Supplementary Information

Native Group-Directed Double Heck Arylation of Internal Alkenes via Selective *β*-H Elimination

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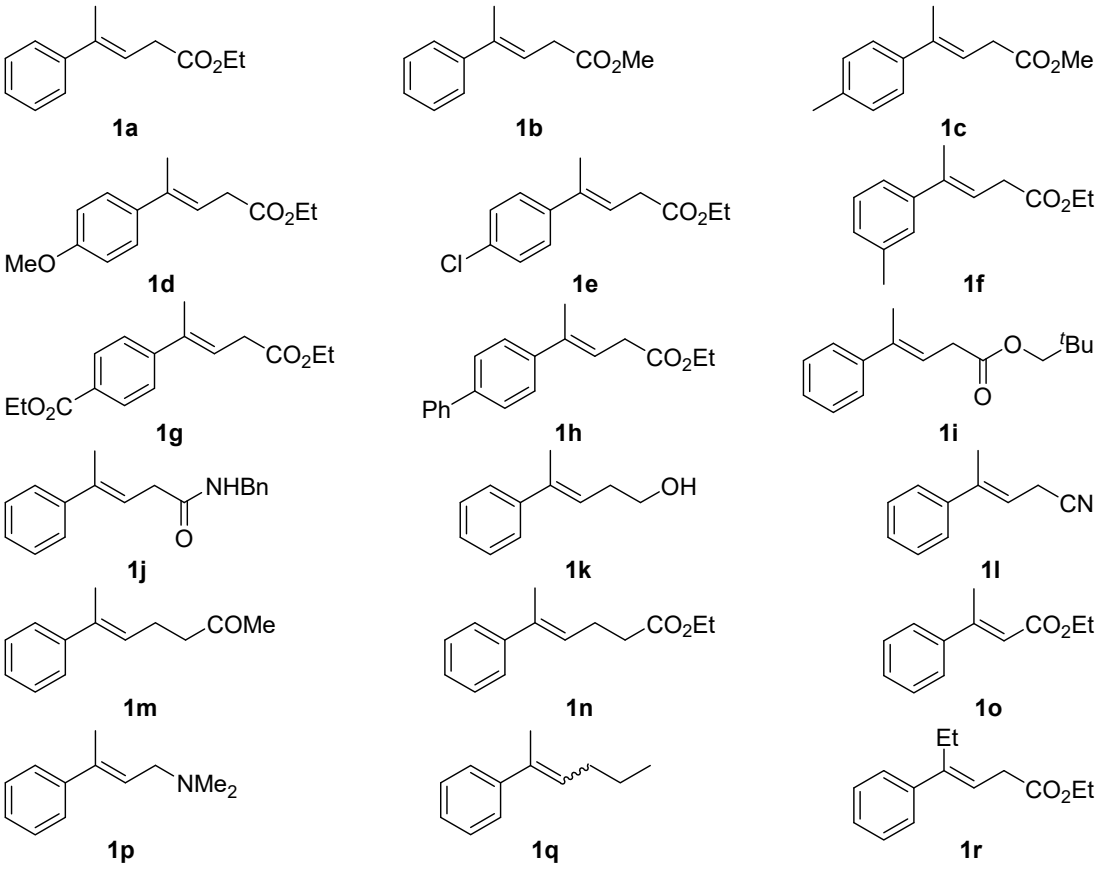
1. General Information

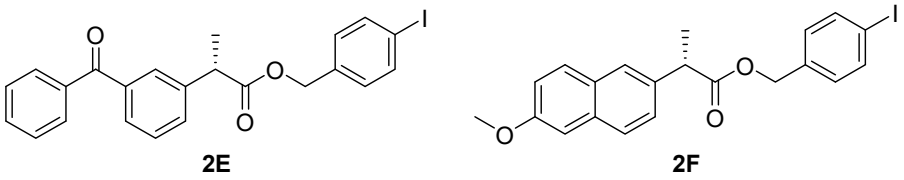
Unless otherwise noted, all reactions were performed in Schlenk tubes under an atmosphere of air with dry solvents, and checked for completion by TLC analysis and plates were visualized with short-wave UV light (254 nm). For reactions that require heating, oil bath or hotplate was used as the heat source. Chemical reagents were purchased from commercial supplies (Accela, Acros Organics, Adamas-beta®, Alfa Aesar, Aladdin, Bidepharmatech, Energy Chemical, TCI Chemicals, Innochem, J&K Chemicals, Laajoo, Leyan, Sigma-Aldrich, Sinocompound, and 3A Chemicals) and used directly without further purification. Flash chromatography was performed with Sepaflash columns produced by Santai Technologies. NMR spectra were recorded at 20 ℃ (293 K) on Bruker-BioSpin AVANCE III HD 400, AVANCE III HD 500, JEOL JNM-ECZ400S and JEOL JNM-ECZ600R NMR spectrometers using $CDCl_3$ as solutions. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. Signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; hept, heptet; m, multiplet. Coupling constants (*J*) are given in hertz (Hz). High-resolution mass spectra were recorded on a Bruker Impact II UHR TOF LC/MS Mass Spectrometry (Operation Mode: ESI Positive Ion Mode or ESI Negative Ion Mode).

2. Synthesis of Starting Materials

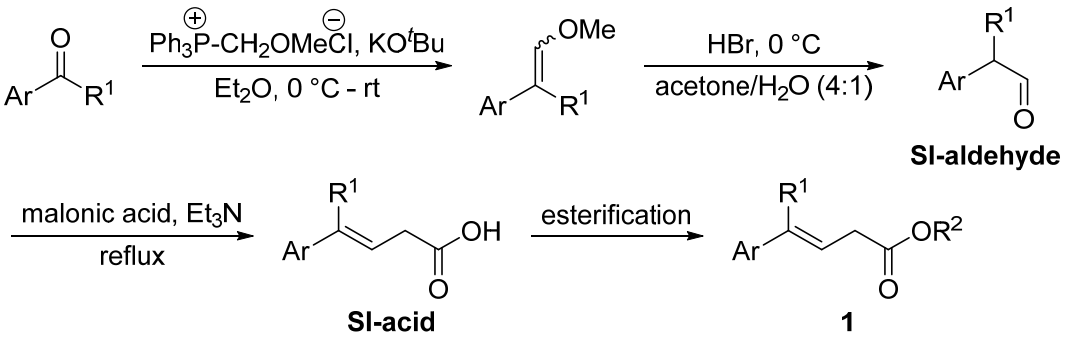
Alkene substrate



Aryl Iodide substrate



Synthesis of **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1n**, **1r**



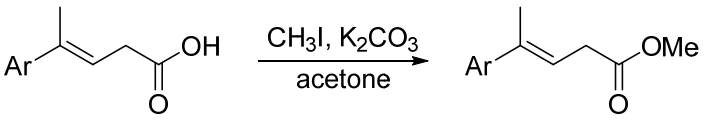
SI-aldehydes were prepared according to known method.[1] In a two-necked round bottom flask, a suspension of (methoxymethyl)triphenyl phosphonium chloride (10.28 g, 30 mmol, 1.5 equiv.) in 100 mL diethyl ether was cooled to 0 °C under nitrogen

atmosphere. With continuous stirring, potassium *tert*-butoxide (4.00 g, 36 mmol, 1.8 equiv.) was added in portions to give a dark red solution. This reaction mixture was allowed to stir at 0 ℃ for 30 minutes, and a solution of the ketone substrate (20 mmol, 1.0 equiv.) in 20 mL diethyl ether was added dropwise through a dropping funnel. After stirring for another 30 minutes at 0 ℃, the mixture was allowed to warm up to ambient temperature, at which it was stirred for another 24 hours. After the completion of the reaction, water was added to quench the reaction and extraction was carried out using ethyl acetate (40 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the enol ether intermediate.

The enol ether was dissolved in a mixed solvent of 20 mL acetone and 5 mL water. The solution was cooled to 0 ℃ with continuous stirring. 2.5 mL of HBr (48%) was added dropwise and the reaction was left to stir at 0 ℃ for another 30 minutes before it was allowed to warm up to ambient temperature. After which the reaction mixture was left to stir for another 24 hours. The reaction was quenched carefully with the addition of saturated aqueous solution of sodium bicarbonate. After removal of acetone under reduced pressure, the aqueous phase was extracted with CH_2Cl_2 (20 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired aldehyde, most of which are known compounds.[2-8]

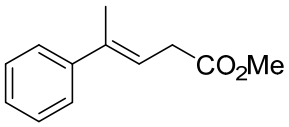
SI-acids were prepared according to known method.[9] A mixture of **SI-aldehyde** (10 mmol, 1.0 equiv.), triethylamine (2.1 mL, 15 mmol, 1.5 equiv.) and malonic acid (1.04 g, 10 mmol, 1.0 equiv.) was refluxed overnight. After cooling to room temperature, diethyl ether (30 mL) was added and the mixture was acidified by the addition of an aqueous 1 M HCl solution (to pH = 1). The aqueous phase was extracted with diethyl ether (30 mL × 2) and the combined organic phases were washed with an aqueous 1 M NaOH solution (to pH = 10). After separation, this aqueous phase was acidified by addition of an aqueous 1 M HCl solution (to pH = 1) and extracted with diethyl ether (30 mL × 2). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired acid, most of which are known compounds.[10,11]

Synthesis of methyl esters **1b**, **1c**



SI-acid **1**

SI-acid (5 mmol, 1.0 equiv.) and K_2CO_3 (2.1 g, 15 mmol, 3.0 equiv.) were placed in a 50 mL round bottom flask. Acetone (10 mL) and iodomethane (0.62 mL, 10 mmol, 2.0 equiv.) were added dropwise, and the mixture was heated at 70 ℃ for 10 hours. After cooling to room temperature, 20 mL water was added and the mixture was extracted with EtOAc (20 mL × 3), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford the desired methyl ester.

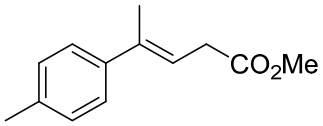


1b

1b,[12] 821 mg, 86% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 1H), 5.95 (t, *J* = 7.0 Hz, 1H), 3.72 (s, 3H), 3.26 (d, *J* = 7.1 Hz, 2H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.48, 143.13, 138.21, 128.33, 127.20, 125.90, 119.27, 52.02, 34.39, 16.30.



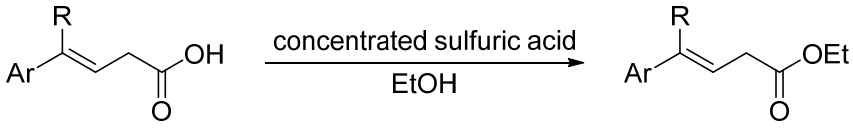
1c

1c,[12] 816 mg, 80% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.91 (t, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 3.24 (d, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 2.03 (s, 3H).

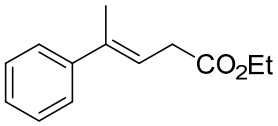
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.57, 140.25, 137.99, 136.90, 129.01, 125.75, 118.43, 51.99, 34.38, 21.14, 16.28.

Synthesis of ethyl esters **1a**, **1d**, **1e**, **1f**, **1g**, **1h**, **1n**, **1r**



SI-acid 1

SI-acid (5 mmol) was dissolved in EtOH (50 mL), and one drop of concentrated H_2SO_4 was added. The solution was refluxed for 3 hours. After cooling at 0 ℃, the mixture was treated with a saturated solution of $NaHCO_3$ and extracted with ether (30 mL × 3). The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA = 98:2) to afford the desired ethyl ester.[13]

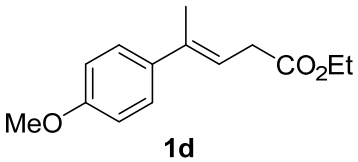


1a

1a, 908 mg, 89% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 5.95 (t, *J* = 7.1 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.23 (d, *J* = 7.1 Hz, 2H), 2.04 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.03, 143.22, 138.10, 128.34, 127.18, 125.92, 119.49, 60.82, 34.65, 16.33, 14.35.

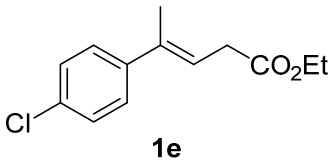


1d

1d, 1.01 g, 86% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.88 (t, *J* = 7.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.23 (d, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.21, 158.90, 137.41, 135.75, 126.95, 117.87, 113.66, 60.80, 55.41, 34.66, 16.36, 14.37.

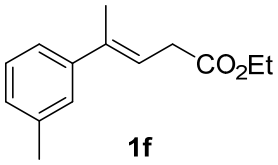


1e

1e, 940 mg, 79% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 5.94 (t, *J* = 7.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.84, 141.56, 136.97, 132.88, 128.40, 127.18, 120.03, 60.88, 34.55, 16.25, 14.33.

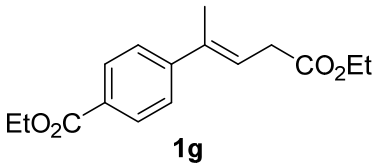


1f

1f, 817 mg, 75% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.17 (m, 3H), 7.09–7.04 (m, 1H), 5.94 (t, *J* = 7.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.04 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.07, 143.23, 138.18, 137.82, 128.21, 127.90, 126.69, 123.02, 119.26, 60.79, 34.63, 21.59, 16.38, 14.34.

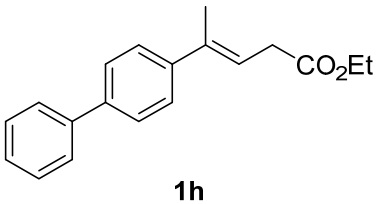


1g

1g, 869 mg, 63% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.07 (t, *J* = 7.1 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.27 (d, *J* = 7.1 Hz, 2H), 2.07 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.70, 166.57, 147.48, 137.33, 129.63, 129.05, 125.74, 121.49, 60.96, 60.91, 34.60, 16.17, 14.43, 14.31.

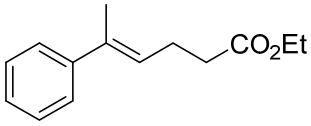


1h

1h, 910 mg, 65% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 5.95 (t, *J* = 7.1 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.19 (d, *J* = 7.1 Hz, 2H), 2.01 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.01, 142.08, 140.86, 139.96, 137.58, 128.87, 127.33, 127.07, 127.03, 126.29, 119.53, 60.86, 34.70, 16.27, 14.36.

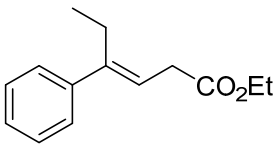


1n

1n, 676 mg, 62% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.27–7.19 (m, 1H), 5.73 (t, *J* = 6.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.60–2.49 (m, 2H), 2.47–2.40 (m, 2H), 2.06 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.37, 143.76, 136.28, 128.31, 126.87, 126.22, 125.81, 60.52, 34.35, 24.47, 15.99, 14.40.



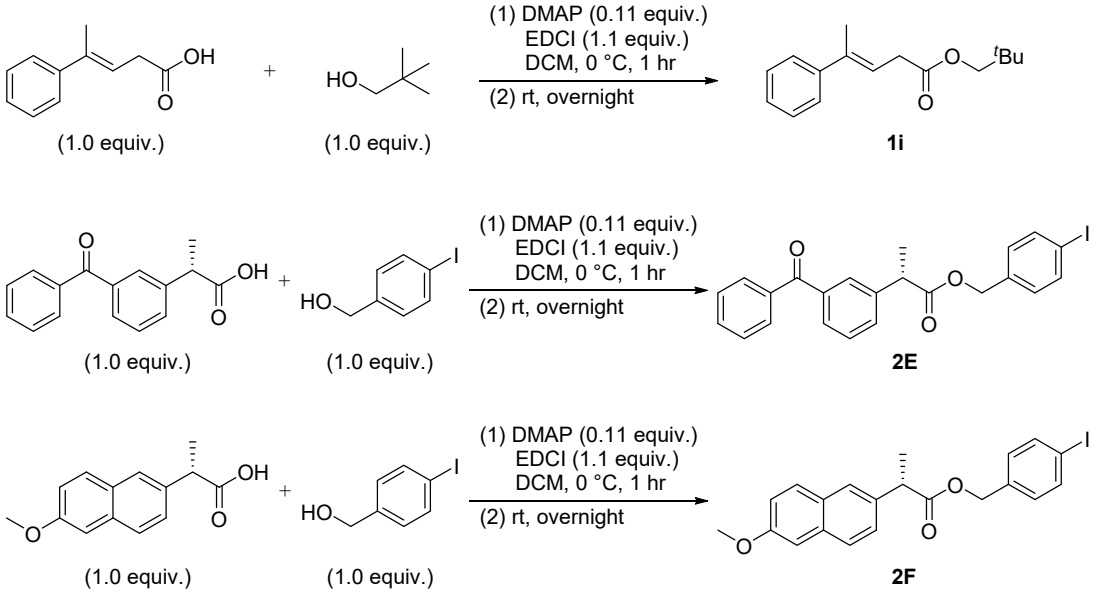
1r

1r, 469 mg, 43% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27–7.23 (m, 1H), 5.82 (t, *J* = 7.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 7.2 Hz, 2H), 2.52 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H).

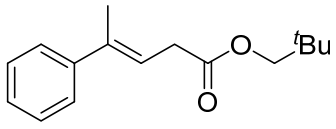
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.12, 144.87, 142.28, 128.34, 127.12, 126.55, 119.04, 60.83, 34.30, 23.42, 14.35, 13.40.

Synthesis of **1i**, **2E**, **2F**



These compounds were prepared according to reported literature procedure.[14,15]

The acid (3.0 mmol, 1.0 equiv.), hydroxyl compound (3.0 mmol, 1.0 equiv.), DMAP (0.33 mmol, 0.11 equiv.) and EDCI (3.3 mmol, 1.1 equiv.) were dissolved in DCM (30 mL) and stirred at 0 ℃ for 1 hour. Then the reaction was allowed to warm up to room temperature and stirred overnight. Upon completion, the reaction mixture was washed with 60 mL H_2O. Then the aqueous layer was separated and extracted with DCM (30 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product.

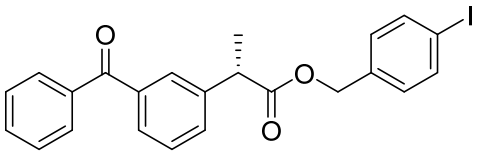


1i

1i, 627 mg, 85% yield, colorless oil, as a *E*/*Z* mixture, *E*/*Z* = 8:1

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.35–7.29 (m, 2H), 7.27–7.23 (m, 1H), 5.96 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 2H), 3.28 (d, *J* = 7.2 Hz, 2H), 2.07 (s, 3H), 0.95 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.11, 143.28, 138.21, 128.35, 127.16, 125.91, 119.50, 74.12, 34.70, 31.47, 26.56, 16.38.

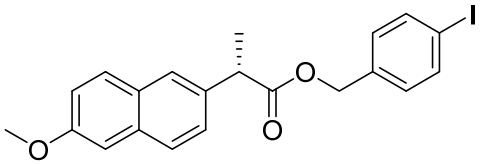


2E

2E, 1.16 g, 82% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.73 (m, 3H), 7.70–7.39 (m, 8H), 6.97 (d, *J* = 8.3 Hz, 2H), 5.04 (s, 2H), 3.84 (q, *J* = 7.2 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.52, 173.80, 140.65, 138.05, 137.72, 137.52, 135.57, 132.69, 131.63, 130.18, 129.91, 129.34, 129.22, 128.72, 128.47, 94.04, 65.99, 45.45, 18.45.



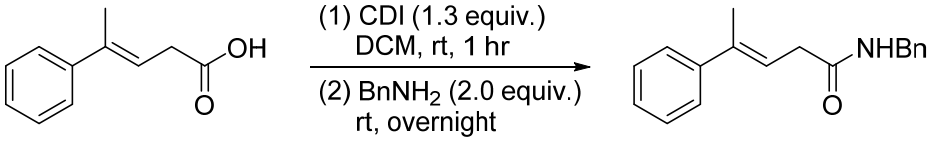
2F

2F, 1.07 g, 80% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (t, *J* = 8.7 Hz, 2H), 7.63–7.56 (m, 3H), 7.37 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.17–7.10 (m, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 5.03 (s, 2H), 3.92 (s, 3H), 3.89 (q, *J* = 7.1 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.45, 157.76, 137.65, 135.73, 135.43, 133.80, 129.89, 129.38, 128.97, 127.29, 126.30, 126.09, 119.18, 105.64, 93.87, 65.83, 55.43, 45.50, 18.54.

Synthesis of amide **1j**

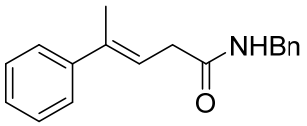


1j

This compound was prepared according to reported literature procedure.[16]

To an oven-dried 250 mL round bottom flask equipped with a magnetic stir-bar was added (*E*)-4-phenylpent-3-enoic acid (1.76 g, 10 mmol) and dry DCM (100 mL) under N_2 atmosphere. 1,1-Carbonyldiimidazole (CDI) (2.11 g, 13 mmol, 1.3 equiv.) was added slowly and the mixture was stirred at room temperature for 1 hour. Then Benzylamine (2.18 mL, 20 mmol, 2.0 equiv.) was added dropwise and the reaction

was stirred overnight. Upon completion, the reaction mixture was poured into a separatory funnel containing DCM and 10% HCl. The organic layers were collected and washed with saturated sodium bicarbonate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford the desired product **1j** (1.33 g, 5 mmol, 50% yield) as a white solid.



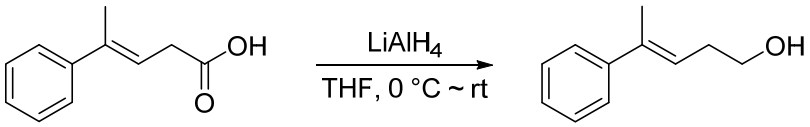
1j

1j, 1.33 g, 50% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.24 (m, 10H), 5.99 (brs, 1H), 5.95 (t, *J* = 7.6 Hz, 1H), 4.46 (d, *J* = 5.8 Hz, 2H), 3.24 (d, *J* = 7.6 Hz, 2H), 2.07 (s, 3H).

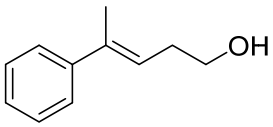
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.82, 142.70, 140.22, 138.29, 128.84, 128.45, 127.77, 127.64, 127.53, 125.85, 119.66, 43.75, 36.81, 16.24.

Synthesis of **1k**



1k

A suspension of $LiAlH_4$ (0.34 g, 8.86 mmol, 2.6 equiv.) in dry THF (5 mL) was added dropwise to a cooled solution of (*E*)-4-phenylpent-3-enoic acid (0.60 g, 3.4 mmol, 1.0 equiv.) in dry THF (5 mL) over 5 min at 0 ℃. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The reaction was quenched with a saturated aqueous solution of Na_2SO_4 and then diluted with EtOAc. The suspension was filtered through a thin pad of Celite, extracted with EtOAc, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 9/1) to afford the desired product.



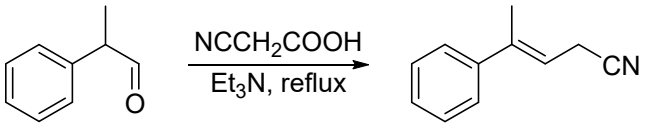
1k

1k, 360 mg, 65% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.22 (m, 5H), 5.78 (t, *J* = 7.2 Hz, 1H), 3.75 (t, *J* = 6.5 Hz, 2H), 2.50 (q, *J* = 6.7 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.61, 137.78, 128.34, 126.96, 125.75, 123.87, 62.44, 32.45, 16.15.

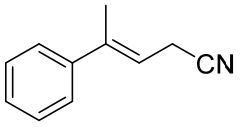
Synthesis of **1l**



1l

This compound was prepared according to reported literature procedure.[16]

A mixture of 2-phenylpropanal (1.3 mL, 10 mmol, 1.0 equiv.), triethylamine (3.5 mL, 25 mmol, 2.5 equiv.) and cyanoacetic acid (1.7 g, 20 mmol, 2.0 equiv.) was refluxed overnight. After cooling to room temperature, the mixture was acidified by the addition of an aqueous 1N HCl solution (pH = 1). The aqueous phase was extracted with diethyl ether three times. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80/1) to afford the desired product.



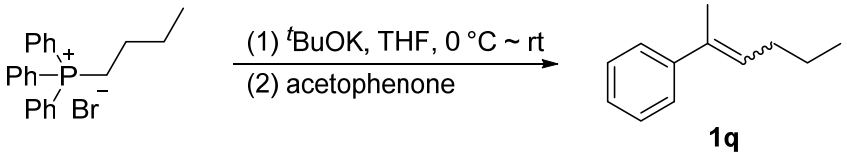
1l

1l, 1.3 g, 83% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.22 (m, 5H), 5.67 (t, *J* = 7.0 Hz, 1H), 3.19 (d, *J* = 7.0 Hz, 2H), 2.05 (s, 3H).

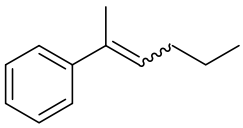
^{13}C NMR (101 MHz, $CDCl_3$): δ 141.88, 141.19, 128.38, 127.74, 125.76, 118.12, 114.56, 16.83, 16.22.

Synthesis of **1q**



1q

n-Butyl(tripheny)phosphonium bromide (4.39 g, 11 mmol, 1.1 equiv.) was suspended in anhydrous Et_2O (15 mL) in an oven-dried flask under N_2. The suspension was vigorously stirred as KO^{t}Bu (1.23 g, 11 mmol, 1.1 equiv.) was added. After stirring at room temperature (25 ℃) for 0.5 hour, the mixture was cooled to 0 ℃, and a solution of freshly distilled acetophenone (1.2 mL, 10 mmol, 1.0 equiv.) in anhydrous Et_2O (10 mL) was added slowly. After stirring for another 15 hours at room temperature (25 ℃), the reaction mixture was cooled to 0 ℃ and quenched with 10 mL water. Then the aqueous phase was separated and extracted with ethyl acetate (15 mL × 3), the combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether) to afford the product (1.04 g, 65% yield) as a *Z*/*E* (*Z*/*E* = 7.5:1) mixture.



1q

1q, 1.04 g, 65% yield, colorless oil.[17]

(*Z*)-**1q**, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.20–7.15 (m, 2H), 5.46 (t, *J* = 7.3 Hz, 1H), 2.02 (s, 3H), 1.94 (q, *J* = 7.4 Hz, 2H), 1.40–1.29 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

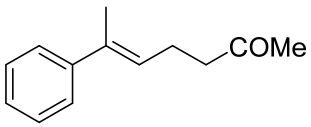
^{13}C NMR (101 MHz, $CDCl_3$): δ 142.45, 136.20, 128.14, 128.13, 127.92, 126.47, 31.33, 25.75, 23.44, 13.95.

(*E*)-**1q**, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40–7.18 (m, 5H), 5.79 (t, *J* = 7.2 Hz, 1H), 2.17 (q, *J* = 7.3 Hz, 2H), 2.03 (s, 3H), 1.53–1.42 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.21, 134.82, 128.73, 128.27, 126.56, 125.74, 31.01, 22.96, 15.92, 14.07.

Synthesis of **1m** & **1p**

The compound **1m** was prepared according to reported literature procedure.[18,19]

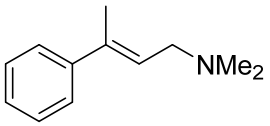


1m

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 5.70 (t, *J* = 7.1 Hz, 1H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.47 (q, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 208.57, 143.73, 136.06, 128.32, 126.85, 126.46, 125.77, 43.48, 30.16, 23.25, 15.95.

The compound **1p** was prepared according to reported literature procedure.[19]



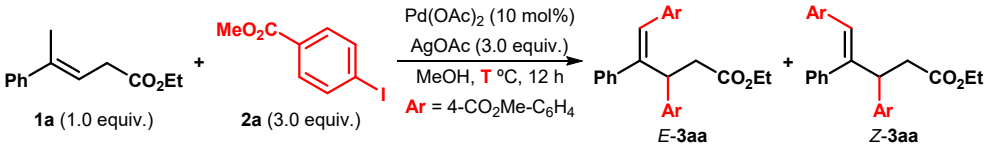
1p

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 5.91 (t, *J* = 6.9 Hz, 1H), 3.25 (d, *J* = 6.9 Hz, 2H), 2.40 (s, 6H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.11, 139.14, 128.40, 127.36, 125.88, 123.25, 57.34, 44.85, 16.38.

3. Optimization of Reaction Conditions

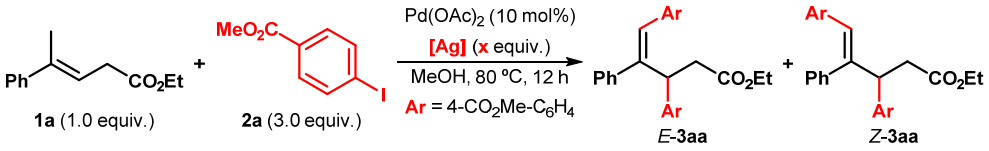
Table S1. Optimization of temperature



Entry	T °C	Yield of **3aa** (*E*+*Z*)
1	room temperature	9%+24%
2	40°C	15%+35%
3	50°C	20%+49%
4	60°C	21%+51%
5	70°C	23%+66%
6	80°C	21%+73%
7	90°C	24%+69%

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), AgOAc (0.6 mmol, 3.0 equiv.), MeOH (2 mL), heated at T °C for 12 hours. Yields (*E*-**3aa** + *Z*-**3aa**) were determined by ^1H NMR analysis of crude reaction mixtures using 1,1,2,2-tetrachloroethane as the internal standard.

Table S2. Optimization of Ag salts

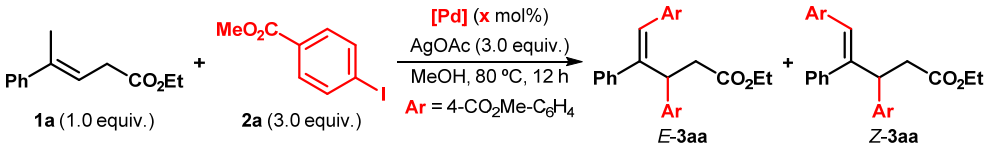


Entry	[Ag]	x equiv.	Yield of **3aa** (*E*+*Z*)
1	AgOAc	1	5%+19%
2	AgOAc	1.5	13%+45%
3	AgOAc	2	15%+54%
4	AgOAc	3	21%+73%
5	Ag_2CO_3	3	15%+50%
6	$AgNO_3$	3	trace
7	Ag_2SO_4	3	trace
8	AgTFA	3	22%+65%

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), $Pd(OAc)_2$ (0.02 mmol,

10 mol%), **Ag** salt (**x** equiv.), MeOH (2 mL), heated at 80 °C for 12 hours. Yields (*E*-**3aa** + *Z*-**3aa**) were determined by ^{1}H NMR analysis of crude reaction mixtures using 1,1,2,2-tetrachloroethane as the internal standard.

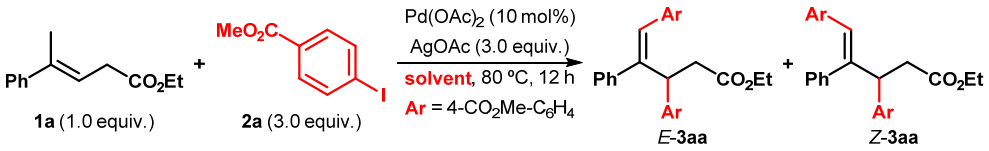
Table S3. Optimization of palladium catalysts



Entry	[Pd]	x mol%	Yield of **3aa** (*E*+*Z*)
1	$Pd(OAc)_2$	10	21%+73%
2	$Pd(OAc)_2$	5	24%+62%
3	$Pd(Ph_3P)_4$	10	trace
4	$Pd(dba)_2$	10	13%+48%
5	$Pd(OPiv)_2$	10	20%+70%
6	$PdCl_2$	10	14%+56%
7	$Pd(acac)_2$	10	9%+31%

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), **Pd** catalyst (**x** mol%), AgOAc (0.6 mmol, 3.0 equiv.), MeOH (2 mL), heated at 80 °C for 12 hours. Yields (*E*-**3aa** + *Z*-**3aa**) were determined by ^{1}H NMR analysis of crude reaction mixtures using 1,1,2,2-tetrachloroethane as the internal standard.

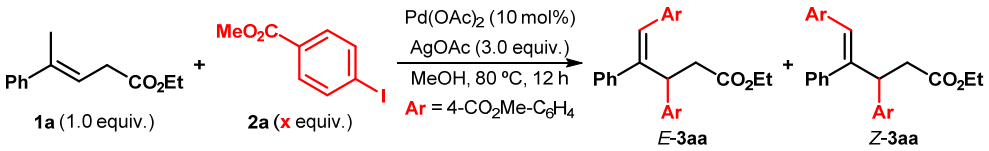
Table S4. Optimization of solvents



Entry	Solvent	Yield of **3aa** (*E*+*Z*)
1	THF	17%+29%
2	DCM	19%+29%
3	DCE	16%+29%
4	HFIP	13%+17%
5	EtOH	23%+50%
6	MeCN	trace
7	NMA	trace

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), AgOAc (0.6 mmol, 3.0 equiv.), **solvent** (2 mL), heated at 80 °C for 12 hours. Yields (*E*-**3aa** + *Z*-**3aa**) were determined by ^1H NMR analysis of crude reaction mixtures using 1,1,2,2-tetrachloroethane as the internal standard.

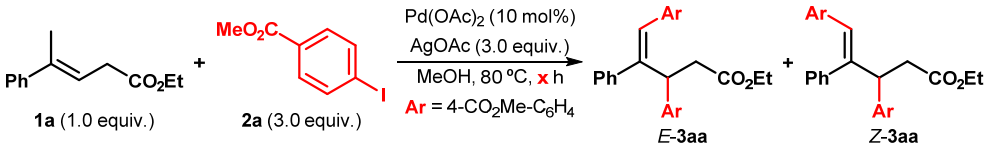
Table S5. Optimization of substrate equivalent



Entry	**2a** (**x** equiv.)	Yield of **3aa** (*E*+*Z*)
1	2	17%+62%
2	4	20%+71%

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (**x** equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), AgOAc (0.6 mmol, 3.0 equiv.), MeOH (2 mL), heated at 80 °C for 12 hours. Yields (*E*-**3aa** + *Z*-**3aa**) were determined by ^1H NMR analysis of crude reaction mixtures using 1,1,2,2-tetrachloroethane as the internal standard.

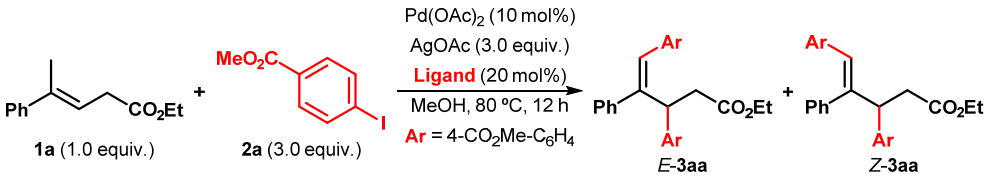
Table S6. Optimization of reaction time



Entry	**x** hrs	Yield of **3aa** (*E*+*Z*)
1	0.5	16%+39%
2	1	21%+50%
3	2	21%+56%
4	4	21%+58%
5	8	21%+60%
6	12	21%+73%

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), AgOAc (0.6 mmol, 3.0 equiv.), MeOH (2 mL), heated at 80 °C for **x** hours. Yields (*E*-**3aa** + *Z*-**3aa**) were determined by ^1H NMR analysis of crude reaction mixtures using 1,1,2,2-tetrachloroethane as the internal standard.

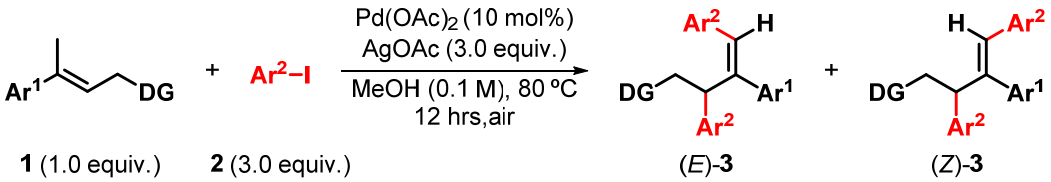
Table S7. Optimization of ligands



Entry	Ligand	Yield of **3aa** (*E*+*Z*)
1	None	21%+73%
2	Fmoc-L-phenylglycine	5%+9%
3	*N*-(*tert*-Butoxycarbonyl)-L-phenylalanine	26%+63%
4	*N*-Acetyl-L-phenylalanine	27%+63%
5	*N*-Carbobenzyloxy-L-alanine	25%+59%
6	*N*-Acetyl-D-alanine	26%+59%
7	(*S*)-(–)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl	11%+20%
8	Bis (2-diphenylphosphinophenyl)ether	None
9	Trimethylphosphine	29%+59%
10	1,2-Bis(diphenylphosphino)benzene	None
11	Tri(2-furyl)phosphine	None

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), AgOAc (0.6 mmol, 3.0 equiv.), MeOH (2 mL), **Ligand** (0.04 mmol, 20 mol%), heated at 80 °C for 12 hours. Yields (*E*-**3aa** + *Z*-**3aa**) were determined by ^{1}H NMR analysis of crude reaction mixtures using 1,1,2,2-tetrachloroethane as the internal standard.

4. General Procedure

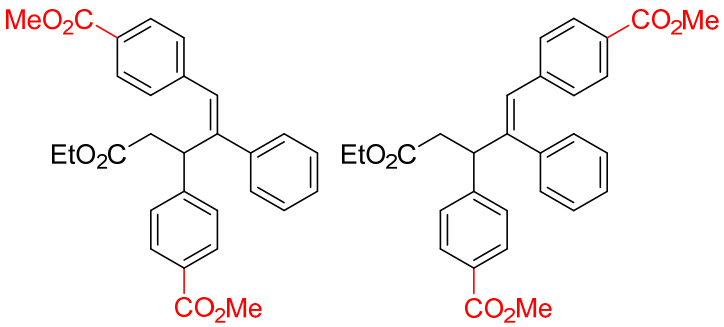


1 (1.0 equiv.) **2** (3.0 equiv.) (*E*)-**3** (*Z*)-**3**

General Procedure A: To an oven-dried 35 mL Schlenk tube (equipped with a magnetic stir bar), aryl iodide **2** (0.6 mmol, 3 equiv.), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 10 mol%) and AgOAc (100 mg, 0.6 mmol, 3 equiv.) were added, followed by addition of MeOH (2 mL) and alkene **1** (0.2 mmol). The tube was sealed with a screw cap, and the reaction mixture was warmed and stirred vigorously at 80 ℃. After the reaction was complete (approximately 12 hours), the resulting solution was filtered through a short pad made from a 1:1 mixture of celite and silica gel (2.5 cm in diameter, 5 cm in length), which was then washed with ethyl acetate (15 mL). The combined organic solutions were concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (1.5 cm in diameter, 15 cm in length, eluent: ethyl acetate / petroleum ether) to yield the desired product **3**.

5. Characterization of Products

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 9:1), the product **3aa** was obtained in 96% yield, *E*/*Z* = 1:3.5 (91 mg, colorless oil).



E-**3aa** *Z*-**3aa**

Dimethyl 4,4'-(5-ethoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3aa**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.26–7.19 (m, 3H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 5.08 (t, *J* = 7.7 Hz, 1H), 4.07–4.00 (m, 2H), 3.93 (s, 3H), 3.89 (s, 3H), 2.93 (dd, *J* = 15.7, 7.3 Hz,1H), 2.79 (dd, *J* = 15.8, 8.2 Hz, 1H), 1.14 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.62, 166.96, 146.58, 144.98, 142.04, 140.56, 130.28, 129.97, 128.89, 128.84, 128.65, 128.11, 128.03, 127.61, 127.33, 60.76, 52.32, 52.22, 41.29, 37.17, 14.17.

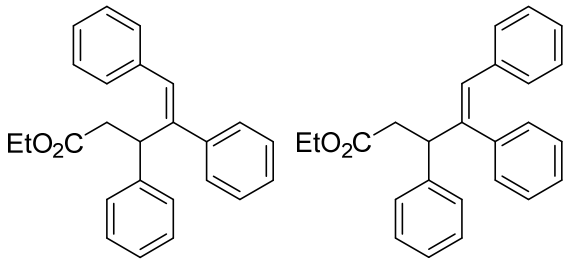
HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{29}O_6$ $[M+H]^+$: 473.1959, found: 473.1961.

Dimethyl 4,4'-(5-ethoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3aa**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.25–7.19 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.87–6.84 (m, 2H), 6.59 (s, 1H),4.42 (t, *J* = 7.9 Hz, 1H), 4.12–4.05 (m, 2H), 3.89 (s, 3H), 3.83 (s, 3H), 3.00 (dd, *J* = 15.6, 7.9 Hz, 1H), 2.85 (dd, *J* = 15.7, 8.1 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.55, 166.99, 166.88, 146.30, 146.27, 141.39, 139.15, 130.95, 129.82, 129.22, 129.08, 128.97, 128.69, 128.32, 127.67, 127.05, 60.76, 52.17, 52.05, 50.91, 38.63, 14.27.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ab** was obtained in 91% yield, *E*/*Z* = 1:3.6 (64.8 mg, colorless oil).



E-**3ab** *Z*-**3ab**

Ethyl (*E*)-3,4,5-triphenylpent-4-enoate (*E*-**3ab**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.29–7.17 (m, 7H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 7.0 Hz, 2H), 6.73 (s, 1H), 5.11 (t, *J* = 7.7 Hz, 1H), 4.05–3.98 (m, 2H), 2.90 (dd, *J* = 15.4, 7.2 Hz, 1H), 2.74 (dd, *J* = 15.4, 8.2 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): 172.15, 143.97, 141.58, 141.42, 137.52, 131.45, 128.90, 128.85, 128.58, 128.46, 127.84, 127.60, 127.23, 127.10, 126.57, 60.55, 40.94, 37.47, 14.17.

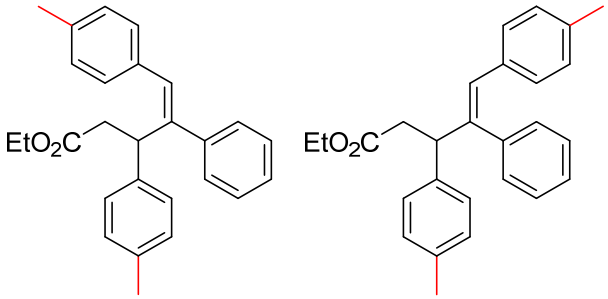
HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{25}O_2$ $[M+H]^+$: 357.1849, found: 357.1850.

Ethyl (*Z*)-3,4,5-triphenylpent-4-enoate (*Z*-**3ab**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27–7.17 (m, 8H), 7.07–7.02(m, 3H), 6.91–6.82 (m, 4H), 6.56 (s, 1H), 4.32 (t, *J* = 8.0 Hz, 1H), 4.11–4.05 (m, 2H), 2.96 (dd, *J* = 15.4, 8.3 Hz, 1H), 2.82 (dd, *J* = 15.4, 7.7 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.05, 144.37, 141.28, 140.14, 136.92, 129.23, 129.21, 128.43, 128.42, 128.28, 127.93, 127.38, 127.14, 126.83, 126.63, 60.57, 50.97, 39.15, 14.32.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ac** was obtained in 92% yield, *E*/*Z* = 1:3.8 (70.7 mg, colorless oil).



E-**3ac** *Z*-**3ac**

Ethyl (*E*)-4-phenyl-3,5-di-*p*-tolylpent-4-enoate (*E*-**3ac**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.9 Hz, 2H), 7.24–7.03 (m, 9H), 7.01 (d, *J* = 7.1 Hz, 2H), 6.69 (s, 1H), 5.07 (t, *J* = 7.7 Hz, 1H), 4.05–3.99 (m, 2H), 2.88 (dd, *J* = 15.4, 7.2 Hz, 1H), 2.70 (dd, *J* = 15.4, 8.3 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.30, 143.46, 141.68, 138.63, 136.72, 136.01, 134.66, 131.33, 129.18, 128.82, 127.81, 127.45, 60.50, 40.52, 37.60, 21.34, 21.12, 14.19.

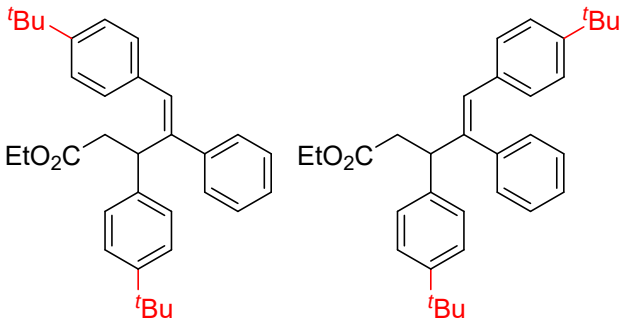
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{29}O_2$ $[M+H]^+$: 385.2162, found: 385.2164.

Ethyl (*Z*)-4-phenyl-3,5-di-*p*-tolylpent-4-enoate (*Z*-**3ac**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.18 (m, 3H), 7.10–7.04 (m, 4H), 6.91–6.87 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.51 (s, 1H), 4.26 (t, *J* = 8.0 Hz, 1H), 4.12–4.04 (m, 2H), 2.93 (dd, *J* = 15.4, 8.4 Hz, 1H), 2.78 (dd, *J* = 15.4, 7.7 Hz, 1H), 2.30 (s, 3H), 2.20 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.20, 143.59, 140.48, 138.36, 136.31, 136.25, 134.12, 129.28, 129.11, 128.67, 128.42, 128.12, 127.10, 127.02, 60.53, 50.57, 39.29, 21.18, 14.34.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ad** was obtained in 79% yield, *E*/*Z* = 1:3 (74.0 mg, colorless oil).



E-**3ad** *Z*-**3ad**

Ethyl (*E*)-3,5-bis(4-(*tert*-butyl)phenyl)-4-phenylpent-4-enoate (*E*-**3ad**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.22–7.15 (m, 5H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.74 (s, 1H), 5.14 (t, *J* = 7.6 Hz, 1H), 4.05–3.99 (m, 2H), 2.90 (dd, *J* = 15.3, 7.0 Hz, 1H), 2.70 (dd, *J* = 15.3, 8.3 Hz, 1H), 1.33 (s, 9H), 1.30 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.42, 149.88, 149.29, 143.33, 141.76, 138.64, 134.65, 131.39, 128.73, 128.66, 128.36, 127.91, 125.47, 125.41, 40.30, 39.12, 34.65, 31.28, 14.32.

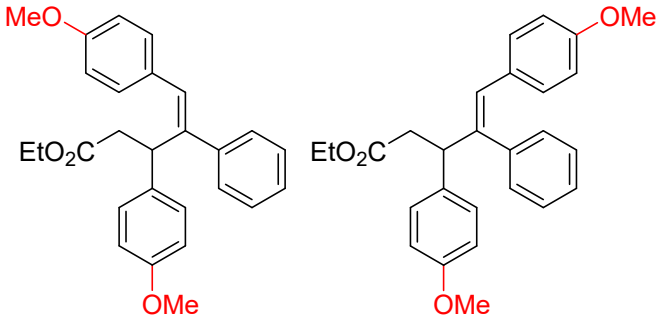
HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{40}NaO_2$ $[M+Na]^+$: 491.2921, found: 491.2919.

Ethyl (*Z*)-3,5-bis(4-(*tert*-butyl)phenyl)-4-phenylpent-4-enoate (*Z*-**3ad**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.22–7.19 (m, 3H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.91–6.87 (m, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 6.52 (s, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.93 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.79 (dd, *J* = 15.4, 7.3 Hz, 1H), 1.29 (s, 9H), 1.21 (s, 9H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.23, 149.58, 149.54, 143.59, 140.54, 138.32, 134.07, 129.27, 128.88, 128.44, 127.84, 127.16, 127.04, 125.22, 124.92, 60.51, 50.64, 39.15, 34.50, 31.50, 31.31, 14.34.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ae** was obtained in 71% yield, *E*/*Z* = 1:4 (59.0 mg, colorless oil).



E-**3ae** *Z*-**3ae**

Ethyl (*E*)-3,5-bis(4-methoxyphenyl)-4-phenylpent-4-enoate (*E*-**3ae**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.26–7.18 (m, 3H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.64 (s, 1H), 5.06 (t, *J* = 7.7 Hz, 1H), 4.05–3.99 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 2.86 (dd, *J* = 15.4, 7.3 Hz, 1H), 2.70 (dd, *J* = 15.3, 8.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.34, 158.64, 158.21, 143.05, 141.76, 133.73, 130.78, 130.05, 129.61, 128.83, 128.59, 127.82, 127.08, 113.98, 113.82, 60.53, 55.37, 55.31, 40.12, 37.72, 14.21.

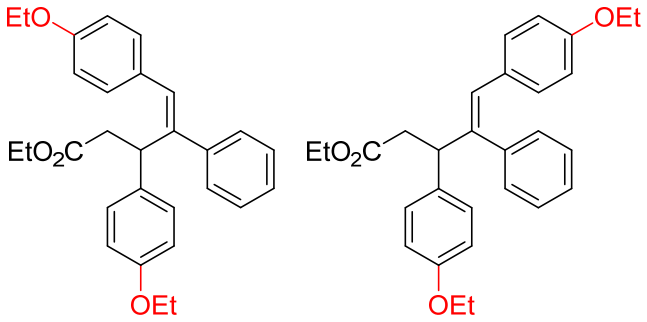
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{28}NaO_4$ $[M+Na]^+$: 439.1880, found: 439.1882.

Ethyl (*Z*)-3,5-bis(4-methoxyphenyl)-4-phenylpent-4-enoate (*Z*-**3ae**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.18 (m, 3H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.87 (dd, *J* = 6.2, 2.8 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.7 Hz, 2H), 6.46 (s, 1H), 4.23 (t, *J* = 8.0 Hz, 1H), 4.12–4.04 (m, 2H), 3.77 (s, 3H), 3.69 (s, 3H), 2.91 (dd, *J* = 15.3, 8.2 Hz, 1H), 2.76 (dd, *J* = 15.3, 7.9 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.23, 158.36, 158.24, 142.62, 140.43, 133.53, 130.36, 130.16, 129.36, 129.24, 128.49, 127.02, 126.48, 113.72, 113.37, 60.53, 55.29, 55.21, 50.24, 39.32, 14.35.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3af** was obtained in 63% yield, *E*/*Z* = 1:4.2 (56.0 mg, colorless oil).



E-**3af** *Z*-**3af**

Ethyl (*E*)-3,5-bis(3-ethoxyphenyl)-4-phenylpent-4-enoate (*E*-**3af**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.23–7.15 (m, 3H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.00–6.96 (m, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.63 (s, 1H), 5.06 (t, *J* = 7.7 Hz, 1H), 4.11–3.95 (m, 6H), 2.86 (dd, *J* = 15.4, 7.3 Hz, 1H), 2.69 (dd, *J* = 15.4, 8.1 Hz, 1H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.32, 158.01, 157.56, 142.96, 141.80, 133.58, 130.80, 130.14, 129.89, 128.83, 128.56, 127.78, 127.03, 114.49, 114.34, 63.48, 63.42, 40.10, 37.71, 14.98, 14.21.

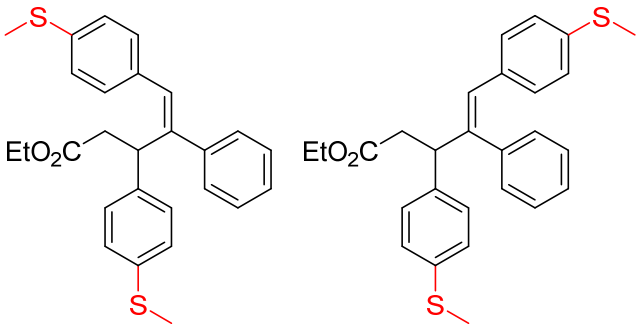
HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{32}NaO_4$ $[M+Na]^+$: 467.2193, found: 467.2192.

Ethyl (*Z*)-3,5-bis(3-ethoxyphenyl)-4-phenylpent-4-enoate (*Z*-**3af**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.18 (m, 3H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.90–6.84 (m, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.46 (s, 1H), 4.22 (t, *J* = 8.0 Hz, 1H), 4.12–4.03 (m, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 3.91 (q, *J* = 7.0 Hz, 2H), 2.90 (dd, *J* = 15.3, 8.1 Hz, 1H), 2.76 (dd, *J* = 15.3, 7.9 Hz, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.28, 157.74, 157.62, 142.53, 140.47, 133.41, 130.36, 129.48, 129.38, 129.24, 128.48, 126.99, 126.52, 114.26, 113.91, 63.43, 63.35, 60.54, 50.26, 39.33, 15.01, 14.92, 14.36.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 8:1), the product **3ag** was obtained in 42% yield, *E*/*Z* = 1:3 (37.8 mg, colorless oil).



Ethyl (*E*)-3,5-bis(4-(methylthio)phenyl)-4-phenylpent-4-enoate (*E*-**3ag**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.24–7.19 (m, 3H), 7.17–7.13 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.66 (s, 1H), 5.04 (t, *J* = 7.6 Hz, 1H), 4.06–4.01 (m, 2H), 2.87 (dd, *J* = 15.6, 7.3 Hz, 1H), 2.71 (dd, *J* = 15.5, 8.2 Hz, 1H), 2.50 (s, 3H), 2.46 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.13, 143.65, 141.34, 138.45, 137.30, 136.45, 134.21, 130.94, 129.36, 128.08, 127.93, 127.31, 126.66, 126.57, 60.63, 40.49, 37.48, 15.84, 14.23.

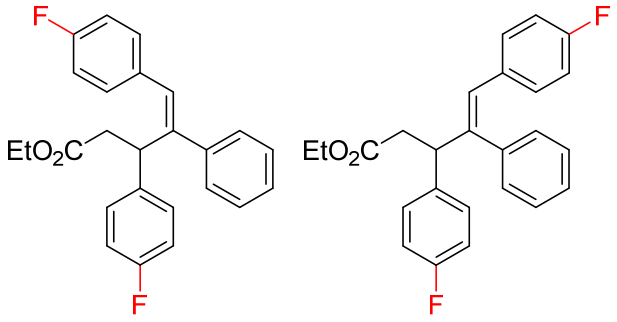
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{28}NaO_2S_2$ $[M+Na]^+$: 471.1423, found: 471.1422.

Ethyl (*Z*)-3,5-bis(4-(methylthio)phenyl)-4-phenylpent-4-enoate (*Z*-**3ag**)

^{1}H NMR (600 MHz, $CDCl_3$): 7.24–7.19 (m, 3H), 7.17–7.13 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.89–6.86 (m, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 6.47 (s, 1H), 4.26 (t, *J* = 8.0 Hz, 1H), 4.11–4.04 (m, 2H), 2.92 (dd, *J* = 15.5, 8.1 Hz, 1H), 2.77 (dd, *J* = 15.4, 7.9 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.99, 143.86, 140.04, 138.19, 136.76, 136.62, 133.67, 129.57, 129.20, 128.76, 128.59, 127.26, 126.78, 126.59, 125.87, 60.63, 50.50, 39.06, 15.93, 15.66, 14.35.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ah** was obtained in 87% yield, *E*/*Z* = 1:2.8 (68.2 mg, colorless oil).



E-**3ah** *Z*-**3ah**

Ethyl (*E*)-3,5-bis(4-fluorophenyl)-4-phenylpent-4-enoate (*E*-**3ah**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.26–7.21 (m, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.08–6.93 (m, 6H), 6.63 (s, 1H), 4.99 (t, *J* = 7.7 Hz, 1H), 4.16–3.96 (m, 2H), 2.86 (dd, *J* = 15.5, 7.4 Hz, 1H), 2.73 (dd, *J* = 15.5, 8.1 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.97, 162.02 (d, *J* = 242.1 Hz), 161.70 (d, *J* = 245.9 Hz), 144.19, 141.04, 137.11 (d, *J* =3.4 Hz), 133.36 (d, *J* = 3.6 Hz), 130.56 (d, *J* = 7.9 Hz), 130.34, 129.09 (d, *J* = 7.9 Hz), 128.84, 127.98, 127.45, 115.61 (d, *J* = 21.2 Hz), 115.33 (d, *J* = 21.2 Hz), 60.71, 40.40, 37.60, 14.24.

^{19}F NMR (376 MHz, $CDCl_3$): δ –114.95, –116.38.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{23}F_2O_2$ $[M+H]^+$: 393.1661, found: 393.1663.

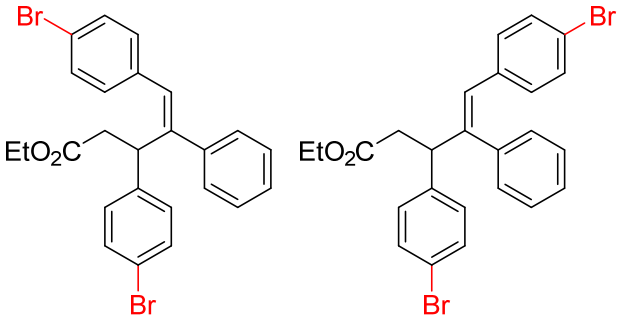
Ethyl (*Z*)-3,5-bis(4-fluorophenyl)-4-phenylpent-4-enoate (*Z*-**3ah**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.18 (m, 3H), 7.13 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.87–6.77 (m, 4H), 6.74 (t, *J* = 8.7 Hz, 2H), 6.49 (s, 1H), 4.29 (t, *J* = 8.0 Hz, 1H), 4.14–4.03 (m, 2H), 2.94 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.78 (dd, *J* = 15.4, 8.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.85, 161.79 (d, *J* = 245.0 Hz), 161.50 (d, *J* = 246.8 Hz), 144.06, 139.61, 136.87 (d, *J* = 3.1 Hz), 132.83 (d, *J* = 3.3 Hz), 130.72 (d, *J* = 7.8 Hz), 129.72 (d, *J* = 7.9 Hz), 129.19, 128.63, 127.38, 126.20, 115.27 (d, *J* = 21.3 Hz), 114.87 (d, *J* = 21.2 Hz), 60.66, 50.23, 39.14, 14.31.

^{19}F NMR (376 MHz, $CDCl_3$): δ –115.10, –116.01.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ai** was obtained in 85% yield, *E*/*Z* = 1:3.5 (87.0 mg, colorless oil).



E-**3ai** *Z*-**3ai**

Ethyl (*E*)-3,5-bis(4-bromophenyl)-4-phenylpent-4-enoate (*E*-**3ai**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.27–7.19 (m, 5H), 6.98–6.94 (m, 4H), 6.62 (s, 1H), 4.93 (t, *J* = 7.7 Hz, 1H), 4.05–4.00 (m, 2H), 2.84 (dd, *J* = 15.7, 7.3 Hz, 1H), 2.71 (dd, *J* = 15.7, 8.3 Hz,1H), 1.18–1.12 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.79, 144.28, 140.74, 140.38, 136.20, 131.81, 130.53, 130.49, 129.34, 128.04, 121.27, 40.61, 37.29, 14.22.

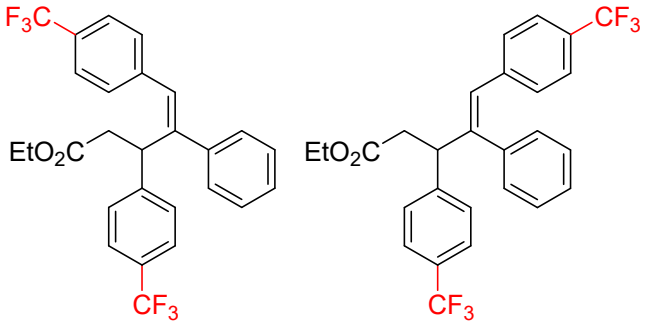
HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{22}NaBr_2O_2$ $[M+Na]^+$: 536.9860, found: 536.9863.

Ethyl (*Z*)-3,5-bis(4-bromophenyl)-4-phenylpent-4-enoate (*Z*-**3ai**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.26–7.20 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.88–6.82 (m, 2H), 6.69 (d, *J* = 8.3 Hz, 2H), 6.45 (s, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 4.14–4.02 (m, 2H), 2.93 (dd, *J* = 15.5, 7.9 Hz, 1H), 2.77 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.67, 144.83, 140.09, 139.35, 135.60, 131.59, 131.10, 130.73, 129.99, 129.04, 128.73, 127.56, 126.45, 120.83, 120.67, 60.75, 50.40, 38.83, 14.32.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3aj** was obtained in 89% yield, *E*/*Z* = 1:2.7 (87.5 mg, colorless oil).



E-**3aj** *Z*-**3aj**

Ethyl (*E*)-4-phenyl-3,5-bis(4-(trifluoromethyl)phenyl)pent-4-enoate (*E*-**3aj**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.31–7.22 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.75 (s, 1H), 5.02 (t, *J* = 7.6 Hz, 1H), 4.15–3.99 (m, 2H), 2.92 (dd, *J* = 15.7, 7.3 Hz, 1H), 2.79 (dd, *J* = 15.8, 8.1 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.65, 145.35, 145.05, 140.93, 140.41, 130.67, 129.18, 128.70, 128.20, 127.94, 127.86, 125.69 (q, *J* = 3.7 Hz), 125.53 (q, *J* = 3.7 Hz), 60.90, 41.19, 37.29, 14.21.

^{19}F NMR (376 MHz, $CDCl_3$): δ –62.43, –62.50.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{22}NaF_6O_2$ $[M+Na]^+$: 515.1416, found: 515.1418.

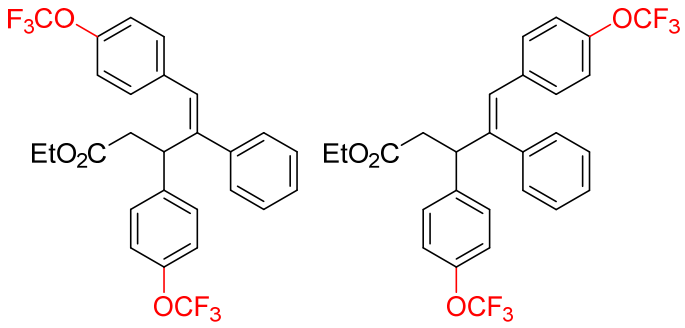
Ethyl (*Z*)-4-phenyl-3,5-bis(4-(trifluoromethyl)phenyl)pent-4-enoate (*Z*-**3aj**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 4H), 7.26–7.21 (m, 3H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.90–6.83 (m, 2H), 6.58 (s, 1H), 4.42 (t, *J* = 8.0 Hz, 1H), 4.14–4.05 (m, 2H), 3.00 (dd, *J* = 15.7, 7.9 Hz, 1H), 2.84 (dd, *J* = 15.7, 8.0 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.50, 146.21, 145.03, 140.17, 139.00, 129.33, 129.32 (q, *J* = 32.4 Hz), 128.96, 128.84, 128.61, 128.59 (q, *J* = 32.4 Hz), 127.83, 126.69, 125.50 (q, *J* = 3.8 Hz), 124.90 (d, *J* = 3.9 Hz), 124.23 (q, *J* = 272.1 Hz), 124.17 (q, *J* = 271.8 Hz), 60.86, 50.76, 38.73, 14.26.

^{19}F NMR (376 MHz, $CDCl_3$): δ –62.41, –62.60.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ak** was obtained in 87% yield, *E*/*Z* = 1:2.3 (91.1 mg, colorless oil).



E-**3ak** *Z*-**3ak**

Ethyl (*E*)-4-phenyl-3,5-bis(4-(trifluoromethoxy)phenyl)pent-4-enoate (*E*-**3ak**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.28–7.21 (m, 5H), 7.11 (s, 4H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.67 (s, 1H), 5.00 (t, *J* = 7.7 Hz, 1H), 4.14–3.98 (m, 2H), 2.87 (dd, *J* = 15.6, 7.3 Hz, 1H), 2.75 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.79, 148.27, 147.98, 144.53, 140.70, 139.99, 135.94, 130.29, 128.91, 128.71, 128.06, 127.63, 121.12, 120.93, 120.59 (q, *J* = 257.2 Hz), 120.54 (q, *J* = 257.1 Hz), 60.77, 40.56, 37.43, 14.13.

^{19}F NMR (376 MHz, $CDCl_3$): δ –57.76, –57.88.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{22}F_6NaO_4$ $[M+Na]^+$: 547.1314, found: 547.1310.

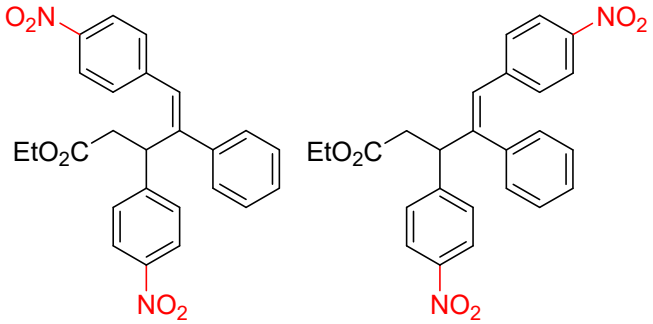
Ethyl (*Z*)-4-phenyl-3,5-bis(4-(trifluoromethoxy)phenyl)pent-4-enoate (*Z*-**3ak**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.21 (m, 3H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.87–6.80 (m, 4H), 6.51 (s, 1H), 4.33 (t, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.95 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.80 (dd, *J* = 15.5, 8.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.68, 148.14, 147.76, 144.89, 139.72, 139.22, 135.30, 130.42, 129.55, 129.04, 128.76, 127.62, 126.20, 120.92, 120.53 (q, *J* = 256.9 Hz), 120.45 (q, *J* = 257.3 Hz), 120.39, 60.76, 50.37, 38.91, 14.25.

^{19}F NMR (376 MHz, $CDCl_3$): δ –57.86, –57.89.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 8:1), the product **3al** was obtained in 80% yield, *E*/*Z* = 1:3.7 (71.4 mg, colorless oil).



E-**3al** *Z*-**3al**

Ethyl (*E*)-3,5-bis(4-nitrophenyl)-4-phenylpent-4-enoate (*E*-**3al**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.35–7.24 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 5.05 (t, *J* = 7.6 Hz, 1H), 4.18–4.03 (m, 2H), 2.96 (dd, *J* = 16.0, 7.3 Hz, 1H), 2.85 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.27, 148.44, 146.98, 146.91, 145.77, 143.80, 139.68, 130.29, 129.72, 128.54, 128.44, 128.35, 128.23, 124.15, 123.85, 61.10, 41.37, 37.03, 14.23.

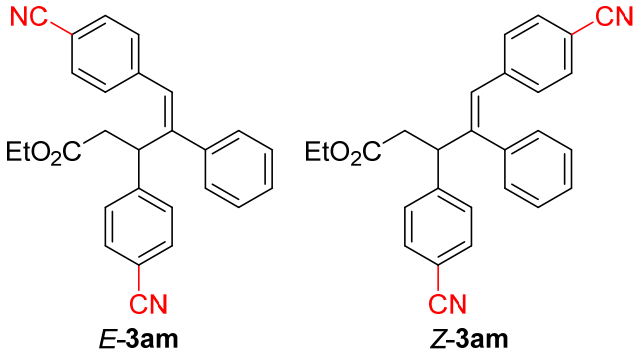
HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{22}N_2NaO_6$ $[M+Na]^+$: 469.1370, found: 469.1370.

Ethyl (*Z*)-3,5-bis(4-nitrophenyl)-4-phenylpent-4-enoate (*Z*-**3al**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.32–7.22 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.64 (s, 1H), 4.51 (t, *J* = 7.9 Hz, 1H), 4.16–4.05 (m, 2H), 3.06 (dd, *J* = 15.8, 7.7 Hz, 1H), 2.89 (dd, *J* = 15.8, 8.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.07, 148.24, 147.68, 147.06, 146.22, 143.15, 138.24, 129.78, 129.15, 129.08, 128.76, 128.31, 126.39, 123.84, 123.31, 61.03, 50.76, 38.39, 14.27.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 8:1), the product **3am** was obtained in 75% yield, *E*/*Z* = 1:3.2 (60.5 mg, colorless oil).



E-**3am** *Z*-**3am**

Ethyl (*E*)-3,5-bis(4-cyanophenyl)-4-phenylpent-4-enoate (*E*-**3am**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 7.1 Hz, 2H), 6.71 (s, 1H), 4.98 (t, *J* = 7.6 Hz, 1H), 4.13–4.01 (m, 2H), 2.90 (dd, *J* = 16.0, 7.3 Hz, 1H), 2.78 (dd, *J* = 15.9, 8.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.40, 146.50, 145.43, 141.85, 139.87, 132.63, 132.45, 130.54, 129.58, 128.57, 128.37, 128.30, 128.13, 118.91, 118.77, 111.14, 110.95, 61.06, 41.39, 36.94, 14.24.

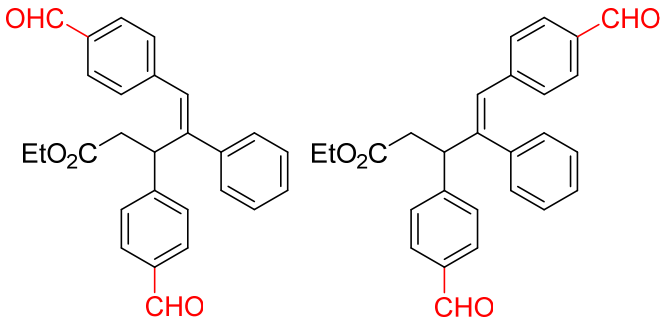
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{22}N_2NaO_2$ $[M+Na]^+$: 429.1573, found: 429.1571.

Ethyl (*Z*)-3,5-bis(4-cyanophenyl)-4-phenylpent-4-enoate (*Z*-**3am**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.30–7.20 (m, 5H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.85–6.79 (m, 2H), 6.55 (s, 1H), 4.41 (t, *J* = 7.9 Hz, 1H), 4.14–4.04 (m, 2H), 3.00 (dd, *J* = 15.7, 7.7 Hz, 1H), 2.84 (dd, *J* = 15.7, 8.1 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.14, 147.01, 146.20, 141.09, 138.38, 132.38, 131.77, 129.63, 129.03, 128.97, 128.74, 128.14, 126.61, 118.89, 118.78, 111.03, 110.19, 60.95, 50.94, 38.32, 14.25.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 8:1), the product **3an** was obtained in 74% yield, *E*/*Z* = 1:4.3 (61.0 mg, colorless oil).



E-**3an** *Z*-**3an**

Ethyl (*E*)-3,5-bis(4-formylphenyl)-4-phenylpent-4-enoate (*E*-**3an**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.04 (s, 1H), 9.98 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.30–7.20 (m, 5H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.78 (s, 1H), 5.11 (t, *J* = 7.6 Hz, 1H), 4.08–4.02 (m, 2H), 2.96 (dd, *J* = 15.8, 7.4 Hz, 1H), 2.83 (dd, *J* = 15.8, 8.0 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.91, 191.88, 171.53, 148.24, 145.37, 143.58, 140.30, 135.19, 135.10, 130.95, 130.18, 130.00, 129.49, 128.62, 128.25, 128.16, 127.88, 60.88, 41.59, 37.14, 14.20.

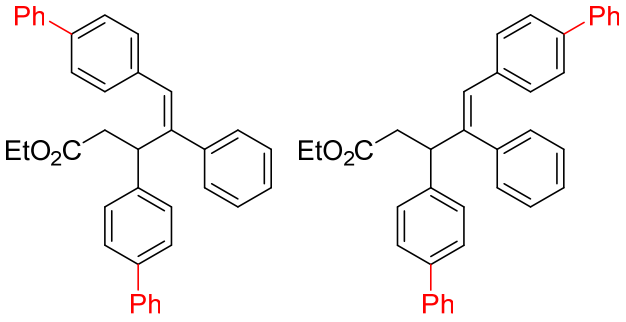
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{25}O_4$ $[M+H]^+$: 413.1747, found: 413.1747.

Ethyl (*Z*)-3,5-bis(4-formylphenyl)-4-phenylpent-4-enoate (*Z*-**3an**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.97 (s, 1H), 9.86 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.30–7.20 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 7.7 Hz, 2H), 6.63 (s, 1H), 4.46 (t, *J* = 7.9 Hz, 1H), 4.14–4.06 (m, 2H), 3.03 (dd, *J* = 15.7, 7.8 Hz, 1H), 2.89 (dd, *J* = 15.7, 8.1 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.97, 191.78, 171.39, 147.96, 147.01, 142.93, 138.92, 135.35, 134.58, 130.04, 129.69, 129.45, 128.97, 128.91, 128.84, 127.93, 127.11, 60.88, 51.12, 38.56, 14.29.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 6:1), the product **3ao** was obtained in 45% yield, *E*/*Z* = 1:2.5 (45.7 mg, white solid).



E-**3ao** *Z*-**3ao**

Ethyl (*E*)-3,5-di([1,1'-biphenyl]-4-yl)-4-phenylpent-4-enoate (*E*-**3ao**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.56 (m, 8H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.30–7.21 (m, 5H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.80 (s, 1H), 5.22 (t, *J* = 7.6 Hz, 1H), 4.14–4.01 (m, 2H), 2.97 (dd, *J* = 15.5, 7.2 Hz, 1H), 2.80 (dd, *J* = 15.5, 8.2 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.23, 144.01, 141.47, 140.87, 140.77, 140.72, 139.86, 139.36, 136.54, 131.26, 129.42, 128.93, 128.90, 128.85, 128.06, 127.97, 127.43, 127.36, 127.34, 127.31, 127.19, 127.13, 127.07, 60.66, 40.79, 37.60, 14.24.

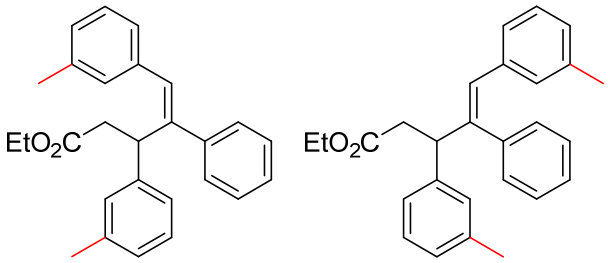
HRMS (ESI, *m*/*z*) calcd for $C_{37}H_{32}NaO_2$ $[M+Na]^+$: 531.2295, found: 531.2293.

Ethyl (*Z*)-3,5-di([1,1'-biphenyl]-4-yl)-4-phenylpent-4-enoate (*Z*-**3ao**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.38–7.20 (m, 12H), 6.99–6.90 (m, 3H), 6.62 (s, 1H), 4.39 (t, *J* = 7.7 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.01 (dd, *J* = 15.4, 8.2 Hz, 1H), 2.86 (dd, *J* = 15.4, 7.6 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.05, 144.47, 140.84, 140.67, 140.41, 140.17, 139.59, 139.26, 135.95, 129.65, 129.27, 128.86, 128.79, 128.71, 128.61, 127.30, 127.28, 127.11, 127.07, 126.91, 126.61, 60.65, 50.78, 39.12, 14.37.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ap** was obtained in 88% yield, *E*/*Z* = 1:3.2 (67.6 mg, colorless oil).



E-**3ap** *Z*-**3ap**

Ethyl (*E*)-4-phenyl-3,5-di-*m*-tolylpent-4-enoate (*E*-**3ap**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–6.83 (m, 13H), 6.69 (s, 1H), 5.07 (t, *J* = 7.7 Hz, 1H), 4.08–3.96 (m, 2H), 2.88 (dd, *J* = 15.3, 7.3 Hz, 1H), 2.72 (dd, *J* = 15.3, 8.2 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.19, 143.86, 141.60, 137.97, 137.49, 131.47, 129.73, 128.86, 128.46, 128.42, 128.27, 127.81, 127.79, 127.24, 127.15, 125.83, 124.62, 60.46, 40.90, 37.57, 21.65, 21.61, 14.15.

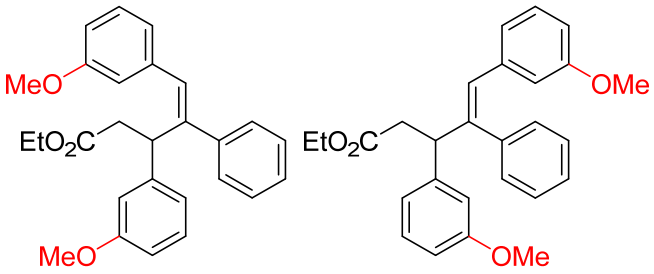
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{28}NaO_2$ $[M+Na]^+$: 407.1982, found: 407.1981.

Ethyl (*Z*)-4-phenyl-3,5-di-*m*-tolylpent-4-enoate (*Z*-**3ap**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.11 (m, 4H), 7.03–6.84 (m, 7H), 6.70 (s, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.51 (s, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 4.12–4.05 (m, 2H), 2.94 (dd, *J* = 15.4, 8.4 Hz, 1H), 2.79 (dd, *J* = 15.4, 7.6 Hz, 1H), 2.29 (s, 3H), 2.13 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.16, 144.23, 141.27, 140.38, 137.91, 137.38, 136.89, 130.25, 129.25, 129.14, 128.38, 128.25, 127.79, 127.57, 127.44, 127.36, 127.07, 126.16, 125.24, 60.55, 50.89, 39.22, 21.59, 21.41, 14.34.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3aq** was obtained in 81% yield, *E*/*Z* = 1:3 (67.4 mg, colorless oil).



E-**3aq** *Z*-**3aq**

Ethyl (*E*)-3,5-bis(3-methoxyphenyl)-4-phenylpent-4-enoate (*E*-**3aq**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.8 Hz, 1H), 7.25–7.15 (m, 4H), 7.10–7.00 (m, 4H), 6.83 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.80–6.73 (m, 2H), 6.71 (s, 2H), 5.09 (t, *J* = 7.7 Hz, 1H), 4.13–3.98 (m, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 2.88 (dd, *J* = 15.4, 7.0 Hz, 1H), 2.72 (dd, *J* = 15.4, 8.5 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.18, 159.75, 159.71, 144.12, 143.43, 141.43, 138.96, 131.44, 129.60, 129.41, 128.80, 127.92, 127.32, 121.36, 119.85, 114.22, 113.41, 112.97, 112.22, 60.60, 55.31, 55.24, 40.96, 37.44, 14.22.

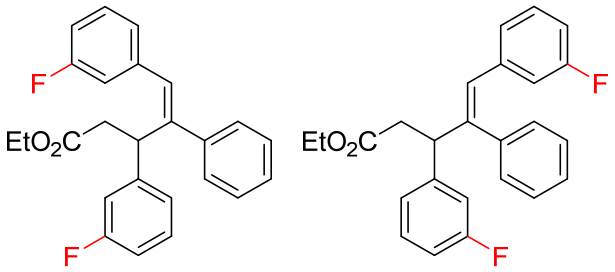
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{29}O_4$ $[M+H]^+$: 417.2060, found: 417.2062.

Ethyl (*Z*)-3,5-bis(3-methoxyphenyl)-4-phenylpent-4-enoate (*Z*-**3aq**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.14 (m, 4H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.93–6.87 (m, 2H), 6.80–6.70 (m, 3H), 6.59 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.55–6.50 (m, 2H), 6.30 (s, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.41 (s, 3H), 2.94 (dd, *J* = 15.4, 8.5 Hz, 1H), 2.79 (dd, *J* = 15.4, 7.6 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.04, 159.63, 159.01, 144.41, 142.91, 140.23, 138.21, 129.38, 129.31, 128.90, 128.52, 127.38, 127.21, 122.24, 120.73, 114.14, 113.50, 113.33, 112.16, 60.64, 55.28, 54.84, 51.01, 39.11, 14.37.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ar** was obtained in 84% yield, *E*/*Z* = 1:3.3 (65.8 mg, colorless oil).



E-**3ar** *Z*-**3ar**

Ethyl (*E*)-3,5-bis(3-fluorophenyl)-4-phenylpent-4-enoate (*E*-**3ar**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.15 (m, 7H), 7.03–6.87 (m, 5H), 6.82 (d, *J* = 10.5 Hz, 1H), 6.68 (s, 1H), 5.02 (t, *J* = 7.7 Hz, 1H), 4.14–4.00 (m, 2H), 2.87 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.72 (dd, *J* = 15.5, 8.3 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.65, 162.90 (d, *J* = 246.1 Hz), 162.89 (d, *J* = 246.1 Hz), 144.47, 143.93 (d, *J* = 6.8 Hz), 140.60, 139.40 (d, *J* = 7.7 Hz), 130.47 (d, *J* = 2.0 Hz), 130.08 (d, *J* = 8.5 Hz), 129.87 (d, *J* = 8.4 Hz), 128.60, 127.94, 127.52, 124.52 (d, *J* = 2.9 Hz), 123.12 (d, *J* = 2.8 Hz), 115.66 (d, *J* = 21.7 Hz), 114.57 (d, *J* = 22.0 Hz), 114.10 (d, *J* = 21.1 Hz), 113.59 (d, *J* = 21.0 Hz), 60.67, 40.69 (d, *J* = 1.4 Hz), 37.17, 14.07. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –112.81, –112.85.

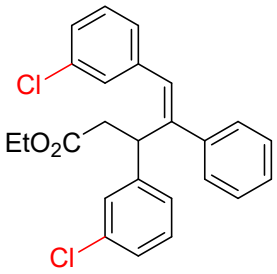
HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{22}F_2NaO_2$ $[M+Na]^+$: 415.1480, found: 415.1482.

Ethyl (*Z*)-3,5-bis(3-fluorophenyl)-4-phenylpent-4-enoate (*Z*-**3ar**)

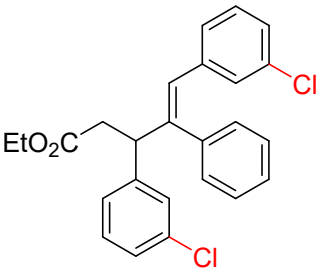
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–6.98 (m, 5H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.93–6.85 (m, 4H), 6.74 (td, *J* = 8.4, 2.0 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.51 (s, 1H), 6.48 (d, *J* = 10.8 Hz, 1H), 4.32 (t, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 2.95 (dd, *J* = 15.5, 8.1 Hz, 1H), 2.80 (dd, *J* = 15.5, 7.9 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.58, 162.86 (d, *J* = 245.8 Hz), 162.39 (d, *J* = 244.5 Hz), 145.20, 143.65 (d, *J* = 6.8 Hz), 139.21, 138.89 (d, *J* = 7.9 Hz), 129.86 (d, *J* = 8.2 Hz), 129.25 (d, *J* = 8.4 Hz), 128.92, 128.63, 127.57, 126.60 (d, *J* = 2.4 Hz), 125.07 (d, *J* = 2.7 Hz), 123.94 (d, *J* = 2.7 Hz), 115.60 (d, *J* = 22.3 Hz), 115.06 (d, *J* = 21.5 Hz), 113.84 (d, *J* = 21.1 Hz), 113.61 (d, *J* = 21.3 Hz), 60.67, 50.58 (d, *J* = 1.3 Hz), 38.78, 14.23. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –113.01, –113.66.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3as** was obtained in 88% yield, *E*/*Z* = 1:3.2 (74.6 mg, colorless oil).



E-**3as**



Z-**3as**

Ethyl (*E*)-3,5-bis(3-chlorophenyl)-4-phenylpent-4-enoate (*E*-**3as**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.36–7.13 (m, 8H), 7.09 (s, 1H), 7.00–6.96 (m, 3H), 6.65 (s, 1H), 4.97 (t, *J* = 7.7 Hz, 1H), 4.10–4.01 (m, 2H), 2.86 (dd, *J* = 15.5, 7.1 Hz, 1H), 2.73 (dd, *J* = 15.5, 8.3 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

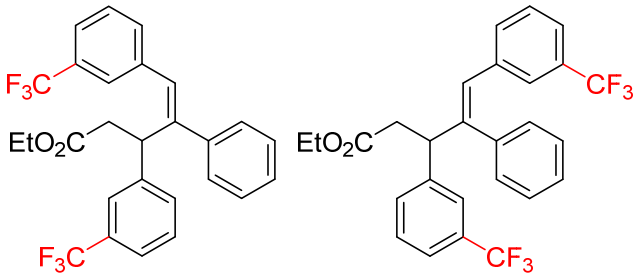
Ethyl (*Z*)-3,5-bis(3-chlorophenyl)-4-phenylpent-4-enoate (*Z*-**3as**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25–7.14 (m, 6H), 7.07–7.03 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.90–6.86 (m, 2H), 6.84 (s, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.47 (s, 1H), 4.30 (t, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.94 (dd, *J* = 15.6, 8.1 Hz, 1H), 2.79 (dd, *J* = 15.6, 7.9 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.54, 171.48, 145.30, 144.61, 143.34, 143.07, 140.52, 139.11, 139.02, 138.46, 134.41, 134.36, 134.25, 133.72, 130.33, 129.87, 129.69, 129.17, 129.07, 128.93, 128.64, 128.31, 127.99, 127.73, 127.60, 127.31, 127.20, 127.15, 126.89, 126.72, 126.43, 125.74, 60.68, 50.50, 40.82, 38.74, 37.16, 14.25, 14.13.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{23}Cl_2O_2$ $[M+H]^+$: 425.1070, found: 425.1069.

Following the **General Procedure** A, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3at** was obtained in 86% yield, *E*/*Z* = 1:3.1 (84.6 mg, colorless oil).



E-**3at** *Z*-**3at**

Ethyl (*E*)-4-phenyl-3,5-bis(3-(trifluoromethyl)phenyl)pent-4-enoate (*E*-**3at**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.60–7.50 (m, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30–7.21 (m, 5H), 6.97 (d, *J* = 6.6 Hz, 2H), 6.72 (s, 1H), 4.96 (t, *J* = 7.7 Hz, 1H), 4.14–3.99 (m, 2H), 2.89 (dd, *J* = 15.7, 7.4 Hz, 1H), 2.80 (dd, *J* = 15.7, 8.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.39, 145.08, 142.13, 140.33, 137.91, 131.96, 130.97 (q, *J* = 32.1 Hz), 130.93, 130.72 (q, *J* = 32.1 Hz), 130.34, 129.10, 128.89, 128.65, 128.04, 127.70, 125.68 (q, *J* = 3.9 Hz), 124.34 (q, *J* = 3.8 Hz), 124.08 (q, *J* = 272.1 Hz), 124.00 (q, *J* = 272.4 Hz), 123.97 (q, *J* = 3.9 Hz), 123.62 (q, *J* = 3.8 Hz), 60.75, 41.23, 37.29, 14.03. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –62.70, –62.75.

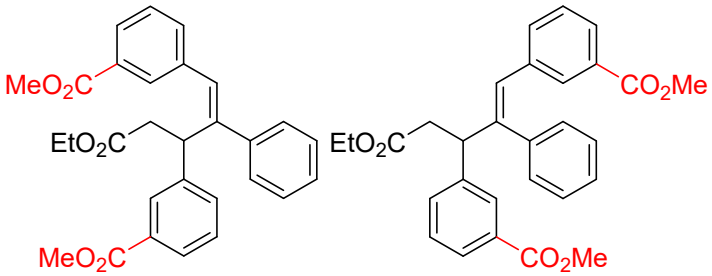
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{22}F_6NaO_2$ $[M+Na]^+$: 515.1416, found: 515.1417.

Ethyl (*Z*)-4-phenyl-3,5-bis(3-(trifluoromethyl)phenyl)pent-4-enoate (*Z*-**3at**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.35 (m, 4H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.26–7.20 (m, 3H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.89–6.82 (m, 2H), 6.58 (s, 1H), 4.44 (t, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.02 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.85 (dd, *J* = 15.5, 8.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.41, 145.73, 141.88, 138.72, 137.25, 132.17, 131.67, 130.74 (q, *J* = 32.2 Hz), 130.27 (q, *J* = 32.1 Hz), 128.91, 128.76, 128.29, 127.75, 126.55, 125.90 (q, *J* = 3.9 Hz), 124.94 (q, *J* = 3.8 Hz), 124.11 (q, *J* = 272.4 Hz), 123.95 (q, *J* = 272.3 Hz), 123.88 (q, *J* = 3.8 Hz), 123.34 (q, *J* = 3.8 Hz), 60.75, 50.71, 38.66, 14.12. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –62.57, –63.02.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 9:1), the product **3au** was obtained in 83% yield, *E*/*Z* = 1:2.1 (78.8 mg, colorless oil).



