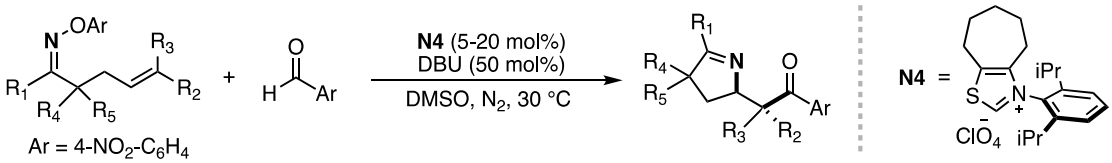


62a

Synthesized according to General Procedure **1**. Orange oil, *E:Z* 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.15 (m, 3H), 7.38 – 7.20 (m, 11H), 5.86 (q, J = 8.0 Hz, 1H), 3.84 – 3.84 (m, 0.5H), 3.07 – 2.87 (m, 2H), 2.78 – 2.74 (m, 0.5H), 2.65 – 2.55 (m, 1H), 2.49 – 2.41 (m, 1H), 2.27 – 2.20 (m, 0.5H), 2.06 – 1.92 (m, 4.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 162.1, 160.1, 143.5, 143.3, 142.2, 142.1, 140.3, 139.4, 136.9, 136.4, 131.1, 130.7, 130.5, 129.1, 129.0, 128.5, 128.1, 128.1, 126.7, 126.5, 125.7, 125.6, 125.6, 125.5, 125.5, 125.4, 124.8, 114.3, 41.1, 33.5, 30.8, 28.5, 27.6, 27.1, 25.0, 24.7, 16.0, 15.9. HRMS (ESI) *m/z* calcd for $C_{26}H_{25}N_2O_3^+$ ([M+H$^+$]), 413.18597, found: 413.18518.

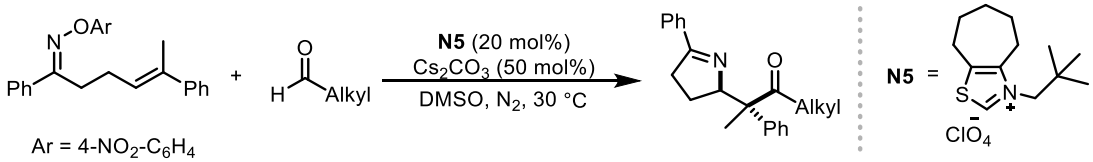
2.4 General procedure

2.4.1 Reaction with aromatic aldehydes



To an oven-dried reaction tube equipped with a stir bar was added *O*-aryl oxime (0.1 mmol, 1.0 equiv), thiazolium salt **N4** (5–20 mol%) and aromatic aldehydes (0.15 mmol, 1.5 equiv). The tube was sealed and placed under nitrogen before DBU (0.05 mmol, 0.5 equiv) and DMSO (1 mL) were added. Then the system was stirred at 30 ℃ for 12 h. The reaction mixture was purified by silica gel column chromatography to afford the desired pyrroline product.

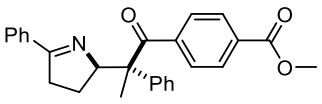
2.4.2 Reaction with aliphatic aldehydes



To an oven-dried reaction tube equipped with a stir bar was added *O*-aryl oxime (0.1 mmol, 1.0 equiv), thiazolium salt **N5** (20 mol%), Cs_2CO_3 (0.05 mmol, 0.5 equiv) and aliphatic aldehydes (0.15 mmol, 1.5 equiv). The tube was sealed and placed under nitrogen before DMSO (1 mL) was added. Then the system was stirred at 30 ℃ for 12 h. The reaction mixture was purified by silica gel column chromatography to afford the desired pyrroline product.

2.5 Characterization data for 3 – 62

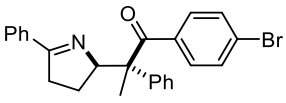
methyl 4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



3

White solid, d.r. > 19:1, m.p. 138 – 139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.70 – 7.68 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.16 (m, 8H), 5.16 – 5.12 (m, 1H), 3.78 (s, 3H), 2.77 – 2.69 (m, 1H), 2.53 – 2.44 (m, 1H), 2.03 – 1.93 (m, 1H), 1.74 – 1.65 (m, 1H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 173.4, 166.3, 142.1, 140.2, 134.4, 131.8, 130.3, 129.0, 128.9, 128.7, 128.2, 127.7, 127.5, 127.2, 77.3, 59.2, 52.1, 35.0, 24.8, 19.4. HRMS (ESI) *m/z* calcd for $C_{27}H_{26}NO_3^+$([M+H$^+$]), 412.19072, found: 412.19032.

1-(4-bromophenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one

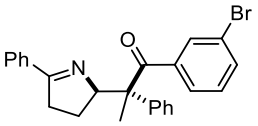


4

Yellow oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.16 (m, 12H), 5.09 (t, *J* = 8.0 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.41 – 2.34 (m, 1H), 2.04 – 1.95

(m, 1H), 1.74 – 1.65 (m, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 173.5, 140.4, 136.3, 134.4, 131.0, 131.0, 130.3, 128.5, 128.2, 127.7, 127.6, 127.1, 126.1, 77.5, 59.0, 35.0, 25.0, 20.3. HRMS (ESI) *m/z* calcd for $C_{25}H_{23}BrNO^+$ ([M+H$^+$]), 432.09575, found: 432.09596.

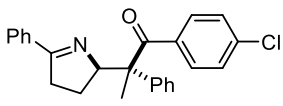
1-(3-bromophenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



5

Yellow oil, d.r. 15:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.60 (t, *J* = 4.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 0.2H), 7.39 – 7.37 (m, 1H), 7.32 – 7.19 (m, 9H), 6.98 (t, *J* = 8.0 Hz, 1H), 5.14 – 5.11 (m, 1H), 2.77 – 2.68 (m, 1H), 2.51 – 2.42 (m, 1H), 2.03 – 1.94 (m, 1H), 1.74 – 1.65 (m, 1H), 1.55 (s, 3H), 1.41 (s, 0.2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 173.4, 140.3, 139.8, 134.4, 133.9, 132.3, 130.3, 129.2, 128.6, 128.2, 127.7, 127.5, 127.2, 122.1, 77.4, 59.1, 35.0, 24.8, 19.9. HRMS (ESI) *m/z* calcd for $C_{25}H_{23}BrNO^+$ ([M+H$^+$]), 432.09575, found: 432.09590.

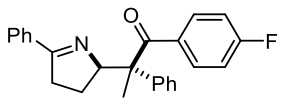
1-(4-chlorophenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



6

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.31 – 7.24 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.18 (t, *J* = 8.0 Hz, 1H), 2.82 – 2.73 (m, 1H), 2.49 – 2.41 (m, 1H), 2.12 – 2.03 (m, 1H), 1.83 – 1.74 (m, 1H), 1.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0 173.5, 140.5, 137.4, 135.9, 134.5, 130.9, 130.3, 128.5, 128.2, 128.0, 127.7, 127.1, 77.6, 59.0, 35.0, 25.0, 20.4. HRMS (ESI) *m/z* calcd for $C_{25}H_{23}ClNO^+$ ([M+H$^+$]), 388.14627, found: 388.14589.

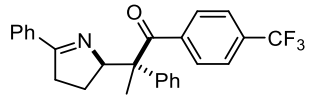
1-(4-fluorophenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



7

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.57 – 7.53 (m, 2H), 7.37 – 7.35 (m, 3H), 7.34 – 7.29 (m, 4H), 7.27 – 7.24 (m, 1H), 6.89 (t, *J* = 8.0 Hz, 2H), 5.18 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.45 – 2.36 (m, 1H), 2.12 – 2.03 (m, 1H), 1.83 – 1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6 173.6, 165.6, 163.1, 140.5, 134.5, 133.5, 133.5, 132.2, 132.1, 130.2, 128.4, 128.2, 127.6, 127.6, 127.1, 114.9, 114.7, 77.7, 59.0, 34.9, 25.0, 20.7. HRMS (ESI) *m/z* calcd for $C_{25}H_{23}FNO^+$ ([M+H$^+$]), 372.17582, found: 372.17494.

2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(4-(trifluoromethyl)phenyl)propan-1-one

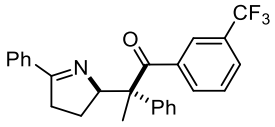


8

White solid, d.r. > 19:1, m.p. 135 – 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H), 7.43 – 7.38 (m, 4H), 7.32 – 7.20 (m, 8H), 5.14 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.79 –

2.70 (m, 1H), 2.56 – 2.47 (m, 1H), 2.04 – 1.95 (m, 1H), 1.76 – 1.67 (m, 1H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 173.5, 141.5, 140.2, 134.3, 132.3 (q, *J* = 32.3 Hz), 130.4, 129.3, 128.8, 128.3 127.7, 127.5, 127.4, 124.8 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.9 Hz), 77.2, 59.2, 35.1, 24.9, 19.4. HRMS (ESI) *m/z* calcd for $C_{26}H_{23}F_3NO^+$ ([M+H$^+$]), 422.17263, found: 422.17242.

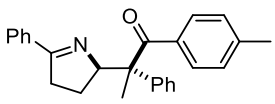
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(3-(trifluoromethyl)phenyl)propan-1-one



9

White solid, d.r. 15:1, m.p. 109 – 112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 0.2H), 7.70 – 7.67 (m, 3H), 7.51 – 7.46 (m, 2H), 7.34 – 7.26 (m, 7H), 7.24 – 7.18 (m, 2H), 5.14 – 5.05 (m, 1H), 2.78 – 2.70 (m, 1H), 2.55 – 2.46 (m, 1H), 2.06 – 1.96 (m, 1H), 1.77 – 1.70 (m, 1H), 1.54 (s, 3H), 1.45 (s, 0.2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 173.5, 140.3, 138.6, 134.3, 132.4, 130.4, 130.3 (q, *J* = 32.2 Hz), 128.8, 128.3, 127.7, 127.5, 127.5, 127.3, 126.2 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.9 Hz), 77.3, 59.1, 35.0, 24.8, 19.9. HRMS (ESI) *m/z* calcd for $C_{26}H_{23}F_3NO^+$ ([M+H$^+$]), 422.17263, found: 422.17238.

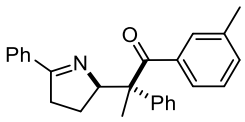
(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(*p*-tolyl)propan-1-one



10

Yellow oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.10 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.71 – 2.59 (m, 1H), 2.29 – 2.18 (m, 4H), 2.05 – 1.95 (m, 1H), 1.75 – 1.65 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 173.6, 141.9, 140.7, 134.6, 134.4, 130.2, 129.8, 128.5, 128.2, 128.2, 127.7, 127.7, 126.8, 78.0, 59.0, 34.9, 25.2, 21.4, 21.0. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO^+$ ([M+H$^+$]), 368.20089, found: 368.20068.

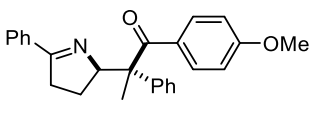
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(m-tolyl)propan-1-one



11

Yellow oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.35 – 7.16 (m, 9H), 7.11 – 7.08 (m, 2H), 7.01 -6.97 (m, 1H), 5.16 – 5.12 (m, 1H), 2.73 – 2.64 (m, 1H), 2.39 – 2.30 (m, 1H), 2.19 (s, 3H), 2.03 – 1.92 (m, 1H), 1.73 – 1.66 (m, 1H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 173.5, 140.7, 137.6, 137.6, 134.6, 132.0, 130.3, 130.0, 128.4, 128.2, 127.7, 127.7, 127.5, 126.9, 126.5, 77.9, 56.0, 34.9, 25.0, 21.3, 20.3. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO^+$ ([M+H$^+$]), 368.20089, found: 368.20089.

1-(4-methoxyphenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one

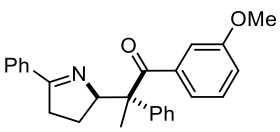


12

White solid, d.r. > 19:1, m.p. 98 – 100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.66 (m, 2H), 7.53 – 7.49 (m, 2H), 7.33 – 7.26 (m, 3H), 7.23 – 7.12 (m, 5H), 6.67 – 6.63 (m, 2H), 5.09 – 5.05 (m, 1H), 3.69 (s, 3H), 2.68 – 2.60 (m, 1H),

2.20 – 2.11 (m, 1H), 2.07 – 1.97 (m, 1H), 1.74 (s, 3H), 1.72 – 1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 173.7, 162.1, 140.9, 134.6, 132.2, 130.2, 129.3, 128.2, 128.1, 127.9, 127.7, 126.8, 113.0, 78.2, 58.9, 55.2, 34.8, 25.3, 21.8. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_2^+$ ([M+H$^+$]), 384.19581, found: 384.19577.

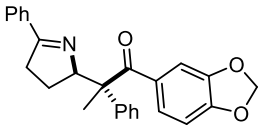
1-(3-methoxyphenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



13

White solid, d.r. > 19:1, m.p. 156 – 158 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.31 – 7.16 (m, 8H), 7.05 – 7.00 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.82 (dd, *J* = 8.0, 4.0 Hz, 1H), 5.16 – 5.12 (m, 1H), 3.58 (s, 3H), 2.73 – 2.65 (m, 1H), 2.42 – 2.33 (m, 1H), 2.02 – 1.92 (m, 1H), 1.74 – 1.65 (m, 1H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 173.4, 158.9, 140.7, 138.9, 134.6, 130.2, 128.7, 128.4, 128.2, 127.7, 127.6, 127.0, 121.9, 117.79, 113.99, 77.8, 59.0, 55.1, 34.9, 25.0, 20. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_2^+$ ([M+H$^+$]), 384.19581, found: 384.19595.

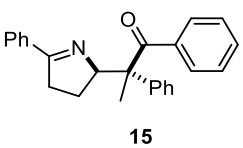
1-(benzo[d][1,3]dioxol-5-yl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



14

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.40 – 7.32 (m, 3H), 7.30 – 7.19 (m, 5H), 7.16 – 7.14 (m, 1H), 7.11 (d, *J* = 4.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.91 – 5.90 (m, 2H), 5.15 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.34 – 2.25 (m, 1H), 2.13 – 2.03 (m, 1H), 1.83 – 1.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 173.6, 150.2, 147.1, 140.8, 134.6, 131.2, 130.2, 128.2, 128.2, 127.7, 127.6, 126.9, 125.8, 110.0, 107.3, 101.4, 78.1, 59.0, 34.8, 25.2, 21.4. HRMS (ESI) *m/z* calcd for $C_{26}H_{24}NO_3^+$ ([M+H$^+$]), 398.17507, found: 398.17416.

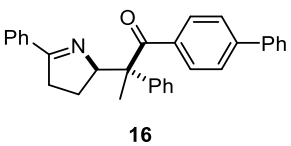
1,2-diphenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



15

Yellow solid, d.r. > 19:1, m.p. 127 – 128 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.42 (d, *J* = 4.0 Hz, 2H), 7.36 – 7.04 (m, 11H), 5.11 – 5.15 (m, 1H), 2.74 – 2.61 (m, 1H), 2.42 – 2.26 (m, 1H), 2.04 – 1.91 (m, 1H), 1.76 – 1.66 (m, 1H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 173.5, 140.6, 137.6, 134.5, 131.2, 130.2, 129.4, 128.3, 128.2, 127.8, 127.7, 127.0, 59.0, 34.9, 25.0, 20.4. HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO^+$ ([M+H$^+$]), 354.18524, found: 354.18500.

1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one

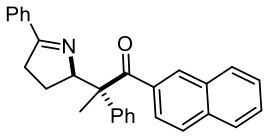


16

White solid, d.r. > 19:1, m.p. 133 – 135 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.23 (m, 11H), 5.22 (t, *J* = 8.0 Hz, 1H), 2.80 – 2.72 (m, 1H),

2.43 – 2.35 (m, 1H), 2.14 – 2.05 (m, 1H), 1.85 – 1.77 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 173.5, 143.9, 140.7, 140.0, 136.0, 134.6, 130.2, 130.2, 128.8, 128.4, 128.2, 127.8, 127.8, 127.7, 127.1, 127.0, 126.4, 77.9, 59.1, 34.9, 25.1, 20.8. HRMS (ESI) *m/z* calcd for $C_{31}H_{28}NO^+$ ([M+H$^+$]), 430.21654, found: 430.21611.

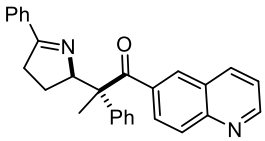
(1-(naphthalen-2-yl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



17

White solid, d.r. > 19:1, m.p. 164 – 169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.78 – 7.73 (m, 3H), 7.69 – 7.62 (m, 3H), 7.49 – 7.23 (m, 10H), 5.27 (t, *J* = 8.0 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.46 – 2.39 (m, 1H), 2.14 – 2.03 (m, 1H), 1.86 – 1.77 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 173.5, 140.8, 134.8, 134.6, 134.5, 132.1, 130.6, 130.2, 129.4, 128.4, 128.2, 127.8, 127.7, 127.7, 127.4, 127.4, 127.0, 126.2, 125.9, 77.9, 59.2, 34.9, 25.1, 20.6. HRMS (ESI) *m/z* calcd for $C_{29}H_{26}NO^+$ ([M+H$^+$]), 404.20089, found: 404.20105.

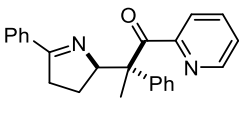
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(quinolin-6-yl)propan-1-one



18

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.90 (m, 1H), 8.03 – 8.01 (m, 1H), 7.96 – 7.94 (m, 2H), 7.83 – 7.77 (m, 3H), 7.43 – 7.29 (m, 9H), 5.30 – 5.26 (m, 1H), 2.86 – 2.77 (m, 1H), 2.58 – 2.49 (m, 1H), 2.16 – 2.07 (m, 1H), 1.88 – 1.81 (m, 1H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 173.5, 151.9, 148.9, 140.6, 137.3, 135.8, 134.4, 130.3, 130.2, 129.5, 128.9, 128.6, 128.2, 127.7, 127.6, 127.2, 127.1, 121.4, 77.6, 59.2, 35.0, 24.9, 20.2. HRMS (ESI) *m/z* calcd for $C_{28}H_{25}N_2O^+$ ([M+H$^+$]), 405.19614, found: 405.19514.

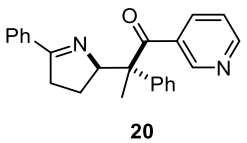
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(pyridin-2-yl)propan-1-one



19

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 4.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.75 (m, 2H), 7.72 – 7.68 (m, 1H), 7.40 – 7.34 (m, 5H), 7.26 – 7.13 (m, 4H), 5.84 (t, *J* = 8.0 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.66 – 2.57 (m, 1H), 2.18 – 2.09 (m, 1H), 1.91 – 1.82 (m, 1H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 173.1, 154.3, 147.7, 141.8, 136.3, 134.6, 130.2, 128.2, 127.9, 127.8, 127.4, 126.1, 125.4, 124.1, 77.4, 58.9, 35.2, 24.9, 18.9. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}N_2O^+$ ([M+H$^+$]), 355.18049, found: 355.18042.

2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(pyridin-3-yl)propan-1-one

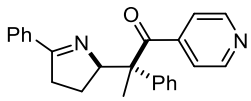


20

White solid, d.r. > 19:1, m.p. 138 – 139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 8.55 (d, *J* = 4.0 Hz, 1H), 8.46 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.69 – 7.63 (m, 3H), 7.34 – 7.18 (m, 8H), 7.09 (dd, *J* = 8.0, 4.0 Hz, 1H), 5.12 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.56 – 2.47 (m, 1H), 2.07 – 1.98 (m, 1H), 1.79 – 1.69 (m, 1H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 173.5, 151.3, 150.2, 139.9, 136.6, 134.3, 133.7, 130.4, 128.8, 128.2, 127.7, 127.5, 127.4, 122.7, 77.0, 59.3, 35.1, 24.8, 19.8. HRMS (ESI)

m/z calcd for $C_{24}H_{23}N_2O^+$ ([M+H$^+$]), 355.18049, found: 355.18032.

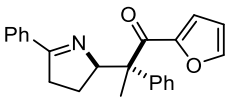
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(pyridin-4-yl)propan-1-one



21

White solid, d.r. > 19:1, m.p. 146 – 147 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.31 (m, 8H), 7.13 (d, *J* = 4.0 Hz, 2H), 5.22 (t, *J* = 8.0 Hz, 1H), 2.92 – 2.84 (m, 1H), 2.74 – 2.66 (m, 1H), 2.14 – 2.05 (m, 1H), 1.85 – 1.76 (m, 1H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 173.4, 149.7, 145.6, 139.7, 134.1, 130.5, 128.9, 128.3, 127.7, 127.5, 127.4, 122.2, 76.6, 59.2, 35.1, 24.5, 18.4. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}N_2O^+$ ([M+H$^+$]), 355.18049, found: 355.17980.

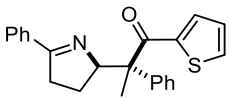
1-(furan-2-yl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



22

Yellow oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 4.0 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.20 – 7.12 (m, 5H), 6.71 (d, *J* = 4.0 Hz, 1H), 6.25 (d, *J* = 4.0 Hz, 1H), 5.17 (s, 1H), 2.78 – 2.70 (m, 1H), 2.20 – 2.10 (m, 2H), 1.83 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 151.4, 145.5, 140.0, 131.4, 128.4, 128.0, 128.0, 127.0, 119.3, 111.5, 76.4, 58.5, 34.8, 25.0, 21.1. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}NO_2^+$ ([M+H$^+$]), 344.16451, found: 344.16385.

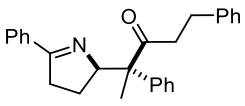
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(thiophen-2-yl)propan-1-one



23

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 4.0 Hz, 2H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.27 – 7.21 (m, 3H), 7.07 (d, *J* =4.0 Hz, 1H), 6.8 6– 6.83 (m, 1H), 5.12 (t, *J* = 8.0 Hz, 1H), 2.79– 2.70 (m, 1H), 2.33 – 2.24 (m, 1H), 2.23 – 2.13 (m, 1H), 1.89 – 1.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 173.8, 142.9, 140.8, 134.6, 133.5, 132.2, 130.2, 128.5, 128.2, 127.9, 127.6, 127.4, 127.0, 77.80, 59.5, 34.9, 25.3, 22.8. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}NOS^+$ ([M+H$^+$]), 360.14166, found: 360.14116.

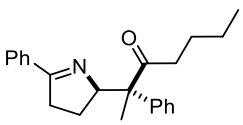
1,4-diphenyl-4-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)pentan-3-one



24

Colorless oil, d.r. = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.42 – 7.34 (m, 3.2H), 7.30 – 7.10 (m, 7.8H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.28 (t, *J* = 8.0 Hz, 0.8H), 5.03 (t, *J* = 8.0 Hz, 0.2H), 2.92 – 2.78 (m, 4H), 2.75 – 2.61 (m, 2H), 2.14 – 2.01 (m, 1H), 1.70 – 1.57 (m, 1H), 1.41 (s, 2.4H), 1.36 (s, 0.6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 210.4, 173.4, 173.3, 141.8, 141.6, 141.5, 141.0, 134.8, 134.7, 130.7, 130.6, 128.8, 128.7, 128.6, 128.5, 128.5, 128.1, 128.0, 127.4, 127.1, 127.0, 126.2, 162.0, 77.7, 77.6, 60.6, 60.1, 40.8, 40.2, 35.4, 35.4, 30.6, 25.3, 25.0, 17.9, 17.2. HRMS (ESI) *m/z* calcd for $C_{27}H_{28}NO^+$ ([M+H$^+$]), 382.21654, found: 382.21658.

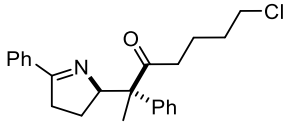
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)heptan-3-one



25

Colorless oil, d.r. = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.43 – 7.31 (m, 7H), 7.28 – 7.22 (m, 1H), 5.29 (t, *J* = 8.0 Hz, 0.8H), 5.07 (t, *J* = 8.0 Hz, 0.2H), 2.91– 2.82 (m, 1H), 2.72 – 2.64 (m, 1H), 2.57 – 2.28 (m, 2H), 2.26 – 2.15 (m, 0.2H), 2.10 – 2.01 (m, 0.8H), 1.71 – 1.61 (m, 1H), 1.52 (dt, *J* = 16.0, 8.0 Hz, 2H), 1.44 (s, 2.4H), 1.40 (s, 0.6H), 1.22 – 1.13 (m, 2H), 0.82 – 0.77 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.1, 211.3, 173.0, 172.9, 141.8, 140.9, 134.6, 134.5, 130.3, 130.3, 128.4, 128.3, 128.2, 127.8, 127.7, 127.3, 126.8, 126.7, 76.6, 60.4, 59.9, 38.3, 37.8, 35.2, 35.1, 29.1, 26.3, 26.2, 25.1, 24.7, 22.2, 17.6, 16.9, 13.8. HRMS (ESI) *m/z* calcd for $C_{23}H_{28}NO^+$ ([M+H$^+$]), 334.21654, found: 334.21664.

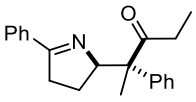
7-chloro-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)heptan-3-one



26

Colorless oil, d.r. = 4:1. ^{1}H NMR (400 MHz, CDCl3) δ 7.81 – 7.76 (m, 2H), 7.43 – 7.30 (m, 7H), 7.27 – 7.24 (m, 1H), 5.32 (t, *J* = 8.0 Hz, 0.8H), 5.07 (t, *J* = 8.0 Hz, 0.2H), 3.43 – 3.38 (m, 2H), 2.94 – 2.90 (m, 1H), 2.80 – 2.72 (m, 1H), 2.64 – 2.57 (m, 0.8H), 2.48 – 2.41 (m, 0.8H), 2.38 – 2.35 (m, 0.4H), 2.23 – 2.15(m, 0.2H), 2.13 – 2.03 (m, 0.8H), 1.73 – 1.61 (m, 5H), 1.42 (s, 0.6H), 1.40 (s, 2.4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 210.4, 173.1, 173.0, 141.4, 140.9, 134.5, 134.3, 130.4, 130.3, 128.6, 128.3, 128.2, 127.8, 127.7, 127.1, 127.0, 126.9, 76.5, 60.4, 59.9, 44.7, 44.6, 37.5, 36.8, 35.2, 31.8, 25.1, 24.7, 21.3, 21.3, 17.7, 16.6. HRMS (ESI) *m/z* calcd for $C_{23}H_{27}ClNO^+$ ([M+H$^+$]), 368.17757, found: 368.17747.

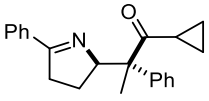
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)pentan-3-one



27

Colorless oil, d.r. = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.43 – 7.31 (m, 7H), 7.26 – 7.23 (m, 1H), 5.29 (t, *J* = 8.0 Hz, 0.75H), 5.06 (t, *J* = 8.0 Hz, 0.25H), 2.90 – 2.78 (m, 1.25H), 2.73 – 2.64 (m, 0.75H), 2.62 – 2.52 (m, 0.75H), 2.48 – 2.31 (m, 1.25H), 2.24 – 2.00 (m, 1H), 1.70 – 1.60 (m, 1H), 1.45 (s, 2.25H), 1.41 (s, 0.75H), 1.05 – 0.96 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 212.8, 212.0, 173.0, 172.9, 141.9, 141.1, 134.5, 134.4, 130.3, 130.2, 128.4, 128.2, 128.2, 128.2, 127.8, 127.7, 127.2, 126.8, 126.7, 77.5, 76.7, 60.3, 59.8, 35.2, 35.1, 31.8, 31.3, 25.1, 24.7, 17.7, 17.0, 8.5, 8.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{24}NO^+$ ([M+H$^+$]), 306.18524, found: 306.18511.

1-cyclopropyl-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one

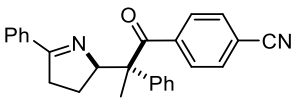


28

Colorless oil, d.r. =2.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 0.57H), 7.76 (d, *J* = 8.0 Hz, 1.43H), 7.52 (d, *J* = 8.0 Hz, 0.57H), 7.41 – 7.21 (m, 7.43H), 5.14 – 5.07 (m, 1H), 2.93 – 2.72 (m, 1.27H), 2.43 – 2.35 (m, 0.73H), 2.24 – 2.07 (m, 1H), 1.97 – 1.90 (m, 0.73H), 1.80 – 1.61 (m, 3.60H), 1.42 (s, 0.86H), 1.11 – 1.01 (m, 2H), 0.80 – 0.68 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 212.1, 211.8, 173.3, 172.9, 142.4, 140.8, 134.7, 134.6, 130.3, 130.2, 128.3, 128.2, 128.2, 128.1, 128.0,

127.8, 127.6, 126.7, 126.6, 76.9, 76.8, 60.7, 60.6, 35.1, 34.9, 25.3, 25.2, 20.2, 18.9, 18.7, 18.2, 12.0, 11.7, 11.7, 11.3. HRMS (ESI) *m/z* calcd for $C_{22}H_{24}NO^+$ ([M+H$^+$]), 318.18524, found: 318.18534.

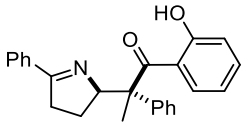
4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzonitrile



29

White solid, d.r. > 19:1, m.p. 128 – 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.5 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.23 (m, 8H), 5.12 (t, *J* = 8.0 Hz, 1H), 2.82 – 2.74 (m, 1H), 2.62 – 2.53 (m, 1H), 2.06 – 1.97 (m, 1H), 1.77 – 1.69 (m, 1H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 173.5, 142.3, 140.0, 134.1, 131.5, 130.5, 129.3, 128.9, 128.3, 127.7, 127.5, 127.4, 118.1, 114.1, 76.9, 59.2, 35.1, 24.7, 19.2. HRMS (ESI) *m/z* calcd for $C_{26}H_{23}N_2O^+$ ([M+H$^+$]), 379.18049, found: 379.18023.

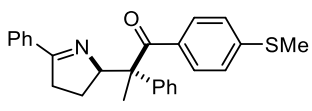
1-(2-hydroxyphenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



30

Colorless oil, d.r. 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.53 (s, 0.25H), 12.36 (s, 0.75H), 7.80 – 7.78 (m, 0.5H), 7.74 – 7.72 (m, 1.5H), 7.54 (d, *J* = 4.0 Hz, 0.5H), 7.38 – 7.31 (m, 3.5H), 7.26 – 7.18 (m, 5.25H), 7.06 – 7.04 (m, 0.75H), 6.96 – 6.93 (m, 1H), 6.47 (t, *J* = 8.0 Hz, 1H), 5.21 – 5.12 (m, 1H), 2.77 – 2.68 (m, 1H), 2.31 – 2.22 (m, 0.75H), 2.18 – 1.99 (m, 1.25H), 1.87 – 1.78 (m, 3H), 1.72 – 1.66 (m, 0.25H), 1.57 (s, 0.75H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 208.3, 174.2, 173.1, 163.5, 162.5, 143.3, 140.6, 135.0, 134.4, 134.2, 131.7, 131.7, 130.3, 130.3, 1284, 128.2, 128.2, 127.7, 127.6, 127.6, 126.9, 126.8, 126.6, 118.9, 118.7, 118.0, 117.8, 117.7, 78.0, 77.9, 59.9, 59.9, 34.8, 25.2, 25.0, 22.1, 21.1. HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_2^+$ ([M+H$^+$]), 370.18016, found: 370.17938.

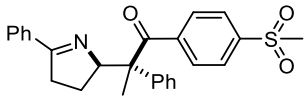
1-(4-(methylthio)phenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



31

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.66 (m, 2H), 7.43 – 7.39 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 – 7.15 (m, 5H), 7.00 – 6.97 (m, 2H), 5.10 – 5.06 (m, 1H), 2.71 – 2.62 (m, 1H), 2.35 (s, 3H), 2.28 – 2.19 (m, 1H), 2.07 – 1.97 (m, 1H), 1.76 – 1.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 173.6, 143.7, 140.7, 134.6, 133.1, 130.2, 130.2, 128.3, 128.2, 127.8, 127.6, 126.9, 124.4, 78.0, 59.0, 34.9, 25.2, 21.2, 14.7. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NOS^+$ ([M+H$^+$]), 400.17296, found: 400.17291.

1-(4-(methylsulfonyl)phenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one

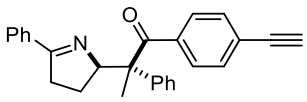


32

White solid, d.r. > 19:1, m.p. 184 – 187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 4H), 7.53 – 7.51 (m, 2H), 7.44 – 7.30 (m, 8H), 5.23 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.97 (s,

3H), 2.92 – 2.84 (m, 1H), 2.74 – 2.65 (m, 1H), 2.15 – 2.06 (m, 1H), 1.86 – 1.77 (m, 1H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 173.5, 143.5, 141.8, 140.0, 134.1, 130.5, 129.6, 128.9, 128.3, 127.7, 127.5, 127.3, 126.8, 76.7, 59.3, 44.2, 35.1, 24.6, 19.0. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_3S^+$ ([M+H$^+$]), 432.16279, found: 432.16196.

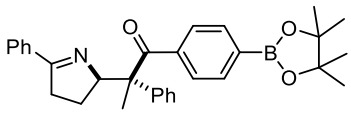
1-(4-ethynylphenyl)-2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one



33

White solid, d.r. > 19:1, m.p. 127 – 129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.75 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.24 (m, 10H), 5.21 – 5.18 (m, 1H), 3.12 (s, 1H), 2.82 – 2.74 (m, 1H), 2.49 – 2.42 (m, 1H), 2.11 – 2.02 (m, 1H), 1.82 – 1.73 (m, 1H), 1.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 173.5, 140.4, 137.5, 134.4, 131.5, 130.3, 129.3, 128.5, 128.2, 127.7, 127.6, 127.1, 124.9, 82.9, 79.39, 77.6, 59.0, 34.9, 24.9, 20.1. HRMS (ESI) *m/z* calcd for $C_{27}H_{24}NO^+$ ([M+H$^+$]), 378.18524, found: 378.18453.

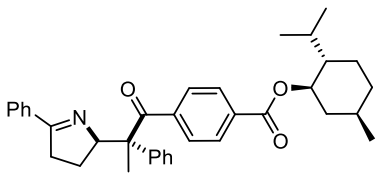
2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one



34

White solid, d.r. > 19:1, m.p. 160 – 164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.27 (m, 8H), 5.26 – 5.22 (m, 1H), 2.84 – 2.76 (m, 1H), 2.52 – 2.43 (m, 1H), 2.14 – 2.04 (m, 1H), 1.85 – 1.76 (m, 1H), 1.71 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 173.5, 140.5, 139.9, 134.5, 134.1, 130.2, 128.4, 128.3, 128.2, 127.7, 127.0, 83.9, 77.7, 59.1, 34.9, 25.0, 24.8, 20.0. HRMS (ESI) *m/z* calcd for $C_{31}H_{35}BNO_3^+$ ([M+H$^+$]), 480.27045, found: 480. 26983.

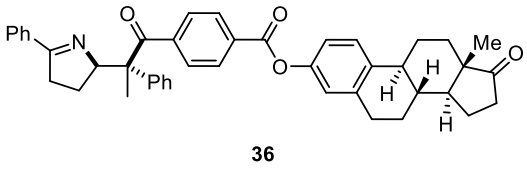
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



35

White solid, d.r. > 19:1, m.p. 74 – 78 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.81 – 7.76 (m, 2H), 7.49 – 7.44 (m, 2H), 7.41 – 7.27 (m, 8H), 5.25 – 5.20 (m, 1H), 4.89 (td, *J* = 8.0, 4.0 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.61 – 2.51 (m, 1H), 2.09 – 2.04 (m, 2H), 1.92 – 1.87 (m, 1H), 1.84 – 1.75 (m, 1H), 1.70 (d, *J* = 12.0 Hz, 2H), 1.62 – 1.58 (m, 3H), 1.53 – 1.47 (m, 2H), 1.15 – 1.00 (m, 2H), 0.94 – 0.85 (m, 7H), 0.75 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 173.4, 173.3, 165.3, 141.8, 141.8, 140.4, 140.3, 134.4, 132.6, 130.3, 128.9, 128.7, 128.6, 128.2, 127.7, 127.6, 127.5, 127.4, 127.2, 77.3, 75.1, 59.2, 59.2, 47.2, 40.8, 35.0, 34.2, 31.4, 26.4, 24.8, 23.5, 22.0, 20.7, 19.6. HRMS (ESI) m/z calcd for $C_{36}H_{42}NO_3^+$ ([M+H$^+$]), 536.31592, found: 536.31519.

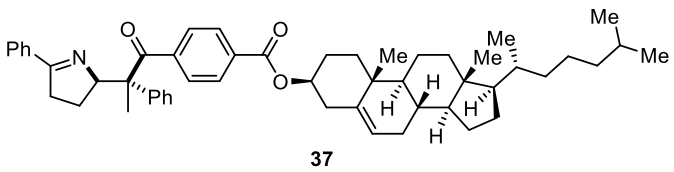
(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl-4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



36

White solid, d.r. > 19:1, m.p. 115 – 118 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.26 (m, 9H), 6.94 – 6.90 (m, 2H), 5.25 (t, *J* = 8.0 Hz, 1H), 2.92 – 2.81 (m, 3H), 2.63 – 2.58 (m, 1H), 2.54 – 2.47 (m, 1H), 2.43 – 2.39 (m, 1H), 2.32 – 2.28 (m, 1H), 2.19 – 1.95 (m, 6H), 1.86 – 1.77 (m, 1H), 1.68 – 1.43 (m, 10H), 1.28 – 1.26 (m, 1H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 173.6, 164.7, 148.6, 142.7, 140.2, 138.1, 137.5, 134.3, 131.3, 130.5, 129.5, 129.0, 128.8, 128.3, 127.8, 127.5, 127.3, 126.4, 121.5, 118.7, 59.2, 50.4, 47.9, 44.1, 38.0, 35.8, 35.1, 31.5, 29.4, 26.3, 25.7, 24.8, 21.5, 19.4, 13.8. HRMS (ESI) *m/z* calcd for $C_{44}H_{44}NO_4^+$ ([M+H$^+$]), 650.32649, found: 650.32718.

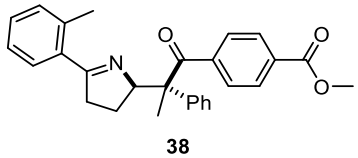
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



37

White solid, d.r. > 19:1, m.p. 90 – 93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.76 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.25 (m, 8H), 5.39 (d, *J* = 4.0 Hz, 1H), 5.22 (t, *J* = 8.0 Hz, 1H), 4.86 – 4.78 (m, 1H), 2.85 – 2.77 (m, 1H), 2.59 – 2.51 (m, 1H), 2.41 (d, *J* = 8.0 Hz, 2H), 2.09 – 1.96 (m, 4H), 1.88 – 1.76 (m, 3H), 1.69 – 1.66 (m, 1H), 1.61 (s, 3H), 1.58 – 1.42 (m, 6H), 1.41 – 1.30 (m, 3H), 1.27 – 1.25 (m, 1H), 1.21 – 1.06 (m, 7H), 1.04 (s, 3H), 1.02 – 0.95 (m, 3H), 0.93 – 0.89 (m, 3H), 0.87 – 0.85 (m, 6H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 173.4, 165.2, 141.8, 140.3, 139.4, 134.4, 132.6, 130.3, 128.9, 128.9, 128.6, 128.2, 127.7, 127.5, 127.2, 122.8, 77.3, 74.8, 59.2, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 36.9, 36.6, 36.1, 35.7, 35.0, 31.9, 31.8, 28.2, 28.0, 27.8, 24.8, 24.2, 23.8, 22.8, 22.5, 21.0, 19.6, 19.3, 18.7, 11.8. HRMS (ESI) *m/z* calcd for $C_{53}H_{68}NO_3^+$ ([M+H$^+$]), 766.51937, found: 766.51772.

methyl 4-(2-phenyl-2-(5-(*o*-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate

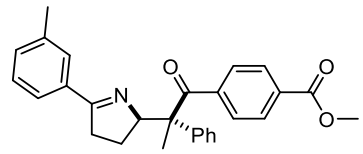


38

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 12.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.32 (m, 6H), 7.27 (d, *J* = 4.0 Hz, 1H), 7.22 – 7.18 (m, 2H), 5.29 (t, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 2.95 – 2.87 (m, 1H), 2.61 – 2.56 (m, 1H), 2.45 (s, 3H), 2.12 – 2.06 (m, 1H), 1.88 – 1.79 (m, 1H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 166.2, 141.5, 139.8, 137.7, 132.0, 131.3, 129.8, 129.2, 129.0, 128.9, 127.5, 125.6, 77.4, 58.8, 52.2, 38.1, 24.6, 22.0, 19.7. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_3^+$

([M+H$^+$]), 426.20637, found: 426.20615.

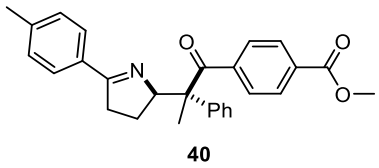
methyl 4-(2-phenyl-2-(5-(*m*-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



39

White solid, d.r. > 19:1, m.p. 102 – 104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.88 (m, 2H), 7.61 (s, 1H), δ 7.59 – 7.54 (m, 1H), δ 7.51 – 7.46 (m, 2H), 7.37 – 7.20 (m, 7H), 5.22 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.86 (s, 3H), 2.84 – 2.75 (m, 1H), 2.60 – 2.52 (m, 1H), 2.37 (s, 3H), 2.09 – 1.99 (m, 1H), 1.81 – 1.71 (m, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 173.5, 166.3, 142.1, 140.3, 137.8, 134.3, 131.8, 131.1, 128.9, 128.9, 128.6, 128.2, 128.1, 127.5, 127.2, 124.9, 77.3, 59.1, 52.1, 35.1, 24.7, 21.3, 19.4. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_3^+$ ([M+H$^+$]), 426.20637, found: 426.20581.

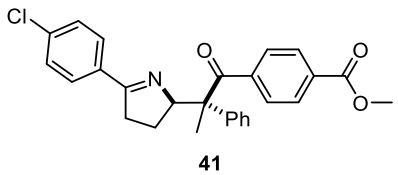
methyl 4-(2-phenyl-2-(5-(*p*-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



40

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.25 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.22 (t, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 2.84 – 2.75 (m, 1H), 2.58 – 2.50 (m, 1H), 2.36 (s, 3H), 2.09 – 2.00 (m, 1H), 1.81 – 1.72 (m, 1H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 173.3, 166.3, 142.1, 140.5, 140.2, 131.7, 131.6, 128.9, 128.9, 128.9, 128.6, 127.7, 127.5, 127.2, 77.1, 59.1, 52.2, 35.0, 24.7, 21.4, 19.3. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_3^+$ ([M+H$^+$]), 426.20637, found: 426.20520.

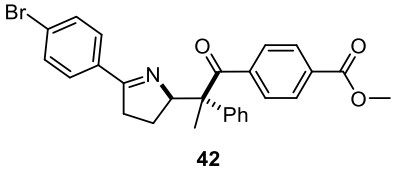
methyl 4-(2-(5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropanoyl)benzoate



41

White solid, d.r. > 19:1, m.p. 142 – 143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.27 (m, 7H), 5.21 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 2.81 – 2.72 (m, 1H), 2.56 – 2.48 (m, 1H), 2.10 – 2.00 (m, 1H), 1.82 – 1.75 (m, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 172.3, 166.2, 141.8, 140.0, 136.3, 132.7, 131.9, 129.0, 129.0, 128.9, 128.7, 128.4, 127.4, 127.3, 77.4, 59.0, 52.2, 34.9, 24.8, 19.4. HRMS (ESI) *m/z* calcd for $C_{27}H_{25}ClNO_3^+$ ([M+H$^+$]), 446.15175, found: 446.15148.

methyl 4-(2-(5-(4-bromophenyl)-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropanoyl)benzoate

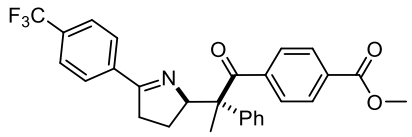


42

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.48 (dd, *J* = 12.0, 8.0 Hz, 4H), 7.34 – 7.28 (m, 5H), 5.20 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 2.81 – 2.73 (m, 1H), 2.56 – 2.47 (m, 1H), 2.10 –

2.00 (m, 1H), 1.83 – 1.73 (m, 1H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 172.5 166.2, 141.7, 140.0, 133.1, 131.9, 131.4, 129.2, 129.0, 128.9, 128.7, 127.4, 127.3, 124.9, 77.4, 59.0, 52.2, 34.9, 24.8, 19.4. HRMS (ESI) *m/z* calcd for $C_{27}H_{25}BrNO_3^+$ ([M+H$^+$]), 490.10123, found: 490.10058.

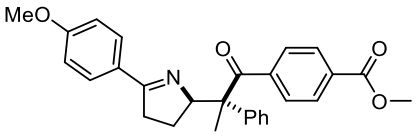
methyl 4-(2-phenyl-2-(5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrol-2-yl) propanoyl)benzoate



43

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 4H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.35 – 7.27 (m, 5H), 5.25 (t, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 2.85 – 2.77 (m, 1H), 2.59 – 2.53 (m, 1H), 2.13 – 2.04 (m, 1H), 1.85 – 1.76 (m, 1H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 172.4, 166.2, 141.6, 139.9, 137.5, 131.9 (q, *J* = 32.3 Hz), 129.0, 129.0, 128.7, 128.0, 127.4, 127.4, 125.2 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.6 Hz), 77.7, 59.0, 52.2, 35.0, 24.8, 19.5. HRMS (ESI) *m/z* calcd for $C_{28}H_{25}F_3NO_3^+$ ([M+H$^+$]), 480.17810, found: 480.17744.

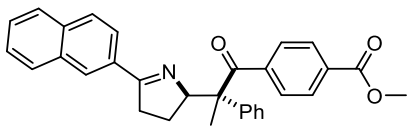
methyl 4-(2-(5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropan oyl)benzoate



44

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.27 (m, 5H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.22 – 5.19 (m, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.83 – 2.75 (m, 1H), 2.59 – 2.50 (m, 1H), 2.09 – 1.99 (m, 1H), 1.82 – 1.73 (m, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 172.7, 166.3, 161.3, 142.2, 140.3, 131.7, 129.3, 128.9, 128.9, 128.6, 127.5, 127.2, 127.2 113.5, 77.0, 59.2, 55.2, 52.2, 34.9, 24.8, 19.3. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_4^+$ ([M+H$^+$]), 442.20128, found: 442.20066.

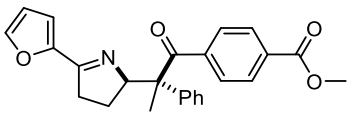
methyl 4-(2-(5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropanoy l)benzoate



45

White solid, d.r. > 19:1, m.p. 84 – 88 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), δ 7.85 – 7.81 (m, 3H), 7.51 – 7.45 (m, 4H), 7.38 – 7.24 (m, 5H), 5.30 – 5.26 (m, 1H), 3.85 (s, 3H), 2.95 – 2.87 (m, 1H), 2.71 – 2.62 (m, 1H), 2.13 – 2.03 (m, 1H), 1.86 – 1.77 (m, 1H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 173.4, 166.3, 142.0, 140.2, 134.3, 132.8, 131.8, 131.8, 129.0, 128.9, 128.6, 128.6, 128.2, 127.9, 127.7, 127.5, 127.2, 126.9, 126.2, 124.7, 77.3, 59.1, 52.2, 34.9, 24.8, 19.4. HRMS (ESI) *m/z* calcd for $C_{31}H_{28}NO_3^+$ ([M+H$^+$]), 462.20637, found: 462.20565.

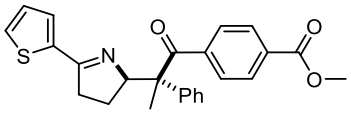
methyl 4-(2-(5-(furan-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropanoyl)benzoate



46

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.88 (m, 2H), δ 7.52 – 7.50 (m, 3H), 7.34 – 7.27 (m, 5H), 6.75 (d, *J* = 4.0 Hz, 1H), 6.44 (dd, *J* = 4.0, 4.0 Hz, 1H), 5.23 – 5.19 (m, 1H), 3.87 (s, 3H), 2.71 – 2.62 (m, 1H), 2.45 – 2.36 (m, 1H), 1.95 – 1.86 (m, 1H), 1.73 – 1.63 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 166.2, 164.4, 149.8, 144.4, 141.2, 139.8, 132.0, 129.2, 128.9, 128.6, 127.4, 127.2, 111.4, 77.8, 58.6, 52.2, 34.7, 24.4, 19.3. HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_4^+$ ([M+H$^+$]), 402.16998, found: 402.16945.

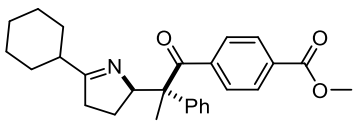
methyl 4-(2-phenyl-2-(5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



47

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.37 (m, 1H), 7.35 – 7.26 (m, 5H), 7.20 (d, *J* = 4.0 Hz, 1H), 7.02 – 7.00 (m, 1H), 5.15 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 2.80 – 2.71 (m, 1H), 2.47 – 2.38 (m, 1H), 2.13 – 2.04 (m, 1H), 1.85 – 1.76 (m, 1H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 168.1, 166.3, 141.6, 139.9, 139.3, 131.9, 129.1, 129.0, 129.0, 128.9, 128.5, 127.6, 127.2, 127.2, 77.3, 59.1, 52.2, 35.6, 25.1, 19.9. HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_3S^+$ ([M+H$^+$]), 418.14714, found: 418.14677.

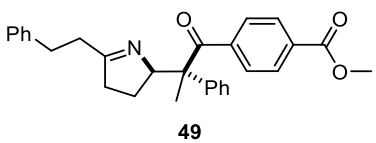
methyl 4-(2-(5-cyclohexyl-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropanoyl)benzoate



48

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.27 (m, 5H), 4.96 (t, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 2.32 – 2.24 (m, 2H), 2.06 – 1.99 (m, 1H), 1.84 – 1.56(m, 10H), 1.31 – 1.16 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$)) δ 203.2, 183.0, 166.3, 141.7, 140.1, 131.8, 129.1, 128.9, 128.6, 127.5, 127.2, 76.4, 58.7, 52.2, 42.5, 34.5, 30.4, 30.3, 26.0, 25.8, 24.3, 19.1. HRMS (ESI) *m/z* calcd for $C_{27}H_{32}NO_3^+$ ([M+H$^+$]), 418.23767, found: 418.23677.

methyl 4-(2-(5-phenethyl-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropanoyl)benzoate

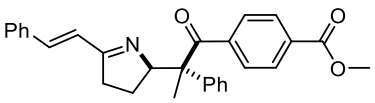


49

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* =12.0 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.35 – 7.24 (m, 7H), 7.18 – 7.15 (m, 3H), 5.02 – 4.98 (m, 1H), 3.87 (s, 3H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.67 – 2.52 (m, 2H), 2.32 – 2.24 (m, 1H), 2.11 – 2.02 (m, 1H), 1.83 – 1.74 (m, 1H), 1.59 – 1.52 (m, 1H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 178.3, 166.3, 141.7, 141.4, 140.1, 131.9, 129.0, 128.9, 128.6, 128.3, 128.3, 127.4, 127.2, 125.9, 76.9, 58.5, 52.1, 37.4, 35.1, 32.4, 24.6, 18.8. HRMS (ESI) *m/z* calcd for $C_{29}H_{30}NO_3^+$ ([M+H$^+$]),

440.22202, found: 440.22149.

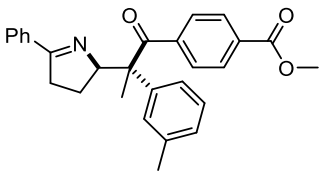
methyl 4-(2-phenyl-2-(5-((E)-styryl)-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



50

Colorless oil, d.r. 12:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.50 – 7.46 (m, 4H), 7.39 – 7.28 (m, 8H), 7.13 (d, *J* = 16.0 Hz, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 5.19 (t, *J* = 8.0 Hz, 1H), 5.10 (t, *J* = 8.0 Hz, 0.08H), 3.87 (s, 3H), 2.65 – 2.46 (m, 2H), 1.84 – 1.75 (m, 1H), 1.65 – 1.57 (m, 4H), 1.53 (s, 0.25H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 174.2, 166.2, 141.5, 140.0, 138.8, 135.8, 132.0, 129.1, 129.0, 128.9, 128.8, 128.7, 127.3, 127.1, 124.9, 77.3, 58.4, 52.2, 33.3, 24.3, 18.2. HRMS (ESI) *m/z* calcd for $C_{29}H_{28}NO_3^+$ ([M+H$^+$]), 438.20637, found: 438.20593.

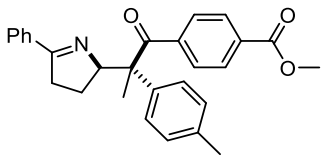
methyl4-(2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-2-(*m*-tolyl)propanoyl)benzoate



51

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.79 – 7.77 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.25 – 7.21 (m, 1H), 7.16 – 7.09 (m, 3H), 5.22 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 2.86 – 2.78 (m, 1H), 2.62 – 2.53 (m, 1H), 2.30 (s, 3H), 2.10 – 2.00 (m, 1H), 1.83 – 1.74 (m, 1H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 173.3, 166.3, 142.3, 140.1, 138.3, 134.4, 131.8, 130.3, 129.0, 128.9, 128.5, 128.2, 128.0, 127.7, 124.5, 77.2, 59.0, 52.2, 35.0, 24.8, 21.5, 19.2. HRMS (ESI) m/z calcd for $C_{28}H_{28}NO_3^+$ ([M+H$^+$]), 426.20637, found: 426.20536.

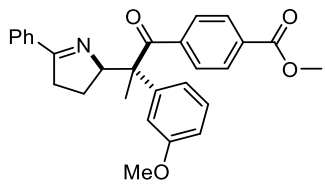
methyl 4-(2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-2-(*p*-tolyl)propanoyl)benzoate



52

White solid, d.r. > 19:1, m.p. 75 – 80 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 2H), 7.79 – 7.77 (m, 2H), 7.47 – 7.45 (m, 2H), 7.42 – 7.34 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.22 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 2.87 – 2.78 (m, 1H), 2.66 – 2.57 (m, 1H), 2.34 (s, 3H), 2.10 – 2.00 (m, 1H), 1.81 – 1.72 (m, 1H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 173.3, 166.4, 142.3, 137.1, 136.9, 134.4, 131.7, 130.3, 129.4, 128.9, 128.9, 128.2, 127.7, 127.3, 77.3, 58.8, 52.2, 35.0, 24.7, 21.0, 19.2. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_3^+$ ([M+H$^+$]), 426.20637, found: 426.20533.

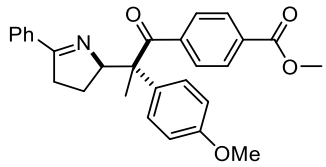
methyl 4-(2-(3-methoxyphenyl)-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propane yl)benzoate



53

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.79 – 7.77 (m, 2H), 7.51 – 7.49 (m, 2H), 7.40 – 7.34 (m, 3H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.85 – 6.82 (m, 1H), 5.24 – 5.20 (m, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 2.87 – 2.78 (m, 1H), 2.67 – 2.59 (m, 1H), 2.10 – 2.01 (m, 1H), 1.84 – 1.75 (m, 1H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 173.3, 166.3, 159.8, 142.2, 141.9, 134.3, 131.8, 130.3, 129.6, 129.0, 128.8, 128.2, 127.7, 119.9, 113.5, 112.3, 77.2. 59.0, 55.1, 52.1, 35.0, 24.7, 19.2. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_4^+$ ([M+H$^+$]), 442.20128, found: 442.20048.

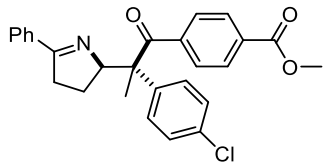
methyl 4-(2-(4-methoxyphenyl)-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan oyl)benzoate



54

White solid, d.r. > 19:1, m.p. 58 – 62 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 2H), 7.79 – 7.77 (m, 2H), 7.48 – 7.46 (m, 2H), 7.42 – 7.34 (m, 3H), 7.28 – 7.24 (m, 2H), 6.89 – 6.86 (m, 2H), 5.20 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 2.87 – 2.78 (m, 1H), 2.64 – 2.55 (m, 1H), 2.11 – 2.01 (m, 1H), 1.81 – 1.71 (m, 1H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 173.2, 166.3, 158.7, 142.3, 134.4, 132.1, 131.7, 130.3, 129.0, 128.9, 128.6, 128.2, 127.7, 114.0, 77.4, 58.5, 55.2, 52.1, 35.0, 24.7, 19.4. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_4^+$ ([M+H$^+$]), 442.20128, found: 442.20043.

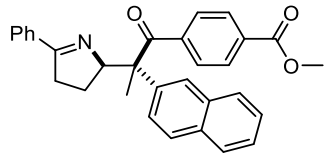
methyl 4-(2-(4-chlorophenyl)-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoy l)benzoate



55

White solid, d.r. > 19:1, m.p. 119 – 123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.78 – 7.76 (m, 2H), 7.50 – 7.48 (m, 2H), 7.43 – 7.35 (m, 3H), 7.33 – 7.26 (m, 4H), 5.19 – 5.15 (m, 1H), 3.88 (s, 3H), 2.87 – 2.79 (m, 1H), 2.64 – 2.55 (m, 1H), 2.14 – 2.04 (m, 1H), 1.76 – 1.67 (m, 1H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 173.5, 166.2, 141.6, 139.0, 134.2, 133.3, 132.1, 130.4, 129.1, 129.0, 128.9, 128.8, 128.3, 127.7, 77.4, 58.8, 52.2, 35.0, 24.8, 20.0. HRMS (ESI) *m/z* calcd for $C_{27}H_{25}ClNO_3^+$ ([M+H$^+$]), 446.15175, found: 446.15100.

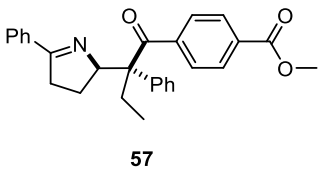
methyl 4-(2-(naphthalen-2-yl)-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



56

White solid, d.r. > 19:1, m.p. 80 – 84 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 8H), 7.51 – 7.46 (m, 5H), 7.41 – 7.34 (m, 3H), 5.38 – 5.34 (m, 1H), 3.83 (s, 3H), 2.86 – 2.77 (m, 1H), 2.66 – 2.57 (m, 1H), 2.10 – 2.01 (m, 1H), 1.85 – 1.75 (m, 1H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 173.4, 166.2, 142.2, 137.8, 134.3, 133.3, 132.3, 131.8, 130.4, 129.0, 128.8, 128.4, 128.2, 128.0, 127.7, 127.5, 126.3, 126.2, 125.3, 77.4, 59.2, 52.1, 35.1, 24.8, 19.3. HRMS (ESI) *m/z* calcd for $C_{31}H_{28}NO_3^+$ ([M+H$^+$]), 462.20637, found: 462.20532.

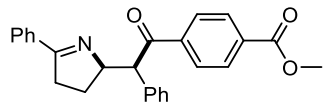
methyl 4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)butanoyl)benzoate



57

Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 2H), δ 7.71 – 7.69 (m, 4H), 7.38 – 7.32 (m, 3H), 7.18 – 7.15 (m, 5H), 5.16 – 5.13 (m, 1H), 3.88 (s, 3H), 3.21 – 3.12 (m, 1H), 2.66 – 2.58 (m, 1H), 2.37 – 2.17 (m, 2H), 1.90 – 1.81 (m, 1H), 1.79 – 1.71 (m, 1H), 0.92 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 174.2, 166.3, 139.7, 134.6, 132.7, 130.1, 129.9, 129.0, 128.9, 128.2, 127.7, 127.5, 127.0, 73.5, 63.7, 52.3, 34.6, 28.2, 25.4, 9.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}NO_3^+$ ([M+H$^+$]), 426.20637, found: 426.20552.

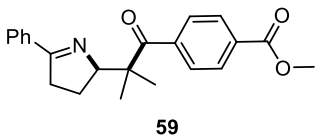
methyl 4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)acetyl)benzoate



58

Colorless oil, d.r. 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 4H), 7.76 – 7.73 (m, 2H), 7.42 – 7.20 (m, 8H), 5.12 (dd, *J* = 16.0, 8.0 Hz, 0.66H), 4.96 (dd, *J* = 16.0, 8.0 Hz, 0.33H), 4.75 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 2H), 3.88 (s, 1H), 3.07 – 2.90 (m, 0.66H), 2.84 – 2.75 (m, 0.66H), 2.71 – 2.62 (m, 0.66H), 2.42 – 2.33 (m, 0.33H), 2.08 – 2.01 (m, 0.66H), 1.83 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 198.7, 173.5, 173.3, 166.2, 166.0, 140.6, 140.2, 137.2, 135.8, 134.4, 134.2, 133.5, 133.3, 130.4, 130.4, 129.6, 129.6,129.1, 129.0, 128.8, 128.7, 128.2, 127.7, 127.7, 127.4, 127.3, 76.3, 75.3, 60.3, 59.3, 52.3, 52.3, 35.1, 34.7, 27.8, 26.6. HRMS (ESI) *m/z* calcd for $C_{26}H_{24}NO_3^+$ ([M+H$^+$]), 398.17507, found: 398.17431.

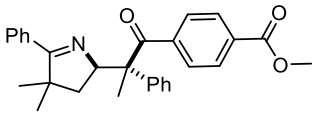
methyl 4-(2-methyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate



59

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.85 – 7.82 (m, 2H), 7.73 – 7.71 (m, 2H), 7.45 – 7.37 (m, 3H), 4.68 – 4.64 (m, 1H), 3.92 (s, 3H), 3.01 – 2.88 (m, 2H), 2.14 – 2.05 (m, 1H), 1.85 – 1.74 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 172.7, 166.4, 144.7, 134.3, 131.2, 130.5, 129.1, 128.4, 127.7, 127.2, 79.1, 52.2, 52.0, 35.2, 23.9, 22.6, 21.3. HRMS (ESI) *m/z* calcd for $C_{22}H_{24}NO_3^+$ ([M+H$^+$]), 350.17507, found: 350.17505.

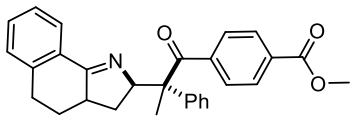
methyl 4-(-2-(4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-2-phenylpropanoyl)benzoate



61

Yellow oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 2H), 7.63 – 7.61 (m, 2H), 7.50 – 7.48 (m, 2H), 7.38 – 7.28 (m, 8H), 5.11 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.87 (s, 3H), 1.75 – 1.70 (m, 4H), 1.60 – 1.54 (m, 1H), 1.37 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 179.8, 166.3, 141.7, 140.1, 134.8, 132.0, 129.3, 129.1, 129.0, 128.7, 128.0, 127.8, 127.4, 127.3, 72.5, 58.0, 52.2, 49.7, 43.7, 26.7, 26.4, 19.2. HRMS (ESI) *m/z* calcd for $C_{29}H_{30}NO_3^+$ ([M+H$^+$]), 440.22202, found: 440.22107.

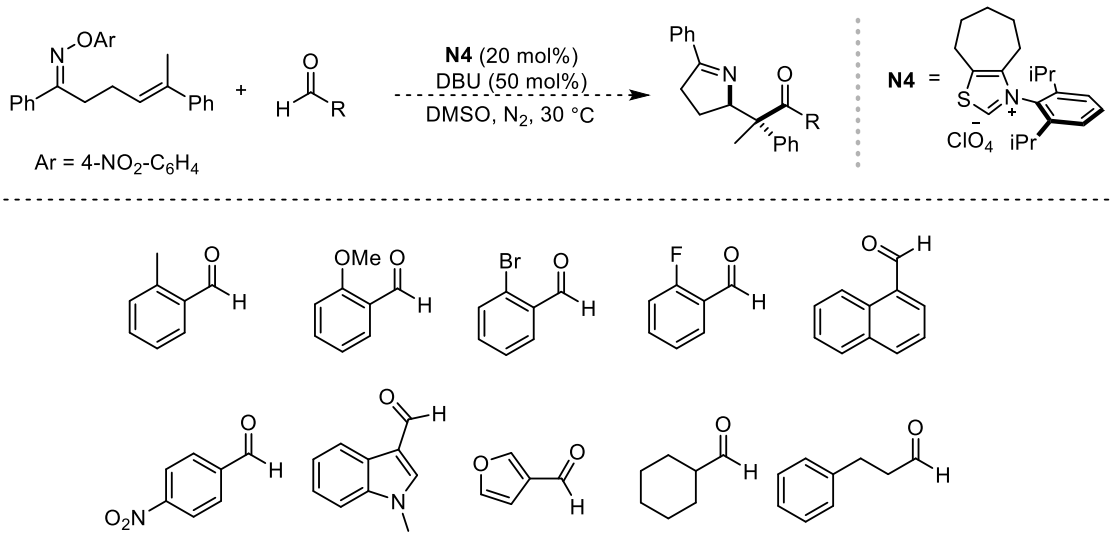
methyl 4-(2-phenyl-2-(3,3a,4,5-tetrahydro-2H-benzo[g]indol-2-yl)propanoyl)benzoate

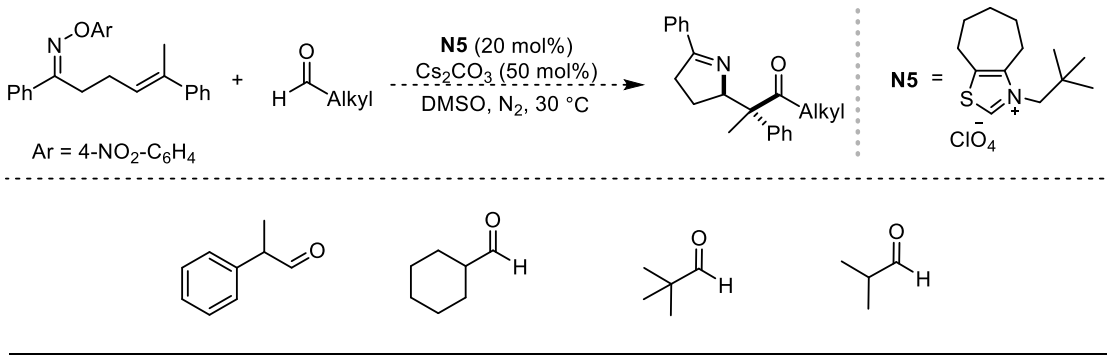


62

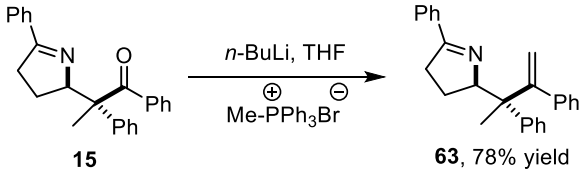
Yellow solid, d.r. 3:2, m.p. 106 – 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.04 (m, 1H), 7.91 – 7.88 (m, 2H), 7.51 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.20 (m,5H), 7.13 (t, *J* = 8.0 Hz, 1H), 5.24 – 5.22 (m, 0.4H), 5.08 – 5.03 (m, 0.6H), 3.87 (s, 3H), 3.00 – 2.91 (m, 0.6H), 2.86 – 2.77 (m, 2H), 2.28 – 2.22 (m, 0.4H), 2.14 – 2.08 (m, 1H), 1.96 – 1.84 (m, 1H), 1.67 (s, 1.2H), 1.57 (s, 1.8H), 1.53 – 1.39 (m, 1H), 1.26 – 1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 203.1, 175.5, 173.2, 166.3, 166.3, 142.5, 141.4, 140.8, 140.7, 140.5, 140.2, 132.0, 131.7, 130.7, 130.5, 130.1, 130.0, 130.0, 129.8, 129.2, 129.0, 129.0, 128.8, 128.7, 128.6, 128.5, 127.8, 127.3, 127.2, 127.1, 126.2, 126.2, 126.1, 76.1, 75.3, 59.7, 57.9, 52.2, 52.2, 46.9, 46.5, 32.8, 32.3, 30.3, 29.8, 29.7, 29.4, 20.5, 18.3. HRMS (ESI) *m/z* calcd for $C_{29}H_{28}NO_3^+$ ([M+H$^+$]), 438.20637, found: 438.20576.

2.6 Unsuccessful aldehydes



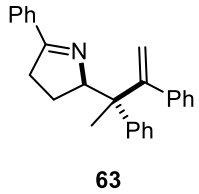


3. Further transformation of the products



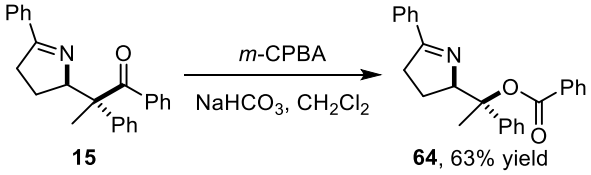
To a stirred solution of Ph_3PCH_3Br (0.2 mmol) in THF (1 mL) was added *n*-butyllithium (0.2 mmol) at −78 ℃. The reaction mixture was stirred for 1 h at room temperature. Then ketone **15** (0.1 mmol) was added at 0 ℃ and the reaction was stirred at room temperature for 12 h. The resulting solution was quenched with saturated aqueous NH_4Cl (2 mL), diluted with water (2 mL) and extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with brine (2 × 2 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give **63** (27.5 mg, 78% yield).[9]

2-(2,3-diphenylbut-3-en-2-yl)-5-phenyl-3,4-dihydro-2H-pyrrole



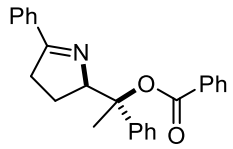
63

White solid, d.r. > 19:1, m.p. 111 – 113 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.42 – 7.36 (m, 5H), 7.31 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 7.13 – 7.04 (m, 3H), 6.85 – 6.82 (m, 2H), 5.71 (d, *J* = 4.0 Hz, 1H), 5.26 (d, *J* = 4.0 Hz, 1H), 5.03 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.82 – 2.73 (m, 1H), 2.71 – 2.62 (m, 1H), 1.85 – 1.76 (m, 1H), 1.73 – 1.63 (m, 1H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 155.4, 144.7, 143.4, 135.0, 130.1, 129.1, 128.3, 127.9, 127.7, 127.1, 126.3, 126.0, 115.0, 78.1, 51.5, 34.9, 25.4, 19.1. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}N^+$ ([M+H$^+$]), 352.20598, found: 352.20563.



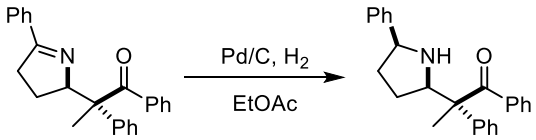
To a 10 mL reaction tube containing a stir bar was charged with **15** (0.1 mmol), *m*-CPBA (0.2 mmol), $NaHCO_3$ (0.2 mmol), and CH_2Cl_2 (1 mL). The solution was stirred at room temperature for 12 h. The resulting mixture was concentrated in vacuo and purified by silica gel column chromatography to give **64** (23.5 mg, 63% yield).[9]

1-phenyl-1-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethyl benzoate



64

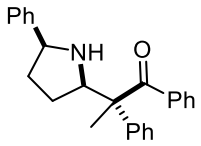
Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.45 – 7.43 (m, 2H), 7.40 – 7.30 (m, 9H), 7.24 – 7.20 (m, 2H), 4.36 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.50 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.31 – 2.23 (m, 1H), 1.92 (s, 3H), 1.43 – 1.33 (m, 1H), 1.15 – 1.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 140.4, 137.1, 135.4, 131.5, 129.4, 129.1, 128.9, 128.2, 127.9, 127.4, 127.1, 126.7, 85.8, 71.9, 56.4, 28.7, 20.6, 18.8. HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_2^+$ ([M+H$^+$]), 370.18016, found: 370.17979.



15 **65**, 83% yield

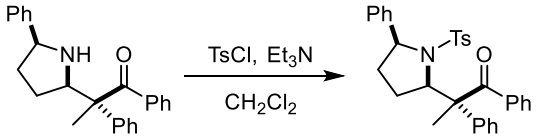
Pyrroline **15** (0.10 mmol) in EtOAc (1 mL) was hydrogenated in the presence of 10% Pd/C (8.0 mg) at room temperature for 24 h. The reaction mixture was filtered through a short pad of silica with CH_2Cl_2. The residue was concentrated in vacuo and the crude product was purified by silica gel column chromatography to give **65** (29.5 mg, 83% yield).[10]

1,2-diphenyl-2-(5-phenylpyrrolidin-2-yl)propan-1-one



65

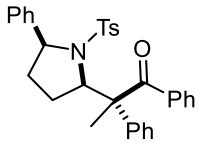
Colorless oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.33 (m, 9H), 7.32 – 7.26 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 3H), 4.24 (t, *J* = 8.0 Hz, 1H), 4.18 – 4.15 (m, 1H), 2.66 (s, 1H), 2.00 – 1.93 (m, 1H), 1.77 (s, 3H), 1.56 – 1.41 (m, 2H), 1.34 – 1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 145.6, 141.8, 137.3, 131.5, 129.4, 128.9, 128.1, 127.9, 127.1, 126.6, 126.6, 64.3, 62.1, 58.7, 34.4, 25.8, 16.6. HRMS (ESI) *m/z* calcd for $C_{25}H_{26}NO^+$ ([M+H$^+$]), 356.20089, found: 356.20031.



65 **66**, 83% yield

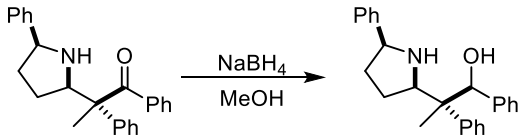
To a solution of the compound **65** (0.1 mmol) in CH_2Cl_2 (1.0 mL) was added Et_3N (0.2 mmol) and *p*-TsCl (0.11 mmol). The reaction mixture was stirred for 16 hours. Then it was washed with 1 M HCl (2 mL), and washed with saturated aqueous Na_2CO_3 (3 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give **66** as a white solid (42 mg, 83% yield).

1,2-diphenyl-2-(-5-phenyl-1-tosylpyrrolidin-2-yl)propan-1-one



66

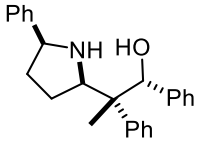
White solid, d.r. > 19:1, m.p. 93 – 96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.28 (m, 9H), 7.25 – 7.19 (m, 5H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 2H), 4.95 (t, *J* = 8.0 Hz, 1H), 4.79 (t, *J* = 8.0 Hz, 1H), 2.48 (s, 3H), 1.91 (s, 3H), 1.62 – 1.49 (m, 2H), 1.19 – 1.10 (m, 1H), 0.96 – 0.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 143.7, 142.1, 139.2, 137.8, 134.0, 131.0, 129.8, 128.9, 128.5, 128.2, 128.0, 127.7, 127.3, 126.9, 126.6, 67.0, 64.8, 57.5, 30.9, 29.3, 21.8, 21.6. HRMS (ESI) *m/z* calcd for $C_{32}H_{32}NO_3S^+$ ([M+H$^+$]), 510.20974, found: 510.20914.



65 **67**, 73% yield

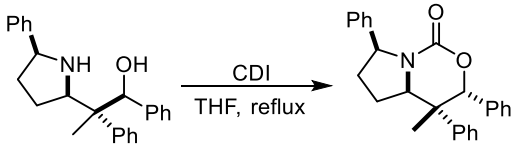
To a solution of compound **65** (0.2 mmol) in MeOH (5 mL), $NaBH_4$ (0.4 mmol, 2 equiv) was added at 0 ℃. The reaction mixture was then allowed to stir at room temperature for 1 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was quenched with saturated aqueous NH_4Cl solution (4 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the alcohol **67** as a white solid (52 mg, 73% yield).

1,2-diphenyl-2-(5-phenylpyrrolidin-2-yl)propan-1-ol



67

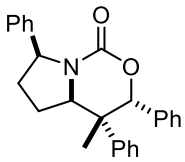
White solid, d.r. > 19:1, m.p. 42 – 45 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.12 – 7.07 (m, 3H), 6.95 – 6.93 (m, 2H), 5.12 (s, 1H), 4.13 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.92 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.16 – 2.08 (m, 1H), 1.93 – 1.81 (m, 2H), 1.78 – 1.68 (m, 1H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.9, 141.5, 128.4, 128.4, 128.1, 127.7, 127.2, 127.1, 127.0, 126.7, 126.3, 81.0, 64.7, 62.7, 47.9, 34.4, 26.8, 19.6. HRMS (ESI) *m/z* calcd for $C_{25}H_{28}NO^+$ ([M+H$^+$]), 358.21654, found: 358.21620.



67 **68**, 84% yield

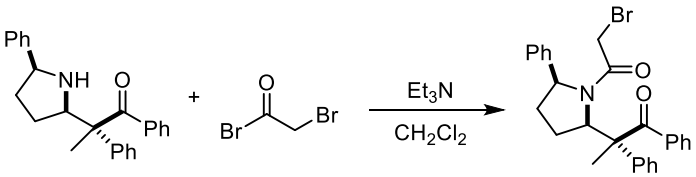
The reaction was carried out with alcohol **67** (0.1 mmol) in THF (2 mL). After addition of carbonyldiimidazole (CDI, 0.2 mmol), the reaction was heated to reflux for 12 h. The resulting mixture was concentrated in vacuo and purified by silica gel column chromatography to give **68** as a white solid (32 mg, 84% yield).[11]

4-methyl-3,4,7-triphenylhexahydro-1H-pyrrolo[1,2-c][1,3]oxazin-1-one



68

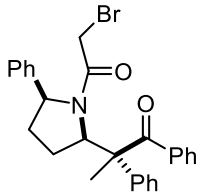
White solid, d.r. > 19:1, m.p. 208 – 210 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.27 – 7.20 (m, 4H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.01 (m, 4H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 4.30 (t, *J* = 80 Hz, 1H), 2.44 – 2.33 (m, 1H), 1.96 – 1.91 (m, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 143.0, 140.3, 137.2, 128.4, 128.3, 127.6, 127.3, 127.2, 127.0, 126.9, 126.7, 126.3, 89.3, 61.5, 58.6, 42.2, 32.5, 25.5, 20.0. HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_2^+$ ([M+H$^+$]), 384.19581, found: 384.19500.



65 **69**, 90% yield

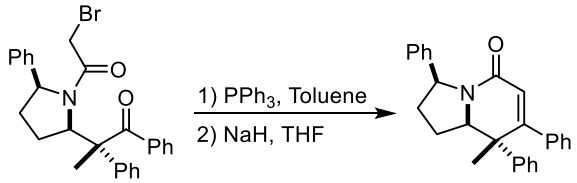
The reaction was carried out with ketone **65** (0.2 mmol) and Et_3N (0.2 mmol) in dry CH_2Cl_2 (2 mL). After addition of bromoacetyl bromide (0.3 mmol), the reaction was cooled to 0 ℃. Then the mixture was stirred for 4 h at room temperature. The resulting solution was quenched with 1 M HCl (4 mL), and washed with saturated aqueous Na_2CO_3 (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give **69** as a white solid (86 mg, 90% yield).[12]

2-(1-(2-bromoacetyl)-5-phenylpyrrolidin-2-yl)-1,2-diphenylpropan-1-one



69

White solid, d.r. > 19:1, m.p. 67 – 70 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 6H), 7.30 – 7.24 (m, 4H), 7.21 – 7.16 (m, 5H), 5.40 (t, *J* = 8.0 Hz, 1H), 5.07 (t, *J* = 8.0 Hz, 1H), 3.73 – 3.67 (m, 2H), 2.26 – 2.17 (m, 1H), 1.86 – 1.71 (m, 5H), 1.19 – 1.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 169.0, 142.2, 140.0, 138.3, 130.6, 128.8, 128.6, 128.4, 127.9, 127.6, 127.3, 127.2, 125.6, 66.1, 63.5, 57.6, 33.4, 28.5, 27.9, 21.2. HRMS (ESI) *m/z* calcd for $C_{27}H_{27}BrNO_2^+$ ([M+H$^+$]), 476.12197, found: 476.12172.

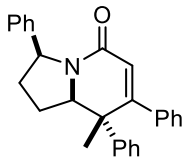


69 **70**, 69% yield

The reaction was carried out with **69** (0.15 mmol) in toluene (1.5 mL). After addition of PPh_3 (0.18 mmol) slowly, the reaction was stirred for 2 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in dry THF (1.5 ml). NaH (0.18 mmol) was added, and the mixture was stirred for 12 h at room temperature. After evaporation of the organic solvent under reduced pressure, the

crude mixture was purified by silica gel column chromatography to give **70** as a white solid (39 mg, 69% yield).[9, 12]

8-methyl-3,7,8-triphenyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one

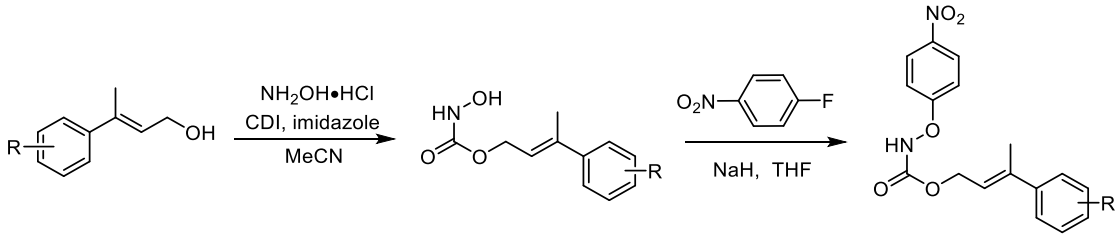


70

White solid, d.r. > 19:1, m.p. 196 – 197 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 5H), 7.25 – 7.08 (m, 10H), 6.35 (s, 1H), 5.27 (d, *J* = 12.0 Hz, 1H), 4.17 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.24 – 2.11 (m, 1H), 2.03 – 1.91 (m, 5H), 1.33 – 1.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 160.9, 142.9, 142.8, 137.4, 128.3, 128.2, 128.1, 127.9, 127.7, 126.8, 126.5, 126.2, 124.4, 70.2, 59.4, 47.5, 31.9, 25.2, 17.9. HRMS (ESI) *m/z* calcd for $C_{27}H_{26}NO^+$ ([M+H$^+$]), 380.20089, found: 380.20007.

4. Amidoacylation of olefins through N-heterocyclic carbene catalysis

4.1 Synthesis of *O*-aryl carbamate

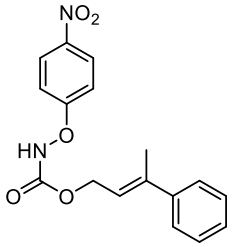


A 250 ml round-bottom flask was charged with allylic alcohol (20 mmol), CH_3CN (100 mL), *N*,*N*'-carbonyldiimidazole (30 mmol, 1.5 equiv). The mixture was stirred at room temperature. After alcohol was fully converted to corresponding intermediate (monitored by TLC), the imidazole (80 mmol, 4 equiv) and $NH_2OH{\cdot}HCl$ (100 mmol, 5 equiv) were added to the suspension. After the intermediate was fully consumed (monitored by TLC), the reaction was quenched with HCl (1 M). The aqueous phase was extracted with EA (50 mL × 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude mixture was purified by flash chromatography on silica gel (PE/EA = 3/1-1/1) to afford the corresponding *N*-allyloxycarbonyl-*O*-benzoyl hydroxylamine.[13]

In a dry Schlenk tube equipped with a stirring bar, the *N*-allyloxycarbonyl-*O*-benzoyl hydroxylamine (1.0 equiv.) was added, dissolved in anhydrous THF (0.2 M), and stirred for 15 minutes at 0 ℃. NaH (1.1 equiv., 60%) was added and the reaction mixture was stirred for 1 hour. 4-Fluoronitrobenzene (1.1 equiv.) was added portion wise and the reaction mixture was allowed to warm up to room temperature overnight. The mixture was diluted with H_2O and EtOAc, the layers were separated and the aqueous phase was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography to give *O*-aryl carbamate.[14]

4.2 Characterization data for *O*-aryl carbamate

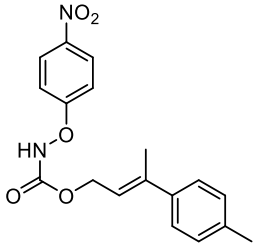
(*E*)-3-phenylbut-2-en-1-yl (4-nitrophenoxy)carbamate



76

White solid, m.p. 81 – 82 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 2H), 8.11 – 8.09 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.88 (t, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 8.0 Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.2, 143.1, 142.1, 141.8, 128.3, 127.8, 125.8, 125.7, 120.0, 113.5, 64.0, 16.2. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}N_2O_5^+$ ([M+H$^+$]), 329.1132, found: 329.1130.

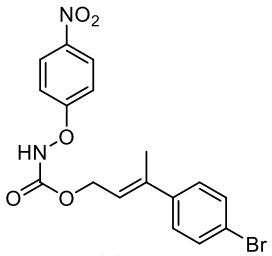
(*E*)-3-(p-tolyl)but-2-en-1-yl (4-nitrophenoxy)carbamate



93a

White solid, m.p. 104 – 105 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 2H), 7.99 (d, J = 4.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.89 – 5.85 (m, 1H), 4.93 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.3, 143.0, 141.7, 139.1, 137.7, 129.0, 125.7, 125.6, 119.0, 113.4, 64.0, 21.0, 16.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}N_2O_5^-$ ([M−H$^+$]), 341.11430, found: 341.11388.

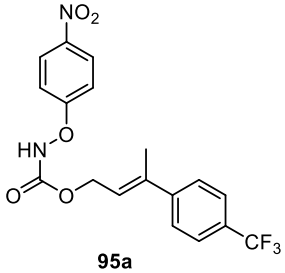
(*E*)-3-(4-bromophenyl)but-2-en-1-yl (4-nitrophenoxy)carbamate



94a

White solid, m.p. 117 – 118 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 2H), 8.05 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.23 (dd, *J* = 16, 8.0 Hz, 4H), 5.87 (t, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 8.0 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 157.1, 143.2, 141.0, 140.6, 131.4, 127.4, 125.8, 121.8, 120.6, 113.5, 63.8, 16.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{14}BrN_2O_5^-$ ([M−H$^+$]), 405.00916, found: 405.00946.

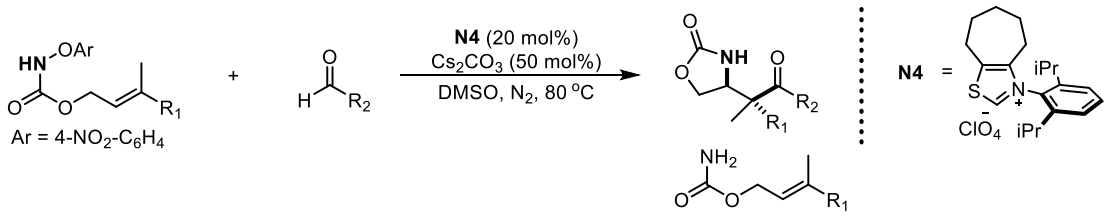
(*E*)-3-(4-(trifluoromethyl)phenyl)but-2-en-1-yl (4-nitrophenoxy)carbamate



95a

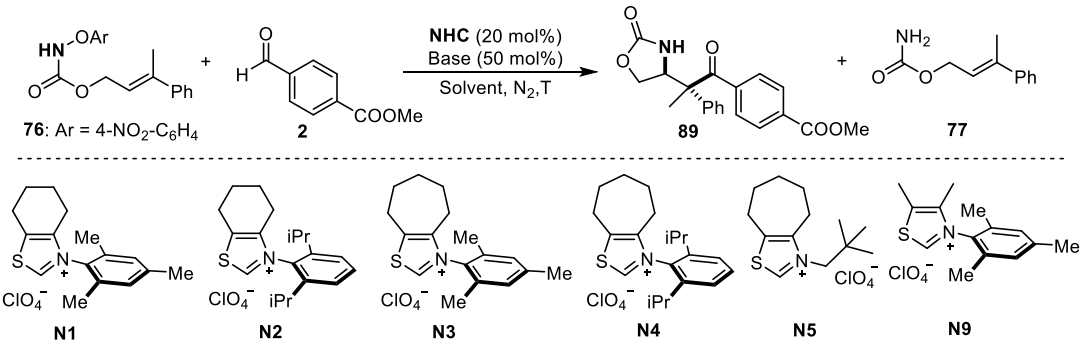
White solid, m.p. 135 – 136 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 2H), 7.98 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.94 (t, *J* = 8.0 Hz, 1H), 4.95 (d, *J* = 8.0 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.1, 145.7, 143.3, 140.4, 129.8 (q, *J* = 32.4 Hz), 126.2, 125.8, 125.3 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 270.6 Hz), 122.1, 113.5, 63.8, 16.3. HRMS (ESI) m/z calcd for C18H14F3N2O5- ([M-H+]), 395.08603, found: 395.08625.

4.3 General procedure



To an oven-dried reaction tube equipped with a stir bar was added *O*-aryl carbamate (0.2 mmol, 1.0 equiv), thiazolium salt **N4** (20 mol%), Cs_2CO_3 (0.10 mmol, 0.5 equiv) and aldehyde (0.30 mmol, 1.5 equiv). The tube was sealed and placed under nitrogen before DMSO (2 mL) was added. Then the system was stirred at 80 ℃ for 12 h. The reaction mixture was purified by silica gel column chromatography to afford the desired oxazolidinone product.

4.4 Optimization of the amidoacylation of olefins



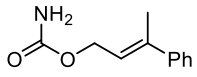
Entry[a]	NHC	Solvent	Base	Yield[b](89)	Yield[b](77)	d.r.
1	**N1**	CH_3CN	Cs_2CO_3	28%	52%	>19:1
2	**N2**	CH_3CN	Cs_2CO_3	32%	46%	>19:1
3	**N3**	CH_3CN	Cs_2CO_3	33%	42%	>19:1
4	**N4**	CH_3CN	Cs_2CO_3	36%	40%	>19:1
5	**N5**	CH_3CN	Cs_2CO_3	27%	24%	>19:1
6	**N9**	CH_3CN	Cs_2CO_3	30%	42%	>19:1
7	**N4**	DMSO	Cs_2CO_3	42%	44%	>19:1
8	**N4**	THF	Cs_2CO_3	25%	24%	>19:1
9	**N4**	CH_2Cl_2	Cs_2CO_3	26%	25%	>19:1
10	**N4**	Toluene	Cs_2CO_3	13%	18%	>19:1
11	**N4**	EtOAc	Cs_2CO_3	22%	28%	>19:1
12	**N4**	Trifluorotoluene	Cs_2CO_3	21%	32%	>19:1
13	**N4**	Acetone	Cs_2CO_3	22%	35%	>19:1
14	**N4**	DMA	Cs_2CO_3	trace	trace	>19:1
15	**N4**	DMF	Cs_2CO_3	trace	trace	>19:1

16	**N4**	DMSO	DBU	28%	47%	>19:1
17	**N4**	DMSO	Na_2CO_3	32%	42%	>19:1
18	**N4**	DMSO	K_2CO_3	35%	44%	>19:1
19	**N4**	DMSO	$NaHCO_3$	26%	50%	>19:1
20	**N4**	DMSO	K_3PO_4	27%	40%	>19:1
21	**N4**	DMSO	Li_2CO_3	18%	36%	>19:1
22[c]	**N4**	DMSO	Cs_2CO_3	40%	40%	>19:1
23[d]	**N4**	DMSO	Cs_2CO_3	38%	36%	>19:1
24[e]	**N4**	DMSO	Cs_2CO_3	28%	60%	>19:1
25[f]	**N4**	DMSO	Cs_2CO_3	48%(48%)	35%(32%)	>19:1
26[g]	**N4**	DMSO	Cs_2CO_3	25%	28%	>19:1
27[h]	**N4**	DMSO	Cs_2CO_3	20%	30%	>19:1
28[i]	**N4**	DMSO	Cs_2CO_3	38%	48%	>19:1

[a]Reaction was carried out with **76** (0.1 mmol), **2** (0.15 mmol), **NHC** (0.02 mmol), and Cs_2CO_3 (0.05 mmol) in CH_3CN (1 mL) at 60 ℃ for 12 h. [b]Yields based on ^1H NMR analysis using 1,3,5-trimethoxybenzene as an external standard and isolated yields are given in parentheses. [c]DMSO, 2 ml. [d]DMSO, 0.5 ml. [e]30 ℃. [f]80 ℃. [g]100 ℃. [h]Cs_2CO_3, 0.02 mmol. [i]Cs_2CO_3, 0.1 mmol.

4.5 Characterization data for 77 – 98

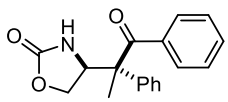
(*E*)-3-phenylbut-2-en-1-yl carbamate



77

White solid, m.p. 116 – 117 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 5.92 – 5.88 (m, 1H), 4.88 (s, 2H), 4.78 (d, *J* = 8.0 Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 142.5, 140.0, 128.2, 127.4, 125.8, 121.6, 62.3, 16.1. HRMS (ESI) *m/z* calcd for $C_{11}H_{14}NO_2^+$ ([M+H$^+$]), 192.1019, found: 192.1018.

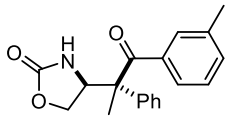
4-(1-oxo-1,2-diphenylpropan-2-yl)oxazolidin-2-one



78

White solid, d.r. > 19:1, m.p. 98 – 99 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 6H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.22 (m,2H), 5.78 (s, 1H), 4.64 – 4.60 (m,1H), 4.03 – 3.95 (m, 2H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 159.3, 137.8, 134.9, 132.7, 129.8, 129.7, 128.4, 128.2, 126.6, 65.4, 58.5, 57.8, 15.6. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_3^+$ ([M+H$^+$]), 296.1281, found: 296.1279.

4-(1-oxo-2-phenyl-1-(m-tolyl)propan-2-yl)oxazolidin-2-one

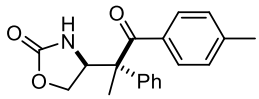


79

White solid, d.r. > 19:1, m.p. 160 – 162 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.13 – 7.05 (m, 2H), 5.86 (s, 1H), 4.64 – 4.60 (m, 1H), 4.02 – 3.95 (m, 2H), 2.25 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 159.3, 138.1, 137.9, 134.9, 133.4,

130.4, 129.6, 128.3, 127.9, 126.9, 126.6, 65.5, 58.5, 57.8, 21.2, 15.6. HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NO_3^+$ ([M+H$^+$]), 310.14377, found: 310.14316.

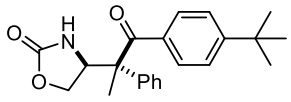
4-(1-oxo-2-phenyl-1-(p-tolyl)propan-2-yl)oxazolidin-2-one



80

White solid, d.r. > 19:1, m.p. 100 – 102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 5H), 7.31 – 7.27 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.82 (s, 1H), 4.61 – 4.58 (m, 1H), 4.02 – 3.94 (m, 2H), 2.30 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 159.3, 143.6, 138.1, 132.0, 130.0, 129.6, 128.9, 128.3, 126.5, 65.5, 58.6, 57.6, 21.4, 15.7. HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NO_3^+$ ([M+H$^+$]), 310.1438, found: 310.1434.

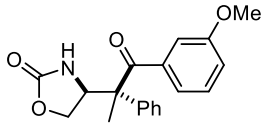
4-1-(4-(tert-butyl)phenyl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



81

White solid, d.r. > 19:1, m.p. 102 – 104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 7H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.92 (s, 1H), 4.61 (t, *J* = 8.0 Hz, 1H), 4.03 – 3.95 (m, 2H), 1.74 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 159.3, 156.5, 138.1, 132.0, 129.9, 129.6, 128.3, 126.6, 125.2, 65.5, 58.6, 57.7, 35.0, 30.9, 15.7. HRMS (ESI) *m/z* calcd for $C_{22}H_{26}NO_3^+$ ([M+H$^+$]), 352.1907, found: 352.1906.

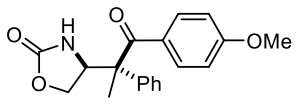
4-(1-(3-methoxyphenyl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



82

White solid, d.r. > 19:1, m.p. 75 – 76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 7.14 – 7.10 (m, 1H), 7.02 – 6.94 (m, 3H), 5.89 (s, 1H), 4.62 (t, *J* = 8.0 Hz, 1H), 4.00 – 3.95 (m, 2H), 3.65 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 159.2, 137.9, 136.1, 129.7, 129.2, 128.4, 126.6, 122.3, 119.2, 114.2, 65.5, 58.5, 57.9, 55.2, 15.5. HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NO_4^+$ ([M+H$^+$]), 326.13868, found: 326.13797.

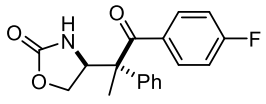
4-(1-(4-methoxyphenyl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



83

White solid, d.r. > 19:1, m.p. 175 – 176 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.30 – 7.27 (m, 2H), 6.74 – 6.71 (m, 2H), 5.90 (s, 1H), 4.60 – 4.56 (m, 1H), 4.02 – 3.92 (m, 2H), 3.78 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 163.0, 159.2, 138.5, 132.4, 129.6, 128.3, 127.2, 126.5, 113.5, 65.5, 58.7, 57.5, 55.3, 15.8. HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NO_4^+$ ([M+H$^+$]), 326.13868, found: 326.13853.

4-(1-(4-fluorophenyl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one

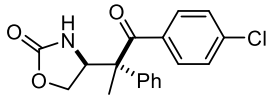


84

White solid, d.r. > 19:1, m.p. 180 – 181 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.45 – 7.35 (m, 3H), 7.30 – 7.27 (m, 2H), 6.91 (t, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 4.60 (t, *J* = 8.0 Hz, 1H), 4.03 – 3.96 (m, 2H), 1.74 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 200.9, 166.4, 163.8, 159.3, 137.7, 132.6, 132.5, 131.0, 130.9, 129.8, 128.5, 126.5, 115.5, 115.3, 65.4, 58.6, 57.7, 15.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}FNO_3^+$ ([M+H$^+$]), 314.11870, found: 314.11783.

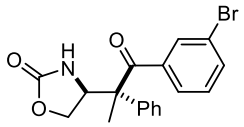
4-(1-(4-chlorophenyl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



85

White solid, d.r. > 19:1, m.p. 89 – 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 5H), 7.28 (d, *J* =8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.87 (s, 1H), 4.59 (t, *J* = 8.0 Hz, 1H), 4.03 – 3.96 (m, 2H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 159.2, 139.2, 137.6, 133.0, 131.3, 129.8, 128.6, 126.5, 65.4, 58.5, 57.8, 15.5. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}ClNO_3^+$ ([M+H$^+$]), 330.08915, found: 330.08849.

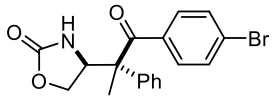
4-(1-(3-bromophenyl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



86

White solid, d.r. > 19:1, m.p. 147 – 148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.30 – 7.25 (m, 3H), 7.08 (t, *J* = 8.0 Hz, 1H), 5.97 (s, 1H), 4.62 (t, *J* = 8.0 Hz, 1H), 3.99 (d, *J* = 8.0 Hz, 2H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 159.3, 137.2, 136.6, 135.5, 132.8), 129.8, 129.7, 128.7, 128.2, 126.5, 122.5, 65.4, 58.4, 57.9, 15.4. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}BrNO_3^+$ ([M+H$^+$]), 374.03863, found: 374.03790.

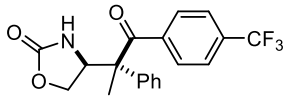
4-(1-(4-bromophenyl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



87

White solid, d.r. > 19:1, m.p. 105 – 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 9H), 5.89 (s, 1H), 4.59 (t, *J* = 8.0 Hz, 1H), 4.02 – 3.95 (m, 2H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 159.3, 137.4, 133.4, 131.5, 131.3, 129.8, 128.6, 127.9, 126.5, 65.4, 58.5, 57.7, 15.6. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}BrNO_3^+$ ([M+H$^+$]), 374.0386, found: 374.0390.

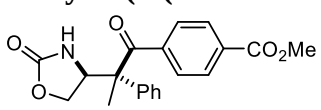
4-(1-oxo-2-phenyl-1-(4-(trifluoromethyl)phenyl)propan-2-yl)oxazolidin-2-one



88

White solid, d.r. > 19:1, m.p. 79 – 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 4H), 7.47 – 7.38 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.11 (s, 1H), 4.65 (t, *J* = 8.0 Hz, 1H), 4.05 – 4.01 (m, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 159.3, 138.0, 137.0, 133.8 (q, *J* = 32.6 Hz), 130.0, 129.9, 128.8, 126.6, 125.28 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 271.1 Hz), 65.4, 58.3, 58.0, 15.3. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}F_3NO_3^+$ ([M+H$^+$]), 364.1155, found: 364.1150.

methyl 4-(2-(2-oxooxazolidin-4-yl)-2-phenylpropanoyl)benzoate

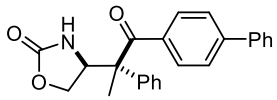


89

White solid, d.r. > 19:1, m.p. 100 – 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.37 (m, 6H), 7.32 – 7.29 (m, 2H), 6.20 (s, 1H), 4.65 (t, *J* = 8.0 Hz, 1H), 4.03 – 4.01 (m, 2H), 3.89 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 165.9, 159.4, 138.5, 137.1, 133.2, 129.8, 129.5,

129.3, 128.6, 126.6, 65.4, 58.3, 57.9, 52.4, 15.3. HRMS (ESI) *m/z* calcd for $C_{20}H_{20}NO_5^+$ ([M+H$^+$]), 354.1336, found: 354.1331.

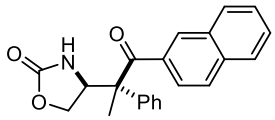
4-(1-([1,1'-biphenyl]-4-yl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



90

White solid, d.r. > 19:1, m.p. 110 – 111 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 4.50 (m, 4H), 7.47 – 7.32 (m, 10H), 5.96 (s, 1H), 4.65 – 4.61 (m, 1H), 4.04 – 3.96 (m, 2H), 1.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 159.2, 145.3, 139.5, 138.0, 133.4, 130.5, 129.7, 128.9, 128.4, 128.2, 127.1, 126.8, 126.6, 65.5, 58.6, 57.8, 15.6. HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO_3^+$ ([M+H$^+$]), 372.15942, found: 372.15892.

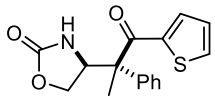
4-(1-(naphthalen-2-yl)-1-oxo-2-phenylpropan-2-yl)oxazolidin-2-one



91

White solid, d.r. > 19:1, m.p. 100 – 102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.56 – 7.51 (m, 2H), 7.47 – 7.43 (m, 3H), 7.40 – 7.36 (m, 3H), 6.03 (s, 1H), 4.68 – 4.65 (m, 1H), 4.07 – 3.99 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4 159.3, 138.0, 135.0, 132.0, 132.0, 131.89, 129.7, 129.6, 128.7, 128.5, 127.9, 127.5, 126.7, 126.6, 125.2, 65.5, 58.6, 57.9, 15.7. HRMS (ESI) *m/z* calcd for $C_{22}H_{20}NO_3^+$ ([M+H$^+$]), 346.1438, found: 346.1436.

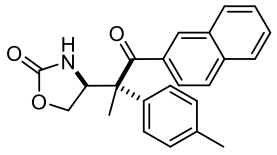
4-(1-oxo-2-phenyl-1-(thiophen-2-yl)propan-2-yl)oxazolidin-2-one



92

Yellow oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 4.0 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 4.0 Hz, 1H), 6.88 (t, *J* = 4.0 Hz, 1H), 5.91 (s, 1H), 4.58 (t, *J* = 8.0 Hz, 1H), 3.98 – 3.93 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 159.1, 140.8, 138.0, 134.2, 134.0, 129.5, 128.6, 127.8, 127.1, 65.4, 58.2, 57.7, 16.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}NO_3S^+$ ([M+H$^+$]), 302.08454, found: 302.08408.

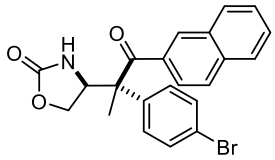
4-1-(naphthalen-2-yl)-1-oxo-2-(p-tolyl)propan-2-yl)oxazolidin-2-one



93

Yellow oil, d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.24 (s, 4H), 5.88 (s, 1H), 4.66 – 4.63 (m, 1H), 4.06 – 3.98 (m, 2H), 2.36 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 159.3, 138.3, 135.0, 134.9, 132.2, 132.1, 131.9, 130.4, 129.6, 128.6, 127.9, 127.5, 126.6, 126.5, 125.3, 65.5, 58.6, 57.6, 21.0, 15.6. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}NO_3^+$ ([M+H$^+$]), 360.15942, found: 360.15844.

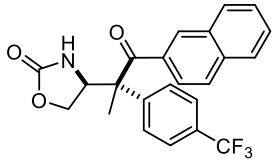
4-(2-(4-bromophenyl)-1-(naphthalen-2-yl)-1-oxopropan-2-yl)oxazolidin-2-one



94

White solid, d.r. > 19:1, m.p. 123 – 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.79 – 7.69 (m, 3H), 7.59 – 7.46 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.63 – 4.60 (m, 1H), 4.08 – 4.01 (m, 2H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 159.2, 137.2, 135.1, 132.8, 132.0, 131.9, 131.7, 129.6, 128.8, 128.4, 128.1, 127.5, 126.8, 125.1, 122.7, 65.4, 58.5, 57.7, 16.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{19}BrNO_3^+$ ([M+H$^+$]), 424.05428, found: 424.05355.

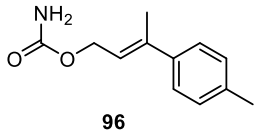
4-(1-(naphthalen-2-yl)-1-oxo-2-(4-(trifluoromethyl)phenyl)propan-2-yl)oxazolidi n-2-one



95

White solid, d.r. > 19:1, m.p. 117 – 118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.69 (m, 4H), 7.58 – 7.46 (m, 5H), 6.13 (s, 1H), 4.69 – 4.65 (m, 1H), 4.08 – 3.99 (m, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 159.2, 142.3, 135.1, 132.0, 132.0, 131.5, 130.7 (q, *J* = 32.6 Hz) , 129.6, 128.9, 128.2, 127.6, 127.2, 126.9, 126.6 (q, *J* = 3.6 Hz), 125.0, 126.6 (q, *J* = 270.6 Hz) , 65.4, 58.7, 58.1, 16.2. HRMS (ESI) *m/z* calcd for $C_{23}H_{19}F_3NO_3^+$ ([M+H$^+$]), 414.13115, found: 414.13027.

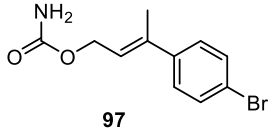
(*E*)-3-(p-tolyl)but-2-en-1-yl carbamate



96

White solid, m.p. 99 – 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.90 – 5.86 (m, 1H), 4.77 (d, *J* = 8.0 Hz, 4H), 2.34 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 139.9, 139.7, 137.3, 128.93, 125.7, 120.7, 62.3, 21.0, 16.1. HRMS (ESI) *m/z* calcd for $C_{12}H_{16}NO_2^+$ ([M+H$^+$]), 206.11756, found: 206.11723.

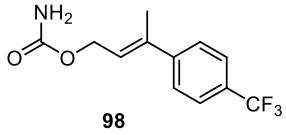
(*E*)-3-(4-bromophenyl)but-2-en-1-yl carbamate



97

Yellow solid, m.p. 119 – 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.25 (m, 2H), 5.91 – 5.87 (m, 1H), 4.76 (d, *J* = 8.0 Hz, 4H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 141.4, 138.8, 131.3, 127.5, 122.3, 121.4, 62.1, 16.1. HRMS (ESI) *m/z* calcd for $C_{11}H_{13}BrNO_2^+$ ([M+H$^+$]), 270.01242, found: 270.01268.

(*E*)-3-(4-(trifluoromethyl)phenyl)but-2-en-1-yl carbamate

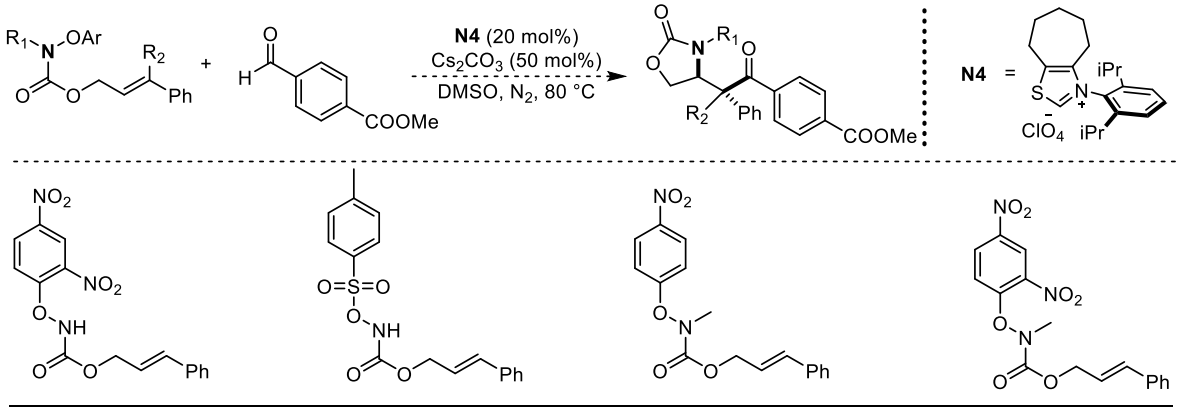


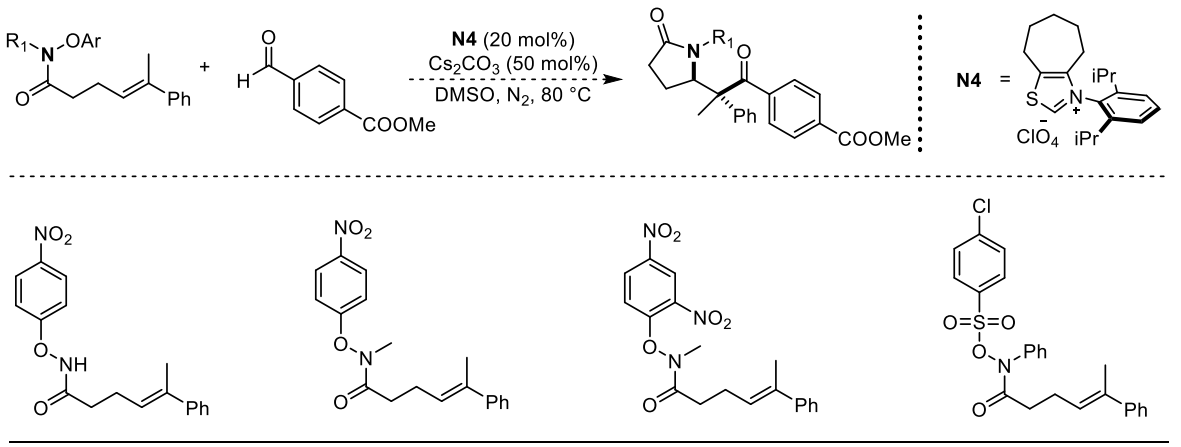
98

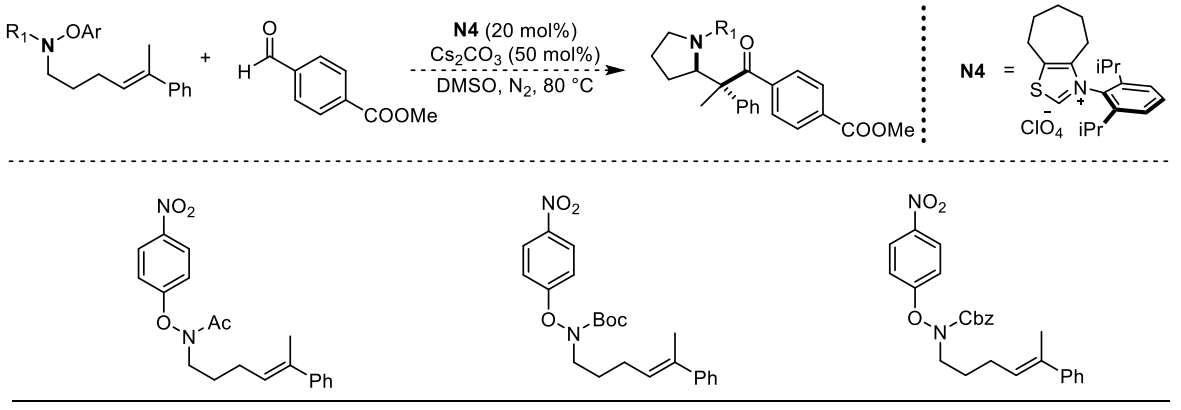
Yellow solid, m.p. 101 – 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 5.95 (t, *J* = 8.0 Hz, 1H), 4.81 – 4.74 (m, 4H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 146.1, 138.6, 129.4 (q, *J* = 32.4

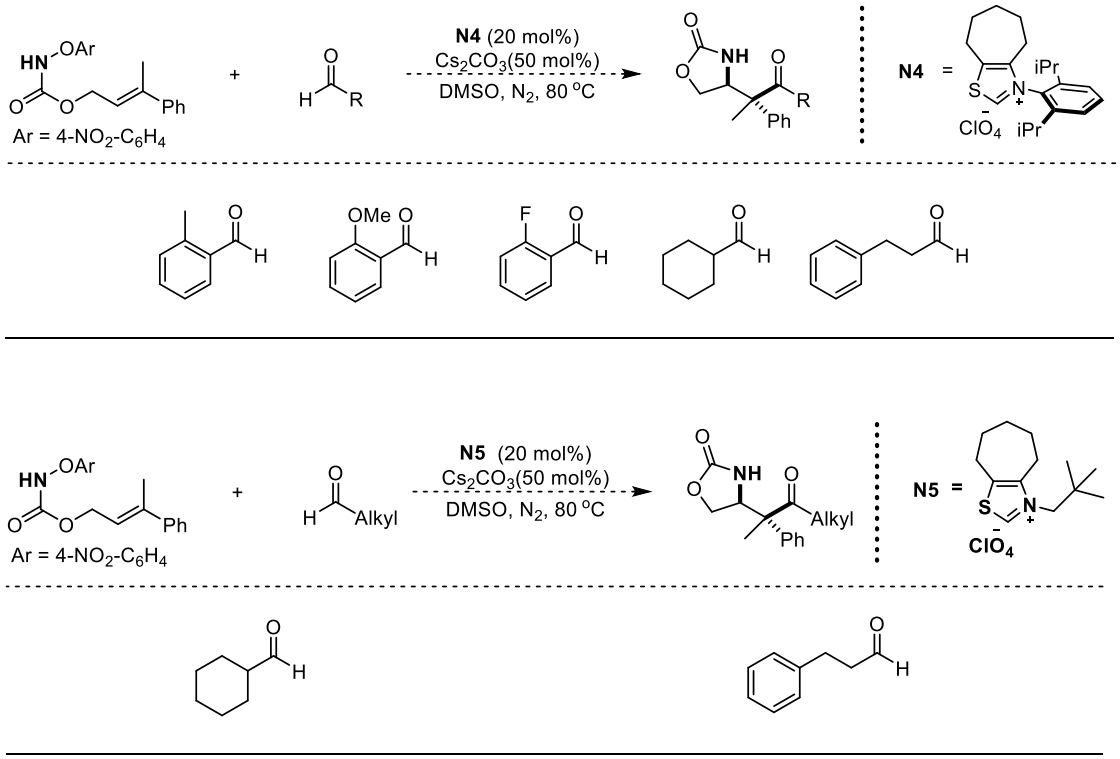
Hz), 126.1, 125.2 (q, J = 3.6 Hz), 124.2 (q, J = 270.1 Hz), 123.8, 62.1, 16.1. HRMS (ESI) *m/z* calcd for $C_{12}H_{13}F_3NO_2^+$ ([M+H$^+$]), 260.08929, found: 260.08909.

4.6 Unsuccessful substrates





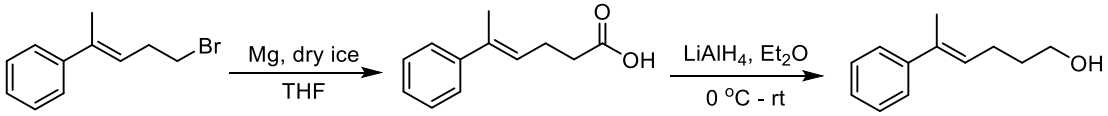




5. Oxyacylation of olefins through N-heterocyclic carbene catalysis

Building on the mechanistic understanding of this NHC-catalyzed radical reaction, we moved on to evaluate whether this strategy could be applied to the generation of alkoxy radicals. Several alkoxy radical precursors (**S1**: $E_{p/2}$ = −1.31 V vs SCE, **S2**: $E_{p/2}$ = −0.93 V vs SCE) were synthesized. However, none of them led to the desired tetrahydrofuran derivative.

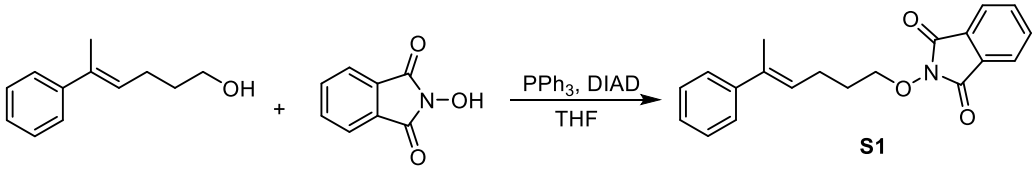
5.1 Synthesis of (*E*)-2-((5-phenylhex-4-en-1-yl)oxy)isoindoline-1,3-dione (S1)



Under N_2, alkyl bromide (4.5 g, 20 mmol) was added dropwise to a three-neck flask that contains magnesium (576 mg, 24 mmol) and 50 mL THF. After refluxing for 4 h, the solution was cooled down to room temperature and added to a Schlenk flask that contains excess dry ice. The system was stirred overnight and quenched by 20 mL saturated NH_4Cl solution, followed by 10 mL 1N HCl. The aqueous phase was extracted with diethyl ether (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the alkyl carboxylic acid.[15]

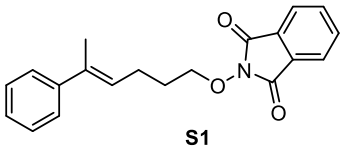
Under N_2, $LiAlH_4$ (0.42 g, 11 mmol) was added to 40 mL Et_2O. The suspension was cooled to 0 ℃. To the suspension was added 10 mL Et_2O solution of acid (1.90 g, 10 mmol). The reaction was stirred at room temperature overnight. Saturated NH_4Cl solution (30 mL) was then added to quench the reaction. The aqueous phase was

extracted with diethyl ether (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the aliphatic alcohol.[15]

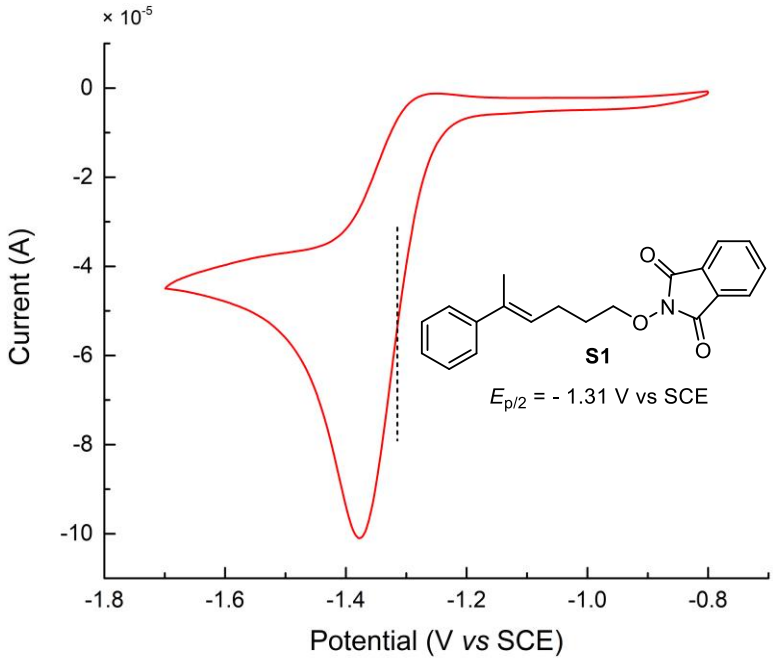


The reaction was carried out with aliphatic alcohol (0.71 g, 4.0 mmol), PPh_3 (1.26 g, 4.8 mmol), and N-hydroxyphthalimide (0.78 g, 4.8 mmol) in THF (15 mL). Diisopropyl azodicarboxylate (0.96 mL, 4.8 mmol) was added over 10 min at room temperature. The resulting mixture was stirred for 12 h, taken up in EtOAc (20 mL), washed with saturated $NaHCO_3$ (3 × 15 mL) and brine (2 × 20 mL). The organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the *N*-alkoxyphthalimides.[16]

(*E*)-2-((5-phenylhex-4-en-1-yl)oxy)isoindoline-1,3-dione

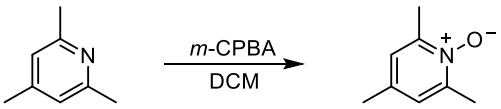


White solid, m.p. 64 – 65 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.74 – 7.71 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 5.79 (t, *J* = 8.0 Hz, 1H), 4.26 (t, *J* = 8.0 Hz, 2H), 2.45 (q, *J* = 8.0 Hz, 2H), 2.08 (s, 3H), 1.98 – 1.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 143.6, 135.9, 134.4, 128.9, 128.1, 126.7, 126.5, 125.6, 123.4, 77.9, 28.1, 24.8, 15.8. HRMS (ESI) *m/z* calcd for $C_{20}H_{20}NO_3^+$ ([M+H$^+$]), 322.14377, found: 322.14356.

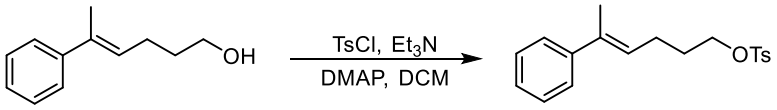


Cyclic voltammogram of *N*-alkoxyphthalimides **S1**

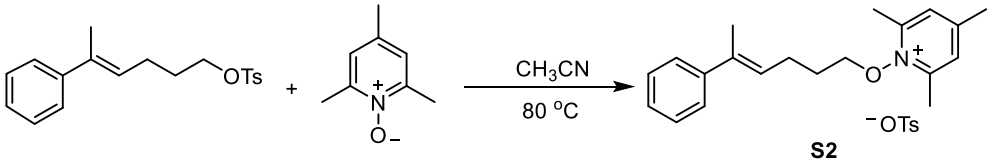
5.2 Synthesis of (*E*)-2,4,6-trimethyl-1-((5-phenylhex-4-en-1-yl)oxy)pyridin-1-ium trifluoromethanesulfonate (S2)



In a round-bottom flask, 2,4,6-trimethyl-pyridine (1.21 g, 10.0 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (20 mL). The reaction mixture was cooled to 0 ℃, and 3-chloroperbenzoicacid (*m*-CPBA) (3.5 g, 20 mmol, 2.0 eq.) was added portionwise. After warming to room temperature, the reaction mixture was stirred overnight. The mixture was diluted with CH_2Cl_2 (20 ml) and an aqueous KOH solution (6 M) was added. Extraction with CH_2Cl_2, dried over anhydrous Na_2SO_4, and removal of the solvent afforded the product as a yellow liquid.[17]



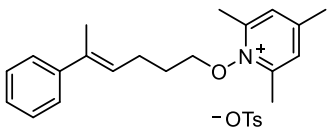
To a solution of alcohol (1.76 g, 10.0 mmol, 1.0 equiv), Et_3N (2.1 ml, 15.0 mmol, 1.5 equiv) and DMAP (122.2 mg, 1.0 mmol, 0.1 equiv) in CH_2Cl_2 (30 mL) was added TsCl (2.09 g, 11.0 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the alkyl tosylate.[18]



S2

To a solution of alkyl tosylate (1.6 g, 4.8 mmol, 1.2 equiv) in CH_3CN (8 mL) was added 2,4,6-trimethylpyridine 1-oxide (0.69 g, 4.0 mmol, 1.0 equiv) at room temperature. The reaction mixture was stirred at 80 ℃ for 24 hours, then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (MeOH/CH_2Cl_2 = 20:1) to afford **S2** as a yellow oil.[19]

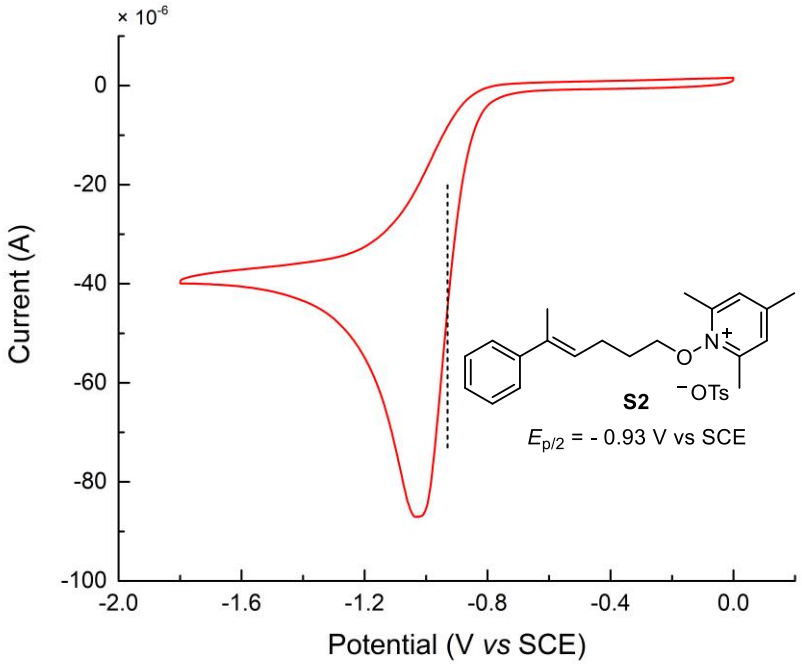
(*E*)-2,4,6-trimethyl-1-((5-phenylhex-4-en-1-yl)oxy)pyridin-1-ium 4-methylbenzenesulfonate



S2

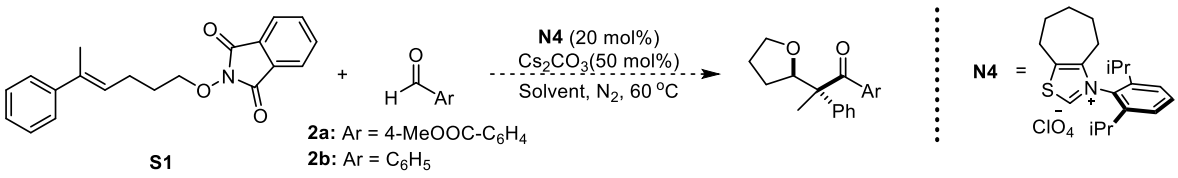
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 2H), 7.36 – 7.28 (m, 4H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.71 (t, *J* = 8.0 Hz, 1H), 4.47 (t, *J* = 8.0 Hz, 2H), 2.75 (s, 6H), 2.42 – 2.36 (m, 5H), 2.28 (s, 3H), 2.03 – 1.97 (m, 5H).. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 151.4, 144.3, 143.0, 138.3, 136.2, 128.7, 128.0, 128.9, 126.6, 125.6, 125.3, 79.3, 27.4, 24.4, 21.3, 20.9, 17.2, 15.7. HRMS (ESI) *m/z* calcd for $C_{20}H_{26}NO^+$

([M]), 296.20089, found: 296.20064.



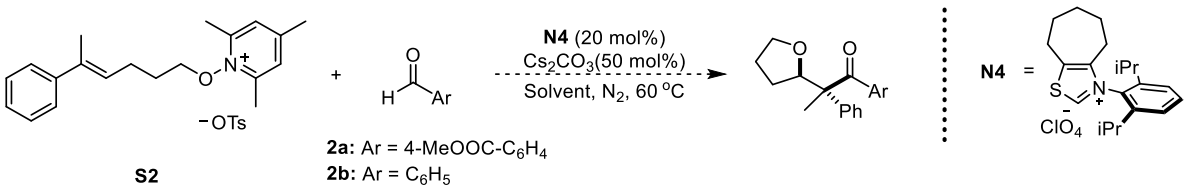
Cyclic voltammogram of *N*-alkoxypyridinium tosylate **S2**

5.3 Reaction development



Entry[a]	**2**	Solvent	Yield (%)
1	**2a**	DMSO	N.R.
2	**2b**	DMSO	N.R.
3	**2a**	CH_3CN	N.R.
4	**2b**	CH_3CN	N.R.

Reaction was carried out with **S1** (0.2 mmol), **2** (0.3 mmol), **N4** (20 mol%), and Cs_2CO_3 (0.1 mmol) in solvent (2 mL) at 60 ℃ for 12 h.



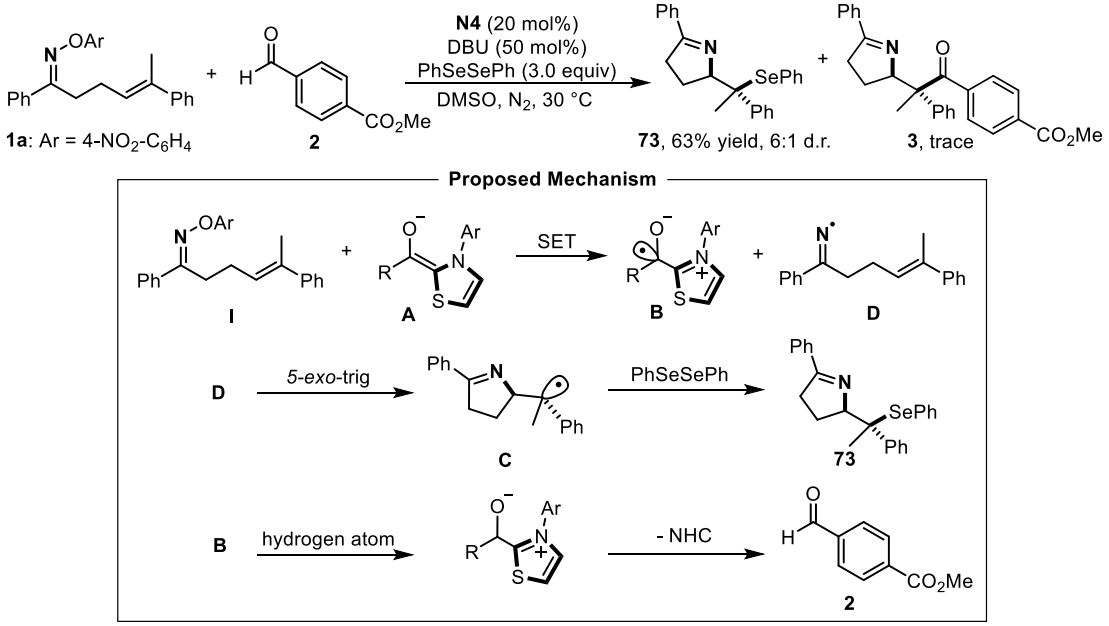
Entry[a]	**2**	Solvent	Yield (%)
1	**2a**	DMSO	N.R.
2	**2b**	DMSO	N.R.
3	**2a**	CH_3CN	N.R.
4	**2b**	CH_3CN	N.R.

