Supporting Information
For the article entitled

Weinreb Amide Directed Cross-Coupling Reaction of Electron-deficient Alkenes Catalyzed by Rhodium Catalyst

Feifei Li, Chunbing Yu, Jian Zhang* and Guofu Zhong*

College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China.

E-mail: zhangjian@hznu.edu.cn;

zgf@hznu.edu.cn

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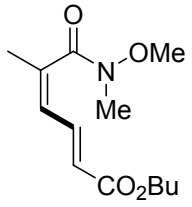
General Methods

All commercially available reagents for the cross-coupling reaction were used as received: AR grade 1, 2-dichloroethane, was obtained from TCI and used as received. $[RhCp^*Cl_2]_2$, $[RuCl_2(p\text{-cymene})]_2$ and $AgSbF_6$ were obtained from Energy Chemical. $Cu(OAc)_2$ was purchased from Alfa Aesar. The desired Weinreb acrylamides and the corresponding acrylic acid were prepared according to the reported method.[1-5] All cross-coupling reactions were run in vials under sealed argon atmosphere. Thin-layer chromatography (TLC) was conducted with pre-coated silica gel plate (0.2 mm thickness) and visualized with UV and potassium permanganate staining, followed by heating on a hot plate. Flash chromatography was performed using silica gel 60 with distilled solvents. ^{1}H NMR spectra were performed on a Bruker 500 NMR spectrometer and are reported in ppm downfield from $SiMe_4$ (δ = 0.0) and relative to the signal of chloroform-*d* (δ = 7.27 ppm, singlet). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}CNMR spectra were recorded on a 500 (125 MHz) or ECA-400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.23 ppm). IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectral analysis (HRMS) was performed on Waters Q-Tof Permies Mass Spectrometer.

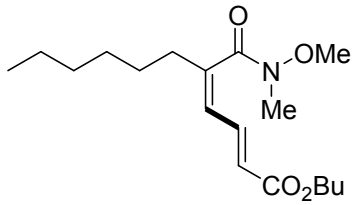
General Procedure for Cross-Coupling of Acrylamides with Alkenes

An oven-dried screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%, 0.005 mmol), $AgSbF_6$ (10 mol%, 0.02 mmol), $Cu(OAc)_2$ (2.0 equiv, 0.4 mmol) and DCE (1 mL). Then, acrylamide (1.0 equiv, 0.2 mmol) and acrylate (2.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 120 ℃ with stirring for 16 hours. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures).

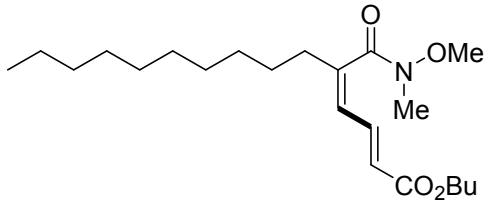
Characterization Data for the Butadienes



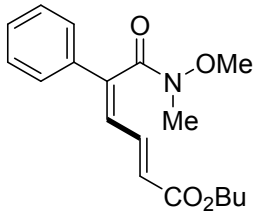
(*2E*, *4Z*)-Butyl 6-(methoxy(methyl)amino)-5-methyl-6-oxohexa-2,4-dienoate (**3a**)：This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 80 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.13 (d, *J* = 11.5 Hz, 1H), 5.89 (d, *J* = 15.0 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 3.61 (s, 3H), 3.26 (s, 3H), 2.08 (s, 3H), 1.66-1.60 (m, 2H), 1.39 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 166.7, 142.8, 140.1, 126.2, 122.1, 64.3, 61.8, 32.1, 31.1, 20.7, 19.1, 13.7. HR-MS (ESI): Calculated for $C_{16}H_{21}NO_4$: $[M+H]^+$ 256.1543. Found: m/z 256.1542. FTIR (KBr, cm^{-1}): ν 3507.68, 2957.85, 2932.54, 2857.87, 1715.65, 1652.43, 1634.89, 1273.67, 1147.72, 995.68.



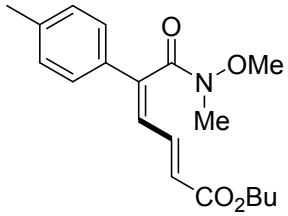
(*2E*,*4Z*)-Butyl 6-(methoxy(methyl)amino)-5-hexyl-6-oxohexa-2,4-dienoate (**3b**): This compound was prepared by the general procedure described above and was obtained as an orange oil, yield = 51 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 15.0 Hz, 11.5 Hz, 1H), 6.12 (d, *J* = 11.5 Hz, 1H), 5.90 (d, *J* = 15.0 Hz, 1H), 4.13 (t, *J* = 6.5 Hz, 2H), 3.57 (s, 3H), 3.27 (s, 3H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.60-1.66 (m, 2H), 1.47-1.53 (m, 2H), 1.25-1.42 (m, 8H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.8, 147.8, 140.4, 124.9, 122.2, 64.3, 61.7, 34.6, 32.1, 31.6, 30.7, 29.0, 27.5, 22.6, 19.2, 14.1, 13.7. HR-MS (ESI): Calculated for $C_{18}H_{31}NO_4$: $[M+H]^+$ 326.2326. Found: m/z 326.2332. FTIR (KBr, cm^{-1}): ν 3507.68, 2957.85, 2932.54, 2857.87, 1715.65, 1652.43, 1634.89, 1455.86, 1385.22, 1273.67, 1147.72, 995.68.



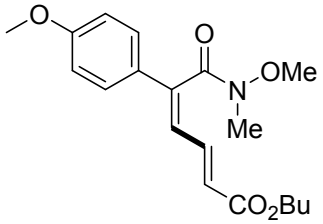
(*2E*,*4Z*)-Butyl 6-(methoxy(methyl)amino)-5-decyl-6-oxohexa-2,4-dienoate (**3c**): this compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 45%.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 15.0 Hz, 12.0 Hz, 1H), 6.12 (d, *J* = 12.0 Hz, 1H), 5.87 (d, *J* = 15.0 Hz, 1H), 4.13 (t, *J* = 6.5 Hz, 2H), 3.57 (s, 3H), 3.27(s, 3H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.60-1.67 (m, 2H), 1.47-1.53 (m, 2H), 1.36-1.41 (m, 2H), 1.30- 1.22 (m, 16H), 0.94 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.8, 147.8, 140.4, 124.9, 122.1, 66.4, 64.3, 61.7, 34.6, 31.9, 30.7, 29.7, 29.6, 29.5, 29.4, 29.3, 27.5, 22.7, 19.2, 14.1, 13.7. HR-MS (ESI): Calculated for $C_{22}H_{39}NO_4$: $[M+H]^+$ 324.1576. Found: m/z 324.1578. FTIR (KBr, cm^{-1}): ν 2925.67, 1715.95, 1660.33, 1455.58, 1273.96, 1147.04



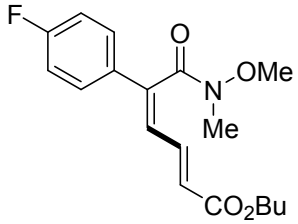
(*2E,4Z*)-Butyl 6-(methoxy(methyl)amino)-5-phenyl-6-oxohexa-2,4-dienoate (**3d**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.50 (m, 5H), 6.72 (d, *J* = 12.0 Hz, 1H), 6.08 (d, *J* = 16.5 Hz, 1H), 4.17 (t, *J* = 6.5 Hz, 2H), 3.41 (s, 3H), 3.36 (s, 3H), 1.61-1.69 (m, 2H), 1.34-1.45 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 166.6, 144.8, 140.0, 135.2, 129.2, 128.9, 126.1, 124.5, 124.2, 64.5, 61.6, 32.3, 30.7, 19.2, 13.7. HR-MS (ESI): Calculated for $C_{18}H_{23}NO_4$: $[M+H]^+$ 324.1576. Found: m/z 324.1578. FTIR (KBr, cm^{-1}): ν 3473.03, 2948.71, 2357.99, 1715.84, 1657.10, 1434.96, 1360.86, 1244.09, 1161.29, 1080.86, 997.07, 901.38, 761.69.



(*2E,4Z*)-Butyl 6-(methoxy(methyl)amino)- 5-(*p*-tolyl)-6-oxohexa-2,4-dienoate (**3e**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 71 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 15.0 Hz, 11.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 11.5 Hz, 1H), 6.06 (d, *J* = 15.0 Hz, 1H), 4.16 (t, *J* = 6.5 Hz, 2H), 3.41 (s, 3H), 3.36 (s, 3H), 2.36 (s, 3H), 1.62-1.68 (m, 2H), 1.37-1.44 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 166.7, 144.7, 140.2, 139.5, 132.3, 129.6, 125.9, 123.6, 123.5, 64.4, 61.5, 32.3, 30.7, 21.2, 19.2, 13.7. HR-MS (ESI): Calculated for $C_{19}H_{25}NO_4$: $[M+H]^+$ 318.1700. Found: m/z 318.1694. FTIR (KBr, cm^{-1}): ν 3473.03, 2948.71, 2357.99, 1715.84, 1657.10, 1434.96, 1360.86, 1244.09, 1161.29, 1080.86, 997.07, 901.38, 761.69.

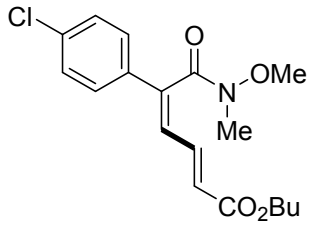


(*2E,4Z*)-Butyl 6-(methoxy(methyl)amino)-5-(4-methoxyphenyl)-6-oxohexa-2,4-dienoate (**3f**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 76 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.43 (m, 3H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 11.5 Hz, 1H), 6.04 (d, *J* = 15.0 Hz, 1H), 4.16 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 3.43 (s, 3H), 3.37 (s, 3H), 1.62-1.68 (m, 2H), 1.37-1.43 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 166.7, 160.5, 144.4, 140.4, 130.3, 127.6, 123.1, 122.4, 114.3, 64.4, 61.5, 55.4, 32.2, 30.6, 19.2, 13.7. HR-MS (ESI): Calculated for $C_{19}H_{25}NO_4$: $[M+H]^+$ 348.1805. Found: m/z 348.1808. FTIR (KBr, cm^{-1}): ν 2958.93, 1712.47, 1651.65, 1601.02, 1512.10, 1384.98, 1253.58, 1180.25, 1140.08, 1030.62.

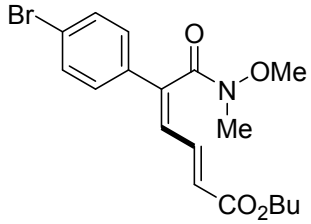


(*2E,4Z*)-Butyl 6-(methoxy(methyl)amino)-5-(4-fluorophenyl)-6-oxohexa-2,4-dienoate (**3g**): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 90 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.36 (m, 3H), 7.10- 7.03 (m, 2H), 6.66 (d, *J* = 11.5 Hz, 1H), 6.08 (d, *J* = 15.0 Hz, 1H), 4.16 (q, *J* = 6.5 Hz, 2H), 3.43 (s, 3H), 3.36 (s, 3H), 1.71-1.62 (m, 2H), 1.47-1.36 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 166.5, 163.2 (d, *J* = 248.60 Hz), 143.6, 139.9, 131.4 (d, *J* = 3.25 Hz), 127.9 (d, *J* = 8.125 Hz), 124.4 (d, *J* = 1.38 Hz), 124.3, 116.0 (d, *J* = 21.75), 64.5, 61.7, 32.3, 30.7, 19.2, 13.7. HR-MS (ESI): Calculated for $C_{18}H_{22}FNO_4$: $[M+H]^+$ 336.1606. Found: m/z 336.1614. FTIR (KBr, cm^{-1}): ν

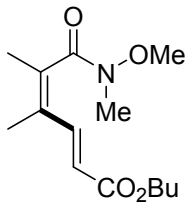
2959.29, 1712.77, 1652.17, 1600.39, 1508.20, 1384.88, 1239.60, 1141.51, 1005.96, 836.68. Melting point: 81-82℃.



（*2E, 4Z*)-Butyl 6-(methoxy(methyl)amino)-5-(4-chlorophenyl)-6-oxohexa-2, 4-dienoate (**3h**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.43 (m, 5H), 6.70 (d, *J* = 12.0 Hz, 1H), 6.10 (d, *J* = 15.0 Hz, 1H), 4.16 (t, *J* = 7.0 Hz, 2H), 3.43 (s, 3H), 3.36 (s, 3H), 1.70 - 1.62 (m,2H), 1.45 - 1.36 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 166.4, 143.4, 139.7, 135.2, 133.7, 129.2, 127.3, 125.0, 124.7, 64.5, 61.7, 32.3, 30.7, 19.2, 13.8. HR-MS (ESI): Calculated for $C_{18}H_{22}ClNO_4$: $[M+H]^+$ 352.1310. Found: m/z 352.1301. FTIR (KBr ,cm^{-1}): ν 2958.57, 2358.07, 2651.89, 1714.14, 1385.07, 1238.27, 1184.84, 1142.15, 1011.82. Melting point: 75-76℃

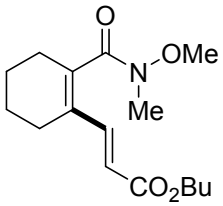


(*2E,4Z*)-Butyl 6-(methoxy(methyl)amino)-5-(4-bromophenyl)-6-oxohexa-2,4-dienoate (**3i**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 76 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.40 (dd, *J* = 11.5 Hz, 15.0 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 11.5 Hz, 1H), 6.10 (d, *J* = 15.0 Hz, 1H), 4.17 (t, *J* = 6.5 Hz, 2H), 3.42 (s, 3H), 3.36 (s, 3H), 1.61- 1.71 (m, 2H), 1.34- 1.47 (m, 2H), 0.92-0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 166.4, 143.5, 139.7, 134.2, 132.1, 127.5, 125.0, 124.8, 123.5, 64.5, 61.7, 32.3, 30.7, 19.2, 13.7. HR-MS (ESI): Calculated for $C_{18}H_{22}BrNO_4$: $[M+H]^+$ 396.0805. Found: m/z 396.0796. FTIR (KBr, cm^{-1}): ν 2958.86, 1712.63, 1658.44, 1625.00, 1385.50, 1238.12, 1184.74, 1142.02, 1007.82, 979.32, 825.94. Melting point: 94-95℃.

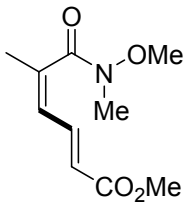


(*2E,4Z*)-Butyl 6-(methoxy(methyl)amino)-4,5-dimethyl-6-oxohexa-2,4-dienoate (**3j**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 50%. ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 15.5 Hz, 1H), 5.92 (d, *J* = 15.5 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 3.55 (s, 3H), 3.29 (s, 3H), 2.02 (s, 3H), 1.87 (s, 3H), 1.68 -1.57 (m, 2H), 1.40 (m, 2H). 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}CNMR (125 MHz, $CDCl_3$): δ 171.8, 167.1, 143.4,

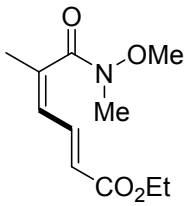
139.2, 129.4, 118.4, 64.3, 61.6, 32.2, 30.7, 19.2, 17.0, 13.7, 13.1. HR-MS (ESI): Calculated for $C_{14}H_{23}NO_4$: $[M+H]^+$ 328.2952. Found: m/z 382.2940. FTIR (KBr, cm^{-1}): ν 2924.97, 1713.67, 1651.89, 1622.61, 1385.01, 1286.55, 1173.88, 983.81.



Butyl (*E*)-3-(2-methoxy(methyl)carbamoylcyclohex-1-enyl) acrylate (**3k**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 56%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 16.0 Hz, 1H), 5.89 (d, *J* = 15.5 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 3.56 (s, 3H), 3.28 (s, 3H), 2.38 (brs, 2H), 2.24 (brs, 2H), 1.60-1.74 (m, 6H), 1.35-1.43 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 167.1, 142.7, 142.0, 130.0, 117.5, 64.2, 61.7, 32.3, 30.7, 27.6, 24.2, 21.7, 21.6, 19.2, 13.7. HR-MS (ESI): Calculated for $C_{16}H_{25}NO_4$: $[M+H]^+$ 296.1856. Found: m/z 296.1849. FTIR (KBr, cm^{-1}): ν 2933.90, 1713.10, 1651.82, 1626.82, 1380.32, 1295.65, 1171.77, 983.61

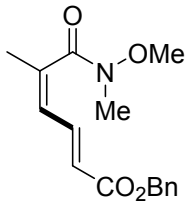


(*2E,4Z*)-Methyl 6-(methoxy(methyl)amino)-5-methyl-6-oxohexa-2,4-dienoate (**3l**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 65%.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 12.0 Hz, 15.5 Hz, 1H), 6.14 (d, *J* = 12.0 Hz, 1H), 5.89 (d, *J* = 15.5 Hz, 1H), 3.73 (s, 3H), 3.61 (s, 3H), 3.28 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 167.1, 143.1, 140.3, 126.3, 121.8, 61.8, 51.61, 32.1, 20.7. HR-MS (ESI): Calculated for $C_{10}H_{15}NO_4$: $[M+H]^+$ 214.1074. Found: m/z 214.1082. FTIR (KBr, cm^{-1}): ν 3507.85, 2933.95, 1715.44, 1651.74, 1455.36, 1275.87, 1149.14, 992.02, 753.77.

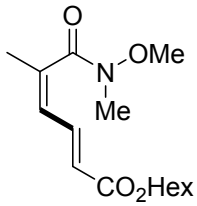


(*2E, 4Z*)-Ethyl 6-(methoxy(methyl)amino)-5-methyl-6-oxohexa-2,4-dienoate (**3m**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 74 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.13 (d, *J* = 11.5 Hz, 1H), 5.88 (d, *J* = 15.5 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.60 (s, 3H), 3.28 (s, 3H), 2.07 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.7, 142.8, 140.1, 126.3, 122.2, 61.8, 60.4, 32.2, 20.7, 14.3. HR-MS (ESI): Calculated for $C_{11}H_{17}NO_4$: $[M+H]^+$ 228.1230.

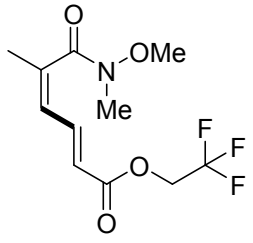
Found: m/z 228.1235. FTIR (KBr, cm^{-1}): ν 2934.16, 1715.47, 1651.98, 1455.31, 1385.12, 1332.33, 1275.93, 1151.58, 993.68,



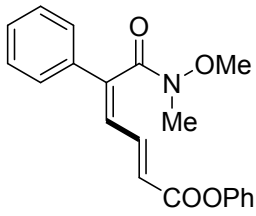
(*2E, 4Z*)-Benzyl 6-(methoxy(methyl) amino)-5-methyl-6-oxohexa-2, 4-dienoate (**3n**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 67 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30- 7.36 (m, 6H), 6.12 (d, *J* = 11.5 Hz, 1H), 5.93 (d, *J* = 15.0 Hz, 1H), 5.18 (s, 2H), 3.58(s, 3H), 3.26 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.5, 143.2, 140.7, 136.0, 128.6, 128.3, 128.2, 126.2, 121.7, 66.2, 61.8, 32.1, 20.9. HR-MS (ESI): Calculated for $C_{16}H_{19}NO_4$: $[M+H]^+$ 290.1387. Found: m/z 290.1395. FTIR (KBr, cm^{-1}): ν 2934.16, 1715.47, 1651.75, 1455.38, 1385.05, 1333.38, 1275.92, 1149.20, 992.26.



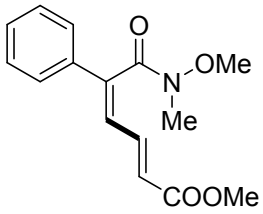
(*2E, 4Z*)-Hexyl 6-(methoxy(methyl)amino)-5-methyl-6-oxohexa-2, 4-dienoate (**3o**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 57 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.14 (d, *J* = 11.5 Hz, 1H), 5.89 (d, *J* = 15.0 Hz, 1H), 4.13 (t, *J* = 6.5 Hz, 2H), 3.64 (s, 3H), 3.27 (s, 3H), 2.10 (s, 3H), 1.72 - 1.58 (m, 2H), 1.38-1.25 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.7, 142.8, 140.1, 125.4, 122.2, 64.6, 31.4, 29.5, 28.9, 25.3, 22.6, 20.7, 18.4, 14.1. HR-MS (ESI): Calculated for $C_{16}H_{22}NO_4$: $[M+H]^+$ 284.1856. Found: m/z 284.1849. FTIR (KBr, cm^{-1}): ν 2932.80, 1715.73, 1658.47, 1455.72, 1384.50, 1331.79, 1275.58, 1150.58, 995.12.



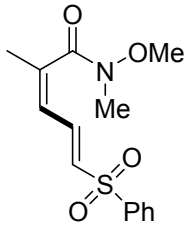
(*2E,4Z*)-2,2,2-Trifluoroethyl 6-(methoxy(methyl)amino)-5-methyl-6-oxohexa-2,4-dienoate (**3p**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 81%. ^{1}H NMR (500 MHz, CDCl3): δ 7.38 (dd, *J* = 15.5, 12.0 Hz, 1H), 6.17 (d, *J* = 11.5 Hz, 1H), 5.94 (d, *J* = 15.0 Hz, 1H), 4.51 (q, *J* = 8.5 Hz, 2H), 3.59 (s, 3H), 3.28 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 164.9, 144.7, 142.6, 125.8, 123.0 (q, *J* = 280.1 Hz), 119.6, 61.8, 60.4 (q, *J* = 36.4 Hz), 29.7, 20.8. HR-MS (ESI): Calculated for $C_{11}H_{14}F_3NO_4$: $[M+H]^+$ 282.0948. Found: m/z 282.0953. FTIR (KBr, cm^{-1}): ν 2920.43, 2849.49, 1732.40, 1651.61, 1455.40, 1287.85, 1167.97.



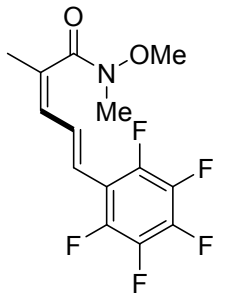
(*2E,4Z*)-Phenyl 6-(methoxy(methyl)amino)-5-phenyl-6-oxohexa-2, 4-dienoate (**3q**): This compound was prepared by the general procedure described above and was obtained as a white solid. Yield = 79%. ^{1}H NMR (400 MHz, CDCl3) δ = 7.61 (dd, *J* = 14.5, 18.5Hz, 1H), 7.32-7.50 (m, 7H), 7.12-7.25 (m, 3H), 6.81 (d, *J* = 14.5 Hz, 1H), 6.27 (d, *J* = 19.0 Hz, 1H), 3.41 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ = 169.0, 164.8, 150.8, 145.9, 141.9, 135.1, 129.5, 129.4, 129.0, 126.2, 125.8, 124.3, 123.1, 121.6, 61.5, 32.2. HR-MS (ESI): Calculated for $C_{20}H_{19}NO_4$: $[M+H]^+$ 338.1387, Found: m/z 338.1381. FTIR (KBr, cm^{-1}): ν 3851.26, 3686.72, 3667.84, 3626.88, 3564.88, 2923.81, 2357.11, 1732.11, 1651.73, 1574.62, 1385.57, 1194.69, 1122.17, 688.33. Melting point: 113-114℃



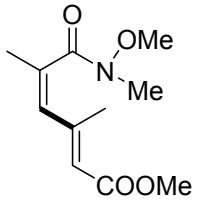
(*2E, 4Z*)-Methyl 6-(methoxy(methyl)amino)-5-phenyl-6-oxohexa-2,4-dienoate (**3r**): This compound was prepared by the General Procedure described above and was obtained as a yellow solid. Yield = 68 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53- 7.32 (m, 6H), 6.72 (d, *J* = 11.5 Hz, 1H), 6.09 (d, *J* = 15.0 Hz, 1H), 3.76 (s, 3H), 3.47 (s, 3H), 3.38(s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ = 169.0, 166.7, 144.9, 140.3, 135.2, 129.2, 128.9, 126.0, 124.5, 123.7, 61.6, 51.7, 32.3. HR-MS (ESI): Calculated for $C_{15}H_{17}NO_4$: $[M+H]^+$ 276.1230, Found: m/z 276.1226. Melting point: 96-97℃.



