Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Olefination of aldehydes with alpha-halo redox-active esters

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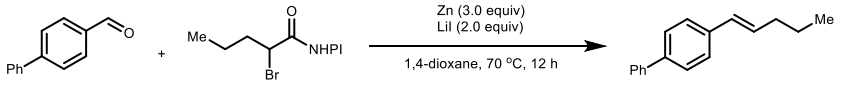
1. General Information

Commercial reagents were purchased from Energy, TCI, J&K, Accela, Macklin or Adamas and used without further purification. The anhydrous solvents used in the experiments were all purchased and used directly. All reactions were carried out with the oven-dried glassware or Schlenk tube. Analytical thin layer chromatography (TLC) was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China). Column chromatography was performed on 200-300 mesh silica gel or 300-400 mesh silica gel (General-Reagent, China). Aldehydes of **2a**-**2v** were commercially available. Aldehydes of **2w**-**2aa** were synthesized according to reported methods.[1] All NHPI esters were synthesized according to reported methods.[2]

^{1}H NMR (400 MHz or 600 MHz) and ^{13}C NMR (101 MHz or 151 MHz) were recorded on an NMR spectrometer with $CDCl_3$ as the solvent. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). High resolution mass spectrometry data of new compounds were recorded on an LTQ Orbitrap Elite LC/MS (ESI or APCI). GC-MS data were collected by an Agilent 5977B instrument. Cyclic Voltammetry measurements were carried out with a CHI600E apparatus. UV-vis spectra were collected by a Shimadzu UV-2600 ultra-violet and visible spectrophotometer. The room temperature ranges from 20 ℃ to 34 ℃.

2. Experimental procedures

4-(pent-1-en-1-yl)-1,1'-biphenyl (3a)



1a, 0.2 mmol **2a**, 2.0 equiv **3a**, 95%, E/Z = 1.8:1

Under the argon atmosphere, 4-biphenylcarboxaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0

mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3a** as a white solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 42.2 mg (95%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62-7.55 (m, 3H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.44-7.39 (m, 3H), 7.37-7.30 (m, 2H), 6.46-6.38 (m, 1H), 6.30-6.23 (m, 1H), 2.23-2.17 (m, 2H), 1.53-1.48 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H).

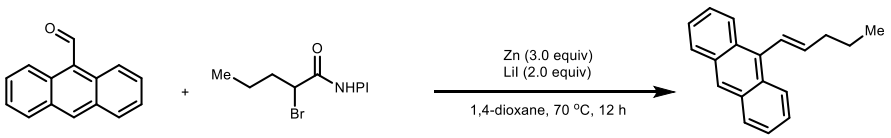
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62-7.55 (m, 3H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.44-7.39 (m, 3H), 7.37-7.30 (m, 2H), 6.46-6.38 (m, 1H), 5.72-5.66 (m, 1H), 2.38-2.33 (m, 2H), 1.53-1.48 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.93, 139.56, 137.06, 131.21, 129.22, 128.77, 128.75, 127.19, 126.90, 126.34, 35.20, 22.58, 13.74.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.92, 139.22, 136.93, 133.32, 129.49, 128.77, 128.45, 127.13, 126.99, 126.82, 30.87, 23.19, 13.87.

Spectroscopic data are in accordance with that reported in the literature.[3]

9-(pent-1-en-1-yl)anthracene (3b)



1b, 0.2 mmol **2a**, 2.0 equiv **3b**, 70%, E/Z = 3.9:1

Under the argon atmosphere, anthracene-9-carbaldehyde **1b** (0.2 mmol, 41.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford

3b yield as a yellow solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 34.5 mg (70%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.32-8.27 (m, 2H), 8.00-7.90 (m, 2H), 7.47-7.37 (m, 4H), 7.10 (d, *J* = 16.4 Hz, 1H), 6.06-5.94 (m, 1H), 2.50-2.41 (qd, *J* = 7.2, 1.6 Hz, 2H), 1.78-1.62 (m, 2H), 1.10 (t, *J* = 7.2 Hz, 3H).

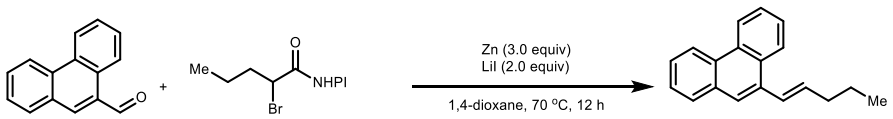
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.19-8.14 (m, 2H), 8.00-7.90 (m, 2H), 7.47-7.37 (m, 4H), 6.97 (d, *J* = 11.2 Hz, 1H), 6.28-6.20 (m, 1H), 2.50-2.41 (qd, *J* = 7.2 Hz, 1.6 Hz, 2H), 1.78-1.62 (m, 2H), 0.71 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.42, 136.56, 133.73, 131.54, 129.65, 128.57, 126.49, 126.25, 125.78, 125.54, 125.08, 125.03, 35.80, 22.68, 13.96.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.42, 136.56, 133.73, 131.41, 129.48, 128.57, 126.49, 126.25, 125.92, 125.35, 125.13, 125.03, 31.22, 22.21, 13.77.

HRMS (APCI) calcd for $(C_{19}H_{19})^+$ $[M + H]^+$: 247.1481, found: 247.1479.

9-(pent-1-en-1-yl)phenanthrene (3c)



Under the argon atmosphere, phenanthrene-9-carbaldehyde **1c** (0.2 mmol, 41.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate =100:1) to afford **3c** as a white solid.

R_f = 0.7 (eluent: petroleum ether/EtOAc = 50:1).

Yield 43.5 mg (89%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.2 Hz, 1H), 8.66 (d, *J* = 7.6 Hz, 1H), 8.22-8.16 (m, 1H), 7.90-7.84 (m, 1H), 7.79 (s, 1H), 7.70-7.55 (m, 4H), 7.12 (d, *J* = 15.6 Hz, 1H), 6.37-6.26 (m, 1H), 2.41-2.31 (m, 2H), 1.70-1.58 (m, 2H), 1.09-1.01 (m, 3H).

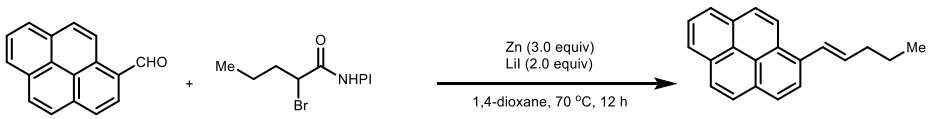
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 7.2 Hz, 1H), 8.66 (d, J = 7.6 Hz, 1H), 8.12-8.07 (m, 1H), 7.90-7.84 (m, 1H), 7.79 (s, 1H), 7.70-7.55 (m, 4H), 6.90 (d, J = 11.6 Hz, 1H), 6.05-5.96 (m, 1H), 2.25-2.17 (m, 2H), 1.49-1.40 (m, 2H), 1.09-1.01 (m, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.74, 134.64, 130.88, 130.38, 129.98, 128.46, 127.67, 126.66, 126.48, 126.33, 126.14, 124.83, 124.29, 123.02, 122.49, 35.49, 22.61, 13.82.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.78, 133.45, 131.68, 131.44, 129.90, 128.49, 127.27, 126.87, 126.64, 126.46, 126.37, 125.81, 124.83, 124.29, 122.88, 122.52, 30.76, 22.99, 13.82.

Spectroscopic data are in accordance with that reported in the literature.[4]

1-(pent-1-en-1-yl)pyrene (3d)



1d, 0.2 mmol **2a**, 2.0 equiv **3d**, 80%, E/Z = 3.3:1

Under the argon atmosphere, pyrene-1-carbaldehyde **1d** (0.2 mmol, 46.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3d** as a yellow solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 43.3 mg (80%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 9.2 Hz, 1H), 8.20-8.11 (m, 4H), 8.11 -

8.02 (m, 3H), 8.02-7.89 (m, 1H), 7.44 (d, *J* = 15.6 Hz, 1H), 6.51-6.41 (m, 1H), 2.42 (q, *J* =6.8 Hz, 2H), 1.72-1.61 (m, 2H), 1.08 (td, *J* = 7.2 Hz, 2.0 Hz, 3H).

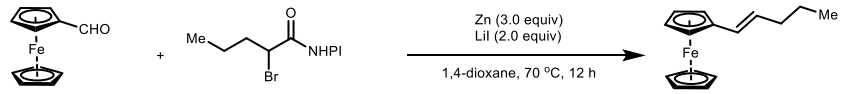
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.2 Hz, 1H), 8.20-8.11 (m, 4H), 8.11 - 8.02 (m, 3H), 8.02-7.89 (m, 1H), 7.18 (d, *J* = 11.6 Hz, 1H), 6.11-6.02 (m, 1H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.51-1.44 (m, 2H), 0.88 (td, *J* = 7.6 Hz, 2.4 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.77, 131.58, 131.04, 130.33, 127.77, 127.49, 127.22, 127.21, 127.18, 127.13, 126.85, 125.86, 125.04, 125.01, 124.99, 124.77, 123.97, 123.36, 35.84, 22.72, 13.88.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.89, 131.42, 130.25, 128.87, 127.77, 127.54, 127.48, 127.18, 127.13, 127.02, 125.06, 125.01, 124.99, 124.91, 124.72, 124.35, 30.85, 22.90, 13.81.

HRMS (APCI) calcd for $(C_{21}H_{19})^+$ $[M + H]^+$: 271.1481, found: 271.1479.

Ferrocene pent-1-ene (3e)



1e, 0.2 mmol **2a**, 2.0 equiv **3e**, 88%, E/Z = 1.8:1

Under the argon atmosphere, ferrocenecarboxaldehyde **1e** (0.2 mmol, 43.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether) to afford **3e** as a brown liquid.

R_f = 0.9 (eluent: petroleum ether).

Yield 44.7 mg (88%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10-6.01 (m, 1H), 5.83-5.73 (m, 1H), 4.30 (dt, *J* = 11.2 Hz, 2.0 Hz, 2H), 4.16 (dt, *J* = 13.6 Hz, 1.6 Hz, 2H), 4.09 (d, *J* = 4.0 Hz, 5H), 2.05 (qd, *J* = 7.2 Hz, 1.6 Hz, 2H), 1.49-1.38 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10-6.01 (m, 1H), 5.49-5.41 (m, 1H), 4.30 (dt, *J* = 11.2 Hz, 2.0 Hz, 2H), 4.16 (dt, *J* = 13.6 Hz, 1.6 Hz, 2H), 4.09 (d, *J* = 4.0 Hz, 5H), 2.23

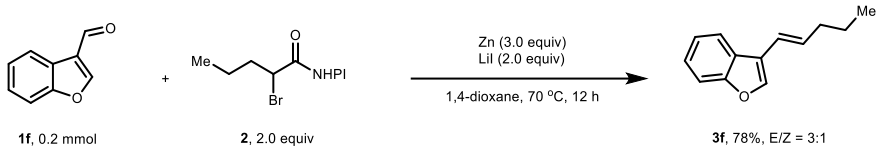
(qd, J = 7.2 Hz, 1.6 Hz, 2H), 1.49-1.38 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ128.30, 126.69, 84.42, 69.06, 68.14, 66.30, 35.11, 22.61, 13.66.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.76, 125.82, 82.45, 69.09, 68.27, 66.30, 31.11, 22.94, 13.97.

HRMS (APCI) calcd for $(C_{15}H_{19}Fe)^+$ $[M + H]^+$: 255.0831, found: 255.0829.

3-(pent-1-en-1-yl)benzofuran (3f)



1f, 0.2 mmol **2**, 2.0 equiv **3f**, 78%, E/Z = 3:1

Under the argon atmosphere, benzofuran-3-carbaldehyde **1f** (0.2 mmol, 29.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3f** as a colorless liquid.

$\mathbf{R_f}$ = 0.7 (eluent: petroleum ether/EtOAc = 50:1).

Yield 29.0 mg (78%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 1H), 7.58 (s, 1H), 7.50-7.44 (m, 1H), 7.33-7.22 (m, 2H), 6.47-6.37 (m, 1H), 6.36-6.26 (m, 1H), 2.30-2.17 (m, 2H), 1.56-1.47 (m, 2H), 0.98 (t, J = 7.6 Hz, 3H).

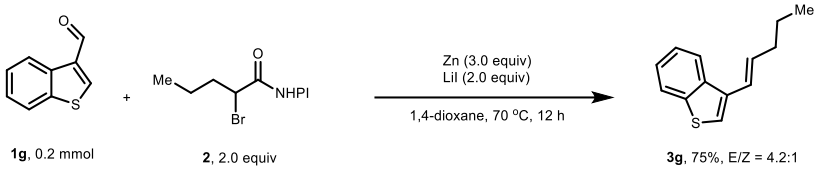
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 1H), 7.62 (s, 1H), 7.50-7.44 (m, 1H), 7.33-7.22 (m, 2H), 6.47-6.37 (m, 1H), 5.88-5.79 (m, 1H), 2.30-2.17 (m, 2H), 1.56-1.47 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.78, 142.12, 132.19, 124.41, 122.72, 120.80, 119.68, 119.24, 116.61, 111.59, 35.62, 22.71, 13.73.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.73, 142.02, 134.41, 126.25, 122.57, 120.80, 119.52, 119.24, 116.61, 111.35, 31.97, 22.62, 13.89.

HRMS (APCI) calcd for $(C_{13}H_{15}O)^+$ $[M + H]^+$: 187.1117, found: 187.1116.

3-(pent-1-en-1-yl)benzo[b]thiophene (3g)



1g, 0.2 mmol **2**, 2.0 equiv **3g**, 75%, E/Z = 4.2:1

Under the argon atmosphere, benzo[*b*]thiophene-3-carbaldehyde **1g** (0.2 mmol, 32.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3g** as a colorless liquid.

R_f = 0.7 (eluent: petroleum ether/EtOAc = 50:1).

Yield 30.5 mg (75%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.42-7.30 (m, 3H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.32-6.22 (m, 1H), 2.46 (q, *J* = 7.6 Hz, 2H), 1.59-1.45 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

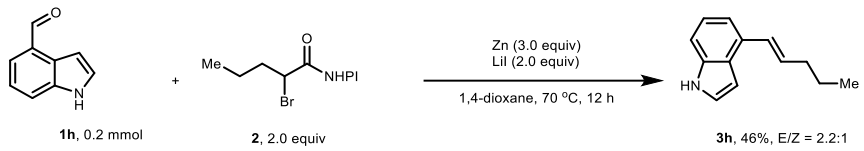
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.37-7.23 (m, 3H), 6.57 (d, *J* = 11.6 Hz, 1H), 5.91-5.82 (m, 1H), 2.31 (q, *J* = 7.2 Hz, 2H), 1.59-1.45 (m, 2H), 0.94 (t, *J* = 8.0 Hz, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.48, 137.92, 134.65, 133.03, 124.29, 124.06, 122.85, 122.23, 122.02, 120.47, 35.44, 22.58, 13.75.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.64, 139.12, 134.94, 132.86, 124.33, 124.04, 123.01, 122.63, 122.11, 120.87, 31.44, 22.97, 13.86.

HRMS (APCI) calcd for $(C_{13}H_{15}S)^+$ $[M + H]^+$: 203.0889, found: 203.0891.

4-(pent-1-en-1-yl)-1H-indole (3h)



1h, 0.2 mmol **2**, 2.0 equiv **3h**, 46%, E/Z = 2.2:1

Under the argon atmosphere, 1*H*-indole-4-carbaldehyde **1h** (0.2 mmol, 29.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford **3h** as a colorless liquid.

R_f = 0.4 (eluent: petroleum ether/EtOAc = 50:1).

Yield 17.0 mg (46%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.21-7.17 (m, 2H), 7.16-7.13 (m, 1H), 6.80-6.74 (m, 1H), 6.73 (t, *J* = 2.4 Hz, 1H), 6.42-6.35 (m, 1H), 2.34-2.24 (m, 2H), 1.55 (q, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

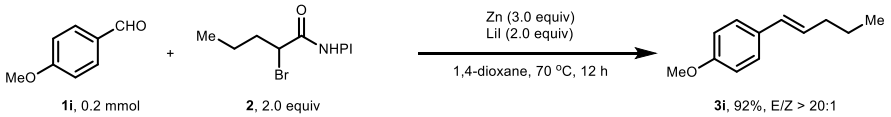
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.22-7.16 (m, 2H), 7.14-7.05 (m, 1H), 6.80-6.74 (m, 1H), 6.57 (t, *J* = 2.4 Hz, 1H), 5.83-5.76 (m, 1H), 2.34-2.24 (m, 2H), 1.47 (q, *J* = 7.2 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.20, 133.27, 131.90, 128.27, 126.66, 123.99, 122.16, 116.85, 109.56, 101.28, 35.60, 22.75, 13.78.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.76, 134.73, 130.46, 128.27, 125.85, 123.76, 121.72, 119.69, 109.56, 101.60, 31.19, 23.21, 13.87.

HRMS (ESI) calcd for $(C_{13}H_{16}N)^+$ $[M + H]^+$: 186.1277, found: 186.1282.

(*E*)-1-methoxy-4-(pent-1-en-1-yl)benzene (3i)



1i, 0.2 mmol **2**, 2.0 equiv **3i**, 92%, E/Z > 20:1

Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3i** as a colorless liquid.

R_f = 0.7 (eluent: petroleum ether/EtOAc = 50:1).

Yield 32.4 mg (92%).

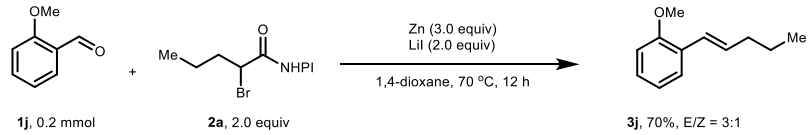
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.12-6.00 (m, 1H), 3.79 (s, 3H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.53-1.41 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.66, 130.86, 129.25, 128.84, 126.99, 113.93, 55.29, 35.11, 22.69, 13.73.

Spectroscopic data are in accordance with that reported in the literature.[5]

1-methoxy-2-(pent-1-en-1-yl)benzene (3j)



Under the argon atmosphere, 2-methoxybenzaldehyde **1j** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3j** as a colorless oil.

R_f = 0.7 (eluent: petroleum ether/EtOAc = 50:1).

Yield 24.6 mg (70%).

NMR spectroscopy:

(E): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.27-7.12 (m, 1H), 6.96-6.79 (m, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.25-6.15 (m, 1H), 3.83 (s, 3H), 2.20 (m, 2H), 1.57-1.42 (m, 2H), 0.99-0.89 (m, 3H).

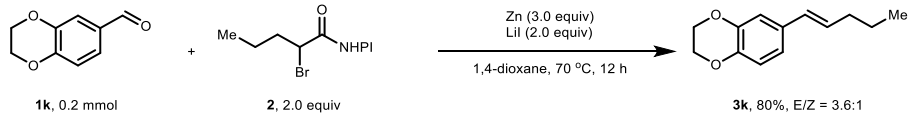
(Z): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.27-7.12 (m, 1H), 6.96-6.79 (m, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 5.76-5.68 (m, 1H), 3.83 (s, 3H), 2.20 (m, 2H), 1.57-1.42 (m, 2H), 0.99-0.89 (m, 3H).

(E): ^{13}C NMR (101 MHz, CDCl3) δ 156.30, 131.71, 130.06, 127.78, 126.39, 124.43, 120.66, 110.84, 55.48, 35.59, 22.70, 13.80.

(Z):^{13}C NMR (101 MHz, CDCl3) δ 157.04, 132.91, 130.06, 127.96, 127.08, 124.17, 120.01, 110.41, 55.45, 30.81, 23.15, 13.92.

GCMS: calcd for $C_{12}H_{16}O$ [M], 176.1, found 176.1.

6-(pent-1-en-1-yl)-2,3-dihydrobenzo[b][1,4]dioxine (3k)



1k, 0.2 mmol **2**, 2.0 equiv **3k**, 80%, E/Z = 3.6:1

Under the argon atmosphere, 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde **1k** (0.2 mmol, 32.8 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford **3k** as a colorless liquid.

R$_f$ = 0.7 (eluent: petroleum ether/EtOAc = 50:1).

Yield 32.7 mg (80%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 6.85-6.71 (m, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.24 (dt, *J* = 16.00 Hz, 6.8 Hz, 1H), 4.31-4.27 (m, 2H),

4.26-4.22 (m, 2H), 2.27-2.15 (m, 2H), 1.56-1.42 (m, 2H), 0.94 (dt, *J* = 6.4 Hz, 3H).

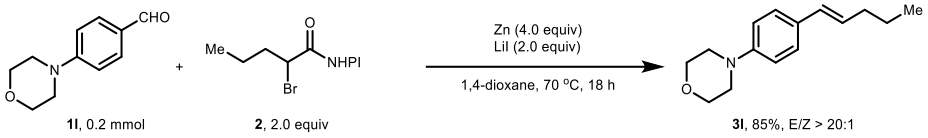
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 6.85-6.71 (m, 2H), 6.45 (d, *J* = 12.0 Hz, 1H), 5.75 (dt, *J* = 11.6 Hz, 7.6 Hz, 1H), 4.31-4.27 (m, 2H), 4.26-4.22 (m, 2H), 2.27-2.15 (m, 2H), 1.56-1.42 (m, 2H), 0.96 (dt, *J* = 7.6 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.64, 140.59, 132.33, 127.27, 123.60, 120.73, 118.58, 115.60, 64.36, 64.12, 35.56, 22.61, 13.77.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ143.48, 141.18, 133.63, 126.90, 123.16, 122.21, 120.21, 115.88, 64.49, 64.15, 30.91, 23.06, 13.89.

HRMS (APCI) calcd for $(C_{13}H_{17}O_2)^+$ $[M + H]^+$: 205.1223, found: 205.1222.

4-(4-(pent-1-en-1-yl)phenyl)morpholine (3l)



Under the argon atmosphere, 4-morpholinobenzaldehyde **1l** (0.2 mmol, 38.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.8 mmol, 52.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 18 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford **3l** as a colorless liquid.

R_f = 0.6 (eluent: petroleum ether/EtOAc = 50:1).

Yield 39.3 mg (85%).

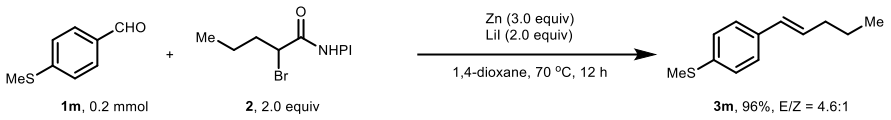
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.30 (d, *J* = 15.60 Hz, 1H), 6.12-6.03 (m, 1H), 3.89 -3.83 (m, 4H), 3.19-3.10 (m, 4H), 2.16 (q, *J* = 7.6 Hz, 2H), 1.53-1.42 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.18, 130.10, 129.32, 128.49, 126.76, 115.70, 66.91, 49.42, 35.14, 22.72, 13.73.

HRMS (ESI) calcd for $(C_{15}H_{22}NO)^+$ $[M + H]^+$: 232.1696, found: 232.1700.

methyl(4-(pent-1-en-1-yl)phenyl)sulfane (3m)



Under the argon atmosphere, 4-(methylthio)benzaldehyde **1m** (0.2 mmol, 30.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3m** as a brown liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 37.0 mg (96%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 16.2 Hz, 1H), 6.21-6.14 (m, 1H), 2.47 (s, 3H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.51-1.45 (m, 2H), 0.95 (t, *J* = 7.8 Hz, 3H).

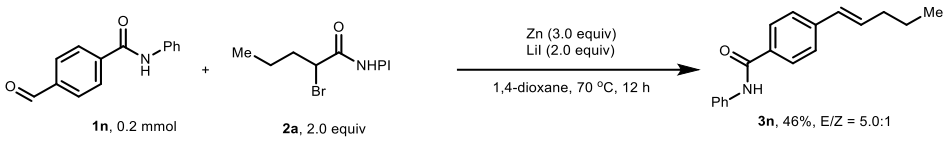
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 12.0 Hz, 1H), 5.66-5.61 (m, 1H), 2.48 (s, 3H), 2.29 (q, *J* = 7.2 Hz, 2H), 1.51-1.45 (m, 2H), 0.95 (t, *J* = 7.8 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.48, 135.20, 130.62, 129.26, 127.04, 126.36, 35.12, 22.55, 16.21, 13.72.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.31, 134.90, 132.92, 129.23, 128.22, 126.49, 30.77, 23.14, 16.02, 13.84.

Spectroscopic data are in accordance with that reported in the literature.[3]

4-(pent-1-en-1-yl)-N-phenylbenzamide (3n)



Under the argon atmosphere, 4-formyl-*N*-phenylbenzamide **1n** (0.2 mmol, 45.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford **3n** yield as a white solid.

R_f = 0.6 (eluent: petroleum ether/EtOAc = 10:1).

Yield 24.4 mg (46%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 3H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.39-6.29 (m, 1H), 2.23 (q, *J* = 6.8 Hz, 2H), 1.56-1.46 (m, 2H), 1.00-0.92 (m, 3H).

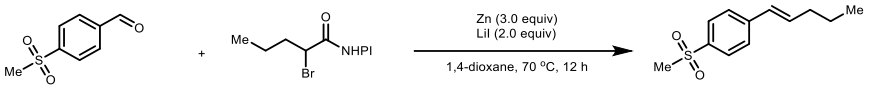
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 3H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 11.2 Hz, 1H), 5.82-5.74 (m, 1H), 2.31 (q, *J* = 7.2 Hz, 2H), 1.56-1.46 (m, 2H), 1.00-0.92 (m, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.40, 141.59, 138.03, 133.76, 132.92, 129.09, 129.01, 127.32, 126.16, 124.47, 120.18, 35.19, 22.37, 13.74.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.40, 141.59, 138.03, 135.12, 132.92, 129.01, 127.97, 126.90, 124.51, 120.18, 30.79, 23.02, 13.81.

HRMS (ESI) calcd for $(C_{18}H_{20}NO)^+$ $[M + H]^+$: 266.1539, found: 266.1544.

1-(methylsulfonyl)-4-(pent-1-en-1-yl)benzene (3o)



Under the argon atmosphere, 4-(methylsulfonyl)benzaldehyde **1o** (0.2 mmol, 36.8 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to afford **3o** as a yellow solid.

R_f = 0.5 (eluent: petroleum ether/EtOAc = 5:1).

Yield 24.0 mg (53%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.48-6.38 (m, 2H), 3.04 (s, 3H), 2.26-2.21 (m, 2H), 1.56-1.48 (m, 2H), 0.99-0.93 (m, 3H).

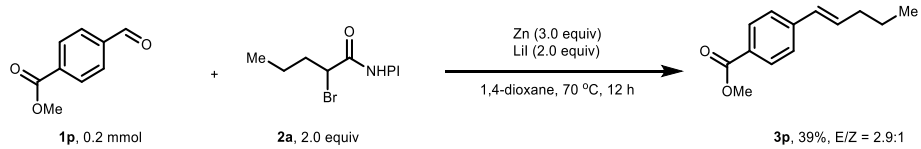
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.48-6.38 (m, 1H), 5.87-5.81 (m, 1H), 3.06 (s, 3H), 2.31-2.27 (m, 2H), 1.56-1.48 (m, 2H), 0.99-0.93 (m, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.46, 138.27, 135.63, 128.42, 127.69, 126.55, 44.61, 35.17, 22.23, 13.69.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.46, 136.46, 134.31, 129.46, 127.26, 126.55, 44.61, 30.72, 29.92, 13.76.

HRMS (ESI) calcd for $(C_{12}H_{17}SO_2)^+$ $[M + H]^+$: 225.0944, found: 225.0947.

methyl-4-(pent-1-en-1-yl)benzoate (3p)



Under the argon atmosphere, methyl 4-formylbenzoate **1p** (0.2 mmol, 32.8 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0

equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to afford **3p** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 30:1).

Yield 16.0 mg (39%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.47-6.31 (m, 2H), 3.90 (s, 3H), 2.25-2.17 (m, 2H), 1.56-1.45 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

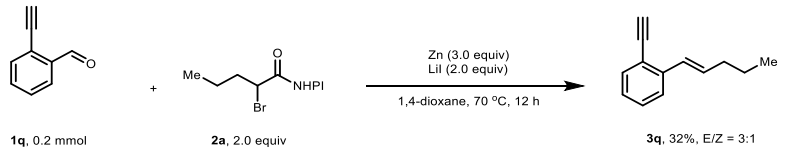
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.47-6.31 (m, 1H), 5.80-5.72 (m, 1H), 3.91 (s, 3H), 2.34-2.26 (m, 2H), 1.56-1.45 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.02, 142.50, 133.99, 129.88, 129.21, 128.66, 125.76, 51.96, 35.19, 22.34, 13.71.

(*Z*): δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.02, 142.50, 135.22, 129.44, 128.27, 128.14, 125.76, 51.96, 30.79, 23.00, 13.78.

Spectroscopic data are in accordance with that reported in the literature.[6]

1-ethynyl-2-(pent-1-en-1-yl)benzene (3q)



1q, 0.2 mmol **2a**, 2.0 equiv **3q**, 32%, E/Z = 3:1

Under the argon atmosphere, 2-ethynylbenzaldehyde **1q** (0.2 mmol, 26.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column

chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3q** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 11.0 mg (32%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.33-7.24 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.36-6.25 (m, 1H), 3.31 (s, 1H), 2.24 (q, *J* = 7.2 Hz, 2H), 1.55-1.42 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

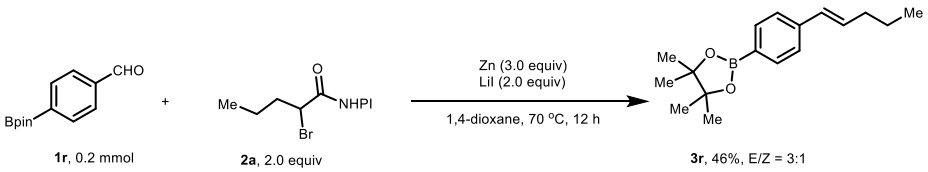
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.33-7.24 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 11.6 Hz, 1H), 5.83-5.75 (m, 1H), 3.28 (s, 1H), 2.24 (q, *J* = 7.2 Hz, 2H), 1.55-1.42 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.08, 133.31, 133.11, 128.84, 127.70, 126.39, 124.58, 120.08, 82.30, 81.38, 35.27, 22.48, 13.73.

(*Z*):^{13}C NMR (101 MHz, $CDCl_3$) δ 140.08, 134.15, 132.88, 128.84, 128.28, 127.26, 124.58, 120.08, 82.30, 81.32, 30.72, 23.00, 13.81.

Spectroscopic data are in accordance with that reported in the literature.[7]

4,4,5,5-tetramethyl-2-(4-(pent-1-en-1-yl)phenyl)-1,3,2-dioxaborolane (3r)



Under the argon atmosphere, 4-formylphenylboronic acid pinacol cyclic ester **1r** (0.2 mmol, 21.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3r** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 25.0 mg (46%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 2.20 (q, *J* = 7.2 Hz, 2H), 1.55-1.41 (m, 2H), 1.34 (s, 12H), 0.95 (t, *J* = 7.2 Hz, 3H).

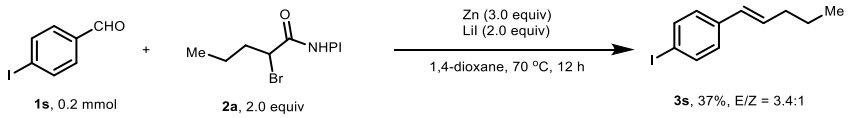
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.42 (d, *J* = 12.0 Hz, 1H), 5.70 (dt, *J* = 11.6 Hz, 7.2 Hz, 1H), 2.30 (q, *J* = 7.2 Hz, 2H), 1.55-1.41 (m, 2H), 1.34 (s, 12H), 0.92 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.73, 135.02, 132.19, 129.99, 125.25, 83.68, 35.18, 24.86, 22.45, 13.73.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.73, 134.58, 133.90, 128.92, 128.09, 83.72, 30.75, 24.86, 23.10, 13.80.

HRMS (ESI) calcd for $(C_{17}H_{26}BO_2)^+$ $[M + H]^+$: 273.2020, found: 273.2012.

1-iodo-4-(pent-1-en-1-yl)benzene (3s)



1s, 0.2 mmol **2a**, 2.0 equiv **3s**, 37%, E/Z = 3.4:1

Under the argon atmosphere, 4-iodobenzaldehyde **1s** (0.2 mmol, 46.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3s** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 20.0 mg (37%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H),

6.29 (d, *J* = 16.2 Hz, 1H), 6.23 (dt, *J* = 16.2 Hz, 6.6 Hz, 1H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.52-1.42 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

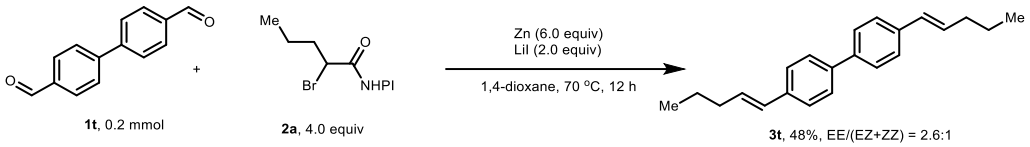
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.31 (d, *J* = 13.6 Hz, 1H), 5.69 (dt, *J* = 11.4 Hz, 7.2 Hz, 1H), 2.26 (qd, *J* = 7.8 Hz, 1.8 Hz, 2H), 1.52-1.42 (m, 2H), 0.93 (t, *J* = 7.8 Hz, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.49, 137.19, 132.05, 130.66, 128.88, 127.77, 35.11, 22.42, 13.75.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ137.47, 137.19, 134.02, 130.66, 128.88, 127.82, 30.67, 23.06, 13.85.

Spectroscopic data are in accordance with that reported in the literature.[8]

4,4'-di-pent-1-en-1-yl)-1,1'-biphenyl (3t)



Under the argon atmosphere, [1,1'-biphenyl]-4,4'-dicarbaldehyde **1t** (0.2 mmol, 42.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.8 mmol, 262.0 mg, 2.0 equiv), Zn power (0.6 mmol, 80.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3t** as a white solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 27.8 mg (48%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.50 (m, 4H), 7.45-7.34 (m, 4H), 6.43 (d, *J* = 16.0 Hz, 2H), 5.75-5.66 (m, 2H), 2.23 (q, *J* = 7. 2 Hz, 4H), 1.58-1.47 (m, 4H), 0.99 (t, *J* = 7.6 Hz, 6H).

(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.50 (m, 4H), 7.45-7.34 (m, 4H), 6.46 (d, *J* =

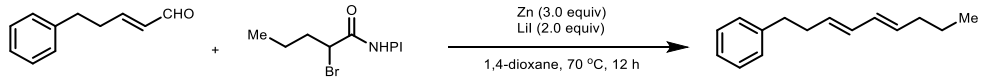
11.6 Hz, 2H), 6.33-6.23 (m, 2H), 2.38 (qd, *J* = 7.6 Hz, 2.00 Hz, 4H), 1.58-1.47 (m, 4H), 0.98 (t, *J* = 7.6 Hz, 6H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.20, 136.94, 133.26, 131.12, 129.51, 129.22, 128.47, 126.90, 126.53, 126.34, 35.21, 22.59, 13.75.

^{13}C NMR (101 MHz, $CDCl_3$) δ138.86, 136.81, 133.30, 131.16, 129.51, 129.25, 128.47, 126.99, 126.62, 126.36, 30.88, 23.19, 13.88.

HRMS (APCI) calcd for $(C_{22}H_{27})^+$ $[M + H]^+$: 291.2107, found: 291.2105.

((3E,5E)-nona-3,5-dien-1-yl)benzene (3u)



1u, 0.2 mmol **2a**, 2.0 equiv **3u**, 50%, E/Z = 1.4:1

Under the argon atmosphere, (*E*)-5-phenylpent-2-enal **1u** (0.2 mmol, 32.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3u** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 20.2 mg (50%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 2H), 7.27-7.18 (m, 3H), 6.14-5.95 (m, 2H), 5.78-5.67 (m, 1H), 5.67-5.58 (m, 1H), 2.74 (q, *J* = 8.0 Hz, 2H), 2.50-2.37 (m, 2H), 2.17 (q, *J* = 7.6 Hz, 1H), 2.07 (q, *J* = 7.2 Hz, 1H), 1.49-1.38 (m, 2H), 0.97-0.89 (m, 3H).

(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 2H), 7.27-7.18 (m, 3H), 6.43-6.32 (m, 1H), 6.14-5.95 (m, 1H), 5.67-5.58 (m, 1H), 5.41-5.32 (m, 1H), 2.74 (q, *J* = 8.0 Hz, 2H), 2.50-2.37 (m, 2H), 2.17 (q, *J* = 7.6 Hz, 1H), 2.07 (q, *J* = 7.2 Hz, 1H), 1.49-1.38 (m, 2H), 0.97-0.89 (m, 3H).

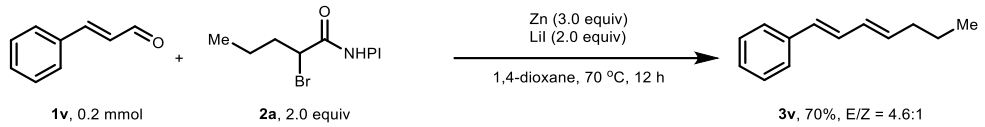
(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.97, 132.78, 130.96, 130.35, 128.42, 128.31,

126.30, 125.80, 35.92, 34.71, 34.47, 22.56, 13.71.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.90, 132.29, 131.10, 130.43, 128.62, 128.45, 126.30, 125.82, 35.88, 34.47, 29.77, 22.89, 13.77.

Spectroscopic data are in accordance with that reported in the literature.[9]

((1E,3E)-hepta-1,3-dien-1-yl)benzene (3v)



Under the argon atmosphere, cinnamaldehyde **1v** (0.2 mmol, 26.5 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3v** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 24.0 mg (70%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23-7.15 (m, 1H), 6.76 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.25-6.13 (m, 1H), 5.87-5.77 (m, 1H), 2.13 (q, *J* = 7.6 Hz, 2H), 1.51-1.39 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

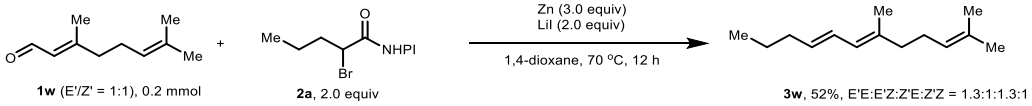
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23-7.15 (m, 1H), 7.07 (dd, *J* = 15.2 Hz, 11.2 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.25-6.13 (m, 1H), 5.58-5.49 (m, 1H), 2.27 (q, *J* = 7.6 Hz, 2H), 1.51-1.39 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.74, 135.75, 130.68, 129.97, 129.51, 128.54, 127.06, 126.14, 34.95, 22.50, 13.72.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.12, 131.98, 128.89, 128.57, 127.32, 126.33, 124.57, 30.06, 22.90, 13.79.

Spectroscopic data are in accordance with that reported in the literature.[10]

2,6-dimethyldodeca-2,6,8-triene (3w)



Under the argon atmosphere, Citral **1w** (0.2 mmol, 30.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3w** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 20.0 mg (52%).

NMR spectroscopy:

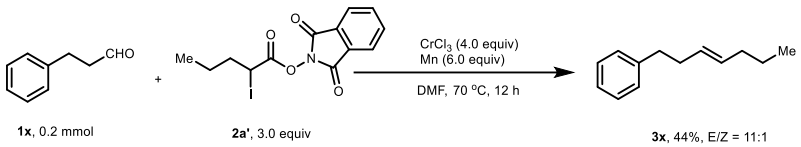
(*E'E and ZE'*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.29-6.15 (m, 1H), 6.08, (d, *J* = 10.2 Hz, 1H), 5.62-5.51 (m, 1H), 5.17-5.08 (m, 1H), 2.20-2.01 (m, 6H), 1.77-1.72 (m, 2H), 1.68 (s, 3H), 1.61 (d, *J* = 6.0 Hz, 3H), 1.46-1.37 (m, 2H), 0.95-0.87 (m, 3H).

(*E'Z and Z'Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.29-6.15 (m, 1H), 5.83-5.78 (m, 1H), 5.38-5.29 (m, 1H), 5.17-5.08 (m, 1H), 2.20-2.01 (m, 6H), 1.77-1.72 (m, 2H), 1.68 (s, 3H), 1.61 (d, *J* = 6.0 Hz, 3H), 1.46-1.37 (m, 2H), 0.95-0.87 (m, 3H).

(*E'E, ZE', E'Z and Z'Z*): ^{13}C NMR (151 MHz, $CDCl_3$) ^{13}C NMR (151 MHz, CDCl3) δ 138.68, 138.42, 136.55, 136.35, 132.33, 132.07, 131.80, 131.78, 131.61, 131.58, 129.87, 129.65, 126.80, 126.60, 125.56, 124.80, 124.67, 124.49, 124.16, 124.15, 124.14, 124.11, 120.75, 120.01, 40.28, 39.91, 35.07, 35.00, 32.46, 32.29, 29.72, 29.62, 29.56, 26.83, 26.68, 25.71, 24.19, 23.71, 22.95, 22.93, 22.78, 22.75, 17.72, 17.69, 17.67, 16.57, 16.45, 13.85, 13.77, 13.72.

Spectroscopic data are in accordance with that reported in the literature.[11]

hept-3-en-1-ylbenzene (3x)



Under the argon atmosphere, 3-phenylpropanal **1x** (0.2 mmol, 27.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-iodopentanoate **2a'** (0.6 mmol, 223.0 mg, 3.0 equiv), $CrCl_3$ (0.8 mmol, 126.0 mg, 2.0 equiv) and Mn power (1.2 mmol, 66.0 mg, 6.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous DMF (0.5 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether) to afford **3x** as a colorless liquid. $\mathbf{R_f}$ = 0.9 (eluent: petroleum ether/EtOAc = 100:1).

Yield 15.4 mg (44%).

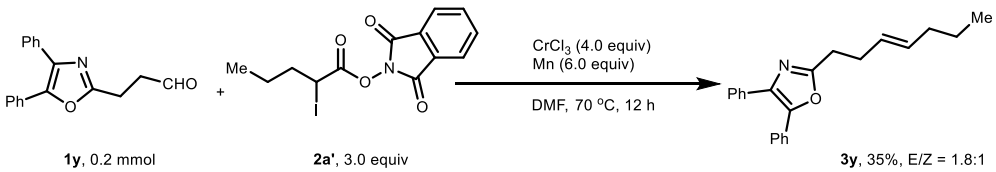
NMR spectroscopy:

(*E* and *Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2H), 7.26-7.20 (m, 3H), 5.50-5.38 (m, 2H), 2.74-2.66 (m, 2H), 2.43-2.31 (m, 2H), 2.05-1.97 (m, 2H), 1.40-1.32 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H).

(*E* and *Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.19, 130.95, 130.49, 129.51, 128.86, 128.46, 128.25, 125.75, 125.68, 36.20, 36.06, 34.68, 34.47, 29.30, 29.19, 22.77, 22.67, 13.76, 13.63.

Spectroscopic data are in accordance with that reported in the literature.[12]

2-(hept-3-en-1-yl)-4,5-diphenyloxazole (3y)



Under the argon atmosphere, 3-(4,5-diphenyloxazol-2-yl) propanal **1y** (0.2 mmol, 55.5 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-iodopentanoate **2a'** (0.6 mmol, 223.0

mg, 3.0 equiv), $CrCl_3$ (0.8 mmol, 126.0 mg, 2.0 equiv) and Mn power (1.2 mmol, 66.0 mg, 6.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous DMF (0.5 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate =100:1) to afford **3y** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 22.0 mg (35%).

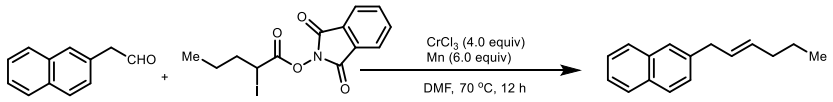
NMR spectroscopy:

(*E* and *Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.36 (q, *J* = 7.2 Hz, 4H), 7.33-7.29 (m, 2H), 5.56-5.45 (m, 2H), 2.91 (q, *J* = 7.8 Hz, 2H), 2.63-2.58 (m, 1H), 2.56-2.51 (m, 1H), 2.05-1.93 (m, 2H), 1.39-1.30 (m, 2H), 0.90-0.83 (m, 3H).

(*E* and *Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.22, 163.17, 145.17, 145.11, 135.12, 135.07, 132.70, 132.67, 132.07, 131.63, 129.24, 129.21, 128.60, 128.52, 128.31, 128.29, 128.08, 127.96, 127.42, 126.46, 126.44, 34.58, 30.17, 29.29, 28.56, 28.44, 25.05, 22.74, 22.55, 13.72, 13.53.

HRMS (ESI) calcd for $(C_{22}H_{24}NO)^+$ $[M + H]^+$: 318.1852, found: 318.1853.

hept-3-en-1-ylbenzene (3z)



Under the argon atmosphere, 2-(naphthalen-2-yl)acetaldehyde **1z** (0.2 mmol, 34.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-iodopentanoate **2a'** (0.6 mmol, 223.0 mg, 3.0 equiv), $CrCl_3$ (0.8 mmol, 126.0 mg, 2.0 equiv) and Mn power (1.2 mmol, 66.0 mg, 6.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous DMF (0.5 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether) to afford **3z** as a colorless liquid.

R_f = 0.9 (eluent: petroleum ether/EtOAc = 100:1).

Yield 15.5 mg (37%).

NMR spectroscopy:

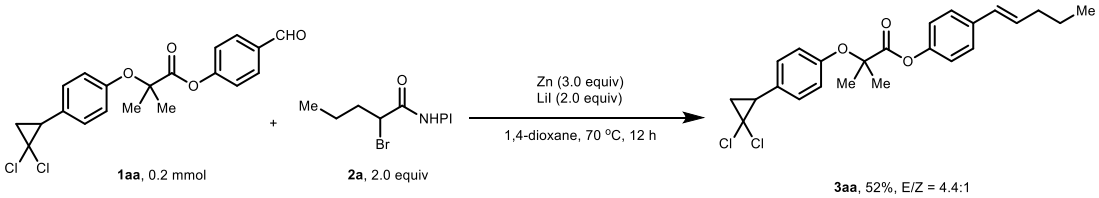
(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.74 (m, 3H), 7.62 (s, 1H), 7.49-7.37 (m, 2H), 7.34 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 5.72-5.51 (m, 2H), 3.57 (d, *J* = 6.8 Hz, 2H), 2.23-2.14 (m, 2H), 1.51-1.41 (m, 2H), 1.01-0.88 (m, 3H).

(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.74 (m, 3H), 7.67 (s, 1H), 7.49-7.37 (m, 2H), 7.34 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 5.72-5.51 (m, 2H), 3.49 (d, *J* = 6.8 Hz, 2H), 2.33-2.23 (m, 2H), 1.51-1.41 (m, 2H), 1.01-0.88 (m, 3H).

(*E* and *Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.78, 133.70, 132.03, 131.73, 131.10, 129.85, 128.02, 128.00, 127.92, 127.81, 127.60, 127.45, 127.32, 126.22, 126.09, 125.88, 125.39, 125.25, 125.13, 123.62, 33.67, 32.85, 31.57, 29.41, 22.87, 22.31, 13.97, 13.86.

Spectroscopic data are in accordance with that reported in the literature.[13]

4-(pent-1-en-1-yl)phenyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (3aa)



Under the argon atmosphere, 4-formylphenyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate **1aa** (0.2 mmol, 78.6 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to afford **3aa** as a colorless liquid.

R$_f$ = 0.6 (eluent: petroleum ether/EtOAc = 15:1).

Yield 45.0 mg (52%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.95-6.90 (m, 2H), 6.89-6.86 (m, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.20-6.17 (m, 1H), 2.85 (dd, *J* = 10.2 Hz, 7.8 Hz, 1H), 2.17 (q, *J* = 6.6 Hz, 2H), 1.94 (dd, *J* = 10.2 Hz, 7.2 Hz, 1H), 1.79 (t, *J* = 7.8 Hz, 1H), 1.75 (s, 6H), 1.51-1.44 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

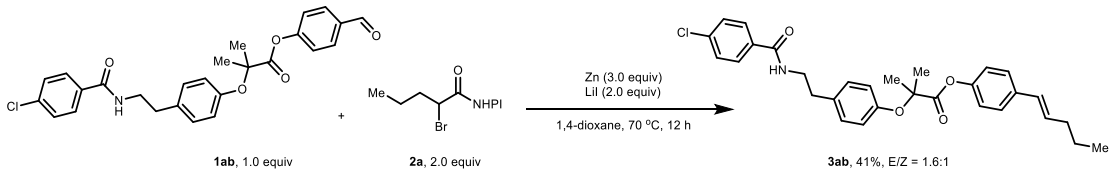
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.95-6.90 (m, 2H), 6.89-6.86 (m, 2H), 6.36 (d, *J* = 13.2 Hz, 1H), 5.68-5.63 (m, 1H), 2.85 (dd, *J* = 10.2 Hz, 7.8 Hz, 1H), 2.26 (q, *J* = 6.6 Hz, 2H), 1.94 (dd, *J* = 10.2 Hz, 7.2 Hz, 1H), 1.79 (t, *J* = 7.8 Hz, 1H), 1.75 (s, 6H), 1.51-1.44 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.87, 155.05, 149.29, 136.08, 131.47, 129.81, 128.87, 128.46, 126.80, 121.23, 118.66, 79.37, 60.86, 35.06, 34.86, 25.85, 25.51, 22.48, 13.71.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.87, 155.05, 148.93, 136.08, 133.44, 129.75, 128.87, 128.46, 127.85, 120.87, 118.66, 79.37, 60.86, 35.06, 30.59, 25.85, 25.51, 23.07, 13.82.

HRMS (ESI) calcd for $(C_{24}H_{27}O_3Cl_2)^+$ $[M + H]^+$: 433.1332, found: 433.1339.

4-(pent-1-en-1-yl)phenyl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate (3ab)



Under the argon atmosphere, 4-formylphenyl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate **1ab** (0.2 mmol, 93.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture

was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to afford **3ab** as a colorless liquid.

R_f = 0.4 (eluent: petroleum ether/EtOAc = 5:1).

Yield 41.5 mg (41%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 9.6 Hz, 2.4 Hz, 2H), 7.40-7.34 (m, 2H), 7.34-7.25 (m, 2H), 7.17-7.12 (m, 2H), 6.97-6.91 (m, 4H), 6.42-6.33 (m, 1H), 6.20-6.12 (m, 1H), 6.07 (s, 1H), 3.68 (q, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 6.6 Hz, 2H), 2.19 (qd, *J* = 6.6 Hz, 1.6 Hz, 2H), 1.74 (s, 6H), 1.52-1.41 (m, 2H), 0.97-0.88 (m, 3H).

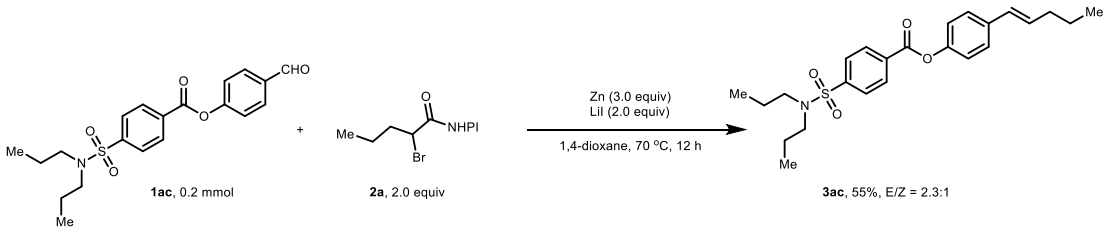
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 9.6 Hz, 2.4 Hz, 2H), 7.40-7.34 (m, 2H), 7.34-7.25 (m, 2H), 7.17-7.12 (m, 2H), 6.99-6.90 (m, 4H), 6.42-6.33 (m, 1H), 6.07 (s, 1H), 5.71-5.62 (m, 1H), 3.68 (q, *J* = 6.8 Hz 2H), 2.89 (t, *J* = 6.6 Hz, 2H), 2.27 (qd, *J* = 6.6 Hz, 1.6 Hz, 2H), 1.76 (s, 6H), 1.52-1.41 (m, 2H), 0.97-0.88 (m, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.93, 166.39, 154.19, 149.31, 137.63, 136.11, 134.47, 133.00, 132.68, 131.54, 129.62, 128.82, 128.24, 126.83, 121.15, 119.51, 79.32, 41.22, 35.06, 34.74, 25.45, 22.47, 13.70.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.93, 166.39, 154.19, 148.96, 137.63, 135.89, 134.47, 133.49, 132.71, 131.54, 129.78, 128.82, 128.24, 123.55, 120.81, 119.55, 79.32, 41.22, 34.74, 30.59, 25.45, 23.06, 13.81.

HRMS (ESI) calcd for $(C_{30}H_{33}NO_4Cl)^+$ $[M + H]^+$: 506.2093, found: 506.2103.

4-(pent-1-en-1-yl)phenyl 4-(N,N-dipropylsulfamoyl)benzoate (3ac)



Under the argon atmosphere, 4-formylphenyl 4-(*N,N*-dipropylsulfamoyl)benzoate **1ac** (0.2 mmol, 77.9 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar.

Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to afford **3ac** as a colorless liquid.

R_f = 0.6 (eluent: petroleum ether/EtOAc = 15:1).

Yield 47.0 mg (55%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33-8.29 (m, 2H), 7.96-7.92 (m, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 15.6 Hz 1H), 6.22 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 3.15-3.10 (m, 4H), 2.20 (qd, *J* = 7.8 Hz, 1.8 Hz, 2H), 1.60-1.54 (m, 4H), 1.53-1.46 (m, 2H), 0.99-0.93 (m, 3H), 0.89 (t, *J* = 7.2 Hz, 6H).

