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Palladium-catalyzed stereoselective decarboxylative allylation of azlactones: access to (*Z*)-trisubstituted allylic amino acid derivatives

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Supporting Information

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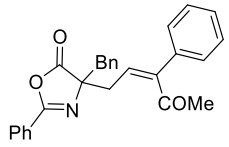
1. General experimental information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52 ppm). Melting points were recorded on a Büchi Melting Point B-545. The HRMS were recorded by Agilent 6545 LC/Q-TOF mass spectrometer.

2. General experimental procedures for synthesis of compounds 3

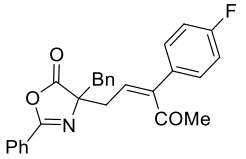
Method A: To a flame dried reaction tube were added $Pd(PPh_3)_2Cl_2$ (3.5 mg, 5 mol%) and ligand **L4** (5.8 mg, 10 mol%), followed by addition distilled chlorobenzene (1.0 mL). Then vinyl methylene cyclic carbonates **1** (0.1 mmol) and azlatones **2** (0.1 mmol) were added at 0 ^{o}C under an argon atmosphere. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 ～ 15:1) to give the corresponding product **3**.

Method B: To a flame dried reaction tube were added $Pd(PPh_3)_2Cl_2$ (3.5 mg, 5 mol%) and ligand **L4** (5.8 mg, 10 mol%), followed by addition distilled CH_2Cl_2 (1.0 mL). Then vinyl methylene cyclic carbonates **1** (0.1 mmol), *N*-acyl amino acids **4** (0.12 mmol, 1.2 equiv) and DCC (0.12 mmol, 1.2 equiv) were added at 0 ^{o}C under an argon atmosphere. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1～15:1) to give the corresponding product **3**.



(*Z*)-4-benzyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3aa)

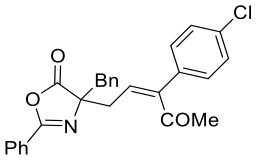
Colourless oil, method A: 36.4 mg, 89% yield; method B: 28.0 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.57 – 7.50 (m, 1H), 7.47 – 7.40 (m, 2H), 7.32 – 7.27 (m, 3H), 7.22 – 7.09 (m, 7H), 5.81 (t, *J* = 7.8 Hz, 1H), 3.29 (d, *J* = 13.5 Hz, 1H), 3.22 (d, *J* = 13.4 Hz, 1H), 3.13 – 3.00 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 179.1, 160.3, 147.8, 137.4, 134.2, 132.8, 130.3, 128.9, 128.4, 128.3, 127.9, 127.4, 127.3, 126.8, 125.6, 74.6, 43.3, 36.7, 30.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}NO_3$ 410.1751; Found: 410.1753.



(Z)-4-benzyl-4-(3-(4-fluorophenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ba)

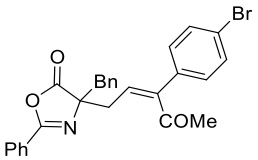
Colourless oil, method A: 34.8 mg, 81% yield; method B: 21.8 mg, 51% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.41 (m, 2H), 7.21 – 7.13 (m, 5H), 7.12 – 7.05 (m, 2H), 7.02 – 6.95 (m, 2H), 5.76 (t, *J* = 7.7 Hz, 1H), 3.27 (d, *J* = 13.5 Hz, 1H),

3.21 (d, *J* = 13.5 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.3, 179.0, 162.8 (d, *J* = 249.2 Hz), 160.3, 146.7, 134.1, 133.5 (d, *J* = 3.4 Hz), 132.9, 130.3, 129.1 (d, *J* = 8.2 Hz), 128.9, 128.3, 127.9, 127.5, 127.0, 125.5, 115.9 (d, *J* = 21.5 Hz), 74.6, 43.3, 36.7, 30.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}FNO_3$ 428.1656; Found: 428.1660.



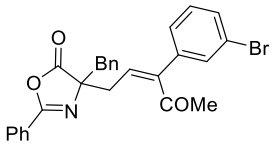
(Z)-4-benzyl-4-(3-(4-chlorophenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ca)

Colourless oil, method B: 31.9 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.50 – 7.44 (m, 1H), 7.40 – 7.33 (m, 2H), 7.21 – 7.17 (m, 2H), 7.13 – 7.03 (m, 5H), 6.99 – 6.93 (m, 2H), 5.71 (t, *J* = 7.7 Hz, 1H), 3.19 (d, *J* = 13.4 Hz, 1H), 3.12 (d, *J* = 13.4 Hz, 1H), 3.03 – 2.89 (m, 2H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 179.0, 160.3, 146.6, 135.8, 134.5, 134.1, 132.9, 130.3, 129.1, 128.9, 128.6, 128.3, 127.9, 127.5, 127.4, 125.5, 74.5, 43.3, 36.7, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO_3$ 444.1361; Found: 444.1366.



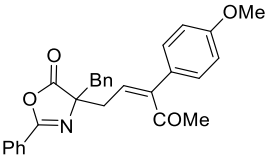
(Z)-4-benzyl-4-(3-(4-bromophenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3da)

White solid, method A, 43.2 mg, 89% yield; method B: 36.6 mg, 75% yield; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.86 – 7.79 (m, 2H), 7.63 – 7.56 (m, 1H), 7.53 – 7.46 (m, 3H), 7.33 – 7.25 (m, 2H), 7.20 – 7.10 (m, 6H), 5.92 (t, *J* = 7.7 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.19 (d, *J* = 13.5 Hz, 1H), 3.02 – 2.91 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.9, 178.3, 159.2, 145.1, 139.1, 134.1, 132.8, 130.9, 130.6, 129.9, 129.4, 128.9, 127.8, 127.3, 127.0, 125.8, 124.9, 122.0, 73.6, 41.9, 35.9, 30.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}BrNO_3$ 488.0856; Found: 488.0861.



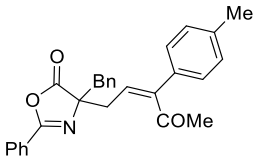
(*Z*)-4-benzyl-4-(3-(3-bromophenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ea)

White solid, method A, 23.0 mg, 47% yield; method B: 39.0 mg, 80% yield, m.p. 114.3-114.9 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 – 7.77(m, 2H), 7.64 – 7.57 (m, 1H), 7.55 – 7.47 (m, 3H), 7.35 – 7.27 (m, 2H), 7.23 – 7.07 (m, 6H), 5.94 (t, *J* = 7.7 Hz, 1H), 3.29 (d, *J* = 13.4 Hz, 1H), 3.20 (d, *J* = 13.5 Hz, 1H), 3.03 – 2.92 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 202.4, 178.5, 159.3, 145.1, 139.2, 134.4, 133.1, 131.1, 130.9, 130.1, 129.4, 129.1, 128.0, 127.9, 127.5, 127.2, 126.0, 125.0, 122.1, 73.7, 41.9, 35.9, 30.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}BrNO_3$ 488.0856; Found: 488.0856.



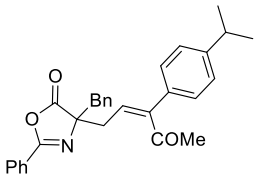
(Z)-4-benzyl-4-(3-(4-methoxyphenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3fa)

Colourless oil, method A, 25.8 mg, 59% yield; method B: 24.7 mg, 56% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 – 7.78 (m, 2H), 7.66 – 7.59 (m, 1H), 7.56 – 7.48 (m, 2H), 7.22 – 7.12 (m, 5H), 7.11 – 7.05 (m, 2H), 6.93 – 6.86 (m, 2H), 5.73 (t, *J* = 7.8 Hz, 1H), 3.73 (s, 3H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.20 (d, *J* = 13.5 Hz, 1H), 2.93 (dd, *J* = 7.9, 2.6 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 203.5, 178.6, 159.3, 159.2, 146.5, 134.4, 133.0, 130.0, 129.1, 128.8, 128.0, 127.9, 127.4, 127.1, 125.0, 123.3, 114.3, 73.9, 55.2, 42.0, 40.2, 30.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_4$ 440.1856; Found: 440.1863.



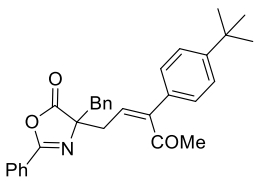
(Z)-4-benzyl-4-(4-oxo-3-(p-tolyl)pent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ga)

Colourless oil, method A, 34.5 mg, 82% yield; method B: 32.1 mg, 76% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.47 – 7.41 (m, 2H), 7.19 – 7.13 (m, 5H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.98 (m, 2H), 5.76 (t, *J* = 7.7 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.09 – 3.00 (m, 2H), 2.32 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.0, 179.1, 160.3, 147.7, 138.3, 134.5, 134.2, 132.8, 130.3, 129.5, 128.9, 128.3, 127.9, 127.4, 127.2, 125.8, 125.6, 74.7, 43.3, 36.7, 30.9, 21.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_3$ 424.1907; Found: 424.1911.



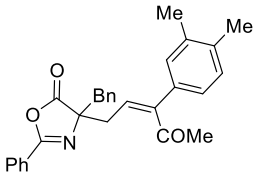
(Z)-4-benzyl-4-(3-(4-isopropylphenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ha)

Colourless oil, method A, 34.8 mg, 77% yield; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.88 – 7.80 (m, 2H), 7.68 – 7.59 (m, 1H), 7.56 – 7.49 (m, 2H), 7.24 – 7.18 (m, 4H), 7.17 – 7.12 (m, 3H), 7.10 – 7.06 (m, 2H), 5.80 (t, *J* = 7.8 Hz, 1H), 3.29 (d, *J* = 13.6 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.00 – 2.91 (m, 2H), 2.85 (p, *J* = 6.9 Hz, 1H), 2.17 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 203.5, 178.6, 159.2, 148.6, 146.8, 134.4, 134.1, 133.1, 130.1, 129.2, 128.0, 127.5, 127.2, 126.9, 126.6, 125.0, 124.5, 73.9, 42.0, 35.8, 33.1, 30.8, 23.7, 23.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{30}NO_3$ 452.2220; Found: 452.2225.



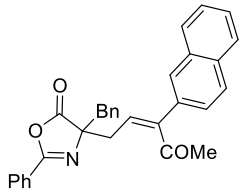
(Z)-4-benzyl-4-(3-(4-(tert-butyl)phenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ia)

Colourless oil, method A, 40.6 mg, 87% yield; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.86 – 7.80 (m, 2H), 7.66 – 7.59 (m, 1H), 7.54 – 7.50 (m, 2H), 7.38 – 7.34 (m, 2H), 7.21 – 7.17 (m, 2H), 7.16 – 7.11 (m, 3H), 7.11 – 7.07 (m, 2H), 5.80 (t, *J* = 7.8 Hz, 1H), 3.28 (d, *J* = 13.6 Hz, 1H), 3.20 (d, *J* = 13.6 Hz, 1H), 2.99 – 2.90 (m, 2H), 2.17 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 203.5, 178.6, 159.2, 150.9, 146.7, 134.4, 133.7, 133.1, 130.0, 129.2, 128.0, 127.5, 127.2, 126.3, 125.7, 125.0, 124.5, 73.9, 42.0, 35.8, 34.3, 31.0, 30.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{32}NO_3$ 466.2377; Found: 466.2383.



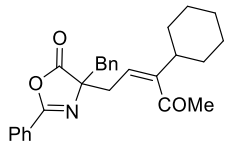
(Z)-4-benzyl-4-(3-(3,4-dimethylphenyl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ja)

White solid, method A, 27.2 mg, 62% yield; method B: 32.8 mg, 75% yield; m.p. 137.1-137.9 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 7.19 – 7.08 (m, 5H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), 5.70 (t, *J* = 7.9 Hz, 1H), 3.26 (d, *J* = 13.5 Hz, 1H), 3.17 (d, *J* = 13.5 Hz, 1H), 2.96 – 2.87 (m, 2H), 2.17 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 203.4, 178.8, 159.7, 147.5, 137.0, 136.9, 134.7, 133.3, 130.4, 130.2, 129.3, 128.3, 128.2, 127.8, 127.5, 125.5, 124.8, 124.4, 74.4, 42.5, 36.4, 30.9, 19.7, 19.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{28}NO_3$ 438.2064; Found: 438.2070.



(Z)-4-benzyl-4-(3-(naphthalen-2-yl)-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ka)

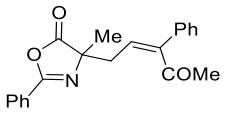
Colourless oil, method A, 40.2 mg, 88% yield; method B: 22.5 mg, 49% yield; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.91 – 7.81 (m, 5H), 7.66 – 7.60 (m, 2H), 7.55 – 7.47 (m, 4H), 7.36 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.22 – 7.13 (m, 5H), 6.02 (t, *J* = 7.8 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.24 (d, *J* = 13.6 Hz, 1H), 3.07 – 2.98 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 203.3, 178.6, 159.3, 146.8, 134.4, 134.0, 133.1, 132.8, 132.5, 130.1, 129.2, 128.5, 128.1, 128.0, 127.6, 127.5, 127.2, 126.7, 126.6, 125.9, 125.8, 125.0, 124.5, 74.0, 42.0, 36.0, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}NO_3$ 460.1907; Found: 460.1912.



(Z)-4-benzyl-4-(3-cyclohexyl-4-oxopent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3la)

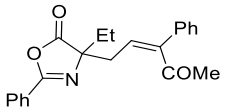
Colourless oil, method A, 15.9 mg, 38% yield; method B: 36.3 mg, 87% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 – 7.73 (m, 2H), 7.67 – 7.59 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.01 (m, 5H), 5.22 (t, *J* = 7.8 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.13 (d, *J* = 13.4 Hz, 1H), 2.77 (d, *J* = 7.8 Hz, 2H), 2.21 (s, 3H), 2.21 - 2.13 (m, 1H), 1.67 – 1.45 (m, 5H), 1.26 – 1.13 (m, 2H), 1.08 – 0.90 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 204.9, 178.6, 159.0, 152.1, 134.4, 133.0, 130.0,

129.1, 128.0, 127.4, 127.1, 125.0, 120.0, 74.1, 42.0, 38.9, 35.6, 31.8, 31.6, 30.4, 25.8, 25.8, 25.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{29}NaNO_3$ 438.2040; Found: 438.2042.



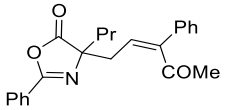
(Z)-4-methyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ab)

Colourless oil, method A, 27.3 mg, 82% yield; method B: 18.2 mg, 55% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.61 – 7.57 (m, 1H), 7.53 – 7.47 (m, 2H), 7.29 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.15 – 7.10 (m, 2H), 5.77 (t, *J* = 7.7 Hz, 1H), 2.97 – 2.86 (m, 2H), 2.18 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.6, 180.2, 160.3, 147.7, 137.4, 133.0, 129.0, 128.9, 128.4, 128.1, 127.3, 126.9, 125.8, 69.5, 37.5, 30.9, 23.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}NO_3$ 334.1438; Found: 334.1443.



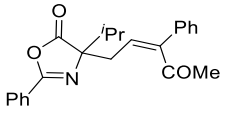
(Z)-4-ethyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ac)

Colourless oil, method A, 16.8 mg, 48% yield; method B: 24.5 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 2H), 7.62 – 7.56 (m, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.11 (dd, *J* = 6.7, 2.9 Hz, 2H), 5.76 (t, *J* = 7.8 Hz, 1H), 3.03 – 2.85 (m, 2H), 2.17 (s, 3H), 2.06 – 1.97 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 179.8, 160.5, 147.6, 137.5, 133.0, 129.0, 128.9, 128.3, 128.1, 127.3, 126.9, 125.8, 74.0, 36.6, 30.9, 30.3, 8.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_3$ 348.1594; Found: 348.1598.



(Z)-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-phenyl-4-propyloxazol-5(4H)-one (3ad)

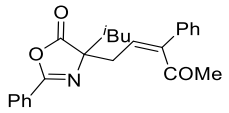
Colourless oil, method A, 19.1 mg, 53% yield; method B: 25.0 mg, 69% yield; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 – 7.92 (m, 2H), 7.64 – 7.55 (m, 1H), 7.54 – 7.45 (m, 2H), 7.31 – 7.22 (m, 3H), 7.11 (dt, *J* = 5.8, 3.0 Hz, 2H), 5.81 – 5.68 (m, 1H), 2.97 (ddd, *J* = 14.8, 7.6, 3.7 Hz, 1H), 2.89 (ddd, *J* = 14.9, 7.9, 3.7 Hz, 1H), 2.17 (d, *J* = 3.8 Hz, 3H), 1.99 – 1.87 (m, 2H), 1.31 (dqt, *J* = 16.4, 7.8, 4.6 Hz, 1H), 1.25 – 1.16 (m, 1H), 0.95 – 0.85 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.7, 179.9, 160.4, 147.6, 137.4, 133.0, 129.0, 128.8, 128.3, 128.1, 127.3, 126.9, 125.7, 73.5, 39.2, 36.9, 30.9, 17.4, 14.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}NO_3$ 362.1751; Found: 362.1755.



(Z)-4-isopropyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3ae)

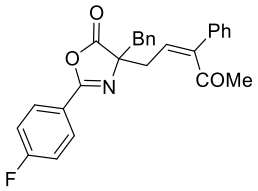
Colourless oil, method A, 28.9 mg, 80% yield; method B: 25.3 mg, 70% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.94 (m, 2H), 7.63 – 7.54 (m, 1H), 7.50 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.27 (dd, *J* = 5.6, 2.4 Hz, 3H), 7.14 – 7.00 (m, 2H), 5.69 (t, *J* = 7.8 Hz, 1H), 3.03 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.93 (dd, *J* = 14.8, 8.1 Hz, 1H), 2.24 (q, *J* = 7.0 Hz, 1H), 2.16 (d, *J* = 1.4 Hz, 3H), 1.09 (d,

J = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 203.8, 179.8, 160.4, 147.7, 137.5, 132.9, 129.0, 128.8, 128.3, 128.1, 127.3, 127.2, 125.8, 76.7, 34.8, 34.5, 30.8, 17.2, 16.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}NO_3$ 362.1751; Found: 362.1755.



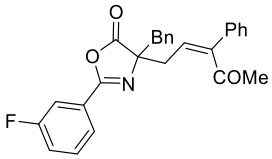
(Z)-4-isobutyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-phenyloxazol-5(4H)-one (3af)

Colourless oil, method A, 17.6 mg, 47% yield; method B: 21.5 mg, 57% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.98 (m, 2H), 7.63 – 7.55 (m, 1H), 7.55 – 7.47 (m, 2H), 7.32 – 7.23 (m, 3H), 7.15 – 7.04 (m, 2H), 5.71 (t, *J* = 7.8 Hz, 1H), 2.99 – 2.82 (m, 2H), 2.15 (q, *J* = 1.1 Hz, 3H), 2.06 – 1.97 (m, 1H), 1.91 – 1.81 (m, 1H), 1.71 – 1.62 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 180.4, 160.1, 147.9, 137.4, 133.0, 129.0, 128.8, 128.3, 128.1, 127.3, 126.6, 125.8, 73.1, 45.8, 38.0, 30.8, 25.1, 24.2, 23.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}NO_3$ 376.1907; Found: 376.1910.



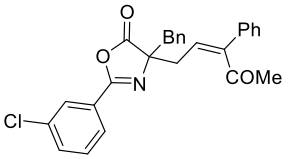
(Z)-4-benzyl-2-(4-fluorophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3ag)

Colourless oil, method A, 37.9 mg, 89% yield; method B: 23.2 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.30 (t, *J* = 3.3 Hz, 3H), 7.19 – 7.08 (m, 9H), 5.80 (t, *J* = 7.8 Hz, 1H), 3.27 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 178.8, 165.6 (d, *J* = 255.8 Hz), 159.4, 147.7, 137.4, 134.1, 130.4, 130.3, 128.9, 128.4, 128.3, 127.4, 127.3, 126.8, 121.8 (d, *J* = 3.1 Hz), 116.2 (d, *J* = 22.4 Hz), 74.6, 43.3, 36.7, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}NO_3$ 428.1656; Found: 428.1667.



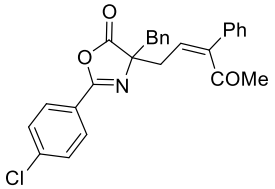
(Z)-4-benzyl-2-(3-fluorophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3ah)

Colourless oil, method B, 19.1 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 1H), 7.61 – 7.54 (m, 1H), 7.45 – 7.38 (m, 1H), 7.31 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.25 – 7.17 (m, 2H), 7.16 (dd, *J* = 6.6, 2.4 Hz, 4H), 7.12 (dd, *J* = 6.7, 3.0 Hz, 2H), 5.79 (t, *J* = 7.7 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 13.4 Hz, 1H), 3.12 – 2.99 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 178.6, 162.7 (d, *J* = 249.0 Hz), 159.3 (d, *J* = 3.3 Hz), 147.8, 137.4, 134.0, 130.7 (d, *J* = 8.0 Hz), 130.3, 128.9, 128.4, 128.3, 127.6 (d, *J* = 8.3 Hz), 127.5, 127.3, 126.7, 123.7 (d, *J* = 3.2 Hz), 120.0 (d, *J* = 21.4 Hz), 114.9 (d, *J* = 23.9 Hz), 74.8, 43.2, 36.6, 30.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{22}NaNO_3$ 450.1476; Found: 450.1481.



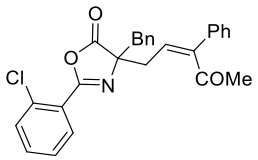
(Z)-4-benzyl-2-(3-chlorophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3ai)

Colourless oil, method A, 36.3 mg, 82% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 1H), 7.77 – 7.71 (m, 1H), 7.52 – 7.48 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.22 – 7.11 (m, 7H), 5.79 (t, *J* = 7.7 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.22 (d, *J* = 13.5 Hz, 1H), 3.10 – 3.01 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.6, 178.5, 159.2, 147.8, 137.4, 135.1, 134.0, 132.9, 130.3, 130.2, 128.9, 128.4, 128.3, 127.9, 127.5, 127.4, 127.3, 126.7, 126.0, 74.7, 43.2, 36.7, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO_3$ 444.1361; Found: 444.1362.



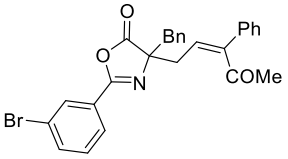
(Z)-4-benzyl-2-(4-chlorophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3aj)

Colourless oil, method B, 35.1 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.22 – 7.03 (m, 7H), 5.79 (t, *J* = 7.7 Hz, 1H), 3.27 (d, *J* = 13.4 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.12 – 3.00 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 178.7, 159.5, 147.8, 139.3, 137.4, 134.1, 130.2, 129.3, 129.2, 128.9, 128.4, 128.3, 127.5, 127.3, 126.7, 124.0, 77.5, 43.2, 36.6, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO_3$ 444.1361; Found: 444.1360.



(Z)-4-benzyl-2-(2-chlorophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3ak)

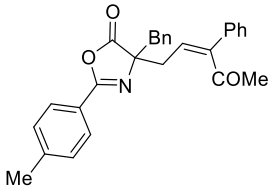
Colourless oil, method B, 22.9 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 3H), 7.32 (dd, *J* = 5.3, 2.0 Hz, 3H), 7.29 – 7.25 (m, 1H), 7.25 – 7.15 (m, 7H), 5.85 (t, *J* = 7.7 Hz, 1H), 3.36 – 3.23 (m, 2H), 3.11 (d, *J* = 7.7 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 178.8, 159.2, 147.8, 137.3, 134.1, 133.6, 132.9, 131.2, 131.0, 130.4, 128.9, 128.4, 127.6, 127.3, 126.9, 126.6, 125.6, 74.9, 43.3, 36.6, 30.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO_3$ 444.1361; Found: 444.1365.



(Z)-4-benzyl-2-(3-bromophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3al)

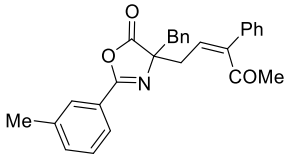
Colourless oil, method A, 30.5 mg, 63% yield; method B: 26.1 mg, 54% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (t, *J* = 1.8 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.68 – 7.64 (m, 1H), 7.33 – 7.28 (m, 4H), 7.20 – 7.12 (m, 7H), 5.79 (t, *J* = 7.7 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.22 (d, *J* = 13.5 Hz,

1H), 3.10 – 3.01 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.5, 178.5, 159.1, 147.8, 137.4, 135.8, 134.0, 130.8, 130.5, 130.2, 128.9, 128.4, 128.3, 127.5, 127.4, 127.3, 126.7, 126.5, 123.0, 74.7, 43.2, 36.7, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}BrNO_3$ 488.0856; Found: 488.0857.



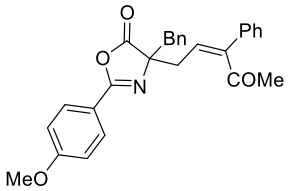
(Z)-4-benzyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-(p-tolyl)oxazol-5(4H)-one (3am)

Colourless oil, method B, 25.9 mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.13 (m, 6H), 7.11 – 7.07 (m, 4H), 7.06 – 7.02 (m, 2H), 5.71 (t, *J* = 7.7 Hz, 1H), 3.19 (d, *J* = 13.4 Hz, 1H), 3.12 (d, *J* = 13.4 Hz, 1H), 2.97 (dd, *J* = 7.7, 2.7 Hz, 2H), 2.32 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 179.2, 160.4, 147.7, 143.6, 137.4, 134.3, 130.3, 129.6, 128.9, 128.4, 128.3, 127.9, 127.4, 127.3, 126.9, 122.8, 74.6, 43.3, 36.7, 30.9, 21.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_3$ 424.1907; Found: 424.1914.



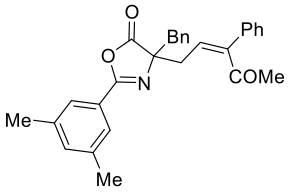
(Z)-4-benzyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-(m-tolyl)oxazol-5(4H)-one (3an)

Colourless oil, method A, 34.6 mg, 82% yield; method B: 27.5 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.62 (m, 2H), 7.38 – 7.26 (m, 5H), 7.24 – 7.05 (m, 7H), 5.80 (t, *J* = 7.8 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.10 – 3.01 (m, 2H), 2.38 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 179.1, 160.5, 147.7, 138.8, 137.4, 134.2, 133.7, 130.3, 128.9, 128.8, 128.4, 128.3, 128.3, 127.4, 127.3, 126.9, 125.5, 125.2, 74.6, 43.3, 36.7, 30.9, 21.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_3$ 424.1907; Found: 424.1919.



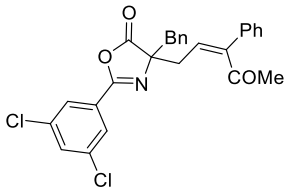
(Z)-4-benzyl-2-(4-methoxyphenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3ao)

Colourless oil, method B, 33.4 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.22 – 7.08 (m, 7H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.80 (t, *J* = 7.7 Hz, 1H), 3.84 (s, 3H), 3.26 (d, *J* = 13.4 Hz, 1H), 3.19 (d, *J* = 13.4 Hz, 1H), 3.10 – 2.98 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 179.2, 163.3, 160.0, 147.6, 137.4, 134.3, 130.3, 129.8, 128.8, 128.3, 128.2, 127.4, 127.3, 126.9, 117.8, 114.3, 74.5, 55.5, 43.3, 36.8, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_4$ 440.1856; Found: 440.1860.



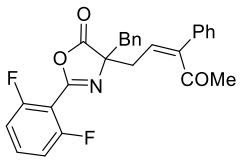
(Z)-4-benzyl-2-(3,5-dimethylphenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3ap)

Colourless oil, method A, 36.8 mg, 84% yield; method B: 29.6 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.32 – 7.27 (m, 3H), 7.21 – 7.14 (m, 6H), 7.14 – 7.10 (m, 2H), 5.79 (t, *J* = 7.7 Hz, 1H), 3.27 (d, *J* = 13.5 Hz, 1H), 3.20 (d, *J* = 13.4 Hz, 1H), 3.05 (d, *J* = 7.7 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 179.1, 160.7, 147.7, 138.6, 137.4, 134.7, 134.2, 130.3, 128.9, 128.4, 128.3, 127.4, 127.3, 126.9, 125.7, 125.4, 74.5, 43.3, 36.8, 30.9, 21.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{28}NO_3$ 438.2064; Found: 438.2072.



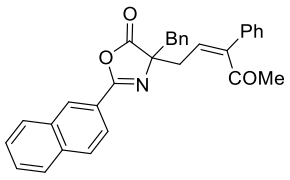
(Z)-4-benzyl-2-(3,5-dichlorophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3aq)

Colourless oil, method B, 30.2 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.32 – 7.25 (m, 2H), 7.25 – 7.18 (m, 6H), 5.84 (t, *J* = 7.7 Hz, 1H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.27 (d, *J* = 13.3 Hz, 1H), 3.12 (d, *J* = 7.7 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 178.5, 158.4, 147.8, 138.7, 137.3, 134.6, 134.0, 132.0, 131.1, 130.3, 128.9, 128.5, 128.4, 127.6, 127.4, 127.3, 126.5, 123.9, 75.0, 43.3, 36.6, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{22}Cl_2NO_3$ 478.0971; Found: 478.0978.



