

Supporting Information

Phosphine-Catalyzed Regiodivergent Annulations of γ -Substituted Allenates with Conjugated Dienes

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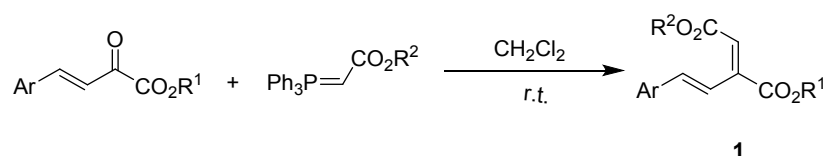
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1. General Experimental Details

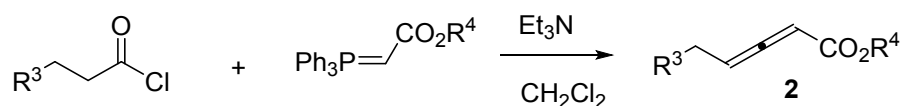
All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-ToF HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4 °C/min, the thermometer was not corrected. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification.

2. General procedure for synthesis of diene



The general procedure was followed at r.t. with β , γ -unsaturated α -keto esters¹ (5 mmol, 1.0 equiv) and ylide (5 mmol, 1.0 equiv) in 50 mL of DCM. When completed, the resulting mixture was carefully evaporated to remove most of the solvent, and the residue was extracted by petroleum ether (b.p. 30 - 60 °C, 4 \times 30 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 20% EtOAc in petroleum ether) to provide the diene **1** as yellow oil.

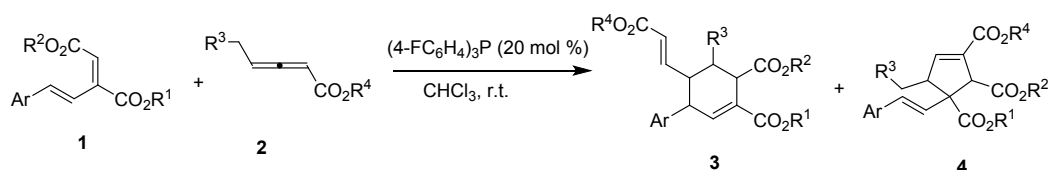
3. General procedure for synthesis of γ -substituted allenates.



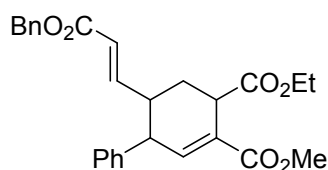
Allenate **2** is a known compound and synthesized according to a similar method developed by Hansen. To a solution of yield (0.1 mol) in dichloromethane (400 mL) was added 1.1 equivalent of triethylamine (0.11 mol). After stirred for about 15 minutes, 1.1 equivalent of acyl chloride (0.11 mol) was added dropwise. Then the

reaction mixture was allowed to be warmed up to room temperature and stirred overnight. The resulting mixture was carefully evaporated to remove most of the solvent, and the residue was extracted by petroleum ether (b.p. 30 - 60 °C, 5 × 100 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 5% EtOAc in petroleum ether) to provide the allenolate **2** as yellow oil.²

4. General procedure for synthesis of **3**.



To a dry flask filled with nitrogen were added **1** (0.3 mmol) and **2** (0.45 mmol) in 3 mL CHCl₃. (4-FC₆H₄)₃P (0.06 mmol) was added. This solution was stirred at r.t. until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh) column (eluant: 20% EtOAc in petroleum ether) to afford **3**.

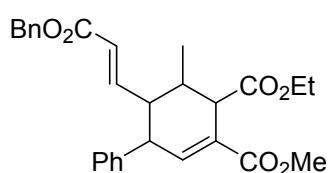


4-Ethyl 3-methyl (*E*)-6-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate **3a**.

The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenolate (84.7 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3a** (107.6 mg, 80% yield) and [3 + 2] adduct (2.7 mg, 2% yield).

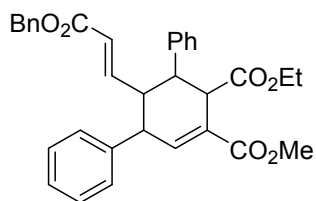
White solid. **MP**: 123 - 124 °C. ¹H NMR (300 MHz, CDCl₃) δ 1.27 (t, *J* = 7.1 Hz, 3H, CH₃), 1.84 (dd, *J* = 24.4, 11.7 Hz, 1H, CH), 2.29 – 2.57 (m, 2H, CH₂), 3.39 – 3.44 (m, 1H, CH), 3.60 – 3.66 (m, 1H, CH), 3.74 (s, 3H, COOCH₃), 4.13 – 4.23 (m, 2H, COOCH₂), 5.12 (s, 2H, COOCH₂Ph), 5.68 (d, *J* = 15.8 Hz, 1H, HC=C), 6.86 (dd,

$J = 15.8, 7.9$ Hz, 1H, C=CH), 7.02 (t, $J = 2.1$ Hz, 1H, HC=C), 7.02 – 7.10 (m, 2H, ArH), 7.26 – 7.36 (m, 8H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 14.2 (s, CH_3), 31.8 (s, CH_2), 42.0 (s, CH), 43.5 (s, CH), 47.8 (s, CH), 51.9 (s, COOCH_3), 61.0 (s, COOCH_2), 66.2 (s, COOCH_2Ph), 122.0 (s, CH), 127.4 (s, CH), 128.1 (s, 2CH), 128.2 (s, 2CH), 128.2 (s, CH), 128.5 (s, 2CH), 128.5 (s, C), 128.8 (s, 2CH), 135.9 (s, C), 141.2 (s, C), 143.0 (s, CH), 149.5 (s, CH), 165.8 (s, C), 166.7 (s, C), 173.8 (s, C) ppm. IR (KBr): 2029, 1727, 1370, 1270, 1114, 1032, 733, 700, 524 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{27}\text{H}_{29}\text{O}_6$ $[\text{M}+\text{H}]^+$: 449.1959, found: 449.1957.



4-Ethyl 3-methyl (E)-6-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-5-methyl-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3b.

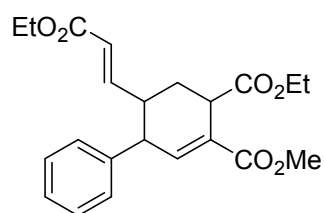
The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenolate (63.1 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3b** (102.1 mg, 85% yield) and [3 + 2] adduct (6.9 mg, 5% yield). Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.04 (d, $J = 6.4$ Hz, 3H, CH_3), 1.29 (t, $J = 7.1$ Hz, 3H, CH_3), 2.01 – 2.20 (m, 2H, 2CH), 3.15 – 3.20 (m, 1H, CH), 3.44 – 3.49 (m, 1H, CH), 3.72 (s, 3H, COOCH_3), 4.16 – 4.30 (m, 2H, COOCH_2), 5.05 – 5.14 (m, 2H, COOCH_2Ph), 5.41 (d, $J = 15.6$ Hz, 1H, HC=C), 6.70 (dd, $J = 15.6, 9.8$ Hz, 1H, HC=C), 7.00 – 7.03 (m, 2H, HC=C; ArH), 7.07 (t, $J = 2.1$ Hz, 1H, ArH), 7.21–7.25 (m, 1H, ArH), 7.27–7.33 (m, 5H, ArH), 7.36 – 7.53 (m, 2H, ArH). ^{13}C NMR (75 MHz, CDCl_3) δ 14.2 (s, CH_3), 18.4 (s, CH_3), 36.5 (s, CH), 48.1 (s, CH), 49.8 (s, CH), 51.5 (s, CH), 51.9 (s, COOCH_3), 61.0 (s, COOCH_2), 66.1 (s, COOCH_2Ph), 123.9 (s, CH), 127.2 (s, CH), 128.0 (s, 2CH), 128.2 (s, CH), 128.3 (s, 2CH), 128.5 (s, 2CH), 128.6 (s, C), 128.7 (s, 2CH), 135.9 (s, C), 141.3 (s, C), 143.1 (s, CH), 148.9 (s, CH), 165.5 (s, C), 166.5 (s, C), 173.9 (s, C). IR (KBr): 2980, 1715, 1388, 1257, 1116, 1033, 751, 705, 523 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6$ $[\text{M}+\text{H}]^+$: 463.2115., found: 463.2116.



4'-Ethyl 5'-methyl (*E*)-2'-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-1', 2', 3', 4'-tetrahydro-[1, 1': 3', 1''-terphenyl]-4', 5'-dicarboxylate **3c.**

The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenolate (118.9 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3c** (121.2 mg, 77% yield) and [3 + 2] adduct (7.9 mg, 5% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 0.90 (t, *J* = 7.1 Hz, 3H, CH₃), 2.79 (dd, *J* = 21.2, 10.1 Hz, 1H, CH), 3.18 (t, *J* = 11.2 Hz, 1H, CH), 3.63 – 3.68 (m, 1H, CH), 3.74 – 3.79 (m, 4H, COOCH₃; CH), 3.89 – 3.96 (m, 2H, COOCH₂), 4.93 – 5.02 (m, 2H, COOCH₂Ph), 5.13 (d, *J* = 15.6 Hz, 1H, HC=C), 6.54 (dd, *J* = 15.6, 9.7 Hz, 1H, C=CH), 7.04 – 7.10 (m, 1H, CH=C), 7.12 – 7.18 (m, 6H, ArH), 7.21 – 7.23 (m, 1H, ArH), δ 7.25 – 7.33 (m, 8H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 13.8 (s, CH₃), 48.9 (s, CH), 49.8 (s, CH), 50.0 (s, CH), 50.1 (s, CH), 52. (s, COOCH₃), 60.6 (s, COOCH₂), 65.7 (s, COOCH₂Ph), 123.7 (s, CH), 127.3 (s, CH), 127.4 (s, CH), 127.5 (s, 2CH), 128.0 (s, CH), 128.0 (s, 2CH), 128.4 (s, 2CH), 128.4 (s, 2CH), 128.7 (s, 2CH), 128.8 (s, 2CH), 129.0 (s, C), 136.0 (s, C), 139.7 (s, C), 140.9 (s, C), 143.3 (s, CH), 147.9 (s, CH), 165.2 (s, C), 166.3 (s, C), 173.4 (s, C) ppm. IR (KBr): 2982, 1732, 1334, 1219, 1080, 1017, 759, 702, 528 cm⁻¹. HRMS (ESI, *m/z*): Calcd for C₃₃H₃₃O₆ [M+H]⁺: 525.2272, found: 525.2275.

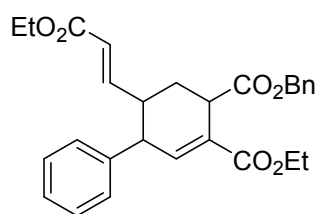


4-Ethyl 3-methyl (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate **3d.**

The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3d** (92.7 mg, 80% yield) and [3 + 2] adduct (9.2 mg, 8% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.21 – 1.28 (m, 6H, 2CH₃), 1.81 – 1.89

(m, 1H, CH), 2.26 – 2.55 (m, 2H, CH₂), 3.38 – 3.43 (m, 1H, CH), 3.60 – 3.64 (m, 1H, CH), 3.72 (s, 3H, COOCH₃), 4.07 – 4.13 (m, 2H, COOCH₂), 4.16 – 4.19 (m, 2H, COOCH₂), 5.61 (d, *J* = 15.2 Hz, 1H, HC=C), 6.78 (dd, *J* = 15.7, 7.9 Hz, 1H, C=CH), 6.99 (t, *J* = 2.1 Hz, 1H, HC=C), 7.06 – 7.08 (m, 2H, ArH), 7.23 – 7.27 (m, 2H, ArH), 7.29 – 7.32 (m, 1H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, 2CH₃), 31.8 (s, CH₂), 42.0 (s, CH), 43.4 (s, CH), 47.7 (s, CH), 51.8 (s, COOCH₃), 60.3 (s, COOCH₂), 61.0 (s, COOCH₂), 122.3 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.8 (s, C), 128.8 (s, 2CH), 141.2 (s, C), 143.0 (s, CH), 148.8 (s, CH), 166.0 (s, C), 166.7 (s, C), 173.8 (s, C) ppm. IR (KBr): 2982, 1727, 1697, 1280, 1119, 1041, 745, 700, 529 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₂H₂₇O₆ [M+H]⁺: 387.1802, found: 387.1804.

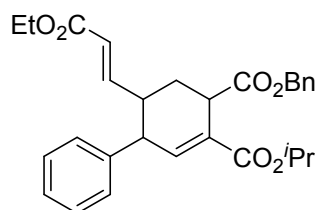


4-Benzyl 3-ethyl (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3e.

The reaction of diene (100.9 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3e** (117.9 mg, 85% yield) and [3 + 2] adduct (4.2 mg, 3% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.17 – 1.26 (m, 6H, 2CH₃), 1.85 (dd, *J* = 24.4, 11.9 Hz, 1H, CH₂), 2.28 – 2.55 (m, 2H, CH₂, CH), 3.39 – 3.44 (m, 1H, CH), 3.67 – 3.74 (m, 1H, CH), 4.09 – 4.16 (m, 4H, 2COOCH₂), 5.17 (dd, *J* = 34.1, 12.3 Hz, 2H, COOCH₂), 5.60 (d, *J* = 15.7 Hz, 1H, HC=C), 6.79 (dd, *J* = 15.7, 8.0 Hz, 1H, C=CH), 7.02 (t, *J* = 2.1 Hz, 1H, HC=C), 7.02 – 7.10 (m, 2H, ArH), 7.25 – 7.27 (m, 1H, ArH), 7.28 – 7.30 (m, 2H, ArH), 7.35 – 7.39 (m, 5H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 14.2 (s, CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.5 (s, CH), 47.8 (s, CH), 60.4 (s, CH₂, COOCH₂), 60.9 (s, CH₂, COOCH₂), 66.8 (s, COOCH₂), 122.3 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.3 (s, 2CH), 128.3 (s, CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 128.9 (s, C), 135.7 (s, C), 141.2 (s, C), 142.9 (s, CH), 148.7 (s, CH), 166.1 (s, C), 166.3 (s, C), 173.7 (s, C) ppm. IR (KBr): 2982, 1728, 1370, 1262,

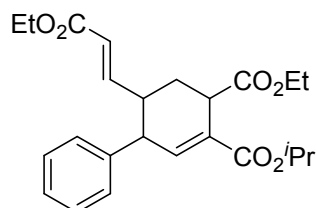
1113, 1035, 753, 703, 523 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6$ $[\text{M}+\text{H}]^+$: 463.2115, found: 463.2117.



4-Benzyl 3-isopropyl (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate **3f.**

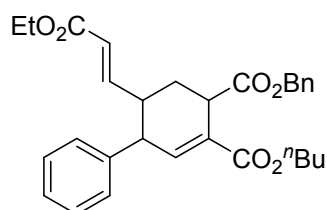
The reaction of diene (105.1 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3f** (110.1 mg, 77% yield) and [3 + 2] adduct (4.3 mg, 3% yield).

Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.18 – 1.24 (m, 9H, 3 CH_3), 1.85 (dd, J = 24.1, 11.9 Hz, 1H, CH), 2.29 – 2.34 (m, 1H, CH), 2.51 (dd, J = 19.0, 9.6 Hz, 1H, CH), 3.41 (d, J = 9.7 Hz, 1H, CH), 3.70 – 3.73 (m, 1H, CH), 4.13 (dd, J = 14.0, 6.9 Hz, 2H, CO_2CH_2), 5.00 – 5.10 (m, 1H, CH), 5.16 (dd, J = 25.8, 12.3 Hz, 2H, $\text{CO}_2\text{CH}_2\text{Ph}$), 5.60 (d, J = 15.7 Hz, 1H, $\text{HC}=\text{C}$), 6.79 (dd, J = 15.7, 7.9 Hz, 1H, $\text{C}=\text{CH}$), 7.00 – 7.04 (m, 1H, $\text{HC}=\text{C}$), 7.08 – 7.11 (m, 2H, ArH), 7.27 – 7.37 (m, 8H, ArH) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 14.2 (s, CH_3), 21.7 (s, CH_3), 21.8 (s, CH_3), 31.9 (s, CH_2), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 60.4 (s, COOCH_2), 66.8 (s, COOCH_2Ar), 68.5 (s, COOCH), 122.3 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 129.2 (s, C), 135.7 (s, C), 141.3 (s, C), 142.5 (s, CH), 148.8 (s, CH), 165.8 (s, C), 166.1 (s, C), 173.7 (s, C) ppm. **IR (KBr)**: 3029, 1727, 1371, 1261, 1110, 1034, 752, 704, 526 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{29}\text{H}_{33}\text{O}_6$ $[\text{M}+\text{H}]^+$: 477.2272, found: 477.2274.



4-Ethyl 3-isopropyl (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate **3g.**

The reaction of diene (86.5 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3g** (104.5 mg, 84% yield) and [3 + 2] adduct (10.0 mg, 8% yield). Colorless oil. **¹H NMR (300 MHz, CDCl₃)** δ 1.22 – 1.31 (m, 12H, 4CH₃), 1.83 (dd, J = 24.1, 12.0 Hz, 1H, CH), 2.28 – 2.56 (m, 2H, CH₂, CH), 3.40 – 3.43 (m, 1H, CH), 3.62 – 3.65 (m, 1H, CH), 4.09 – 4.21 (m, 4H, 2COOCH₂), 5.03 – 5.11 (m, 1H, COOCH), 5.62 (d, J = 15.8 Hz, 1H, HC=C), 6.80 (dd, J = 15.7, 7.8 Hz, 1H, C=CH), 6.93 – 6.98 (m, 1H, HC=C), 7.09 – 7.11 (m, 2H, ArH), 7.28 – 7.35 (m, 3H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 14.1 (s, CH₃), 14.2 (s, CH₃), 21.7 (s, CH₃), 21.8 (s, CH₃), 32.0 (s, CH₂), 42.1 (s, CH), 43.2 (s, CH), 47.8 (s, CH), 60.3 (s, COOCH₂), 61.0 (s, COOCH₂), 68.4 (s, COOCH), 122.2 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.8 (s, 2CH), 129.4 (s, C), 141.4 (s, C), 142.3 (s, CH), 148.9 (s, CH), 165.8 (s, C), 166.1 (s, C), 173.9 (s, C) ppm. **IR (KBr):** 3007, 1732, 1371, 1255, 1117, 1033, 750, 705, 526 cm⁻¹. **HRMS (ESI, m/z):** Calcd for C₂₄H₃₁O₆ [M+H]⁺: 415.2115, found: 415.2117.

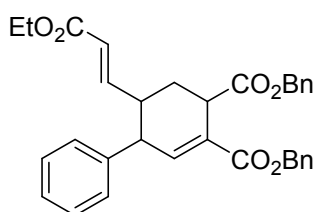


4-Benzyl 3-butyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate **3h.**

The reaction of diene (109.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3h** (116.3 mg, 79% yield) and [3 + 2] (5.8 mg, 2% yield).

White solid. **MP:** 74 - 75 °C. **¹H NMR (300 MHz, CDCl₃)** δ 0.90 (t, J = 7.4 Hz, 3H, CH₃), 1.24 (t, J = 7.1 Hz, 3H, CH₃), 1.30 – 1.37 (m, 2H, CH₂), 1.51 – 1.60 (m, 2H, CH₂), 1.85 (dd, J = 24.3, 11.8 Hz, 1H, CH), 2.28 – 2.35 (m, 1H, CH), 2.45 – 2.55 (m, 1H, CH), 3.39 – 3.44 (m, 1H, CH), 3.67 – 3.75 (m, 1H, CH), 4.02 – 4.16 (m, 4H, 2COOCH₂), 5.16 (dd, J = 36.3, 12.3 Hz, 2H, COOCH₂Ph), 5.60 (d, J = 15.8 Hz, 1H, HC=C), 6.79 (dd, J = 15.7, 8.0 Hz, 1H, C=CH), 7.01 (t, J = 2.1 Hz, 1H, HC=C), 7.07 – 7.10 (m, 2H, ArH), 7.26 – 7.30 (m, 2H, ArH), 7.32 – 7.35 (m, 2H, ArH), 7.36 – 7.38

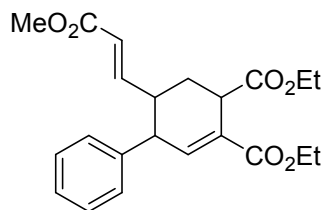
(m, 4H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 13.7 (s, CH_3), 14.2 (s, CH_3), 19.1 (s, CH_2), 30.5 (s, CH_2), 31.9 (s, CH_2), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 60.4 (s, CH_2), 64.8 (s, CH_2), 66.8 (s, CH_2), 122.3 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.3 (s, 2CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 128.9 (s, C), 135.7 (s, C), 141.3 (s, C), 142.8 (s, CH), 148.7 (s, CH), 166.1 (s, C), 166.3 (s, C), 173.7 (s, C) ppm. IR (KBr): 3003, 1728, 1372, 1259, 1117, 1030, 751, 705, 527 cm^{-1} . RMS (ESI, m/z): Calcd for $\text{C}_{30}\text{H}_{35}\text{O}_6$ $[\text{M}+\text{H}]^+$: 491.2428, found: 491.2430.



Dibenzy l (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate **3i.**

The reaction of diene (119.5 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3i** (141.6 mg, 90% yield) and [3 + 2] adduct (3.2 mg, 2% yield).

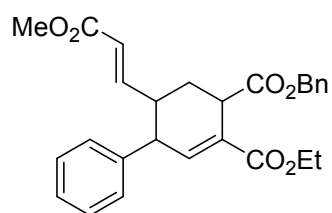
Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.24 (t, $J = 7.1$ Hz, 3H, CH_3), 1.80 – 1.92 (m, 1H, CH), 2.30 – 2.36 (m, 1H, CH), 2.51 (dd, $J = 18.6, 8.8$ Hz, 1H, CH), 3.42 (d, $J = 9.7$ Hz, 1H), 3.72 – 3.76 (m, 1H, CH), 4.13 (dd, $J = 14.0, 6.9$ Hz, 2H, COOCH_2), 4.98 – 5.18 (m, 4H, $2\text{COOCH}_2\text{Ph}$), 5.60 (d, $J = 15.8$ Hz, 1H, $\text{HC}=\text{C}$), 6.79 (dd, $J = 15.7, 8.0$ Hz, 1H, $\text{C}=\text{CH}$), 7.07 – 7.09 (m, 3H, $\text{HC}=\text{C}$, ArH), 7.26 – 7.30 (m, 13H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 14.2 (s, CH_3), 31.9 (s, CH_2), 42.1 (s, CH), 43.5 (s, CH), 47.8 (s, CH), 60.4 (s, COOCH_2), 66.6 (s, COOCH_2), 66.8 (s, COOCH_2), 122.4 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.2 (s, CH), 128.2 (s, CH), 128.3 (s, 2CH), 128.3 (s, 2CH), 128.5 (s, 2CH), 128.5 (s, 2CH), 128.7 (s, C), 128.8 (s, 2CH), 135.7 (s, C), 135.7 (s, C), 141.1 (s, C), 143.5 (s, CH), 148.6 (s, CH), 166.1 (s, C), 166.1 (s, C), 173.6 (s, C) ppm. IR (KBr): 3002, 1715, 1362, 1221, 1165, 1005, 751, 700, 529 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{33}\text{H}_{33}\text{O}_6$ $[\text{M}+\text{H}]^+$: 525.2272, found: 525.2271.



Diethyl (*E*)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1,1'-biphenyl]-3,4-dicarboxylate **3j.**

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3j** (99.7 mg, 86% yield) and [3 + 2] adduct (4.6 mg, 4% yield).

White solid. **MP**: 87 - 88 °C. **¹H NMR (300 MHz, CDCl₃)** δ 1.24 – 1.30 (m, 6H, 2CH₃), 1.84 (q, J = 11.8 Hz, 1H, CH), 2.27 – 2.56 (m, 2H, CH₂), 3.39 – 3.44 (m, 1H, CH), 3.60 – 3.64 (m, 1H, CH), 3.67 (s, 3H, COOCH₃), 4.14 – 4.24 (m, 4H, 2COOCH₂), 5.62 (d, J = 15.8 Hz, 1H, HC=C), 6.81 (dd, J = 15.8, 8.0 Hz, 1H, C=CH), 7.00 (t, J = 2.0 Hz, 1H, HC=C), 7.08 – 7.10 (m, 2H, ArH), 7.26 – 7.35 (m, 3H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 14.1 (s, 2CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.5 (s, COOCH₃), 60.9 (s, COOCH₂), 61.0 (s, COOCH₂), 121.7 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.8 (s, 2CH), 129.1 (s, C), 141.3 (s, C), 142.6 (s, CH), 149.1 (s, CH), 166.3 (s, C), 166.5 (s, C), 173.9 (s, C) ppm. **IR (KBr)**: 3001, 1733, 1335, 1217, 1092, 1037, 779, 704, 528 cm⁻¹. **HRMS (ESI, m/z)**: Calcd for C₂₂H₂₇O₆ [M+H]⁺: 387.1802, found: 387.1801.

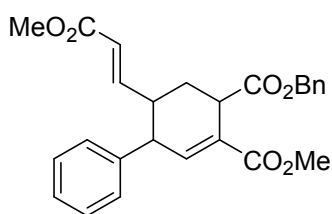


4-Benzyl 3-ethyl (*E*)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1,1'-biphenyl]-3,4-dicarboxylate **3k.**

The reaction of diene (100.9 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3k** (107.6 mg, 80% yield) and [3 + 2] adduct (4.0 mg, 3% yield).

White solid. **MP**: 70 - 71 °C. **¹H NMR (300 MHz, CDCl₃)** δ 1.20 (t, J = 7.1 Hz, 3H, CH₃), 1.85 (q, J = 11.9 Hz, 1H, CH), 2.28 – 2.56 (m, 2H, CH₂), 3.39 – 3.44 (m, 1H,

CH), 3.67 (s, 3H, COOCH₃), 3.70 – 3.75 (m, 1H, CH), 4.21 – 4.06 (m, 2H, CO₂CH₂), 5.17 (q, $J = 34.1, 12.3$ Hz, 2H, CO₂CH₂Ph), 5.60 (d, $J = 16.1$ Hz, 1H, C=CH), 6.80 (dd, $J = 15.7, 8.0$ Hz, 1H, C=CH), 7.02 (t, $J = 2.0$ Hz, 1H, HC=C), 7.10 – 7.06 (m, 2H, ArH), 7.39 – 7.25 (m, 8H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.5 (s, COOCH₃), 60.9 (s, COOCH₂), 66.8 (s, COOCH₂Ph), 121.9 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.3 (s, 2CH), 128.3 (s, CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 128.9 (s, C), 135.8 (s, C), 141.2 (s, C), 142.8 (s, CH), 149.0 (s, CH), 166.2 (s, C), 166.5 (s, C), 173.7 (s, C) ppm. IR (KBr): 2960, 1714, 1699, 1283, 1119, 1038, 760, 700, 530 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₇H₂₉O₆ [M+H]⁺: 449.1959, found: 449.1960.

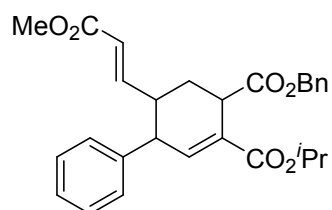


4-Benzyl 3-methyl (*E*)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate **3I.**

The reaction of diene (97.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3I** (93.8 mg, 72% yield) and [3 + 2] adduct (5.2 mg, 4% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.85 (q, $J = 11.9$ Hz, 1H, CH), 2.28 – 2.56 (m, 2H, CH₂), 3.39 – 3.44 (m, 1H, CH), 3.63 (s, 3H, COOCH₃), 3.67 (s, 3H, COOCH₃), 3.70 – 3.73 (m, 1H, CH), 5.18 (q, $J = 12.2$ Hz, 2H, COOCH₂Ph), 5.58 – 5.63 (m, 1H, CH=C), 6.80 (dd, $J = 15.8, 8.0$ Hz, 1H, C=CH), 7.02 (t, $J = 2.1$ Hz, 1H, CH=C), 7.06 – 7.09 (m, 2H, ArH), 7.21 – 7.26 (m, 1H, ArH), 7.28 – 7.34 (m, 3H, ArH), 7.36 – 7.39 (m, 4H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 31.9 (s, CH₂), 42.1 (s, CH), 43.5 (s, CH), 47.8 (s, CH), 51.6 (s, COOCH₃), 51.9 (s, COOCH₃), 66.8 (s, COOCH₂Ph), 122.0 (s, CH), 127.4 (s, CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.4 (s, 2CH), 128.6 (s, 2CH), 128.6 (s, C), 128.8 (s, 2CH), 135.8 (s, C), 141.1 (s, C), 143.2 (s, CH), 149.0 (s, CH), 166.5 (s, C), 166.6 (s, C), 173.6 (s, C) ppm. IR (KBr): 2993, 1715, 1699, 1284, 1109, 1035, 760, 702, 533 cm⁻¹. HRMS (ESI, m/z): Calcd for

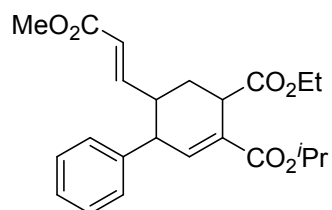
C₂₆H₂₇O₆ [M+H]⁺: 435.1802, found: 435.1804.



