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Supporting Information

For the article entitled

Acylsilane directed aromatic C-H alkenylations by ruthenium catalysis

Xiunan Lu,[a] Cong Shen,[a] Keke Meng,[a] Li Zhao,*[a,b] Tingyan Li,[a] Yalin Sun,[a] Jian Zhang,*[a] and Guofu Zhong*[a]

[a] *College of Materials, Chemistry and Chemical Engineering,* [b] *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China*

lizhao@hznu.edu.cn;
zhangjian@hznu.edu.cn;
zgf@hznu.edu.cn

Supporting Information

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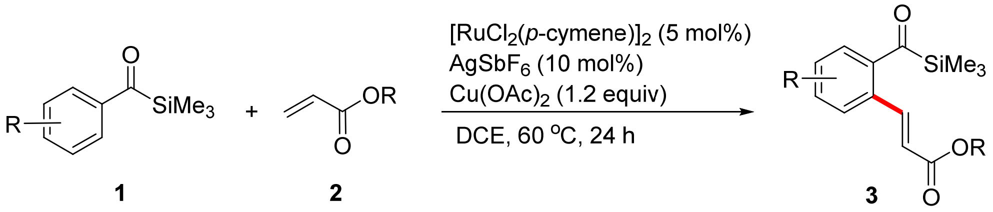
General methods

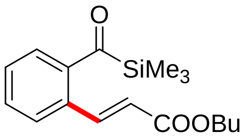
Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent), and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. 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}). $[Ru(p\text{-cymene})Cl_2]_2$, $AgSbF_6$ and $Cu(OAc)_2$ were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification. Aroylsilanes were prepared from aroyl chlorides by reported method.[7]

General Procedure for the Cross-Coupling between Aroylsilanes and Alkenes



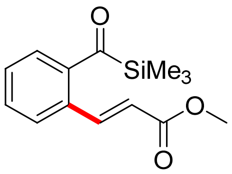
An screw-cap vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%, 0.01 mmol), $AgSbF_6$ (10 mol%, 0.02 mmol), $Cu(OAc)_2$ (1.2 equiv , 0.24 mmol) and DCE (1 mL). Then, aroylsilane **1** (1.0 equiv, 0.2 mmol) and alkene **2** (2.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 ℃ with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures).

Characterization Data



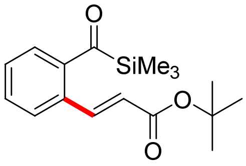
Butyl (E)-3-(2-((trimethylsilyl)carbonyl)phenyl) acrylate (3aa)

Following the general procedure, **3aa** was obtained as a yellow liquid, yield = 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.31 (s, 9H), 0.96 (t, J = 7.4 Hz, 3H), 1.46 - 1.40 (m, 2H), 1.72 - 1.65 (m, 2H), 4.21 (t, J = 6.7 Hz, 2H), 6.27 (d, J = 15.8 Hz, 1H), 7.48 - 7.46 (m, 2H), 7.54 - 7.52 (m, 1H), 7.61 - 7.58 (m, 1H), 7.91 (d, J = 15.9 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.83, 21.26, 32.80, 66.52, 123.05, 130.14, 130.55, 131.51, 133.03, 134.36, 145.41, 145.43, 168.65, 244.29.



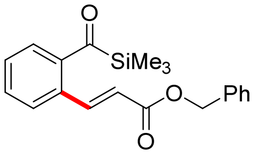
Methyl (E)-3-(2-((trimethylsilyl)carbonyl) phenyl) acrylate (3ab)

Following the general procedure, **3ab** was obtained as a yellow liquid, yield = 74%. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.25 (s, 9H), 3.73 (s, 3H), 6.20 (d, J = 15.9 Hz, 1H), 7.43 - 7.38 (m, 2H), 7.53 - 7.49 (m, 2H), 7.87 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 53.77, 122.51, 130.17, 130.85, 131.46, 133.09, 134.35, 145.06, 145.77, 168.98, 243.89.



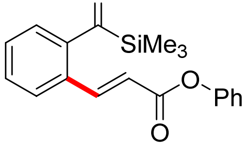
tert-Butyl (E)-3-(2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ac)

Following the general procedure, **3ac** was obtained as a yellow liquid, yield = 56%. ^{1}H NMR (400 Hz, CDCl$_3$): δ = 0.22 (s, 9H), 1.45 (s, 9H), 6.12 (d, *J* = 15.8 Hz,1H), 7.42 - 7.35 (m, 3H), 7.53 - 7.49 (m, 1H), 7.72 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 30.27, 82.67, 125.22, 130.11, 130.16, 131.31, 132.85, 134.53, 144.19, 145.75, 167.85, 244.73. HRMS (ESI): m/z for $C_{17}H_{24}O_3Si$ $[M+H]^+$: 327.1382, found: 327.1387. FTIR (KBr, cm^{-1}): 3132.39, 2977.77, 2931.78, 1712.50, 1633.83, 1451.40, 1368.72, 1150.09, 842.95.



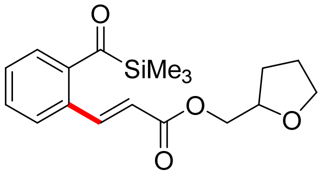
Benzyl (E)-3-(2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ad)

Following the general procedure, **3ad** was obtained as a yellow liquid, yield = 71%. ^{1}H NMR (400 Hz, CDCl$_3$): δ = 0.23 (s, 9H), 5.17 (s, 2H), 6.24 (d, *J* = 15.8 Hz, 1H), 7.41 - 7.25 (m, 7H), 7.52 - 7.46 (m, 2H), 7.90 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 68.38, 122.53, 130.15, 130.24, 130.27, 130.60, 130.67, 131.56, 133.05, 134.28, 138.11, 145.36, 146.12, 168.34, 244.06.



phenyl (E)-3-(2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ae)

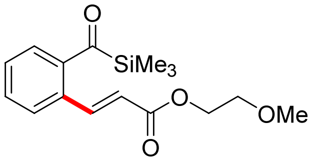
Following the general procedure, **3ad** was obtained as a yellow liquid, yield = 71%. ^{1}H NMR (400 Hz, CDCl$_3$): δ = 0.25 (s, 9H), 6.39 (d, *J* = 12.0 Hz, 1H), 7.11-7.09 (m, 2H), 7.17 - 7.14 (m, 1H), 7.33 - 7.30 (m, 2H), 7.44-7.41 (m, 2H), 7.59-7.52 (m, 2H), 8.05 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 121.91, 123.65, 127.74, 130.29, 130.92, 131.38, 131.78, 133.16, 134.12, 145.21, 147.52, 152.79, 166.90, 243.78.



(3af)

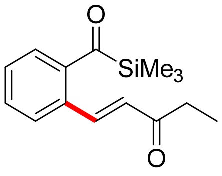
(E)-(2-(3-((tetrahydrofuran-2-yl)methoxy)prop-1-en-1-yl)phenyl)(trimethylsilyl) methanone

Following the general procedure, **3af** was obtained as a yellow liquid, yield = 90%. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.24 (s, 9H), 1.65 - 1.57 (m ,1H), 1.99 - 1.83 (m, 3H), 3.77 - 3.71(m, 1H), 3.88 - 3.82 (m, 1H), 4.14 - 4.05 (m, 2H), 4.22 (dd, *J* = 10.8 Hz, *J* = 3.1 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 7.42 - 7.38 (m, 2H), 7.53 - 7.47 (m, 2H), 7.90 - 7.86 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 27.75, 30.01, 68.62, 70.53, 78.57, 122.40, 130.13, 130.75, 131.47, 133.07, 134.28, 145.21, 146.02, 168.49, 243.89.



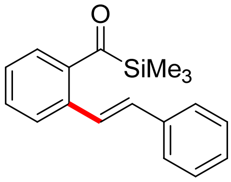
2-Methoxyethyl (E)-3-(2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ag)

Following the general procedure, **3ag** was obtained as a yellow liquid, yield = 86%. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.24 (s, 9H), 3.34 (s, 3H), 3.59 (m, 2H), 4.30-4.27 (m, 2H), 6.26 (d, *J* = 15.8 Hz, 1H), 7.42-7.39 (m, 2H), 7.53-7.47 (m, 2H), 7.87 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 61.09, 65.69, 72.58, 122.45, 130.13, 130.67, 131.54, 133.06, 134.29, 145.37, 146.04, 168.51, 244.05. HRMS (ESI): m/z for $C_{16}H_{22}O_4Si$ $[M+H]^+$: 307.136, found: 307.136. FTIR (KBr, cm^{-1}): 3132.65, 2957.54, 1634.10, 1400.75, 1174.27, 1273.20.



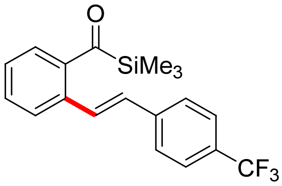
(E)-1-(2-((trimethylsilyl)carbonyl)phenyl) pent-1-en-3-one (3ah)

Following the general procedure, **3ah** was obtained as a yellow liquid, yield = 41%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.33 (s, 9H), 1.17 (t, *J* = 7.3 Hz, 3H), 2.73 (q, *J* = 7.3 Hz, 2H), 6.525 (d, *J* = 16.2 Hz, 1H), 7.49 (d, *J* = 20.2 Hz, 2H), 7.63 (m, 2H), 7.88 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 10.06, 35.19, 130.10, 131.05, 131.28, 131.33, 133.14, 134.69, 143.44, 144.53, 203.06, 243.64. HRMS (ESI): m/z for $C_{15}H_{20}O_2Si$ $[M+H]^+$: 261.1305, found: 261.1302. FTIR (KBr, cm^{-1}): 3132.68, 2969.94, 1714.17, 1400.61, 1668.55, 844.16.



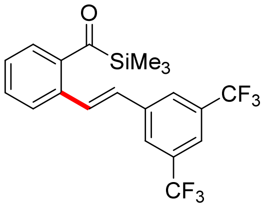
(E)-(2-styrylphenyl)(trimethylsilyl) methanone (3ai)

Following the general procedure, **3ai** was obtained as a yellow liquid, yield = 61%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.18 (s, 9H), 6.80 (d, *J* = 16.2 Hz, 1H), 7.175 (t, *J* = 7.0 Hz, 1H), 7.27 (m, 1H), 7.38 (m, 5H), 7.57 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 128.80, 129.02, 129.24, 129.28, 129.93, 130.16, 130.70, 132.67, 134.54, 137.19, 139.15, 144.40, 245.52. HRMS (ESI): m/z for $C_{18}H_{20}OSi$ $[M+H]^+$: 281.1351, found: 281.1356. FTIR (KBr, cm^{-1}): 3125.59, 1607.18, 1400.59, 1249.26, 1196.31, 963.73, 841.55, 759.55, 691.30.



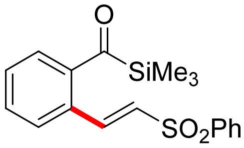
(E)-(2-(4-(trifluoromethyl)styryl)phenyl)(trimethylsilyl) methanone (3aj)

Following the general procedure, **3aj** was obtained as a yellow solid, m.p.: 62.5 °C, yield = 72%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.22 (s, 9H), 6.84 (d, *J* = 16.2 Hz, 1H), 7.35 - 7.32 (m, 1H), 7.42 - 7.38 (m, 1H), 7.53 - 7.46 (m, 6H), 7.60 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): 0.21, 126.13 (q, $J_{C\text{-}F}$ = 270.1 Hz), 127.55 (q, $J_{C\text{-}F}$ = 3.75 Hz), 128.79, 129.40, 129.69, 130.93, 131.34 (q, $J_{C\text{-}F}$ = 32.25 Hz), 131.77, 132.31, 132.90, 136.48, 142.62, 143.89, 244.76. ^{19}F NMR (471 MHz, $CDCl_3$): δ = -62.42. HRMS (ESI): m/z for $C_{19}H_{19}F_3OSi$ $[M+H]^+$: 349.1231, found: 349.123. FTIR (KBr, cm^{-1}): 3132.99, 3024.30, 2354.21, 1614.13, 1423.83, 1165.14, 1122.85, 842.59, 744.86.



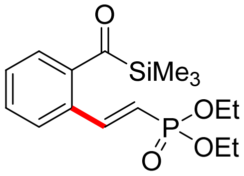
2-Methoxyethyl (E)-3-(2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ak)

Following the general procedure, **3ak** was obtained as a yellow solid, m.p.: 63.1 °C, yield = 71%. ^{1}H NMR (500 Hz, CDCl$_3$): δ = 0.25 (s, 9H), 6.85 (d, *J* = 16.2 Hz, 1H), 7.43 - 7.36 (m, 2H), 7.58 - 7.55 (m, 3H), 7.67 (s, 1H), 7.81 (s, 2H). ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 122.83 (q, J_{C-F} = 15.0 Hz), 125.19 (q, J_{C-F} = 271.13 Hz), 128.30, 128.32, 129.56 (q, J_{C-F} = 47.00 Hz), 129.62, 130.03, 130.35, 131.54, 133.13, 133.52, 133.73, 133.99, 136.05, 141.29, 143.47, 243.96. ^{19}F NMR (471 MHz, CDCl$_3$): δ = -62.95, -63.25. HRMS (ESI): m/z for $C_{20}H_{18}F_6OSi$ [M+H]$^+$: 417.1103, found: 417.1104. FTIR (KBr, cm^{-1}): 3132.74,2351.40, 2323.36, 1614.58, 1478.37, 1176.75, 1133.79, 843.54, 683.18.



(E)-(2-(2-(phenylsulfonyl)vinyl)phenyl)(trimethylsilyl) methanone (3al)

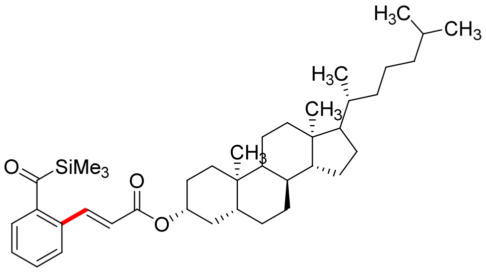
Following the general procedure, **3al** was obtained as a yellow liquid, yield = 75%. ^{1}H NMR (400 Hz, CDCl$_3$): δ = 0.26 (s, 9H), 6.60 (d, *J* = 15.3 Hz, 1H), 7.61 - 7.41 (m, 7H), 7.89 (d, *J* = 15.3 Hz, 1H), 7.96 (dd. *J* = 8.2 Hz, *J* = 1.4 Hz, 2H). ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 129.71, 130.63, 131.10, 131.23, 131.50, 132.05, 132.35, 133.32, 135.28, 142.54, 144.63, 144.68, 242.59. HRMS (ESI): m/z for $C_{17}H_{24}O_3Si$ [M+H]$^+$: 345.098, found: 345.0975. FTIR (KBr, cm^{-1}): 3132.09, 3001.87, 1651.42, 1557.17, 1455.10, 1445.82, 1398.78, 1145.79, 840.19.



Diethyl(E)-(2-((trimethylsilyl)carbonyl)styryl) phosphonate (3am)

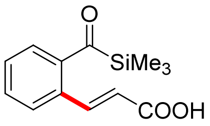
Following the general procedure, **3am** was obtained as a yellow solid, m.p.: 74.2 °C. yield = 54%.

^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.24 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 6H), 4.13 - 4.07 (m, 4H), 6.08 - 6.00 (m, 1H), 7.42 - 7.38 (m, 2H), 7.52 - 7.48 (m, 2H), 7.602 (dd, *J* = 22.4 Hz, *J* = 17.4 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 18.43 (d, $J_{C\text{-}P}$= 6.3 Hz), 64.06 (d, $J_{C\text{-}P}$= 5.0 Hz), 118.9 (d, $J_{C\text{-}P}$= 189.0 Hz), 130.02, 130.75, 131.31, 133.05, 135.00 (d, $J_{C\text{-}P}$ = 23.8 Hz), 144.80 (s), 149.25 (d, $J_{C\text{-}P}$ = 7.5 Hz), 243.87. HRMS (ESI): m/z for $C_{16}H_{25}O_4PSi$ $[M+H]^+$: 341.1326, found: 341.1332. FTIR (KBr, cm^{-1}): 3132.32, 1651.35, 1621.20, 1455.02, 1400.98, 1252.33, 1026.58.



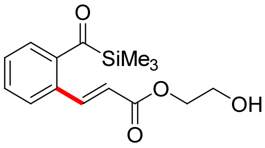
(3R,5R,8S,10R,13S,14R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl) hexadecahydro-1H-cyclopenta [a] phenanthren-3-yl (E)-3-(2-((trimethylsilyl)carbonyl)phenyl) acrylate (3an)

Following the general procedure, **3an** was obtained as a colourless solid, yield = 55%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.30 (s, 9H), 0.65 (s, 4H), 0.87 – 0.83 (m, 11H), 0.90 (d, *J* = 6.5 Hz, 4H), 1.99 – 0.96 (m, 37H), 6.24 (d, *J* = 15.8 Hz, 1H), 7.50 - 7.44 (m, 3H), 7.59 - 7.56 (m, 1H), 7.88 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 14.15, 14.33, 20.75, 23.29, 24.65, 24.90, 25.91, 26.29, 29.64, 30.09, 30.33, 30.70, 34.08, 36.16, 37.56, 37.88, 38.24, 38.73, 38.86, 41.59, 42.06, 44.66, 46.76, 56.31, 58.42, 76.07, 123.75, 130.06, 130.25, 131.48, 132.92, 134.45, 144.99, 145.68, 168.08, 244.67. HRMS (ESI): m/z for $C_{40}H_{62}O_3Si$ $[M+H]^+$: 619.4539, found: 619.4541. FTIR (KBr, cm^{-1}): 2935.18, 2866.61, 1713.04, 1633.78, 1614.43, 1383.98, 1175.37, 844.74.



(E)-2-(3-butoxy-3-oxoprop-1-en-1-yl) benzoic acid (3ao)

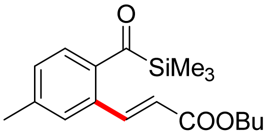
Compound **3ao** was obtained as a yellow solid, m.p.: 140 °C, yield = 24%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.33 (s, 9H), 6.30 (d, *J* = 15.0 Hz, 1H), 7.53-7-49 (m, 2H), 7.64-7.60 (m, 2H), 8.05 (d, *J* = 5.0 Hz, 1H), ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 121.86, 130.31, 130.95, 131.77, 133.13, 134.03, 145.16, 147.99, 173.61, 243.79. HRMS (ESI): m/z for $C_{16}H_{25}O_4PSi$ [M+H]$^+$: 249.0941, found: 249.0936. FTIR (KBr, cm^{-1}): 3673.66, 3667.69, 3646.24, 3441.47, 1682.46, 1660.43, 1633.87, 1384.30.



(3ap)

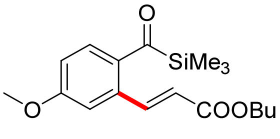
2-hydroxyethyl (E)-3-(2-((trimethylsilyl) carbonyl) phenyl) acrylate

Compound **3ap** was obtained as a yellow liquid, yield = 90%. ^{1}H NMR (500 Hz, CDCl$_3$): δ = 0.33 (s, 9H), 3.91-3.90 (q, 2H), 4.35 (t, *J* = 5.0 Hz, 2H), 6.31 (d, *J* = 5.0 Hz, 1H), 7.51-7.47 (m, 2H), 7.61 - 7.58 (m, 2H), 7.98 (d, *J* = 15.0 Hz, 1H), ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 63.22, 68.31, 122.20, 129.46, 130.20, 131.02, 131.53, 133.18, 144.87, 146.39, 168.82, 243.89. HRMS (ESI): m/z for $C_{16}H_{25}O_4PSi$ [M+H]$^+$: 293.1204, found: 293.1196. FTIR (KBr, cm^{-1}): 3646.09, 3453.06, 1714.29, 1651.45, 1633.74, 1614.89, 1384.25.



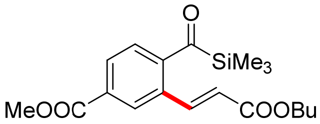
Butyl (E)-3-(5-methyl-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ba)

Following the general procedure, **3ba** was obtained as a yellow liquid, yield = 76%. ^{1}H NMR (400 Hz, CDCl$_3$): δ = 0.24 (s, 9H), 0.88 (t, *J* = 7.4 Hz, 3H), 1.38 - 1.33 (m, 2H), 1.64 - 1.57 (m, 2H), 2.33 (s, 3H), 4.13 (t, *J* = 6.7 Hz, 2H), 6.18 (d, *J* = 15.8 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.31 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 Hz, CDCl$_3$): δ = 0.21, 15.65, 21.09, 23.37, 32.65, 66.31, 122.60, 130.76, 131.33, 131.89, 134.64, 142.35, 143.49, 145.85, 168.61, 242.69.



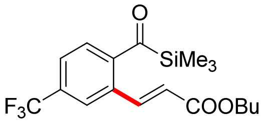
Butyl (E)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ca)

Following the general procedure, **3ca** was obtained as a yellow liquid, yield = 64%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.25 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H), 1.36 (q, J = 22.5 Hz, 2H), 1.625 (m, 2H), 3.81 (s, 3H), 4.13 (t, J = 6.7 Hz, 2H), 6.15 (d, J = 15.8 Hz, 1H), 6.91 (m, 2H), 7.62 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 15.8 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.39, 20.83, 32.39, 57.17, 66.09, 115.36, 115.83, 122.55, 134.29, 137.10, 137.30, 146.22, 163.30, 168.30, 239.37. HRMS (ESI): m/z for $C_{18}H_{26}O_4Si$ $[M+H]^+$: 335.1676, found: 335.1673. FTIR (KBr, cm^{-1}): 3132.64, 2354.21, 1712.15, 1399.57, 1266.36, 1224.3, 1171.03.



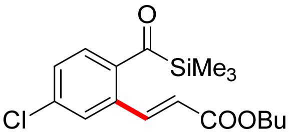
Methyl (E)-3-(3-butoxy-3-oxoprop-1-en-1-yl)-4-((trimethylsilyl)carbonyl) benzoate (3da)

Following the general procedure, **3da** was obtained as a yellow liquid, yield = 86%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.22 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H), 1.35 (dt, J = 14.4 Hz, J = 7.3 Hz, 2H), 1.64 - 1.58 (m, 2H), 3.88 (s, 3H), 4.14 (t, J = 6.7 Hz, 2H), 6.31 (d, J = 15.9 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 15.9 Hz, 1H). 8.03 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 8.20 (d, J = 1.2 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 16.10, 21.55, 33.08, 54.91, 66.99, 124.60, 129.83, 131.46, 132.76, 134.26, 134.47, 143.97, 149.58, 168.23, 168.62, 245.62.



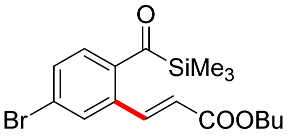
Butyl (E)-3-(5-(trifluoromethyl)-2-((trimethylsilyl)carbonylphenyl) acrylate (3ea)

Following the general procedure, **3ea** was obtained as a yellow liquid, yield = 64%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.23 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H), 1.39 - 1.33 (m, 2H), 1.64 - 1.58 (m, 2H), 4.14 (t, J = 6.7 Hz, 2H), 6.27 (d, J = 15.9 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.77 - 7.72 (m, 2H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 16.09, 21.55, 33.07, 67.11, 125.21, 125.77 (q, $J_{C\text{-}F}$ = 271.13 Hz), 127.21 (q, $J_{C\text{-}F}$ = 3.8 Hz), 128.49 (q, $J_{C\text{-}F}$ = 3.8 Hz), 130.33, 134.86 (q, $J_{C\text{-}F}$ = 32.75 Hz), 135.13, 143.57, 148.82, 168.40, 244.97. ^{19}F NMR (471 MHz, $CDCl_3$): δ = -63.06. HRMS (ESI): m/z for $C_{19}H_{19}F_3OSi$ $[M+H]^+$: 349.1244, found: 349.123. FTIR (KBr, cm^{-1}): 3132.65, 2963.07, 1715.50, 1633.77, 1400.88, 1333.92, 1170.74, 1132.45, 846.51.