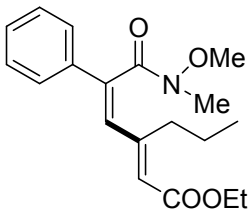
(*2Z, 4E*)-*N*-Methoxy-*N*, 2-dimethyl-5-(phenylsulfonyl)penta-2, 4-dienamide (**3s**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85-7.87 (m, 2H), 7.51-7.63 (m, 3H), 7.27 (dd, *J* = 12.0 Hz, 14.5 Hz, 1H), 6.37 (d, *J* = 14.5 Hz, 1H), 6.07 (d, *J* = 11.5 Hz, 1H), 3.60 (s, 3H), 3.29 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 146.0, 140.4, 138.1, 133.4, 130.5, 129.3, 127.6, 123.7, 62.0, 32.2, 20.9. HR-MS (ESI): Calculated for $C_{14}H_{17}NO_4S$: $[M+H]^+$ 296.0951. Found: m/z 296.0940. FTIR (KBr, cm^{-1}): ν 3508.32, 2936.77, 1651.10, 1588.18, 1446.15, 1386.44, 1306.73, 1145.48, 1084.92, 992.41, 825.61, 752.45, 608.18.



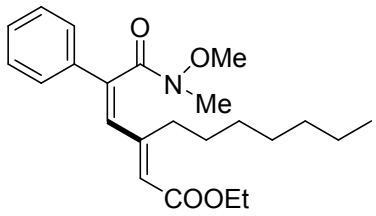
(2*Z*, *4E*)-*N*-methoxy-*N*, 2-dimethyl-5-(perfluorophenyl) penta-2,4-dienamide (**3t**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 30%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (dd, *J* = 16.0, 11.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.19 (d, *J* = 11.0 Hz, 1H), 3.66 (s, 3H), 3.29 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.65 (m), 143.63 (m), 140.77 (m), 138.78 (m), 136.70 (m), 133.52, 128.99, 116.61 (m), 112.19 (m), 67.96, 25.60, 20.47. HR-MS (ESI): Calculated for $C_{14}H_{12}F_5NO_4$: $[M+H]^+$ 322.0861. Found: m/z 322.0854. FTIR (KBr, cm^{-1}): ν 2935.81, 1651.77, 1519.63, 1495.53, 960.06. melting point: 42-43℃.



(*2E,4Z*)-Methyl 6-(methoxy(methyl)amino)-3,5-dimethyl-6-oxohexa-2,4-dienoate (**3u**): This compound was prepared by the general procedure described above and was obtained as an orange oil. Yield = 78 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (s, 1H), 5.80 (s, 1H), 3.69 (s, 3H), 3.63 (s, 3H), 3.23 (s, 3H), 2.25 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.0, 167.2, 151.8, 136.5, 131.3, 119.1, 61.6, 51.1, 32.4, 22.3, 16.0. HR-MS (ESI): Calculated for $C_{11}H_{17}NO_4$: $[M+H]^+$ 214.1082. Found: m/z 214.1082. FTIR (KBr, cm^{-1}): ν 2948.84, 2358.22, 1715.85, 1675.15, 1434.98, 1381.73, 1360.88, 1244.18, 1161.33, 997.15



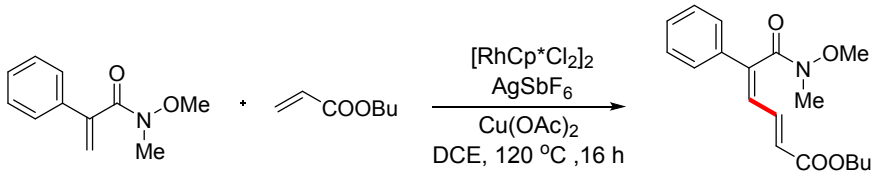
(*2E,4Z*)-Ethyl 6-(methoxy(methyl)amino)-5-phenyl-3-propyl-6-oxohexa-2,4-dienoate (**3v**): This compound was prepared by the general procedure described above and was obtained as an orange oil, yield = 65 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.34 (m, 5H), 6.40 (s, 1H), 5.96 (s, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.28 (s, 3H), 3.26 (s, 3H), 2.73 (t, *J* = 8.0, 2H), 1.61-1.53 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 166.4, 156.3, 139.5, 136.9, 129.9, 128.8, 128.6, 126.4, 118.6, 61.2, 59.8, 33.5, 32.5, 22.3, 14.3, 14.2. HR-MS (ESI): Calculated for $C_{14}H_{23}NO_4$: $[M+H]^+$ 332.1856. Found: m/z 332.1859. FTIR (KBr, cm^{-1}): ν 2964.33, 1713.30, 1652.03, 1372.84, 1265.24, 1150.06, 1035.11, 695.10.



(*E*)-ethyl 3-((Z)-3-(methoxy(methyl)amino)-3-oxo-2-phenylprop-1-en-1-yl)dec-2-enoate (3w)

This compound was prepared by the general procedure described above and was obtained as an orange oil, yield = 46 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.23 (m, 5H), 6.33 (s, 1H), 5.87 (s, 1H), 4.11-4.06 (m, 2H), 3.21 (s, 3H), 3.19 (s, 3H), 2.69 – 2.63 (m, 2H), 1.50 – 1.39 (m, 2H), 1.33 – 1.14 (m, 11H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 166.4, 156.5, 139.4, 136.9, 129.9, 129.1, 128.8, 126.4, 118.3, 61.3, 59.8, 32.5, 31.87, 31.8, 29.9, 29.2, 29.0, 22.7, 14.3, 14.1. HR-MS (ESI): Calculated for $C_{23}H_{33}NO_4$: $[M+H]^+$ 388.2482. Found: m/z 388.2478. FTIR (KBr, cm^{-1}): ν 2926.95, 1659.01, 1626.68, 1446.67, 1151.09, 1044.45, 695.11.

Gram-scaled synthesis

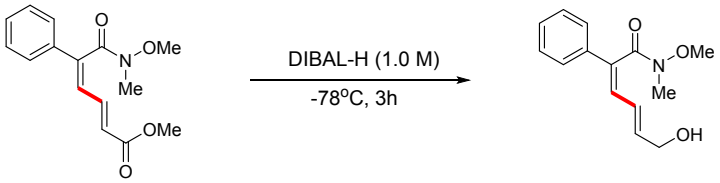


1d, 0.4 g **2a** **3d**, 0.54 g (83%)

N-Methoxy-*N*-methyl-2-phenylacrylamide (2.1 g, 11.0 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (34 mg, 0.055 mmol, 0.5 mol%), $AgSbF_6$ (0.22 mmol, 2.0 mol%), $Cu(OAc)_2$ (4.4 g, 22.0 mmol, 2.0 equiv), were charged into an oven-dried 100 mL sealed tube. The tube was evacuated and refilled with Ar. After addition of butyl acrylate (3.16 mL, 22.0 mmol, 2.0 equiv) and DCE (30 mL), the sealed tube was heated to 120℃with stirring for 48 hours. After cooling down, the mixture was diluted with DCM, filtrated and concentrated in vacuo. The resulting residue was directly purified by column chromatography to give product as yellow oil (2.8 g, 82%).

Selective reduction

Synthesis of 4q

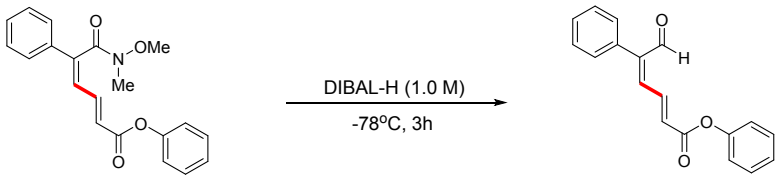


3q **4q**, yield = 61%

To a solution of the butadiene **3q** (27.5 mg, 0.1 mmol, 1.0 equiv) in anhydrous THF (1 mL) at -78 °C was added DIBAL-H (1.0 M in heptane, 0.3 mL, 0.3 mmol) carefully over 5 min. The resulting solution was stirred at -78 °C for 1 h and quenched with saturated aqueous NH_4Cl (0.1 mL). The mixture was warmed to ambient temperature. The layer was separated and extracted with ethyl

acetate (5 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Concentration in vacuo and purification by column chromatography afforded the alcohol **4q** (15 mg, 61%) as a yellow oil, and the unreacted acrylamide **1d** was recovered (25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.39 (m, 5H), 6.65 (d, *J* = 11.5 Hz, 1H), 6.45 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H), 6.06-6.13 (m, 1H), 4.26 (d, *J* = 5.0 Hz, 2H), 3.90 (s, 1H), 3.40 (s, 2H), 3.34 (s, 2H), 3.12 (s, 1H), 1.70 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.2, 137.7, 136.3, 136.2, 129.0, 128.7, 128.0, 127.3, 125.6, 125.5, 63.2, 61.6, 32.2. FTIR (KBr, cm^{-1}): ν 3851.14, 3673.62, 3626.76, 3417.43, 2932.41, 1644.68, 1446.35, 1385.56, 1102.77, 1006.29, 694.16, 495.65. HR-MS (ESI): Calculated for$C_{14}H_{17}NO_3$: $[M+H]^+$ 248.1281, Found: m/z 248.1273.

Synthesis of 4p



3p **4p**, yield = 58%

To a solution of the butadiene **3p** (33.7 mg, 0.1 mmol, 1.0 equiv) in anhydrous THF (1mL) at -78 °C was added DIBAL-H (1.0 M in heptane, 0.3 mL, 0.3 mmol, 3.0 equiv) carefully over 20 min. The resulting solution was stirred at -78 °C for 2 h and quenched with saturated aqueous NH_4Cl (0.1 mL). The mixture was warmed to ambient temperature. The layer was separated and extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Concentration in vacum and purification by column chromatography afforded the aldehyde **4p** in 58% yield as yellow solid, and the unreacted acrylamide **1d** was recovered (about 30%).. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.50 (s, 1H), 8.43 (dd, *J* = 12.5 Hz, 15.0 Hz, 1H), 7.16-7.45 (m, 11H), 6.45 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 190.1, 161.3, 150.6, 143.2, 139.3, 138.3, 135.4, 129.5, 129.3, 128.7, 128.4, 128.3, 126.1, 121.5. FTIR (KBr, cm-1): ν 3851.05,3708.76, 3667.67, 3626.70, 3564.67, 1732.23, 1682.42, 1651.67, 1538.57, 1505.36, 499.88. HR-MS (ESI): Calculated for $C_{18}H_{14}O_3$: $[M+H]^+$ 279.1016, Found: m/z 279.1023. Melting point: 100-101℃.

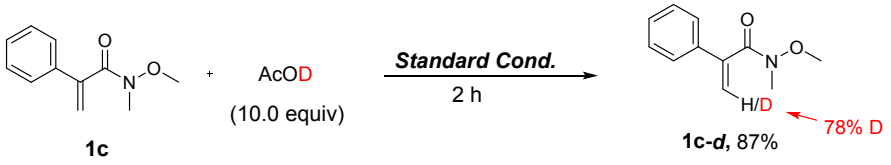
Synthesis of 4r

Carboxylic acid **3x** was obtained as a white solid in 95% yield from ester **3q** by hydrolysis using LiOH (aq.) as the base according to reported method.[8d-e] Melting point: 147℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 15.1, 11.9 Hz, 1H), 7.49-7.36 (m, 5H), 6.76 (d, *J* = 11.8 Hz, 1H), 6.09 (d, *J* = 15.0 Hz, 1H), 3.42 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 169.0, 145.9, 142.3, 135.0, 129.5, 128.9, 126.2, 124.2, 123.1, 61.7, 32.3. FTIR (KBr, cm-1): ν 3756.99, 3667.89, 2934.78, 2358.55, 2339.32, 1651.63, 1621.68, 1386.07, 1288.40, 980.05. HR-MS (ESI): Calculated for $C_{14}H_{15}NO_4$: $[M+H]^+$ 262.1074, Found: m/z 262.1076.

To a solution of acid **3x** (26.1 mg, 0.1 mmol, 1.0 equiv) in anhydrous THF (1mL) was added DIBAL-H (1.5 M in toluene, 0.2 mL, 0.3 mmol, 3.0 equiv) carefully over 20 min at -78 °C. The resulting solution was stirred at -78 °C for 2 h and quenched with saturated aqueous NH_4Cl (0.1 mL). The mixture was warmed to ambient temperature and was extracted with ethyl acetate (5 mL

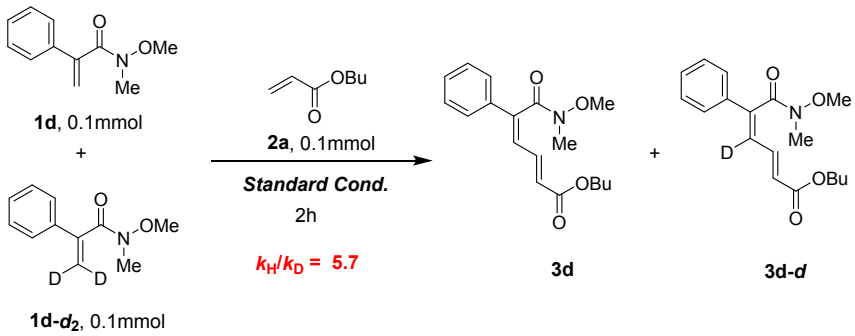
× 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Concentration in vacuum and purification by column chromatography afforded the aldehyde **4r** in 68% yield as a yellow solid. Melting point: 94.5℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.28 (dd, *J* = 15.1, 12.3 Hz, 1H), 7.40-7.30 (m, 5H), 7.07 (d, *J* = 12.3 Hz, 1H), 6.19 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 171.1, 143.4, 139.0, 139.0, 135.3, 129.3, 128.7, 128.3, 128.2. FTIR (KBr, cm^{-1}): ν 3730.86, 3667.49, 1732.16, 1682.42, 1614.47, 1538.31, 1455.25, 1309.22. HR-MS (ESI): Calculated for $C_{12}H_{10}O_3$: $[M+H]^+$ 203.0703, Found: m/z 203.0708.

Deuterium Labeled Experiments



1c **1c-*d*, 87%**

An oven-dried screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%, 0.0025 mmol), $AgSbF_6$ (0.1 equiv., 0.02 mmol), $Cu(OAc)_2$ (2.0 equiv, 0.4 mmol), DCE (1 mL) and AcOD (10 equiv., 5.0 mmol). Then, acrylamides (0.2 mmol) was added into the solution. The vial was sealed under argon and heated to 120 ℃ with stirring for 2 hour. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures) on silica gel (33.2 mg, 87% recovered). The D % of **1c-*d*** was estimated by ^{1}HNMR.



A 15 mL screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%) and DCE (1.0 mL). The *N*-methoxy- *N*-methyl-2-phenylacrylamide **1c** (19.1 mg, 0.1 mmol, 1.0 equiv) and **1c-*d*$_2$** (19.3 mg, 0.1 mmol, 1.0 equiv.) were added into the solution in sequence. The vial was sealed under Ar and heated to 120 ℃with stirring for 2 hours. After cooling down, the mixture was diluted with ethyl acetate, filtrated, concentrated in vacuo and purified by column chromatography affording the mixed products **3d** and **3d-*d*** (8.2 mg, 26%) as colorless oil, and a mixture of **1c**/**1c-*d*$_2$** was recovered (29.5 mg, 77%). The ratio of **3d**/**3d-*d*** was determined by ^{1}H NMR to be 5.7:1.

References

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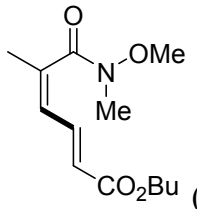
[2] I. Fleming, D. Lee, *J. Chem. Soc. - Perk. Trans. 1*, **1998**, 2701.

[3] J. Z. Hamilton, N. T. Kadunce, M. D. McDonald, L. Rios, A. R. Matlin, *Tetrahedron Lett.* **2015**, *56*, 6622.

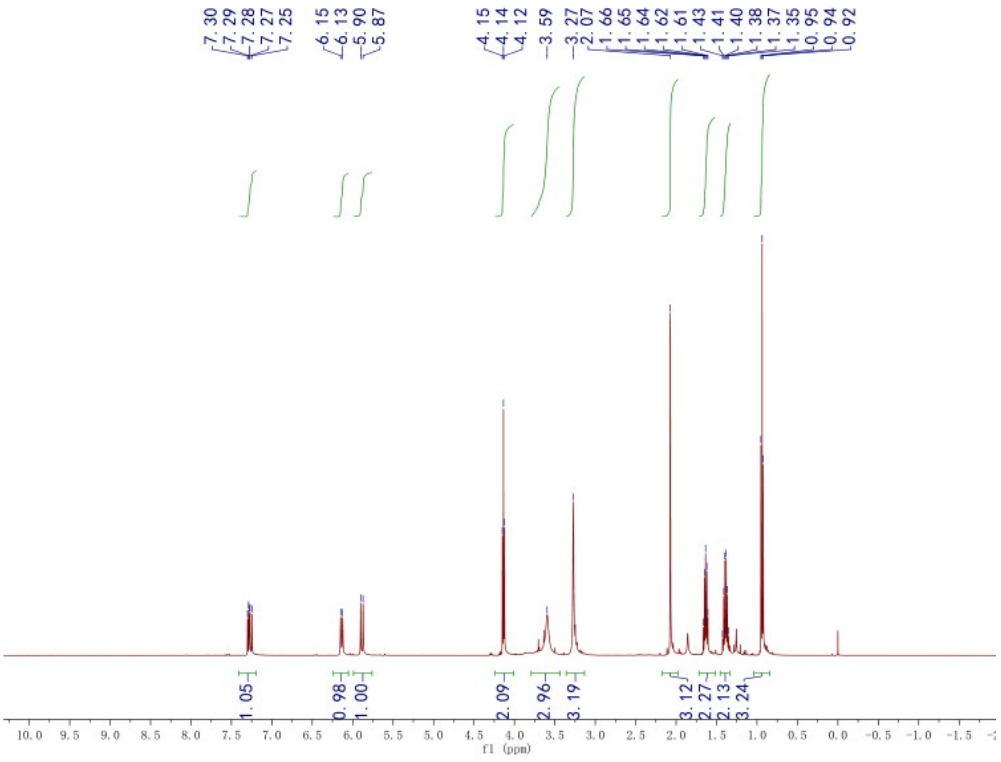
[4] J. Zhang, T. P. Loh, *Chem. Commun*. **2012**, *48*, 11232.

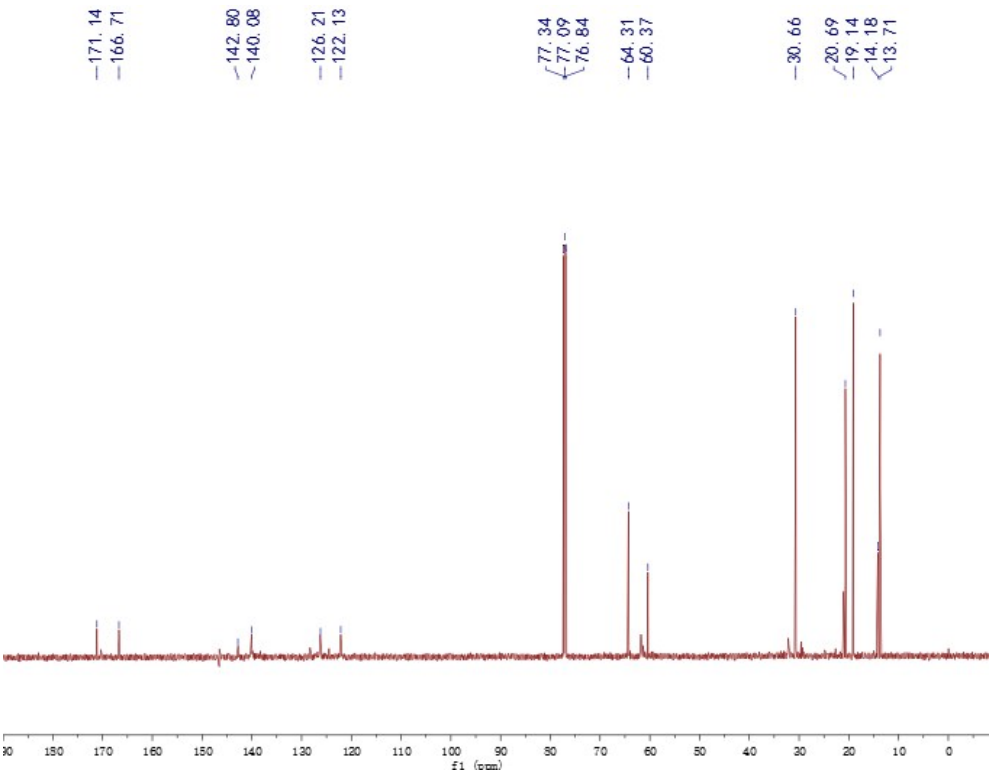
[5] X. H. Hu, J. Zhang, X. F. Yang, Y. H. Xu, T. P. Loh, *J. Am. Chem. Soc*. **2015**, *137*, 3169.