E-**3au** *Z*-**3au**

Dimethyl 3,3'-(5-ethoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3au**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.94–7.86 (m, 1H), 7.81 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.40–7.30 (m, 2H), 7.28–7.18 (m, 3H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.75 (s, 1H), 5.03 (t, *J* = 7.7 Hz, 1H), 4.12–4.00 (m, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 2.94 (dd, *J* = 15.6, 7.1 Hz, 1H), 2.82 (dd, *J* = 15.6, 8.4 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.69, 167.04, 167.02, 144.64, 141.79, 140.78, 137.60, 133.18, 132.28, 130.80, 130.47, 130.37, 130.32, 130.20, 129.86, 128.74, 128.60, 128.58, 128.32, 127.99, 127.53, 60.67, 52.24, 52.18, 41.00, 37.32, 14.13.

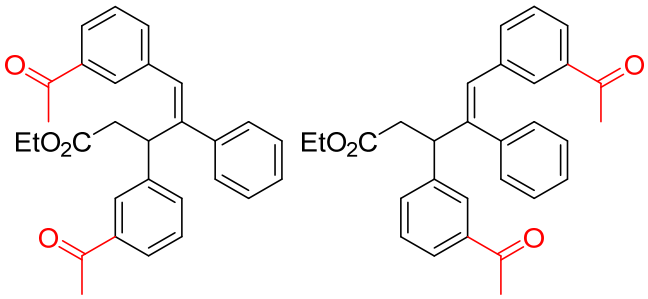
HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{28}NaO_6$ $[M+Na]^+$: 495.1778, found: 495.1776.

Dimethyl 3,3'-(5-ethoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3au**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.63 (s, 1H), 7.40–7.40 (m, 2H), 7.28–7.18 (m, 3H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.92–6.84 (m, 2H), 6.59 (s, 1H), 4.42 (t, *J* = 7.9 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.81 (s, 3H), 3.02 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.87 (dd, *J* = 15.5, 7.9 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.67, 167.07, 166.97, 145.31, 141.49, 139.31, 137.00, 133.26, 132.93, 130.59, 129.34, 129.05, 128.71, 128.68, 128.54, 128.27, 128.01, 127.94, 127.76, 127.48, 126.82, 60.69, 52.21, 52.06, 50.64, 38.82, 14.25.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 9:1), the product **3av** was obtained in 88% yield, *E*/*Z* = 1:2.8 (77.4 mg, colorless oil).



E-**3av** *Z*-**3av**

Ethyl (*E*)-3,5-bis(3-acetylphenyl)-4-phenylpent-4-enoate (*E*-**3av**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.80–7.77 (m, 1H), 7.66 (s, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.36–7.31 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.26–7.20 (m, 3H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.74 (s, 1H), 5.02 (t, *J* = 7.7 Hz, 1H), 4.08–4.00 (m, 2H), 2.92 (dd, *J* = 15.7, 7.2 Hz, 1H), 2.81 (dd, *J* = 15.7, 8.3 Hz, 1H), 2.60 (s, 3H), 2.48 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.03, 171.73, 144.74, 141.91, 140.66, 137.75, 137.39, 137.19, 133.43, 132.30, 130.76, 128.97, 128.95, 128.69, 128.03, 127.61, 127.44, 127.04, 126.77, 41.06, 37.27, 26.68, 14.16.

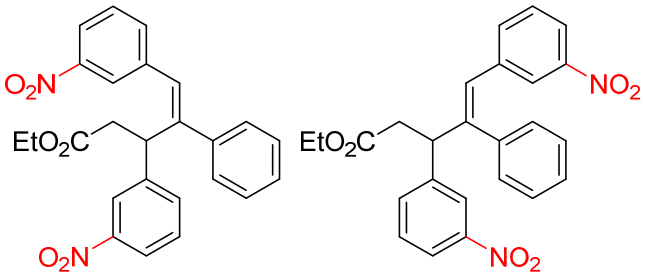
HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{29}O_4$ $[M+H]^+$: 441.2060, found: 441.2059.

Ethyl (*Z*)-3,5-bis(3-acetylphenyl)-4-phenylpent-4-enoate (*Z*-**3av**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.76 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.40–7.34 (m, 3H), 7.26–7.19 (m, 3H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.91–6.86 (m, 2H), 6.58 (s, 1H), 4.41 (t, *J* = 7.9 Hz, 1H), 4.12–4.02 (m, 2H), 3.01 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.86 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.53 (s, 3H), 2.22 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.20, 198.12, 171.62, 145.26, 141.58, 139.39, 137.22, 136.90, 136.63, 133.88, 133.02, 129.29, 129.10, 128.79, 128.74, 128.29, 128.01, 127.63, 127.19, 126.80, 126.26, 60.72, 50.77, 38.72, 26.76, 26.41, 14.26.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 6:1), the product **3aw** was obtained in 84% yield, *E*/*Z* = 1:2 (75.0 mg, light yellow solid).



E-**3aw** *Z*-**3aw**

Ethyl (*E*)-3,5-bis(3-nitrophenyl)-4-phenylpent-4-enoate (*E*-**3aw**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.92 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.49–7.39 (m, 2H), 7.33–7.24 (m, 3H), 6.97 (d, *J* = 7.0 Hz, 2H), 6.78 (s, 1H), 5.01 (t, *J* = 7.7 Hz, 1H), 4.18–4.04 (m, 2H), 2.97 (dd, *J* = 15.9, 7.3 Hz, 1H), 2.87 (dd, *J* = 15.9, 8.1 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.26, 148.59, 148.42, 145.61, 143.16, 139.82, 138.69, 134.94, 133.85, 129.90, 129.87, 129.63, 128.59, 128.39, 128.20, 123.88, 122.46, 122.42, 122.16, 61.13, 41.16, 37.18, 14.25.

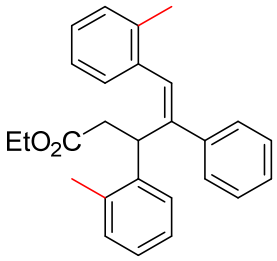
HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{22}N_2NaO_6$ $[M+Na]^+$: 469.1370, found: 469.1369.

Ethyl (*Z*)-3,5-bis(3-nitrophenyl)-4-phenylpent-4-enoate (*Z*-**3aw**)

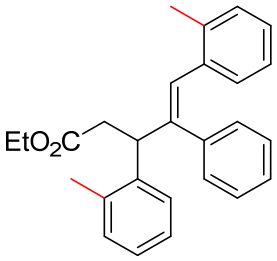
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.73 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.30–7.24 (m, 3H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.91–6.84 (m, 2H), 6.62 (s, 1H), 4.50 (t, *J* = 7.9 Hz, 1H), 4.16–4.06 (m, 2H), 3.06 (dd, *J* = 15.8, 7.7 Hz, 1H), 2.90 (dd, *J* = 15.8, 8.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.17, 148.43, 148.06, 146.65, 142.96, 138.16, 138.10, 134.95, 134.61, 129.56, 129.17, 128.89, 128.83, 128.31, 126.10, 123.98, 123.09, 122.38, 121.76, 61.04, 50.50, 38.52, 14.31.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ax** was obtained in 92% yield, *E*/*Z* = 1:2.4 (70.4 mg, colorless oil).



E-**3ax**



Z-**3ax**

Ethyl (*E*)-4-phenyl-3,5-di-*o*-tolylpent-4-enoate (*E*-**3ax**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 6.7 Hz, 1H), 7.28–6.86 (m, 11H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.46 (s, 1H), 4.95 (dd, *J* = 9.9, 6.1 Hz, 1H), 4.01–3.92 (m, 2H), 3.01 (dd, *J* = 15.8, 9.9 Hz, 1H), 2.94 (dd, *J* = 15.8, 6.1 Hz, 1H), 2.21 (s, 3H), 1.87 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.69, 143.93, 142.00, 138.94, 136.93, 136.83, 136.46, 130.28, 130.22, 130.12, 128.65, 127.56, 127.48, 127.42, 127.00, 126.34, 125.74, 125.28, 60.44, 39.24, 38.91, 19.20, 14.11.

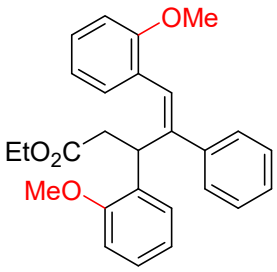
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{28}NaO_2$ $[M+Na]^+$: 407.1982, found: 407.1981.

Ethyl (*Z*)-4-phenyl-3,5-di-*o*-tolylpent-4-enoate (*Z*-**3ax**)

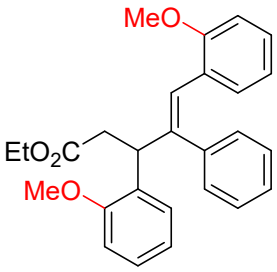
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–6.86 (m, 11H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 6.45 (s, 1H), 4.63 (t, *J* = 8.0 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.94 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.82 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.24, 144.30, 140.29, 139.58, 136.69, 136.29, 130.68, 129.68, 129.57, 129.24, 128.02, 126.98, 126.91, 126.70, 126.67, 126.50, 126.12, 125.17, 60.57, 45.56, 39.22, 20.18, 19.80, 14.26.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1), the product **3ay** was obtained in 57% yield, *E*/*Z* = 1:1.2 (47.3 mg, colorless oil).



E-**3ay**



Z-**3ay**

Ethyl (*E*)-3,5-bis(2-methoxyphenyl)-4-phenylpent-4-enoate (*E*-**3ay**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.32–6.69 (m, 11H), 6.65 (s, 1H), 6.57 (d, *J* = 7.4 Hz, 1H), 5.15 (t, *J* = 7.9 Hz, 1H), 4.02–3.90 (m, 2H), 3.77 (s, 3H), 3.58 (s, 3H), 2.91 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.81 (dd, *J* = 15.6, 7.1 Hz, 1H), 1.08 (t, *J* = 7.1 Hz, 3H).

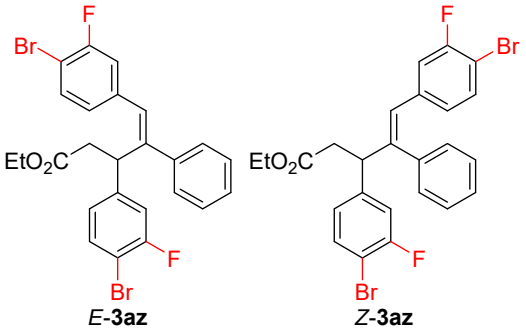
Ethyl (*Z*)-3,5-bis(2-methoxyphenyl)-4-phenylpent-4-enoate (*Z*-**3ay**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–6.69 (m, 12H), 6.56 (s, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 4.80 (t, *J* = 8.1 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 2.90 (d, *J* = 8.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.54, 172.35, 157.62, 157.42, 157.39, 143.52, 142.79, 141.36, 130.43, 130.17, 129.93, 129.78, 129.47, 129.40, 128.51, 128.47, 128.17, 128.01, 127.70, 127.51, 127.45, 127.09, 126.93, 126.77, 126.70, 122.60, 120.45, 120.15, 119.87, 119.84, 110.80, 110.32, 110.26, 60.39, 60.26, 55.60, 55.59, 55.38, 55.02, 43.27, 38.70, 37.67, 37.29, 14.31, 14.16.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{28}NaO_4$ $[M+Na]^+$: 439.1880, found: 439.1882.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3az** was obtained in 76% yield, *E*/*Z* = 1:3.2 (83.3 mg, colorless oil).



Ethyl (*E*)-3,5-bis(4-bromo-3-fluorophenyl)-4-phenylpent-4-enoate (*E*-**3az**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.29–7.22 (m, 4H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 10.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.62 (s, 1H), 4.92 (t, *J* = 7.7 Hz, 1H), 4.14–4.03 (m, 2H), 2.85 (dd, *J* = 15.8, 7.1 Hz, 1H), 2.72 (dd, *J* = 15.8, 8.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.45, 159.15 (d, *J* = 247.7 Hz), 159.11 (d, *J* = 247.7 Hz), 144.70, 143.03 (d, *J* = 6.2 Hz), 140.09, 138.44 (d, *J* = 7.1 Hz), 133.76, 133.50, 129.86, 128.55, 128.20, 127.91, 125.79 (d, *J* = 3.3 Hz), 124.42 (d, *J* = 3.2 Hz), 116.86 (d, *J* = 22.6 Hz), 115.80 (d, *J* = 22.9 Hz), 107.91 (d, *J* = 21.0 Hz), 107.25 (d, *J* = 21.0 Hz), 60.94, 40.50, 37.07, 14.19.

^{19}F NMR (376 MHz, $CDCl_3$): δ –106.61, –106.63.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{20}NaBr_2F_2O_2$ $[M+Na]^+$: 570.9690, found: 570.9682.

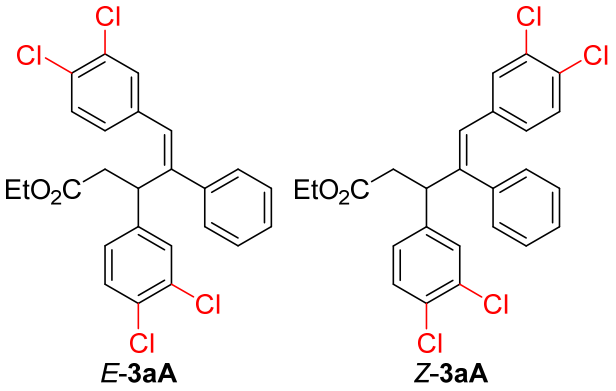
Ethyl (*Z*)-3,5-bis(4-bromo-3-fluorophenyl)-4-phenylpent-4-enoate (*Z*-**3az**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.7 Hz, 1H), 7.23–7.12 (m, 4H), 6.87 (dd, *J* = 9.6, 1.6 Hz, 1H), 6.82–6.74 (m, 3H), 6.45 (d, *J* = 10.0 Hz, 2H), 6.36 (s, 1H), 4.21 (t, *J* = 7.9 Hz, 1H), 4.07–3.97 (m, 2H), 2.85 (dd, *J* = 15.6, 7.8 Hz, 1H), 2.69 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.33, 159.06 (d, *J* = 247.7 Hz), 158.59 (d, *J* = 246.2 Hz), 145.62, 142.80 (d, *J* = 6.2 Hz), 138.62, 137.93 (d, *J* = 7.2 Hz), 133.47, 132.86, 128.97, 128.81, 128.01, 126.18 (d, *J* = 3.1 Hz), 125.95 (d, *J* = 1.5 Hz), 125.20 (d, *J* = 3.1 Hz), 116.72 (d, *J* = 23.3 Hz), 116.30 (d, *J* = 22.4 Hz), 107.41 (d, *J* = 20.7 Hz), 107.22 (d, *J*= 21.0 Hz), 60.91, 50.27, 38.60, 14.31.

^{19}F NMR (376 MHz, $CDCl_3$): δ –107.03, –107.95.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3aA** was obtained in 82% yield, *E*/*Z* = 1:2.7 (80.7 mg, colorless oil).



Ethyl (*E*)-3,5-bis(3,4-dichlorophenyl)-4-phenylpent-4-enoate (*E*-**3aA**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 1.4 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.30–7.24 (m, 4H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 2H), 6.91 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.60 (s, 1H), 4.88 (t, *J* = 7.7 Hz, 1H), 4.14–4.03 (m, 2H), 2.84 (dd, *J* = 15.7, 7.2 Hz, 1H), 2.73 (dd, *J* = 15.7, 8.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.43, 144.91, 141.41, 140.14, 137.12, 132.81, 132.67, 131.44, 130.95, 130.81, 130.70, 130.48, 129.61, 128.63, 128.22, 128.16, 127.93, 127.02, 60.96, 40.54, 37.19, 14.24.

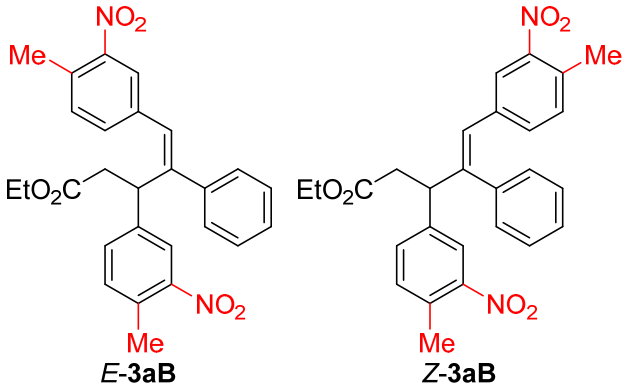
HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{20}Cl_4NaO_2$ $[M+Na]^+$: 515.0110, found: 515.0107.

Ethyl (*Z*)-3,5-bis(3,4-dichlorophenyl)-4-phenylpent-4-enoate (*Z*-**3aA**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.3 Hz, 1H), 7.30–7.23 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 6.89–6.83 (m, 2H), 6.61 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.41 (s, 1H), 4.28 (t, *J* = 7.9 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.92 (dd, *J* = 15.6, 7.8 Hz, 1H), 2.76 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.34, 145.63, 141.19, 138.62, 136.57, 132.59, 132.03, 131.09, 131.02, 130.66, 130.48, 130.19, 129.87, 128.97, 128.89, 128.31, 128.00, 127.67, 125.70, 60.92, 50.06, 38.65, 14.32.

Following **the General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3aB** was obtained in 87% yield, *E*/*Z* = 1:2.3 (82.5 mg, colorless oil).



Ethyl (*E*)-3,5-bis(4-methyl-3-nitrophenyl)-4-phenylpent-4-enoate (*E*-**3aB**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.69 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.30–7.22 (m, 3H), 6.90 (t, *J* = 7.0 Hz, 2H), 6.71 (s, 1H), 4.95 (t, *J* = 7.6 Hz, 1H), 4.14–4.04 (m, 2H), 2.93 (dd, *J* = 15.9, 7.3 Hz, 1H), 2.81 (dd, *J* = 15.9, 8.1 Hz, 1H), 2.63 (s, 3H), 2.57 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

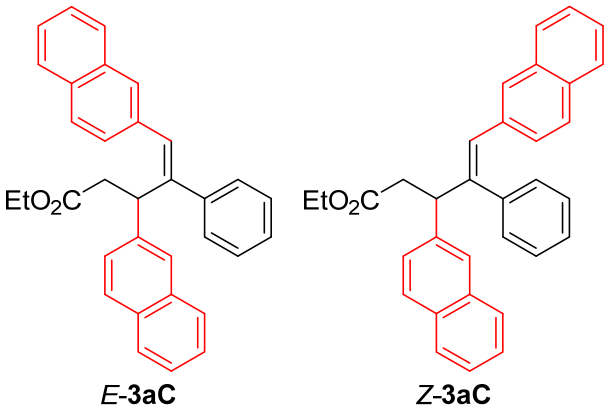
Ethyl (*Z*)-3,5-bis(4-methyl-3-nitrophenyl)-4-phenylpent-4-enoate (*Z*-**3aB**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.48 (s, 1H), 7.30–7.22 (m, 5H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.52 (s, 1H), 4.41 (t, *J* = 7.9 Hz, 1H), 4.14–4.04 (m, 2H), 3.00 (dd, *J* = 15.8, 7.7 Hz, 1H), 2.84 (dd, *J* = 15.8, 8.2 Hz, 1H), 2.56 (s, 3H), 2.45 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.38, 171.32, 149.34, 149.19, 149.17, 148.89, 145.88, 145.17, 140.54, 140.34, 140.09, 138.49, 136.24, 135.70, 133.31, 133.25, 133.10, 133.05, 132.97, 132.63, 132.49, 132.36, 132.27, 131.98, 129.65, 129.10, 128.87, 128.56, 128.31, 128.14, 128.02, 125.79, 125.18, 125.02, 124.27, 123.61, 61.02, 60.96, 50.06, 40.69, 38.56, 37.21, 20.43, 20.38, 20.29, 20.25, 14.31, 14.22.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{26}N_2NaO_6$ $[M+Na]^+$: 497.1683, found: 497.1681.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 6:1), the product **3aC** was obtained in 81% yield, *E*/*Z* = 1:2.6 (73.9 mg, colorless oil).



E-**3aC** *Z*-**3aC**

Ethyl (*E*)-3,5-di(naphthalen-2-yl)-4-phenylpent-4-enoate (*E*-**3aC**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.96–7.15 (m, 18H), 6.93 (s, 1H), 5.37 (t, *J* = 7.6 Hz, 1H), 4.13–4.01 (m, 2H), 3.13–3.03 (m, 1H), 2.90 (dd, *J* = 15.4, 8.3 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H).

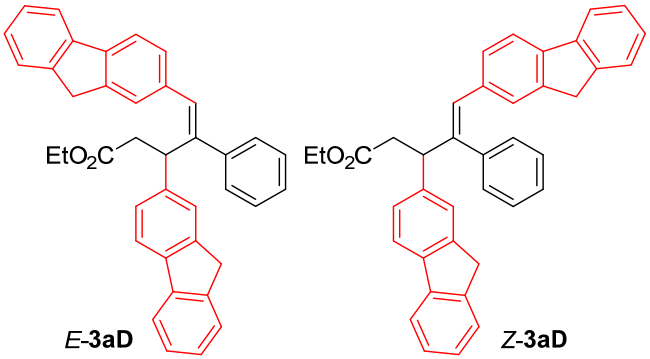
Ethyl (*Z*)-3,5-di(naphthalen-2-yl)-4-phenylpent-4-enoate (*Z*-**3aC**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–6.87 (m, 19H), 6.78 (s, 1H), 4.56 (t, *J* = 7.9 Hz, 1H), 4.13–4.03 (m, 2H), 3.09 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.97 (dd, *J* = 15.5, 8.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.18, 172.10, 144.66, 144.18, 141.51, 140.17, 139.25, 138.86, 135.06, 134.56, 133.58, 133.52, 133.44, 133.27, 132.59, 132.53, 132.34, 132.24, 131.77, 129.38, 128.89, 128.66, 128.59, 128.26, 128.19, 128.17, 128.06, 128.02, 127.97, 127.91, 127.79, 127.77, 127.72, 127.64, 127.51, 127.35, 127.32, 127.19, 127.10, 126.92, 126.71, 126.65, 126.37, 126.28, 126.12, 126.08, 126.05, 125.99, 125.84, 125.77, 125.75, 125.70, 60.67, 60.65, 51.07, 41.32, 39.23, 37.61, 14.35, 14.23.

HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{28}NaO_2$ $[M+Na]^+$: 479.1982, found: 479.1982.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3aD** was obtained in 34% yield, *E*/*Z* = 1:2.7 (36.2 mg, colorless oil).



Ethyl (*E*)-3,5-di(9*H*-fluoren-2-yl)-4-phenylpent-4-enoate (*E*-**3aD**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 9.5, 8.0 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.69 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.57–7.50 (m, 3H), 7.41–7.17 (m, 9H), 7.07–7.01 (m, 2H), 6.81 (s, 1H), 5.28 (t, *J* = 7.7 Hz, 1H), 4.14–4.00 (m, 2H), 3.94 (s, 2H), 3.82 (s, 2H), 3.00 (dd, *J* = 15.4, 7.5 Hz, 1H), 2.83 (dd, *J* = 15.4, 8.0 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.29, 144.03, 143.64, 143.60, 143.48, 141.70, 141.63, 141.62, 140.74, 140.39, 140.24, 136.17, 131.72, 128.95, 127.89, 127.80, 127.25, 126.93, 126.87, 126.83, 126.66, 126.34, 125.55, 125.17, 124.35, 120.02, 120.01, 119.90, 119.84, 60.62, 41.28, 37.81, 37.14, 37.06, 14.26.

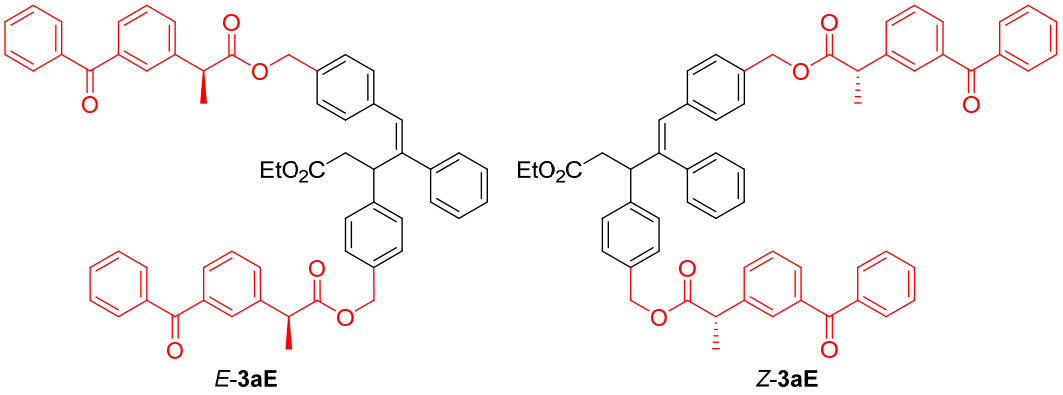
HRMS (ESI, *m*/*z*) calcd for $C_{39}H_{32}NaO_2$ $[M+Na]^+$: 555.2295, found: 555.2295.

Ethyl (*Z*)-3,5-di(9*H*-fluoren-2-yl)-4-phenylpent-4-enoate (*Z*-**3aD**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 8.7 Hz, 2H), 7.40 (s, 1H), 7.38–7.16 (m, 8H), 7.03 (s, 1H), 6.96–6.91 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 4.42 (t, *J* = 8.0 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 2H), 3.67 (s, 2H), 3.03 (dd, *J* = 15.4, 8.1 Hz, 1H), 2.89 (dd, *J* = 15.4, 7.9 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.20, 144.16, 143.57, 143.54, 143.45, 142.97, 141.68, 141.53, 140.50, 140.42, 140.26, 140.12, 135.65, 129.37, 128.52, 128.08, 127.69, 127.17, 127.00, 126.85, 126.80, 126.64, 125.90, 125.16, 125.02, 119.89, 119.80, 119.35, 60.63, 51.21, 39.37, 36.99, 36.88, 14.38.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3aE** was obtained in 27% yield, *E*/*Z* = 1:3.5 (47.9 mg, colorless oil).



E-**3aE** *Z*-**3aE**

(((*E*)-5-ethoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)bis(4,1-phenylene))bis(methylene) (2*S*,2'*S*)-bis(2-(3-benzoylphenyl)propanoate) (*E*-**3aE**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.06 (m, 29H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.69 (s, 1H), 5.20–5.00 (m, 5H), 4.06–3.98 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 2.87 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.71 (dd, *J* = 15.6, 8.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 6H), 1.12 (t, *J* = 7.1 Hz, 3H).

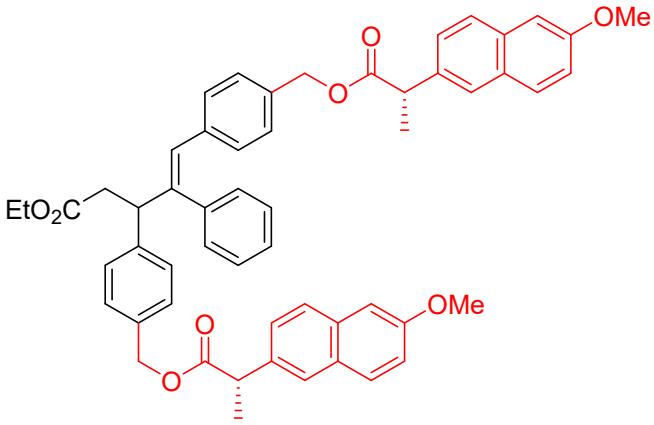
(((*Z*)-5-ethoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)bis(4,1-phenylene))bis(methylene) (2*S*,2'*S*)-bis(2-(3-benzoylphenyl)propanoate) (*Z*-**3aE**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.06 (m, 25H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.50 (s, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 5.06 (d, *J* = 12.4 Hz, 1H), 5.00 (d, *J* = 12.6 Hz, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 4.29 (t, *J* = 7.9 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.85 (q, *J* = 7.2 Hz, 2H), 2.93 (dd, *J* = 15.6, 8.3 Hz, 1H), 2.77 (dd, *J* = 15.6, 7.7 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 6H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.58, 173.99, 173.91, 172.01, 171.89, 144.64, 144.03, 141.57, 141.29, 141.11, 140.78, 140.72, 140.61, 139.85, 137.99, 137.55, 137.42, 136.79, 135.08, 135.02, 134.57, 134.35, 134.12, 134.07, 132.62, 131.63, 131.08, 130.17, 129.40, 129.29, 129.15, 129.11, 129.06, 128.71, 128.66, 128.54, 128.41, 128.29, 128.11, 128.04, 127.93, 127.70, 127.58, 127.39, 127.32, 126.99, 66.54, 66.44, 66.41, 60.62, 50.66, 45.48, 45.45, 40.66, 39.00, 37.37, 18.55, 18.49, 14.31, 14.18.

HRMS (ESI, *m*/*z*) calcd for $C_{59}H_{52}NaO_8$ $[M+Na]^+$: 911.3554, found: 911.3561.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product *Z*-**3aF** was obtained in 40% yield (67.2 mg, colorless oil), *E*/*Z* = 1:4.4.



Z-**3aF**

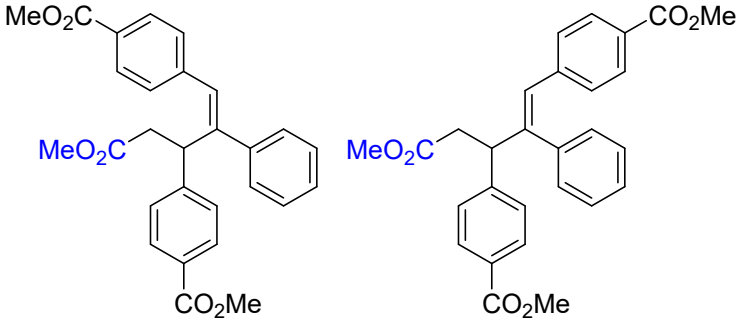
(((*Z*)-5-ethoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)bis(4,1-phenylene))bis(methylene) (2*S*,2'*S*)-bis(2-(6-methoxynaphthalen-2-yl)propanoate) (*Z*-**3aF**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.62 (m, 5H), 7.60 (s, 1H), 7.41–7.33 (m, 2H), 7.20–7.07 (m, 11H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 7.0 Hz, 2H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.49 (s, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 5.04 (d, *J* = 12.5 Hz, 1H), 5.01 (d, *J* = 12.6 Hz, 1H), 4.92 (d, *J* = 12.6 Hz, 1H), 4.28 (t, *J* = 8.0 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.93–3.81 (m, 2H), 2.91 (dd, *J* = 15.5, 8.3 Hz, 1H), 2.76 (dd, *J* = 15.5, 7.7 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.54 (d, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.62, 174.58, 171.96, 157.72, 144.58, 141.16, 139.90, 139.89, 136.72, 135.61, 134.56, 134.29, 133.79, 133.77, 129.40, 129.27, 129.14, 129.00, 128.98, 128.54, 128.33, 128.07, 127.63, 127.30, 127.26, 127.23, 127.03, 126.37, 126.12, 126.07, 119.09, 105.65, 105.63, 66.32, 66.29, 60.66, 55.42, 50.67, 45.55, 45.51, 39.04, 18.66, 14.32.

HRMS (ESI, *m*/*z*) calcd for $C_{55}H_{52}NaO_8$ $[M+Na]^+$: 863.3554, found: 863.3558.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ba** was obtained in 89% yield, *E*/*Z* = 1:2.6 (81.5 mg, colorless oil).



E-**3ba** *Z*-**3ba**

Dimethyl 4,4'-(5-methoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3ba**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.28–7.18 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 5.05 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.60 (s, 3H), 2.93 (dd, *J* = 15.7, 7.2 Hz, 1H), 2.80 (dd, *J* = 15.7, 8.2 Hz, 1H).

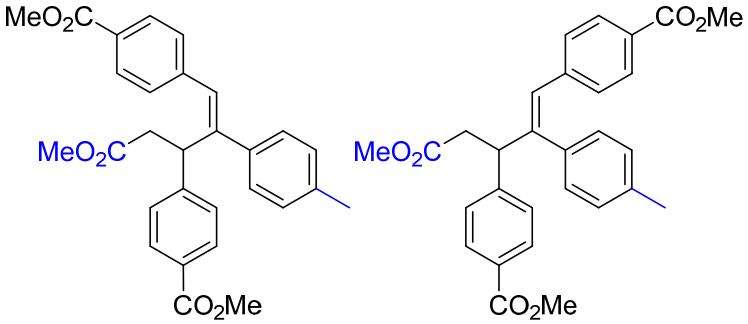
Dimethyl 4,4'-(5-methoxy-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3ba**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.23–7.19 (m, 3H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.57 (s, 1H), 4.42 (t, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.62 (s, 3H), 3.01 (dd, *J* = 15.7, 7.8 Hz, 1H), 2.87 (dd, *J* = 15.7, 8.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.09, 172.03, 166.99, 166.97, 166.90, 146.53, 146.32, 146.24, 144.95, 142.07, 141.40, 140.53, 139.15, 131.05, 129.99, 129.88, 129.84, 129.24, 129.11, 128.99, 128.97, 128.89, 128.84, 128.71, 128.30, 128.16, 128.06, 127.71, 127.70, 127.62, 127.10, 52.23, 52.17, 52.06, 51.94, 51.88, 50.84, 41.34, 38.40, 36.94.

HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{26}NaO_6$ $[M+Na]^+$: 481.1622, found: 481.1621.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ca** was obtained in 84% yield, *E*/*Z* = 1:3 (79.3 mg, colorless oil).



E-**3ca** *Z*-**3ca**

Dimethyl 4,4'-(5-methoxy-5-oxo-2-(*p*-tolyl)pent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3ca**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.73 (s, 1H), 5.04 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.59 (s, 3H), 2.93 (dd, *J* = 15.8, 7.1 Hz, 1H), 2.80 (dd, *J* = 15.8, 8.2 Hz, 1H), 2.31 (s, 3H).

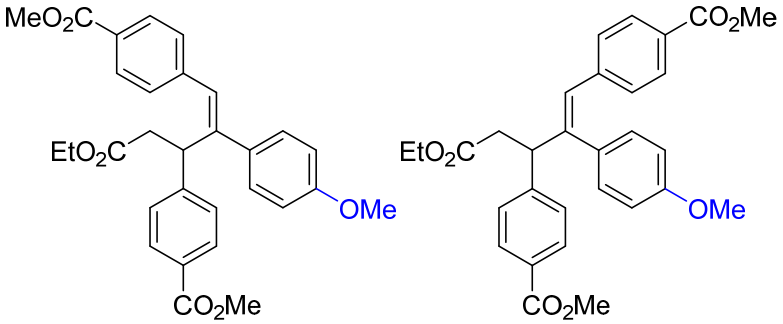
Dimethyl 4,4'-(5-methoxy-5-oxo-2-(*p*-tolyl)pent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3ca**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 7.1 Hz, 2H), 6.54 (s, 1H), 4.40 (t, *J* = 7.8 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.62 (s, 3H), 3.00 (dd, *J* = 15.7, 7.7 Hz, 1H), 2.85 (dd, *J* = 15.7, 8.1 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.12, 172.07, 167.00, 166.96, 166.92, 146.66, 146.38, 144.81, 142.20, 141.60, 137.57, 137.43, 137.39, 136.02, 130.69, 129.94, 129.83, 129.81, 129.41, 129.21, 129.08, 128.88, 128.81, 128.78, 128.74, 128.63, 128.52, 128.29, 128.03, 127.59, 126.94, 52.20, 52.15, 52.03, 51.90, 51.85, 50.85, 41.29, 38.39, 36.97, 21.28, 21.18.

HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{28}NaO_6$ $[M+Na]^+$: 495.1778, found: 495.1781.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3da** was obtained in 83% yield, *E*/*Z* = 1:3.9 (83.4 mg, colorless oil).



E-**3da** *Z*-**3da**

Dimethyl 4,4'-(5-ethoxy-2-(4-methoxyphenyl)-5-oxopent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3da**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.73 (s, 1H), 5.05 (t, *J* = 7.6 Hz, 1H), 4.08–4.00 (m, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.78 (s, 3H), 2.93 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.77 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

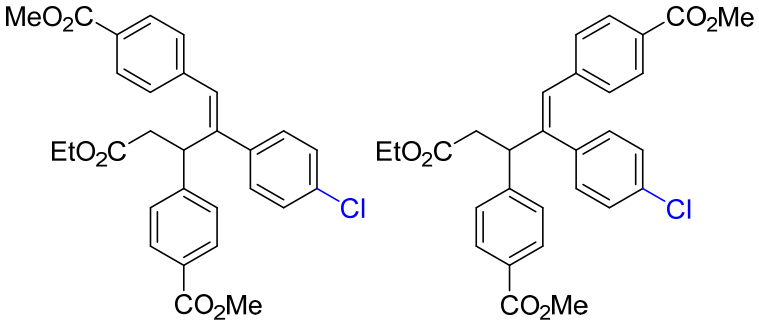
Dimethyl 4,4'-(5-ethoxy-2-(4-methoxyphenyl)-5-oxopent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3da**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 6.55 (s, 1H), 4.39 (t, *J* = 7.9 Hz, 1H), 4.13–4.05 (m, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H), 2.98 (dd, *J* = 15.6, 7.9 Hz, 1H), 2.84 (dd, *J* = 15.6, 8.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.75, 171.69, 167.08, 167.05, 167.01, 159.17, 159.08, 146.80, 146.52, 146.05, 144.52, 142.28, 141.73, 132.97, 131.23, 130.80, 130.48, 130.23, 129.99, 129.86, 129.82, 129.29, 129.12, 128.89, 128.87, 128.77, 128.66, 128.34, 128.06, 127.62, 127.04, 114.13, 113.45, 60.79, 55.34, 55.24, 52.26, 52.21, 52.10, 51.03, 41.35, 38.71, 37.30, 14.32, 14.23.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}NaO_7$ $[M+Na]^+$: 525.1884, found: 525.1884.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ea** was obtained in 60% yield, *E*/*Z* = 1:2.8 (60.7 mg, colorless oil).



E-**3ea** *Z*-**3ea**

Dimethyl 4,4'-(2-(4-chlorophenyl)-5-ethoxy-5-oxopent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3ea**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.22–7.12 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 5.06 (t, *J* = 7.6 Hz, 1H), 4.15–4.05 (m, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 2.91 (dd, *J* = 15.5, 7.1 Hz, 1H), 2.75 (dd, *J* = 15.5, 8.4 Hz, 1H), 1.15 (t, *J* = 7.3 Hz, 3H).

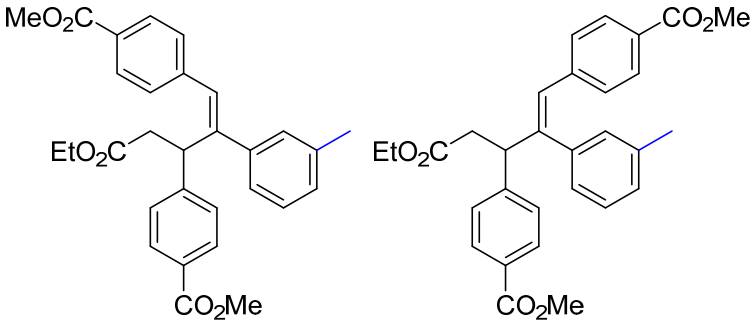
Dimethyl 4,4'-(2-(4-chlorophenyl)-5-ethoxy-5-oxopent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3ea**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 6.64 (s, 1H), 4.38 (t, *J* = 7.9 Hz, 1H), 4.11–4.01 (m, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 2.99 (dd, *J* = 15.6, 8.2 Hz, 1H), 2.85 (dd, *J* = 15.6, 7.7 Hz, 1H), 1.17 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.46, 171.43, 166.91, 166.89, 166.82, 166.79, 146.18, 145.95, 144.93, 143.91, 141.67, 141.03, 138.99, 137.63, 133.68, 131.42, 130.47, 130.05, 130.03, 129.95, 129.92, 129.37, 129.10, 128.98, 128.85, 128.82, 128.41, 128.24, 127.55, 127.53, 60.86, 52.26, 52.22, 52.13, 50.73, 41.23, 38.64, 37.01, 14.29, 14.19.

HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{27}ClNaO_6$ $[M+Na]^+$: 529.1388, found: 529.1386.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3fa** was obtained in 88% yield, *E*/*Z* = 1:3.0 (85.5 mg, colorless oil).



E-**3fa** *Z*-**3fa**

Dimethyl 4,4'-(5-ethoxy-5-oxo-2-(*m*-tolyl)pent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3fa**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.11–7.01(m, 2H), 6.82 (s, 1H), 6.74–8.68 (m, 2H), 5.06 (t, *J* = 7.6 Hz, 1H), 4.14–4.01 (m, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 2.92 (dd, *J* = 15.5, 7.3 Hz, 1H), 2.78 (dd, *J* = 15.5, 7.7 Hz, 1H), 2.27 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

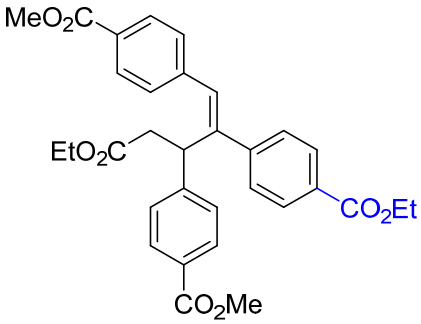
Dimethyl 4,4'-(5-ethoxy-5-oxo-2-(*m*-tolyl)pent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3fa**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.10–7.02 (m, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.71 (s, 1H), 6.62 (d, *J* = 7.1 Hz, 1H), 6.53 (s, 1H), 4.40 (t, *J* = 7.9 Hz, 1H), 4.14–4.01 (m, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 2.98 (dd, *J* = 15.6, 7.8 Hz, 1H), 2.84 (dd, *J* = 15.4, 8.1 Hz, 1H), 2.23 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

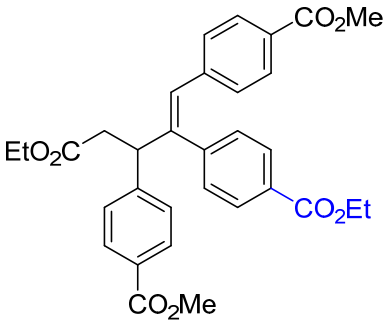
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.69, 171.61, 167.04, 167.01, 166.99, 166.95, 146.73, 146.53, 146.40, 145.16, 142.16, 141.49, 140.59, 139.13, 138.34, 137.64, 130.74, 130.31, 129.97, 129.81, 129.77, 129.54, 129.41, 129.23, 129.07, 128.88, 128.82, 128.62, 128.56, 128.44, 128.38, 128.09, 127.87, 127.68, 127.35, 126.92, 126.07, 125.69, 60.75, 52.34, 52.23, 52.18, 52.06, 50.98, 41.37, 38.69, 37.27, 21.55, 21.51, 14.29, 14.21.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}NaO_6$ $[M+Na]^+$: 509.1935, found: 509.1937.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ga** was obtained in 73% yield, *E*/*Z* = 1:2.5 (79.5 mg, colorless oil).



E-**3ga**



Z-**3ga**

Dimethyl 4,4'-(5-ethoxy-2-(4-(ethoxycarbonyl)phenyl)-5-oxopent-1-ene-1,3-diyl) (*E*)-dibenzoate (*E*-**3ga**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.98–7.86 (m, 4H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 5.09 (t, *J* = 7.7 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.10–4.00 (m, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 2.93 (dd, *J* = 15.6, 7.1 Hz, 1H), 2.76 (dd, *J* = 15.6, 8.4 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

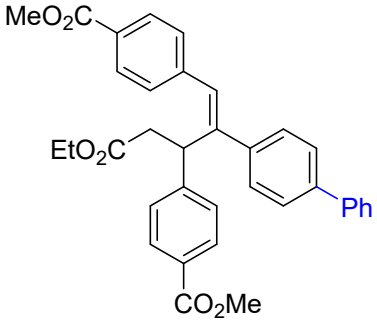
Dimethyl 4,4'-(5-ethoxy-2-(4-(ethoxycarbonyl)phenyl)-5-oxopent-1-ene-1,3-diyl) (*Z*)-dibenzoate (*Z*-**3ga**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 1H), 4.42 (t, *J* = 7.9 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.15–4.04 (m, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 3.01 (dd, *J* = 15.6, 8.1 Hz, 1H), 2.86 (dd, *J* = 15.6, 7.8 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.3 Hz, 3H).

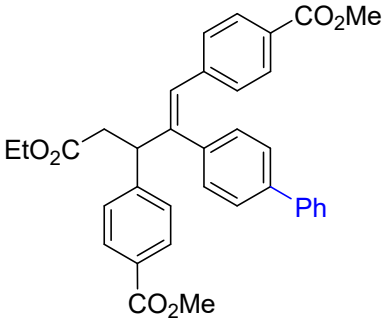
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.41, 171.35, 166.87, 166.85, 166.76, 166.35, 166.29, 146.14, 145.83, 145.28, 145.21, 144.27, 144.17, 141.55, 140.89, 131.74, 130.29, 130.03, 129.94, 129.92, 129.88, 129.73, 129.72, 129.35, 129.28, 129.17, 129.15, 129.11, 128.84, 128.71, 128.48, 128.24, 127.54, 127.52, 127.33, 61.14, 61.10, 60.86, 60.85, 52.30, 52.25, 52.19, 52.10, 50.62, 41.25, 38.66, 37.04, 14.40, 14.38, 14.28, 14.19.

HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{32}NaO_8$ $[M+Na]^+$: 567.1989, found: 567.1990.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ha** was obtained in 53% yield, *E*/*Z* = 1:3.1 (58.1 mg, colorless oil).



***E*-3ha**



***Z*-3ha**

Dimethyl 4,4'-(2-([1,1'-biphenyl]-4-yl)-5-ethoxy-5-oxopent-1-ene-1,3-diyl) (*E*)-dibenzoate (*E*-**3ha**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.60–7.52 (m, 4H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.36–7.30 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 5.11 (t, *J* = 7.6 Hz, 1H), 4.10–4.00 (m, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 2.98 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.83 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

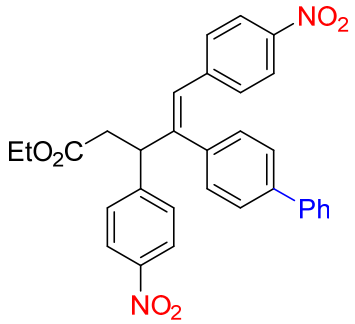
Dimethyl 4,4'-(2-([1,1'-biphenyl]-4-yl)-5-ethoxy-5-oxopent-1-ene-1,3-diyl) (*Z*)-dibenzoate (*Z*-**3ha**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.45–7.38 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 4.45 (t, *J* = 7.9 Hz, 1H), 4.15–4.03 (m, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 3.02 (dd, *J* = 15.6, 7.9 Hz, 1H), 2.87 (dd, *J* = 15.6, 7.9 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.68, 171.58, 167.01, 166.98, 166.91, 146.66, 146.34, 145.97, 144.61, 142.05, 141.44, 140.52, 140.46, 140.37, 140.32, 139.58, 138.17, 131.07, 130.01, 129.91, 129.48, 129.32, 129.15, 129.09, 128.98, 128.91, 128.89, 128.74, 128.37, 128.22, 127.64, 127.56, 127.53, 127.35, 127.30, 127.28, 127.06, 127.02, 126.73, 60.82, 52.25, 52.21, 52.19, 52.08, 50.88, 41.30, 38.77, 37.29, 14.31, 14.22.

HRMS (ESI, *m*/*z*) calcd for $C_{35}H_{32}NaO_6$ $[M+Na]^+$: 571.2091, found: 571.2093.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 6:1), the product *Z*-**3hl** was obtained in 43% yield (44.9 mg, light yellow solid), *E*/*Z* = 1:6.



Z-**3hl**

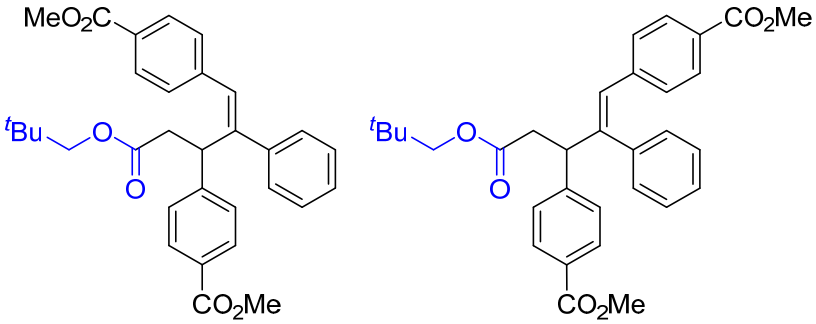
Ethyl (*Z*)-4-([1,1'-biphenyl]-4-yl)-3,5-bis(4-nitrophenyl)pent-4-enoate (*Z*-**3hl)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.48–7.33 (m, 5H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.65 (s, 1H), 4.54 (t, *J* = 7.9 Hz, 1H), 4.16–4.08 (m, 2H), 3.07 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.91 (dd, *J* = 15.8, 8.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.11, 148.29, 147.38, 147.17, 146.34, 143.20, 141.02, 139.97, 137.18, 129.86, 129.30, 129.20, 129.00, 127.86, 127.64, 127.04, 126.61, 123.94, 123.44, 61.09, 50.74, 38.54, 14.32.

HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{26}N_2NaO6$ $[M+Na]^+$: 545.1683, found: 545.1684.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3ia** was obtained in 73% yield, *E*/*Z* = 1:3.3 (75.2 mg, colorless oil).



E-**3ia** *Z*-**3ia**

Dimethyl 4,4'-(5-(neopentyloxy)-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3ia**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.30–7.18 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.73 (s, 1H), 5.10 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.76–3.66 (m, 2H), 2.97 (dd, *J* = 15.6, 7.9 Hz, 1H), 2.83 (dd, *J* = 15.6, 7.4 Hz, 1H), 0.81 (s, 9H).

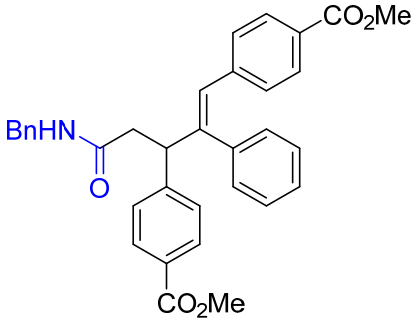
Dimethyl 4,4'-(5-(neopentyloxy)-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3ia**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.24–7.19 (m, 3H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.59 (s, 1H), 4.43 (t, *J* = 7.9 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.76–3.66 (m, 2H), 3.03 (dd, *J* = 15.6, 7.7 Hz, 1H), 2.89 (dd, *J* = 15.6, 8.1 Hz, 1H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.76, 167.00, 166.98, 166.97, 166.91, 146.53, 146.36, 146.30, 145.17, 142.05, 141.39, 140.56, 139.09, 130.81, 130.31, 130.03, 129.87, 129.83, 129.24, 129.11, 129.00, 128.92, 128.90, 128.87, 128.73, 128.68, 128.33, 128.13, 128.06, 127.71, 127.68, 127.35, 127.15, 74.23, 52.24, 52.19, 52.07, 50.97, 41.37, 38.60, 37.24, 31.30, 31.23, 26.45, 26.40.

HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{34}NaO_6$ $[M+Na]^+$: 537.2248, found: 537.2249.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 6:1), the product *Z*-**3ja** was obtained in 40% yield (42.5 mg, colorless oil), *E*/*Z* = 1:2.5.



Z-**3ja**

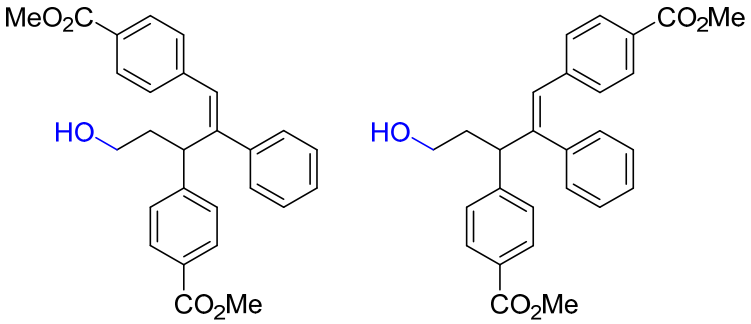
Dimethyl 4,4'-(5-(benzylamino)-5-oxo-2-phenylpent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3ja**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.24–7.10 (m, 6H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.60 (s, 1H), 6.00 (t, *J* = 5.6 Hz, 1H), 4.52 (t, *J* = 7.7 Hz, 1H), 4.33 (d, *J* = 5.7 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 2.90 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.72 (dd, *J* = 14.4, 8.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.42, 167.06, 166.99, 146.67, 146.54, 141.52, 139.32, 138.05, 129.90, 129.23, 129.18, 129.01, 128.84, 128.68, 128.66, 128.44, 128.06, 127.67, 127.63, 127.50, 126.92, 52.20, 52.09, 51.01, 43.57, 40.90.

HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{31}NNaO_5$ $[M+Na]^+$: 556.2094, found: 556.2094.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 5:1), the product **3ka** was obtained in 58% yield, *E*/*Z* = 1:2.1 (49.5 mg, colorless oil).



E-**3ka** *Z*-**3ka**

Dimethyl 4,4'-(5-hydroxy-2-phenylpent-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3ka**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.26–7.17 (m, 5H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.79 (s, 1H), 4.67 (dd, *J* = 8.5, 6.8 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.29–2.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.16, 167.01, 147.62, 145.83, 142.32, 140.80, 131.15, 130.03, 129.78, 128.92, 128.87, 128.68, 128.49, 128.07, 128.05, 127.61, 60.75, 52.31, 52.23, 41.36, 34.25.

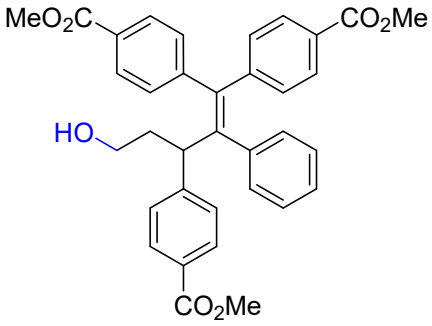
HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{26}NaO_5$ $[M+Na]^+$: 453.1672, found:453.1675.

Dimethyl 4,4'-(5-hydroxy-2-phenylpent-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3ka**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.21–7.14 (m, 3H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.82–6.76 (m, 2H), 6.63 (s, 1H), 4.04 (t, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.72 (dt, *J* = 10.6, 6.2 Hz, 1H), 3.61 (dt, *J* = 10.6, 6.6 Hz, 1H), 2.31–2.05 (m, 2H), 2.03 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.17, 167.03, 147.44, 147.42, 141.71, 139.61, 129.74, 129.22, 129.07, 128.88, 128.57, 127.89, 127.46, 126.80, 60.53, 52.17, 52.07, 51.02, 35.80.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 5:1), the product **4ka** was obtained in 32% yield (36.1 mg, colorless oil).



4ka

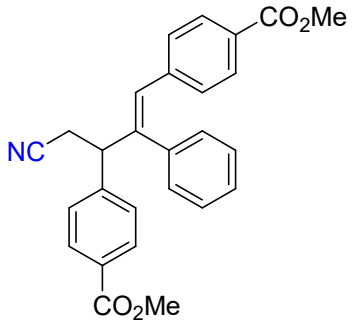
Trimethyl 4,4',4''-(5-hydroxy-2-phenylpent-1-ene-1,1,3-triyl)tribenzoate (**4ka**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.10–6.99 (m, 5H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.1 Hz, 2H), 4.36 (t, *J* = 7.6 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.79 (s, 3H), 3.75–3.60 (m, 2H), 2.14–1.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.14, 166.90, 146.97, 146.69, 146.56, 144.35, 140.21, 137.93, 130.69, 130.25, 130.07, 129.89, 129.60, 129.32, 129.01, 128.59, 128.51, 127.92, 127.65, 127.13, 60.76, 52.39, 52.24, 52.11, 44.49, 34.83.

HRMS (ESI, *m*/*z*) calcd for $C_{35}H_{32}NaO_7$ $[M+Na]^+$: 587.2040, found: 587.2042.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product *Z*-**3la** was obtained in 48% yield (40.8 mg, colorless oil), *E*/*Z* = 1:5.3.



Z-**3la**

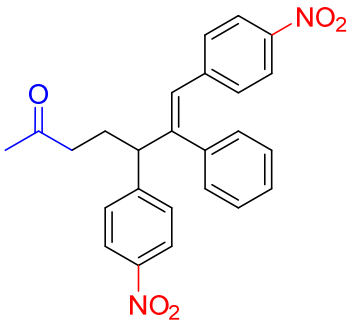
Dimethyl 4,4'-(4-cyano-2-phenylbut-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3la**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.28–7.20 (m, 3H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.85 (dd, *J* = 8.0, 1.4 Hz, 2H), 6.64 (s, 1H), 4.25 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 2.92 (dd, *J* = 16.7, 7.9 Hz, 1H), 2.84 (dd, *J* = 16.7, 7.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.85, 166.75, 143.94, 143.81, 140.64, 137.66, 130.22, 129.79, 129.33, 129.26, 129.15, 129.05, 128.99, 128.61, 128.26, 128.09, 118.12, 52.36, 52.16, 51.04, 21.82.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{23}NNaO_4$ $[M+Na]^+$: 448.1519, found: 448.1516.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product *Z*-**3ml** was obtained in 50% yield (43 mg, colorless oil), *E*/*Z* = 1:5.



Z-**3ml**

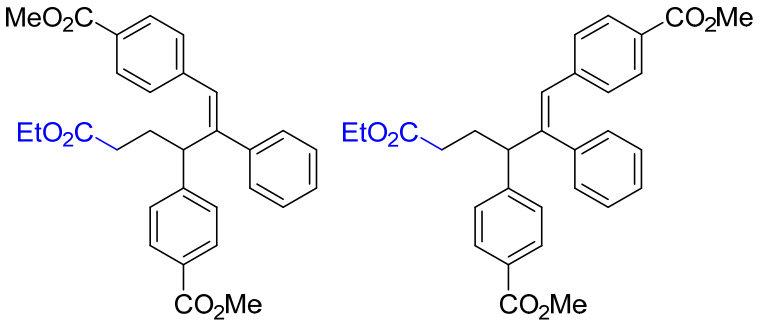
(*Z*)-5,7-Bis(4-nitrophenyl)-6-phenylhept-6-en-2-one (*Z*-**3ml**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.32–7.20 (m, 5H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 7.2 Hz, 2H), 6.67 (s, 1H), 3.88 (t, *J* = 7.6 Hz, 1H), 2.57–2.41 (m, 2H), 2.39–2.29 (m, 1H), 2.23–2.13 (m, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.73, 149.18, 148.68, 147.06, 146.24, 143.36, 138.73, 129.82, 129.29, 129.06, 128.63, 128.20, 126.21, 123.88, 123.37, 54.06, 41.31, 30.30, 26.88.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{22}N_2NaO_5$ $[M+Na]^+$: 453.1421, found: 453.1421.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 8:1), the product **3na** was obtained in 52% yield, *E*/*Z* = 1:4.2 (50.6 mg, colorless oil).



E-**3na** *Z*-**3na**

Dimethyl 4,4'-(6-ethoxy-6-oxo-2-phenylhex-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3na**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.28–7.15 (m, 7H), 6.99 (d, *J* = 6.9 Hz, 2H), 6.78 (s, 1H), 4.42 (t, *J* = 8.0 Hz, 1H), 4.06–3.97 (m, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 2.42–2.14 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.09, 167.08, 166.93, 147.15, 145.54, 142.21, 140.43, 131.32, 129.94, 129.78, 128.82, 128.80, 128.68, 128.58, 128.11, 128.03, 127.62, 60.57, 52.27, 44.47, 32.08, 26.61, 14.25.

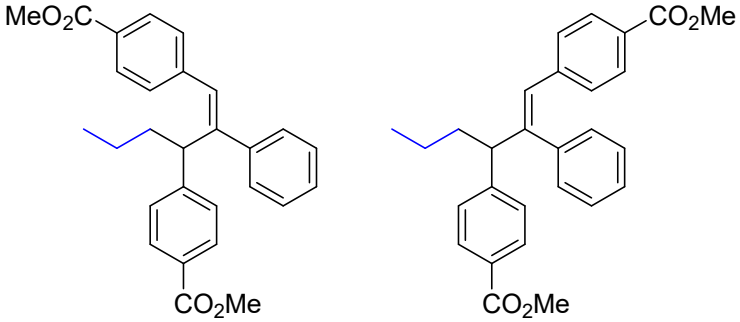
HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}NaO_6$ $[M+Na]^+$: 509.1935, found: 509.1934.

Dimethyl 4,4'-(6-ethoxy-6-oxo-2-phenylhex-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3na**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.28–7.15 (m, 5H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.64 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.86–3.76 (m, 1H), 3.83 (s, 3H), 2.42–2.14 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.26, 167.07, 166.94, 147.02, 141.59, 139.60, 129.84, 129.26, 129.12, 128.84, 128.80, 128.65, 128.54, 128.07, 127.54, 127.00, 60.60, 54.41, 52.18, 52.07, 32.56, 28.35, 14.33.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **3qa** was obtained in 46% yield, *E*/*Z* = 1:5.1 (39 mg, colorless oil).



E-**3qa** *Z*-**3qa**

Dimethyl 4,4'-(2-phenylhex-1-ene-1,3-diyl)(*E*)-dibenzoate (*E*-**3qa**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.95–7.90 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.27–7.14 (m, 5H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.91–3.86 (m, 1H), 2.00–1.78 (m, 2H), 1.48–1.24 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.01, 146.83, 144.43, 142.66, 140.96, 130.39, 130.31, 129.88, 129.60, 128.91, 128.72, 128.18, 127.81, 52.34, 52.25, 45.03, 33.81, 20.88, 14.22.

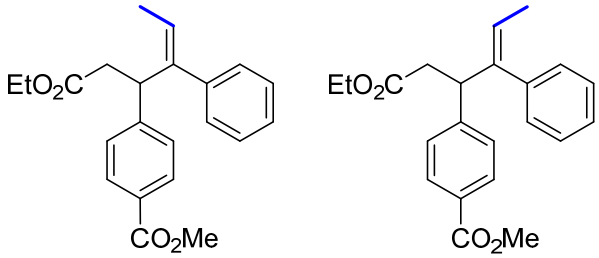
HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{28}NaO_4$ $[M+Na]^+$: 451.1880, found: 451.1882.

Dimethyl 4,4'-(2-phenylhex-1-ene-1,3-diyl)(*Z*)-dibenzoate (*Z*-**3qa**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.25–7.14 (m, 5H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 7.7 Hz, 2H), 6.61 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.76 (t, *J* = 7.5 Hz, 1H), 2.00–1.78 (m, 2H), 1.48–1.24 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.20, 166.99, 148.23, 148.07, 141.91, 140.00, 129.65, 129.23, 129.07, 128.85, 128.56, 128.54, 128.41, 127.86, 127.36, 126.56, 55.10, 52.13, 52.05, 35.42, 21.07, 14.18.

Following the **General Procedure A**, after purification by flash chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1), the product **5ra** was obtained in 67% yield, *E*/*Z* = 1:1.8 (47.3 mg, colorless oil).



E-**5ra** *Z*-**5ra**

Methyl (*E*)-4-(1-ethoxy-1-oxo-4-phenylhex-4-en-3-yl)benzoate (*E*-**5ra**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.27–7.11 (m, 5H), 6.81 (d, *J* = 7.0 Hz, 2H), 5.68 (q, *J* = 7.1 Hz, 1H), 4.84 (t, *J* = 7.7 Hz, 1H), 4.14–4.01 (m, 2H), 3.90 (s, 3H), 2.88 (dd, *J* = 15.4, 7.5 Hz, 1H), 2.72 (dd, *J* = 15.4, 8.0 Hz, 1H), 1.95 (d, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

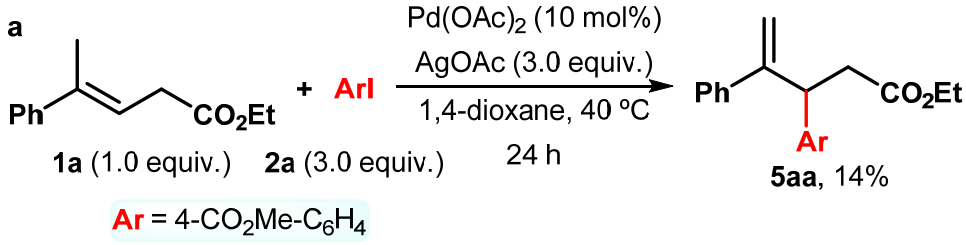
Methyl (*Z*)-4-(1-ethoxy-1-oxo-4-phenylhex-4-en-3-yl)benzoate (*Z*-**5ra**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.27–7.11 (m, 5H), 6.86 (d, *J* = 7.0 Hz, 2H), 5.66 (q, *J* = 6.8 Hz, 1H), 4.22 (t, *J* = 8.0 Hz, 1H), 4.14–4.01 (m, 2H), 3.88 (s, 3H), 2.87 (dd, *J* = 15.4, 7.8 Hz, 1H), 2.72 (dd, *J* = 15.4, 8.3 Hz, 1H), 1.49 (d, *J* = 6.7 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

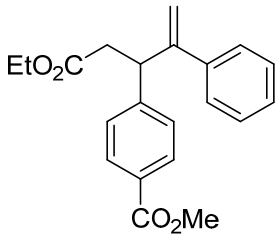
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.08, 171.91, 167.14, 167.12, 147.61, 147.44, 143.00, 142.27, 141.76, 139.63, 129.75, 129.64, 129.12, 128.63, 128.50, 128.35, 128.25, 128.06, 127.80, 127.64, 126.84, 126.81, 126.70, 122.89, 60.67, 60.55, 52.15, 52.11, 49.75, 41.16, 38.97, 37.17, 14.80, 14.34, 14.26.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{24}NaO_4$ $[M+Na]^+$: 375.1567, found: 375.1572.

6. Control Experiments



To an oven-dried 35 mL Schlenk tube with previously placed magnetic stir-bar were added aryl iodide **2a** (0.6 mmol, 3 equiv.), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 10 mol%), AgOAc (100 mg, 0.6 mmol, 3 equiv.), followed by addition of 1,4-dioxane (2 mL) and alkene **1a** (0.2 mmol). The tube was sealed with a screw cap and the reaction mixture was stirred vigorously at 40 °C. After stirring for 24 hours, the resultant solution was filtered through a short pad of 1:1 mixture of Celite and silica gel, and the column was washed with ethyl acetate (15 mL). The combined organic solutions were concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to afford the compound **5aa** (9.5 mg, 14% yield).



5aa

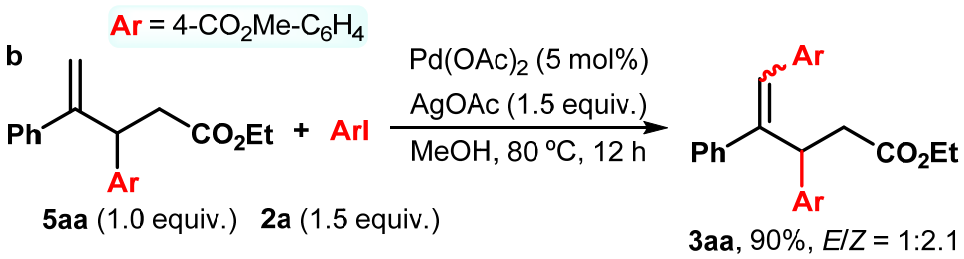
Methyl 4-(5-ethoxy-5-oxo-2-phenylpent-1-en-3-yl)benzoate (**5aa**)

9.5 mg, 14% yield, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.45–7.07 (m, 5H), 5.41 (s, 1H), 5.17 (s, 1H), 4.51 (t, *J* = 7.8 Hz, 1H), 4.12–4.00 (m, 2H), 3.87 (s, 3H), 2.95 (dd, *J* = 15.6, 7.5 Hz, 1H), 2.79 (dd, *J* = 15.6, 8.3 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

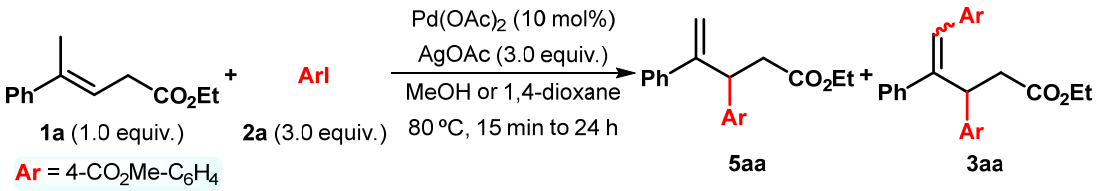
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.76, 167.09, 150.15, 147.22, 141.47, 129.95, 128.76, 128.37, 128.19, 127.72, 126.93, 113.89, 60.75, 52.18, 46.46, 40.25, 14.26.

HRMS (ESI, *m/z*) calcd for $C_{21}H_{22}NaO_4$ $[M+Na]^+$: 361.1410, found: 361.1412.



To an oven-dried 35 mL Schlenk tube with previously placed magnetic stir-bar were added aryl iodide **2a** (0.3 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5mol%), AgOAc (50.0 mg, 0.3 mmol, 1.5 equiv.), followed by addition of MeOH (2 mL) and **5aa** (68 mg, 0.2 mmol). The tube was sealed with a screw cap and the reaction mixture was stirred vigorously at 80 °C. After stirring for 12 hours, the resultant solution was filtered through a short pad of 1:1 mixture of Celite and silica gel, and the column was washed with ethyl acetate (15 mL). The combined organic solutions were concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to afford the desired **3aa** (85 mg, 90% yield, *E*/*Z* = 1:2.1).

Kinetic data of the model reaction in MeOH or 1,4-dioxane



The model reaction was conducted according to **General Procedure A** in either methanol or 1,4-dioxane for a duration ranging from 15 min to 24 hours. Following rapid cooling in a dry ice/acetone bath (−78°C), the reaction mixture was filtered through a short pad of Celite/silica gel (1:1 w/w), and thoroughly washed with ethyl acetate. The combined filtrate was concentrated under reduced pressure. The yields of **3aa** and **5aa** were determined by crude ^1H NMR analysis, using 1,1,2,2-tetrachloroethane as the internal standard. The average yields from two sets of experiments were plotted as yield (%) versus reaction time (hours).

x/hours Yield/%	0.25	0.5	1	1.5	2	3	4	8	12	16	20	24
3aa (MeOH)	34	44	66	81	85	87	87	90	91	91	92	93
5aa(MeOH)	0											
3aa(1,4-Dioxane)	0	0	0	0	0	0	10	21	43	76	82	90
5aa(1,4-Dioxane)	0	0	0	0	12	16	18	16	14	11	4	0

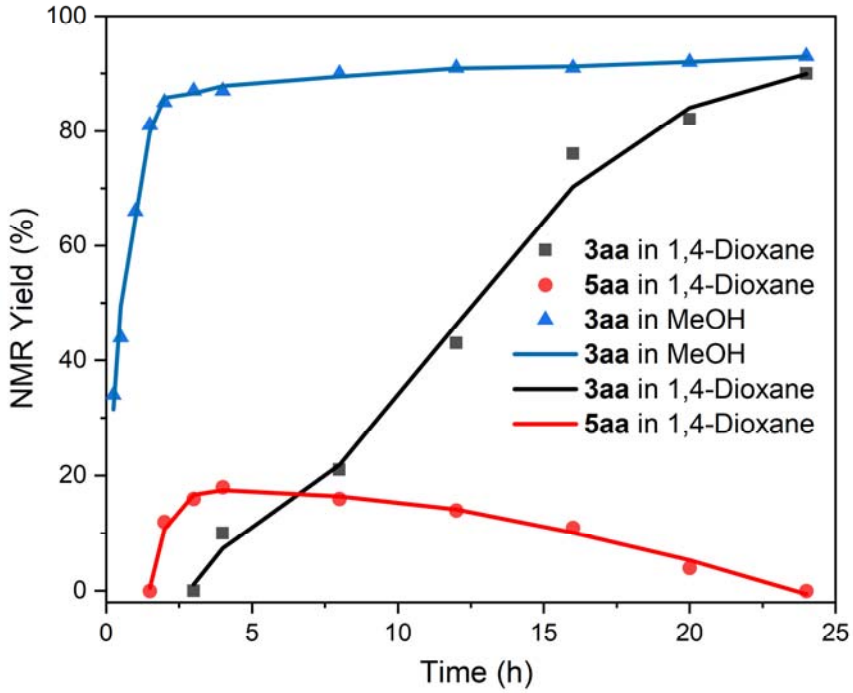
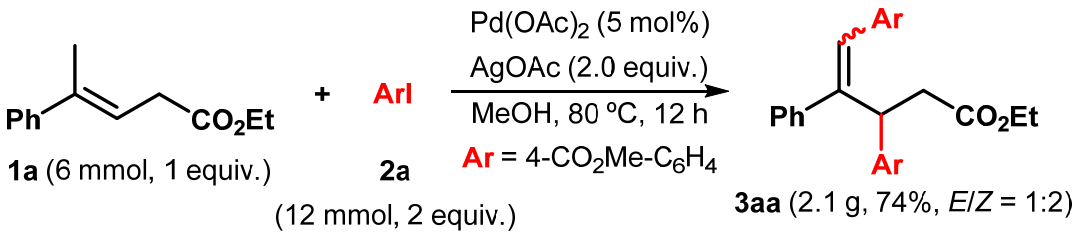


Figure S1. Kinetic investigation in different solvents

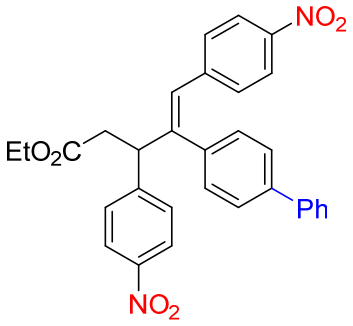
7. Gram-Scale Experiment



Gram-Scale Experiment: To an oven-dried 100 mL Schlenk tube (equipped with a magnetic stir bar), aryl iodide **2a** (3.15 g, 12 mmol, 2 equiv.), $Pd(OAc)_2$ (67.4 mg, 0.3 mmol, 5 mol%) and AgOAc (2.0 g, 12 mmol, 2 equiv.) were added, followed by addition of MeOH (60 mL) and alkene **1a** (1.22 g, 6 mmol, 1 equiv.). The tube was sealed with a screw cap, and the reaction mixture was warmed and stirred vigorously at 80 °C. After the reaction was complete (approximately 12 hours), the resulting solution was filtered through a short pad made from a 1:1 mixture of celite and silica gel (8 cm in diameter, 5 cm in length), which was then washed with ethyl acetate (60 mL). The combined organic solutions were concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (4 cm in diameter, 15 cm in length, eluent: ethyl acetate / petroleum ether) to afford the desired product **3aa** in 74% yield (2.1 g, light-yellow oil).

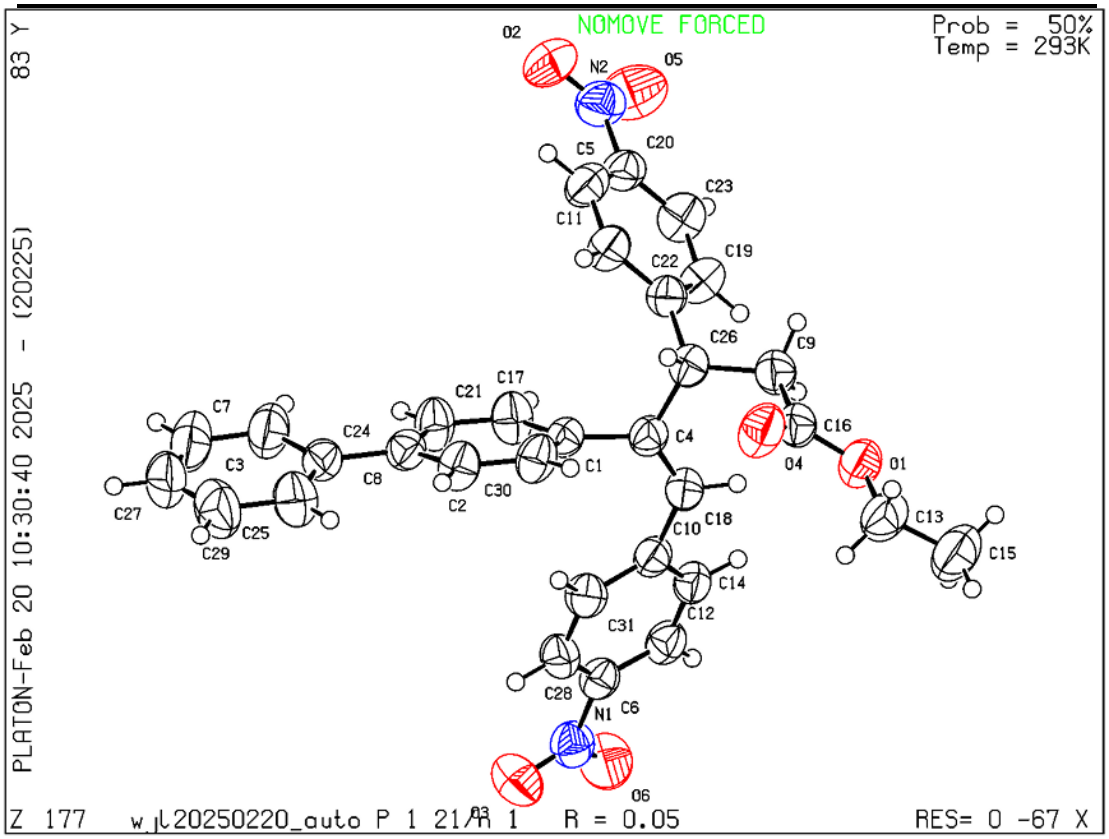
8. X-Ray Crystallographic Data of *Z*-3hl

After purification by flash chromatography on silica gel, the crystal was grown in a mixed solution of DCM/hexane, and the structure was determined by X-ray diffraction. Single-crystal X-ray diffraction (SCXRD) data were recorded using Rigaku Synergy S (Cu-Kα λ = 1.54184 Å). Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement. The relevant report was generated by Olex2 1.5.