4-Benzyl 3-isopropyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3m.

The reaction of diene (105.1 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3m** (110.0 mg, 80% yield) and [3+2] adduct (6.9 mg, 5% yield).

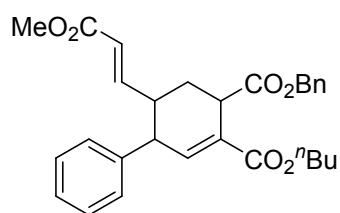
White solid. **MP:** 78 - 79 °C. **¹H NMR (300 MHz, CDCl₃)** δ 1.18 – 1.24 (m, 6H, 2CH₃), 1.77 – 1.91 (m, 1H, CH), 2.28 – 2.35 (m, 1H, CH), 2.47 – 2.56 (m, 1H, CH), 3.39 – 3.43 (m, 1H, CH), 3.66 (s, 3H, COOCH₃), 3.70– 3.74 (m, 1H, CH), 5.00 – 5.08 (m, 1H, COOCH), 5.11 – 5.23 (m, 2H, COOCH₂Ph), 5.52 – 5.66 (m, 1H, CH=C), 6.80 (dd, *J* = 15.7, 8.0 Hz, 1H, C=CH), 6.95 – 7.03 (m, 1H, CH=C), 7.08 – 7.10 (m, 2H, ArH), 7.26 – 7.37 (m, 8H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.7(s, CH₃), 21.8 (s, CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.5 (s, COOCH₃), 66.8 (s, COOCH₂Ph), 68.5 (s, COOCH), 121.9 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.2 (s, 2CH), 128.2 (s, CH), 128.3 (s, CH), 128.6(s, 2CH), 128.8 (s, 2CH), 129.2 (s, C), 135.7 (s, C), 141.3 (s, C), 142.5 (s, CH), 149.1 (s, CH), 165.8 (s, C), 166.5 (s, C), 173.7 (s, C) ppm. **IR (KBr):** 3003, 1715, 1361, 1221, 1165, 1005, 735, 703, 530 cm⁻¹. **HRMS (ESI, m/z):** Calcd for C₂₈H₃₁O₆ [M+H]⁺: 463.2115, found: 463.2116.



4-Ethyl 3-isopropyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3n.

The reaction of diene (86.5 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1)

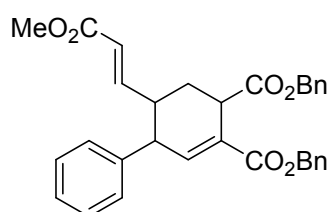
afforded the product **3n** (102.1mg, 85% yield) and [3 + 2] adduct (8.4 mg, 7% yield). White solid. **MP**: 94 - 95 °C. **¹H NMR (300 MHz, CDCl₃)** δ 1.22 – 1.30 (m, 9H, 3CH₃), 1.77 – 1.89 (m, 1H, CH), 2.26 – 2.55 (m, 2H), 3.40 (d, *J* = 9.6 Hz, 1H, CH), 3.57 – 3.61 (m, 1H, CH), 3.66 (s, 3H, COOCH₃), 4.17 (q, *J* = 7.1 Hz, 2H, COOCH₂), 5.02 – 5.10 (m, 1H, COOCH), 5.61 (d, *J* = 15.7 Hz, 1H, CH=C), 6.80 (dd, *J* = 15.7, 8.0 Hz, 1H, C=CH), 6.92 – 7.01 (m, 1H, CH=C), 7.08 – 7.10 (m, 2H, ArH), 7.25 – 7.34 (m, 3H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 14.1 (s, CH₃), 21.7 (s, CH₃), 21.8 (s, CH₃), 32.0 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.5 (s, COOCH₃), 61.0 (s, COOCH₂Ph), 68.4 (s, COOCH), 121.8 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.8 (s, 2CH), 129.4 (s, C), 141.3 (s, C), 142.3 (s, CH), 149.2 (s, CH), 165.8 (s, C), 166.5 (s, C), 173.9 (s, C) ppm. **IR (KBr)**: 2981, 1716, 1372, 1267, 1178, 1002, 752, 702, 530 cm⁻¹. **HRMS (ESI, m/z)**: Calcd for C₂₃H₂₉O₆ [M+H]⁺: 401.1959, found: 401.1960.



4-Benzyl 3-butyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate **3o.**

The reaction of diene (109.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3o** (98.6 mg, 69% yield) and [3 + 2] adduct (11.5 mg, 8% yield). Colorless oil. **¹H NMR (300 MHz, CDCl₃)** δ 0.91 (t, *J* = 7.3 Hz, 3H, CH₃), 1.28 – 1.38 (m, 2H, CH₂), 1.51 – 1.60 (m, 2H, CH₂), 1.85 (q, *J* = 12.0 Hz, 1H, CH), 2.29 – 2.34 (m, 1H, CH), 2.51 (q, *J* = 9.0 Hz, 1H, CH), 3.40 – 3.43 (m, 1H, CH), 3.67 (s, 3H, COOCH₃), 3.70– 3.73 (m, 1H, CH), 3.99 – 4.16 (m, 2H, COOCH₂), 5.17 (q, *J* = 12.3 Hz, 2H, COOCH₂Ph), 5.60 (d, *J* = 15.7 Hz, 1H, CH=C), 6.80 (dd, *J* = 15.7, 8.1 Hz, 1H, C=CH), 7.02 – 7.10 (m, 3H, CH=C, ArH), 7.26 – 7.37 (m, 8H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 13.7 (s, CH₃), 19.1 (s, CH₂), 30.5 (s, CH₂), 31.9 (s, CH), 42.1 (s, CH), 43.7 (s, CH), 47.8 (s, CH), 51.6 (s, COOCH₃), 64.8 (s, COOCH₂), 66.8

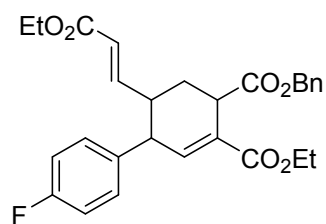
(s, COOCH₂Ph), 121.9 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.3 (s, 2CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 128.9 (s, C), 135.7 (s, C), 141.2 (s, C), 142.8 (s, CH), 149.0 (s, CH), 166.3 (s, C), 166.5 (s, C), 173.7 (s, C) ppm. **IR (KBr)**: 3029, 1727, 1379, 1270, 1163, 1032, 733, 700, 520 cm⁻¹. **HRMS (ESI, m/z)**: Calcd for C₂₉H₃₃O₆ [M+H]⁺: 477.2272, found: 477.2273.



Dibenzyl 6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3p.

The reaction of diene (119.5 mg, 0.3 mmol, 1.0 equiv) and allenolate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3p** (85.7 mg, 56% yield) and [3 + 2] adduct (6.1 mg, 4% yield).

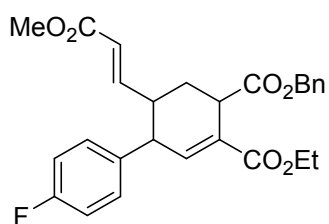
Colorless oil. **¹H NMR (300 MHz, CDCl₃)** δ 1.87 (q, *J* = 12.0 Hz, 1H, CH), 2.29 – 2.56 (m, 2H, CH₂), 3.41 – 3.44 (m, 1H, CH), 3.68 (s, 3H, CH₃), 3.72 – 3.77 (m, 1H, CH), 4.99 – 5.14 (m, 4H, 2COOCH₂), 5.61 (d, *J* = 15.7 Hz, 1H, HC=C), 6.80 (dd, *J* = 15.7, 8.0 Hz, 1H, C=CH), 7.08 – 7.09 (m, 3H, HC=C, ArH), 7.30 – 7.35 (m, 13H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 31.9 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.6 (s, COOCH₃), 66.7 (s, COOCH₂), 66.8 (s, COOCH₂), 122.0 (s, CH), 127.4 (s, CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.3(s, 2CH), 128.3 (s, 2CH), 128.5 (s, 2CH), 128.6 (s, 2CH), 128.7 (s, C), 128.9 (s, 2CH), 135.7(s, C), 135.7 (s, C), 141.1 (s, C), 143.5 (s, CH), 149.0 (s, CH), 166.0 (s, C), 166.5 (s, C), 173.6 (s, C) ppm. **IR (KBr)**: 2982, 1733, 1433, 1269, 1170, 1009, 732, 704, 541 cm⁻¹. **HRMS (ESI, m/z)**: Calcd for C₃₂H₃₀O₆Na [M+Na]⁺: 533.1935, found: 533.1934.



4-Benzyl 3-ethyl 6-(3-ethoxy-3-oxoprop-1-en-1-yl)-4'-fluoro-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3q.

The reaction of diene (106.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3q** (113.8 mg, 79% yield) and [3 + 2] adduct (11.5 mg, 8% yield).

Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.17 – 1.26 (m, 6H, 2 CH_3), 1.76 – 1.90(m, 1H, CH), 2.28 – 2.49(m, 2H, CH_2), 3.38 – 3.43 (m, 1H, CH), 3.66 – 3.74 (m, 1H, CH), 4.05 – 4.18 (m, 4H, 2 COOCH_2), 5.16 (q, $J = 12.3$ Hz, 2H, COOCH_2Ph), 5.59 (d, $J = 15.7$ Hz, 1H, $\text{HC}=\text{C}$), 6.76 (dd, $J = 15.7, 8.1$ Hz, 1H, $\text{C}=\text{CH}$), 6.97 – 7.05 (m, 5H, $\text{HC}=\text{C}$, ArH), 7.33 – 7.38 (m, 5H, ArH) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 14.1 (s, CH_3), 14.2 (s, CH_3), 31.9 (s, CH_2), 42.1 (s, CH), 43.8 (s, CH), 47.0 (s, CH), 60.4 (s, COOCH_2), 61.0 (s, COOCH_2), 66.8 (s, COOCH_2Ph), 115.7 (d, $J = 21.4$ Hz, 2CH), 122.6 (s, CH), 128.3 (s, CH), 128.3 (s, 2CH), 128.6 (s, 2CH), 129.1 (s, C), 129.7 (d, $J = 8.0$ Hz, 2CH), 135.7 (s, C), 137.0 (d, $J = 3.2$ Hz, C), 142.5 (s, CH), 148.4 (s, CH), 161.9 (d, $J = 245.8$ Hz, C), 166.0 (s, C), 166.1 (s, C), 173.6 (s, C) ppm. **IR** (KBr): 2987, 1733, 1433, 1269, 1184, 1003, 735, 708, 541 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{28}\text{H}_{30}\text{FO}_6$ [$\text{M}+\text{H}$] $^+$: 481.2021, found: 481.2022.

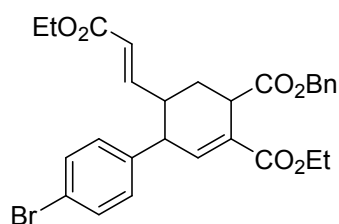


4-Benzyl 3-ethyl 6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3r.

The reaction of diene (106.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3r** (123.2 mg, 88% yield) and [3 + 2] adduct (4.2 mg, 3% yield).

Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.20 (t, $J = 7.1$ Hz, 3H, CH_3), 1.84 (q, $J = 12.0$ Hz, 1H, CH), 2.27 – 2.50 (m, 2H, CH_2), 3.38 – 3.43 (m, 1H, CH), 3.67 (s, 3H, COOCH_3), 3.72 – 3.81 (m, 1H, CH), 4.06 – 4.19 (m, 2H, COOCH_2), 5.16 (q, $J = 12.3$ Hz, 2H, COOCH_2Ph), 5.59 (d, $J = 15.7$ Hz, 1H, $\text{HC}=\text{C}$), 6.76 (dd, $J = 15.7, 8.2$ Hz,

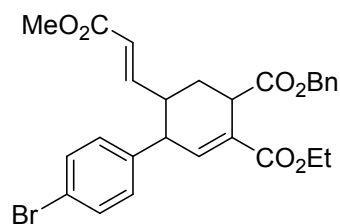
1H, C=CH), 6.97 – 7.07 (m, 5H, HC=C, ArH), 7.32 – 7.37 (m, 5H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.9 (s, CH), 47.0 (s, CH), 51.6 (s, CH₃), 61.0 (s, COOCH₂), 66.8 (s, COOCH₂Ph), 115.7 (d, *J* = 21.4 Hz, 2CH), 122.2 (s, CH), 128.3 (s, 2CH), 128.3 (s, CH), 128.6 (s, 2CH), 129.1 (s, C), 129.7 (d, *J* = 8.0 Hz, 2CH), 135.7 (s, C), 137.0 (d, *J* = 3.2 Hz, C), 142.4 (s, CH), 148.7 (s, CH), 161.9 (d, *J* = 246.0 Hz, C), 166.1 (s, C), 166.4 (s, C), 173.5 (s, C) ppm. IR (KBr): 2951, 1731, 1435, 1270, 1184, 1008, 732, 708, 542 cm⁻¹. HRMS (ESI, *m/z*): Calcd for C₂₇H₂₈FO₆ [M+H]⁺: 467.1864, found: 467.1866.



4-Benzyl 3-ethyl (*E*)-4'-bromo-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3,4-dicarboxylate 3s.

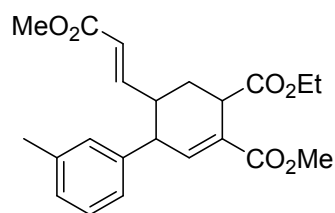
The reaction of diene (124.6 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3s** (123.4 mg, 76% yield) and [3 + 2] adduct (9.2 mg, 6% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.20 – 1.25 (m, 6H, 2CH₃), 1.78 – 1.97 (m, 1H, CH), 2.19 – 2.46 (m, 2H, CH₂), 3.30 – 3.40 (m, 1H, CH), 3.57 – 3.76 (m, 1H, CH), 3.99 – 4.28 (m, 4H, 2COOCH₂), 5.16 (dd, *J* = 33.4, 12.0 Hz, 2H, COOCH₂Ph), 5.52 – 5.71 (m, 1H, HC=C), 6.75 (dd, *J* = 15.2, 7.8 Hz, 1H, C=CH), 6.95 – 7.05 (m, 3H, HC=C, ArH), 7.28 – 7.45 (m, 7H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 14.2 (s, CH₃), 31.9 (s, CH₂), 42.0 (s, CH), 43.6 (s, CH), 47.2 (s, CH), 60.5 (s, COOCH₂), 61.0 (s, COOCH₂Ph), 66.8 (s, COOCH₂Ph), 121.2 (s, C), 122.7 (s, CH), 128.31 (s, 2CH), 128.32 (s, CH), 128.6 (s, 2CH), 129.3 (s, C), 129.9 (s, 2CH), 131.9 (s, 2CH), 135.7 (s, C), 140.3 (s, C), 142.0 (s, CH), 148.2 (s, CH), 166.0 (s, C), 166.1 (s, C), 173.5 (s, C) ppm. IR (KBr): 2980, 1715, 1368, 1267, 1094, 1033, 751, 698, 519 cm⁻¹. HRMS (ESI, *m/z*): Calcd for C₂₈H₃₀BrO₆ [M+H]⁺: 541.1220, found: 541.1218.



4-Benzyl 3-ethyl (*E*)-4'-bromo-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1,1'-biphenyl]-3, 4-dicarboxylate **3t.**

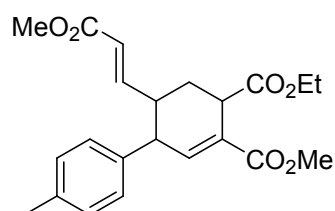
The reaction of diene (124.6 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3t** (120.2 mg, 76% yield) and [3 + 2] adduct (11.0 mg, 7% yield). Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.20 (t, $J = 7.1$ Hz, 6H, 2 CH_3), 1.77 – 1.89 (m, 1H, CH), 2.18 – 2.50 (m, 2H, CH_2), 3.35 – 3.41 (m, 1H, CH), 3.66 – 3.73 (m, 4H, CH, COOCH_3), 4.05 – 4.18 (m, 2H, COOCH_2), 5.16 (q, $J = 12.3$ Hz, 2H, COOCH_2Ph), 5.57– 5.63 (m, 1H, $\text{CH}=\text{C}$), 6.75 (dd, $J = 15.7, 8.2$ Hz, 1H, $\text{C}=\text{CH}$), 6.94 – 6.97 (m, 3H, $\text{CH}=\text{C}$, ArH), 7.33 – 7.39 (m, 5H, ArH), 7.42 – 7.45 (m, 2H, ArH) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 14.1 (s, CH_3), 31.9 (s, CH_2), 42.0 (s, CH), 43.7 (s, CH), 47.2 (s, CH), 51.6 (s, COOCH_3), 61.0 (s, COOCH_2), 66.8 (s, COOCH_2Ph), 121.3 (s, C), 122.3 (s, CH), 128.30 (s, 2CH), 128.33 (s, CH), 128.6 (s, 2CH), 129.4 (s, C), 129.9 (s, 2CH), 132.0 (s, 2CH), 135.7 (s, C), 140.2 (s, C), 141.9 (s, CH), 148.5 (s, CH), 166.1 (s, C), 166.4 (s, C), 173.5 (s, C) ppm. IR (KBr): 2932, 1727, 1384, 1280, 1119, 1041, 745, 697, 533 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{27}\text{H}_{28}\text{BrO}_6$ [$\text{M}+\text{H}$] $^+$: 527.1064, found: 527.1063.



4-Ethyl 3-methyl (*E*)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-3'-methyl-1, 4, 5, 6-tetrahydro-[1,1'-biphenyl]-3, 4-dicarboxylate **3u.**

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3u** (99.7 mg, 86% yield) and [3 + 2] adduct (2.3 mg, 3% yield). Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.25 – 1.29 (m, 3H, CH_3), 1.76 – 1.88

(m, 1H, CH), 2.28 – 2.32 (m, 4H, CH, CH₃), 2.47 – 2.56 (m, 1H, CH), 3.37 (d, $J = 9.7$ Hz, 1H, CH), 3.56 – 3.61 (m, 1H, CH), 3.67 (s, 3H, COOCH₃), 3.73 (s, 3H, COOCH₃), 4.14 – 4.23 (m, 2H, COOCH₂), 5.64 (d, $J = 15.8$ Hz, 1H, CH=C), 6.81 (dd, $J = 15.8, 7.9$ Hz, 1H, C=CH), 6.88 – 6.99 (m, 3H, CH=C, ArH), 7.04 – 7.07 (m, 1H, ArH), 7.16 – 7.21 (m, 1H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.2 (s, CH₃), 21.4 (s, CH₃), 31.9 (s, CH₂), 42.0 (s, CH), 43.3 (s, CH), 47.7 (s, CH), 51.5 (s, COOCH₃), 51.9 (s, COOCH₃), 61.0 (s, COOCH₂), 121.8 (s, CH), 125.3 (s, CH), 128.1 (s, CH), 128.6 (s, C), 128.7 (s, CH), 128.7 (s, CH), 138.5 (s, C), 141.1 (s, C), 143.2 (s, CH), 149.2 (s, CH), 166.5 (s, C), 166.8 (s, C), 173.9 (s, C) ppm. IR (KBr): 2980, 1731, 1435, 1270, 1184, 1036, 732, 708, 542 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₂H₂₇O₆ [M+H]⁺: 387.1802, found: 387.1801.

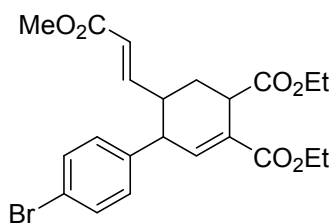


4-Ethyl 3-methyl (*E*)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-4'-methyl-1, 4, 5, 6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate **3v.**

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3v** (90.4 mg, 78% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.27 (t, $J = 7.1$ Hz, 3H, CH₃), 1.82 (q, $J = 12.0$ Hz, 1H, CH), 2.26 – 2.29 (m, 1H, CH), 2.32 (s, 3H, CH₃), 2.45 – 2.54 (m, 1H, CH), 3.36 – 3.39 (m, 1H, CH), 3.60 – 3.64 (m, 1H, CH), 3.67 (s, 3H, COOCH₃), 3.73 (s, 3H, COOCH₃), 4.14 – 4.23 (m, 2H, COOCH₂), 5.63 (d, $J = 15.8$ Hz, 1H, HC=C), 6.80 (dd, $J = 15.8, 7.9$ Hz, 1H, C=CH), 6.95 – 6.99 (m, 3H, CH=C, ArH), 7.10 – 7.13 (m, 2H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.2 (s, CH₃), 21.0 (s, CH₃), 31.9 (s, CH₂), 42.0 (s, CH), 43.4 (s, CH), 47.4 (s, CH), 51.5 (s, COOCH₃), 51.9 (s, COOCH₃), 61.0 (s, COOCH₂), 121.8 (s, CH), 128.0 (s, 2CH), 128.6 (s, C), 129.5 (s, 2CH), 136.9 (s, C), 138.1 (s, C), 143.4 (s, CH), 149.3 (s, CH), 166.5 (s, C), 166.8 (s, C), 173.9 (s, C) ppm. IR (KBr): 2957, 1723, 1434, 1260, 1161, 1032, 732, 705, 541

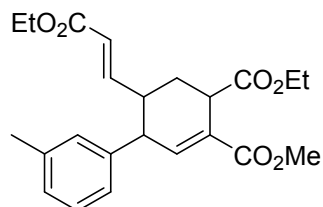
cm⁻¹. **HRMS** (ESI, m/z): Calcd for C₂₂H₂₇O₆ [M+H]⁺: 387.1802, found: 387.1803.



Diethyl (*E*)-4'-bromo-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate **3w.**

The reaction of diene (124.6 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3w** (113.1 mg, 81% yield) and [3 + 2] adduct (12.6 mg, 9% yield).

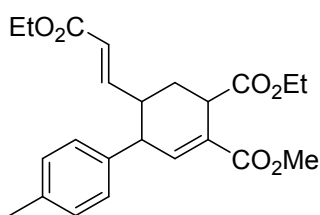
Colorless oil. **¹H NMR (300 MHz, CDCl₃)** δ 1.24 – 1.29 (m, 3H, CH₃), 1.82 (q, *J* = 12.0 Hz, 1H, CH), 2.26 – 2.50 (m, 2H, CH₂), 3.37 – 3.41 (m, 1H, CH), 3.60 – 3.64 (m, 1H, CH), 3.68 (s, 3H, COOCH₃), 4.12 – 4.25 (m, 4H, 2COOCH₂), 5.62 (d, *J* = 15.7 Hz, 1H, HC=C), 6.76 (dd, *J* = 15.7, 8.2 Hz, 1H, C=CH), 6.93 – 6.98 (m, 3H, HC=C, ArH), 7.39 – 7.45 (m, 2H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 14.1 (s, 2CH₃), 31.9 (s, CH₂), 42.0 (s, CH), 43.6 (s, CH), 47.2 (s, CH), 51.6 (s, COOCH₃), 61.0 (s, COOCH₂), 61.1 (s, COOCH₂), 121.2 (s, C), 122.2 (s, CH), 129.5 (s, C), 129.9 (s, 2CH), 132.0 (s, 2CH), 140.3 (s, C), 141.8 (s, CH), 148.6 (s, CH), 166.1 (s, C), 166.4 (s, C), 173.7 (s, C) ppm. **IR (KBr):** ν = 2951, 1731, 1435, 1270, 1184, 1008, 732, 708, 542 cm⁻¹. **HRMS** (ESI, m/z): Calcd for C₂₂H₂₆BrO₆ [M+H]⁺: 465.0907, found: 465.0906.



4-Ethyl 3-methyl (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-3'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate **3x.**

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3x** (87.7 mg, 73% yield) and [3 + 2] adduct (15.6 mg, 13% yield).

Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.24 – 1.27 (m, 6H, 2 CH_3), 1.77 – 1.89 (m, 1H, CH), 2.24 – 2.29 (m, 1H, CH), 2.33(s, 3H, CH_3), 2.51 (dd, $J = 18.5, 8.9$ Hz, 1H, CH), 3.36 – 3.39 (m, 1H, CH), 3.61 – 3.65 (m, 1H, CH), 3.74 (s, 3H, COOCH_3), 4.09 – 4.21 (m, 4H, COOCH_2), 5.63 (d, $J = 15.7$ Hz, 1H, $\text{HC}=\text{C}$), 6.80 (dd, $J = 15.8, 7.7$ Hz, 1H, $\text{C}=\text{CH}$), 6.88 – 6.94 (m, 2H, $\text{HC}=\text{C}$; ArH), 6.96 – 6.99 (m, 1H, ArH), 7.05 – 7.07 (m, 1H, ArH), 7.17 – 7.22 (m, 1H, ArH) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 14.2 (s, 2 CH_3), 21.4 (s, CH_3), 31.8 (s, CH_2), 42.0 (s, CH), 43.2 (s, CH), 47.7 (s, CH), 51.9 (s, COOCH_3), 60.3 (s, COOCH_2), 61.0 (s, COOCH_2), 122.2 (s, CH), 125.3 (s, CH), 128.1 (s, CH), 128.6 (s, C), 128.7 (s, CH), 128.8 (s, CH), 138.5 (s, C), 141.1 (s, C), 143.3 (s, CH), 148.9 (s, CH), 166.2 (s, C), 166.8 (s, C), 173.9 (s, C) ppm. **IR (KBr)**: 2982, 1727, 1435, 1269, 1163, 1036, 734, 698, 554 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{23}\text{H}_{29}\text{O}_6$ $[\text{M}+\text{H}]^+$: 401.1959, found: 401.1960.



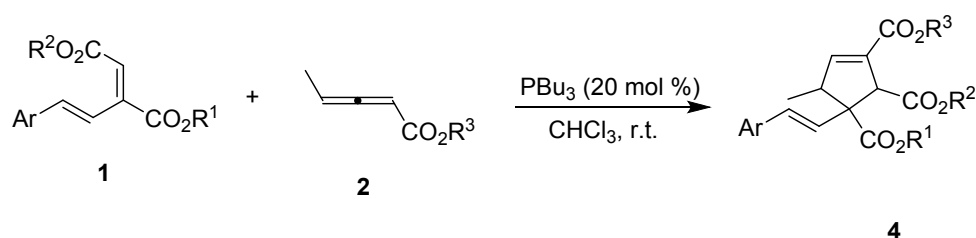
4-Ethyl 3-methyl (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-4'-methyl-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate **3y.**

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **3y** (105.7 mg, 88% yield) and [3 + 2] adduct (6.0 mg, 5% yield).

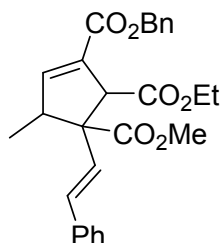
Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.26 (dd, $J = 15.3, 7.6$ Hz, 6H, 2 CH_3), 1.83 (dd, $J = 24.1, 12.0$ Hz, 1H, CH), 2.27 – 2.29 (m, 1H, CH), 2.33 (s, 3H, CH_3), 2.49 (dd, $J = 18.7, 8.9$ Hz, 1H, CH), 3.38 (d, $J = 9.7$ Hz, 1H, CH), 3.61 – 3.64 (m, 1H, CH), 3.74 (s, 3H, COOCH_3), 4.10 – 4.21 (m, 4H, 2 COOCH_2), 5.64 (d, $J = 15.8$ Hz, 1H, $\text{HC}=\text{C}$), 6.80 (dd, $J = 15.7, 7.8$ Hz, 1H, $\text{C}=\text{CH}$), 6.90 – 6.96 (m, 1H, $\text{HC}=\text{C}$), 6.99 – 7.04 (m, 2H, ArH), 7.11 – 7.13 (m, 2H, ArH) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 14.2 (s, CH_3), 14.2 (s, CH_3), 21.1 (s, CH_3), 31.9 (s, CH_2), 42.0 (s, CH), 43.4 (s, CH), 47.4 (s, CH), 51.9 (s, COOCH_3), 60.3 (s, COOCH_2), 61.0 (s, COOCH_2), 122.2 (s, CH), 128.0 (s, 2CH), 128.6 (s, C), 129.5 (s, 2CH), 136.9 (s, C), 138.2 (s, C),

143.4 (s, CH), 149.0 (s, CH), 166.1 (s, C), 166.8 (s, C), 173.9 (s, C) ppm. **IR (KBr)**: 2989, 1716, 1435, 1257, 1092, 1037, 735, 692, 551 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{23}\text{H}_{29}\text{O}_6$ $[\text{M}+\text{H}]^+$: 401.1959, found: 401.1961.

5. General procedure for synthesis of 4.



To a dry flask filled with nitrogen were added **1** (0.3 mmol) and **2** (0.45 mmol) in 3 mL CHCl_3 . PBU_3 (0.06 mmol) was added. This solution was stirred at r.t. until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh) column (eluant: 20% EtOAc in petroleum ether) to afford **4**.

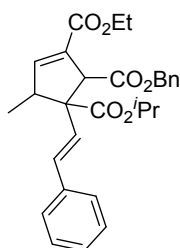


3-Benzyl 2-ethyl 1-methyl (*E*)-5-methyl-1-styrylcyclopent-3-ene- 1, 2, 3-tricarboxylate **4a**.