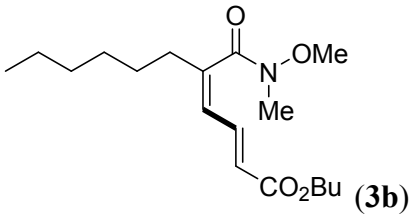
^{1}H, ^{13}C Spectra



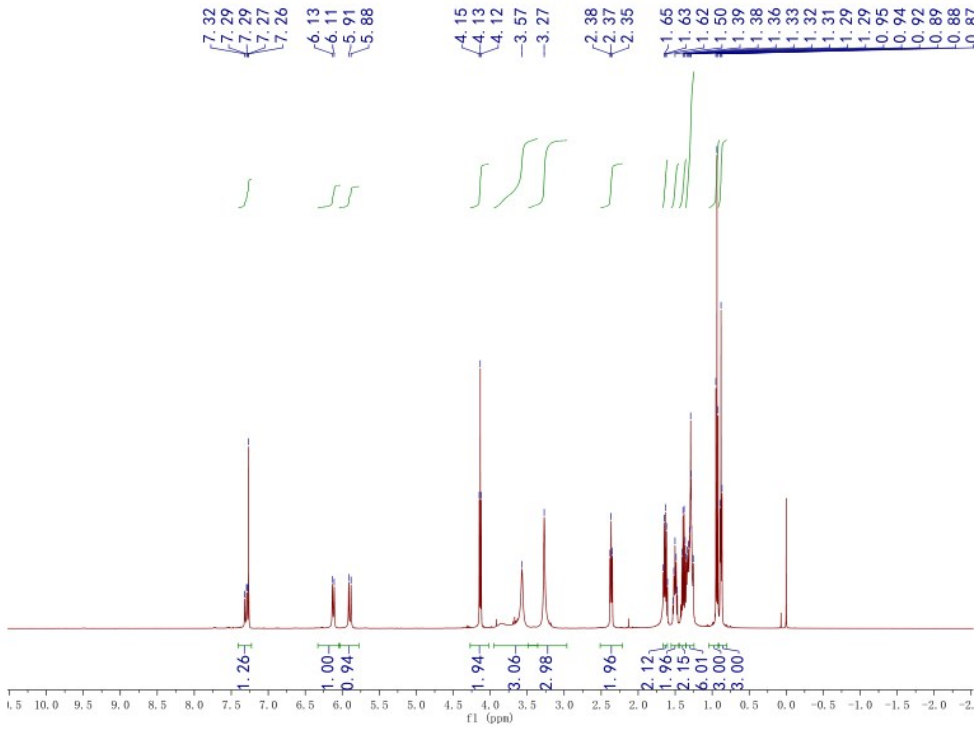
(3a)






O
N
OMe
Me
CO2Bu

(**3b**)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7.29
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7.26
6.13
6.11
5.91
5.88
4.15
4.13
4.12
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3.27
2.38
2.37
2.35
1.65
1.63
1.62
1.50
1.39
1.38
1.36
1.33
1.32
1.31
1.29
1.29
0.95
0.94
0.92
0.89
0.88
1.26
1.00
0.94
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2.12
1.96
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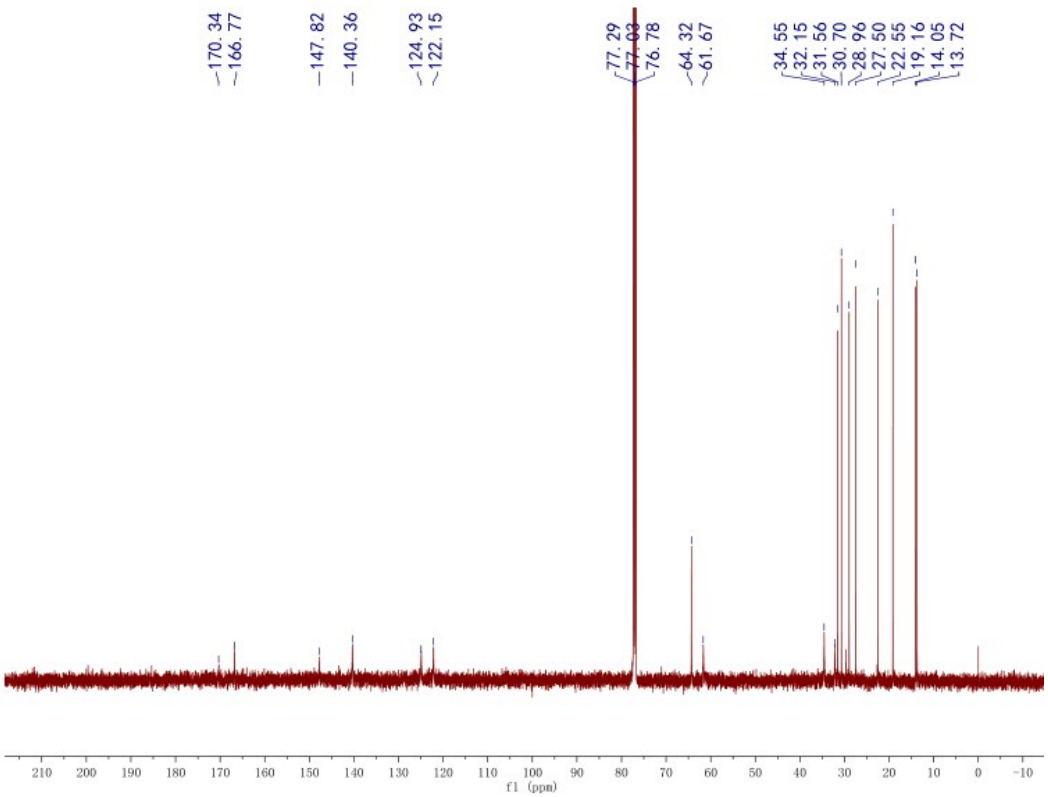
3.00
3.00
f1 (ppm)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124.93
122.15
77.29
77.03
76.78
64.32
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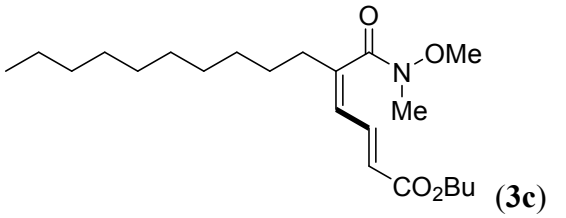
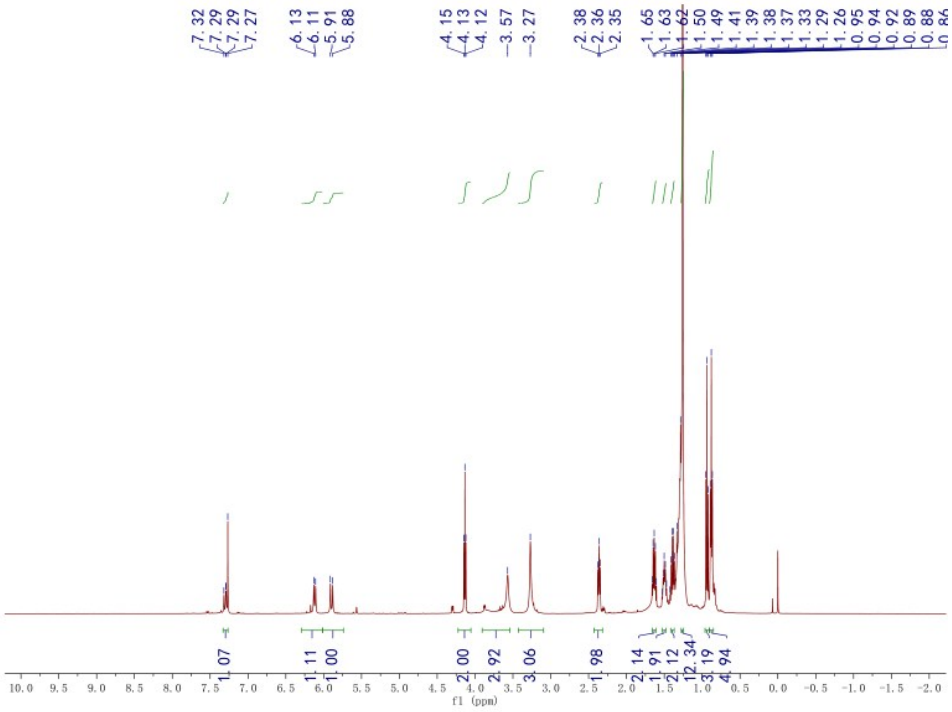
31.56
30.70
28.96
27.50
22.55
19.16
14.05
13.72
f1 (ppm)


O
OMe
N
Me
CO2Bu

(**3c**)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5.88
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4.13
4.12
3.57
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2.36
2.35
1.65
1.63
1.62
1.50
1.49
1.41
1.39
1.38
1.37
1.33
1.29
1.26
0.95
0.94
0.92
0.89
0.88
1.07
1.11
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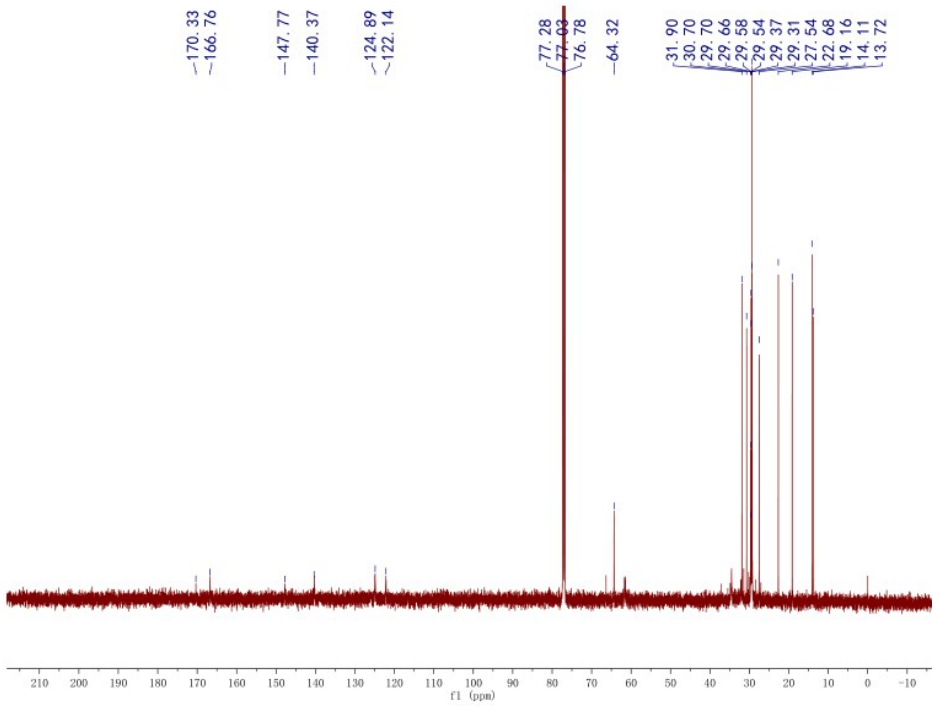
f1 (ppm)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29.31
27.54
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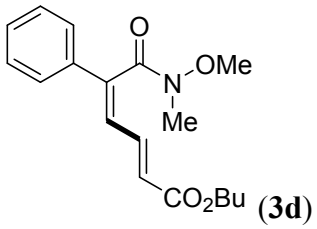
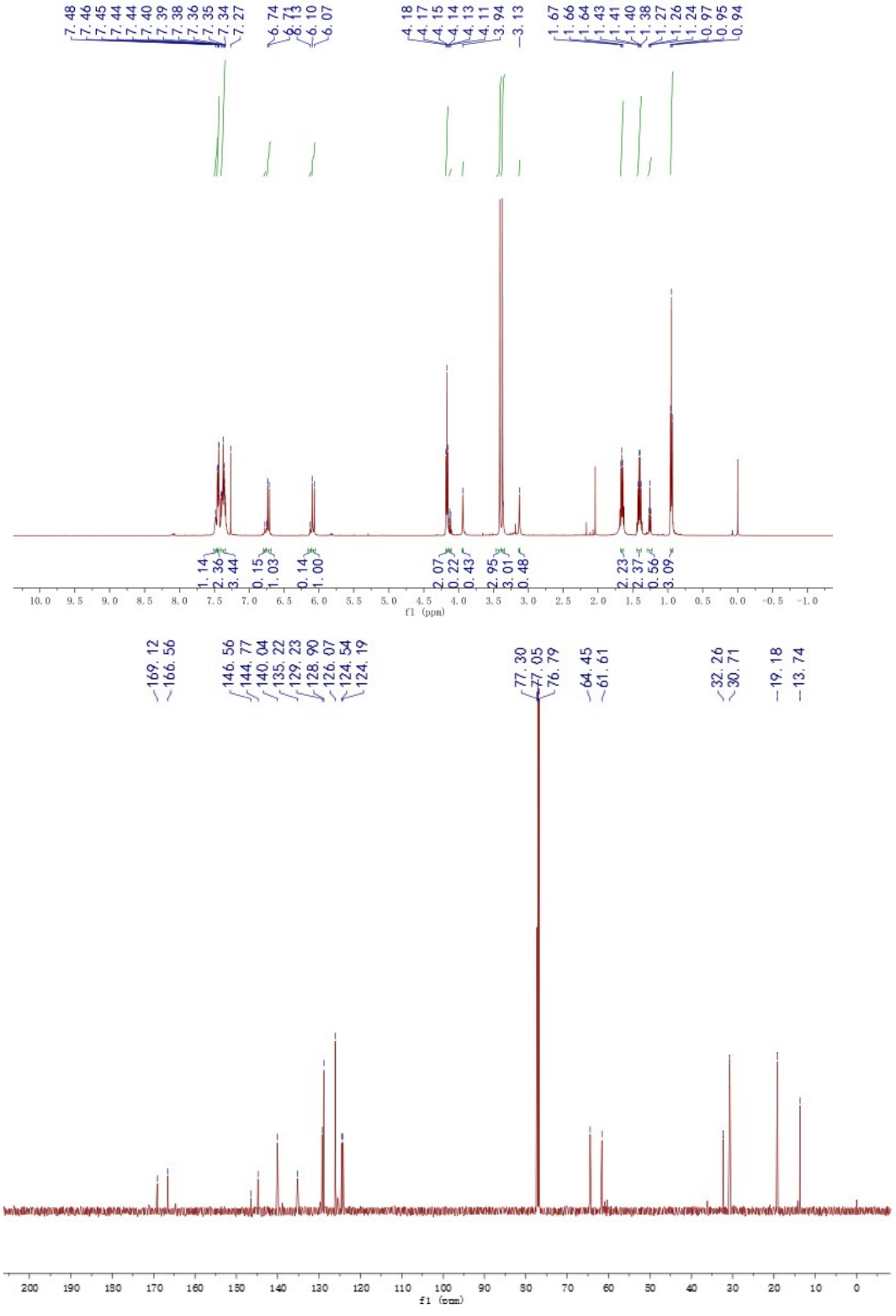
19.16
14.11
13.72
f1 (ppm)


O
N
OMe
Me
CO2Bu

(3d)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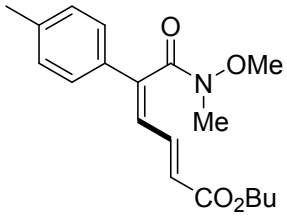
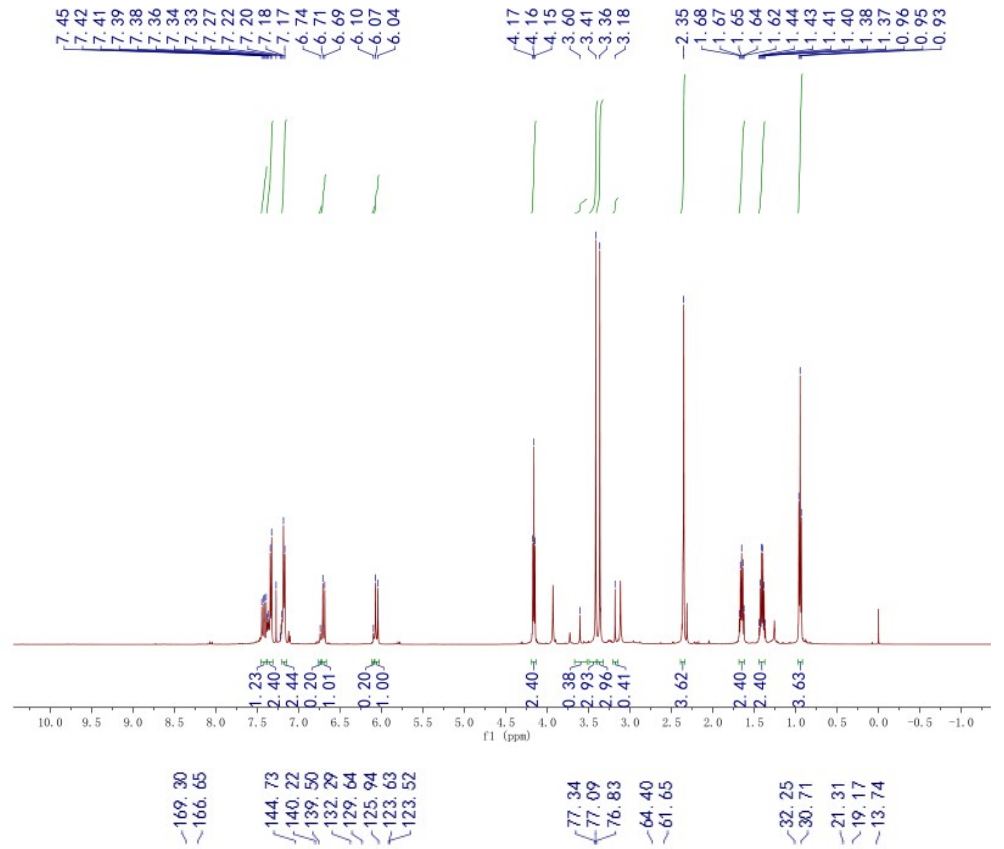
6.74 6.73 6.10 6.07
4.18 4.17 4.15 4.14 4.13 4.11 3.94 3.13
1.67 1.66 1.64 1.43 1.41 1.40 1.38 1.27 1.26 1.24 0.97 0.95 0.94
1.14 2.36 3.44 0.15 1.03 0.14 1.00 2.07 0.22 0.43 2.95 3.01 0.48 2.23 2.37 0.56 3.09
f1 (ppm)
169.12 166.56 146.56 144.77 140.04 135.22 129.23 128.90 126.07 124.54 124.19 77.30 77.05 76.79 64.45 61.61 32.26 30.71 19.18 13.74
f1 (ppm)


O
N
OMe
Me
CO2Bu

(3e)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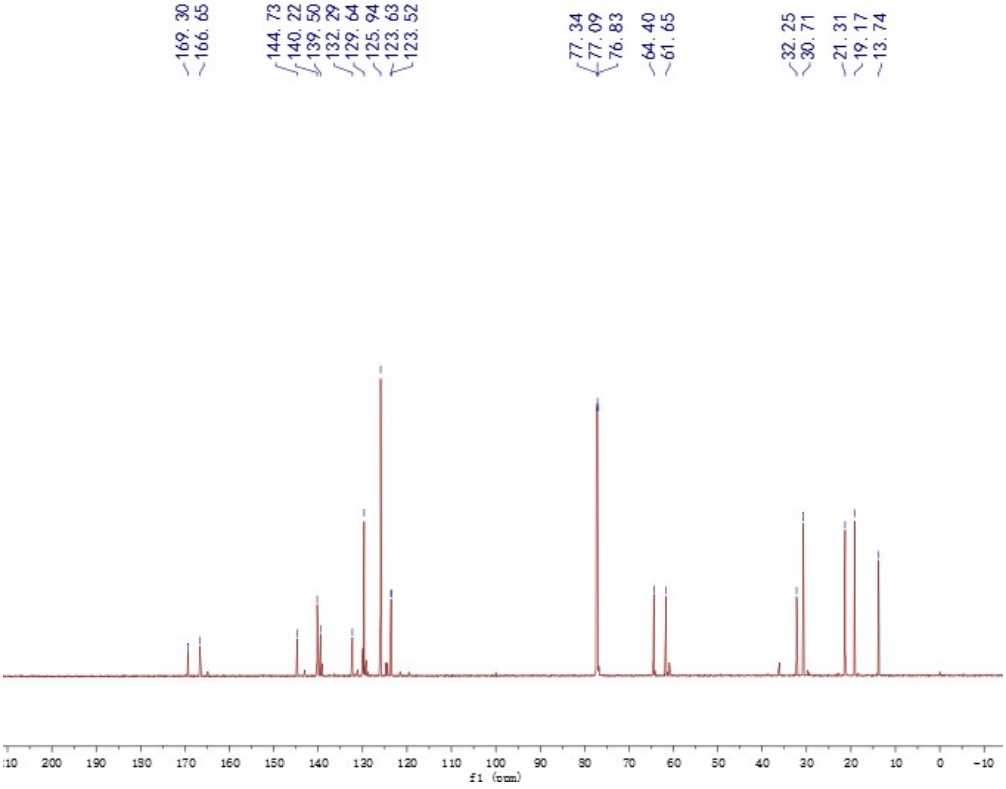
4.17 4.16 4.15 3.60 3.41 3.36 3.18
2.35 1.68 1.67 1.65 1.64 1.62 1.44 1.43 1.41 1.40 1.38 1.37 0.96 0.95 0.93
1.23 2.40 2.44 0.20 1.01 0.20 1.00 2.40 0.38 2.93 2.96 0.41 3.62 2.40 2.40 3.63
f1 (ppm)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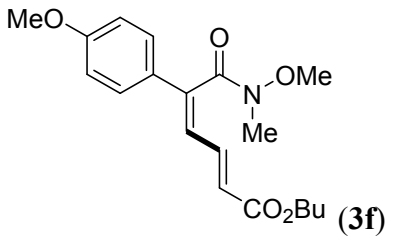
f1 (ppm)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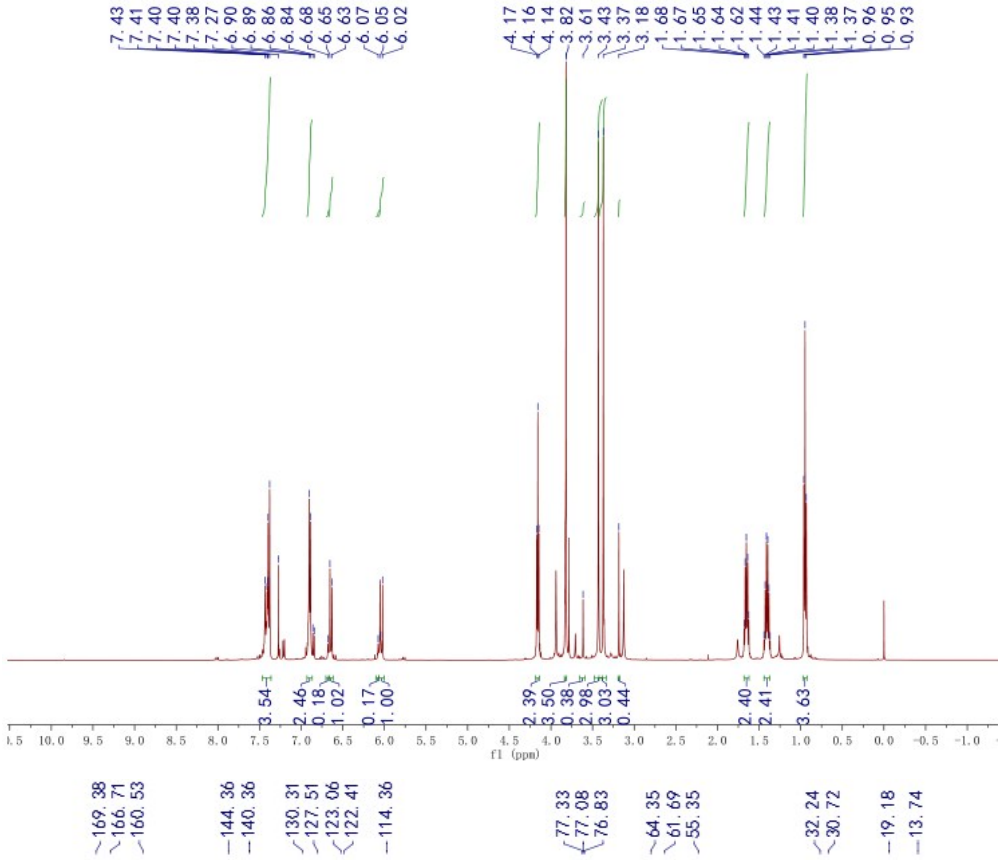
O
N
OMe
Me
CO2Bu