Reaction was carried out with **S2** (0.2 mmol), **2** (0.3 mmol), **N4** (20 mol%), and Cs_2CO_3 (0.1 mmol) in solvent (2 mL) at 60 ℃ for 12 h.

6. Mechanistic studies

6.1 Radical trapping experiments

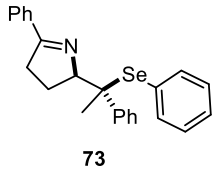
6.1.1 PhSeSePh trapping experiment



To an oven-dried reaction tube equipped with a stir bar was added *O*-aryl oxime **1a** (0.1 mmol, 1.0 equiv), thiazolium salt **N4** (20 mol%), aldehyde **2** (0.15 mmol, 1.5 equiv) and diphenyl diselenide (0.3 mmol, 3.0 equiv). The tube was sealed and placed under nitrogen before DBU (0.05 mmol, 0.5 equiv) and DMSO (1 mL) were added. Then the system was stirred at 30 ℃ for 12 h. The reaction mixture was purified by silica gel column chromatography to afford the selenide **73** (25.5 mg, 63% yield).[20]

Entry	Deviation from standard conditions	Yield of **73**	Recovery of **1a**
1	none	63%	-
2	without **N4**	not detected	96%
3	without **N4**, **2**, and DBU	not detected	93%

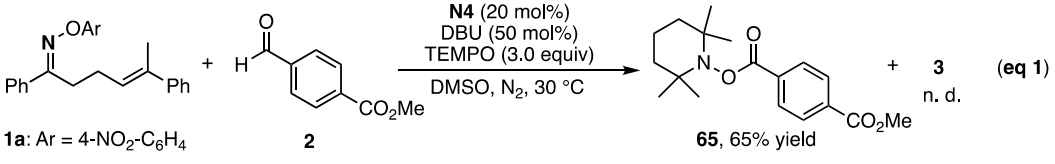
5-phenyl-2-(1-phenyl-1-(phenylselanyl)ethyl)-3,4-dihydro-2H-pyrrole

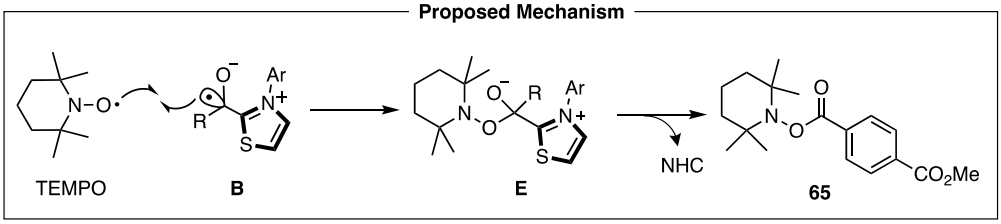


73

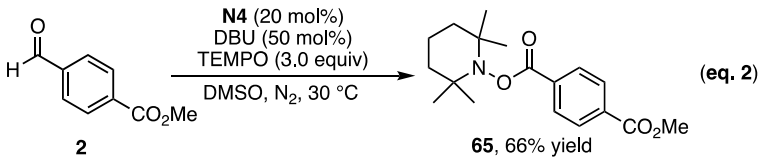
White solid, d.r. 6:1, m.p. 196 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 1.7H), 7.86 – 7.84 (m, 0.3H), 7.52 – 7.50 (m, 0.3H), 7.44 – 7.38 (m, 4.7H), 7.27 – 7.05 (m, 8H), 5.24 – 5.20 (m, 0.85H), 4.85 – 4.82 (m, 0.15H), 2.90 – 2.77 (m, 1.85H), 2.56 – 2.44 (m, 0.15H), 2.22 – 2.08 (m, 0.28H), 1.97 – 1.88 (m, 1H), 1.75 (s, 0.44H), 1.68 (s, 2.56H), 1.62 – 1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 144.0, 137.7, 137.3, 134.5, 130.4, 130.4, 129.0, 128.9, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 126.2, 82.1, 81.5, 56.5, 56.0, 35.3, 25.4, 25.2. HRMS (ESI) *m/z* calcd for $C_{24}H_{24}NSe^+$ ([M+H$^+$]), 406.10685, found: 406.10744.

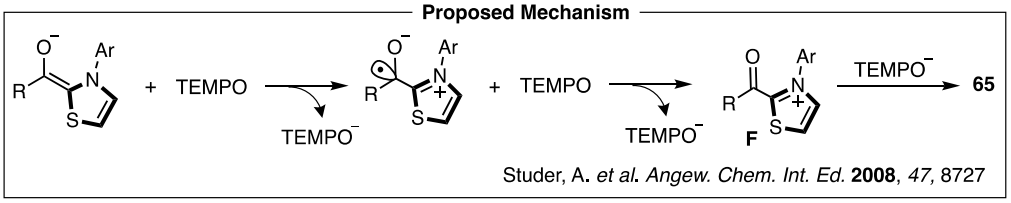
6.1.2.TEMPO trapping experiment





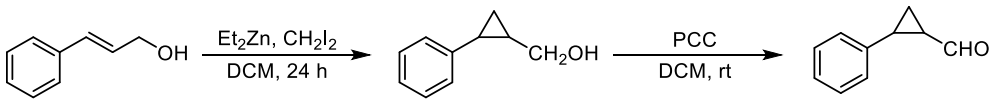
When TEMPO was added to the reaction of **1a** with **2** under standard conditions, the pyrroline **3** was not formed. Instead, the adduct **65** was obtained in 65% yield (eq. 1), indicating the involvement of the ketyl radical **B**. However, According to Studer's study,[21] we currently could not exclude an alternative mechanism that the Breslow intermediate gets oxidized to the corresponding acyl thiazoliums **F** by TEMPO (eq. 2).





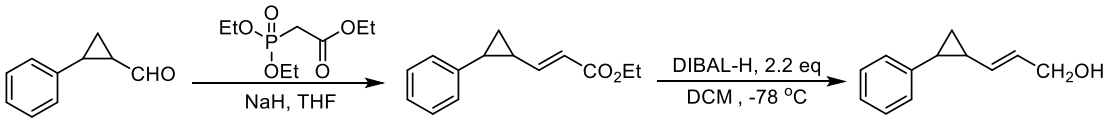
6.2 Radical clock experiment

6.2.1 Synthesis of 4*E* 1-phenyl-5-(2-phenylcyclopropyl)pent-4-en-1-one O-(4-nitrophenyl) oxime



To a 500 mL round-bottomed flask was added CH_2I_2 (28.5 mmol, 1.2 equiv.) and dry DCM (135 mL) under nitrogen atmosphere. To another nitrogen backfilled 250 mL round-bottomed flask was added cinnamyl alcohol (3.1 g, 23.4 mmol, 1.0 equiv.) and dry DCM (60 mL). A solution of Et_2Zn (1 M in Hexane, 29.4 mmol, 1.25 equiv.) was added, dropwise, to each flask at 0 ℃. After 30 min, the solution of cinnamyl alcohol was transferred to the 500 mL flask at 0 ℃. The reaction mixture was stirred at 0 ℃ for 30 min. Then, the ice bath was removed and the reaction was stirred for 24 h at room temperature. Saturated aqueous NH_4Cl (75 ml) and HCl (2 M, 300 mL) were added. The mixture was transferred to a separation funnel, the layers were separated and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The cyclic product was obtained in quantitative yield, and it was used without purification.[22]

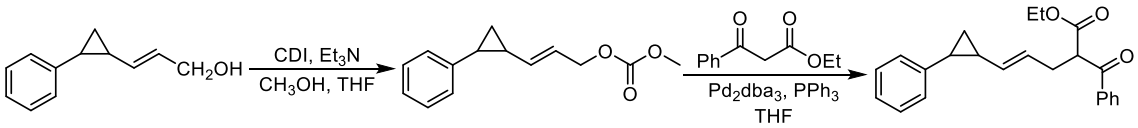
Then pyridinium chlorochromate (6.46 g, 30 mmol, 1.5 equiv.) was added slowly to a DCM (50 mL) solution of (2-phenylcyclopropyl)methanol (2.96 g, 20.0 mmol, 1.0 equiv.). The reaction mixture was stirred for 1 h at room temperature and then filtered over celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the aldehyde in 84% yield.[22]



To a solution of NaH (60% in mineral oil; 0.9 g, 22.5 mmol, 1.5 equiv.) in THF (45 mL) was added triethyl phosphonoacetate (5.0 g, 22.5 mmol, 1.5 equiv) dropwise at 0 ℃. The resulting mixture was stirred at 0 ℃ for 30 min, before 2-phenylcyclopropane-1-carbaldehyde (2.2 g, 15 mmol, 1.0 equiv.) was added at room temperature. The mixture was stirred for 12 h and quenched with saturated aqueous NH_4Cl. The resulting slurry was diluted with EtOAc and washed with water and brine. The organic layer was separated and dried over $MgSO_4$. Then, the drying agent was removed by filtration, and the resulting solution was concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the alkenoate (2.4 g, 75%).[4]

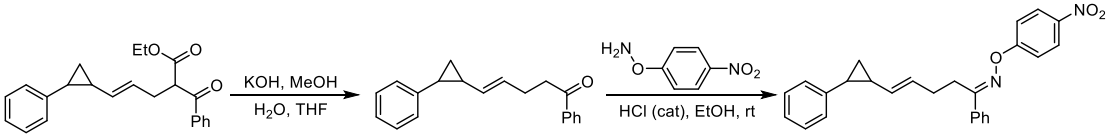
To a solution of the alkenoate (2.16 g, 10 mmol, 1.0 equiv.) in CH_2Cl_2 (80 mL) was added DIBAL-H (1.02 M in hexane, 2.2 equiv.) at –78 ℃. After stirring for 2 h,

saturated aqueous NH_4Cl was added and the mixture was vigorously stirred for 10 min. The reaction mixture was then filtered through celite and the filtrate was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the allylic alcohol (1.56 g, 90%).[4]



A 250 mL round-bottom flask was charged with allylic alcohol (1.4 g, 8 mmol, 1.0 equiv.), THF (20 mL), and *N*,*N*'-carbonyldiimidazole (1.95 g, 12 mmol, 1.5 equiv.). The mixture was stirred at room temperature. After the alcohol was fully converted to the corresponding intermediate (monitored by TLC), triethylamine (1.67 mL, 12 mmol, 1.5 equiv.) and methanol (0.65 mL, 16 mmol, 2.0 equiv.) were added to the suspension. After the intermediate was fully consumed (monitored by TLC), the mixture was diluted with H_2O and the layers were separated. The aqueous phase was extracted with EA (50 mL × 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude mixture was purified by flash chromatography on silica gel to afford the carbonate (1.54 g, 83%).[13]

A 50 ml round-bottom flask was charged with Pd_2dba_3 (229 mg, 0.25 mmol, 0.05 equiv.) and PPh_3 (393 mg, 1.5 mmol, 0.3 equiv.). The flask was evacuated and back-filled with nitrogen three times. THF (15 mL) was added and the mixture was stirred at room temperature. After 15 min, (*E*)-methyl (3-(2-phenylcyclopropyl)allyl) carbonate (1.16 g, 5 mmol, 1.0 equiv.) and ethyl benzoylacetate (1.06 g, 5.5 mmol, 1.1 equiv.) were added as a combined solution in THF (10 mL). The reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was concentrated in vacuo. Purification of the residue by flash chromatography on silica gel afforded the title compound (1.25 g, 72%) as a yellow oil.[23]

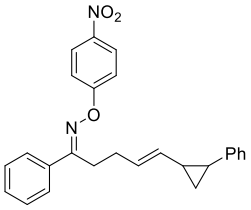


To a solution of ethyl (*E*)-2-benzoyl-5-(2-phenylcyclopropyl)pent-4-enoate (1.0 g, 2.9 mmol, 1.0 equiv.) in THF (15 mL) was added KOH (729 mg, 13.0 mmol, 4.5 equiv.), MeOH (3.2 mL) and H_2O (8.0 mL). The reaction mixture was heated at reflux for 3 hours. Then the mixture was cooled to room temperature and 1M HCl (40 mL) was added. The mixture was stirred for 10 minutes followed by extraction with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (80 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. Purification of the residue by flash chromatography on silica gel afforded the desired ketone (520 mg, 65%).[23]

A solution of the ketone (520 mg, 1.9 mmol, 1.0 equiv.) in EtOH (20 mL) was treated with *O*-(4-nitrophenyl)hydroxylamine (293 mg, 1.9 mmol, 1.0 equiv.) and stirred at room temperature overnight. H_2O was added and EtOH was removed in vacuo. The mixture was diluted with EtOAc and the organic layer was separated. The aqueous

layer was extracted with EtOAc and the combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to give the *O*-aryloxime (650 mg, 83%).[6]

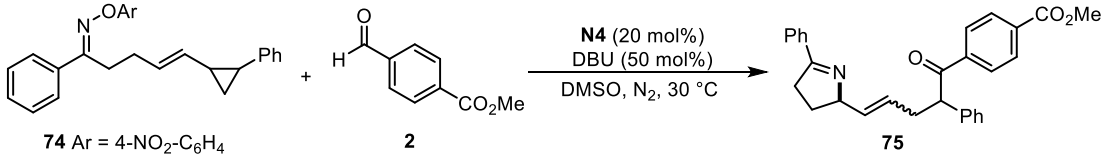
4*E*-1-phenyl-5-(2-phenylcyclopropyl)pent-4-en-1-one *O*-(4-nitrophenyl) oxime

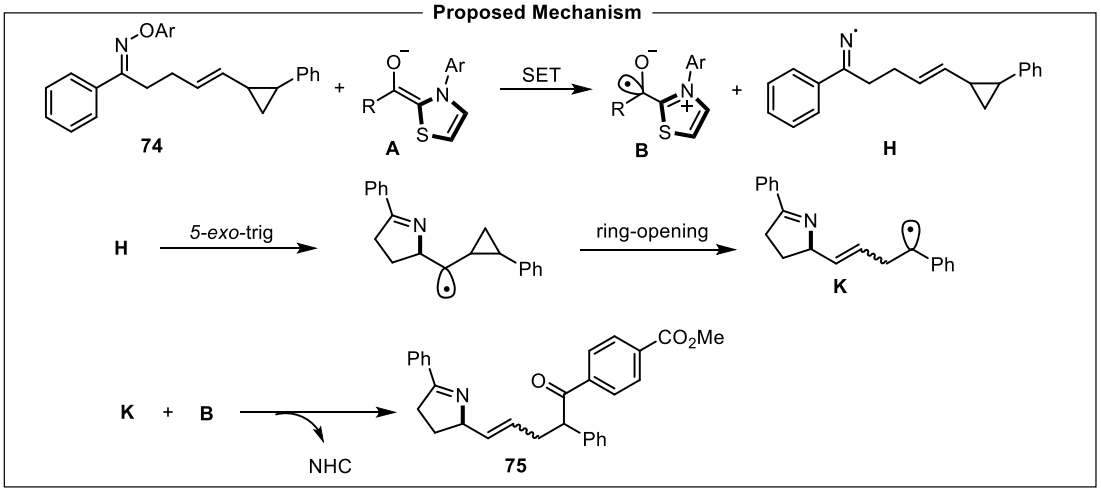


74

Orange oil, *E:Z* 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (t, *J* = 12 Hz, 2H), 7.75 – 7.73 (m, 1.5H), 7.46 – 7.34 (m, 5H), 7.25 – 7.21 (m, 2.5H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 2H), 5.58 – 5.51 (m, 1H), 5.21 – 5.12 (m, 1H), 3.03 (t, *J* = 8.0 Hz, 1.5H), 2.77 (t, *J* = 8.0 Hz, 0.5H), 2.37 – 2.26 (m, 2H), 1.85 – 1.77 (m, 1H), 1.63 – 1.53 (m, 1H), 1.13 – 1.09 (m, 1H), 1.05 – 0.97 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.5, 163.4, 142.3, 142.3, 142.1, 134.1, 133.9, 133.7, 132.7, 130.3, 129.5, 128.7, 128.3, 128.3, 127.6, 126.9, 126.7, 126.6, 125.7, 125.6, 125.5, 125.5, 114.5, 114.3, 35.4, 29.5, 29.2, 27.6, 26.4, 26.2, 24.9, 16.7. HRMS (ESI) *m/z* calcd for $C_{26}H_{24}N_2NaO_3^+$ ([M+Na$^+$]), 435.16791, found: 435.16717.

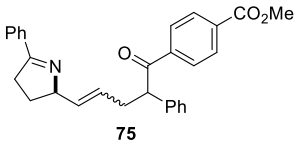
6.2.2 General procedure





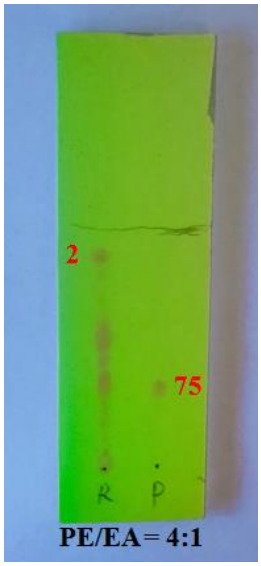
To an oven-dried reaction tube equipped with a stir bar was added *O*-aryl oxime **74** (0.2 mmol, 1.0 equiv), thiazolium salt **N4** (20 mol%), DBU (0.1 mmol, 0.5 equiv) and **2** (0.3 mmol, 1.5 equiv). The tube was sealed and placed under nitrogen before DMSO (2 mL) was added. Then the system was stirred at 30 ℃ for 12 h. The reaction mixture was purified by silica gel column chromatography to afford the desired fragmentation product **75**.

methyl-4-(2-phenyl-5-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)pent-4-enoyl)benzoat e



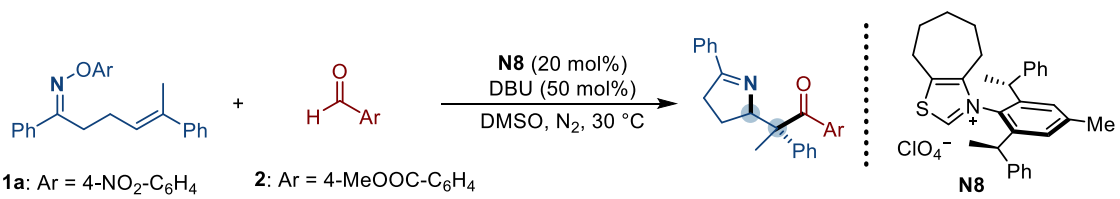
75

Yellow oil. A mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.08 (m, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 8.0 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.28 – 7.27 (m, 3H), 7.22 – 7.18 (m, 1H), 5.67 – 5.52 (m, 2H), 4.63 – 4.59 (m, 2H), 3.91 (s, 3H), 3.01 – 2.81 (m, 3H), 2.61 – 2.51 (m, 1H), 2.22 – 2.14 (m, 1H), 1.67 – 1.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 198.9, 173.5, 166.2, 140.0, 139.9, 138.7, 138.5, 134.4, 134.3, 134.1, 133.5, 130.6, 130.5, 130.0, 129.7, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 127.8, 127.2, 126.1, 115.7, 74.1, 73.9, 54.3, 54.1, 52.4, 36.8, 36.6, 35.0, 29.5. HRMS (ESI) *m/z* calcd for $C_{29}H_{28}NO_3^+$ ([M+H$^+$]), 438.20637, found: 438.20539.



6.3 Reaction with chiral NHC

6.3.1 Iminoacylation with chiral NHC

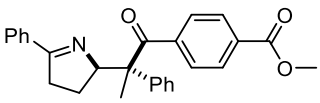


1a: Ar = 4-NO_2-C_6H_4 **2**: Ar = 4-MeOOC-C_6H_4 **N8**

Entry	NHC	Yield	d.r.	ee
1	**N4**	91%	>19:1	0%
2	**N8**	81%	>19:1	3%

Reaction was carried out with **1a** (0.2 mmol), **2** (0.3 mmol), **N8** (20 mol%), and DBU (0.1 mmol) in DMSO (2 mL) at 30 ℃ for 12 h.

methyl 4-(2-phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propanoyl)benzoate

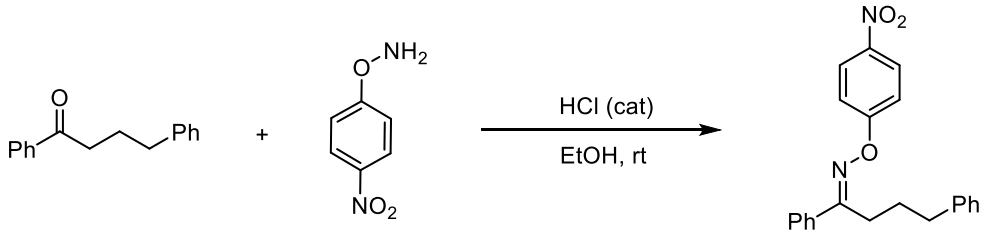


3

HPLC: Daicel Chiralcel AD-H column, elute: *n*-hexane/*i*-PrOH = 70/30, λ = 254 nm, 30 °C, 0.6 mL/min, t_R(major) = 12.8 min, t_R(minor) = 15.7 min.

6.3.2 Intramolecular 1,5-H-atom abstraction of *O*-aryloximes

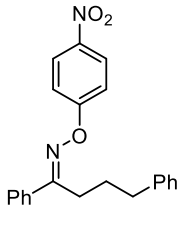
6.3.2.1 Synthesis of *O*-aryloximes



71

A solution of the ketone (448 mg, 2 mmol) in EtOH (20 ml) was treated with the *O*-(4-nitrophenyl)hydroxylamine (308 mg, 2 mmol) and HCl (1-3 drops). Upon addition of HCl the mixture became a yellow solution and over time the product crystallized out. Once the reaction was judged complete by TLC analysis the pure product was filtered washing with cold *n*-hexane and dried under high vacuum for 2 h.

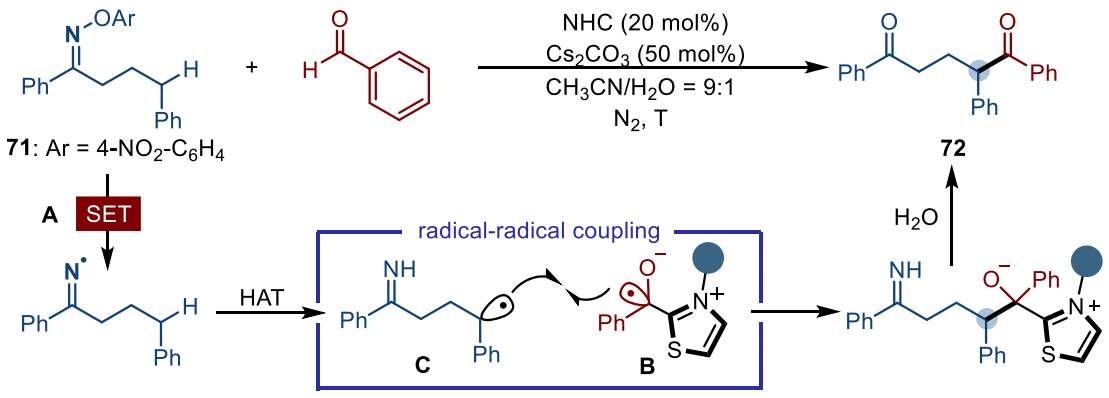
(*E*)-1,4-diphenylbutan-1-one *O*-(4-nitrophenyl) oxime



71

White solid, m.p. 75 – 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.48 – 7.41 (m, 3H), 7.33 – 7.27 (m, 4H), 7.24 – 7.17 (m, 3H), 2.98 (t, *J* = 8.0 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.02 – 1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.9, 142.4 141.1, 134.1 130.4, 128.7, 128.5, 128.4 126.9, 126.1, 125.7, 114.4, 35.7, 28.2, 27.0. HRMS (ESI) *m/z* calcd for $C_{22}H_{21}N_2O_3^+$ ([M+H$^+$]), 361.15467, found: 361.15419.

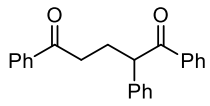
6.3.2.2 General procedure and reaction development



To an oven-dried reaction tube equipped with a stir bar was added *O*-aryl oxime **71** (0.2 mmol, 1.0 equiv), thiazolium salt **N4** or **N8** (20 mol%), benzaldehyde (0.30 mmol, 1.5 equiv) and Cs_2CO_3 (0.1 mmol, 0.5 equiv). The tube was sealed and placed under nitrogen before CH_3CN (1.8 ml) and H_2O (0.2 mL) were added. Then the system was stirred for 12 h. The reaction mixture was purified by silica gel column chromatography to afford the 1,5-dione **72**.

Entry	NHC	T	Yield	ee
1	**N4**	80 ℃	51%	0%
2	**N8**	80 ℃	54%	0%
3	**N4**	30 ℃	12%	0%
4	**N8**	30 ℃	10%	16%

1,2,5-triphenylpentane-1,5-dione

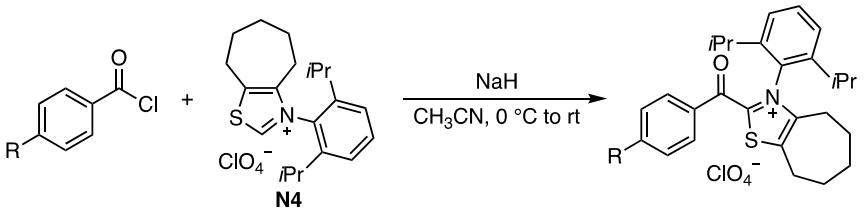


72

White solid, m.p. 97 – 98 ℃. HPLC: Daicel Chiralcel AD-H column, elute: *n*-hexane/*i*-PrOH = 70/30, λ = 254 nm, 30 ℃, 0.6 mL/min, t_R(minor) = 13.6 min, t_R(major) = 15.3 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.35 (m, 6H), 7.32 – 7.25 (m, 4H), 7.22 – 7.18 (m, 1H), 4.77 (t, *J* = 8.0 Hz, 1H), 3.05 – 2.88 (m, 2H), 2.63 – 2.54 (m, 1H), 2.33 – 2.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 199.6, 139.1, 136.8, 136.6, 133.0, 132.9, 129.0, 128.8, 128.5, 128.5, 128.3, 128.0, 127.2, 52.4, 36.0, 28.3. HRMS (ESI) *m/z* calcd for $C_{23}H_{21}O_2^+$ ([M+H$^+$]), 329.1536, found: 329.1538.

6.4 Cyclic voltammetry experiments

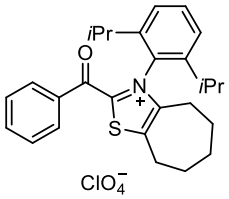
6.4.1. Synthesis of acyl thiazolium salts



N4

The reaction was carried out with NaH (60% in mineral oil, 4.5 mmol, 3 equiv) in a round-bottomed flask under nitrogen atmosphere. After addition of CH_3CN, the reaction was cooled to 0 ℃. A solution of the NHC precursor (1.5 mmol, 1 equiv) and benzoyl chloride (4.5 mmol, 3 equiv) in CH_3CN was added portion-wise to the stirred solution over 1 h. The reaction was warmed up to room temperature and stirred for 6 h at room temperature. The resulting mixture was concentrated in vacuo. The residue is triturated in Et_2O until a precipitate was obtained. Then it is washed with Et_2O for several times and dried under vacuum. Recrystallization from dry petroleum ether and CH_2Cl_2 led to pale yellow or colorless crystals.[24]

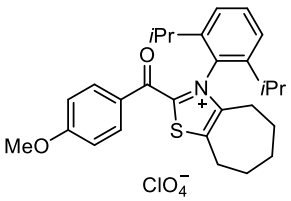
2-benzoyl-3-(2,6-diisopropylphenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[d]thiazol-3-ium perchlorate



F1

Yellow crystalline (220 mg, 28%), m.p. 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.62 – 7.59 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.38 (m, 2H), 2.69 – 2.67 (m, 2H), 2.30 – 2.23 (m, 2H), 2.01 (m, 2H), 1.73 (m, 2H), 1.19 (d, *J* = 8.0 Hz, 6H), 1.10 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 155.8, 152.8, 145.0, 144.7, 136.0, 134.9, 132.1, 131.4, 130.8, 129.6, 125.1, 30.7, 28.9, 28.7, 27.7, 25.9, 25.3, 24.2, 23.8. HRMS (ESI) *m/z* calcd for $C_{27}H_{32}NOS^{+}$, 418.21991, found: 418.21924.

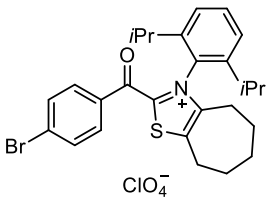
3-(2,6-diisopropylphenyl)-2-(4-methoxybenzoyl)-5,6,7,8-tetrahydro-4H-cyclohept a[*d*]thiazol-3-ium perchlorate



F2

Yellow crystalline (450 mg, 55%), m.p. 210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.37 – 3.35 (m, 2H), 2.66 – 2.64 (m, 2H), 2.30 – 2.23 (m, 2H), 2.04 – 1.99 (m, 4H), 1.74 (m, 2H), 1.18 (d, *J* = 8.0 Hz, 6H), 1.10 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 166.3, 157.4, 152.0, 145.2, 143.3, 134.0, 132.1, 131.3, 127.6, 125.1, 115.1, 56.0, 30.7, 28.8, 28.7, 27.8, 26.0, 25.4, 24.3, 23.8. HRMS (ESI) *m/z* calcd for $C_{28}H_{34}NO_2S^{+}$, 448.23048, found: 448.22916.

2-(4-bromobenzoyl)-3-(2,6-diisopropylphenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[*d*]thiazol-3-ium perchlorate



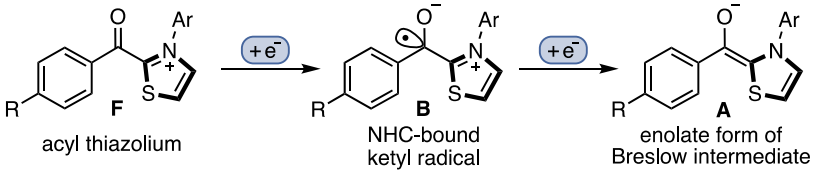
F3

Yellow crystalline (510 mg, 57%), m.p. 228 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.37 –3.35 (m, 2H), 2.68 – 2.65 (m, 2H), 2.28 – 2.22 (m, 2H), 2.04 – 2.00 (m, 4H), 1.74 – 1.72 (m, 2H), 1.19 (d, *J* = 8.0 Hz, 6H), 1.10 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 155.4, 152.9, 145.1, 144.8, 133.7, 133.1, 132.3, 132.2, 131.3, 125.2, 30.7, 29.0, 28.7, 27.8, 25.9, 25.3, 24.2, 23.9. HRMS (ESI) *m/z* calcd for $C_{27}H_{31}BrNOS^{+}$, 496.13042, found: 496.12943.

6.4.2. Electrochemical studies

Cyclic voltammograms were recorded using a CH Instruments 656E potentiostat and a glassy carbon working electrode, a Ag/AgCl reference electrode, and a Pt counter electrode. The voltammograms were recorded at room temperature under nitrogen atmosphere in 0.1 M tetrabutylammonium hexafluorophosphate in MeCN containing **1a** or **F** (1 mM). The scan rate was 100 mV s^{-1}. All potentials are reported in V vs SCE. The $E_{1/2}$ of the Fc/Fc^{+} redox couple used as a standard is 0.42 V vs SCE in acetonitrile under our conditions.[24a]

Table S1. Reduction potentials of acyl thiazolium[a]



entry	acyl thiazolium	$E_{1/2}^{1}$ [**F**/**B**]	$E_{1/2}^{2}$ [**B**/**A**]
1	**F1**	–0.53	–1.32
2	**F2**	–0.60	–1.36
3	**F3**	–0.50	–1.29

[a]All potentials are given in volts versus the saturated calomel electrode (SCE). Measurements were performed in MeCN at room temperature.

Figure S1. Cyclic voltammogram of acyl thiazolium **F1**.

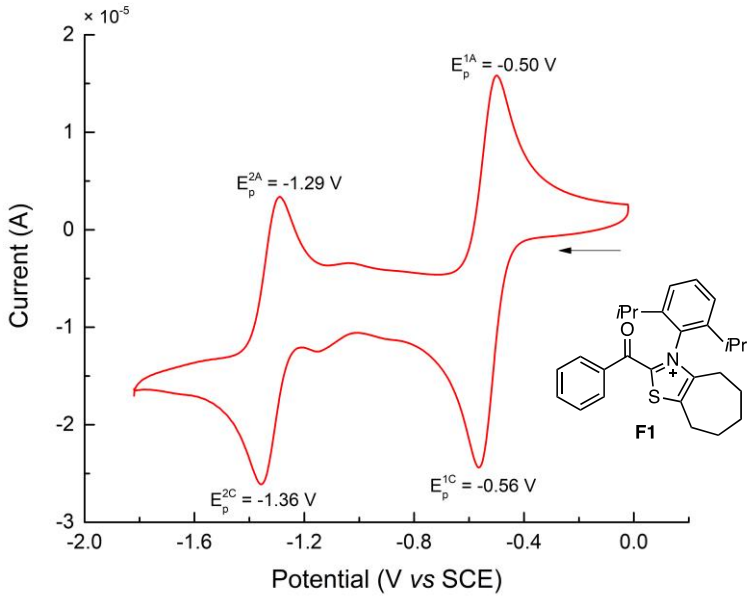


Figure S2. Cyclic voltammogram of acyl thiazolium **F2**.

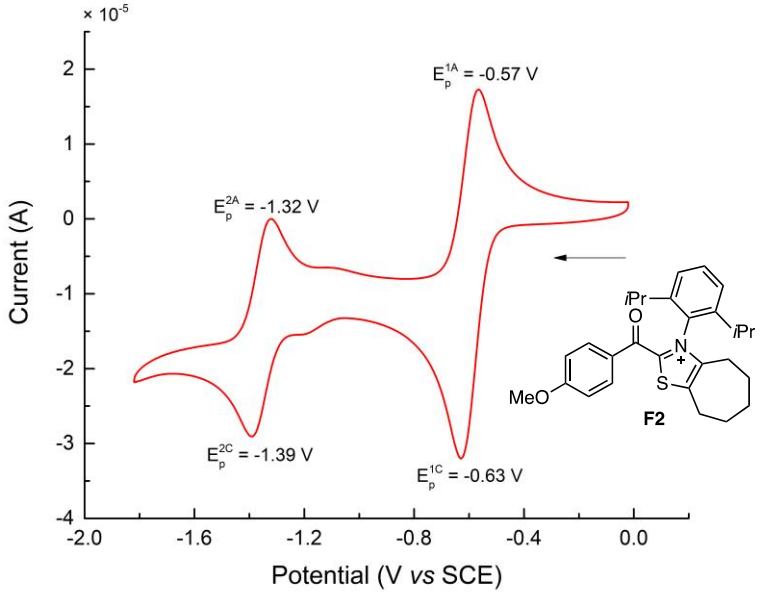


Figure S3. Cyclic voltammograms of acyl thiazolium **F3**.

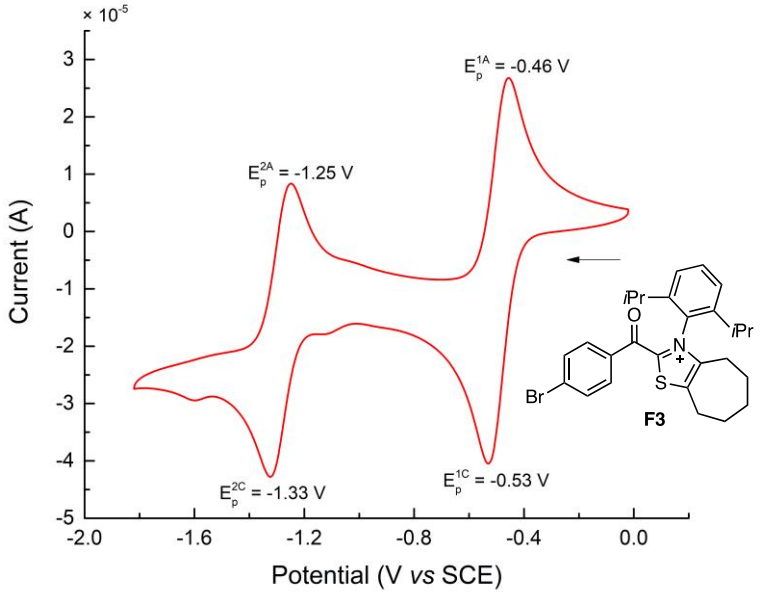


Figure S4. Cyclic voltammogram of *O*-aryl oxime **1a**.

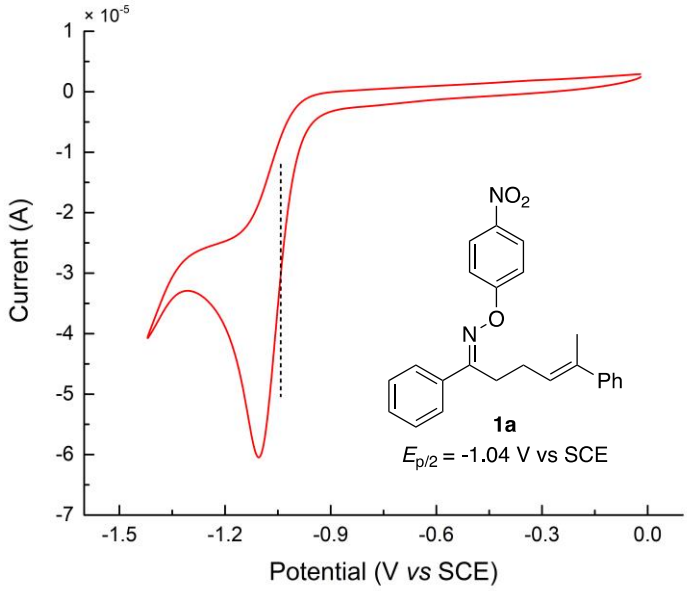
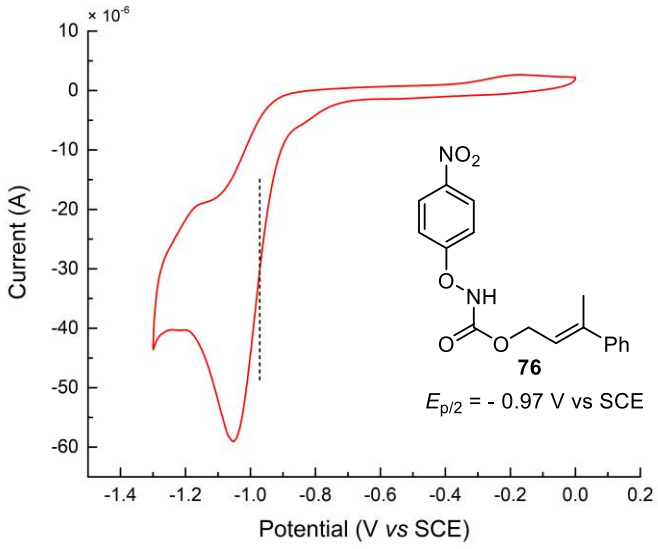
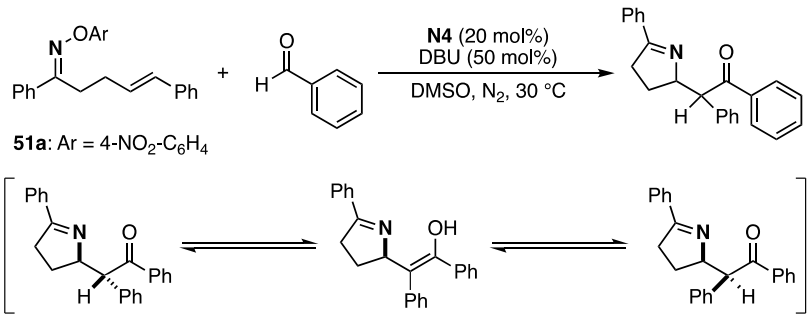


Figure S5. Cyclic voltammogram of *O*-aryl carbamate **76**.



6.5. Enolized epimerization.

Table S2. Epimerization



entry	temperature	yield	d.r.
1	30 °C	95%	2:3
2	60 °C	93%	2:1
3[a]	30 °C	96%	2:1

[a]After completion of the reaction, the mixture was stirred at 60 °C for additional 12 h.

We examined the iminoacylation reaction with oxime **51a** containing disubstituted olefin (Table S2). The desired pyrroline was obtained with 2:1 d.r. (entry 1). Further evaluation of the reaction temperature led to a d.r. of 1:2 (entry 2). We reasoned that this poor diastereoselectivity may be due to enolized racemization. To probe this hypothesis, we conducted the reaction at 30 °C. After 12 h, the resulting solution was allowed to stir at 60 °C. The two diastereomeres of product **51** were found to undergo epimerization to each other (entry 3).

6.6. Computational methods

Density functional theory (DFT) computations were performed with Gaussian 16.[25] The (u)ωB97X-D functional was used to optimize molecular geometries.[26] Geometry optimizations were completed with the def2-SVP basis set[27] and the SMD solvation model accounting for the effect of DMSO.[28] Frequency calculations were conducted at the same level of theory used for the geometry optimizations in order to obtain thermal Gibbs free energies and characterize the stationary points on the potential energy surface. Gibbs free energies were corrected using Goodvibes, which corrects the vibrational frequencies *via* the approximation for the quasi-harmonic correction, as proposed by Truhlar.[29] Single point energies were obtained using the def2-TZVPP basis set.[27] Intrinsic reaction coordinate (IRC) calculations were performed to verify that a transition state (TS) connects the reactant and the product on the potential energy surface.

Conformation searches were executed by Grimme's Conformer-Rotamer Ensemble Sampling Tool (CREST) to find the lowest energy conformers.[30] CYLview was employed to visualize molecular structures.[31]

6.6.1. Energies and Cartesian coordinates of calculated structures

Table S3. Energies of the optimized structures with the quasi-harmonic correction
(u)ωB97X-D/def2-SVP/SMD=DMSO

Structure	E	ZPE	H	T.S	T.qh-S	G(T)	qh-G(T)
N4’	-1230.366745	0.429933	-1229.914203	0.072894	0.069278	-1229.987097	-1229.983482
13’	-459.619737	0.143747	-459.466275	0.043679	0.043429	-459.509954	-459.509704
1a	-1261.519423	0.413033	-1261.080349	0.085096	0.076693	-1261.165445	-1261.157042
DBU-H$^+$	-462.144264	0.262465	-461.871178	0.045237	0.045009	-461.916414	-461.916187
DBU	-461.648462	0.247580	-461.390340	0.045374	0.044848	-461.435714	-461.435188
INT1	-1689.995408	0.575953	-1689.387403	0.095028	0.087497	-1689.482431	-1689.474900
INT2	-1689.510791	0.563417	-1688.915259	0.094715	0.087673	-1689.009973	-1689.002931
INT3	-1261.611478	0.410263	-1261.175008	0.085748	0.077516	-1261.260756	-1261.252525
INT4	-1689.422816	0.565277	-1688.825456	0.095305	0.088328	-1688.920761	-1688.913783
INT5	-510.958703	0.095793	-510.854412	0.041438	0.041230	-510.895850	-510.895642
INT6	-511.442754	0.109297	-511.324747	0.041907	0.041362	-511.366655	-511.366109
INT7	-750.669760	0.311509	-750.340237	0.067096	0.061419	-750.407333	-750.401657
INT8	-750.707520	0.313009	-750.377388	0.063410	0.059835	-750.440799	-750.437223
INT9	-2440.159211	0.884272	-2439.227420	0.126902	0.115873	-2439.354322	-2439.343293
PRODUCT	-1209.786289	0.451681	-1209.308896	0.082438	0.075862	-1209.391334	-1209.384759
TS1	-1689.983889	0.575024	-1689.376899	0.094536	0.087594	-1689.471435	-1689.464492
TS2	-750.658388	0.310881	-750.330326	0.063560	0.060054	-750.393886	-750.390380
TS3	-2440.136217	0.880859	-2439.207196	0.129185	0.117487	-2439.336381	-2439.324683
TS3’	-2440.134585	0.881226	-2439.205267	0.129632	0.117072	-2439.334900	-2439.322339
TS4	-2440.147154	0.883138	-2439.216537	0.128076	0.115834	-2439.344613	-2439.332371

Table S4. Single point energies
(u)ωB97X-D/def2-TZVPP/SMD=DMSO

Structure	E
N4’	-1231.385642
13’	-460.127965
1a	-1262.889579
DBU-H$^+$	-462.635392
DBU	-462.141733
INT1	-1691.517457
INT2	-1691.029143
INT3	-1262.990742
INT4	-1690.940043
INT5	-511.543686
INT6	-512.023062
INT7	-751.468467
INT8	-751.501322
INT9	-2442.460978
PRODUCT	-1211.080117

TS1	-1691.506231
TS2	-751.456013
TS3	-2442.438034
TS3’	-2442.436310
TS4	-2442.450404
TS3a	-2211.357168
TS3a’	-2211.359427

XYZ STRUCTURES

N4’

Charge: 0

C	0.057054	-0.668312	1.975189
N	-0.009818	-0.348011	0.671210
C	1.134798	-0.506127	-0.129716
C	2.181142	-0.984149	0.590200
S	1.656715	-1.207497	2.238333
C	3.572725	-1.263692	0.105150
H	3.545199	-2.115582	-0.597322
H	4.190045	-1.588269	0.955909
C	4.243316	-0.066345	-0.577812
H	4.200283	0.804375	0.099120
H	5.310231	-0.308992	-0.707181
C	3.672127	0.312173	-1.945857
H	4.332682	1.073384	-2.392094
H	3.727103	-0.567890	-2.611825
C	2.242198	0.856276	-1.964919
H	2.166869	1.736286	-1.303164
H	2.025800	1.214211	-2.984002
C	1.149812	-0.150529	-1.586548
H	1.283988	-1.074194	-2.176148
H	0.169371	0.254267	-1.870154
C	-1.242689	0.167599	0.130461
C	-1.432351	1.558643	0.106695
C	-2.649459	2.037071	-0.388683
C	-3.625475	1.159573	-0.853157
C	-3.399094	-0.213830	-0.841268
C	-2.197167	-0.739526	-0.355600
C	-1.958556	-2.240721	-0.328481
C	-2.311383	-2.912619	-1.656768
H	-2.023100	-3.974972	-1.630812
H	-1.782422	-2.438599	-2.498295
H	-3.391934	-2.870914	-1.866040

C	-2.711887	-2.878606	0.843592
H	-2.408560	-2.426456	1.800577
H	-3.800293	-2.744338	0.732510
H	-2.506394	-3.959487	0.895503
H	-0.884925	-2.407484	-0.157108
H	-4.171057	-0.889633	-1.216437
H	-4.571585	1.551162	-1.234372
H	-2.837879	3.112907	-0.411395
C	-0.370653	2.516176	0.623471
C	-0.109976	3.673776	-0.341987
H	0.120446	3.307573	-1.354610
H	-0.974762	4.352163	-0.414572
H	0.747488	4.270538	0.005936
C	-0.740242	3.017601	2.023229
H	-1.682058	3.589864	2.001543
H	0.048208	3.675761	2.421176
H	-0.868771	2.176727	2.722449
H	0.571885	1.957032	0.715871

There are no imaginary frequencies

13'

Charge: 0

O	3.669912	-0.410360	-0.000065
O	-2.230315	-1.007468	0.000111
C	0.101816	-0.905321	0.000053
H	0.109995	-1.998607	0.000053
C	2.579079	-0.930090	-0.000027
C	1.294679	-0.185947	0.000024
C	-1.130281	-0.234506	0.000060
C	1.281819	1.217322	0.000013
H	2.225674	1.765501	-0.000002
C	-1.144461	1.166107	0.000022
H	-2.085690	1.716735	0.000019
C	0.061194	1.877454	0.000012
H	0.029215	2.969563	0.000004
C	-3.498667	-0.392316	-0.000126
H	-3.650722	0.228481	-0.899093
H	-3.650853	0.229036	0.898422
H	-4.238442	-1.202396	0.000075
H	2.472980	-2.041908	-0.000032

There are no imaginary frequencies

1a

Charge: 0

N	-1.520658	-0.238509	-0.987992
C	2.120306	-2.695596	-0.007754
C	-0.261436	-2.992877	-0.554991
H	-0.396967	-3.276053	0.496091
C	-2.568392	-0.797138	-0.513194
C	-3.658479	-0.085196	0.212039
C	3.186747	-1.791459	-0.150370
H	3.190272	-1.079513	-0.978125
C	0.978381	-2.671882	-0.969004
C	2.170634	-3.600884	1.066119
H	1.380366	-4.346112	1.183919
C	1.284661	-2.193724	-2.365694
H	1.388409	-1.095520	-2.391707
H	0.498744	-2.464142	-3.081448
H	2.233008	-2.616689	-2.730989
C	-2.693881	-2.287696	-0.675612
H	-3.625471	-2.478687	-1.234479
H	-2.867661	-2.708318	0.329967
C	4.240565	-1.767003	0.762716
H	5.048768	-1.042649	0.633189
C	-1.528209	-3.000736	-1.361389
H	-1.376091	-2.575554	-2.362342
H	-1.841916	-4.049095	-1.507279
C	-3.368943	0.660221	1.363320
H	-2.338180	0.738400	1.716378
C	3.225688	-3.581193	1.976176
H	3.240353	-4.299406	2.799861
C	-4.984338	-0.194148	-0.221965
H	-5.221287	-0.773619	-1.117372
C	4.264322	-2.659776	1.833612
H	5.091750	-2.645341	2.547006
C	-4.393386	1.290208	2.064886
H	-4.159591	1.863603	2.964864
C	-5.713214	1.191080	1.619904
H	-6.514809	1.690687	2.168949
C	-6.005979	0.450710	0.475501
H	-7.036556	0.369906	0.122411
O	-1.545737	1.150587	-0.859664

C	-0.336621	1.702222	-0.643379
C	-0.257589	3.092250	-0.817826
C	0.781154	0.968273	-0.225160
C	0.938447	3.748356	-0.582125
H	-1.144025	3.640975	-1.140022
C	1.980519	1.629005	0.005060
H	0.706834	-0.108198	-0.075078
C	2.050017	3.007654	-0.175693
H	1.019110	4.826841	-0.715193
H	2.860585	1.076512	0.333819
N	3.314590	3.694794	0.069825
O	4.272499	3.027790	0.409645
O	3.348361	4.900868	-0.078271

There are no imaginary frequencies

DBU-H$^+$

Charge: 1

N	0.287545	-0.631999	-0.390062
N	1.460603	1.335016	-0.129120
C	-0.942216	-1.361663	-0.724589
C	-2.009456	-1.293808	0.363559
C	-2.803132	0.010151	0.374036
C	-1.969041	1.276706	0.549845
C	-0.916342	1.506162	-0.545741
C	0.329116	0.689920	-0.360419
C	2.740739	0.685170	0.103143
C	2.485922	-0.672465	0.729606
C	1.476493	-1.443413	-0.099270
H	1.417565	2.348269	-0.095451
H	3.420491	-1.244947	0.790365
H	-0.638395	-2.401770	-0.892822
H	-1.335372	-0.990569	-1.683531
H	-1.527763	-1.466900	1.340814
H	-2.705246	-2.131513	0.201706
H	-3.556596	-0.032771	1.176148
H	-3.362324	0.088075	-0.574693
H	-1.472997	1.278832	1.534650
H	-2.642963	2.146164	0.540445
H	-1.341972	1.280413	-1.536547
H	-0.618246	2.562298	-0.564251
H	3.333211	1.330293	0.763658

H	3.282079	0.584612	-0.851163
H	2.103555	-0.539946	1.753643
H	1.915903	-1.775829	-1.053692
H	1.139539	-2.336393	0.443968

There are no imaginary frequencies

DBU

Charge: 0

N	-0.318859	0.602189	-0.393950
N	-1.468470	-1.448185	-0.138972
C	0.895438	1.315860	-0.764000
C	1.983621	1.307521	0.310088
C	2.779029	0.005815	0.368409
C	1.945787	-1.257288	0.579188
C	0.900107	-1.532810	-0.511927
C	-0.393580	-0.765088	-0.349461
C	-2.706021	-0.714507	0.040041
C	-2.488835	0.617581	0.746539
C	-1.465430	1.426083	-0.029015
H	-3.425945	1.186745	0.834177
H	0.596539	2.351790	-0.976666
H	1.298673	0.918101	-1.710321
H	1.512176	1.517390	1.286015
H	2.678543	2.139311	0.109666
H	3.533576	0.076868	1.168902
H	3.341391	-0.102119	-0.576578
H	1.442449	-1.221744	1.561140
H	2.631137	-2.118873	0.618355
H	1.340233	-1.337434	-1.504815
H	0.611220	-2.591338	-0.493001
H	-3.413258	-1.340259	0.608826
H	-3.183162	-0.531915	-0.942923
H	-2.118967	0.428720	1.768295
H	-1.925947	1.854592	-0.938494
H	-1.108051	2.273136	0.578698

There are no imaginary frequencies

INT1

Charge: 0

O	0.697567	-2.235343	0.565068
O	5.734772	0.861741	1.083361
C	3.613990	-0.093045	0.850982
H	3.333631	0.442537	1.763271
C	1.242712	-1.056839	0.705273
C	2.694628	-0.902022	0.190498
C	4.925995	0.053157	0.369244
C	3.091266	-1.597048	-0.959574
H	2.370957	-2.245785	-1.461322
C	5.315762	-0.631570	-0.787026
H	6.327551	-0.541876	-1.183757
C	4.388026	-1.453396	-1.438062
H	4.700327	-1.989916	-2.338205
C	7.064260	1.041456	0.658055
H	7.115782	1.490596	-0.348523
H	7.626047	0.091754	0.655839
H	7.533568	1.727335	1.374682
C	0.422474	0.115422	0.076069
N	-0.898021	0.125135	-0.081874
C	-1.439677	1.345211	-0.521286
C	-0.480383	2.284271	-0.725843
S	1.079059	1.625813	-0.359045
C	-0.665494	3.696455	-1.194104
H	-1.038056	3.677239	-2.232978
H	0.314563	4.194575	-1.226251
C	-1.623953	4.514160	-0.321390
H	-1.295891	4.451448	0.730209
H	-1.523847	5.569816	-0.618715
C	-3.097878	4.122708	-0.432727
H	-3.691676	4.866690	0.122508
H	-3.411034	4.207336	-1.488780
C	-3.475832	2.733675	0.083537
H	-3.175728	2.629126	1.140215
H	-4.573404	2.647734	0.061853
C	-2.911322	1.552883	-0.715873
H	-3.103073	1.708701	-1.791421
H	-3.448049	0.638992	-0.435100
C	-1.777849	-1.007478	0.144890
C	-2.275521	-1.225437	1.433451
C	-3.236260	-2.230290	1.588301
C	-3.675463	-2.974316	0.498117
C	-3.152689	-2.735211	-0.770772
C	-2.193546	-1.740605	-0.975852

C	-1.554431	-1.539812	-2.338778
C	-2.559470	-1.547365	-3.489605
H	-3.037281	-2.531981	-3.613322
H	-2.049040	-1.311610	-4.436394
H	-3.353588	-0.799473	-3.337641
C	-0.452862	-2.593043	-2.517284
H	0.160075	-2.375591	-3.406945
H	0.183377	-2.612923	-1.615772
H	-0.896214	-3.594909	-2.647102
H	-1.065996	-0.553848	-2.346612
H	-3.494170	-3.337523	-1.615437
H	-4.428721	-3.753297	0.638111
H	-3.640586	-2.437885	2.581942
C	-1.741858	-0.482423	2.644103
C	-2.849815	0.164094	3.476387
H	-3.453704	0.857199	2.869772
H	-3.528226	-0.588505	3.908704
H	-2.414795	0.735178	4.311511
C	-0.875646	-1.441499	3.472112
H	-0.165104	-1.965619	2.812321
H	-1.502916	-2.198887	3.971150
H	-0.321996	-0.896448	4.253028
H	-1.089432	0.329604	2.290246
H	1.284156	-0.662482	1.772277

There are no imaginary frequencies

INT2

Charge: –1

O	-0.717167	-1.909469	-1.028419
O	-5.536460	1.565402	-0.395290
C	-3.502048	0.425668	-0.473771
H	-3.053041	1.419393	-0.484727
C	-1.213946	-0.805696	-0.593814
C	-2.721068	-0.735913	-0.530926
C	-4.903614	0.370584	-0.439613
C	-3.400717	-1.972447	-0.586233
H	-2.790337	-2.871455	-0.681232
C	-5.560859	-0.864325	-0.458124
H	-6.648421	-0.934688	-0.422915
C	-4.786039	-2.027946	-0.537382
H	-5.292175	-2.997384	-0.565892

C	-6.941202	1.587420	-0.367781
H	-7.344177	1.081516	0.526685
H	-7.378790	1.121378	-1.267674
H	-7.240178	2.643148	-0.338233
C	-0.434049	0.218381	-0.088661
N	1.000480	0.144147	-0.036130
C	1.605553	1.343348	0.360324
C	0.755111	2.320316	0.729277
S	-0.931851	1.770571	0.672402
C	1.097681	3.731363	1.114827
H	1.671792	3.738749	2.060472
H	0.166627	4.279732	1.325917
C	1.892227	4.496335	0.048995
H	1.363066	4.417335	-0.916708
H	1.894164	5.565759	0.318478
C	3.346629	4.051067	-0.117527
H	3.843223	4.745113	-0.815958
H	3.864498	4.172638	0.851556
C	3.579587	2.622598	-0.615179
H	3.105903	2.483593	-1.602684
H	4.663248	2.492729	-0.771392
C	3.101476	1.514468	0.331301
H	3.460528	1.735756	1.351878
H	3.575167	0.567474	0.044974
C	1.703002	-1.090933	0.127564
C	2.542038	-1.535906	-0.915280
C	3.281352	-2.706823	-0.730010
C	3.190330	-3.431498	0.456931
C	2.355907	-2.984018	1.476270
C	1.610626	-1.806708	1.335811
C	0.677255	-1.367267	2.450860
C	1.371680	-1.282467	3.811366
H	1.726568	-2.266516	4.157884
H	0.674009	-0.898918	4.573076
H	2.238261	-0.603017	3.776869
C	-0.545816	-2.292289	2.489513
H	-1.331778	-1.885722	3.146605
H	-0.954617	-2.417561	1.475086
H	-0.271298	-3.290276	2.871820
H	0.317024	-0.359166	2.205910
H	2.284100	-3.559747	2.403225
H	3.770927	-4.348698	0.585684
H	3.931096	-3.068417	-1.531452
C	2.578161	-0.806317	-2.247477

C	3.991533	-0.587759	-2.786250
H	4.629510	-0.071497	-2.050927
H	4.485031	-1.536302	-3.053562
H	3.961063	0.030697	-3.697568
C	1.681086	-1.542669	-3.248792
H	0.687339	-1.702674	-2.797119
H	2.108055	-2.527596	-3.505765
H	1.577966	-0.967420	-4.183927
H	2.129653	0.183008	-2.081534

There are no imaginary frequencies

INT3

Charge: –1

N	1.533461	-0.008722	-0.929171
C	-1.919398	2.756393	-0.087258
C	0.424110	2.850792	-0.836659
H	0.645081	3.300757	0.139095
C	2.625384	0.566837	-0.594729
C	3.720432	-0.078655	0.185737
C	-3.036081	1.906061	-0.018584
H	-3.133092	1.076403	-0.720937
C	-0.852669	2.519389	-1.104516
C	-1.849945	3.816868	0.832949
H	-1.018417	4.523841	0.782860
C	-1.277565	1.825570	-2.373884
H	-1.432614	0.747458	-2.198103
H	-0.531747	1.922563	-3.172255
H	-2.228875	2.232628	-2.749805
C	2.809263	2.007721	-0.995685
H	3.705862	2.065564	-1.635836
H	3.067402	2.572993	-0.083065
C	-4.021234	2.082346	0.952589
H	-4.869623	1.394083	0.988832
C	1.629941	2.667202	-1.712273
H	1.389632	2.100427	-2.621580
H	1.975137	3.662997	-2.041616
C	3.458563	-0.631240	1.447551
H	2.441693	-0.614345	1.845378
C	-2.836137	3.997745	1.800581
H	-2.756787	4.832867	2.501181
C	5.029453	-0.095795	-0.309600

H	5.247036	0.333442	-1.290817
C	-3.925558	3.127788	1.870199
H	-4.698672	3.270227	2.629023
C	4.489320	-1.194283	2.195256
H	4.275261	-1.617393	3.179589
C	5.791079	-1.220742	1.689752
H	6.597411	-1.667836	2.276047
C	6.058222	-0.672561	0.436264
H	7.074086	-0.689809	0.034604
O	1.482375	-1.344442	-0.578435
C	0.194582	-1.802724	-0.435028
C	-0.071456	-3.120988	-0.826588
C	-0.819173	-1.025740	0.141364
C	-1.334781	-3.665838	-0.648447
H	0.731940	-3.712553	-1.273197
C	-2.091084	-1.554129	0.312916
H	-0.606101	0.000984	0.447877
C	-2.374060	-2.886077	-0.079665
H	-1.561988	-4.688918	-0.946132
H	-2.893554	-0.964868	0.754754
N	-3.646878	-3.415610	0.088682
O	-4.557830	-2.684497	0.595231
O	-3.868594	-4.616915	-0.268788

There are no imaginary frequencies

INT4

Charge: 0

O	-0.771190	-1.913104	-1.151653
O	-5.425992	0.766216	1.018613
C	-3.417282	0.041120	0.078727
H	-2.947212	0.303414	1.029392
C	-1.204092	-0.792991	-0.822054
C	-2.674995	-0.506472	-0.966517
C	-4.800708	0.241800	-0.052434
C	-3.322462	-0.879172	-2.155029
H	-2.745414	-1.328539	-2.965458
C	-5.439324	-0.108613	-1.247335
H	-6.511335	0.040755	-1.379091
C	-4.689022	-0.668334	-2.286616
H	-5.195485	-0.943245	-3.215262
C	-6.818362	0.970849	0.962099

H	-7.364057	0.025549	0.801517
H	-7.095130	1.685064	0.168177
H	-7.113367	1.389356	1.932513
C	-0.369593	0.250772	-0.320604
N	0.958375	0.111307	0.033420
C	1.591336	1.305028	0.375241
C	0.778135	2.387712	0.300318
S	-0.835478	1.930212	-0.194078
C	1.128206	3.818346	0.587593
H	1.350091	3.929069	1.664126
H	0.246527	4.447054	0.392518
C	2.312325	4.346795	-0.229548
H	2.122439	4.159587	-1.300443
H	2.346145	5.440854	-0.103562
C	3.677010	3.779520	0.163448
H	4.451603	4.332838	-0.392202
H	3.856908	3.992444	1.232673
C	3.891731	2.285308	-0.083289
H	3.725603	2.051900	-1.148901
H	4.948421	2.053212	0.124142
C	3.037007	1.345594	0.775561
H	3.101531	1.656135	1.832720
H	3.454475	0.332001	0.728336
C	1.564604	-1.169648	0.271675
C	2.441323	-1.698331	-0.688621
C	3.030317	-2.936560	-0.420059
C	2.752983	-3.618613	0.762164
C	1.888926	-3.066510	1.702775
C	1.282614	-1.825376	1.480671
C	0.334394	-1.241508	2.516005
C	0.993861	-1.122322	3.892074
H	1.248788	-2.109155	4.310171
H	0.310412	-0.628985	4.600882
H	1.917857	-0.525351	3.841405
C	-0.963984	-2.052989	2.581171
H	-1.690594	-1.569551	3.253123
H	-1.424565	-2.148293	1.586593
H	-0.776152	-3.069596	2.963936
H	0.068234	-0.223236	2.199094
H	1.681927	-3.608429	2.629012
H	3.218549	-4.588567	0.953258
H	3.711701	-3.379434	-1.150639
C	2.718245	-0.977406	-1.996267
C	4.215702	-0.804612	-2.257883

H	4.718338	-0.310857	-1.411783
H	4.714018	-1.772116	-2.429979
H	4.377276	-0.186696	-3.155137
C	2.016041	-1.692546	-3.154839
H	0.943751	-1.808469	-2.938372
H	2.443045	-2.696453	-3.314987
H	2.131699	-1.123629	-4.091110
H	2.280842	0.028897	-1.921605

There are no imaginary frequencies

INT5

Charge: –1

O	-3.454390	0.000001	0.000001
C	-2.212052	0.000000	0.000000
C	-1.420099	1.225144	0.000024
C	-1.420100	-1.225144	-0.000024
C	-0.047774	1.220897	0.000026
H	-1.968810	2.171930	0.000037
C	-0.047774	-1.220898	-0.000027
H	-1.968811	-2.171930	-0.000037
C	0.662718	-0.000001	-0.000000
H	0.516113	2.155562	0.000042
H	0.516112	-2.155563	-0.000044
N	2.083840	-0.000001	0.000000
O	2.679007	-1.074830	-0.000101
O	2.679008	1.074831	0.000101

There are no imaginary frequencies

INT6

Charge: 0

O	3.415050	0.083534	-0.000006
C	2.079272	0.019527	-0.000003
C	1.385751	-1.200772	0.000033
C	1.369434	1.230556	-0.000037
C	-0.001254	-1.210877	0.000034
H	1.938923	-2.143590	0.000061
C	-0.015526	1.222560	-0.000034
H	1.921640	2.171789	-0.000066

C	-0.690479	0.000677	0.000001
H	-0.550221	-2.152165	0.000061
H	-0.578254	2.155723	-0.000059
N	-2.149631	-0.008869	0.000002
O	-2.729386	1.059875	0.000020
O	-2.715703	-1.084942	-0.000014
H	3.792451	-0.807436	0.000021

There are no imaginary frequencies

INT7

Charge: 0

N	-1.195442	0.903305	1.321308
C	3.076590	-0.000349	-0.020490
C	1.118221	1.244801	-0.833037
H	1.167257	0.597200	-1.716969
C	-1.838324	0.836871	0.243795
C	-3.091052	0.011840	0.165718
C	4.372250	0.179831	0.491705
H	4.630932	1.108068	1.005885
C	2.041523	1.065992	0.129485
C	2.789355	-1.216923	-0.662881
H	1.779576	-1.405350	-1.035343
C	2.121519	1.907677	1.377517
H	2.312576	1.277811	2.260233
H	1.196130	2.467930	1.558668
H	2.947359	2.635894	1.317757
C	-1.377988	1.597317	-0.990983
H	-2.137758	2.369326	-1.194915
H	-1.407699	0.900999	-1.845298
C	5.349946	-0.803219	0.340882
H	6.352823	-0.632347	0.740190
C	0.002164	2.247070	-0.874343
H	0.024627	2.924845	-0.009720
H	0.136073	2.877754	-1.768976
C	-3.355109	-0.941726	1.160918
H	-2.637908	-1.084951	1.972360
C	3.764668	-2.200801	-0.812184
H	3.512254	-3.139196	-1.312364
C	-4.007808	0.179141	-0.879579
H	-3.827374	0.915065	-1.665015
C	5.052464	-1.997816	-0.314224

H	5.816583	-2.770451	-0.428227
C	-4.515072	-1.708557	1.112613
H	-4.706867	-2.450374	1.891227
C	-5.427554	-1.533479	0.070053
H	-6.337877	-2.136299	0.031505
C	-5.171113	-0.589555	-0.923090
H	-5.880689	-0.447744	-1.741404

There are no imaginary frequencies

INT8

Charge: 0

N	-0.724750	-0.255520	-0.347380
C	3.013136	-0.280201	0.016334
C	0.556811	0.419704	-0.125643
H	0.842565	0.850420	-1.101077
C	-1.679919	0.490417	0.058081
C	-3.100052	0.097029	-0.097484
C	4.031122	-1.184294	0.435588
H	3.761611	-2.077084	1.002570
C	1.638955	-0.517763	0.338862
C	3.439407	0.860193	-0.723773
H	2.708778	1.596808	-1.062744
C	1.242546	-1.652034	1.231876
H	1.384405	-2.630499	0.738171
H	0.182833	-1.583416	1.511927
H	1.840840	-1.677969	2.157905
C	-1.244661	1.809676	0.660519
H	-1.789173	2.058247	1.582565
H	-1.442986	2.618698	-0.063655
C	5.367801	-0.964057	0.131050
H	6.120018	-1.682696	0.466602
C	0.250054	1.566631	0.871667
H	0.434890	1.216965	1.899788
H	0.876492	2.451405	0.696948
C	-3.428525	-1.163946	-0.619699
H	-2.621084	-1.841324	-0.904741
C	4.779170	1.071715	-1.020019
H	5.068425	1.960320	-1.587061
C	-4.133464	0.970622	0.266135
H	-3.901643	1.958071	0.670903
C	5.757398	0.164210	-0.598564

H	6.810141	0.335221	-0.834740
C	-4.758371	-1.541999	-0.770621
H	-5.000848	-2.527148	-1.176155
C	-5.782648	-0.664111	-0.405131
H	-6.827367	-0.961154	-0.524279
C	-5.467274	0.591692	0.111139
H	-6.263562	1.282868	0.396825

There are no imaginary frequencies

INT9

Charge: 0

O	-0.077200	-0.416960	1.399373
O	-1.914054	3.534324	-2.718167
N	-3.335798	-0.983396	0.294847
C	-0.085191	-2.654033	-0.715099
C	-1.129102	1.817984	-1.343969
H	-0.581948	1.480978	-2.226347
C	-2.181702	-1.874222	0.365237
H	-1.740977	-1.749584	1.368730
C	-4.416290	-1.647966	0.423657
C	-0.261512	-0.183866	0.123609
C	-5.740161	-0.982124	0.439360
C	0.096999	-3.380444	-1.900632
H	-0.449392	-3.111151	-2.805198
C	-1.053191	1.144236	-0.128839
C	-1.045820	-1.460789	-0.614753
C	0.646854	-3.065962	0.410608
H	0.517736	-2.497617	1.329735
C	-1.683918	-1.139611	-1.968582
H	-2.396821	-0.314295	-1.870766
H	-2.247488	-2.007102	-2.346838
H	-0.959994	-0.868675	-2.750400
C	-4.220374	-3.138284	0.600221
H	-4.924147	-3.737172	0.004129
H	-4.387174	-3.401234	1.659468
C	-1.926748	2.962948	-1.492897
C	0.992428	-4.449982	-1.968582
H	1.114394	-4.988602	-2.911979
C	-2.756036	-3.296991	0.182344
H	-2.700200	-3.603337	-0.874537
H	-2.214191	-4.048830	0.770521

C	-6.909035	-1.706022	0.707491
H	-6.855064	-2.778441	0.907851
C	1.548293	-4.126103	0.345170
H	2.113815	-4.407597	1.238065
C	-1.746647	1.665054	0.970192
H	-1.639149	1.138649	1.918691
C	-5.837289	0.396416	0.189458
H	-4.925621	0.961174	-0.018348
C	-2.664869	3.442804	-0.406758
H	-3.298375	4.325935	-0.494842
C	1.730838	-4.826166	-0.848492
H	2.436162	-5.659151	-0.903085
C	-8.149341	-1.066540	0.727844
H	-9.052696	-1.642678	0.941562
C	-8.235323	0.301863	0.476679
H	-9.206643	0.802152	0.490919
C	-2.551146	2.787617	0.824762
H	-3.108141	3.174693	1.682522
C	-7.074271	1.031962	0.206543
H	-7.135997	2.104784	0.008365
C	-2.681235	4.692873	-2.931100
H	-2.363340	5.522014	-2.275614
H	-3.758112	4.507675	-2.775580
H	-2.522741	4.989157	-3.975955
C	1.147564	-0.007512	-0.563221
N	2.243480	0.402632	0.090754
C	3.436513	0.338705	-0.642375
C	3.234010	-0.065160	-1.922571
S	1.564054	-0.405749	-2.165718
C	4.265891	-0.295129	-2.984439
H	4.770709	0.662269	-3.199208
H	3.763616	-0.597677	-3.914782
C	5.307261	-1.350336	-2.594535
H	4.784663	-2.268295	-2.275104
H	5.875975	-1.611084	-3.500854
C	6.297506	-0.908443	-1.516379
H	7.061698	-1.695300	-1.410496
H	6.831285	-0.008329	-1.870279
C	5.715946	-0.623481	-0.130180
H	5.183414	-1.514206	0.243204
H	6.554066	-0.447640	0.562245
C	4.786427	0.596437	-0.044620
H	5.257271	1.441318	-0.573614
H	4.672913	0.908809	1.000719

C	2.233104	1.095272	1.371777
C	2.527567	0.399041	2.554491
C	2.596086	1.139467	3.736133
C	2.392299	2.516443	3.738659
C	2.132043	3.181983	2.547667
C	2.057640	2.489603	1.332196
C	1.863697	3.272570	0.039373
C	3.185722	3.896003	-0.423344
H	3.564198	4.609495	0.326528
H	3.039082	4.443171	-1.367853
H	3.964370	3.139699	-0.590948
C	0.786734	4.352350	0.161421
H	0.543332	4.753123	-0.834643
H	-0.136741	3.953858	0.602383
H	1.126272	5.198638	0.779467
H	1.530573	2.575890	-0.742691
H	1.997016	4.265249	2.557107
H	2.448703	3.075637	4.675579
H	2.815543	0.626170	4.675444
C	2.782370	-1.095831	2.598267
C	4.208124	-1.405495	3.067806
H	4.966303	-0.867193	2.482252
H	4.345052	-1.128341	4.125640
H	4.413658	-2.484118	2.978491
C	1.758454	-1.800615	3.492816
H	0.743847	-1.523389	3.177625
H	1.897656	-1.522910	4.550408
H	1.874998	-2.894146	3.422696
H	2.661002	-1.487138	1.577757

There are no imaginary frequencies

PRODUCT

Charge: 0

O	-0.294804	-0.718099	2.118879
O	-5.106441	-1.046949	-1.224044
N	2.160426	-0.056064	0.411847
C	-1.161217	1.760281	0.077648
C	-3.046221	-0.833494	-0.157353
H	-3.009182	0.167824	-0.586194
C	1.154268	0.990043	0.579312
H	1.049677	1.158955	1.663556

C	3.268843	0.465363	0.050619
C	-0.812325	-0.513272	1.042841
C	4.489833	-0.349726	-0.152950
C	-1.553235	2.412990	-1.096815
H	-1.231692	2.036798	-2.069093
C	-2.027523	-1.320898	0.660886
C	-0.238304	0.536048	0.060472
C	-1.596091	2.281794	1.304346
H	-1.301580	1.796594	2.238463
C	-0.088817	-0.103271	-1.328068
H	0.439758	-1.063199	-1.243099
H	0.504540	0.540194	-1.994072
H	-1.055449	-0.287264	-1.813601
C	3.239643	1.970150	-0.106660
H	3.748338	2.313280	-1.018838
H	3.761946	2.431873	0.748965
C	-4.174934	-1.617444	-0.437437
C	-2.361548	3.549244	-1.046906
H	-2.655176	4.042340	-1.976813
C	1.734900	2.249558	-0.095838
H	1.364067	2.346059	-1.127741
H	1.465290	3.170027	0.437718
C	5.717040	0.255781	-0.454184
H	5.787341	1.341987	-0.542521
C	-2.406901	3.414124	1.356342
H	-2.737915	3.797856	2.324346
C	-2.137475	-2.609421	1.208516
H	-1.345129	-2.986113	1.856883
C	4.432377	-1.747858	-0.040482
H	3.476458	-2.218516	0.197582
C	-4.272320	-2.907706	0.095976
H	-5.135303	-3.540444	-0.113420
C	-2.794577	4.053270	0.178592
H	-3.431302	4.940302	0.215980
C	6.862193	-0.519358	-0.639750
H	7.812865	-0.033856	-0.872155
C	6.793416	-1.907196	-0.529380
H	7.690050	-2.514007	-0.676796
C	-3.246860	-3.390544	0.913329
H	-3.327927	-4.398911	1.326045
C	5.573743	-2.520006	-0.229091
H	5.514856	-3.607463	-0.140986
C	-6.270009	-1.775447	-1.541122
H	-6.846945	-2.036518	-0.637854

H	-6.035118	-2.698320	-2.097887
H	-6.882876	-1.124691	-2.177128

There are no imaginary frequencies

TS1

Charge: 0

O	0.886586	-2.390666	1.066584
O	5.477934	1.382136	0.855708
C	3.555292	0.058407	0.957166
H	3.187602	0.739286	1.730778
C	1.425587	-1.280559	1.158415
C	2.788608	-1.026324	0.542557
C	4.816784	0.302612	0.393149
C	3.294703	-1.908899	-0.419478
H	2.698203	-2.777126	-0.705238
C	5.312635	-0.565663	-0.587936
H	6.289972	-0.403374	-1.043471
C	4.544571	-1.667742	-0.978352
H	4.945367	-2.348553	-1.734085
C	6.750316	1.677966	0.331050
H	6.709880	1.878713	-0.753168
H	7.470528	0.863320	0.518249
H	7.099251	2.582724	0.844633
C	0.383625	0.175781	0.122128
N	-0.930285	0.158544	-0.107093
C	-1.538440	1.369622	-0.488429
C	-0.630329	2.376097	-0.572007
S	0.942775	1.757881	-0.155565
C	-0.862262	3.802440	-0.975019
H	-1.107752	3.830363	-2.051394
H	0.078207	4.361710	-0.861260
C	-1.967755	4.509979	-0.185832
H	-1.752167	4.426035	0.893232
H	-1.916696	5.582295	-0.432679
C	-3.387454	4.018718	-0.469804
H	-4.092281	4.708278	0.022453
H	-3.586629	4.099789	-1.553584
C	-3.715365	2.598594	-0.007353
H	-3.498917	2.500068	1.070045
H	-4.799241	2.440492	-0.122590
C	-3.008437	1.469678	-0.765128

H	-3.155277	1.606781	-1.850851
H	-3.485375	0.514215	-0.510043
C	-1.695105	-1.065607	-0.017079
C	-2.259479	-1.426044	1.211226
C	-3.029532	-2.593981	1.248492
C	-3.215761	-3.362811	0.105277
C	-2.638195	-2.978838	-1.103589
C	-1.868580	-1.816327	-1.191614
C	-1.193385	-1.403702	-2.490034
C	-2.001220	-1.755193	-3.738227
H	-2.056042	-2.842660	-3.903774
H	-1.524154	-1.315420	-4.627571
H	-3.029507	-1.365744	-3.678270
C	0.217949	-1.999470	-2.549096
H	0.758064	-1.640310	-3.439329
H	0.797152	-1.727067	-1.655326
H	0.172695	-3.100014	-2.595480
H	-1.085288	-0.308006	-2.476133
H	-2.792710	-3.595989	-1.990632
H	-3.818441	-4.272981	0.153299
H	-3.485488	-2.906470	2.191246
C	-2.047537	-0.610977	2.474190
C	-3.369093	-0.055619	3.011310
H	-3.893077	0.542551	2.250047
H	-4.044737	-0.866448	3.328283
H	-3.188352	0.589591	3.885484
C	-1.307823	-1.441175	3.528952
H	-0.417144	-1.913400	3.087483
H	-1.953978	-2.240740	3.927300
H	-1.001314	-0.808059	4.376487
H	-1.407827	0.247540	2.222357
H	1.271000	-0.654844	2.074248

1 imaginary frequency: –197.18 cm^{-1}

TS2

Charge: 0

N	-0.567144	-0.129551	0.189562
C	2.990074	0.068007	0.044597
C	0.901582	1.268263	-0.516043
H	0.935177	0.728601	-1.468080
C	-1.602922	0.494682	-0.178335

C	-2.957447	-0.118036	0.010846
C	4.307431	0.155347	0.537419
H	4.618386	1.031776	1.109534
C	2.011177	1.141861	0.302941
C	2.640841	-1.089489	-0.681488
H	1.615924	-1.217400	-1.034954
C	2.243786	2.026754	1.494684
H	2.562025	1.440616	2.371174
H	1.345324	2.590738	1.774817
H	3.041254	2.764014	1.297201
C	-1.467551	1.845660	-0.858401
H	-2.278584	2.529996	-0.570549
H	-1.557526	1.681835	-1.946447
C	5.238517	-0.851147	0.290515
H	6.256485	-0.749471	0.674966
C	-0.092991	2.391912	-0.491340
H	-0.137753	2.857789	0.502891
H	0.207134	3.176863	-1.204586
C	-3.124307	-1.189088	0.901899
H	-2.261933	-1.552689	1.464849
C	3.571219	-2.097133	-0.920916
H	3.269577	-2.986435	-1.480039
C	-4.067460	0.349112	-0.704721
H	-3.962773	1.177891	-1.407787
C	4.877557	-1.982708	-0.441756
H	5.606652	-2.774160	-0.630771
C	-4.373170	-1.778422	1.072899
H	-4.490089	-2.607736	1.774523
C	-5.474121	-1.310157	0.351876
H	-6.454662	-1.773147	0.485847
C	-5.317376	-0.247889	-0.537024
H	-6.173643	0.122612	-1.105439

1 imaginary frequency: –492.10 cm^{-1}

TS3

Charge: 0

O	-0.283943	-0.071321	1.379381
O	-2.163066	3.827535	-2.756298
N	-3.251430	-1.164671	0.062154
C	0.091423	-2.240408	-1.377670
C	-1.283156	2.198152	-1.341149

H	-0.563786	2.038689	-2.143450
C	-1.996877	-1.908529	-0.019486
H	-1.466227	-1.709713	0.936107
C	-4.211199	-1.945779	0.369197
C	-0.245107	0.414602	0.222935
C	-5.589098	-1.441073	0.577814
C	0.660507	-2.376216	-2.666128
H	0.173944	-1.917457	-3.527777
C	-1.263723	1.464593	-0.155194
C	-1.094167	-1.427274	-1.131605
C	0.759600	-2.903495	-0.320316
H	0.361104	-2.825684	0.689893
C	-1.785201	-0.838933	-2.327844
H	-2.617979	-0.194327	-2.021693
H	-2.203022	-1.631916	-2.979961
H	-1.111206	-0.242424	-2.962374
C	-3.812820	-3.396072	0.541293
H	-4.522533	-4.094350	0.074508
H	-3.781024	-3.636749	1.618431
C	-2.245565	3.193912	-1.566805
C	1.830063	-3.106090	-2.875953
H	2.235944	-3.186961	-3.887947
C	-2.423544	-3.400052	-0.098536
H	-2.494826	-3.709063	-1.154219
H	-1.716542	-4.074741	0.400262
C	-6.609552	-2.293094	1.019610
H	-6.397567	-3.346720	1.214267
C	1.929407	-3.621383	-0.530259
H	2.421896	-4.105222	0.317921
C	-2.225596	1.760609	0.826622
H	-2.199404	1.192434	1.755524
C	-5.889011	-0.090014	0.339133
H	-5.093705	0.575726	-0.003106
C	-3.202867	3.475806	-0.588017
H	-3.958748	4.247390	-0.736096
C	2.482830	-3.725591	-1.811682
H	3.402776	-4.291762	-1.975531
C	-7.901919	-1.806237	1.220511
H	-8.687458	-2.481592	1.567558
C	-8.189564	-0.463899	0.979079
H	-9.201956	-0.083305	1.134554
C	-3.173375	2.748615	0.607480
H	-3.915616	2.968567	1.379345
C	-7.177959	0.393570	0.537167

H	-7.397644	1.446801	0.346239
C	-3.096133	4.837819	-3.051737
H	-3.034485	5.675765	-2.336330
H	-4.129831	4.451566	-3.061689
H	-2.849433	5.211074	-4.053821
C	1.085816	0.469035	-0.420586
N	2.228268	0.377187	0.307876
C	3.401945	0.352331	-0.449903
C	3.170444	0.456896	-1.781836
S	1.471773	0.585307	-2.084827
C	4.180726	0.426495	-2.889121
H	4.823906	1.320405	-2.810867
H	3.658533	0.505335	-3.854013
C	5.052722	-0.835109	-2.885366
H	4.397315	-1.721580	-2.869284
H	5.600041	-0.864664	-3.840824
C	6.073940	-0.922770	-1.749631
H	6.712102	-1.802321	-1.933425
H	6.741685	-0.044063	-1.801838
C	5.516359	-1.027847	-0.328415
H	4.858765	-1.910048	-0.241223
H	6.360639	-1.198235	0.358078
C	4.760514	0.212591	0.164620
H	5.347364	1.116652	-0.070882
H	4.668239	0.182584	1.256495
C	2.289790	0.769123	1.705904
C	2.515479	-0.187996	2.705977
C	2.639425	0.264275	4.022011
C	2.545474	1.618159	4.329527
C	2.334837	2.546999	3.317006
C	2.209141	2.145498	1.982194
C	2.046499	3.205811	0.901501
C	3.352289	3.985871	0.718096
H	3.616553	4.542774	1.631602
H	3.255301	4.711915	-0.104364
H	4.188307	3.310329	0.478401
C	0.863944	4.137828	1.178334
H	0.708479	4.815711	0.324425
H	-0.065726	3.568976	1.331948
H	1.035246	4.762163	2.069693
H	1.835272	2.709103	-0.054148
H	2.278088	3.609915	3.563369
H	2.643526	1.951812	5.365271
H	2.808609	-0.460584	4.822126

C	2.602847	-1.671215	2.407559
C	3.937473	-2.277230	2.849133
H	4.795439	-1.745219	2.411829
H	4.049039	-2.253542	3.945206
H	3.998418	-3.330929	2.533742
C	1.422591	-2.412292	3.041788
H	0.475914	-1.954103	2.722359
H	1.476758	-2.375499	4.142201
H	1.426348	-3.473521	2.745278
H	2.525618	-1.791039	1.319262

1 imaginary frequency: –472.30 cm^{-1}

TS3'

Charge: 0

O	0.227902	-1.587632	0.660625
O	-2.352767	3.616615	2.107387
N	-3.008398	-0.969278	-0.752520
C	-1.185464	1.733929	1.386137
H	-0.607042	2.451215	0.807779
C	-1.762578	-1.284448	-1.440680
H	-1.217657	-1.988485	-0.774495
C	-3.963603	-1.672693	-1.220540
C	0.123499	-0.340878	0.549892
C	-5.327308	-1.606780	-0.645206
C	-0.950987	0.360429	1.344387
C	-0.784879	-0.155008	-1.675286
C	-3.568623	-2.595905	-2.353125
H	-4.292172	-2.597164	-3.180979
H	-3.509775	-3.630043	-1.970671
C	-2.217707	2.274452	2.169552
C	-2.197321	-2.033969	-2.729977
H	-2.300613	-1.314196	-3.558712
H	-1.478878	-2.804681	-3.038413
C	-6.359338	-2.416036	-1.137838
H	-6.167362	-3.109442	-1.959528
C	-1.763657	-0.476425	2.133431
H	-1.572402	-1.548672	2.103693
C	-5.601723	-0.728774	0.416127
H	-4.795842	-0.104640	0.808202
C	-3.025665	1.435000	2.938999
H	-3.833244	1.829611	3.556124

C	-7.638603	-2.348129	-0.584458
H	-8.433544	-2.985985	-0.977924
C	-7.901474	-1.470175	0.465947
H	-8.903624	-1.416533	0.898107
C	-2.776460	0.056667	2.913290
H	-3.401222	-0.605299	3.518684
C	-6.877789	-0.659963	0.965177
H	-7.076913	0.028264	1.790205
C	-3.394663	4.226132	2.828876
H	-3.292409	4.063603	3.915585
H	-4.384704	3.862193	2.504344
H	-3.330647	5.302733	2.625863
C	1.340538	0.398743	0.170452
N	2.568886	-0.188339	0.176915
C	3.608479	0.631752	-0.273742
C	3.191107	1.878278	-0.602502
S	1.482672	2.025488	-0.363381
C	4.012633	2.999049	-1.164815
H	4.754088	3.314781	-0.410386
H	3.362395	3.868589	-1.341407
C	4.732617	2.626882	-2.466574
H	3.997243	2.211707	-3.177125
H	5.113714	3.556844	-2.917348
C	5.907454	1.660470	-2.303994
H	6.418451	1.576240	-3.276807
H	6.641475	2.109116	-1.610822
C	5.576592	0.247750	-1.817771
H	4.864984	-0.235154	-2.509436
H	6.500694	-0.350431	-1.855396
C	5.026136	0.158707	-0.388542
H	5.654002	0.767215	0.284250
H	5.101244	-0.873596	-0.027658
C	2.891333	-1.347383	0.990949
C	3.177058	-2.582034	0.389025
C	3.557390	-3.638060	1.220959
C	3.656833	-3.469673	2.598867
C	3.386960	-2.230229	3.166927
C	3.008481	-1.139782	2.375596
C	2.756891	0.205270	3.041637
C	4.033894	0.745991	3.691283
H	4.379074	0.093352	4.509132
H	3.854462	1.746857	4.114323
H	4.849348	0.829734	2.955842
C	1.600790	0.122586	4.042334

H	1.362330	1.122863	4.436764
H	0.693441	-0.279891	3.567441
H	1.853908	-0.523507	4.898327
H	2.461052	0.932275	2.274145
H	3.478796	-2.099926	4.248033
H	3.953027	-4.309108	3.232387
H	3.776317	-4.613660	0.779978
C	3.059037	-2.810328	-1.105840
C	4.368304	-3.306935	-1.724674
H	5.207743	-2.630602	-1.504826
H	4.636552	-4.308969	-1.353430
H	4.268421	-3.376171	-2.819360
C	1.905405	-3.774752	-1.400719
H	0.984201	-3.426264	-0.911687
H	2.133693	-4.786384	-1.027586
H	1.726769	-3.850093	-2.485158
H	2.818439	-1.843747	-1.570304
C	0.404506	-0.670024	-2.445440
H	1.271079	0.005853	-2.425227
H	0.719142	-1.631999	-2.025534
H	0.162996	-0.838844	-3.511694
C	-1.222265	1.205416	-1.963323
C	-2.379688	1.791692	-1.385025
C	-0.464880	2.042573	-2.823598
C	-2.736451	3.110029	-1.638166
H	-2.997237	1.185698	-0.726604
C	-0.827158	3.364931	-3.074118
H	0.414516	1.647318	-3.332012
C	-1.960541	3.914795	-2.478376
H	-3.632145	3.520047	-1.163968
H	-0.212819	3.969664	-3.746703
H	-2.243278	4.952502	-2.671875

1 imaginary frequency: –465.69 cm^{-1}

TS4

Charge: 0

O	-0.363128	-0.397631	1.467918
O	-1.551995	3.611562	-2.736487
N	-3.496489	-1.057613	0.382153
C	-0.183917	-2.586923	-0.654594
C	-1.098661	1.841889	-1.286733

H	-0.506225	1.429561	-2.102738
C	-2.373544	-1.986534	0.340901
H	-1.967819	-2.046298	1.363759
C	-4.600354	-1.694621	0.329047
C	-0.617233	-0.195653	0.271753
C	-5.905387	-0.994903	0.385272
C	0.014314	-3.297480	-1.846565
H	-0.550677	-3.044187	-2.743726
C	-1.198516	1.189636	-0.061233
C	-1.204862	-1.445641	-0.546840
C	0.572302	-2.978508	0.460003
H	0.427191	-2.444470	1.395182
C	-1.769856	-1.064482	-1.915608
H	-2.510067	-0.262146	-1.819610
H	-2.281983	-1.916228	-2.385593
H	-0.990577	-0.729076	-2.614642
C	-4.458638	-3.198714	0.247308
H	-5.125036	-3.647745	-0.503310
H	-4.728354	-3.638872	1.222790
C	-1.743784	3.064282	-1.515859
C	0.954172	-4.325655	-1.933064
H	1.088879	-4.850850	-2.882203
C	-2.968806	-3.350803	-0.075550
H	-2.833799	-3.526436	-1.153290
H	-2.493539	-4.187324	0.452875
C	-7.107503	-1.713155	0.423094
H	-7.094199	-2.805310	0.413792
C	1.521444	-3.995241	0.376080
H	2.106985	-4.258131	1.261536
C	-1.925586	1.808030	0.966968
H	-1.986000	1.310177	1.934743
C	-5.951082	0.408542	0.402166
H	-5.013773	0.968701	0.373672
C	-2.514227	3.647308	-0.504540
H	-3.031815	4.594472	-0.658588
C	1.723785	-4.675103	-0.825357
H	2.466800	-5.473423	-0.894988
C	-8.330683	-1.043681	0.477142
H	-9.260667	-1.616121	0.507816
C	-8.365547	0.349733	0.491184
H	-9.323418	0.873906	0.531645
C	-2.582061	3.012004	0.738272
H	-3.162748	3.475175	1.540357
C	-7.170958	1.074541	0.453398

H	-7.193064	2.166926	0.463846
C	-2.135229	4.860426	-3.015793
H	-1.774742	5.644675	-2.328208
H	-3.236939	4.820034	-2.966246
H	-1.839065	5.125025	-4.038873
C	1.285521	0.020872	-0.660294
N	2.370969	0.377789	0.043629
C	3.624136	0.193698	-0.576783
C	3.496827	-0.289218	-1.838072
S	1.814655	-0.521971	-2.182854
C	4.590588	-0.634295	-2.803769
H	5.134330	0.288313	-3.072779
H	4.140715	-1.009913	-3.734619
C	5.582341	-1.670128	-2.263338
H	5.021472	-2.550844	-1.905624
H	6.203148	-2.013882	-3.105931
C	6.510785	-1.159604	-1.160870
H	7.257512	-1.942763	-0.951670
H	7.076758	-0.291622	-1.544306
C	5.847436	-0.772269	0.162075
H	5.278435	-1.630202	0.557631
H	6.643095	-0.561020	0.894069
C	4.933078	0.459469	0.103927
H	5.458890	1.266499	-0.433929
H	4.748985	0.838373	1.117356
C	2.266059	1.112646	1.292006
C	2.446841	0.459388	2.522397
C	2.378972	1.234648	3.684931
C	2.142517	2.602215	3.626855
C	1.977035	3.227129	2.395554
C	2.040936	2.501459	1.201584
C	1.926524	3.231520	-0.130783
C	3.302533	3.694720	-0.624171
H	3.761066	4.390046	0.097743
H	3.204616	4.220769	-1.586870
H	3.995462	2.855763	-0.771790
C	0.962590	4.417807	-0.076618
H	0.727782	4.754858	-1.097800
H	0.017458	4.150613	0.415886
H	1.398647	5.275529	0.460009
H	1.524652	2.524572	-0.870013
H	1.801893	4.303734	2.362601
H	2.091692	3.188379	4.547515
H	2.515024	0.753371	4.656258

C	2.731473	-1.027286	2.652033
C	4.128155	-1.278683	3.233540
H	4.915605	-0.747671	2.682544
H	4.178626	-0.950594	4.284404
H	4.363790	-2.354495	3.210095
C	1.676564	-1.723785	3.519135
H	0.666314	-1.469011	3.174686
H	1.772705	-1.423887	4.575162
H	1.807490	-2.816877	3.477030
H	2.690651	-1.468805	1.644930

1 imaginary frequency: –126.78 cm^{-1}

TS3a

Charge: 0

O	-0.133011	-0.922800	0.865548
O	-1.782868	4.530629	-0.971326
N	-3.193012	-1.123219	-0.661772
C	-1.003866	2.388065	-0.487229
H	-0.310665	2.567855	-1.308057
C	-1.998162	-1.821445	-1.129434
H	-1.439633	-2.109249	-0.213198
C	-4.202947	-1.900688	-0.695466
C	-0.076253	0.031555	0.052540
C	-5.536479	-1.465478	-0.216782
C	-1.020335	1.196681	0.237553
C	-1.079648	-0.942130	-1.945791
C	-1.743741	0.164258	-2.713610
H	-2.521879	0.647597	-2.110577
H	-2.228921	-0.220598	-3.632924
H	-1.037431	0.942899	-3.041582
C	-3.910043	-3.291889	-1.215504
H	-4.676444	-3.659425	-1.913158
H	-3.879500	-3.996331	-0.365803
C	-1.893553	3.432505	-0.193477
C	-2.534869	-3.086901	-1.852967
H	-2.645008	-2.878699	-2.929794
H	-1.871968	-3.954688	-1.746361
C	-6.610082	-2.363559	-0.159543
H	-6.473431	-3.401285	-0.471647
C	-1.942509	1.071161	1.291417
H	-1.943998	0.143042	1.861470

C	-5.739543	-0.138112	0.194489
H	-4.902657	0.562393	0.152503
C	-2.812257	3.295531	0.851099
H	-3.511347	4.093288	1.103056
C	-7.859761	-1.945750	0.300176
H	-8.687543	-2.657561	0.341646
C	-8.051278	-0.625614	0.704480
H	-9.030317	-0.298158	1.062552
C	-2.818079	2.104892	1.586784
H	-3.530092	1.994042	2.408871
C	-6.986099	0.277886	0.650014
H	-7.130399	1.314021	0.965625
C	-2.643300	5.617911	-0.734585
H	-2.508988	6.034985	0.278218
H	-3.702707	5.339702	-0.869043
H	-2.385203	6.389840	-1.470699
C	1.244987	0.293594	-0.559096
N	2.388636	-0.185644	-0.005303
C	3.545467	0.066951	-0.747126
C	3.301820	0.777654	-1.875890
S	1.612786	1.129130	-2.007814
C	4.289928	1.193443	-2.923953
H	4.998431	1.915083	-2.481079
H	3.760172	1.731884	-3.723552
C	5.066428	0.018550	-3.531169
H	4.347734	-0.738542	-3.886046
H	5.595291	0.393446	-4.421724
C	6.095771	-0.634558	-2.606849
H	6.664399	-1.370885	-3.197717
H	6.825639	0.131290	-2.288248
C	5.553918	-1.339824	-1.361542
H	4.834454	-2.125243	-1.651024
H	6.393803	-1.852342	-0.866535
C	4.899330	-0.415903	-0.326671
H	5.547580	0.460381	-0.156145
H	4.821925	-0.932390	0.637101
C	2.500435	-0.474800	1.414476
C	2.670278	-1.792810	1.862987
C	2.847512	-1.994792	3.233990
C	2.858447	-0.924753	4.123535
C	2.701334	0.372870	3.650458
C	2.525812	0.628621	2.285720
C	2.425208	2.071259	1.808973
C	3.782007	2.771378	1.936048

H	4.100677	2.836764	2.988970
H	3.726187	3.795772	1.535440
H	4.562117	2.230196	1.378118
C	1.319039	2.844048	2.532103
H	1.200872	3.843315	2.084490
H	0.352413	2.323155	2.456074
H	1.549646	2.984910	3.600109
H	2.163215	2.075400	0.743167
H	2.726958	1.209704	4.352425
H	2.996791	-1.103571	5.192455
H	2.975065	-3.012242	3.611817
C	2.643378	-2.981604	0.923482
C	3.936302	-3.799261	0.980494
H	4.824340	-3.178246	0.790481
H	4.066184	-4.281884	1.962630
H	3.914480	-4.596838	0.220979
C	1.421577	-3.858910	1.209809
H	0.506473	-3.250918	1.176622
H	1.495256	-4.328473	2.204434
H	1.342464	-4.668384	0.466417
H	2.540763	-2.590019	-0.096735
H	-0.259153	-1.441864	-2.416910

There are no frequencies

TS3a'

Charge: 0

O	-0.053286	-0.760000	1.086157
O	-2.382629	4.293747	-1.120868
N	-3.196855	-1.064955	-0.610296
C	-1.299751	2.338541	-0.463716
H	-0.661198	2.535668	-1.322180
C	-1.947404	-1.765193	-0.881409
H	-1.467513	-1.924041	0.108985
C	-4.173415	-1.885066	-0.608983
C	-0.082411	0.157864	0.229283
C	-5.550697	-1.448000	-0.281705
C	-1.142664	1.224019	0.358713
C	-0.899167	-1.041106	-1.695943
C	-3.791791	-3.318118	-0.911971
H	-4.484398	-3.810758	-1.609444
H	-3.805634	-3.900320	0.026126

C	-2.326634	3.270080	-0.241961
C	-2.378161	-3.138201	-1.466533
H	-2.410755	-3.077045	-2.566870
H	-1.694355	-3.952288	-1.192742
C	-6.609072	-2.364930	-0.239863
H	-6.427919	-3.421039	-0.451189
C	-2.029233	1.067425	1.441681
H	-1.898513	0.198916	2.086493
C	-5.812078	-0.097172	0.000376
H	-4.986332	0.617228	-0.021701
C	-3.207954	3.099291	0.827445
H	-4.013102	3.808375	1.021562
C	-7.901212	-1.941739	0.074210
H	-8.716776	-2.668071	0.104277
C	-8.150690	-0.597932	0.348435
H	-9.162853	-0.266889	0.593139
C	-3.037017	1.990466	1.666406
H	-3.719610	1.854659	2.509408
C	-7.100821	0.323999	0.310683
H	-7.289519	1.378239	0.527360
C	-3.413010	5.241899	-0.990764
H	-3.358823	5.778774	-0.028144
H	-4.410056	4.778510	-1.086282
H	-3.280527	5.964952	-1.805641
C	1.187531	0.479938	-0.445783
N	2.379389	-0.007743	-0.003983
C	3.479403	0.338190	-0.795623
C	3.145741	1.129238	-1.843965
S	1.441075	1.431944	-1.853220
C	4.049293	1.648840	-2.921385
H	4.780308	2.344025	-2.473122
H	3.456388	2.241394	-3.633731
C	4.792621	0.538994	-3.674490
H	4.060443	-0.207824	-4.026921
H	5.241897	0.986831	-4.574965
C	5.903912	-0.150775	-2.880843
H	6.443474	-0.826597	-3.564008
H	6.637265	0.611802	-2.562682
C	5.475963	-0.958810	-1.653814
H	4.762965	-1.748006	-1.948409
H	6.365194	-1.475253	-1.259154
C	4.870950	-0.138419	-0.507278
H	5.508230	0.740209	-0.309708
H	4.874201	-0.732800	0.413716

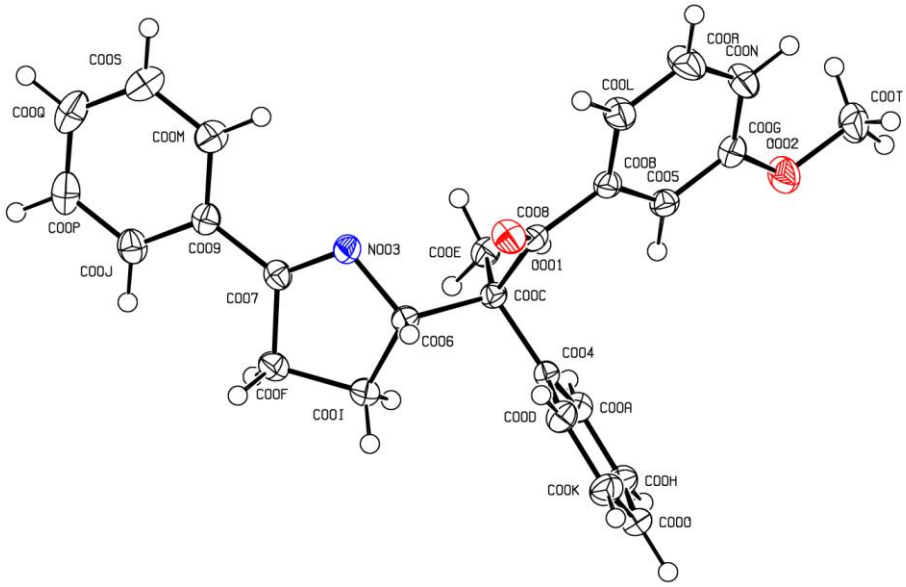
C	2.606109	-0.429523	1.367406
C	2.842128	-1.779770	1.666476
C	3.131843	-2.110640	2.992579
C	3.191766	-1.133816	3.982072
C	2.973039	0.199043	3.654371
C	2.685695	0.581960	2.339329
C	2.487755	2.057879	2.025393
C	3.769660	2.853730	2.287113
H	4.047811	2.833221	3.353029
H	3.632708	3.907223	1.996792
H	4.614149	2.449122	1.707472
C	1.294037	2.634162	2.792031
H	1.099171	3.670991	2.475795
H	0.382634	2.046099	2.606772
H	1.479353	2.644385	3.878209
H	2.261289	2.166831	0.956775
H	3.033732	0.963707	4.432708
H	3.416928	-1.413748	5.013901
H	3.310279	-3.156141	3.255783
C	2.764403	-2.875252	0.620271
C	4.064348	-3.677505	0.518847
H	4.932665	-3.028492	0.331164
H	4.261661	-4.246136	1.441657
H	3.999590	-4.402152	-0.308075
C	1.568833	-3.790293	0.905308
H	0.652232	-3.193624	1.019507
H	1.725661	-4.364406	1.832962
H	1.424788	-4.511632	0.085237
H	2.595963	-2.392486	-0.352590
C	0.285487	-1.948033	-1.912950
H	1.187936	-1.422627	-2.256026
H	0.529641	-2.456256	-0.973370
H	0.072733	-2.730478	-2.665440
H	-1.155028	-0.375822	-2.493961

There are no frequencies

---

7. X-Ray crystallographic Data

7.1 Diffraction data of compound 13 (CCDC 2161395)



Bond precision: C-C = 0.0022 A Wavelength=0.71073

Cell:	a=8.73400	b=27.63100	c=9.16300
	alpha=90	beta=114.9000	gamma=90
Temperature:	120 K		
	Calculated	Reported 2006	
Volume	2005.746		
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C26 H25 N O2	C26 H25 N O2	
Sum formula	C26 H25 N O2	C26 H25 N O2	
Mr	383.47	383.47	
Dx,g cm-3	1.270	1.270	
Z	4	4	
Mu (mm-1)	0.080	0.080	
F000	816.0	816.0	
F000’	816.34		
h,k,lmax	11,35,11	11,35,11	
Nref	4616	4599	
Tmin,Tmax	0.980,0.986	0.636,0.729	
Tmin’	0.976		

Correction method= # Reported T Limits: Tmin=0.636 Tmax=0.729 AbsCorr =

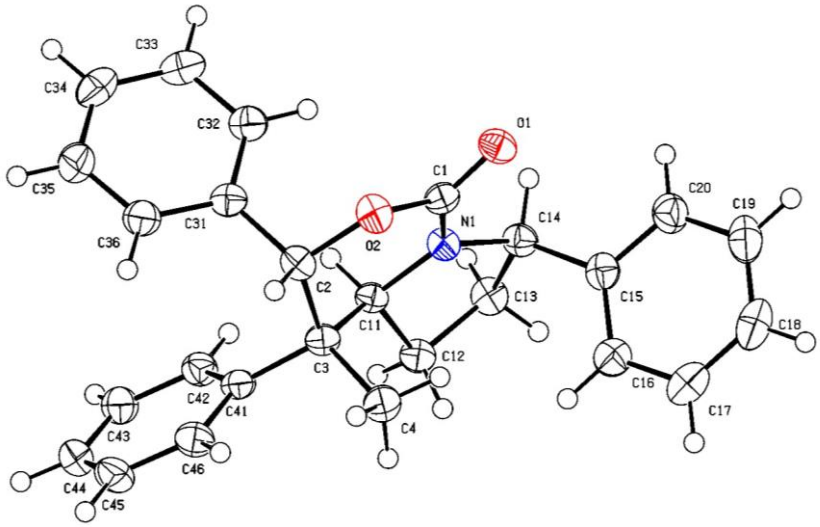
NONE

Data completeness= 0.996 Theta(max)= 27.517

R(reflections)= 0.0479(3415) wR2(reflections)= 0.1270(4599)

S = 1.046 Npar= 264

7.2 Diffraction data of compound 68 (CCDC 2155949)



Bond precision:	C-C = 0.0022 A	Wavelength=0.71073
Cell:	a=13.0638(4)	b=14.3536(4) c=11.9261(3)
	alpha=90	beta=116.328(1) gamma=90
Temperature:	173 K	
	Calculated	Reported
Volume	2004.32(10)	2004.32(10)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H25 N O2	C26 H25 N O2
Sum formula	C26 H25 N O2	C26 H25 N O2
Mr	383.47	383.47
Dx,g cm-3	1.271	1.271
Z	4	4
Mu (mm-1)	0.080	0.080
F000	816.0	816.0
F000’	816.34	
h,k,lmax	16,17,14	16,17,14

Nref	4130	4096
Tmin,Tmax	0.970,0.981	0.956,1.000
Tmin’	0.970	

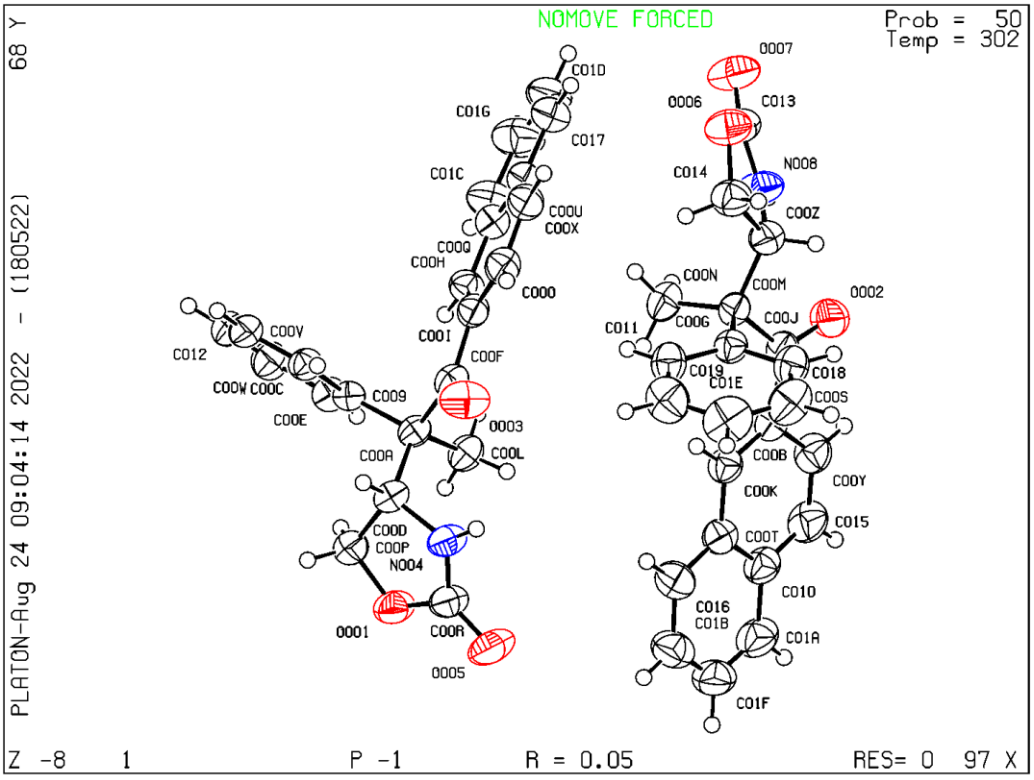
Correction method= # Reported T Limits: Tmin=0.956 Tmax=1.000 AbsCorr = NUMERICAL

Data completeness= 0.992 Theta(max)= 26.435

wR2(reflections)= 0.0918(4096) R(reflections)= 0.0392(3279)

S = 1.088 Npar= 264

7.3 Diffraction data of compound 91 (CCDC 2205064)



Bond precision: C-C = 0.0023 A Wavelength=1.54178

Cell:	a=7.7664(2)	b=13.1204(4) c=17.9064(5)
	alpha=93.283(1)	beta=101.361(1) gamma=95.285(1)
Temperature:	302 K	
	Calculated	Reported
Volume	1775.95(9)	1775.95(9)
Space group	P -1	P -1

Hall group	-P 1		-P 1
Moiety formula	C22 H19 N	O3	C22 H19 N O3
Sum formula	C22 H19 N	O3	C22 H19 N O3
Mr	345.38		345.38
Dx,g cm-3	1.292		1.292
Z	4		4
Mu (mm-1)	0.693		0.693
F000	728.0		728.0
F000’	730.21		
h,k,lmax	9,16,22		9,16,22
Nref	7076		6915
Tmin,Tmax	4340		4278
Tmin’	0.972		

Correction method= Not given

Data completeness= 0.977 Theta(max)= 72.671

R(reflections)= 0.0461(5709) wR2(reflections)= 0.1258(6915)

S = 1.067 Npar= 471

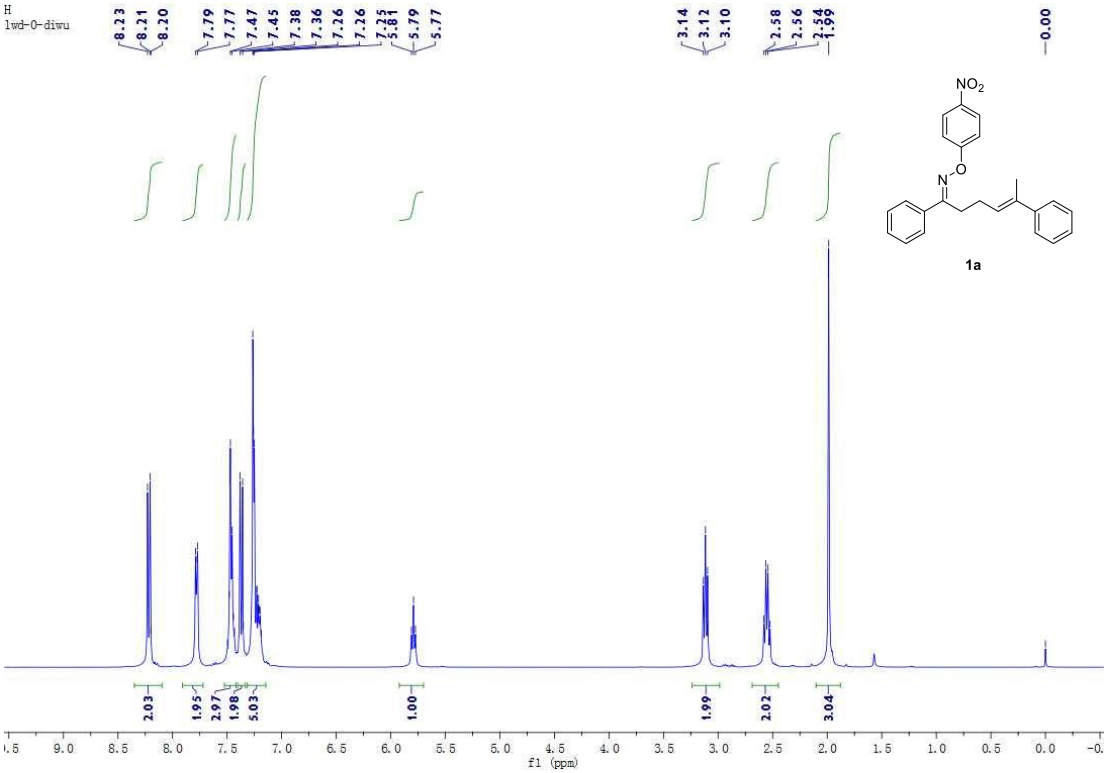
8. References

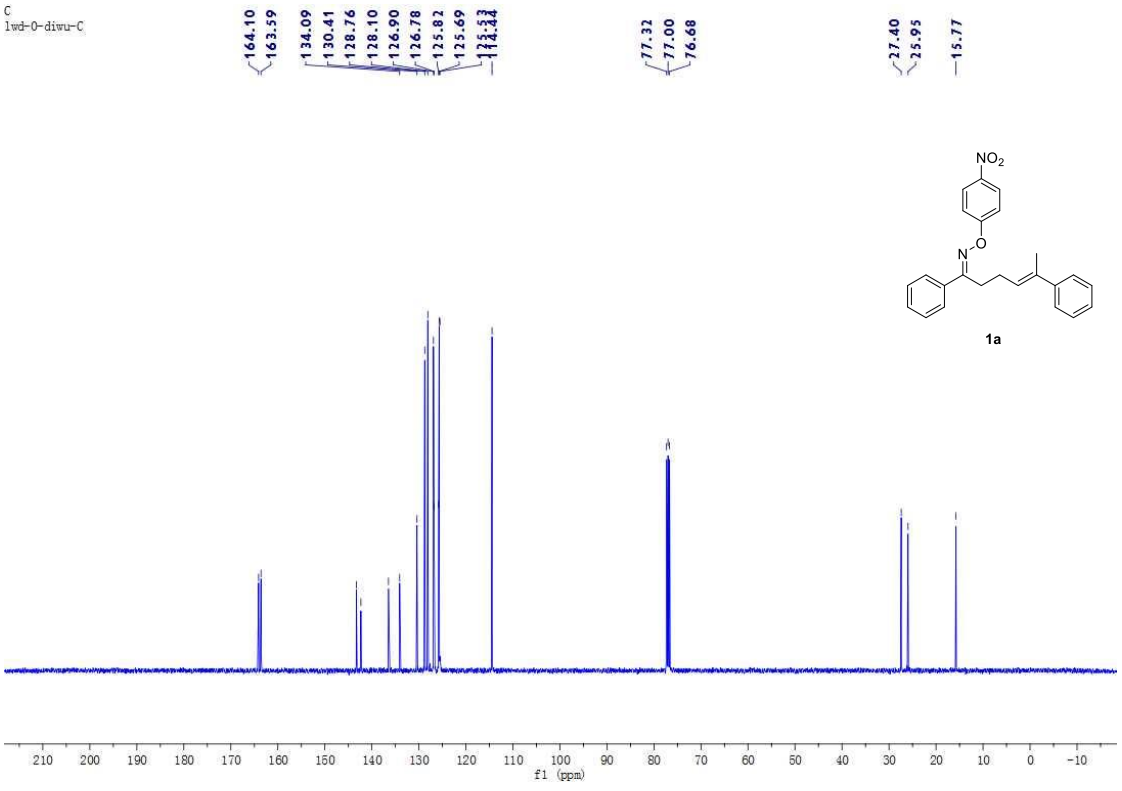
(1) Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. *Eur. J. Org. Chem.* **2011**, 5475−5484.
(2) Ling, K. B.; Smith, A, D. *Chem. Commun.*, **2011**, *47*, 373–375.
(3) Han, Y.-X.; Corey, E. J. *Org. Lett.* **2019**, *21*, 283−286.
(4) Hojoh, K.; Ohmiya, H.; Sawamura, M. *J. Am. Chem.Soc.* **2017**, *139*, 2184−2187.
(5) Lin, Q.-C.; Hu, B.-W.; Xu, X.; Dong, S.-X.; Liu, X.-H.; Feng, X.-M. *Chem. Sci.*, **2020**, *11*, 3068–3073.
(6) Davies, J.; Booth, S. G.; Essafi, S.; Dryfe, R. A. W.; Leonori, D. *Angew. Chem. Int. Ed.* **2015**, *127*, 14223−14227.
(7) Li, G.; Kuo, J. L.; Han, A.; Abuyuan, J. M.; Young, L. C.; Norton, J. R.; Palmer, J. H. *J. Am. Chem. Soc.* **2016**, *138*, 7698−7704.
(8) Peng, X.-G.; Tong, B. M. K.; Hirao, H.; Chiba, S. *Angew. Chem. Int. Ed.* **2014**, *126*, 1990 −1993.
(9) Liu, W.-D.; Xu, G.-Q.; Hu, X.-Q.; Xu, P.-F. *Org. Lett.* **2017**, *19*, 6288−6291.
(10) Faulkner, A.; Scott, J. S.; Bower, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 7224−7230.
(11) Millet, R.; Träff, A. M.; Petrus, M. L.; Bäckvall, J. E. *J. Am. Chem. Soc.* **2010**, *132*, 15182−15184.
(12) Szczesniak, P.; Pieczykolan, M.; Stecko, S. *J. Org. Chem.* **2016**, *81*, 1057−1074.
(13) Ren, X.; Guo. Q.-H.; Chen. J.-H.; Xie. H.-J.; Xu, Q.; Lu, Z. *Chem. Eur. J.* **2016**, *22*, 18695 – 18699.

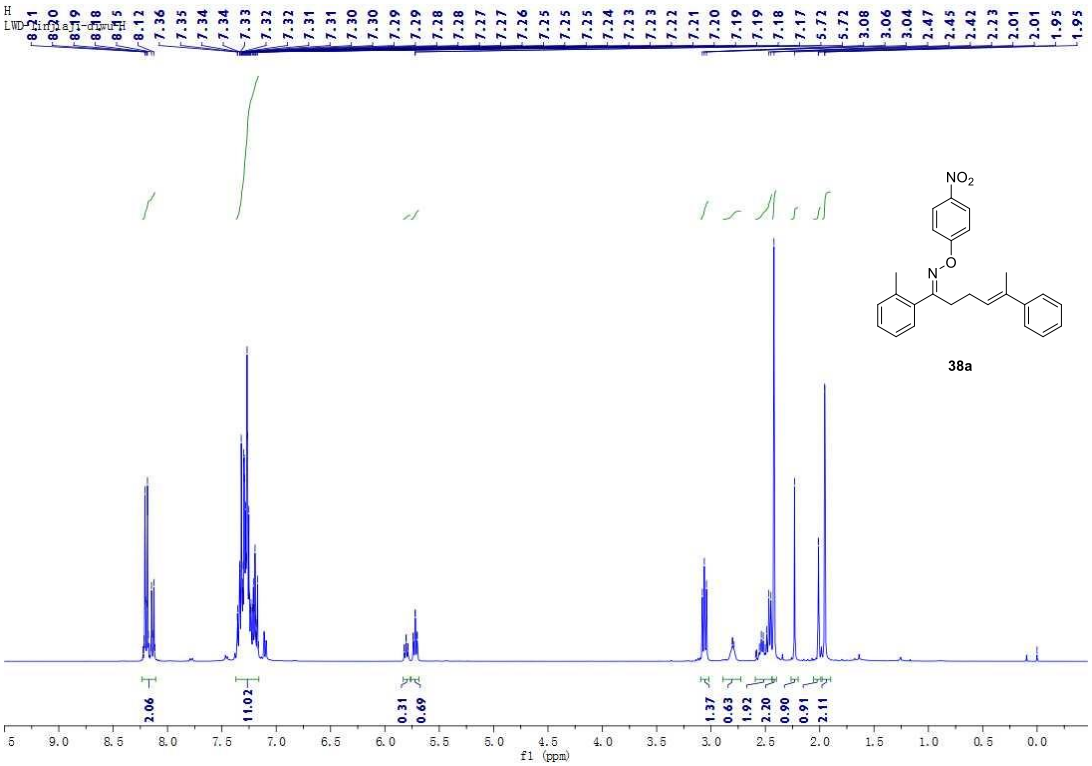
(14) Davies, J.; Svejstrup, T. D.; Fernandez Reina, D.; Sheikh, N. S.; Leonori, D. *J. Am. Chem. Soc.* **2016**, *138*, 8092−8095.
(15) Li, G.; Kuo, J, L.; Han, A.; Abuyuan, J. M.; Young, L. C.; Norton, J. R.; Palmer, J. H.; *J. Am. Chem. Soc.* **2016**, *138*, 7698−7704.
(16) Cong, F.; Lv, X.-Y.; Day, C. S.; Martin, R. *J. Am. Chem. Soc.* **2020**, *142*, 20594−20599.
(17) Dutta, L. Q. S.; Pflüger, P. M.; Sandfort, F.; Bellotti, Peter.; Glorius, F.; *ACS Catal.* **2022**, *12*, 2499−2504.
(18) Duan, J.-C.; Du, Y.-F.; Pang, X.-B.; Shu, X.-Z. *Chem. Sci.* **2019**, *10*, 8706–8712
(19) Bao, X.; Wang, Q.; Zhu, J.-P. *Angew. Chem. Int. Ed*. **2019**, *58*, 2139 –2143.
(20) Gao, Y.; Quan, Y.-S.; Li, Z.-J.; Gao, L.-Y.; Zhang, Z.-H.; Zou, X.; Yan, R.; Qu, Y.-Y.; Guo, K. *Org. Lett.* **2021**, *23*, 183−189.
(21) Guin, J.; Sarkar, S. D.; Grimme, S.; Studer, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 8727–8730.
(22) Jang, Y. Ho.; Youn, S. W. *Org. Lett*. **2014**, *16*, 3720−3723.
(23) Faulkner, A.; Race, N. J.; Scottb, J. S.; Bower, J. F. *Chem. Sci*. **2014**, *5*, 2416–2421
(24) (a) Delfau, L.; Nichilo, S.; Molton, F.; Broggi, J.; Mendivil, E. T.; Martin, D. *Angew. Chem. Int. Ed.* **2021**, *60*, 26783–26789. (b) Ren, S.-C.; Lv, W.-X.; Yang, X.; Yan, J.-L.; Xu, J.; Wang, F.-X.; Hao, L.; Chai, H.-F.; Jin, Z.-C.; Chi, Y. R. *ACS Catal.* **2021**, *11*, 2925−2934.
(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobfayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; and Fox, D. J. *Gaussian 16*; Gaussian, Inc.: Wallingford, CT, **2016**.
(26) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections†. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.
(27) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.
(28) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the

Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
(29) (a) Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Use of Solution-Phase Vibrational Frequencies in Continuum Models for the Free Energy of Solvation *J. Phys. Chem. B* **2011**, *115*, 14556–14562; (b) Luchini, G.; Alegre-Requena J. V.; Guan, Y.; Funes-Ardoiz, I.; Paton, R. S. (**2019**). GoodVibes*: GoodVibes 3.0.1* DOI: 10.5281/zenodo.595246.
(30) (a) Grimme, S.; Bannwarth, C.; Shushkov, P. A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All spd-Block Elements (z = 1-86). *J. Chem. Theory Comput.* **2017**, *13*, 1989–2009. (b) Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-xTB–An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671. (c) Pracht, P.; Caldeweyher, E.; Ehlert, S.; Grimme, S. A Robust Non-Self-Consistent Tight-Binding Quantum Chemistry Method for Large Molecules. *ChemRxiv* **2019,** https://doi.org/10.26434/chemrxiv.8326202.v1
(31) Legault, C. Y. *CYLview*, 1.0b; Universite′ de Sherbrooke, **2009**; http://www.cylview.org.