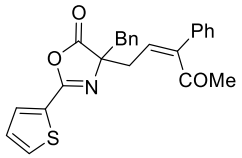
(Z)-4-benzyl-2-(2,6-difluorophenyl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3ar)

Colourless oil, method B, 36.4 mg, 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 1H), 7.30 – 7.23 (m, 3H), 7.18 (d, *J* = 7.0 Hz, 3H), 7.16 – 7.10 (m, 4H), 6.95 – 6.85 (m, 2H), 5.71 (t, *J* = 7.7 Hz, 1H), 3.23 (d, *J* = 13.5 Hz, 1H), 3.18 (d, *J* = 13.5 Hz, 1H), 3.11 – 2.96 (m, 2H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 178.3, 161.1 (dd, J_1 = 262.6 Hz, J_2 = 5.4 Hz), 153.7 (d, *J* = 2.2 Hz), 148.1, 137.3, 133.9 (d, *J* = 10.4 Hz), 133.7, 130.4, 128.9, 128.4, 127.6, 127.4, 126.1, 112.4, 112.3 (d, *J* = 1.8 Hz), 112.2 (d, *J* = 1.6 Hz), 112.1, 74.8, 43.2, 36.5, 30.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{22}F_2NO_3$ 446.1562; Found: 446.1561.



(Z)-4-benzyl-2-(naphthalen-2-yl)-4-(4-oxo-3-phenylpent-2-en-1-yl)oxazol-5(4H)-one (3as)

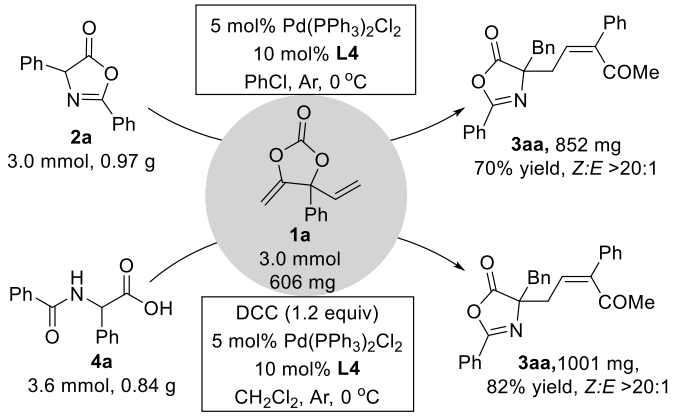
Colourless oil, method A, 34.0 mg, 74% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.7 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.84 – 7.74 (m, 3H), 7.52 – 7.47 (m, 1H), 7.47 – 7.42 (m, 1H), 7.19 – 7.15 (m, 3H), 7.14 – 7.10 (m, 2H), 7.09 – 7.00 (m, 5H), 5.75 (t, *J* = 7.7 Hz, 1H), 3.23 (d, *J* = 13.5 Hz, 1H), 3.16 (d, *J* = 13.5 Hz, 1H), 3.07 – 2.96 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.7, 179.0, 160.4, 147.8, 137.4, 135.4, 134.2, 132.6, 130.3, 129.4, 129.2, 128.9, 128.5, 128.3, 128.3, 128.0, 127.4, 127.3, 127.1, 126.8, 123.5, 122.7, 74.8, 43.4, 36.8, 30.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{25}NaNO_3$ 482.1727; Found: 482.1732.



(Z)-4-benzyl-4-(4-oxo-3-phenylpent-2-en-1-yl)-2-(thiophen-2-yl)oxazol-5(4H)-one (3at)

Colourless oil, method A, 17.3 mg, 42% yield; method B: 20.0 mg, 48% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 2H), 7.33 – 7.27 (m, 3H), 7.23 – 7.15 (m, 5H), 7.15 – 7.10 (m, 2H), 7.10 – 7.04 (m, 1H), 5.86 – 5.72 (m, 1H), 3.26 (dd, *J* = 13.6, 3.8 Hz, 1H), 3.20 (dd, *J* = 13.5, 3.8 Hz, 1H), 3.11 – 3.00 (m, 2H), 2.20 (d, *J* = 3.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.7, 178.4, 156.1, 147.8, 137.4, 134.1, 132.0, 131.9, 130.3, 128.9, 128.4, 128.3, 128.2, 128.0, 127.4, 127.3, 126.7, 74.6, 43.3, 36.7, 30.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}NO_3S$ 416.1315; Found: 416.1324.

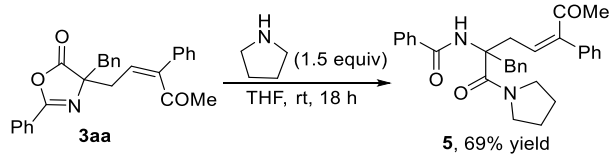
3. Scale-up Experiment



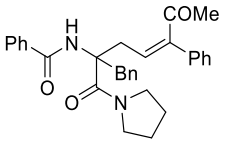
Method A: To a flame dried reaction tube were added $Pd(PPh_3)_2Cl_2$ (105.3 mg, 5 mol%) and ligand **L4** (174 mg, 10 mol%), followed by addition distilled chlorobenzene (30.0 mL). Then vinyl methylene cyclic carbonate **1a** (3.0 mmol, 606 mg) and azlatone **2a** (3.0 mmol, 970 mg) were added at 0 °C under an argon atmosphere. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the corresponding product **3aa** in 70% yield.

Method B: To a flame dried reaction tube were added $Pd(PPh_3)_2Cl_2$ (105.3 mg, 5 mol%) and ligand **L4** (174 mg, 10 mol%), followed by addition distilled CH_2Cl_2 (30.0 mL). Then vinyl methylene cyclic carbonate **1a** (3.0 mmol, 606 mg), *N*-acyl amino acid **4a** (3.6 mmol, 840 mg) and DCC (36 mmol, 1.2 equiv) were added at 0 °C under an argon atmosphere. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the corresponding product **3aa** in 82% yield.

4. Synthesis of compound 5



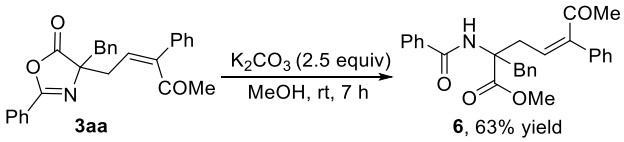
To a sealed tube equipped with compound **3aa** (81.8 mg, 0.2 mmol) in 2 mL THF were added pyrrolidine (21.5 mg, 1.5 equiv). The reaction mixture stirred at room temperature for 18 h. After completion, the resulting mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give the corresponding product **5** in 69% yield.



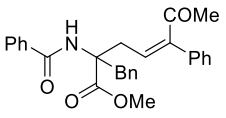
(Z)-*N*-(2-benzyl-1,6-dioxo-5-phenyl-1-(pyrrolidin-1-yl)hept-4-en-2-yl)benzamide (5)

Colourless oil, 66.2 mg, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (bs, 1H), 7.78 – 7.70 (m, 2H), 7.54 – 7.47 (m, 1H), 7.46 – 7.33 (m, 5H), 7.13 – 7.16 (m, 3H), 7.12 – 7.04 (m, 2H), 6.97 – 6.88 (m, 2H), 6.78 (dd, *J* = 9.3, 4.8 Hz, 1H), 4.05 – 3.88 (m, 2H), 3.59 – 3.49 (m, 2H), 3.44 (d, *J* = 11.4 Hz, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.89 (dd, *J* = 16.3, 9.2 Hz, 1H), 2.84 – 2.72 (m, 1H), 2.23 (s, 3H), 1.88 – 1.70 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 168.8, 166.4, 144.5, 138.0, 135.9, 135.4, 135.3, 131.6, 129.8, 129.4, 128.7, 128.4, 128.3, 128.0, 127.1, 127.0, 65.3, 38.0, 33.7, 27.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{33}N_2O_3$ 481.2486; Found: 481.2469.

5. Synthesis of compound 6



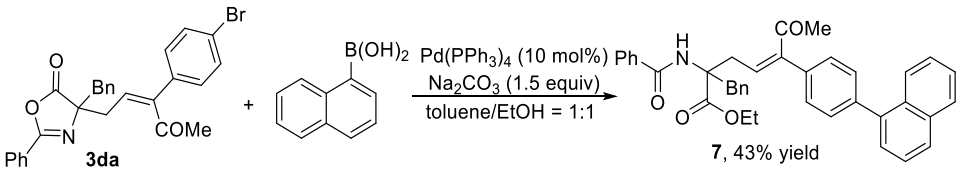
To a sealed tube equipped with compound **3aa** (81.8 mg, 0.2 mmol) in 2 mL MeOH were added K_2CO_3 (69 mg, 2.5 equiv). The reaction mixture stirred at room temperature for 7 h. After completion, the resulting mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the corresponding product **6** in 63% yield.



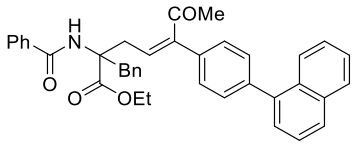
methyl (Z)-2-benzamido-2-benzyl-6-oxo-5-phenylhept-4-enoate (6)

white solid, 55.6 mg, 63% yield; m.p. 89.1-90.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 2H), 7.48 – 7.41 (m, 1H), 7.40 – 7.27 (m, 5H), 7.11 – 7.06 (m, 3H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.93 (s, 1H), 6.87 (dd, *J* = 6.8, 2.7 Hz, 2H), 6.71 – 6.62 (m, 1H), 3.79 (dd, *J* = 13.5, 2.0 Hz, 1H), 3.65 (s, 3H), 3.64 – 3.55 (m, 1H), 2.98 (d, *J* = 13.5 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 173.0, 167.0, 145.3, 136.6, 135.7, 135.6, 134.9, 131.9, 129.7, 129.5, 128.8, 128.5, 128.4, 127.9, 127.2, 127.0, 65.7, 53.0, 40.5, 35.6, 27.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{28}NO_4$ 442.2013; Found: 442.2018.

6. Synthesis of compound 7



Under arogen atmosphere, compound **3da** (48.8 mg, 0.1 mmol), naphthalen-1-ylboronic acid (20.6 mg, 1.2 equiv), Na_2CO_3 (15.9 mg, 1.5 equiv), and $Pd(PPh_3)_4$ (5.7 mg, 10 mol%) were successively added to mixed solvents of toluene (1.5 mL) and EtOH (1.5 mL). The resulting mixture was stirred at reflux for 20 h. The reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 3:1) to afford the corresponding products **7** in 43% yield.

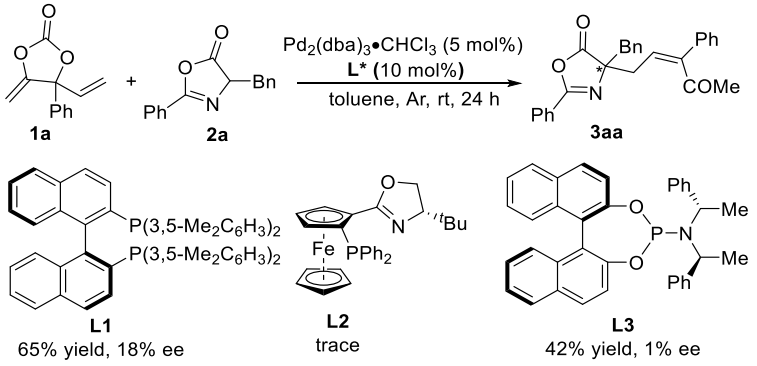


ethyl (Z)-2-benzamido-2-benzyl-5-(4-(naphthalen-1-yl)phenyl)-6-oxohept-4-enoate (7)

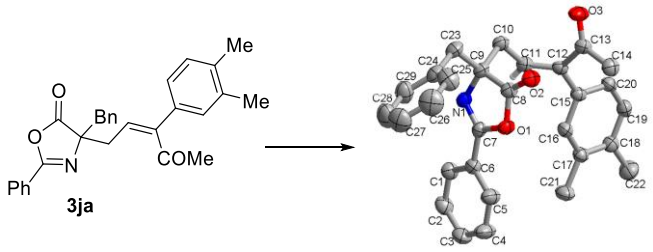
Colourless oil, 25.1 mg, 43% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 2H), 7.78 – 7.68 (m, 3H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.37 – 7.29 (m, 3H), 7.21 – 7.11 (m, 6H), 7.08 – 6.94 (m, 4H), 5.69 (t, *J* = 7.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.76 (d, *J* = 13.6 Hz, 1H), 3.51 (dd, *J* = 15.1, 8.0 Hz, 1H), 3.36 (d, *J* = 13.6 Hz, 1H), 2.91 (dd, *J* = 15.1, 7.4 Hz, 1H), 2.07 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 172.9, 167.1, 146.5, 141.4, 139.3, 137.5, 136.2, 135.4, 133.9, 133.4, 131.5, 130.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.3, 127.2, 127.1, 126.4, 126.0, 125.9, 125.8, 125.5, 65.2, 62.4, 40.3, 35.9, 30.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{36}NO_4$ 582.2639; Found: 582.2643.

7. The preliminary attempt to the asymmetric decarboxylative allylation

In a flame dried reaction tube were added $Pd_2(dba)_3$ $CHCl_3$ (5.0 mg, 5 mol%) and ligand **L*** (10 mol%). Then, distilled chlorobenzene (0.3 mL) was added and stirred for 30 minutes at rt. Vinyl methylene cyclic carbonate **1a** (0.1mmol, 20.2 mg) and azlatone **2a** (0.1 mmol, 25.1 mg) were added under an argon atmosphere. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the corresponding product **3aa** (The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm)).



8. X-Ray crystal data for compound 3ja



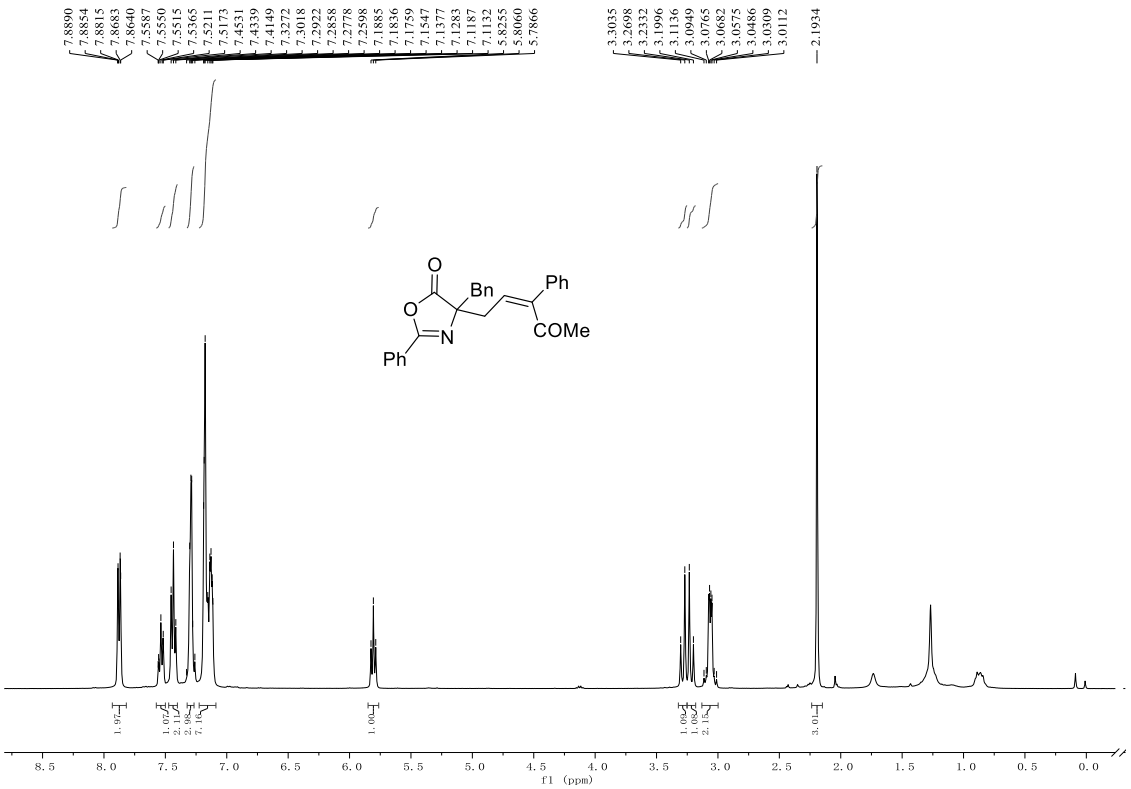
ORTEP of **3ja** (at 50% level)

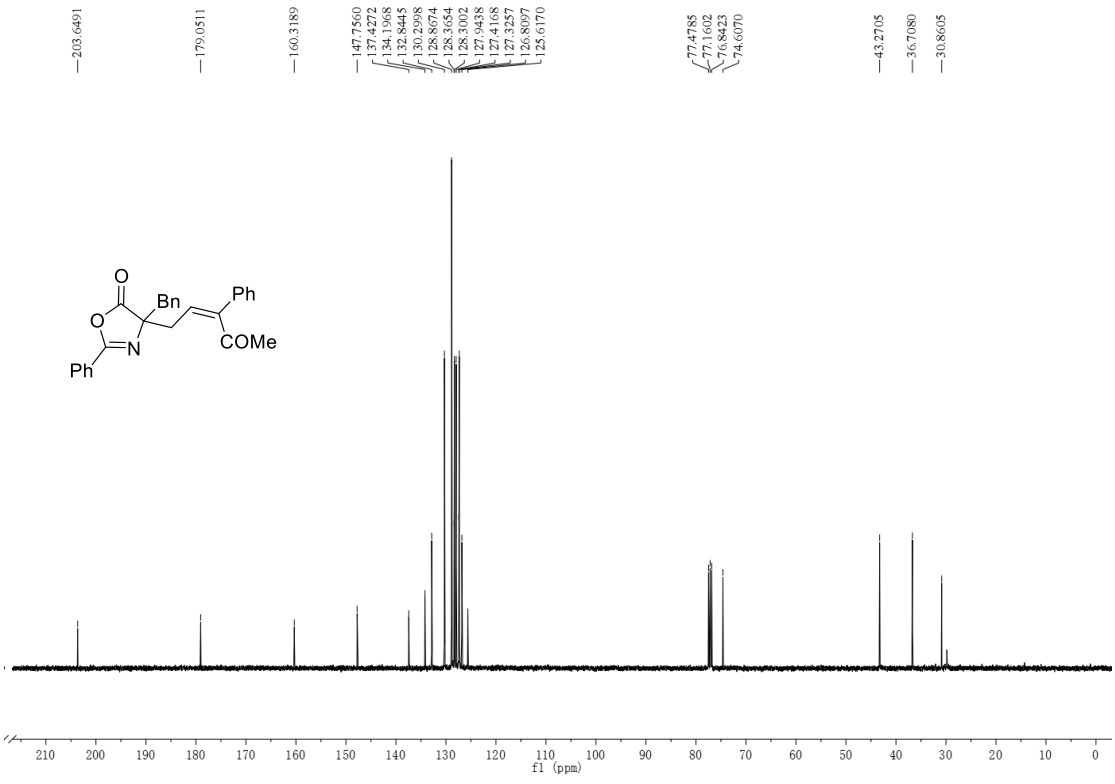
Crystal data and structure refinement for **3ja** (CCDC-2184568)

Identification code	202112381
Empirical formula	$C_{29}H_{27}NO_3$
Formula weight	437.51
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	8.29455(17)
b/Å	18.4338(4)
c/Å	16.1206(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2464.84(9)
Z	4
ρ_{calc}g/cm^3	1.179
μ/mm^{-1}	0.602
F(000)	928.0
Crystal size/mm^3	0.14 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	7.284 to 134.144
Index ranges	-6 ≤ h ≤ 9, -21 ≤ k ≤ 22, -11 ≤ l ≤ 19
Reflections collected	8291
Independent reflections	3209 [R_{int} = 0.0325, R_{sigma} = 0.0374]
Data/restraints/parameters	3209/1/301
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0405, wR_2 = 0.1004
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	0.09/-0.14
Flack parameter	0.3(3)

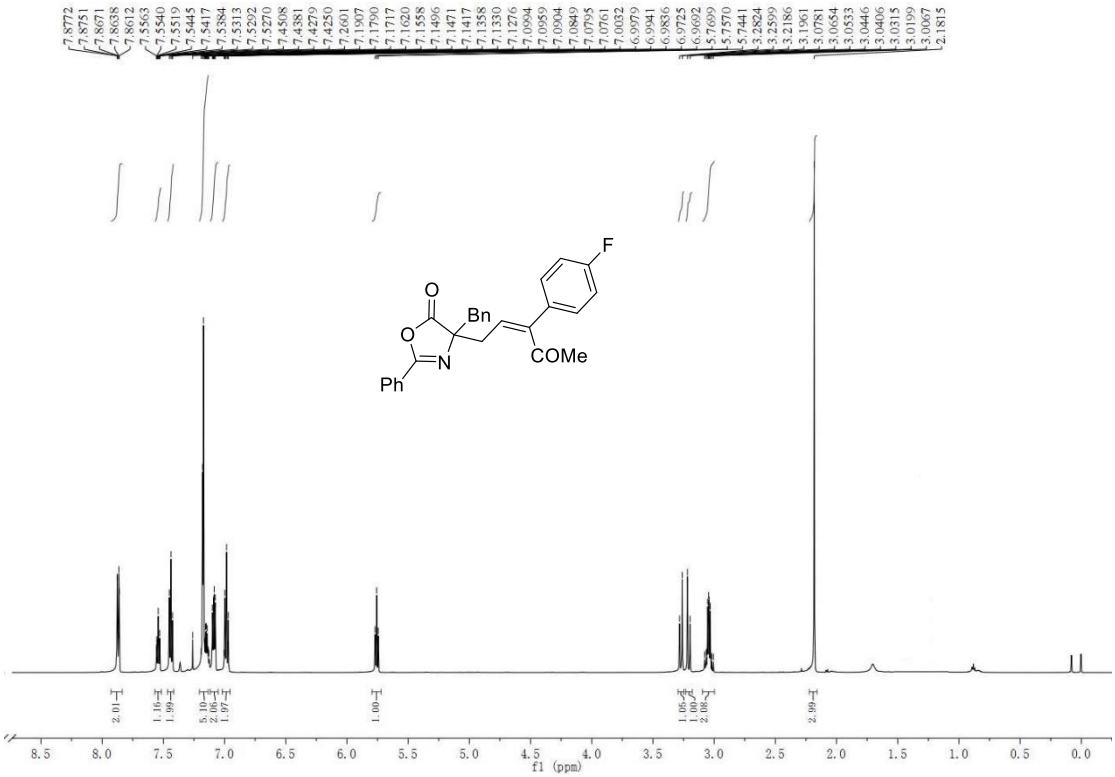
9. ^{1}H, and ^{13}C NMR spectra for compounds 3