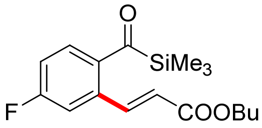
Butyl (E)-3-(5-chloro-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3fa)

Following the general procedure, **3fa** was obtained as a yellow liquid, yield = 84%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.23 (s, 9H), 0.88 (t, *J* = 7.4 Hz, 3H), 1.39 - 1.32 (m, 2H), 1.58 (m, 2H), 4.13 (t, *J* = 6.7 Hz, 2H), 6.20 (d, *J* = 15.8 Hz, 1H), 7.37 - 7.35 (m, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.81, 21.25, 32.78, 66.70, 124.32, 130.20, 131.35, 132.12, 136.42, 139.24, 143.33, 144.06, 168.29, 242.74. HRMS (ESI): m/z for $C_{17}H_{23}O_3SiCl$ $[M+H]^+$: 339.1175, found: 339.1178. FTIR (KBr, cm^{-1}): 3646.19, 3132.94, 1714.74, 1651.56, 1644.78, 1557.28, 1470.63, 1399.82.



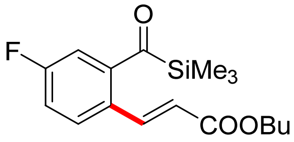
Butyl (E)-3-(5-bromo-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ga)

Following the general procedure, **3ga** was obtained as a yellow liquid, yield = 78%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.23 (s, 9H), 0.88 (t, *J* = 7.5 Hz, 3H), 1.39 - 1.32 (m, 2H), 1.63 - 1.58 (m, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 6.20 (d, *J* = 16.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.52 (dd, *J* = 2.0 Hz, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 1.5 Hz, 1H), 7.75 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.83, 21.27, 32.80, 66.72, 124.30, 127.63, 132.11, 133.13, 134.35, 136.48, 143.80, 143.93, 168.28, 243.00. HRMS (ESI): m/z for $C_{17}H_{23}BrO_3Si$ $[M+H]^+$: 383.0670, found: 383.0673. FTIR (KBr, cm^{-1}): 3132.40, 1714.65, 1633.80, 1538.48, 1505.05, 1455.21, 1400.12, 1174.28, 843.53.



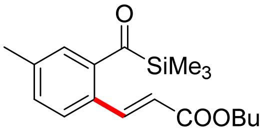
Butyl (E)-3-(5-fluoro-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ha)

Following the general procedure, **3ha** was obtained as a yellow liquid, yield = 77%. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.25 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H), 1.38 - 1.33 (m, 2H), 1.65 - 1.58 (m, 2H), 4.14 (t, *J* = 6.7 Hz, 2H), 6.19 (d, *J* = 15.8 Hz, 1H), 7.11 - 7.07 (m, 1H), 7.21 - 7.18 (m, 1H), 7.56 - 7.53 (m, 1H), 7.85 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.71, 21.14, 32.65, 66.59, 117.01 (d, $J_{C\text{-}F}$ = 22.5 Hz), 118.15 (d, $J_{C\text{-}F}$ = 21.3 Hz), 123.97, 133.52 (d, $J_{C\text{-}F}$ = 8.8 Hz), 137.65 (d, $J_{C\text{-}F}$ = 8.8 Hz), 141.21 (d, $J_{C\text{-}F}$ = 3.8 Hz), 144.39 (d, $J_{C\text{-}F}$ = 1.3 Hz), 165.7 (d, $J_{C\text{-}F}$ = 251.25 Hz), 168.26, 241.74. ^{19}F NMR (471 MHz, $CDCl_3$): δ = -107.50 - -107.56 (m).



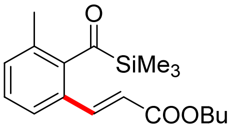
Butyl (E)-3-(4-fluoro-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ia)

Following the general procedure, **3ia** was obtained as a yellow liquid, yield = 82%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.26 (s, 9H), 0.96 (t, *J* = 7.4 Hz, 3H), 1.47 - 1.39 (m, 2H), 1.71 - 1.65 (m, 2H), 4.21 (t, *J* = 6.5 Hz, 2H). 6.36 (dd, *J* = 16.2 Hz, *J* = 0.9 Hz, 1H), 7.11 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.20 (d, *J* = 18.9 Hz, 1H), 7.44 - 7.40 (m, 1H), 7.69 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 16.08, 21.53, 33.06, 66.98, 120.22 (d, $J_{C\text{-}F}$ = 23.8 Hz), 122.25 (d, $J_{C\text{-}F}$ = 12.5 Hz), 124.84 (d, $J_{C\text{-}F}$ = 3.8 Hz), 128.0 (d, $J_{C\text{-}F}$ = 10.0 Hz), 133.12 (d, $J_{C\text{-}F}$ = 8.8 Hz), 138.17, 149.16, 163.47 (d, $J_{C\text{-}F}$ = 255.0 Hz), 168.76, 245.31. ^{19}F NMR (471 MHz, $CDCl_3$): δ = -111.06 (dd, *J* = 14.13 Hz, *J* = 4.71 Hz). HRMS (ESI): m/z for $C_{17}H_{23}FO_3Si$ $[M+H]^+$: 323.1475, found: 323.1473. FTIR (KBr, cm^{-1}): 3132.52, 1715.46, 1682.54, 1634.03, 1538.47, 1399.73, 1249.01, 1174.99, 845.04.



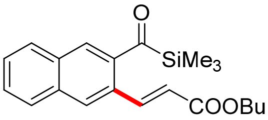
Butyl (E)-3-(4-methyl-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ja)

Following the general procedure, **3ja** was obtained as a yellow liquid, yield = 75%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.22 (s, 9H), 0.88 (t, *J* = 7.4 Hz, 3H), 1.39 - 1.31 (m, 2H), 1.63 - 1.57 (m, 2H), 2.34 (s, 3H), 4.12 (t, *J* = 6.7 Hz, 2H), 6.16 (d, *J* = 15.8 Hz, 1H), 7.20 - 7.16 (m, 2H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.85, 21.30, 23.50, 32.85, 66.51, 122.29, 129.94, 130.60, 131.47, 133.64, 142.01, 145.06, 146.10, 168.82, 245.20. HRMS (ESI): m/z for $C_{18}H_{26}O_3Si$ $[M+H]^+$: 319.1724, found: 319.1724. FTIR (KBr, cm^{-1}): 3564.64, 3132.80, 1714.66, 1644.84, 1614.83, 1470.68, 1400.04.



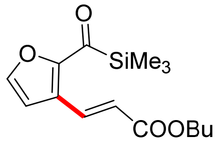
Butyl (E)-3-(3-methyl-2-((trimethylsilyl)carbonyl)phenyl) acrylate (3ka)

Following the general procedure, **3ka** was obtained as a yellow liquid, yield = 17%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.21 (s, 9H), 0.95 (t, *J* = 15Hz, 3H), 1.43 - 1.39 (m, 2H), 1.67 - 1.64 (m, 2H), 2.15 (s, 3H), 4.18 (t, *J* = 6.5 Hz, 2H), 6.27 (d, *J* = 15.8 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.28 - 7.25 (m, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 16.65, 21.96, 22.10, 33.63, 67.47, 123.95, 127.28, 131.61, 132.87, 135.31, 135.37, 144.34, 149.35, 169.29, 255.55. HRMS (ESI): m/z for $C_{18}H_{26}O_3Si$ $[M+H]^+$: 319.1722, found: 319.1724. FTIR (KBr, cm^{-1}): 3125.39, 2964.54, 2348.60, 1715.10, 1454.21, 1311.21, 1257.81, 1176.64, 842.19.



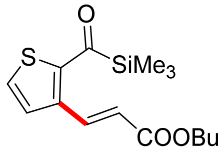
Butyl (E)-3-(3-((trimethylsilyl)carbonyl)naphthalen-2-yl) acrylate (3la)

Following the general procedure, **3la** was obtained as a yellow liquid, yield = 73%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.30 (s, 9H), 0.89 (t, *J* = 7.5 Hz, 3H), 1.41 - 1.34 (m, 2H), 1.65 - 1.60 (m, 2H), 4.15 (t, *J* = 6.5 Hz, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 7.54 - 7.48 (m, 2H), 7.85 - 7.79 (m, 2H), 7.96 (d, *J* = 23.1 Hz, 2H), 8.03 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.50, 20.95, 32.51, 66.18, 122.33, 129.41, 130.03, 130.16, 130.30, 130.47, 132.09, 132.26, 134.49, 135.67, 142.25, 145.97, 168.45, 242.45. HRMS (ESI): m/z for $C_{21}H_{26}O_3Si$ $[M+H]^+$: 355.1718, found: 355.1724. FTIR (KBr, cm^{-1}): 3125.14, 3057.94, 2958.99, 2867.29, 2357.01, 1712.31, 1605.87, 1398.66, 843.67.



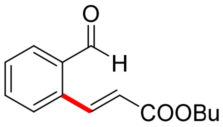
Butyl (E)-3-(2-((trimethylsilyl)carbonyl)furan-3-yl) acrylate (3ma)

Following the general procedure, **3ma** was obtained as a yellow liquid, yield = 51%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.26 (s, 9H), 0.89 (t, *J* = 7.5 Hz, 3H), 1.38 - 1.33 (m, *J* = 22.5 Hz, 2H), 1.64 - 1.58 (m, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 6.31 (d, *J* = 16.2 Hz, 1H), 6.67 (d, *J* = 1.5 Hz, 1H), 7.44 (d, *J* = 1.5 Hz, 1H), 8.12 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 16.75, 22.16, 33.73, 67.56, 112.97, 126.67, 126.74, 137.39, 148.28, 156.99, 169.45, 228.59. HRMS (ESI): m/z for $C_{15}H_{22}O_4Si$ $[M+H]^+$: 317.1169, found: 317.1168. FTIR (KBr, cm^{-1}): 3143.86, 2960.19, 2348.60, 1715.28, 1402.26, 1309.88, 1175.69, 845.23, 828.45.



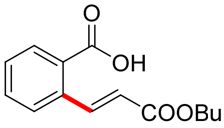
Butyl (E)-3-(2-((trimethylsilyl)carbonyl)thiophen-3-yl) acrylate (3na)

Following the general procedure, **3na** was obtained as a yellow liquid, yield = 46%. ^{1}HNMR (500 Hz, $CDCl_3$): δ = 0.31 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H), 1.36 (m, *J* = 22.5 Hz, 2H), 1.63 (m, *J* = 14.9 Hz, 2H), 4.14 (t, *J* = 6.8 Hz, 2H), 6.30 (d, *J* = 16.5 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.45 (d, *J* = 5.1 Hz, 1H), 8.26 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 0.21, 15.67, 21.08, 32.67, 66.49, 124.39, 128.95, 132.65, 139.47, 139.82, 146.47, 168.75, 229.59. HRMS (ESI): m/z for $C_{15}H_{22}O_4Si$ $[M+H]^+$: 295.1359, found: 295.136. FTIR (KBr, cm^{-1}): 3132.95, 2357.01, 1714.95, 1400.22, 1252.34, 1171.03, 1022.43, 848.60.



Butyl (E)-3-(2-formylphenyl) acrylate (4)

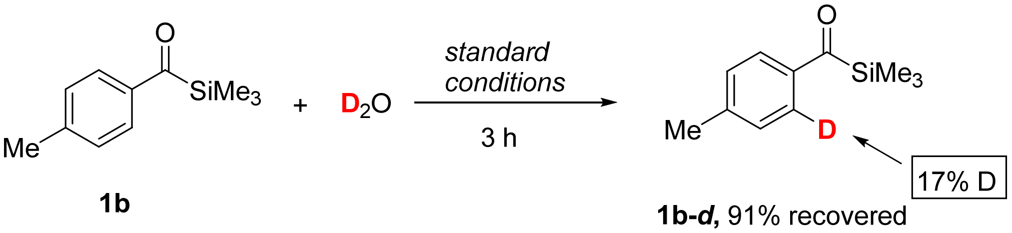
Compound **4** was obtained as a yellow liquid, yield = 65%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.90 (t, *J* =7.5 Hz, 3H), 1.42 - 1.34 (m, 2H), 1.67 - 1.61 (m, 2H), 4.17 (t, *J* = 6.5 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 7.58 - 7.47 (m, 3H), 7.82 - 7.80 (m, 1H), 8.45 (d, *J* = 16.0 Hz, 1H), 10.24 (s, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 12.73, 18.17, 29.70, 63.70, 122.26, 126.96, 128.85, 131.16, 132.81, 132.88, 135.67, 139.86, 165.29, 190.75.



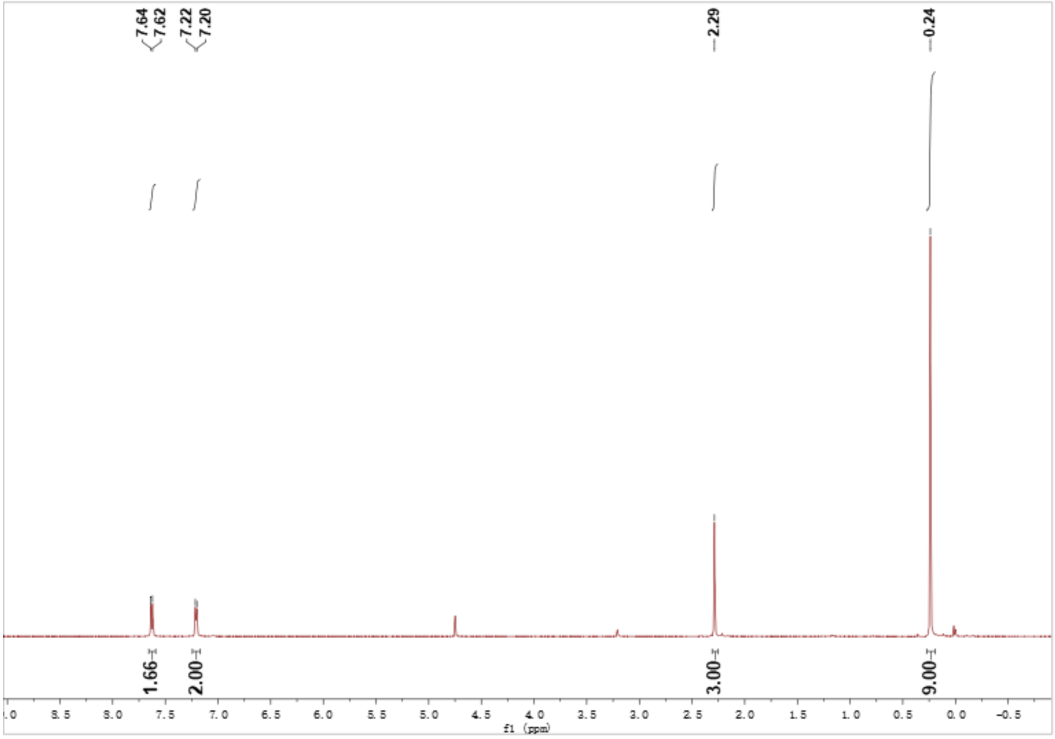
(E)-2-(3-butoxy-3-oxoprop-1-en-1-yl) benzoic acid (5)

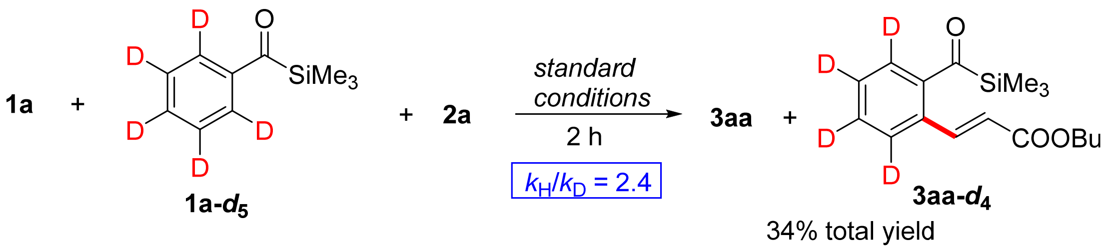
Compound **5** was obtained as a colourless solid, yield = 73%. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.90 (t, *J* = 7.4 Hz, 3H), 1.42 - 1.34 (m, 2H), 1.66 - 1.60 (m, 2H), 4.16 (t, *J* = 6.5 Hz, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 7.42 - 7.39 (m, 1H), 7.57 - 7.50 (m, 2H), 8.04 (d, *J* = 7.5 Hz, 1H), 8.49 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 13.76, 19.22, 30.72, 64.63, 121.35, 128.17, 128.68, 129.46, 131.63, 133.17, 137.21, 143.80, 166.84, 171.27.

Ru-Catalyzed H/D Exchange in 1b

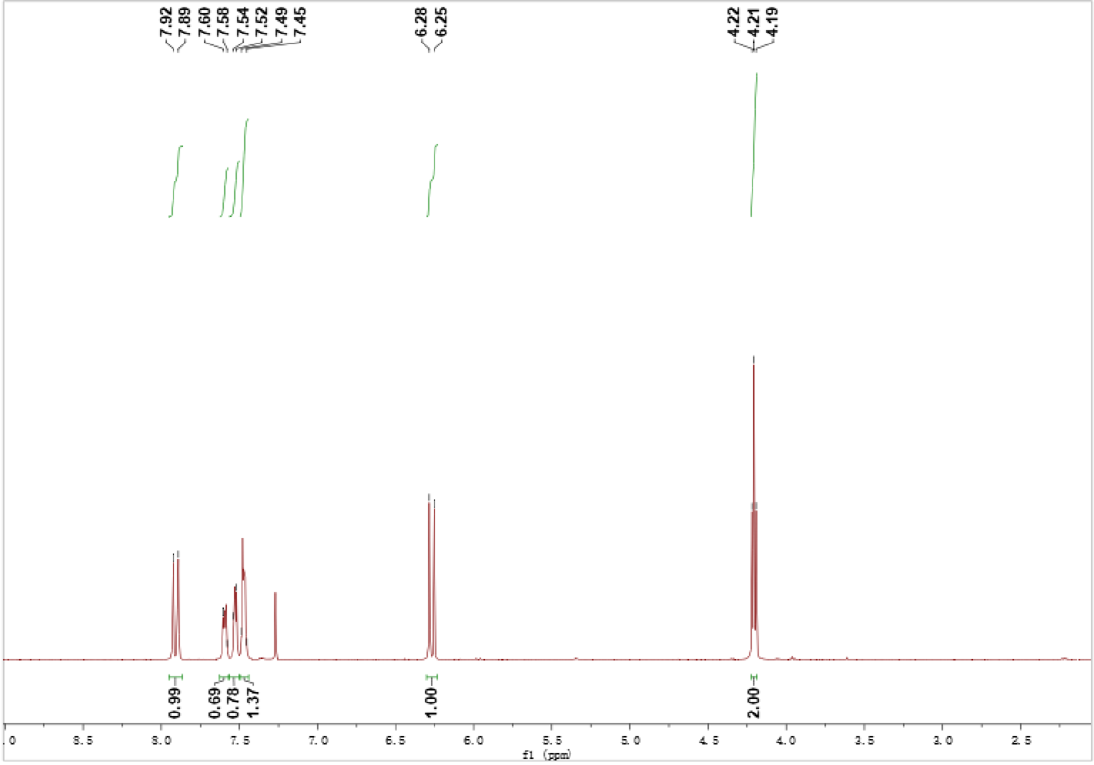


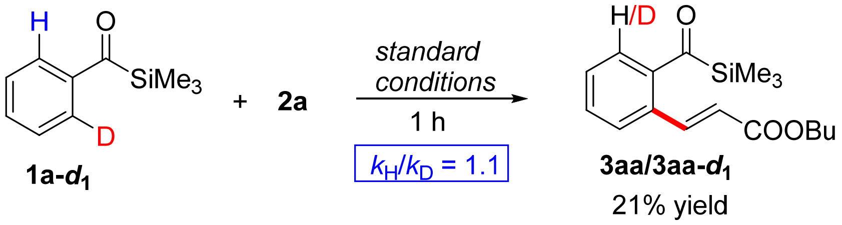
An screw-cap vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.01 mmol), $AgSbF_6$ (10 mol %, 0.02 mmol), Cu(OAc)$_2$ (1.2 equiv , 0.24 mmol) and DCE (1 mL). Then, **1b** (1.0 equiv , 0.2 mmol) and Deuterium oxide (10.0 equiv, 2.0 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 ℃ with stirring for 3 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures), providing deuterium labeled **1b** as a yellow oil (35 mg, 91%). The D-incorporation was determined by ^{1}H NMR.



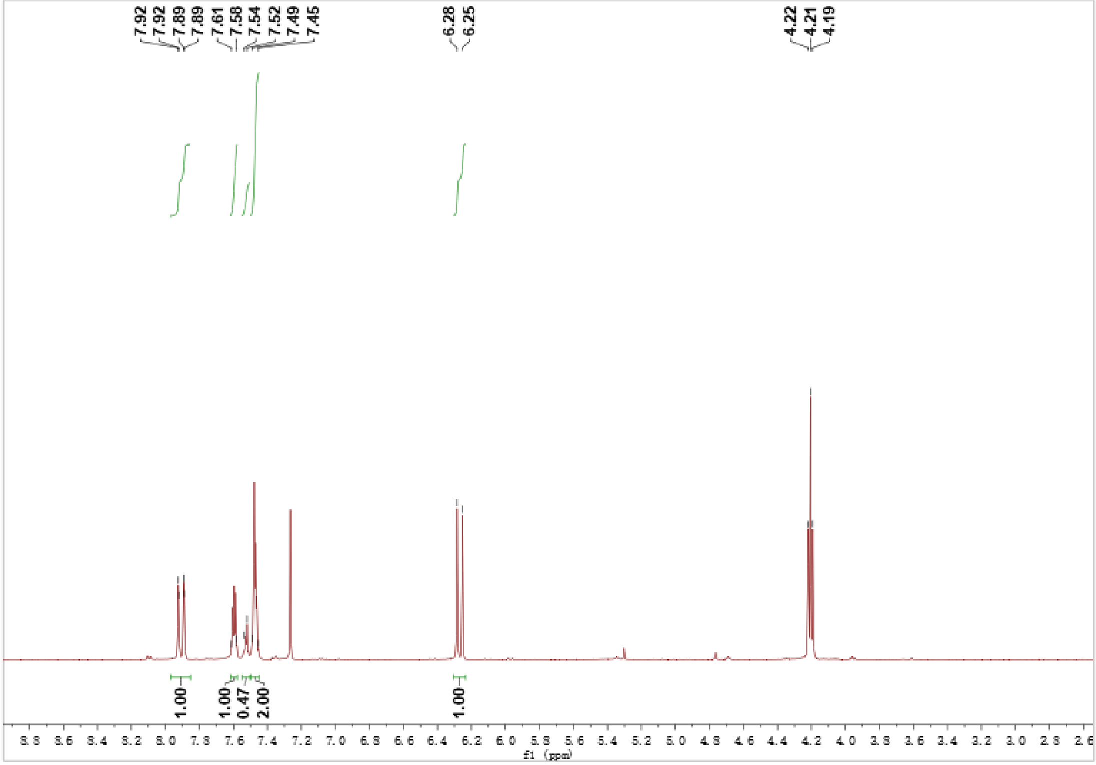


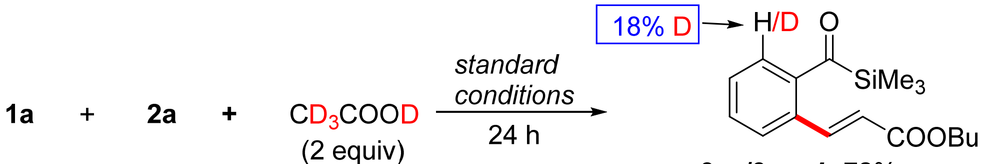
An screw-cap vial was charged with [Ru(p-cymene)Cl$_2$]$_2$ (10 mol %, 0.01 mmol), AgSbF$_6$ (20 mol %, 0.02 mmol), Cu(OAc)$_2$ (2.4 equiv, 0.24 mmol) and DCE (1 mL). Then, **1a** (1.0 equiv , 0.1 mmol), **D-5** (1,0 equiv, 0.1 mmol) and **2a** (2.0 equiv, 0.2 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 ℃ with stirring for 2 h. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography. **3aa/3aa-*d*$_4$** was obtained as yellow liquid (21 mg, 34% total yield). The KIE was determined by ^{1}H NMR.