9. Copies of ^{1}H NMR and ^{13}C NMR spectra



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NO2
N
O
38a
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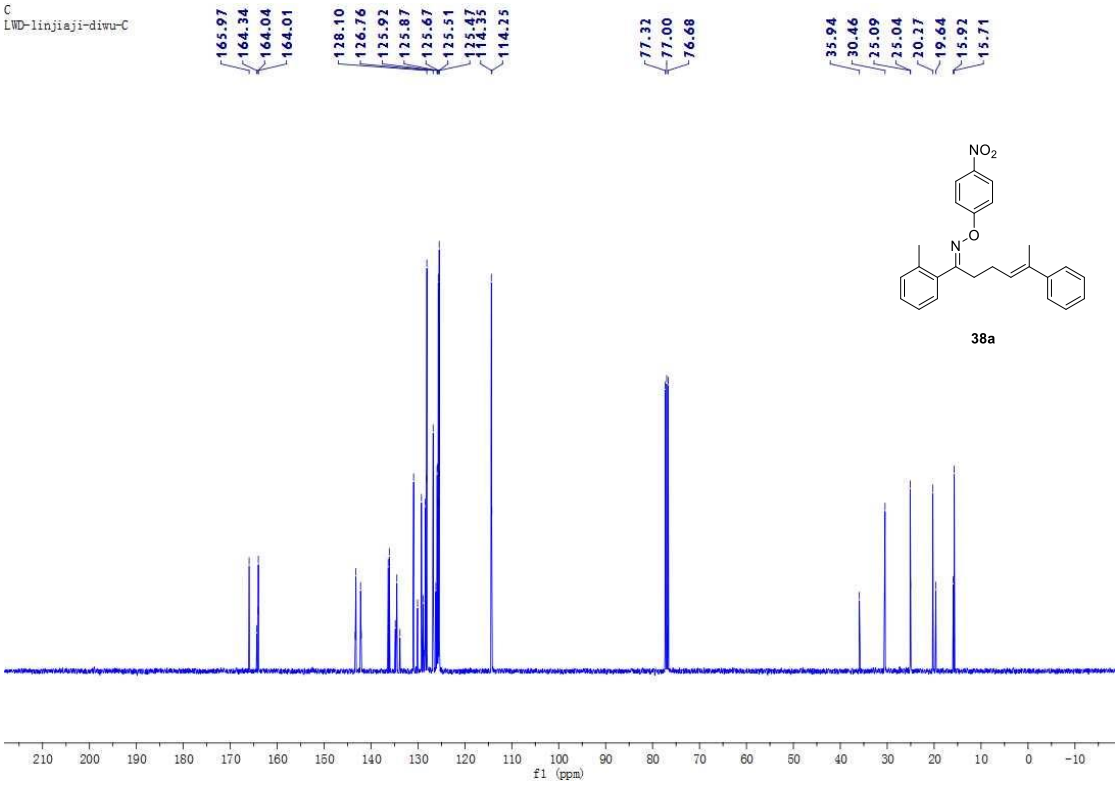
f1 (ppm)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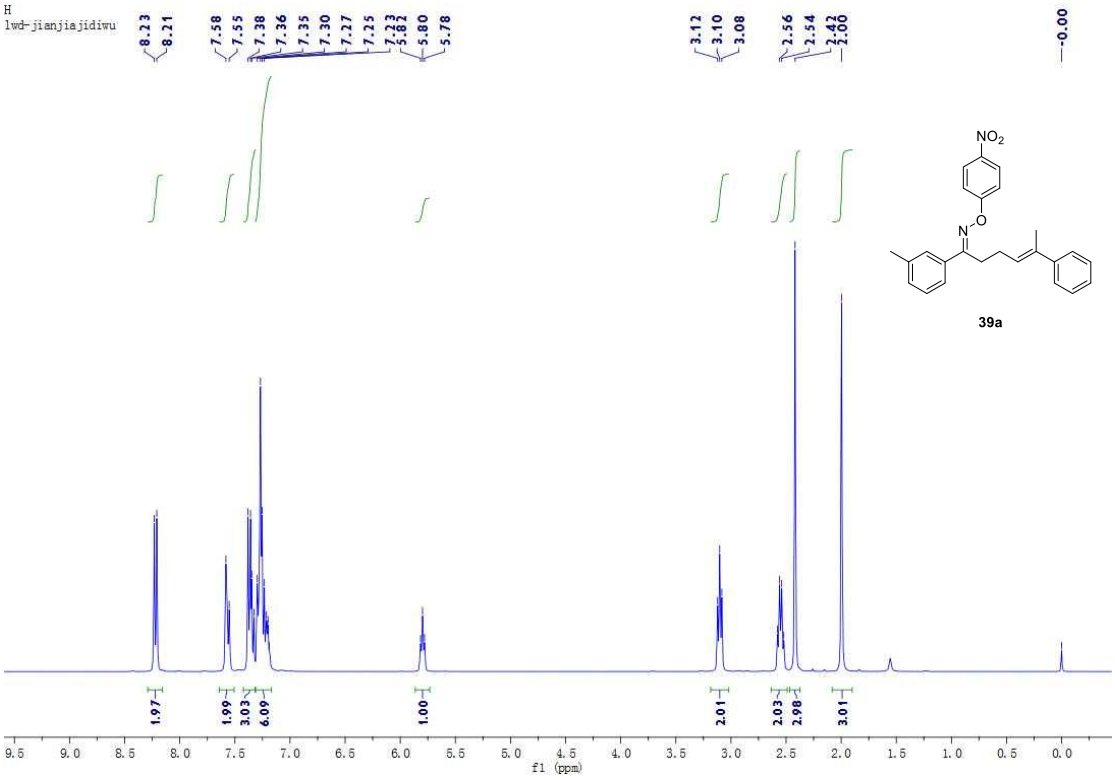
NO2
N
O
38a
f1 (ppm)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5.78
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3.10
3.08
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2.54
2.42
2.00
-0.00
1.97
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1.00
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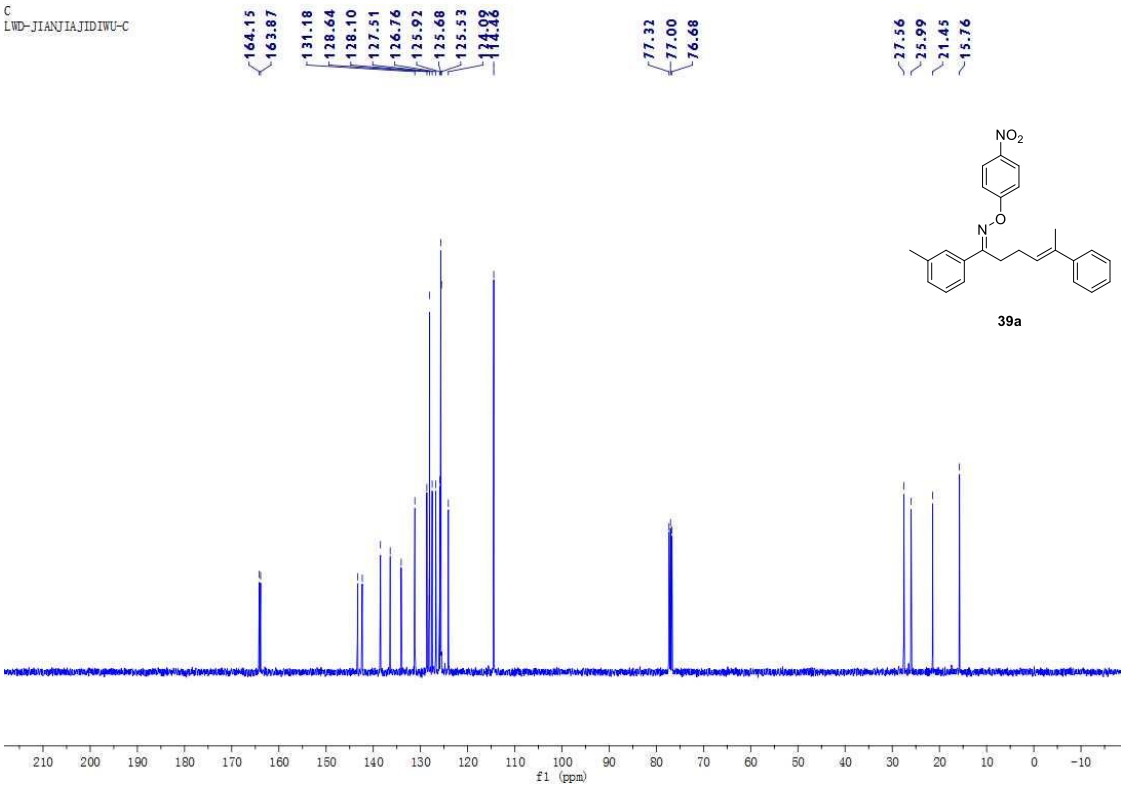
2.03
2.98
3.01
f1 (ppm)

NO2
N
O

39a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125.68
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76.68
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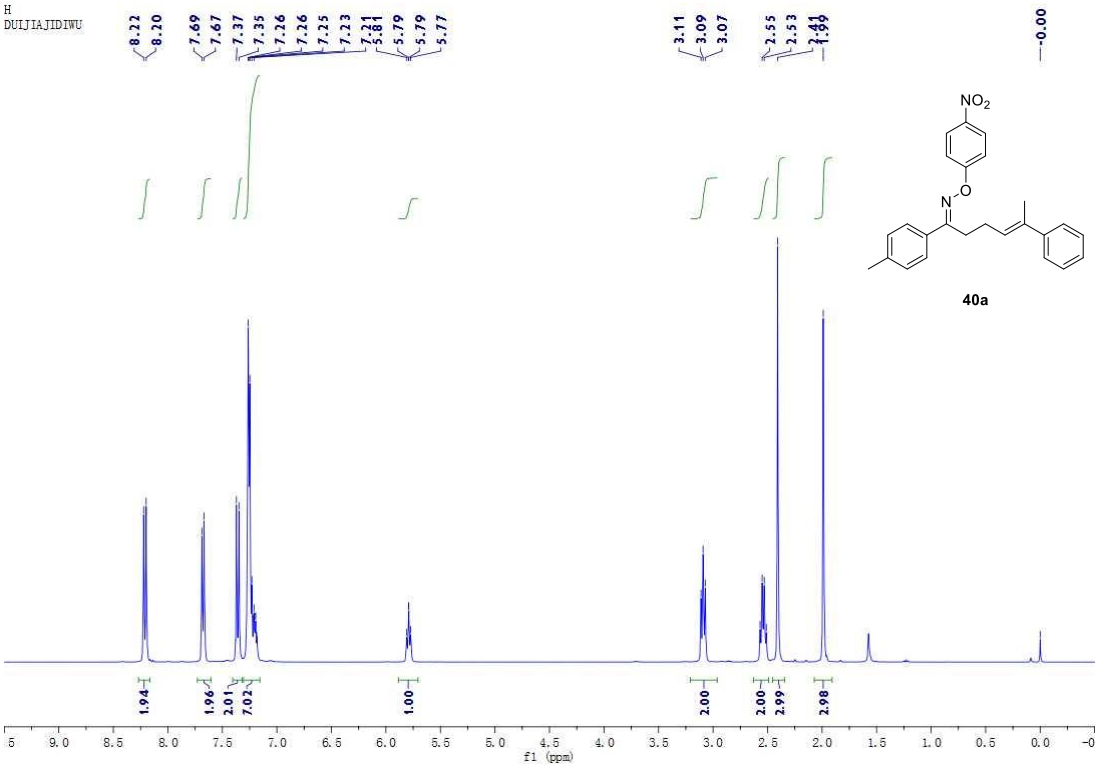
f1 (ppm)

NO2
N
O

39a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5.79
5.77
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3.09
3.07
2.55
2.53
2.41
1.99
0.00
1.94
1.96
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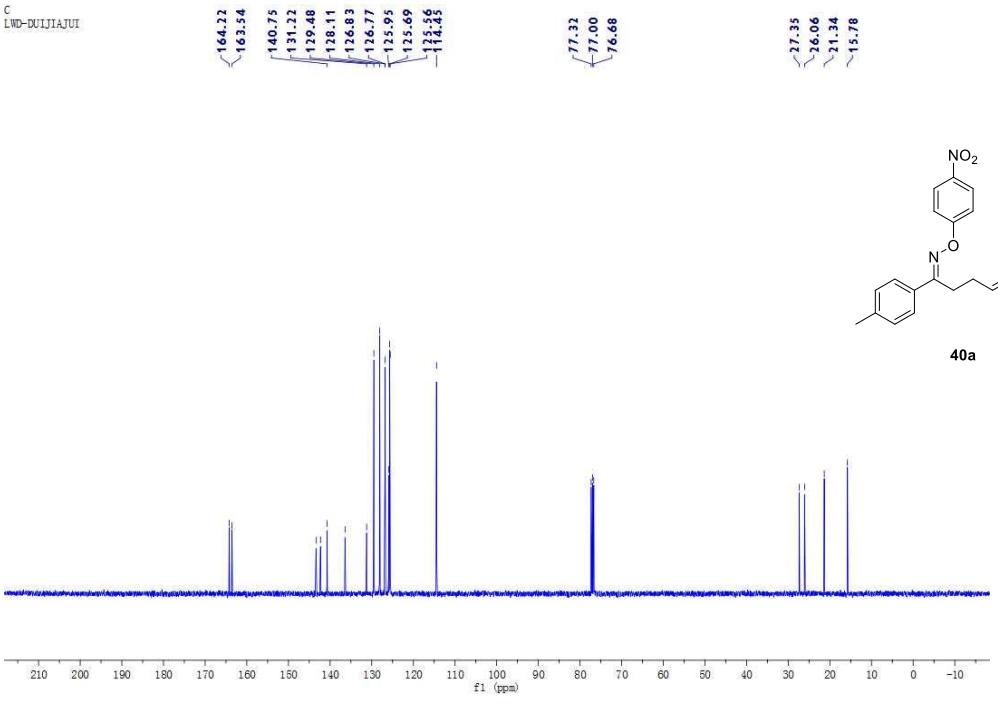
1.00
2.00
2.00
2.99
2.98
f1 (ppm)

NO2
N
O

40a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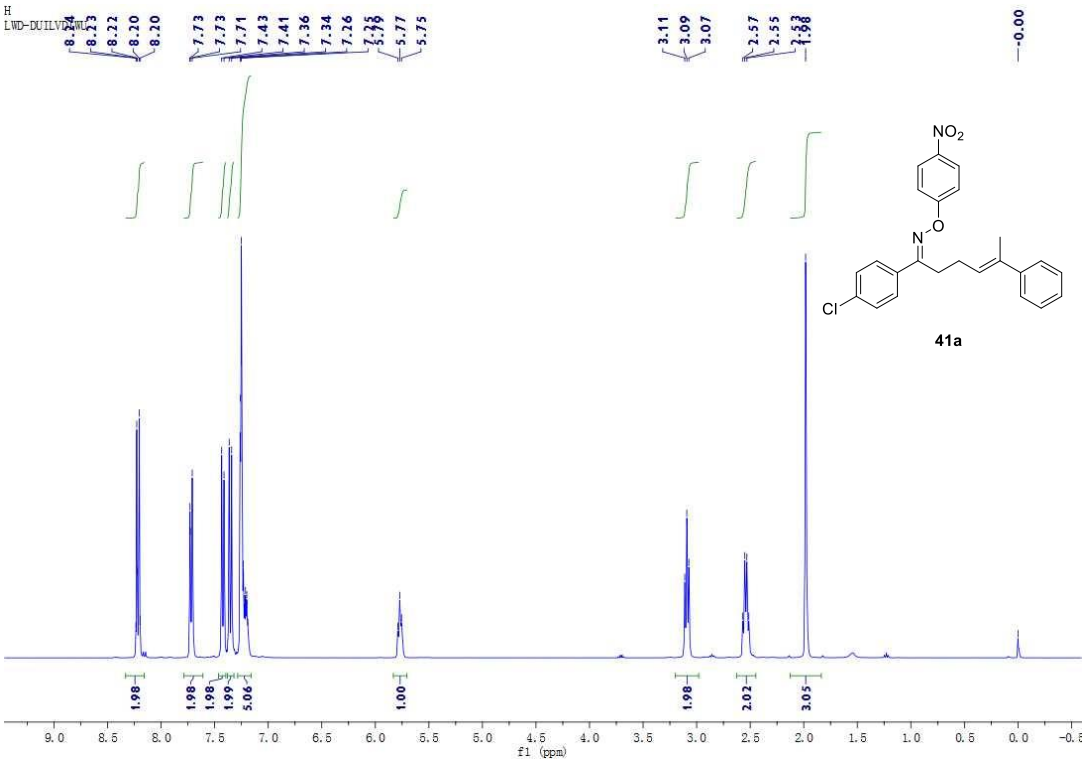
f1 (ppm)

NO2
N
O

40a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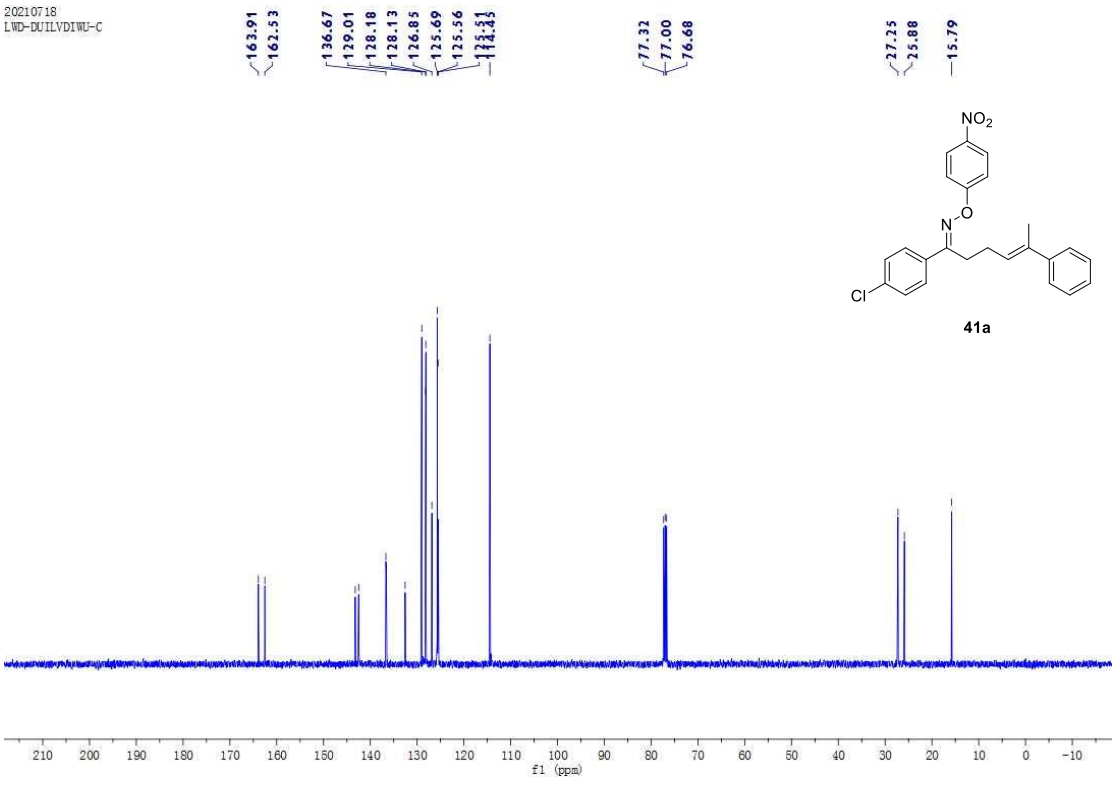
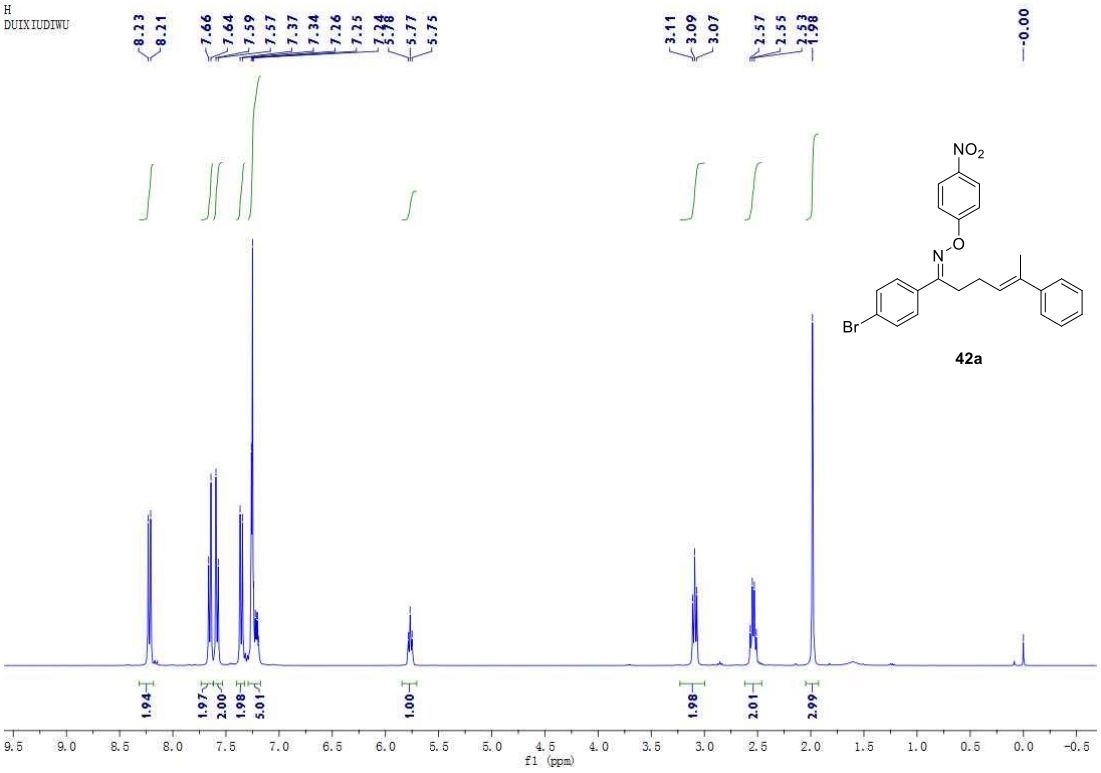
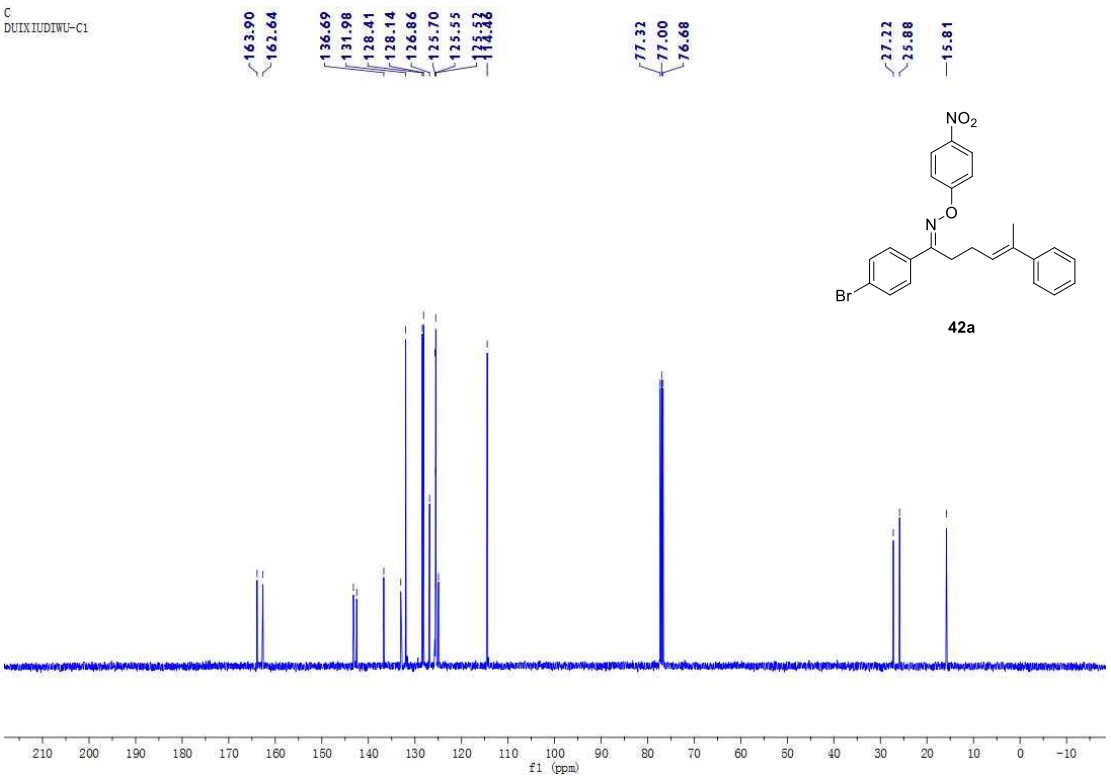
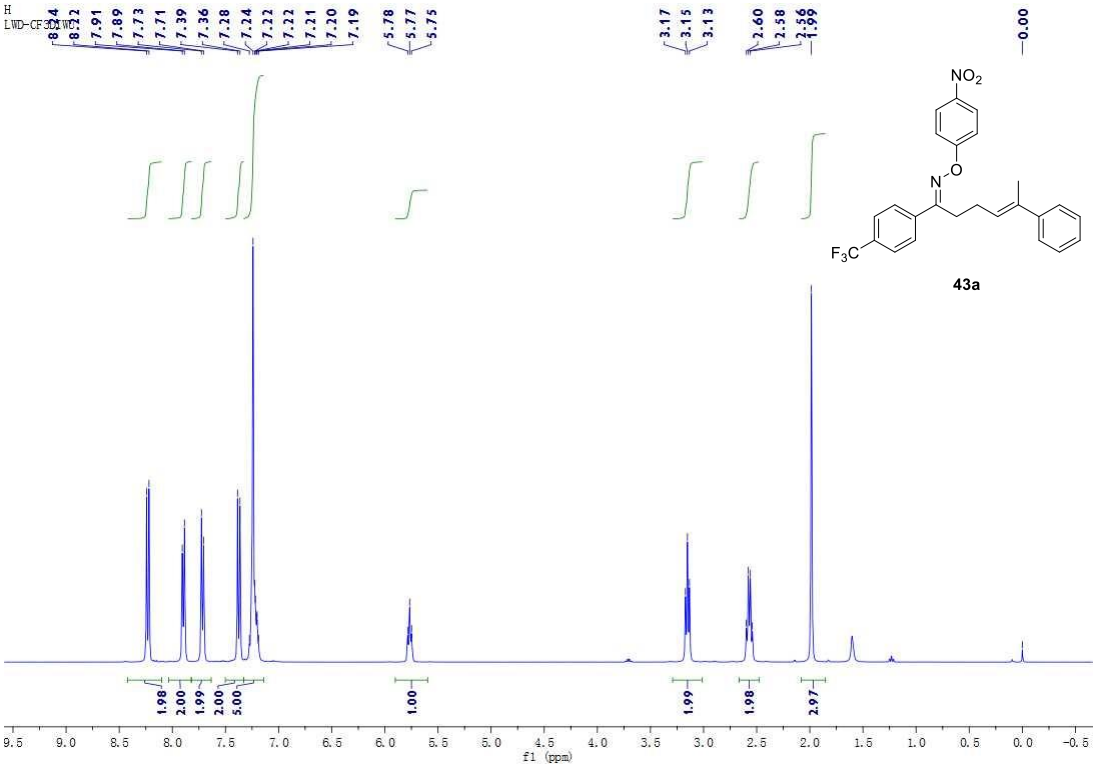
7.43
7.41
7.36
7.34
7.26
5.77
5.75
3.11
3.09
3.07
2.57
2.55
-0.00
NO2
O
N
Cl
41a
1.98
1.98
1.99
5.06
1.00
1.98
2.02
3.05
f1 (ppm)


20210718
LWD-DUILVDIWU-C
163.91
161.53
136.67
129.01
128.18
128.13
126.85
125.69
125.56
77.32
77.00
76.68
27.25
25.88
15.79
NO2
O
N
Cl
41a
f1 (ppm)

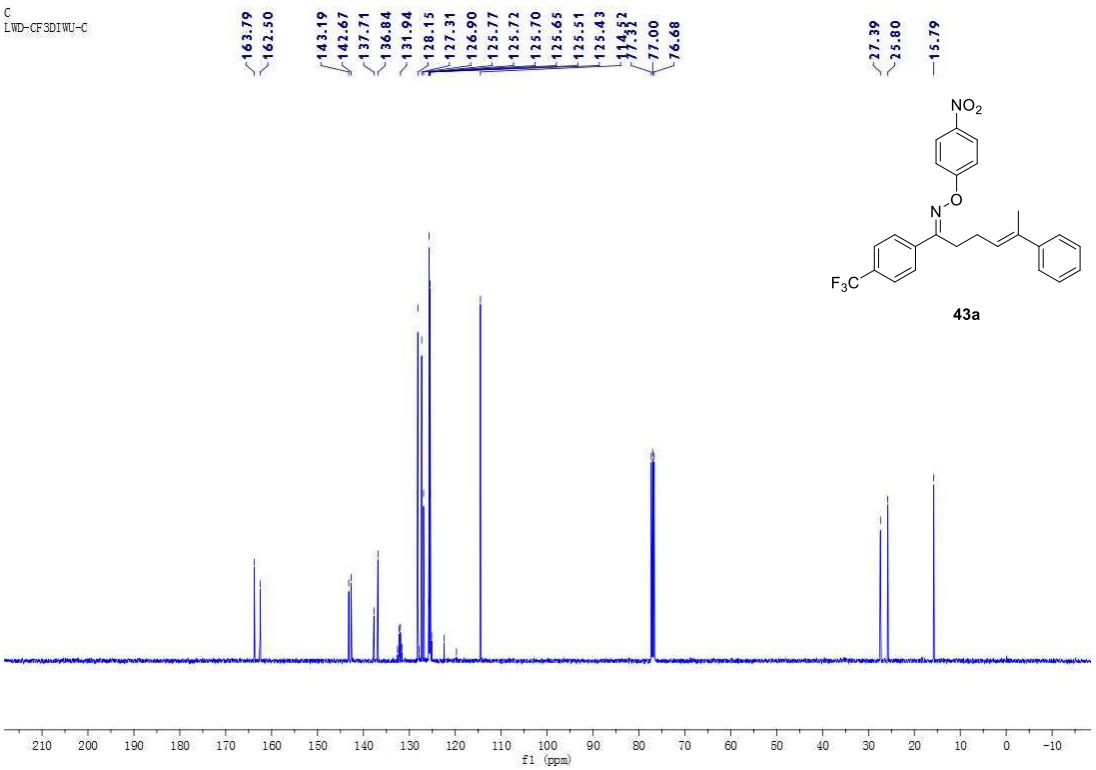

H
DUIXIUDIWU
8.23
8.21
7.66
7.64
7.59
7.57
7.37
7.34
7.26
7.25
5.77
5.75
3.11
3.09
3.07
2.57
2.55
2.53
1.98
0.00
NO2
N
O
Br
42a
1.94
1.97
2.00
1.98
5.01
1.00
1.98
2.01
2.99
f1 (ppm)


C
DUIXIUDIWU-C1
163.90
161.64
136.69
131.98
128.41
128.14
126.86
125.70
125.55
77.32
77.00
76.68
27.22
25.88
15.81
NO2
N
O
Br
42a
f1 (ppm)


H
LWD-CF3D1WU
8.24
8.22
7.91
7.89
7.73
7.71
7.39
7.36
7.28
7.24
7.22
7.22
7.21
7.20
7.19
5.78
5.77
5.75
3.17
3.15
3.13
2.60
2.58
2.56
1.99
0.00
1.98
2.00
1.99
2.00
5.00
1.00
1.99
1.98
2.97
f1 (ppm)

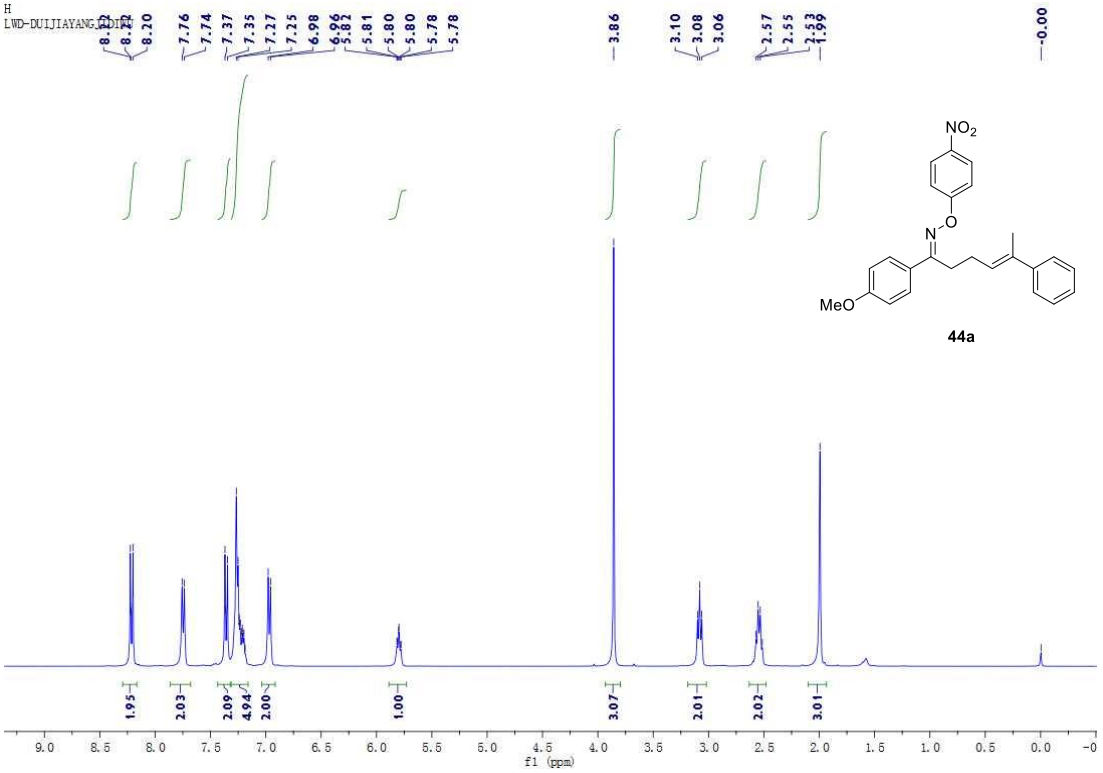
NO2
N
O
F3C

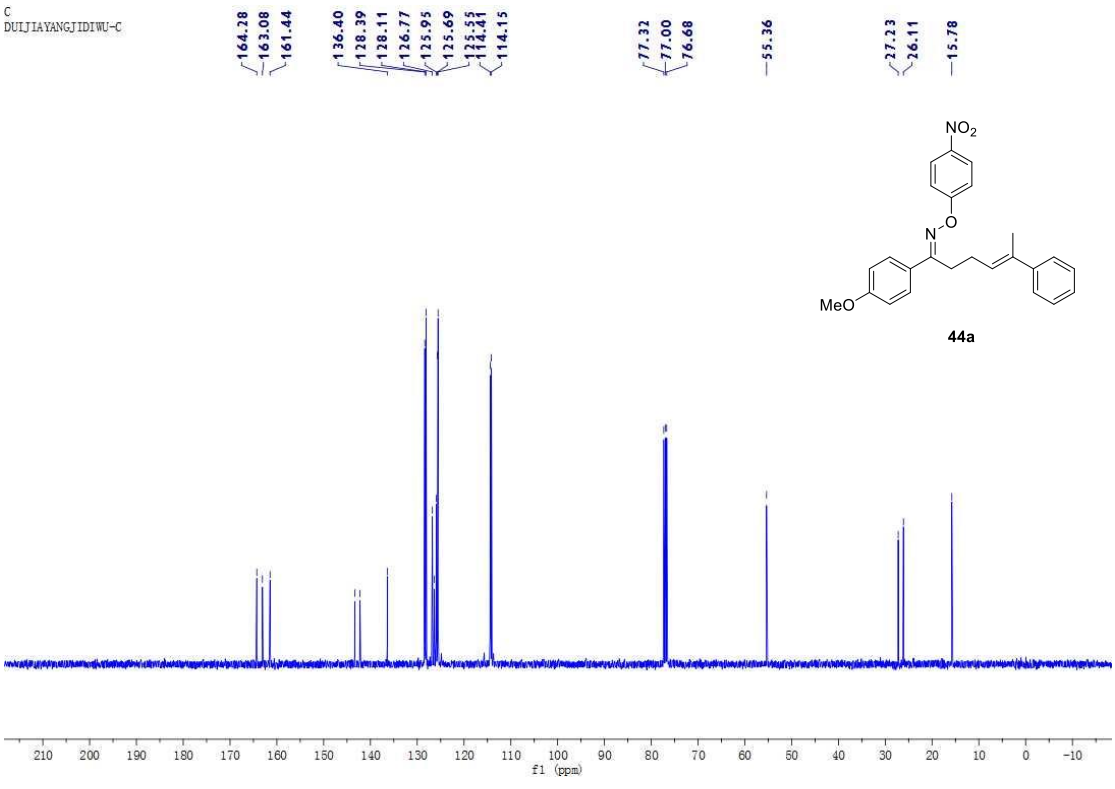
43a

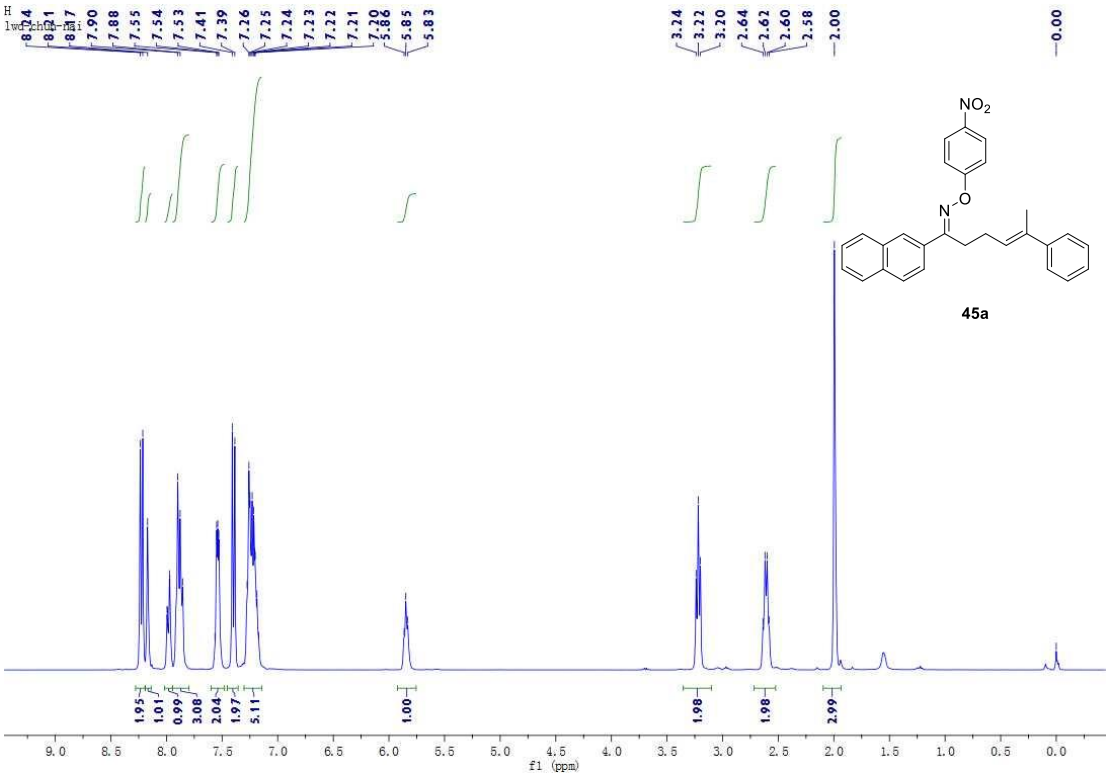

C
LWD-CF3D1WU-C
163.79
162.50
143.19
142.67
137.71
136.84
131.94
128.15
127.31
126.90
125.77
125.72
125.70
125.65
125.51
125.43
114.32
111.92
77.00
76.68
27.39
25.80
15.79
f1 (ppm)

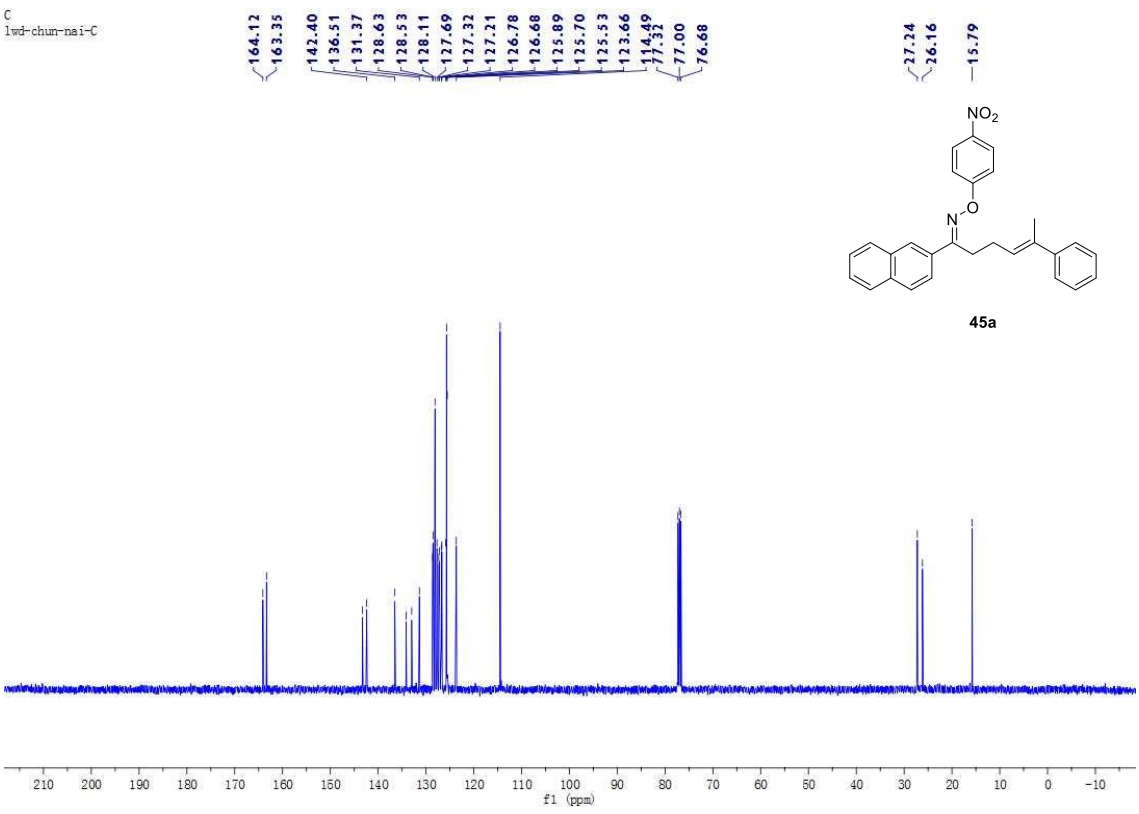
NO2
N
O
F3C

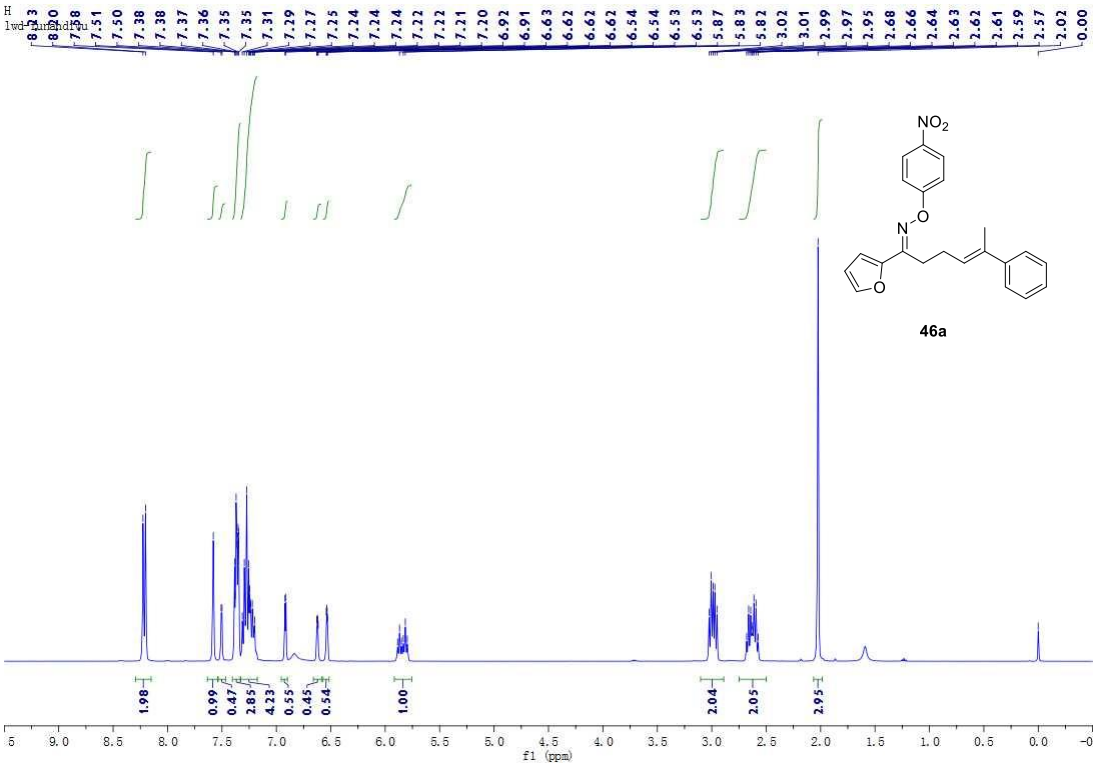
43a


H
LWD-DULJIAYANGJIDIWU-H
8.21
8.20
7.76
7.74
7.37
7.35
7.27
7.25
6.98
5.82
5.81
5.80
5.80
5.78
5.78
3.86
3.10
3.08
3.06
2.57
2.55
2.53
1.99
-0.00
NO2
N
O
MeO
44a
1.95
2.03
2.09
4.94
2.00
1.00
3.07
2.01
2.02
3.01
f1 (ppm)


C
DULJIAYANGJIDIWU-C
164.28
163.08
161.44
136.40
128.39
128.11
126.77
125.95
125.69
77.32
77.00
76.68
55.36
27.23
26.11
15.78
NO2
N
O
MeO
44a
f1 (ppm)

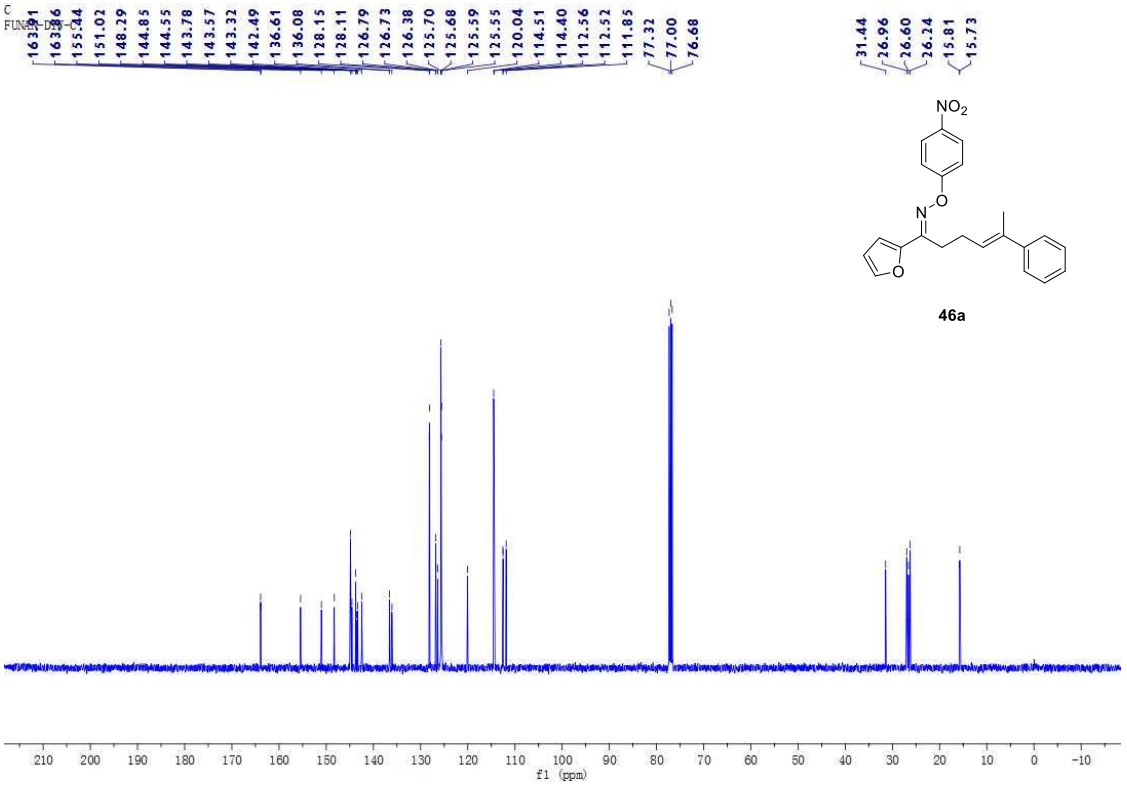

H
lwd-chun-nai
8.24
8.21
8.17
7.90
7.88
7.55
7.54
7.53
7.41
7.39
7.26
7.25
7.24
7.23
7.22
7.21
7.20
5.85
5.83
3.24
3.22
3.20
2.64
2.62
2.60
2.58
2.00
0.00
NO2
N
O
45a
1.95
1.01
0.99
3.08
2.04
1.97
5.11
1.00
1.98
1.98
2.99
f1 (ppm)


C
lwd-chun-nai-C
164.12
163.35
142.40
136.51
131.37
128.63
128.53
128.11
127.69
127.32
127.21
126.78
126.68
125.89
125.70
125.53
123.66
114.49
77.32
77.00
76.68
27.24
26.16
15.79
NO2
N
O
45a
f1 (ppm)


8.33
8.20
7.58
7.51
7.50
7.38
7.38
7.37
7.36
7.35
7.35
7.31
7.29
7.27
7.25
7.24
7.24
7.24
7.22
7.22
7.21
7.20
6.92
6.91
6.63
6.62
6.62
6.62
6.54
6.54
6.53
6.53
5.87
5.83
5.82
3.02
3.01
2.99
2.97
2.95
2.68
2.66
2.64
2.63
2.62
2.61
2.59
2.57
2.02
0.00
1.98
0.99
0.47
2.85
4.23
0.55
0.45
0.54
1.00
2.04
2.05
2.95
f1 (ppm)

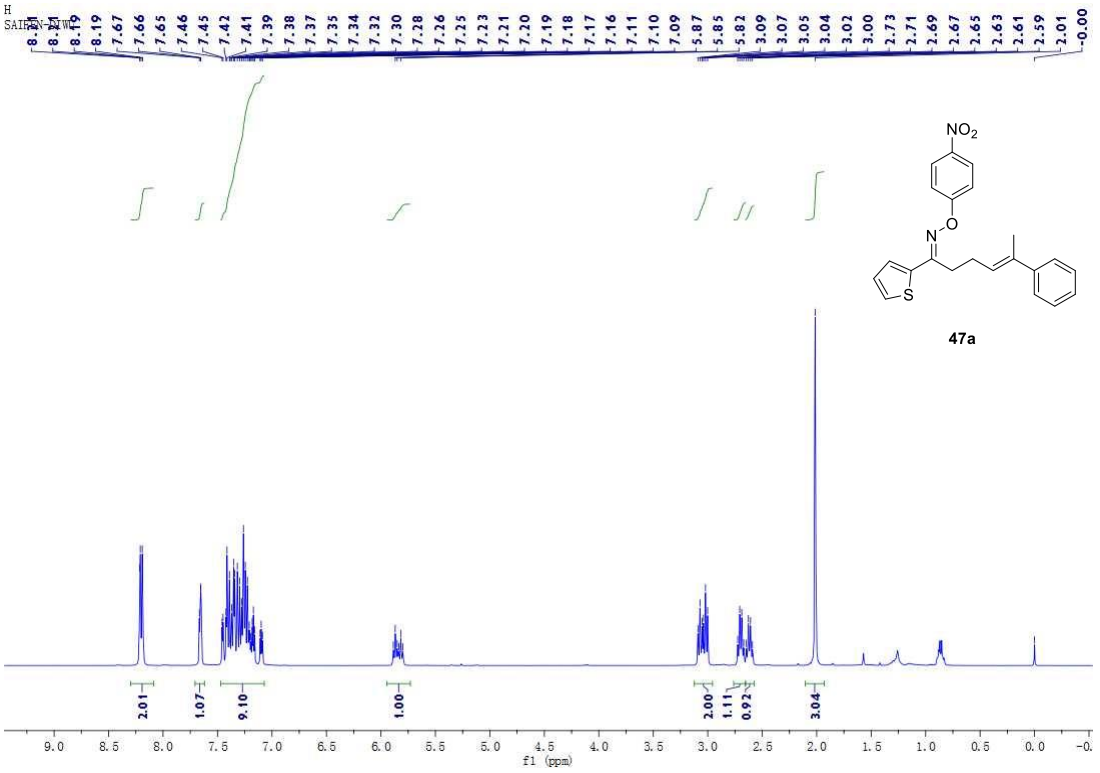
NO2
N
O
O

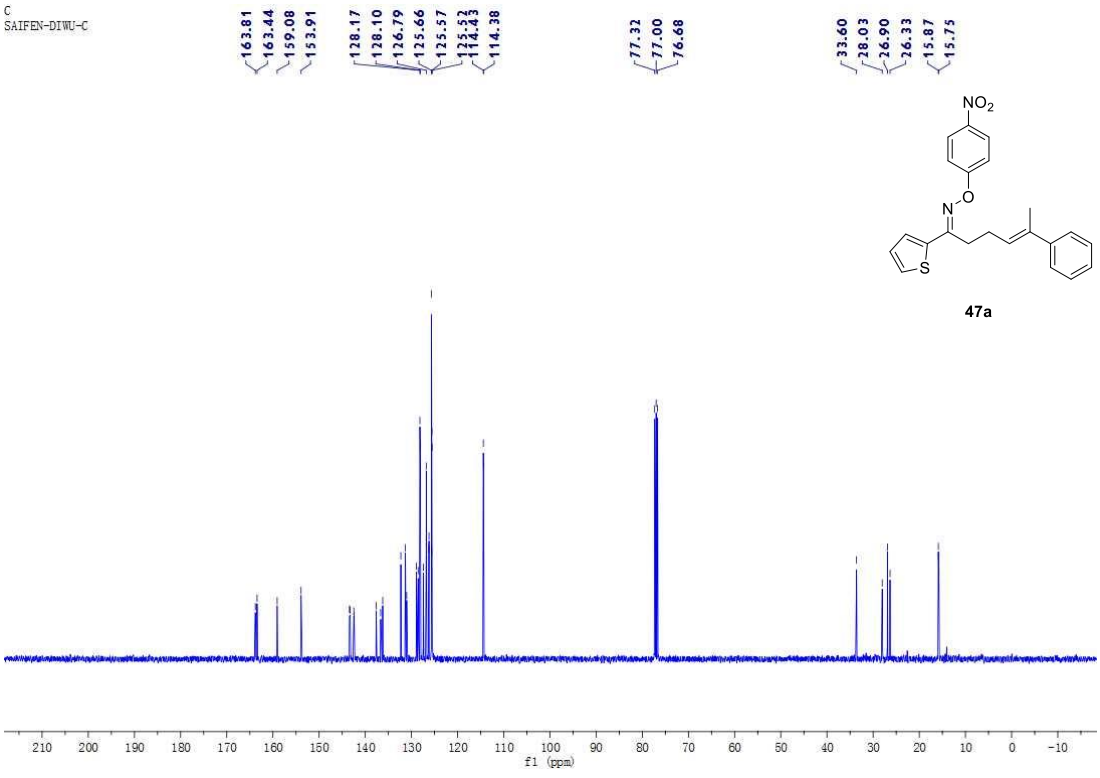
46a

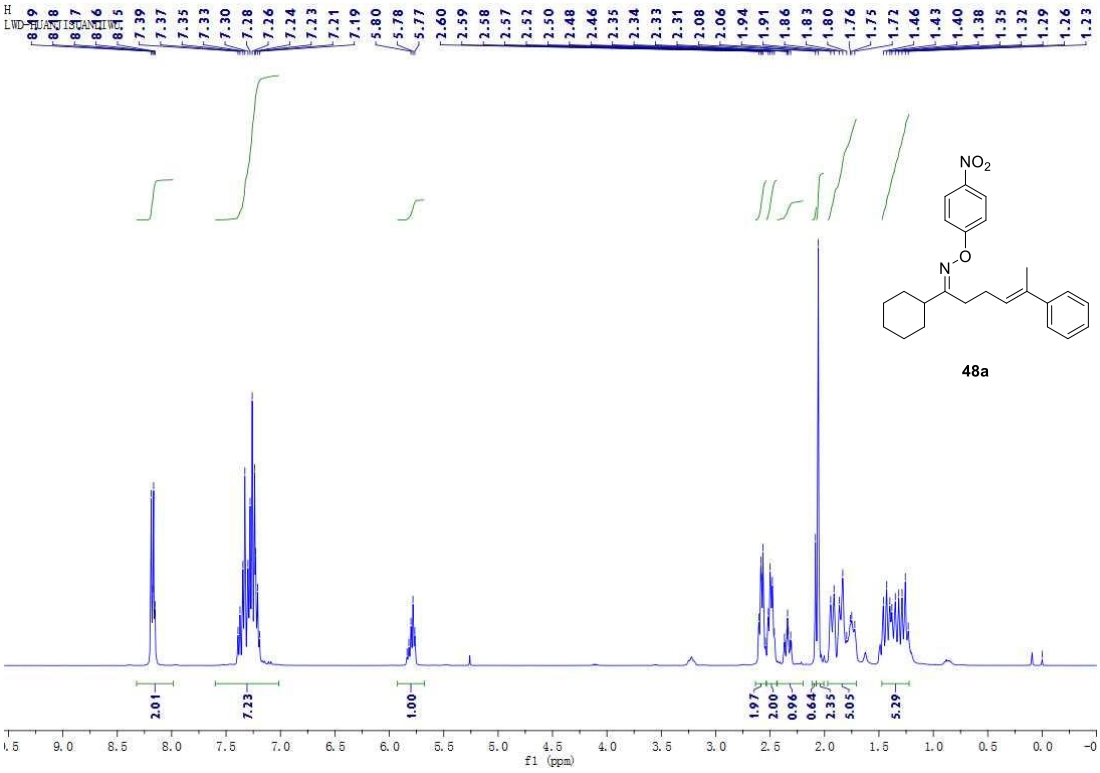

163.91
163.86
155.44
151.02
148.29
144.85
144.55
143.78
143.57
143.32
142.49
136.61
136.08
128.15
128.11
126.79
126.73
126.38
125.70
125.68
125.59
125.55
120.04
114.51
114.40
112.56
112.52
111.85
77.32
77.00
76.68
31.44
26.96
26.60
26.24
15.81
15.73
f1 (ppm)

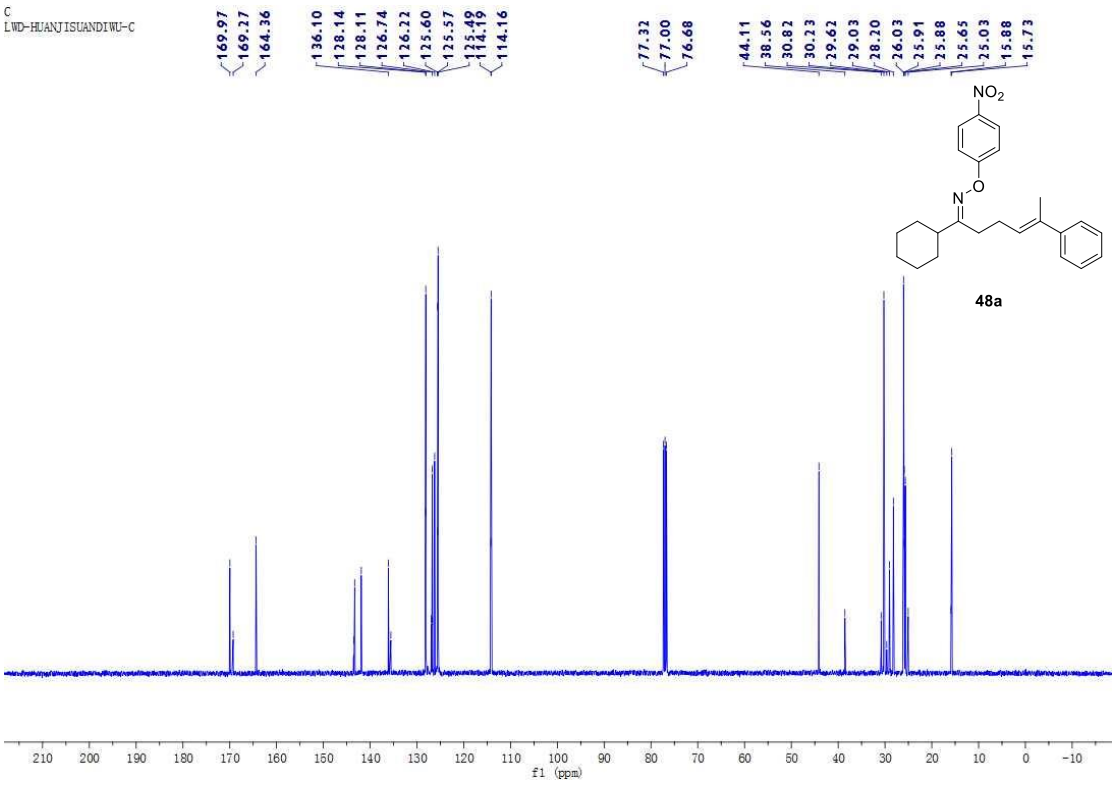
NO2
N
O
O

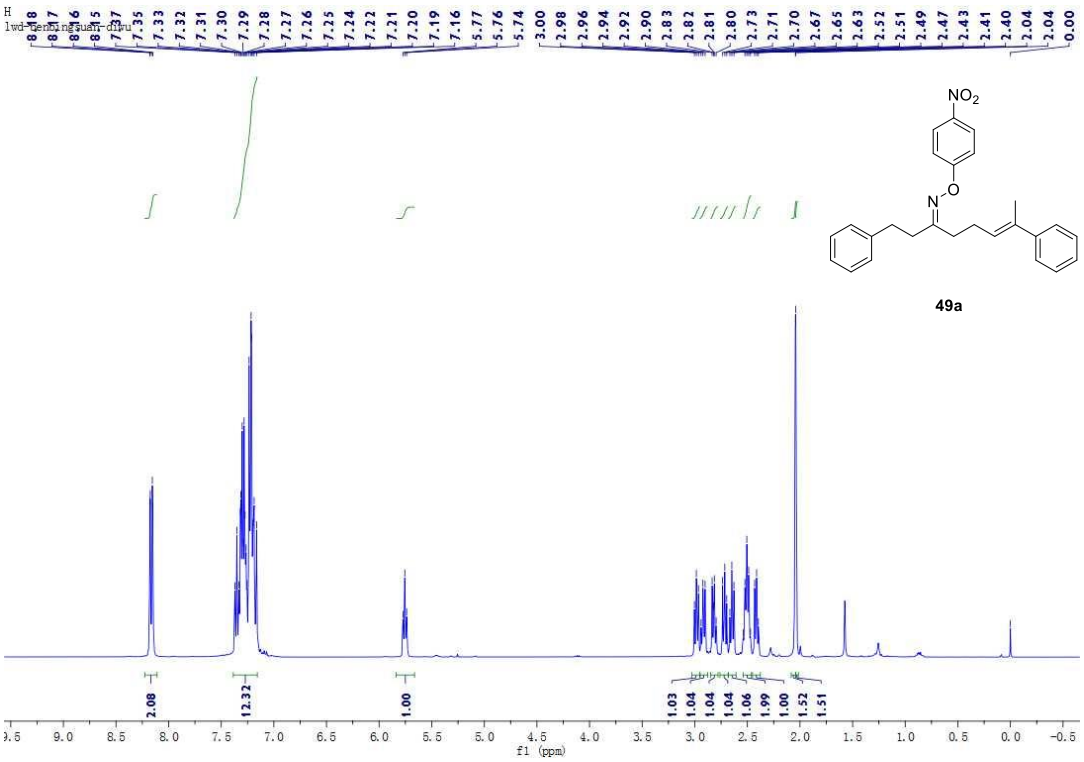
46a

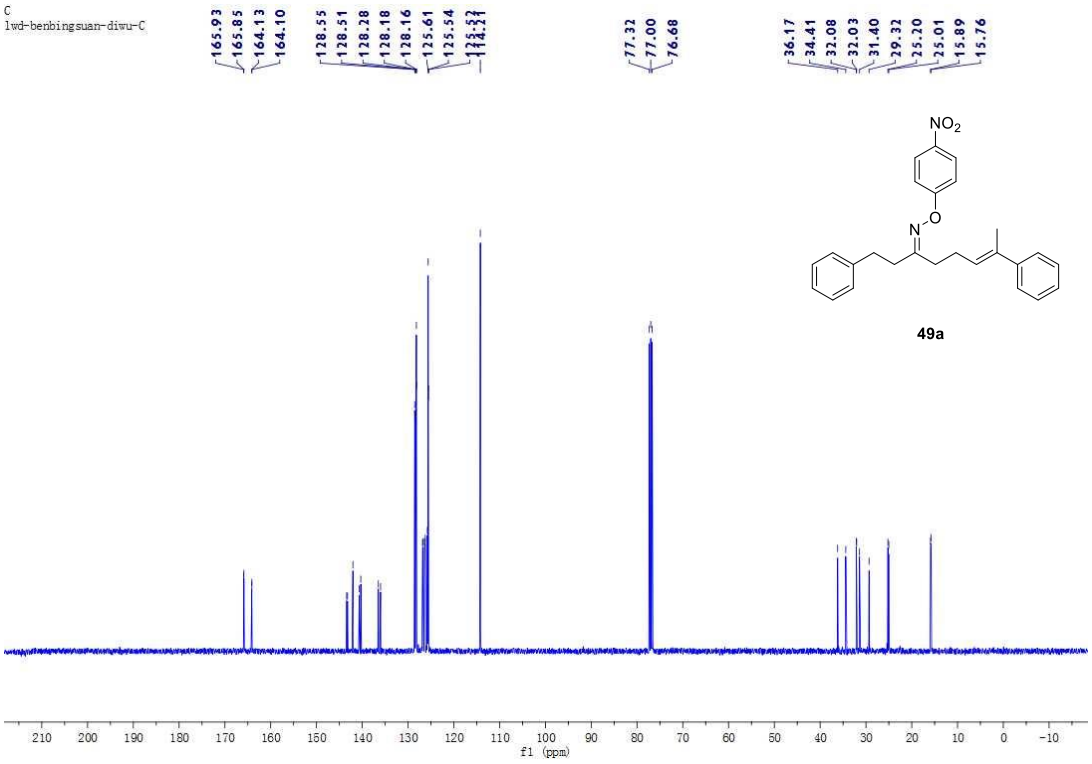

H
8.21
8.19
7.67
7.66
7.65
7.46
7.45
7.42
7.41
7.39
7.38
7.37
7.35
7.34
7.32
7.30
7.28
7.26
7.25
7.23
7.21
7.20
7.19
7.18
7.17
7.16
7.11
7.10
7.09
5.87
5.85
5.82
3.09
3.07
3.05
3.04
3.02
3.00
2.73
2.71
2.69
2.67
2.65
2.63
2.61
2.59
2.01
-0.00
NO2
N
O
S
47a
2.01
1.07
9.10
1.00
2.00
1.11
0.92
3.04
f1 (ppm)

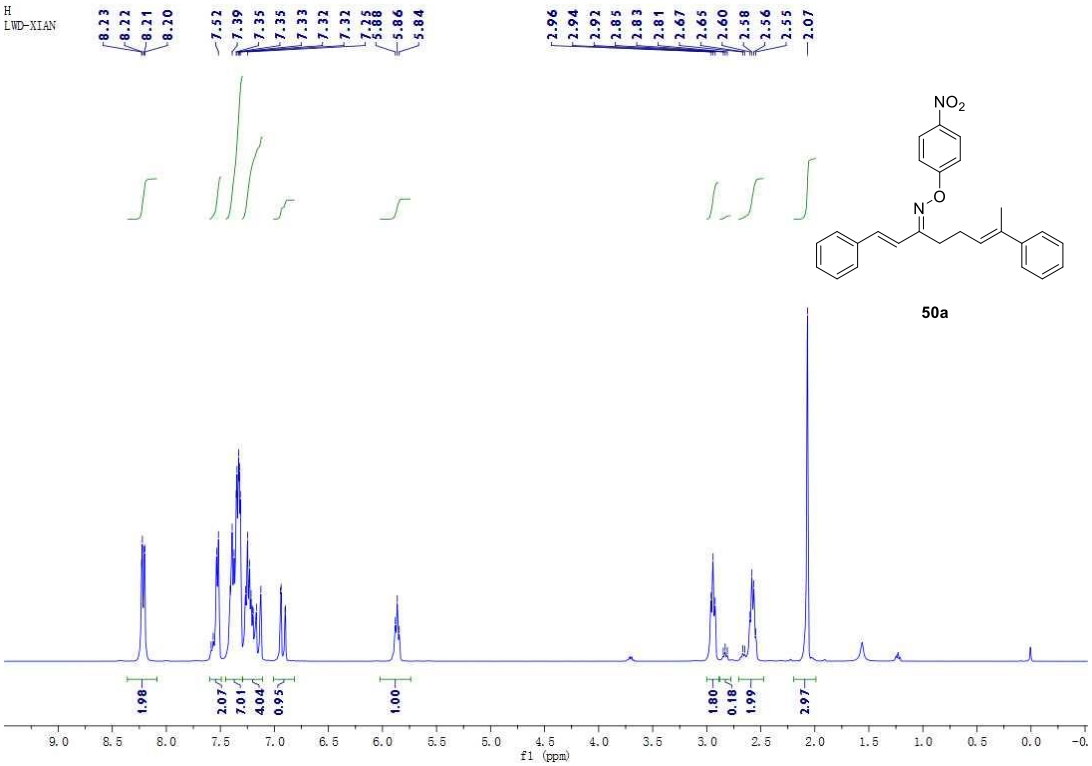

C
SAIFEN-DIWU-C
163.81
163.44
159.08
153.91
128.17
128.10
126.79
125.66
125.57
125.52
114.43
114.38
77.32
77.00
76.68
33.60
28.03
26.90
26.33
15.87
15.75
NO2
N
O
S
47a
f1 (ppm)

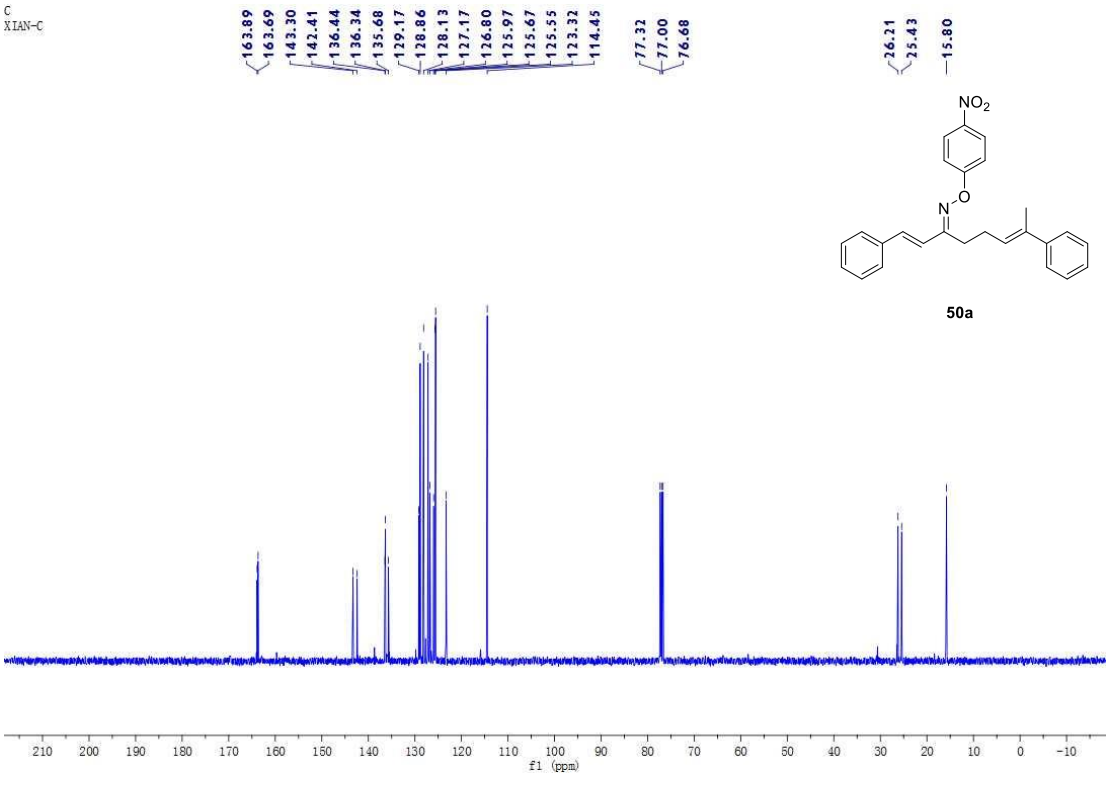

H
LWD-HUANJISUANDIWU-H
NO2
N
O
48a
f1 (ppm)

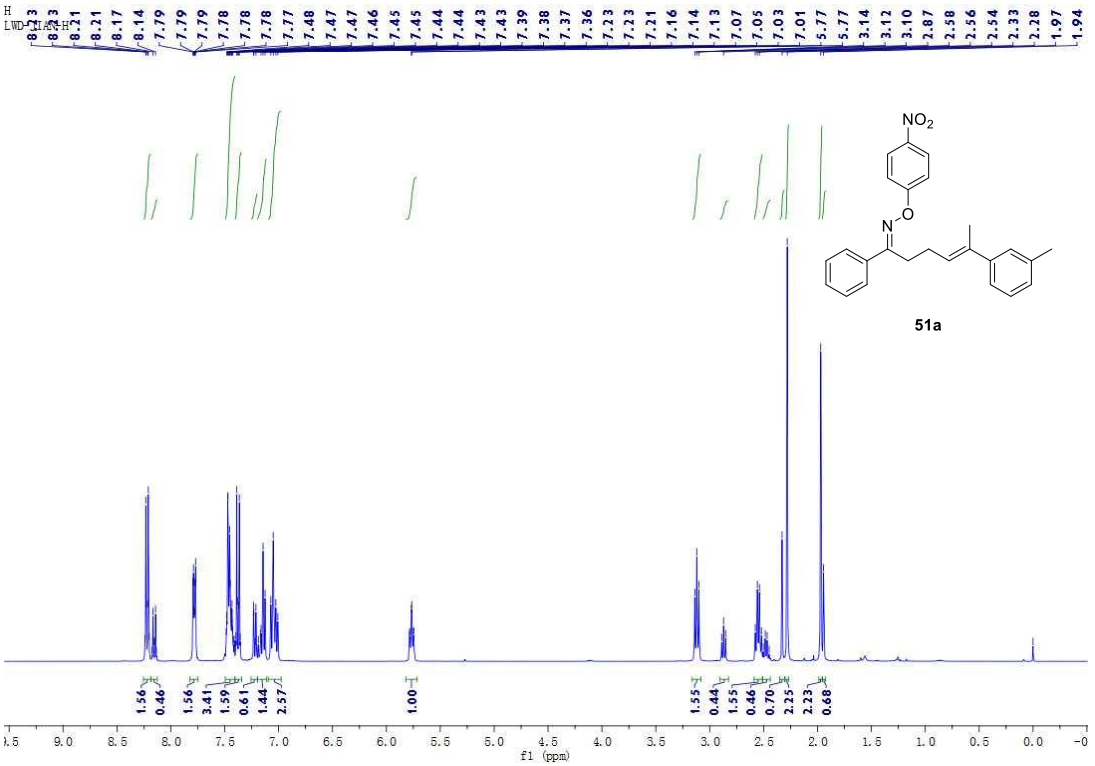

C
LWD-HUANJISUANDIWU-C
NO2
N
O
48a
f1 (ppm)

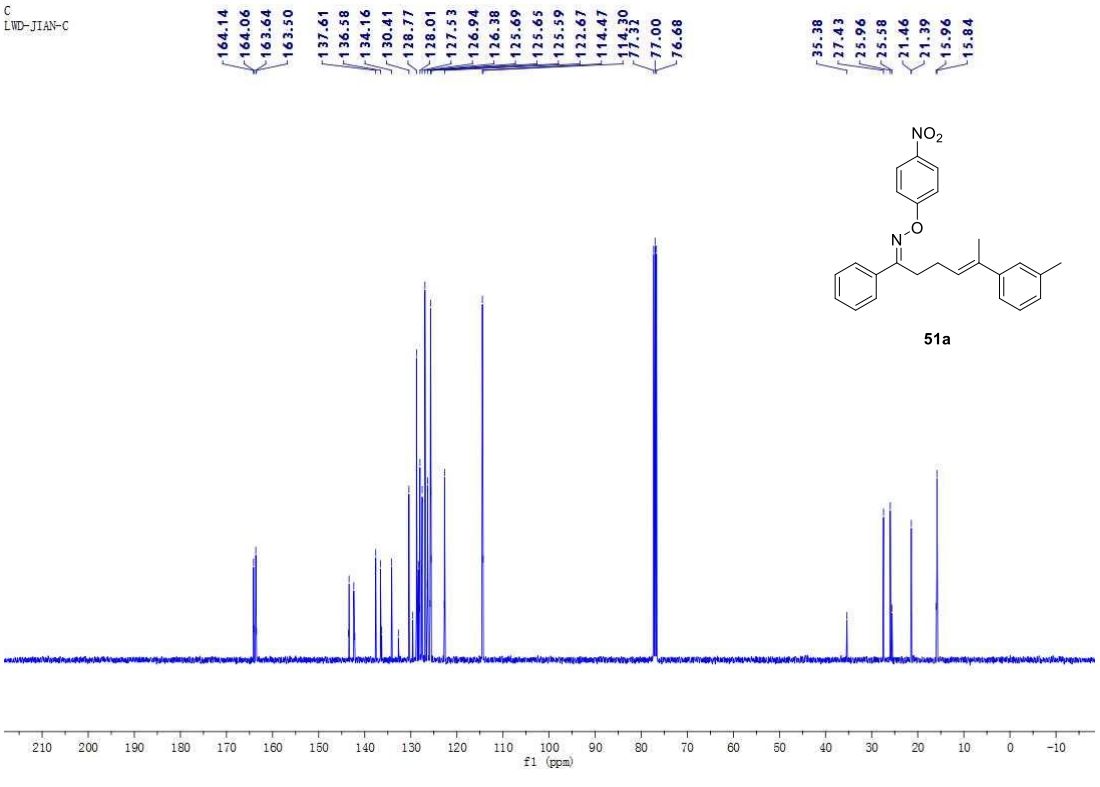

H
lwd-benbingsuan-diwu
8.18
8.17
8.06
8.05
7.37
7.35
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.22
7.21
7.20
7.19
7.16
5.77
5.74
3.00
2.98
2.96
2.94
2.92
2.90
2.83
2.82
2.81
2.80
2.73
2.71
2.70
2.67
2.65
2.63
2.52
2.51
2.49
2.47
2.43
2.41
2.40
2.04
2.04
0.00
NO2
N
O
49a
2.08
12.32
1.00
1.03
1.04
1.04
1.04
1.06
1.99
1.00
1.52
1.51
f1 (ppm)

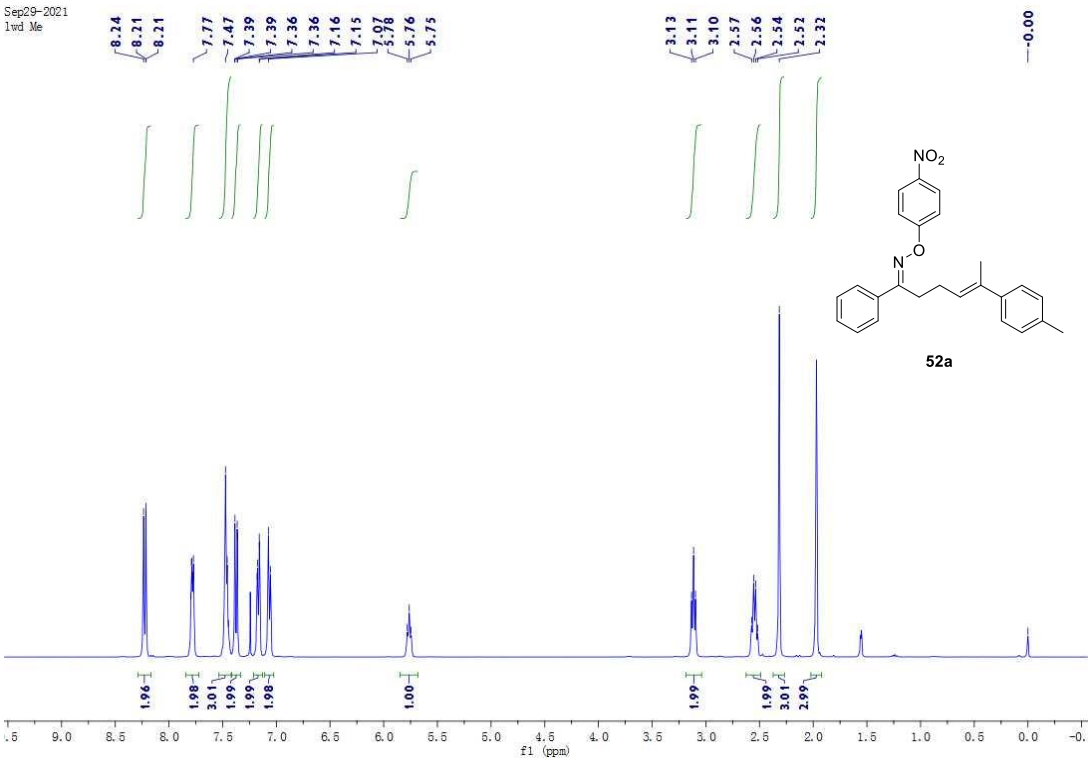

C
lwd-benbingsuan-diwu-C
165.93
165.85
164.13
164.10
128.55
128.51
128.28
128.18
128.16
125.61
125.54
77.32
77.00
76.68
36.17
34.41
32.08
32.03
31.40
29.32
25.20
25.01
15.89
15.76
NO2
N
O
49a
f1 (ppm)

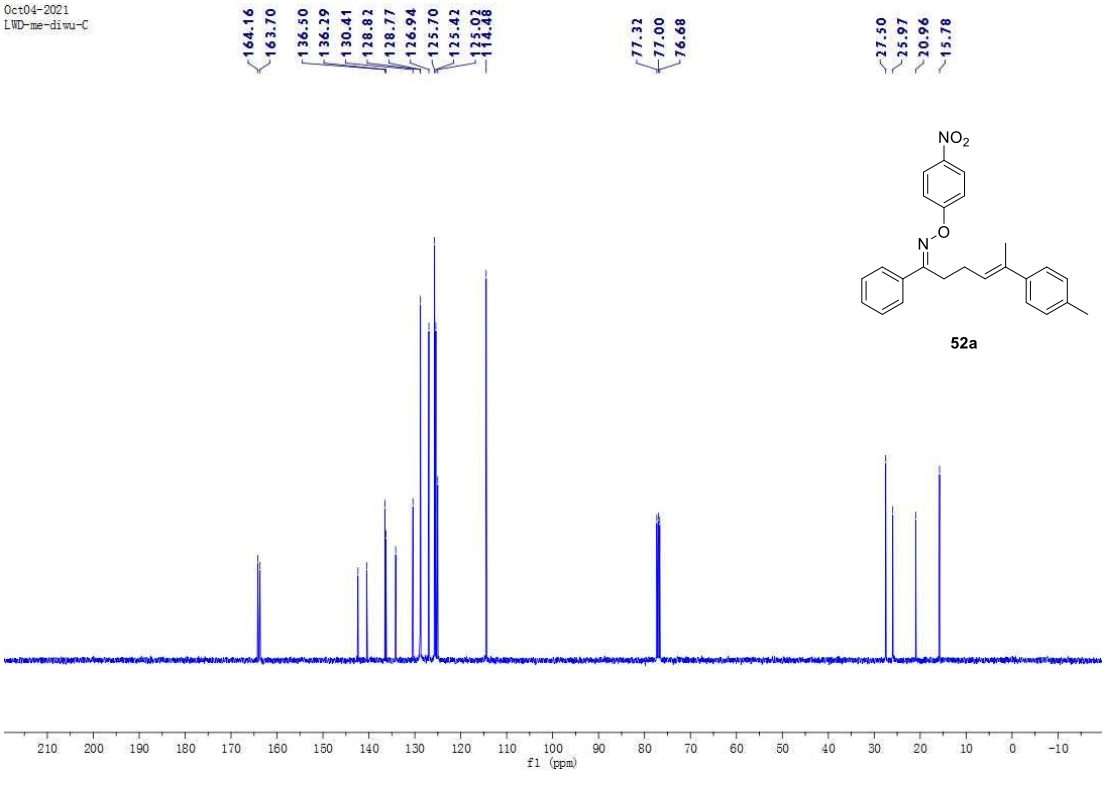

H
LWD-XIAN
8.23
8.22
8.21
8.20
7.52
7.39
7.35
7.35
7.33
7.32
7.32
7.25
5.88
5.86
5.84
2.96
2.94
2.92
2.85
2.83
2.81
2.67
2.65
2.60
2.58
2.56
2.55
2.07
NO2
N
O
50a
1.98
2.07
7.01
4.04
0.95
1.00
1.80
0.18
1.99
2.97
f1 (ppm)

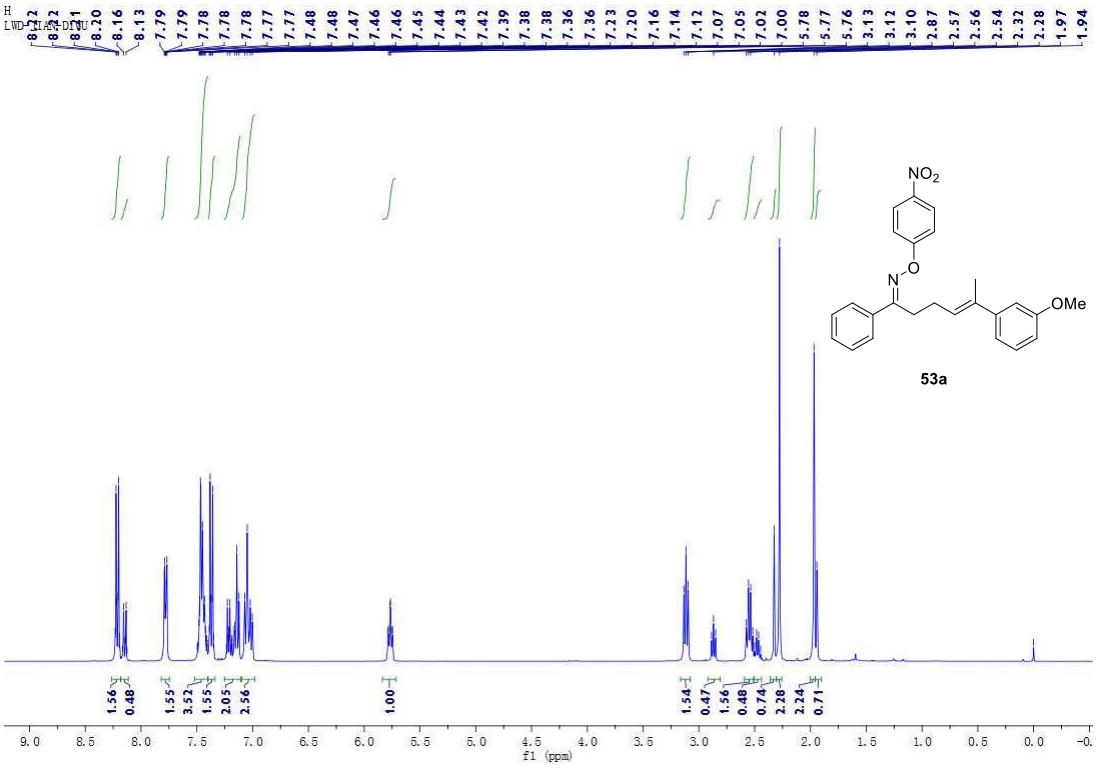

C
XIAN-C
163.89
163.69
143.30
142.41
136.44
136.34
135.68
129.17
128.86
128.13
127.17
126.80
125.97
125.67
125.55
123.32
114.45
77.32
77.00
76.68
26.21
25.43
15.80
NO2
N
O
50a
f1 (ppm)

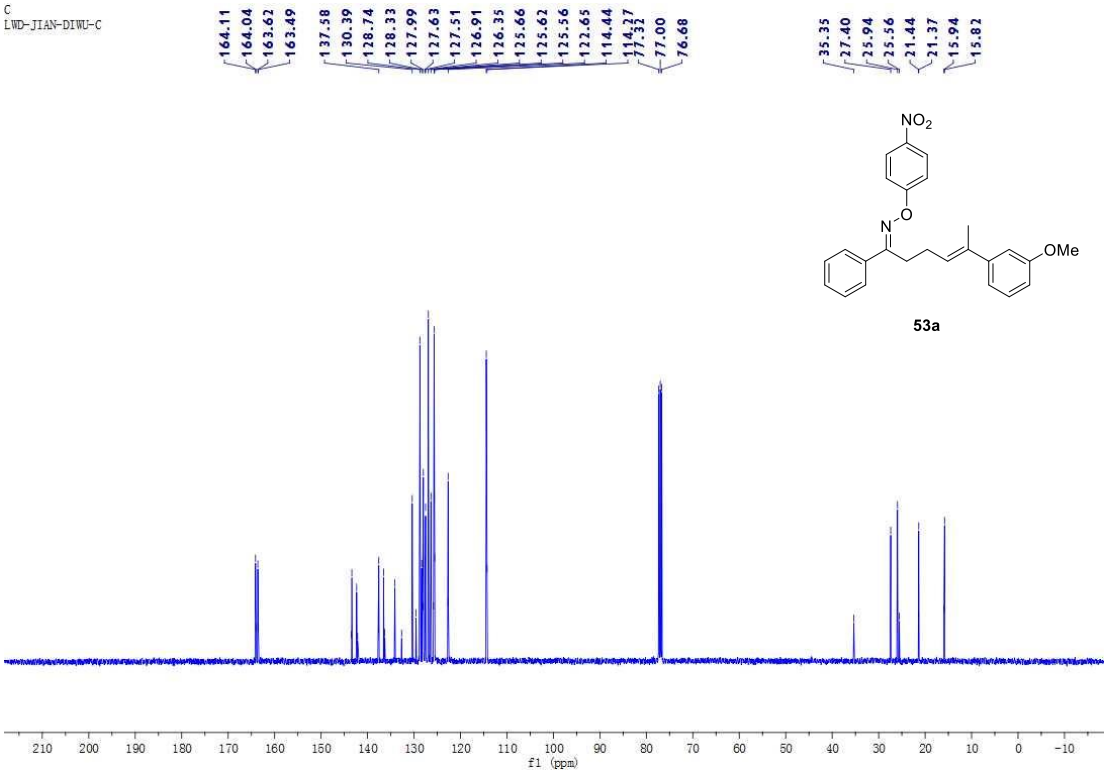

H
LWD-JIAN-H
8.23
8.23
8.21
8.21
8.17
8.14
7.79
7.79
7.79
7.78
7.78
7.78
7.77
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.39
7.38
7.37
7.36
7.23
7.23
7.21
7.16
7.14
7.13
7.07
7.05
7.03
7.01
5.77
5.77
3.14
3.12
3.10
2.87
2.58
2.56
2.54
2.33
2.28
1.97
1.94
NO2
N
O
51a
1.56
0.46
1.56
3.41
1.59
0.61
1.44
2.57
1.00
1.55
0.44
1.55
0.46
0.70
2.25
2.23
0.68
f1 (ppm)

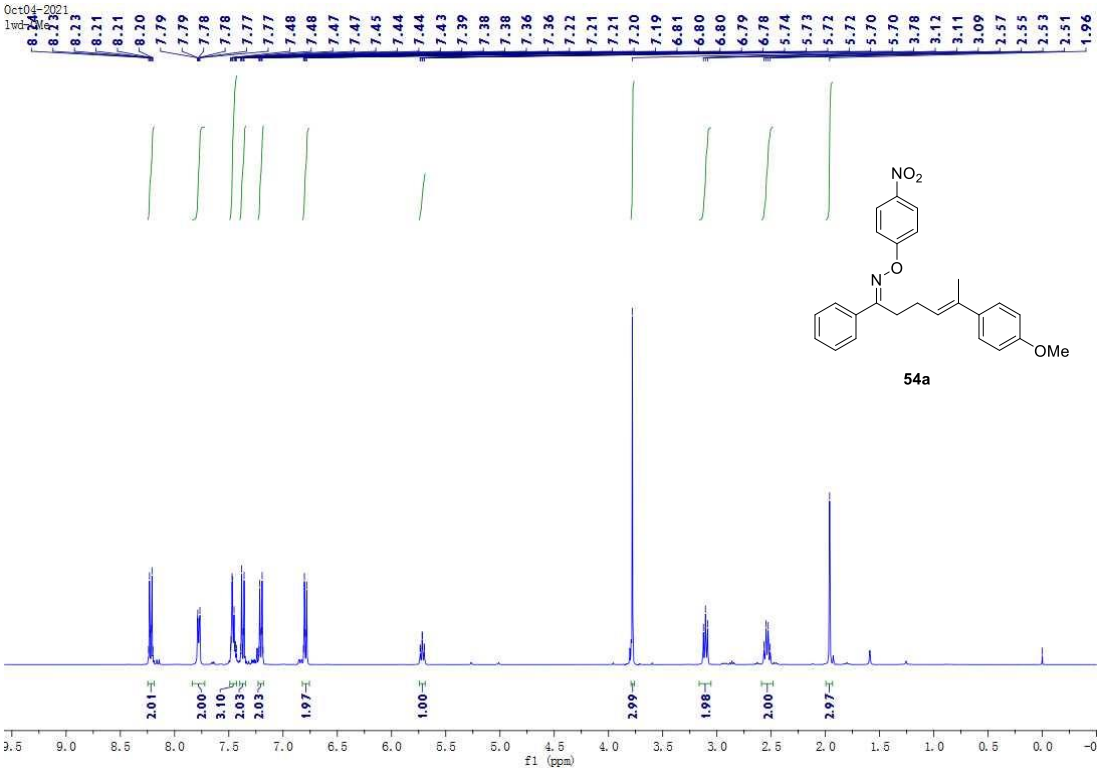

C
LWD-JIAN-C
164.14
164.06
163.64
163.50
137.61
136.58
134.16
130.41
128.77
128.01
127.53
126.94
126.38
125.69
125.65
125.59
122.67
114.47
114.30
77.32
77.00
76.68
35.38
27.43
25.96
25.58
21.46
21.39
15.96
15.84
NO2
N
O
51a
f1 (ppm)

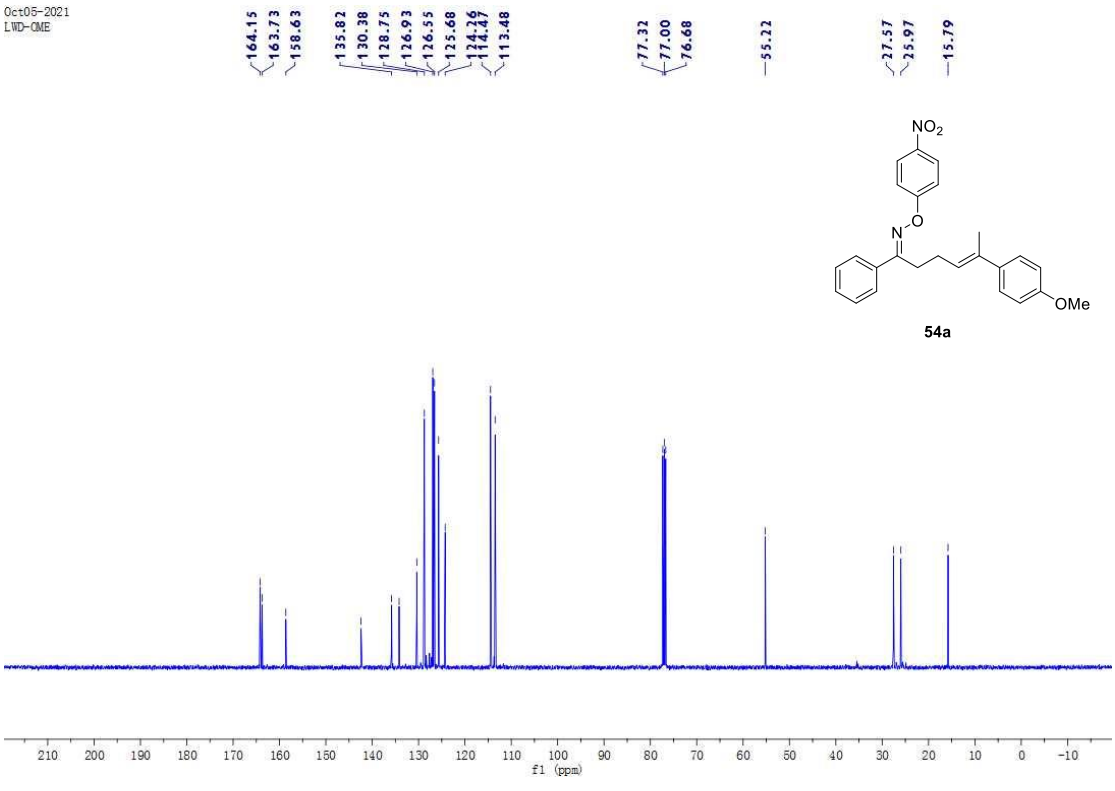

Sep29-2021
lwd Me
8.24
8.21
8.21
7.77
7.47
7.39
7.39
7.36
7.36
7.16
7.15
7.07
5.78
5.76
5.75
3.13
3.11
3.10
2.57
2.56
2.54
2.52
2.32
-0.00
NO2
N
O
52a
1.96
1.98
3.01
1.99
1.99
1.98
1.00
1.99
1.99
3.01
2.99
f1 (ppm)

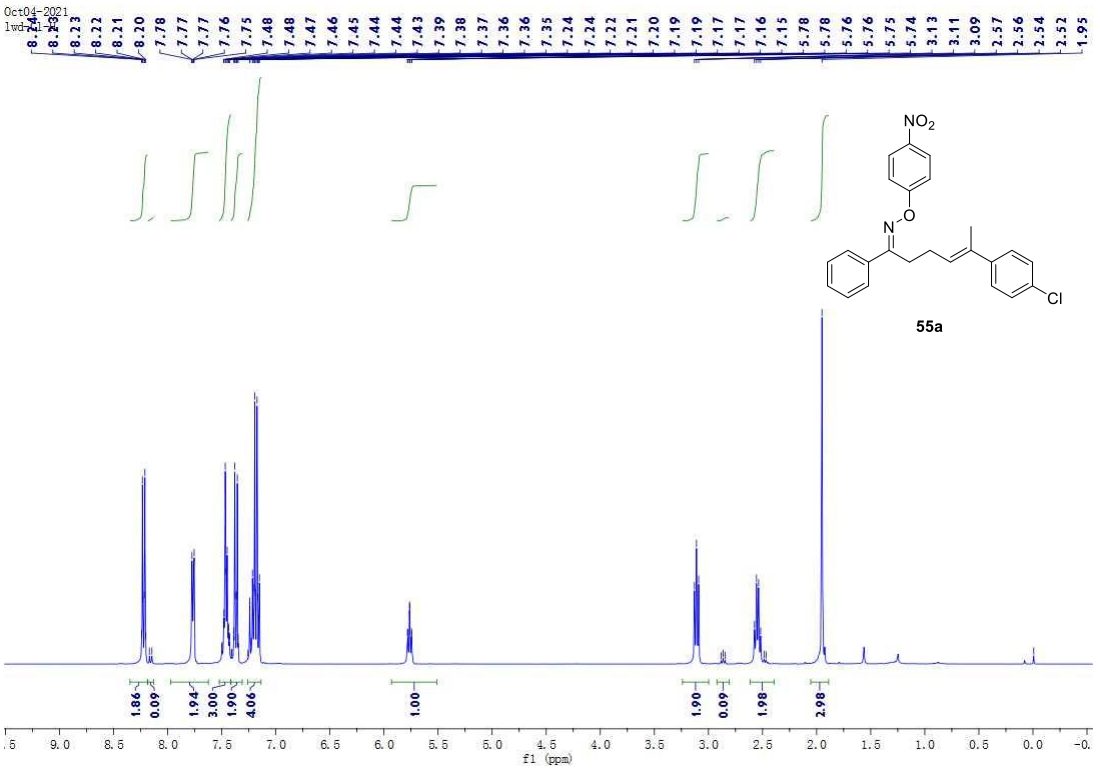

Oct04-2021
LWD-me-diwu-C
164.16
163.70
136.50
136.29
130.41
128.82
128.77
126.94
125.70
125.42
125.02
114.48
77.32
77.00
76.68
27.50
25.97
20.96
15.78
NO2
N
O
52a
f1 (ppm)

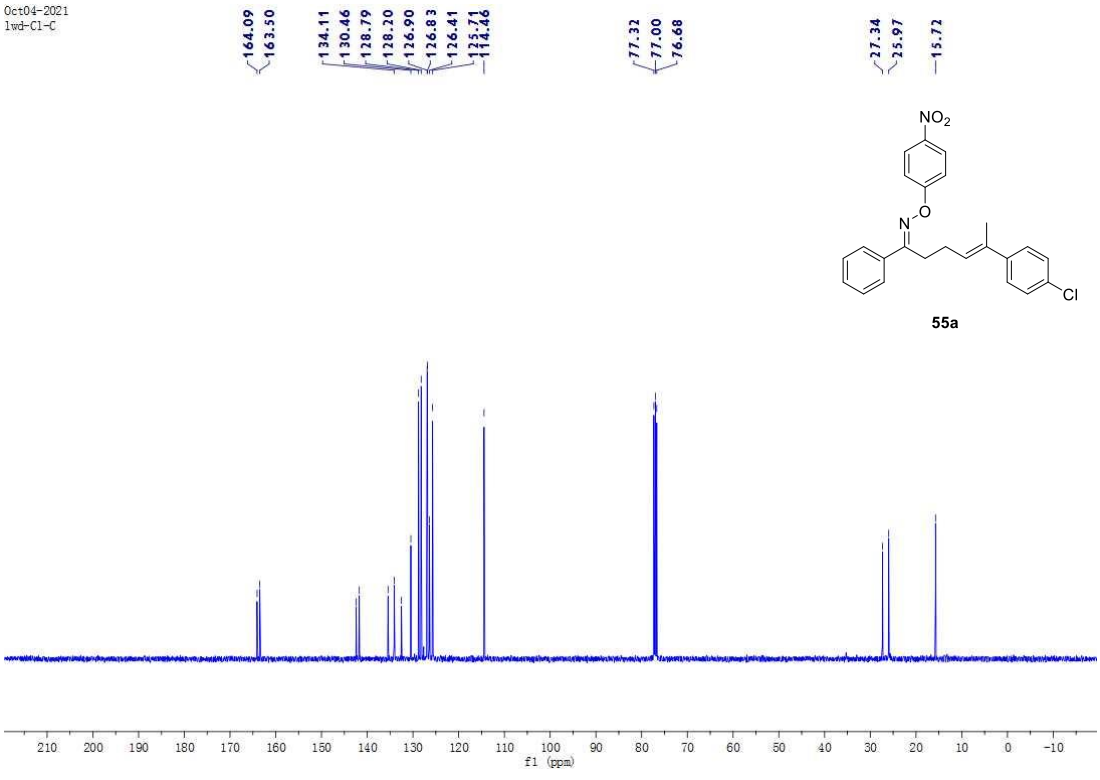

H
LWD-JIAN-DIWU
8.22
8.21
8.20
8.16
8.13
7.79
7.78
7.77
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.39
7.38
7.36
7.23
7.20
7.16
7.14
7.12
7.07
7.05
7.02
7.00
5.78
5.77
5.76
3.13
3.12
3.10
2.87
2.57
2.56
2.54
2.32
2.28
1.97
1.94
NO2
N
O
OMe
53a
1.56
0.48
1.55
3.52
1.55
2.05
2.56
1.00
1.54
0.47
1.56
0.48
0.74
2.28
2.24
0.71
f1 (ppm)

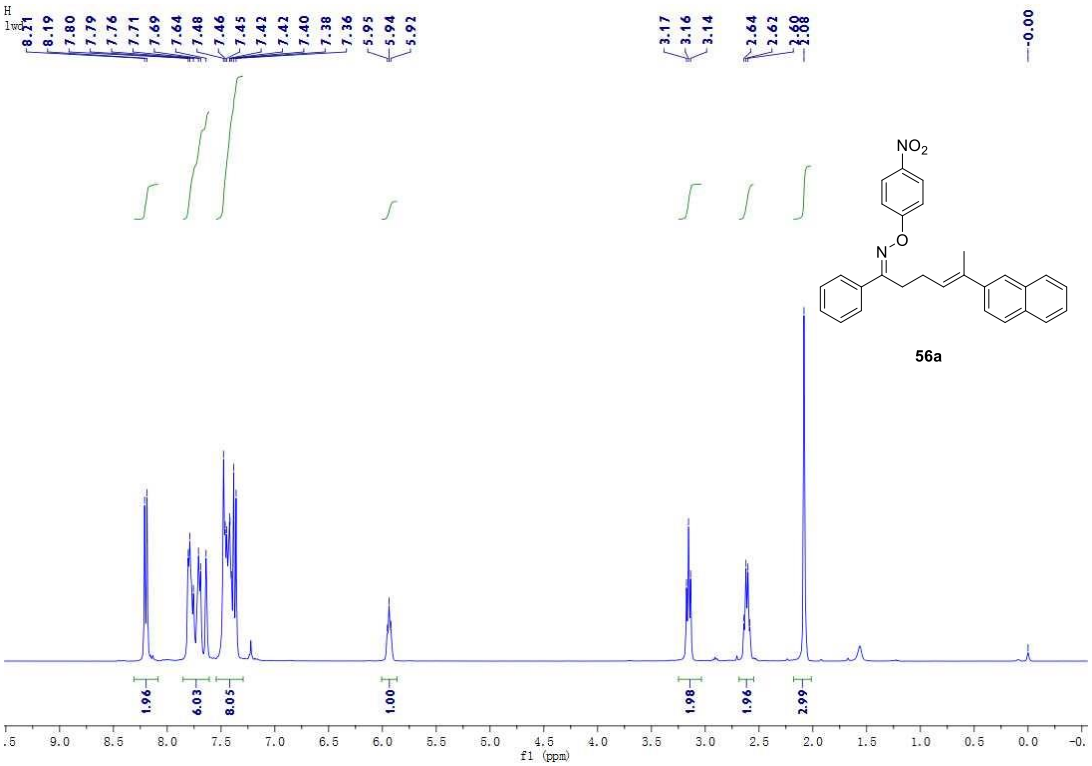

C
LWD-JIAN-DIWU-C
164.11
164.04
163.62
163.49
137.58
130.39
128.74
128.33
127.99
127.63
127.51
126.91
126.35
125.66
125.62
125.56
122.65
114.44
114.27
77.32
77.00
76.68
35.35
27.40
25.94
25.56
21.44
21.37
15.94
15.82
NO2
N
O
OMe
53a
f1 (ppm)

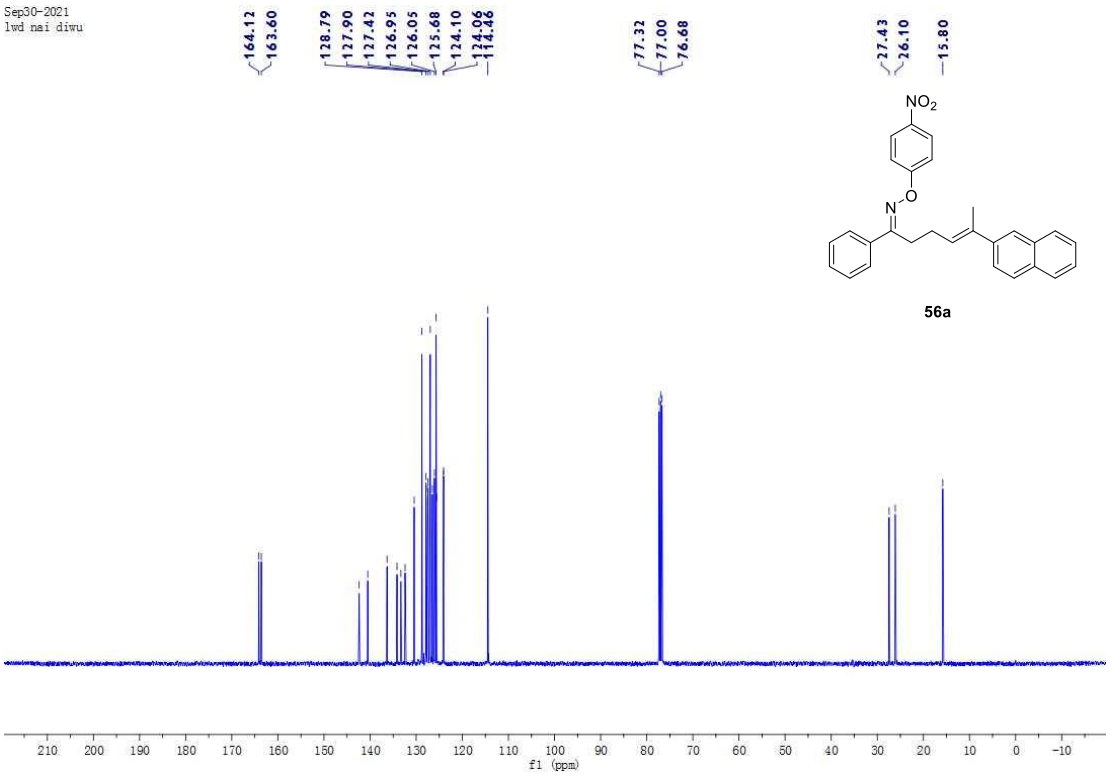

Oct04-2021
lwd-AM-2
8.24
8.23
8.21
8.21
8.20
7.79
7.79
7.78
7.78
7.77
7.77
7.48
7.48
7.47
7.47
7.45
7.44
7.44
7.43
7.39
7.38
7.38
7.36
7.22
7.21
7.21
7.20
7.19
6.81
6.80
6.80
6.79
6.78
5.74
5.73
5.72
5.72
5.70
5.70
3.78
3.12
3.11
3.09
2.57
2.55
2.53
2.51
1.96
NO2
N
O
OMe
54a
2.01
2.00
3.10
2.03
2.03
1.97
1.00
2.99
1.98
2.00
2.97
f1 (ppm)

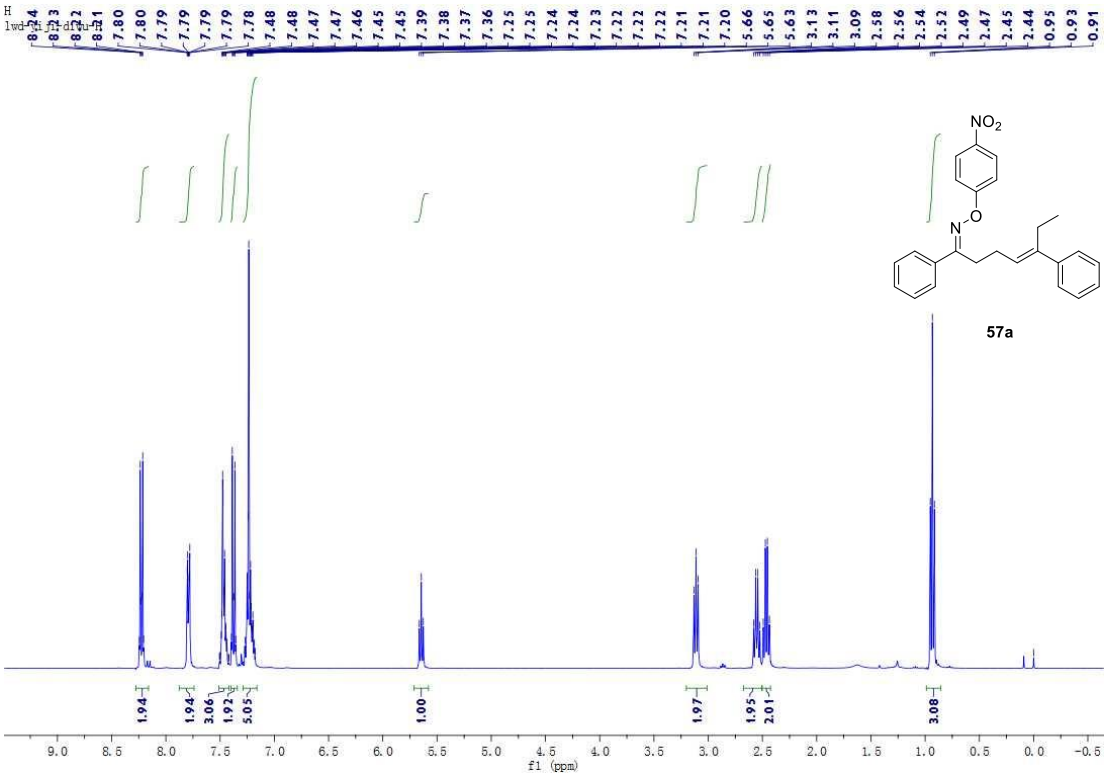

Oct05-2021
LWD-OME
164.15
163.73
158.63
135.82
130.38
128.75
126.93
126.55
125.68
114.26
114.17
113.48
77.32
77.00
76.68
55.22
27.57
25.97
15.79
NO2
N
O
OMe
54a
f1 (ppm)

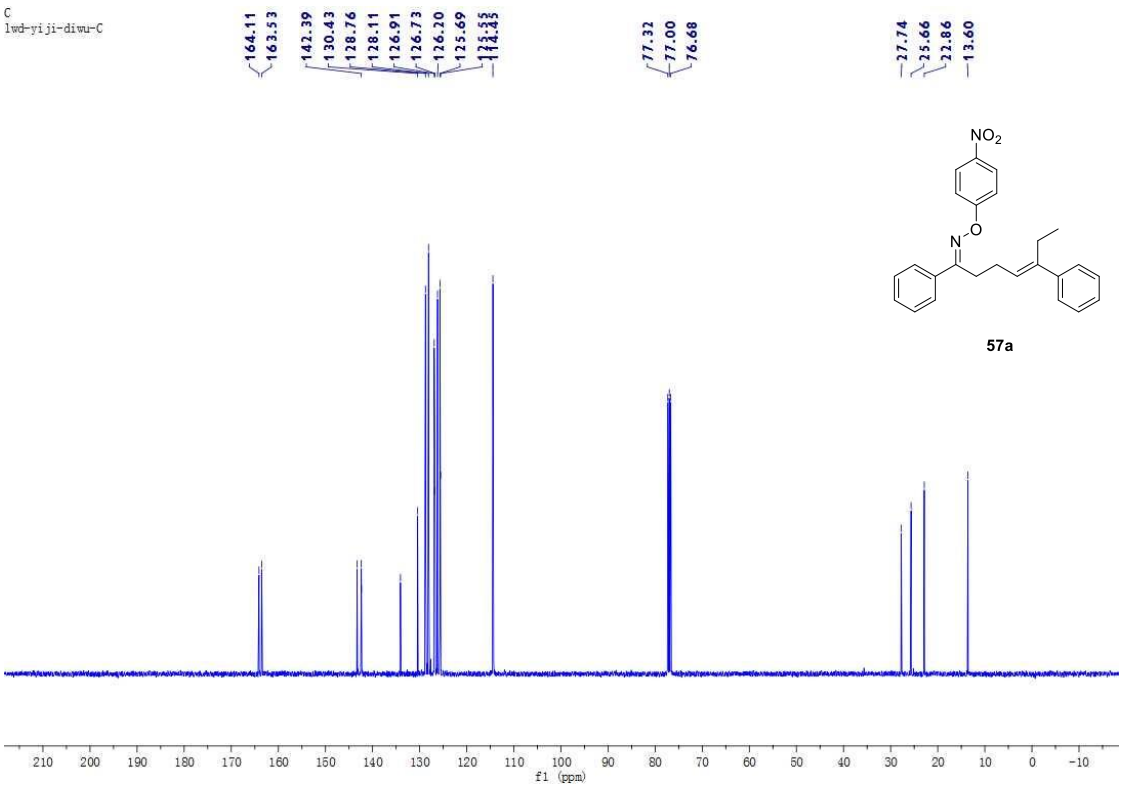

Oct04-2021
lwd-Cl-H
8.24
8.23
8.22
8.21
8.20
7.78
7.77
7.77
7.76
7.75
7.48
7.48
7.47
7.46
7.45
7.44
7.44
7.43
7.39
7.38
7.37
7.36
7.35
7.24
7.24
7.22
7.21
7.20
7.19
7.19
7.17
7.17
7.16
7.15
5.78
5.78
5.76
5.76
5.75
5.74
3.13
3.11
3.09
2.57
2.56
2.54
2.52
1.95
NO2
O
N
Cl
55a
1.86
0.09
1.94
3.00
1.90
4.06
1.00
1.90
0.09
1.98
2.98
f1 (ppm)

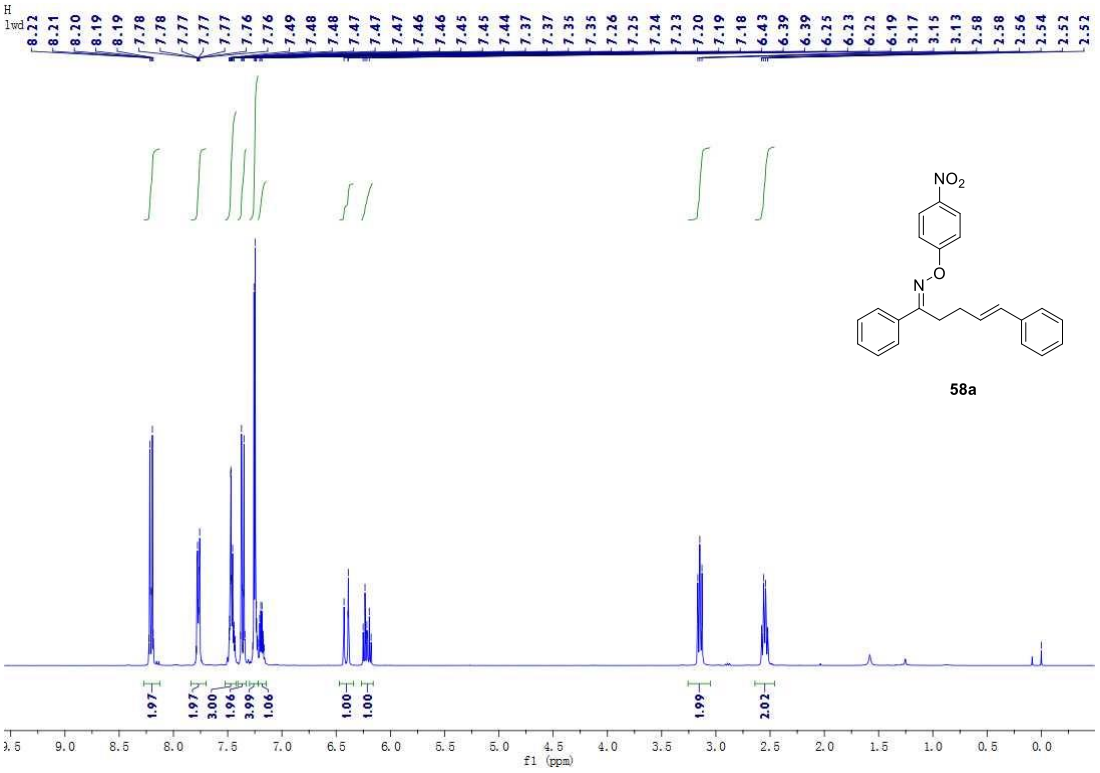

Oct04-2021
lwd-Cl-C
164.09
163.50
134.11
130.46
128.79
128.20
126.90
126.83
126.41
125.71
114.46
77.32
77.00
76.68
27.34
25.97
15.72
NO2
O
N
Cl
55a
f1 (ppm)

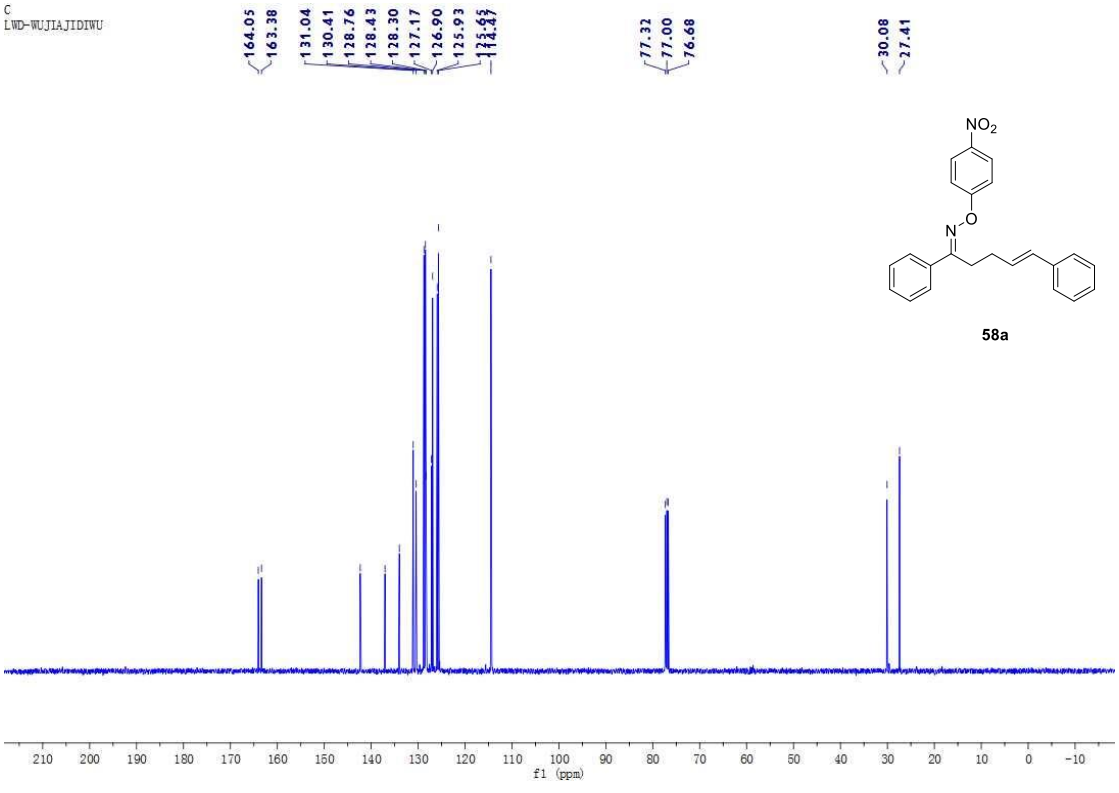

8.21
8.19
7.80
7.79
7.76
7.71
7.69
7.64
7.48
7.46
7.45
7.42
7.42
7.40
7.38
7.36
5.95
5.94
5.92
3.17
3.16
3.14
2.64
2.62
2.60
2.08
0.00
NO2
N
O
56a
1.96
6.03
8.05
1.00
1.98
1.96
2.99
f1 (ppm)

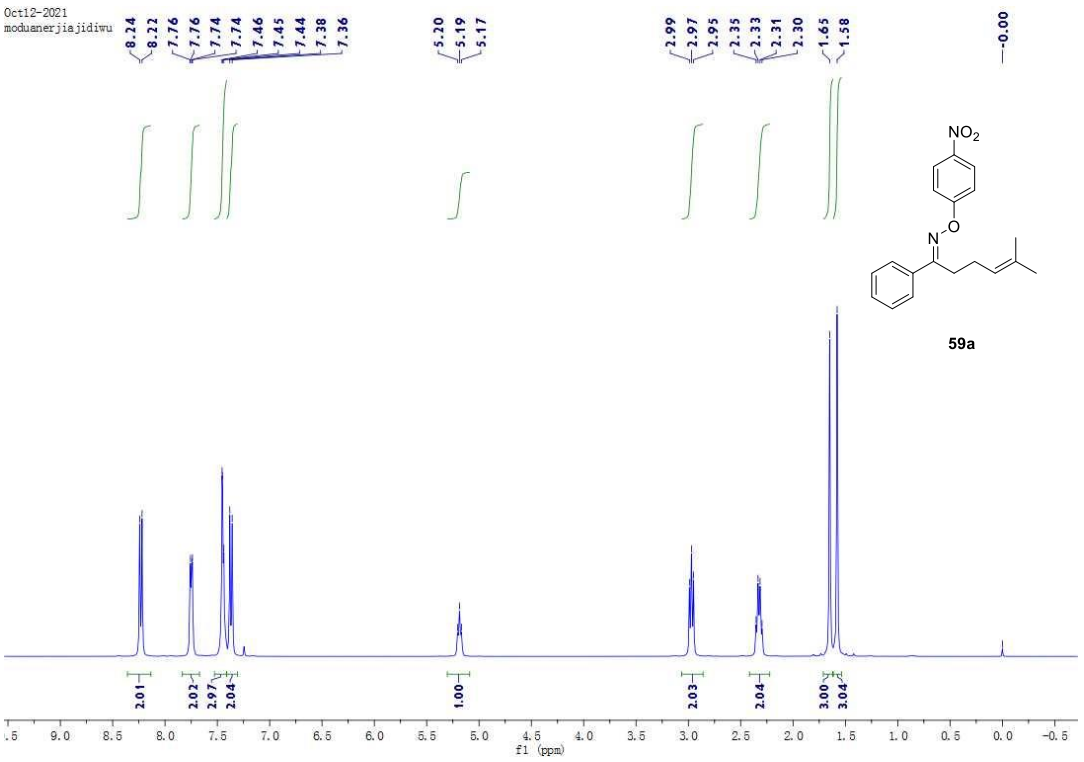

Sep30-2021
lwd nai diwu
164.12
163.60
138.79
137.90
137.42
136.95
136.05
135.68
134.10
134.06
134.46
77.32
77.00
76.68
27.43
26.10
15.80
NO2
N
O
56a
f1 (ppm)

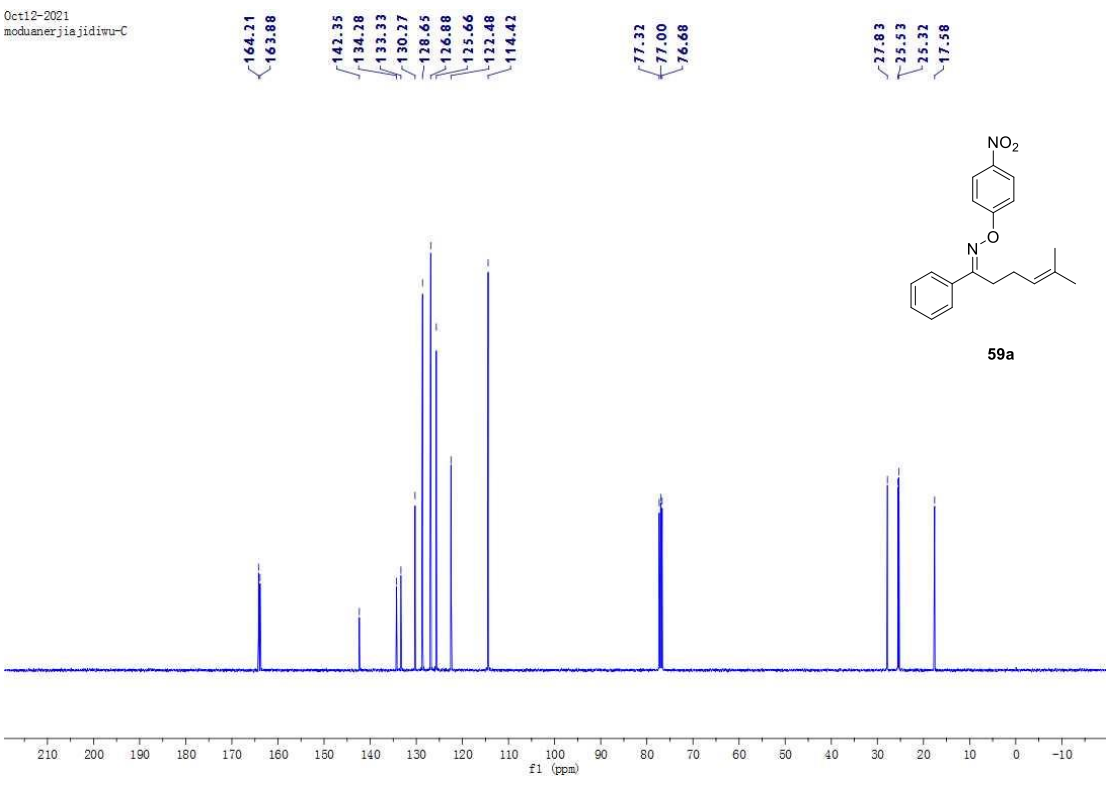

H
lwd-yiji-diwu-H
8.24
8.23
8.22
8.21
7.80
7.80
7.79
7.79
7.79
7.79
7.78
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.39
7.38
7.37
7.36
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.20
5.66
5.65
5.63
3.13
3.11
3.09
2.58
2.56
2.54
2.52
2.49
2.47
2.45
2.44
0.95
0.93
0.91
NO2
N
O
57a
1.94
1.94
3.06
1.92
5.05
1.00
1.97
1.95
2.01
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

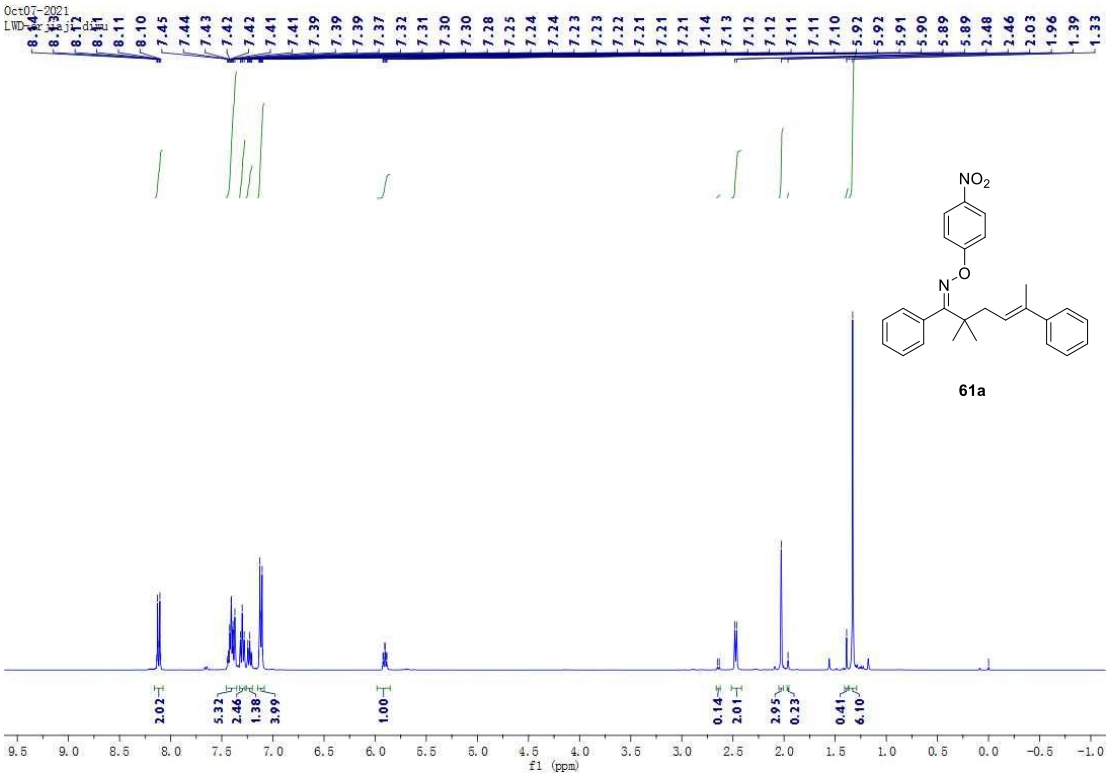

C
lwd-yiji-diwu-C
164.11
163.53
142.39
130.43
128.76
128.11
126.91
126.73
126.20
125.69
114.45
77.32
77.00
76.68
27.74
25.66
22.86
13.60
NO2
N
O
57a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