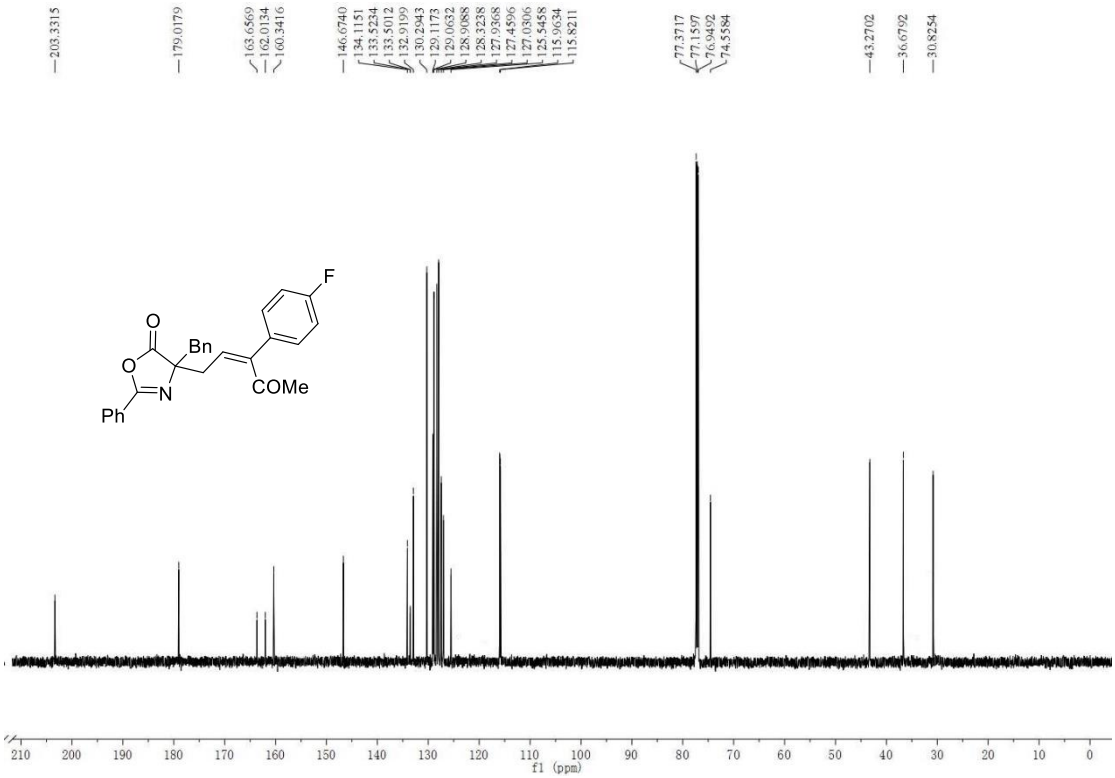
^{1}H, ^{13}C NMR of compound **3aa**



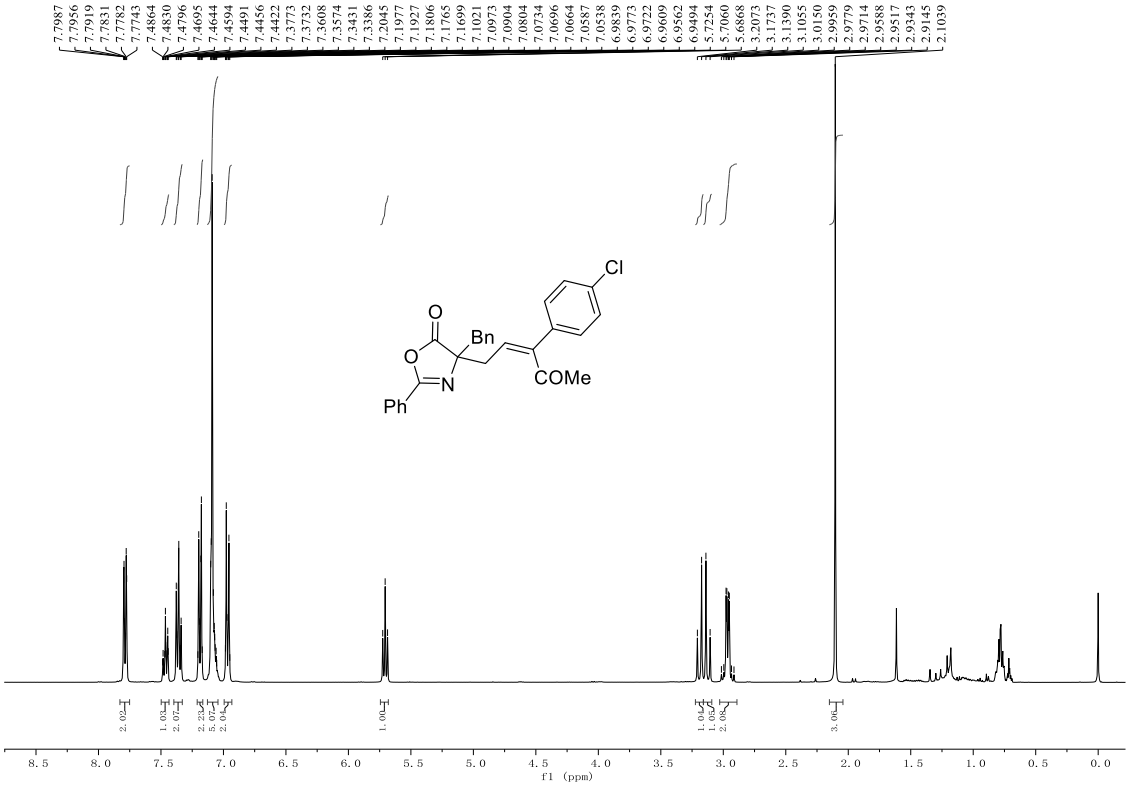


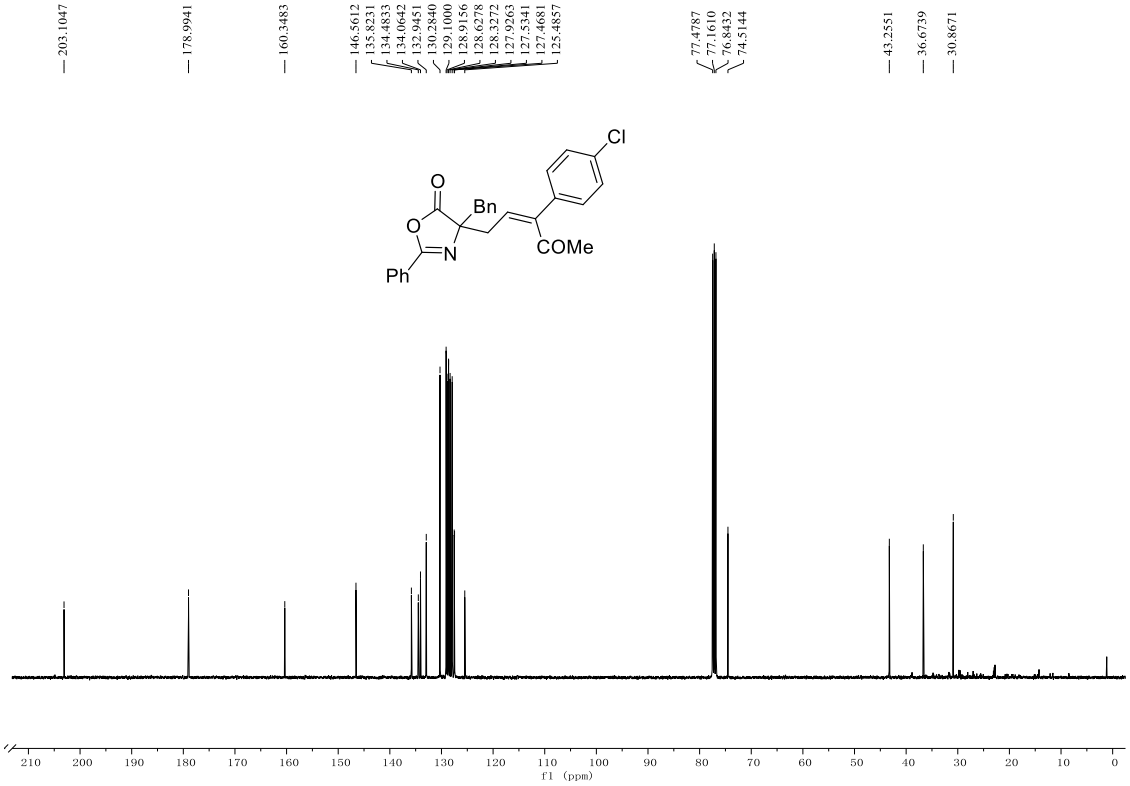
^{1}H, ^{13}C NMR of compound **3ba**



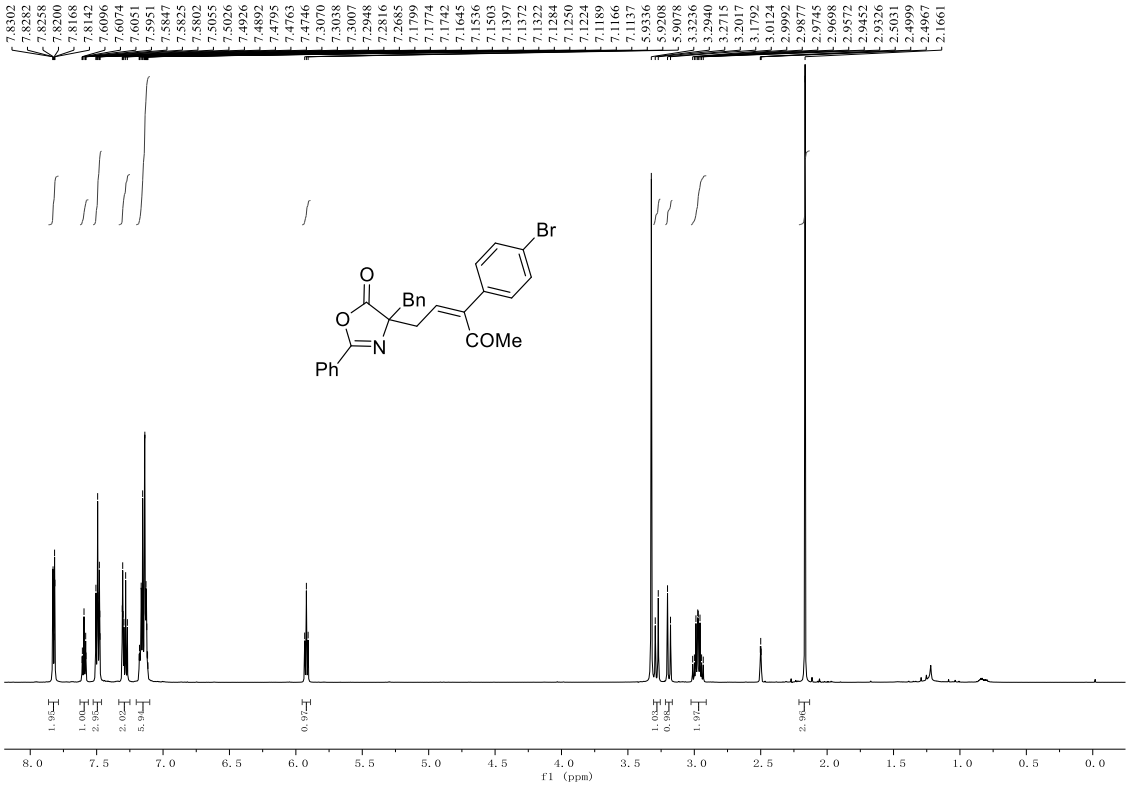


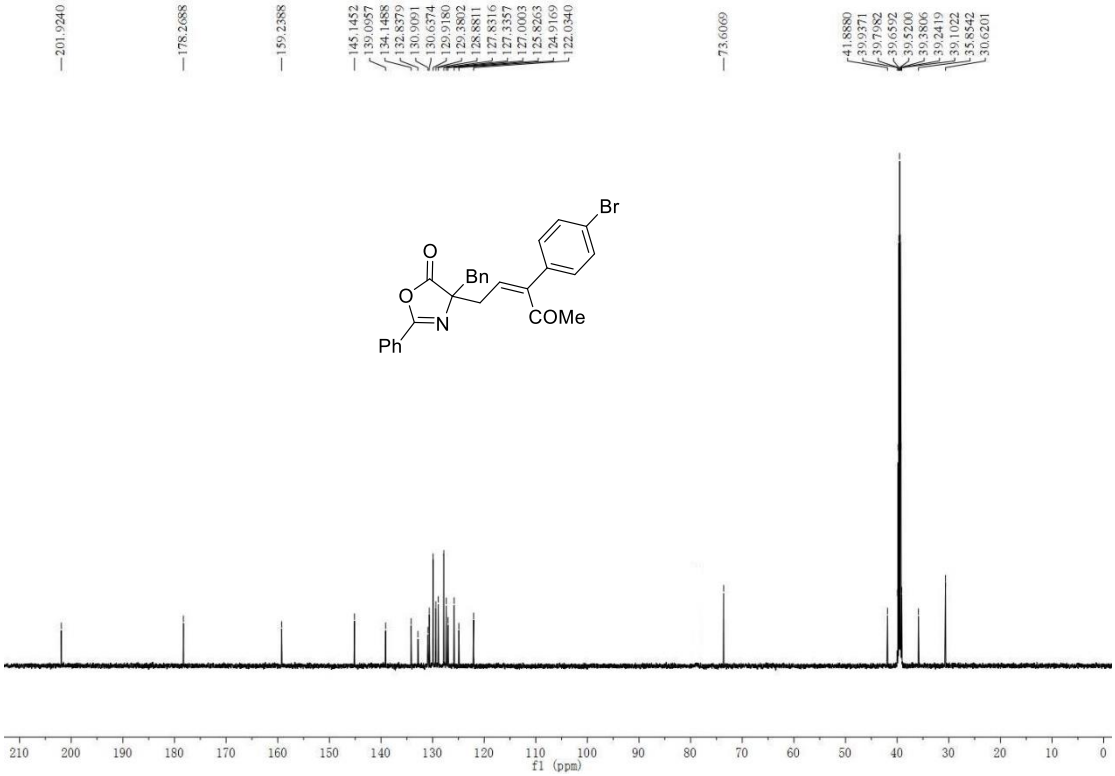
^{1}H, ^{13}C NMR of compound **3ca**



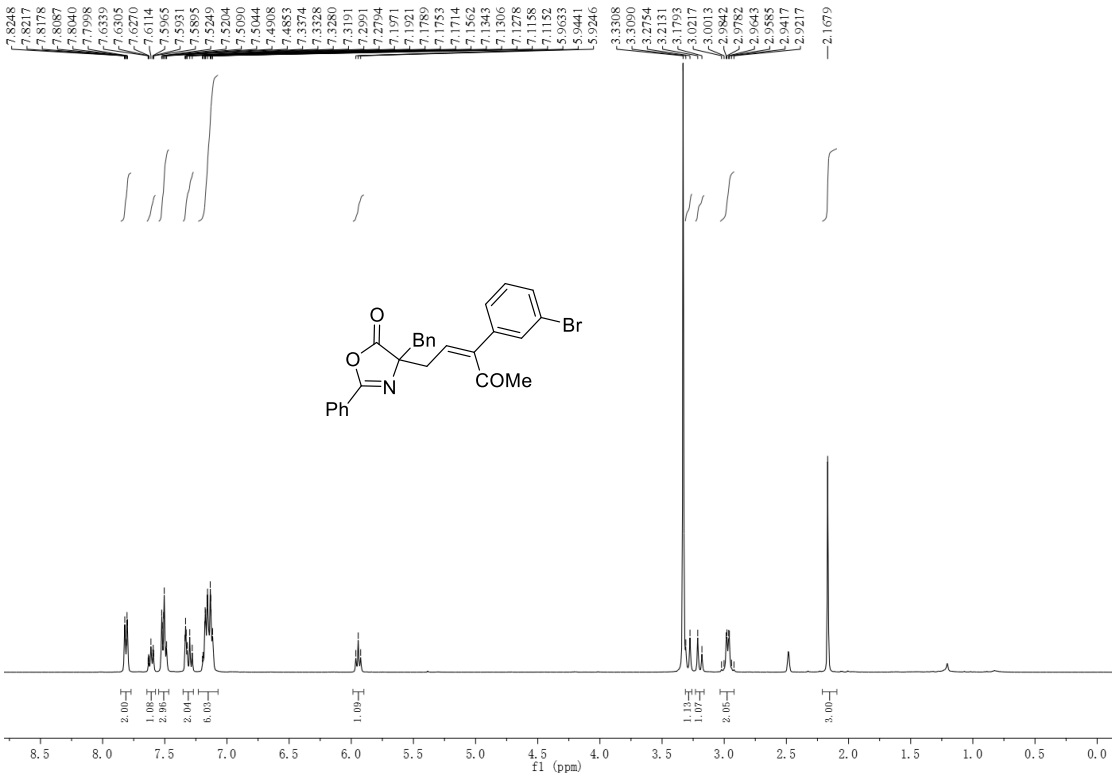


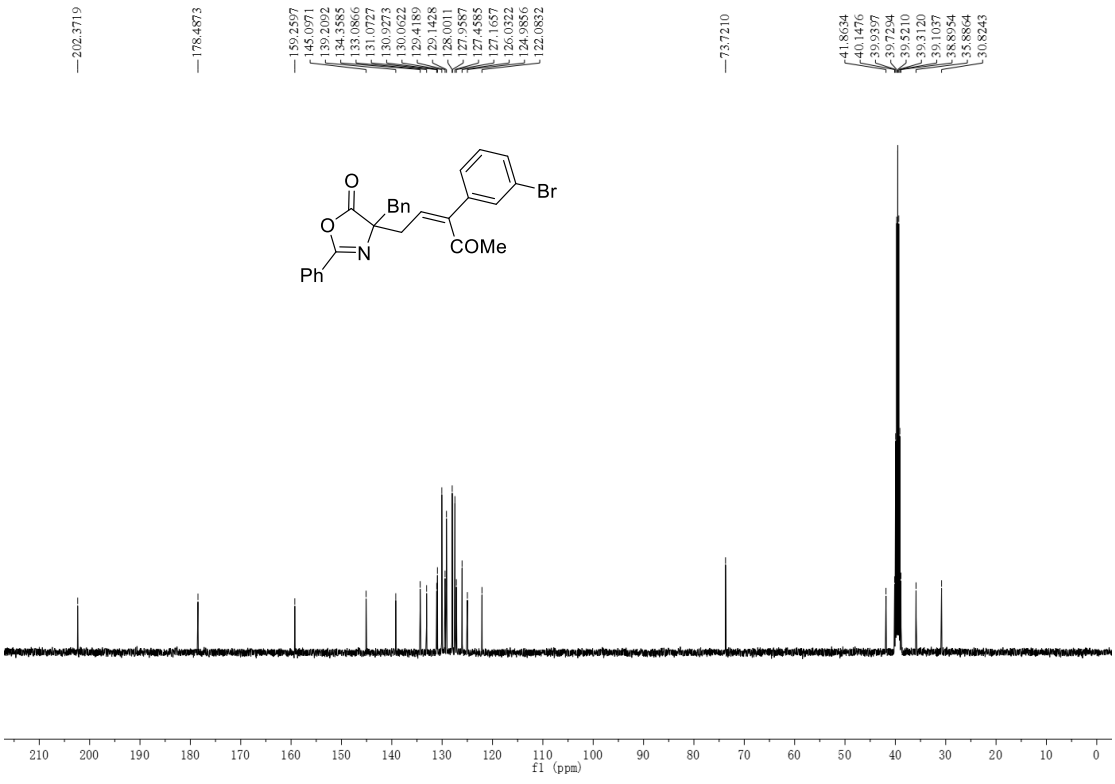
^{1}H, ^{13}C NMR of compound **3da**



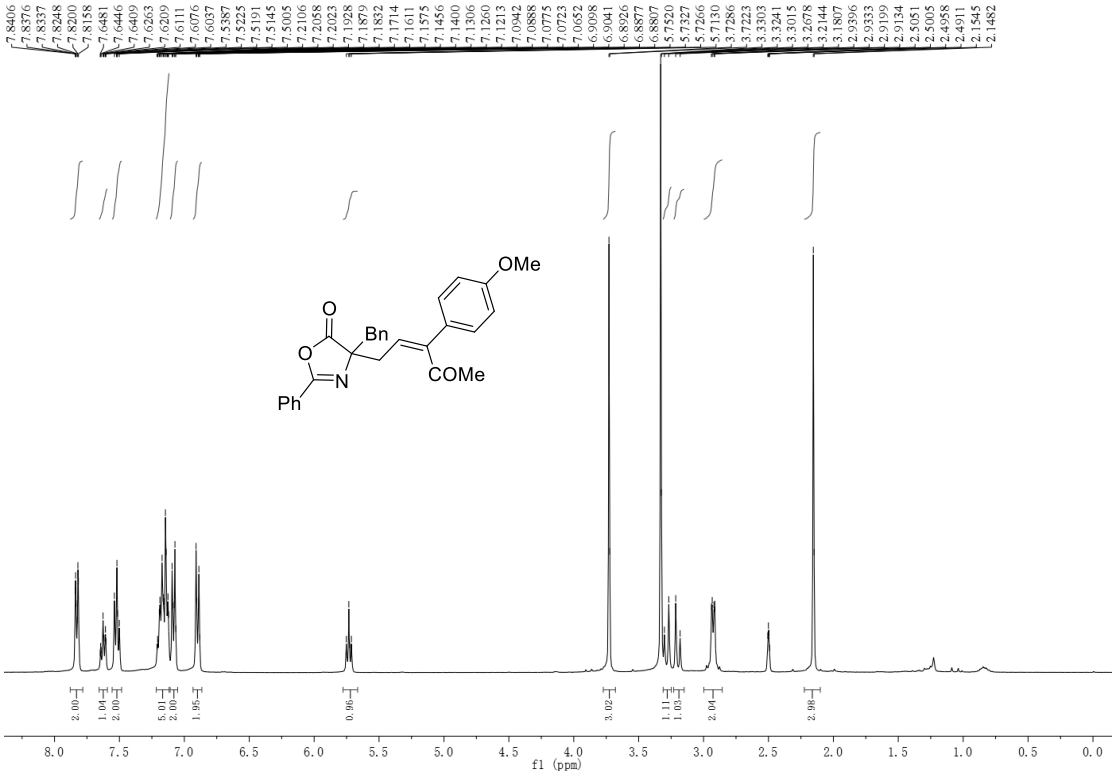


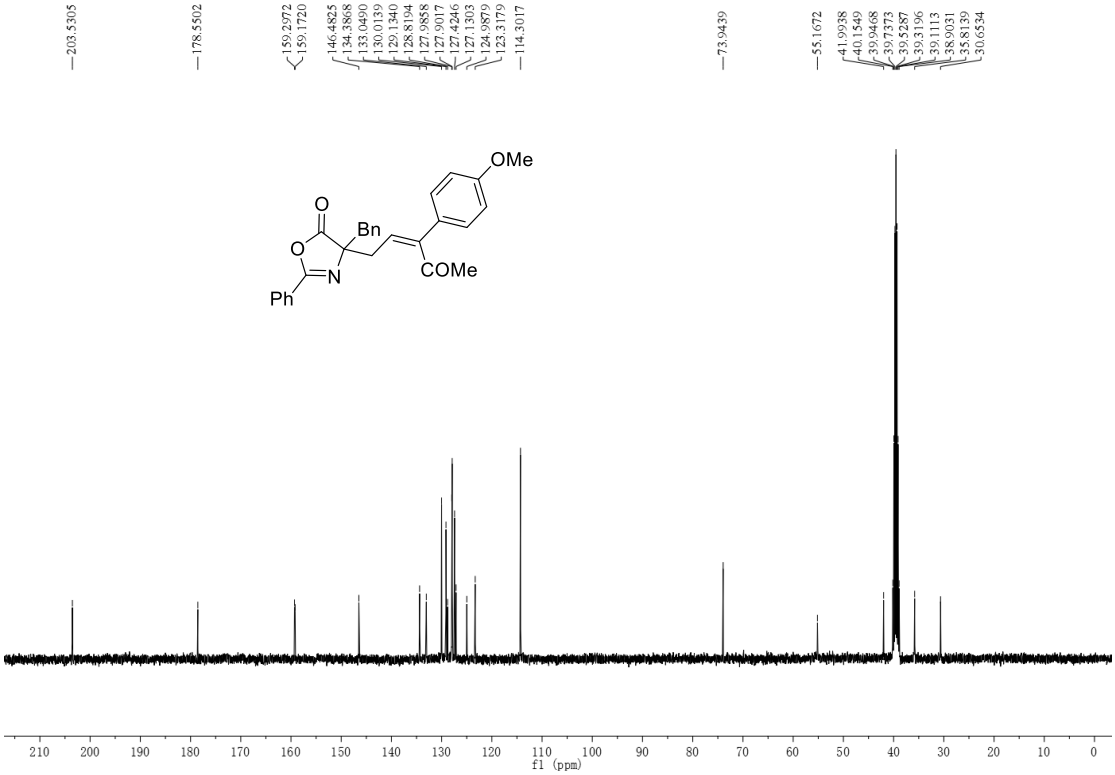
^{1}H, ^{13}C NMR of compound **3ea**



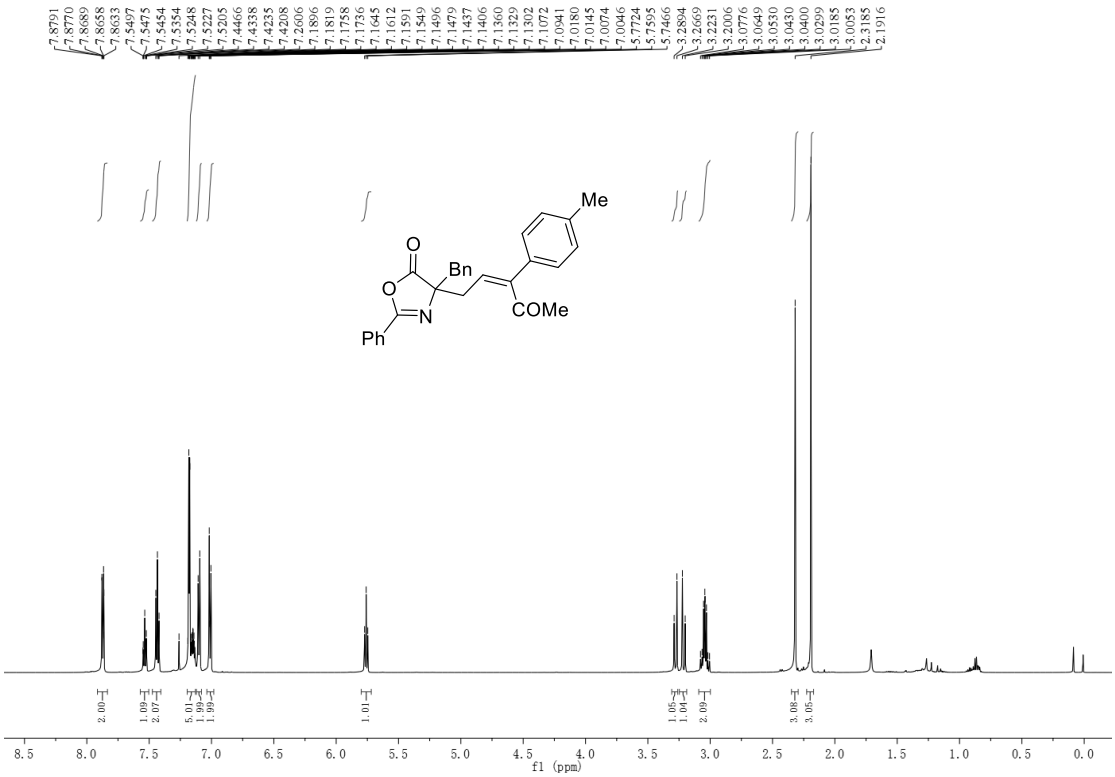


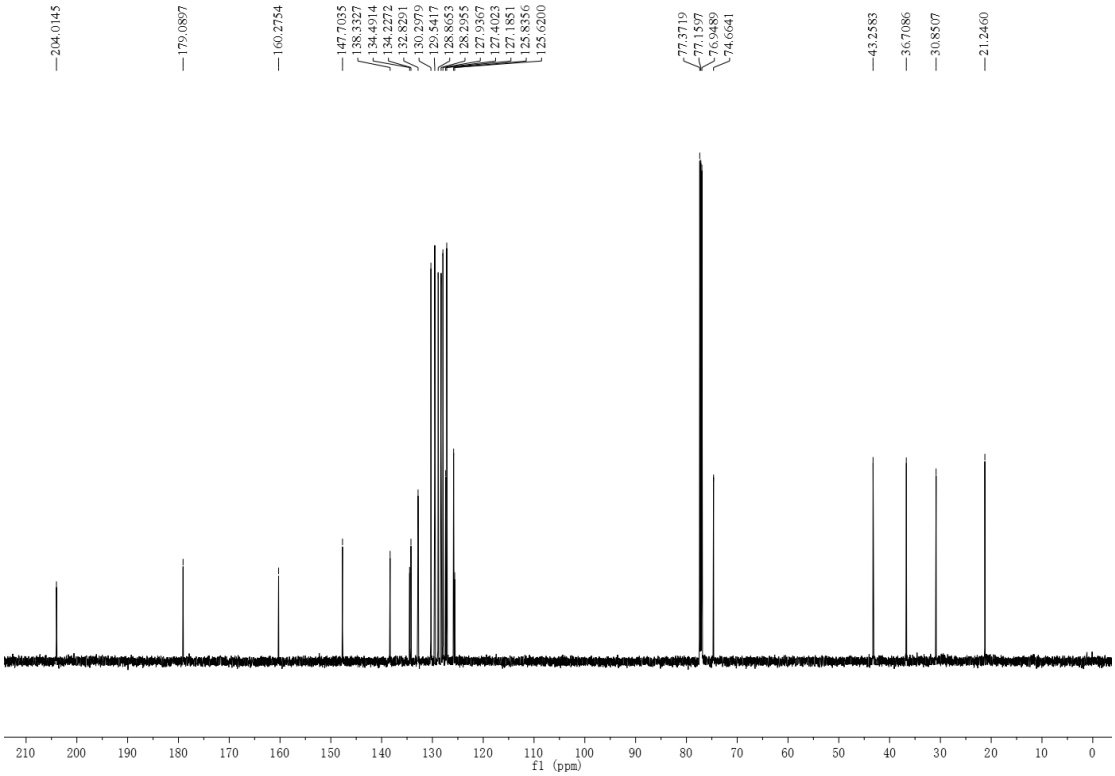
^{1}H, ^{13}C NMR of compound **3fa**



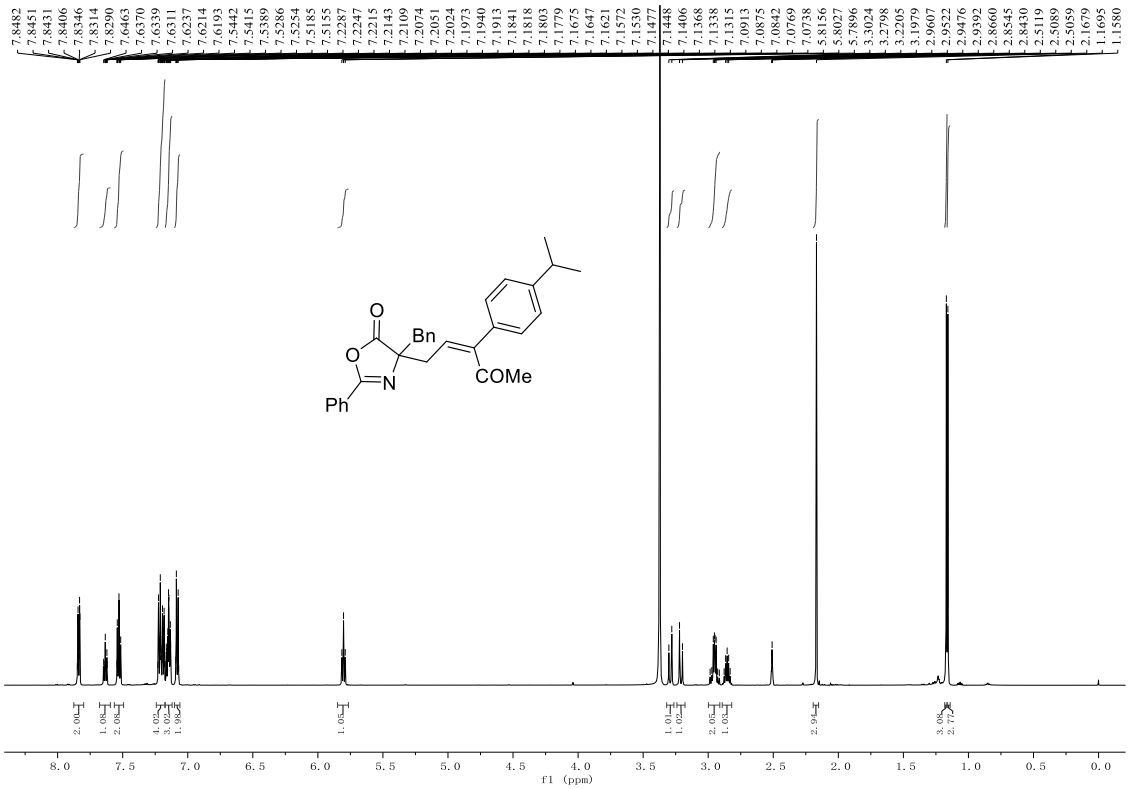