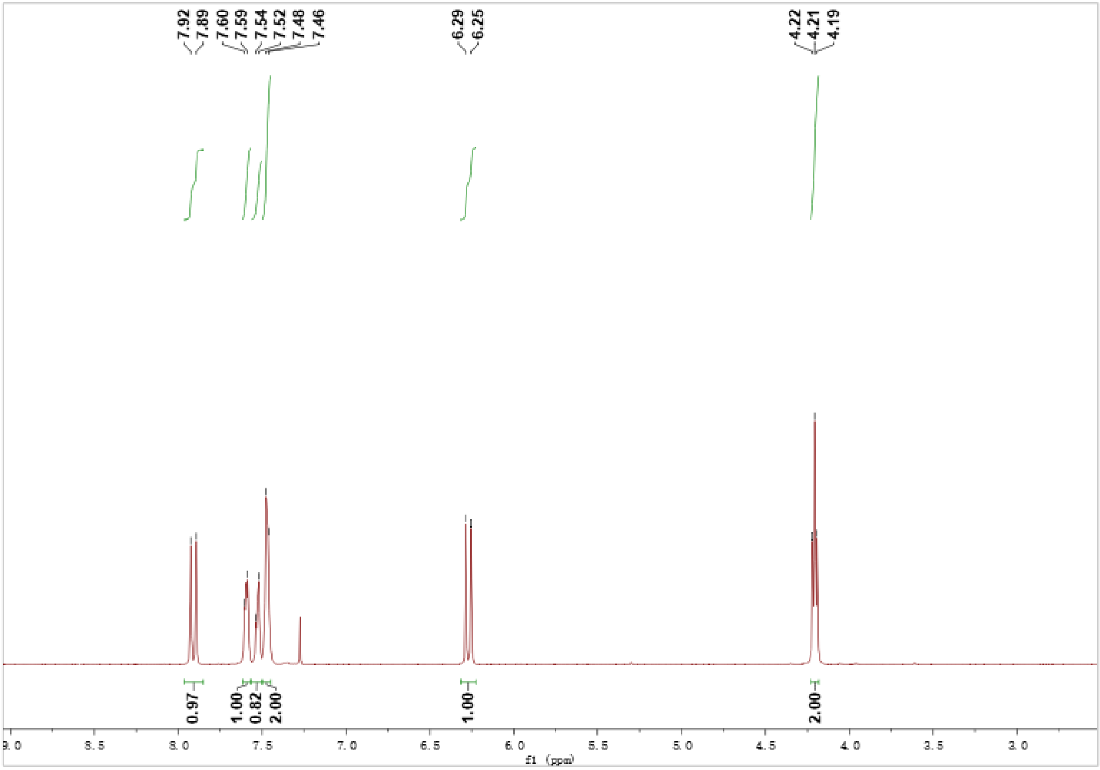
An screw-cap vial was charged with [Ru(p-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol), $AgSbF_6$ (10 mol %, 0.01 mmol), $Cu(OAc)_2$ (1.2 equiv, 0.12 mmol) and DCE (1 mL). Then, **1a-*d*$_1$**[5,7] (1.0 equiv, 0.1 mmol) and **2a** (1,0 equiv, 0.1 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 ℃ with stirring for 1 h. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography. Product **3aa/3aa-*d*$_1$** was obtained as a yellow oil (6.5 mg, 21%). The KIE was determined by ^{1}H NMR.



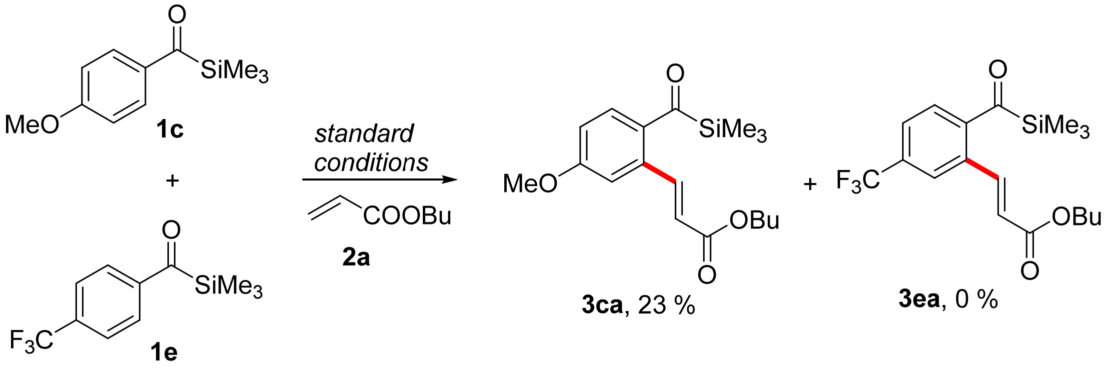


3aa/3aa-*d*$_1$ 72%

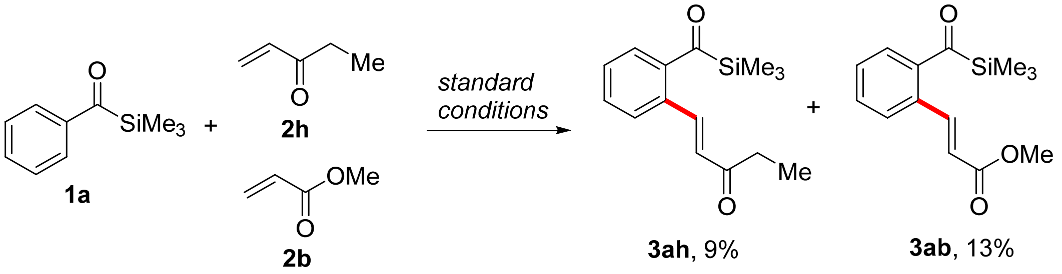
An screw-cap vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.01 mmol), $AgSbF_6$ (10 mol %, 0.02 mmol), Cu(OAc)$_2$ (1.2 equiv, 0.24 mmol) and DCE (1 mL), CD_3COOD (2.0 equiv, 0.4 mmol). Then, **1a** (1.0 equiv, 0.2 mmol) and **2a** (2,0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 ℃ with stirring for 24 h. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography. **3aa/3aa-*d*$_1$** was obtained as yellow oil (43.8 mg, 72%). The D-incorporation was determined by ^{1}H NMR.



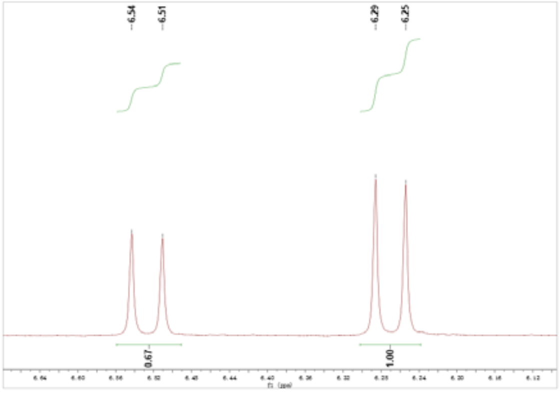
Competition Experiments



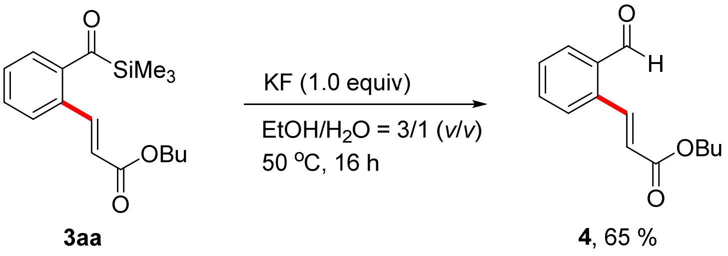
An screw-cap vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.01 mmol), $AgSbF_6$ (10 mol %, 0.02 mmol), $Cu(OAc)_2$ (1.2 equiv, 0.24 mmol) and DCE (1 mL). Then, **1c** (1.0 equiv, 0.2 mmol), **1e** (1.0 equiv, 0.2 mmol) and **2a** (4.0 equiv, 0.8 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 ℃ with stirring for 4 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). Only product **3ca** was obtained as yellow oil (15.4 mg, 23%) and no **3ea** was detected.



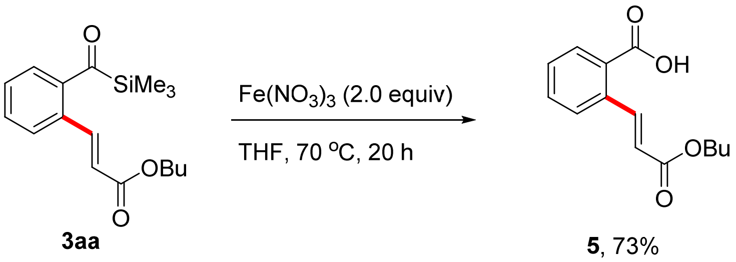
A screw-cap vial was charged with [Ru(p-cymene)Cl$_2$]$_2$ (5 mol %, 0.01 mmol), AgSbF$_6$ (10 mol %, 0.02 mmol), Cu(OAc)$_2$ (1.2 equiv , 0.24 mmol) and DCE (1 mL). Then, **1a** (1.0 equiv , 0.2 mmol), **2h** (2.0 equiv , 0.4 mmol) and **2b** (2.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 ℃ with stirring for 4 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The ratio of **3ah/3ab** was determined by ^{1}H NMR (11.5 mg **3ah/3ab** mixture).



Synthetic Application



A screw-cap vial was charged with KF (1.0 equiv, 0.1 mmol), EtOH/H_2O = 3/1 (0.75 mL/ 0.25 mL). Then **3aa** (1.0 equiv, 0.2 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 50 ℃ with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). Compound **4** was obtained as a yellow liquid (30.2 mg, yield = 65%).



A screw-cap vial was charged with $Fe(NO_3)_3$ (2.0 equiv, 0.4 mmol), THF (1 mL). Then **3aa** (1.0 equiv, 0.2 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 70 ℃ with stirring for 20 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). Compound **5** was obtained as a colourless solid (36.2 mg, yield = 73%).

References:

1. A. Hayashi, S. Suzuki, J. Tsuji, K. Yamamoto, *Organometallics,* **1987**, *6*, 974.

2. P. Becker, D. L. Priebbenow, R. Pirwerdjan, C. Bolm, *Angew. Chem. Int. Ed*. **2014**, *53*, 269.

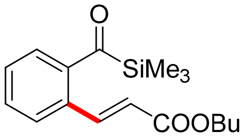
3. D. Schinzer, C. H. Heathcock, *Tetrahedron Letters,* **1981**, *22*, 1881.

4. L. Wang, X. Liu, M. He, *Chem. Asian J.* **2018**, *13*, 765-769.

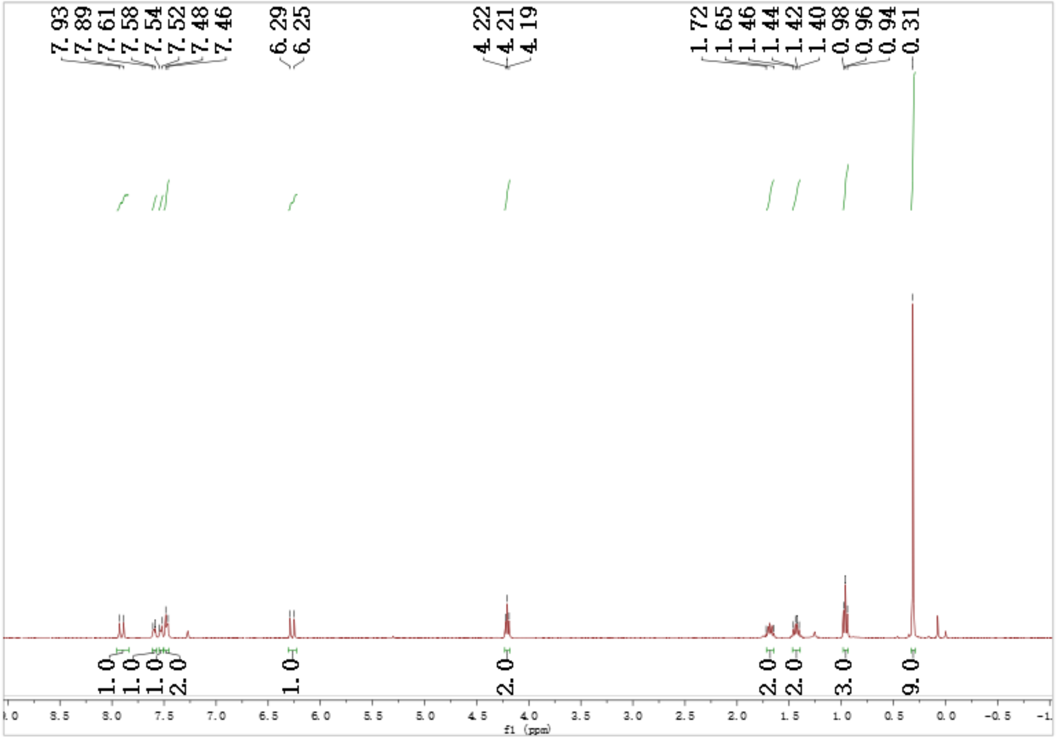
5. H. Sajiki, T. Kurita, H. Esaki, K. Hirota, *Org. Lett*. **2004**, *6*, 20.

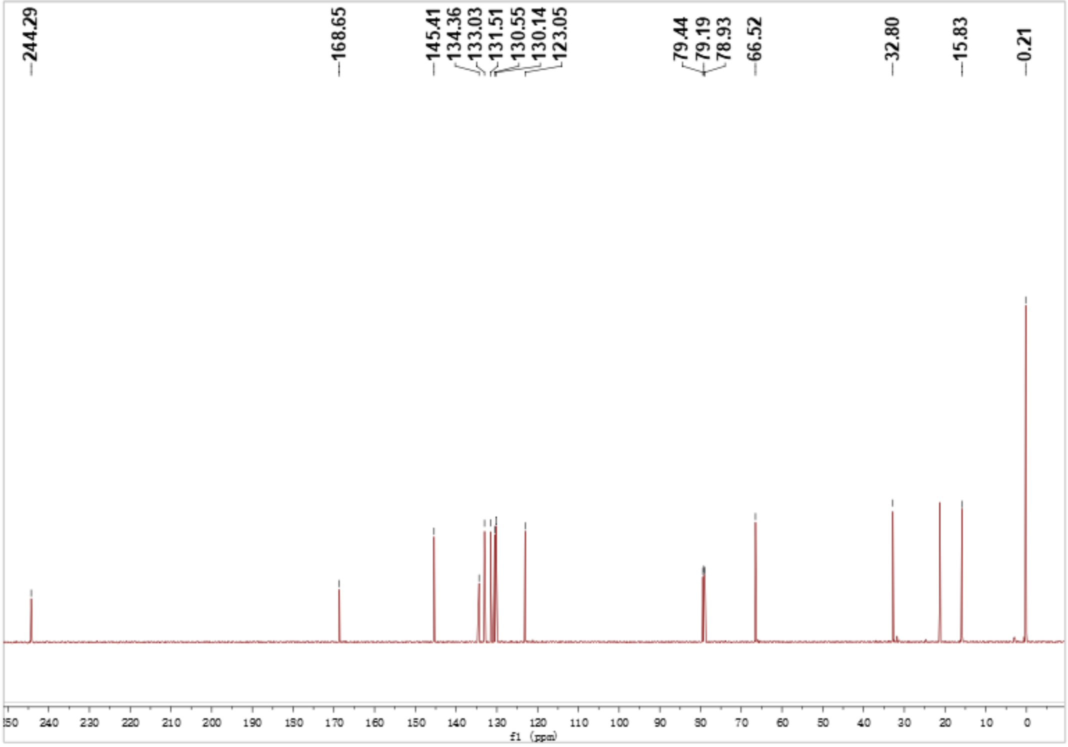
6. D. A. Tocher, R. O. Gould, T. A. Stephenson, *J. Chem. Soc. Dalton Trans.* **1983**, 1571-1581.

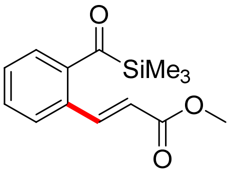
$^1H/^{13}C$ NMR Charts:



(3aa)



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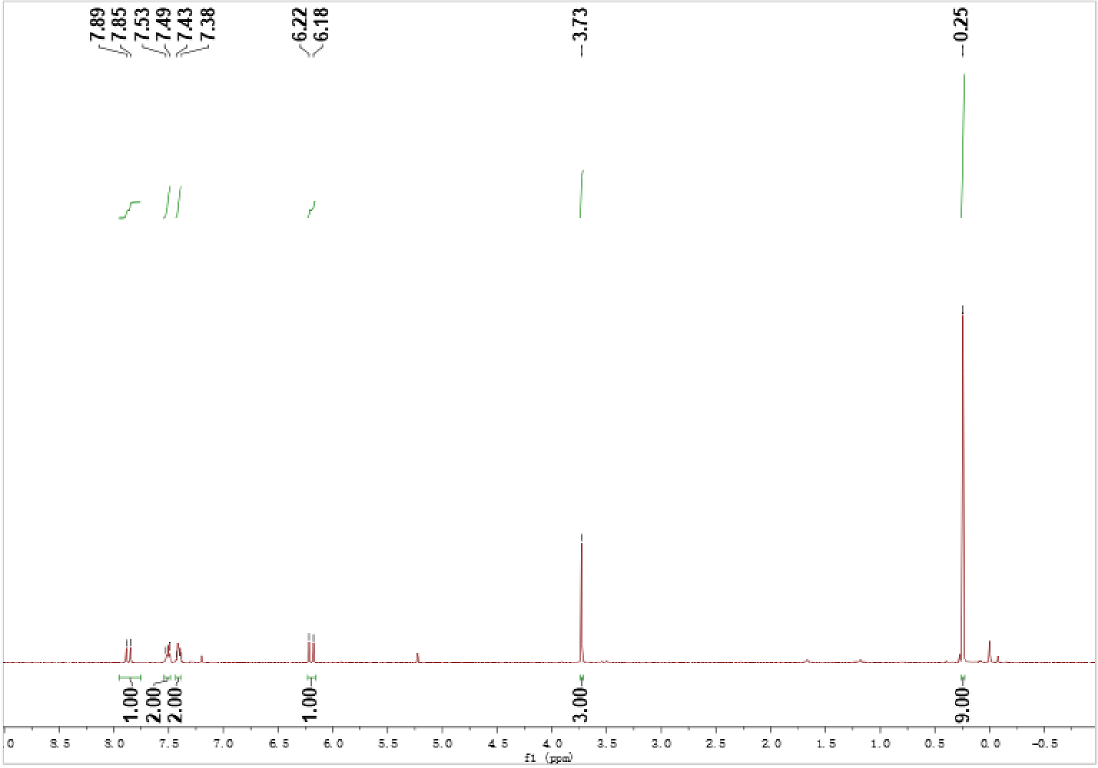
O
O

(3ab)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2.00
1.00
3.00
9.00
8.5
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7.5
7.0
6.5
6.0
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5.0
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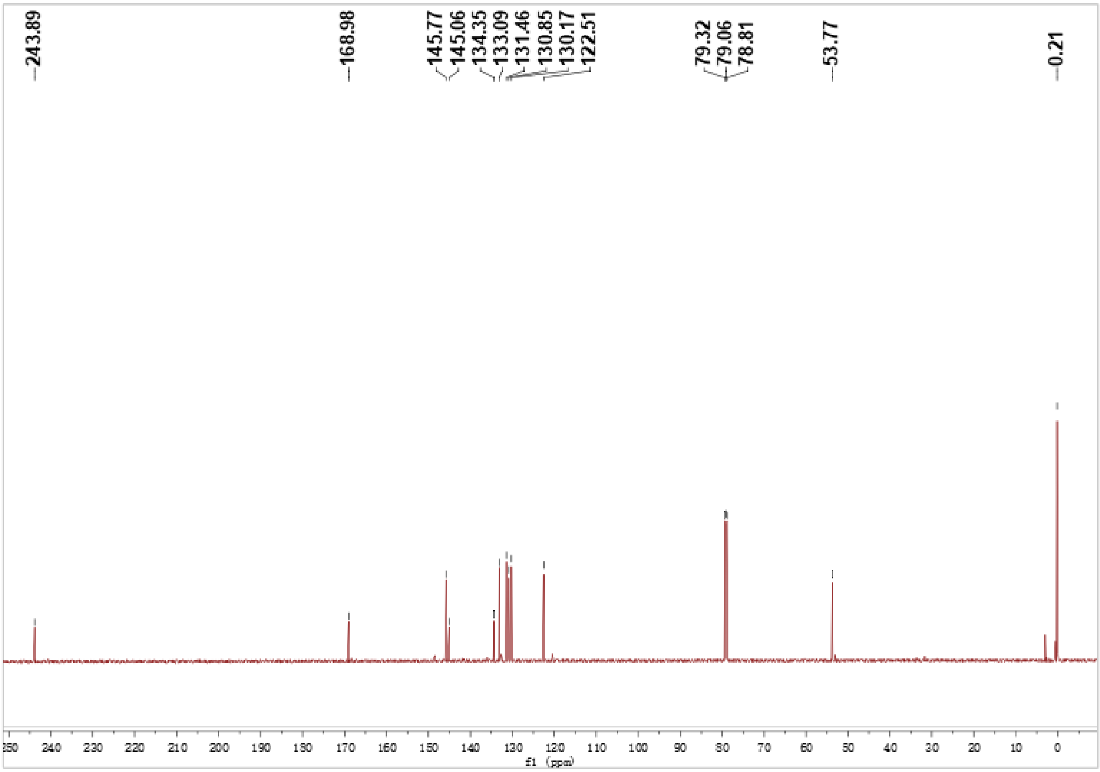
f1 (ppm)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78.81
53.77
0.21
240
230
220
210
200
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180
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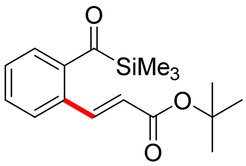
50
40
30
20
10
0
f1 (ppm)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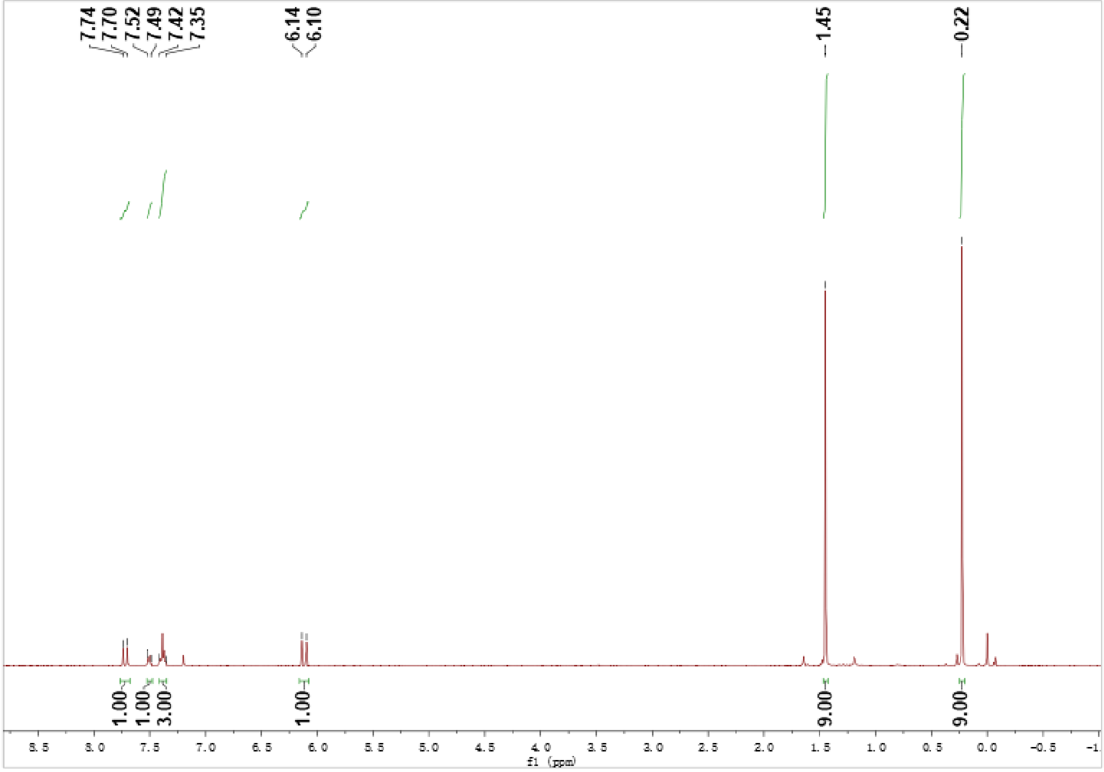
O
O