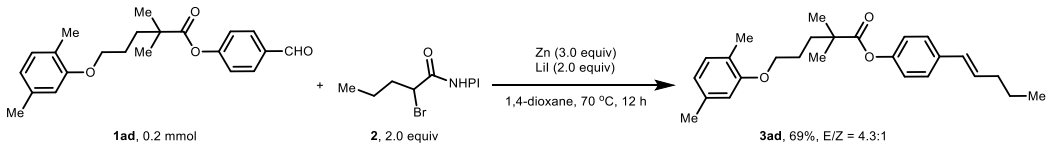
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33-8.29 (m, 2H), 7.96-7.92 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 6.41 (d, *J* = 12.0 Hz 1H), 5.70 (dt, *J* = 12.0 Hz, 7.2 Hz, 1H), 3.15-3.10 (m, 4H), 2.32 (qd, *J* = 7.8 Hz, 1.8 Hz, 2H), 1.60-1.54 (m, 4H), 1.53-1.46 (m, 2H), 0.99-0.93 (m, 3H), 0.89 (t, *J* = 7.2 Hz, 6H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.92, 149.38, 144.93, 136.23, 131.63, 130.78, 129.90, 128.87, 127.17, 126.95, 121.43, 49.95, 35.08, 22.50, 21.94, 13.71, 11.16.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.92, 149.01, 144.96, 136.02, 134.72, 133.57, 132.93, 128.87, 127.84, 123.94, 121.09, 49.95, 30.63, 23.09, 21.94, 13.83, 11.16.

HRMS (ESI) calcd for $(C_{24}H_{32}NO_4S)^+$ $[M + H]^+$: 430.2047, found: 430.2053.

4-(pent-1-en-1-yl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3ad)



Under the argon atmosphere, 4-formylphenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **1ad** (0.2 mmol, 70.9 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was

stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1) to afford **3ad** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 20:1).

Yield 54.4 mg (69%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.64 (s, 1H), 6.36 (d, *J* = 16.2 Hz, 1H), 6.21-6.15 (m, 1H), 3.99 (s, 2H), 2.32 (s, 3H), 2.22-2.16 (m, 5H), 1.89 (s, 4H), 1.53-1.46 (m, 2H), 1.38 (d, *J* = 4.72 Hz, 6H), 0.96 (t, *J* = 7.8 Hz, 3H).

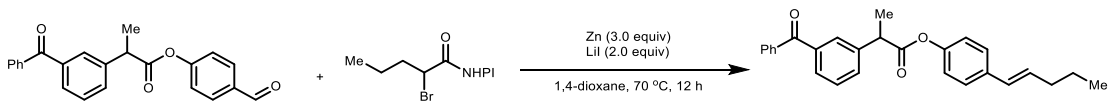
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.64 (s, 1H), 6.40 (d, *J* = 11.4 Hz, 1H), 5.70-65.64 (m, 1H), 3.99 (s, 2H), 2.32 (s, 3H), 2.22-2.16 (m, 5H), 1.89 (s, 4H), 1.53-1.46 (m, 2H), 1.38 (d, *J* = 4.72 Hz, 6H), 0.96 (t, *J* = 7.8 Hz, 3H).

(*E*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.42, 156.91, 149.79, 136.51, 135.62, 131.13, 130.37, 129.72, 129.01, 126.77, 121.51, 120.76, 111.96, 67.81, 42.44, 37.19, 35.11, 25.30, 25.19, 22.54, 21.44, 15.84, 13.77.

(*Z*): ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.42, 156.91, 149.40, 136.51, 135.40, 133.23, 131.13, 130.37, 129.72, 128.00, 126.77, 123.65, 121.15, 67.81, 42.46, 37.19, 30.63, 25.30, 25.19, 23.14, 21.44, 15.84, 13.88.

HRMS (ESI) calcd for $(C_{26}H_{35}O_3)^+$ $[M + H]^+$: 395.2581, found: 395.2586.

4-(pent-1-en-1-yl)phenyl 2-(3-benzoylphenyl)propanoate (3ae)



1ae,0.2 mmol **2a**, 2.0 equiv **3ae**, 73%, E/Z = 3.4:1

Under the argon atmosphere, 4-formylphenyl 2-(3-benzoylphenyl)propanoate **1ae** (0.2 mmol, 71.6 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar.

Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1) to afford **3ae** as a colorless liquid.

R_f = 0.5 (eluent: petroleum ether/EtOAc = 40:1).

Yield 58.2 mg (73%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.72 (dt, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.65-7.61 (m, 1H), 7.61-7.55 (m, 1H), 7.48 (q, *J* = 7.6 Hz, 3H), 7.32-7.27 (m, 1H), 7.26-7.21 (m, 1H), 6.98-6.90 (m, 2H), 6.39-6.29 (m, 1H), 6.20-6.10 (m, 1H), 4.07-3.98 (m, 1H), 2.20-2.11 (m, 2H), 1.65 (d, *J* = 7.2 Hz, 3H), 1.51-1.42 (m, 2H), 0.96-0.87 (m, 3H).

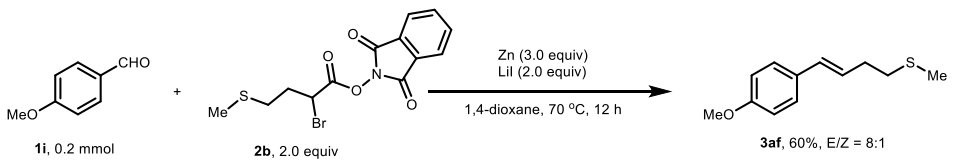
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.72 (dt, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.65-7.61 (m, 1H), 7.61-7.55 (m, 1H), 7.48 (q, *J* = 7.6 Hz, 3H), 7.32-7.27 (m, 1H), 7.26-7.21 (m, 1H), 6.98-6.90 (m, 2H), 6.39-6.29 (m, 1H), 5.69-5.60 (m, 1H), 4.07-3.98 (m, 1H), 2.30-2.21 (m, 2H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.51-1.42 (m, 2H), 0.96-0.87 (m, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.40, 172.56, 149.49, 140.40, 138.16, 137.51, 135.87, 133.33, 132.54, 131.51, 130.08, 129.30, 129.19, 128.92, 128.77, 128.35, 126.75, 121.26, 45.55, 35.06, 22.49, 18.50, 13.71.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.40, 172.59, 149.12, 140.40, 138.16, 137.51, 135.64, 133.33, 132.54, 131.32, 129.70, 129.30, 129.19, 128.92, 128.77, 127.91, 126.75, 120.90, 45.55, 30.59, 23.08, 18.52, 13.81.

HRMS (ESI) calcd for $(C_{27}H_{27}O_3)^+$ $[M + H]^+$: 399.1955, found: 399.1960.

(4-(4-methoxyphenyl)but-3-en-1-yl)(methyl)sulfane (3af)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0

equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-4-(methylthio)butanoate **2b** (0.4 mmol, 143.2 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3af** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 25.0 mg (60%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.09 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 3.79 (s, 3H), 2.65-2.59 (m, 2H), 2.49 (q, *J* = 6.8 Hz, 2H), 2.14 (s, 3H).

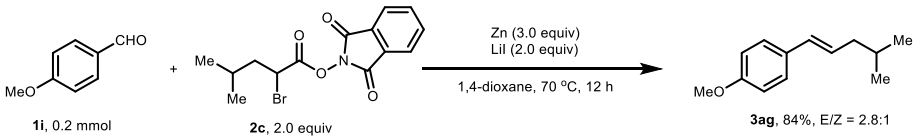
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 12.8 Hz, 1H), 5.60-5.55 (m, 1H), 3.81 (s, 3H), 2.65-2.59 (m, 2H), 2.49 (q, *J* = 6.8 Hz, 2H), 2.09 (s, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.88, 130.55, 129.93, 127.19, 126.32, 113.95, 55.31, 34.19, 32.90, 15.67.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.38, 130.24, 129.93, 129.62, 128.85, 113.65, 55.31, 34.19, 32.90, 15.48.

HRMS (ESI) calcd for $(C_{12}H_{17}OS)^+$ $[M + H]^+$: 209.0995, found: 209.0998.

1-methoxy-4-(4-methylpent-1-en-1-yl)benzene (3ag)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-4-methylpentanoate **2c** (0.4 mmol, 136.1 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane

(1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3ag** (32.0 mg) in 84% yield as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 32.0 mg (84%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.84 (dd, *J* = 8.8 Hz, 2H), 6.32 (d, *J* = 15.6 Hz, 1H), 6.14-6.03 (m, 1H), 3.81 (s, 3H), 2.08 (t, *J* = 6.80 Hz, 2H), 1.77-1.65 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 6H).

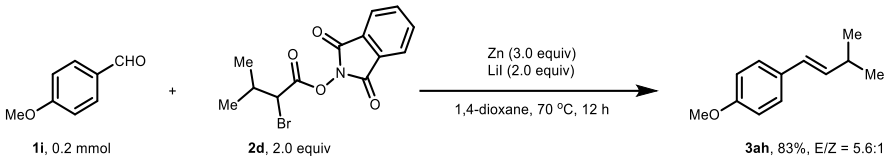
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.88 (dd, *J* = 8.8 Hz, 2H), 6.39 (d, *J* = 12.4 Hz, 1H), 5.65-5.56 (m, 1H), 3.82 (s, 3H), 2.22 (t, *J* = 6.4 Hz, 2H), 1.77-1.65 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 6H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.67, 130.15, 129.98, 127.73, 127.01, 113.93, 55.29, 42.42, 28.69, 22.38.

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.15, 130.87, 130.63, 130.49, 128.69, 113.54, 55.23, , 37.63, 29.09, 22.44.

Spectroscopic data are in accordance with that reported in the literature.[14]

1-methoxy-4-(3-methylbut-1-en-1-yl)benzene (3ah)



1i, 0.2 mmol **2d**, 2.0 equiv **3ah**, 83%, E/Z = 5.6:1

Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-3-methylbutanoate **2d** (0.4 mmol, 130.5 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3ah** yield as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 29.0 mg (83%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 2H), 6.90-6.82 (m, 2H), 6.30 (d, *J* = 16.0 Hz 1H), 6.07 (dd, *J* = 16.0 Hz, 6.8 Hz, 1H), 3.81 (s, 3H), 2.50-2.40 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 6H).

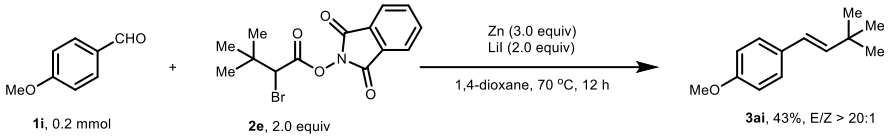
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 2H), 6.90-6.82 (m, 2H), 6.25 (d, *J* = 11.6 Hz 1H), 5.40 (dd, *J* = 11.6 Hz, 10.4 Hz, 1H), 3.82 (s, 3H), 2.50-2.40 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 6H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.63, 135.96, 127.04, 126.17, 113.92, 55.30, 31.50, 22.59.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.18, 139.11, 130.80, 129.81, 125.84, 113.60, 55.30, 27.12, 23.25.

Spectroscopic data are in accordance with that reported in the literature.[15]

(E)-1-(3,3-dimethylbut-1-en-1-yl)-4-methoxybenzene (3ai)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-3,3-dimethylbutanoate **2e** (0.4 mmol, 136.1 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3ai** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 16.2 mg (43%).

NMR spectroscopy:

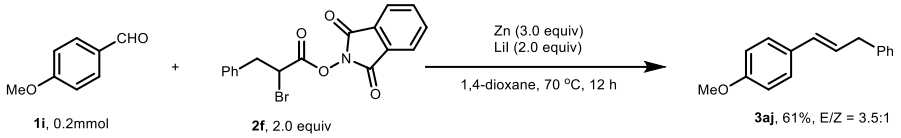
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.25

(d, *J* = 16.0 Hz, 1H), 6.12 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.64, 139.86, 130.90, 127.06, 123.90, 113.93, 55.30, 33.22, 29.70.

Spectroscopic data are in accordance with that reported in the literature.[16]

1-methoxy-4-(3-phenylprop-1-en-1-yl)benzene (3aj)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-3-phenylpropanoate **2f** (0.4 mmol, 149.7 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3aj** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 27.5 mg (61%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.23 (m, 7H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.27 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 3.84 (s, 3H), 3.58 (d, *J* = 6.4 Hz, 2H).

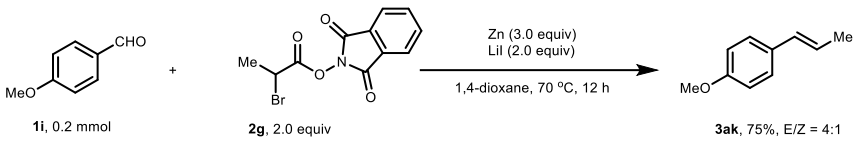
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.23 (m, 7H), 6.93 (d, *J* = 9.2 Hz, 2H), 6.58 (d, *J* = 11.6 Hz, 1H), 6.27 (dt, *J* = 11.2 Hz, 7.6 Hz, 1H), 3.86 (s, 3H), 3.73 (d, *J* = 7.6 Hz, 2H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.92, 140.50, 130.50, 129.95, 128.68, 128.49, 127.27, 127.11, 126.14, 113.99, 55.31, 39.37.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.53, 141.00, 130.39, 129.50, 129.21, 128.53, 128.38, 126.05, 113.74, 55.28, 34.71.

Spectroscopic data are in accordance with that reported in the literature.[17]

1-methoxy-4-(prop-1-en-1-yl)benzene (3ak)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopropanoate **2g** (0.4 mmol, 119.2 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3ak** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 22.2 mg (75%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 16.4 Hz, 1H), 6.14-6.02 (m, 1H), 3.79 (s, 3H), 1.84 (dd, *J* = 6.4 Hz, 1.6 Hz, 3H).

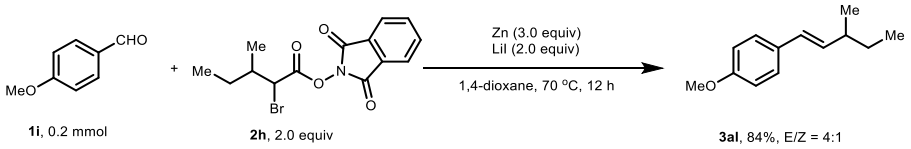
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 10.8 Hz, 1H), 5.74-5.64 (m, 1H), 3.80 (s, 3H), 1.88 (dd, *J* = 7.2 Hz, 1.6 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.59, 130.35, 126.89, 123.50, 113.91, 55.28, 18.44.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.11, 130.83, 130.02, 129.28, 125.13, 113.56, 55.26, 14.62.

Spectroscopic data are in accordance with that reported in the literature.[18]

1-methoxy-4-(3-methylpent-1-en-1-yl)benzene (3al)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0

equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-3-methylpentanoate **2h** (0.4 mmol, 136.1 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3al** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 32.0 mg (84%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.30 (d, *J* = 16.2 Hz, 1H), 5.96 (dd, *J* = 15.6 Hz, 7.8 Hz, 1H), 3.81 (s, 3H), 2.23-2.19 (m, 1H), 1.44-1.38 (m, 2H), 1.06 (d, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.8 Hz, 3H).

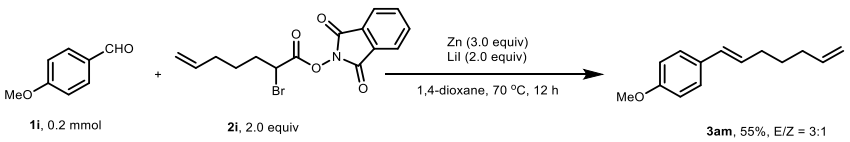
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 12.6 Hz, 1H), 5.37-5.33 (m, 1H), 3.82 (s, 3H), 2.69-2.63 (m, 1H), 1.44-1.38 (m, 2H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 7.8 Hz, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.61, 134.70, 130.85, 127.45, 127.03, 113.91, 55.31, 38.89, 29.93, 20.34, 11.88.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.13, 138.07, 130.65, 129.79, 126.94, 113.56, 55.24, 33.77, 30.42, 20.69, 11.84.

Spectroscopic data are in accordance with that reported in the literature.[19]

1-(hepta-1,6-dien-1-yl)-4-methoxybenzene (3am)



1i, 0.2 mmol **2i**, 2.0 equiv **3am**, 55%, E/Z = 3:1

Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromohept-6-enoate **2i** (0.4 mmol, 141.8 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture

was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3am** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 22.3. mg (55%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.36 (d, *J* = 16.8 Hz, 1H), 6.14-6.09 (m, 1H), 5.92-5.81 (m, 1H), 5.10-4.96 (m, 2H), 3.83 (s, 3H), 2.24 (q, *J* = 7.2 Hz, 2H), 2.17-2.09 (m, 2H), 1.63-1.55 (m, 2H).

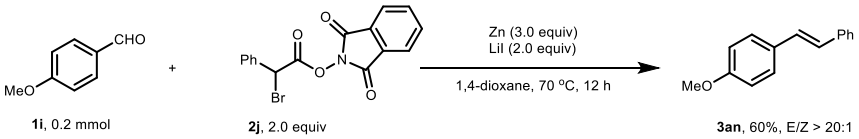
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 13.2 Hz, 1H), 5.92-5.81 (m, 1H), 5.62-5.57 (m, 1H), 5.10-4.96 (m, 2H), 3.84 (s, 3H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.17-2.09 (m, 2H), 1.63-1.55 (m, 2H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.70, 138.75, 129.93, 129.44, 128.53, 127.00, 114.57, 113.95, 55.29, 33.26, 32.41, 28.74.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.22, 138.63, 131.14, 130.75, 130.46, 128.47, 114.61, 113.58, 55.25, 33.42, 29.29, 28.08.

HRMS (ESI) calcd for $(C_{14}H_{19}O)^+$ $[M + H]^+$: 203.1430, found: 203.1435.

(E)-1-methoxy-4-styrylbenzene (3an)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-2-phenylacetate **2j** (0.4 mmol, 144.1 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3an** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 25.2 mg (60%).

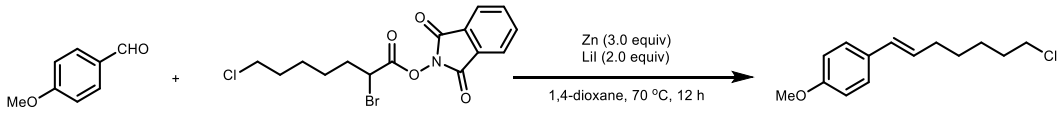
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.43 (m, 4H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.27-7.22 (m, 1H), 7.08 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.36, 137.70, 130.20, 128.65, 128.26, 127.74, 127.22, 126.67, 126.28, 114.18, 55.34.

Spectroscopic data are in accordance with that reported in the literature.[20]

1-(7-chlorohept-1-en-1-yl)-4-methoxybenzene (3ao)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-7-chloroheptanoate **2k** (0.4 mmol, 155.5 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3ao** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 38.2 mg (80%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.42-6.33 (m, 1H), 6.14-6.04 (m, 1H), 3.83 (s, 3H), 3.60-3.51 (m, 2H), 2.28-2.19 (m, 2H), 1.87-1.76 (m, 2H), 1.57-1.47 (p, *J* = 3.6 Hz, 4H).

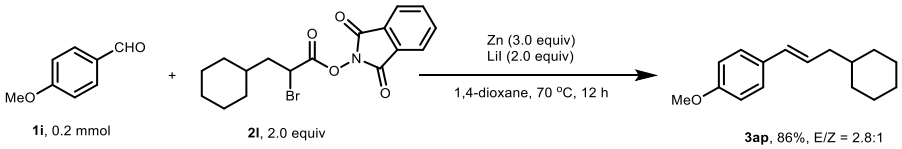
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.42-6.33 (m, 1H), 5.63-5.55 (m, 1H), 3.84 (s, 3H), 3.60-3.51 (m, 2H), 2.40-2.33 (m, 2H), 1.87-1.76 (m, 2H), 1.57-1.47 (p, *J* = 3.6 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.74, 129.93, 129.49, 128.37, 127.02, 113.96, 55.29, 45.04, 32.79, 32.55, 28.78, 26.47.

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.26, 131.01, 130.67, 130.39, 128.56, 113.61, 55.26, 45.04, 32.50, 29.27, 28.41, 26.60.

HRMS (ESI) calcd for $(C_{14}H_{20}ClO)^+$ $[M + H]^+$: 239.1197, found: 239.1193.

1-(3-cyclohexylprop-1-en-1-yl)-4-methoxybenzene (3ap)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-3-cyclohexylpropanoate **2l** (0.4 mmol, 152.1 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford **3ap** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 40.0 mg (86%).

NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.13-6.03 (m, 1H), 3.80 (s, 3H), 2.08 (td, *J* = 7.2 Hz, 1.6 Hz, 2H), 1.80-1.61 (m, 6H), 1.41-1.34 (m, 1H), 1.27-1.12 (m, 4H).

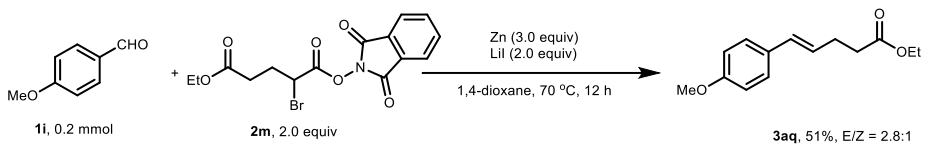
(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 11.6 Hz, 1H), 5.64-5.56 (m, 1H), 3.82 (s, 3H), 2.21 (td, *J* = 6.8 Hz, 1.6 Hz, 2H), 1.80-1.61 (m, 6H), 1.41-1.34 (m, 1H), 1.27-1.12 (m, 4H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.63, 130.02, 129.97, 127.59, 126.98, 113.92, 55.30, 41.04, 38.31, 33.22, 26.61, 26.38.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.12, 130.87, 130.63, 130.35, 128.63, 113.53, 55.23, 38.76, 36.29, 33.27, 26.58, 26.38.

Spectroscopic data are in accordance with that reported in the literature.[21]

Ethyl -5-(4-methoxyphenyl)pent-4-enoate (3aq)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1-(1,3-dioxoisoindolin-2-yl) 5-ethyl 2-bromopentanedioate **2m** (0.4 mmol, 152.1 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3aq** as a colorless liquid.

R_f = 0.7 (eluent: petroleum ether/EtOAc = 40:1).

Yield 23.9 mg (51%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.06 (dt, *J* = 16.2 Hz, 6.0 Hz, 1H), 4.18-4.10 (m, 2H), 3.79 (s, 3H), 2.53-2.48 (m, 2H), 2.47-2.41 (m, 2H), 1.27-1.21 (m, 3H).

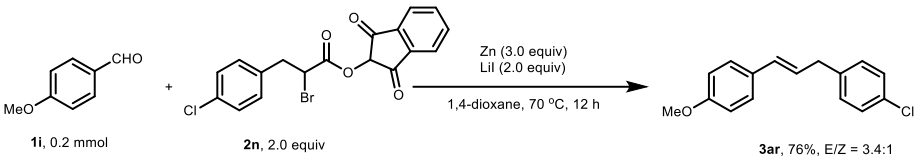
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 10.8 Hz, 1H), 6.55-6.49 (m, 1H), 4.18-4.10 (m, 2H), 3.81 (s, 3H), 2.67-2.62 (m, 2H), 2.47-2.41 (m, 2H), 1.27-1.21 (m, 3H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.10, 158.87, 130.30, 129.95, 127.16, 126.32, 113.93, 60.38, 55.29, 34.25, 28.33, 14.28.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.10, 158.38, 130.24, 129.53, 128.82, 126.32, 113.66, 60.38, 55.29, 34.51, 24.10, 14.24.

Spectroscopic data are in accordance with that reported in the literature.[22]

1-chloro-4-(3-(4-methoxyphenyl)allyl)benzene (3ar)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxo-2,3-dihydro-1H-inden-2-yl 2-bromo-3-(4-chlorophenyl)propanoate **2n** (0.4 mmol, 163.1 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford **3ar** resulting in 76% yield (39.3 mg) as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 39.3 mg (76%).

NMR spectroscopy:

(*E*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.13-7.09 (m, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 16.2 Hz, 1H), 6.20-6.13 (m, 1H), 3.81 (s, 3H), 3.48 (d, *J* = 6.6 Hz, 2H).

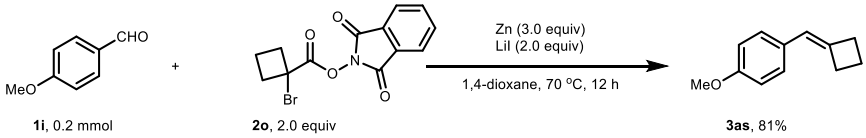
(*Z*): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.13-7.09 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 10.8 Hz, 1H), 5.75-5.69 (m, 1H), 3.82 (s, 3H), 3.62 (d, *J* = 7.8 Hz, 2H).

(*E*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.00, 139.44, 131.51, 130.94, 130.45, 127.29, 126.27, 119.93, 113.99, 55.32, 38.69.

(*Z*): ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.59, 139.95, 131.55, 130.12, 130.08, 130.00, 129.91, 128.35, 119.83, 113.76, 55.29, 34.07.

Spectroscopic data are in accordance with that reported in the literature.[23]

1-(cyclobutylidenemethyl)-4-methoxybenzene (3as)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0

equiv), 1,3-dioxoisoindolin-2-yl 1-bromocyclobutane-1-carboxylate **2o** (0.4 mmol, 129.6 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3as** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 28.0 mg (81%).

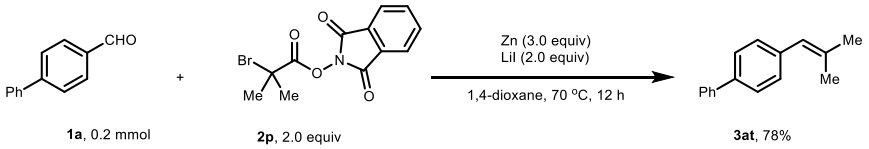
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.03 (s, 1H), 3.80 (s, 3H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.87 (t, *J* = 8.4 Hz, 2H), 2.16-2.04 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.67, 142.17, 130.95, 128.17, 120.19, 113.82, 55.26, 32.56, 32.50, 18.32.

Spectroscopic data are in accordance with that reported in the literature.[24]

4-(2-methylprop-1-en-1-yl)-1,1'-biphenyl (3at)



Under the argon atmosphere, 4-Biphenylcarboxaldehyde **1a** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-2-methylpropanoate **2p** (0.4 mmol, 124.8 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3at** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 32.5 mg (78%).

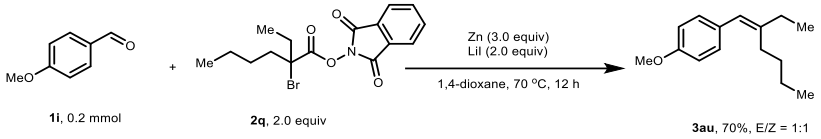
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37-7.28 (m, 3H), 6.31 (s, 1H), 1.94 (d, *J* = 5.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.02, 138.53, 137.79, 135.81, 129.13, 128.74, 127.07, 126.96, 126.74, 124.76, 27.00, 19.54.

Spectroscopic data are in accordance with that reported in the literature.[25]

1-(2-ethylpent-1-en-1-yl)-4-methoxybenzene (3au)



1i, 0.2 mmol **2q**, 2.0 equiv **3au**, 70%, E/Z = 1:1

Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-2-ethylhexanoate **2q** (0.4 mmol, 147.3 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3au** as a colorless liquid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 30.5 mg (70%).

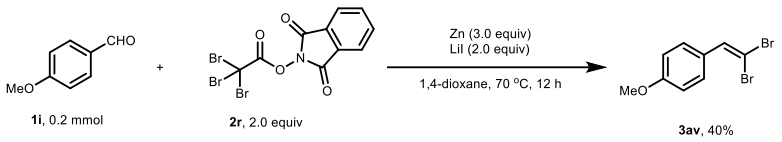
NMR spectroscopy:

(*E and Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.8, 3.2 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.18 (s, 1H), 3.80 (s, 3H), 2.27-2.12 (m, 4H), 1.51-1.41 (m, 2H), 1.39-1.30 (m, 2H), 1.08 (dt, *J* = 12.8 Hz, 7.6 Hz, 3H), 0.91 (dt, *J* = 19.2 Hz, 7.2 Hz, 3H).

(*E and Z*):^{13}C NMR (101 MHz, $CDCl_3$) δ 157.72, 157.68, 144.08, 143.83, 131.39, 131.32, 129.69, 129.65, 123.69, 123.04, 113.51, 113.48, 55.23, 36.53, 30.58, 30.52, 30.45, 30.01, 23.59, 22.95, 22.59, 14.06, 13.99, 13.05, 12.90.

HRMS (APCI) calcd for $(C_{15}H_{23}O)^+$ $[M + H]^+$: 219.1743, found: 219.1743.

1-(2,2-dibromovinyl)-4-methoxybenzene (3av)



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.2 mmol, 27.2 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2,2,2-tribromoacetate **2r** (0.4 mmol, 176.4 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) to afford **3av** as a yellow solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 23.0 mg (40%).

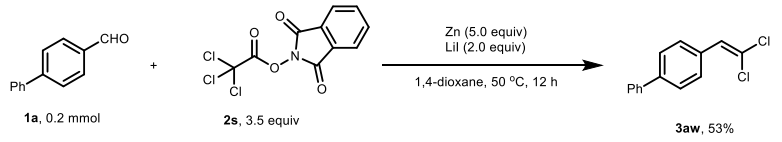
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.43 (s, 1H), 6.92 (d, *J* = 9.6 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.68, 136.32, 129.90, 127.83, 113.81, 87.30, 55.31.

Spectroscopic data are in accordance with that reported in the literature.[26]

1-(2,2-dibromovinyl)-4-methoxybenzene (3aw)



Under the argon atmosphere, 4-methoxybenzaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2,2,2-tribromoacetate **2s** (0.7 mmol, 216.0 mg, 3.5 equiv), Zn power (1.0 mmol, 65.0 mg, 5.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 50 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford

3aw as a white solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 40:1).

Yield 26.0 mg (53%).

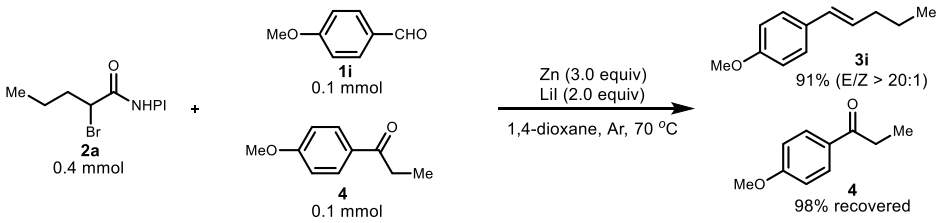
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 6H), 7.48-7.42 (m, 2H), 7.37 (tt, *J* = 7.2 Hz, 2.0 Hz, 1H), 6.90 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.22, 140.31, 132.37, 129.09, 128.87, 128.23, 127.66, 127.11, 127.03, 120.99.

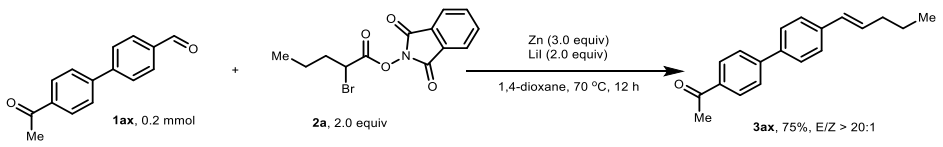
Spectroscopic data are in accordance with that reported in the literature.[27]

The chemoselectivity of this decarboxylative olefination.



Under the argon atmosphere, 4-methoxybenzaldehyde **1i** (0.1 mmol, 13.6 mg, 1.0 equiv), 1-(4-methoxyphenyl)propan-1-one **4** (0.1 mmol, 16.4 mg, 1.0 equiv) 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3i** resulting in 91% yield (16.0 mg) as a colorless liquid and the **4** was recovered (15.0 mg, 98%) as a colorless liquid.

1-(2-ethylpent-1-en-1-yl)-4-methoxybenzene (3ax)



Under the argon atmosphere, 4'-acetyl-[1,1'-biphenyl]-4-carbaldehyde **1ax** (0.2

mmol, 44.8 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromo-2-ethylhexanoate **2a** (0.4 mmol, 130.5 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3ax** as a white solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 40.0 mg (75%).

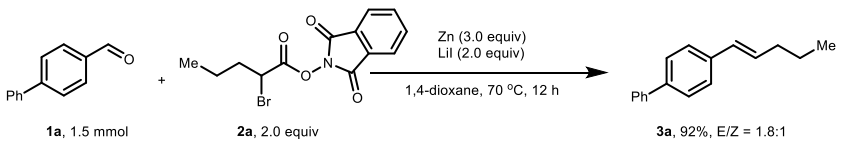
NMR spectroscopy:

(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 2H), 7.71-7.66 (m, 2H), 7.60-7.55 (m, 2H), 7.47-7.41 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.35-6.26 (m, 1H), 2.63 (s, 3H), 2.23 (q, *J* = 7.9, 7.5 Hz, 2H), 1.53 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

(*E*):^{13}C NMR (151 MHz, $CDCl_3$) δ 197.68, 145.43, 138.07, 138.05, 135.74, 131.96, 129.28, 128.93, 127.32, 126.88, 126.50, 35.20, 26.61, 22.51, 13.73.

HRMS (APCI) calcd for $(C_{19}H_{21}O)^+$ $[M + H]^+$: 265.1587, found: 265.1587.

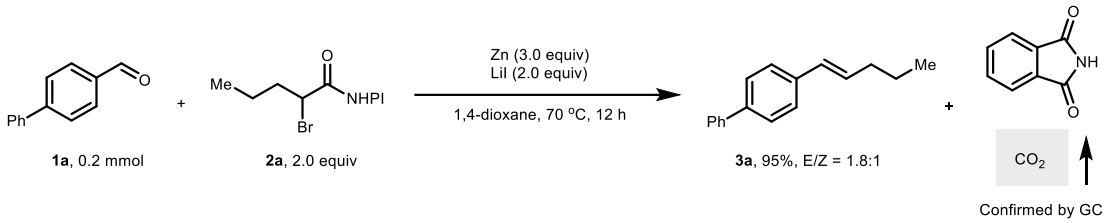
3. Scaled-up reaction



Under the argon atmosphere, 4-biphenylcarboxaldehyde **1a** (1.5 mmol, 274.0 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (3.0 mmol, 978.0 mg, 2.0 equiv), Zn power (4.5 mmol, 292.5 mg, 3.0 equiv) and LiI (4.0 mmol, 540.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (15.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3a** (307.0 mg) in 92 % yield as a white solid.

4. Mechanistic studies

4.1 The detection of phthalimide and CO_2



Under the argon atmosphere, 4-biphenylcarboxaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. Then, the reaction mixture was analyzed by GC-MS. The molecular weight of the by-products of phthalimide and CO_2 were detected by GC-MS.

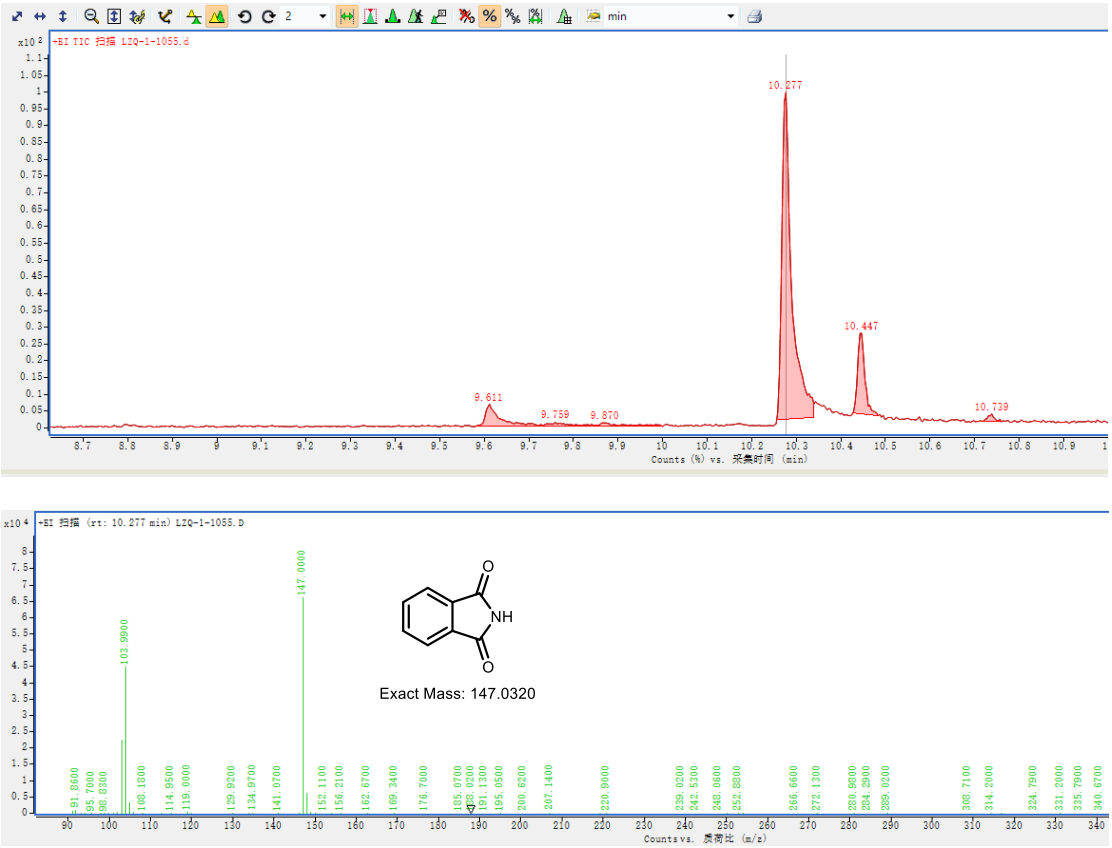


Figure S1. GC-MS of the reaction mixtures for by-product phthalimide

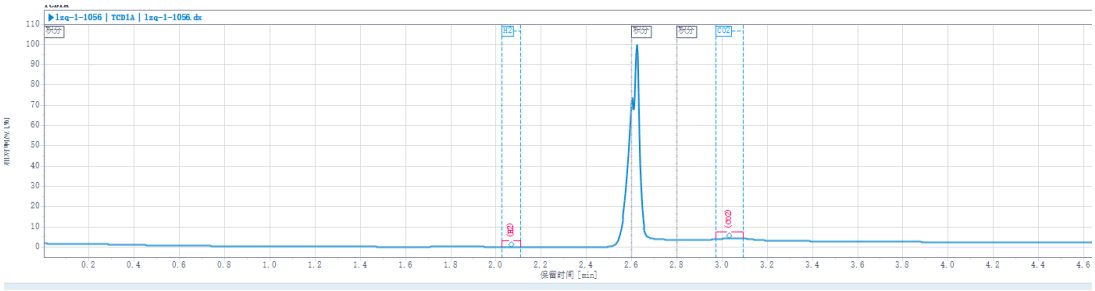


Figure S2. Blank control experiment

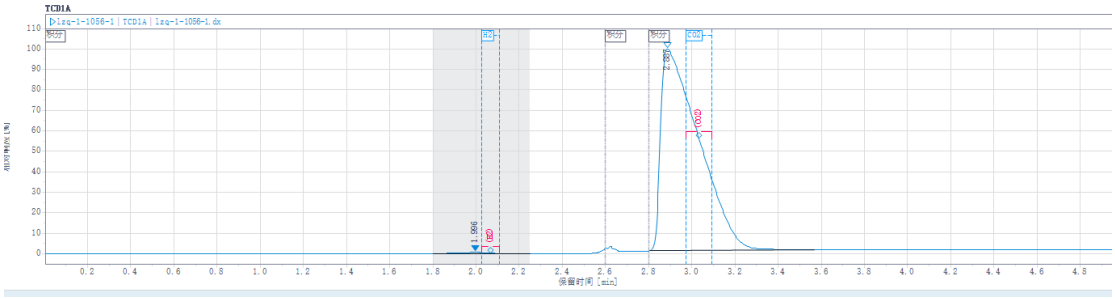
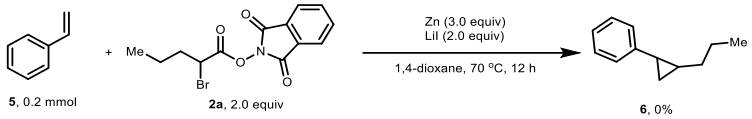


Figure S3. The CO_2 detection of the reaction

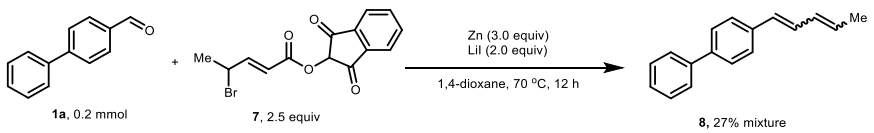
4.2 Control reaction to rule out the potential carbenoid intermediate



5, 0.2 mmol　　**2a**, 2.0 equiv　　**6**, 0%

Under the argon atmosphere, styrene **5** (0.2 mmol, 23.0 μL, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.5 mg, 2.0 equiv), Zn power (1.0 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was detected by TLC and GC-MS. The (2-propylcyclopropyl)benzene **6** was not observed.

4.3 Control experiment with 4-bromobut-2-enoic acid-derived NHPI ester



1a, 0.2 mmol　　**7**, 2.5 equiv　　**8**, 27% mixture

Under the argon atmosphere, 4-phenylbenzaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxo-2,3-dihydro-1H-inden-2-yl (E)-4-bromopent-2-enoate **7** (0.5 mmol, 161.5 mg, 2.5 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0

mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **8** resulting in 27% yield (12.0 mg) as a white solid.

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 12.0 mg (27%).

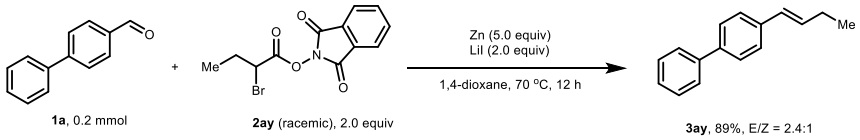
NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.57 (m, 2H), 7.56-7.48 (m, 2H), 7.47-7.39 (m, 4H), 7.37-7.30 (m, 1H), 7.18-7.08 (m, 0.22H), 6.80 (dd, *J* = 16.0 Hz, 10.4 Hz, 0.86H), 6.56 (d, *J* = 15.6 Hz, 0.19H) 6.47 (d, *J* = 16.0 Hz, 0.86H), 6.30-6.17 (m, 1H), 5.91-5.81 (m, 0.86H), 5.67-5.57 (m, 0.2H), 1.84 (dd, *J* = 6.8 Hz, 1.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.79, 139.79, 136.79, 131.94, 131.40, 130.44, 129.68, 129.48, 129.27, 128.76, 127.26, 127.23, 127.20, 126.89, 126.87, 126.74, 126.54, 18.35.

HRMS (APCI) calcd for $(C_{17}H_{17})^+$ $[M + H]^+$: 221.1325, found: 221.1327.

4.4 Relation between the stereochemistry



Under the argon atmosphere, 4-phenylbenzaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromobutanoate **2ay** (0.4 mmol, 125.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford 4-(but-1-en-1-yl)-1,1'-biphenyl **3ay** as a colorless liquid .

R_f = 0.8 (eluent: petroleum ether/EtOAc = 50:1).

Yield 37.0 mg (89%).

NMR spectroscopy:

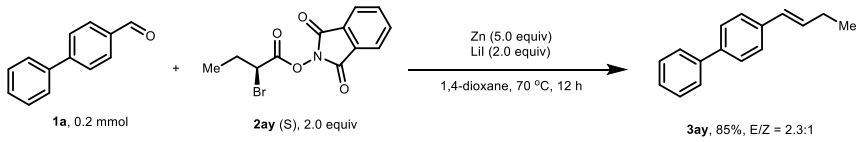
(*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.51 (m, 4H), 7.47-7.39(m, 3H), 7.39-7.30 (m, 2H), 6.43 (d, *J* = 15.2 Hz, 1H), 6.37-6.27 (m, 1H), 2.31-2.22 (m, 2H), 1.15-1.07 (m, 3H).

(*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.51 (m, 4H), 7.47-7.39(m, 3H), 7.39-7.30 (m, 2H), 6.43 (d, *J* = 15.2 Hz, 1H), 5.74-5.63 (m, 1H), 2.46-2.36 (m, 2H), 1.15-1.07 (m, 3H).

(*E*):^{13}C NMR (151 MHz, $CDCl_3$) δ 140.91, 139.53, 137.06, 132.87, 129.19, 128.74, 128.39, 127.18, 126.89, 126.33, 26.13, 13.66.

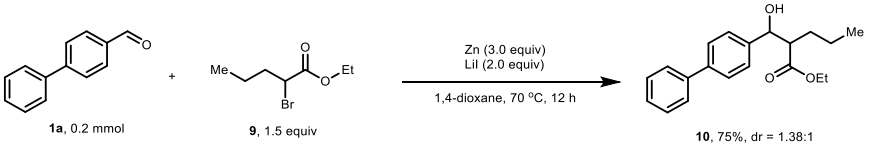
(*Z*):^{13}C NMR (151 MHz, $CDCl_3$) δ 140.91, 139.24, 136.85, 135.01, 129.19, 128.77, 127.85, 127.13, 126.99, 126.82, 22.12, 14.48.

Spectroscopic data are in accordance with that reported in the literature.[28]



Under the argon atmosphere, 4-phenylbenzaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl (*S*)-2-bromobutanoate **2ay** (0.4 mmol, 125.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3ay** resulting in 85% yield (35.0 mg) as a colorless liquid.

4.5 Control reactions for the nucleophilic addition step



Under the argon atmosphere, 4-phenylbenzaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0

equiv), ethyl 2-bromopentanoate **9** (0.3 mmol, 62.7 mg, 1.5 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 ºC for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to afford **10** (dr = 1.38:1) as a white solid.

R_f = 0.4 (eluent: petroleum ether/EtOAc = 5:1).

Yield 46.5 mg (75%).

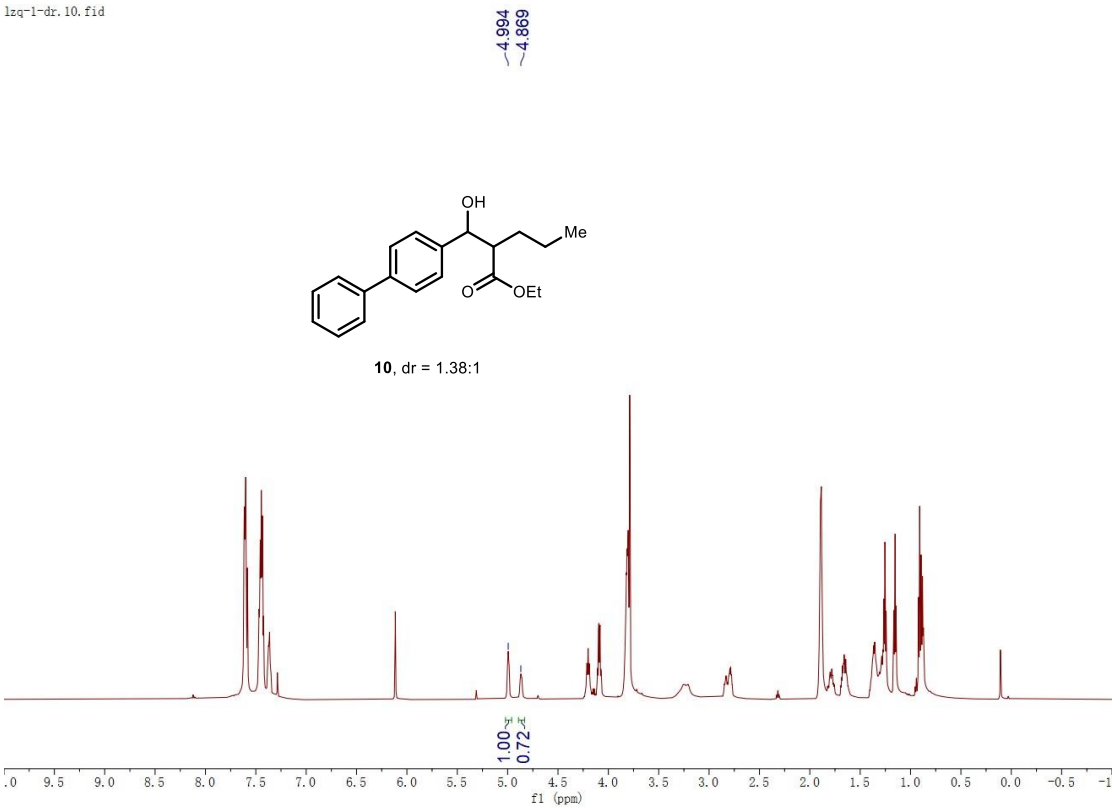


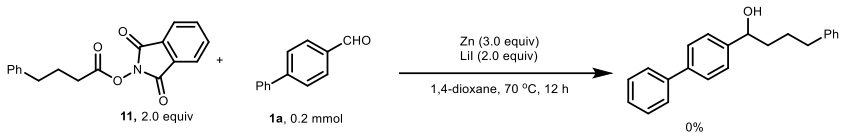
Figure S4. ^{1}H NMR of **10** (reaction mixture, $CDCl_3$, 400 MHz).

NMR spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.34 (t, *J* = 7.2 Hz, 1H), 4.98 (dd, *J* = 5.6 Hz, 2.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.86 (d, *J* = 3.2 Hz, 1H), 2.79-2.70 (m, 1H), 1.82-1.70 (m, 1H), 1.67-1.56 (m, 1H), 1.35-1.25 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H).

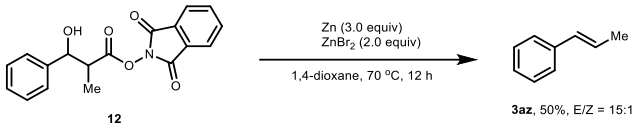
^{13}C NMR (151 MHz, $CDCl_3$) δ 175.15, 140.80, 140.69, 140.55, 128.77, 127.30, 127.05, 126.99, 126.67, 74.07, 60.53, 52.76, 29.21, 20.81, 14.11, 13.96.

HRMS (ESI) calcd for $(C_{20}H_{25}O_3)^+$ $[M + H]^+$: 313.1798, found: 313.1803.

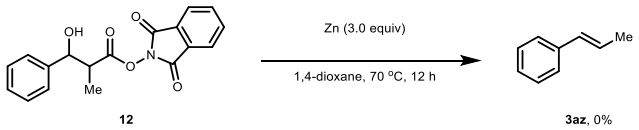


Under the argon atmosphere, 4-phenylbenzaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate **11** (0.4 mmol, 123.7 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was detected by TLC and GC-MS. The 1-([1,1'-biphenyl]-4-yl)-4-phenylbutan-1-ol was not observed.

4.6 Control reactions for the elimination step

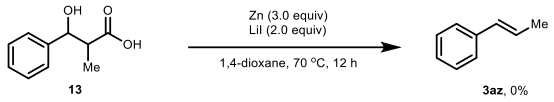


Under the argon atmosphere, 1,3-dioxoisoindolin-2-yl 3-hydroxy-2-methyl-3-phenylpropanoate **12** (0.2 mmol, 65.0 mg, 1.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and $ZnBr_2$ (0.4 mmol, 90.4 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford **3az** resulting in 50% yield (11.8 mg) as a colorless liquid.

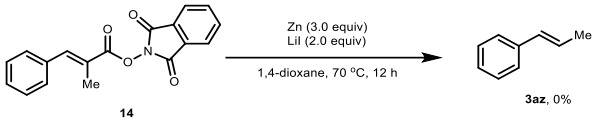


Under the argon atmosphere, 1,3-dioxoisoindolin-2-yl 3-hydroxy-2-methyl-3-phenylpropanoate **12** (0.2 mmol, 65.0 mg, 1.0 equiv) and Zn power (0.6 mmol, 39.2

mg, 3.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was detected by TLC and GC-MS. The **3az** was not observed.

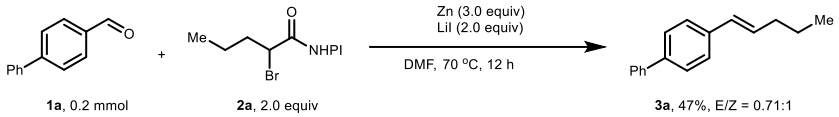


Under the argon atmosphere, 3-hydroxy-2-methyl-3-phenylpropanoic acid **13** (0.2 mmol, 36.1 mg, 1.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was detected by TLC and GC-MS. The **3az** was not observed.



Under the argon atmosphere, 1,3-dioxoisoindolin-2-yl 1,3-dioxoisoindolin-2-yl (E)-2-methyl-3-phenylacrylate (0.2 mmol, 61.4 mg, 1.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous 1,4-dioxane (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was detected by TLC and GC-MS. The **3az** was not observed.

4.7 Solvent effect on the E/Z selectivity



Under the argon atmosphere, 4-biphenylcarboxaldehyde **1a** (0.2 mmol, 36.4 mg, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 2-bromopentanoate **2a** (0.4 mmol, 131.0 mg, 2.0 equiv), Zn power (0.6 mmol, 39.2 mg, 3.0 equiv) and LiI (0.4 mmol, 54.0 mg, 2.0 equiv) were added to a 10 mL Schlenk tube with a magnetic bar. Anhydrous DMF (1.0 mL) was charged and the solution was stirred at 70 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residual was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford **3a** (21.0 mg) in 47 % yield as a white solid.

