

Switching the Z/E Selectivity in the Palladium(II)-Catalyzed Decarboxylative Heck Arylations of trans-Cinnamaldehydes by Solvent

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1. General Information

All experiments were carried out under air. All work-up and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). Nuclear magnetic resonance (NMR) spectra were recorded on Varian MERCURY plus-300 spectrometer (^1H 300 MHz, ^{13}C 75 MHz) spectrometer or a Varian MERCURY plus-400 spectrometer (^1H 400 MHz, ^{13}C 100 MHz) or a Varian MERCURY plus-500 spectrometer (^1H 500 MHz, ^{13}C 125 MHz). Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) with the solvent resonance as the internal standard (CDCl_3 : δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) with the solvent as the internal standard (CDCl_3 : δ 77.0 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Infrared spectra were recorded on a Perkin Elmer ATR-FTIR spectrometer and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI and APCI). X-ray determination was resolved by Rigaku AFC63 four-circle diffractometer. All calculations were performed with Gaussian 09. Molecular geometries were fully optimized with the B3LYP method. The LanL2DZ basis sets with effective core potentials (ECPs) were employed for Pd, and the 6-31G basis set was used for H, C, N, O.

Unless stated otherwise, commercial reagents were used without further purification.

2. General procedure of THF-Condition

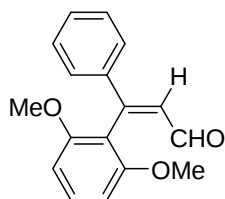
An oven-dried reaction tube was charged with PdCl_2 (3.54 mg, 0.02 mmol), tri(*p*-tolyl)phosphine (12.16 mg, 0.04 mmol), DCM (1 mL) and MeCN (1 mL) and then stirred for 2 hours. After removing the solvent under vacuum, aromatic acid (**1**, 0.4 mmol), AgIO_3 (56.56 mg, 0.2 mmol), *trans*-cinnamaldehyde (**2**, 0.2 mmol) and THF (2 mL) were added to the reaction tube. The reaction tube was sealed and heated at 120 °C (oil bath temperature) for 3–24 h (TLC monitored). The black sediment was removing and the filtrate was concentrated in vacuo to give the crude mixture. ^1H NMR experiment of the crude mixture was performed to determine the *Z/E* ratios and NMR yields of product (using mesitylene as internal standard). The corresponding pure *Z*-isomer product was then obtained by purifying the mixture using preparative TLC.

3. General procedure of DMF-Condition

An oven-dried reaction tube was charged with PdCl_2 (3.54 mg, 0.02 mmol), aromatic acid (**1**, 0.4 mmol), AgIO_3 (56.56 mg, 0.2 mmol), *trans*-cinnamaldehyde (**2**, 0.2 mmol) and DMF (2 mL). The reaction tube was sealed and heated at 120 °C (oil bath temperature) for 0.3–4 h (TLC monitored). The mixture was diluted by EtOAc (20 mL), washed with saturated brine (3 x 20 mL). The organic phase was dried with Na_2SO_4 and evaporated in vacuum. ^1H NMR experiment of the crude mixture was performed to determine the *Z/E* ratios and NMR yields of product (using mesitylene as internal standard). The corresponding pure *E*-isomer product was then obtained by purifying the mixture using preparative TLC.

4. Experimental characterization data for compounds

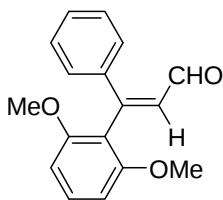
(*Z*)-3-(2,6-dimethoxyphenyl)-3-phenylacrylaldehyde (**3a-Z**)



Prepared under THF-condition, reaction time: 24 hours, 32.7 mg, Yield: 61 %; white solid; m.p. 88–90 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.40 (d, J = 8.0 Hz, 1H), 7.41–7.32 (m, 6H), 6.69 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 8.4 Hz, 2H), 3.68 (s, 7H); ^{13}C NMR (125 MHz, CDCl_3) δ 194.21, 157.96, 155.10, 138.65, 130.53, 129.91, 128.49, 127.58, 126.82, 113.64, 103.84, 55.91; IR (neat) ν (cm^{-1}): 3001, 2938, 2837, 1654, 1578, 1468, 1425; HRMS (ESI): $[\text{M}+\text{Na}]^+$ calcd. For $\text{C}_{17}\text{H}_{16}\text{NaO}_3$:

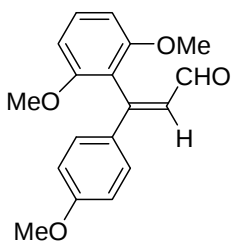
291.0992; Found: 291.0983.

(E)-3-(2,6-dimethoxyphenyl)-3-phenylacrylaldehyde(3a-E)



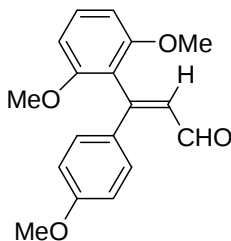
Prepared under DMF-condition, reaction time: 1 hour, 37.6 mg, Yield: 70 %; light yellow solid; m.p. 134~135 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.74 (d, *J* = 8.1 Hz, 1H), 7.37–7.22 (m, 6H), 6.58 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 8.1 Hz, 1H), 3.69 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 193.81, 157.17, 156.74, 138.32, 132.23, 130.13, 129.53, 128.64, 127.73, 119.57, 104.21, 55.89; IR (neat) ν (cm⁻¹): 3007, 2928, 2838, 1659, 1584, 1470, 1431; HRMS (ESI): [M+H]⁺ calcd. For C₁₇H₁₇O₃: 269.1172; Found: 269.1172.

(Z)-3-(2,6-dimethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3b-Z)



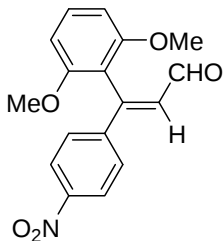
Prepared under THF-condition, reaction time: 24 hours, 39.0 mg, Yield: 65 %; white solid; m.p. 130-131 °C; ¹H NMR(400 MHz, CDCl₃) δ 9.35 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.34 (m, 3H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 3.68 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 194.11, 161.29, 157.93, 154.83, 130.66, 130.38, 128.47, 125.59, 113.96, 113.75, 103.84, 55.93, 55.31; IR (neat) ν (cm⁻¹): 3006, 2941, 2843, 1647, 1599, 1586, 1511, 1470, 1432; HRMS (ESI): [M+H]⁺ calcd. For C₁₈H₁₉O₄: 299.1278; Found: 299.1281.

(E)-3-(2,6-dimethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3b-E)



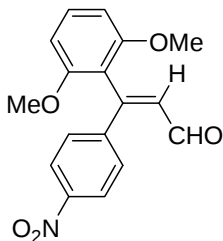
Prepared under DMF-condition, reaction time: 2 hours, 39.0 mg, Yield: 65%; white solid; m.p. 168-170 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.76 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 6.15 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 193.77, 160.20, 157.17, 156.37, 131.40, 131.08, 130.01, 128.47, 119.76, 113.23, 104.21, 55.94, 55.27; IR (neat) ν (cm⁻¹): 3010, 2937, 2832, 1659, 1602, 1585, 1511, 1470, 1430; HRMS (ESI): [M+H]⁺ calcd. For C₁₈H₁₉O₄: 299.1278; Found: 299.1282.

(Z)-3-(2,6-dimethoxyphenyl)-3-(4-nitrophenyl)acrylaldehyde(3c-Z)



Prepared under THF-condition, reaction time: 17 hours, 20.0 mg, Yield: 32%; light yellow solid; m.p. 152~154 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.42 (d, *J* = 7.8 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 7.42 (t, *J* = 8.4 Hz, 1H), 6.67 – 6.65 (m, 3H), 3.69 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 193.49, 157.87, 152.03, 148.25, 145.84, 131.35, 130.17, 127.59, 123.69, 112.35, 103.91, 55.87; IR (neat) ν (cm⁻¹): 3010, 2942, 2840, 1671, 1589, 1512, 1470, 1433, 1342; HRMS (ESI): [M+Na]⁺ calcd. For C₁₇H₁₅NNaO₅: 336.0842; Found: 336.0848.

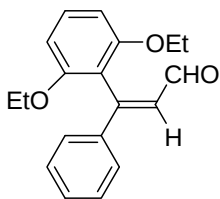
(E)-3-(2,6-dimethoxyphenyl)-3-(4-nitrophenyl)acrylaldehyde(3c-E)



Prepared under DMF-condition, reaction time: 0.3 hour, 34.0 mg, Yield: 54%; light yellow solid; m.p. 102~104 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.68 (d,

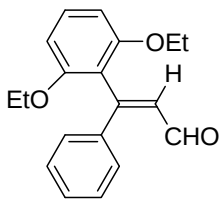
$J = 8.2$ Hz, 1H), 8.19 (d, $J = 8.9$ Hz, 2H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.31 (t, $J = 8.4$ Hz, 1H), 6.31 (d, $J = 8.2$ Hz, 1H), 3.70 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.35, 157.11, 153.75, 147.65, 145.23, 133.61, 130.96, 130.25, 123.02, 117.96, 104.11, 55.82; IR (neat) ν (cm^{-1}): 3011, 2946, 1672, 1590, 1516, 1470, 1430, 1351; HRMS (ESI): $[\text{M}+\text{Na}]^+$ calcd. For $\text{C}_{17}\text{H}_{15}\text{NNaO}_5$: 336.0842; Found: 336.0848.

(Z)-3-(2,6-diethoxyphenyl)-3-phenylacrylaldehyde(3d-Z)



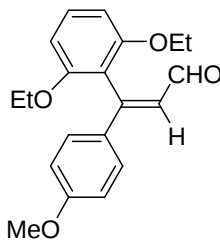
Prepared under THF-condition, reaction time: 16 hours, 42.0 mg, Yield: 71%; white solid; m.p. 72-74 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.43 (d, $J = 8.1$ Hz, 1H), 7.39 – 7.27 (m, 6H), 6.60 (d, $J = 8.1$ Hz, 1H), 6.59 (d, $J = 8.4$ Hz, 2H), 4.02 – 3.80 (m, 4H), 1.09 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 194.35, 157.45, 155.49, 140.03, 130.44, 129.43, 128.27, 127.83, 126.87, 114.53, 104.79, 64.14, 14.45; IR (neat) ν (cm^{-1}): 3031, 2928, 2884, 2858, 1667, 1587, 1576, 1480, 1452; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{21}\text{O}_3$: 297.1485; Found: 297.1484.

(E)-3-(2,6-diethoxyphenyl)-3-phenylacrylaldehyde(3d-E)



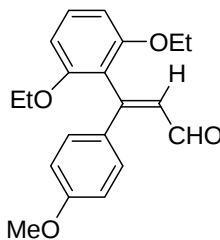
Prepared under DMF-condition, reaction time: 1 hour, 48.0 mg, Yield: 81%; white solid; m.p. 84-85 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.75 (d, $J = 8.1$ Hz, 1H), 7.37 – 7.28 (m, 5H), 7.22 (t, $J = 8.4$ Hz, 1H), 6.53 (d, $J = 8.4$ Hz, 2H), 6.25 (d, $J = 8.1$ Hz, 1H), 3.91 (q, $J = 7.0$ Hz, 4H), 1.17 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.95, 157.00, 156.67, 138.77, 132.24, 130.11, 129.71, 128.50, 127.61, 119.78, 104.89, 64.12, 14.52; IR (neat) ν (cm^{-1}): 3027, 2979, 2933, 2889, 2839, 1660, 1588, 1579, 1480, 1454; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{21}\text{O}_3$: 297.1485; Found: 297.1482.

(Z)-3-(2,6-diethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3e-Z)

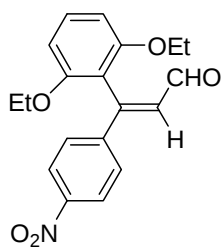


Prepared under THF-condition, reaction time: 12 hours, 46.0 mg, Yield: 71%; white solid; m.p. 117-118 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.38 (d, $J = 8.1$ Hz, 1H), 7.33-7.29 (m, 3H), 6.83 (d, $J = 8.9$ Hz, 2H), 6.59 (d, $J = 8.4$ Hz, 2H), 6.58 (d, $J = 8.1$ Hz, 1H), 4.01 – 3.84 (m, 4H), 3.81 (s, 3H), 1.11 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 194.33, 160.97, 157.39, 155.28, 131.91, 130.24, 128.44, 125.94, 114.66, 113.72, 104.80, 64.13, 55.30, 14.53; IR (neat) ν (cm^{-1}): 3035, 2980, 2934, 2885, 2841, 1658, 1601, 1512, 1457, 1383, 1252; HRMS (APCI): $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{20}\text{H}_{23}\text{O}_4$: 327.1591; Found: 327.1594.

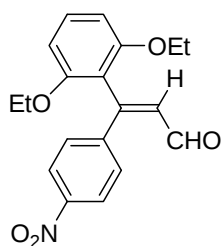
(E)-3-(2,6-diethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3e-E)



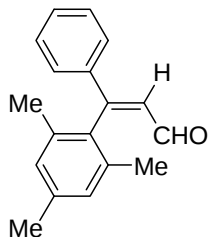
Prepared under DMF-condition, reaction time: 0.5 hour, 40.0 mg, Yield: 61%; white solid; m.p. 74-75 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.76 (d, $J = 8.1$ Hz, 1H), 7.28 – 7.18 (m, 3H), 6.84 (d, $J = 8.7$ Hz, 2H), 6.53 (d, $J = 8.4$ Hz, 2H), 6.18 (d, $J = 8.1$ Hz, 1H), 3.91 (q, $J = 7.0$ Hz, 4H), 3.82 (s, 3H), 1.17 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.92, 160.12, 156.73, 156.66, 131.47, 131.24, 131.16, 129.97, 120.09, 113.09, 104.98, 64.14, 55.30, 14.58; IR (neat) ν (cm^{-1}): 3032, 2981, 2930, 2878, 2838, 1654, 1602, 1508, 1453, 1385, 1249; HRMS (APCI): $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{20}\text{H}_{23}\text{O}_4$: 327.1591; Found: 327.1595.

(Z)-3-(2,6-diethoxyphenyl)-3-(4-nitrophenyl)acrylaldehyde(3f-Z)

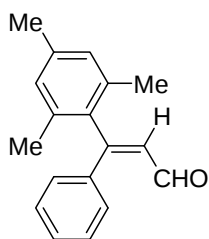
Prepared under THF-condition, reaction time: 12 hours, 24.0 mg, Yield: 35%; light yellow solid; m.p. 92-94 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.44 (d, *J* = 7.9 Hz, 1H), 8.15 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.9 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H); 6.57 (d, *J* = 7.9 Hz, 1H), 4.01 – 3.81 (m, 4H), 1.09 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 193.65, 157.31, 152.36, 148.04, 147.07, 131.26, 130.19, 127.63, 123.54, 112.90, 104.61, 64.09, 14.45; IR (neat) ν (cm⁻¹): 3038, 2978, 2939, 2881, 2860, 1678, 1589, 1516, 1455, 1391, 1346; HRMS (APCI): [M]⁺ calcd. For C₁₉H₁₉NO₅: 341.1263; Found: 341.1269.

(E)-3-(2,6-diethoxyphenyl)-3-(4-nitrophenyl)acrylaldehyde(3f-E)

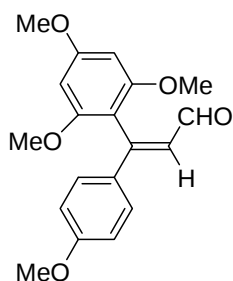
Prepared under DMF-condition, reaction time: 0.3 hour, 36.0 mg, Yield: 53%; white solid; m.p. 94-95 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.68 (d, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.25 (t, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 8.2 Hz, 1H), 3.92 (d, *J* = 7.0 Hz, 4H), 1.19 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 192.46, 156.56, 154.01, 147.61, 145.61, 133.60, 130.92, 130.41, 122.91, 118.07, 104.67, 64.07, 14.54; IR (neat) ν (cm⁻¹): 3043, 2979, 2929, 2881, 2830, 1673, 1591, 1516, 1453, 1391, 1345; HRMS (APCI): [M]⁺ calcd. For C₁₉H₁₉NO₅: 341.1263; Found: 341.1270.

(Z)-3-(2,4,6-trimethylphenyl)-3-phenylacrylaldehyde(3g-Z)

Prepared under THF-condition (0.2 equiv PdCl₂, 0.4 equiv tri(*p*-tolyl)phosphine, 150 °C); reaction time: 24 hours, 15.6 mg, Yield: 31%; white solid; m.p. 72~74 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.33 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.35 (m, 5H), 6.96 (s, 2H), 6.78 (d, *J* = 8.1 Hz, 1H), 2.35 (s, 3H), 2.06 (s, 6H); ¹³C NMR (75 MHz, cdcl₃) δ 193.92, 161.10, 138.03, 137.24, 136.01, 132.53, 130.69, 128.95, 128.43, 127.04, 126.34, 21.09, 20.02; IR (neat) ν (cm⁻¹): 3004, 2916, 2826, 1664, 1589, 1447, 1385, 1332; HRMS (ESI): [M+H]⁺ calcd. For C₁₈H₁₉O: 251.1430; Found: 251.1429.

(E)-3-(2,4,6-trimethylphenyl)-3-phenylacrylaldehyde(3g-E)

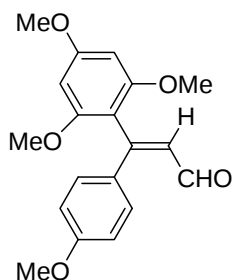
Prepared under DMF-condition (0.2 equiv PdCl₂, 150 °C), reaction time: 4 hours, 22.0 mg, Yield: 40%; white solid; m.p. 112~114 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.90 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.26 (m, 5H), 6.91 (s, 2H), 6.15 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 3H), 2.13 (s, 6H); ¹³C NMR (75 MHz, cdcl₃) δ 193.45, 161.86, 137.93, 137.87, 136.80, 134.92, 131.06, 130.24, 129.76, 128.65, 128.35, 21.02, 20.36; IR (neat) ν (cm⁻¹): 3007, 2917, 2832, 1666, 1595, 1442, 1383, 1332; HRMS (ESI): [M+Na]⁺ calcd. For C₁₈H₁₈NaO: 273.1250; Found: 273.1252.

(Z)-3-(2,4,6-trimethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3h-Z)

Prepared under THF-condition, reaction time: 24 hours, 16.4 mg, Yield: 25%; white solid; m.p. 115-116 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.38 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz,

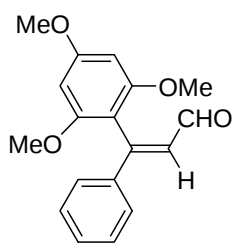
1H), 6.21 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H), 3.66 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 194.11, 161.78, 160.96, 158.52, 154.44, 131.07, 128.23, 125.83, 113.65, 106.22, 90.34, 55.64, 55.19, 55.07; IR (neat) ν (cm⁻¹): 3003, 2938, 2838, 1659, 1583, 1509, 1455, 1413, 1334; HRMS (ESI): [M+Na]⁺ calcd. For C₁₉H₂₀NaO₅: 351.1203; Found: 351.1209.

(E)-3-(2,4,6-trimethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3h-E)



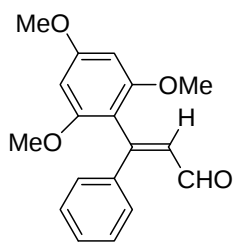
Prepared under DMF-condition, reaction time: 0.5 hour, 41.0 mg, Yield: 63%; white solid; m.p. 120-121 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.71 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.16 (d, *J* = 8.1 Hz, 1H), 6.13 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.63 (s, 6H); ¹³C NMR (75 MHz, cdcl₃) δ 193.96, 161.81, 160.13, 158.34, 156.10, 131.58, 131.03, 128.46, 113.88, 113.14, 90.94, 55.89, 55.36, 55.27; IR (neat) ν (cm⁻¹): 3003, 2935, 2835, 1654, 1582, 1508, 1548, 1412, 1333; HRMS (ESI): [M+Na]⁺ calcd. For C₁₉H₂₀NaO₅: 351.1203; Found: 351.1211.

(Z)-3-(2,4,6-trimethoxyphenyl)-3-phenylacrylaldehyde(3i-Z)



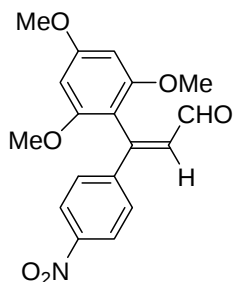
Prepared under THF-condition, reaction time: 24 hours, 14.4 mg, Yield: 24%; white solid; m.p. 108-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.43 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.28 (m, 5H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.21 (s, 2H), 3.88 (s, 3H), 3.66 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 194.35, 162.15, 158.82, 154.94, 139.35, 129.75, 128.41, 127.97, 126.82, 106.41, 90.62, 55.84, 55.42; IR (neat) ν (cm⁻¹): 3008, 2941, 2841, 1656, 1583, 1467, 1332; HRMS (ESI): [M+Na]⁺ calcd. For C₁₈H₁₈NaO₄: 321.1097; Found: 321.1102.

(E)-3-(2,4,6-trimethoxyphenyl)-3-phenylacrylaldehyde(3i-E)



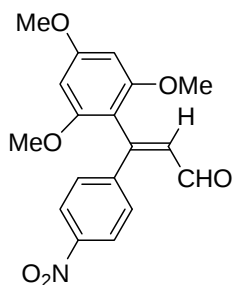
Prepared under DMF-condition, reaction time: 1 hour, 44.0 mg, Yield: 74%; white solid; m.p. 113-114 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.70 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.27 (m, 5H), 6.23 (d, *J* = 8.2 Hz, 1H), 6.14 (s, 2H), 3.83 (s, 3H), 3.63 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 194.02, 161.91, 158.33, 156.50, 139.06, 132.34, 129.52, 128.52, 127.64, 112.55, 90.94, 55.82, 55.36; IR (neat) ν (cm⁻¹): 3006, 2939, 2839, 1666, 1578, 1456, 1329; HRMS (ESI): [M+Na]⁺ calcd. For C₁₈H₁₈NaO₄: 321.1097; Found: 321.1102.

(Z)-3-(2,4,6-trimethoxyphenyl)-3-(4-nitrophenyl)acrylaldehyde(3j-Z)



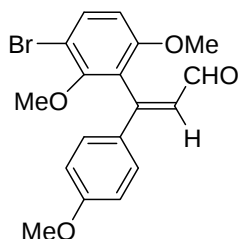
Prepared under THF-condition, reaction time: 17 hours, 14.0 mg, Yield: 20%; light yellow solid; m.p. 120-122 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.45 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.9 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.21 (s, 2H), 3.89 (s, 3H), 3.66 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 193.66, 162.78, 158.81, 151.87, 148.18, 146.63, 130.41, 127.59, 123.62, 105.08, 90.64, 55.79, 55.49; IR (neat) ν (cm⁻¹): 3070, 2939, 2841, 1661, 1585, 1513, 1454, 1413, 1347, 1330, 1229, 1204 ; HRMS (ESI): [M+H]⁺ calcd. For C₁₈H₁₈NO₆: 344.1129; Found: 344.1122.

(E)-3-(2,4,6-trimethoxyphenyl)-3-(4-nitrophenyl)acrylaldehyde(3j-E)



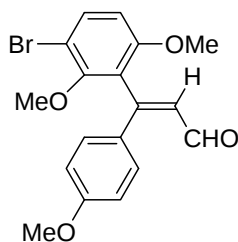
Prepared under DMF-condition, reaction time: 1 hour, 26.0 mg, Yield: 38%; light yellow solid; m.p. 124-126 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.64 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 6.33 (d, J = 8.2 Hz, 1H), 6.13 (s, 2H), 3.84 (s, 3H), 3.64 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.58, 162.56, 158.36, 153.48, 147.58, 146.06, 133.61, 130.21, 122.92, 110.92, 55.72, 55.43; IR (neat) ν (cm^{-1}): 3071, 2940, 2837, 1661, 1585, 1514, 1455, 1413, 1348, 1330, 1230, 1203; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{18}\text{H}_{18}\text{NO}_6$: 344.1129; Found: 344.1121.

(Z)-3-(3-bromo-2,6-dimethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3k-Z)



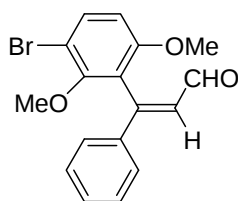
Prepared under THF-condition, reaction time: 17 hours, 14.0 mg, Yield: 19%; colorless gel; ^1H NMR (500 MHz, CDCl_3) δ 9.39 (d, J = 7.4 Hz, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.34 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.69 (dd, J = 12.9, 4.8 Hz, 2H), 3.82 (s, 3H), 3.71 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 193.18, 161.56, 157.26, 155.26, 153.43, 133.94, 130.31, 128.55, 125.83, 121.30, 114.19, 108.52, 108.12, 61.05, 56.21, 55.36; IR (neat) ν (cm^{-1}): 3003, 2937, 2837, 1662, 1593, 1569, 1510, 1461, 1401, 1329; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{18}\text{H}_{18}\text{BrO}_4$: 377.0383; Found: 377.0377.

(E)-3-(3-bromo-2,6-dimethoxyphenyl)-3-(4-methoxyphenyl)acrylaldehyde(3k-E)



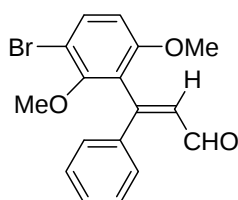
Prepared under DMF-condition, reaction time: 1 hour, 15.8 mg, Yield: 21%; colorless gel; ^1H NMR (400 MHz, CDCl_3) δ 9.79 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 8.9 Hz, 1H), 7.26 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.9 Hz, 1H), 6.17 (d, J = 7.9 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.19, 160.67, 156.57, 155.18, 154.68, 133.56, 131.27, 131.19, 129.76, 126.71, 113.59, 108.55, 108.42, 61.30, 56.18, 55.32; IR (neat) ν (cm^{-1}): 3003, 2938, 2837, 1662, 1601, 1568, 1509, 1462, 1401, 1332; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{18}\text{H}_{18}\text{BrO}_4$: 377.0383; Found: 377.0377.

(Z)-3-(3-bromo-2,6-dimethoxyphenyl)-3-phenylacrylaldehyde(3l-Z)



Prepared under THF-condition, reaction time: 22 hours, 12.0 mg, Yield: 17%; colorless gel; ^1H NMR (400 MHz, CDCl_3) δ 9.43 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.41 – 7.32 (m, 5H), 6.71 (dd, J = 8.5, 3.7 Hz, 2H), 3.71 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.20, 157.29, 155.34, 153.69, 138.35, 134.11, 130.31, 128.73, 127.83, 126.87, 121.17, 108.50, 108.16, 60.94, 56.19; IR (neat) ν (cm^{-1}): 3004, 2937, 2837, 1669, 1603, 1575, 1463, 1403, 1328; HRMS (ESI): $[\text{M}+\text{Na}]^+$ calcd. For $\text{C}_{17}\text{H}_{15}\text{BrNaO}_3$: 369.0097; Found: 369.0093.

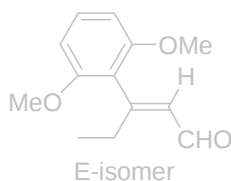
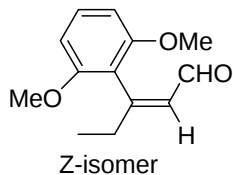
(E)-3-(3-bromo-2,6-dimethoxyphenyl)-3-phenylacrylaldehyde(3l-E)



Prepared under DMF-condition, reaction time: 1 hour, 20.0 mg, Yield: 29%; colorless gel; ^1H NMR (400 MHz, CDCl_3) δ 9.77 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.9 Hz, 1H), 7.40 – 7.30 (m, 5H), 6.65 (d, J = 8.9 Hz, 1H), 6.24 (d, J = 8.0 Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.20, 156.55,

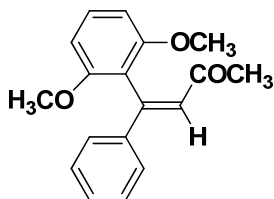
155.54, 154.72, 137.38, 133.71, 132.19, 129.60, 129.30, 128.11, 126.54, 108.57, 108.38, 61.25, 56.16; IR (neat) ν (cm⁻¹): 3002, 2938, 2837, 1665, 1600, 1566, 1462, 1401, 1333; HRMS (ESI): [M+Na]⁺ calcd. For C₁₇H₁₅BrNaO₃: 369.0097; Found: 369.0096.

3-(2,6-dimethoxyphenyl)pent-2-enal(3m)



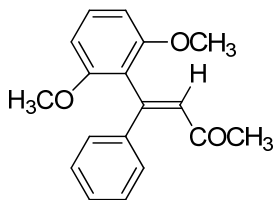
Prepared under THF-condition, reaction time: 3 hours, 5.0 mg, Yield of (Z+E): 11%, Z/E 10:3; Prepared under DMF-condition, reaction time: 0.5 hour, 11.0 mg, Yield of (Z+E): 25%, Z/E 1:4; colorless gel; ¹H NMR (300 MHz, CDCl₃; 400 MHz, CDCl₃) δ 9.26; 10.18 (d, *J* = 8.2 Hz, 1H; d, *J* = 8.3 Hz, 1H), 7.28, 7.24 (t, *J* = 8.4 Hz, 1H; t, *J* = 8.4 Hz, 1H), 6.59; 6.57 (d, *J* = 8.4 Hz, 2H; d, *J* = 8.4 Hz, 2H), 6.13, 5.88 (d, *J* = 8.2 Hz, 1H; d, *J* = 8.3 Hz, 1H), 3.76; 3.76 (s, 6H; s, 6H), 2.49; 2.90 (q, *J* = 7.4 Hz, 2H; q, *J* = 7.6 Hz, 2H), 1.07; 1.03 (t, *J* = 7.4 Hz, 3H; t, *J* = 7.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃; 125 MHz, CDCl₃) δ 194.37, 162.84, 157.07, 129.67, 128.08, 115.29, 103.62, 55.73, 31.12, 11.48; 191.14, 161.68, 156.84, 131.08, 129.35, 118.98, 103.84, 55.75, 25.14, 13.51; IR (neat) ν (cm⁻¹): 3008, 2968, 2837, 1674, 1625, 1592, 1471, 1433, 1248, 1110; 3007, 2970, 2839, 1666, 1626, 1588, 1471, 1432, 1247, 1107; HRMS (APCI): [M+H]⁺ calcd. For (Z+E) C₁₃H₁₇O₃: 221.1172; Found: 221.1176.