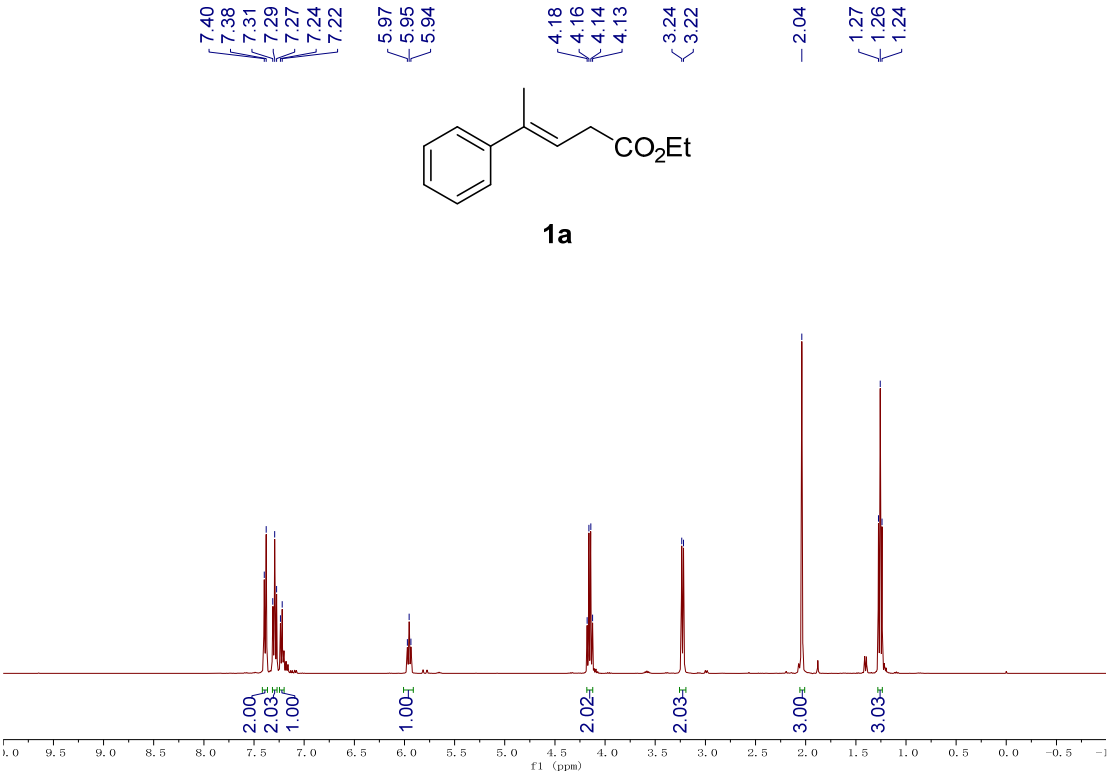


Crystal data and structure for (*Z*)-**3hl**	
Identification code	CCDC 2425608
Empirical formula	$C_{31}H_{26}N_2O_6$
Formula weight	522.54
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å,°)	a = 6.01910(10) α = 90
	b = 21.3231(3) β = 90.459(2)
	c = 20.4562(3) γ = 90
Volume (Å^3)	2625.38(7)
Z	4
Calculated density (g/cm^3)	1.322
Absorption coefficient (mm^{-1})	0.758
F_{000}	1096.0
Crystal size (mm^3)	0.4 × 0.2 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection (°)	5.988 to 133.164
Index ranges	$-7 \le h \le 7$, $-25 \le k \le 24$, $-24 \le l \le 22$

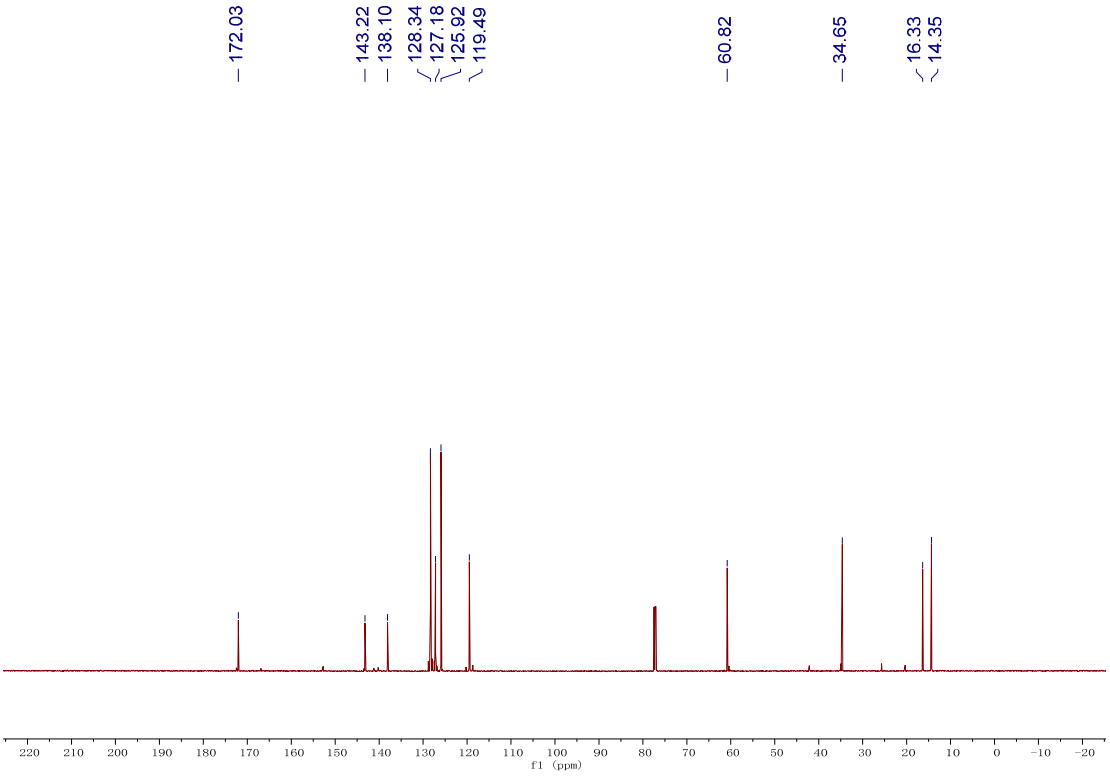
Reflections collected	26692
Independent reflections	4470 [R_{int} = 0.0507, R_{sigma} = 0.0239]
Data / restraints / parameters	4470 / 0 / 353
Goodness-of-fit on F^2	1.067
Final R indexes [I >=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1284
Final R indexes (all data)	R_1 = 0.0623, wR_2 = 0.1339
Largest diff. peak and hole (e Å^{-3})	0.17 / -0.17



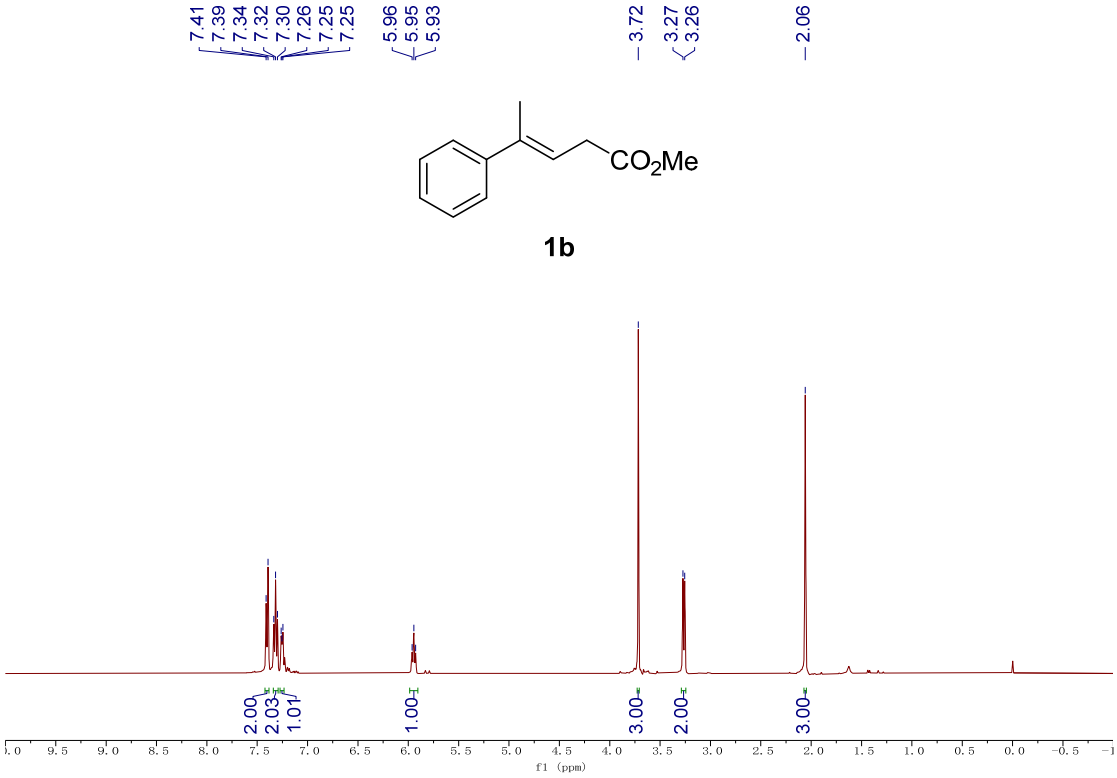
9. NMR Spectra



^{1}H NMR (400 MHz, $CDCl_3$) of **1a**

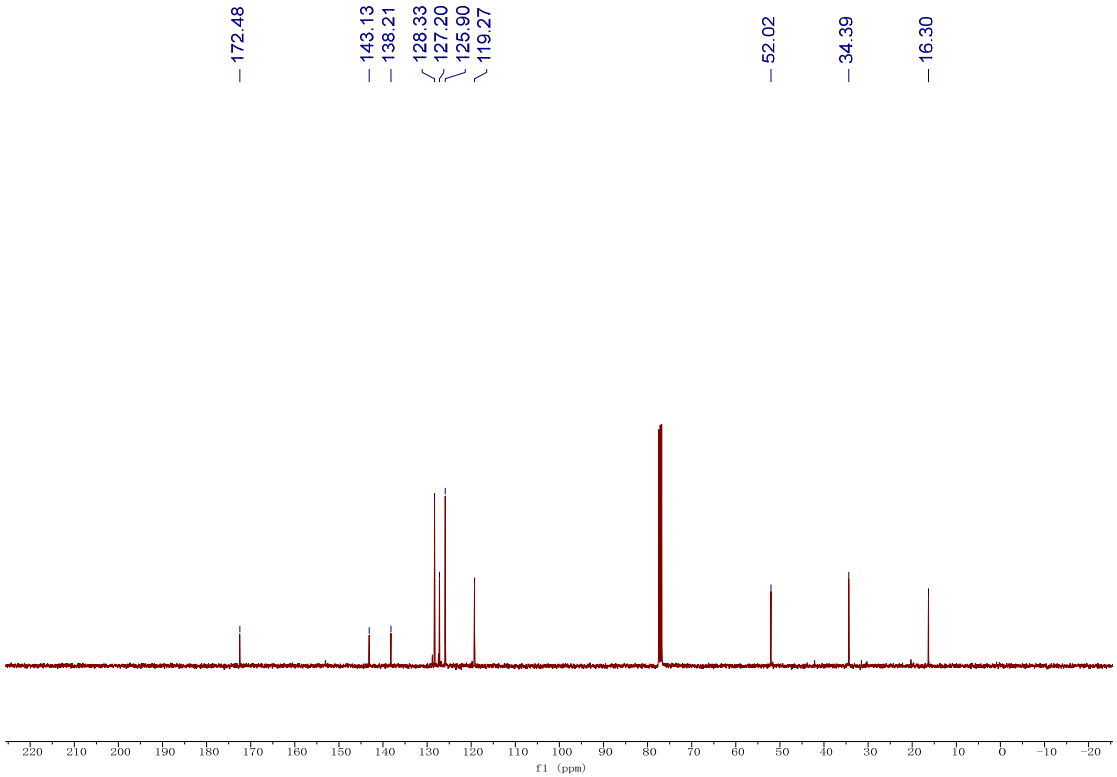


^{13}C NMR (101 MHz, $CDCl_3$) of **1a**

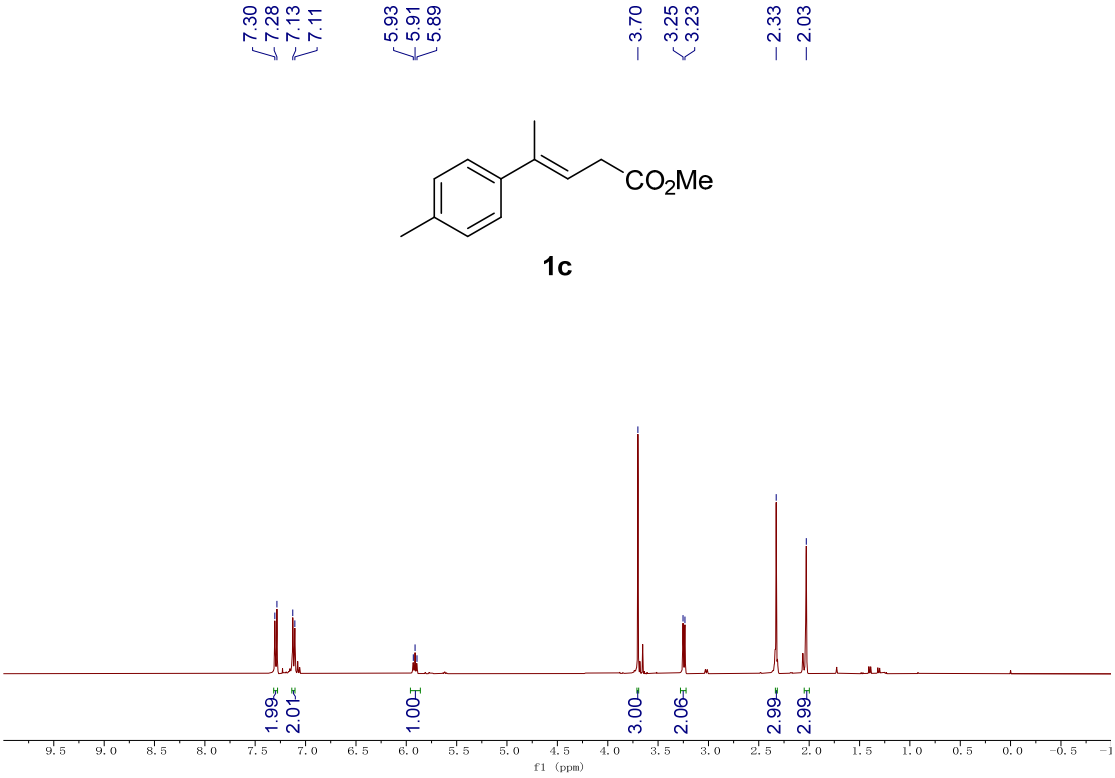


1b

^{1}H NMR (400 MHz, $CDCl_3$) of **1b**

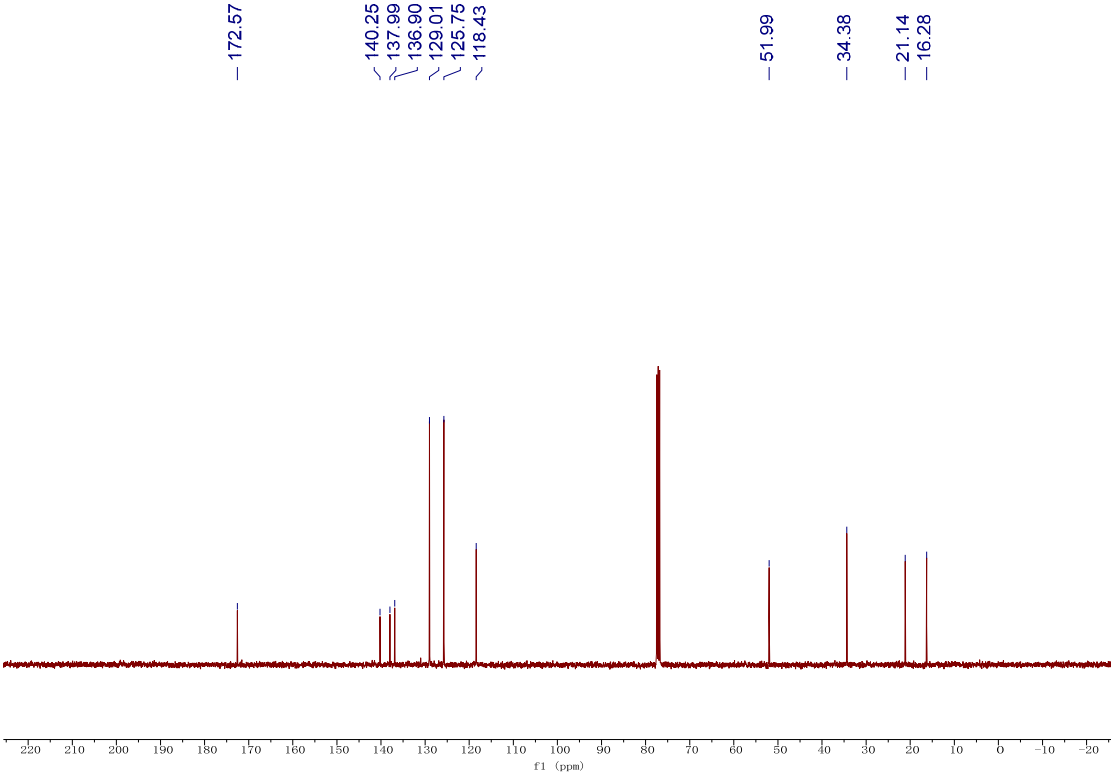


^{13}C NMR (101 MHz, $CDCl_3$) of **1b**

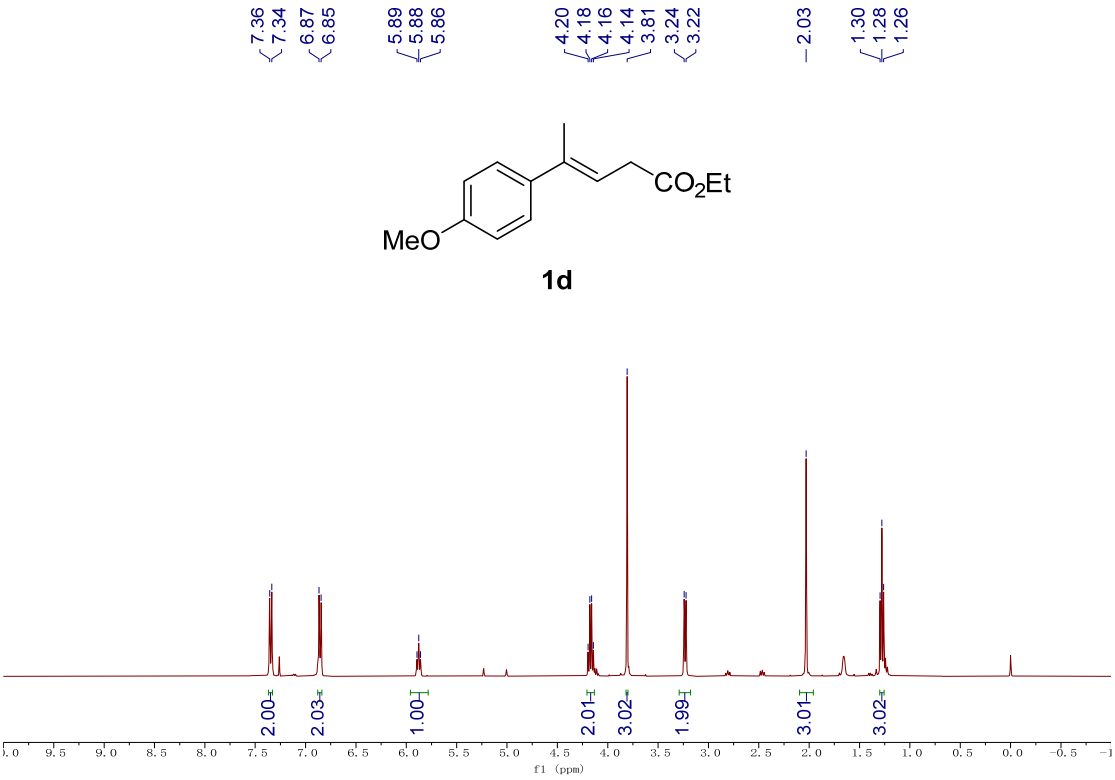


1c

^{1}H NMR (400 MHz, $CDCl_3$) of **1c**

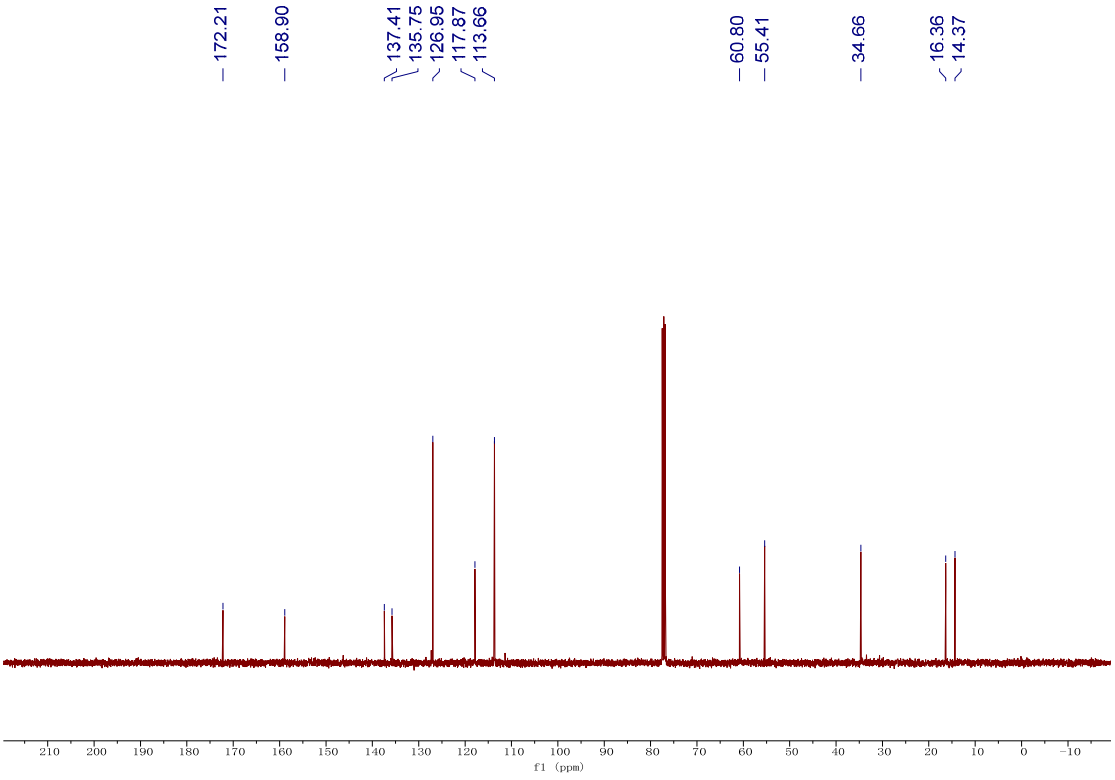


^{13}C NMR (101 MHz, $CDCl_3$) of **1c**

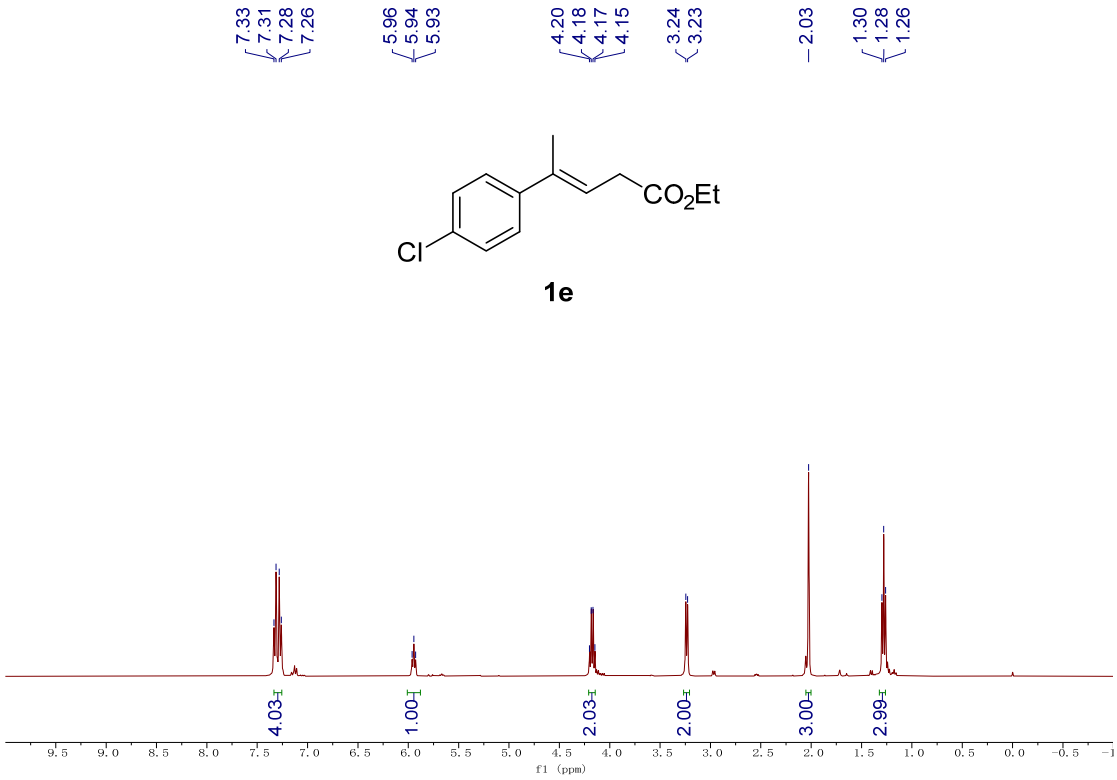


1d

^{1}H NMR (400 MHz, $CDCl_3$) of **1d**

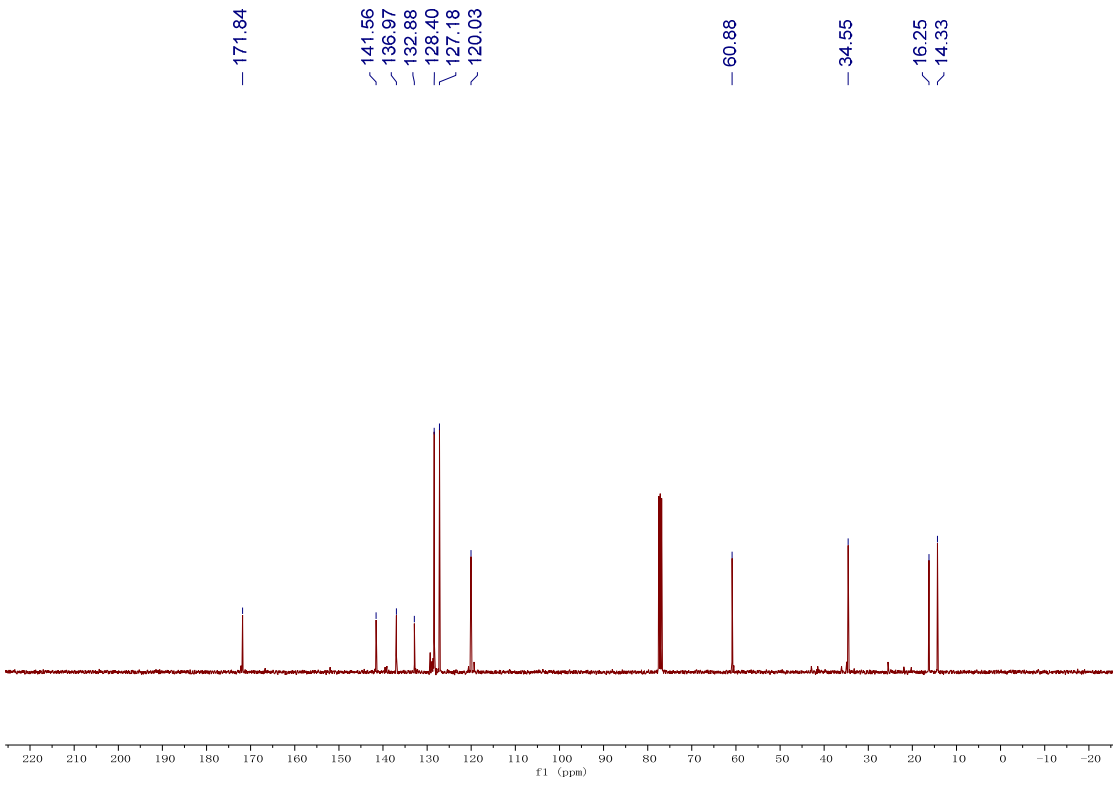


^{13}C NMR (101 MHz, $CDCl_3$) of **1d**

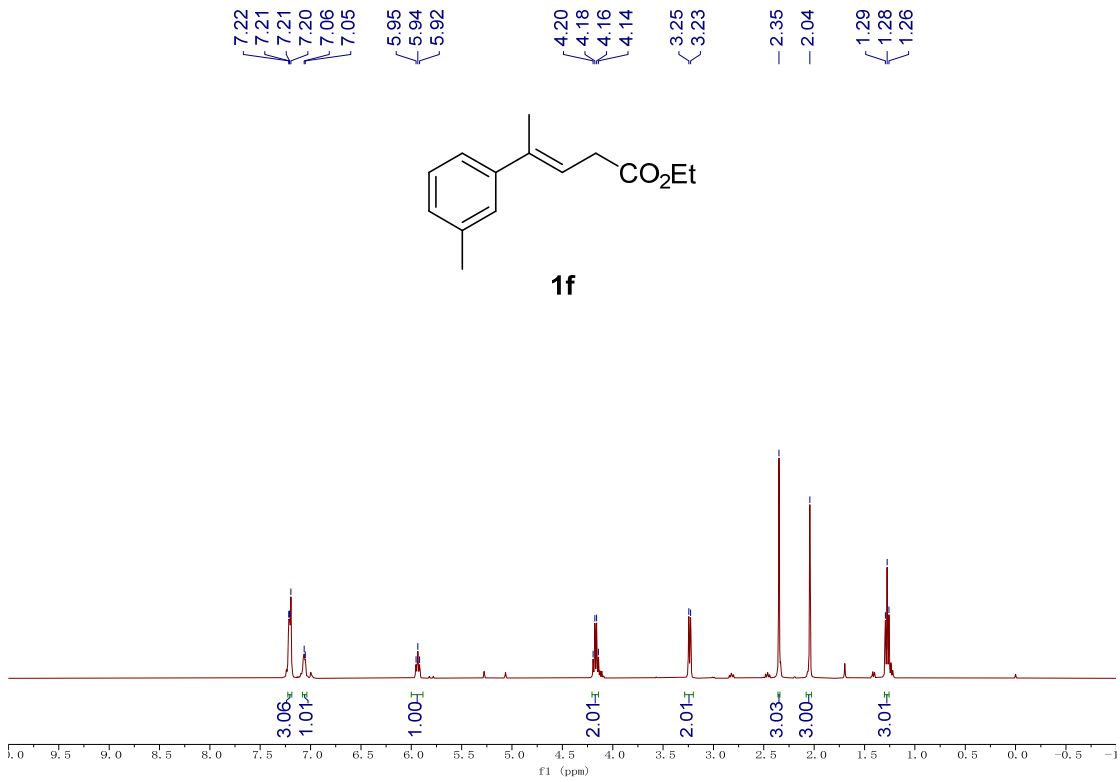


1e

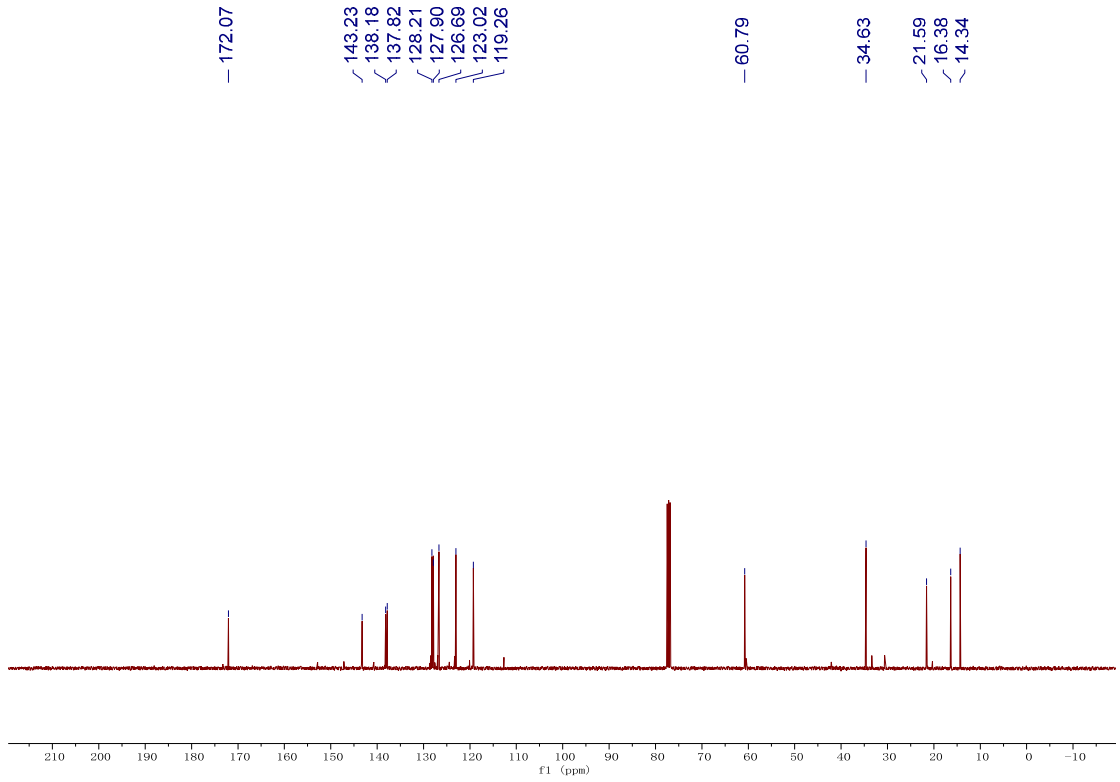
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



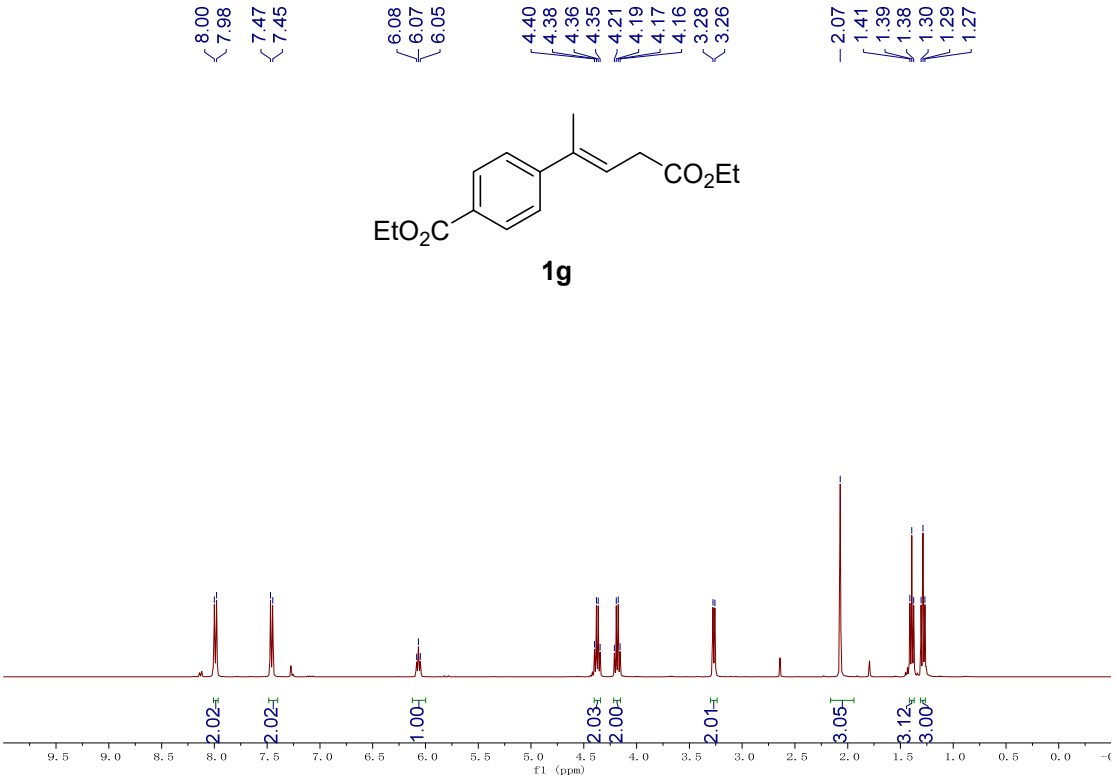
^{13}C NMR (101 MHz, $CDCl_3$) of **1e**



^{1}H NMR (400 MHz, $CDCl_3$) of **1f**

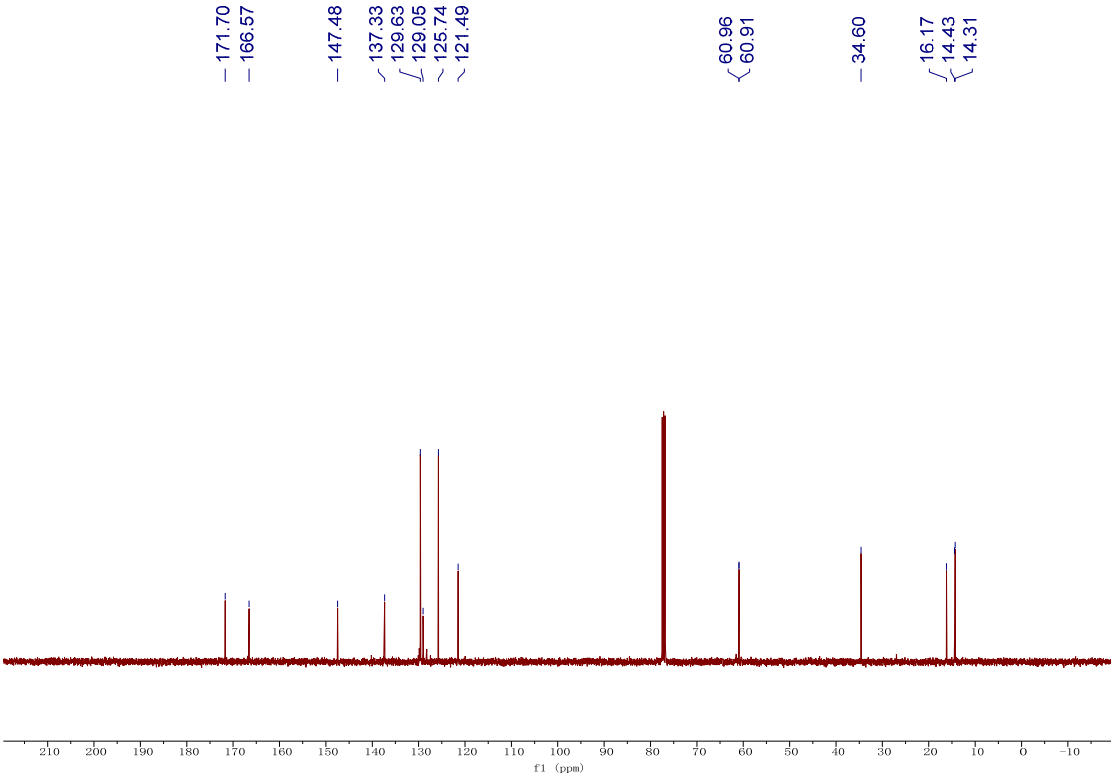


^{13}C NMR (101 MHz, $CDCl_3$) of **1f**

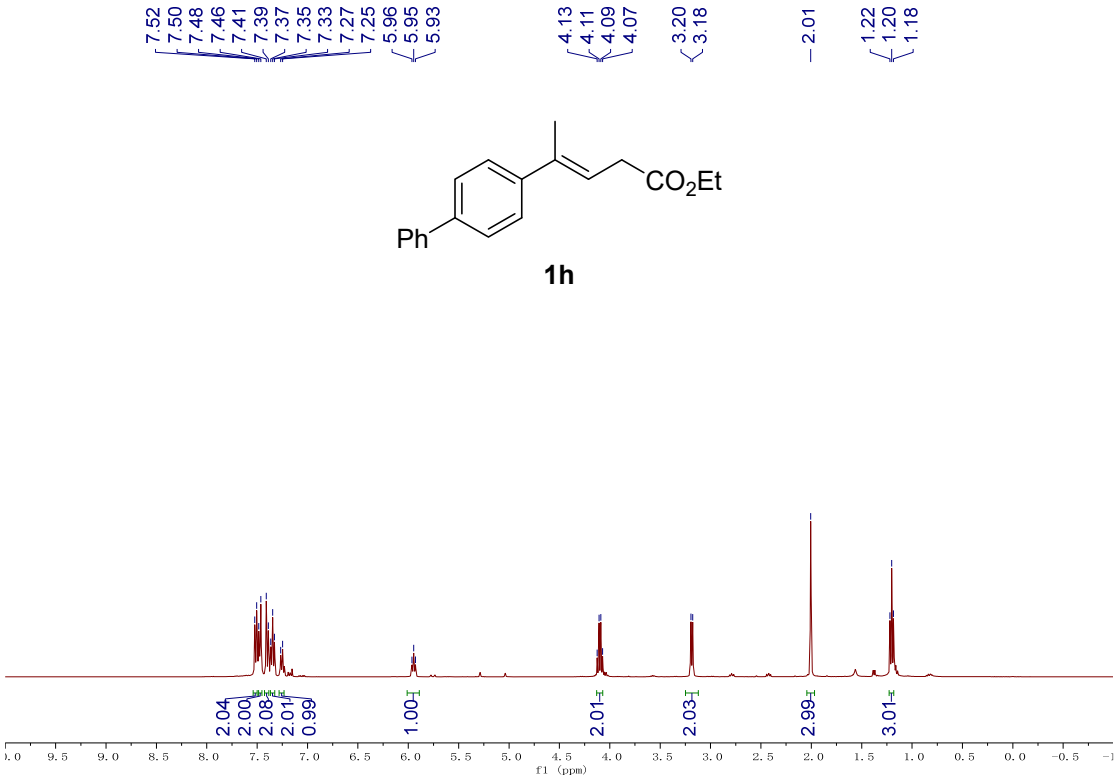


1g

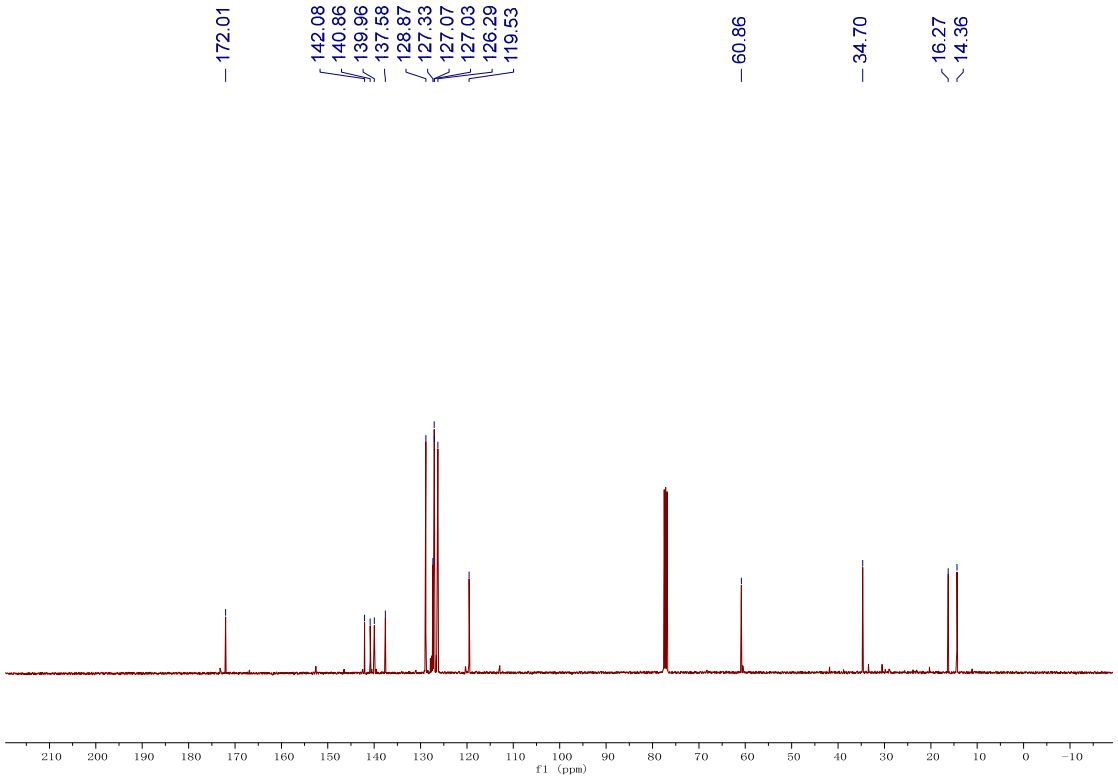
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



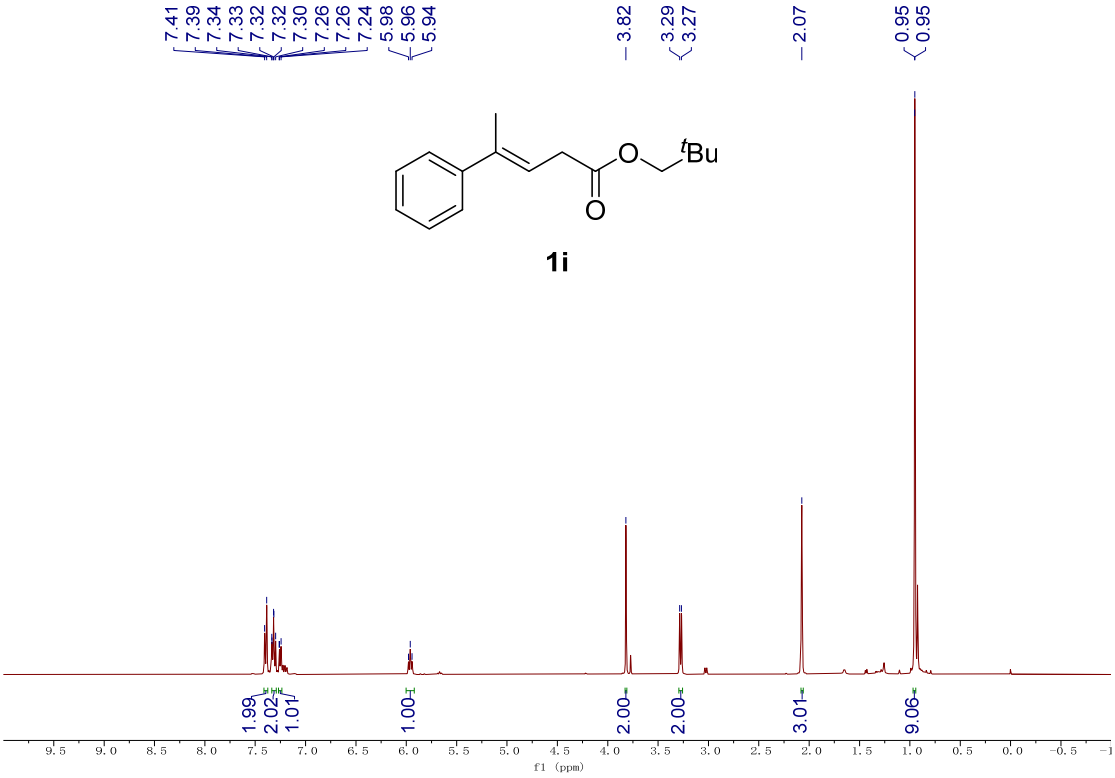
^{13}C NMR (101 MHz, $CDCl_3$) of **1g**



^{1}H NMR (400 MHz, $CDCl_3$) of **1h**

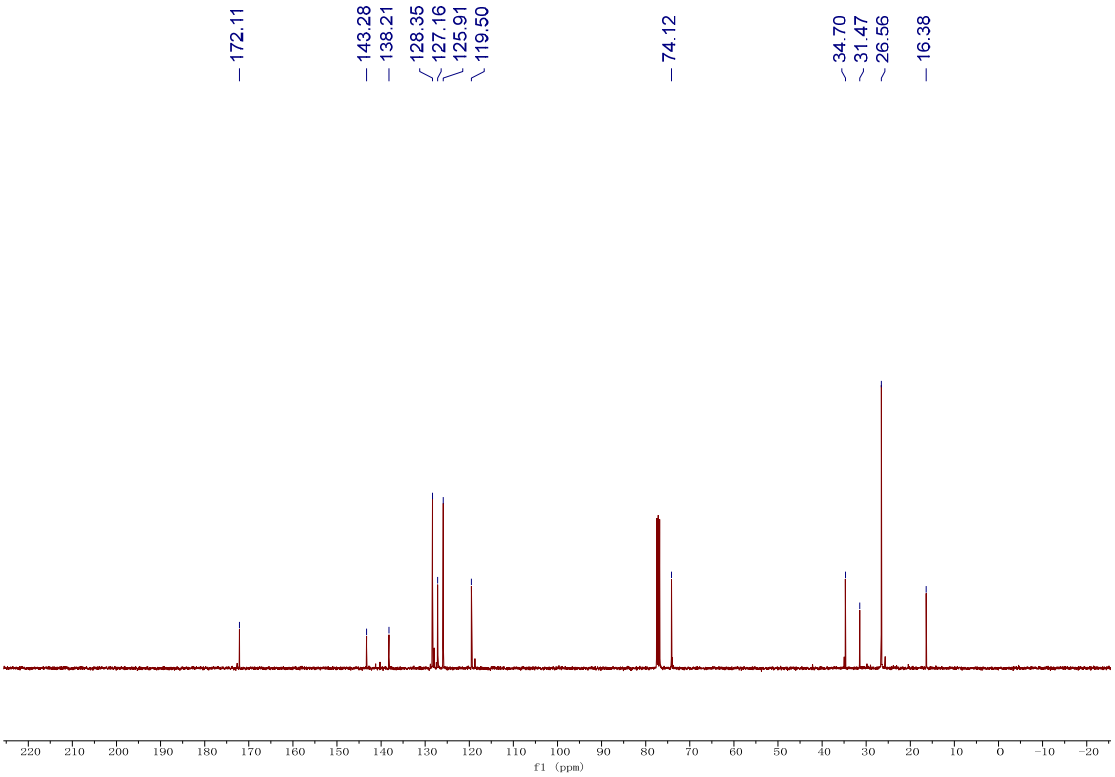


^{13}C NMR (101 MHz, $CDCl_3$) of **1h**

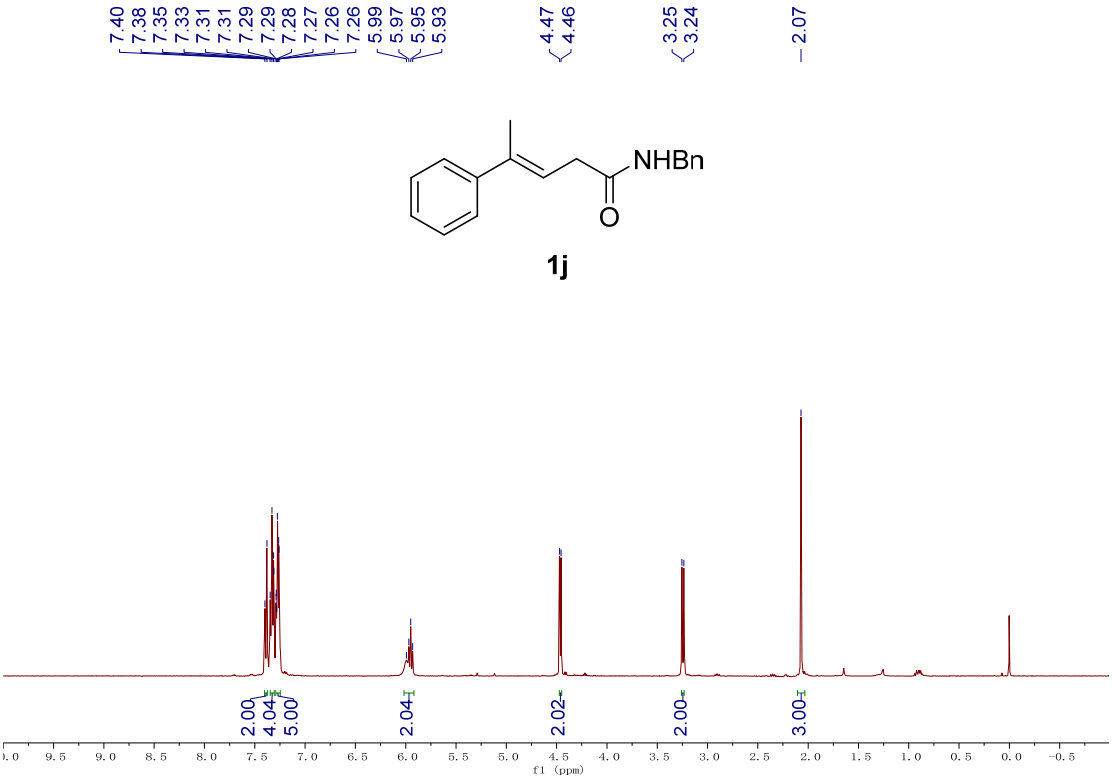


1i

^{1}H NMR (400 MHz, $CDCl_3$) of **1i**

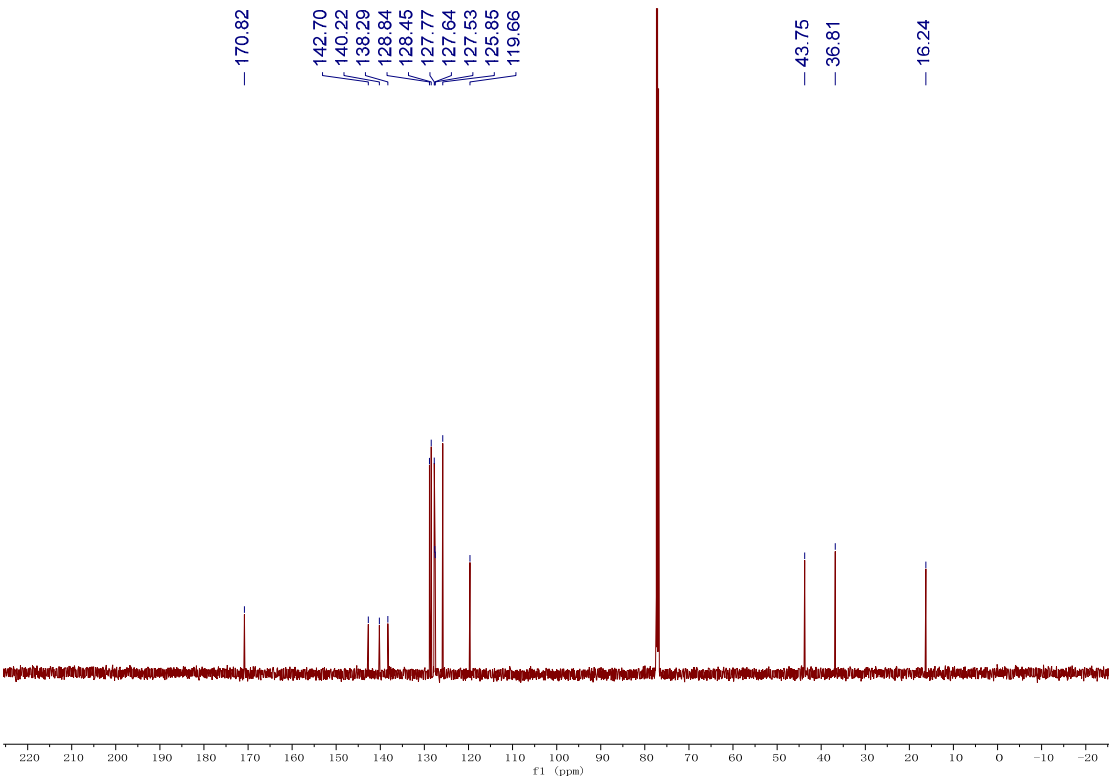


^{13}C NMR (101 MHz, $CDCl_3$) of **1i**

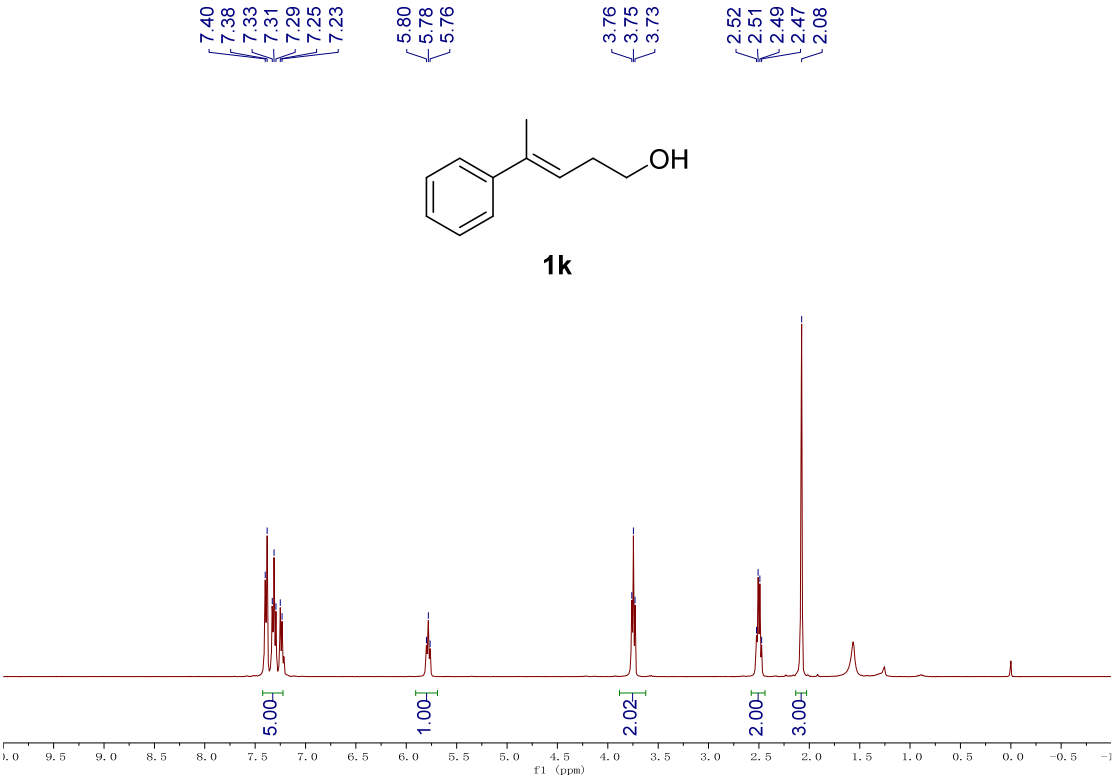


1j

^{1}H NMR (400 MHz, $CDCl_3$) of **1j**

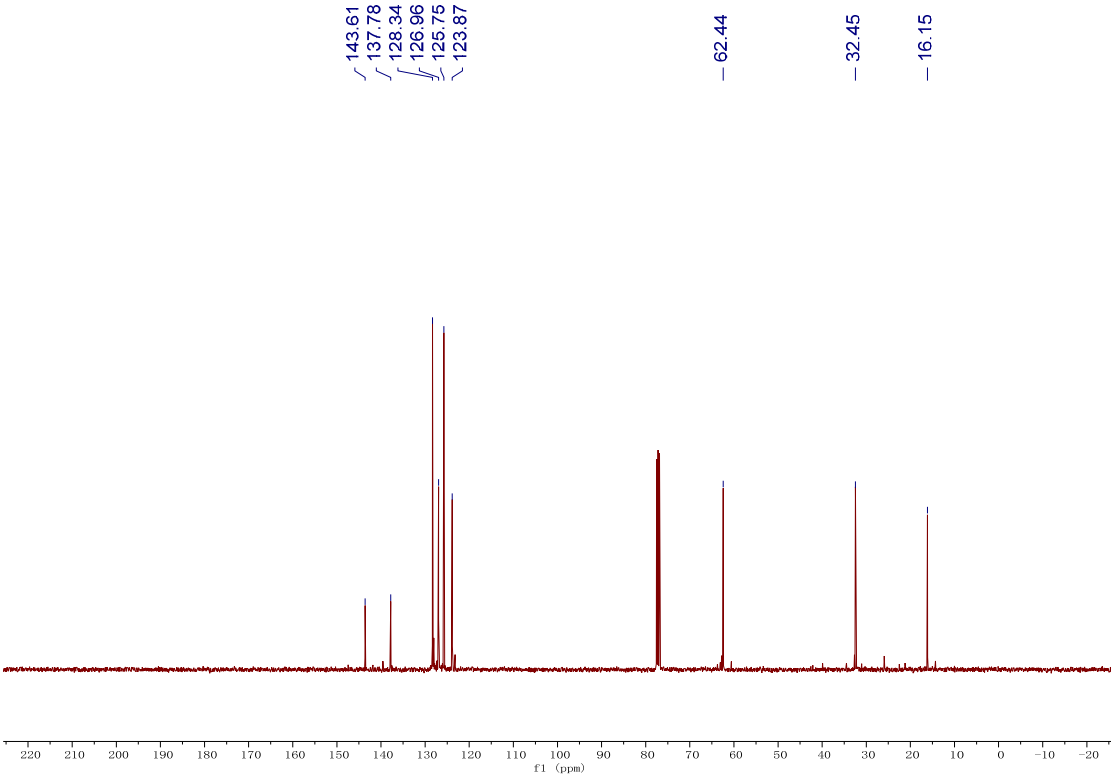


^{13}C NMR (101 MHz, $CDCl_3$) of **1j**

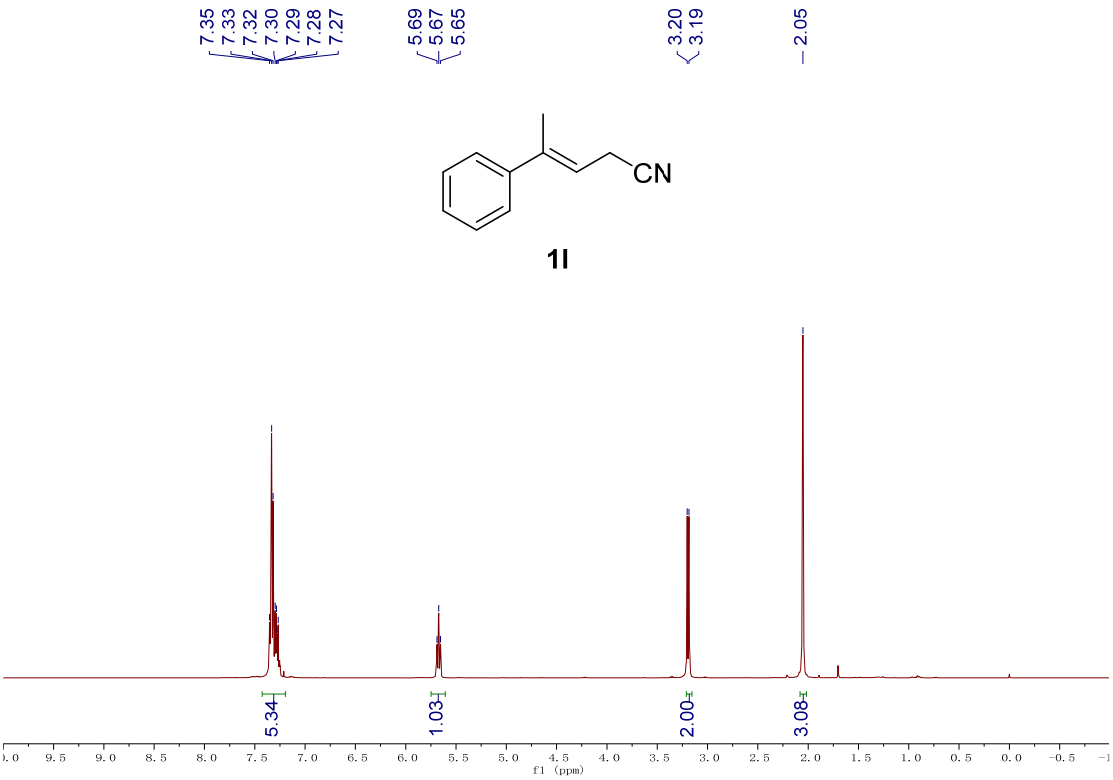


1k

^{1}H NMR (400 MHz, $CDCl_3$) of **1k**

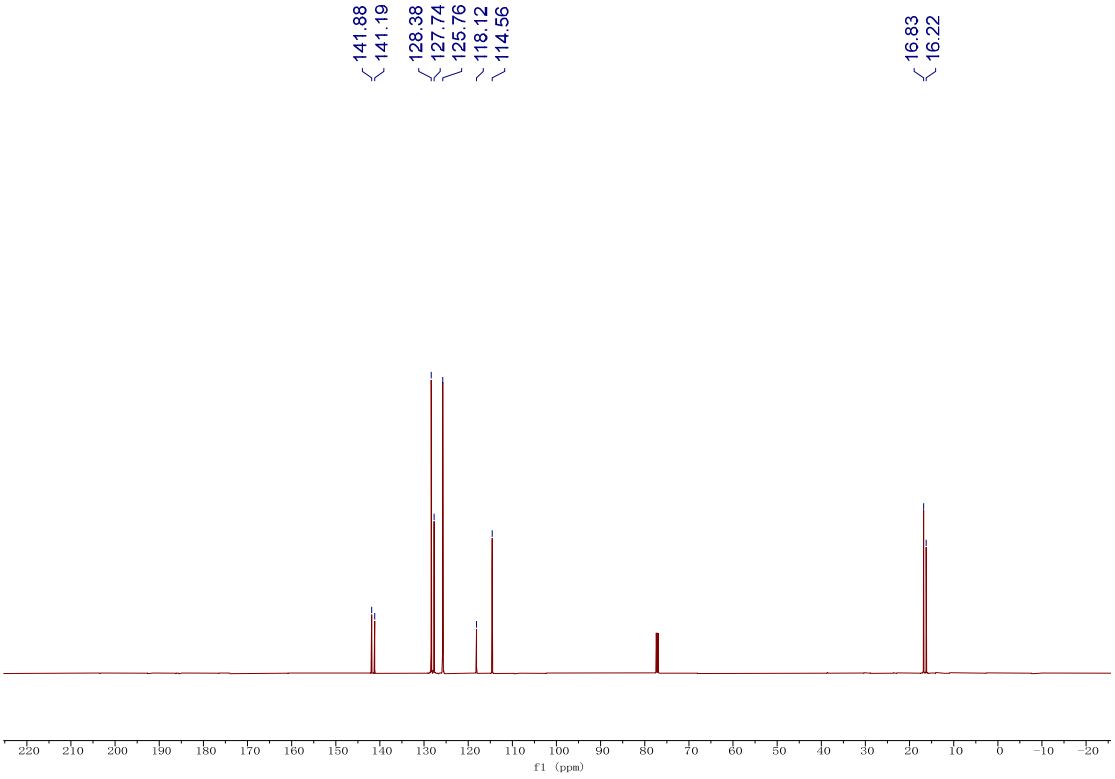


^{13}C NMR (101 MHz, $CDCl_3$) of **1k**

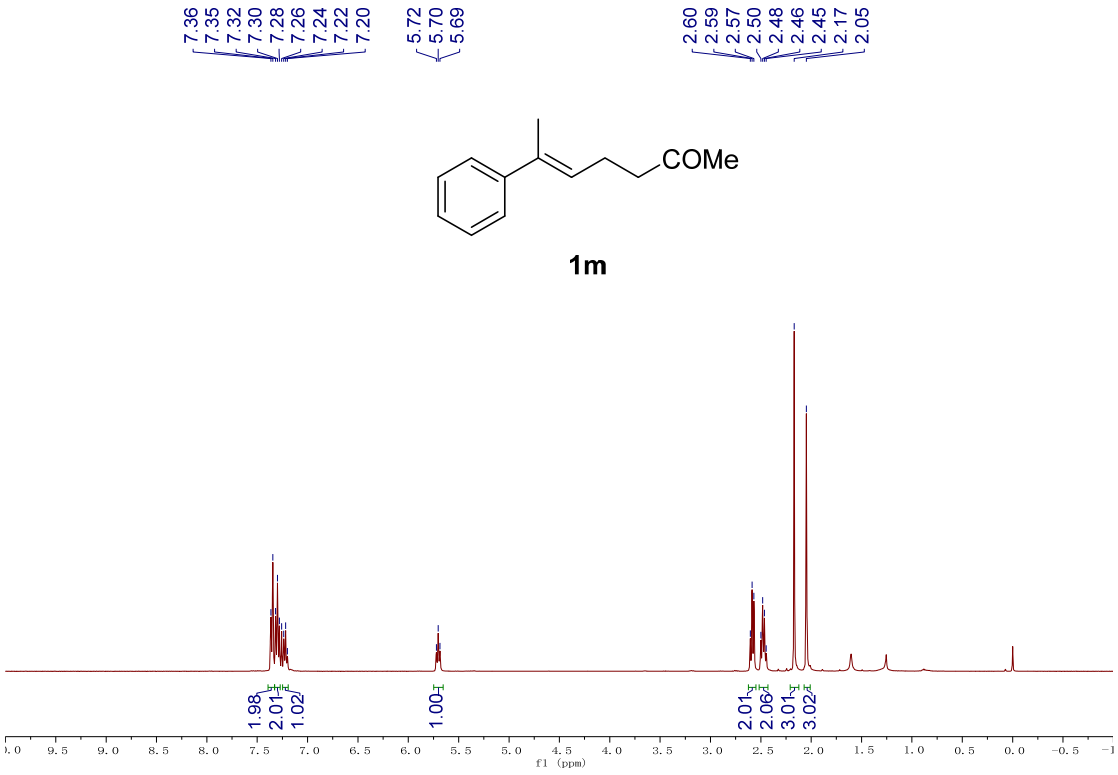


1l

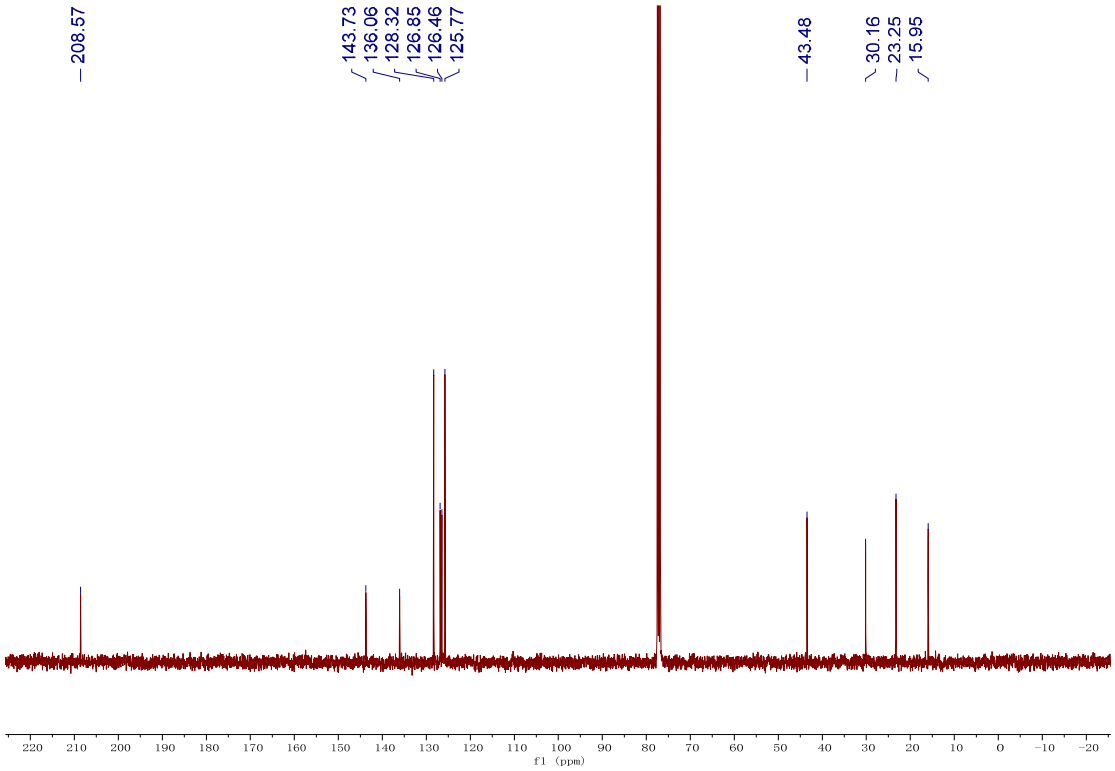
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



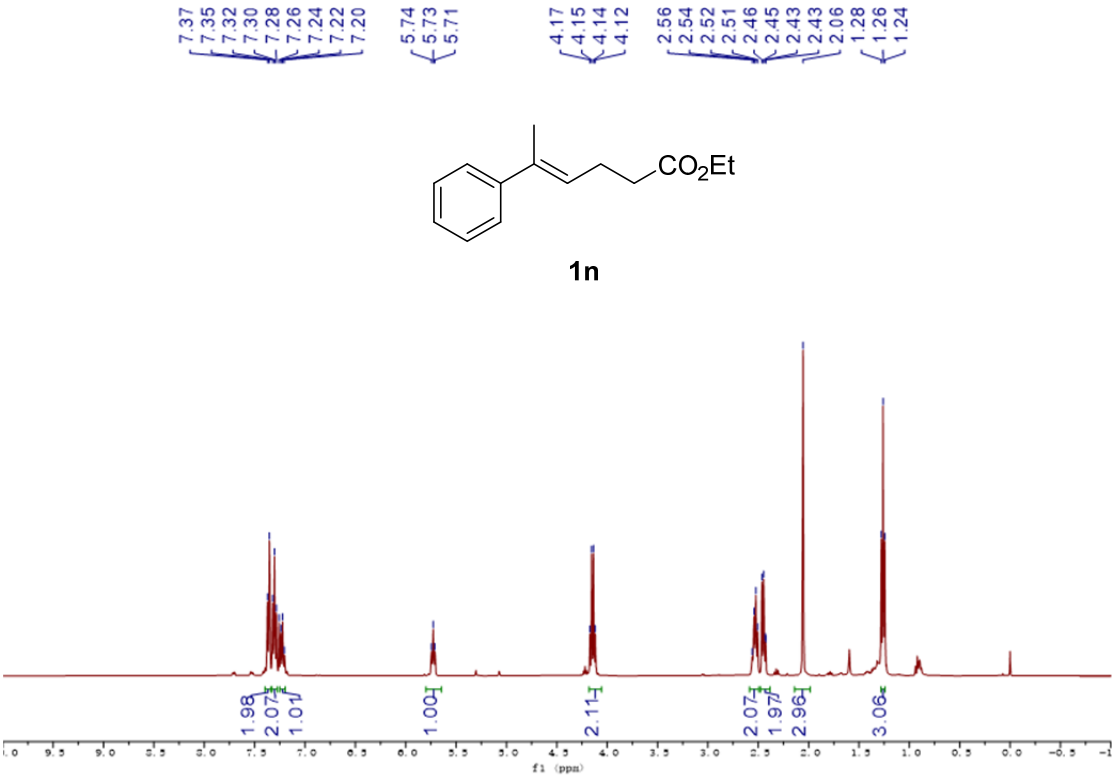
^{13}C NMR (101 MHz, $CDCl_3$) of **1l**



^{1}H NMR (400 MHz, $CDCl_3$) of **1m**

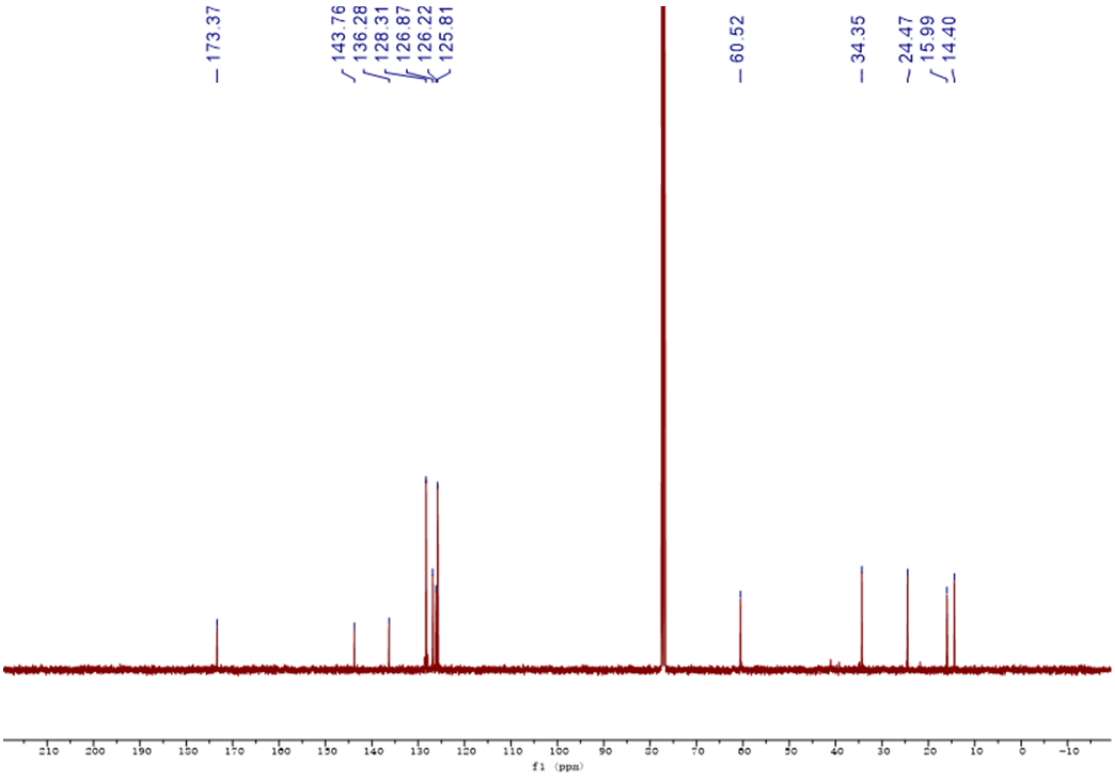


^{13}C NMR (101 MHz, $CDCl_3$) of **1m**

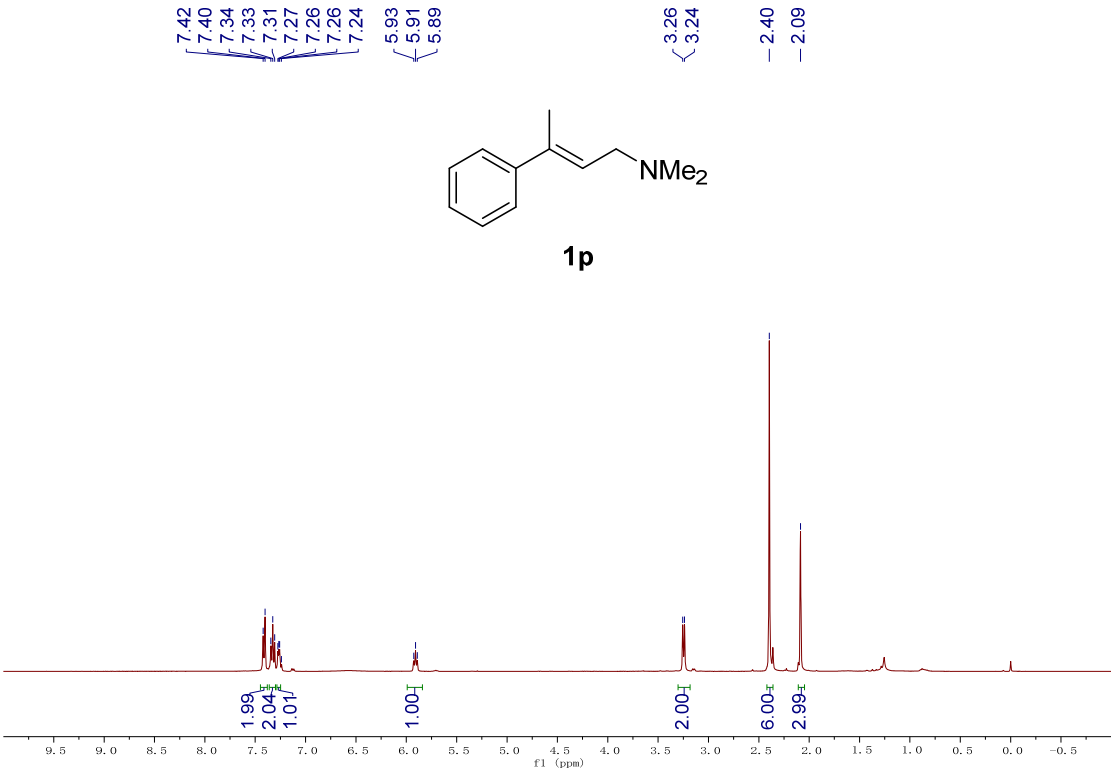


1n

^{1}H NMR (400 MHz, $CDCl_3$) of **1n**

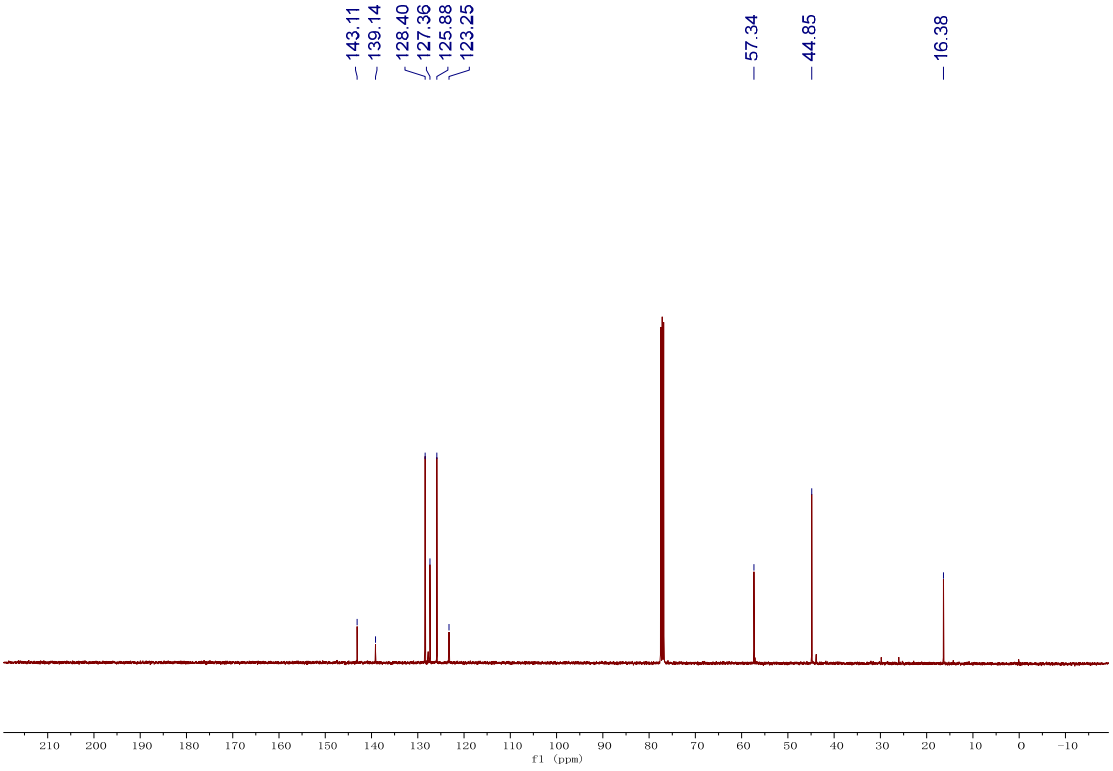


^{13}C NMR (101 MHz, $CDCl_3$) of **1n**

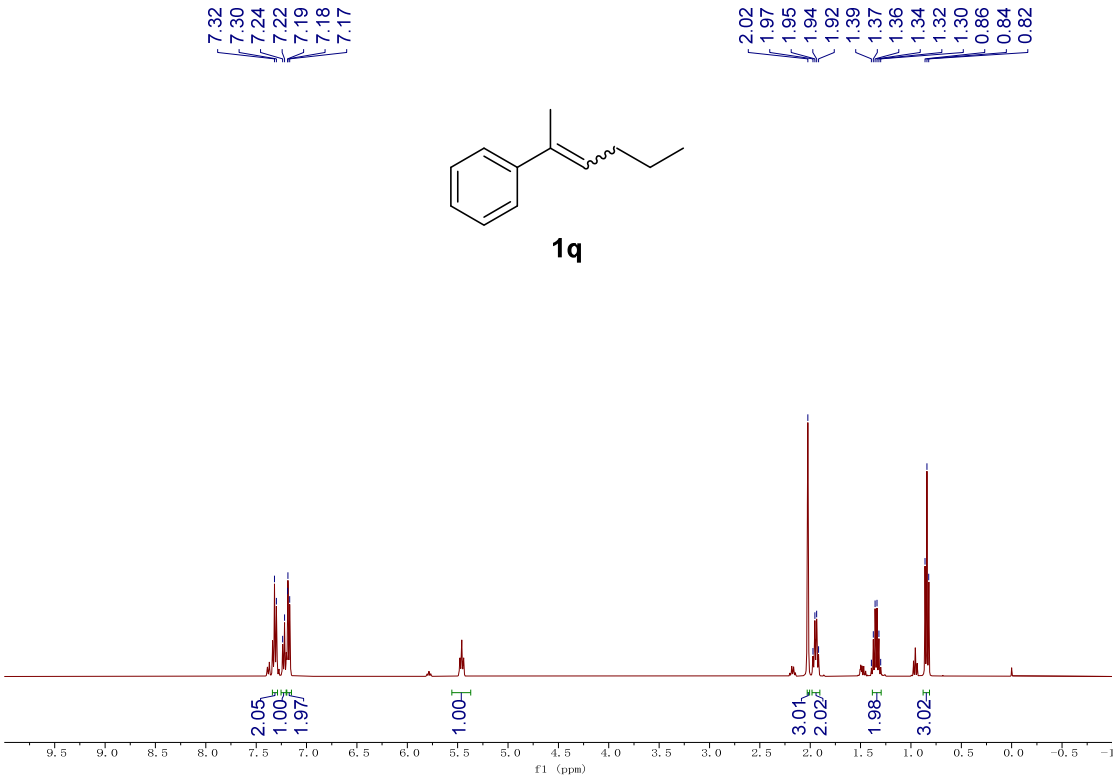


1p

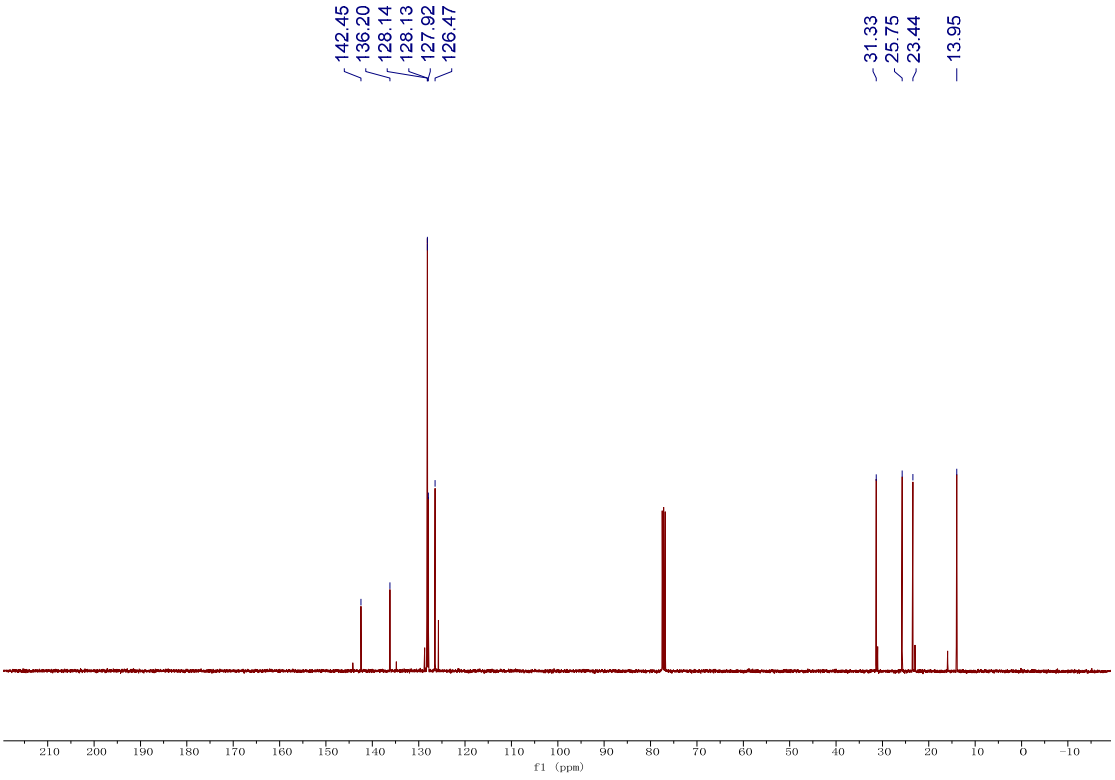
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



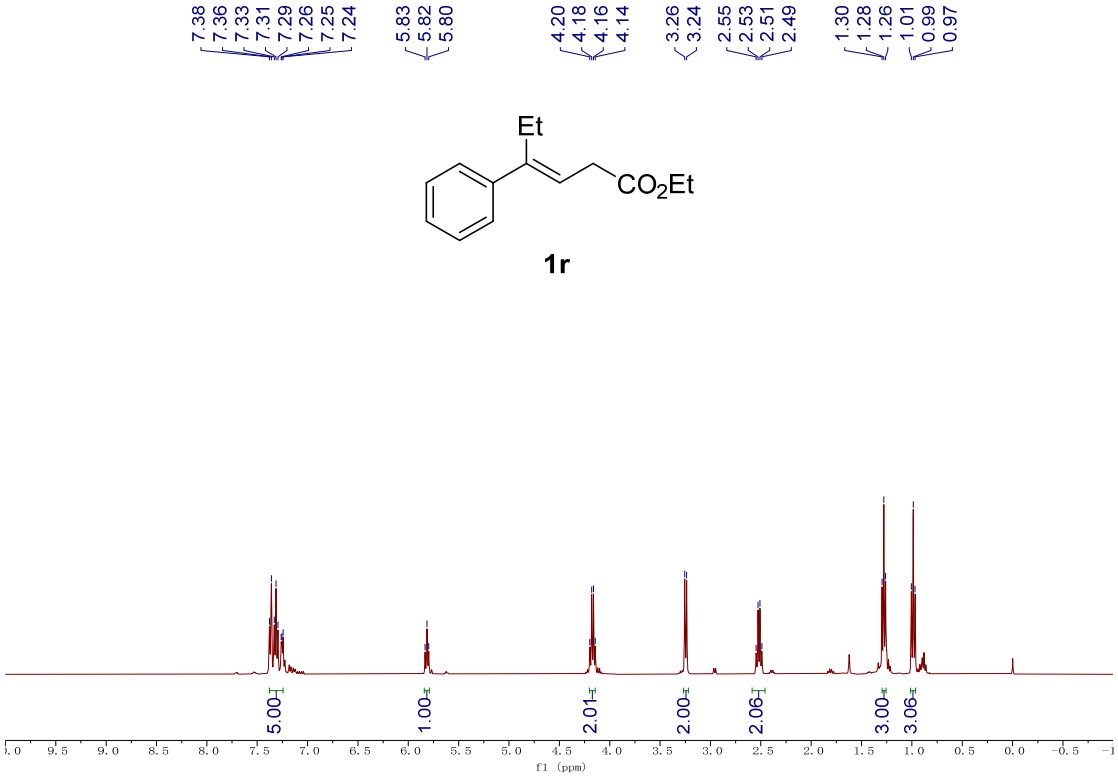
^{13}C NMR (101 MHz, $CDCl_3$) of **1p**



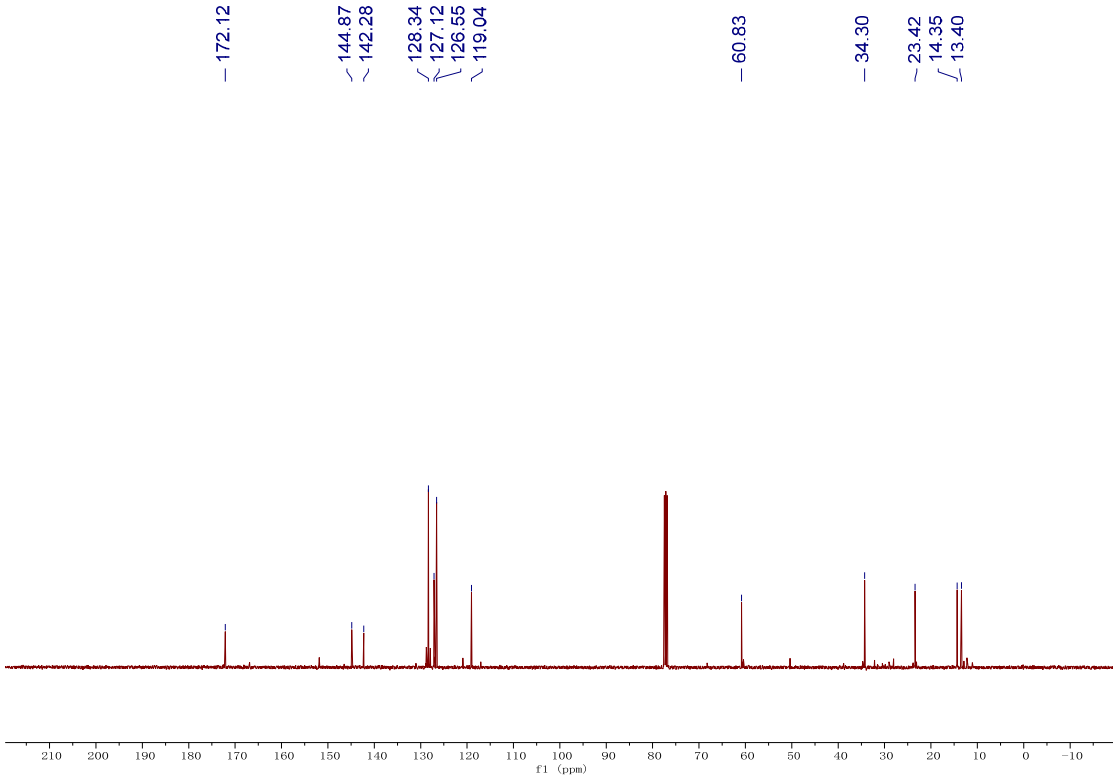
^{1}H NMR (400 MHz, $CDCl_3$) of **1q**



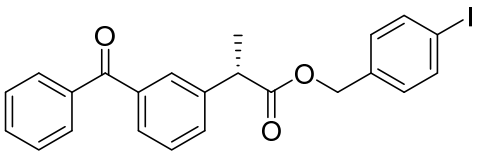
^{13}C NMR (101 MHz, $CDCl_3$) of **1q**



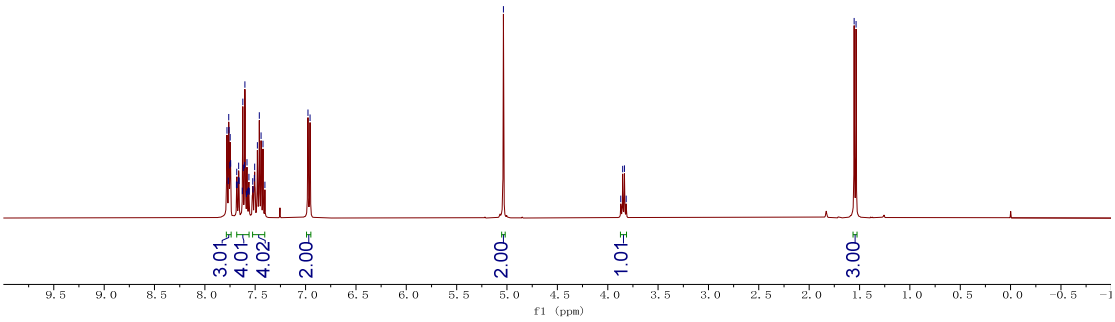
^{1}H NMR (400 MHz, $CDCl_3$) of **1r**



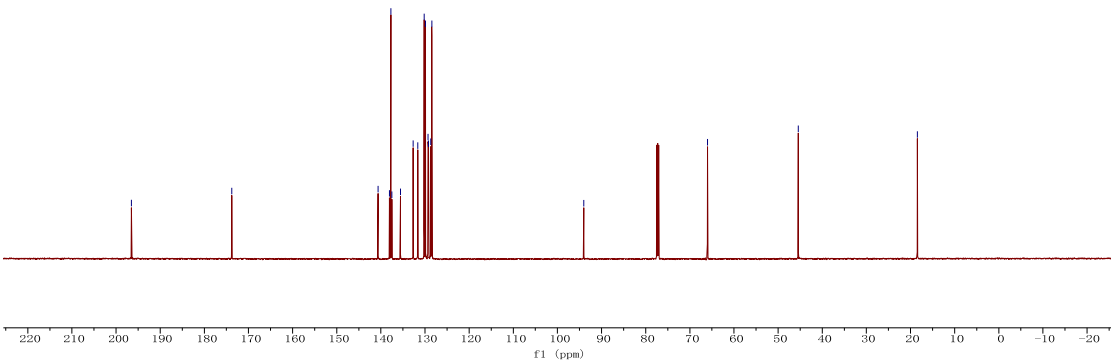
^{13}C NMR (101 MHz, $CDCl_3$) of **1r**