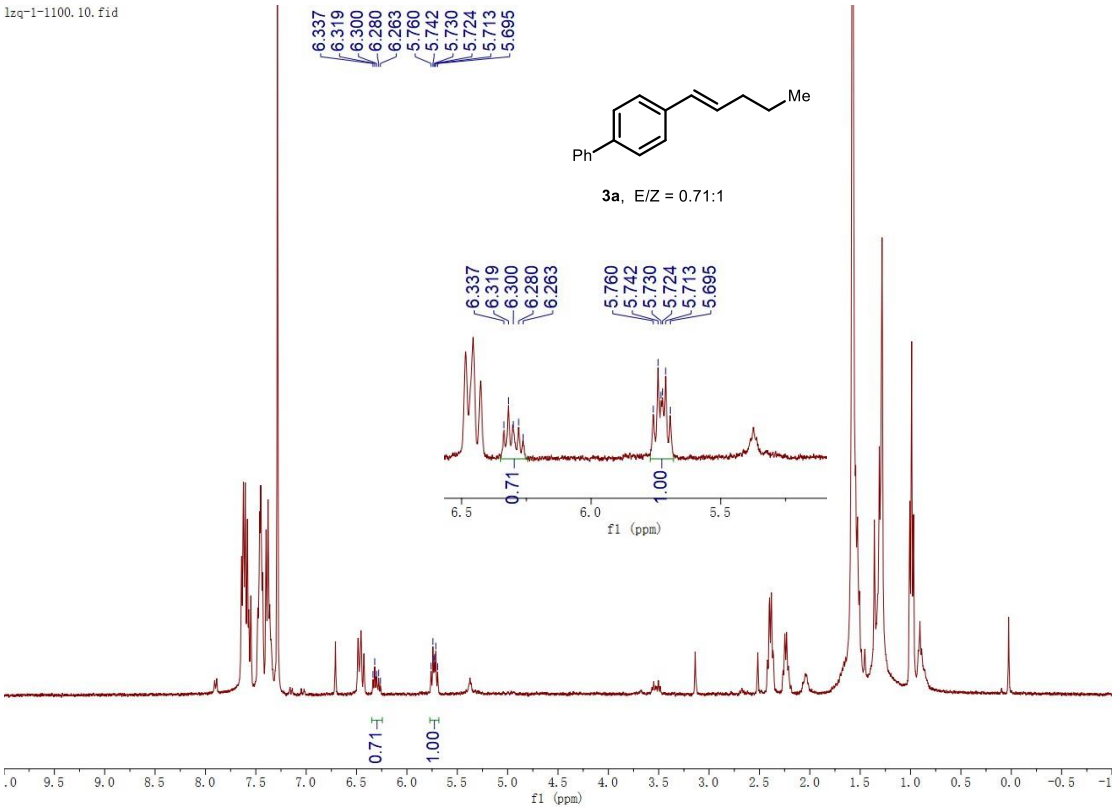
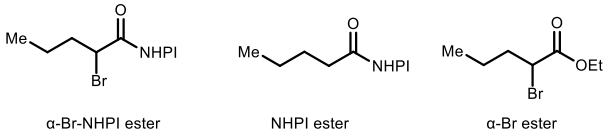


Figure S5. ^{1}H NMR of the reaction mixture ($CDCl_3$, 400 MHz).

4.8 Cyclic Voltammetry experiments

(I) CV measurement of the oxidation potential of α-Br-NHPI ester, NHPI ester, α-Br ester.



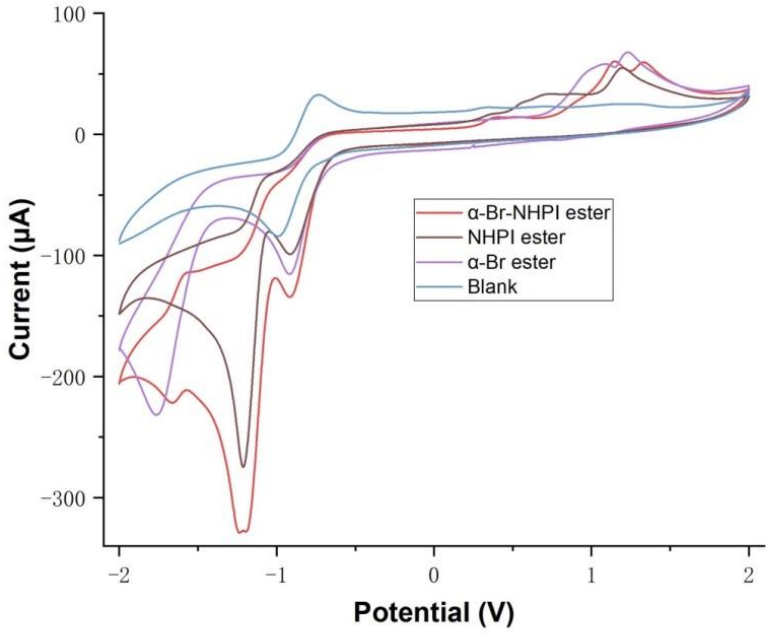


Figure S6. **Cyclic Voltammogram for α-Br-NHPI ester, NHPI ester** and **α-Br ester.** Redox potentials were measured by cyclic voltammetry in degassed MeCN at room temperature (two segments: 2 V to – 2.0 V and then back to 2 V; sweep rate 100 mV/s) under air. The concentration of α-Br-NHPI ester, NHPI ester and α-Br ester. were 10 mM and Bu_4NPF_6 (0.1 M) was employed as the supporting electrolyte. A standard three-electrode assembly consisting of a glassy carbon disk as the working electrode, copper plated with platinum as the counter electrode, and Ag/AgCl (saturated in 3 M KCl) as the reference electrode was used.

(II) CV measurement of the oxidation potential of α-Br-NHPI ester, α-Br-NHPI ester + LiI and α-Br-NHPI ester + $ZnBr_2$

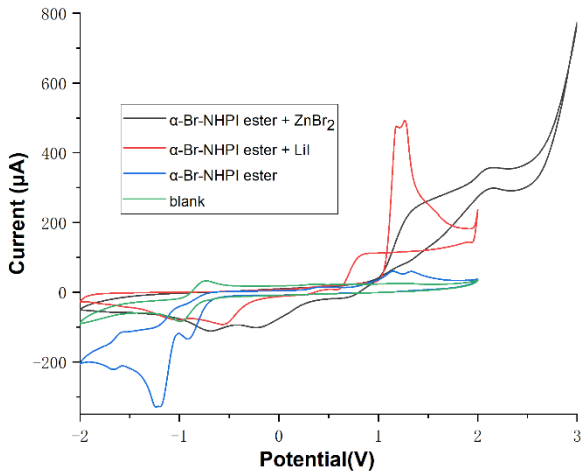
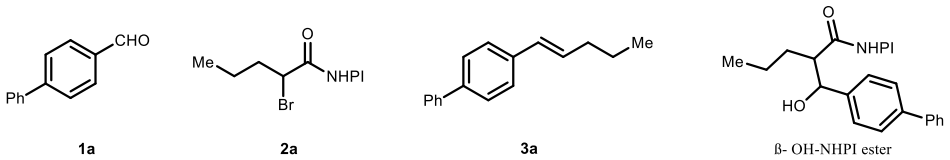


Figure S7. **Cyclic Voltammogram for α-Br-NHPI ester, α-Br-NHPI ester + LiI** and **α-Br-NHPI ester + $ZnBr_2$.** Redox potentials were measured by cyclic voltammetry in degassed MeCN at room temperature (two segments: 2 V to – 2.0 V and then back to 3 V; sweep rate 100 mV/s) under air. The concentration of α-Br-NHPI ester, α-Br-NHPI ester + LiI and α-Br-NHPI ester + $ZnBr_2$ were 10 mM, and Bu_4NPF_6 (0.1 M) was employed as the supporting electrolyte. A standard three-electrode assembly consisting of a glassy carbon disk as the working electrode, copper plated with platinum as the counter electrode, and Ag/AgCl (saturated in 3 M KCl) as the reference electrode was used.

4.9 Analysis of UV-Vis absorption spectra



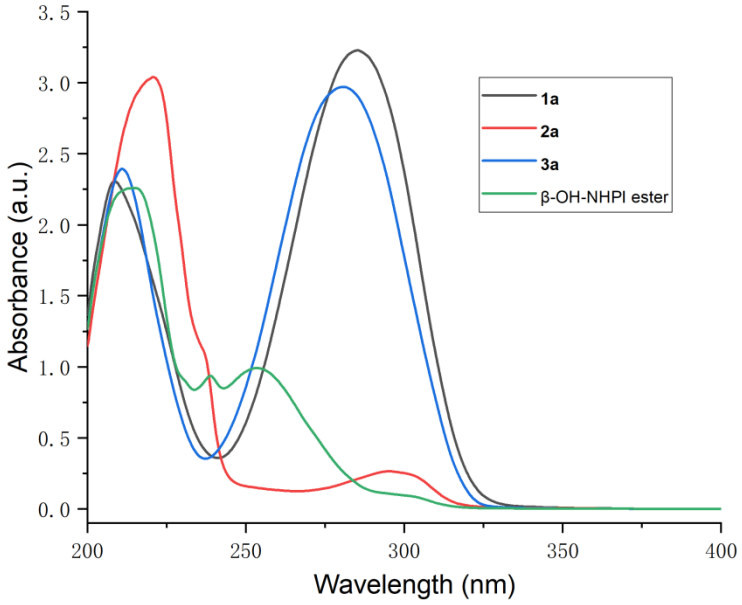


Figure S8. UV-visible absorption spectra of **1a**, **2a**, **3a** and β-OH-NHPI ester recorded at room temperature in MeCN (3×10^{-4} M).

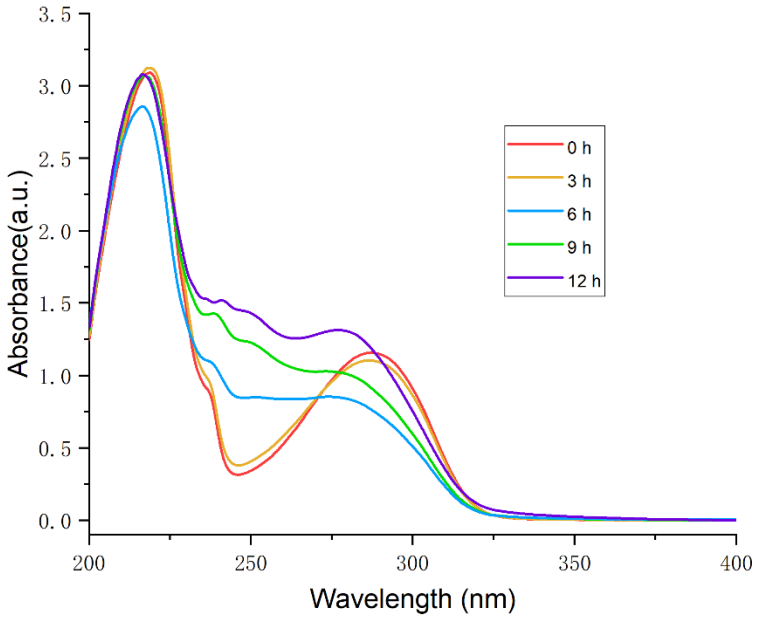


Figure S9. UV-visible absorption spectra of reaction mixture 0 h, 3 h, 6 h, 9 h and 12 h recorded at room temperature in MeCN (3×10^{-4} M).

5. References

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6. Copies of NMR spectra

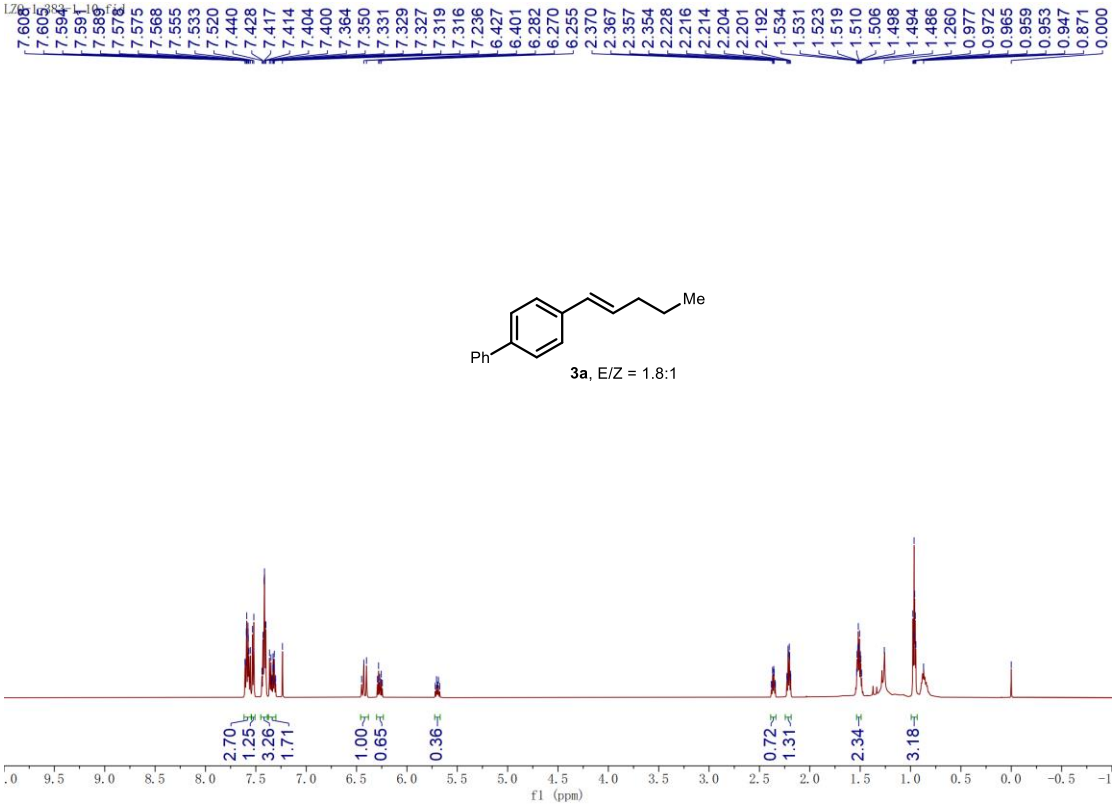

Figure S10. ^{1}H NMR of **3a** (trans/cis mixture, $CDCl_3$, 600 MHz).

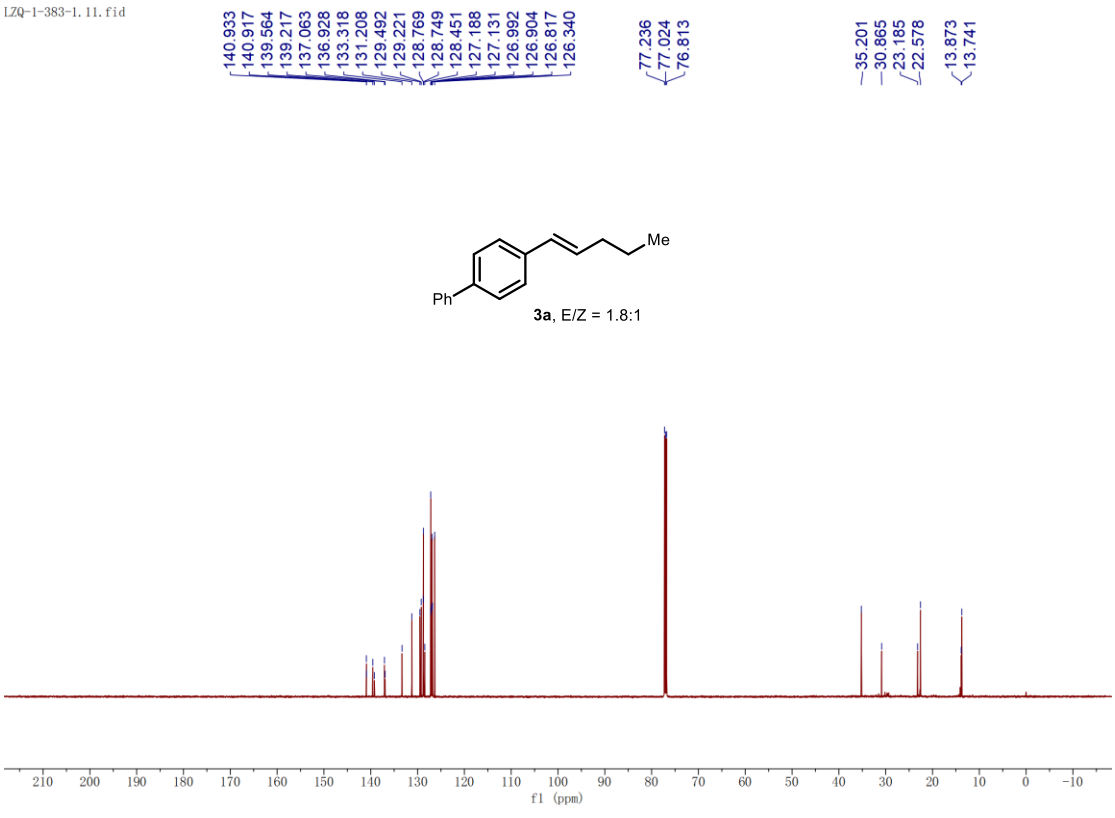

Figure S11. ^{13}C NMR of **3a** (trans/cis mixture, $CDCl_3$, 151 MHz).

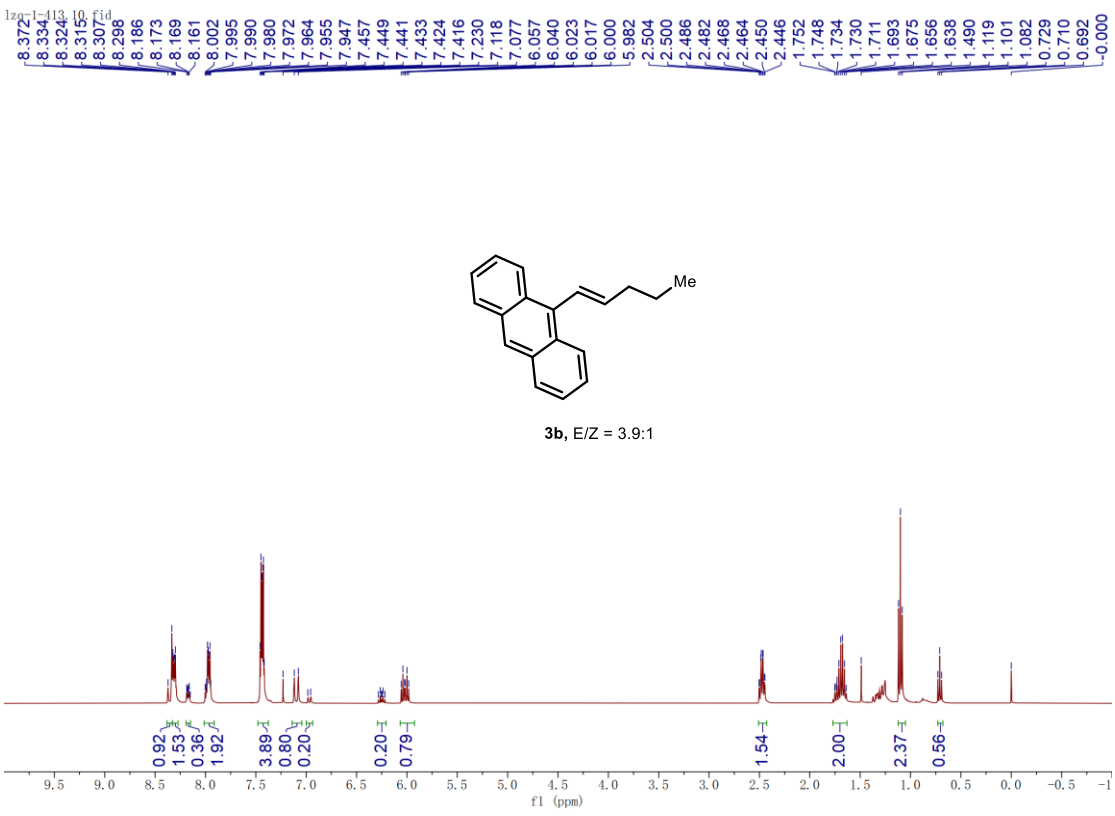

Figure S12. ^{1}H NMR of **3b** (trans/cis mixture, $CDCl_3$, 400 MHz).

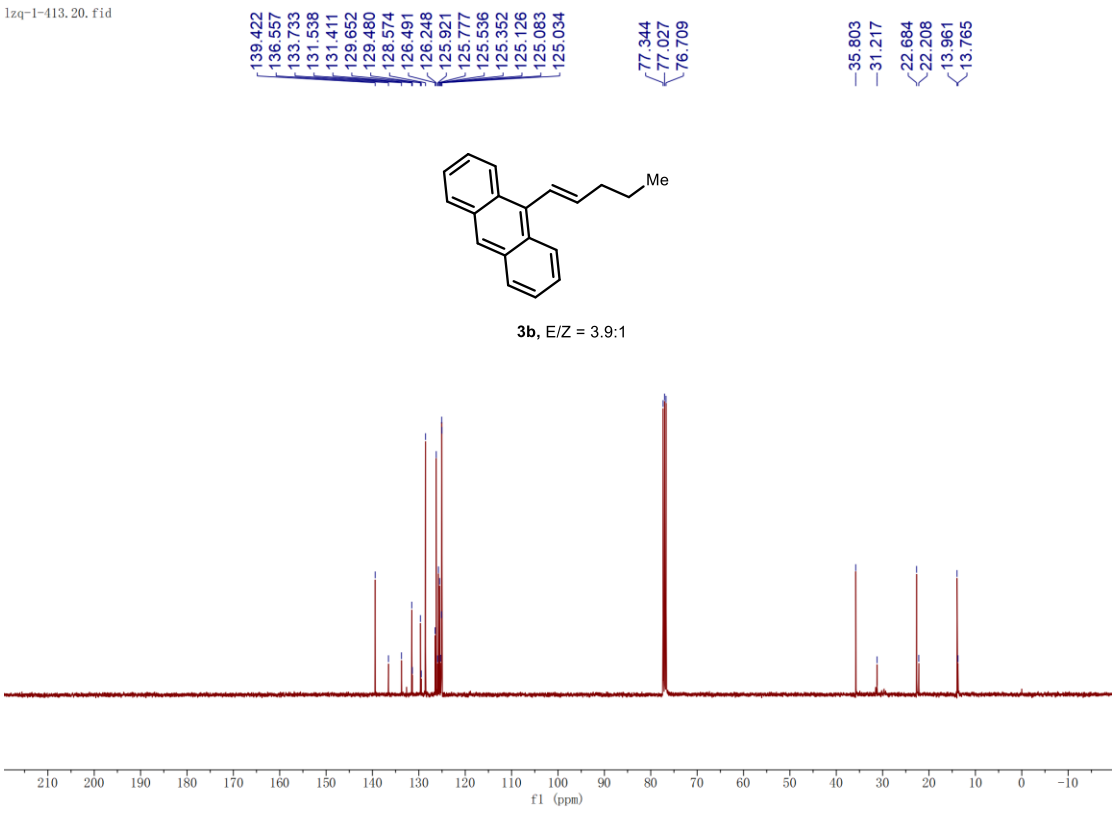

Figure S13. ^{13}C NMR of **3b** (trans/cis mixture, $CDCl_3$, 101 MHz).

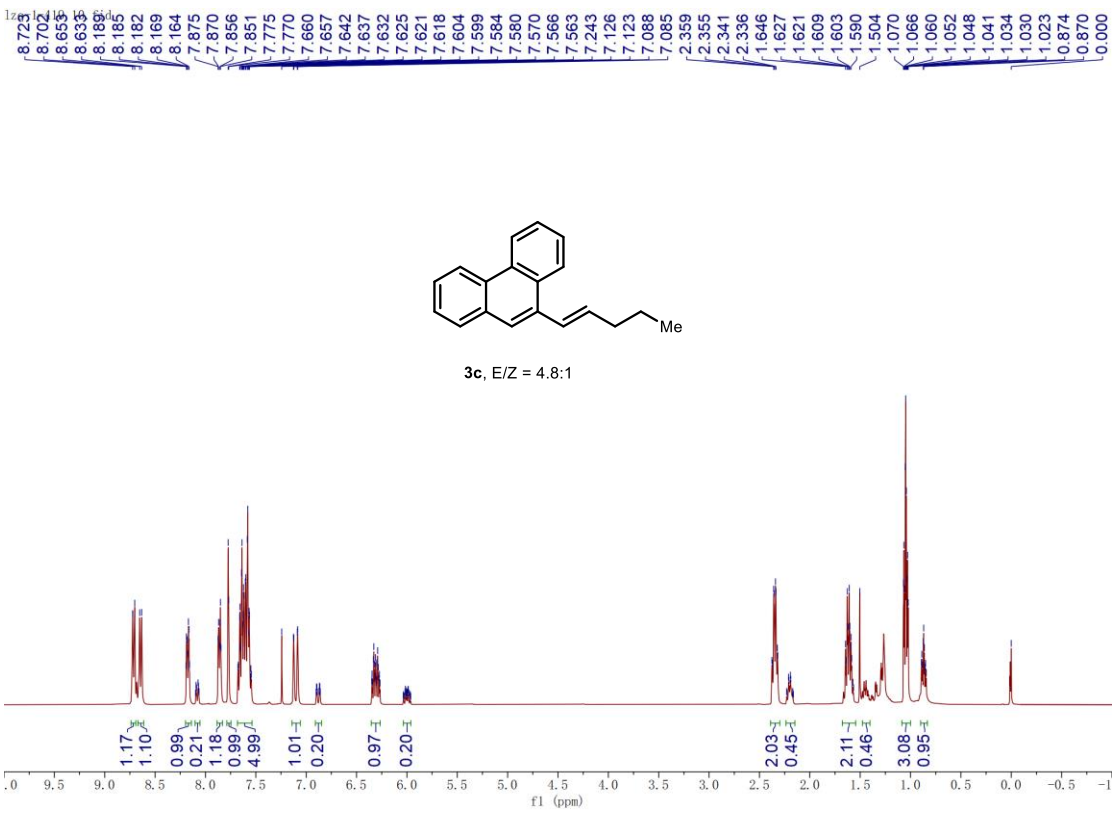

Figure S14. ^{1}H NMR of **3c** (trans/cis mixture, $CDCl_3$, 400 MHz).

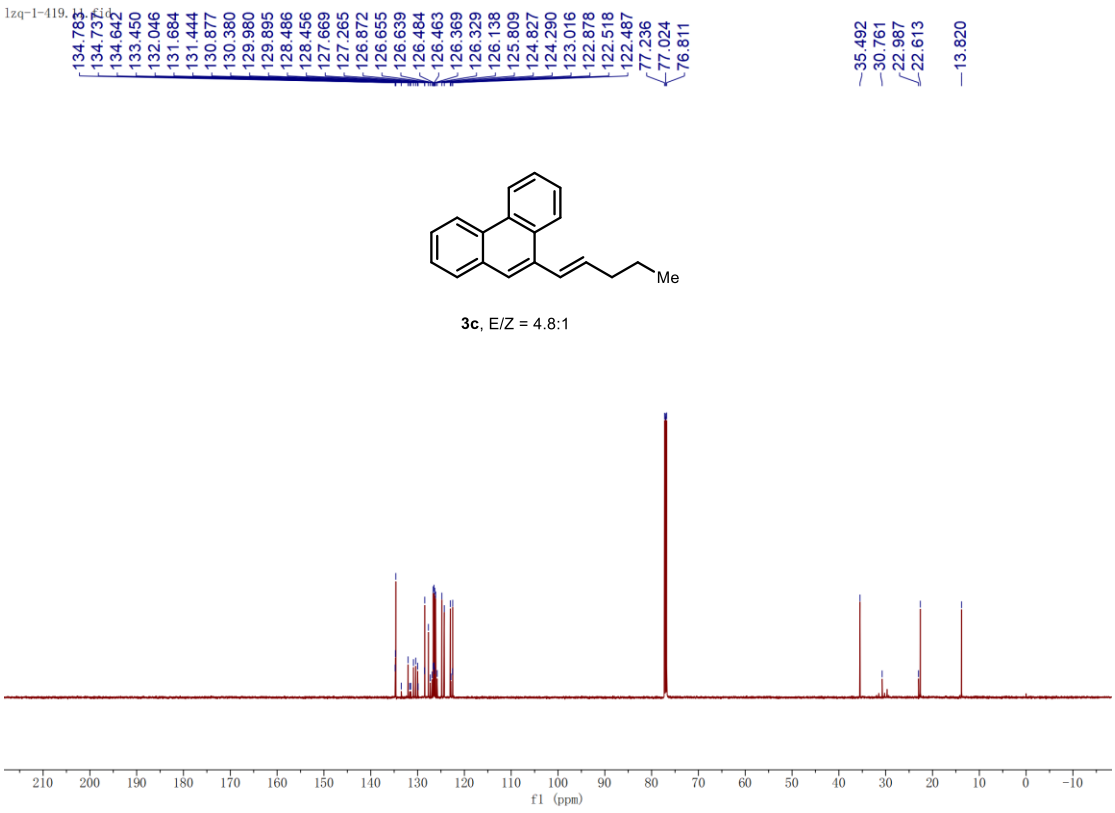

Figure S15. ^{13}C NMR of **3c** (trans/cis mixture, $CDCl_3$, 151 MHz).

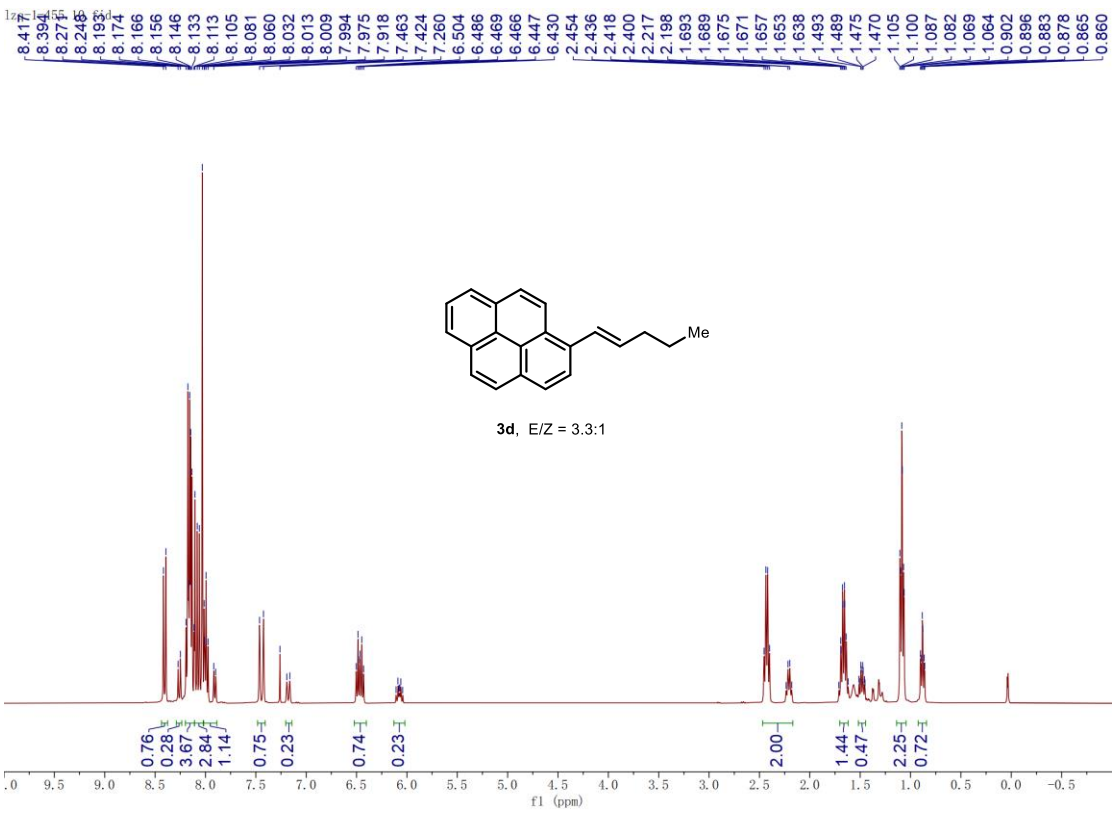

Figure S16. ^{1}H NMR of **3d** (trans/cis mixture, $CDCl_3$, 400 MHz).

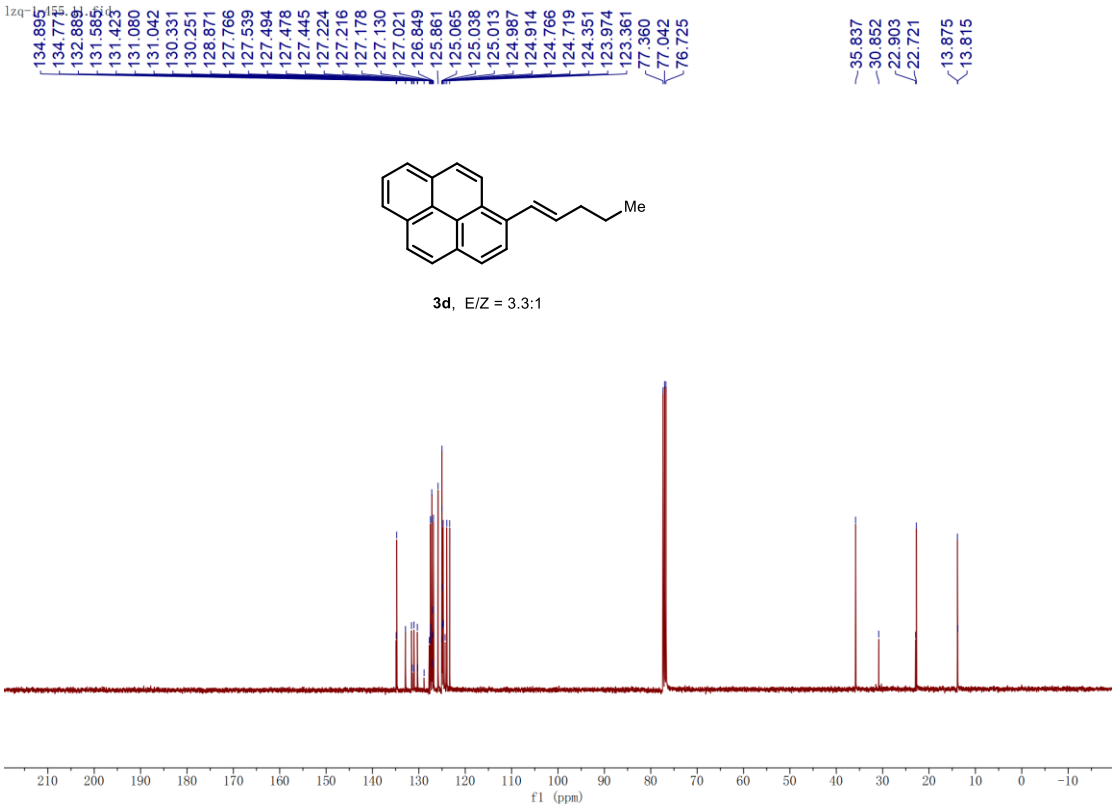

Figure S17. ^{13}C NMR of **3d** (trans/cis mixture, $CDCl_3$, 101 MHz).

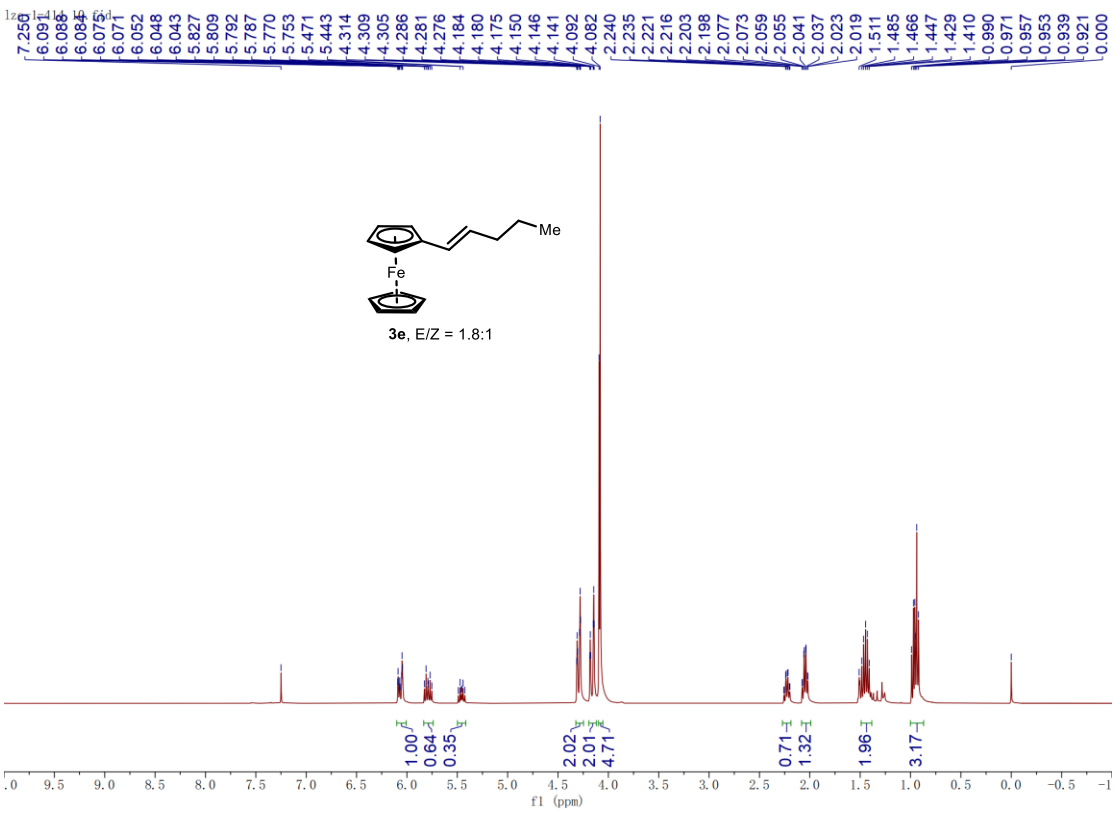

Figure S18. ^{1}H NMR of **3e** (trans/cis mixture, $CDCl_3$, 400 MHz).

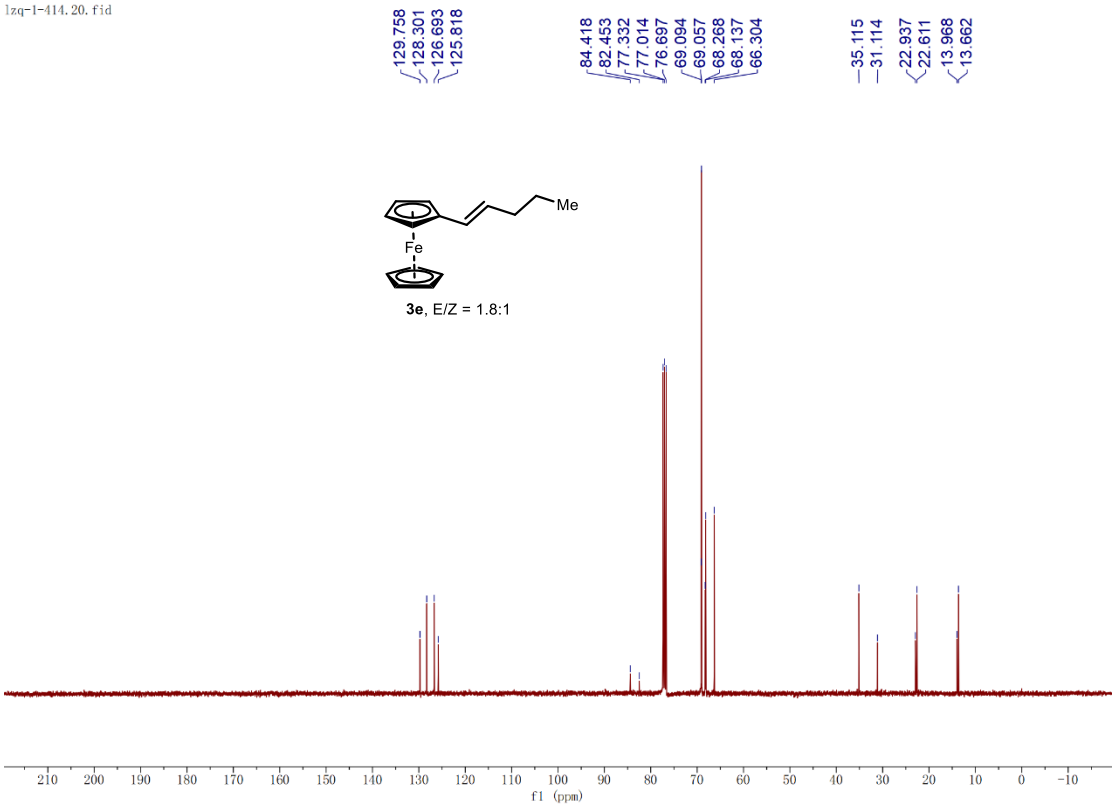

Figure S19. ^{13}C NMR of **3e** (trans/cis mixture, $CDCl_3$, 101 MHz).

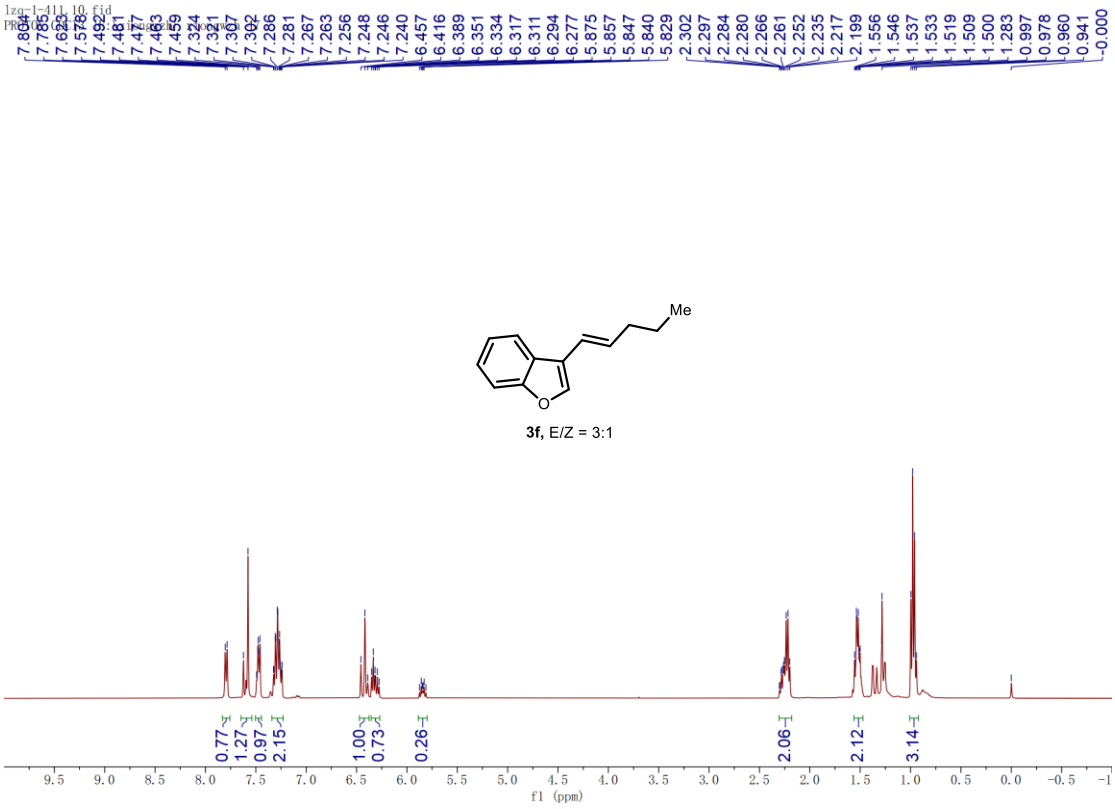

Figure S20. ^{1}H NMR of **3f** (trans/cis mixture, $CDCl_3$, 400 MHz).

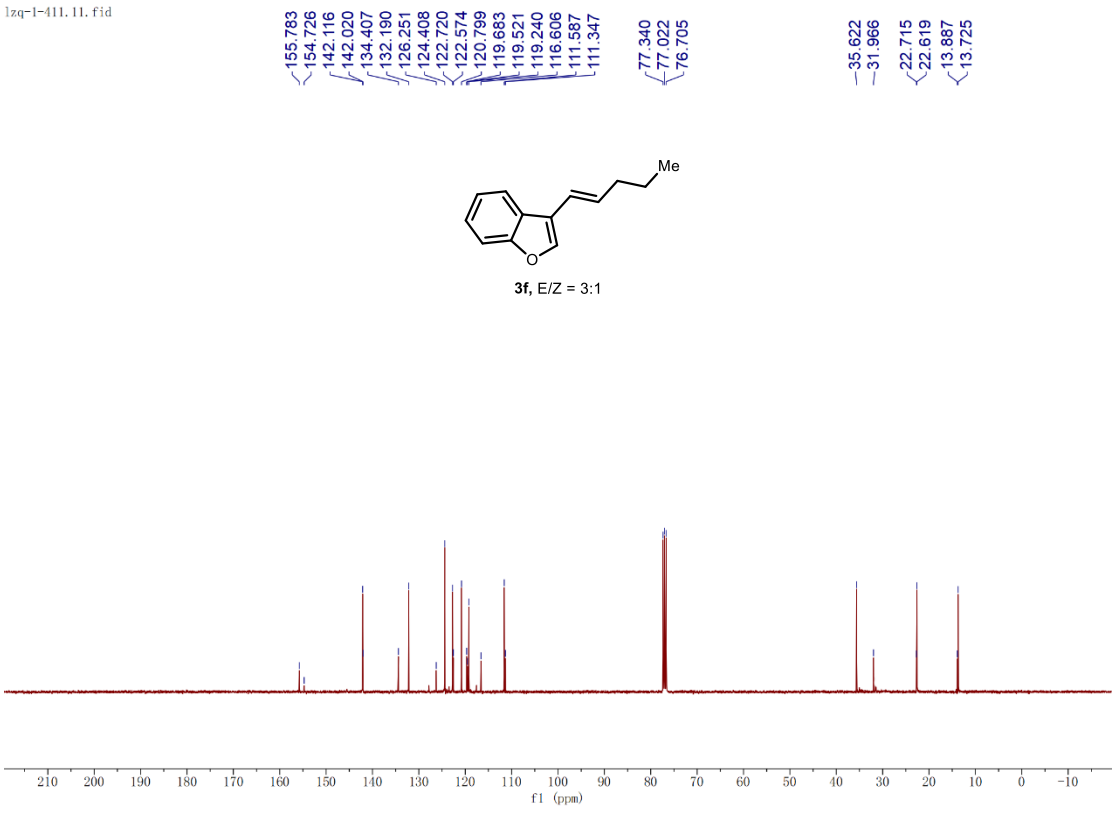

Figure S21. ^{13}C NMR of **3f** (trans/cis mixture, $CDCl_3$, 101 MHz).

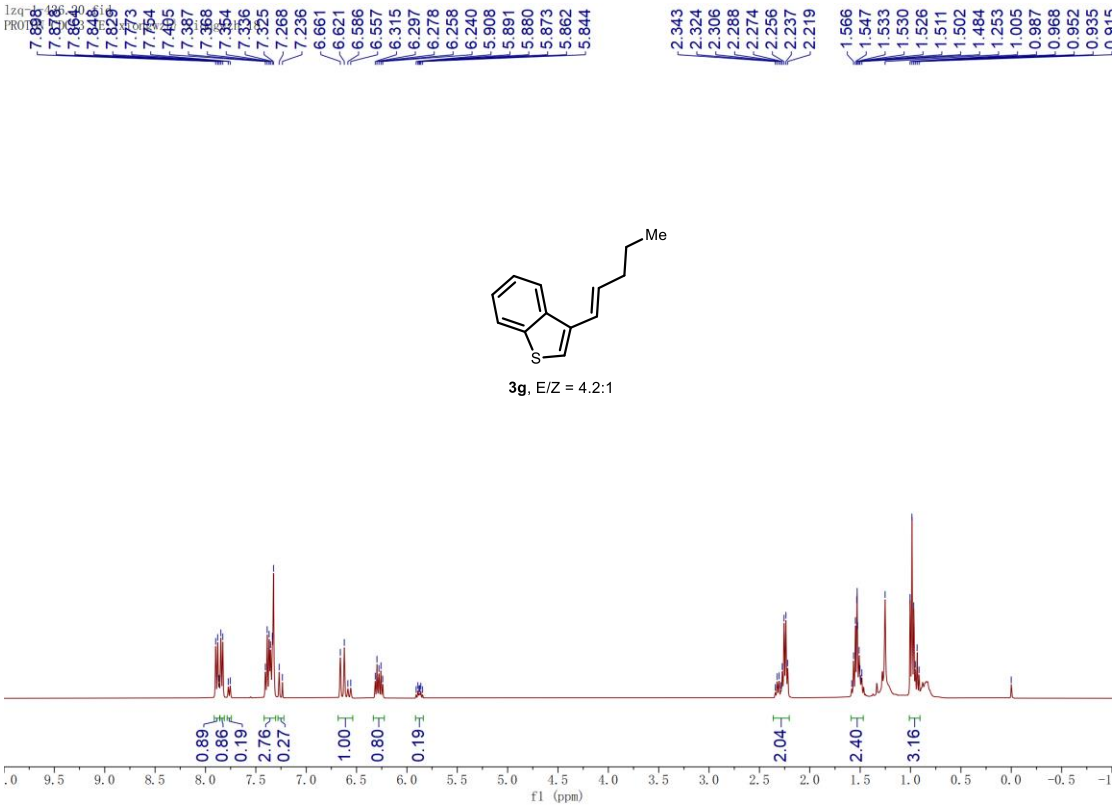

Figure S22. ^{1}H NMR of **3g** (trans/cis mixture, $CDCl_3$, 400 MHz).

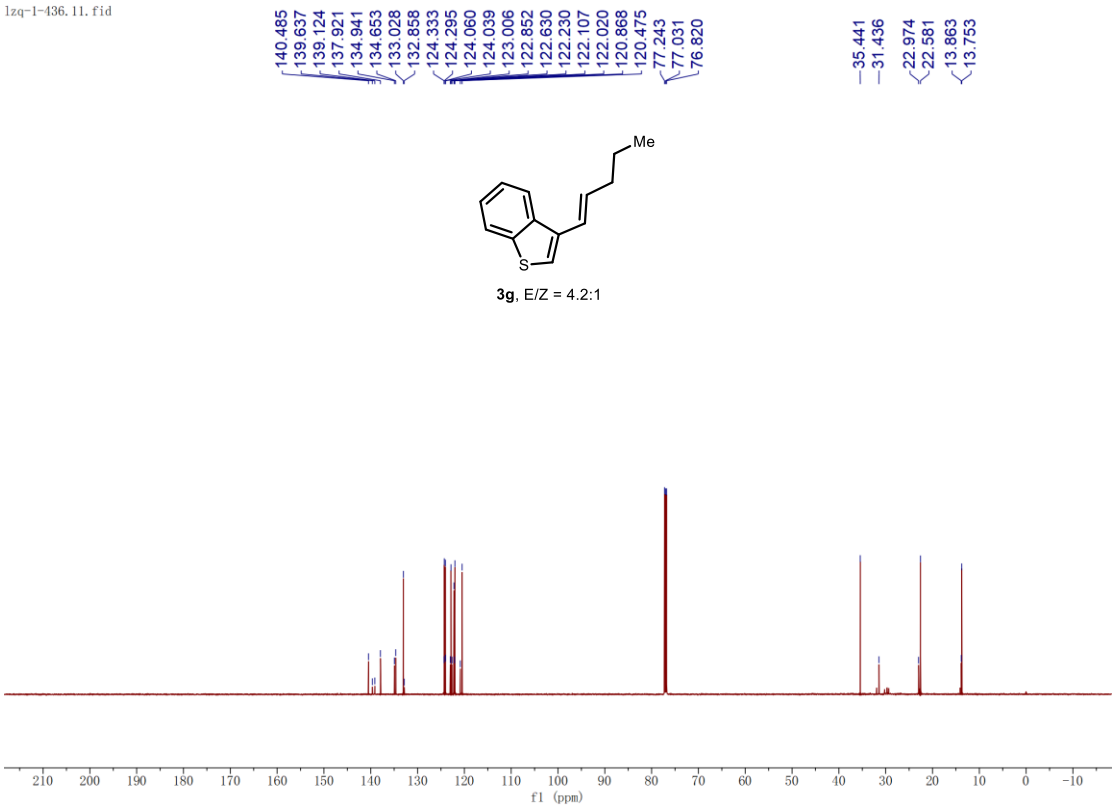

Figure S23. ^{13}C NMR of **3g** (trans/cis mixture, $CDCl_3$, 151 MHz).

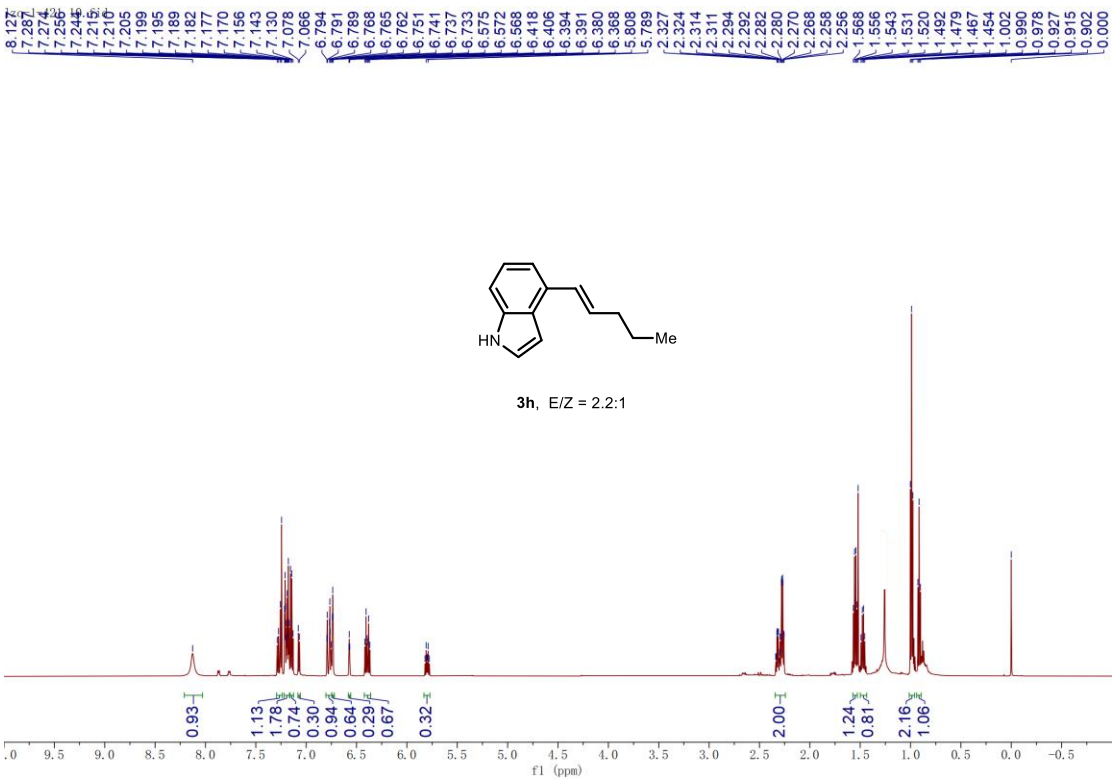

Figure S24. ^{1}H NMR of **3h** (trans/cis mixture, $CDCl_3$, 600 MHz).