The reaction of diene (78.1 mg, 0.3 mmol, 1.0 equiv) and allenoate (84.7 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4a** (117.0 mg, 87% yield).

Colorless oil. **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 0.99 (t, $J = 7.1$ Hz, 3H, CH_3), 1.13 (d, $J = 7.3$ Hz, 3H, CH_3), 3.52 – 3.54 (m, 1H, CH), 3.75 (s, 3H, COOCH_3), 3.86 – 3.94 (m, 2H, COOCH_2), 4.57 (s, 1H, CH), 5.19 (q, $J = 12.5$ Hz, 2H, COOCH_2Ph), 6.40 (q, $J = 16.4$ Hz, 2H, $\text{CH}=\text{CH}$), 6.82 (s, 1H, $\text{CH}=\text{C}$), 7.19 – 7.25 (m, 2H, ArH), 7.25 – 7.34 (m, 8H, ArH) ppm. **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 13.1 (s, CH_3), 14.0 (s, CH_3), 46.6 (s, CH), 51.3 (s, COOCH_3), 56.8 (s, CH), 59.9 (s, COOCH_2), 60.8 (s, C), 65.4 (s,

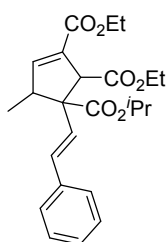
COOCH₂Ph), 125.5 (s, 2CH), 126.4 (s, CH), 126.9 (s, CH), 127.1 (s, 2CH), 127.2 (s, CH), 127.5 (s, 2CH), 127.6 (s, 2CH), 129.7 (s, CH), 131.9 (s, C), 134.8 (s, C), 135.6 (s, C), 147.1 (s, CH), 162.8 (s, C), 169.4 (s, C), 171.9 (s, C) ppm. **IR (KBr)**: 2981, 1733, 1455, 1258, 1119, 1024, 733, 698, 550 cm⁻¹. **HRMS** (ESI, m/z): Calcd for C₂₇H₂₉O₆ [M+H]⁺: 449.1959, found : 449.1957.



2-Benzyl 3-ethyl 1-isopropyl (E)-5-methyl-1-styrylcyclopent-3-ene-1, 2, 3-tricarboxylate 4b.

The reaction of diene (105.1 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4b** (117.3 mg, 82% yield).

Colorless oil. **¹H NMR (300 MHz, CDCl₃)** δ 1.22 – 1.28 (m, 12H, 4CH₃), 3.49 – 3.56 (m, 1H, CH), 4.13 – 4.20 (m, 2H, COOCH₂), 4.65 (s, 1H, CH), 4.99 – 5.05 (m, 2H, COOCH₂Ph), 5.09 – 5.16 (m, 1H, COOCH), 6.23 – 6.38 (m, 2H, CH=CH), 6.79 (s, 1H, CH=C), 7.17 – 7.23 (m, 5H, ArH), 7.26 – 7.35 (m, 5H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 14.1 (s, CH₃), 15.2 (s, CH₃), 21.6 (s, 2CH₃), 47.9 (s, CH), 57.3 (s, CH), 60.7 (s, COOCH₂), 61.6 (s, C), 66.7 (s, COOCH₂Ph), 69.3 (s, COOCH), 125.6 (s, CH), 126.4 (s, 2CH), 127.8 (s, CH), 128.0 (s, CH), 128.3 (s, 2CH), 128.4 (s, 2CH), 128.6 (s, 2CH), 131.8 (s, CH), 132.6 (s, C), 135.7 (s, C), 136.6 (s, C), 148.1 (s, CH), 164.0 (s, C), 171.0 (s, C), 173.0 (s, C) ppm. **IR (KBr)**: 2982, 1723, 1453, 1256, 1116, 1030, 734, 682, 551 cm⁻¹. **HRMS** (ESI, m/z): Calcd for C₂₉H₃₃O₆ [M+H]⁺: 477.2272, found: 477.2276.

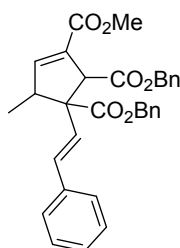


2, 3-Diethyl 1-isopropyl (E)-5-methyl-1-styrylcyclopent-3-ene-1, 2, 3-

tricarboxylate **4c**.

The reaction of diene (86.5 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4c** (90.7 mg, 73% yield).

Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.14 (t, $J = 7.1$ Hz, 3H, CH_3), 1.23 – 1.25 (m, 3H, CH_3), 1.29 – 1.34 (m, 9H, 3CH_3), 3.48 – 3.56 (m, 1H, CH), 4.04 – 4.11 (m, 2H, COOCH_2), 4.18 – 4.23 (m, 2H, COOCH_2), 4.58 (s, 1H, CH), 5.12 – 5.21 (m, 1H, COOCH), 6.33 (q, $J = 16.5$ Hz, 2H, $\text{CH}=\text{CH}$), 6.78 (s, 1H, $\text{CH}=\text{C}$), 7.27 – 7.31 (m, 5H, ArH) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 14.2 (s, 2CH_3), 15.2 (s, CH_3), 21.7 (s, 2CH_3), 47.8 (s, CH), 57.3 (s, CH), 60.6 (s, COOCH_2), 60.8 (s, COOCH_2), 61.5 (s, C), 69.2 (s, COOCH), 125.8 (s, CH), 126.3 (s, 2CH), 127.8 (s, CH), 128.6 (s, 2CH), 131.6 (s, CH), 132.7 (s, C), 136.8 (s, C), 147.9 (s, CH), 164.07 (s, C), 171.16 (s, C), 173.07 (s, C) ppm. IR (KBr): 2980, 1723, 1454, 1257, 1116, 1029, 735, 692, 550 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{24}\text{H}_{31}\text{O}_6$ $[\text{M}+\text{H}]^+$: 415.2115, found: 415.2117.

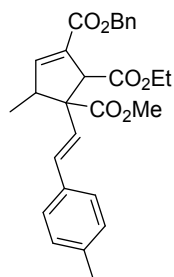


1, 2-Dibenzyl 3-methyl (*E*)-5-methyl-1-styrylcyclopent-3-ene-1, 2, 3-tricarboxylate **4d**.

The reaction of diene (119.5 mg, 0.3 mmol, 1.0 equiv) and allenolate (50.5 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4d** (137.8 mg, 90% yield).

Colorless oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.22 (d, $J = 7.4$ Hz, 3H, CH_3), 3.54 – 3.59 (m, 1H, CH), 3.68 (s, 3H, COOCH_3), 4.69 (t, $J = 1.7$ Hz, 1H, CH), 5.04 (s, 2H, COOCH_2Ph), 5.26 (s, 2H, COOCH_2Ph), 6.19 (q, $J = 16.6$ Hz, 2H, $\text{CH}=\text{CH}$), 6.81 (t, $J = 2.1$ Hz, 1H, $\text{CH}=\text{C}$), 7.09 – 7.12 (m, 2H, ArH), 7.20 – 7.24 (m, 7H, ArH), 7.31–7.35 (m, 6H, ArH) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 15.2 (s, CH_3), 47.9 (s, CH), 51.7 (s, CH), 57.2 (s, COOCH_3), 61.7 (s, C), 66.8 (s, COOCH_2Ph), 67.4 (s, COOCH_2Ph), 125.1 (s, CH), 126.4 (s, 2CH), 127.8 (s, CH), 128.0 (s, CH), 128.35 (s, 2CH), 128.35

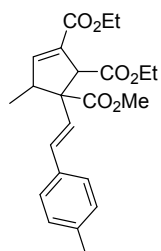
(s, 2CH), 128.37 (s, CH), 128.4 (s, 2CH), 128.5 (s, 2CH), 128.6 (s, 2CH), 132.1 (s, CH), 132.3 (s, C), 135.5 (s, C), 135.6 (s, C), 136.4 (s, C), 148.5 (s, CH), 164.3(s, C), 170.9 (s, C), 173.4 (s, C) ppm. **IR (KBr)**: 2981, 1727, 1454, 1260, 1119, 1041, 745, 696, 550 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{32}\text{H}_{31}\text{O}_6$ $[\text{M}+\text{H}]^+$: 511.2115, found: 511.2116.



3-Benzyl 2-ethyl 1-methyl (*E*)-5-methyl-1-(4-methylstyryl)cyclopent-3-ene-1, 2, 3-tricarboxylate 4e.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (84.7 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4e** (116.5 mg, 84% yield).

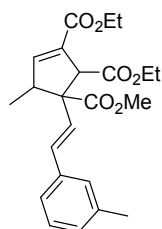
Colorless oil. **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 1.07 (t, $J = 7.1$ Hz, 3H, CH_3), 1.23 – 1.25 (m, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.54 – 3.61 (m, 1H, CH), 3.83 (s, 3H, COOCH_3), 4.00 (q, $J = 7.1$ Hz, 2H, COOCH_2), 4.57 – 4.63 (m, 1H, CH), 5.19 (m, 2H, COOCH_2Ph), 6.18 – 6.32 (m, 2H, $\text{CH}=\text{CH}$), 6.86 – 6.87 (m, 1H, $\text{CH}=\text{C}$), 7.09 – 7.12 (m, 2H, ArH), 7.20 – 7.23 (m, 2H, ArH), 7.35 – 7.38 (m, 5H, ArH) ppm. **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 14.1 (s, CH_3), 15.3 (s, CH_3), 21.2 (s, CH_3), 48.0 (s, CH), 52.8 (s, CH), 57.3 (s, COOCH_3), 61.0 (s, COOCH_2), 61.5 (s, C), 66.4 (s, COOCH_2Ph), 124.3 (s, CH), 126.3 (s, 2CH), 128.2 (s, 2CH), 128.5 (s, 2CH), 129.3 (s, 2CH), 131.8 (s, CH), 132.3 (s, C), 133.7 (s, C), 135.7 (s, C), 137.8 (s, C), 149.0 (s, CH), 163.8 (s, C), 171.1 (s, C), 174.3 (s, C) ppm. **IR (KBr)**: 2980, 1734, 1435, 1264, 1114, 1035, 734, 692, 550 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6$ $[\text{M}+\text{H}]^+$: 463.2115, found: 463.2117.



2, 3-diethyl 1-methyl (*E*)-5-methyl-1-(4-methylstyryl)cyclopent-3-ene- 1, 2, 3-tricarboxylate 4f.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4f** (87.5mg, 76% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.15 (t, *J* = 7.1 Hz, 3H, CH₃), 1.23 – 1.31 (m, 6H, 2CH₃), 2.33 (s, 3H, CH₃), 3.53 – 3.60 (m, 1H, CH), 3.83 (s, 3H, COOCH₃), 4.08 (q, *J* = 7.1 Hz, 2H, COOCH₂), 4.16 – 4.24 (m, 2H, COOCH₂), 4.59 (s, 1H, CH), 6.18 – 6.32 (m, 2H, CH=CH), 6.81 (s, 1H, CH=C), 7.09 – 7.12 (m, 2H, ArH), 7.20 – 7.23 (m, 2H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 14.2 (s, CH₃), 15.3 (s, CH₃), 21.2 (s, CH₃), 47.9 (s, CH), 52.8 (s, CH), 57.3 (s, COOCH₃), 60.6 (s, COOCH₂), 60.9 (s, COOCH₂), 61.5 (s, C), 124.4 (s, CH), 126.3 (s, 2CH), 129.3 (s, 2CH), 131.7 (s, CH), 132.7 (s, C), 133.7 (s, C), 137.7 (s, C), 148.2 (s, CH), 164.0 (s, C), 171.1 (s, C), 174.4 (s, C) ppm. IR (KBr): 2978, 1714, 1454, 1264, 1114, 1035, 735, 693, 550 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₃H₂₉O₆ [M+H]⁺: 401.1959, found: 401.1962.

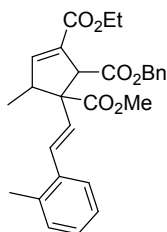


2, 3-Diethyl 1-methyl (*E*)-5-methyl-1-(3-methylstyryl)cyclopent-3-ene- 1, 2, 3-tricarboxylate 4g.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4g** (105.6 mg, 88% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.16 – 1.31 (m, 9H, 3CH₃), 2.33 (s, 3H, CH₃), 3.56 – 3.58 (m, 1H, CH), 3.83 (s, 3H, COOCH₃), 4.06 – 4.23 (m, 4H, 2COOCH₂), 4.55-4.59 (m, 1H, CH), 6.27-6.40 (m, 2H, CH=CH), 6.81 (s, 1H, CH=C), 7.05 – 7.07 (m, 1H, ArH), 7.11 – 7.22 (m, 3H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 14.2 (s, CH₃), 15.3 (s, CH₃), 21.4 (s, CH₃), 47.9 (s, CH), 52.8 (s, CH), 57.3 (s, COOCH₃), 60.7 (s, COOCH₂), 60.9 (s, COOCH₂), 61.6 (s, C), 123.5

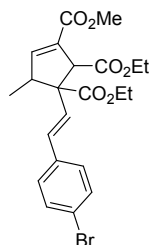
(s, CH), 125.2 (s, CH), 127.0 (s, CH), 128.5 (s, CH), 128.7 (s, CH), 132.0 (s, CH), 132.7 (s, C), 136.5 (s, C), 138.1 (s, C), 148.2 (s, CH), 164.0 (s, C), 171.1 (s, C), 174.3 (s, C) ppm. **IR (KBr)**: 2981, 1711, 1454, 1263, 1116, 1030, 735, 692, 550 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{23}\text{H}_{29}\text{O}_6$ $[\text{M}+\text{H}]^+$: 401.1959, found: 401.1960.



2-Benzyl 3-ethyl 1-methyl (E)-5-methyl-1-(2-methylstyryl)cyclopent-3-ene- 1, 2, 3-tricarboxylate 4h.

The reaction of diene (100.9 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product **4h** (123.5 mg, 89% yield).

Colorless oil. **^1H NMR (300 MHz, CDCl_3)** δ 1.21 – 1.26 (m, 6H, 2 CH_3), 2.24 – 2.28 (m, 3H, CH_3), 3.56 – 3.63 (m, 1H, CH), 3.81 (s, 3H, COOCH_3), 4.13 – 4.20 (m, 2H, COOCH_2), 4.67 (s, 1H, CH), 4.96 – 5.12 (m, 2H, COOCH_2Ph), 6.09 – 6.14 (m, 1H, $\text{CH}=\text{C}$), 6.50 (d, $J = 16.4$ Hz, 1H, $\text{C}=\text{CH}$), 6.82 (s, 1H, $\text{CH}=\text{C}$), 7.12 – 7.27 (m, 4H, ArH) ppm. **^{13}C NMR (75 MHz, CDCl_3)** δ 14.1 (s, CH_3), 15.3 (s, CH_3), 19.6 (s, CH_3), 47.8 (s, CH), 52.7 (s, CH), 57.3 (s, COOCH_3), 60.7 (s, COOCH_2), 61.9 (s, C), 66.8 (s, COOCH_2Ph), 125.7 (s), 126.2 (s), 126.7 (s), 127.8 (s), 128.1 (s), 128.3 (s), 128.3 (s), 130.1 (s), 130.2 (s), 132.6 (s), 135.5 (s), 135.6 (s), 135.8 (s), 148.4(s), 148.4(s), 163.9 (s), 171.0 (s), 174.3(s) ppm. **IR (KBr)**: 2979, 1733, 1455, 1257, 1119, 1024, 733, 698, 550 cm^{-1} . **HRMS** (ESI, m/z): Calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6$ $[\text{M}+\text{H}]^+$: 463.2115, found: 463.2119.



1, 2-Diethyl 3-methyl (E)-1-(4-bromostyryl)-5-methylcyclopent-3-ene- 1, 2, 3-tricarboxylate 4i.

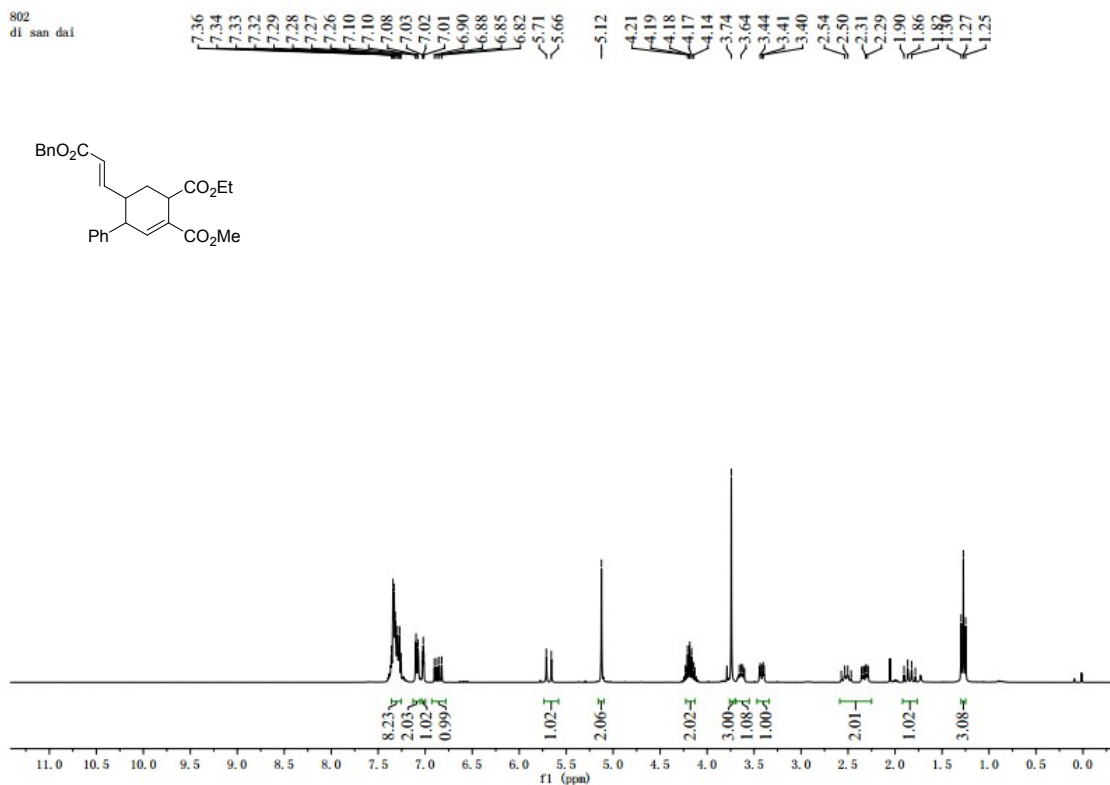
The reaction of diene (106.0 mg, 0.3 mmol, 1.0 equiv) and allenolate (50.5 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1)

afforded the product **4i** (114.4 mg, 82% yield).

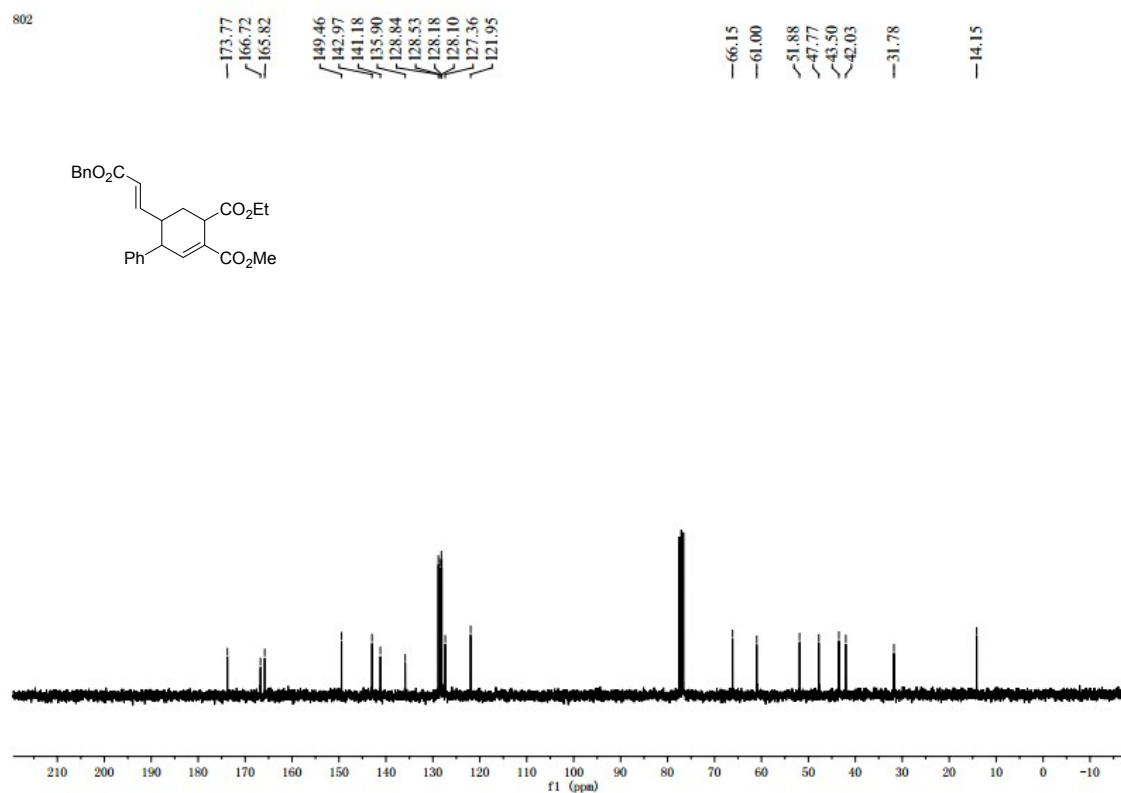
Colorless oil. **¹H NMR (300 MHz, CDCl₃)** δ 1.14 (t, $J = 7.0$ Hz, 3H, CH₃), 1.22 – 1.24 (m, 3H, CH₃), 1.31 – 1.36 (m, 3H, CH₃), 1.53 – 1.59 (m, 1H, CH), 3.75 (s, 3H, COOCH₃), 4.08 (q, $J = 7.1$ Hz, 2H, COOCH₂), 4.30 (q, $J = 14.3, 7.2$ Hz, 2H, COOCH₂), 4.59 (s, 1H, CH), 6.29-6.38 (m, 2H, CH=CH), 6.73-6.86 (m, 1H, CH=C), 7.17 – 7.22 (m, 2H, ArH), 7.41 – 7.44 (m, 2H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 14.2 (s, CH₃), 14.2 (s, CH₃), 15.2 (s, CH₃), 47.9 (s, CH), 51.8 (s, CH), 57.2 (s, COOCH₃), 60.9 (s, COOCH₂), 61.5 (s, C), 61.8 (s, COOCH₂), 121.7 (s, C), 126.5 (s, CH), 127.8 (s, 2CH), 130.6 (s, CH), 131.7 (s, 2CH), 132.4 (s, C), 135.6 (s, C), 148.2 (s, CH), 164.4 (s, C), 171.0 (s, C), 173.4 (s, C) ppm. **IR (KBr):** 2981, 1714, 1435, 1258, 1118, 1032, 735, 693, 550 cm⁻¹. **HRMS (ESI, m/z):** Calcd for C₂₂H₂₆BrO₆ [M+H]⁺: 465.0907, found: 465.0906.

1. H. Audrain, J. Thorhauge, R. G. Hazell, K. A. Joergensen, *J. Org. Chem.*, 2000, **65**, 4487.
2. R. W. Lang, H.-J. Hansen, *Organic Syntheses*. 1990, **62**, 202.

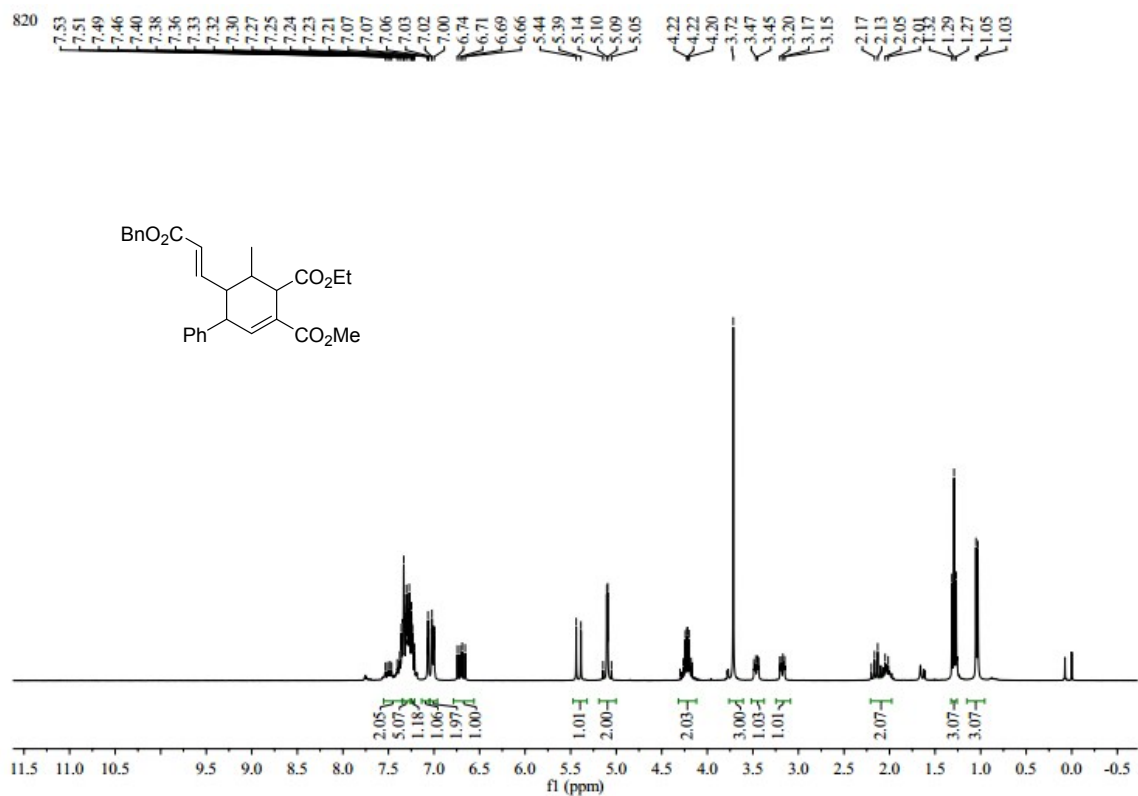
6. Copies of ^1H NMR, ^{13}C NMR Spectra