(3ac)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1.00
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9.00
8.5
8.0
7.5
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6.0
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5.0
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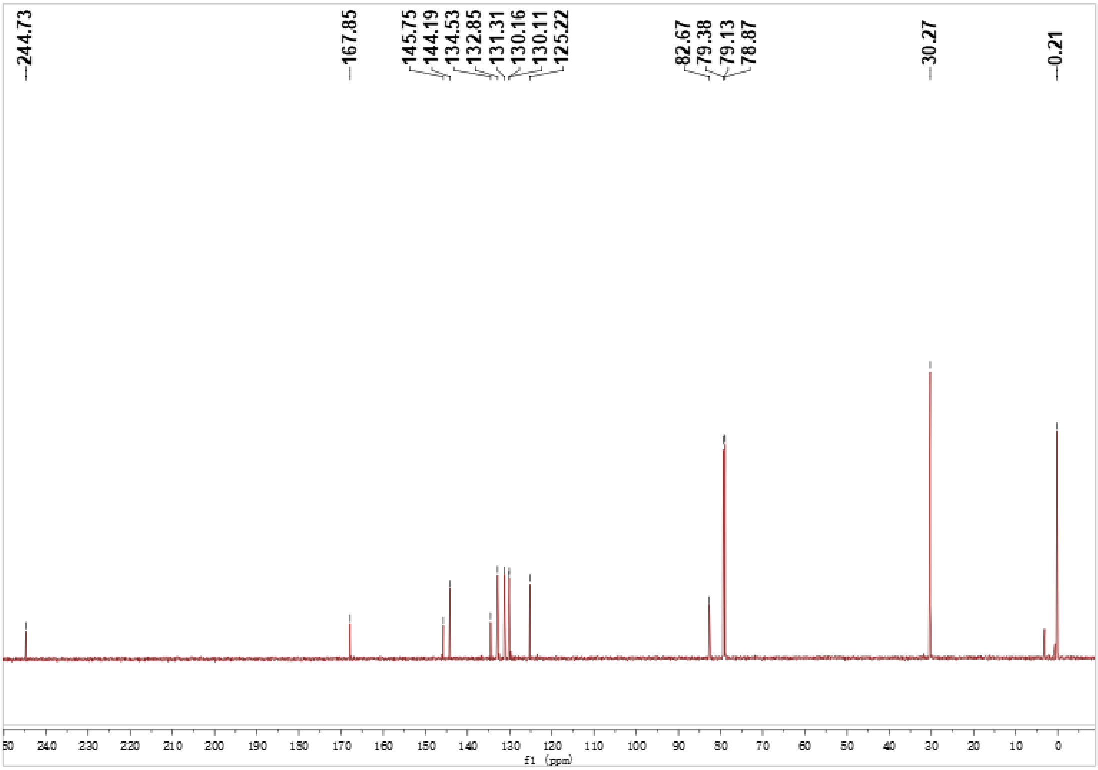
f1 (ppm)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78.87
30.27
0.21
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200
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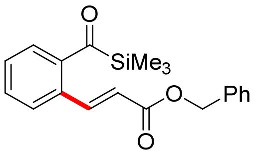
f1 (ppm)



O
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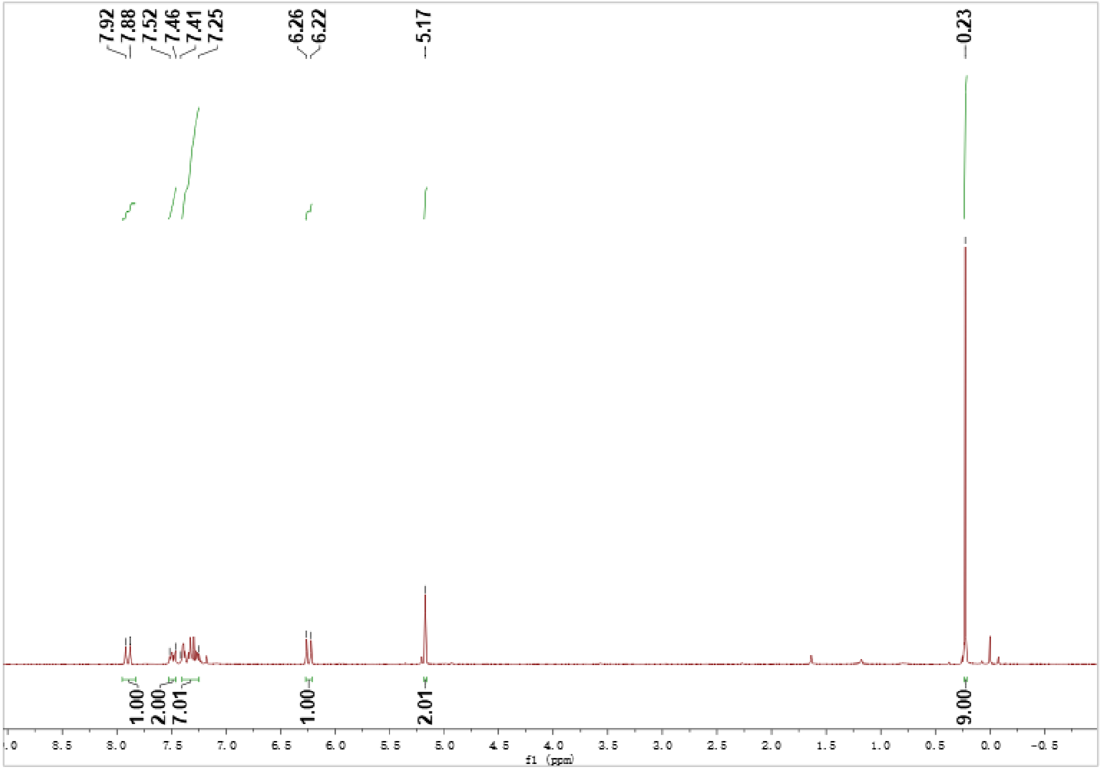
O
Ph
O

(3ad)



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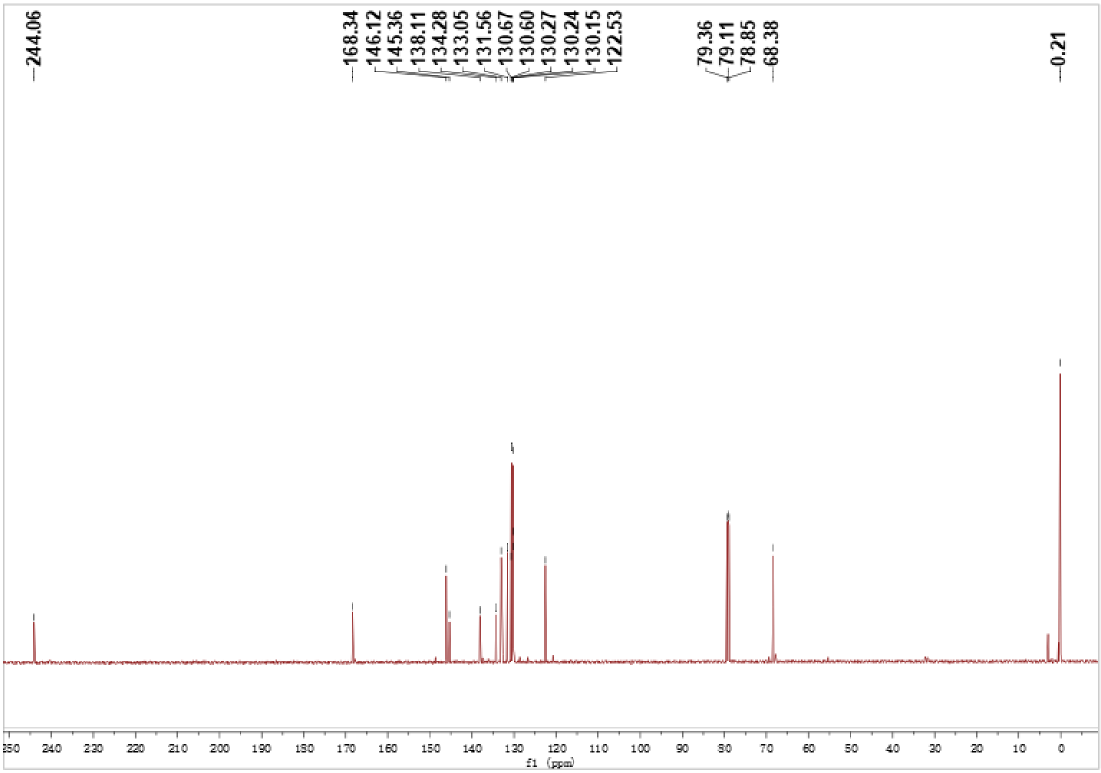

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68.38
0.21
f1 (ppm)
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220
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10
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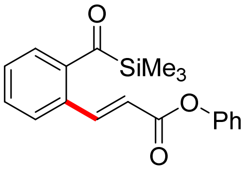
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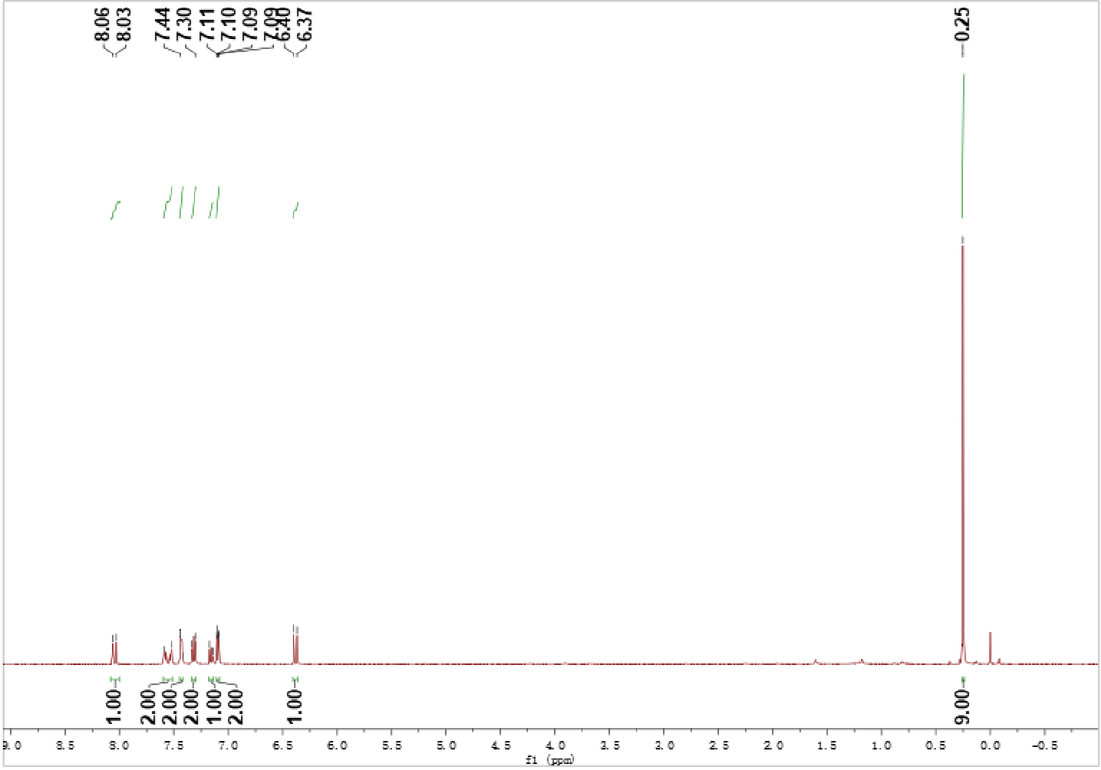
Ph
O

(3ae)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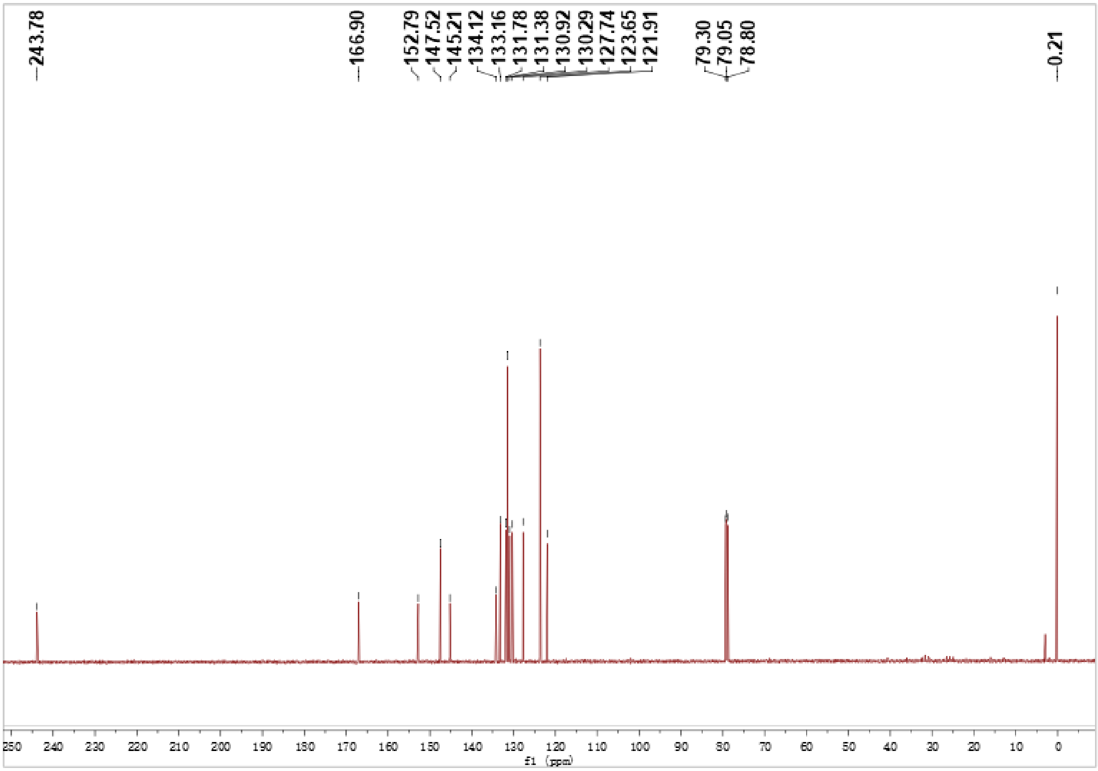
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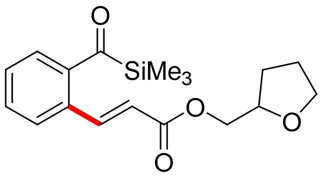
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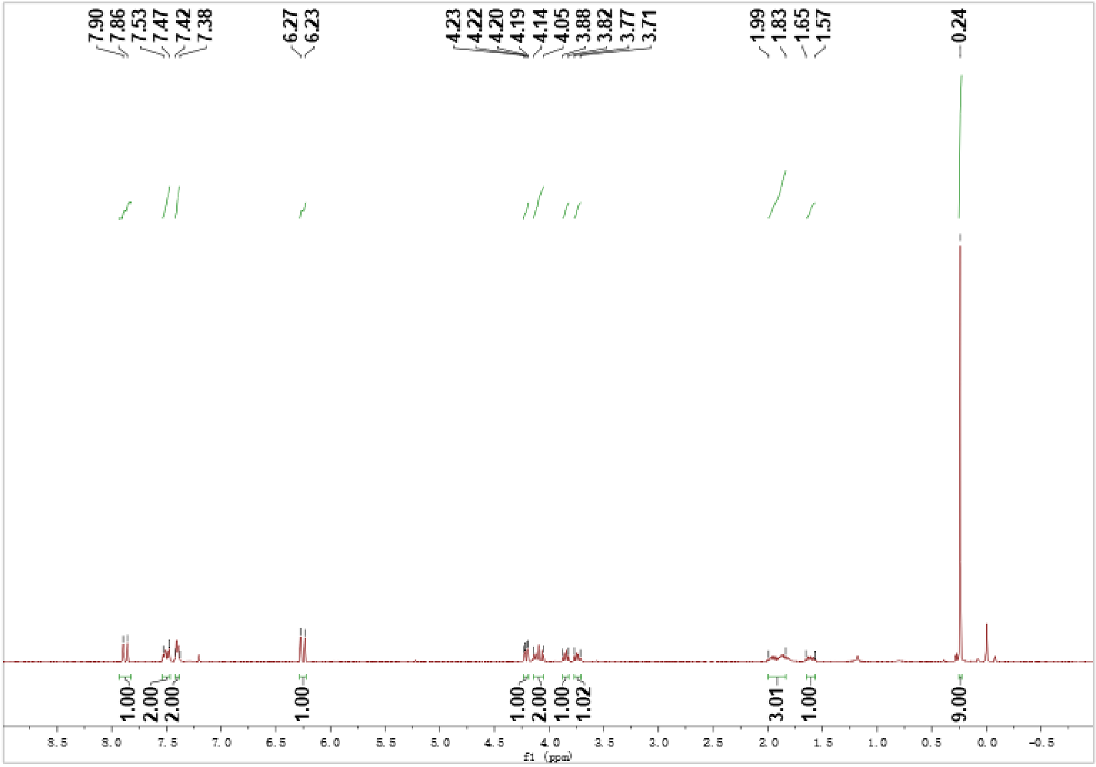
O
O
O