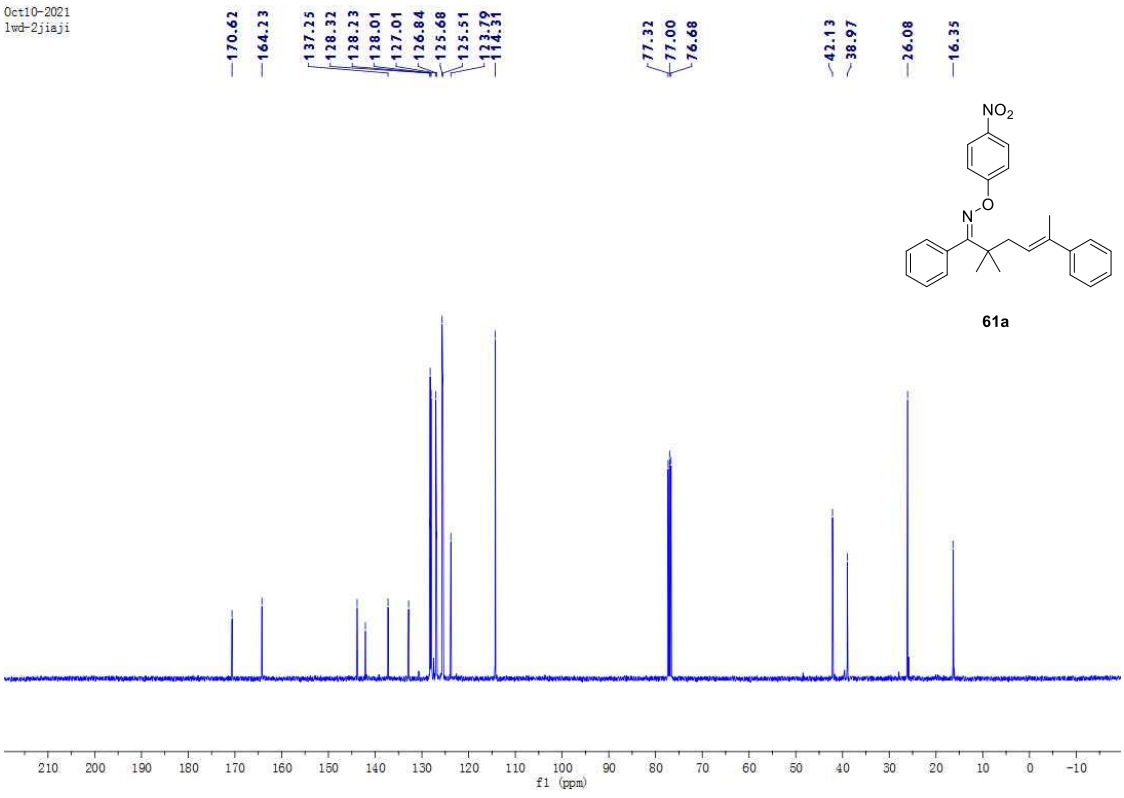

H
lwd
8.22
8.21
8.20
8.19
8.19
7.78
7.78
7.77
7.77
7.77
7.76
7.76
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.37
7.37
7.35
7.35
7.26
7.25
7.24
7.23
7.20
7.19
7.18
6.43
6.39
6.39
6.25
6.23
6.22
6.19
3.17
3.15
3.13
2.58
2.58
2.56
2.54
2.52
2.52
NO2
N
O
58a
1.97
1.97
3.00
1.96
3.99
1.06
1.00
1.00
1.99
2.02
f1 (ppm)

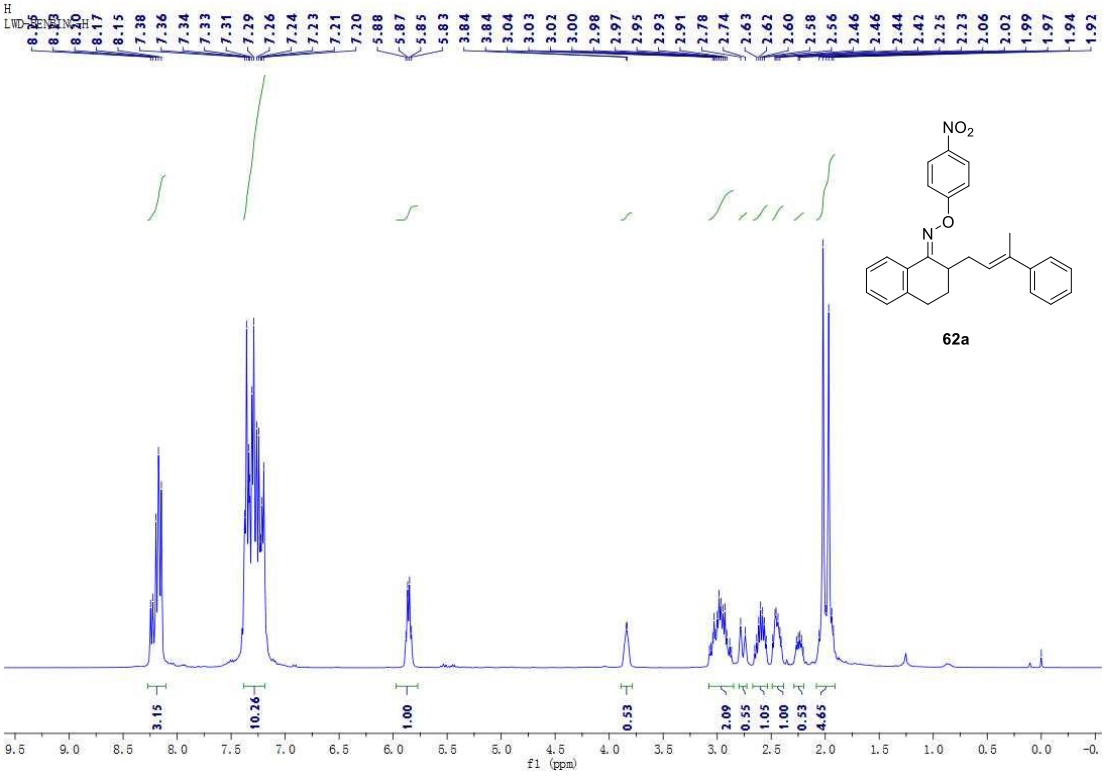

C
LWD-WUJIAJIDIWU
164.05
163.38
131.04
130.41
128.76
128.43
128.30
127.17
126.90
125.93
77.32
77.00
76.68
30.08
27.41
NO2
N
O
58a
f1 (ppm)


Oct12-2021
moduanerjiajidiwu
8.24
8.22
7.76
7.76
7.74
7.74
7.46
7.45
7.44
7.38
7.36
5.20
5.19
5.17
2.99
2.97
2.95
2.35
2.33
2.31
2.30
1.65
1.58
0.00
NO2
O
N
59a
2.01
2.02
2.97
2.04
1.00
2.03
2.04
3.00
3.04
f1 (ppm)

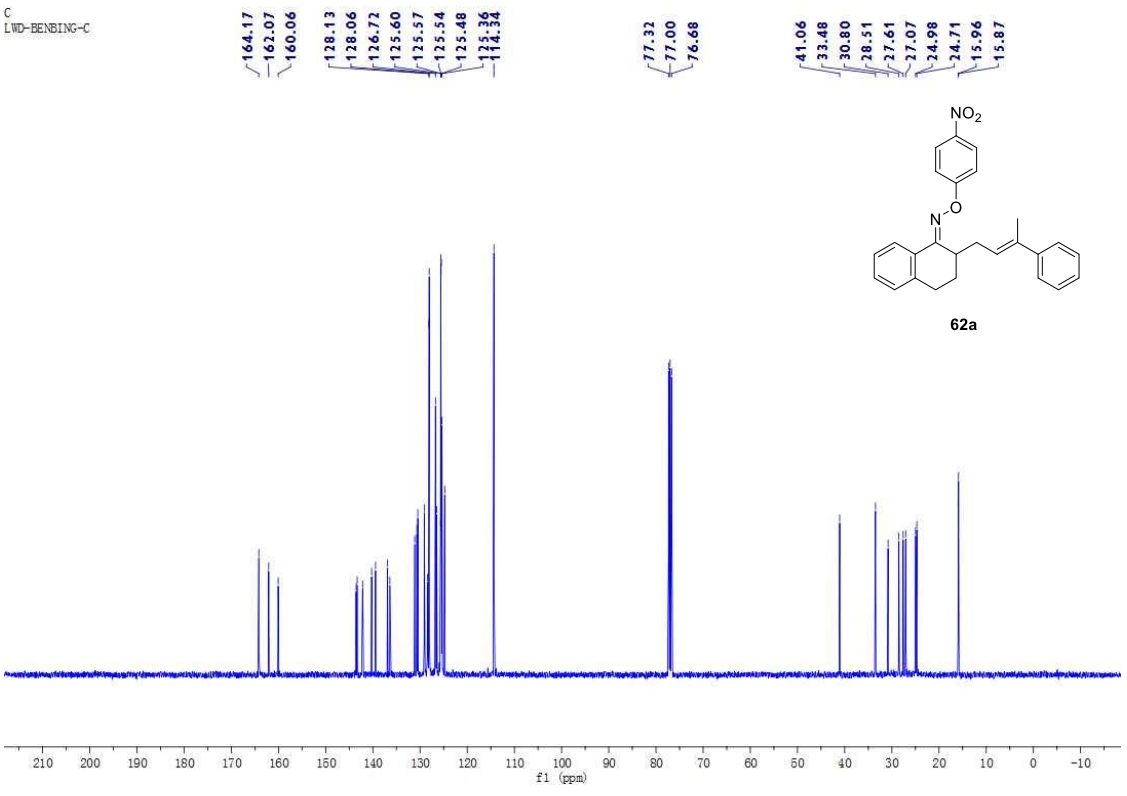

Oct12-2021
moduanerjiajidiwu-C
164.21
163.88
142.35
134.28
133.33
130.27
128.65
126.88
125.66
122.48
114.42
77.32
77.00
76.68
27.83
25.53
25.32
17.58
NO2
O
N
59a
f1 (ppm)


Oct07-2021
LWD-2jiajiaji
NO2
N
O
61a
2.02
5.32
2.46
1.38
3.99
1.00
0.14
2.01
2.95
0.23
0.41
6.10
f1 (ppm)

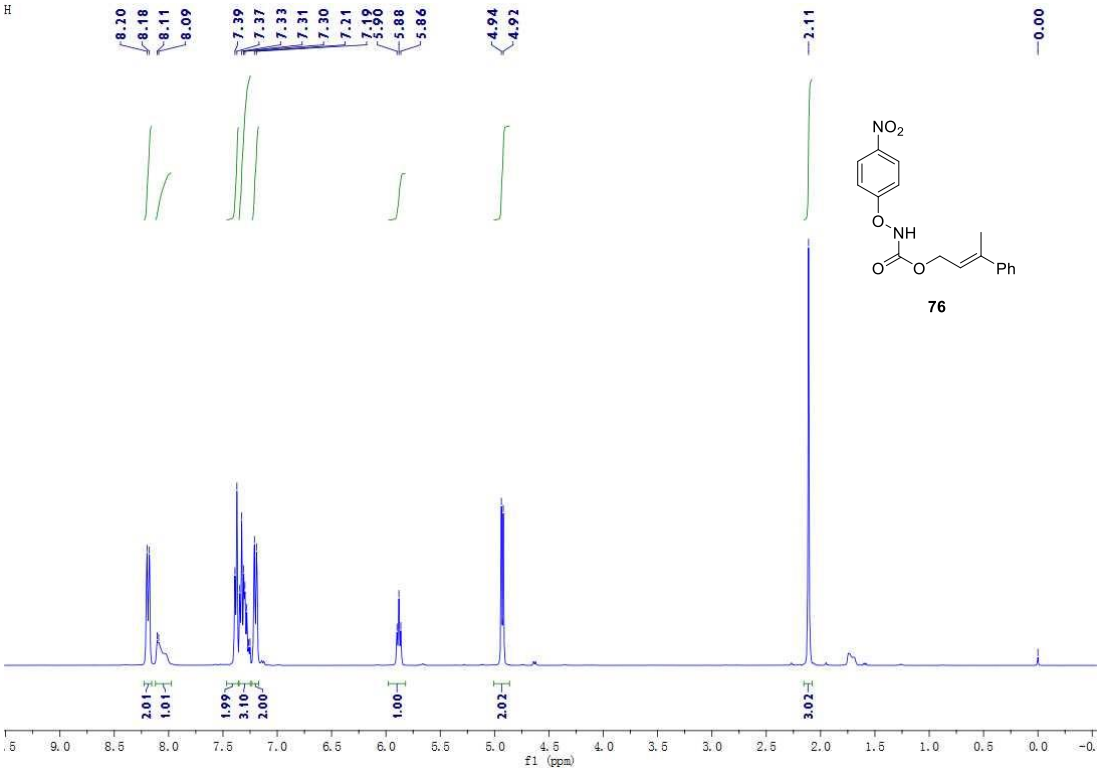

Oct10-2021
lwd-2jiaji
170.62
164.23
137.25
128.32
128.23
128.01
127.01
126.84
125.68
125.51
114.31
77.32
77.00
76.68
42.13
38.97
26.08
16.35
NO2
N
O
61a
f1 (ppm)

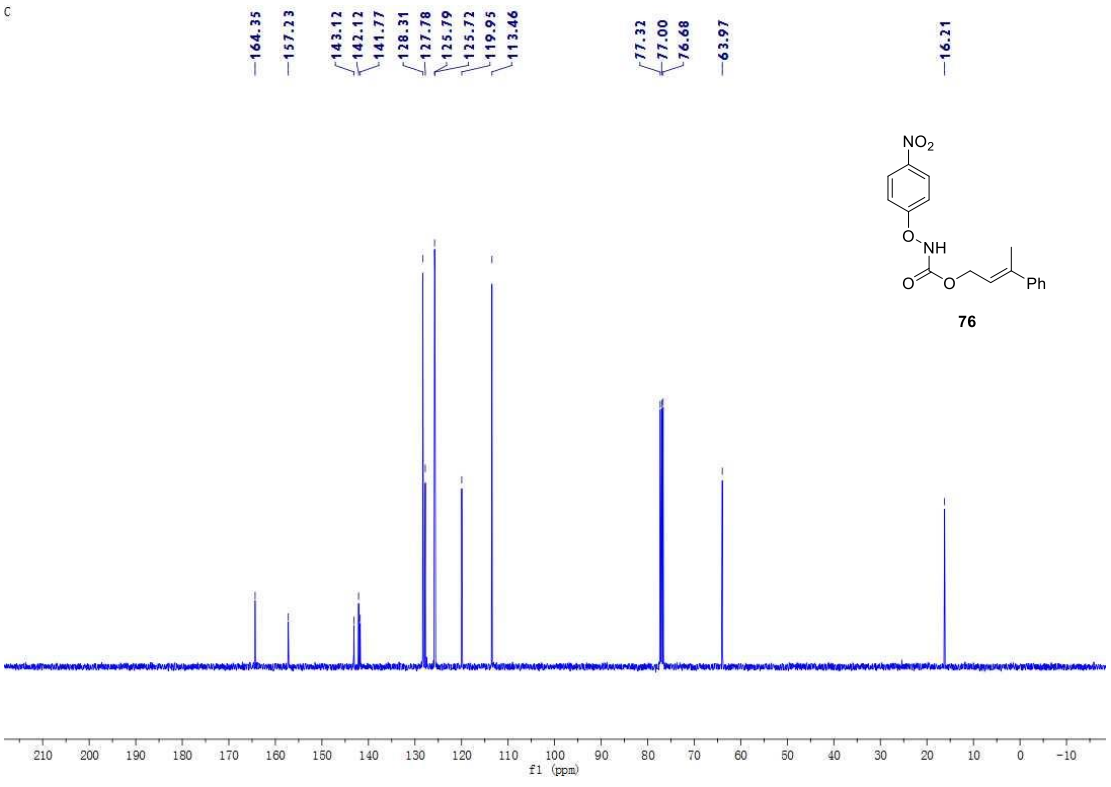

H
LWD-BENBING-H
8.19
8.17
8.15
7.38
7.36
7.34
7.33
7.31
7.29
7.26
7.24
7.23
7.21
7.20
5.88
5.87
5.85
5.83
3.84
3.84
3.04
3.03
3.02
3.00
2.98
2.97
2.95
2.93
2.91
2.78
2.74
2.63
2.62
2.60
2.58
2.56
2.46
2.46
2.44
2.42
2.25
2.23
2.06
2.02
1.99
1.97
1.94
1.92
NO2
N
O
3.15
10.26
1.00
0.53
2.09
0.55
1.05
1.00
0.53
4.65
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

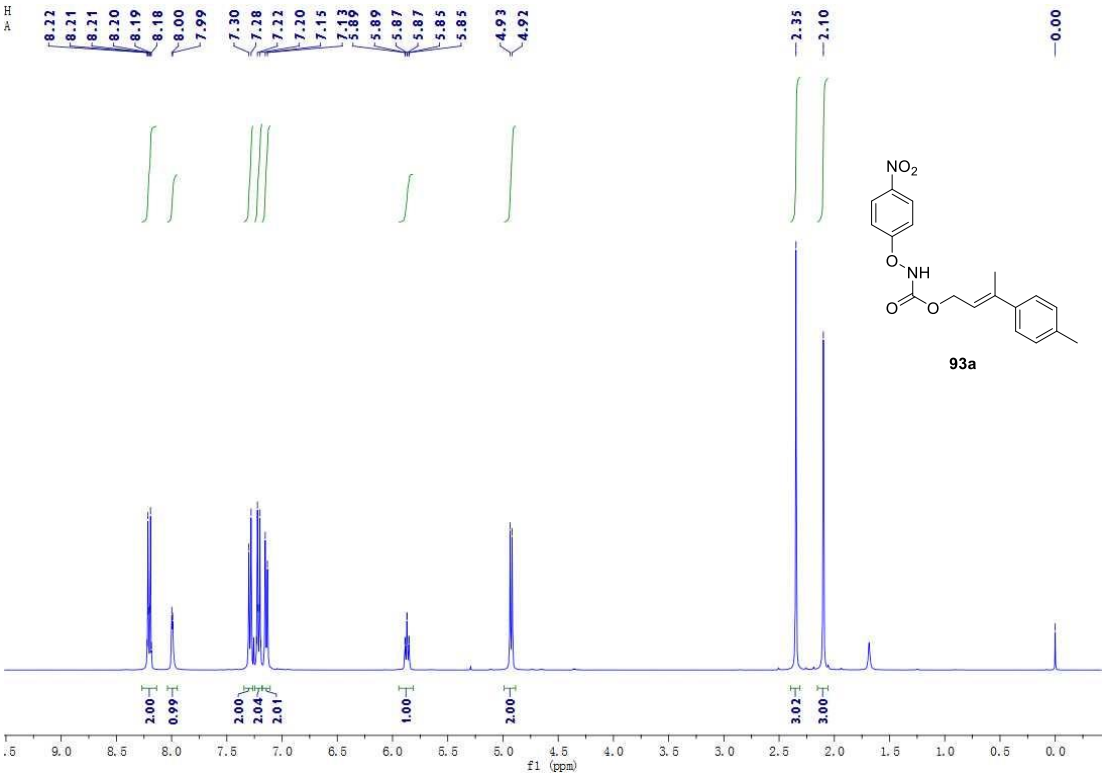
62a

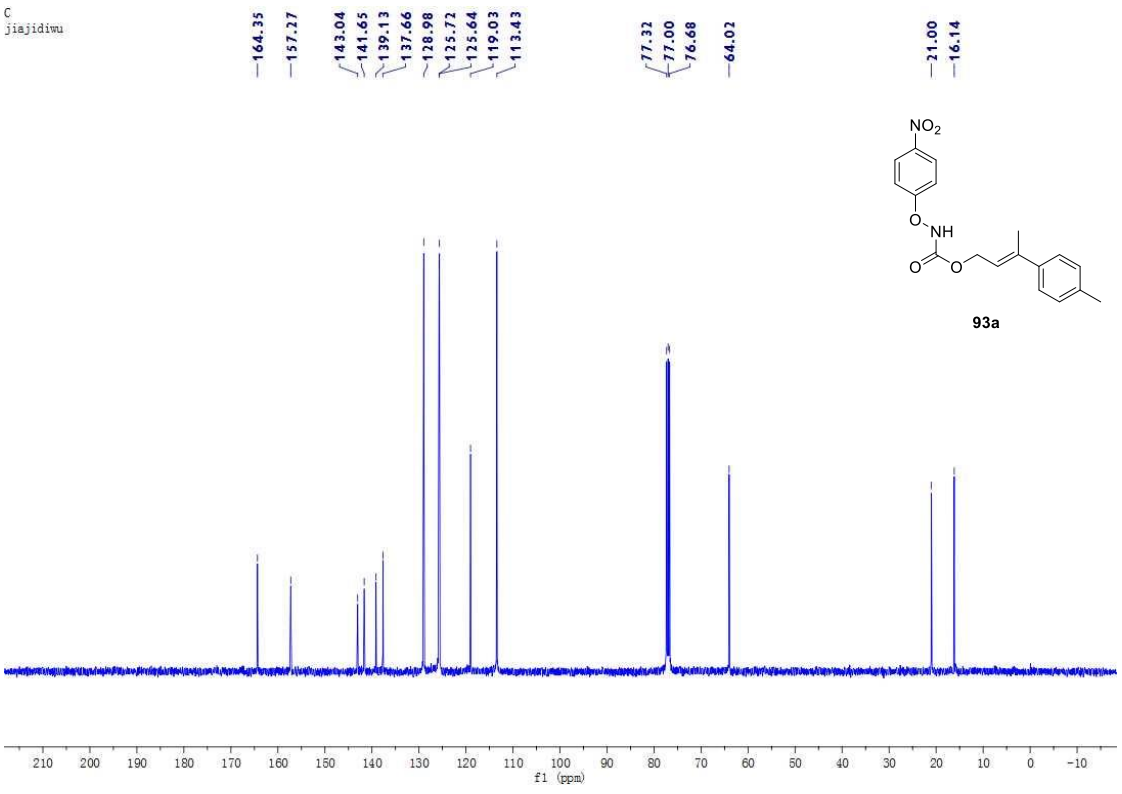

C
LWD-BENBING-C
164.17
162.07
160.06
128.13
128.06
126.72
125.60
125.57
125.54
125.48
77.32
77.00
76.68
41.06
33.48
30.80
28.51
27.61
27.07
24.98
24.71
15.96
15.87
NO2
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

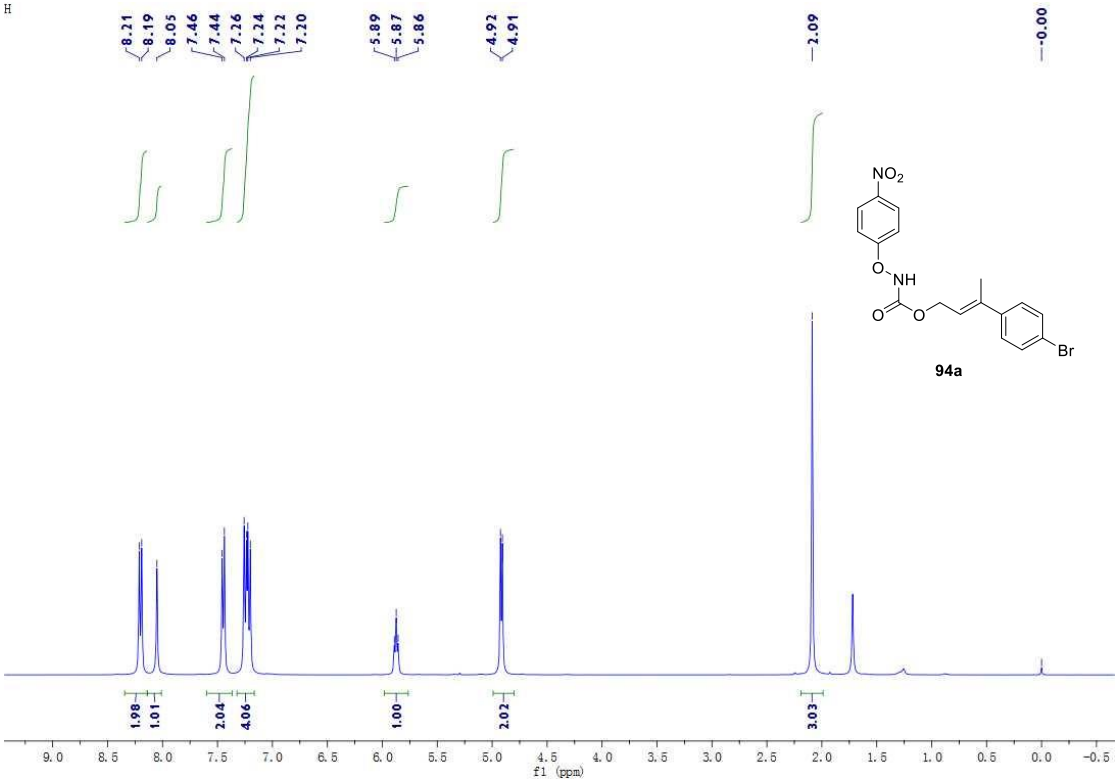
62a

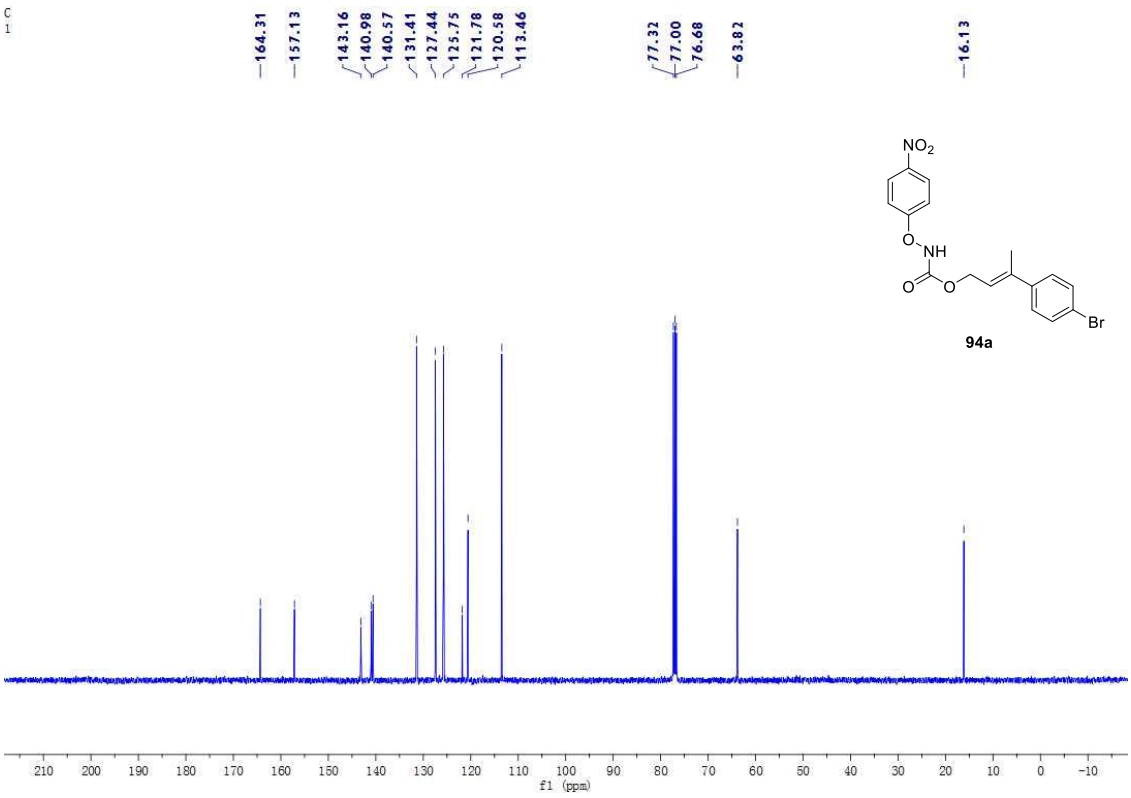

H
8.20
8.18
8.11
8.09
7.39
7.37
7.33
7.31
7.30
7.21
7.19
5.90
5.88
5.86
4.94
4.92
2.11
0.00
2.01
1.01
1.99
3.10
2.00
1.00
2.02
3.02
f1 (ppm)
NO2
O
NH
O
O
Ph
76

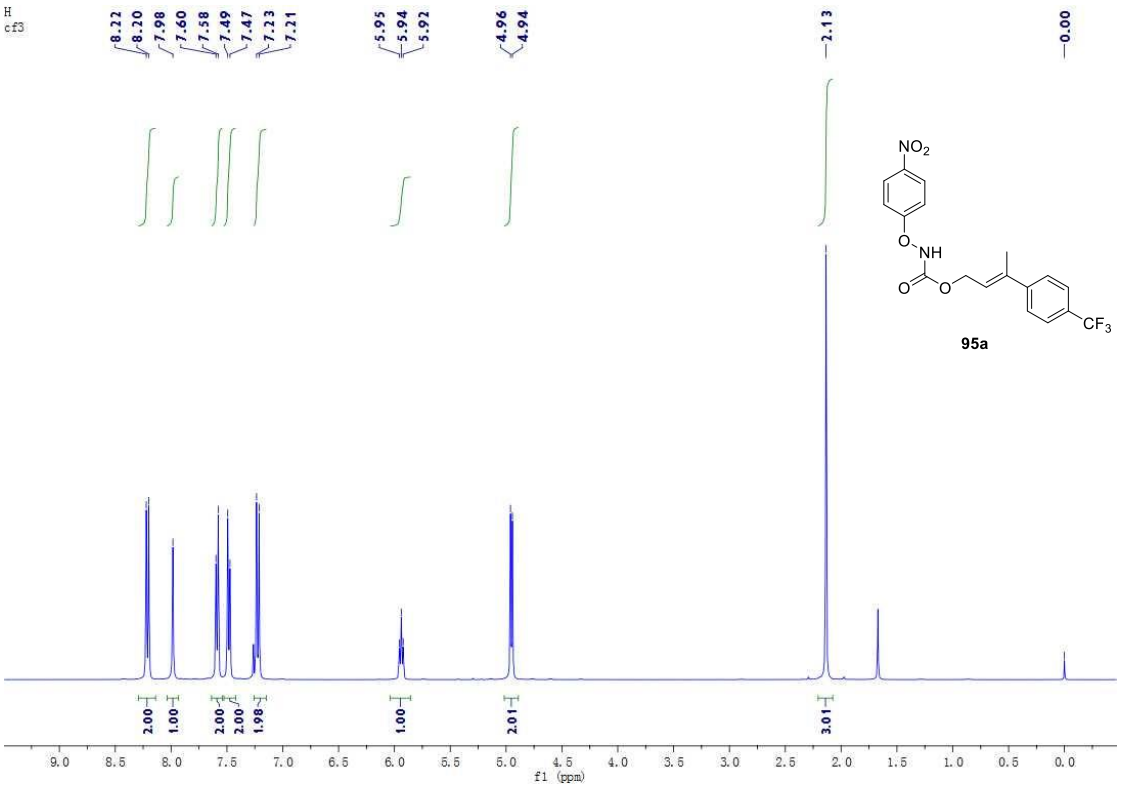

C
164.35
157.23
143.12
142.12
141.77
128.31
127.78
125.79
125.72
119.95
113.46
77.32
77.00
76.68
63.97
16.21
f1 (ppm)
NO2
O
NH
O
O
Ph
76

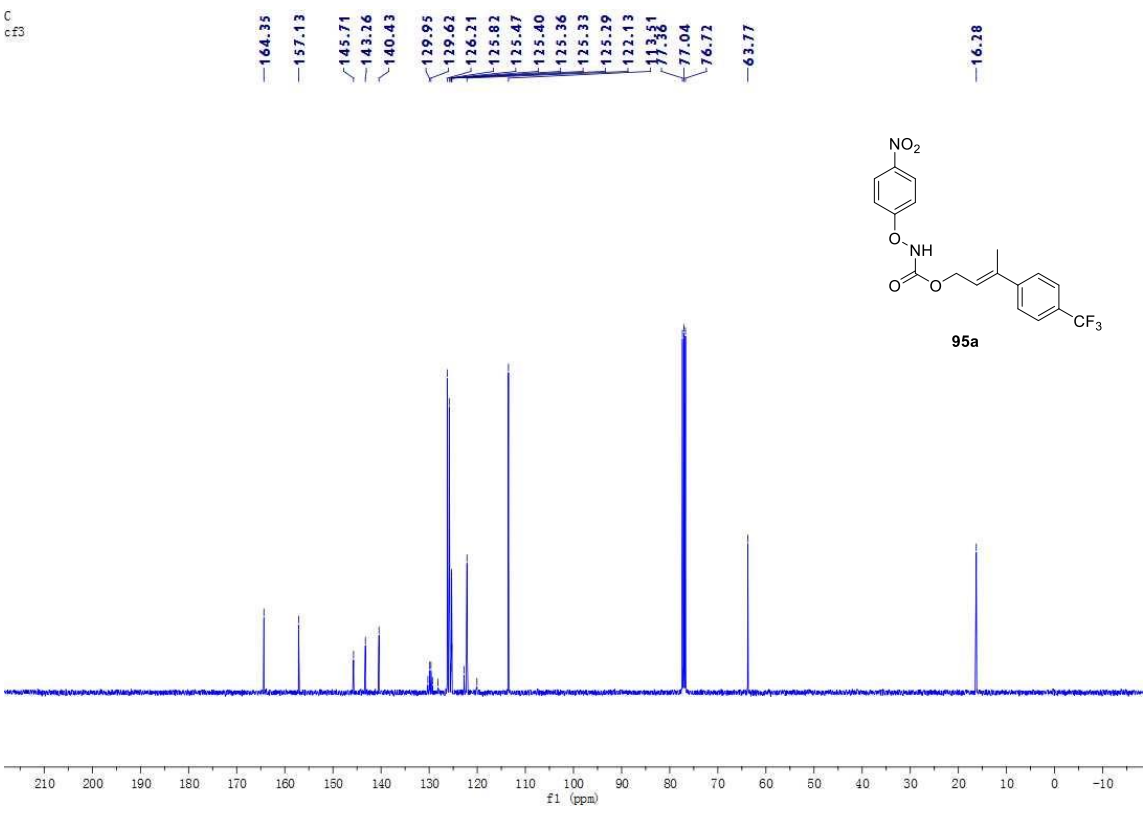

H
A
8.22
8.21
8.21
8.20
8.19
8.18
8.00
7.99
7.30
7.28
7.22
7.20
7.15
7.13
5.89
5.89
5.87
5.87
5.85
5.85
4.93
4.92
2.35
2.10
0.00
2.00
0.99
2.00
2.04
2.01
1.00
2.00
3.02
3.00
f1 (ppm)
NO2
NH
O
O
O
93a

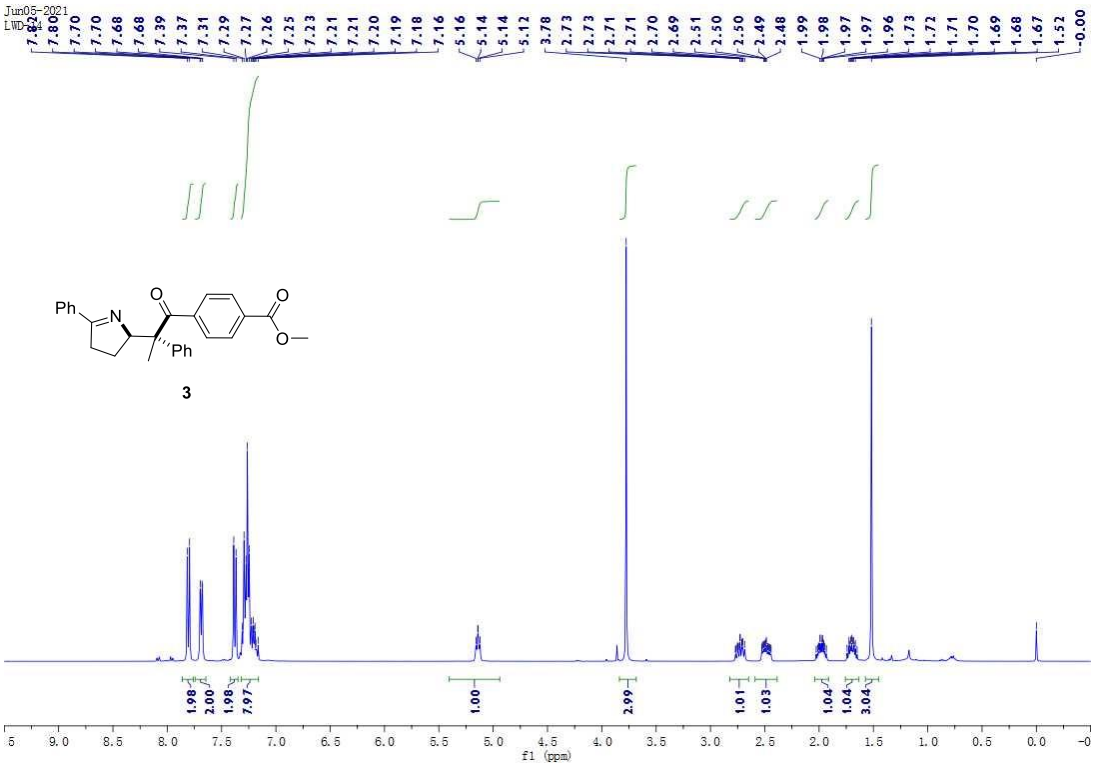

C
jiajidiwu
164.35
157.27
143.04
141.65
139.13
137.66
128.98
125.72
125.64
119.03
113.43
77.32
77.00
76.68
64.02
21.00
16.14
f1 (ppm)
NO2
NH
O
O
O
93a

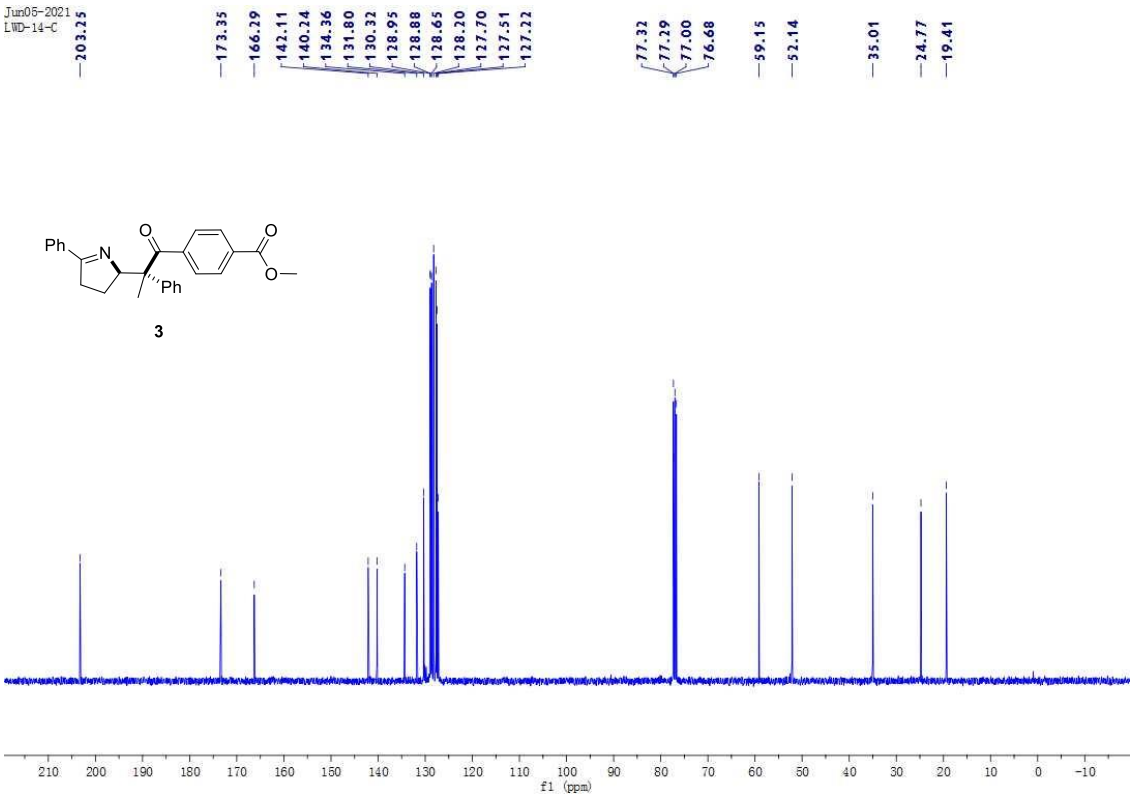

H
8.21
8.19
8.05
7.46
7.44
7.26
7.24
7.22
7.20
5.89
5.87
5.86
4.92
4.91
2.09
0.00
NO2
O
NH
O
O
Br
94a
1.98
1.01
2.04
4.06
1.00
2.02
3.03
f1 (ppm)

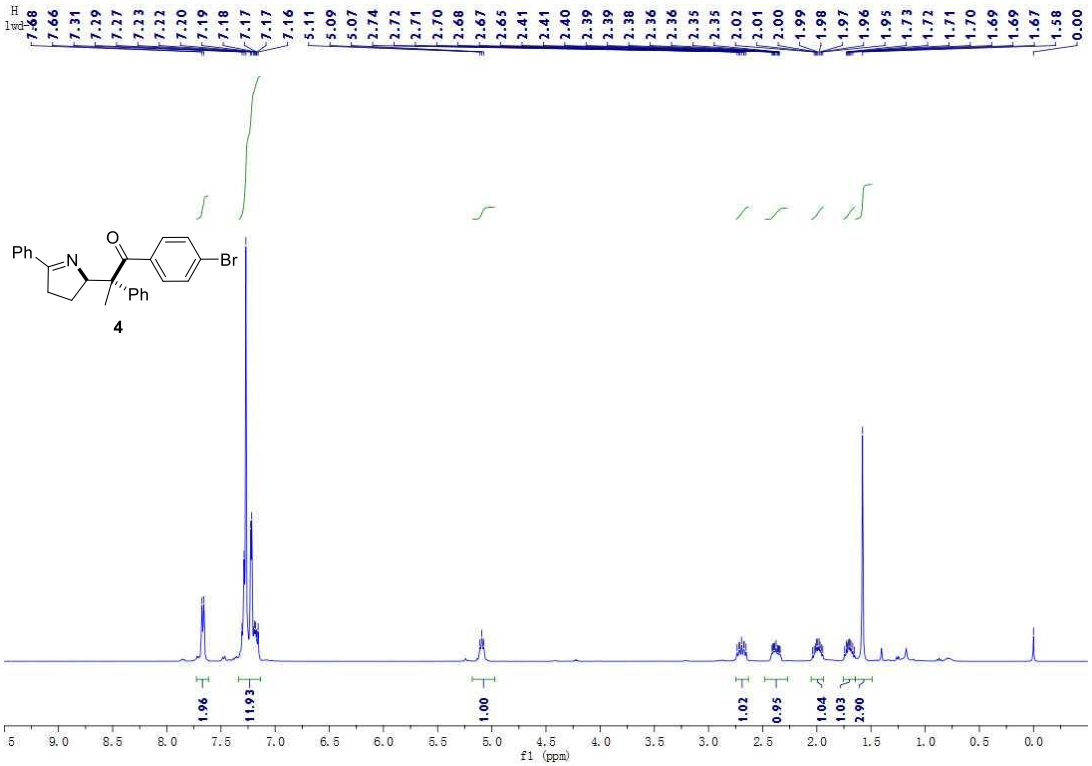

C
1
164.31
157.13
143.16
140.98
140.57
131.41
127.44
125.75
121.78
120.58
113.46
77.32
77.00
76.68
63.82
16.13
NO2
O
NH
O
O
Br
94a
f1 (ppm)

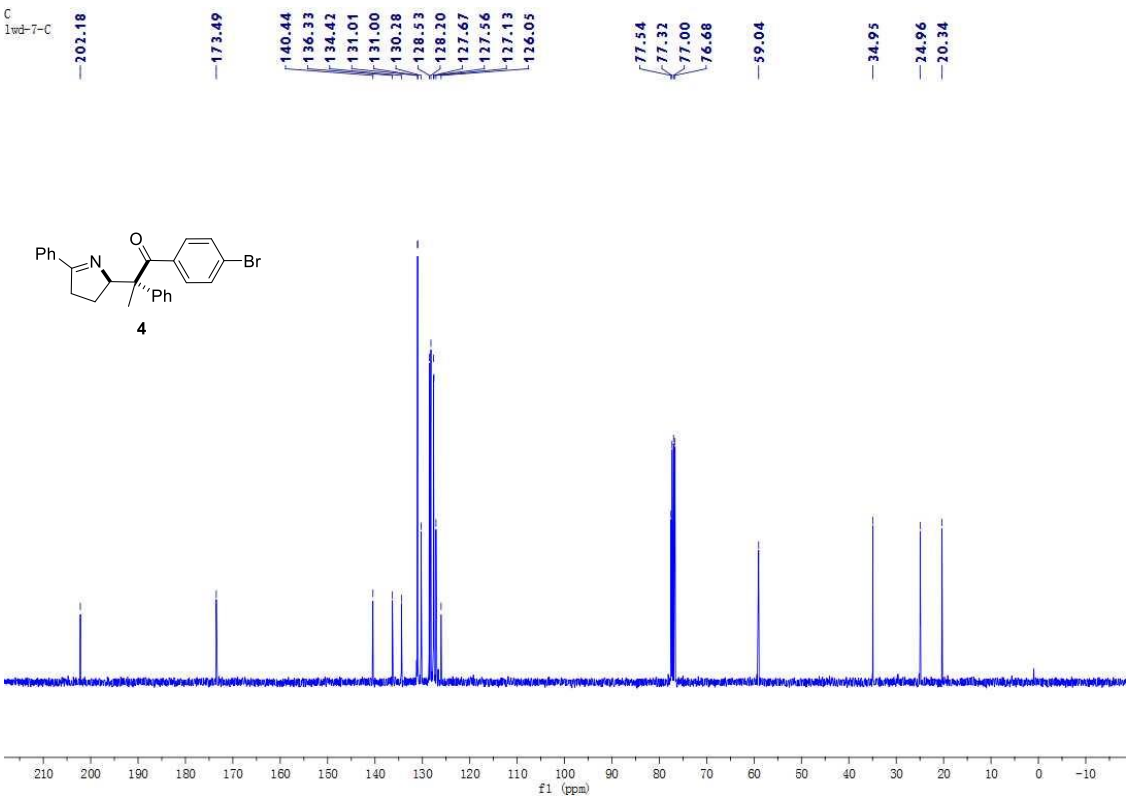

H
cf3
8.22
8.20
7.98
7.60
7.58
7.49
7.47
7.23
7.21
5.95
5.94
5.92
4.96
4.94
2.13
0.00
2.00
1.00
2.00
2.00
1.98
1.00
2.01
3.01
f1 (ppm)
NO2
NH
O
CF3
95a

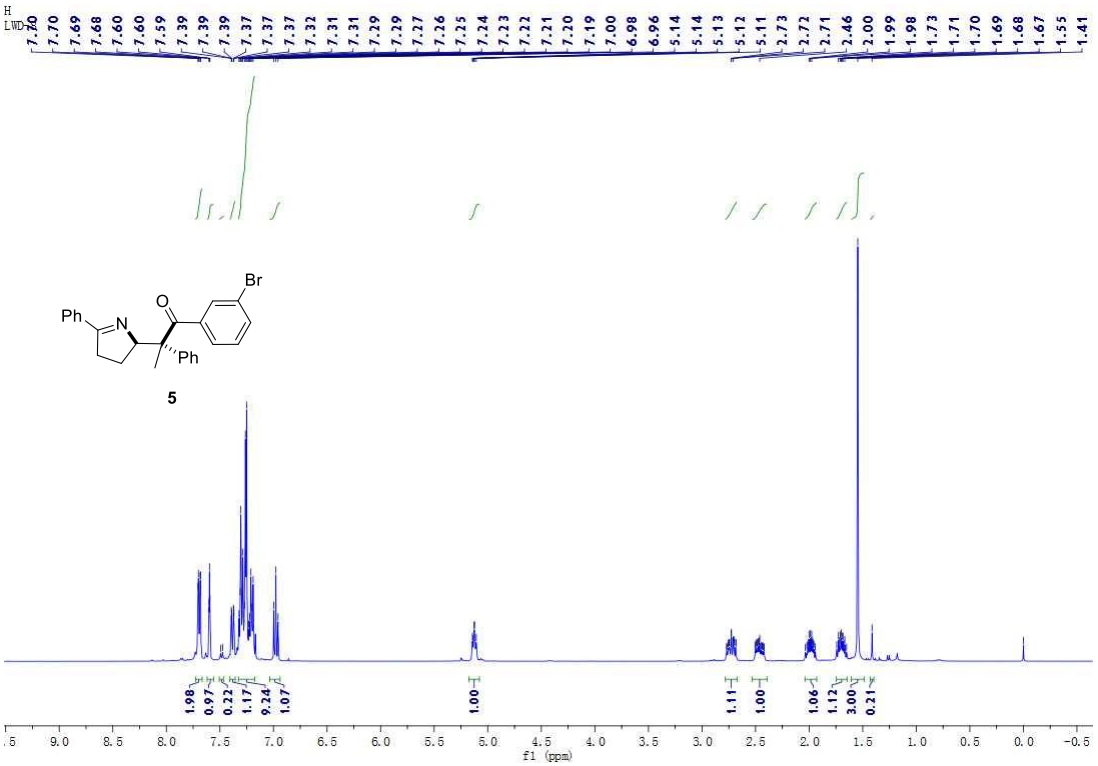

C
cf3
164.35
157.13
145.71
143.26
140.43
129.95
129.62
126.21
125.82
125.47
125.40
125.36
125.33
125.29
122.13
77.04
76.72
63.77
16.28
f1 (ppm)
NO2
NH
O
CF3
95a

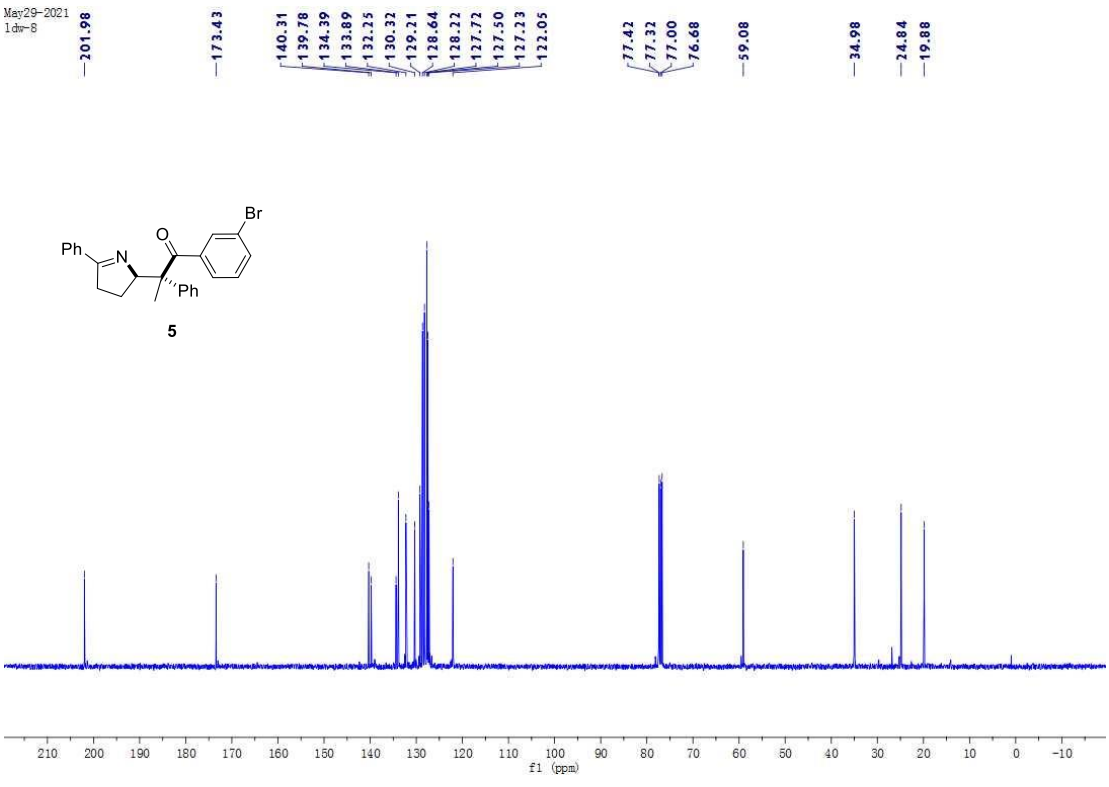

Jun05-2021
LWD-14
Ph
N
O
O
O
Ph
3
1.98
2.00
1.98
7.97
1.00
2.99
1.01
1.03
1.04
1.04
3.04
f1 (ppm)

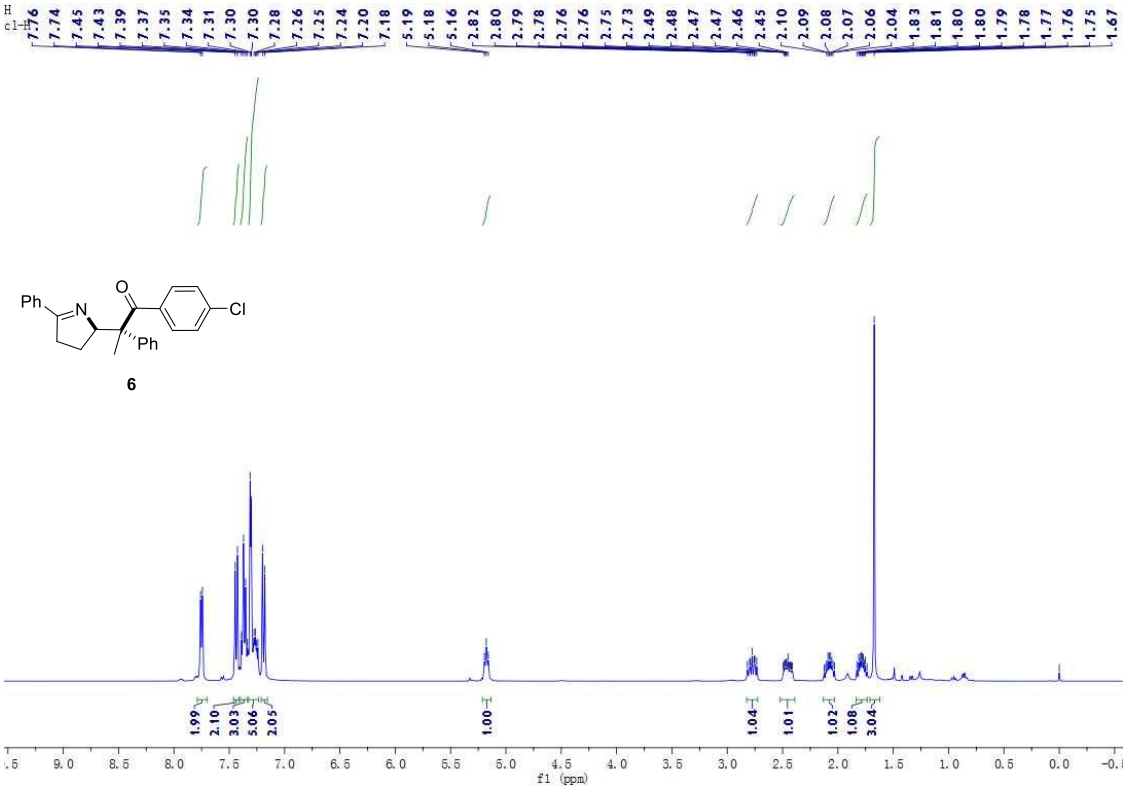

Jun05-2021
LWD-14-C
203.25
173.35
166.29
142.11
140.24
134.36
131.80
130.32
128.95
128.88
128.65
128.20
127.70
127.51
127.22
77.32
77.29
77.00
76.68
59.15
52.14
35.01
24.77
19.41
Ph
N
O
O
O
Ph
3
f1 (ppm)


Ph
N
O
Br
Ph
4
1.96
11.93
1.00
1.02
0.95
1.04
1.03
2.90
f1 (ppm)

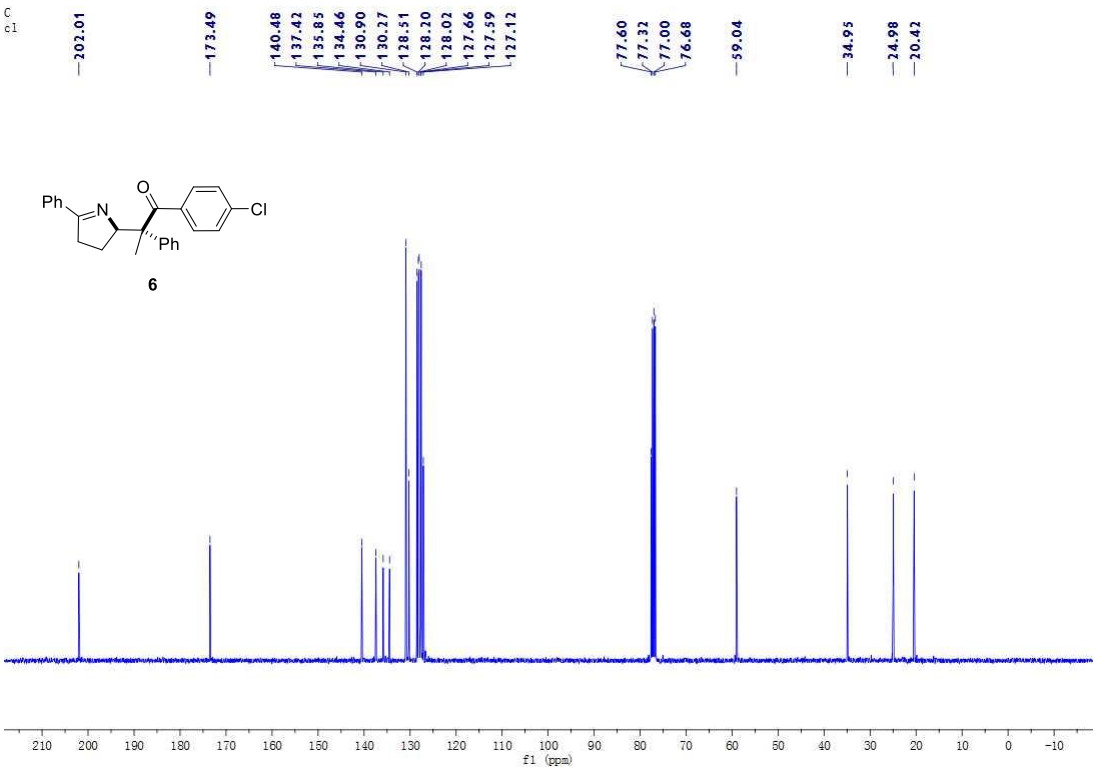

Ph
N
O
Br
Ph
4
f1 (ppm)


H
LWD-400
7.70
7.69
7.68
7.60
7.60
7.59
7.39
7.39
7.39
7.37
7.37
7.37
7.32
7.31
7.31
7.29
7.29
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.00
6.98
6.96
5.14
5.14
5.13
5.12
5.11
2.73
2.72
2.71
2.46
2.00
1.99
1.98
1.73
1.71
1.70
1.69
1.68
1.67
1.55
1.41
Br
O
Ph
N
Ph
5
1.98
0.97
0.22
1.17
9.24
1.07
1.00
1.11
1.00
1.06
1.12
3.00
0.21
f1 (ppm)

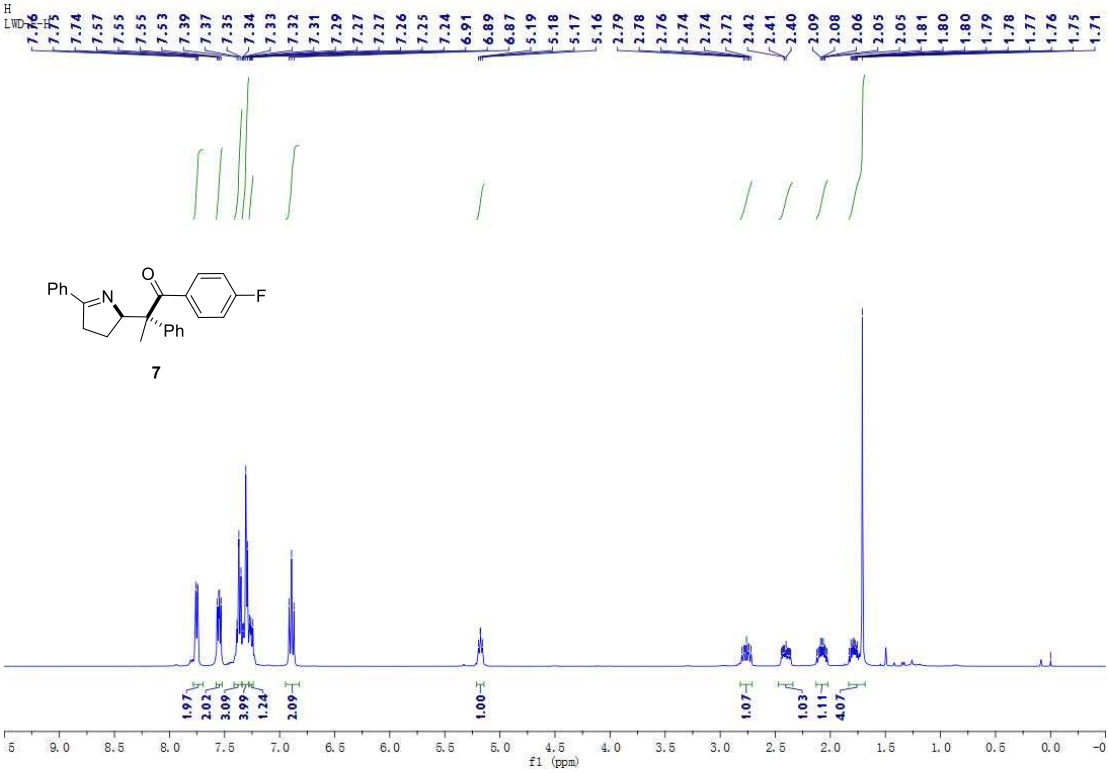

May29-2021
1dw-8
201.98
173.43
140.31
139.78
134.39
133.89
132.25
130.32
129.21
128.64
128.22
127.72
127.50
127.23
122.05
77.42
77.32
77.00
76.68
59.08
34.98
24.84
19.88
Br
O
Ph
N
Ph
5
f1 (ppm)


7.76 7.74 7.45 7.43 7.39 7.37 7.35 7.34 7.31 7.30 7.30 7.28 7.26 7.25 7.24 7.20 7.18
5.19 5.18 5.16 2.82 2.80 2.79 2.78 2.76 2.76 2.75 2.73 2.49 2.48 2.47 2.47 2.46 2.45 2.10 2.09 2.08 2.07 2.06 2.04 1.83 1.81 1.80 1.80 1.79 1.78 1.77 1.76 1.75 1.67
Ph
N
O
Cl
Ph
1.99 2.10 3.03 5.06 2.05 1.00 1.04 1.01 1.02 1.08 3.04
f1 (ppm)

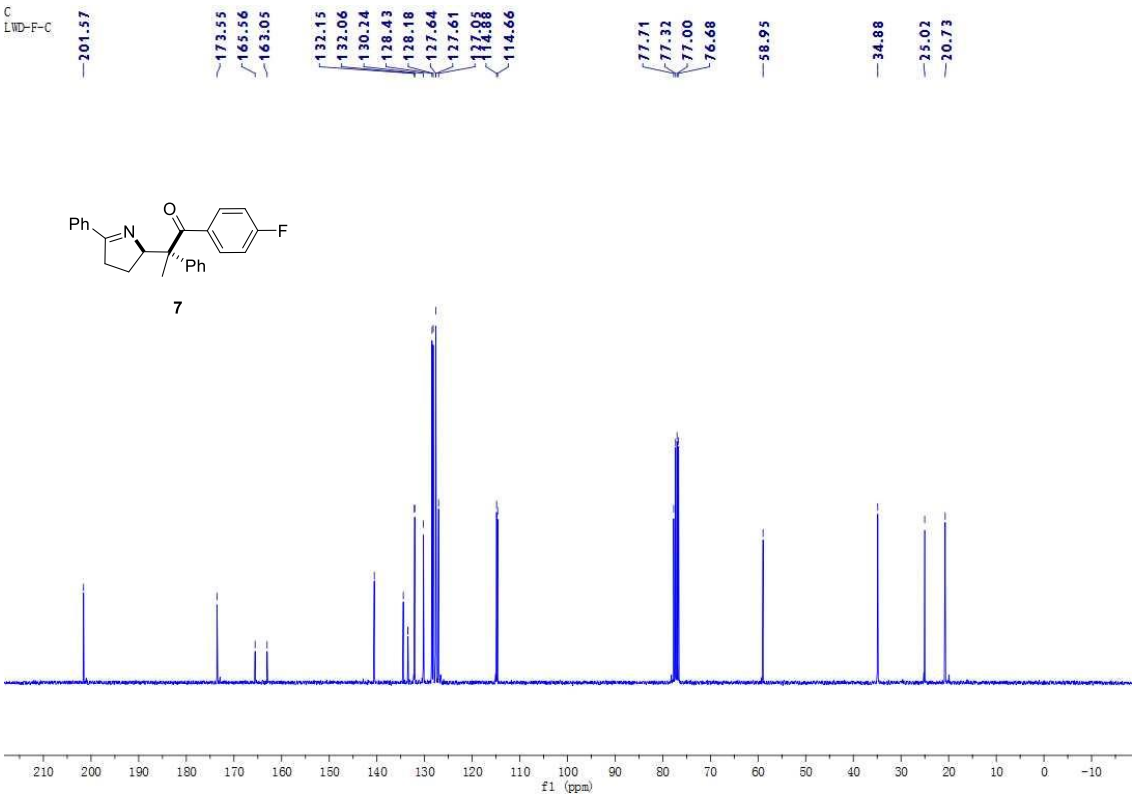
6


202.01 173.49 140.48 137.42 135.85 134.46 130.90 130.27 128.51 128.20 128.02 127.66 127.59 127.12 77.60 77.32 77.00 76.68 59.04 34.95 24.98 20.42
Ph
N
O
Cl
Ph
f1 (ppm)

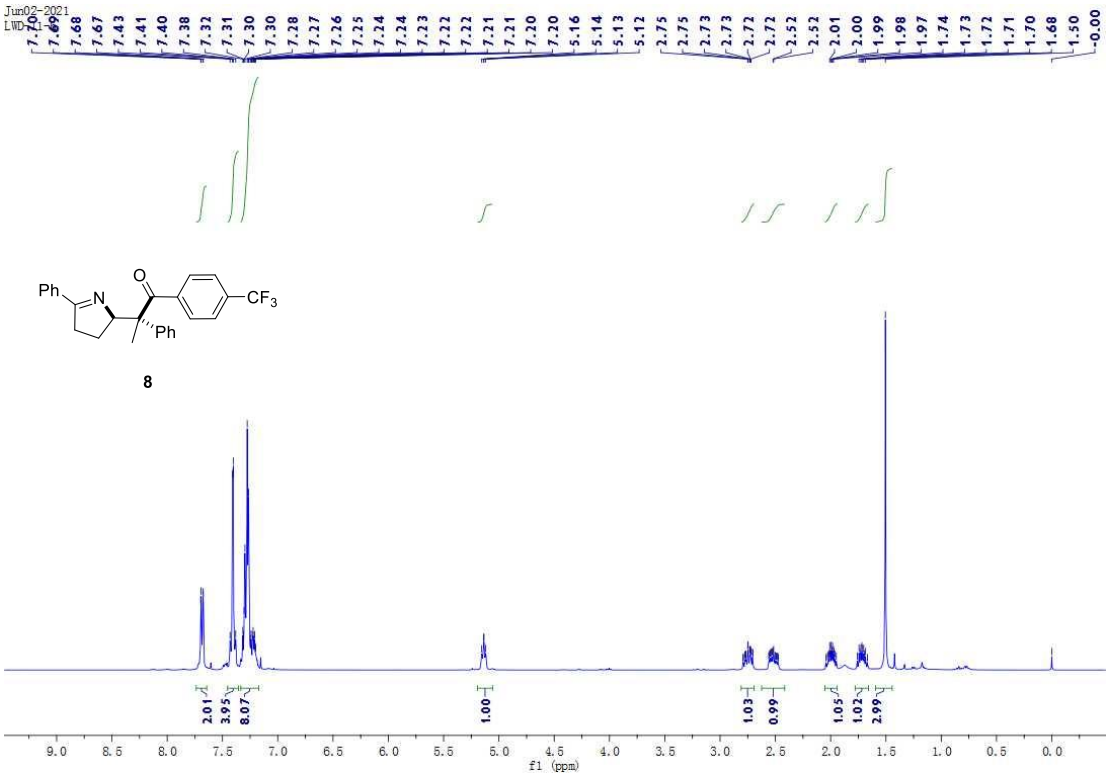
6

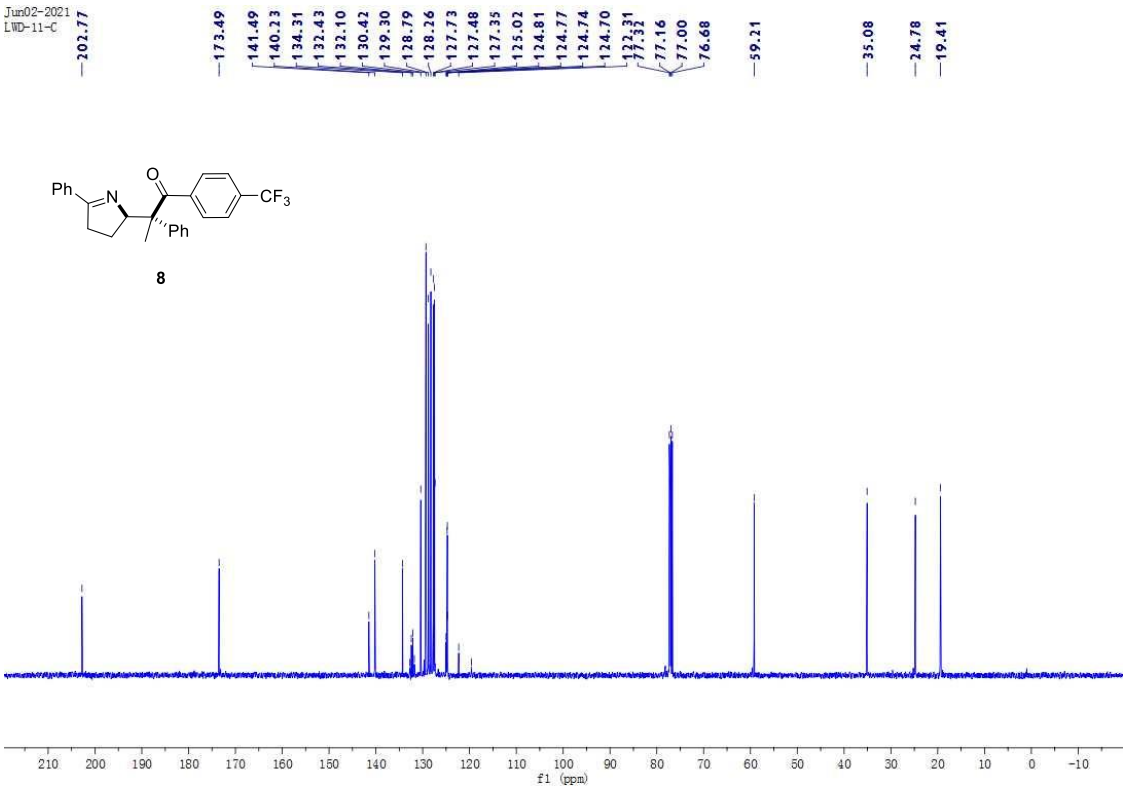

H
LWD-F-H
7.76 7.75 7.74 7.57 7.55 7.55 7.53 7.39 7.37 7.35 7.34 7.33 7.32 7.31 7.29 7.27 7.27 7.26 7.25 7.24 6.91 6.89 6.87 5.19 5.18 5.17 5.16 2.79 2.78 2.76 2.74 2.74 2.72 2.42 2.41 2.40 2.09 2.08 2.06 2.05 2.05 1.81 1.80 1.80 1.79 1.78 1.77 1.76 1.75 1.71
Ph
N
O
F
Ph
1.97 2.02 3.09 3.99 1.24 2.09 1.00 1.07 1.03 1.11 4.07
f1 (ppm)

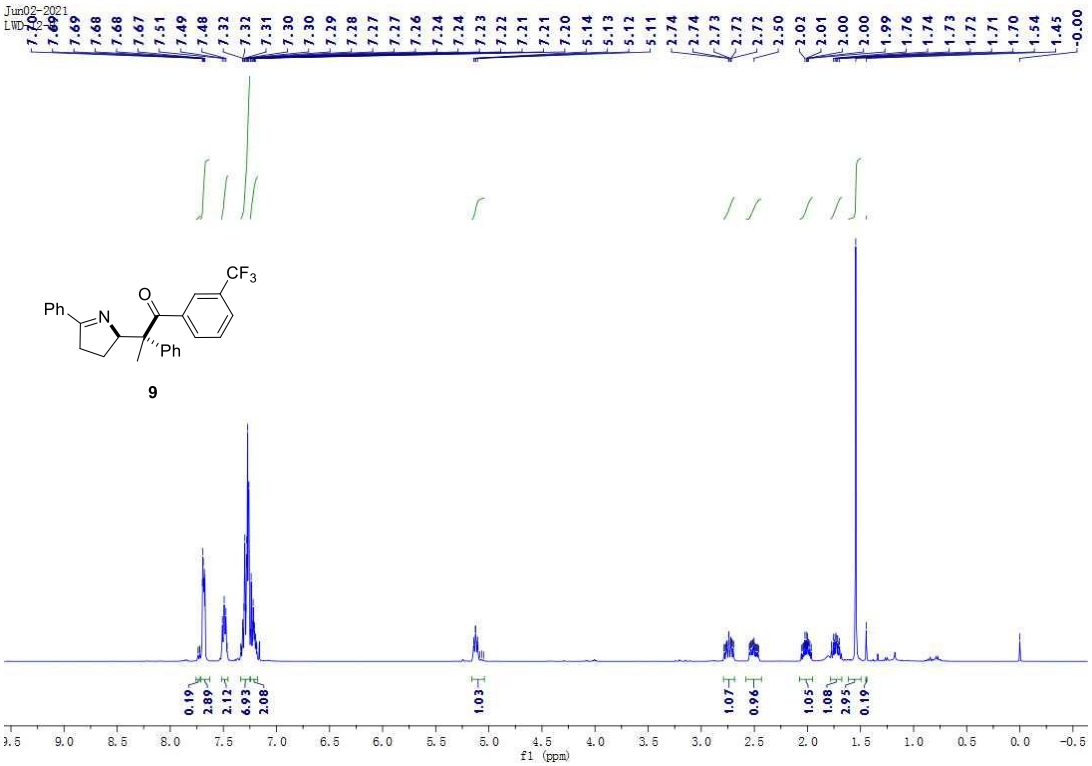
7

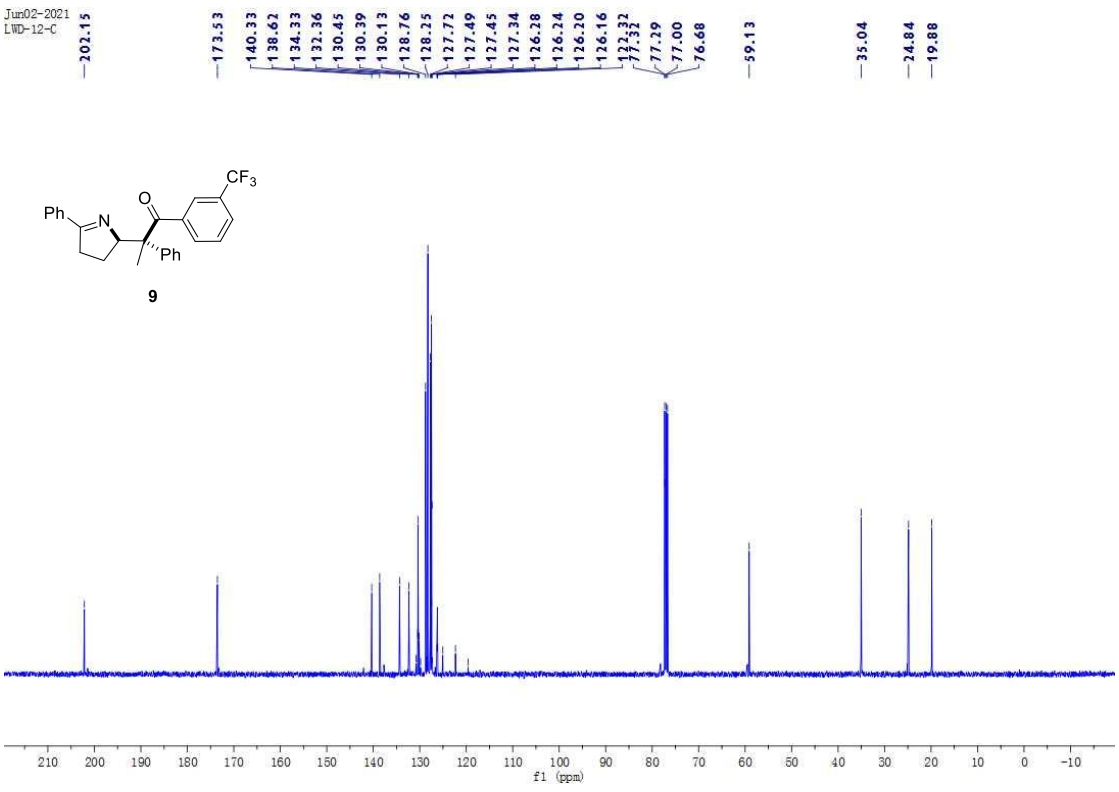

C
LWD-F-C
201.57
173.55 165.56 163.05
132.15 132.06 130.24 128.43 128.18 127.64 127.61 115.05 114.88 114.66
77.71 77.32 77.00 76.68
58.95
34.88
25.02
20.73
Ph
N
O
F
Ph
f1 (ppm)

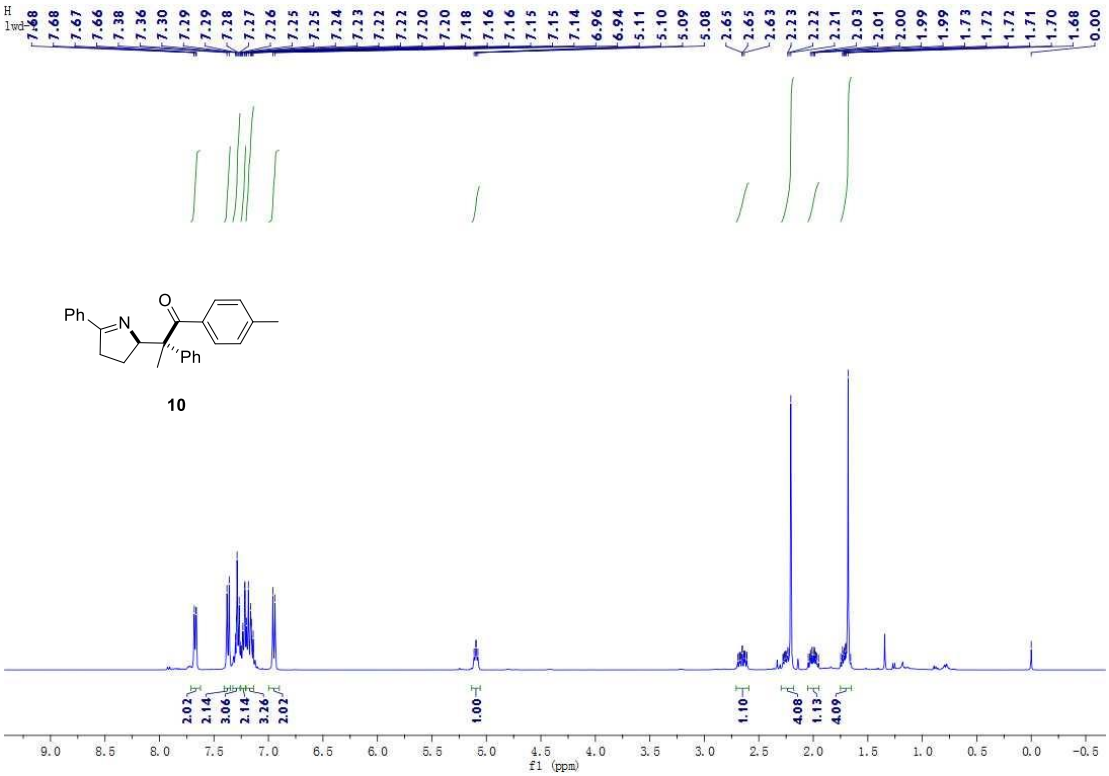
7

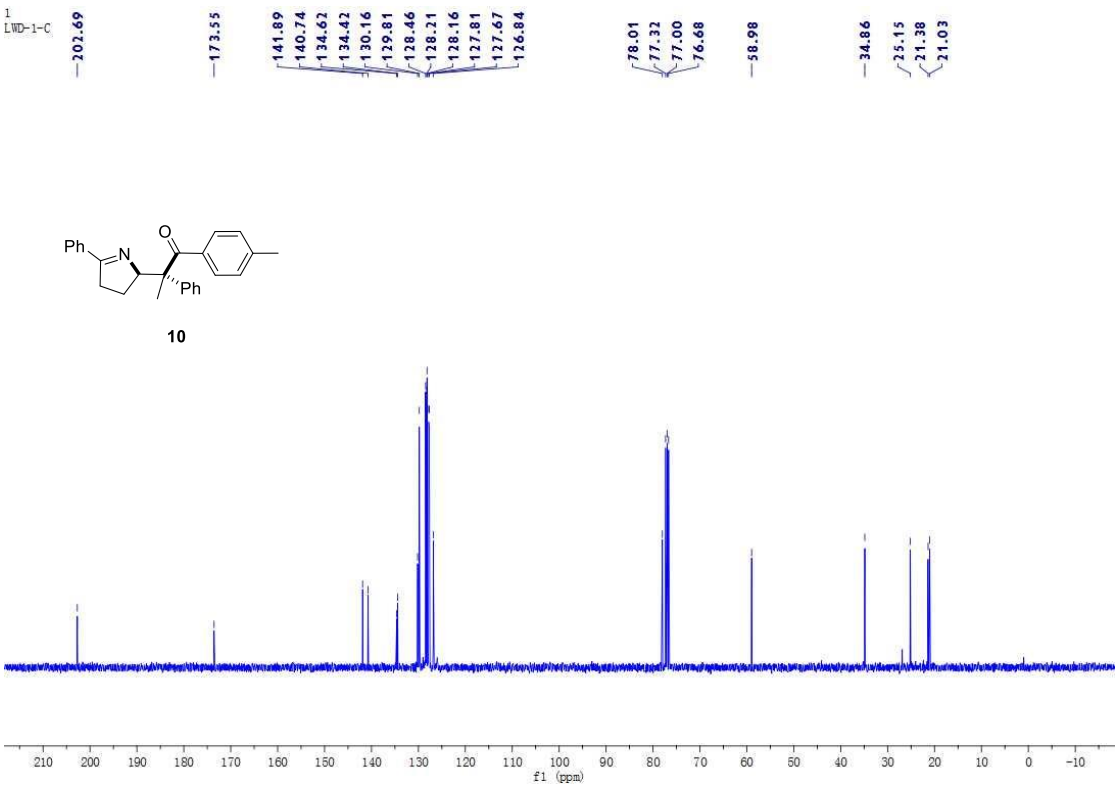

Jun02-2021
LWD-11
Ph
N
O
CF3
Ph
8
2.01
3.95
8.07
1.00
1.03
0.99
1.05
1.02
2.99
f1 (ppm)

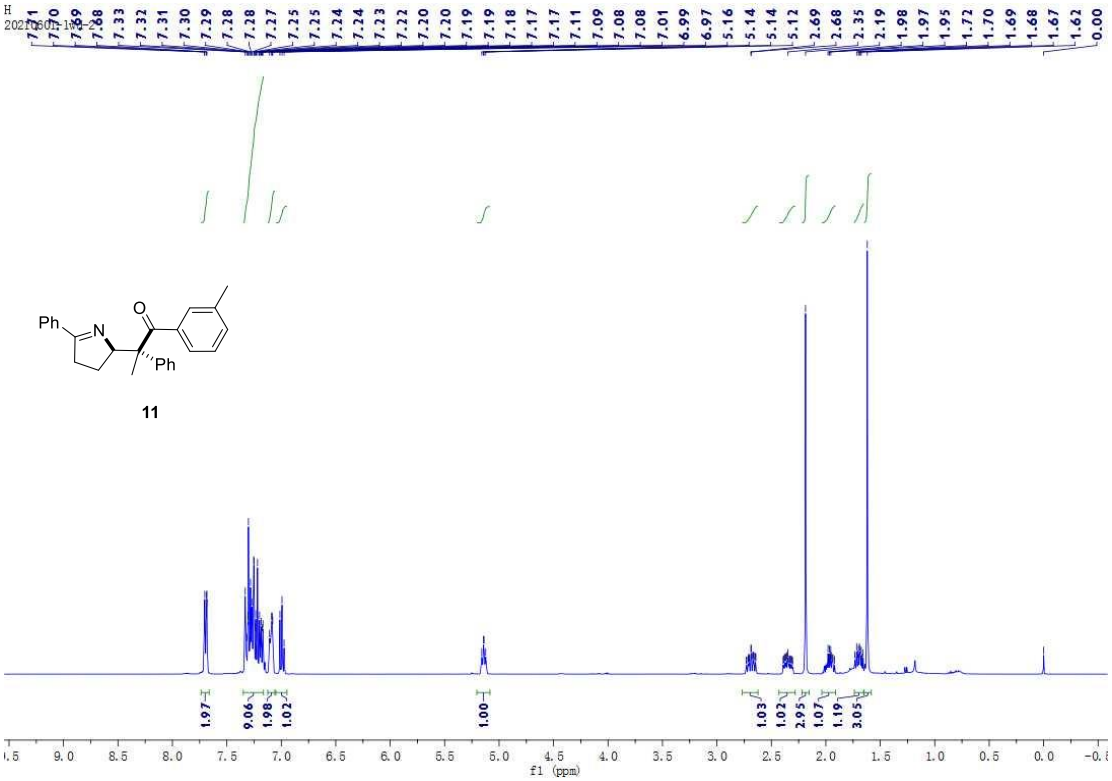

Jun02-2021
LWD-11-C
202.77
173.49
141.49
140.23
134.31
132.43
132.10
130.42
129.30
128.79
128.26
127.73
127.48
127.35
125.02
124.81
124.77
124.74
124.70
77.16
77.00
76.68
59.21
35.08
24.78
19.41
Ph
N
O
CF3
Ph
8
f1 (ppm)

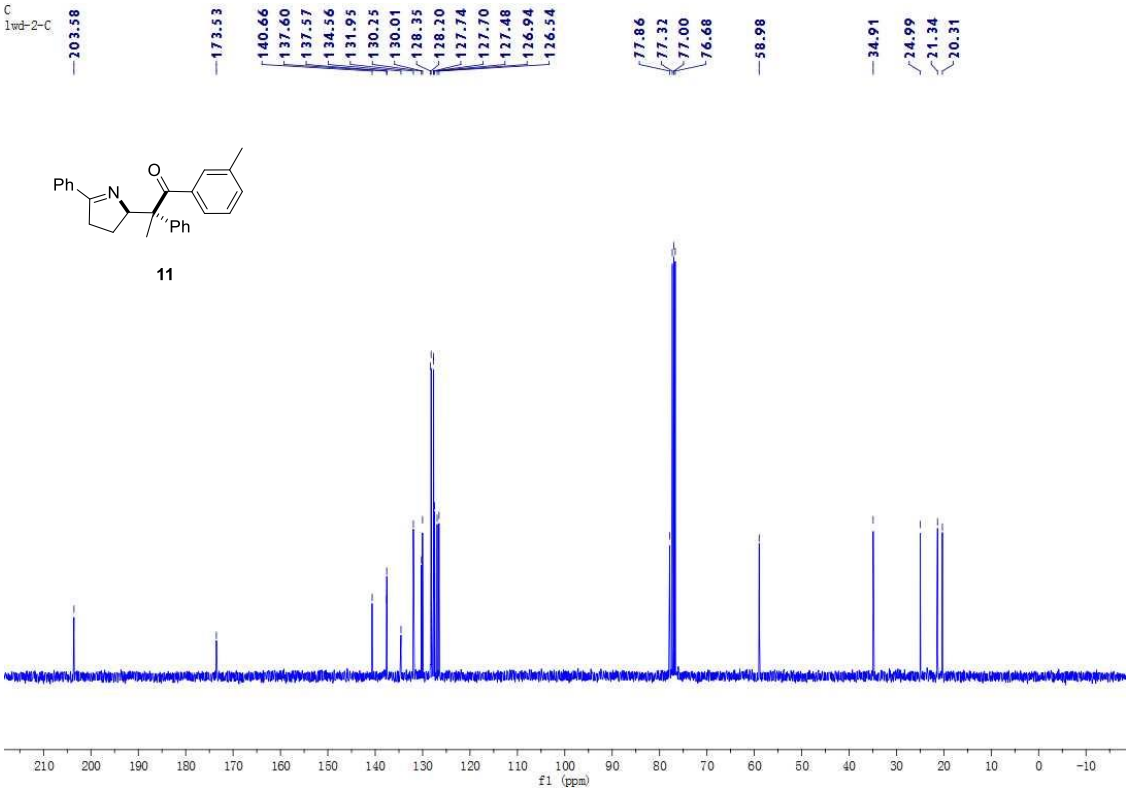

Jun02-2021
LWD-12-H
CF3
O
Ph
N
Ph
9
f1 (ppm)

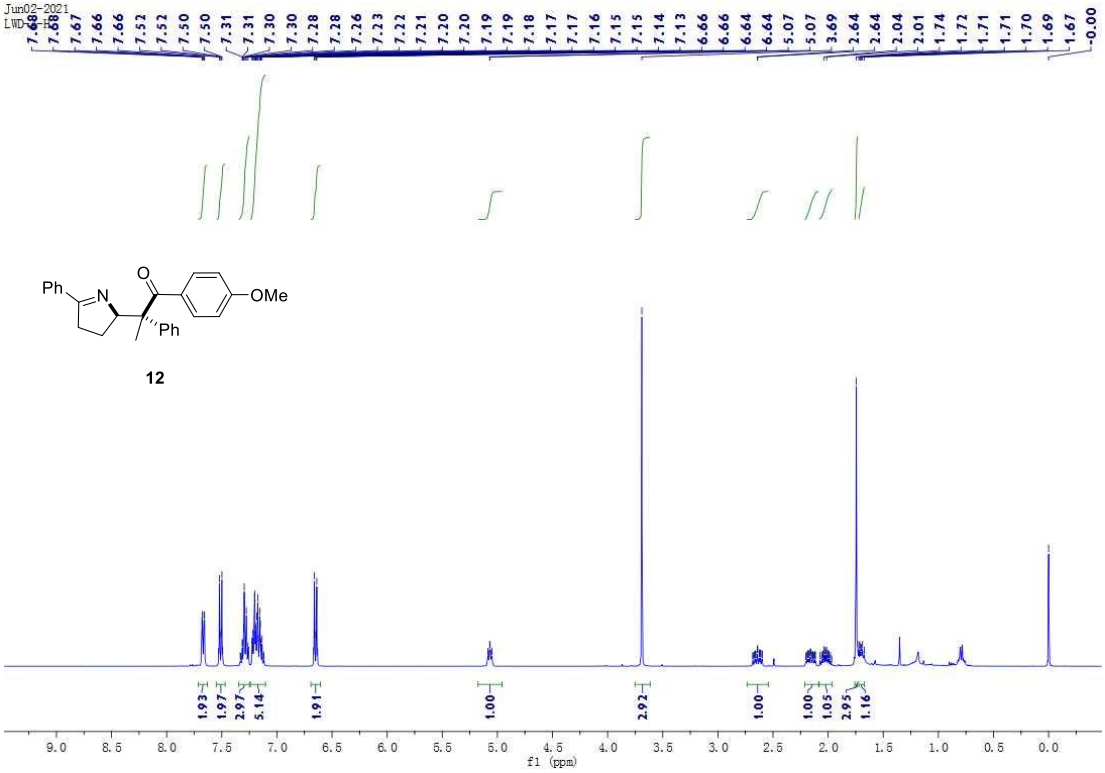

Jun02-2021
LWD-12-C
CF3
O
Ph
N
Ph
9
f1 (ppm)

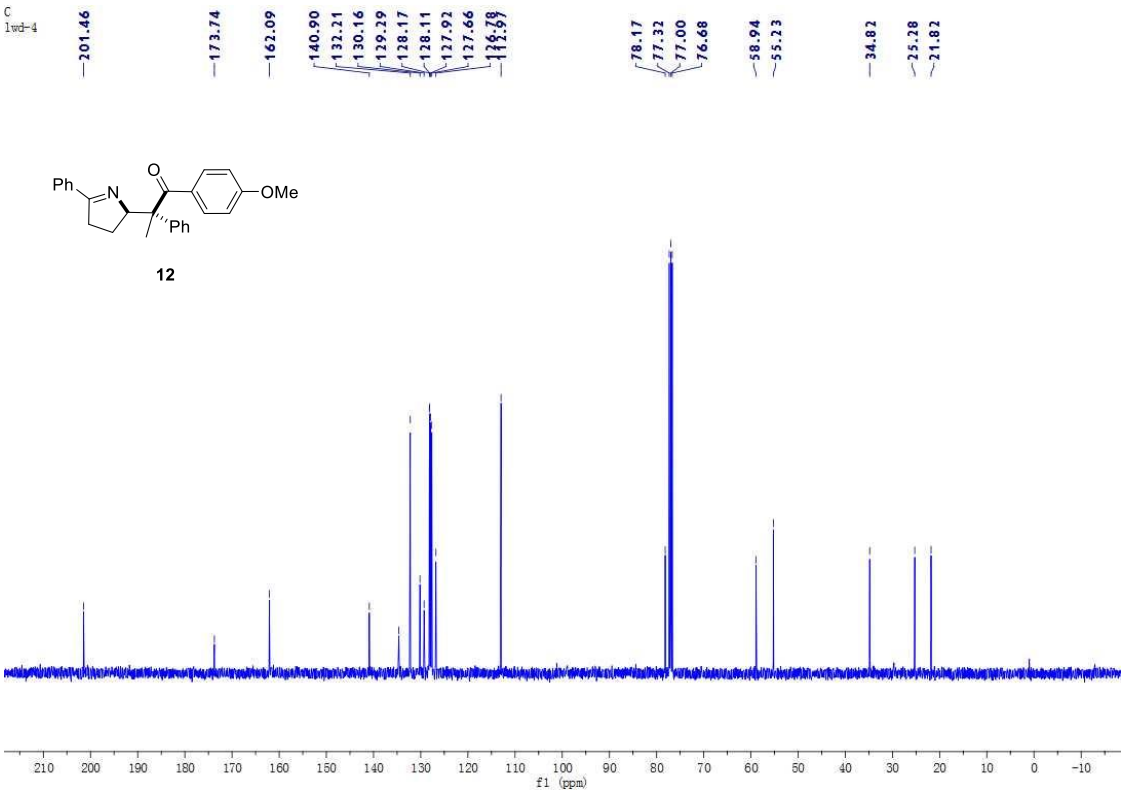

H
lwd-1
7.68 7.68 7.67 7.66 7.38 7.36 7.30 7.29 7.29 7.28 7.27 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.20 7.20 7.18 7.16 7.16 7.15 7.15 7.14 6.96 6.94 5.11 5.10 5.09 5.08 2.65 2.65 2.63 2.23 2.22 2.21 2.03 2.01 2.00 1.99 1.99 1.73 1.72 1.72 1.71 1.70 1.68 0.00
Ph
N
O
Ph
10
2.02 2.14 3.06 2.14 3.26 2.02 1.00 1.10 4.08 1.13 4.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

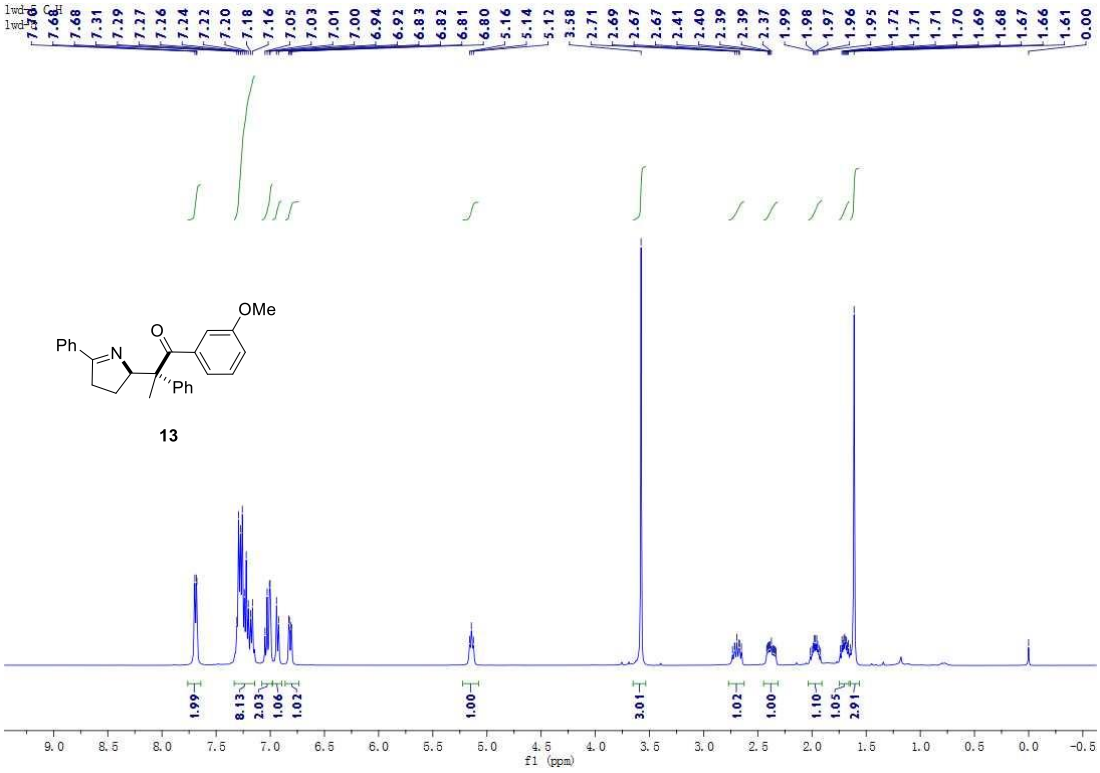

1
LWD-1-C
202.69 173.55 141.89 140.74 134.62 134.42 130.16 129.81 128.46 128.21 128.16 127.81 127.67 126.84 78.01 77.32 77.00 76.68 58.98 34.86 25.15 21.38 21.03
Ph
N
O
Ph
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

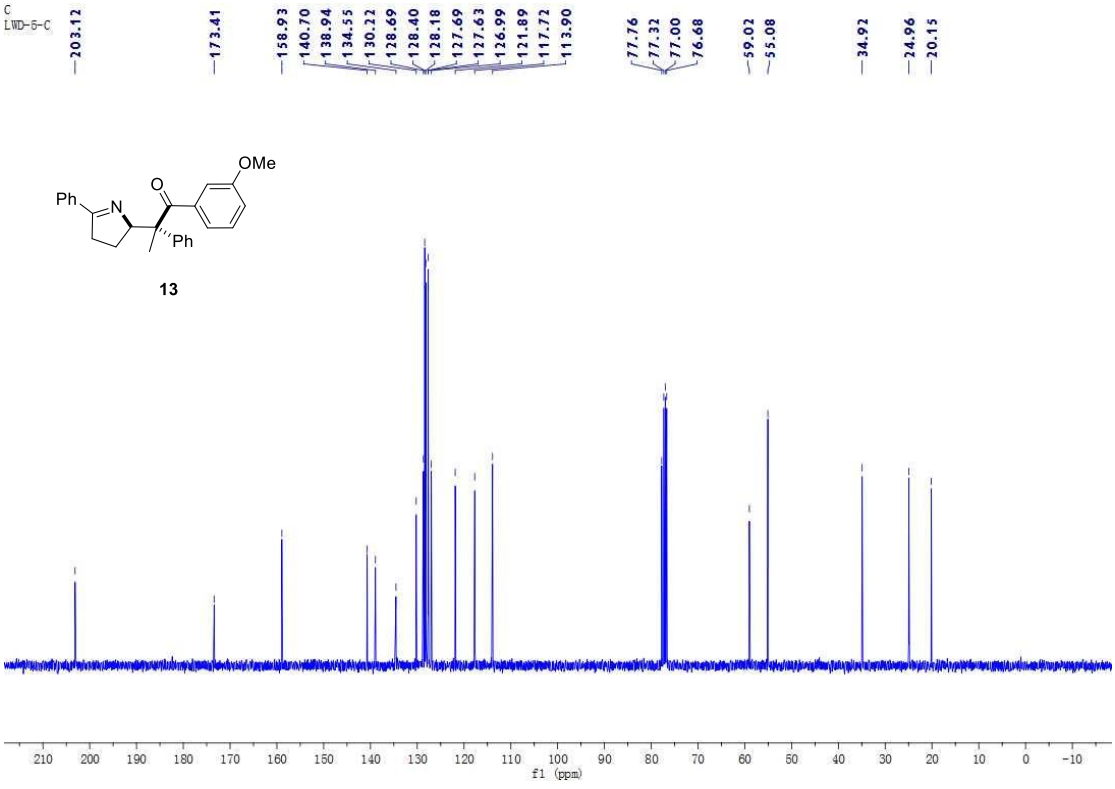

Ph
N
O
Ph
11
1.97
9.06
1.98
1.02
1.00
1.03
1.02
2.95
1.07
1.19
3.05
f1 (ppm)

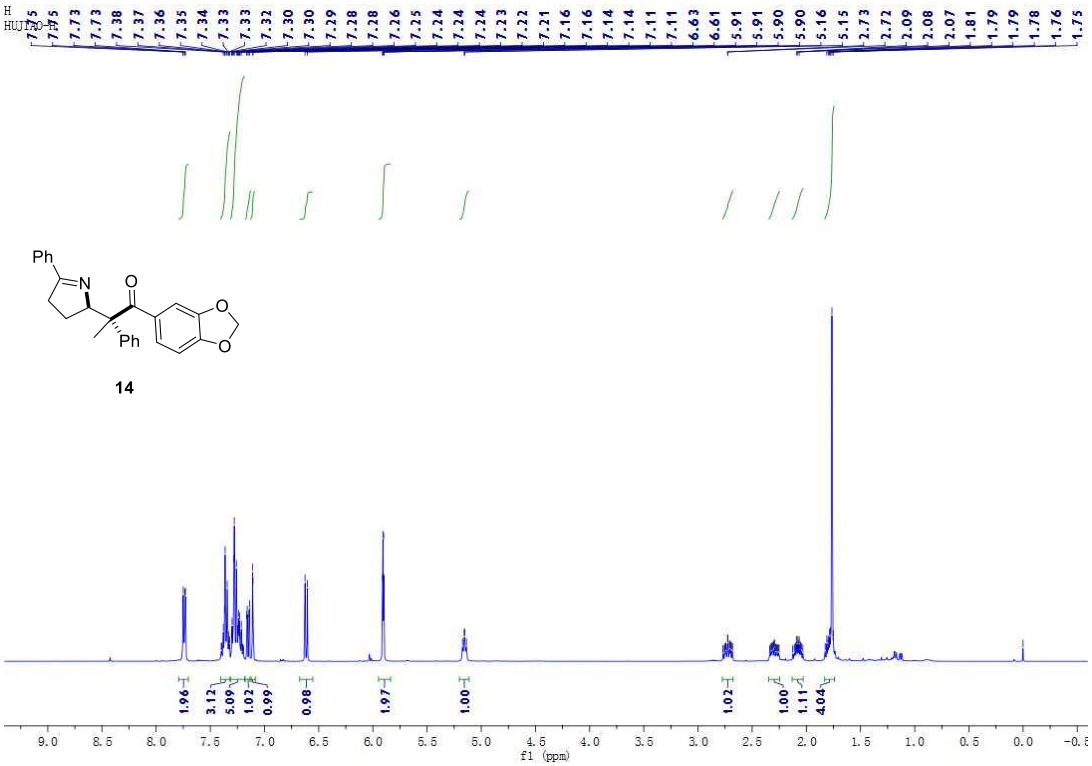

Ph
N
O
Ph
11
203.58
173.53
140.66
137.60
137.57
134.56
131.95
130.25
130.01
128.35
128.20
127.74
127.70
127.48
126.94
126.54
77.86
77.32
77.00
76.68
58.98
34.91
24.99
21.34
20.31
f1 (ppm)

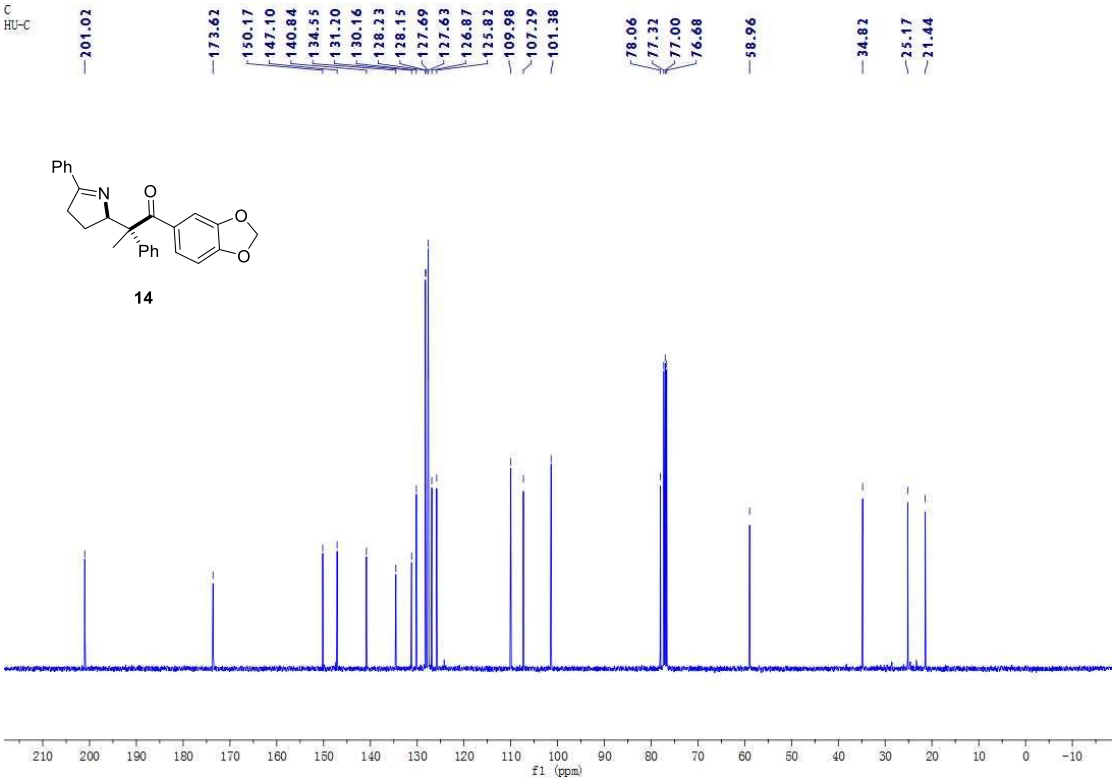

Jun02-2021
LWD-4
7.68
7.68
7.67
7.67
7.66
7.66
7.52
7.52
7.50
7.50
7.31
7.31
7.30
7.30
7.28
7.28
7.26
7.23
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.13
6.66
6.66
6.64
6.64
5.07
5.07
3.69
2.64
2.64
2.04
2.01
1.74
1.72
1.71
1.71
1.70
1.69
1.67
-0.00
Ph
N
O
OMe
Ph
12
1.93
1.97
2.97
5.14
1.91
1.00
2.92
1.00
1.00
1.05
2.95
1.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

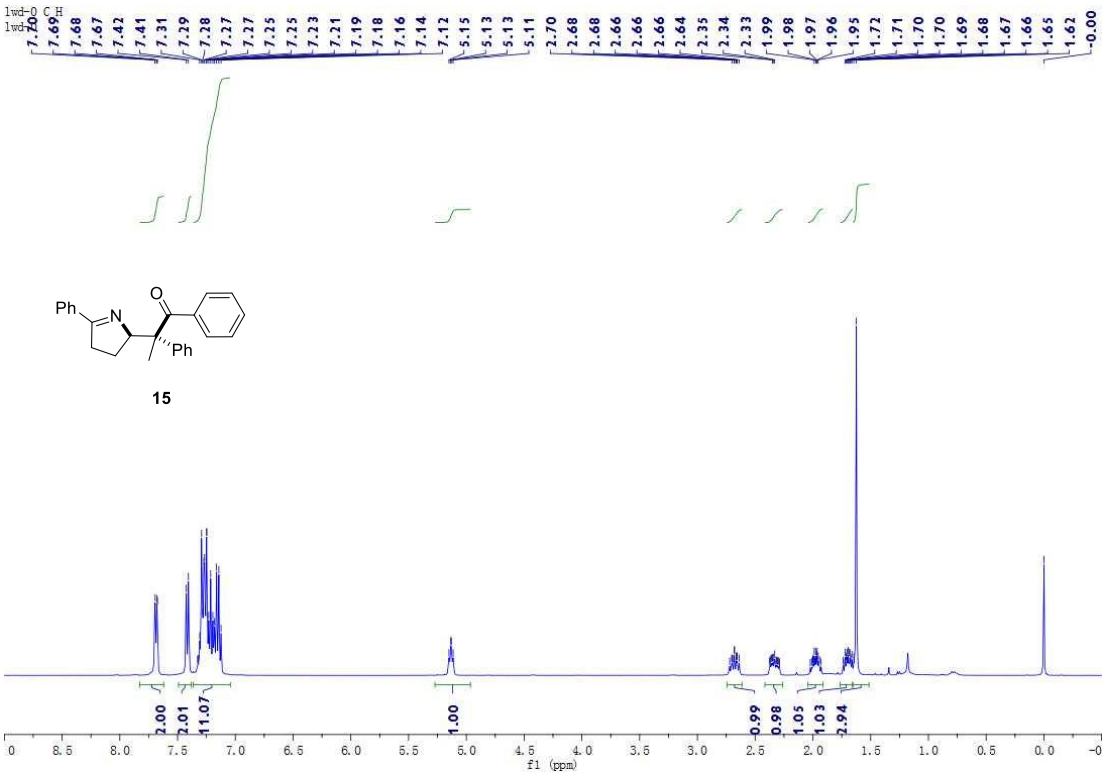

C
lwd-4
201.46
173.74
162.09
140.90
132.21
130.16
129.29
128.17
128.11
127.92
127.66
78.17
77.32
77.00
76.68
58.94
55.23
34.82
25.28
21.82
Ph
N
O
OMe
Ph
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

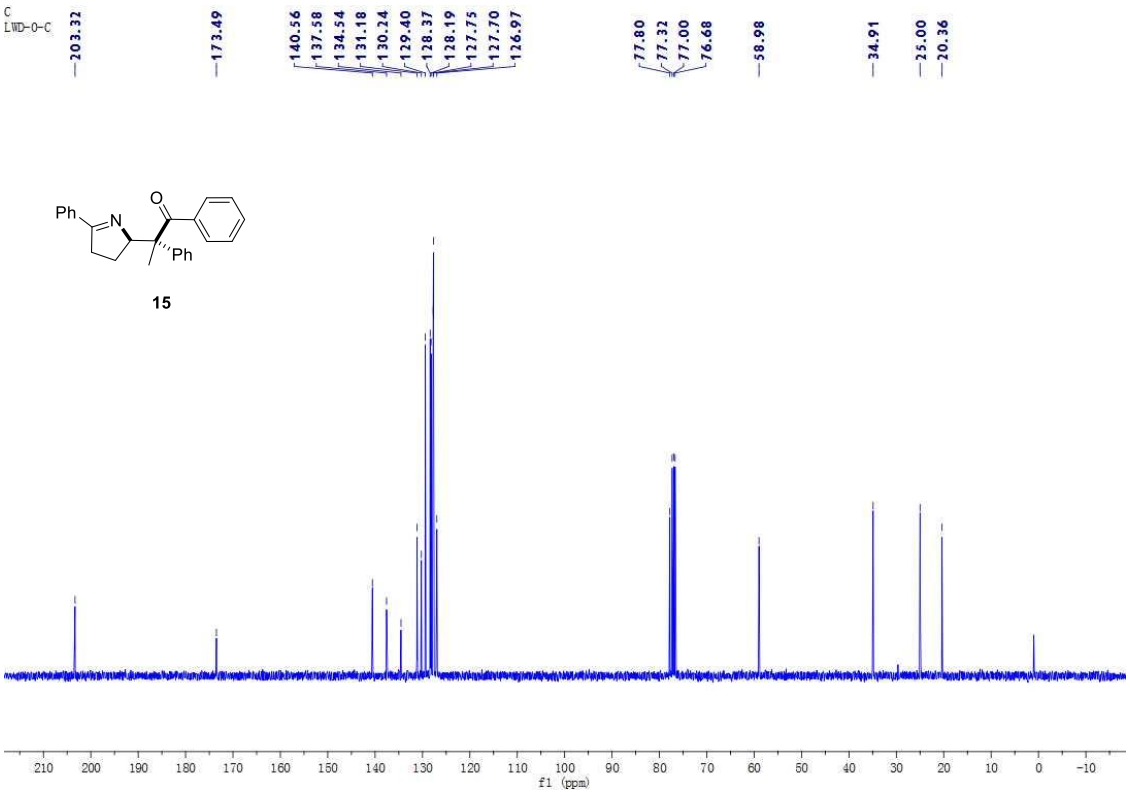

OMe
O
Ph
N
Ph
13
f1 (ppm)

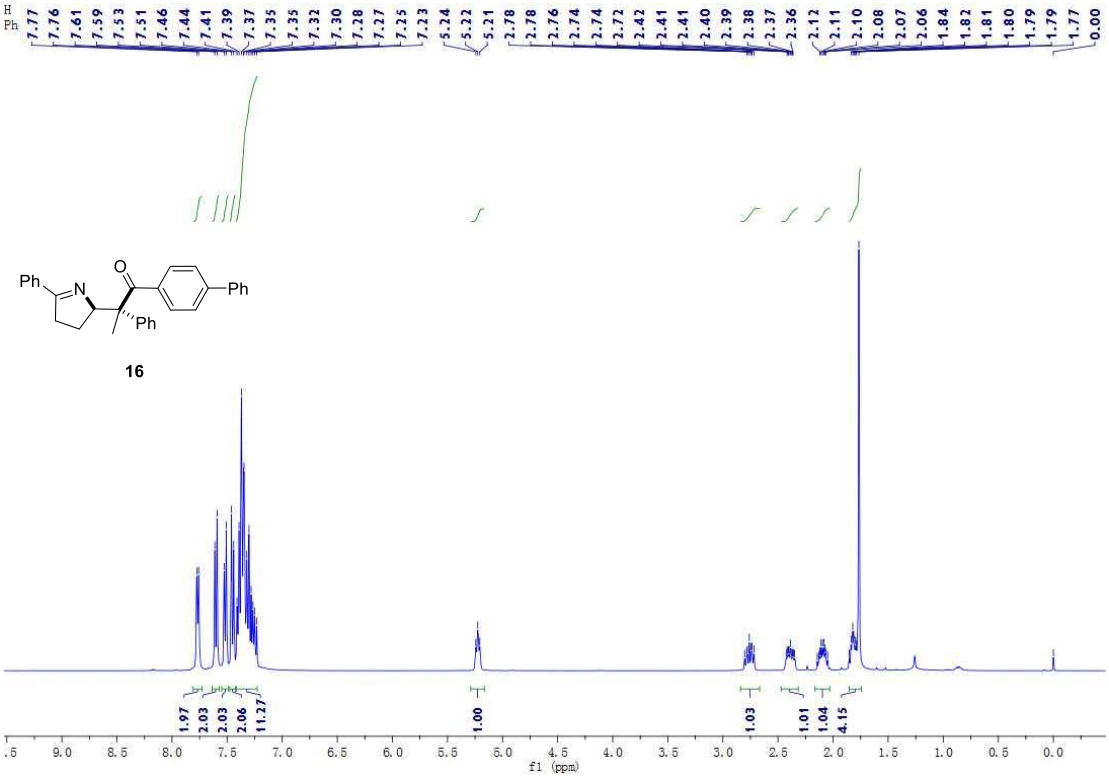

OMe
O
Ph
N
Ph
13
f1 (ppm)


Ph
N
O
O
O
Ph
14
1.96
3.12
5.09
1.02
0.99
0.98
1.97
1.00
1.02
1.00
1.11
4.04
f1 (ppm)

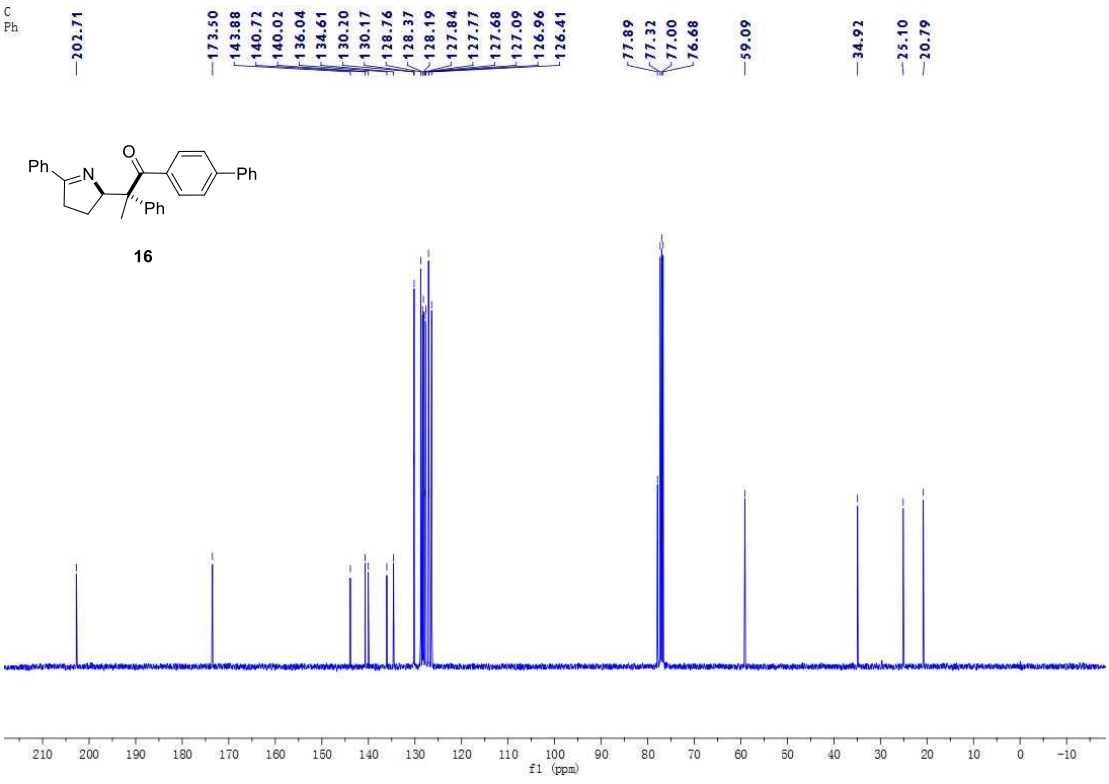

Ph
N
O
O
O
Ph
14
201.02
173.62
150.17
147.10
140.84
134.55
131.20
130.16
128.23
128.15
127.69
127.63
126.87
125.82
109.98
107.39
101.38
78.06
77.32
77.00
76.68
58.96
34.82
25.17
21.44
f1 (ppm)


lwd-0 C H
7.70
7.69
7.68
7.67
7.42
7.41
7.31
7.29
7.28
7.27
7.27
7.25
7.25
7.23
7.21
7.19
7.18
7.16
7.14
7.12
5.15
5.13
5.13
5.11
2.70
2.68
2.68
2.66
2.66
2.66
2.64
2.35
2.34
2.33
1.99
1.98
1.97
1.96
1.95
1.72
1.71
1.70
1.70
1.69
1.68
1.67
1.66
1.65
1.62
0.00
Ph
N
O
Ph
15
2.00
2.01
11.07
1.00
0.99
0.98
1.05
1.03
2.94
f1 (ppm)

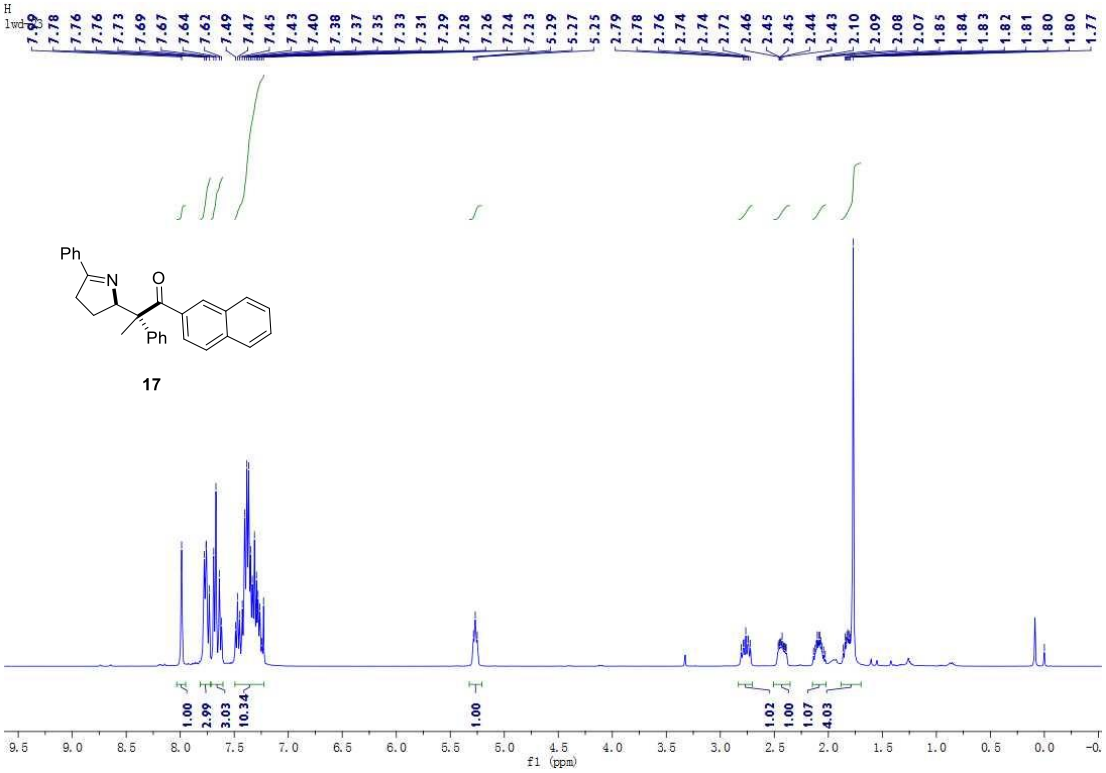

C
LWD-0-C
203.32
173.49
140.56
137.58
134.54
131.18
130.24
129.40
128.37
128.19
127.75
127.70
126.97
77.80
77.32
77.00
76.68
58.98
34.91
25.00
20.36
Ph
N
O
Ph
15
f1 (ppm)

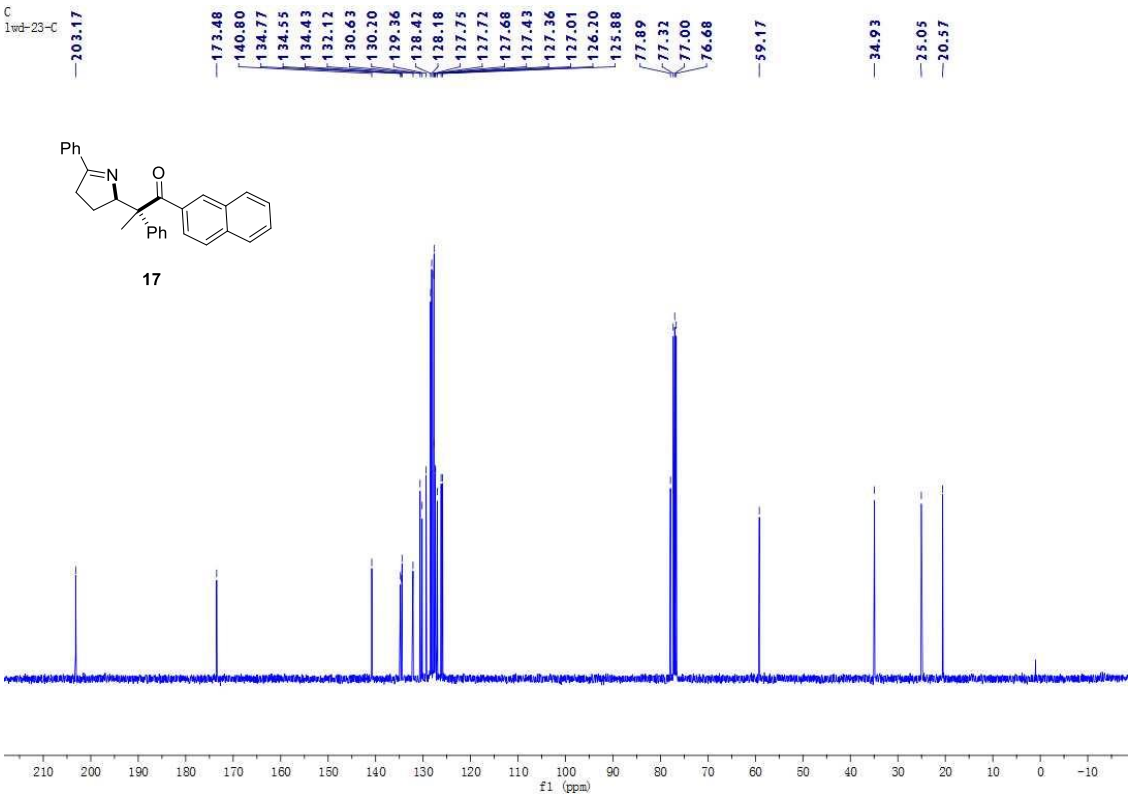

H
Ph
7.77 7.76 7.61 7.59 7.53 7.51 7.46 7.44 7.41 7.39 7.37 7.35 7.35 7.32 7.30 7.28 7.27 7.25 7.23
5.24 5.22 5.21
2.78 2.78 2.76 2.74 2.74 2.72 2.42 2.41 2.41 2.40 2.39 2.38 2.37 2.36
2.12 2.11 2.10 2.08 2.07 2.06 1.84 1.82 1.81 1.80 1.79 1.79 1.77 0.00
Ph
N
O
Ph
Ph
1.97 2.03 2.03 2.06 11.27
1.00
1.03 1.01 1.04 4.15
f1 (ppm)

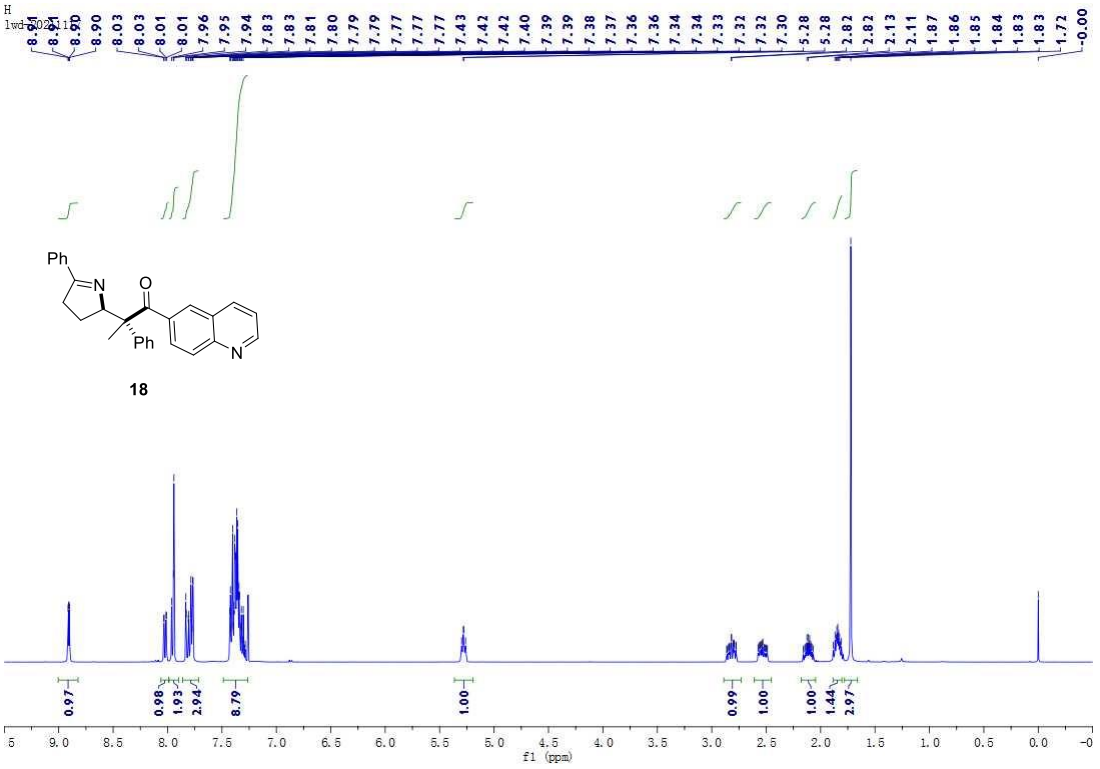
16

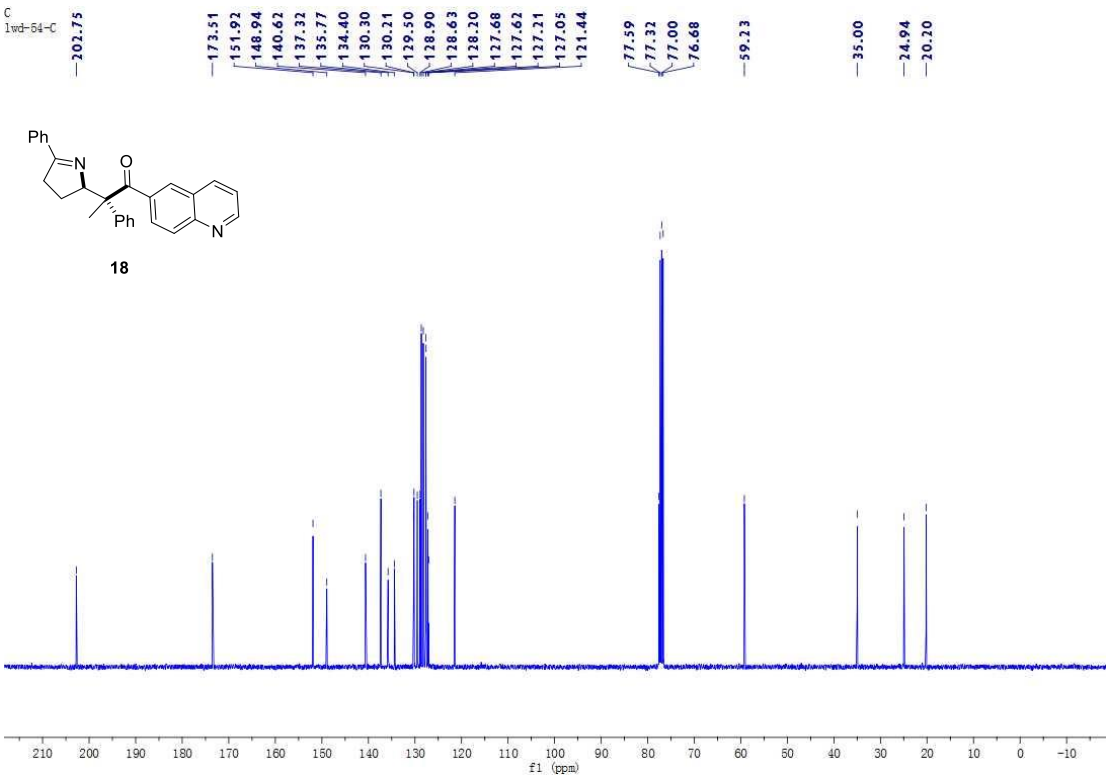

C
Ph
202.71
173.50 143.88 140.72 140.02 136.04 134.61 130.20 130.17 128.76 128.37 128.19 127.84 127.77 127.68 127.09 126.96 126.41
77.89 77.32 77.00 76.68
59.09
34.92
25.10
20.79
Ph
N
O
Ph
Ph
f1 (ppm)