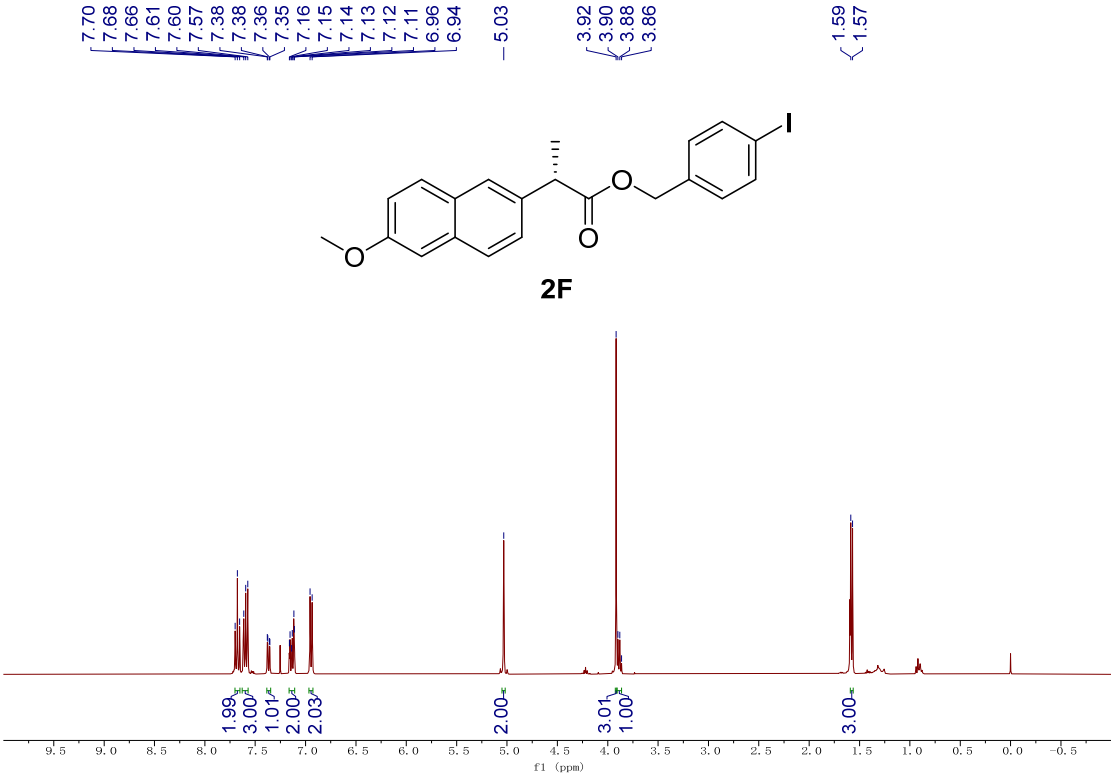
2E



^{1}H NMR (400 MHz, $CDCl_3$) of **2E**

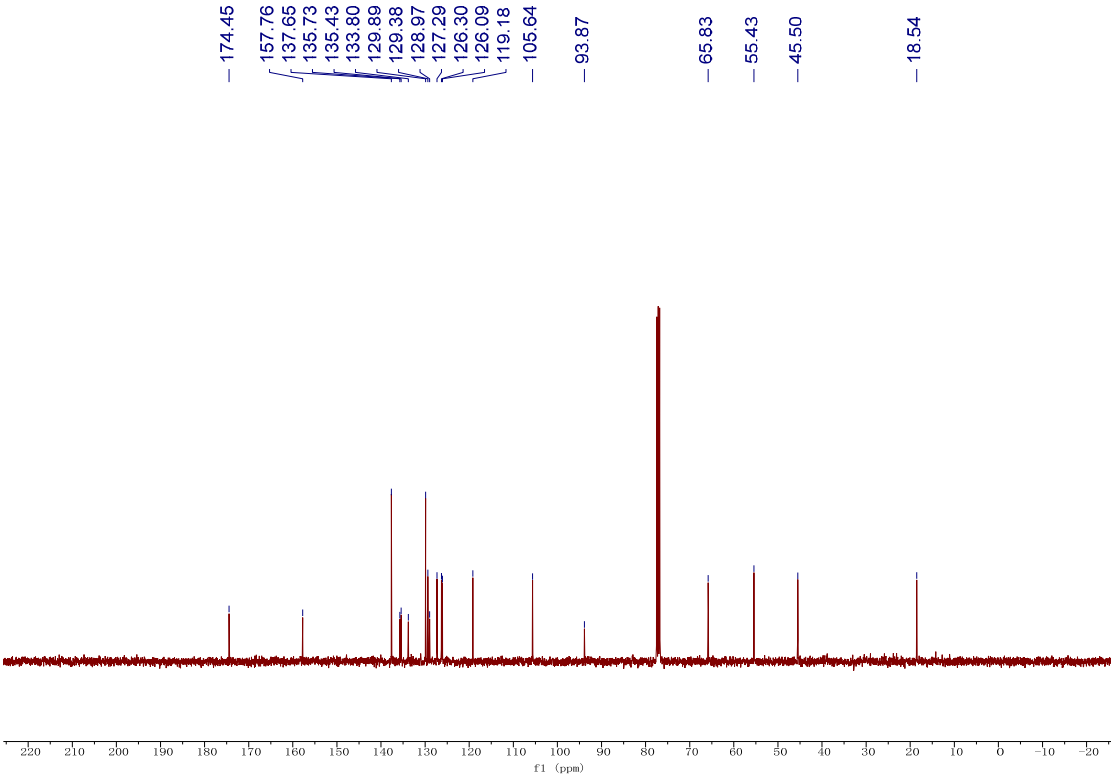


^{13}C NMR (101 MHz, $CDCl_3$) of **2E**

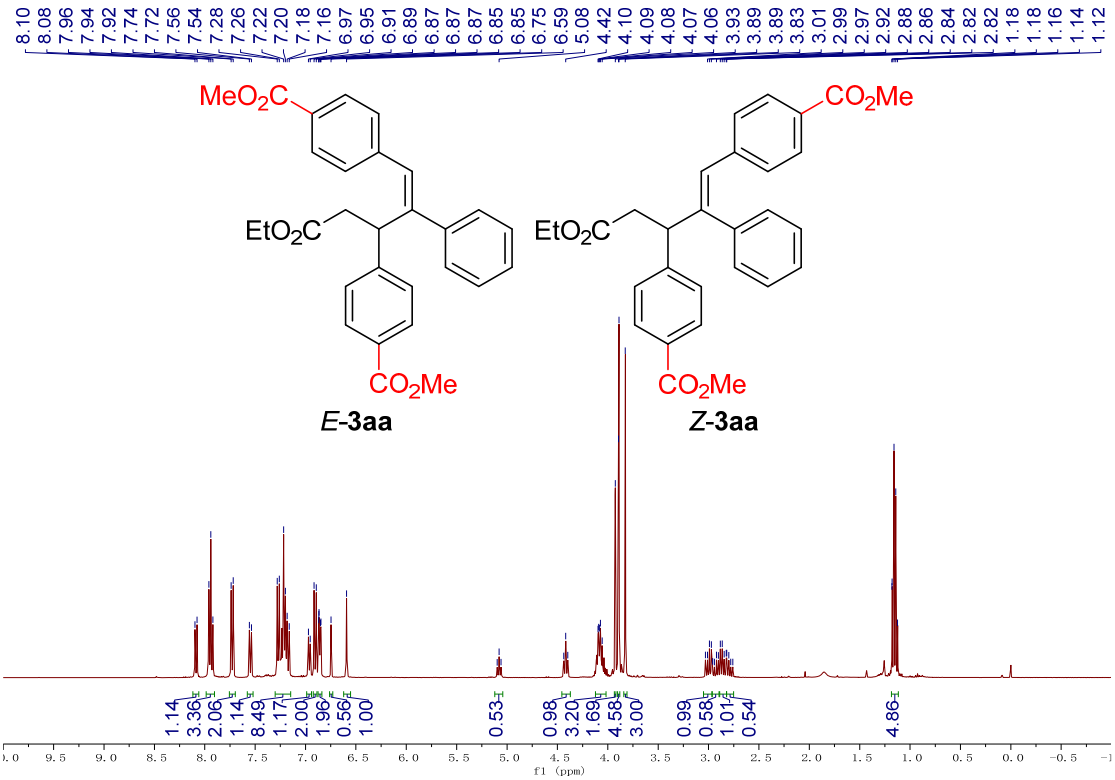


2F

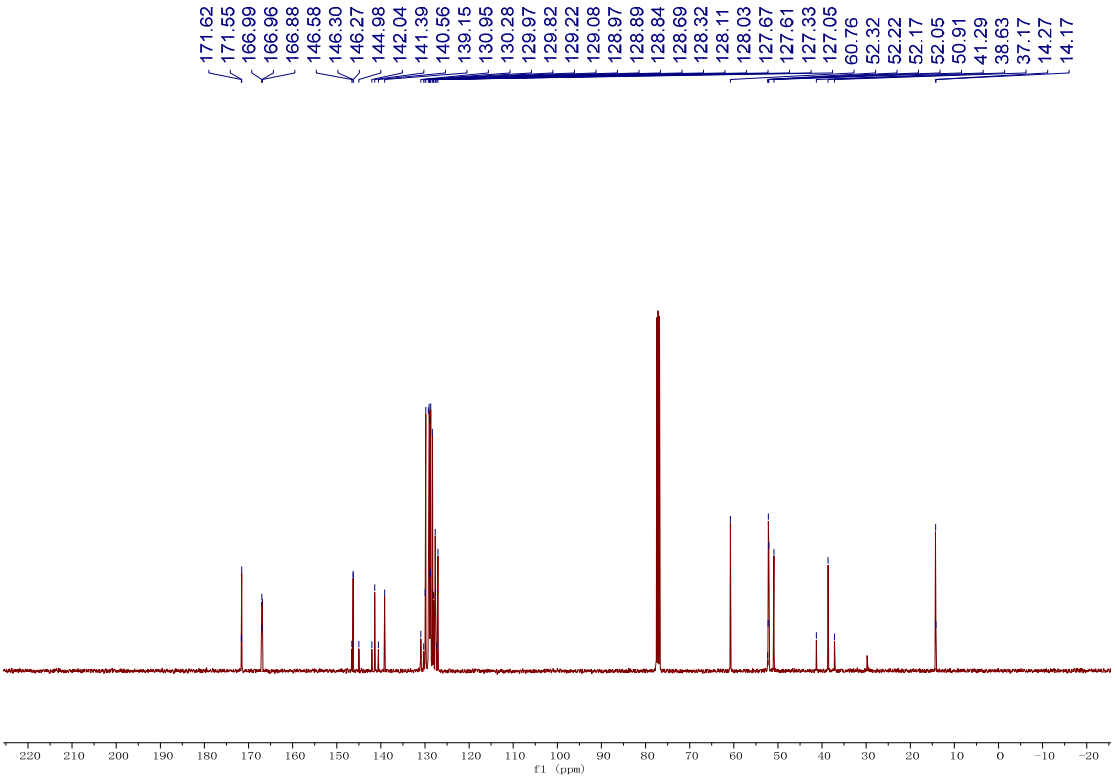
^{1}H NMR (400 MHz, $CDCl_3$) of **2F**



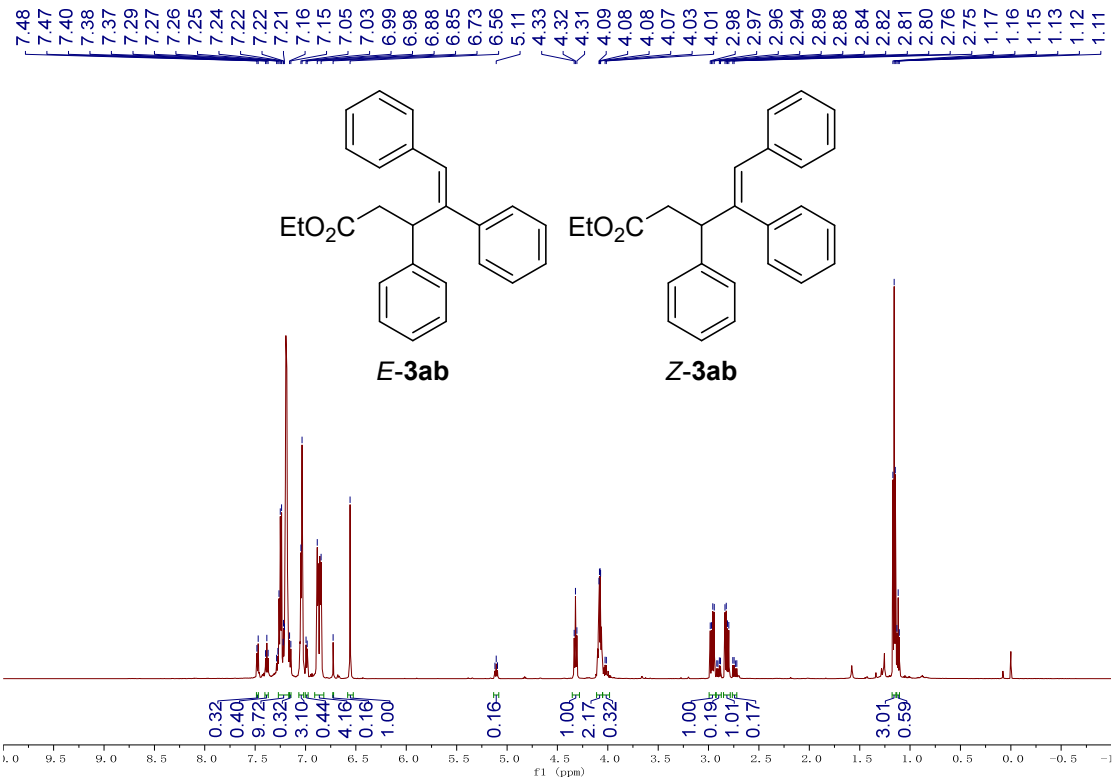
^{13}C NMR (101 MHz, $CDCl_3$) of **2F**



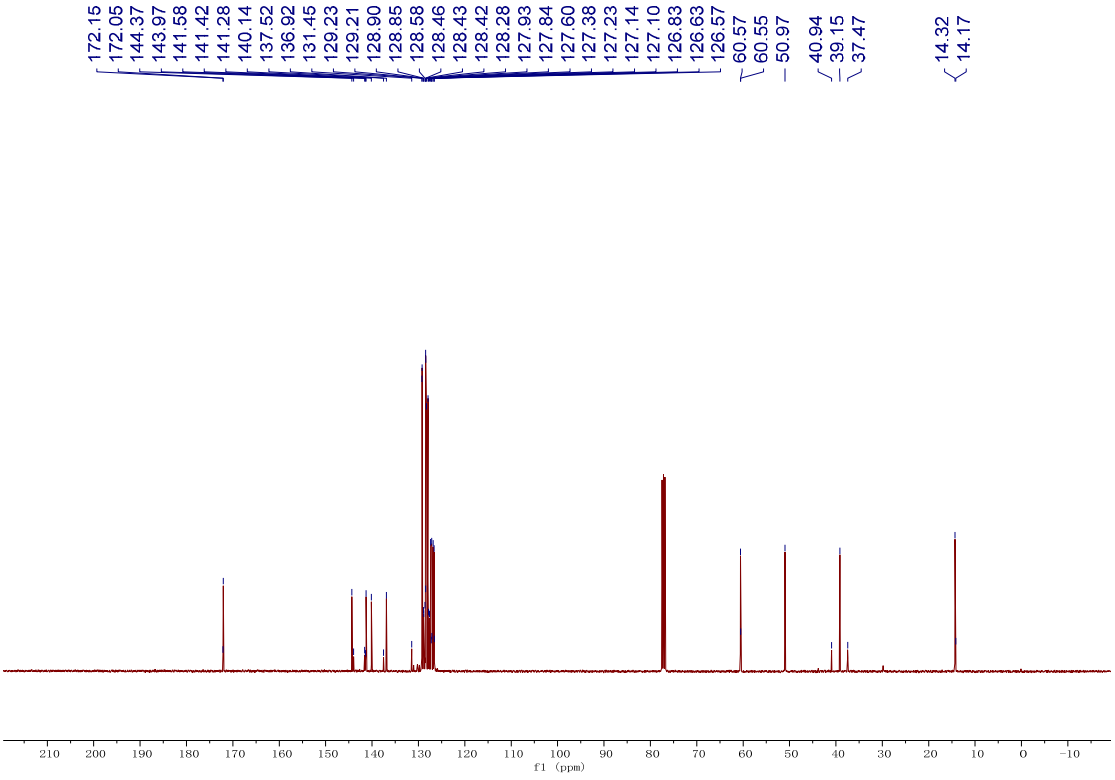
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



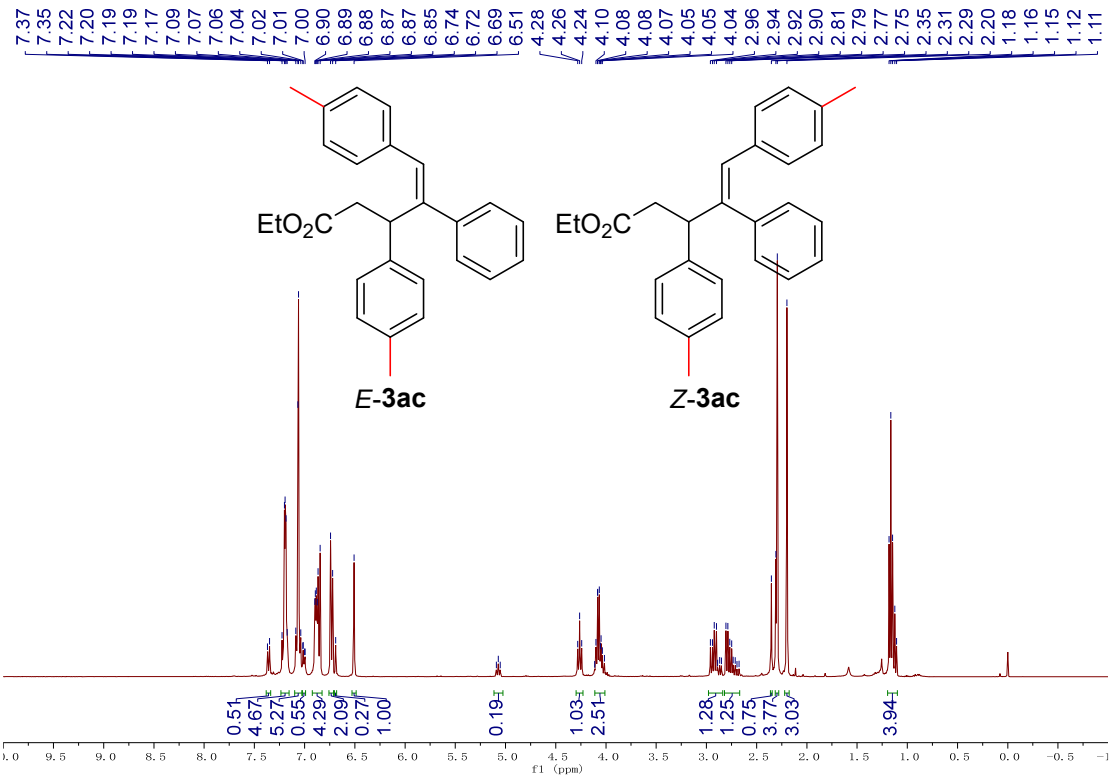
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



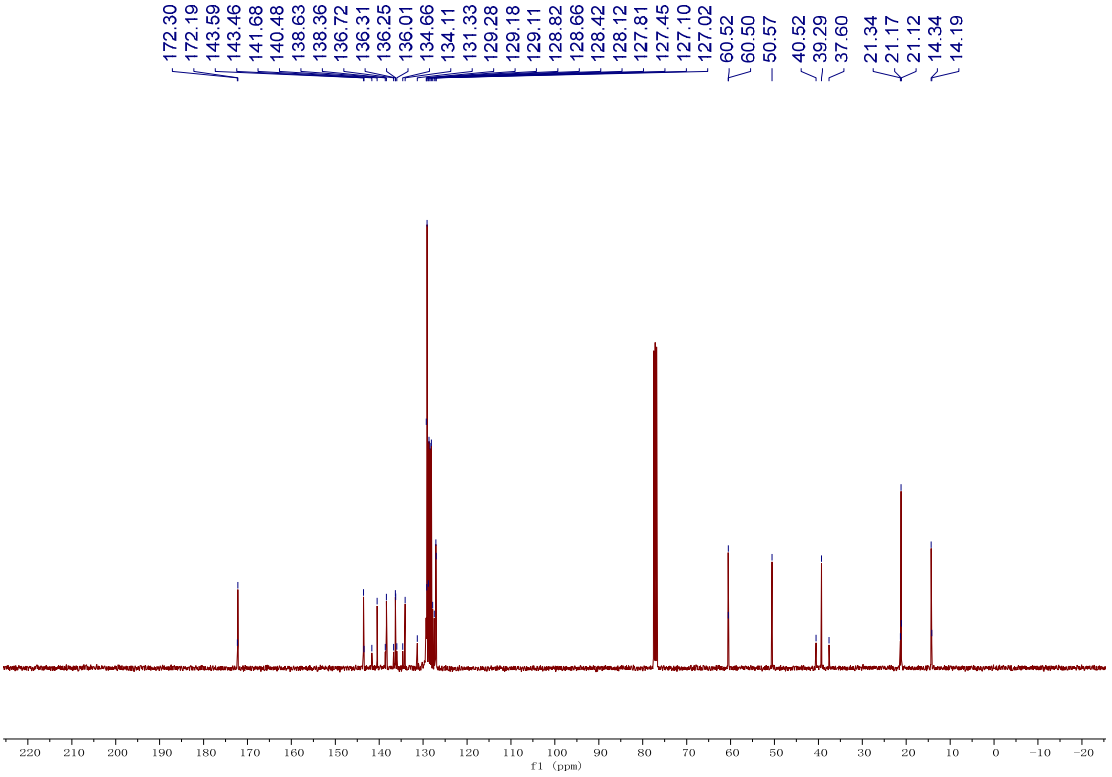
^{1}H NMR (600 MHz, $CDCl_3$) of **3ab**



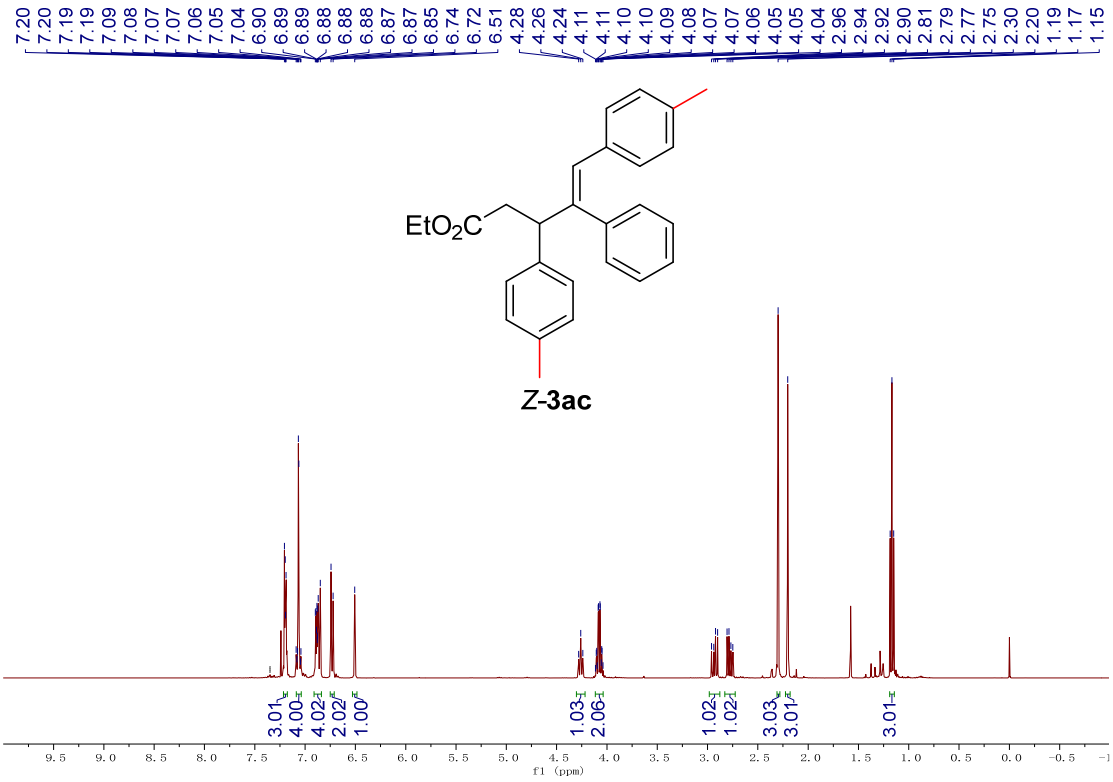
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



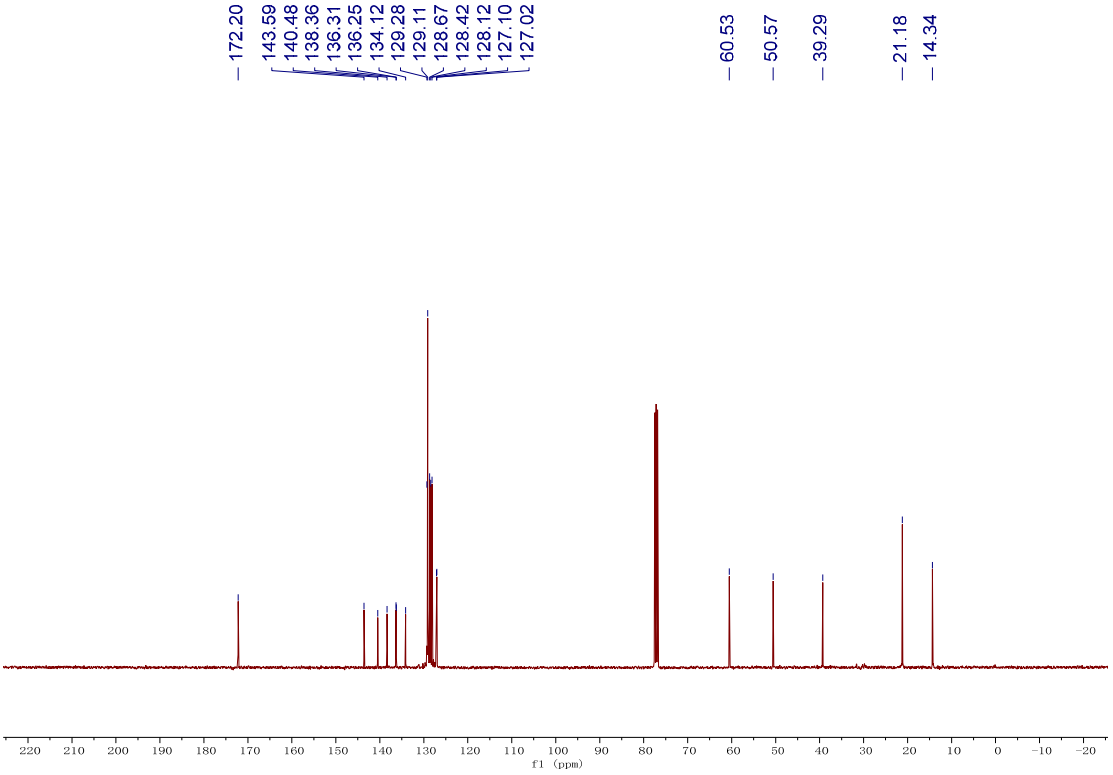
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



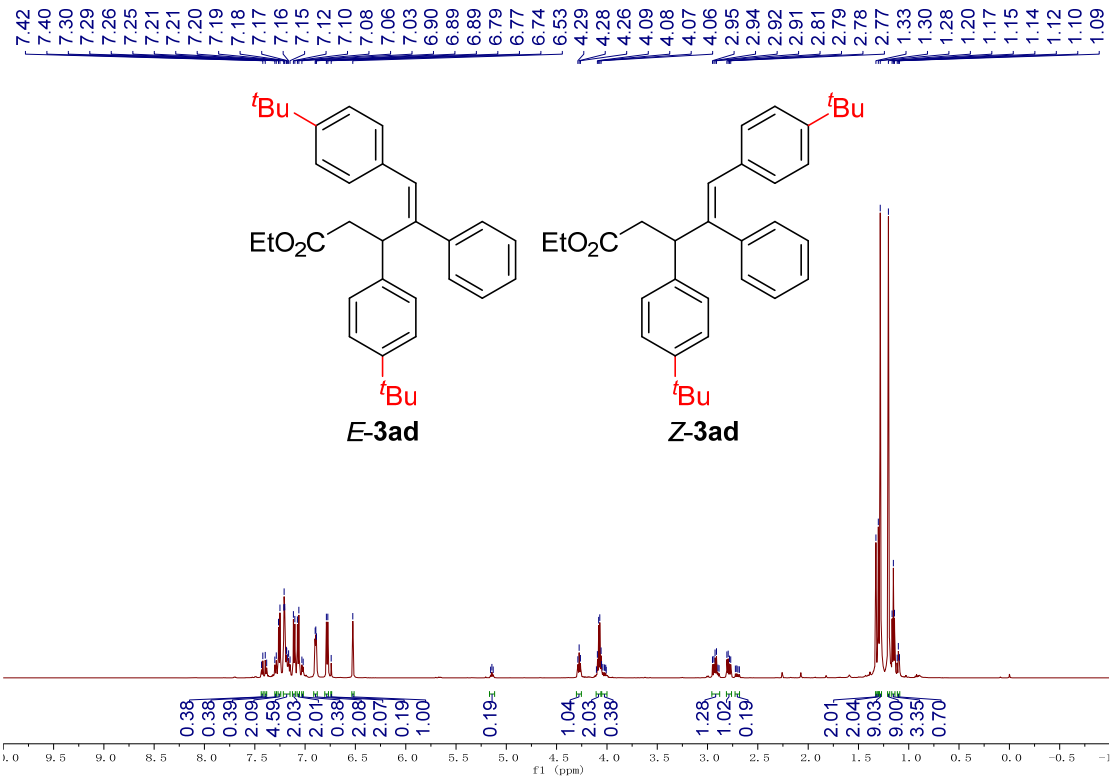
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



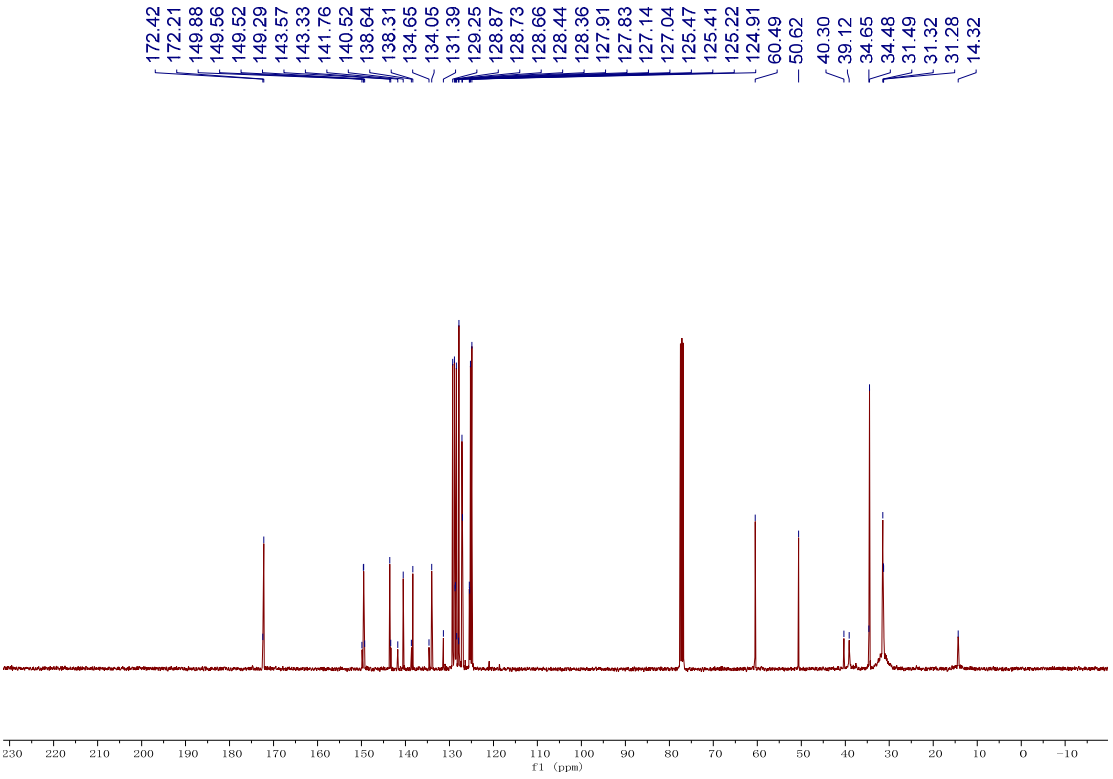
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ac**



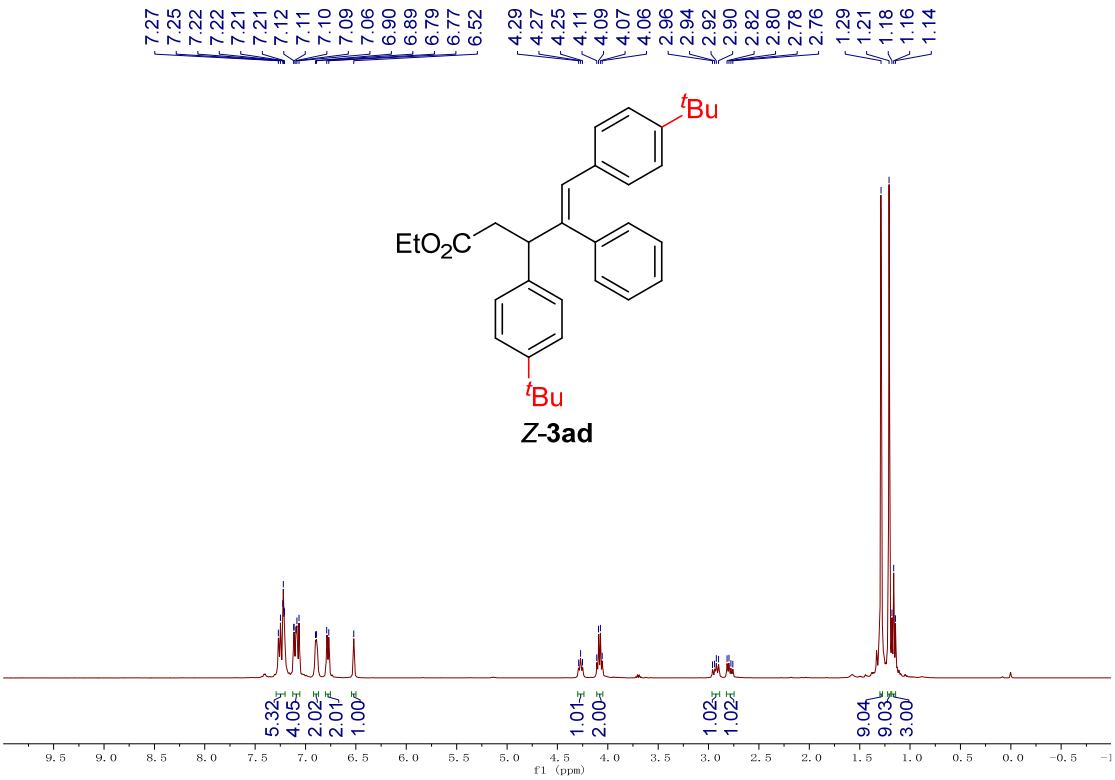
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ac**



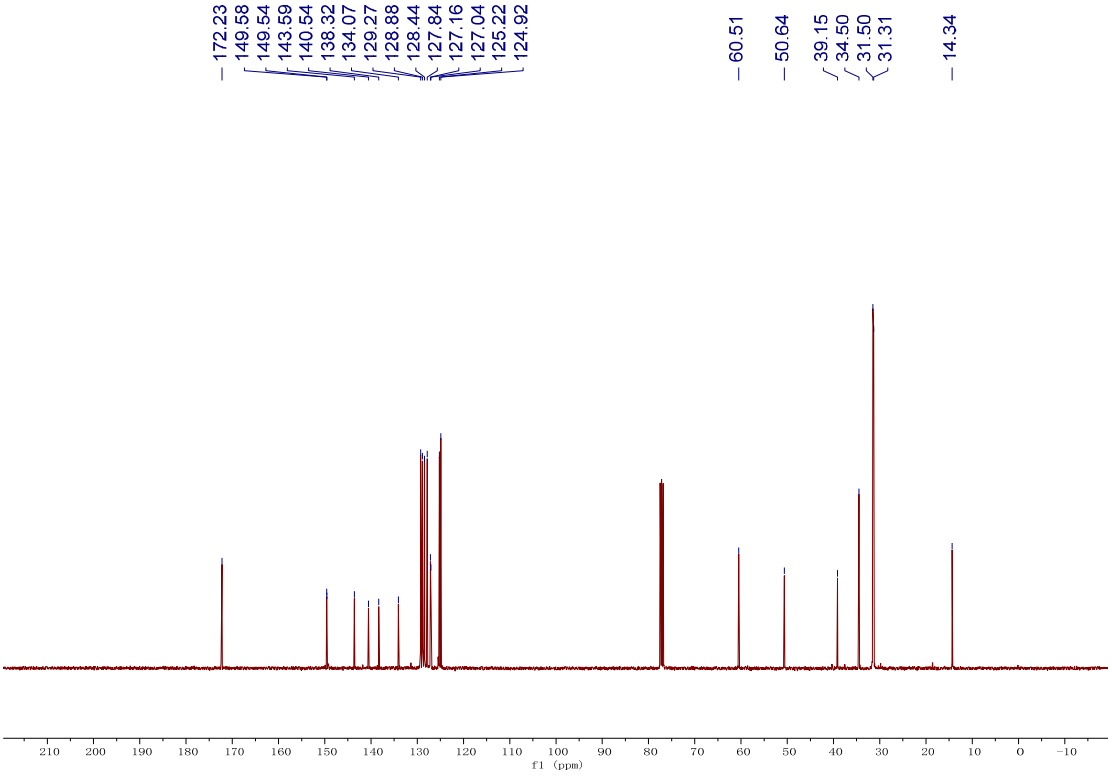
^{1}H NMR (600 MHz, $CDCl_3$) of **3ad**



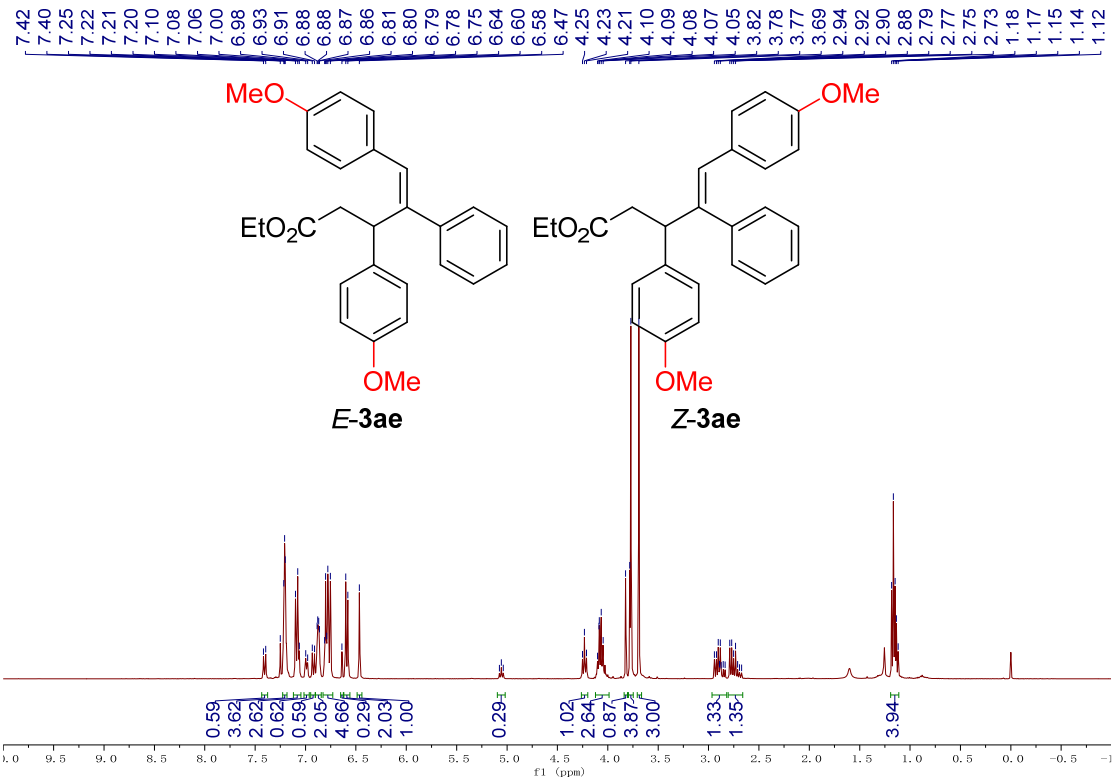
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**



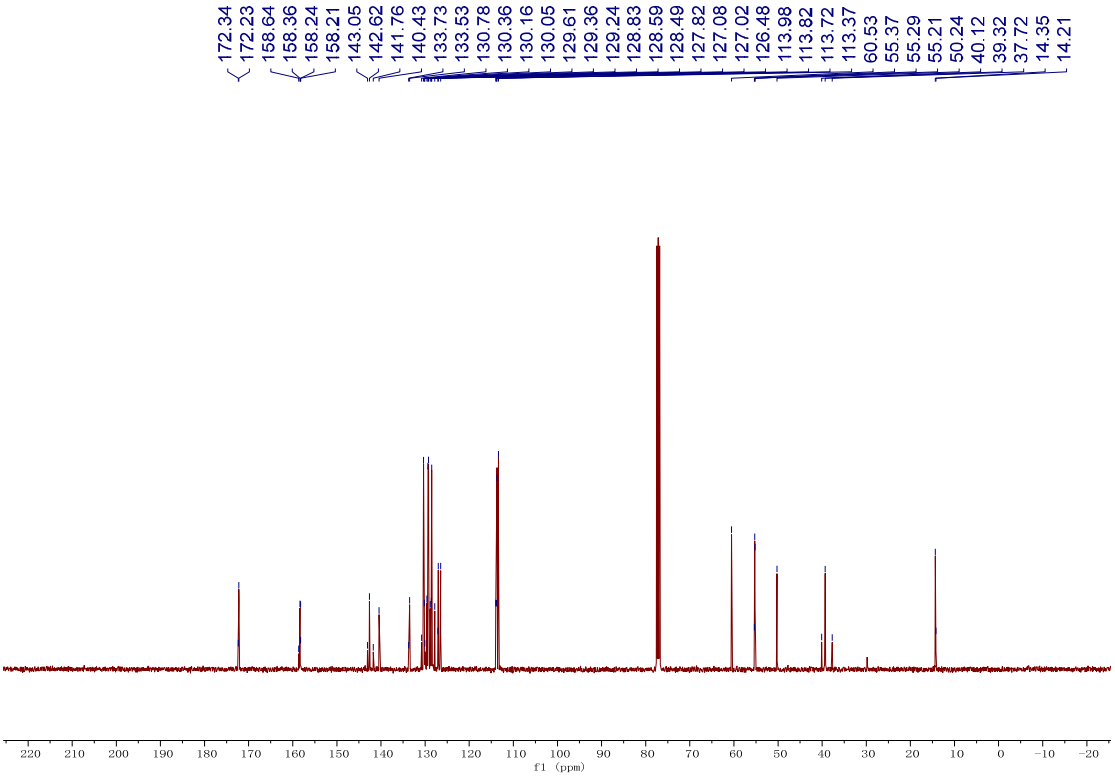
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ad**



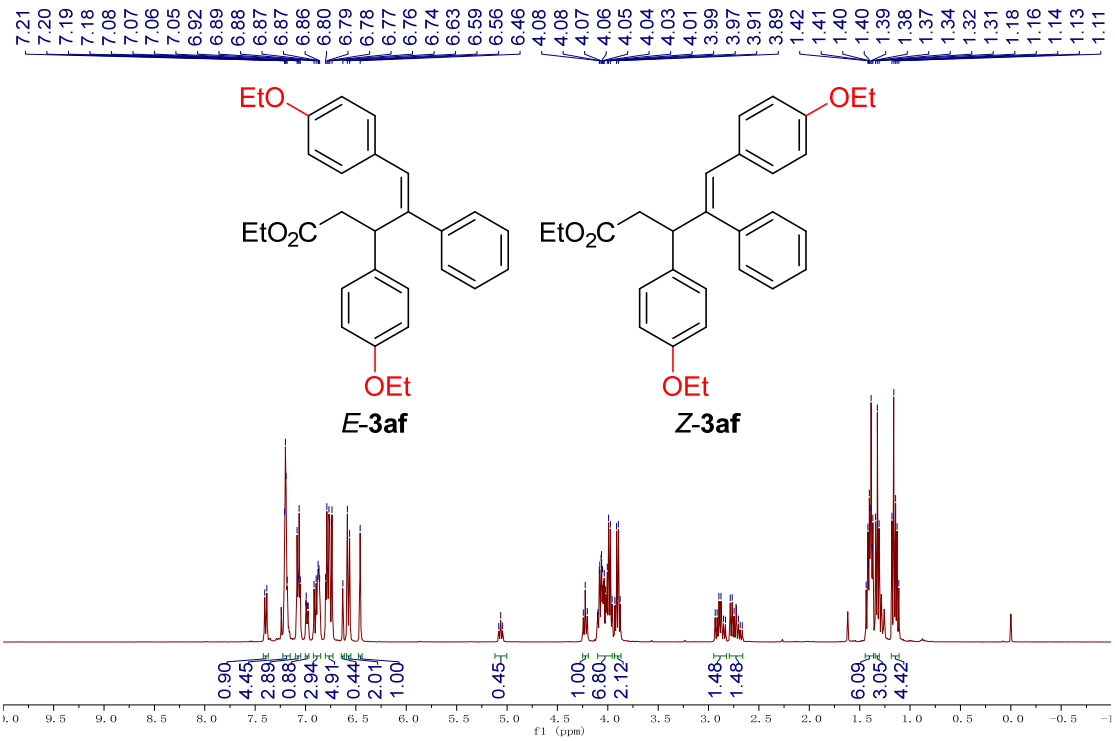
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ad**



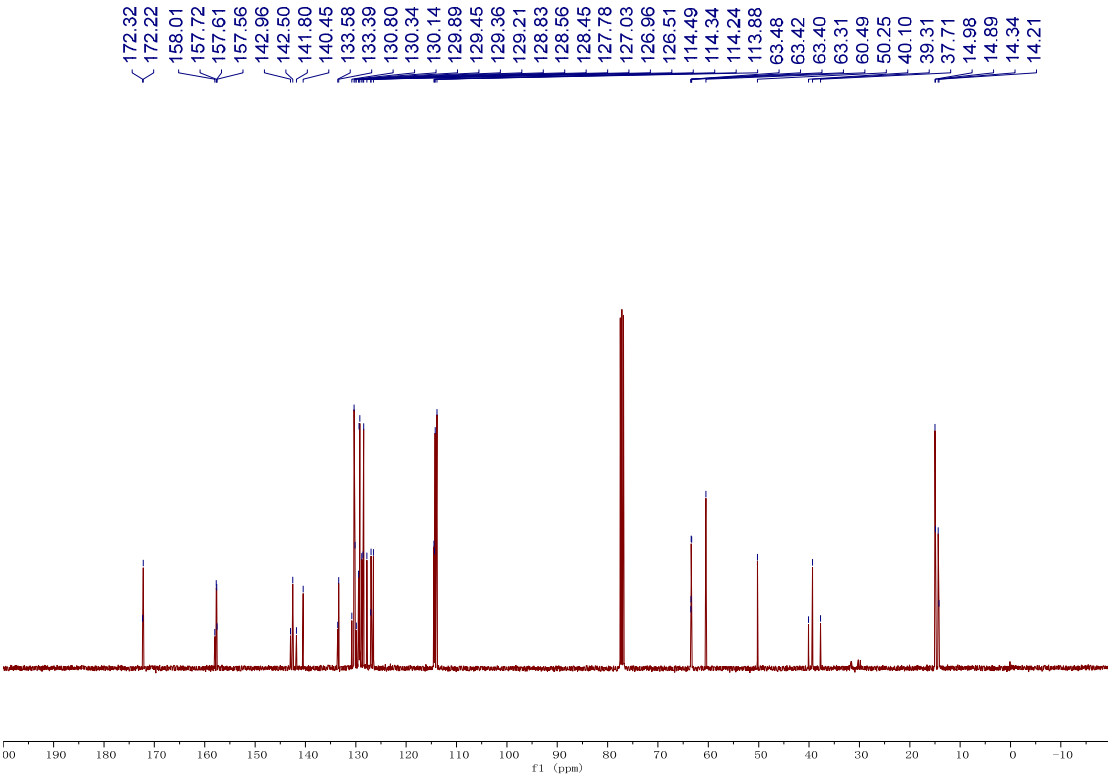
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



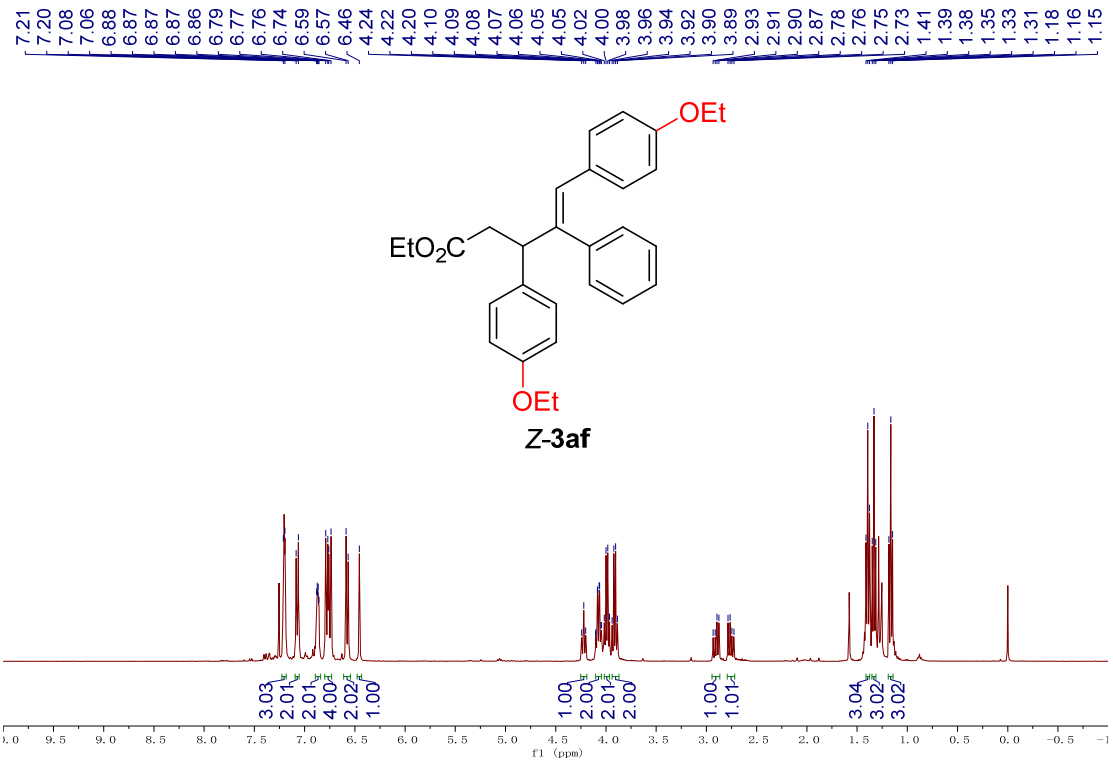
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



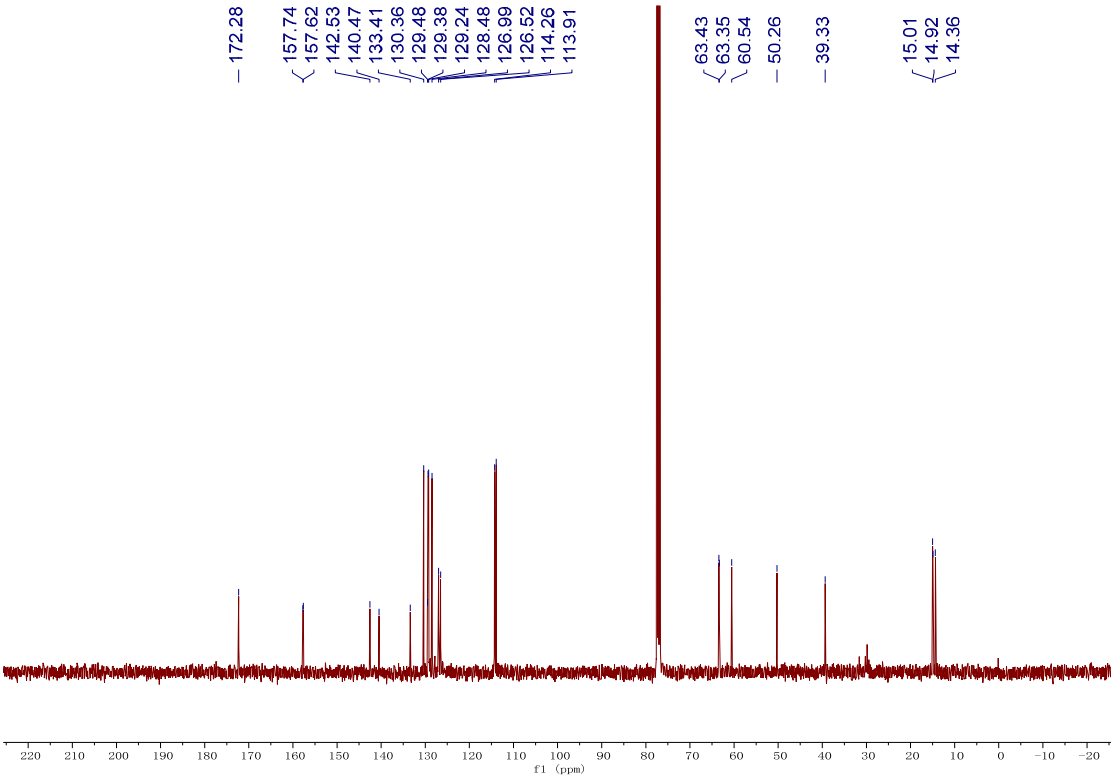
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



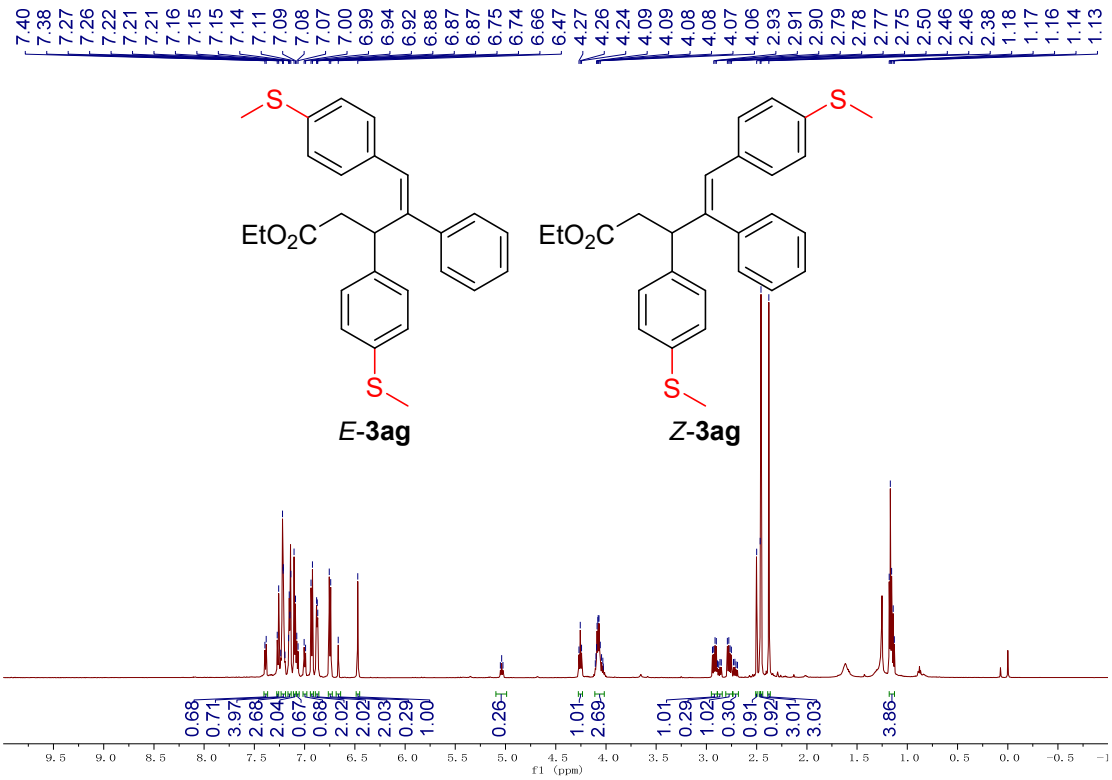
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



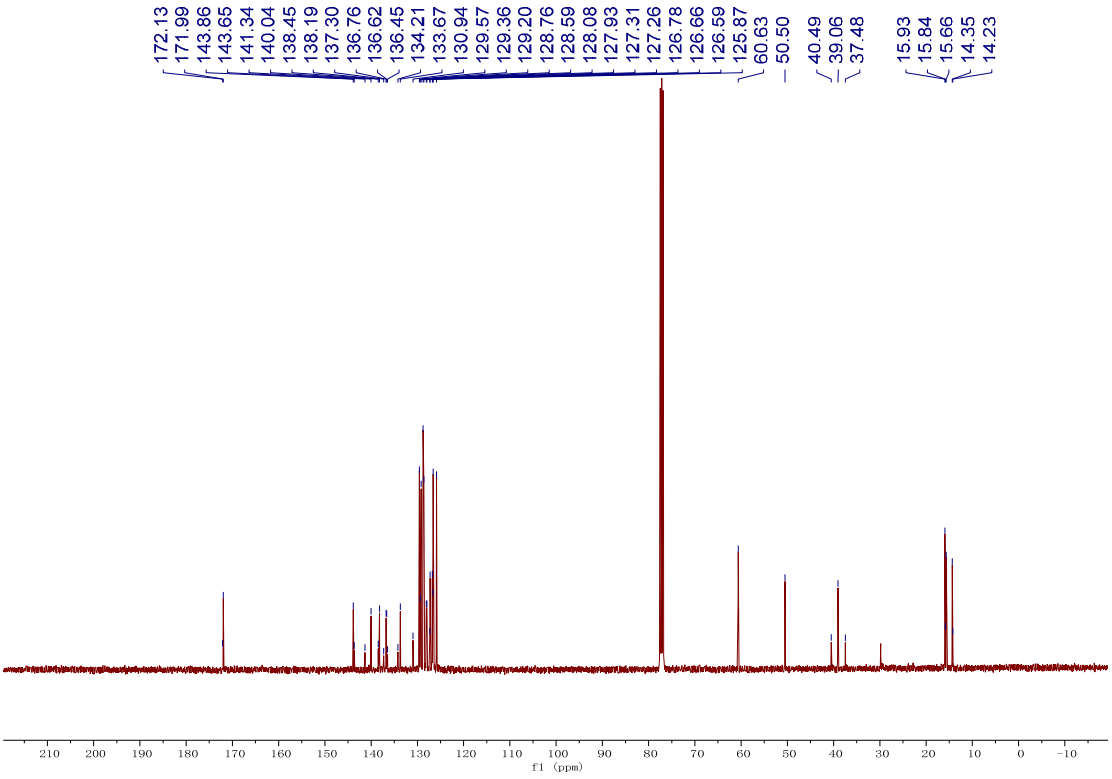
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3af**



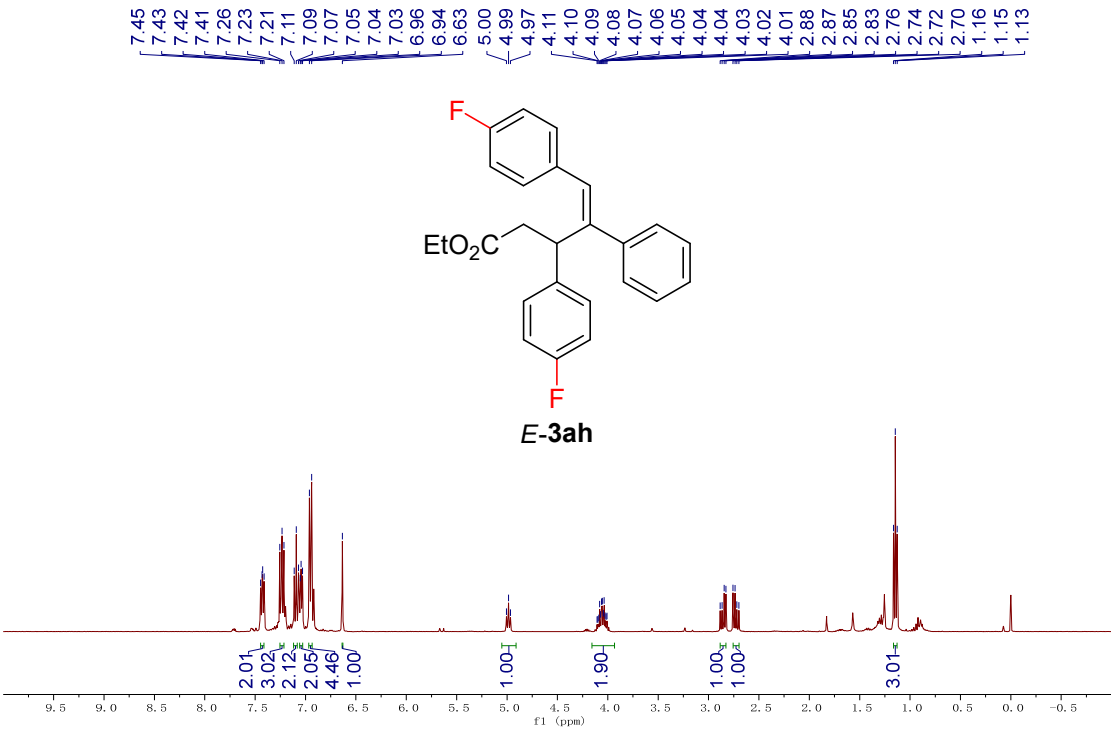
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3af**



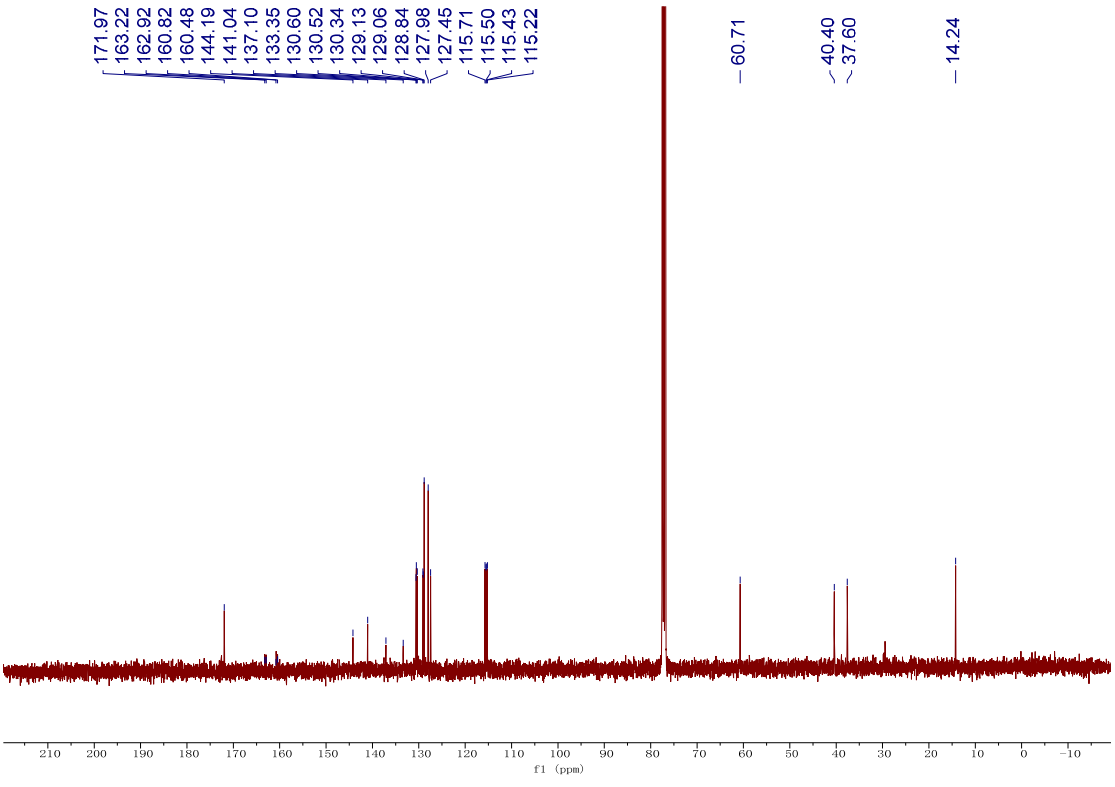
^{1}H NMR (600 MHz, $CDCl_3$) of **3ag**



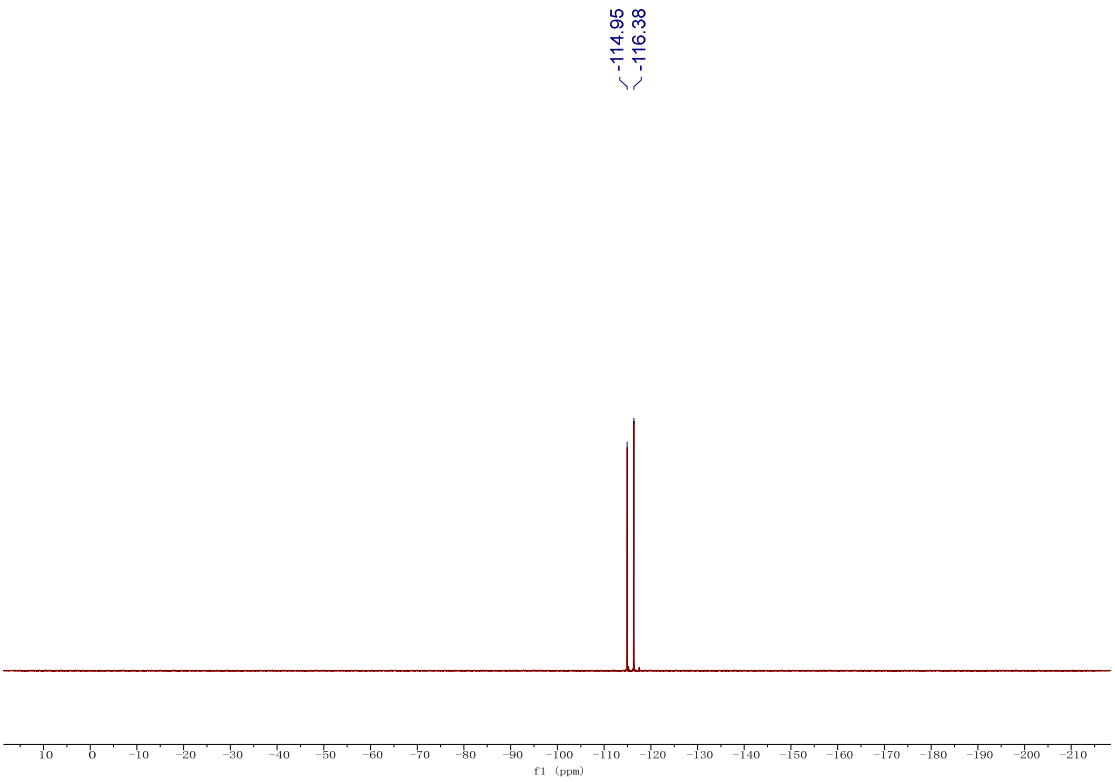
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



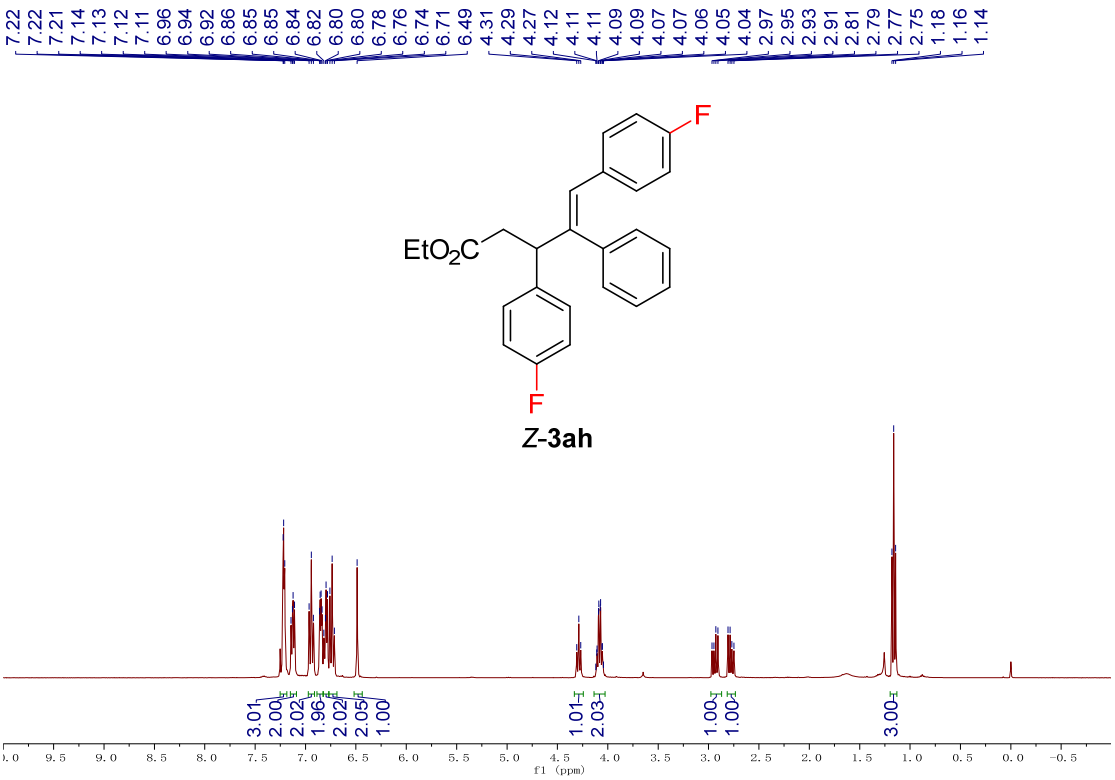
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3ah**



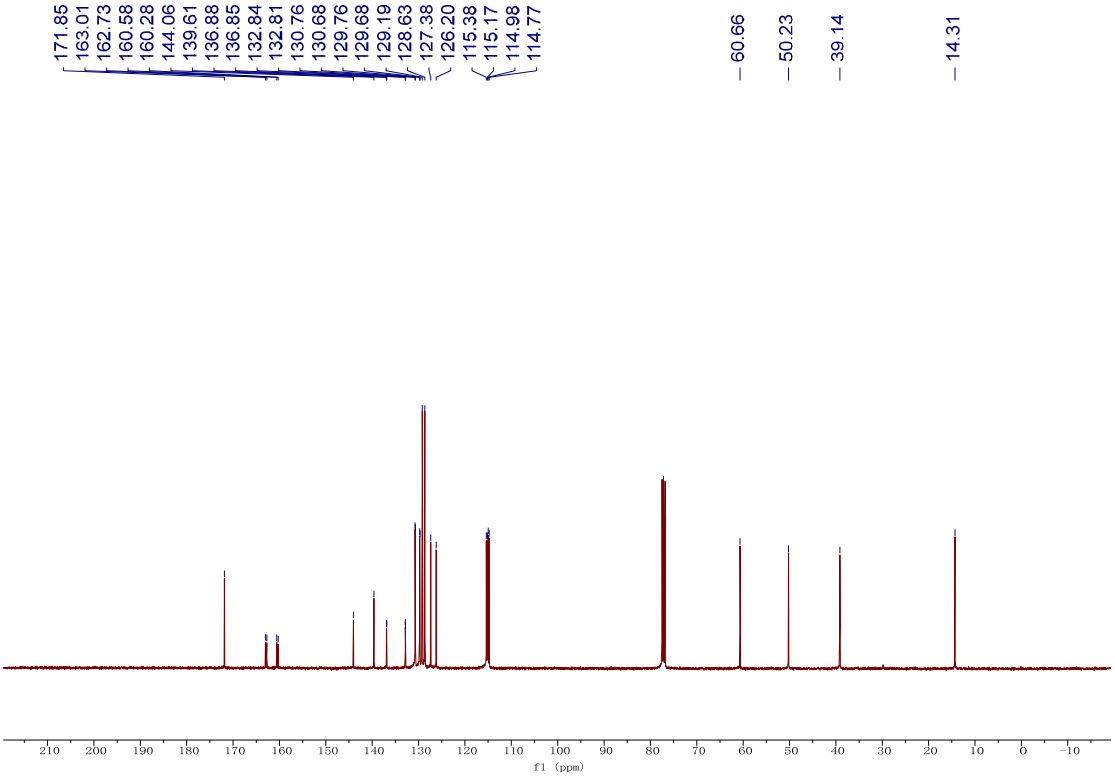
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3ah**



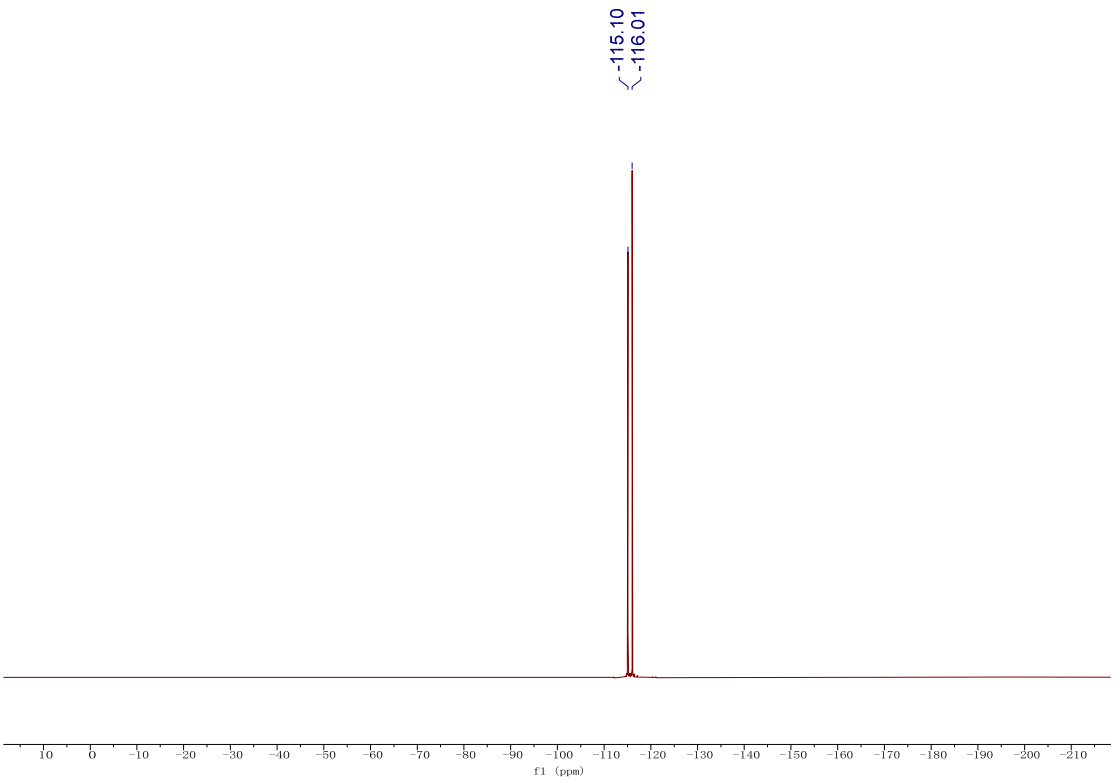
^{19}F NMR (376 MHz, $CDCl_3$) of *E*-**3ah**



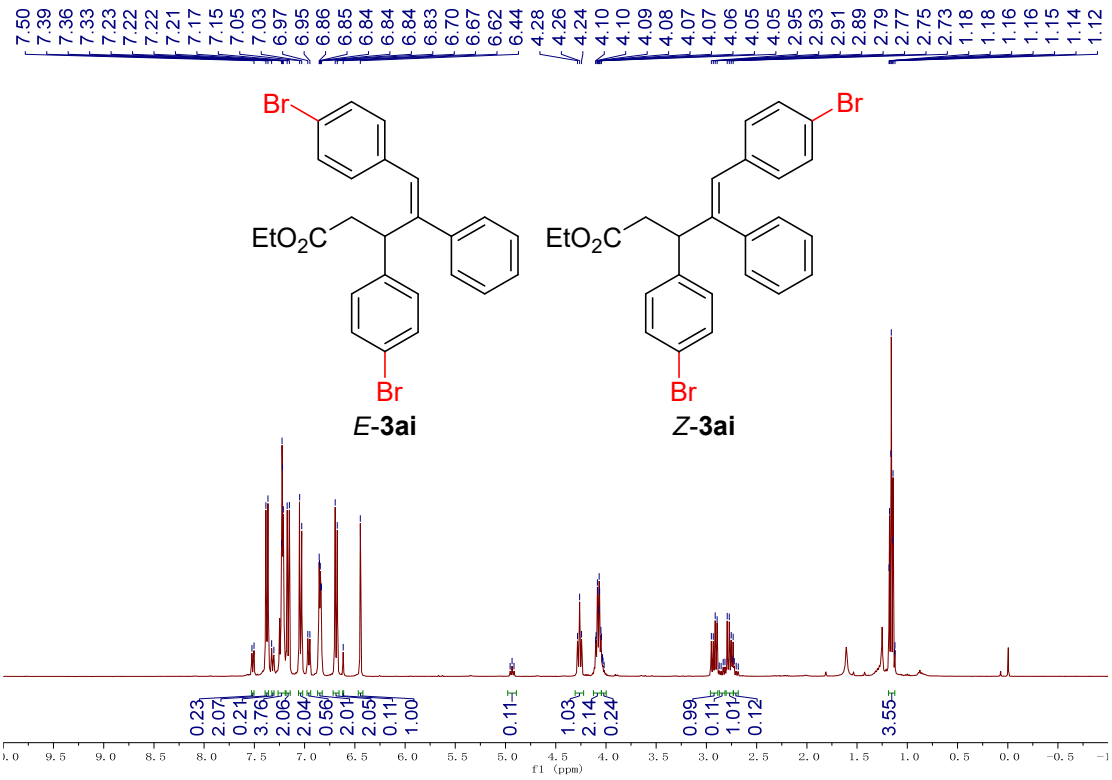
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ah**



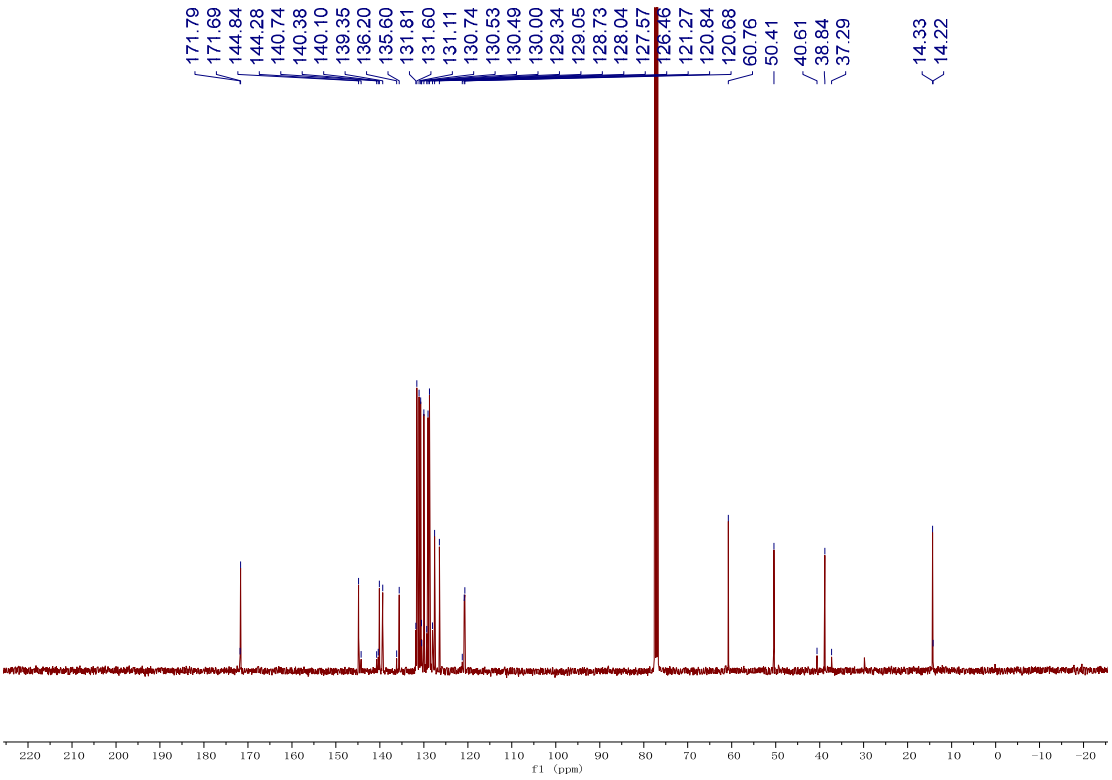
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ah**



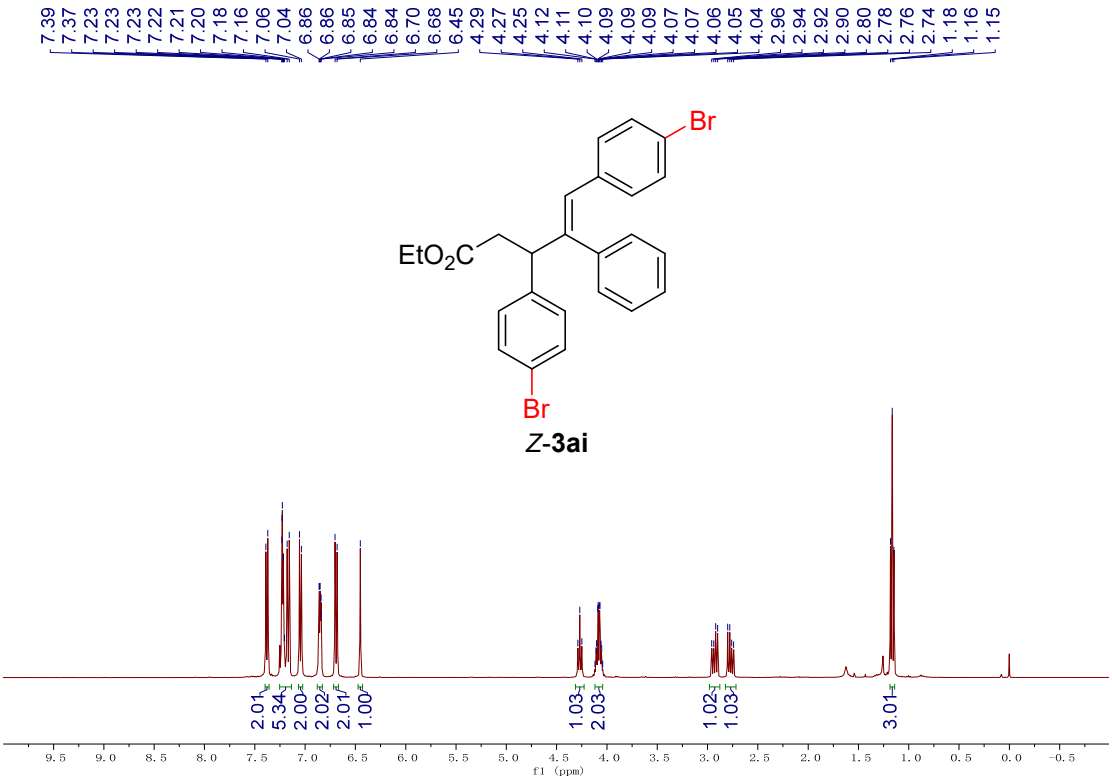
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-**3ah**



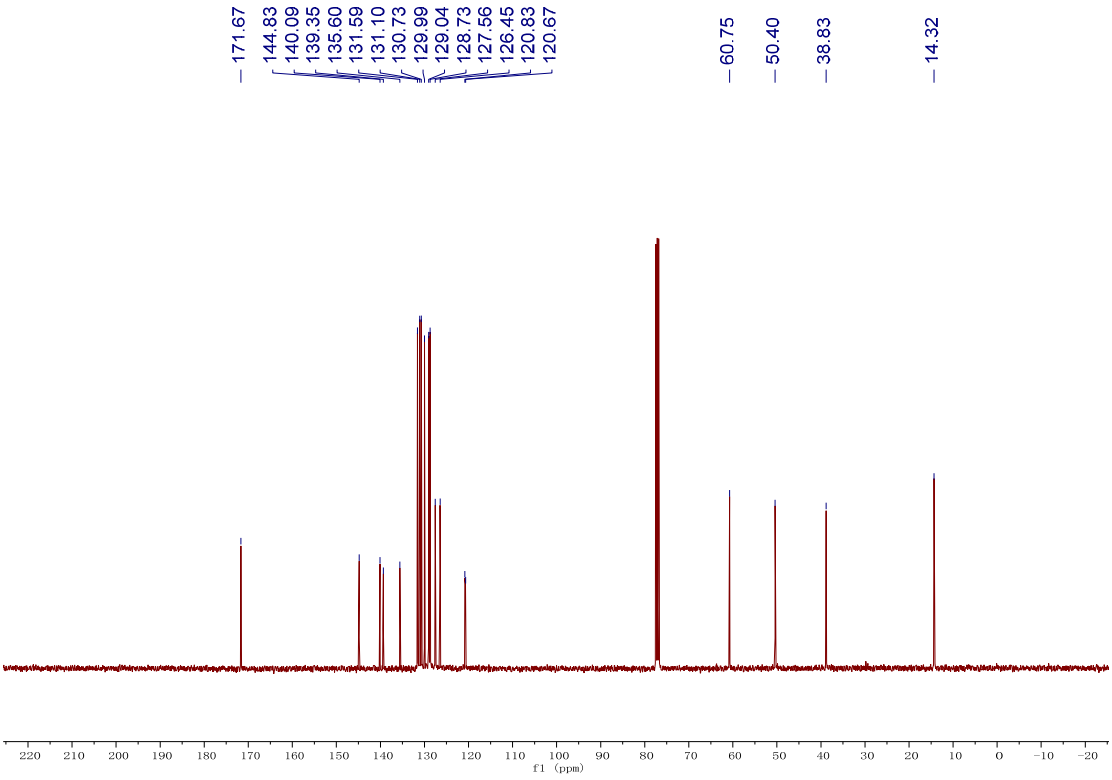
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