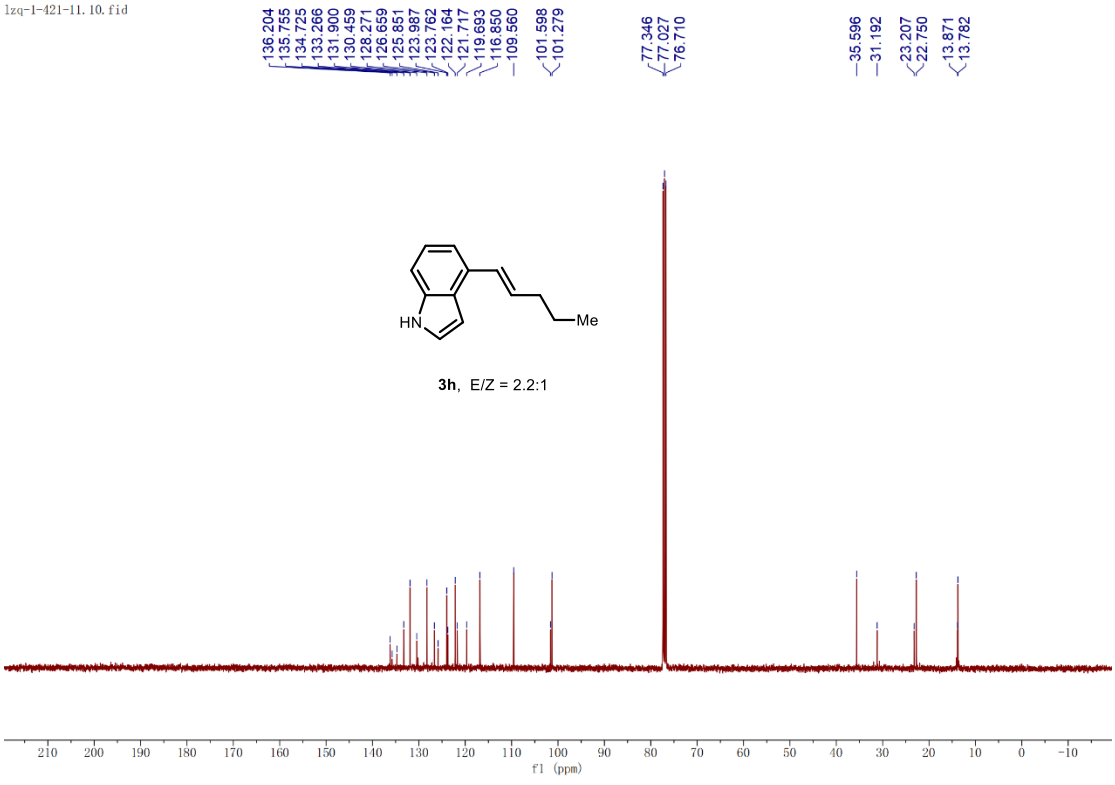

Figure S25. ^{13}C NMR of **3h** (trans/cis mixture, $CDCl_3$, 101 MHz).

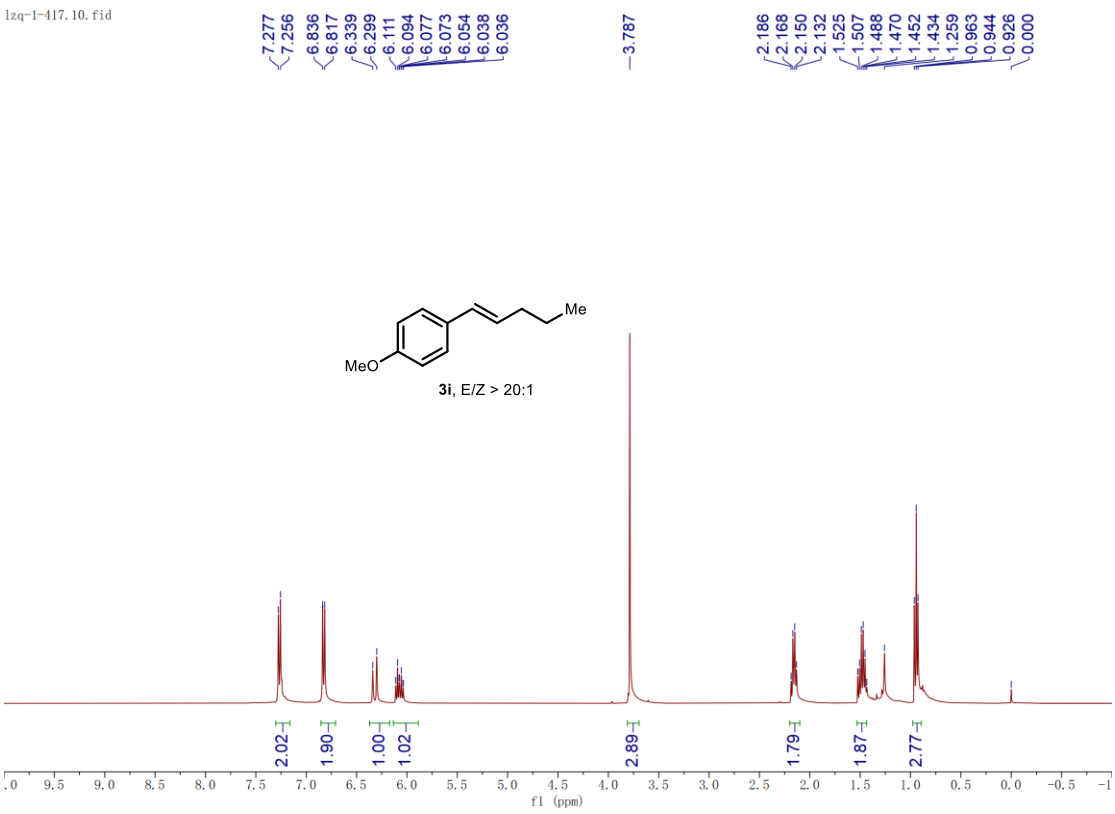

Figure S26. ^{1}H NMR of **3i** (trans, $CDCl_3$, 400 MHz).

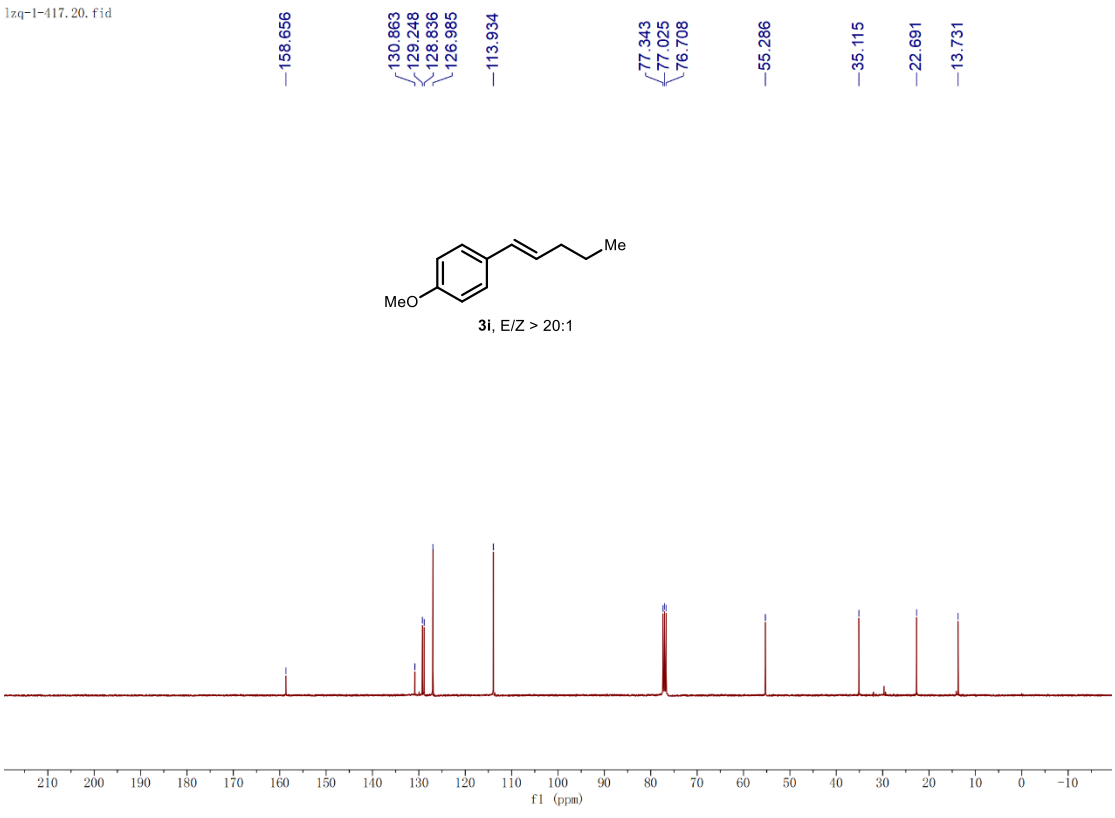

Figure S27. ^{13}C NMR of **3i** (trans, $CDCl_3$, 101 MHz).

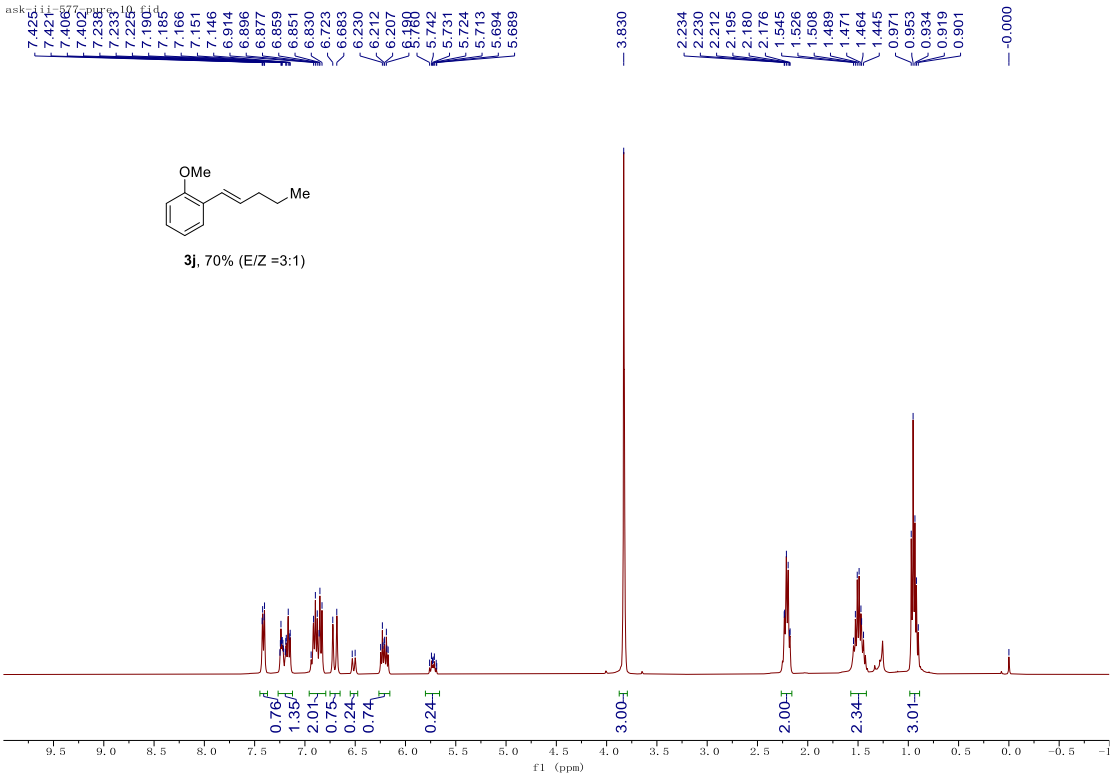

Figure S28. ^{1}H NMR of **3j** (trans/cis mixture, $CDCl_3$, 400 MHz).

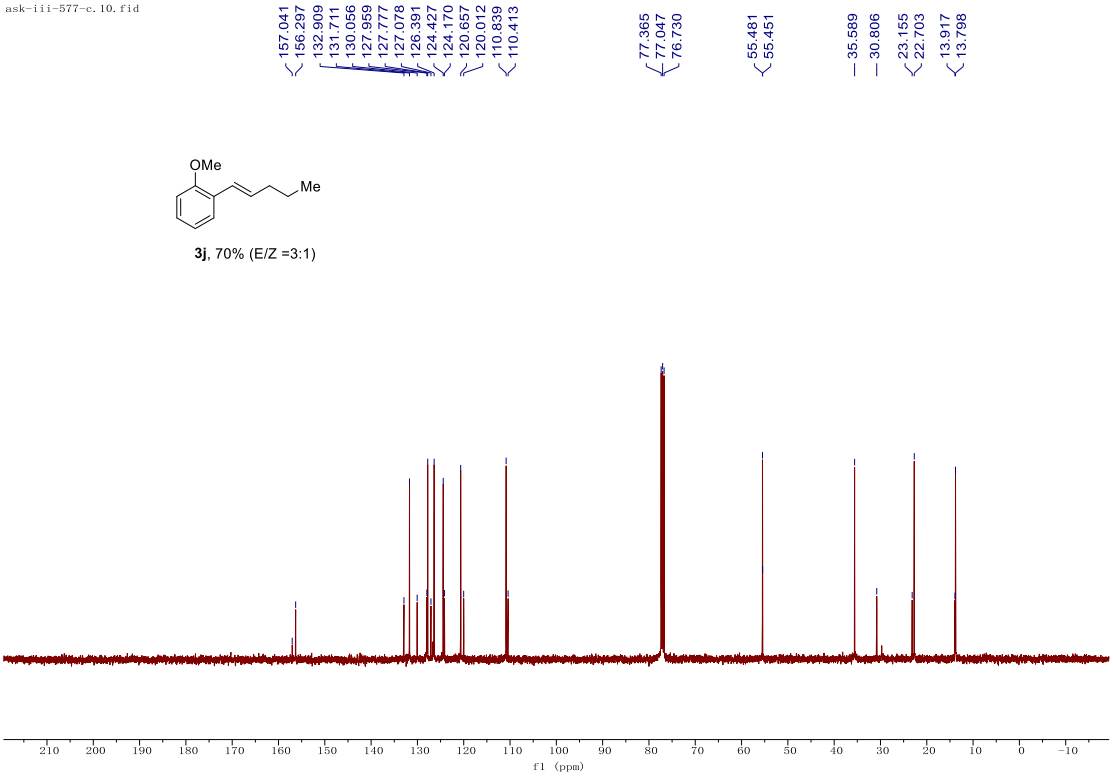

Figure S29. ^{13}C NMR of **3j** (trans/cis mixture, $CDCl_3$, 101 MHz).

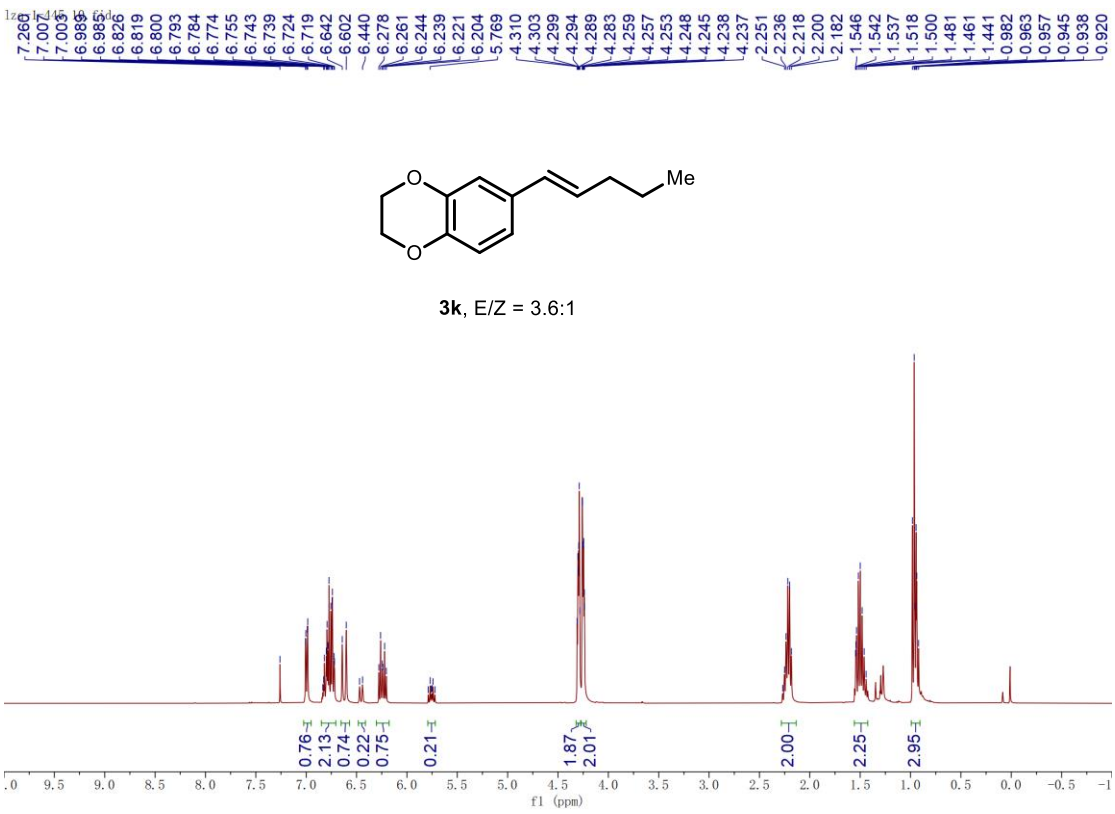

Figure S30. ^{1}H NMR of **3k** (trans/cis mixture, $CDCl_3$, 400 MHz).

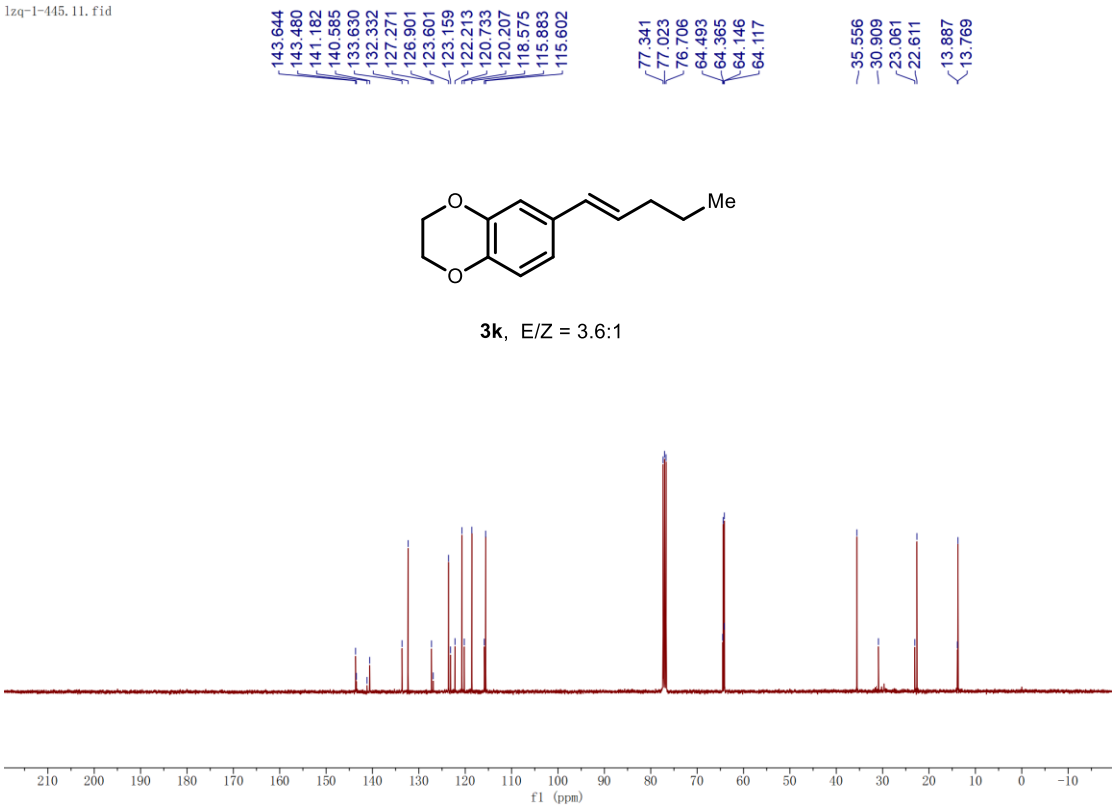

Figure S31. ^{13}C NMR of **3k** (trans/cis mixture, $CDCl_3$, 101 MHz).

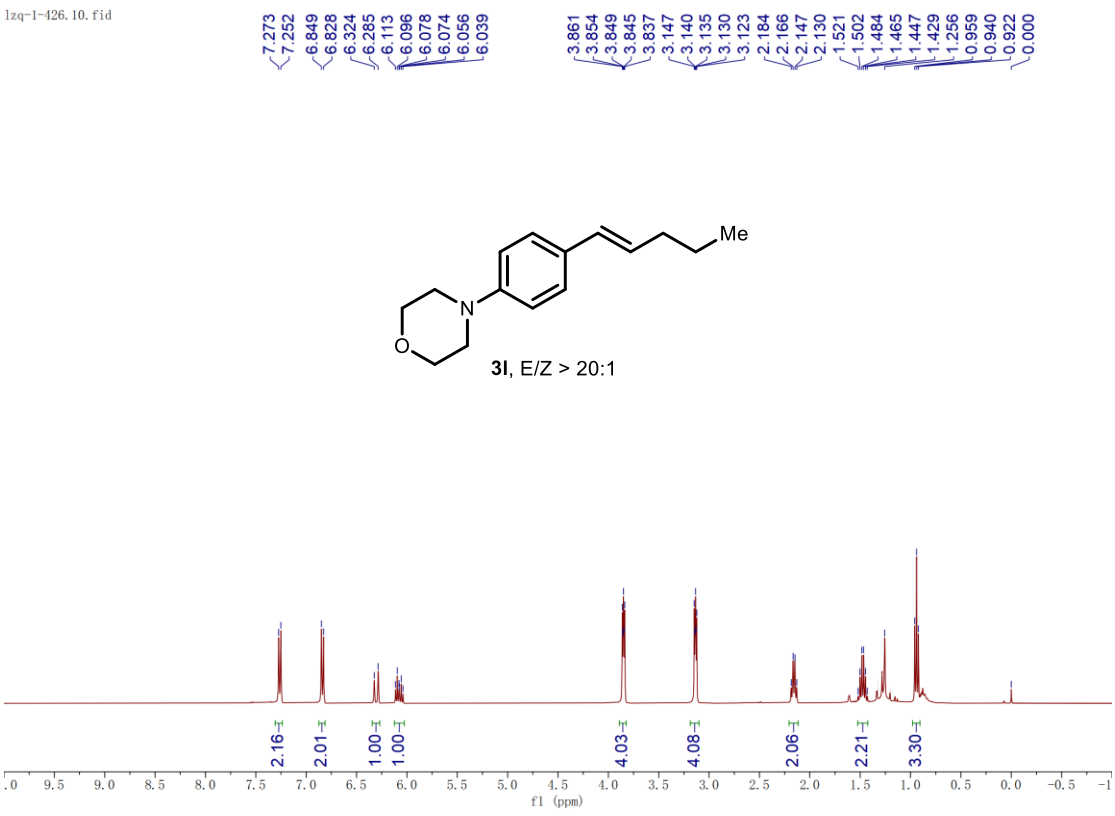

Figure S32. ^{1}H NMR of **3l** (trans, $CDCl_3$, 400 MHz).

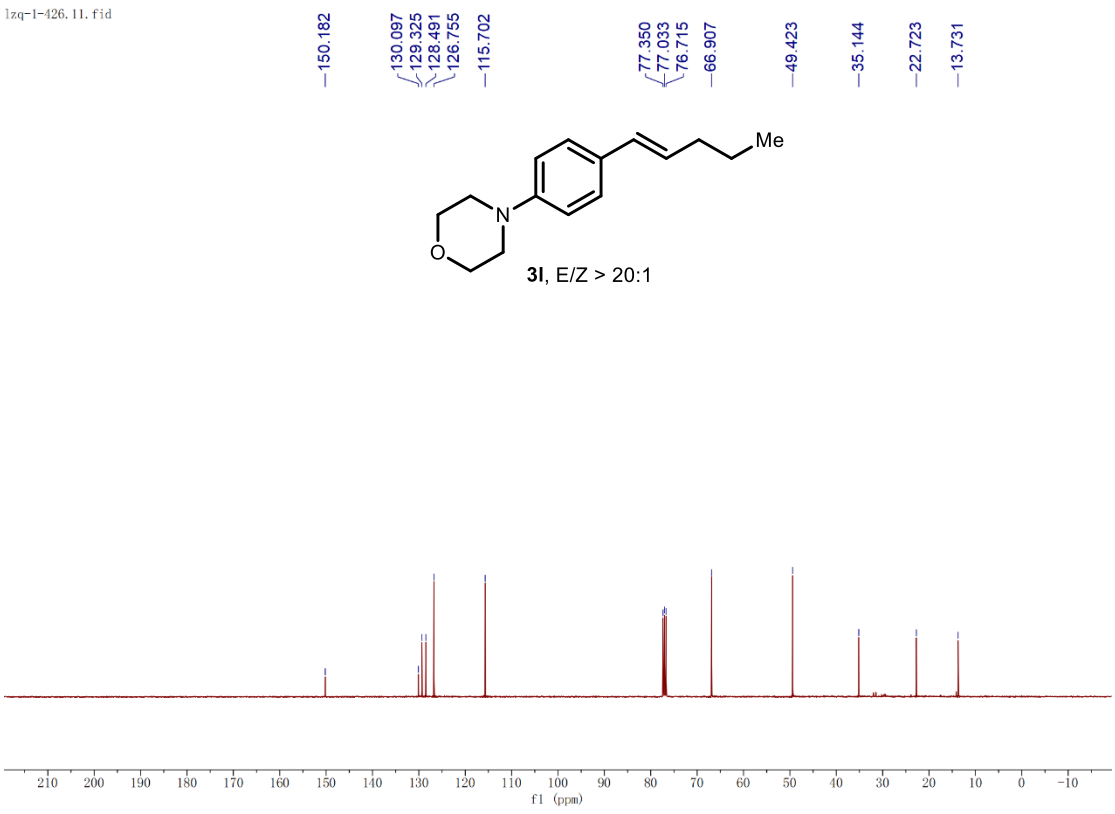

Figure S33. ^{13}C NMR of **3l** (trans, $CDCl_3$, 101 MHz).

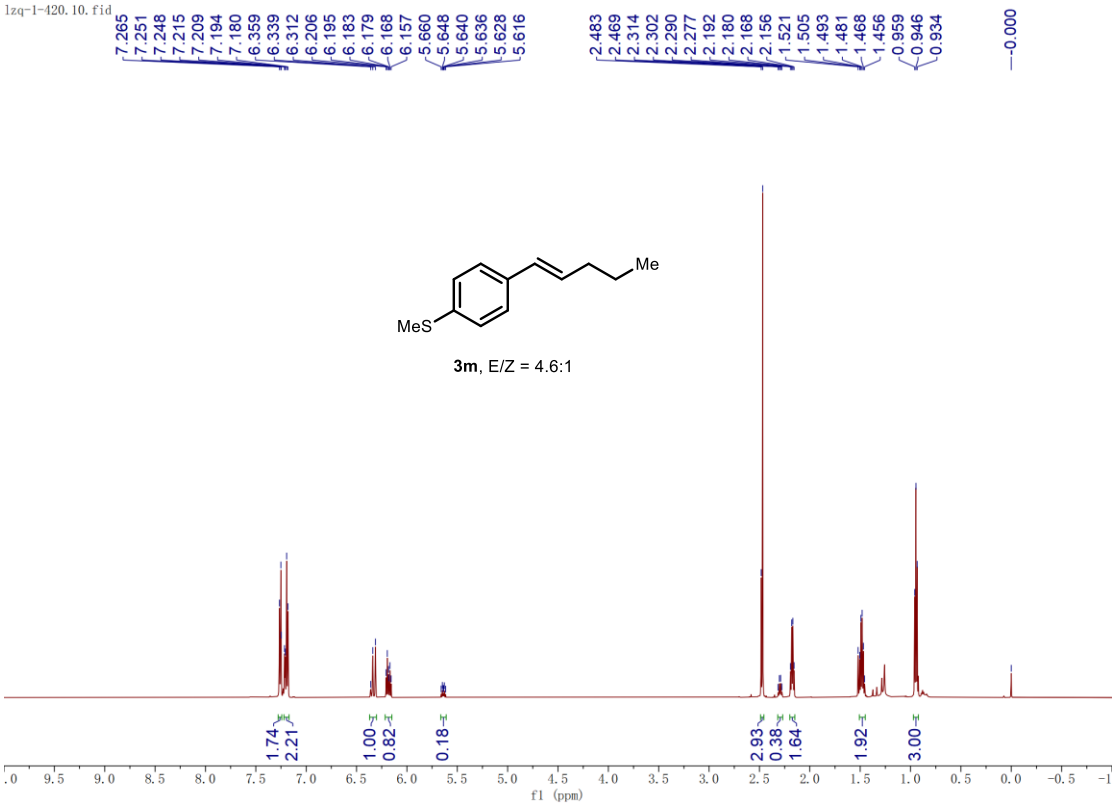

Figure S34. ^{1}H NMR of **3m** (trans/cis mixture, $CDCl_3$, 600 MHz).

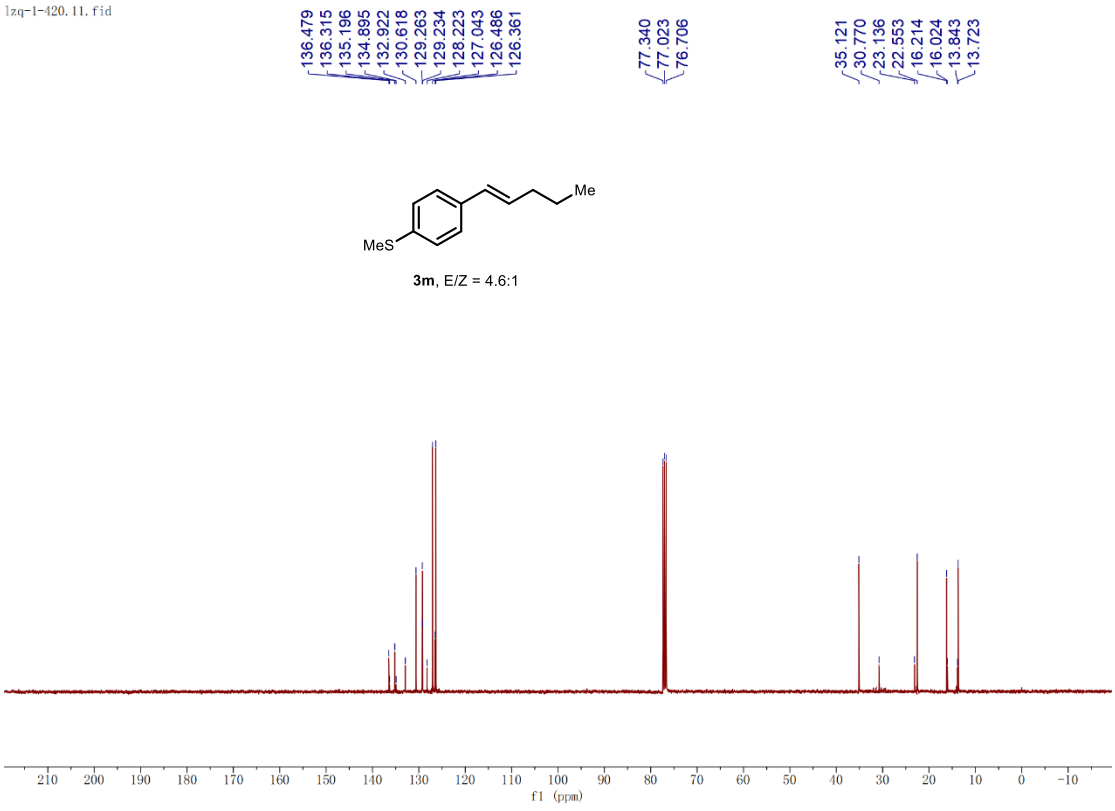

Figure S35. ^{13}C NMR of **3m** (trans/cis mixture, $CDCl_3$, 101 MHz).

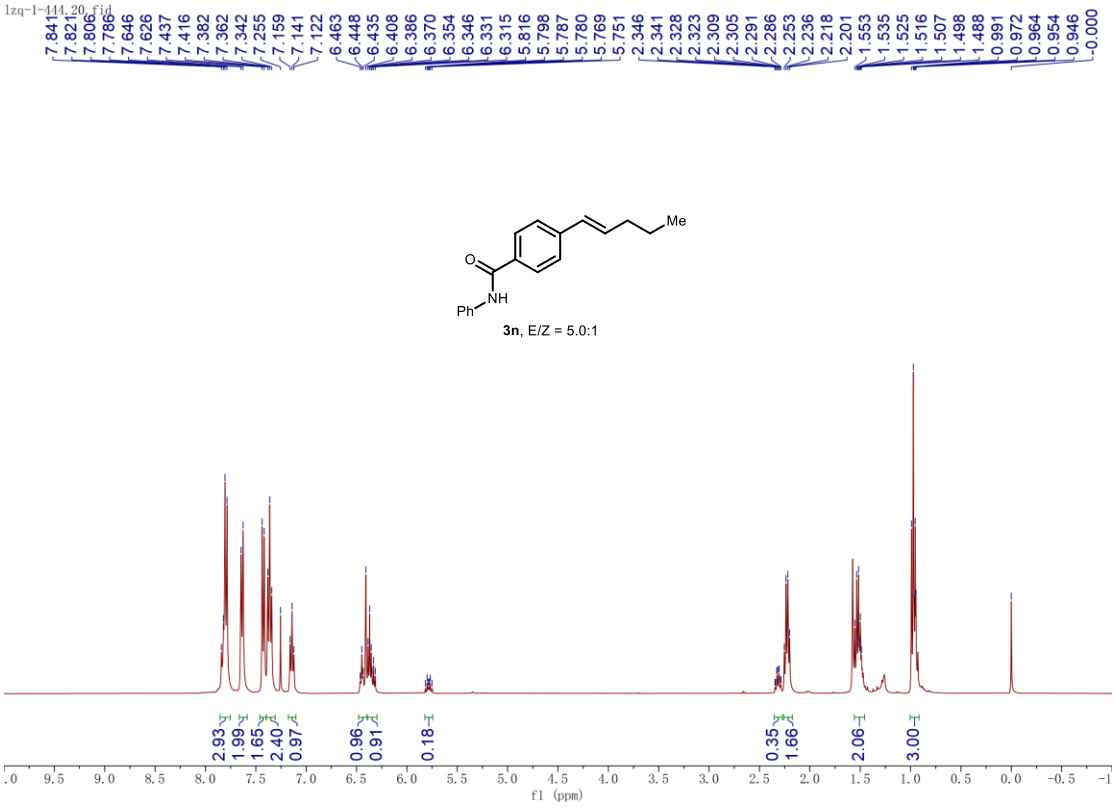

Figure S36. ^{1}H NMR of **3n** (trans/cis mixture, $CDCl_3$, 400 MHz).

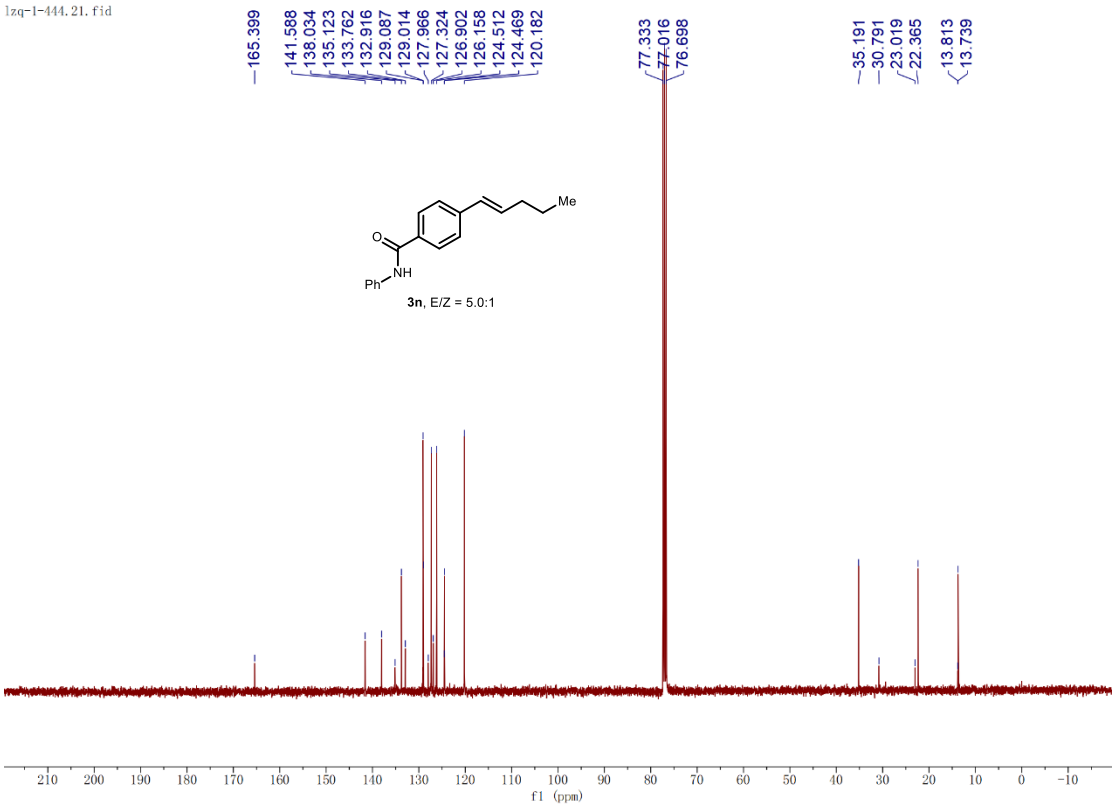

Figure S37. ^{13}C NMR of **3n** (trans/cis mixture, $CDCl_3$, 101 MHz).

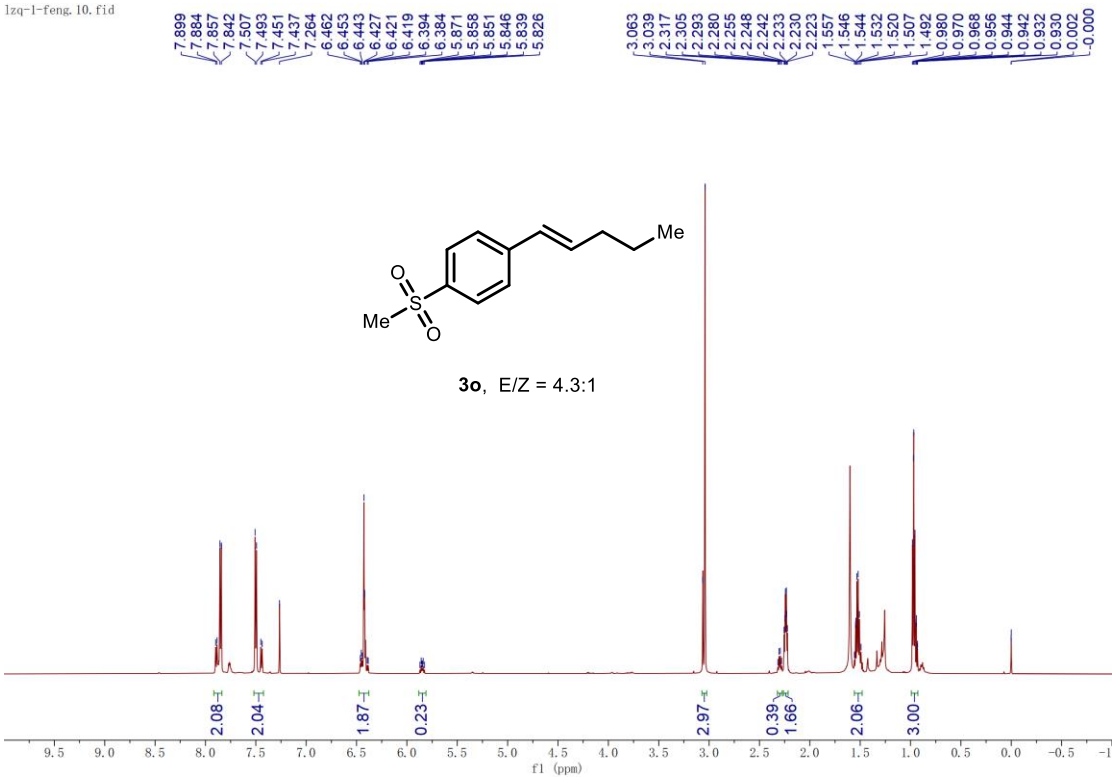

Figure S38. ^{1}H NMR of **3o** (trans/cis mixture, $CDCl_3$, 600 MHz).

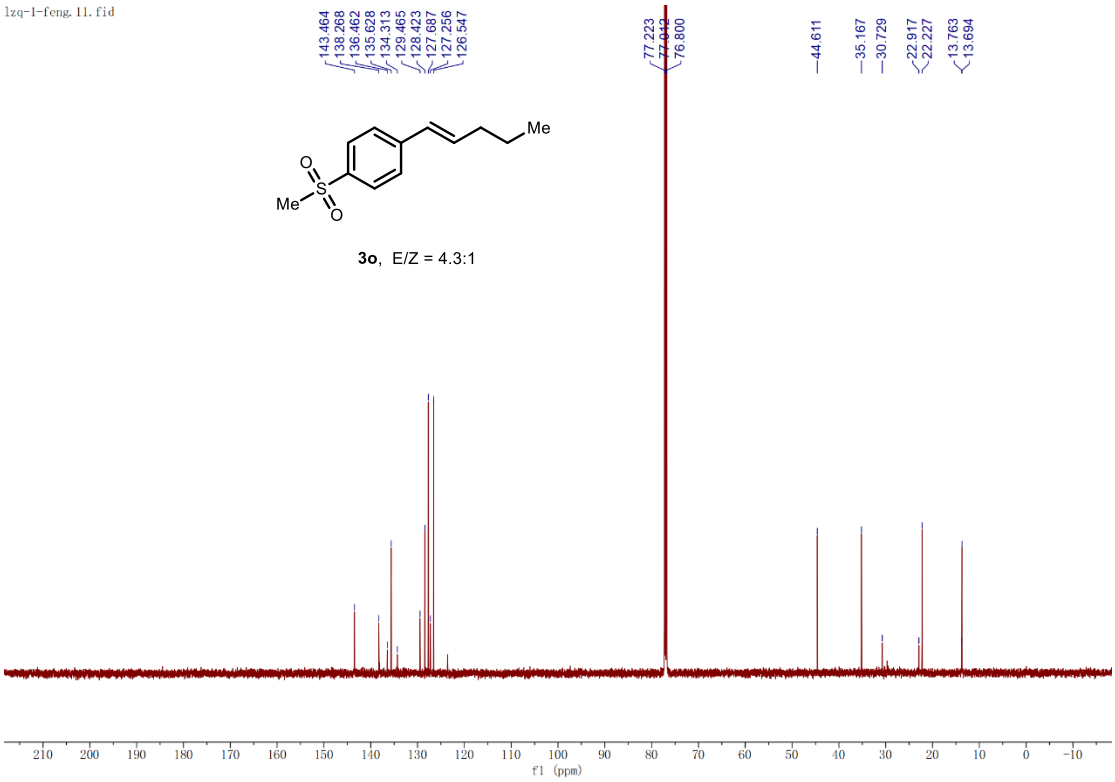

Figure S39. ^{13}C NMR of **3o** (trans/cis mixture, $CDCl_3$, 151 MHz).

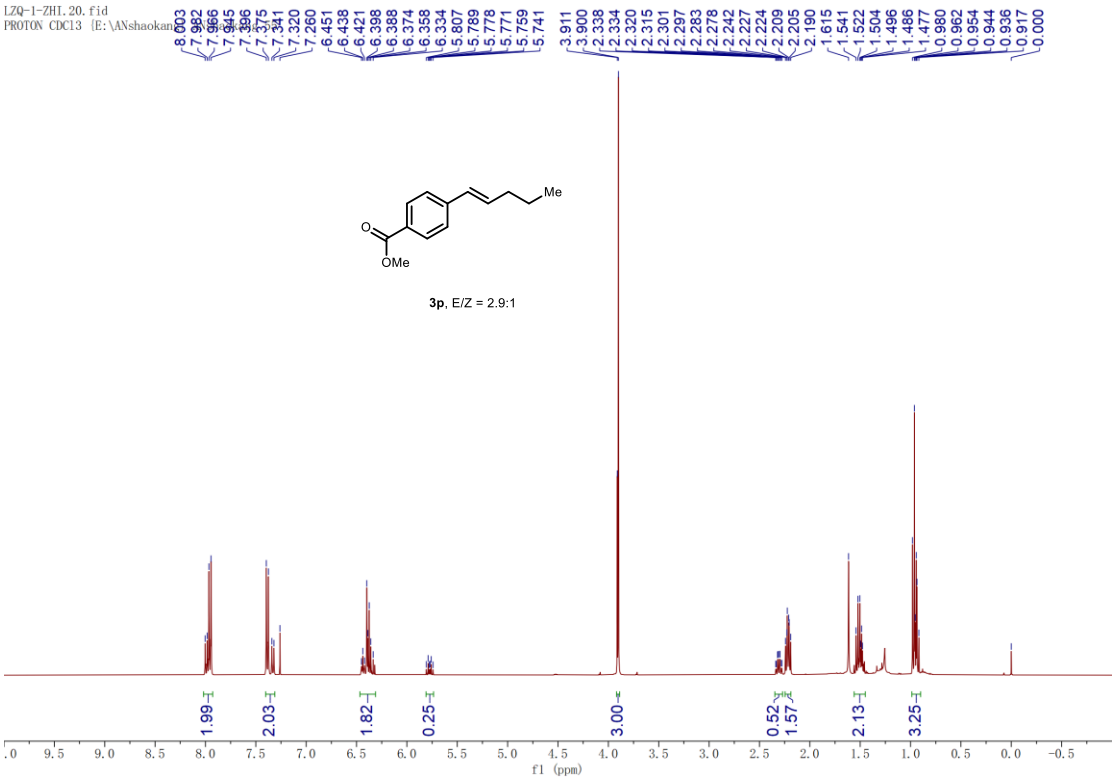

Figure S40. ^{1}H NMR of **3p** (trans/cis mixture, $CDCl_3$, 400 MHz).

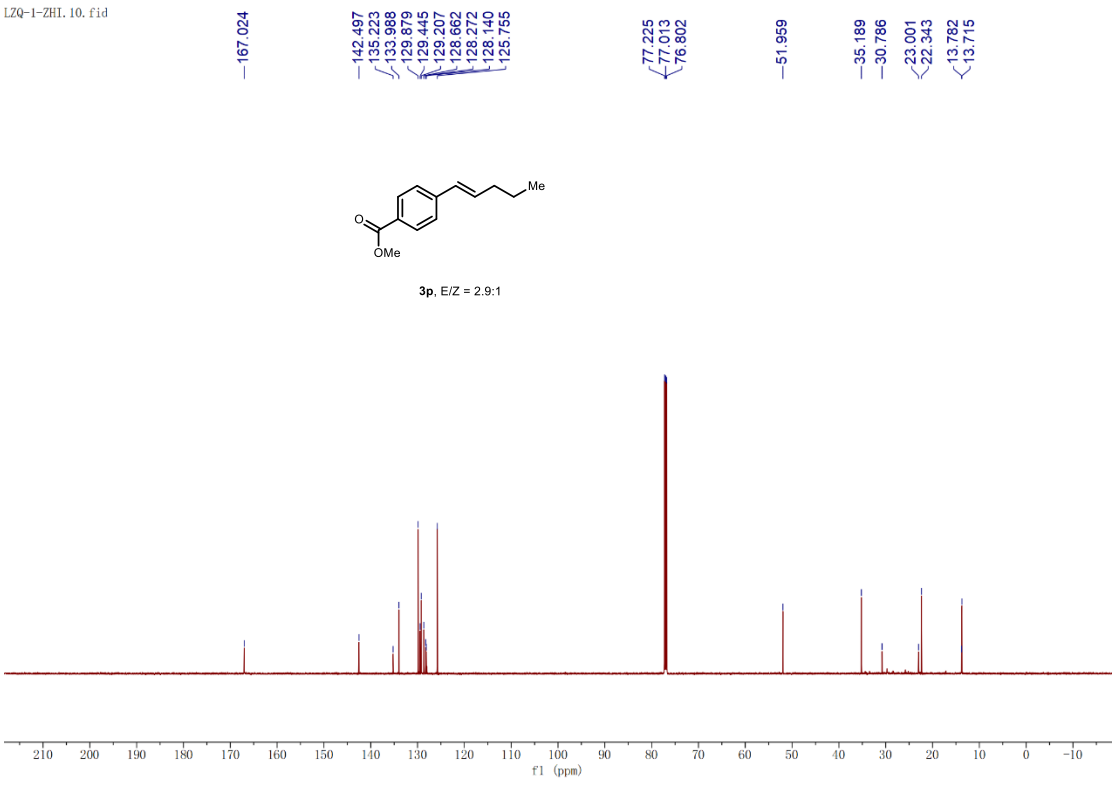

Figure S41. ^{13}C NMR of **3p** (trans/cis mixture, $CDCl_3$, 151 MHz).

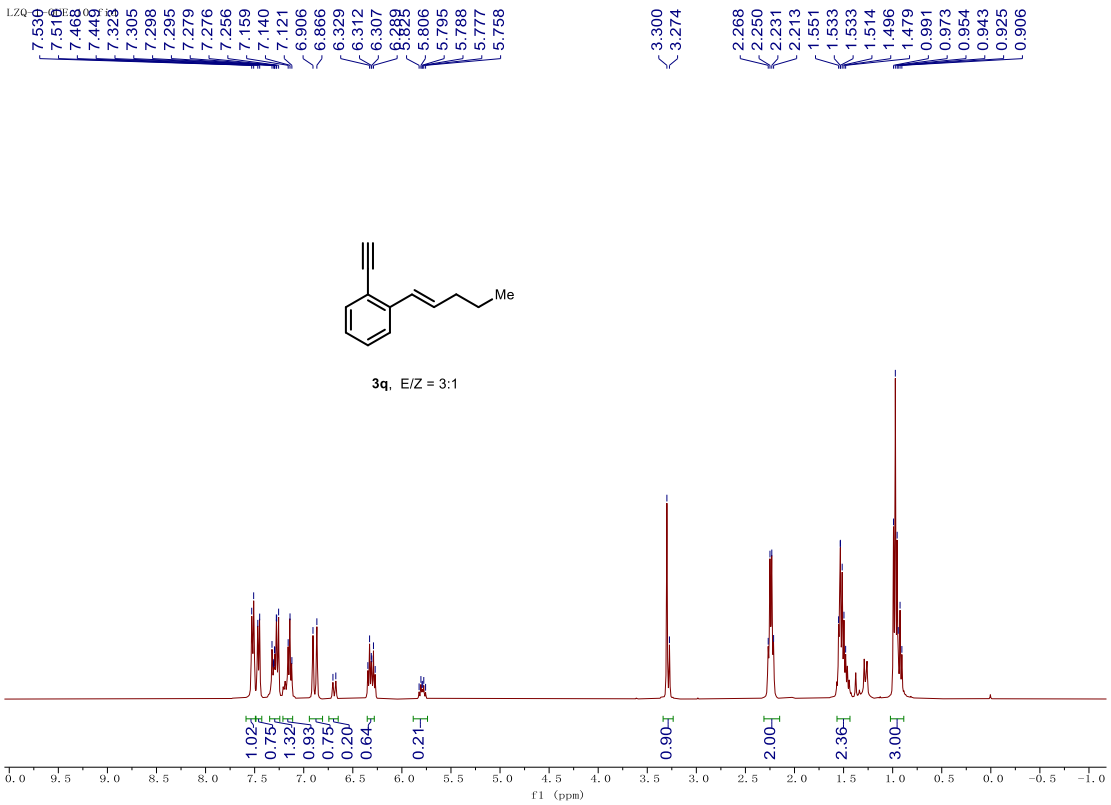

Figure S42. ^{1}H NMR of **3q** (trans/cis mixture, $CDCl_3$, 400 MHz).

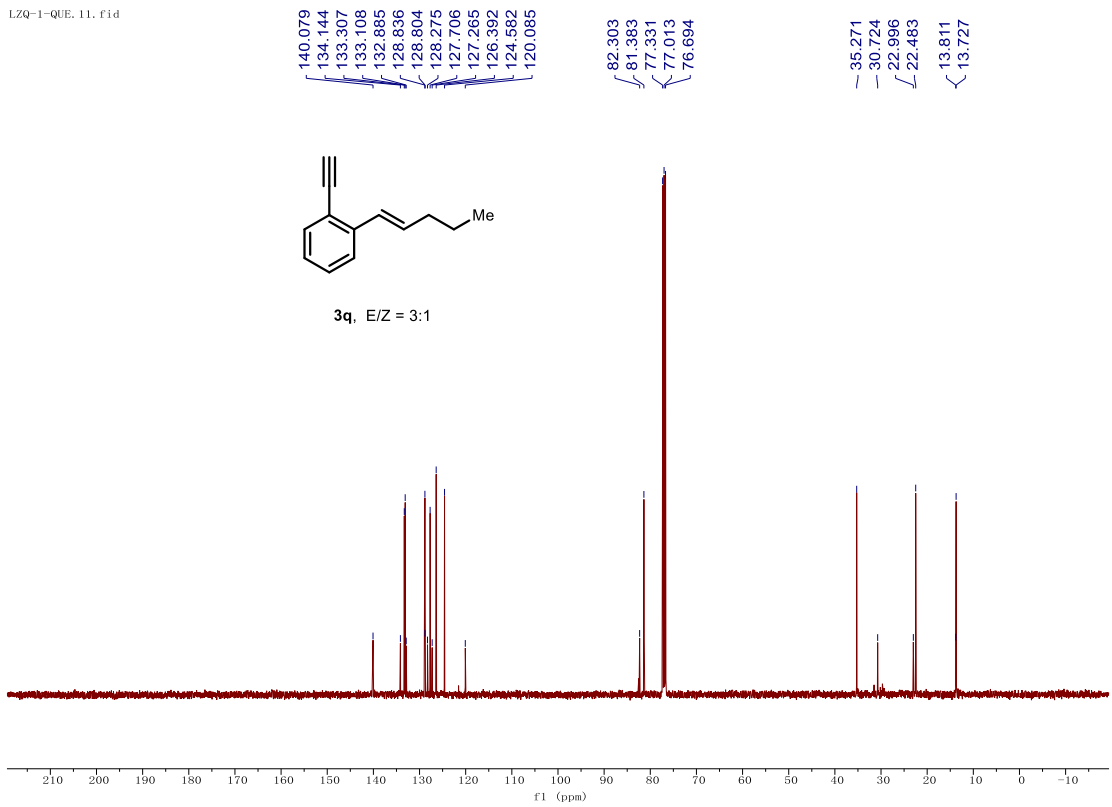

Figure S43. ^{13}C NMR of **3q** (trans/cis mixture, $CDCl_3$, 101 MHz).