(Z)-4-(2,6-dimethoxyphenyl)-4-phenylbut-3-en-2-one(3n-Z)



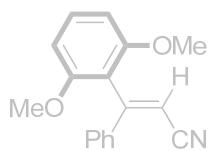
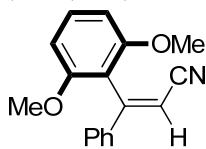
Prepared under THF-condition, reaction time: 12 hours, 46.0 mg, Yield 82 %, Z/E 87:9; Prepared under DMF-condition, reaction time: 0.5 hour, 40.0 mg, Yield 71%, Z/E 78:18; white solid; m.p. 182-183 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.27 (m, 6H), 6.75 (s, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 3.69 (s, 6H), 1.91 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 199.16, 157.27, 146.74, 140.06, 129.99, 129.10, 128.91, 128.29, 126.92, 116.51, 104.14, 55.91, 29.25; IR (neat) ν (cm⁻¹): 1644, 1587, 1470, 1432, 1250, 1107; HRMS (APCI): [M+H]⁺ calcd. For C₁₈H₁₉O₃: 283.1329; Found: 283.1333.

(E)-4-(2,6-dimethoxyphenyl)-4-phenylbut-3-en-2-one(3n-E)



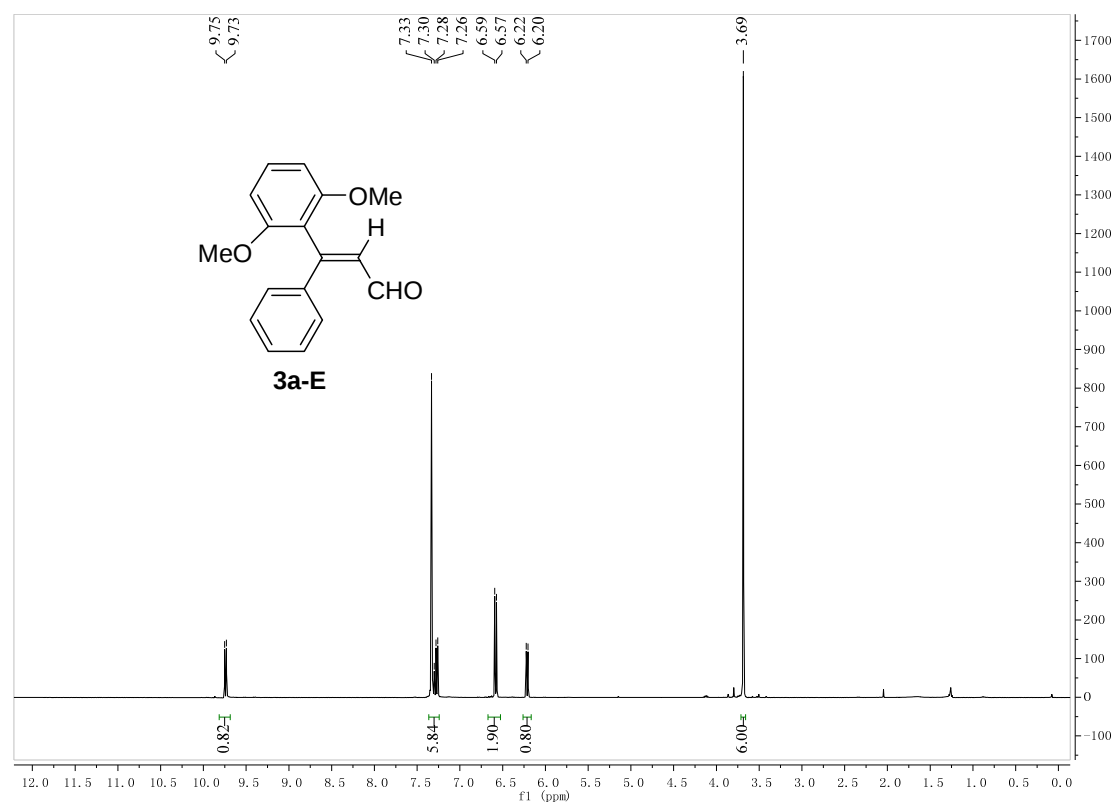
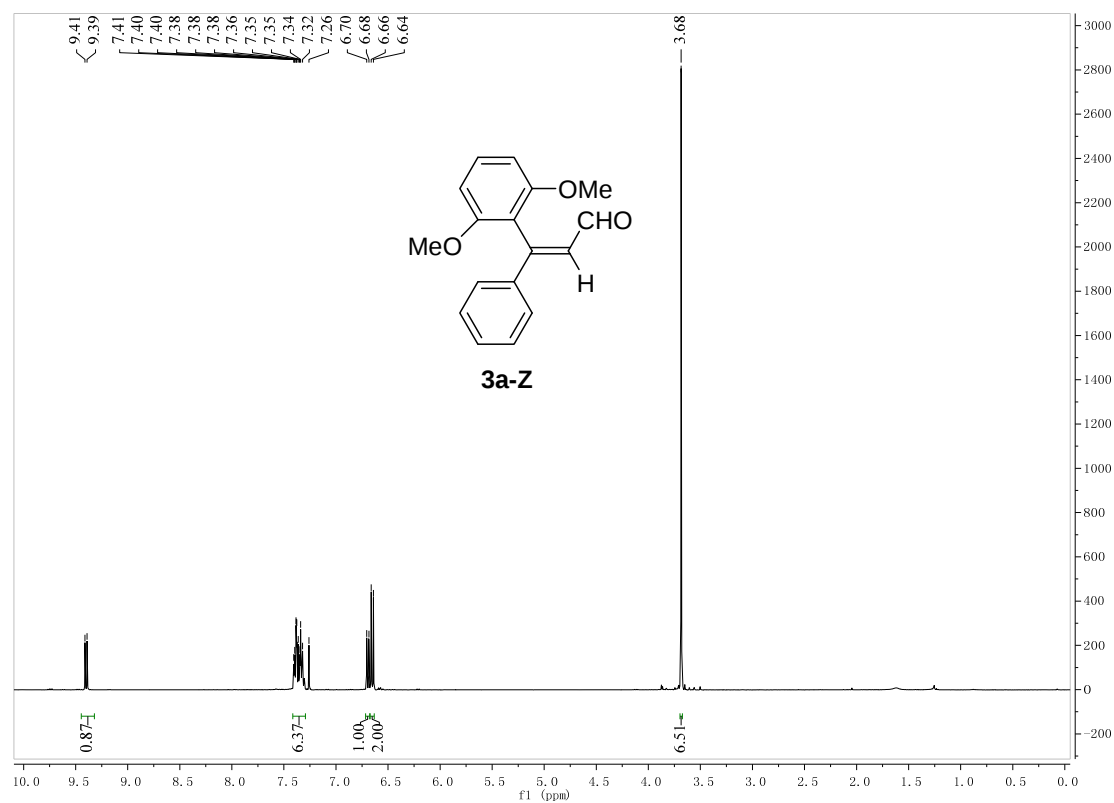
Prepared under THF-condition, reaction time: 12 hours, 6.0 mg, Yield 11 %, E/Z 9:87; Prepared under DMF-condition, reaction time: 0.5 hour, 10.0 mg, Yield 18%, E/Z 18:78; white solid; m.p. 167-168 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.26 (m, 5H), 7.22 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.14 (s, 1H), 3.72 (s, 6H), 1.94 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 201.05, 157.16, 147.74, 140.18, 132.15, 129.30, 128.49, 127.90, 127.70, 120.56, 104.14, 55.88, 30.49; IR (neat) ν (cm⁻¹): 1663, 1585, 1471, 1432, 1250, 1106; HRMS (APCI): [M+H]⁺ calcd. For C₁₈H₁₉O₃: 283.1329; Found: 283.1329.

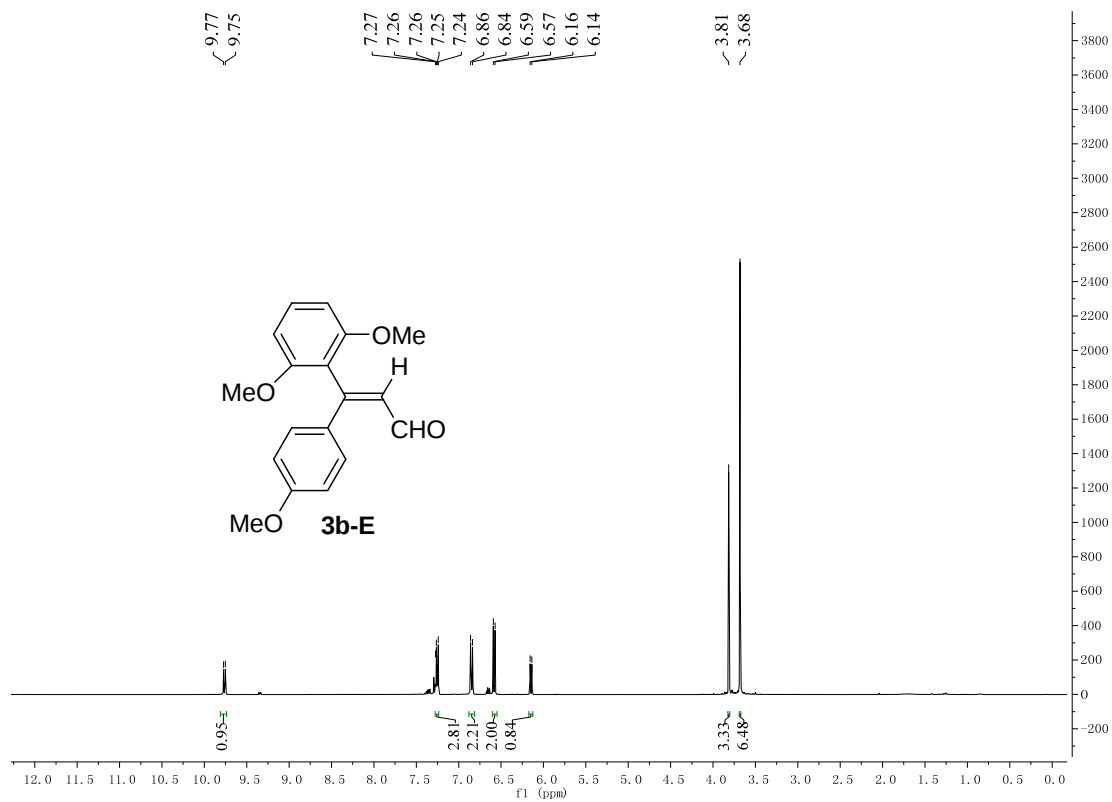
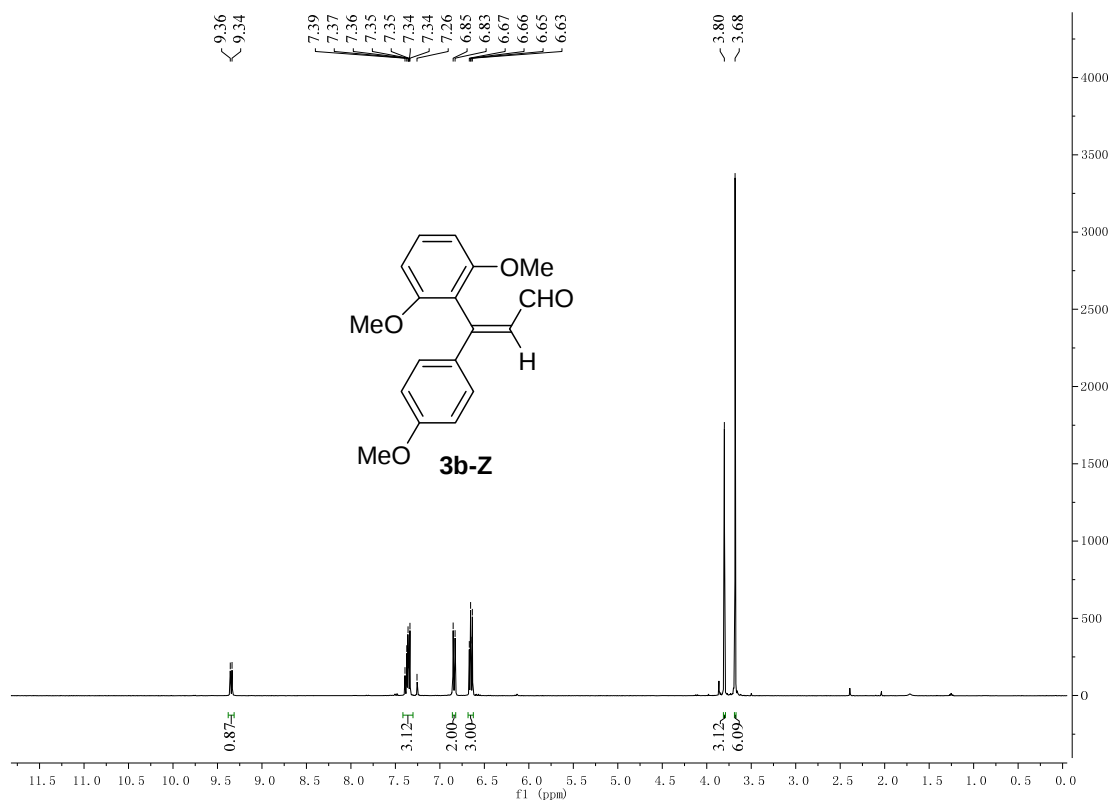
(Z+E)-3-(2,6-dimethoxyphenyl)-3-phenylacrylonitrile(3o)

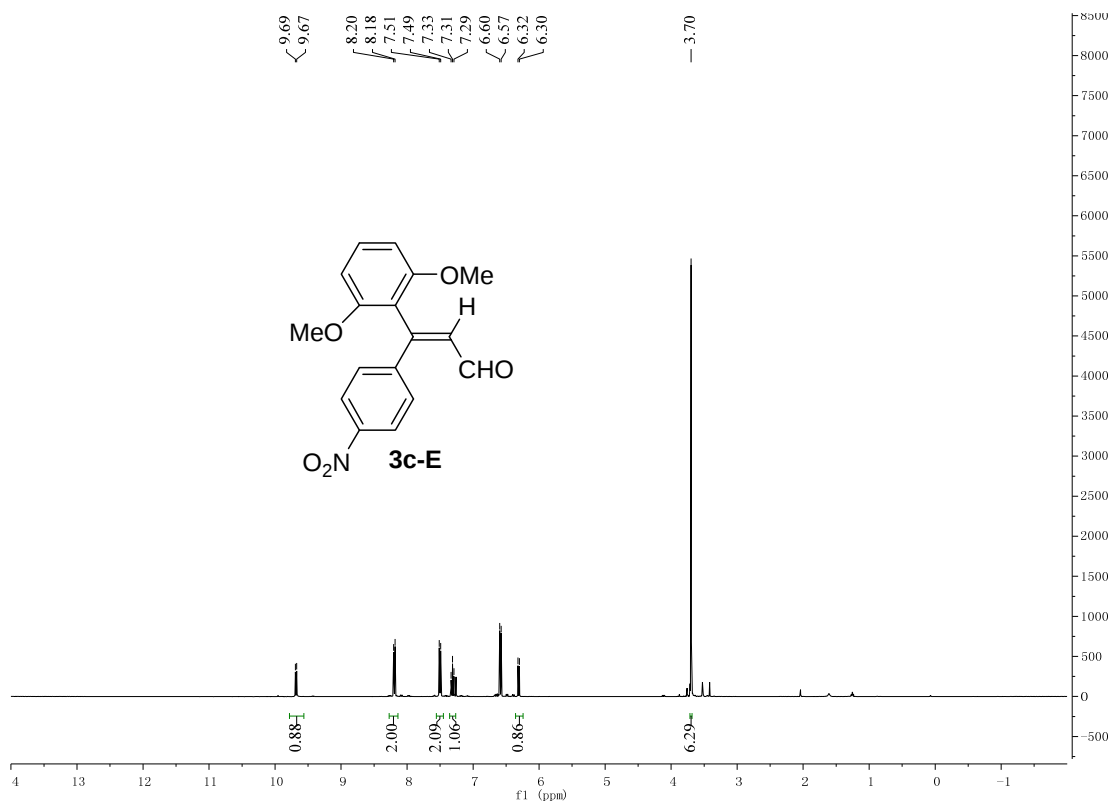
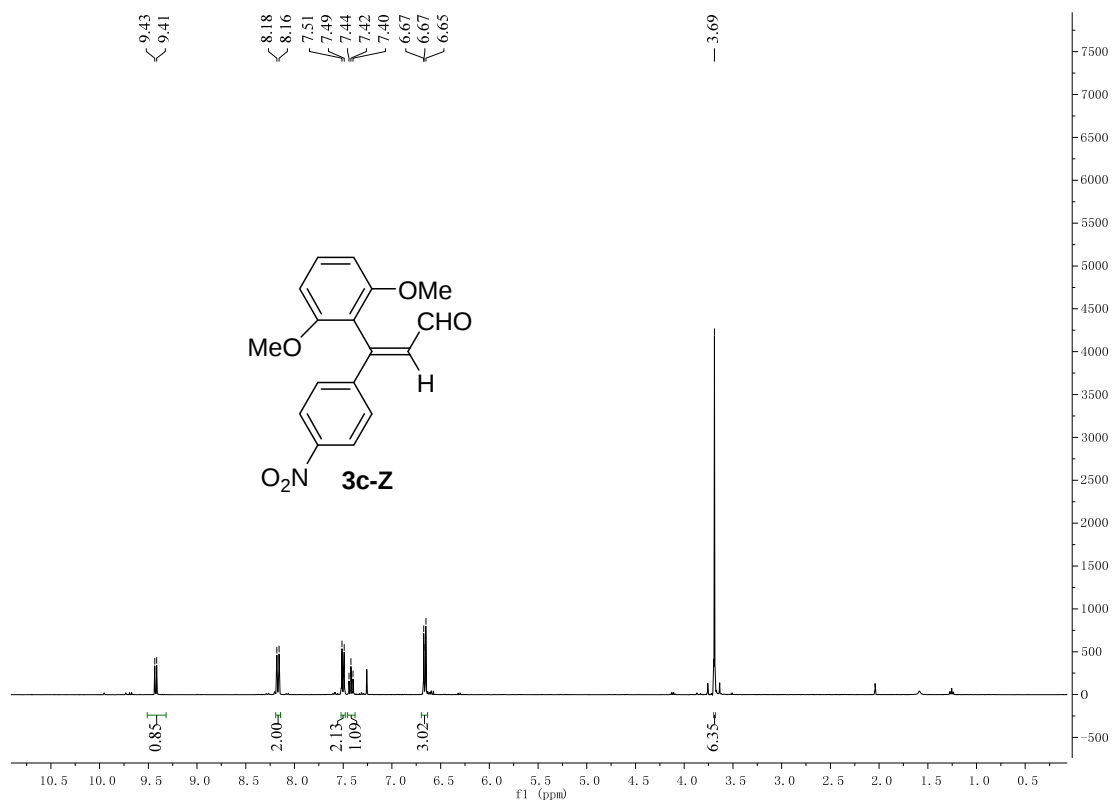


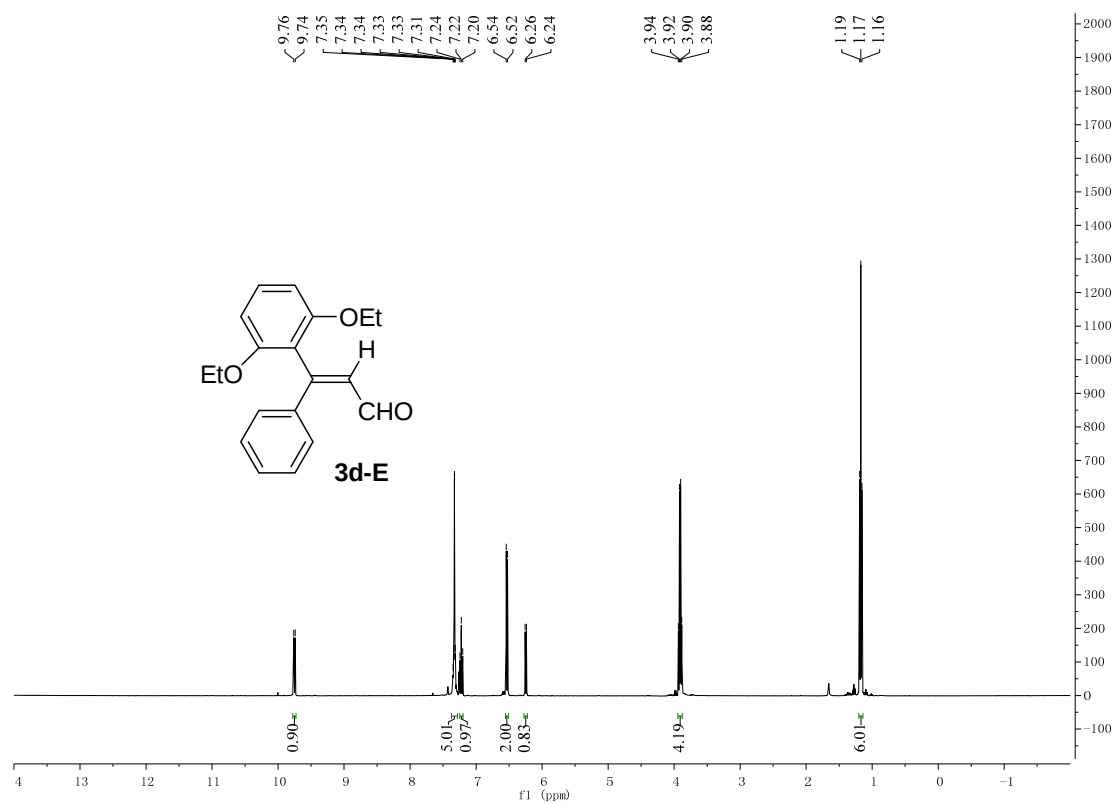
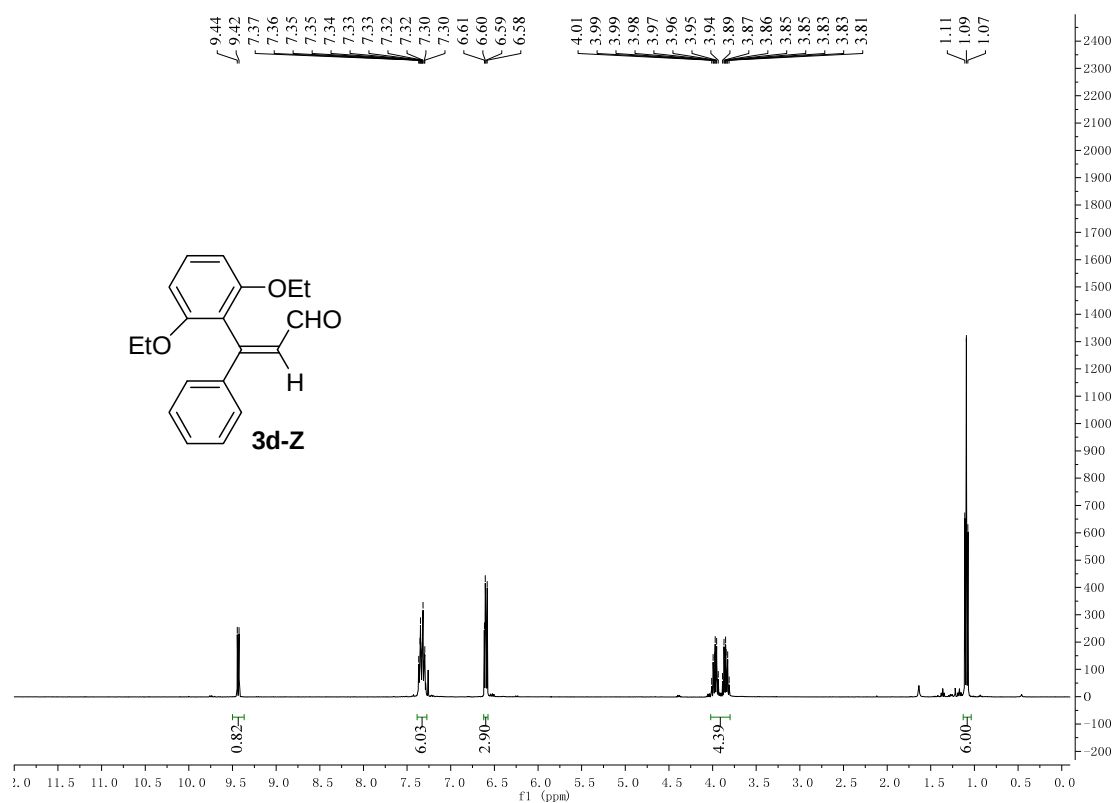
Prepared under THF-condition, reaction time: 10 hours, 32.0 mg, Yield of (Z+E): 60 %, Z/E 43:32;
Prepared under DMF-condition, reaction time: 1 hour, 36.6 mg, Yield of (Z+E): 69%, Z/E 1:8; White solid;
¹H NMR (300 MHz, CDCl₃) δ 7.52- 7.49; 7.53 – 7.48 (m, 2H; m, 2H), 7.38- 7.26; 7.36 – 7.28 (m, 4H; m, 4H), 6.66; 6.59 (d, *J* = 8.4 Hz, 2H; d, *J* = 8.5 Hz, 2H), 6.01; 5.49 (s, 1H; s, 1H), 3.73; 3.68 (s, 6H; s, 6H);
¹³C NMR (125 MHz, 75 MHz, CDCl₃) δ 157.51, 156.44, 137.57, 130.38, 129.84, 128.50, 126.42, 117.84, 117.66, 104.22, 97.84, 55.96; 157.53, 156.34, 138.01, 130.39, 129.27, 128.09, 127.85, 126.44, 117.91, 104.08, 98.76, 55.90;

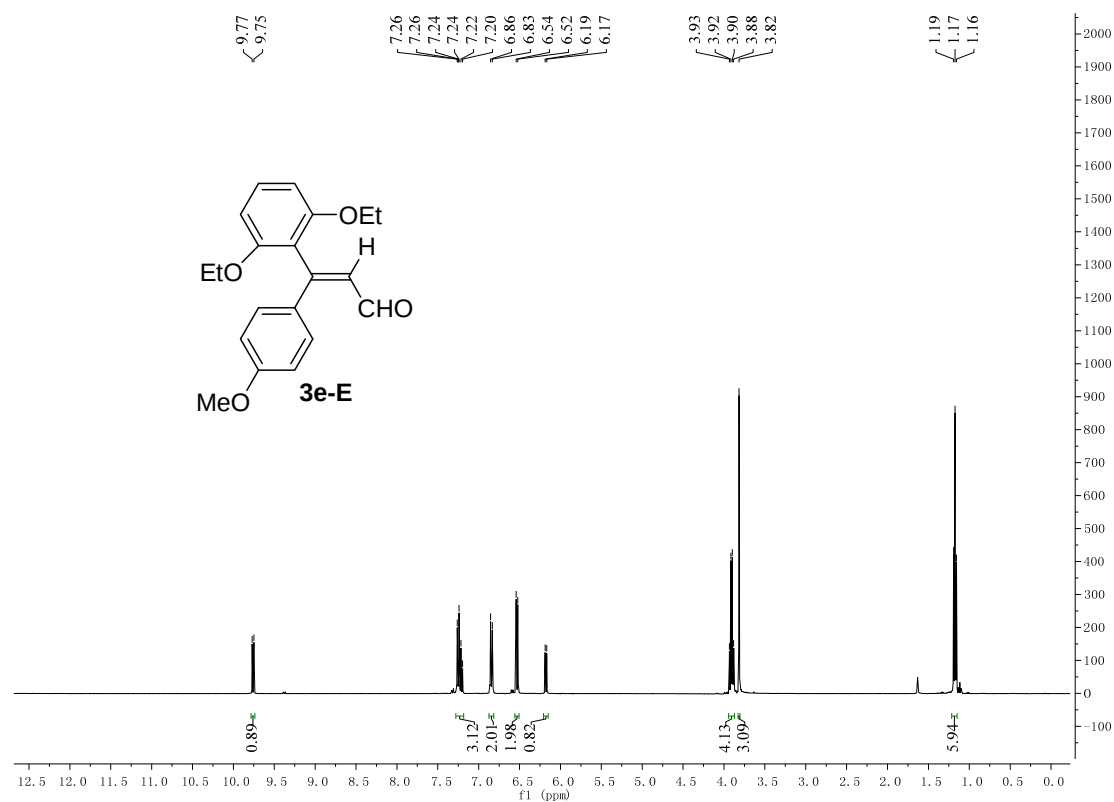
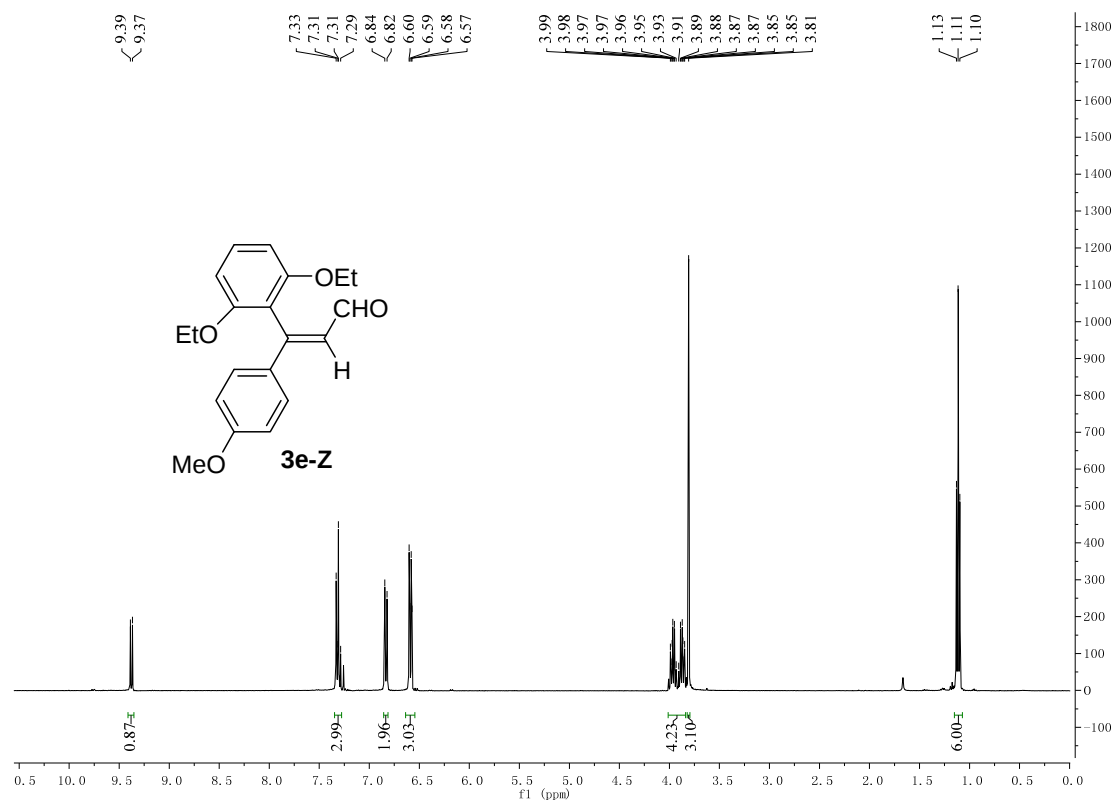
5. Copies of product ^1H NMR and ^{13}C NMR