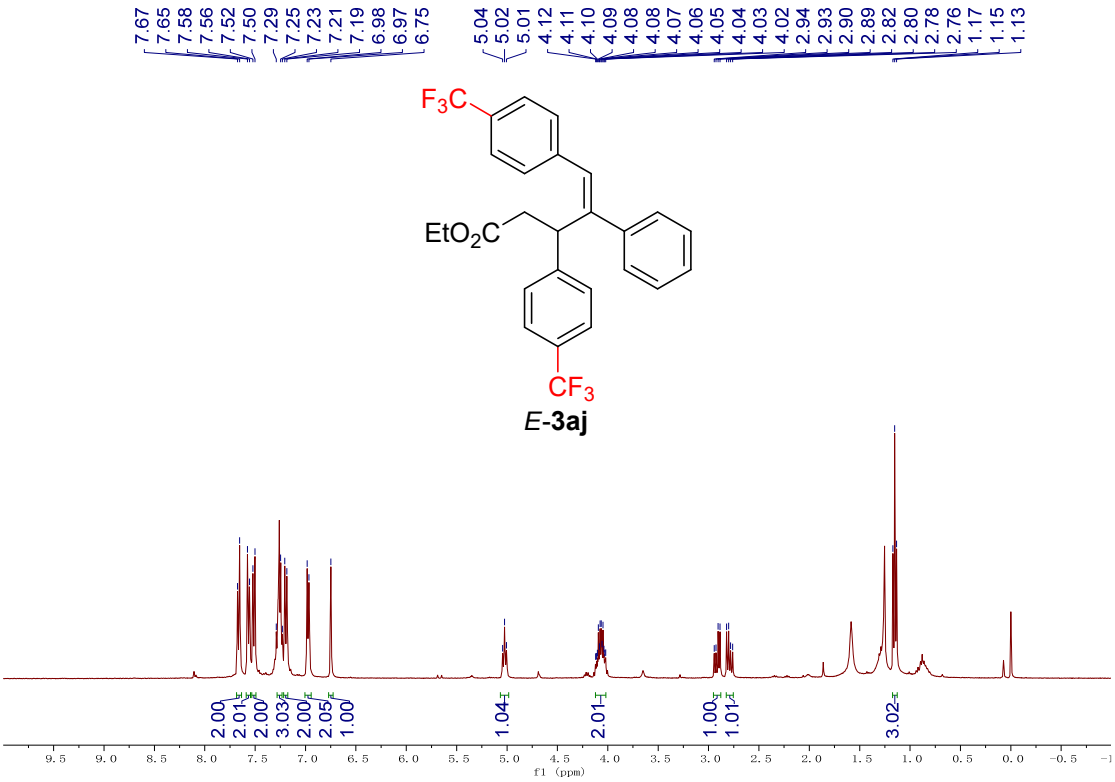
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**



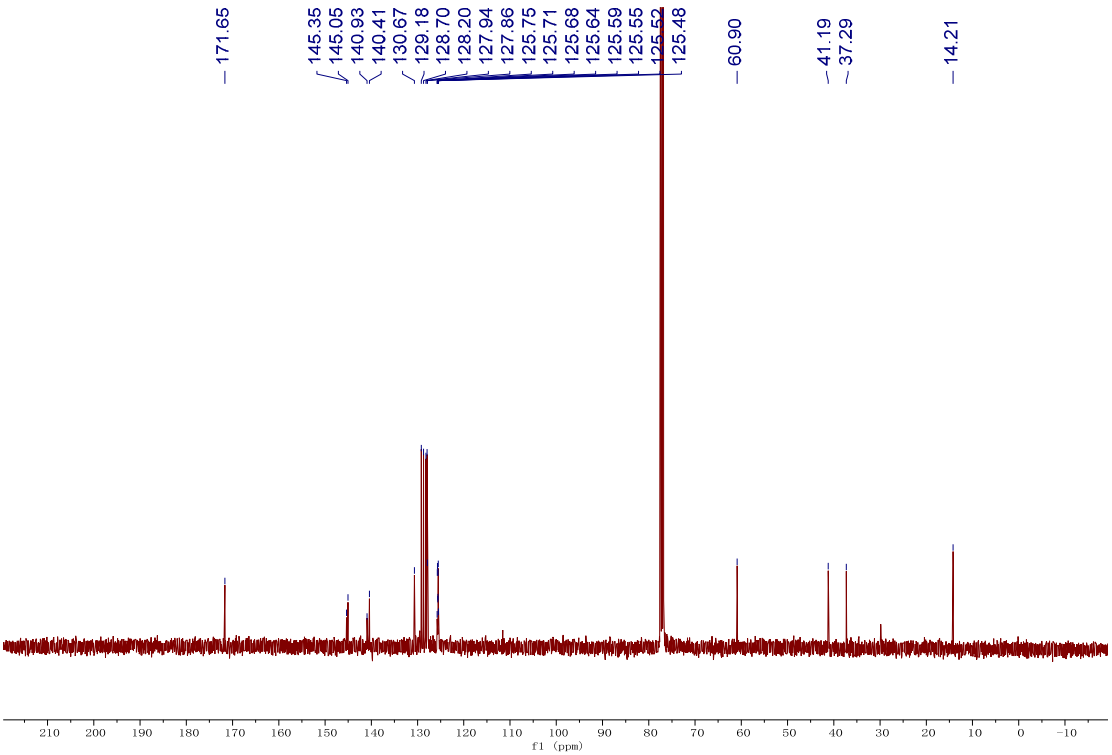
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ai**



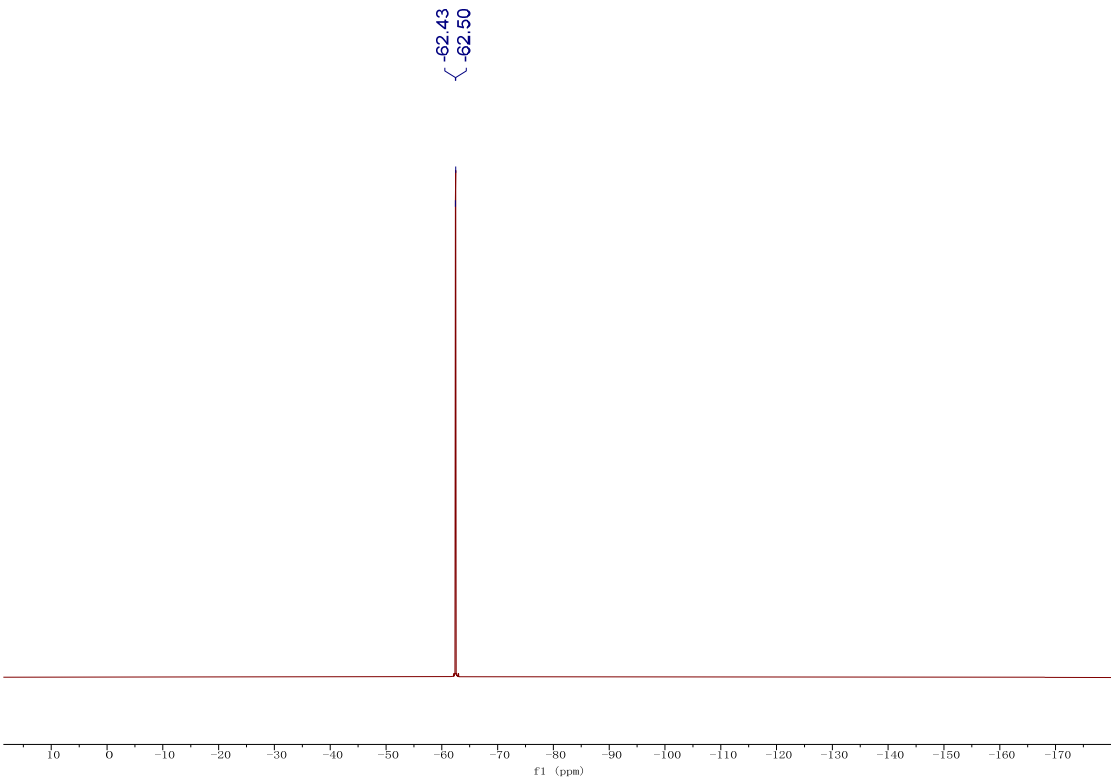
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ai**



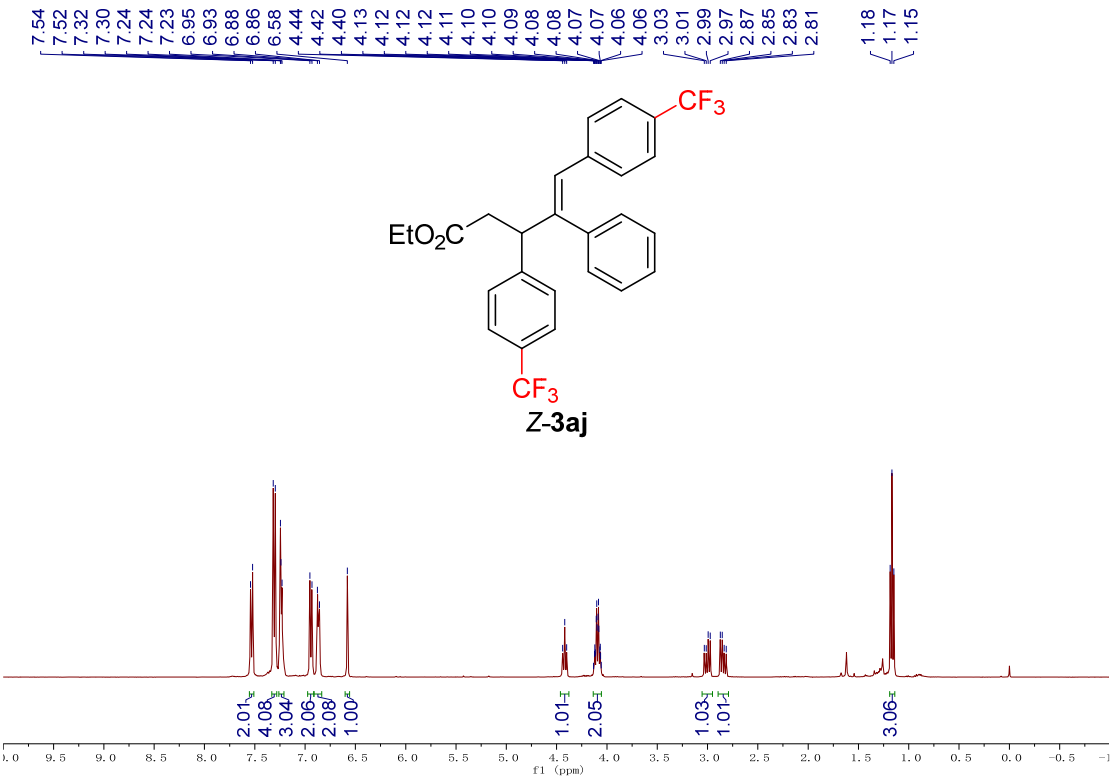
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3aj**



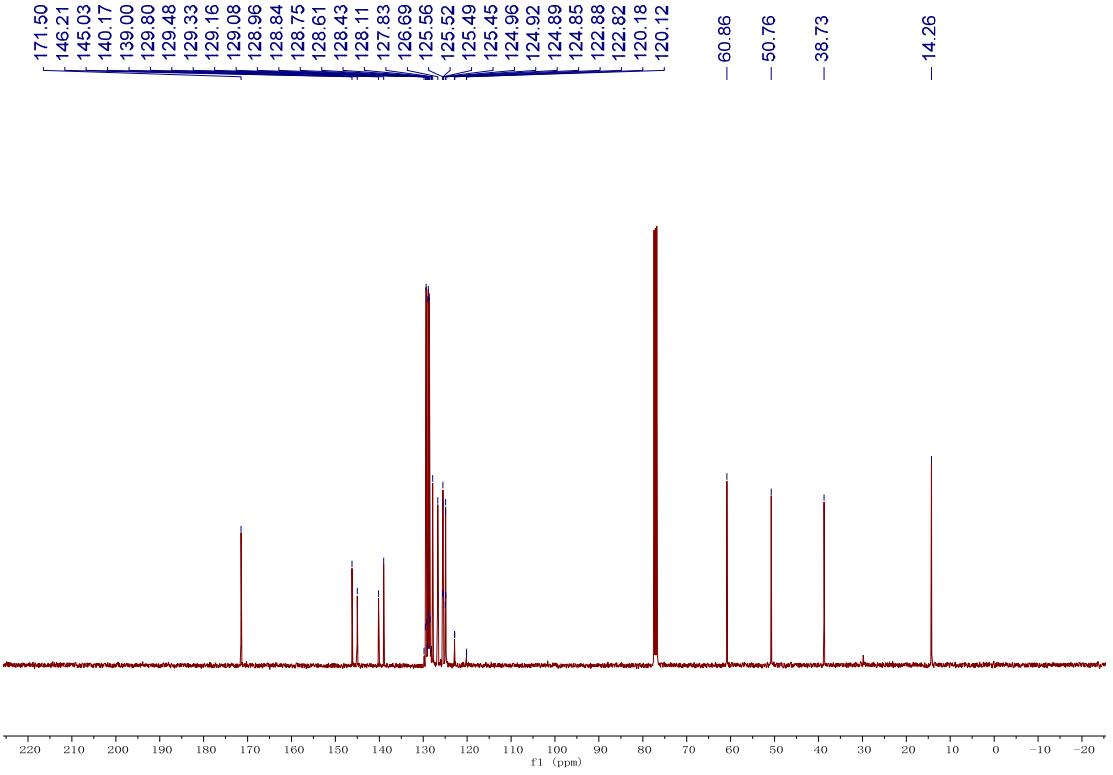
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3aj**



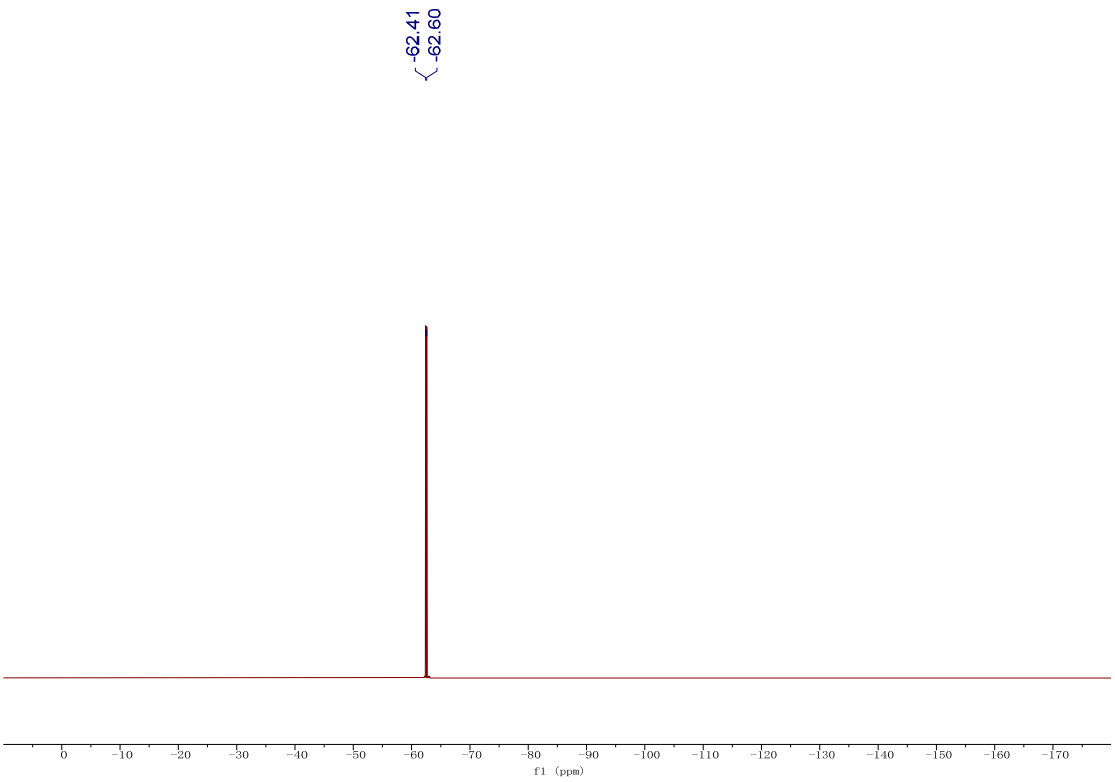
^{19}F NMR (376 MHz, $CDCl_3$) of *E*-**3aj**



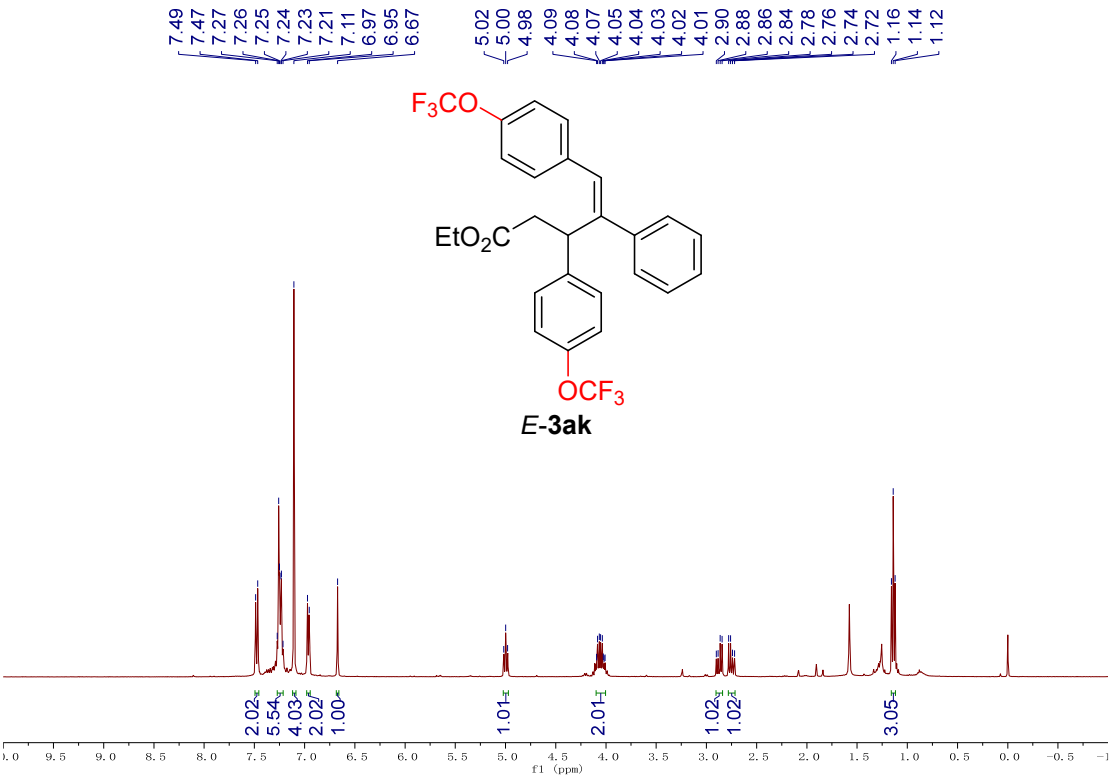
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3aj**



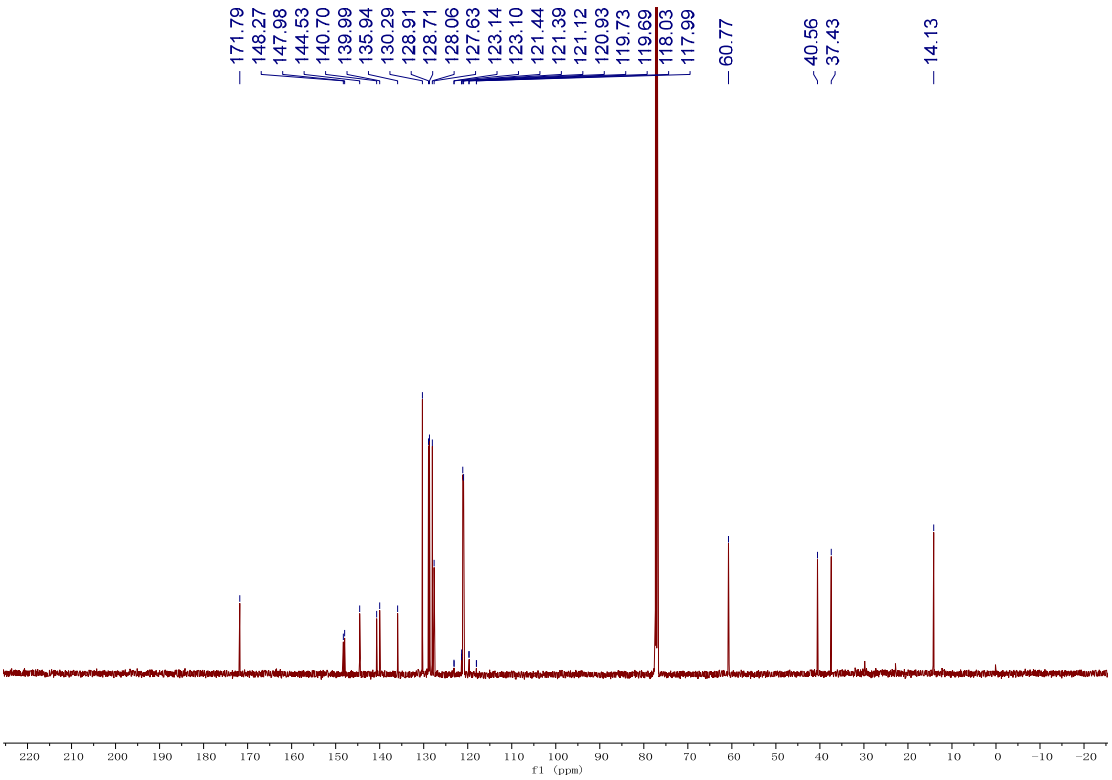
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3aj**



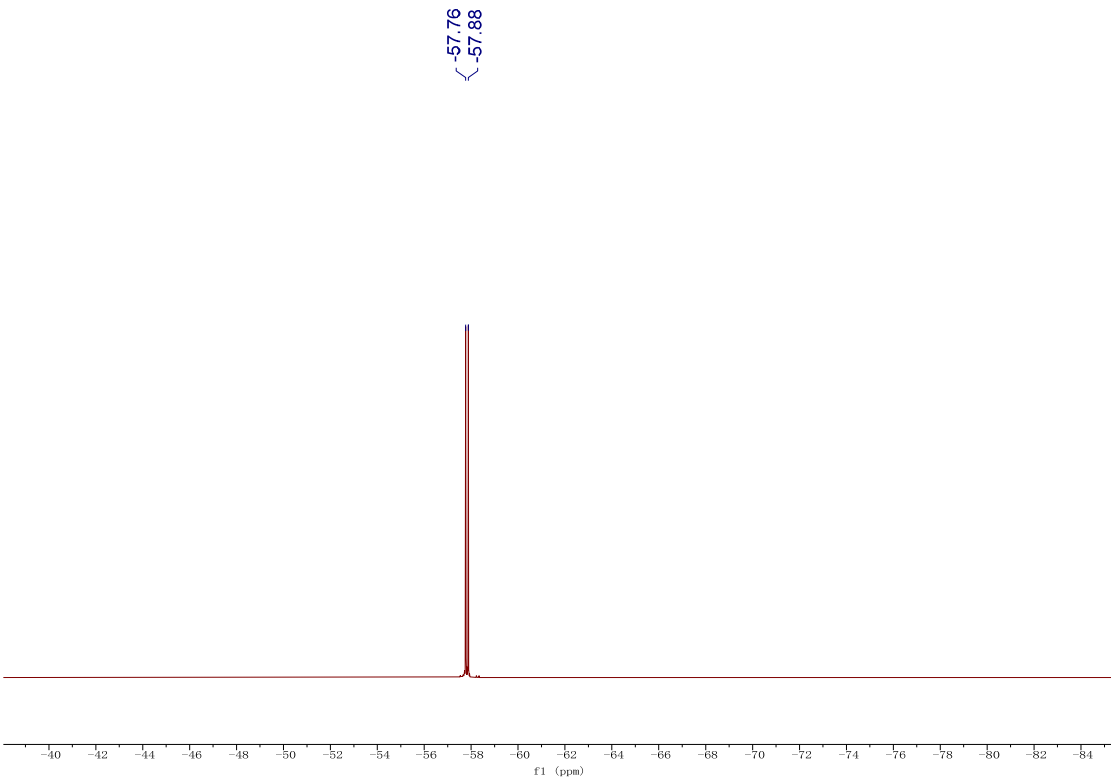
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-**3aj**



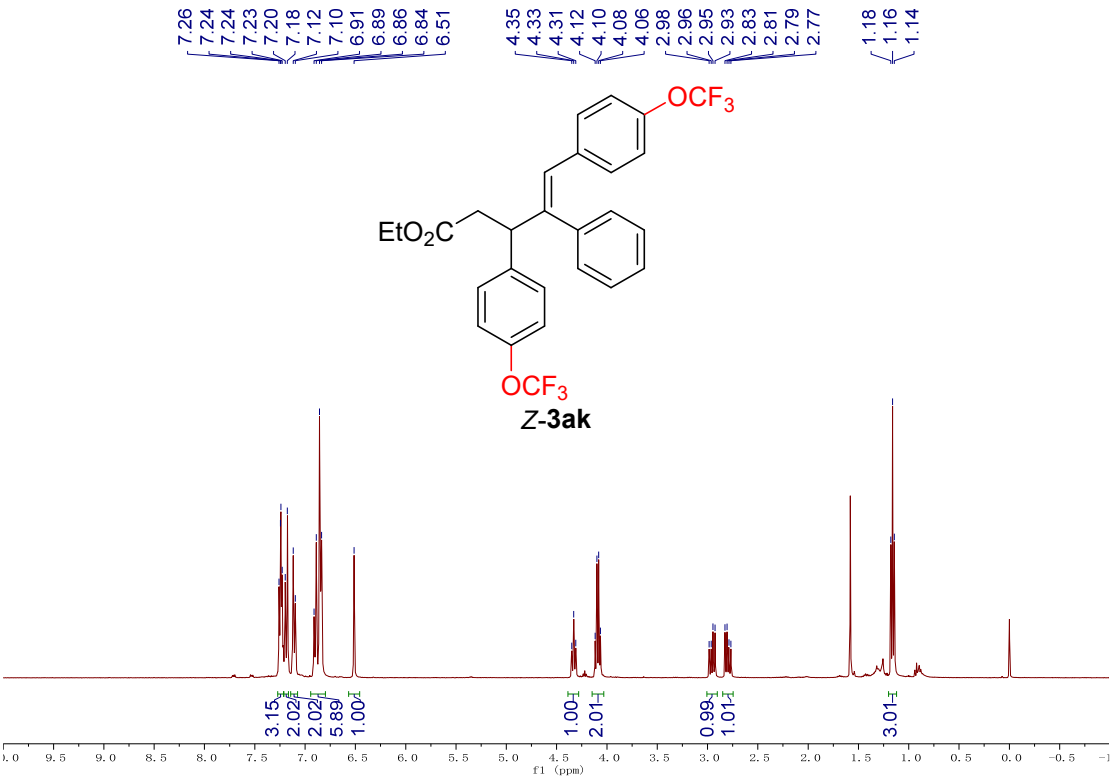
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3ak**



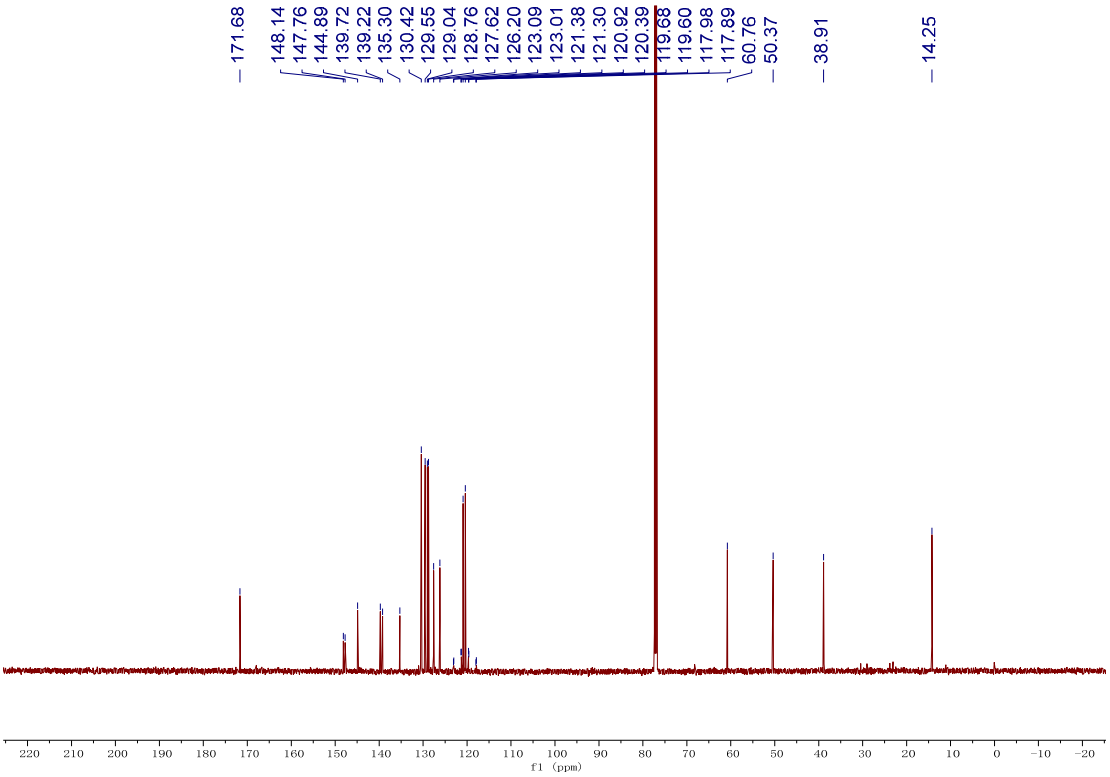
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3ak**



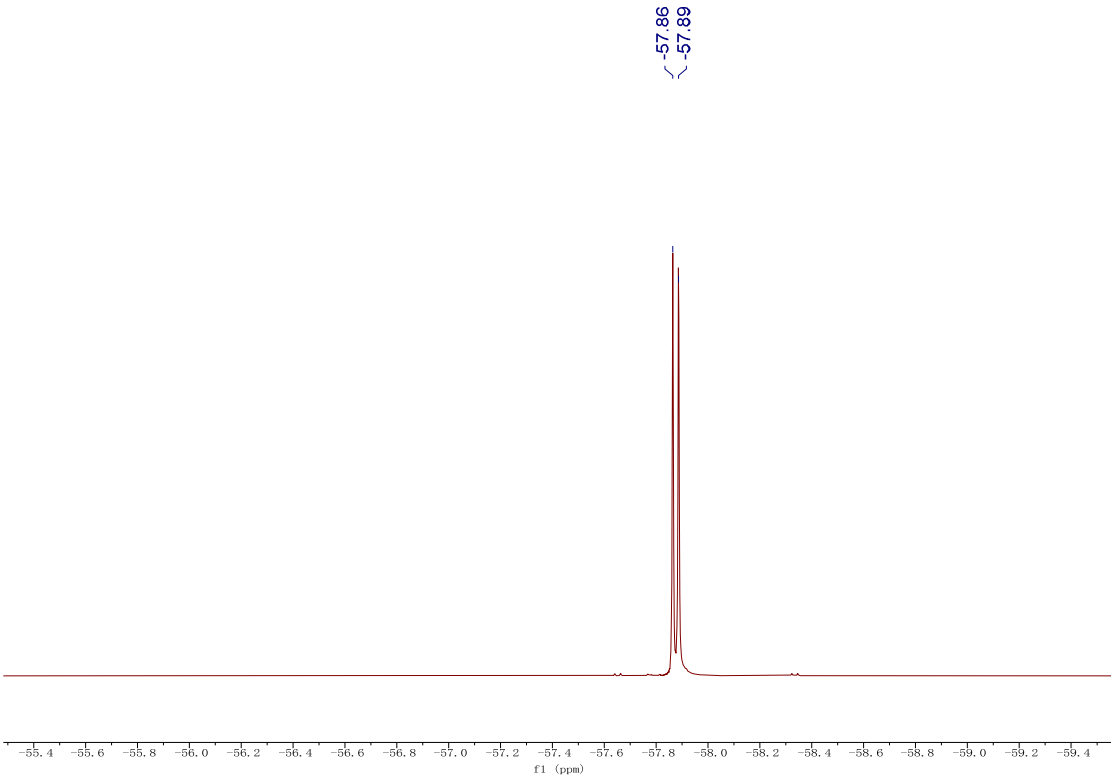
^{19}F NMR (376 MHz, $CDCl_3$) of *E*-**3ak**



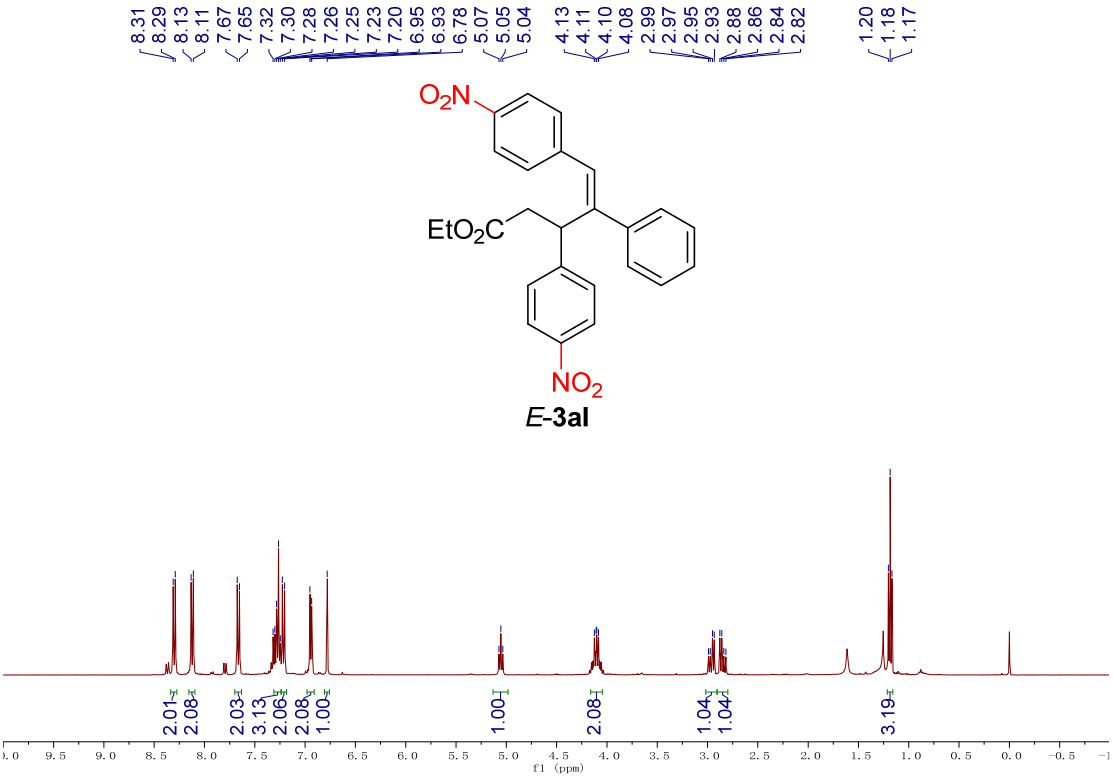
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ak**



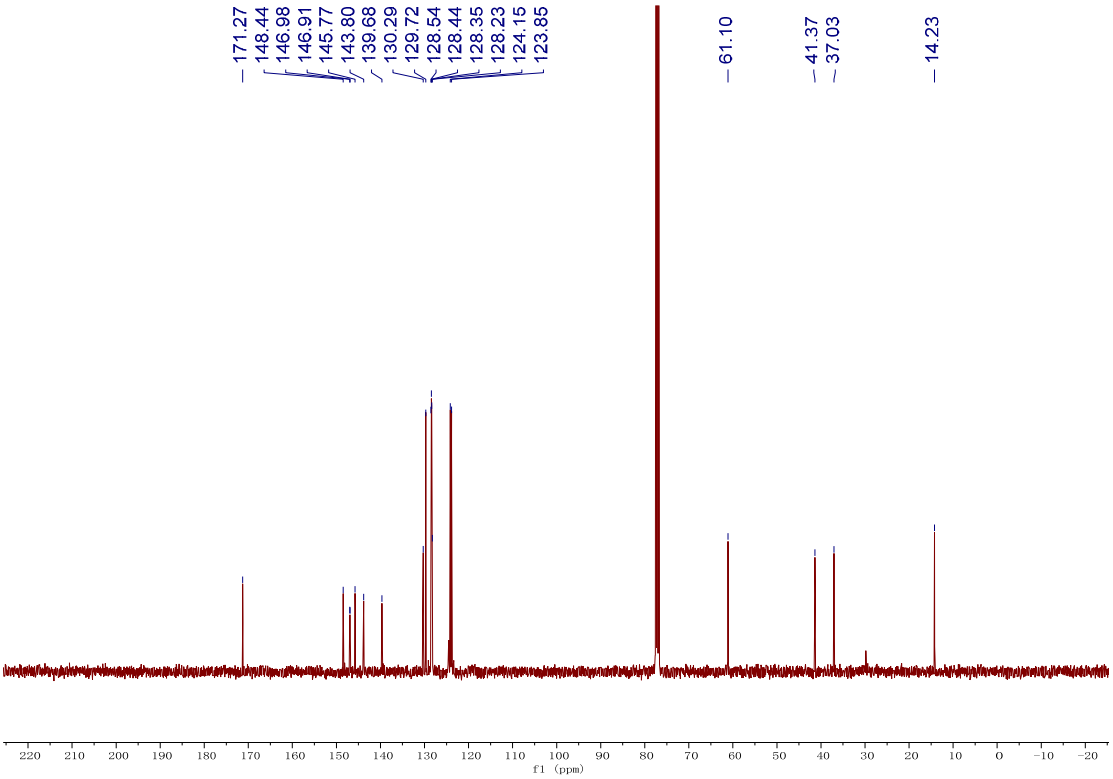
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ak**



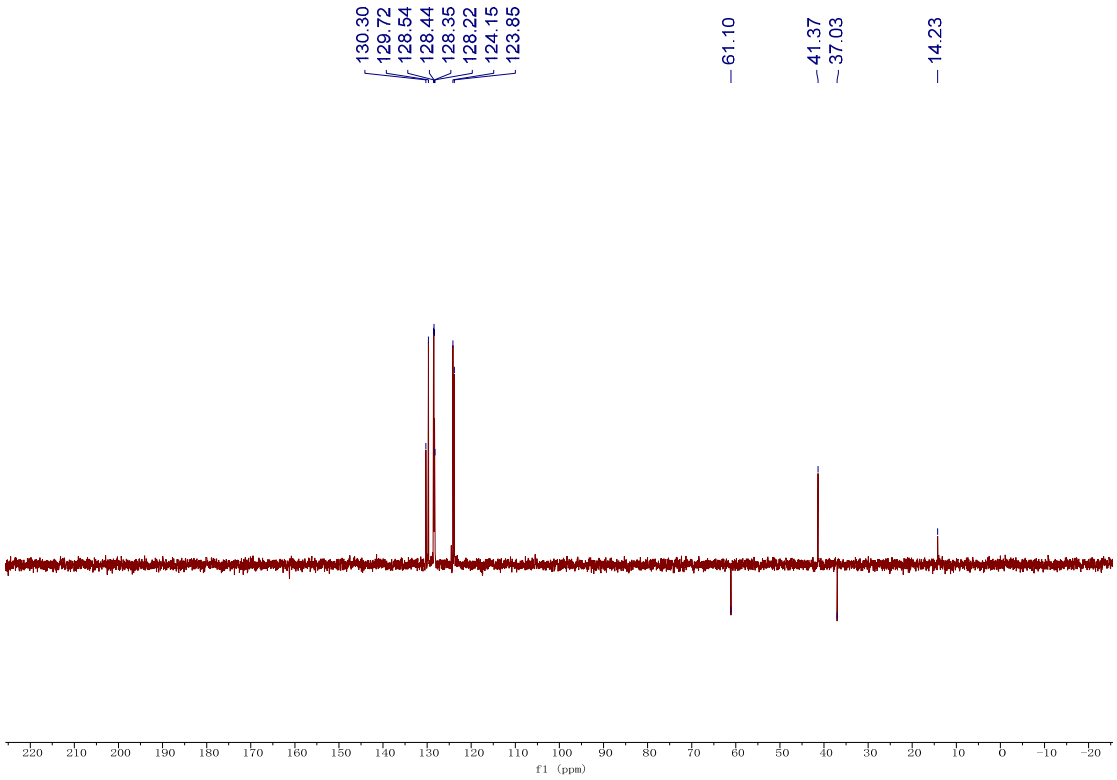
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-**3ak**



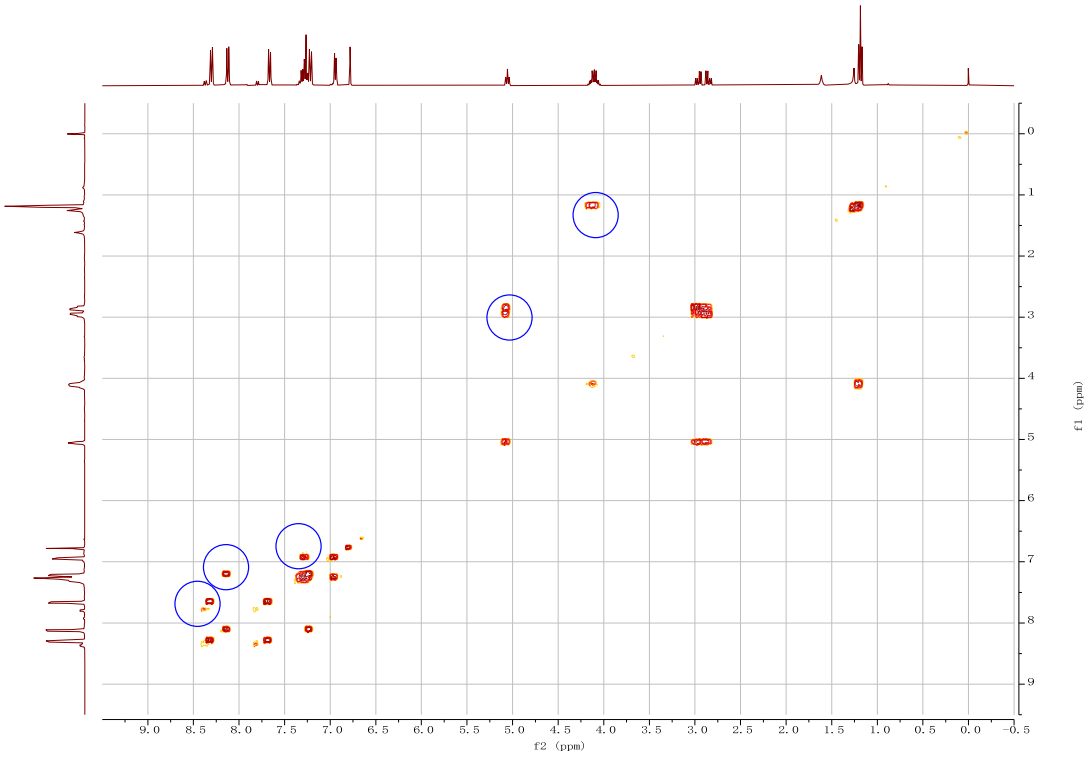
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3al**



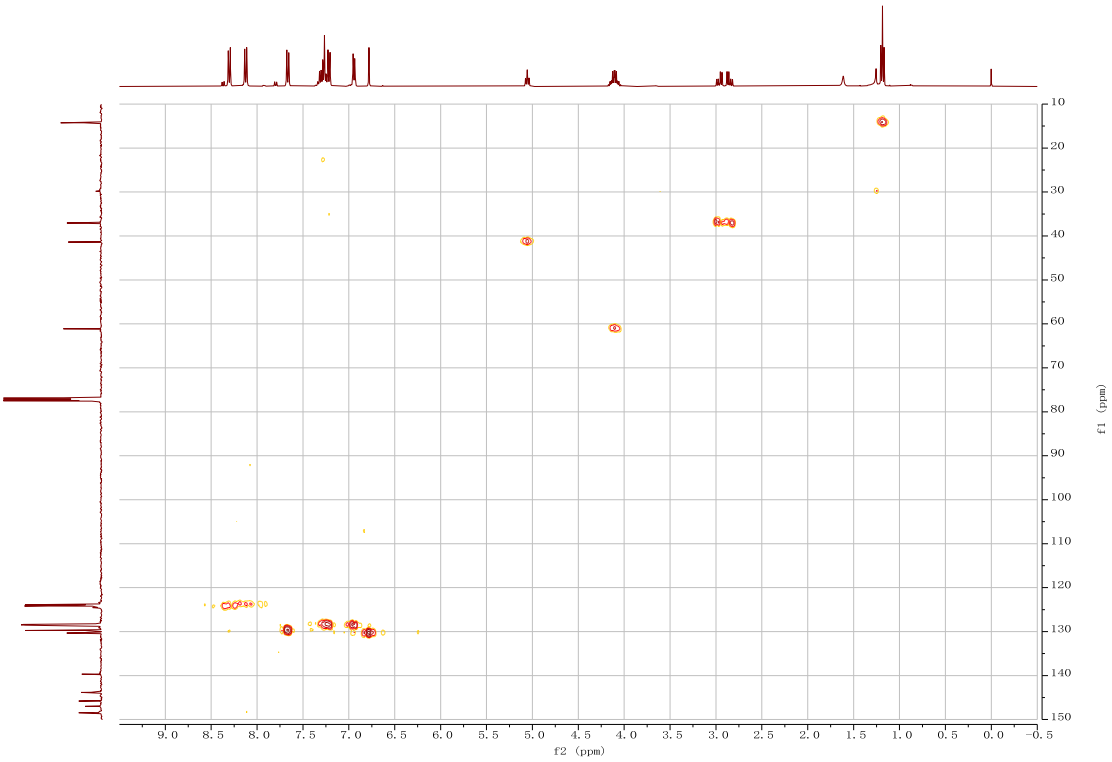
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3al**



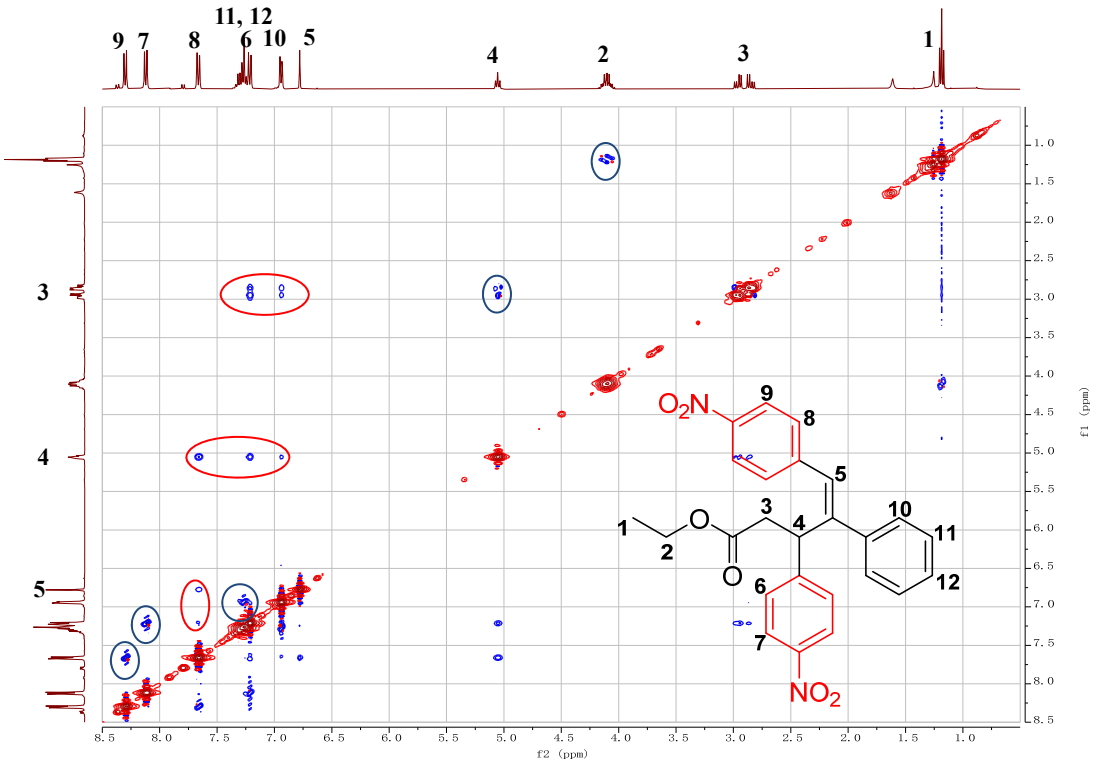
DEPT135 of *E*-**3al**



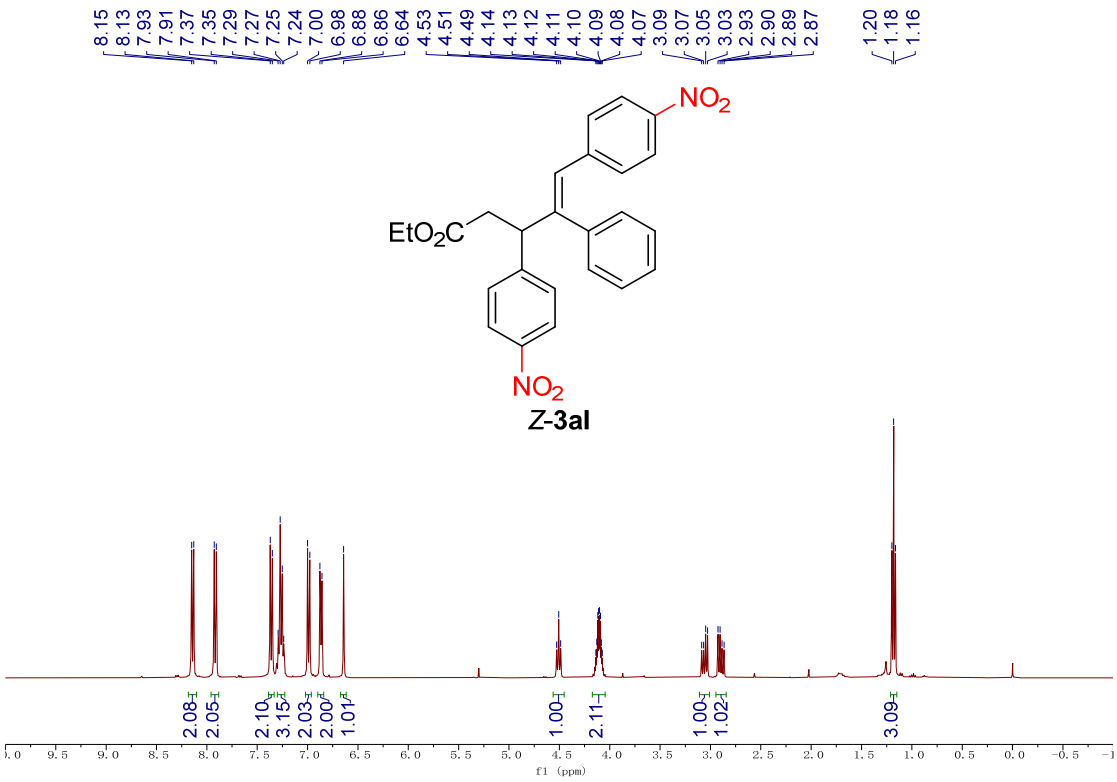
H-H COSY of *E*-**3al**



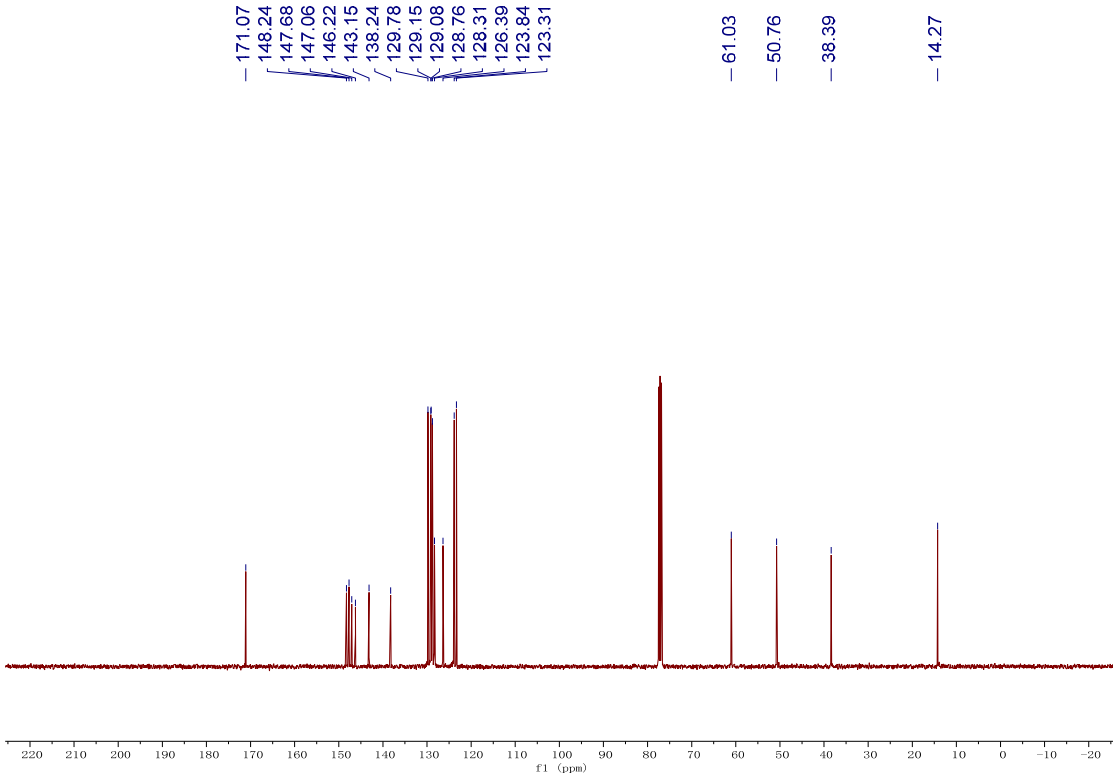
HMQC of *E*-**3al**



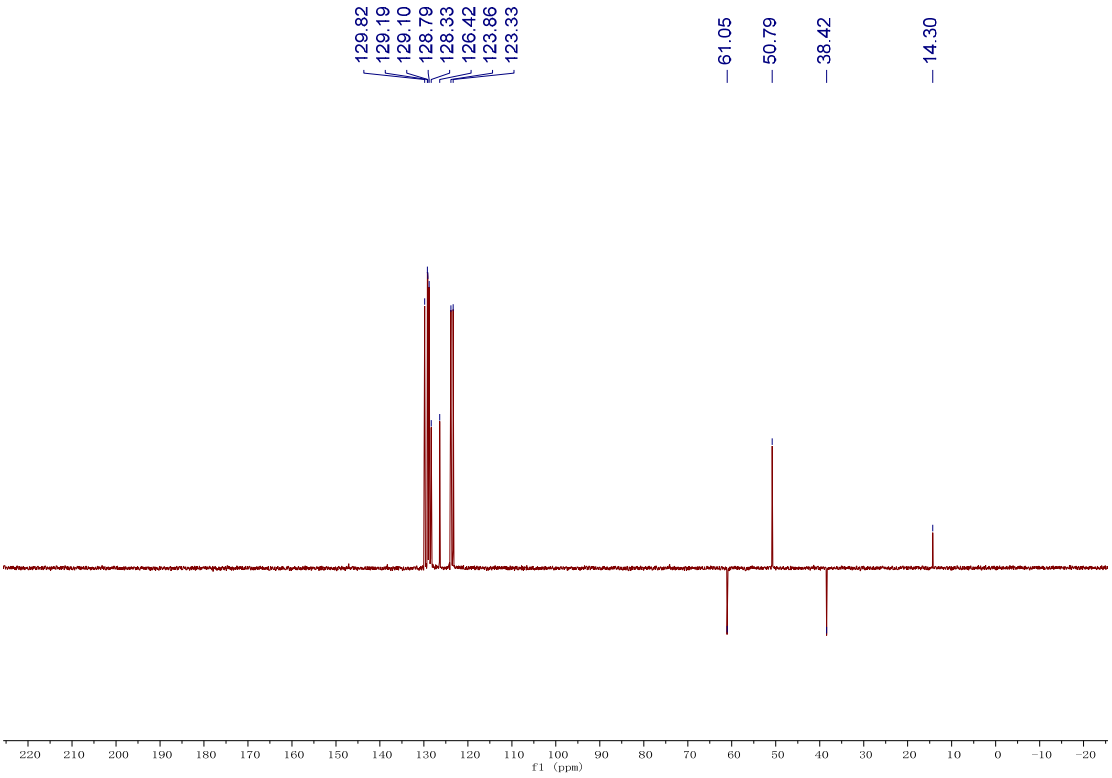
NOESY of *E*-**3al**



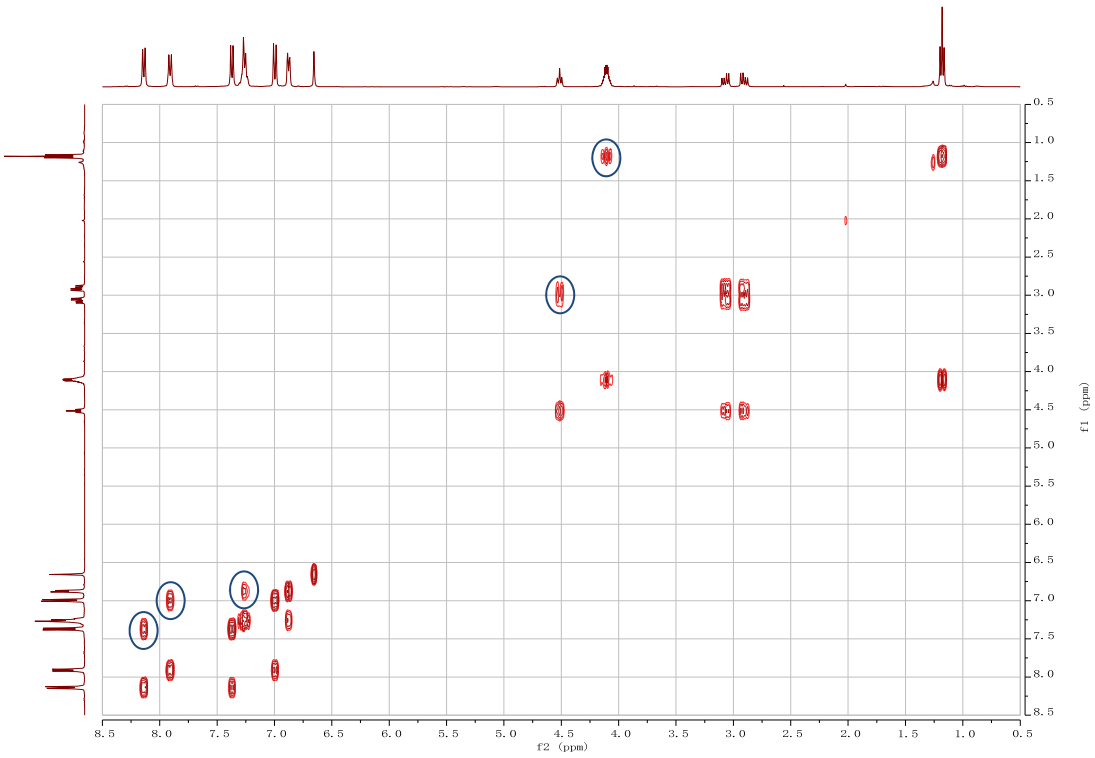
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3al**



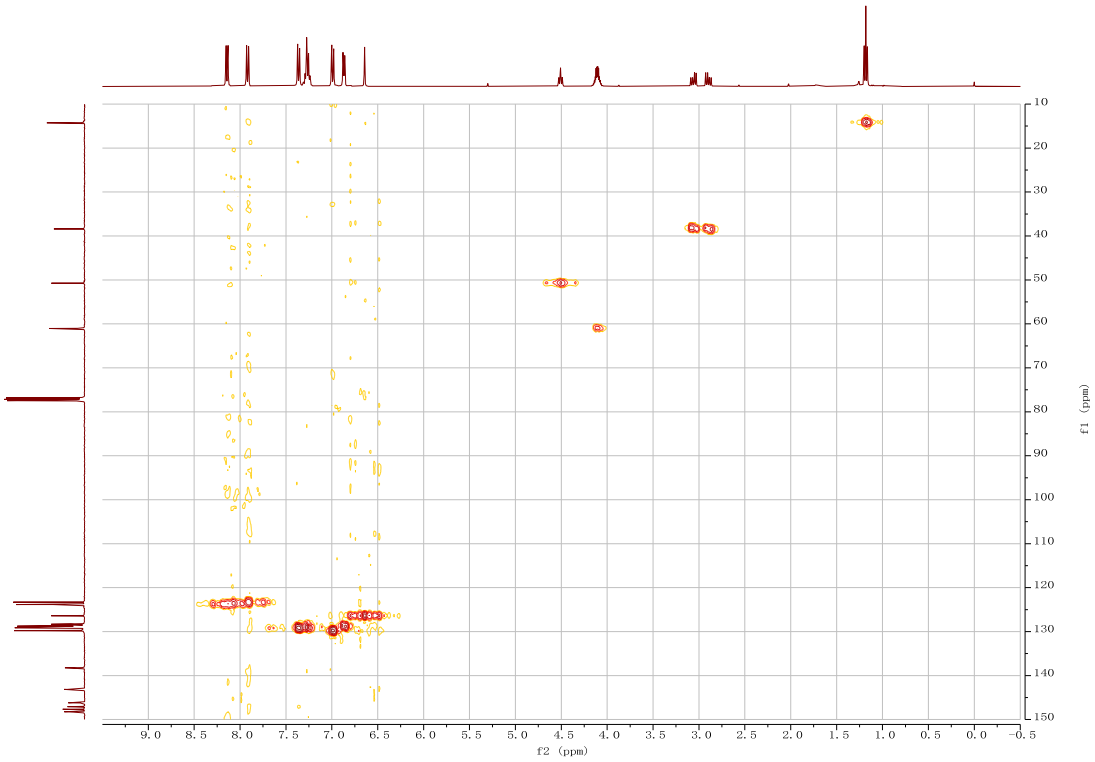
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3al**



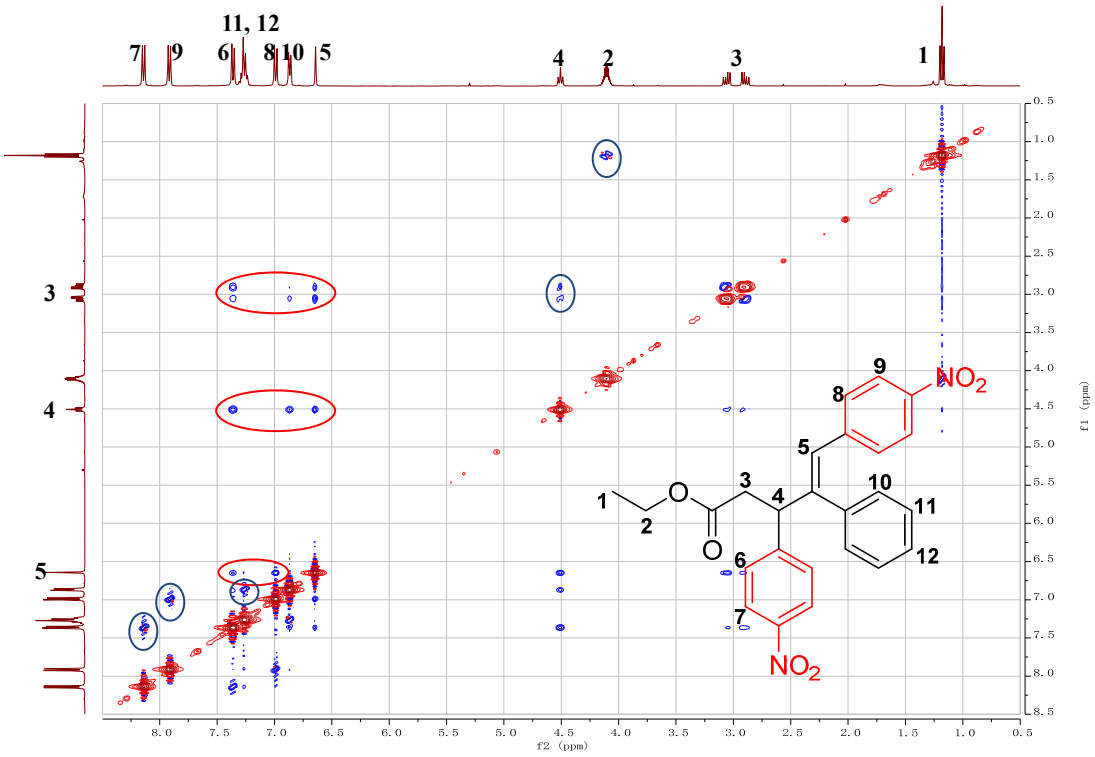
DEPT135 of *Z*-**3al**



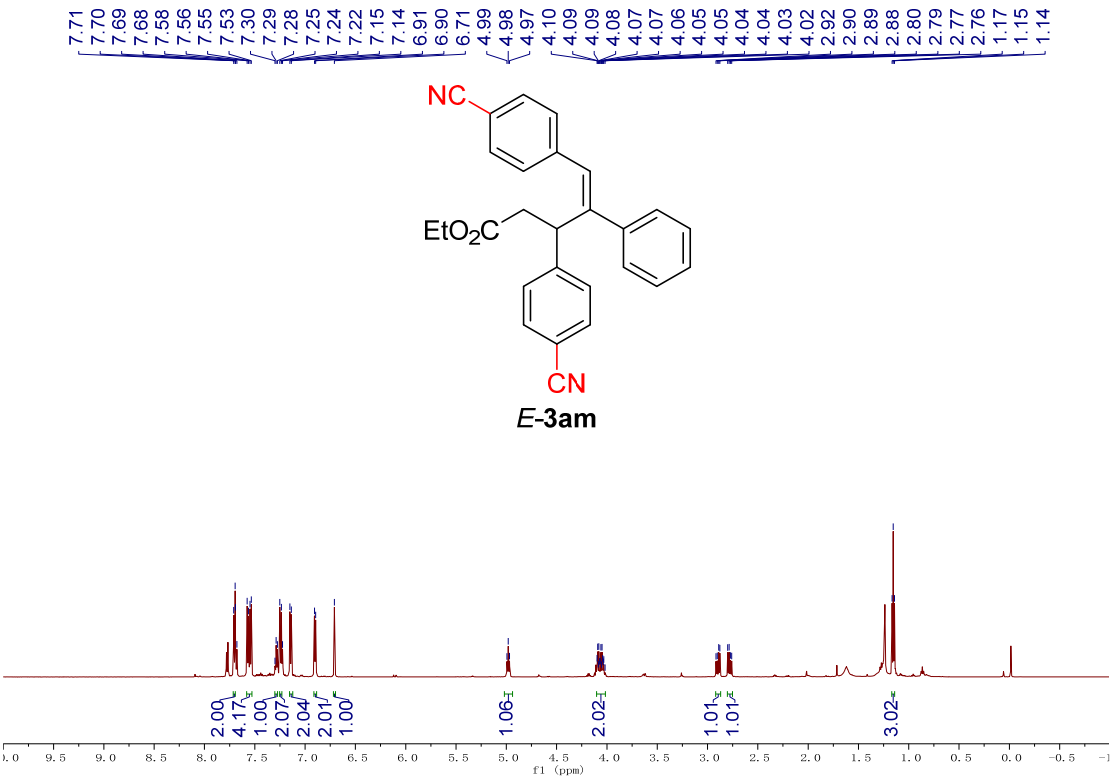
H-H COSY of *Z*-**3al**



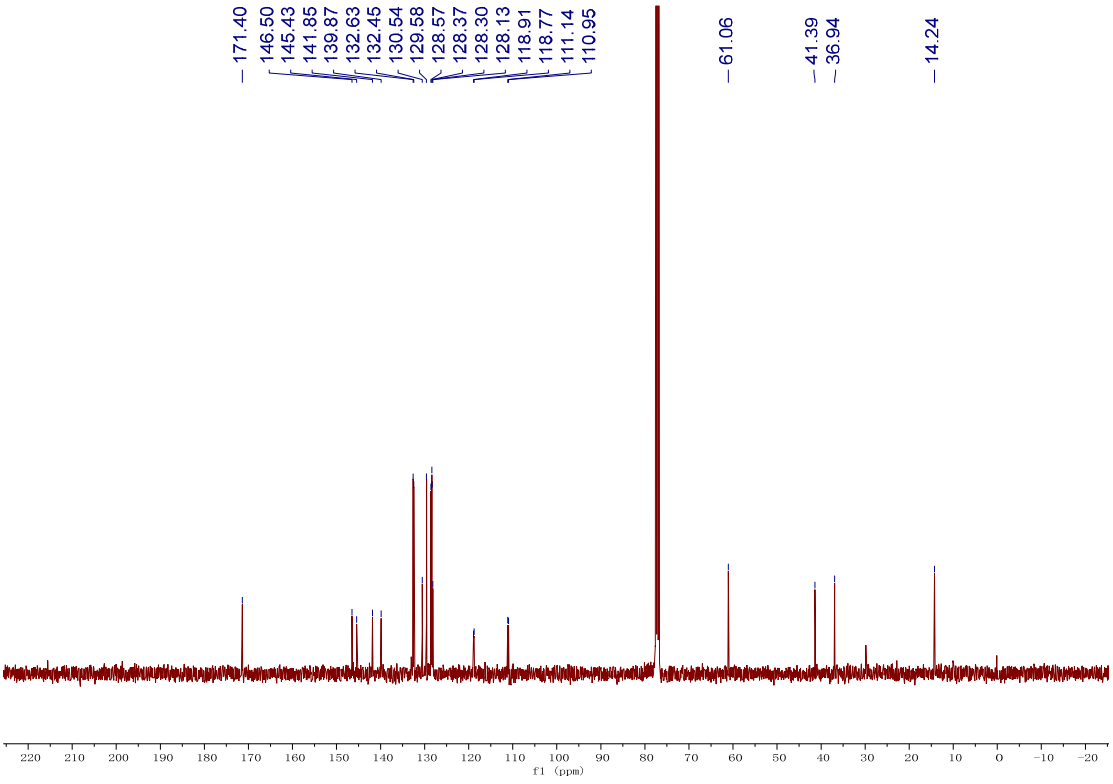
HMQC of *Z*-**3al**



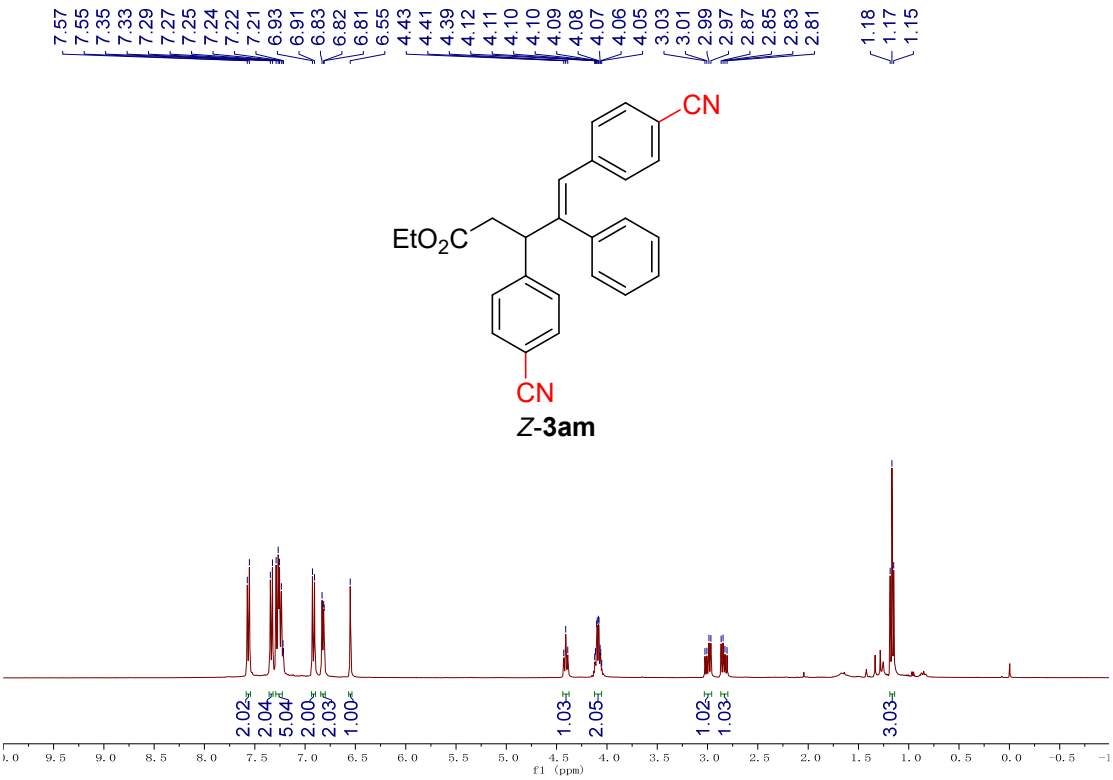
NOESY of *Z*-**3al**



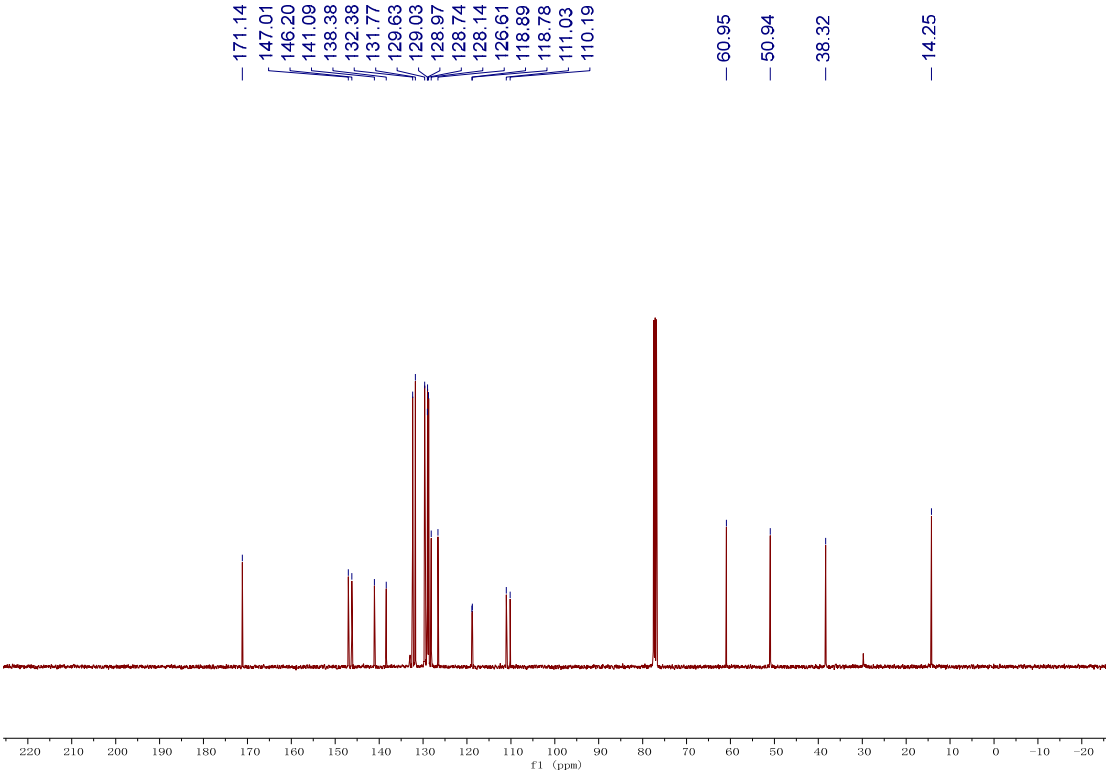
^{1}H NMR (600 MHz, $CDCl_3$) of *E*-**3am**



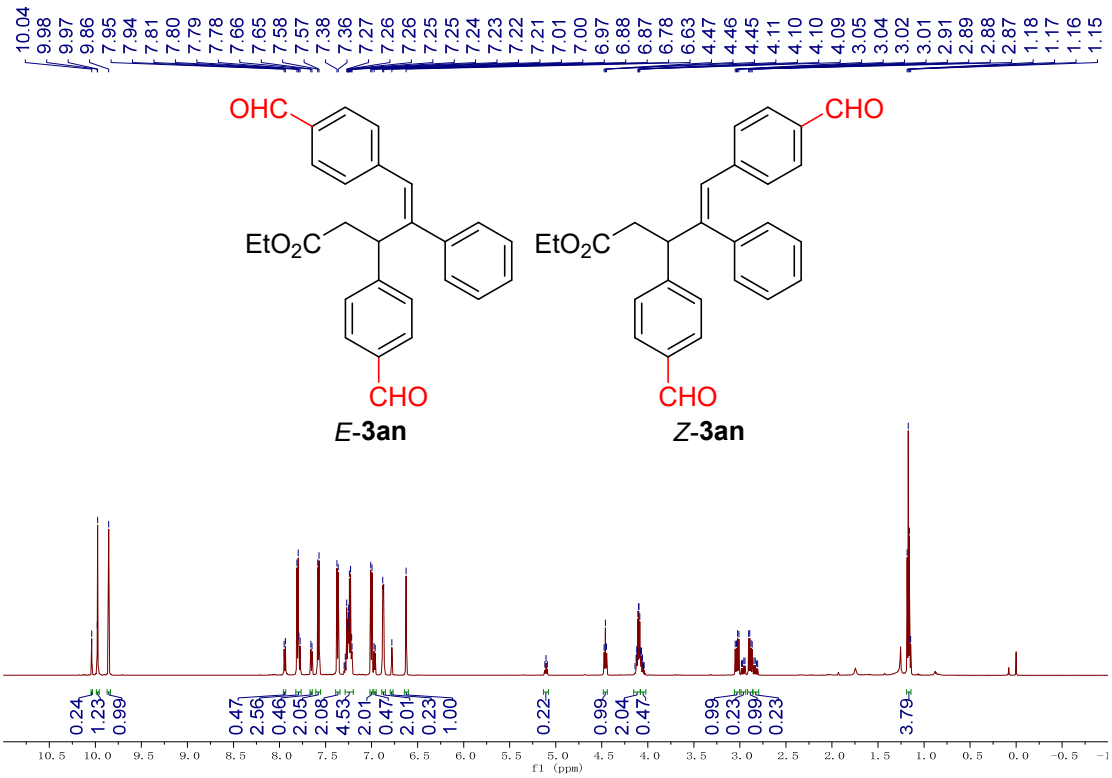
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3am**



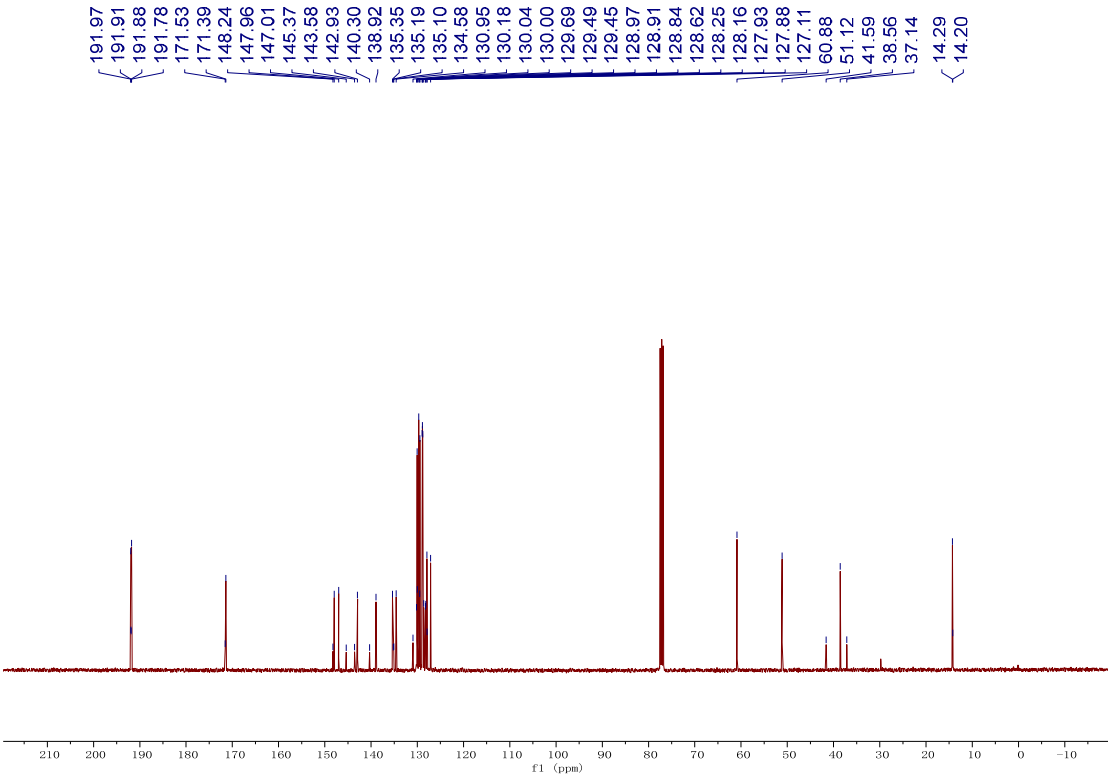
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3am**



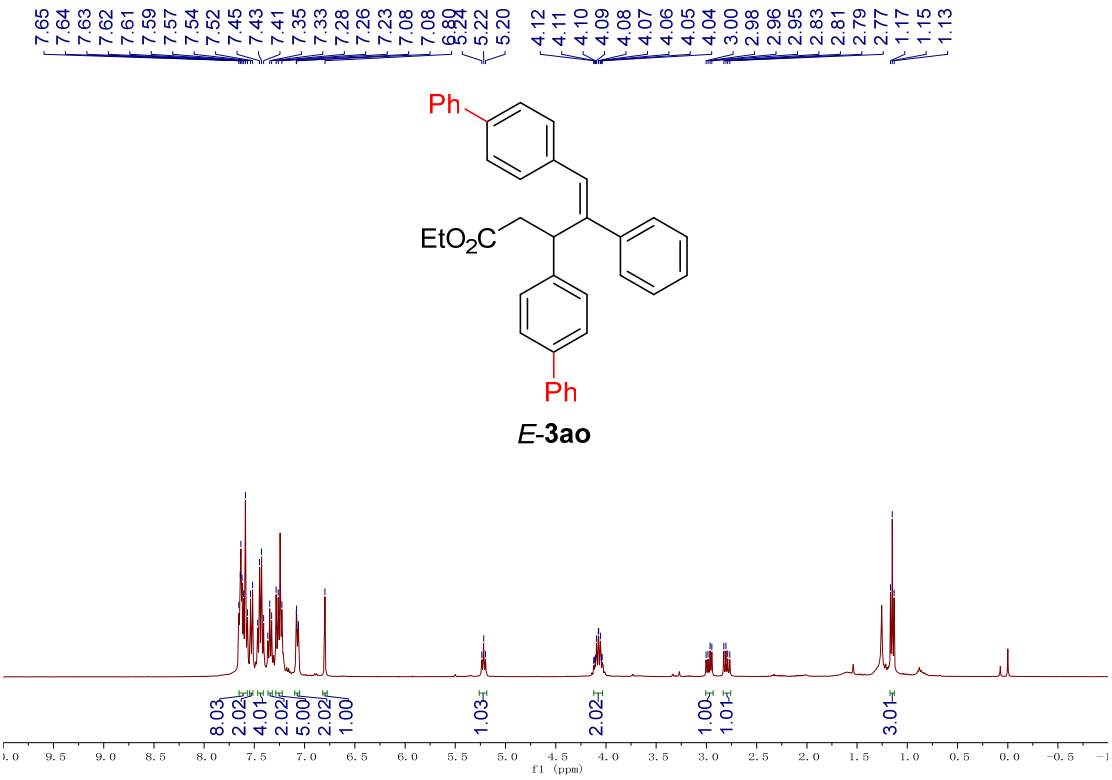
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3am**