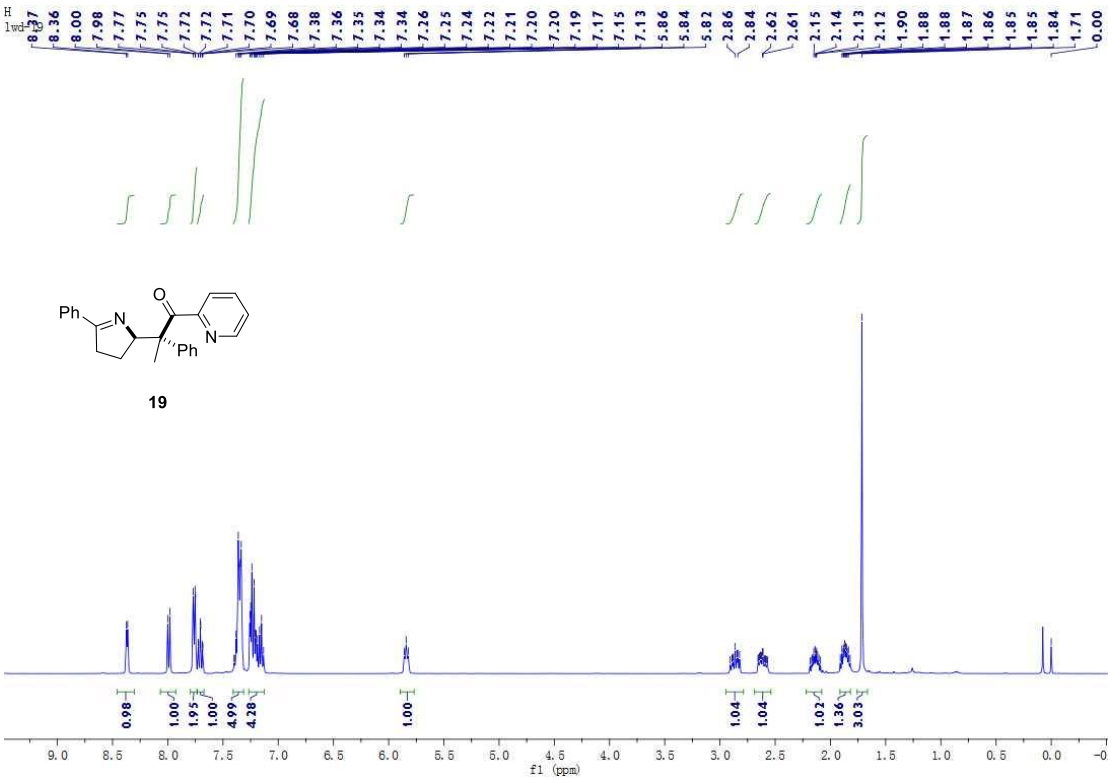
16

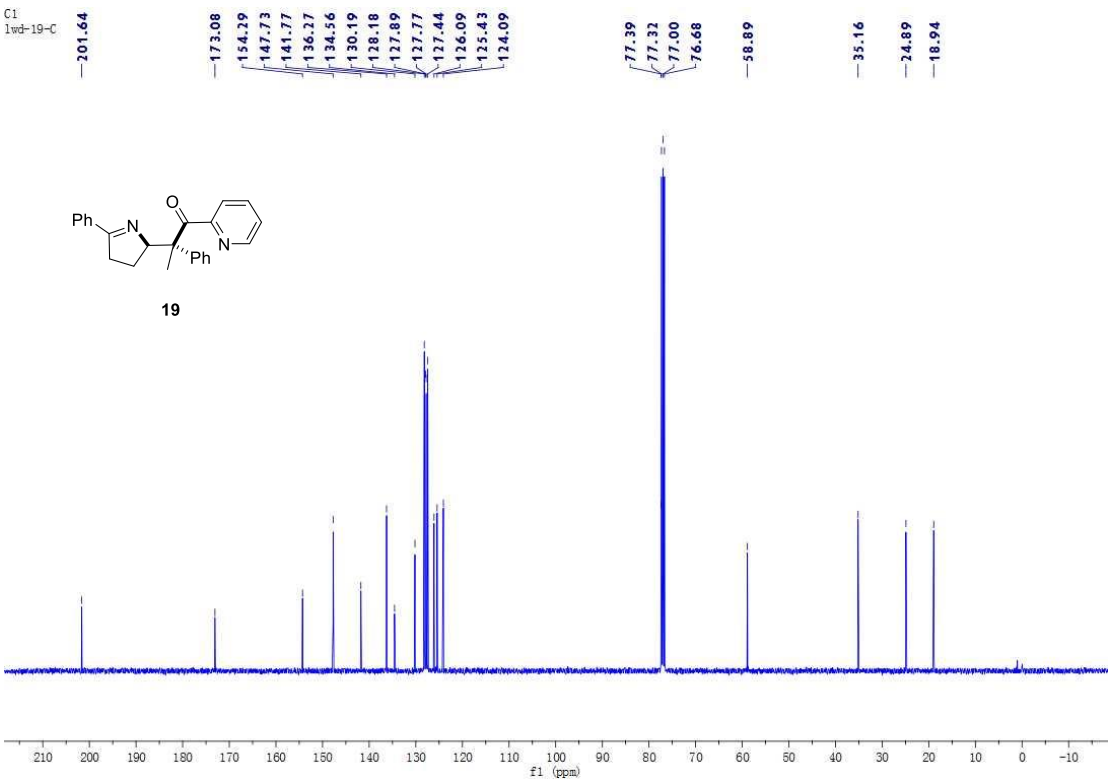

Ph
N
O
Ph
17
1.00
2.99
3.03
10.34
1.00
1.02
1.00
1.07
4.03
f1 (ppm)

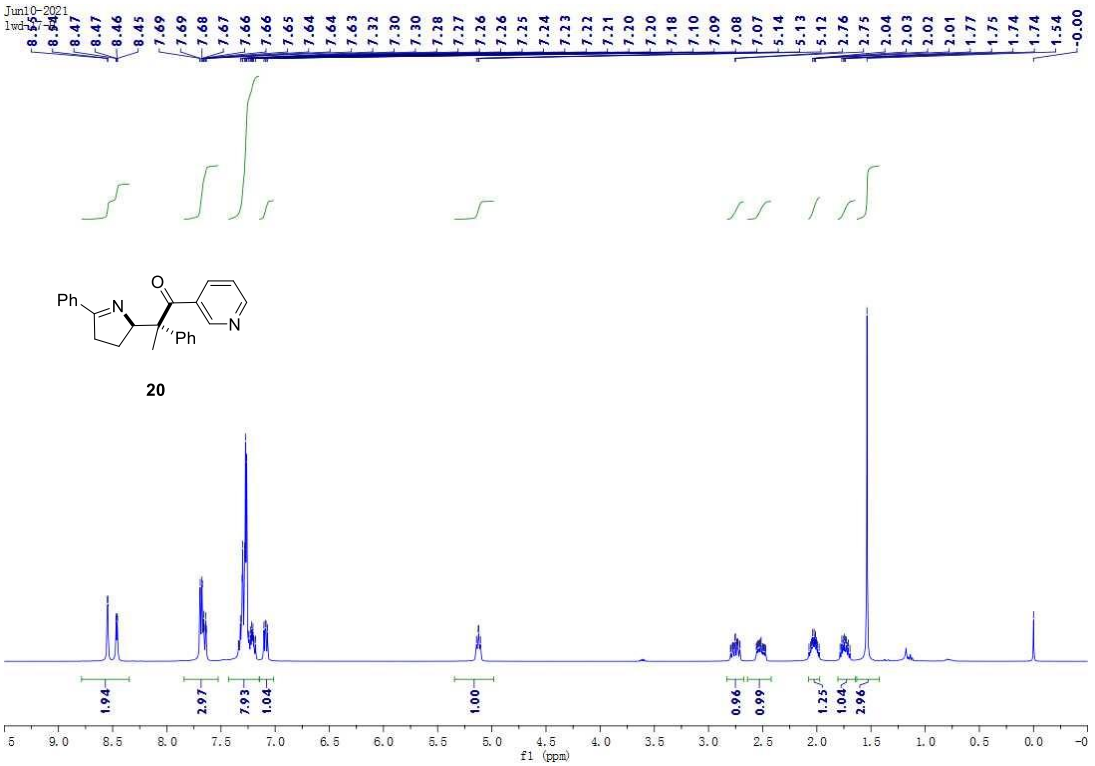

Ph
N
O
Ph
17
f1 (ppm)


Ph
N
O
Ph
N
18
f1 (ppm)

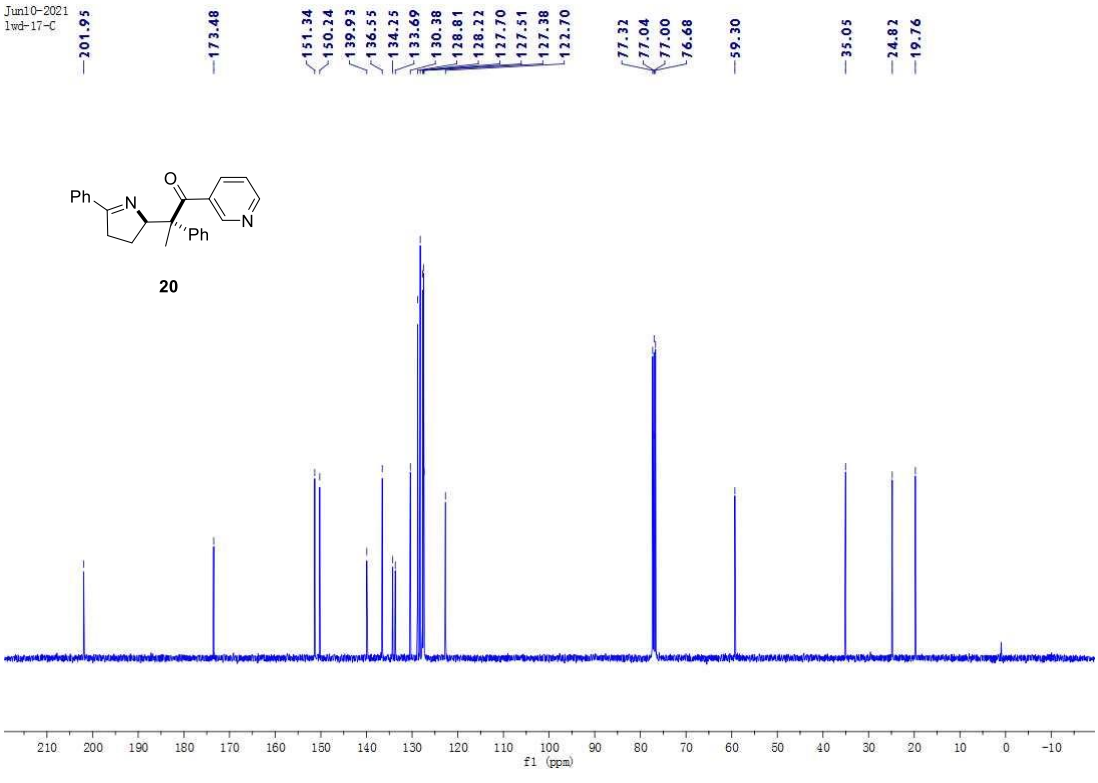

Ph
N
O
Ph
N
18
f1 (ppm)


H
lwd-19
8.37
8.36
8.00
7.98
7.77
7.75
7.75
7.72
7.72
7.71
7.70
7.69
7.68
7.38
7.36
7.35
7.34
7.34
7.26
7.25
7.24
7.22
7.21
7.20
7.19
7.17
7.15
7.13
5.86
5.84
5.82
2.86
2.84
2.62
2.61
2.15
2.14
2.13
2.12
1.90
1.88
1.88
1.87
1.86
1.85
1.85
1.84
1.71
0.00
Ph
N
O
N
Ph
19
0.98
1.00
1.95
1.00
4.99
4.28
1.00
1.04
1.04
1.02
1.36
3.03
f1 (ppm)

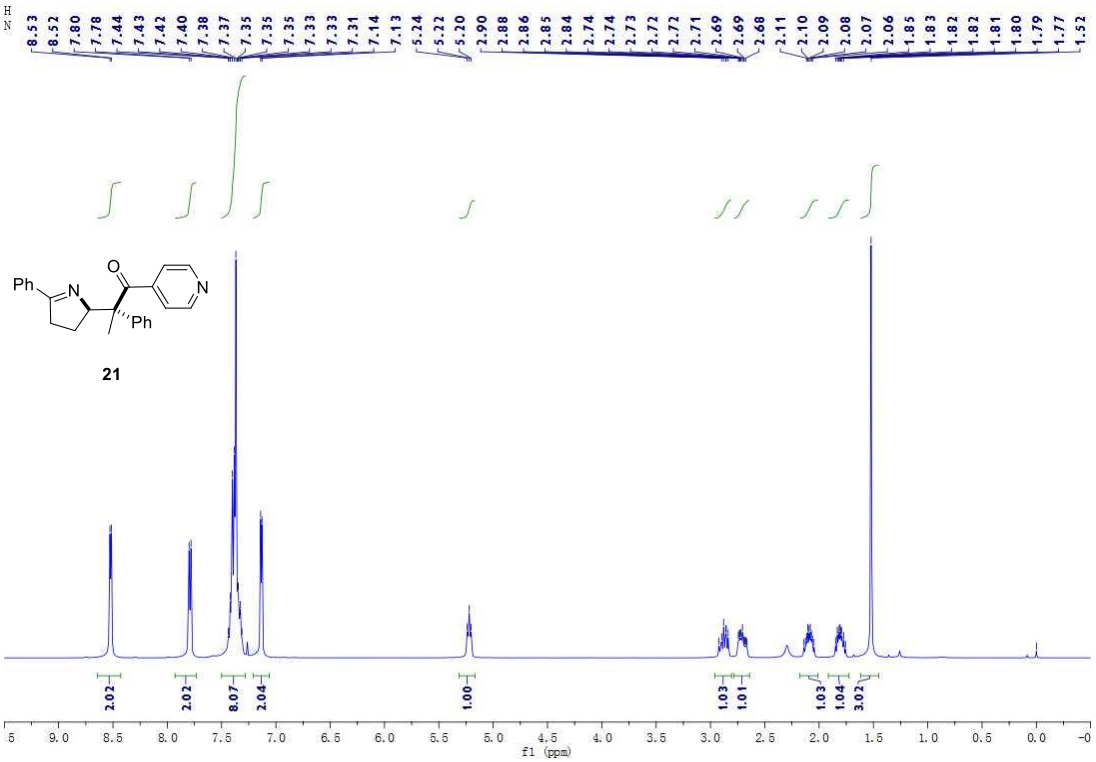

C1
lwd-19-C
201.64
173.08
154.29
147.73
141.77
136.27
134.56
130.19
128.18
127.89
127.77
127.44
126.09
125.43
124.09
77.39
77.32
77.00
76.68
58.89
35.16
24.89
18.94
Ph
N
O
N
Ph
19
f1 (ppm)

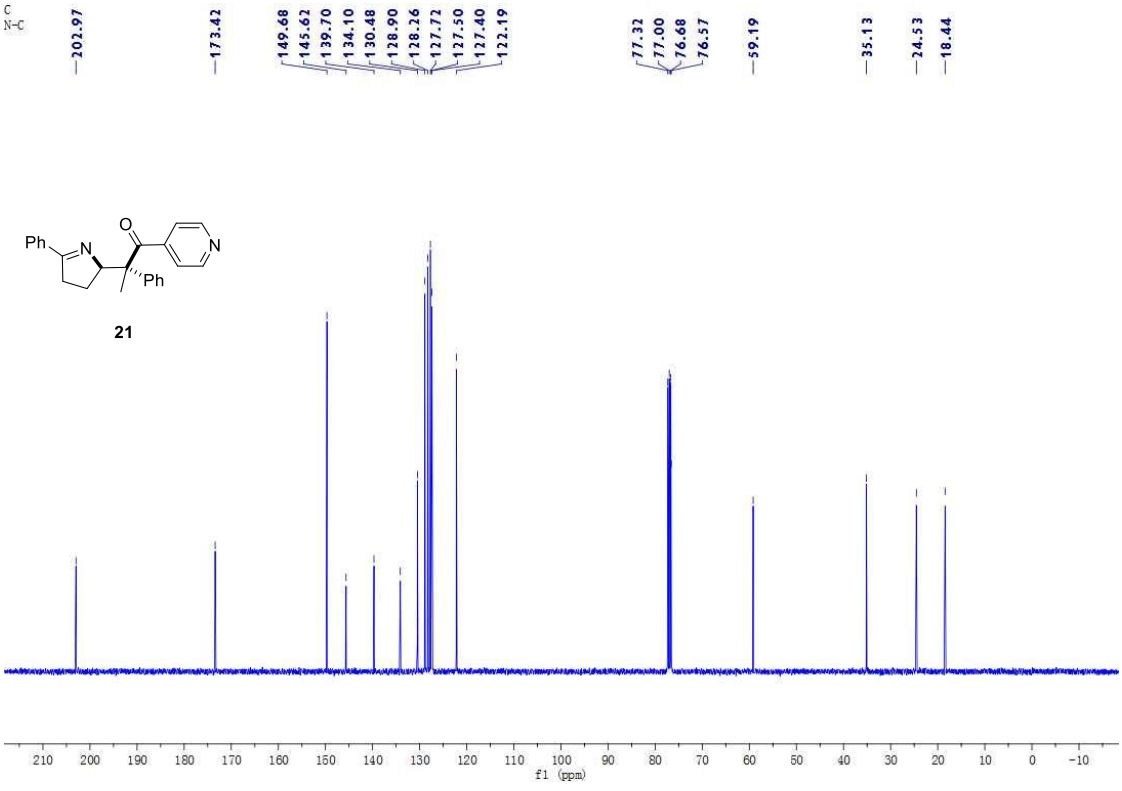

Jun10-2021
lwd-17-H
8.47
8.46
7.69
7.68
7.67
7.66
7.65
7.64
7.63
7.32
7.30
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.18
7.10
7.09
7.08
7.07
5.14
5.13
5.12
2.76
2.75
2.04
2.03
2.02
2.01
1.77
1.75
1.74
1.54
-0.00
Ph
N
O
N
Ph
1.94
2.97
7.93
1.04
1.00
0.96
0.99
1.25
1.04
2.96
f1 (ppm)

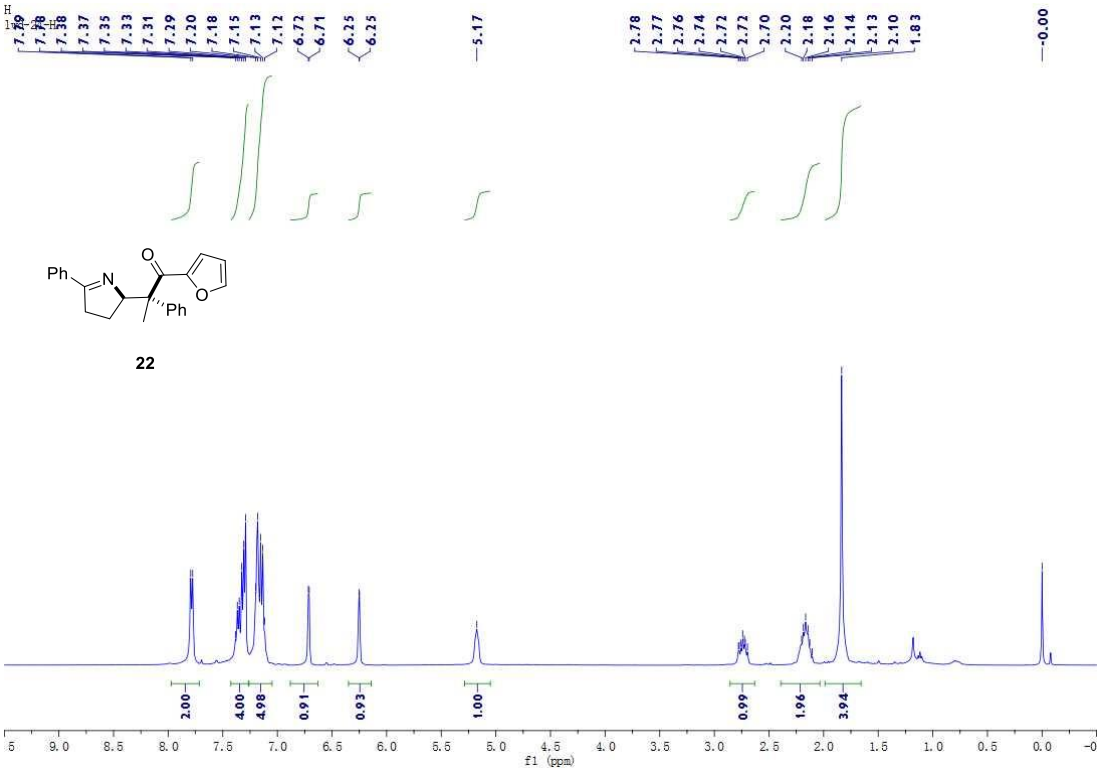
20


Jun10-2021
lwd-17-C
201.95
173.48
151.34
150.24
139.93
136.55
134.25
133.69
130.38
128.81
128.22
127.70
127.51
127.38
122.70
77.32
77.04
77.00
76.68
59.30
35.05
24.82
19.76
Ph
N
O
N
Ph
f1 (ppm)

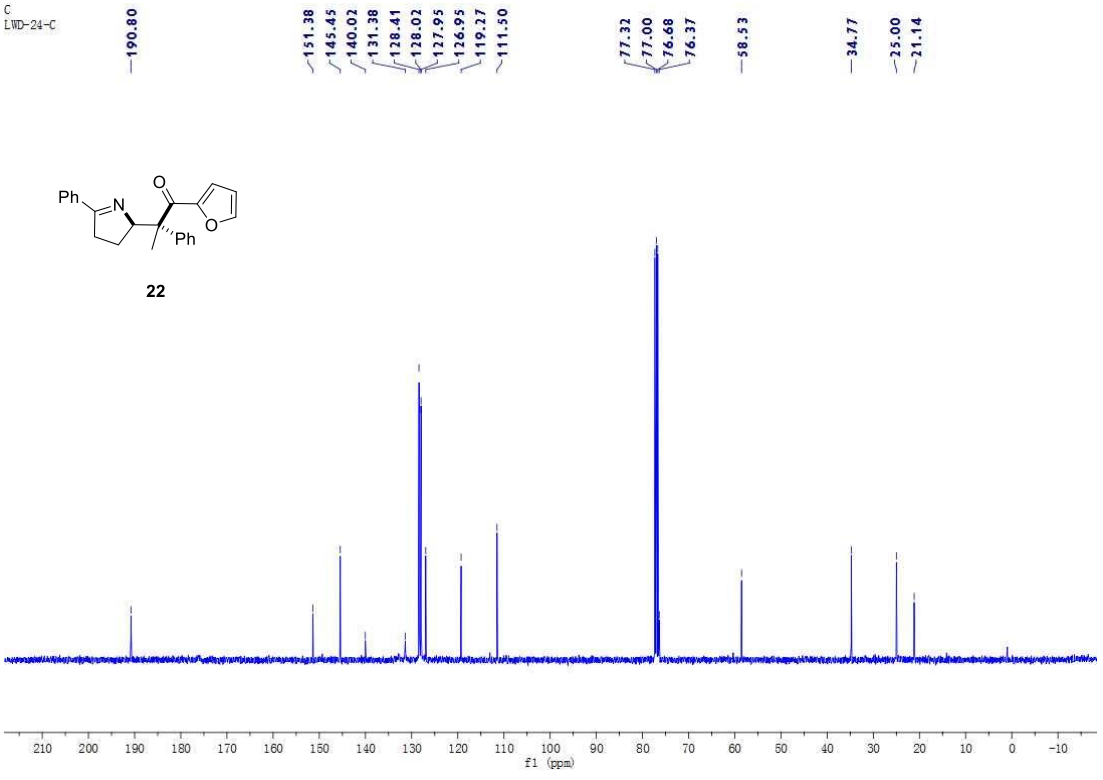
20


8.53 8.52 7.80 7.78 7.44 7.43 7.42 7.40 7.38 7.37 7.35 7.35 7.35 7.33 7.33 7.31 7.14 7.13
5.24 5.22 5.20
2.90 2.88 2.86 2.85 2.84 2.74 2.74 2.73 2.72 2.72 2.71 2.69 2.69 2.68
2.11 2.10 2.09 2.08 2.07 2.06 1.85 1.83 1.82 1.82 1.81 1.80 1.79 1.77 1.52
Ph
N
O
N
Ph
21
2.02 2.02 8.07 2.04 1.00 1.03 1.01 1.03 1.04 3.02
f1 (ppm)

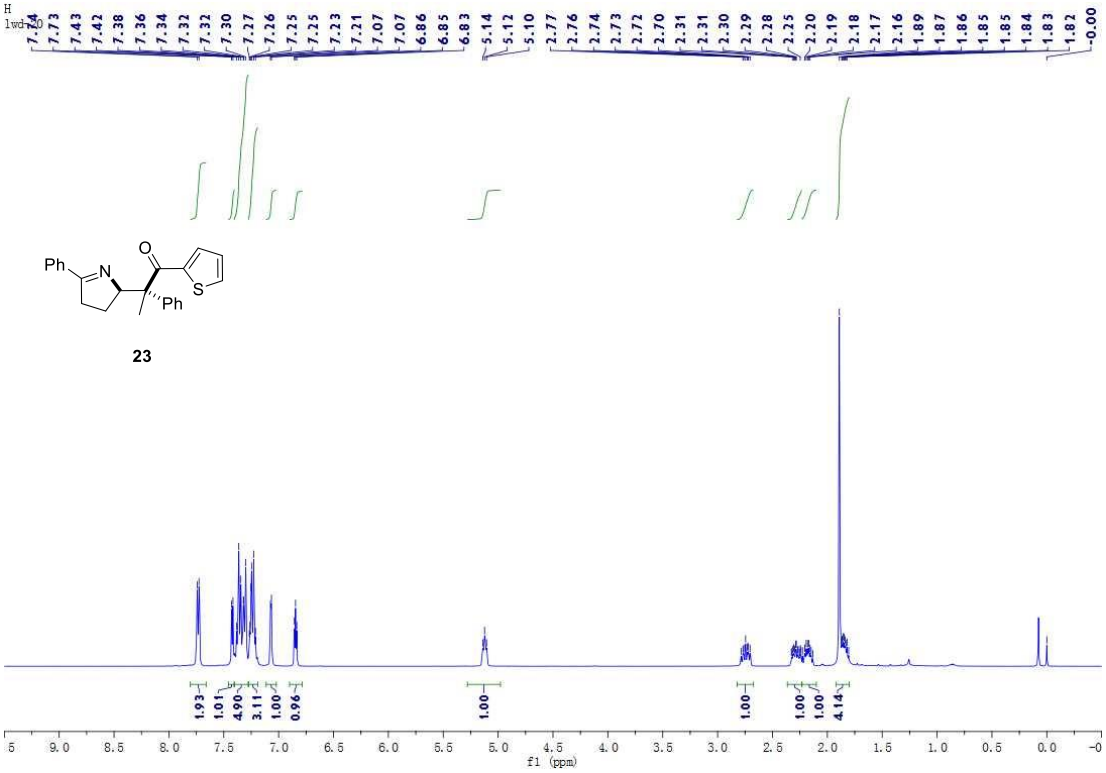

202.97
173.42
149.68 145.62 139.70 134.10 130.48 128.90 128.26 127.72 127.50 127.40 122.19
77.32 77.00 76.68 76.57
59.19
35.13
24.53
18.44
Ph
N
O
N
Ph
21
f1 (ppm)


H
LWD-24-H
7.49
7.48
7.38
7.37
7.35
7.33
7.31
7.29
7.20
7.18
7.15
7.13
7.12
6.72
6.71
6.25
6.25
5.17
2.78
2.77
2.76
2.74
2.72
2.72
2.70
2.20
2.18
2.16
2.14
2.13
2.10
1.83
0.00
Ph
N
O
O
Ph
2.00
4.00
4.98
0.91
0.93
1.00
0.99
1.96
3.94
f1 (ppm)

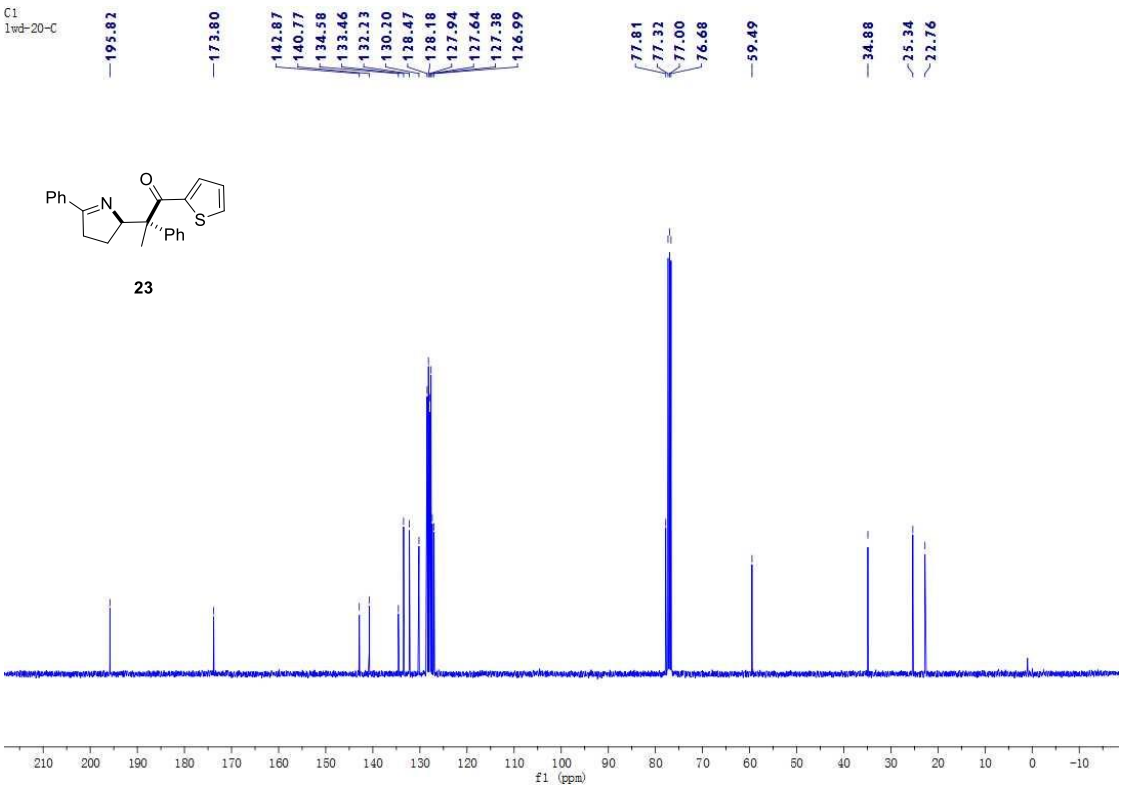
22


C
LWD-24-C
190.80
151.38
145.45
140.02
131.38
128.41
128.02
127.95
126.95
119.27
111.50
77.32
77.00
76.68
76.37
58.53
34.77
25.00
21.14
Ph
N
O
O
Ph
f1 (ppm)

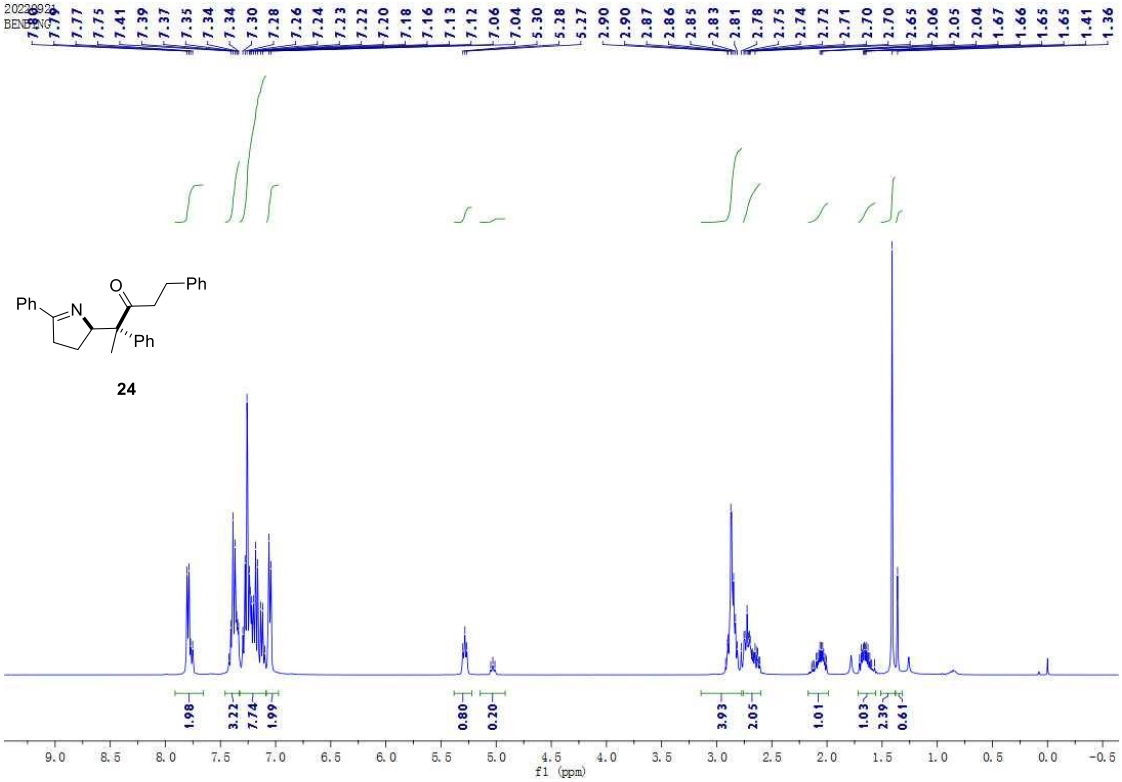
22

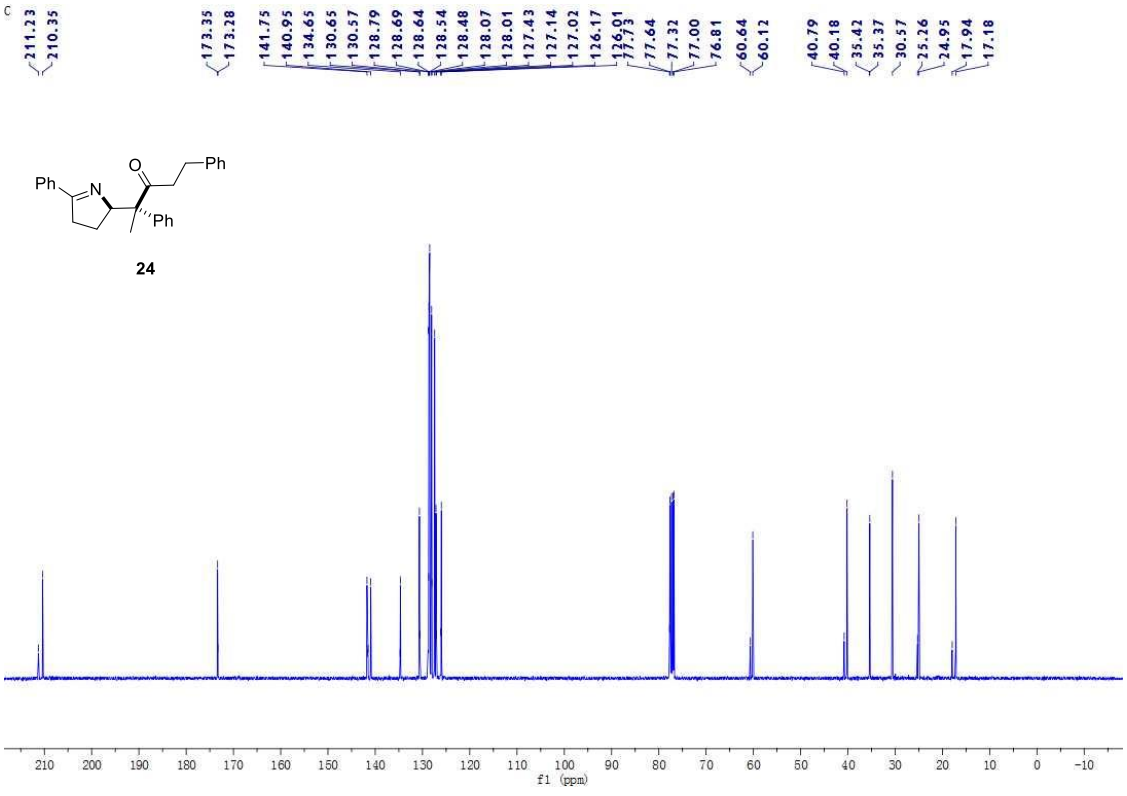

H
lwd-20
7.74
7.73
7.43
7.42
7.38
7.36
7.34
7.32
7.32
7.30
7.27
7.26
7.25
7.25
7.23
7.21
7.07
7.07
6.86
6.85
6.83
5.14
5.12
5.10
2.77
2.76
2.74
2.73
2.72
2.70
2.31
2.31
2.30
2.29
2.28
2.25
2.20
2.19
2.18
2.17
2.16
1.89
1.87
1.86
1.85
1.85
1.84
1.83
1.82
-0.00
Ph
N
O
S
Ph
1.93
1.01
4.90
3.11
1.00
0.96
1.00
1.00
1.00
1.00
4.14
f1 (ppm)

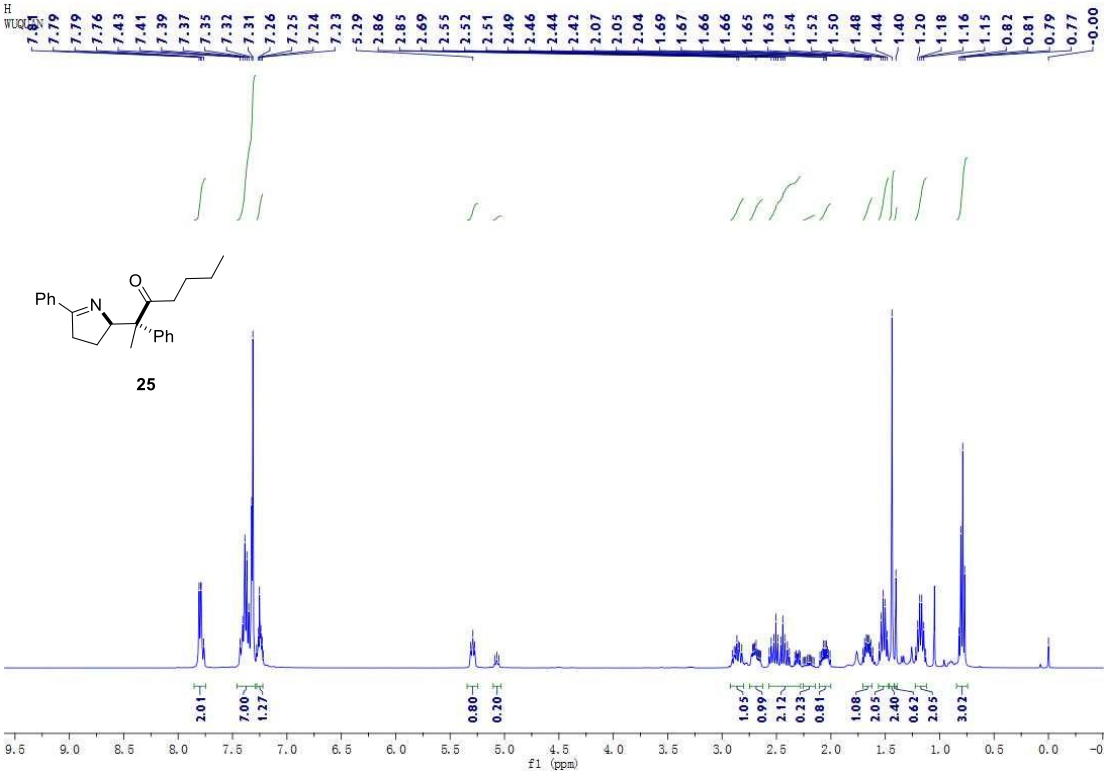
23

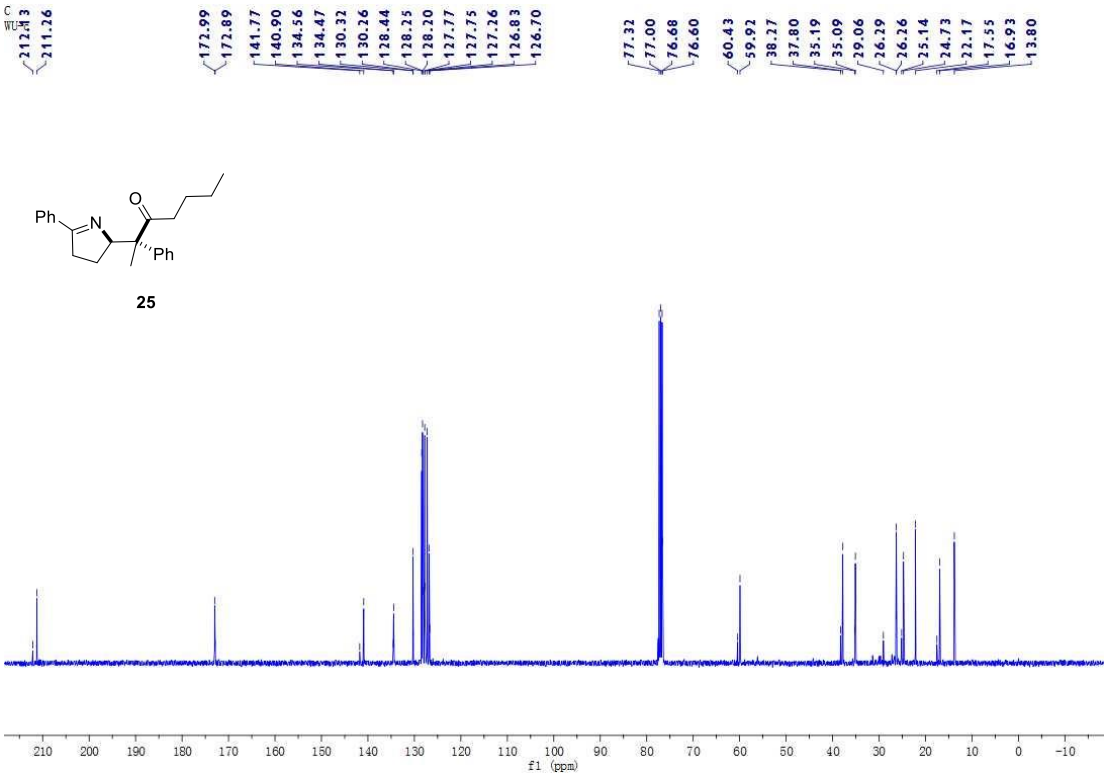

C1
lwd-20-C
195.82
173.80
142.87
140.77
134.58
133.46
132.23
130.20
128.47
128.18
127.94
127.64
127.38
126.99
77.81
77.32
77.00
76.68
59.49
34.88
25.34
22.76
Ph
N
O
S
Ph
f1 (ppm)

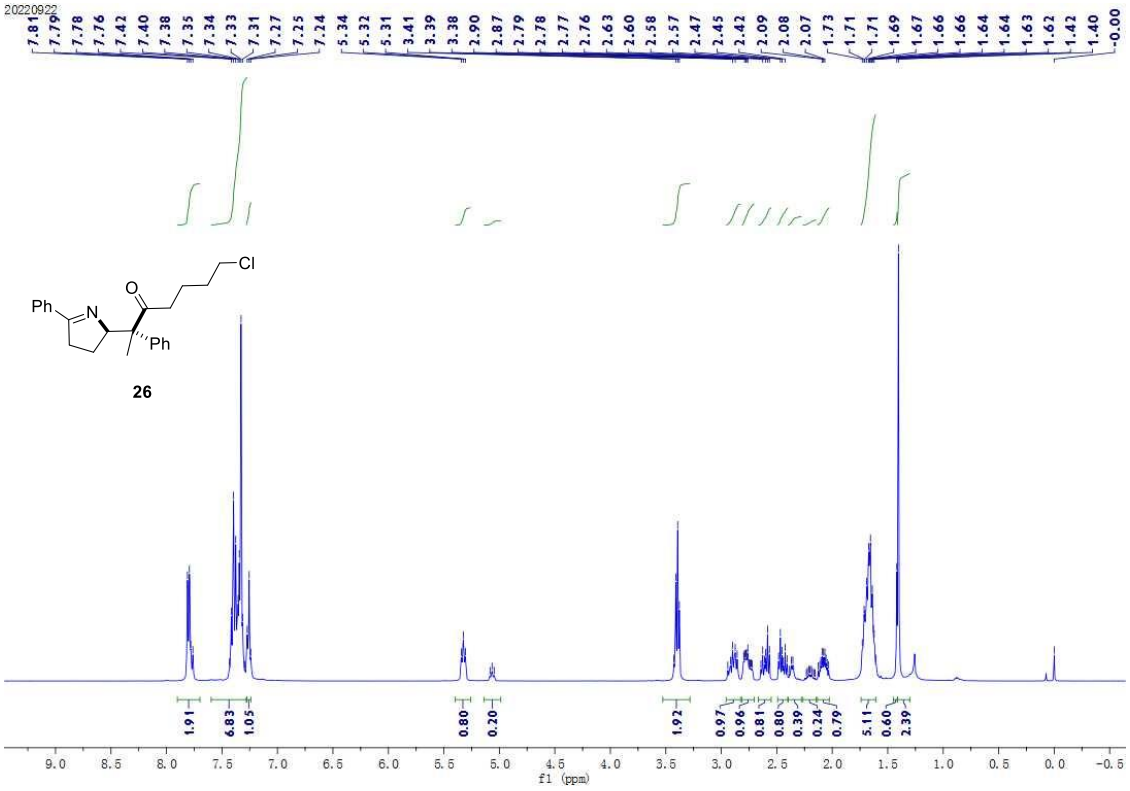
23

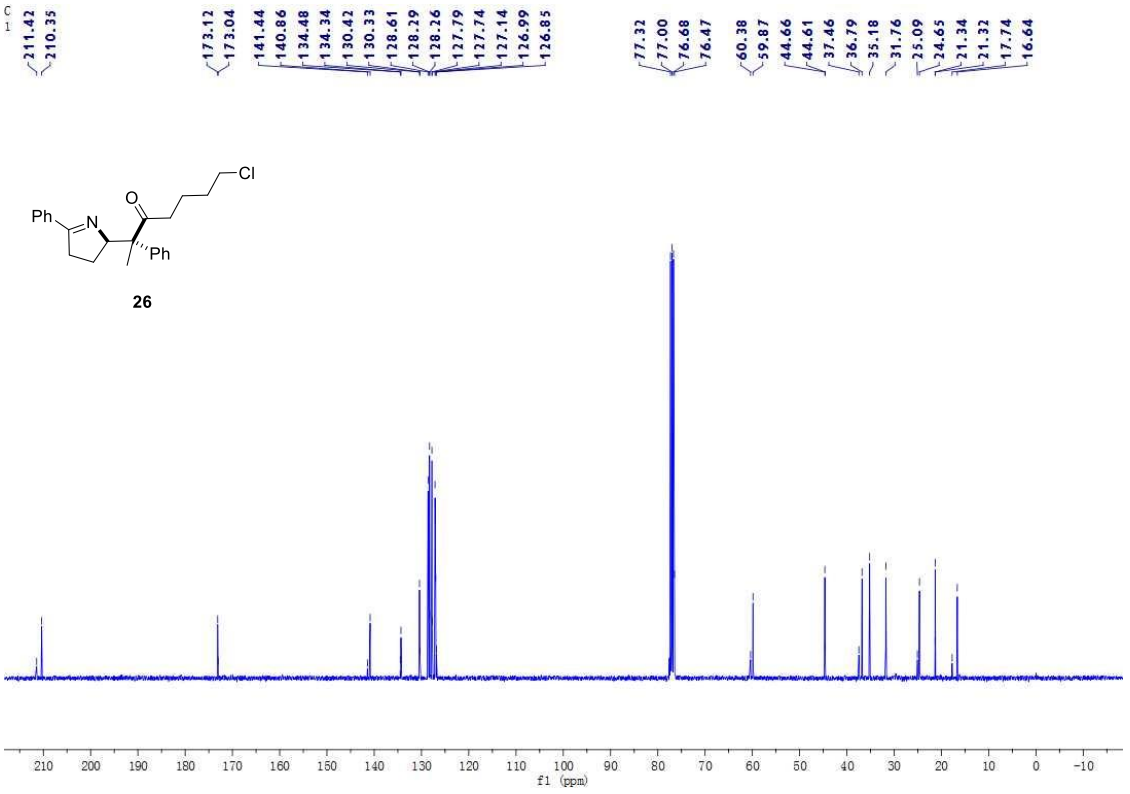

7.77
7.75
7.41
7.39
7.37
7.35
7.34
7.34
7.30
7.28
7.26
7.24
7.23
7.22
7.20
7.18
7.16
7.13
7.12
7.06
7.04
5.30
5.28
5.27
2.90
2.90
2.87
2.86
2.85
2.83
2.81
2.78
2.75
2.74
2.72
2.71
2.70
2.70
2.65
2.06
2.05
2.04
1.67
1.66
1.65
1.65
1.41
1.36
Ph
N
O
Ph
Ph
24
1.98
3.22
7.74
1.99
0.80
0.20
3.93
2.05
1.01
1.03
2.39
0.61
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

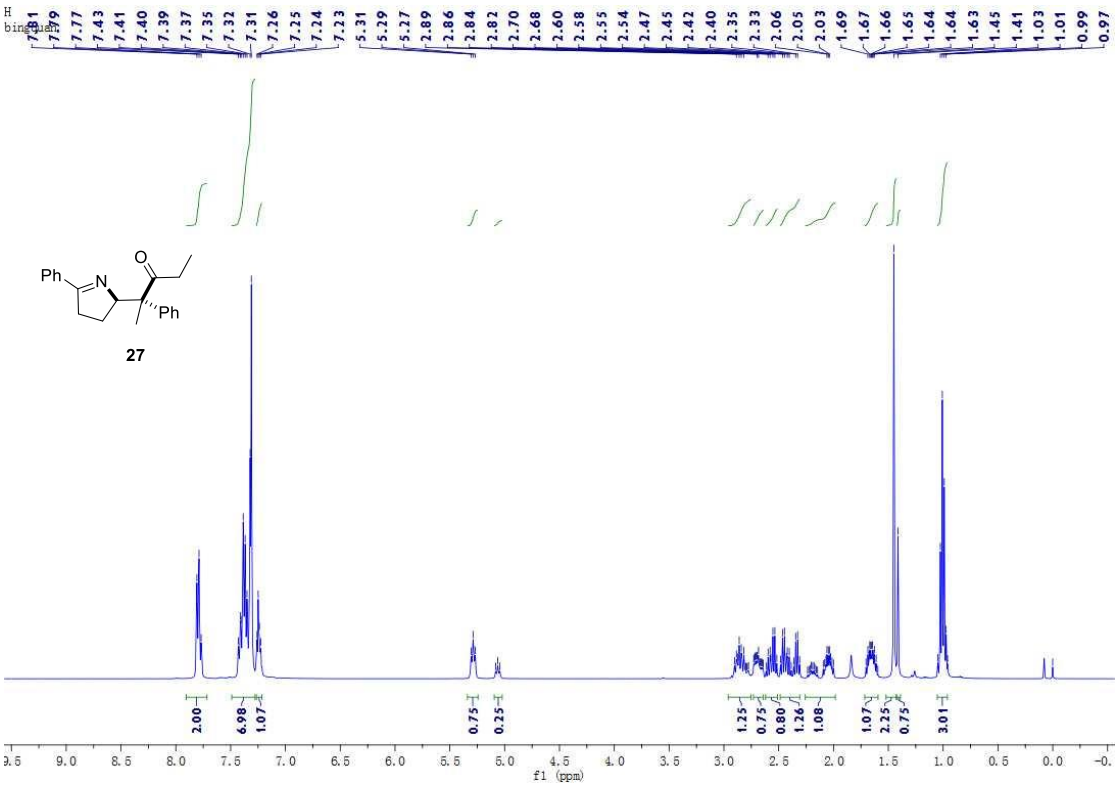

211.23
210.35
173.35
173.28
141.75
140.95
134.65
130.65
130.57
128.79
128.69
128.64
128.54
128.48
128.07
128.01
127.43
127.14
127.02
126.17
126.01
77.73
77.64
77.32
77.00
76.81
60.64
60.12
40.79
40.18
35.42
35.37
30.57
25.26
24.95
17.94
17.18
Ph
N
O
Ph
Ph
24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

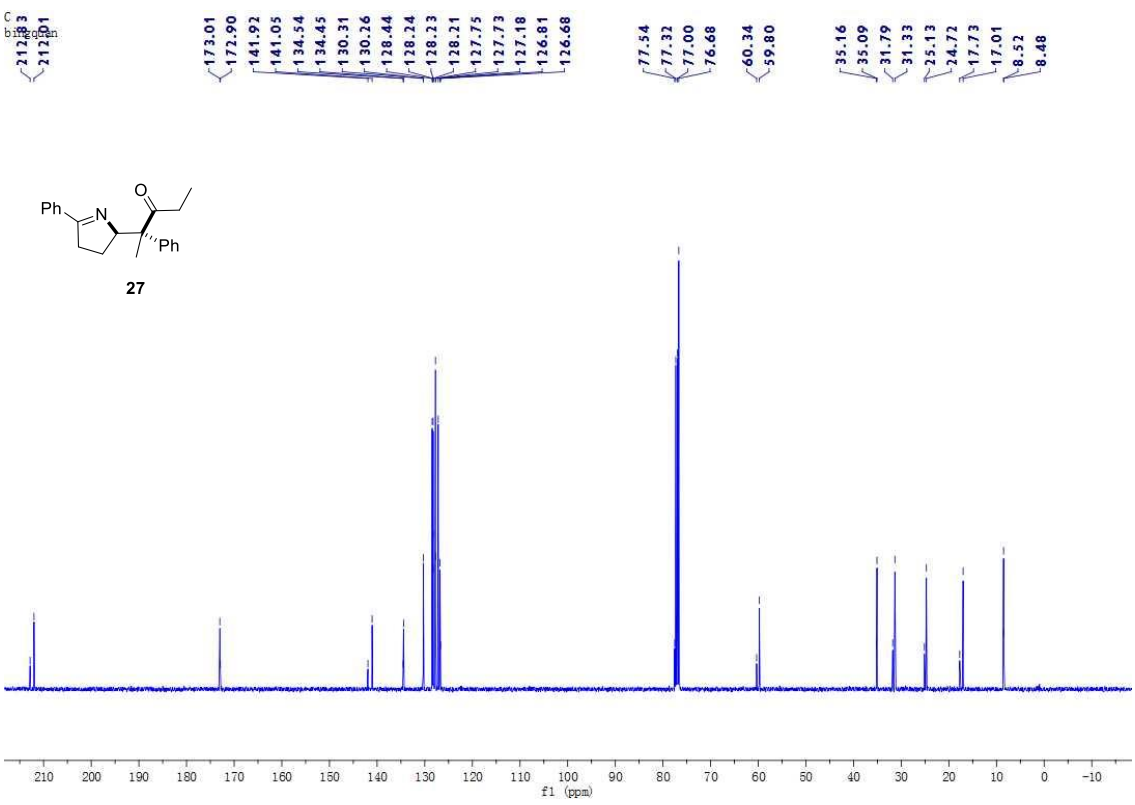

Ph
N
O
Ph
25
2.01
7.00
1.27
0.80
0.20
1.05
0.99
2.12
0.23
0.81
1.08
2.05
2.40
0.62
2.05
3.02
f1 (ppm)

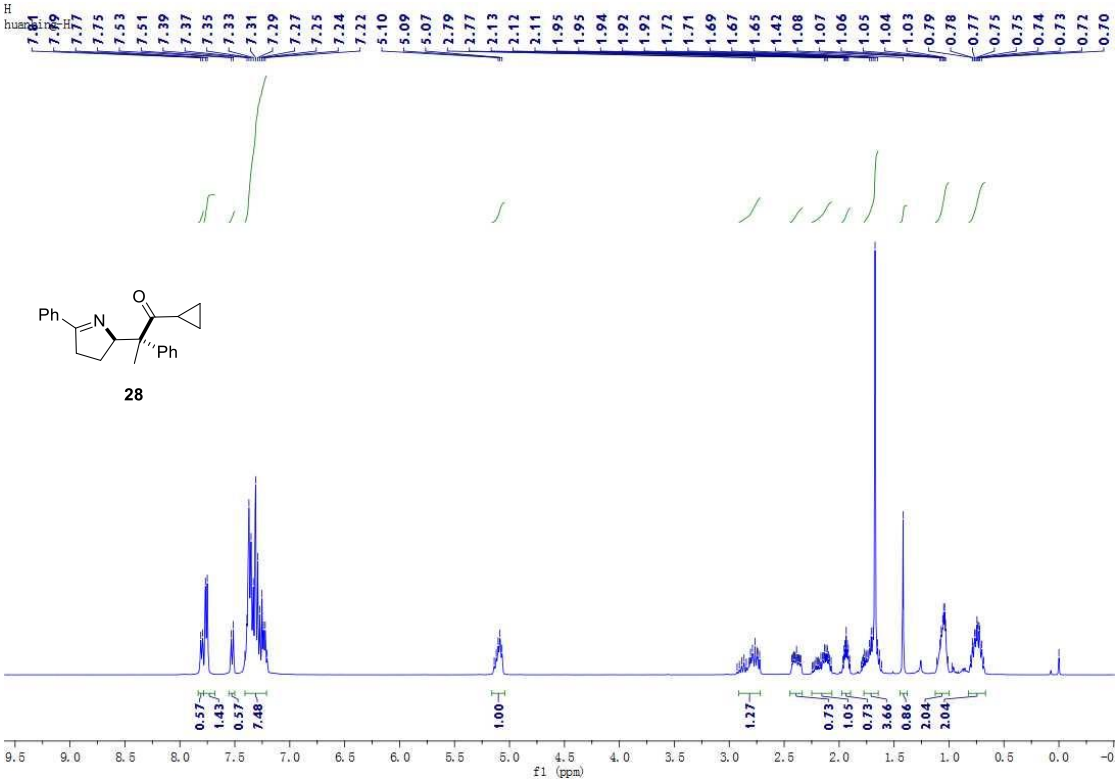

Ph
N
O
Ph
25
f1 (ppm)

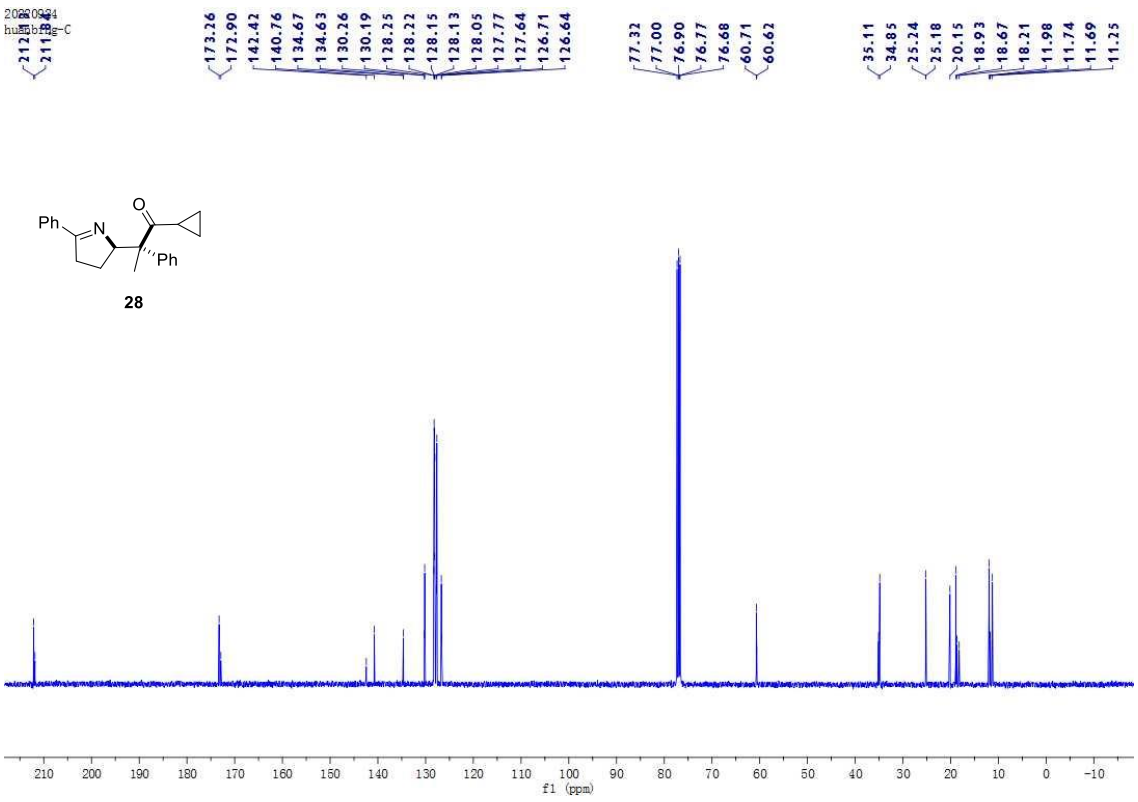

20220922
7.81 7.79 7.78 7.76 7.42 7.40 7.38 7.35 7.34 7.33 7.31 7.27 7.25 7.24
5.34 5.32 5.31 3.41 3.39 3.38 2.90 2.87 2.79 2.78 2.77 2.76 2.63 2.60 2.58 2.57 2.47 2.45 2.42 2.09 2.08 2.07 1.73 1.71 1.71 1.69 1.67 1.66 1.66 1.64 1.64 1.63 1.62 1.42 1.40 0.00
Ph
N
O
Cl
Ph
26
1.91 6.83 1.05 0.80 0.20 1.92 0.97 0.96 0.81 0.80 0.39 0.24 0.79 5.11 0.60 2.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

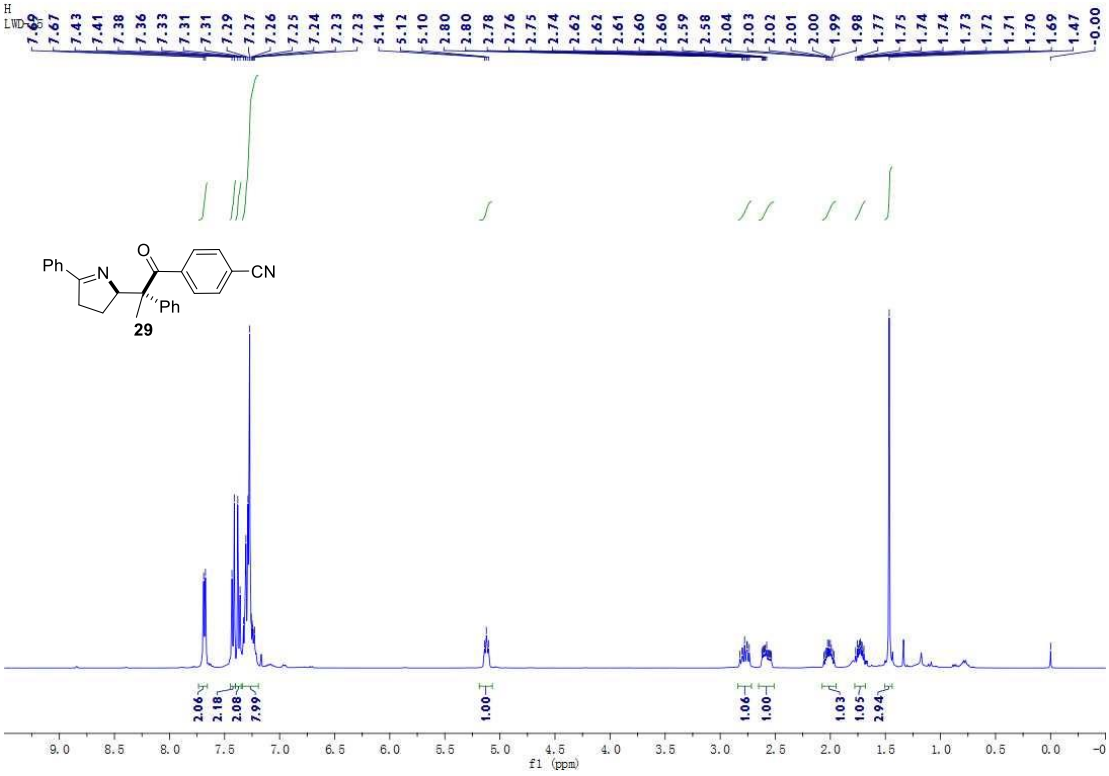

211.42 210.35
173.12 173.04 141.44 140.86 134.48 134.34 130.42 130.33 128.61 128.29 128.26 127.79 127.74 127.14 126.99 126.85
77.32 77.00 76.68 76.47 60.38 59.87 44.66 44.61 37.46 36.79 35.18 31.76 25.09 24.65 21.34 21.32 17.74 16.64
Ph
N
O
Cl
Ph
26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

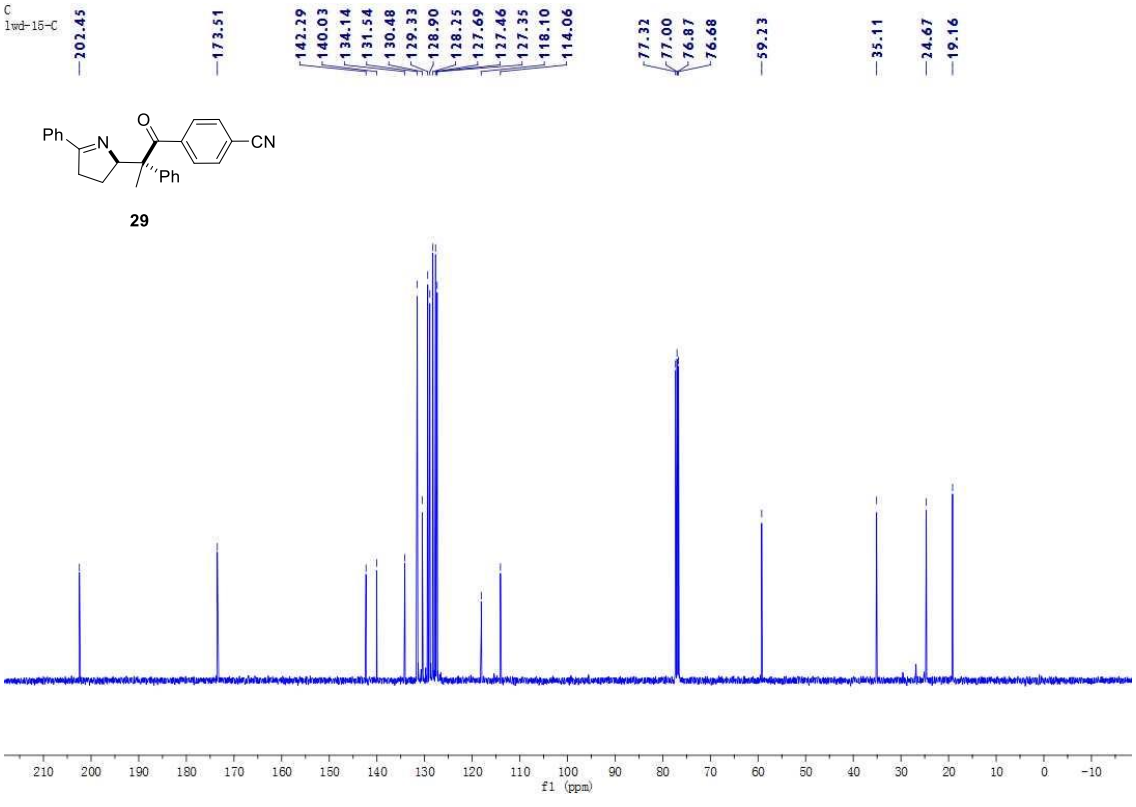

Ph
N
O
Ph
27
f1 (ppm)

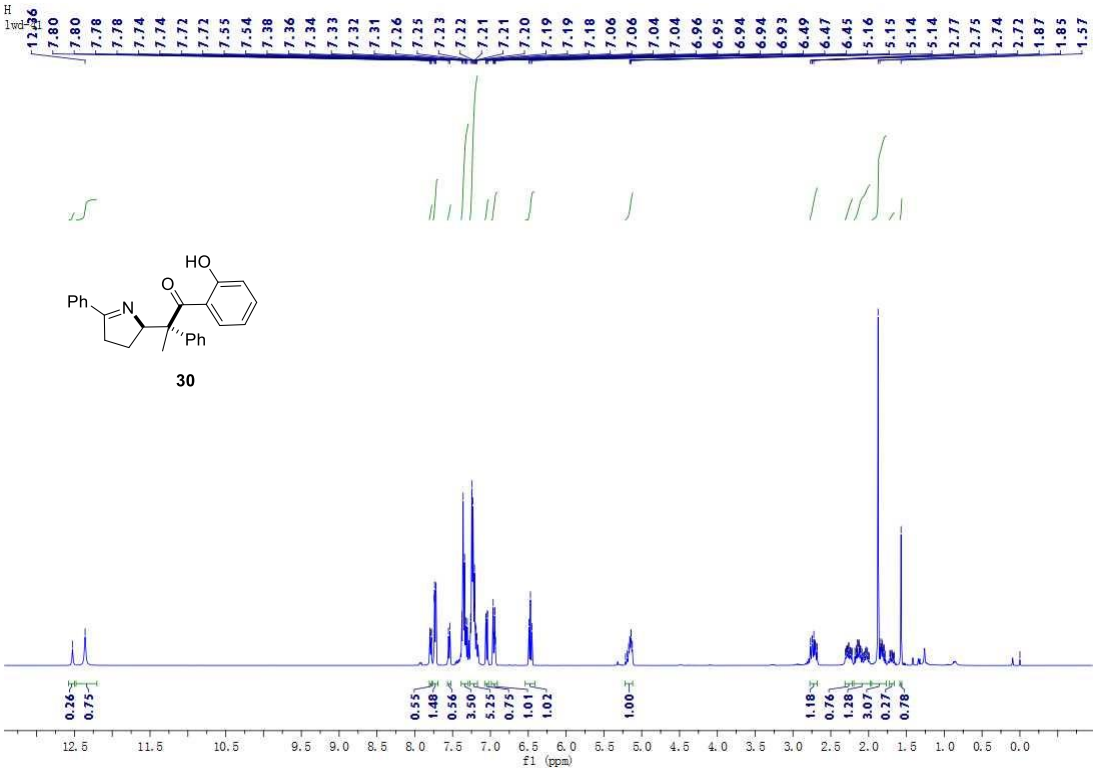

Ph
N
O
Ph
27
f1 (ppm)

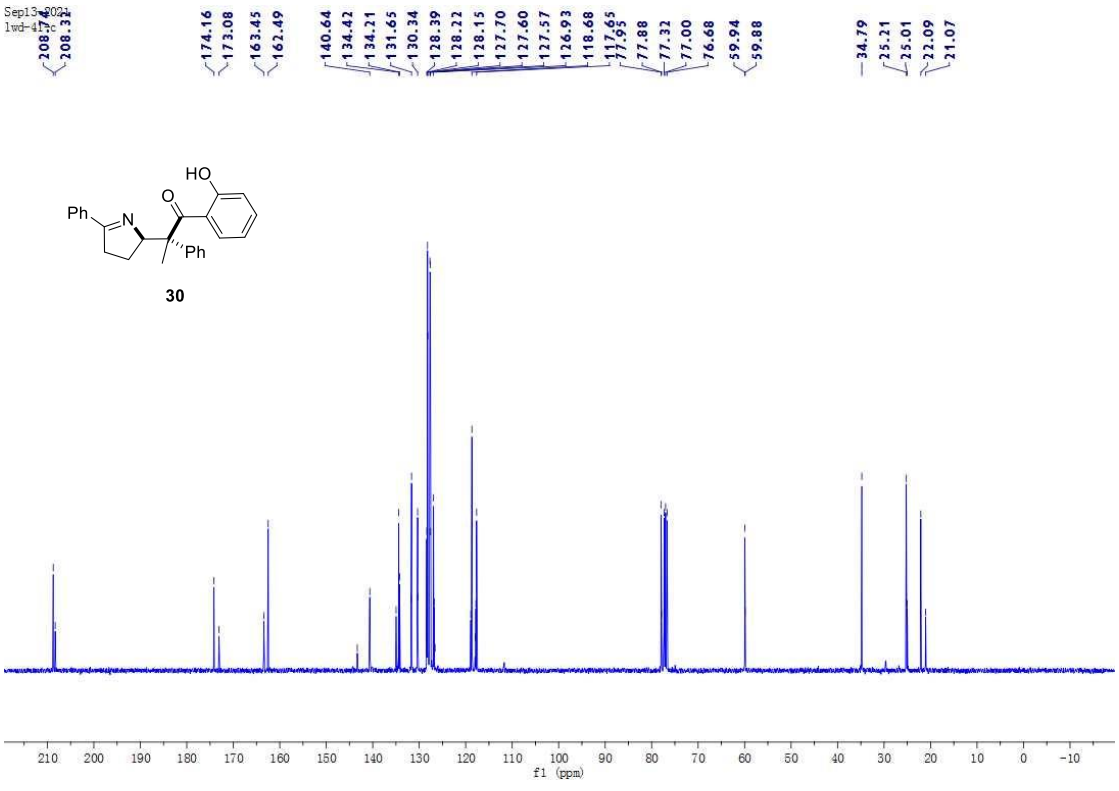

Ph
N
O
Ph
28
0.57
1.43
0.57
7.48
1.00
1.27
0.73
1.05
0.73
3.66
0.86
2.04
2.04
f1 (ppm)

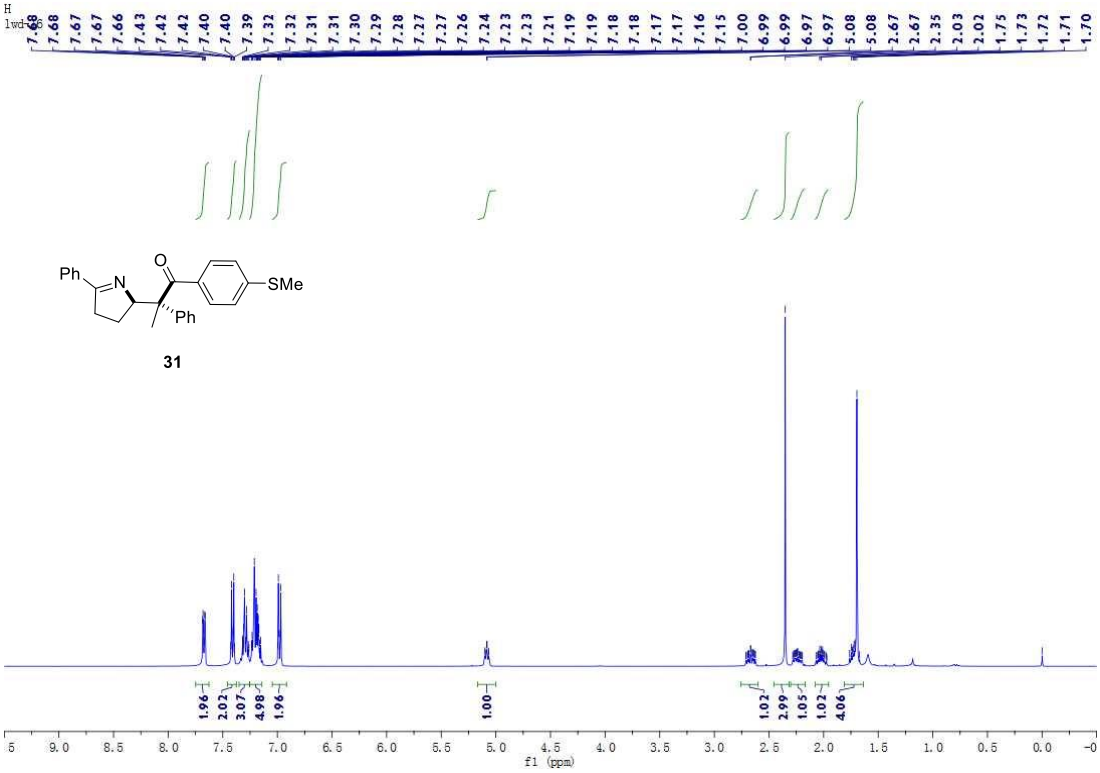

Ph
N
O
Ph
28
f1 (ppm)


H
LWD-15
7.69
7.67
7.43
7.41
7.38
7.36
7.33
7.31
7.31
7.29
7.27
7.26
7.25
7.24
7.23
7.23
5.14
5.12
5.10
2.80
2.78
2.76
2.75
2.74
2.62
2.62
2.61
2.60
2.60
2.59
2.58
2.04
2.03
2.02
2.01
2.00
1.99
1.98
1.77
1.75
1.74
1.74
1.73
1.72
1.71
1.70
1.69
1.47
0.00
Ph
N
O
CN
Ph
29
2.06
2.18
2.08
7.99
1.00
1.06
1.00
1.03
1.05
2.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

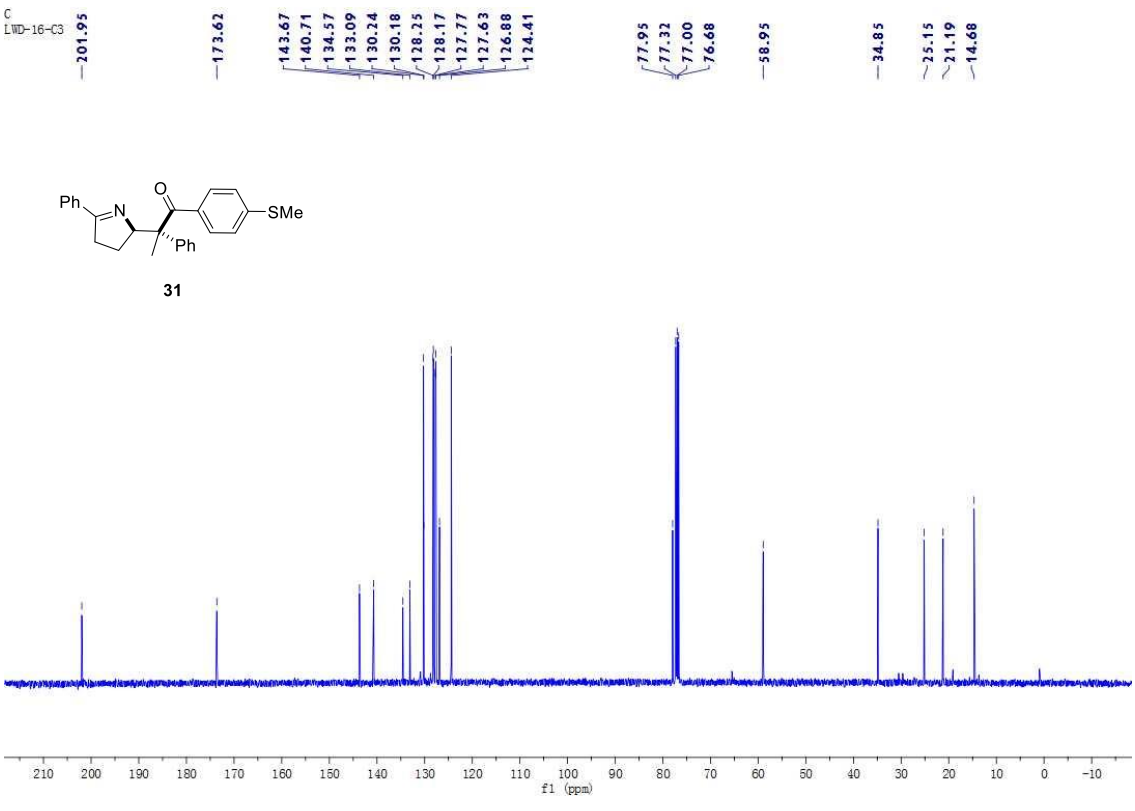

C
lwd-15-C
202.45
173.51
142.29
140.03
134.14
131.54
130.48
129.33
128.90
128.25
127.69
127.46
127.35
118.10
114.06
77.32
77.00
76.87
76.68
59.23
35.11
24.67
19.16
Ph
N
O
CN
Ph
29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
O
Ph
N
Ph
30
f1 (ppm)

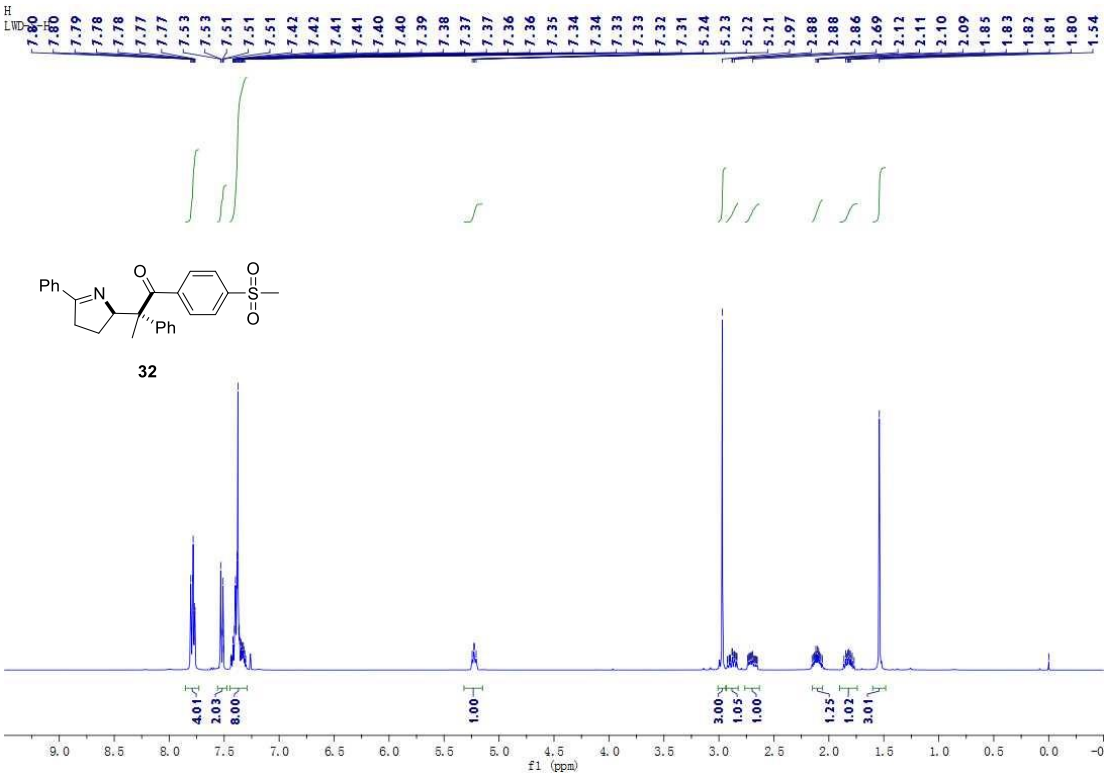

HO
O
Ph
N
Ph
30
f1 (ppm)



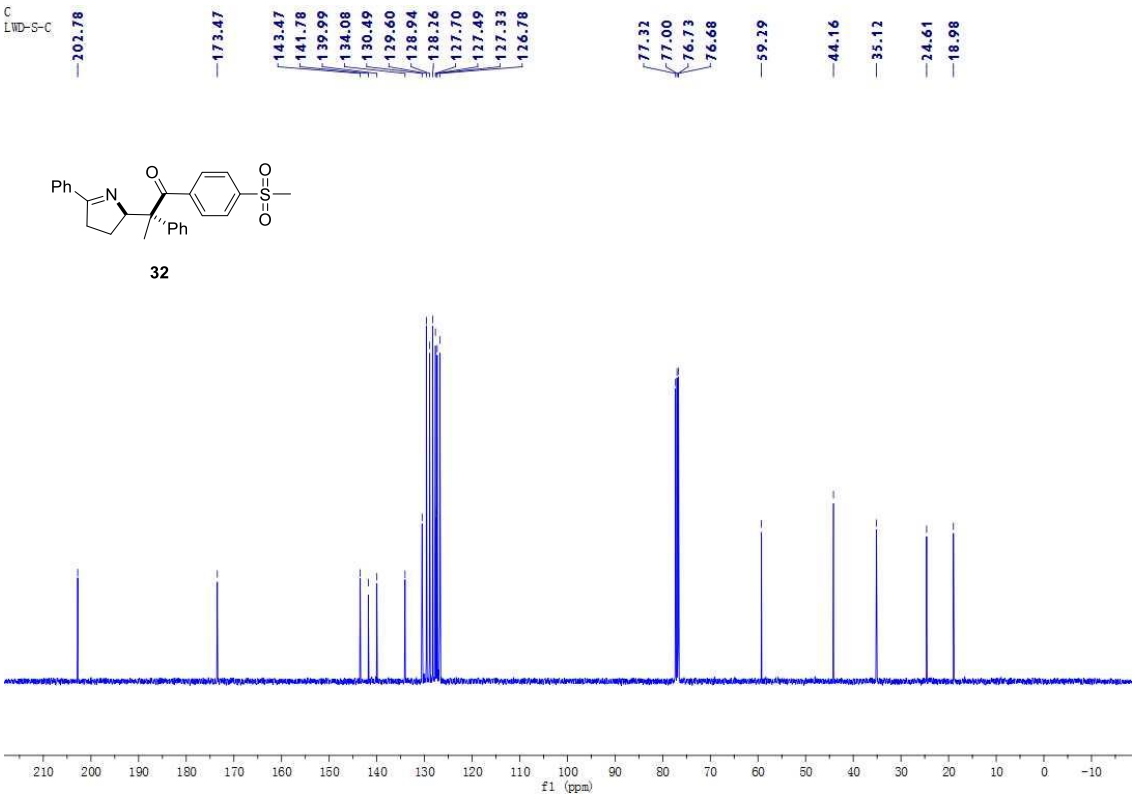
31



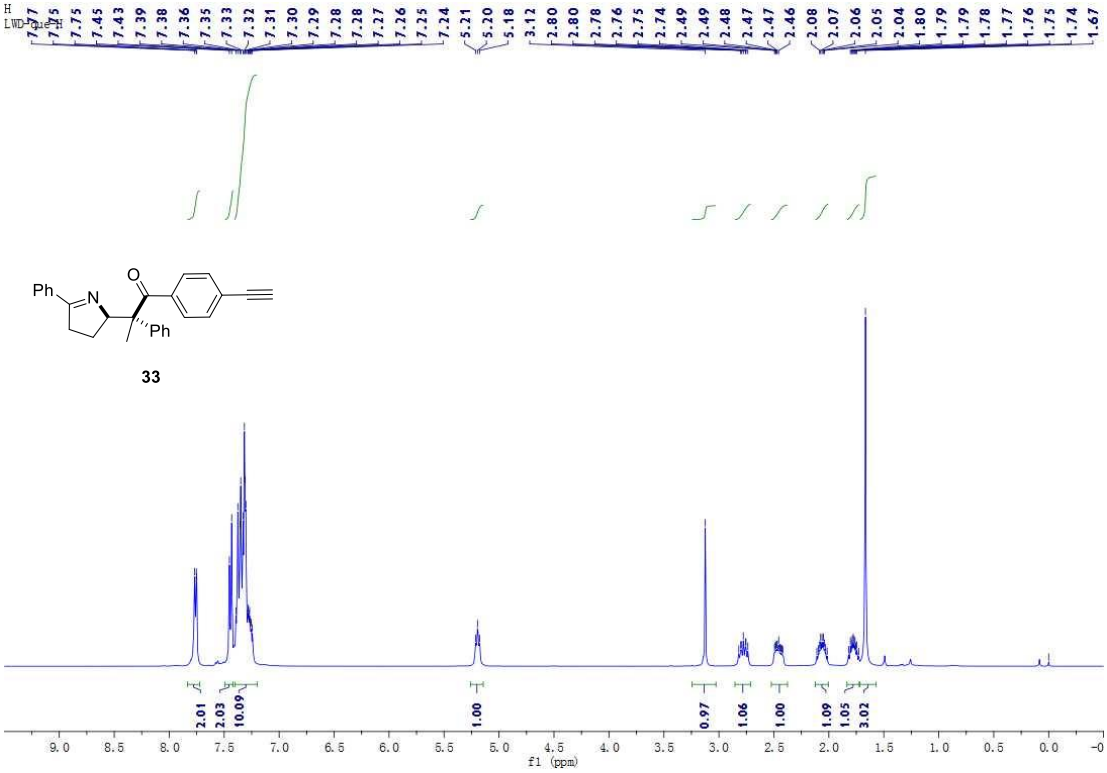
31


H
LWD-S-H
7.80 7.80 7.79 7.78 7.78 7.77 7.77 7.53 7.53 7.51 7.51 7.51 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.31 5.24 5.23 5.22 5.21 2.97 2.88 2.88 2.86 2.69 2.12 2.11 2.10 2.09 1.85 1.83 1.82 1.81 1.80 1.54
Ph
N
O
S
O
O
Ph
4.01
2.03
8.00
1.00
3.00
1.05
1.00
1.25
1.02
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

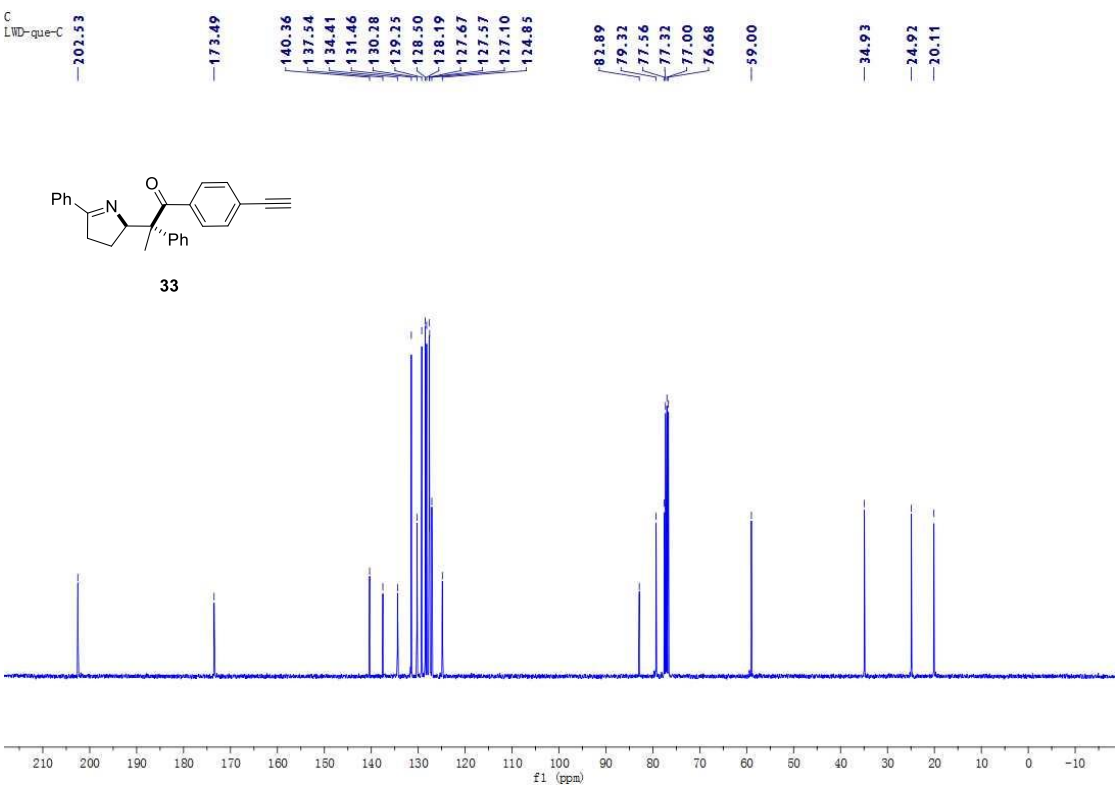
32


C
LWD-S-C
202.78
173.47
143.47
141.78
139.99
134.08
130.49
129.60
128.94
128.26
127.70
127.49
127.33
126.78
77.32
77.00
76.73
76.68
59.29
44.16
35.12
24.61
18.98
Ph
N
O
S
O
O
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

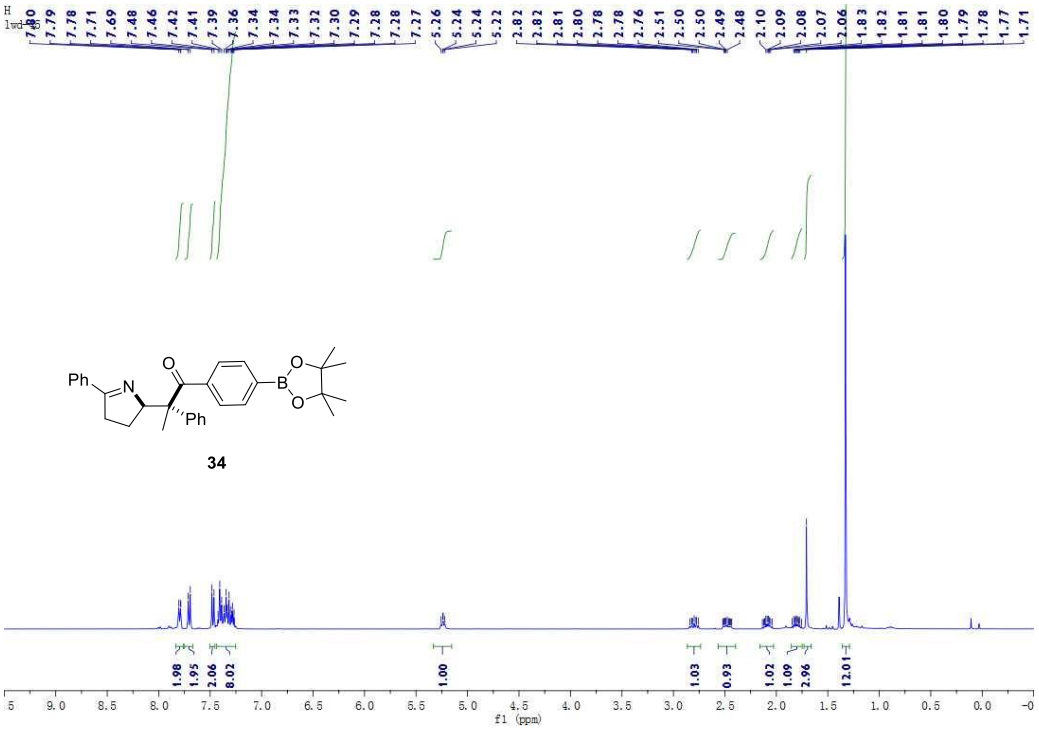
32

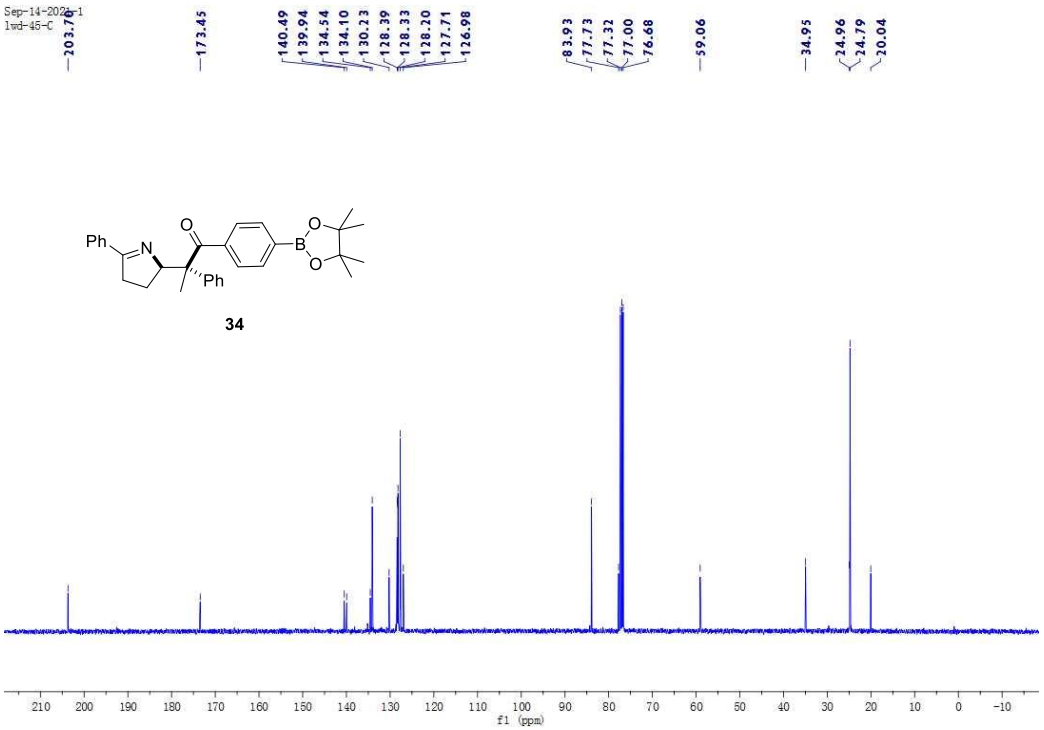

H
LWD-que-H
7.77
7.75
7.45
7.43
7.39
7.38
7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.25
7.24
5.21
5.20
5.18
3.12
2.80
2.80
2.78
2.76
2.75
2.74
2.49
2.49
2.48
2.47
2.47
2.46
2.08
2.07
2.06
2.05
2.04
1.80
1.79
1.79
1.78
1.77
1.76
1.75
1.74
1.67
Ph
N
O
Ph
2.01
2.03
10.09
1.00
0.97
1.06
1.00
1.09
1.05
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

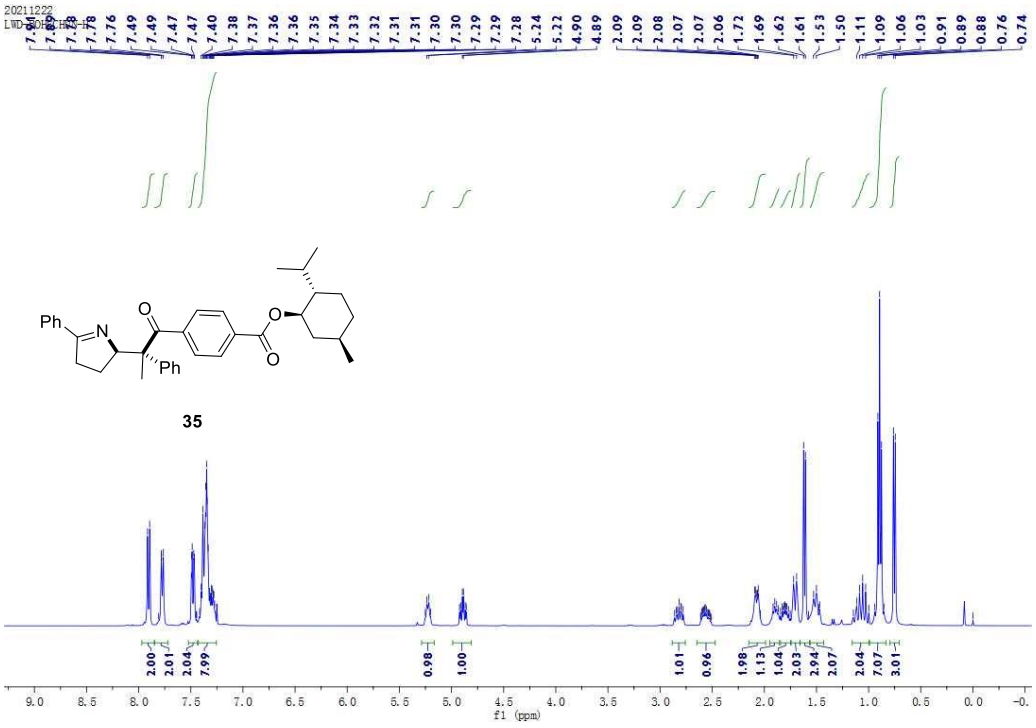
33

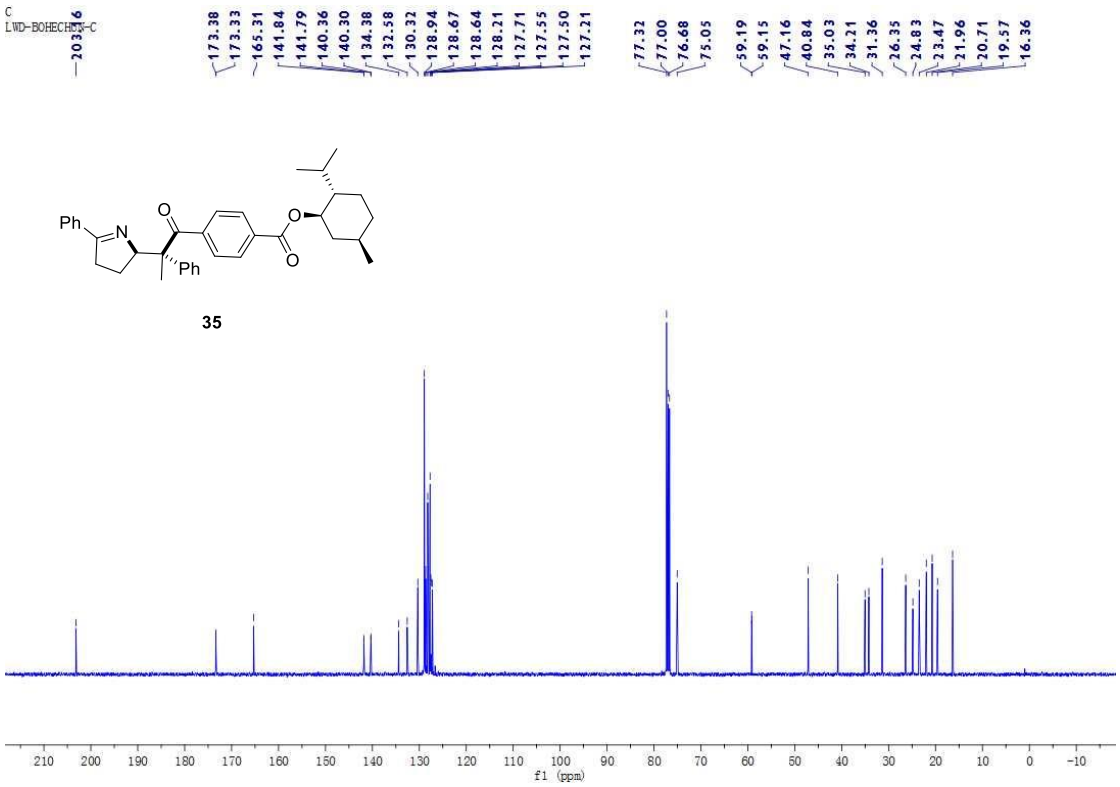

C
LWD-que-C
202.53
173.49
140.36
137.54
134.41
131.46
130.28
129.25
128.50
128.19
127.67
127.57
127.10
124.85
82.89
79.32
77.56
77.32
77.00
76.68
59.00
34.93
24.92
20.11
Ph
N
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

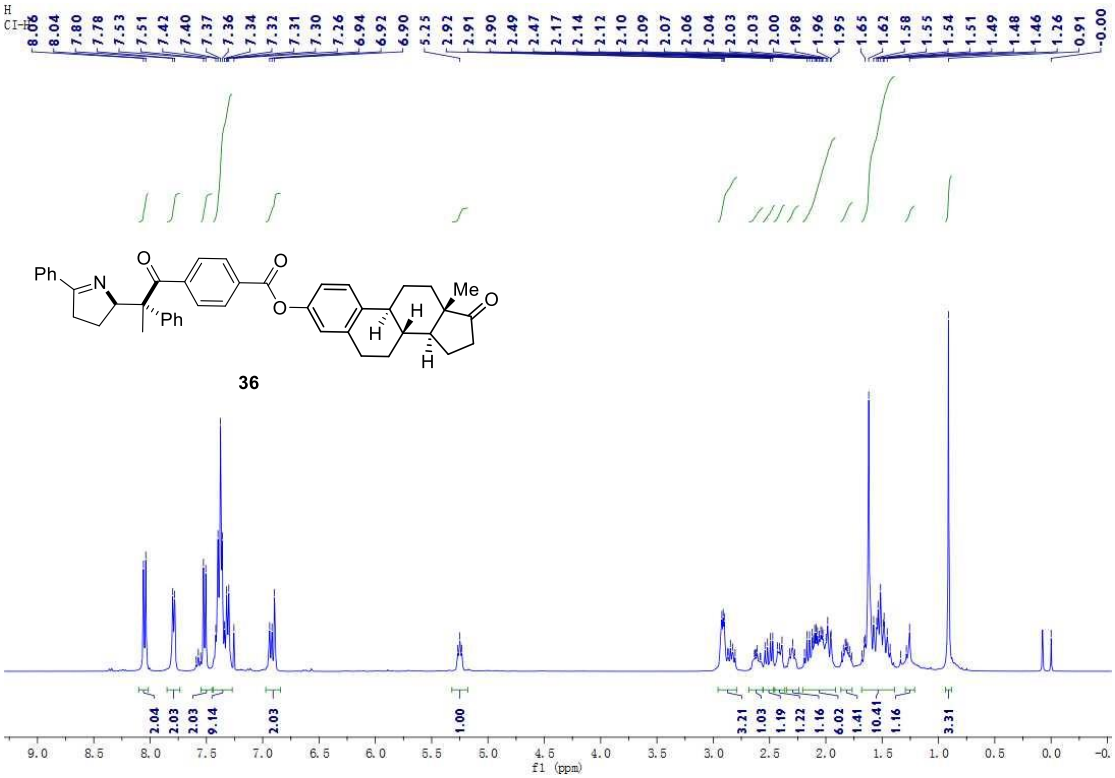
33

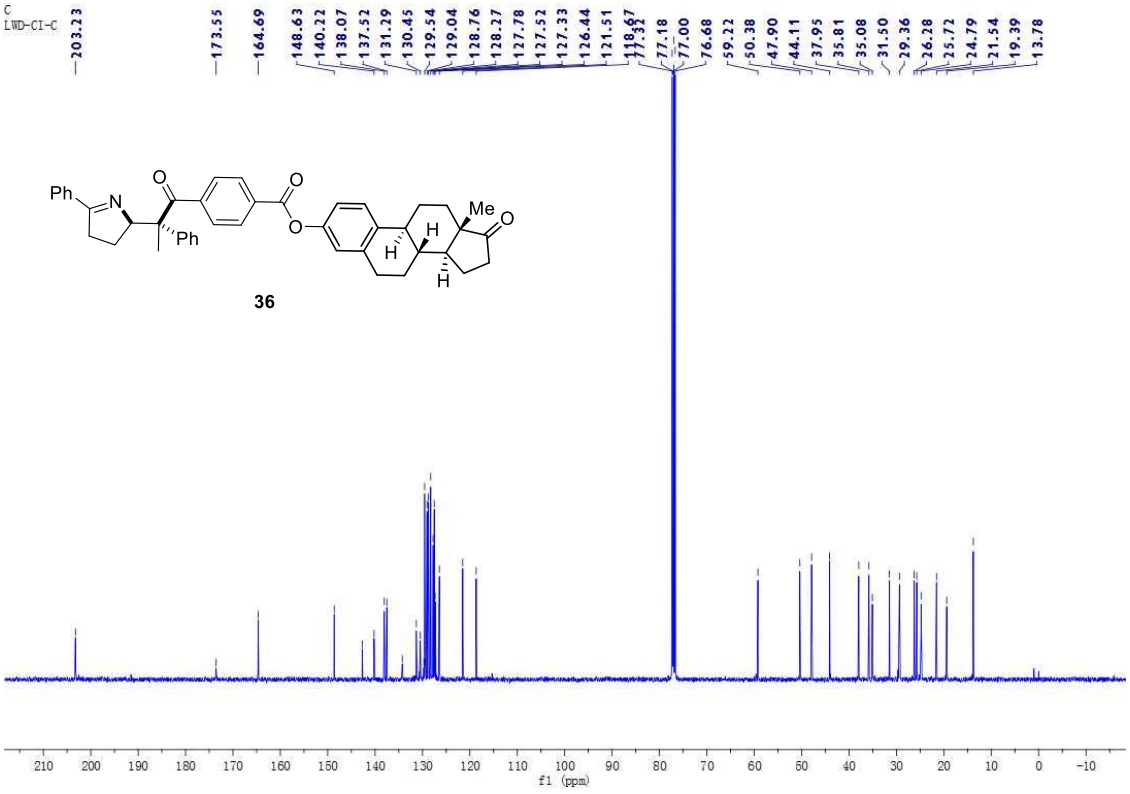

Ph
N
O
B
O
O
Ph
34
1.98
1.95
2.06
8.02
1.00
1.03
0.93
1.02
1.09
2.96
12.01
f1 (ppm)

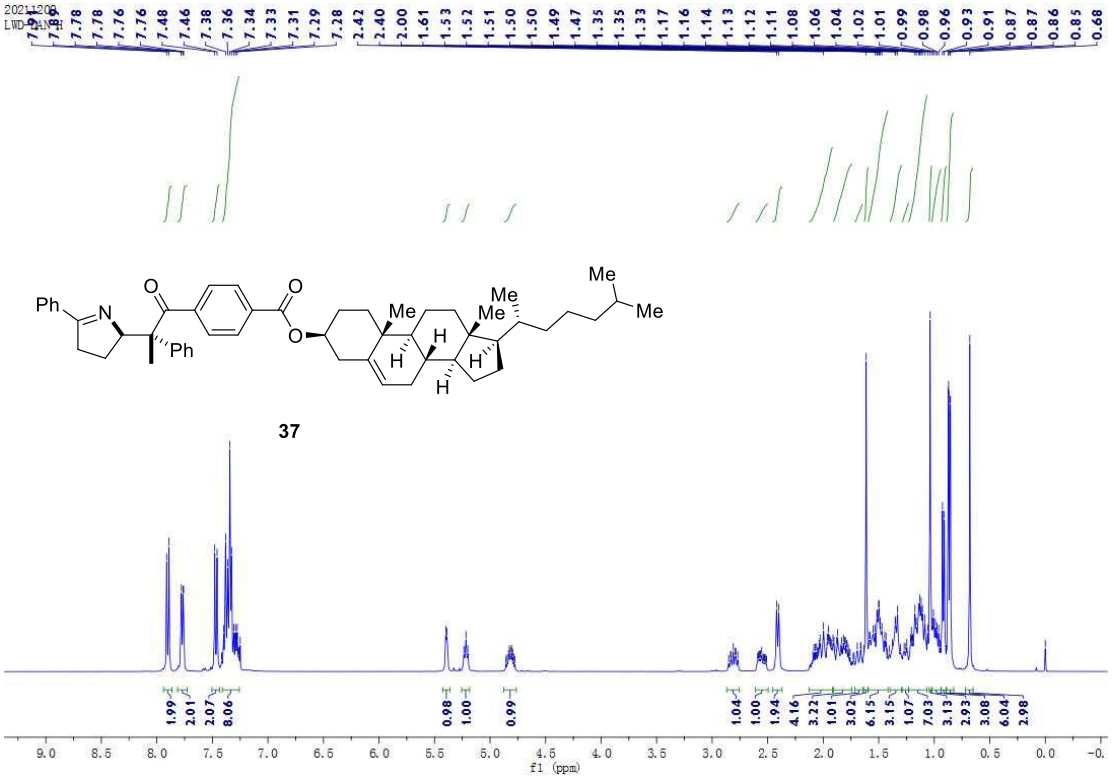

Ph
N
O
B
O
O
Ph
34
203.76
173.45
140.49
139.94
134.54
134.10
130.23
128.39
128.33
128.20
127.71
126.98
83.93
77.73
77.32
77.00
76.68
59.06
34.95
24.96
24.79
20.04
f1 (ppm)

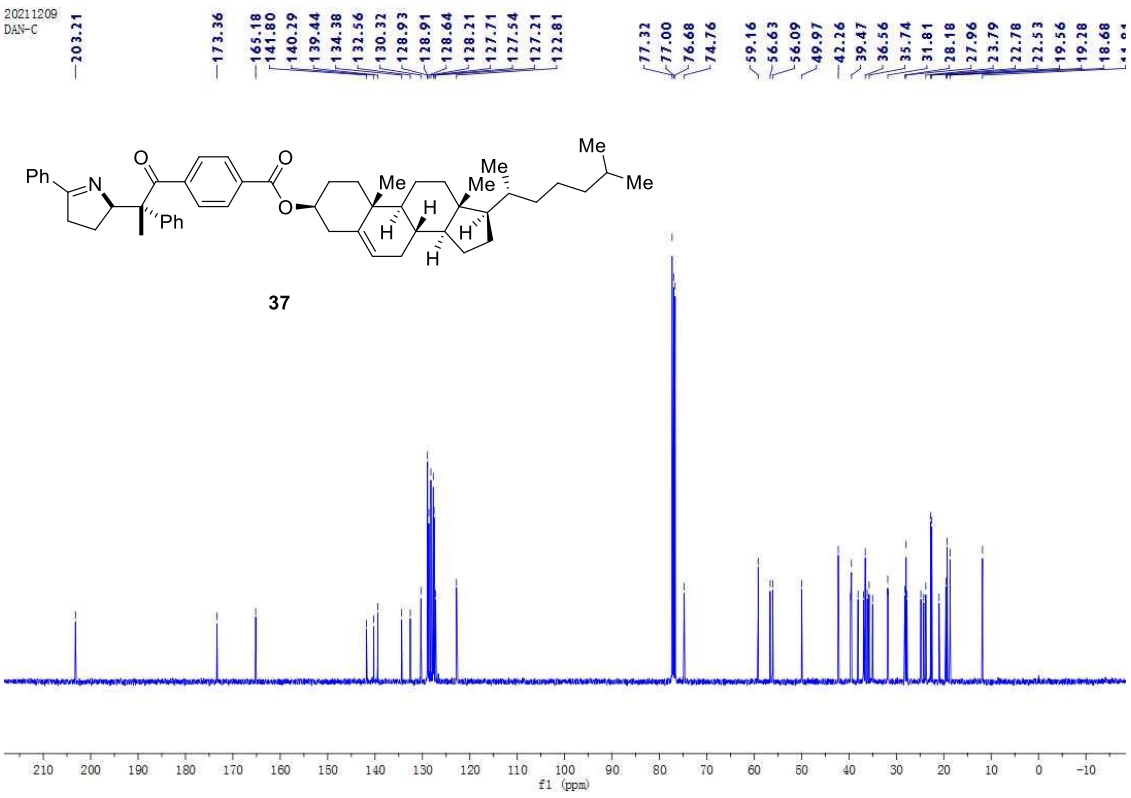

20211222
LWD-BOHECH5-H
7.78 7.76 7.49 7.49 7.47 7.40 7.38 7.37 7.36 7.36 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 5.24 5.22 4.90 4.89 2.09 2.09 2.08 2.07 2.07 2.06 1.72 1.69 1.62 1.61 1.53 1.50 1.11 1.09 1.06 1.03 0.91 0.89 0.88 0.76 0.74
Ph
N
O
O
O
Ph
35
2.00 2.01 2.04 7.99 0.98 1.00 1.01 0.96 1.98 1.13 1.04 2.03 2.94 2.07 2.04 7.07 3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

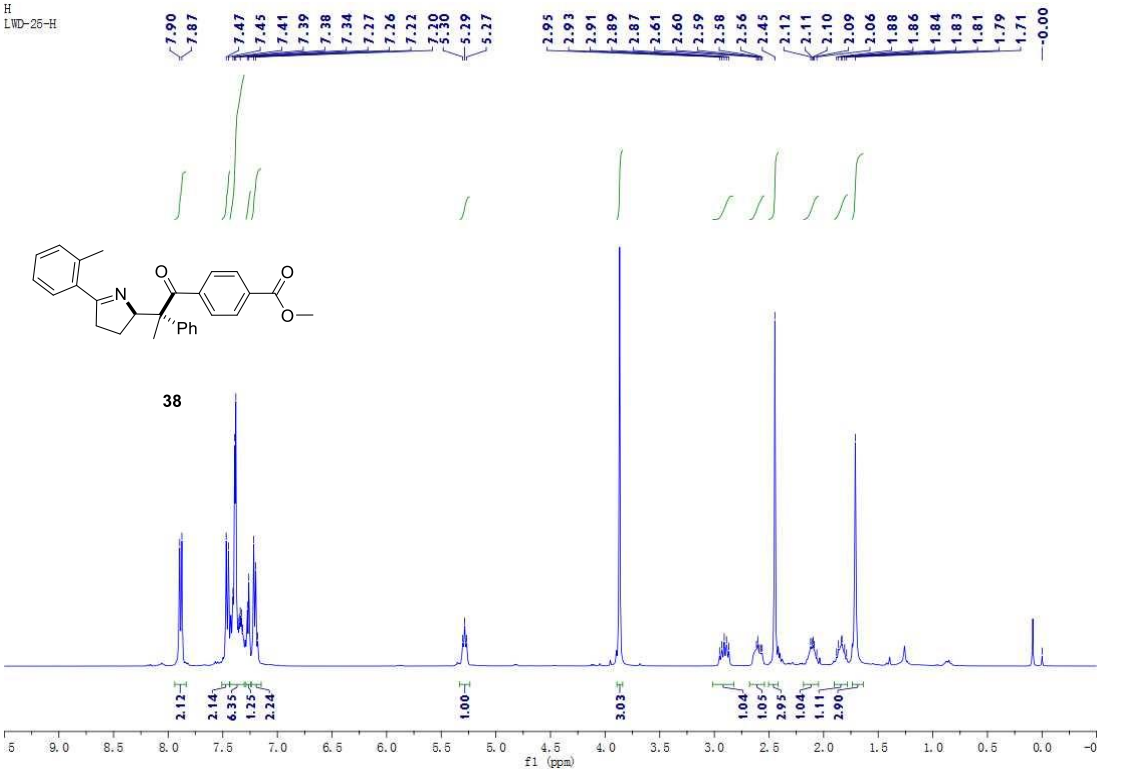

C
LWD-BOHECH5-C
203.16
173.38 173.33 165.31 141.84 141.79 140.36 140.30 134.38 132.58 130.32 128.94 128.67 128.64 128.21 127.71 127.55 127.50 127.21 77.32 77.00 76.68 75.05 59.19 59.15 47.16 40.84 35.03 34.21 31.36 26.35 24.83 23.47 21.96 20.71 19.57 16.36
Ph
N
O
O
O
Ph
35
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
N
O
O
Ph
O
O
Me
O
H
H
H
36
2.04
2.03
2.03
9.14
2.03
1.00
3.21
1.03
1.19
1.22
1.16
6.02
1.41
10.41
1.16
3.31
f1 (ppm)

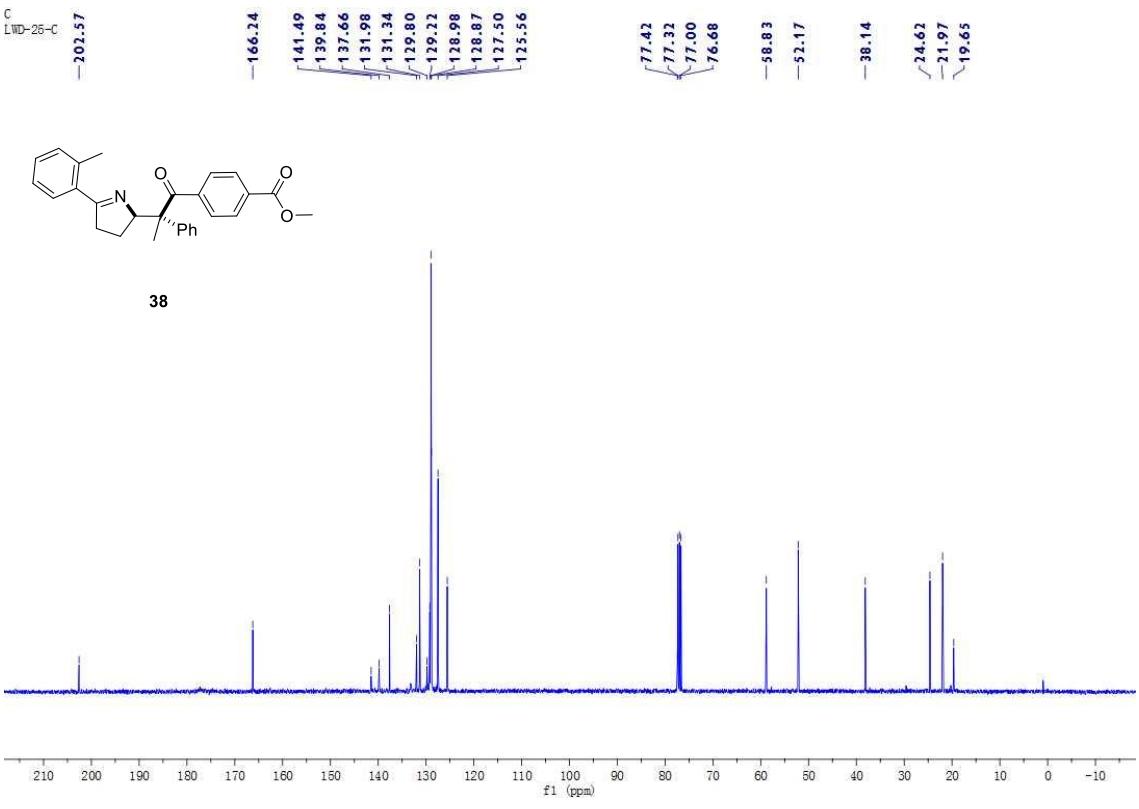

Ph
N
O
O
Ph
O
O
Me
O
H
H
H
36
f1 (ppm)


Ph
N
O
O
Ph
O
Me
Me
Me
Me
H
H
H
H
37
f1 (ppm)

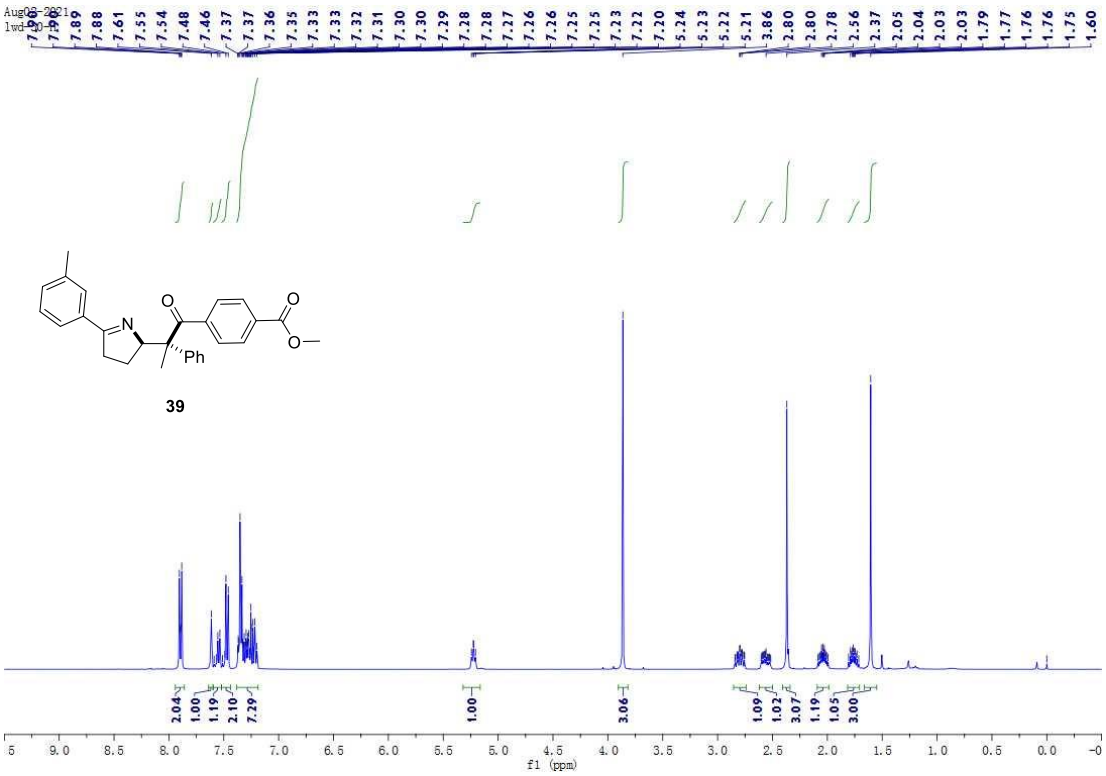

Ph
N
O
O
Ph
O
Me
Me
Me
Me
H
H
H
H
37
f1 (ppm)


H
LWD-26-H
7.90
7.87
7.47
7.45
7.41
7.39
7.38
7.34
7.27
7.26
7.22
7.20
5.30
5.29
5.27
2.95
2.93
2.91
2.89
2.87
2.61
2.60
2.59
2.58
2.56
2.45
2.12
2.11
2.10
2.09
2.06
1.88
1.86
1.84
1.83
1.81
1.79
1.71
-0.00
O
N
O
O
Ph
2.12
2.14
6.35
1.25
2.24
1.00
3.03
1.04
1.05
2.95
1.04
1.11
2.90
f1 (ppm)

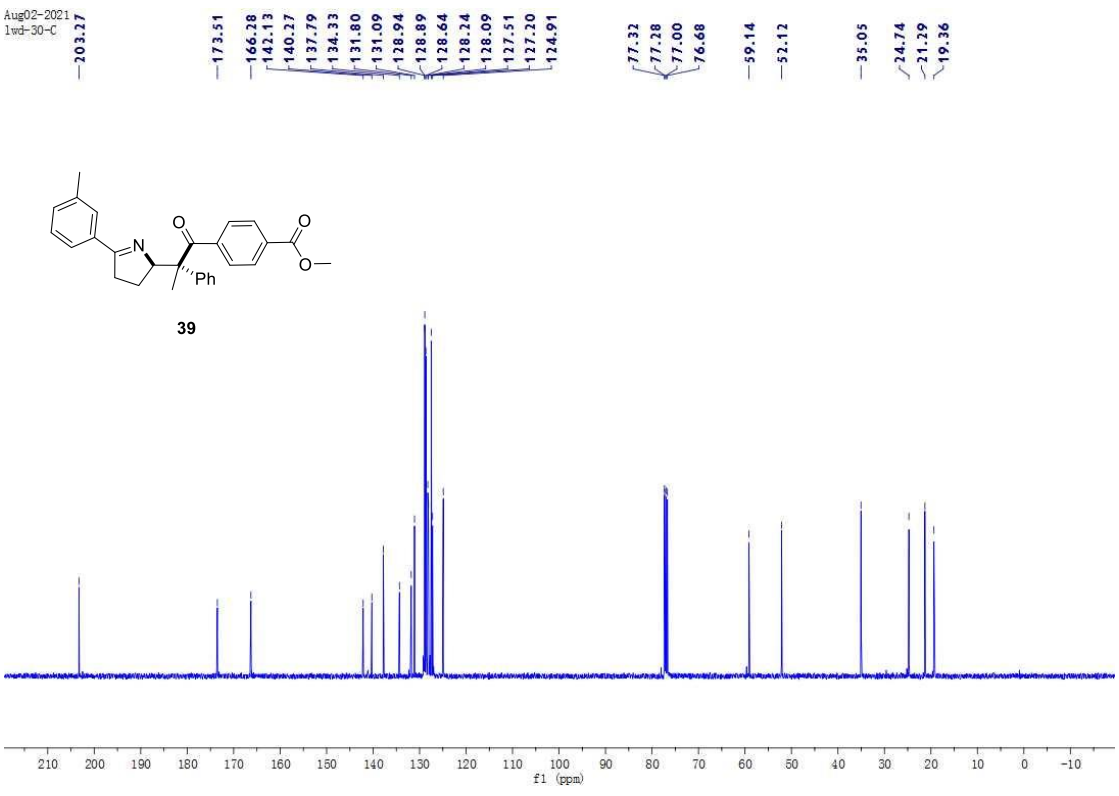
38


C
LWD-26-C
202.57
166.24
141.49
139.84
137.66
131.98
131.34
129.80
129.22
128.98
128.87
127.50
125.56
77.42
77.32
77.00
76.68
58.83
52.17
38.14
24.62
21.97
19.65
O
N
O
O
Ph
f1 (ppm)