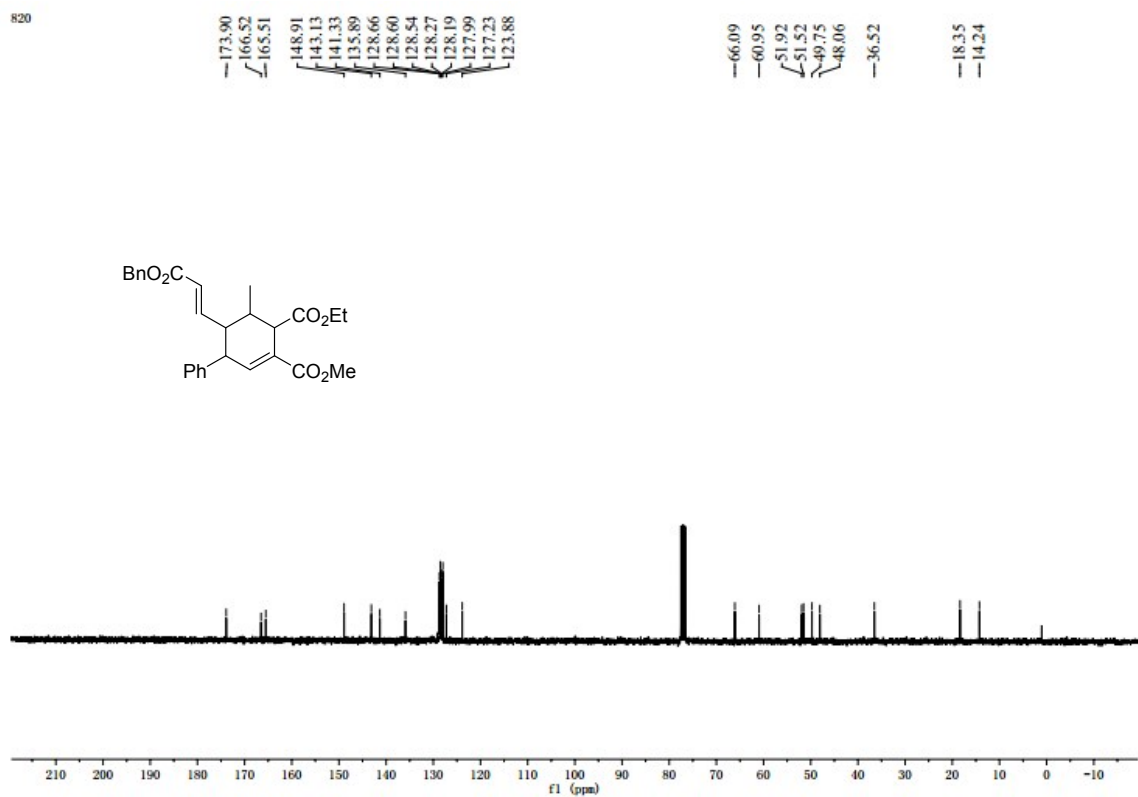
Compound 3a ^1H NMR



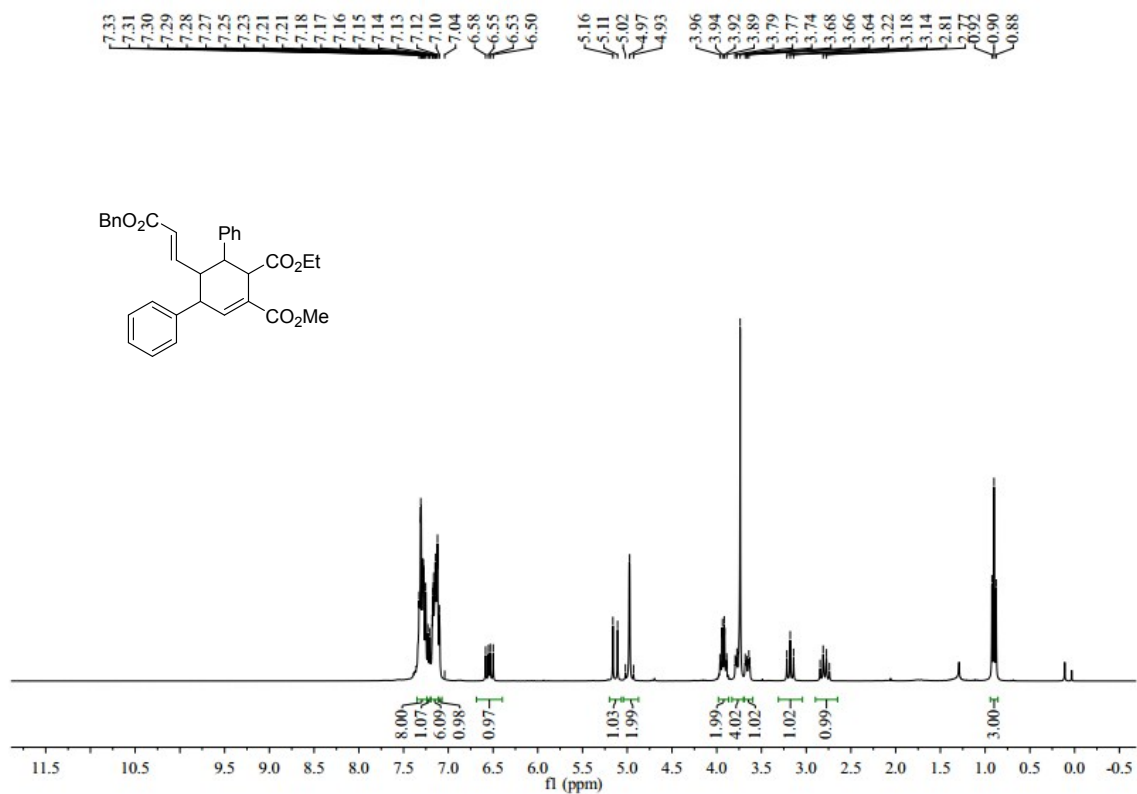
Compound 3a ^{13}C NMR



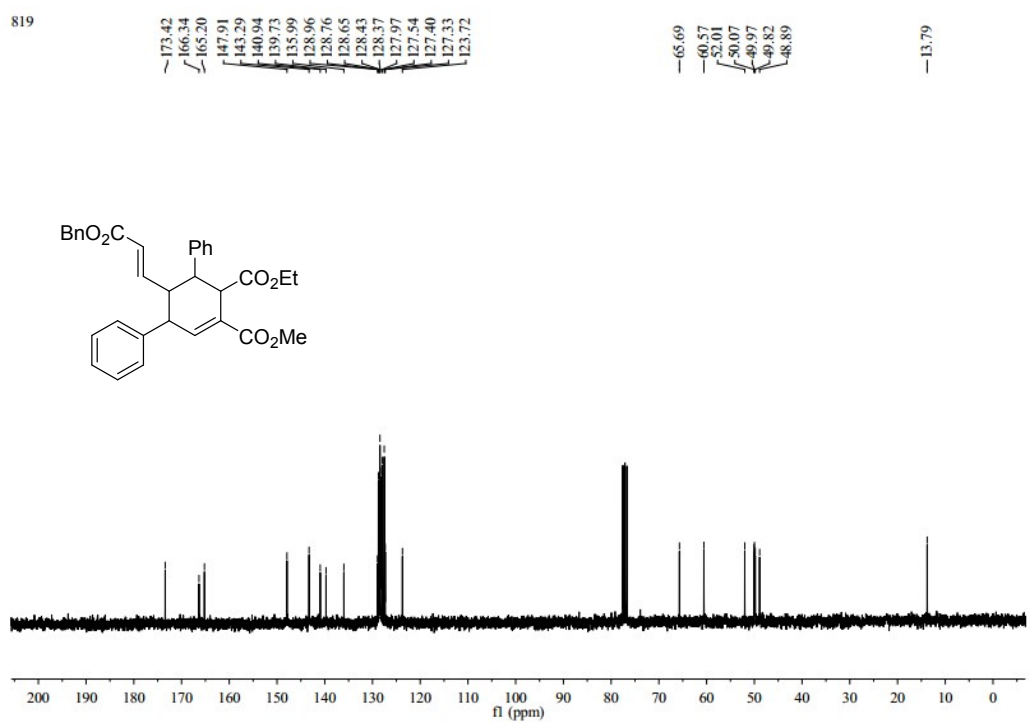
Compound 3b ¹H NMR



Compound 3b ¹³C NMR

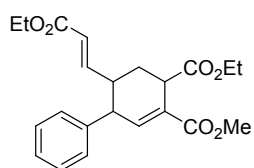


Compound 3c ¹H NMR

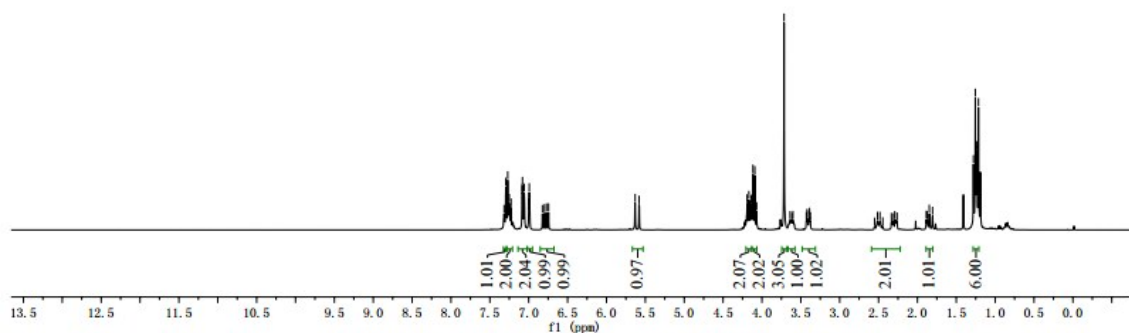


Compound 3c ¹³C NMR

955
yi zhi , fei 955

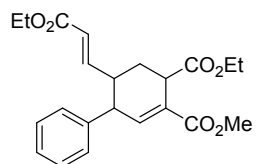


7.32
7.29
7.27
7.25
7.24
7.23
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7.08
7.06
7.00
6.99
6.99
6.82
6.80
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1.21

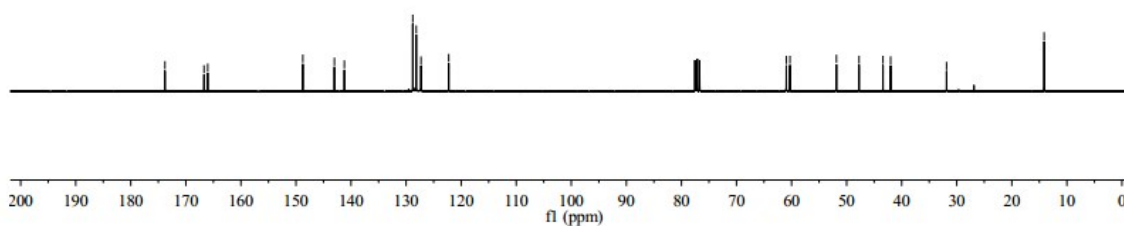


Compound 3d ¹H NMR

955
yi zhi , fei 955



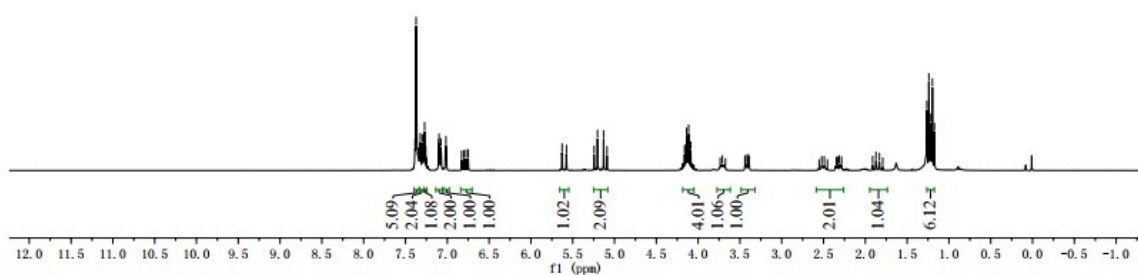
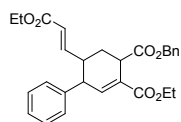
173.8
166.7
166.0
148.8
143.0
141.2
128.8
128.2
127.3
122.3
61.0
60.3
51.8
47.7
43.4
42.0
31.8
14.1



Compound 3d ¹³C NMR

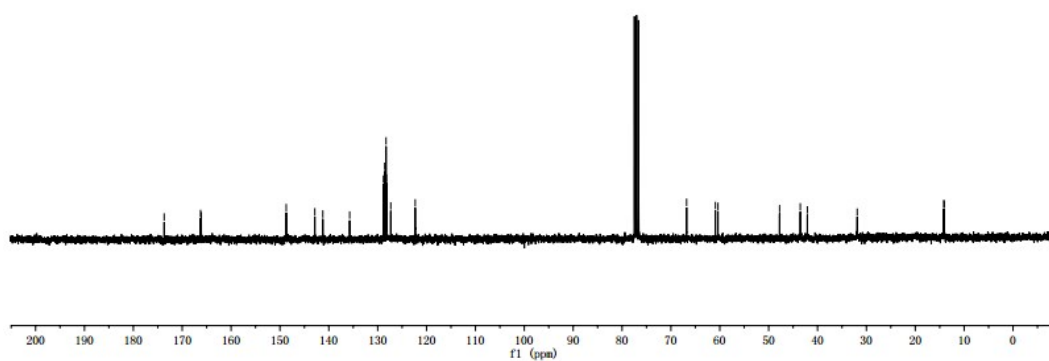
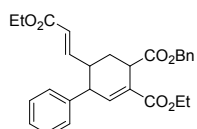
1846

7.39
7.37
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7.30
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7.10
7.08
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7.02
7.01
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6.80
6.78
6.75
5.63
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5.09
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1.17

Compound 3e ¹H NMR

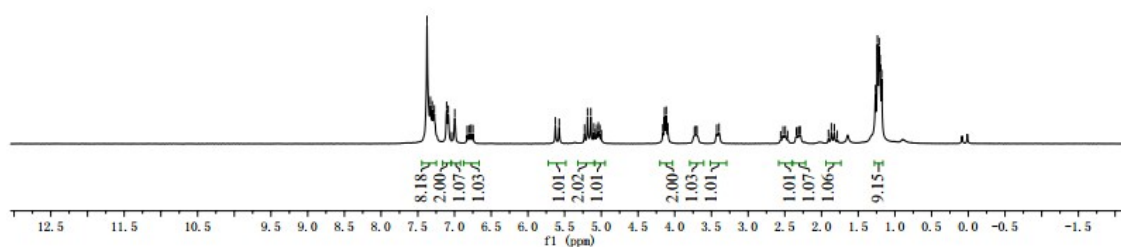
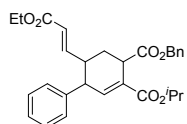
1846

173.7
166.2
166.1
148.7
142.9
141.2
135.7
128.9
128.8
128.6
128.3
128.2
127.3
122.3
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43.5
42.1
31.9
14.2
14.1

Compound 3e ¹³C NMR

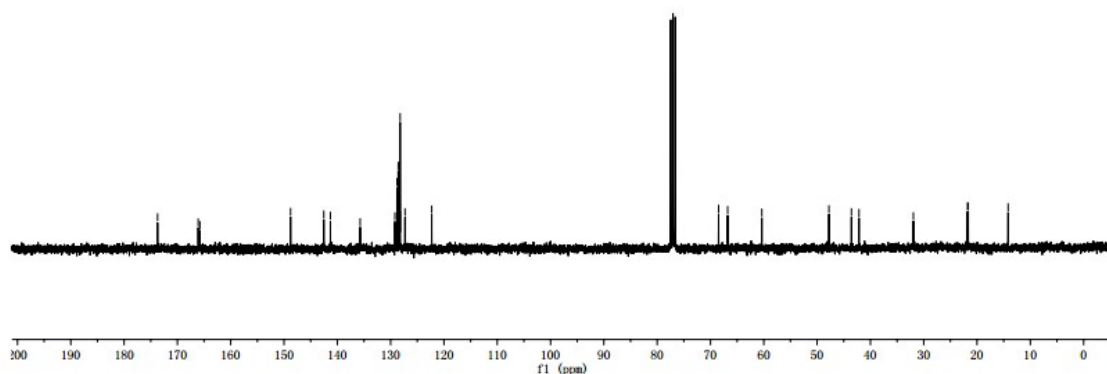
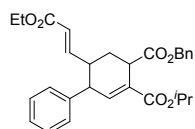
1852
2

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6.77
6.75
5.63
5.57
5.19
5.14
5.10
5.04
4.16
4.14
4.11
4.09
3.43
3.40
2.56
2.52
2.49
2.46
2.34
2.33
2.31
2.29
1.91
1.87
1.82
1.79
1.26
1.24
1.21
1.20
1.18



Compound 3f ¹H NMR

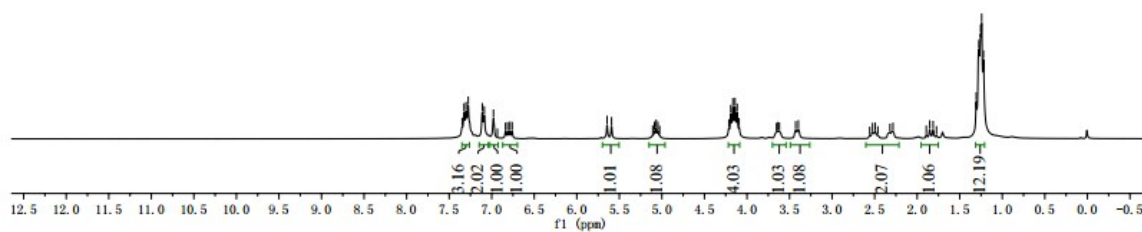
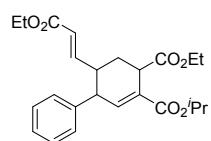
173.72
166.10
165.78
148.77
142.53
141.30
135.71
129.19
128.81
128.57
128.27
128.22
127.30
122.30
68.48
66.78
60.36
47.78
43.56
42.14
31.94
21.78
21.65
14.17



Compound 3f ¹³C NMR

1863
4+2

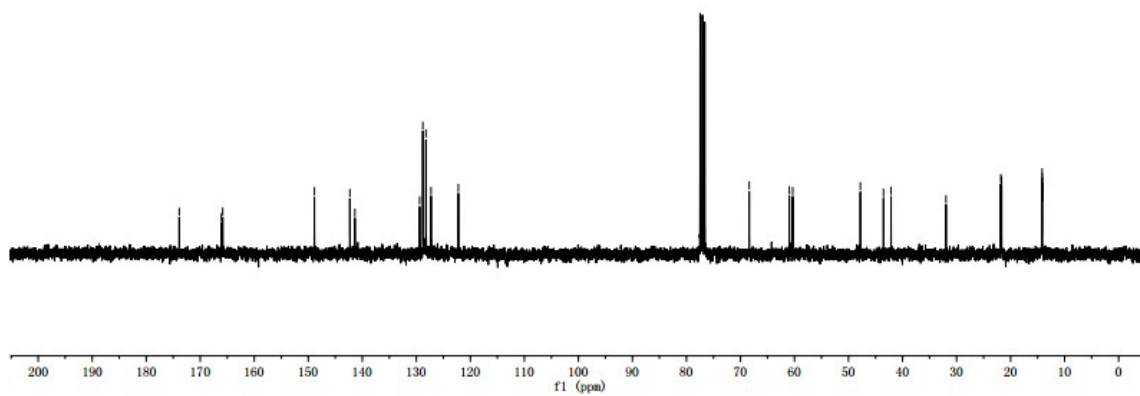
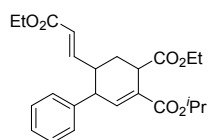
7.35
7.32
7.30
7.28
7.11
7.09
6.98
6.93
6.84
6.81
6.79
6.76
5.64
5.59
5.09
5.07
5.05
4.21
4.19
4.17
4.14
4.12
4.09
3.40
2.52
2.49
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2.28
1.85
1.81
1.27
1.25
1.24
1.22



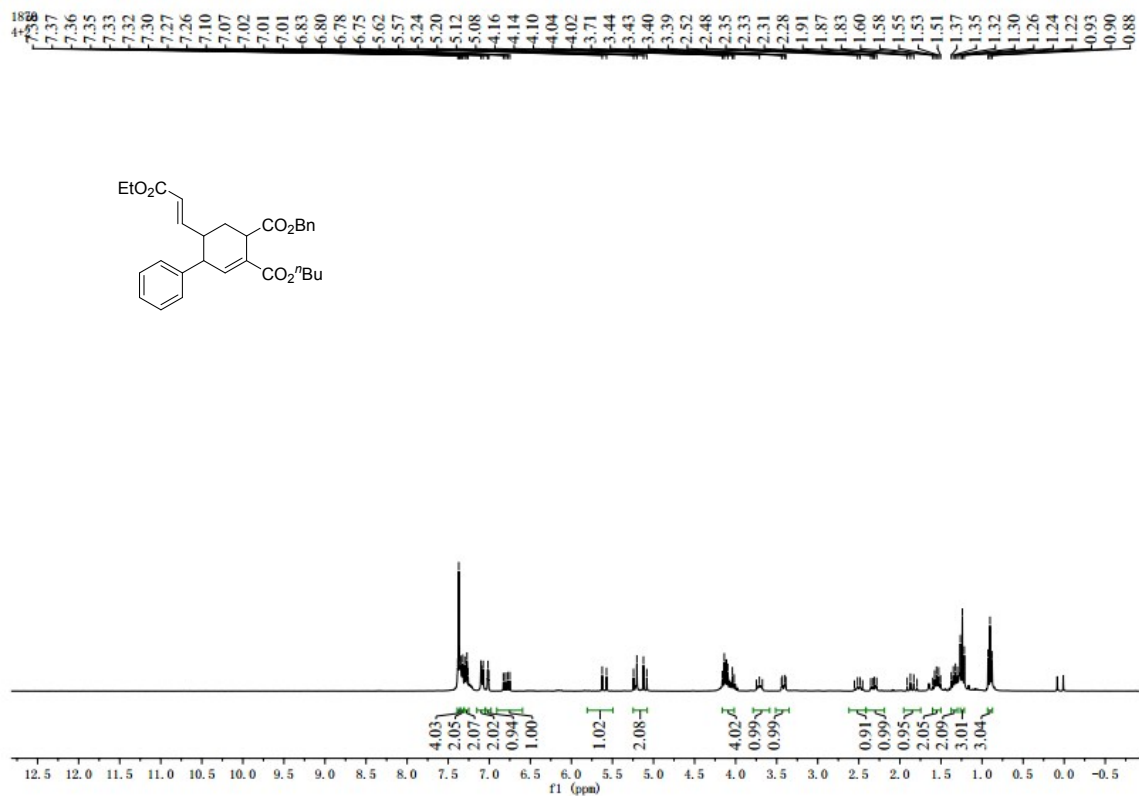
Compound 3g ¹H NMR

1863
4+2

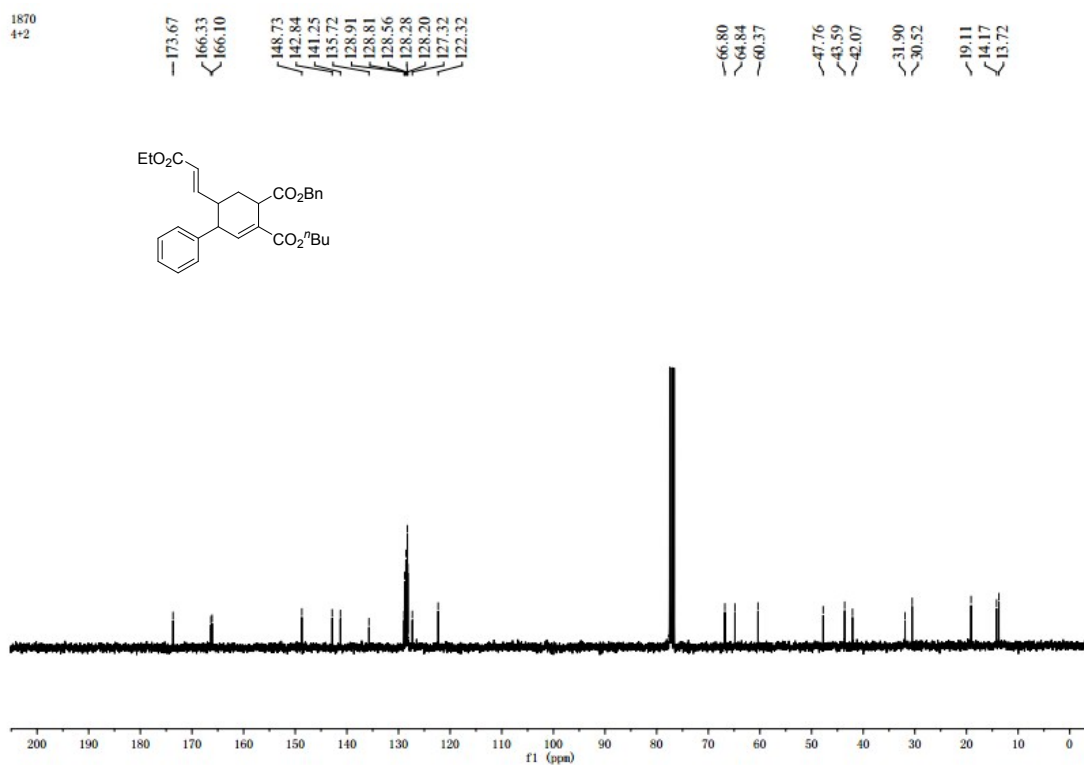
173.9
166.1
165.8
148.9
142.3
141.4
129.4
128.8
128.2
127.3
122.2
68.4
61.0
60.3
47.8
43.5
42.1
32.0
21.8
21.7
14.2
14.1



Compound 3g ¹³C NMR



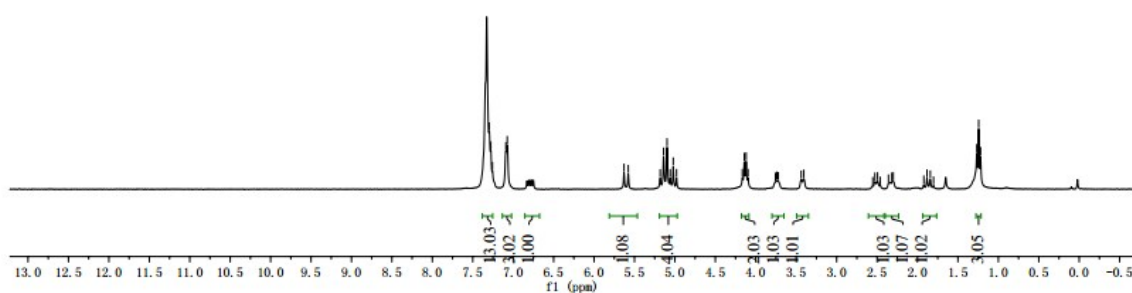
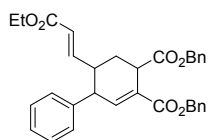
Compound 3h ¹H NMR



Compound 3h ¹³C NMR

1896
4+2

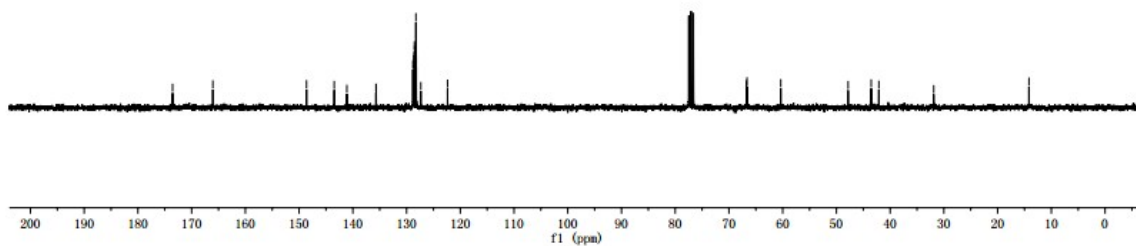
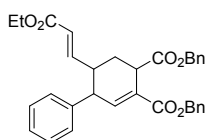
7.30
7.28
7.26
7.09
7.07
5.63
5.58
5.18
5.14
5.10
5.06
5.02
4.98
4.17
4.14
4.12
3.44
3.41
2.53
2.49
2.32
2.30
1.88
1.84
1.24
1.22



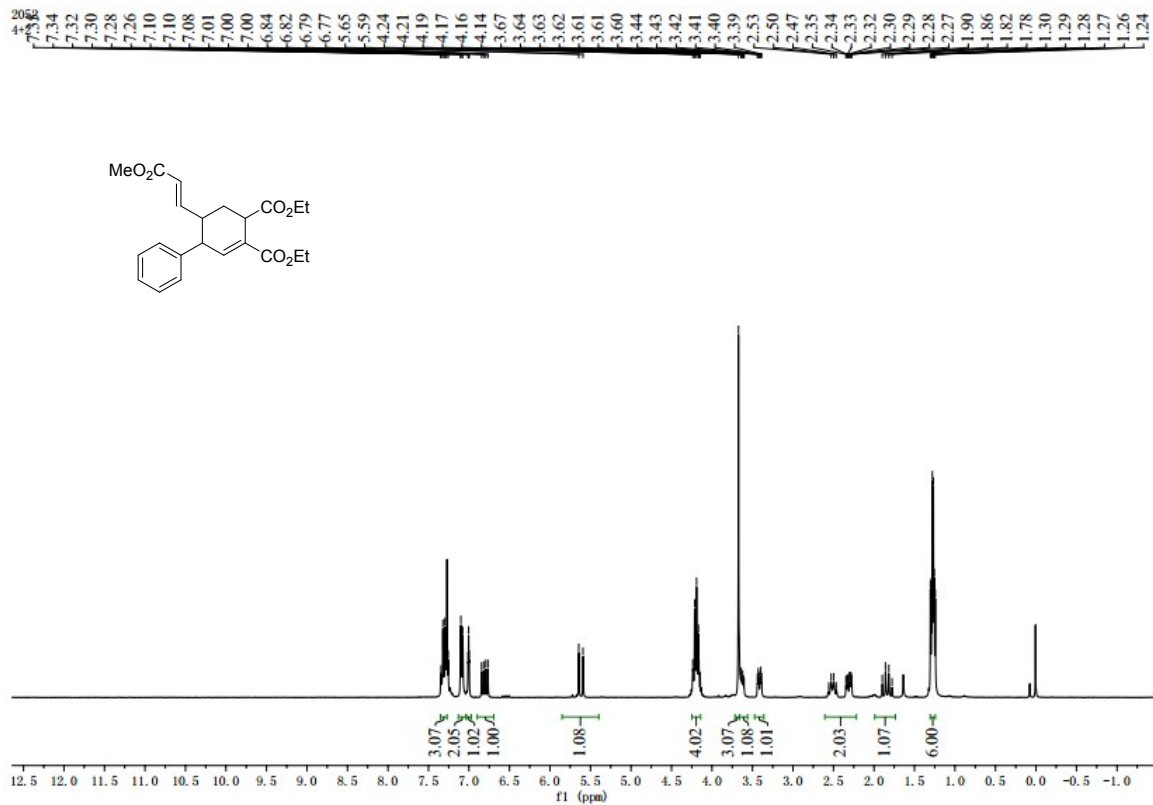
Compound 3i ¹H NMR

1896
4+2

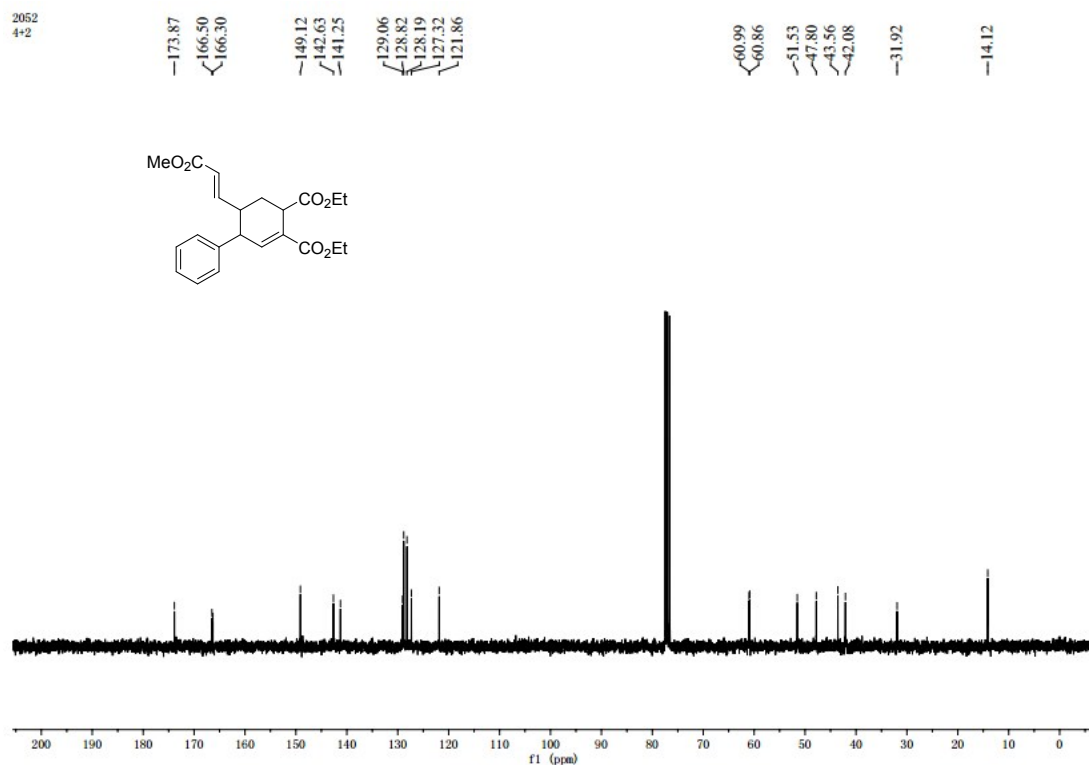
173.55
166.05
148.62
143.47
141.11
135.69
135.65
128.82
128.70
128.54
128.52
128.26
128.24
128.20
127.34
122.37
66.77
66.64
60.35
47.82
43.52
42.10
31.89
14.16



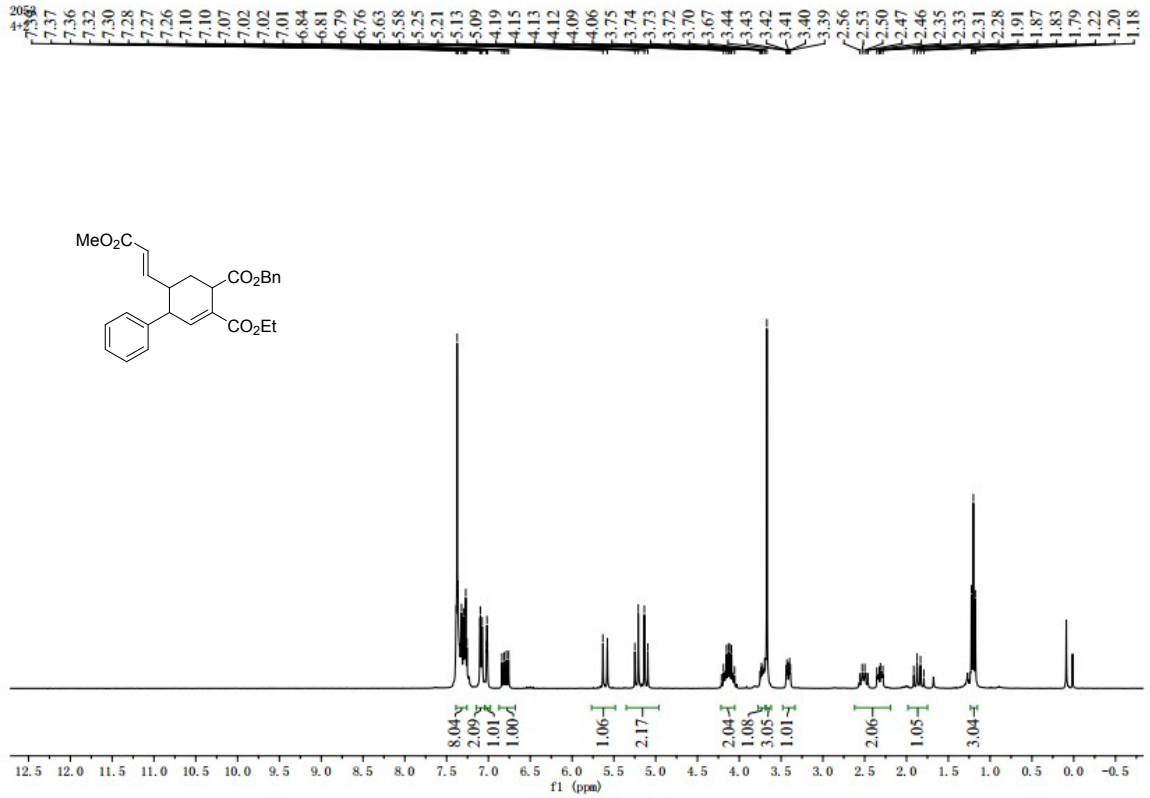
Compound 3i ¹³C NMR



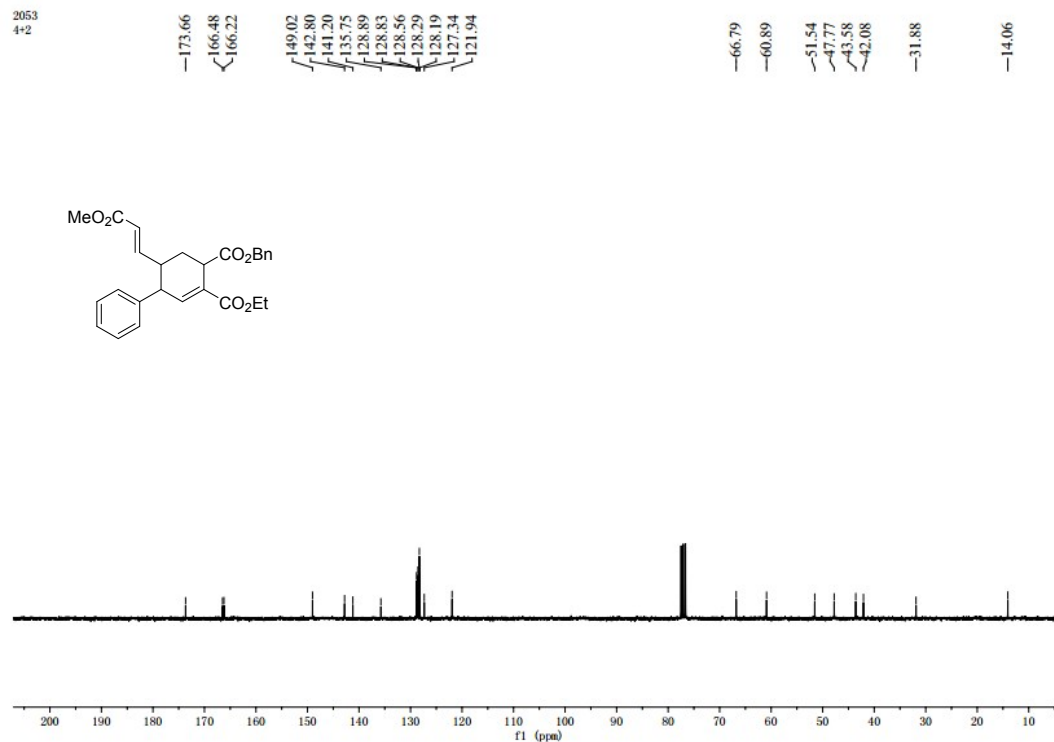
Compound 3j ¹H NMR



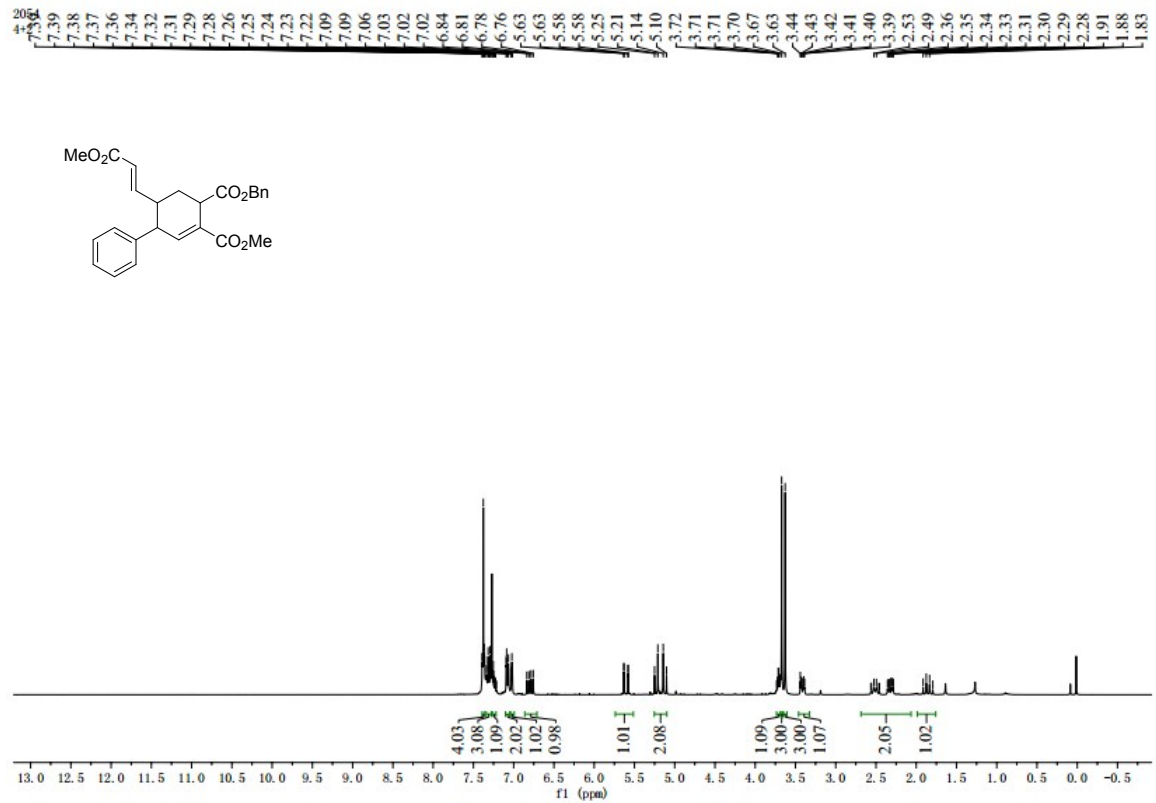
Compound 3j ¹³C NMR



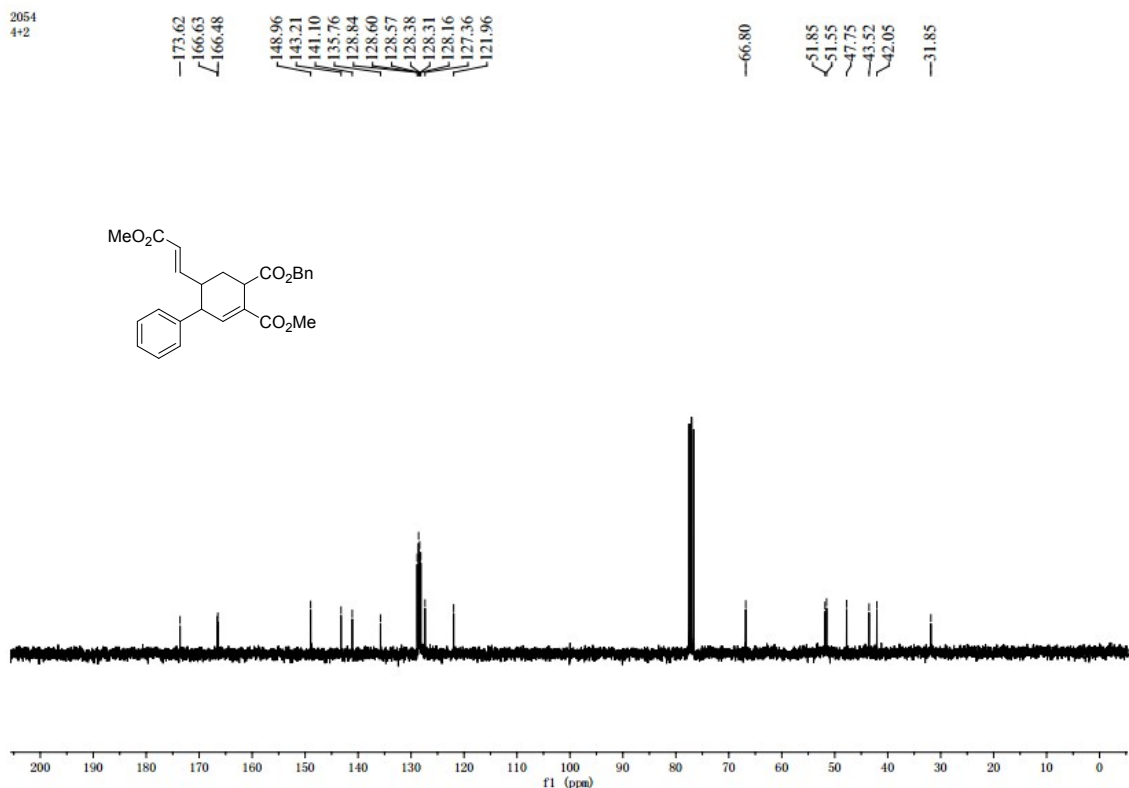
Compound 3k ¹H NMR



Compound 3k ¹³C NMR

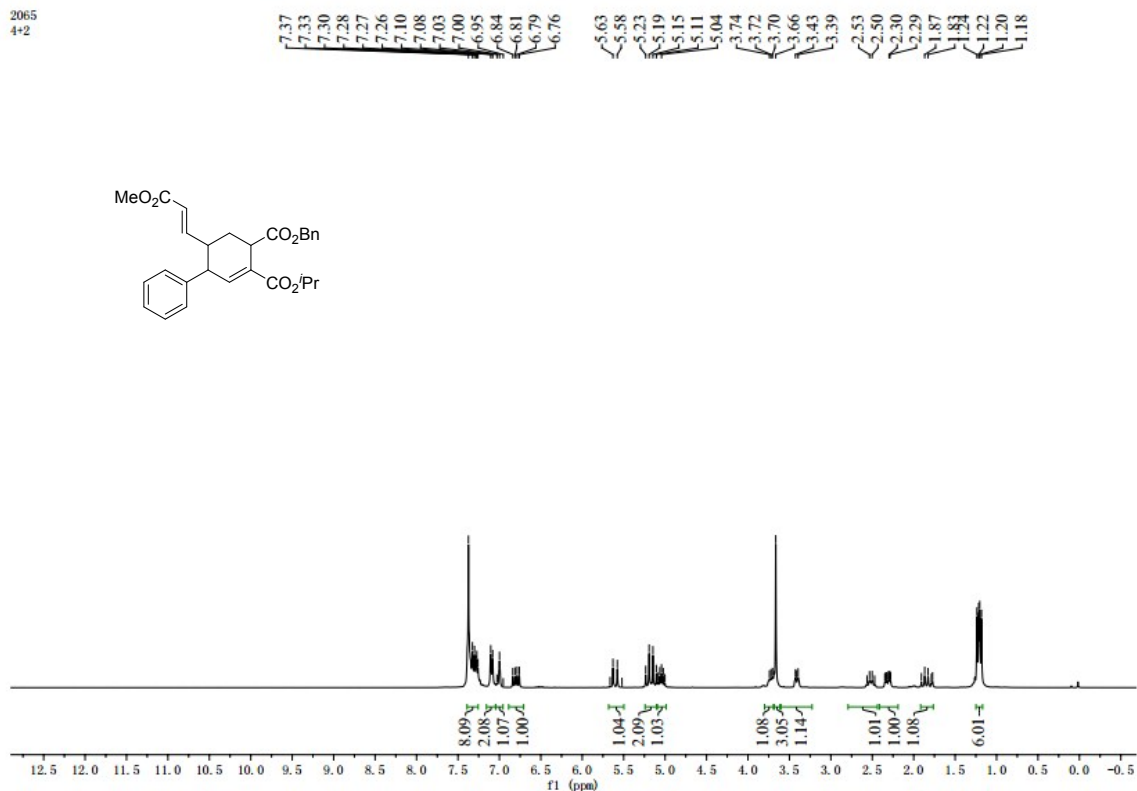
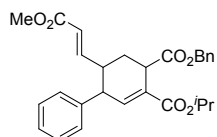


Compound 31 ¹H NMR



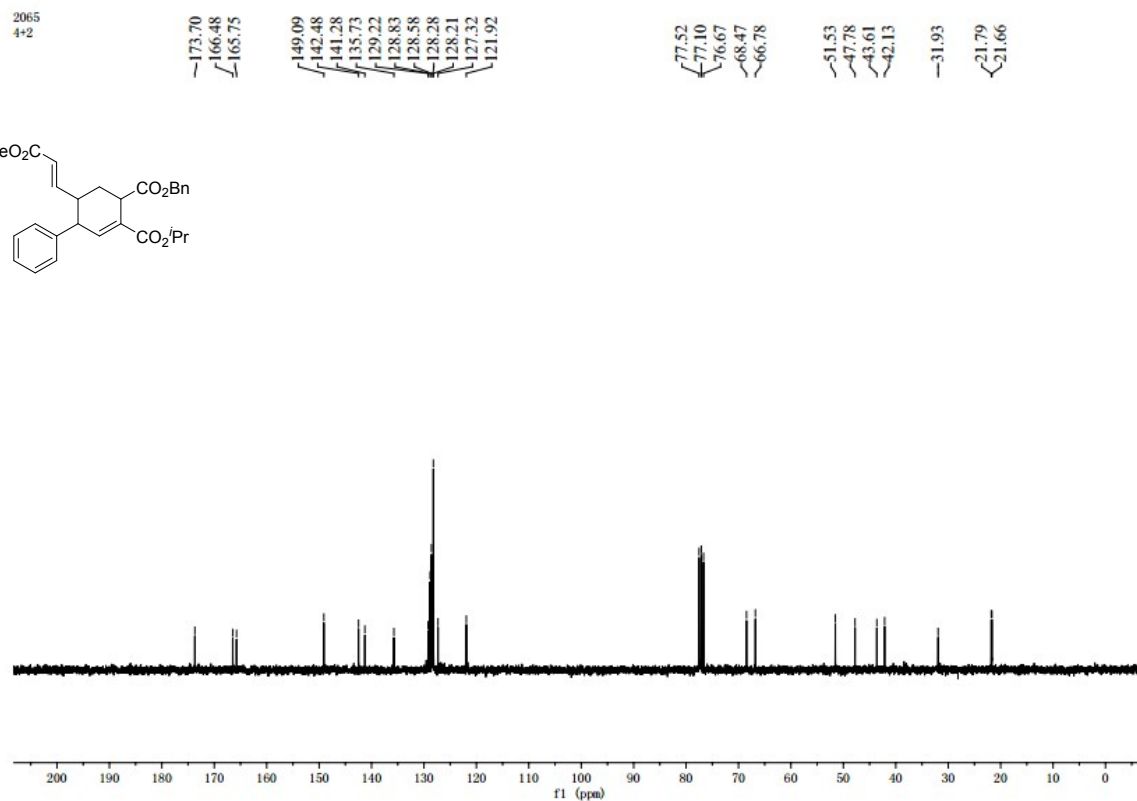
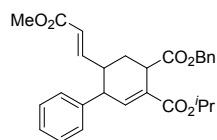
Compound 31 ¹³C NMR

2065
4+2



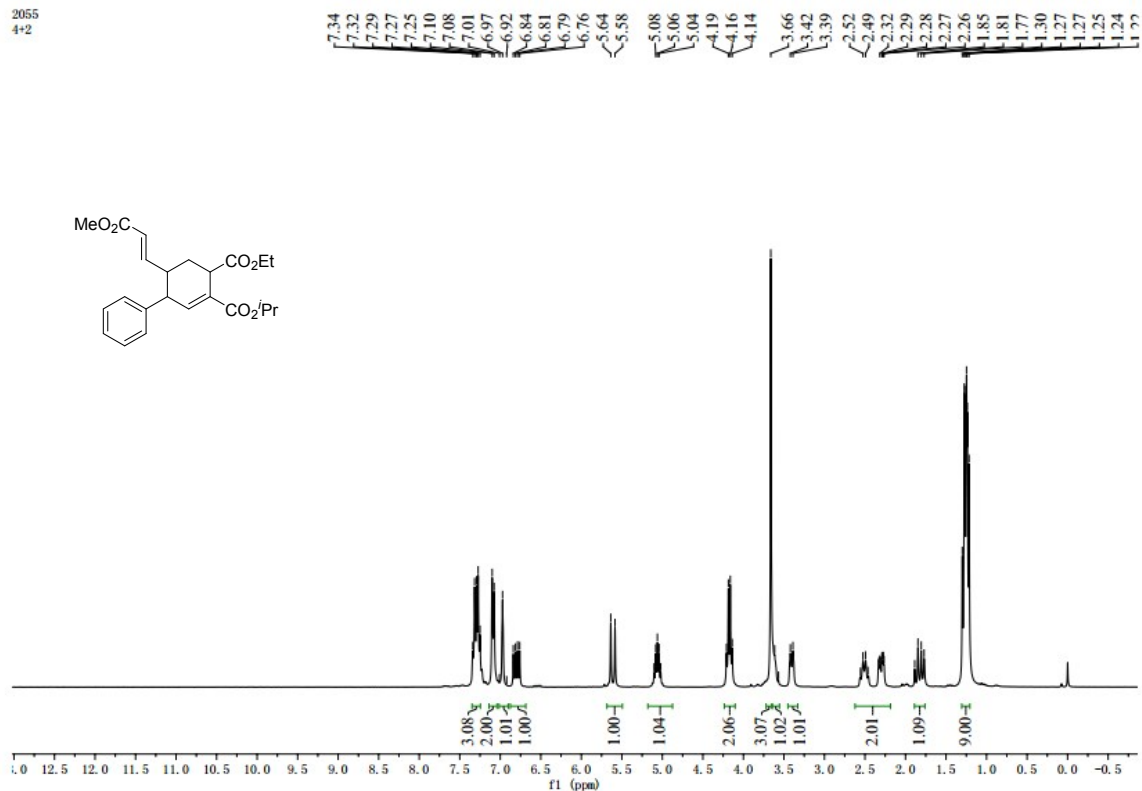
Compound 3m ¹H NMR

2065
4+2



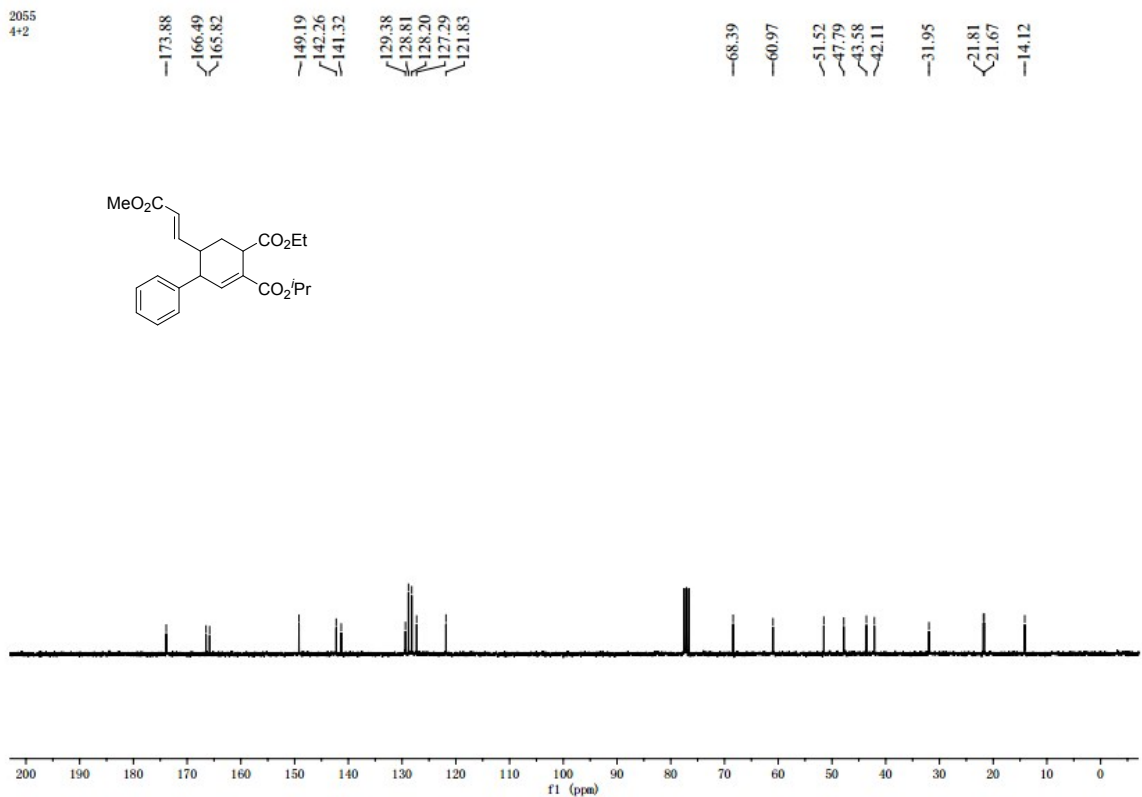
Compound 3m ¹³C NMR

2055
4+2



Compound 3n ¹H NMR

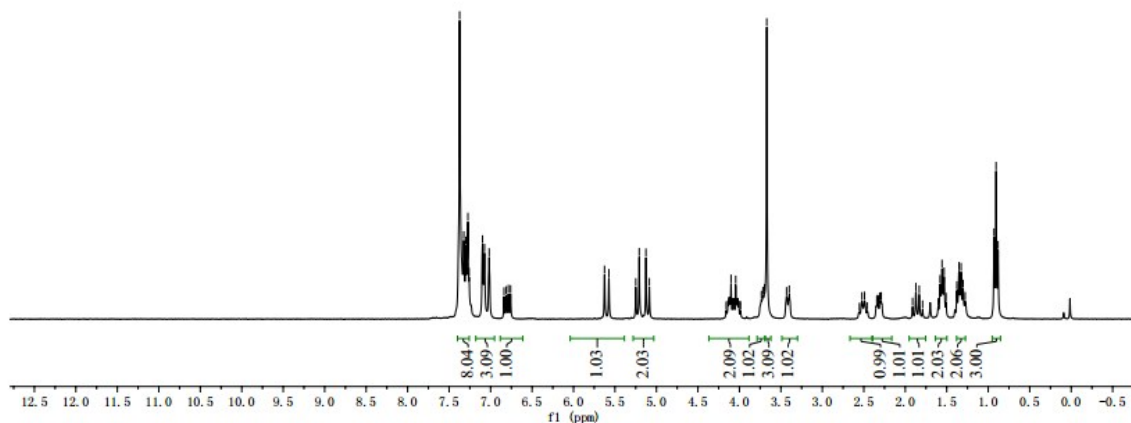
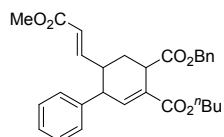
2055
4+2



Compound 3n ¹³C NMR

2064
4+2

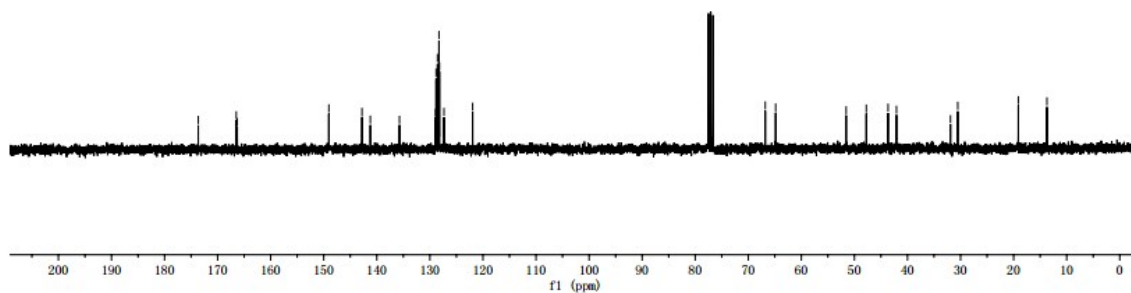
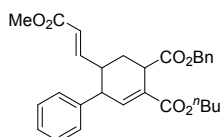
7.37
7.32
7.30
7.27
7.26
7.10
7.07
7.02
6.84
6.81
6.79
6.76
5.63
5.57
5.25
5.21
5.13
5.09
4.10
4.04
3.72
3.70
3.67
3.43
3.40
2.52
2.49
2.29
1.87
1.83
1.58
1.56
1.53
1.38
1.35
1.33
1.30
1.28
0.93
0.91
0.88



Compound 3o ¹H NMR

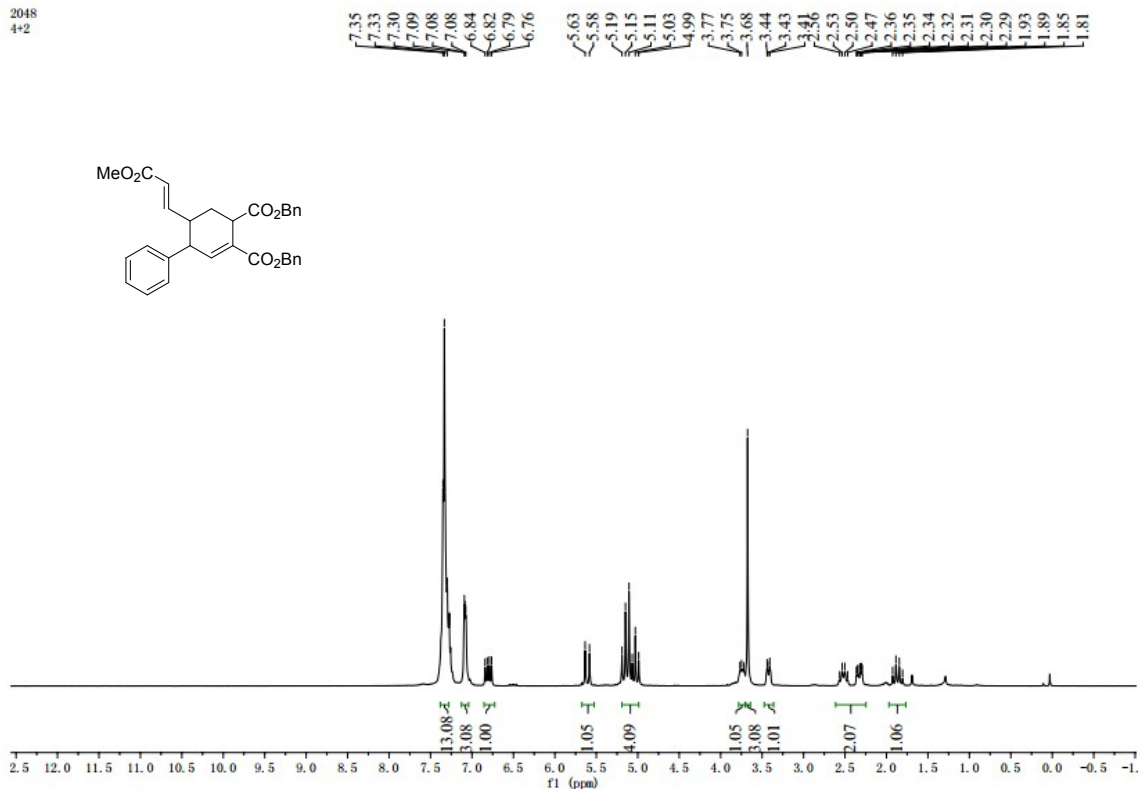
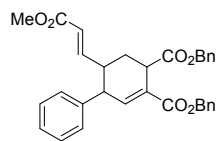
2064
4+2

173.65
166.49
166.30
149.04
142.80
141.22
135.73
128.93
128.83
128.57
128.28
128.19
127.34
121.94
66.80
64.84
51.55
47.76
43.65
42.07
31.90
30.52
19.11
13.72



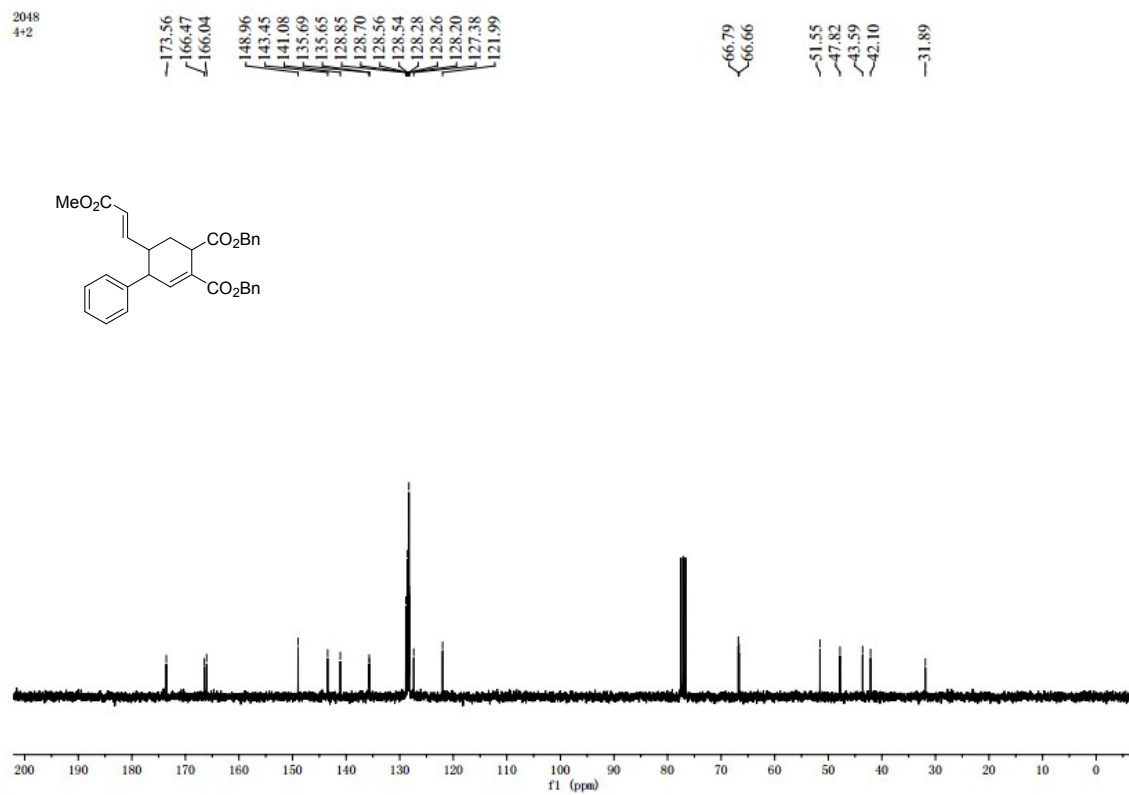
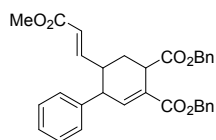
Compound 3o ¹³C NMR

2048
4+2



Compound 3p ¹H NMR

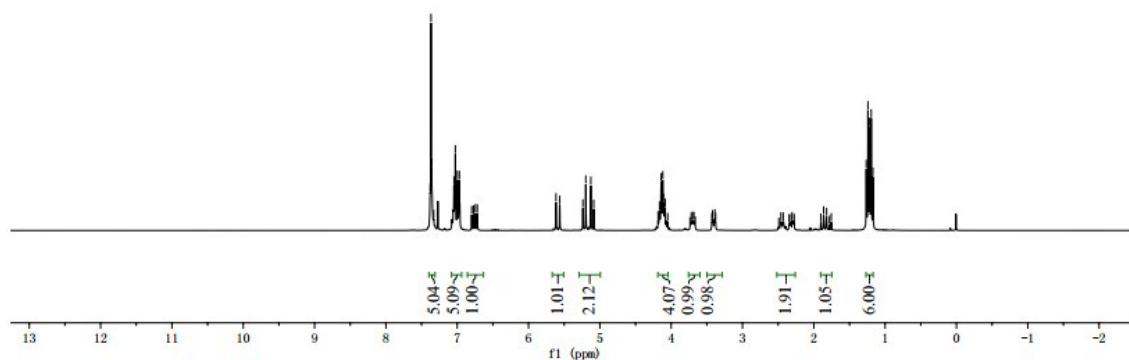
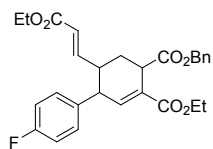
2048
4+2



Compound 3p ¹³C NMR

1989
4+2

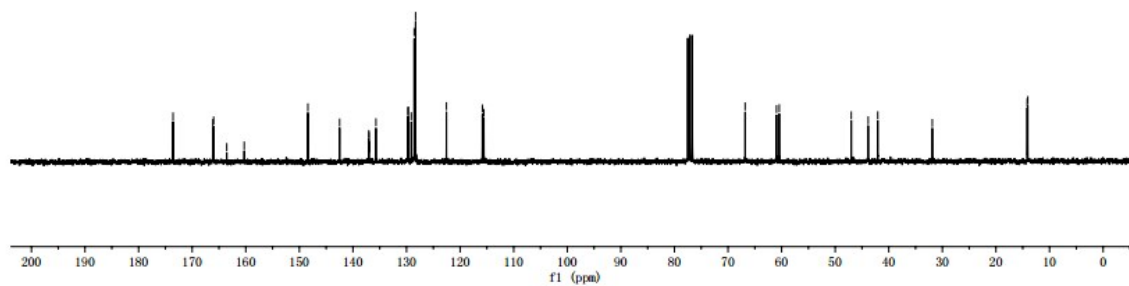
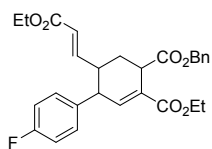
7.38
7.37
7.36
7.33
7.05
7.03
7.00
6.97
6.80
6.77
6.75
6.72
5.61
5.56
5.24
5.20
5.13
4.16
4.14
4.12
4.11
4.08
3.39
2.46
2.43
2.35
2.32
2.30
2.28
1.90
1.86
1.82
1.78
1.76
1.26
1.24
1.22
1.19
1.17



Compound 3q ¹H NMR

1989
4+2

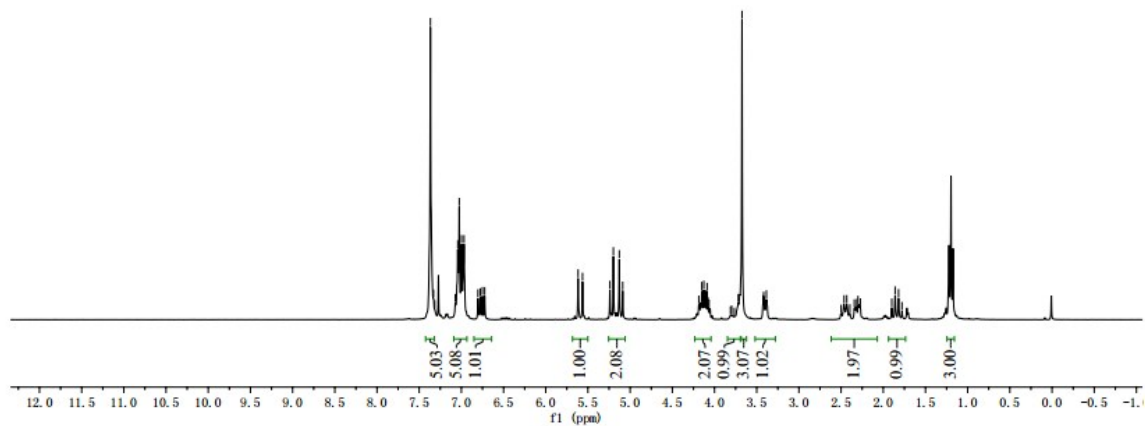
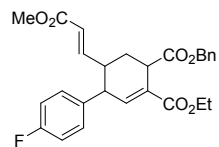
173.57
166.14
166.00
163.55
160.29
148.40
142.49
137.03
136.99
135.70
129.75
129.64
129.12
128.57
128.31
122.56
115.84
115.56
66.81
60.95
60.43
47.00
43.84
42.05
31.88
14.17
14.06



Compound 3q ¹³C NMR

2049
4+2

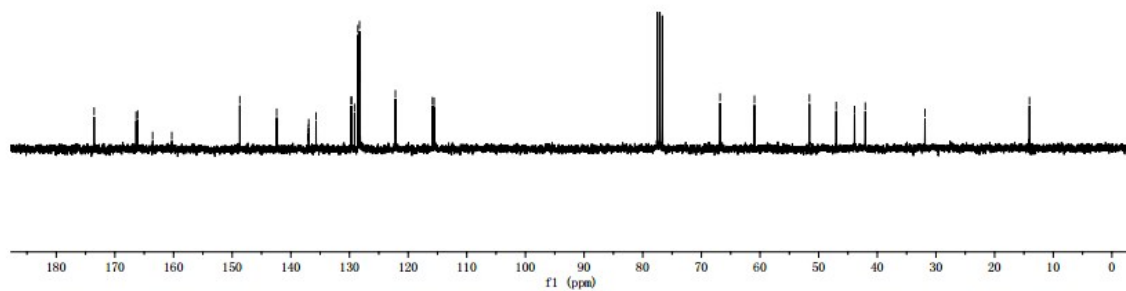
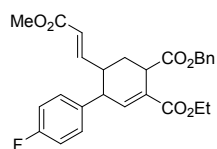
7.37
7.33
7.32
7.07
7.04
7.03
7.00
6.97
6.80
6.78
6.75
6.72
5.62
5.56
5.24
5.20
5.13
5.09
4.15
4.13
4.09
3.72
3.67
3.42
3.38
3.36
2.46
2.43
2.40
2.34
2.31
2.30
2.27
1.90
1.86
1.82
1.78



Compound 3r ¹H NMR

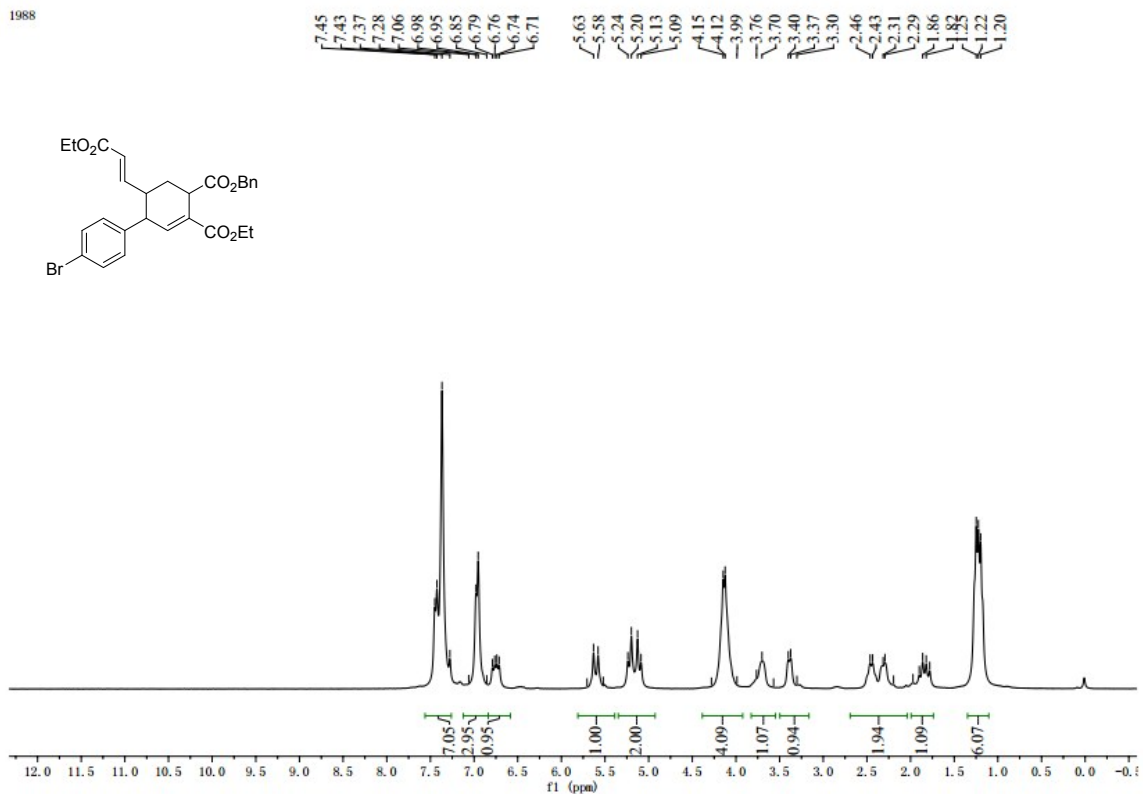
2049
4+2

173.54
166.39
166.11
163.56
160.30
148.70
142.42
136.99
136.95
135.70
129.73
129.62
129.14
128.57
128.31
128.29
122.16
115.85
115.57
66.81
60.95
51.58
47.01
43.88
42.05
31.87
14.05

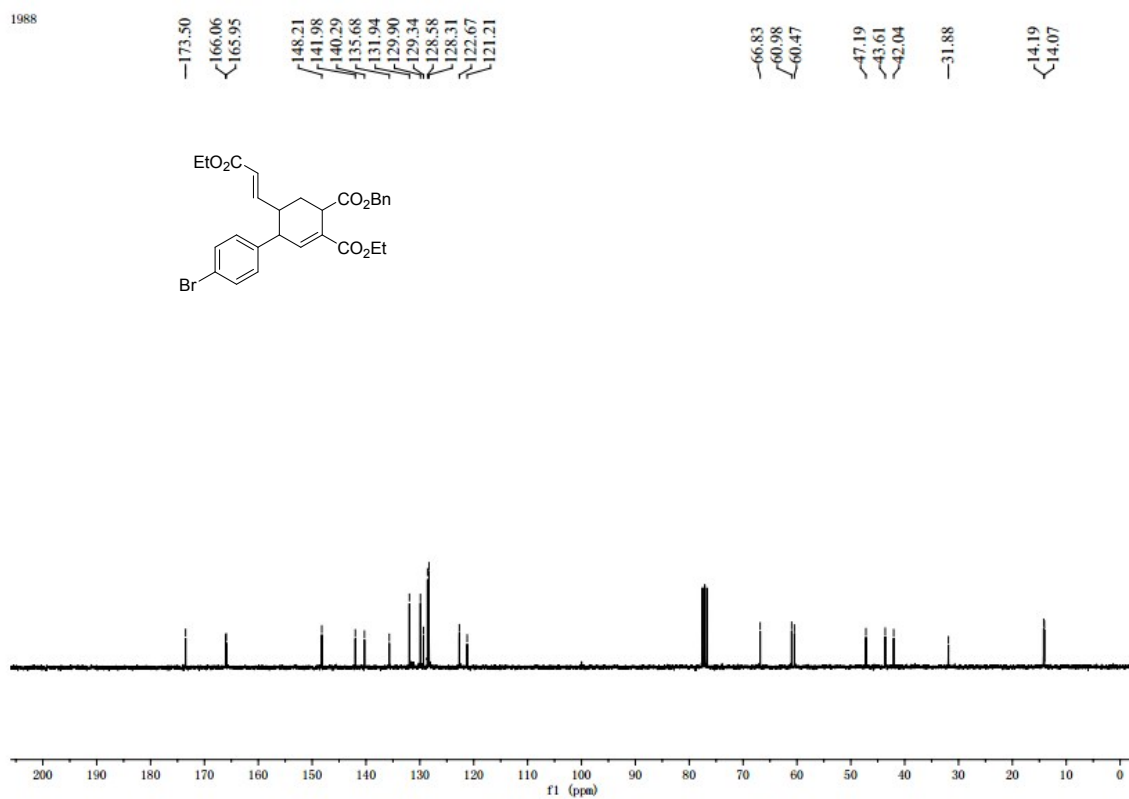


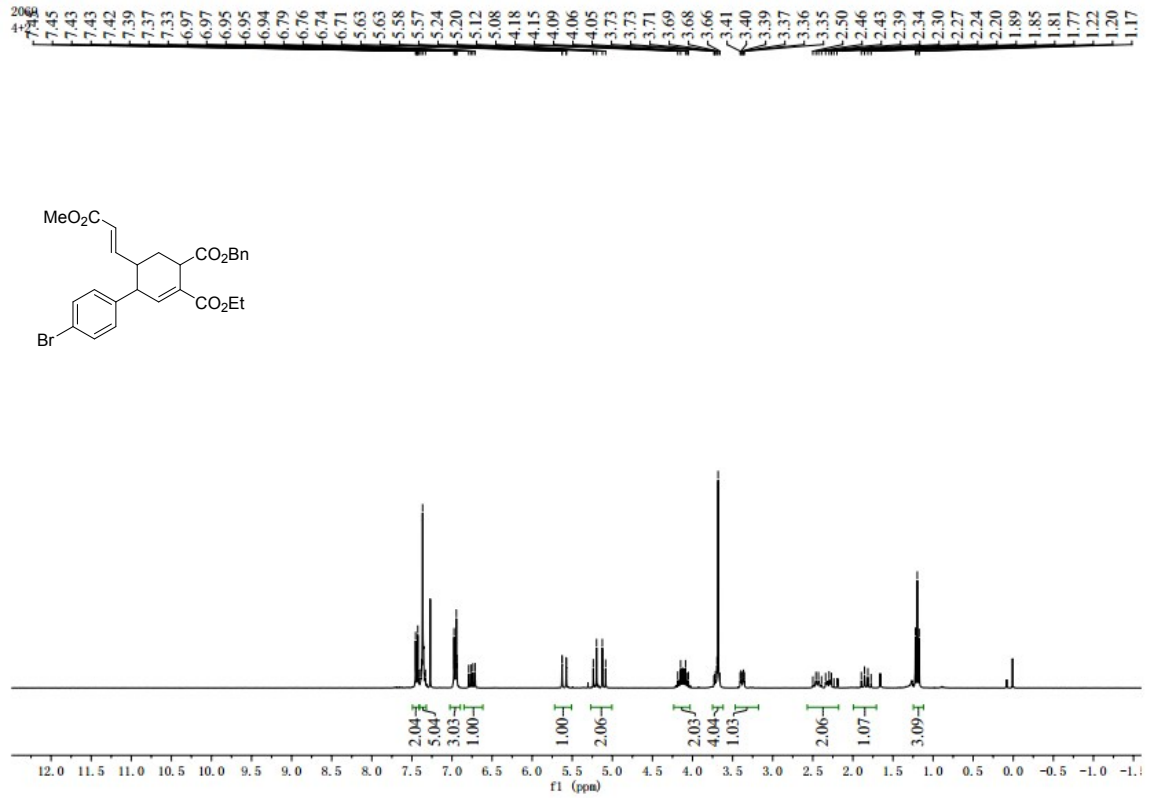
Compound 3r ¹³C NMR

1988

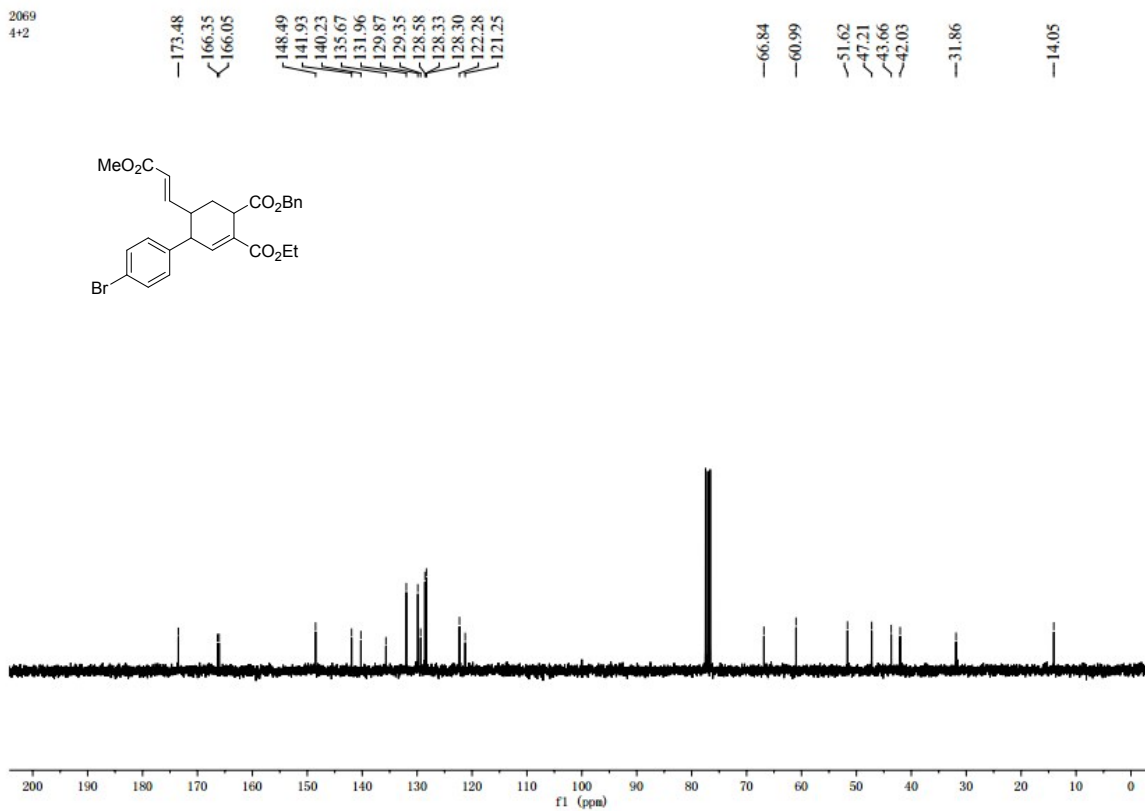
Compound 3s $^1\text{H NMR}$

1988

Compound 3s $^{13}\text{C NMR}$



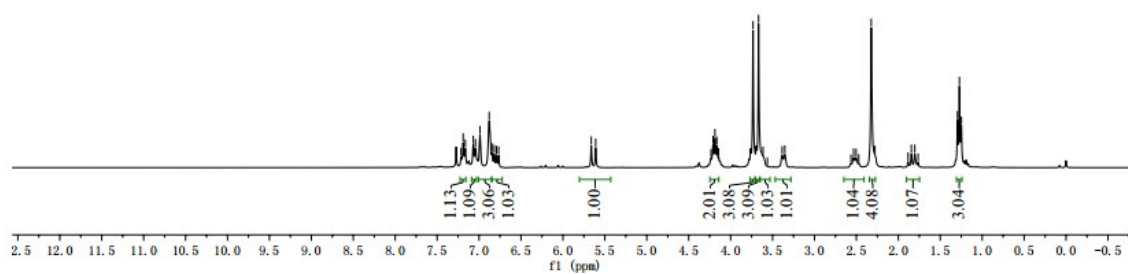
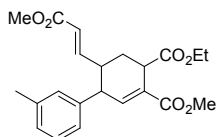
Compound 3t ¹H NMR



Compound 3t ¹³C NMR

2066
4+2

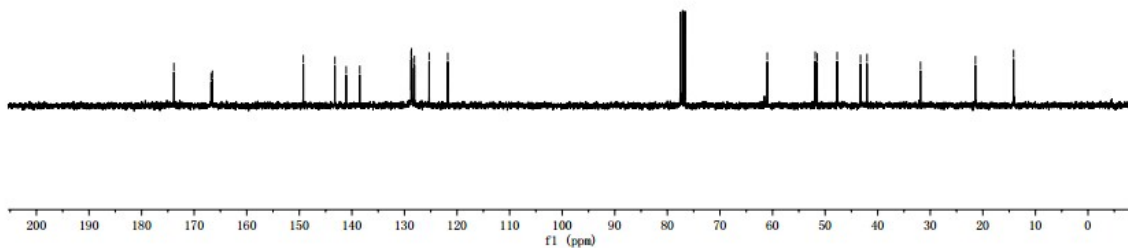
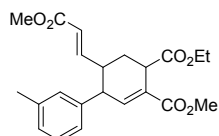
7.21
7.19
7.16
7.07
7.04
6.99
6.88
6.85
6.82
6.79
6.77
5.61
4.23
4.21
4.19
4.16
4.14
3.73
3.67
3.61
3.39
3.35
2.53
2.50
2.32
2.28
1.84
1.89
1.27
1.25



Compound 3u ¹H NMR

2066
4+2

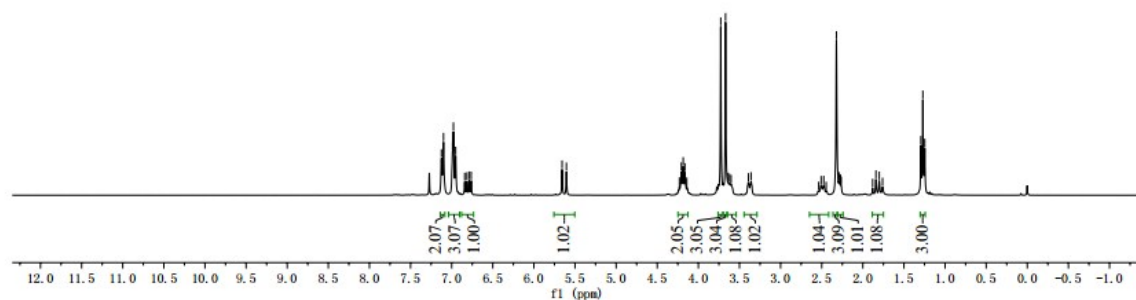
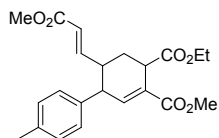
173.85
166.78
166.52
149.24
143.23
141.08
138.50
128.73
128.66
128.58
128.11
125.30
121.77
61.00
51.88
51.51
47.71
43.26
42.03
31.85
21.42
14.15



Compound 3u ¹³C NMR

2057
4+2

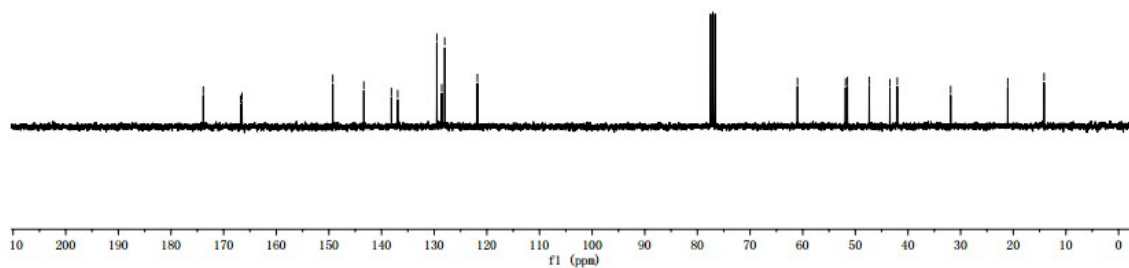
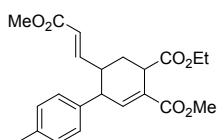
7.13
7.10
6.99
6.98
6.95
6.84
6.82
6.79
6.76
5.66
5.60
4.21
4.18
4.16
3.73
3.67
3.64
3.62
3.60
3.39
3.35
2.51
2.48
2.45
2.32
2.29
2.28
2.27
2.26
1.88
1.84
1.80
1.76
1.29
1.27
1.25



Compound 3v ¹H NMR

2057
4+2

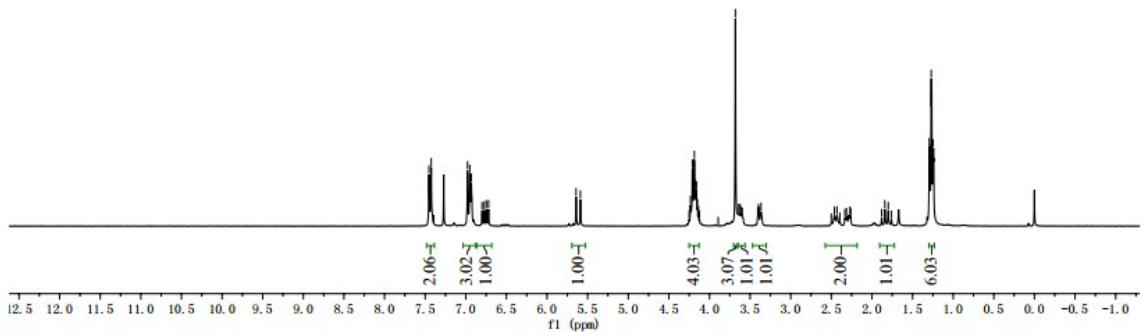
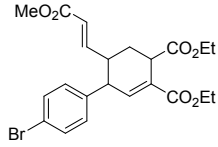
173.86
166.76
166.52
149.26
143.37
138.13
136.94
129.50
128.57
128.00
121.79
60.99
51.87
51.52
47.36
43.44
42.04
31.90
21.04
14.15



Compound 3v ¹³C NMR

2050
4+2

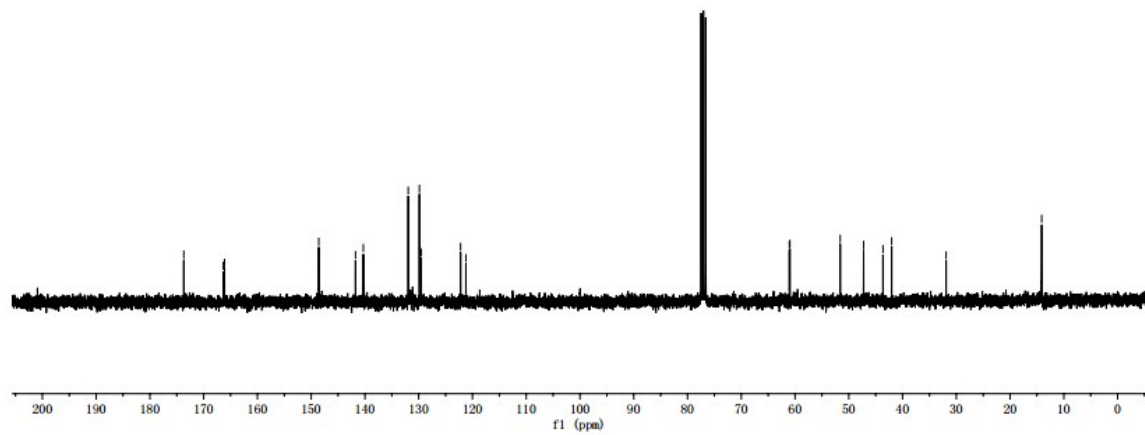
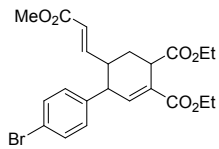
7.45
7.43
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6.95
6.93
6.80
6.77
6.75
6.72
5.64
5.59
4.23
4.21
4.19
4.17
4.16
4.15
3.68
3.62
3.40
3.37
2.46
2.43
2.39
2.33
2.31
2.27
2.26
1.88
1.84
1.80
1.76
1.29
1.27
1.26
1.25
1.24



Compound 3w ¹H NMR

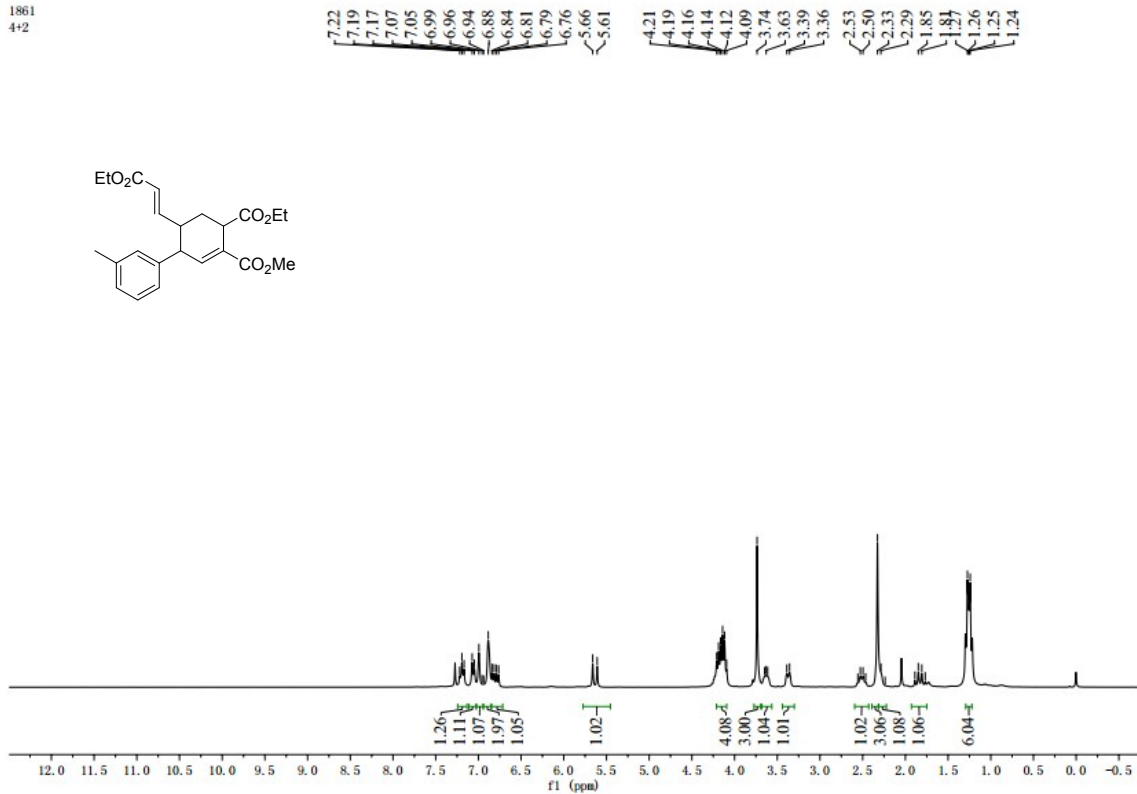
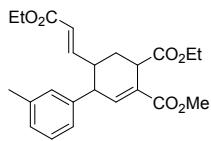
2050
4+2

173.69
166.35
166.12
148.59
141.75
140.30
131.95
129.87
129.53
122.21
121.22
61.05
60.95
51.60
47.24
43.64
42.03
31.90
14.12



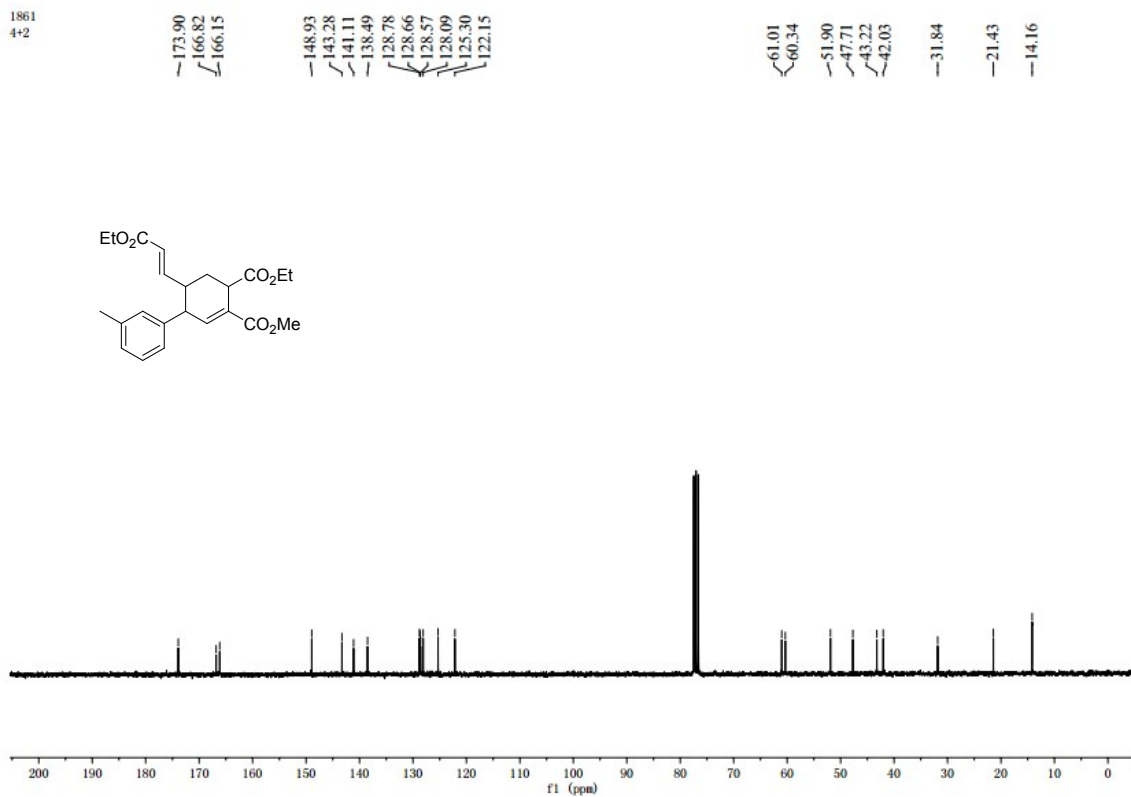
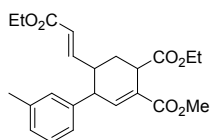
Compound 3w ¹³C NMR

1861
4+2



Compound 3x ¹H NMR

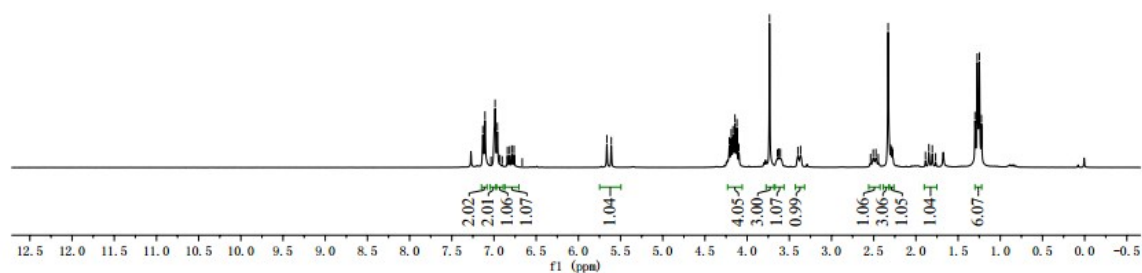
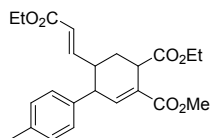
1861
4+2



Compound 3x ¹³C NMR

1849
dierdai4+2

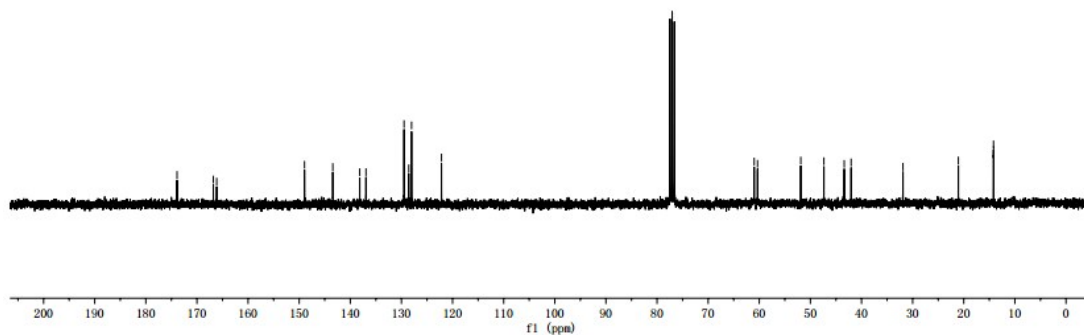
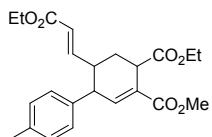
7.13
7.11
7.04
6.99
6.96
6.93
6.90
6.84
6.81
6.79
6.76
6.67
5.66
5.61
4.21
4.19
4.17
4.14
4.12
4.10
3.74
3.62
3.40
3.37
2.33
2.30
2.29
2.28
1.85
1.80
1.27
1.25
1.22



Compound 3y ¹H NMR

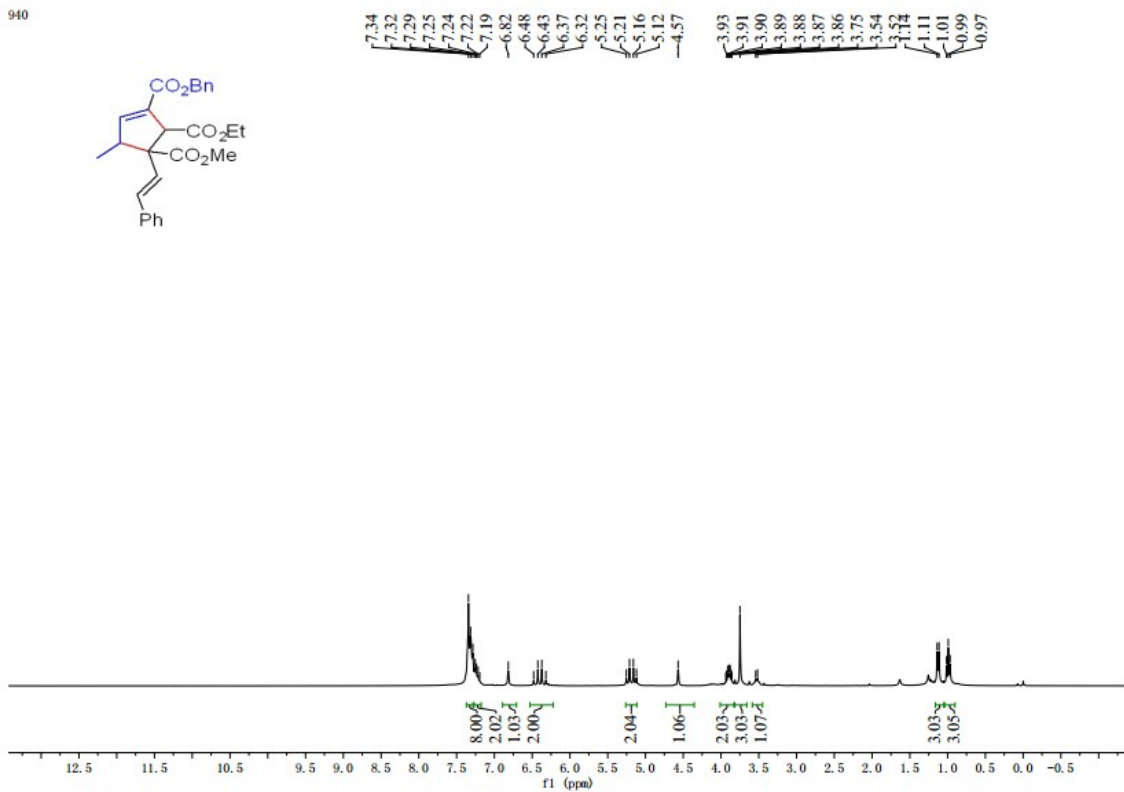
1849
dierdai4+2

173.9
166.8
166.1
149.0
143.4
138.2
136.9
129.5
128.6
128.0
122.2
61.0
60.3
51.9
47.4
43.4
42.0
31.9
21.1
14.2
14.2

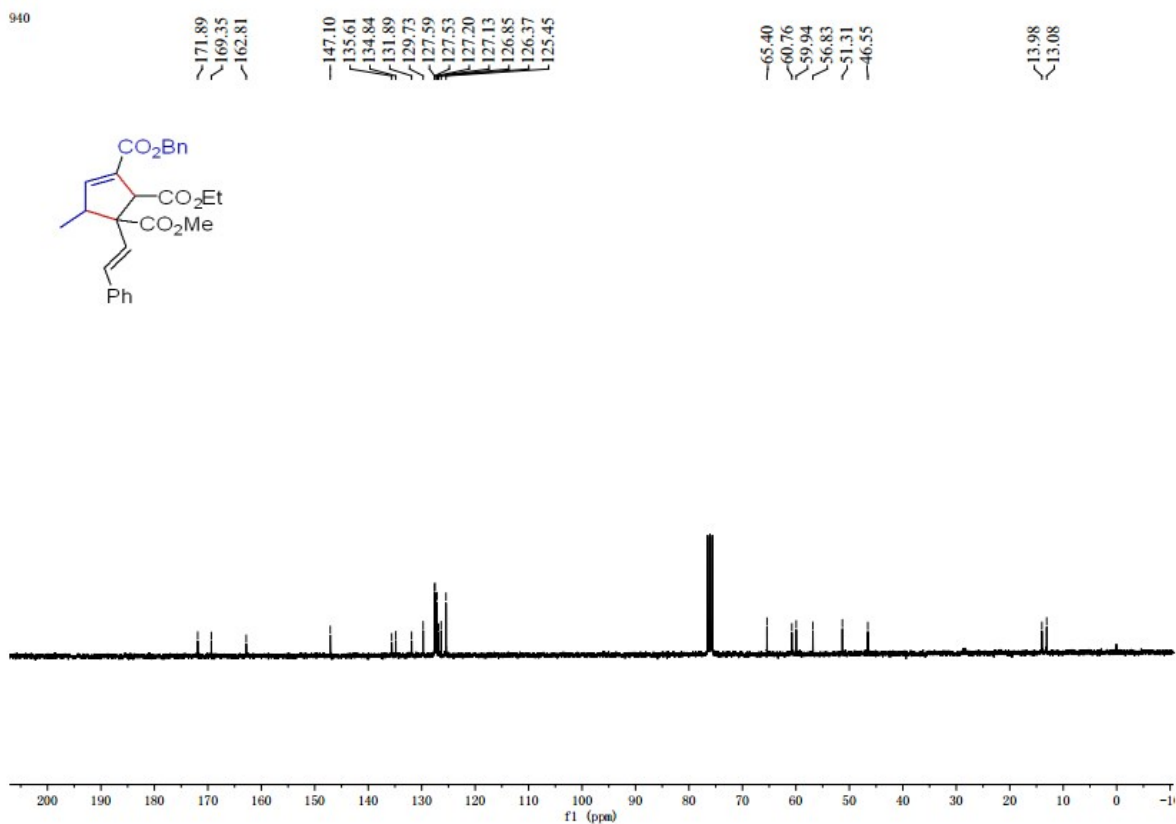


Compound 3y ¹³C NMR

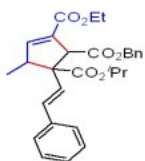
940

Compound 4a $^1\text{H NMR}$

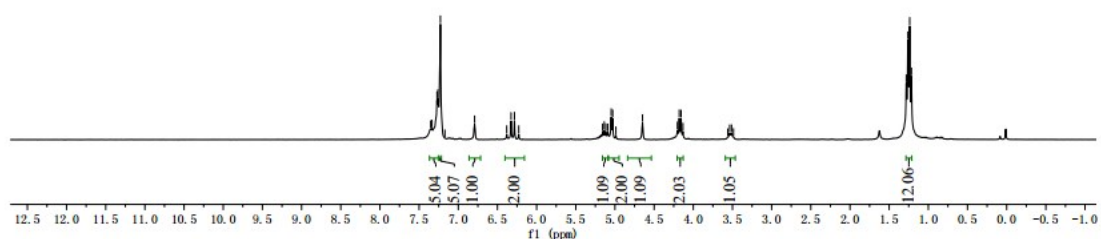
940

Compound 4a $^{13}\text{C NMR}$

1852
1

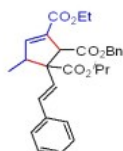


7.35
7.34
7.27
7.26
7.23
7.17
6.79
6.38
6.33
6.28
6.23
5.14
5.05
5.03
4.65
4.20
4.18
4.16
3.56
3.54
3.51
3.49
1.28
1.26
1.24
1.22

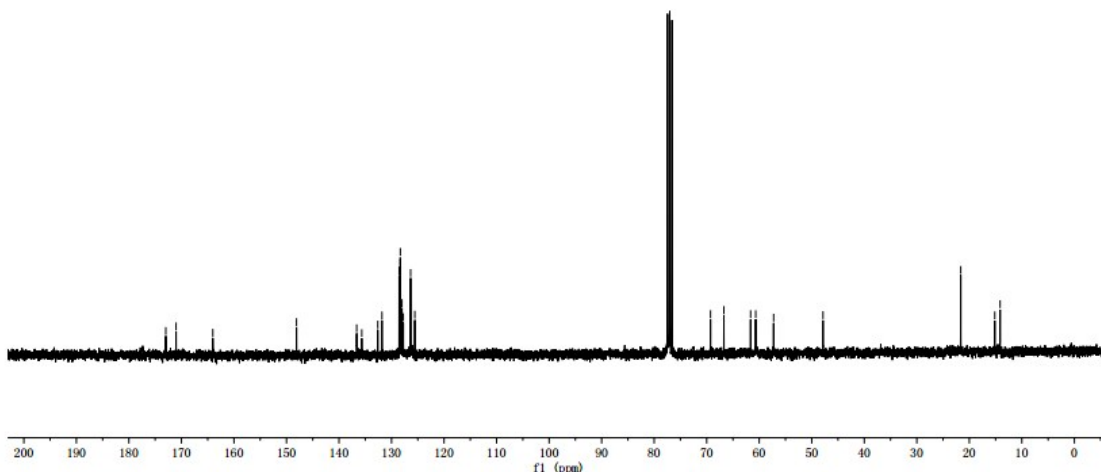


Compound 4b ¹H NMR

1852
1

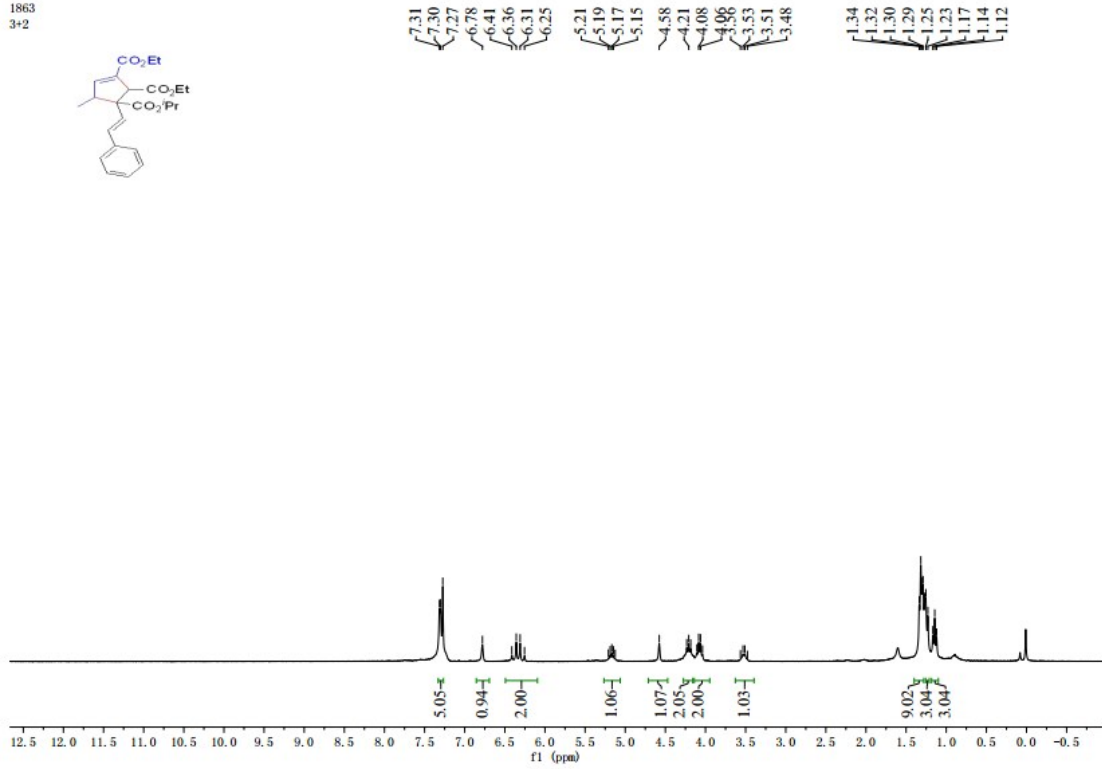
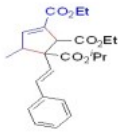


172.98
171.02
164.02
148.10
136.64
135.66
132.61
131.82
128.55
128.35
128.32
128.01
127.76
126.37
125.57
69.27
66.73
61.64
60.67
57.26
47.85
21.63
15.15
14.14



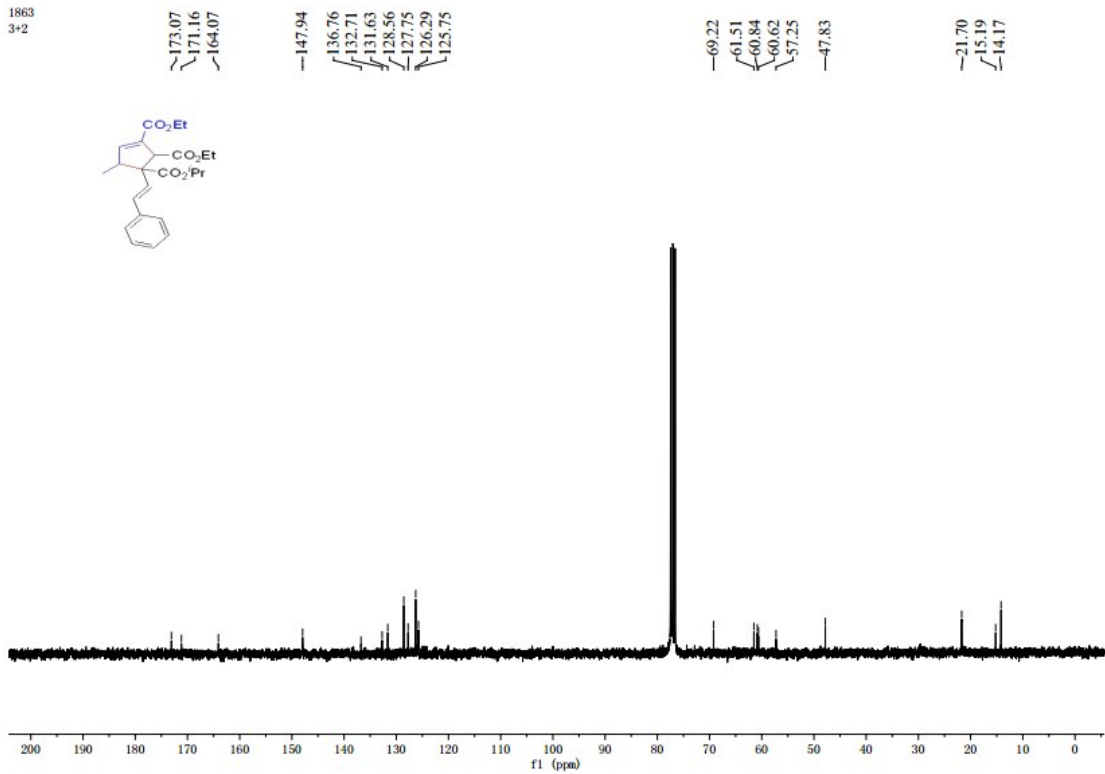
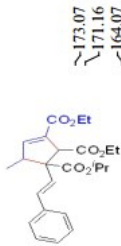
Compound 4b ¹³C NMR

1863
3+2



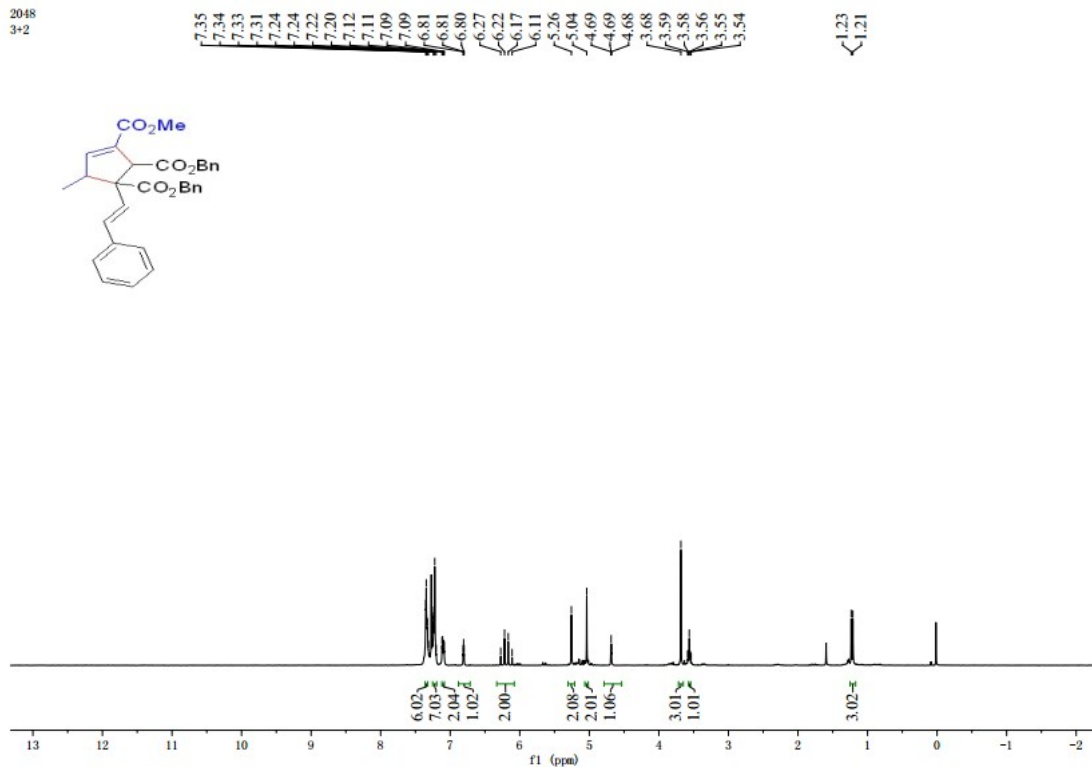
Compound 4c ¹H NMR

1863
3+2



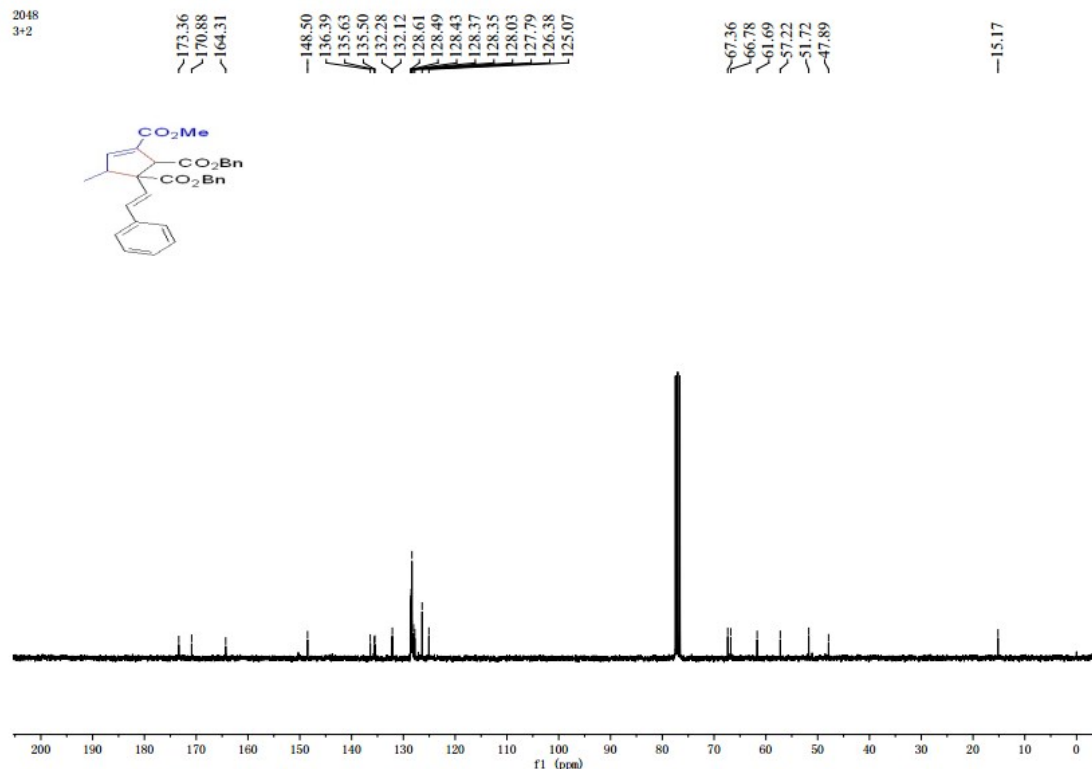
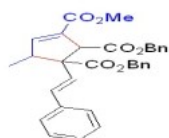
Compound 4c ¹³C NMR

2048
3+2



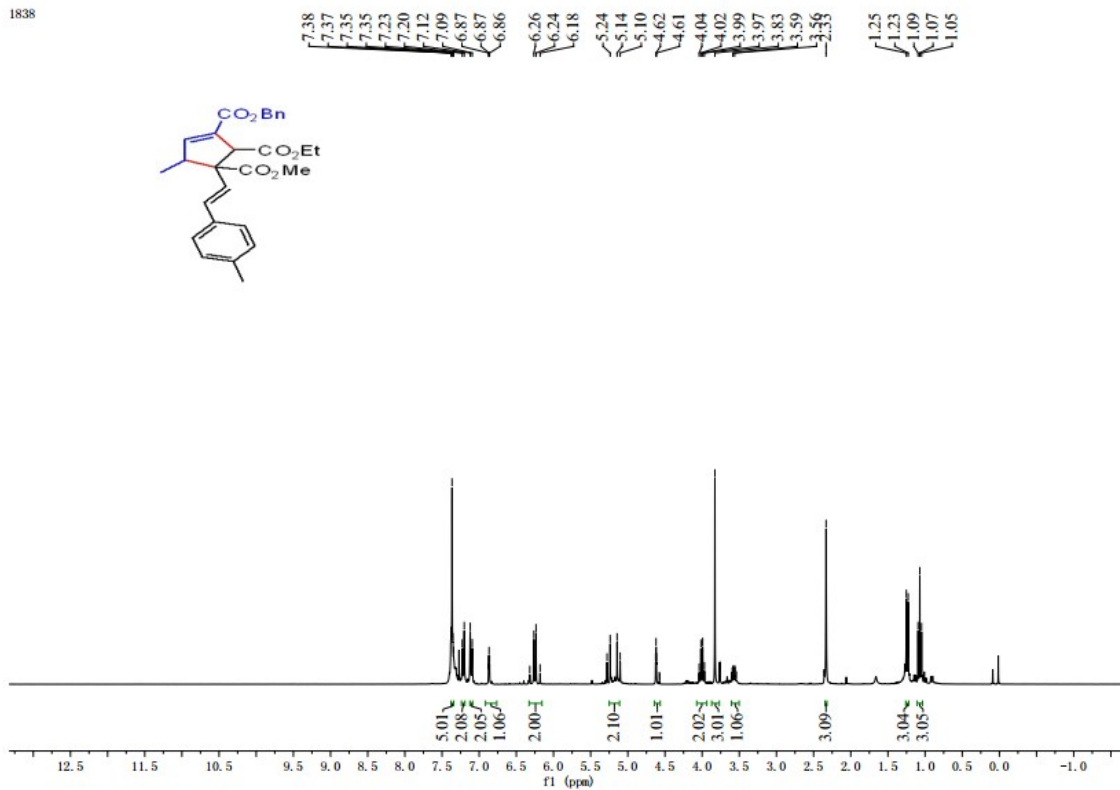
Compound 4d ¹H NMR

2048
3+2

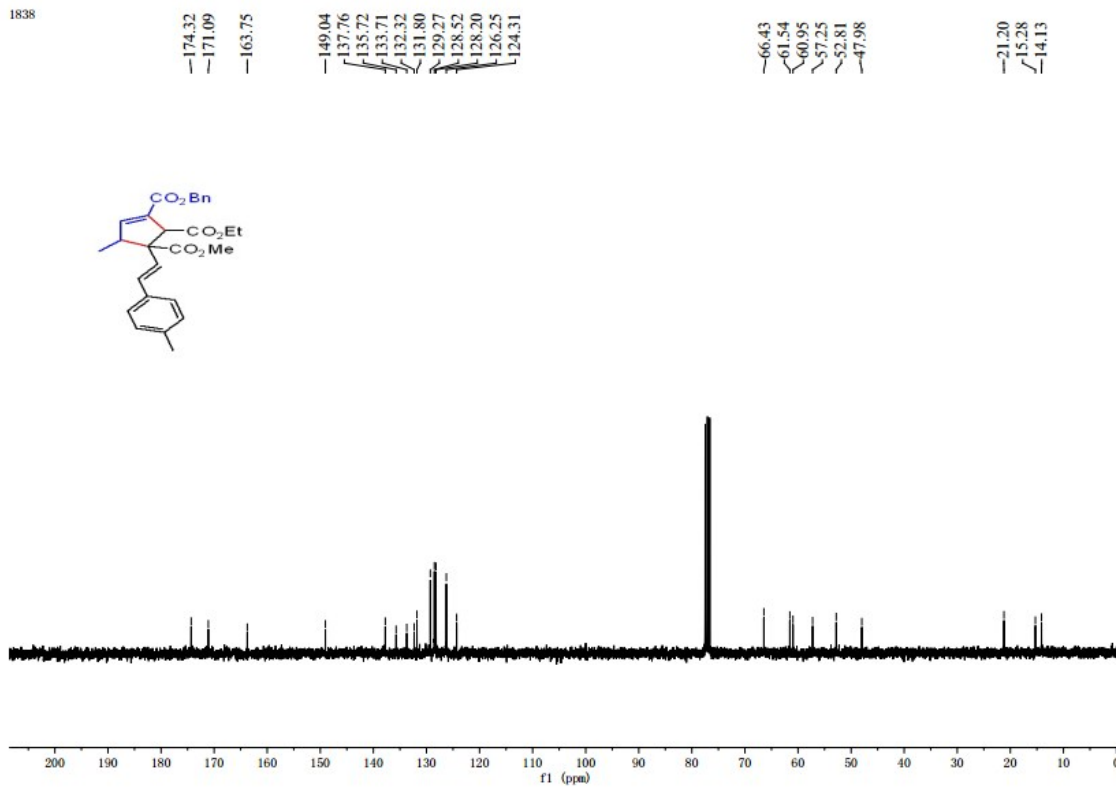


Compound 4d ¹³C NMR

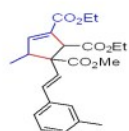
1838

Compound 4e ¹H NMR

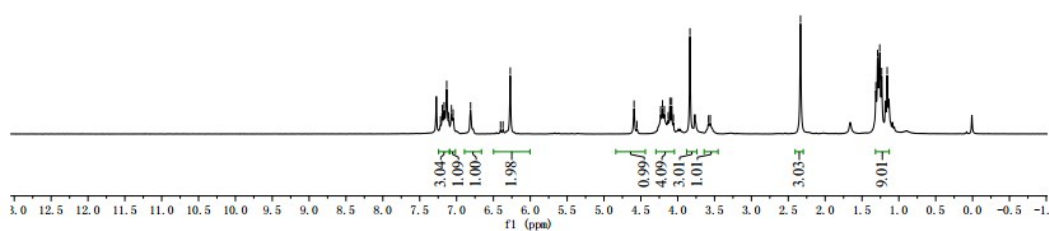
1838

Compound 4e ¹³C NMR

1861
3+2

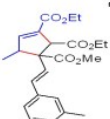


7.22
7.19
7.17
7.13
7.11
7.07
7.05
6.81
6.40
6.37
6.27
4.59
4.55
4.23
4.21
4.18
4.13
4.11
4.08
4.06
3.83
3.58
3.56
-2.33
1.31
1.29
1.23
1.16

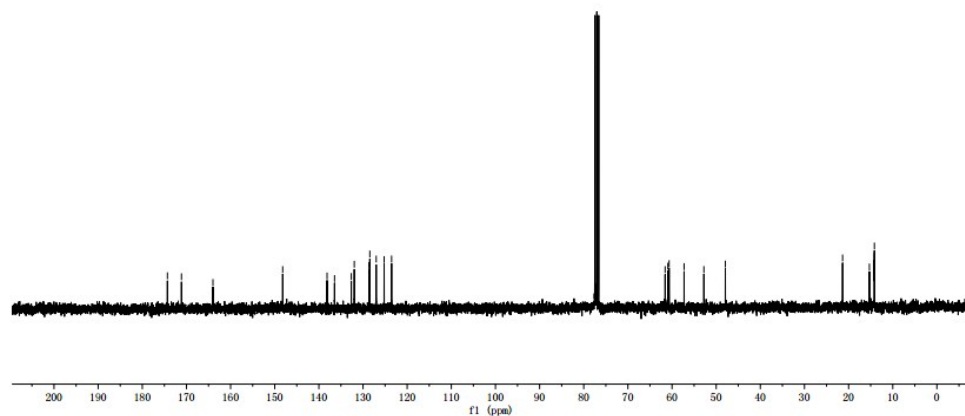


Compound 4g ¹H NMR

1861
3+2

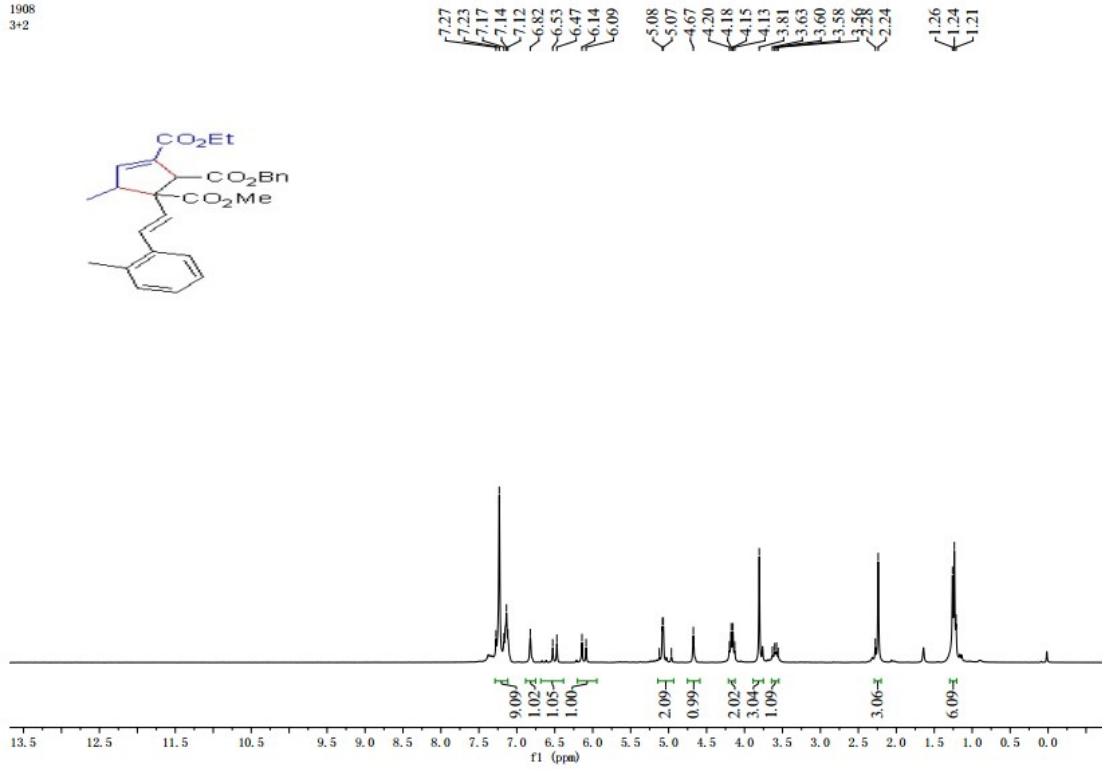


174.31
171.13
164.00
148.20
138.14
136.45
132.66
131.98
128.65
128.46
127.01
125.21
123.53
61.56
60.94
60.66
57.27
52.78
47.92
21.36
15.29
14.20
14.16



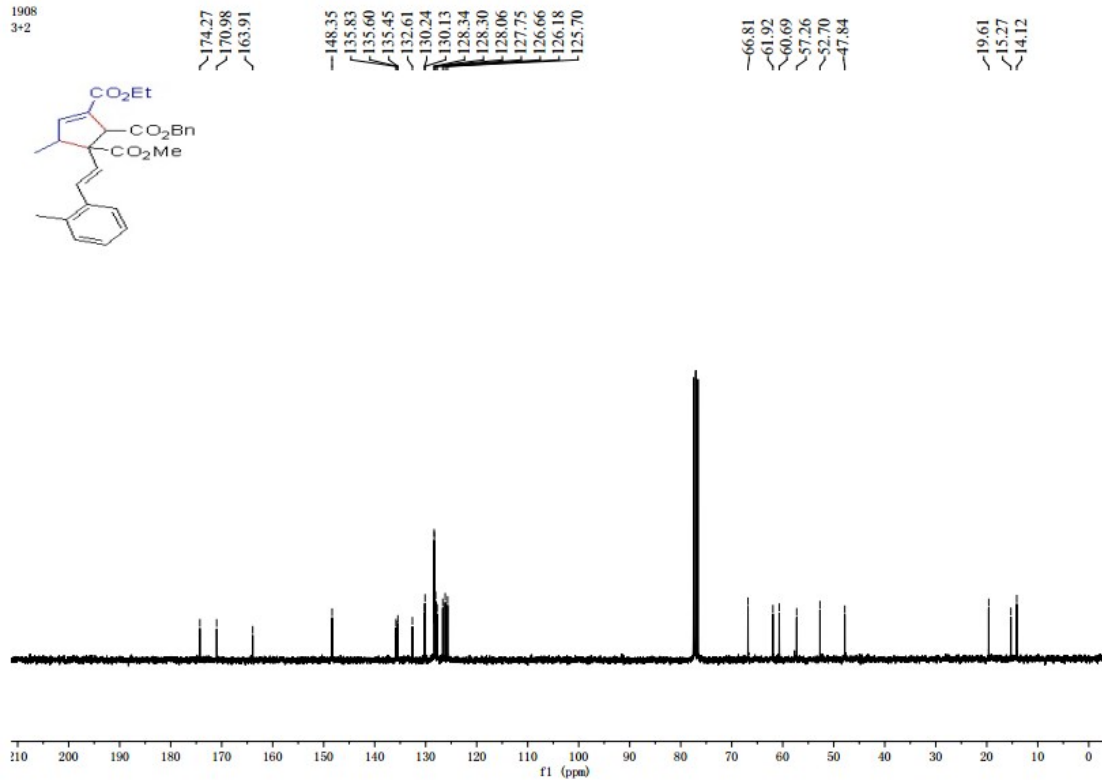
Compound 4g ¹³C NMR

1908
3+2

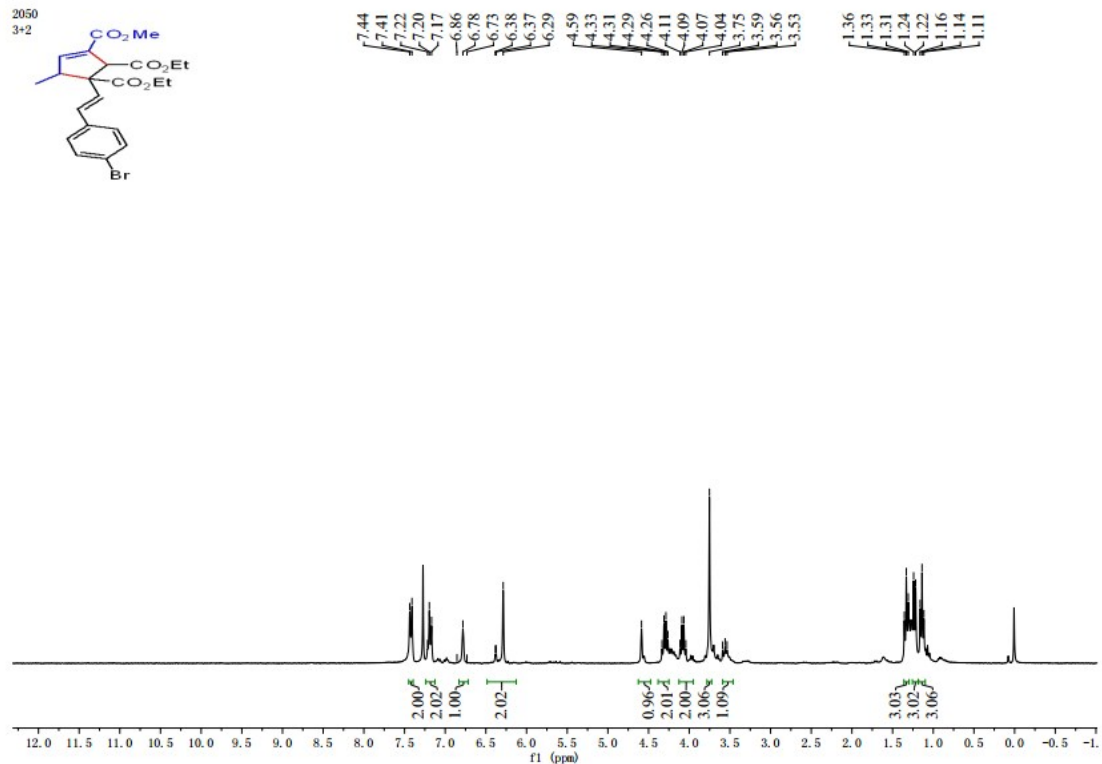


Compound 4h ¹H NMR

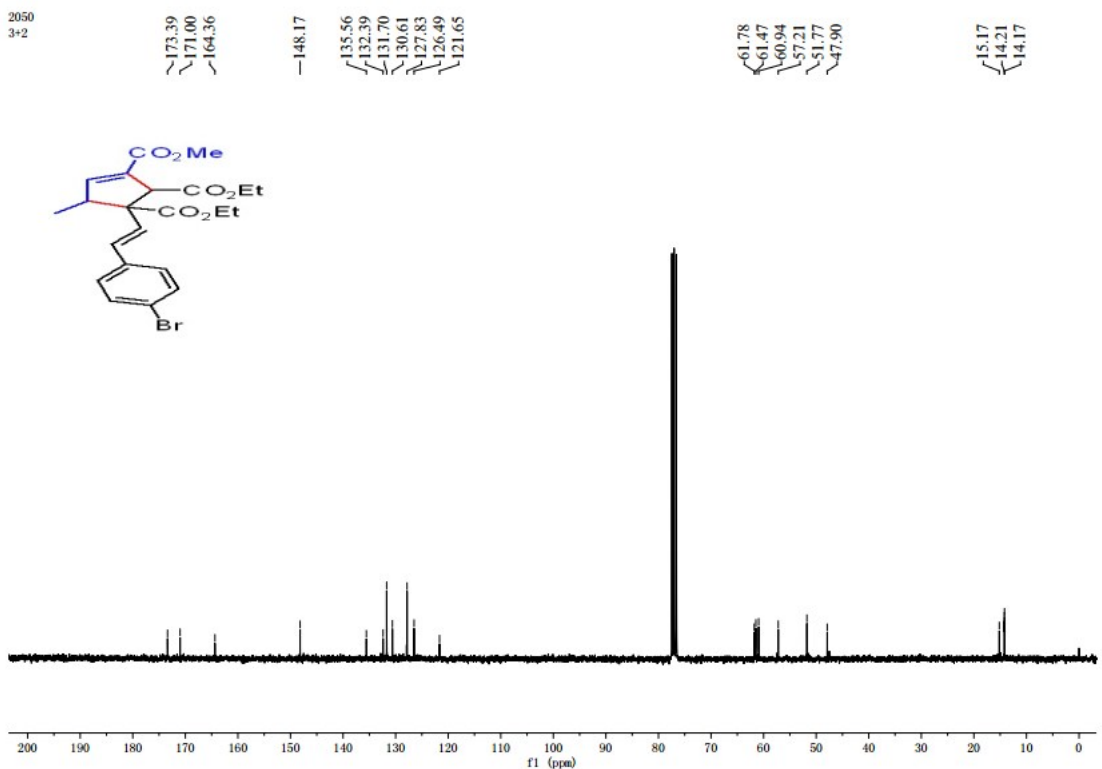
1908
3+2



Compound 4h ¹³C NMR



Compound 4i ^1H NMR



Compound 4i ^{13}C NMR

7. X-ray crystal structure

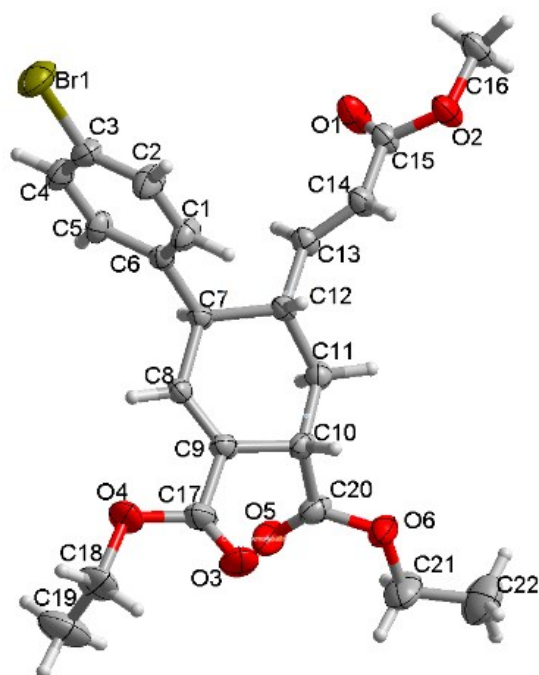
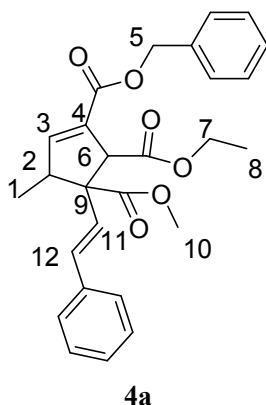


Table 1 Crystal data and structure refinement for 3w

Identification code	20190496
Empirical formula	C ₂₂ H ₂₅ BrO ₆
Formula weight	465.33
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	6.04519(13)
b/Å	20.9360(4)
c/Å	18.0511(4)
α/°	90
β/°	98.534(2)
γ/°	90
Volume/Å ³	2259.30(8)
Z	4
ρ _{calc} /g/cm ³	1.368
μ/mm ⁻¹	2.765
F(000)	960.0
Crystal size/mm ³	0.19 × 0.14 × 0.13
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.446 to 134.14
Index ranges	-5 ≤ h ≤ 7, -24 ≤ k ≤ 25, -21 ≤ l ≤ 21

Reflections collected	8982
Independent reflections	4030 [$R_{\text{int}} = 0.0284$, $R_{\text{sigma}} = 0.0359$]
Data/restraints/parameters	4030/29/293
Goodness-of-fit on F^2	1.032
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0588$, $wR_2 = 0.1584$
Final R indexes [all data]	$R_1 = 0.0708$, $wR_2 = 0.1732$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.03/-0.68

^1H and ^{13}C NMR Spectral Data of 4a



Position	^1H NMR (300 MHz)	^{13}C NMR (75 MHz)
1	1.13 (d, $J = 7.3$ Hz, 3H, CH_3) ppm	14.0 ppm
2	3.52 – 3.54 (m, 1H, CH) ppm	46.6 ppm
3	6.82 (s, 1H, $\text{CH}=\text{C}$) ppm	147.1 ppm
4		131.9 ppm
5	5.19 (q, $J = 12.5$ Hz, 2H, COOCH_2Ph) ppm	65.4 ppm
6	4.57 (s, 1H, CH)	56.8 ppm
7	3.86 – 3.94 (m, 2H, COOCH_2) ppm	59.9 ppm
8	0.99 (t, $J = 7.1$ Hz, 3H, CH_3) ppm	13.1 ppm

9		60.8 ppm
10	3.75 (s, 3H, COOCH ₃) ppm	51.3 ppm
11	6.35 (d, $J = 16.4$ Hz, 1H, C=CH)	126.9 ppm
	ppm	
12	6.45 (d, $J = 16.4$ Hz, 1H, CH=C)	135.6 ppm
	ppm	