^{1}H NMR (600 MHz, $CDCl_3$) of **3an**

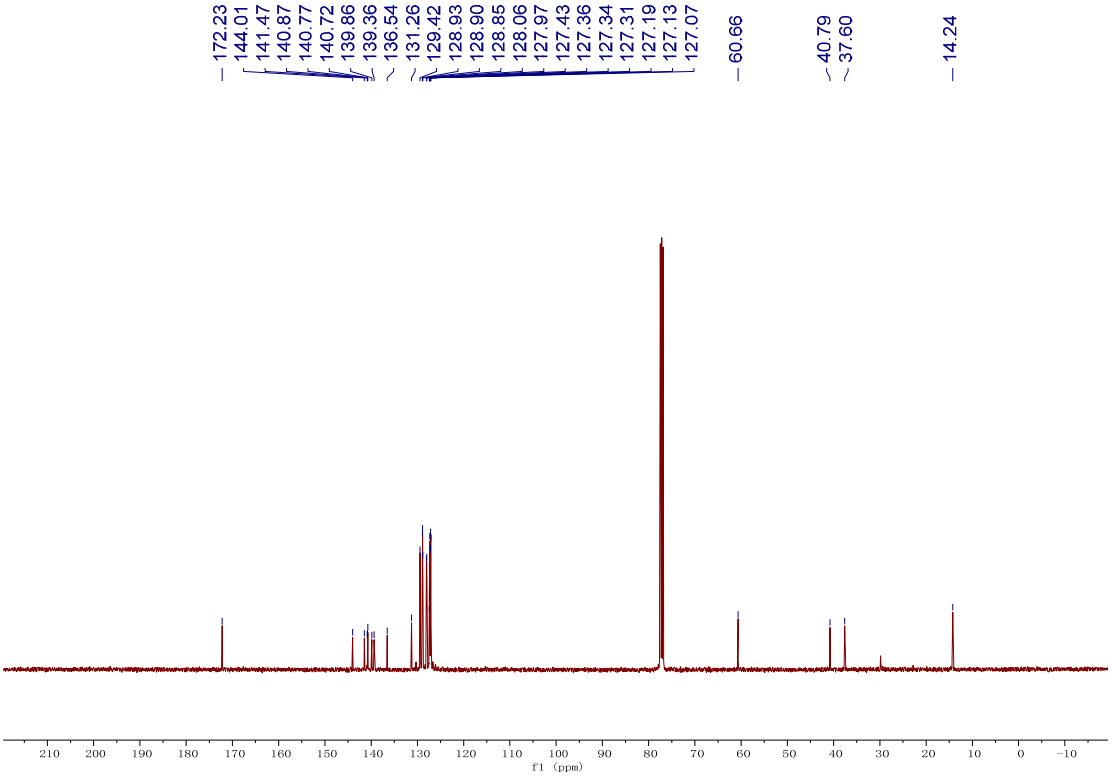


^{13}C NMR (101 MHz, $CDCl_3$) of **3an**

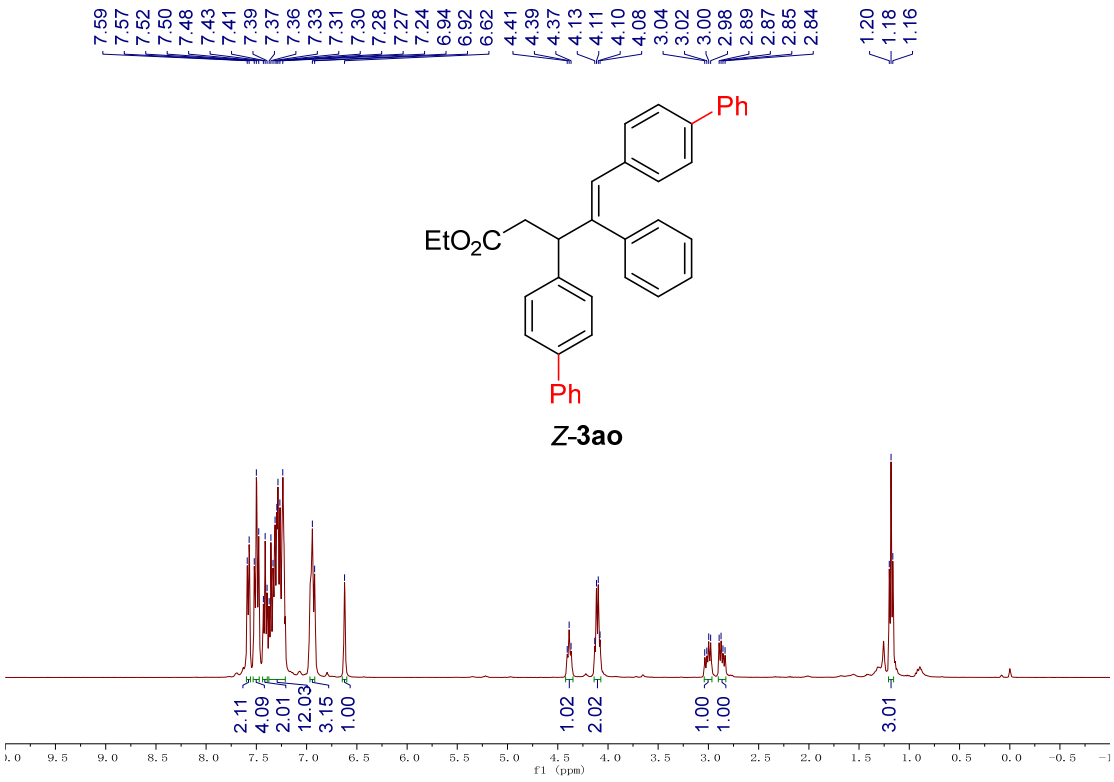


E-**3ao**

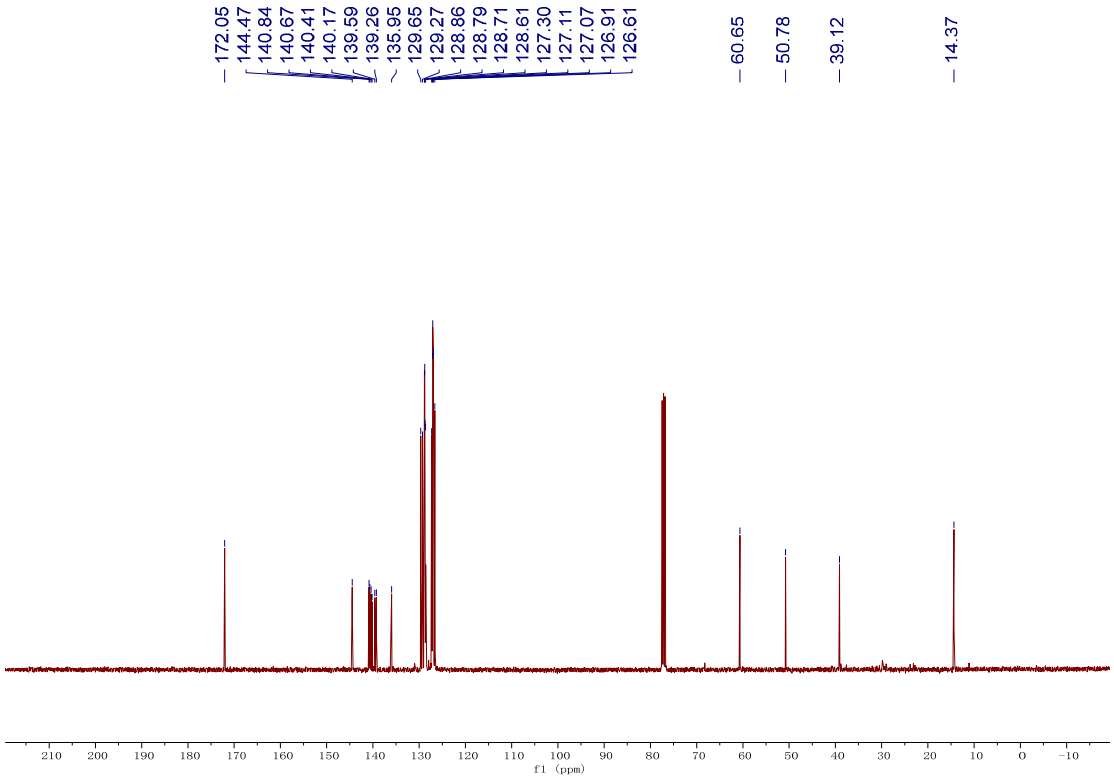
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3ao**



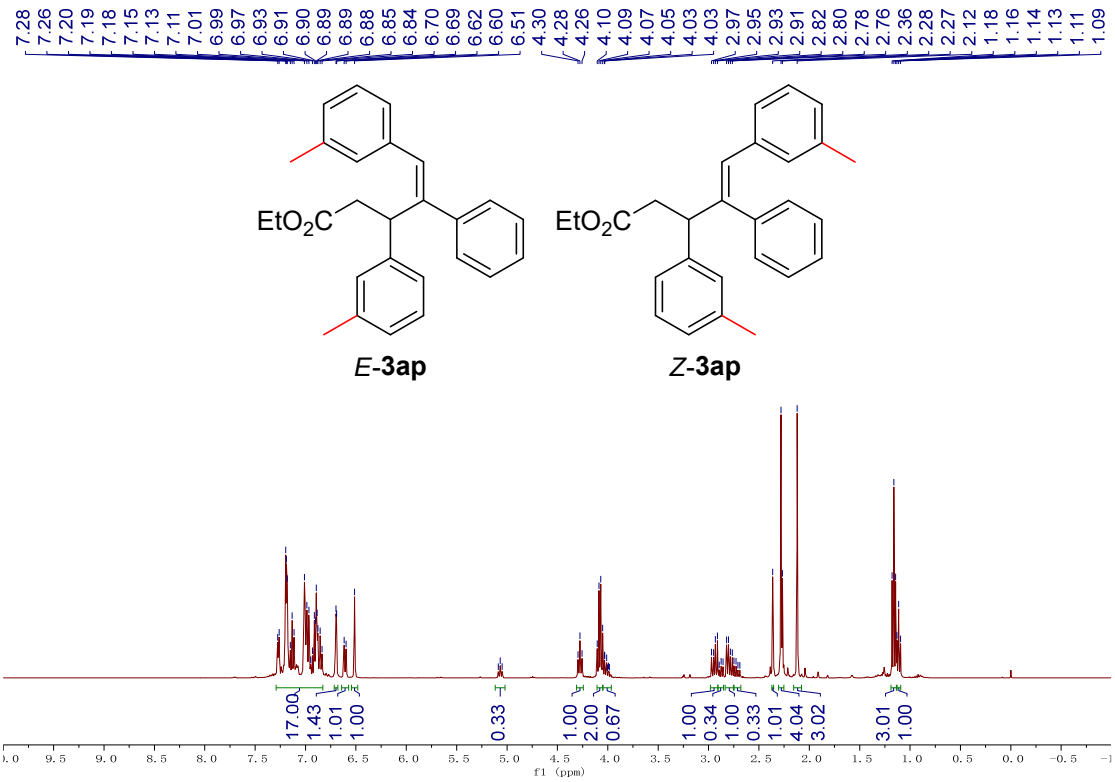
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3ao**



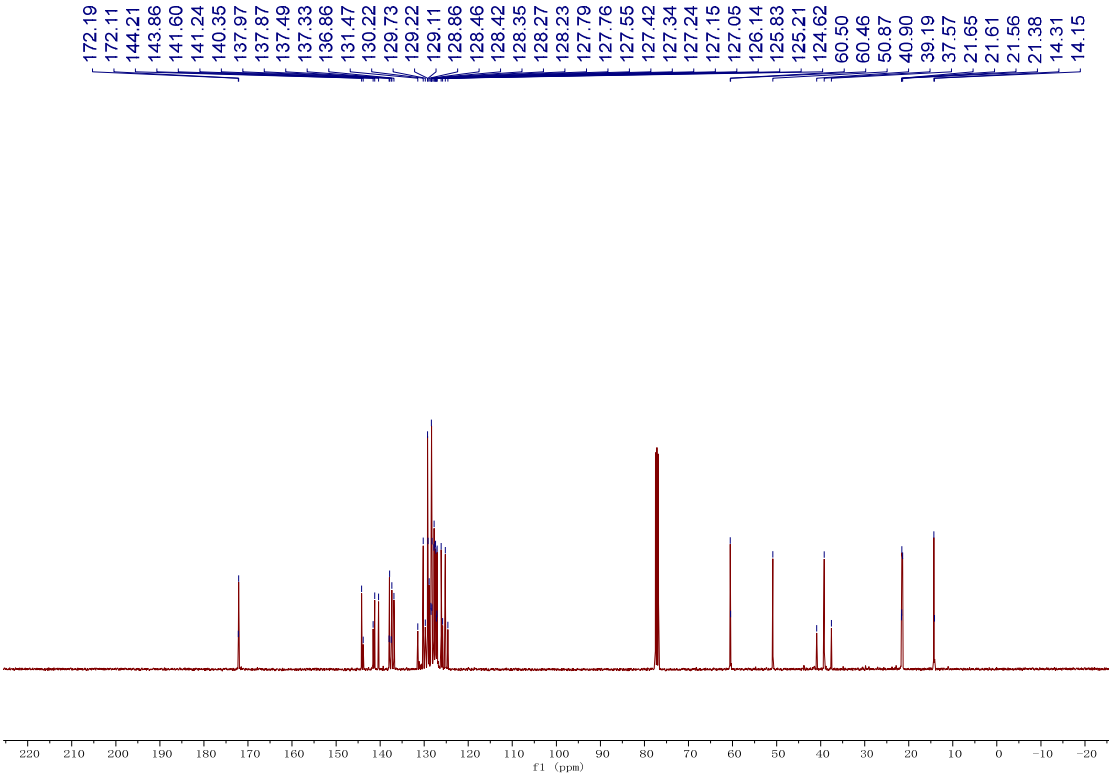
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ao**



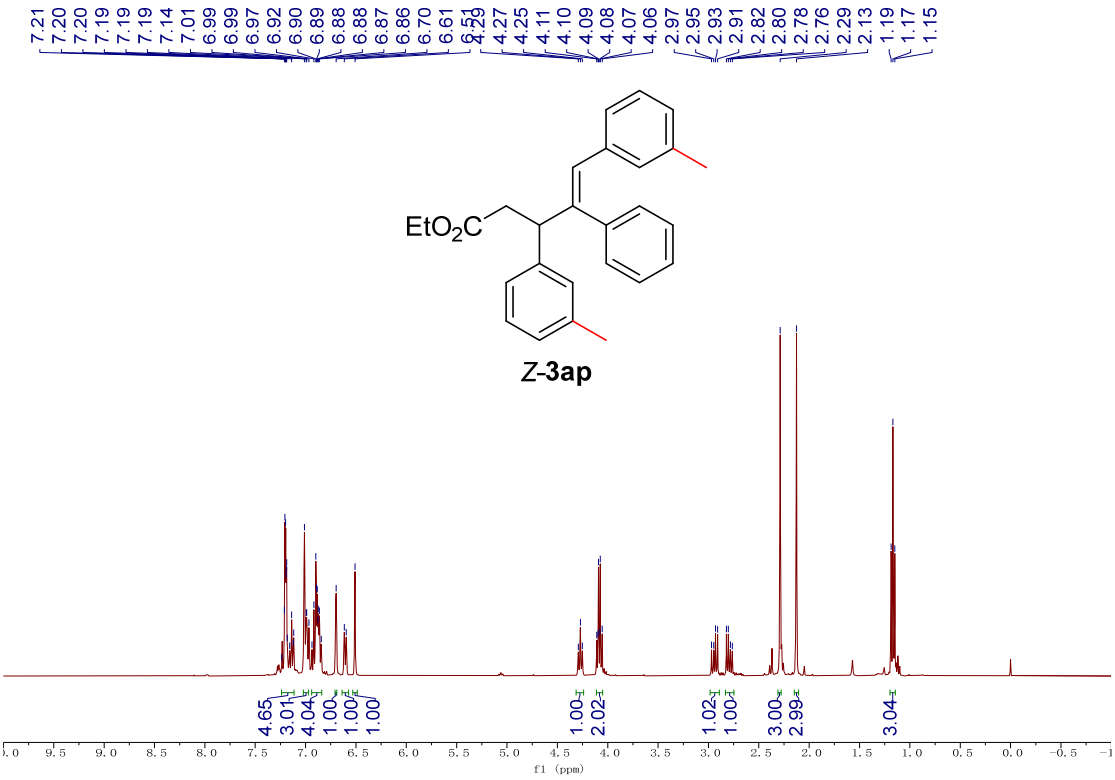
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ao**



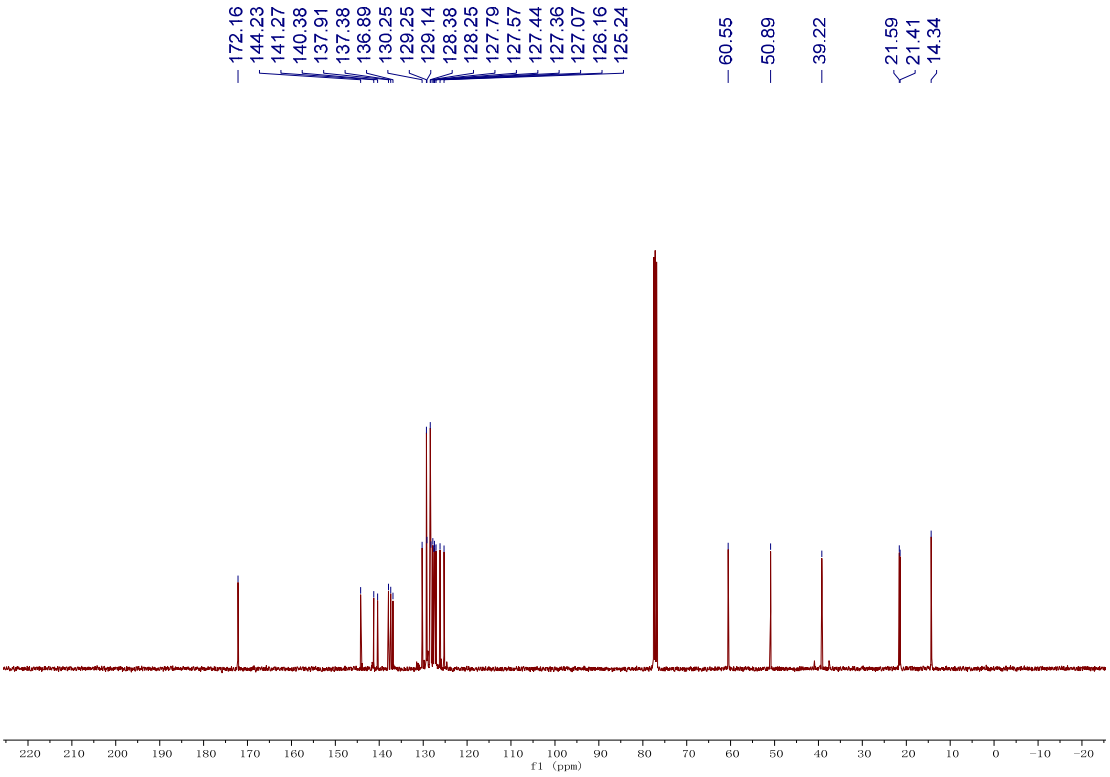
^{1}H NMR (400 MHz, $CDCl_3$) of **3ap**



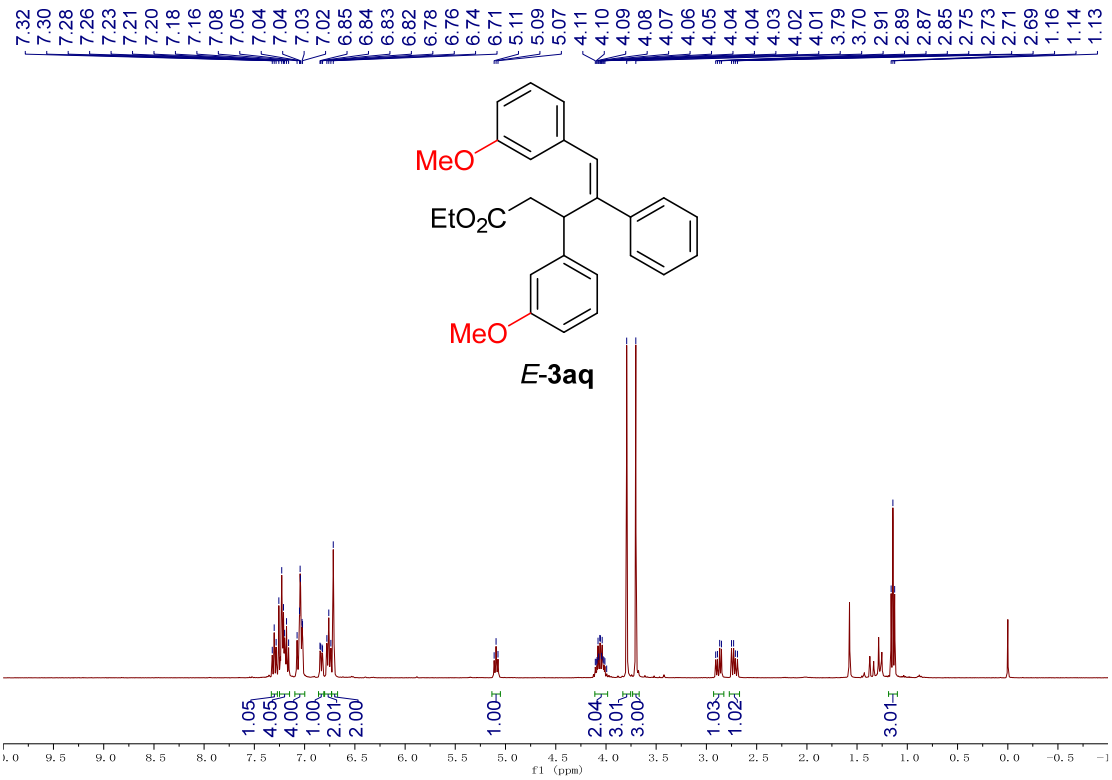
^{13}C NMR (101 MHz, $CDCl_3$) of **3ap**



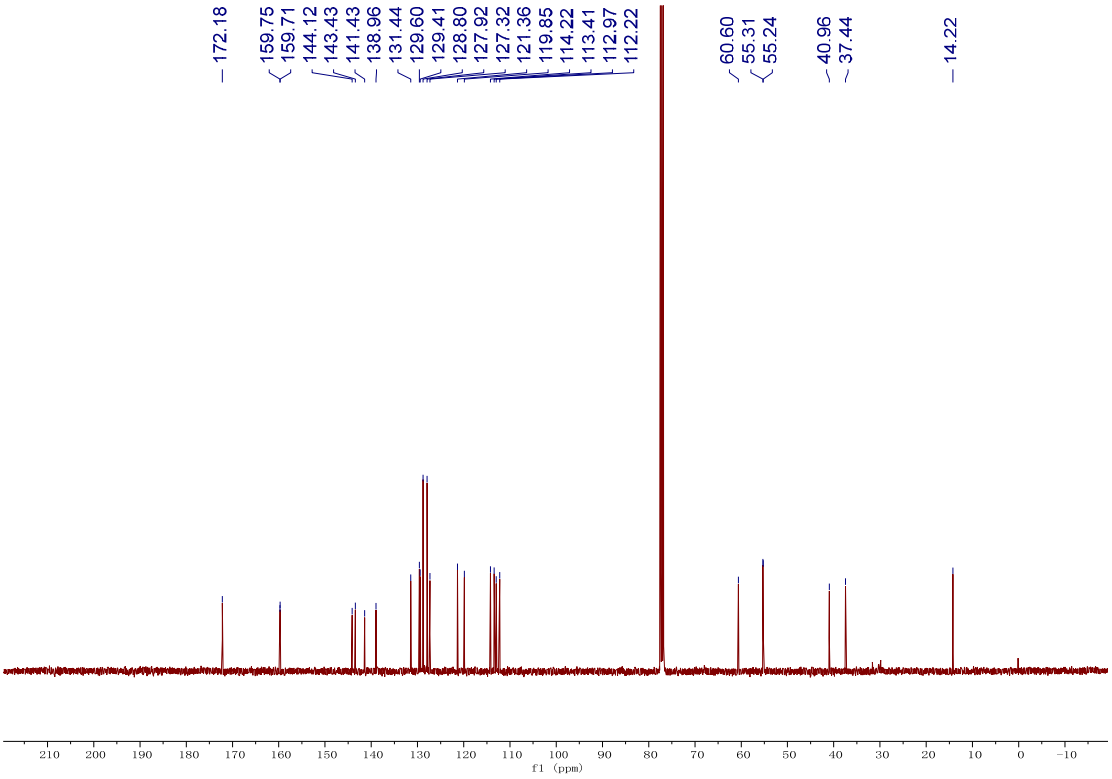
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ap**



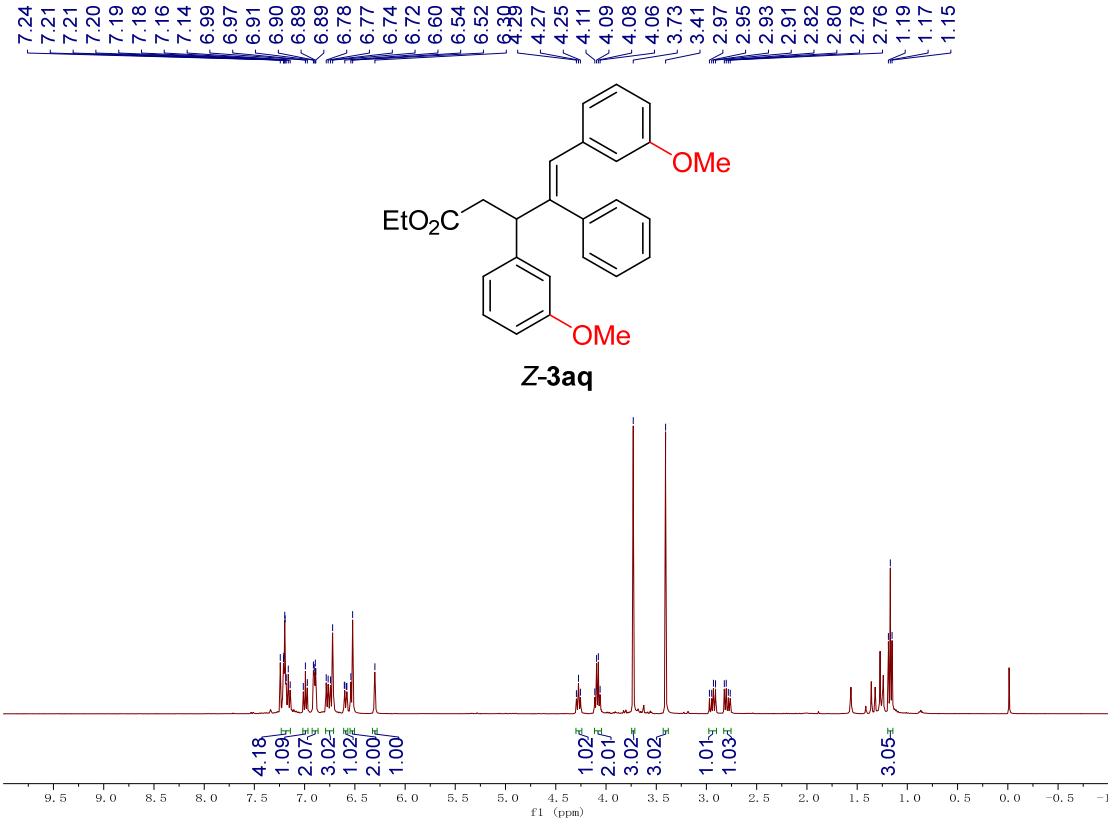
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ap**



^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3aq**

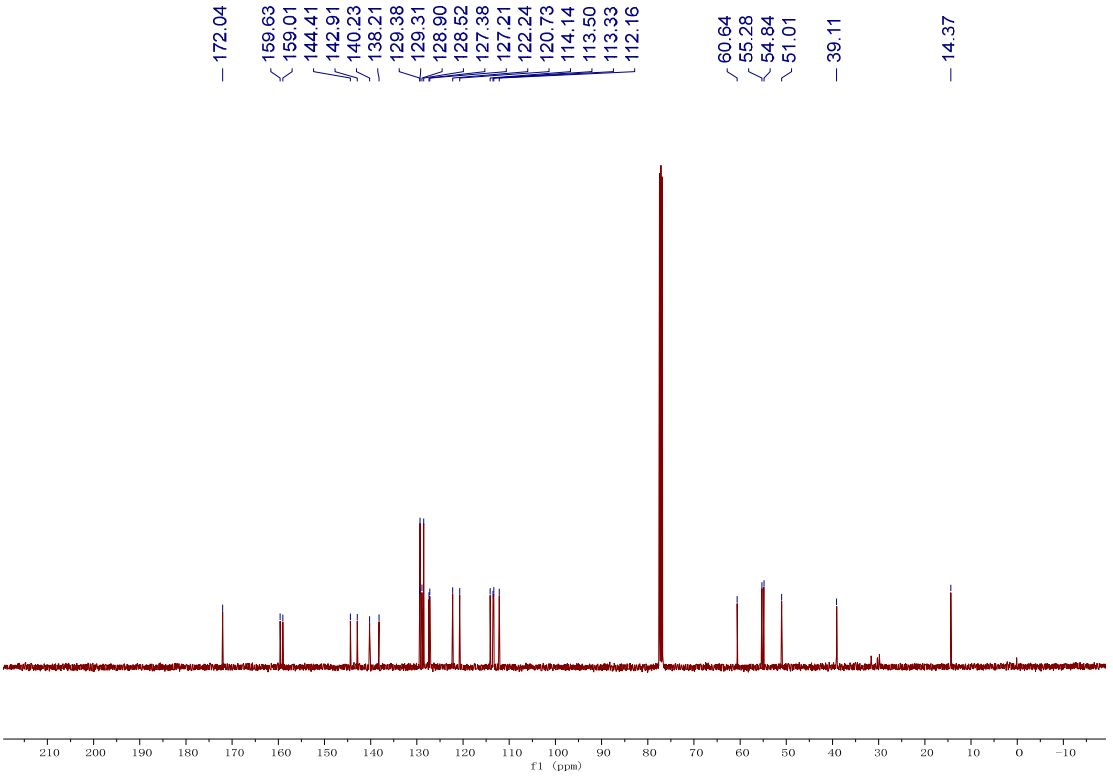


^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3aq**

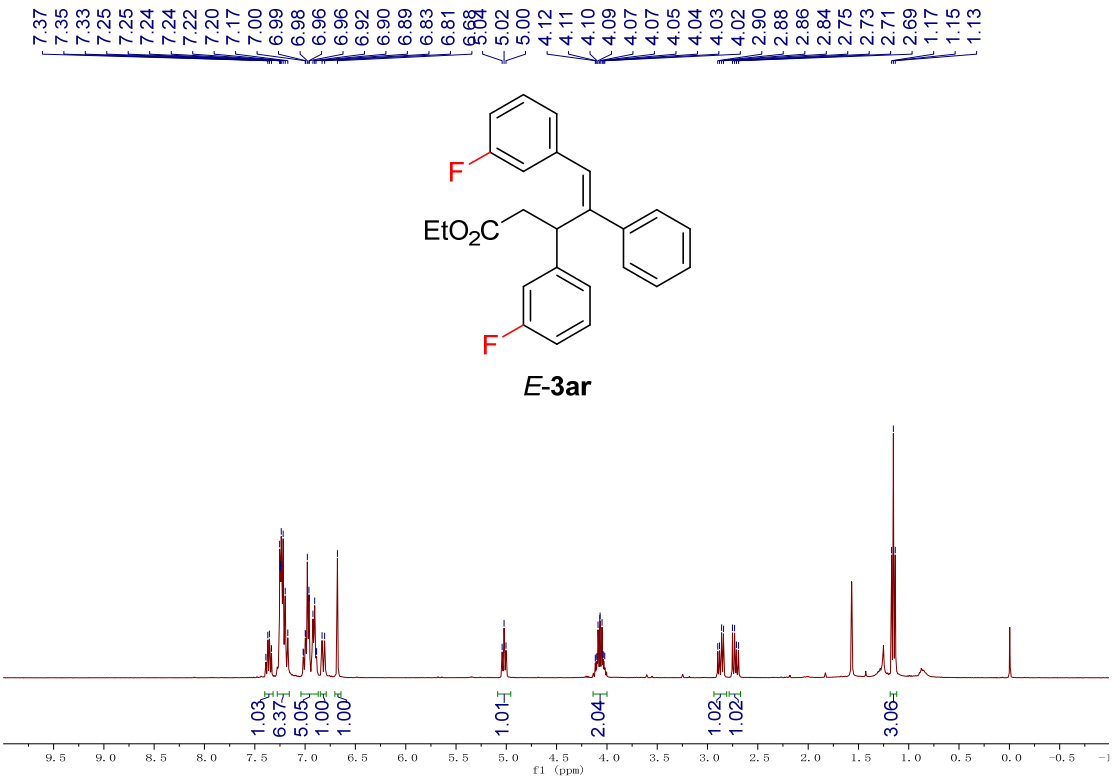


Z-**3aq**

^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3aq**

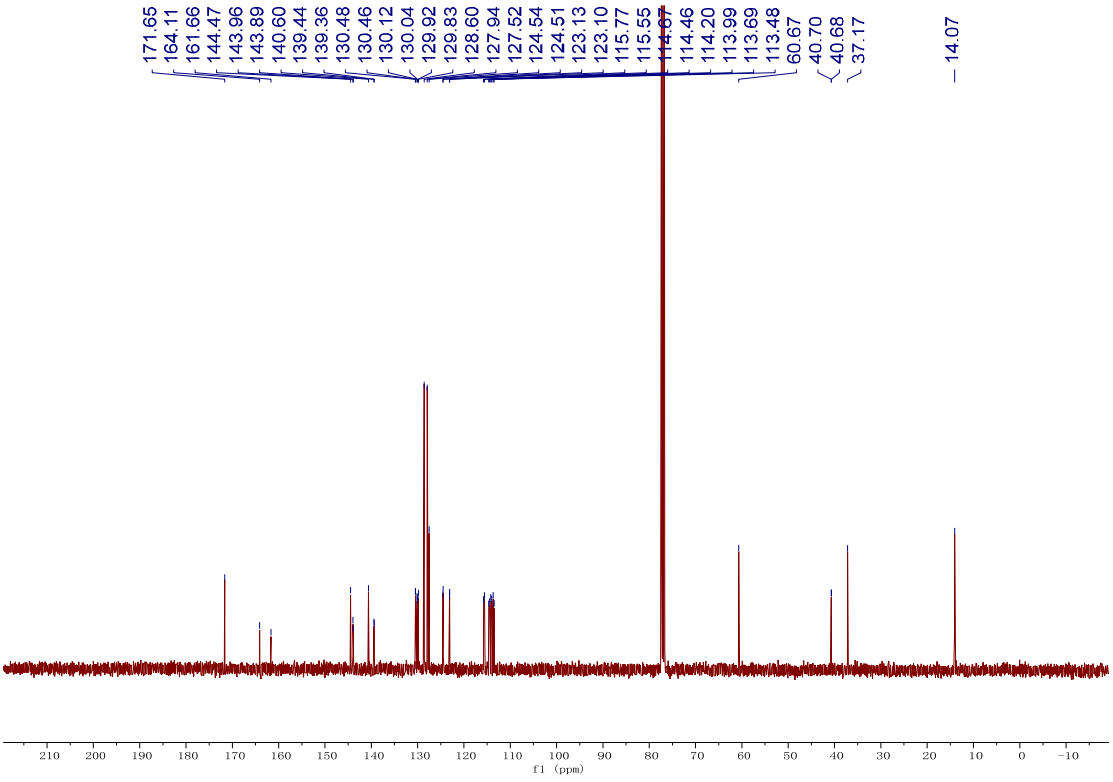


^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3aq**

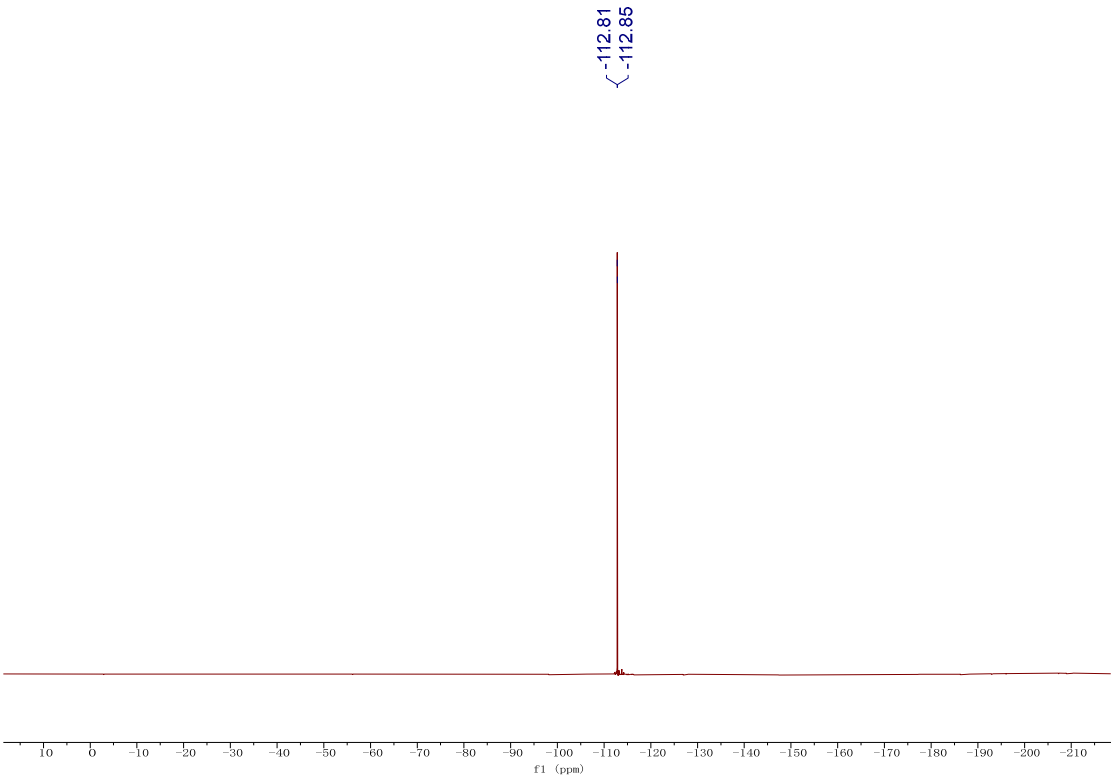


E-**3ar**

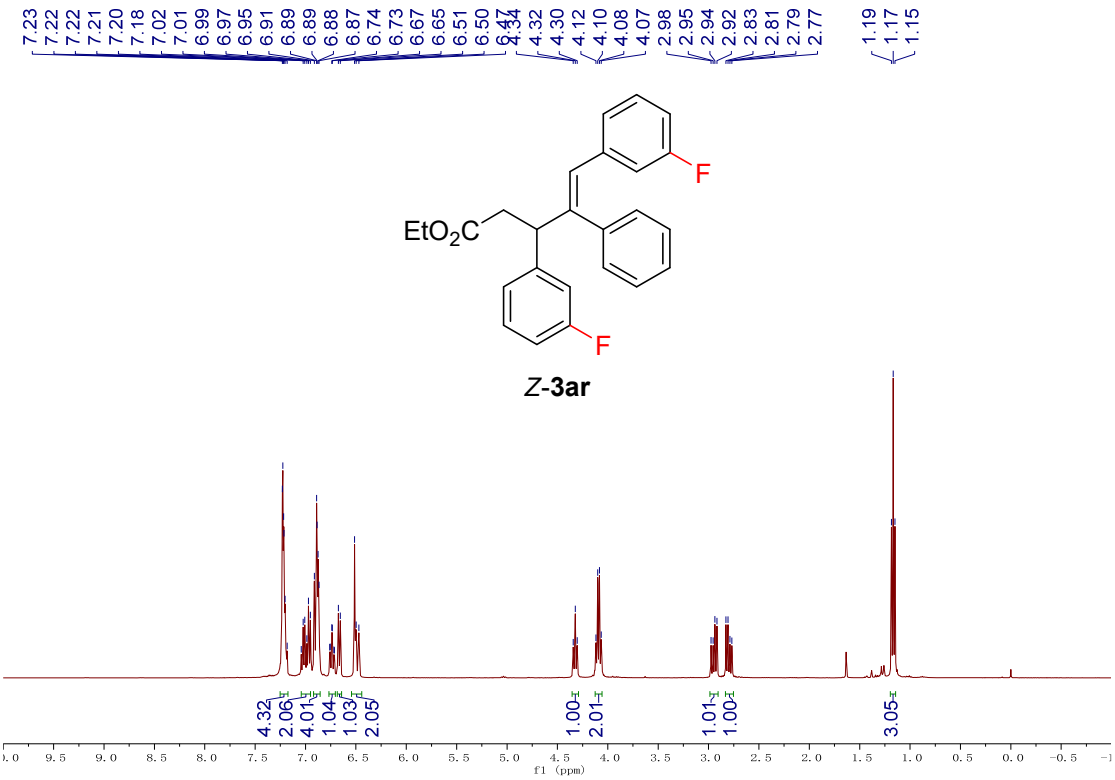
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3ar**



^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3ar**

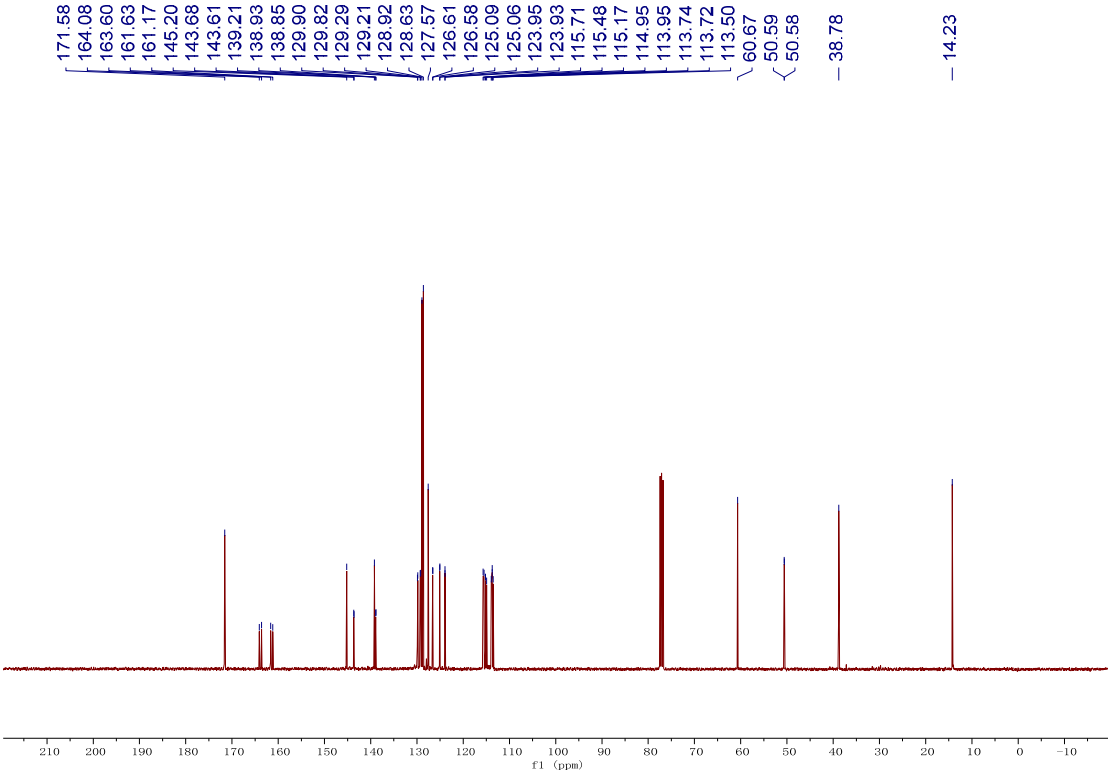


^{19}F NMR (376 MHz, $CDCl_3$) of *E*-**3ar**

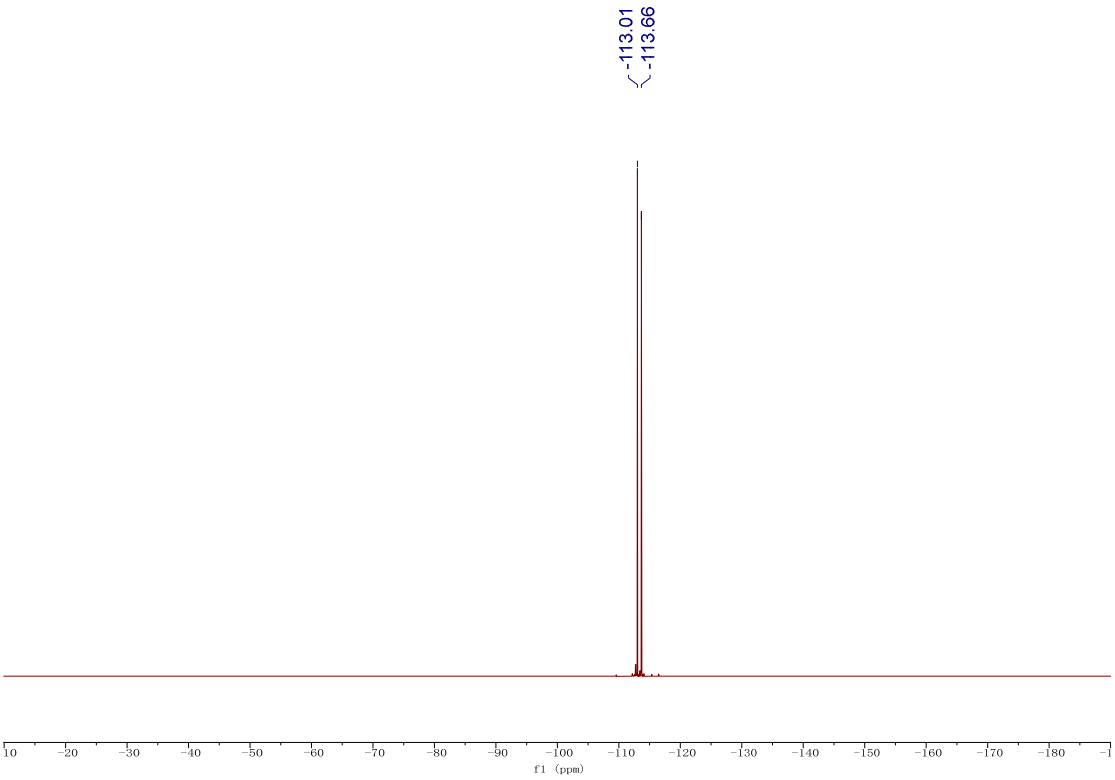


Z-**3ar**

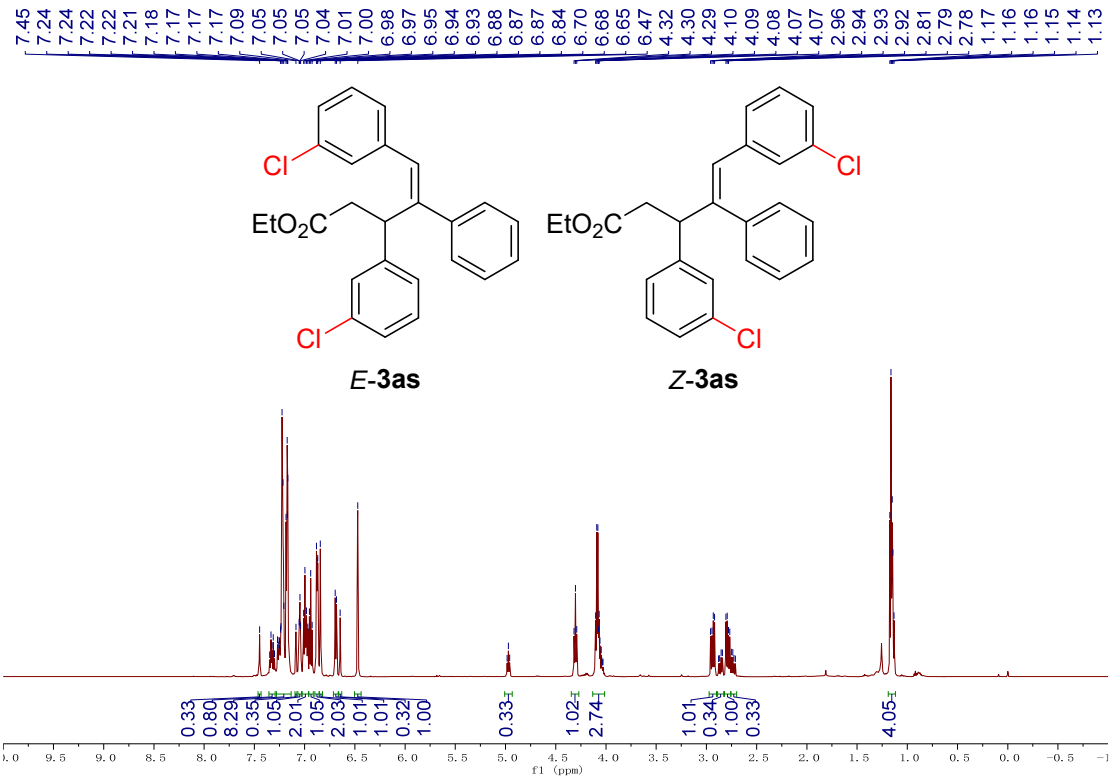
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ar**



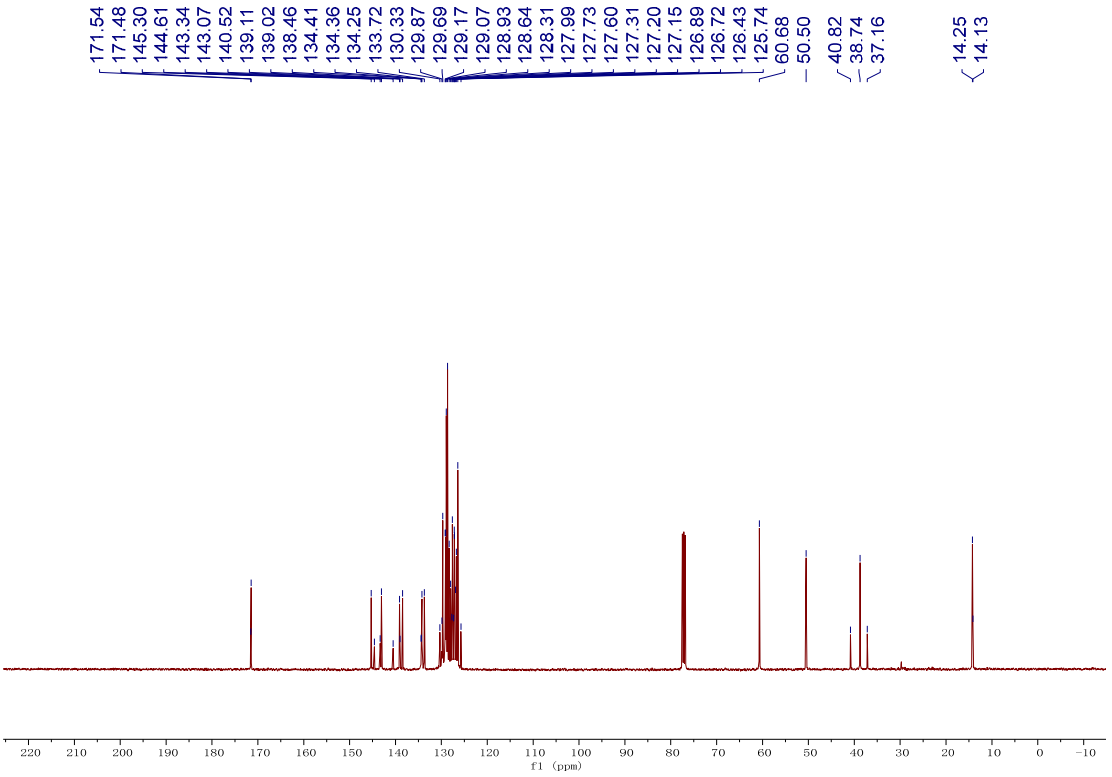
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ar**



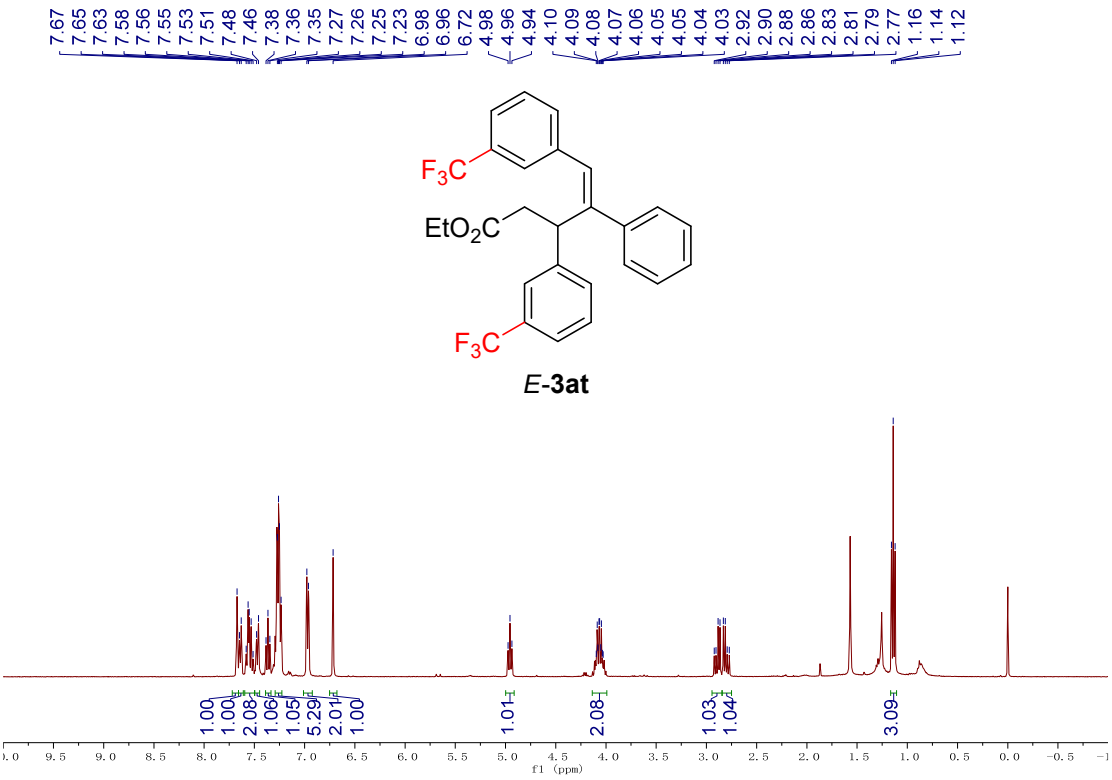
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-**3ar**



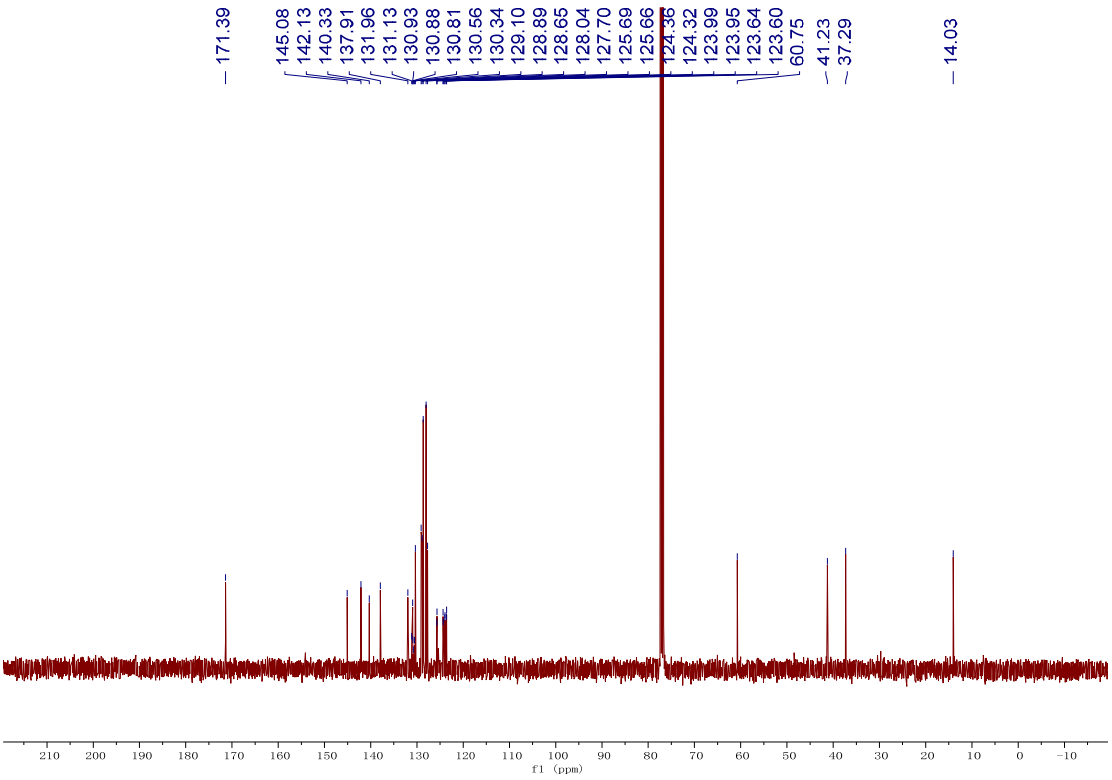
^{1}H NMR (600 MHz, $CDCl_3$) of **3as**



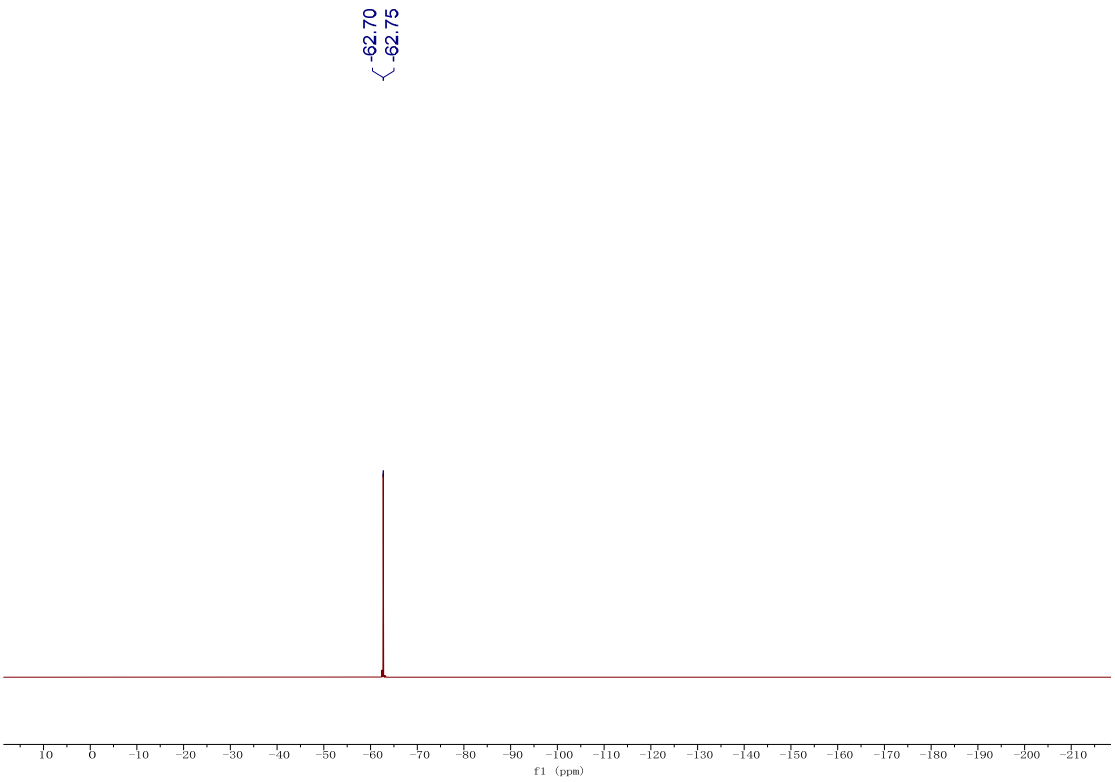
^{13}C NMR (101 MHz, $CDCl_3$) of **3as**



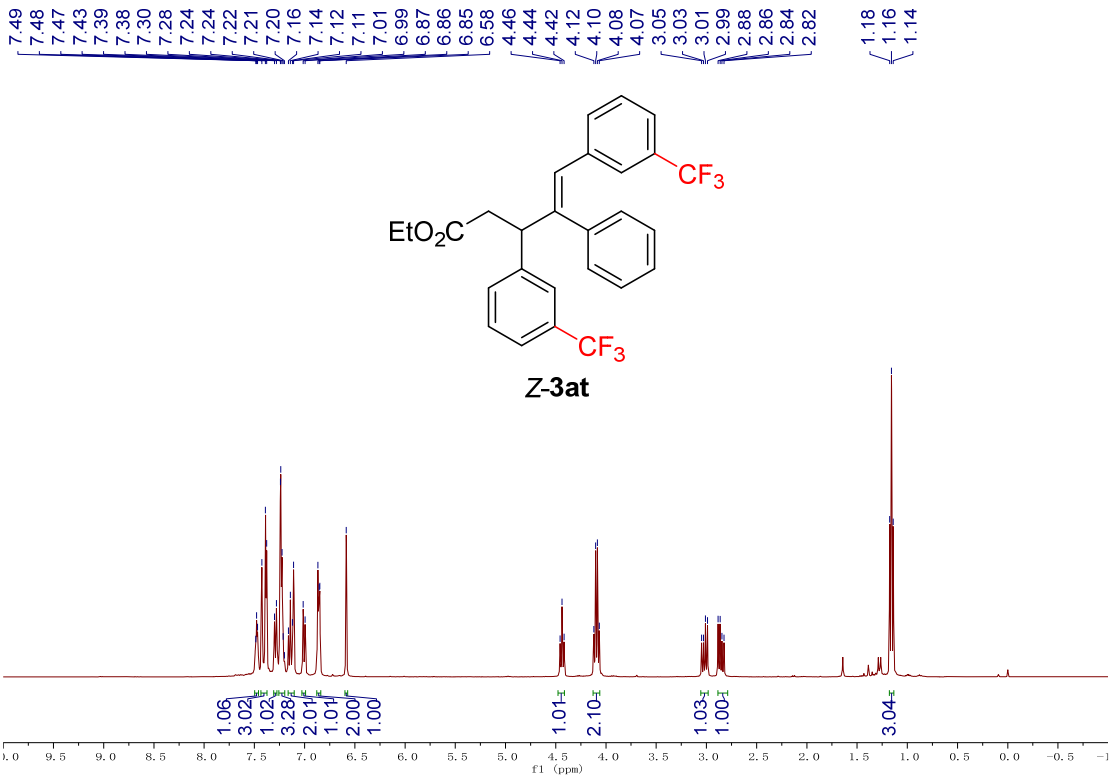
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3at**



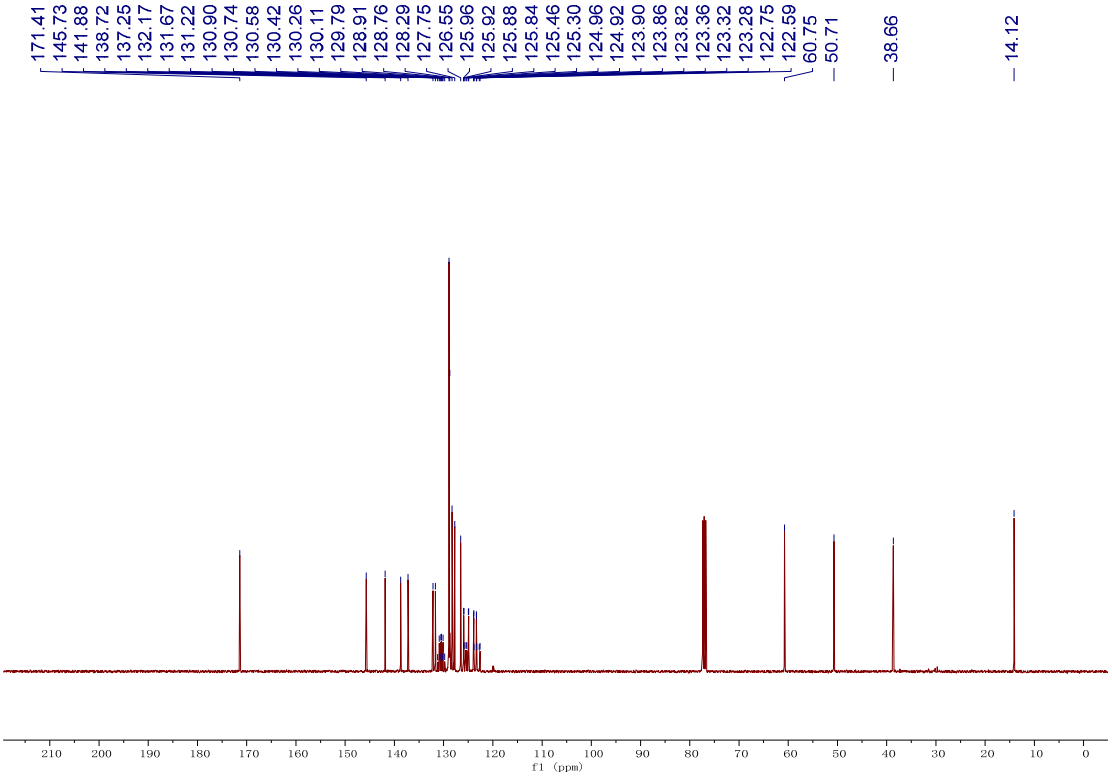
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3at**



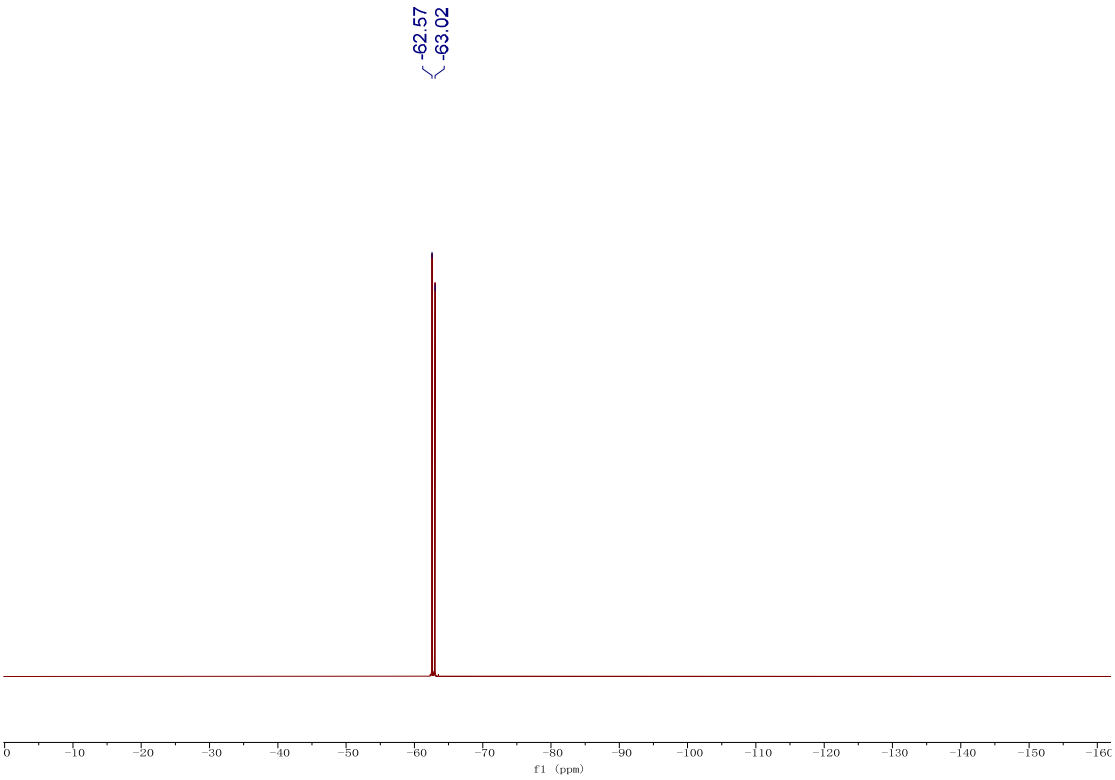
^{19}F NMR (376 MHz, $CDCl_3$) of *E*-**3at**



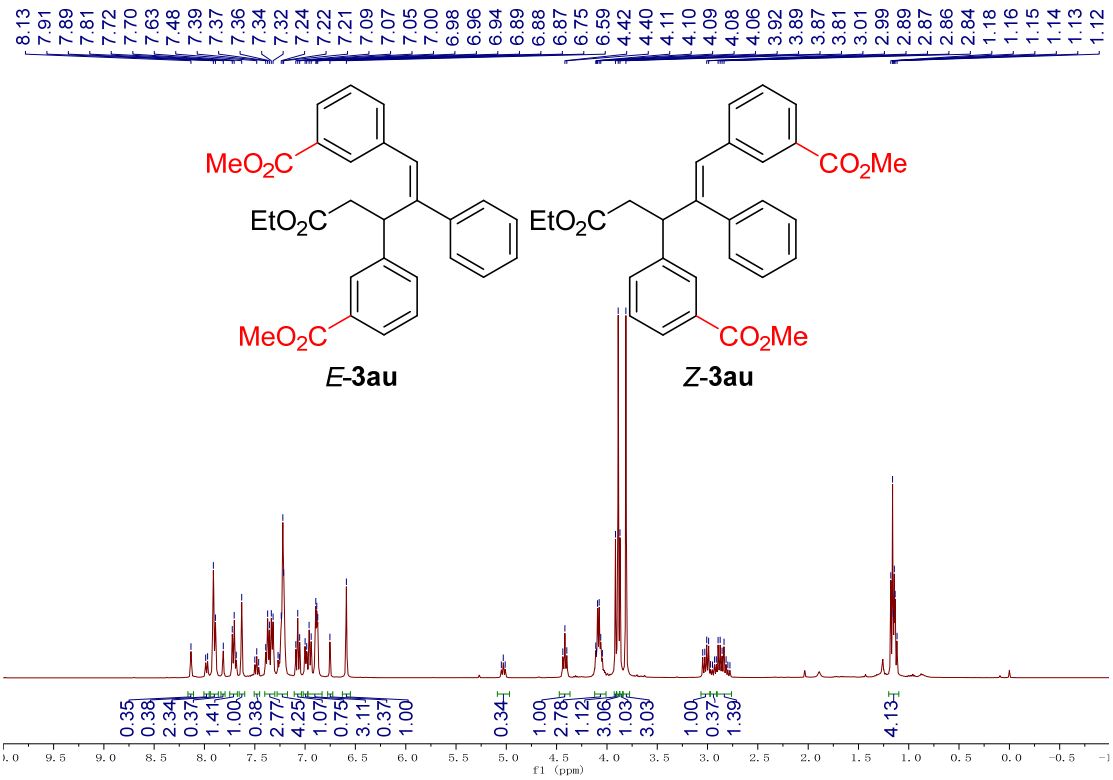
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3at**



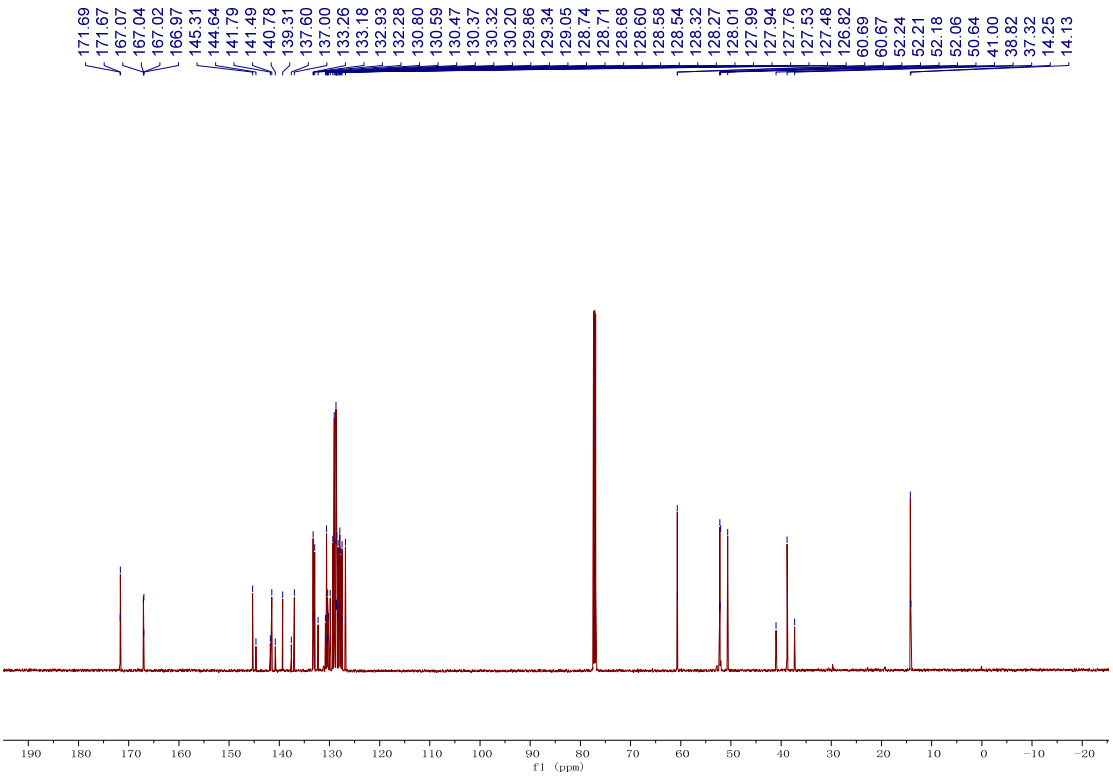
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3at**



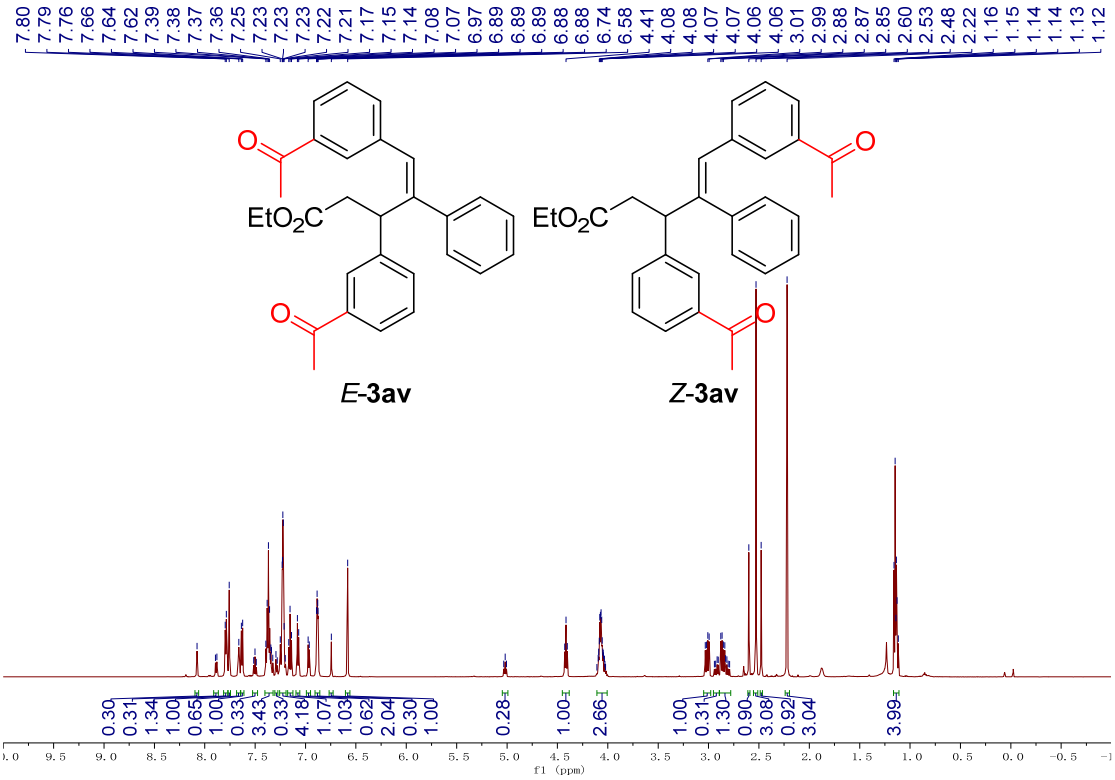
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-**3at**



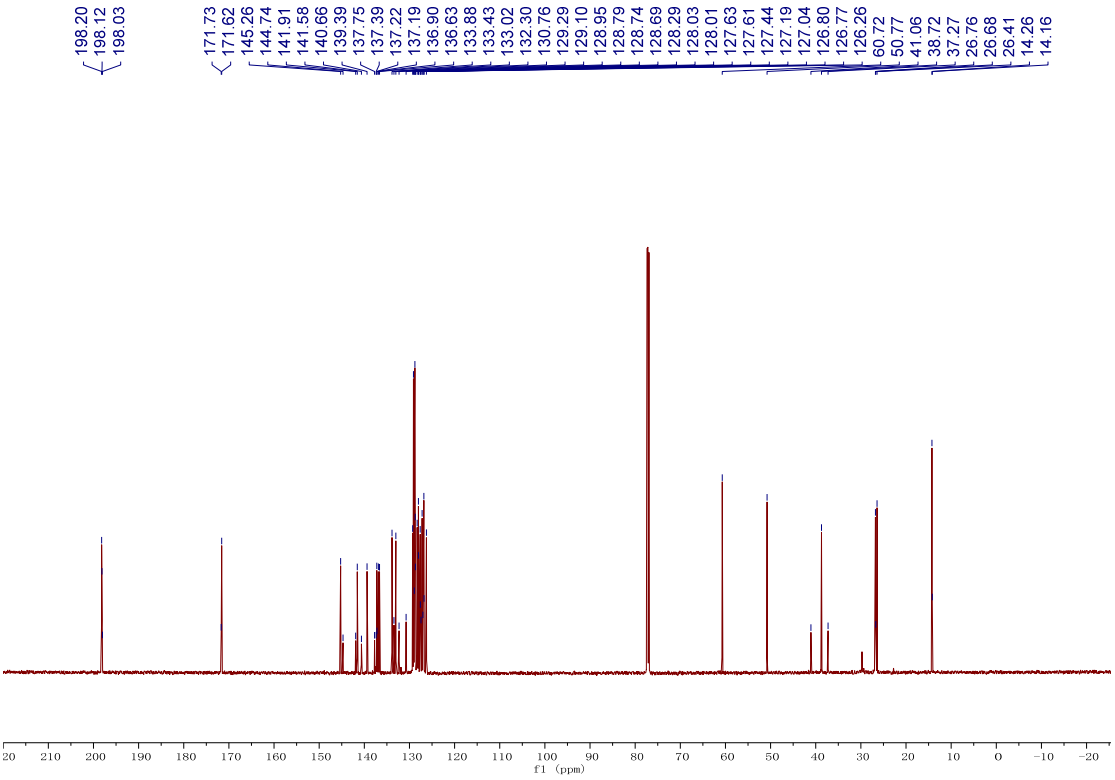
^{1}H NMR (400 MHz, $CDCl_3$) of **3au**



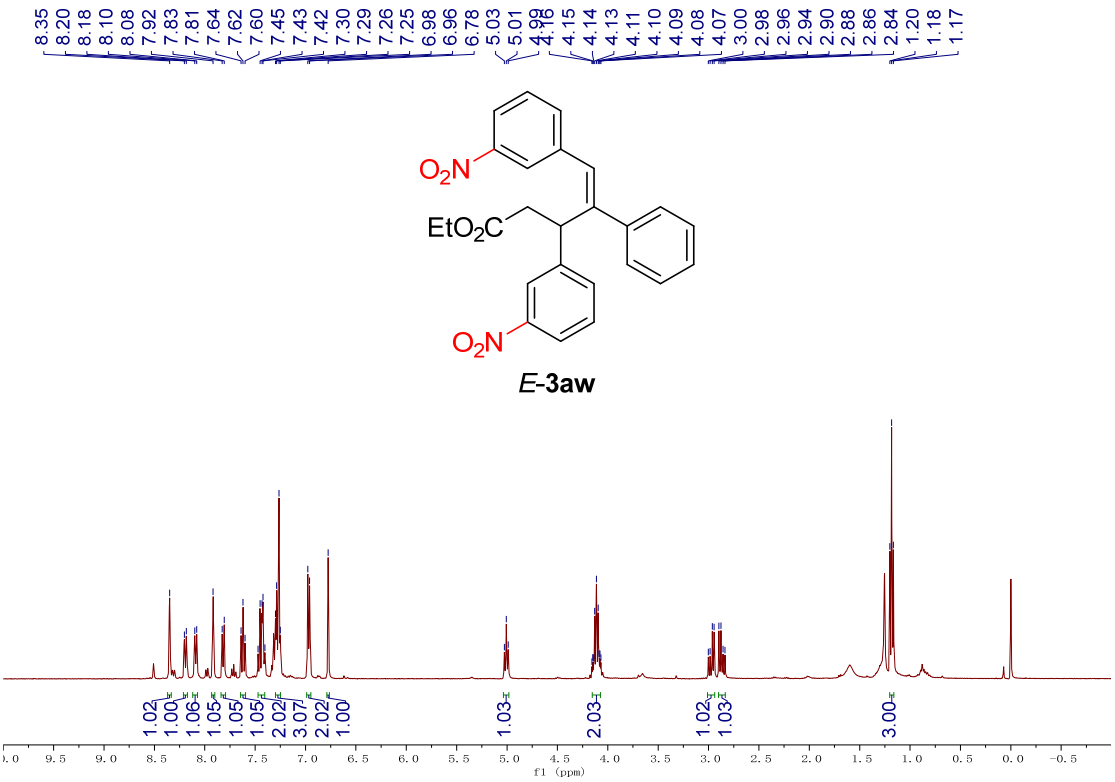
^{13}C NMR (151 MHz, $CDCl_3$) of **3au**



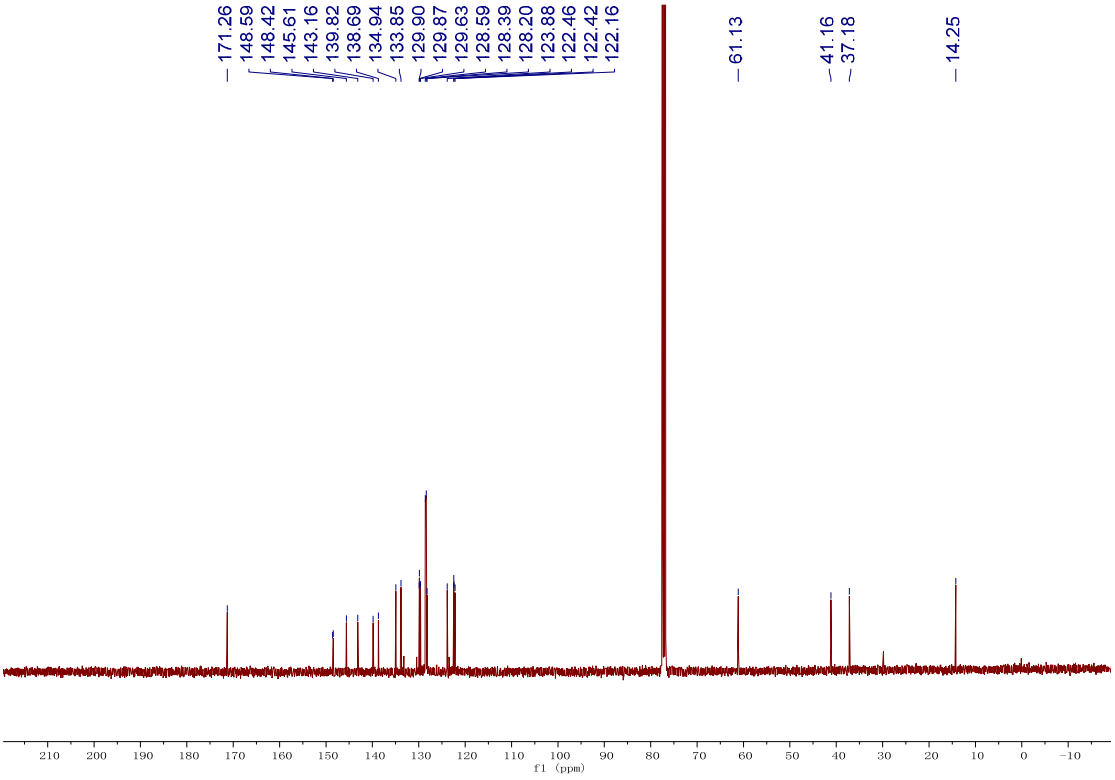
^{1}H NMR (600 MHz, $CDCl_3$) of **3av**



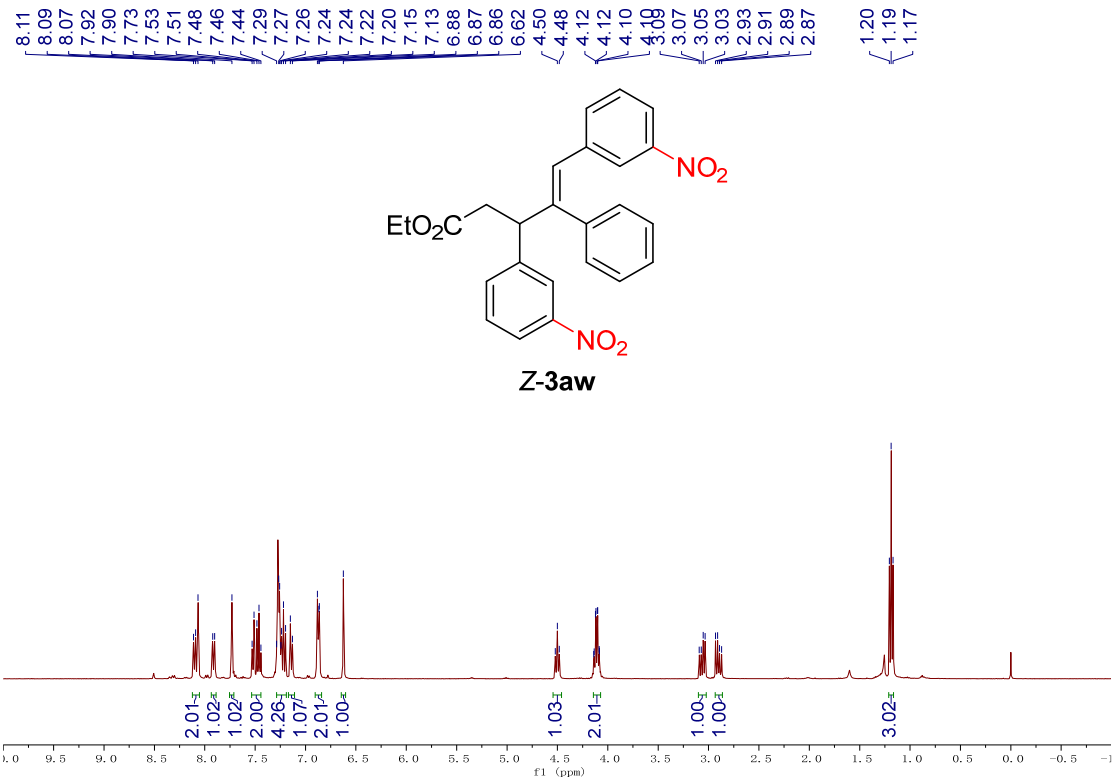
^{13}C NMR (151 MHz, $CDCl_3$) of **3av**



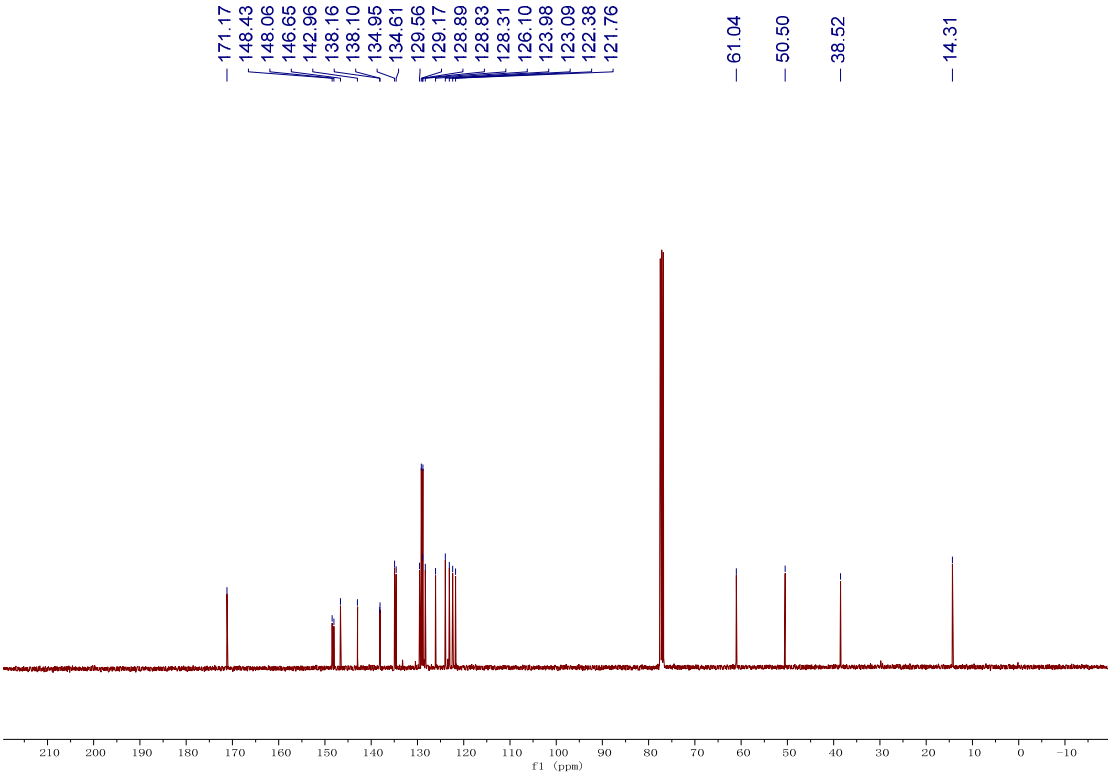
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3aw**