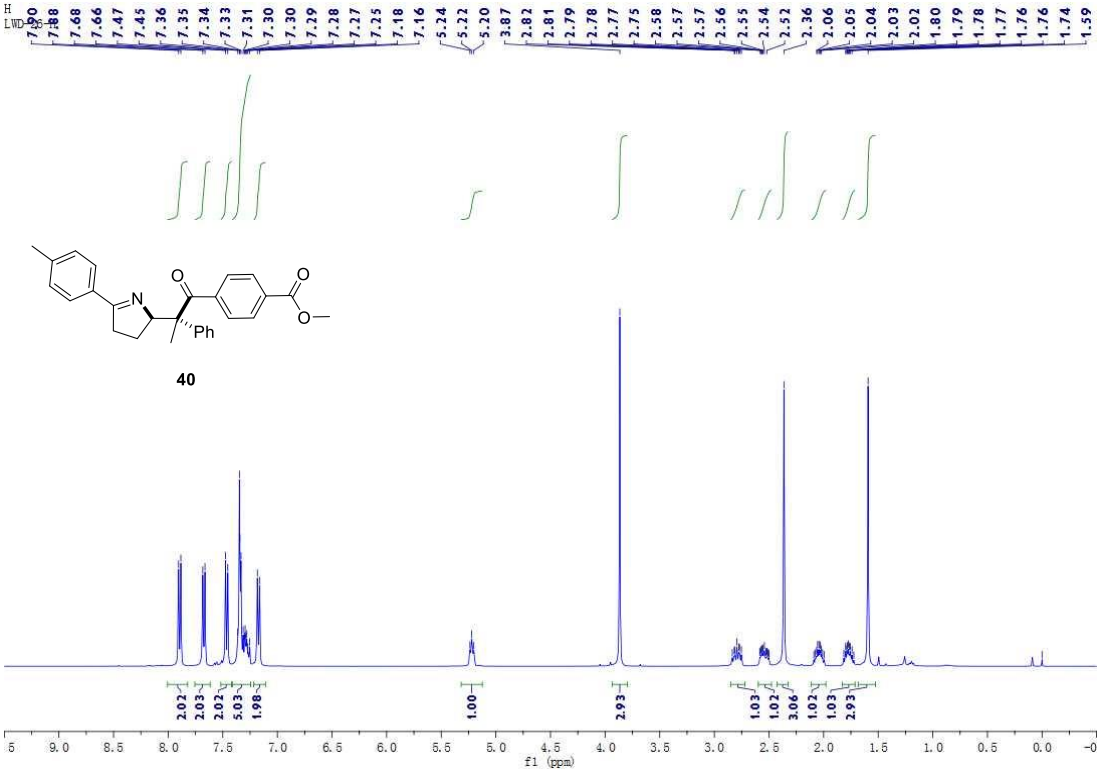
38


Aug02-2021
lwd-30-H
7.90
7.89
7.88
7.61
7.55
7.54
7.48
7.46
7.37
7.37
7.36
7.35
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.23
7.22
7.20
5.24
5.23
5.22
5.21
3.86
2.80
2.80
2.78
2.56
2.37
2.05
2.04
2.03
2.03
1.79
1.77
1.76
1.76
1.75
1.60
O
O
O
N
Ph
2.04
1.00
1.19
2.10
7.29
1.00
3.06
1.09
1.02
3.07
1.19
1.05
3.00
f1 (ppm)

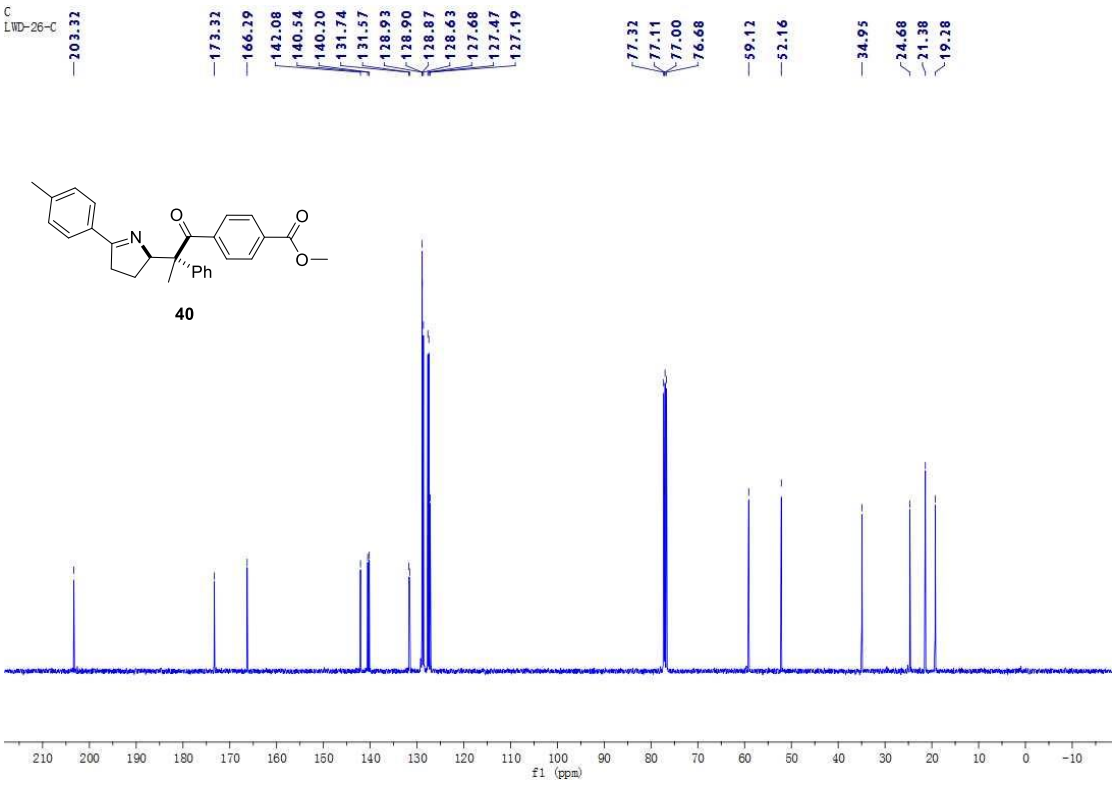
39


Aug02-2021
lwd-30-C
203.27
173.51
166.28
142.13
140.27
137.79
134.33
131.80
131.09
128.94
128.89
128.64
128.24
128.09
127.51
127.20
124.91
77.32
77.28
77.00
76.68
59.14
52.12
35.05
24.74
21.29
19.36
O
O
O
N
Ph
f1 (ppm)

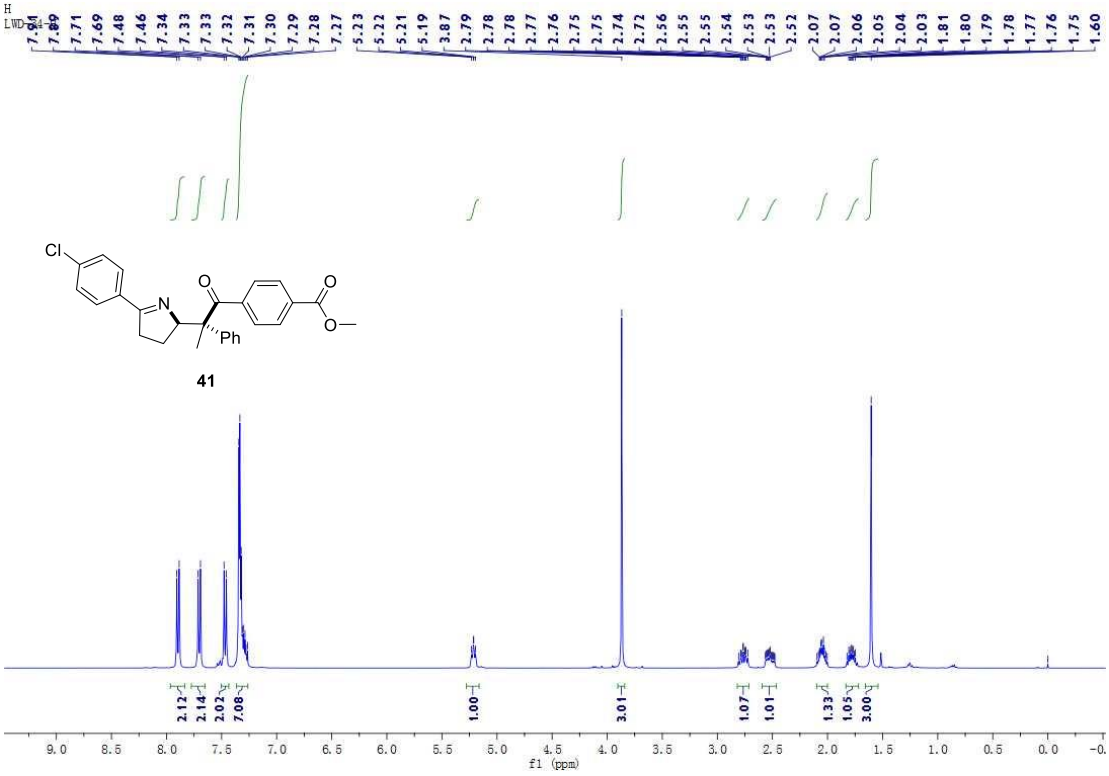
39

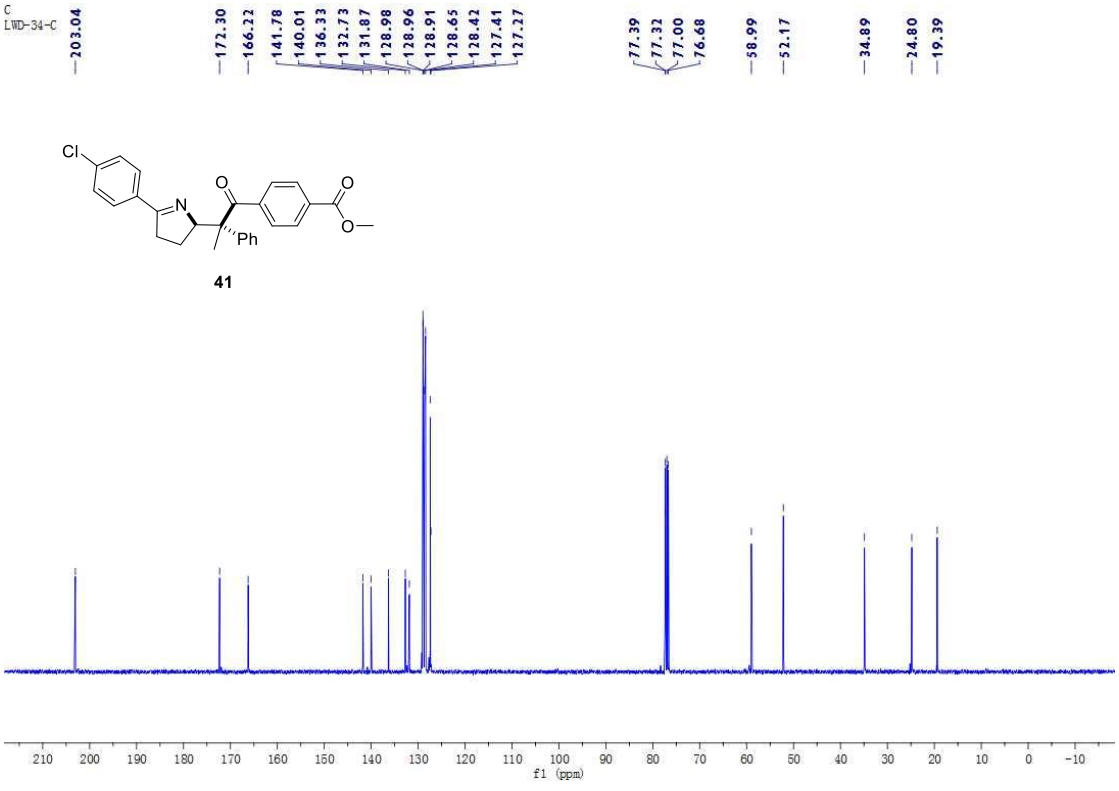

H
LWD-26-H
7.90
7.88
7.68
7.66
7.47
7.45
7.36
7.35
7.34
7.33
7.31
7.30
7.30
7.29
7.28
7.27
7.25
7.18
7.16
5.24
5.22
5.20
3.87
2.82
2.81
2.79
2.78
2.77
2.75
2.58
2.57
2.57
2.56
2.55
2.54
2.52
2.36
2.06
2.05
2.04
2.03
2.02
1.80
1.79
1.78
1.77
1.76
1.76
1.74
1.59
O
N
O
O
Ph
2.02
2.03
2.02
5.03
1.98
1.00
2.93
1.03
1.02
3.06
1.02
1.03
2.93
f1 (ppm)

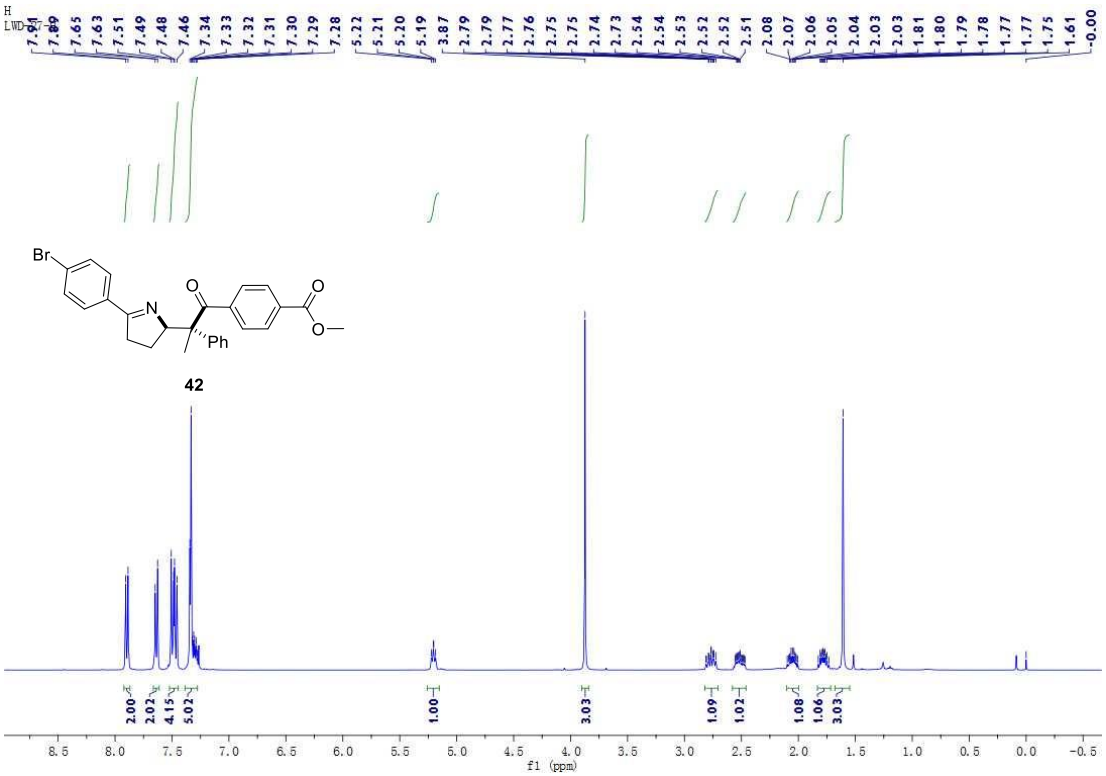
40

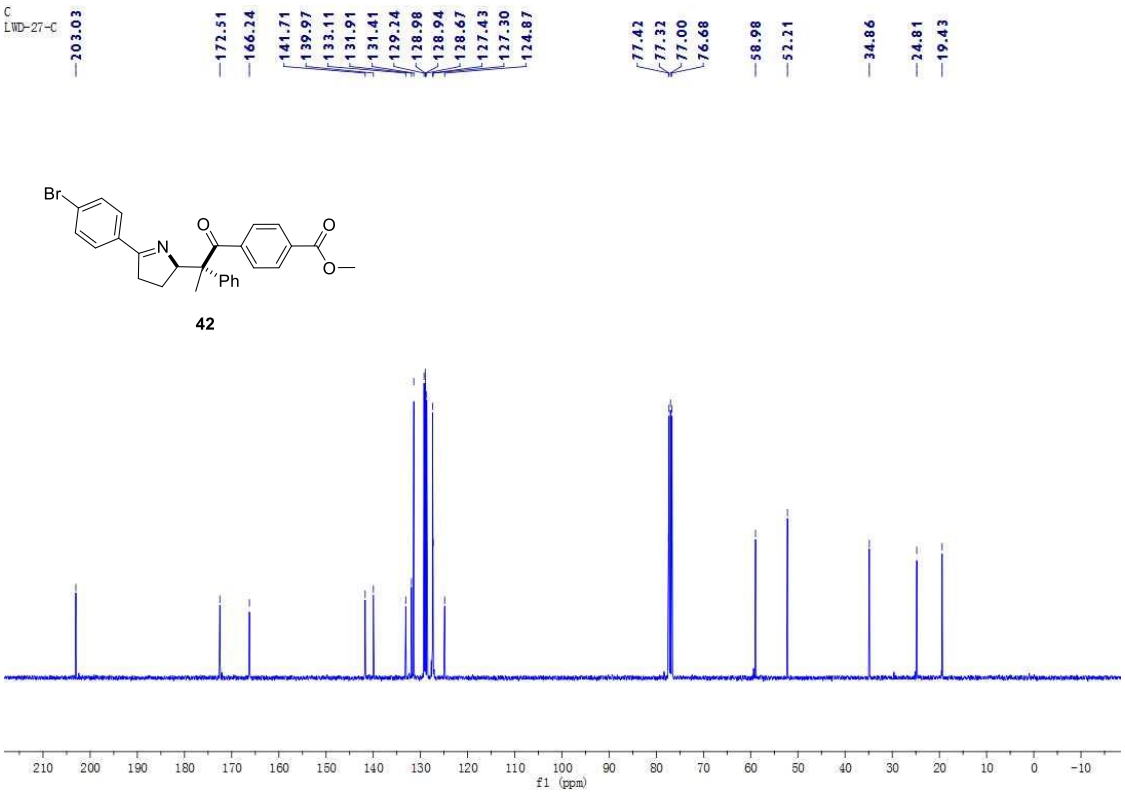

C
LWD-26-C
203.32
173.32
166.29
142.08
140.54
140.20
131.74
131.57
128.93
128.90
128.87
128.63
127.68
127.47
127.19
77.32
77.11
77.00
76.68
59.12
52.16
34.95
24.68
21.38
19.28
O
N
O
O
Ph
f1 (ppm)

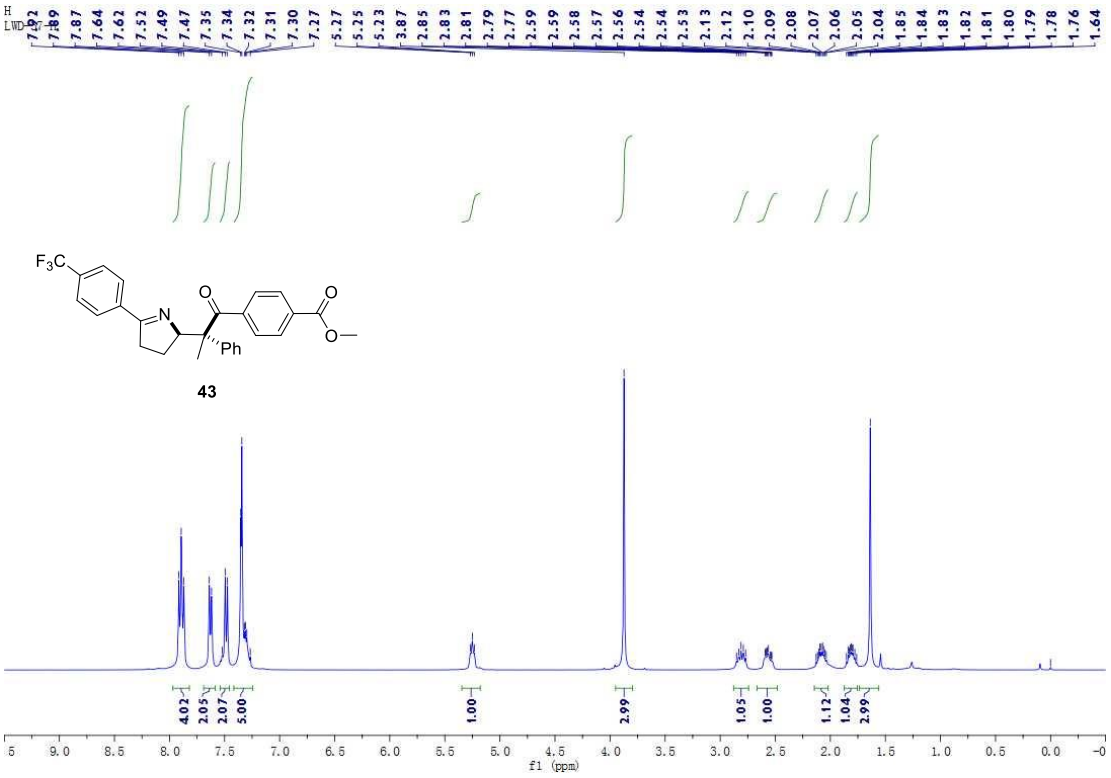
40

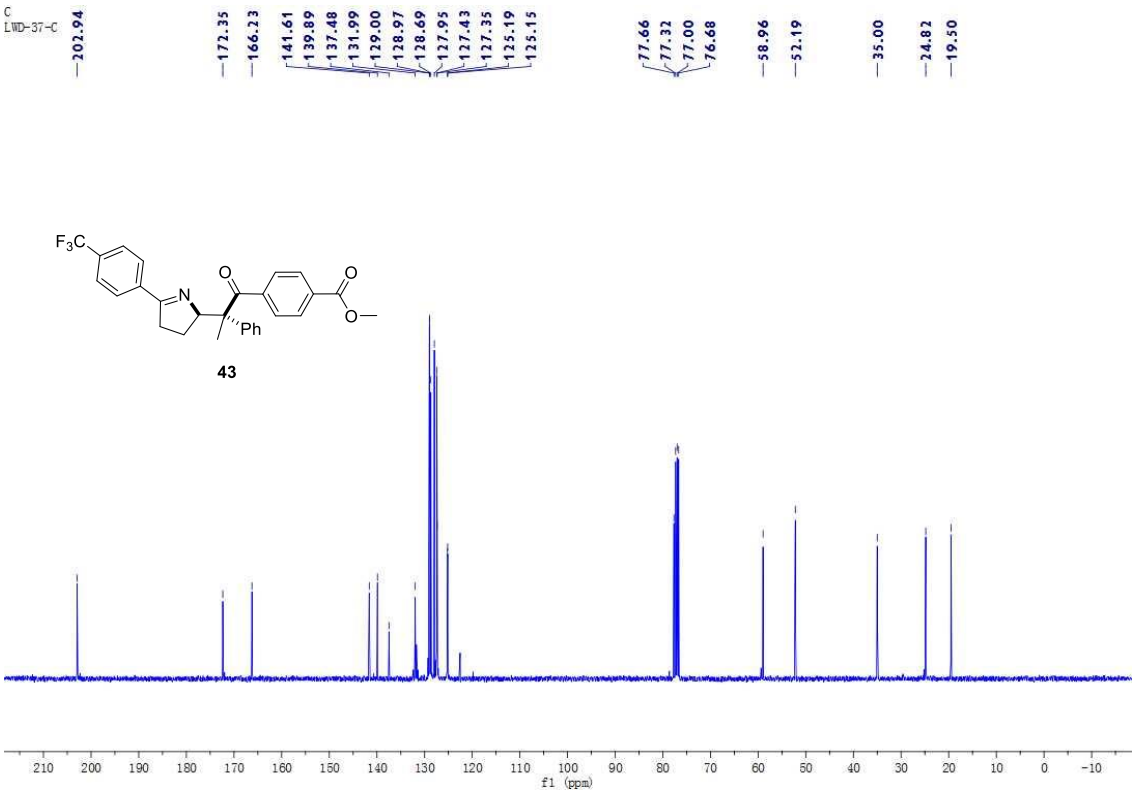

Cl
N
O
O
O
Ph
41
f1 (ppm)

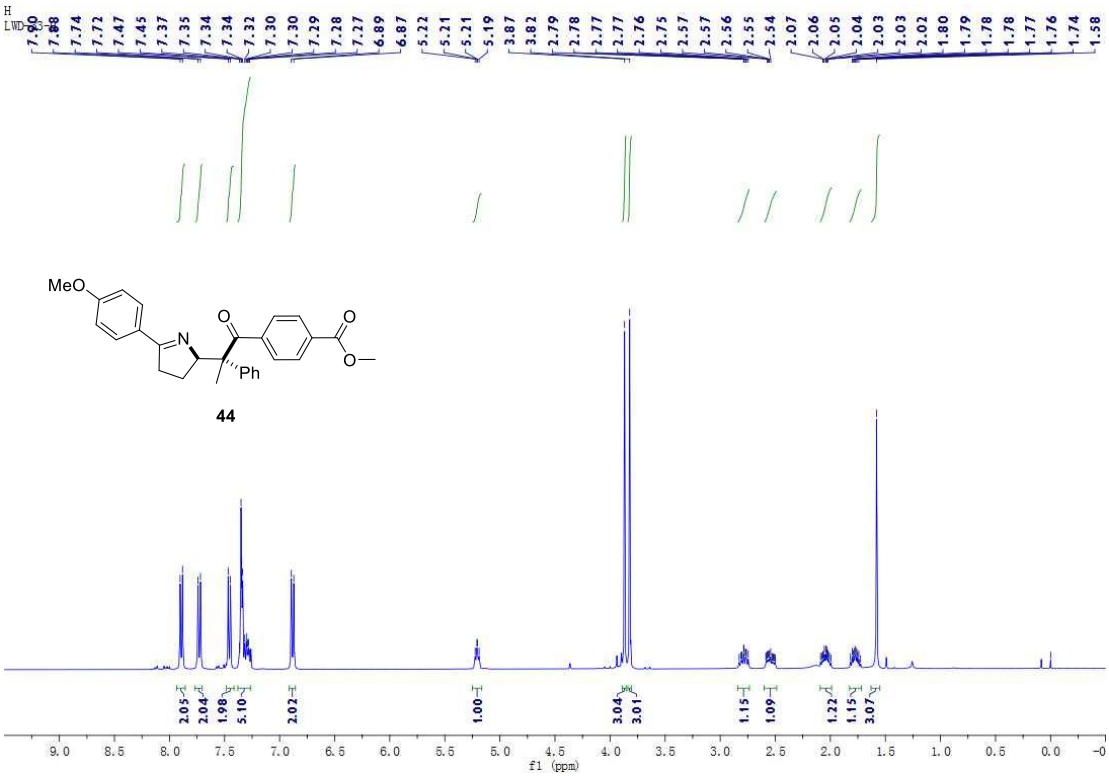

Cl
N
O
O
O
Ph
41
f1 (ppm)

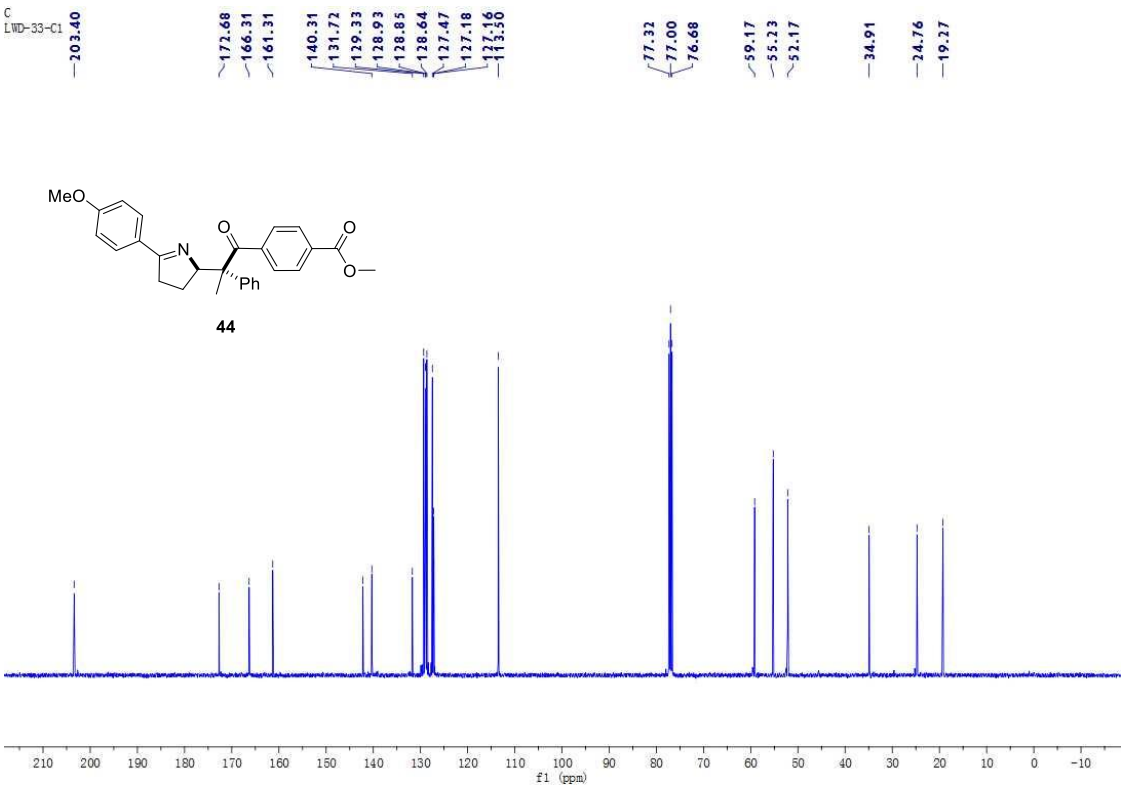

Br
O
N
O
O
Ph
42
f1 (ppm)

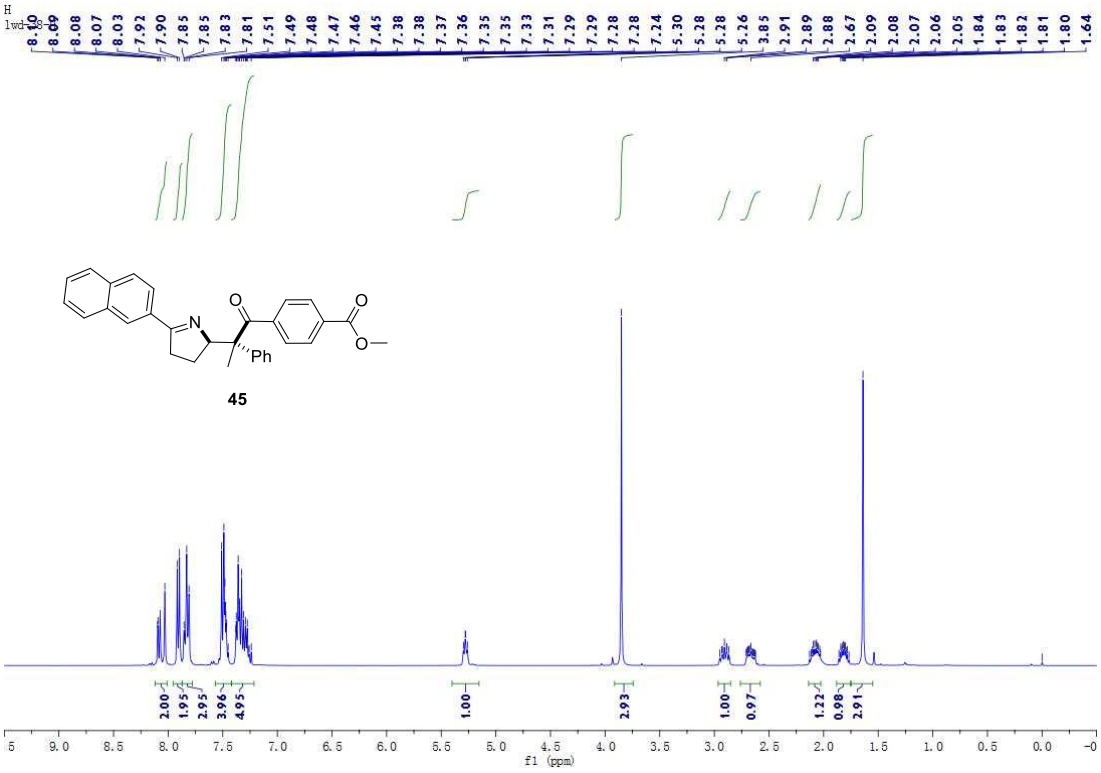

Br
O
N
O
O
Ph
42
f1 (ppm)

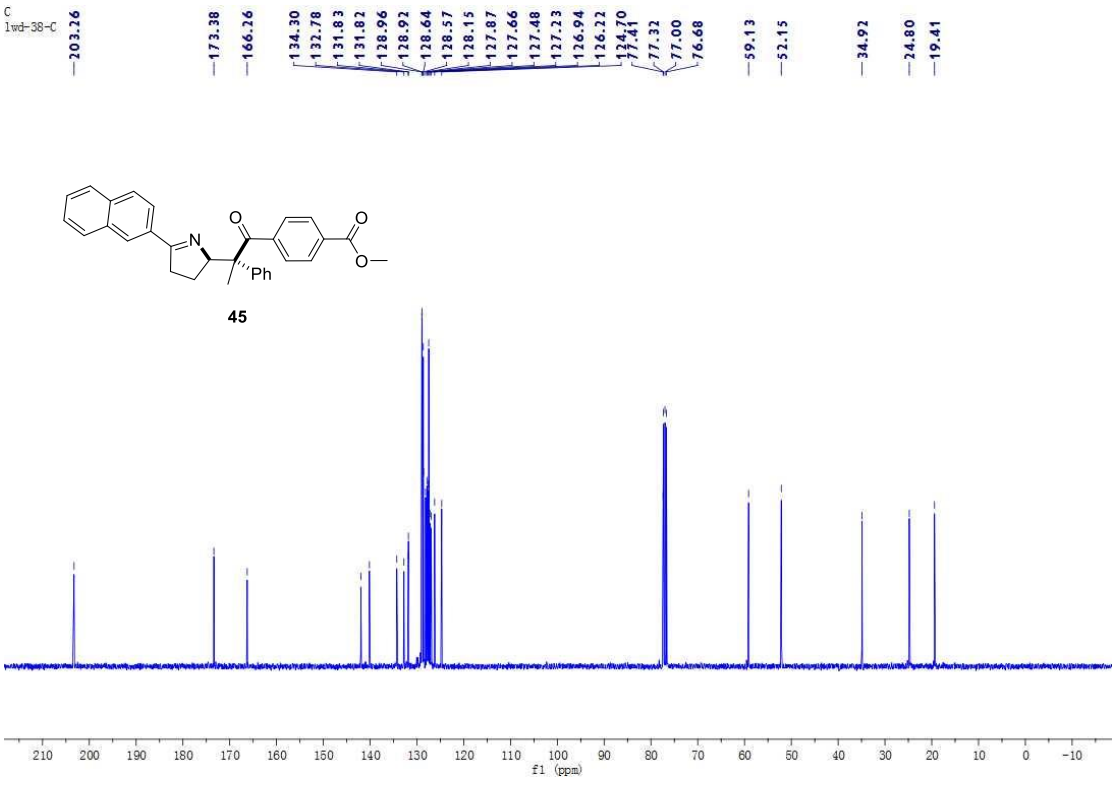

F3C
O
N
Ph
O
O
O—
43
4.02
2.05
2.07
5.00
1.00
2.99
1.05
1.00
1.12
1.04
2.99
f1 (ppm)

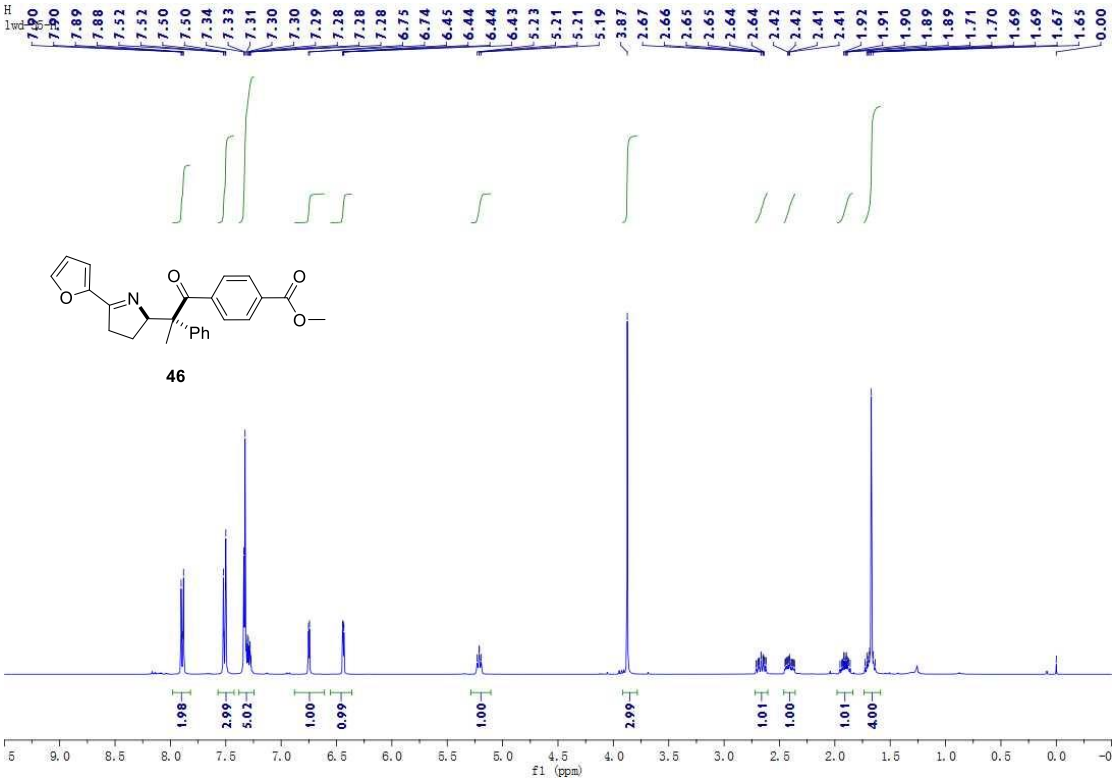

202.94
172.35
166.23
141.61
139.89
137.48
131.99
129.00
128.97
128.69
127.95
127.43
127.35
125.19
125.15
77.66
77.32
77.00
76.68
58.96
52.19
35.00
24.82
19.50
F3C
O
N
Ph
O
O
O—
43
f1 (ppm)

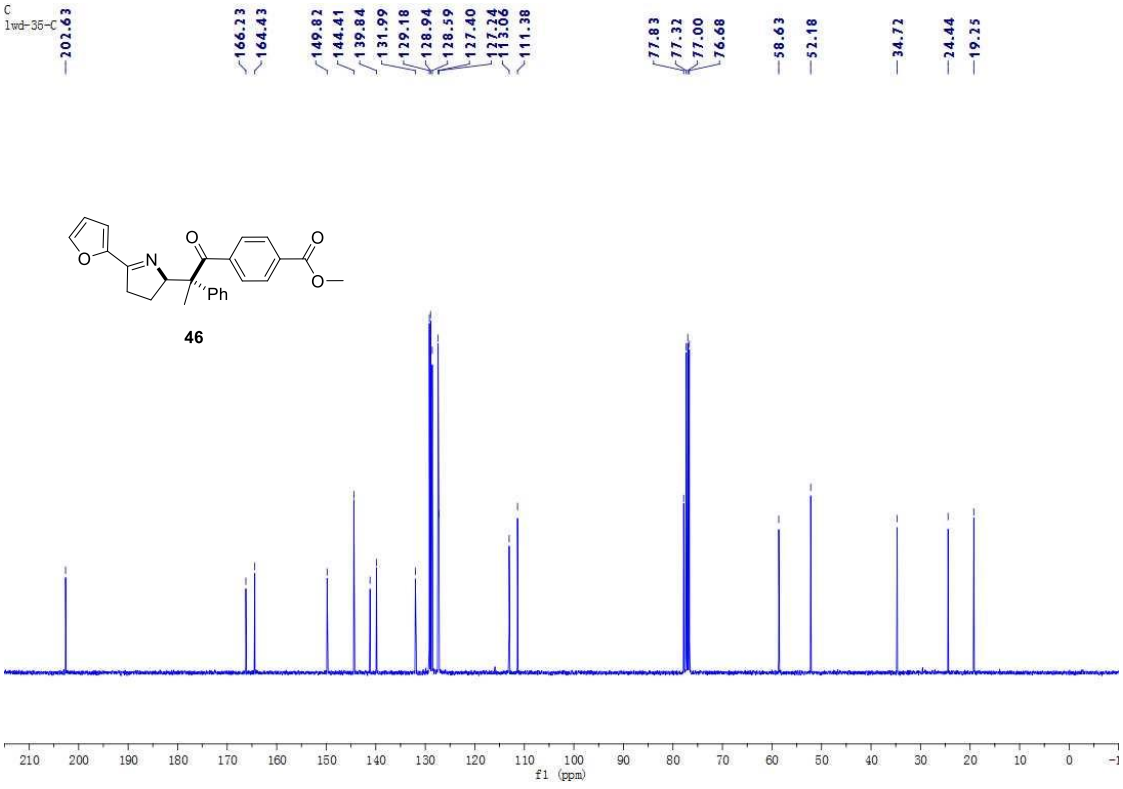

MeO
O
N
O
O
Ph
44
f1 (ppm)

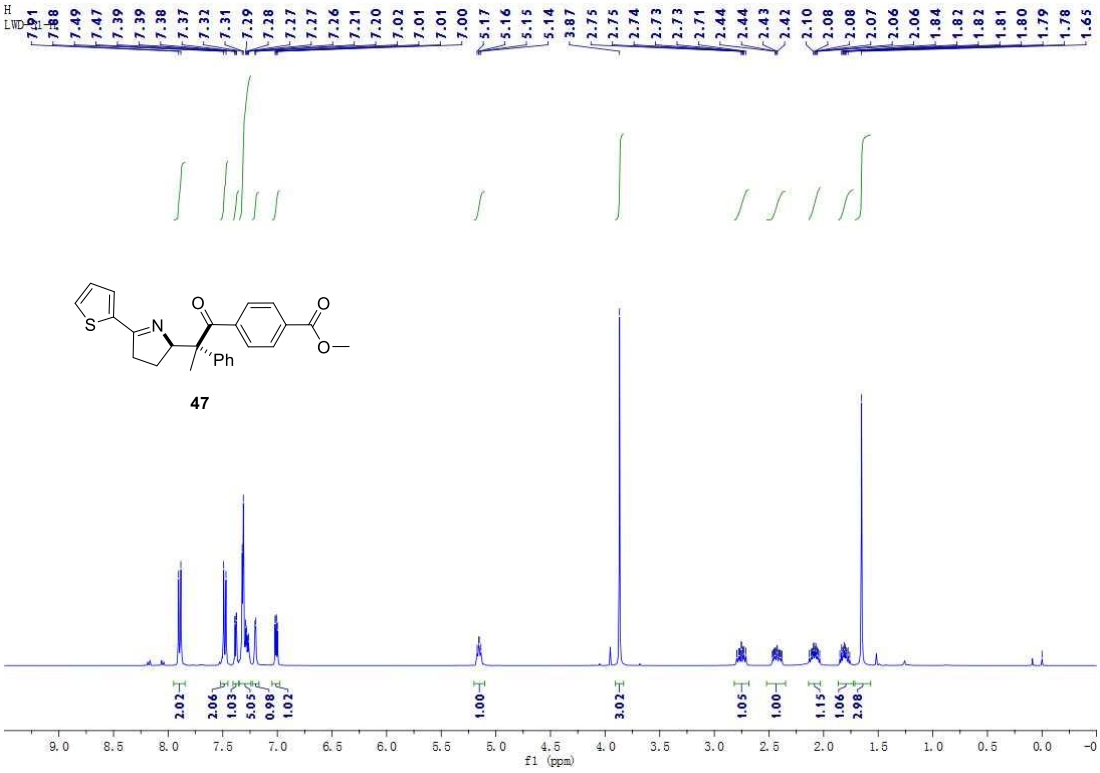

MeO
O
N
O
O
Ph
44
f1 (ppm)

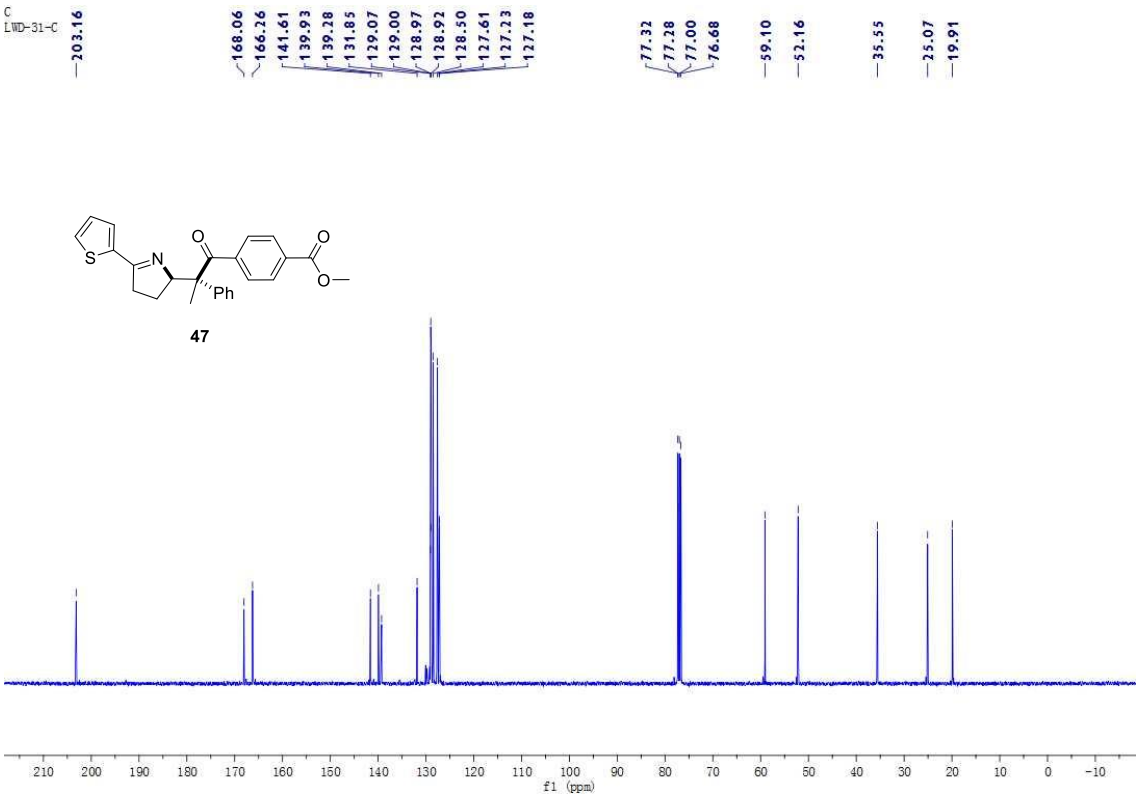

45
f1 (ppm)

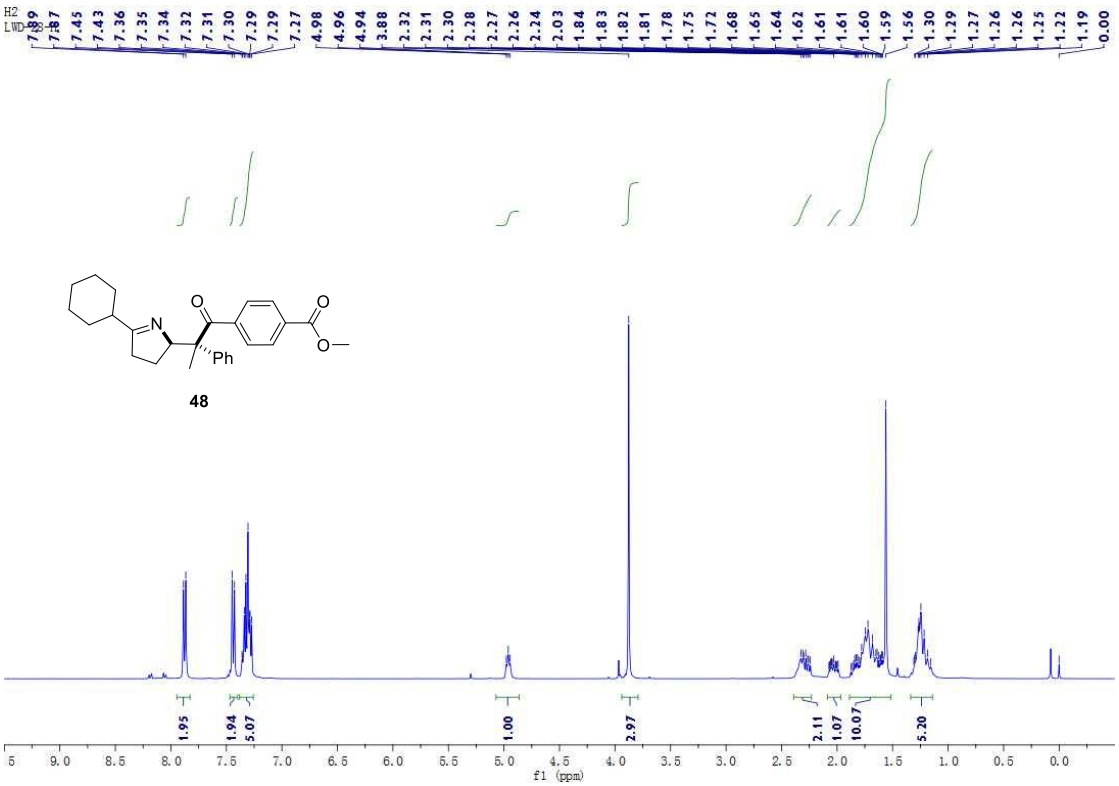

45
f1 (ppm)

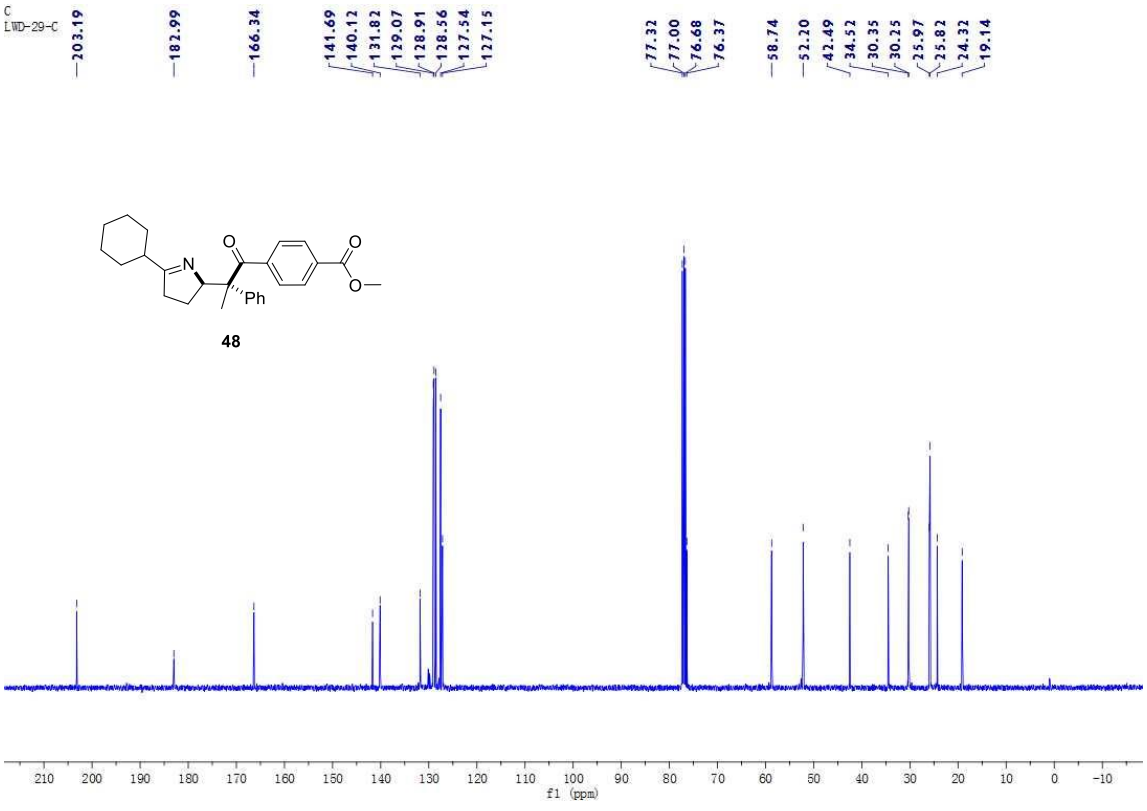

46
f1 (ppm)

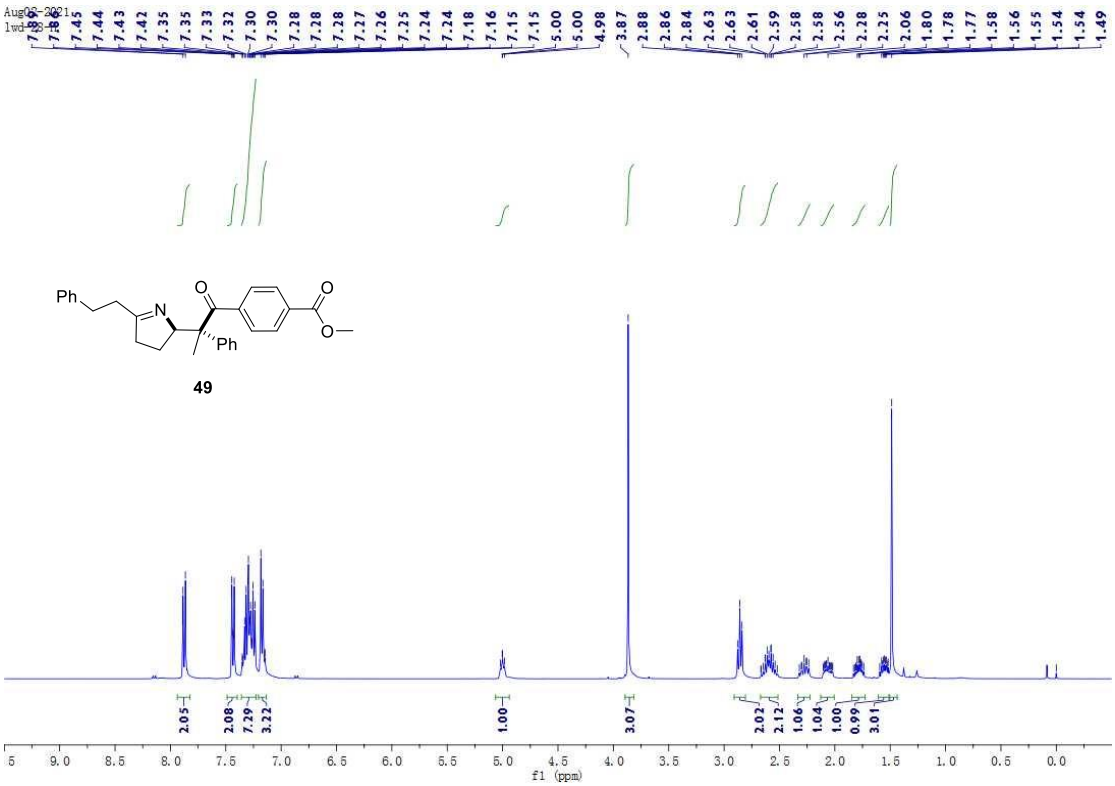

46
f1 (ppm)


H
LWD-31-H
7.91
7.88
7.49
7.47
7.39
7.39
7.38
7.37
7.32
7.31
7.29
7.28
7.27
7.27
7.26
7.21
7.20
7.02
7.01
7.01
7.00
5.17
5.16
5.15
5.14
3.87
2.75
2.75
2.74
2.73
2.73
2.71
2.44
2.44
2.43
2.42
2.10
2.08
2.08
2.07
2.06
2.06
1.84
1.82
1.82
1.81
1.80
1.79
1.78
1.65
O
N
S
O
O
Ph
47
2.02
2.06
1.03
5.05
0.98
1.02
1.00
3.02
1.05
1.00
1.15
1.06
2.98
f1 (ppm)

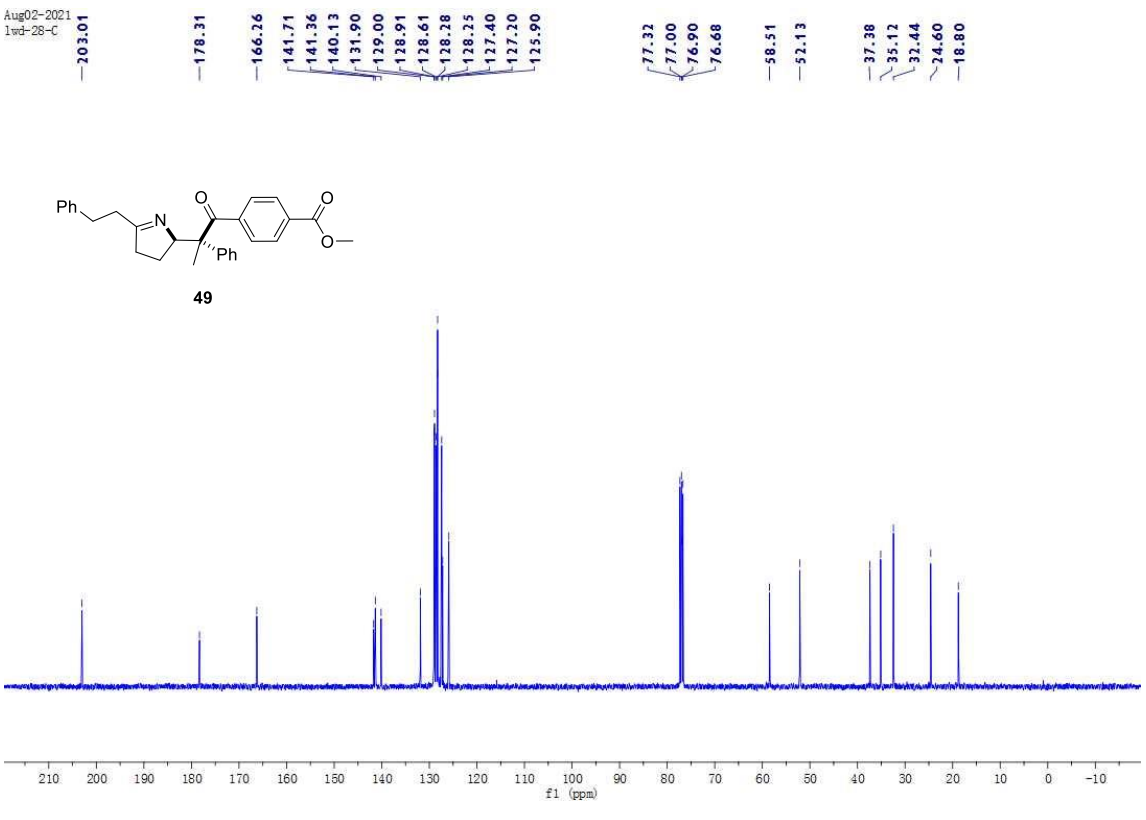

C
LWD-31-C
203.16
168.06
166.26
141.61
139.93
139.28
131.85
129.07
129.00
128.97
128.92
128.50
127.61
127.23
127.18
77.32
77.28
77.00
76.68
59.10
52.16
35.55
25.07
19.91
O
N
S
O
O
Ph
47
f1 (ppm)


H2
LWD-29-H
7.89
7.87
7.45
7.43
7.36
7.35
7.34
7.32
7.31
7.30
7.29
7.29
7.27
4.98
4.96
4.94
3.88
2.32
2.31
2.30
2.28
2.27
2.26
2.24
2.03
1.84
1.83
1.82
1.81
1.78
1.75
1.72
1.68
1.65
1.64
1.62
1.61
1.61
1.60
1.59
1.56
1.30
1.29
1.27
1.26
1.26
1.25
1.22
1.19
0.00
O
N
O
O
Ph
48
1.95
1.94
5.07
1.00
2.97
2.11
1.07
10.07
5.20
f1 (ppm)

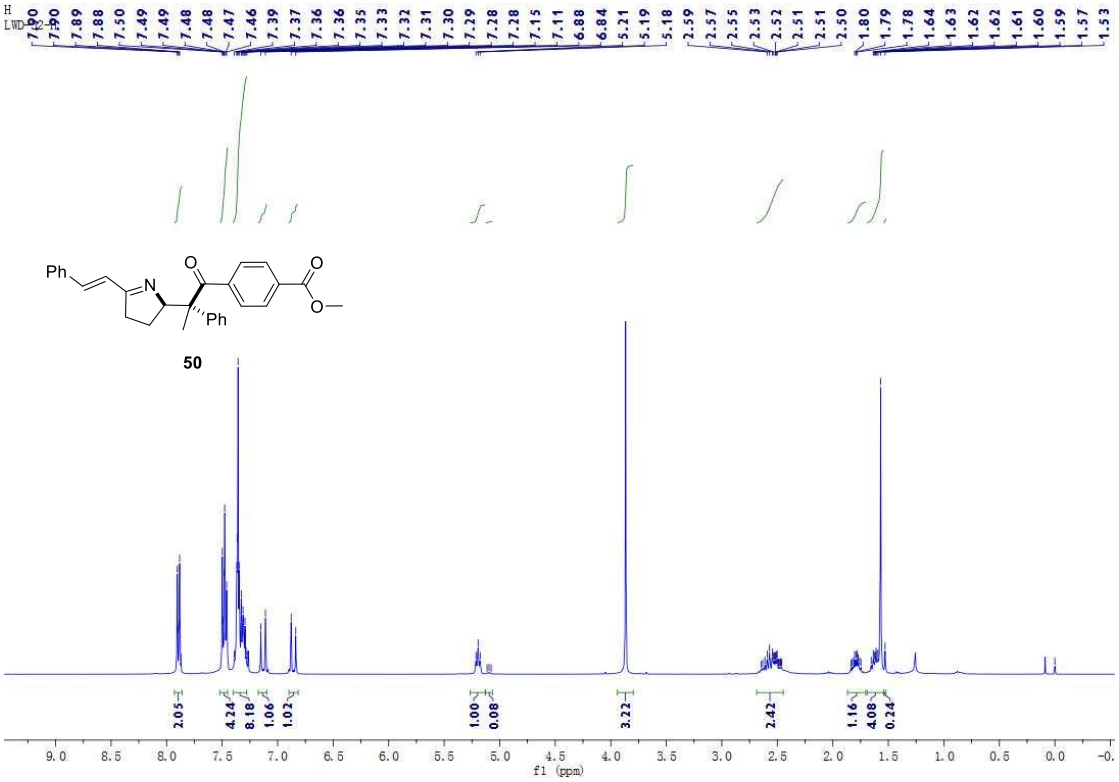

C
LWD-29-C
203.19
182.99
166.34
141.69
140.12
131.82
129.07
128.91
128.56
127.54
127.15
77.32
77.00
76.68
76.37
58.74
52.20
42.49
34.52
30.35
30.25
25.97
25.82
24.32
19.14
O
N
O
O
Ph
48
f1 (ppm)


Aug02-2021
lwd-28-H
7.45 7.44 7.43 7.42 7.35 7.33 7.32 7.30 7.30 7.28 7.28 7.28 7.27 7.26 7.25 7.24 7.24 7.18 7.16 7.15 7.15 5.00 4.98 3.87 2.88 2.86 2.84 2.63 2.63 2.61 2.59 2.58 2.58 2.56 2.28 2.25 2.06 1.80 1.78 1.77 1.58 1.56 1.55 1.54 1.54 1.49
Ph
N
O
O
O
Ph
2.05 2.08 7.29 3.22 1.00 3.07 2.02 2.12 1.06 1.04 1.00 0.99 3.01
f1 (ppm)

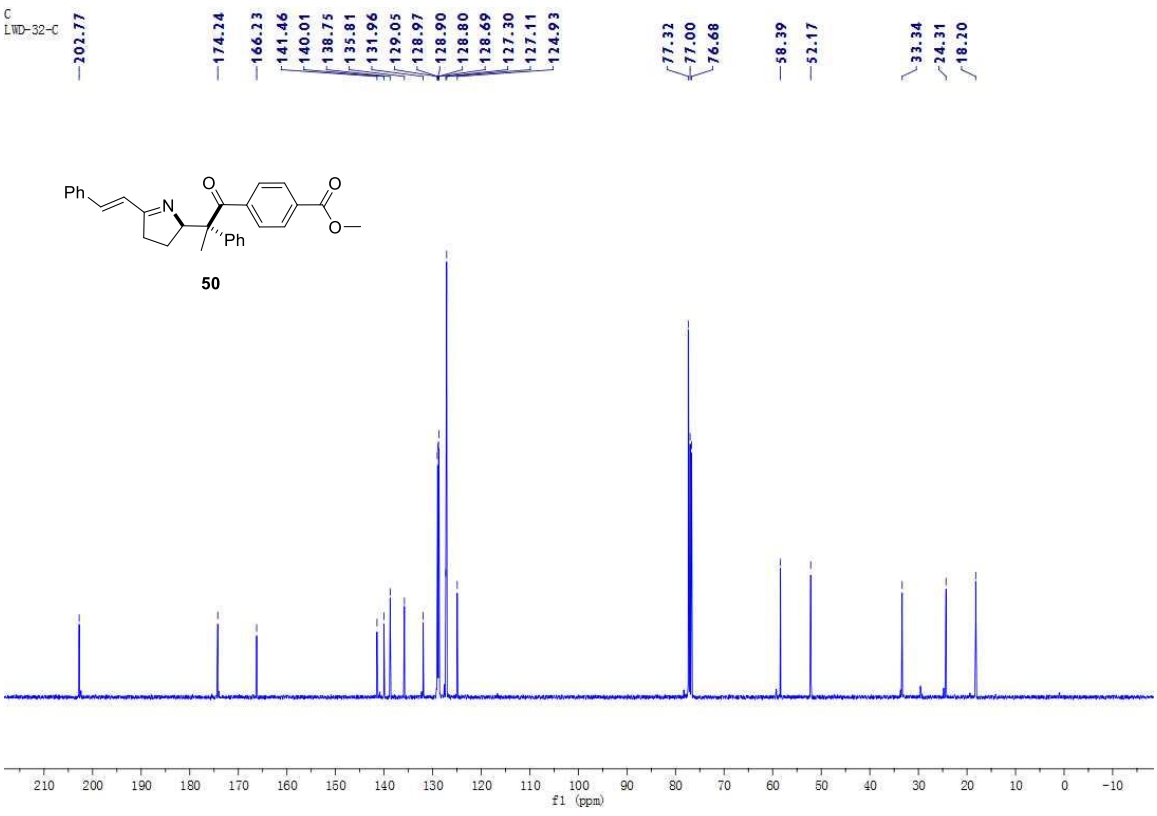
49


Aug02-2021
lwd-28-C
203.01 178.31 166.26 141.71 141.36 140.13 131.90 129.00 128.91 128.61 128.28 128.25 127.40 127.20 125.90 77.32 77.00 76.90 76.68 58.51 52.13 37.38 35.12 32.44 24.60 18.80
Ph
N
O
O
O
Ph
f1 (ppm)

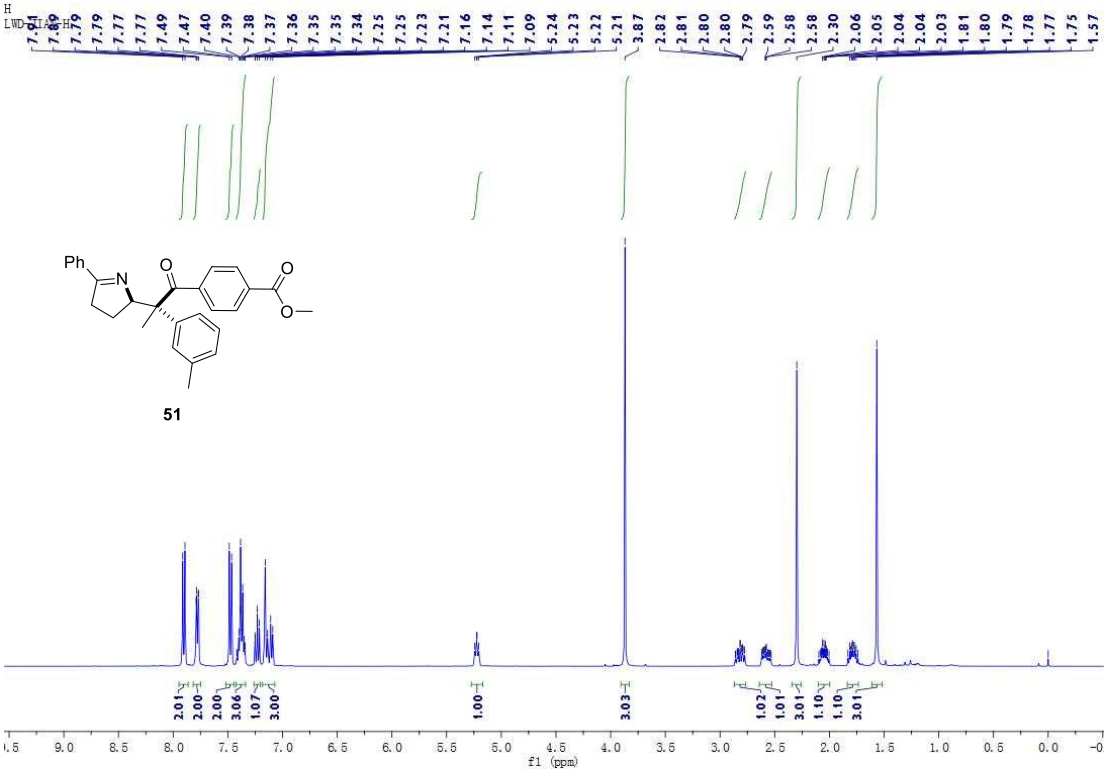
49

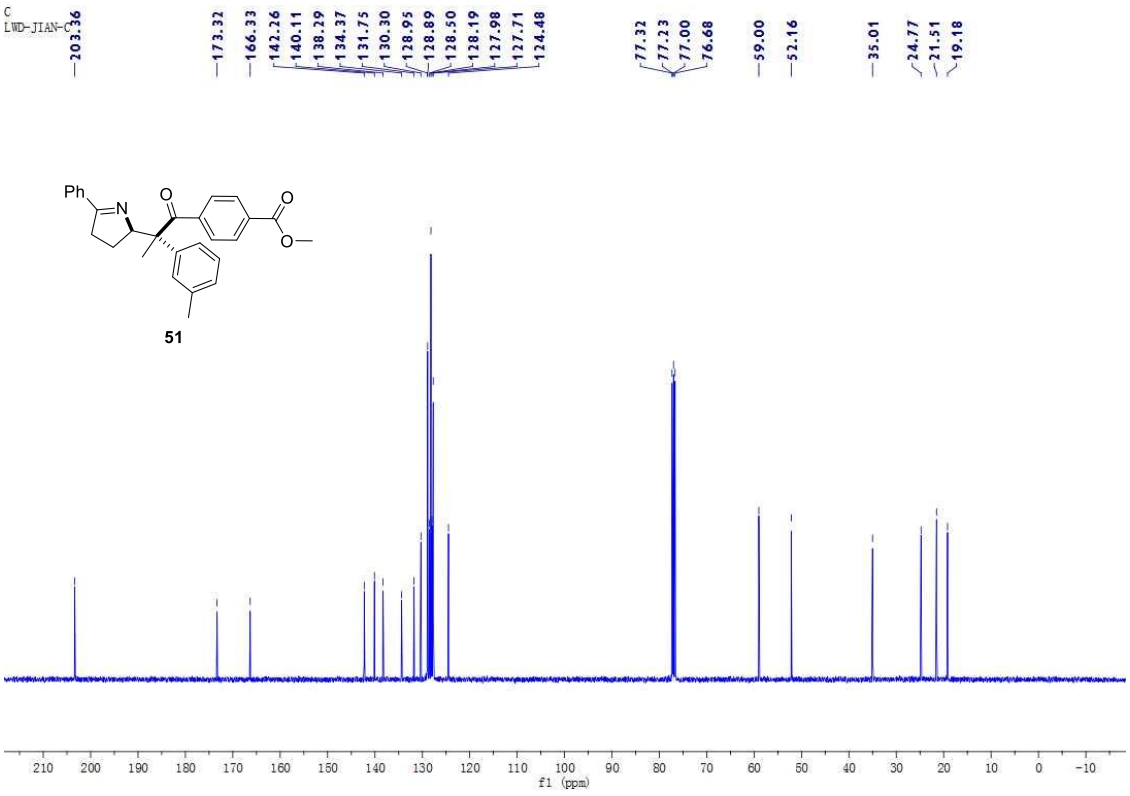

H
LWD-32-H
7.90
7.90
7.89
7.88
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.39
7.37
7.36
7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.15
7.11
6.88
6.84
5.21
5.19
5.18
2.59
2.57
2.55
2.53
2.52
2.51
2.51
2.50
1.80
1.79
1.78
1.64
1.63
1.62
1.62
1.61
1.60
1.59
1.57
1.53
Ph
N
O
O
O
Ph
2.05
4.24
8.18
1.06
1.02
1.00
0.08
3.22
2.42
1.16
4.08
0.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

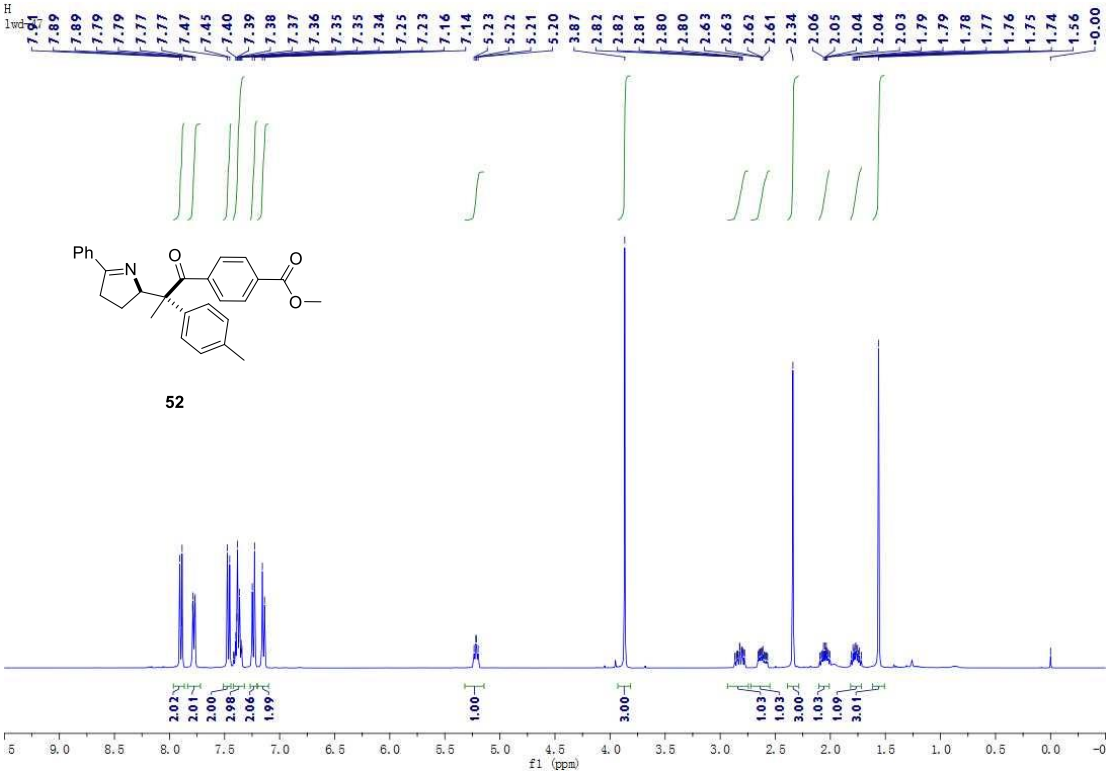
50


C
LWD-32-C
202.77
174.24
166.23
141.46
140.01
138.75
135.81
131.96
129.05
128.97
128.90
128.80
128.69
127.30
127.11
124.93
77.32
77.00
76.68
58.39
52.17
33.34
24.31
18.20
Ph
N
O
O
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

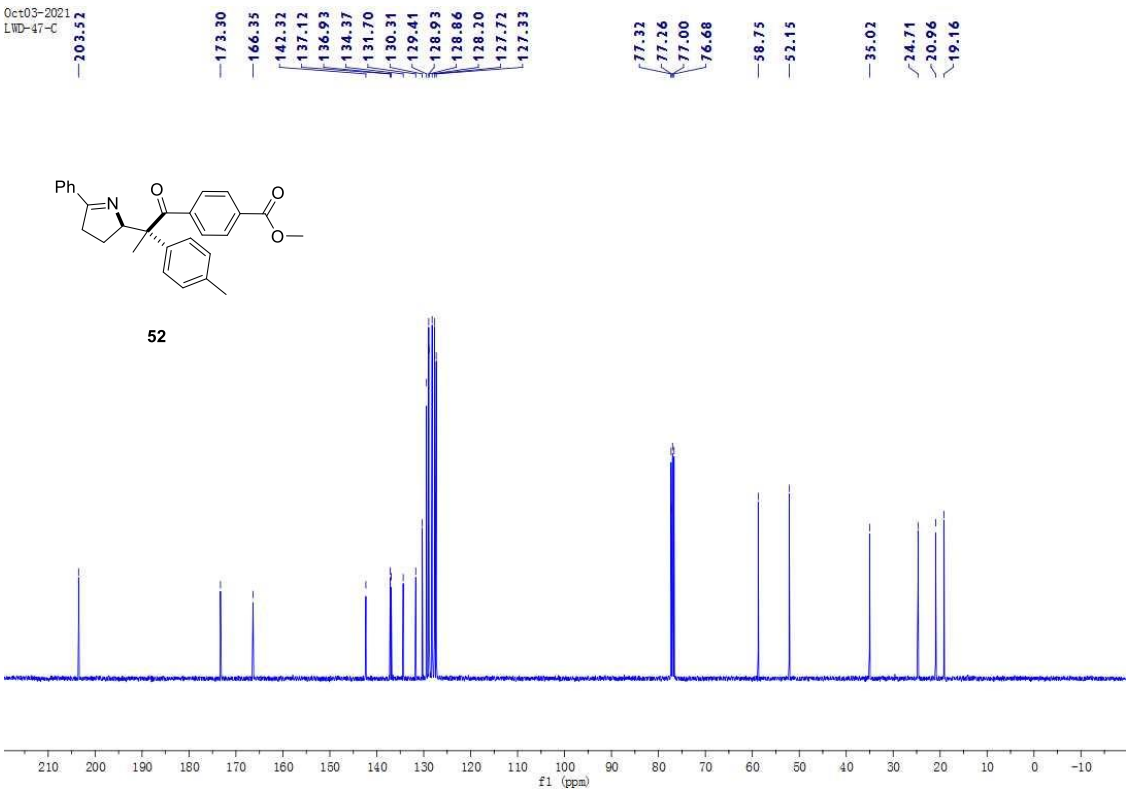
50


Ph
N
O
O
O
51
f1 (ppm)

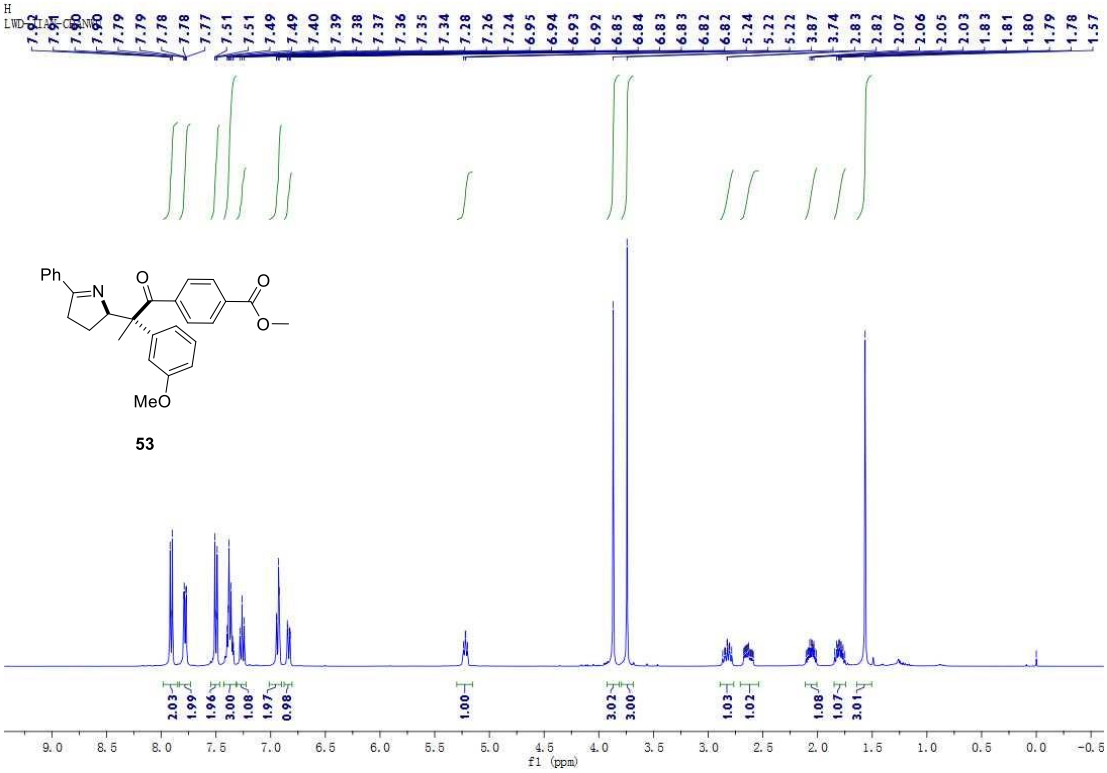

Ph
N
O
O
O
51
f1 (ppm)

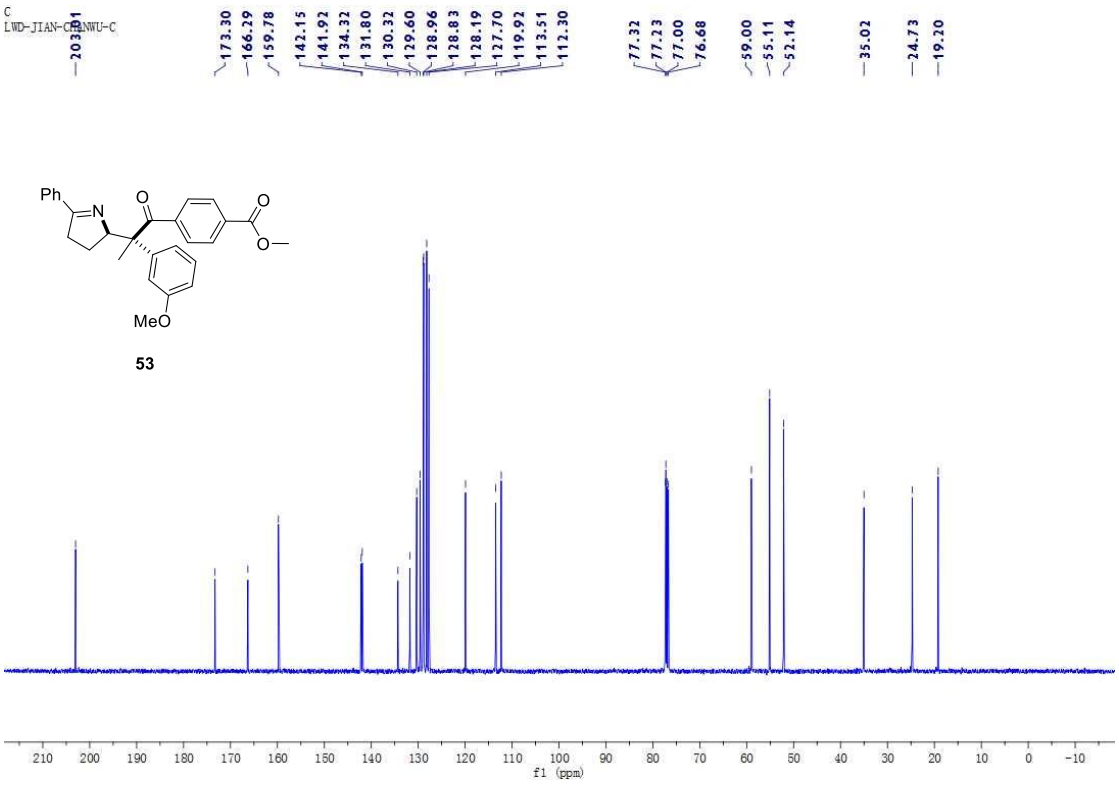

1H
lwd-c-1
7.91
7.89
7.89
7.79
7.79
7.77
7.77
7.47
7.45
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.25
7.23
7.16
7.14
5.23
5.22
5.21
5.20
3.87
2.82
2.82
2.81
2.80
2.80
2.63
2.63
2.62
2.61
2.34
2.06
2.05
2.04
2.04
2.03
1.79
1.79
1.78
1.77
1.76
1.75
1.74
1.56
0.00
Ph
N
O
O
O
2.02
2.01
2.00
2.98
2.06
1.99
1.00
3.00
1.03
1.03
3.00
1.03
1.09
3.01
f1 (ppm)

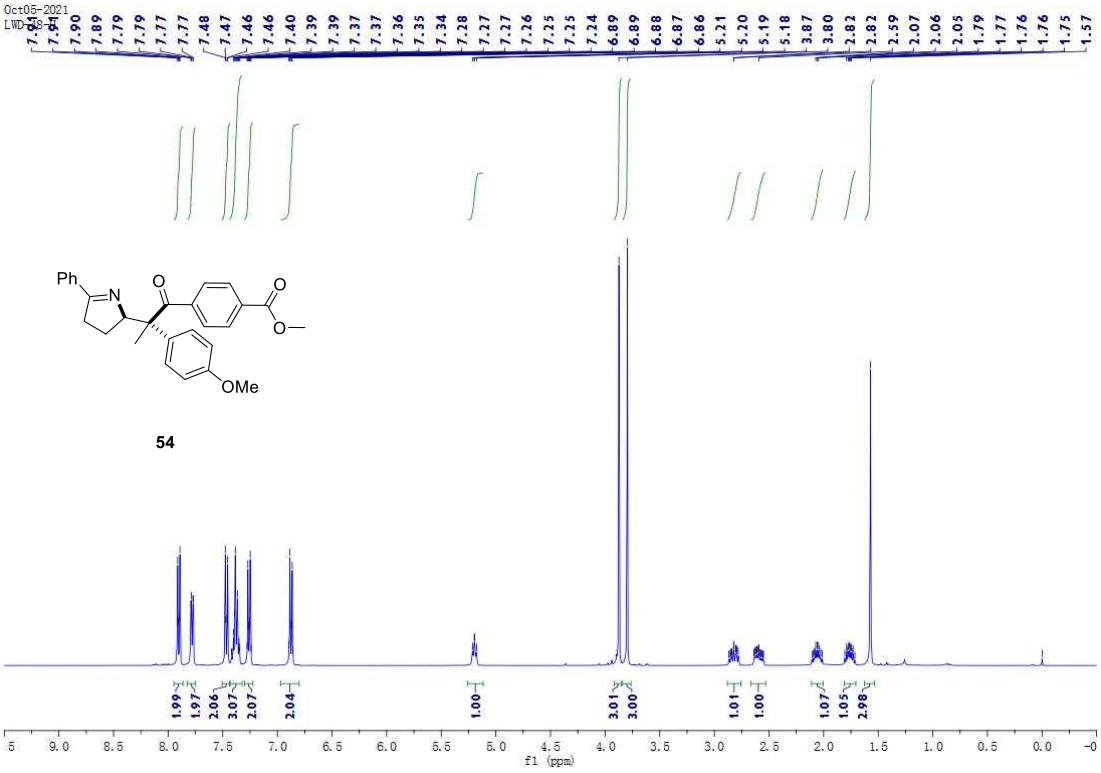
52


Oct03-2021
LWD-47-C
203.52
173.30
166.35
142.32
137.12
136.93
134.37
131.70
130.31
129.41
128.93
128.86
128.20
127.72
127.33
77.32
77.26
77.00
76.68
58.75
52.15
35.02
24.71
20.96
19.16
Ph
N
O
O
O
f1 (ppm)

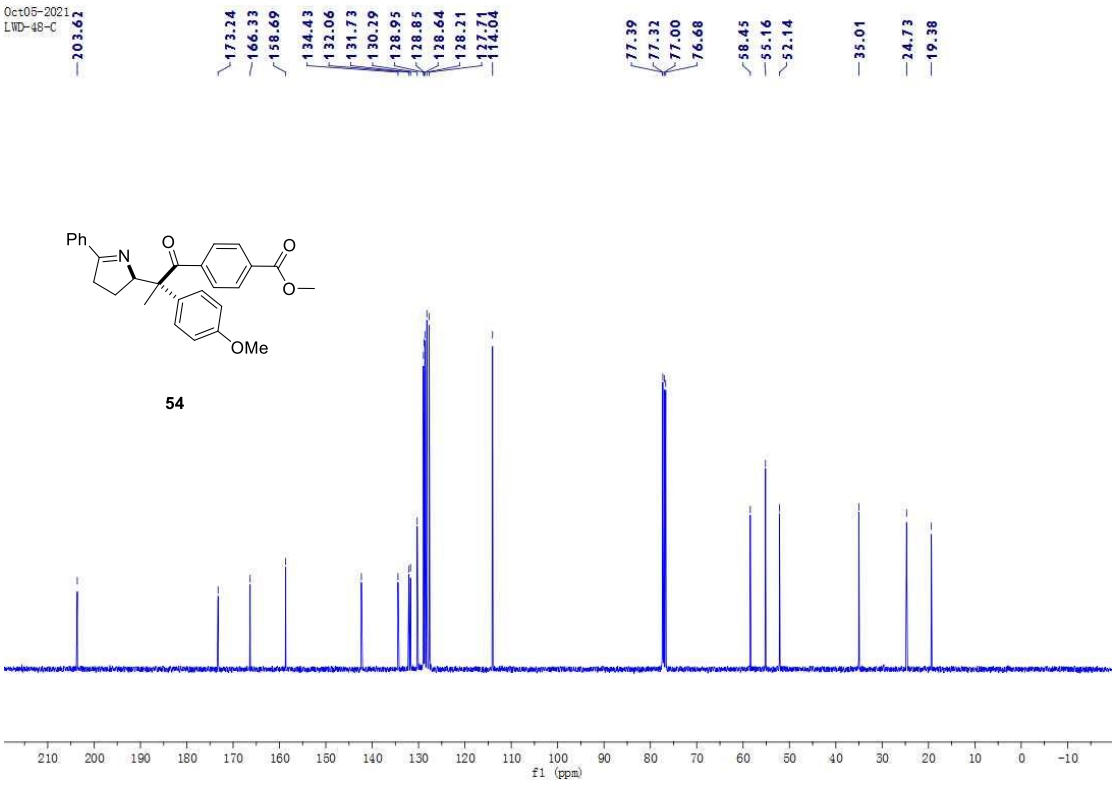
52


Ph
N
O
O
O
MeO
53
f1 (ppm)

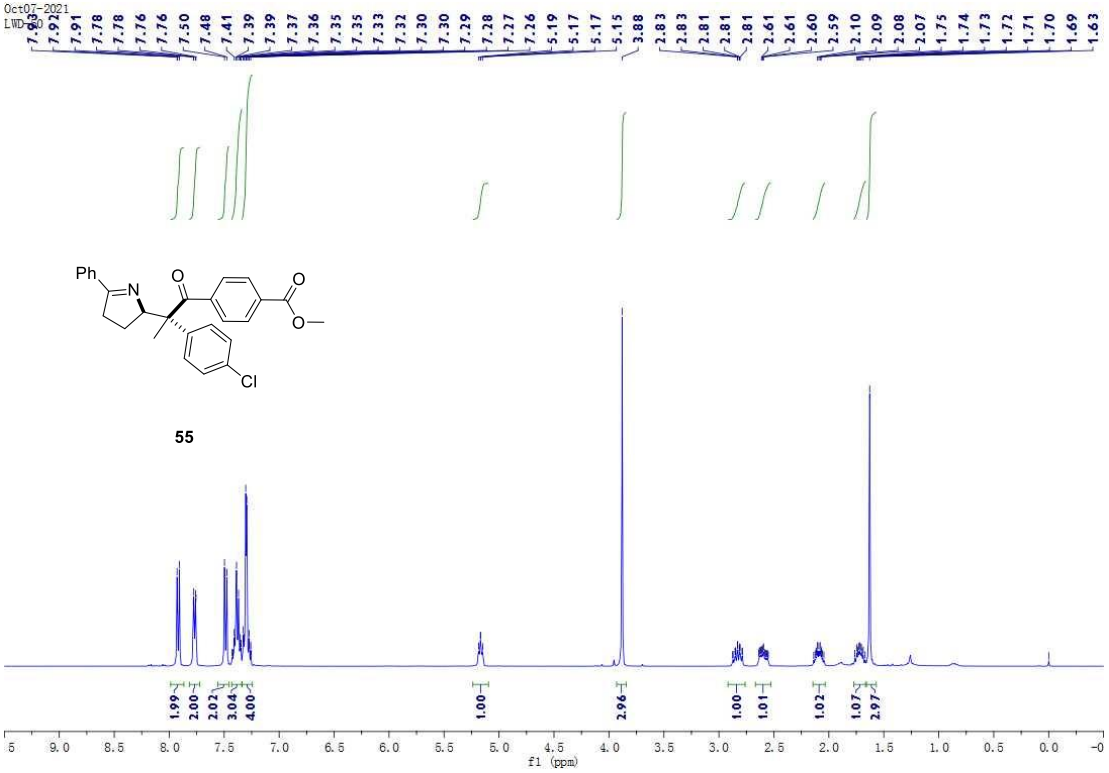

Ph
N
O
O
O
MeO
53
f1 (ppm)


Oct05-2021
LWD-48-H
Ph
N
O
O
O
OMe
f1 (ppm)

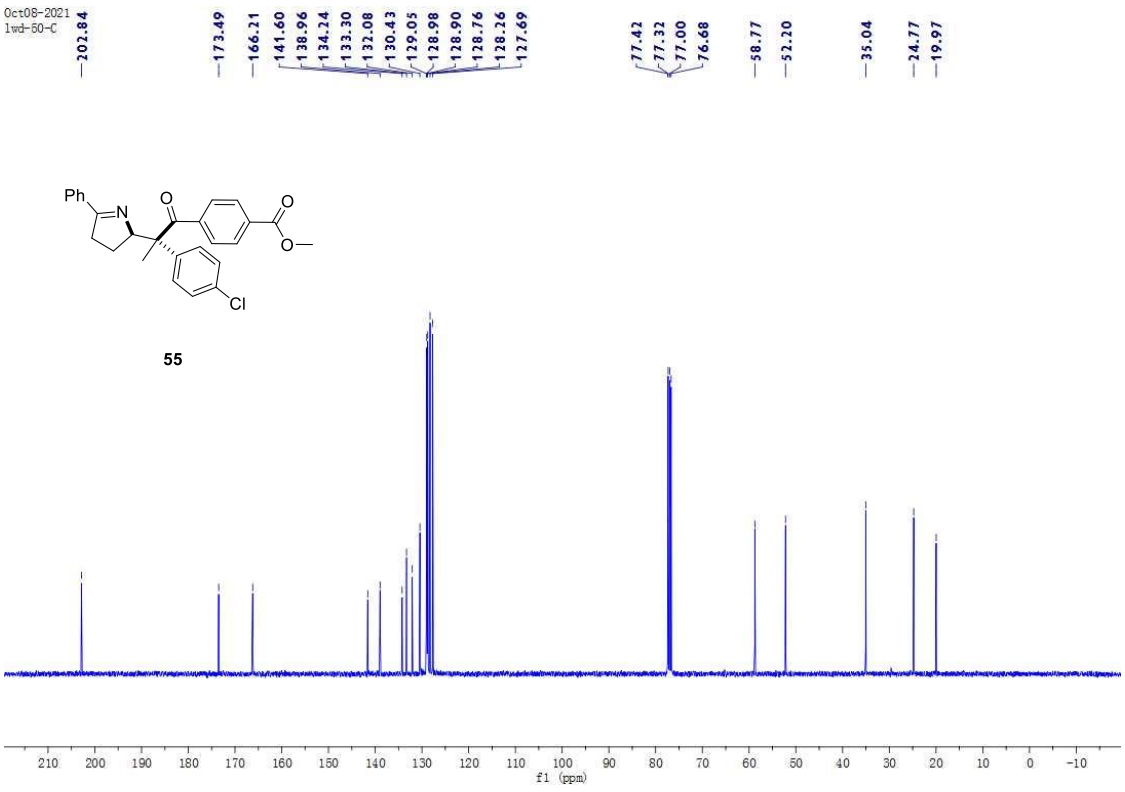
54


Oct05-2021
LWD-48-C
Ph
N
O
O
O
OMe
f1 (ppm)

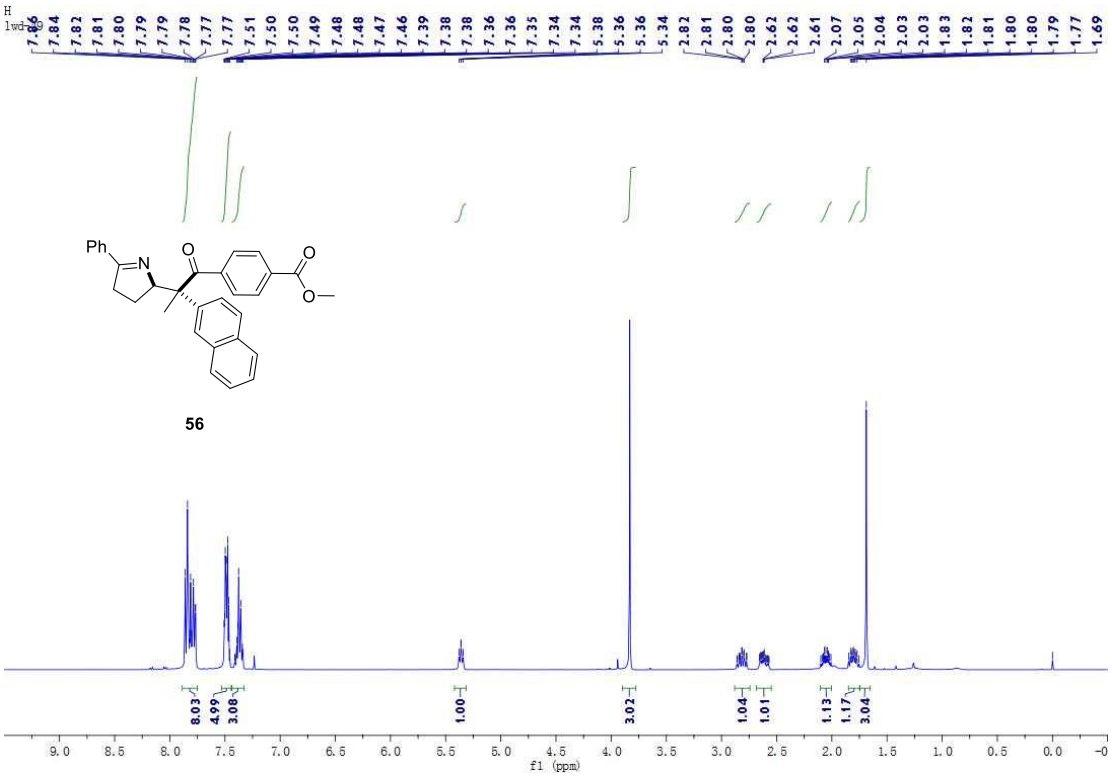
54

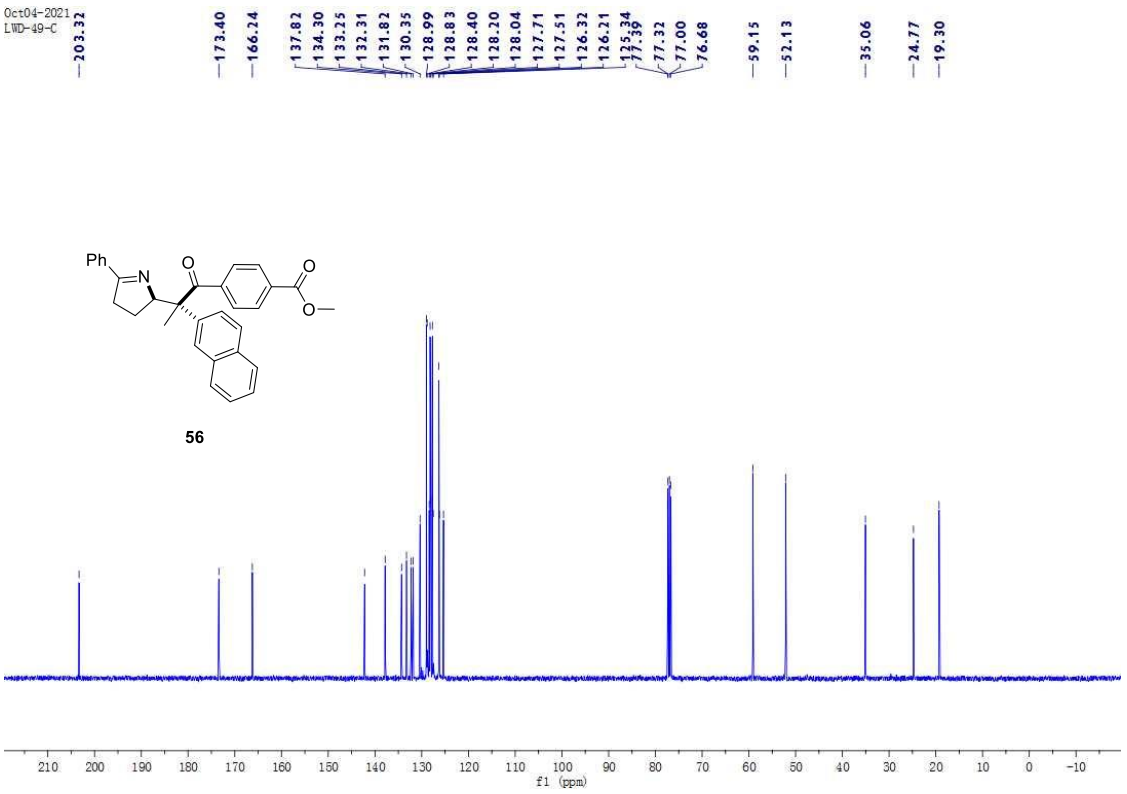

Oct07-2021
LWD-50
7.92
7.91
7.78
7.78
7.76
7.76
7.50
7.48
7.41
7.39
7.39
7.37
7.36
7.35
7.35
7.33
7.32
7.30
7.30
7.29
7.28
7.27
7.26
5.19
5.17
5.17
5.15
3.88
2.83
2.83
2.81
2.81
2.81
2.61
2.61
2.60
2.59
2.10
2.09
2.08
2.07
1.75
1.74
1.73
1.72
1.71
1.70
1.69
1.63
Ph
N
O
O
O
Cl
1.99
2.00
2.02
3.04
4.00
1.00
2.96
1.00
1.01
1.02
1.07
2.97
f1 (ppm)

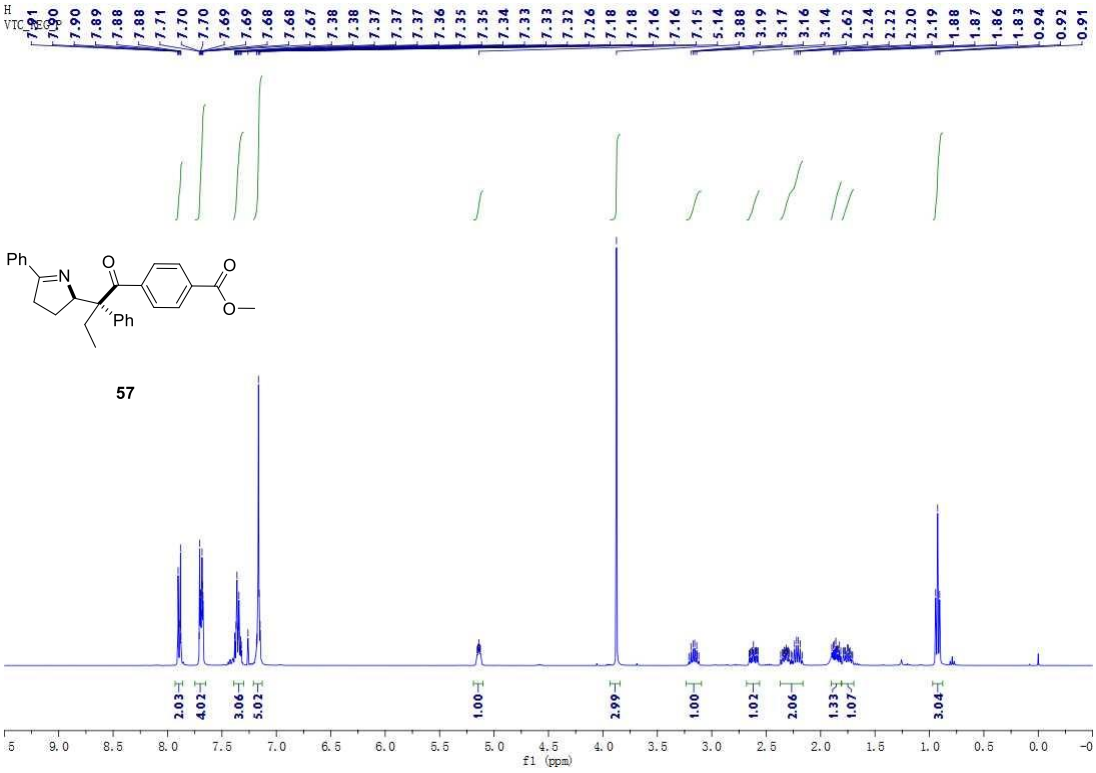
55

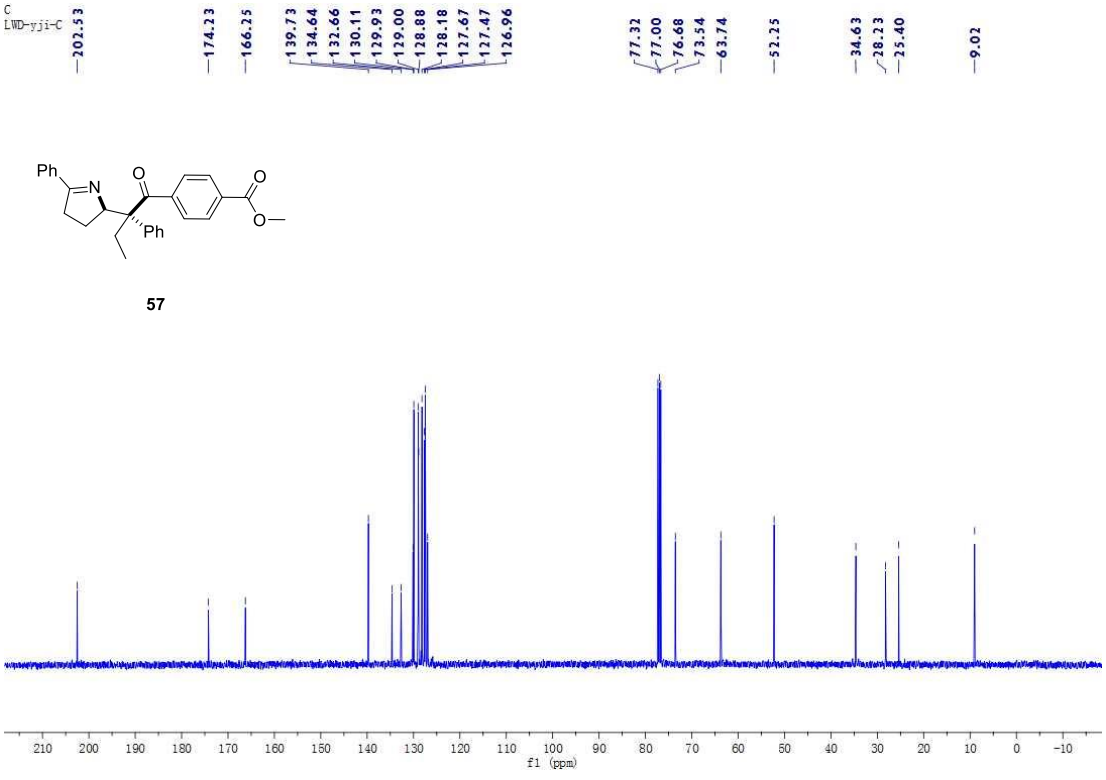

Oct08-2021
lwd-50-C
202.84
173.49
166.21
141.60
138.96
134.24
133.30
132.08
130.43
129.05
128.98
128.90
128.76
128.26
127.69
77.42
77.32
77.00
76.68
58.77
52.20
35.04
24.77
19.97
Ph
N
O
O
O
Cl
f1 (ppm)

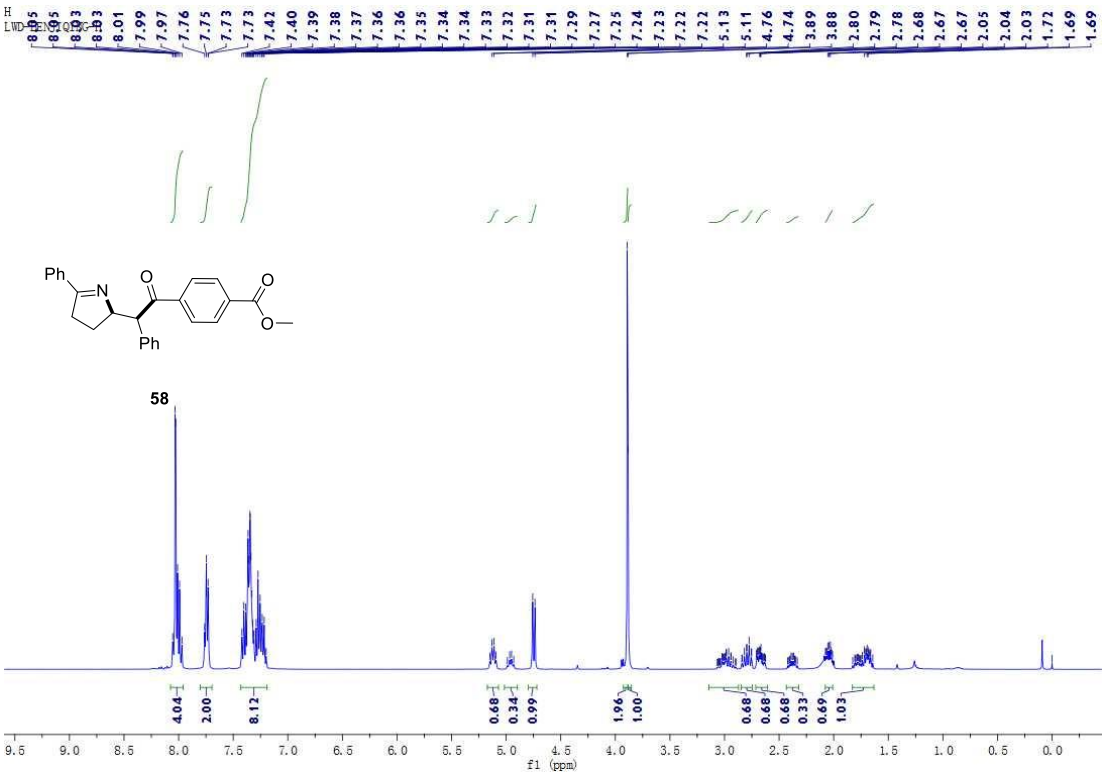
55

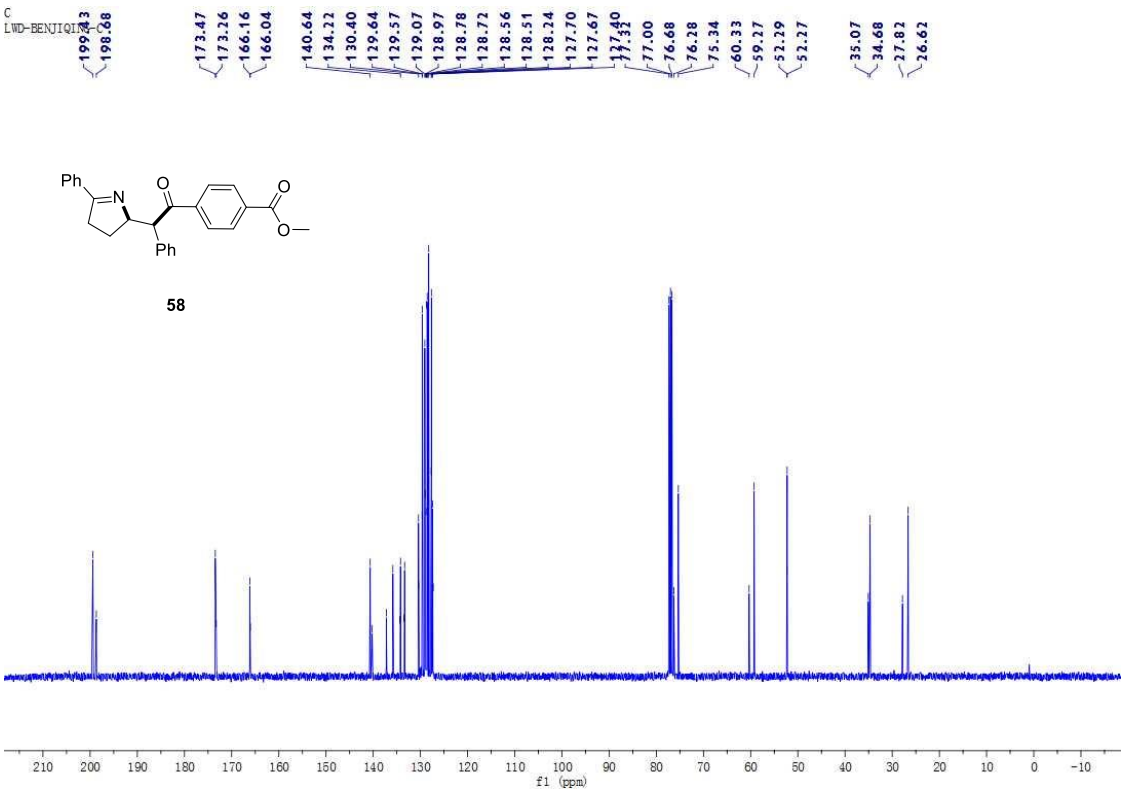

Ph
N
O
O
O
56
8.03
4.99
3.08
1.00
3.02
1.04
1.01
1.13
1.17
3.04
f1 (ppm)

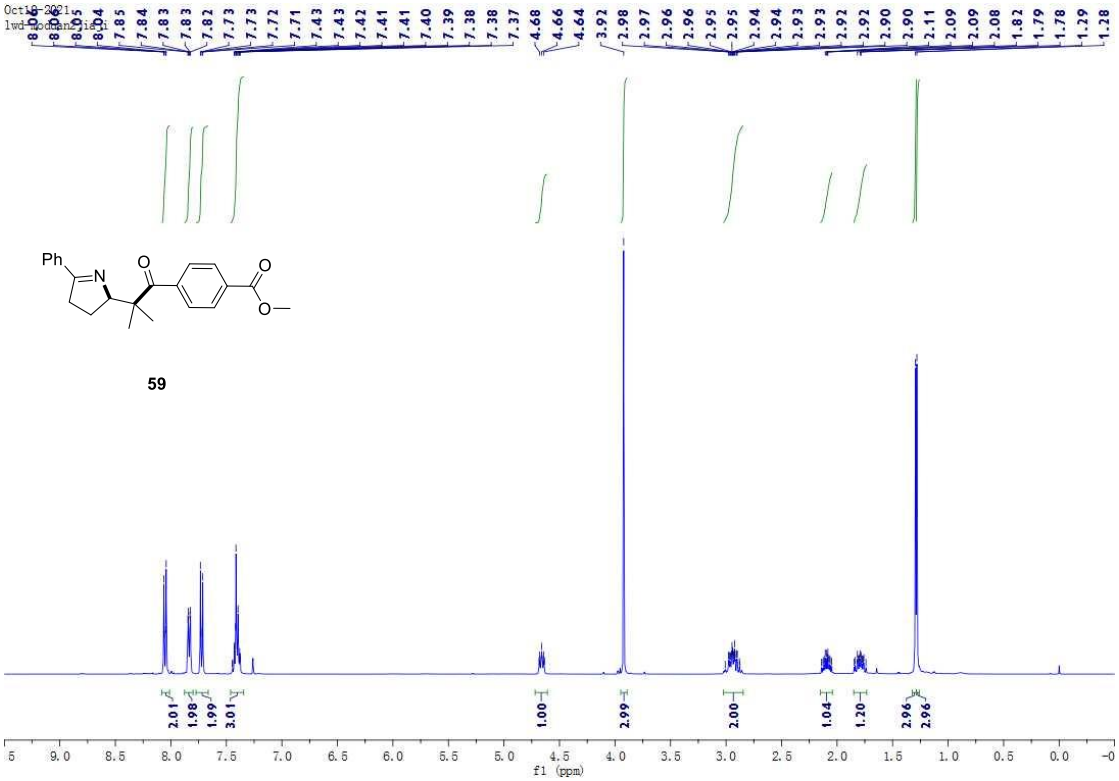

Oct04-2021
LWD-49-C
203.32
173.40
166.24
137.82
134.30
133.25
132.31
131.82
130.35
128.99
128.83
128.40
128.20
128.04
127.71
127.51
126.32
126.21
125.34
77.32
77.00
76.68
59.15
52.13
35.06
24.77
19.30
Ph
N
O
O
O
56
f1 (ppm)


Ph
N
O
O
O
Ph
57
f1 (ppm)

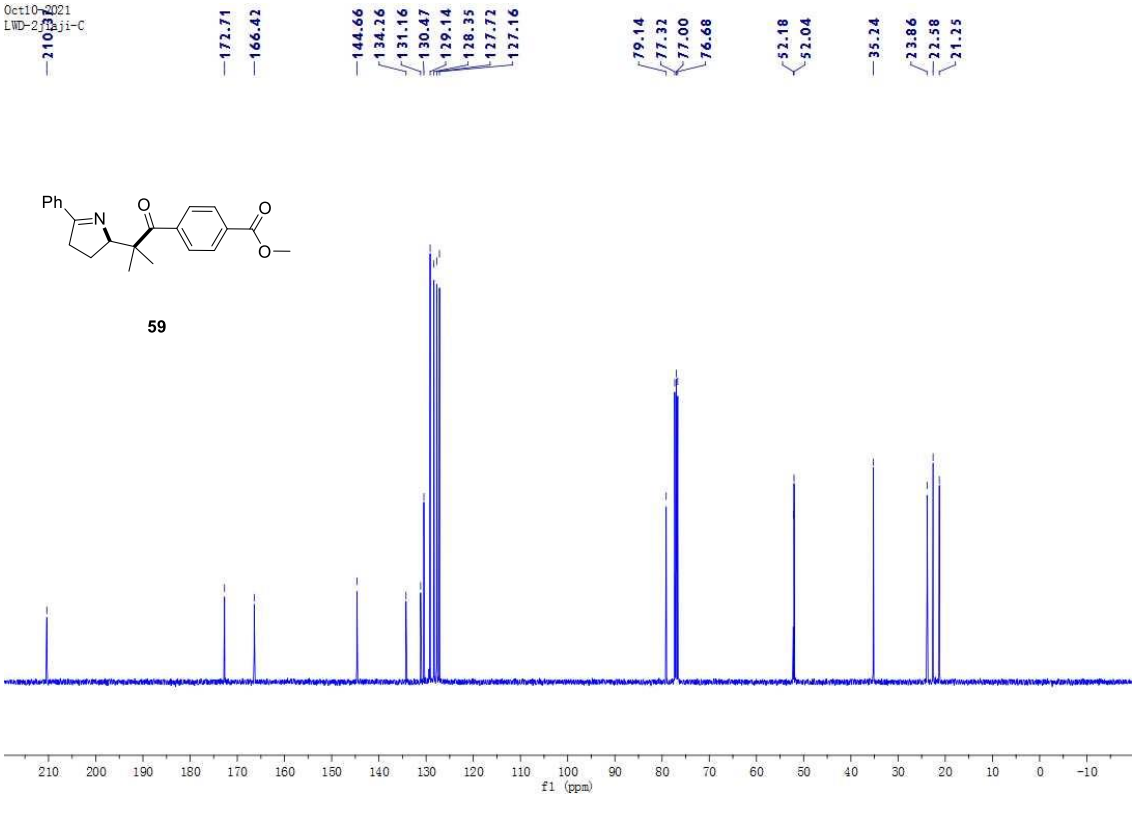

Ph
N
O
O
O
Ph
57
f1 (ppm)


Ph
N
O
O
O
Ph
58
4.04
2.00
8.12
0.68
0.34
0.99
1.96
1.00
0.68
0.68
0.68
0.33
0.69
1.03
f1 (ppm)

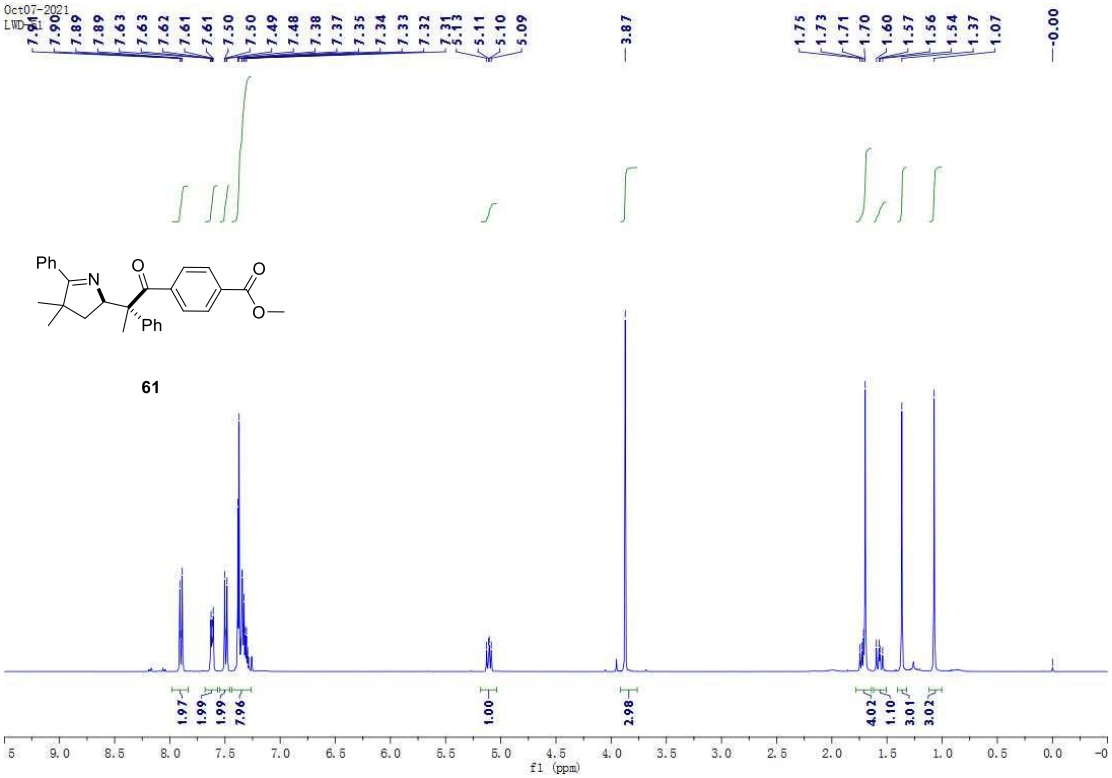

199.43
198.68
173.47
173.26
166.16
166.04
140.64
134.22
130.40
129.64
129.57
129.07
128.97
128.78
128.72
128.56
128.51
128.24
127.70
127.67
77.00
76.68
76.28
75.34
60.33
59.27
52.29
52.27
35.07
34.68
27.82
26.62
Ph
N
O
O
O
Ph
58
f1 (ppm)

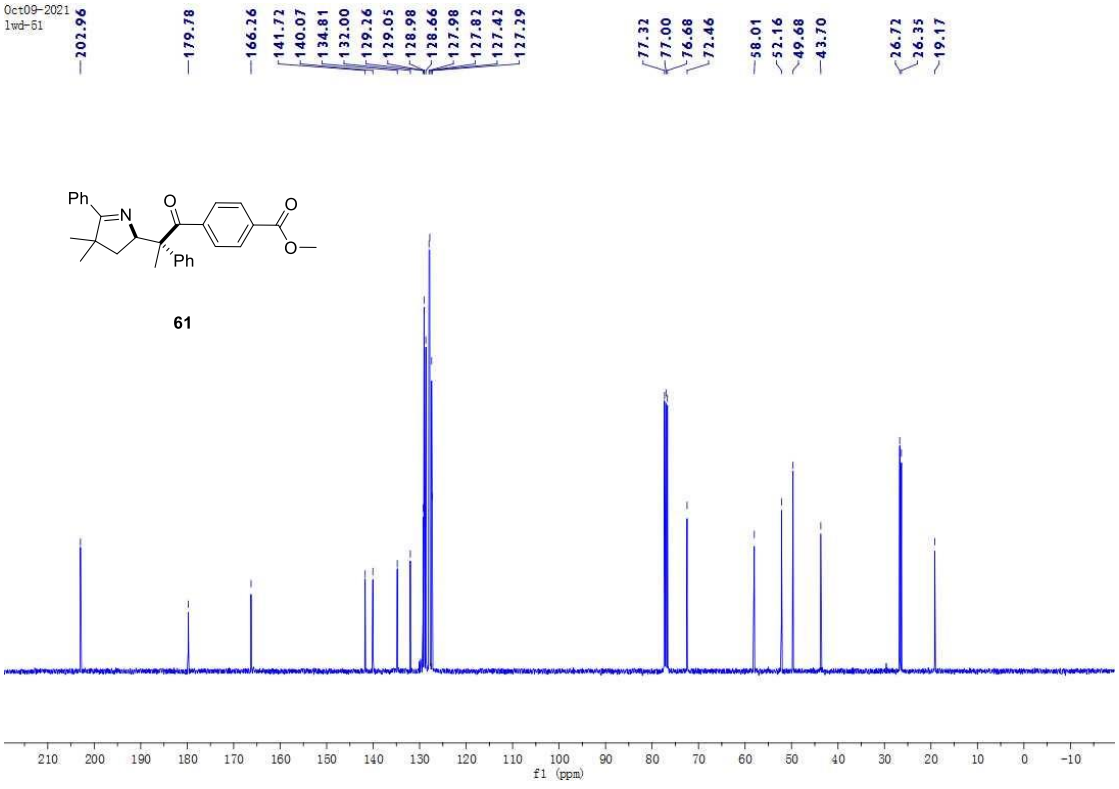

Oct18-2021
lwd-zhuanjieji
8.05
8.05
8.04
7.85
7.84
7.83
7.83
7.82
7.73
7.73
7.72
7.71
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.37
4.68
4.66
4.64
3.92
2.98
2.97
2.96
2.96
2.95
2.95
2.94
2.94
2.93
2.93
2.92
2.92
2.90
2.90
2.11
2.09
2.09
2.08
1.82
1.79
1.78
1.29
1.28
Ph
N
O
O
O
2.01
1.98
1.99
3.01
1.00
2.99
2.00
1.04
1.20
2.96
2.96
f1 (ppm)