(3f)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4.14
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3.18
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1.41
1.40
1.38
1.37
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0.93
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0.18
1.02
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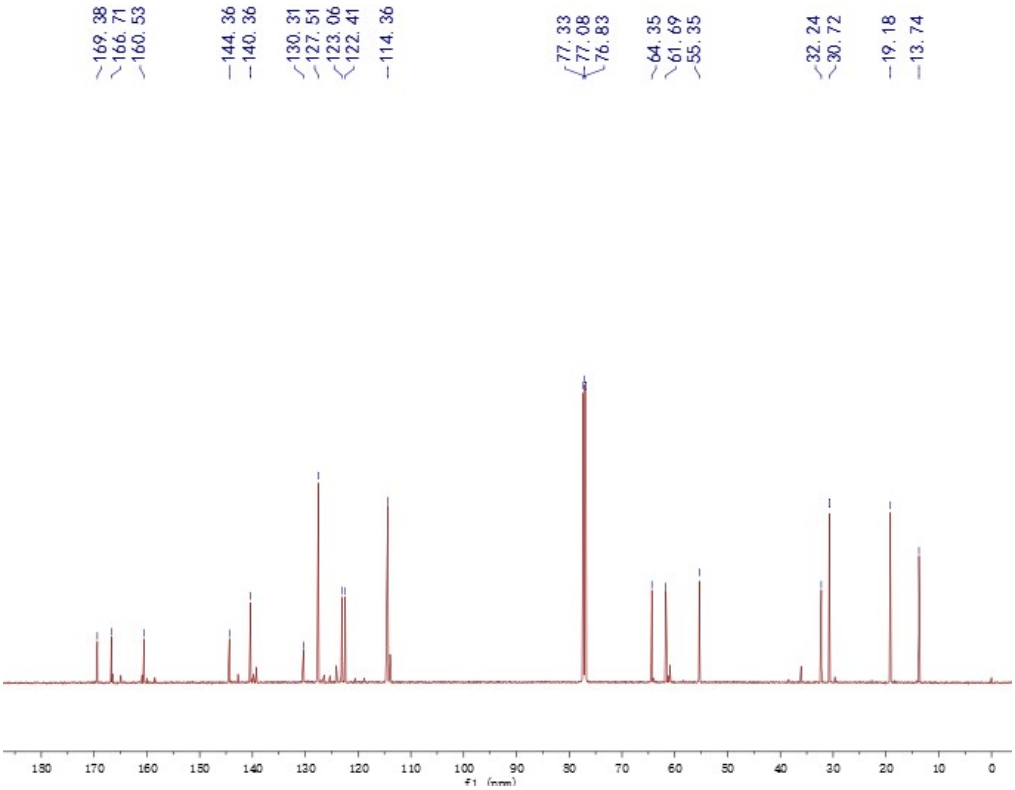
3.63
f1 (ppm)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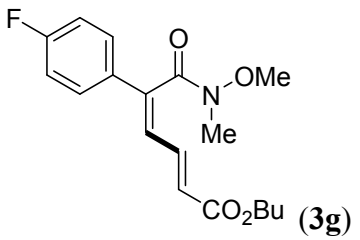
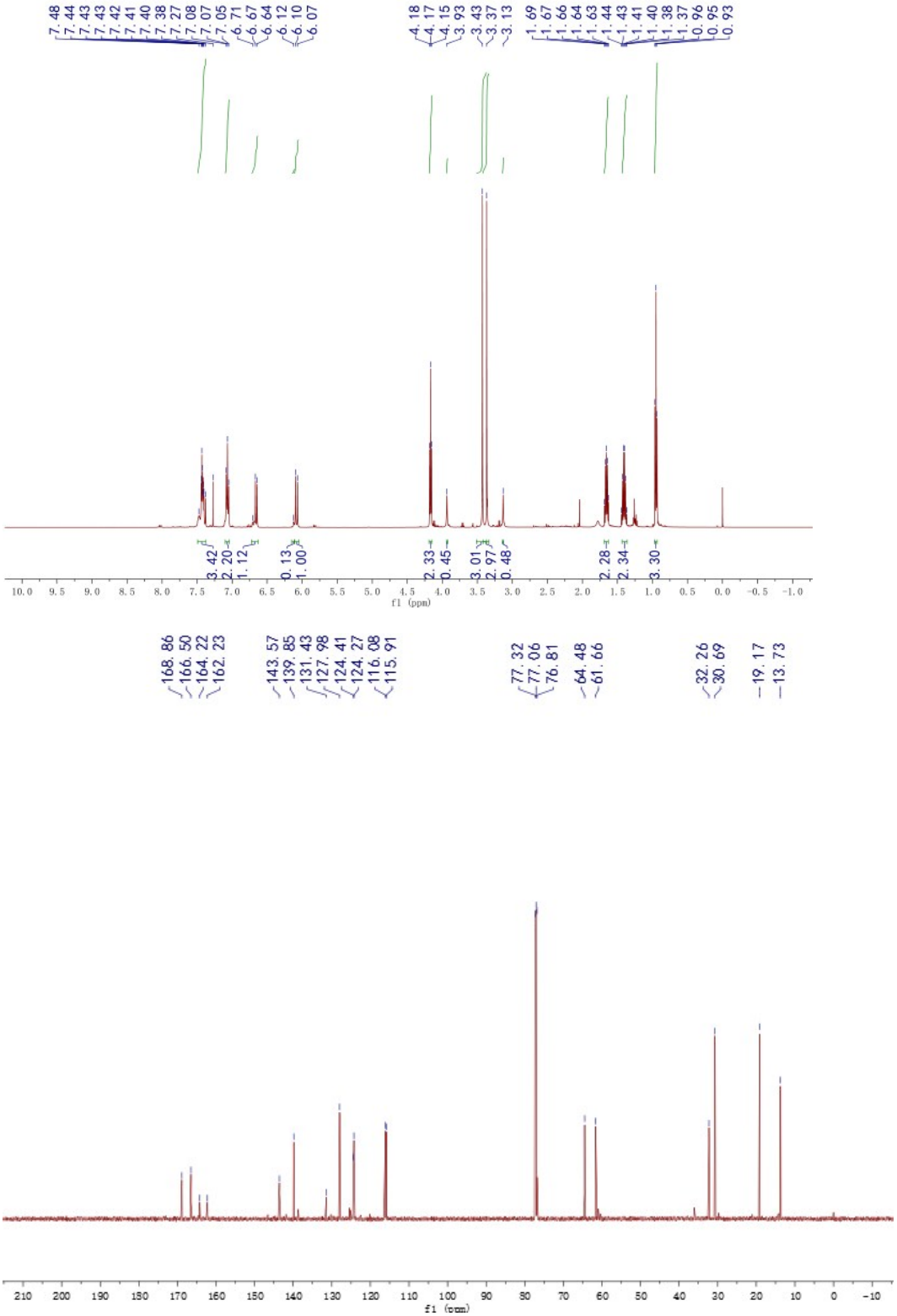
30.72
19.18
13.74
f1 (ppm)


F
O
N
OMe
Me
CO2Bu

(3g)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6.67
6.64
6.12
6.10
6.07
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4.17
4.15
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1.63
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1.43
1.41
1.40
1.38
1.37
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0.95
0.93
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0.13
1.00
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3.01
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2.34
3.30
f1 (ppm)
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162.23
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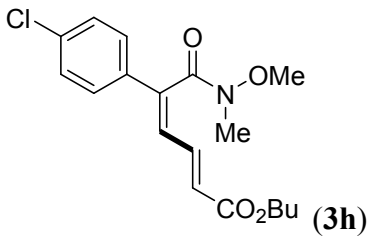
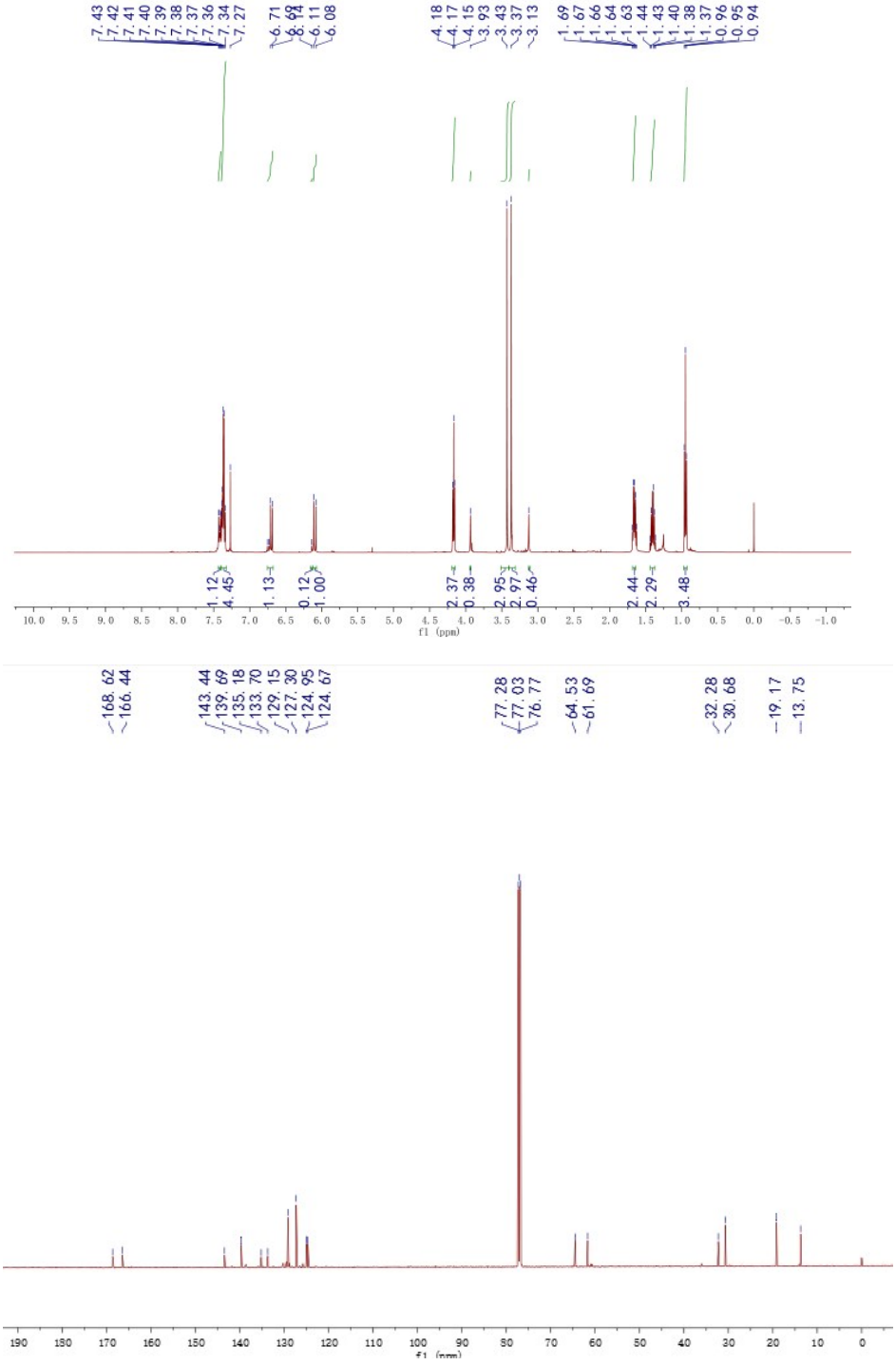
f1 (ppm)


Cl
O
N
OMe
Me
CO2Bu

(**3h**)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3.13
1.69
1.67
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1.64
1.63
1.44
1.43
1.40
1.38
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0.94
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0.12
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f1 (ppm)
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135.18
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129.15
127.30
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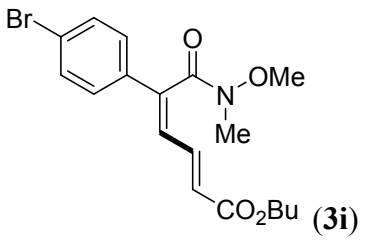
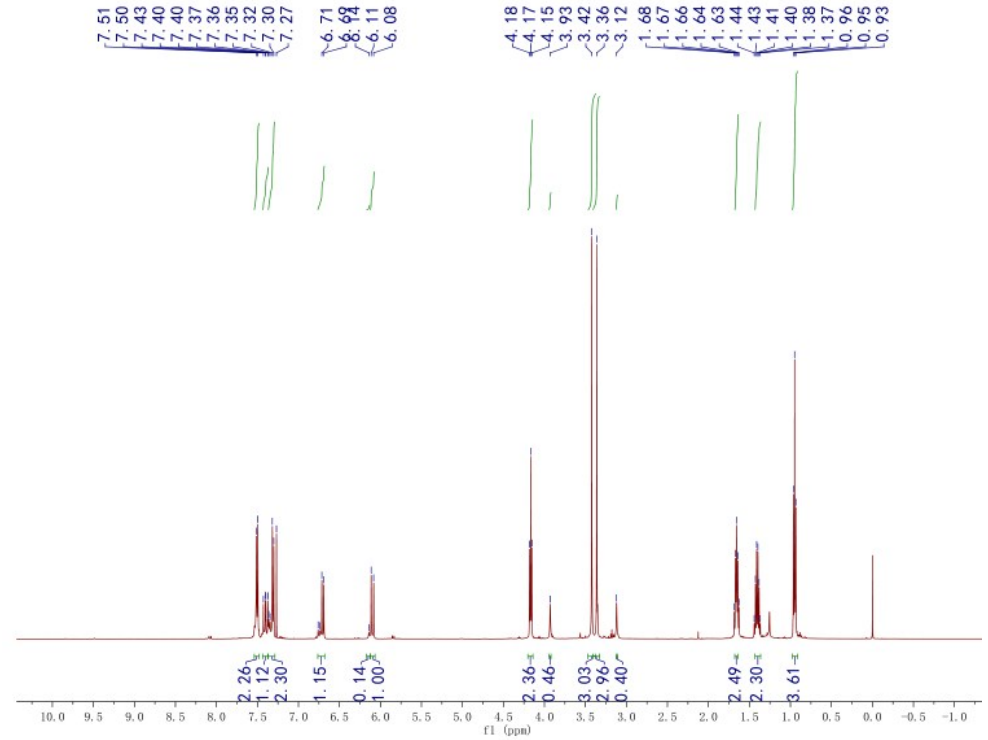

Br
O
N
OMe
Me
CO2Bu

(**3i**)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4.17
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1.68
1.67
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1.64
1.63
1.44
1.43
1.41
1.40
1.38
1.37
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0.95
0.93
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2.30
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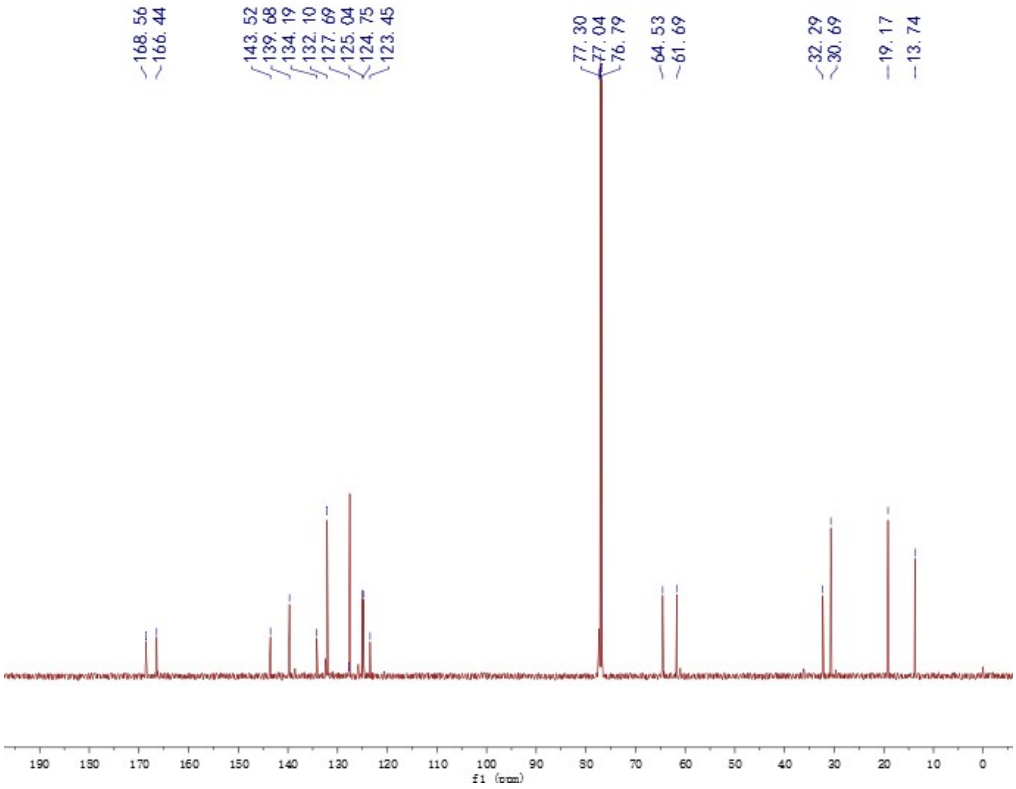
3.61
f1 (ppm)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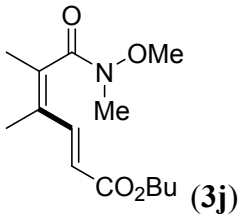
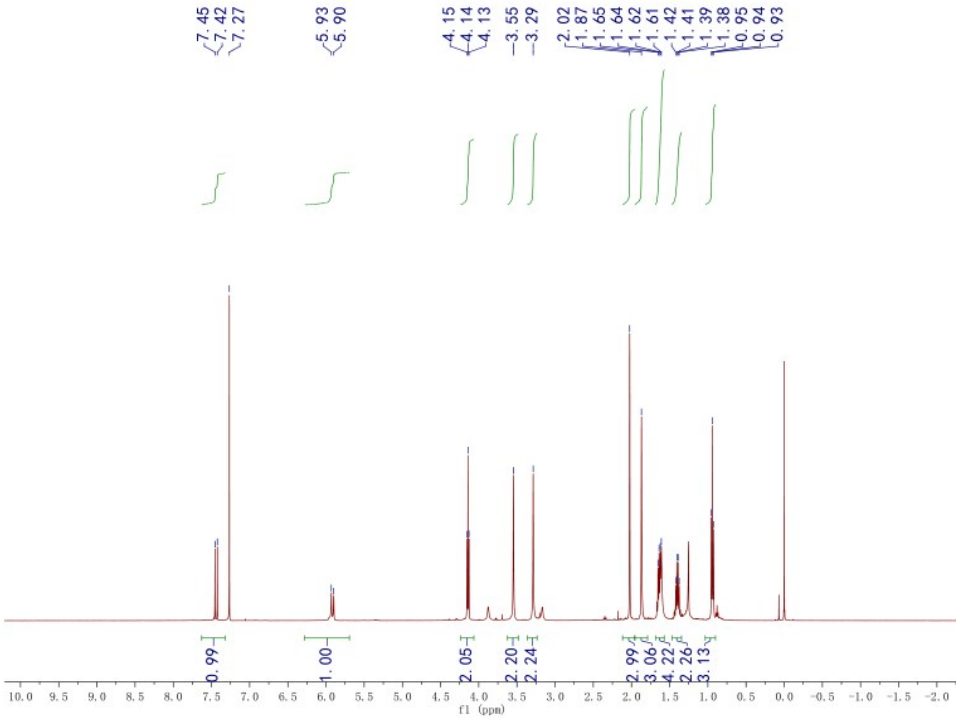
32.29
30.69
19.17
13.74
f1 (ppm)


O
N
OMe
Me
CO2Bu

(**3j**)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1.65
1.64
1.62
1.61
1.42
1.41
1.39
1.38
0.95
0.94
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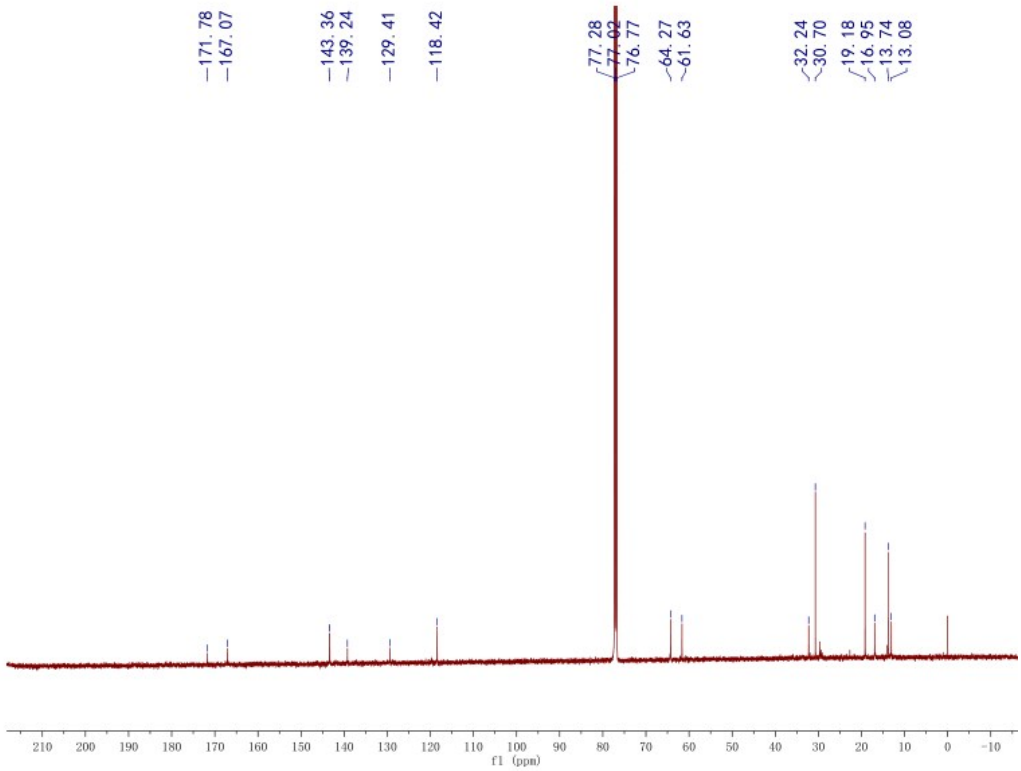
2.26
3.13
f1 (ppm)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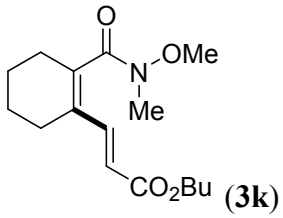
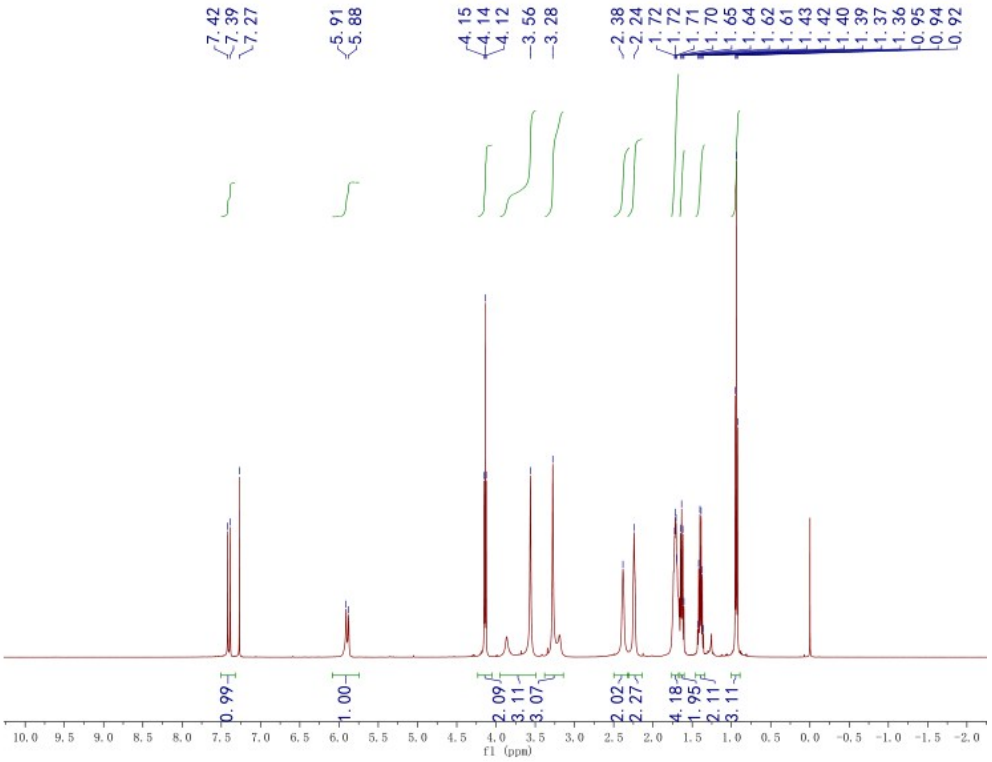
13.08
f1 (ppm)