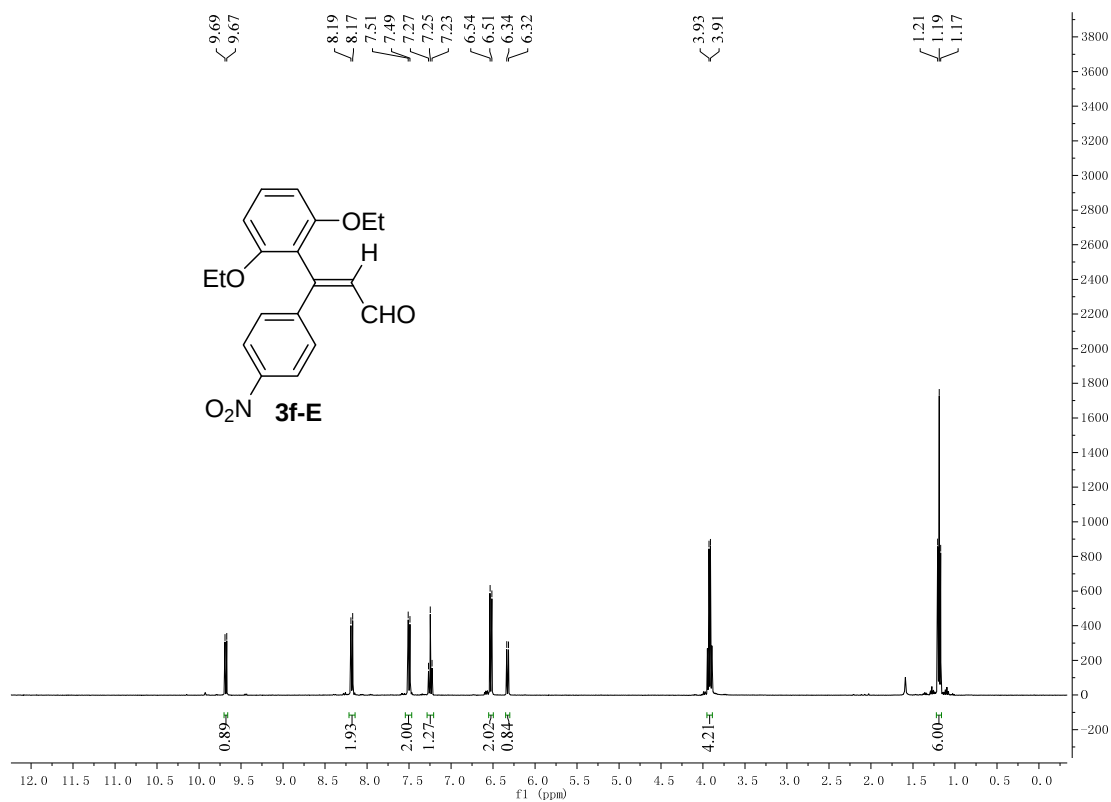
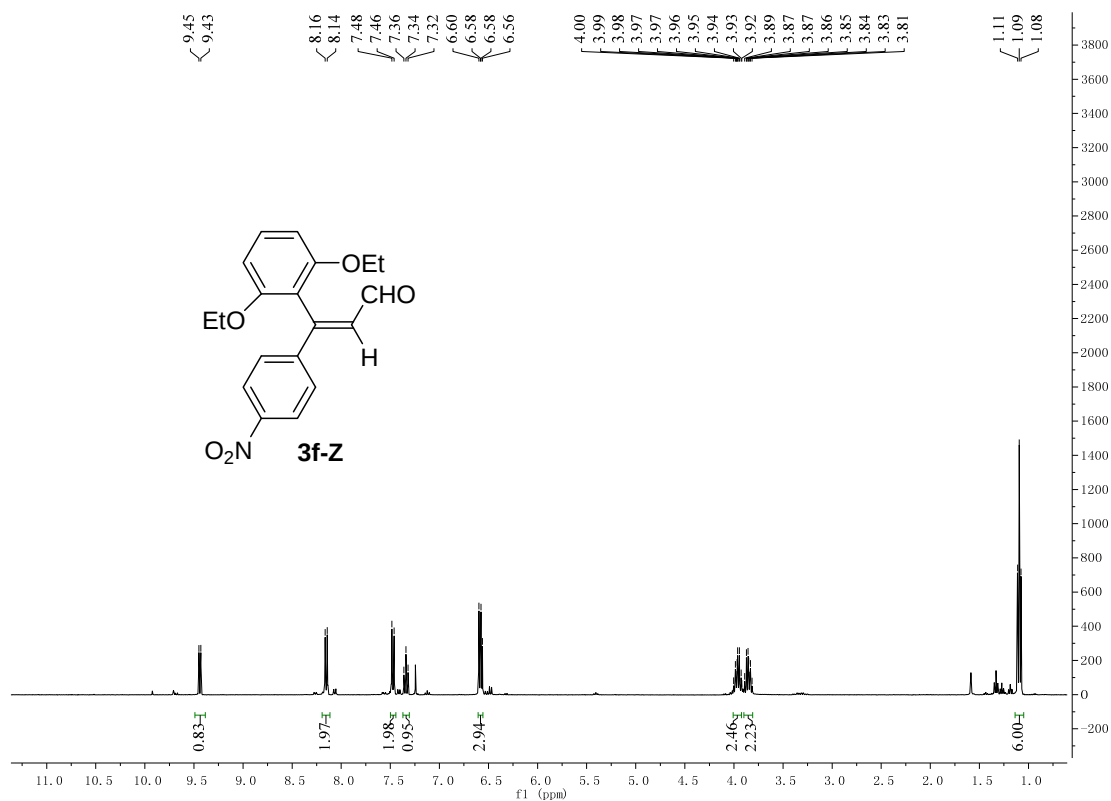


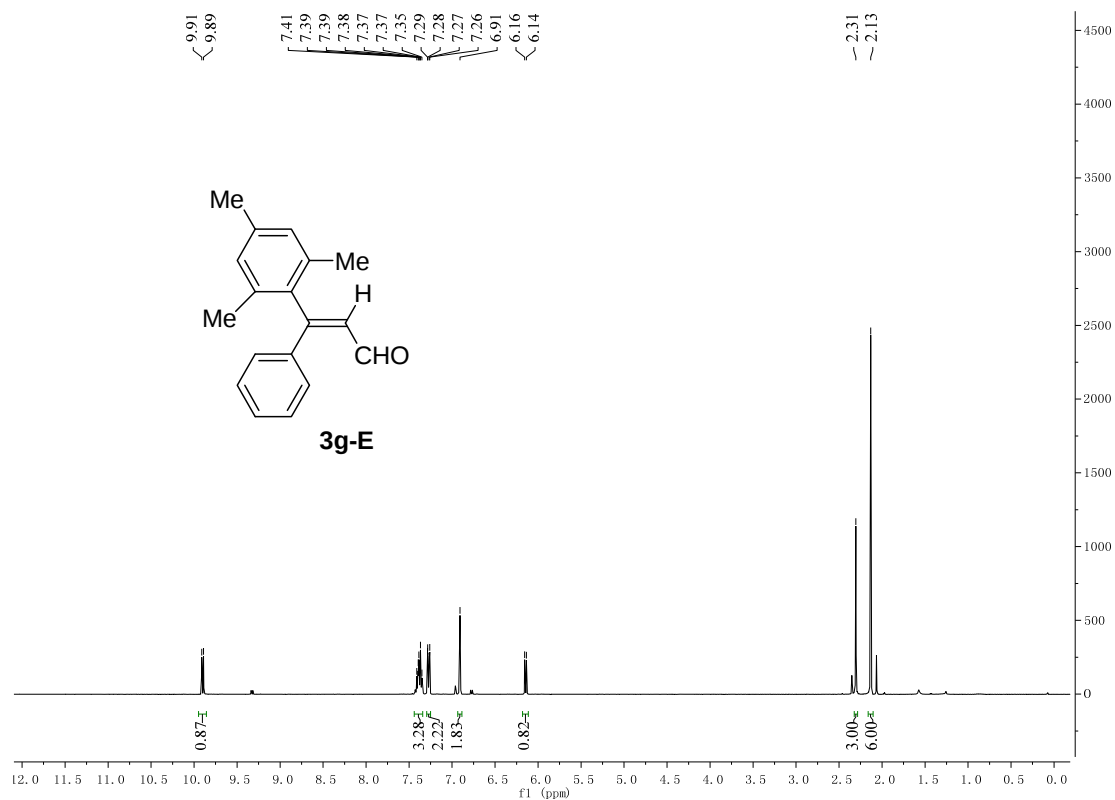
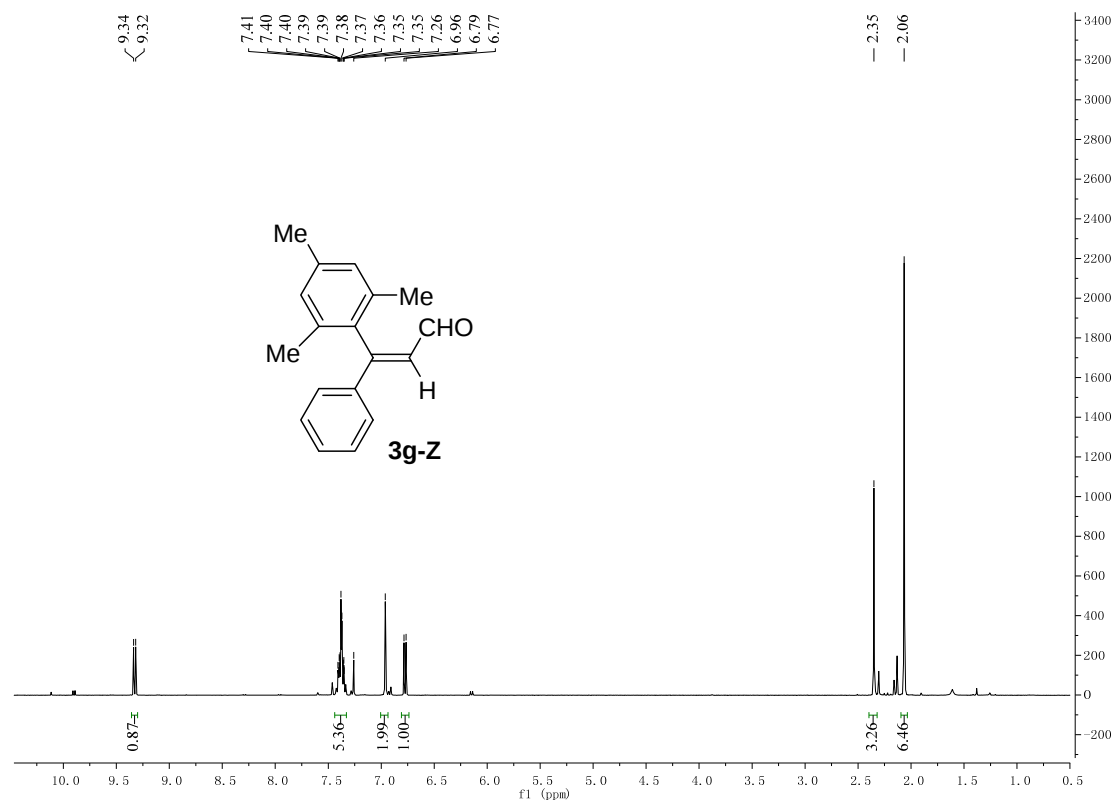


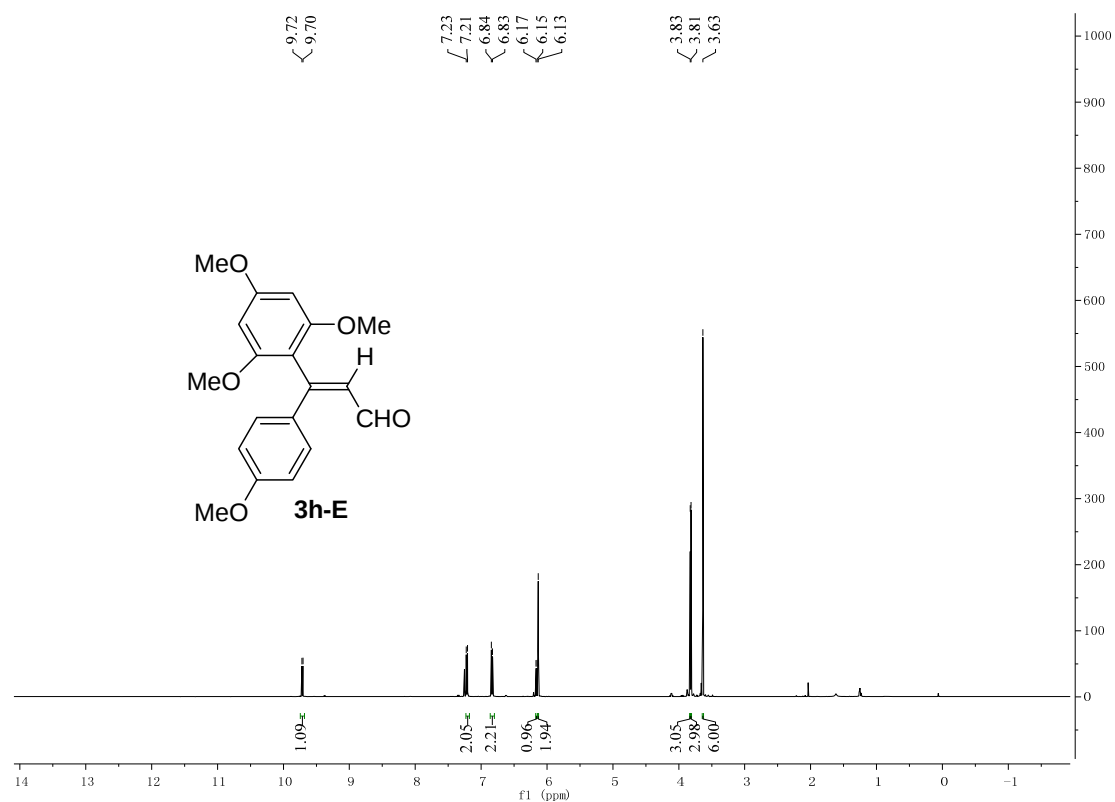
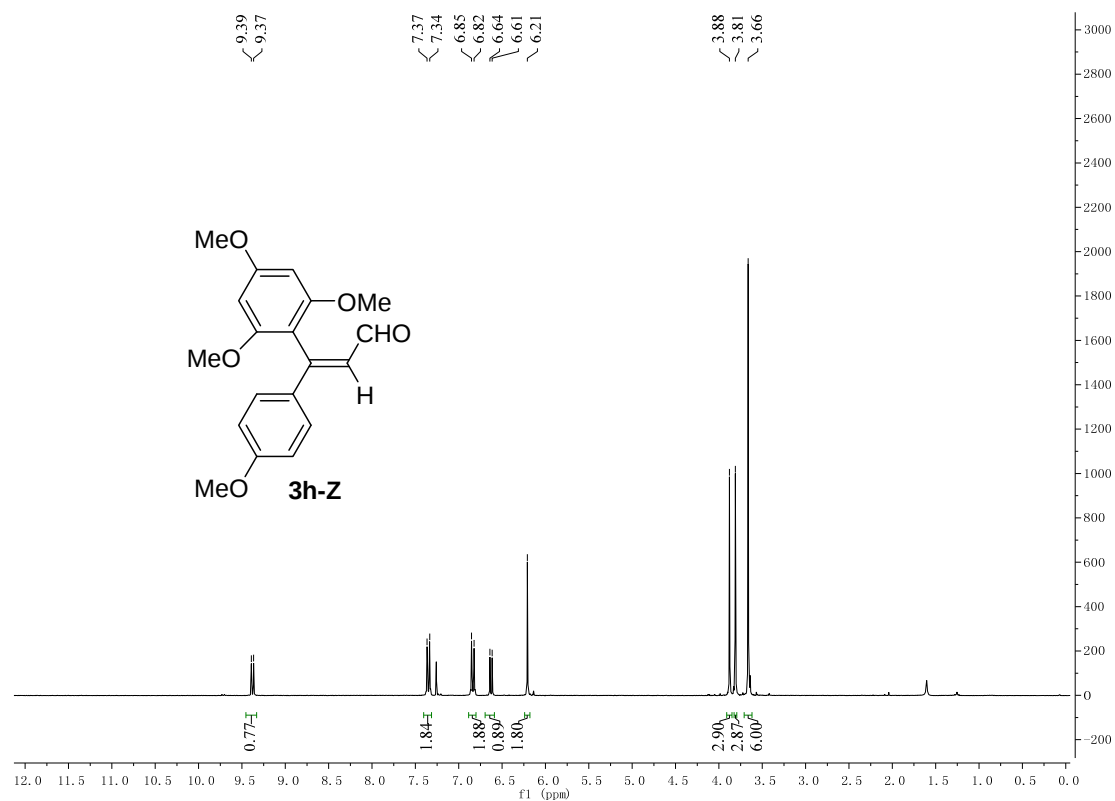


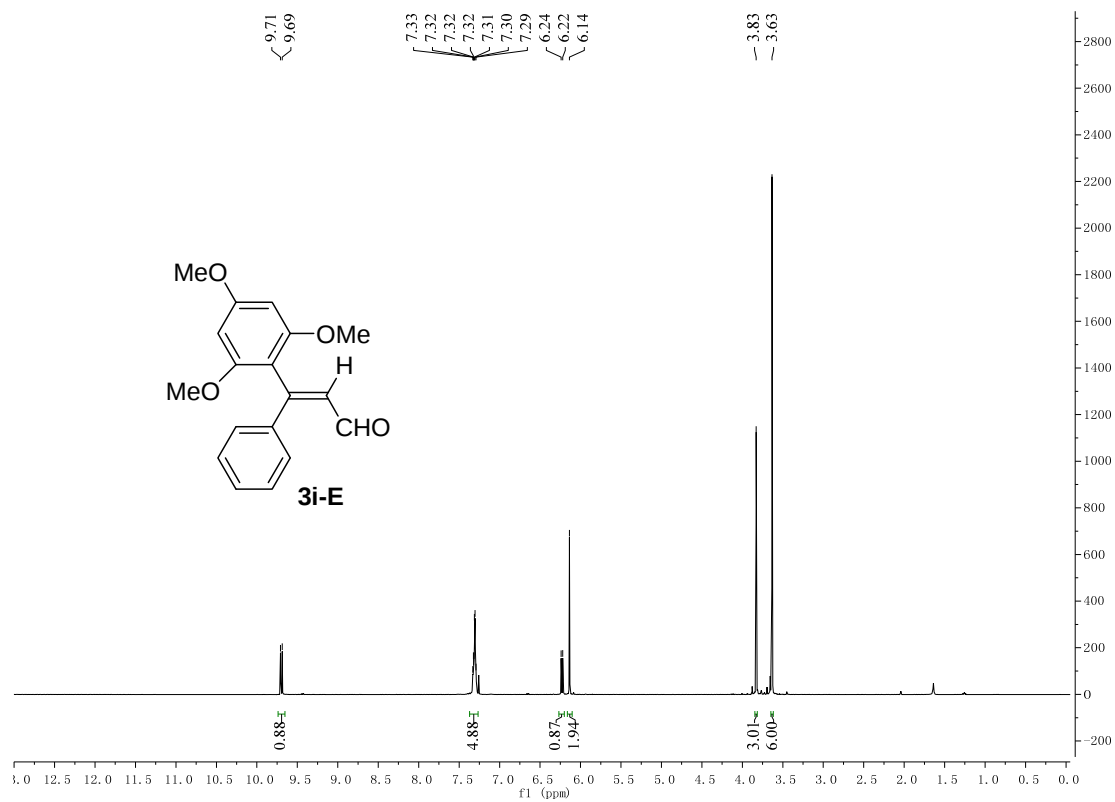
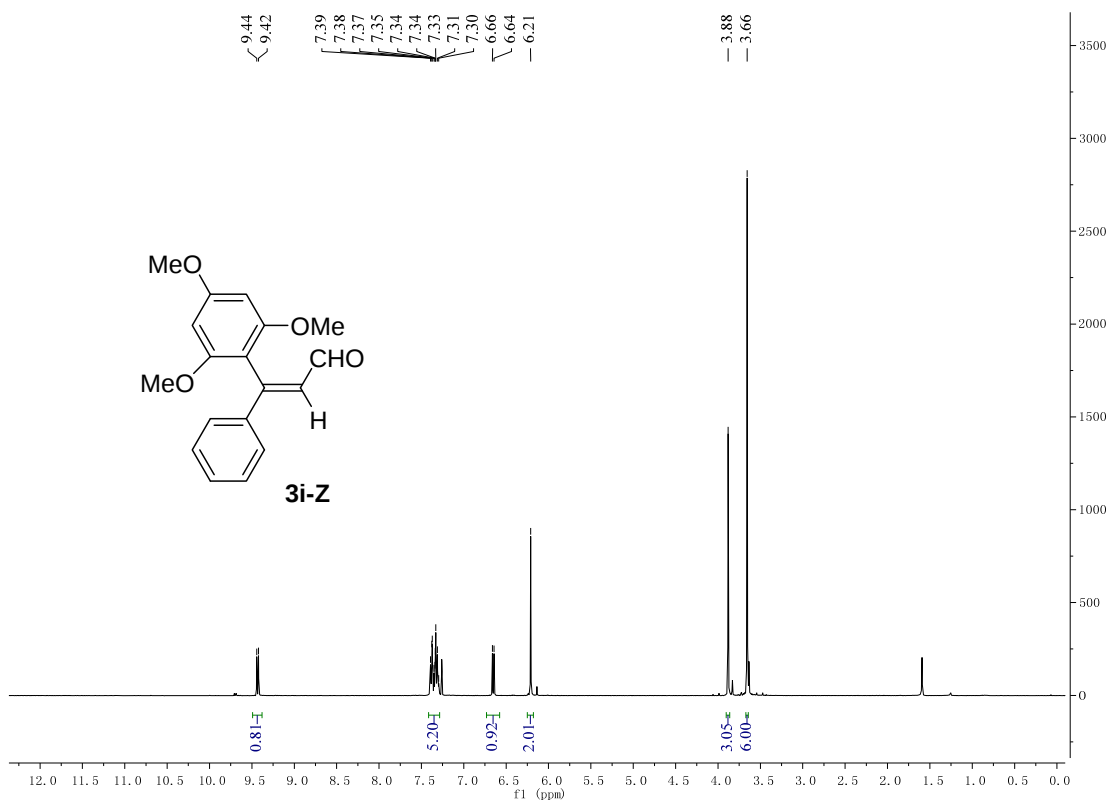


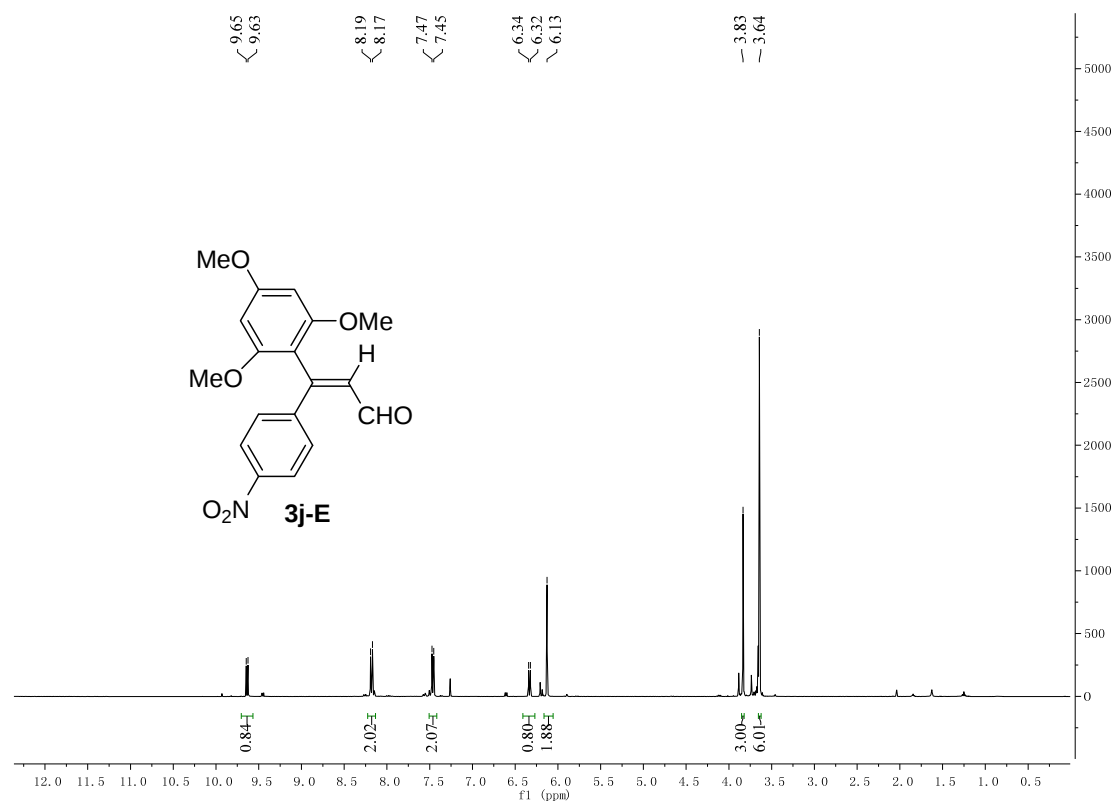
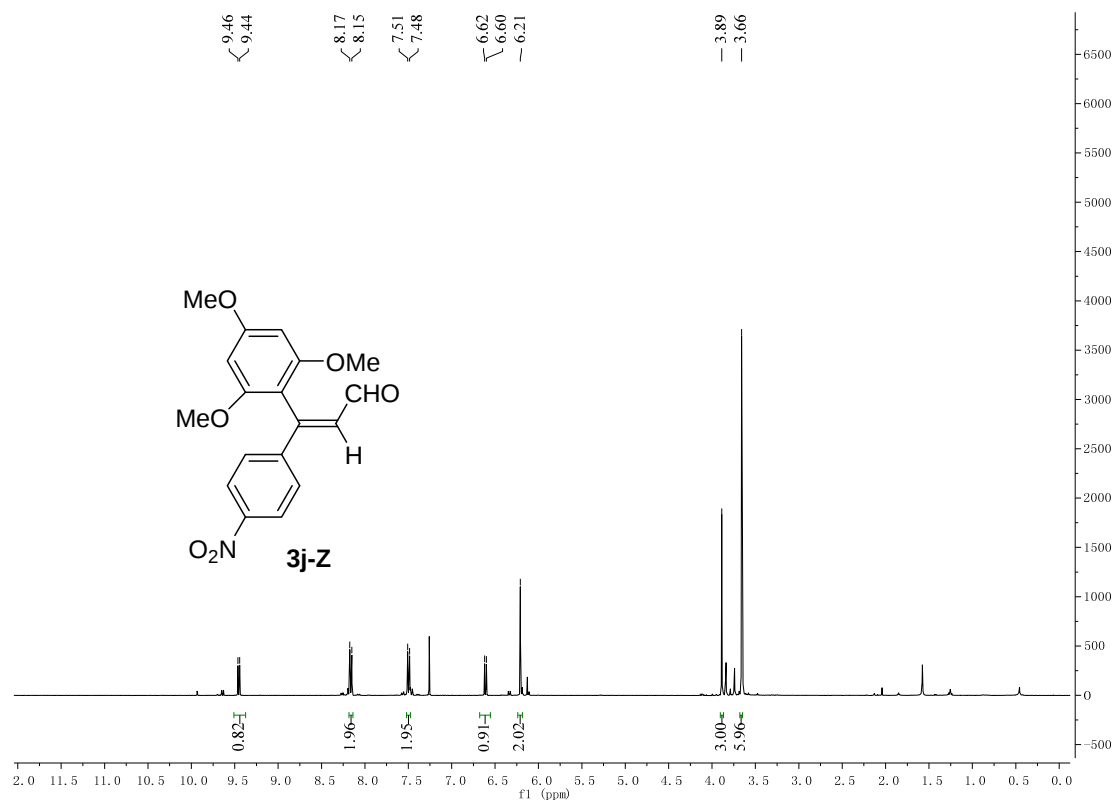