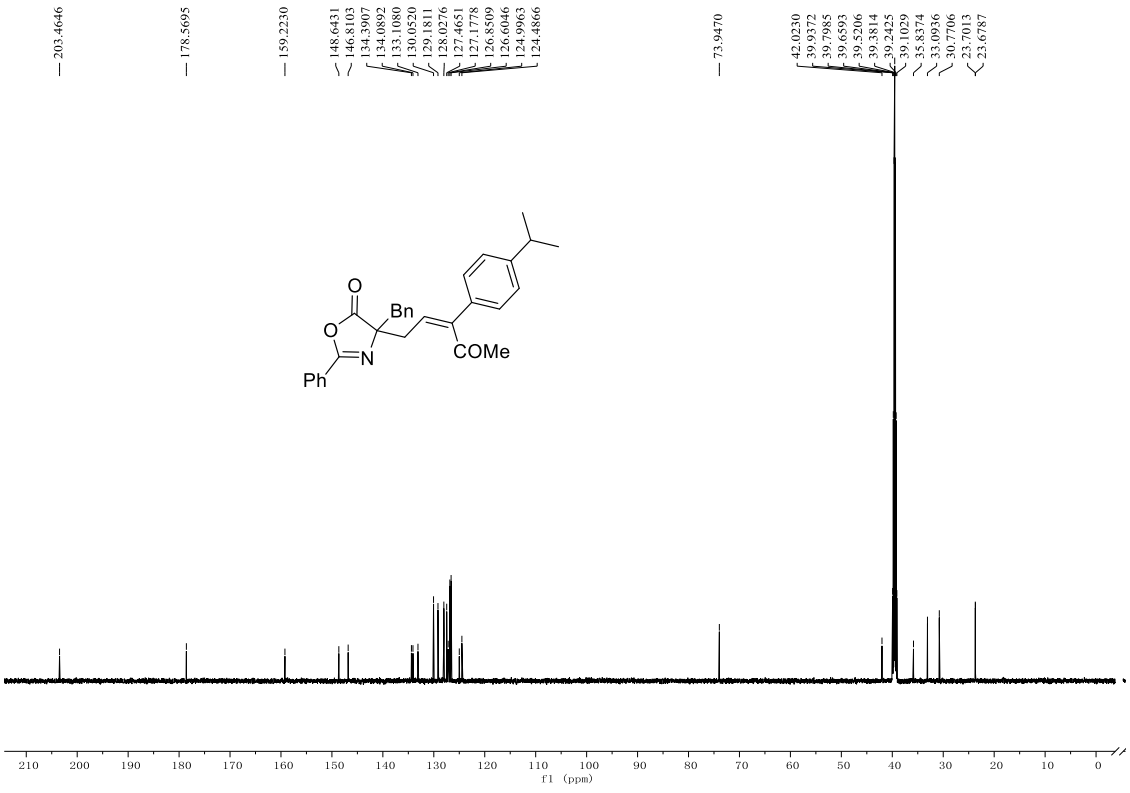
^{1}H, ^{13}C NMR of compound **3ga**



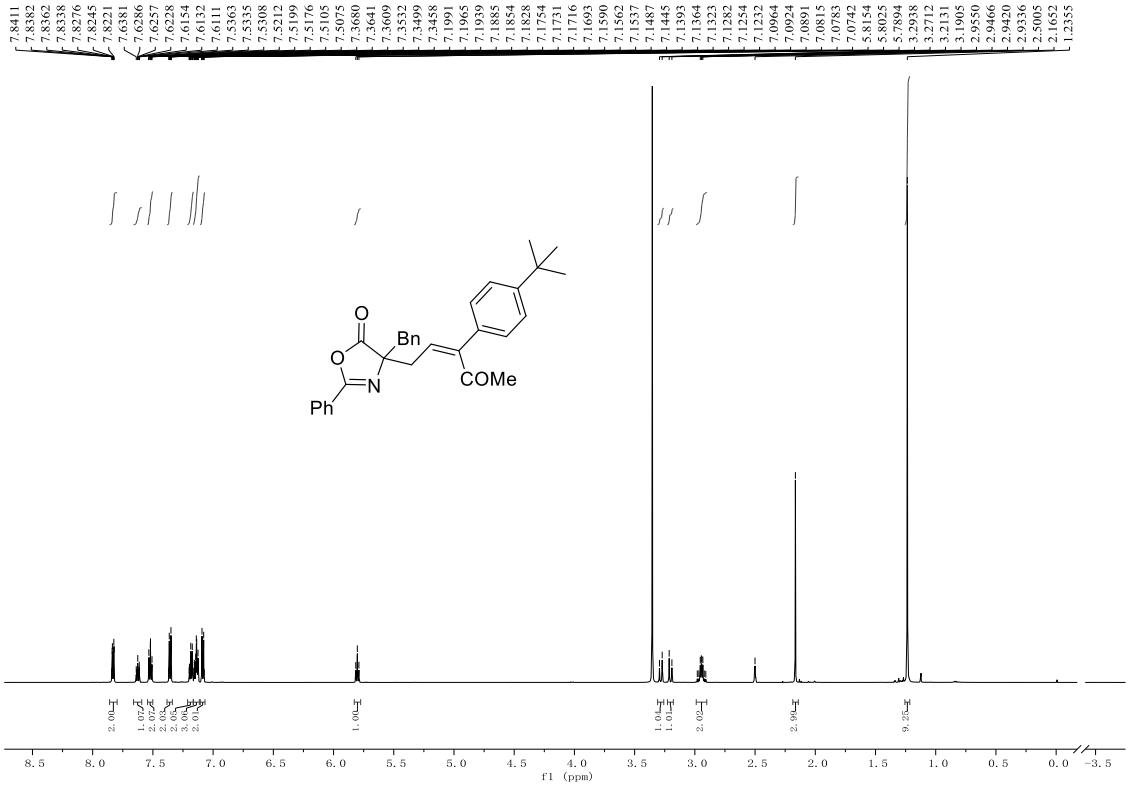


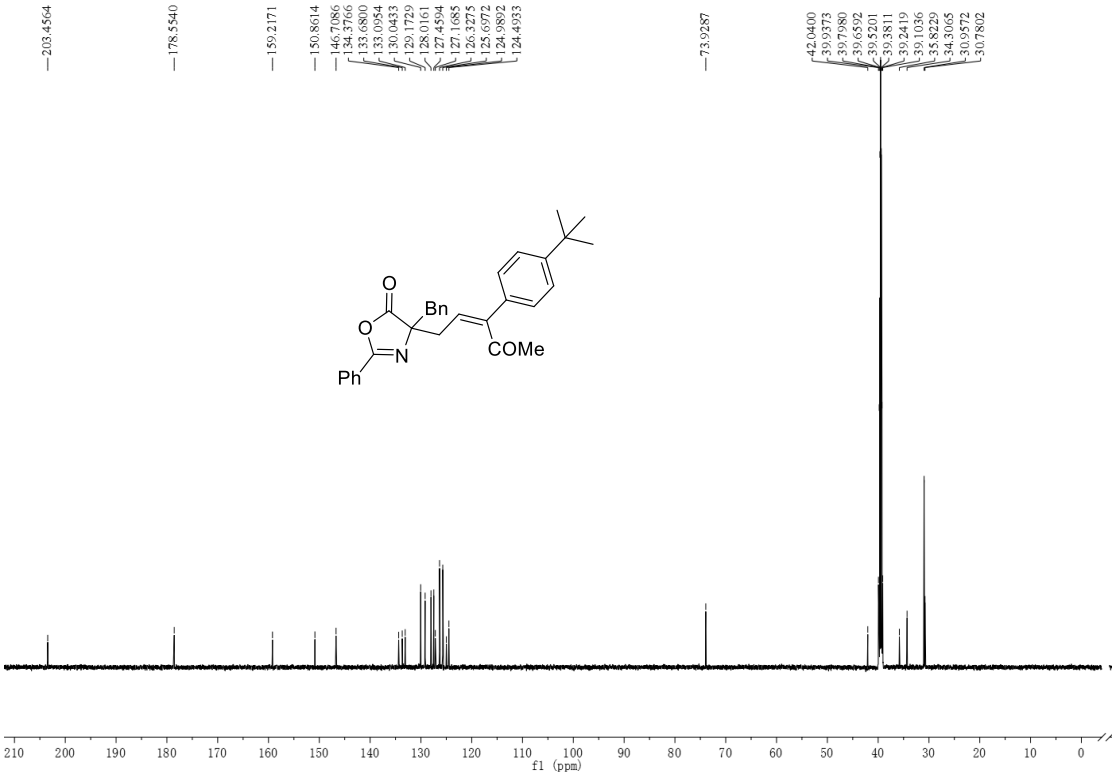
^{1}H, ^{13}C NMR of compound **3ha**



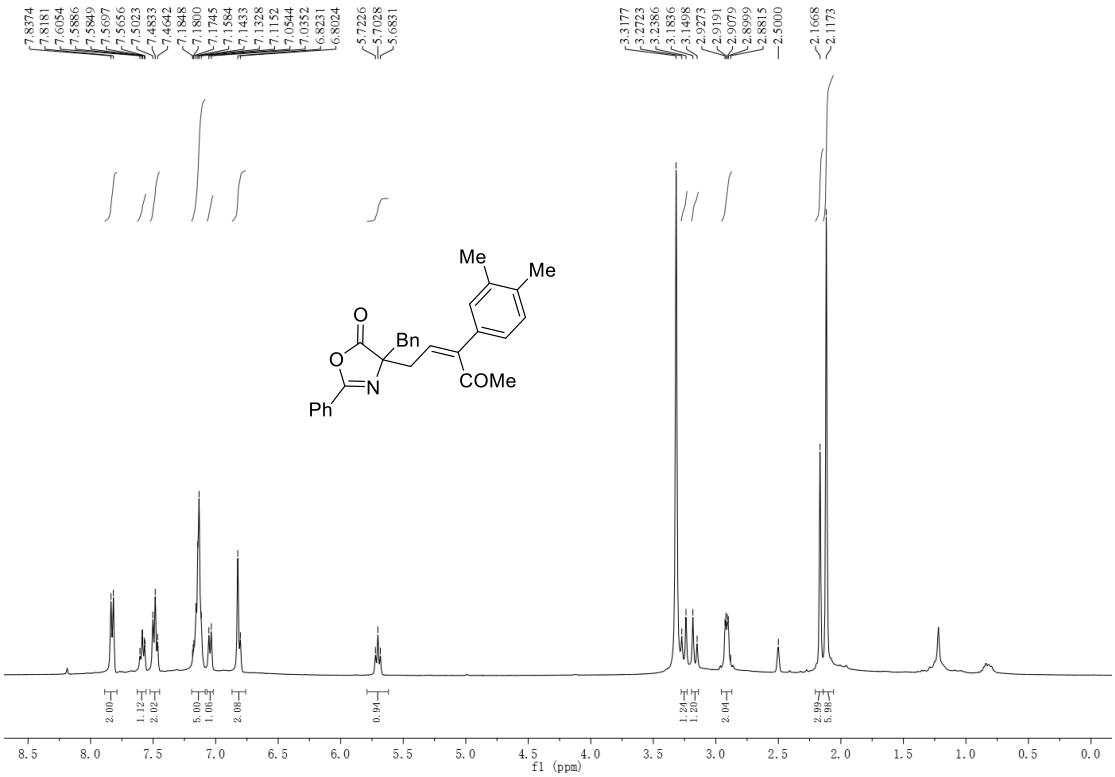


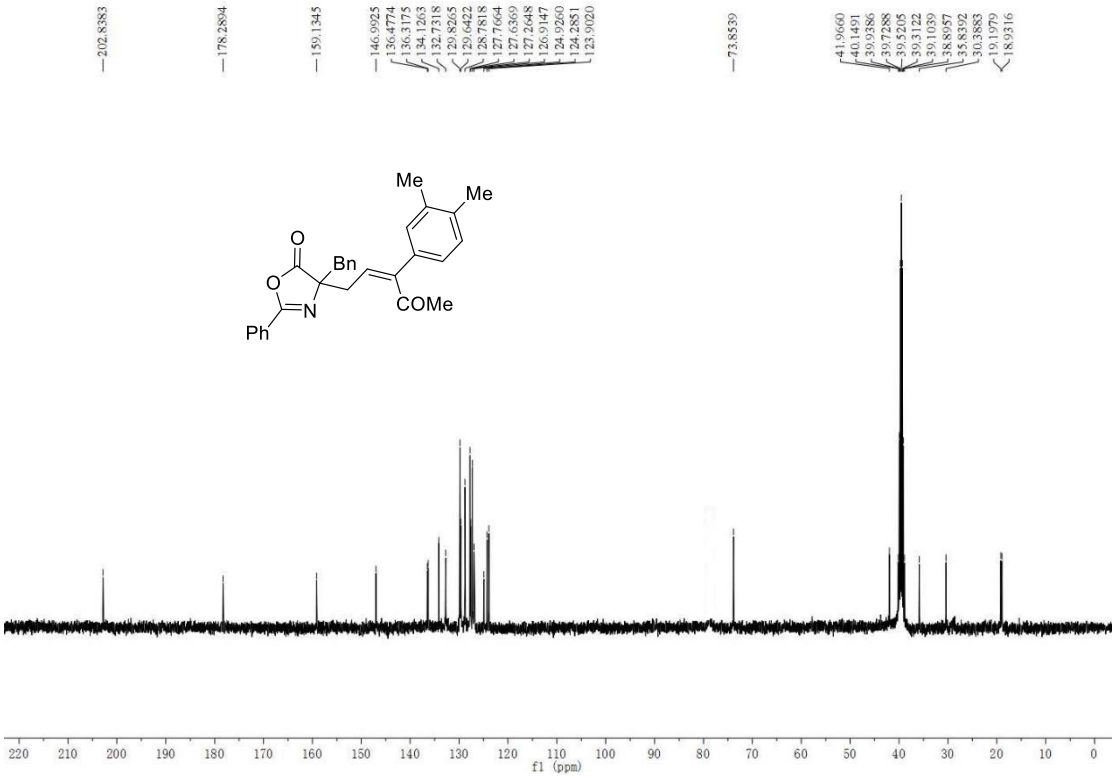
^{1}H, ^{13}C NMR of compound **3ia**



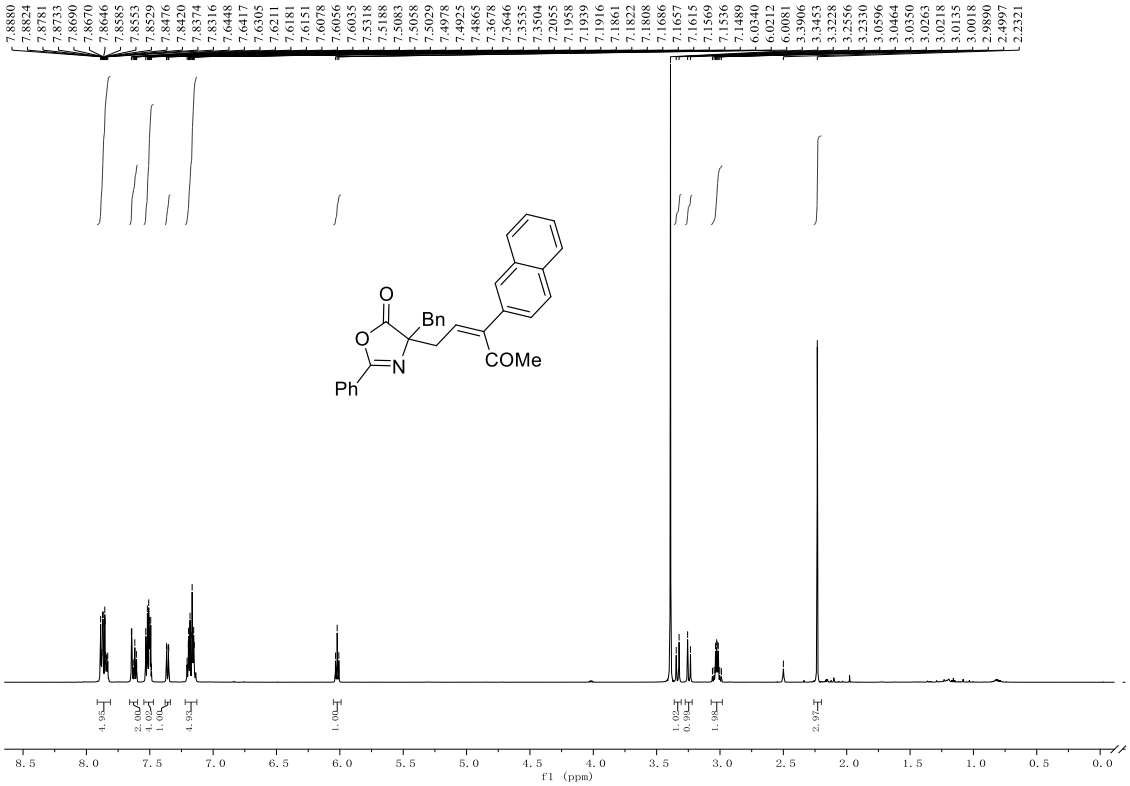


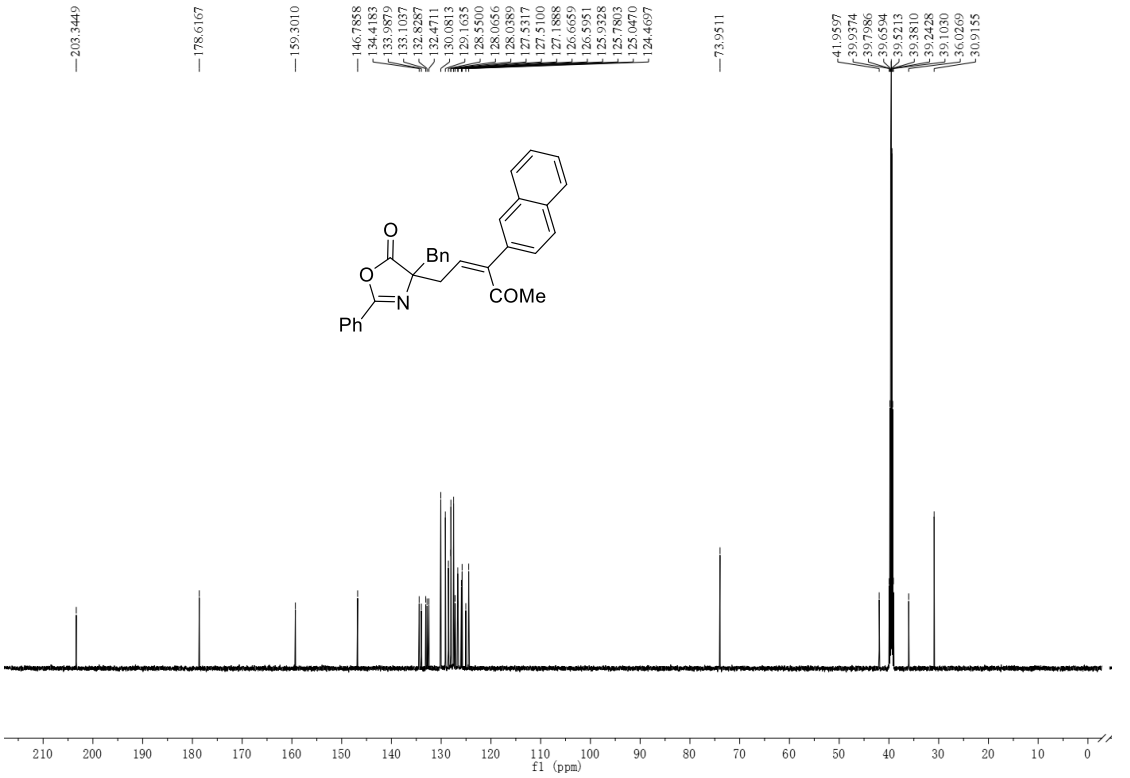
^{1}H, ^{13}C NMR of compound **3ja**



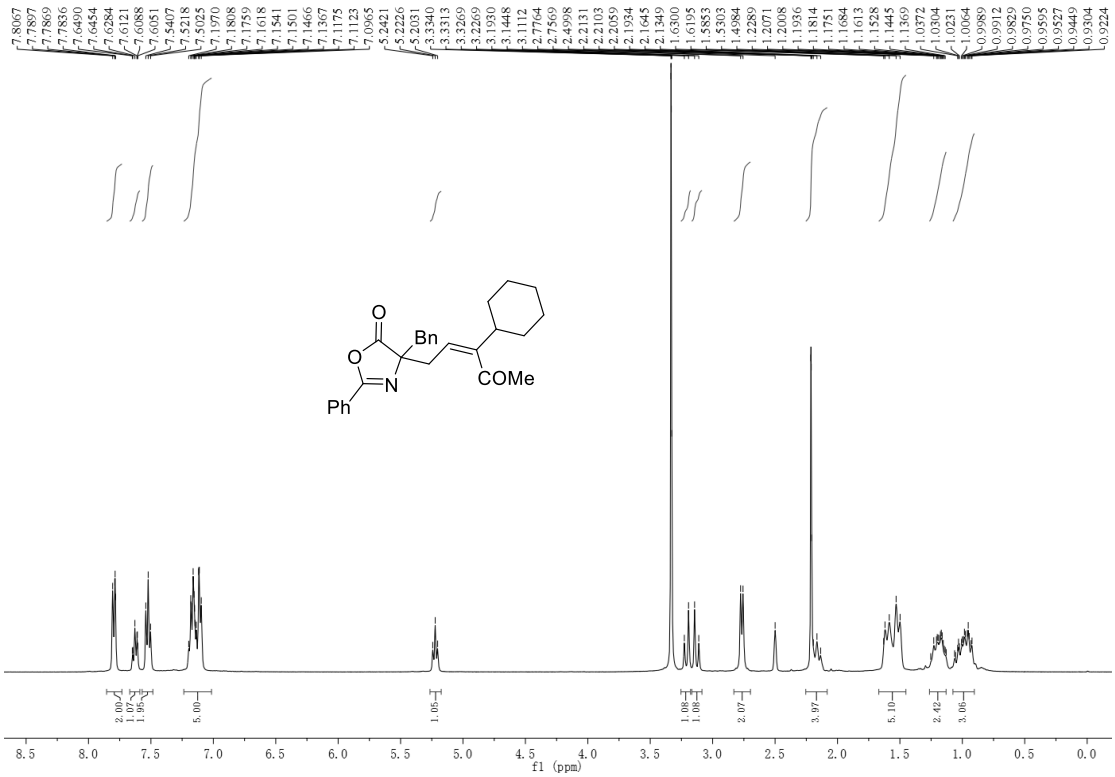


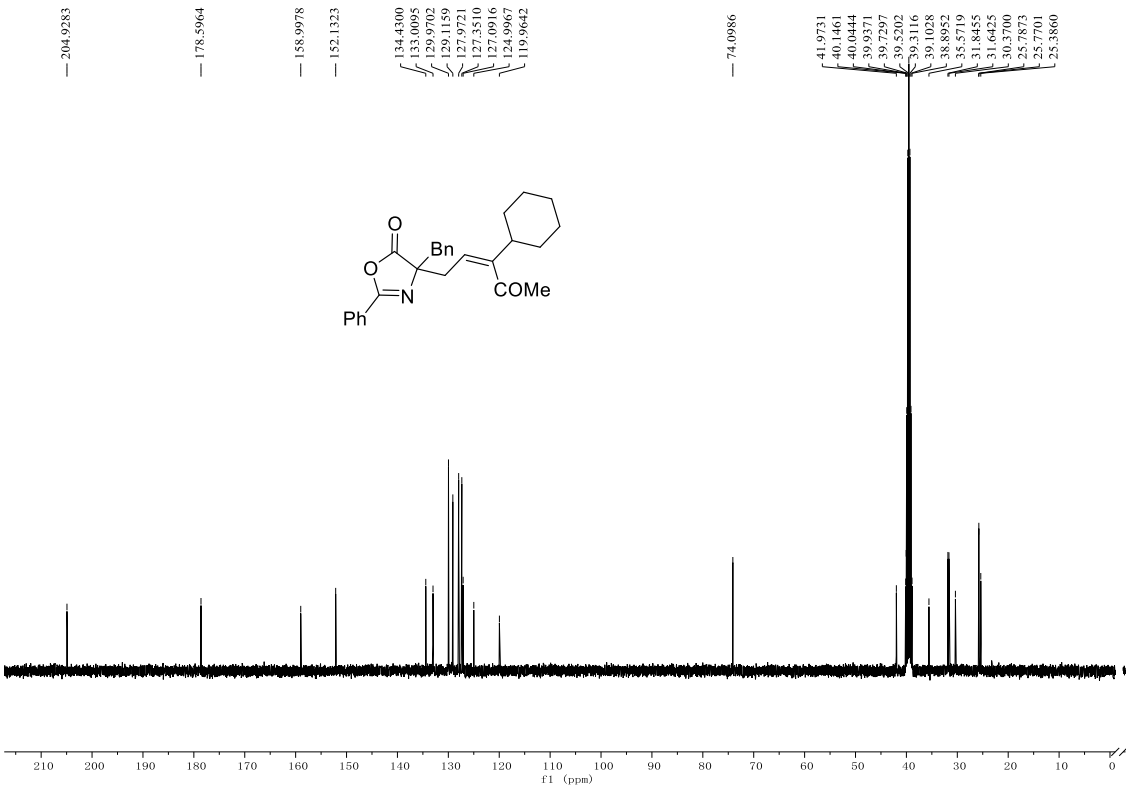
^{1}H, ^{13}C NMR of compound **3ka**



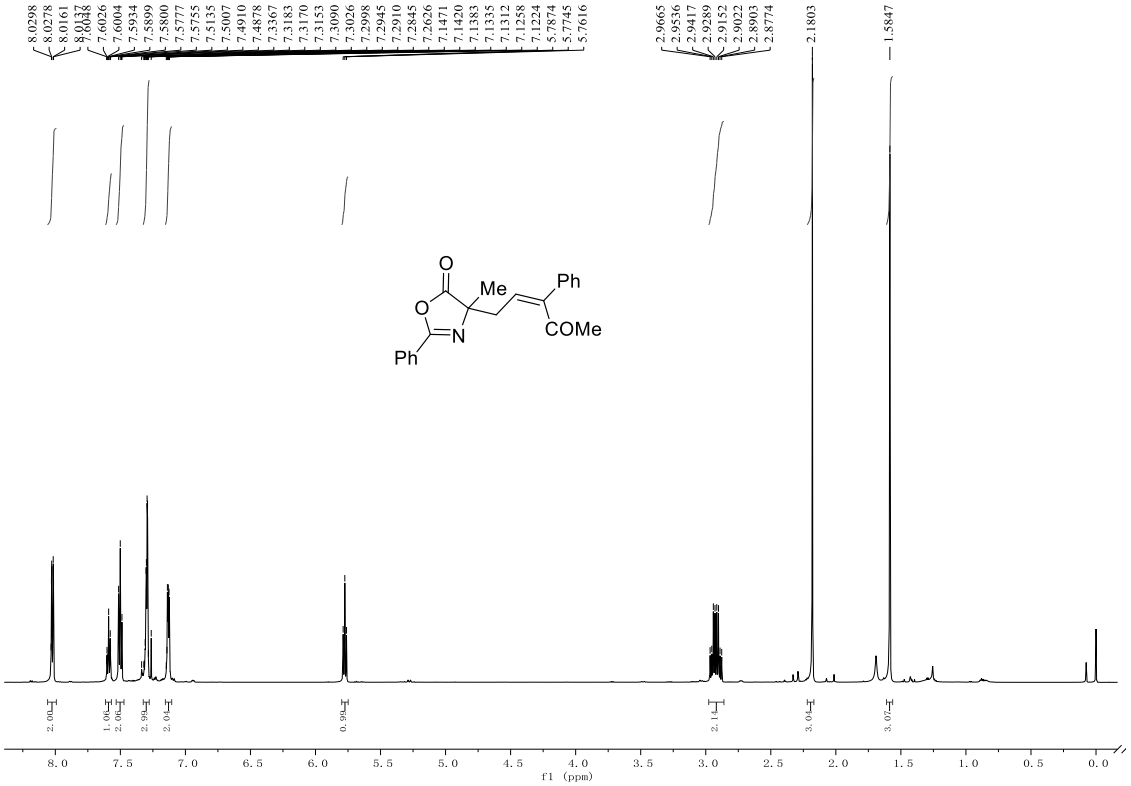


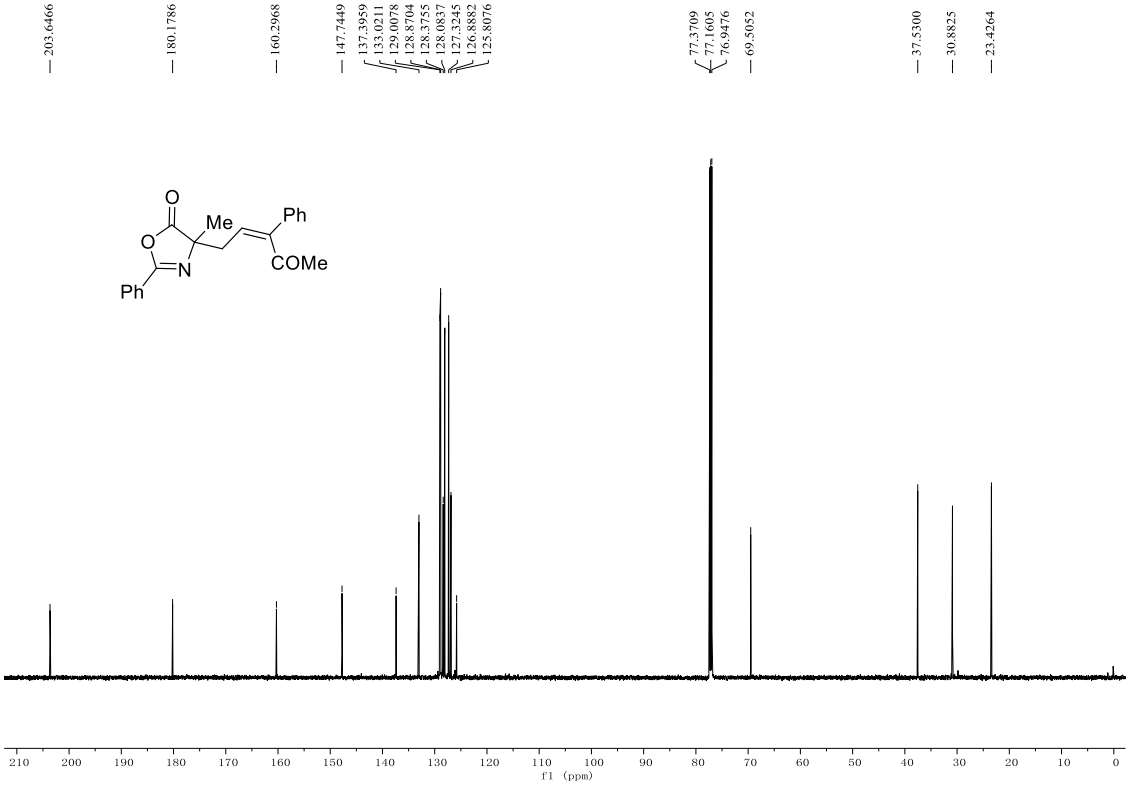
^{1}H, ^{13}C NMR of compound **3la**



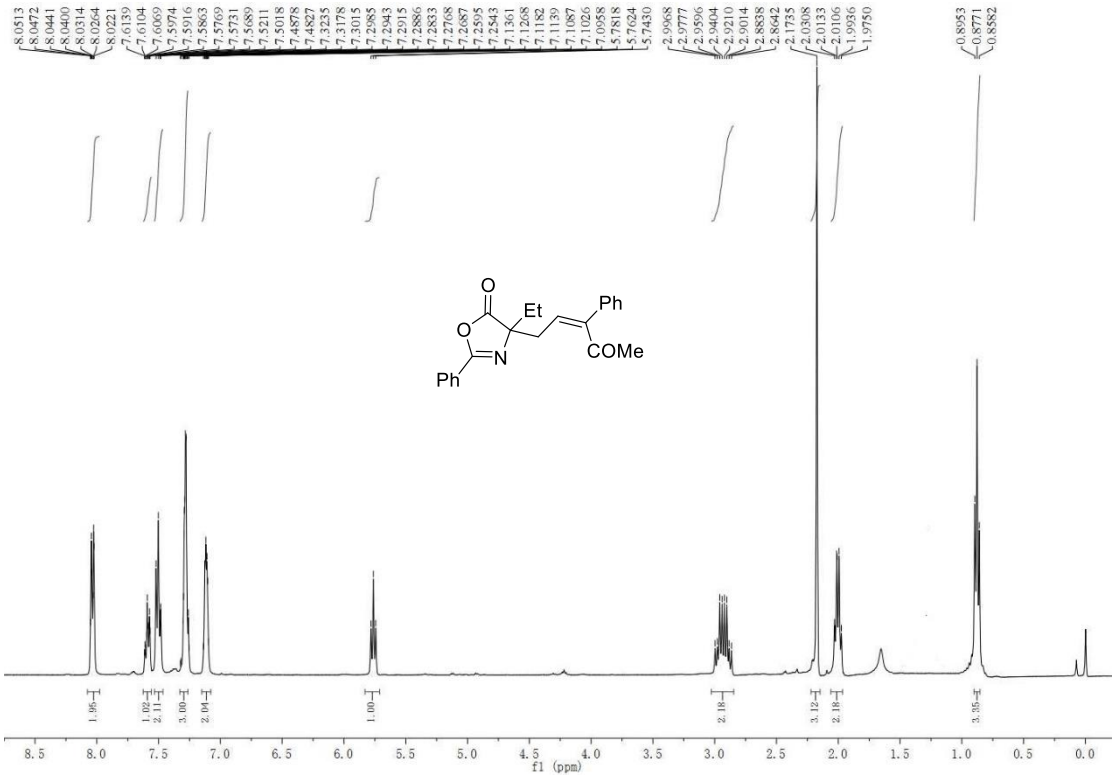


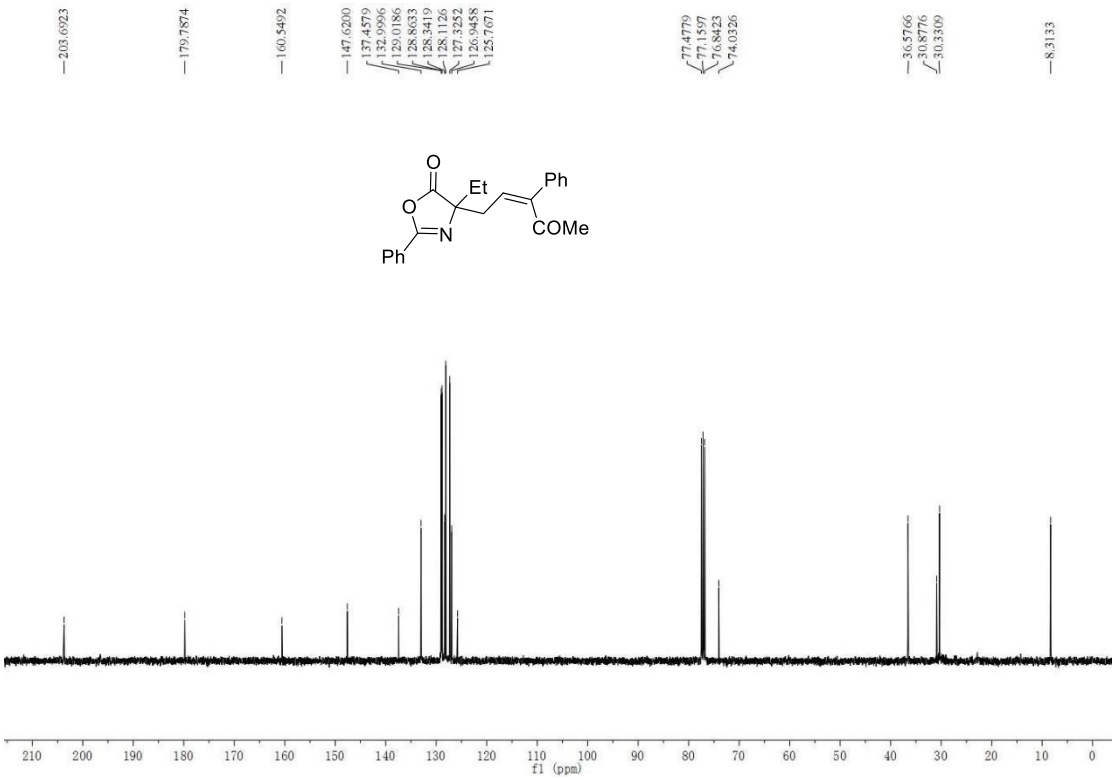
^{1}H, ^{13}C NMR of compound **3ab**



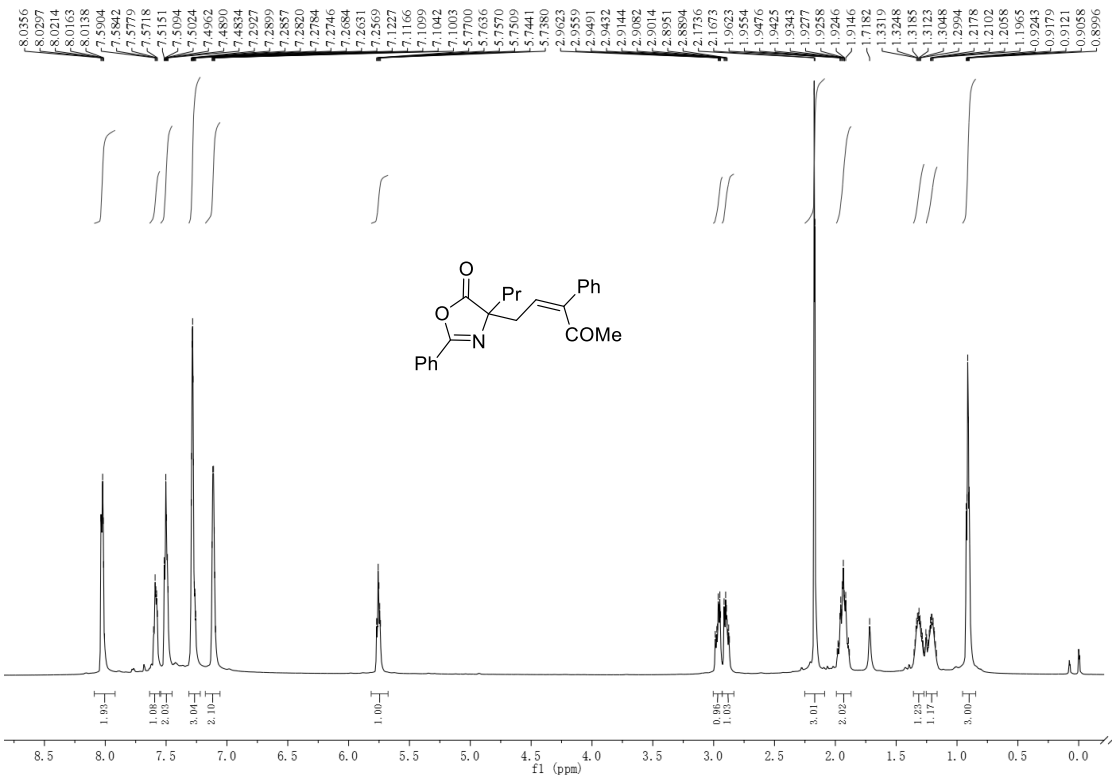


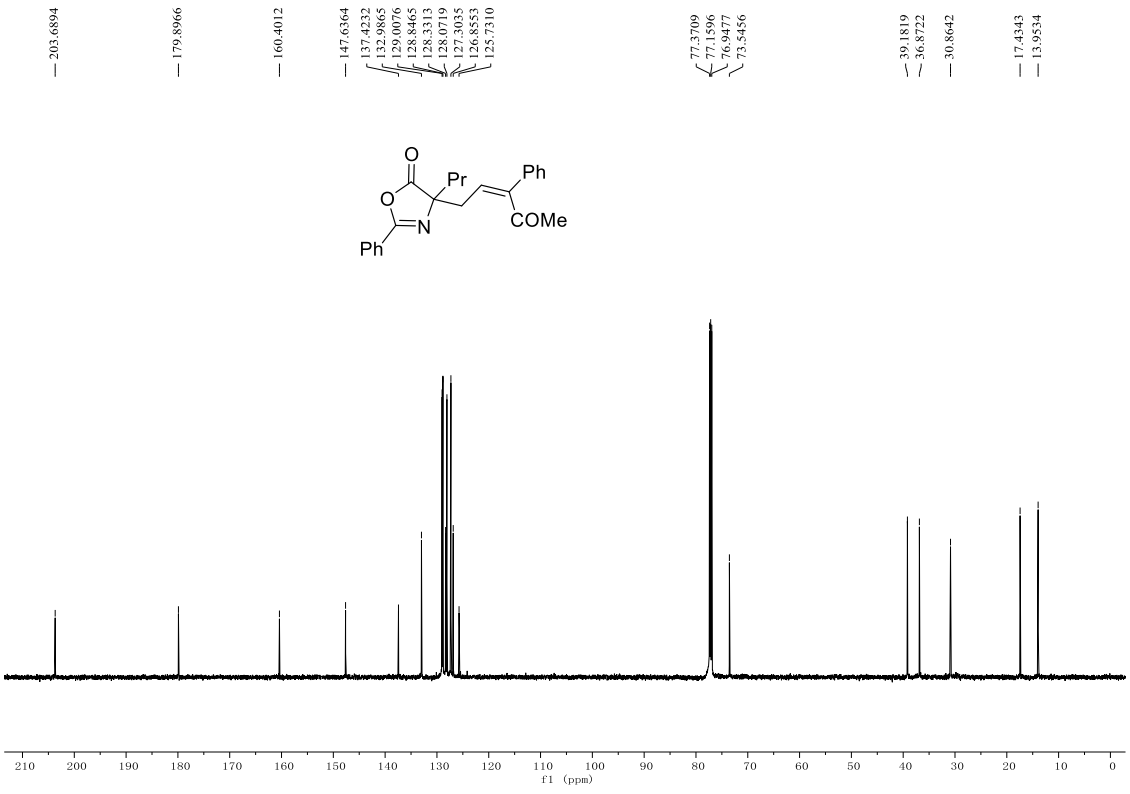
^{1}H, ^{13}C NMR of compound **3ac**



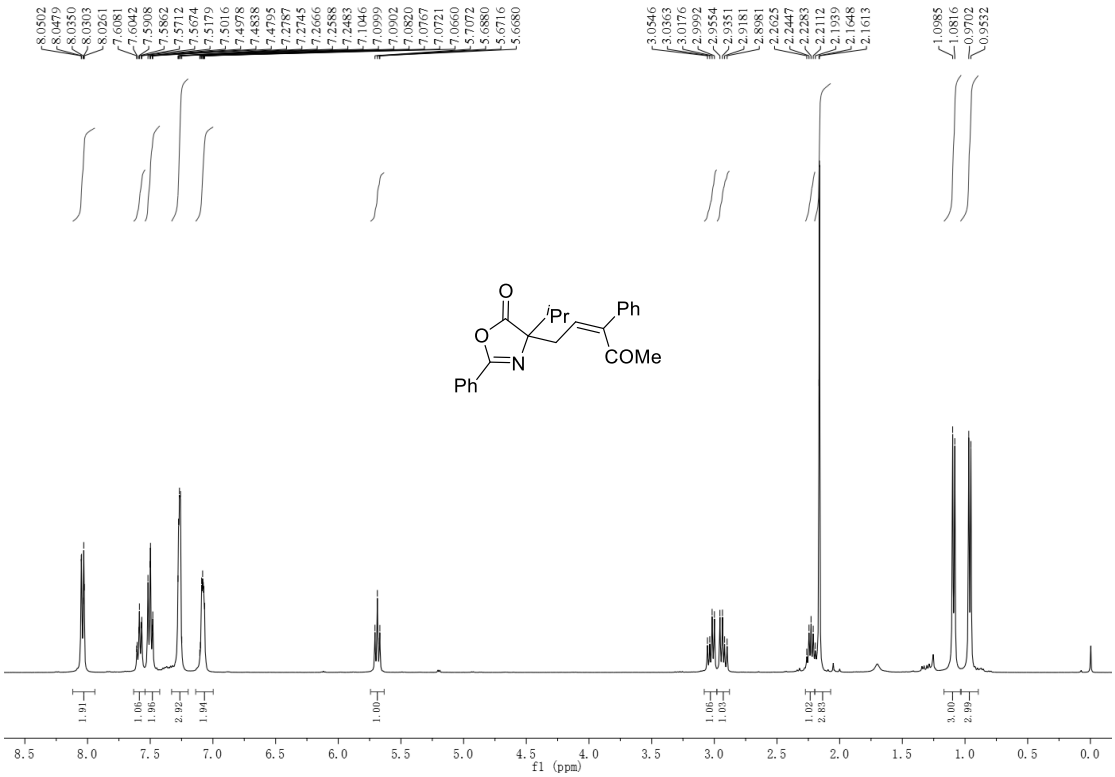


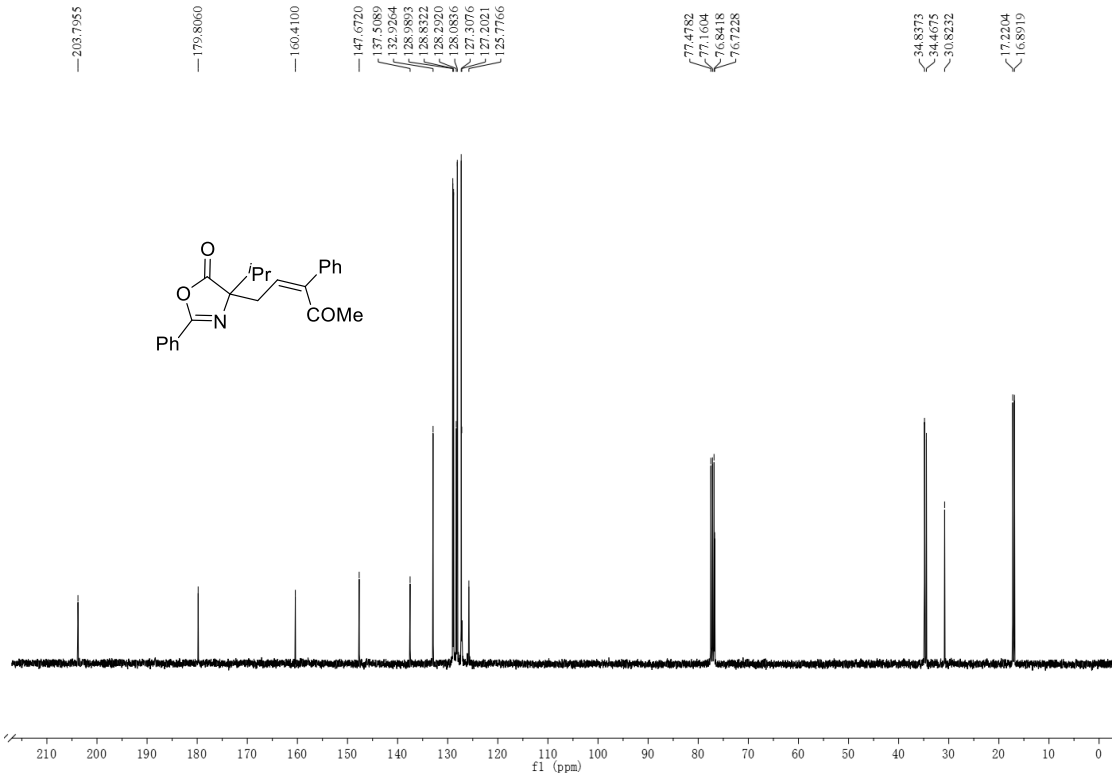
^{1}H, ^{13}C NMR of compound **3ad**



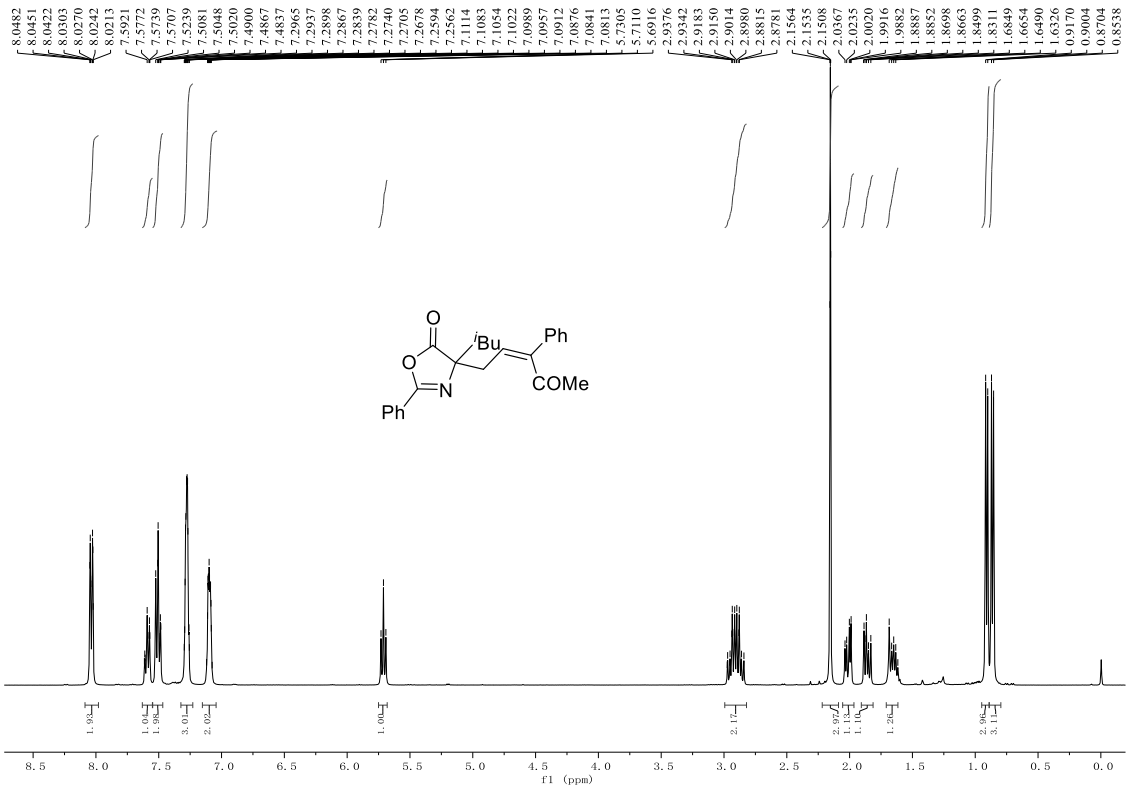


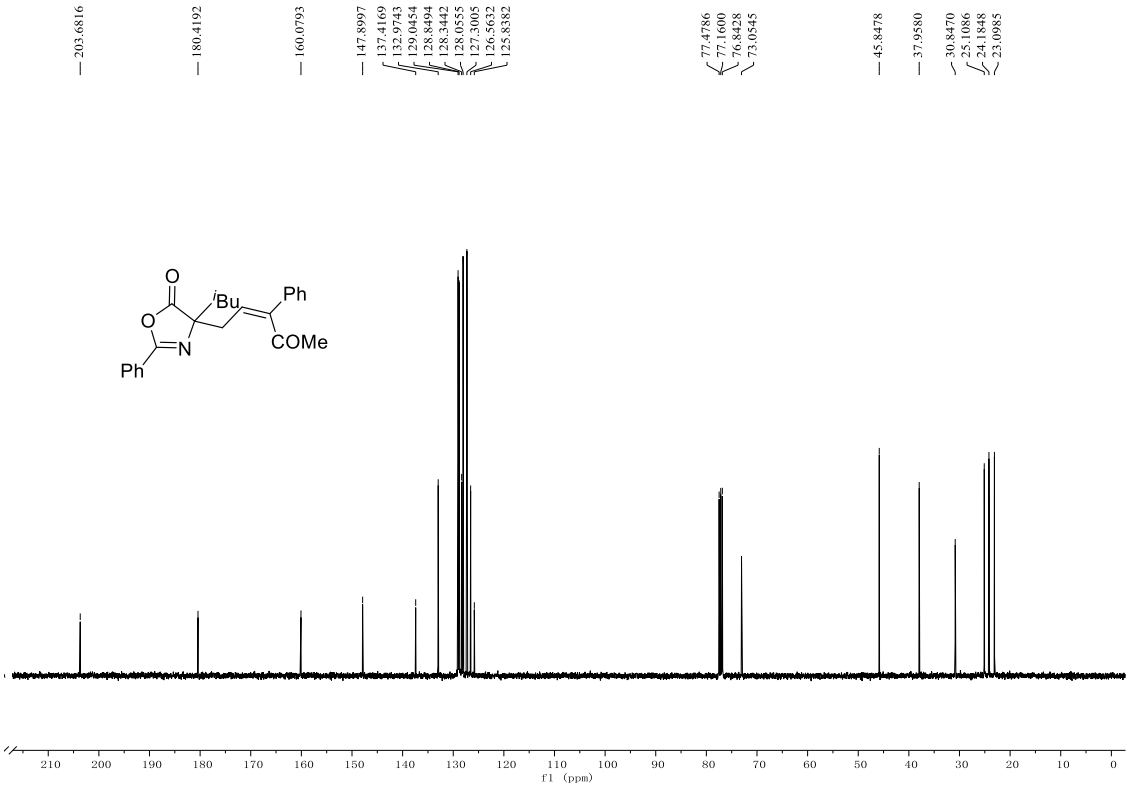
^{1}H, ^{13}C NMR of compound **3ae**



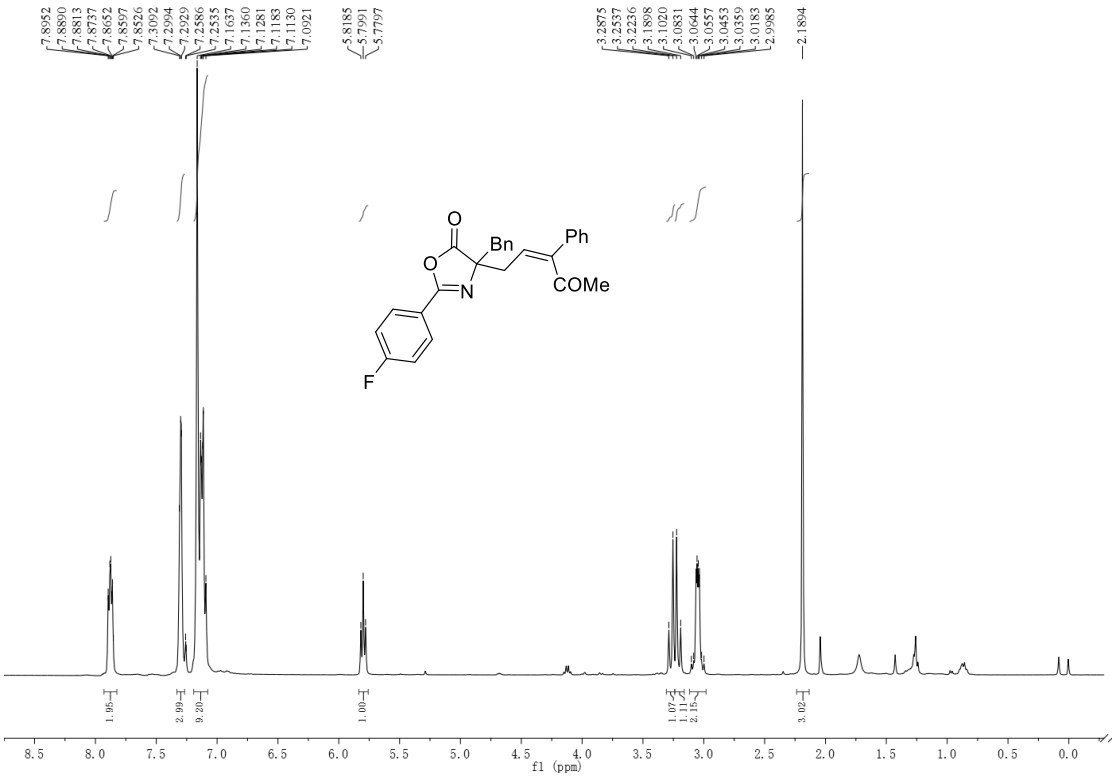


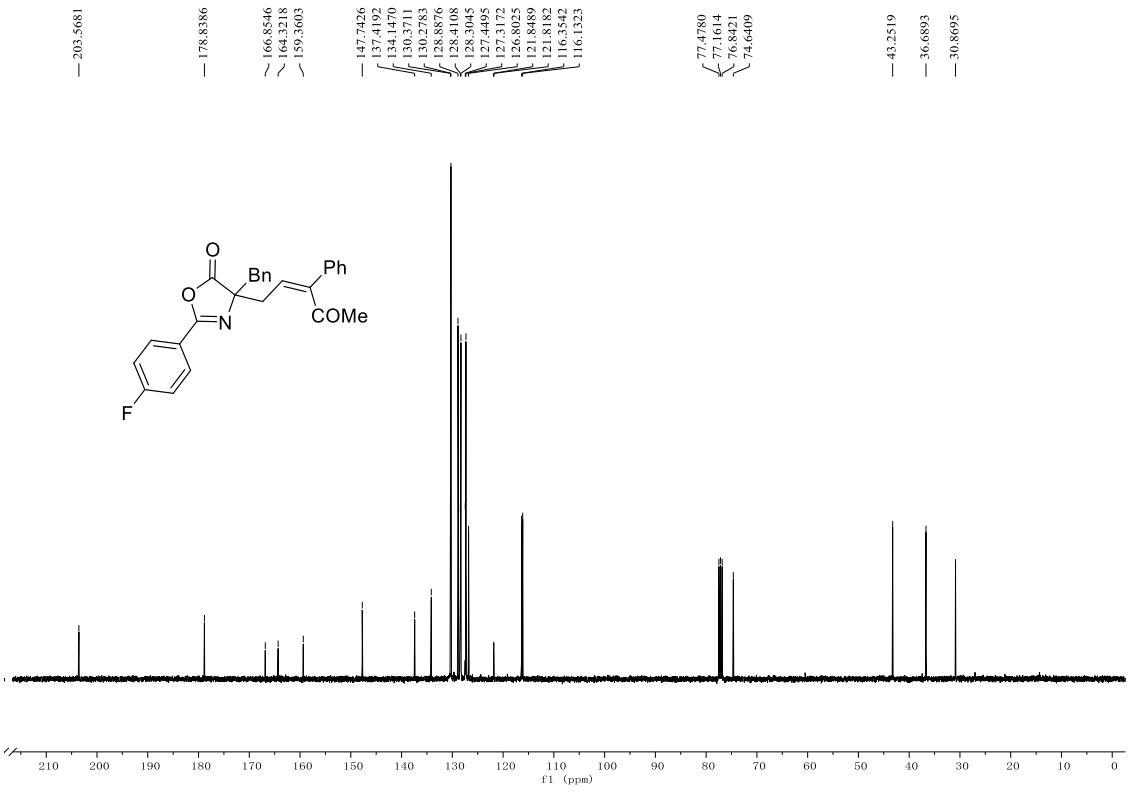
^{1}H, ^{13}C NMR of compound **3af**



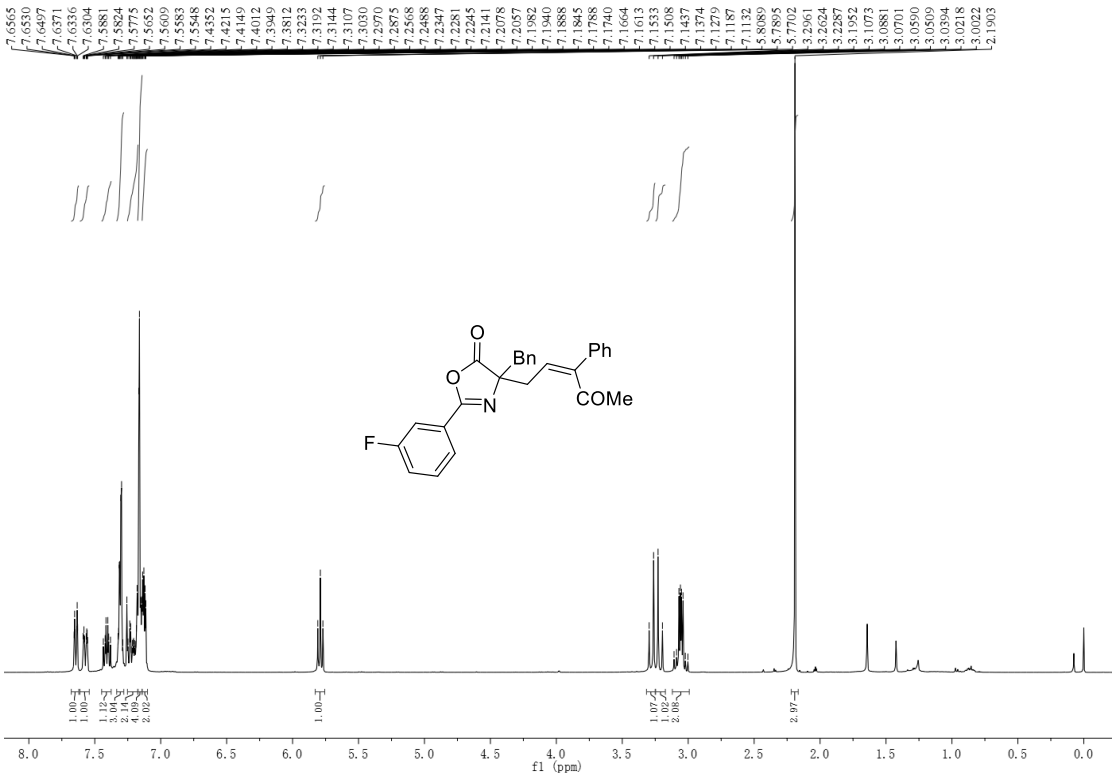


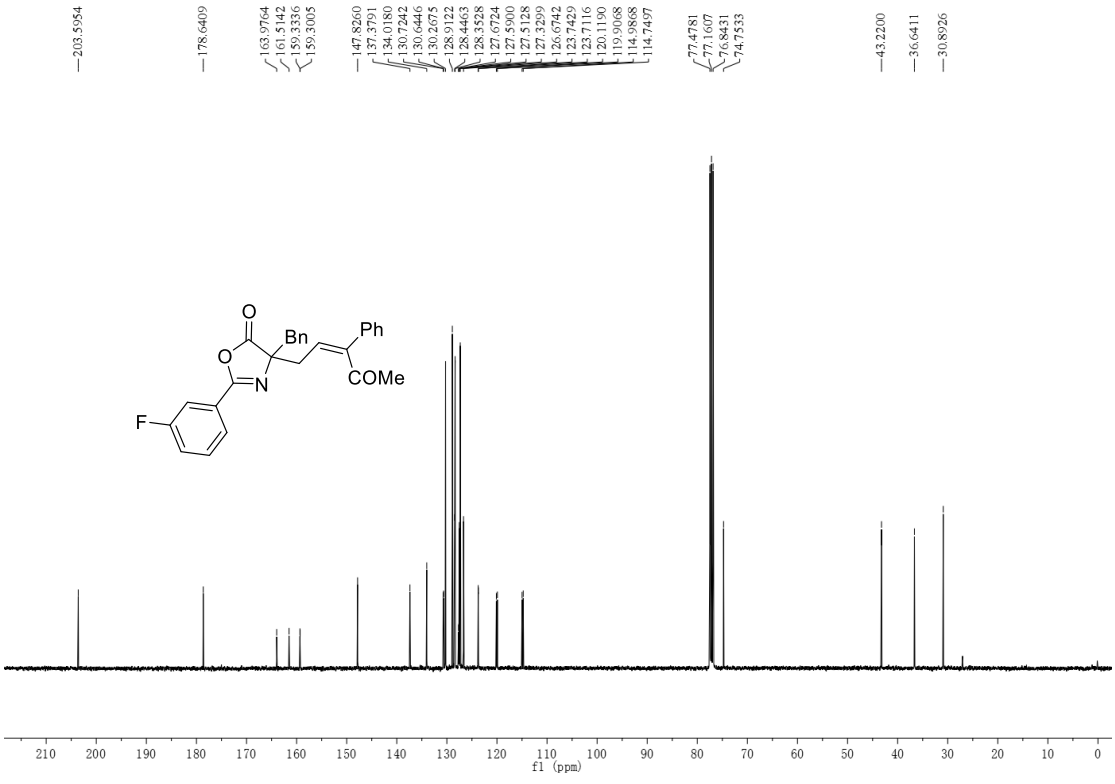
^{1}H, ^{13}C NMR of compound **3ag**



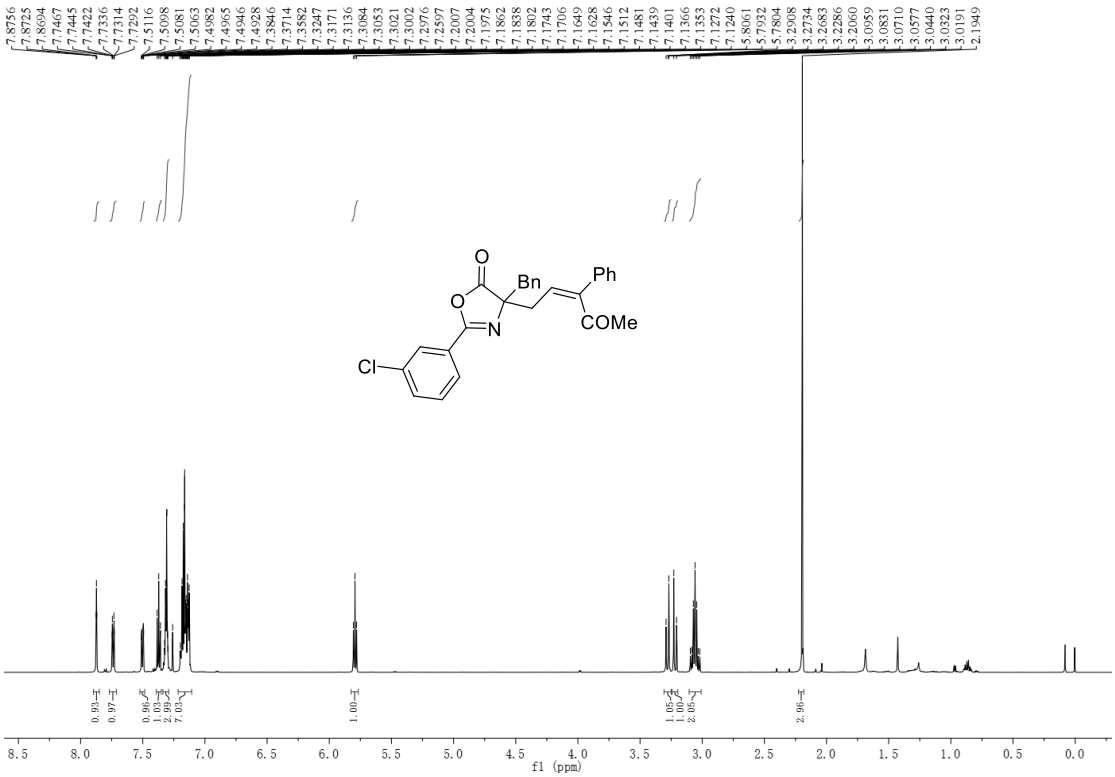


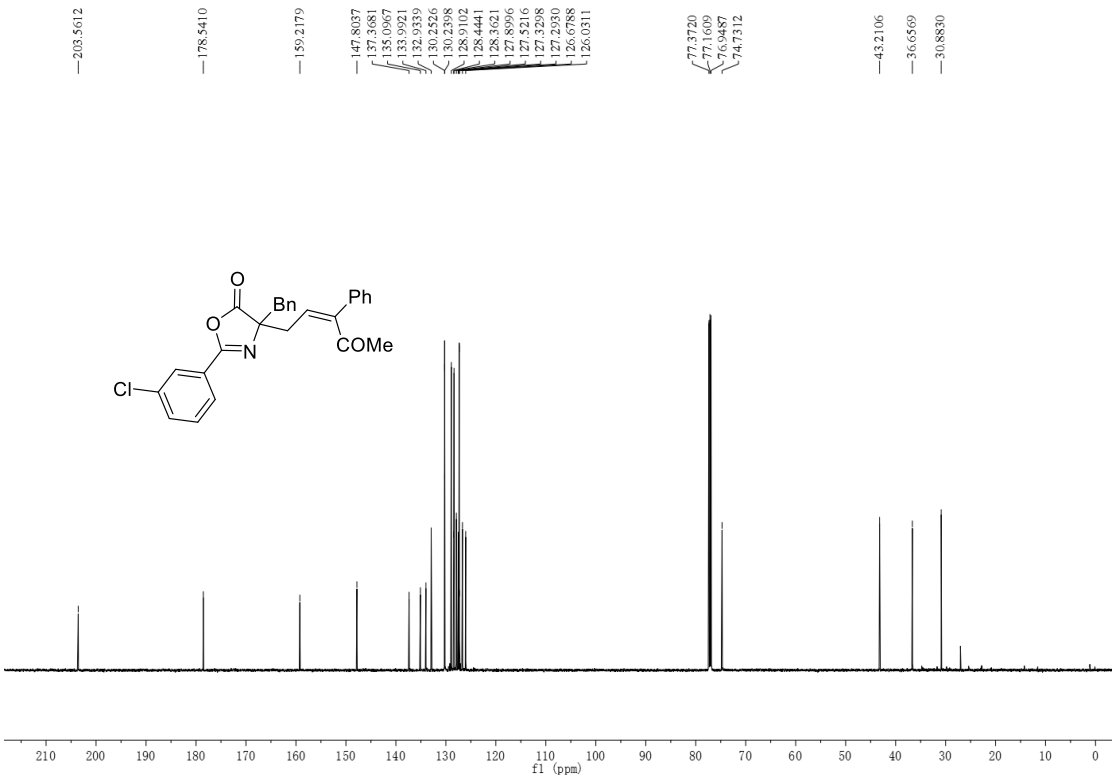
^{1}H, ^{13}C NMR of compound **3ah**



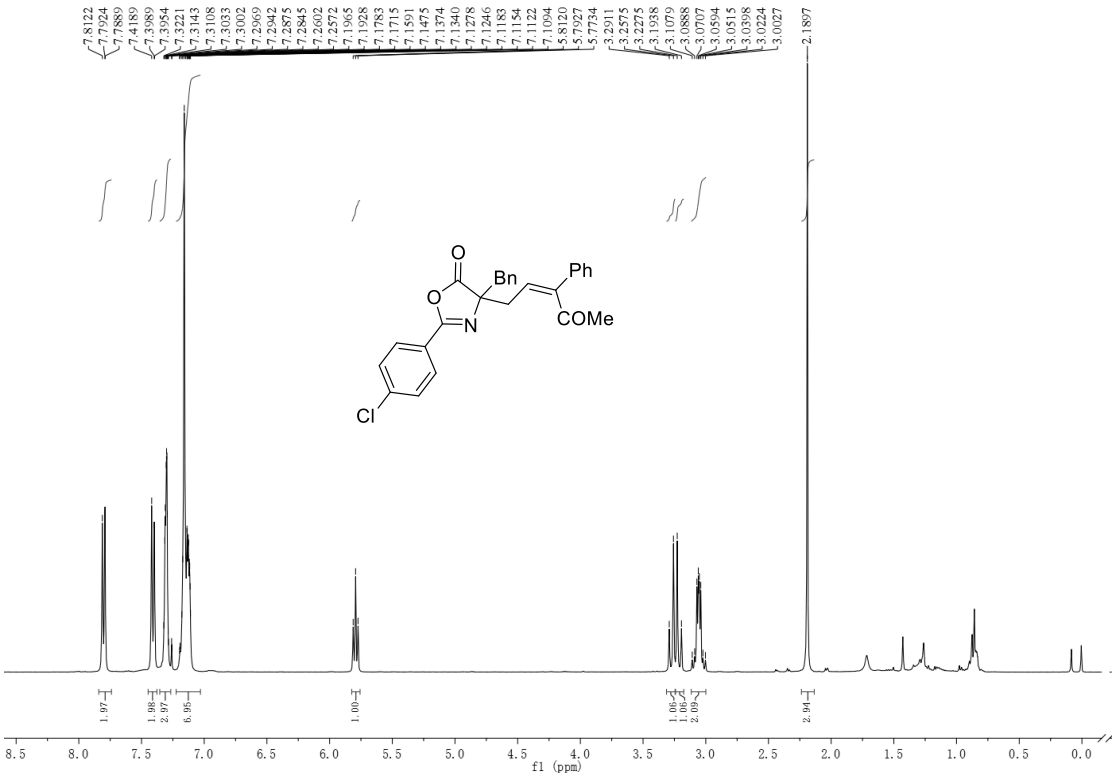


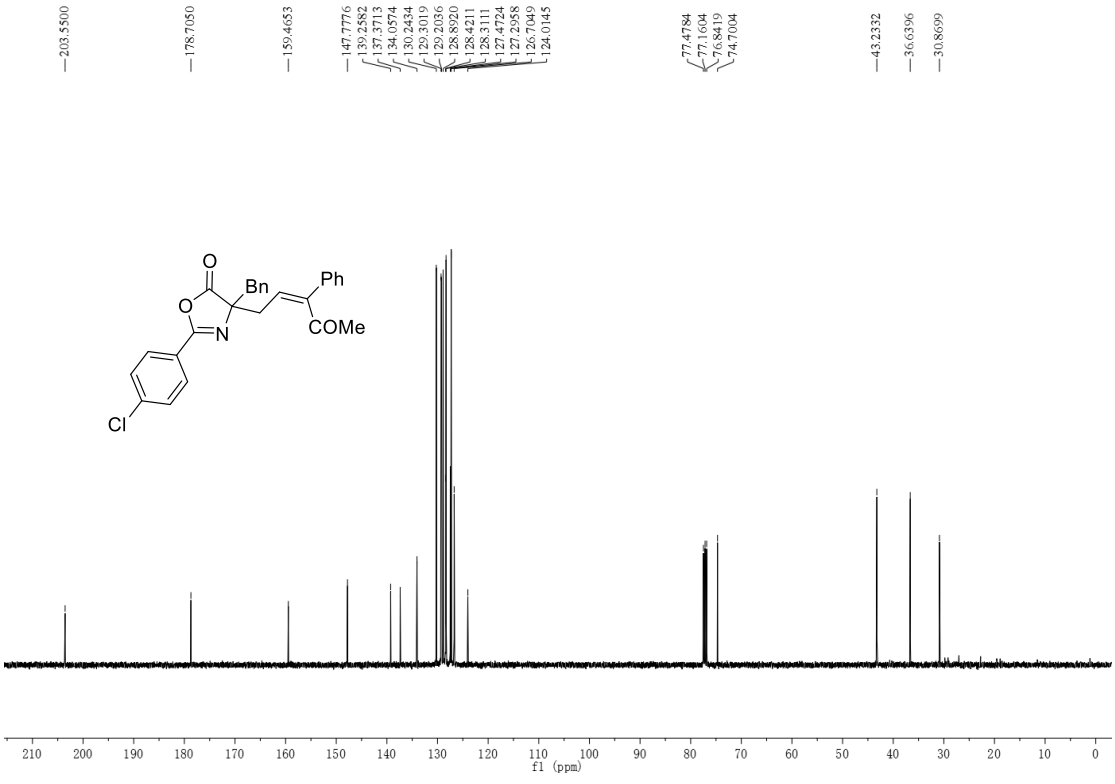
^{1}H, ^{13}C NMR of compound **3ai**



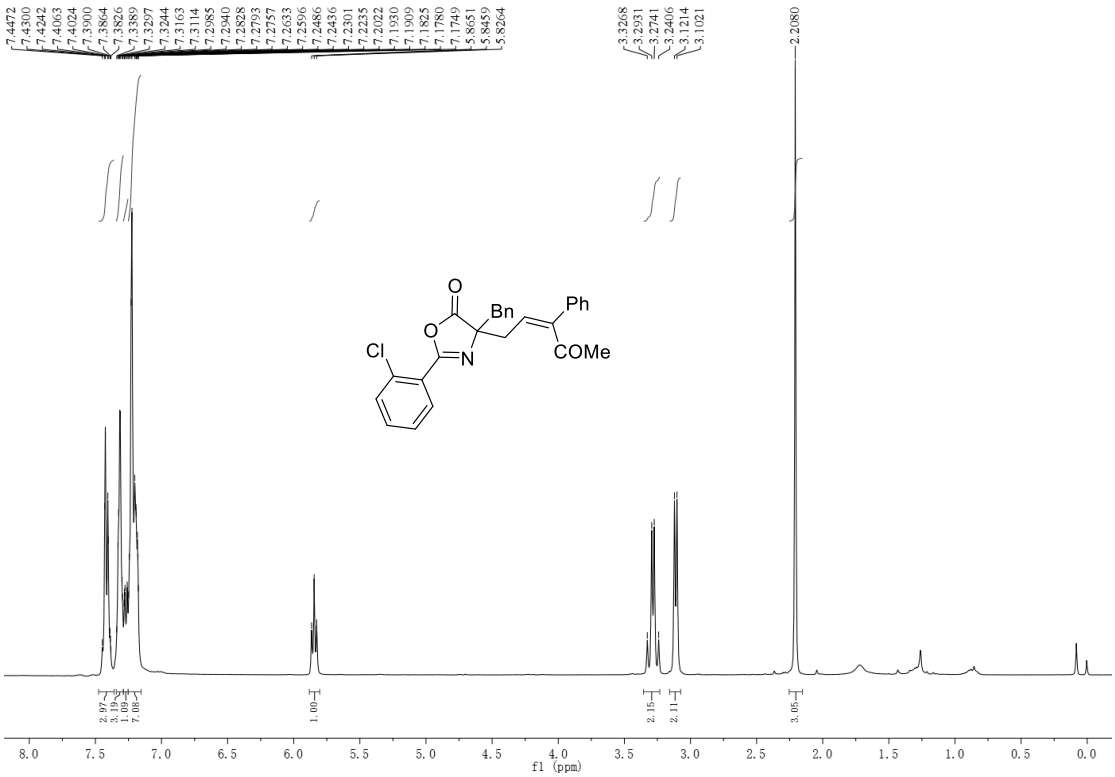


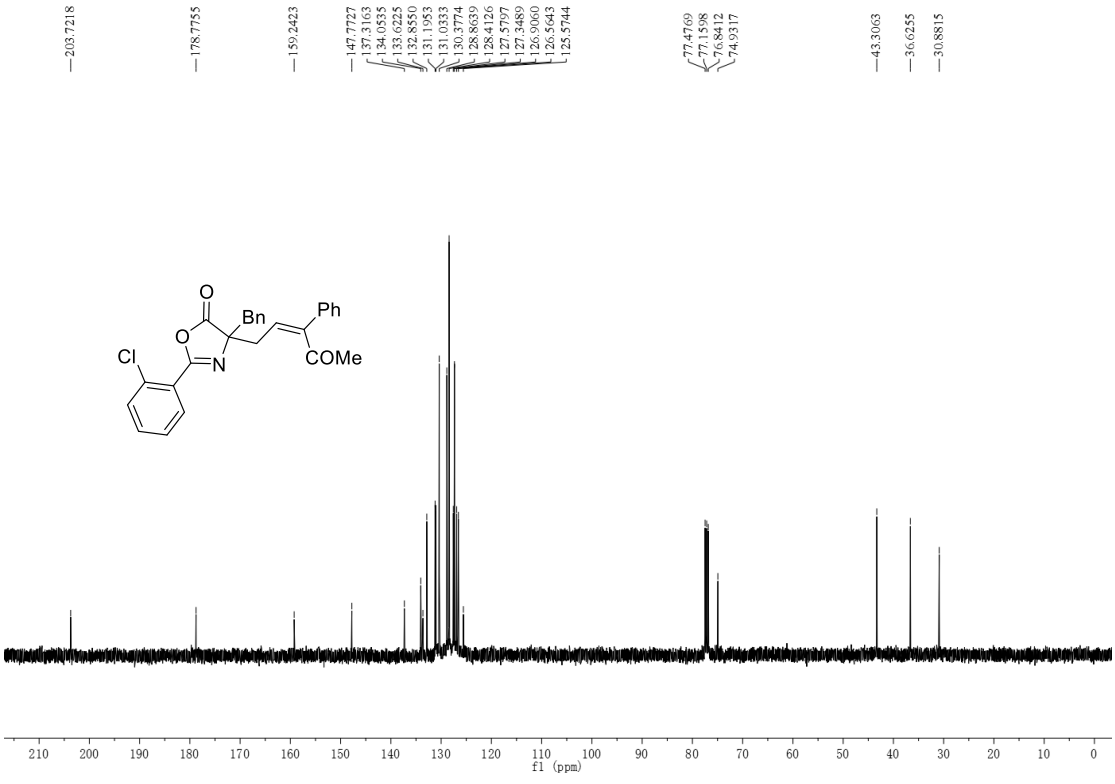
^{1}H, ^{13}C NMR of compound **3aj**



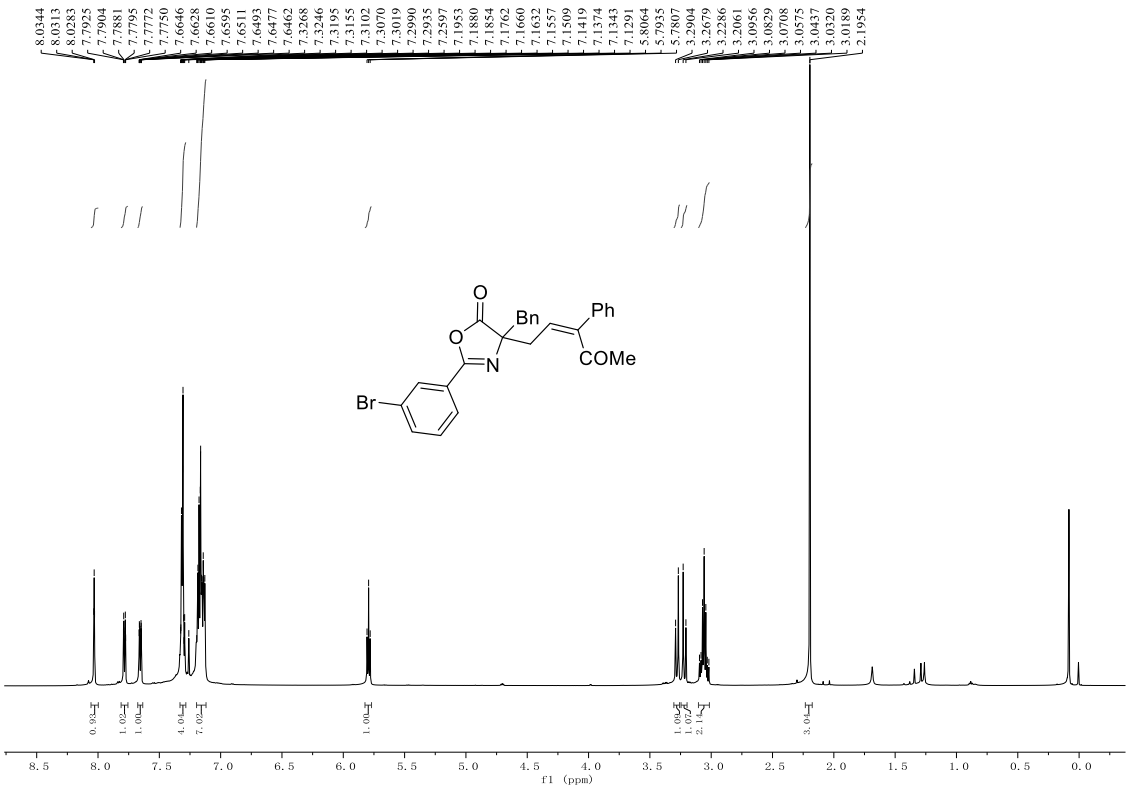


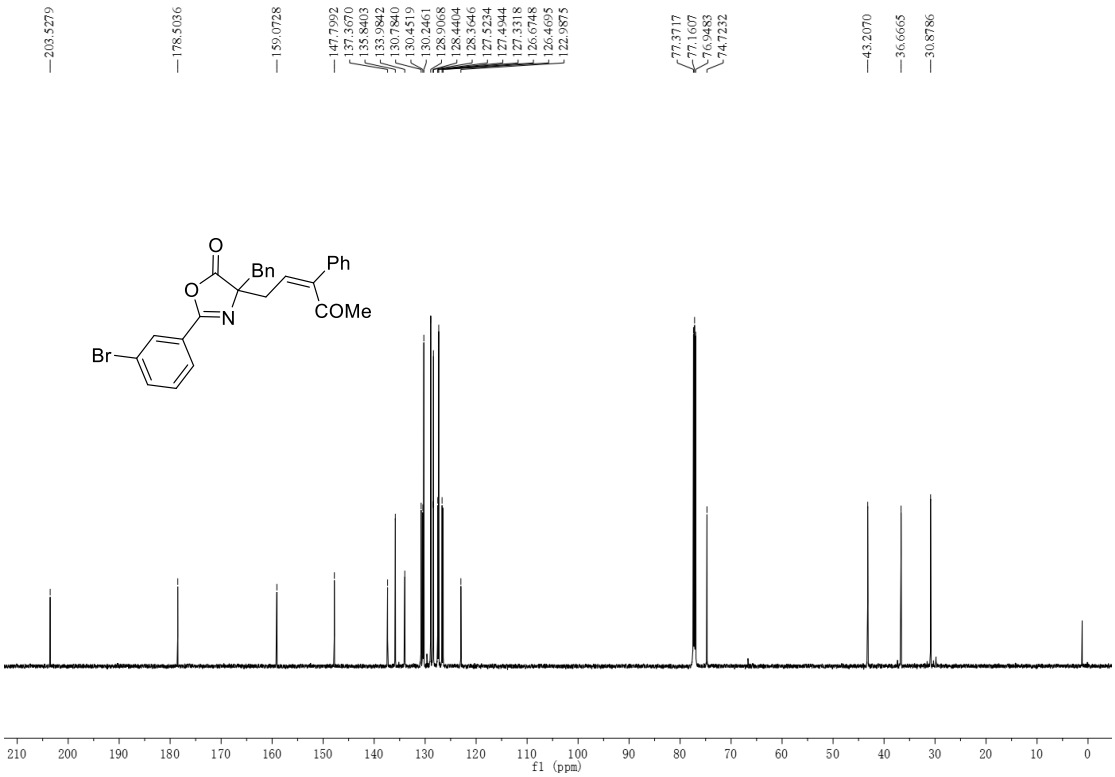
^{1}H, ^{13}C NMR of compound **3ak**



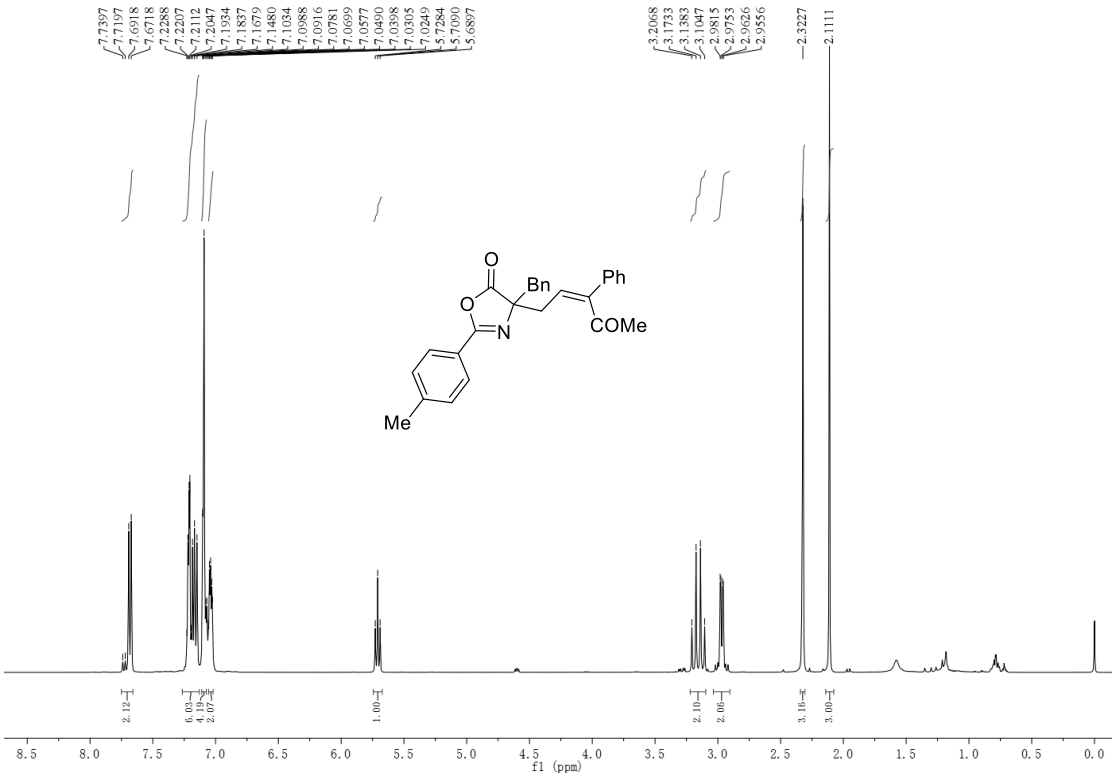


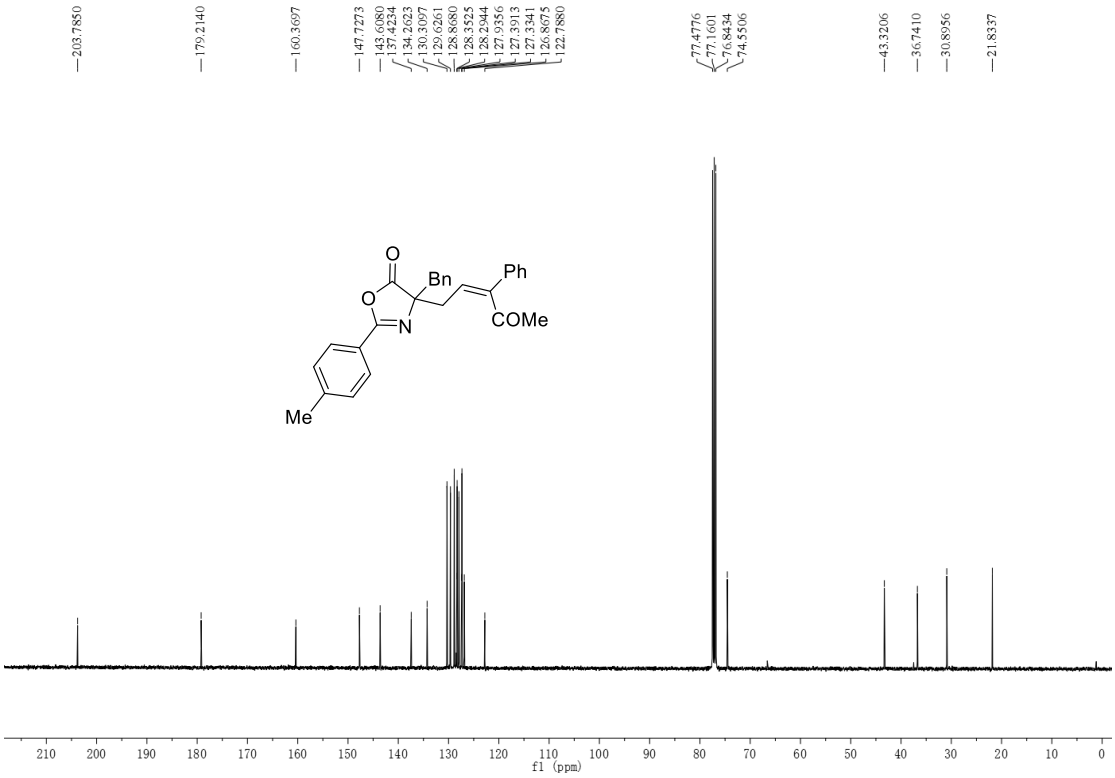
^{1}H, ^{13}C NMR of compound **3al**



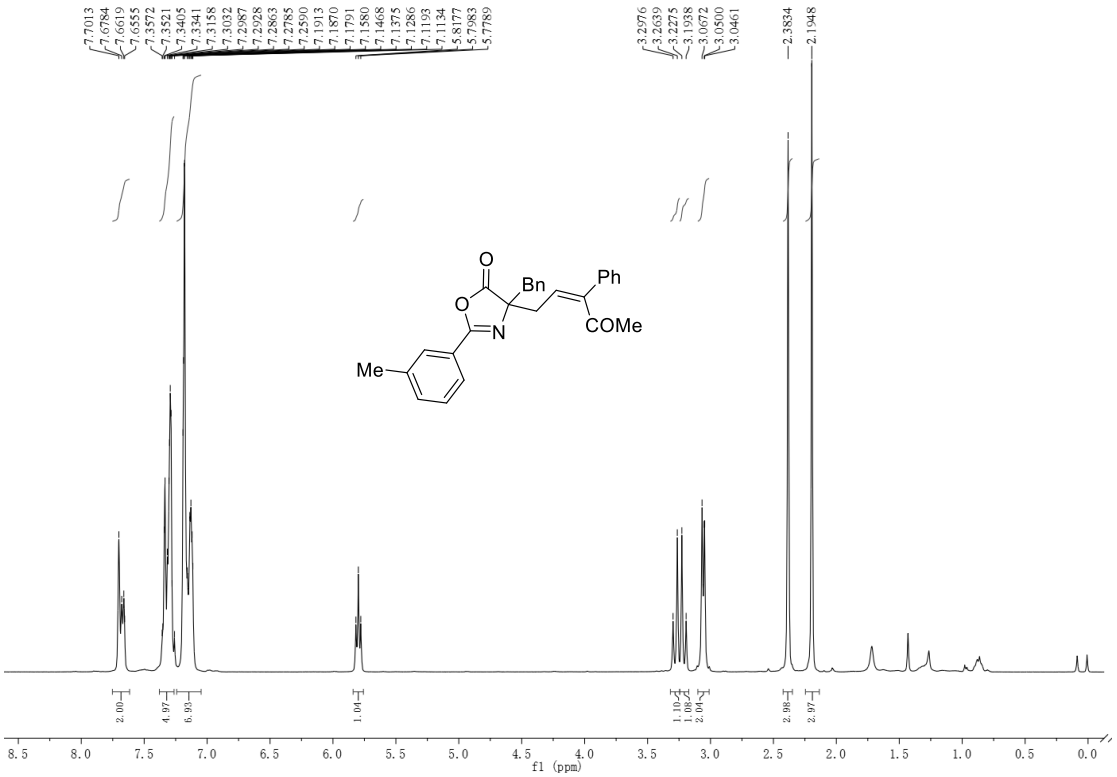


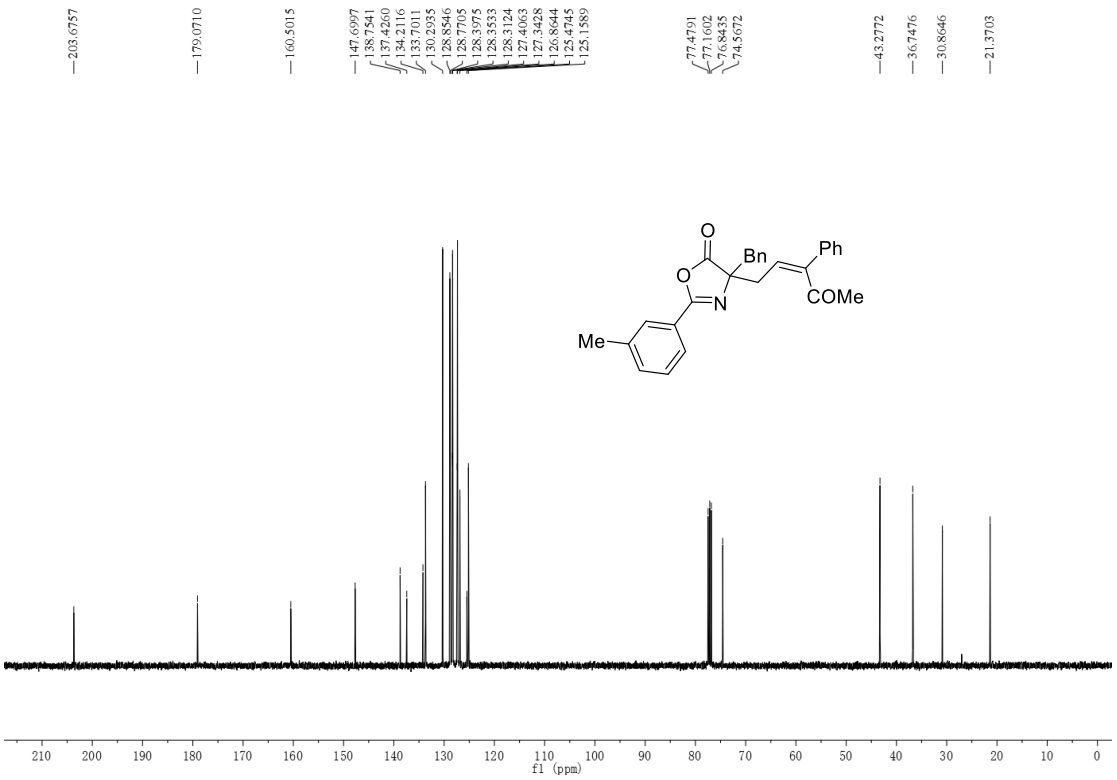
^{1}H, ^{13}C NMR of compound **3am**



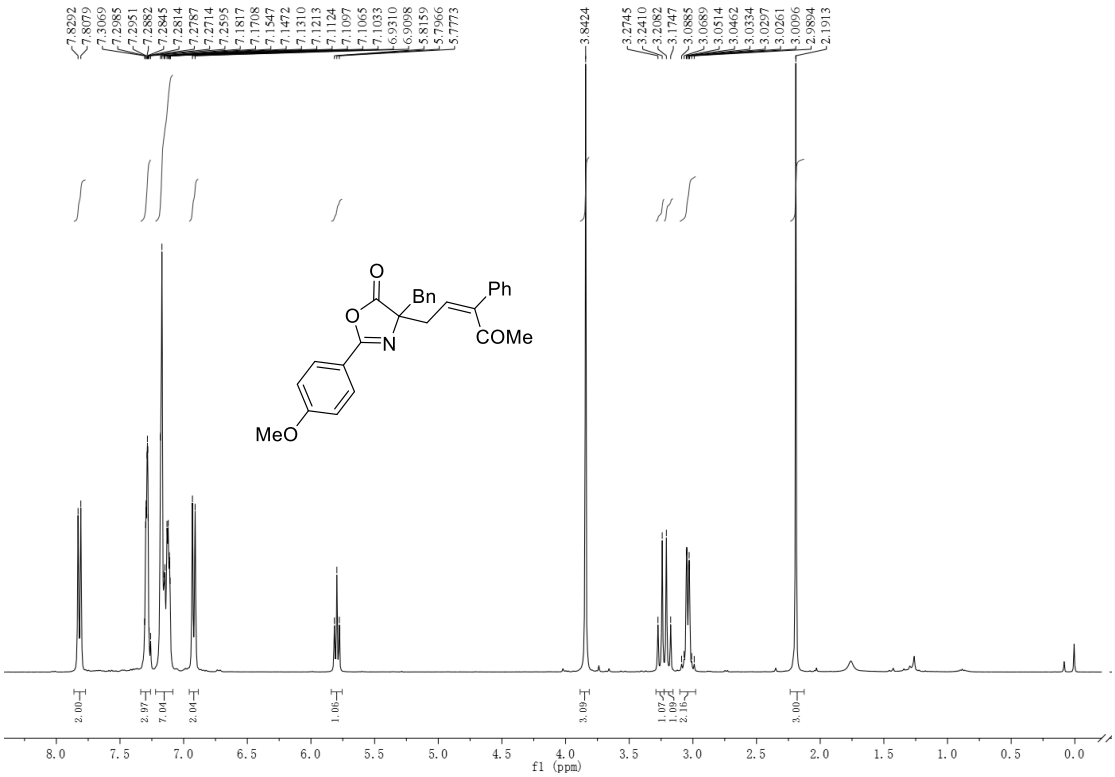