O
N
OMe
Me
CO2Bu

(**3k**)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3.28
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1.64
1.62
1.61
1.43
1.42
1.40
1.39
1.37
1.36
0.95
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0.92
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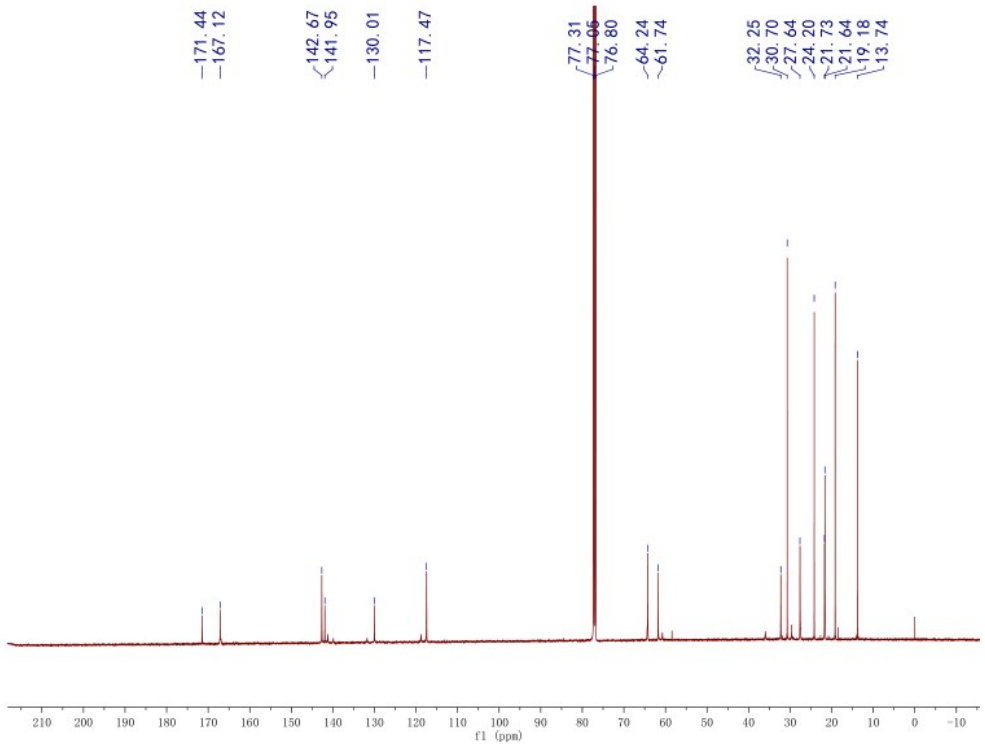
f1 (ppm)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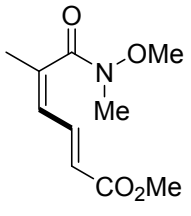
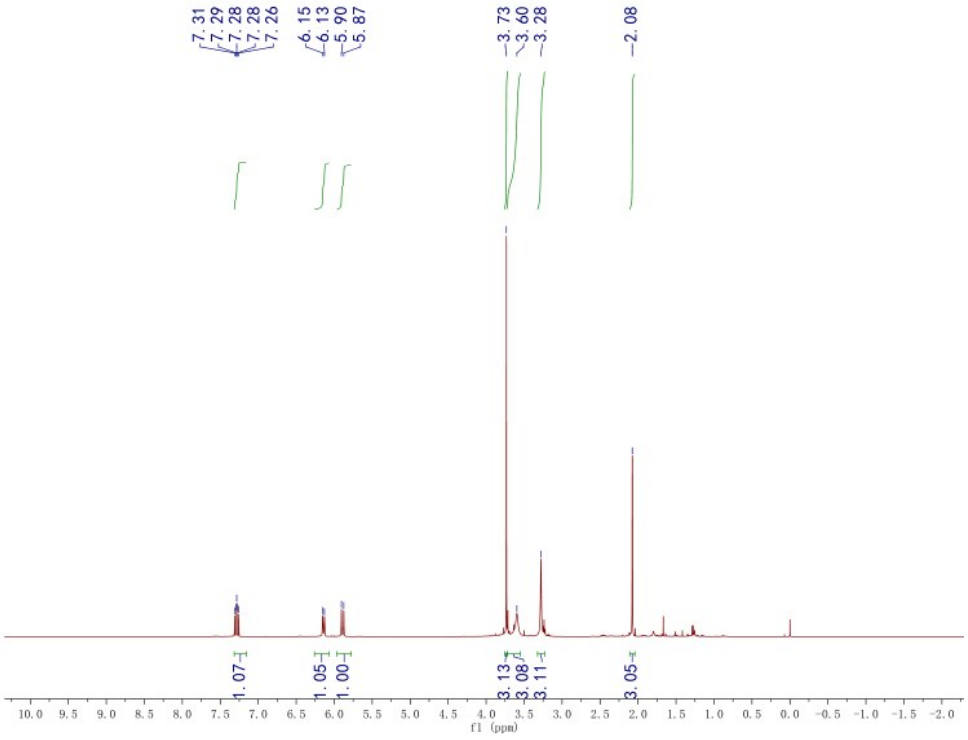
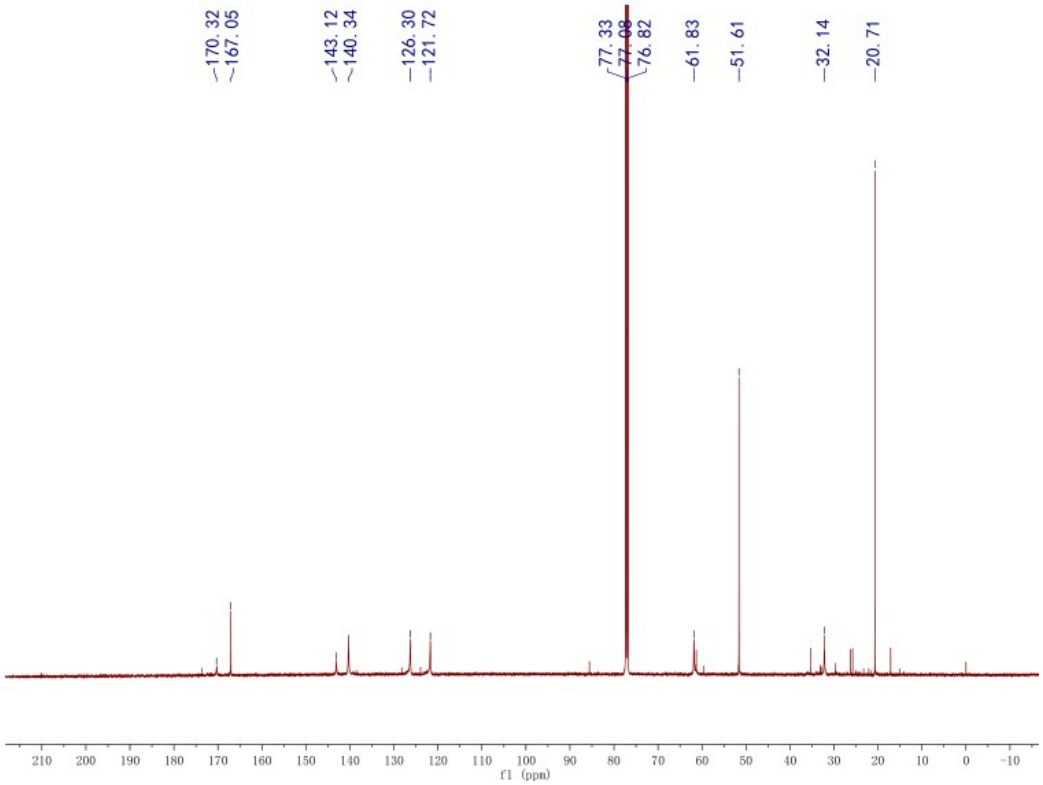
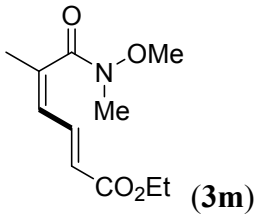
167.12
142.67
141.95
130.01
117.47
77.31
77.06
76.80
64.24
61.74
32.25
30.70
27.64
24.20
21.73
21.64
19.18
13.74
f1 (ppm)


O
N
OMe
Me
CO2Me

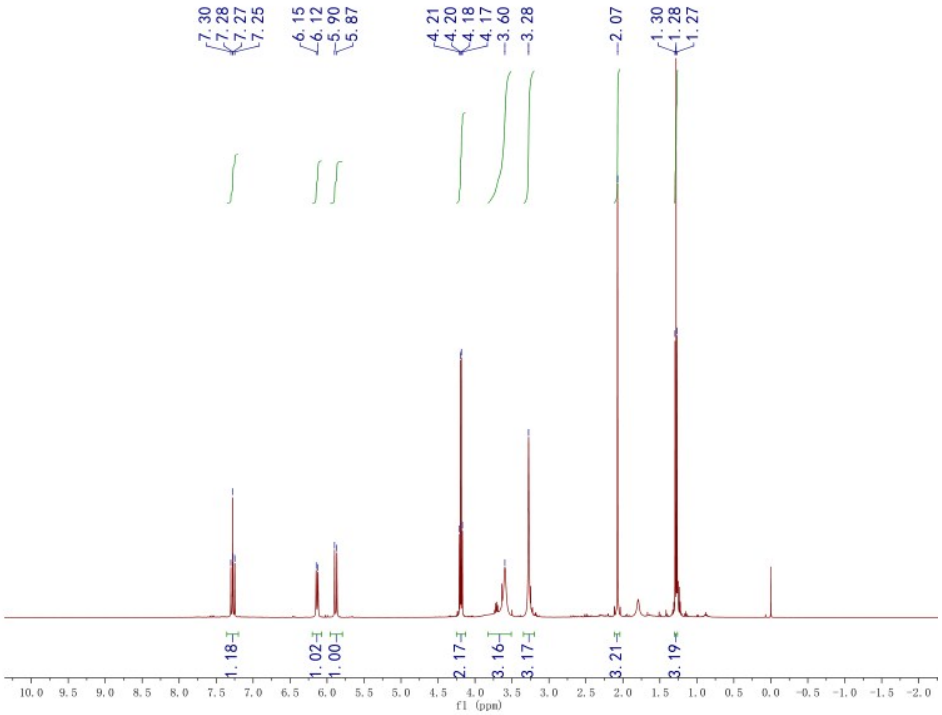
(**3l**)


7.31
7.29
7.28
7.28
7.26
6.15
6.13
5.90
5.87
3.73
3.60
3.28
2.08
1.07
1.05
1.00
3.13
3.08
3.11
3.05
f1 (ppm)


170.32
167.05
143.12
140.34
126.30
121.72
77.33
77.08
76.82
61.83
51.61
32.14
20.71
f1 (ppm)


O
N
OMe
Me
CO2Et

(3m)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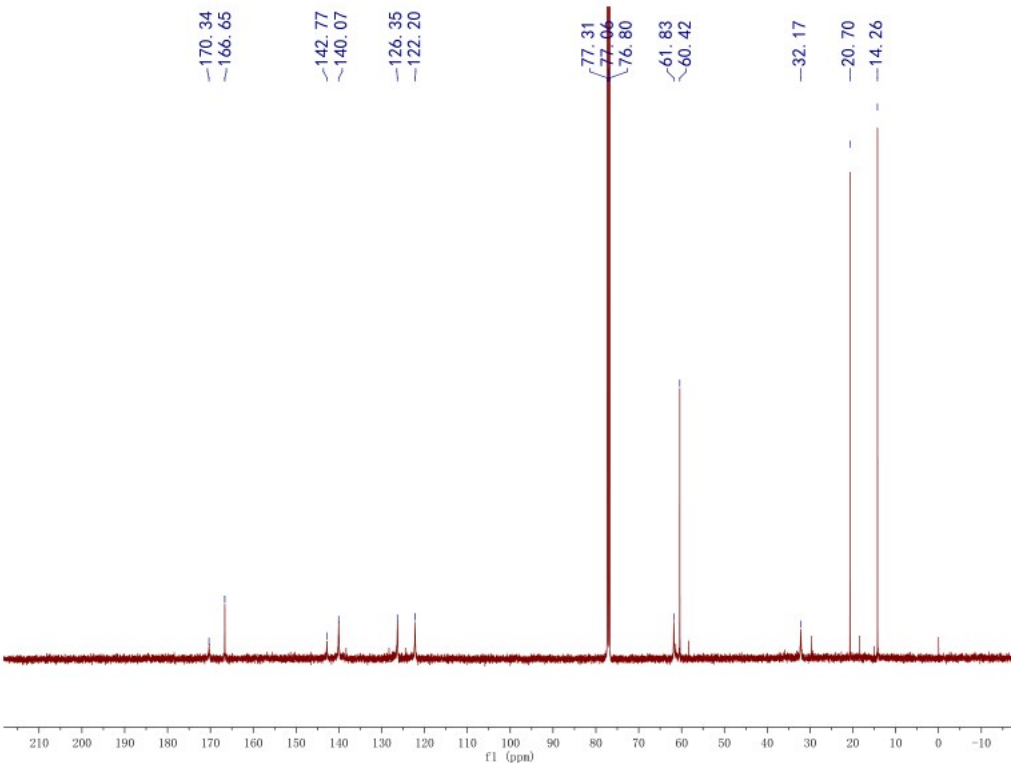
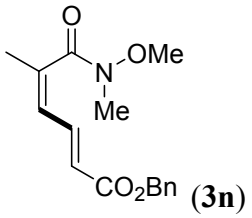
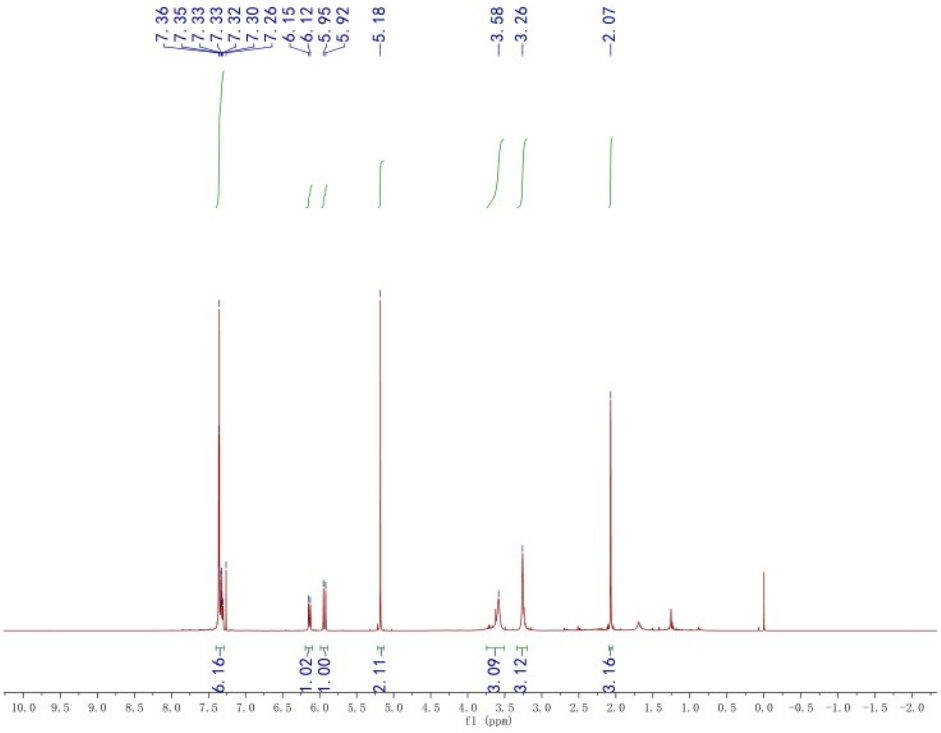
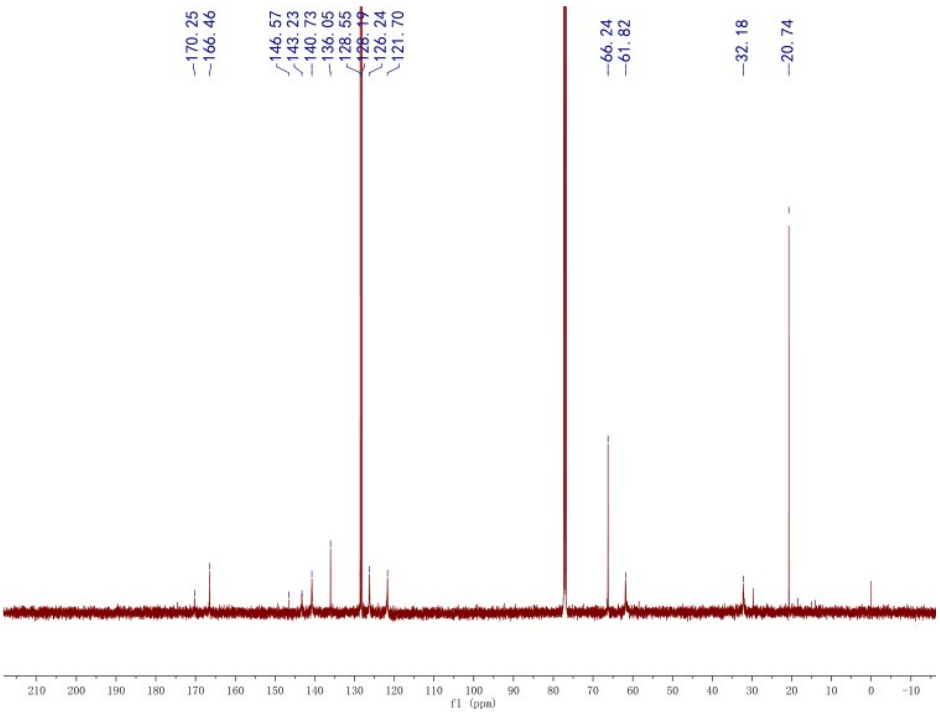
7.28
7.27
7.25
6.15
6.12
5.90
5.87
4.21
4.20
4.18
4.17
3.60
3.28
2.07
1.30
1.28
1.27
1.18
1.02
1.00
2.17
3.16
3.17
3.21
3.19
f1 (ppm)

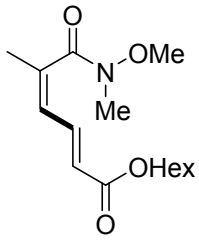

170.34
166.65
142.77
140.07
126.35
122.20
77.31
77.06
76.80
61.83
60.42
32.17
20.70
14.26
f1 (ppm)


O
OMe
N
Me
CO2Bn

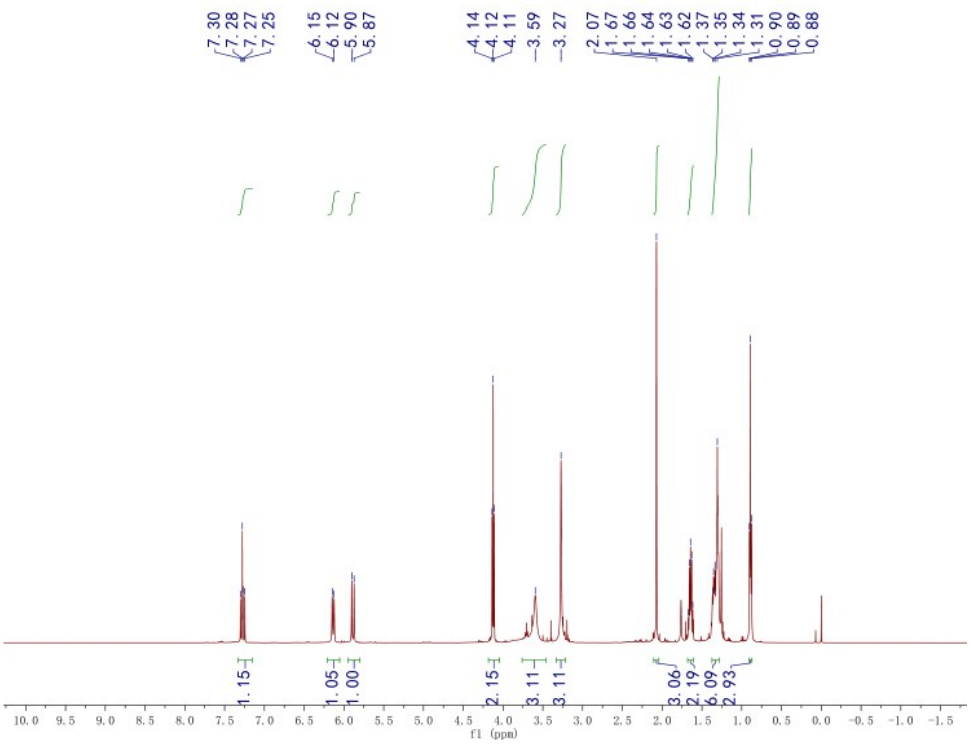
(3n)

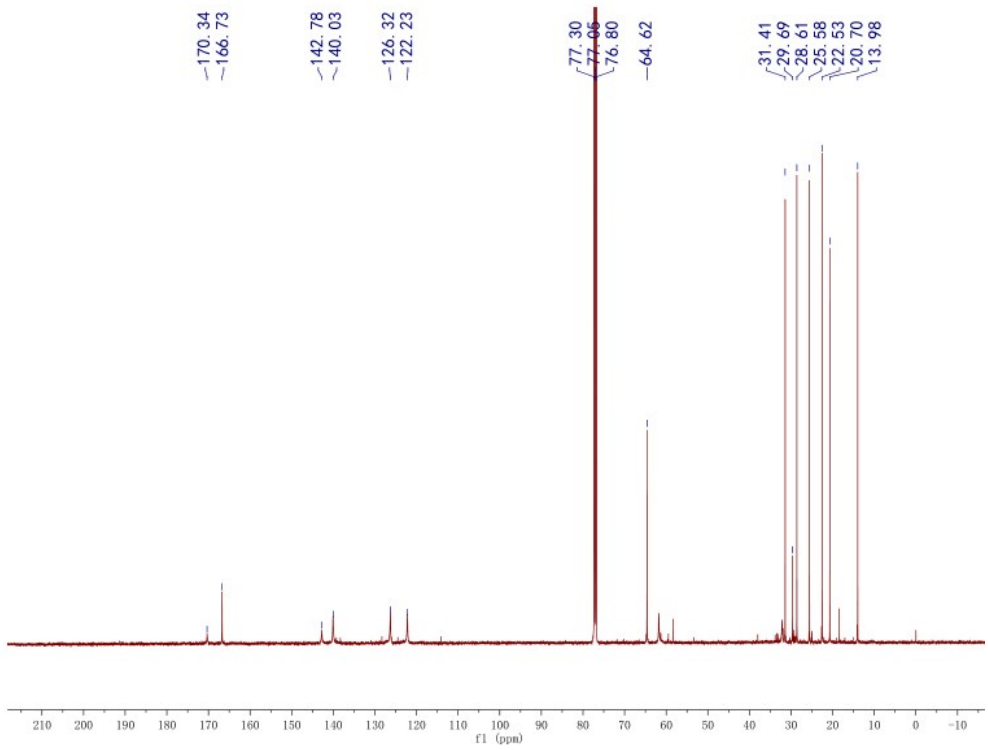

7.36
7.35
7.33
7.33
7.32
7.30
7.26
6.15
6.12
5.95
5.92
5.18
3.58
3.26
2.07
6.16
1.02
1.00
2.11
3.09
3.12
3.16
f1 (ppm)

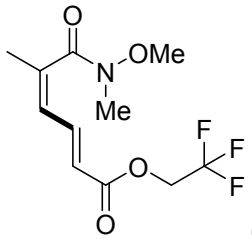

170.25
166.46
146.57
143.23
140.73
136.05
128.55
128.19
126.24
121.70
66.24
61.82
32.18
20.74
f1 (ppm)


O
N
OMe
Me
OHex
O

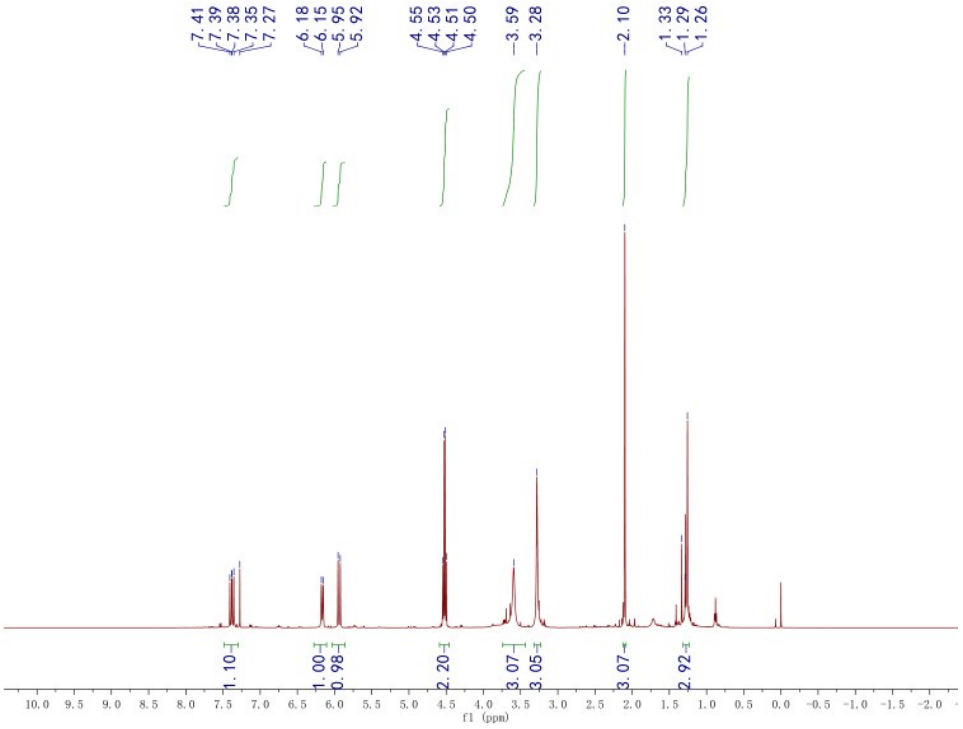
(**3o**)