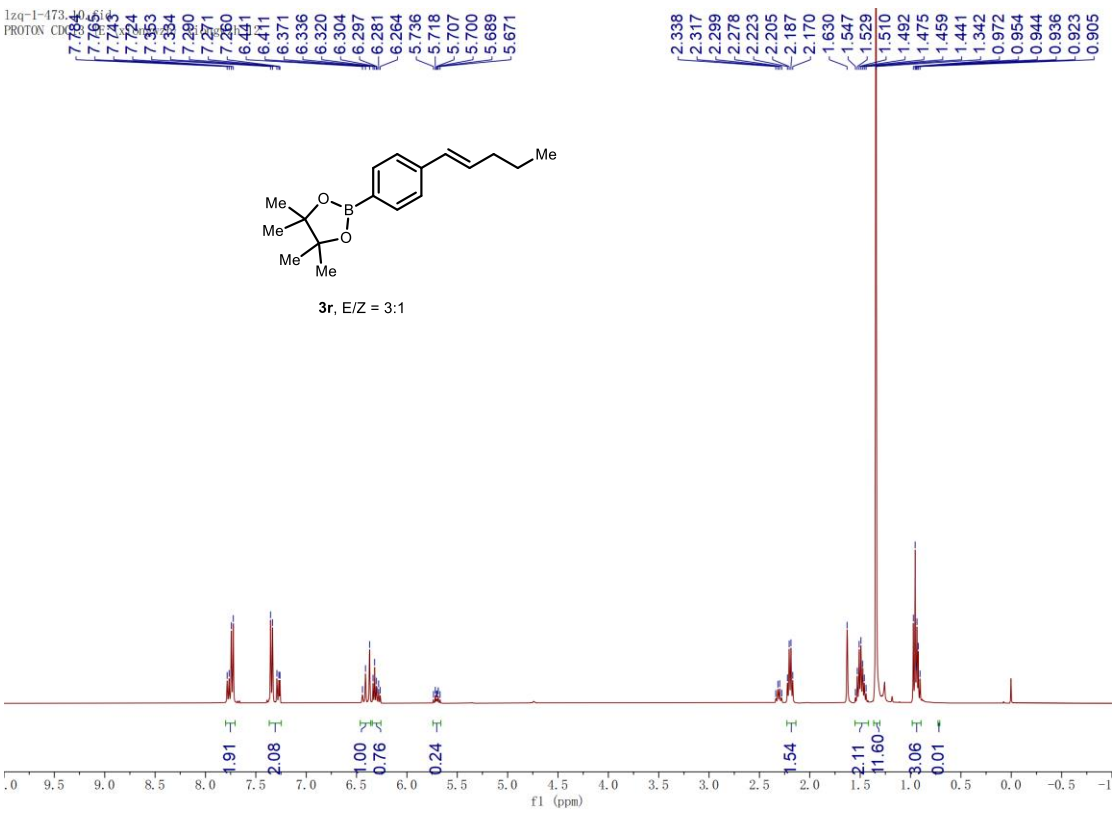

Figure S44. ^{1}H NMR of **3r** (trans/cis mixture, $CDCl_3$, 400 MHz).

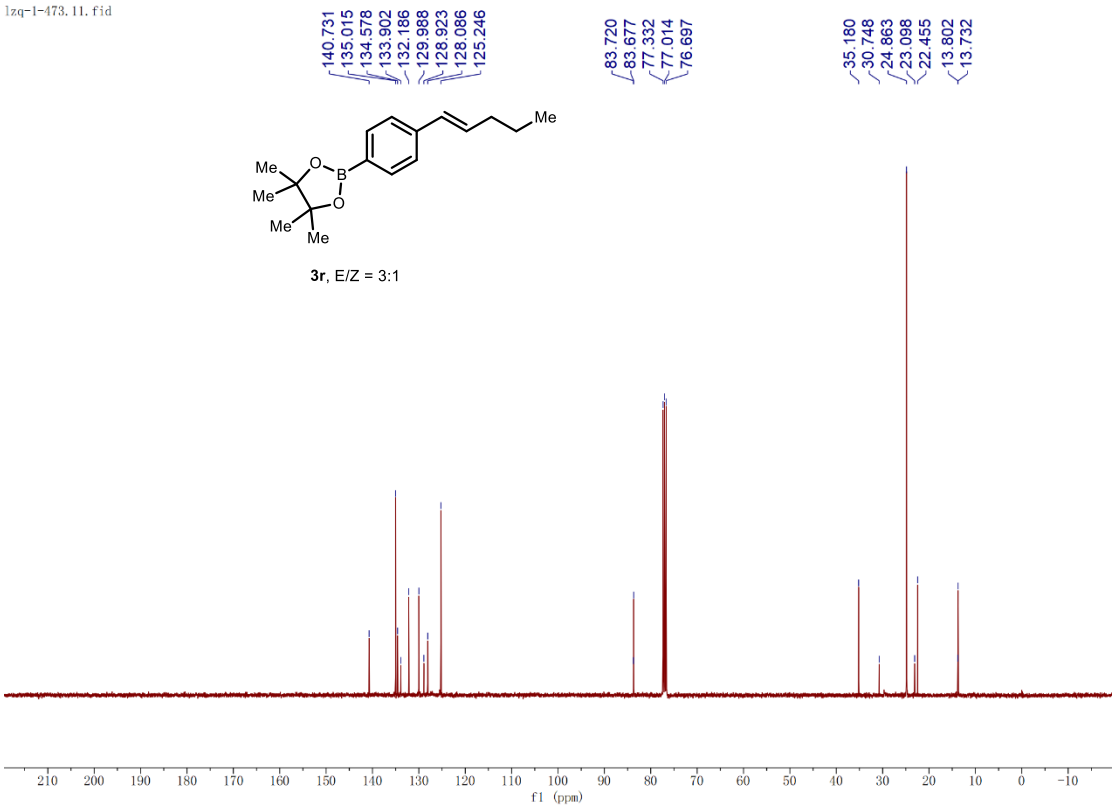

Figure S45. ^{13}C NMR of **3r** (trans/cis mixture, $CDCl_3$, 101 MHz).

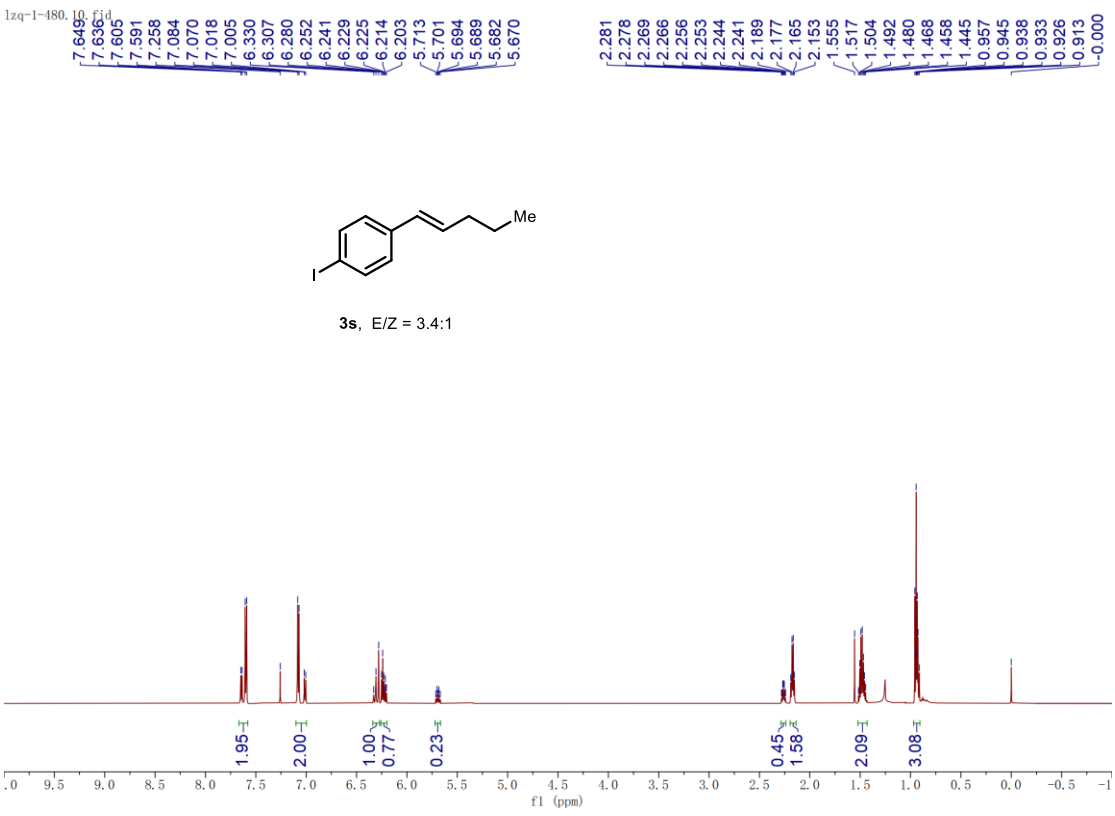

Figure S46. ^{1}H NMR of **3s** (trans/cis mixture, $CDCl_3$, 600 MHz).

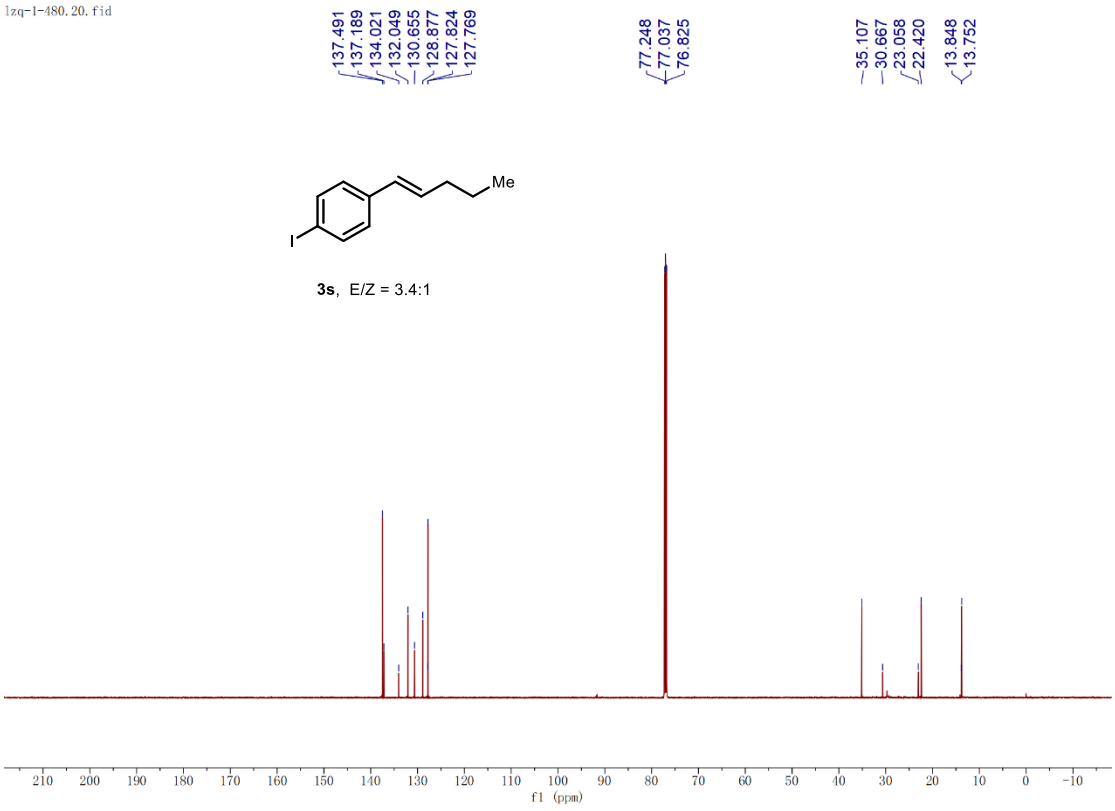

Figure S47. ^{13}C NMR of **3s** (trans/cis mixture, $CDCl_3$, 151 MHz).

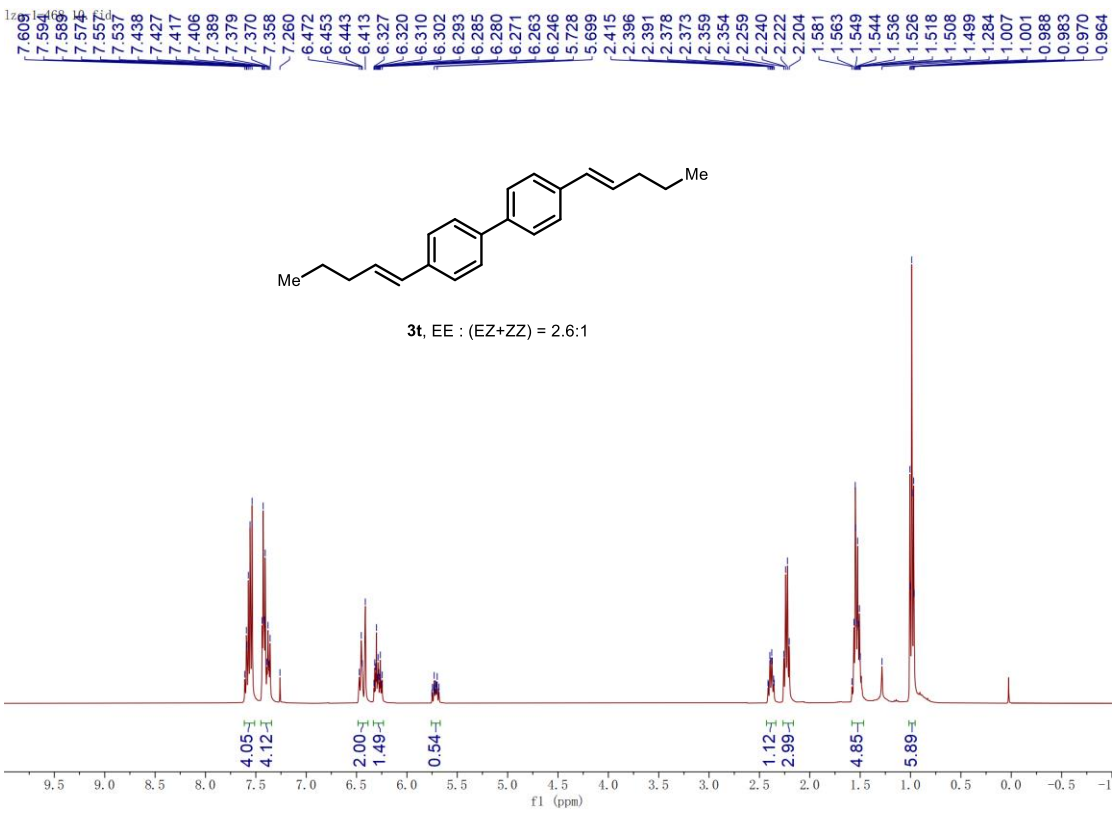

Figure S48. ^{1}H NMR of **3t** (trans/cis mixture, $CDCl_3$, 400 MHz).

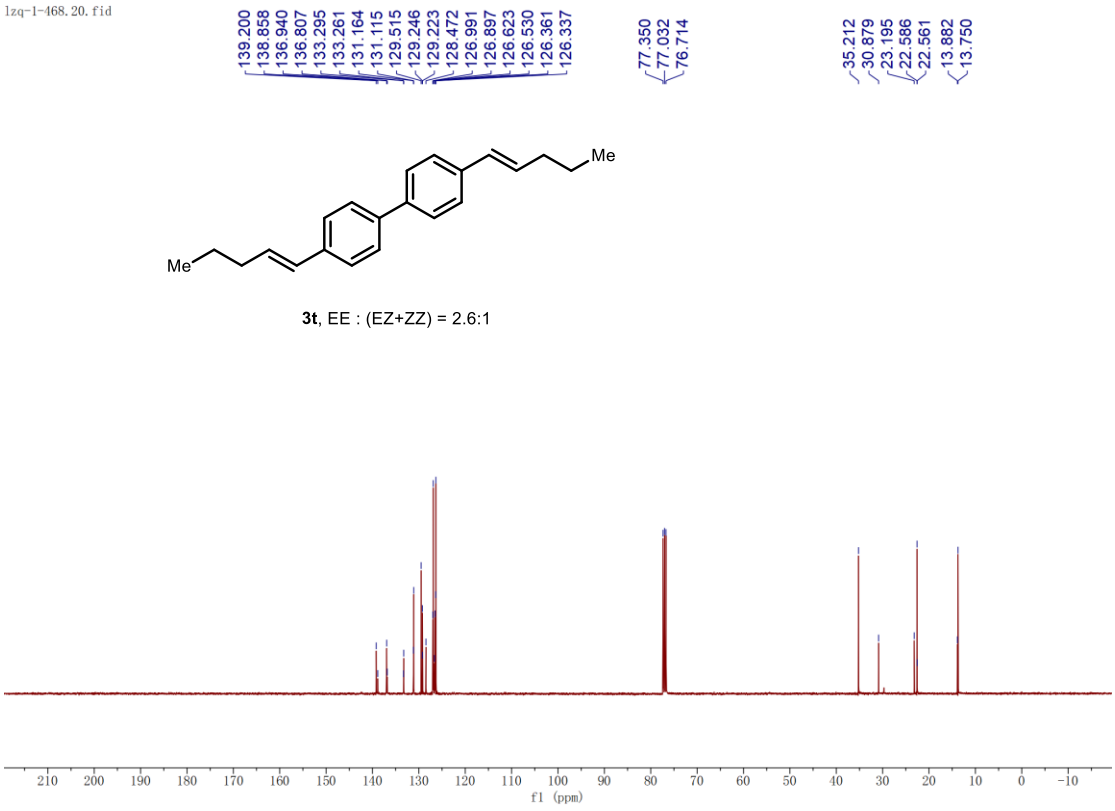

Figure S49. ^{13}C NMR of **3t** (trans/cis mixture, $CDCl_3$, 101 MHz).

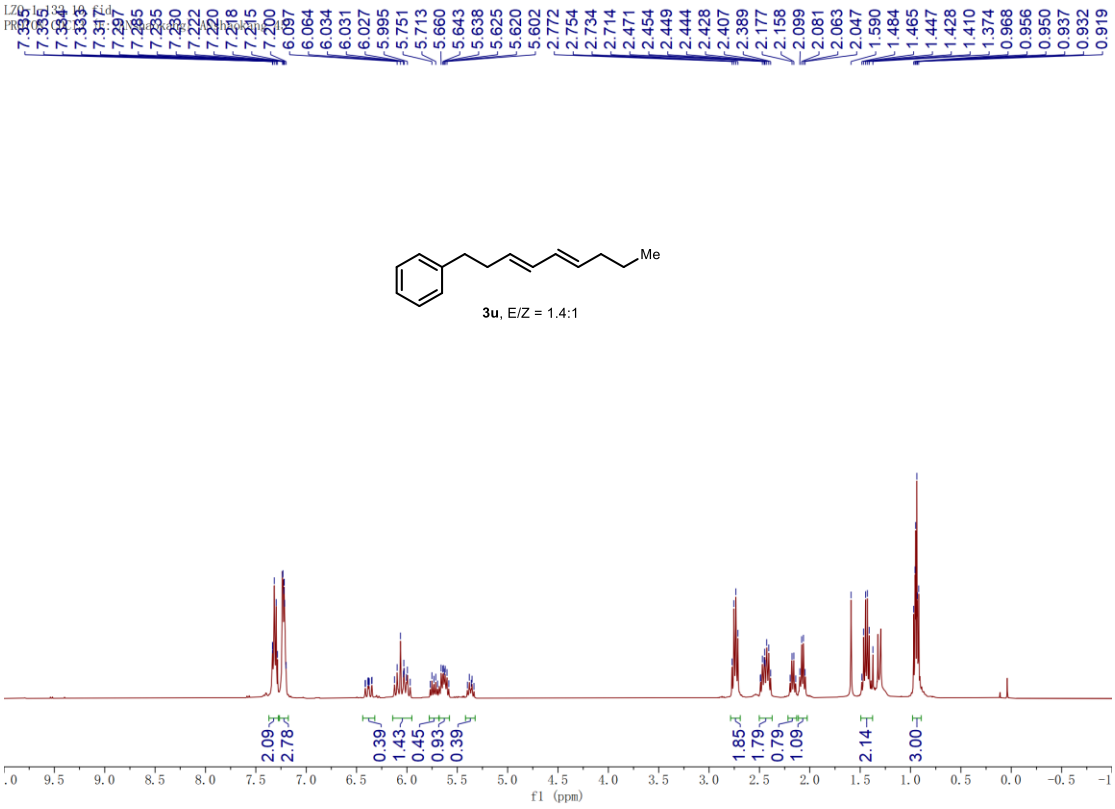

Figure S50. ^{1}H NMR of **3u** (trans/cis mixture, $CDCl_3$, 400 MHz).

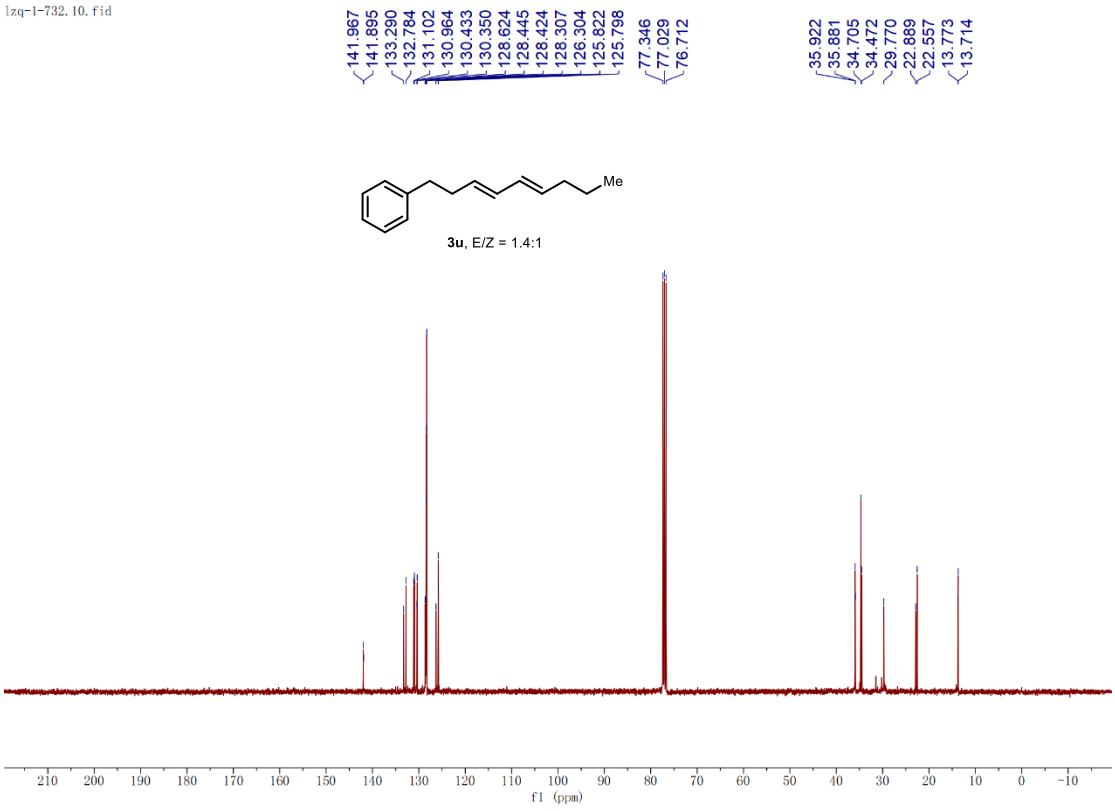

Figure S51. ^{13}C NMR of **3u** (trans/cis mixture, $CDCl_3$, 101 MHz).

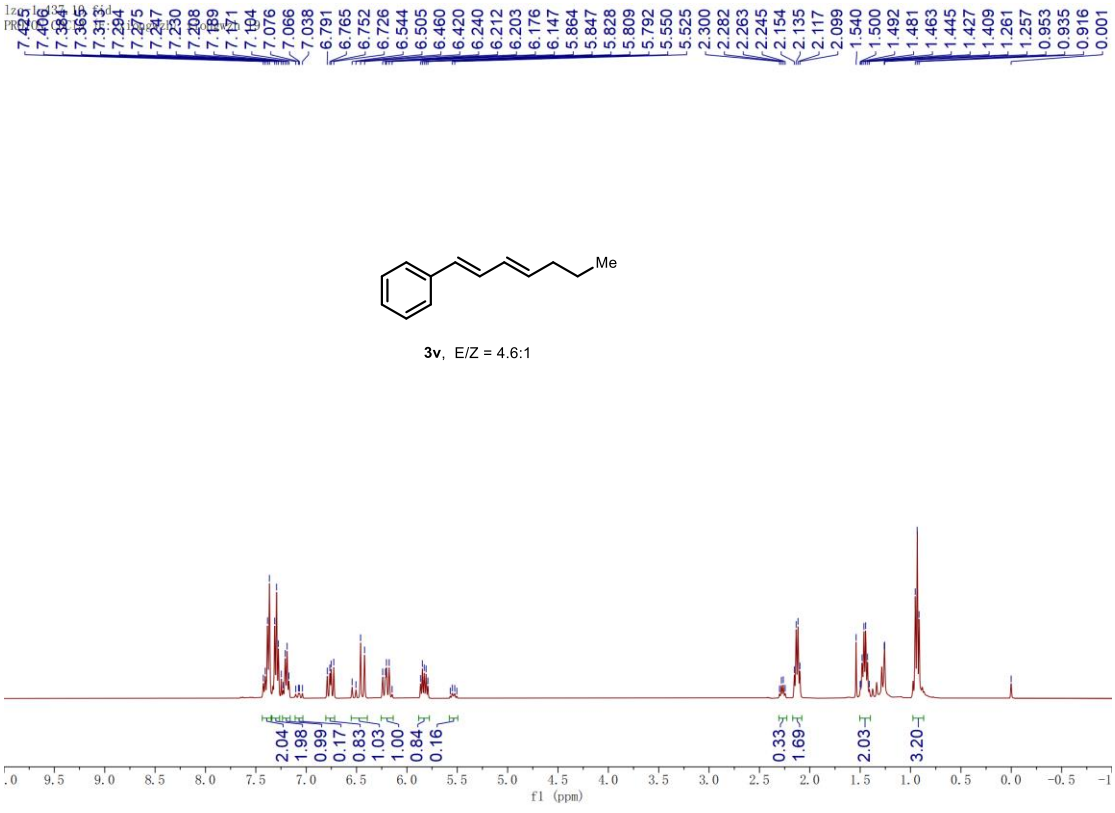

Figure S52. ^{1}H NMR of **3v** (trans/cis mixture, $CDCl_3$, 400 MHz).

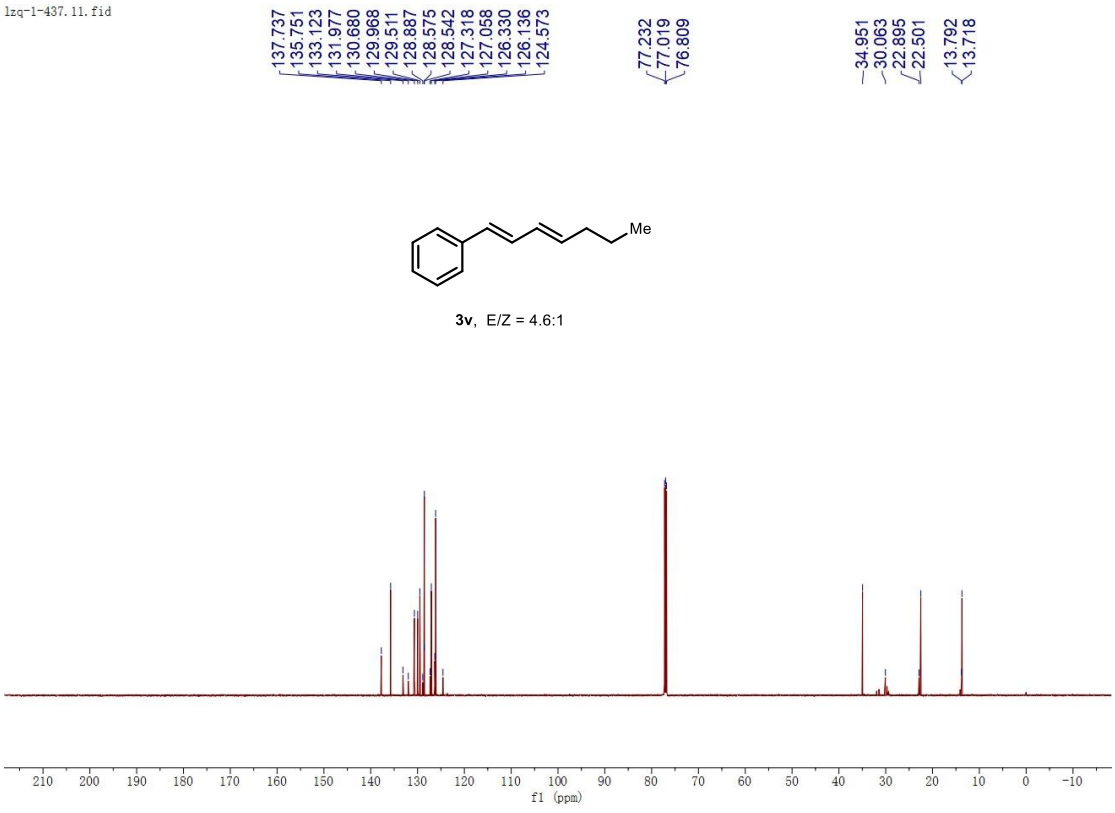

Figure S53. ^{13}C NMR of **3v** (trans/cis mixture, $CDCl_3$, 151 MHz).

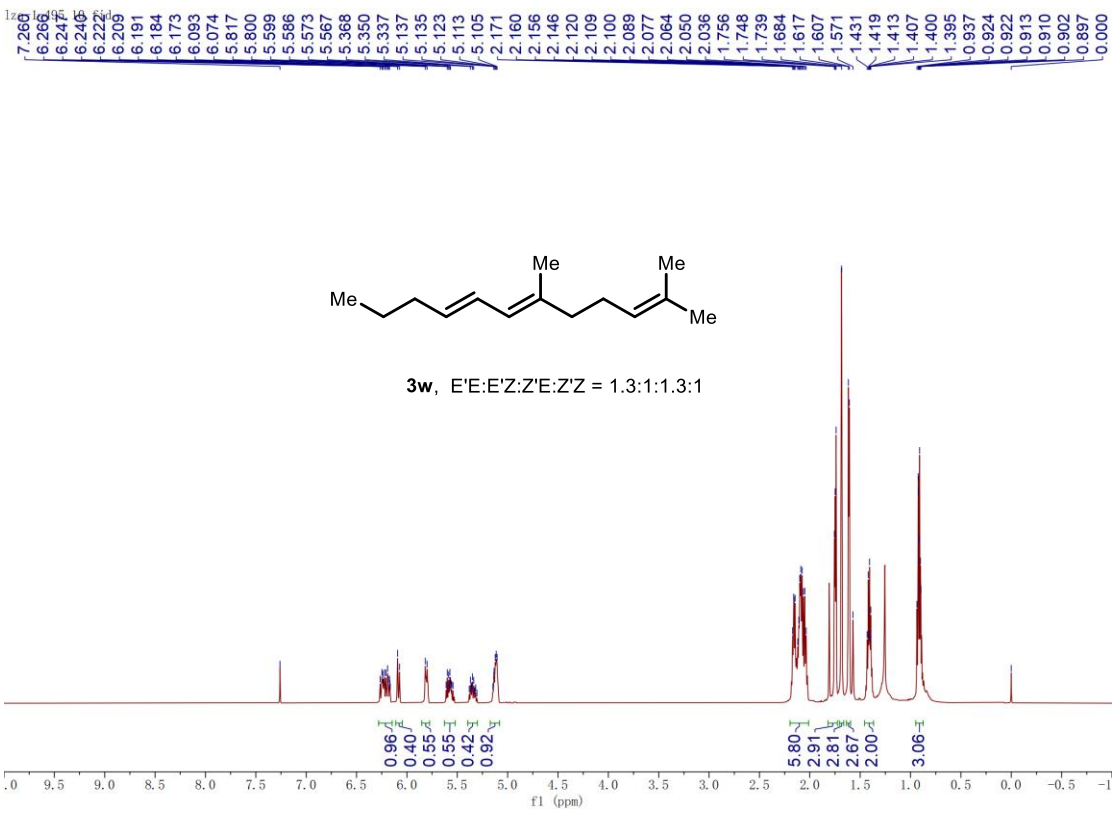

Figure S54. ^{1}H NMR of **3w** (trans/cis mixture, $CDCl_3$, 600 MHz)

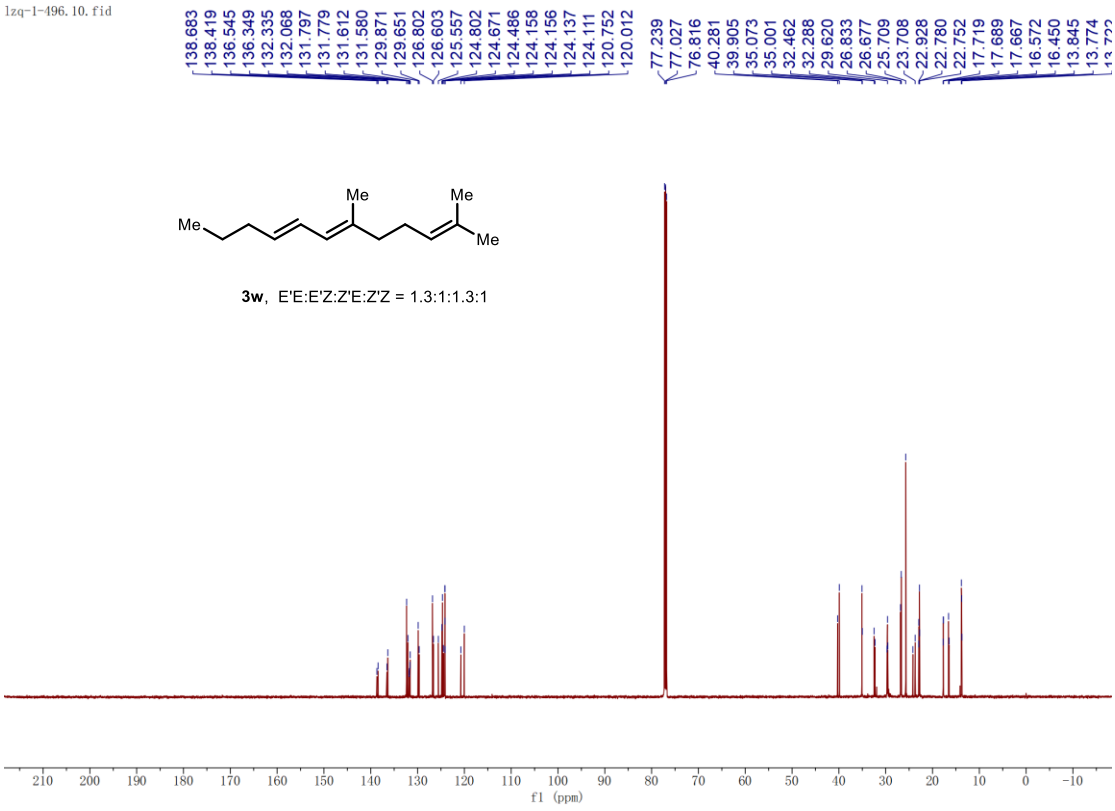

Figure S55. ^{13}C NMR of **3w** (trans/cis mixture, $CDCl_3$, 151 MHz).

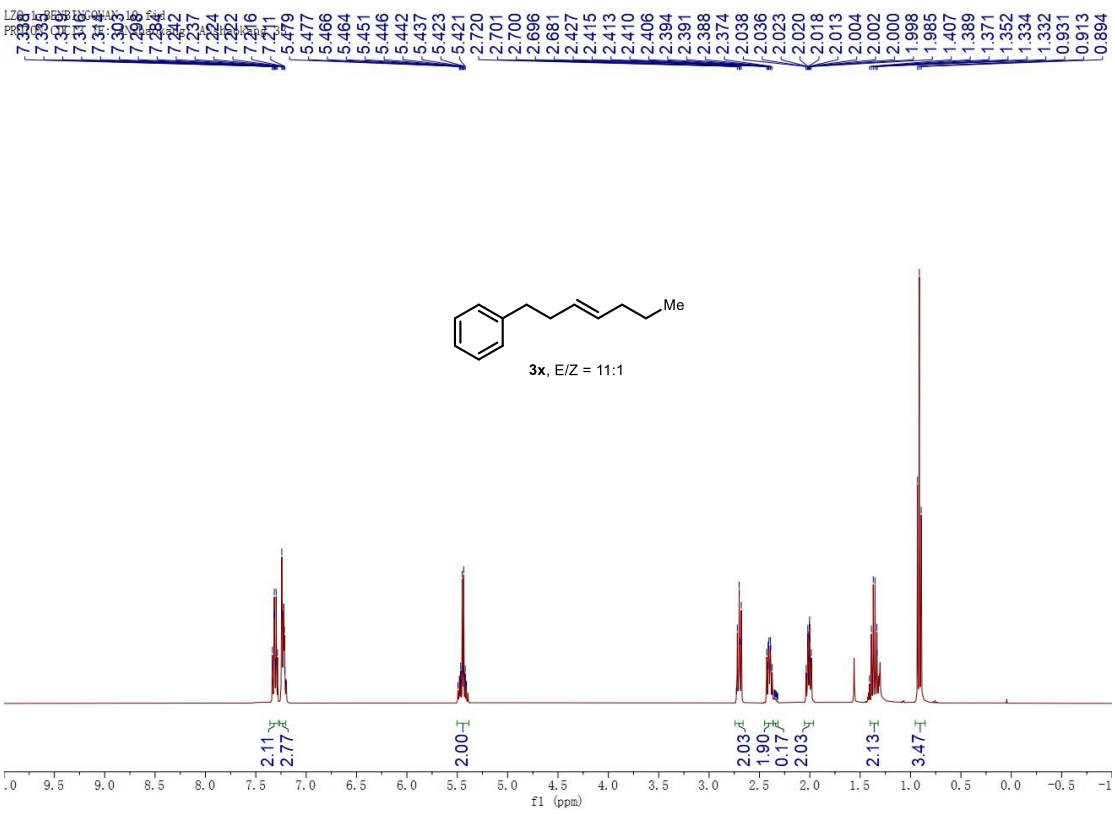

Figure S56. ^{1}H NMR of **3x** (trans/cis mixture, $CDCl_3$, 400 MHz).

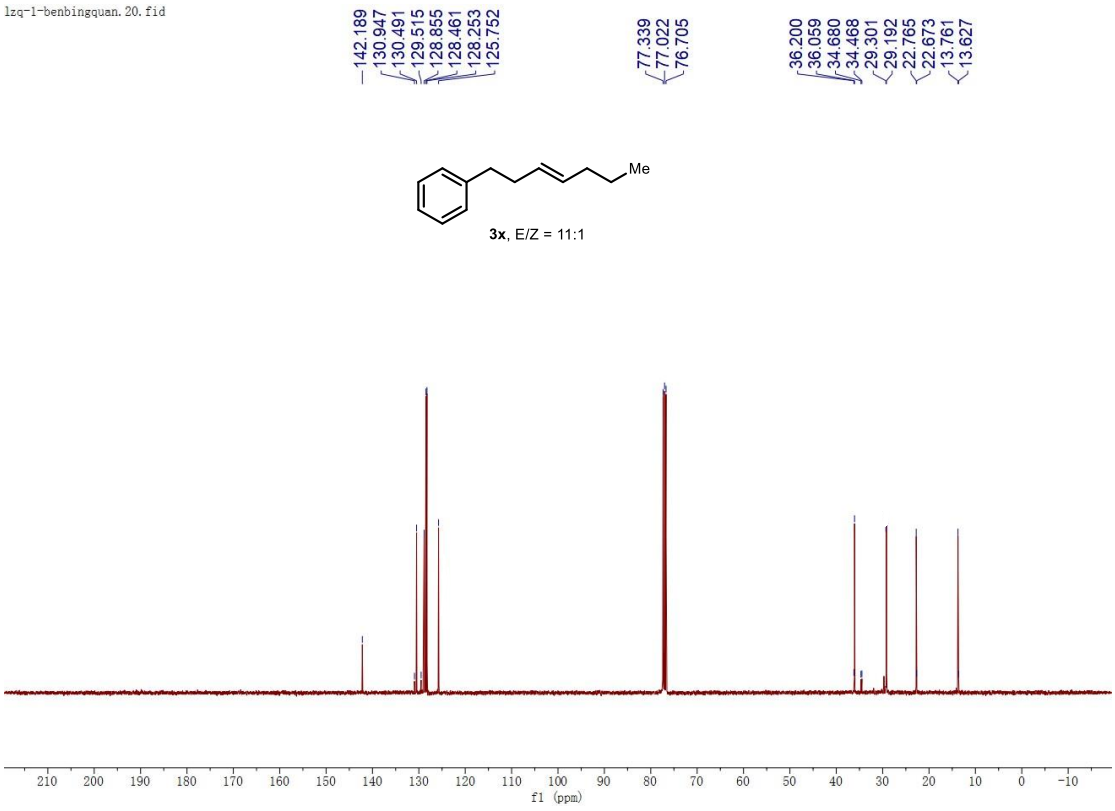

Figure S57. ^{13}C NMR of **3x** (trans/cis mixture, $CDCl_3$, 101 MHz).

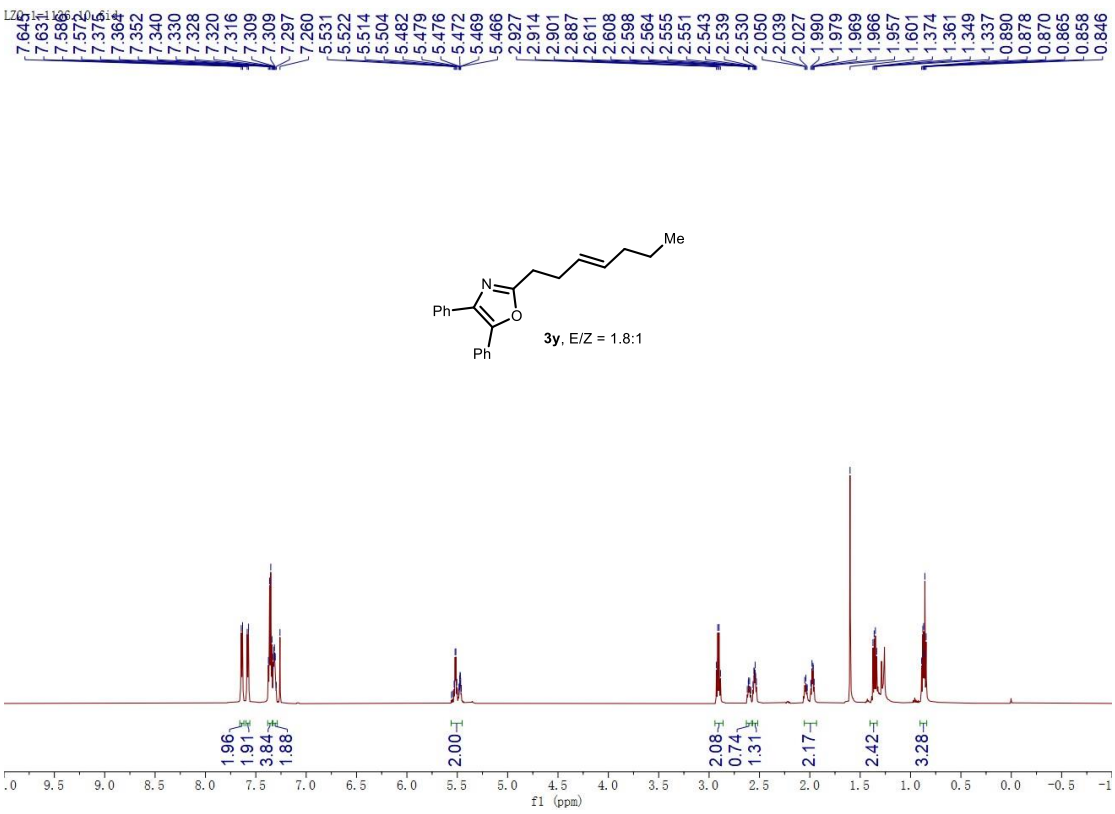

Figure S58. ^{1}H NMR of **3y** (trans/cis mixture, $CDCl_3$, 600 MHz).

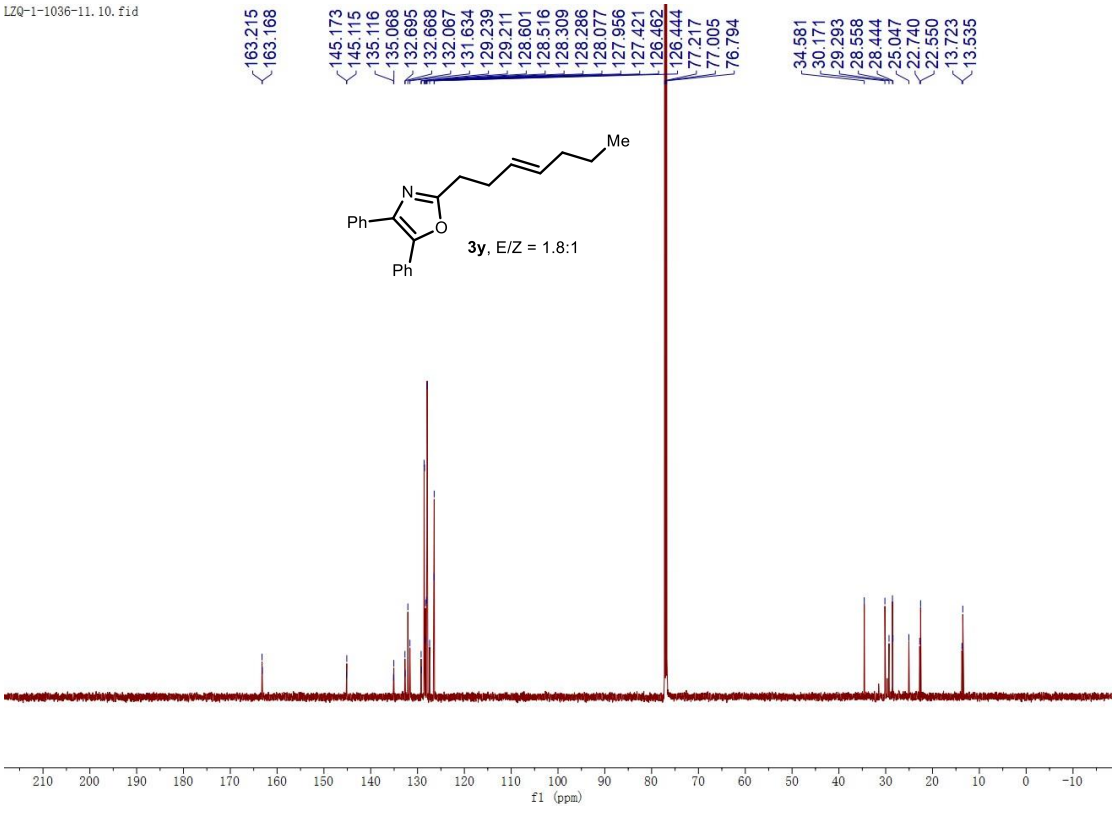

Figure S59. ^{13}C NMR of **3y** (trans/cis mixture, $CDCl_3$, 151 MHz).

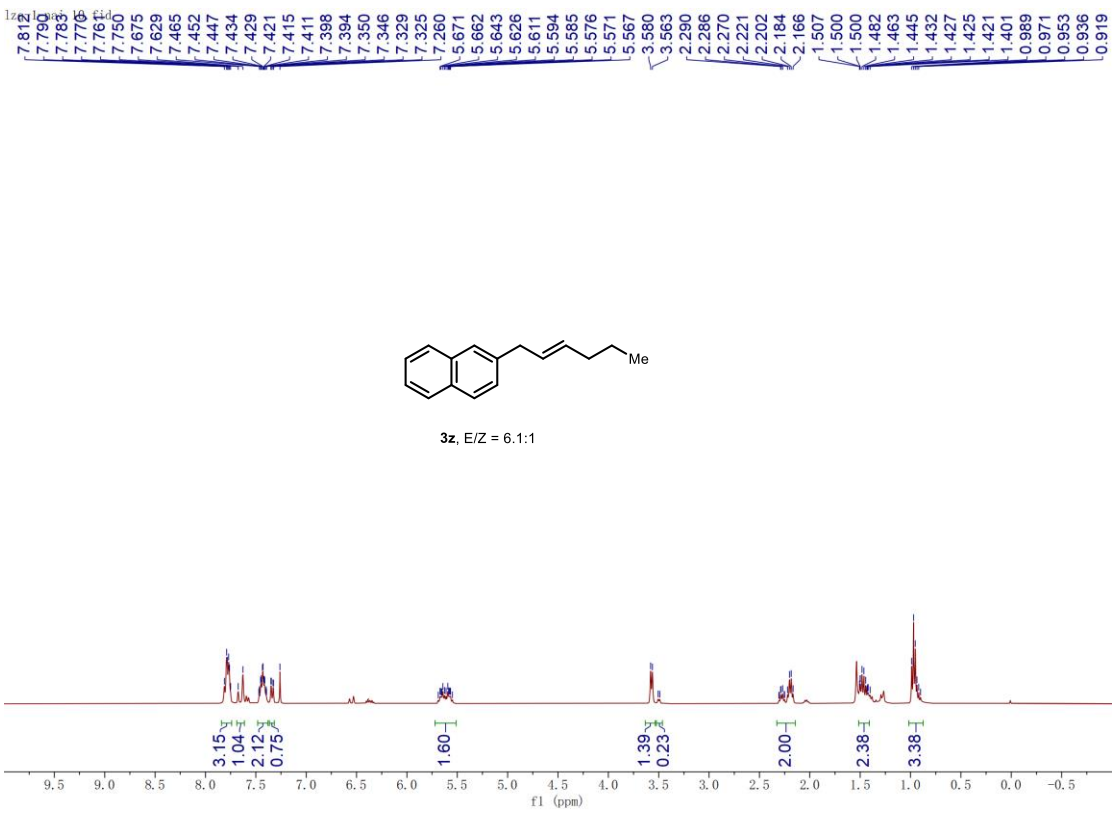

Figure S60. ^{1}H NMR of **3z** (trans/cis mixture, $CDCl_3$, 400 MHz).

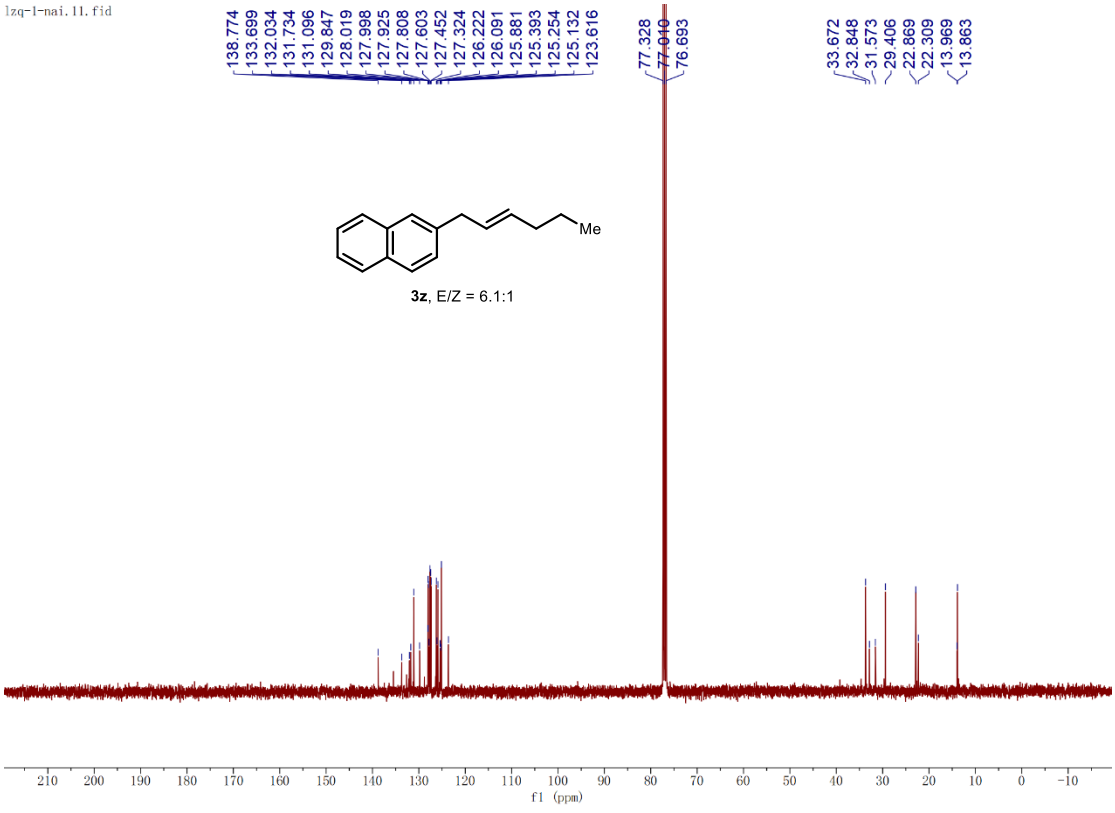

Figure S61. ^{13}C NMR of **3z** (trans/cis mixture, $CDCl_3$, 101 MHz).