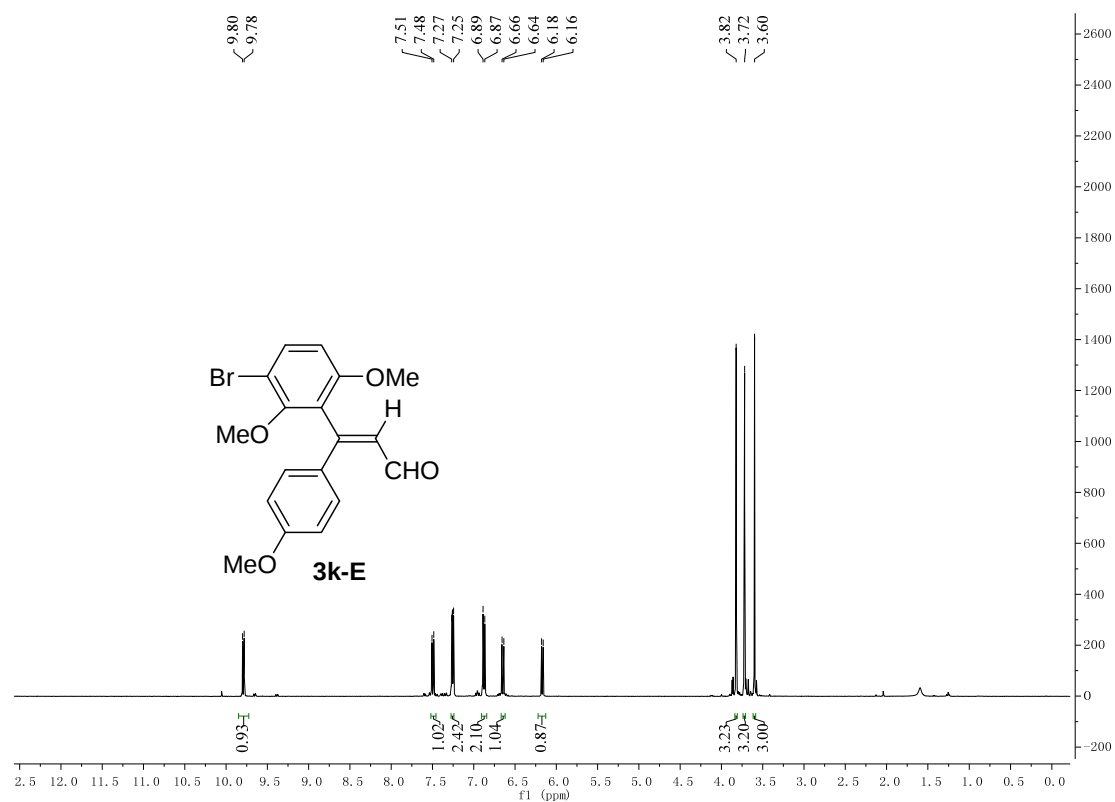
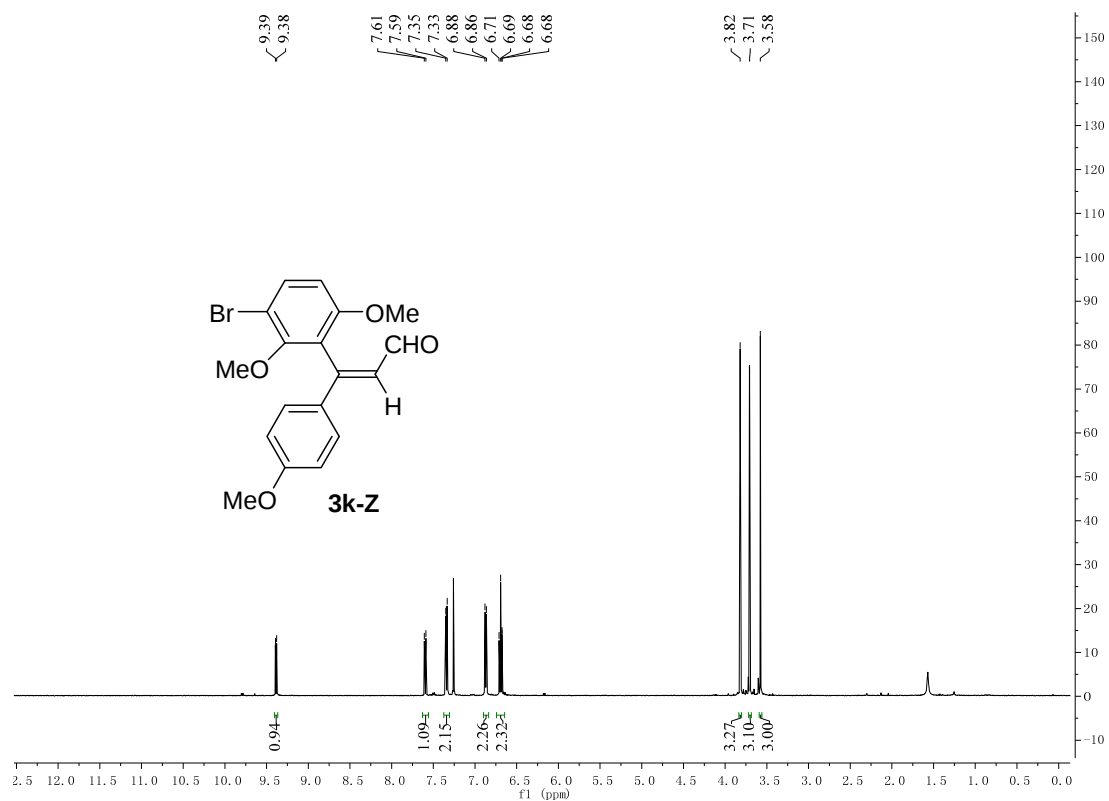


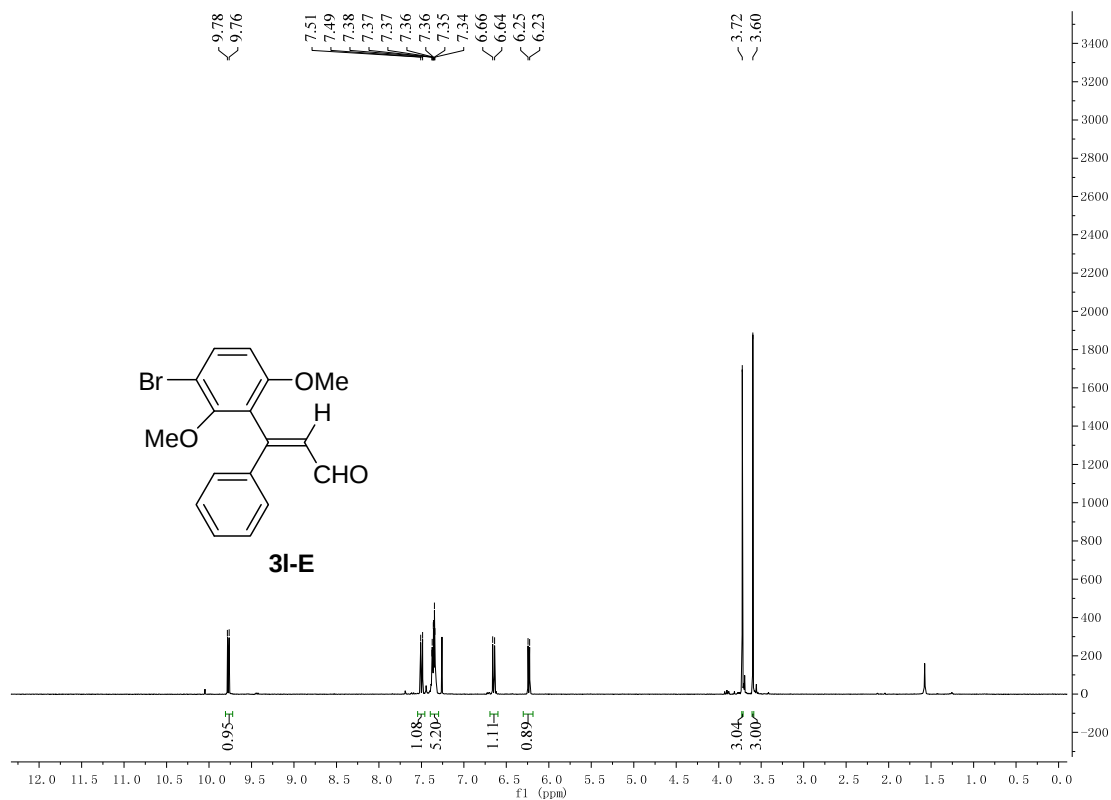
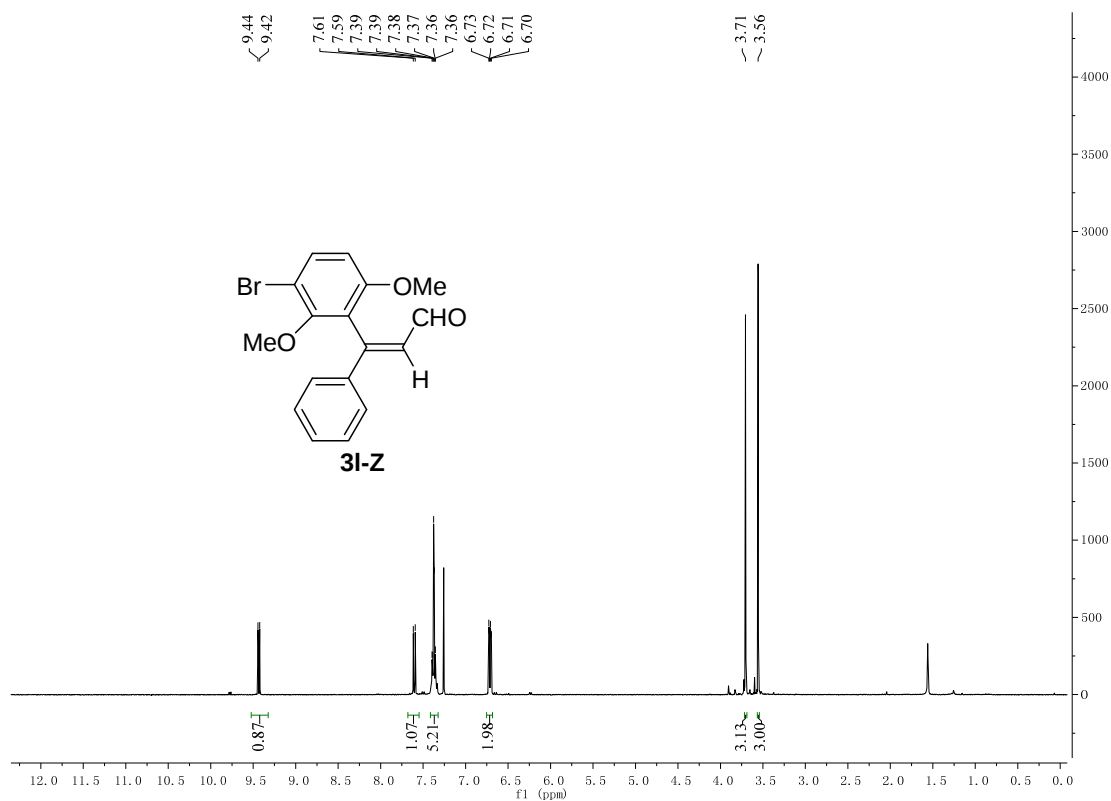


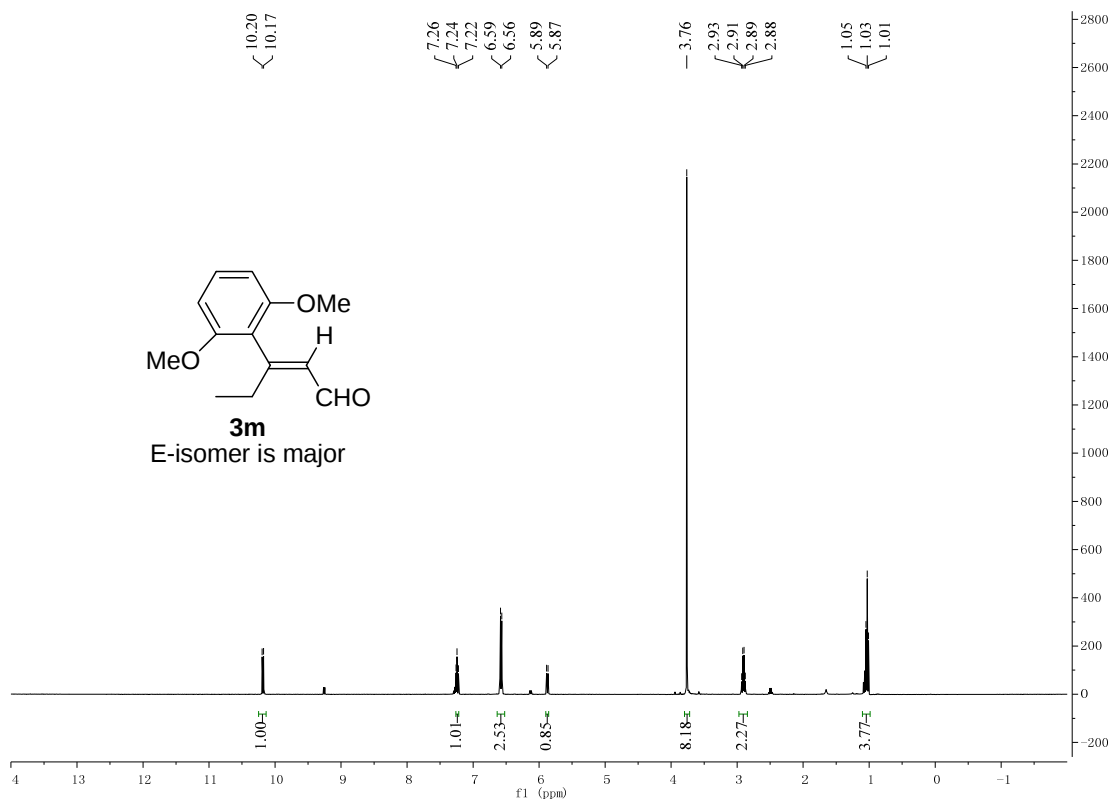
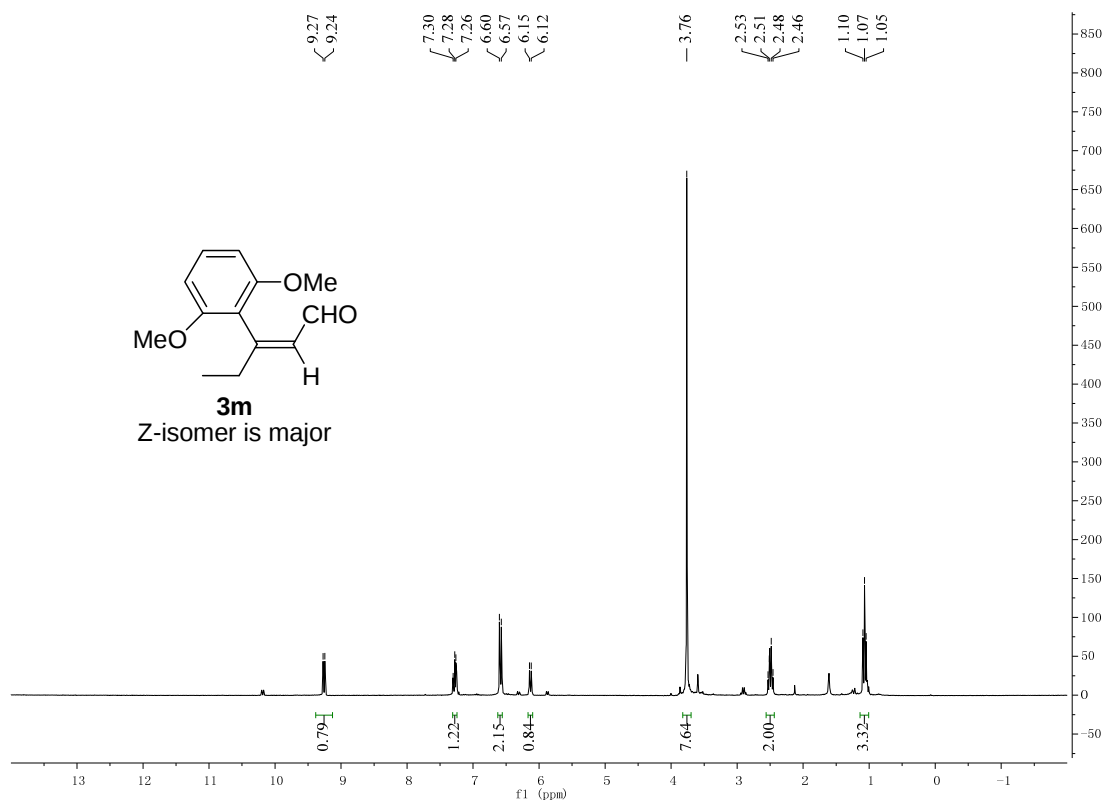


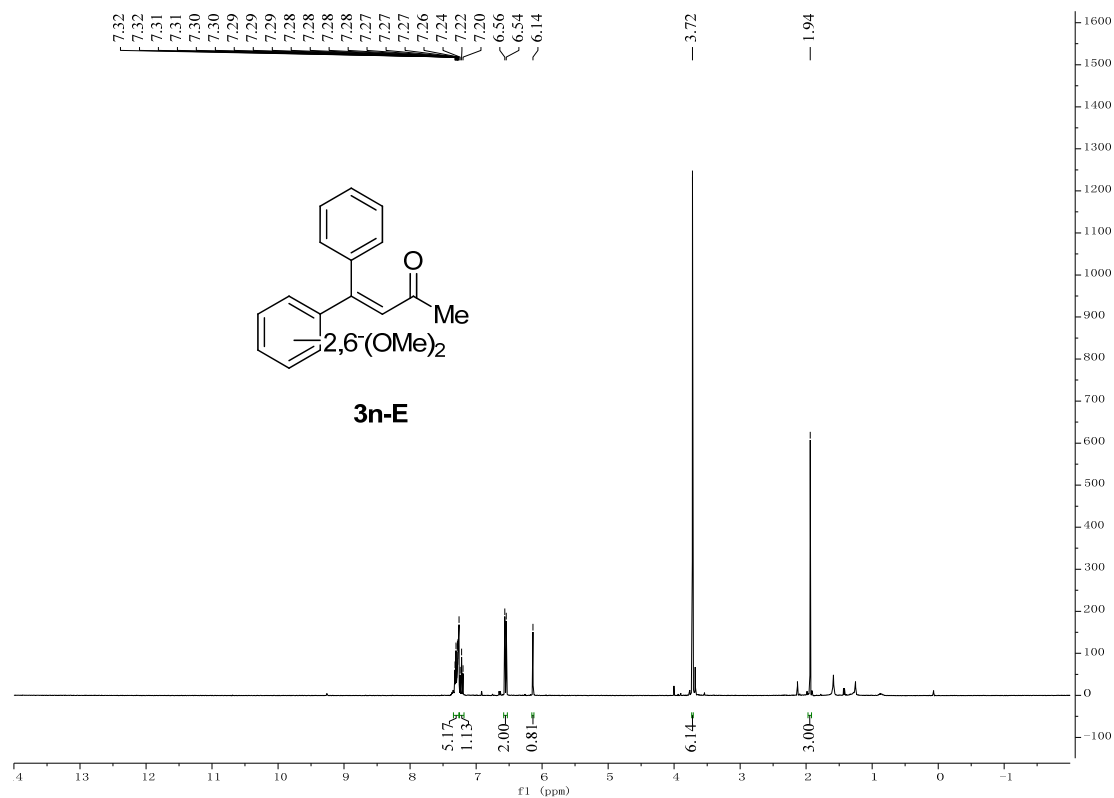
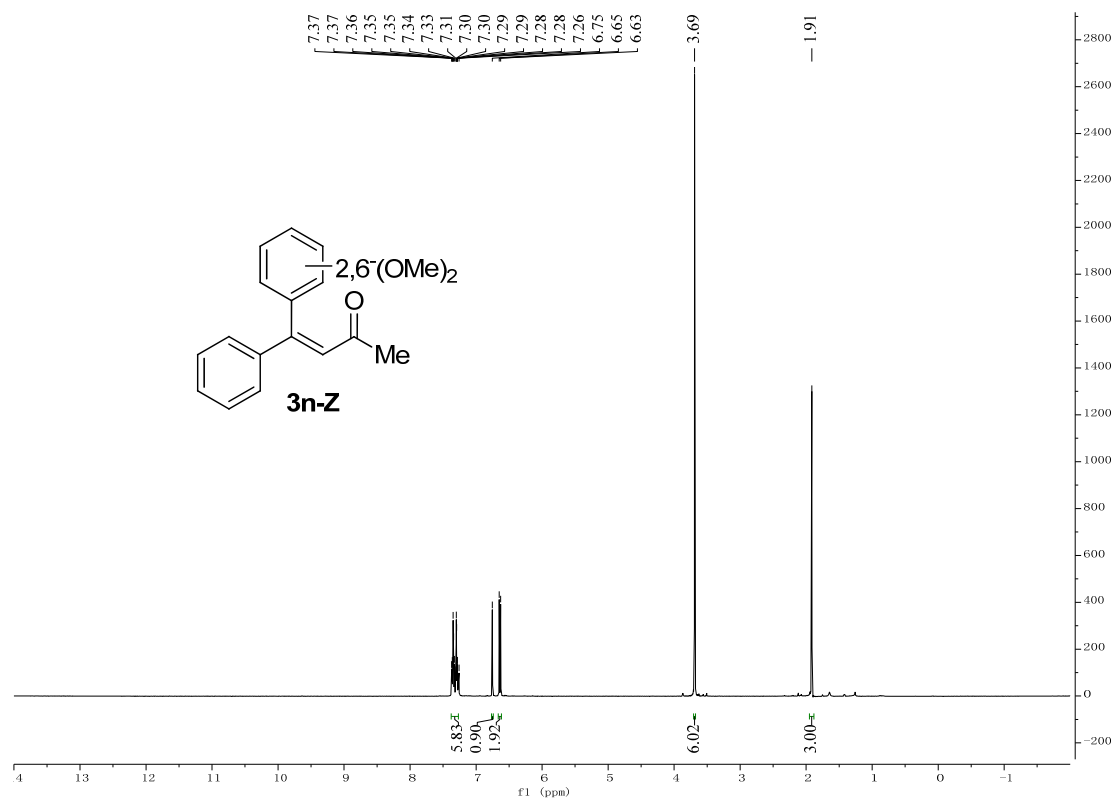


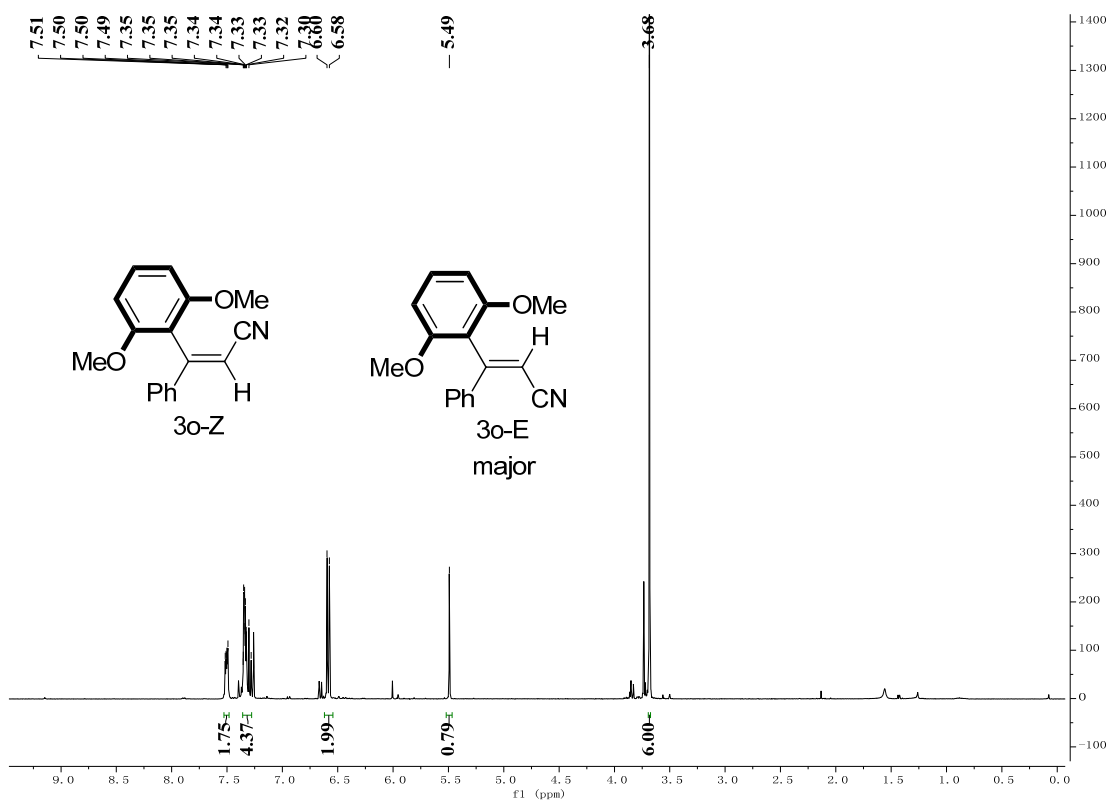
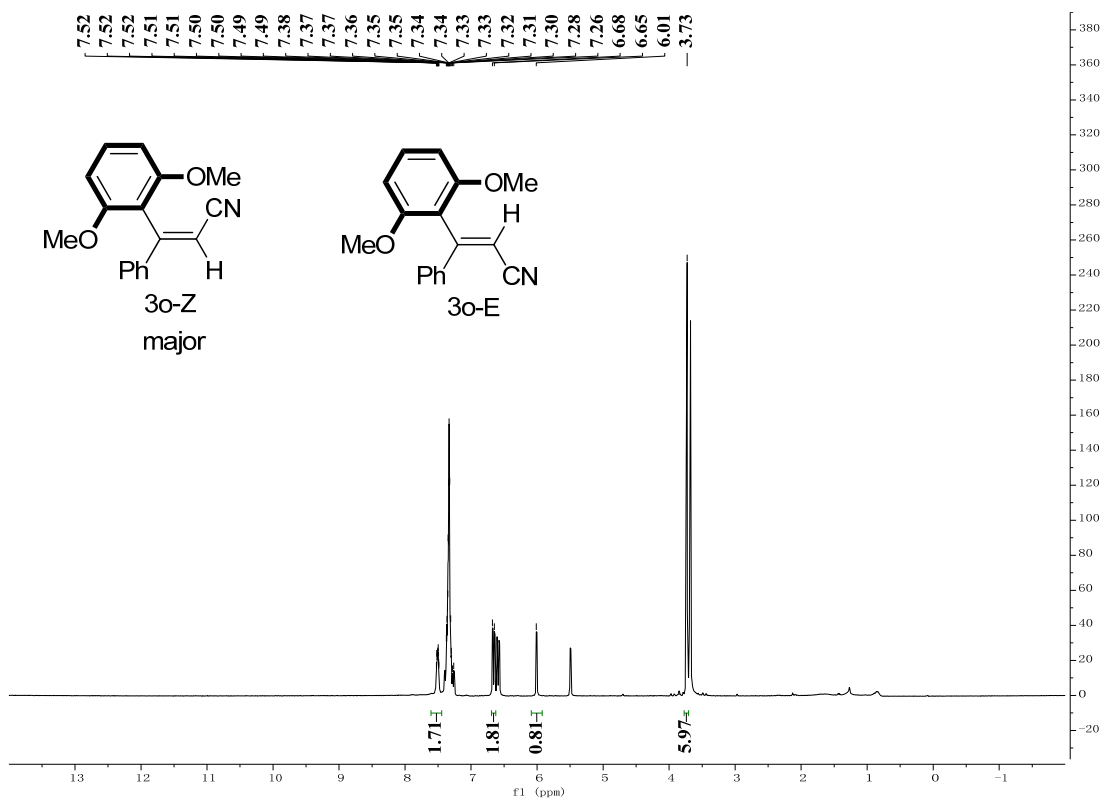


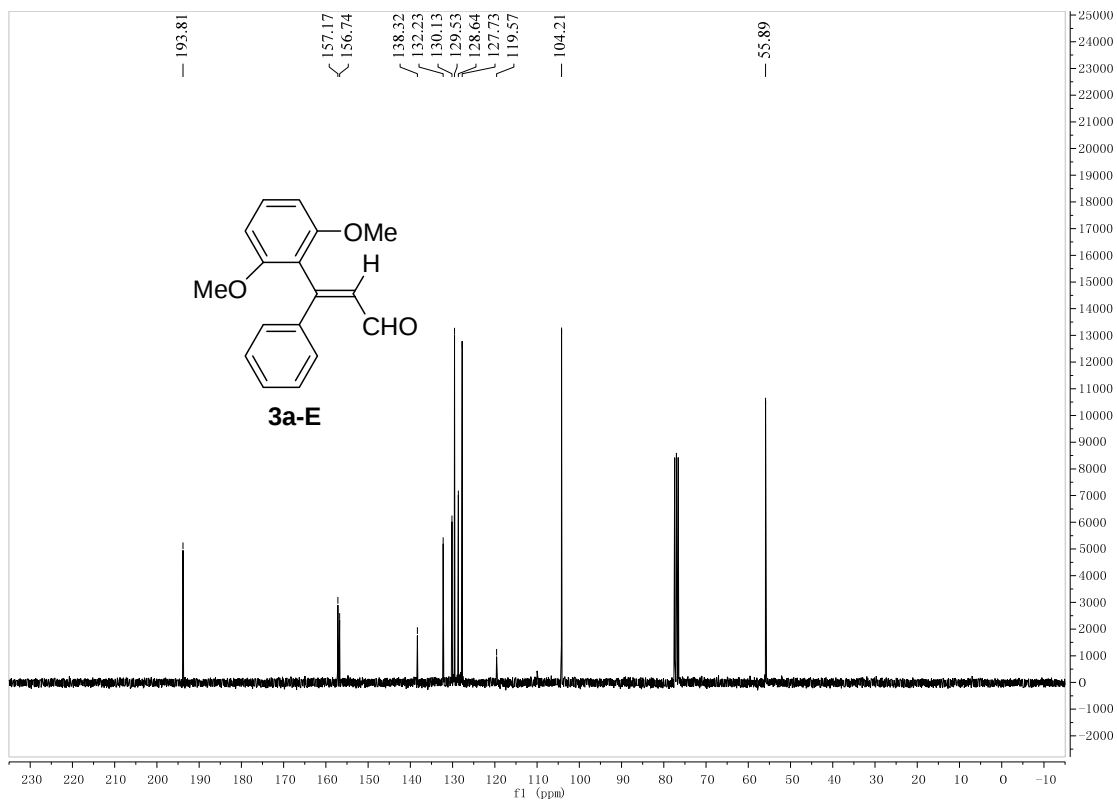
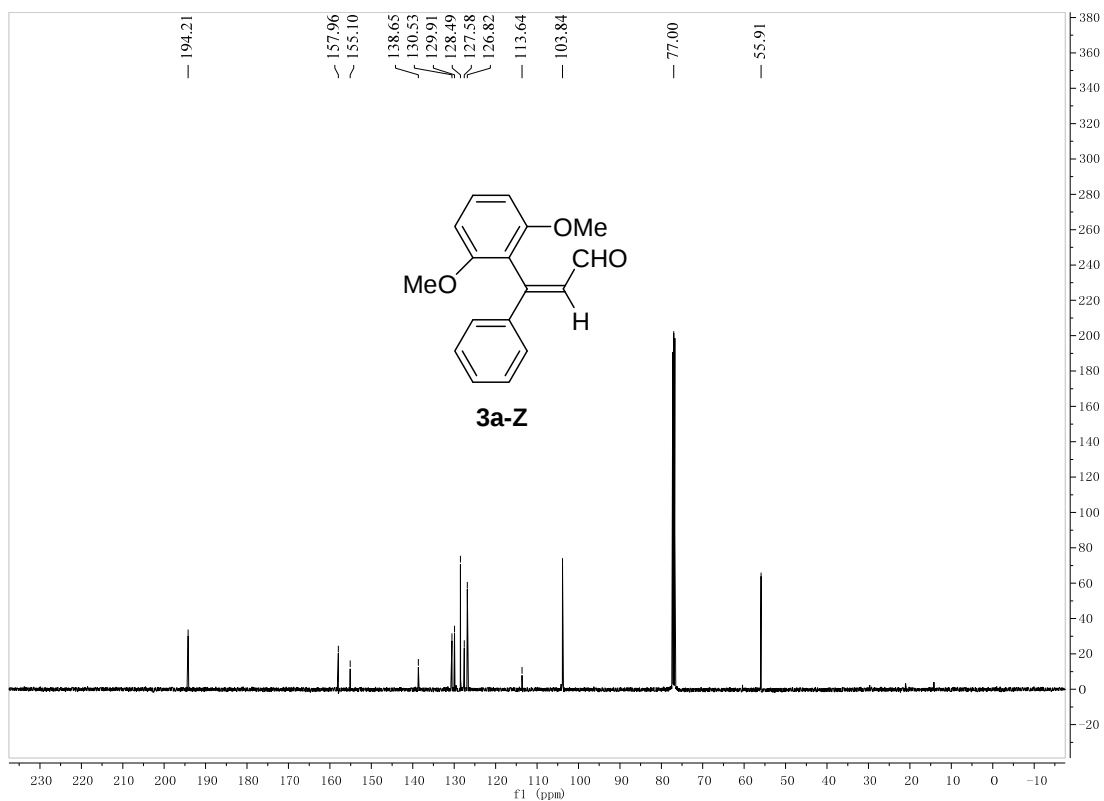