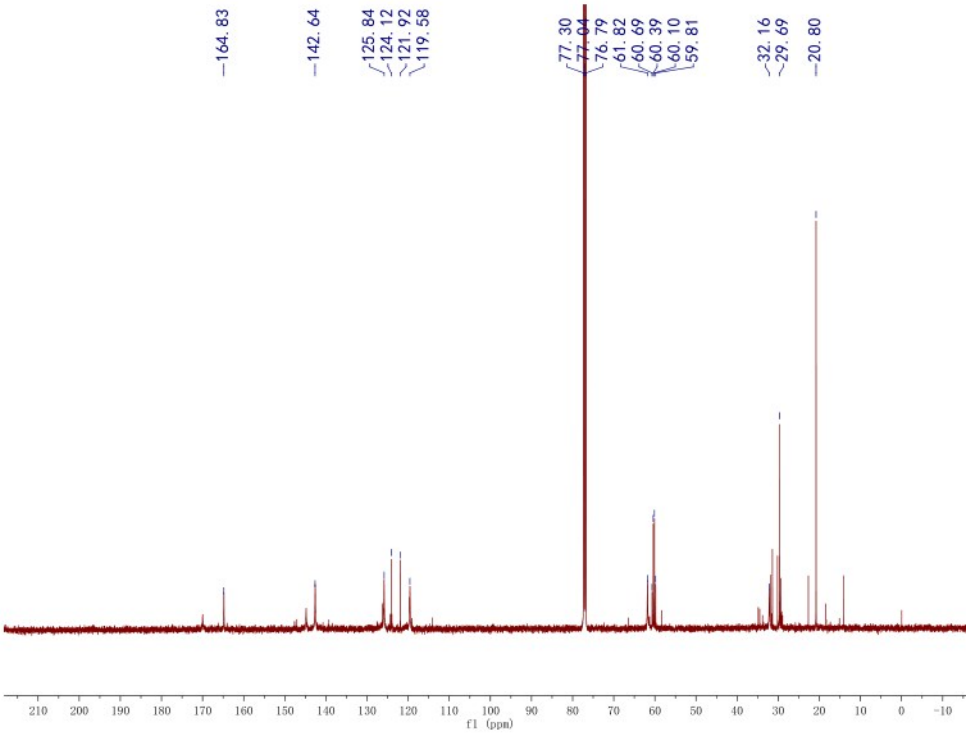

7.30
7.28
7.27
7.25
6.15
6.12
5.90
5.87
4.14
4.12
4.11
3.59
3.27
2.07
1.67
1.66
1.64
1.63
1.62
1.37
1.35
1.34
1.31
0.90
0.89
0.88
1.15
1.05
1.00
2.15
3.11
3.11
3.06
2.19
6.09
2.93
f1 (ppm)

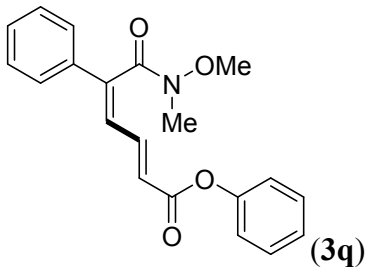

170.34
166.73
142.78
140.03
126.32
122.23
77.30
77.06
76.80
64.62
31.41
29.69
28.61
25.58
22.53
20.70
13.98
f1 (ppm)


O
N
OMe
Me
F
F
F
O
O

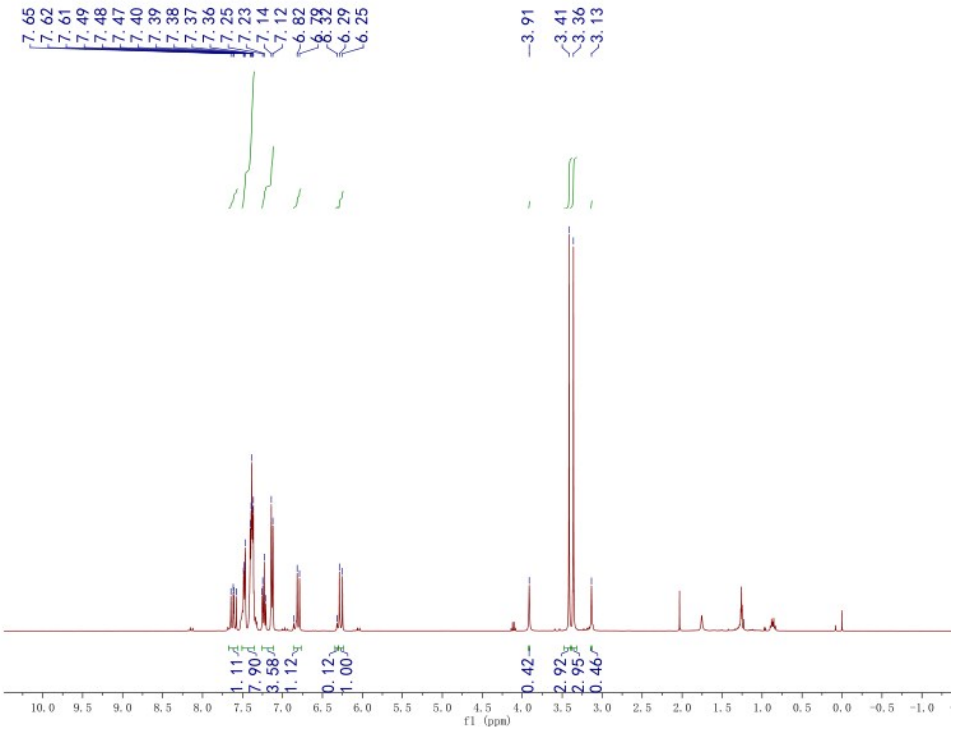
(**3p**)

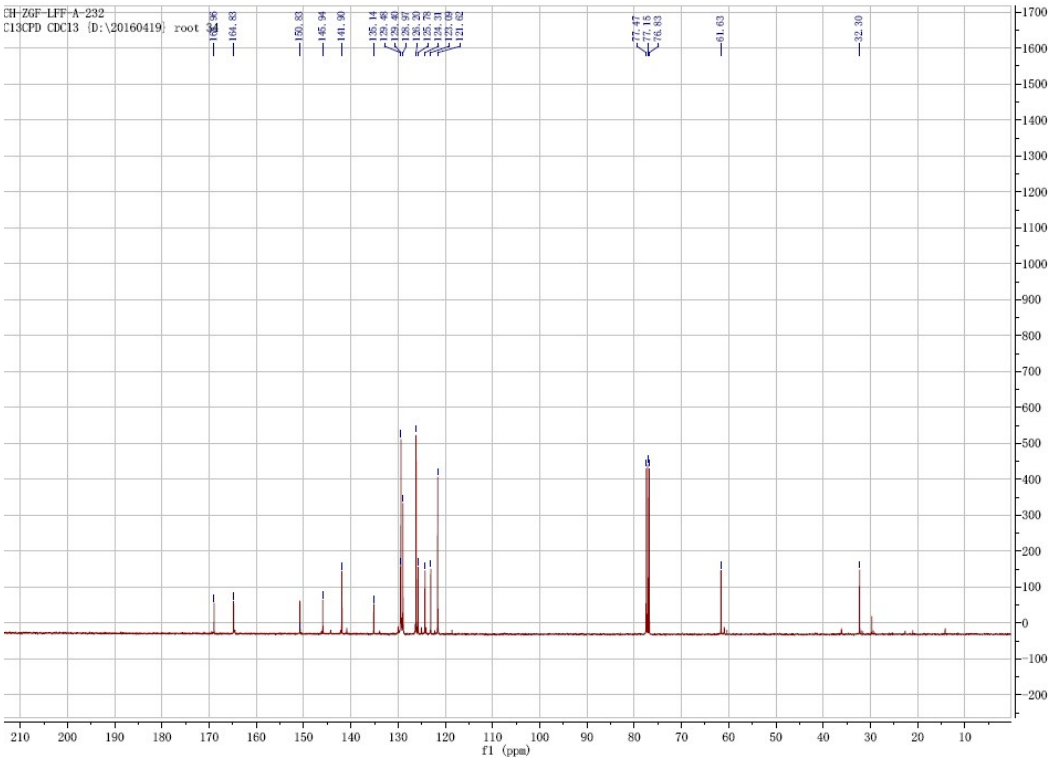

7.41
7.39
7.38
7.35
7.27
6.18
6.15
5.95
5.92
4.55
4.53
4.51
4.50
3.59
3.28
2.10
1.33
1.29
1.26
1.10
1.00
0.98
2.20
3.07
3.05
3.07
2.92
f1 (ppm)

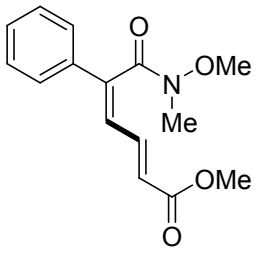

164.83
142.64
125.84
124.12
121.92
119.58
77.30
77.04
76.79
61.82
60.69
60.39
60.10
59.81
32.16
29.69
20.80
f1 (ppm)


O
N
OMe
Me
O
O

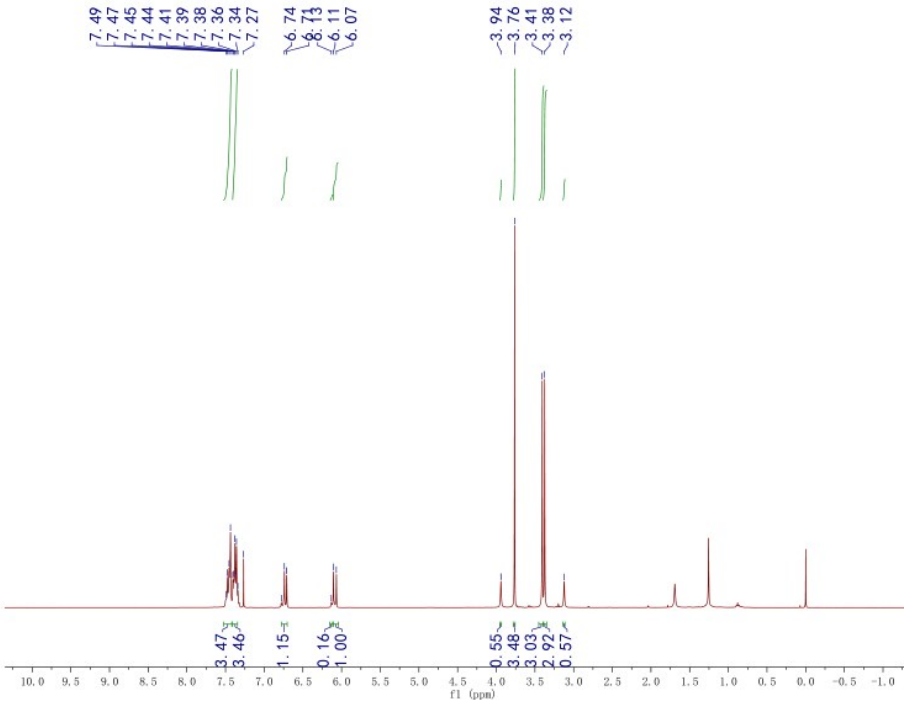
(**3q**)

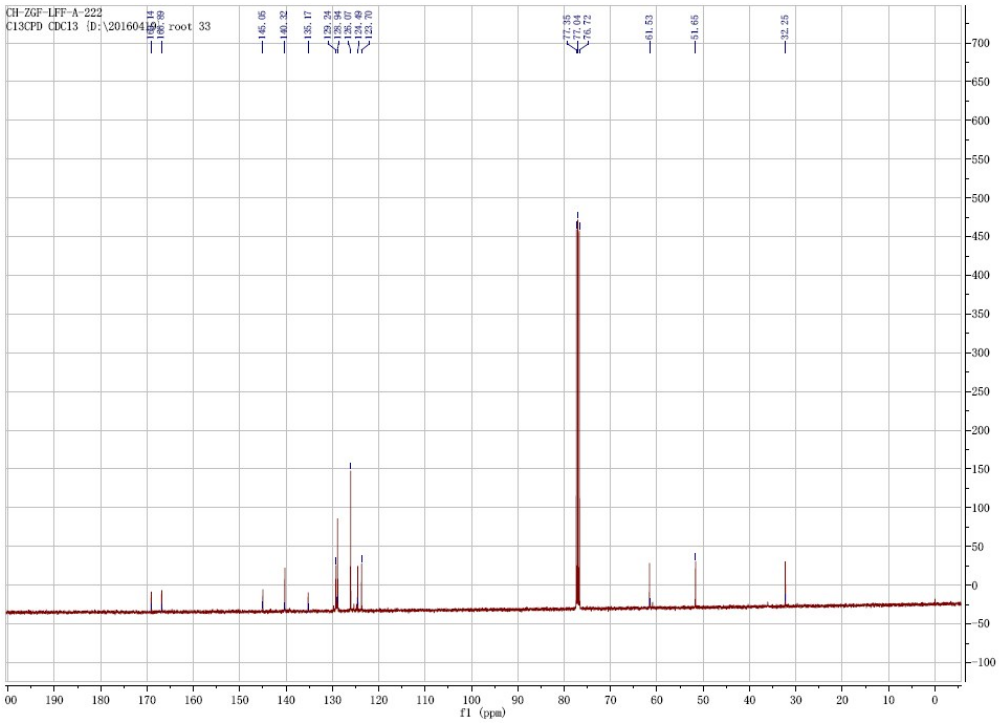

7.65
7.62
7.61
7.49
7.48
7.47
7.40
7.39
7.38
7.37
7.36
7.25
7.23
7.14
7.12
6.82
6.32
6.29
6.25
3.91
3.41
3.36
3.13
1.11
7.90
3.58
1.12
0.12
1.00
0.42
2.92
2.95
0.46
f1 (ppm)

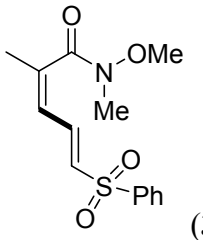

CH-ZGF-LFF-A-232
C13CPD CDCl3 (D:\20160419) root
164.83
150.83
145.94
141.90
135.14
129.48
128.97
126.20
125.78
124.31
121.62
77.47
77.15
76.83
61.63
32.30
f1 (ppm)


O
OMe
N
Me
OMe
O

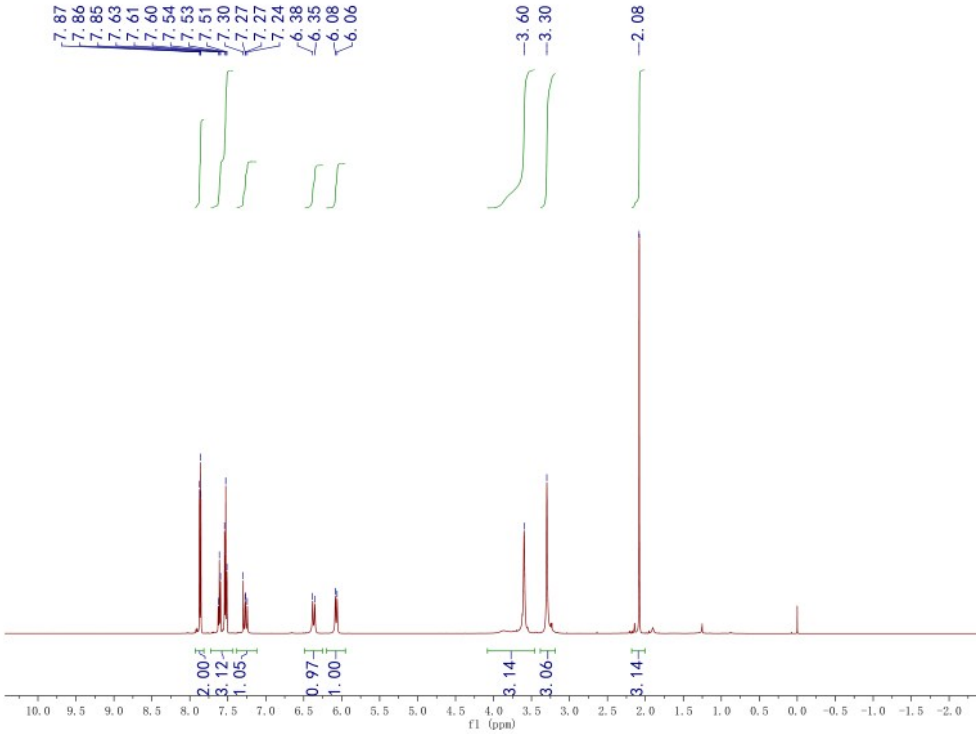
(**3r**)

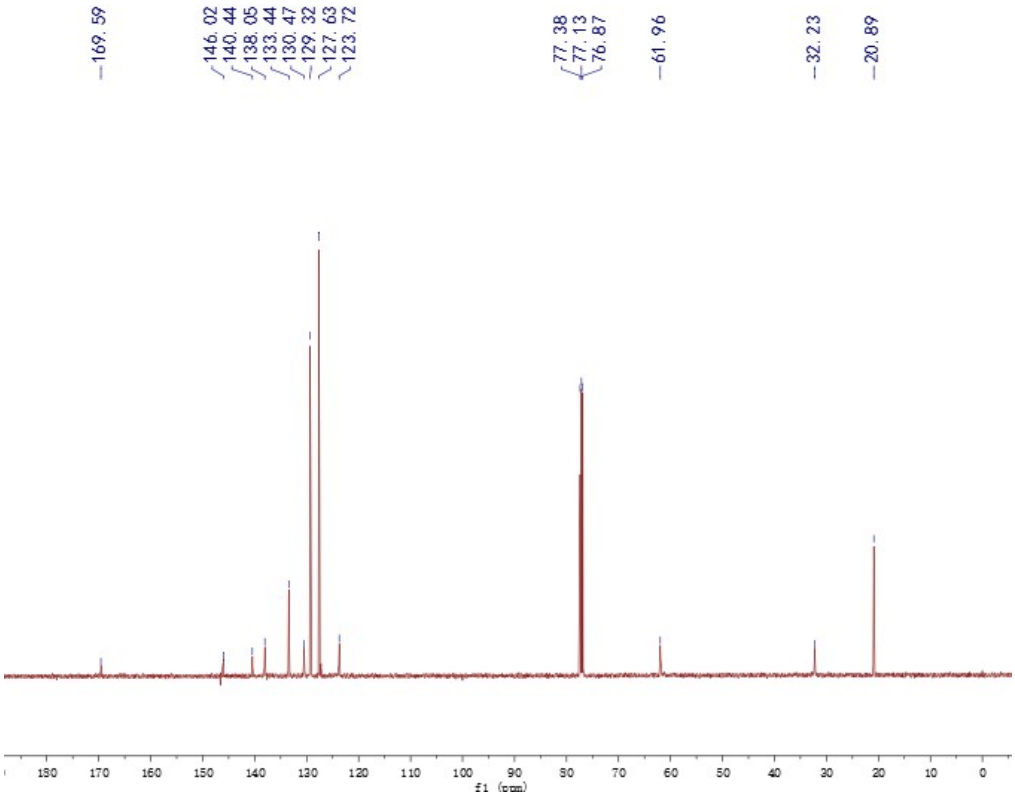

7.49
7.47
7.45
7.44
7.41
7.39
7.38
7.36
7.34
7.27
6.74
6.73
6.13
6.11
6.07
3.94
3.76
3.41
3.38
3.12
3.47
3.46
1.15
0.16
1.00
0.55
3.48
3.03
2.92
0.57
f1 (ppm)

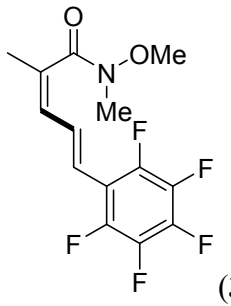

CH-ZGF-LFF-A-222
C13CPD CDC13 {D:\20160418\ root 33
146.05
140.32
135.17
129.24
128.98
128.66
124.49
123.70
77.35
77.04
76.72
61.53
51.65
32.25
f1 (ppm)


O
N
OMe
Me
O
S
O
Ph

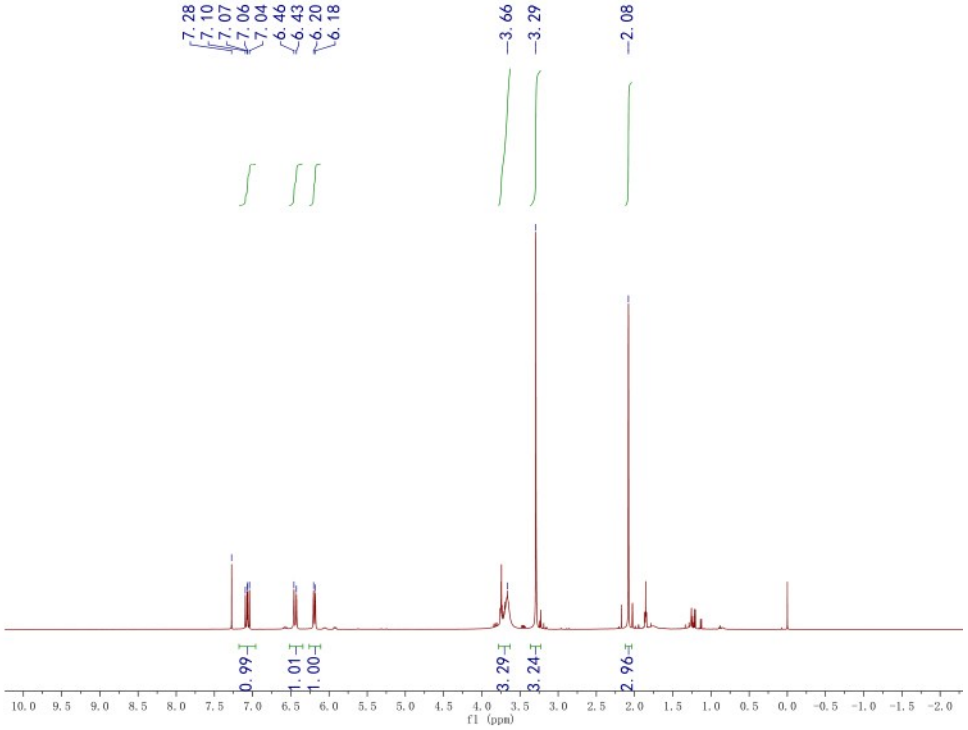
(**3s**)

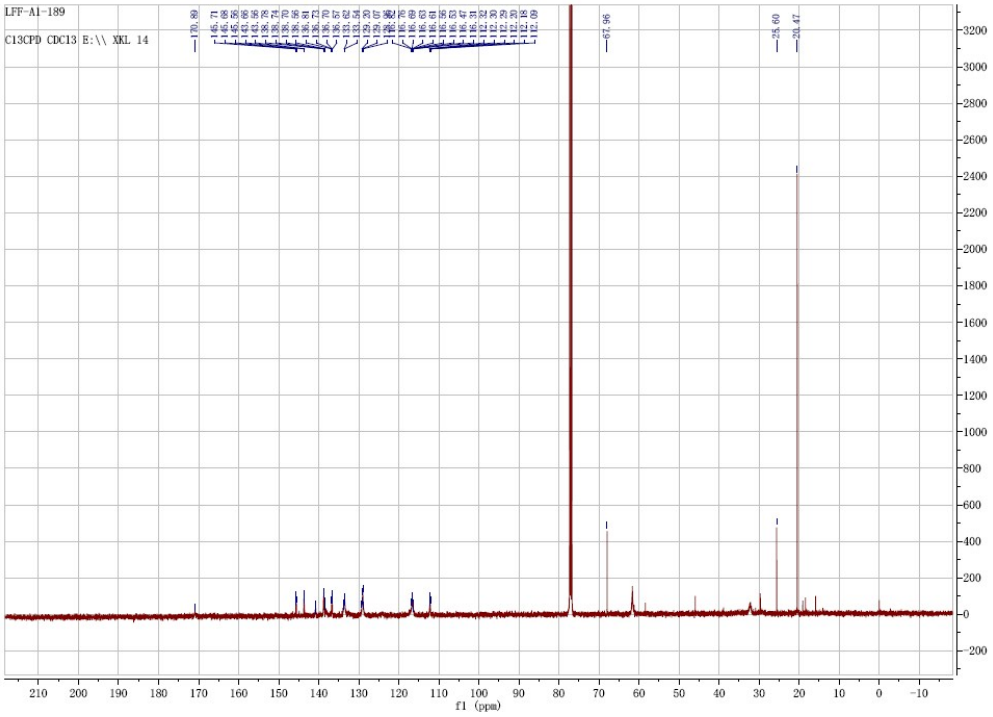

7.87
7.86
7.85
7.63
7.61
7.60
7.54
7.53
7.51
7.30
7.27
7.27
7.24
6.38
6.35
6.08
6.06
3.60
3.30
2.08
2.00
3.12
1.05
0.97
1.00
3.14
3.06
3.14
f1 (ppm)