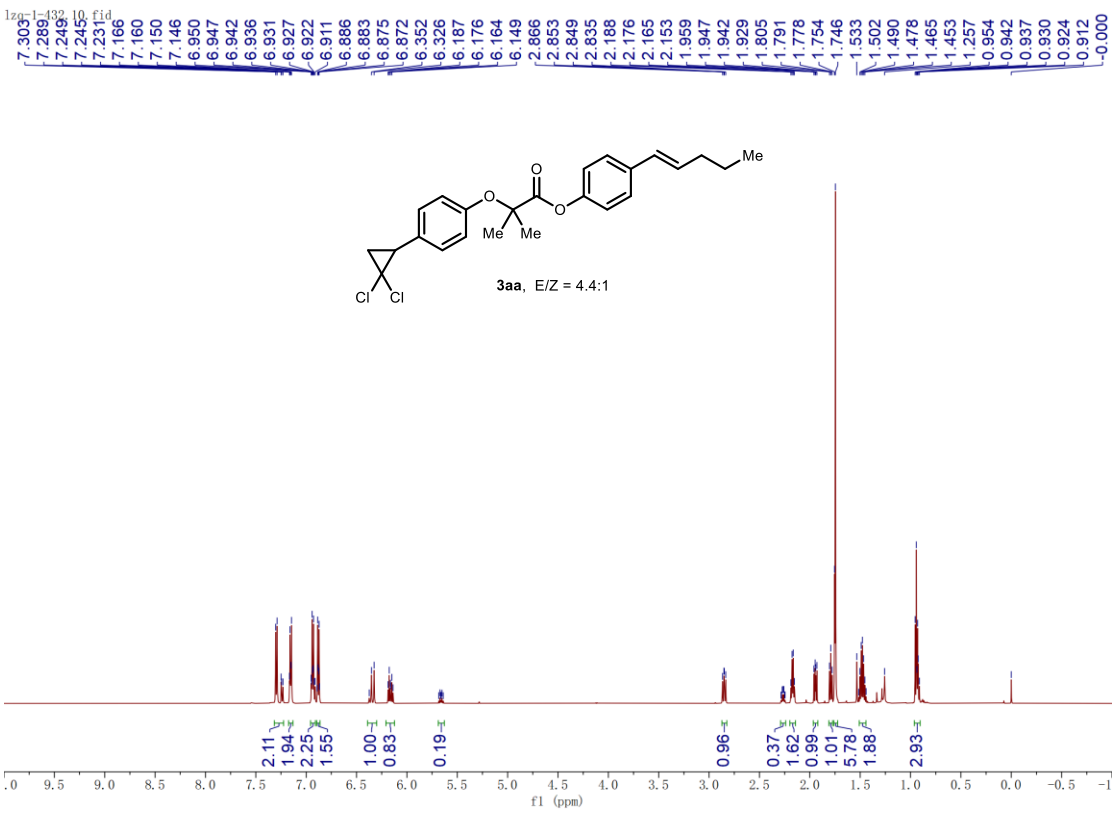

Figure S62. ^{1}H NMR of **3aa** (trans/cis mixture, $CDCl_3$, 600 MHz).

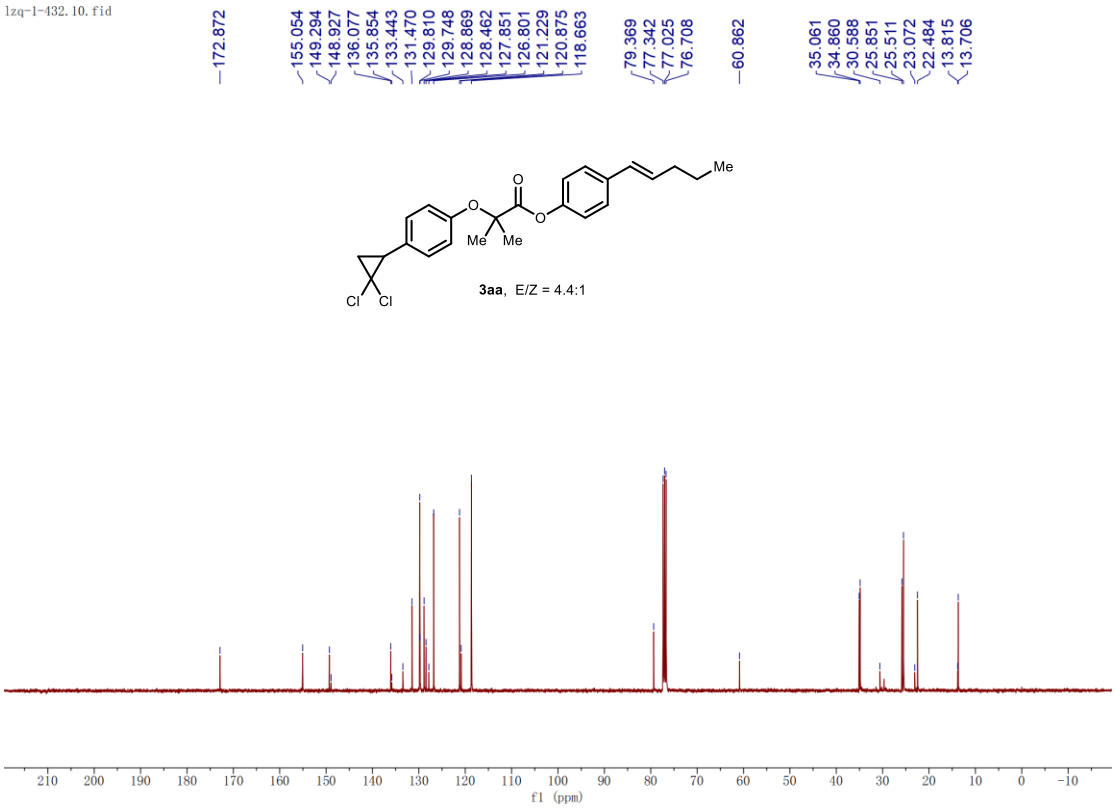

Figure S63. ^{13}C NMR of **3aa** (trans/cis mixture, $CDCl_3$, 101 MHz).

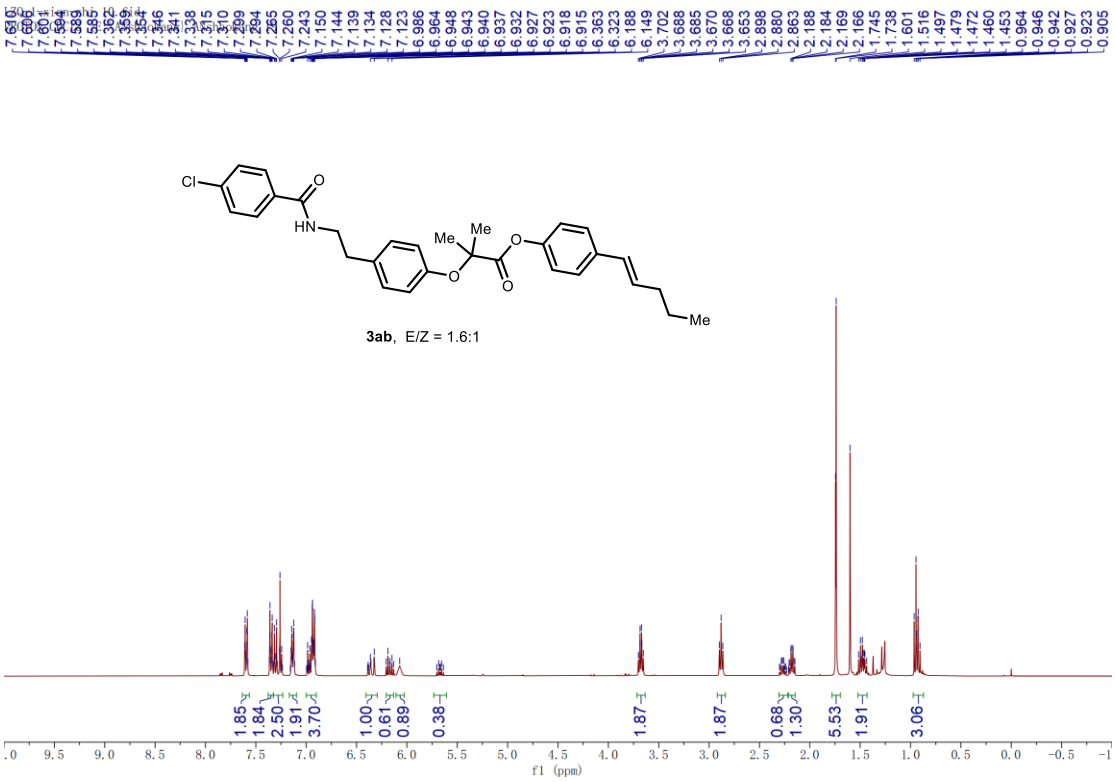

Figure S64. ^{1}H NMR of **3ab** (trans/cis mixture, $CDCl_3$, 600 MHz).

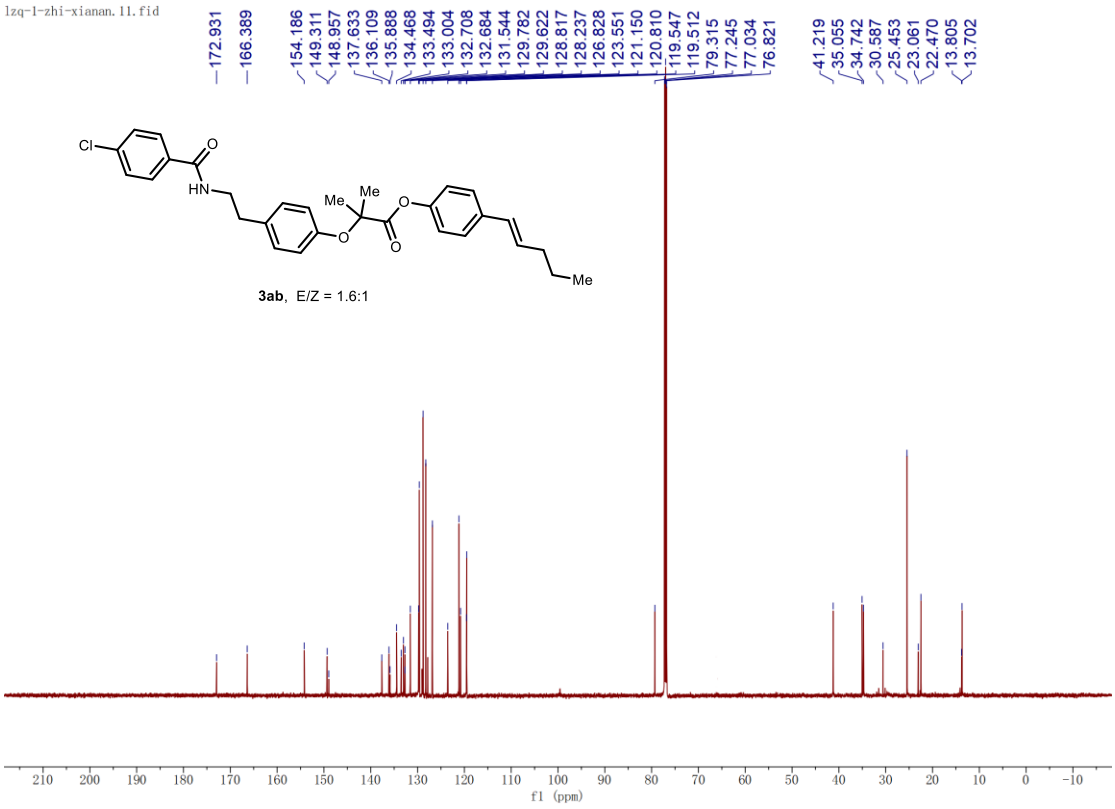

Figure S65. ^{13}C NMR of **3ab** (trans/cis mixture, $CDCl_3$, 151 MHz).

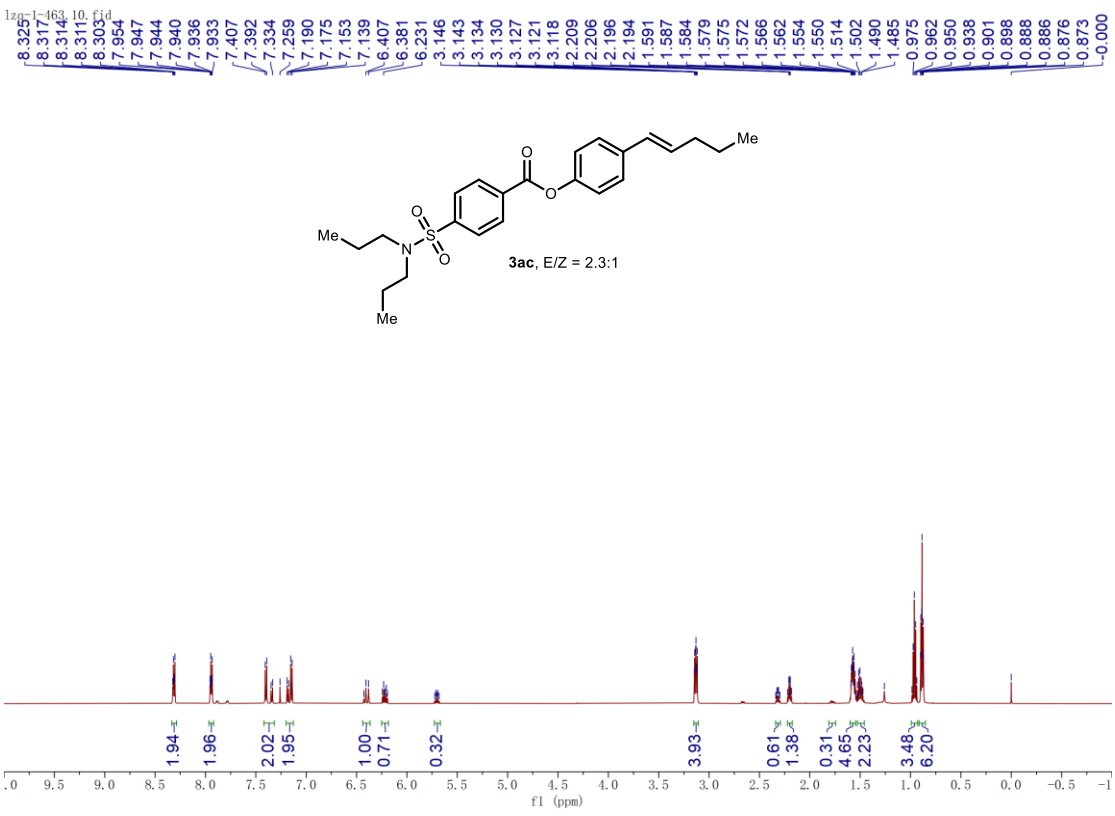

Figure S66. ^{1}H NMR of **3ac** (trans/cis mixture, $CDCl_3$, 600 MHz).

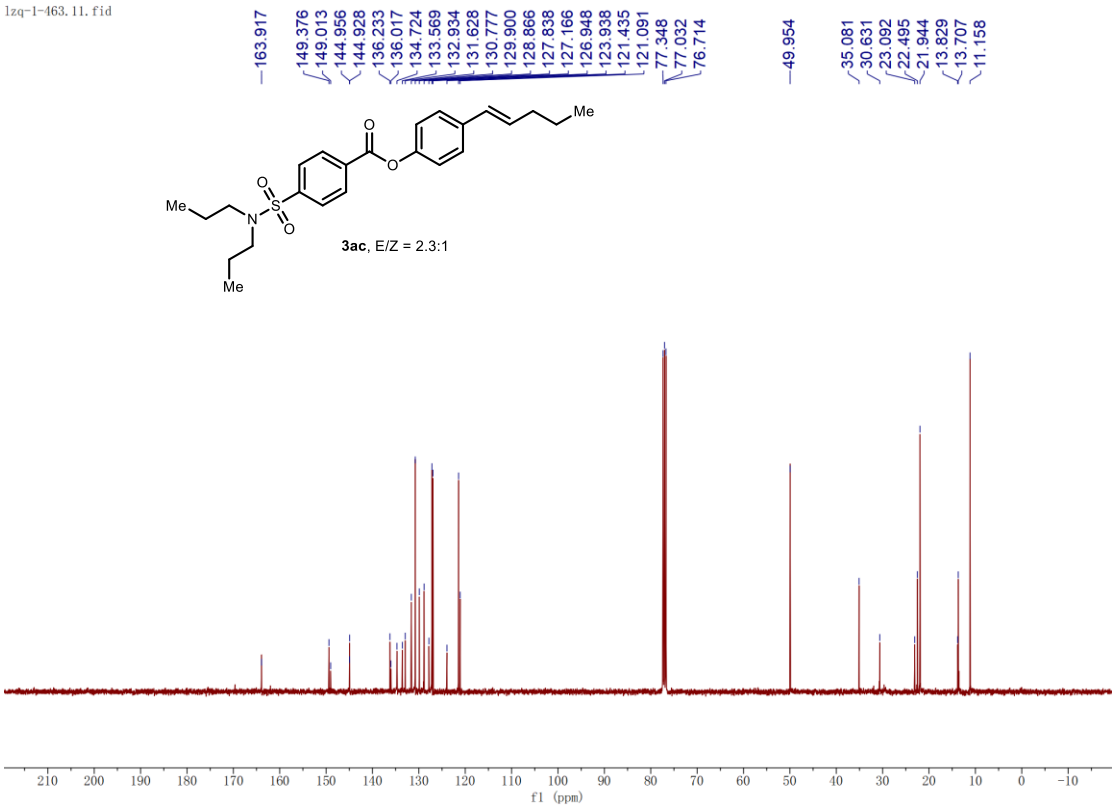

Figure S67. ^{13}C NMR of **3ac** (trans/cis mixture, $CDCl_3$, 101 MHz).

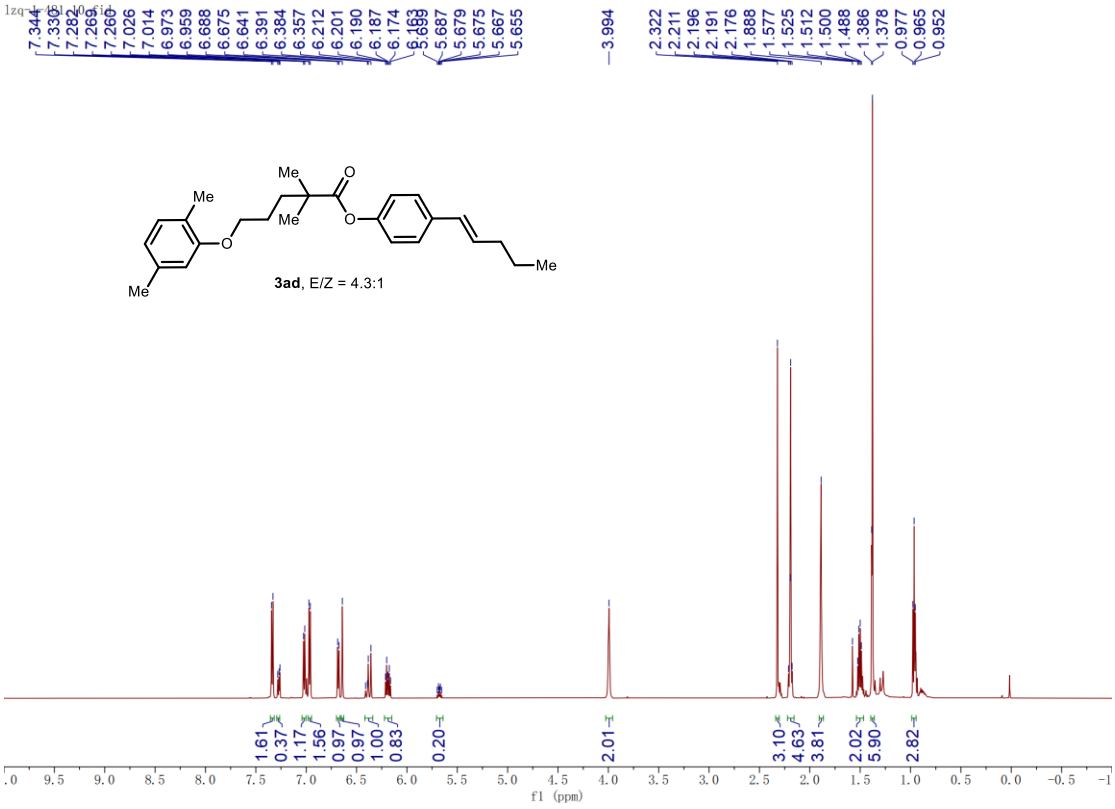

Figure S68. ^{1}H NMR of **3ad** (trans/cis mixture, $CDCl_3$, 600 MHz)

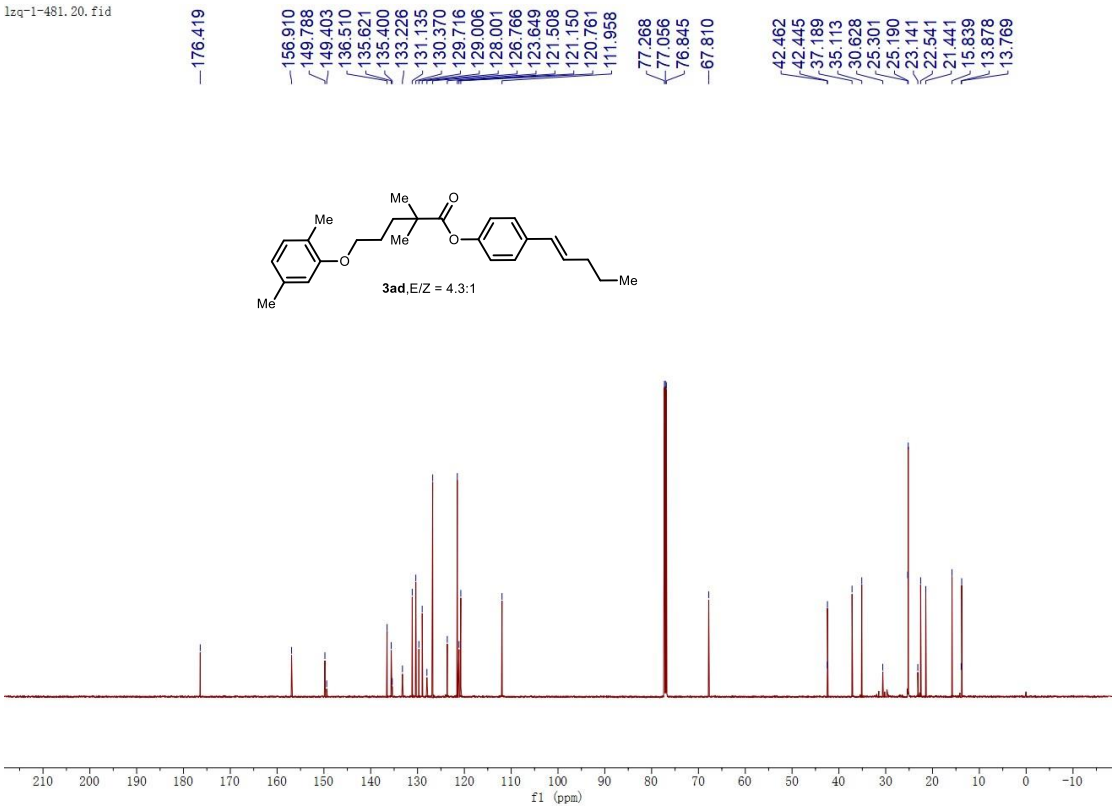

Figure S69. ^{13}C NMR of **3ad** (trans/cis mixture, $CDCl_3$, 151 MHz).

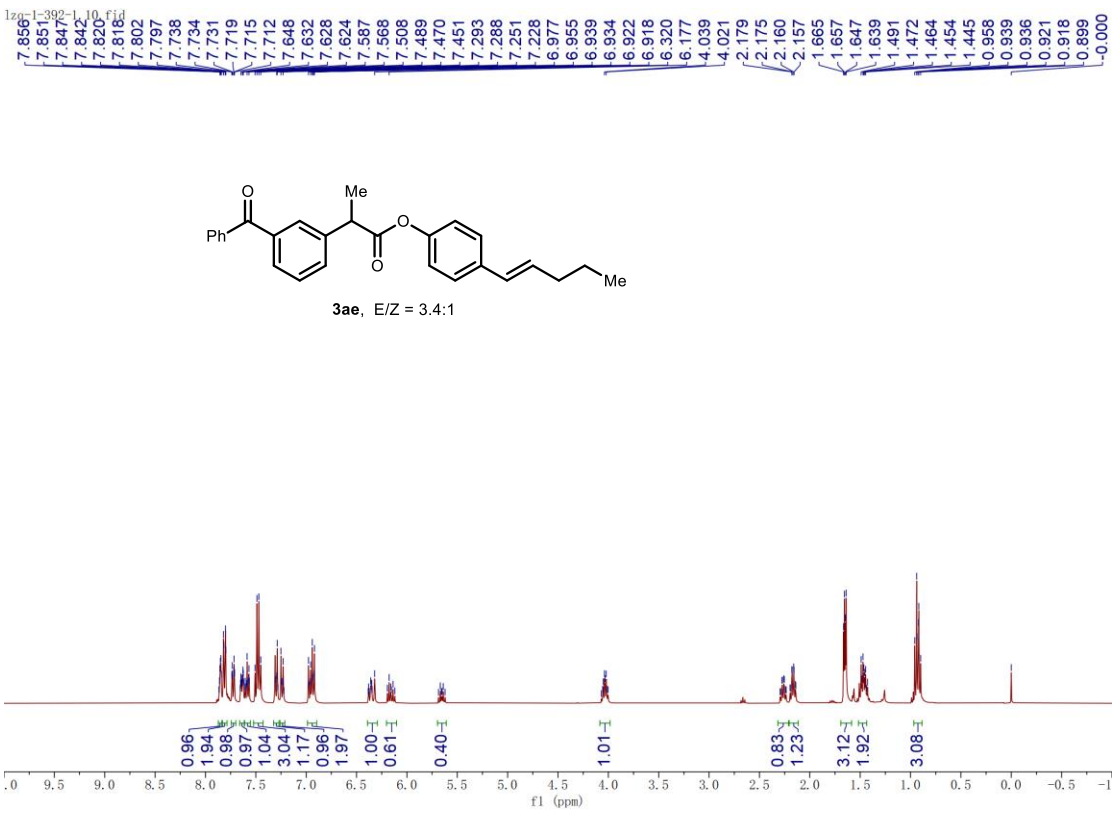

Figure S70. ^{1}H NMR of **3ae** (trans/cis mixture, $CDCl_3$, 400 MHz).

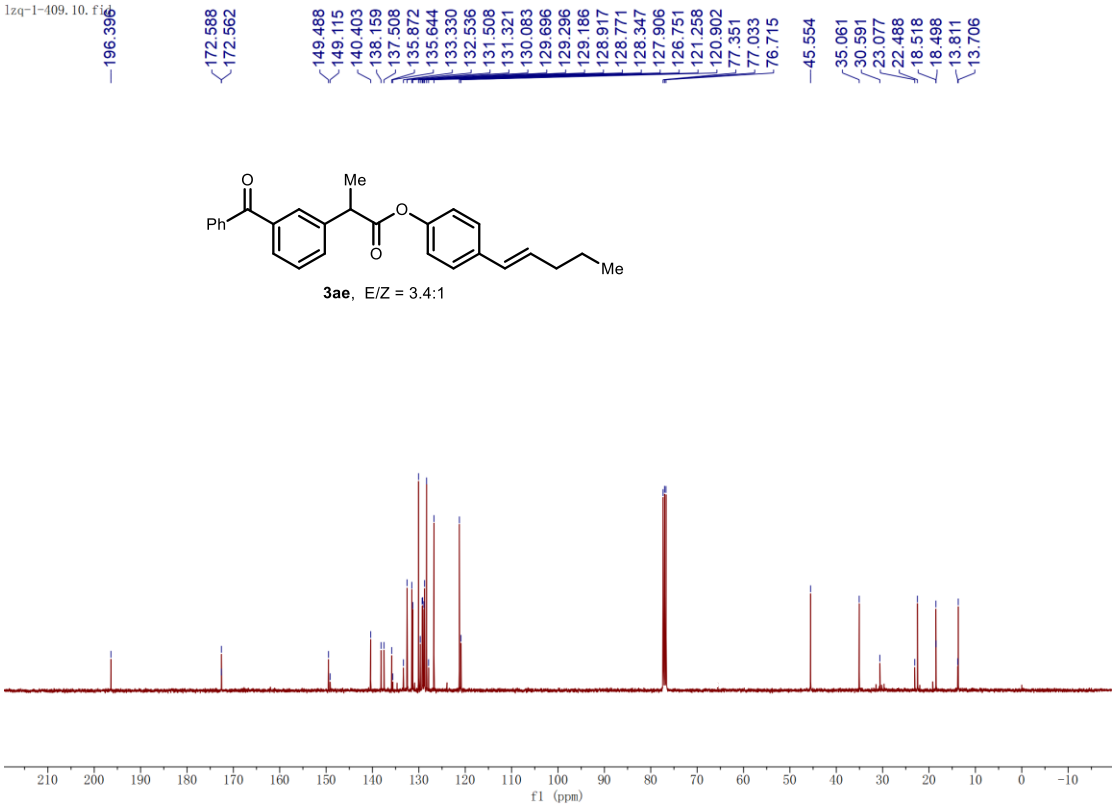

Figure S71. ^{13}C NMR of **3ae** (trans/cis mixture, $CDCl_3$, 101 MHz).

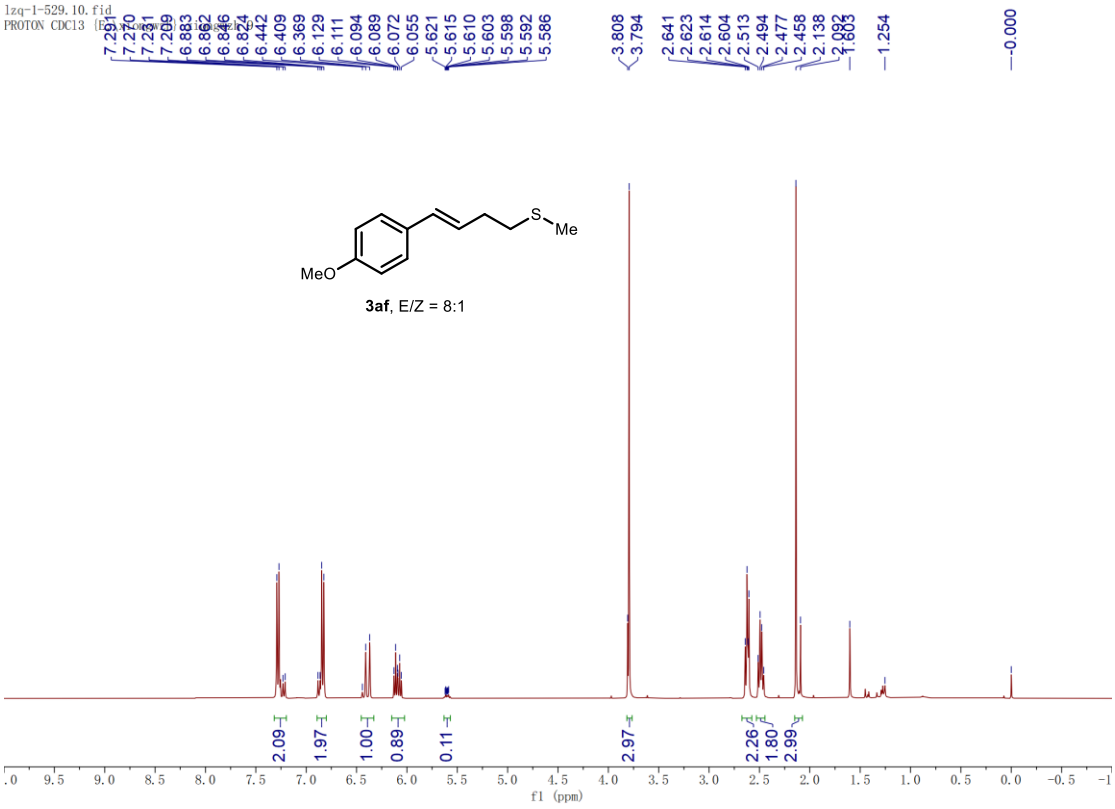

Figure S72. ^{1}H NMR of **3af** (trans/cis mixture, $CDCl_3$, 400 MHz)

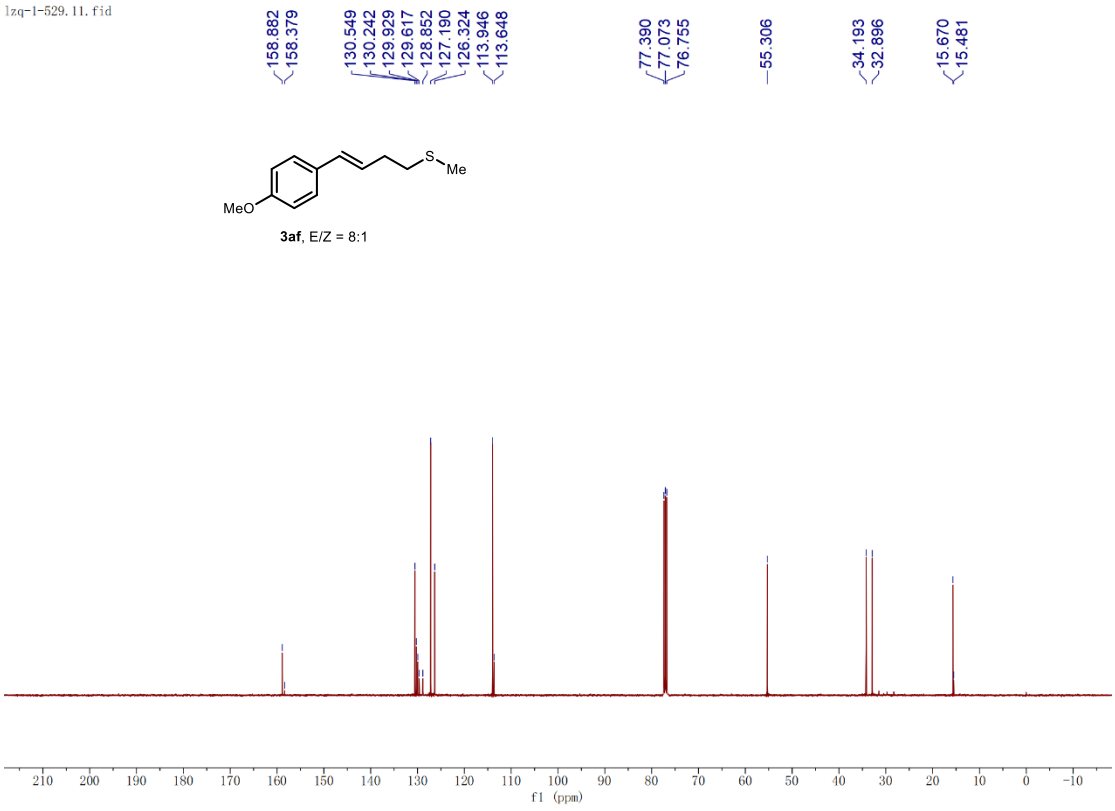

Figure S73. ^{13}C NMR of **3af** (trans/cis mixture, $CDCl_3$, 101 MHz).

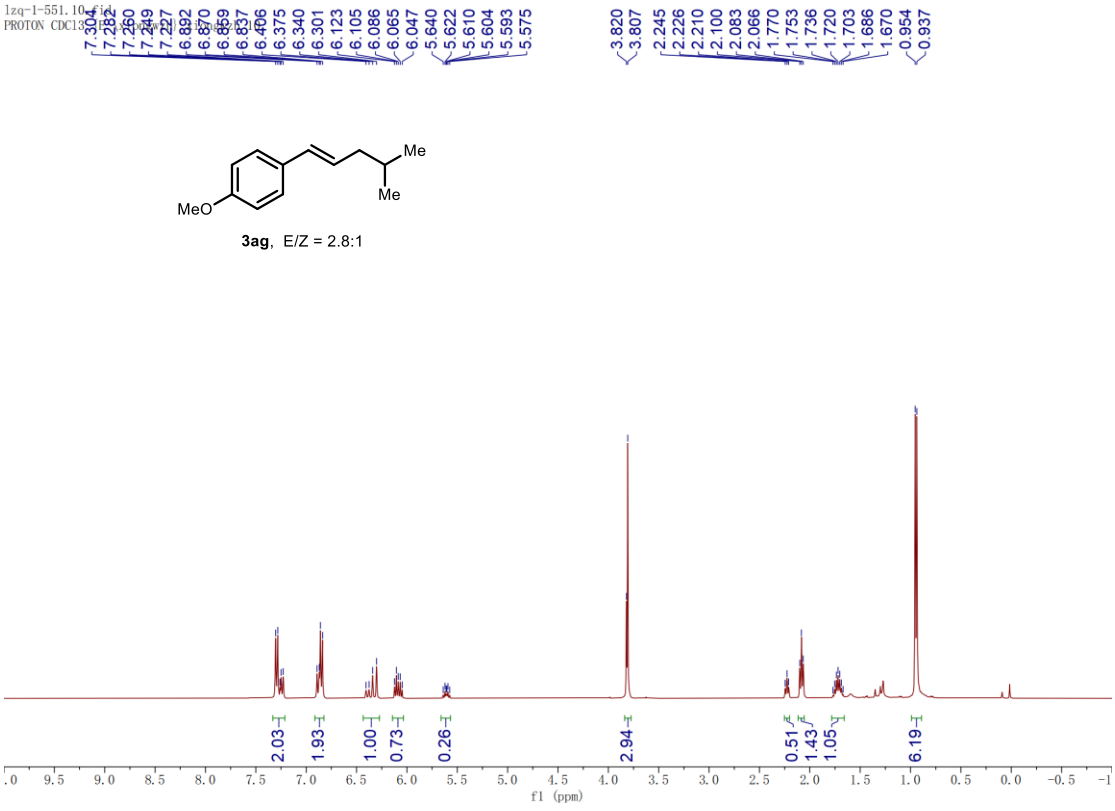

Figure S74. ^{1}H NMR of **3ag** (trans/cis mixture, $CDCl_3$, 400 MHz)

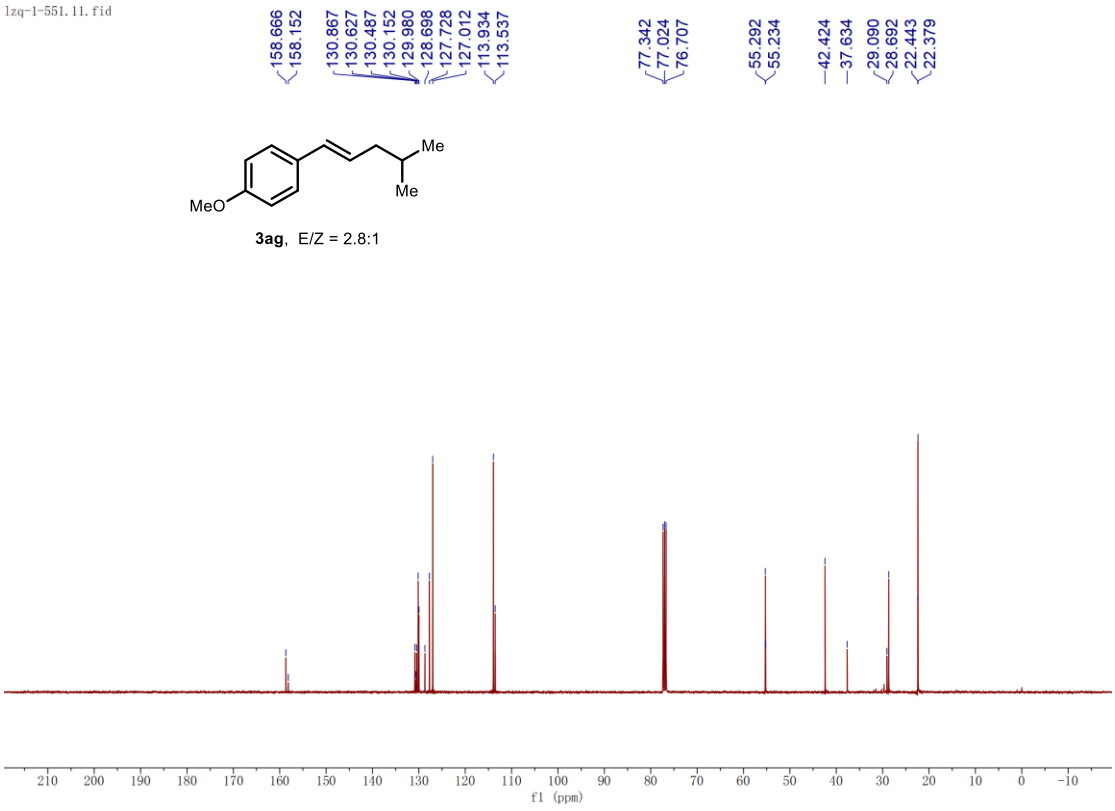

Figure S75. ^{13}C NMR of **3ag** (trans/cis mixture, $CDCl_3$, 101 MHz).

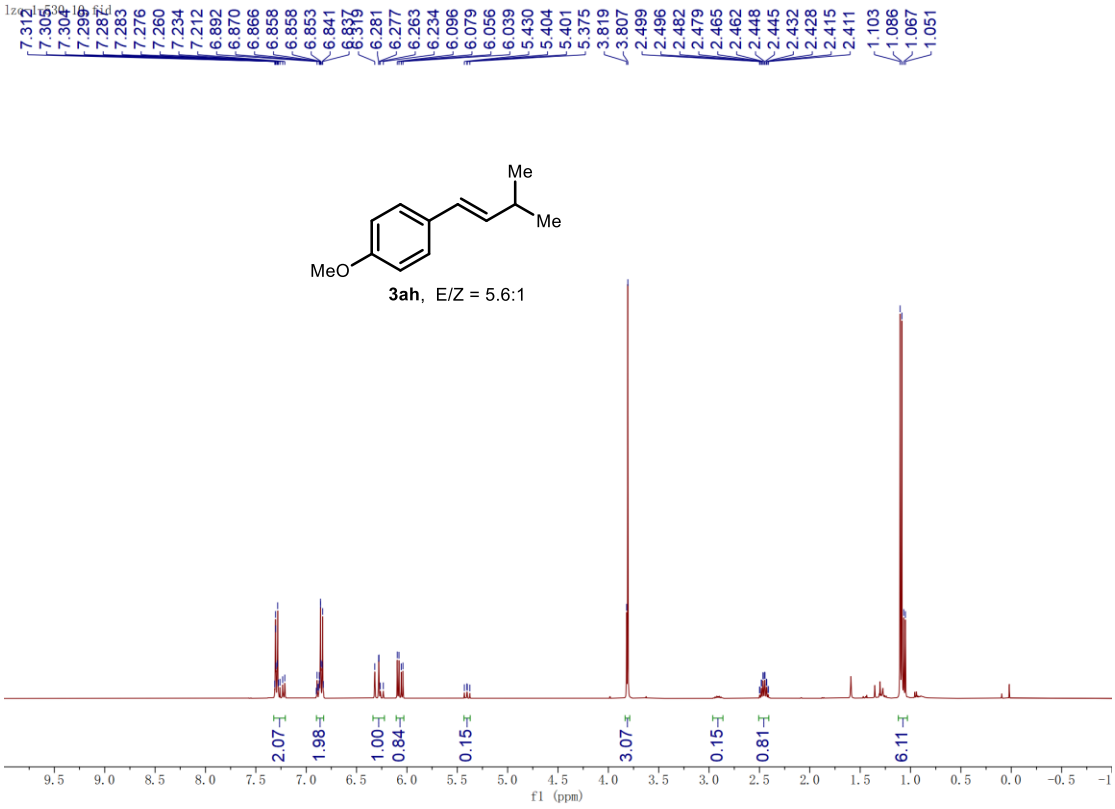

Figure S76. ^{1}H NMR of **3ah** (trans/cis mixture, $CDCl_3$, 400 MHz)

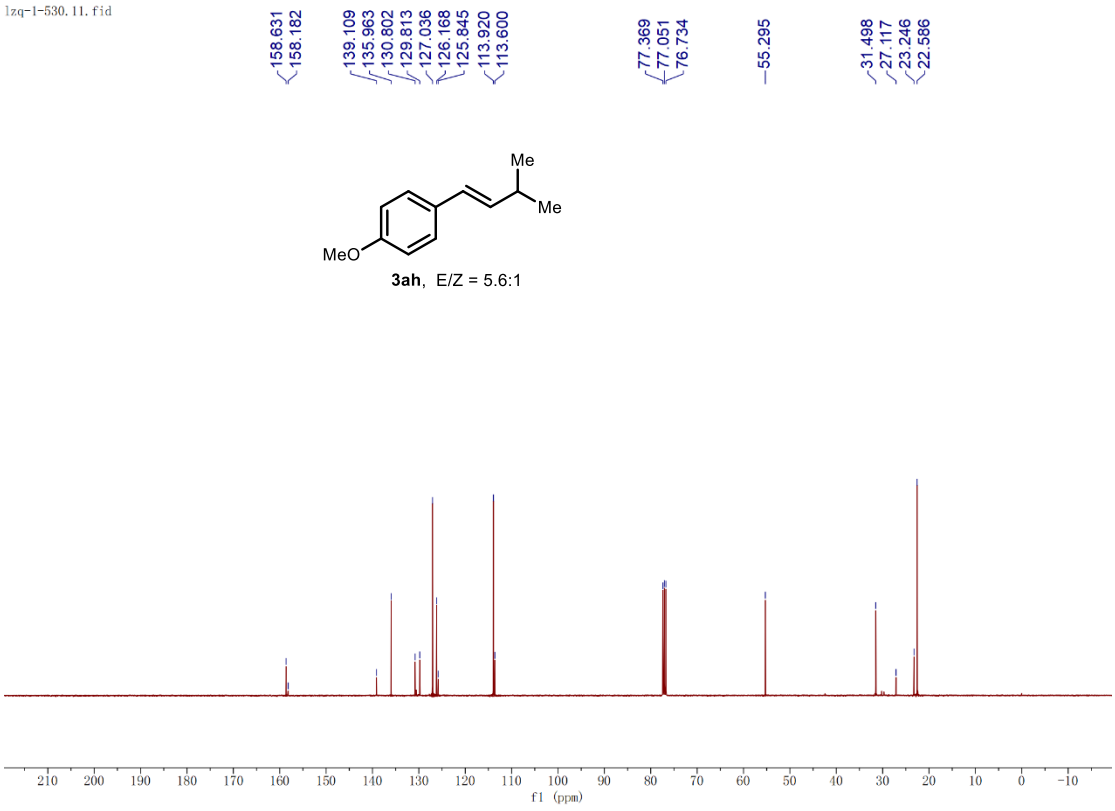

Figure S77. ^{13}C NMR of **3ah** (trans/cis mixture, $CDCl_3$, 101 MHz).

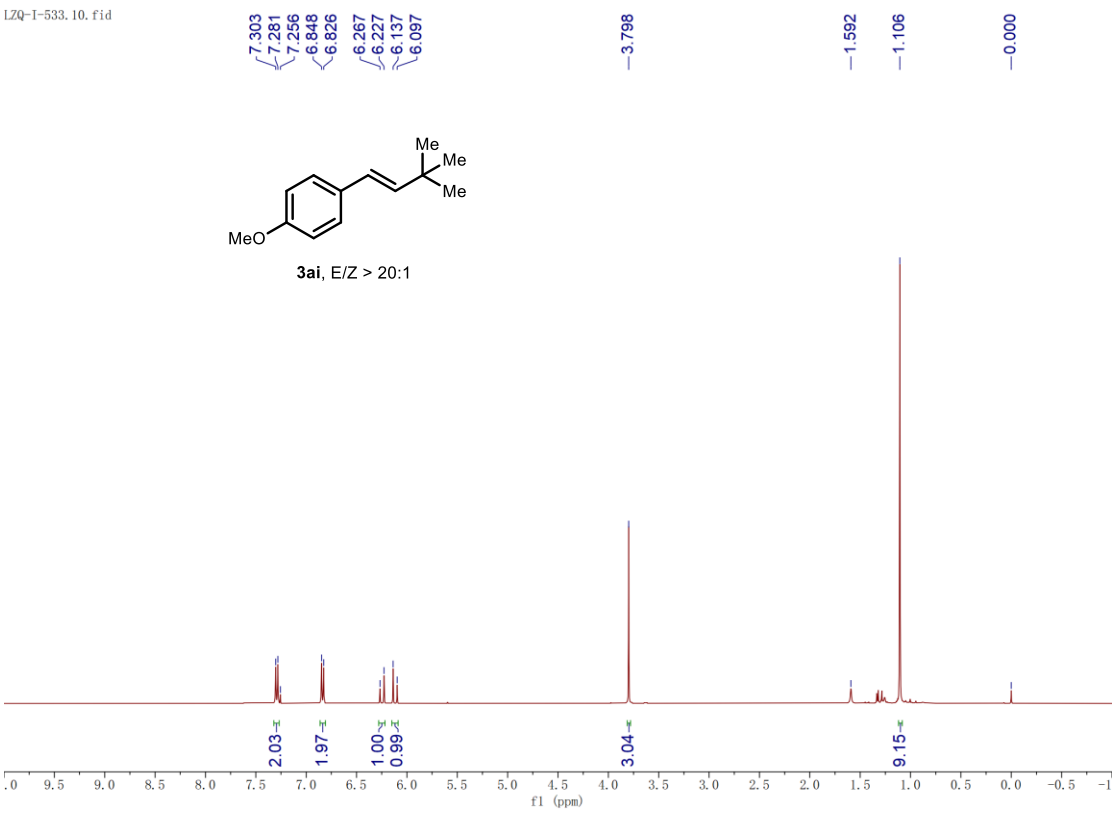

Figure S78. ^{1}H NMR of **3ai** (trans, $CDCl_3$, 400 MHz)

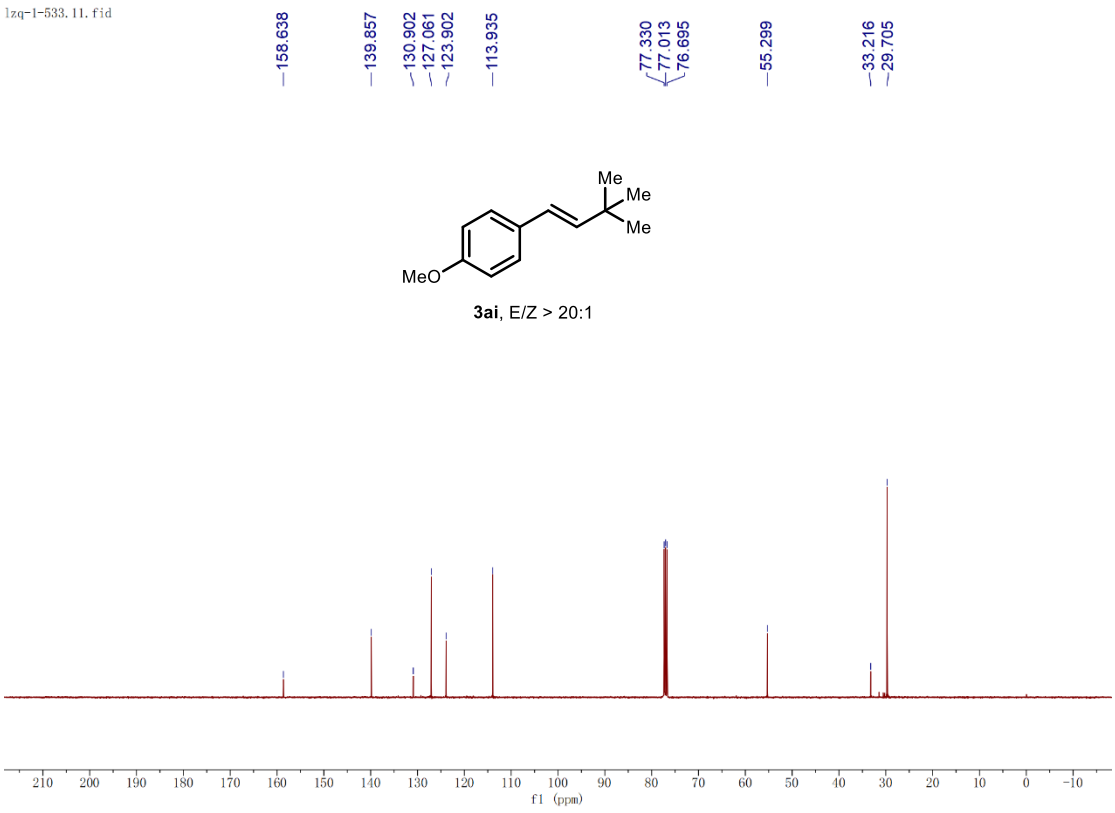

Figure S79. ^{13}C NMR of **3ai** (trans, $CDCl_3$, 101 MHz).