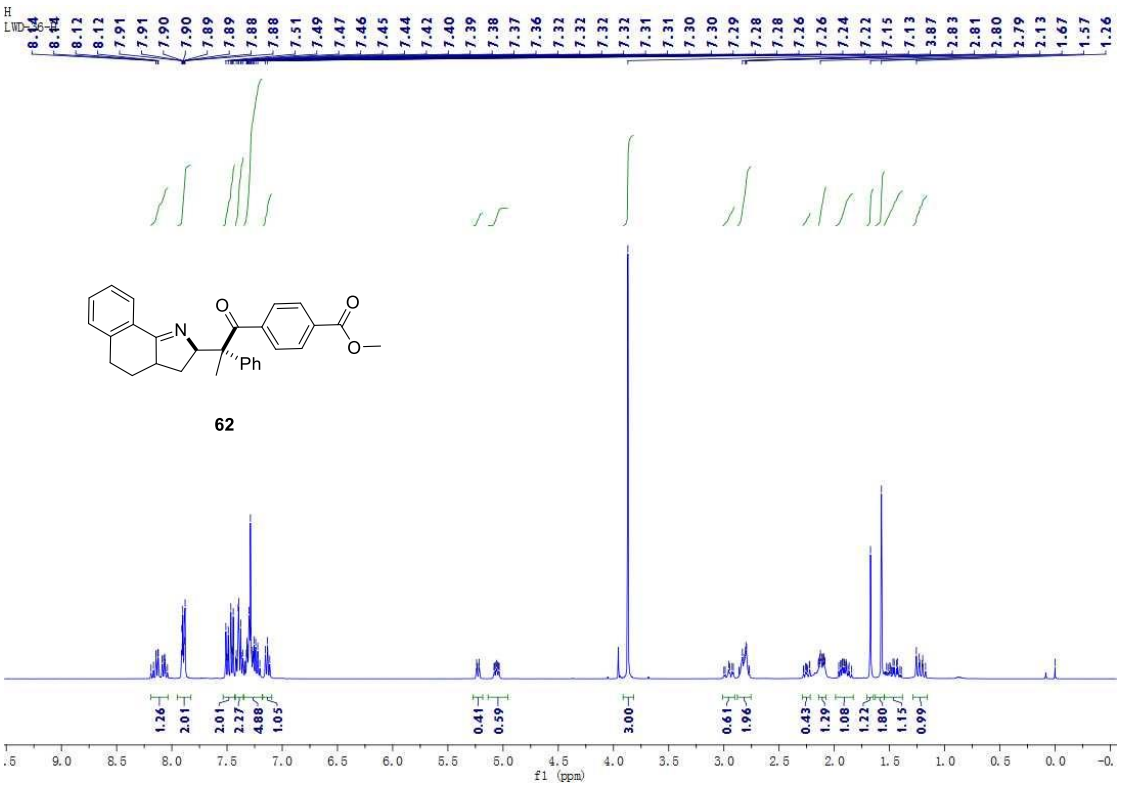
59

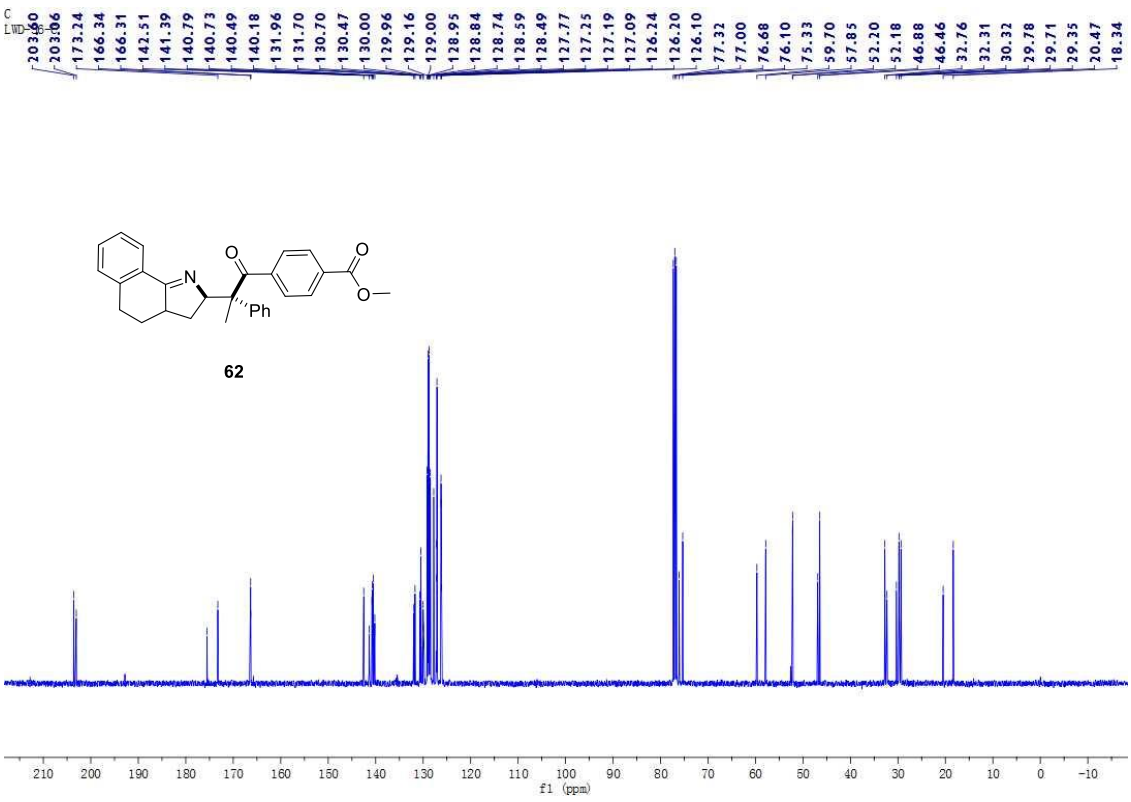

Oct10-2021
LWD-2-zhaji-C
210.03
172.71
166.42
144.66
134.26
131.16
130.47
129.14
128.35
127.72
127.16
79.14
77.32
77.00
76.68
52.18
52.04
35.24
23.86
22.58
21.25
Ph
N
O
O
O
f1 (ppm)

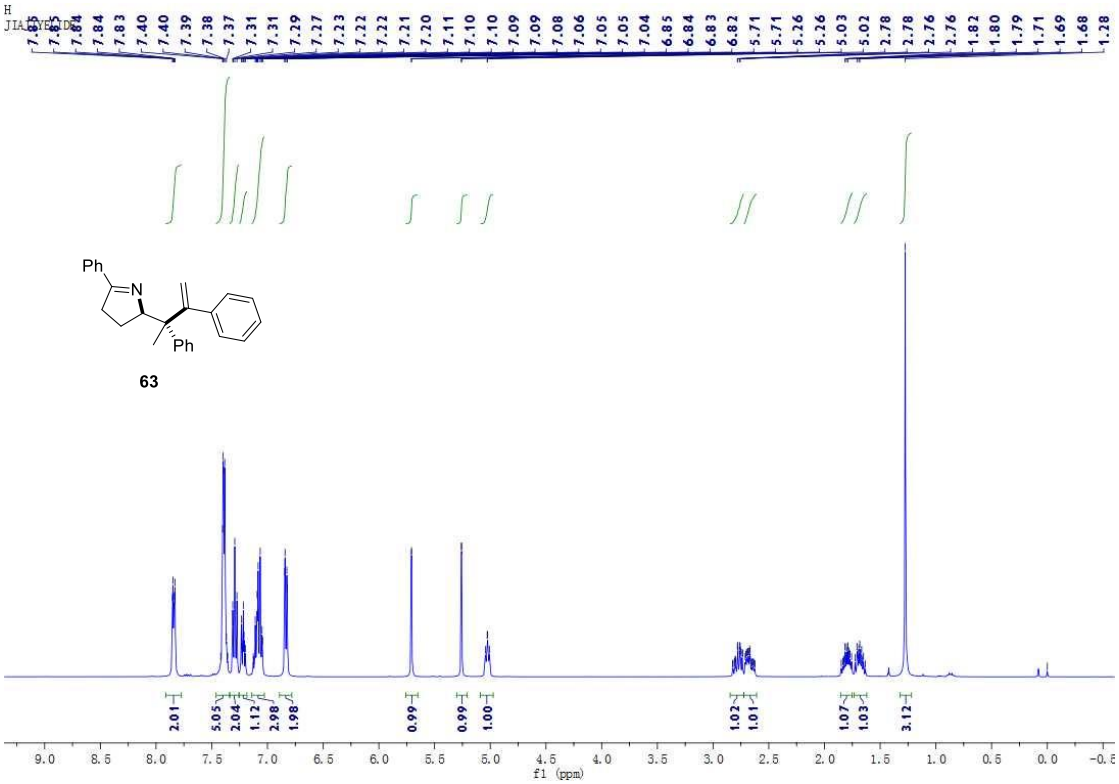
59

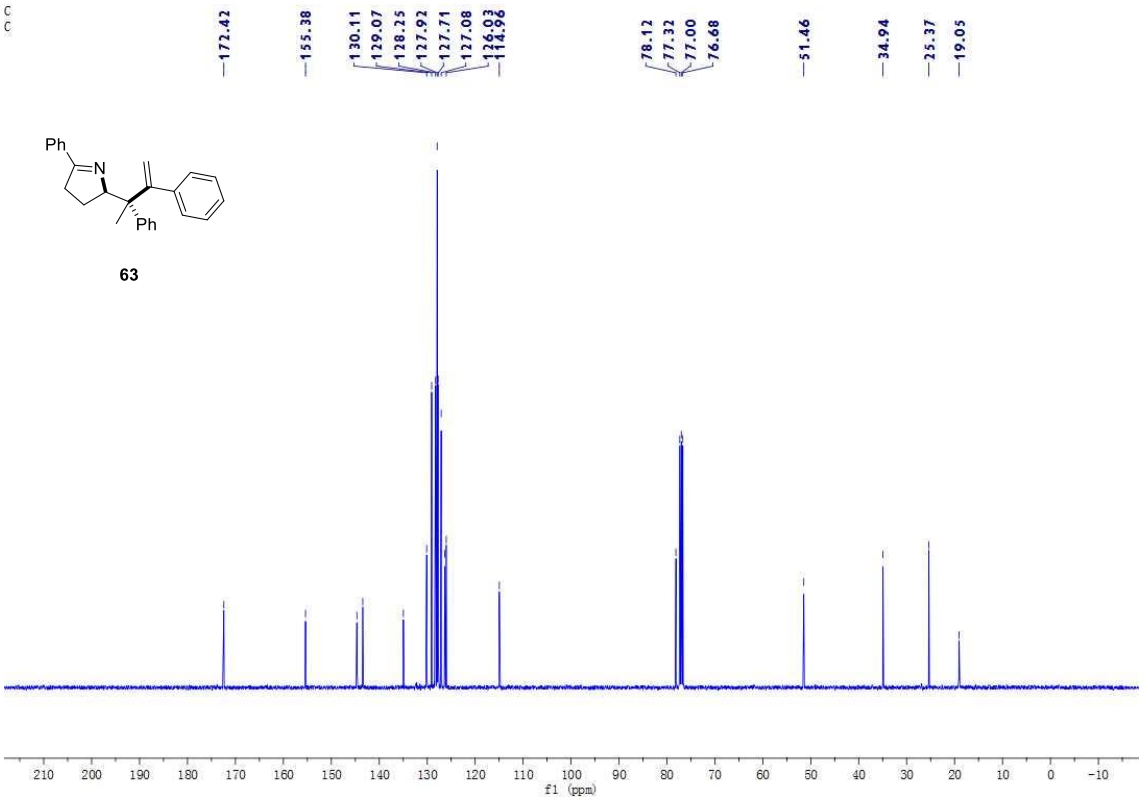

Oct07-2021
LWD-61
7.91
7.90
7.89
7.89
7.63
7.63
7.62
7.61
7.61
7.50
7.50
7.49
7.48
7.38
7.37
7.35
7.34
7.33
7.32
7.31
5.13
5.11
5.10
5.09
3.87
1.75
1.73
1.71
1.70
1.60
1.57
1.56
1.54
1.37
1.07
0.00
Ph
N
O
O
O
Ph
61
1.97
1.99
1.99
7.96
1.00
2.98
4.02
1.10
3.01
3.02
f1 (ppm)

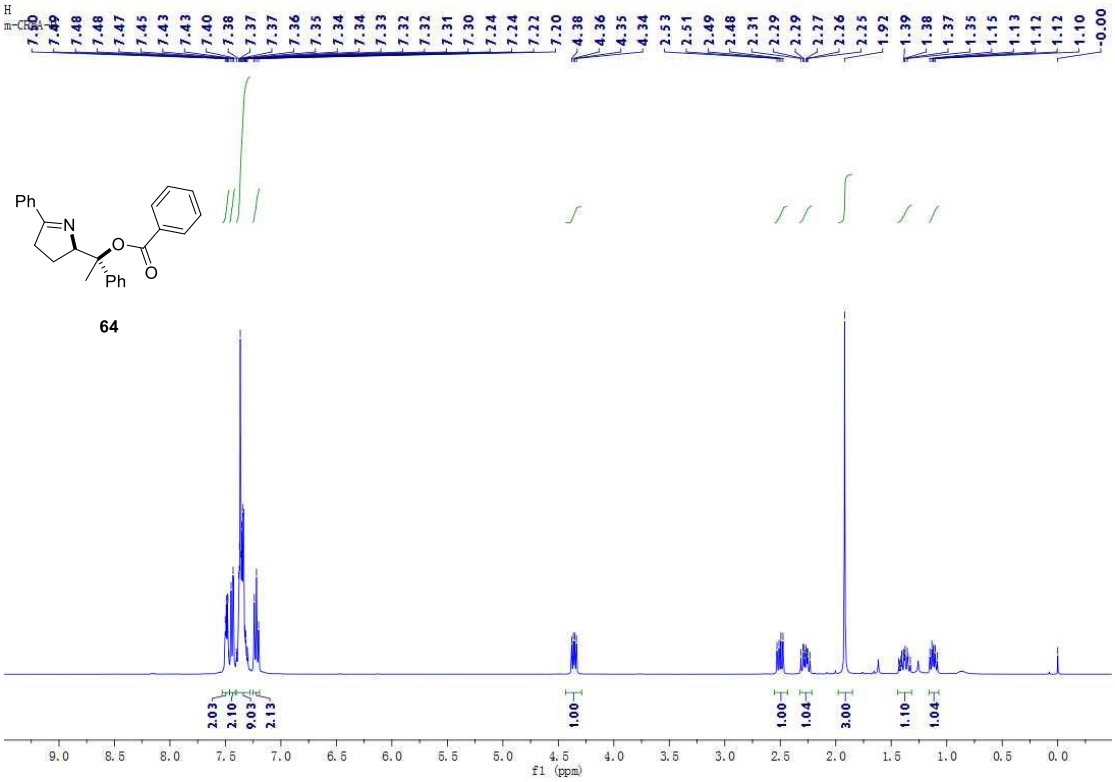

Oct09-2021
lwd-51
202.96
179.78
166.26
141.72
140.07
134.81
132.00
129.26
129.05
128.98
128.66
127.98
127.82
127.42
127.29
77.32
77.00
76.68
72.46
58.01
52.16
49.68
43.70
26.72
26.35
19.17
Ph
N
O
O
O
Ph
61
f1 (ppm)

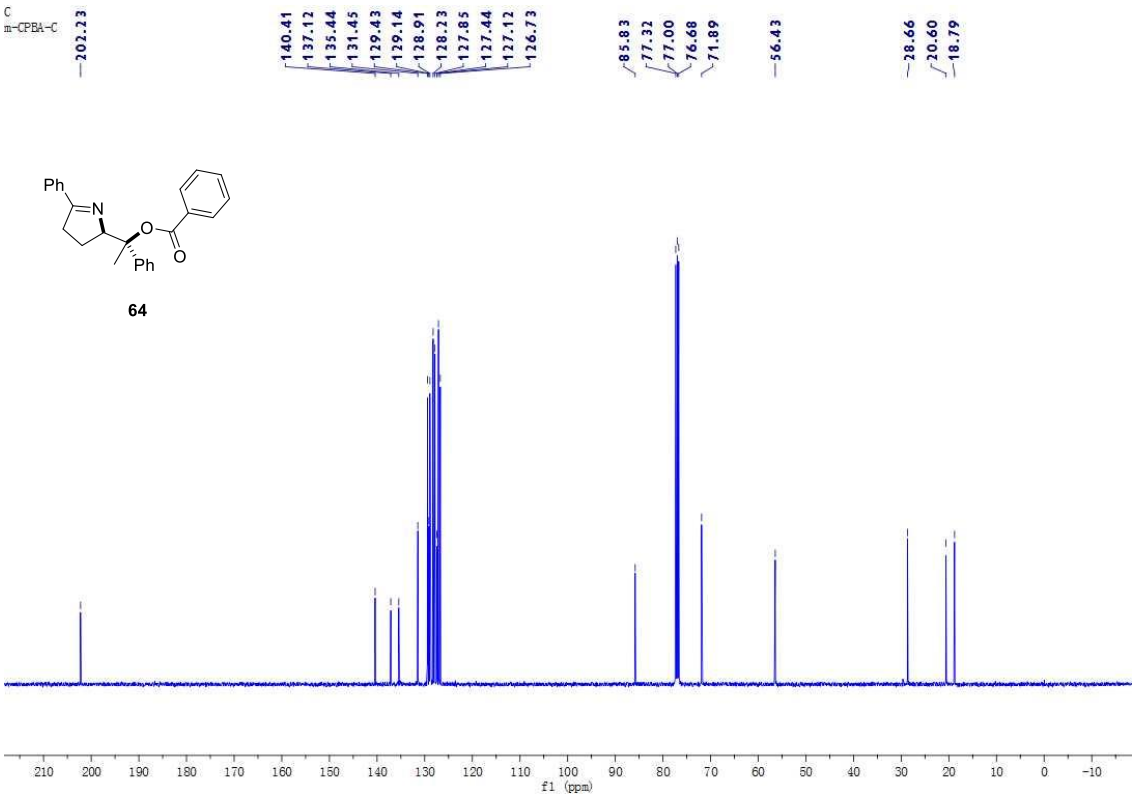

62
f1 (ppm)

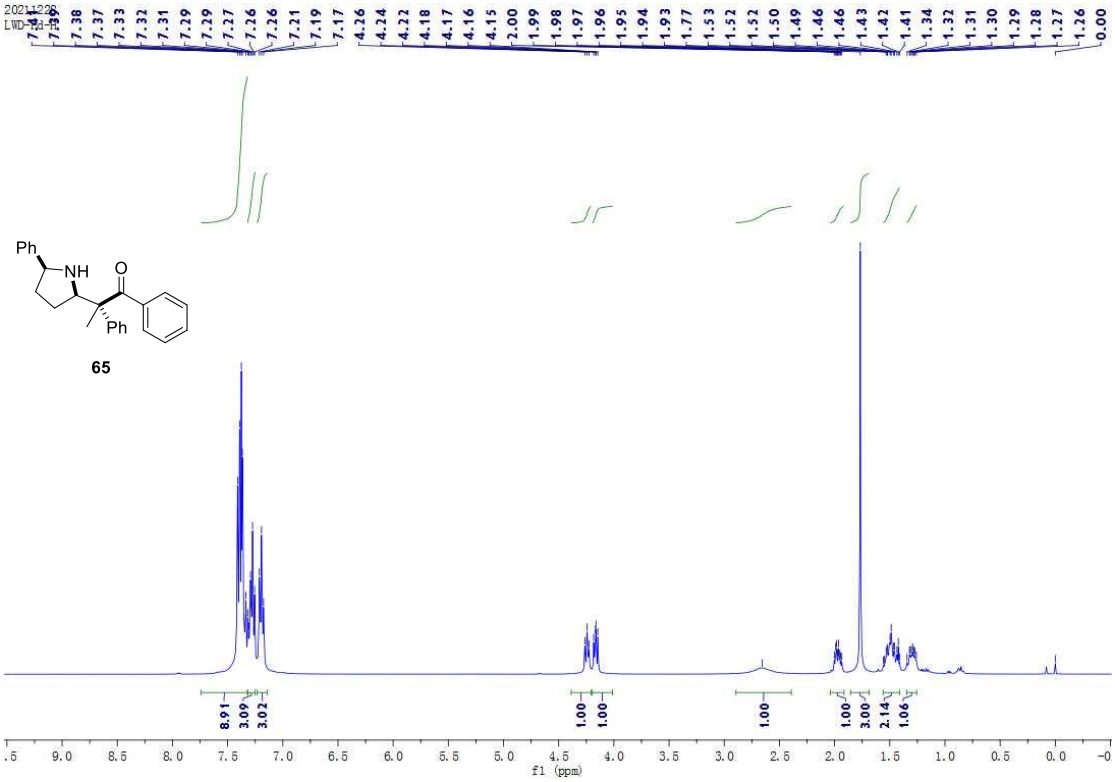

62
f1 (ppm)

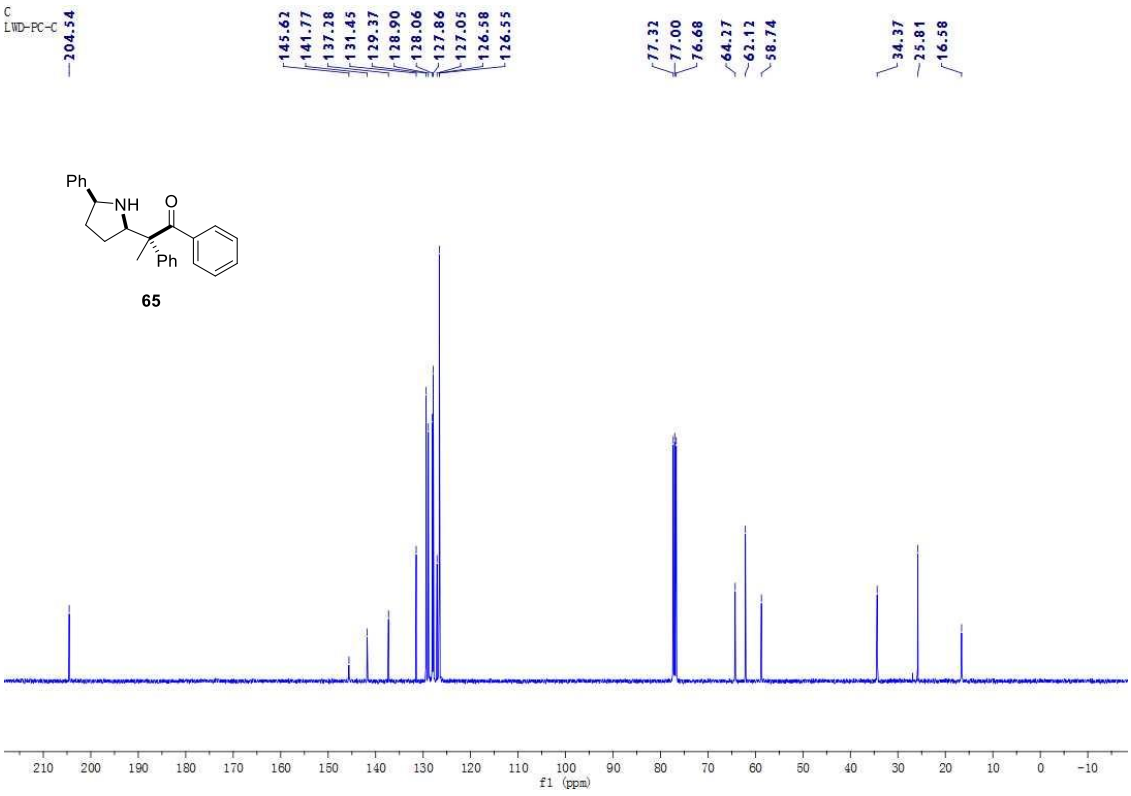

Ph
N
Ph
63
f1 (ppm)

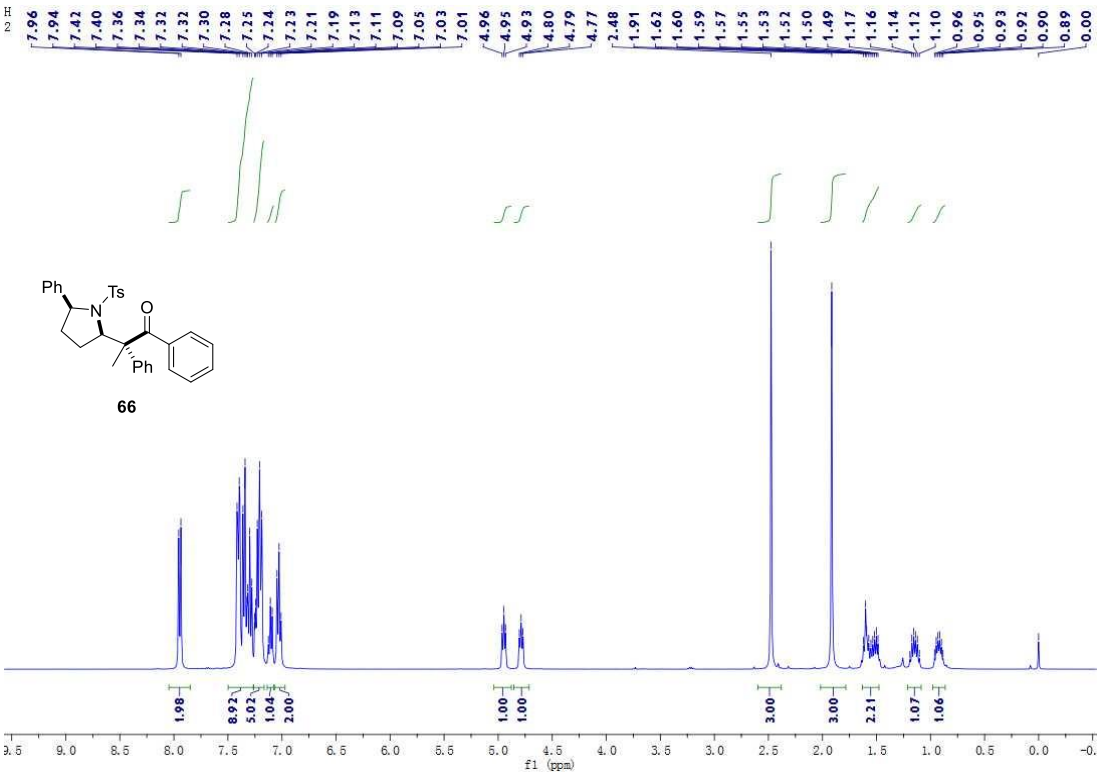

Ph
N
Ph
63
f1 (ppm)

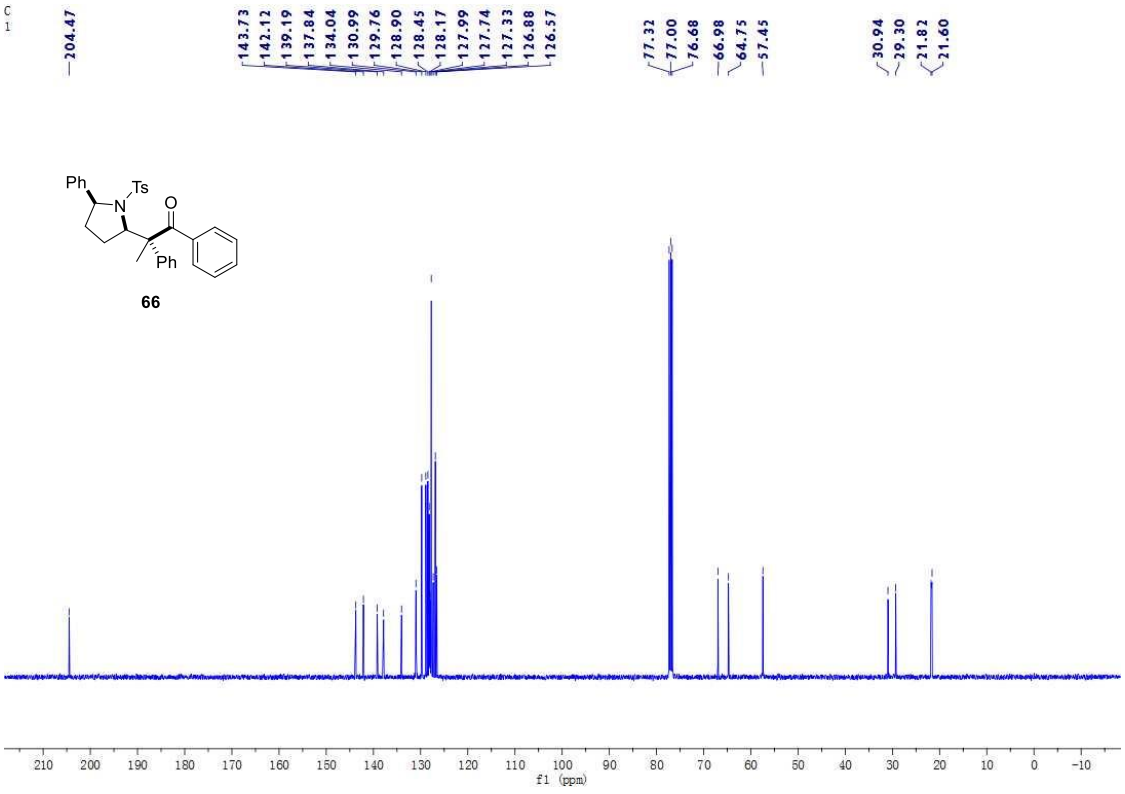

Ph
N
O
O
Ph
64
2.03
2.10
9.03
2.13
1.00
1.00
1.04
3.00
1.10
1.04
f1 (ppm)

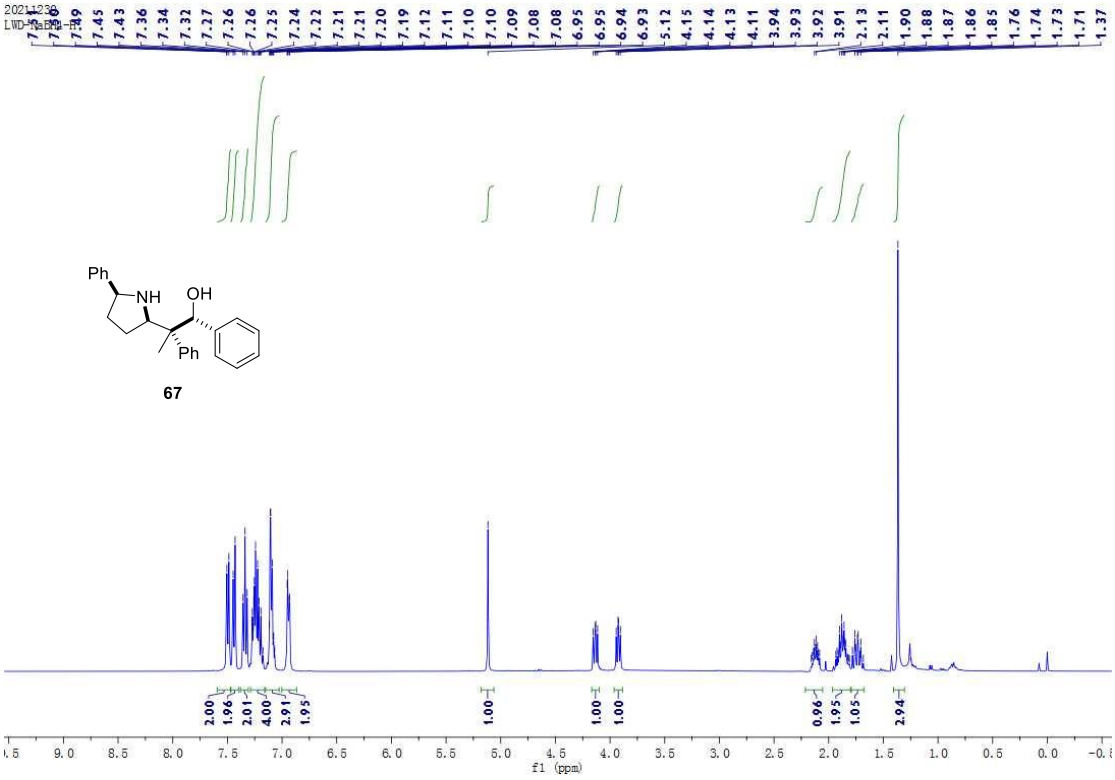

Ph
N
O
O
Ph
64
202.23
140.41
137.12
135.44
131.45
129.43
129.14
128.91
128.23
127.85
127.44
127.12
126.73
85.83
77.32
77.00
76.68
71.89
56.43
38.66
20.60
18.79
f1 (ppm)

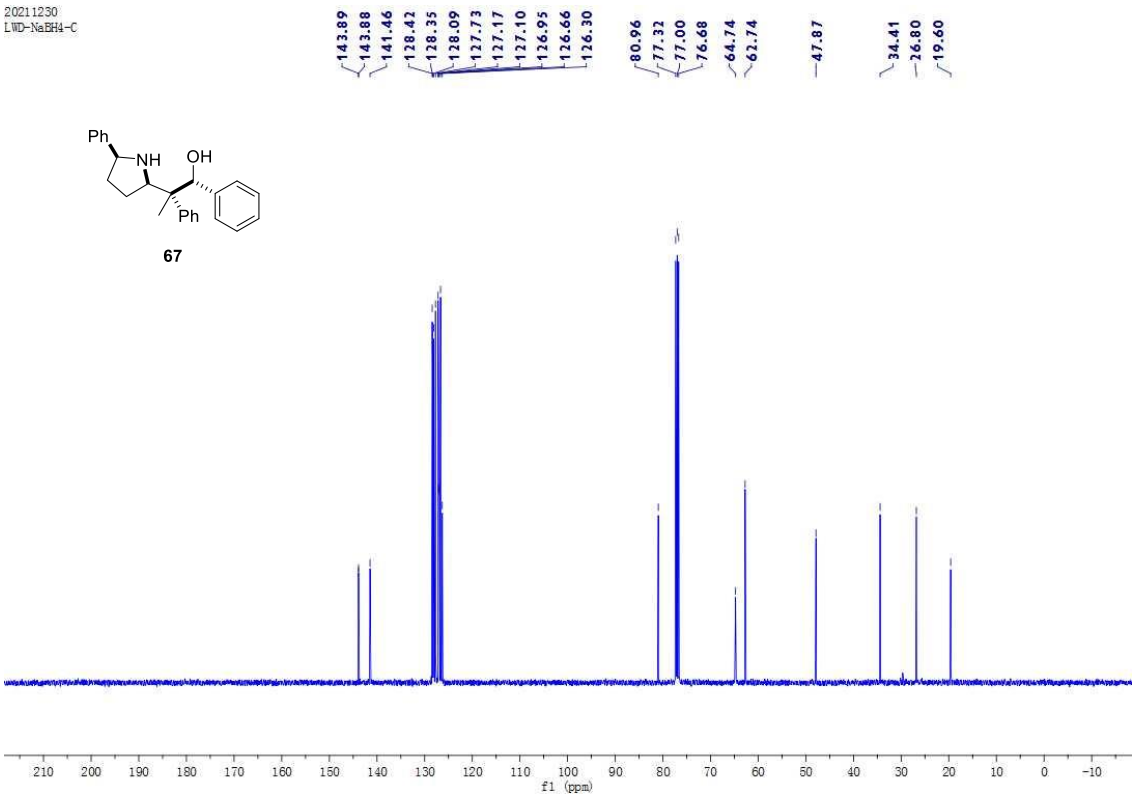

Ph
NH
O
Ph
65
8.91
3.09
3.02
1.00
1.00
1.00
1.00
3.00
2.14
1.06
f1 (ppm)

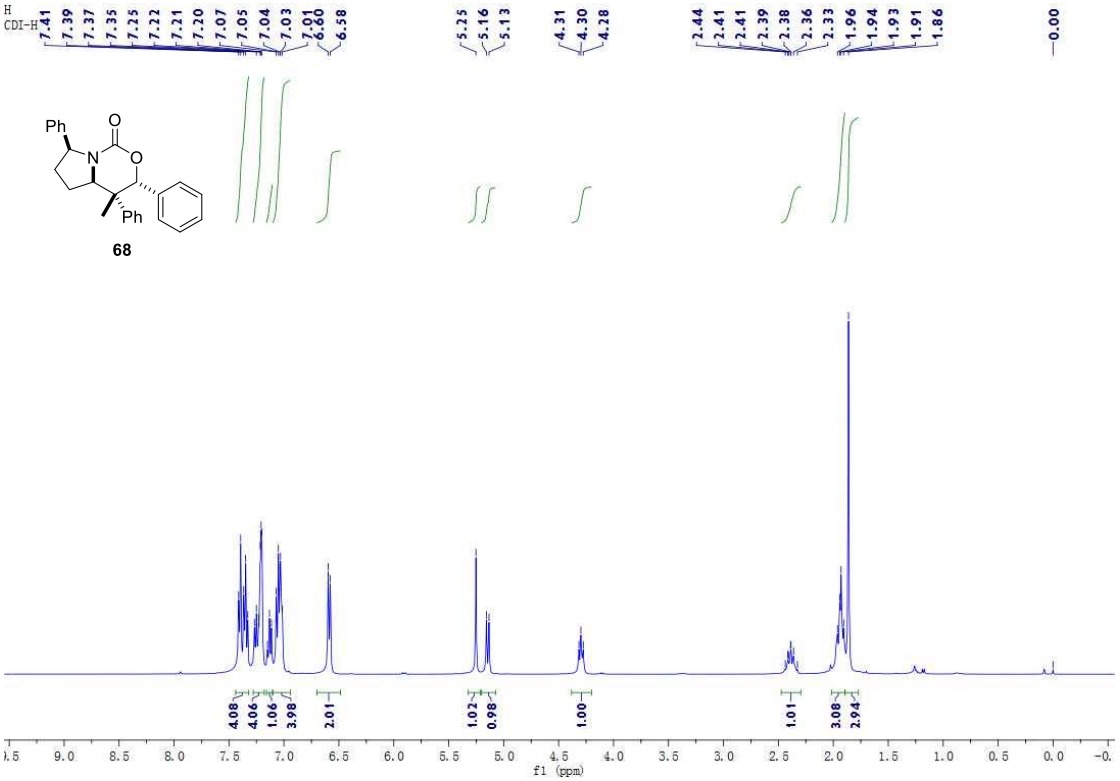

204.54
145.62
141.77
137.28
131.45
129.37
128.90
128.06
127.86
127.05
126.58
126.55
77.32
77.00
76.68
64.27
62.12
58.74
34.37
25.81
16.58
Ph
NH
O
Ph
65
f1 (ppm)

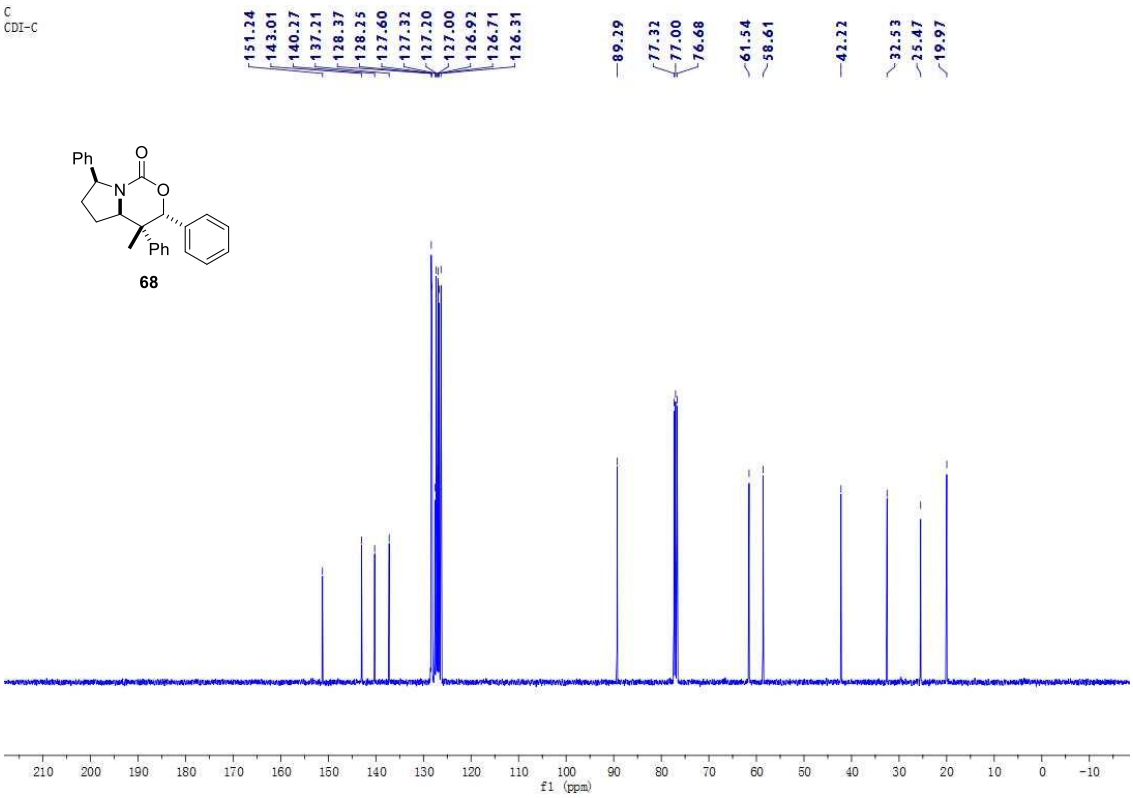

7.96 7.94 7.42 7.40 7.36 7.34 7.32 7.32 7.30 7.28 7.25 7.24 7.23 7.21 7.19 7.13 7.11 7.09 7.05 7.03 7.01
4.96 4.95 4.93 4.80 4.79 4.77
2.48 1.91 1.62 1.60 1.59 1.57 1.55 1.53 1.52 1.50 1.49 1.17 1.16 1.14 1.12 1.10 0.96 0.95 0.93 0.92 0.90 0.89 0.00
Ph
N
Ts
O
Ph
66
1.98 8.92 5.02 1.04 2.00 1.00 1.00 3.00 3.00 2.21 1.07 1.06
f1 (ppm)

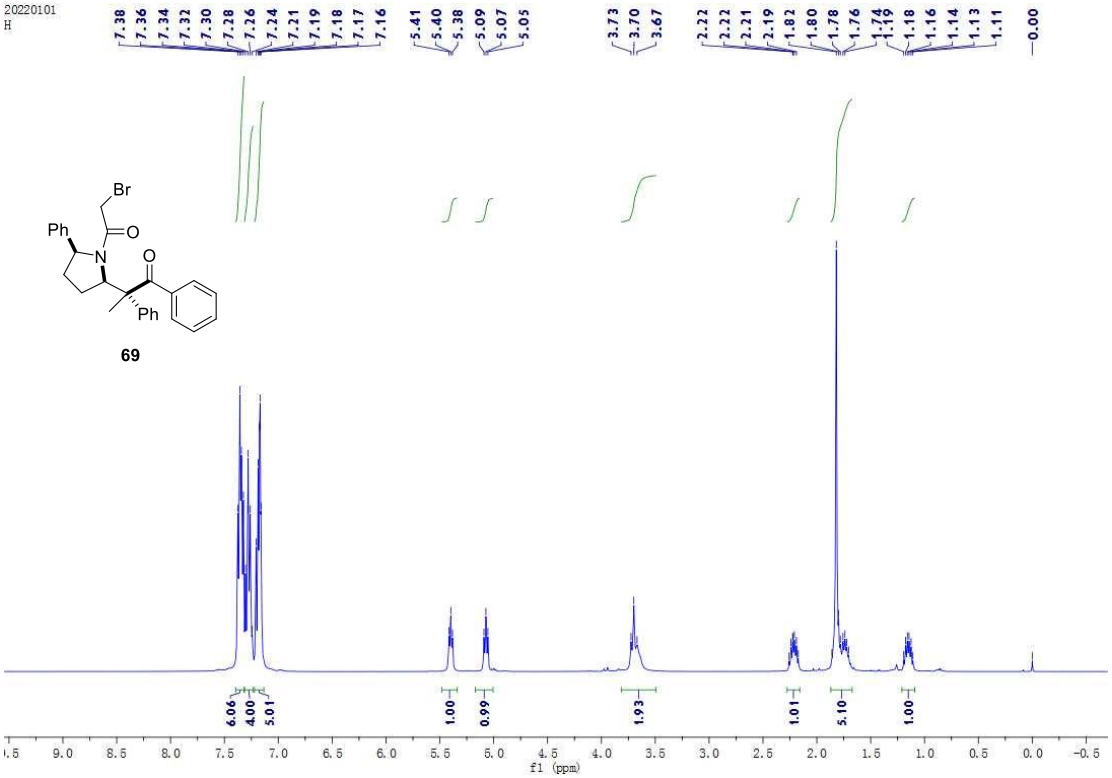

204.47
143.73 142.12 139.19 137.84 134.04 130.99 129.76 128.90 128.45 128.17 127.99 127.74 127.33 126.88 126.57
77.32 77.00 76.68 66.98 64.75 57.45
30.94 29.30 21.82 21.60
Ph
N
Ts
O
Ph
66
f1 (ppm)

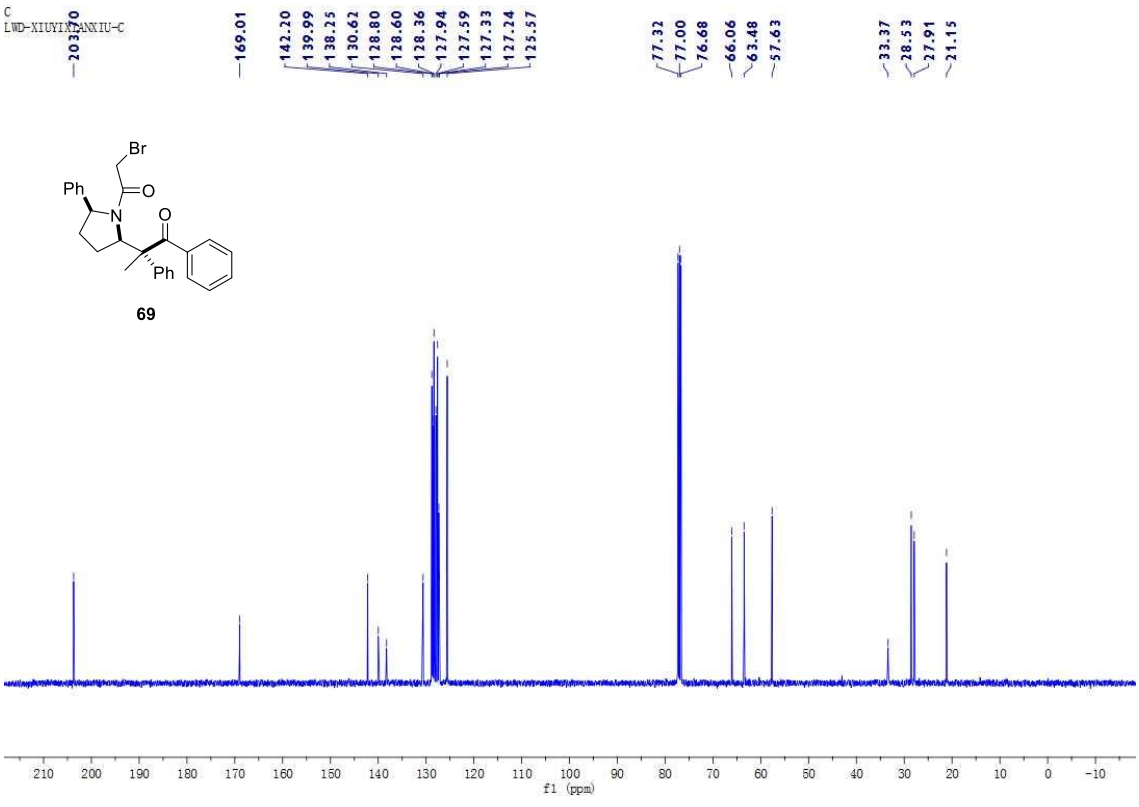

7.49
7.45
7.43
7.36
7.34
7.32
7.27
7.26
7.26
7.25
7.24
7.22
7.21
7.21
7.20
7.19
7.12
7.11
7.10
7.10
7.09
7.08
7.08
6.95
6.95
6.94
6.93
5.12
4.15
4.14
4.13
4.11
3.94
3.93
3.92
3.91
2.13
2.11
1.90
1.88
1.87
1.86
1.85
1.76
1.74
1.73
1.71
1.37
Ph
NH
OH
Ph
67
2.00
1.96
2.01
4.00
2.91
1.95
1.00
1.00
1.00
0.96
1.95
1.05
2.94
f1 (ppm)

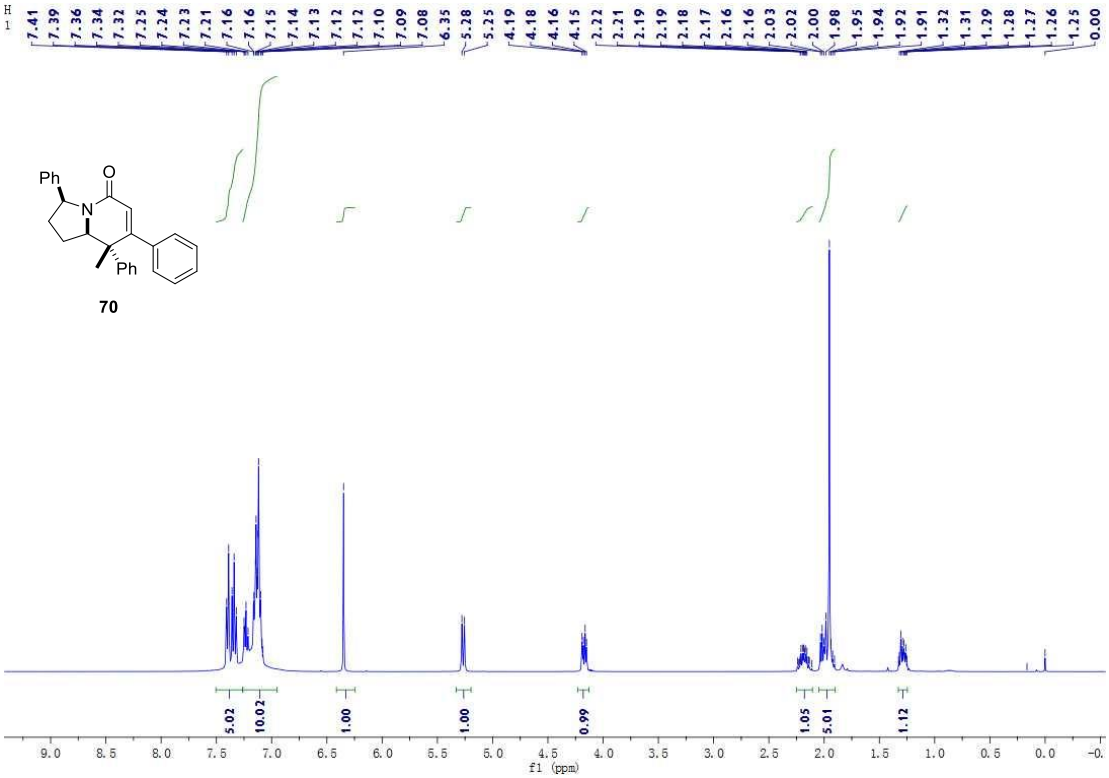

20211230
LWD-NaBH4-C
143.89
143.88
141.46
128.42
128.35
128.09
127.73
127.17
127.10
126.95
126.66
126.30
80.96
77.32
77.00
76.68
64.74
61.74
47.87
34.41
26.80
19.60
Ph
NH
OH
Ph
67
f1 (ppm)


H
CDI-H
7.41
7.39
7.37
7.35
7.25
7.22
7.21
7.20
7.07
7.05
7.04
7.03
7.01
6.60
6.58
5.25
5.16
5.13
4.31
4.30
4.28
2.44
2.41
2.41
2.39
2.38
2.36
2.33
1.96
1.94
1.93
1.91
1.86
0.00
Ph
O
N
O
Ph
68
4.08
4.06
1.06
3.98
2.01
1.02
0.98
1.00
1.01
3.08
2.94
f1 (ppm)

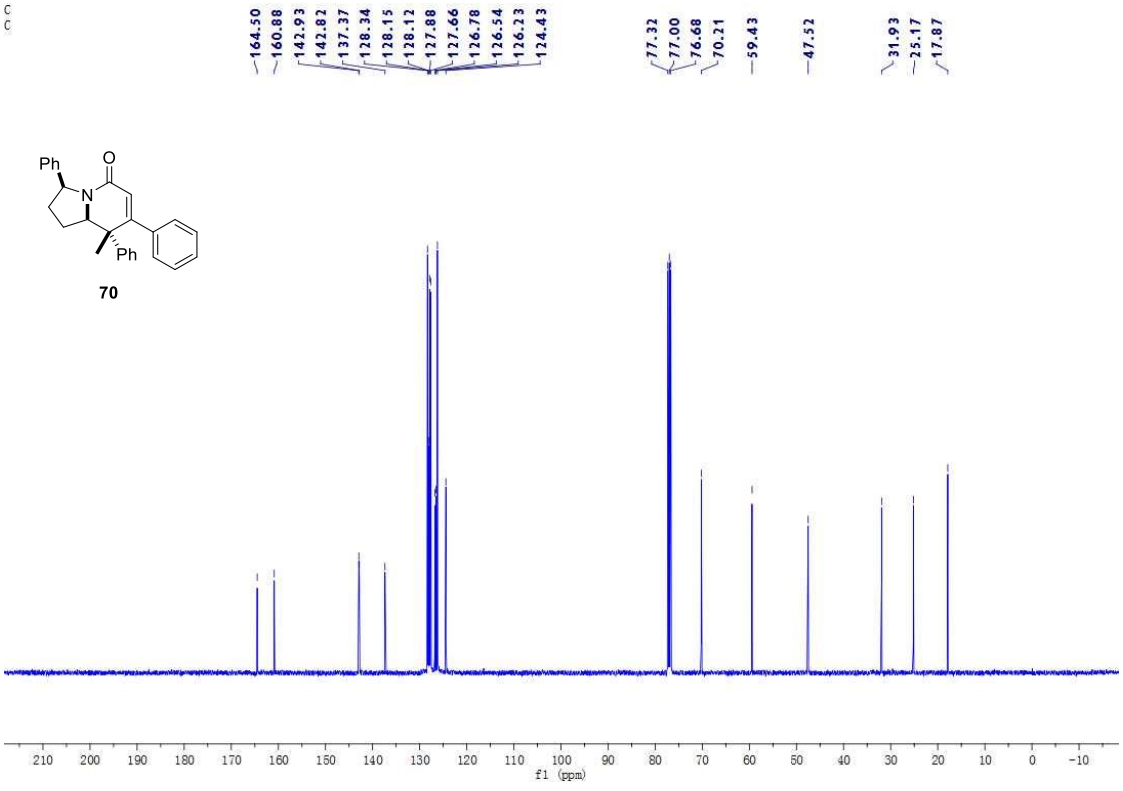

C
CDI-C
151.24
143.01
140.27
137.21
128.37
128.25
127.60
127.32
127.20
127.00
126.92
126.71
126.31
89.29
77.32
77.00
76.68
61.54
58.61
42.22
32.53
25.47
19.97
Ph
O
N
O
Ph
68
f1 (ppm)


20220101
H
7.38
7.36
7.34
7.32
7.30
7.28
7.26
7.24
7.21
7.19
7.18
7.17
7.16
5.41
5.40
5.38
5.09
5.07
5.05
3.73
3.70
3.67
2.22
2.22
2.21
2.19
1.82
1.80
1.78
1.76
1.74
1.19
1.18
1.16
1.14
1.13
1.11
0.00
Br
Ph
N
O
O
Ph
69
6.06
4.00
5.01
1.00
0.99
1.93
1.01
5.10
1.00
f1 (ppm)

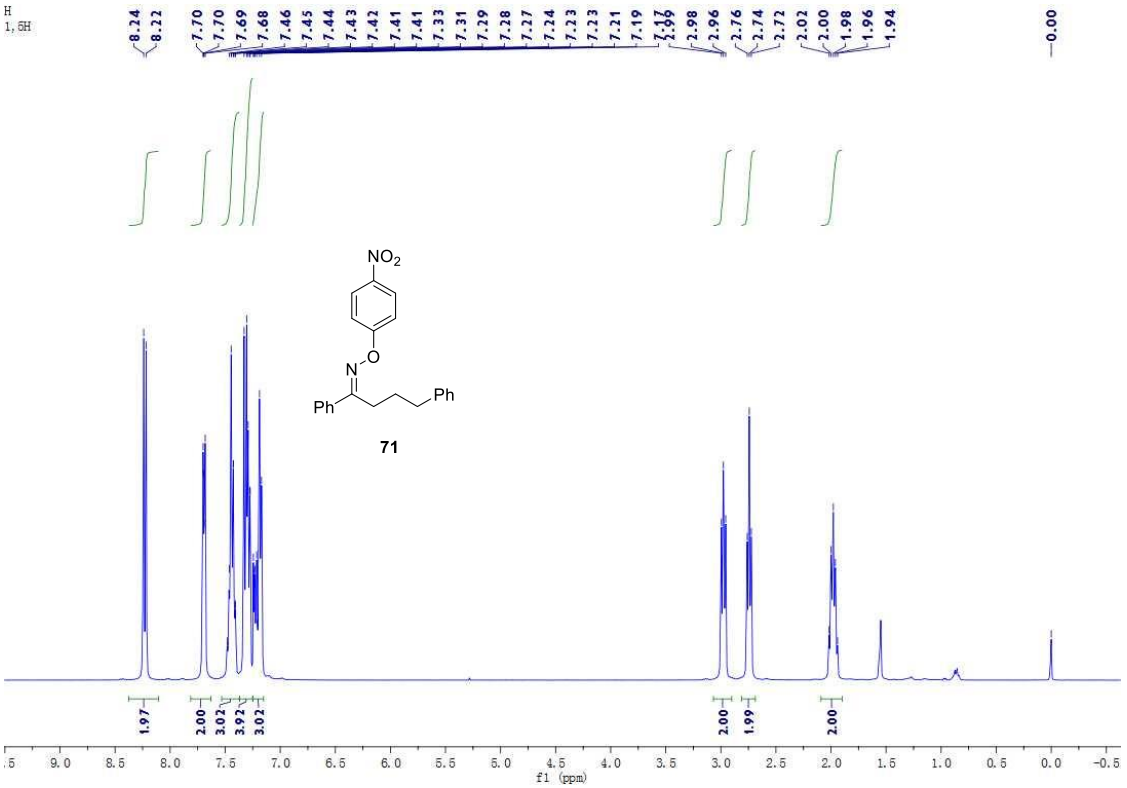

C
LWD-XIUYIXIANXIU-C
203.70
169.01
142.20
139.99
138.25
130.62
128.80
128.60
128.36
127.94
127.59
127.33
127.24
125.57
77.32
77.00
76.68
66.06
63.48
57.63
33.37
28.53
27.91
21.15
Br
Ph
N
O
O
Ph
69
f1 (ppm)

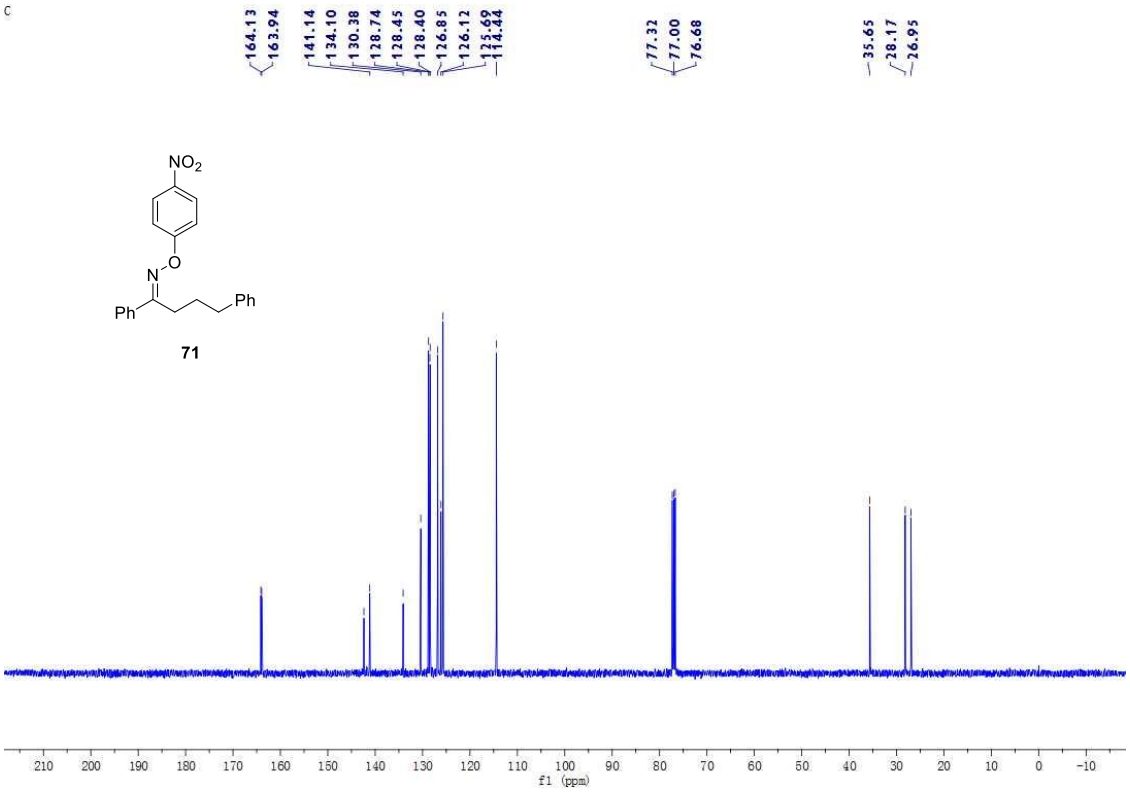

7.41 7.39 7.36 7.34 7.32 7.25 7.24 7.23 7.21 7.16 7.16 7.15 7.14 7.13 7.12 7.12 7.10 7.09 7.08 6.35 5.28 5.25 4.19 4.18 4.16 4.15 2.22 2.21 2.19 2.19 2.18 2.17 2.16 2.16 2.03 2.02 2.00 1.98 1.95 1.94 1.92 1.91 1.32 1.31 1.29 1.28 1.27 1.26 1.25 0.00
Ph
O
N
Ph
5.02
10.02
1.00
1.00
0.99
1.05
5.01
1.12
f1 (ppm)

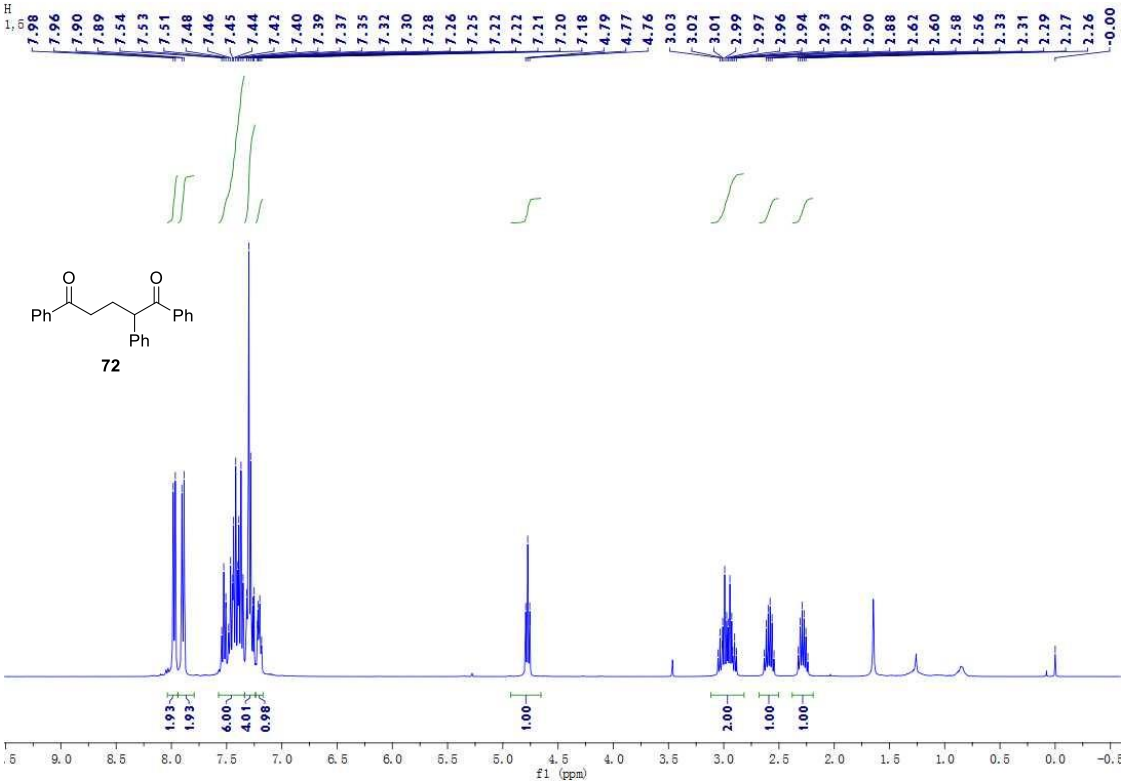
70

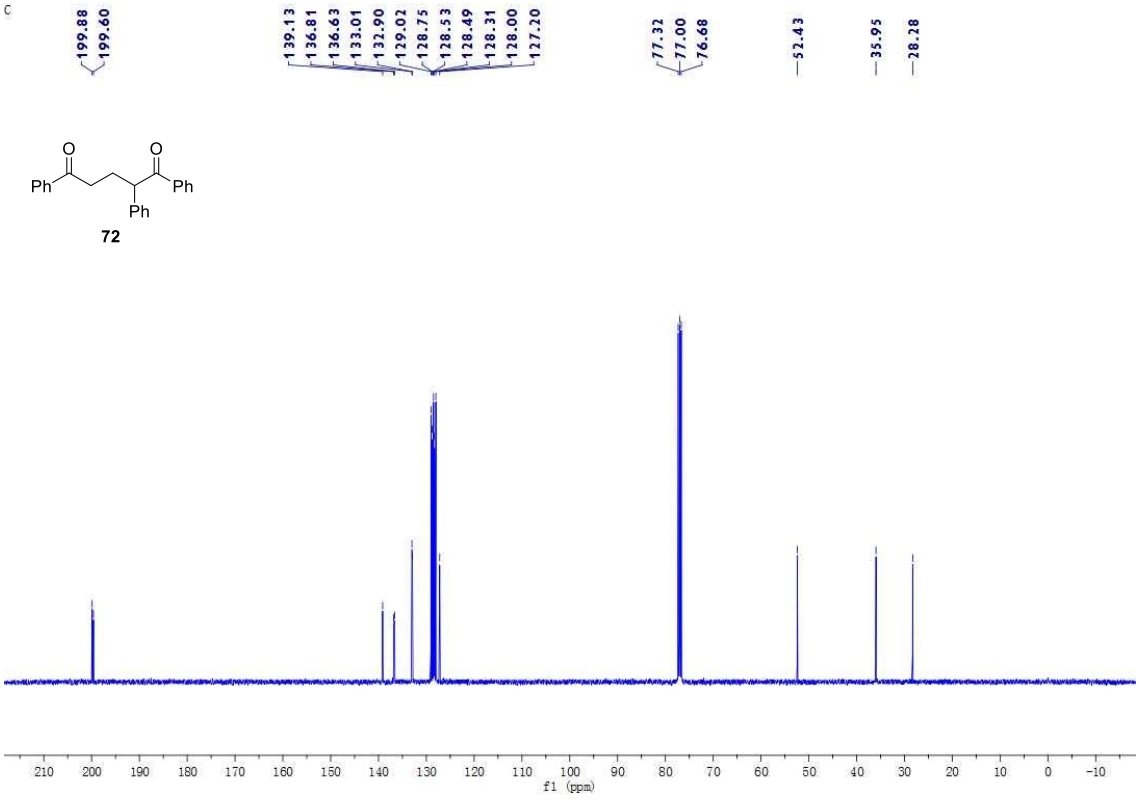

164.50 160.88 142.93 142.82 137.37 128.34 128.15 128.12 127.88 127.66 126.78 126.54 126.23 124.43
77.32 77.00 76.68 70.21 59.43 47.52 31.93 25.17 17.87
Ph
O
N
Ph
f1 (ppm)

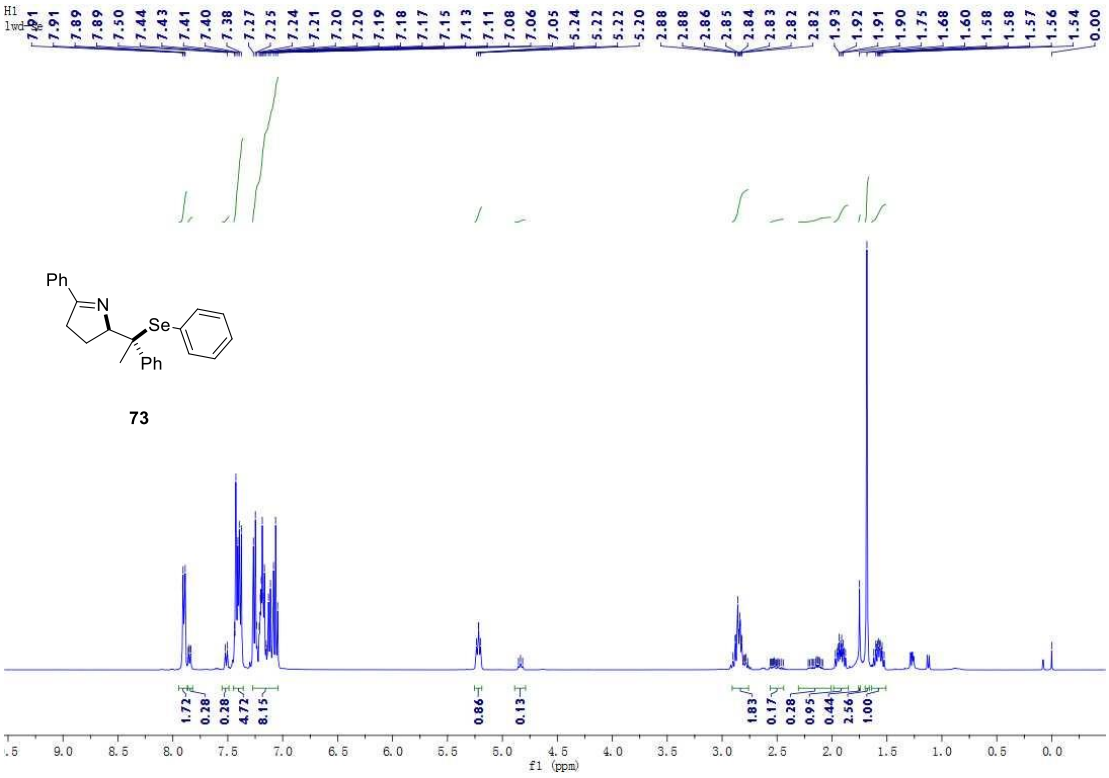
70


H
1.5H
8.24
8.22
7.70
7.70
7.69
7.68
7.46
7.45
7.44
7.43
7.42
7.41
7.41
7.33
7.31
7.29
7.28
7.27
7.24
7.23
7.23
7.21
7.19
7.17
2.98
2.96
2.76
2.74
2.72
2.02
2.00
1.98
1.96
1.94
0.00
NO2
O
N
Ph
Ph
71
1.97
2.00
3.02
3.92
3.02
2.00
1.99
2.00
f1 (ppm)

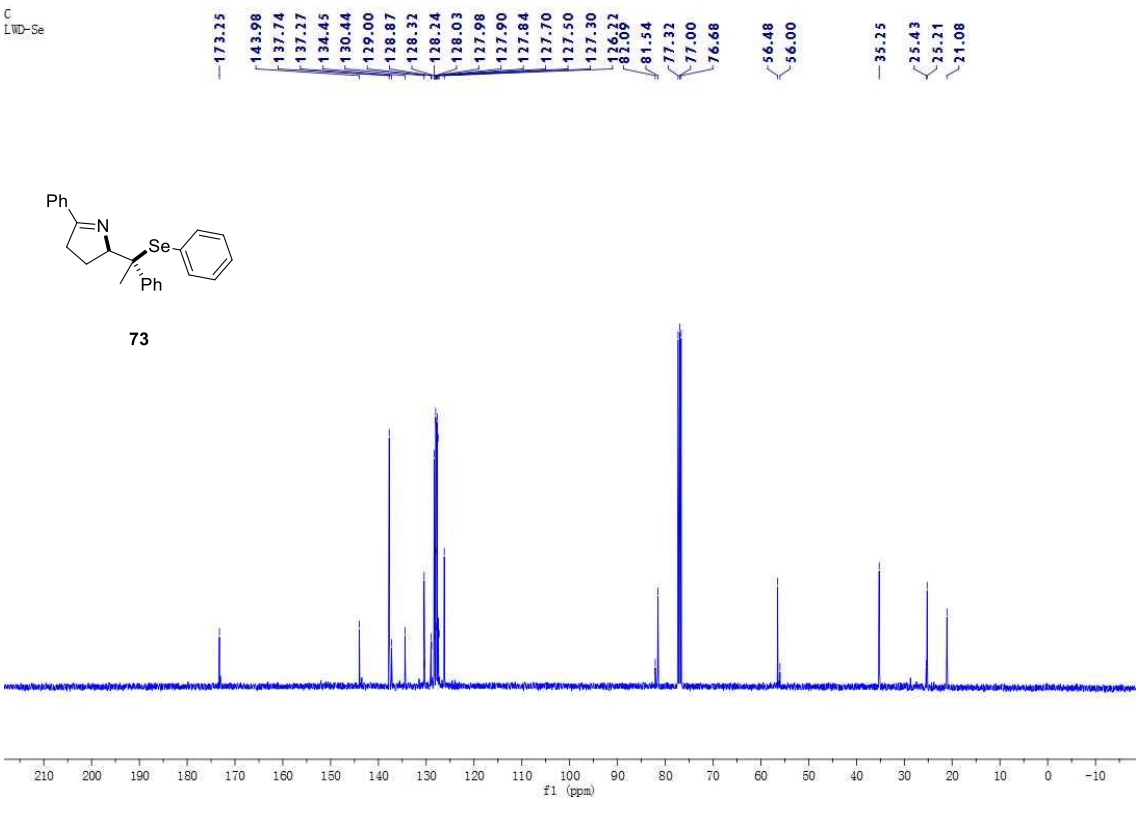

C
164.13
163.94
141.14
134.10
130.38
128.74
128.45
128.40
126.85
126.12
125.69
114.44
77.32
77.00
76.68
35.65
28.17
26.95
NO2
O
N
Ph
Ph
71
f1 (ppm)


7.98 7.96 7.90 7.89 7.54 7.53 7.51 7.48 7.46 7.45 7.44 7.42 7.40 7.39 7.37 7.35 7.32 7.30 7.28 7.26 7.25 7.22 7.22 7.21 7.20 7.18 4.79 4.77 4.76 3.03 3.02 3.01 2.99 2.97 2.96 2.94 2.93 2.92 2.90 2.88 2.62 2.60 2.58 2.56 2.33 2.31 2.29 2.17 2.26 -0.00
Ph
Ph
Ph
72
1.93 1.93 6.00 4.01 0.98 1.00 2.00 1.00 1.00
f1 (ppm)

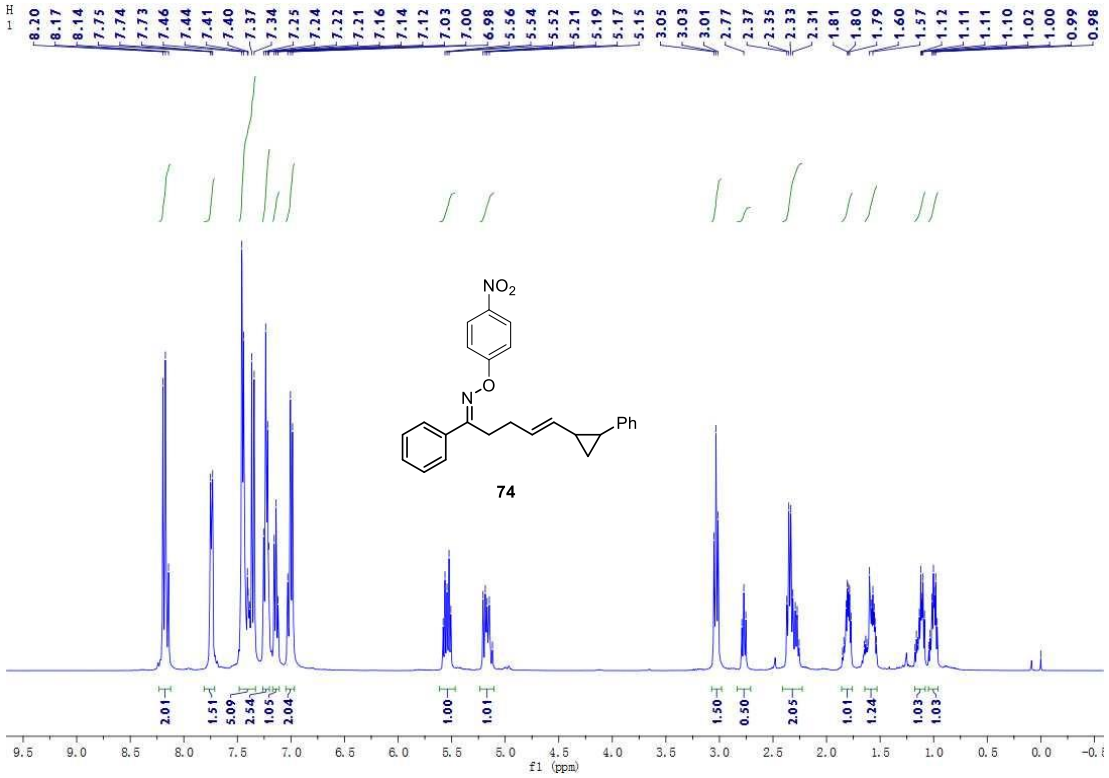

199.88 199.60 139.13 136.81 136.63 133.01 132.90 129.02 128.75 128.53 128.49 128.31 128.00 127.20 77.32 77.00 76.68 52.43 35.95 28.28
Ph
Ph
Ph
72
f1 (ppm)

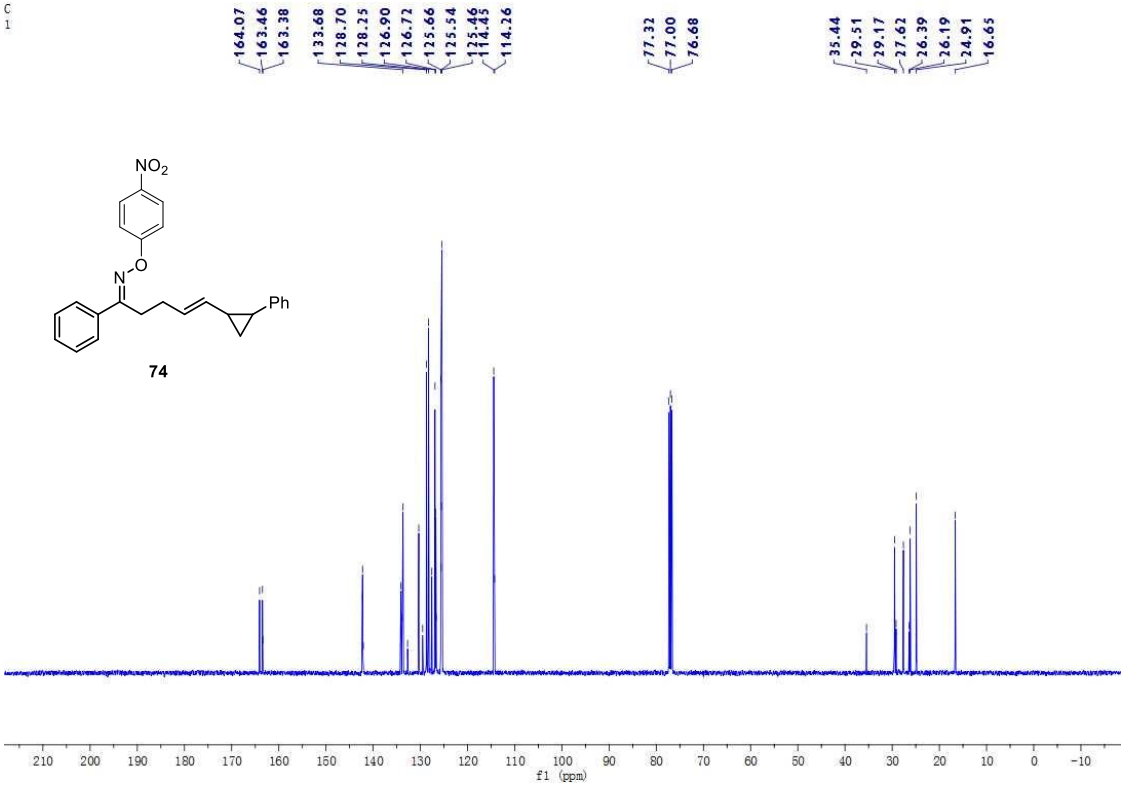

H1
lwd-Se
7.91
7.89
7.50
7.44
7.43
7.41
7.40
7.38
7.27
7.25
7.24
7.21
7.20
7.19
7.18
7.17
7.15
7.13
7.11
7.08
7.06
7.05
5.24
5.22
5.20
2.88
2.86
2.85
2.84
2.83
2.82
1.93
1.92
1.91
1.90
1.75
1.68
1.60
1.58
1.57
1.56
1.54
0.00
Ph
N
Se
Ph
1.72
0.28
0.28
4.72
8.15
0.86
0.13
1.83
0.17
0.28
0.95
0.44
2.56
1.00
f1 (ppm)

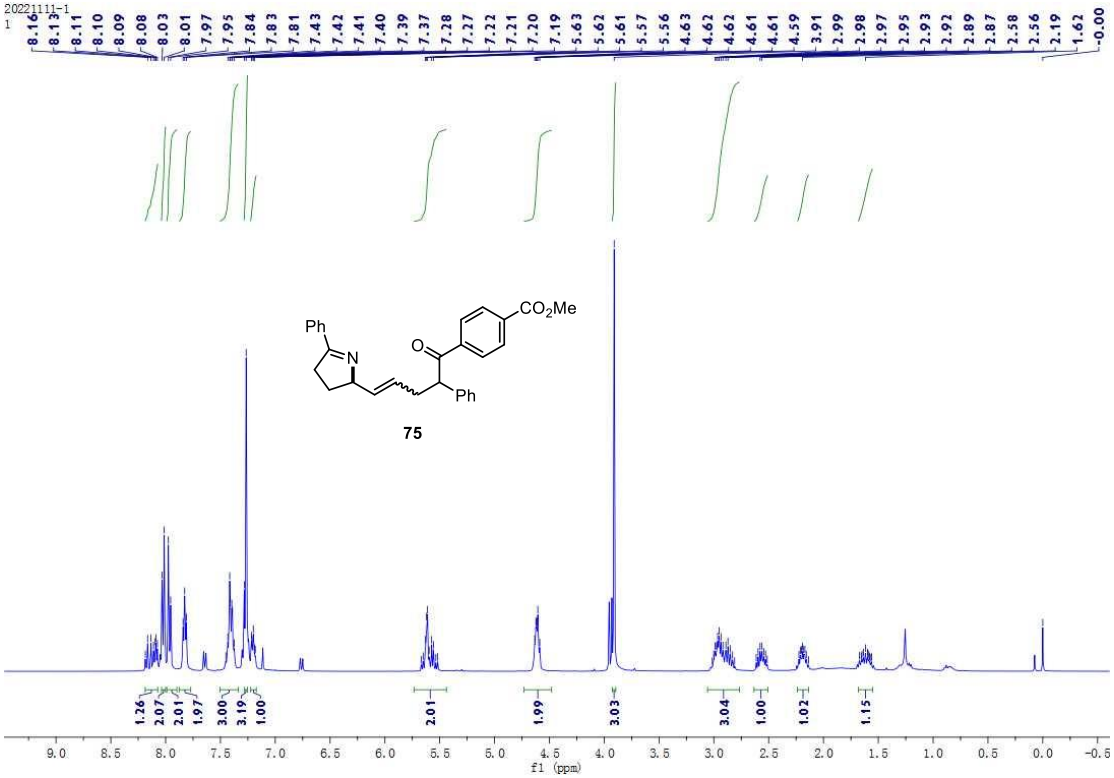
73

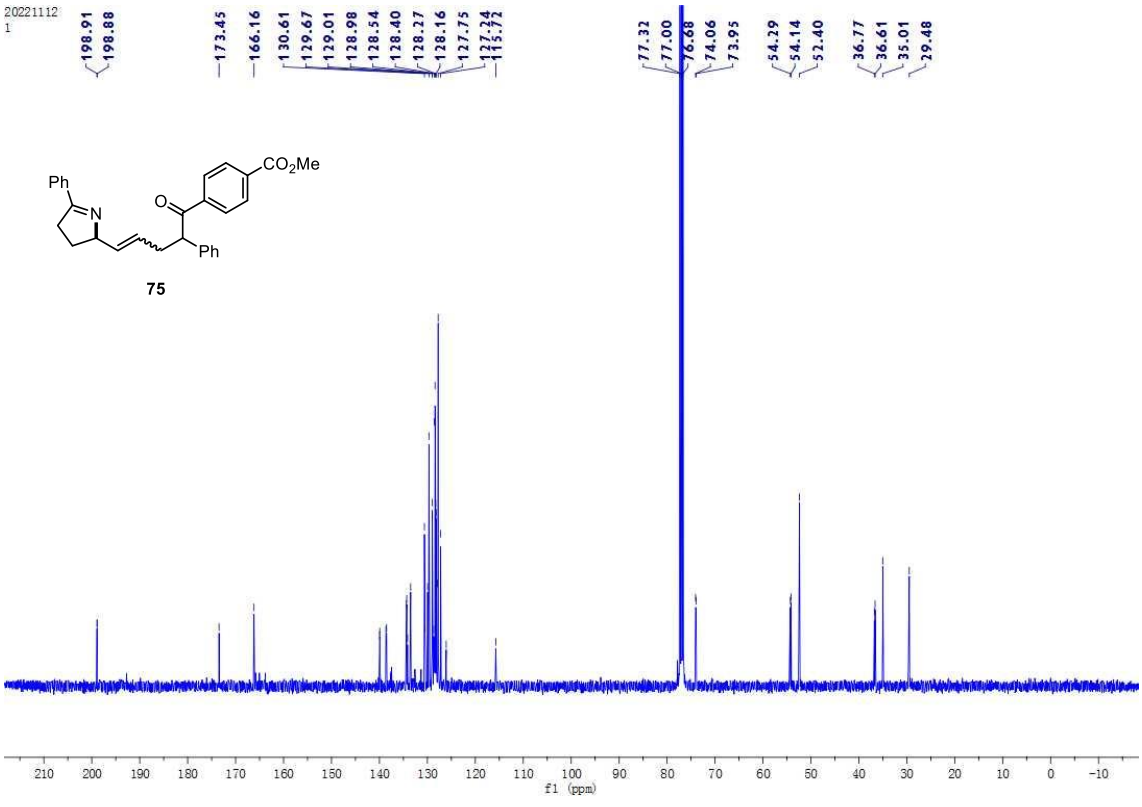

C
LWD-Se
173.25
143.98
137.74
137.27
134.45
130.44
129.00
128.87
128.32
128.24
128.03
127.98
127.90
127.84
127.70
127.50
127.30
126.22
82.09
81.54
77.32
77.00
76.68
56.48
56.00
35.25
25.43
25.21
21.08
Ph
N
Se
Ph
f1 (ppm)

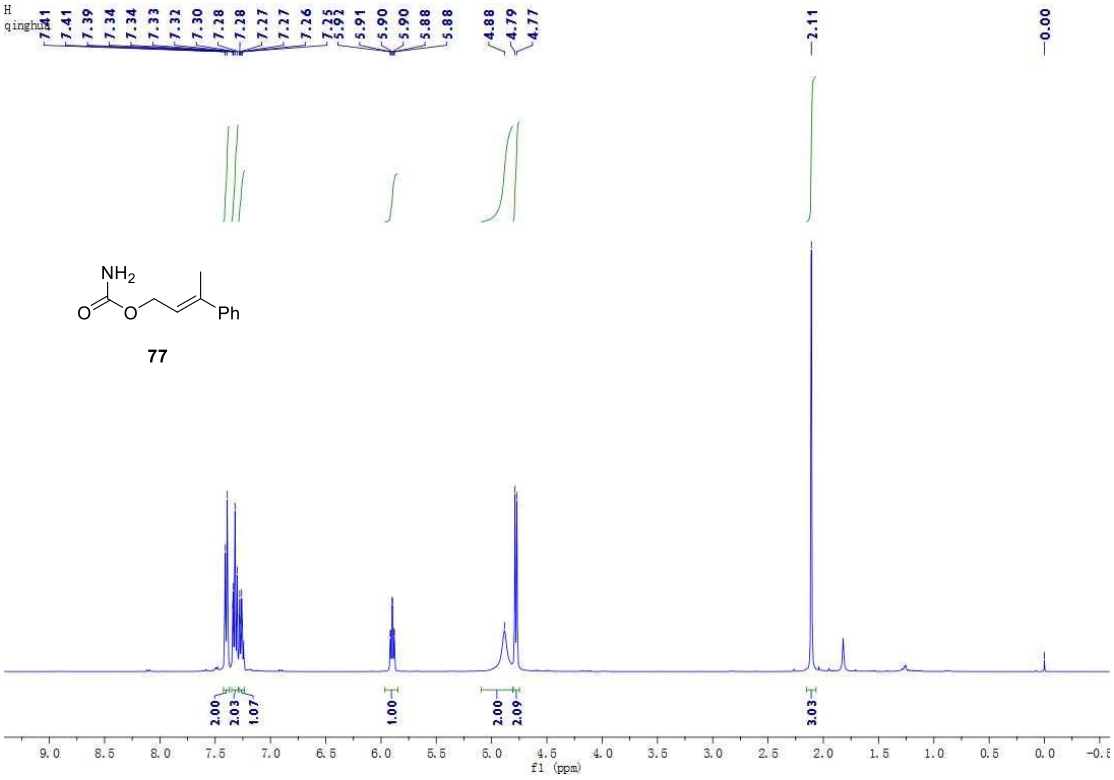
73


8.20 8.17 8.14 7.75 7.74 7.73 7.46 7.44 7.41 7.40 7.37 7.34 7.25 7.24 7.22 7.21 7.16 7.14 7.12 7.03 7.00 6.98 5.56 5.54 5.52 5.21 5.19 5.17 5.15 3.05 3.03 3.01 2.77 2.37 2.35 2.33 2.31 1.81 1.80 1.79 1.60 1.57 1.12 1.11 1.11 1.10 1.02 1.00 0.99 0.98
NO2
O
N
Ph
74
2.01 1.51 5.09 2.54 1.05 2.04 1.00 1.01 1.50 0.50 2.05 1.01 1.24 1.03 1.03
f1 (ppm)

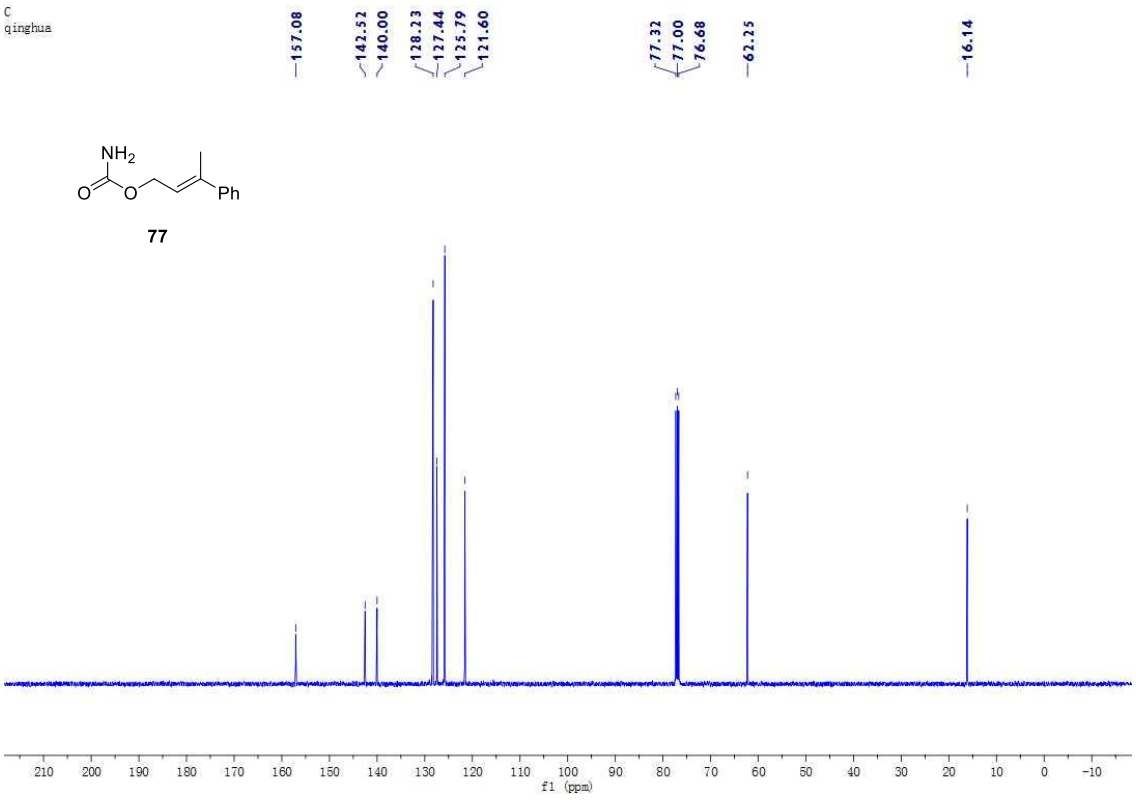

164.07 163.46 163.38 133.68 128.70 128.25 126.90 126.72 125.66 125.54 114.43 114.26 77.32 77.00 76.68 35.44 29.51 29.17 27.62 26.39 26.19 24.91 16.65
NO2
O
N
Ph
74
f1 (ppm)


20221111-1
1
Ph
N
O
CO2Me
Ph
75
f1 (ppm)

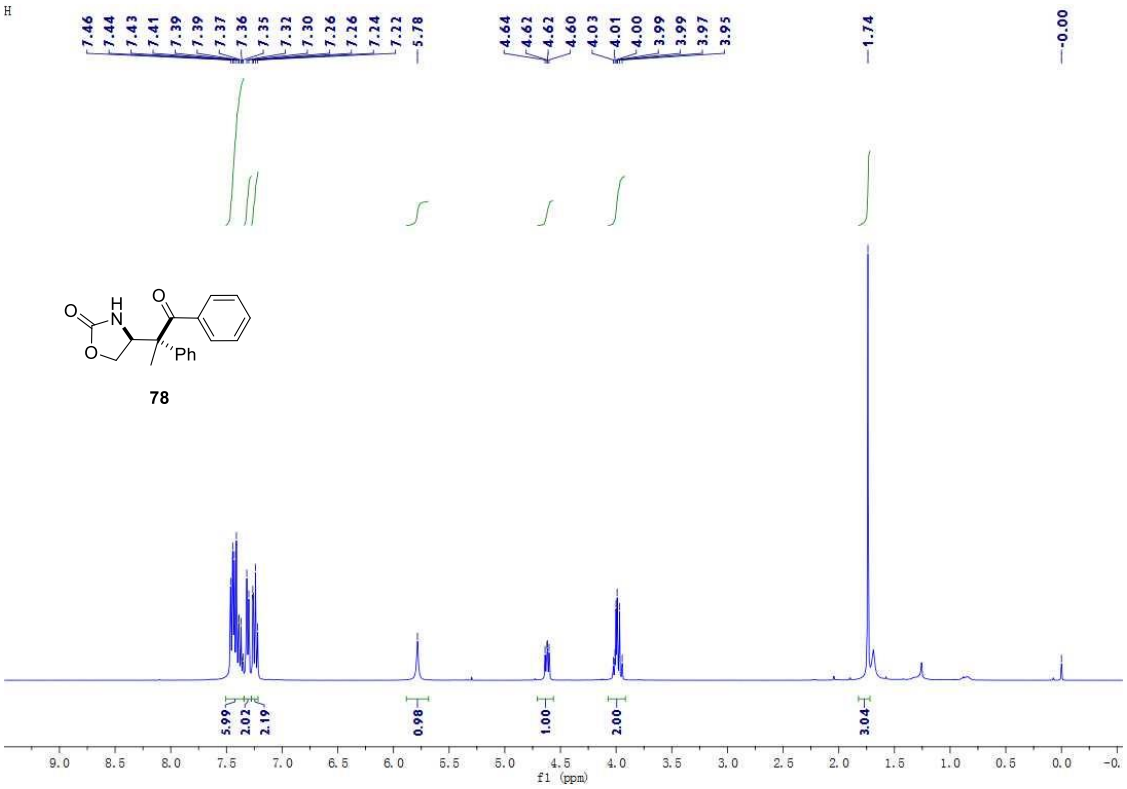

20221112
1
Ph
N
O
CO2Me
Ph
75
f1 (ppm)


H
qinghua
7.41
7.39
7.34
7.34
7.33
7.32
7.30
7.28
7.28
7.27
7.27
7.26
5.91
5.90
5.90
5.88
5.88
4.88
4.79
4.77
2.11
0.00
NH2
O
O
Ph
2.00
2.03
1.07
1.00
2.00
2.09
3.03
f1 (ppm)

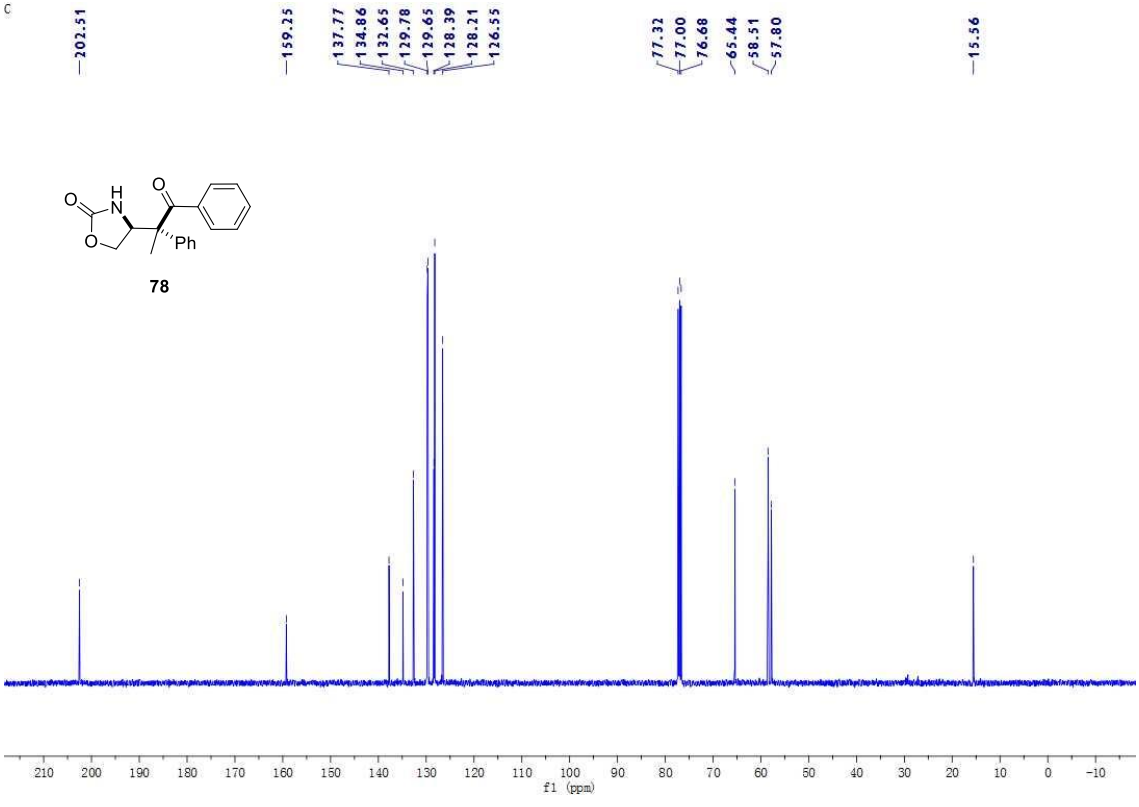
77


C
qinghua
157.08
142.52
140.00
128.23
127.44
125.79
121.60
77.32
77.00
76.68
62.25
16.14
NH2
O
O
Ph
f1 (ppm)

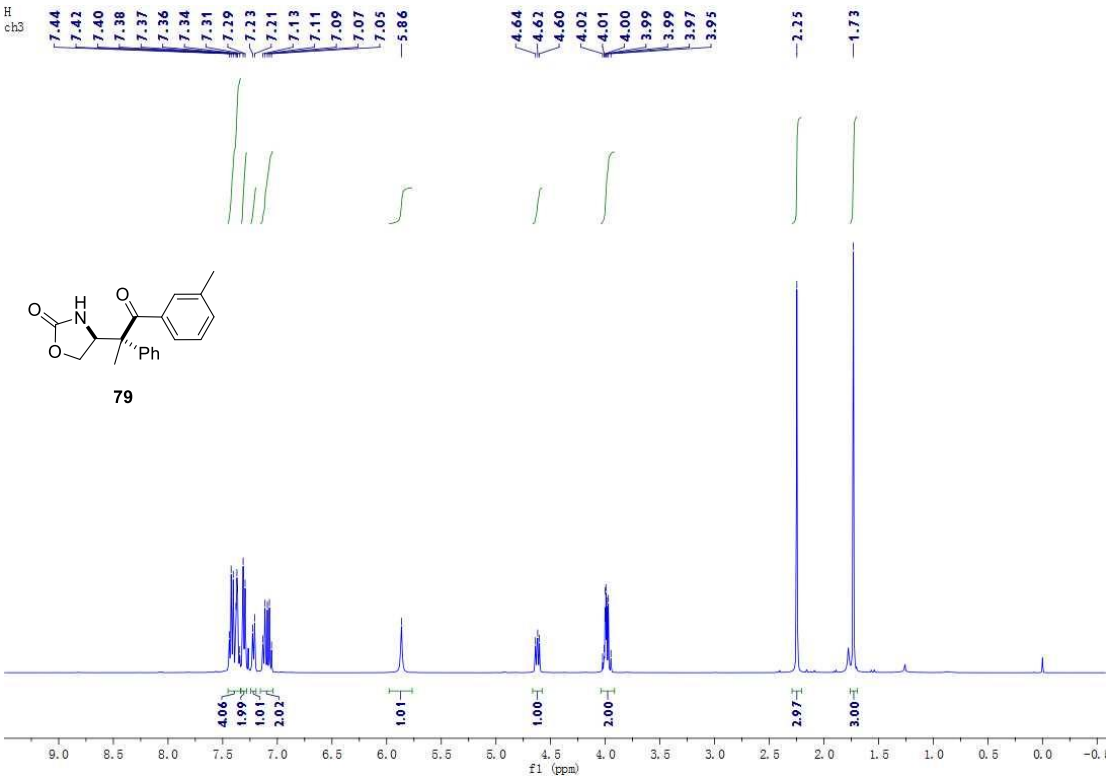
77


H
7.46
7.44
7.43
7.41
7.39
7.39
7.37
7.36
7.35
7.32
7.30
7.26
7.26
7.24
7.22
5.78
4.64
4.62
4.62
4.60
4.03
4.01
4.00
3.99
3.99
3.97
3.95
1.74
0.00
5.99
2.02
2.19
0.98
1.00
2.00
3.04
f1 (ppm)

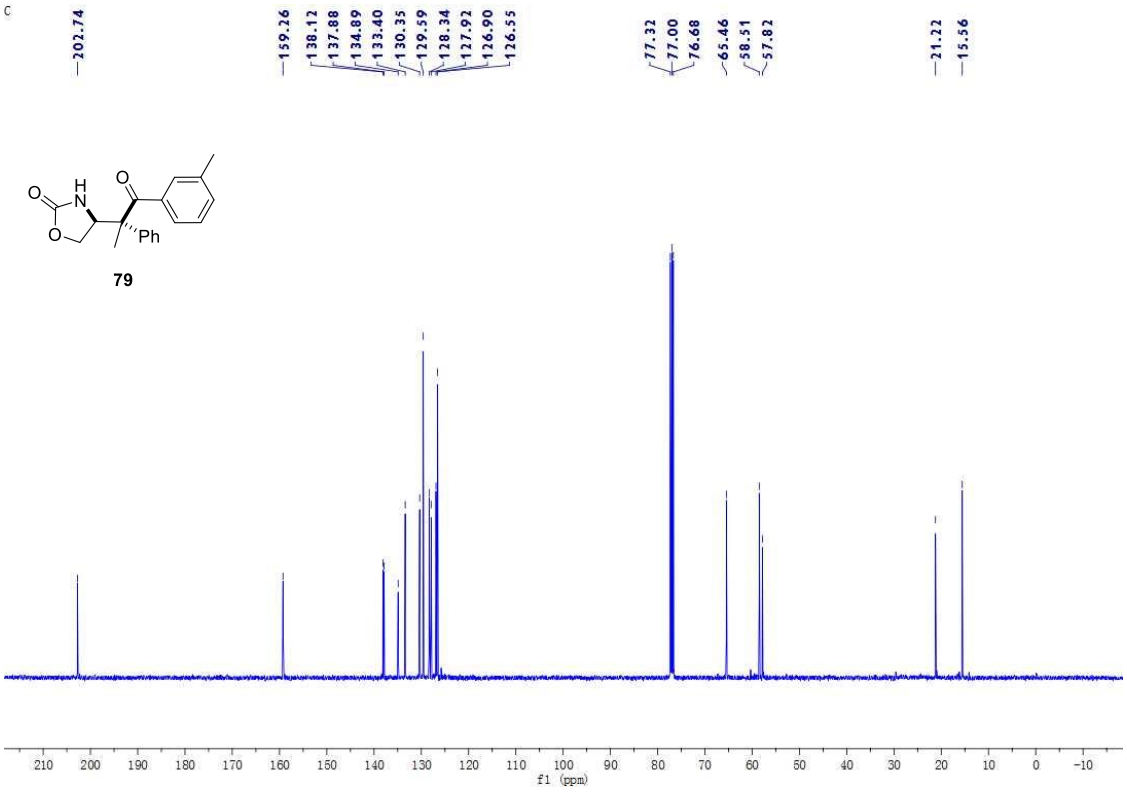
78


C
202.51
159.25
137.77
134.86
132.65
129.78
129.65
128.39
128.21
126.55
77.32
77.00
76.68
65.44
58.51
57.80
15.56
f1 (ppm)

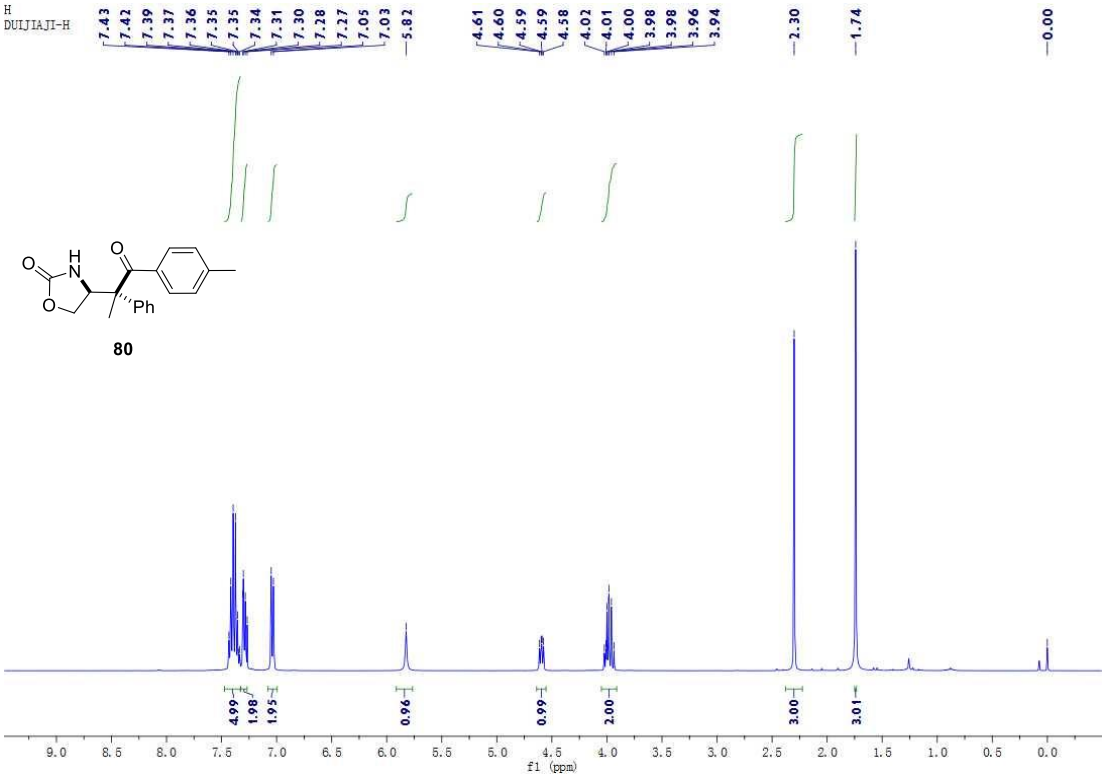
78


H
ch3
7.44
7.42
7.40
7.38
7.37
7.36
7.34
7.31
7.29
7.23
7.21
7.13
7.11
7.09
7.07
7.05
5.86
4.64
4.62
4.60
4.02
4.01
4.00
3.99
3.99
3.97
3.95
2.25
1.73
4.06
1.99
1.01
2.02
1.01
1.00
2.00
2.97
3.00
f1 (ppm)

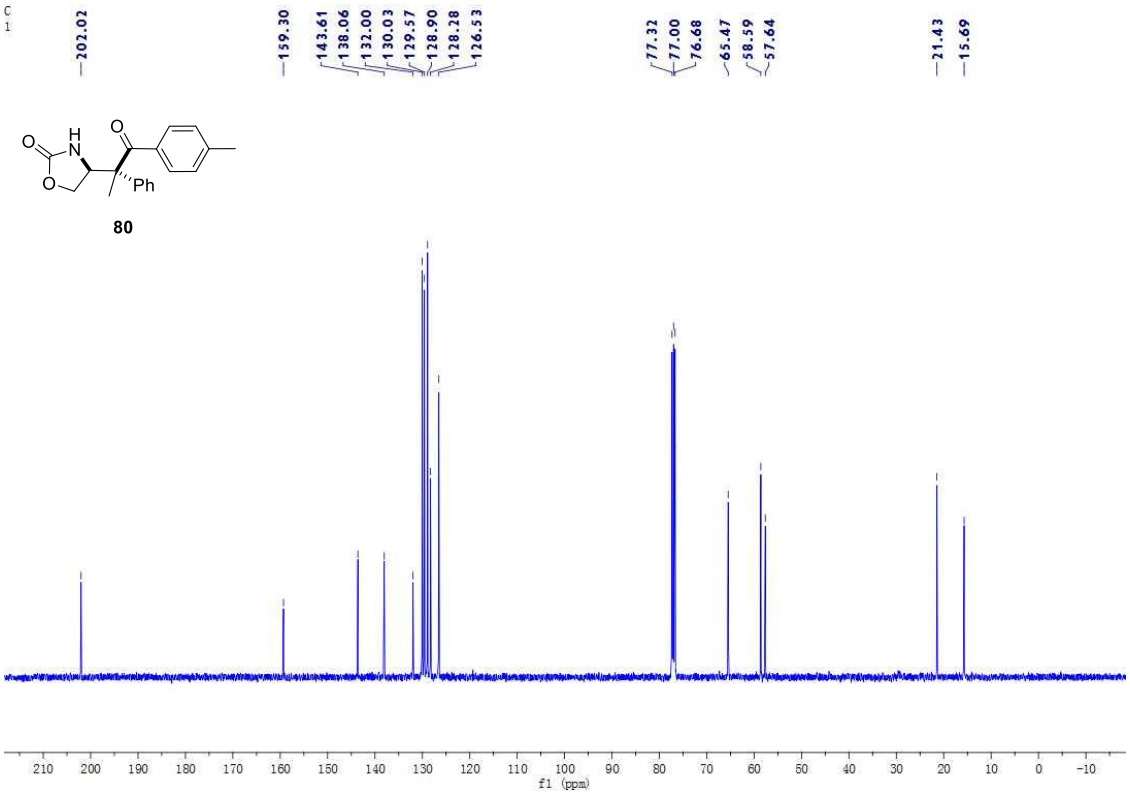
79


C
202.74
159.26
138.12
137.88
134.89
133.40
130.35
129.59
128.34
127.92
126.90
126.55
77.32
77.00
76.68
65.46
58.51
57.82
21.22
15.56
f1 (ppm)

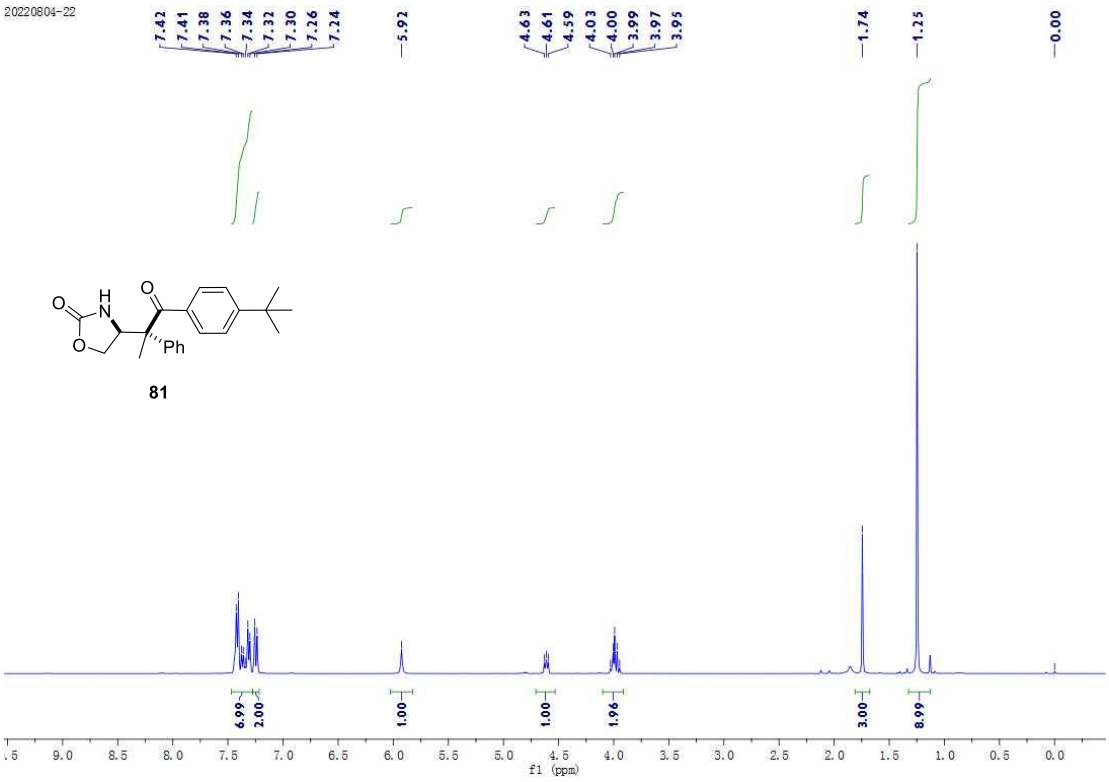
79


H
DUIJIAJI-H
7.43
7.42
7.39
7.37
7.36
7.35
7.35
7.34
7.31
7.30
7.28
7.27
7.05
7.03
5.82
4.61
4.60
4.59
4.59
4.58
4.02
4.01
4.00
3.98
3.98
3.96
3.94
2.30
1.74
0.00
O
H
N
O
O
Ph
4.99
1.98
1.95
0.96
0.99
2.00
3.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

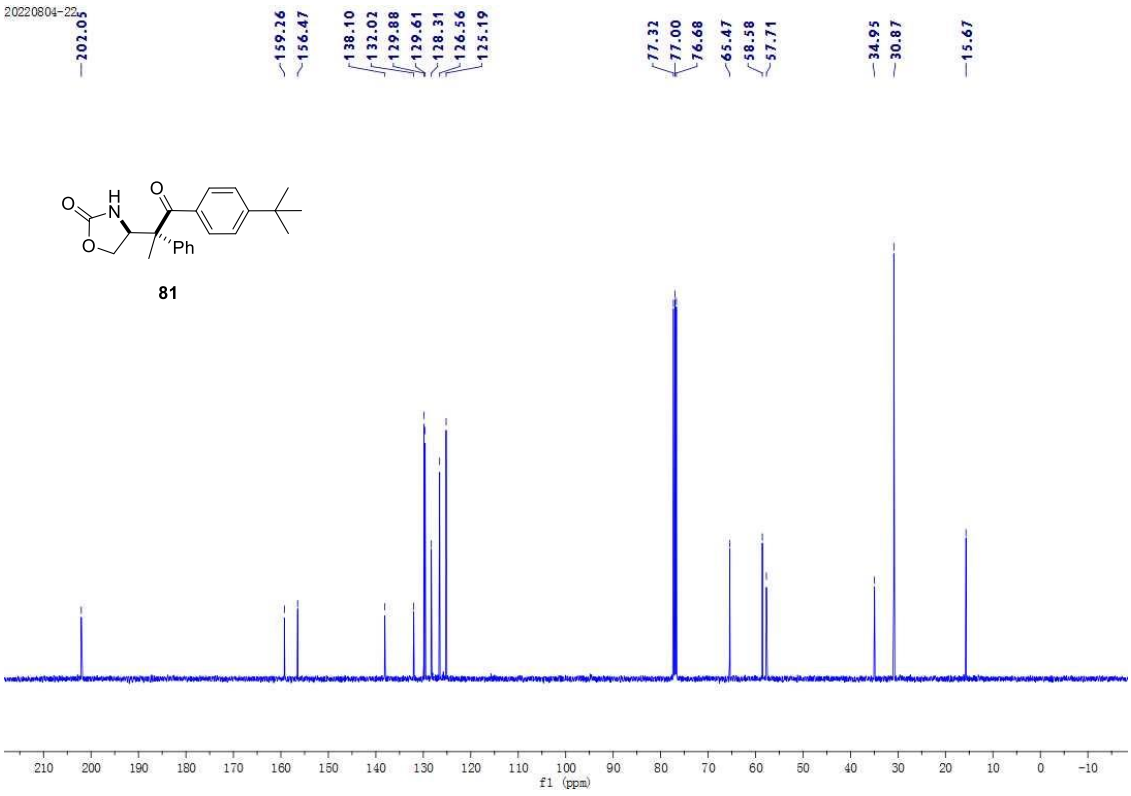
80


C
1
202.02
159.30
143.61
138.06
132.00
130.03
129.57
128.90
128.28
126.53
77.32
77.00
76.68
65.47
58.59
57.64
21.43
15.69
O
H
N
O
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

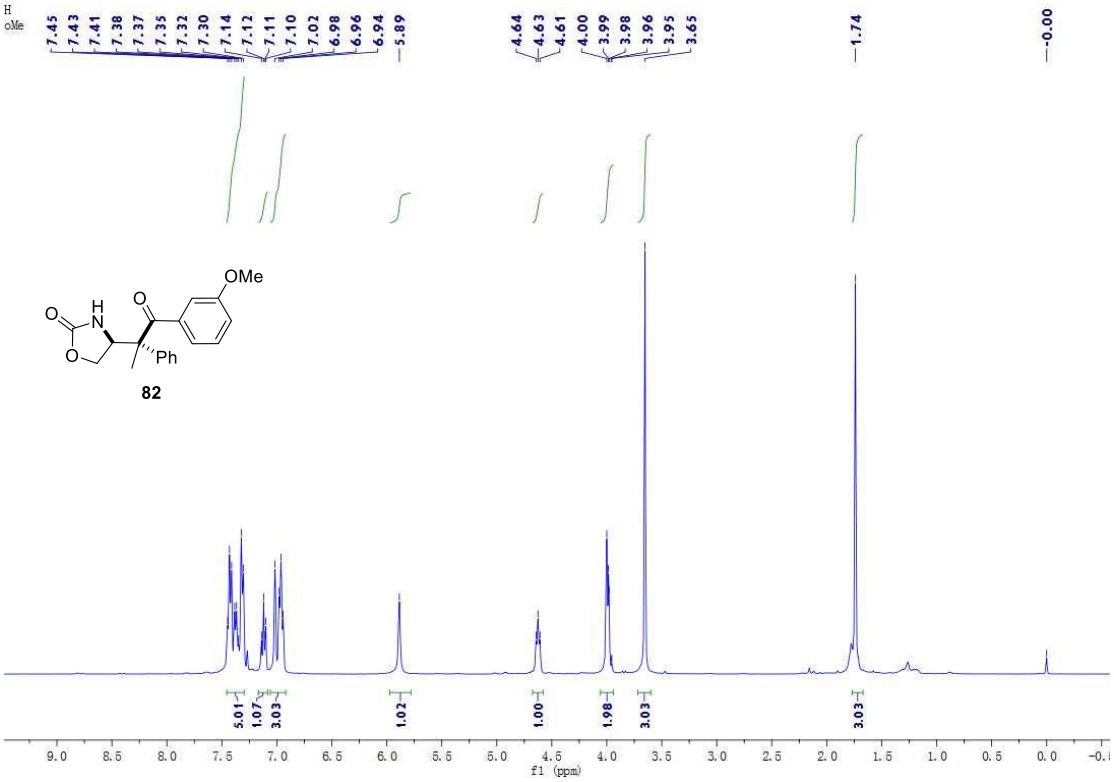
80

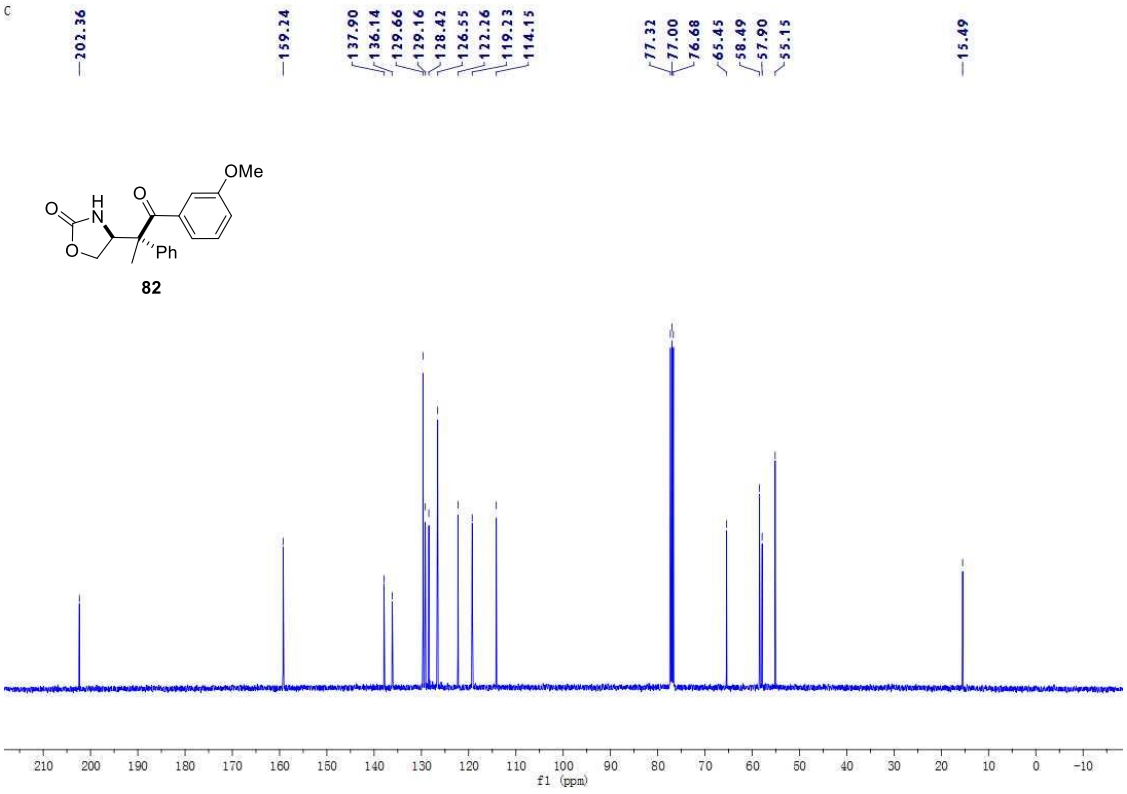

20220804-22
7.42
7.41
7.38
7.36
7.34
7.32
7.30
7.26
7.24
5.92
4.63
4.61
4.59
4.03
4.00
3.99
3.97
3.95
1.74
1.25
0.00
6.99
2.00
1.00
1.00
1.96
3.00
8.99
f1 (ppm)

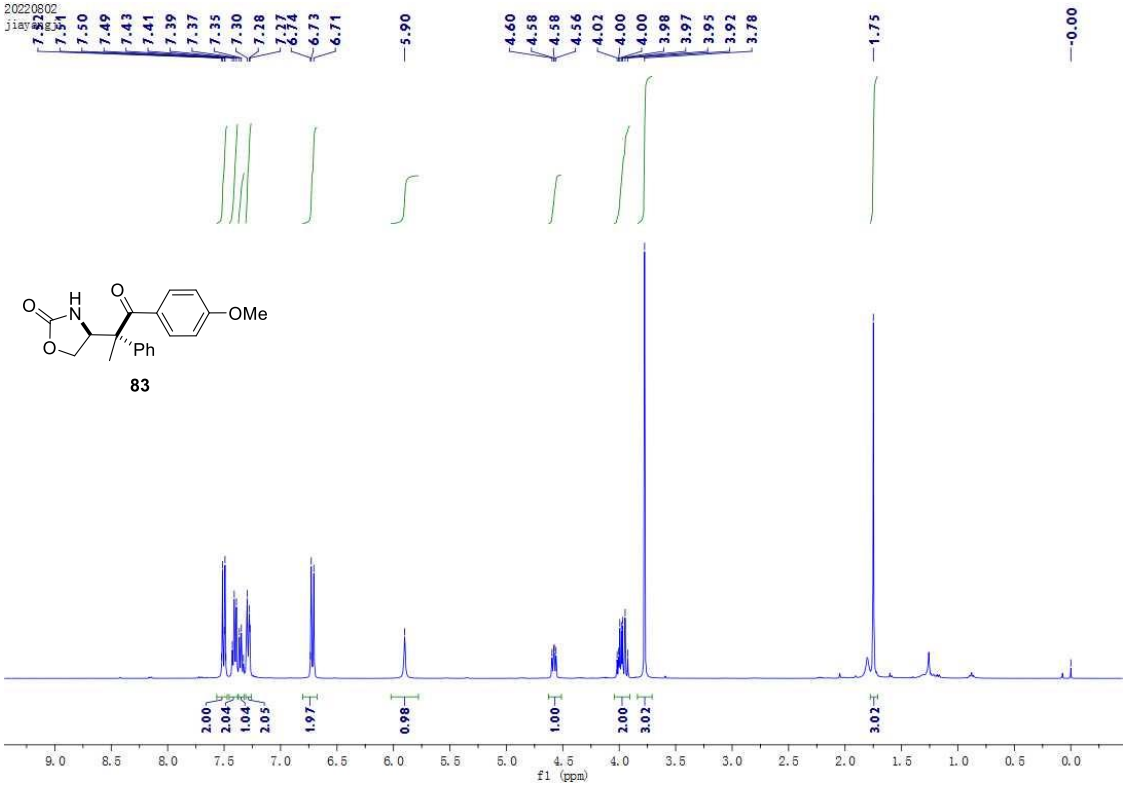
81

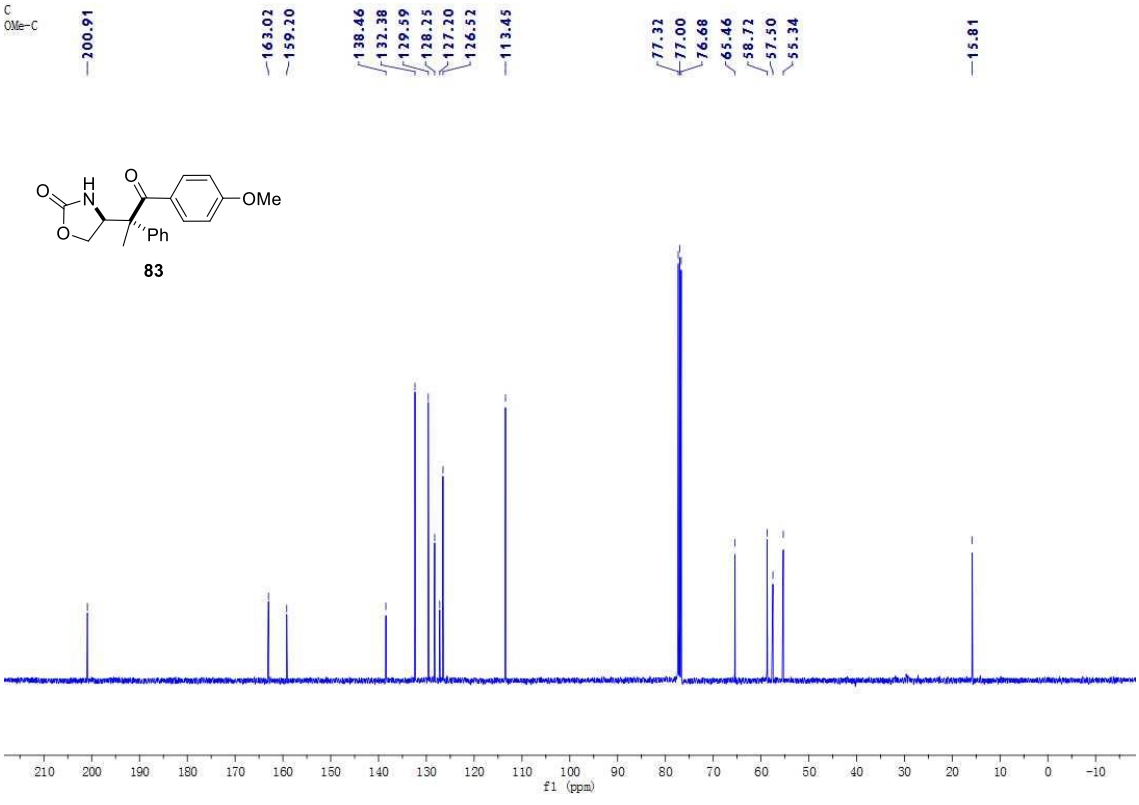

20220804-22
202.05
159.26
156.47
138.10
132.02
129.88
129.61
128.31
126.56
125.19
77.32
77.00
76.68
65.47
58.58
57.71
34.95
30.87
15.67
f1 (ppm)

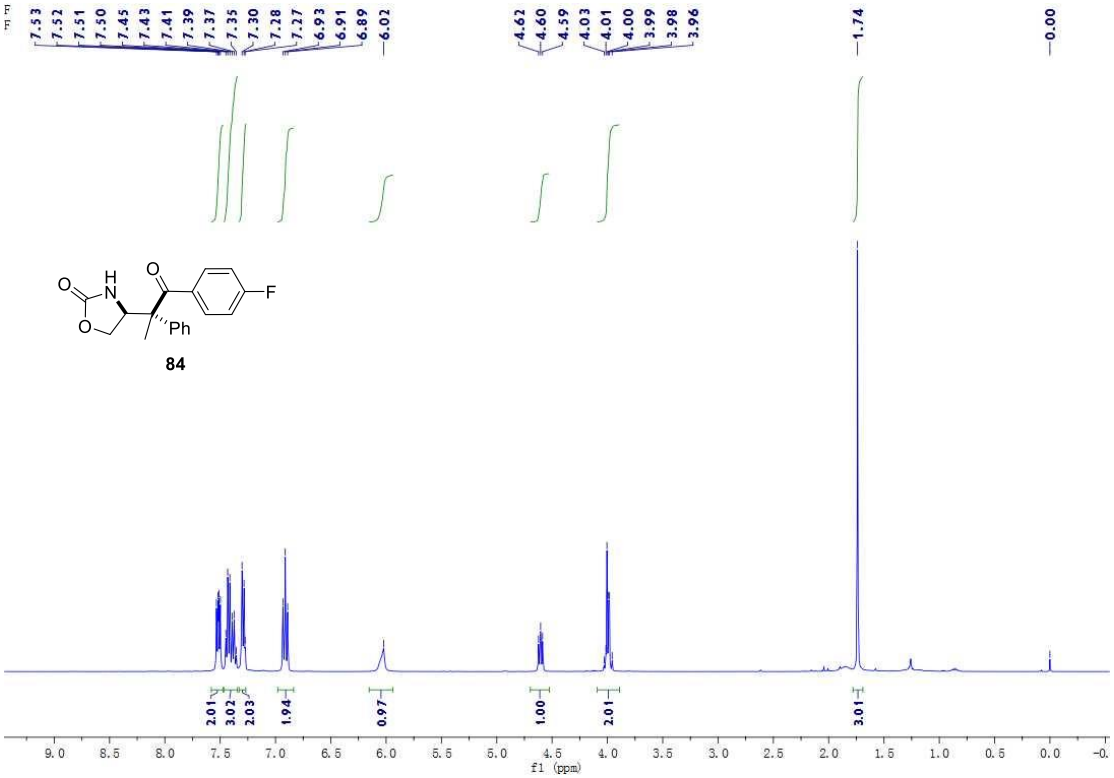
81


7.45
7.43
7.41
7.38
7.37
7.35
7.32
7.30
7.14
7.12
7.11
7.10
7.02
6.98
6.96
6.94
5.89
4.64
4.63
4.61
4.00
3.99
3.98
3.96
3.95
3.65
1.74
0.00
OMe
O
H
N
O
O
Ph
82
5.01
1.07
3.03
1.02
1.00
1.98
3.03
3.03
f1 (ppm)