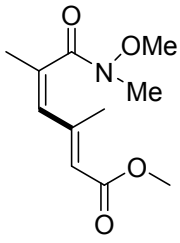

169.59
146.02
140.44
138.05
133.44
130.47
129.32
127.63
123.72
77.38
77.13
76.87
61.96
32.23
20.89
f1 (ppm)


O
N
OMe
Me
F
F
F
F
F

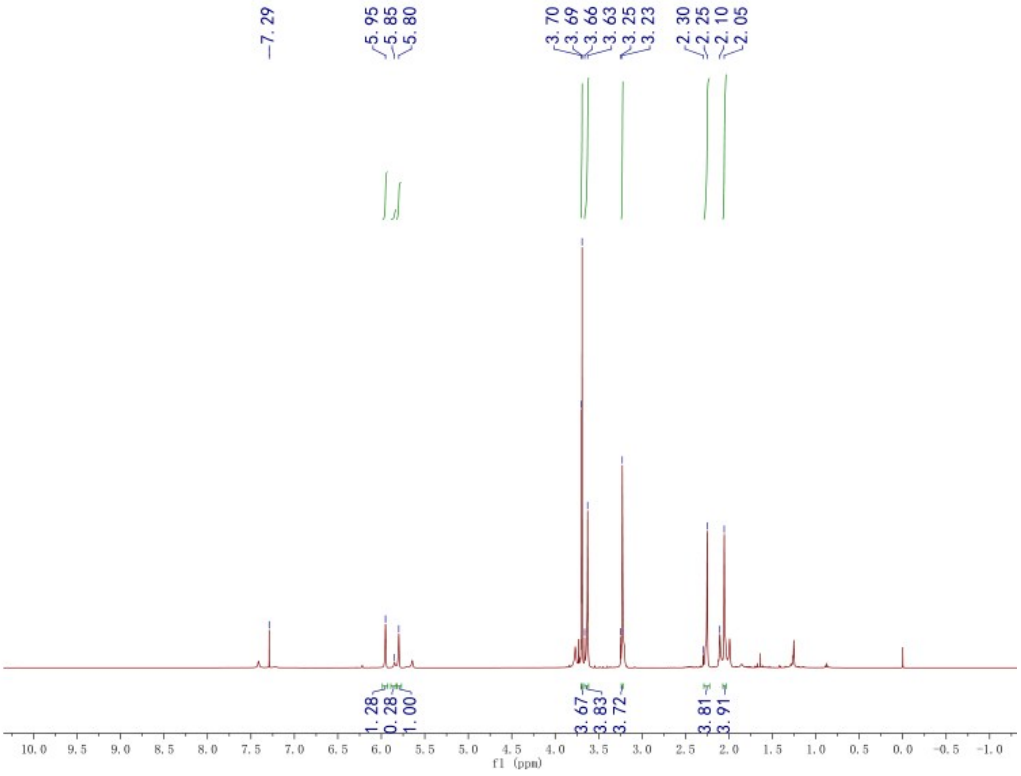
(**3t**)

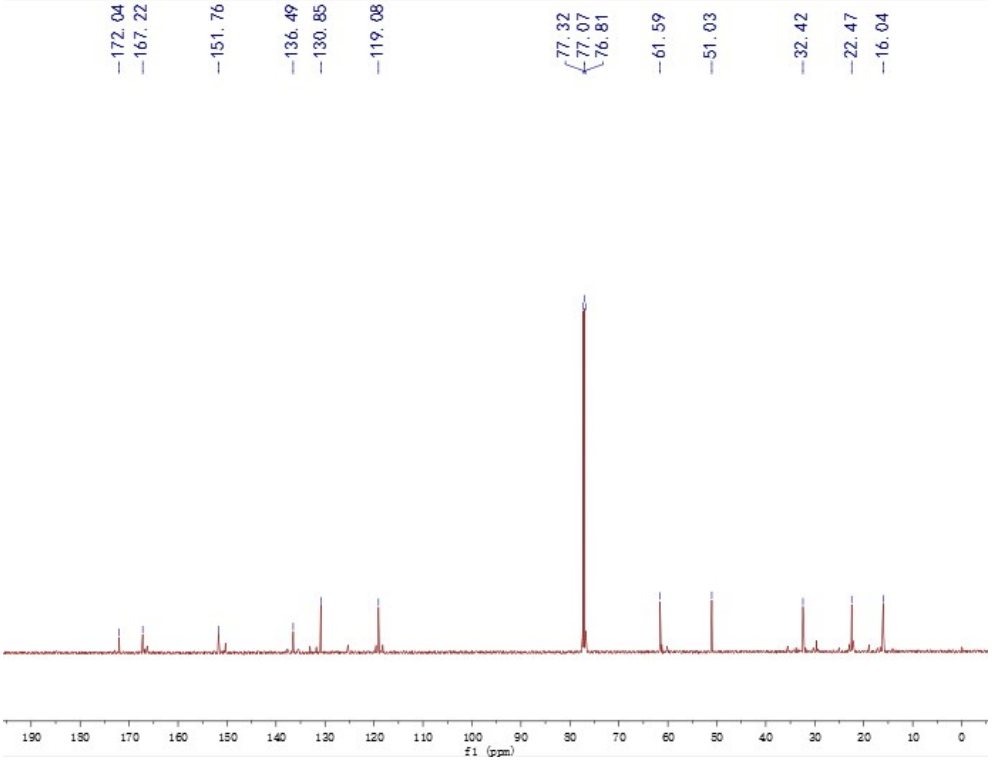

7.28
7.10
7.07
7.06
7.04
6.46
6.43
6.20
6.18
3.66
3.29
2.08
0.99
1.01
1.00
3.29
3.24
2.96
f1 (ppm)

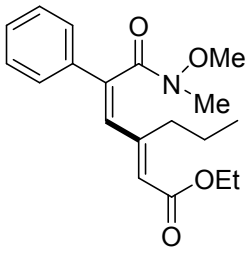

LFF-A1-189
C13CPD CDCl3 E:\\ XKL 14
f1 (ppm)



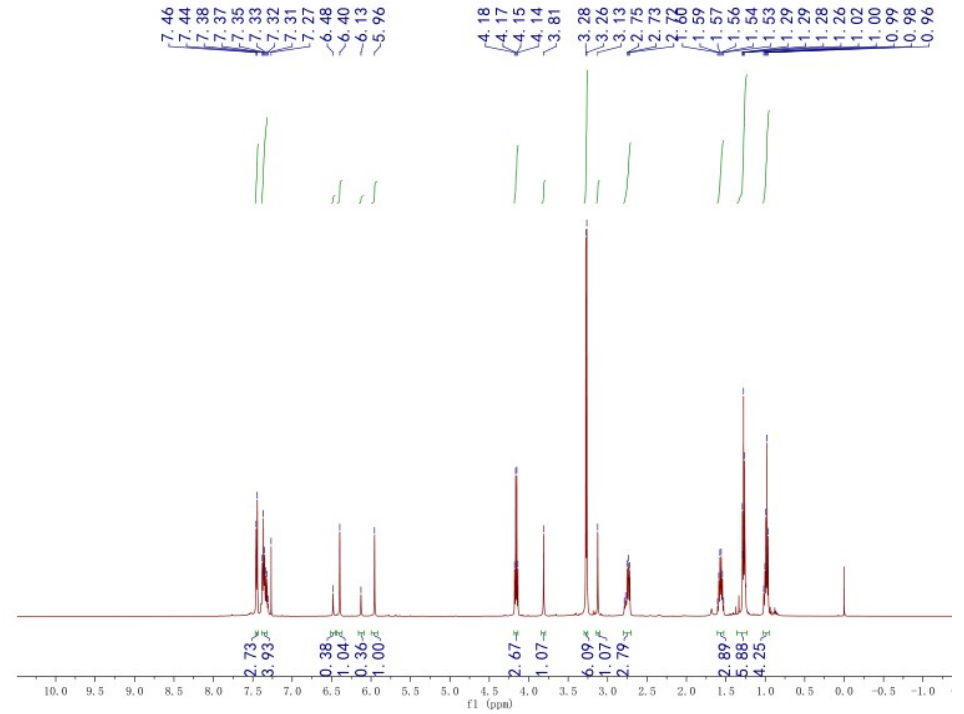
(**3u**)

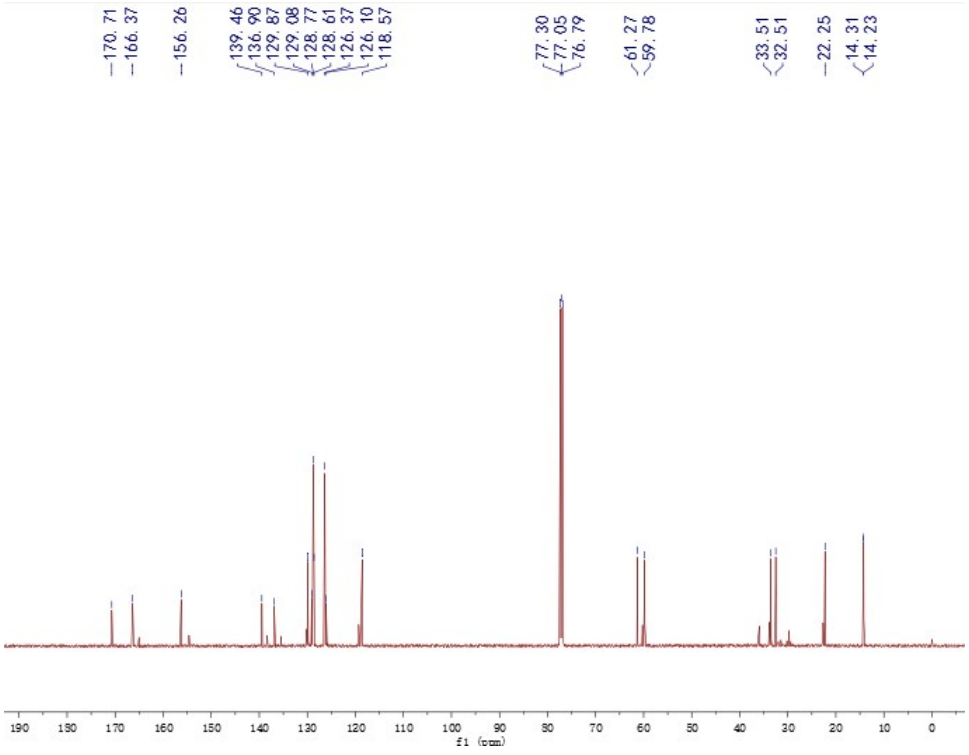

7.29
5.95
5.85
5.80
3.70
3.69
3.66
3.63
3.25
3.23
2.30
2.25
2.10
2.05
1.28
0.28
1.00
3.67
3.83
3.72
3.81
3.91
f1 (ppm)

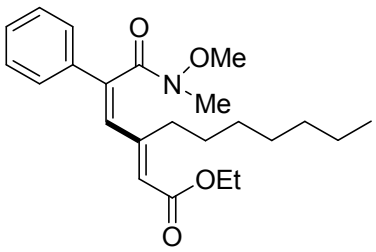

172.04
167.22
151.76
136.49
130.85
119.08
77.32
77.07
76.81
61.59
51.03
32.42
22.47
16.04
f1 (ppm)


O
OMe
N
Me
OEt
O

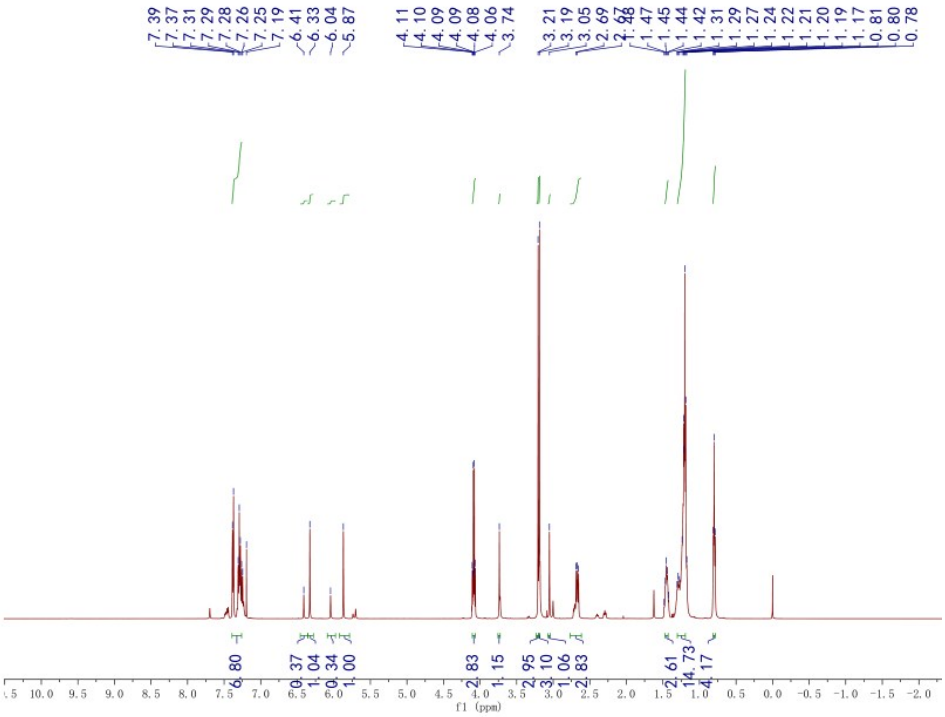
(**3v**)

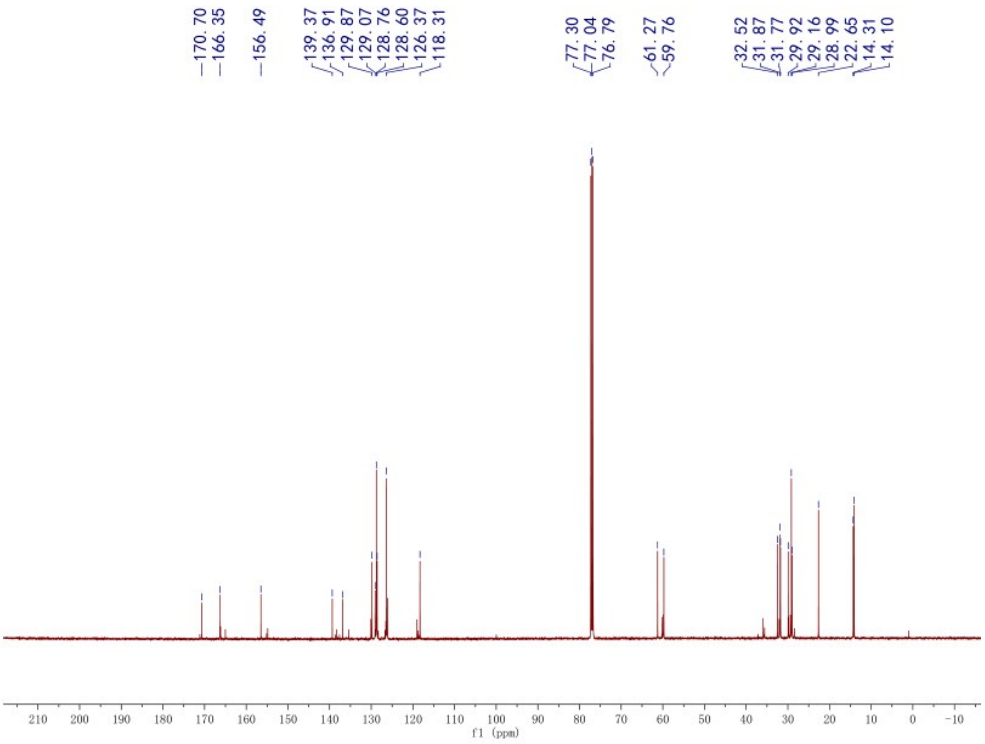

7.46
7.44
7.38
7.37
7.35
7.33
7.32
7.31
7.27
6.48
6.40
6.13
5.96
4.18
4.17
4.15
4.14
3.81
3.28
3.26
3.13
2.75
2.73
1.59
1.57
1.56
1.54
1.53
1.29
1.28
1.26
1.02
1.00
0.99
0.98
0.96
2.73
3.93
0.38
1.04
0.36
1.00
2.67
1.07
6.09
1.07
2.79
2.89
5.88
4.25
f1 (ppm)

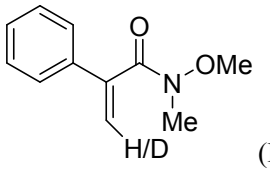

170.71
166.37
156.26
139.46
136.90
129.87
129.08
128.77
128.61
126.37
126.10
118.57
77.30
77.05
76.79
61.27
59.78
33.51
32.51
22.25
14.31
14.23
f1 (ppm)


O
OMe
N
Me
OEt
O

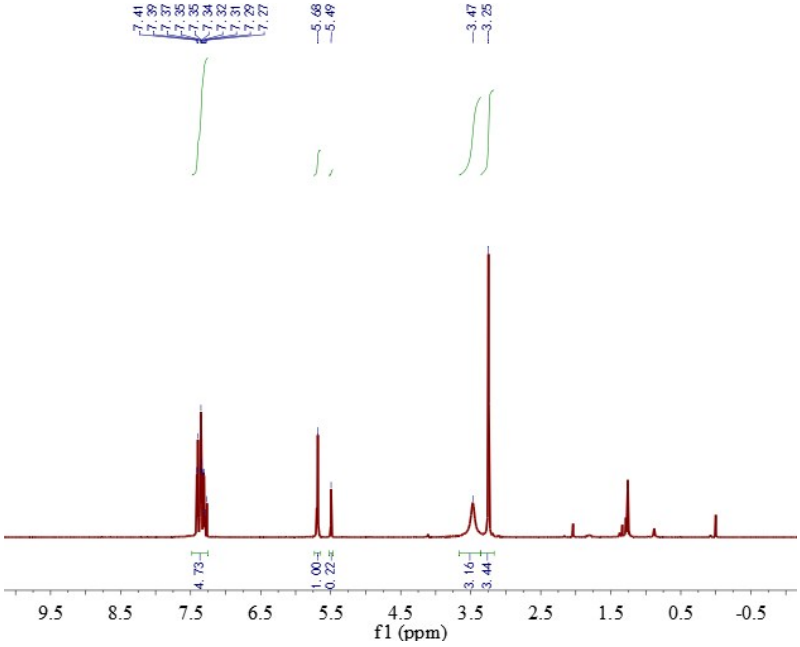
(3w)

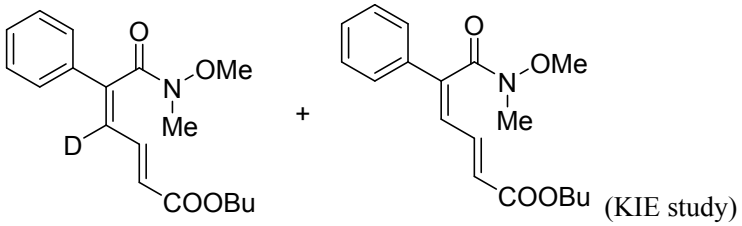

7.39
7.37
7.31
7.29
7.28
7.26
7.25
7.19
6.41
6.33
6.04
5.87
4.11
4.10
4.09
4.09
4.08
4.06
3.74
3.21
3.19
3.05
2.69
1.47
1.45
1.44
1.42
1.31
1.29
1.27
1.24
1.22
1.21
1.20
1.19
1.17
0.81
0.80
0.78
6.80
0.37
1.04
0.34
1.00
2.83
1.15
2.95
3.10
1.06
2.83
2.61
14.73
4.17
f1 (ppm)


170.70
166.35
156.49
139.37
136.91
129.87
129.07
128.76
128.60
126.37
118.31
77.30
77.04
76.79
61.27
59.76
32.52
31.87
31.77
29.92
29.16
28.99
22.65
14.31
14.10
f1 (ppm)

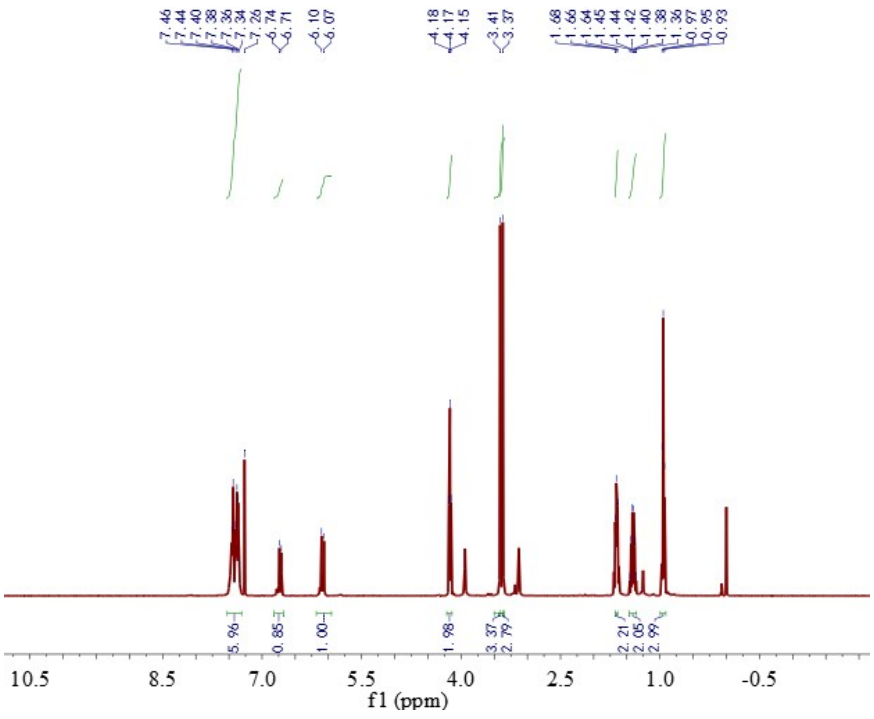


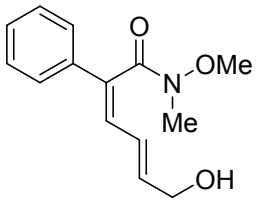
(H/D exchange)