(3af)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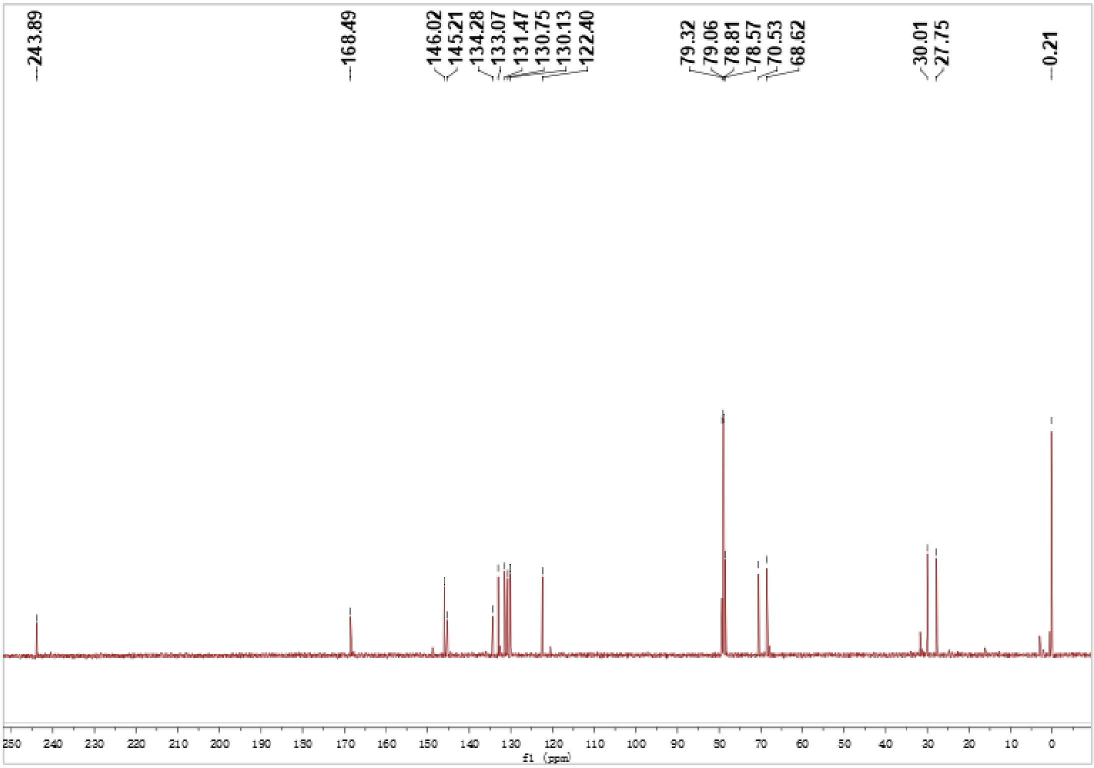
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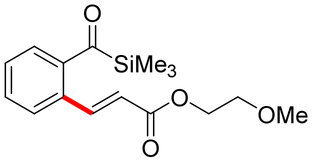
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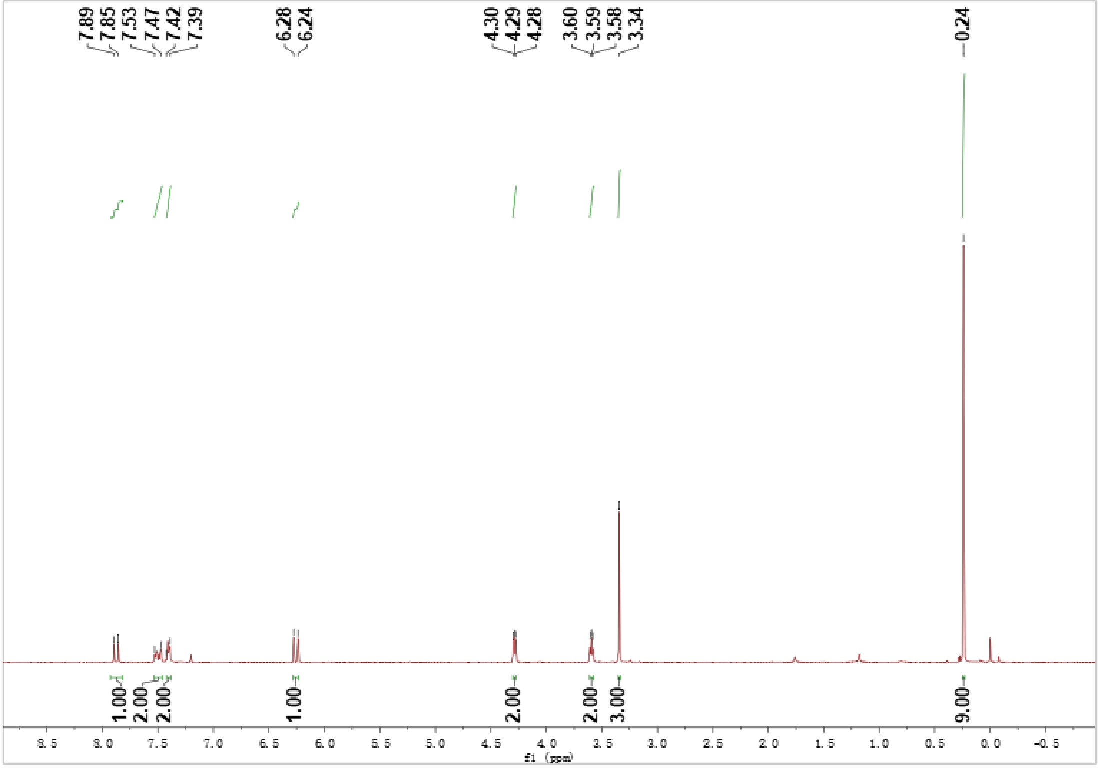
(3ag)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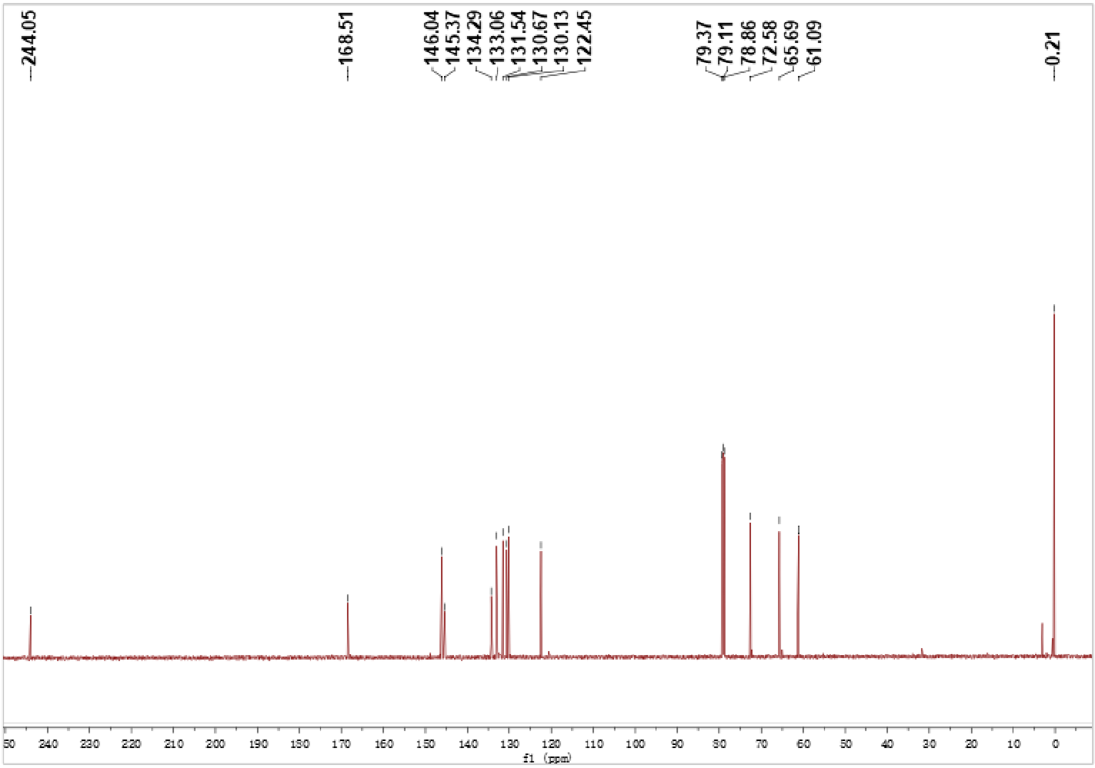
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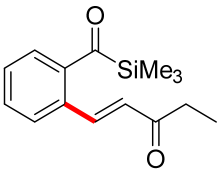
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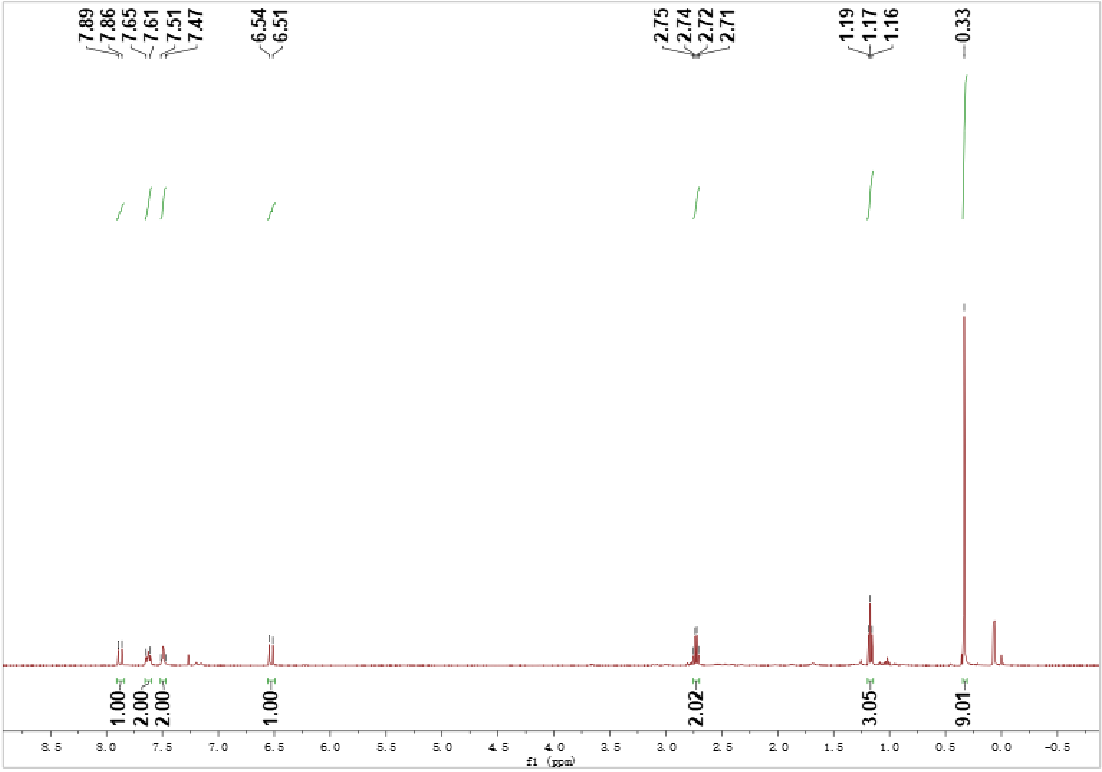
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5.5
5.0
4.5
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3.0
2.5
2.0
1.5
1.0
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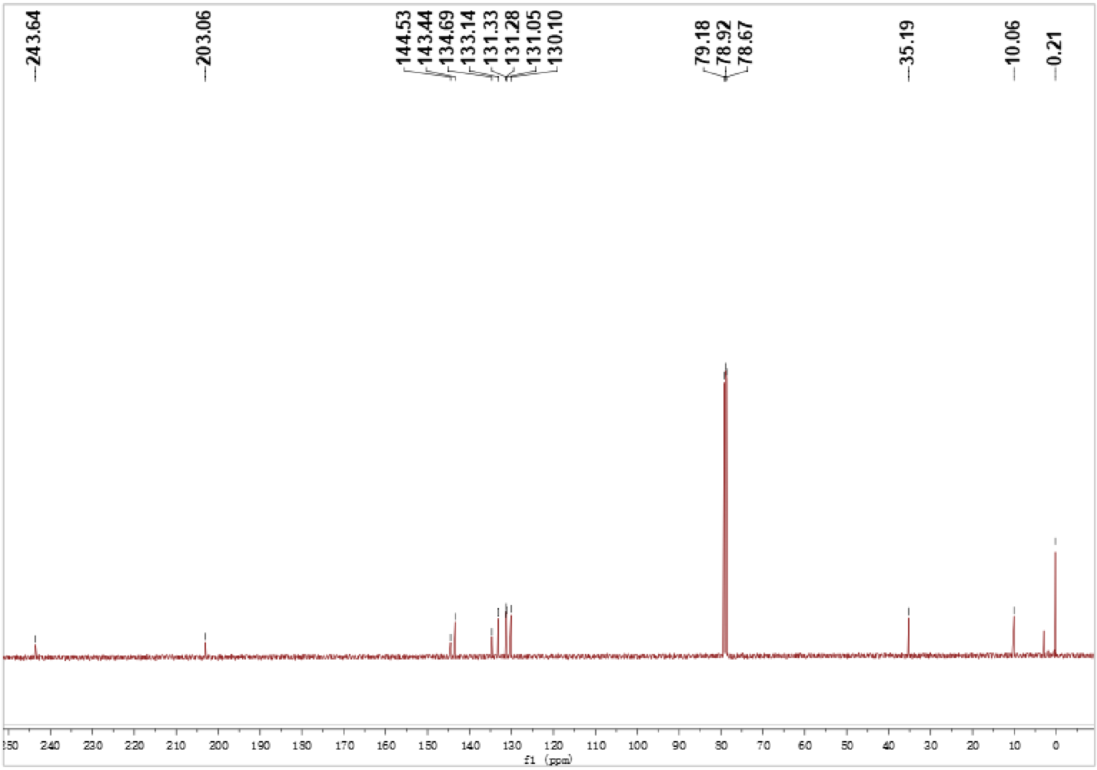
f1 (ppm)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144.53
143.44
134.69
133.14
131.33
131.28
131.05
130.10
79.18
78.92
78.67
35.19
10.06
0.21
240
230
220
210
200
190
180
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90
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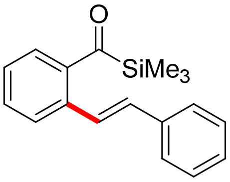
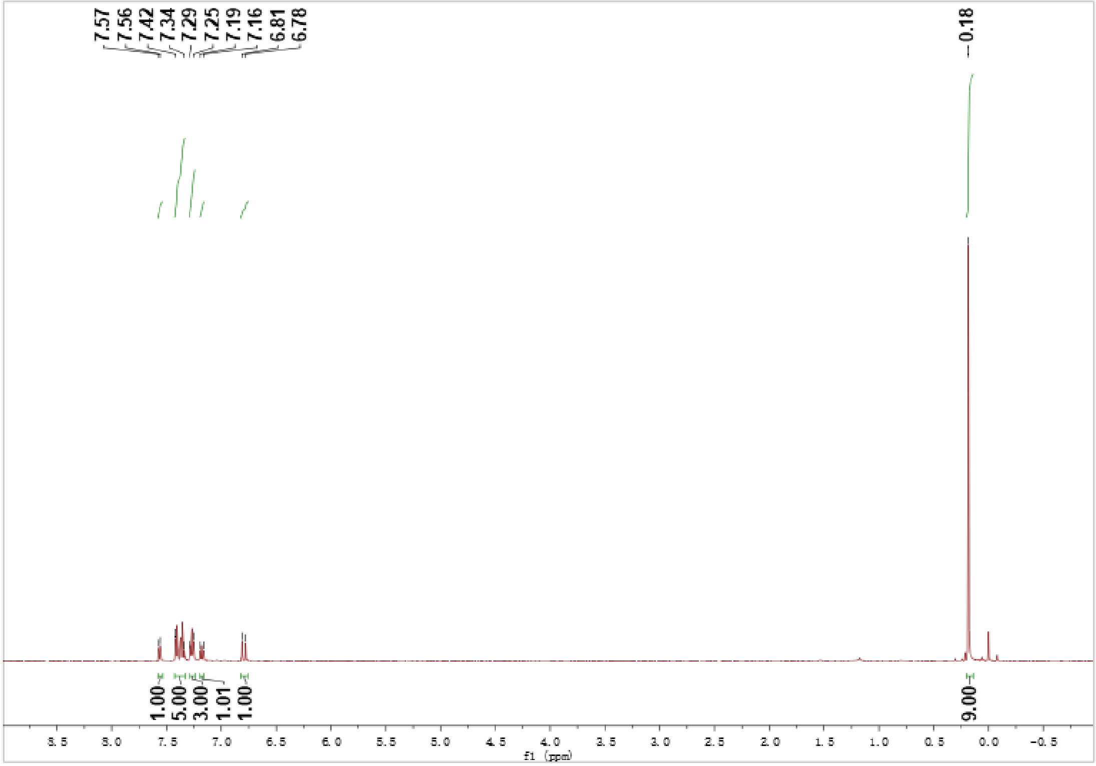
70
60
50
40
30
20
10
0
f1 (ppm)


O
SiMe$_3$

(3ai)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7.25
7.19
7.16
6.81
6.78
0.18
1.00
5.00
3.00
1.01
1.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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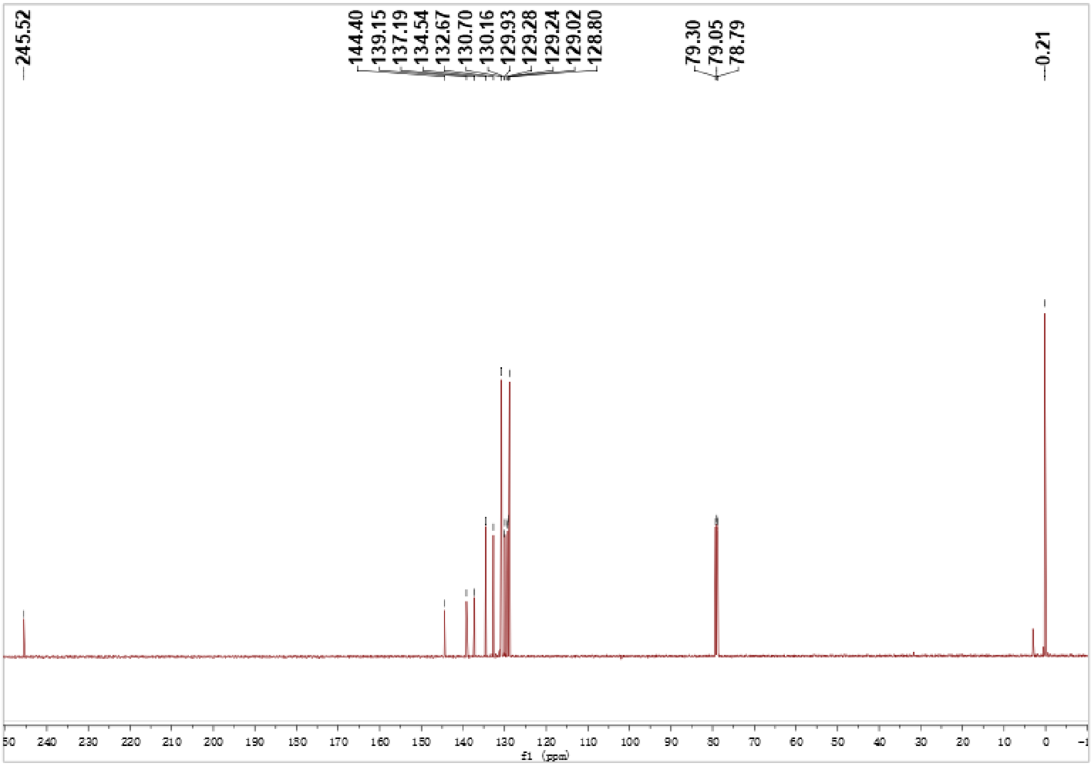
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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137.19
134.54
132.67
130.70
130.16
129.93
129.28
129.24
129.02
128.80
79.30
79.05
78.79
-0.21
250
240
230
220
210
200
190
180
170
160
150
140
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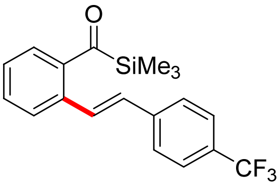
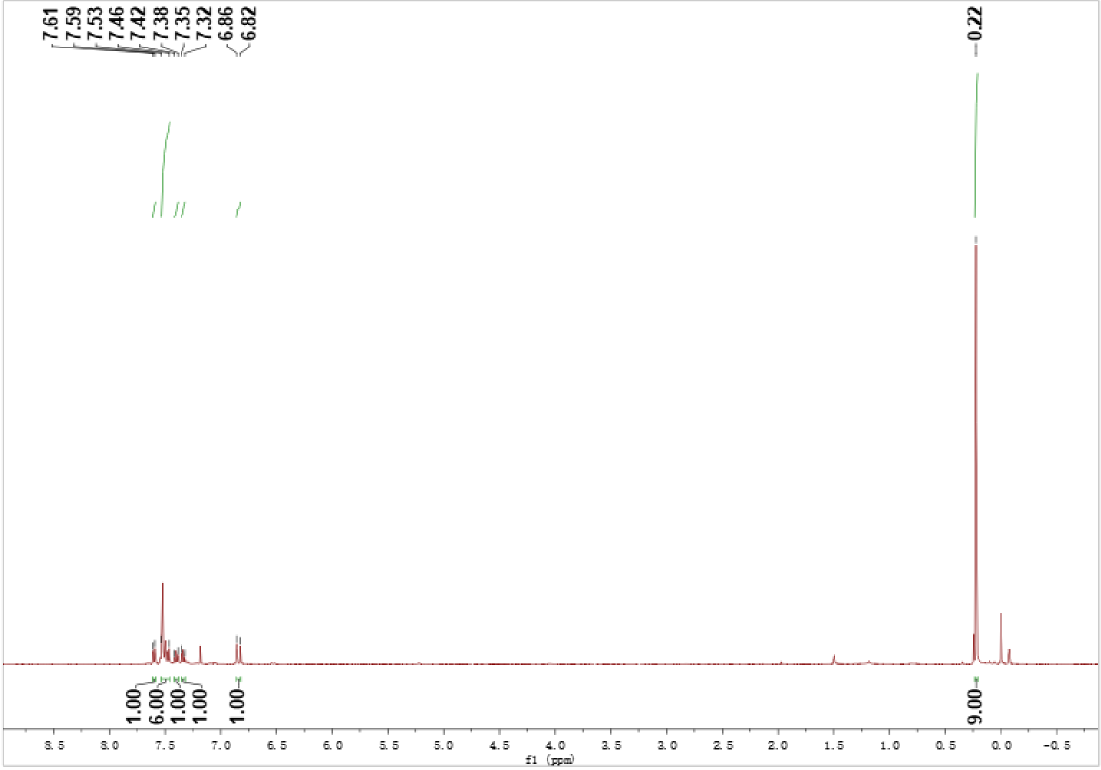
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
SiMe3
CF3

(3aj)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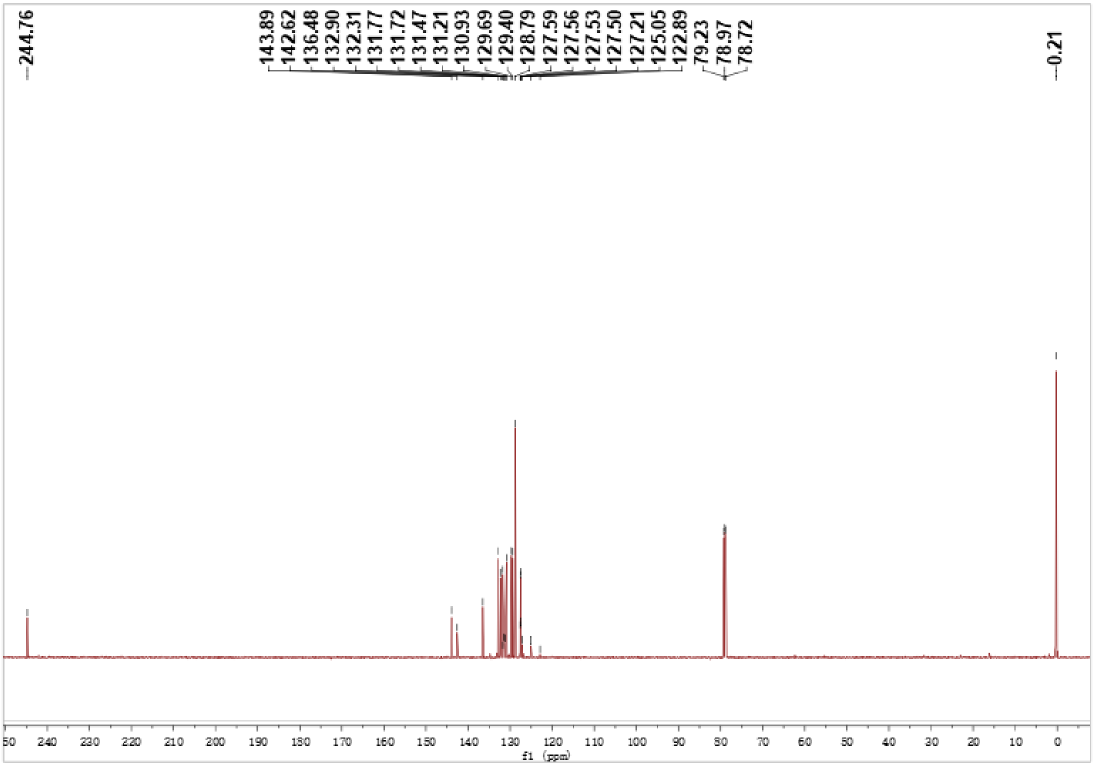
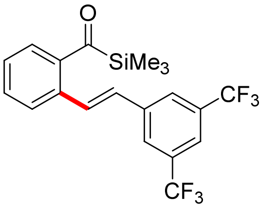
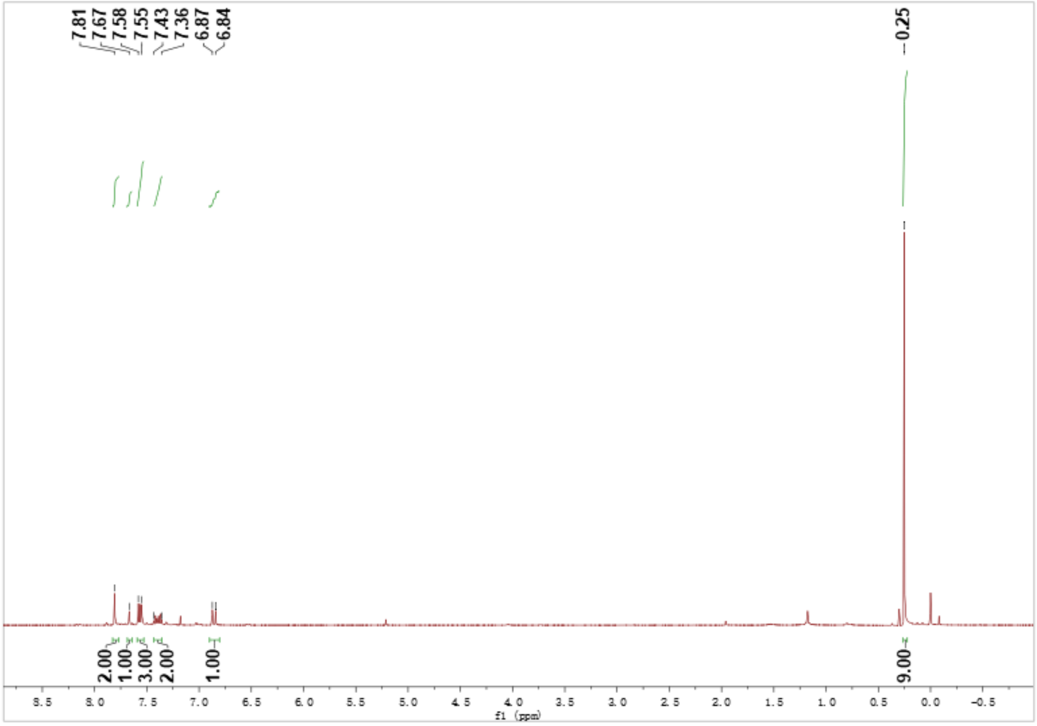
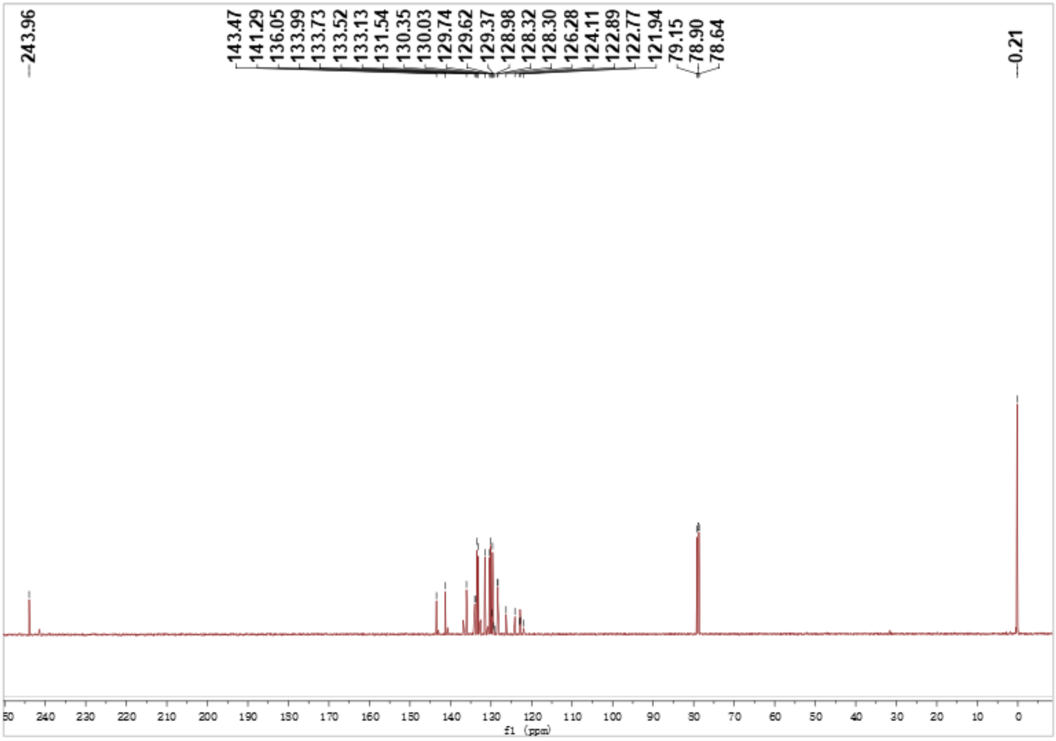
7.59
7.53
7.46
7.42
7.38
7.35
7.32
6.86
6.82
0.22
1.00
6.00
1.00
1.00
1.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


244.76
143.89
142.62
136.48
132.90
132.31
131.77
131.72
131.47
131.21
130.93
129.69
129.40
128.79
127.59
127.56
127.53
127.50
127.21
125.05
122.89
79.23
78.97
78.72
-0.21
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SiMe3
CF3
CF3

(3ak)


7.81
7.67
7.58
7.55
7.43
7.36
6.87
6.84
0.25
2.00
1.00
3.00
2.00
1.00
9.00
8.5
8.0
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
0.0
-0.5
f1 (ppm)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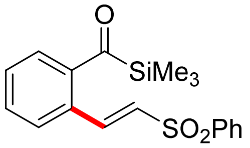
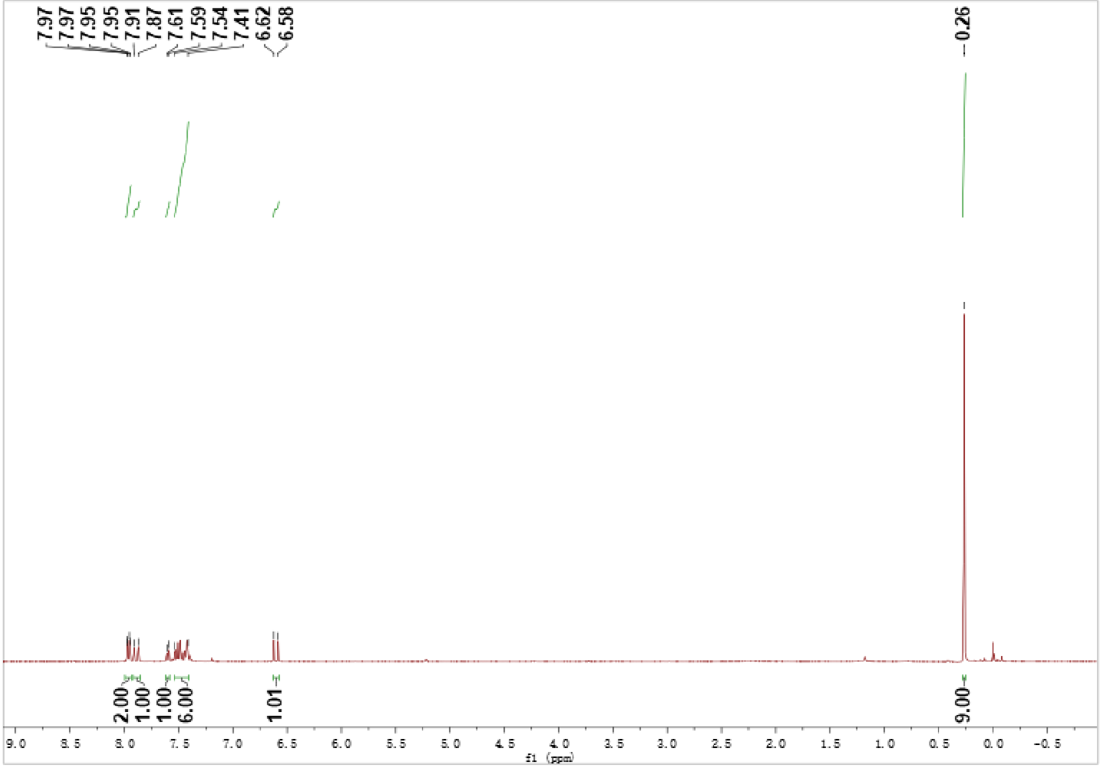
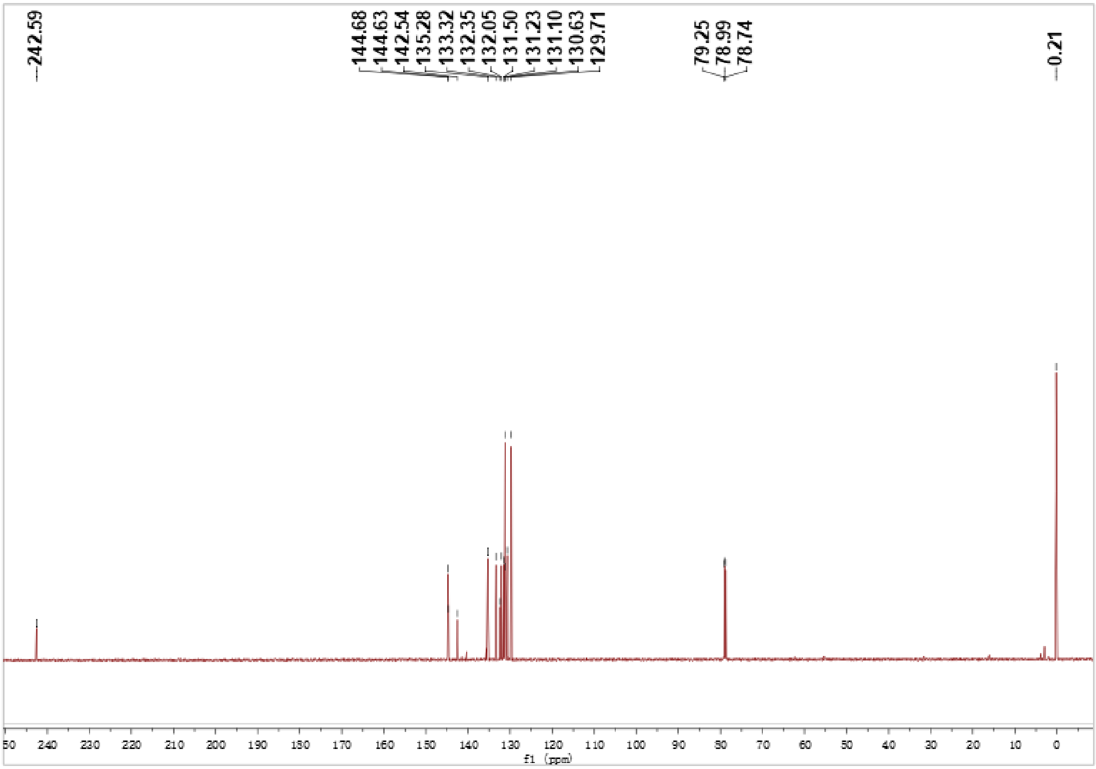
143.47
141.29
136.05
133.99
133.73
133.52
133.13
131.54
130.35
130.03
129.74
129.62
129.37
128.98
128.32
128.30
126.28
124.11
122.89
122.77
121.94
79.15
78.90
78.64
-0.21
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SiMe3
SO2Ph

(3al)


7.97
7.97
7.95
7.95
7.91
7.87
7.61
7.59
7.54
7.41
6.62
6.58
0.26
2.00
1.00
1.00
6.00
1.01
9.00
9.0
8.5
8.0
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
0.0
-0.5
f1 (ppm)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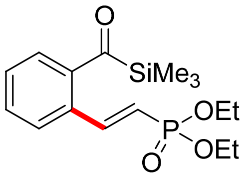
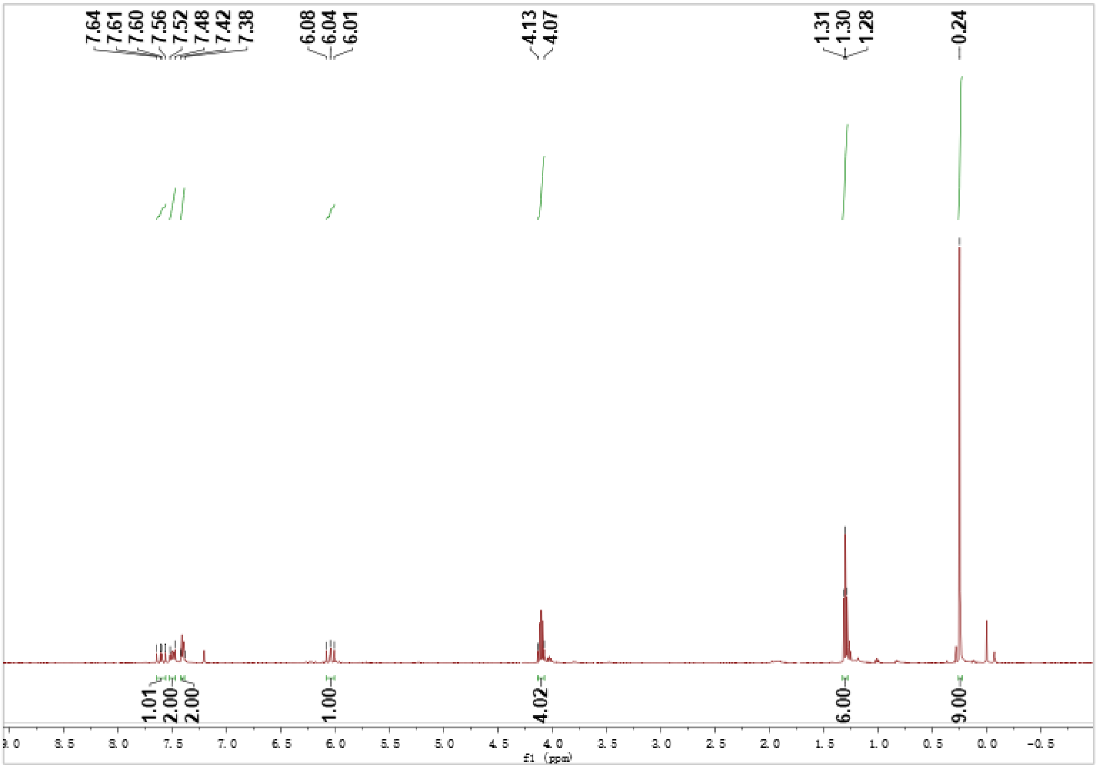
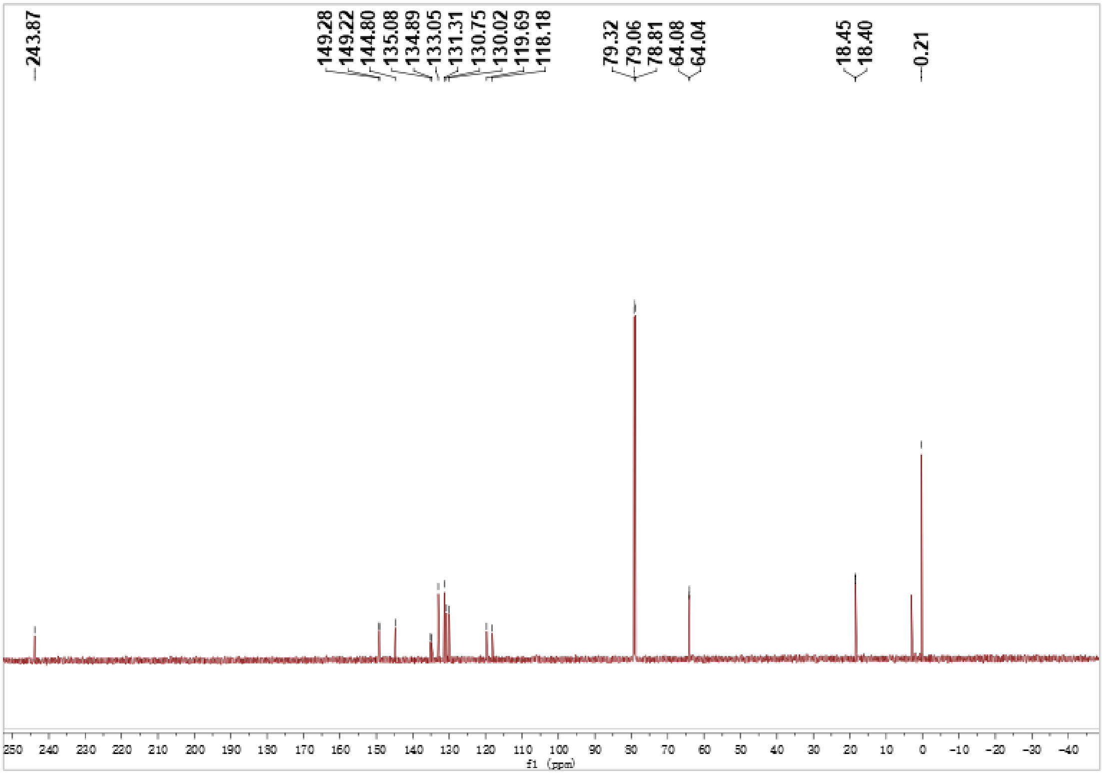
144.63
142.54
135.28
133.32
132.35
132.05
131.50
131.23
131.10
130.63
129.71
79.25
78.99
78.74
-0.21
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SiMe3
OEt
P
OEt
O

(3am)


7.64
7.61
7.60
7.56
7.52
7.48
7.42
7.38
6.08
6.04
6.01
4.13
4.07
1.31
1.30
1.28
0.24
1.01
2.00
2.00
1.00
4.02
6.00
9.00
9.0
8.5
8.0
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
0.0
-0.5
f1 (ppm)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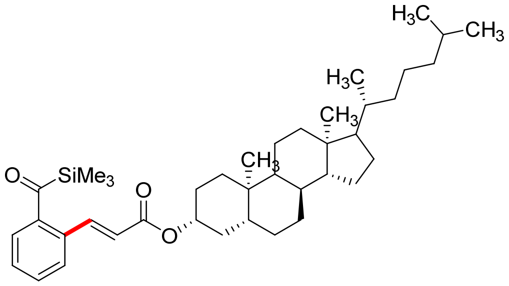
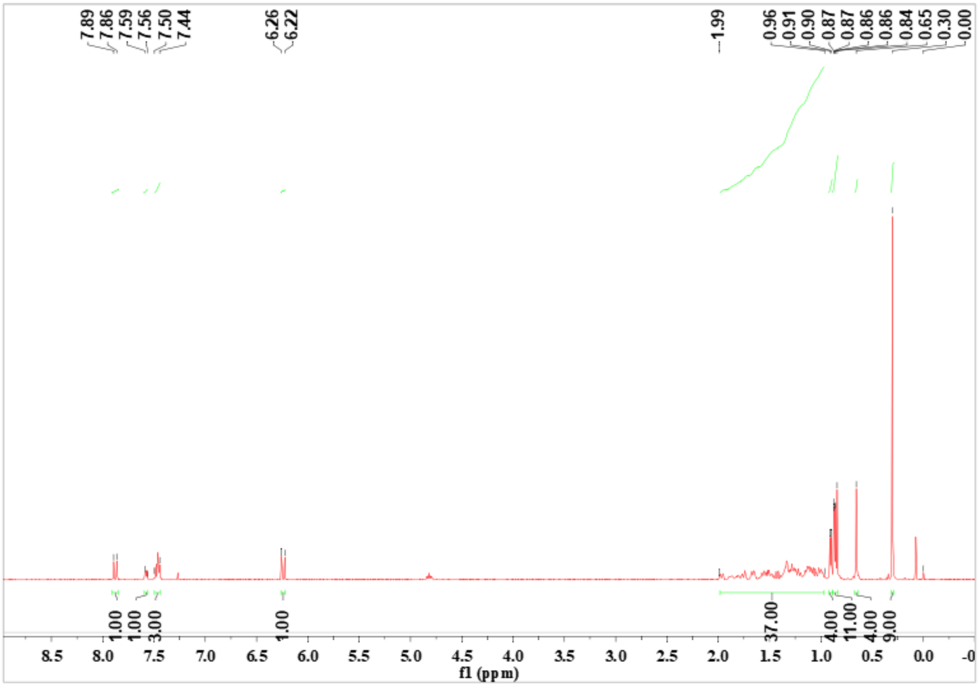
149.22
144.80
135.08
134.89
133.05
131.31
130.75
130.02
119.69
118.18
79.32
79.06
78.81
64.08
64.04
18.45
18.40
-0.21
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


H3C
CH3
H3C
CH3
CH3
O
SiMe3
O
O

(3an)


7.89
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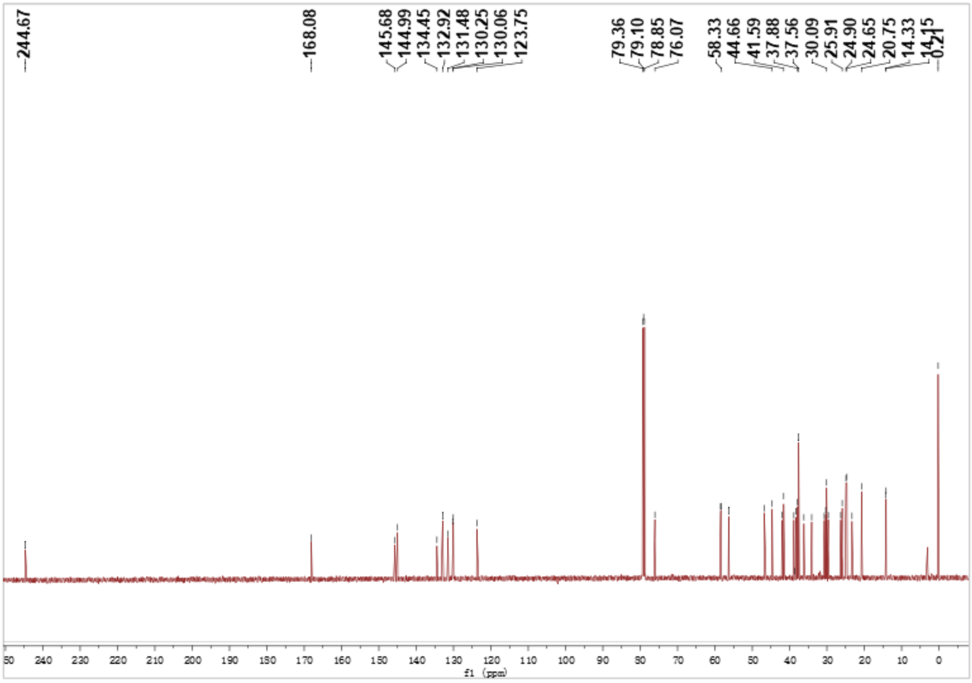
7.56
7.50
7.44
6.26
6.22
1.99
0.96
0.91
0.90
0.87
0.87
0.86
0.86
0.84
0.65
0.30
0.00
1.00
1.00
3.00
1.00
37.00
4.00
11.00
4.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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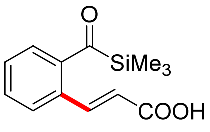
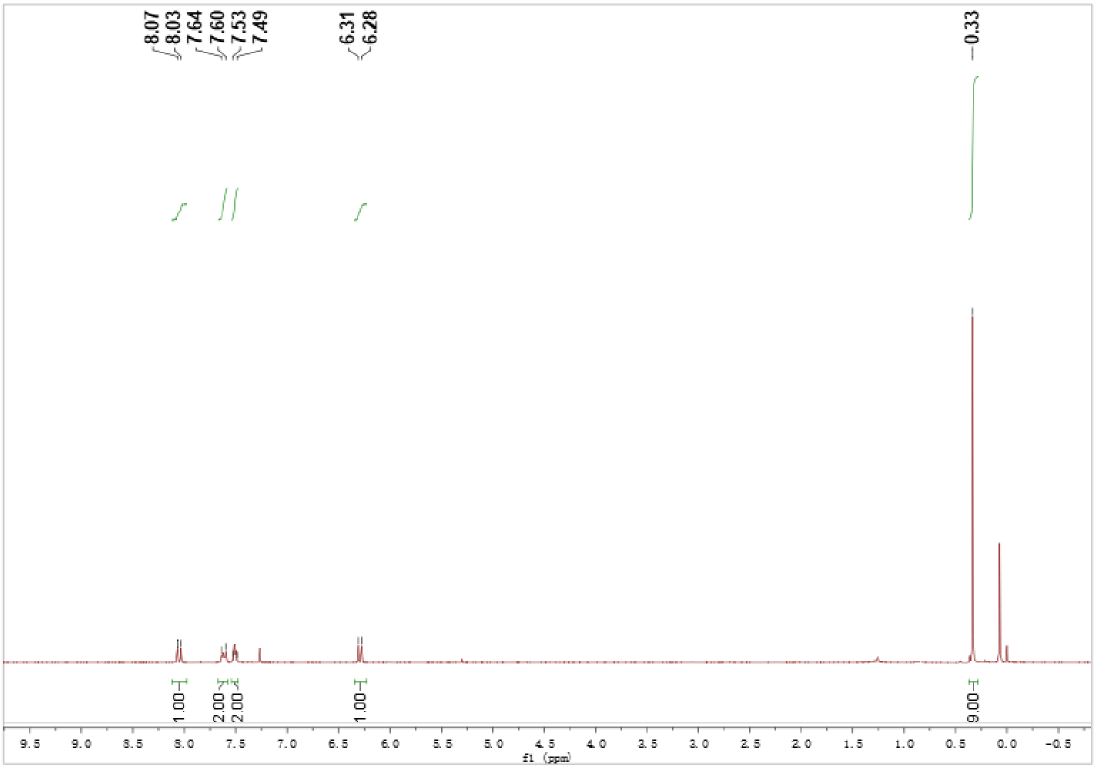
144.99
134.45
132.92
131.48
130.25
130.06
123.75
79.36
79.10
78.85
76.07
58.33
44.66
41.59
37.88
37.56
30.09
25.91
24.90
24.65
20.75
14.33
14.15
0.21
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

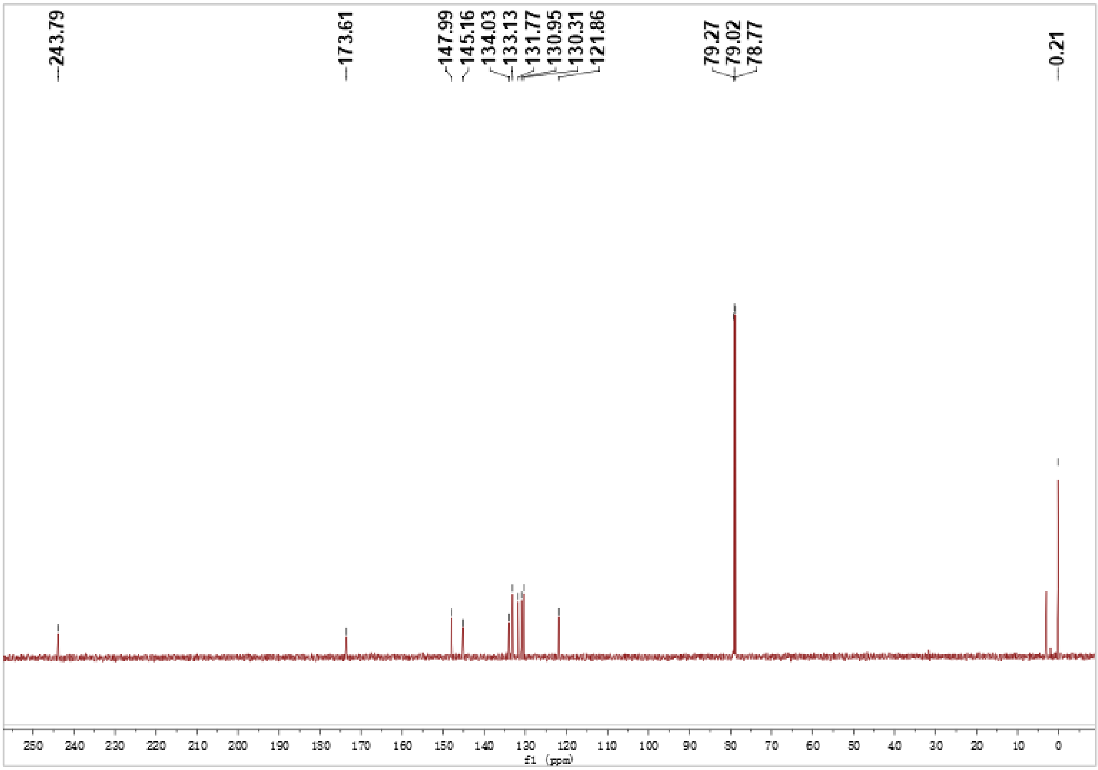


O
SiMe3
COOH

(3ao)



8.07
8.03
7.64
7.60
7.53
7.49
6.31
6.28
0.33
1.00
2.00
2.00
1.00
9.00
9.5
9.0
8.5
8.0
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
0.0
-0.5
f1 (ppm)



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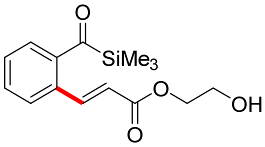
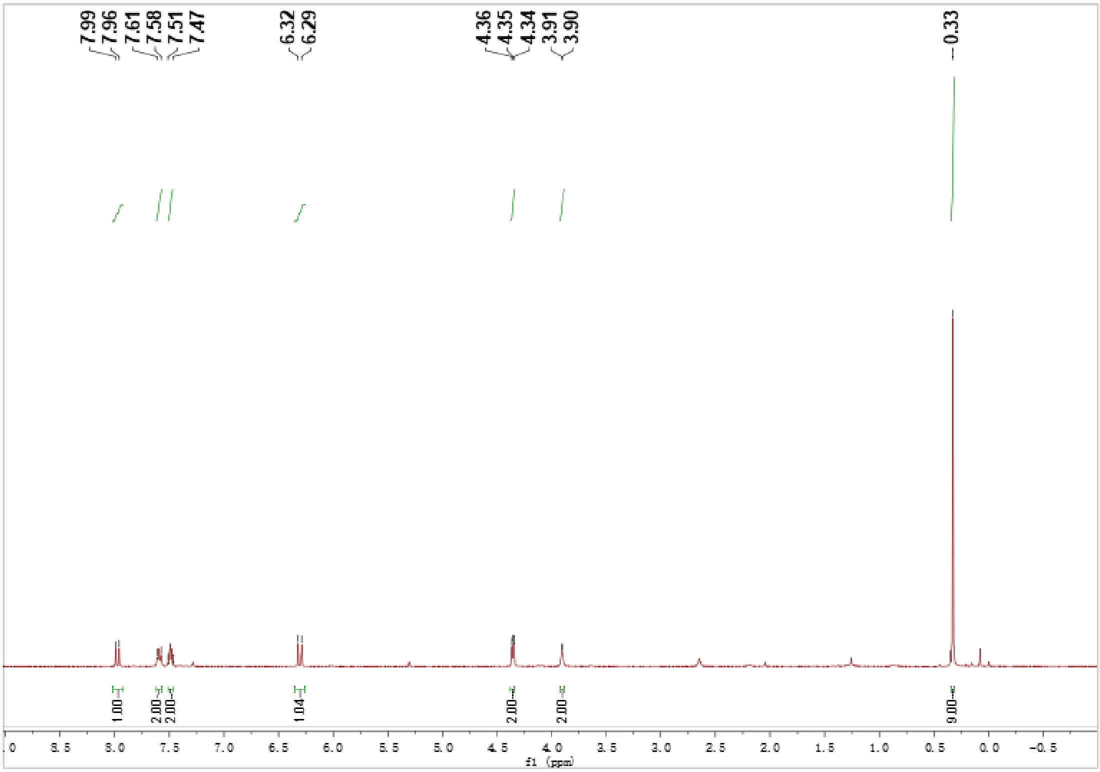
173.61
147.99
145.16
134.03
133.13
131.77
130.95
130.31
121.86
79.27
79.02
78.77
0.21
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

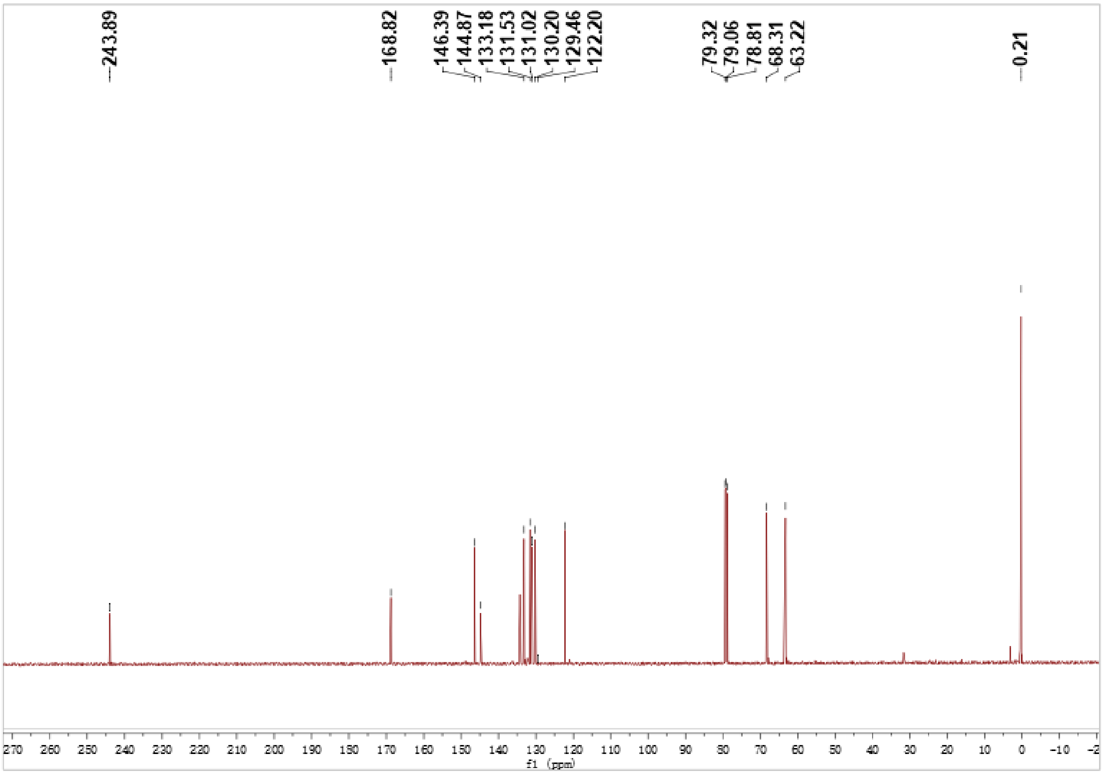


O
SiMe3
O
OH
O

(3ap)



7.99
7.96
7.61
7.58
7.51
7.47
6.32
6.29
4.36
4.35
4.34
3.91
3.90
0.33
1.00
2.00
2.00
1.04
2.00
2.00
9.00
8.5
8.0
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
0.0
-0.5
f1 (ppm)



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168.82
146.39
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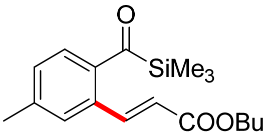
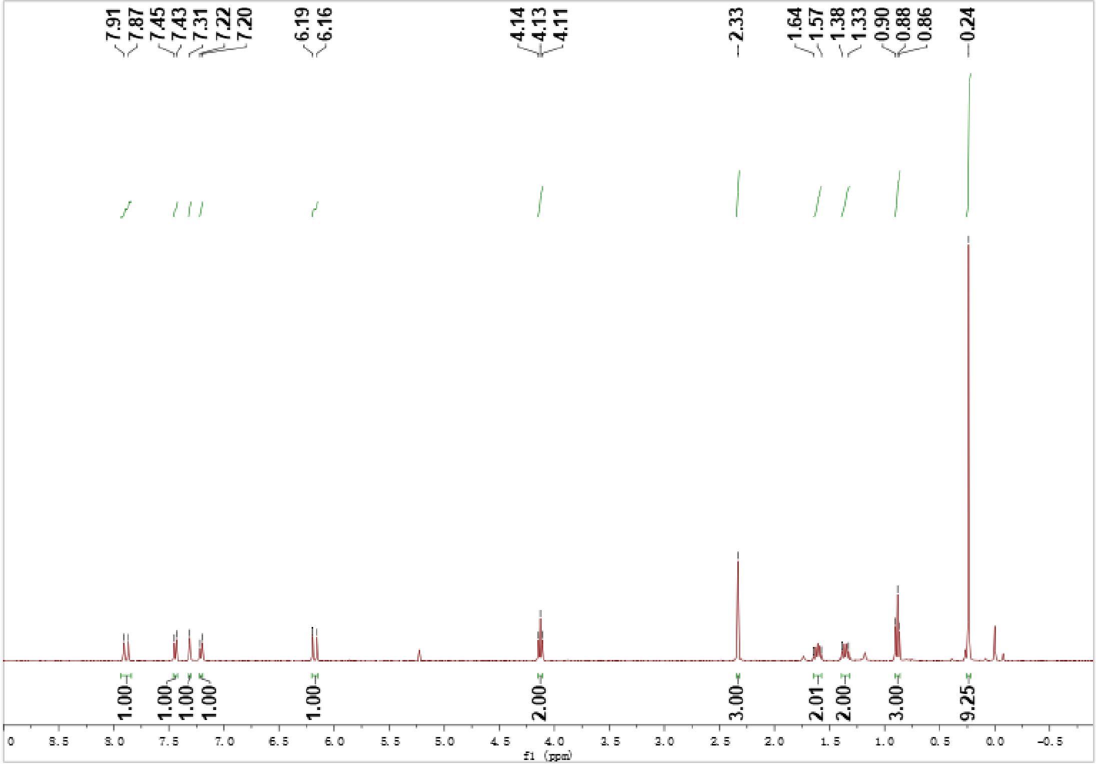
133.18
131.53
131.02
130.20
129.46
122.20
79.32
79.06
78.81
68.31
63.22
0.21
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


O
SiMe3
COOBu

(3ba)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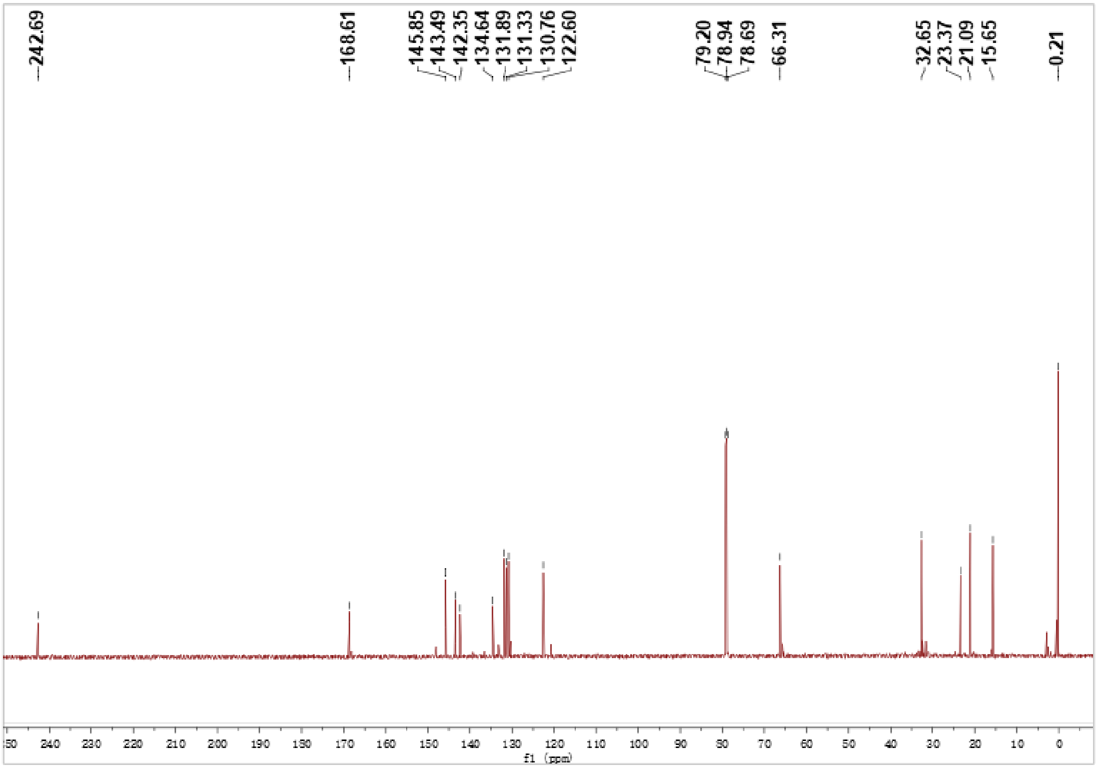
7.22
7.20
6.19
6.16
4.14
4.13
4.11
2.33
1.64
1.57
1.38
1.33
0.90
0.88
0.86
0.24
1.00
1.00
1.00
1.00
1.00
2.00
3.00
2.01
2.00
3.00
9.25
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


242.69
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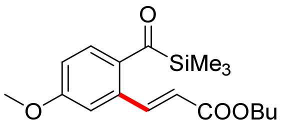
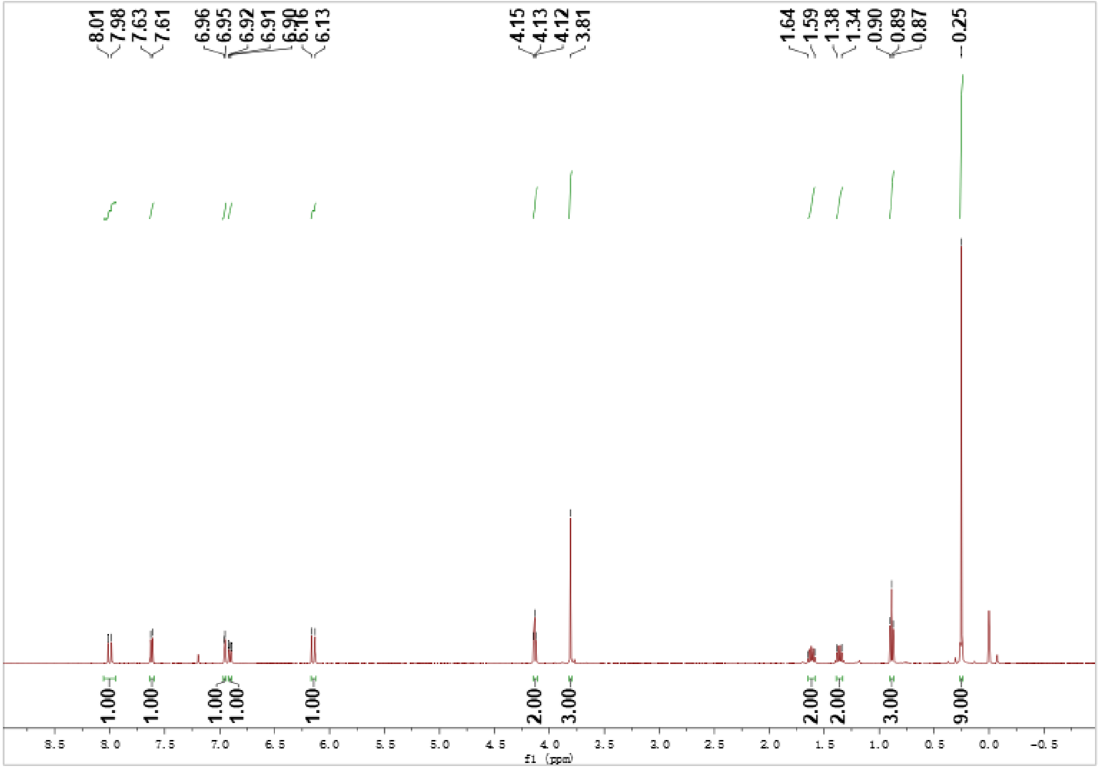
145.85
143.49
142.35
134.64
131.89
131.33
130.76
122.60
79.20
78.94
78.69
66.31
32.65
23.37
21.09
15.65
0.21
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SiMe3
O
COOBu

(3ca)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7.98
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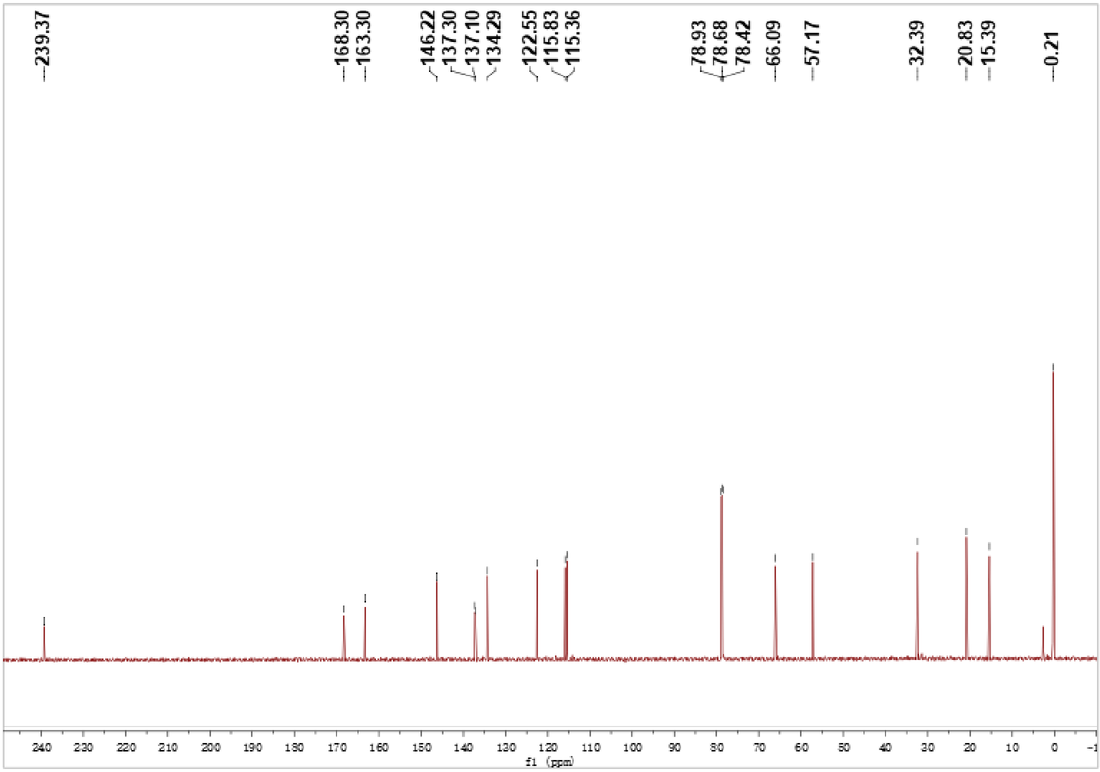
7.61
6.96
6.95
6.92
6.91
6.90
6.16
6.13
4.15
4.13
4.12
3.81
1.64
1.59
1.38
1.34
0.90
0.89
0.87
0.25
1.00
1.00
1.00
1.00
1.00
2.00
3.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