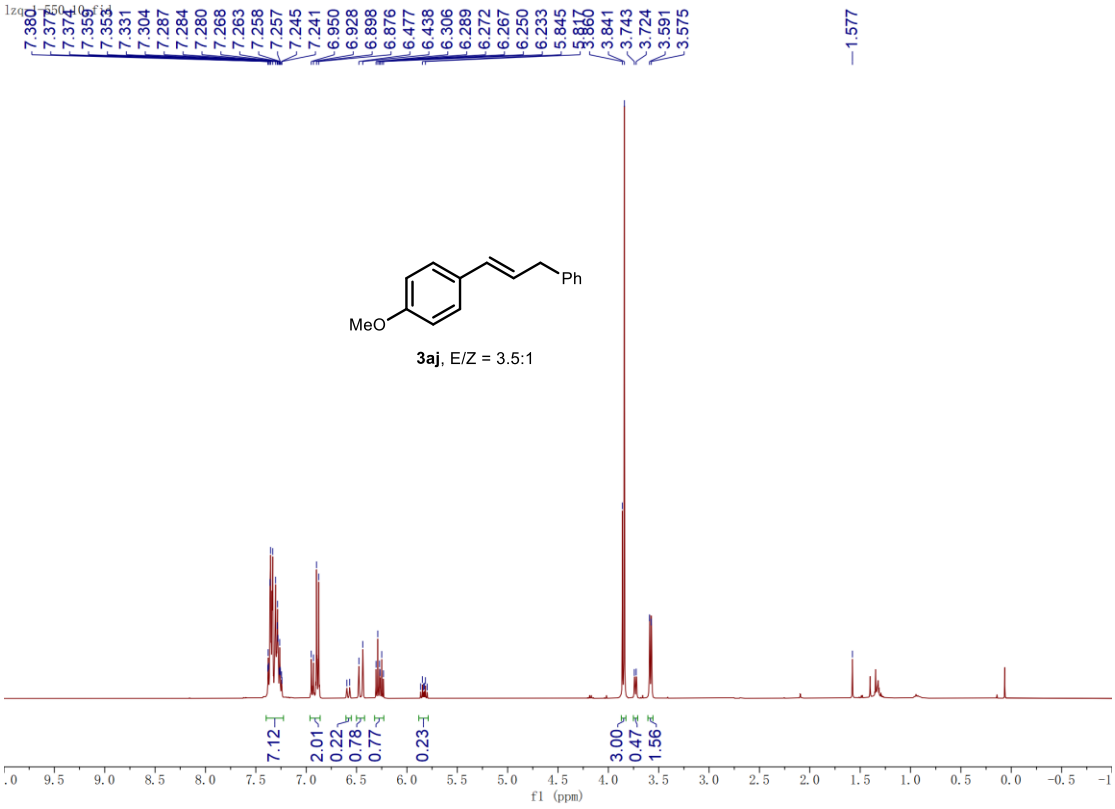

Figure S80. ^{1}H NMR of **3aj** (trans/cis mixture, $CDCl_3$, 400 MHz)

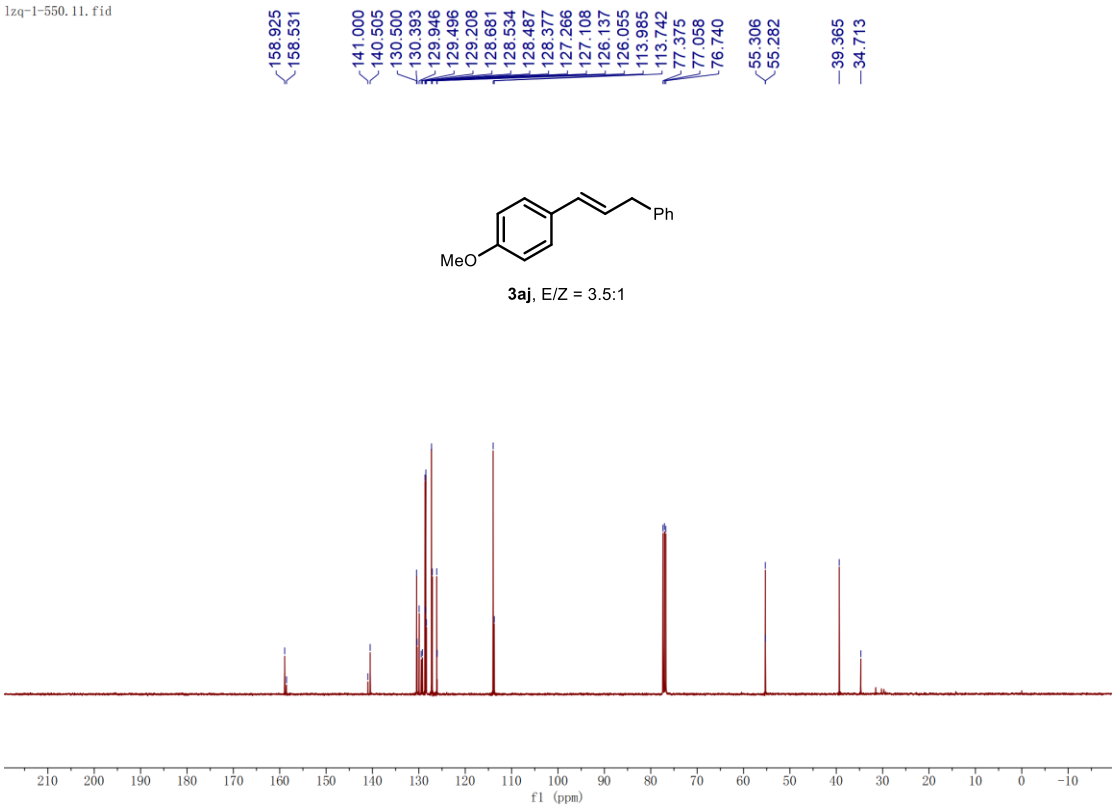

Figure S81. ^{13}C NMR of **3aj** (trans/cis mixture, $CDCl_3$, 101 MHz).

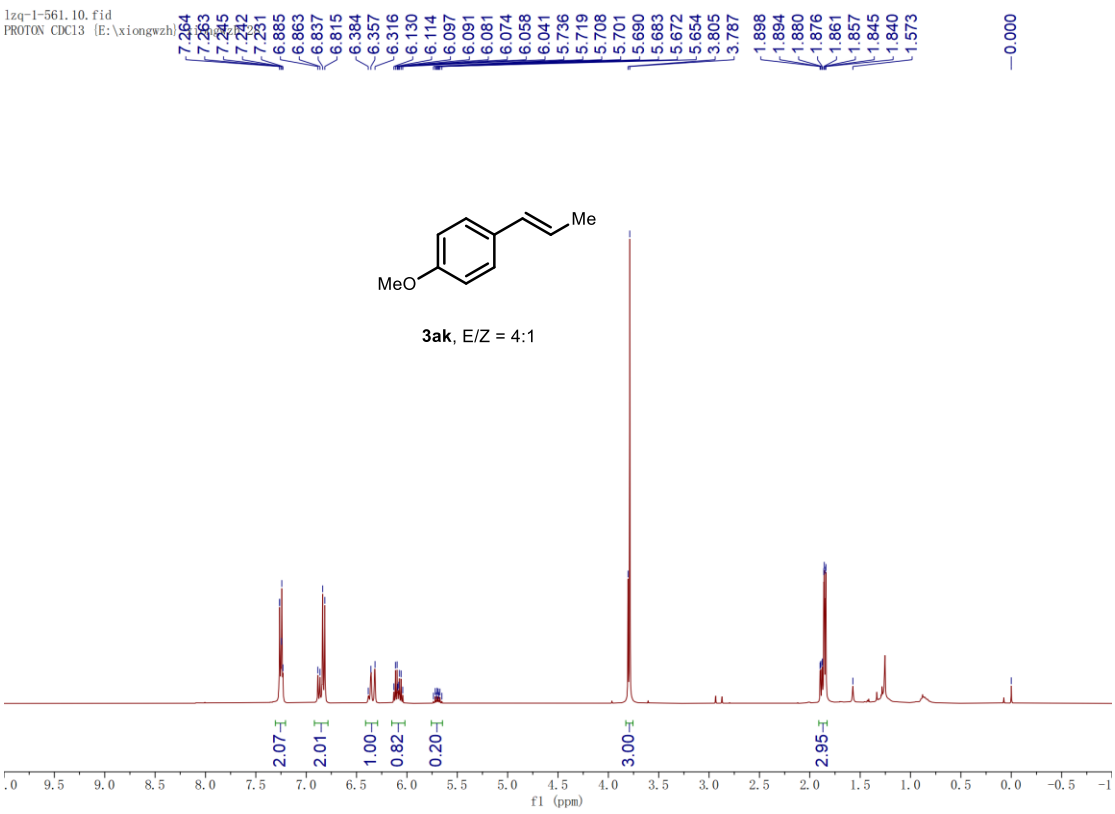

Figure S82. ^{1}H NMR of **3ak** (trans/cis mixture, $CDCl_3$, 400 MHz).

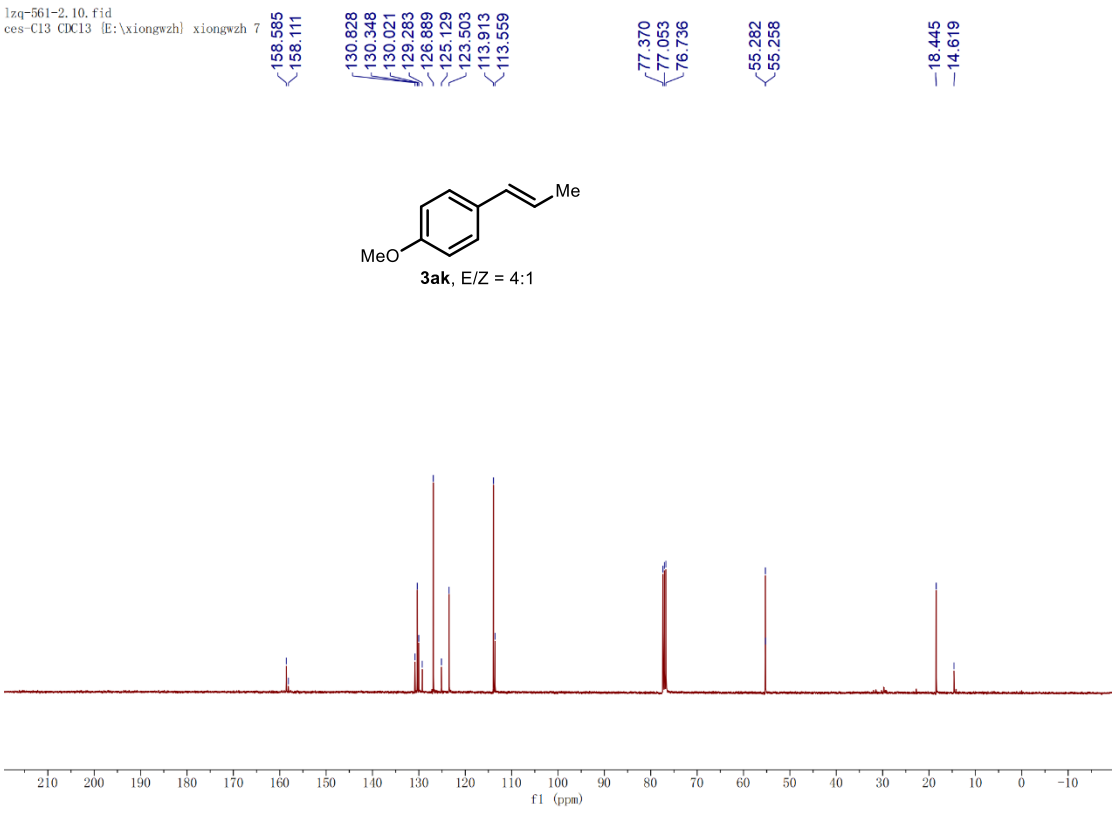

Figure S83. ^{13}C NMR of **3ak** (trans/cis mixture, $CDCl_3$, 101 MHz).

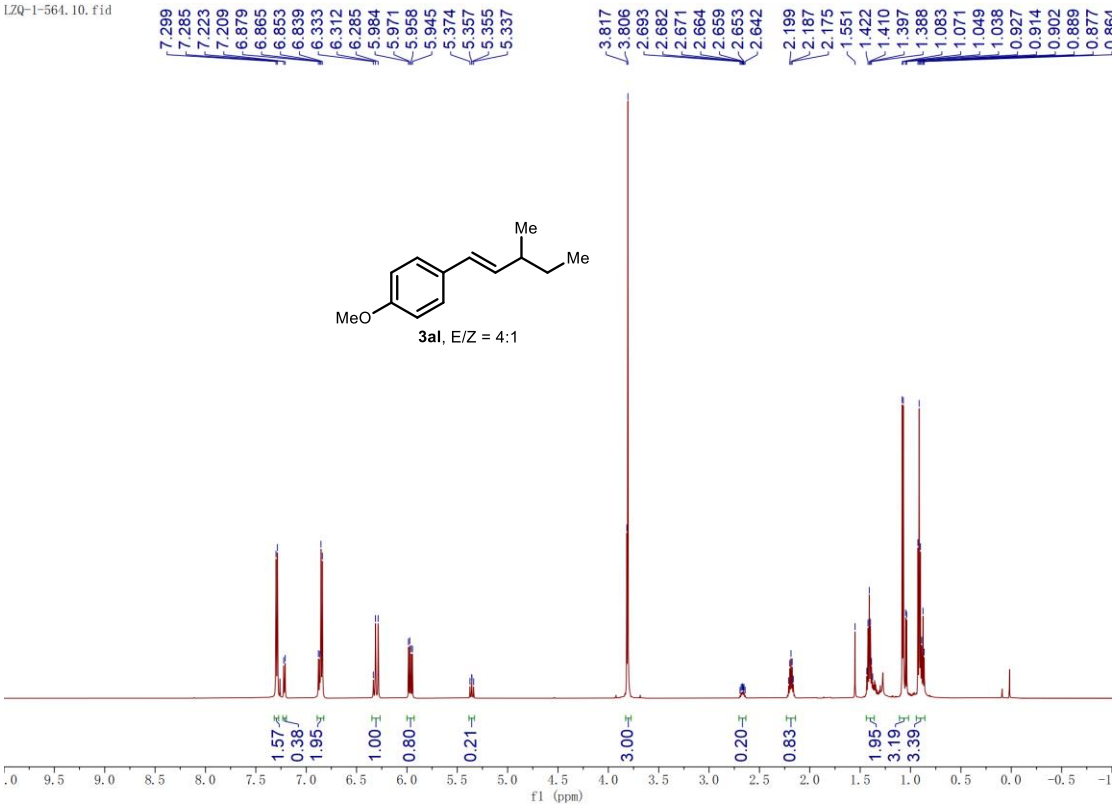

Figure S84. ^{1}H NMR of **3al** (trans/cis mixture, $CDCl_3$, 600 MHz).

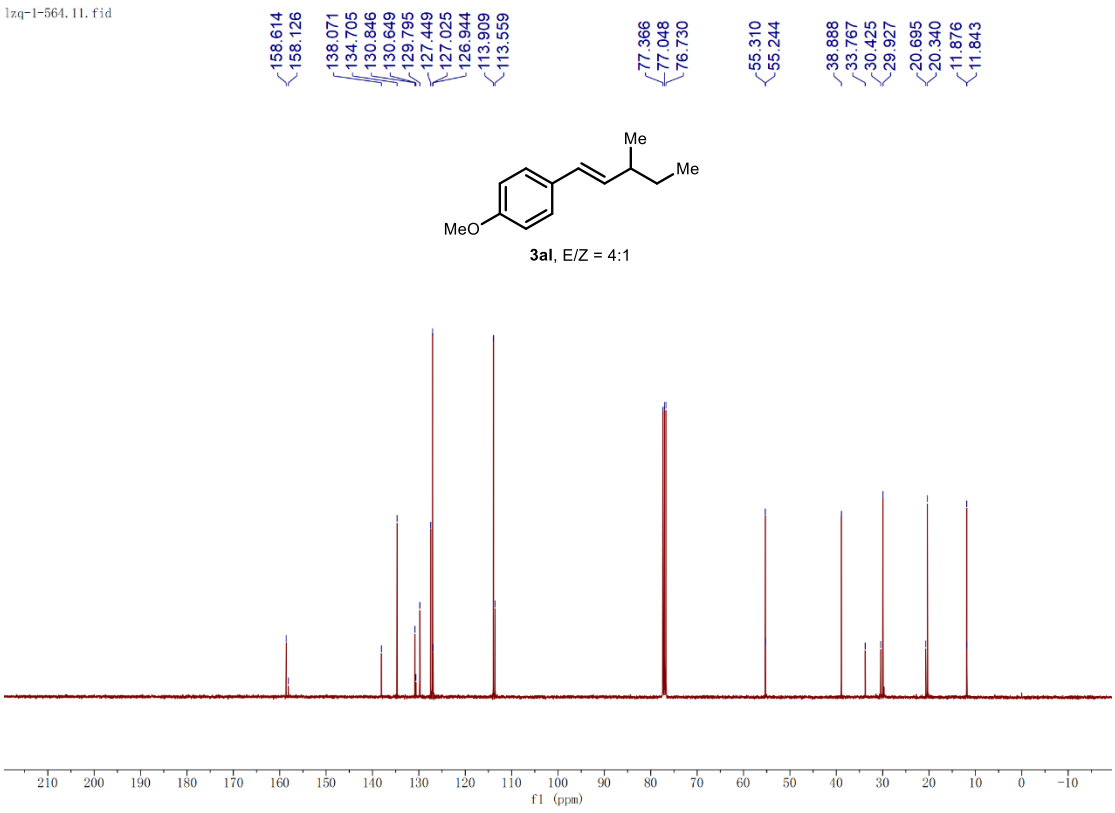

Figure S85. ^{13}C NMR of **3al** (trans/cis mixture, $CDCl_3$, 101 MHz).

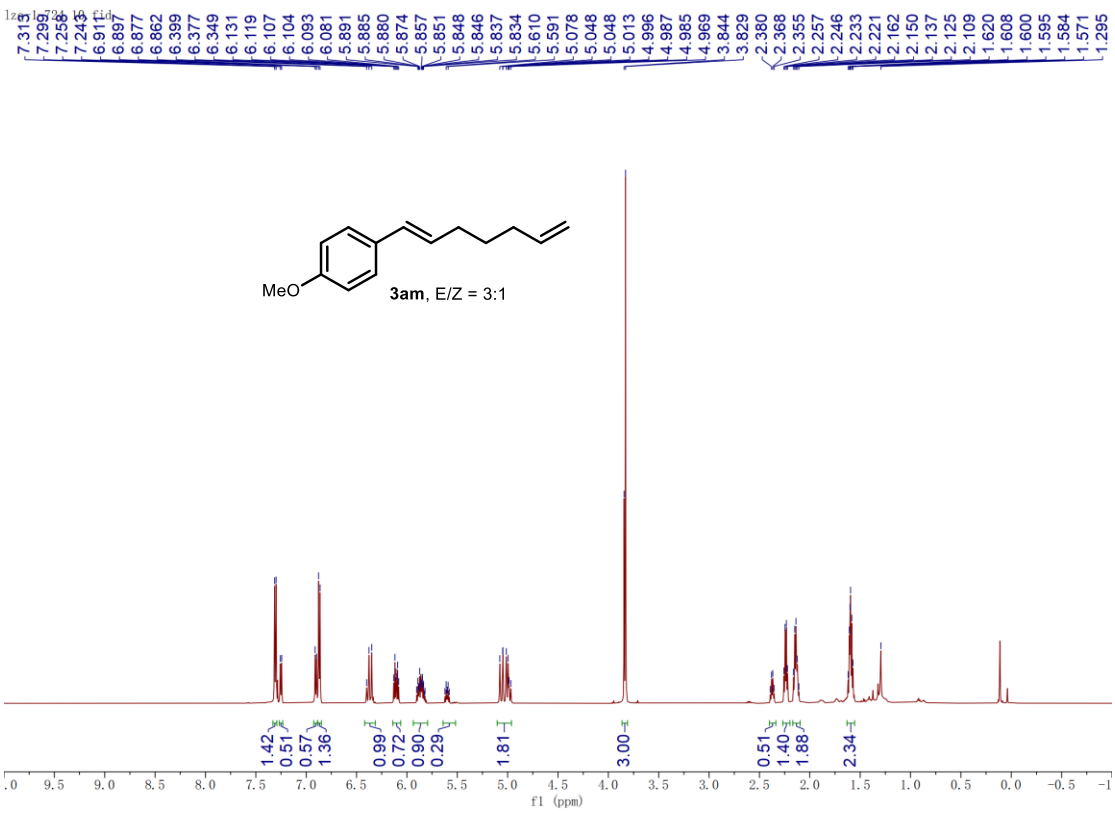

Figure S86. ^{1}H NMR of **3am** (trans/cis mixture, $CDCl_3$, 400 MHz).

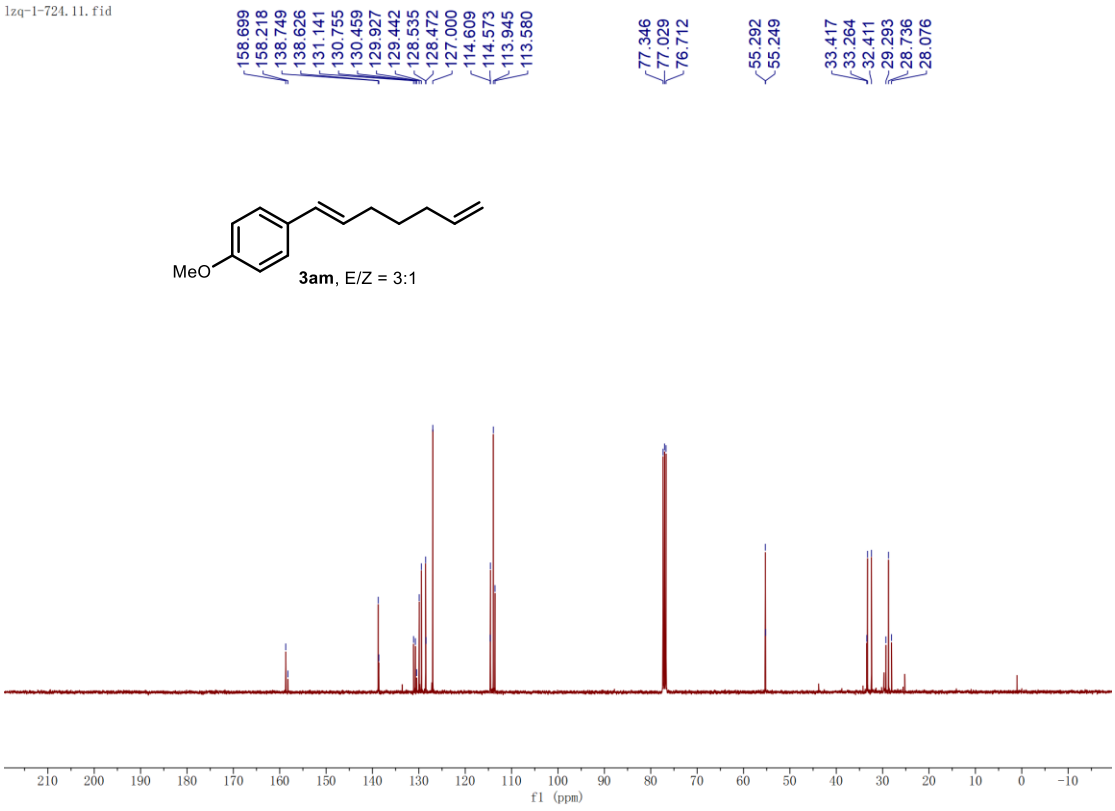

Figure S87. ^{13}C NMR of **3am** (trans/cis mixture, $CDCl_3$, 101 MHz).

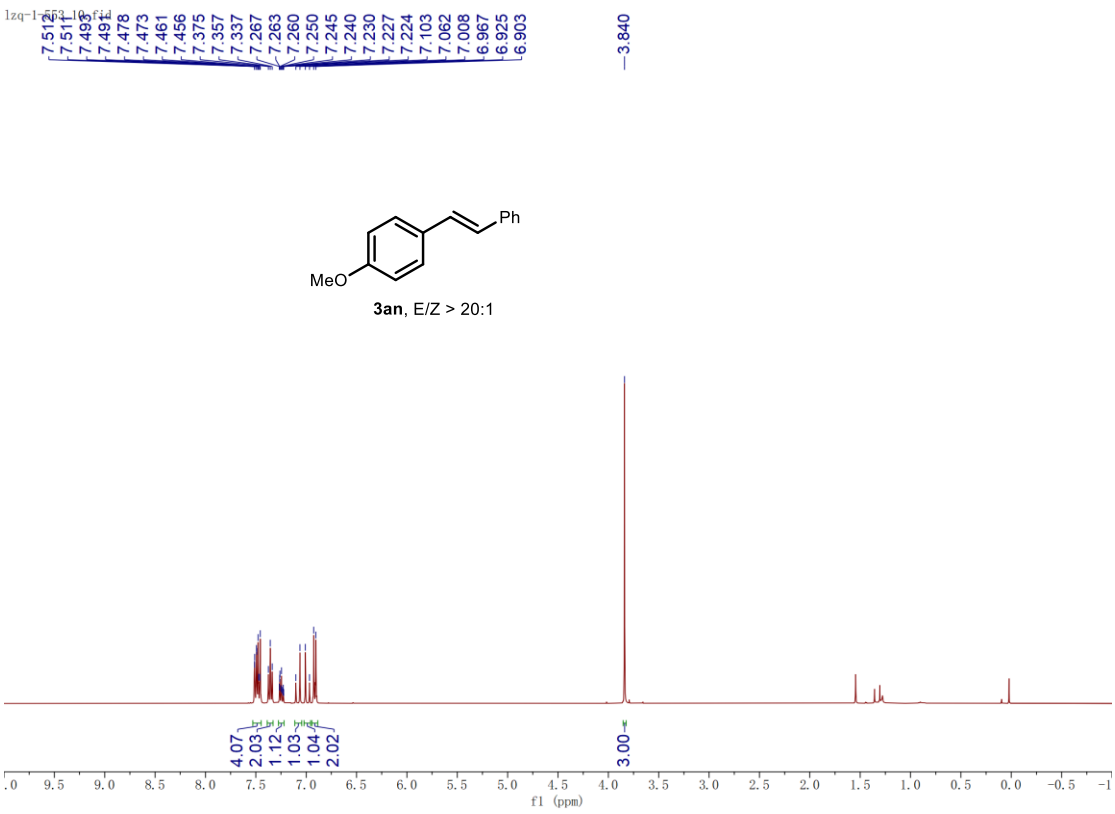

Figure S88. ^{1}H NMR of **3an** (trans, $CDCl_3$, 400 MHz)

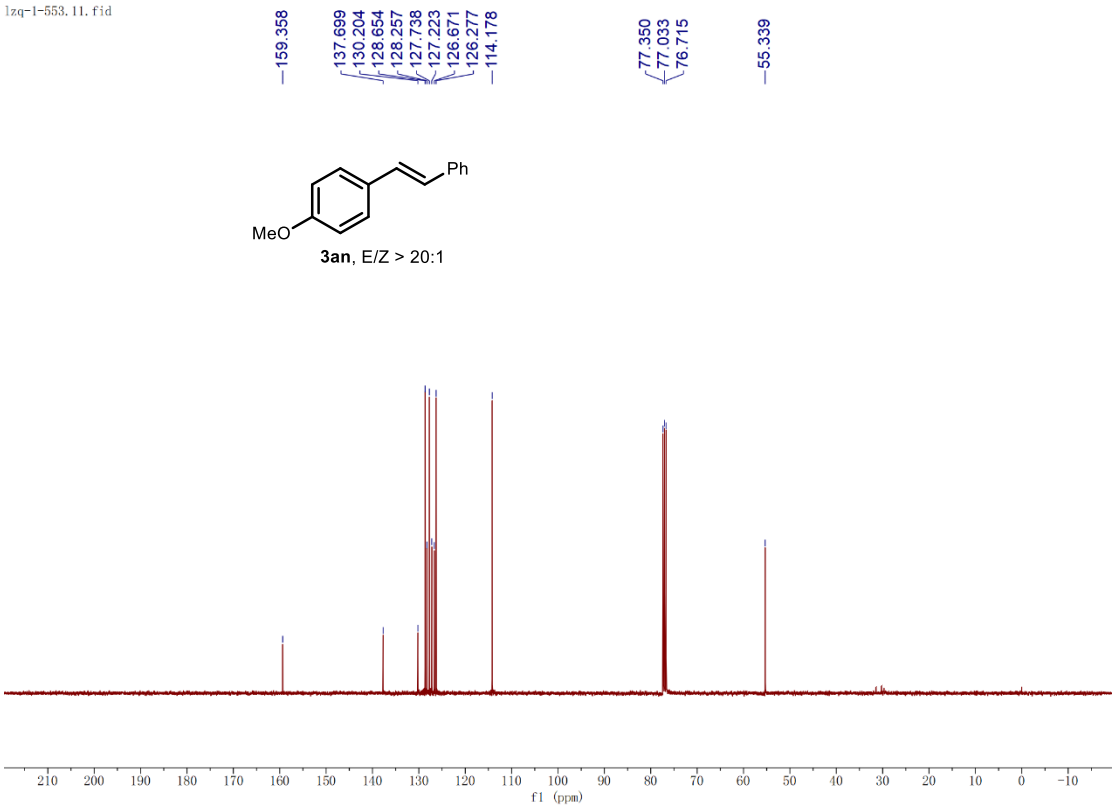

Figure S89. ^{13}C NMR of **3an** (trans, $CDCl_3$, 101 MHz).

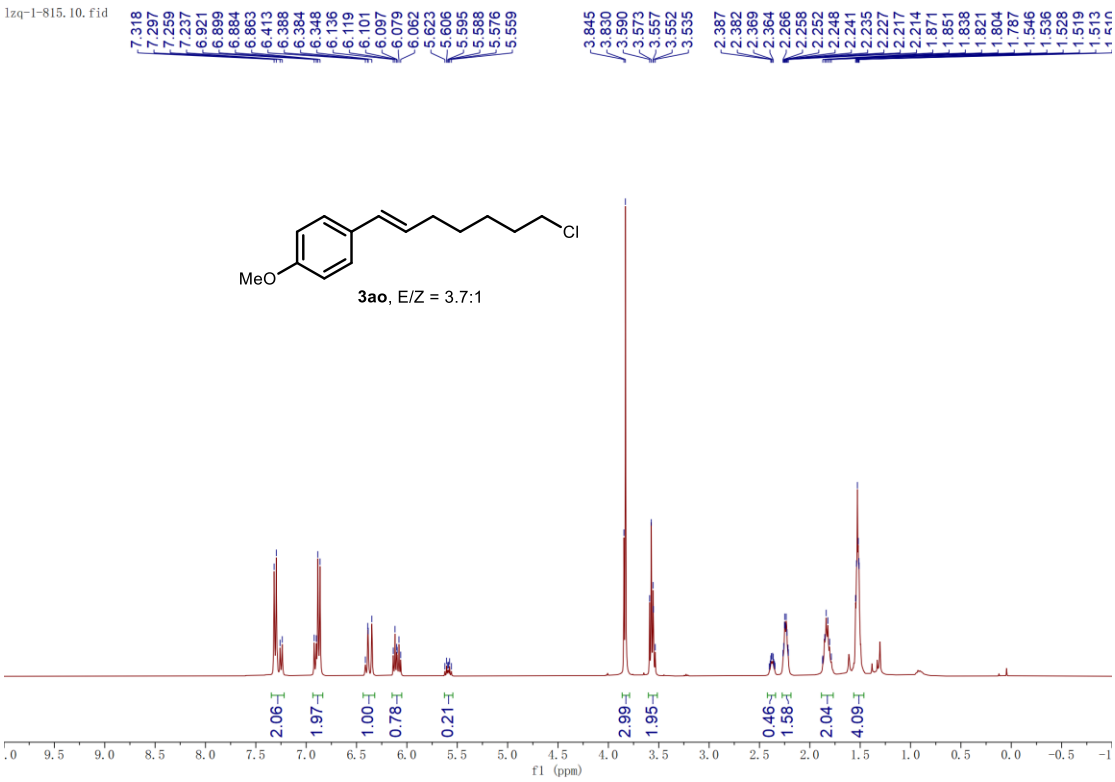

Figure S90. ^{1}H NMR of **3ao** (cis/trans, $CDCl_3$, 400 MHz)

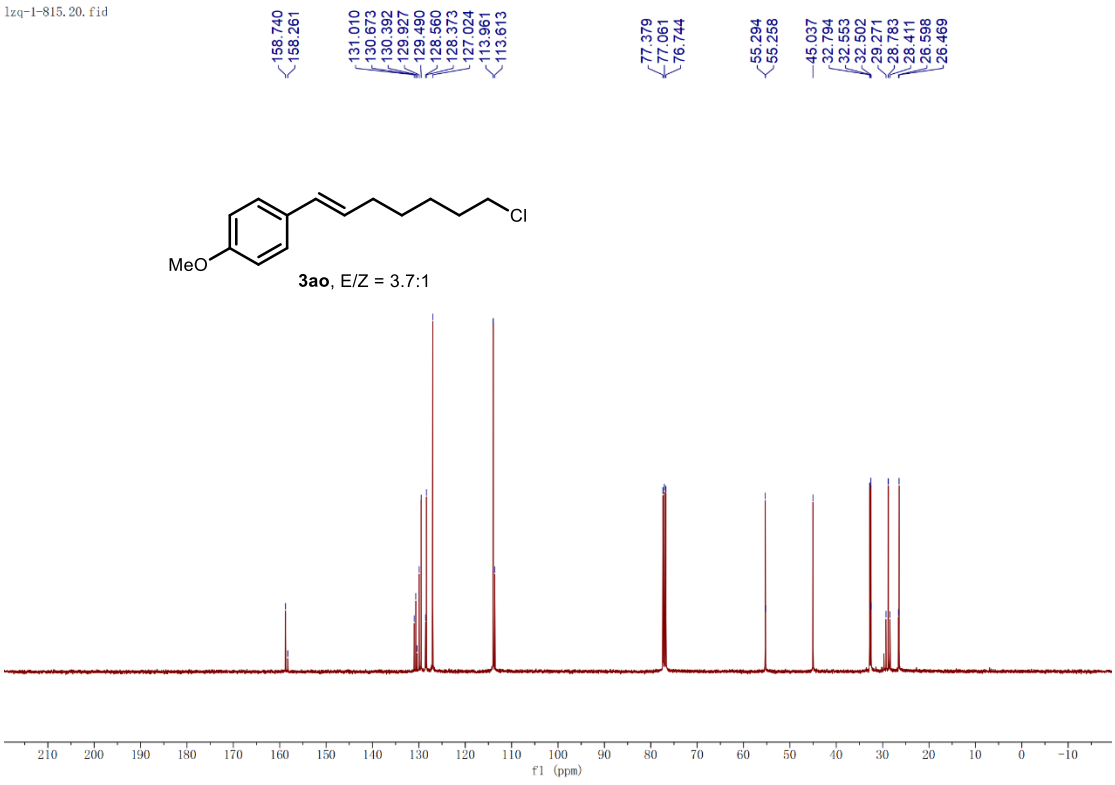

Figure S91. ^{13}C NMR of **3ao** (trans, $CDCl_3$, 101 MHz).

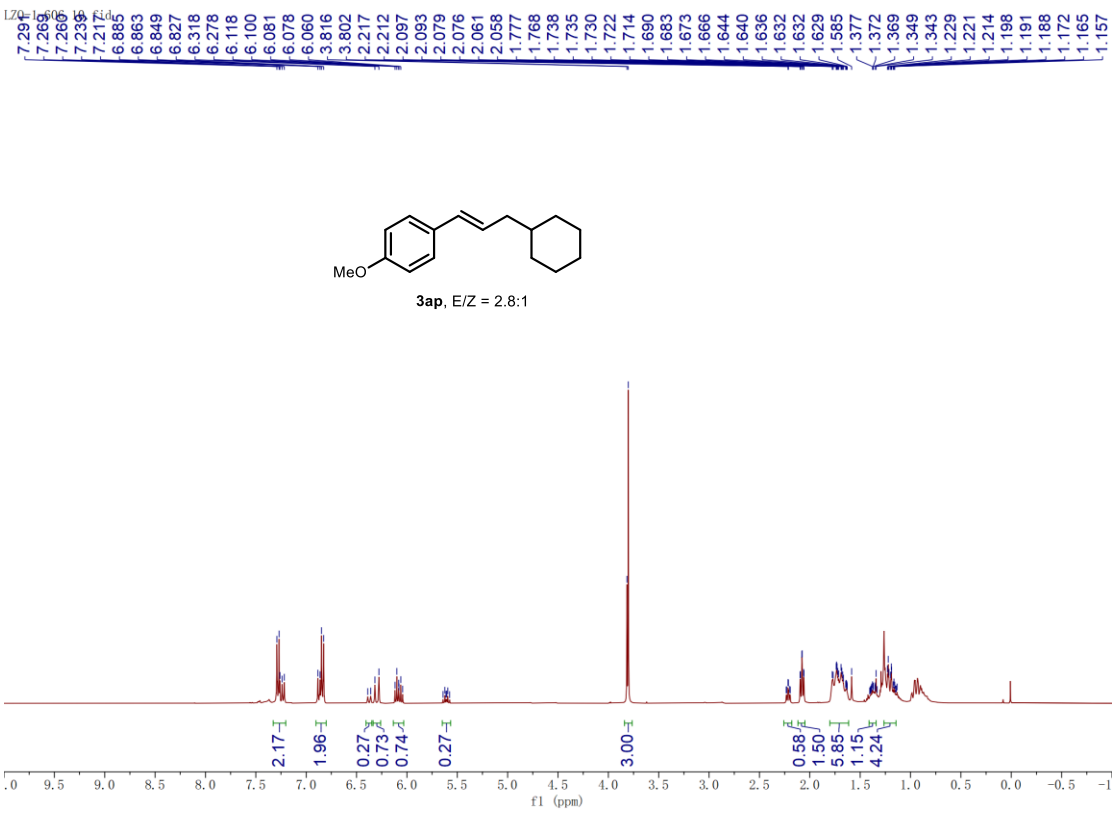

Figure S92. ^{1}H NMR of **3ap** (trans/cis mixture, $CDCl_3$, 400 MHz).

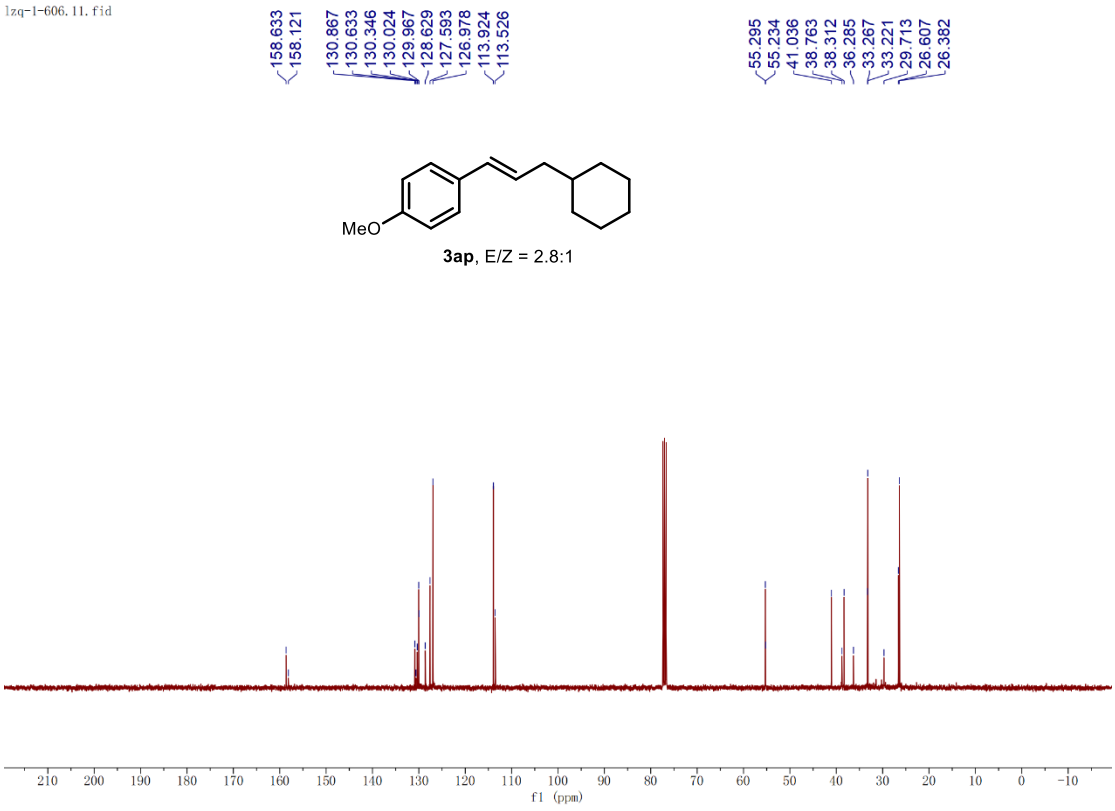

Figure S93. ^{13}C NMR of **3ap** (trans/cis mixture, $CDCl_3$, 101 MHz).

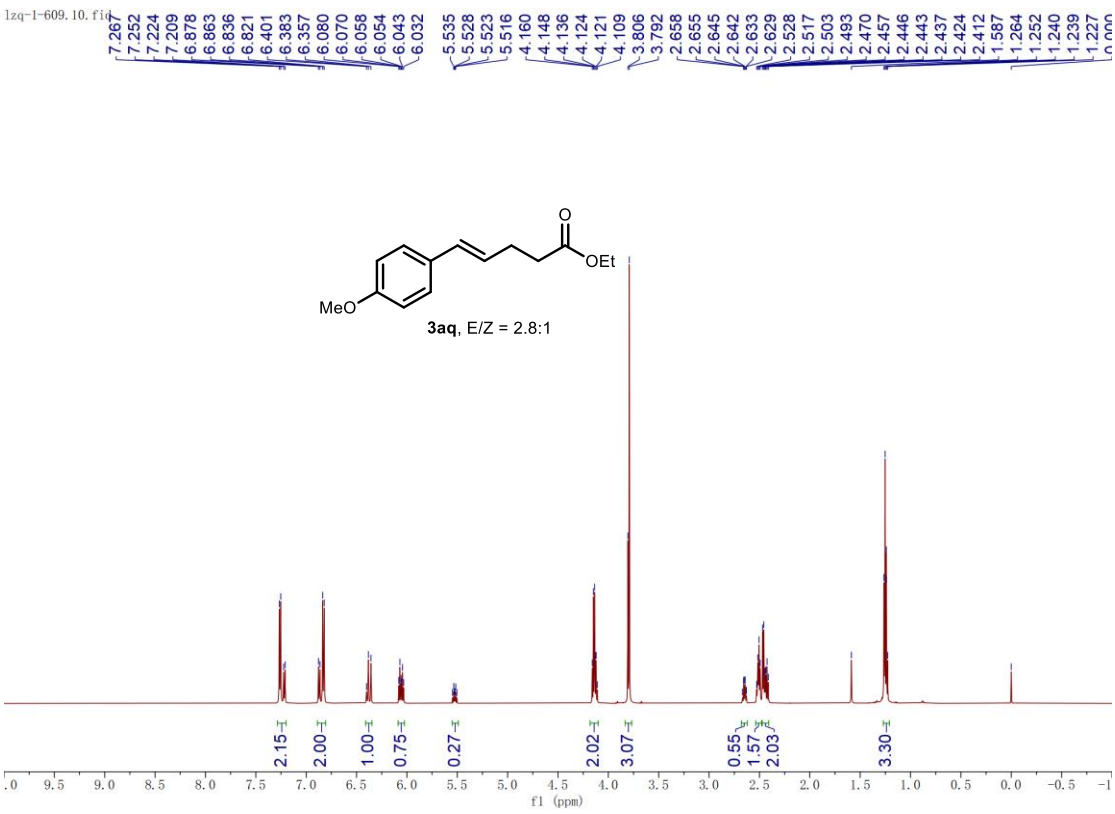

Figure S94. ^{1}H NMR of **3aq** (trans/cis mixture, $CDCl_3$, 600 MHz).

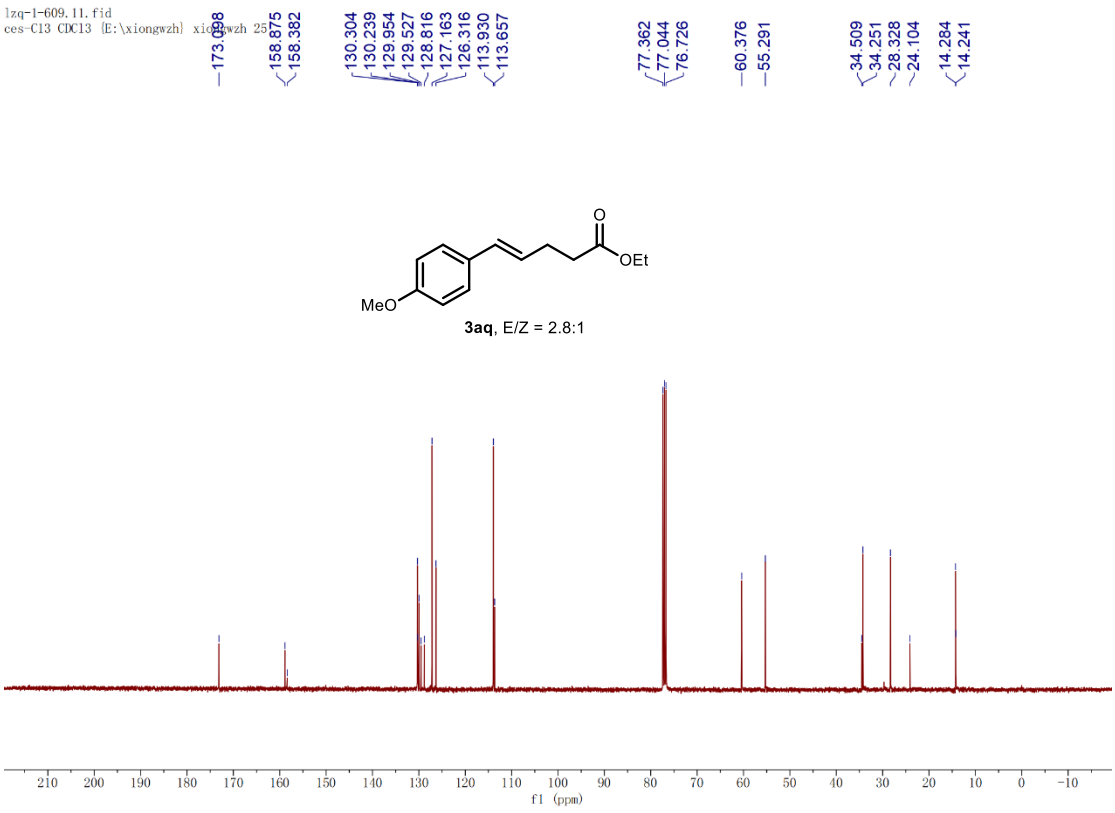

Figure S95. ^{13}C NMR of **3aq** (trans/cis mixture, $CDCl_3$, 101 MHz).

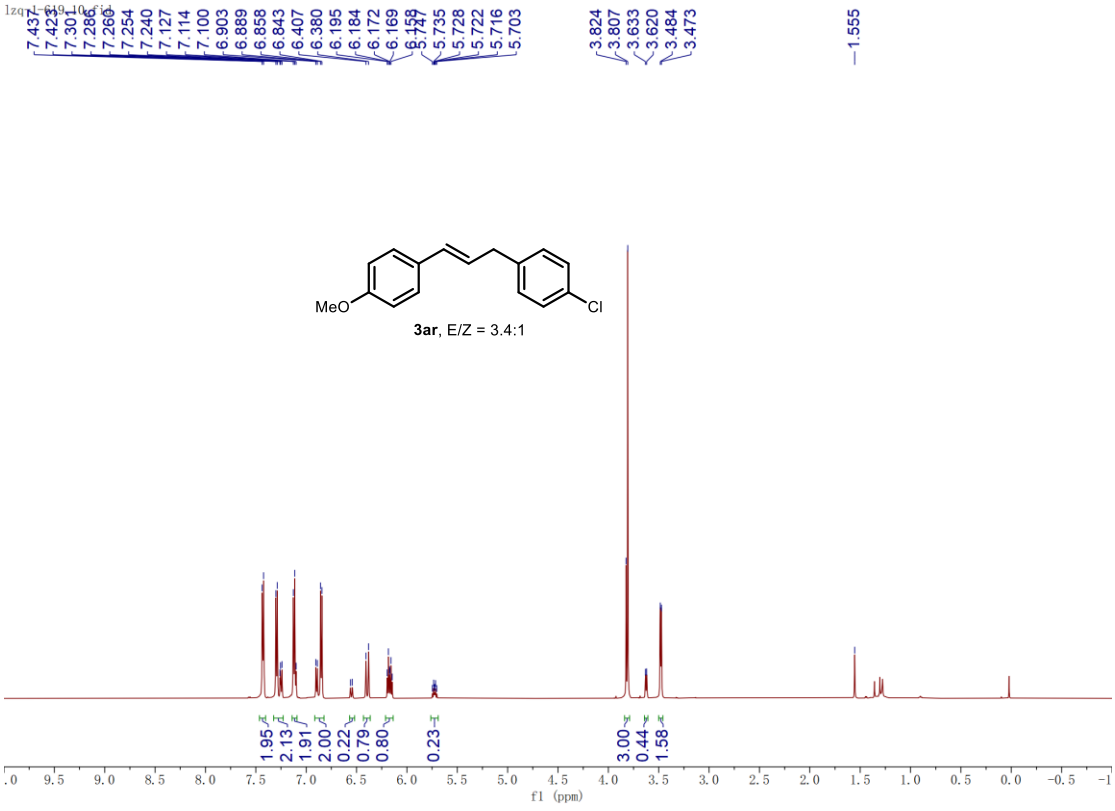

Figure S96. ^{1}H NMR of **3ar** (trans/cis mixture, $CDCl_3$, 600 MHz).

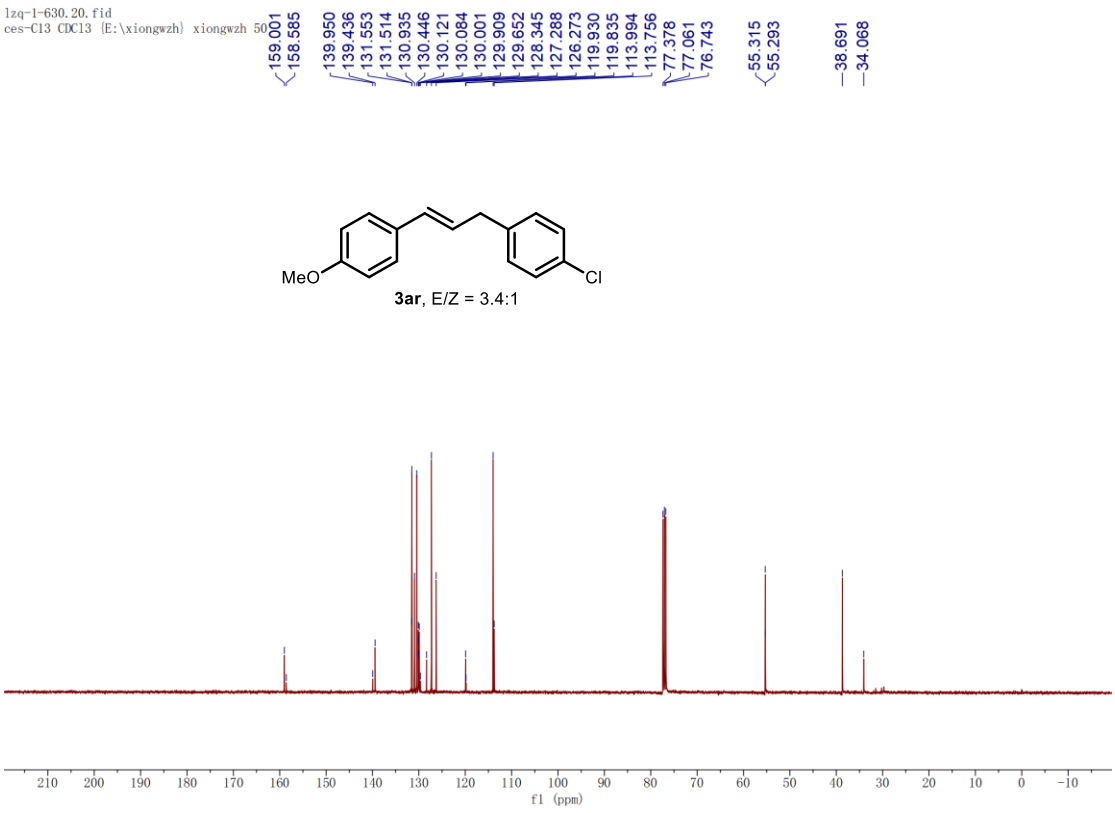

Figure S97. ^{13}C NMR of **3ar** (trans/cis mixture, $CDCl_3$, 101 MHz).

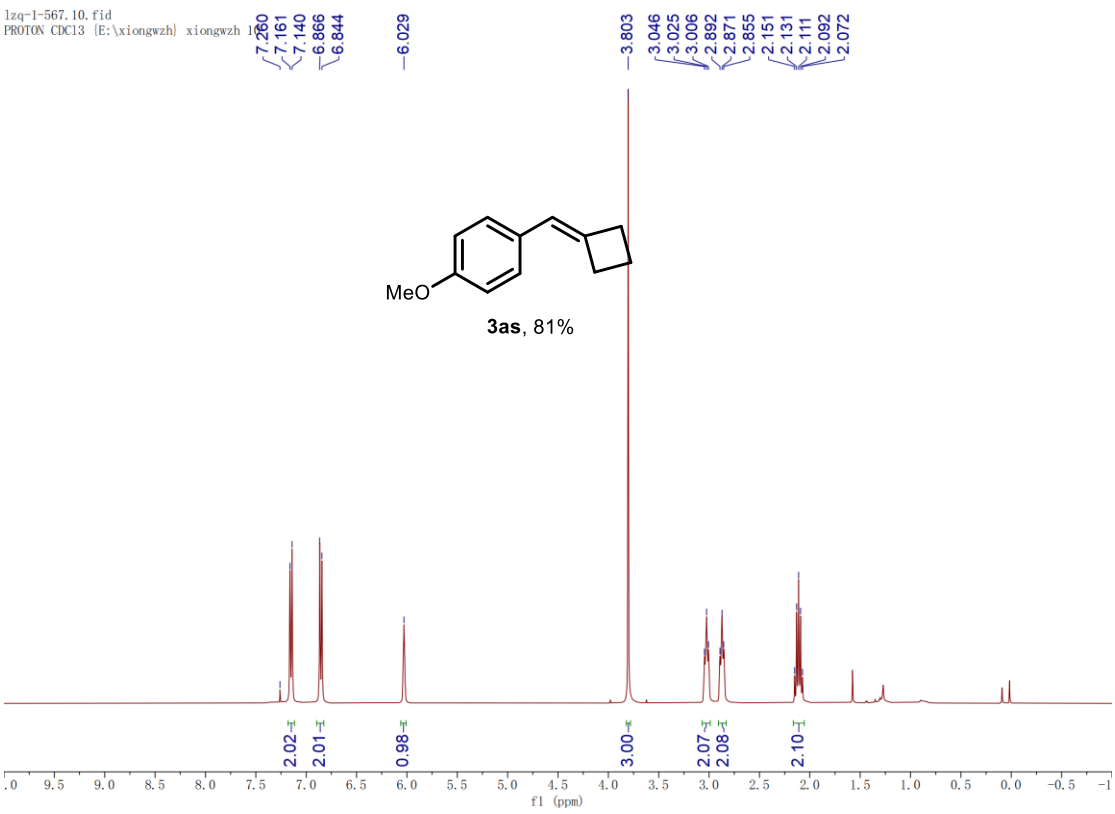

Figure S98. ^{1}H NMR of **3as** ($CDCl_3$, 400 MHz).