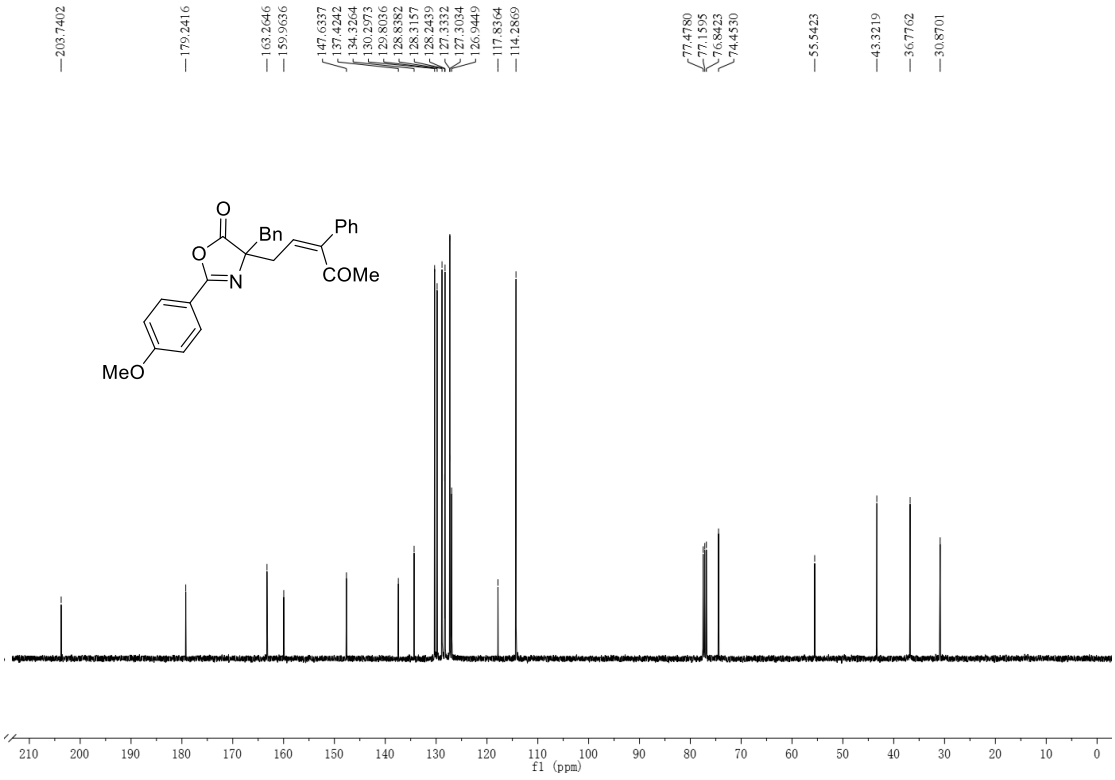
^{1}H, ^{13}C NMR of compound **3an**



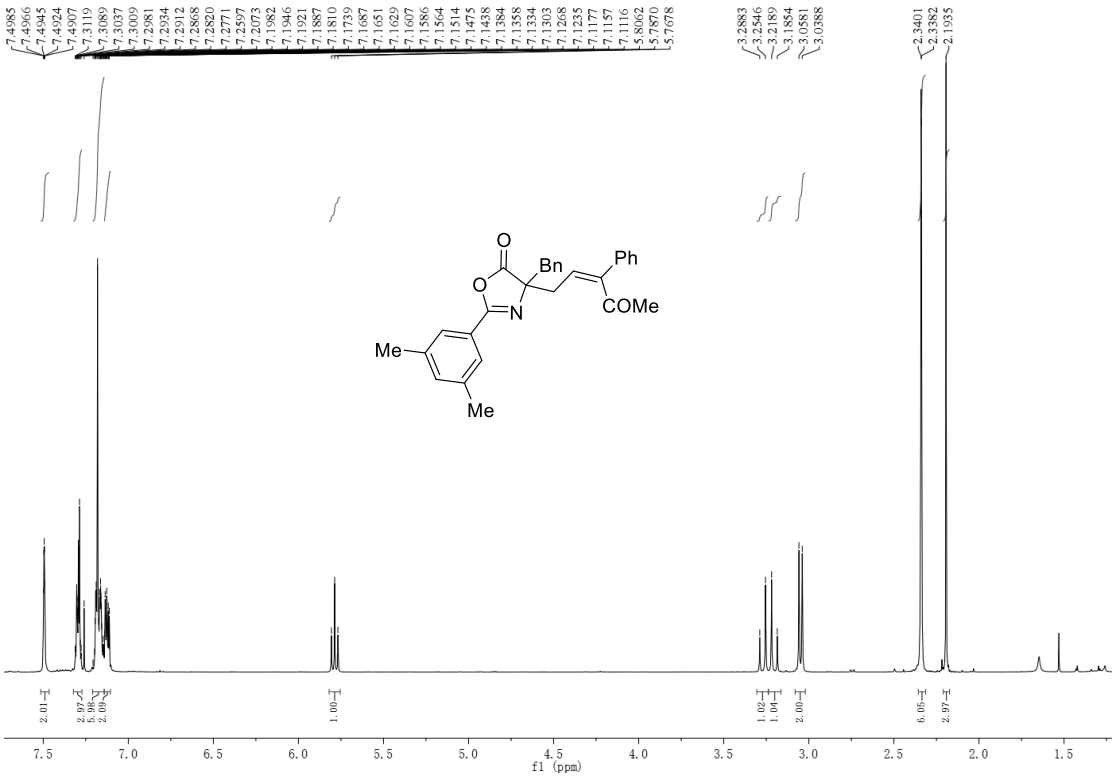


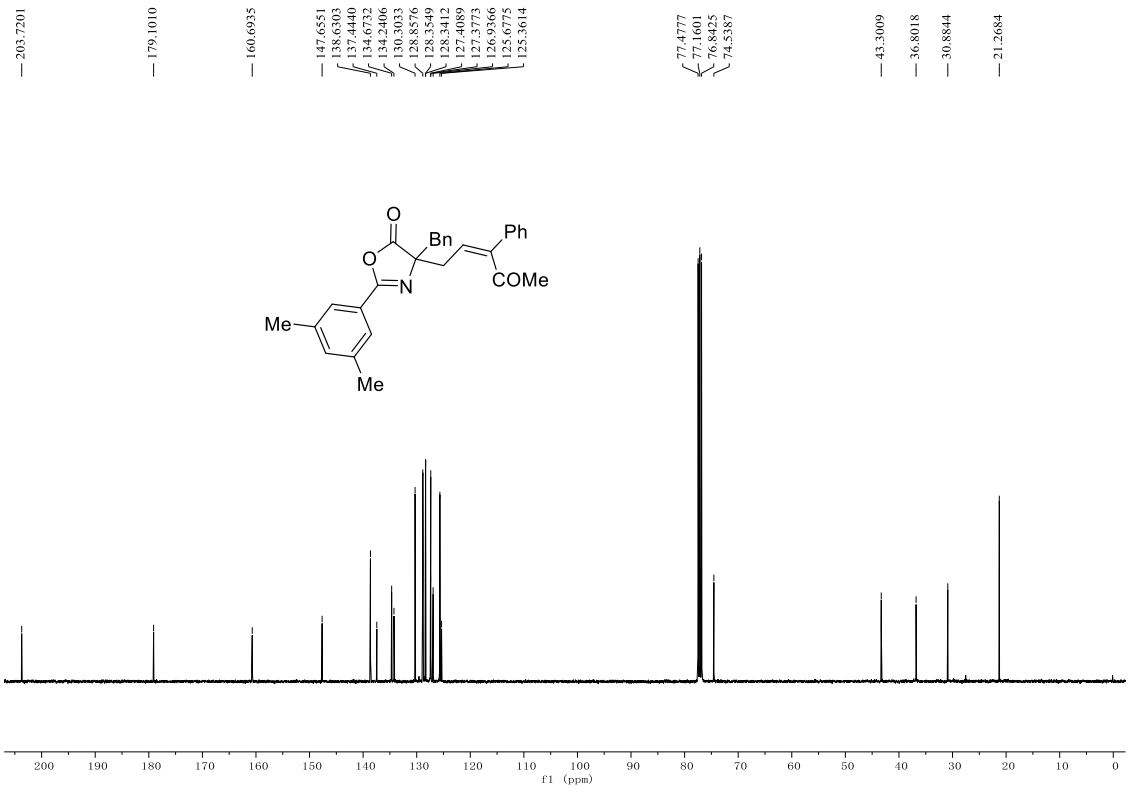
^{1}H, ^{13}C NMR of compound **3ao**



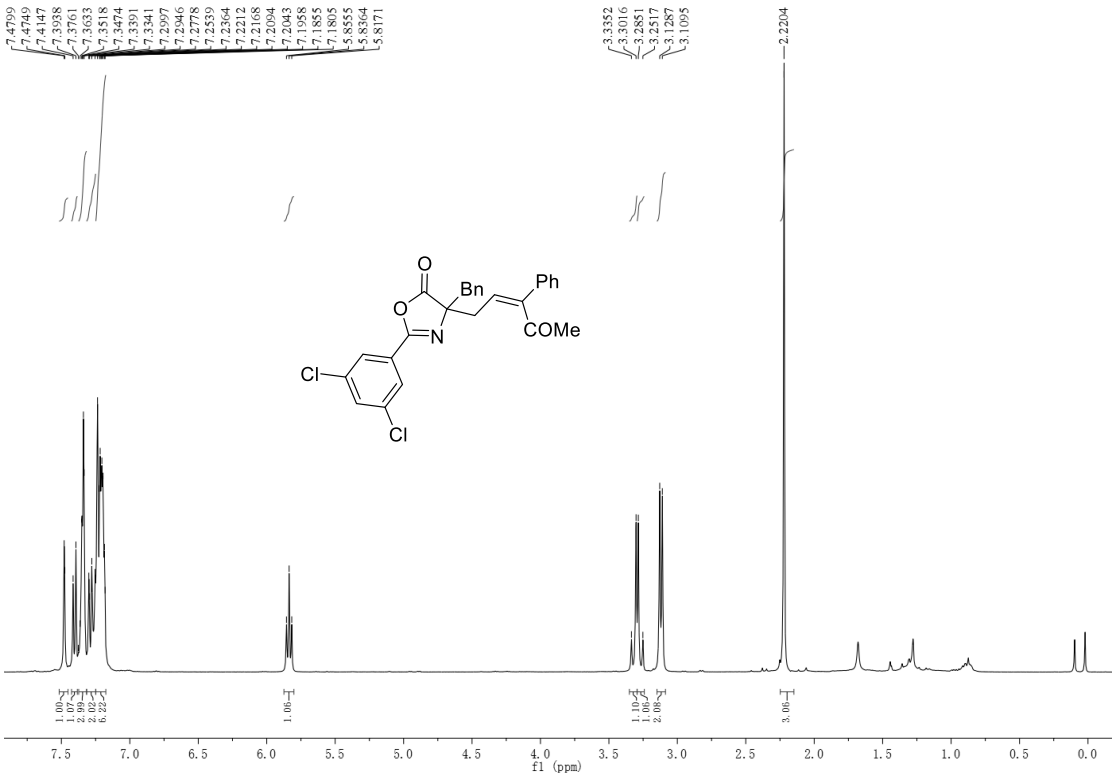


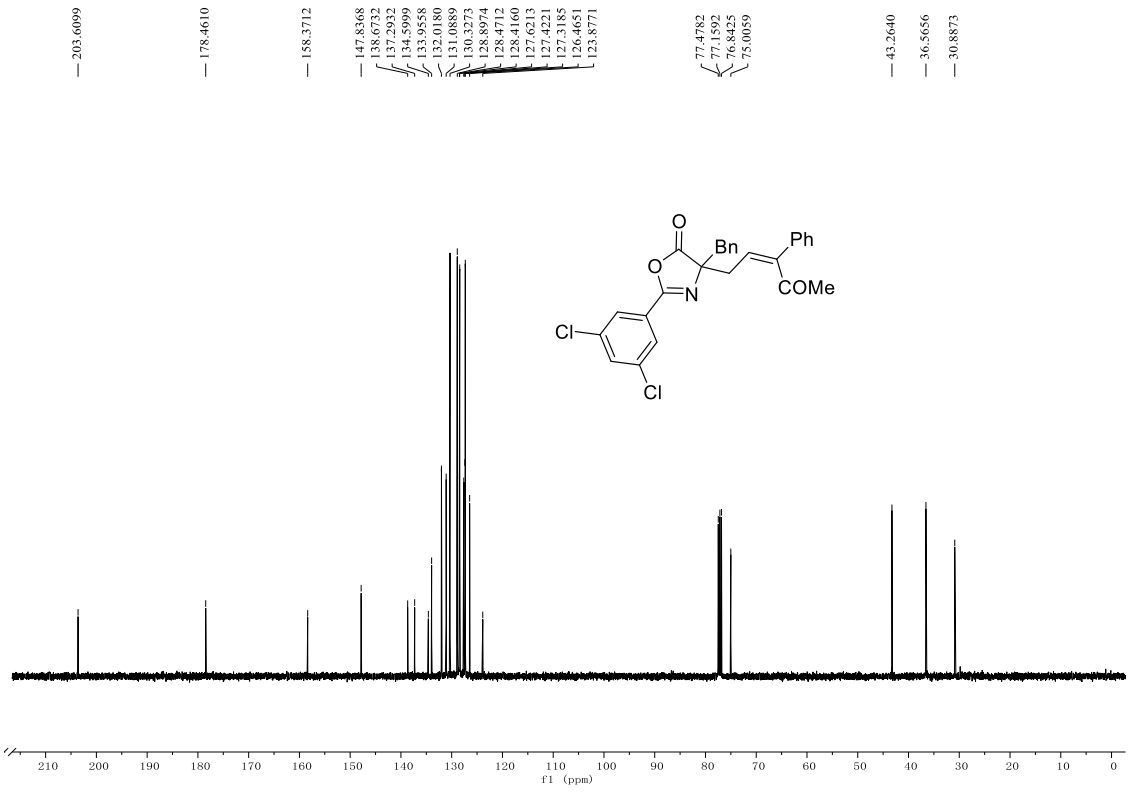
^{1}H, ^{13}C NMR of compound **3ap**



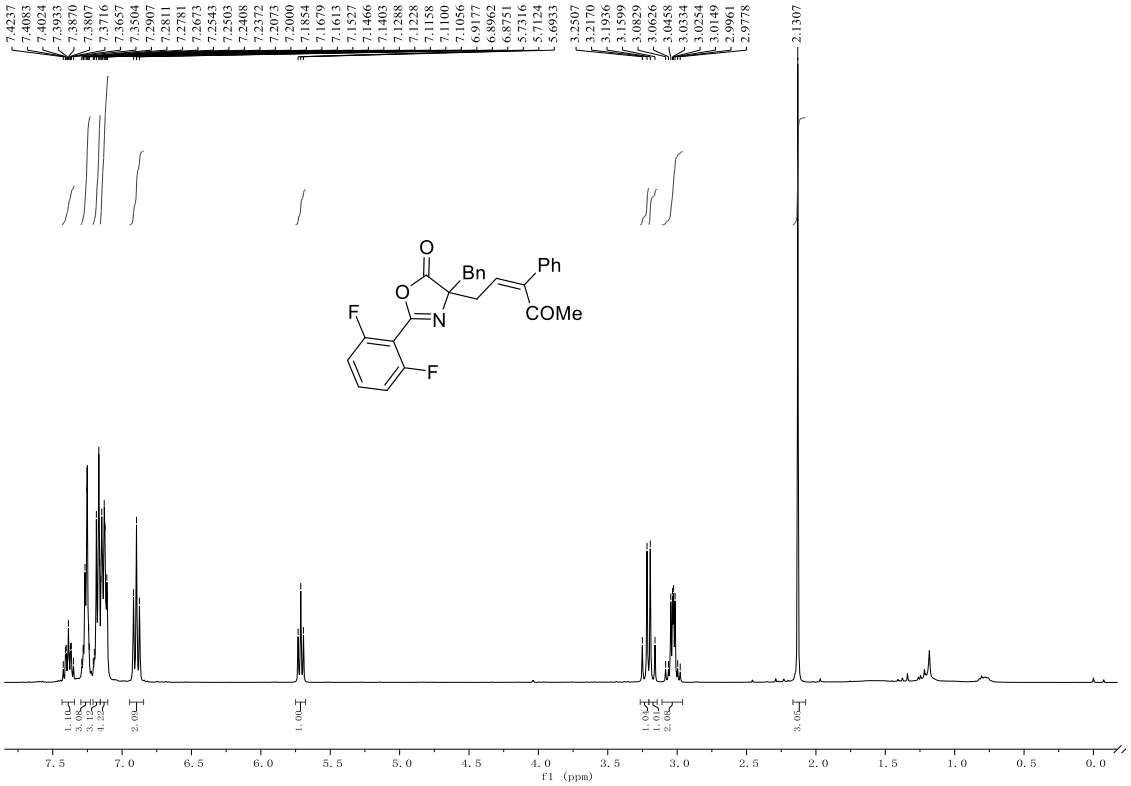


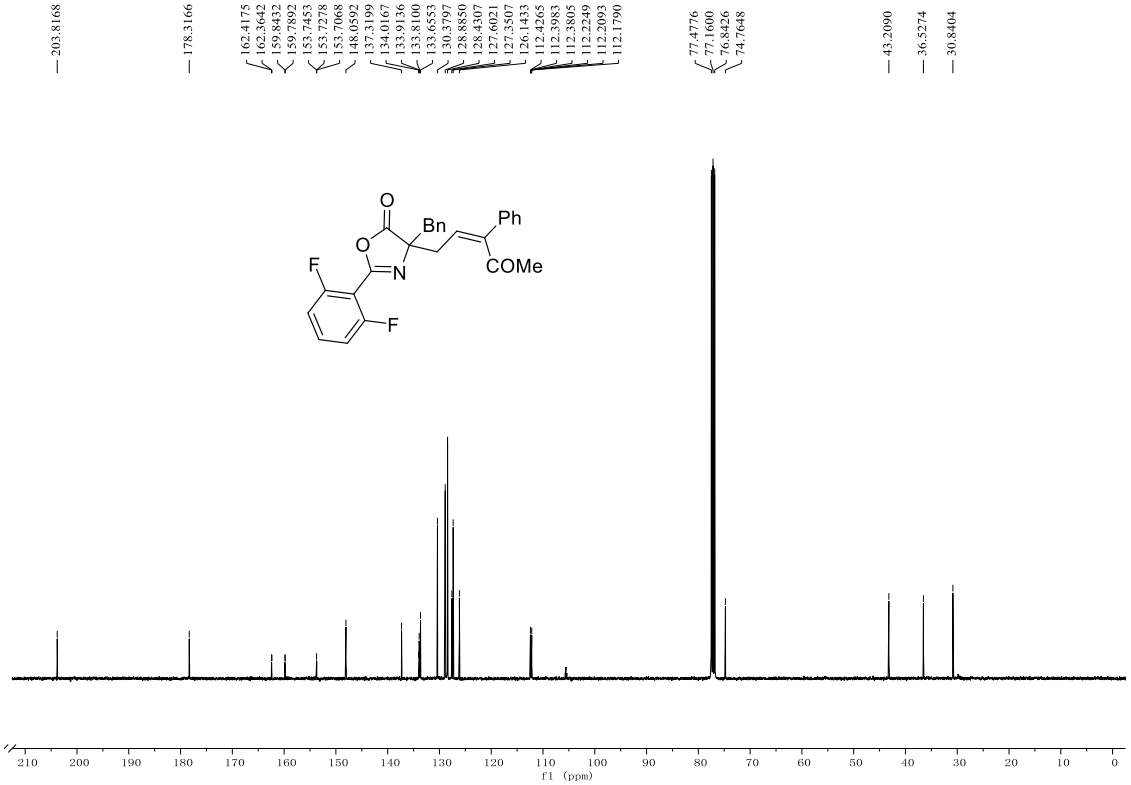
^{1}H, ^{13}C NMR of compound **3aq**



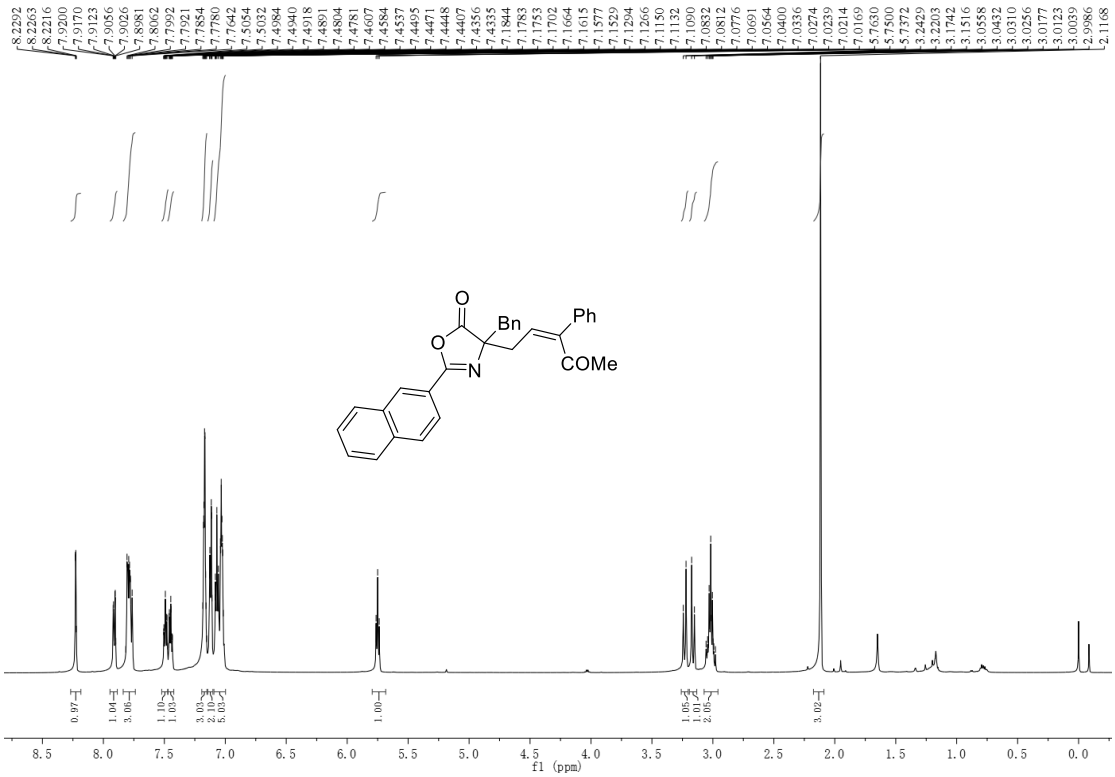


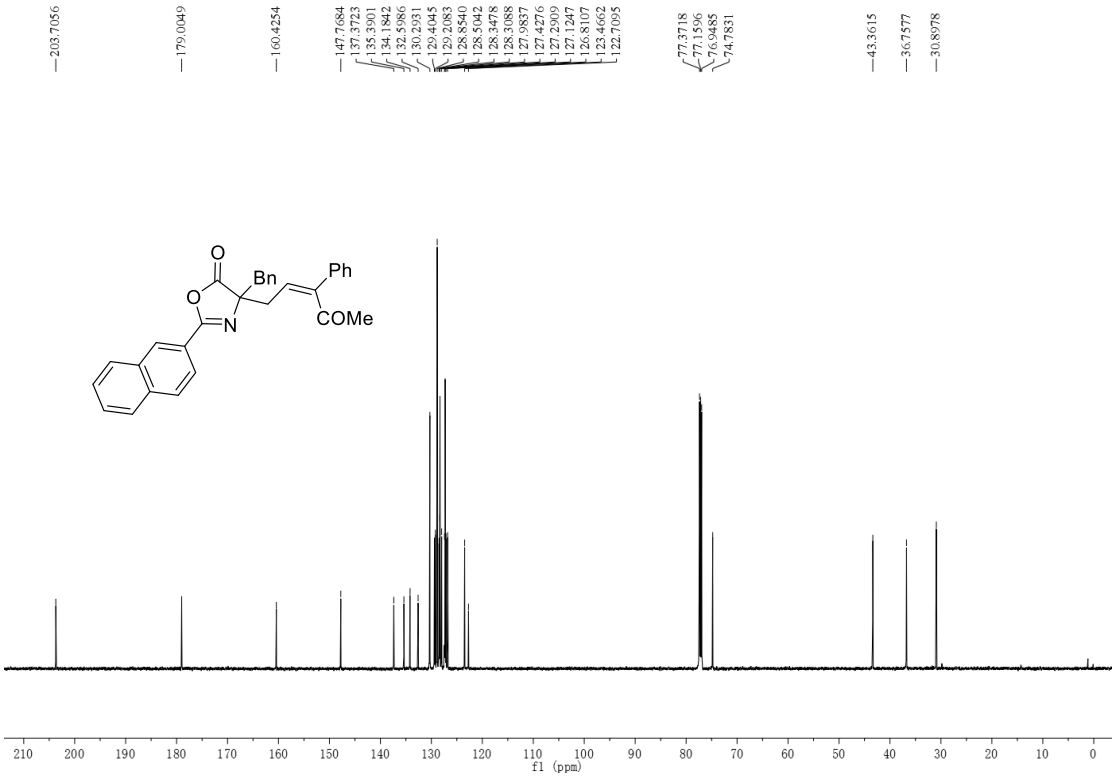
^{1}H, ^{13}C NMR of compound **3ar**



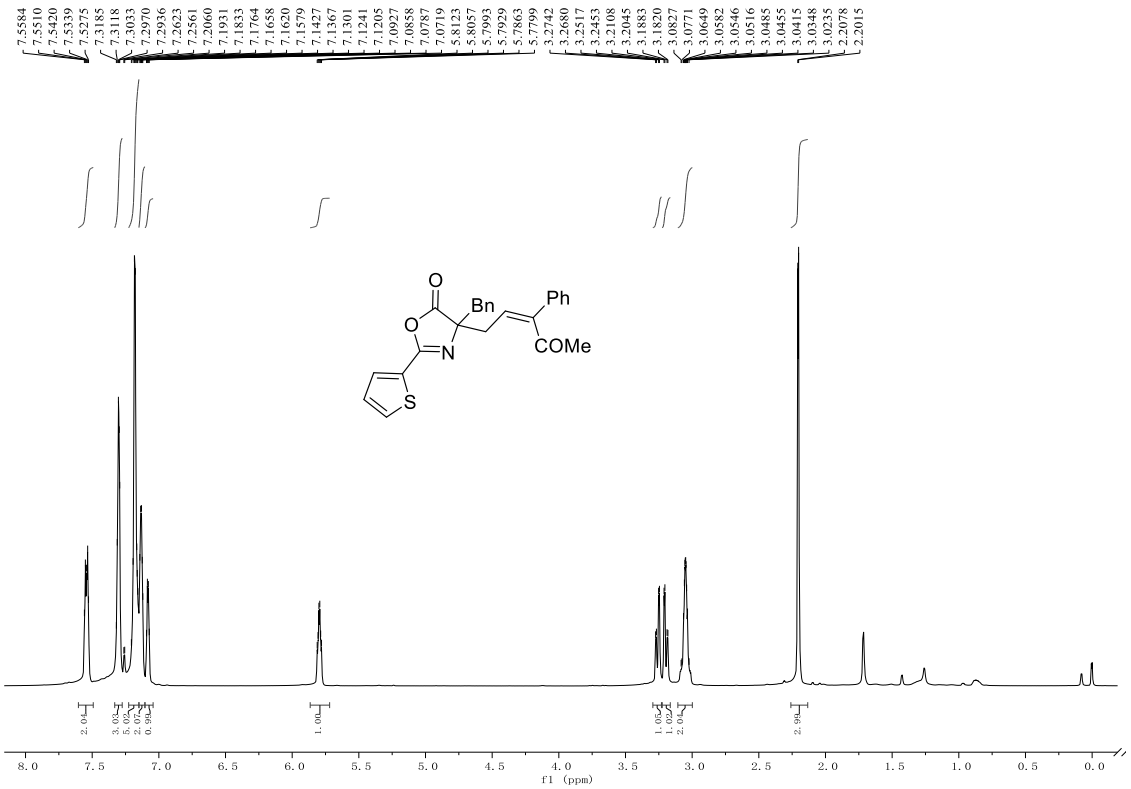


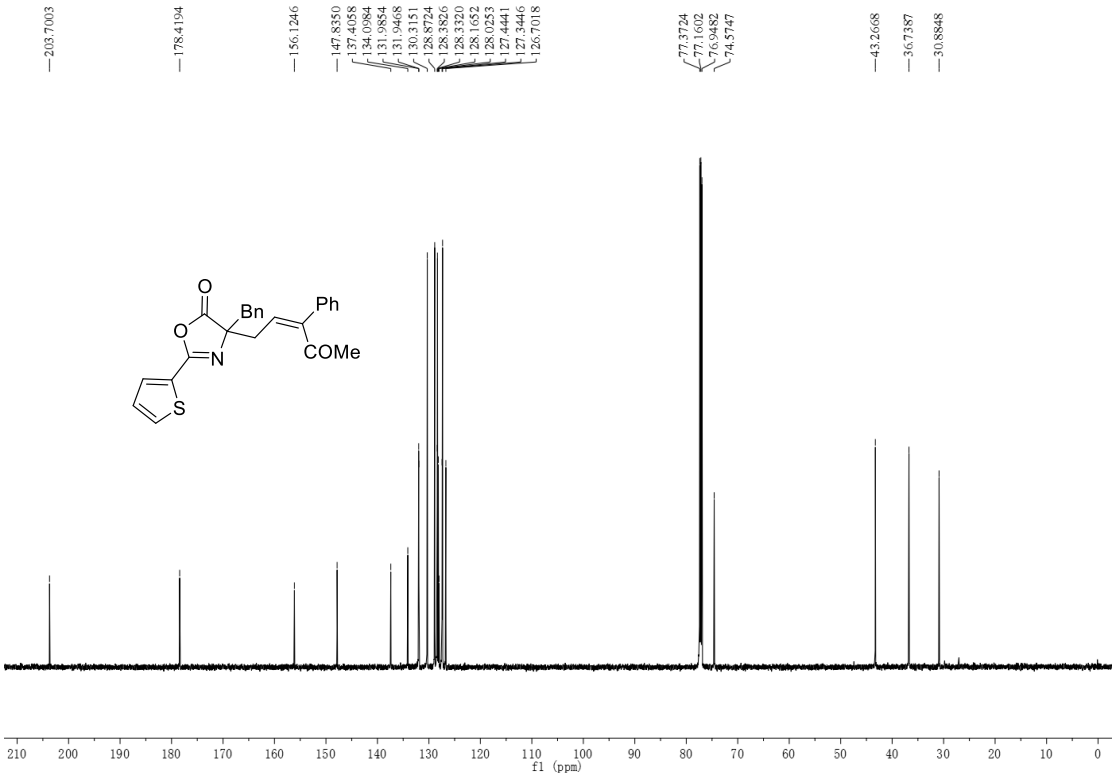
^{1}H, ^{13}C NMR of compound **3as**



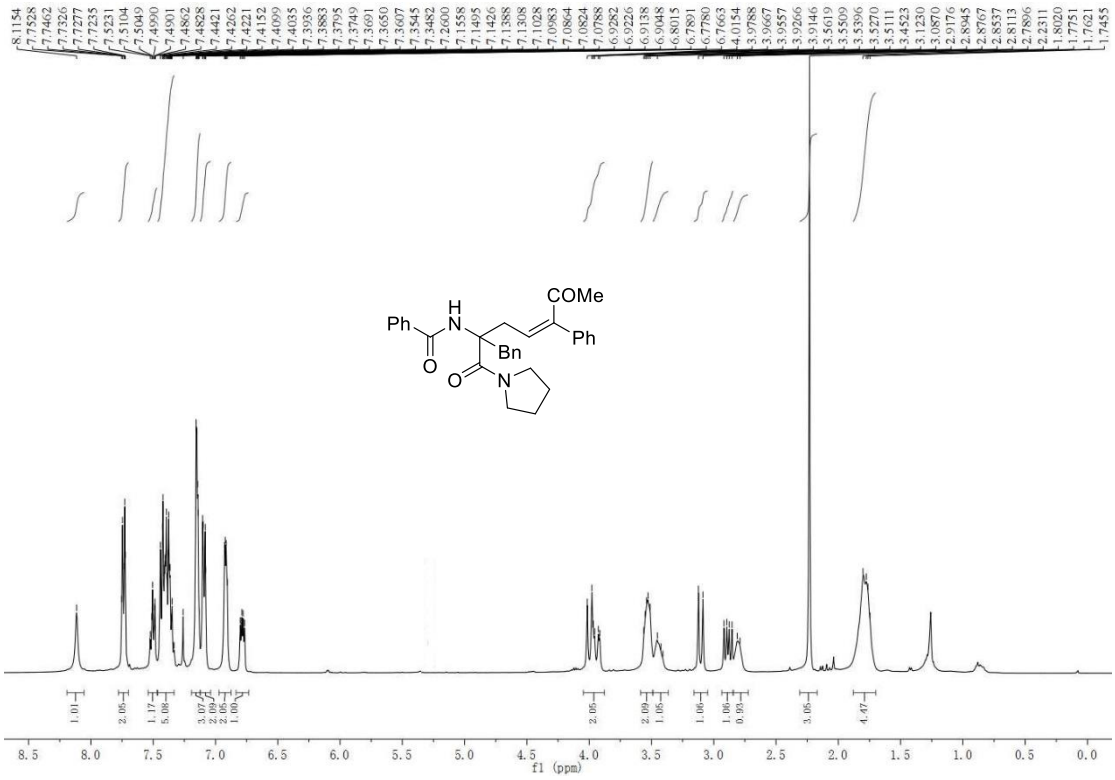


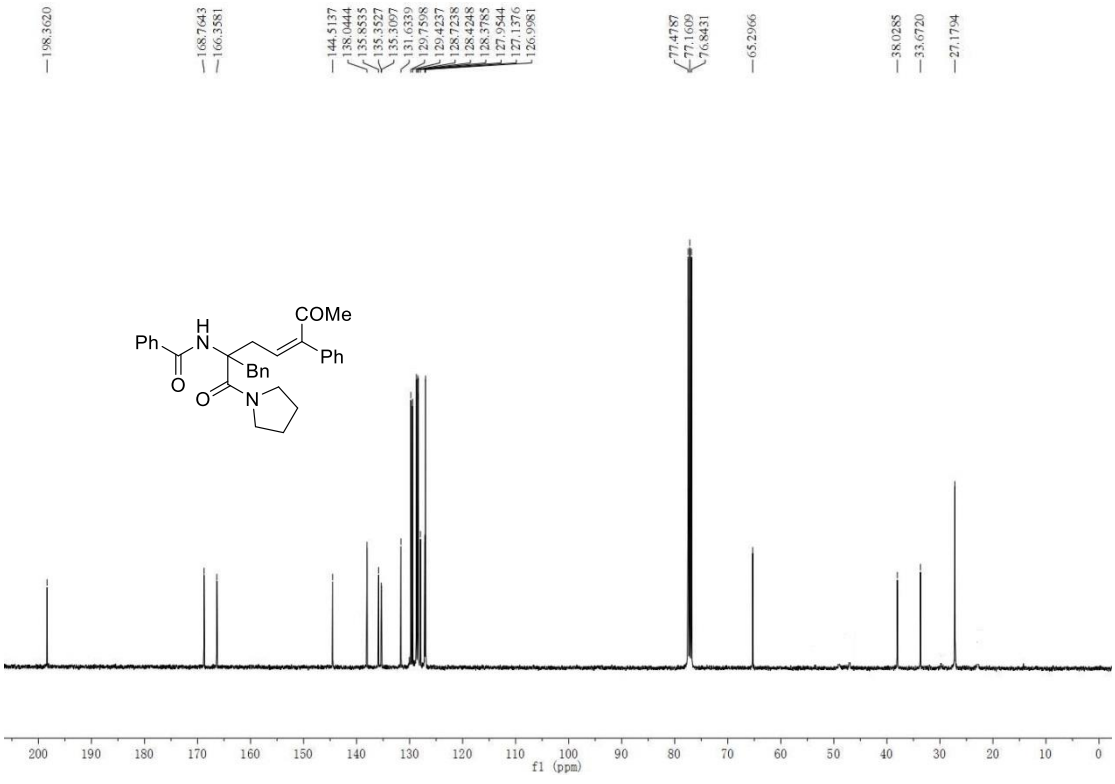
^{1}H, ^{13}C NMR of compound **3at**



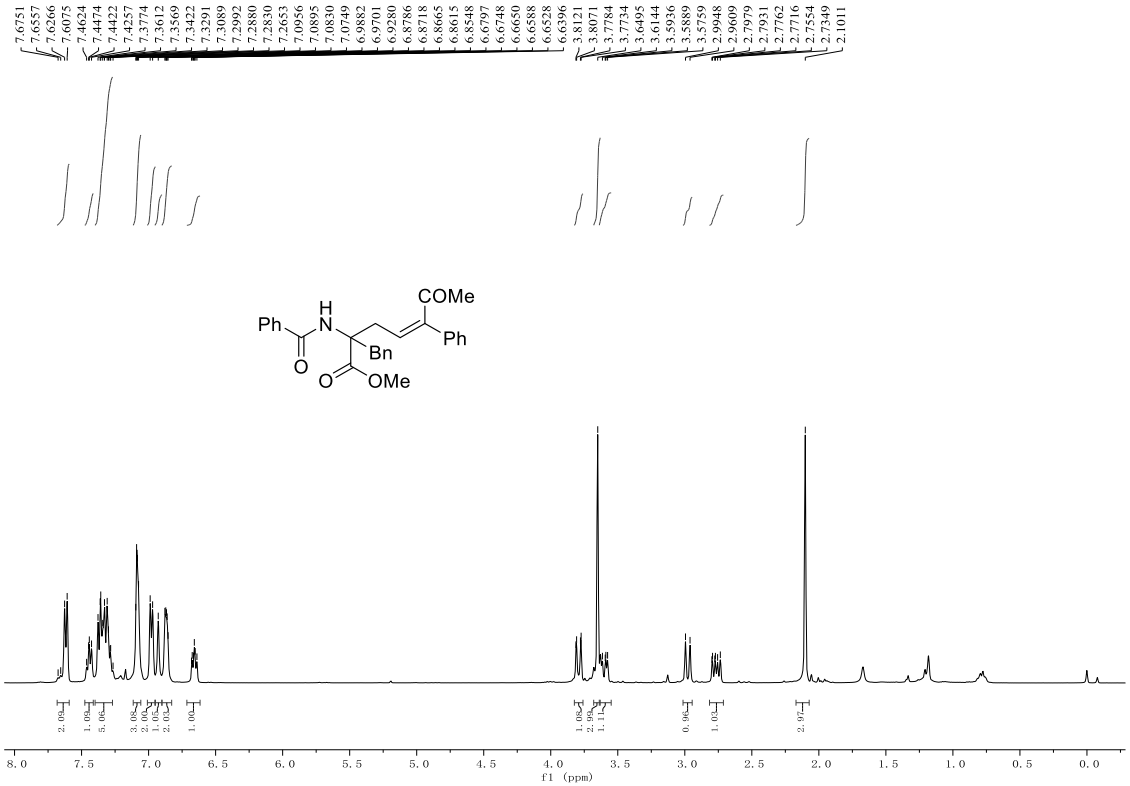


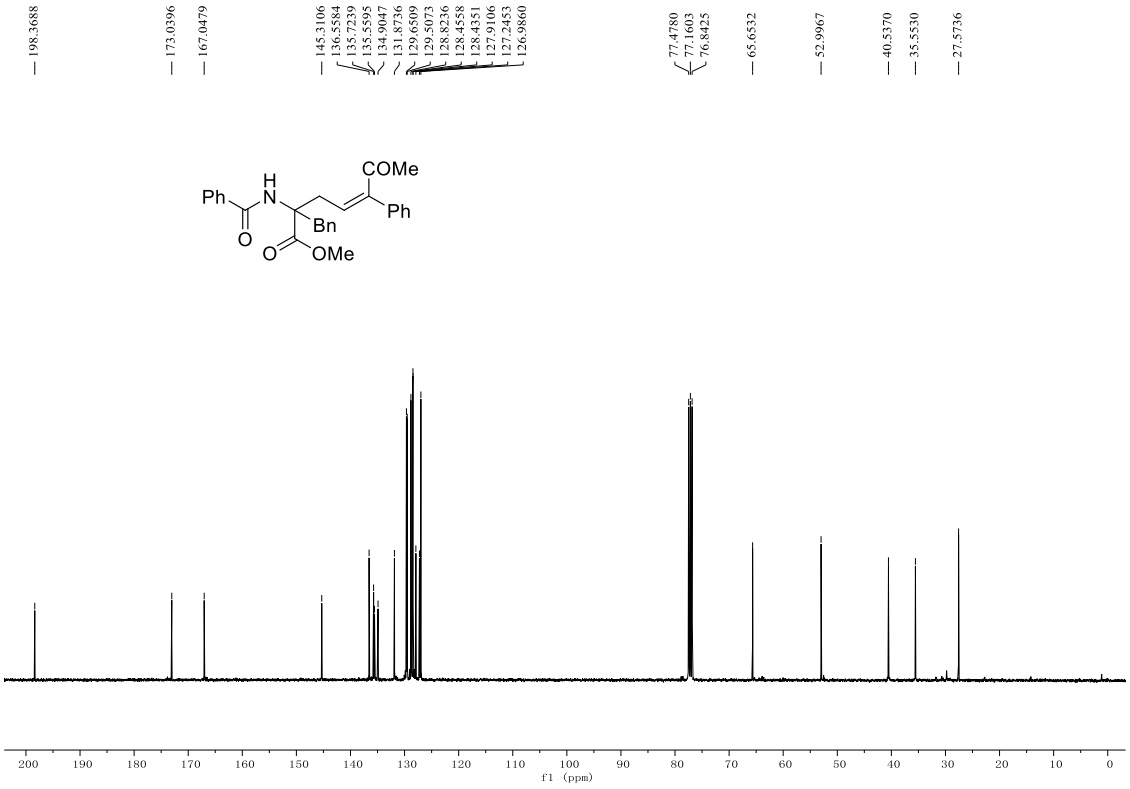
^{1}H, ^{13}C NMR of compound **5**



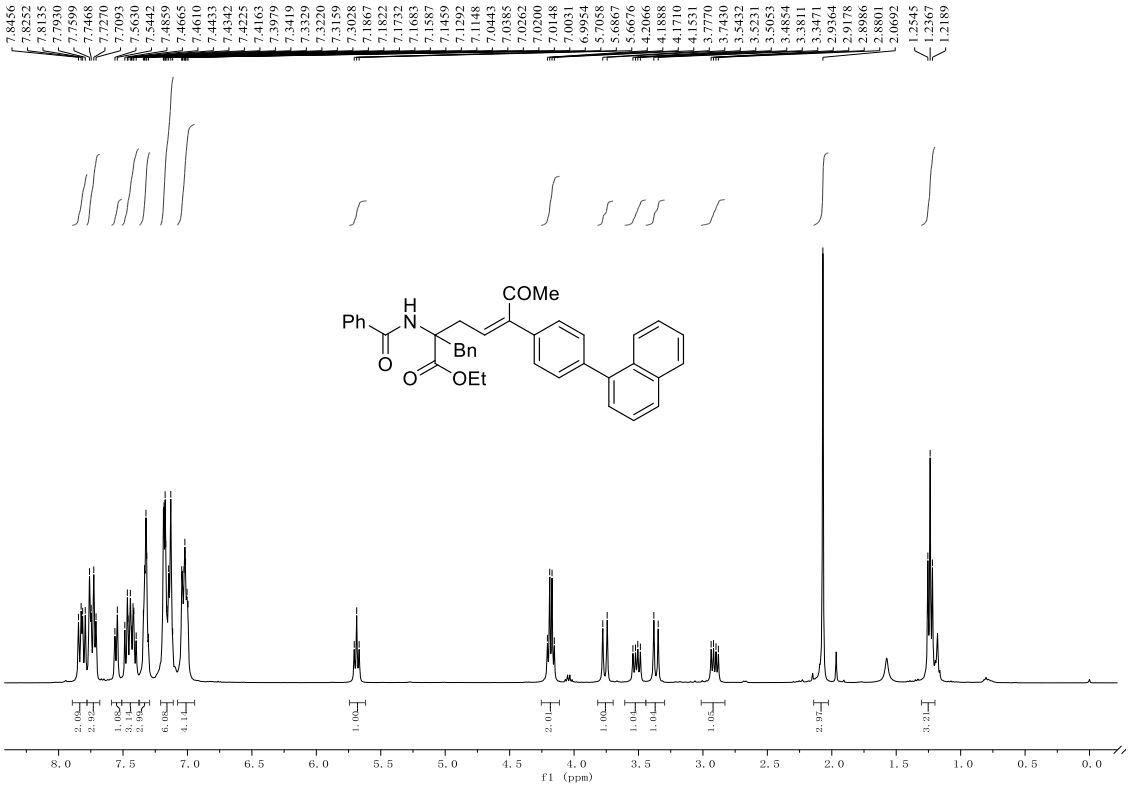


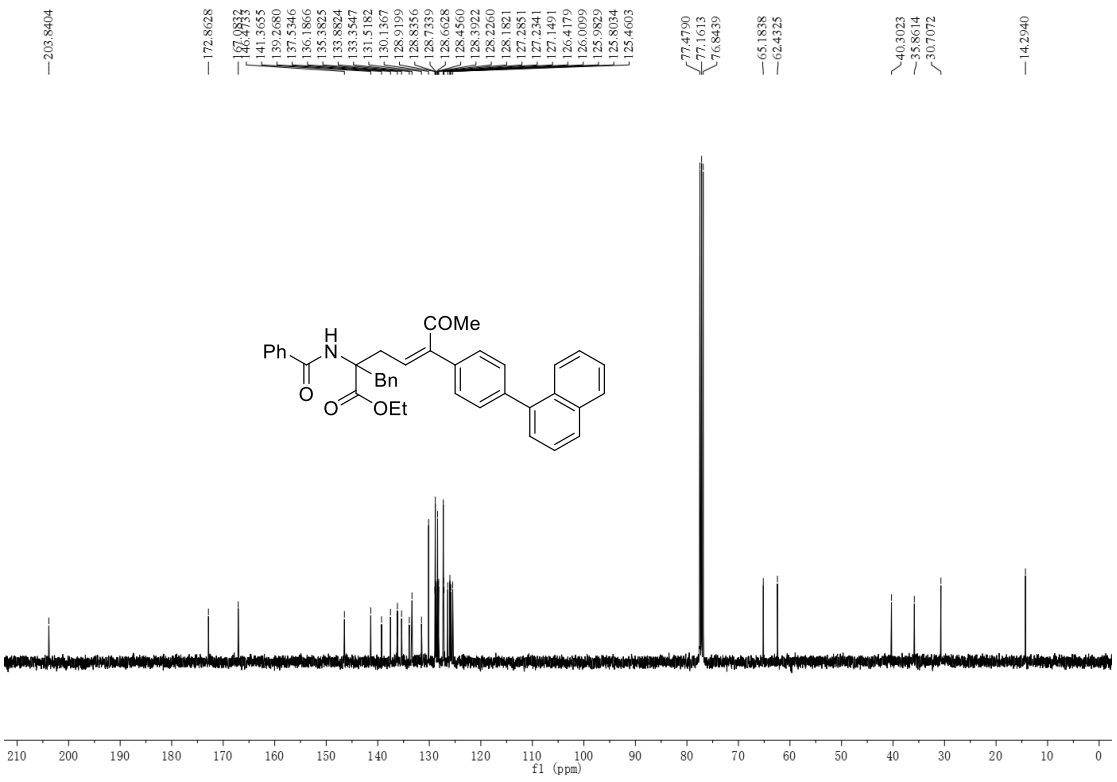
^{1}H, ^{13}C NMR of compound **6**



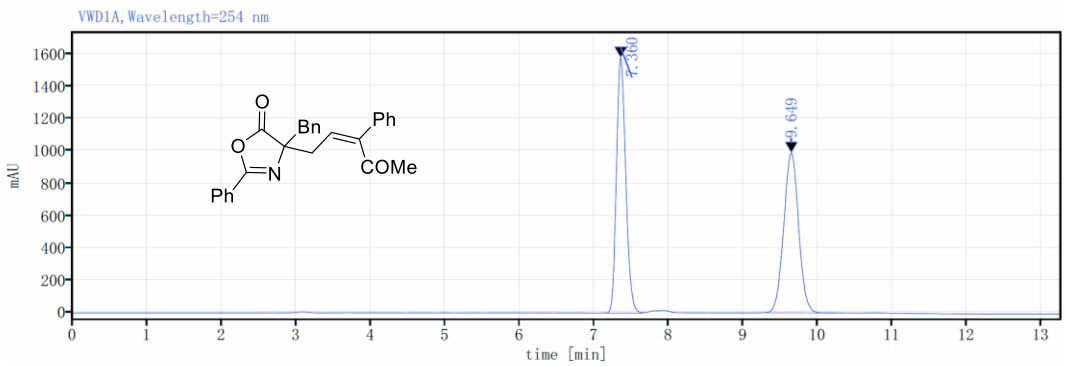


^{1}H, ^{13}C NMR of compound **7**



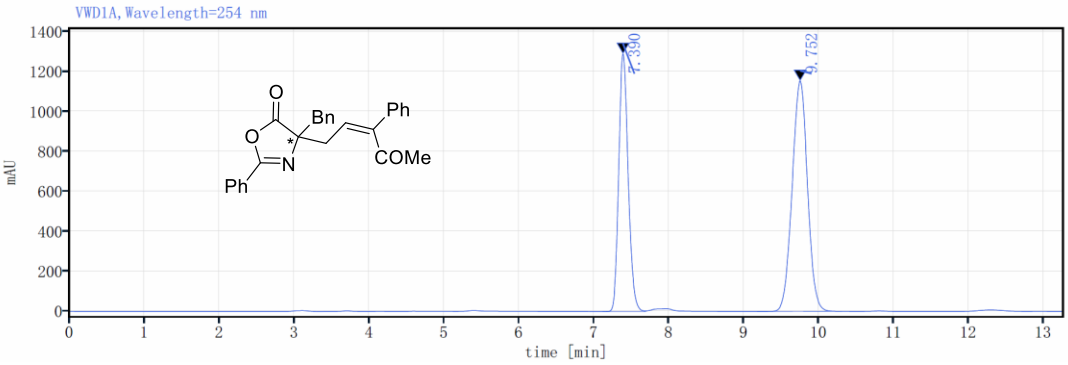


HPLC of **3aa**



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	7.360	13638.29	1577.49	49.93
	9.649	13678.22	987.97	50.07
		27316.51		100.00



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	7.390	11309.71	1290.01	40.81
	9.752	16404.13	1153.75	59.19
		27713.84		100.00