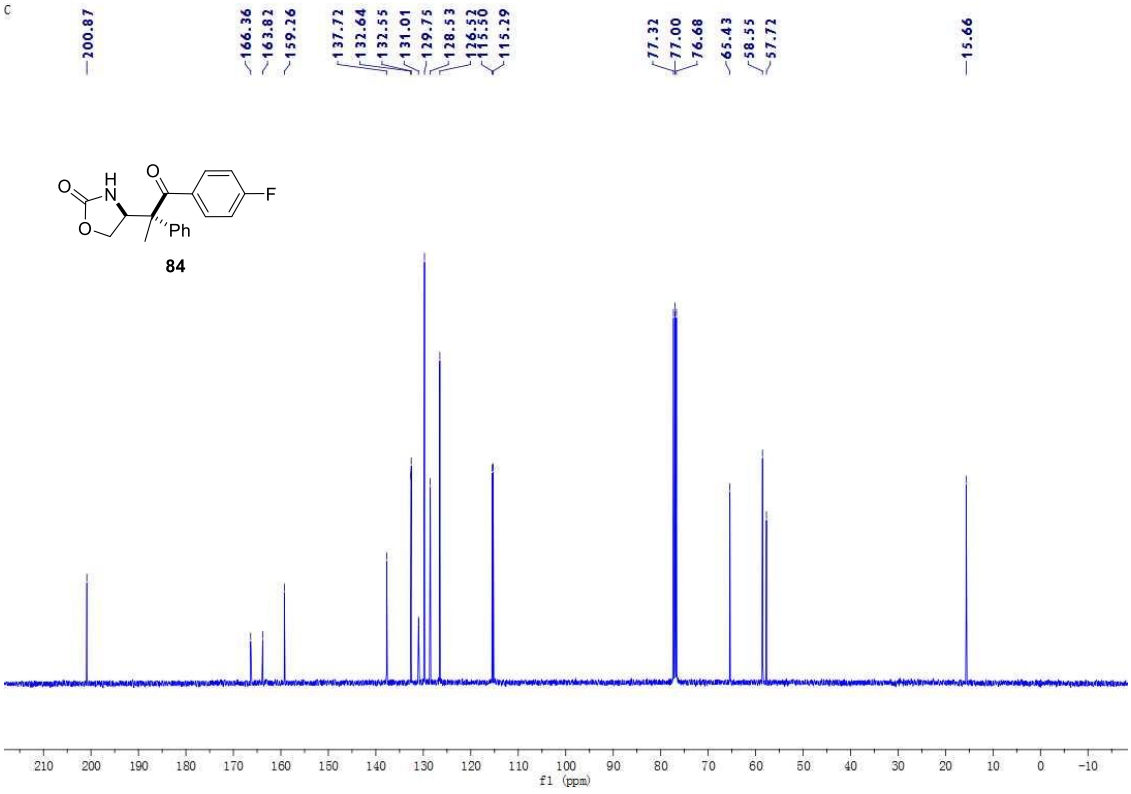

202.36
159.24
137.90
136.14
129.66
129.16
128.42
126.55
122.26
119.23
114.15
77.32
77.00
76.68
65.45
58.49
57.90
55.15
15.49
OMe
O
H
N
O
O
Ph
82
f1 (ppm)


20220802
7.52
7.51
7.50
7.49
7.43
7.41
7.39
7.37
7.35
7.30
7.28
7.27
6.74
6.73
6.71
5.90
4.60
4.58
4.58
4.56
4.02
4.00
4.00
3.98
3.97
3.95
3.92
3.78
1.75
0.00
OMe
Ph
83
2.00
2.04
1.04
2.05
1.97
0.98
1.00
2.00
3.02
3.02
f1 (ppm)

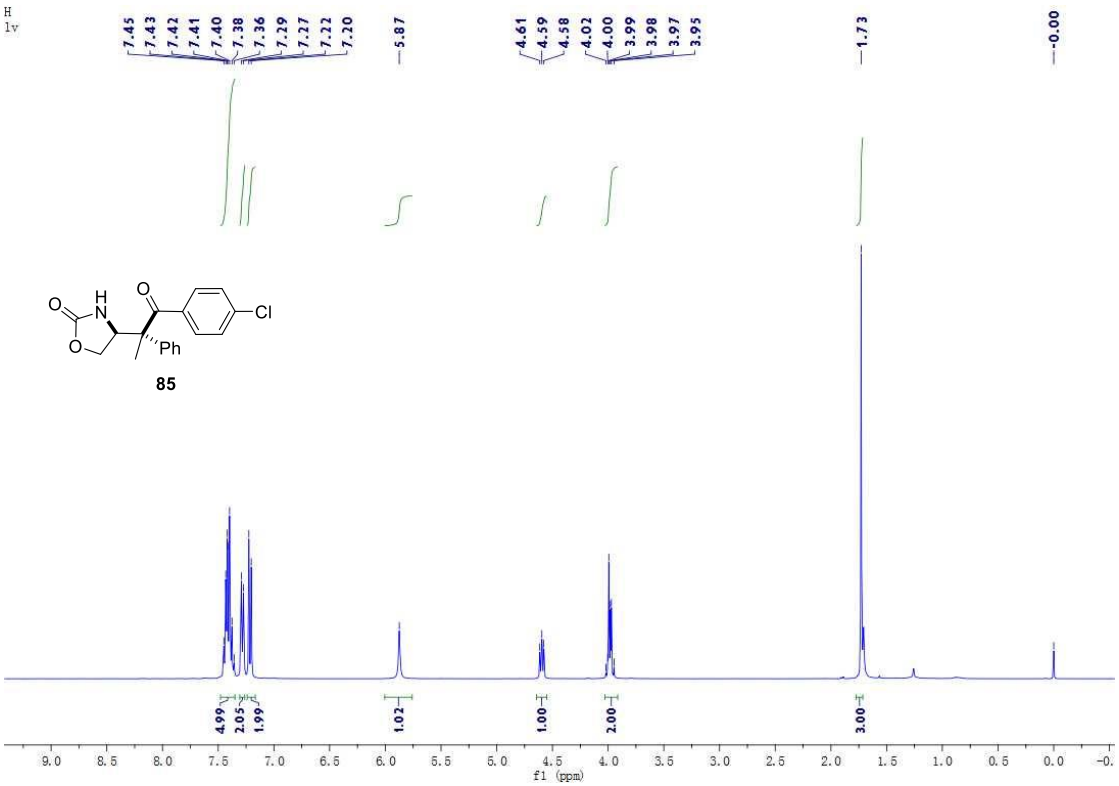

C
OMe-C
200.91
163.02
159.20
138.46
132.38
129.59
128.25
127.20
126.52
113.45
77.32
77.00
76.68
65.46
58.72
57.50
55.34
15.81
OMe
Ph
83
f1 (ppm)

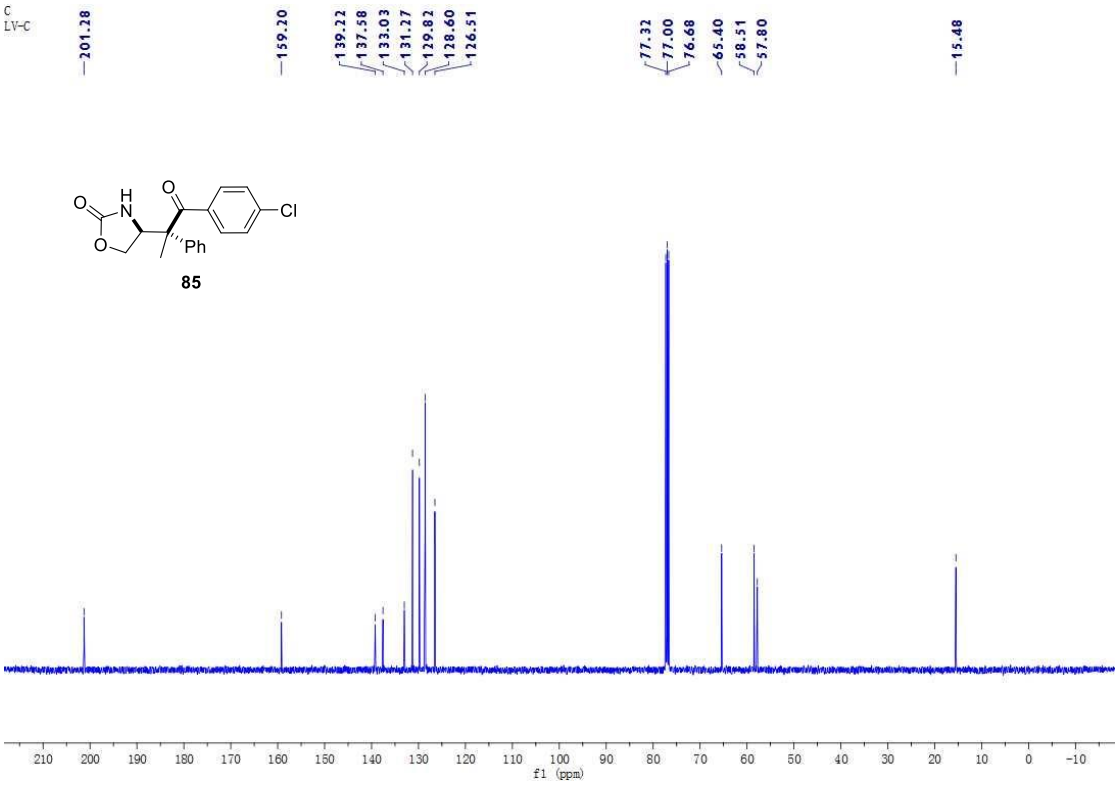

7.53
7.52
7.51
7.50
7.45
7.43
7.41
7.39
7.37
7.35
7.30
7.28
7.27
6.93
6.91
6.89
6.02
4.62
4.60
4.59
4.03
4.01
4.00
3.99
3.98
3.96
1.74
0.00
2.01
3.02
2.03
1.94
0.97
1.00
2.01
3.01
f1 (ppm)

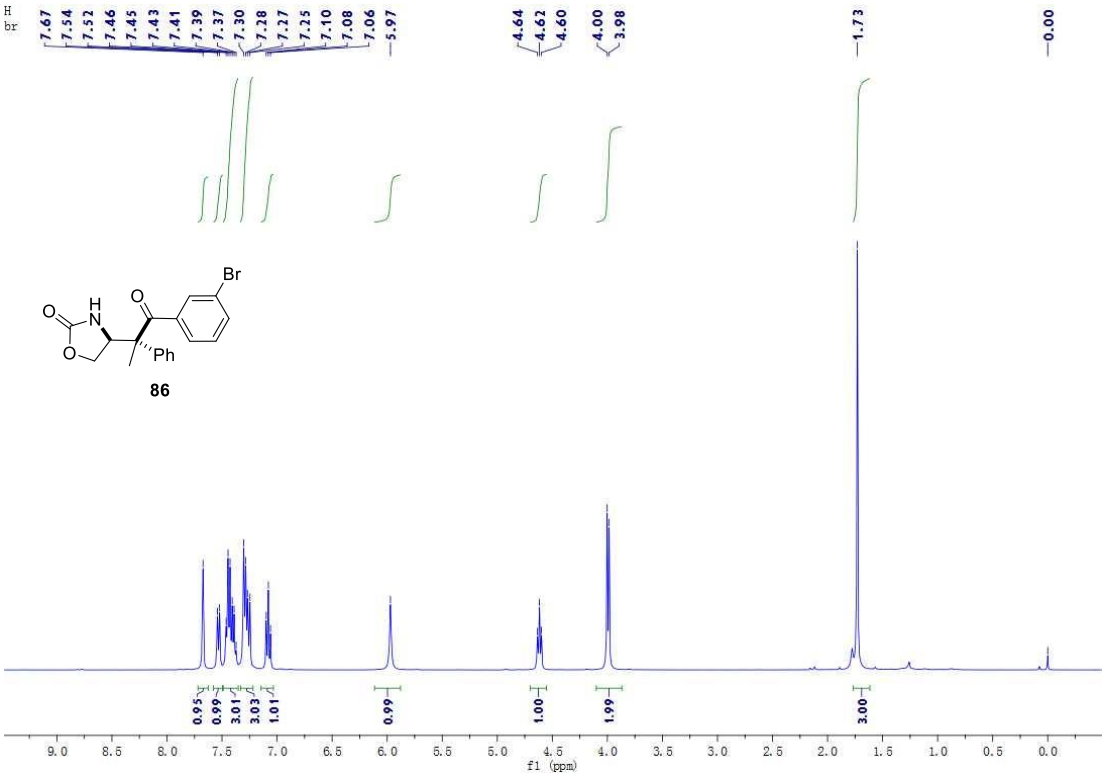
84

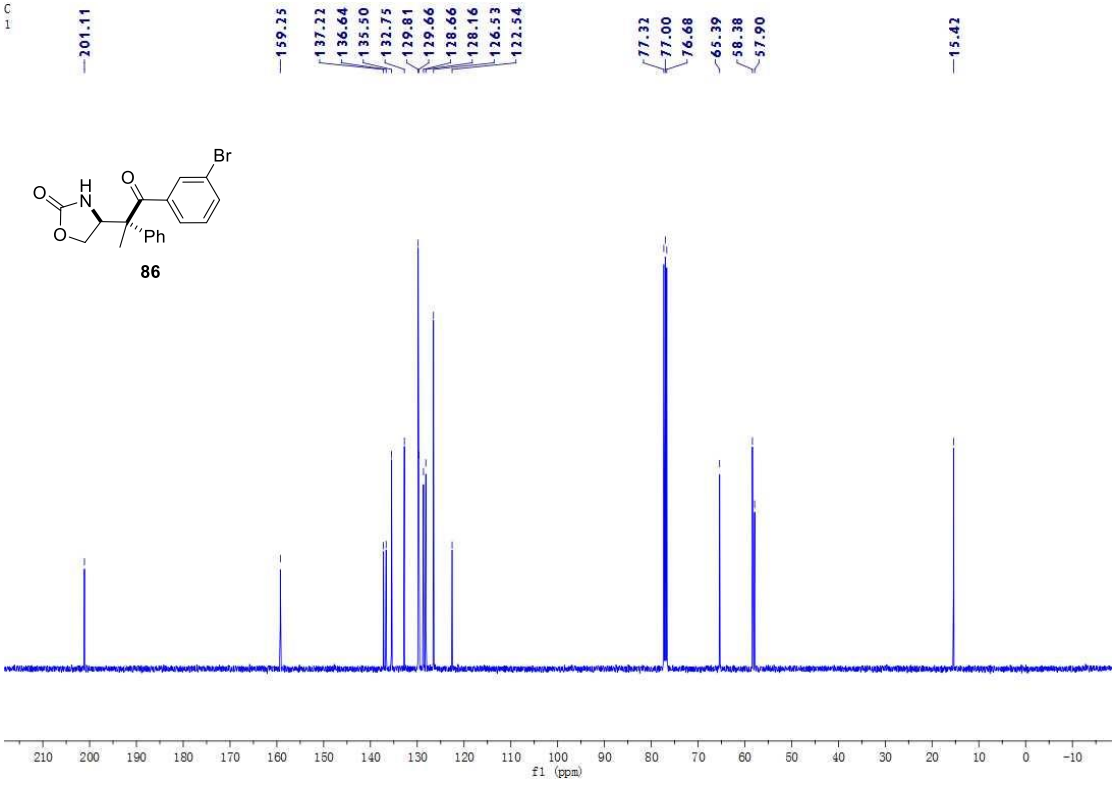

200.87
166.36
163.82
159.26
137.72
132.64
132.55
131.01
129.75
128.53
126.52
115.50
115.29
77.32
77.00
76.68
65.43
58.55
57.72
15.66
f1 (ppm)

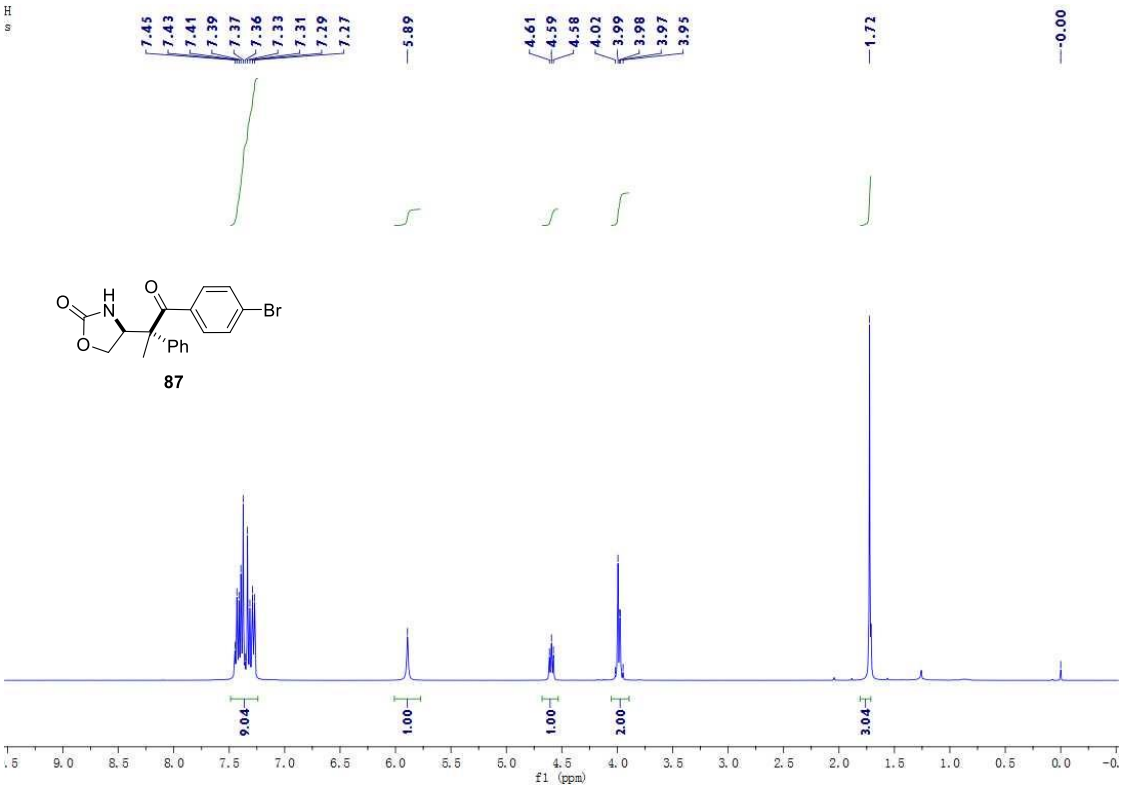
84

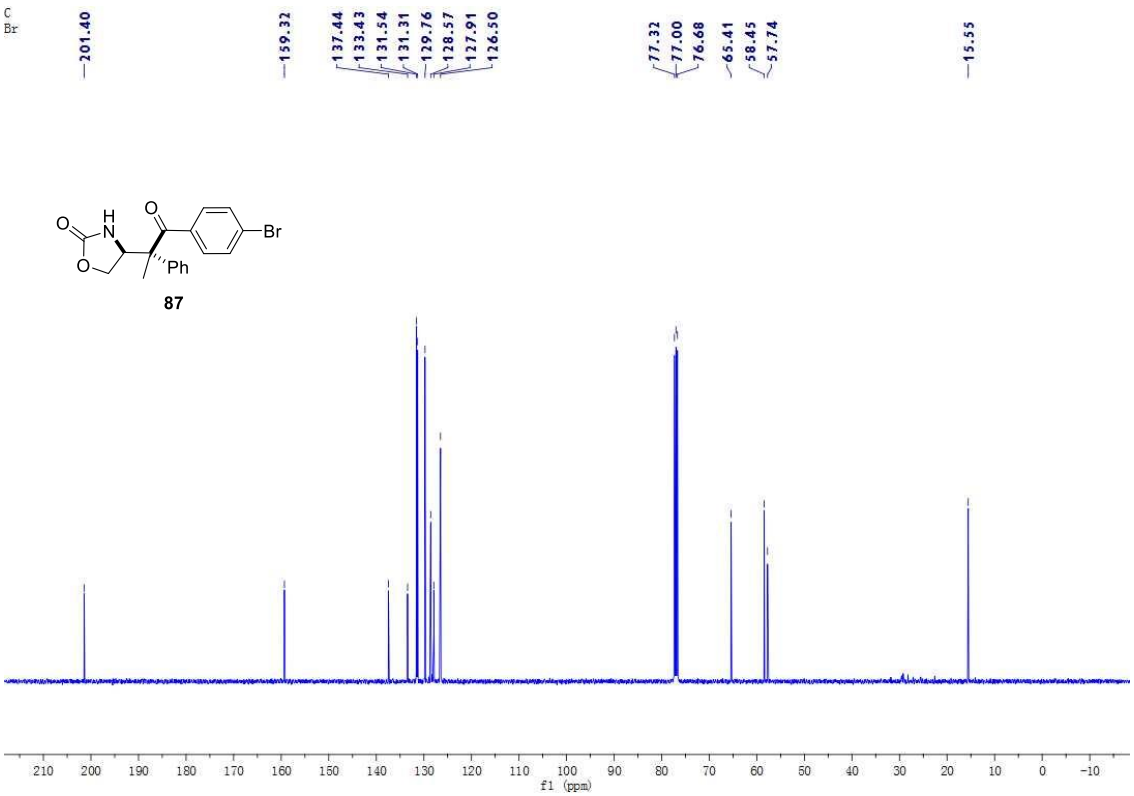

H
lv
7.45
7.43
7.42
7.41
7.40
7.38
7.36
7.29
7.27
7.22
7.20
5.87
4.61
4.59
4.58
4.02
4.00
3.99
3.98
3.97
3.95
1.73
0.00
Cl
Ph
85
4.99
2.05
1.99
1.02
1.00
2.00
3.00
f1 (ppm)

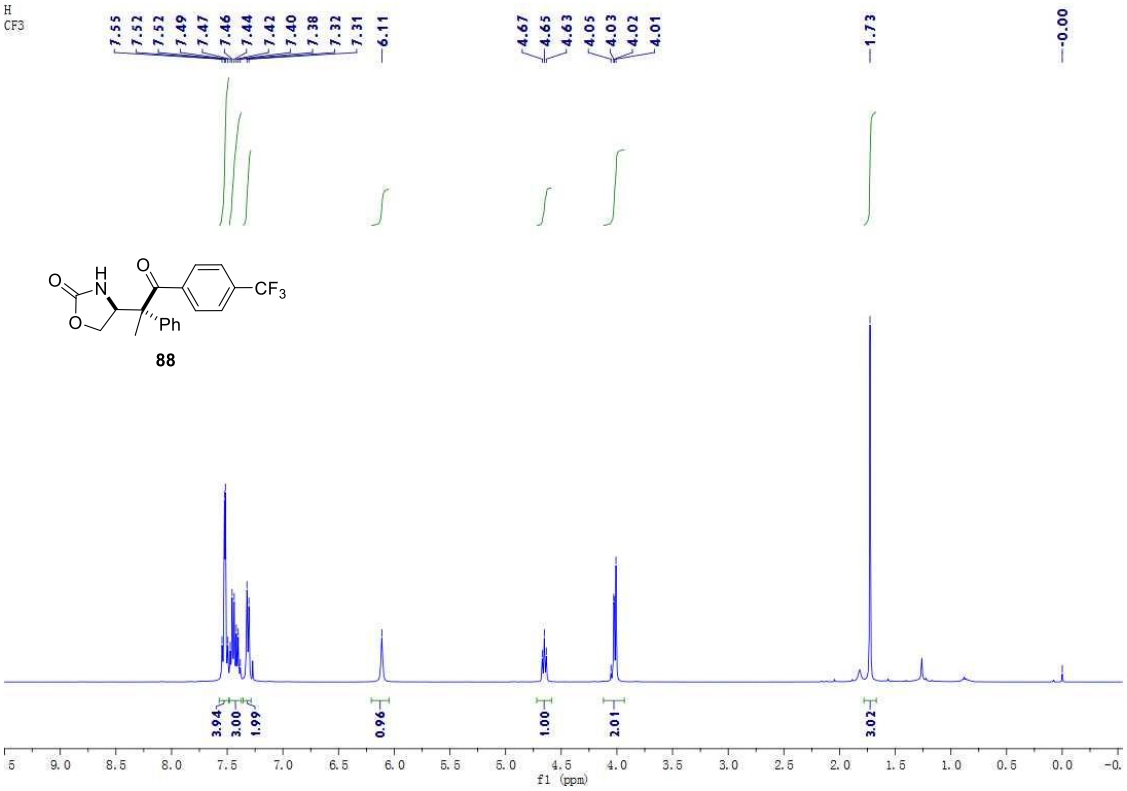

C
LV-C
201.28
159.20
139.22
137.58
133.03
131.27
129.82
128.60
126.51
77.32
77.00
76.68
65.40
58.51
57.80
15.48
Cl
Ph
85
f1 (ppm)


H
br
7.67
7.54
7.52
7.46
7.45
7.43
7.41
7.39
7.37
7.30
7.28
7.27
7.25
7.10
7.08
7.06
5.97
4.64
4.62
4.60
4.00
3.98
1.73
0.00
Br
O
H
N
O
O
Ph
86
0.95
0.99
3.01
3.03
1.01
0.99
1.00
1.99
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

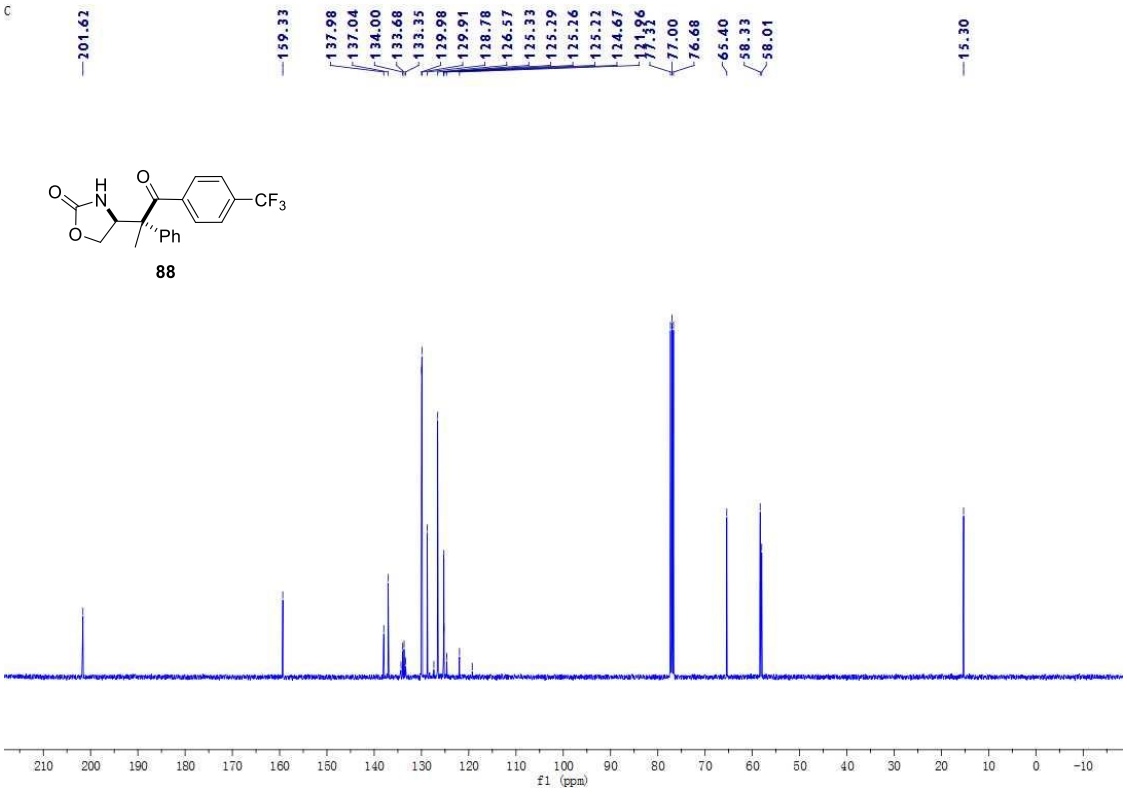

C
1
201.11
159.25
137.22
136.64
135.50
132.75
129.81
129.66
128.66
128.16
126.53
122.54
77.32
77.00
76.68
65.39
58.38
57.90
15.42
Br
O
H
N
O
O
Ph
86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.45
7.43
7.41
7.39
7.37
7.36
7.33
7.31
7.29
7.27
5.89
4.61
4.59
4.58
4.02
3.99
3.98
3.97
3.95
1.72
0.00
Br
Ph
87
9.04
1.00
1.00
2.00
3.04
f1 (ppm)

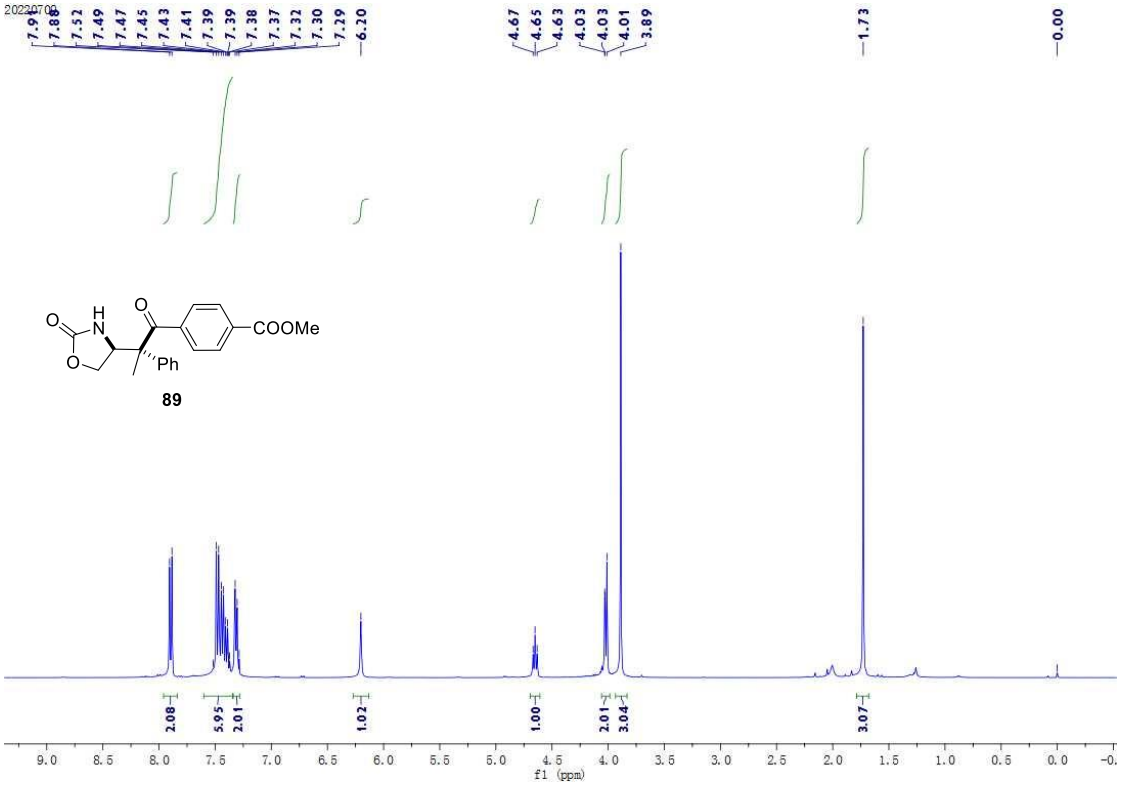

201.40
159.32
137.44
133.43
131.54
131.31
129.76
128.57
127.91
126.50
77.32
77.00
76.68
65.41
58.45
57.74
15.55
Br
Ph
87
f1 (ppm)

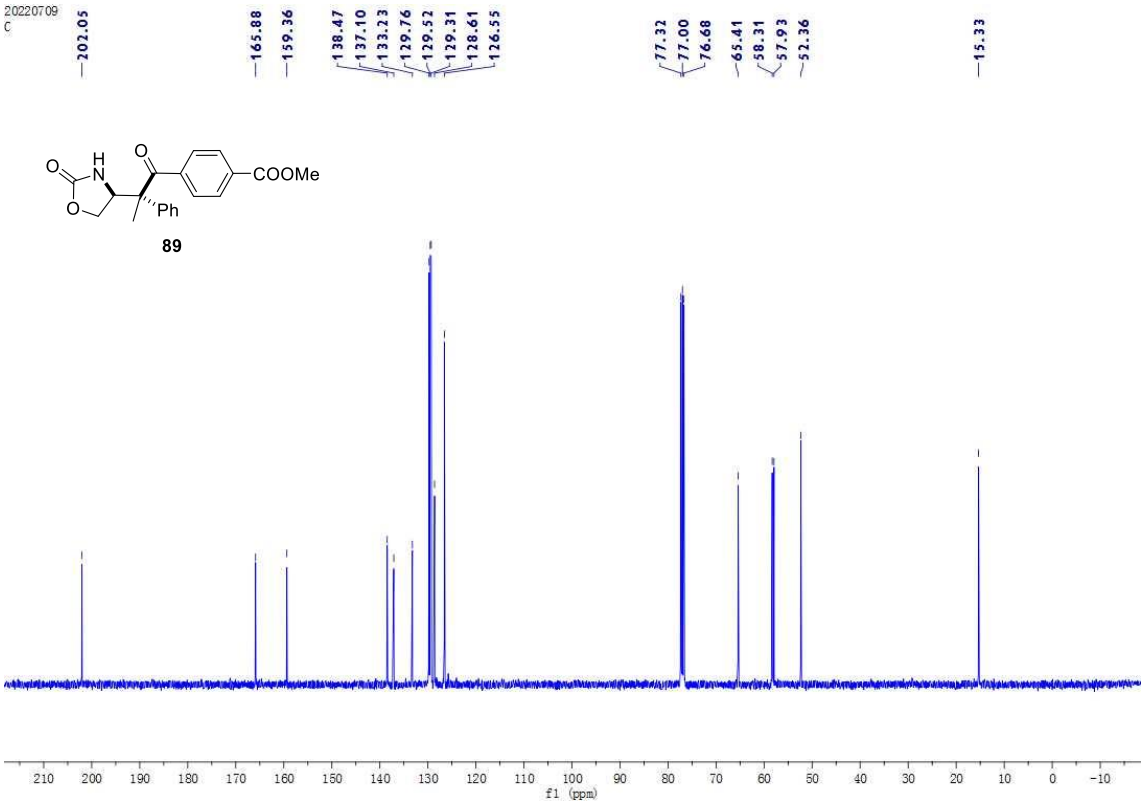

H
CF3
7.55
7.52
7.52
7.49
7.47
7.46
7.44
7.42
7.40
7.38
7.32
7.31
6.11
4.67
4.65
4.63
4.05
4.03
4.02
4.01
1.73
0.00
3.94
3.00
1.99
0.96
1.00
2.01
3.02
f1 (ppm)

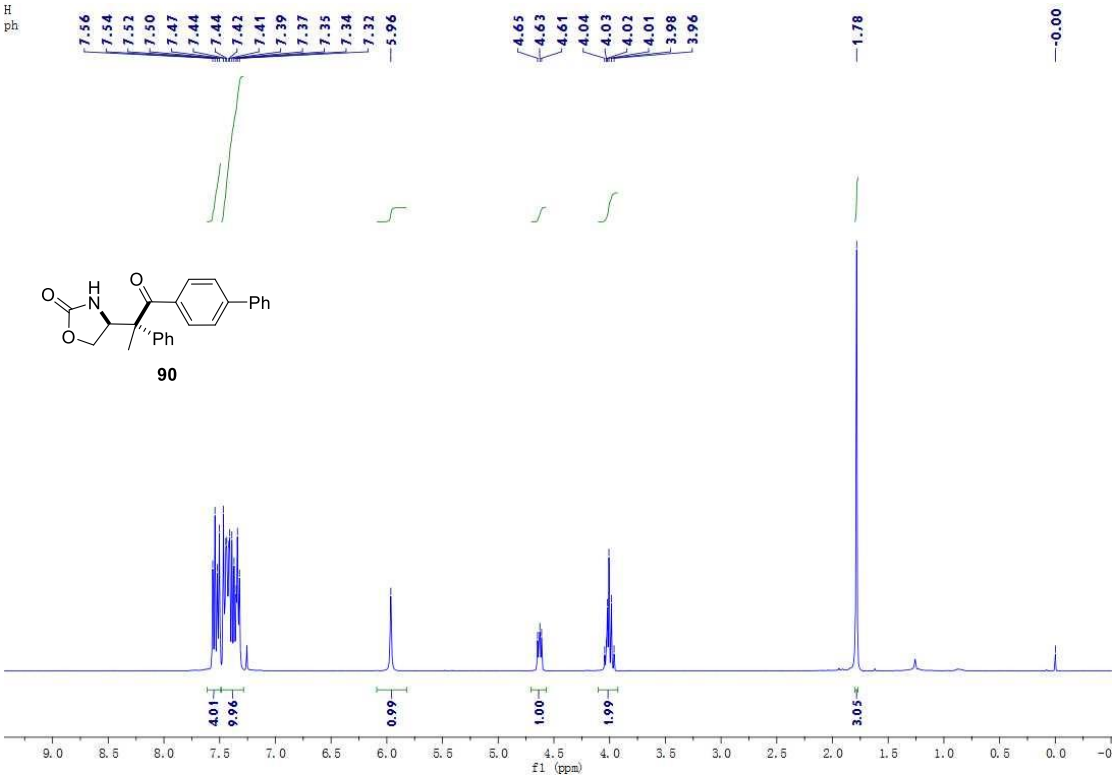
88


C
201.62
159.33
137.98
137.04
134.00
133.68
133.35
129.98
129.91
128.78
126.57
125.33
125.29
125.26
125.22
124.67
77.00
76.68
65.40
58.33
58.01
15.30
f1 (ppm)

88

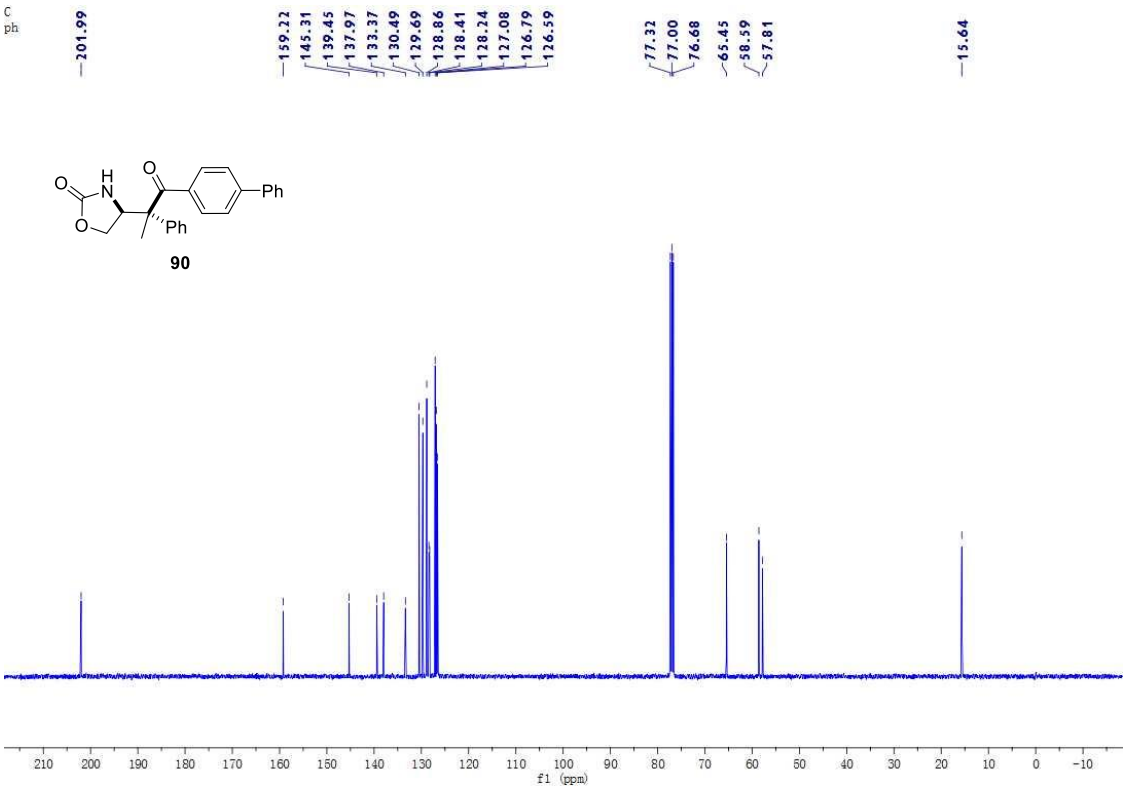

20220709
7.91
7.89
7.52
7.49
7.47
7.45
7.43
7.41
7.39
7.39
7.38
7.37
7.32
7.30
7.29
6.20
4.67
4.65
4.63
4.03
4.03
4.01
3.89
1.73
0.00
O
H
N
O
O
COOMe
Ph
89
2.08
5.95
2.01
1.02
1.00
2.01
3.04
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


20220709
C
202.05
165.88
159.36
138.47
137.10
133.23
129.76
129.52
129.31
128.61
126.55
77.32
77.00
76.68
65.41
58.31
57.93
52.36
15.33
O
H
N
O
O
COOMe
Ph
89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


H
ph
7.56
7.54
7.52
7.50
7.47
7.44
7.44
7.42
7.41
7.39
7.37
7.35
7.34
7.32
5.96
4.65
4.63
4.61
4.04
4.03
4.02
4.01
3.98
3.96
1.78
-0.00
4.01
9.96
0.99
1.00
1.99
3.05
f1 (ppm)

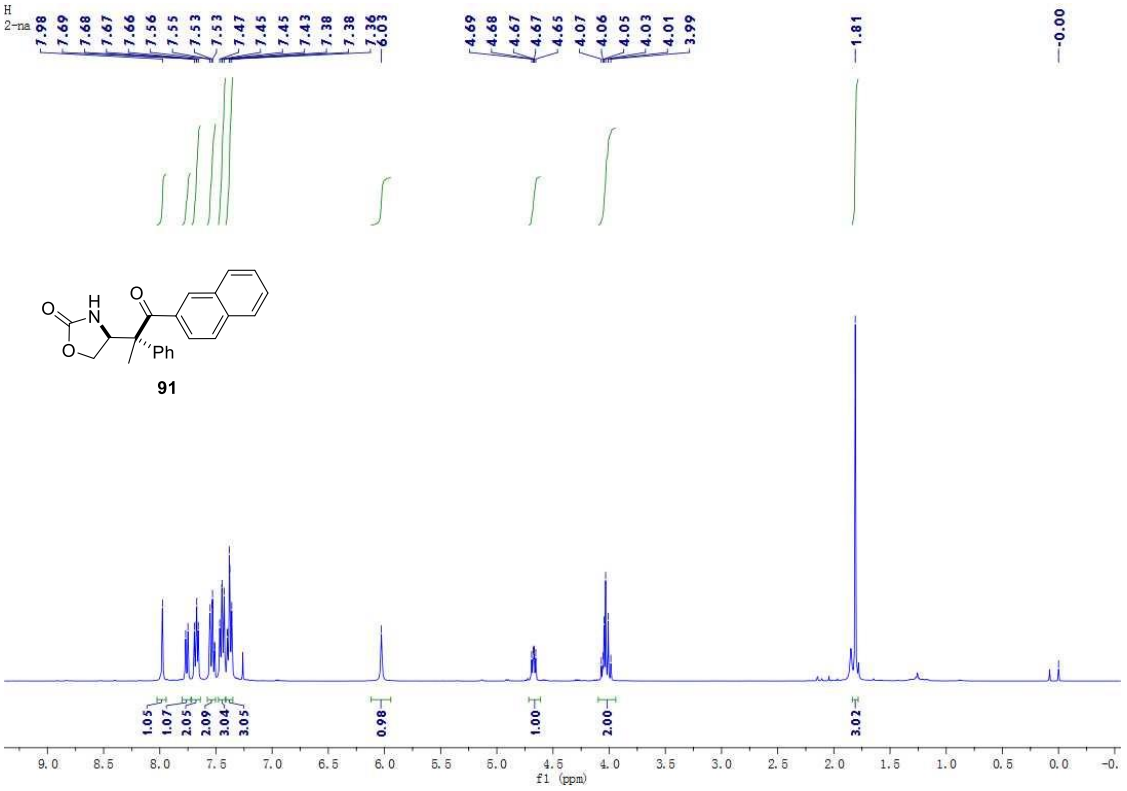
O
H
N
O
O
Ph
Ph

90

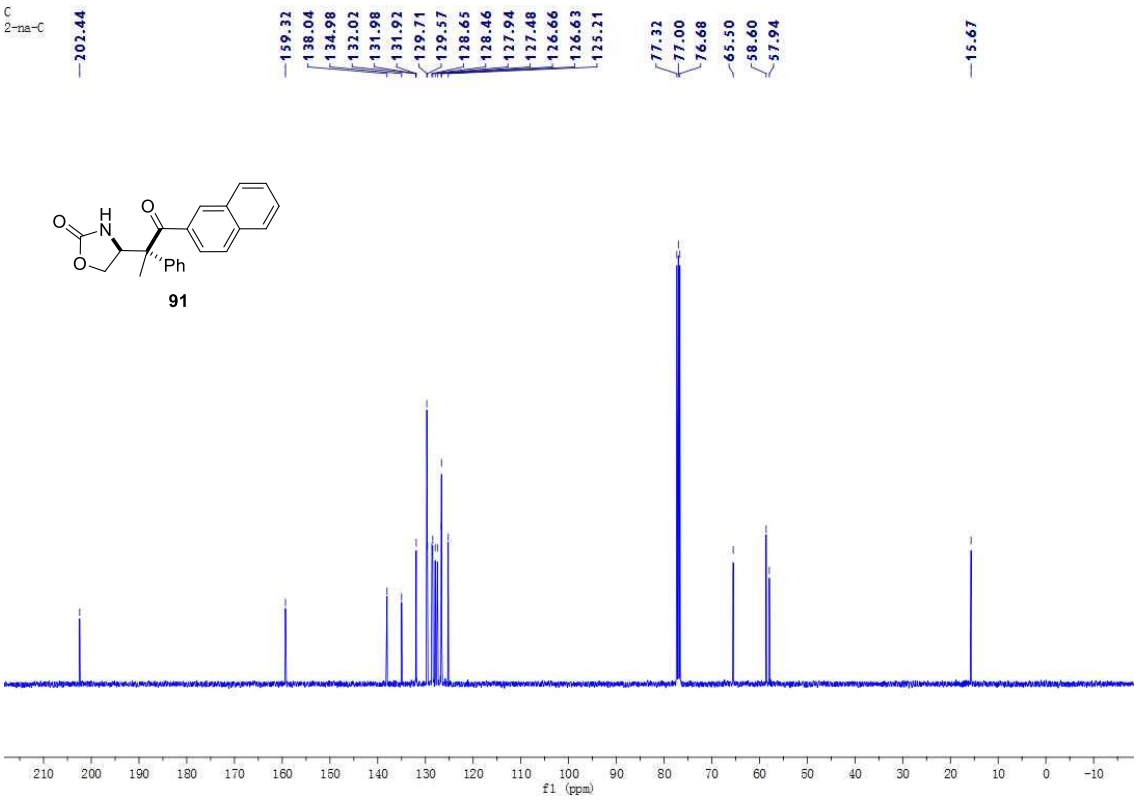

C
ph
201.99
159.22
145.31
139.45
137.97
133.37
130.49
129.69
128.86
128.41
128.24
127.08
126.79
126.59
77.32
77.00
76.68
65.45
58.59
57.81
15.64
f1 (ppm)

O
H
N
O
O
Ph
Ph

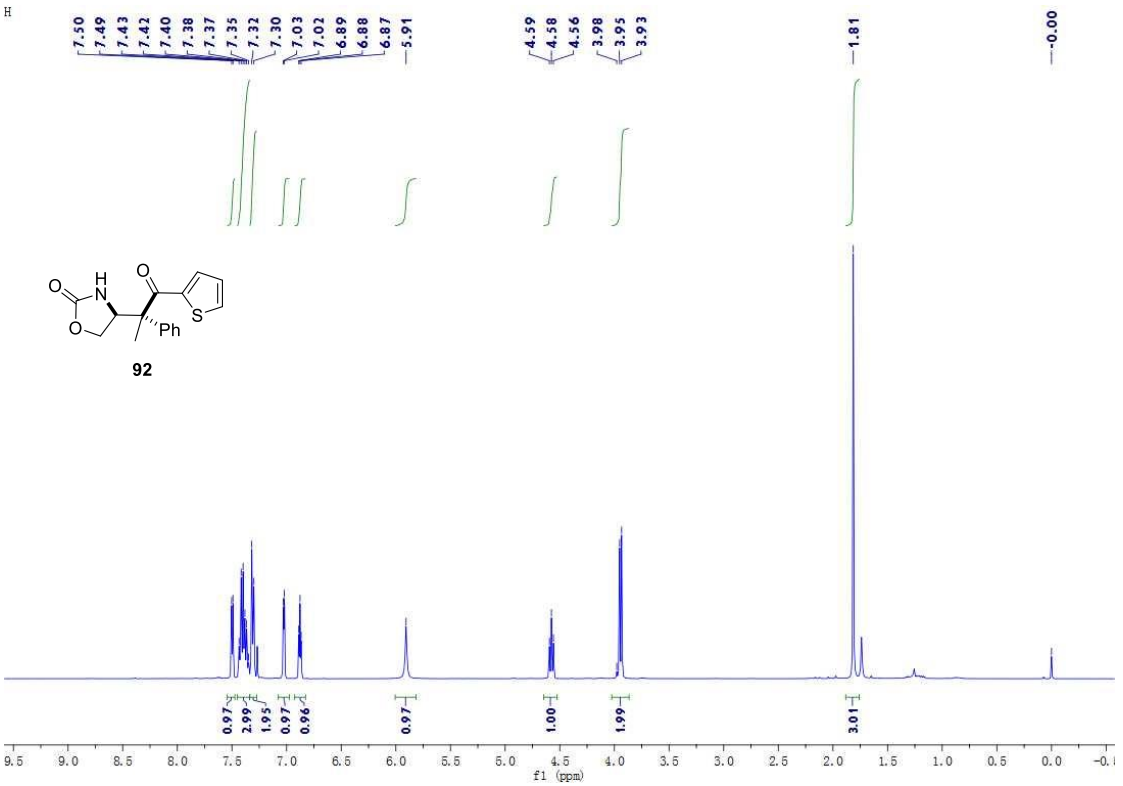
90


H
2-na
7.98
7.69
7.68
7.67
7.66
7.56
7.55
7.53
7.53
7.47
7.45
7.45
7.43
7.38
7.38
7.36
6.03
4.69
4.68
4.67
4.67
4.65
4.07
4.06
4.05
4.03
4.01
3.99
1.81
0.00
O
H
N
O
O
Ph
1.05
1.07
2.05
2.09
3.04
3.05
0.98
1.00
2.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

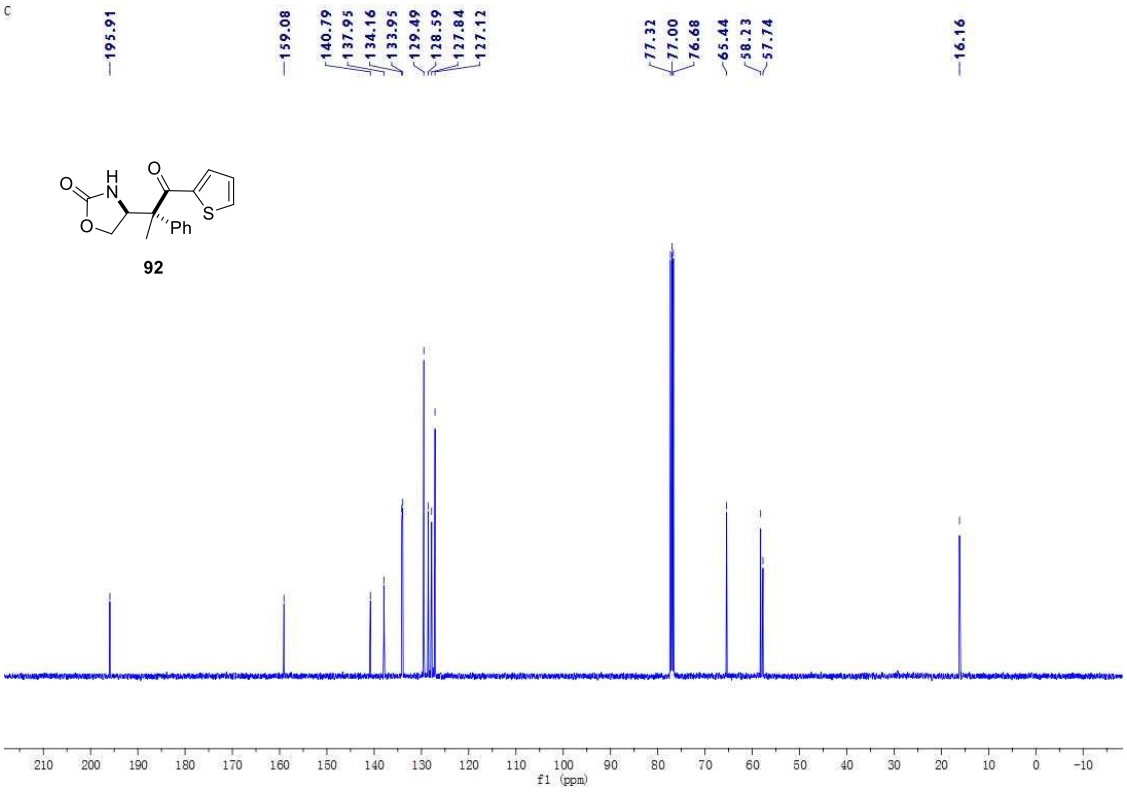
91


C
2-na-C
202.44
159.32
138.04
134.98
132.02
131.98
131.92
129.71
129.57
128.65
128.46
127.94
127.48
126.66
126.63
125.21
77.32
77.00
76.68
65.50
58.60
57.94
15.67
O
H
N
O
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

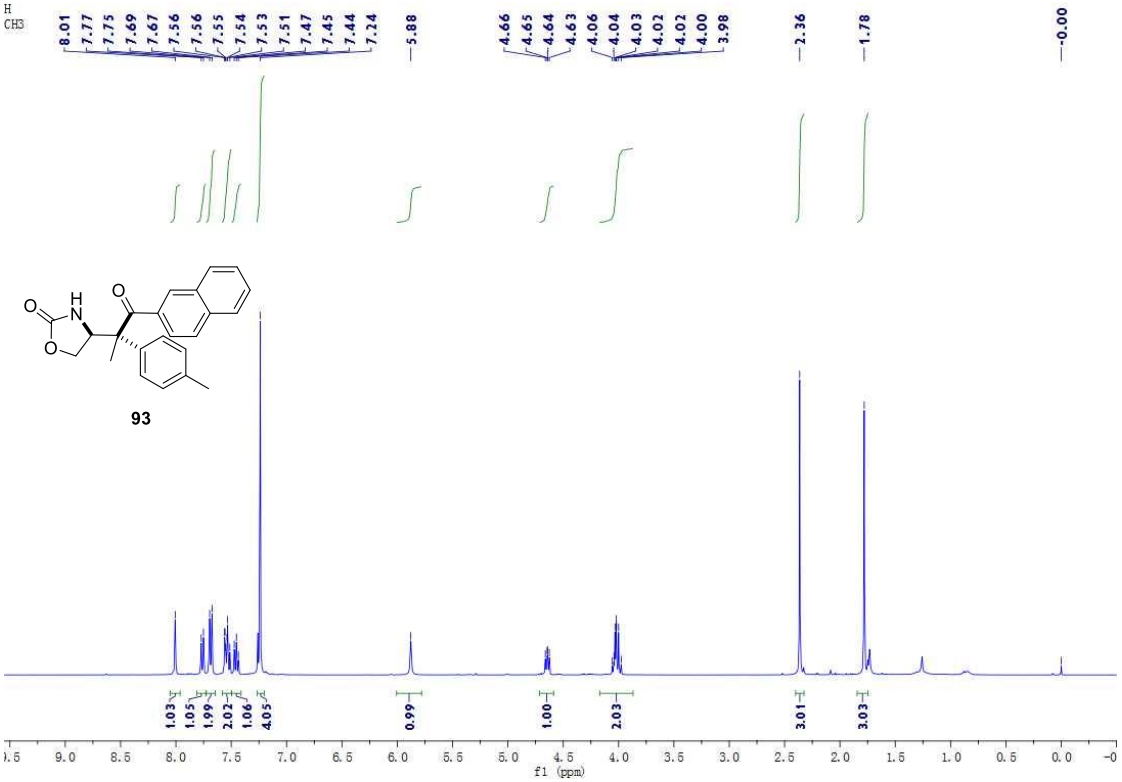
91


H
7.50
7.49
7.43
7.42
7.40
7.38
7.37
7.35
7.32
7.30
7.03
7.02
6.89
6.88
6.87
5.91
4.59
4.58
4.56
3.98
3.95
3.93
1.81
0.00
0.97
2.99
1.95
0.97
0.96
0.97
1.00
1.99
3.01
f1 (ppm)

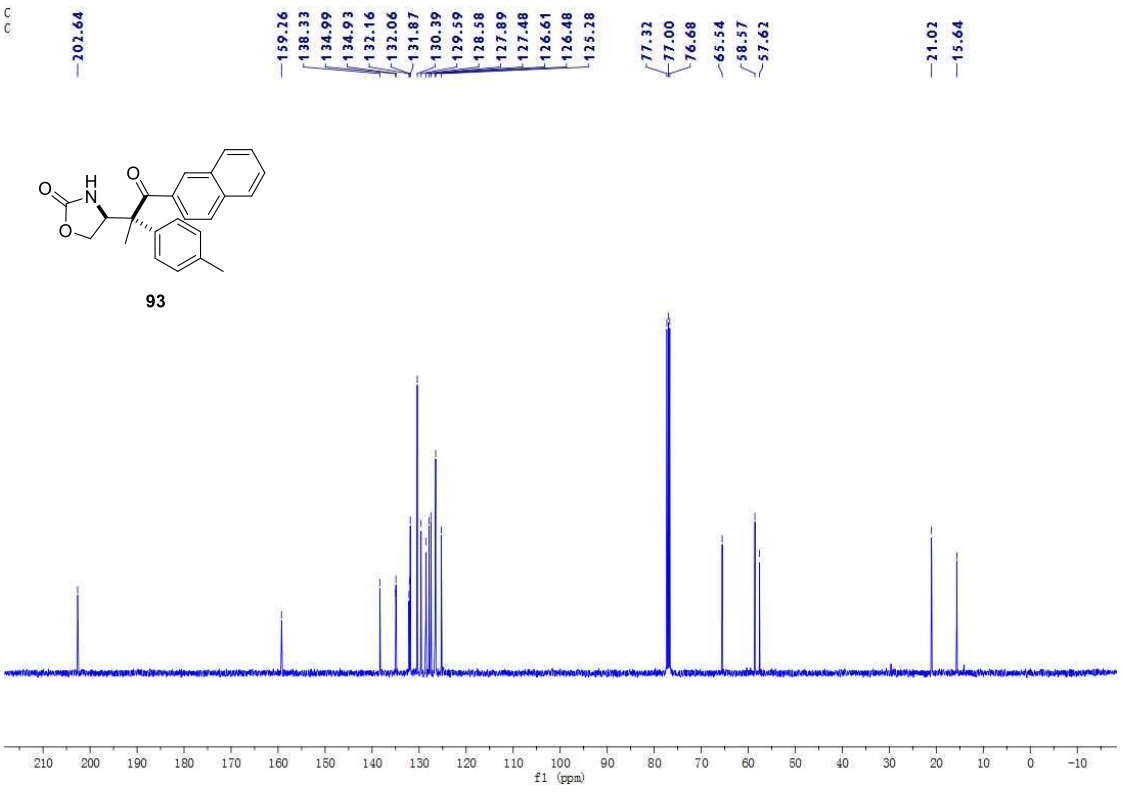
92


C
195.91
159.08
140.79
137.95
134.16
133.95
129.49
128.59
127.84
127.12
77.32
77.00
76.68
65.44
58.23
57.74
16.16
f1 (ppm)

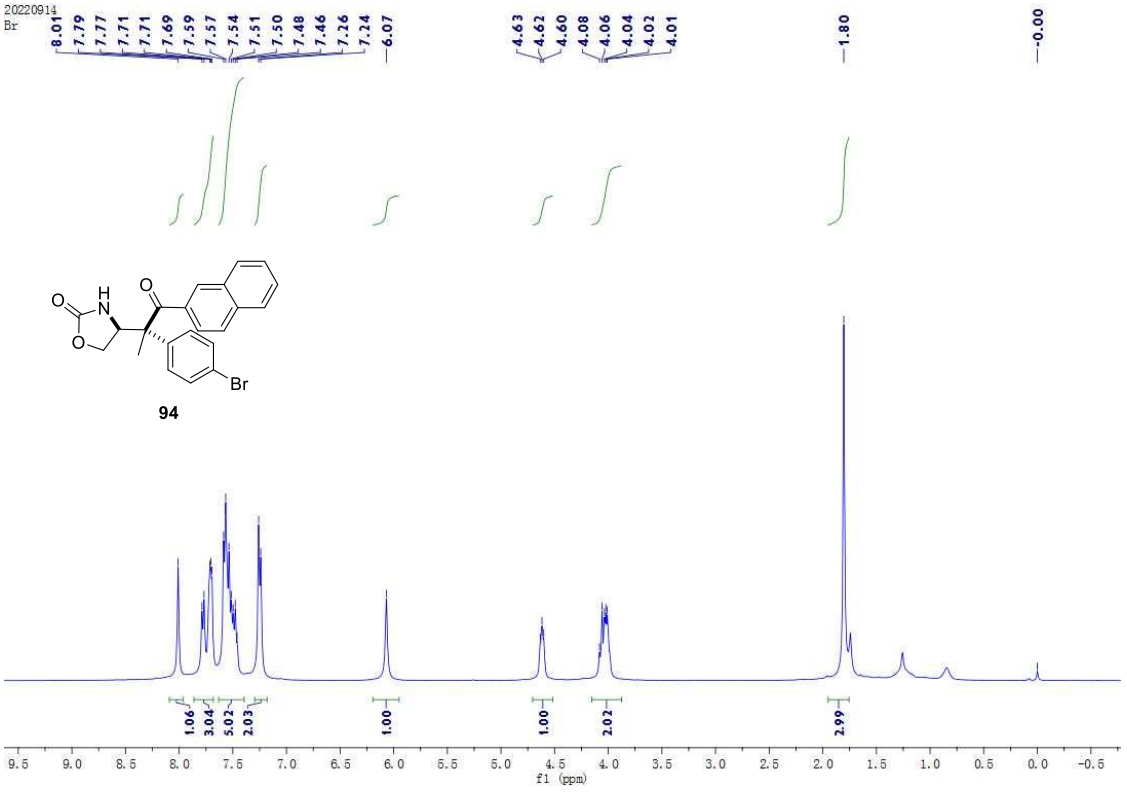
92


8.01
7.77
7.75
7.69
7.67
7.56
7.56
7.55
7.54
7.53
7.51
7.47
7.45
7.44
7.24
5.88
4.66
4.65
4.64
4.63
4.06
4.04
4.03
4.02
4.02
4.00
3.98
2.36
1.78
0.00
1.03
1.05
1.99
2.02
1.06
4.05
0.99
1.00
2.03
3.01
3.03
f1 (ppm)

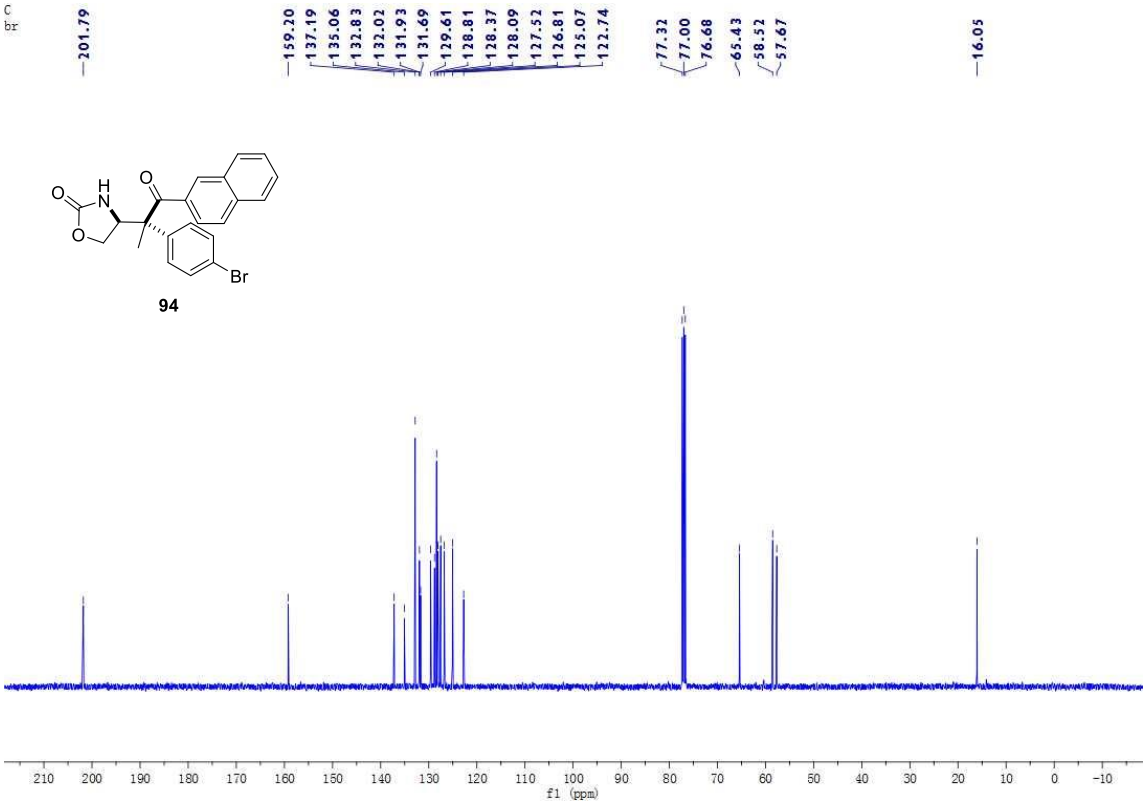
93


202.64
159.26
138.33
134.99
134.93
132.16
132.06
131.87
130.39
129.59
128.58
127.89
127.48
126.61
126.48
125.28
77.32
77.00
76.68
65.54
58.57
57.62
21.02
15.64
f1 (ppm)

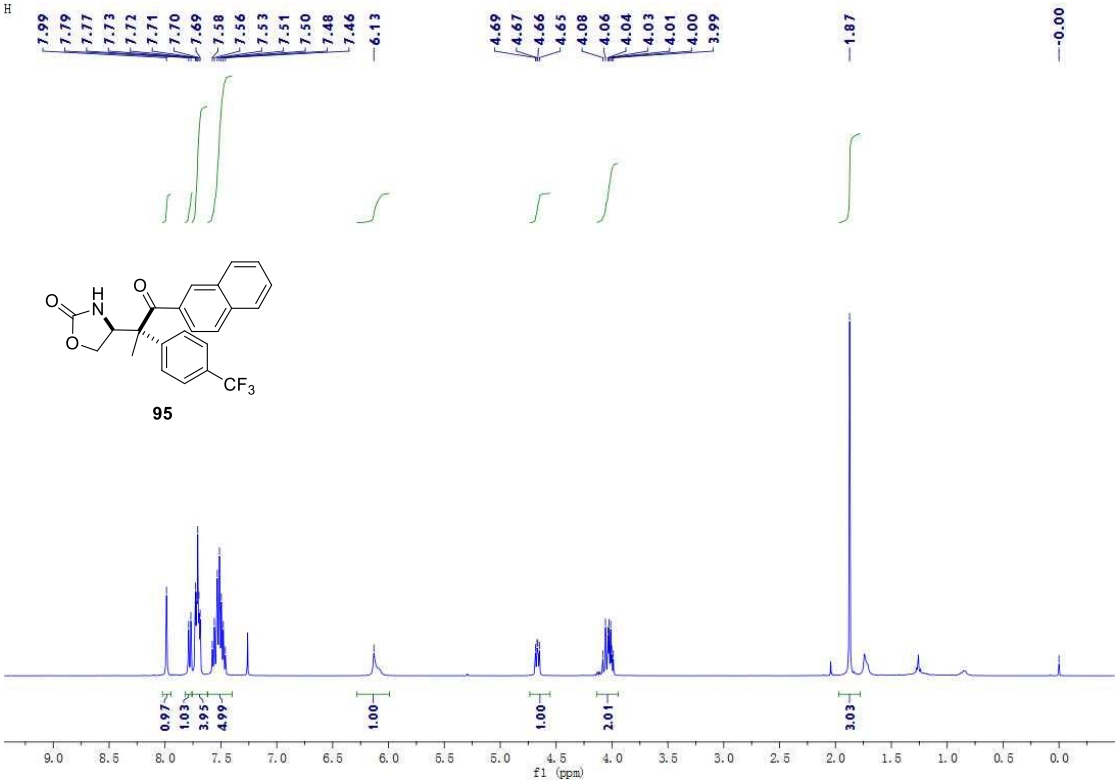
93

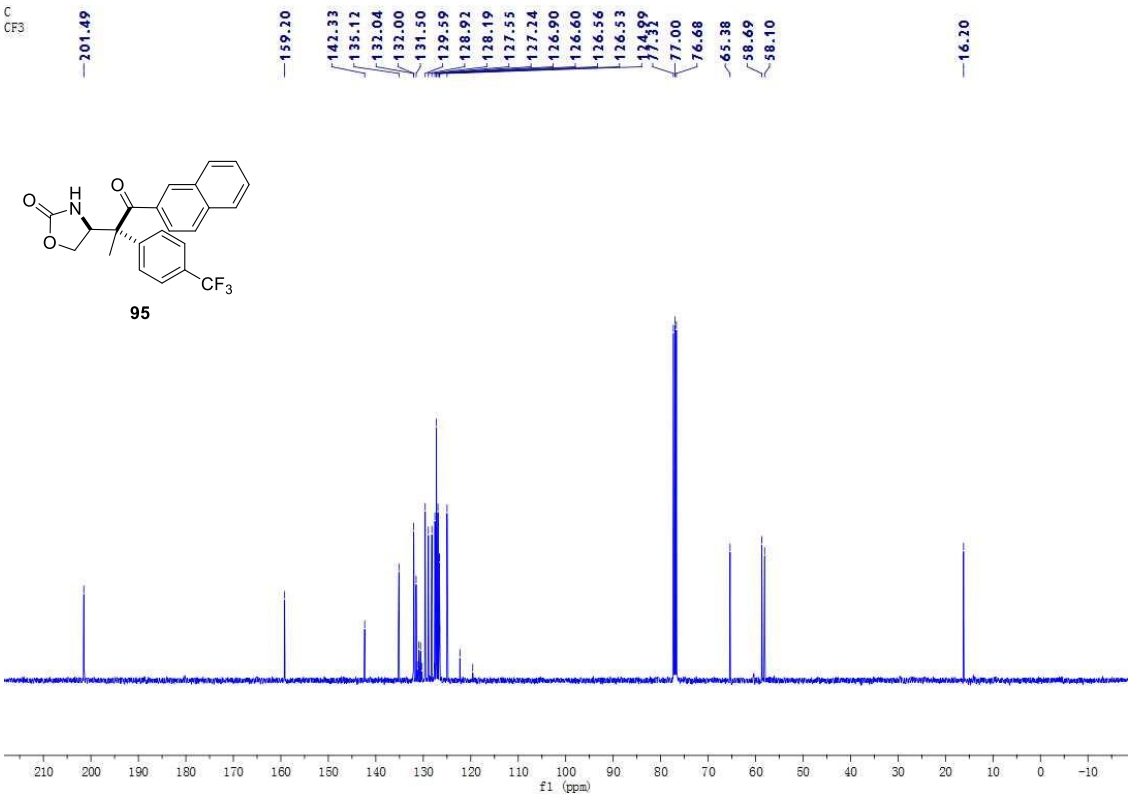

20220914
Br
8.01
7.79
7.77
7.71
7.71
7.69
7.59
7.57
7.54
7.51
7.50
7.48
7.46
7.26
7.24
6.07
4.63
4.62
4.60
4.08
4.06
4.04
4.02
4.01
1.80
0.00
O
H
N
O
O
Br
1.06
3.04
5.02
2.03
1.00
1.00
2.02
2.99
f1 (ppm)

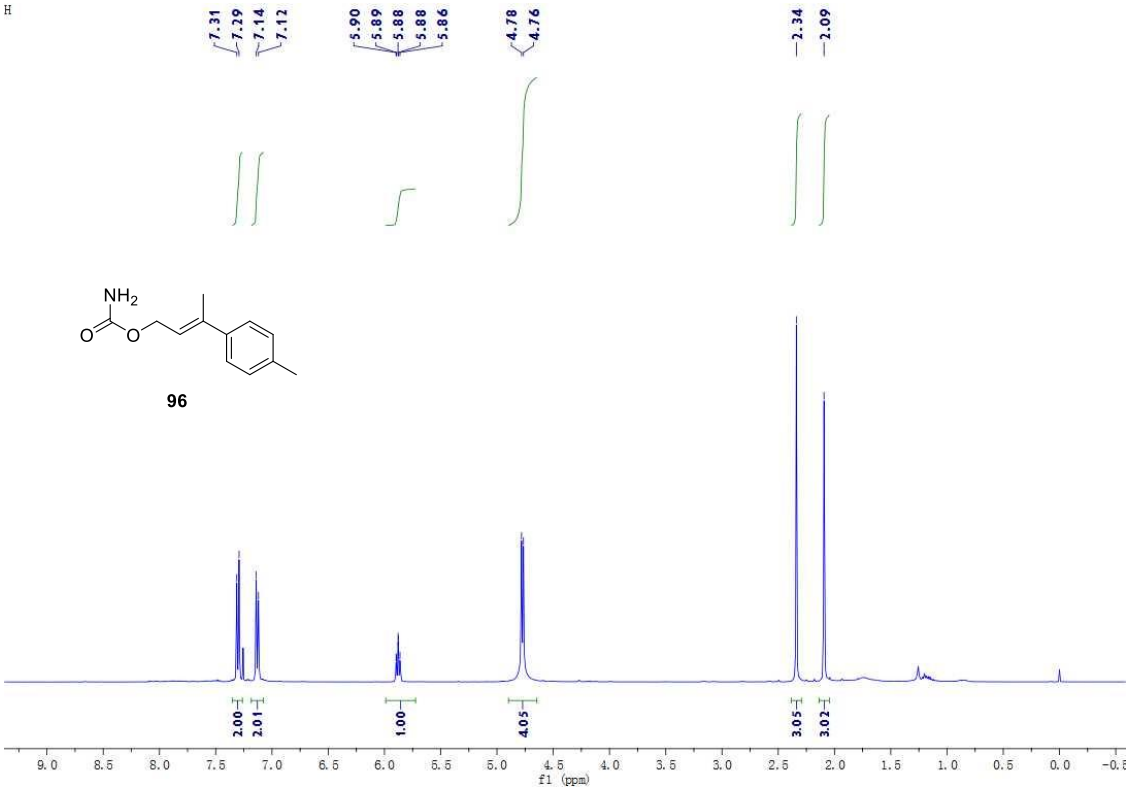
94

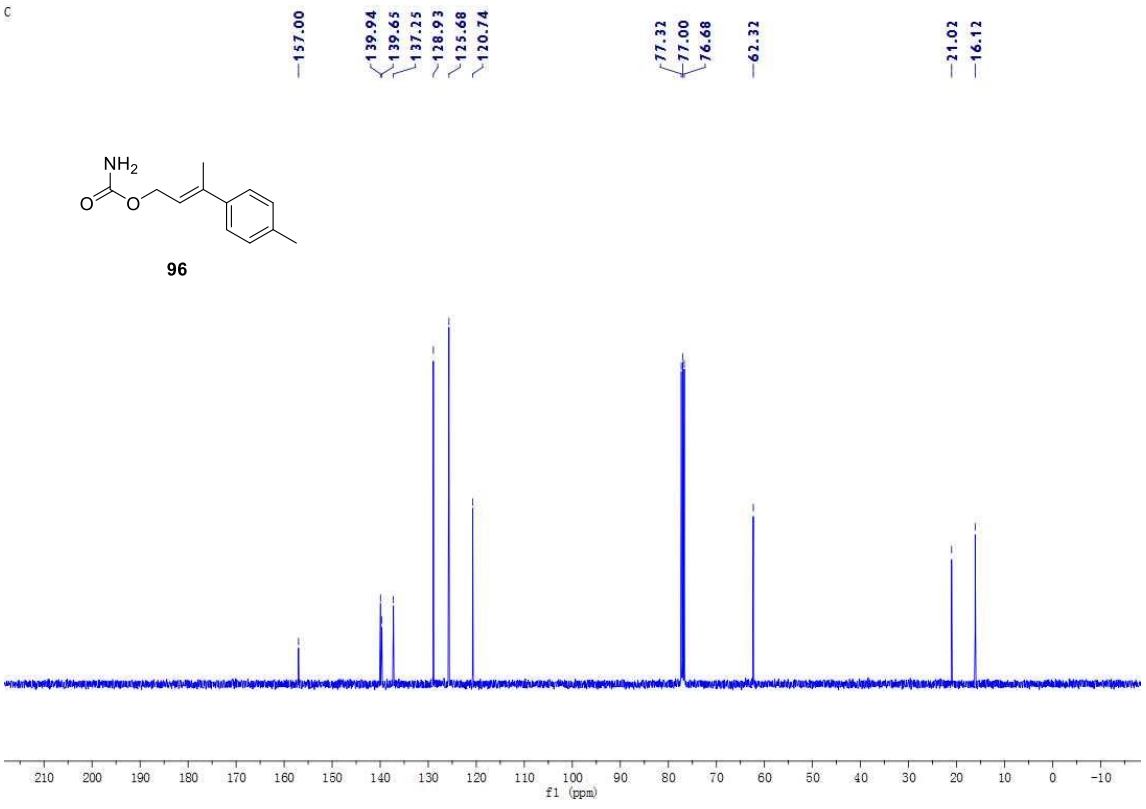

C
br
201.79
159.20
137.19
135.06
132.83
132.02
131.93
131.69
129.61
128.81
128.37
128.09
127.52
126.81
125.07
122.74
77.32
77.00
76.68
65.43
58.52
57.67
16.05
O
H
N
O
O
Br
f1 (ppm)

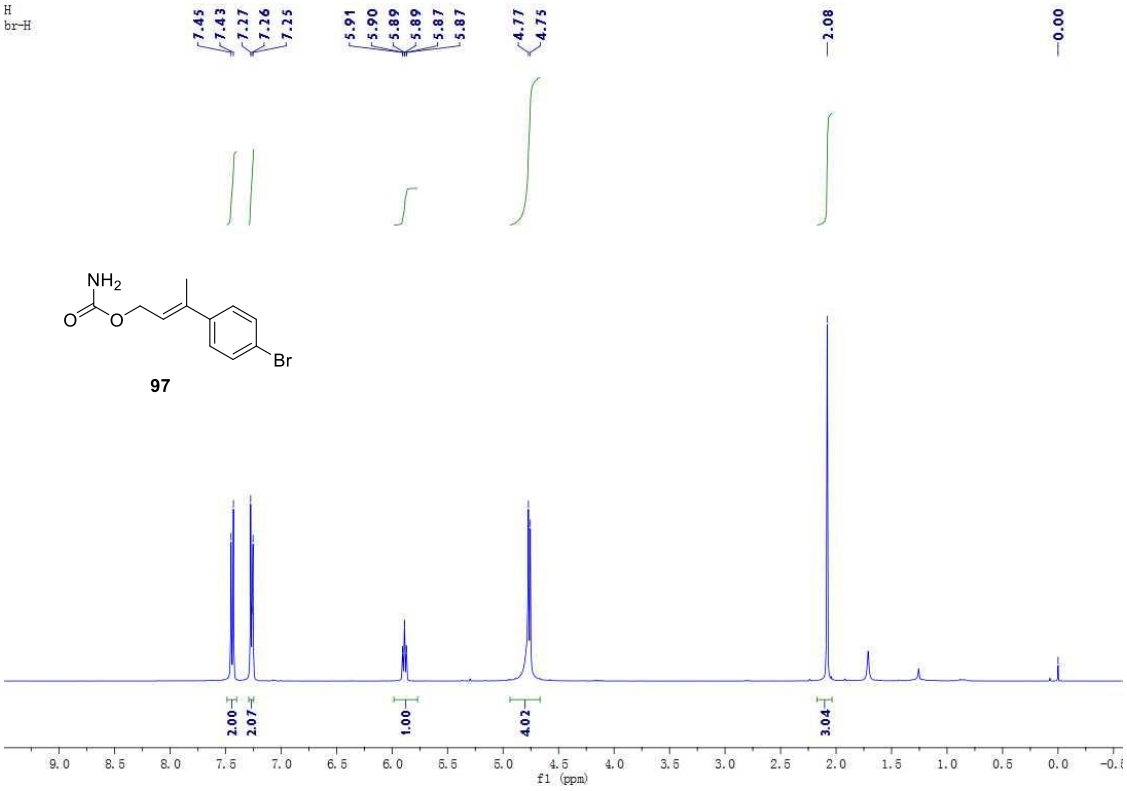
94

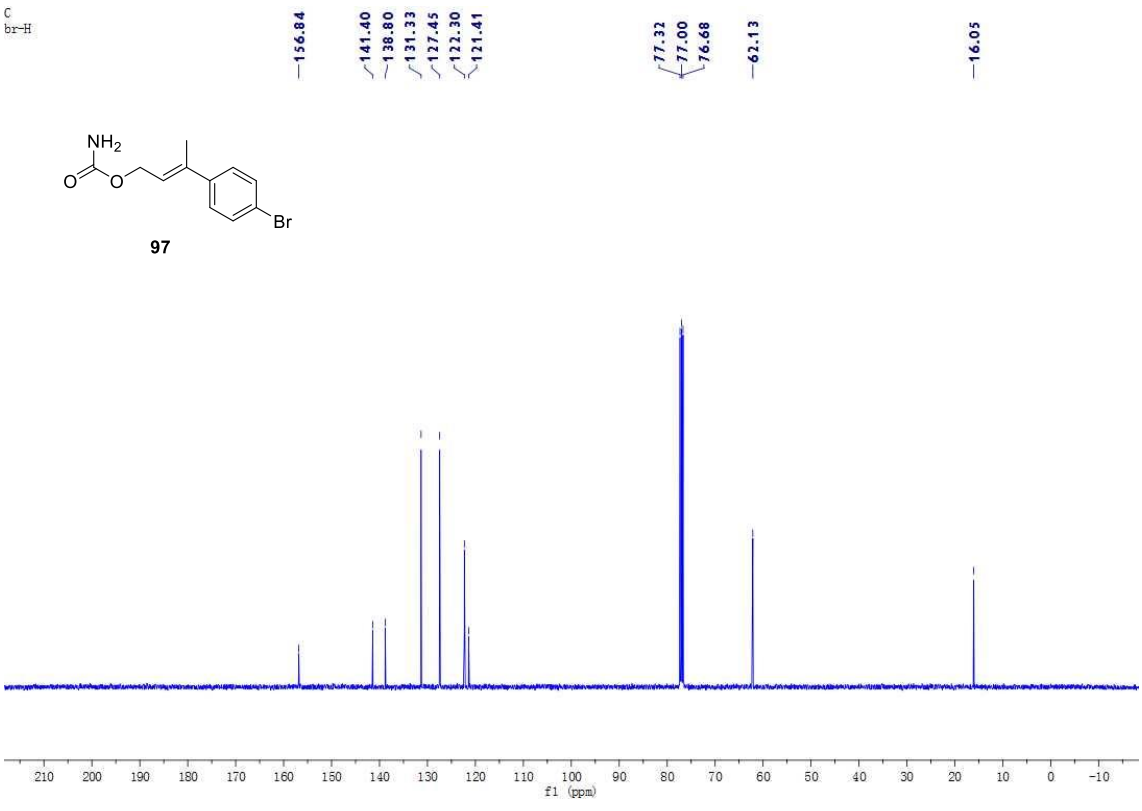

H
7.99
7.79
7.77
7.73
7.72
7.71
7.70
7.69
7.58
7.56
7.53
7.51
7.50
7.48
7.46
6.13
4.69
4.67
4.66
4.65
4.08
4.06
4.04
4.03
4.01
4.00
3.99
1.87
0.00
95
0.97
1.03
3.95
4.99
1.00
1.00
2.01
3.03
f1 (ppm)

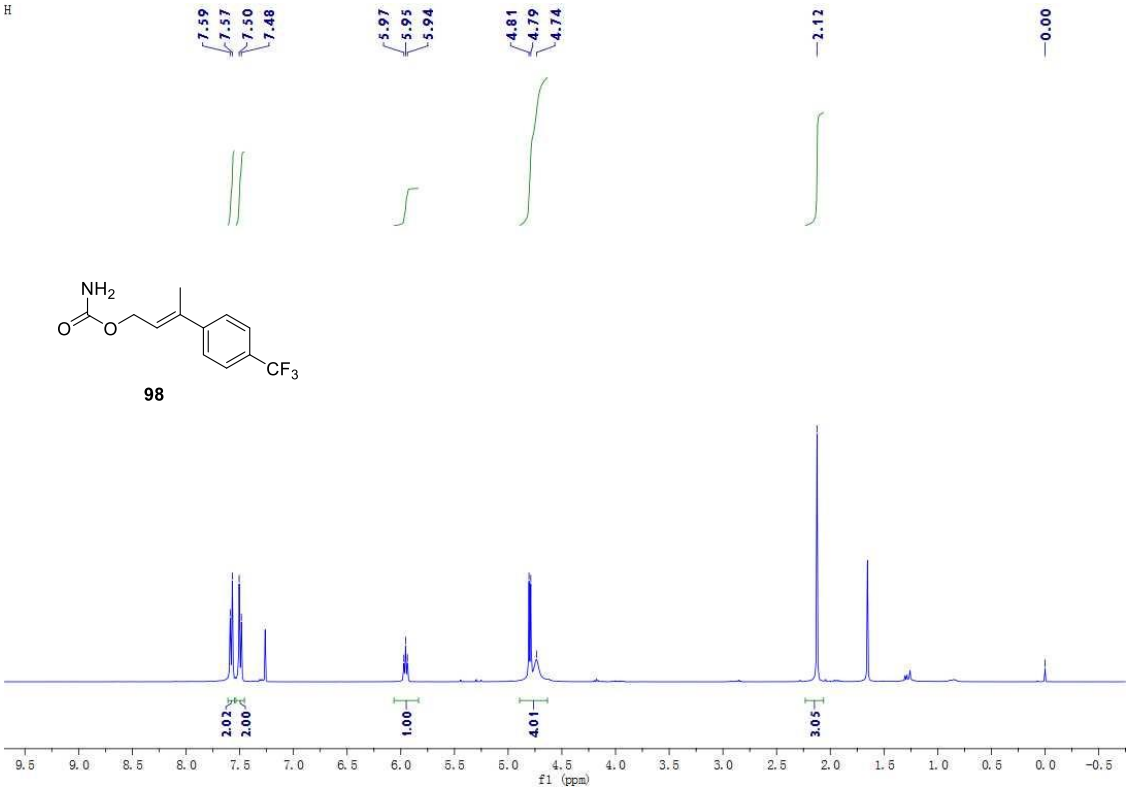

C
CF3
201.49
159.20
142.33
135.12
132.04
132.00
131.50
129.59
128.92
128.19
127.55
127.24
126.90
126.60
126.56
126.53
124.89
77.32
77.00
76.68
65.38
58.69
58.10
16.20
95
f1 (ppm)


H
7.31
7.29
7.14
7.12
5.90
5.89
5.88
5.88
5.86
4.78
4.76
2.34
2.09
NH2
O
O
96
2.00
2.01
1.00
4.05
3.05
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

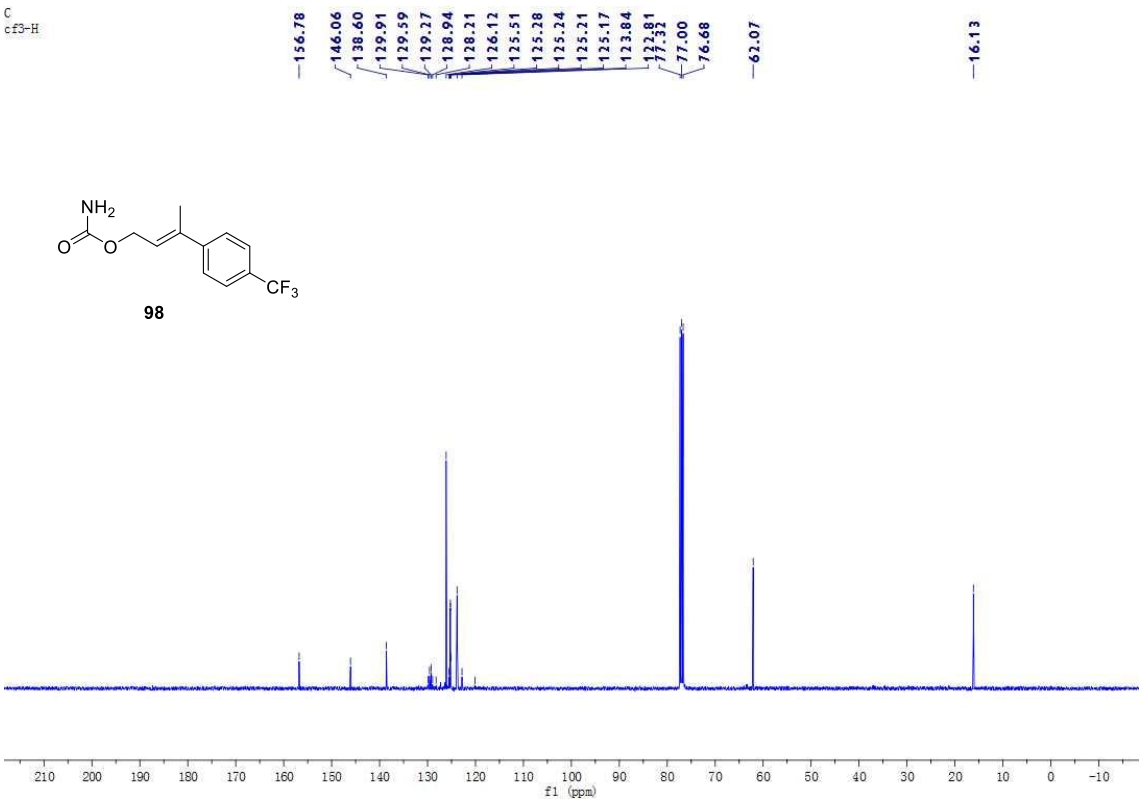

C
157.00
139.94
139.65
137.25
128.93
125.68
120.74
77.32
77.00
76.68
62.32
21.02
16.12
NH2
O
O
96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
br-H
7.45
7.43
7.27
7.26
7.25
5.91
5.90
5.89
5.89
5.87
5.87
4.77
4.75
2.08
0.00
NH2
O
O
Br
97
2.00
2.07
1.00
4.02
3.04
f1 (ppm)

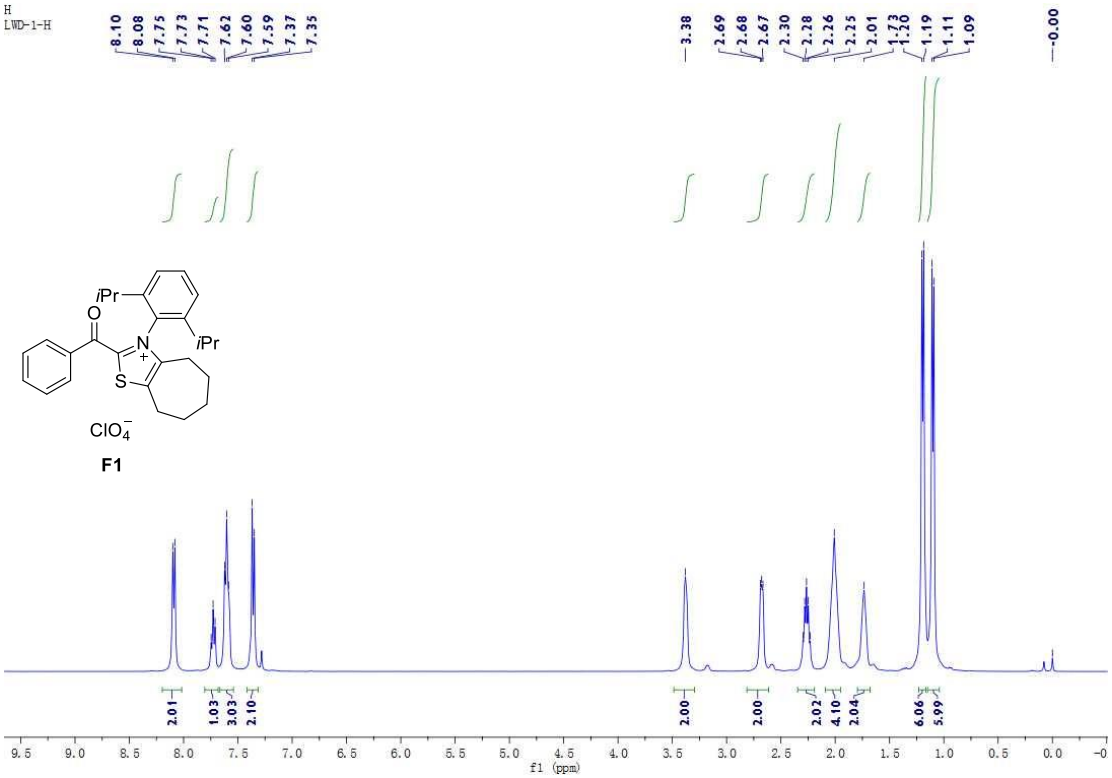

C
br-H
156.84
141.40
138.80
131.33
127.45
122.30
121.41
77.32
77.00
76.68
62.13
16.05
NH2
O
O
Br
97
f1 (ppm)

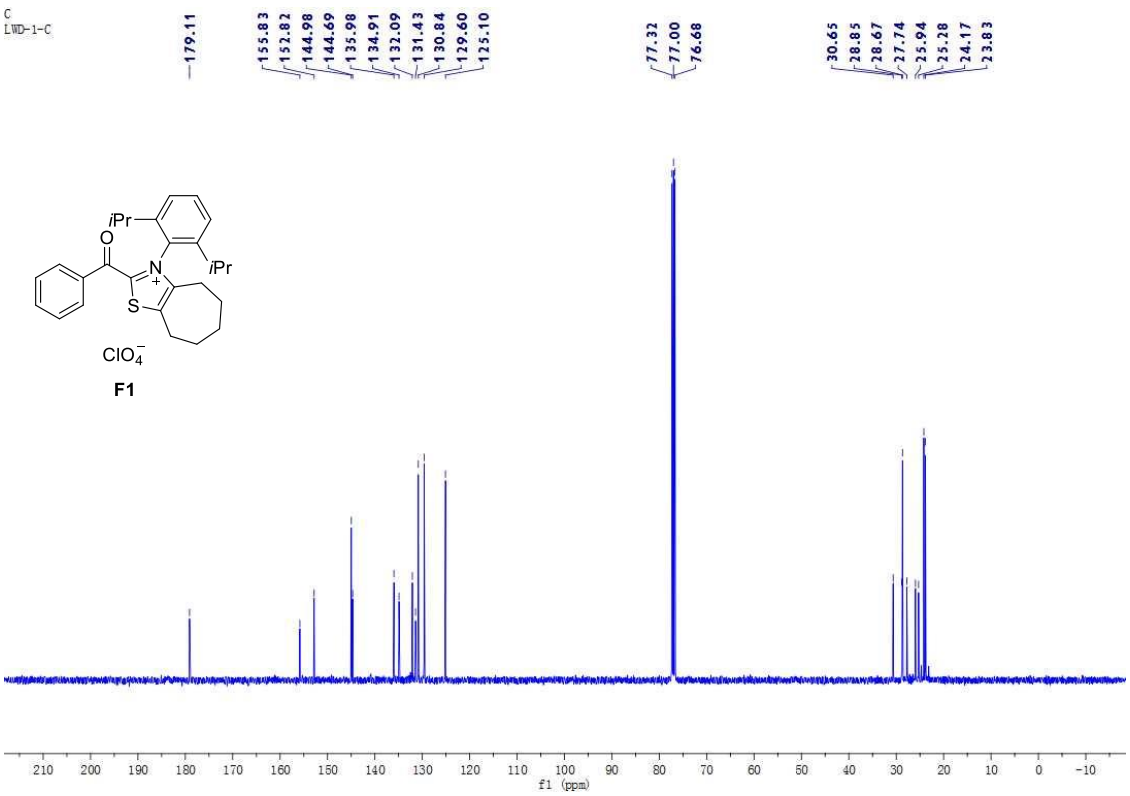

H
7.59
7.57
7.50
7.48
5.97
5.95
5.94
4.81
4.79
4.74
2.12
0.00
NH2
O
O
CF3
2.02
2.00
1.00
4.01
3.05
f1 (ppm)

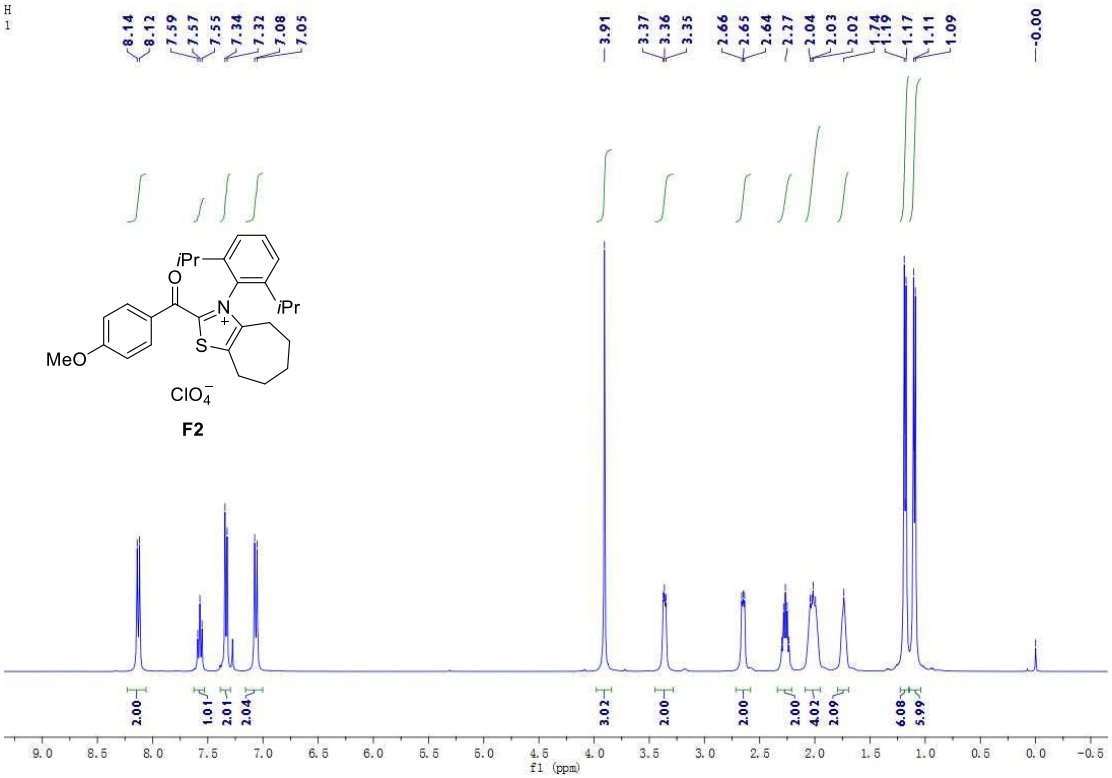
98


C
cf3-H
156.78
146.06
138.60
129.91
129.59
129.27
128.94
128.21
126.12
125.51
125.28
125.24
125.21
125.17
123.84
122.81
77.32
77.00
76.68
62.07
16.13
NH2
O
O
CF3
f1 (ppm)

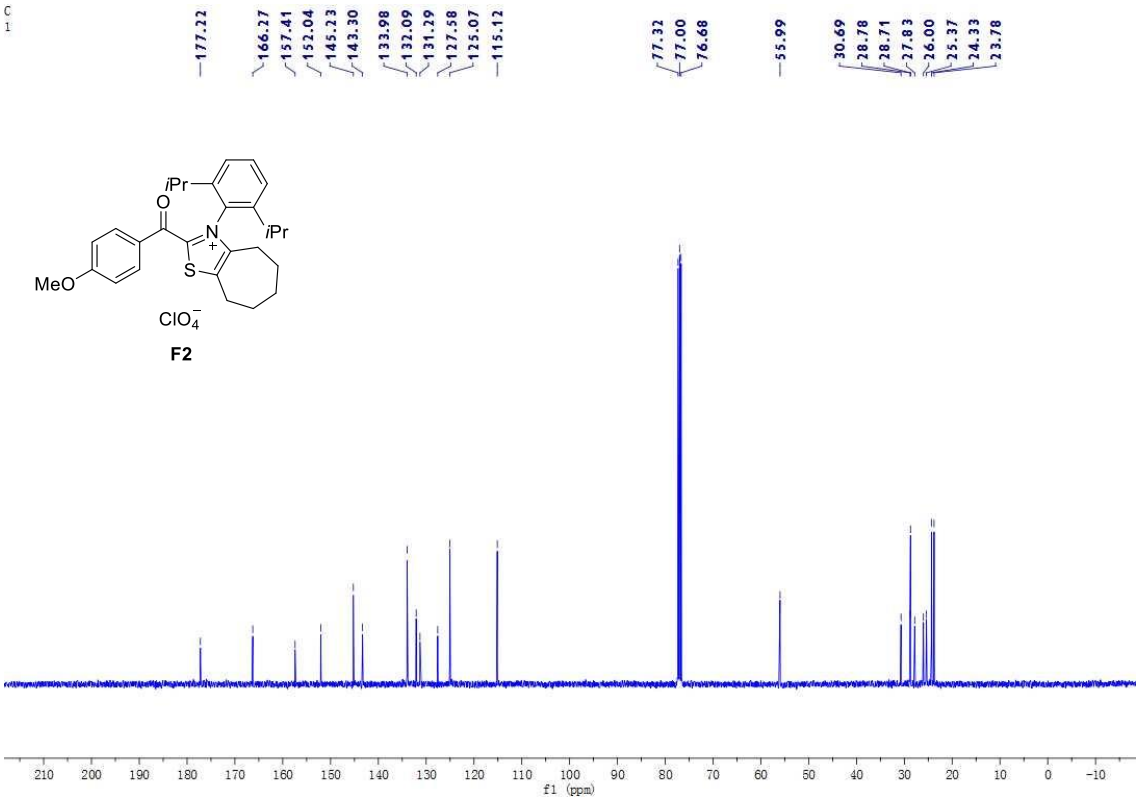
98


H
LWD-1-H
8.10
8.08
7.75
7.73
7.71
7.62
7.60
7.59
7.37
7.35
3.38
2.69
2.68
2.67
2.30
2.28
2.26
2.25
2.01
1.73
1.20
1.19
1.11
1.09
0.00
iPr
iPr
O
N
S
ClO4−
F1
2.01
1.03
3.03
2.10
2.00
2.00
2.02
4.10
2.04
6.06
5.99
f1 (ppm)

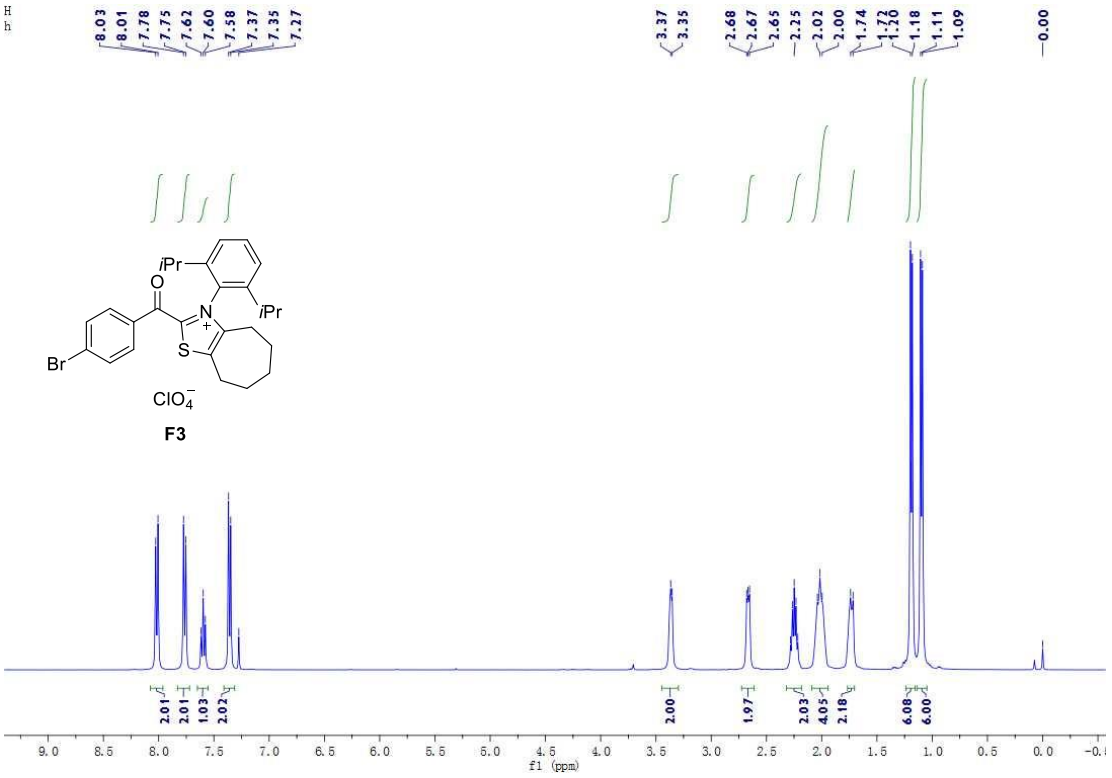

C
LWD-1-C
179.11
155.83
152.82
144.98
144.69
135.98
134.91
132.09
131.43
130.84
129.60
125.10
77.32
77.00
76.68
30.65
28.85
28.67
27.74
25.94
25.28
24.17
23.83
iPr
iPr
O
N
S
ClO4−
F1
f1 (ppm)


8.14
8.12
7.59
7.57
7.55
7.34
7.32
7.08
7.05
3.91
3.37
3.36
3.35
2.66
2.65
2.64
2.27
2.04
2.03
2.02
1.74
1.19
1.17
1.11
1.09
-0.00
iPr
iPr
O
N
S
MeO
ClO4−
2.00
1.01
2.01
2.04
3.02
2.00
2.00
2.00
4.02
2.09
6.08
5.99
f1 (ppm)

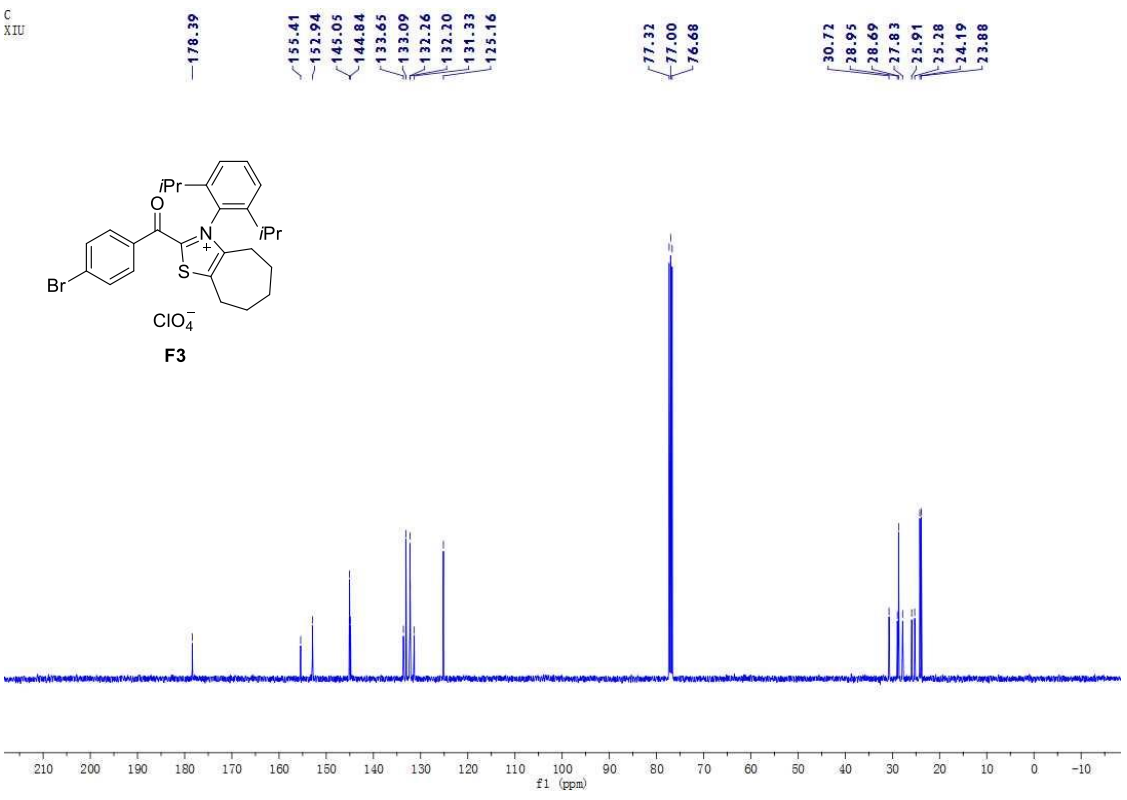
F2


177.22
166.27
157.41
152.04
145.23
143.30
133.98
132.09
131.29
127.58
125.07
115.12
77.32
77.00
76.68
55.99
30.69
28.78
28.71
27.83
26.00
25.37
24.33
23.78
iPr
iPr
O
N
S
MeO
ClO4−
f1 (ppm)

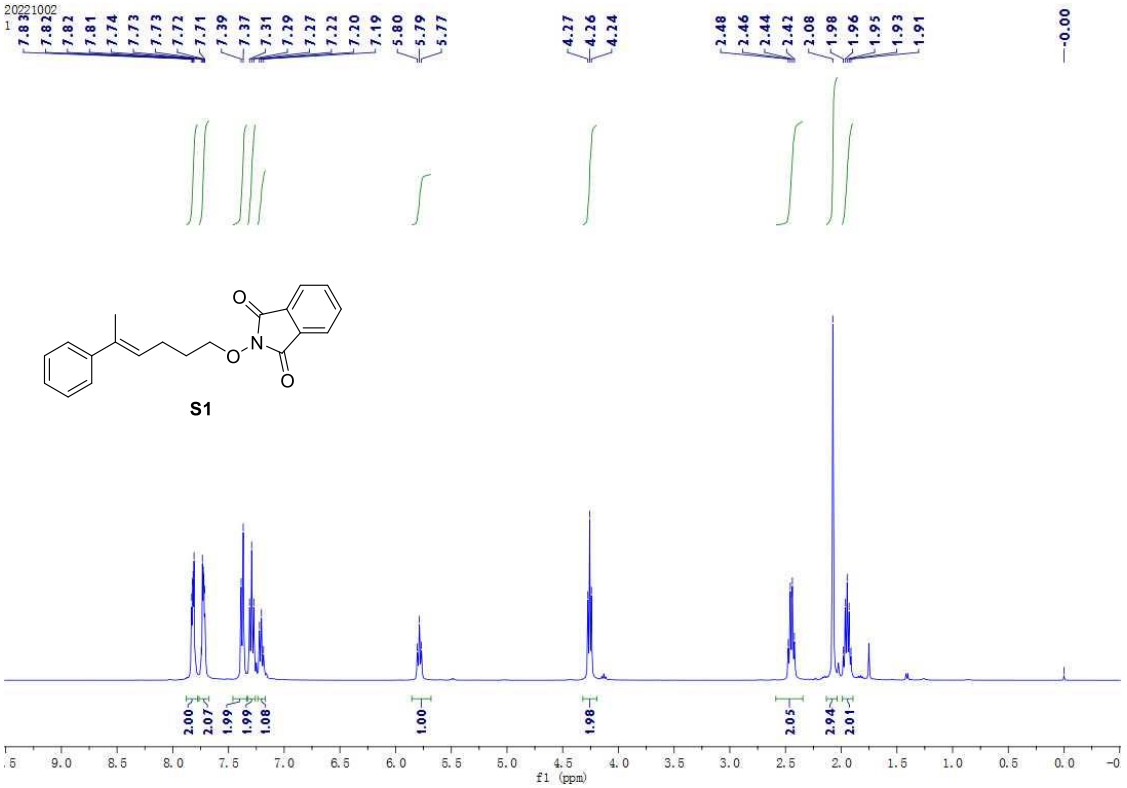
F2

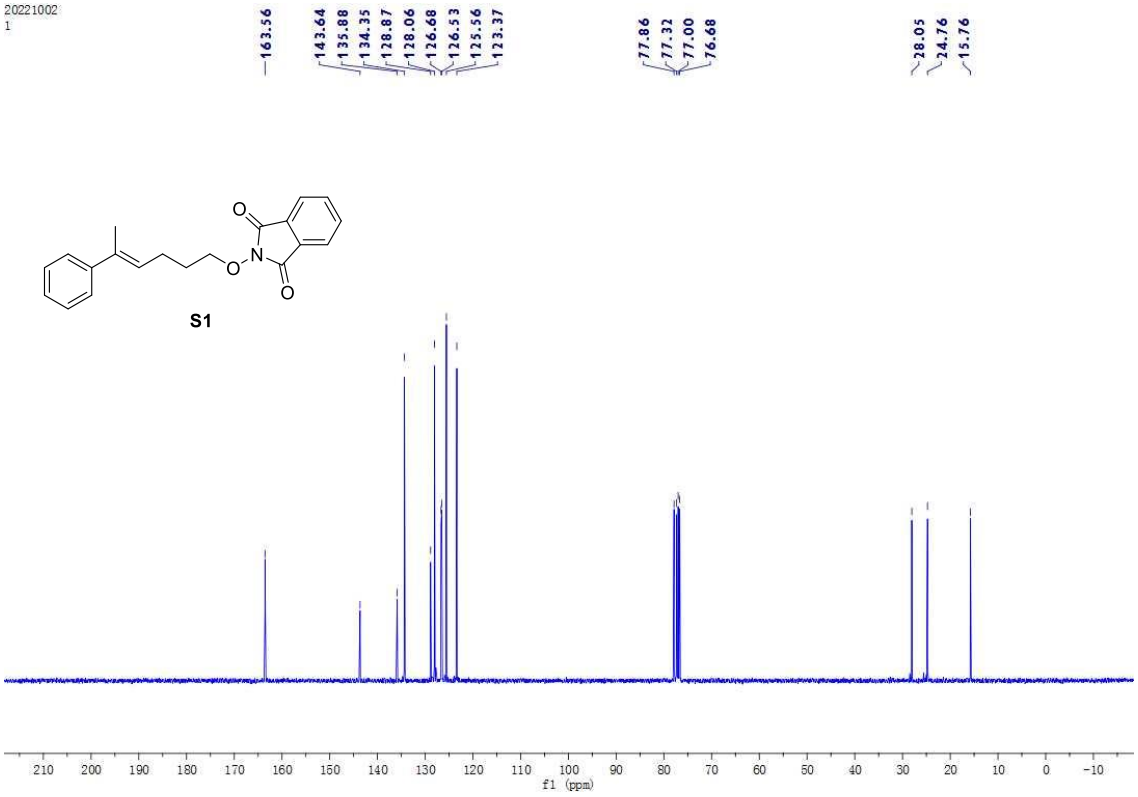

8.03
8.01
7.78
7.75
7.62
7.60
7.58
7.37
7.35
7.27
3.37
3.35
2.68
2.67
2.65
2.25
2.02
2.00
1.74
1.72
1.20
1.18
1.11
1.09
0.00
iPr
iPr
O
N
S
Br
ClO4−
2.01
2.01
1.03
2.02
2.00
1.97
2.03
4.05
2.18
6.08
6.00
f1 (ppm)

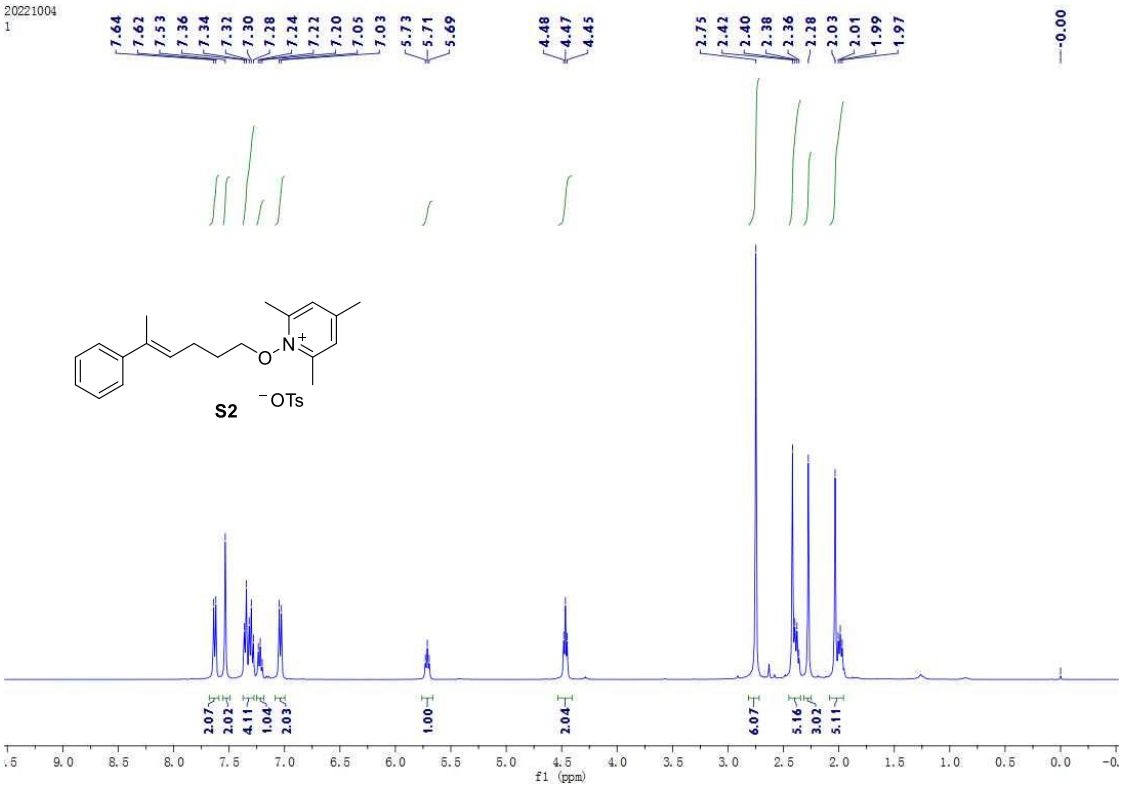
F3

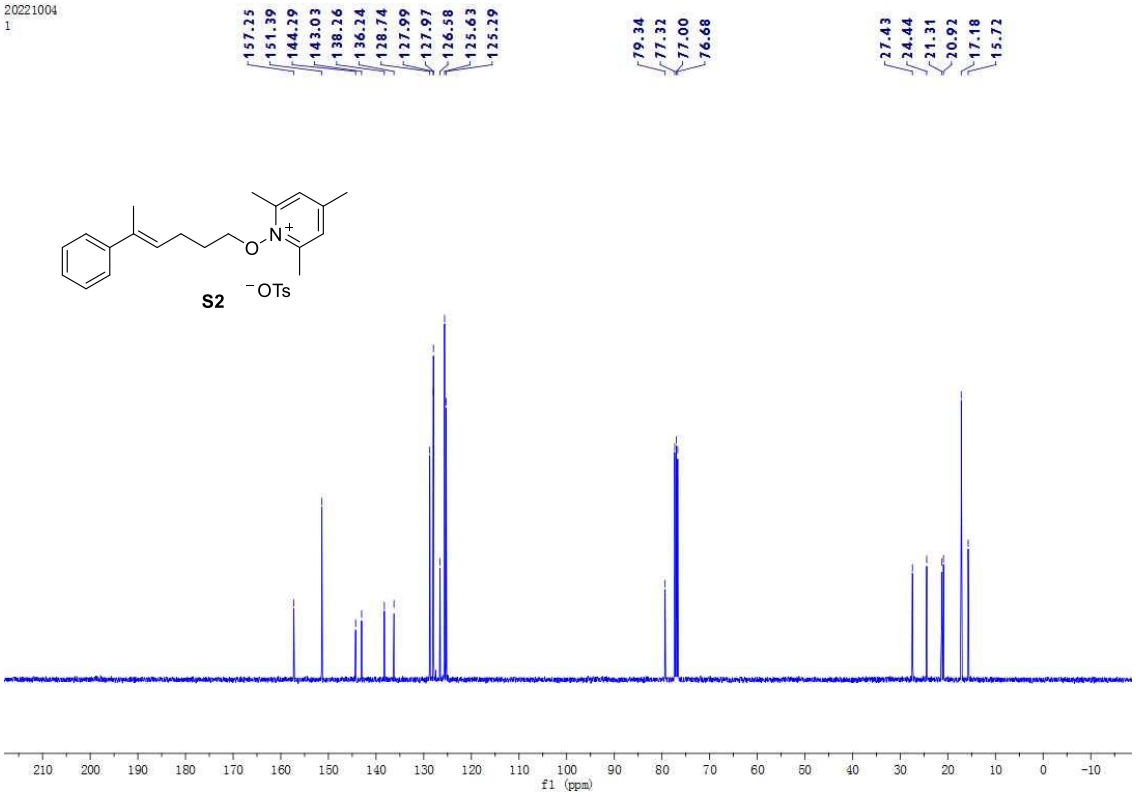

178.39
155.41
152.94
145.05
144.84
133.65
133.09
132.26
132.20
131.33
125.16
77.32
77.00
76.68
30.72
28.95
28.69
27.83
25.91
25.28
24.19
23.88
iPr
iPr
O
N
S
Br
ClO4−
f1 (ppm)

F3


20221002
1
7.83
7.82
7.82
7.81
7.74
7.73
7.73
7.72
7.71
7.39
7.37
7.31
7.29
7.27
7.22
7.20
7.19
5.80
5.79
5.77
4.27
4.26
4.24
2.48
2.46
2.44
2.42
2.08
1.98
1.96
1.95
1.93
1.91
0.00
S1
2.00
2.07
1.99
1.99
1.08
1.00
1.98
2.05
2.94
2.01
f1 (ppm)


20221002
1
163.56
143.64
135.88
134.35
128.87
128.06
126.68
126.53
125.56
123.37
77.86
77.32
77.00
76.68
28.05
24.76
15.76
S1
f1 (ppm)


20221004
1
7.64
7.62
7.53
7.36
7.34
7.32
7.30
7.28
7.24
7.22
7.20
7.05
7.03
5.73
5.71
5.69
4.48
4.47
4.45
2.75
2.42
2.40
2.38
2.36
2.28
2.03
2.01
1.99
1.97
0.00
S2
OTs
2.07
2.02
4.11
1.04
2.03
1.00
2.04
6.07
5.16
3.02
5.11
f1 (ppm)

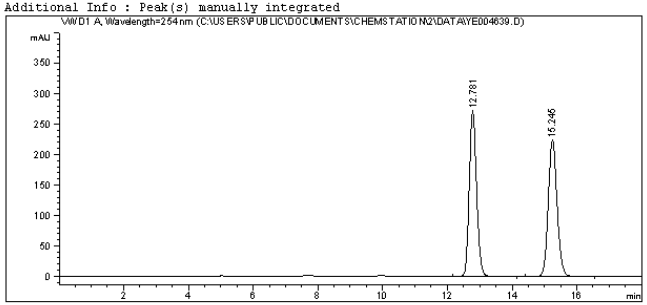

20221004
1
157.25
151.39
144.29
143.03
138.26
136.24
128.74
127.99
127.97
126.58
125.63
125.29
79.34
77.32
77.00
76.68
27.43
24.44
21.31
20.92
17.18
15.72
S2
OTs
f1 (ppm)

10. Copies of HPLC spectra

10.1 HPLC spectra of 3

Data File C:\USERS\PUBLIC\DOCUMENTS\CHEMSTATION\2\DATA\YE004639.D
Sample Name: LWD-5

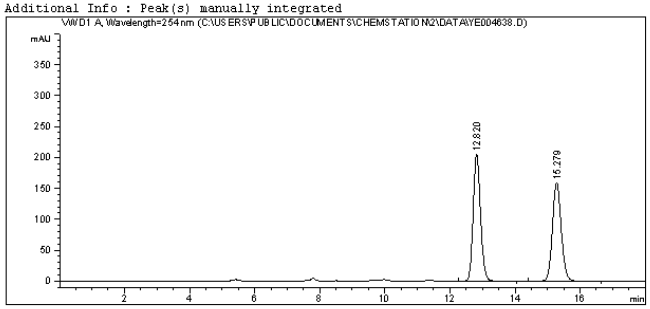
```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260                          Location :     -
Injection Date  : 9/15/2022 11:08:35 AM              Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/15/2022 10:50:03 AM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/15/2022 7:32:19 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 70/30, 0.6 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.781 BB    0.2409 4239.43799  271.83368  50.0468
   2  15.245 BB    0.2929 4231.51611  223.48911  49.9532

Totals :                  8470.95410  495.32278


==========================================================================
                        *** End of Report ***
```


Data File C:\USERS\PUBLIC\DOCUMENTS\CHEMSTATION\2\DATA\YE004638.D
Sample Name: LWD-6

```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260                          Location :     -
Injection Date  : 9/13/2022 9:31:25 PM               Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/13/2022 8:34:05 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/15/2022 7:32:19 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 70/30, 0.6 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```

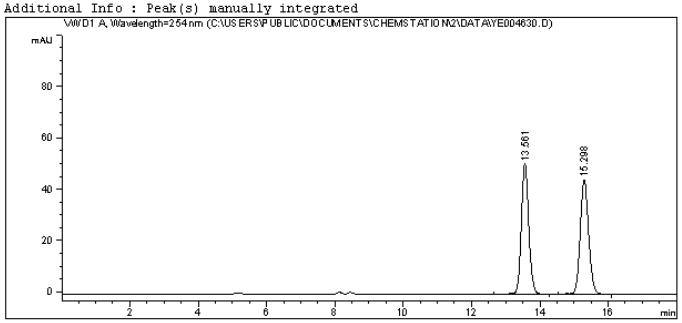



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.820 BB    0.2394 3185.15234  204.89972  51.4183
   2  15.279 BB    0.2913 3009.43481  159.38892  48.5817

Totals :                  6194.58716  364.28864


==========================================================================
                        *** End of Report ***
```

10.2 HPLC spectra of 72

Data File C:\USERS\PUBLIC\DOCUMENTS\CHEMSTATION\2\DATA\YE004630.D
Sample Name: LWD-3

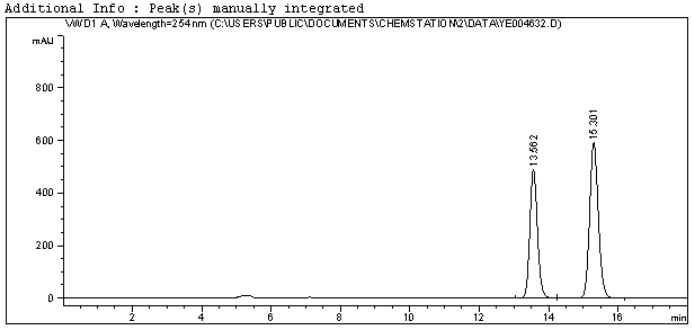
```
======================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260                          Location :     -
Injection Date  : 9/7/2022 8:34:39 PM                Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/7/2022 7:54:33 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/7/2022 9:06:03 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 70/30, 0.6 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.561 VV R  0.2320  766.13458   50.76930  50.0060
   2  15.298 VB R  0.2650  765.95007   44.56546  49.9940

Totals :                  1532.08466   95.33477

======================================================================
                        *** End of Report ***
```


Data File C:\USERS\PUBLIC\DOCUMENTS\CHEMSTATION\2\DATA\YE004632.D
Sample Name: LWD-4

```
======================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260                          Location :     -
Injection Date  : 9/7/2022 9:16:50 PM                Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/7/2022 7:54:33 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\2\Methods\DEF_LC.M
Last changed    : 9/7/2022 9:38:11 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 70/30, 0.6 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.562 BB    0.2358 7441.81006  488.31500  41.8364
   2  15.301 VB R  0.2707 1.0346le4   591.29816  58.1636

Totals :                  1.77879e4  1079.61316

======================================================================
                        *** End of Report ***
```