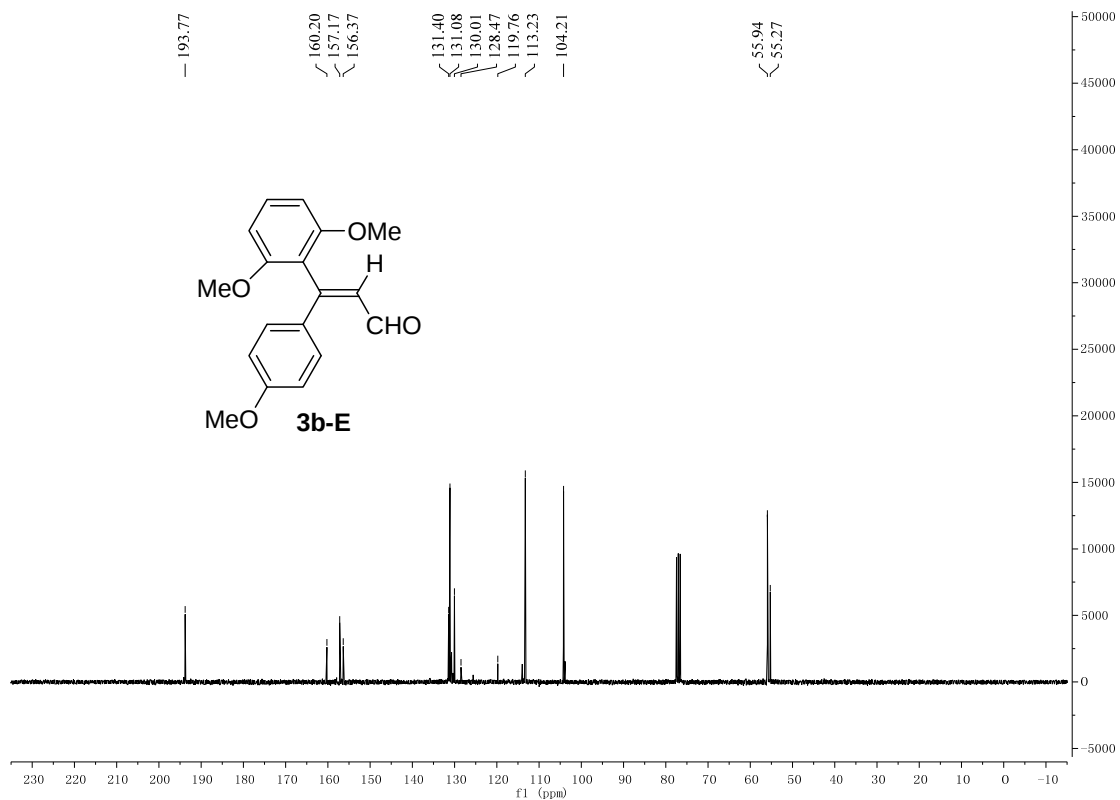
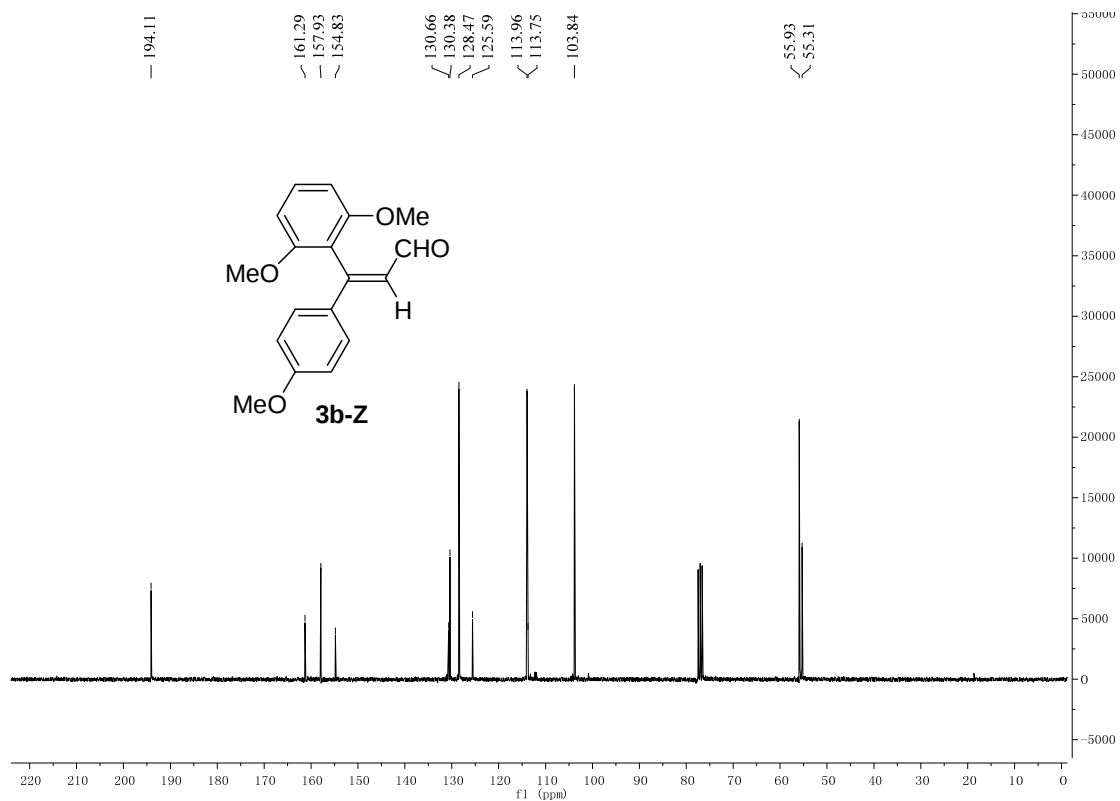


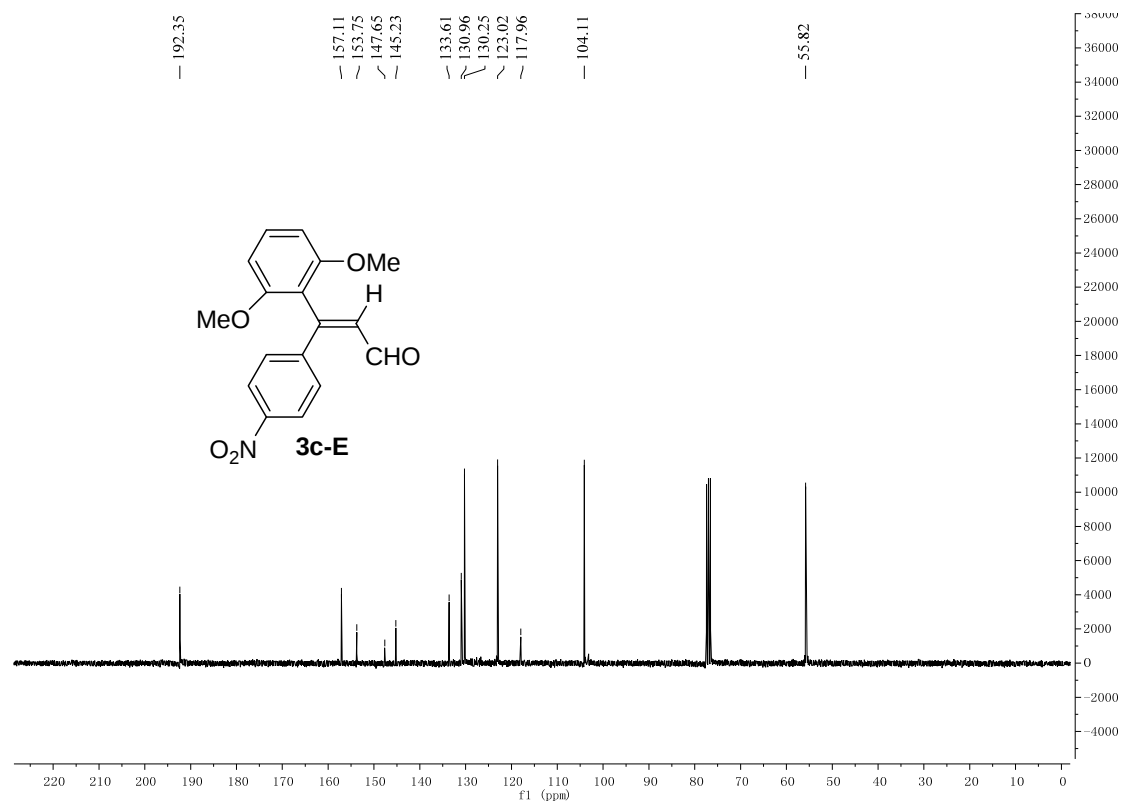
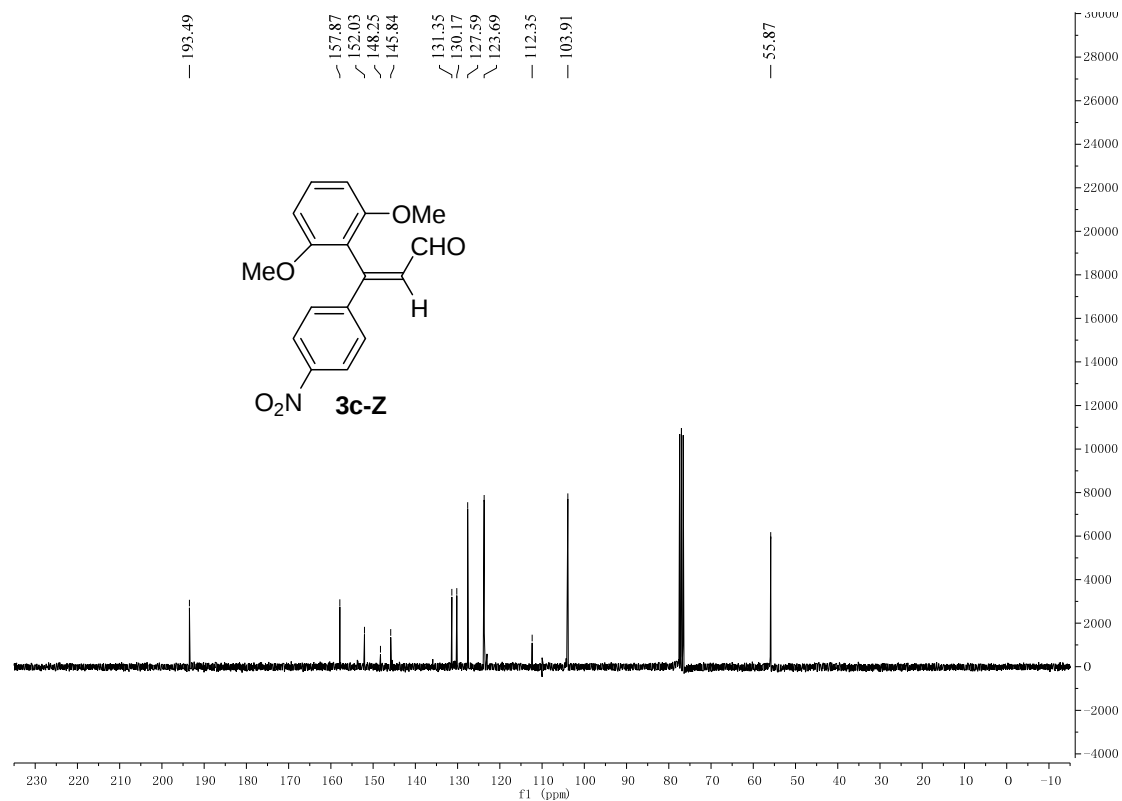


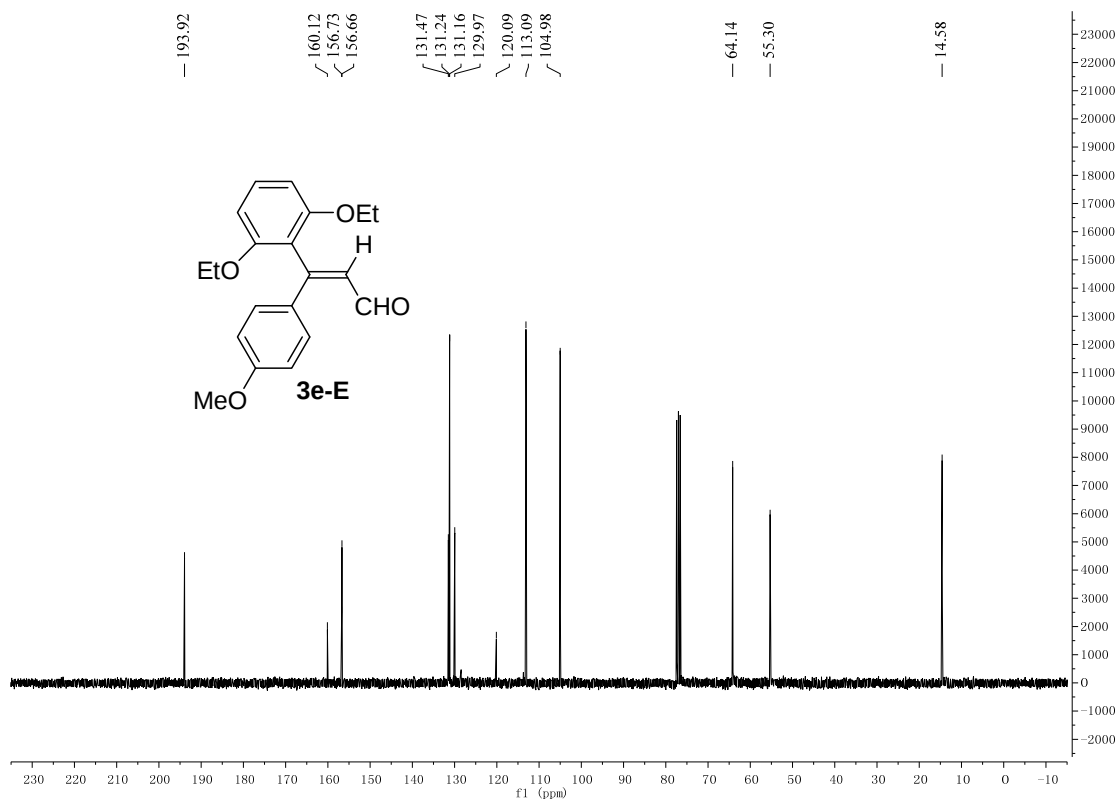
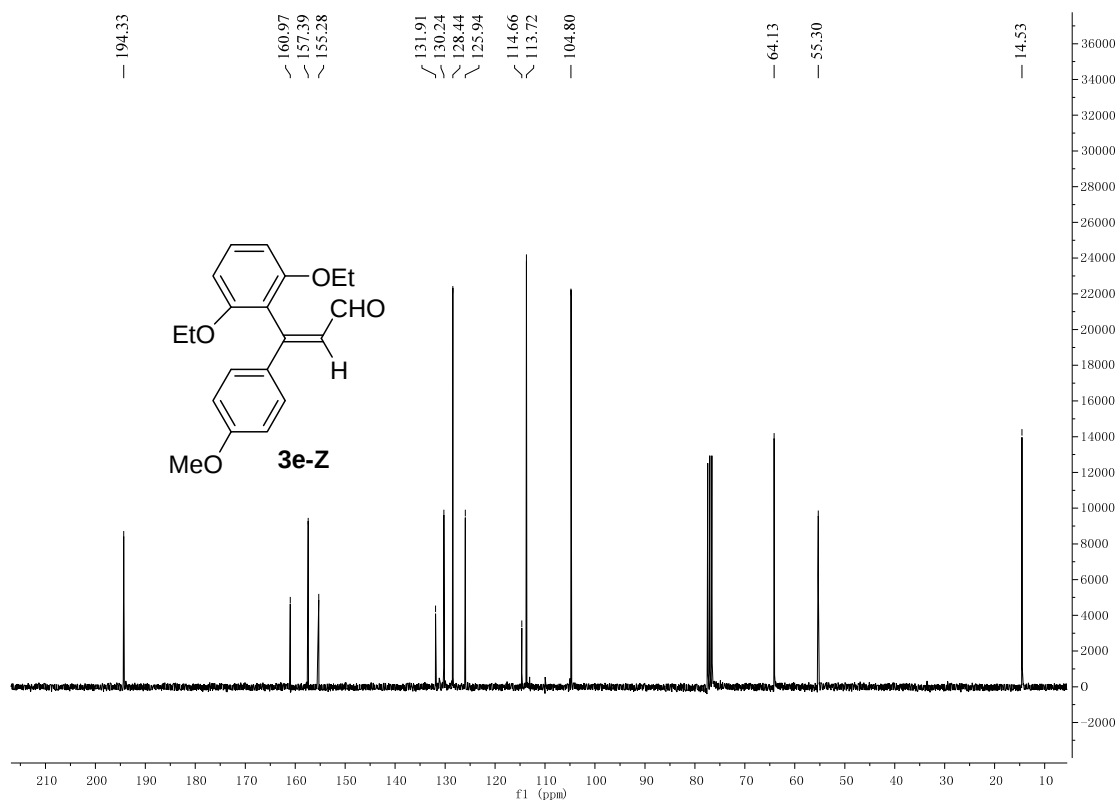


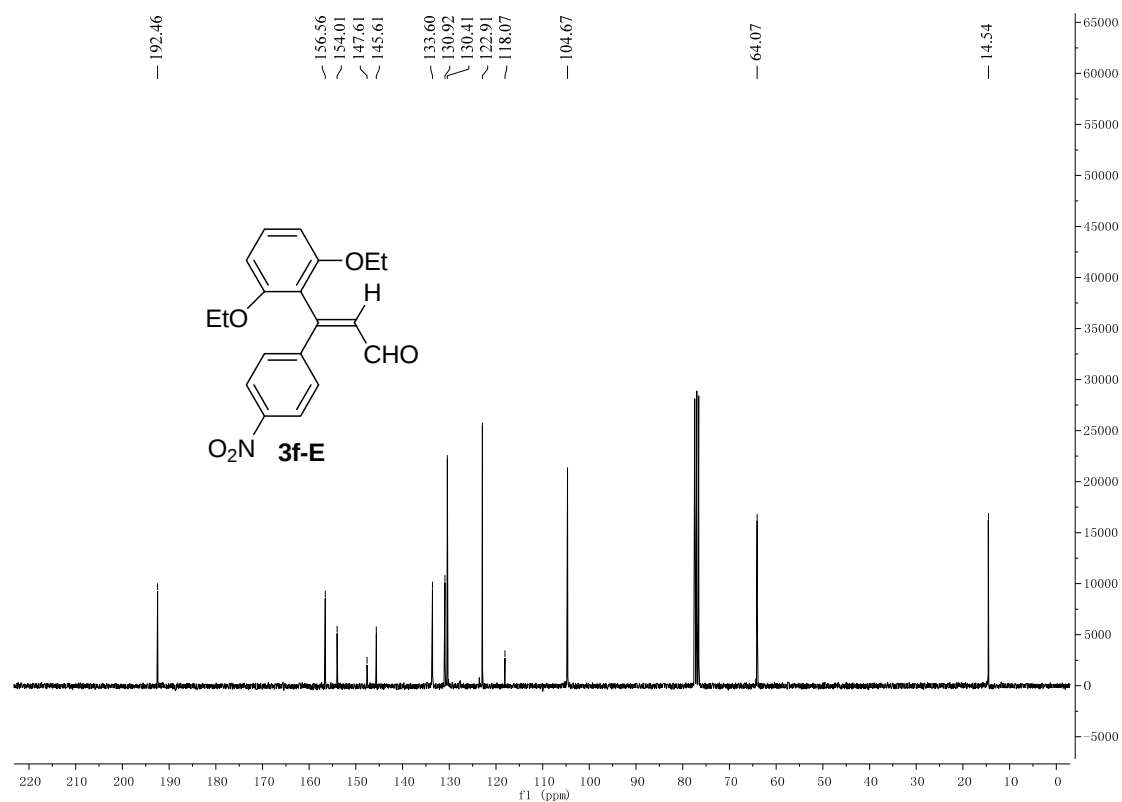
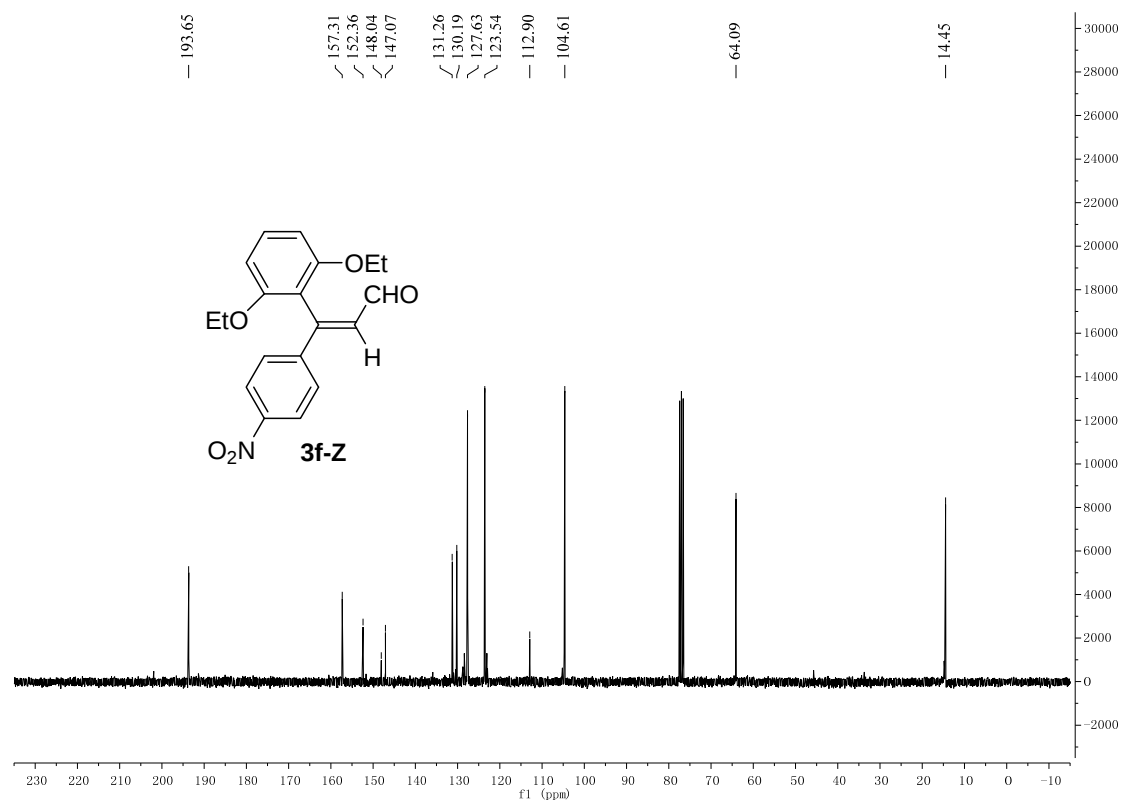


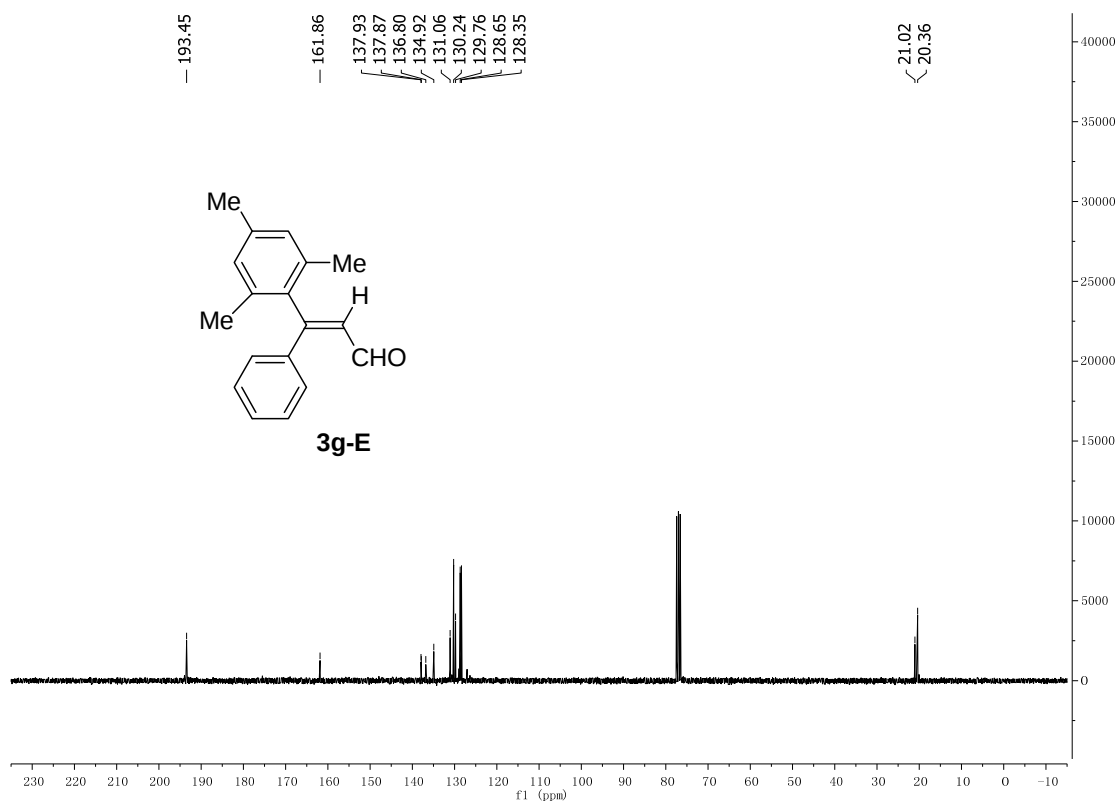
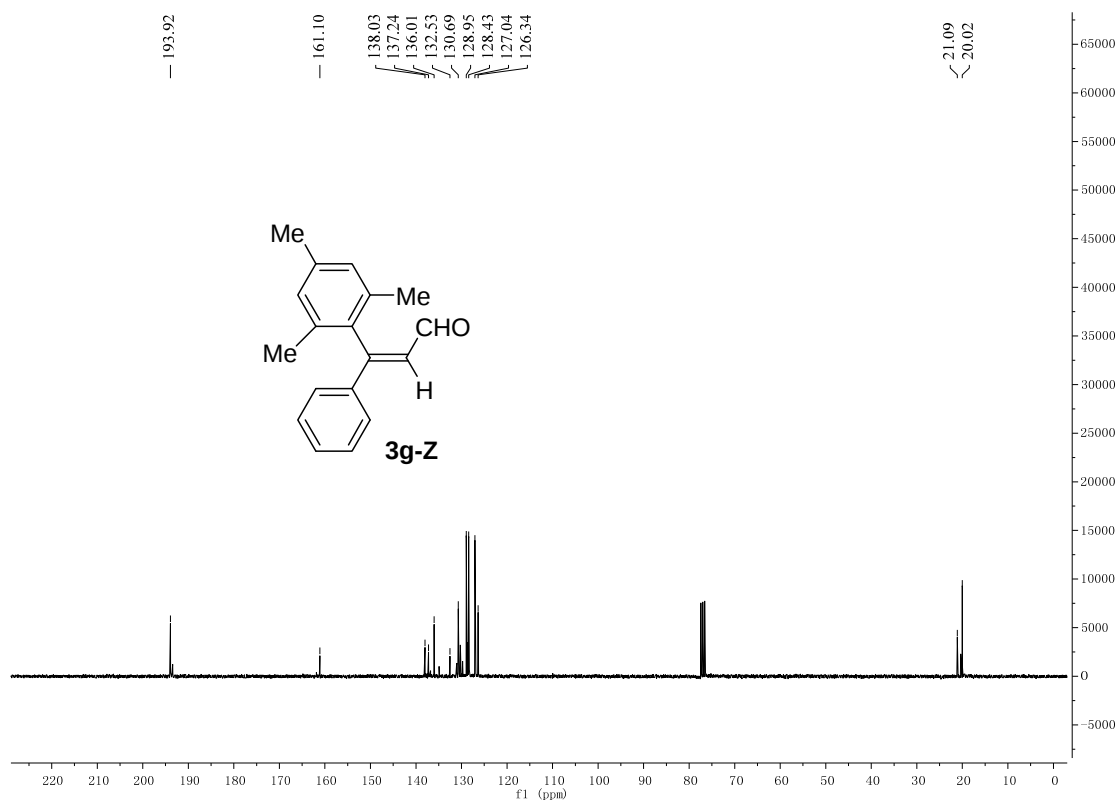