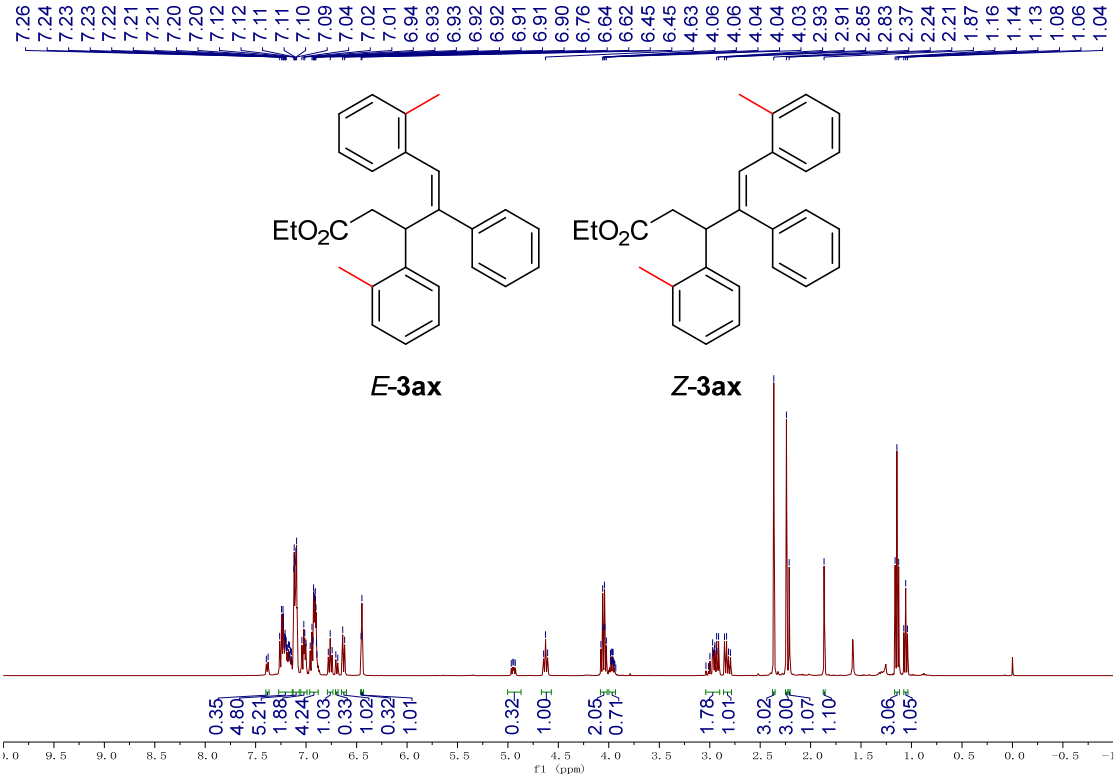
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3aw**



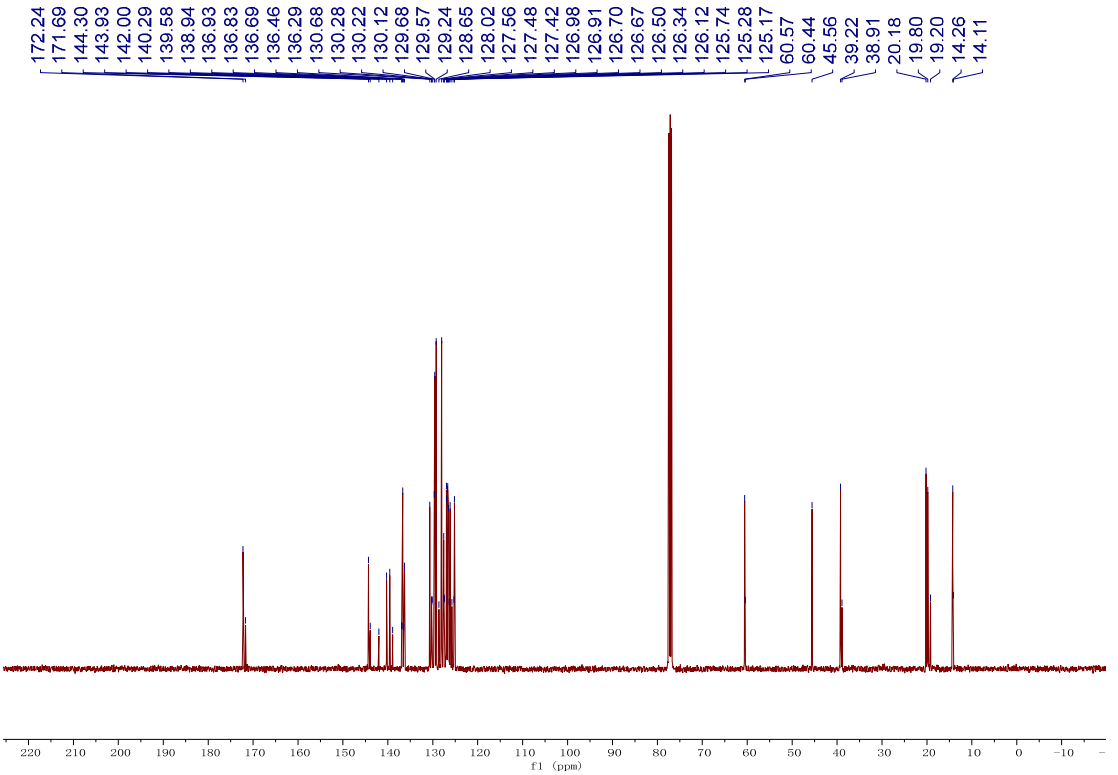
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3aw**



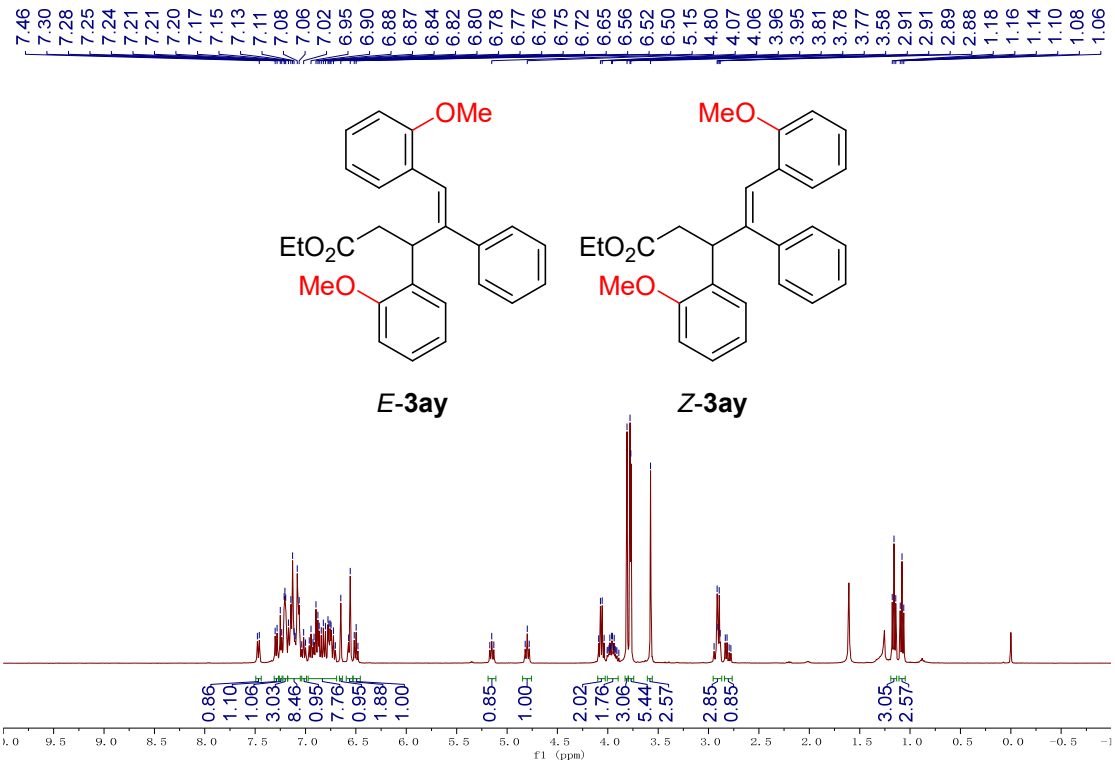
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3aw**



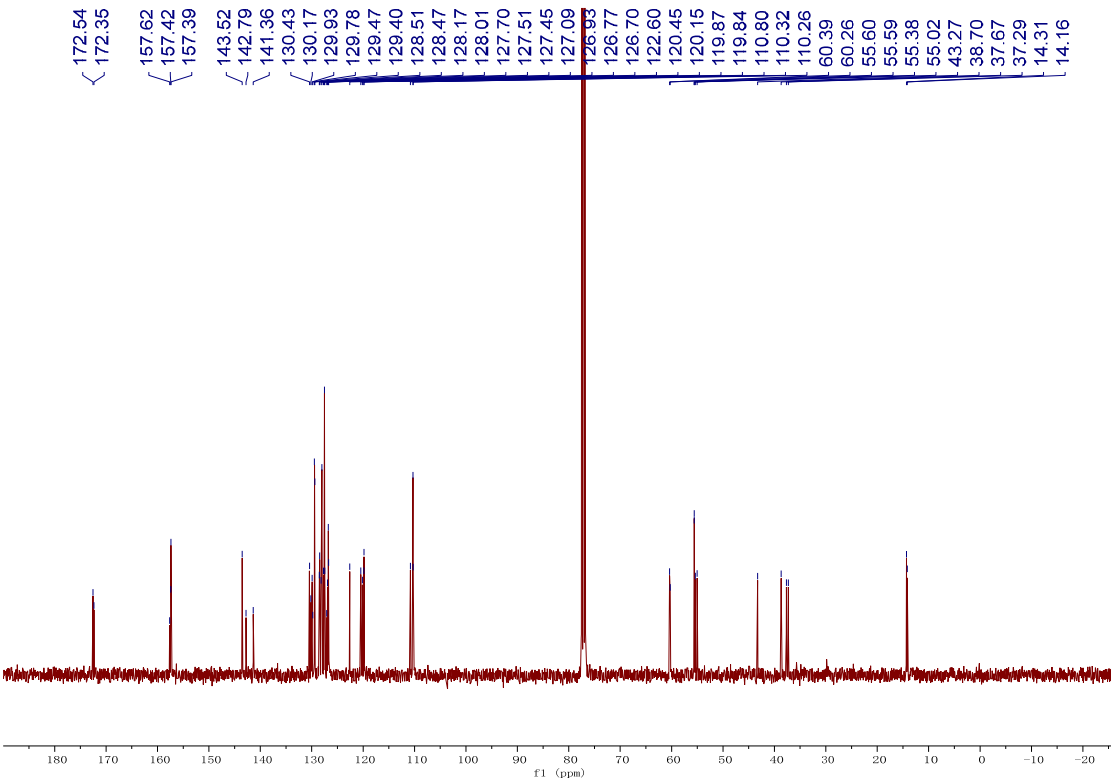
^{1}H NMR (400 MHz, $CDCl_3$) of **3ax**



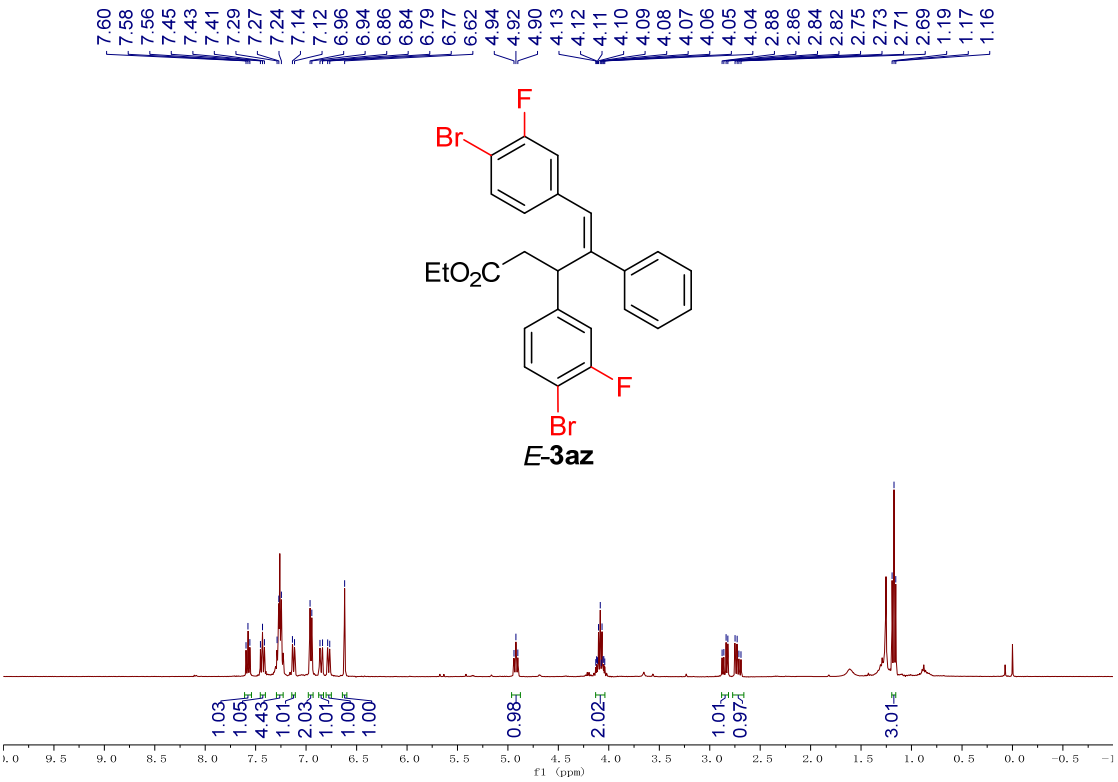
^{13}C NMR (101 MHz, $CDCl_3$) of **3ax**



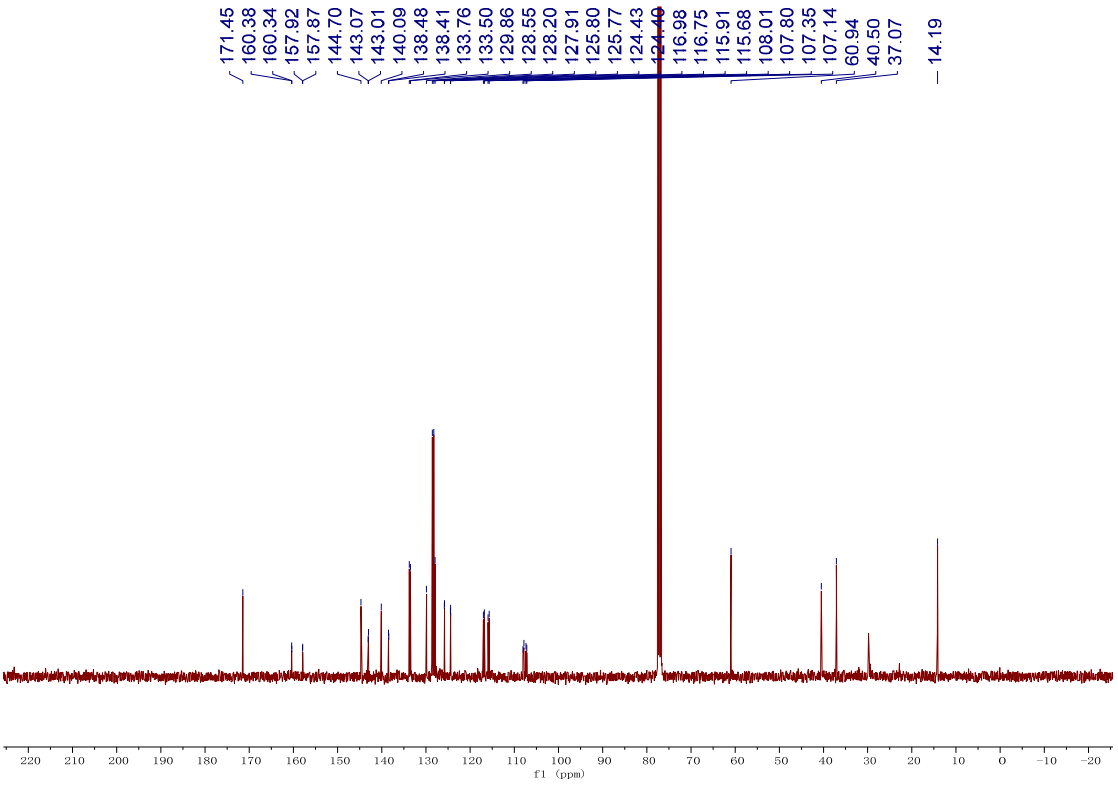
^{1}H NMR (400 MHz, $CDCl_3$) of **3ay**



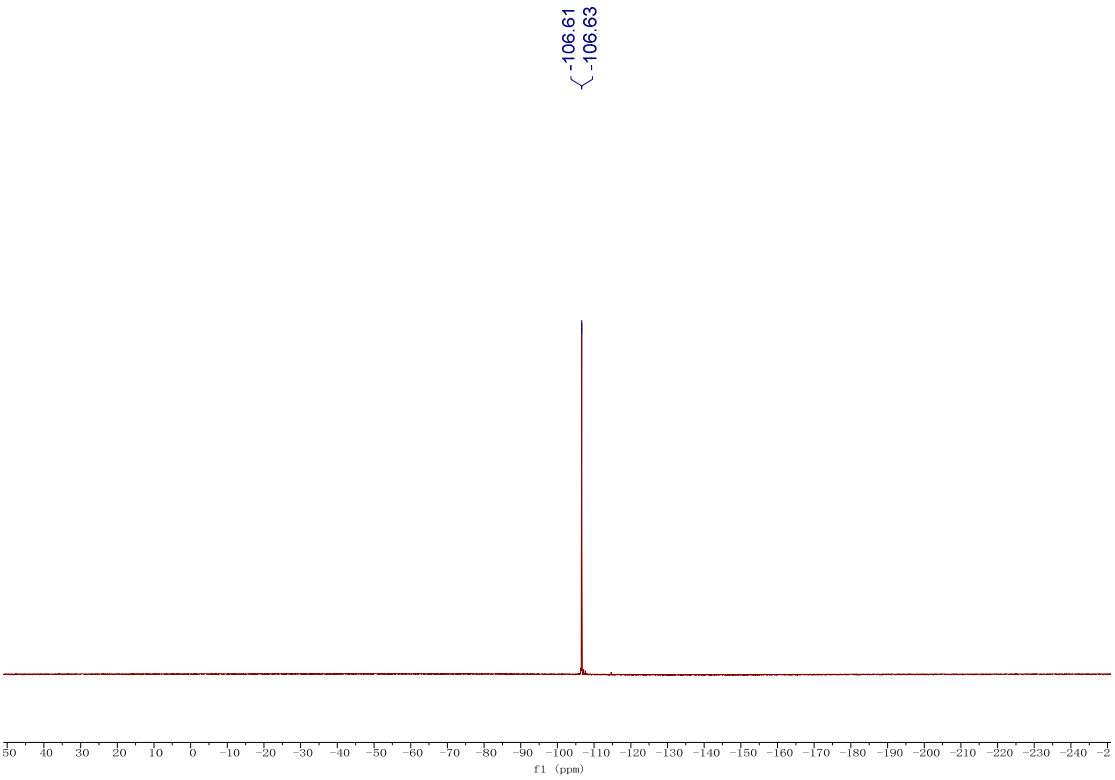
^{13}C NMR (101 MHz, $CDCl_3$) of **3ay**



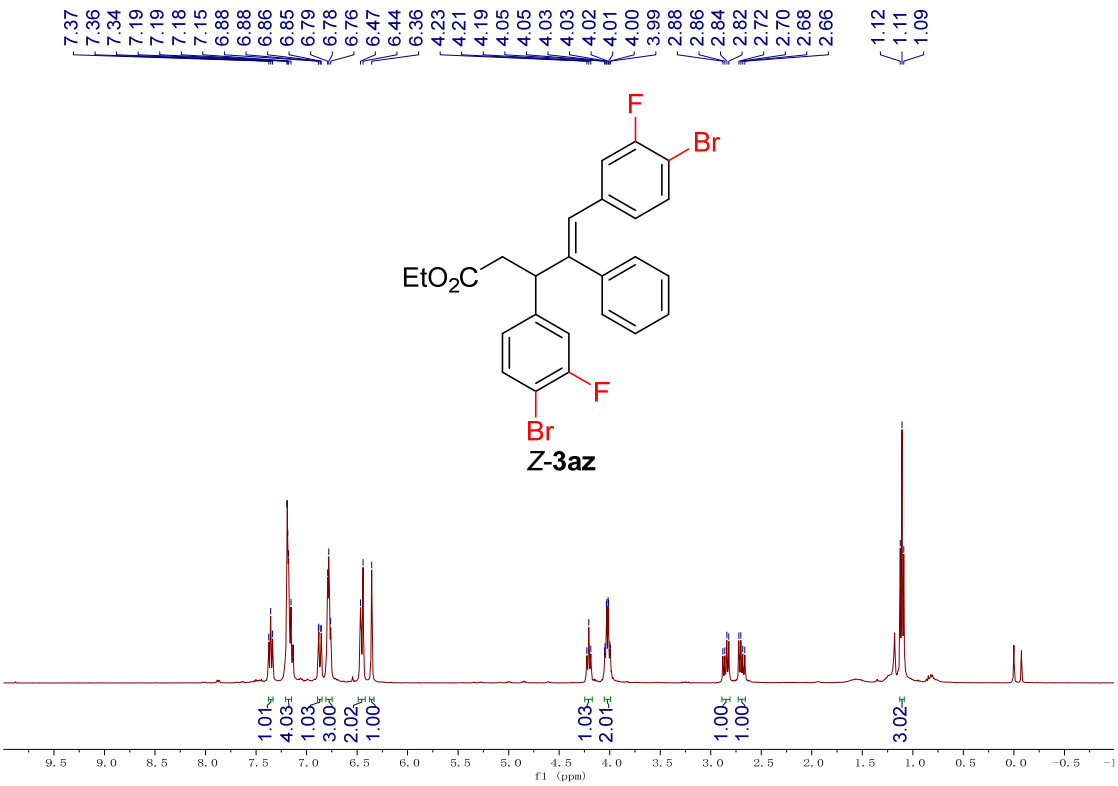
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3az**



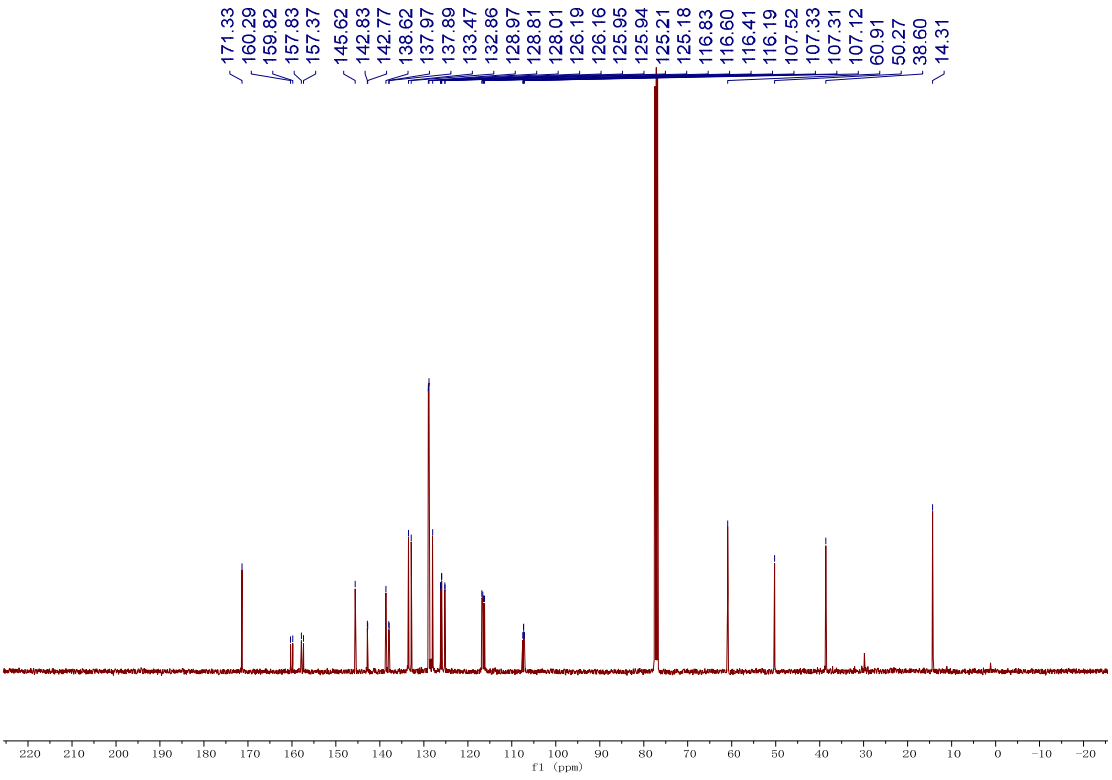
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3az**



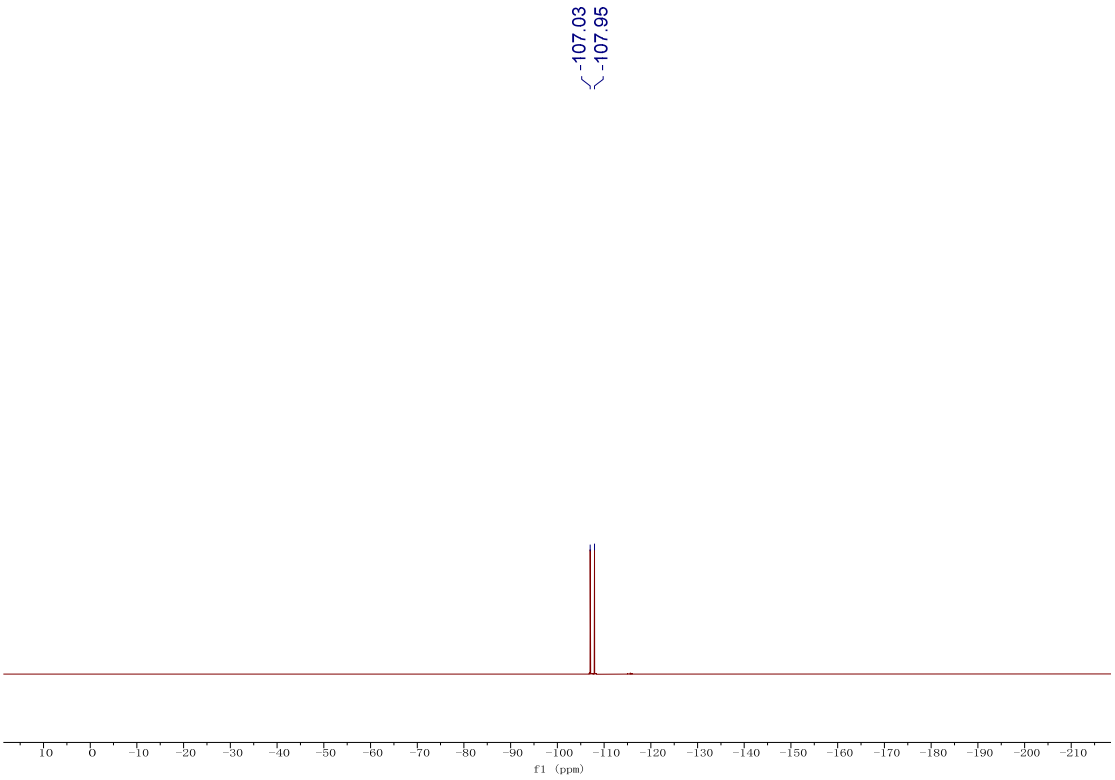
^{19}F NMR (376 MHz, $CDCl_3$) of *E*-**3az**



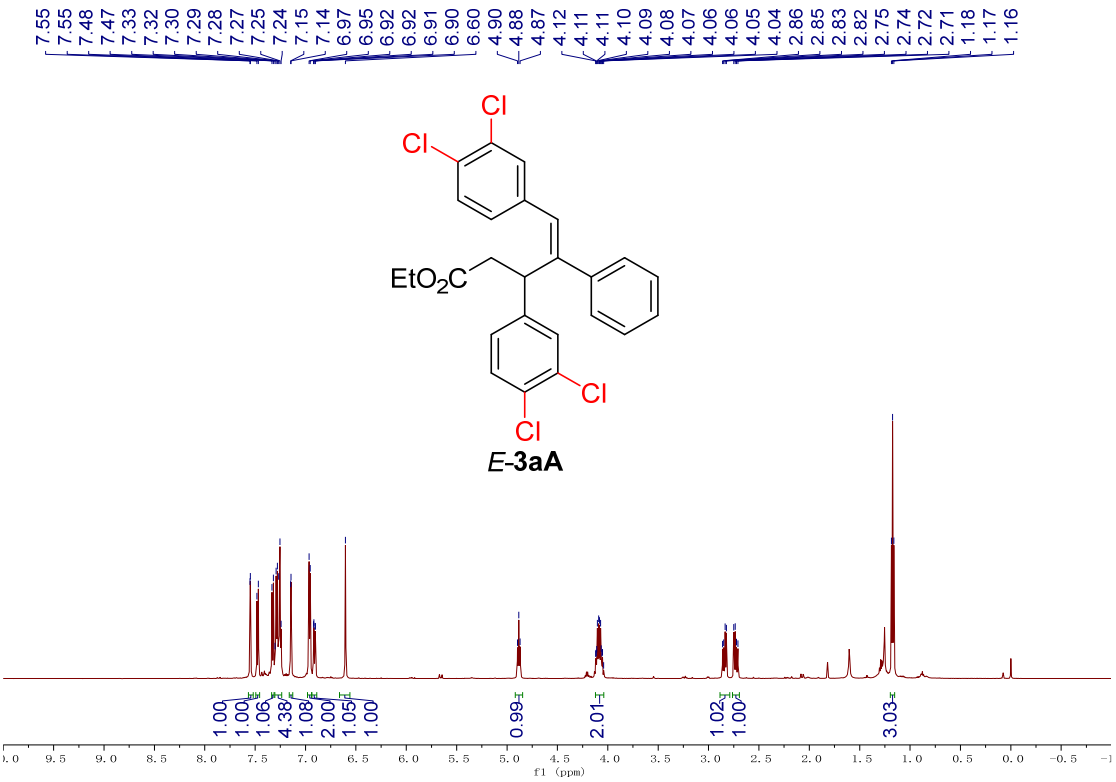
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3az**



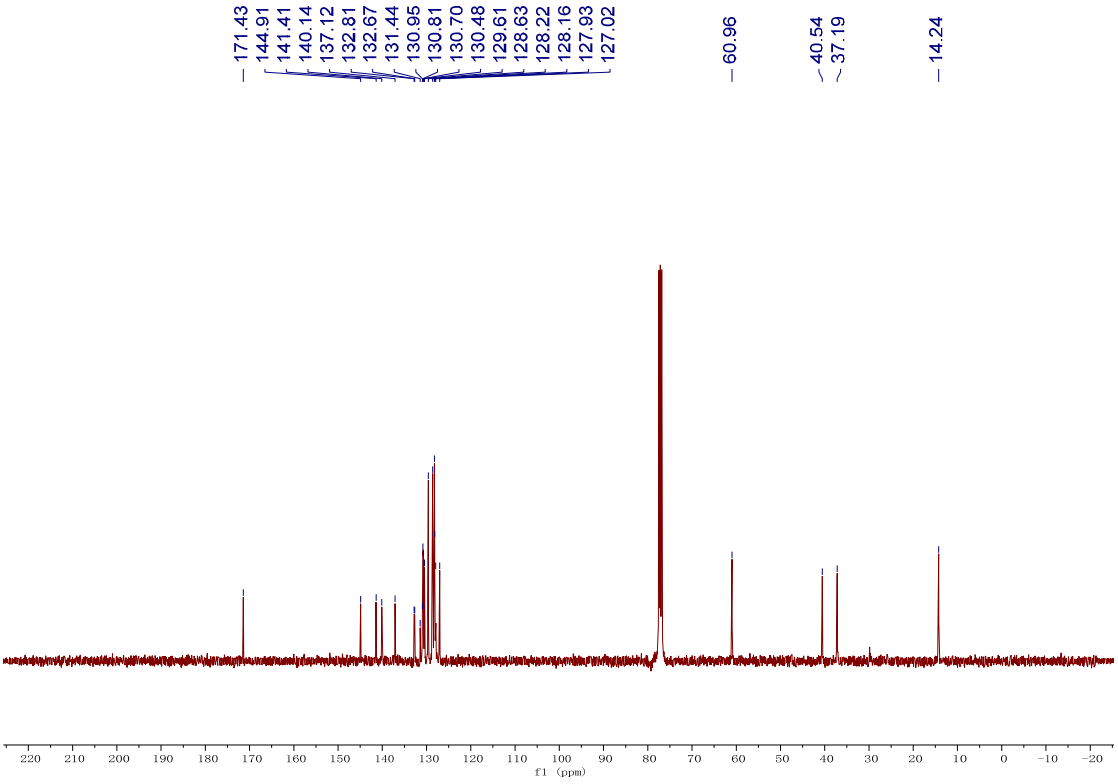
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3az**



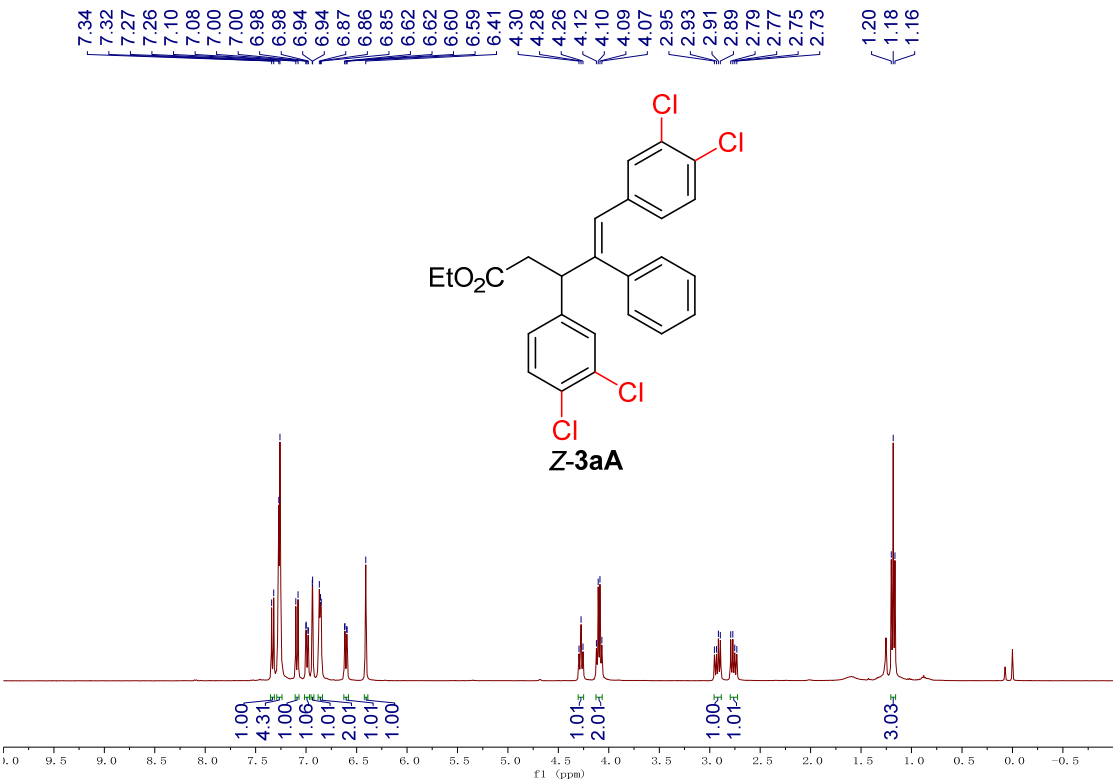
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-**3az**



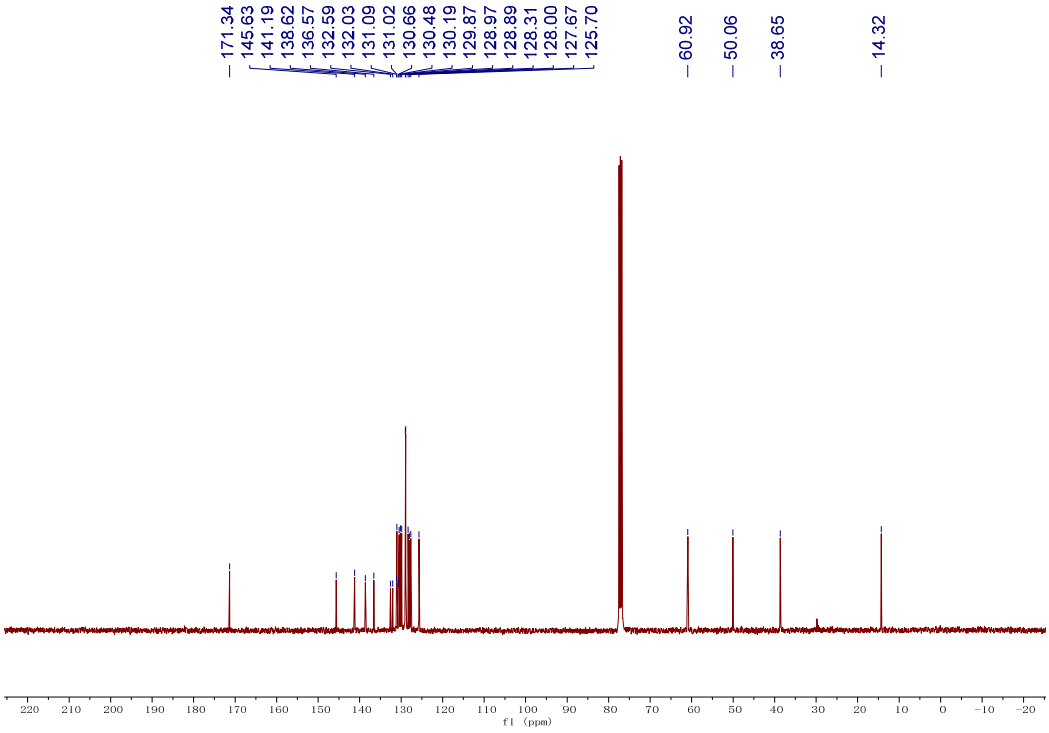
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3aA**



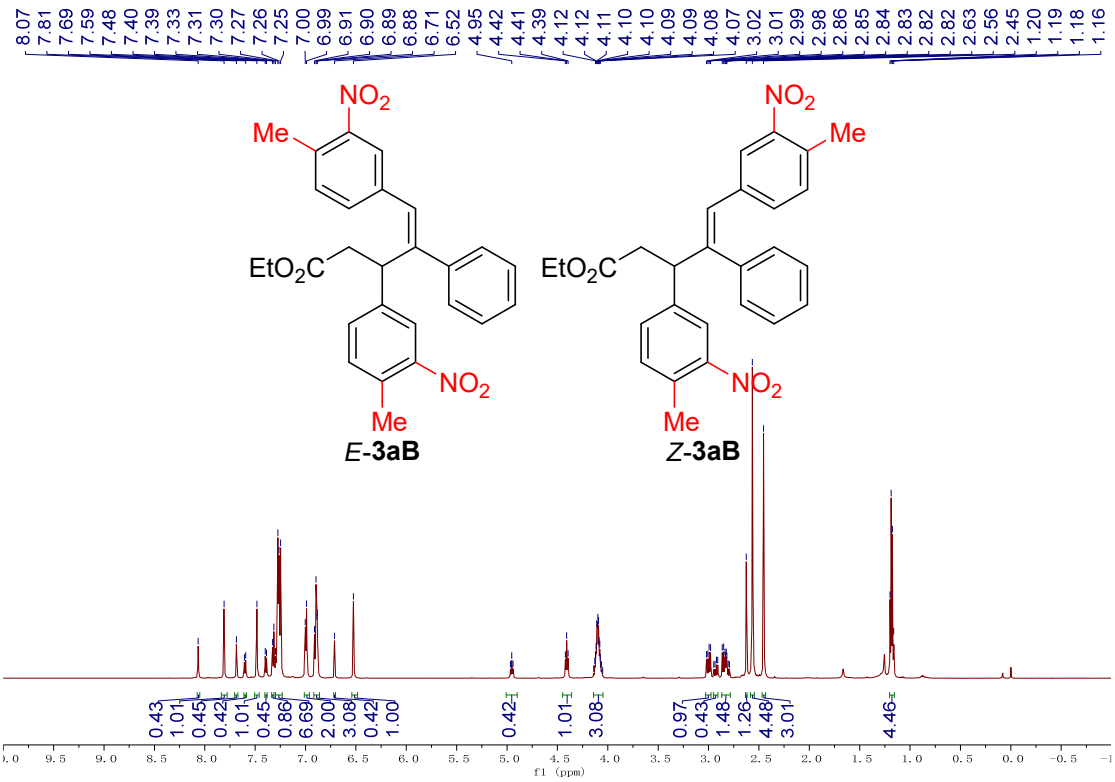
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3aA**



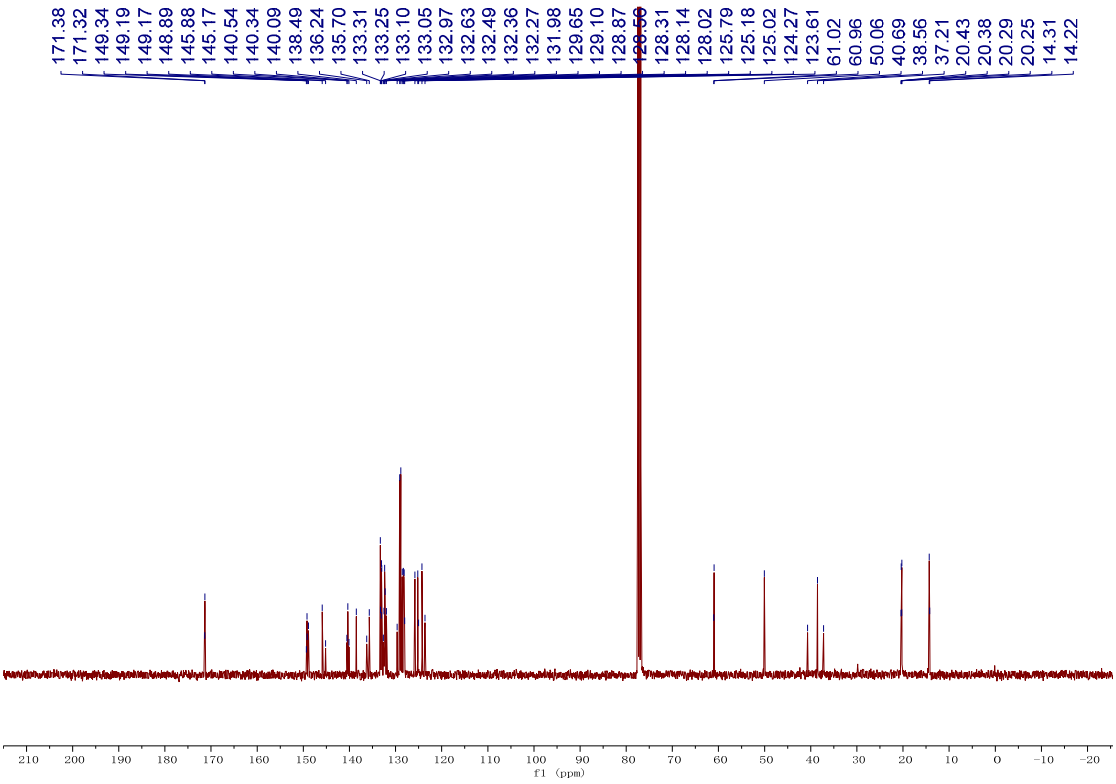
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3aA**



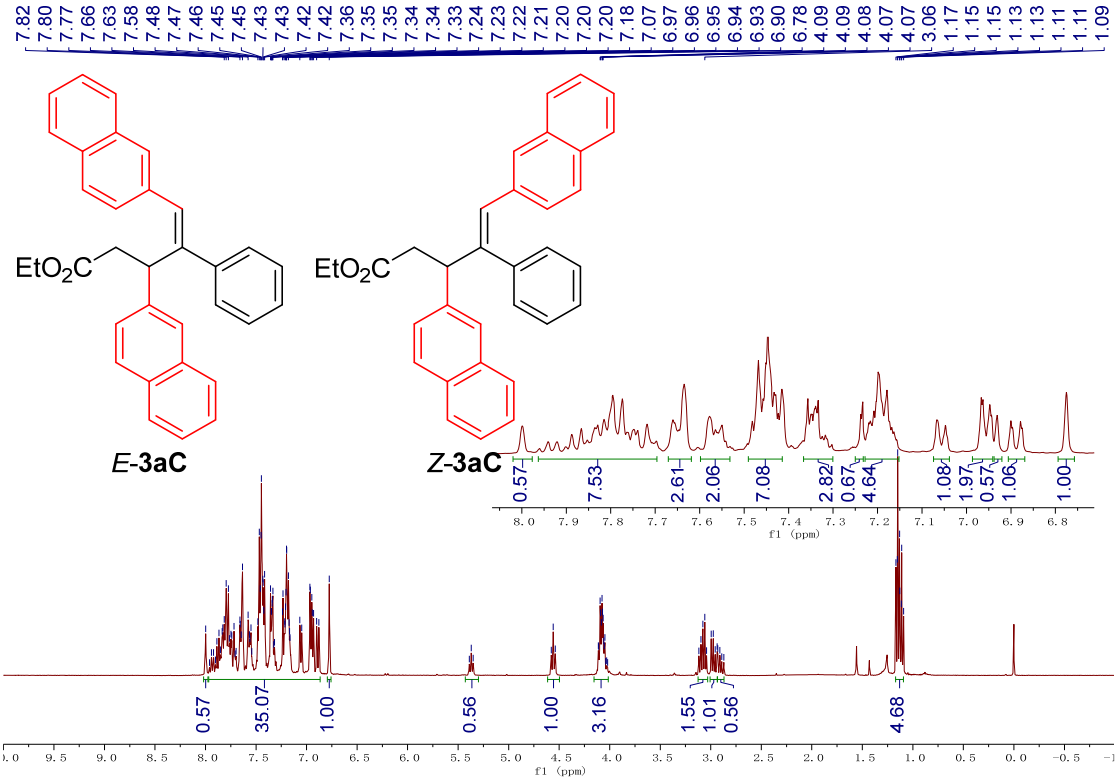
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3aA**



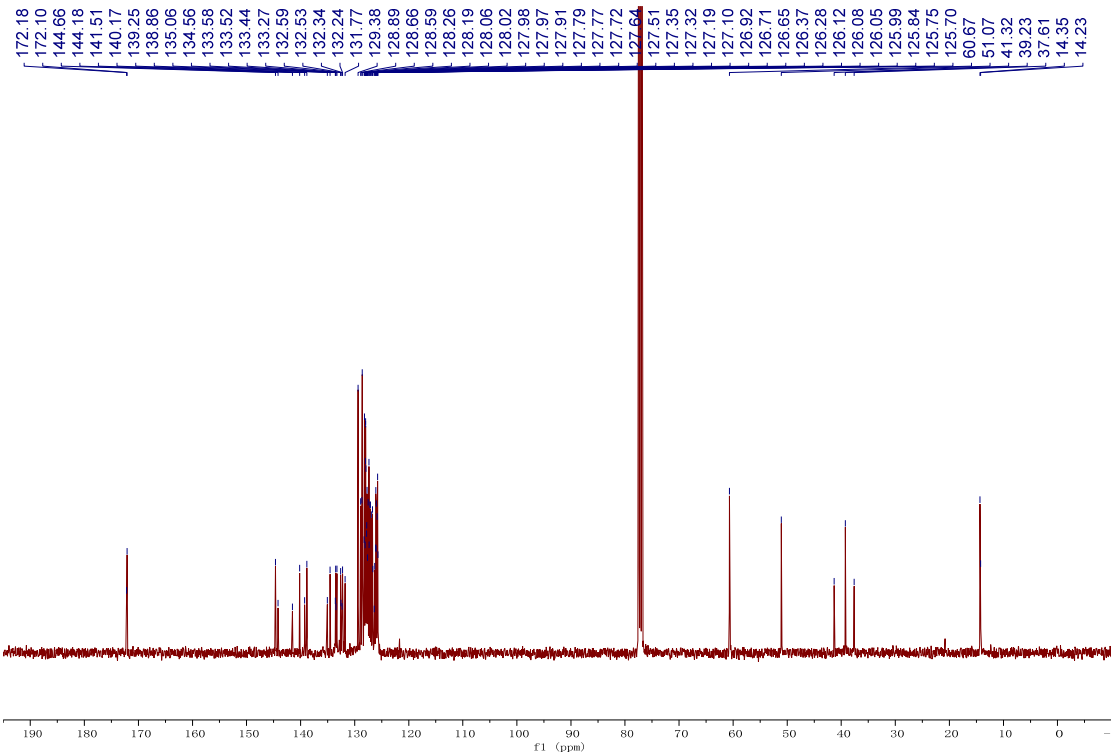
^{1}H NMR (400 MHz, $CDCl_3$) of **3aB**



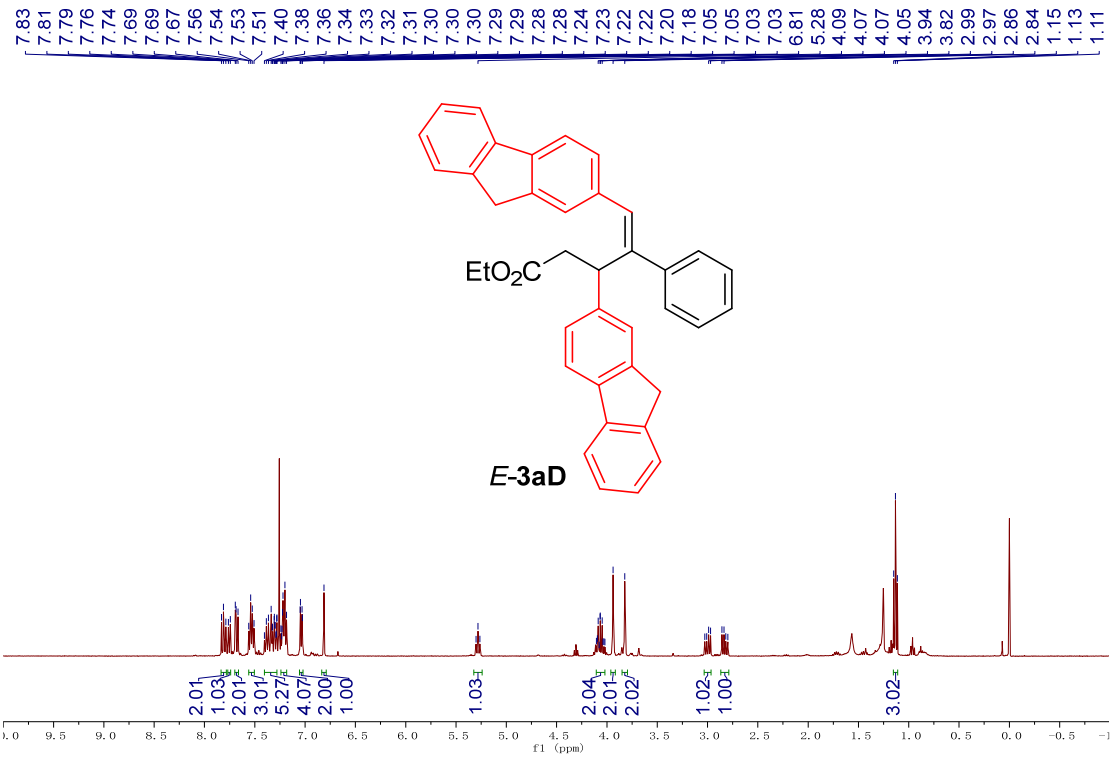
^{13}C NMR (101 MHz, $CDCl_3$) of **3aB**



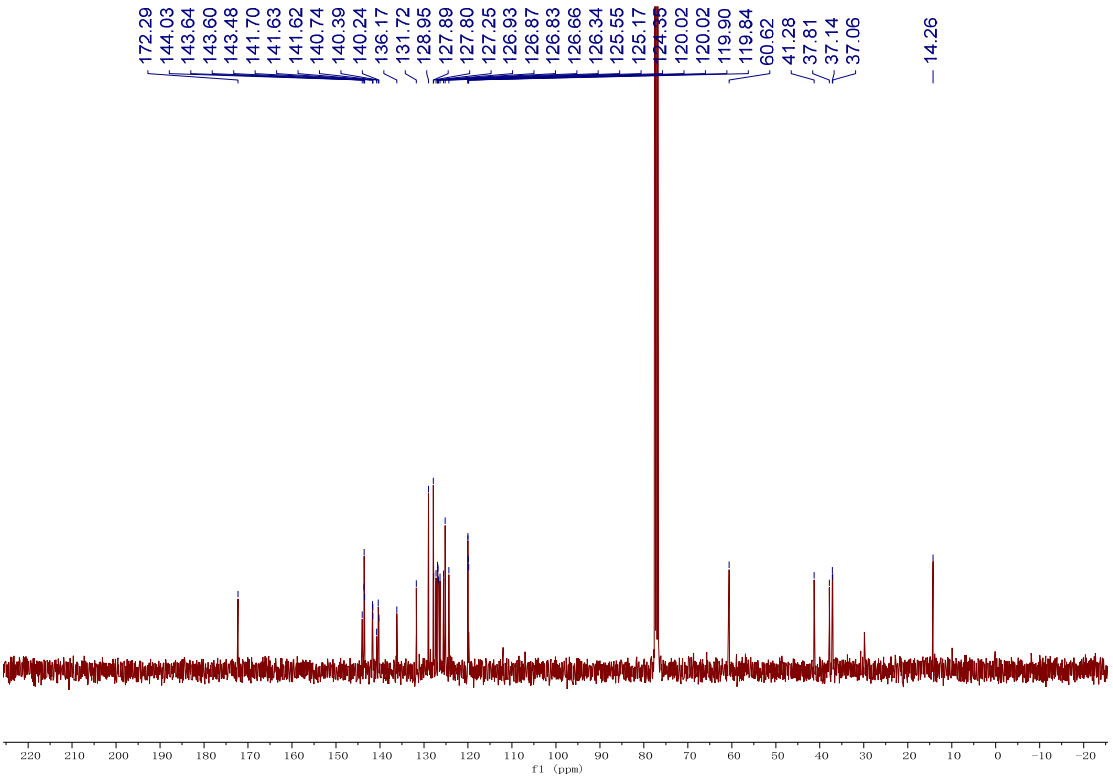
^{1}H NMR (400 MHz, $CDCl_3$) of **3aC**



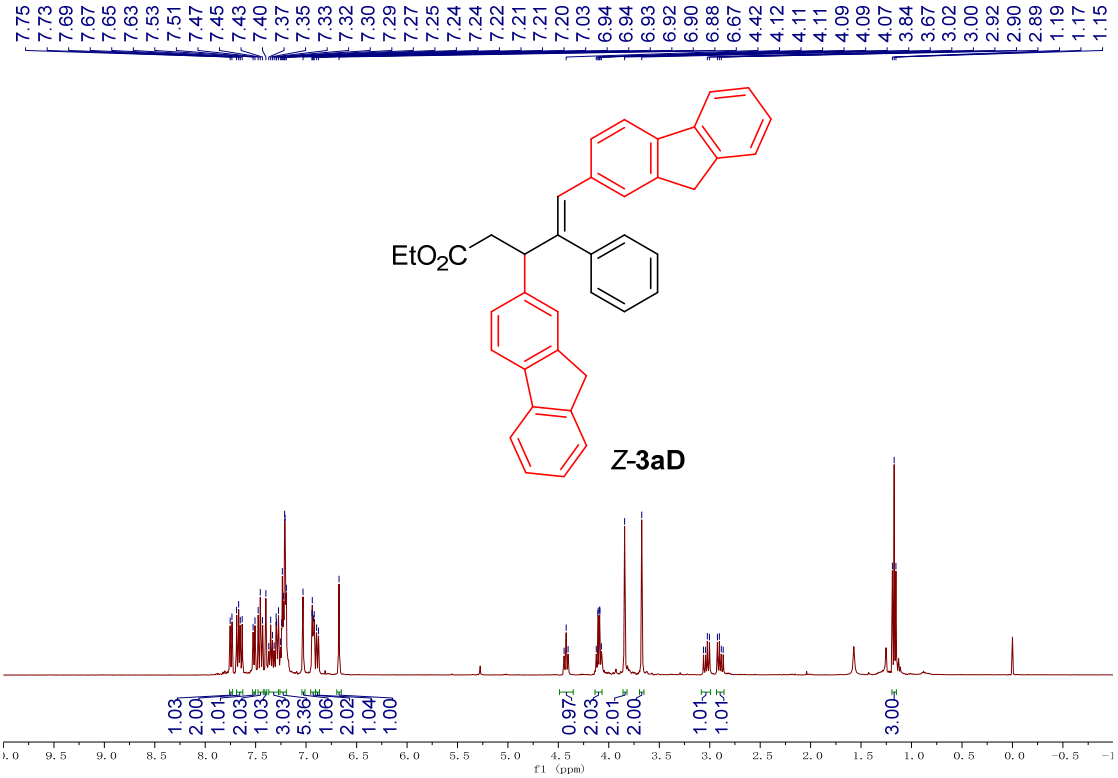
^{13}C NMR (101 MHz, $CDCl_3$) of **3aC**



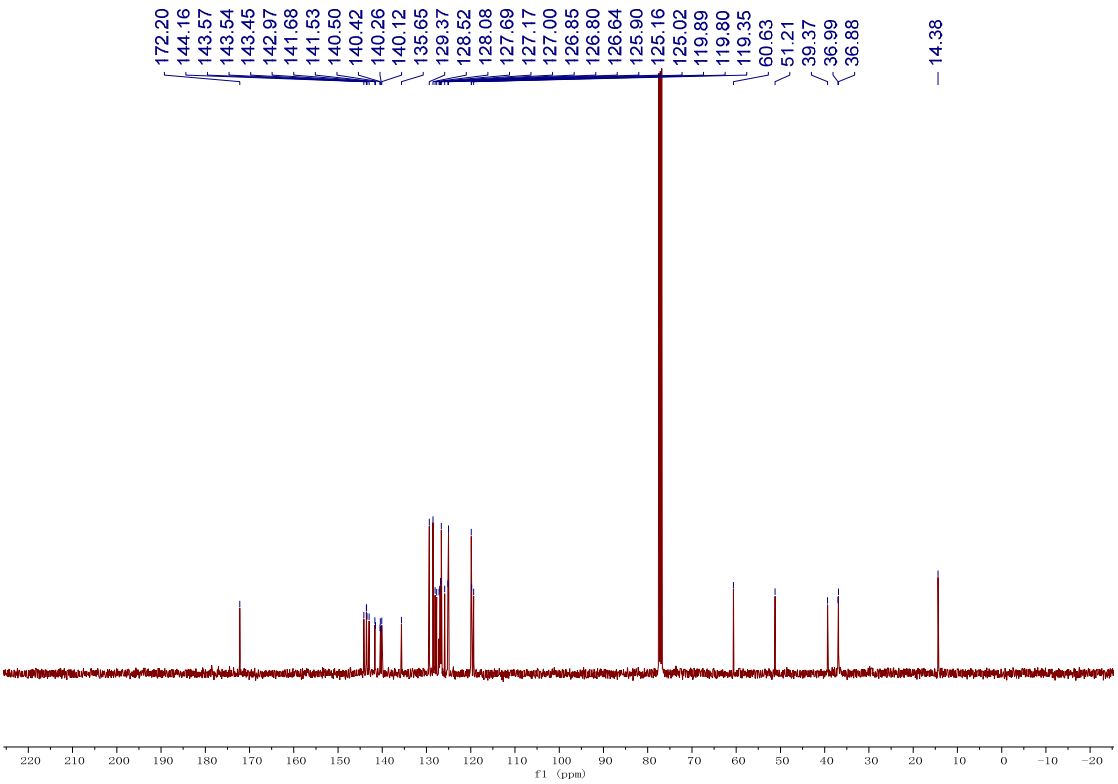
^{1}H NMR (400 MHz, $CDCl_3$) of ***E*-3aD**



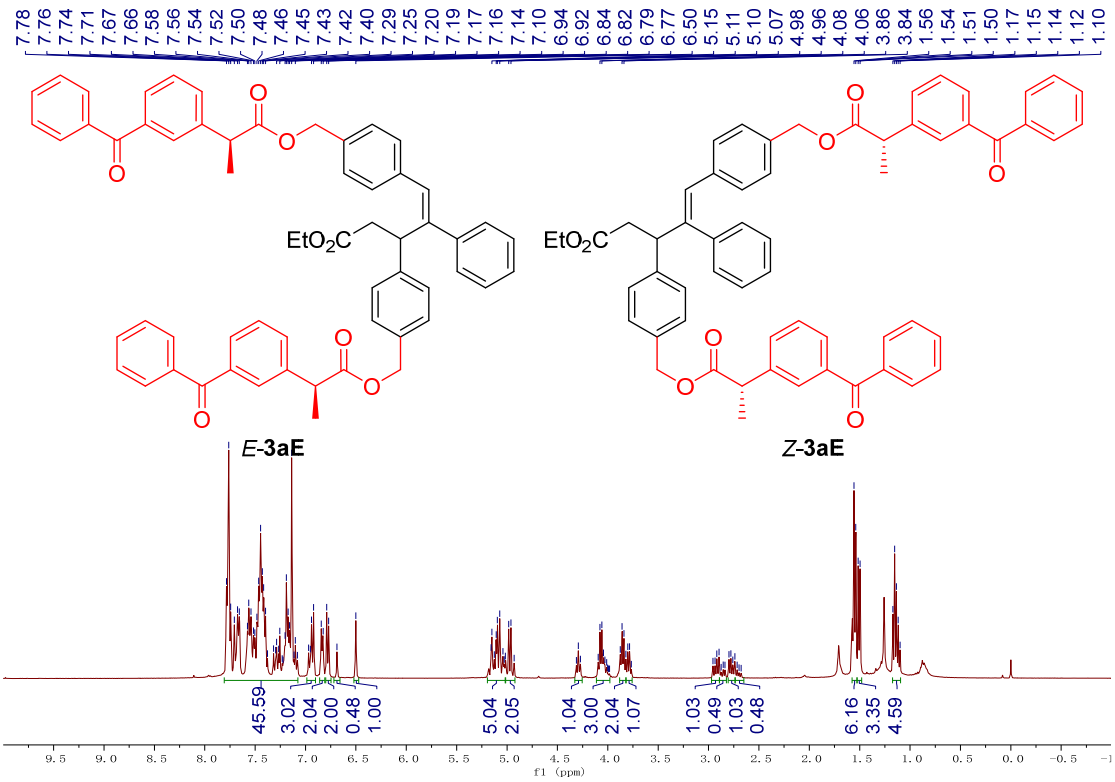
^{13}C NMR (101 MHz, $CDCl_3$) of ***E*-3aD**



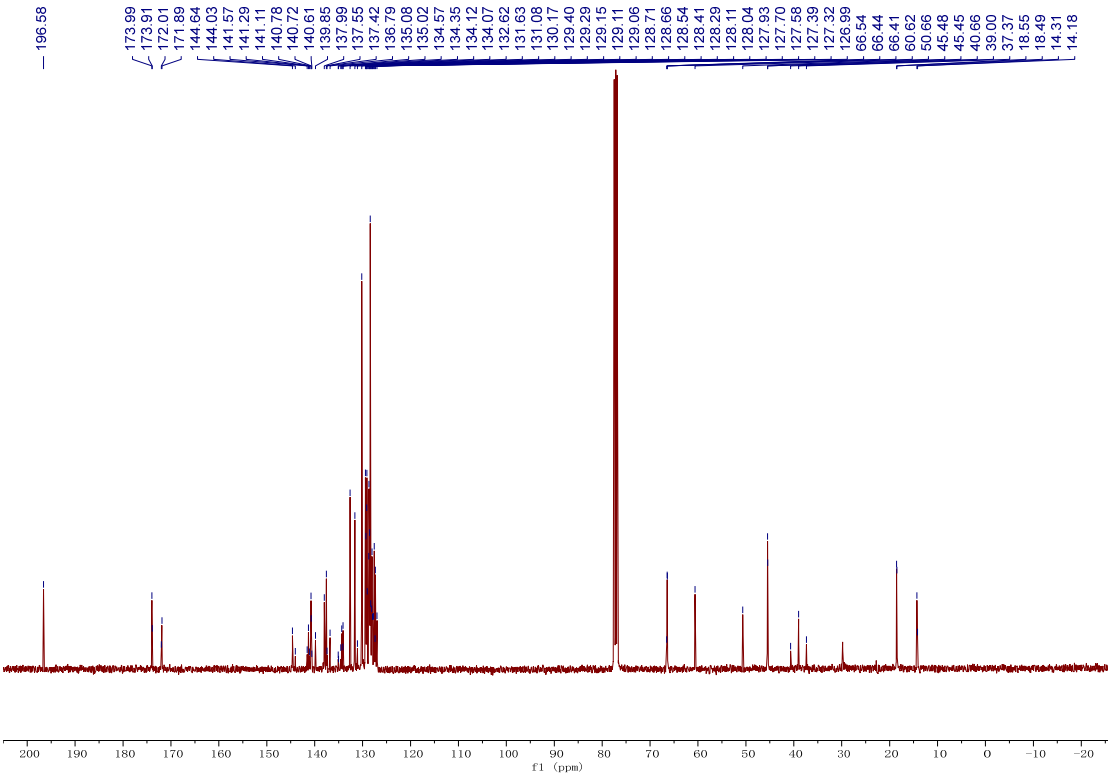
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3aD**



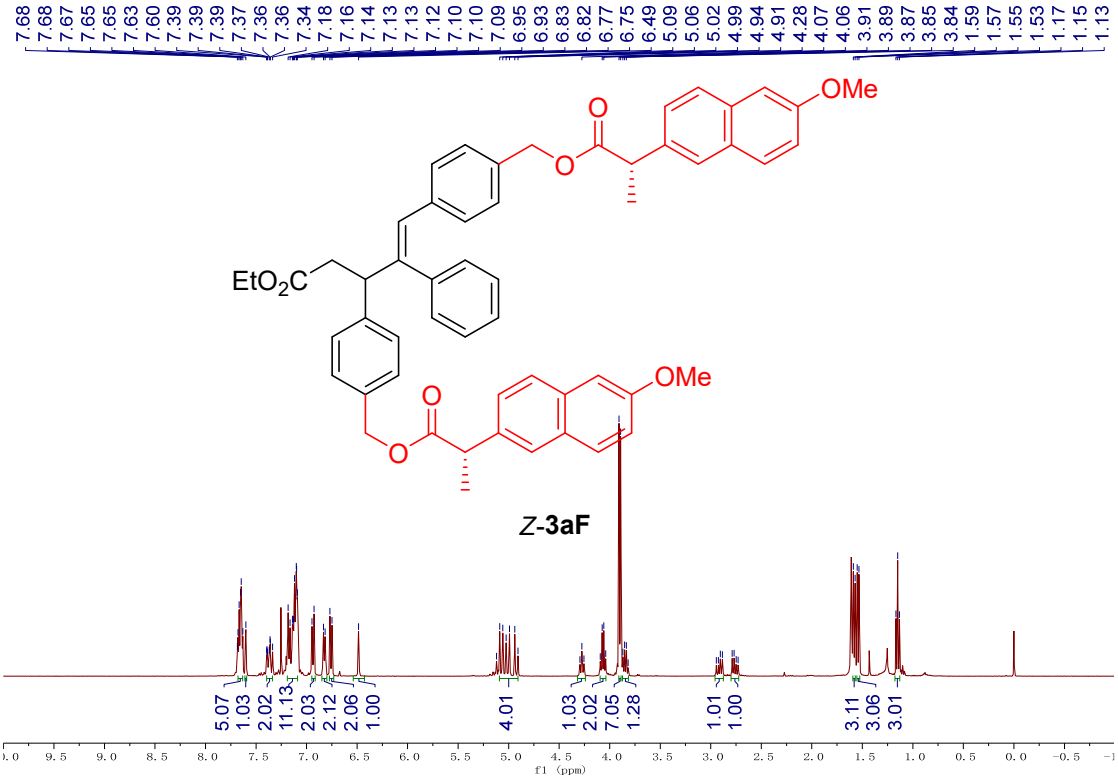
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3aD**



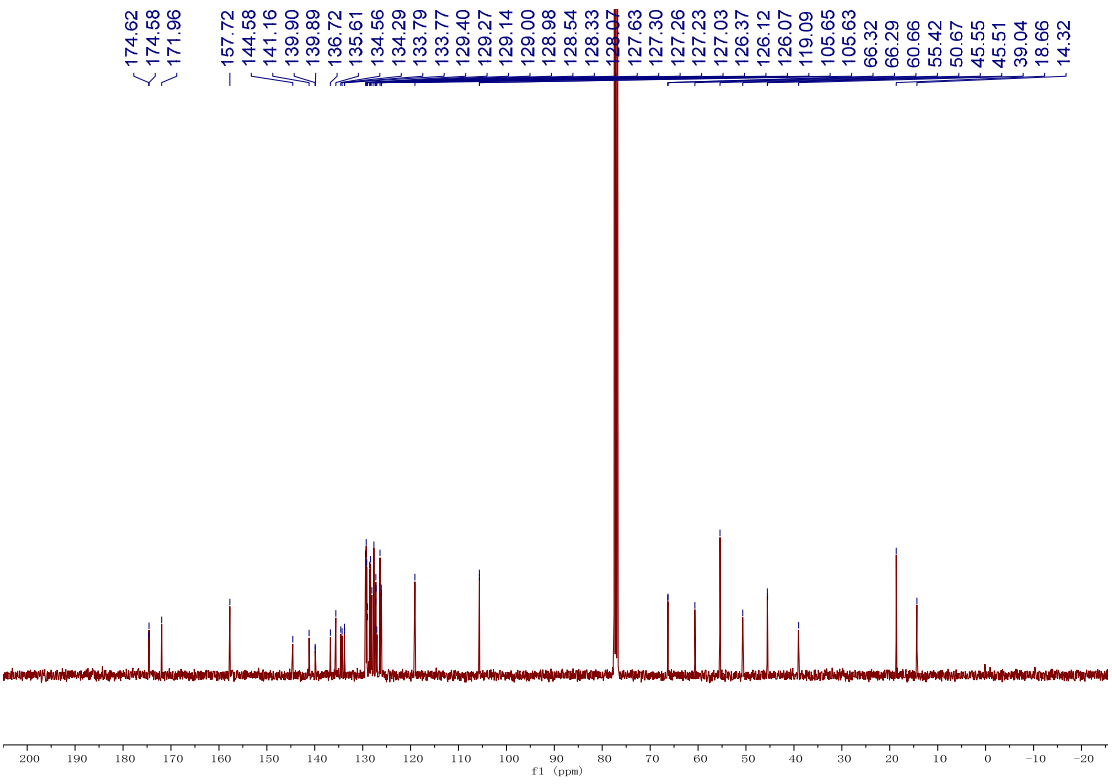
^{1}H NMR (400 MHz, $CDCl_3$) of **3aE**



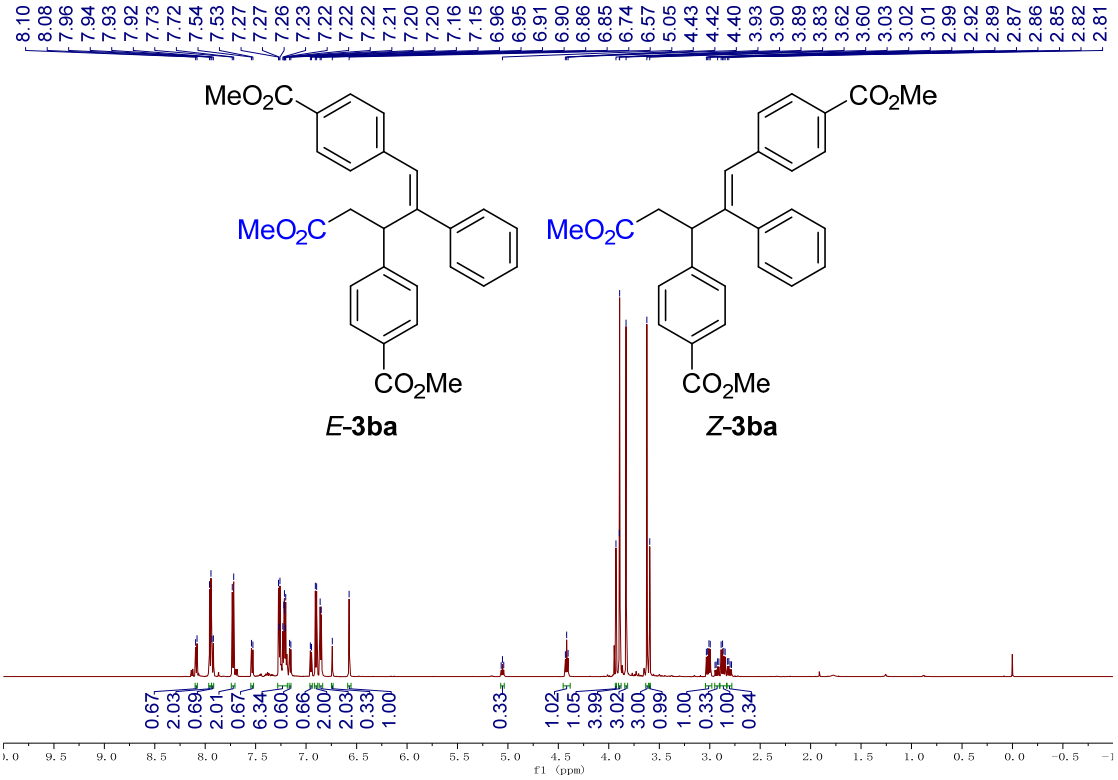
^{13}C NMR (101 MHz, $CDCl_3$) of **3aE**



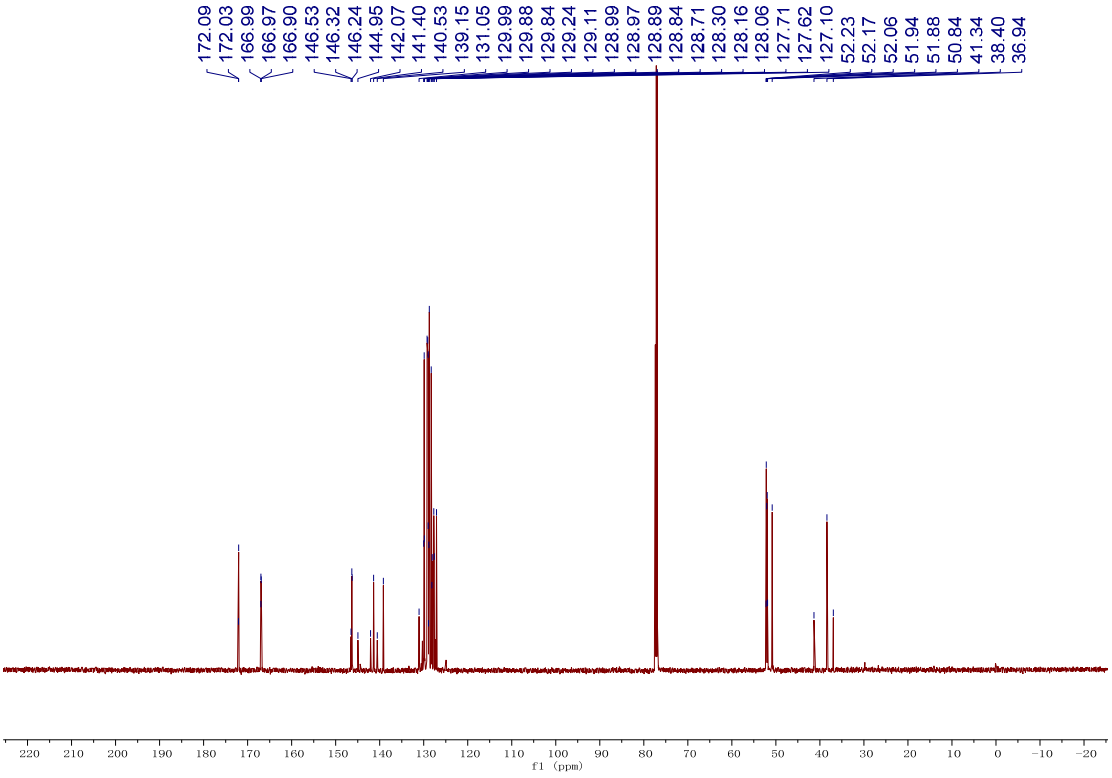
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3aF**



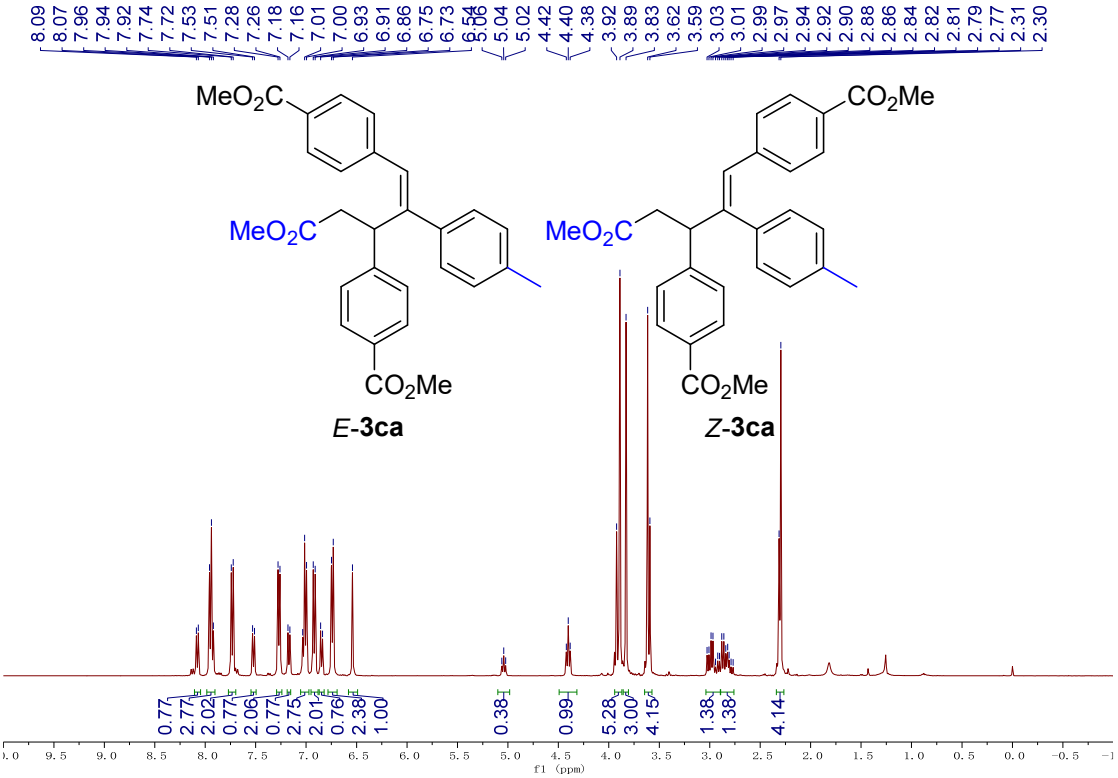
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3aF**



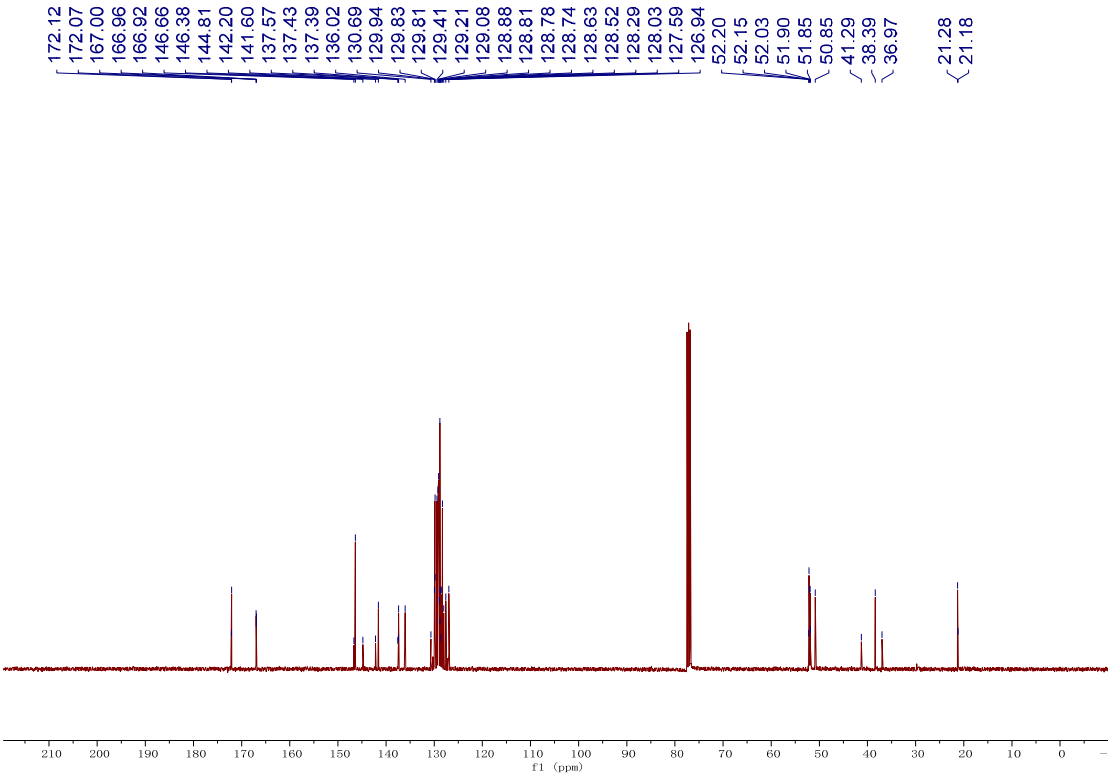
^{1}H NMR (600 MHz, $CDCl_3$) of **3ba**



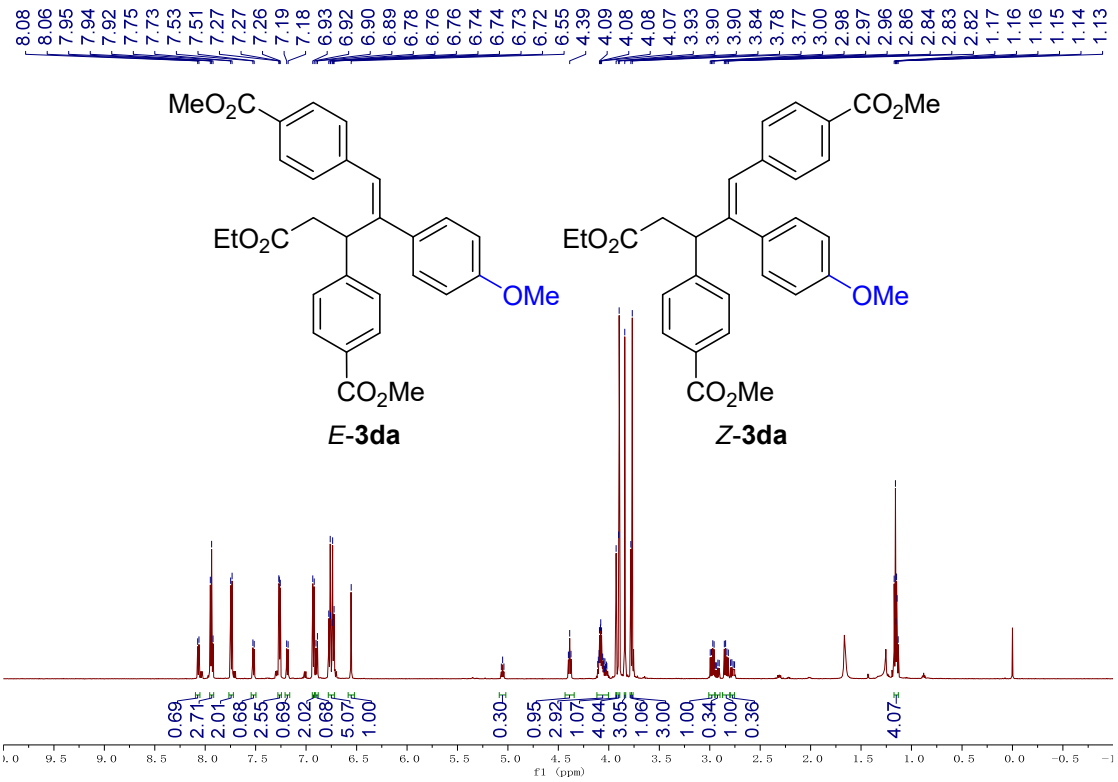
^{13}C NMR (151 MHz, $CDCl_3$) of **3ba**



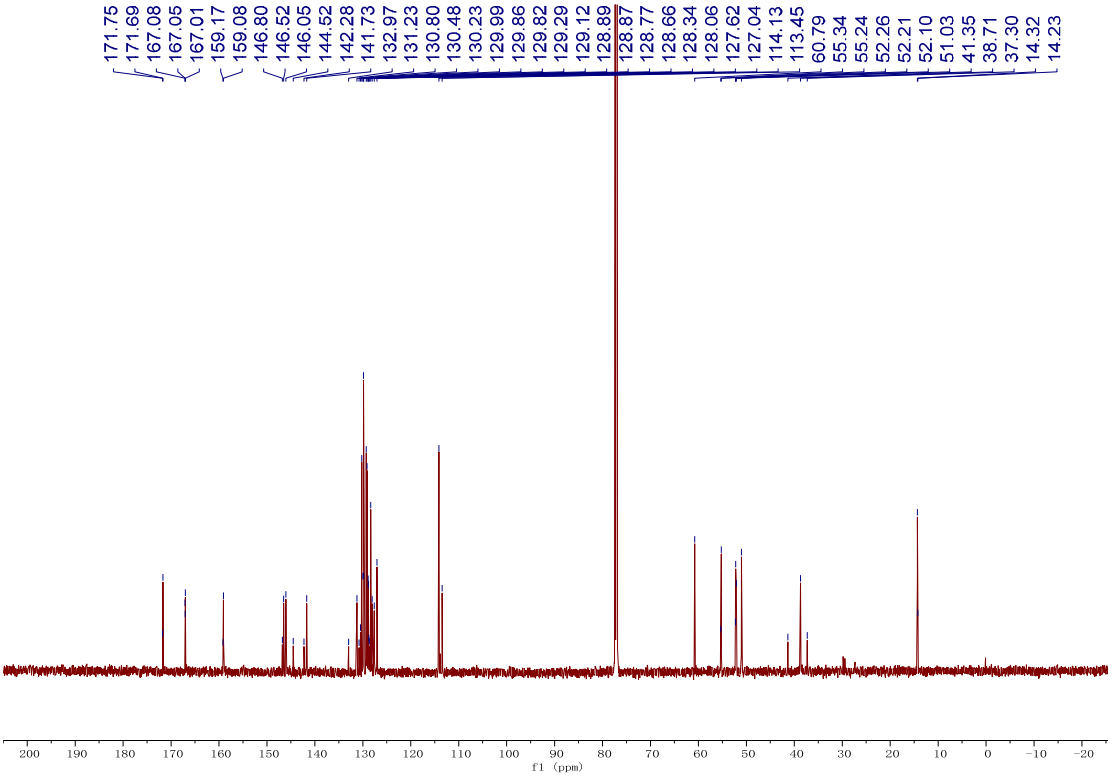
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



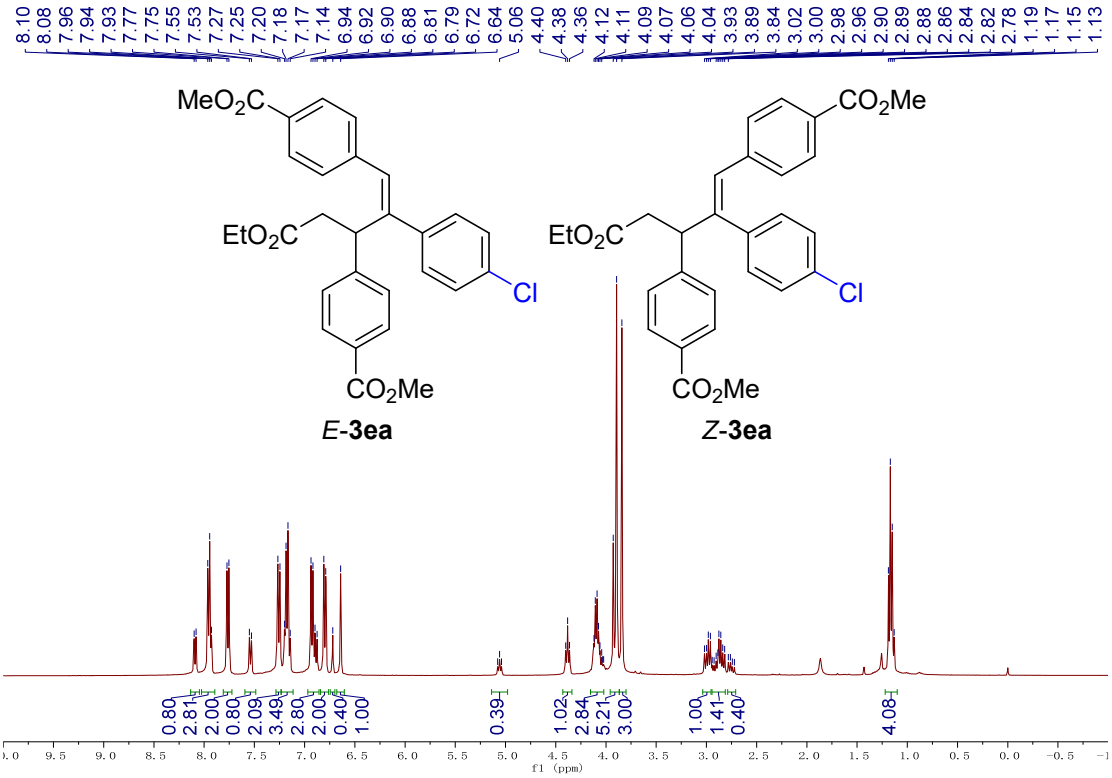
^{13}C NMR (101 MHz, $CDCl_3$) of **3ca**



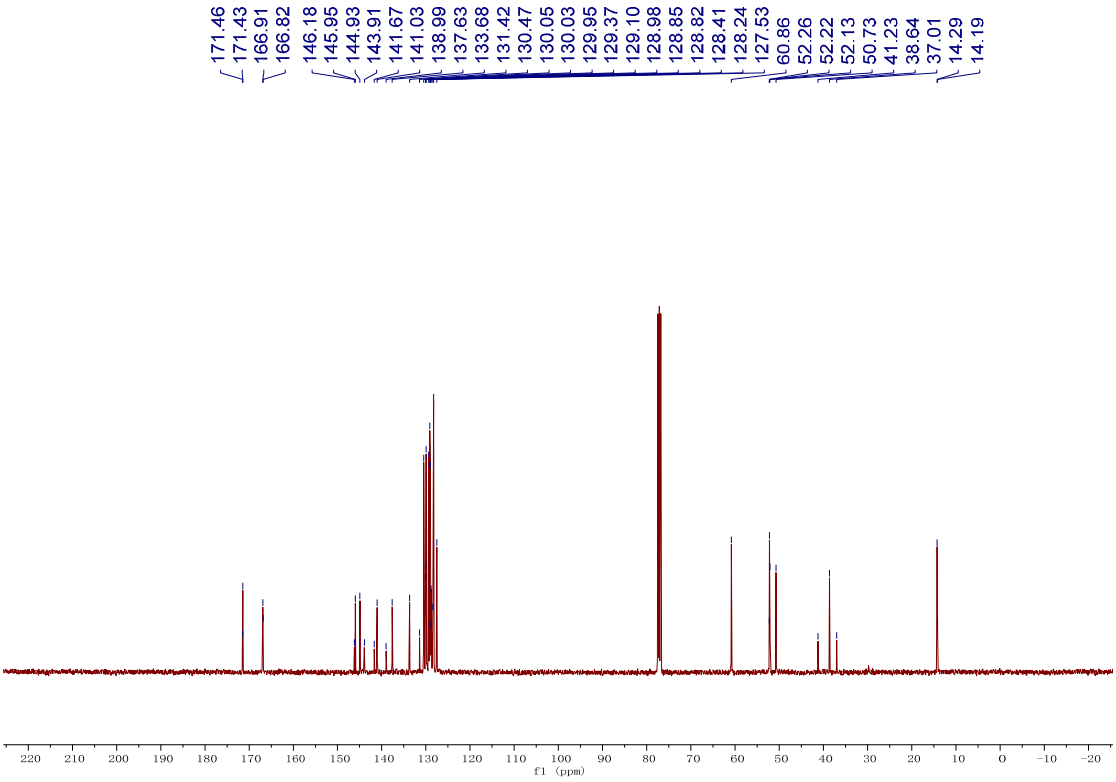
^{1}H NMR (600 MHz, $CDCl_3$) of **3da**



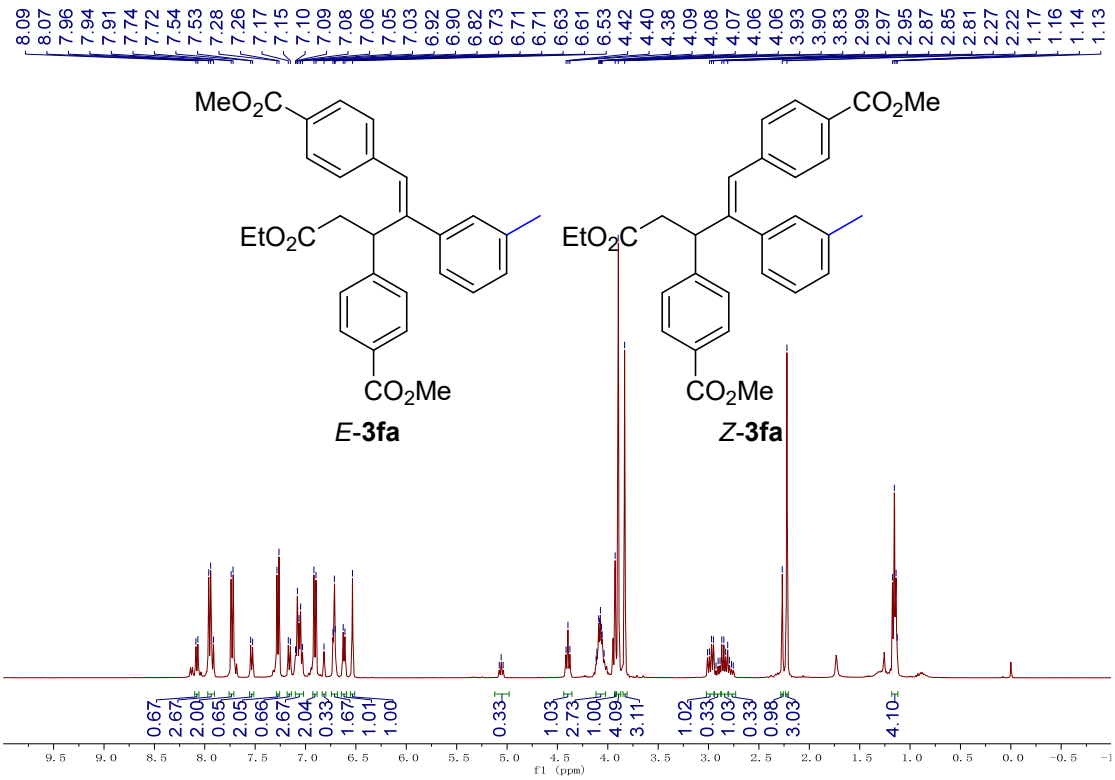
^{13}C NMR (151 MHz, $CDCl_3$) of **3da**



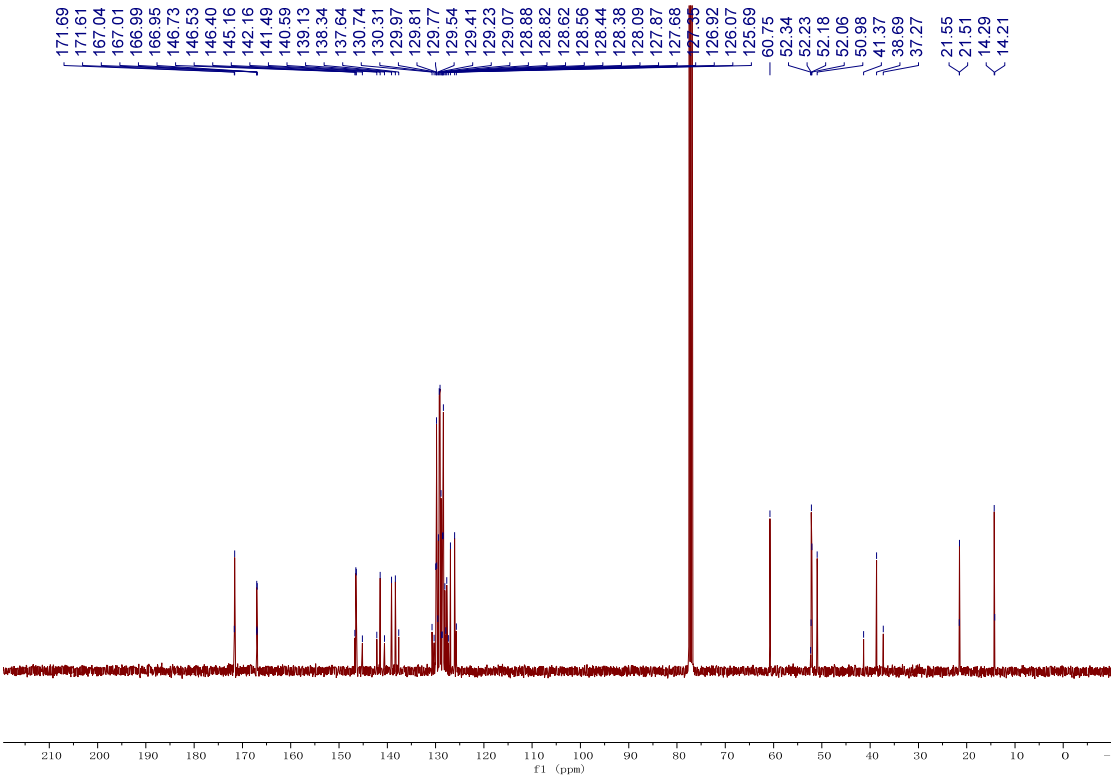
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



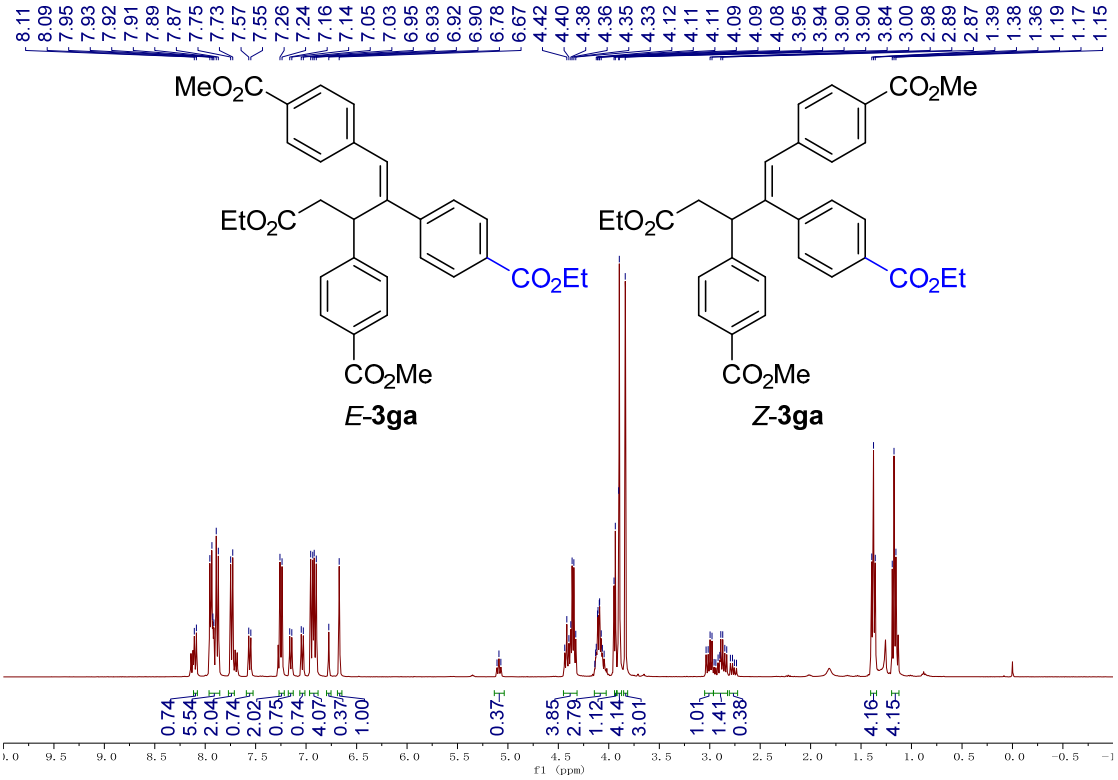
^{13}C NMR (101 MHz, $CDCl_3$) of **3ea**



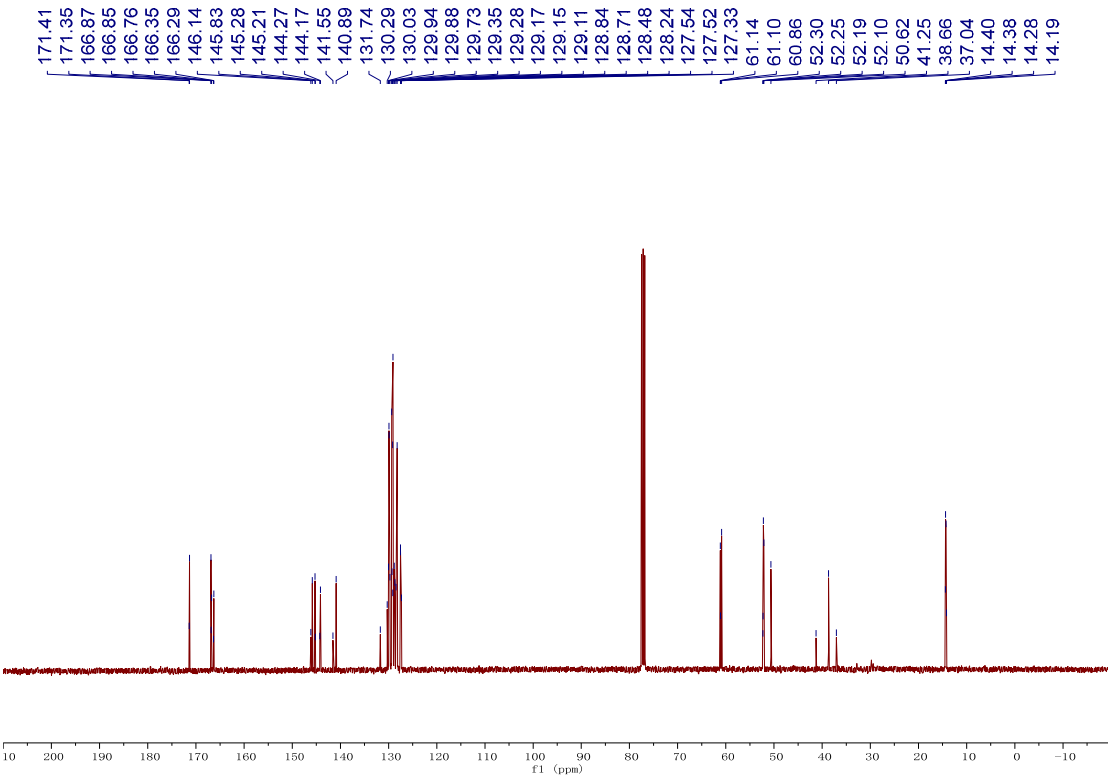
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



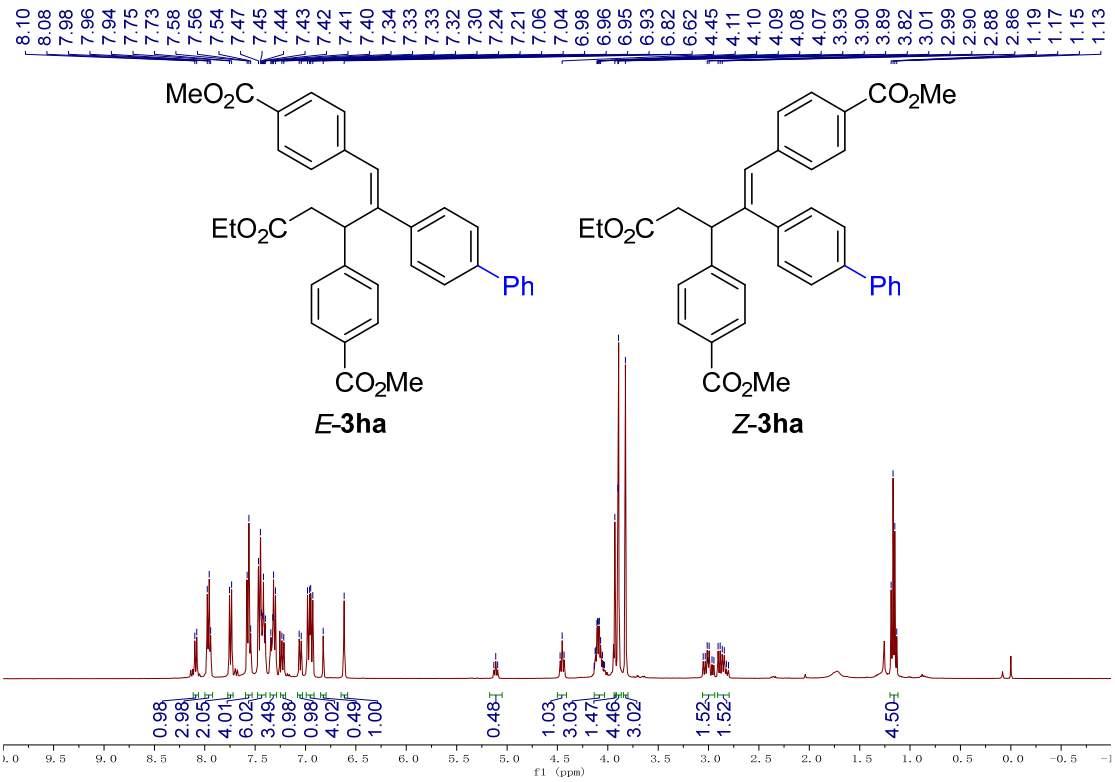
^{13}C NMR (101 MHz, $CDCl_3$) of **3fa**



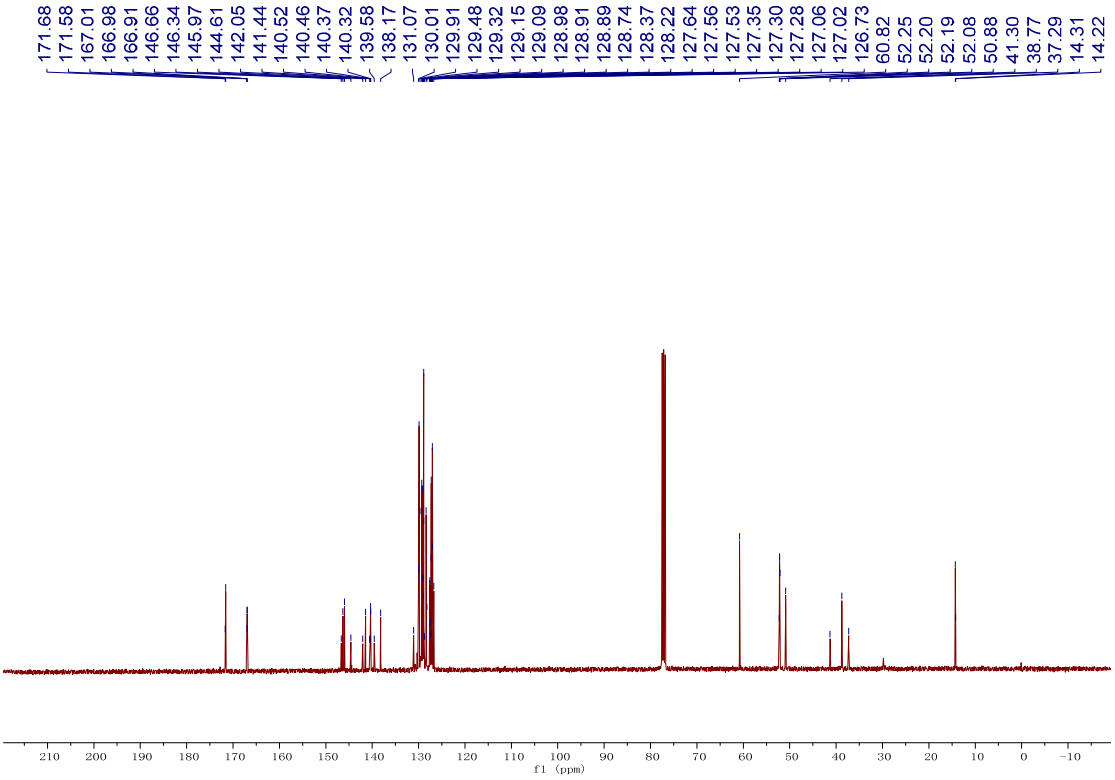
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



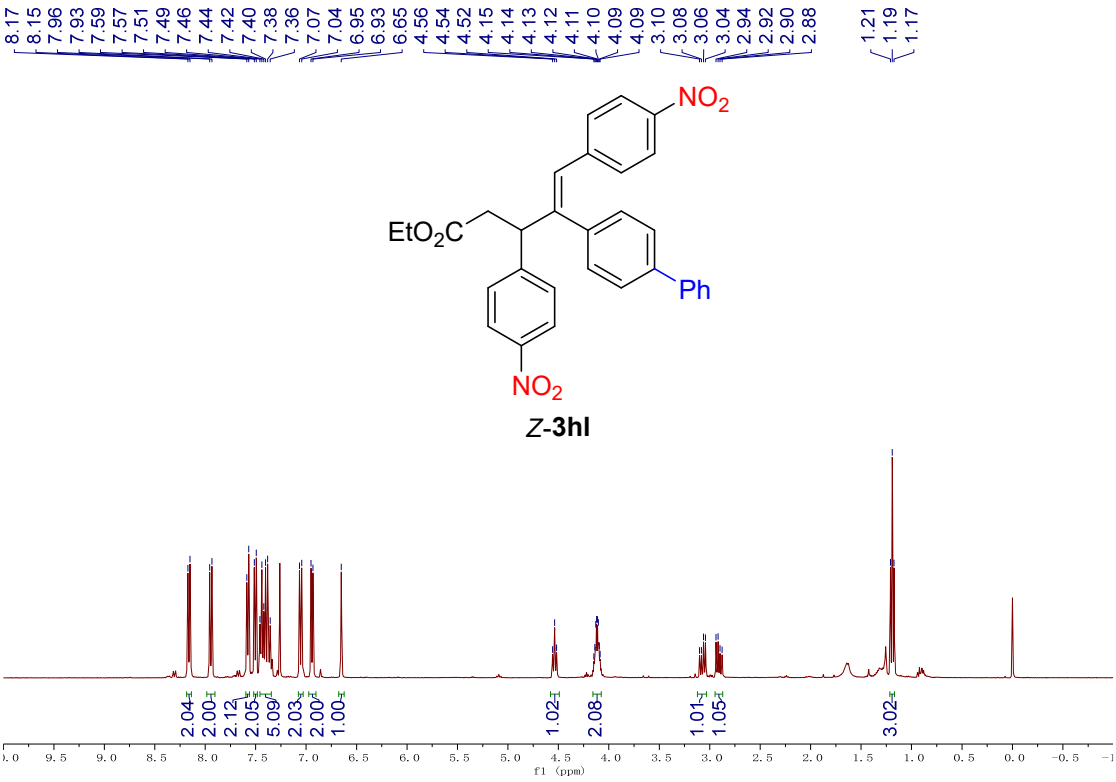
^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**



^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**

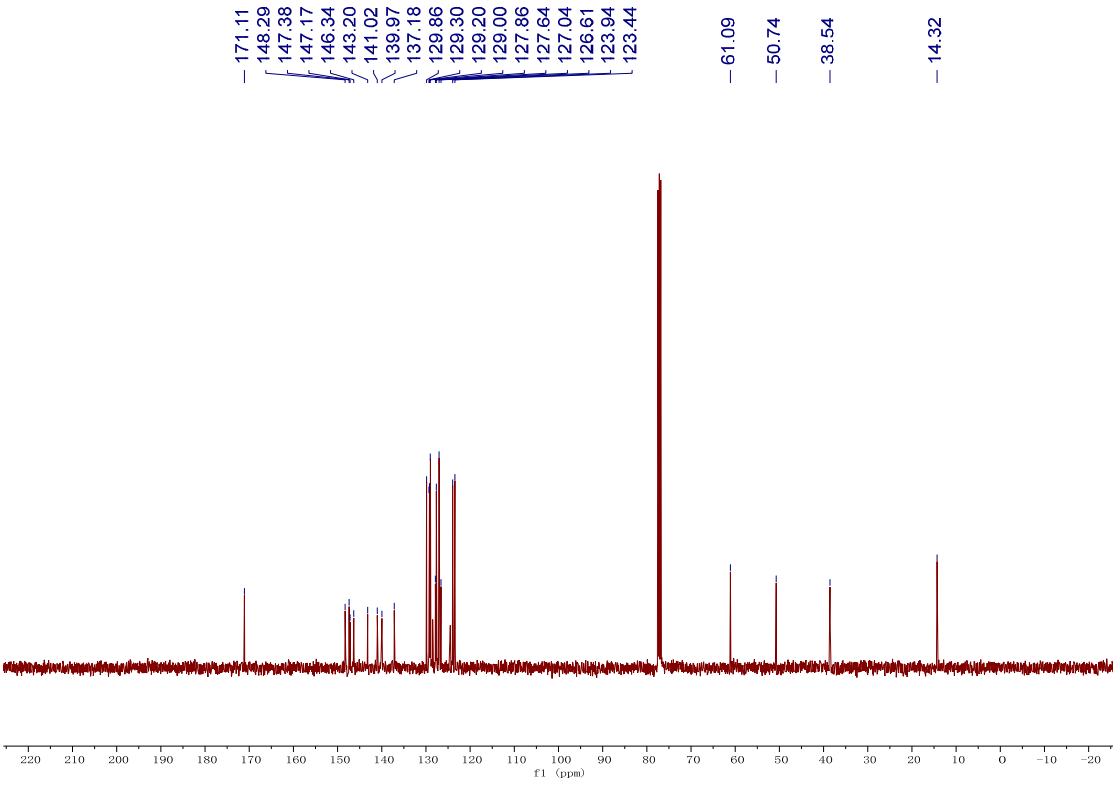


^{13}C NMR (101 MHz, $CDCl_3$) of **3ha**

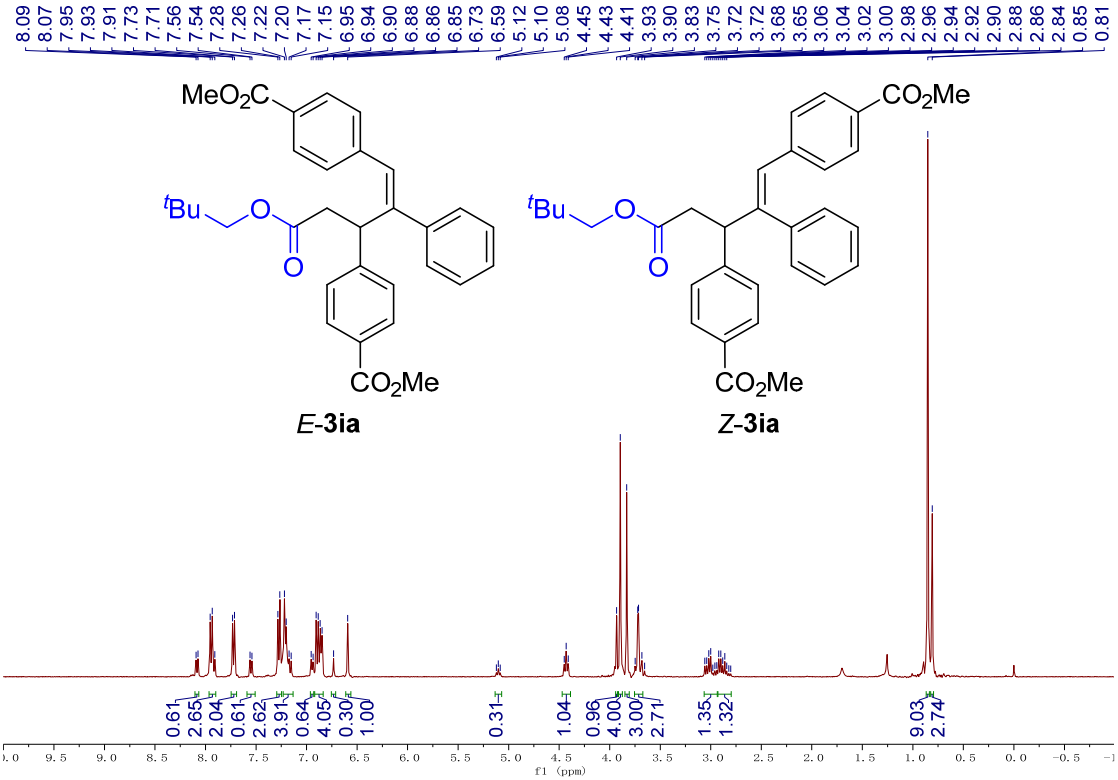


Z-**3hl**

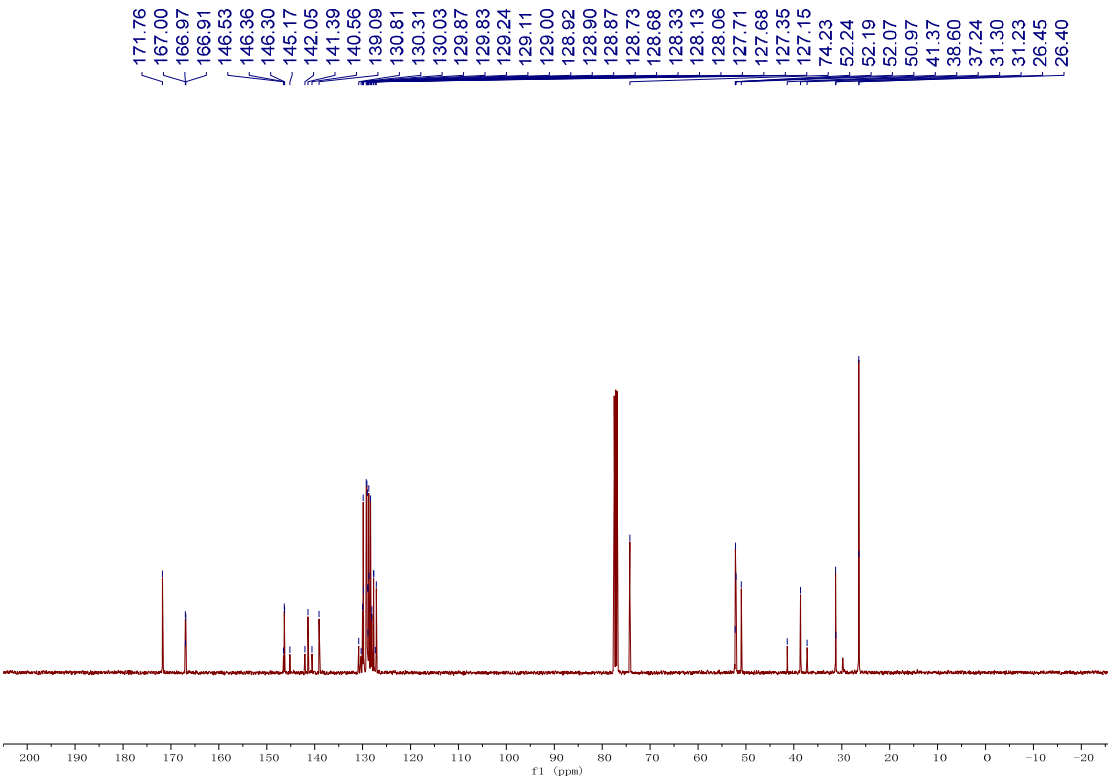
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3hl**



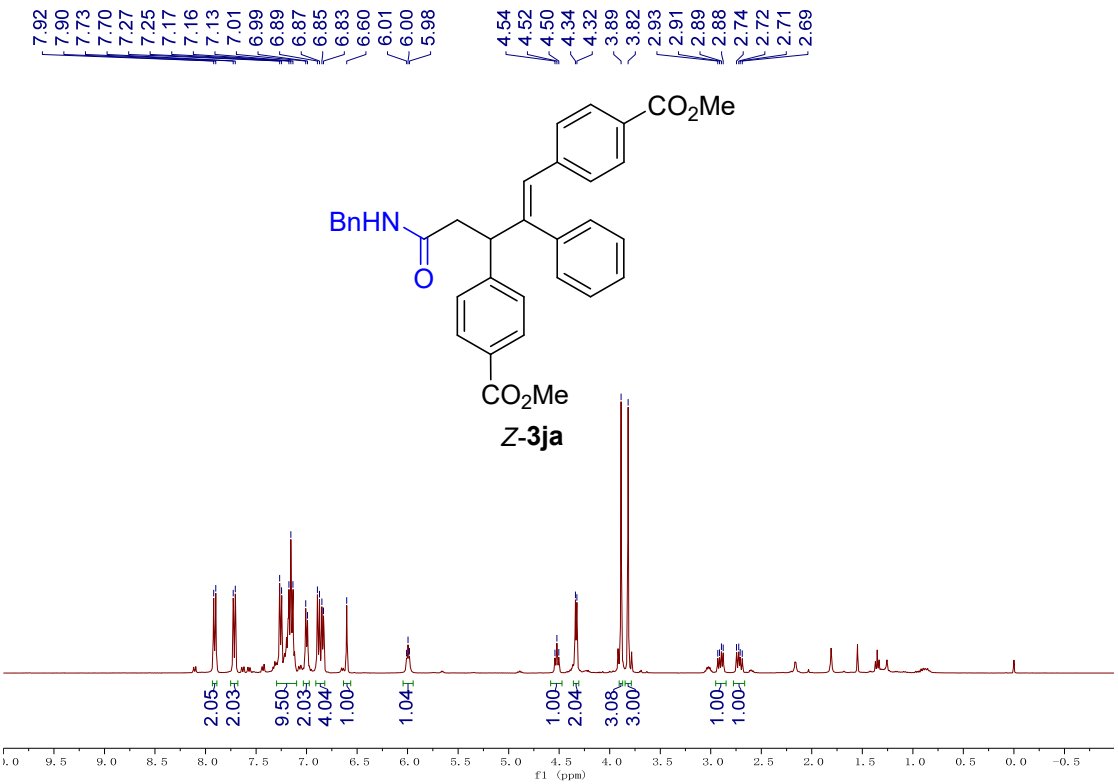
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3hl**



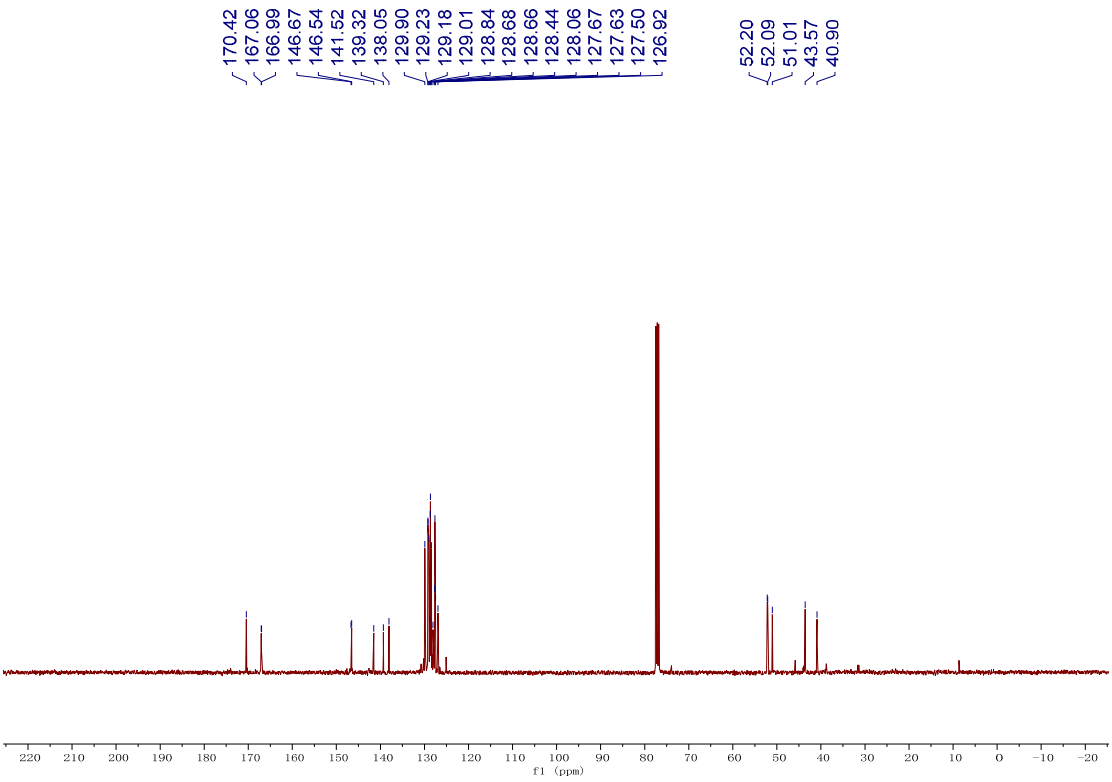
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



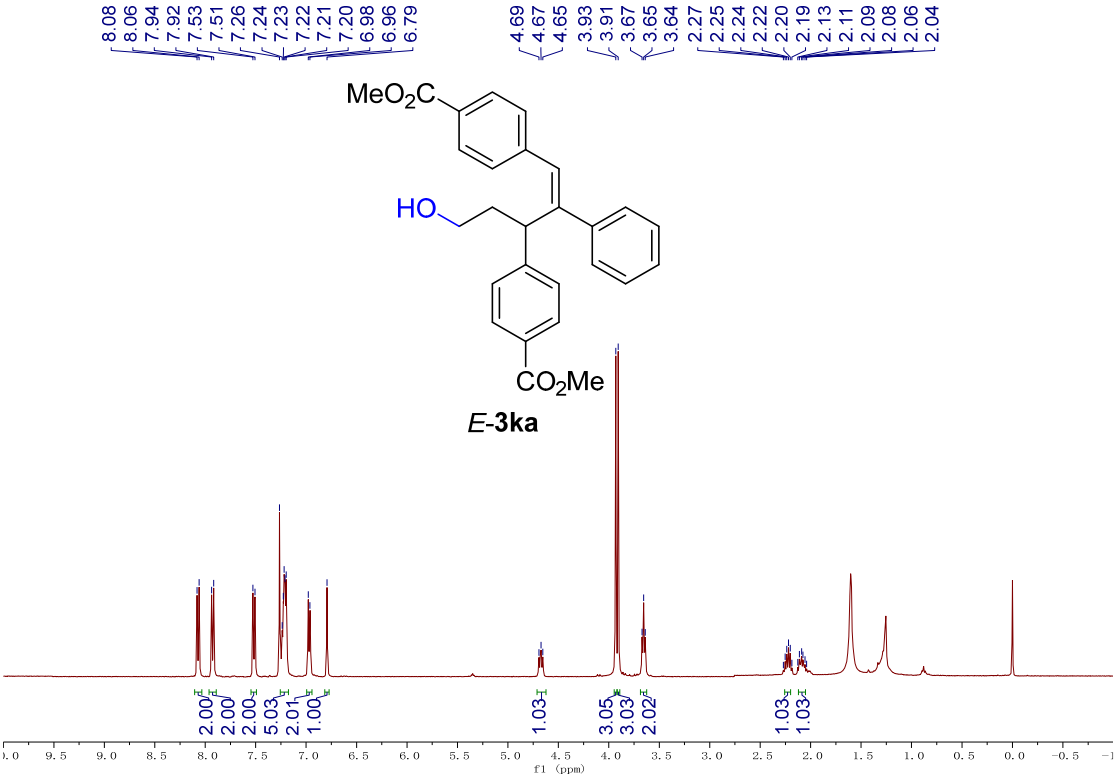
^{13}C NMR (101 MHz, $CDCl_3$) of **3ia**



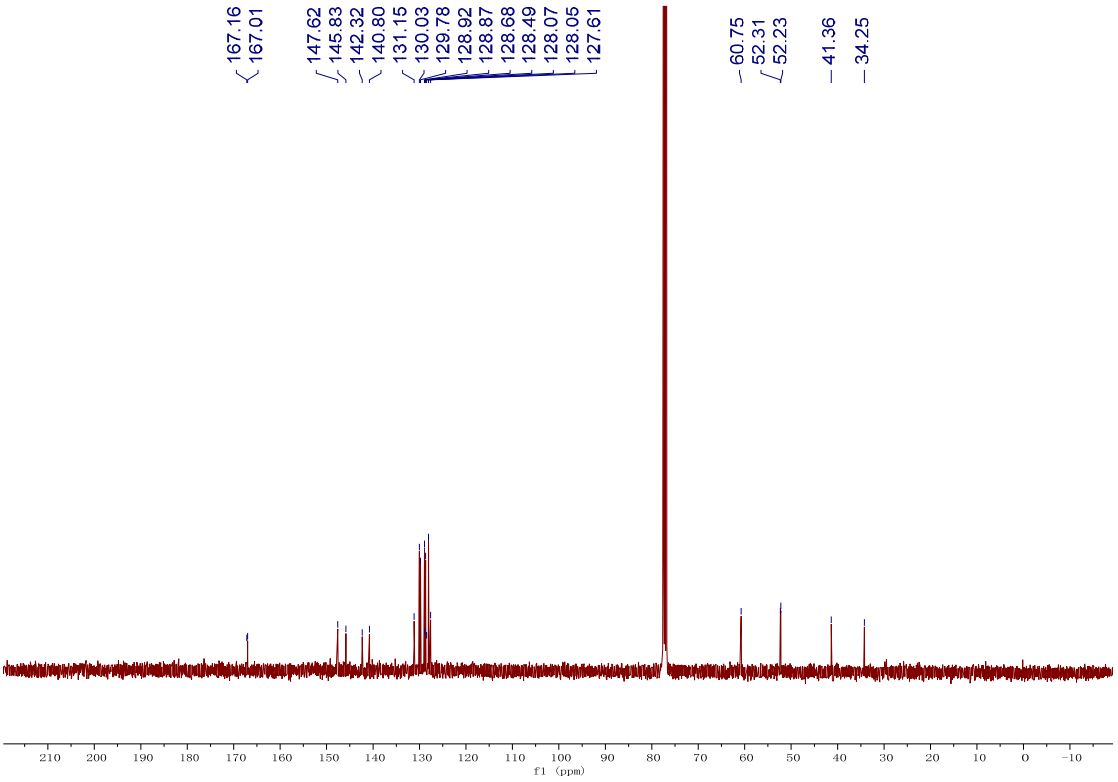
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ja**



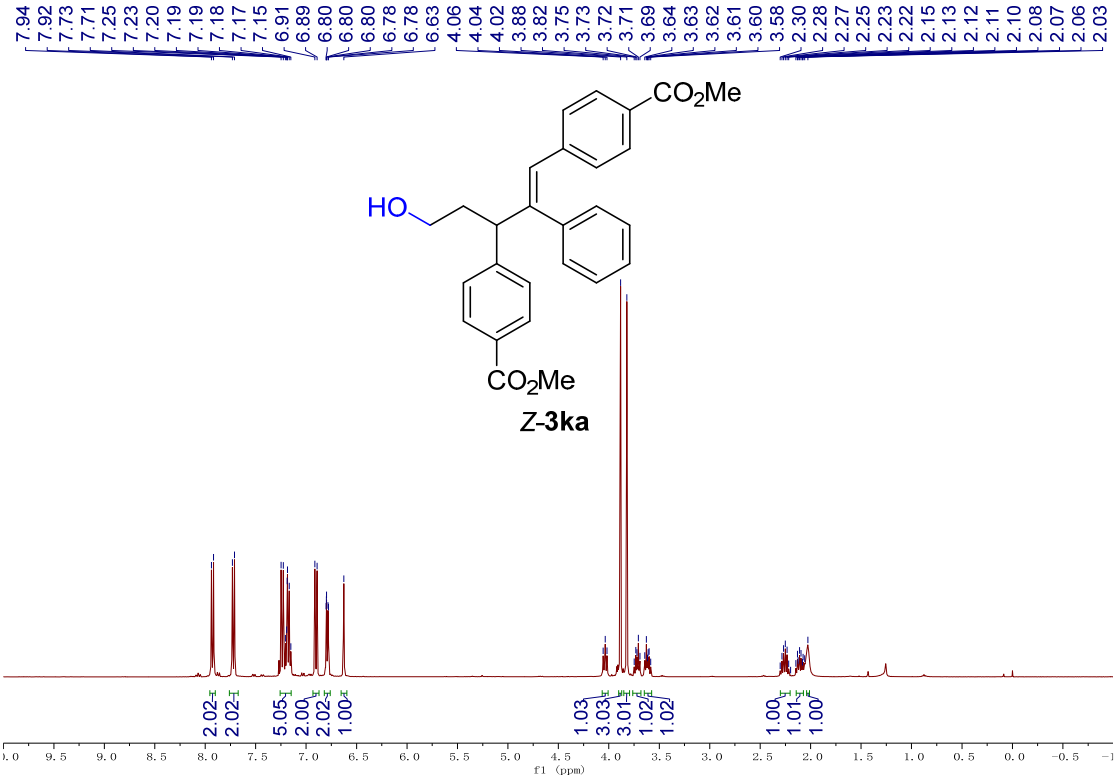
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ja**



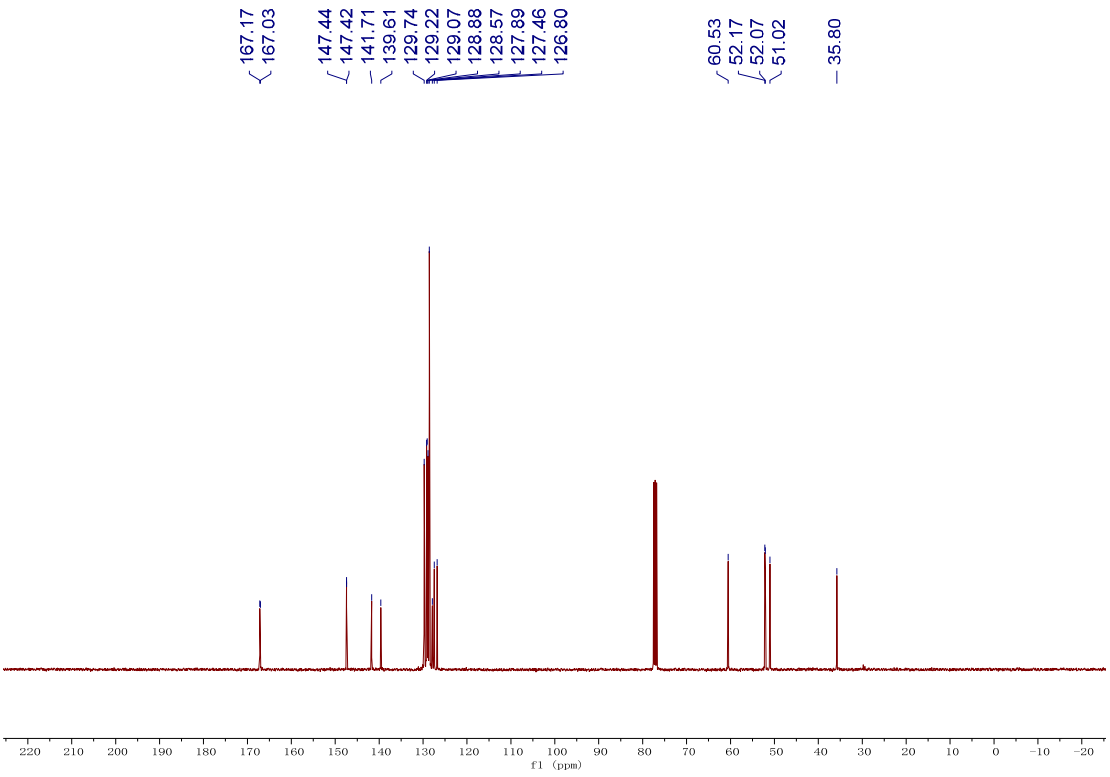
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-**3ka**



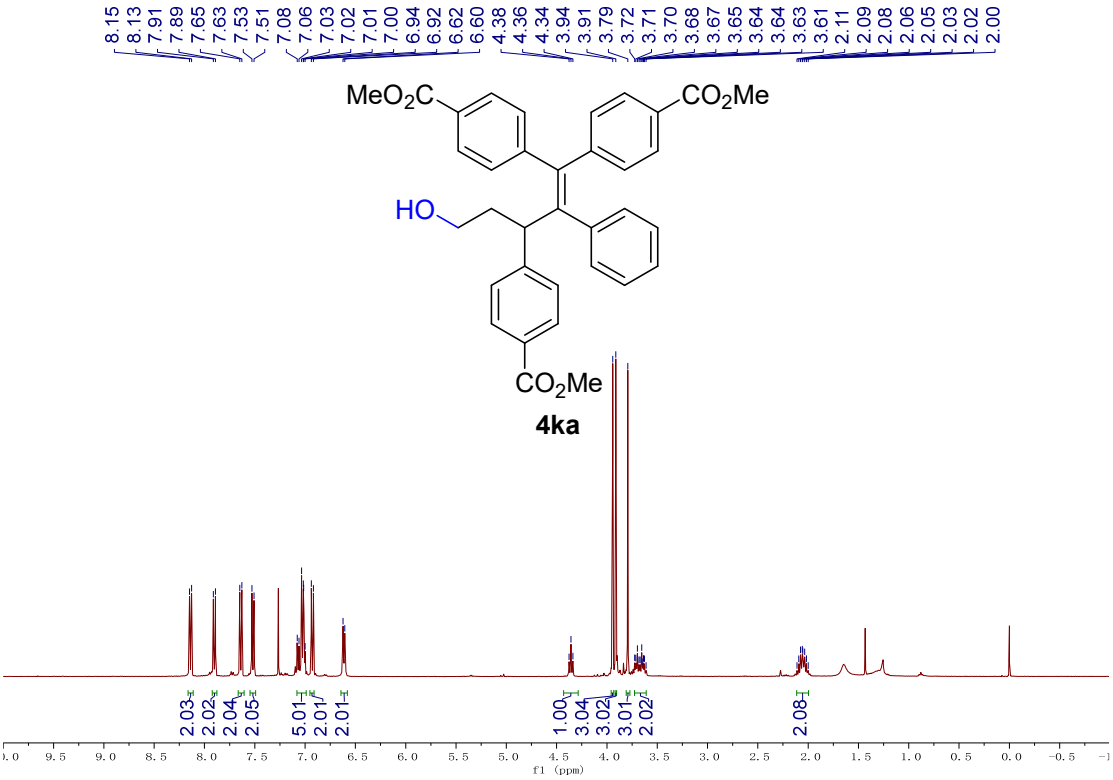
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-**3ka**



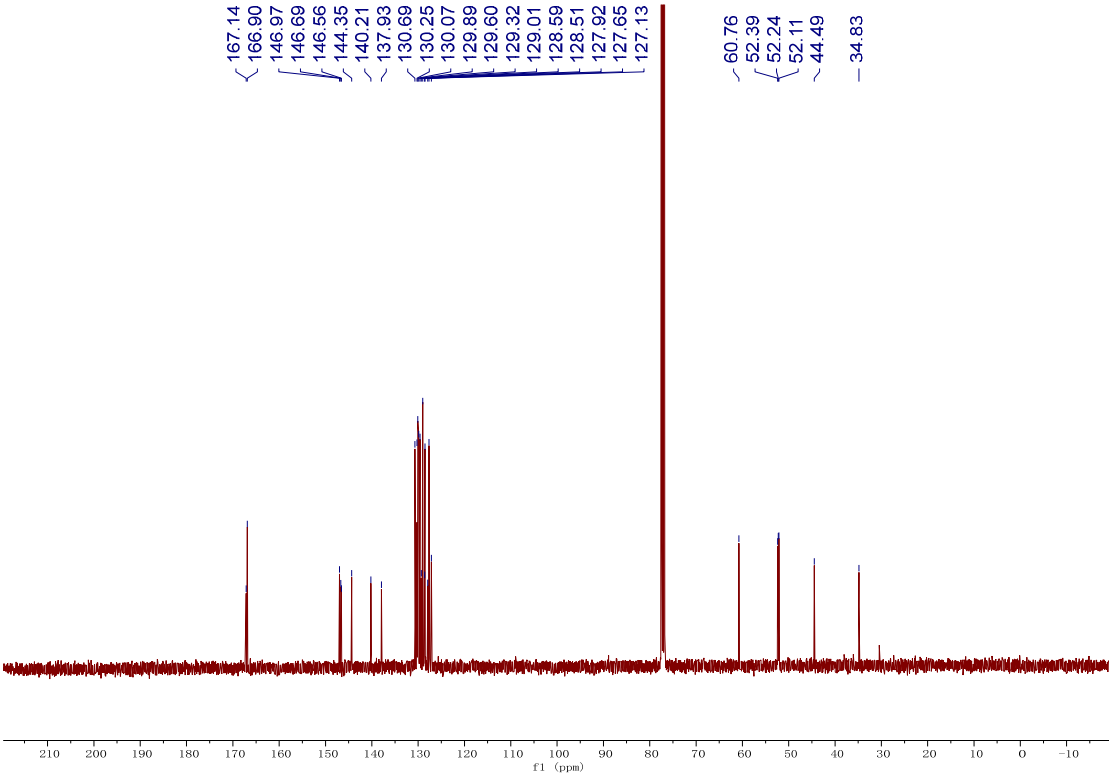
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ka**



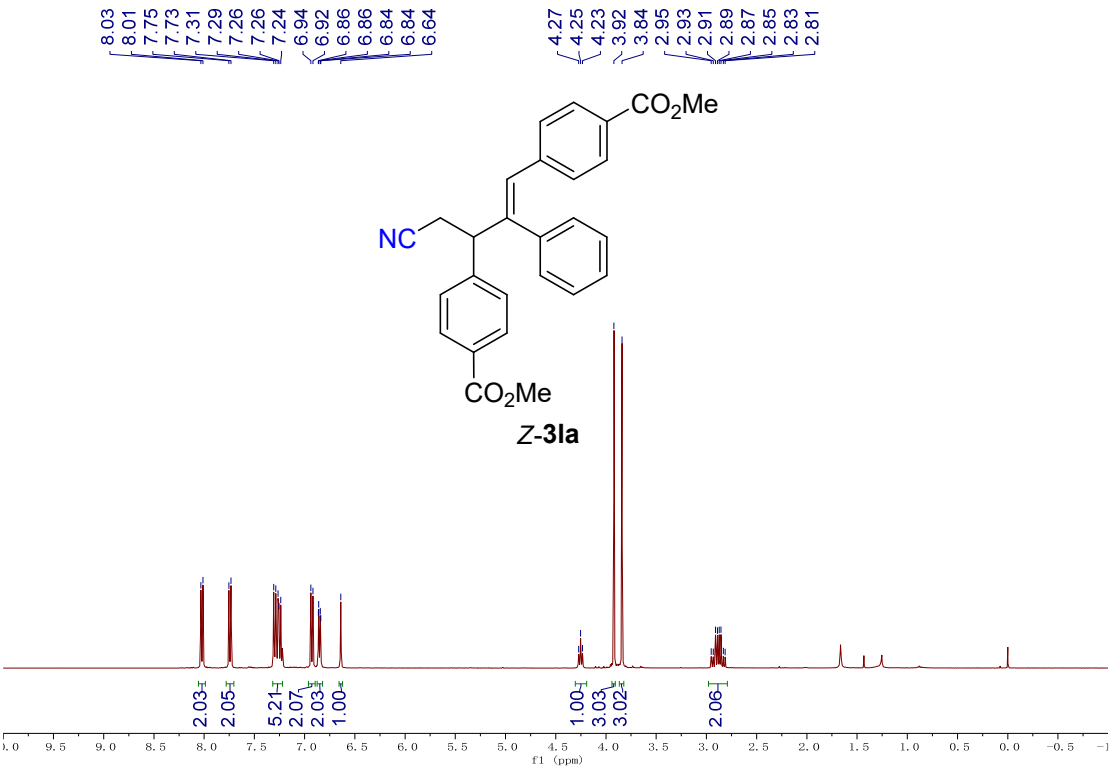
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ka**



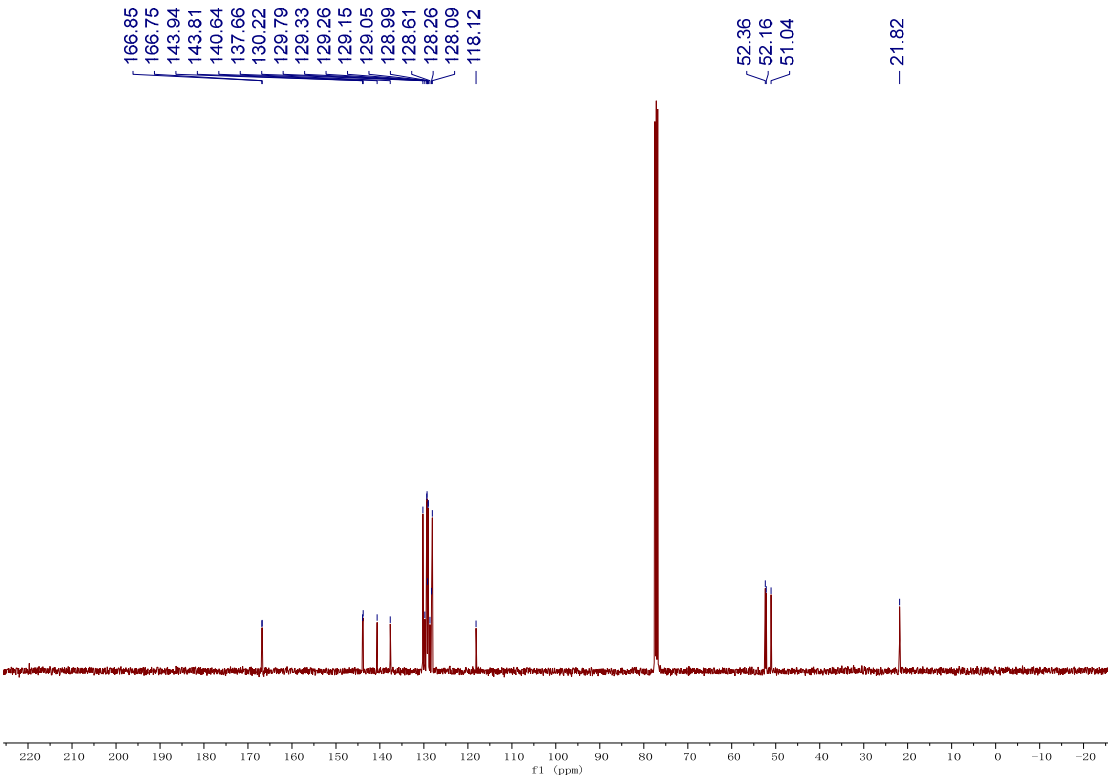
^{1}H NMR (400 MHz, $CDCl_3$) of **4ka**



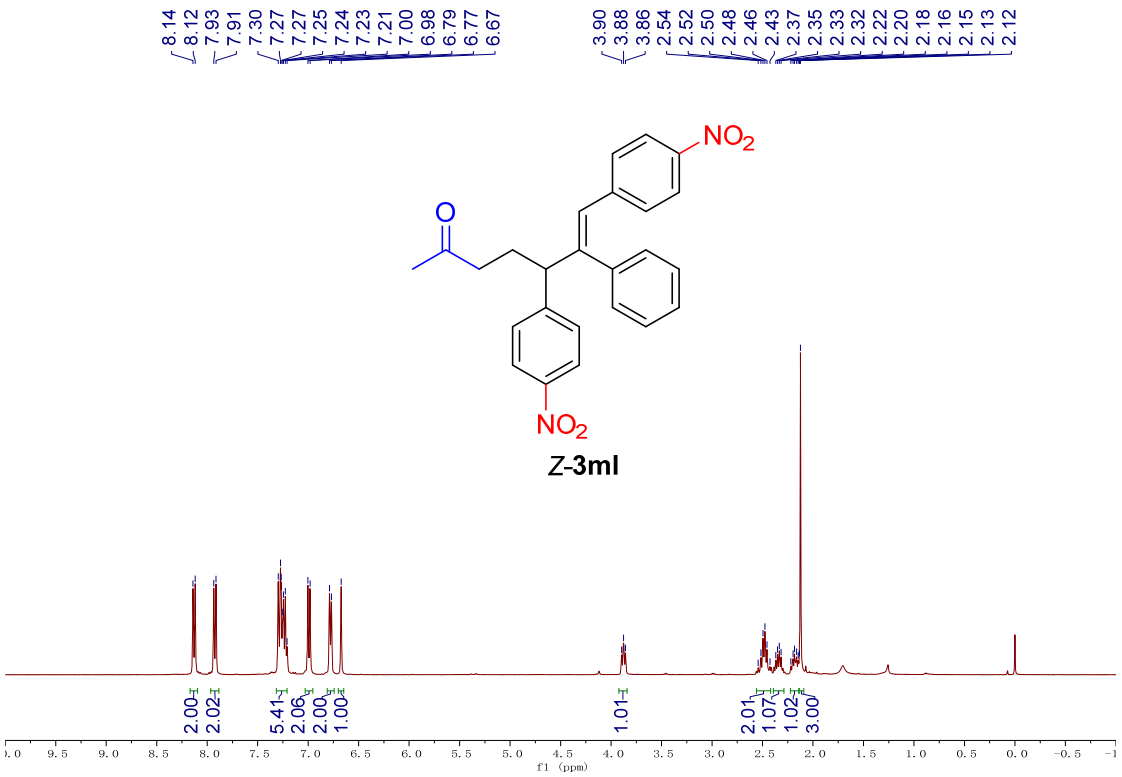
^{13}C NMR (101 MHz, $CDCl_3$) of **4ka**



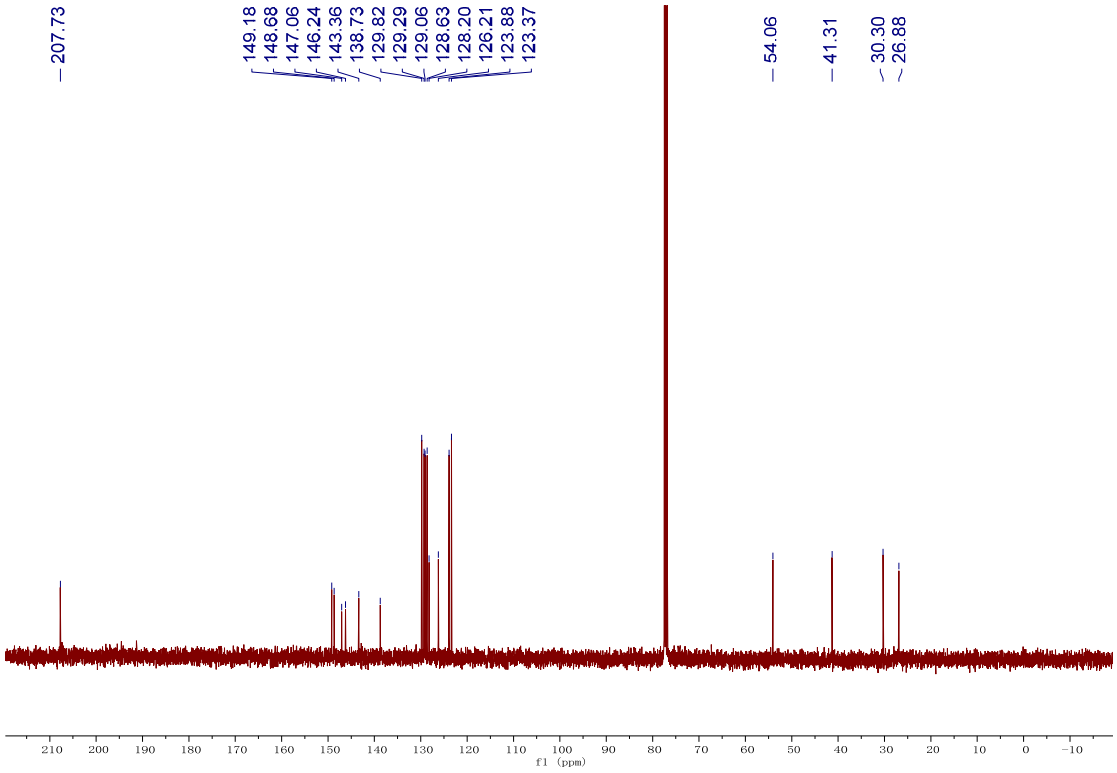
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3la**



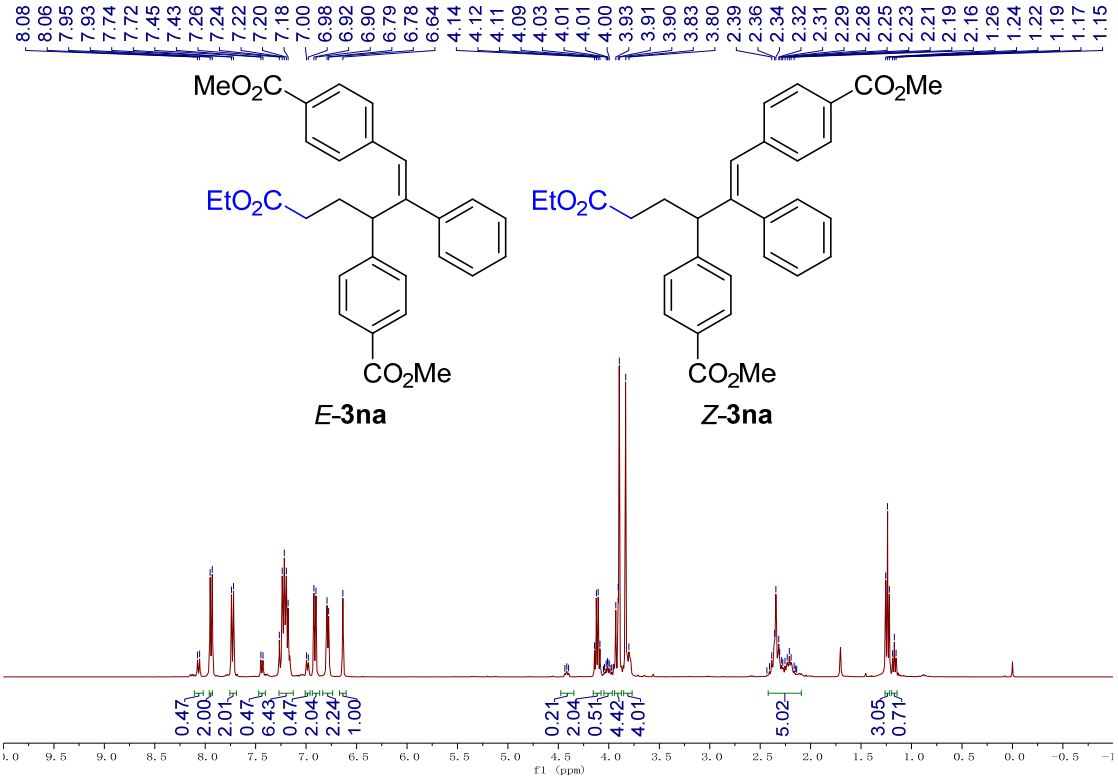
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3la**



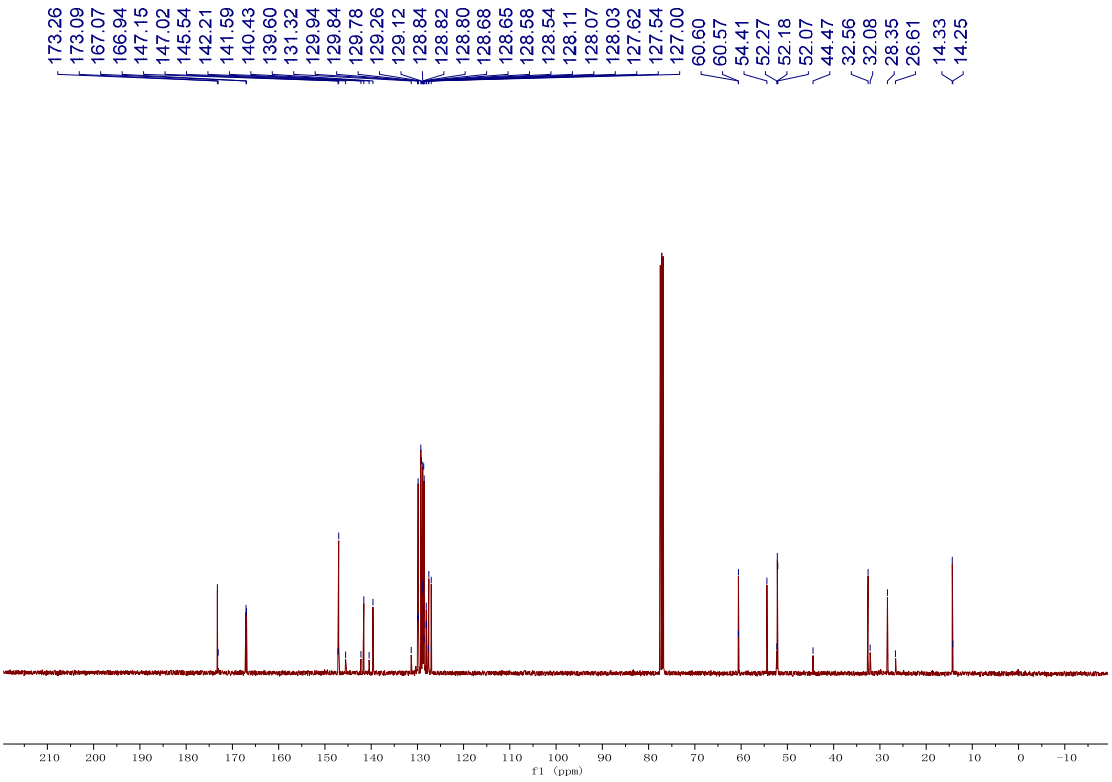
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-**3ml**



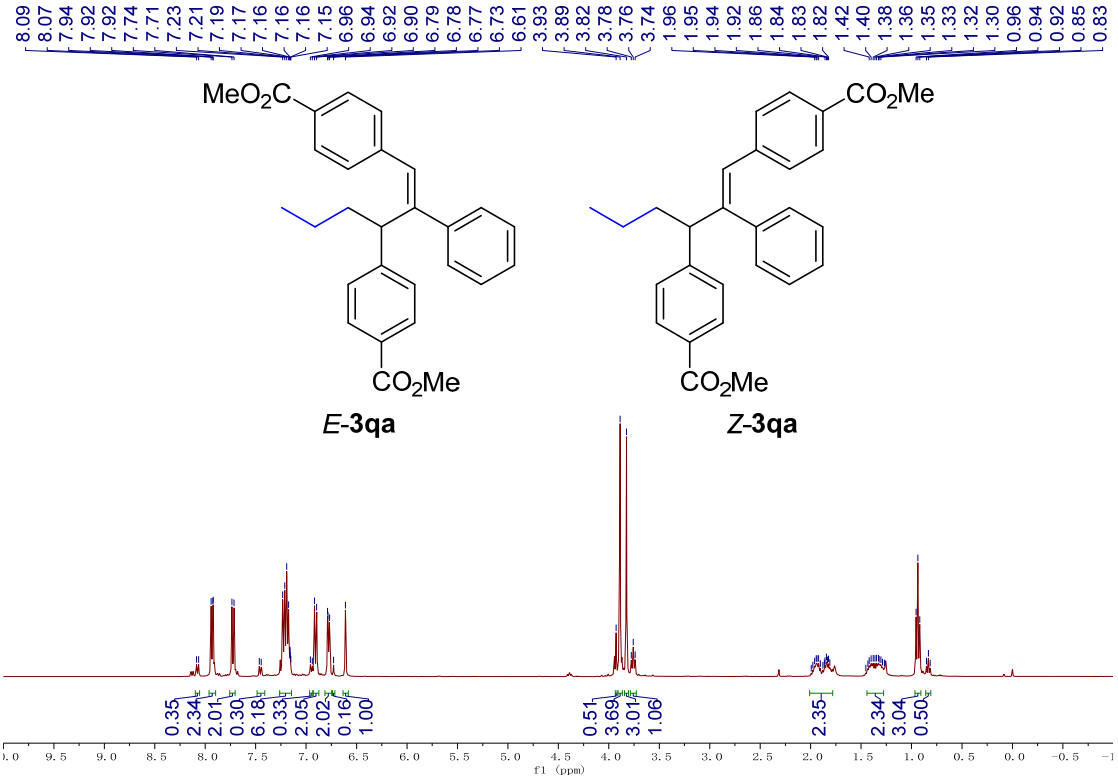
^{13}C NMR (101 MHz, $CDCl_3$) of *Z*-**3ml**



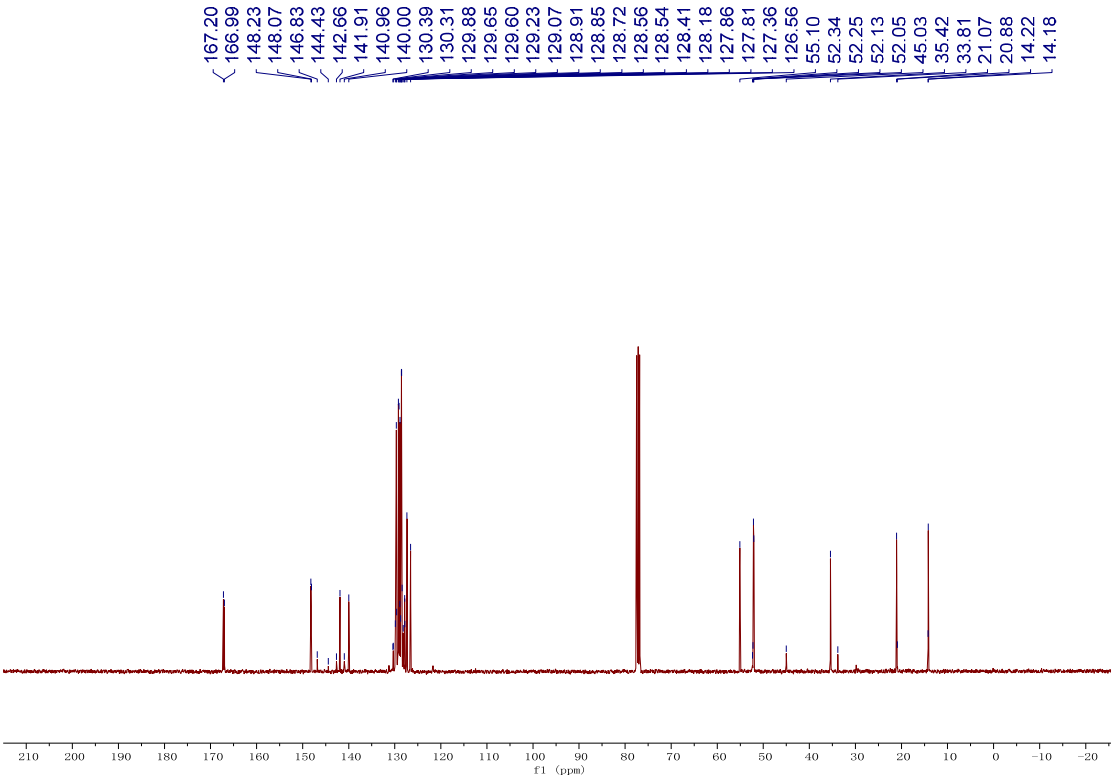
^{1}H NMR (400 MHz, $CDCl_3$) of **3na**



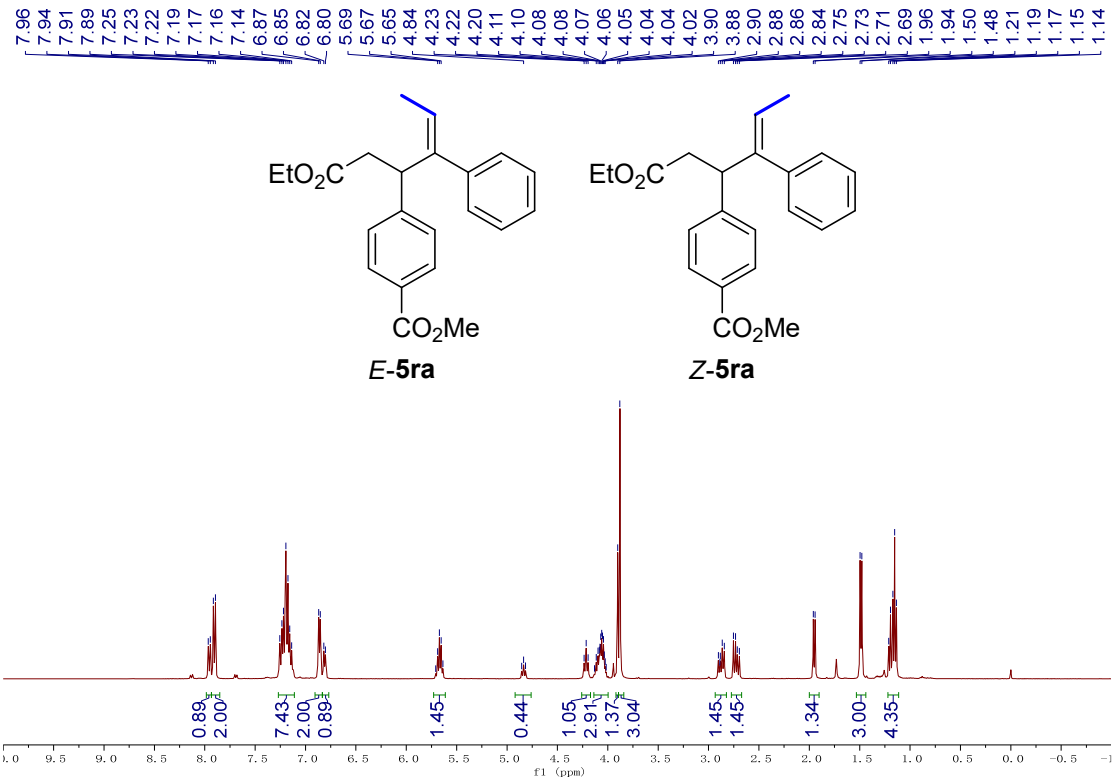
^{13}C NMR (101 MHz, $CDCl_3$) of **3na**



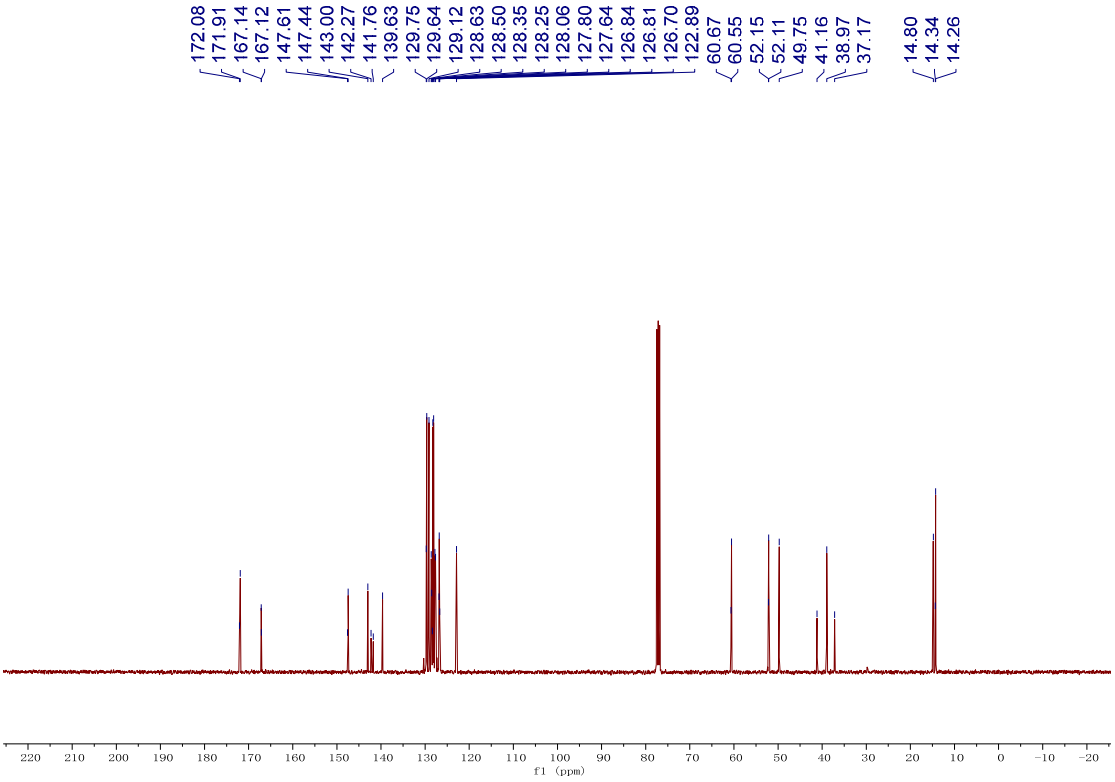
^{1}H NMR (400 MHz, $CDCl_3$) of **3qa**



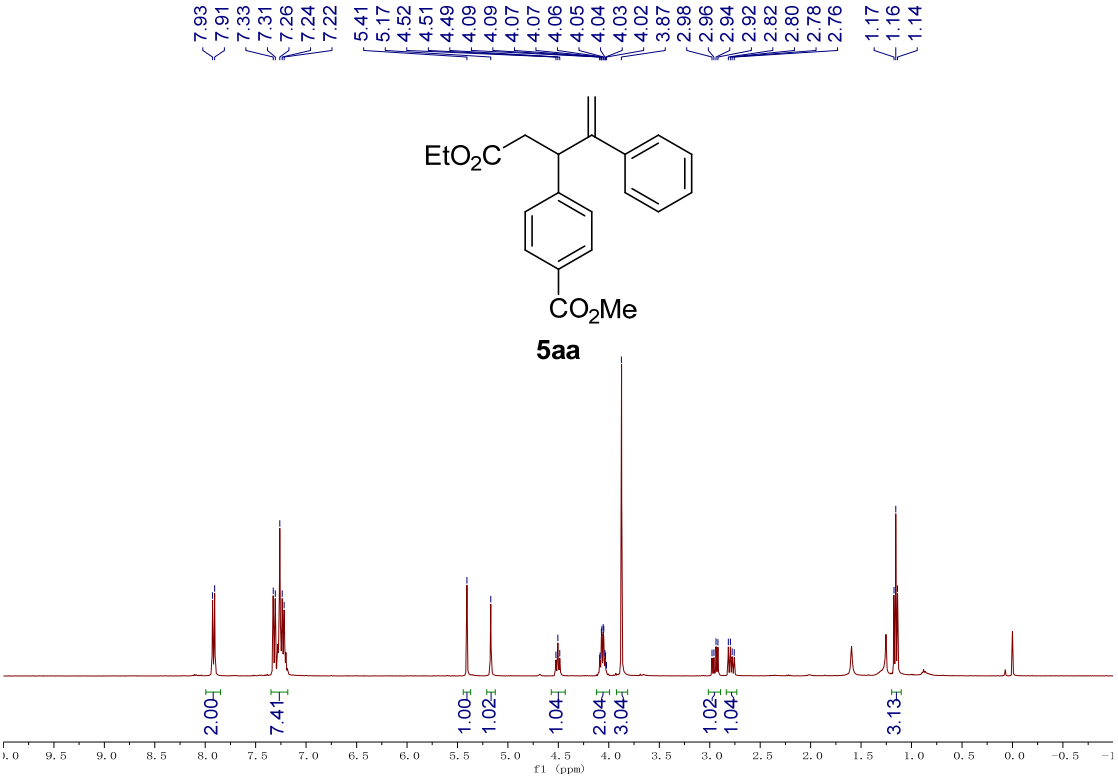
^{13}C NMR (101 MHz, $CDCl_3$) of **3qa**



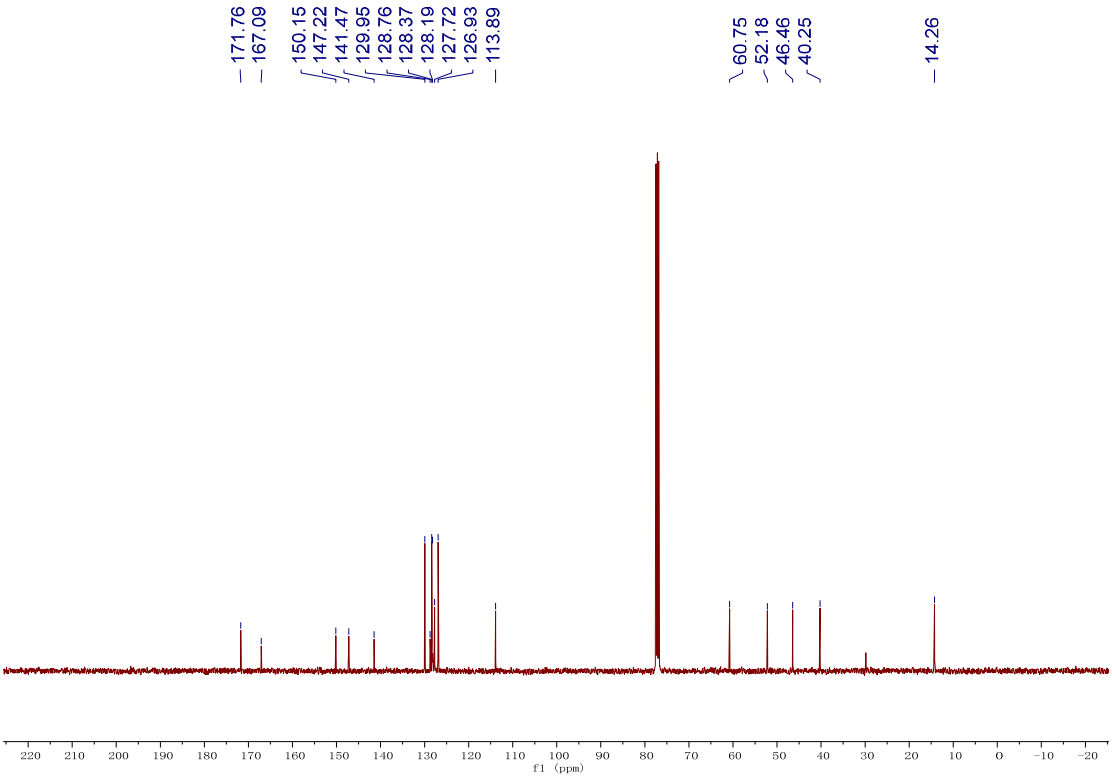
^{1}H NMR (400 MHz, $CDCl_3$) of **5ra**



^{13}C NMR (101 MHz, $CDCl_3$) of **5ra**



^{1}H NMR (400 MHz, $CDCl_3$) of **5aa**



^{13}C NMR (101 MHz, $CDCl_3$) of **5aa**

10. Supplementary References

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