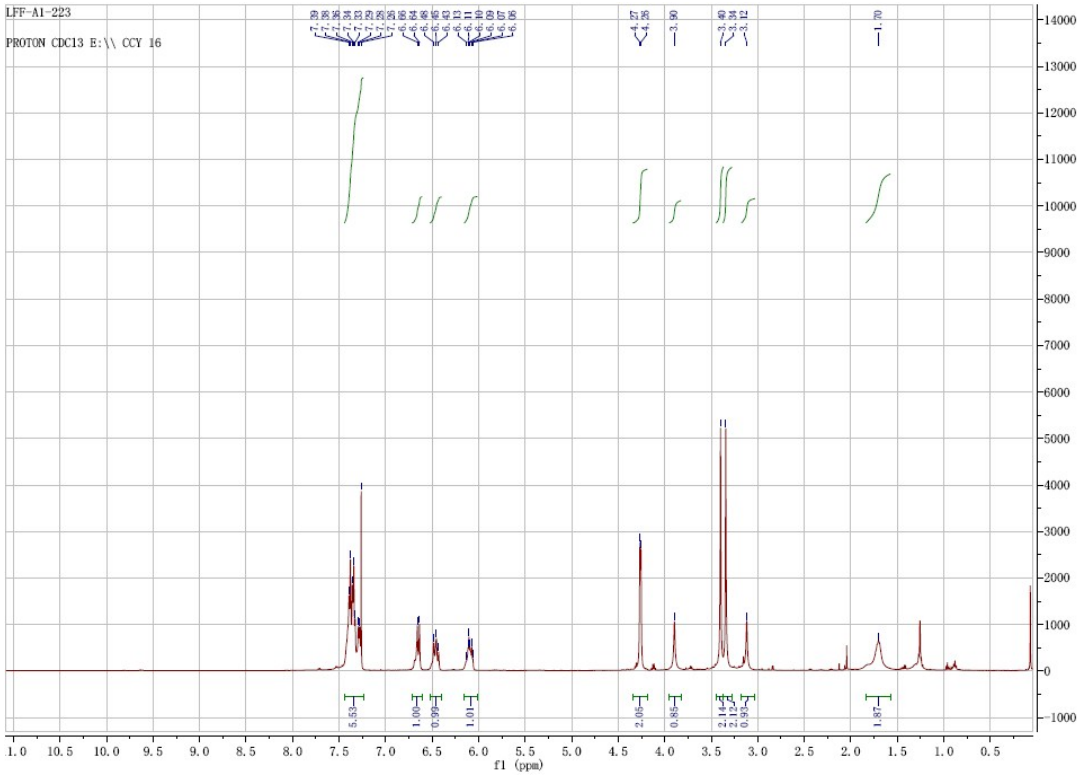


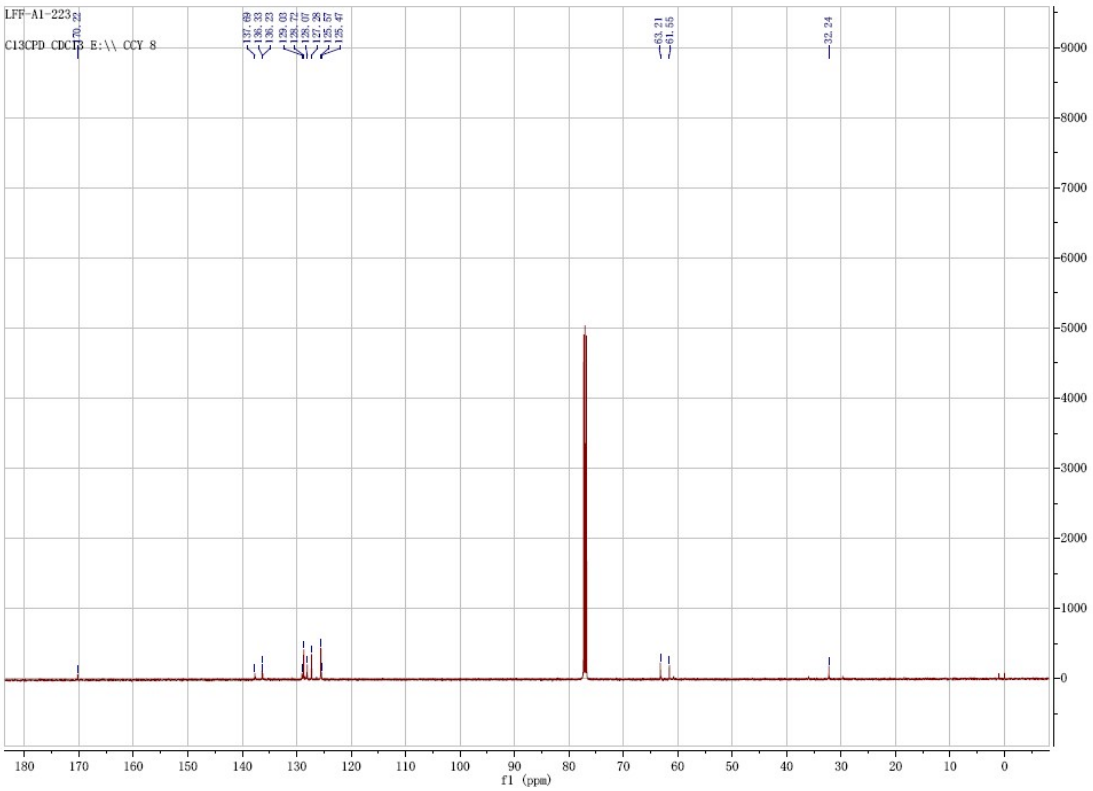
(KIE study)

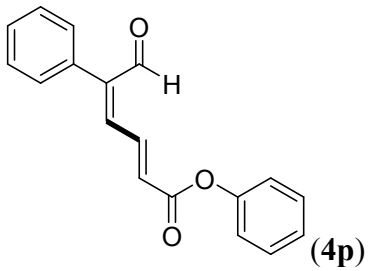



O
N
OMe
Me
OH

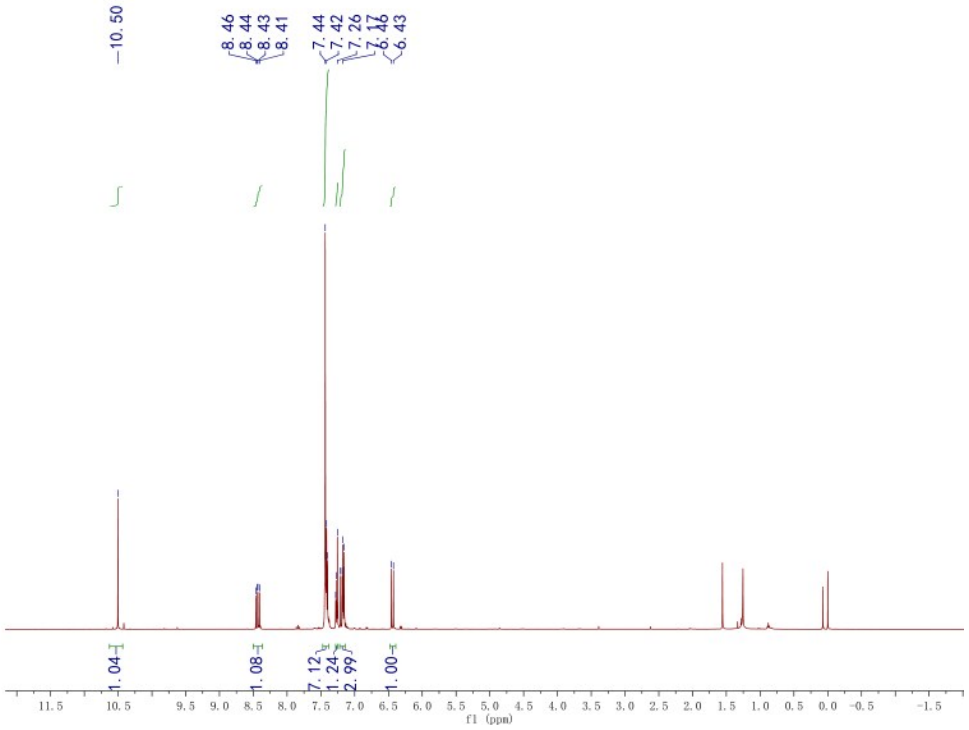
(**4q**)

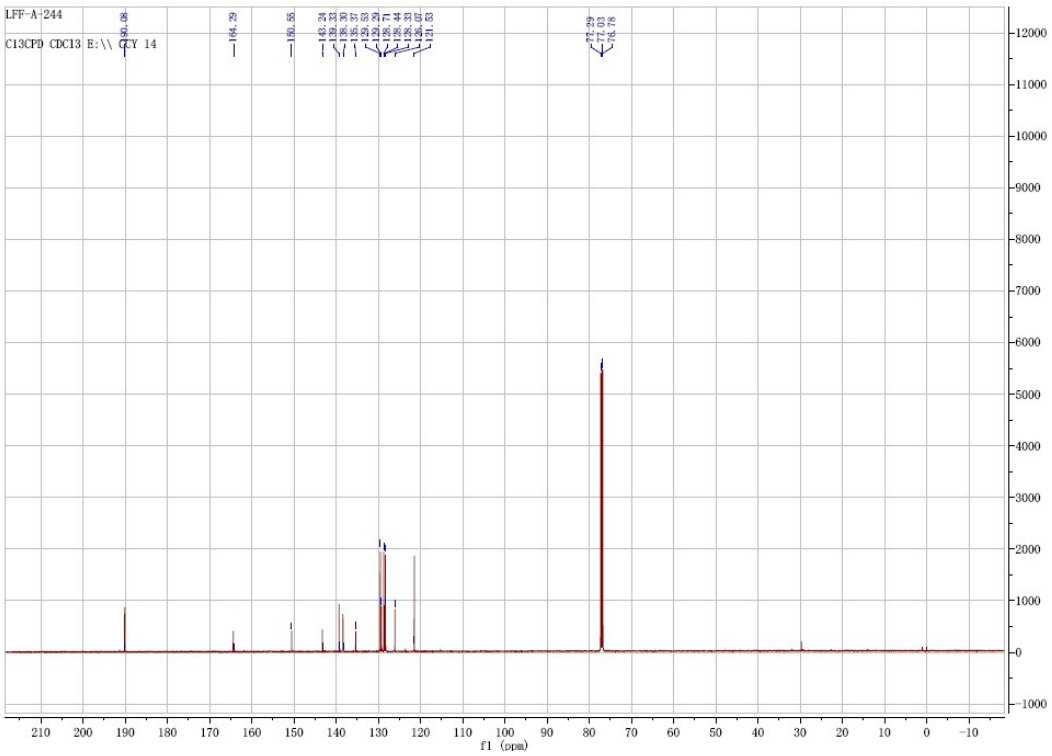

LFF-A1-223
PROTON CDCl3 E:\\ CCY 16
f1 (ppm)

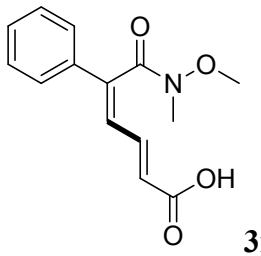

LFF-A1-223
C13CPD CDCl3 E:\\ CCY 8
f1 (ppm)



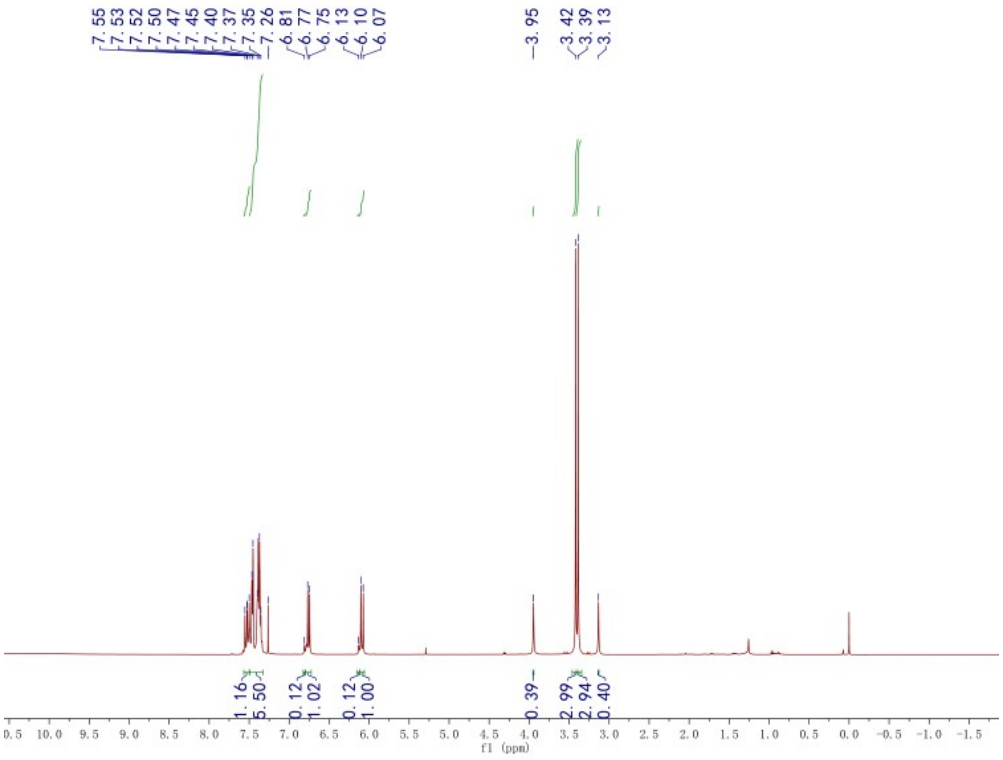
(**4p**)

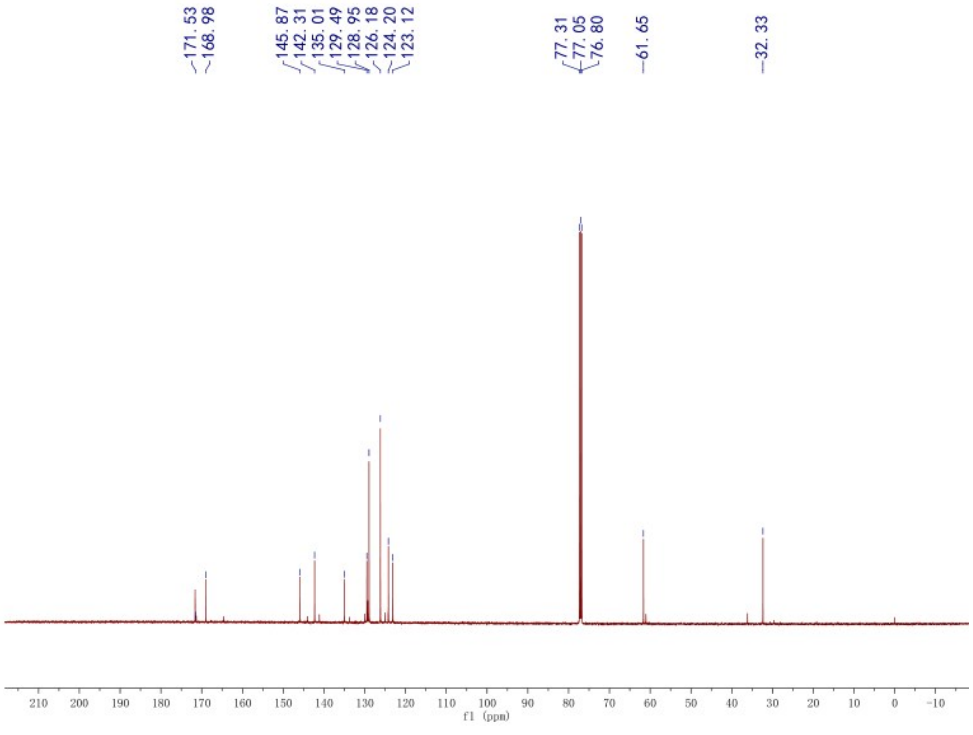

10.50
8.46
8.44
8.43
8.41
7.44
7.42
7.26
7.17
6.46
6.43
1.04
1.08
7.12
1.24
2.99
1.00
f1 (ppm)

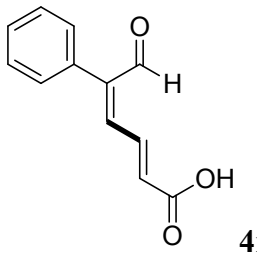

LFF-A-244
C13CPD CDCl3 E:\\ CHY 14
190.08
164.29
150.55
143.24
138.33
136.39
135.37
129.53
129.29
128.71
128.44
128.33
126.07
121.53
77.29
77.03
76.78
f1 (ppm)


O
N
O
OH
O

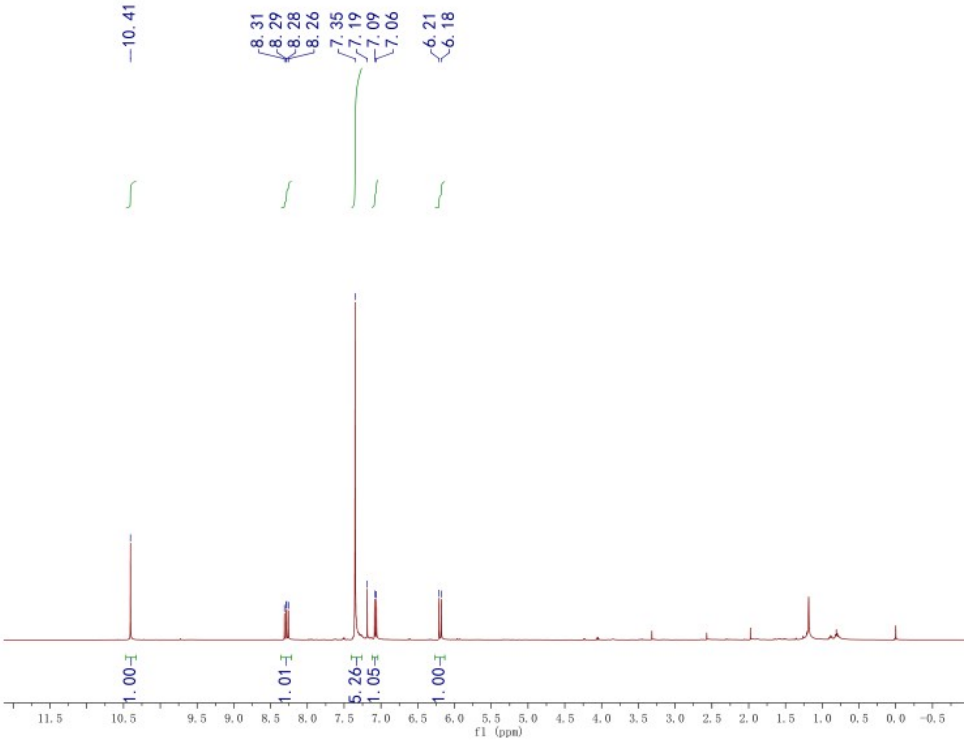
3x

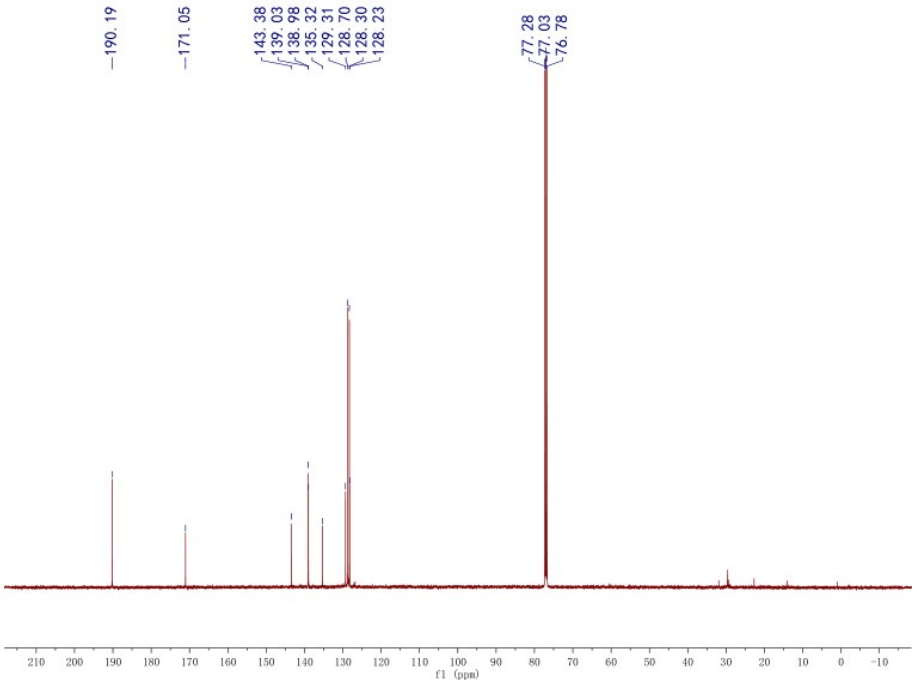

7.55
7.53
7.52
7.50
7.47
7.45
7.40
7.37
7.35
7.26
6.81
6.77
6.75
6.13
6.10
6.07
3.95
3.42
3.39
3.13
1.16
5.50
0.12
1.02
0.12
1.00
0.39
2.99
2.94
0.40
f1 (ppm)

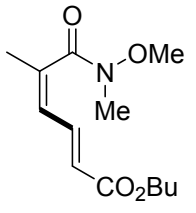

171.53
168.98
145.87
142.31
135.01
129.49
128.95
126.18
124.20
123.12
77.31
77.05
76.80
61.65
32.33
f1 (ppm)


O
H
OH
O

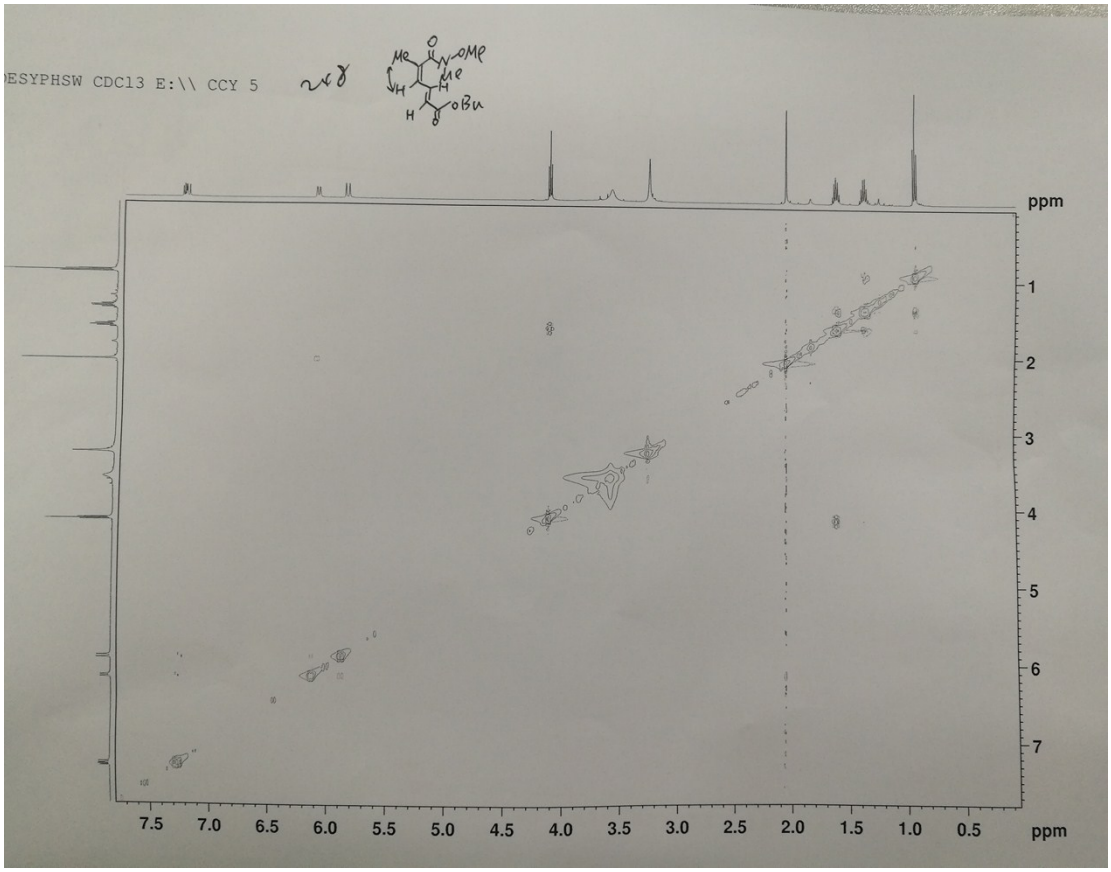
4r


10.41
8.31
8.29
8.28
8.26
7.35
7.19
7.09
7.06
6.21
6.18
1.00
1.01
5.26
1.05
1.00
f1 (ppm)


190.19
171.05
143.38
139.03
138.98
135.32
129.31
128.70
128.30
128.23
77.28
77.03
76.78
f1 (ppm)


O
OMe
N
Me
CO2Bu

(**3a**) (NOE)


ESYPHSW CDCl3 E:\\ CCY 5
ppm
1
2
3
4
5
6
7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm