Supplementary Information

A gold(I)-catalysed three-component reaction via trapping oxonium ylides with allenamides

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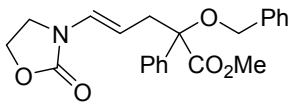
General Information

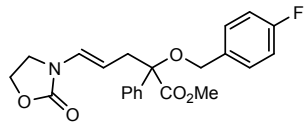
All reactions were carried out in oven dried Schlenk tubes. Extra dry solvents and alcohols **1** were purchased from Energy Chemical and JohnphosAu(MeCN)SbF_6 was purchased from Laajoo. Diazo compounds **2**[1], allenamides **3**[2] were prepared according to the reported literature procedures. Dimerization products of allenamides **5a**[3], O-H insertion product **6a**[4] and three-compound product **13a**[5] have been reported. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). Flash column chromatography was performed using silica gel (300-400 mesh). Melting points were determined on an Electrothermo Mel-Temp DLX 104 device and were uncorrected. All NMR spectra were recorded in $CDCl_3$ on a Bruker spectrometer at 400 or 500 MHz (^{1}H NMR), 101 or 126 MHz (^{13}C NMR) and 376 or 471 MHz (^{19}F NMR). Chemical shifts (δ value) were reported in ppm down field from internal tetramethylsilane (TMS). X-ray diffraction data (**4a**) were recorded on Oxford Diffraction Xcalibur Nova. HRMS (ESI) and LC-MS (ESI) Mass Spectra were recorded on SHIMADZU LCMS-IT-TOF mass spectrometer and Thermo TSQ QUANTUM LC-MS spectrometer, respectively.

General Procedure for the Three-Component Reaction

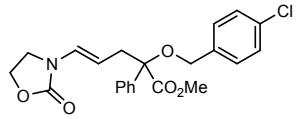
To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6, alcohol **1** (0.40 mmol), and 100 mg 4 Å MS in 4.0 mL 1,2-dichloroethane (DCE), aryldiazoacetate **2** (0.48 mmol) and allenamides **3** (0.48 mmol) in DCE (4.0 mL) were slowly introduced by syringe pump over 0.5 h at 25 ^{o}C under nitrogen atmosphere and the reaction solution was stirred for another 1.5 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtrated and the filtrate was evaporated in vacuum to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc : light petroleum ether = 1:10 ~ 1:2) to give the pure product **4**.



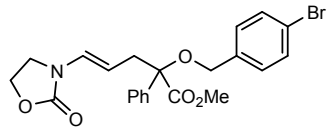
Methyl (*E*)-2-(benzyloxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4a). 132.6 mg, 85% yield. **White solid**, mp = 129-130 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 2H), 7.34 - 7.43 (m, 7H), 7.30 (dd, J = 13.8, 6.6 Hz, 1H), 6.72 (d, J = 14.4 Hz, 1H), 4.68 (dt, J = 14.4, 7.2 Hz, 1H), 4.60 (d, J = 11.1 Hz, 1H), 4.36 (dd, J = 18.1, 9.7 Hz, 3H), 3.76 (s, 3H), 3.63 – 3.46 (m, 2H), 3.18 – 3.06 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 155.3, 139.0, 138.3, 128.5, 128.3, 128.2, 127.5, 127.4, 126.7, 126.4, 104.0, 84.6, 66.6, 62.1, 52.4, 42.4, 36.7; HRMS (ESI$^+$) calculated for $C_{22}H_{23}NO_5Na$ [M+Na]$^+$: 404.1468, found 404.1467.



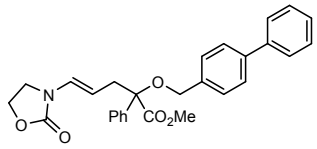
Methyl (*E*)-2-((4-fluorobenzyl)oxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4b). 121.4 mg, 76% yield. **White solid**, mp = 111-112 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 7.3 Hz, 2H), 7.41 – 7.28 (m, 5H), 7.03 - 6.95 (m, 2H), 6.69 (d, J = 14.4 Hz, 1H), 4.65 (dt, J = 14.4 Hz, 7.2 Hz, 1H), 4.52 (d, J = 11.0 Hz, 1H), 4.38 – 4.22 (m, 3H), 3.73 (s, 3H), 3.54 (dq, J = 17.1, 8.8 Hz, 2H), 3.07 (d, J = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 163.3 (d, J = 245.4 Hz), 155.2, 138.9, 134.1 (d, J = 3.1 Hz), 129.2 (d, J = 8.0 Hz), 128.5, 128.2, 126.8, 126.4, 115.1 (d, J = 21.4 Hz), 104.0, 84.8, 66.0, 62.1, 52.3, 42.4, 37.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.10; HRMS (ESI$^+$) calculated for $C_{22}H_{22}FNO_5Na$ [M+Na]$^+$: 422.1374, found 422.1375.



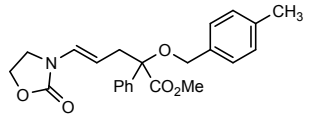
Methyl (*E*)-2-((4-chlorobenzyl)oxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4c). 153.1 mg, 92% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.4 Hz, 2H), 7.38 - 7.33 (m, 2H), 7.33 – 7.27 (m, 5H), 6.69 (d, J = 14.4 Hz, 1H), 4.65 (dt, J = 14.4, 7.3 Hz, 1H), 4.53 (d, J = 11.3 Hz, 1H), 4.34 (t, J = 8.1 Hz, 2H), 4.29 (d, J = 11.3 Hz, 1H), 3.74 (s, 3H), 3.61 – 3.47 (m, 2H), 3.06 (d, J = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 155.2, 138.8, 136.9, 133.2, 128.8, 128.5, 128.4, 128.3, 126.9, 126.4, 103.9, 84.9, 66.0, 62.1, 52.3, 42.4, 37.1; HRMS (ESI$^+$) calculated for $C_{22}H_{22}ClNO_5Na$ [M+Na]$^+$: 438.1079, found 438.1079.



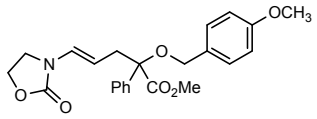
Methyl (*E*)-2-((4-bromobenzyl)oxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4d). 138.1 mg, 75% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 - 7.43 (m, 4H), 7.40 - 7.32 (m, 3H), 7.26 (d, J = 8.1 Hz, 2H), 6.71 (d, J = 14.4 Hz, 1H), 4.65 (dt, J = 14.4, 7.3 Hz, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.36 (t, J = 8.1 Hz, 2H), 4.27 (d, J = 11.4 Hz, 1H), 3.74 (s, 3H), 3.63 – 3.51 (m, 2H), 3.07 (d, J = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 155.3, 138.7, 137.3, 131.4, 129.2, 128.6, 128.4, 126.8, 126.4, 121.3, 103.9, 84.8, 65.9, 62.2, 52.5, 42.4, 37.0; HRMS (ESI$^+$) calculated for $C_{22}H_{22}BrNO_5Na$ [M+Na]$^+$: 482.0574, found 482.0571.



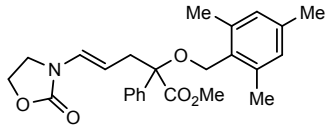
Methyl (*E*)-2-([1,1'-biphenyl]-4-ylmethoxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4e). 155.6 mg, 85% yield. **Colorless oil** ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 - 7.54 (m, 4H), 7.51 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.44 - 7.29 (m, 6H), 6.71 (d, J = 14.4 Hz, 1H), 4.66 (dt, J = 14.4, 7.2 Hz, 1H), 4.60 (d, J = 11.1 Hz, 1H), 4.37 (d, J = 11.1 Hz, 1H), 4.28 (t, J = 8.2 Hz, 2H), 3.73 (s, 3H), 3.56 – 3.42 (m, 2H), 3.15 – 3.03 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 155.3, 140.9, 140.5, 139.0, 137.4, 128.9, 128.6, 128.3, 128.0, 127.3, 127.1, 127.1, 126.7, 126.4, 104.1, 84.7, 66.4, 62.2, 52.5, 42.4, 36.8; HRMS (ESI$^+$) calculated for $C_{28}H_{27}NO_5Na$ [M+Na]$^+$: 480.1781, found 480.1782.



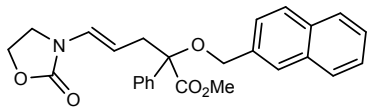
Methyl (*E*)-2-((4-methylbenzyl)oxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4f). 145.5 mg, 92% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 2H), 7.39 - 7.25 (m, 5H), 7.15 (d, J = 7.8 Hz, 2H), 6.68 (d, J = 14.4 Hz, 1H), 4.64 (dt, J = 14.4, 7.3 Hz, 1H), 4.52 (d, J = 10.8 Hz, 1H), 4.35 (t, J = 8.1 Hz, 2H), 4.29 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.61 – 3.49 (m, 2H), 3.15 – 3.01 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 155.3, 139.0, 137.2, 135.2, 129.0, 128.4, 128.2, 127.6, 126.6, 126.3, 104.1, 84.6, 66.5, 62.1, 52.4, 42.4, 36.7, 21.2; HRMS (ESI$^+$) calculated for $C_{23}H_{25}NO_5Na$ [M+Na]$^+$: 418.1625, found 418.1628.



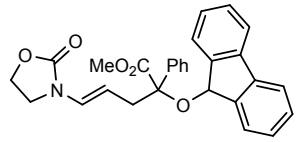
Methyl (*E*)-2-((4-methoxybenzyl)oxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4g). 138.3 mg, 84% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.5 Hz, 2H), 7.38 - 7.26 (m, 5H), 6.86 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 14.4 Hz, 1H), 4.64 (dt, J = 14.4, 7.2 Hz, 1H), 4.49 (d, J = 10.6 Hz, 1H), 4.33 (t, J = 8.1 Hz, 2H), 4.27 (d, J = 10.6 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.60 – 3.45 (m, 2H), 3.13 – 2.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 159.2, 155.2, 139.2, 130.5, 129.1, 128.4, 128.1, 126.7, 126.4, 113.8, 104.2, 84.6, 66.4, 62.1, 55.3, 52.3, 42.5, 36.8; HRMS (ESI$^+$) calculated for $C_{23}H_{25}NO_6Na$ [M+Na]$^+$: 434.1629, found 434.1627.



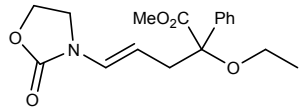
Methyl (*E*)-5-(2-oxooxazolidin-3-yl)-2-phenyl-2-((2,4,6-trimethylbenzyl)oxy)pent-4-enoate (4h). 152.5 mg, 90% yield. **White solid**, mp = 142-143 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 2H), 7.42 - 7.32 (m, 3H), 6.87 (s, 2H), 6.71 (d, J = 14.4 Hz, 1H), 4.75 – 4.68 (m, 1H), 4.67 (d, J = 9.5 Hz, 1H), 4.44 – 4.34 (m, 2H), 4.24 (d, J = 9.5 Hz, 1H), 3.79 (s, 3H), 3.62 – 3.51 (m, 2H), 3.17 – 3.05 (m, 2H), 2.32 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 155.2, 139.2, 138.1, 137.7, 131.2, 129.0, 128.3, 128.2, 126.5, 126.5, 104.6, 84.5, 62.1, 61.0, 52.2, 42.4, 37.1, 21.0, 19.7; HRMS (ESI$^+$) calculated for $C_{25}H_{29}NO_5Na$ [M+Na]$^+$: 446.1938, found 446.1936.



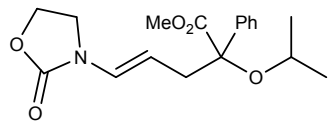
Methyl (*E*)-2-(naphthalen-2-ylmethoxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4i). 136.4 mg, 79% yield. **White solid**, mp = 97-98 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 7.8 Hz, 1H), 7.86 (dd, J = 27.6, 7.6 Hz, 2H), 7.59 – 7.44 (m, 6H), 7.44 - 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 6.70 (d, J = 14.4 Hz, 1H), 5.08 (d, J = 11.2 Hz, 1H), 4.80 (d, J = 11.2 Hz, 1H), 4.65 (dt, J = 14.4, 7.3 Hz, 1H), 4.39 – 4.26 (m, 2H), 3.81 (s, 3H), 3.54 – 3.37 (m, 2H), 3.16 (qd, J = 14.9, 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 155.2, 139.0, 134.0, 133.7, 131.7, 128.5, 128.4, 128.3, 126.6, 126.4, 126.0, 125.7, 125.4, 124.2, 104.2, 84.9, 65.0, 62.1, 52.5, 42.3, 37.0; HRMS (ESI$^+$) calculated for $C_{26}H_{25}NO_5Na$ [M+Na]$^+$: 454.1625, found 454.1628.



Methyl (*E*)-2-((9H-fluoren-9-yl)oxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4j). 109.3 mg, 60% yield. **White solid**, mp = 149-150 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 7.4 Hz, 1H), 7.55 – 7.51 (m, 3H), 7.50 – 7.43 (m, 3H), 7.37 - 7.32 (m, 1H), 7.30 - 7.25 (m, 1H), 7.24 - 7.18 (m, 1H), 7.00 - 6.90 (m, 1H), 6.71 (d, J = 14.5 Hz, 1H), 6.00 (d, J = 7.6 Hz, 1H), 5.89 (s, 1H), 4.91 (ddd, J = 14.5, 9.0, 5.6 Hz, 1H), 4.46 – 4.29 (m, 2H), 3.78 (s, 3H), 3.59 (dd, J = 16.1, 9.1 Hz, 1H), 3.52 (dd, J = 16.0, 9.1 Hz, 1H), 3.34 (dd, J = 14.3, 4.7 Hz, 1H), 3.05 (dd, J = 14.3, 9.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 155.3, 144.7, 144.2, 140.5, 140.4, 139.7, 129.1, 129.1, 128.8, 128.6, 127.5, 127.5, 127.3, 126.7, 126.5, 125.7, 119.6, 119.5, 105.1, 86.0, 78.1, 62.2, 52.3, 42.5, 38.7; HRMS (ESI$^+$) calculated for $C_{28}H_{25}NO_5Na$ [M+Na]$^+$: 478.1625, found 478.1629.

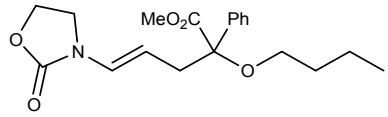


Methyl (E)-2-ethoxy-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4k). 35.8 mg, 28% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.6 Hz, 2H), 7.38 – 7.27 (m, 3H), 6.67 (d, J = 14.3 Hz, 1H), 4.61 (dt, J = 14.1, 7.0 Hz, 1H), 4.39 (t, J = 8.0 Hz, 2H), 3.71 (s, 3H), 3.66 – 3.56 (m, 2H), 3.52 – 3.43 (m, 1H), 3.37 – 3.28 (m, 1H), 3.00 (ddd, J = 21.1, 14.9, 7.2 Hz, 2H), 1.24 (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 155.3, 139.3, 128.4, 128.0, 126.6, 126.2, 104.1, 84.1, 62.1, 59.9, 52.4, 42.5, 35.8, 15.5; HRMS (ESI$^+$) calculated for $C_{17}H_{23}NO_5Na$ [M+Na]$^+$: 342.1312, found 342.1307.

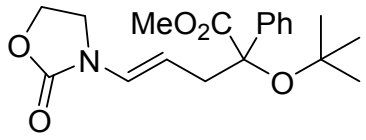


Methyl (E)-2-isopropoxy-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4l). 105.3 mg, 79% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 5H), 6.63 (d, J = 14.4 Hz, 1H), 4.65 (dt, J = 14.2, 7.0 Hz, 1H), 4.36 (t, J = 8.1 Hz, 2H), 3.78 (dt, J = 11.8, 5.9 Hz, 1H), 3.69 (s, 3H), 3.65 – 3.51 (m, 2H), 3.00 (ddd, J = 22.7, 14.9, 7.1 Hz, 2H), 1.16 (d, J = 5.9 Hz, 3H), 1.07 (d, J = 5.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 155.3, 139.9, 128.2, 128.0, 126.4, 126.4, 104.7, 84.3, 67.8, 62.1, 52.2, 42.4, 36.4, 24.2, 23.6; HRMS (ESI$^+$) calculated for $C_{18}H_{23}NO_5Na$ [M+Na]$^+$:

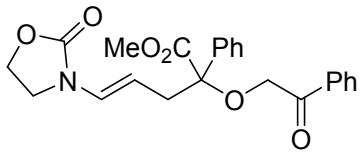
356.1468, found 356.1466.



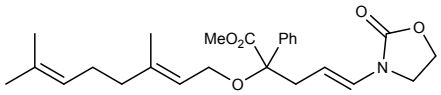
Methyl (E)-2-butoxy-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4m). 116.6 mg, 84% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.26 (m, 3H), 6.65 (d, *J* = 14.4 Hz, 1H), 4.58 (dt, *J* = 14.3, 7.1 Hz, 1H), 4.37 (t, *J* = 8.1 Hz, 2H), 3.70 (s, 3H), 3.66 – 3.52 (m, 2H), 3.43 (dd, *J* = 14.2, 7.1 Hz, 1H), 3.25 (dd, *J* = 14.0, 6.9 Hz, 1H), 3.00 (ddd, *J* = 21.3, 15.0, 7.2 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.45 – 1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 155.3, 139.5, 128.3, 127.9, 126.5, 126.1, 104.1, 83.8 63.9, 62.1, 52.3, 42.4, 35.7, 32.1, 19.3, 13.9; HRMS (ESI$^+$) calculated for $C_{19}H_{25}NO_5Na$ [M+Na]$^+$: 370.1625, found 370.1628.



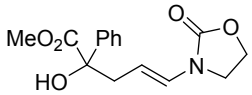
Methyl (*E*)-2-(tert-butoxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4n). 62.5 mg, 45% yield. **White solid**, mp = 203-204 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.42 (d, *J* = 8.1 Hz, 2H), 7.32 - 7.20 (m, 3H), 6.49 (d, *J* = 14.4 Hz, 1H), 4.52 (dt, *J* = 14.2, 7.1 Hz, 1H), 4.33 (t, *J* = 8.1 Hz, 2H), 3.69 (d, *J* = 1.3 Hz, 3H), 3.53 (dd, *J* = 16.9, 8.3 Hz, 1H), 3.46 (dd, *J* = 17.0, 8.2 Hz, 1H), 3.11 (dd, *J* = 15.1, 7.3 Hz, 1H), 2.94 (dd, *J* = 15.1, 6.8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 174.7, 155.2, 142.0, 128.0, 127.4, 126.0, 125.9, 105.5, 82.6, 77.1, 62.0, 52.1, 42.4, 39.4, 30.4; HRMS (ESI$^+$) calculated for $C_{19}H_{25}NO_5Na$ [M+Na]$^+$: 370.1625, found 370.1626.



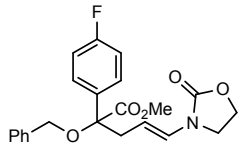
Methyl (*E*)-2-(2-oxo-2-phenylethoxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4o). 127.7 mg, 78% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.88 (d, *J* = 8.0 Hz, 2H), 7.55 - 7.49 (m, 1H), 7.46 – 7.38 (m, 4H), 7.37 - 7.33 (m, 2H), 7.31 (d, *J* = 6.9 Hz, 1H), 6.65 (d, *J* = 14.4 Hz, 1H), 4.89 – 4.77 (m, 2H), 4.51 (d, *J* = 16.1 Hz, 1H), 4.33 (t, *J* = 8.1 Hz, 2H), 3.75 (s, 3H), 3.60 – 3.50 (m, 2H), 3.00 (qd, *J* = 14.7, 7.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 195.5, 172.1, 155.3, 138.1, 135.2, 133.3, 128.7, 128.6, 128.5, 128.1, 126.8, 126.6, 104.2, 85.9, 68.7, 62.2, 52.4, 42.4, 38.7; HRMS (ESI$^+$) calculated for $C_{23}H_{23}NO_6Na$ [M+Na]$^+$: 432.1418, found 432.1417.



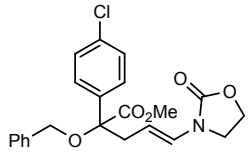
Methyl (*E*)-2-(((*E*)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4p). 138.5 mg, 81% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.7 Hz, 2H), 7.38 - 7.27 (m, 3H), 6.68 (d, J = 14.4 Hz, 1H), 5.40 (t, J = 6.6 Hz, 1H), 5.06 – 5.00 (m, 1H), 4.65 (dt, J = 14.4, 7.3 Hz, 1H), 4.38 (t, J = 8.1 Hz, 2H), 3.95 (dd, J = 10.7, 6.9 Hz, 1H), 3.77 (dd, J = 10.5, 7.1 Hz, 1H), 3.72 (s, 3H), 3.66 – 3.55 (m, 2H), 3.01 (qd, J = 14.9, 7.3 Hz, 2H), 2.01 – 1.96 (m, 4H), 1.74 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 155.3, 140.2, 139.1, 131.9, 128.4, 128.1, 126.6, 126.3, 123.9, 121.5, 104.2, 84.2, 62.1, 61.1, 52.4, 42.5, 36.3, 32.3, 26.7, 25.7, 23.6, 17.7; HRMS (ESI$^+$) calculated for $C_{25}H_{33}NO_5Na$ [M+Na]$^+$: 450.2251, found 450.2253.



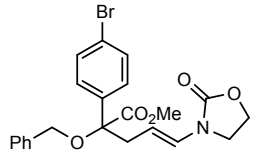
Methyl (*E*)-2-hydroxy-5-(2-oxooxazolidin-3-yl)-2-phenylpent-4-enoate (4q). To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6 and H_2O (40 mmol) in 4.0 mL DCE, aryldiazoacetate **2** (0.4 mmol), allenamide **3**(0.48 mmol) in DCE (4.0 mL) were introduced by syringe pump over 0.5 h at 25 ^{o}C under nitrogen atmosphere and the reaction solution was stirred for another 1.5 h. After the completion of the reaction, the reaction mixture was filtrated and the filtrate was evaporated in vacuum to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc : light petroleum ether = 1:10 ~ 1:2) to give 4n (61.7 mg, 53% yield); **White solid**, mp = 87-88 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.7 Hz, 2H), 7.41 - 7.29 (m, 3H), 6.77 (d, J = 14.4 Hz, 1H), 4.82 (ddd, J = 14.6, 8.2, 6.7 Hz, 1H), 4.41 (t, J = 8.1 Hz, 2H), 3.84 (br, 1H), 3.80 (s, 3H), 3.70 – 3.61 (m, 2H), 2.98 (dd, J = 14.2, 8.4 Hz, 1H), 2.78 (dd, J = 14.2, 6.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 155.3, 141.0, 128.4, 128.0, 127.2, 125.5, 104.0, 78.6, 62.2, 53.4, 42.5, 40.3; HRMS (ESI$^+$) calculated for $C_{15}H_{17}NO_5Na$ [M+Na]$^+$: 314.0999, found 314.1002.



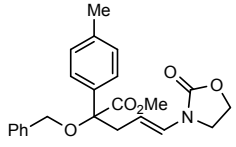
Methyl (*E*)-2-(benzyloxy)-2-(4-fluorophenyl)-5-(2-oxooxazolidin-3-yl)pent-4-enoate (4r). 103.8 mg, 65% yield. **White solid**, mp = 105-106 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.40 – 7.32 (m, 4H), 7.31 - 7.27 (m, 1H), 7.07 - 7.02 (m, 2H), 6.69 (d, J = 14.4 Hz, 1H), 4.65 – 4.52 (m, 2H), 4.39 – 4.32 (m, 3H), 3.74 (s, 3H), 3.61 – 3.48 (m, 2H), 3.15 – 3.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 162.4 (d, J = 247.3 Hz), 155.3, 138.0, 134.8 (d, J = 3.1 Hz), 128.4, 128.2 (d, J = 8.2 Hz), 127.7, 127.5, 126.8, 115.4 (d, J = 21.4 Hz), 103.7, 84.1, 66.6, 62.1, 52.6, 42.4, 36.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.95. HRMS (ESI$^+$) calculated for $C_{22}H_{22}FNO_5Na$ [M+Na]$^+$: 422.1374, found 422.1379.



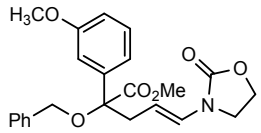
Methyl (*E*)-2-(benzyloxy)-2-(4-chlorophenyl)-5-(2-oxooxazolidin-3-yl)pent-4-enoate (4s). 119.8 mg, 72% yield. **White solid**, mp = 112-113 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.41 - 7.37 (m, 2H), 7.37 – 7.32 (m, 4H), 7.32 - 7.27 (m, 1H), 6.70 (d, J = 14.4 Hz, 1H), 4.61 – 4.53 (m, 2H), 4.39 – 4.33 (m, 3H), 3.74 (s, 3H), 3.61 – 3.47 (m, 2H), 3.07 (qd, J = 15.2, 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 155.3, 137.9, 137.6, 134.1, 128.7, 128.4, 127.8, 127.7, 127.5, 126.9, 103.5, 84.1, 66.7, 62.1, 52.6, 42.4, 36.4; HRMS (ESI$^+$) calculated for $C_{22}H_{22}ClNO_5Na$ [M+Na]$^+$: 438.1079, found 438.1079.



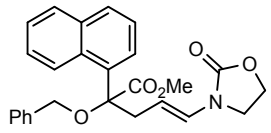
Methyl (*E*)-2-(benzyloxy)-2-(4-bromophenyl)-5-(2-oxooxazolidin-3-yl)pent-4-enoate (4t). 149.1 mg, 81% yield. **White solid**, mp = 117-118 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.3 Hz, 4H), 7.37 - 7.32 (m, 2H), 7.32 - 7.26 (m, 1H), 6.69 (d, J = 14.4 Hz, 1H), 4.62 – 4.52 (m, 2H), 4.35 (dd, J = 17.0, 9.3 Hz, 3H), 3.73 (s, 3H), 3.58 – 3.47 (m, 2H), 3.06 (qd, J = 15.1, 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 155.3, 138.2, 137.9, 131.6, 128.4, 128.1, 127.7, 127.5, 126.9, 122.3, 103.4, 84.2, 66.7, 62.2, 52.6, 42.4, 36.4; HRMS (ESI$^+$) calculated for $C_{22}H_{22}BrNO_5Na$ [M+Na]$^+$: 482.0574, found 482.0573.



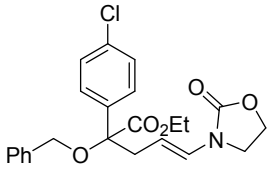
Methyl (*E*)-2-(benzyloxy)-5-(2-oxooxazolidin-3-yl)-2-(p-tolyl)pent-4-enoate (4u). 118.7 mg, 75% yield. **White solid**, mp = 107-108 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.9 Hz, 4H), 7.34 - 7.29 (m, 2H), 7.28 - 7.22 (m, 1H), 7.16 (d, J = 8.1 Hz, 2H), 6.68 (d, J = 14.4 Hz, 1H), 4.67 (dt, J = 14.4, 7.3 Hz, 1H), 4.54 (d, J = 11.2 Hz, 1H), 4.31 (dd, J = 9.9, 5.8 Hz, 3H), 3.72 (s, 3H), 3.60 – 3.44 (m, 2H), 3.12 – 2.99 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 155.2, 138.5, 138.0, 136.0, 129.1, 128.2, 127.4, 127.3, 126.7, 126.4, 104.3, 84.7, 66.5, 62.1, 52.2, 42.5, 36.9, 21.0; HRMS (ESI$^+$) calculated for $C_{23}H_{25}NO_5Na$ [M+Na]$^+$: 418.1625, found 418.1622.



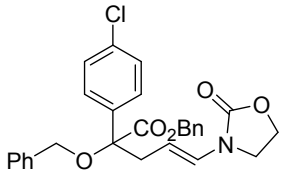
Methyl (*E*)-2-(benzyloxy)-2-(3-methoxyphenyl)-5-(2-oxooxazolidin-3-yl)pent-4-enoate (4v). 121.8 mg, 74% yield. **White solid**, mp = 93-94 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.4 Hz, 2H), 7.36 - 7.26 (m, 4H), 7.08 - 7.04 (m, 2H), 6.85 (dd, J = 8.0, 1.6 Hz, 1H), 6.70 (d, J = 14.4 Hz, 1H), 4.66 (dt, J = 14.4, 7.3 Hz, 1H), 4.56 (d, J = 11.2 Hz, 1H), 4.35 (d, J = 7.3 Hz, 2H), 4.33 (d, J = 3.7 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.60 – 3.50 (m, 2H), 3.12 – 3.02 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 159.7, 155.3, 140.6, 138.3, 129.5, 128.3, 127.5, 127.4, 126.7, 118.7, 113.3, 112.5, 104.0, 84.6, 66.5, 62.1, 55.3, 52.5, 42.4, 36.7; HRMS (ESI$^+$) calculated for $C_{23}H_{25}NO_6Na$ [M+Na]$^+$: 434.1574, found 434.1579.



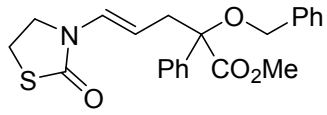
Methyl (*E*)-2-(benzyloxy)-2-(naphthalen-1-yl)-5-(2-oxooxazolidin-3-yl)pent-4-enoate (4w). 120.8 mg, 70% yield. **White solid**, mp = 143-144 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.88 – 7.78 (m, 3H), 7.60 (dd, J = 8.7, 0.9 Hz, 1H), 7.51 - 7.46 (m, 2H), 7.44 - 7.39 (m, 2H), 7.37 - 7.32 (m, 2H), 7.30 - 7.25 (m, 1H), 6.74 (d, J = 14.4 Hz, 1H), 4.65 (dt, J = 14.4, 7.2 Hz, 1H), 4.59 (d, J = 11.1 Hz, 1H), 4.38 (d, J = 11.1 Hz, 1H), 4.32 – 4.24 (m, 2H), 3.74 (s, 3H), 3.51 (dd, J = 16.4, 8.8 Hz, 1H), 3.45 (dd, J = 16.6, 8.7 Hz, 1H), 3.21 (d, J = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 155.3, 138.2, 136.4, 133.0, 128.5, 128.4, 127.6, 126.7, 126.6, 126.4, 125.8, 124.0, 104.0, 84.8, 77.4, 77.2, 76.9, 66.7, 62.1, 52.6, 42.4, 36.5, 29.7; HRMS (ESI$^+$) calculated for $C_{26}H_{25}NO_5Na$ [M+Na]$^+$: 454.1625, found 454.1628.



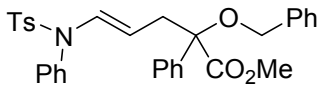
Ethyl (*E*)-2-(benzyloxy)-2-(4-chlorophenyl)-5-(2-oxooxazolidin-3-yl)pent-4-enoate (4x). 67.1 mg, 39% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 7.4 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 6.72 (d, J = 14.3 Hz, 1H), 4.65 – 4.54 (m, 2H), 4.39 (t, J = 8.4 Hz, 3H), 4.29 – 4.19 (m, 2H), 3.62 – 3.52 (m, 2H), 3.14 – 3.00 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 155.2, 138.0, 137.8, 134.0, 128.6, 128.4, 127.8, 127.7, 127.5, 126.9, 103.5, 84.0, 66.7, 62.1, 61.7, 42.4, 36.5, 14.2; HRMS (ESI$^+$) calculated for $C_{23}H_{24}NO_5ClNa$ [M+Na]$^+$: 452.1235, found 452.1235.



Benzyl (*E*)-2-(benzyloxy)-2-(4-chlorophenyl)-5-(2-oxooxazolidin-3-yl)pent-4-enoate (4y). 94.5 mg, 48% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.8 Hz, 2H), 7.35 – 7.26 (m, 10H), 7.25 – 7.22 (m, 2H), 6.65 (d, J = 14.3 Hz, 1H), 5.16 (dd, J = 33.5, 12.1 Hz, 2H), 4.57 – 4.48 (m, 2H), 4.36 – 4.27 (m, 3H), 3.47 – 3.35 (m, 2H), 3.12 – 2.97 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 155.2, 138.0, 137.6, 135.3, 134.1, 128.7, 128.6, 128.6, 128.5, 128.4, 127.9, 127.6, 127.5, 127.0, 103.4, 84.1, 67.3, 66.7, 62.1, 42.3, 36.5; HRMS (ESI$^+$) calculated for $C_{28}H_{26}NO_5ClNa$ [M+Na]$^+$: 514.1392, found 514.1392.



Methyl (E)-2-(benzyloxy)-5-(2-oxothiazolidin-3-yl)-2-phenylpent-4-enoate (4z). 50.9 mg, 32% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 2H), 7.42 – 7.27 (m, 8H), 6.84 (d, J = 14.5 Hz, 1H), 4.74 (dt, J = 14.5, 7.0 Hz, 1H), 4.56 (d, J = 11.1 Hz, 1H), 4.34 (d, J = 11.0 Hz, 1H), 3.74 (s, 3H), 3.64 (dt, J = 17.2, 8.9 Hz, 2H), 3.28 (t, J = 7.4 Hz, 2H), 3.09 (d, J = 7.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 170.3, 139.0, 138.3, 128.5, 128.3, 128.2, 127.5, 127.5, 126.9, 126.4, 105.1, 84.6, 77.3, 77.0, 76.8, 66.6, 52.4, 46.1, 37.0, 24.9; HRMS (ESI$^+$) calculated for $C_{22}H_{23}NO_4SNa$ [M+Na]$^+$: 420.1240, found 420.1243.



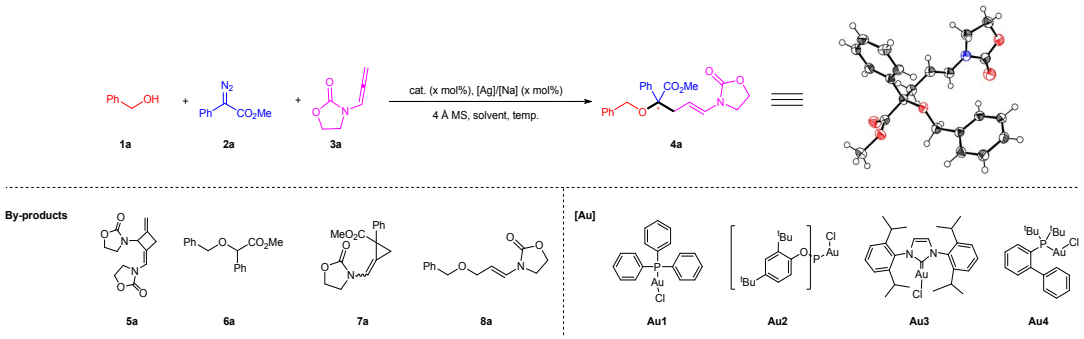
Methyl (E)-2-(benzyloxy)-5-((4-methyl-N-phenylphenyl)sulfonamido)-2-phenylpent-4-enoate (4A). 86.6 mg, 40% yield. **Colorless oil**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 13H), 7.21 (d, *J* = 6.7 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 14.1 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 4.45 (d, *J* = 11.0 Hz, 1H), 4.31 – 4.20 (m, 2H), 3.69 (s, 3H), 2.98 (dd, *J* = 14.7, 7.7 Hz, 1H), 2.88 (dd, *J* = 14.6, 7.3 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 143.7, 139.2, 138.2, 136.5, 135.8, 131.8, 130.2, 129.5, 129.3, 128.8, 128.3, 127.9, 127.4, 127.4, 126.2, 105.4, 84.8, 66.6, 52.3, 37.0, 21.6; HRMS (ESI$^+$) calculated for $C_{32}H_{31}NO_5SNa$ $[M+Na]^+$: 564.1815, found 564.1817.

Condition Optimization:

Initially, the alcohol **1a**, aryldiazoacetate **2a** and allenamide **3a** were used as the model substrates (Table S1). A variety of gold-complexes were evaluated for the model reaction in DCE at 25 ^{o}C (entries 1-8). To our delight, the three-component product **4a** was obtained in moderate yield (62%) combined with the allenamide dimer product **5a** in 5% yield and the O-H inserted product **6a** in 13% when the reaction was catalyzed by JohnphosAuSbF_6 (entry 4). It should be noted that the cyclopropane product **7a** was obtained in good yield (60%) when the reaction was catalyzed by Au4 and $AgSbF_6$ (entry 2). To further improve the yield of three-component product **4a**, we also tried commercially available gold catalyst - JohnphosAu(MeCN)SbF_6. Fortunately, when JohnphosAu(MeCN)SbF_6 was used as catalyst, the yield of **4a** reached 87%. After further optimizing solvent and temperature conditions, the conditions of DCE and 25 ^{o}C were still the best reaction conditions (entry 10-14). When the equivalent of JohnphosAu(MeCN)SbF_6 was reduced to 2.0 mol%, a considerable yield of **4a** (65%) still can be achieved (entry 15). The other transition metal catalysts, which have been reported to decompose the diazo compounds, were then screened under similar conditions, such as silver, palladium, copper, rhodium and boron catalysts (entries 16-21). Unfortunately, these reactions failed to gave the product **4a**. Instead, the O-H inserted product **6a** was obtained as major product (entries 16-20). While the by-

product **8a** was obtained in moderate yield (66%) by addition of **1a** to **3a** when the reaction was promoted by TPFPB (entries 21). Changing the addition sequences or methods gave no better results (entries 22 and 23). In addition, a relatively good yield (84%) of **4a** also can be contained when the reaction was carried out under open air (entry 24).

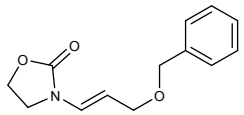
Table S1. Condition Optimization[a]



entry	cat. (x mol%)	[Ag]/[Na] (x mol%)	solvent	temp. (ºC)	time (h)	yield (%)[b] 4a	5a	6a	7a	8a
1[c]	Au1 (5.0)	$AgSbF_6$ (5.0)	DCE	25	5	19	< 5	< 5	23	< 5
2[c, d]	Au2 (5.0)	$AgSbF_6$ (5.0)	DCE	25	4	< 5	6	< 5	60	< 5
3[c]	Au3 (5.0)	$AgSbF_6$ (5.0)	DCE	25	6	< 5	11	< 5	< 5	< 5
4[c]	Au4 (5.0)	$AgSbF_6$ (5.0)	DCE	25	2	62	5	13	< 5	< 5
5[c]	Au4 (5.0)	$AgNTf_2$ (5.0)	DCE	25	2	58	6	13	< 5	< 5
6[c]	Au4 (5.0)	AgOTf (5.0)	DCE	25	5	54	< 5	< 5	< 5	< 5
7[c]	Au4 (5.0)	NaBArF (5.0)	DCE	25	8	26	< 5	58	< 5	< 5
8[e]	Au4 (5.0)	—	DCE	25	24	< 5	< 5	< 5	< 5	< 5
9[c, f]	**JohnphosAu(MeCN)SbF_6 (5.0)**	**—**	**DCE**	25	**2**	**87**	**6**	**6**	**< 5**	**< 5**
10[c]	JohnphosAu(MeCN)SbF_6 (5.0)	—	DCM	25	2	74	8	12	< 5	< 5
11[c]	JohnphosAu(MeCN)SbF_6 (5.0)	—	Toluene	25	2	32	13	26	< 5	< 5
12[c, e]	JohnphosAu(MeCN)SbF_6 (5.0)	—	THF	25	12	< 5	< 5	< 5	< 5	< 5
13[c]	JohnphosAu(MeCN)SbF_6 (5.0)	—	DCE	0	7	46	< 5	12	8	< 5
14[c]	JohnphosAu(MeCN)SbF_6 (5.0)	—	DCE	40	1.5	72	24	< 5	< 5	< 5
15[c]	JohnphosAu(MeCN)SbF_6 (2.0)	—	DCE	25	3	65	< 5	23	< 5	< 5

16	—	$AgSbF_6$ (5.0)	DCE	25	24	< 5	< 5	72	< 5	< 5
17	(η^3-C_3H_5)$_2Pd_2Cl_2$ (5.0)	—	DCE	25	1	< 5	< 5	95	< 5	< 5
18	$Cu(OTf)_2$ (5.0)	—	DCE	25	4	< 5	< 5	75	< 5	< 5
19	$[Rh(COD)Cl]_2$ (2.0)	—	DCE	65	3	< 5	< 5	43	< 5	< 5
20	$Rh_2(OAc)_4$ (2.0)	—	DCE	25	1	< 5	< 5	95	< 5	< 5
21	$(C_6F_5)_3B$ (5.0)	—	DCE	25	2	< 5	< 5	5	< 5	66
22[g]	JohnphosAu(MeCN)SbF_6 (5.0)	—	DCE	25	2	72	< 5	< 5	< 5	< 5
23[h]	JohnphosAu(MeCN)SbF_6 (5.0)	—	DCE	25	2	73	< 5	< 5	< 5	< 5
24[i]	JohnphosAu(MeCN)SbF_6 (5.0)	—	DCE	25	2	84	< 5	5	< 5	< 5

[a]Unless other noted, all reactions were carried out (**1a**/**2a**/**3a** = 0.2/0.24/0.24 mmol) in 4.0 mL solvent under nitrogen atmosphere until **2a** was consumed completely. [b]Determined by ^{1}H NMR spectroscopy analyses using 1,3,5-trimethoxybenzene as an internal standard. [c]The reaction was quenched by addition of pyridine (10 mol%). [d]*Z*-**7a** : *E*-**7a** = 1:2, the rate was determined by crude ^{1}H NMR. [e]All components were unconverted. [f]The isolated yield of **4a** was 85%. [g]Three components added once. [h]Three components added together for 0.5 h. [i]Under air condition.

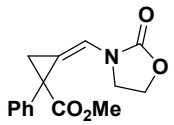


(*E*)-3-(3-(benzyloxy)prop-1-en-1-yl)oxazolidin-2-one (8a). Colorless oil; The product was identified as *E*-configuration by the ^{1}H NMR coupling constant (*J*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 6.91 (d, *J* = 14.3 Hz, 1H), 4.98 (dt, *J* = 14.0, 6.9 Hz, 1H), 4.51 (s, 2H), 4.44 (t, *J* = 8.0 Hz, 2H), 4.05 (d, *J* = 6.9 Hz, 2H), 3.71 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 138.1, 128.5, 127.8, 127.8, 127.7, 106.5, 72.0, 68.7, 62.2, 42.4; HRMS (ESI$^+$) calculated for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$: 256.0944, found 256.0944.

Procedure for Synthesis of 7a and 7b

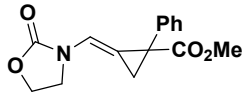
Synthesis of 7a: To a flame-dried 25-mL Schlenk flask charged with a magnetic stirring bar, 5.0 mol% JohnphosAu(MeCN)SbF_6 and 100 mg 4 Å MS, 2.0 mL of DCM were added under nitrogen atmosphere at 25 ^{o}C. methyl phenyldiazoacetate **2a** (0.10 mmol) and allenamide **3a** (0.15 mmol) dissolved in DCM (2.0 mL) were added by syringe pump over 1.0 h. The mixture was stirred for 4.0 h at 25 ^{o}C. Pyridine was used for quenching reaction before the reaction mixture was filtrated, and then the

filtrate was evaporated in vacuum to give the crude product. The crude product was purified by column chromatography (10:1 to 1:1 gradient of hexanes: ethyl acetate as eluents) to afford *Z*-**7a** : *E*-**7a** in total yield of 52% (*Z*-**7a** : *E*-**7a** = 1:2).



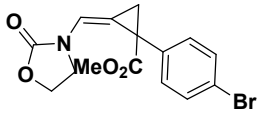
Methyl (*Z*)-2-((2-oxooxazolidin-3-yl)methylene)-1-phenylcyclopropane-1-carboxylate (*Z*-7a).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 1H), 7.29 – 7.22 (m, 2H), 4.40 – 4.29 (m, 1H), 3.92 – 3.83 (m, 1H), 3.80 – 3.69 (m, 2H), 2.57 (dd, J = 7.9, 2.1 Hz, 1H), 1.60 (dd, J = 7.9, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 155.7, 137.4, 129.2, 128.3, 127.7, 116.5, 108.2, 62.5, 52.8, 42.9, 31.3, 20.2. HRMS (ESI$^+$) calculated for $C_{15}H_{15}NO_4Na$ $[M+Na]^+$: 296.0893, found 296.0892.

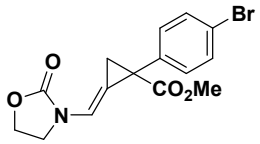


Methyl (*E*)-2-((2-oxooxazolidin-3-yl)methylene)-1-phenylcyclopropane-1-carboxylate (*E*-7a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.34 – 7.27 (m, 3H), 4.49 – 4.37 (m, 2H), 4.06 – 3.97 (m, 1H), 3.94 – 3.85 (m, 1H), 3.66 (s, 3H), 2.57 (dd, J = 7.8, 2.4 Hz, 1H), 1.87 (dd, J = 7.8, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 155.6, 139.1, 128.6, 127.4, 127.3, 116.8, 107.2, 62.4, 52.8, 43.3, 33.4, 21.5. HRMS (ESI$^+$) calculated for $C_{15}H_{15}NO_4Na$ $[M+Na]^+$: 296.0893, found 296.0891.

Synthesis of 7b: The *Z*-**7b** and *E*-**7b** were obtained in the same procedure in total yield of 27% (*Z*-**7a** : *E*-**7a** = 5:22).



Methyl (*Z*)-1-(4-bromophenyl)-2-((2-oxooxazolidin-3-yl)methylene)cyclopropane-1-carboxylate (*Z*-7b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.9 Hz, 2H), 7.23 (s, 1H), 7.16 (d, J = 7.8 Hz, 2H), 4.43 – 4.27 (m, 2H), 3.81 (dd, J = 16.2, 8.5 Hz, 1H), 3.76 (s, 3H), 3.70 (dd, J = 17.5, 8.7 Hz, 1H), 2.59 (d, J = 8.0 Hz, 1H), 1.59 (d, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 155.5, 138.1, 131.7, 131.7, 129.2, 128.3, 121.2, 117.0, 106.9, 62.4, 52.9, 43.2, 21.8. HRMS (ESI$^+$) calculated for $C_{15}H_{14}NO_4Br$ $[M+Na]^+$: 373.9999, found 373.9999.



Methyl (*E*)-1-(4-bromophenyl)-2-((2-oxooxazolidin-3-yl)methylene)cyclopropane-1-carboxylate (*E*-7b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.5 Hz, 2H), 7.38 (s, 1H), 7.24 (d, J = 7.3 Hz, 2H), 4.46 (dd, J = 14.3, 7.5 Hz, 2H), 4.03 (q, J = 8.3 Hz, 1H), 3.91 (q, J = 8.4 Hz, 1H), 3.67 (s, 3H), 2.58 (d, J = 7.8 Hz, 1H), 1.83 (d, J = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 155.6, 136.4, 131.4, 130.9, 121.8, 116.9, 107.6, 62.4, 52.9, 42.9, 30.8, 20.3. HRMS (ESI$^+$) calculated for $C_{15}H_{14}NO_4Br$ [M+Na]$^+$: 373.9999, found 373.9999.

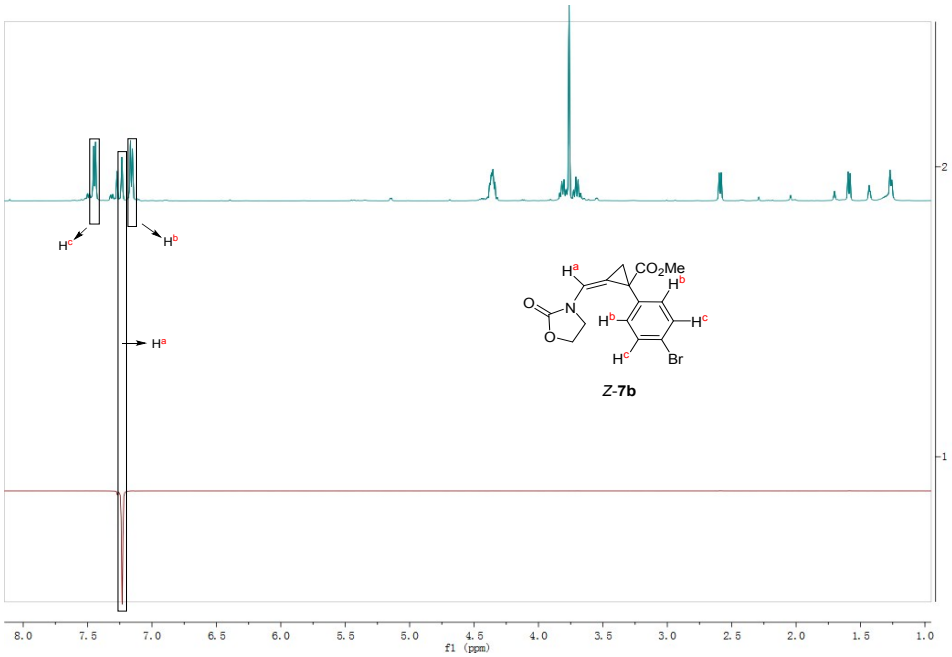


Figure S1. 1D NOE analysis of compound ***Z*-7b**.

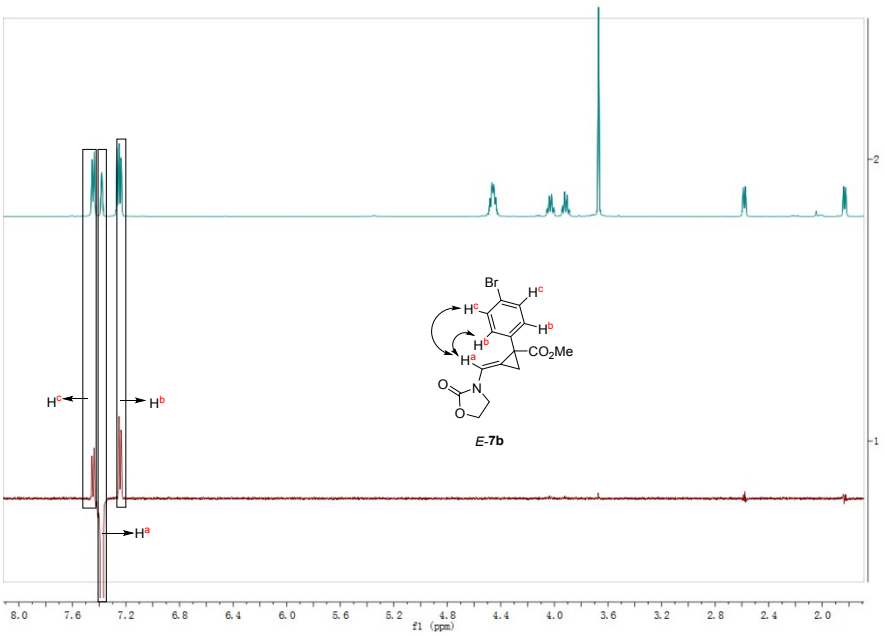
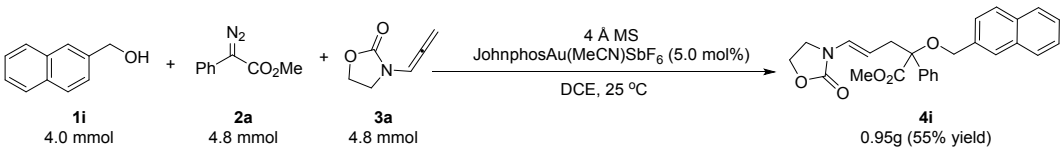


Figure S2. 1D NOE analysis of compound ***E*-7b**.

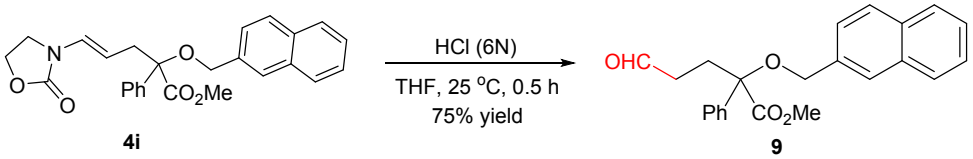
General Procedure for the Scale-Up Reaction



1i 4.0 mmol | **2a** 4.8 mmol | **3a** 4.8 mmol | **4i** 0.95g (55% yield)

To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6, alcohol **1i** (4.0 mmol), 500 mg 4 Å MS in 40 mL DCE, diazoacetate **2a** (4.8 mmol), allenamide **3a** (4.8 mmol) in DCE (40 mL) were introduced by syringe pump over 0.5 h under nitrogen atmosphere at 25 °C and the reaction solution was stirred for another 2.0 h. After the completion of the reaction, the reaction mixture was filtrated and the filtrate was evaporated in vacuum to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc : light petroleum ether = 1:10 ~ 1:2) to give **4i** (0.95g, 55% yield).

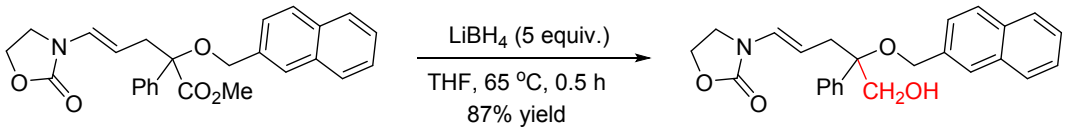
Further Transformations of 4i



4i → **9**

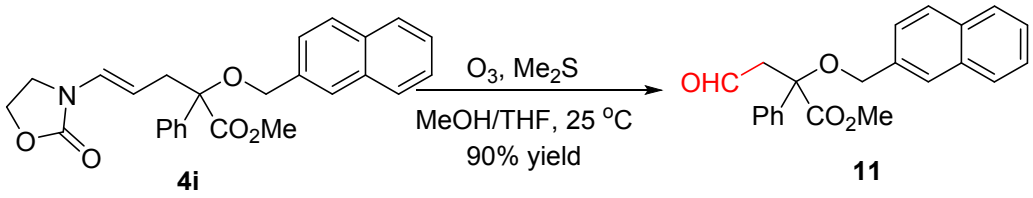
Synthesis of 9: To a solution of **4i** (43.1 mg, 0.10 mmol) in THF (4.0 mL) was added

HCl (6N) (1 mL, 6.0 mmol), the mixture was stirred at 25 °C for 0.5 h. Saturated $NaHCO_3$ was added until neutralization, the reaction mixture was extracted with EtOAc (2×10 mL), the combined organic layers was dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography on silica gel (EtOAc : light petroleum ether = 1:10 ~ 1:5) to give product **9** (27.3 mg, 75% yield, **colorless oil**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (t, J = 1.1 Hz, 1H), 7.83 (d, J = 8.1 Hz, 4H), 7.55 – 7.45 (m, 5H), 7.40 – 7.30 (m, 3H), 4.66 (d, J = 11.2 Hz, 1H), 4.51 (d, J = 11.2 Hz, 1H), 3.77 (s, 3H), 2.77 – 2.61 (m, 2H), 2.50 – 2.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 172.7, 138.8, 135.5, 133.3, 133.0, 128.6, 128.3, 128.1, 128.0, 127.7, 126.1, 126.0, 125.9, 125.6, 83.9, 66.9, 52.6, 38.3, 28.2; HRMS (ESI$^+$) calculated for $C_{23}H_{22}O_4Na$ [M+Na]$^+$: 385.1410, found 385.1411.

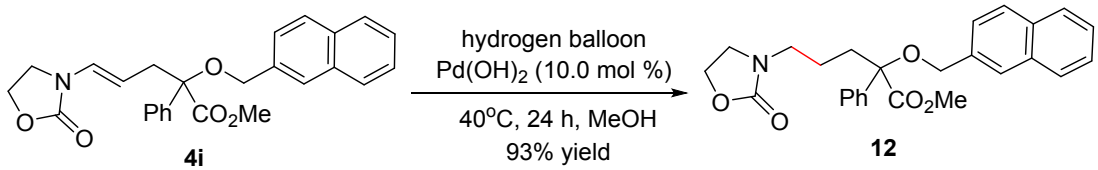


4i **10**

Synthesis of 10: To a 25mL flask with a magnetic stirring bar, **4i** (86.2 mg, 0.2 mmol) in anhydrous THF (2.0 mL) was added $LiBH_4$ (22 mg, 1 mmol, 5 equiv.) at 25 °C, and the reaction mixture was stirred at 65 °C for 0.5 h until the reaction was completed (monitored by TLC). And then H_2O (3.0 mL) was added to quench the reaction, and the aqueous layer was extracted with EtOAc (3×10 mL), the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuum after filtration, and the residue was purified by column chromatography on silica gel (EtOAc : light petroleum ether = 1:3 ~ 1:1) to give product **10** (72.2 mg, 87% yield, **colorless oil**); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H), 7.49 – 7.38 (m, 7H), 7.34 – 7.29 (m, 1H), 6.73 (d, J = 14.4 Hz, 1H), 4.70 (dt, J = 14.5, 7.4 Hz, 1H), 4.51 (q, J = 11.6 Hz, 2H), 4.36 – 4.28 (m, 2H), 3.97 (qd, J = 11.5, 5.0 Hz, 2H), 3.58 – 3.48 (m, 2H), 2.90 – 2.80 (m, 2H), 1.86 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 141.0, 136.1, 133.4, 132.9, 128.6, 128.2, 127.9, 127.8, 127.7, 126.6, 126.5, 126.2, 125.9, 125.9, 125.5, 105.1, 81.6, 65.7, 64.8, 62.1, 42.5, 35.9; HRMS (ESI$^+$) calculated for $C_{25}H_{25}NO_4Na$ [M+Na]$^+$: 426.1676, found 426.1675.

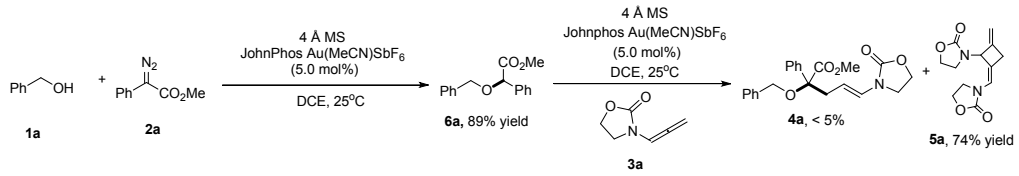


Synthesis of 11: After **4i** (86.2 mg, 0.20 mmol) was dissolved in MeOH (1 mL) and THF (1 mL), ozone was bubbled through the solution for 1.0 h until **4a** consumed completely monitored by TLC. Then, Me_2S (1.25 mL, 17.0 mmol) was added and stirred overnight. The solvent was evaporated and the resulting crude residue was chromatographed (EtOAc : light petroleum ether = 1:10 ~ 1:5) to give product **11** (60.6 mg, 90% yield, **colorless oil**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (t, J = 2.5 Hz, 1H), 7.85 – 7.77 (m, 4H), 7.56 – 7.51 (m, 2H), 7.50 – 7.45 (m, 3H), 7.44 – 7.36 (m, 3H), 4.82 (d, J = 11.1 Hz, 1H), 4.56 (d, J = 11.1 Hz, 1H), 3.82 (s, 3H), 3.40 – 3.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 172.0, 138.1, 135.1, 133.3, 133.0, 128.9, 128.8, 128.2, 128.0, 127.7, 126.4, 126.2, 126.1, 126.0, 125.7, 82.4, 67.6, 52.9, 50.1; HRMS (ESI$^+$) calculated for $C_{22}H_{20}O_4Na$ [M+Na]$^+$: 371.1254, found 371.1259.



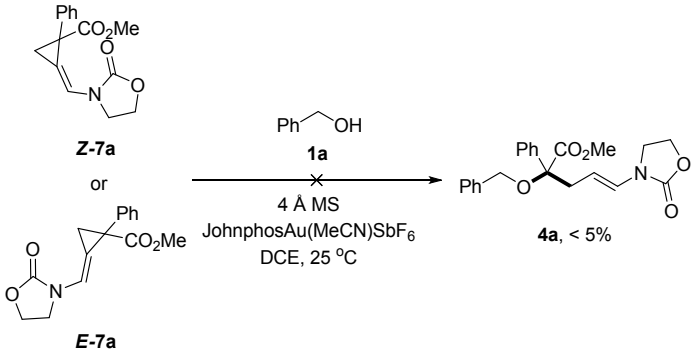
Synthesis of 12: A flask was charged with **4i** (43.1 mg, 0.10 mmol), $Pd(OH)_2$ (10.0 mol%) in 4.0 mL MeOH. The reaction mixture was stirred under a hydrogen atmosphere at 40 ºC for 24 h. The reaction mixture was filtered, and the filtrate were concentrated. Then the crude product was purified by flash chromatography on silica gel (EtOAc : light petroleum ether = 1:5 ~ 1:2) to give the pure product **12** (40.3 mg, 93%, **colorless oil**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.79 (m, 4H), 7.58 - 7.42 (m, 6H), 7.41 - 7.29 (m, 4H), 4.66 (d, J = 11.4 Hz, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.19 (ddd, J = 8.6, 7.3, 2.5 Hz, 2H), 3.78 (s, 3H), 3.33 – 3.20 (m, 4H), 2.50 – 2.36 (m, 1H), 2.33 – 2.25 (m, 1H), 1.50 (td, J = 14.4, 7.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 158.6, 139.3, 135.7, 133.3, 132.9, 128.5, 128.2, 128.1, 127.9, 127.7, 126.1, 126.1, 126.0, 125.9, 125.7, 84.5, 66.8, 61.6, 52.5, 44.1, 44.0, 32.7, 21.3; HRMS (ESI$^+$) calculated for $C_{26}H_{27}NO_5Na$ [M+Na]$^+$: 456.1781, found 456.1784.

Control Experiments

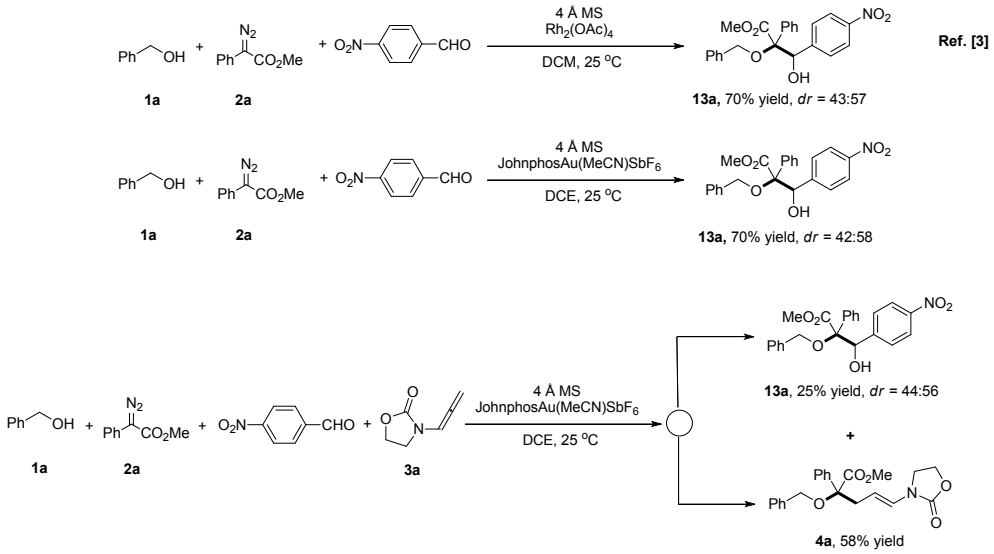


To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6, **1a** (0.4 mmol) and 100 mg 4 Å MS in 4.0 mL DCE, methyl phenyldiazoacetate **2a** (0.48 mmol) in DCE (4.0 mL) were introduced by syringe pump over 0.5 h at 25 °C under nitrogen atmosphere and the reaction solution was stirred for another 1.5 h. After the completion of the reaction, the reaction mixture was filtrated and the filtrate was evaporated in vacuum to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc : light petroleum ether = 1:20 ~ 1:10) to give **6a** in 89% yield.

To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6, **6a** (0.2 mmol), and 50 mg 4 Å MS in 2.0 mL DCE, **3a** (0.24 mmol) in DCE (1.0 mL) were introduced by syringe pump over 0.5 h under nitrogen atmosphere at 25 °C and the reaction solution was stirred for another 1.5 h. The reaction mixture was detected by ^{1}H NMR spectroscopy analyses and LC-MS. Product **4a** was not detected, and 74% of the allenamide dimer product **5a** was detected.



To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6, **1a** (0.2 mmol), *Z*-**7a** or *E*-**7a** (0.2 mmol), and 50 mg 4 Å MS in 2.0 mL DCE under nitrogen atmosphere at 25 °C and the reaction solution was stirred for another 2.0 h. The reaction mixture was detected by ^{1}H NMR spectroscopy analyses and LC-MS, and no three-component product 4a was observed.



To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6, **1a** (0.4 mmol) and *p*-nitrobenzenealdehyde (0.48 mmol) in 4.0 mL DCE, aryldiazoacetate **2a** (0.48 mmol) in DCE (4.0 mL) were introduced by syringe pump over 0.5 h at 25 °C under nitrogen atmosphere and the reaction solution was stirred for another 1.5 h. After the completion of the reaction, the reaction mixture was filtrated and the filtrate was evaporated in vacuum to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc : light petroleum ether = 1:20 ~ 1:10) to give **13a** in 70% yield with 42:58 *d.r.* (determined by ^{1}H NMR analysis).

To a Schlenk tube charged with 5.0 mol% JohnphosAu(MeCN)SbF_6, **1a** (0.4 mmol) and *p*-nitrobenzenealdehyde (0.48 mmol) in 4.0 mL DCE, methyl phenyldiazoacetate **2a** (0.48 mmol) and allenamide **3a** (0.48 mmol) in DCE (4.0 mL) were introduced by syringe pump over 0.5 h at 25 °C under nitrogen atmosphere and the reaction solution was stirred for another 1.5 h. The reaction mixture was detected by ^{1}H NMR spectroscopy analyses and LC-MS, affording 25% of **13a** (*d.r.* = 44:56) and 58% of **4a**.

References

[1] Muthusamy, S.; Sivaguru, M. *Org. Lett.*, **2014**, *16*, 4248 – 4251.

[2] Gholap, S. S.; Takimoto, M.; Hou, Z. *Chem. Eur. J.* **2016**, *22*, 8547 – 8552.

[3] Faustino, H.; Alonso, I.; Mascareñas, J. L.; López, F. *Angew. Chem., Int. Ed.* **2013**, *52*,6526–6530.

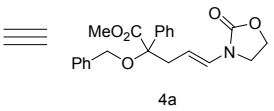
[4] Effenberger, F.; Hopf, M.; Ziegler, T.; Hudelmayer, J. *Chem. Ber.* **1991**, *124*, 1651-1659.

[5] Lu, C.-D.; Liu, H.; Chen, Z.-Y.; Hu, W.-H.; Mi, A.-Q. *Org. Lett.* **2005**, *7*, 83-86.

Single Crystal X-ray Diffraction Data of 4a

Product 4a (CDCC NO.:1878814)

Ellipsoids are drawn at the 50% probability level.



4a

```
Bond precision:  C-C = 0.0021 A          Wavelength=1.54184

Cell:            a=20.9188(7)     b=11.2773(4)       c=8.3717(3)
                 alpha=90         beta=98.639(3)     gamma=90
Temperature:     100 K

                 Calculated                Reported
Volume           1952.54(12)               1952.54(11)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C22 H23 N O5              C22 H23 N O5
Sum formula      C22 H23 N O5              C22 H23 N O5
Mr               381.41                    381.41
Dx,g cm-3        1.298                     1.297
Z                4                         4
Mu (mm-1)        0.755                     0.755
F000             808.0                     808.0
F000'            810.59
h,k,lmax         24,13,10                  24,13,10
Nref             3472                      3467
Tmin,Tmax        0.834,0.927               0.666,1.000
Tmin'            0.797

Correction method= # Reported T Limits: Tmin=0.666 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 67.079

R(reflections)= 0.0398( 2972)     wR2(reflections)= 0.1087( 3467)

S = 1.032                 Npar= 254
```

Alert level C

PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.381	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.597	5	Report

Alert level G

PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O3	109.6	Degree
PLAT793_ALERT_4_G	Model has Chirality at C8 (Centro SPGR)	R	Verify
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	78%	Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	3	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	7	Info

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  5 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  2 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
  1 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
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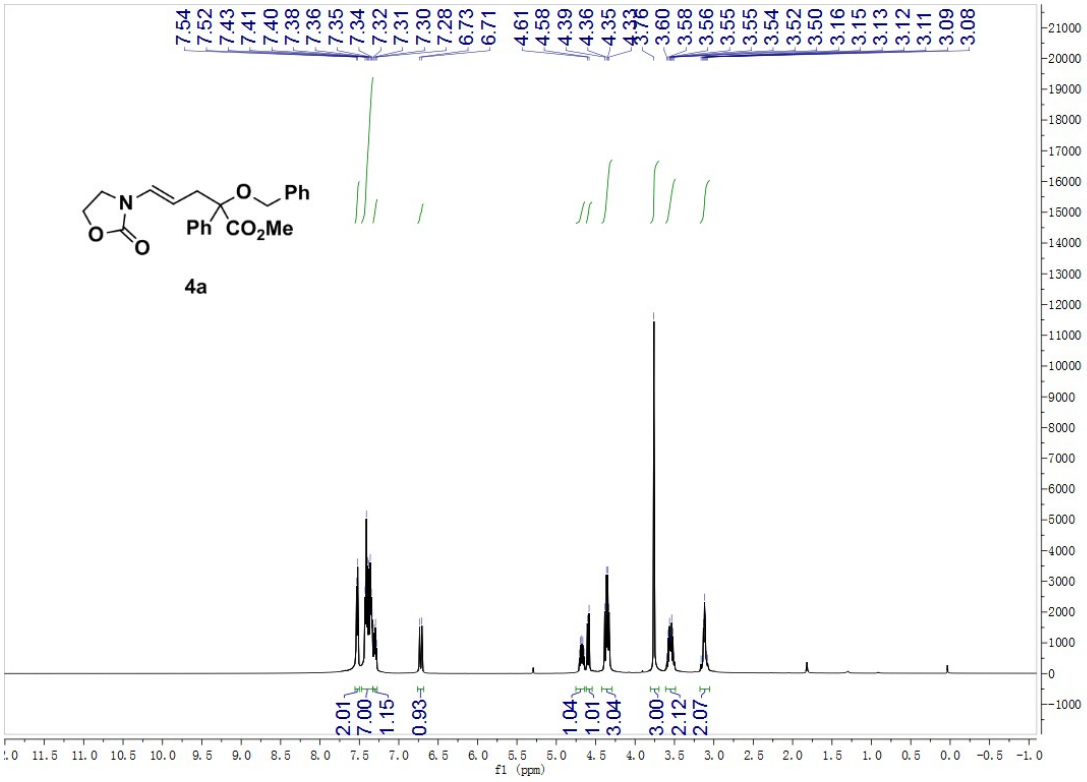
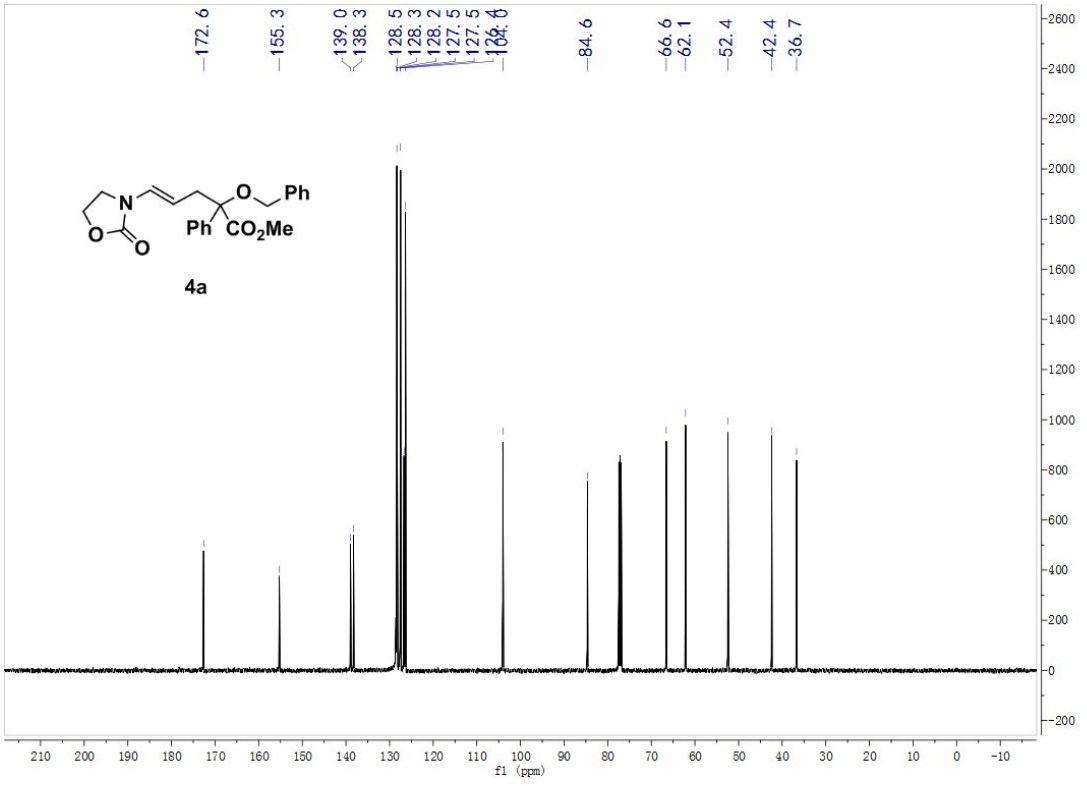
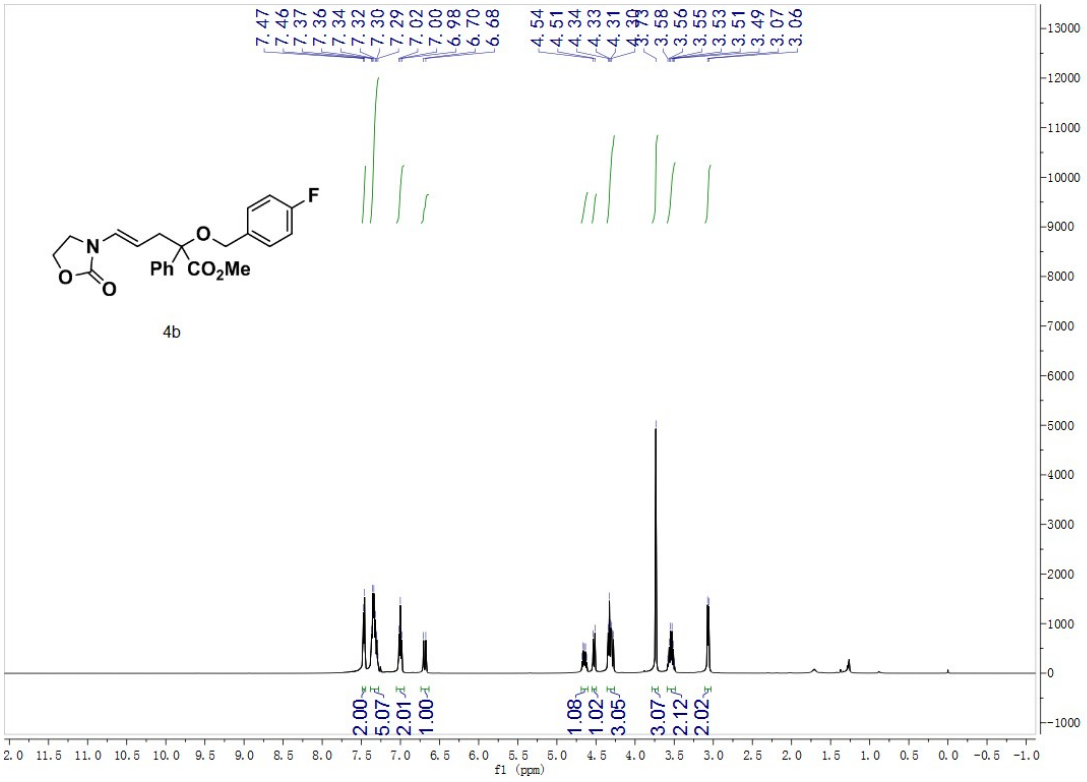
NMR Spectra of Products



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4.51
4.34
4.33
4.31
3.58
3.56
3.55
3.53
3.51
3.49
3.07
3.06
F
N
O
O
O
Ph
CO2Me
4b
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1.08
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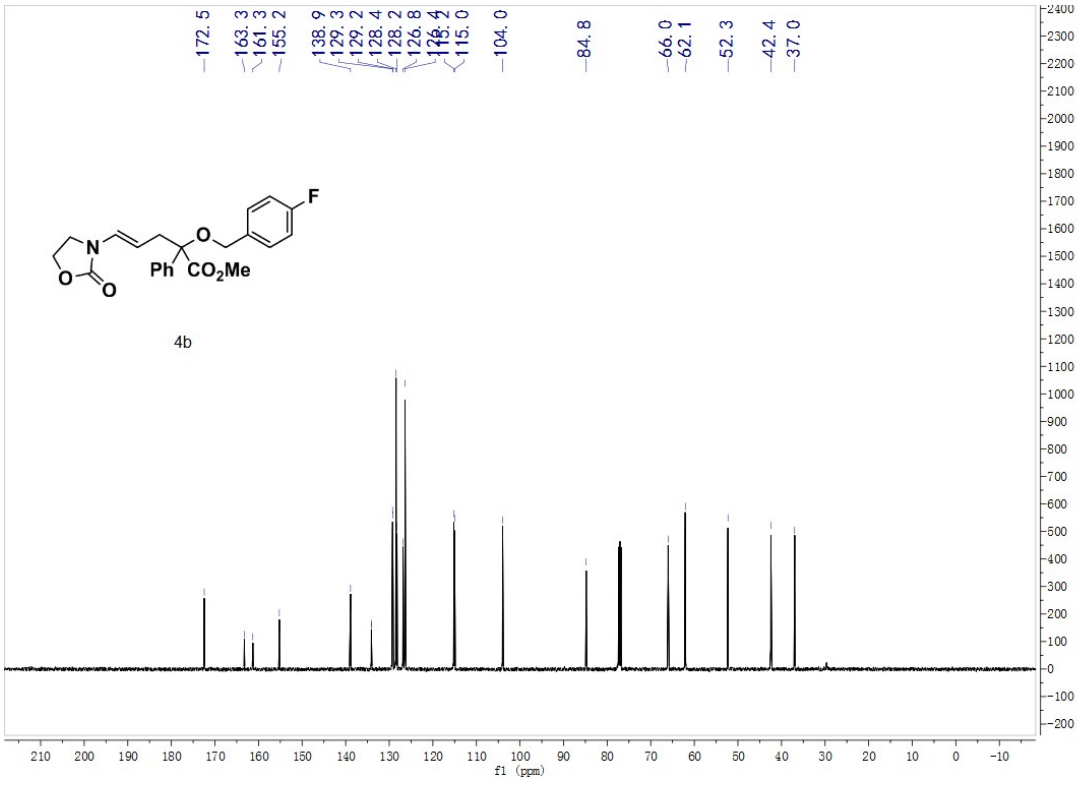
f1 (ppm)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104.0
84.8
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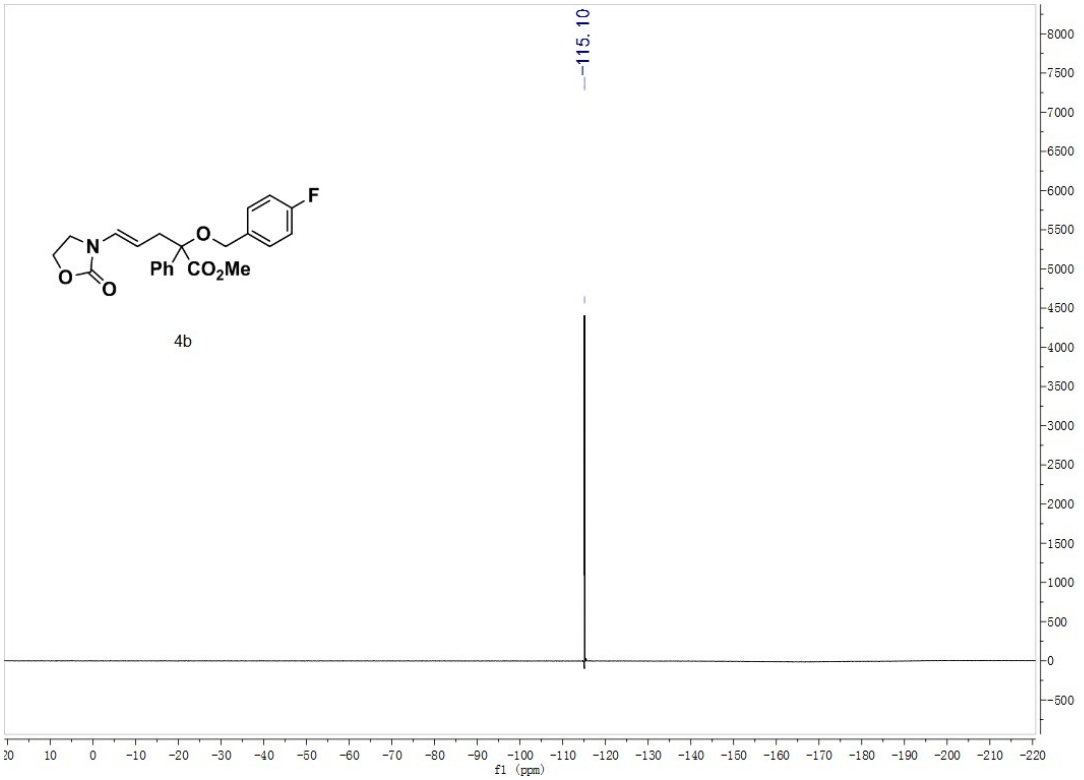
O
O
O
Ph
CO2Me
4b
f1 (ppm)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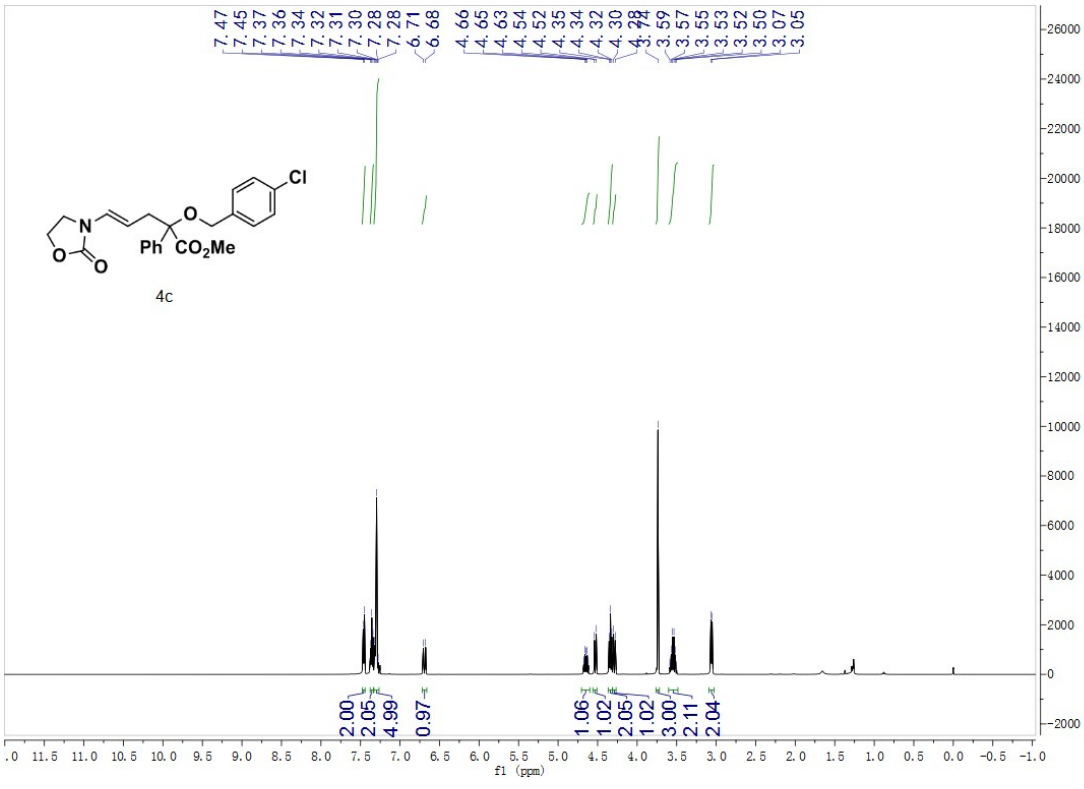
4b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3.52
3.50
3.07
3.05
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O
O
Ph
CO2Me
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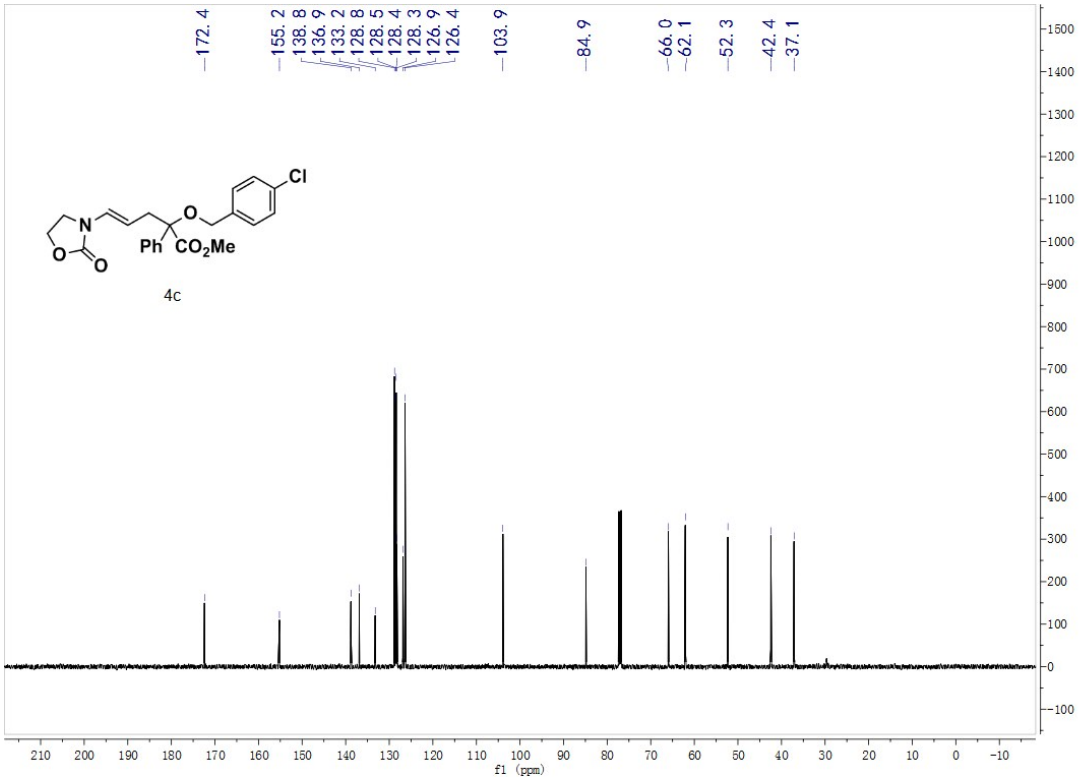
f1 (ppm)

4c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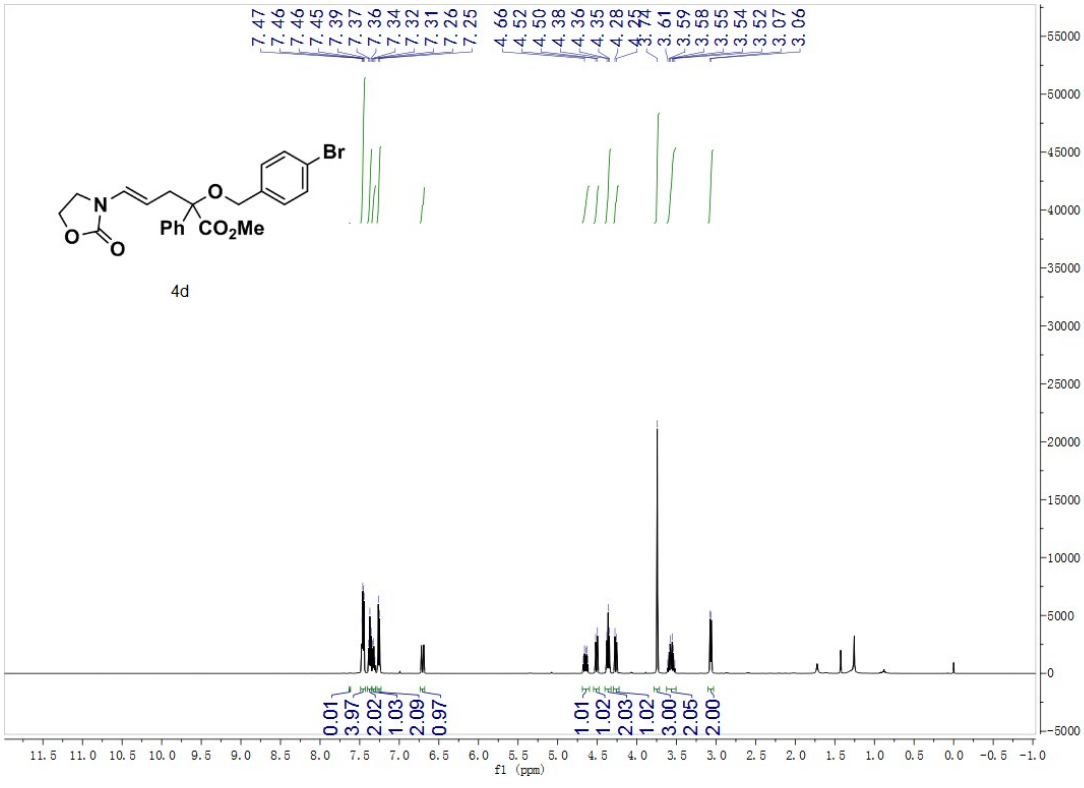
O
O
Ph
CO2Me
f1 (ppm)

4c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O
Ph
CO2Me
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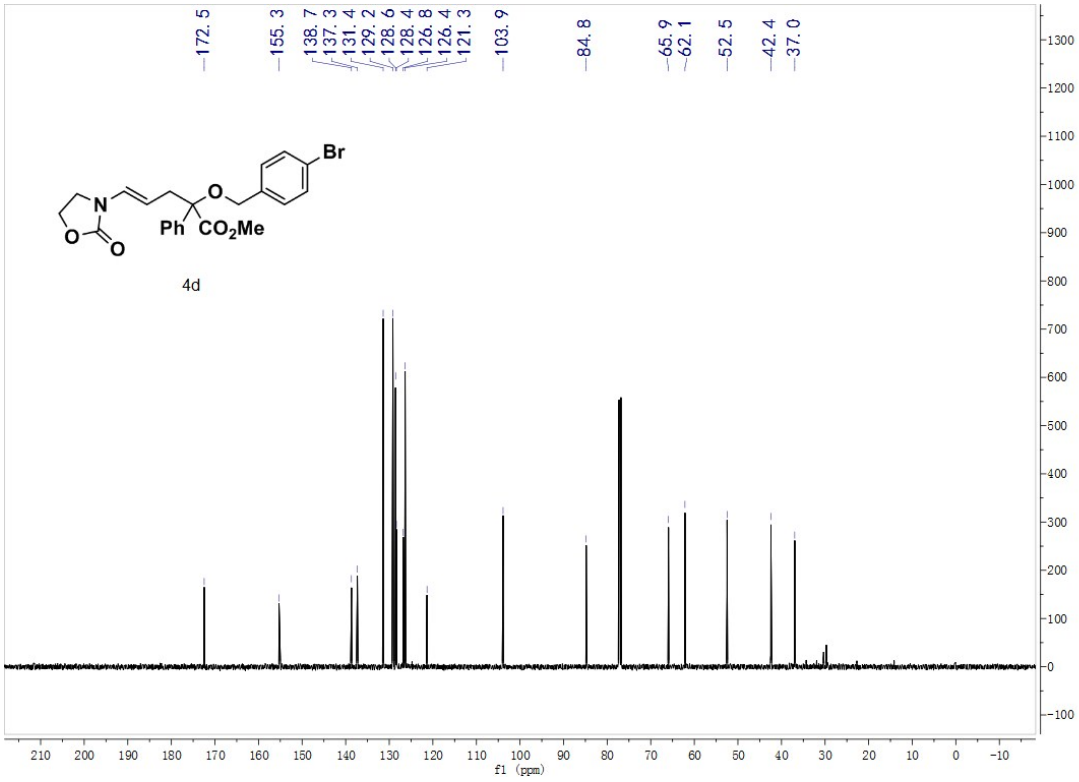
f1 (ppm)

4d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84.8
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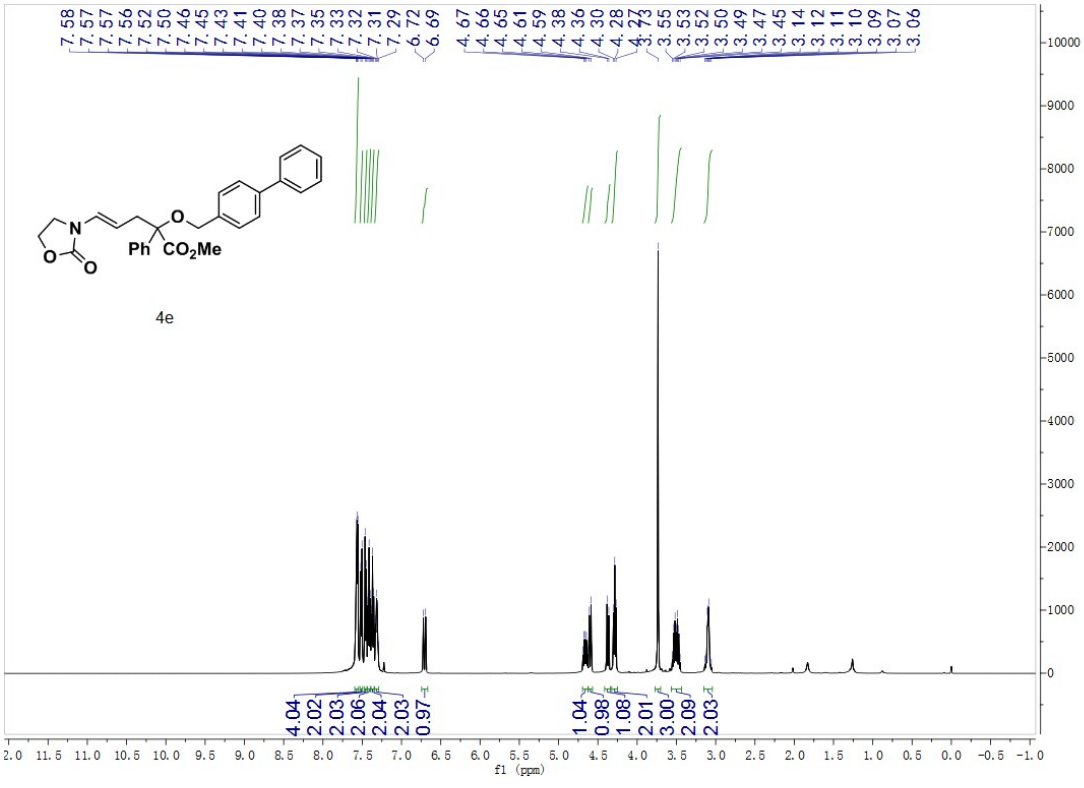
Ph
CO2Me
4d
f1 (ppm)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3.06
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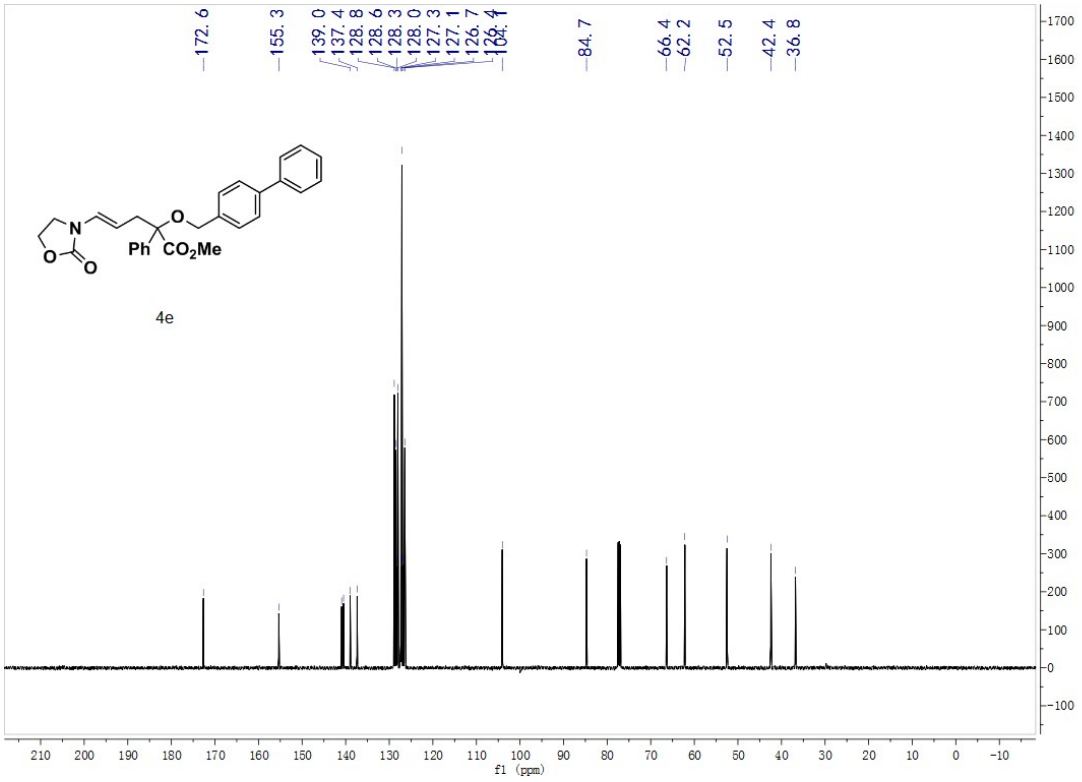
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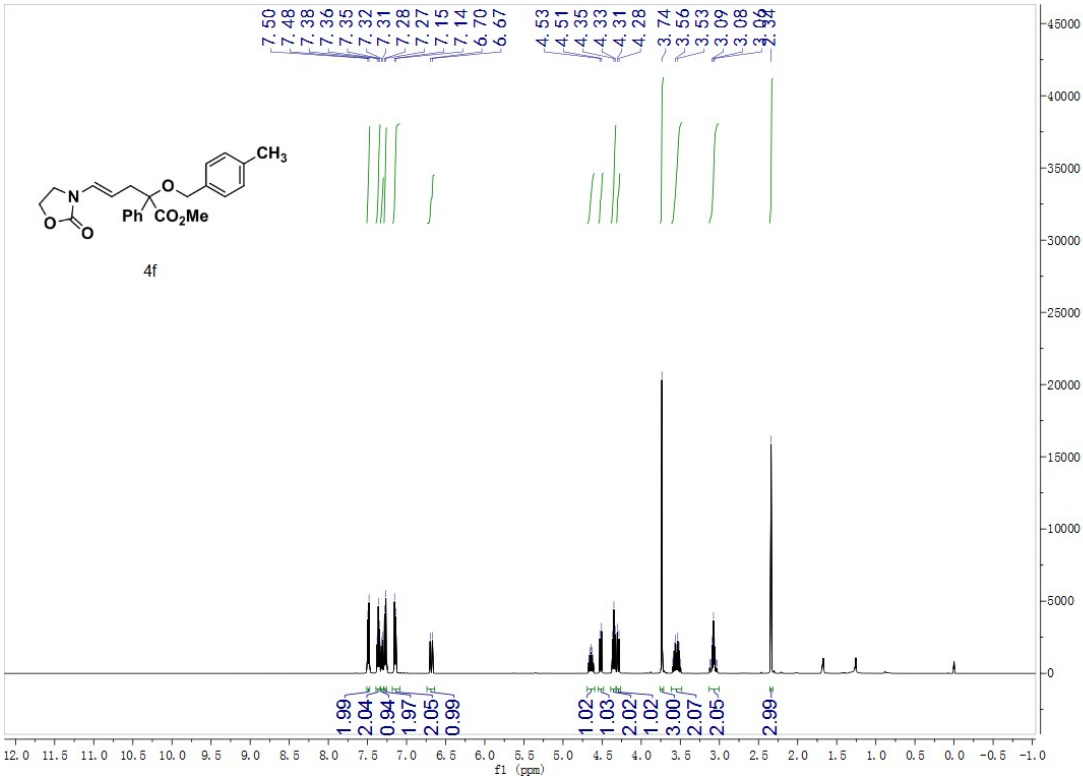
Ph
CO2Me
4e
f1 (ppm)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CH3
Ph
CO2Me
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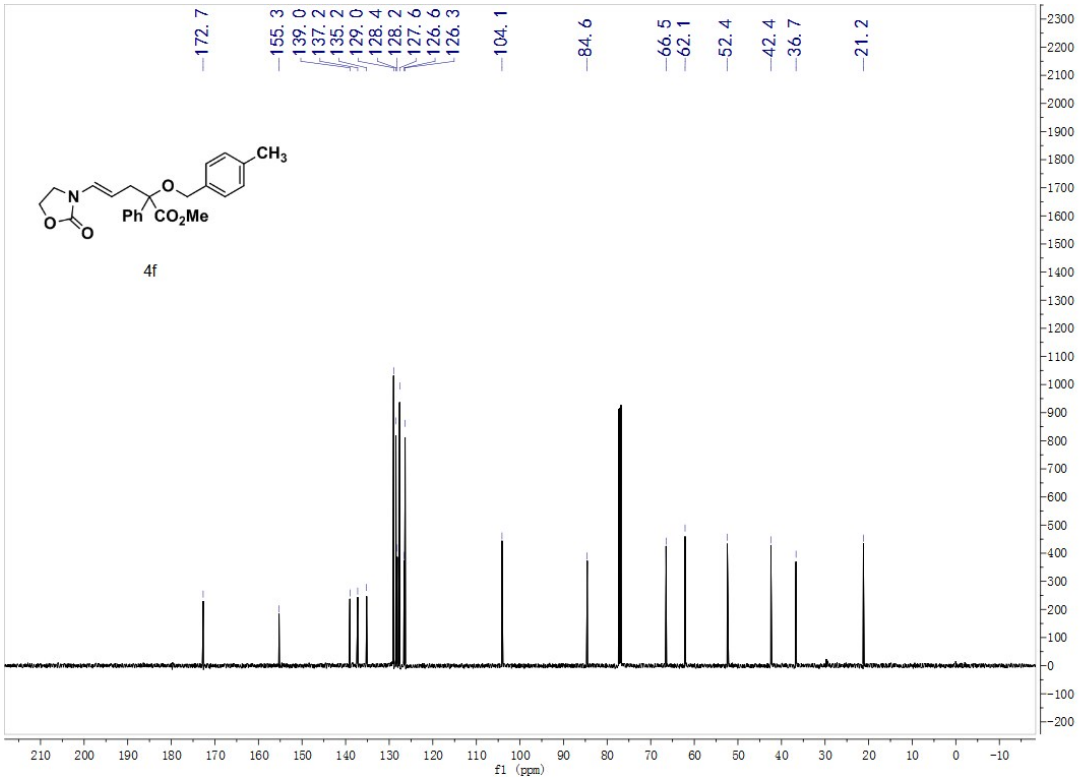
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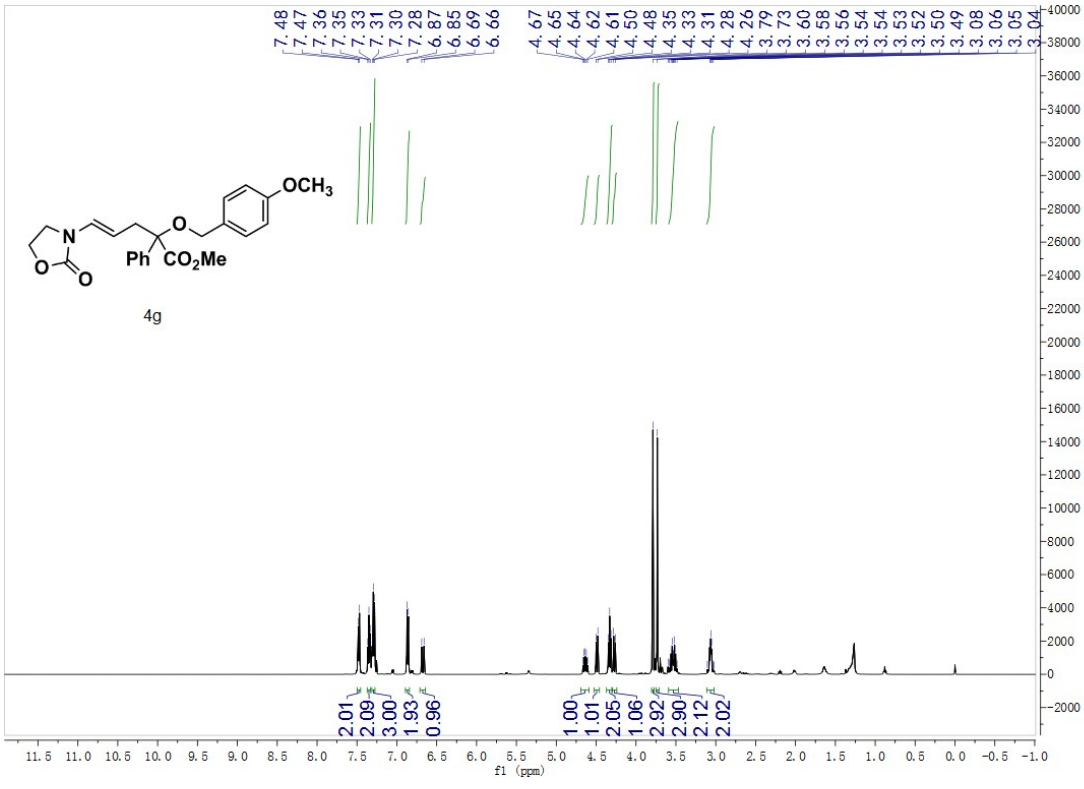
f1 (ppm)

4f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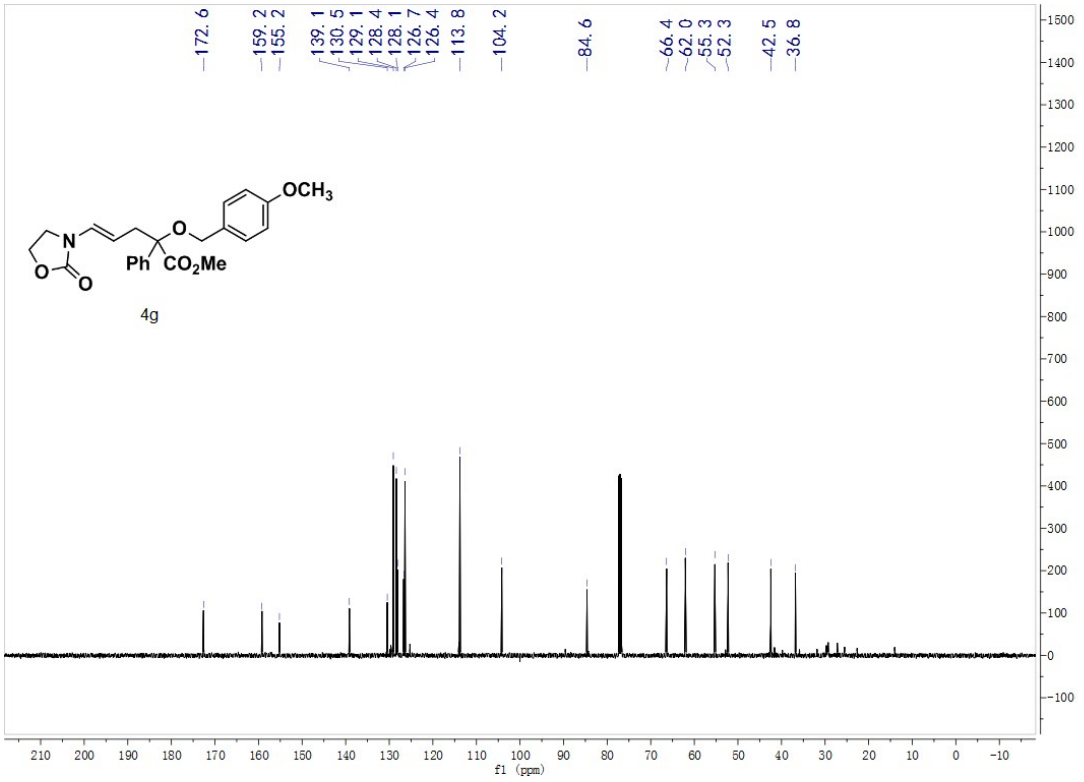
4g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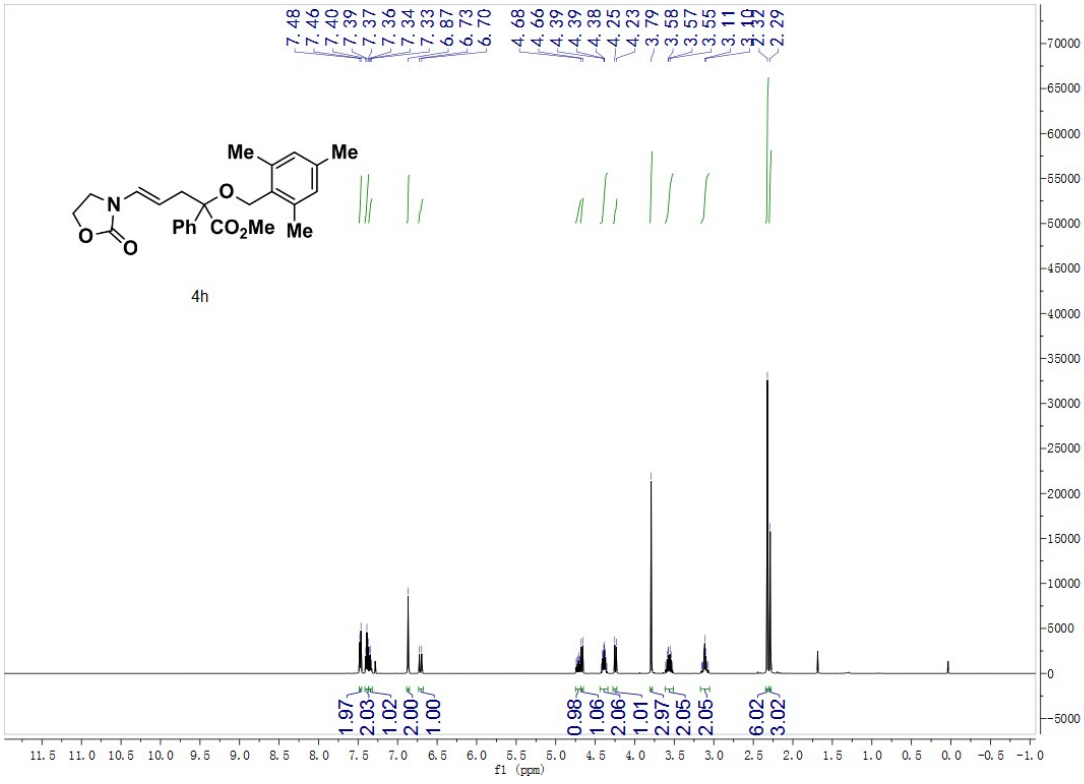
4g
f1 (ppm)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O
Ph
CO2Me
4h
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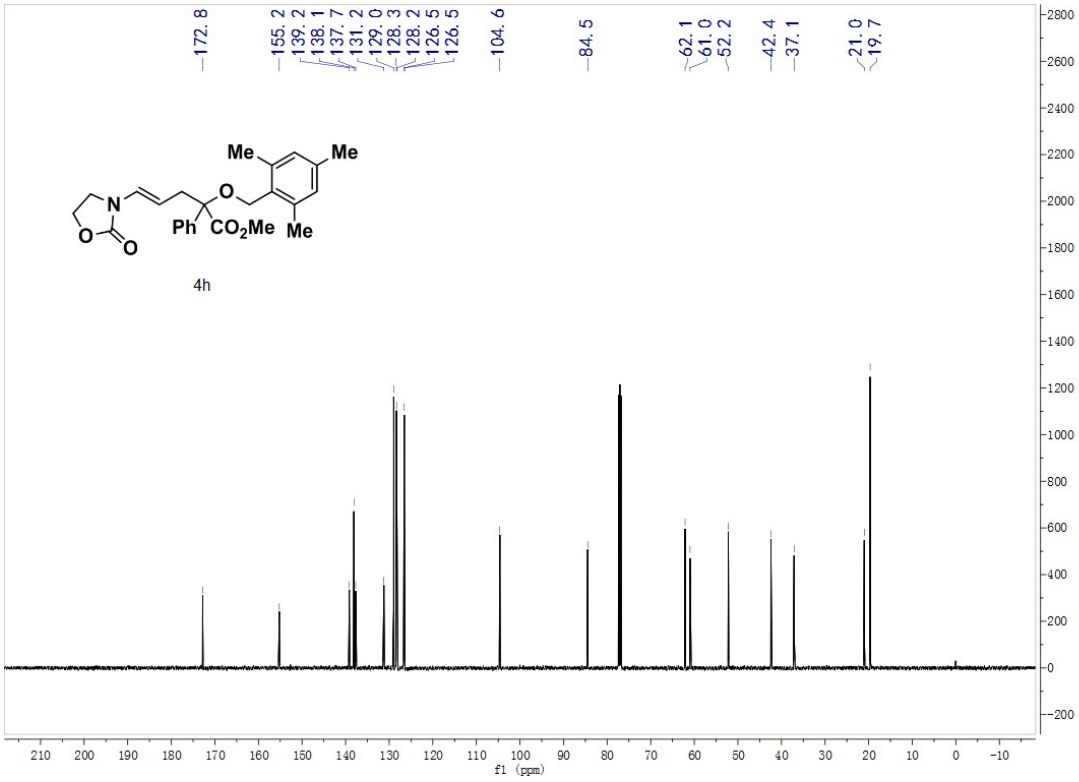
f1 (ppm)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61.0
52.2
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Me
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Ph
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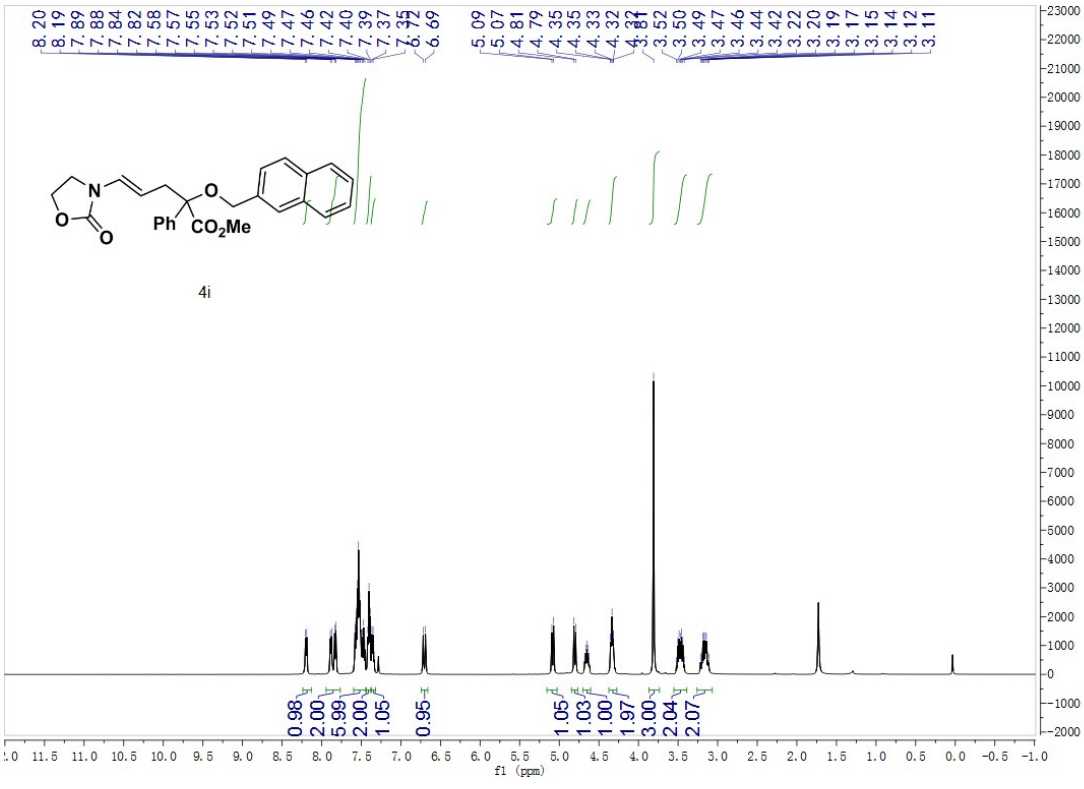
N
O
O
O
f1 (ppm)

4h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3.52
3.50
3.49
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3.46
3.44
3.42
3.22
3.20
3.19
3.17
3.15
3.14
3.12
3.11
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5.99
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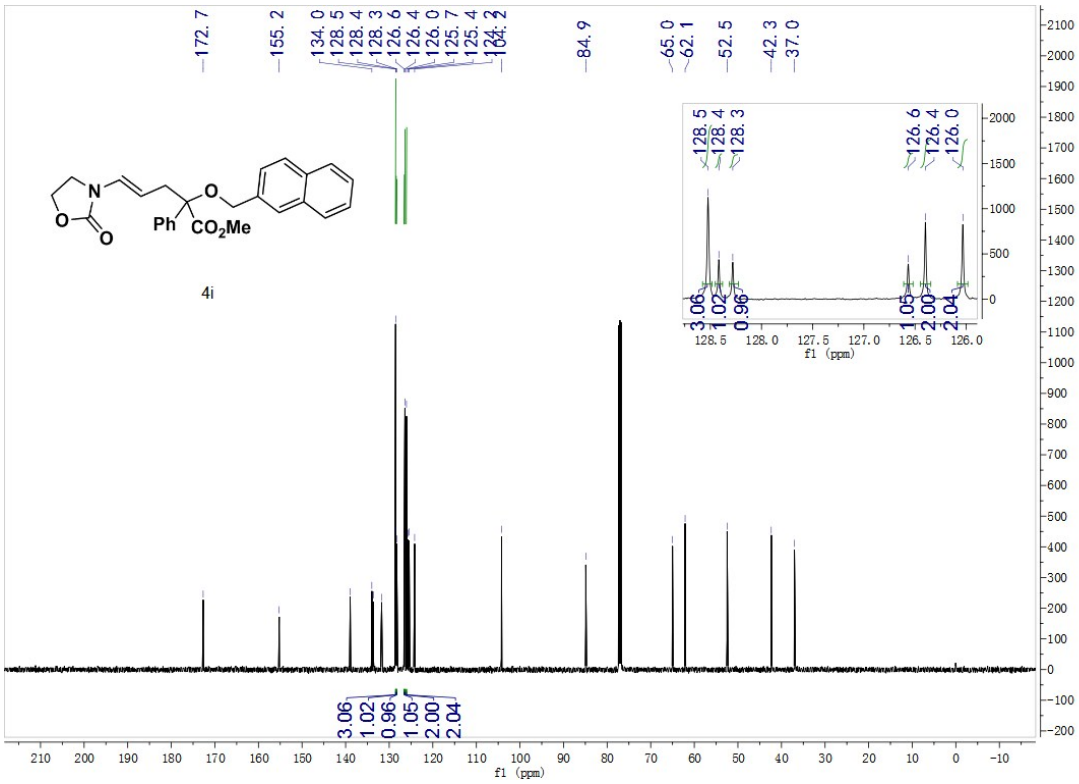
f1 (ppm)

4i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155.2
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128.5
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126.0
125.7
125.4
84.9
65.0
62.1
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37.0
Ph
CO2Me
4i
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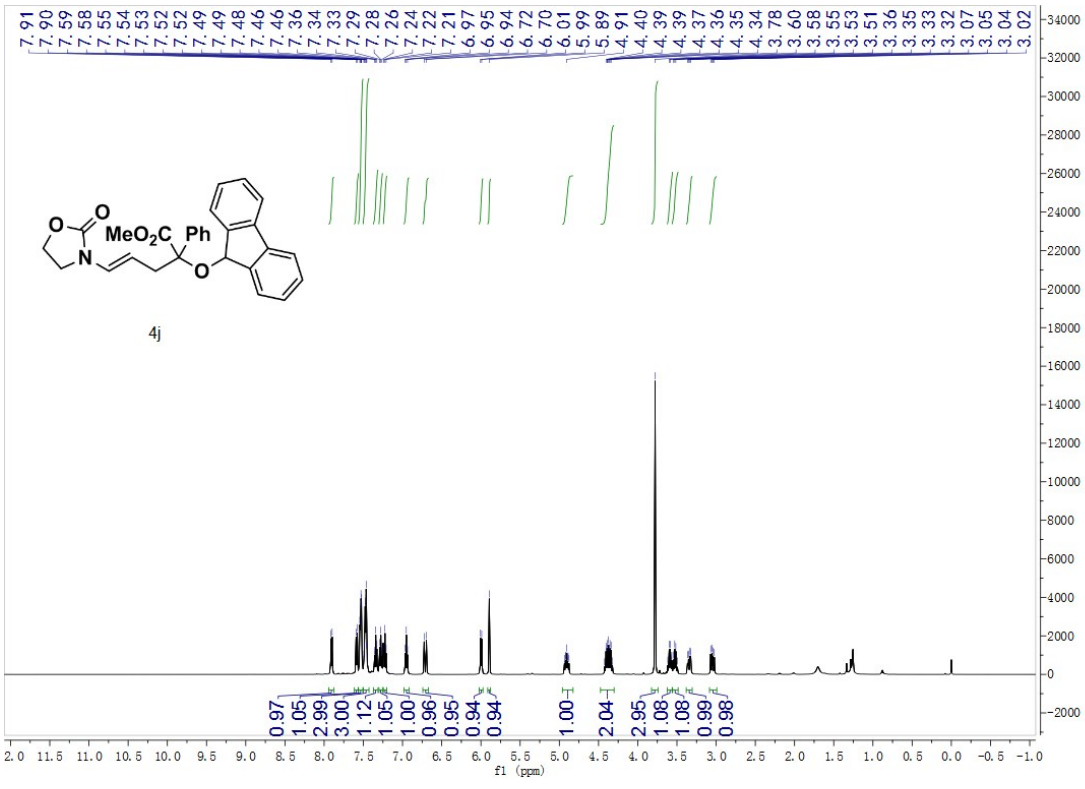
1.05
2.00
2.04
f1 (ppm)


MeO2C
Ph
4j
0.97
1.05
2.99
3.00
1.12
1.05
1.00
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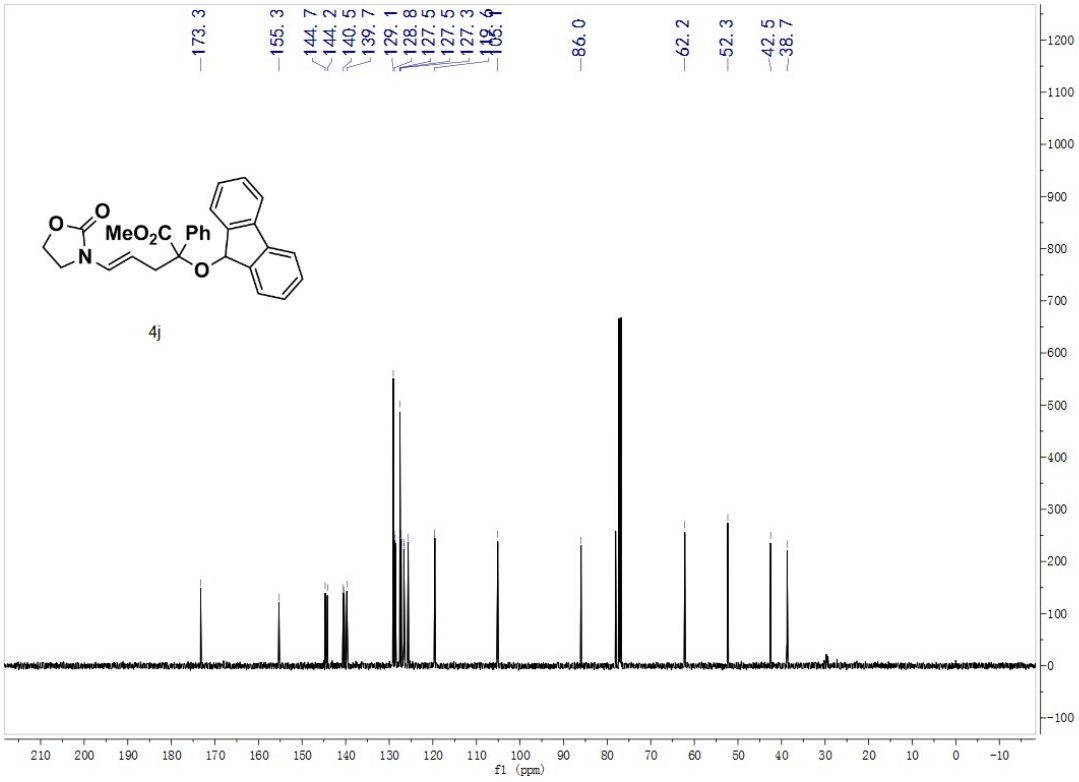
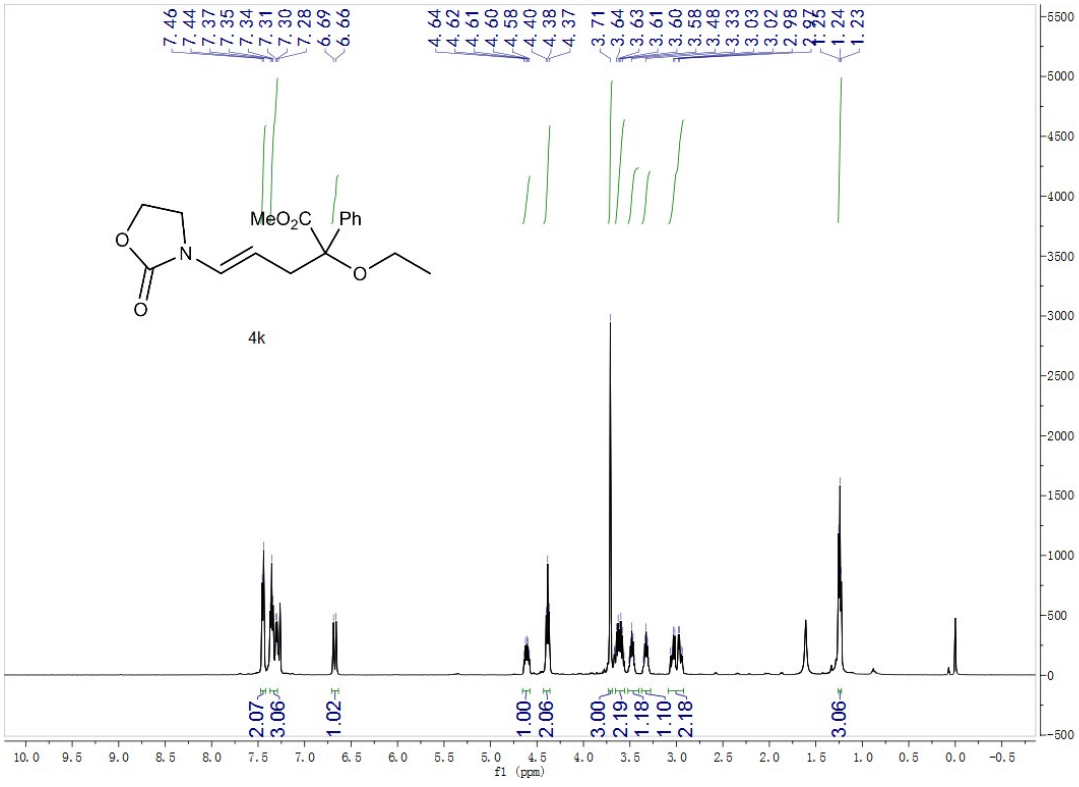
0.95
0.94
0.94
1.00
2.04
2.95
1.08
1.08
0.99
0.98
f1 (ppm)


173.3
155.3
144.7
144.2
140.5
139.7
129.1
128.8
127.5
127.5
127.3
86.0
62.2
52.3
42.5
38.7
MeO2C
Ph
O
N
4j
f1 (ppm)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7.30
7.28
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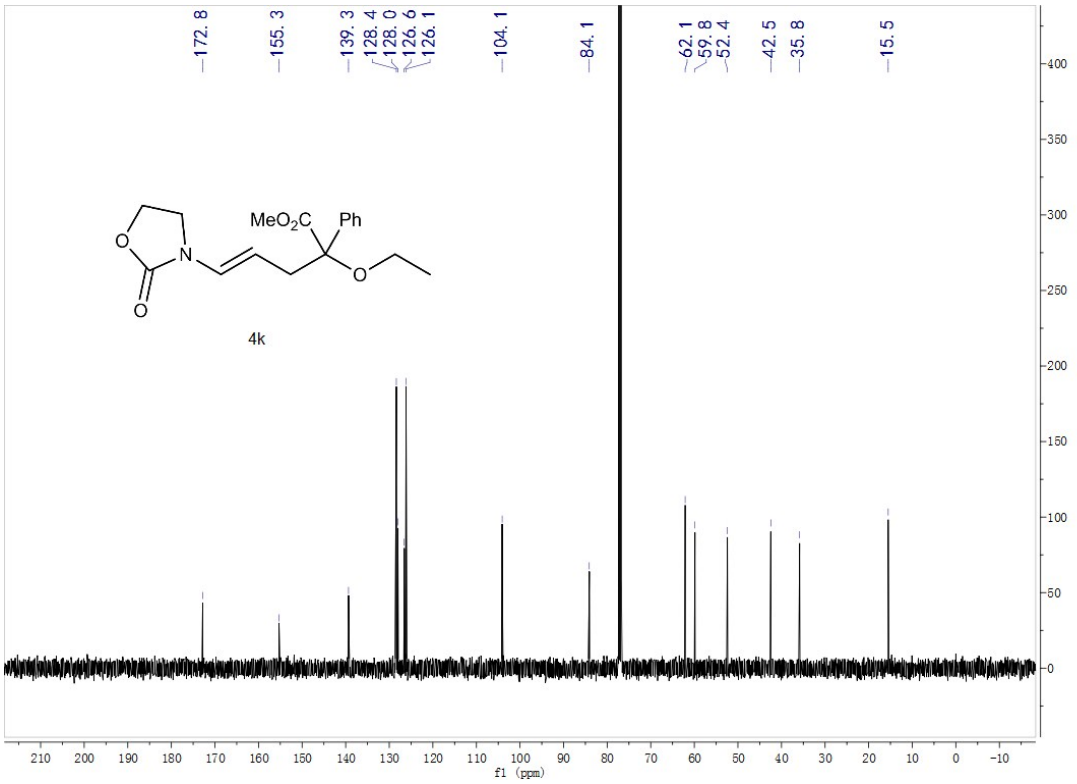
6.66
4.64
4.62
4.61
4.60
4.58
4.40
4.38
4.37
3.71
3.64
3.63
3.61
3.60
3.58
3.48
3.33
3.03
3.02
2.98
1.24
1.23
MeO2C
Ph
O
N
4k
2.07
3.06
1.02
1.00
2.06
3.00
2.19
1.18
1.10
2.18
3.06
f1 (ppm)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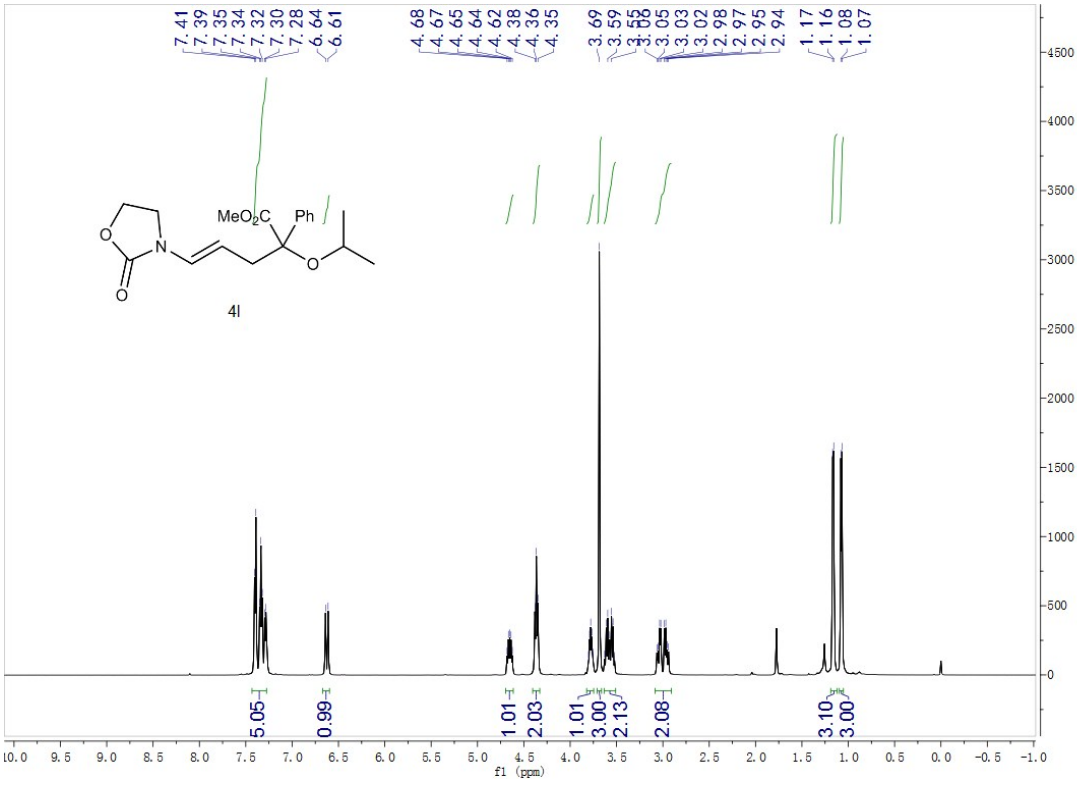
139.3
128.4
128.0
126.6
126.1
104.1
84.1
62.1
59.8
52.4
42.5
35.8
15.5
MeO2C
Ph
O
N
O
O
4k
f1 (ppm)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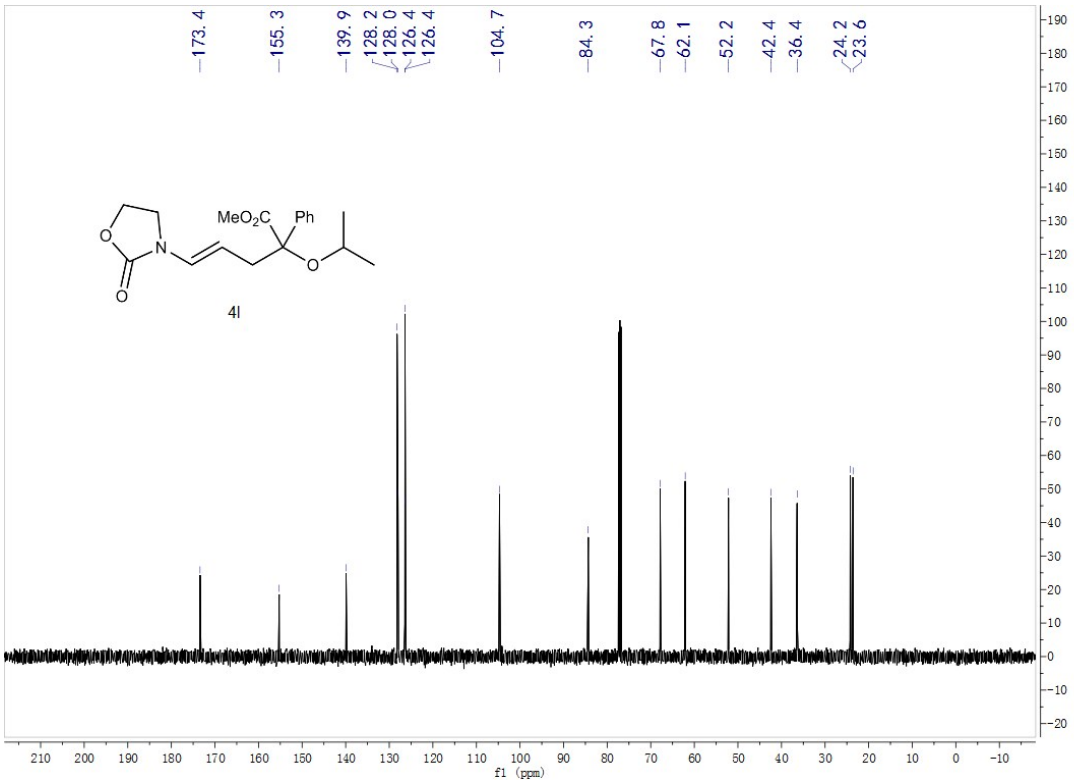
7.28
6.64
6.61
4.68
4.67
4.65
4.64
4.62
4.38
4.36
4.35
3.69
3.59
3.55
3.05
3.03
3.02
2.98
2.97
2.95
2.94
1.17
1.16
1.08
1.07
MeO2C
Ph
O
N
O
O
4l
5.05
0.99
1.01
2.03
1.01
3.00
2.13
2.08
3.10
3.00
f1 (ppm)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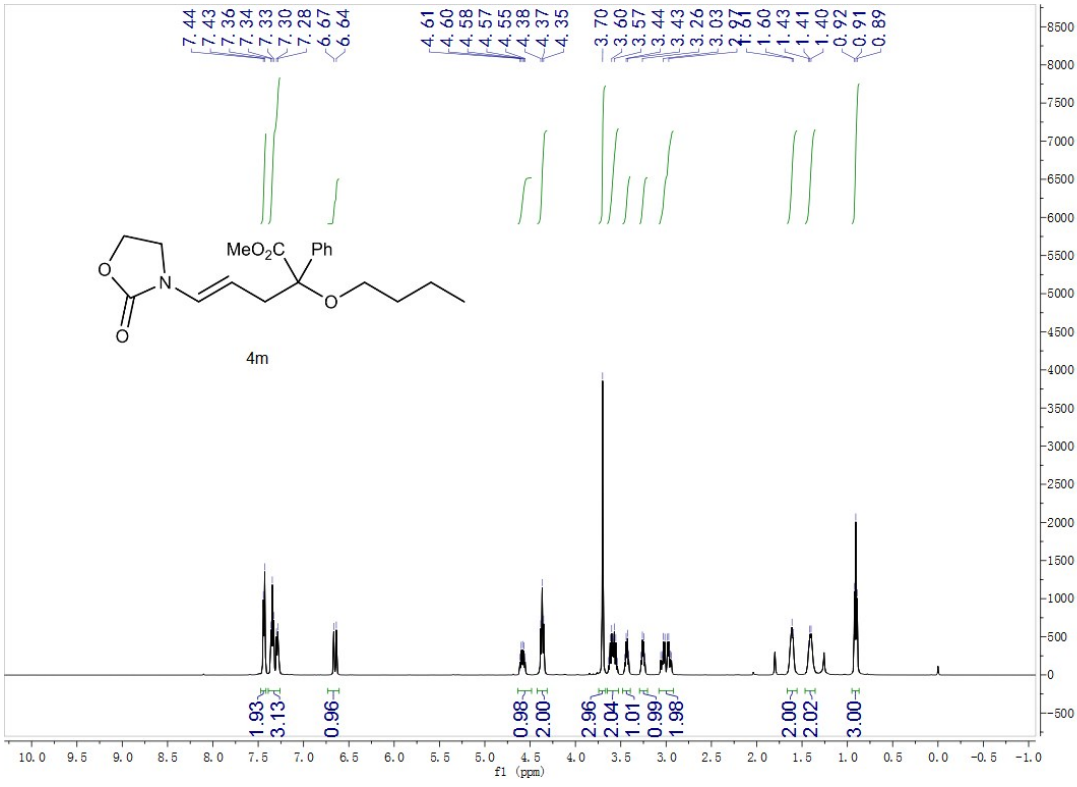
155.3
139.9
128.2
128.0
126.4
126.4
104.7
84.3
67.8
62.1
52.2
42.4
36.4
24.2
23.6
MeO2C
Ph
O
N
O
O
4l
f1 (ppm)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7.43
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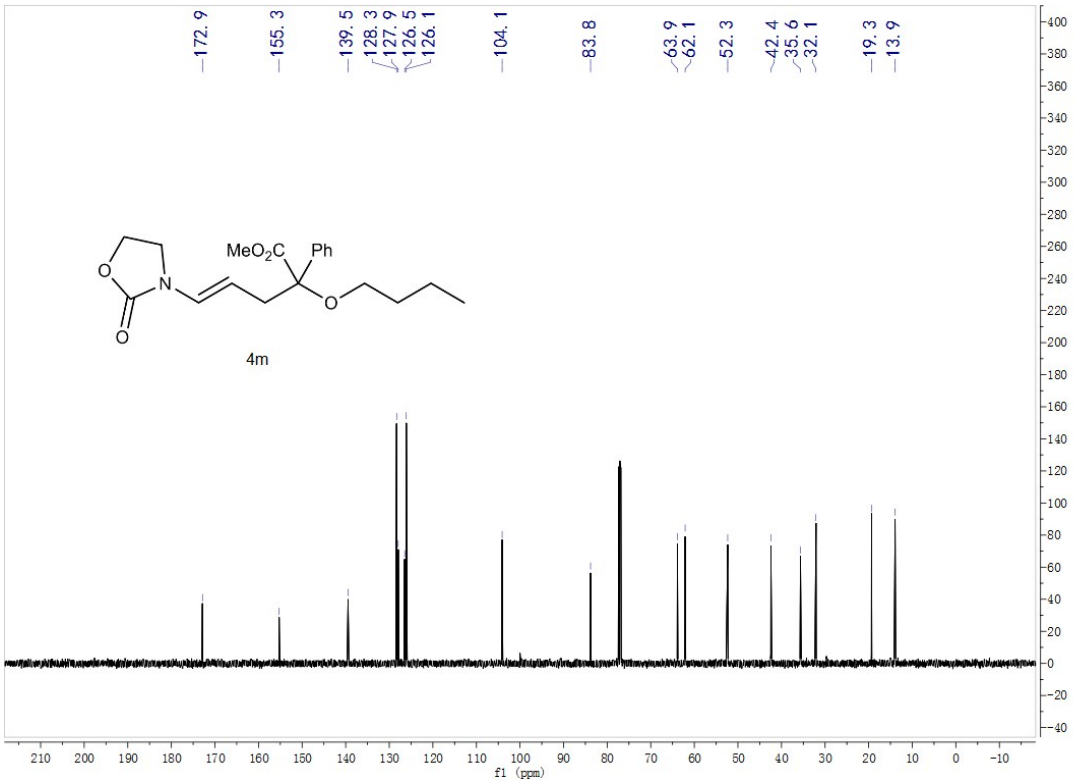
7.33
7.30
7.28
6.67
6.64
4.61
4.60
4.58
4.57
4.55
4.38
4.37
4.35
3.70
3.60
3.57
3.44
3.43
3.26
3.03
2.97
2.61
1.60
1.43
1.41
1.40
0.92
0.91
0.89
MeO2C
Ph
O
N
O
O
4m
1.93
3.13
0.96
0.98
2.00
2.96
2.04
1.01
0.99
1.98
2.00
2.02
3.00
f1 (ppm)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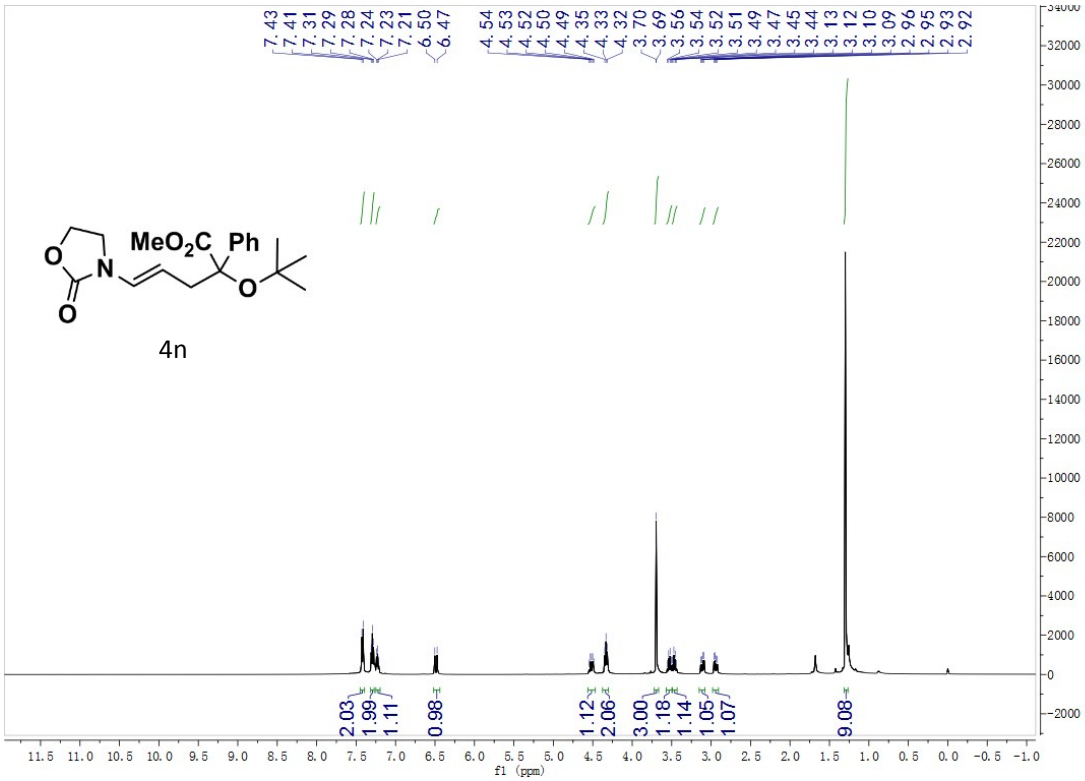
139.5
128.3
127.9
126.5
126.1
104.1
83.8
63.9
62.1
52.3
42.4
35.6
32.1
19.3
13.9
MeO2C
Ph
O
N
O
O
4m
f1 (ppm)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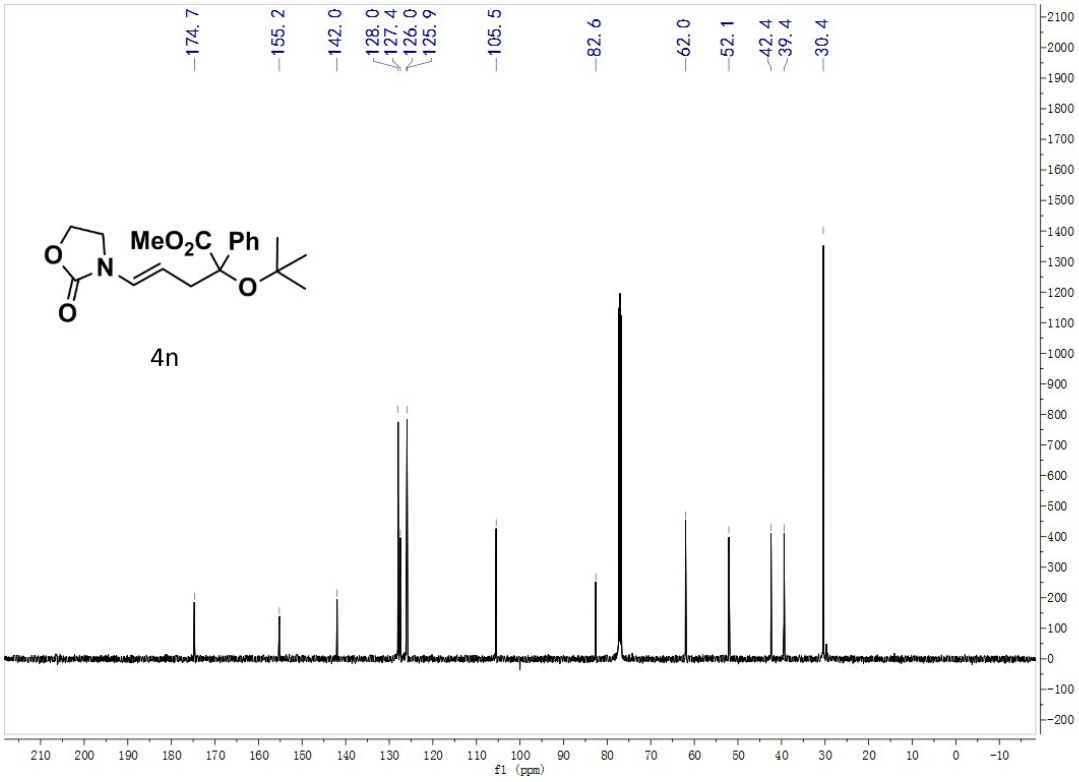
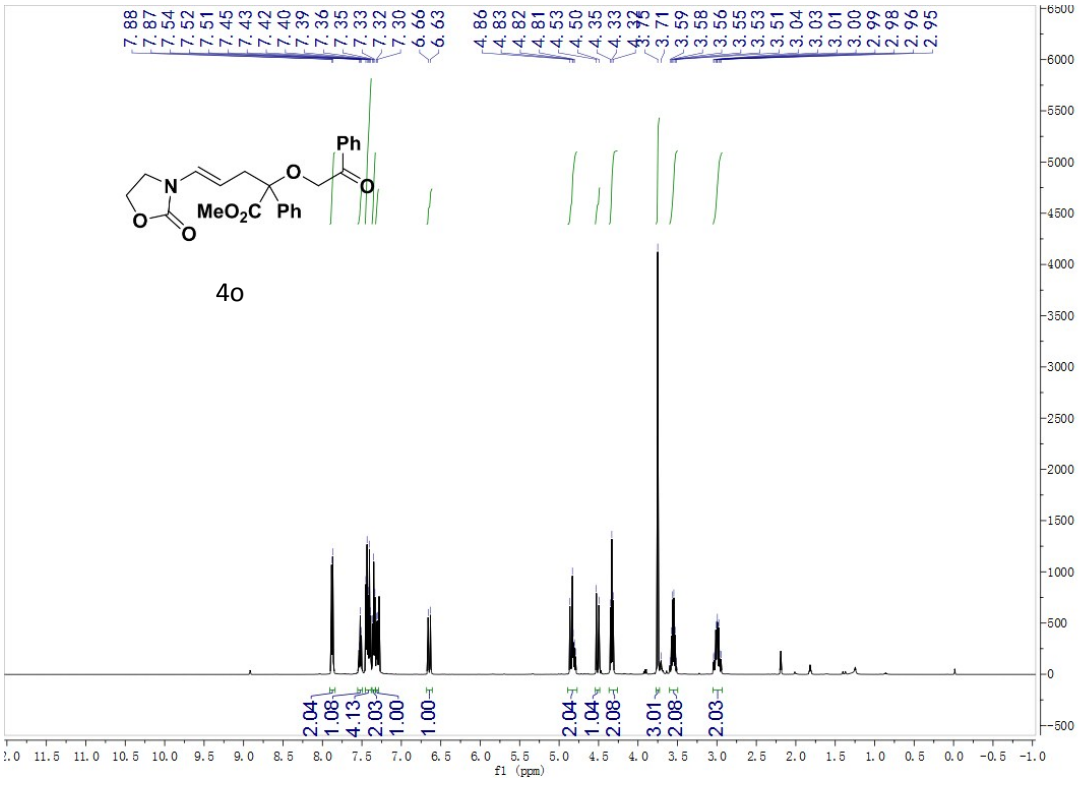
7.24
7.23
7.21
6.50
6.47
4.54
4.53
4.52
4.50
4.49
4.35
4.33
4.32
3.70
3.69
3.56
3.54
3.52
3.51
3.49
3.47
3.45
3.44
3.13
3.12
3.10
3.09
2.96
2.95
2.93
2.92
MeO2C
Ph
O
N
O
O
4n
2.03
1.99
1.11
0.98
1.12
2.06
3.00
1.18
1.14
1.05
1.07
9.08
f1 (ppm)


174.7
155.2
142.0
128.0
127.4
126.0
125.9
105.5
82.6
62.0
52.1
42.4
39.4
30.4
MeO2C Ph
f1 (ppm)

4n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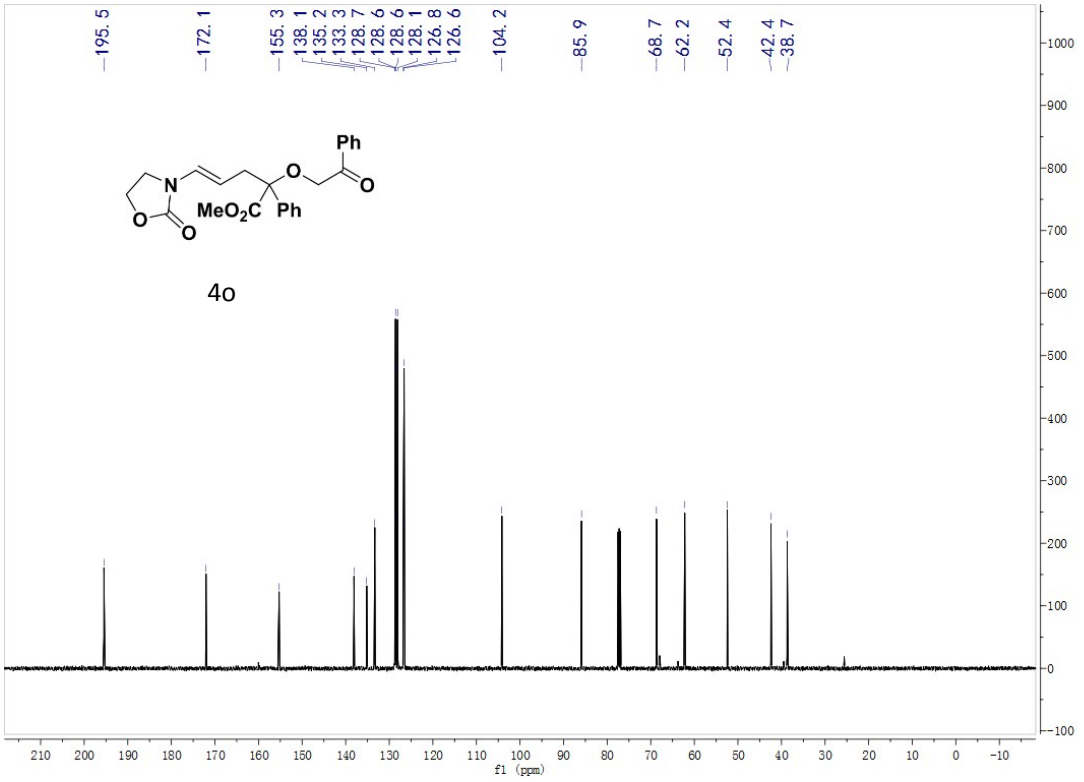
7.45
7.43
7.42
7.40
7.39
7.36
7.35
7.33
7.32
7.30
6.66
6.63
4.86
4.83
4.82
4.81
4.53
4.50
4.35
4.33
3.71
3.59
3.58
3.56
3.55
3.53
3.51
3.04
3.03
3.01
3.00
2.99
2.98
2.96
2.95
Ph
MeO2C Ph
2.04
1.08
4.13
2.03
1.00
1.00
2.04
1.04
2.08
3.01
2.08
2.03
f1 (ppm)

4o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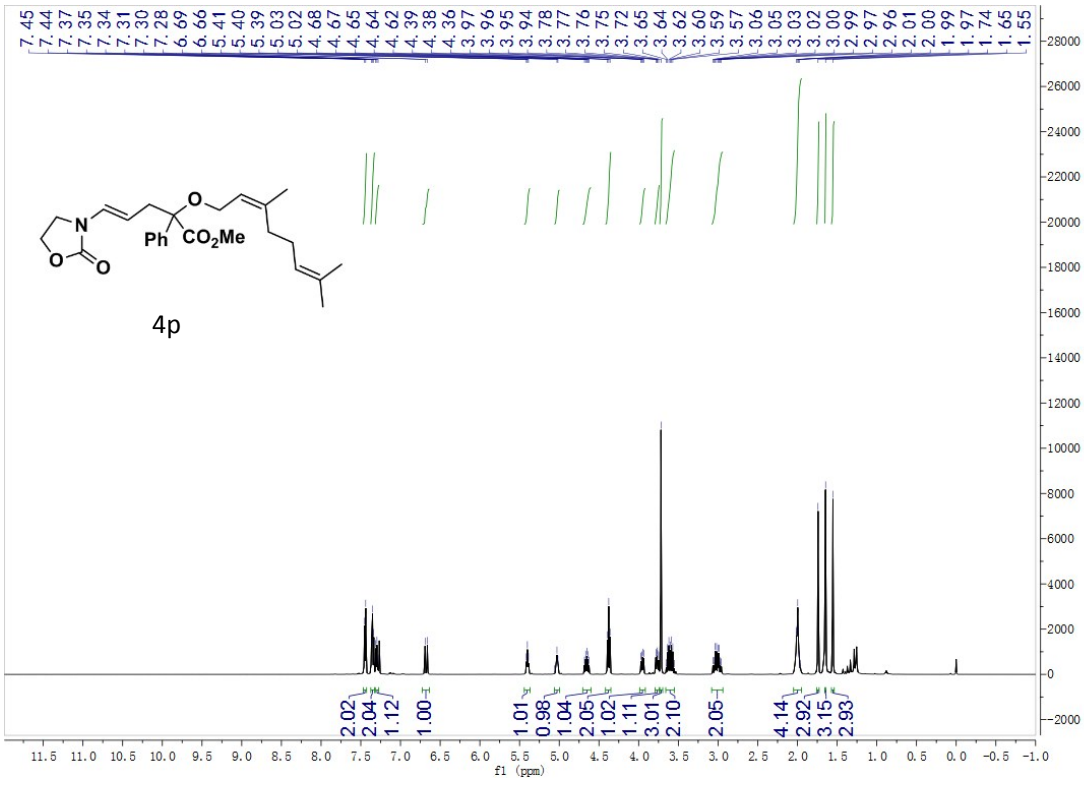
172.1
155.3
138.1
135.2
133.3
128.7
128.6
128.6
128.1
126.8
126.6
104.2
85.9
68.7
62.2
52.4
42.4
38.7
Ph
O
N
O
O
MeO2C
Ph
f1 (ppm)

4o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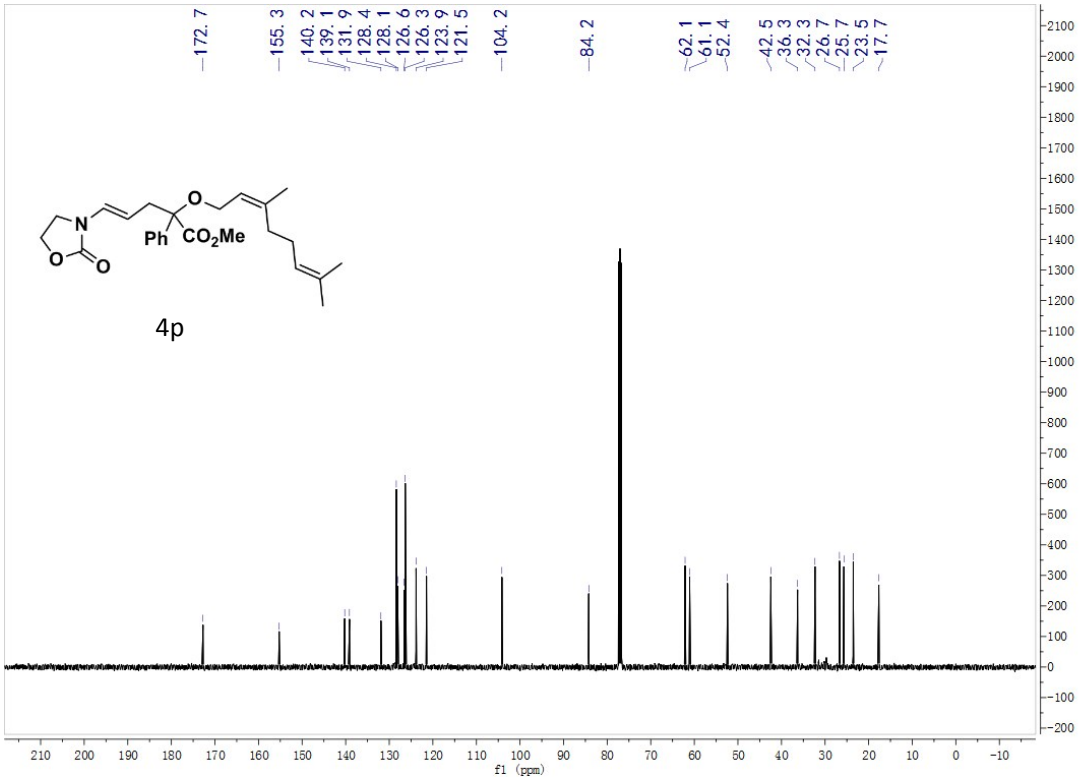
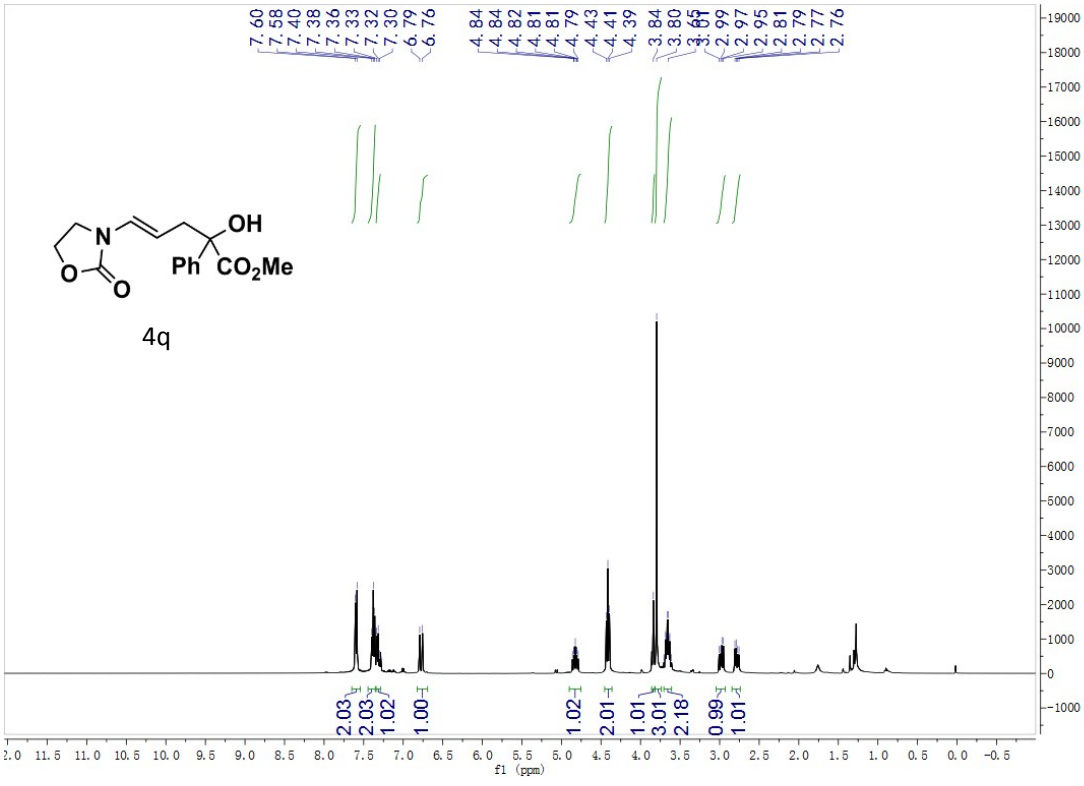
7.44
7.37
7.35
7.34
7.31
7.30
7.28
6.69
6.66
5.41
5.40
5.39
5.03
5.02
4.68
4.67
4.65
4.64
4.62
4.39
4.38
4.36
3.97
3.96
3.95
3.94
3.78
3.77
3.76
3.75
3.72
3.65
3.64
3.62
3.60
3.59
3.57
3.06
3.05
3.03
3.02
3.00
2.99
2.97
2.96
2.01
2.00
1.99
1.97
1.74
1.65
1.55
N
O
O
Ph
CO2Me
2.02
2.04
1.12
1.00
1.01
0.98
1.04
2.05
1.02
1.11
3.01
2.10
2.05
4.14
2.92
3.15
2.93
f1 (ppm)

4p


172.7
155.3
140.2
139.1
131.9
128.4
128.1
126.6
126.3
123.9
121.5
104.2
84.2
62.1
61.1
52.4
42.5
36.3
32.3
26.7
25.7
23.5
17.7
Ph
CO2Me
f1 (ppm)

4p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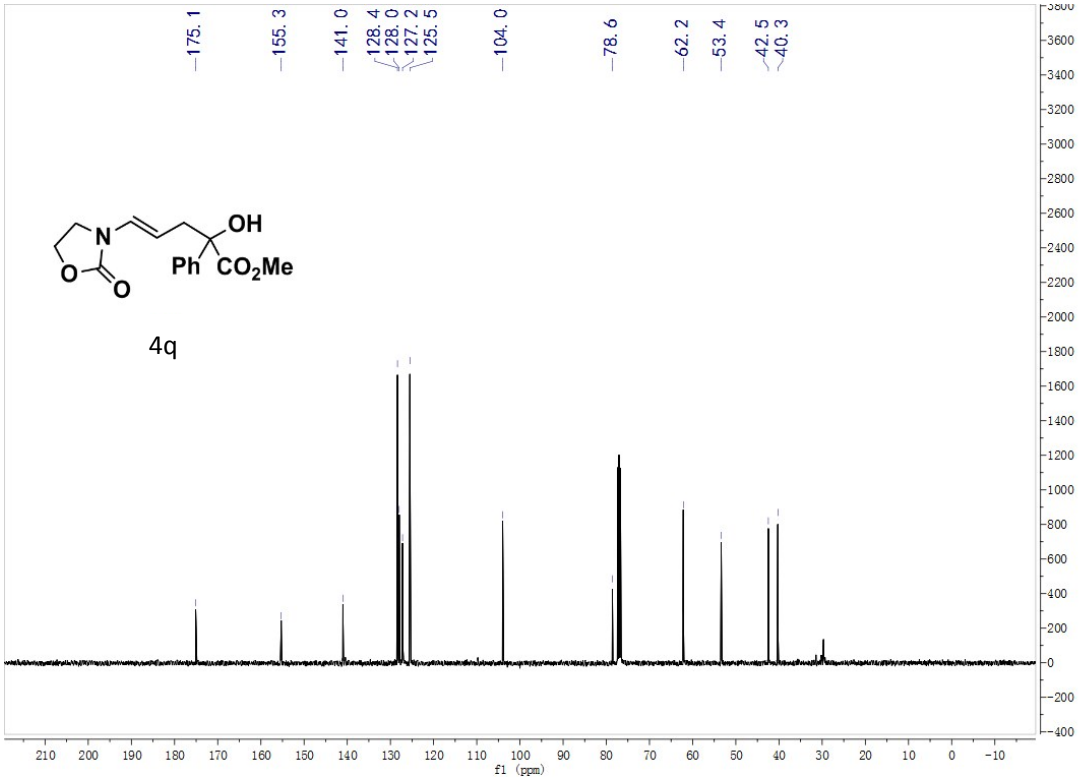
7.33
7.32
7.30
6.79
6.76
4.84
4.84
4.82
4.81
4.81
4.79
4.43
4.41
4.39
3.84
3.80
3.65
3.61
2.99
2.97
2.95
2.81
2.79
2.77
2.76
OH
Ph
CO2Me
2.03
2.03
1.02
1.00
1.02
2.01
1.01
3.01
2.18
0.99
1.01
f1 (ppm)

4q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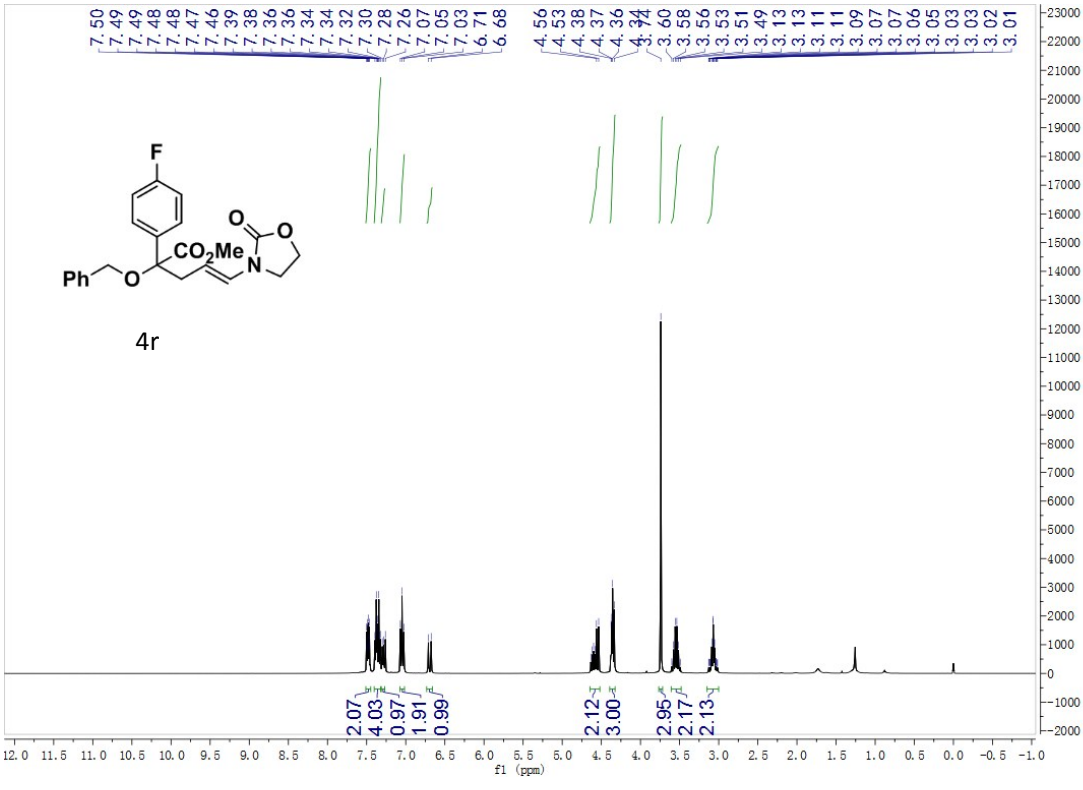
155. 3
141. 0
128. 4
128. 0
127. 2
125. 5
104. 0
78. 6
62. 2
53. 4
42. 5
40. 3
OH
Ph
CO2Me
N
O
O
f1 (ppm)

4q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7. 39
7. 38
7. 36
7. 36
7. 34
7. 34
7. 32
7. 30
7. 28
7. 26
7. 07
7. 05
7. 03
6. 71
6. 68
4. 56
4. 53
4. 38
4. 37
4. 36
3. 60
3. 58
3. 56
3. 53
3. 51
3. 49
3. 13
3. 13
3. 11
3. 11
3. 09
3. 07
3. 07
3. 06
3. 05
3. 03
3. 03
3. 02
3. 01
F
O
O
CO2Me
N
Ph
O
2.07
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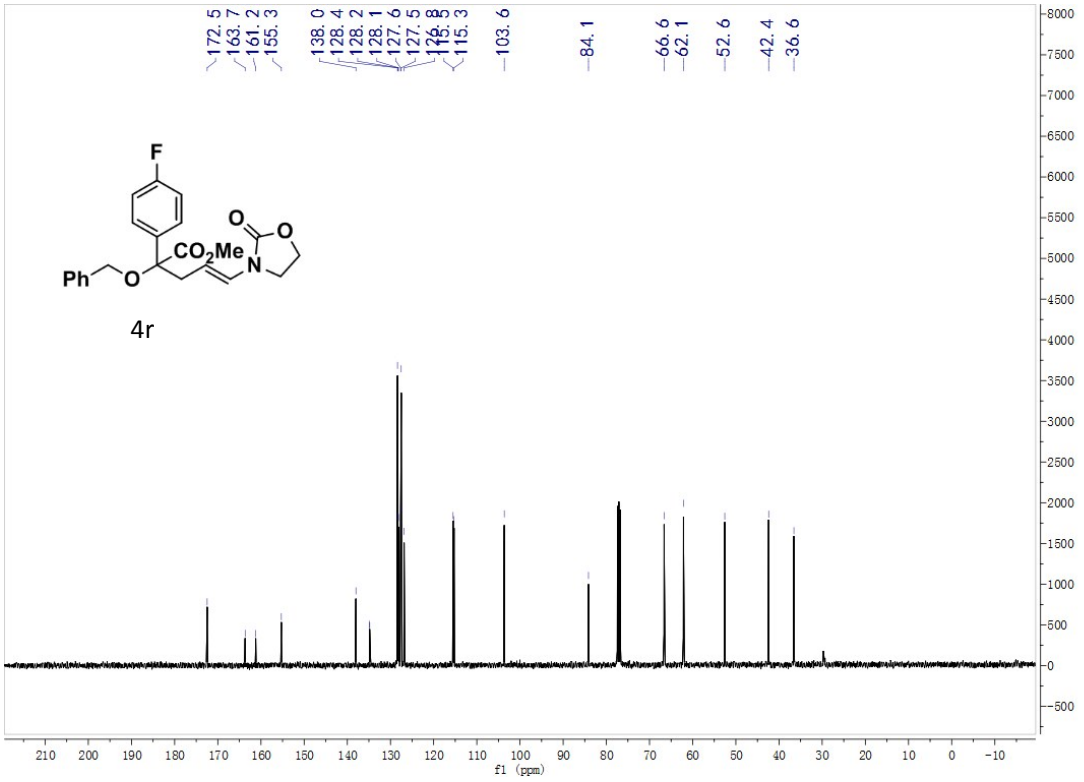
1.91
0.99
2.12
3.00
2.95
2.17
2.13
f1 (ppm)

4r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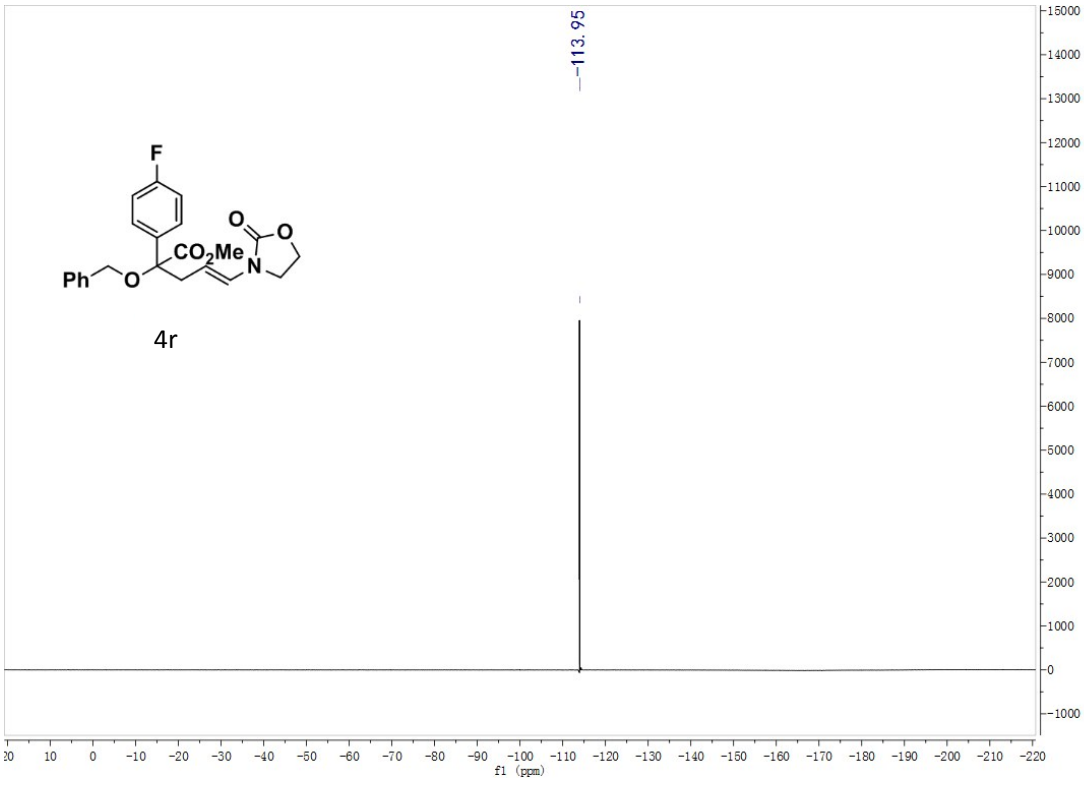
163.7
161.2
155.3
138.0
128.4
128.2
128.1
127.6
127.5
115.3
103.6
84.1
66.6
62.1
52.6
42.4
36.6
F
O
O
CO2Me
N
Ph
O
f1 (ppm)

4r


113.95
F
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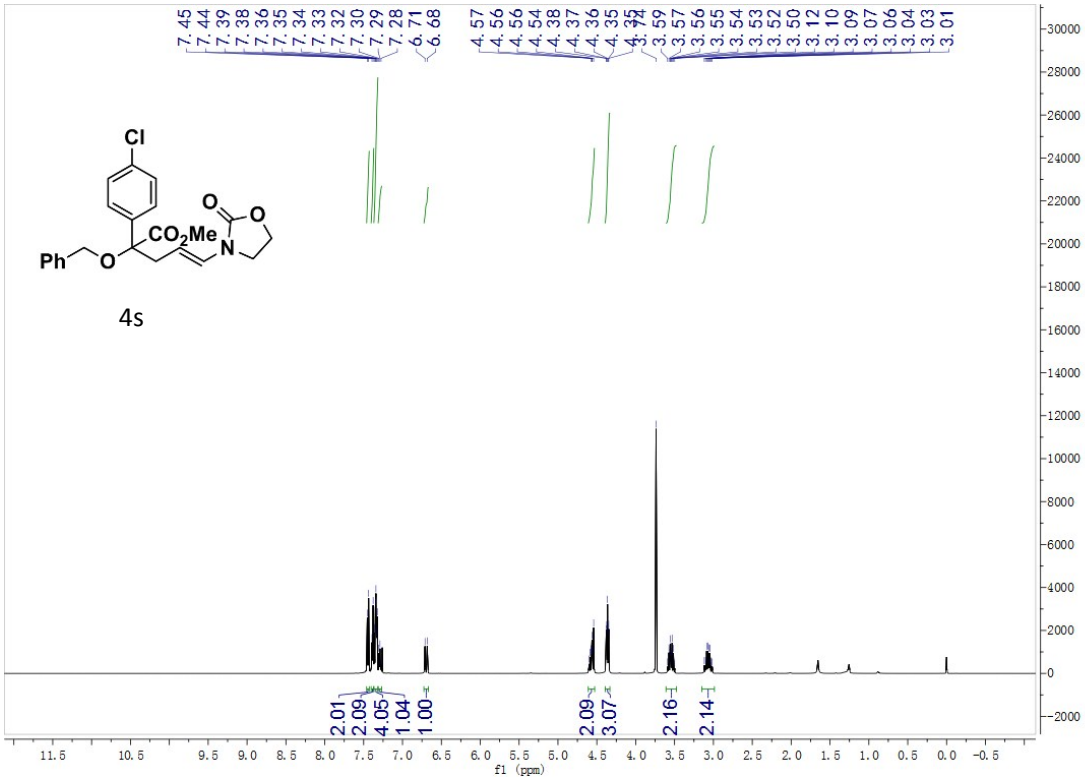
O
CO2Me
N
Ph
O
f1 (ppm)

4r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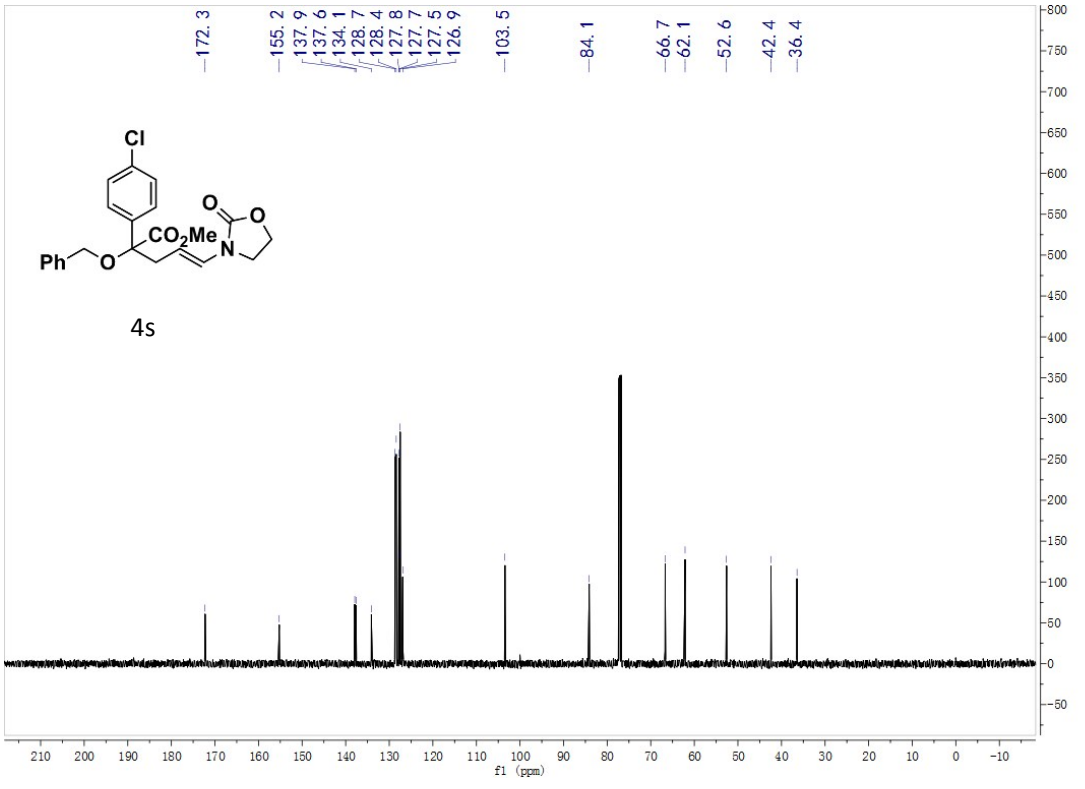
7.29
7.28
6.71
6.68
4.57
4.56
4.56
4.54
4.38
4.37
4.36
4.35
3.59
3.57
3.56
3.55
3.54
3.53
3.52
3.50
3.12
3.10
3.09
3.07
3.06
3.04
3.03
3.01
Cl
O
O
CO2Me
N
Ph
O
2.01
2.09
4.05
1.04
1.00
2.09
3.07
2.16
2.14
f1 (ppm)

4s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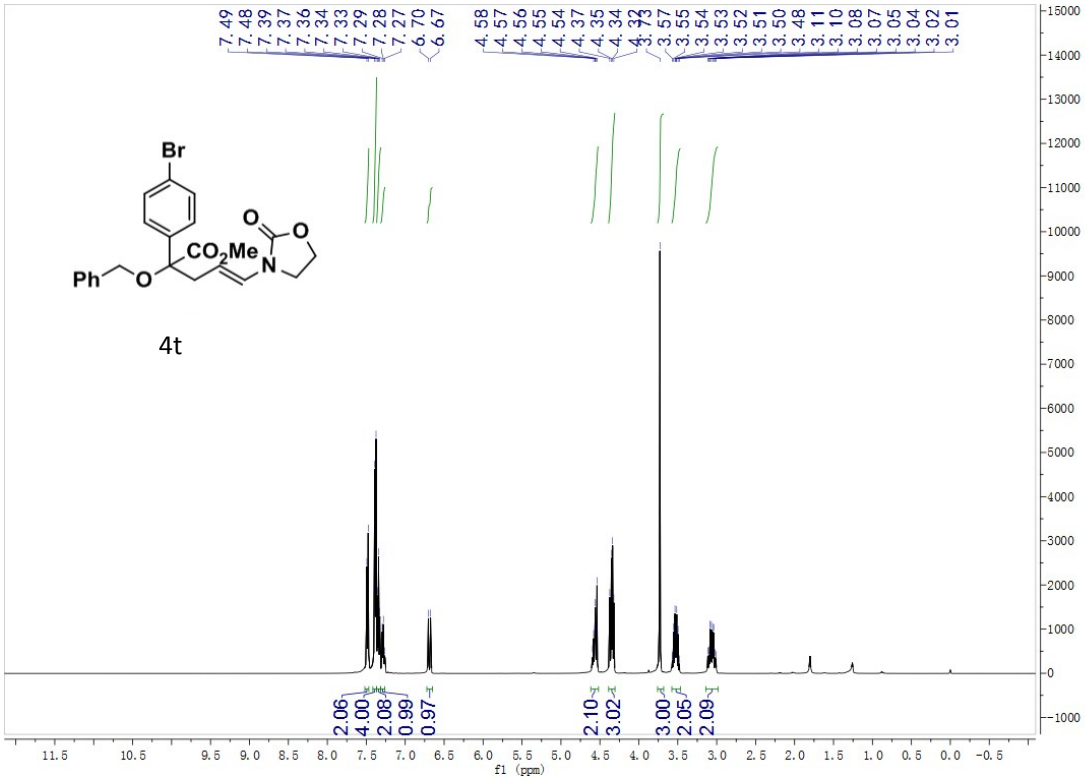
137.6
134.1
128.7
128.4
127.8
127.7
127.5
126.9
103.5
84.1
66.7
62.1
52.6
42.4
36.4
Cl
O
O
CO2Me
N
Ph
O
f1 (ppm)

4s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7.29
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6.67
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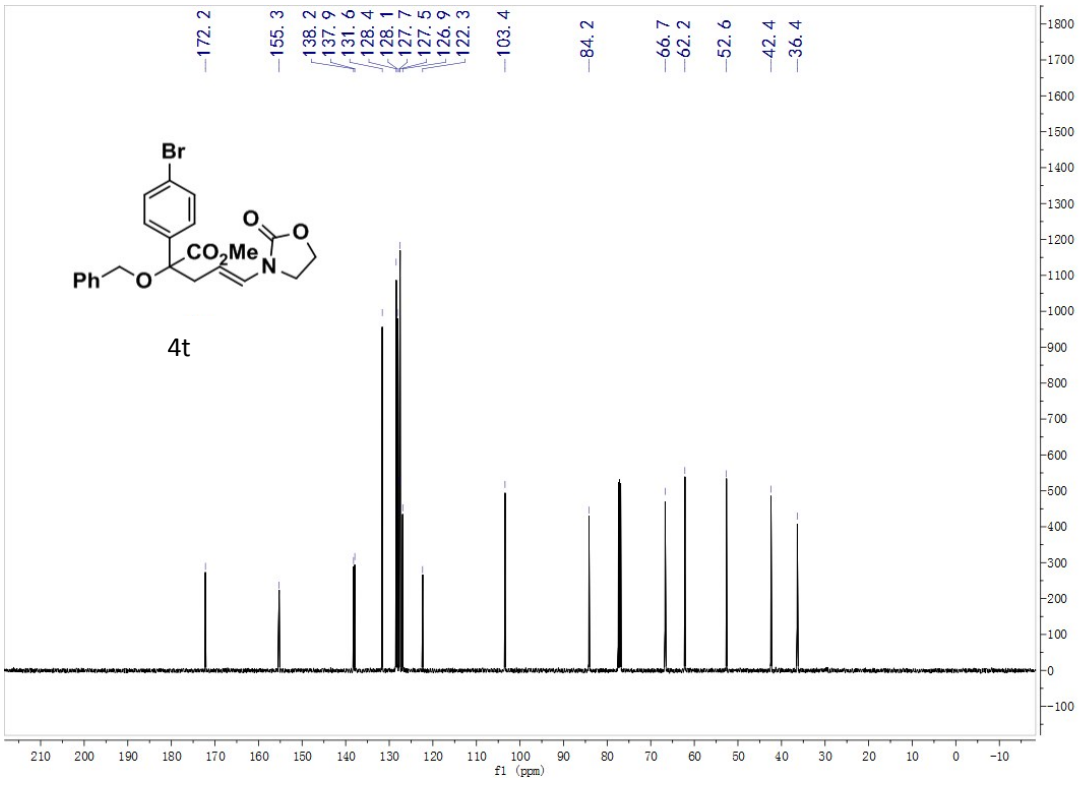
4.57
4.56
4.55
4.54
4.37
4.35
4.34
3.57
3.55
3.54
3.53
3.52
3.51
3.50
3.48
3.11
3.10
3.08
3.07
3.05
3.04
3.02
3.01
Br
O
O
CO2Me
N
Ph
O
2.06
4.00
2.08
0.99
0.97
2.10
3.02
3.00
2.05
2.09
f1 (ppm)

4t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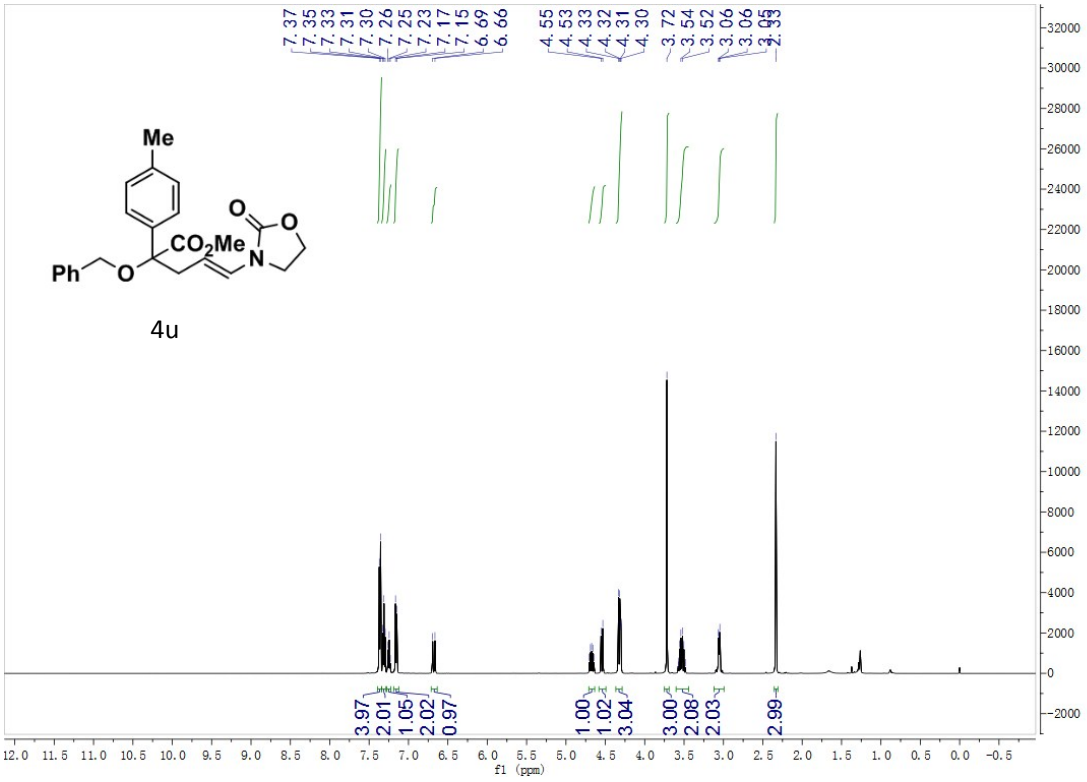
138.2
137.9
131.6
128.4
128.1
127.7
127.5
126.9
122.3
103.4
84.2
66.7
62.2
52.6
42.4
36.4
Br
O
O
CO2Me
N
Ph
O
f1 (ppm)

4t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7.31
7.30
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7.15
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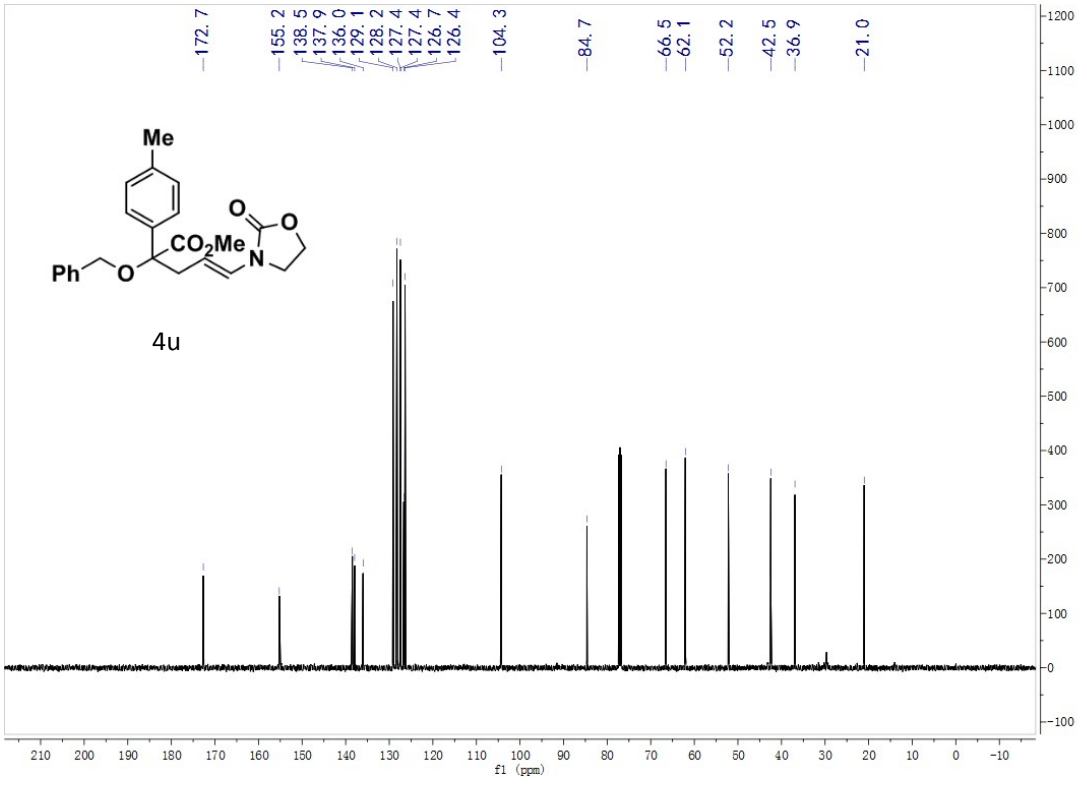
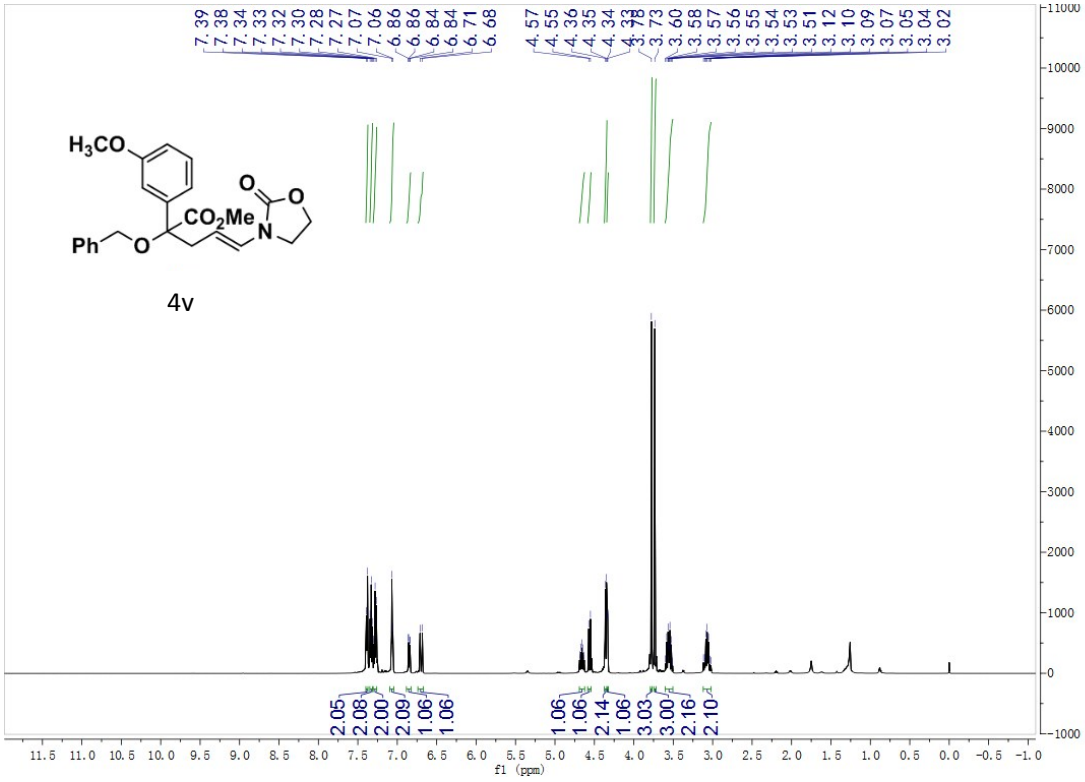
6.66
4.55
4.53
4.33
4.32
4.31
4.30
3.72
3.54
3.52
3.06
3.05
2.33
Me
O
O
CO2Me
N
Ph
O
4u
3.97
2.01
1.05
2.02
0.97
1.00
1.02
3.04
3.00
2.08
2.03
2.99
f1 (ppm)


172.7
155.2
138.5
137.9
136.0
129.1
128.2
127.4
127.4
126.7
126.4
104.3
84.7
66.5
62.1
52.2
42.5
36.9
21.0
Me
O
O
CO2Me
N
Ph
O
4u
f1 (ppm)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7.32
7.30
7.28
7.27
7.07
7.06
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6.86
6.84
6.84
6.71
6.68
4.57
4.55
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4.34
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3.78
3.73
3.60
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3.57
3.56
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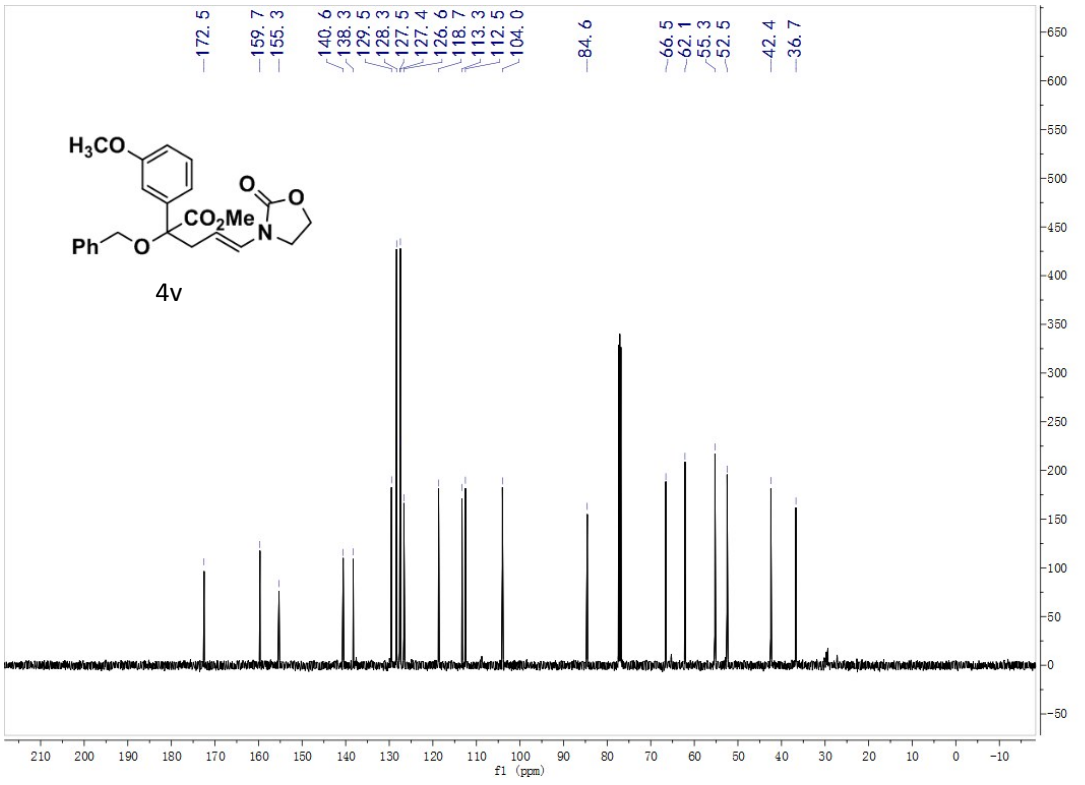
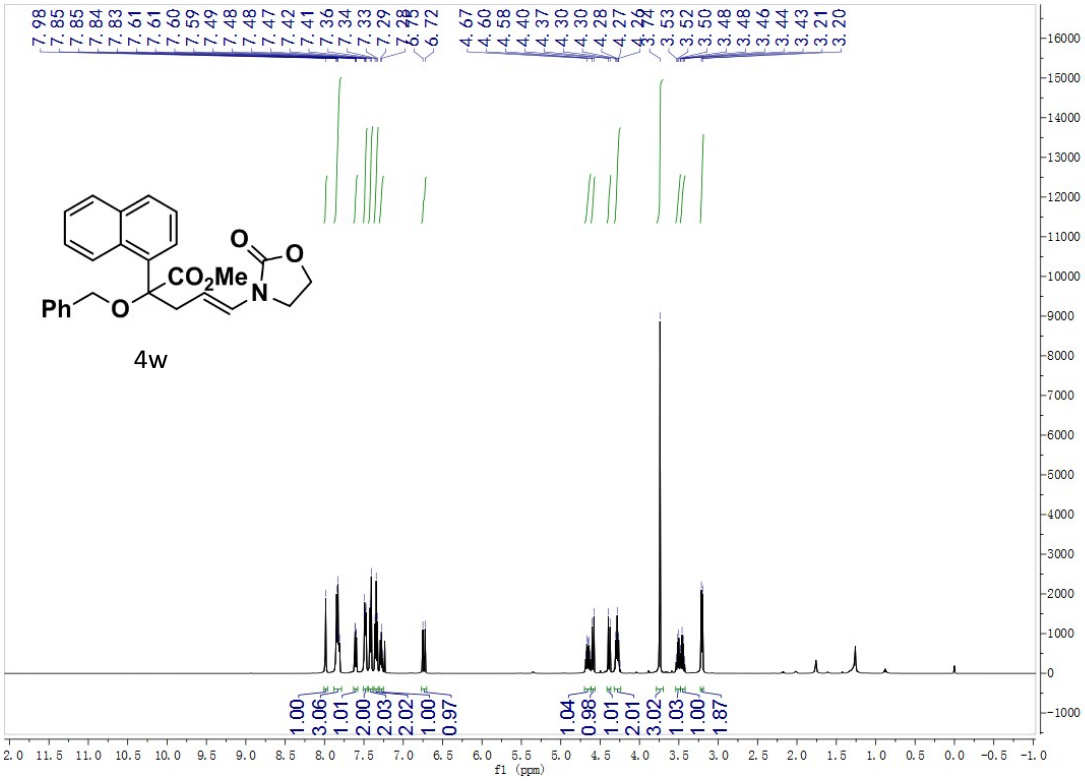
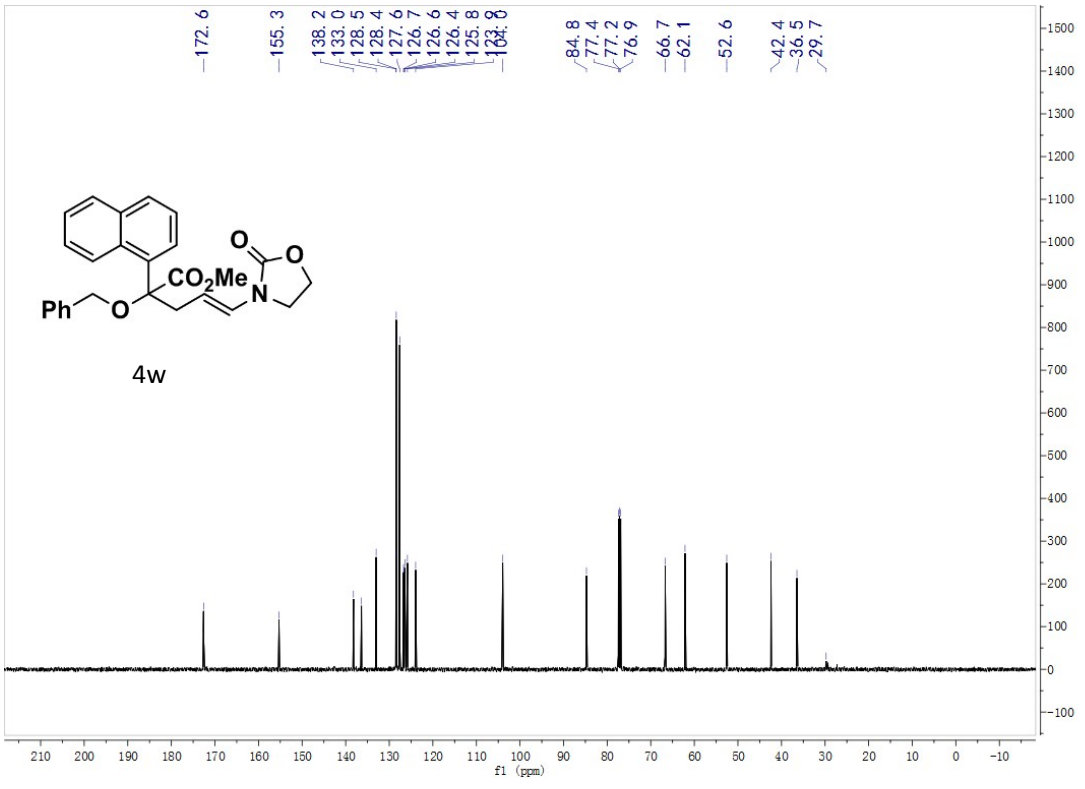
3.54
3.53
3.51
3.12
3.10
3.09
3.07
3.05
3.04
3.02
H3CO
O
O
CO2Me
N
Ph
O
4v
2.05
2.08
2.00
2.09
1.06
1.06
1.06
1.06
2.14
1.06
3.03
3.00
2.16
2.10
f1 (ppm)


172.5
159.7
155.3
140.6
138.3
129.5
128.3
127.5
127.4
126.6
118.7
113.3
112.5
104.0
84.6
66.5
62.1
55.3
52.5
42.4
36.7
H3CO
O
O
CO2Me
N
Ph
O
4v
f1 (ppm)


7.98
7.85
7.85
7.84
7.83
7.61
7.61
7.60
7.59
7.49
7.48
7.48
7.47
7.42
7.41
7.36
7.34
7.33
7.29
6.72
4.67
4.60
4.58
4.40
4.37
4.30
4.30
4.28
4.27
3.53
3.52
3.50
3.48
3.48
3.46
3.44
3.43
3.21
3.20
CO2Me
Ph
O
N
1.00
3.06
1.01
2.00
2.03
2.02
1.00
0.97
1.04
0.98
1.01
2.01
3.02
1.03
1.00
1.87
f1 (ppm)

4w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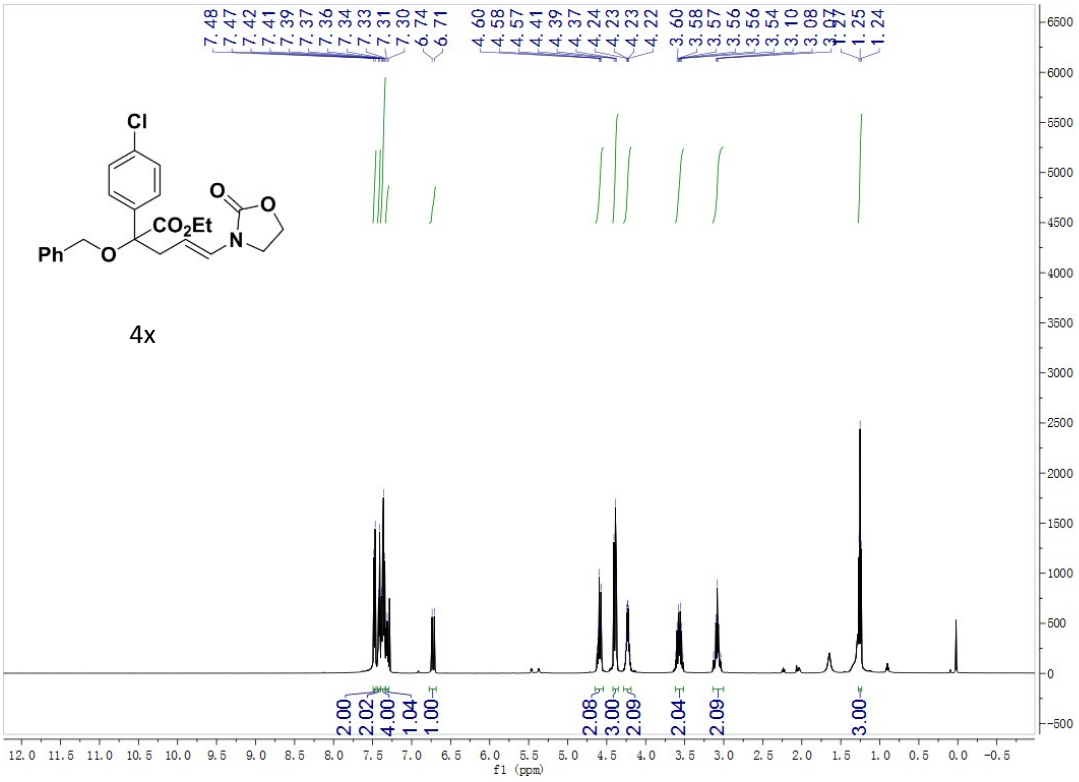
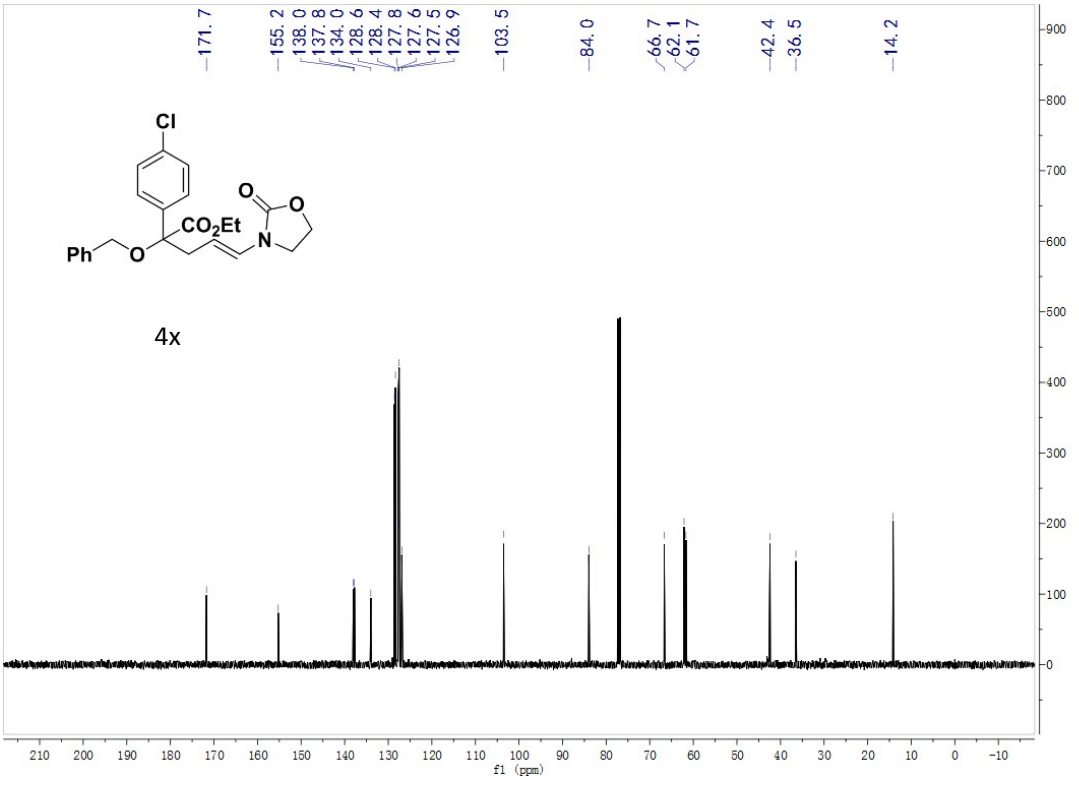
155.3
138.2
133.0
128.5
128.4
127.6
126.7
126.6
126.4
125.8
84.8
77.4
77.2
76.9
66.7
62.1
52.6
42.4
36.5
29.7
CO2Me
Ph
O
N
f1 (ppm)

4w


7.48
7.47
7.42
7.41
7.39
7.37
7.36
7.34
7.33
7.31
7.30
6.74
6.71
4.60
4.58
4.57
4.41
4.39
4.37
4.24
4.23
4.23
4.22
3.60
3.58
3.57
3.56
3.56
3.54
3.10
3.08
1.25
1.24
Cl
CO2Et
Ph
O
N
4x
2.00
2.02
4.00
1.04
1.00
2.08
3.00
2.09
2.04
2.09
3.00
f1 (ppm)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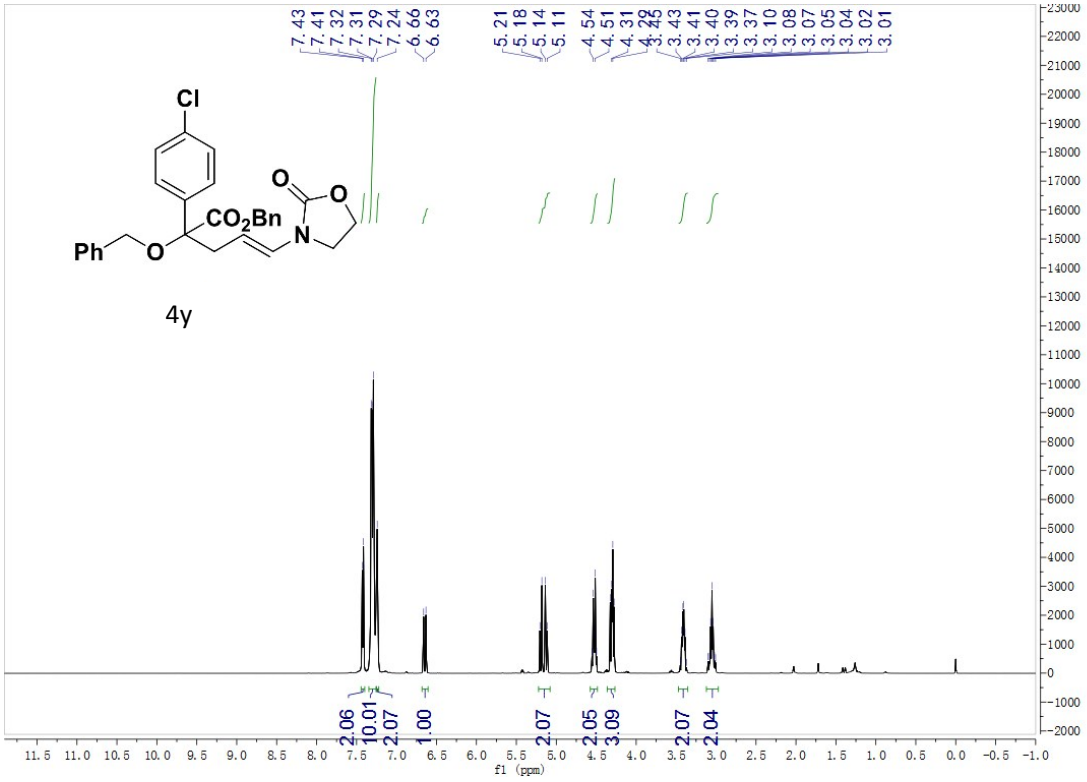
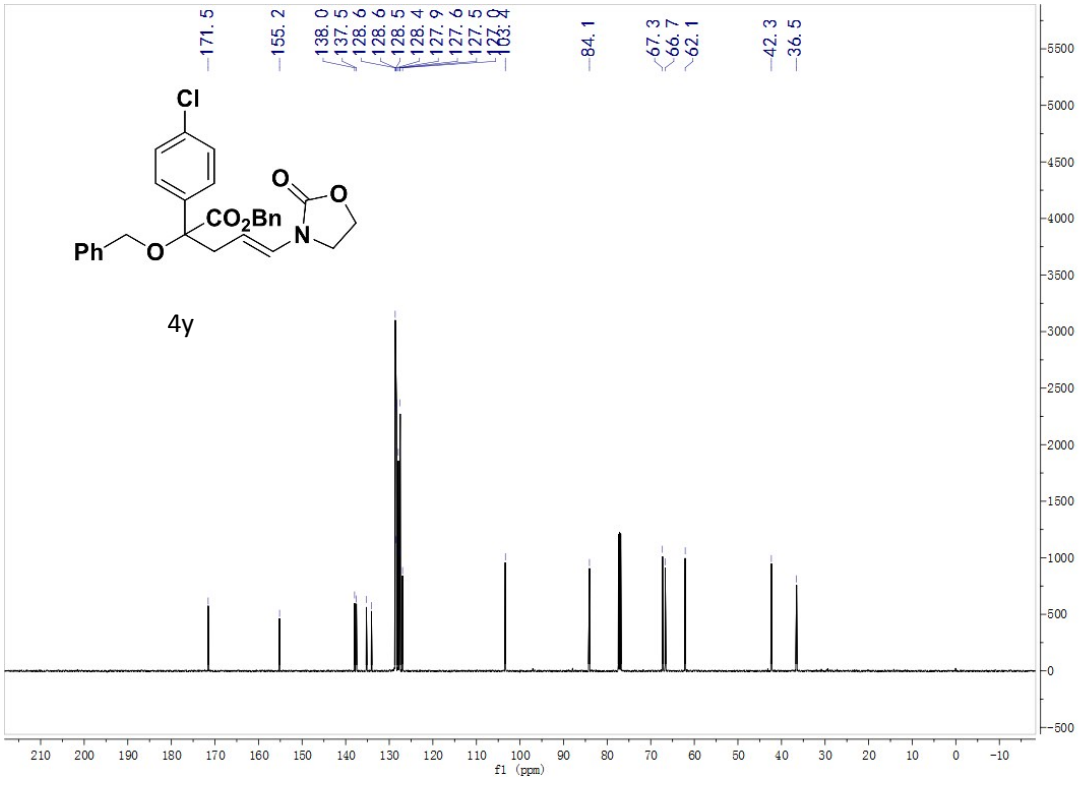
155.2
138.0
137.8
134.0
128.6
128.4
127.8
127.6
127.5
126.9
103.5
84.0
66.7
62.1
61.7
42.4
36.5
14.2
Cl
CO2Et
Ph
O
N
4x
f1 (ppm)


7.43
7.41
7.32
7.31
7.29
7.24
6.66
6.63
5.21
5.18
5.14
5.11
4.54
4.51
4.31
3.43
3.41
3.40
3.39
3.37
3.10
3.08
3.07
3.05
3.04
3.02
3.01
Cl
O
O
CO2Bn
N
Ph
O
4y
2.06
10.01
2.07
1.00
2.07
2.05
3.09
2.07
2.04
f1 (ppm)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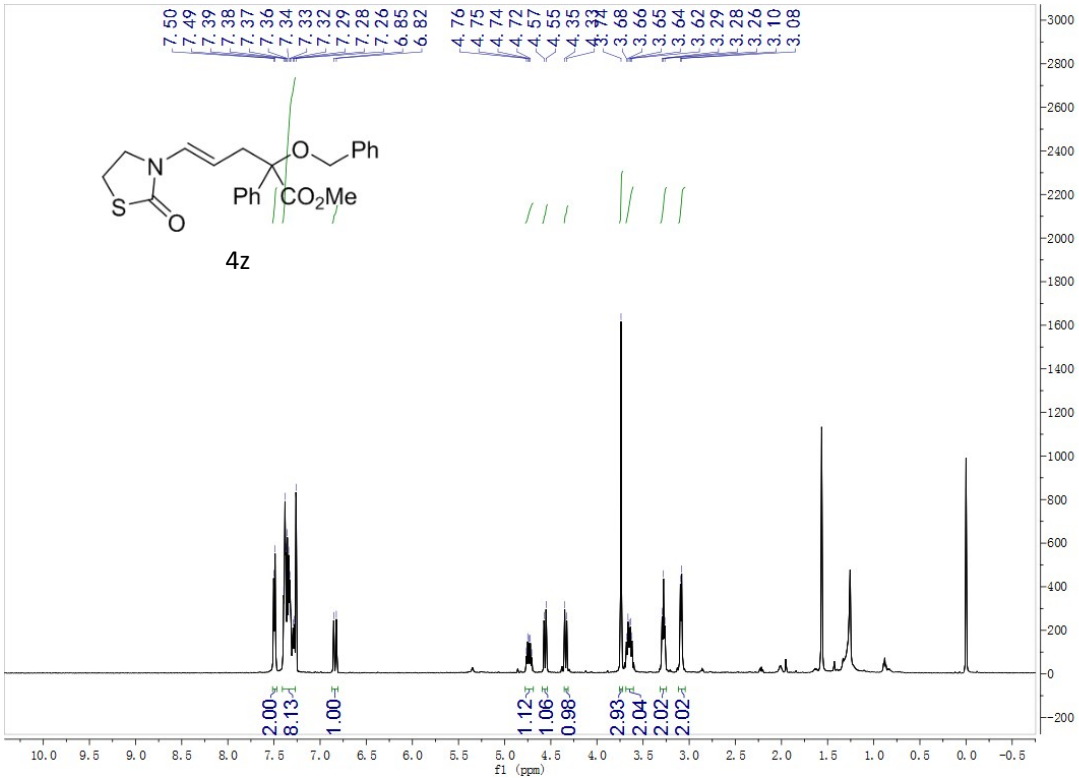
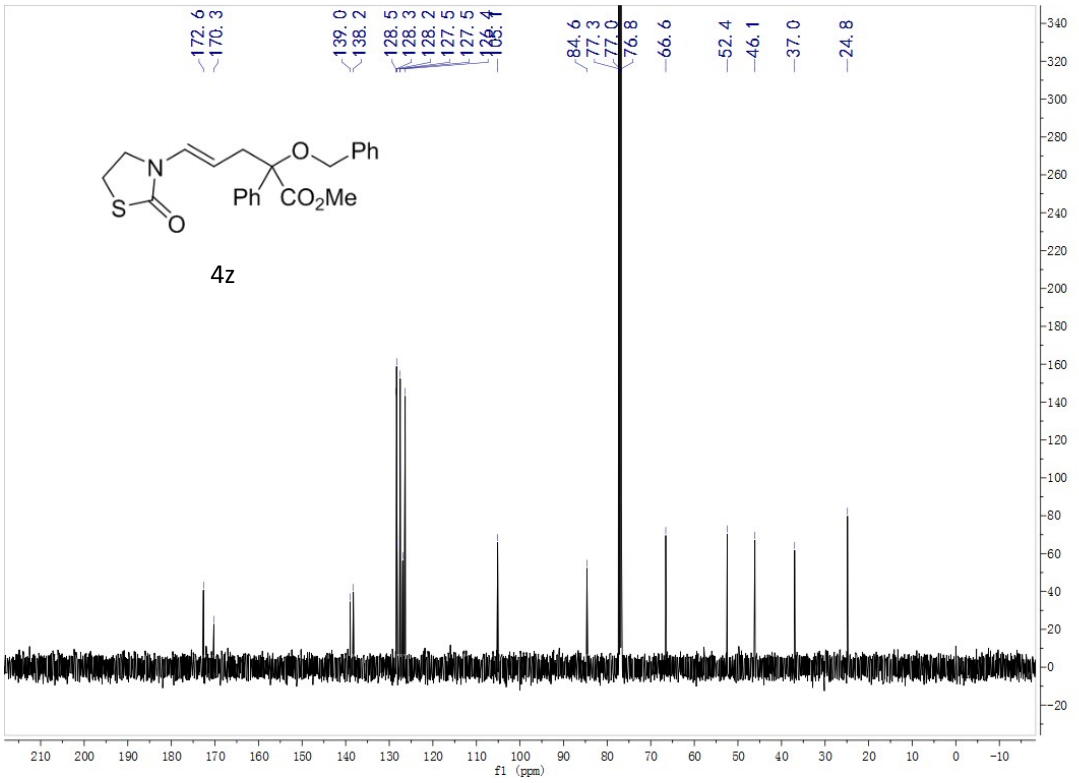
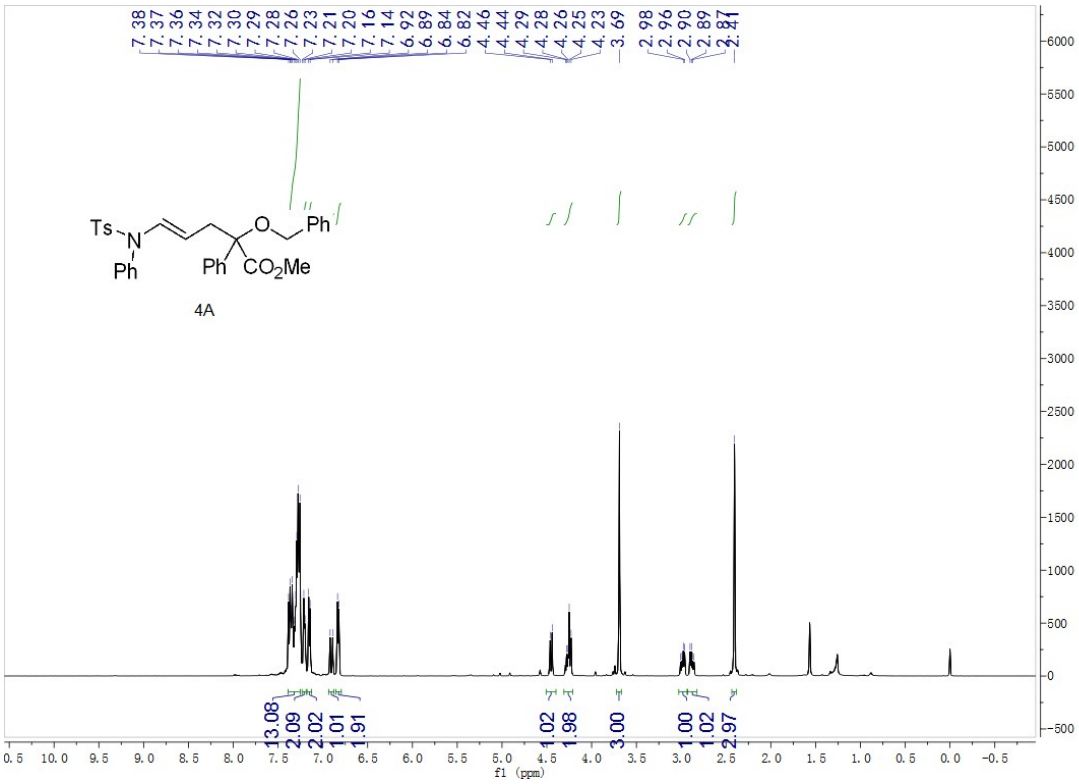
155.2
138.0
137.5
128.6
128.6
128.5
128.4
127.9
127.6
127.5
84.1
67.3
66.7
62.1
42.3
36.5
Cl
O
O
CO2Bn
N
Ph
O
4y
f1 (ppm)

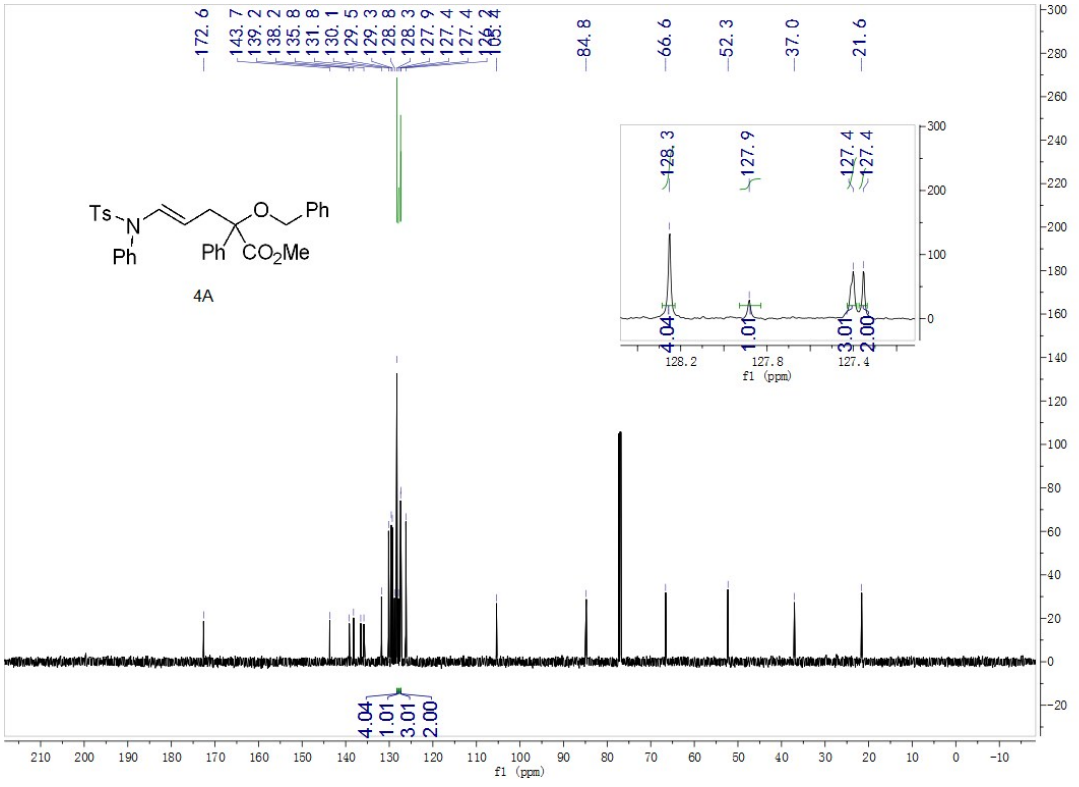

7.50
7.49
7.39
7.38
7.37
7.36
7.34
7.33
7.32
7.29
7.28
7.26
6.85
6.82
4.76
4.75
4.74
4.72
4.57
4.55
4.35
3.68
3.66
3.65
3.64
3.62
3.29
3.28
3.26
3.10
3.08
N
S
O
O
Ph
Ph
CO2Me
2.00
8.13
1.00
1.12
1.06
0.98
2.93
2.04
2.02
2.02
f1 (ppm)

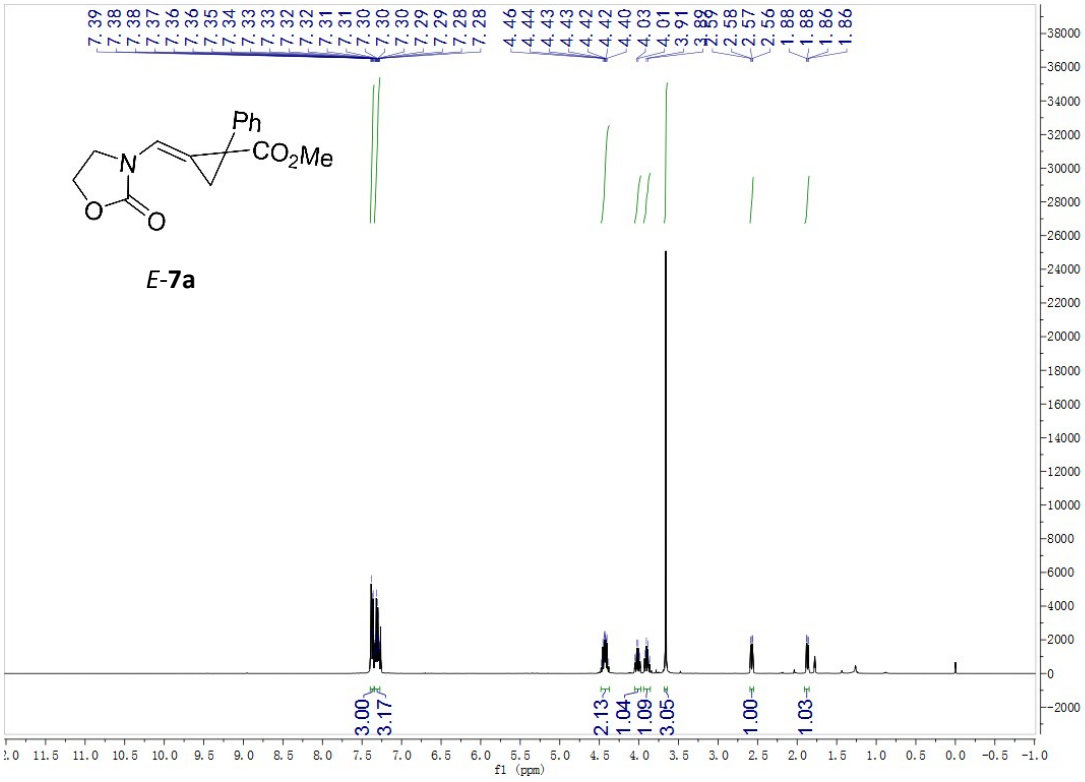
4z

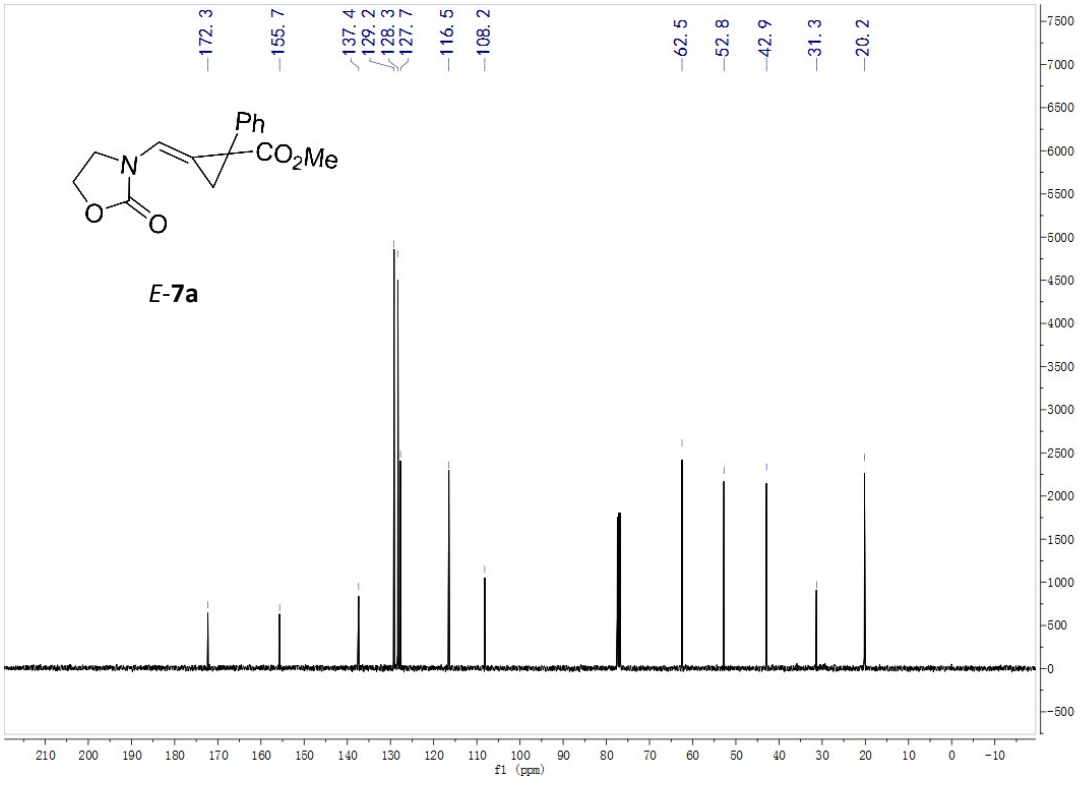

172.6
170.3
139.0
138.2
128.5
128.3
128.2
127.5
127.5
84.6
77.3
77.0
76.8
66.6
52.4
46.1
37.0
24.8
N
S
O
O
Ph
Ph
CO2Me
f1 (ppm)

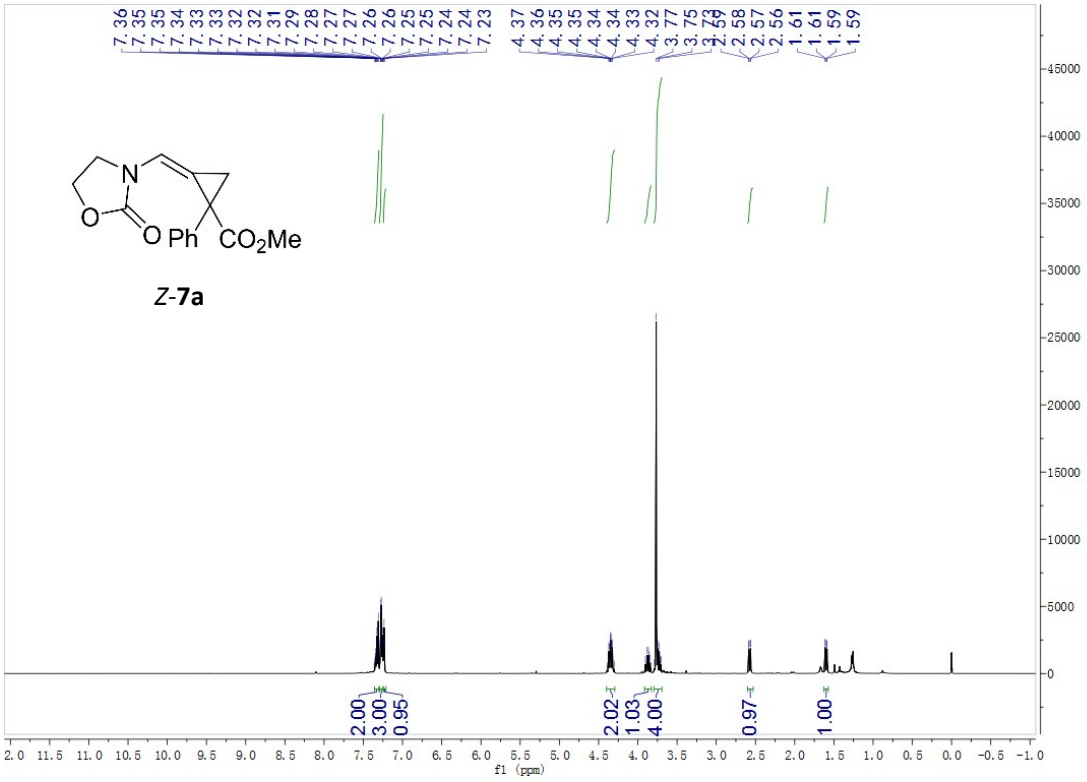
4z


7.38
7.37
7.36
7.34
7.32
7.30
7.29
7.28
7.26
7.23
7.21
7.20
7.16
7.14
6.92
6.89
6.84
6.82
4.46
4.44
4.29
4.28
4.26
4.25
4.23
3.69
2.98
2.96
2.90
2.89
2.87
2.81
Ts
N
Ph
O
Ph
Ph
CO2Me
4A
13.08
2.09
2.02
1.01
1.91
1.02
1.98
3.00
1.00
1.02
2.97
f1 (ppm)

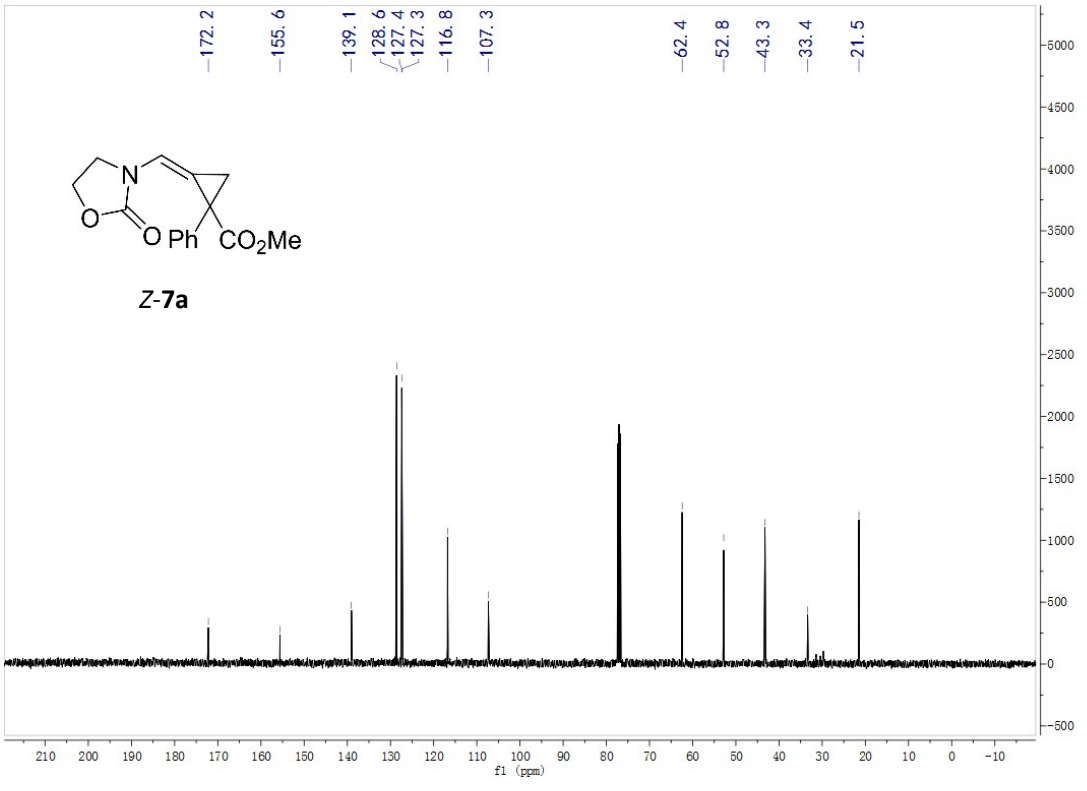

172.6
143.7
139.2
138.2
135.8
131.8
130.1
129.5
129.3
128.8
128.3
127.9
127.4
127.4
84.8
66.6
52.3
37.0
21.6
Ts
N
Ph
O
Ph
Ph
CO2Me
4A
128.3
127.9
127.4
127.4
4.04
1.01
3.01
2.00
f1 (ppm)
4.04
1.01
3.01
2.00
f1 (ppm)


Ph
CO2Me
N
O
O
E-7a
7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28
4.46 4.44 4.43 4.43 4.42 4.42 4.40 4.03 4.01 3.91
2.58 2.57 2.56
1.88 1.86 1.86
3.00 3.17 2.13 1.04 1.09 3.05 1.00 1.03
f1 (ppm)

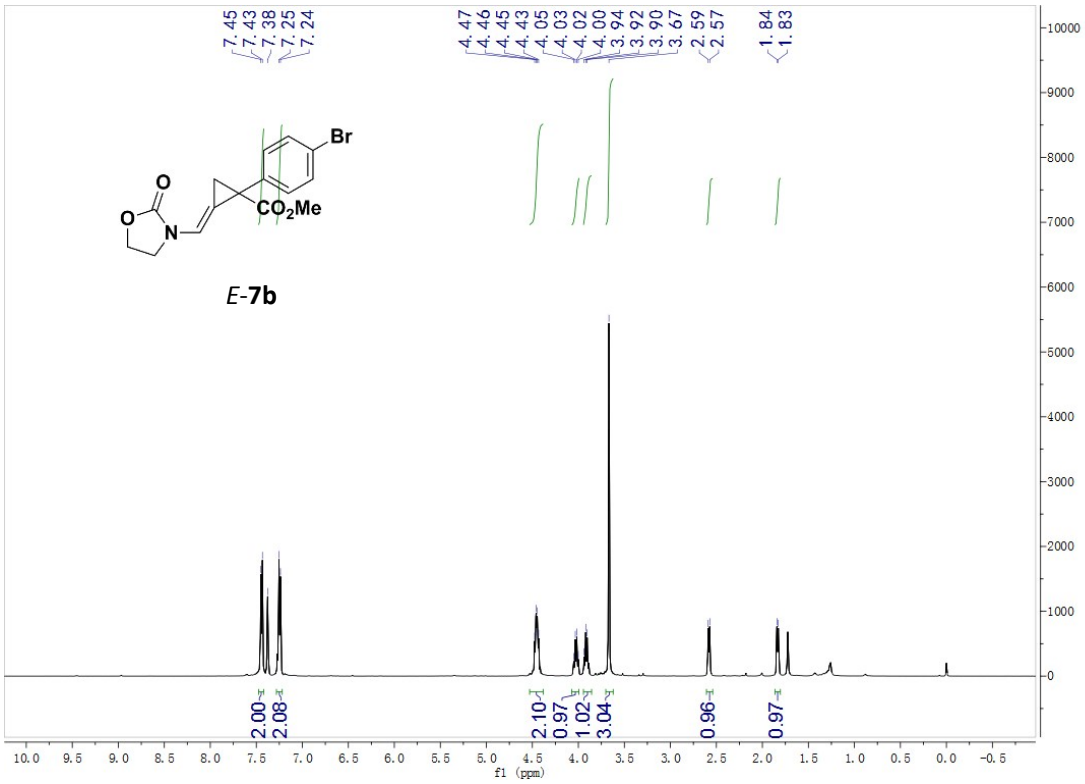

Ph
CO2Me
N
O
O
E-7a
172.3 155.7 137.4 129.2 128.3 127.7 116.5 108.2
62.5 52.8 42.9 31.3 20.2
f1 (ppm)

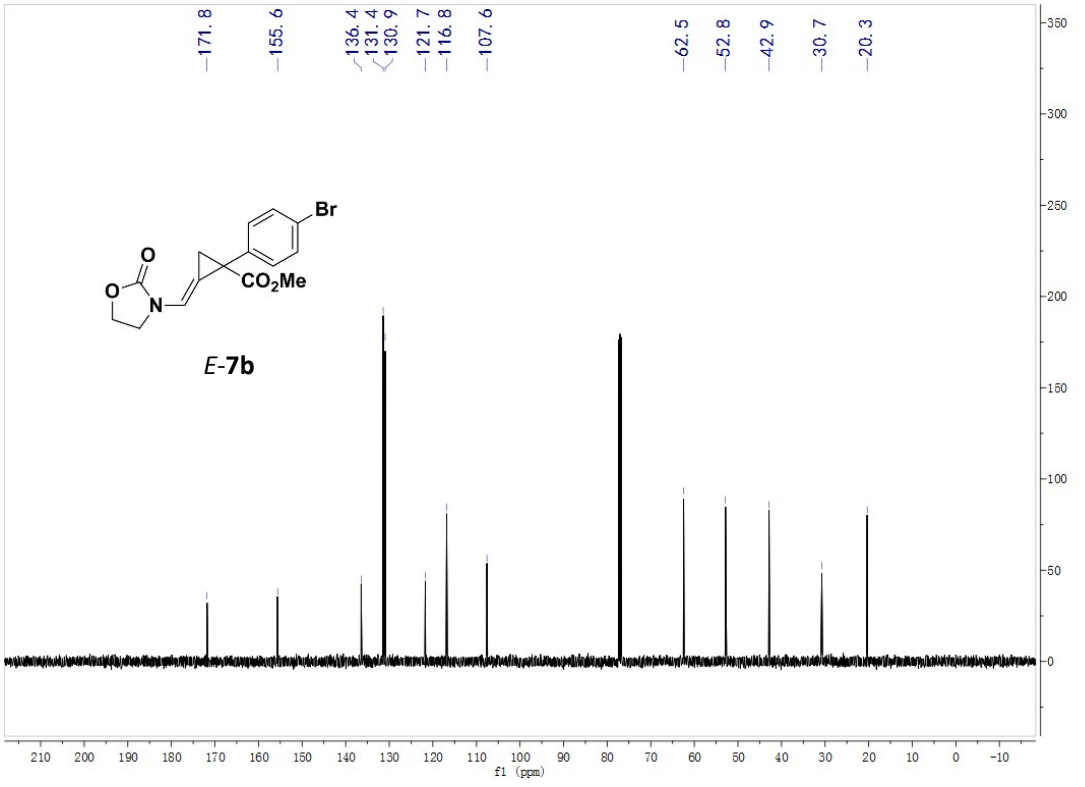

7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.23
4.37 4.36 4.35 4.34 4.34 4.33 4.32 3.77 3.75 2.58 2.57 2.56 1.61 1.61 1.59 1.59
N
O
O Ph CO2Me
2.00 3.00 0.95 2.02 1.03 4.00 0.97 1.00
f1 (ppm)

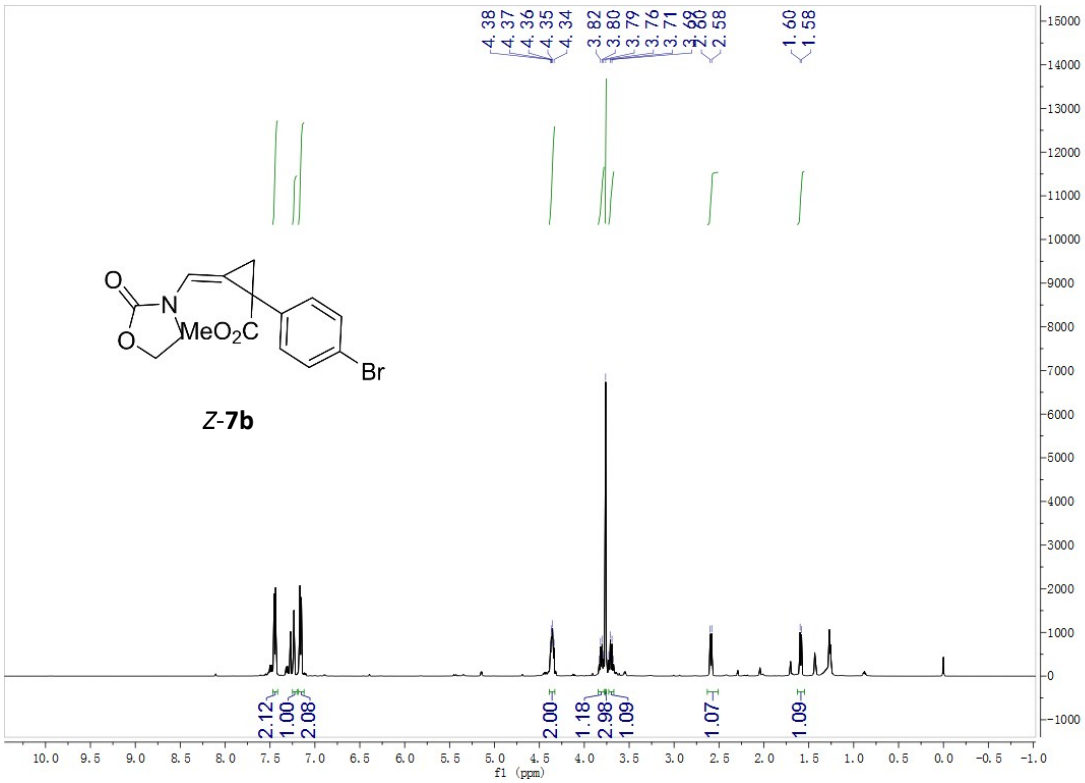
Z-**7a**


172.2 155.6 139.1 128.6 127.4 127.3 116.8 107.3 62.4 52.8 43.3 33.4 21.5
N
O
O Ph CO2Me
f1 (ppm)

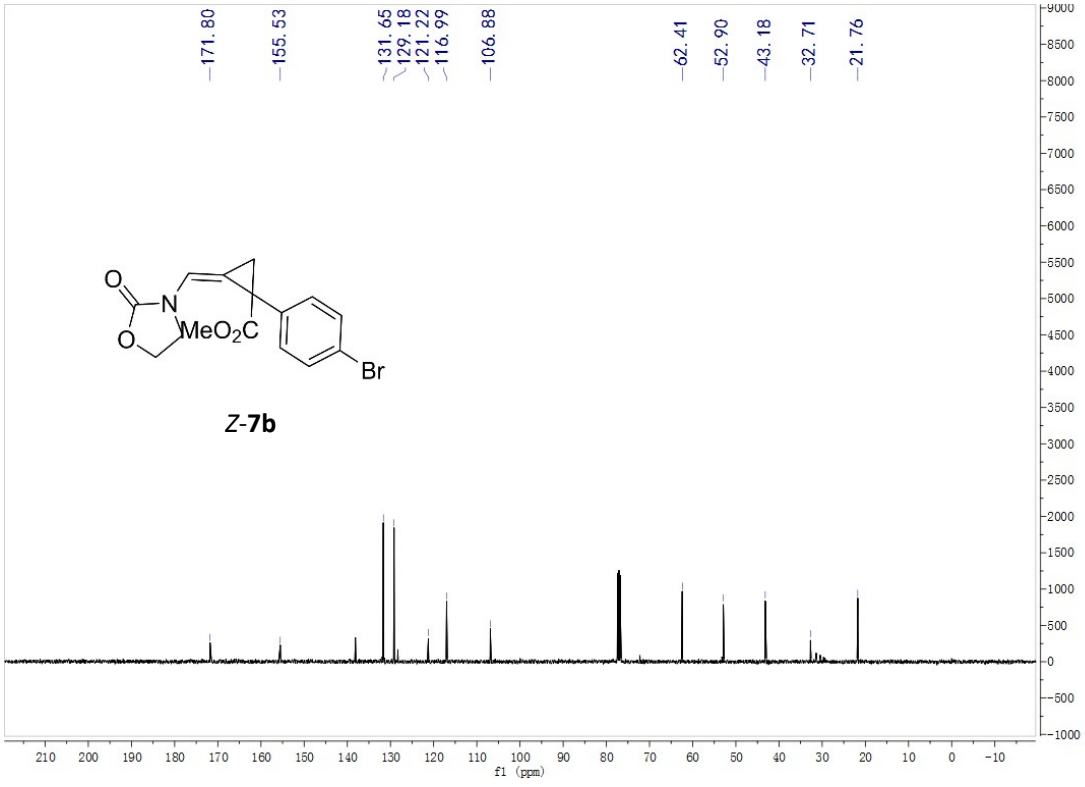
Z-**7a**


7.45
7.43
7.38
7.25
7.24
4.47
4.46
4.45
4.43
4.05
4.03
4.02
4.00
3.94
3.92
3.90
3.67
2.59
2.57
1.84
1.83
Br
O
O
N
CO2Me
E-7b
2.00
2.08
2.10
0.97
1.02
3.04
0.96
0.97
f1 (ppm)

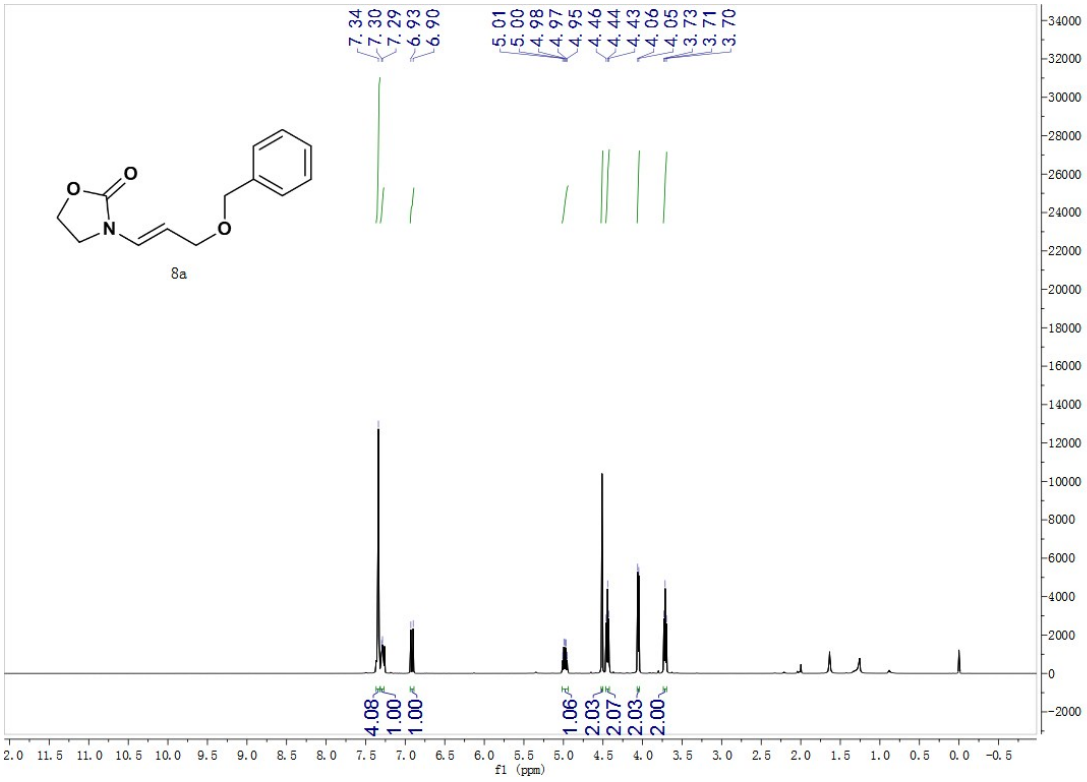

171.8
155.6
136.4
131.4
130.9
121.7
116.8
107.6
62.5
52.8
42.9
30.7
20.3
Br
O
O
N
CO2Me
E-7b
f1 (ppm)

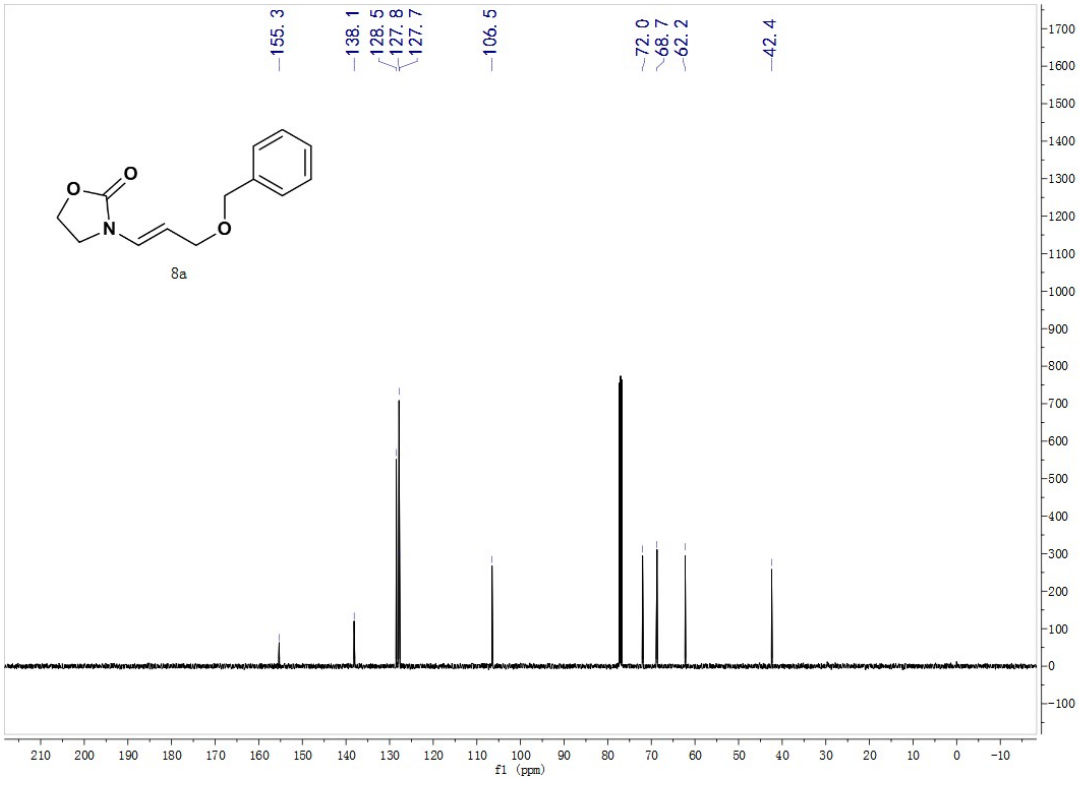

4.38
4.37
4.36
4.35
4.34
3.82
3.80
3.79
3.76
3.71
2.60
2.58
1.60
1.58
O
N
O
MeO2C
Br
2.12
1.00
2.08
2.00
1.18
2.98
1.09
1.07
1.09
f1 (ppm)

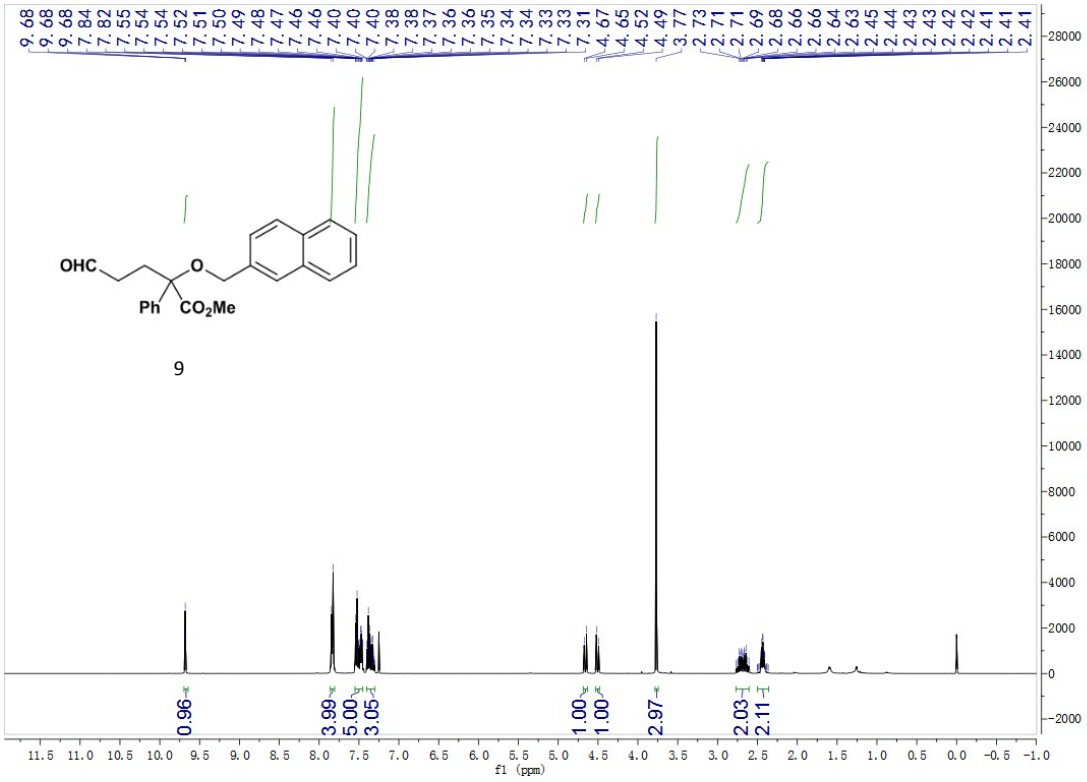
Z-**7b**

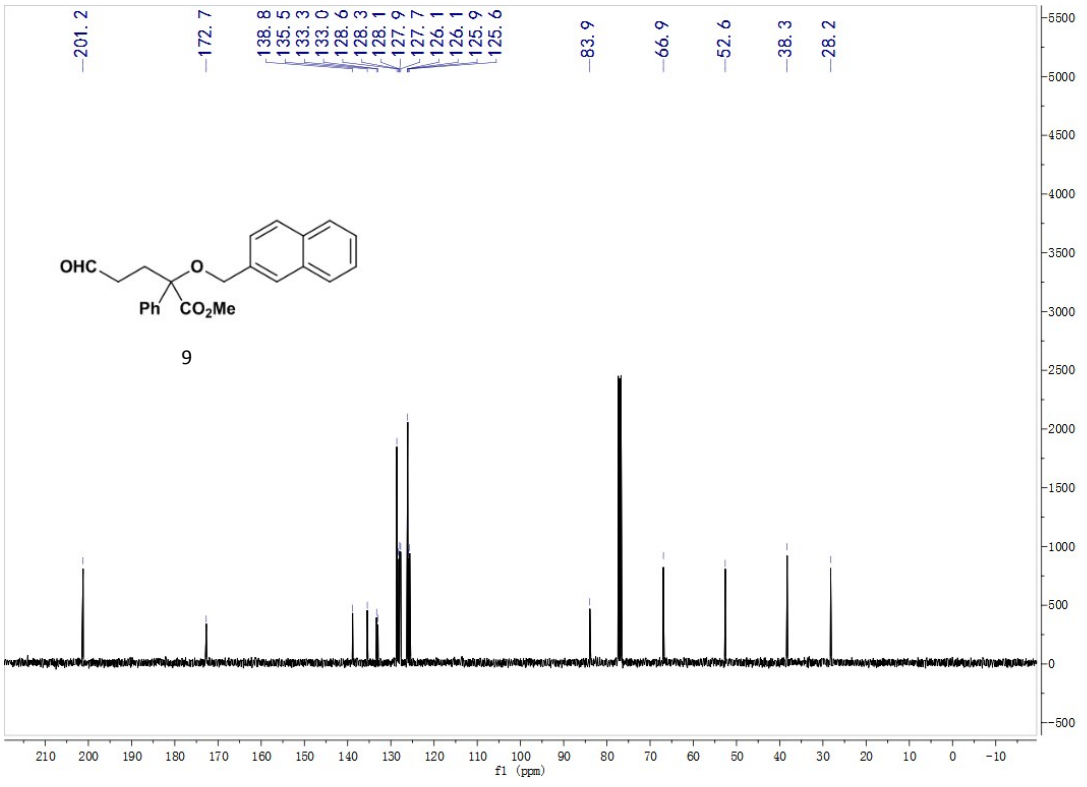

171.80
155.53
131.65
129.18
121.22
116.99
106.88
62.41
52.90
43.18
32.71
21.76
O
N
O
MeO2C
Br
f1 (ppm)

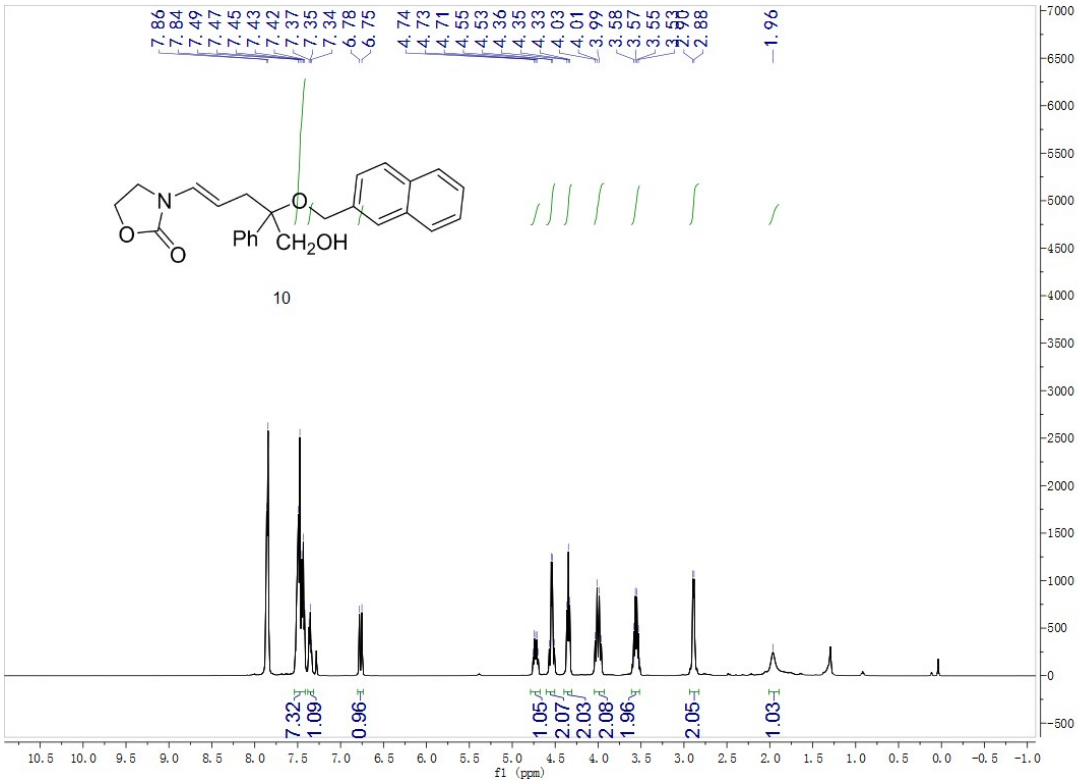
Z-**7b**

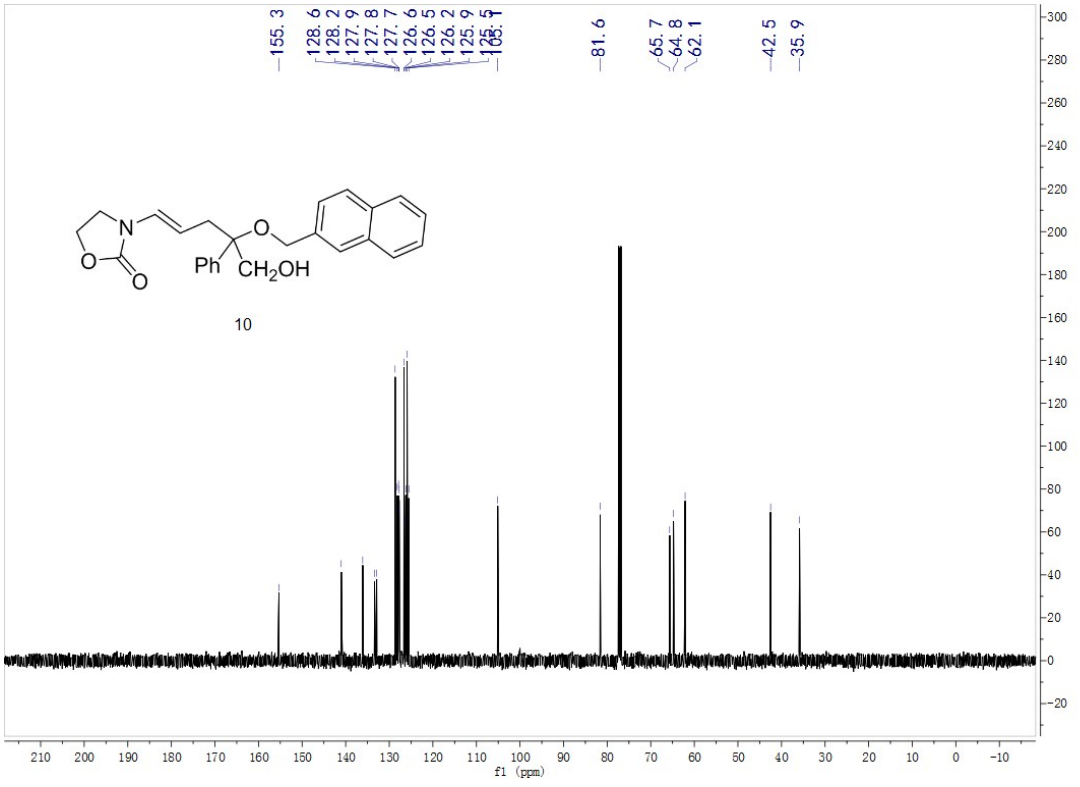

7.34
7.30
7.29
6.93
6.90
5.01
5.00
4.98
4.97
4.95
4.46
4.44
4.43
4.06
4.05
3.73
3.71
3.70
8a
4.08
1.00
1.00
1.06
2.03
2.07
2.03
2.00
f1 (ppm)

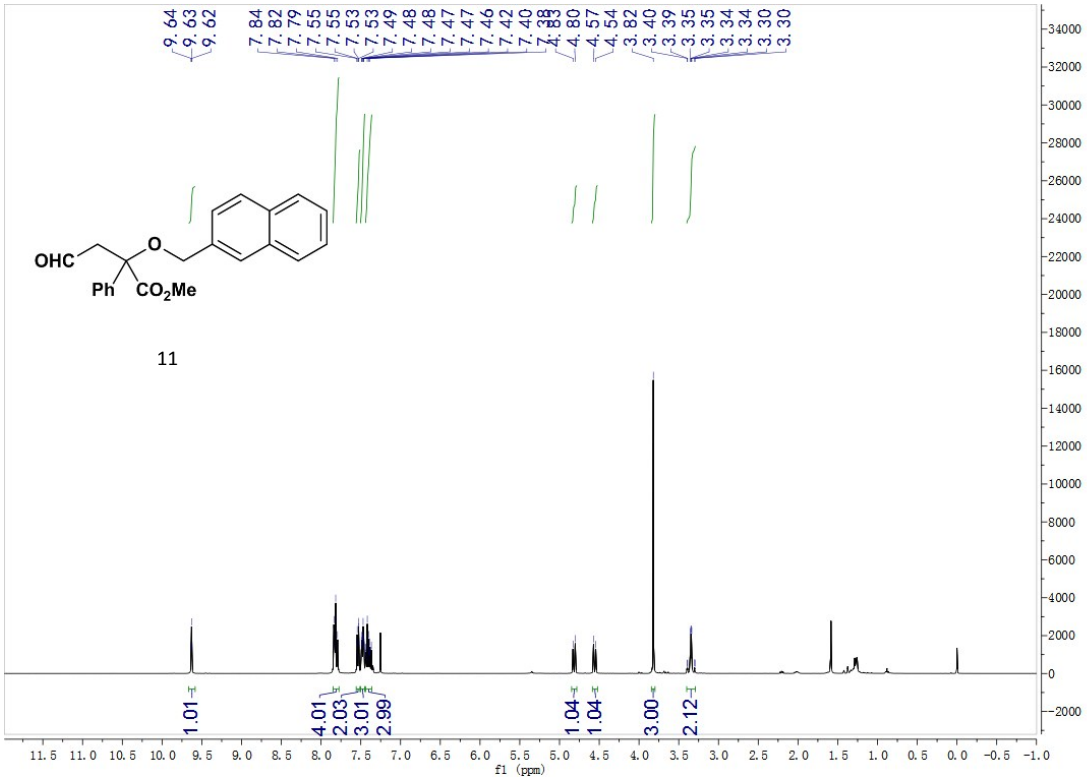

155.3
138.1
128.5
127.8
127.7
106.5
72.0
68.7
62.2
42.4
8a
f1 (ppm)


OHC
O
Ph
CO2Me
9
0.96
3.99
5.00
3.05
1.00
1.00
2.97
2.03
2.11
f1 (ppm)

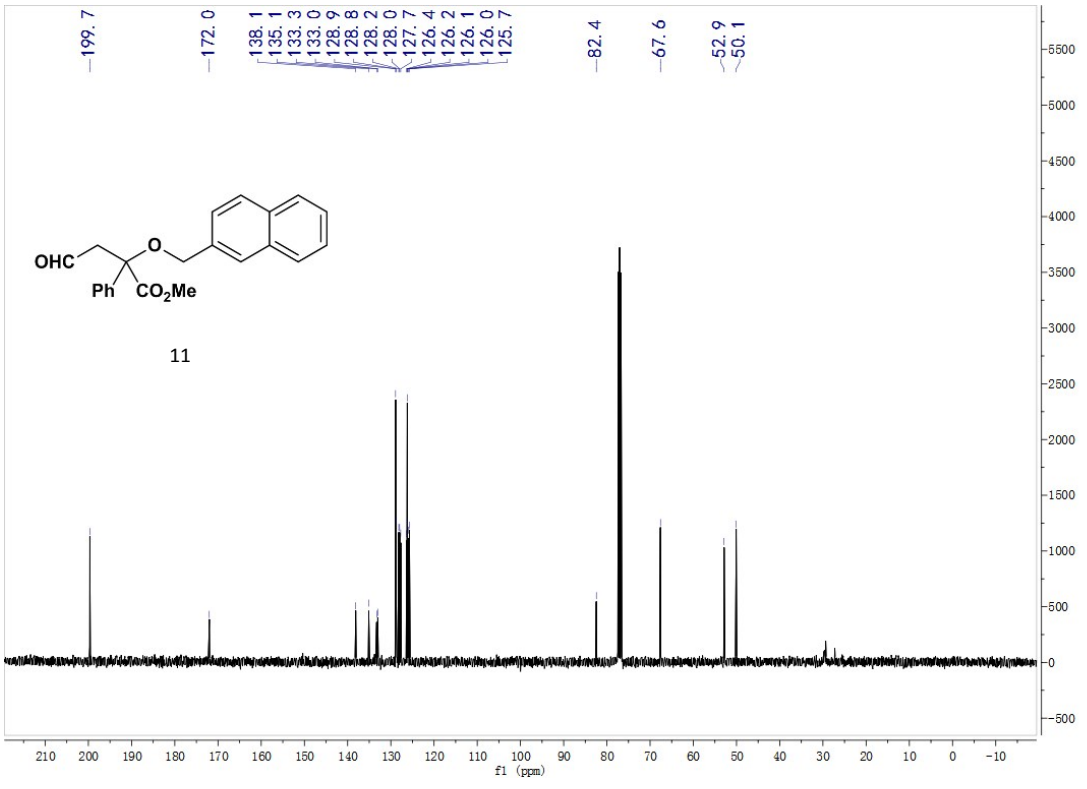

201.2
172.7
138.8
135.5
133.3
133.0
128.6
128.3
128.1
127.9
127.7
126.1
126.1
125.9
125.6
83.9
66.9
52.6
38.3
28.2
OHC
O
Ph
CO2Me
9
f1 (ppm)


7.86
7.84
7.49
7.47
7.45
7.43
7.42
7.37
7.35
7.34
6.78
6.75
4.74
4.73
4.71
4.55
4.53
4.36
4.35
4.33
4.03
4.01
3.99
3.58
3.57
3.55
3.53
2.90
2.88
1.96
Ph
CH2OH
10
7.32
1.09
0.96
1.05
2.07
2.03
2.08
1.96
2.05
1.03
f1 (ppm)

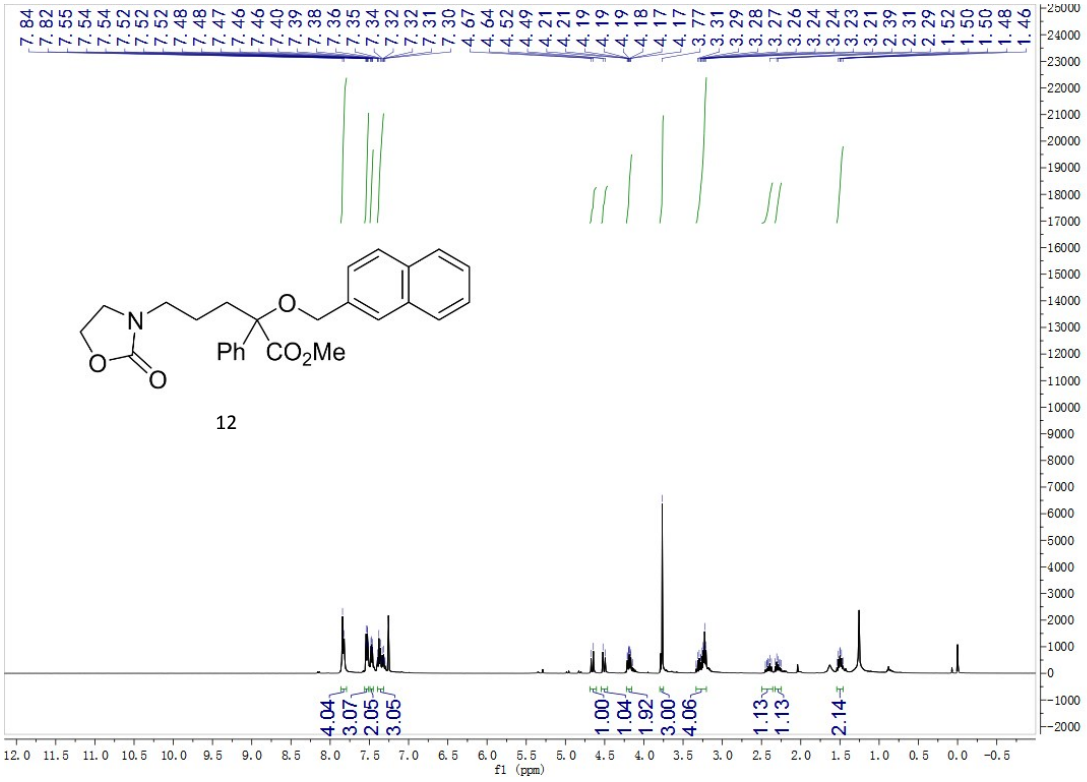

155.3
128.6
128.2
127.9
127.8
127.7
126.6
126.5
126.2
125.9
81.6
65.7
64.8
62.1
42.5
35.9
Ph
CH2OH
10
f1 (ppm)


9.64
9.63
9.62
7.84
7.82
7.79
7.55
7.55
7.53
7.53
7.49
7.48
7.48
7.47
7.47
7.46
7.42
7.40
4.80
4.57
4.54
3.82
3.40
3.39
3.35
3.35
3.34
3.34
3.30
3.30
OHC
O
Ph
CO2Me
1.01
4.01
2.03
3.01
2.99
1.04
1.04
3.00
2.12
f1 (ppm)

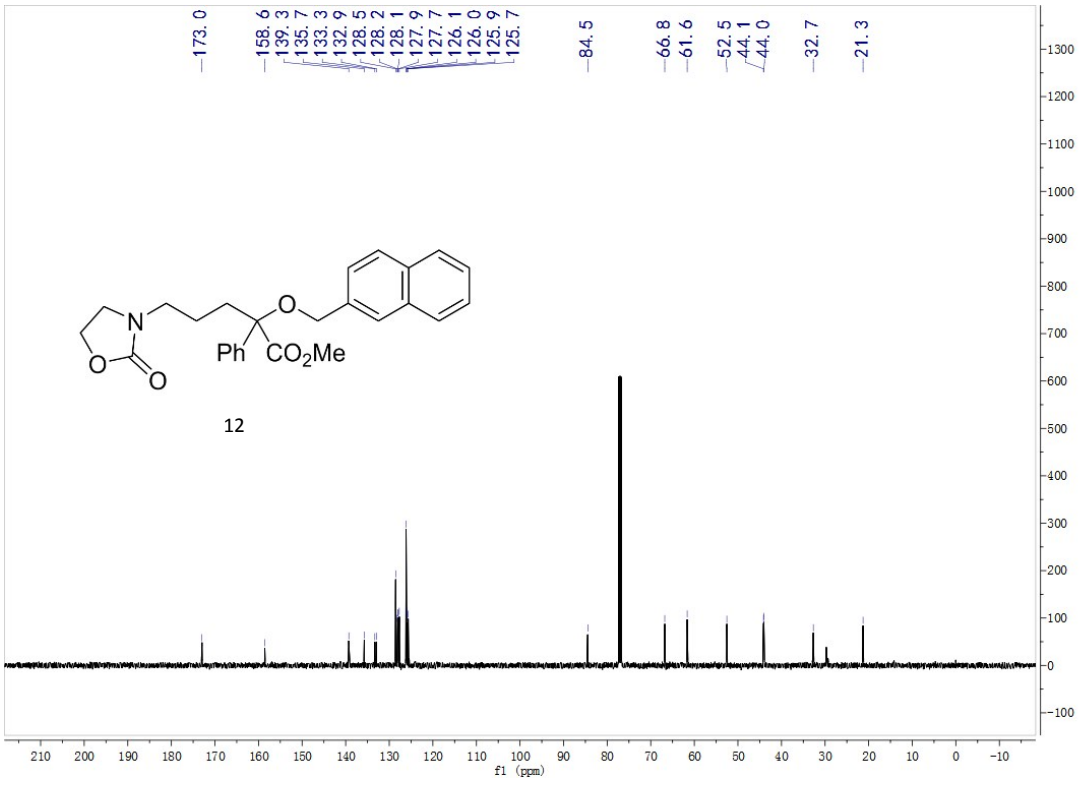
11


199.7
172.0
138.1
135.1
133.3
133.0
128.9
128.8
128.2
128.0
127.7
126.4
126.2
126.1
126.0
125.7
82.4
67.6
52.9
50.1
OHC
O
Ph
CO2Me
f1 (ppm)

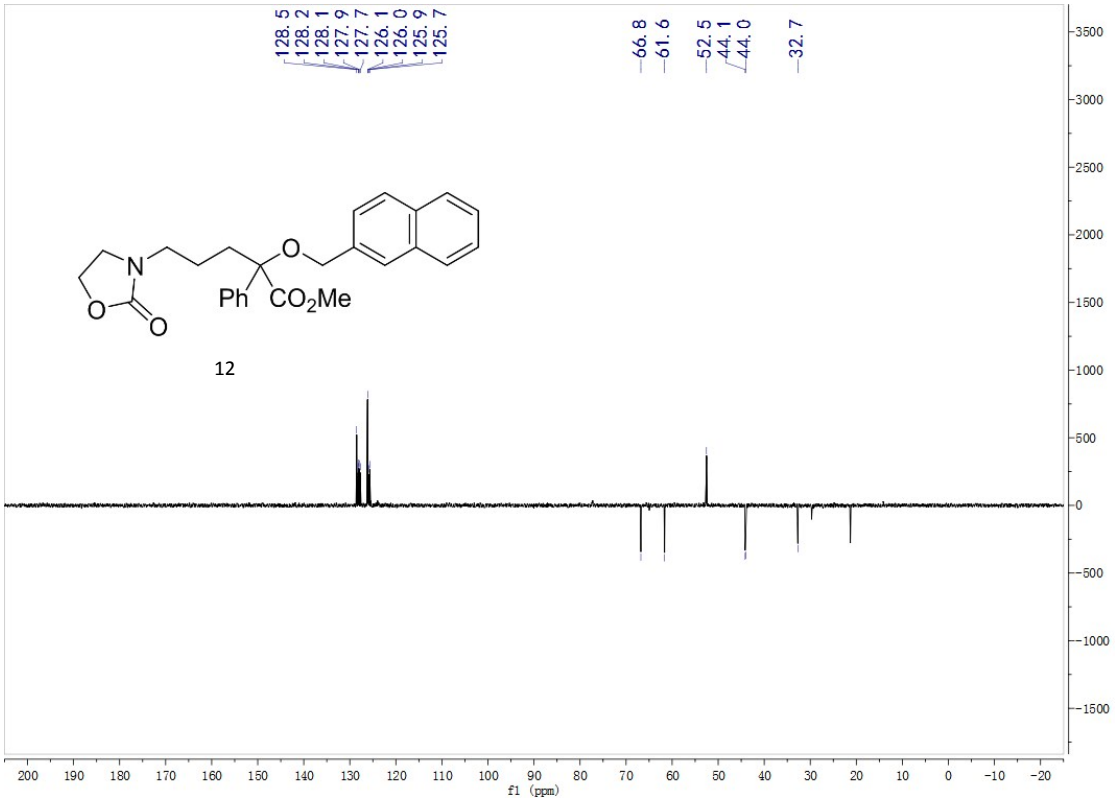
11


7.84 7.82 7.55 7.54 7.54 7.52 7.52 7.52 7.48 7.48 7.47 7.46 7.46 7.40 7.39 7.38 7.36 7.35 7.34 7.32 7.32 7.31 7.30 4.67 4.64 4.52 4.49 4.21 4.21 4.19 4.19 4.19 4.18 4.17 4.17 3.77 3.31 3.29 3.28 3.27 3.26 3.24 3.24 3.23 3.21 2.39 2.31 2.29 1.52 1.50 1.50 1.48 1.46
4.04 3.07 2.05 3.05 1.00 1.04 1.92 3.00 4.06 1.13 1.13 2.14
f1 (ppm)

12


173.0 158.6 139.3 135.7 133.3 132.9 128.5 128.2 128.1 127.9 127.7 126.1 126.0 125.9 125.7 84.5 66.8 61.6 52.5 44.1 44.0 32.7 21.3
f1 (ppm)

12


128.5
128.2
128.1
127.9
127.7
126.1
126.0
125.9
125.7
66.8
61.6
52.5
44.1
44.0
32.7
N
O
O
O
Ph
CO2Me
12
f1 (ppm)