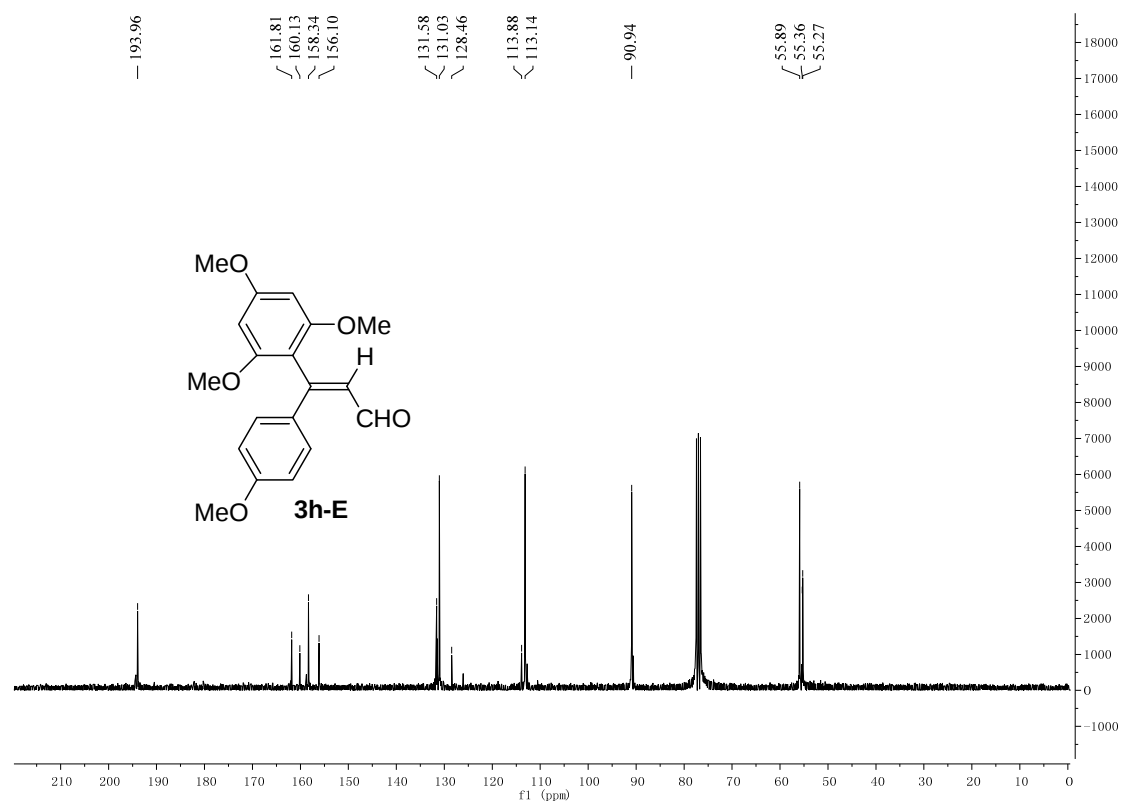
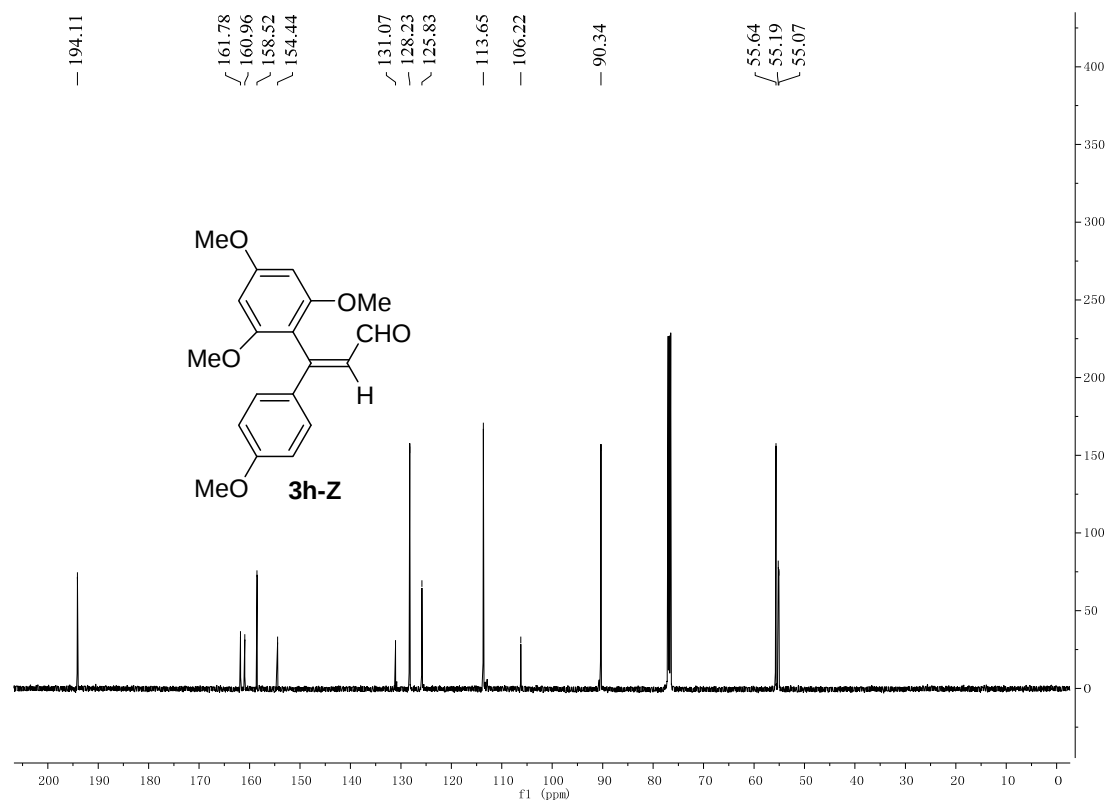


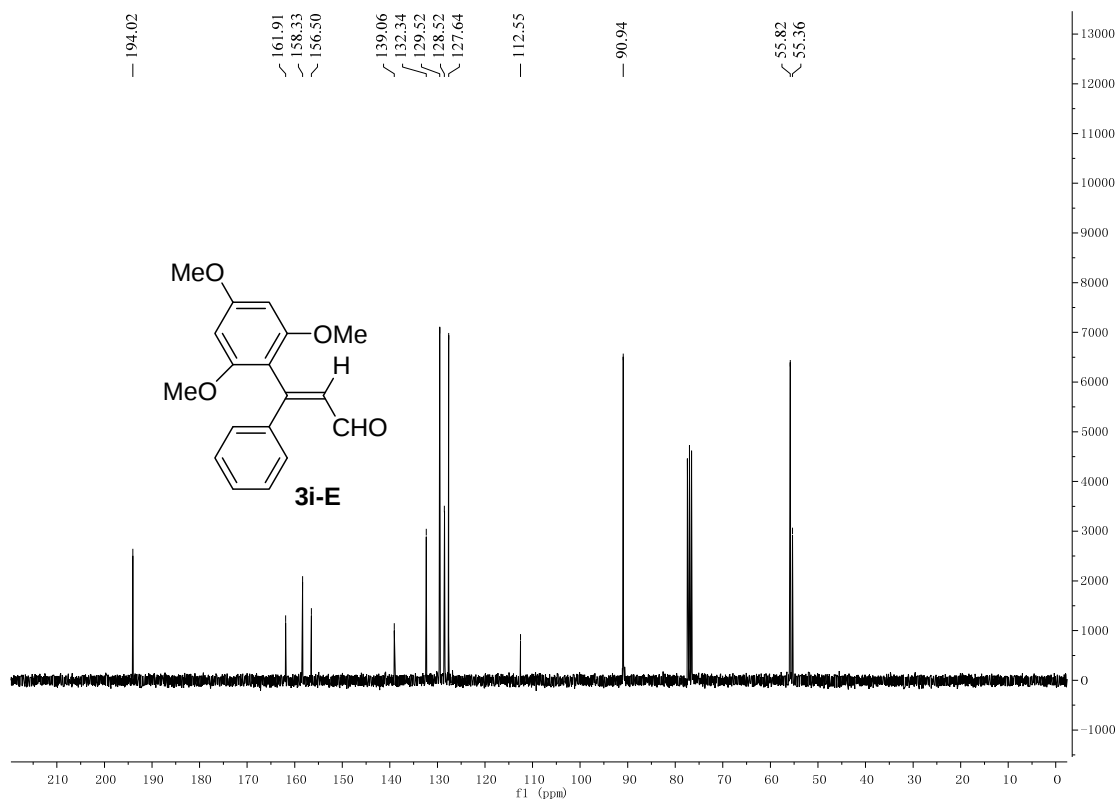
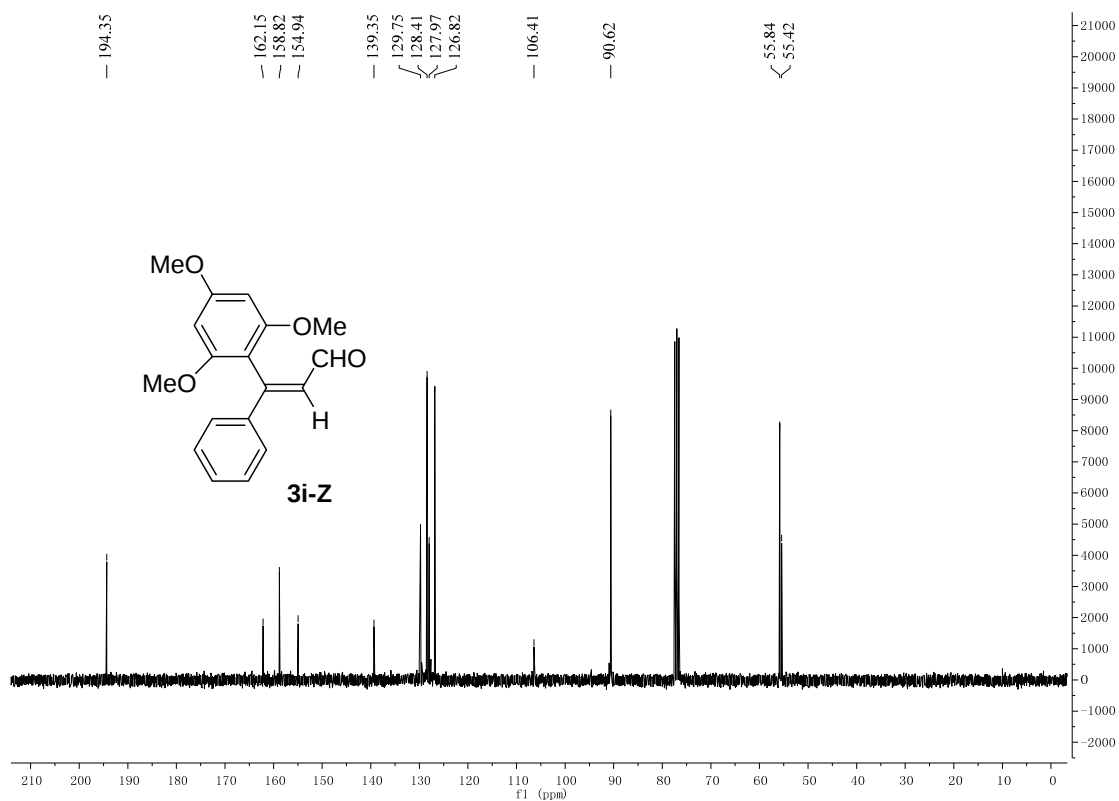


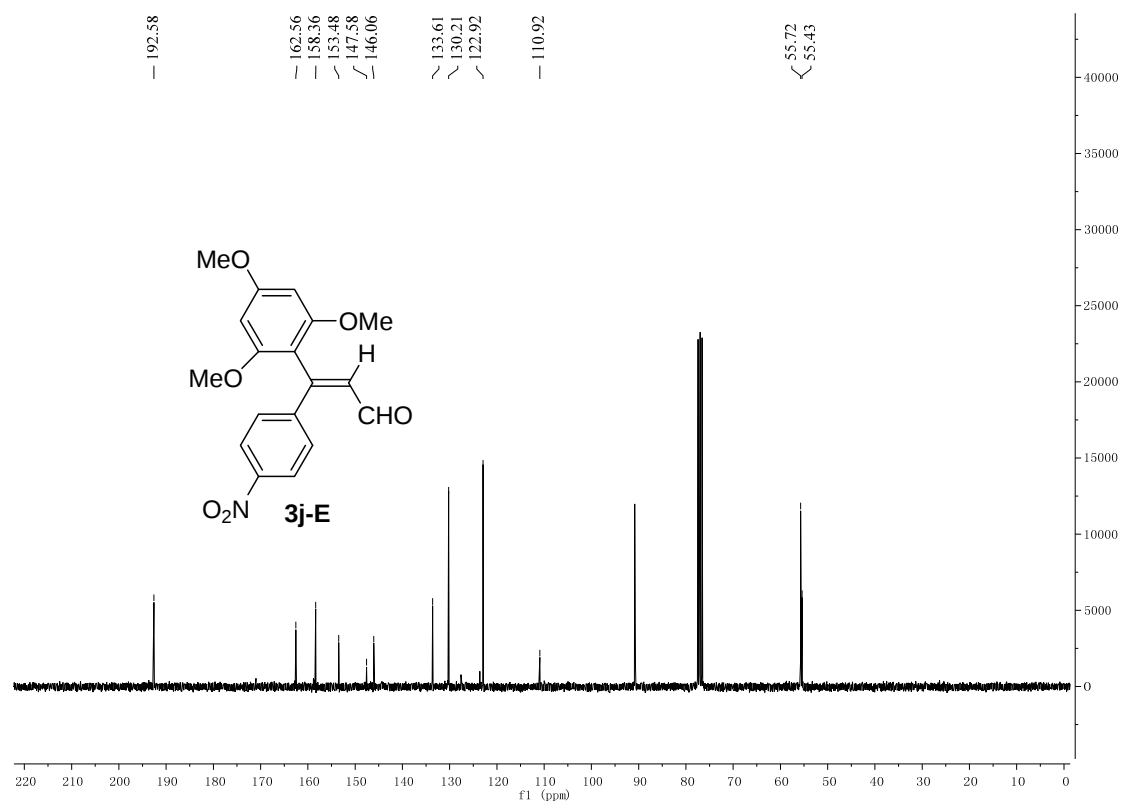
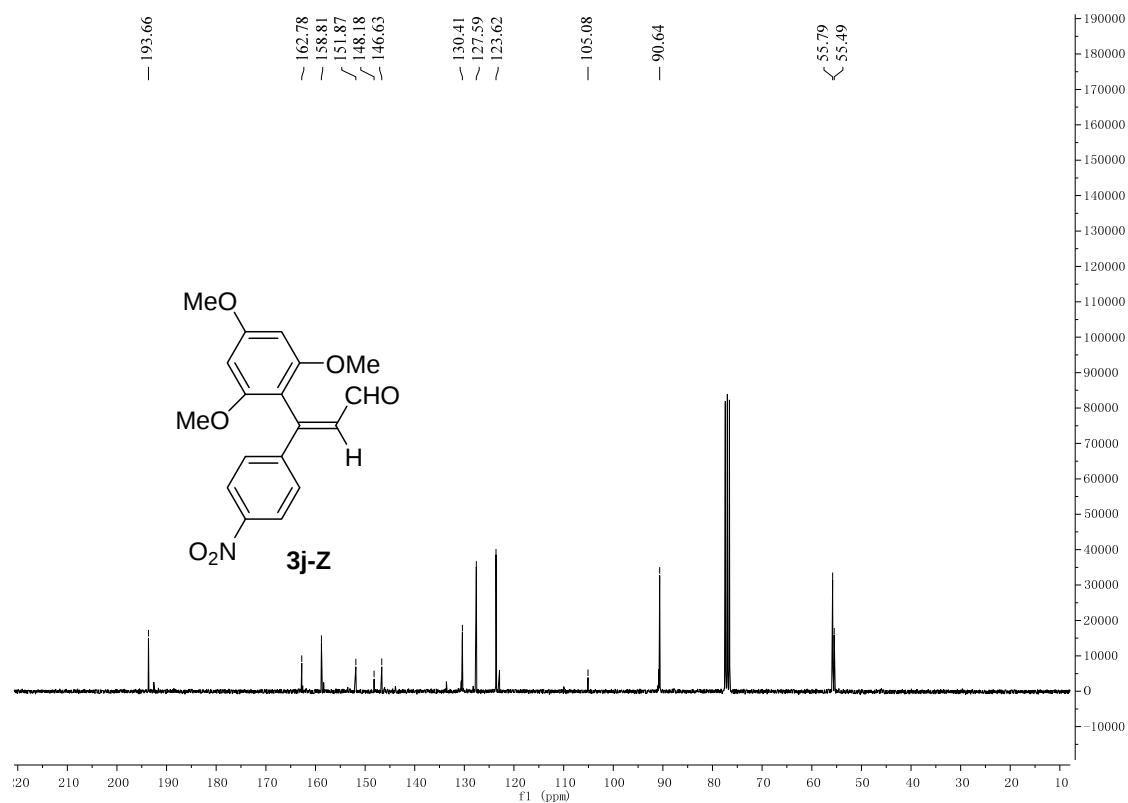


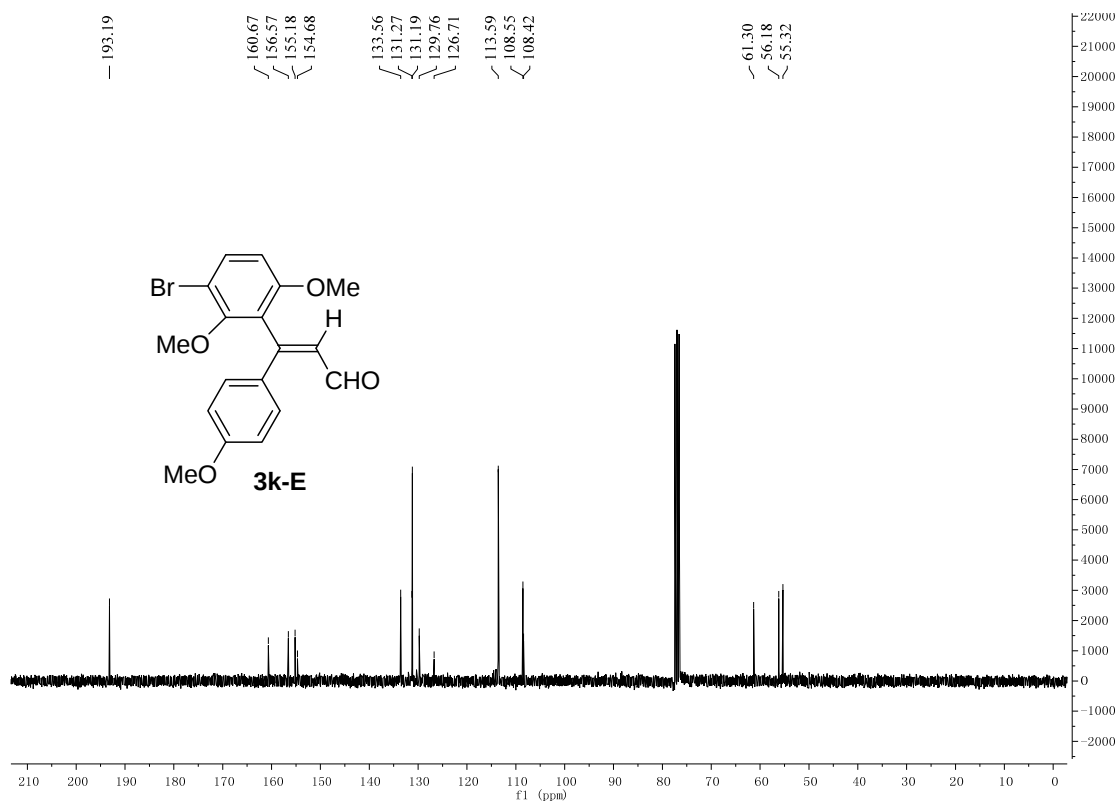
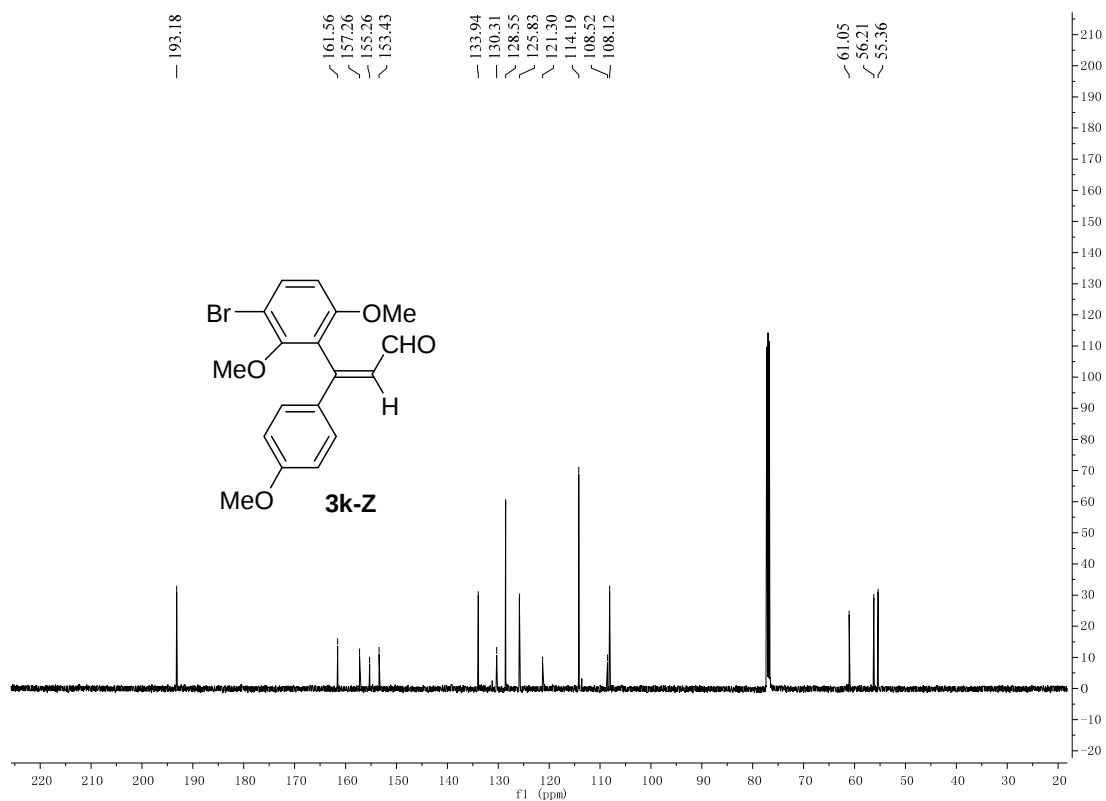


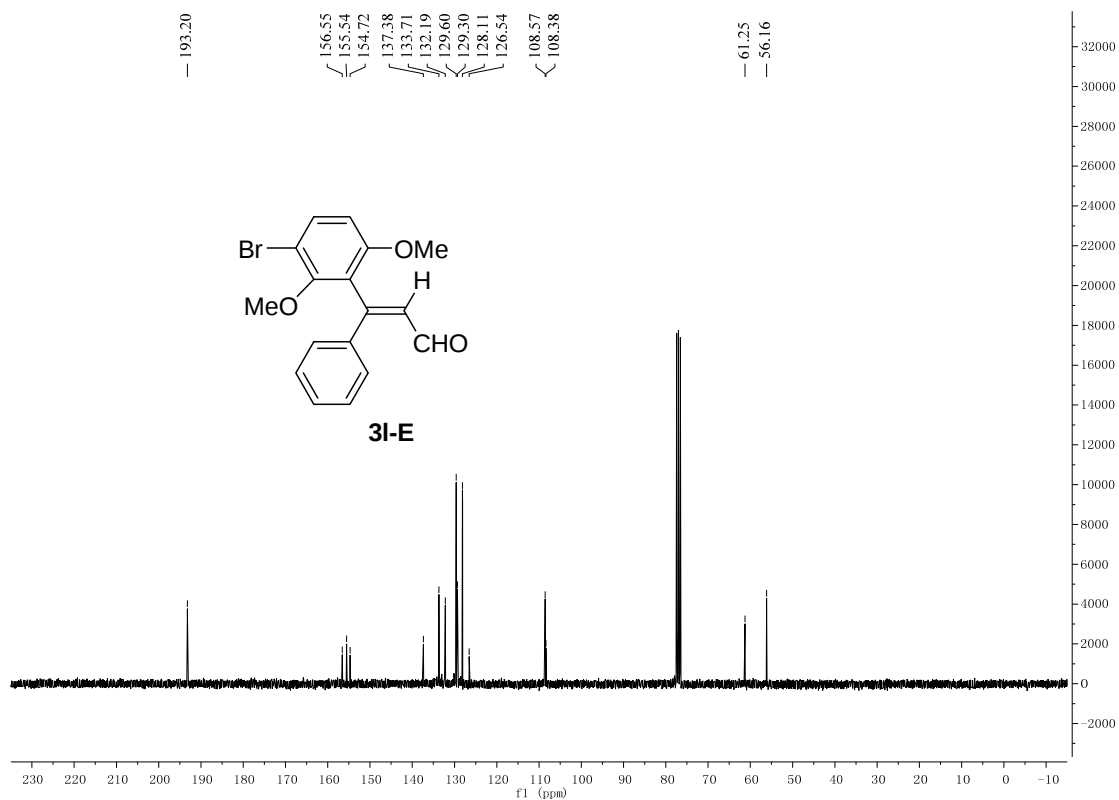
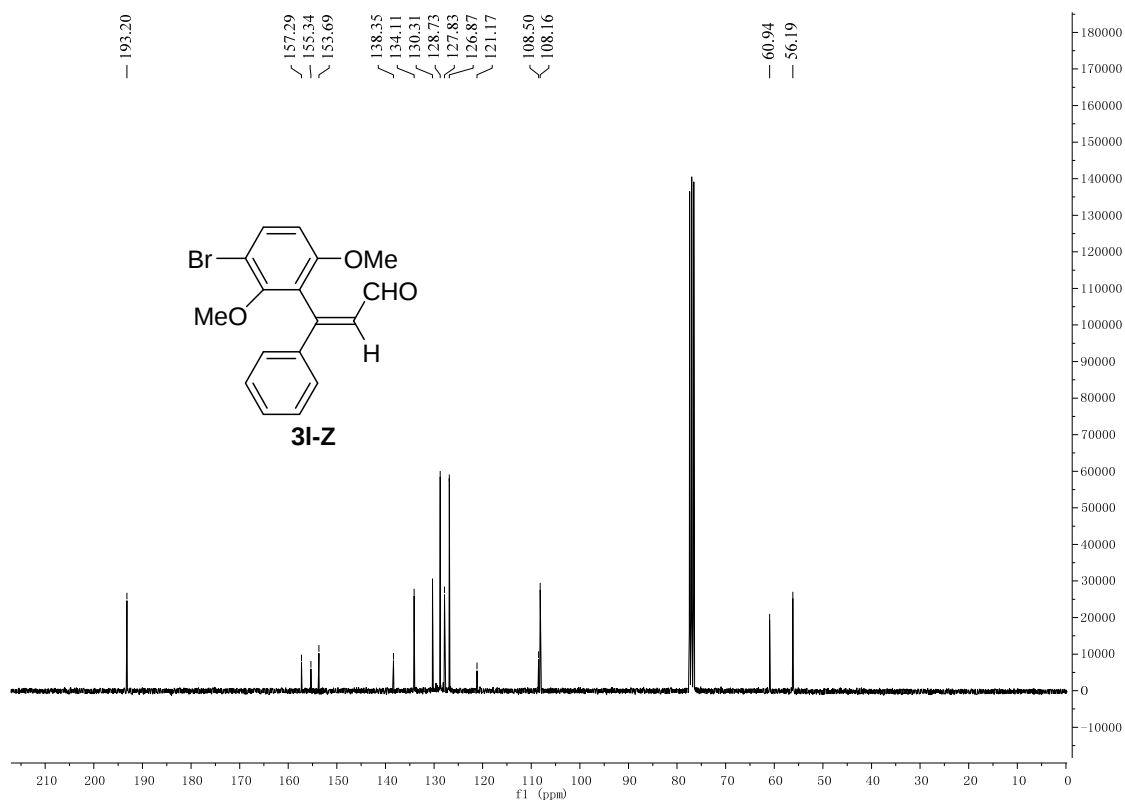


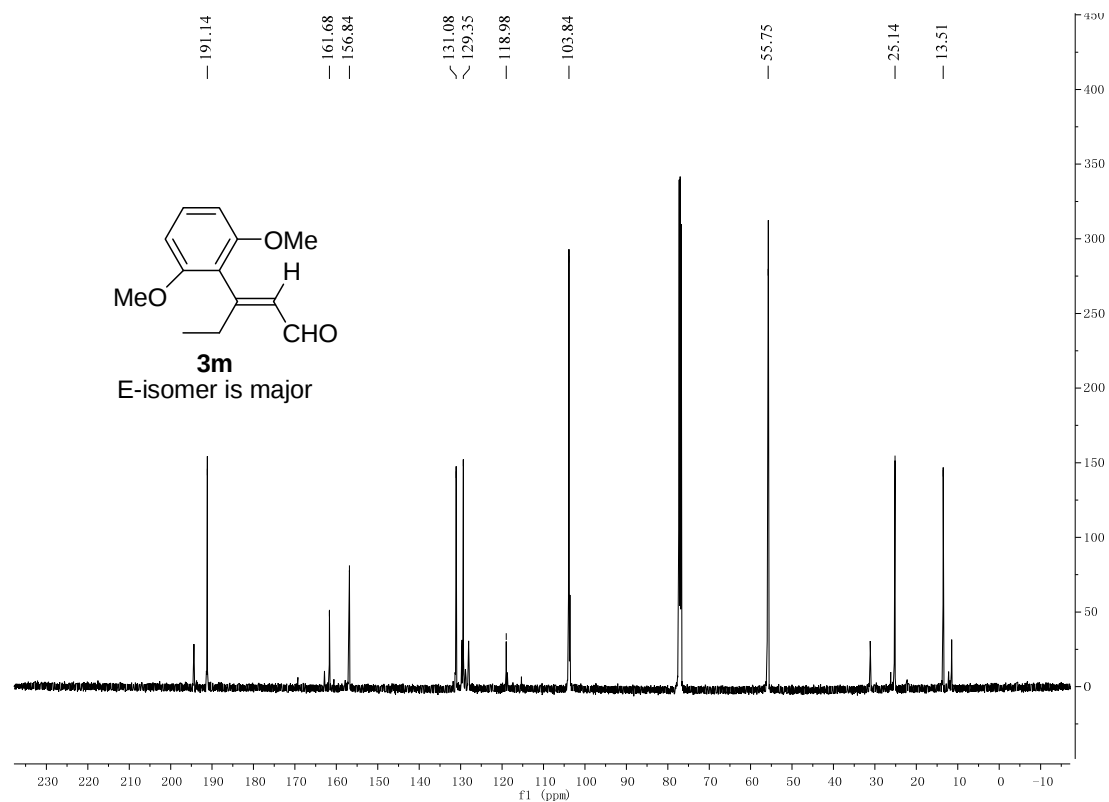
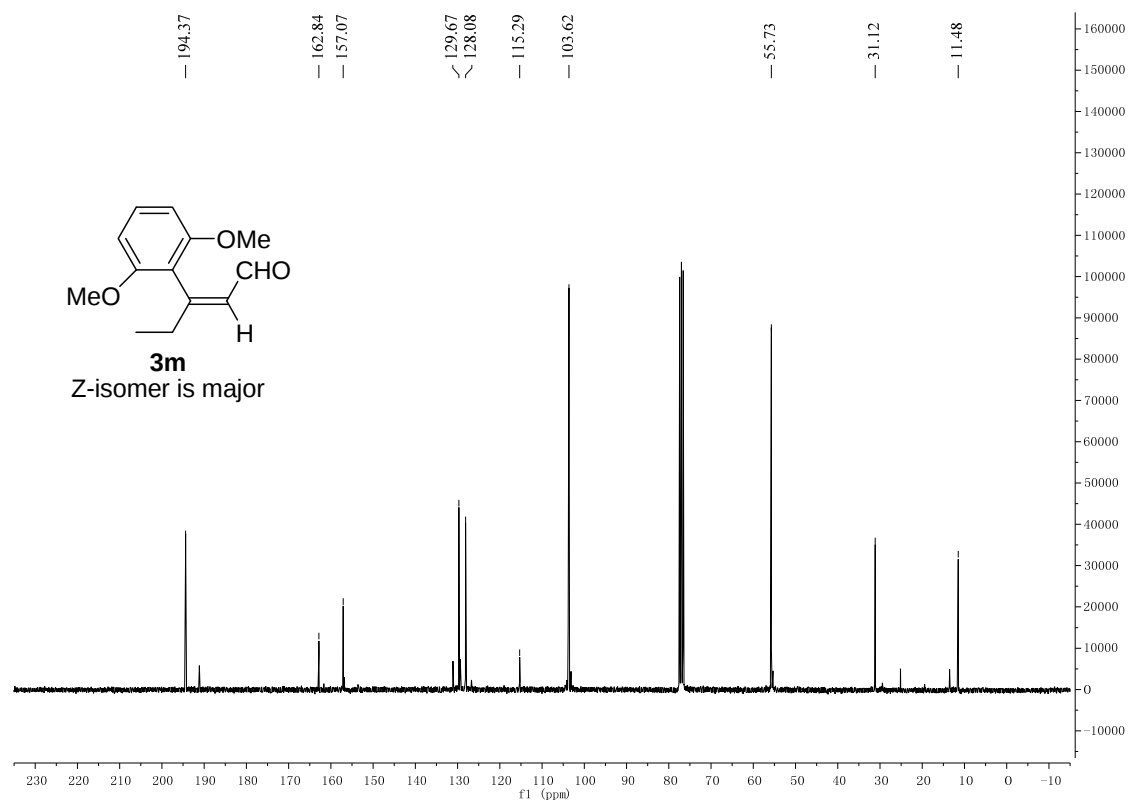


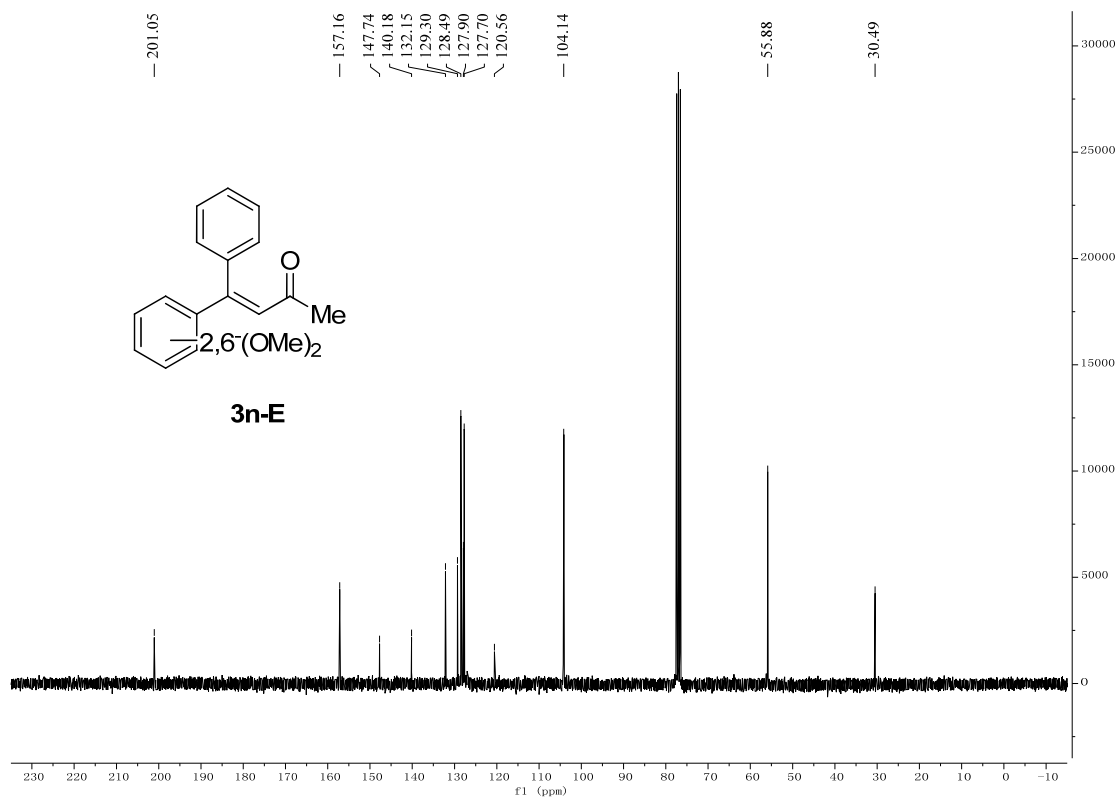
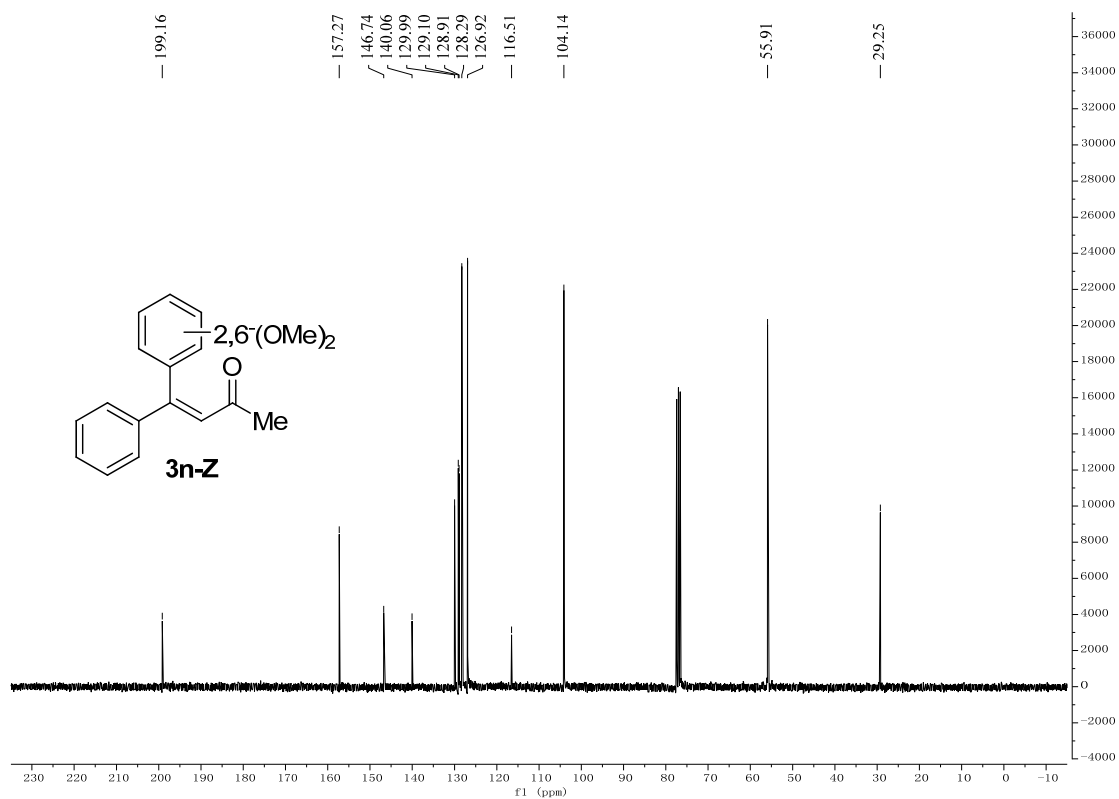


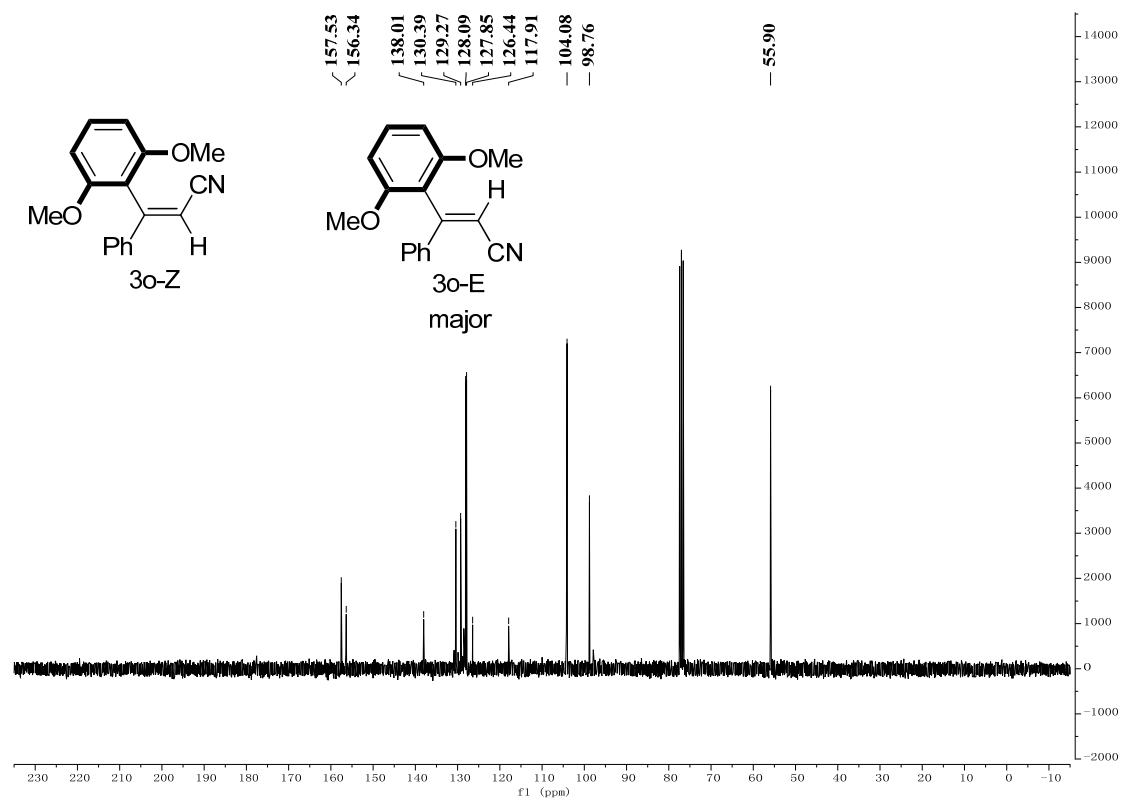
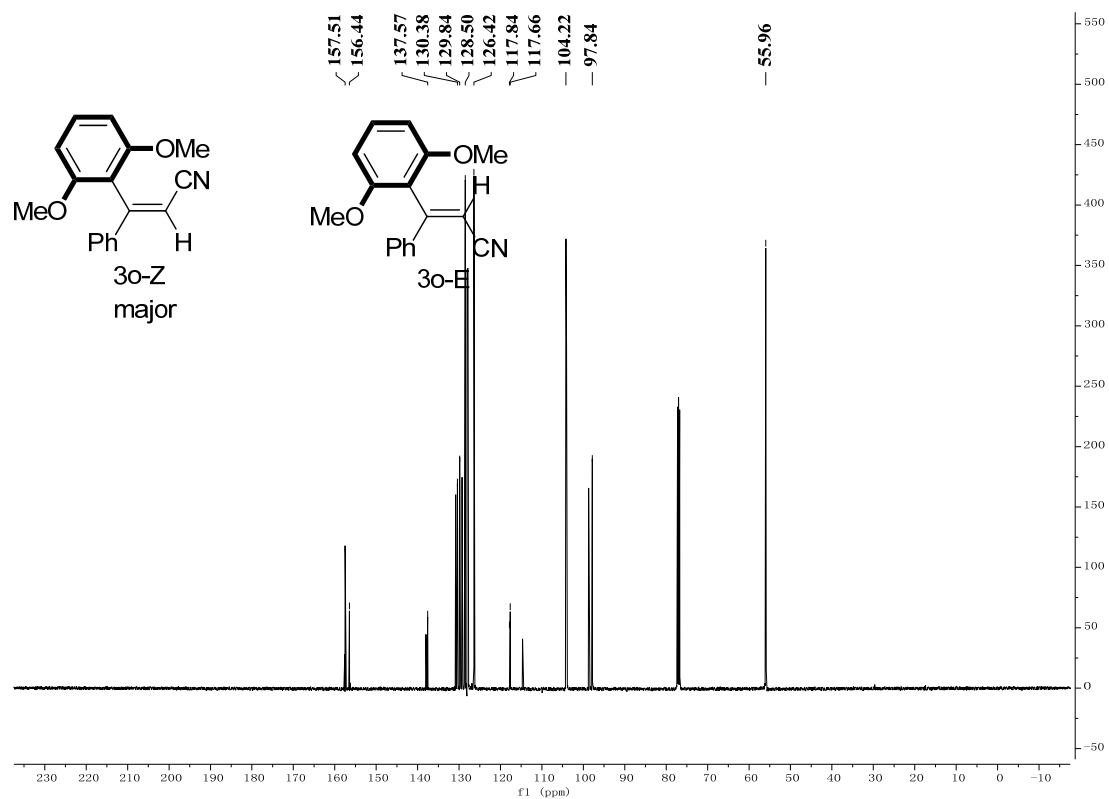




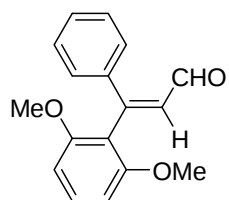




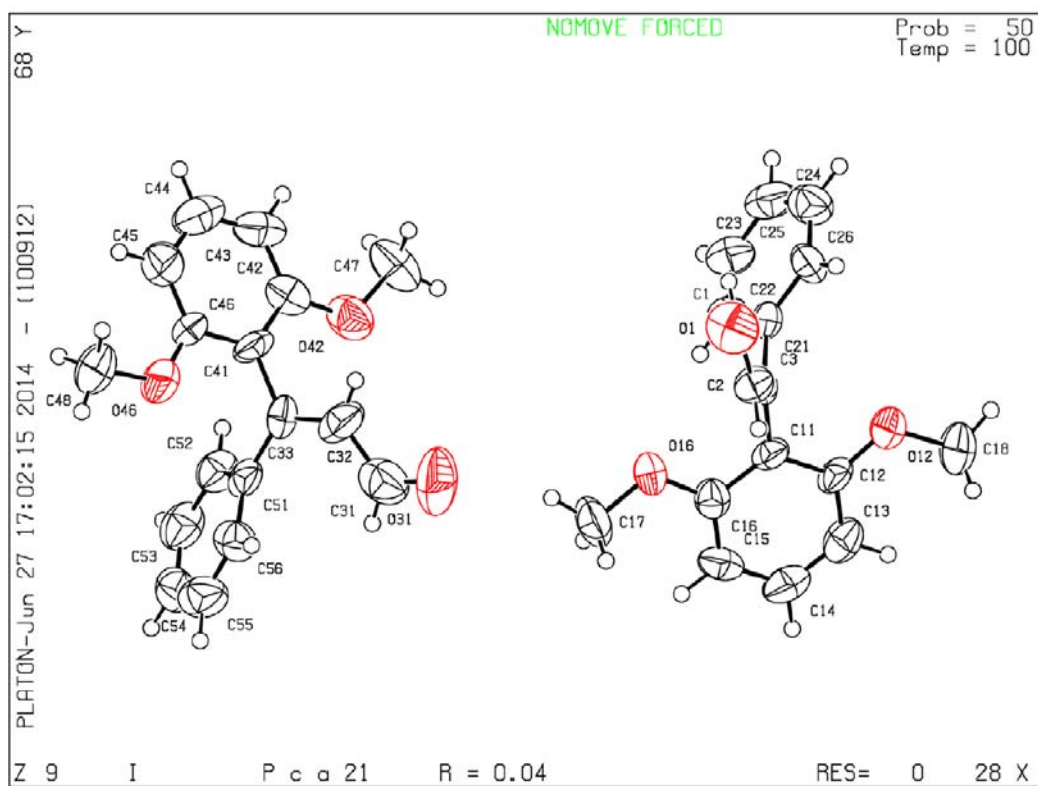




6. Crystallographic data for 3a-E



3a-E



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0144 Å Wavelength=0.71073

Cell: a=16.5918 (15) b=11.0463 (10) c=15.4242 (14)
 alpha=90 beta=90 gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	2826.9 (4)	2826.9 (4)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C17 H16 O3	?
Sum formula	C17 H16 O3	C17 H16 O3
Mr	268.30	268.30
Dx, g cm-3	1.261	1.261
Z	8	8
Mu (mm-1)	0.086	0.086
F000	1136.0	1136.0
F000'	1136.57	
h,k,lmax	14,9,13	14,9,13
Nref	2174 [1146]	2171
Tmin,Tmax	0.996,0.998	0.880,1.000
Tmin'	0.996	

Correction method= MULTI-SCAN

Data completeness= 1.89/1.00 Theta (max)= 18.730

R(reflections)= 0.0424 (1922) wR2(reflections)= 0.1218 (2171)

S = 1.009 Npar= Npar = 361

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT089_ALERT_3_A Poor Data / Parameter Ratio (Zmax < 18) 3.17 Note

Alert level B

PLAT080_ALERT_2_B Maximum Shift/Error 0.19
PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds 0.0144 Ang.

Alert level C

PLAT230_ALERT_2_C Hirshfeld Test Diff for C31 -- C32 .. 5.6 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C32 -- C33 .. 6.9 su
PLAT234_ALERT_4_C Large Hirshfeld Difference O1 -- C1 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C1 -- C2 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C12 -- C13 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C23 -- C24 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C24 -- C25 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O31 -- C31 .. 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C33 -- C41 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C41 -- C42 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C44 -- C45 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C45 -- C46 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C55 -- C56 .. 0.18 Ang.
PLAT334_ALERT_2_C Small Average Benzene C-C Dist. C41 -C46 1.37 Ang.

Alert level G

PLAT005_ALERT_5_G No iucr_refine_instructions_details in the CIF Please Do !
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High . 0.600 Why ?
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2 Note
C17 H16 O3

-
- 1 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
14 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected
- 0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
13 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
-

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

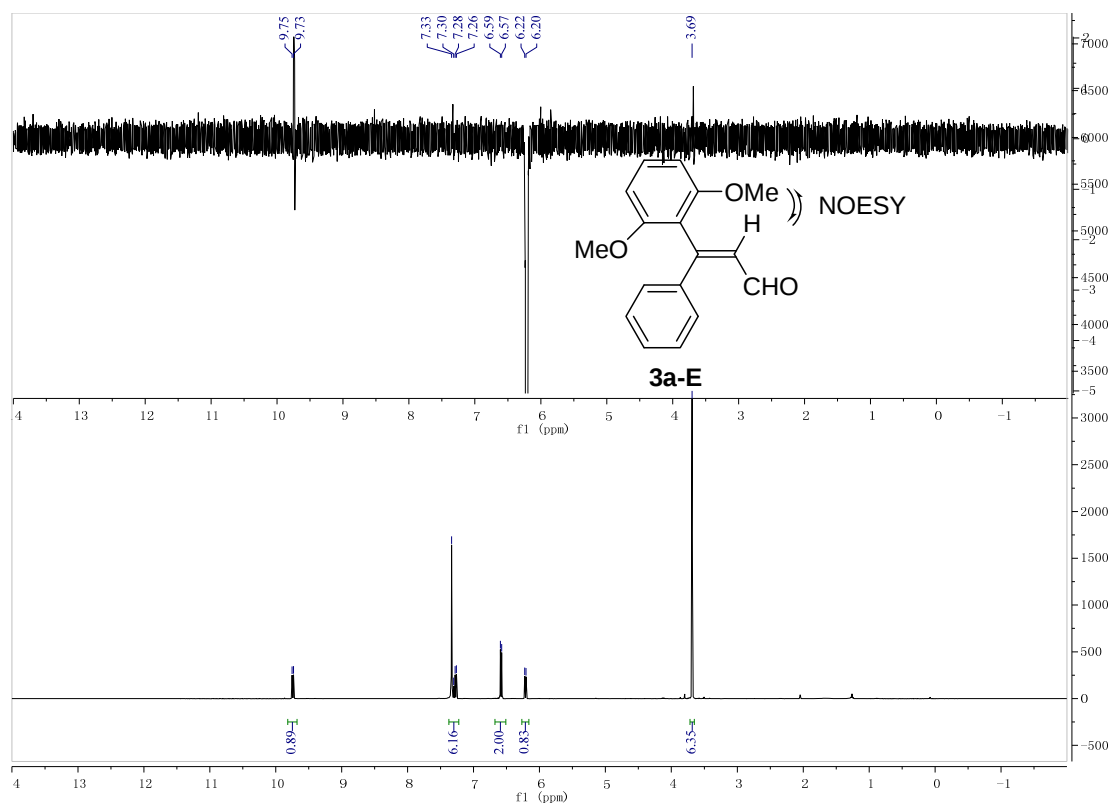
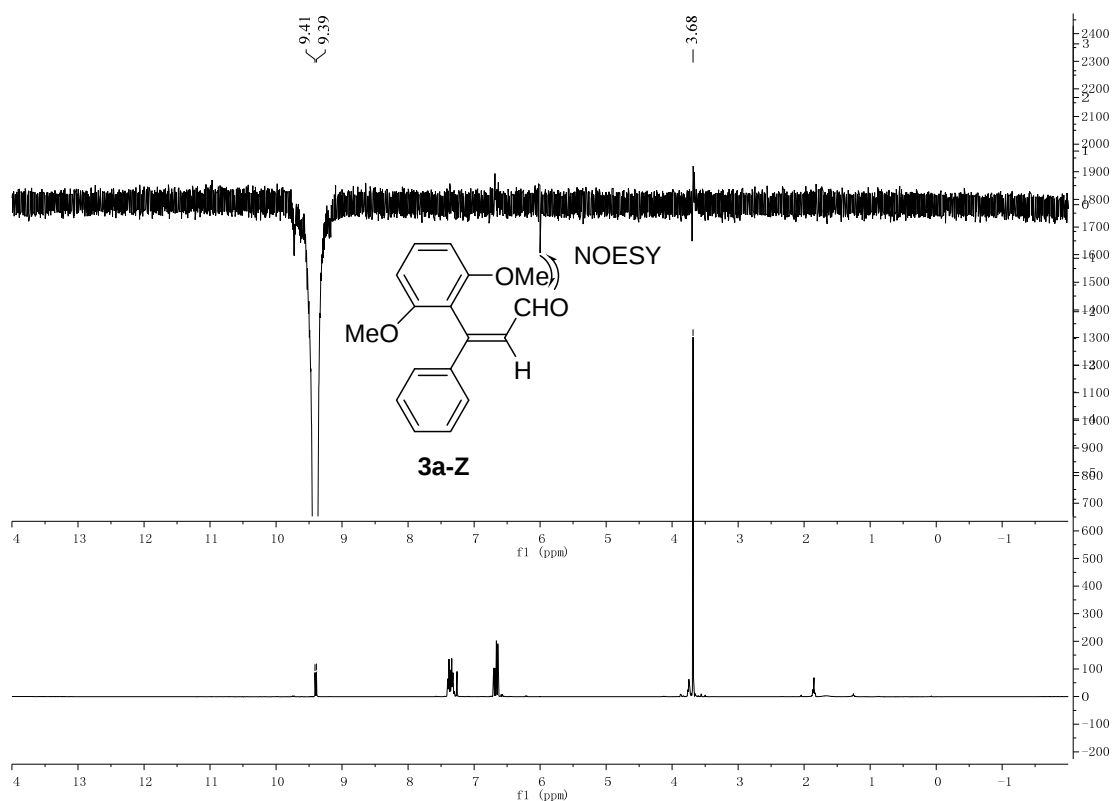
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

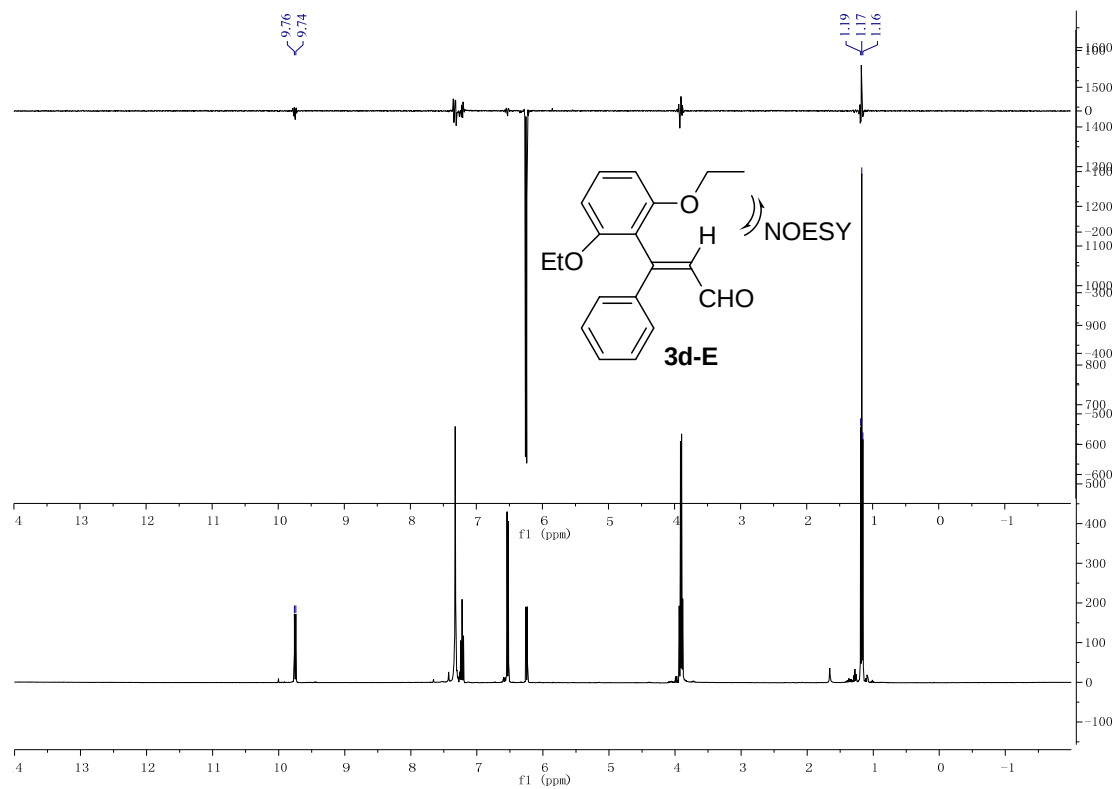
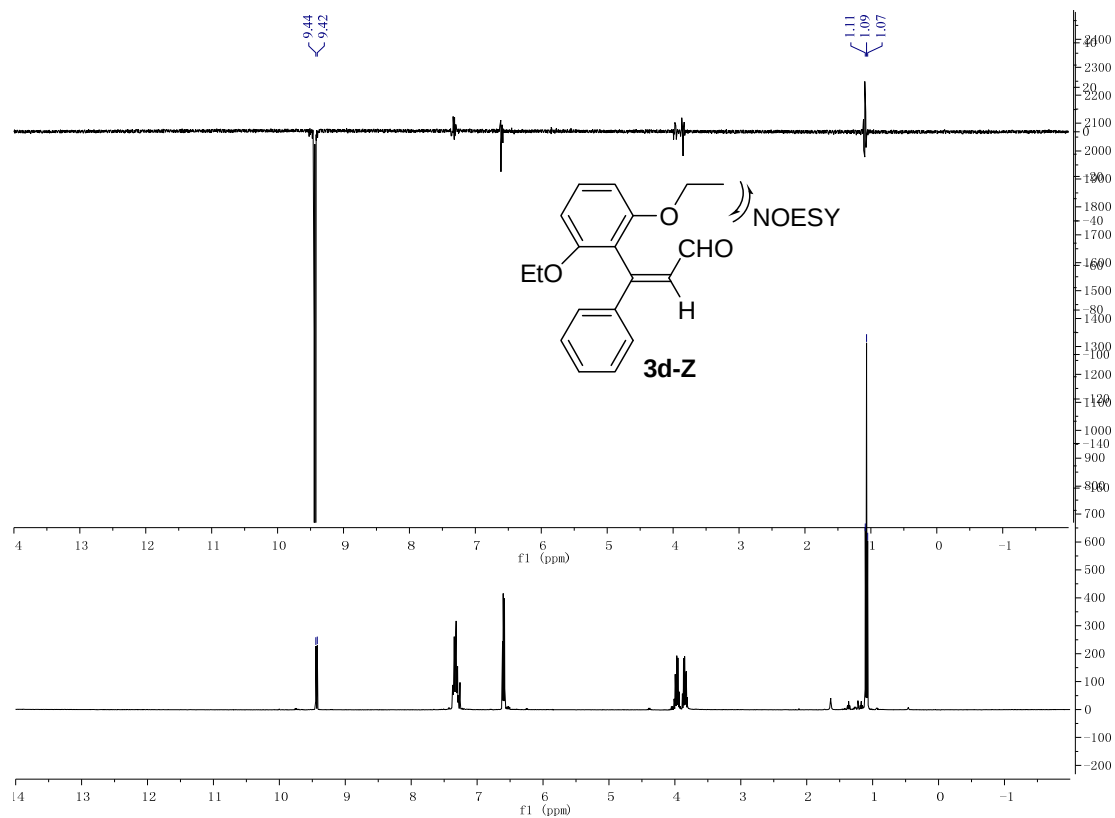
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

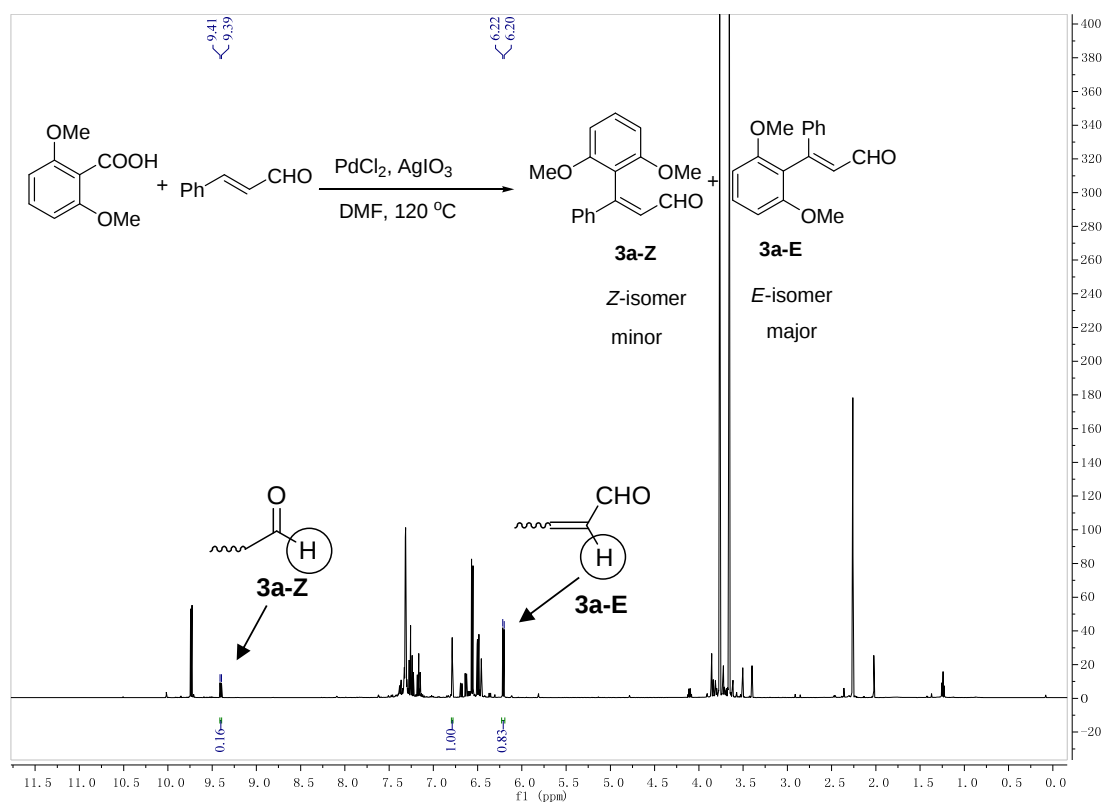
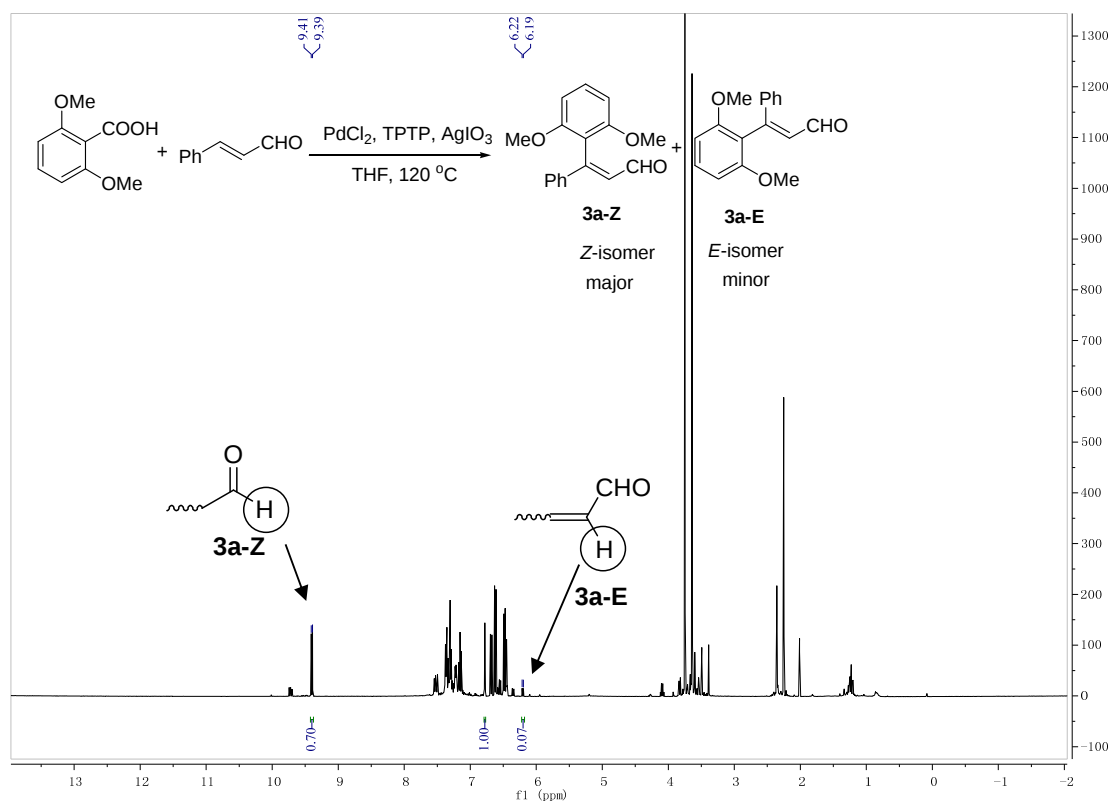
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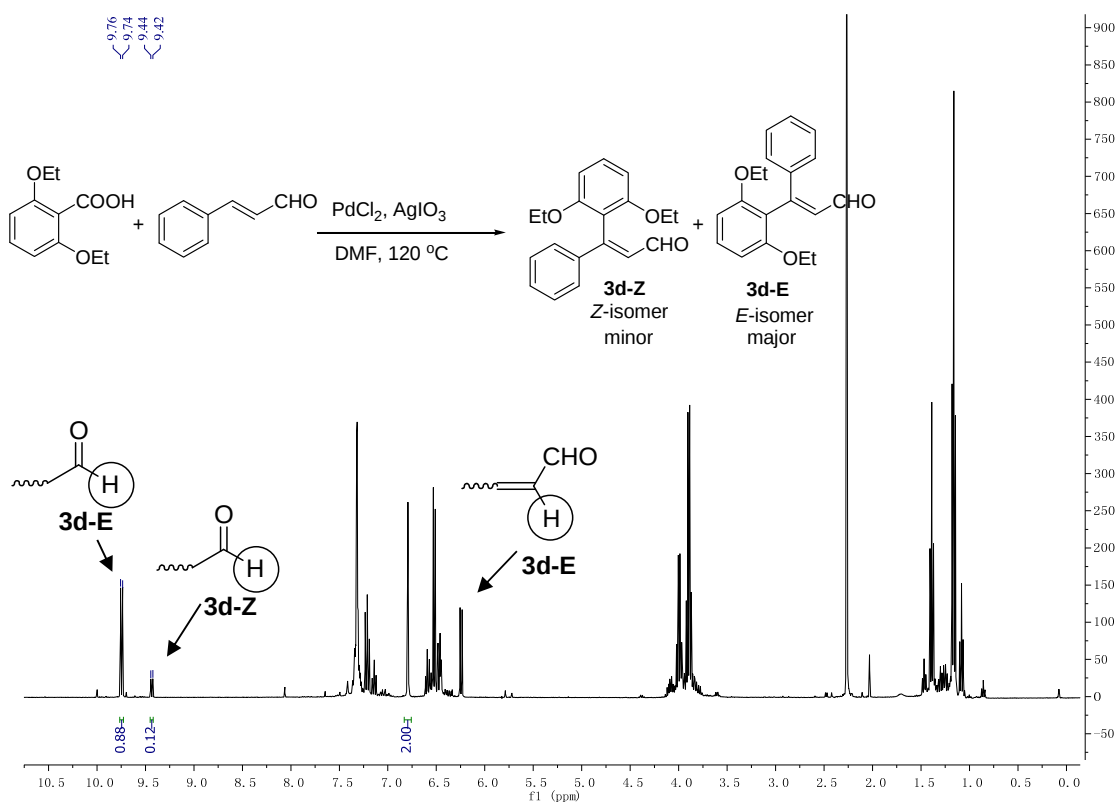
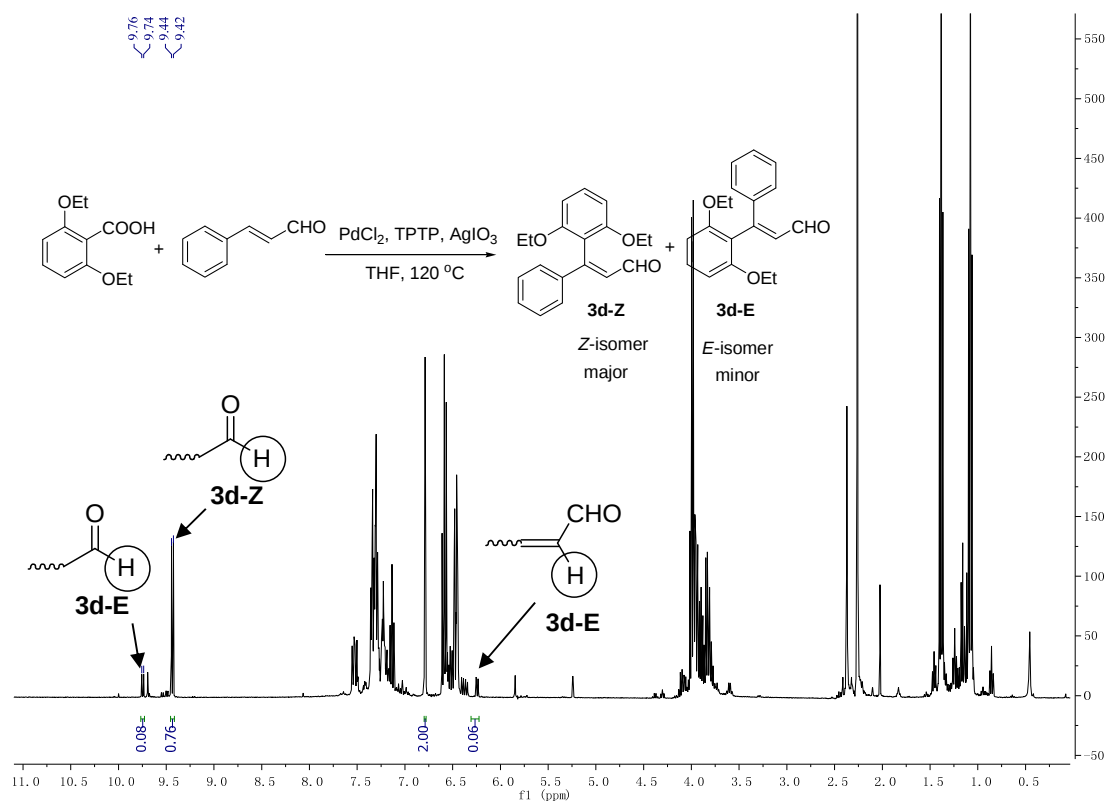
7. Selected NOESY spectra



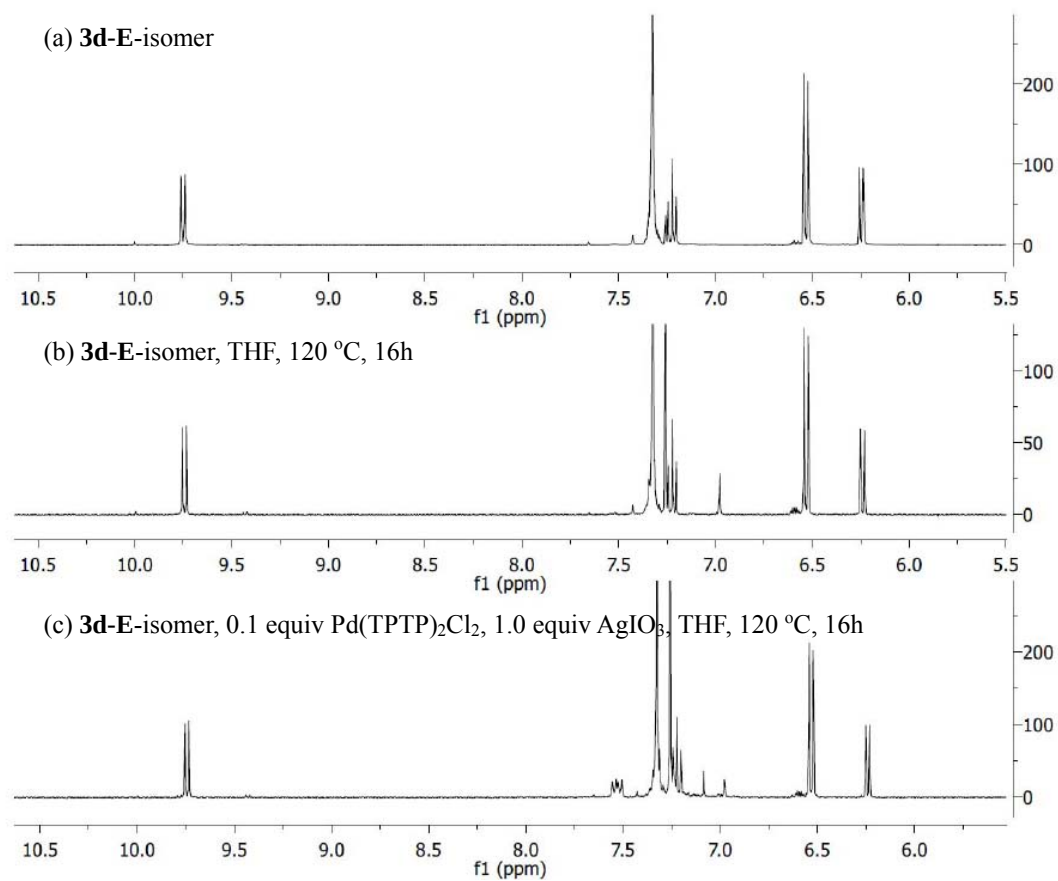


8. Selected ^1H NMR spectra of crude reaction mixtures





9. Isomerization experiments of 3d-E



10. DFT calculations

All calculations were performed with Gaussian 09. Molecular geometries were fully optimized with the B3LYP method. The LanL2DZ basis sets with effective core potentials (ECPs) were employed for Pd, and the 6-31G basis set was used for H, C, N, O.

Table S1 Total Energies, Internal Energies, Enthalpies and Free Energies of 3a-Z and 3a-E

	THF		DMF	
	3a-Z	3a-E	3a-Z	3a-E
$E_0/\text{Hartree}$	-882.552880	-882.549358	-882.555725	-882.552143
$E/\text{Hartree}$	-882.534469	-882.530957	-882.537294	-882.533730
$H/\text{Hartree}$	-882.533525	-882.530013	-882.536350	-882.532786
$G/\text{Hartree}$	-882.601025	-882.597445	-882.604073	-882.600251
$\Delta G_{Z-E}/\text{kcal/mol}$	-2.25		-2.40	

Table S2 Cartesian Coordinates of the Optimized Complexes

(a) 3a-Z in THF				C	2.823241	-1.926372	-2.146963
C	-0.315842	-0.697852	0.453247	H	2.585702	-2.974601	-2.320784
C	-0.070495	-1.743443	1.292737	H	2.799153	-1.377143	-3.093744
H	-0.849658	-2.467814	1.510014	H	3.814806	-1.840681	-1.691186
C	1.205585	-1.990028	1.935588	C	-0.448213	3.261500	1.859744
H	1.999628	-1.247833	1.763542	H	-0.588432	3.963176	1.031223
O	1.426750	-2.982891	2.669115	H	-1.337824	3.245799	2.487212
C	-1.666341	-0.480937	-0.124547	H	0.421850	3.556626	2.455054
C	-1.813694	0.160608	-1.372127	(b) 3a-E in THF			
C	-2.830142	-0.920515	0.543306	C	-0.288679	0.615512	-0.394567
C	-3.077010	0.335846	-1.943303	C	-0.309842	1.734705	-1.175036
C	-4.092252	-0.738698	-0.025516	H	0.593191	2.021559	-1.705482
C	-4.221584	-0.113713	-1.273511	C	-1.417251	2.666985	-1.297812
H	-3.167424	0.822458	-2.909112	H	-2.280653	2.516120	-0.633455
H	-4.975319	-1.074682	0.508343	O	-1.404835	3.641832	-2.087659
H	-5.203325	0.027241	-1.713869	C	0.996270	-0.119613	-0.204115
C	0.766042	0.256599	0.050574	C	1.119325	-1.462483	-0.626543
C	0.734491	1.592157	0.503845	C	2.119127	0.490766	0.399809
C	1.810421	-0.127837	-0.816676	C	2.311173	-2.178185	-0.450282
C	1.708661	2.519472	0.109467	C	3.316299	-0.217379	0.584299
C	2.790518	0.790907	-1.221703	C	3.398438	-1.544131	0.156028
C	2.727363	2.105262	-0.752692	H	2.400646	-3.203452	-0.783370
H	1.683619	3.540689	0.465427	H	4.171050	0.249311	1.054832
H	3.587965	0.495319	-1.889987	H	4.324695	-2.091786	0.294912
H	3.485060	2.817452	-1.062169	C	-1.487554	0.079487	0.303102
H	-0.932410	0.509988	-1.898042	C	-1.386646	-0.347566	1.643436
H	-2.748759	-1.377888	1.523144	C	-2.734264	-0.028046	-0.346536
O	1.785514	-1.451144	-1.238297	C	-2.506680	-0.832940	2.323040
O	-0.307157	1.894553	1.369946				

H	-0.430582	-0.282862	2.151974
C	-3.851908	-0.523139	0.332379
H	-2.814018	0.237959	-1.395036
C	-3.743936	-0.921203	1.670671
H	-2.414718	-1.143860	3.358755
H	-4.801546	-0.607558	-0.186009
H	-4.611599	-1.305750	2.196903
O	1.946508	1.803442	0.819682
O	-0.002214	-1.992021	-1.248557
C	3.053530	2.490298	1.475618
H	3.918955	2.568389	0.809782
H	2.671561	3.484215	1.703107
H	3.340530	1.980907	2.401340
C	0.016161	-3.383936	-1.683824
H	0.781255	-3.545395	-2.450052
H	0.186409	-4.058642	-0.838728
H	-0.972210	-3.559966	-2.105196

(c) **3a-Z** in DMF

C	-0.323637	-0.685940	0.467622
C	-0.088403	-1.716430	1.329416
H	-0.874954	-2.427505	1.563679
C	1.185730	-1.961042	1.974825
H	1.987207	-1.231736	1.784636
O	1.398863	-2.940341	2.730436
C	-1.671426	-0.466166	-0.114639
C	-1.811068	0.161398	-1.370644
C	-2.840317	-0.887798	0.556680
C	-3.071997	0.340524	-1.946150
C	-4.099891	-0.701648	-0.016563
C	-4.221565	-0.090692	-1.272526
H	-3.156617	0.816108	-2.917829
H	-4.986729	-1.023306	0.519669
H	-5.201258	0.053594	-1.716127
C	0.768856	0.248211	0.045849
C	0.762107	1.587935	0.487703
C	1.797625	-0.160728	-0.828738
C	1.746856	2.496152	0.075808
C	2.788024	0.738737	-1.251250
C	2.750136	2.057957	-0.792808
H	1.741550	3.520883	0.422232
H	3.573999	0.425537	-1.925080
H	3.515658	2.755312	-1.116221
H	-0.926296	0.497061	-1.899538

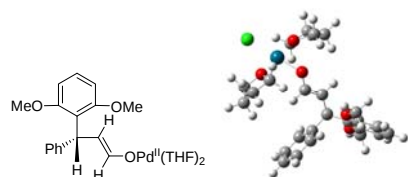
H	-2.765501	-1.334741	1.541810
O	1.746124	-1.487039	-1.239565
O	-0.266909	1.914071	1.360877
C	2.763997	-1.983795	-2.161244
H	2.507323	-3.028826	-2.326971
H	2.734961	-1.438198	-3.109634
H	3.762725	-1.911582	-1.719583
C	-0.378769	3.287626	1.843951
H	-0.514256	3.986165	1.012360
H	-1.262270	3.291842	2.480178
H	0.502291	3.570049	2.428669

(d) **3a-E** in DMF

C	-0.299054	0.604185	-0.403681
C	-0.335039	1.709179	-1.204670
H	0.563583	1.994443	-1.743798
C	-1.451110	2.627864	-1.339685
H	-2.311049	2.481245	-0.670440
O	-1.450144	3.590023	-2.146551
C	0.996399	-0.110735	-0.204903
C	1.144026	-1.450762	-0.628309
C	2.104161	0.517999	0.407976
C	2.346700	-2.146234	-0.445396
C	3.311999	-0.169913	0.599124
C	3.419090	-1.494471	0.169062
H	2.456039	-3.169414	-0.778757
H	4.155728	0.309906	1.076228
H	4.353394	-2.026681	0.313389
C	-1.488535	0.065169	0.306405
C	-1.374074	-0.351028	1.649487
C	-2.739742	-0.057146	-0.332940
C	-2.485249	-0.839512	2.341443
H	-0.414877	-0.275524	2.150521
C	-3.848251	-0.555743	0.358437
H	-2.830612	0.199022	-1.383010
C	-3.726874	-0.942336	1.699116
H	-2.382905	-1.141893	3.378598
H	-4.800880	-0.652307	-0.152096
H	-4.587294	-1.329780	2.234826
O	1.905461	1.826715	0.829534
O	0.034977	-1.998383	-1.258110
C	2.995992	2.529733	1.498926
H	3.865351	2.624938	0.840884
H	2.595552	3.516056	1.727691

H	3.282863	2.020541	2.424423
C	0.082385	-3.389380	-1.699249
H	0.856519	-3.533024	-2.459507
H	0.258402	-4.063728	-0.855380
H	-0.899107	-3.581855	-2.129408

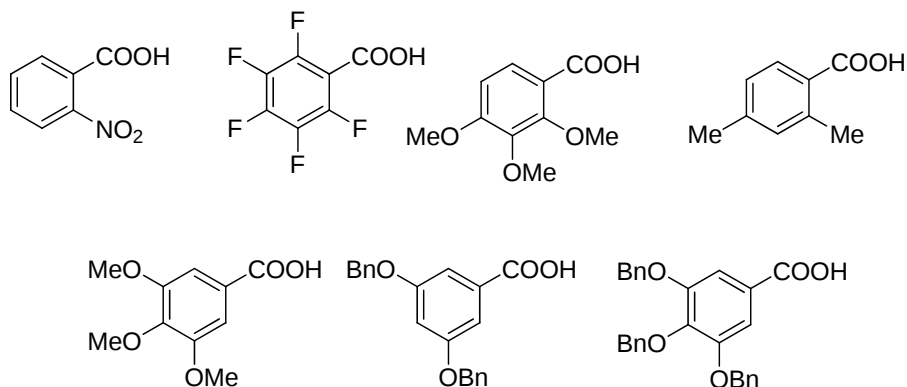
(e) Palladium(II) enolate in THF



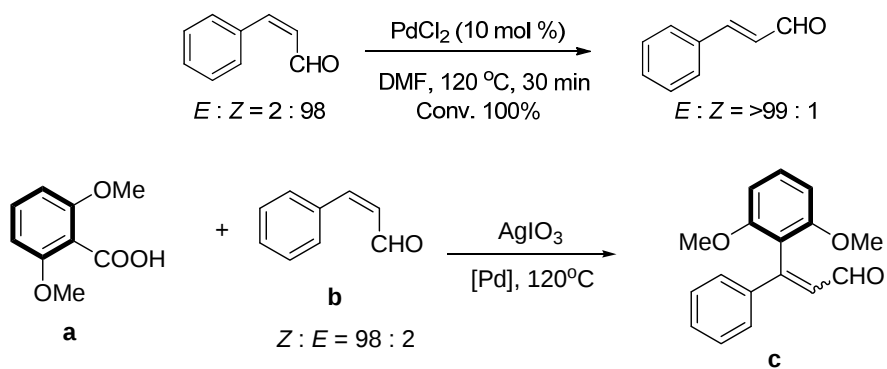
C	-1.059589	-0.516591	0.330989
H	-1.142379	-1.440993	0.905081
C	0.117209	0.158404	0.375807
H	0.251682	1.093936	-0.174976
C	-3.617302	-0.363089	0.279905
C	-4.682135	-1.022820	-0.390047
C	-3.855672	0.039944	1.619364
C	-5.917643	-1.288699	0.238009
C	-5.082662	-0.224672	2.267956
C	-6.103077	-0.887129	1.569688
H	-6.718569	-1.793088	-0.290126
H	-5.248132	0.084835	3.293491
H	-7.049906	-1.087358	2.064564
C	-2.219854	1.253709	-1.136915
C	-2.334700	2.449147	-0.388704
C	-2.025542	1.351043	-2.532698
C	-2.263365	3.703359	-1.023029
H	-2.473710	2.386903	0.686141
C	-1.950212	2.605532	-3.171676
H	-1.936980	0.441448	-3.123785
C	-2.070686	3.788926	-2.417901
H	-2.357368	4.612410	-0.432474
H	-1.802570	2.656921	-4.248169
H	-2.017384	4.759040	-2.906816
O	-2.817081	0.726888	2.255863
O	-4.423270	-1.395930	-1.716578
C	-2.949847	1.071650	3.670550
H	-3.107010	0.175023	4.283308
H	-2.001386	1.539981	3.939814
H	-3.772052	1.780676	3.831692
C	-5.456015	-2.104818	-2.470413

H	-5.711641	-3.058467	-1.991245
H	-6.357872	-1.489587	-2.579434
H	-5.016891	-2.291127	-3.452255
O	1.172289	-0.236016	1.171322
Cl	5.135220	-0.684687	-0.873047
C	-2.295255	-0.133912	-0.479132
H	-2.337034	-0.851047	-1.309219
Pd	2.953660	-0.435340	0.230106
C	3.487396	2.532728	-0.721007
C	3.221557	3.833064	1.313544
C	3.011241	3.907352	-0.221923
H	2.910830	2.140282	-1.561929
H	4.555113	2.502374	-0.952951
H	2.592595	4.548189	1.852744
H	4.269161	4.029821	1.568380
H	1.950918	4.057096	-0.455235
H	3.583338	4.720027	-0.679634
C	1.921505	-3.270795	1.122782
C	1.975760	-4.543903	-0.949496
C	1.161109	-4.370046	0.360072
H	1.284551	-2.567598	1.661564
H	2.703528	-3.669938	1.776492
H	1.379168	-4.985993	-1.753513
H	2.854257	-5.176572	-0.778722
H	0.139510	-4.044663	0.131989
H	1.106866	-5.296575	0.939774
C	2.402180	-3.109633	-1.285317
H	3.343086	-3.019814	-1.830066
H	1.609251	-2.550402	-1.796103
C	2.846164	2.384394	1.652981
H	3.390619	1.965628	2.502380
H	1.771285	2.236281	1.787114
O	2.625998	-2.486921	0.054273
O	3.270144	1.616826	0.443709

11. Other acids that were tested but not effective in this system:



12. Experiments using *cis*-cinnamaldehyde as the substrate:



DMF-conditions	a (36.4 mg, 2 equiv), b (13.1 mg, 1 equiv), PdCl ₂ (1.8 mg, 10 mol %), AgIO ₃ (28.0 mg, 1 equiv), DMF (1.0 mL), 120 °C, 1 h.	NMR Yield = 73 % Z- c : E- c = 14 : 86
THF-conditions	a (43.7 mg, 2 equiv), b (15.4 mg, 1 equiv), PdCl ₂ (TPTP) ₂ (9.4 mg, 10 mol %), AgIO ₃ (33.9 mg, 1 equiv), THF (1.0 mL), 120 °C, 24 h.	NMR Yield = 52 % Z- c : E- c = 85 : 15