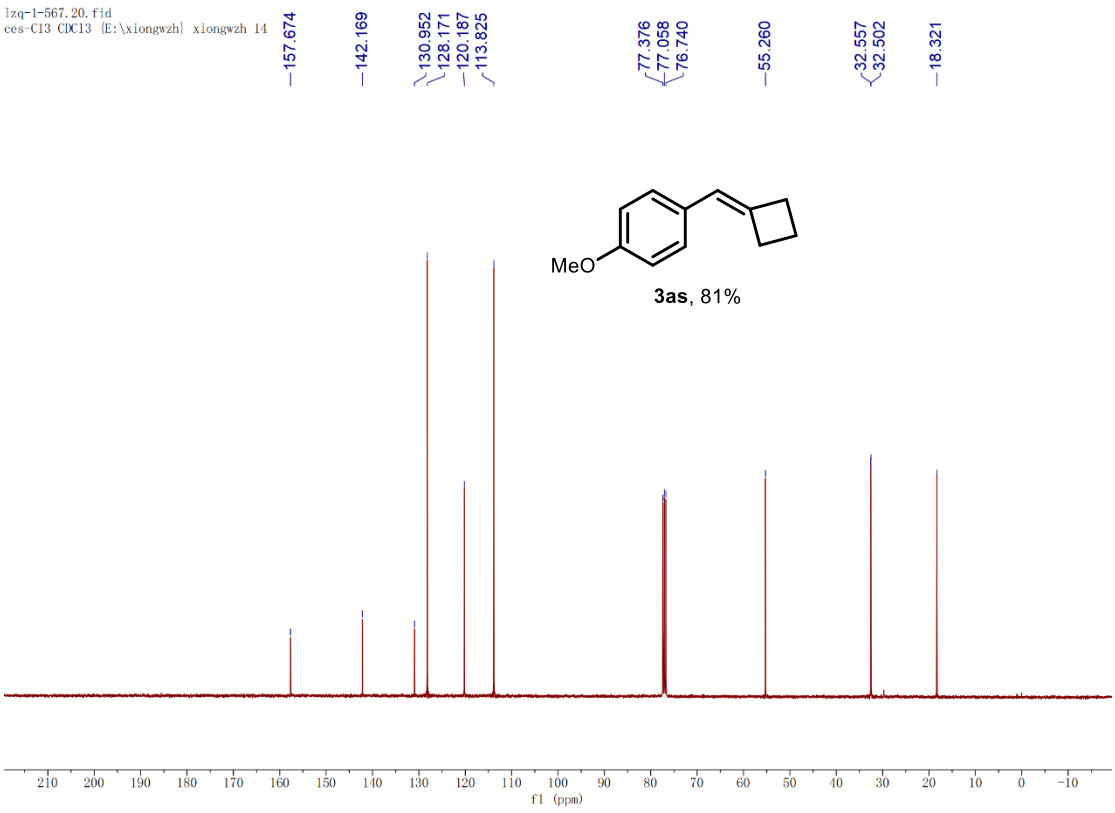

Figure S99. ^{13}C NMR of **3as** ($CDCl_3$, 101 MHz).

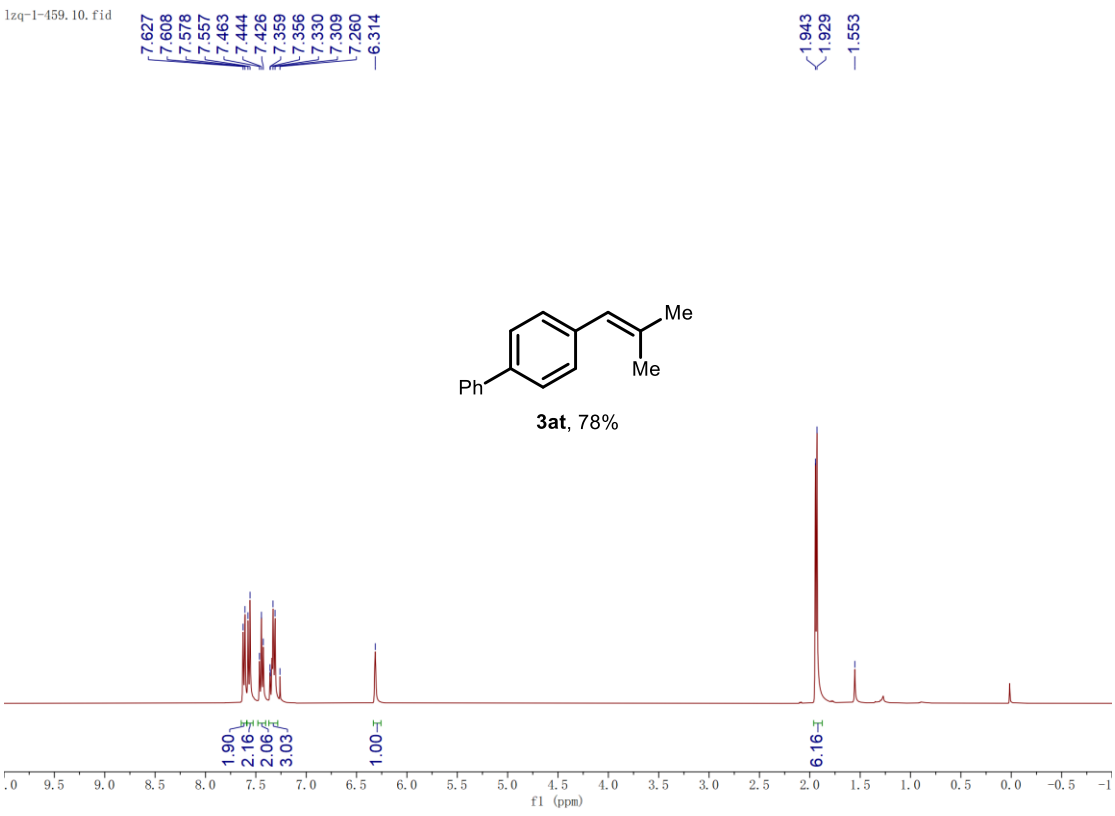

Figure S100. ^{1}H NMR of **3at** (trans/cis mixture, $CDCl_3$, 400 MHz).

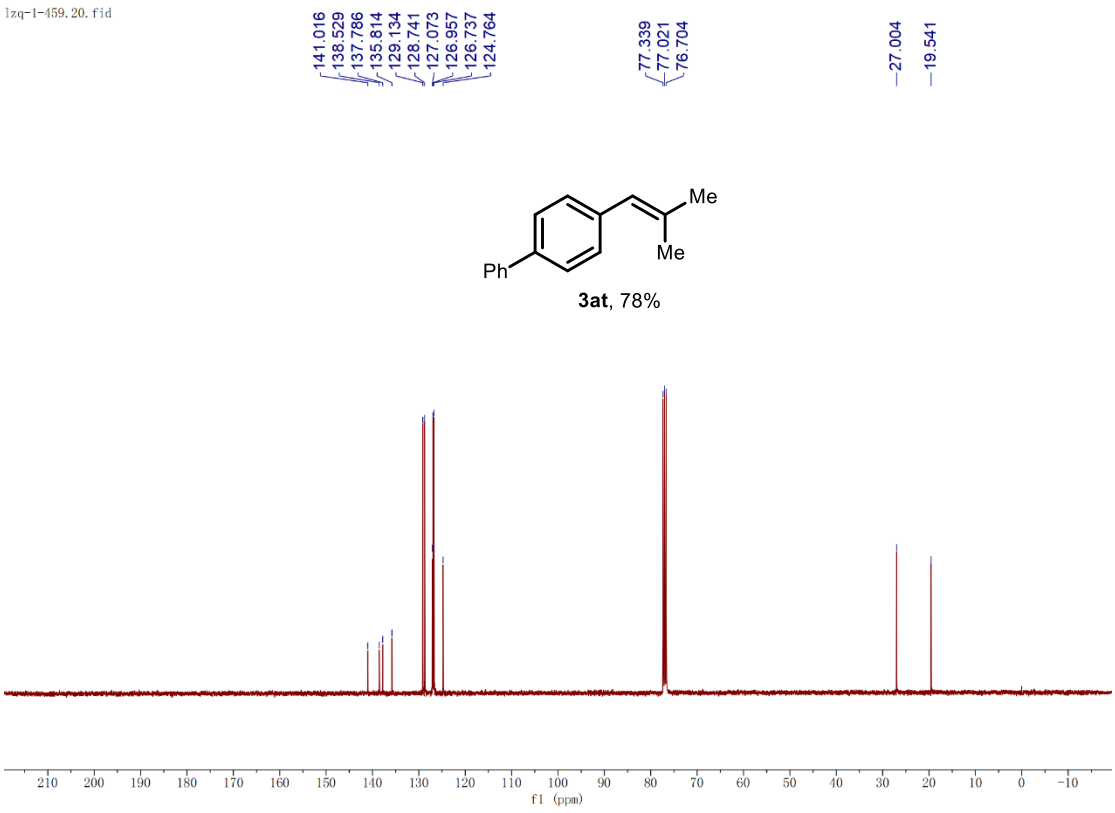

Figure S101. ^{13}C NMR of **3at** (trans/cis mixture, $CDCl_3$, 101 MHz).

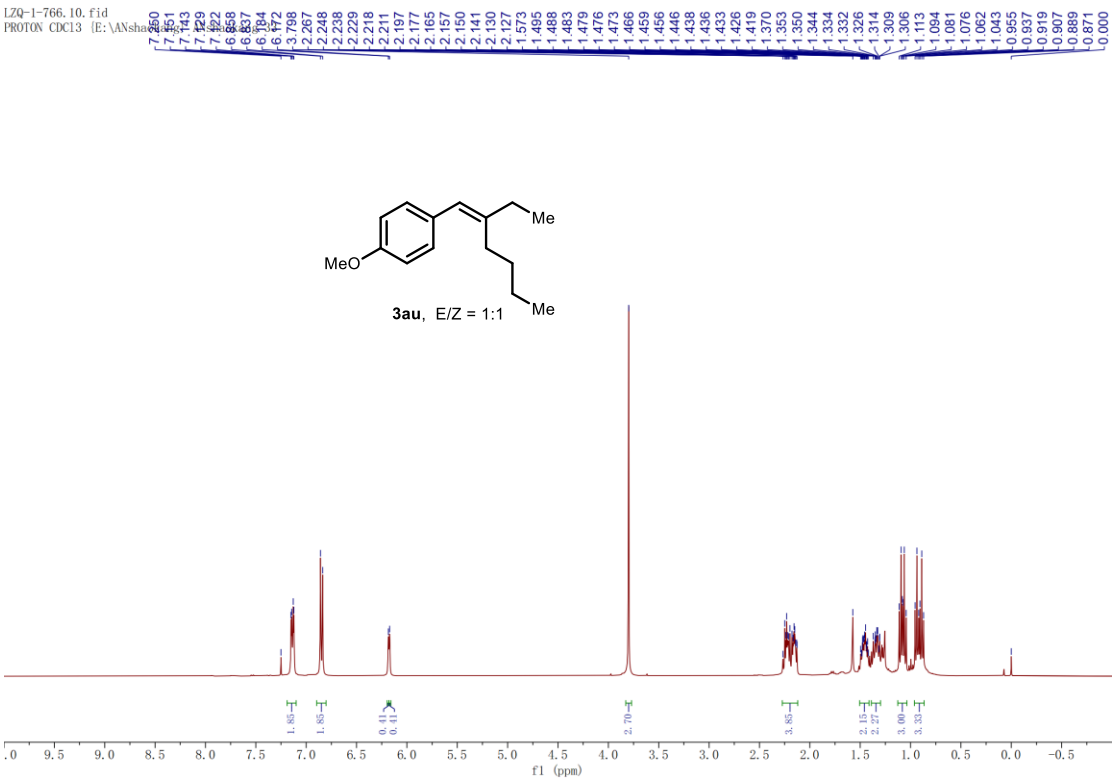

Figure S102. ^{1}H NMR of **3au** (trans/cis mixture, $CDCl_3$, 400 MHz).

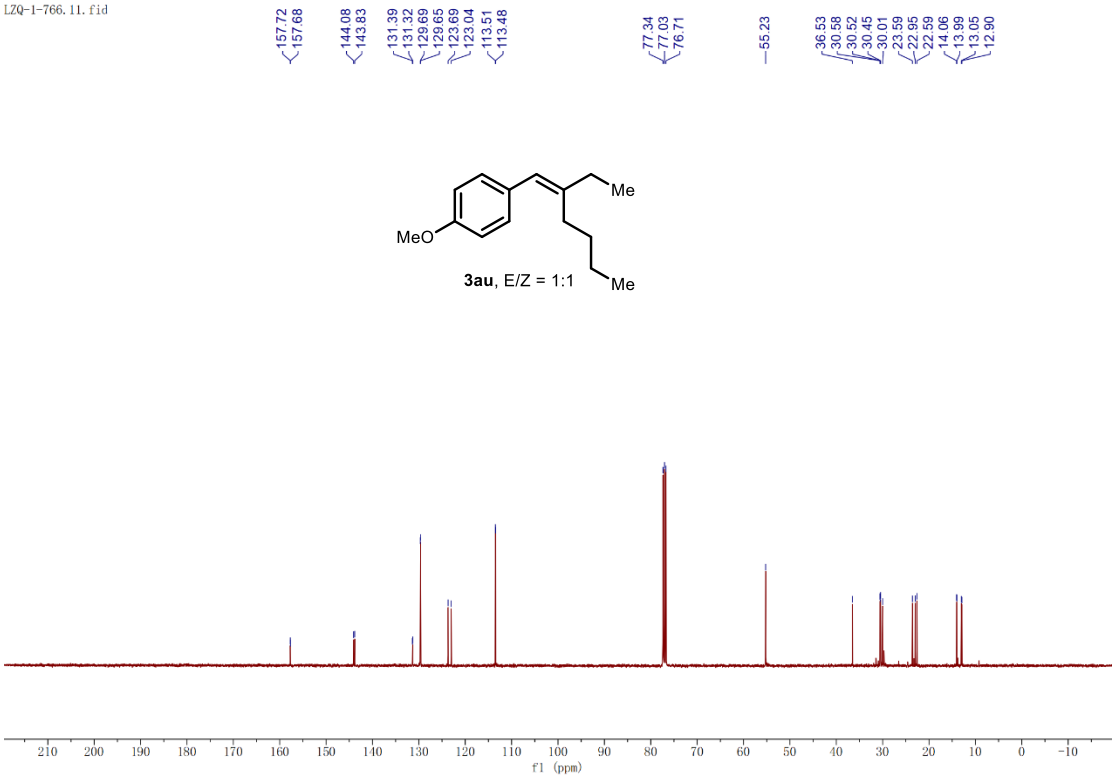

Figure S103. ^{13}C NMR of **3au** (trans/cis mixture, $CDCl_3$, 101 MHz).

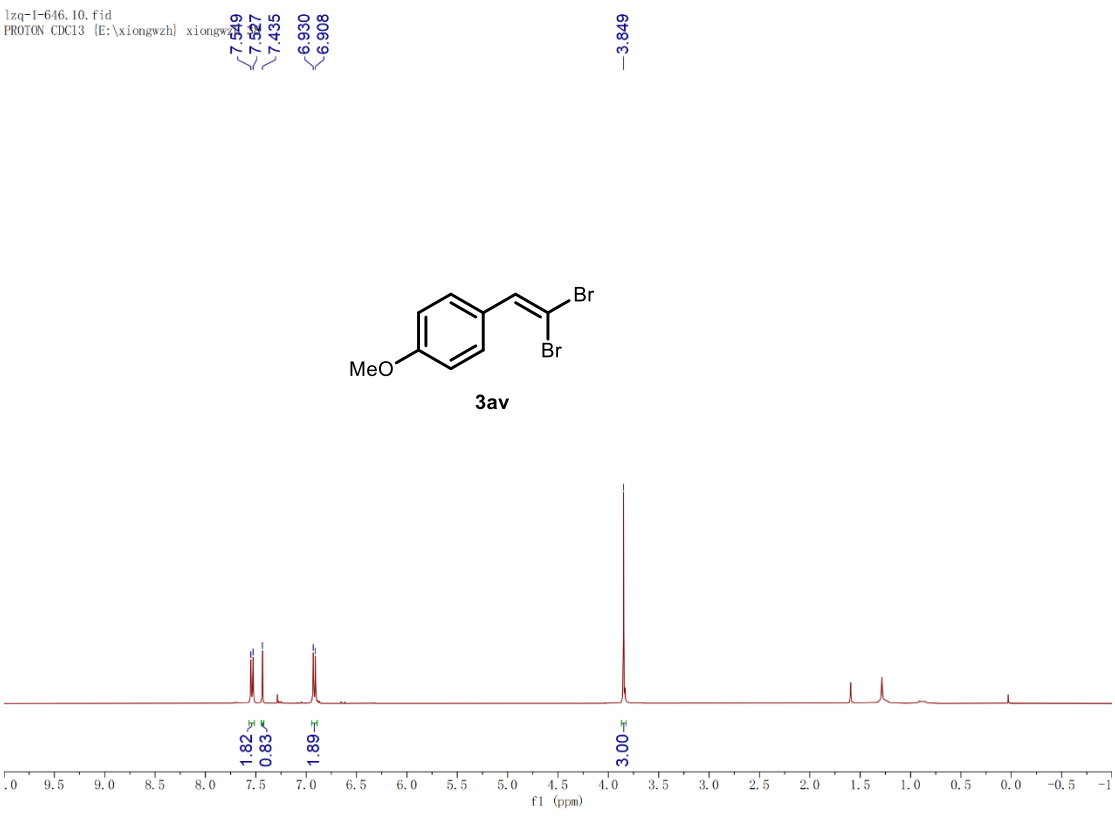

Figure S104. ^{1}H NMR of **3av** ($CDCl_3$, 400 MHz).

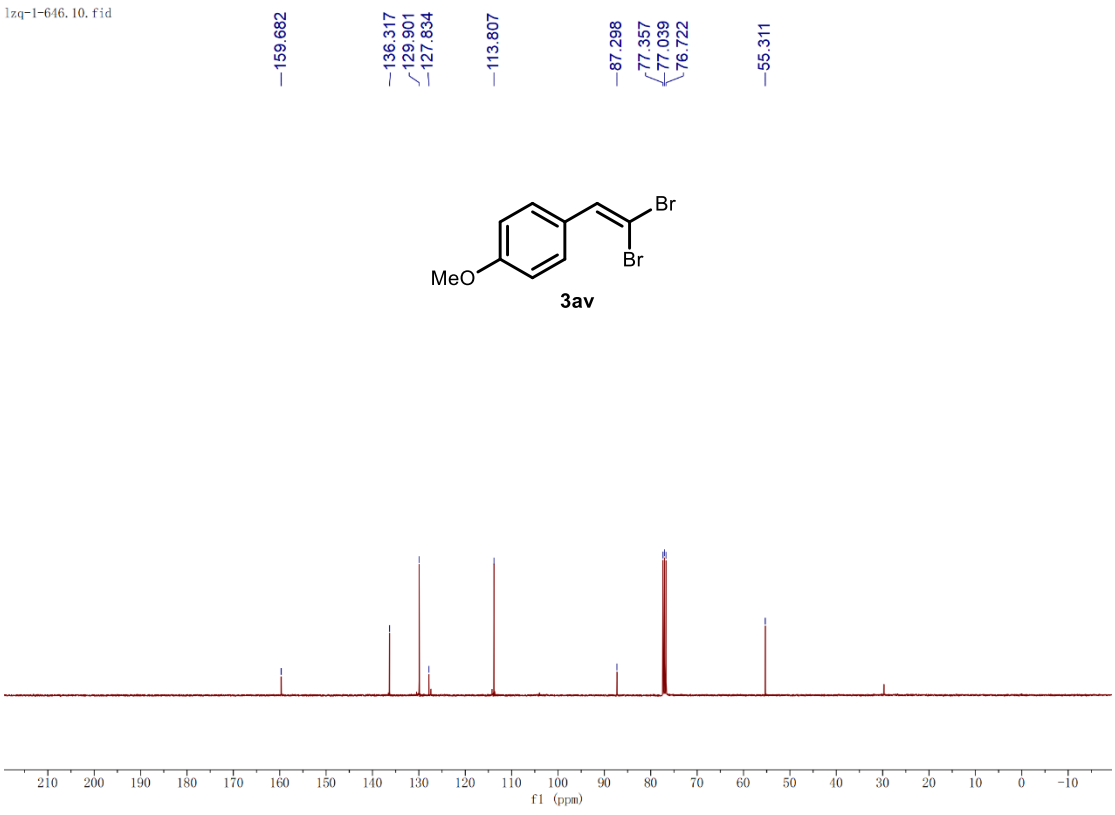

Figure S105. ^{13}C NMR of **3av** ($CDCl_3$, 101 MHz).

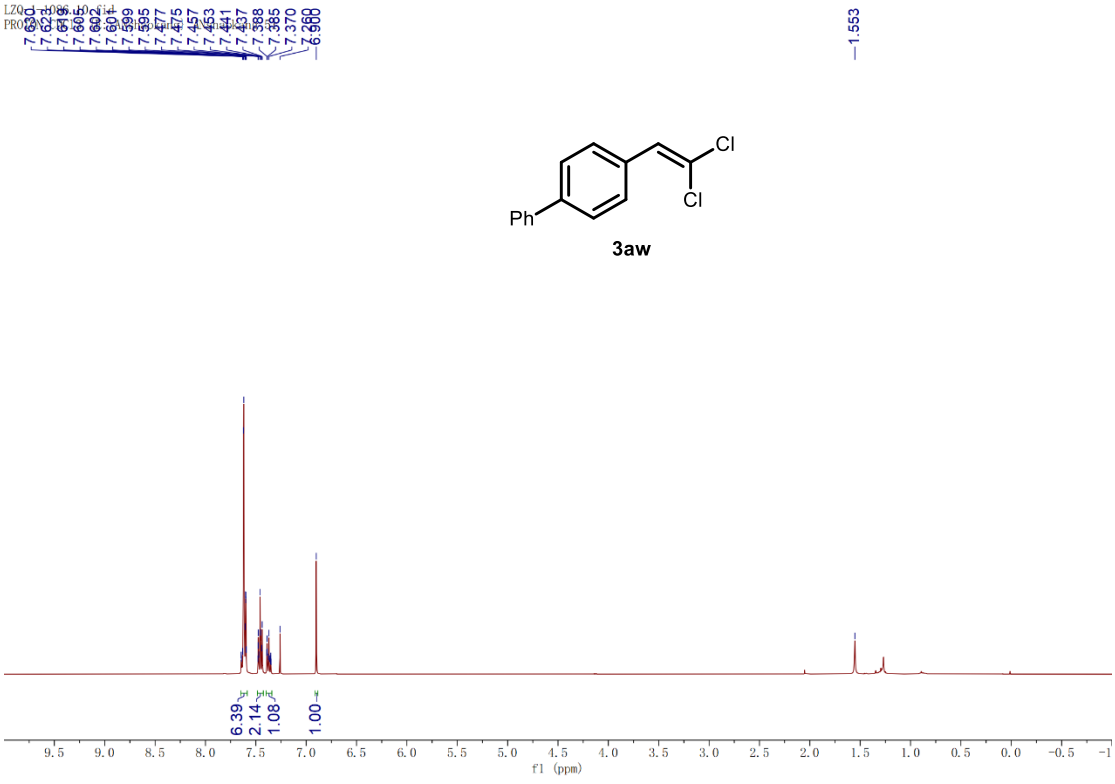

Figure S106. ^{1}H NMR of **3aw** (cis, $CDCl_3$, 400 MHz).

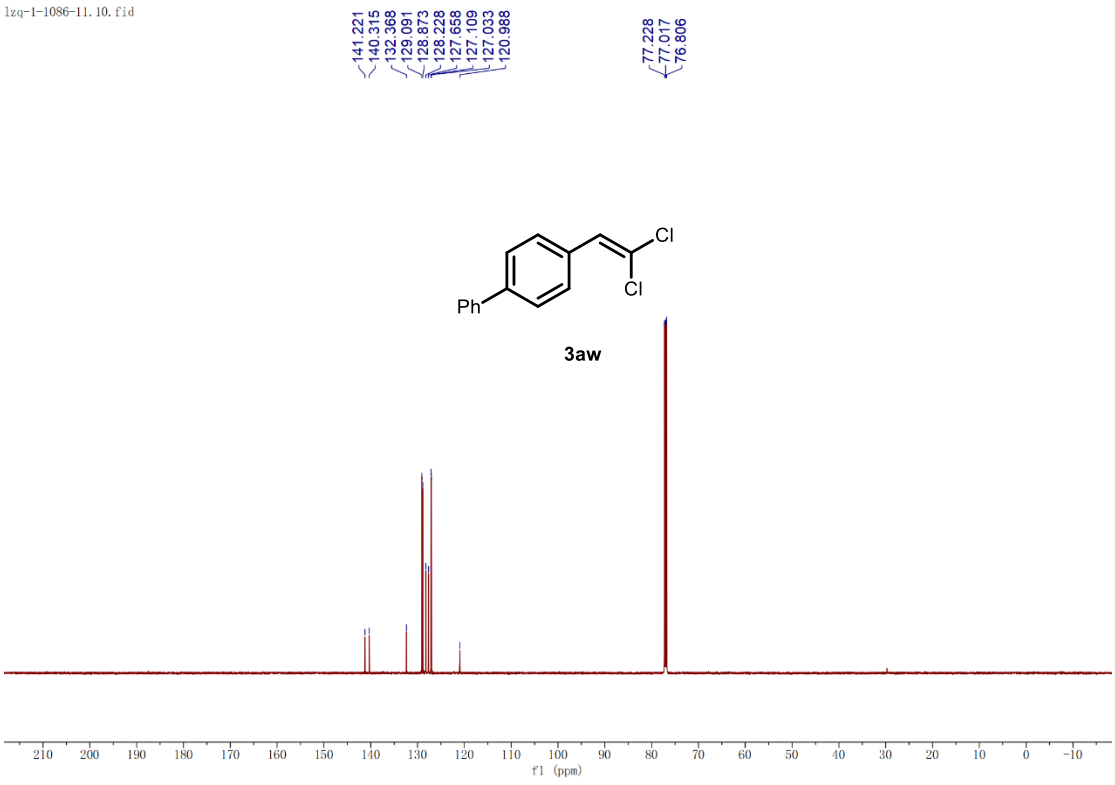

Figure S107. ^{13}C NMR of **3aw** ($CDCl_3$, 151 MHz).

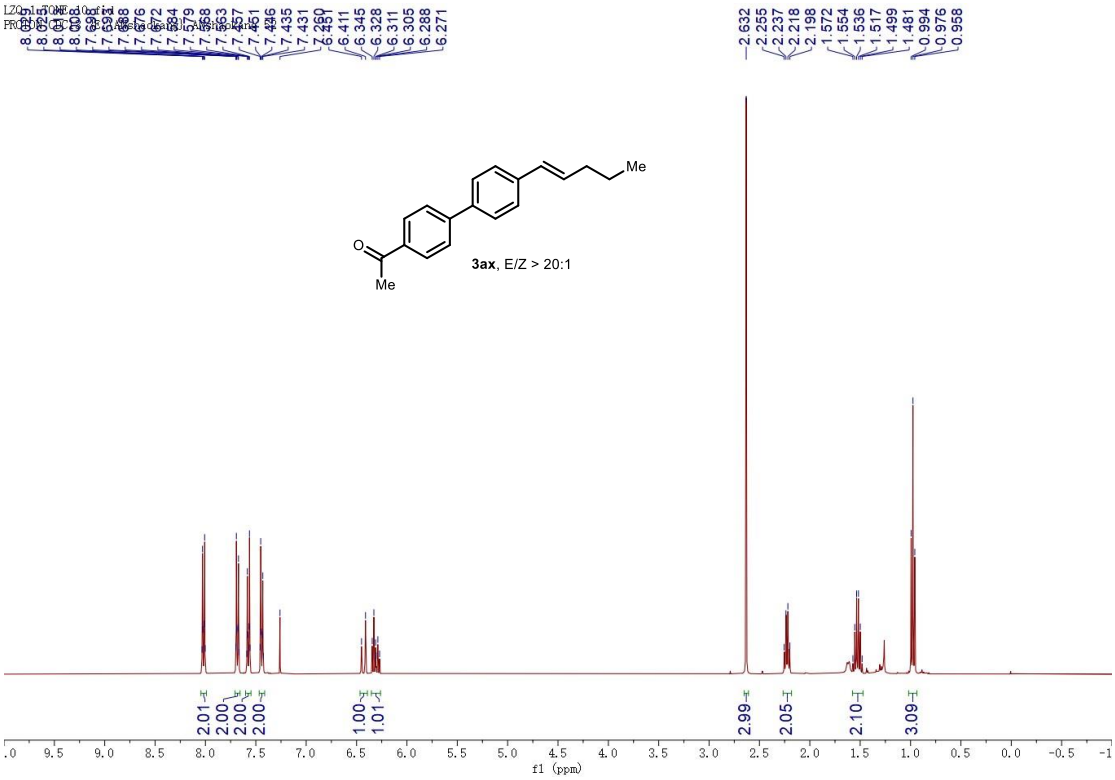

Figure S108. ^{1}H NMR of **3ax** (trans, $CDCl_3$, 400 MHz).

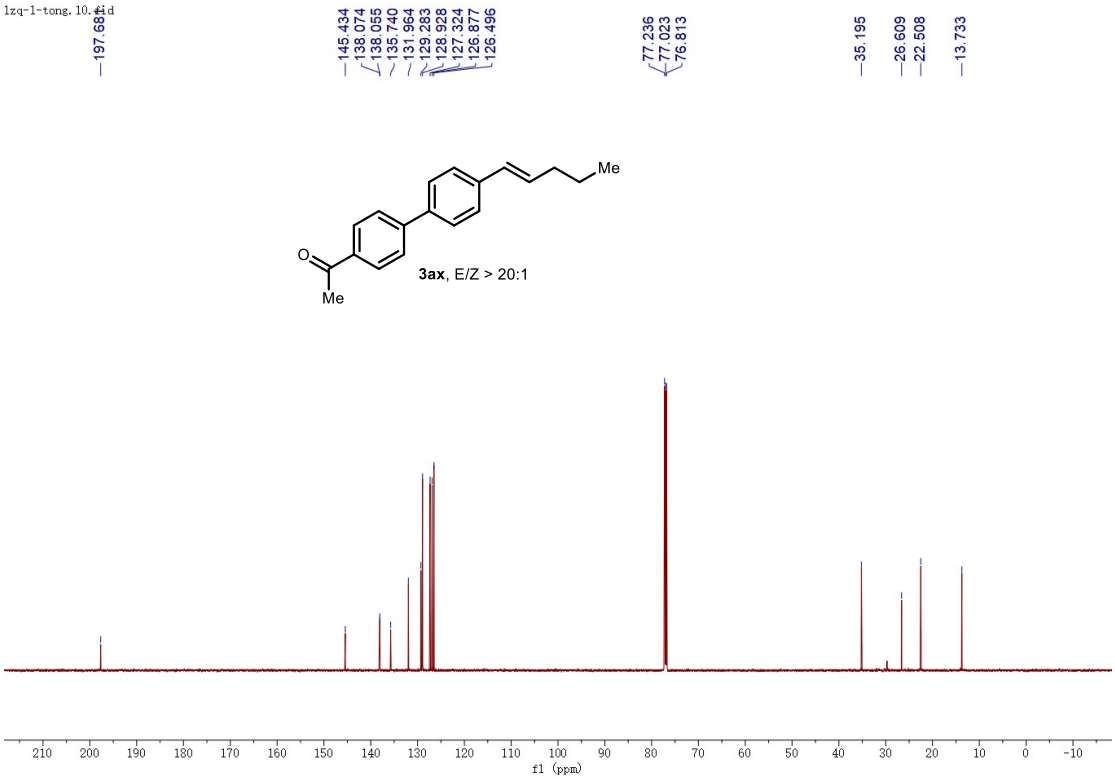

Figure S109. ^{13}C NMR of **3ax** (trans, $CDCl_3$, 151 MHz).

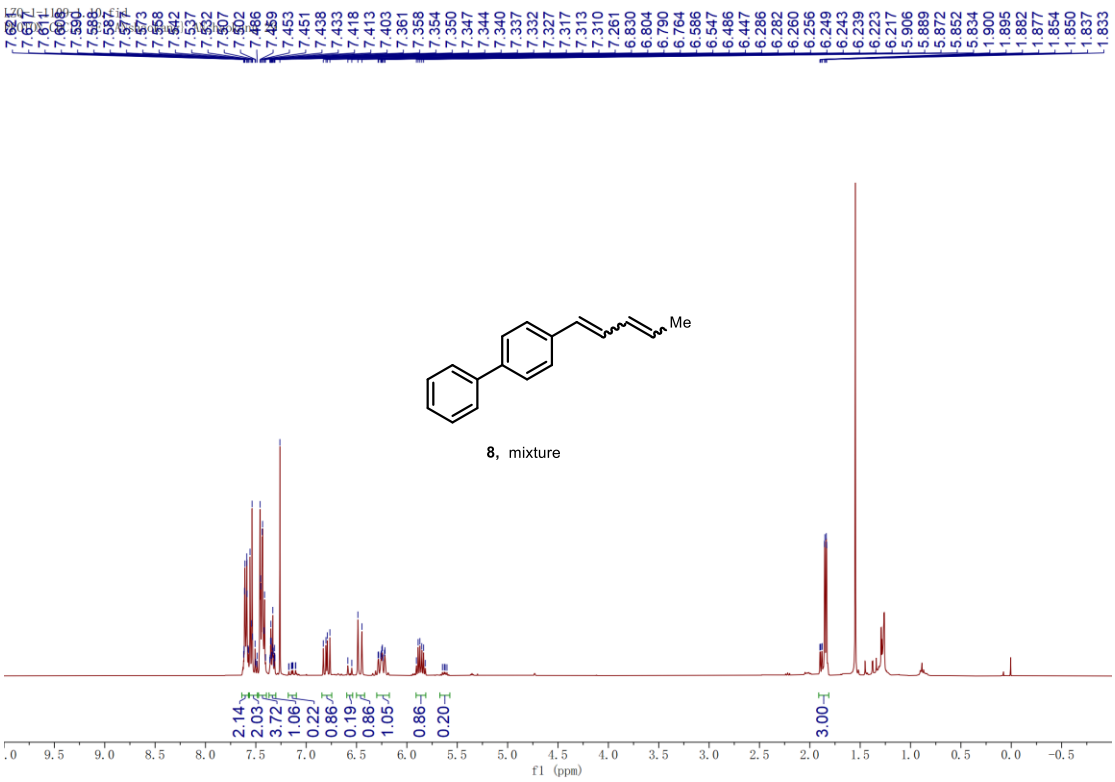

Figure S110. ^{1}H NMR of **8** (trans/cis mixture, $CDCl_3$, 400 MHz).

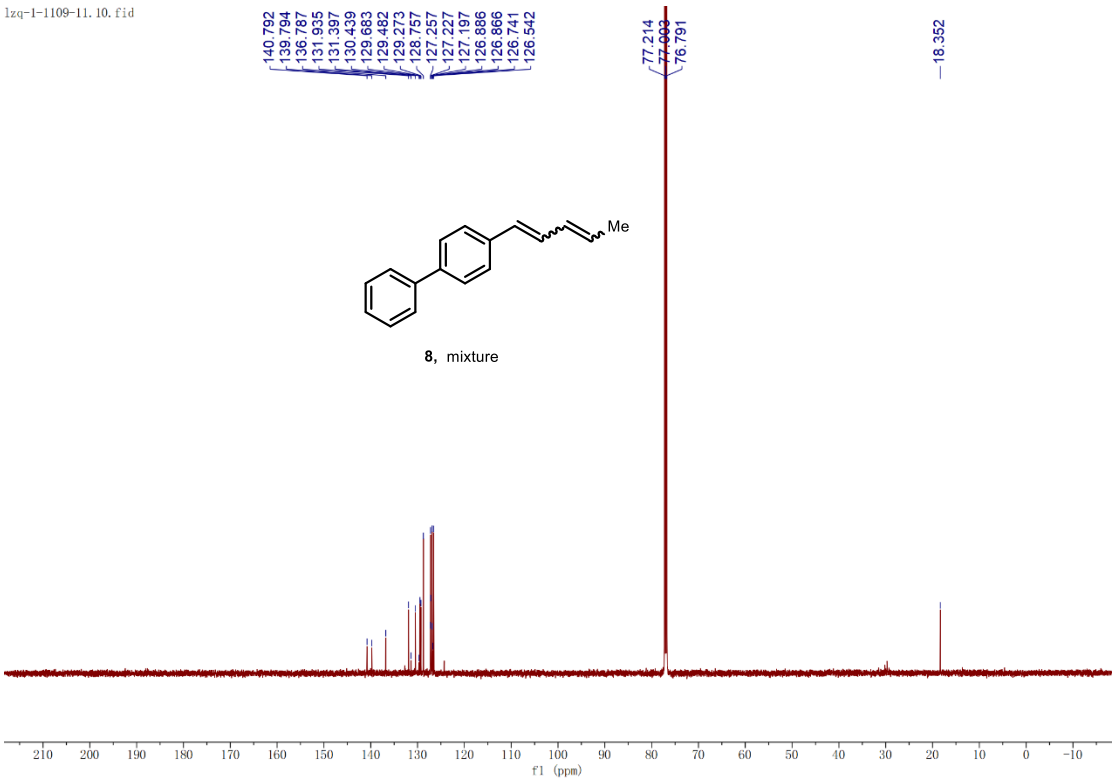

Figure S111. ^{13}C NMR of **8** (trans/cis mixture, $CDCl_3$, 151 MHz).

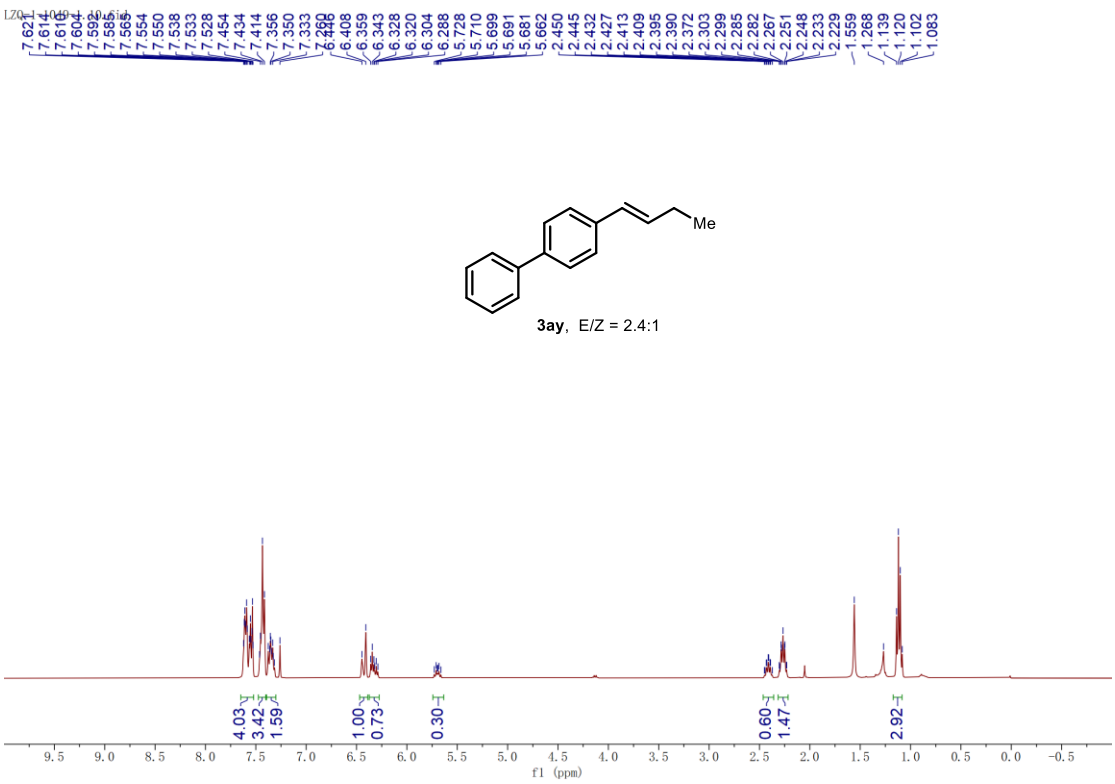

Figure S112. ^{1}H NMR of **3ay** (trans/cis mixture, $CDCl_3$, 400 MHz).

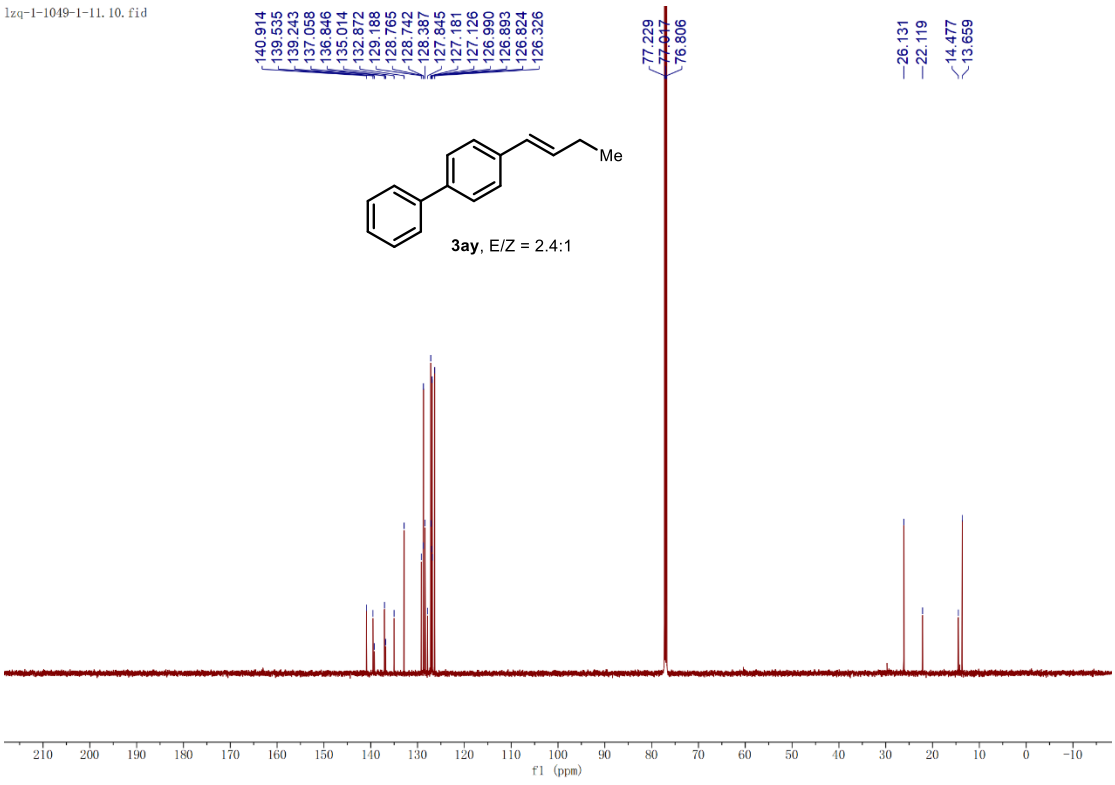

Figure S113. ^{13}C NMR of **3ay** (trans/cis mixture, $CDCl_3$, 101 MHz).

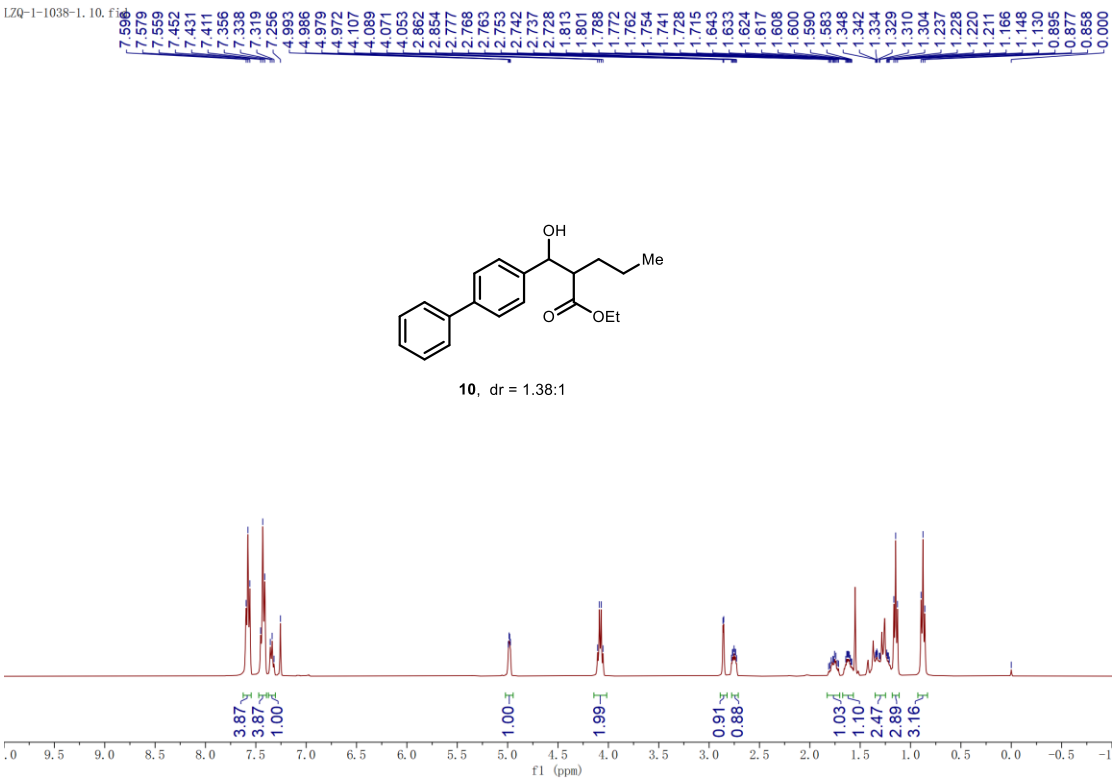

Figure S114. ^{1}H NMR of **10** ($CDCl_3$, 400 MHz).

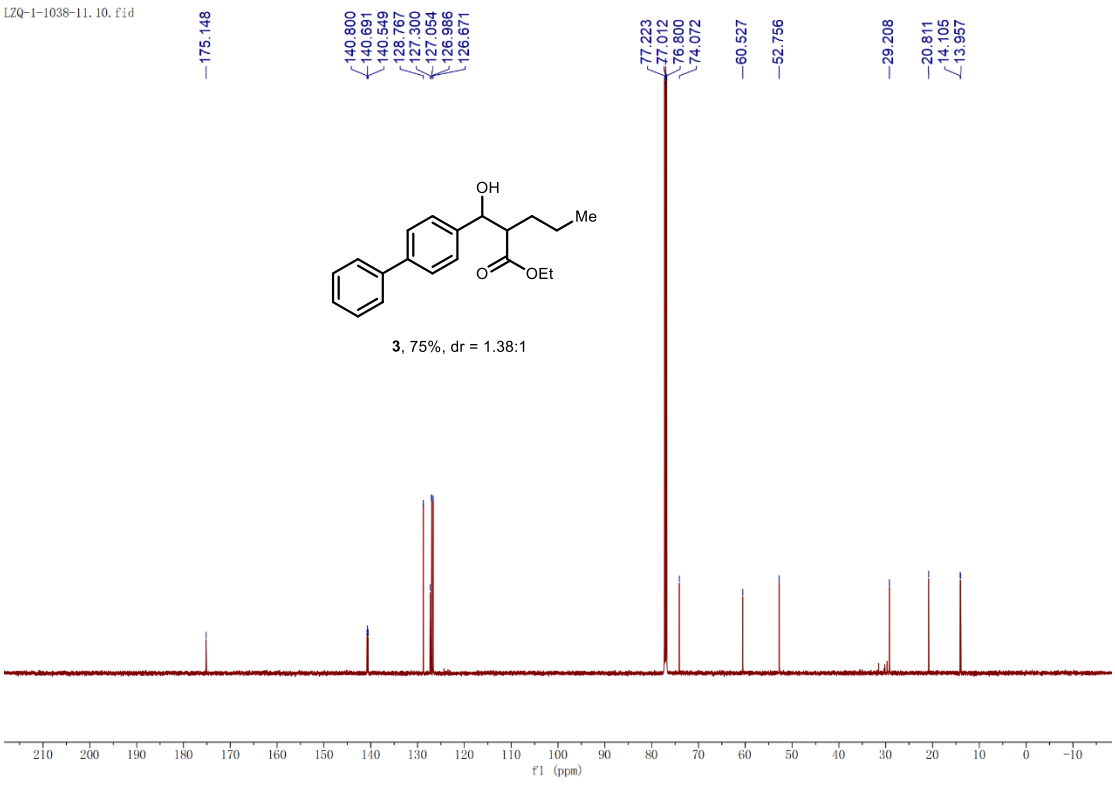

Figure S115. ^{13}C NMR of **10** ($CDCl_3$, 151 MHz).

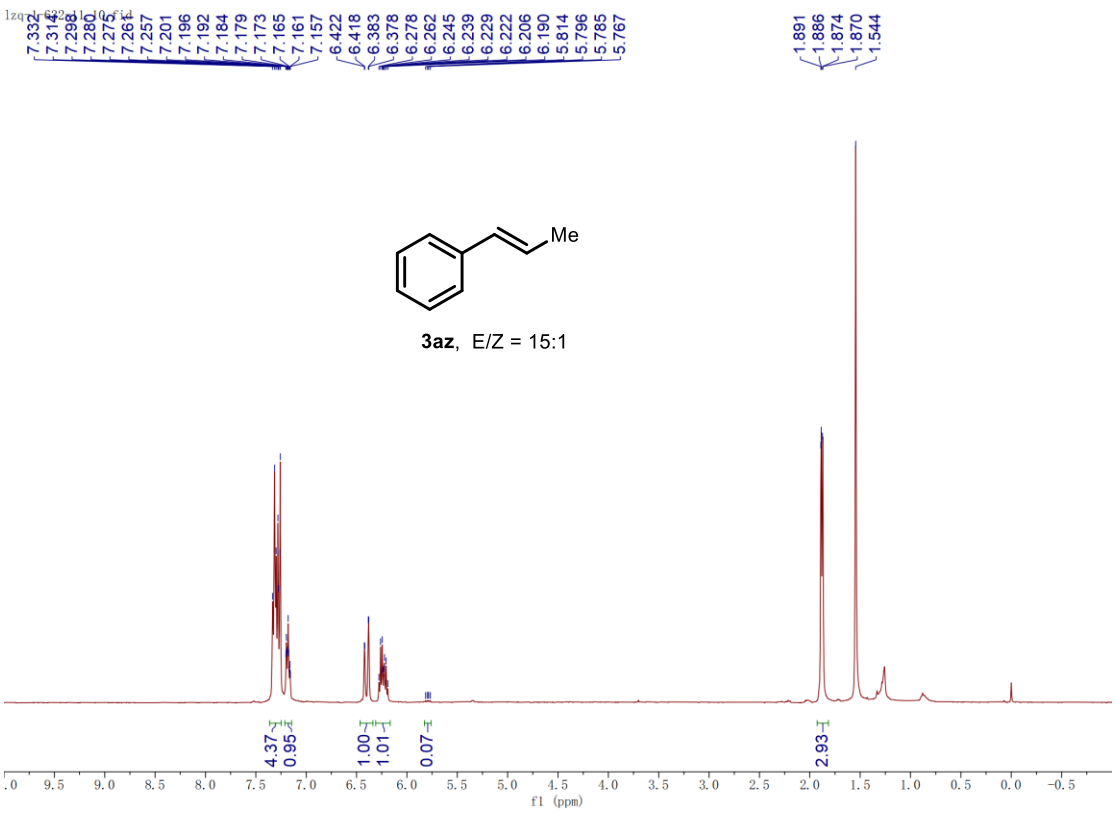

Figure S116. ^{1}H NMR of **3az** (trans/cis mixture, $CDCl_3$, 400 MHz).

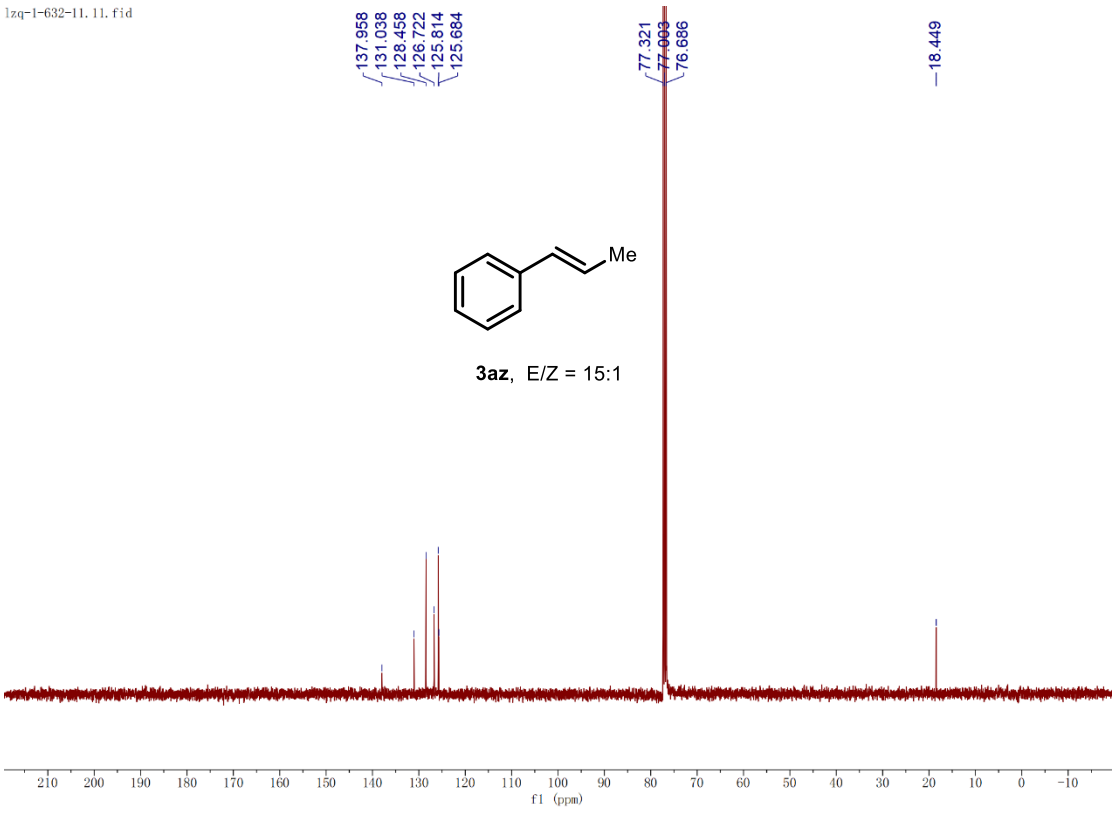

Figure S117. ^{13}C NMR of **3az** (trans/cis mixture, $CDCl_3$, 101 MHz).