239.37
168.30
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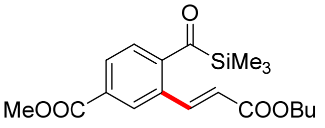
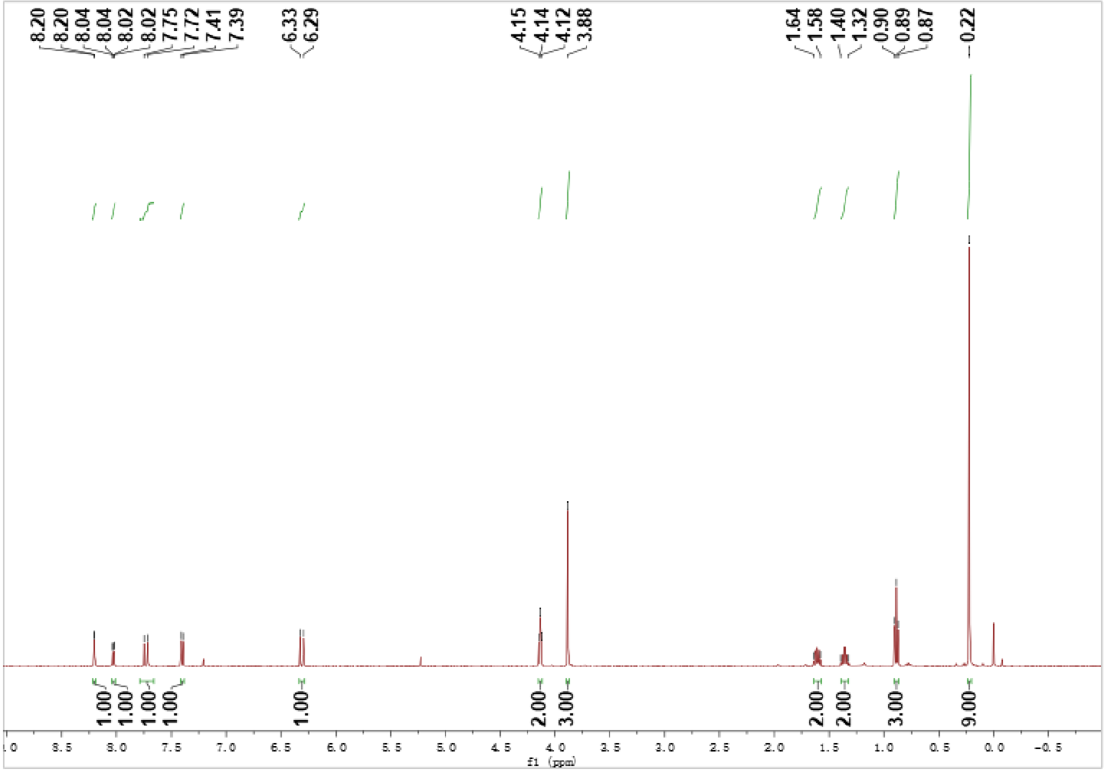
137.30
137.10
134.29
122.55
115.83
115.36
78.93
78.68
78.42
66.09
57.17
32.39
20.83
15.39
0.21
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


O
SiMe3
MeOOC
COOBu

(3da)


8.20
8.20
8.04
8.04
8.02
8.02
7.75
7.72
7.41
7.39
6.33
6.29
4.15
4.14
4.12
3.88
1.64
1.58
1.40
1.32
0.90
0.89
0.87
0.22
1.00
1.00
1.00
1.00
1.00
2.00
3.00
2.00
2.00
3.00
9.00
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5.0
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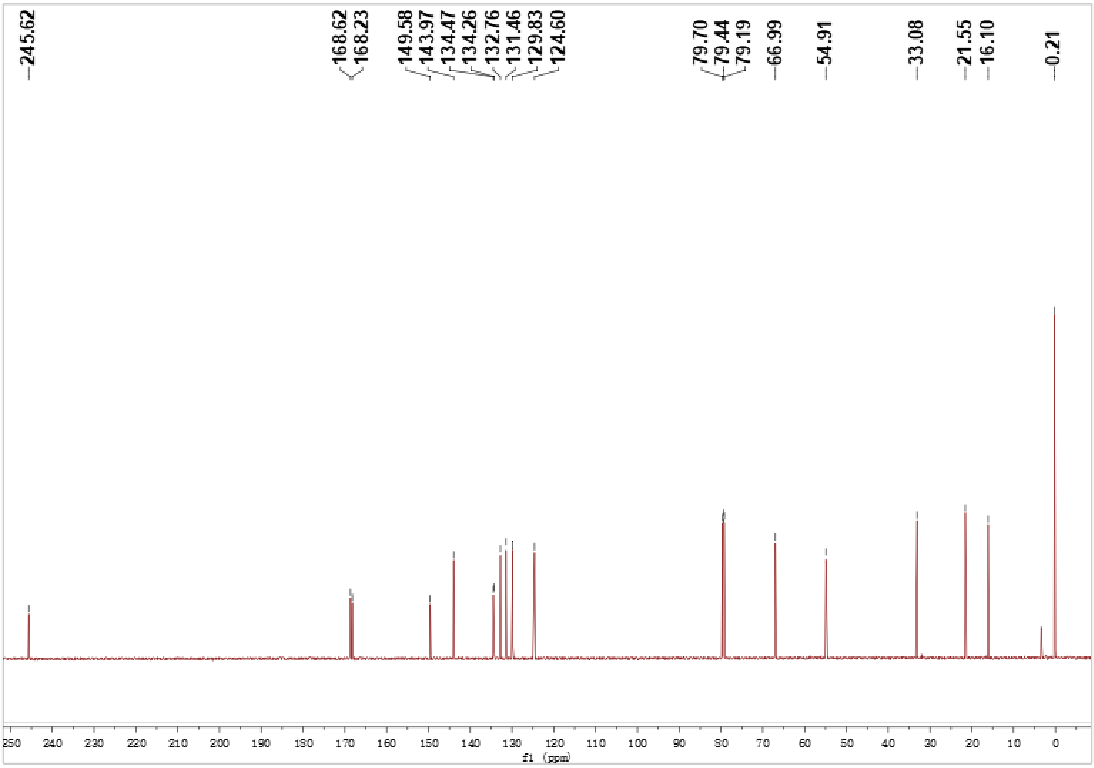
f1 (ppm)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134.26
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129.83
124.60
79.70
79.44
79.19
66.99
54.91
33.08
21.55
16.10
-0.21
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240
230
220
210
200
190
180
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90
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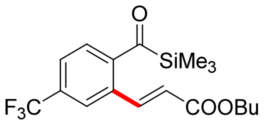
f1 (ppm)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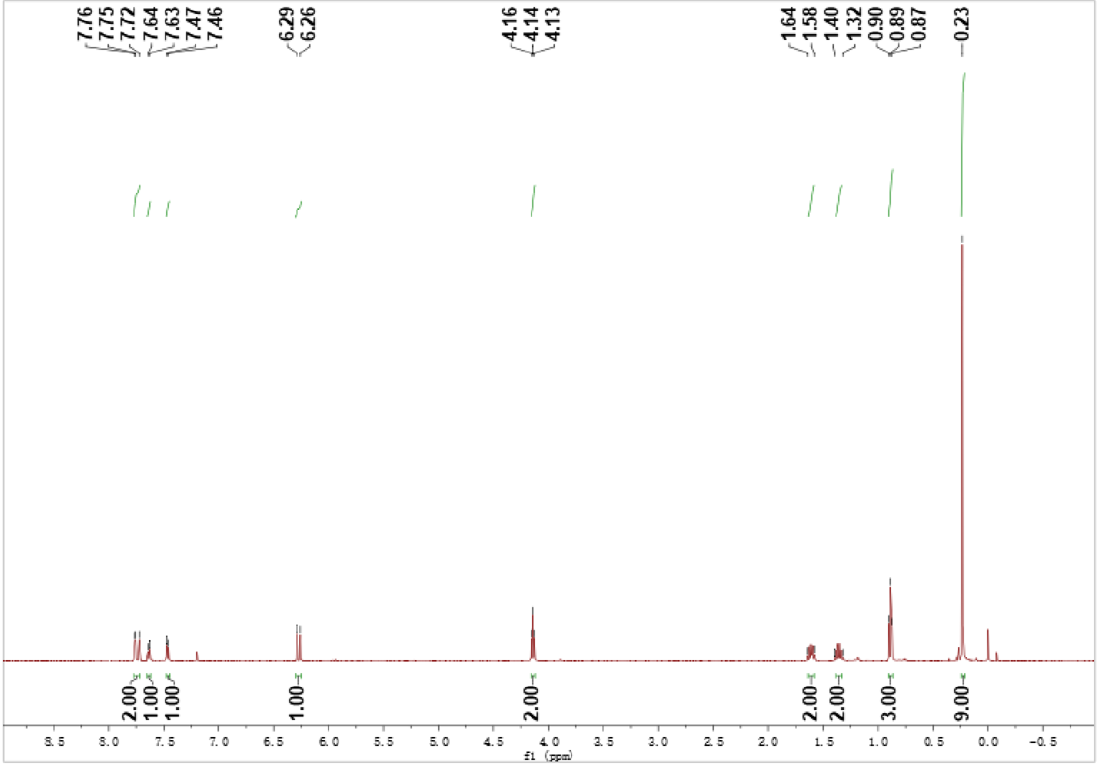
F3C
COOBu

(3ea)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7.72
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7.47
7.46
6.29
6.26
4.16
4.14
4.13
1.64
1.58
1.40
1.32
0.90
0.89
0.87
0.23
2.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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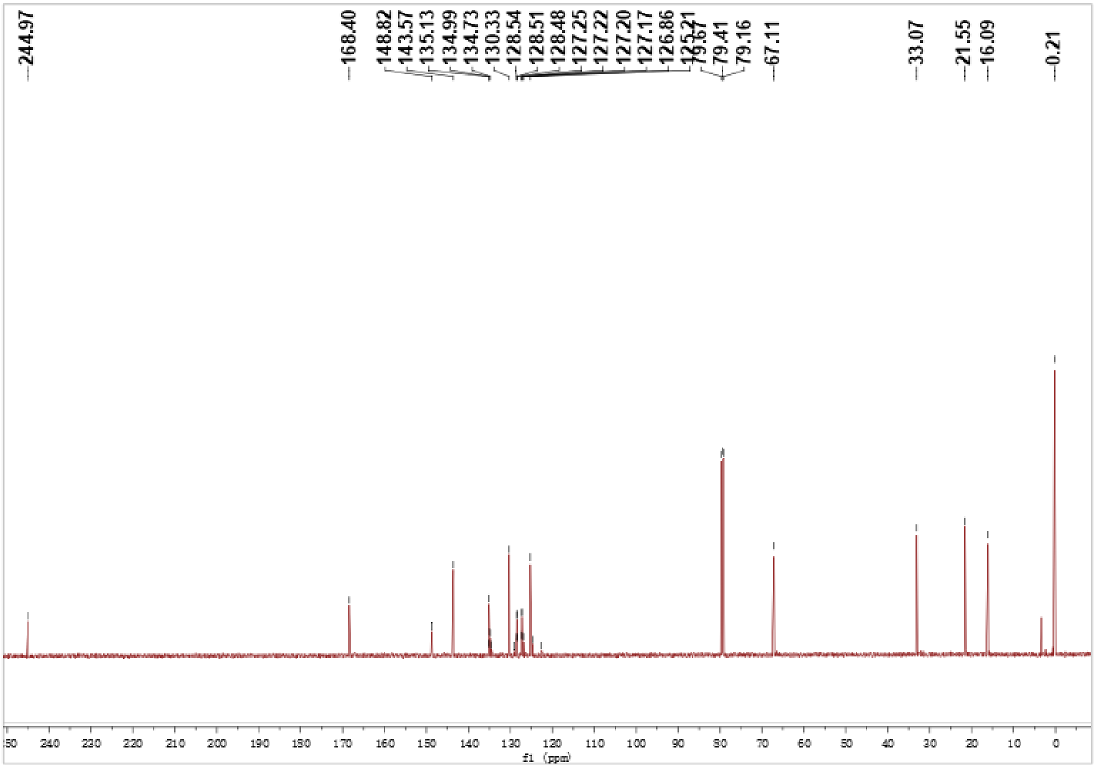
-0.5
f1 (ppm)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127.22
127.20
127.17
126.86
125.21
79.67
79.41
79.16
67.11
33.07
21.55
16.09
-0.21
50
240
230
220
210
200
190
180
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50
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10
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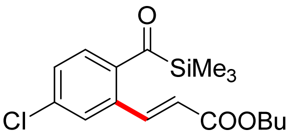
f1 (ppm)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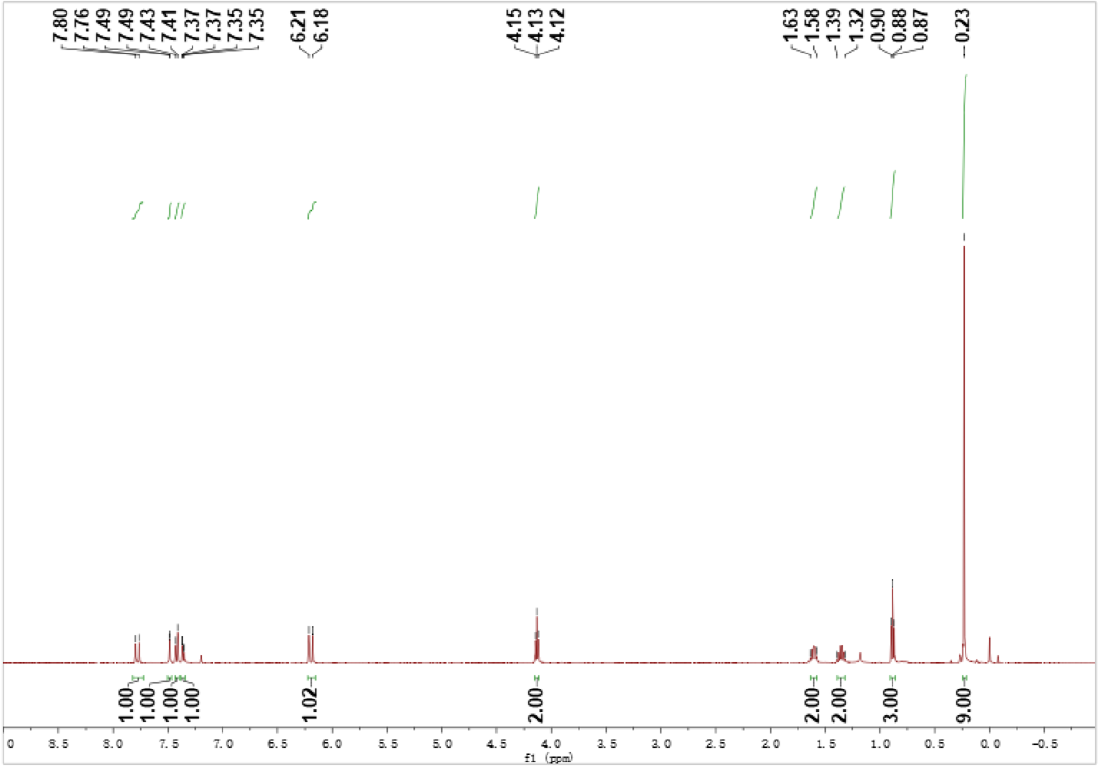
Cl
COOBu

(3fa)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7.37
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7.35
6.21
6.18
4.15
4.13
4.12
1.63
1.58
1.39
1.32
0.90
0.88
0.87
0.23
1.00
1.00
1.00
1.00
1.02
2.00
2.00
2.00
3.00
9.00
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8.0
7.5
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6.5
6.0
5.5
5.0
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3.0
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2.0
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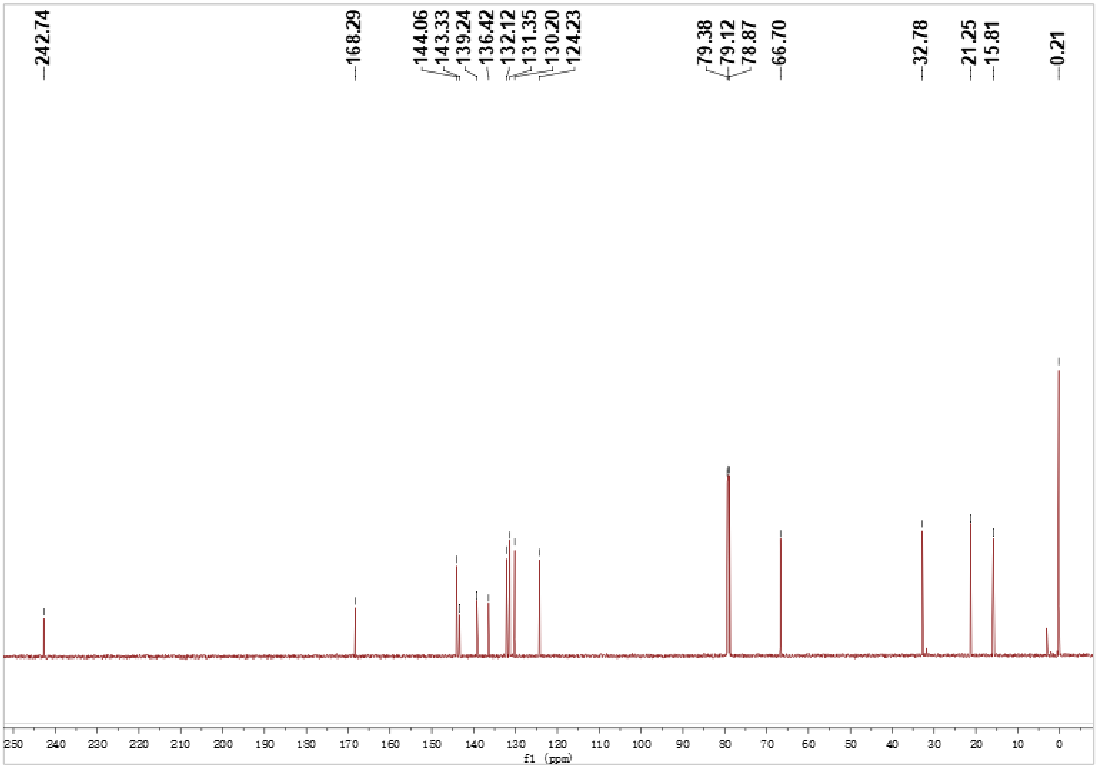
f1 (ppm)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124.23
79.38
79.12
78.87
66.70
32.78
21.25
15.81
0.21
250
240
230
220
210
200
190
180
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130
120
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50
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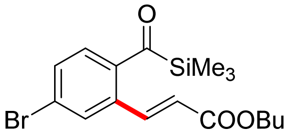
f1 (ppm)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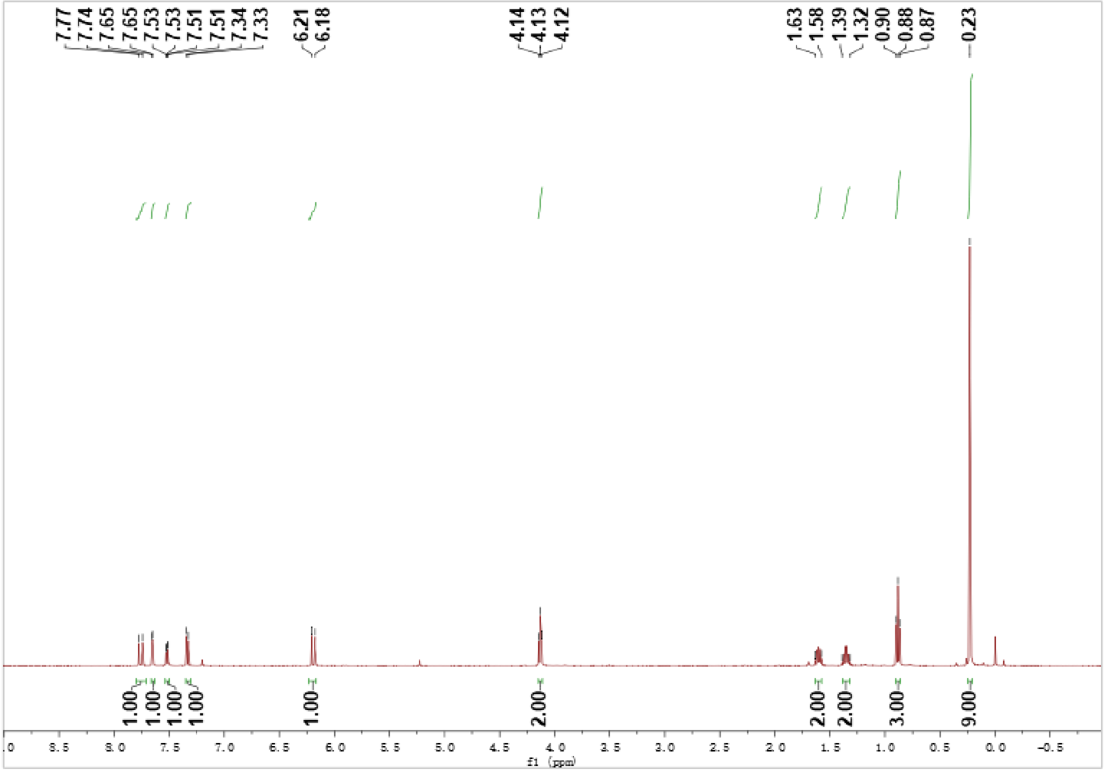
Br
COOBu

(3ga)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7.51
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7.33
6.21
6.18
4.14
4.13
4.12
1.63
1.58
1.39
1.32
0.90
0.88
0.87
0.23
1.00
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
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2.0
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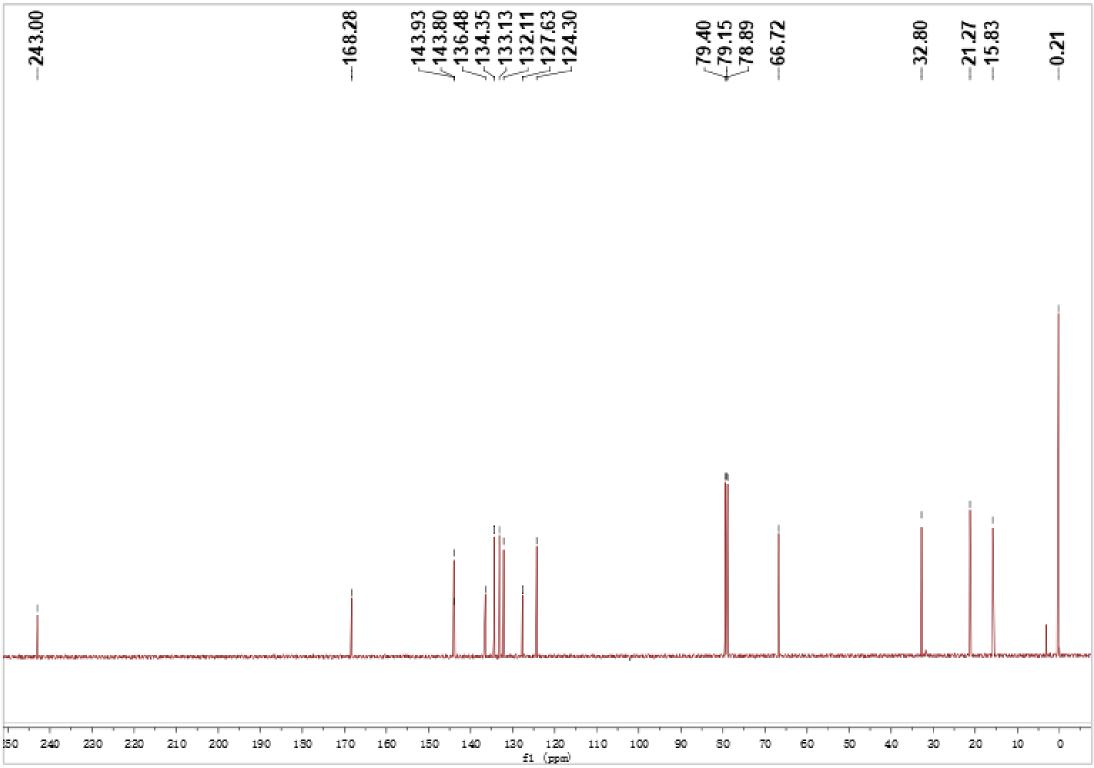
0.0
-0.5
f1 (ppm)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132.11
127.63
124.30
79.40
79.15
78.89
66.72
32.80
21.27
15.83
-0.21
240
230
220
210
200
190
180
170
160
150
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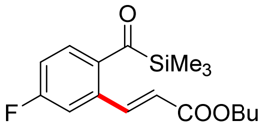
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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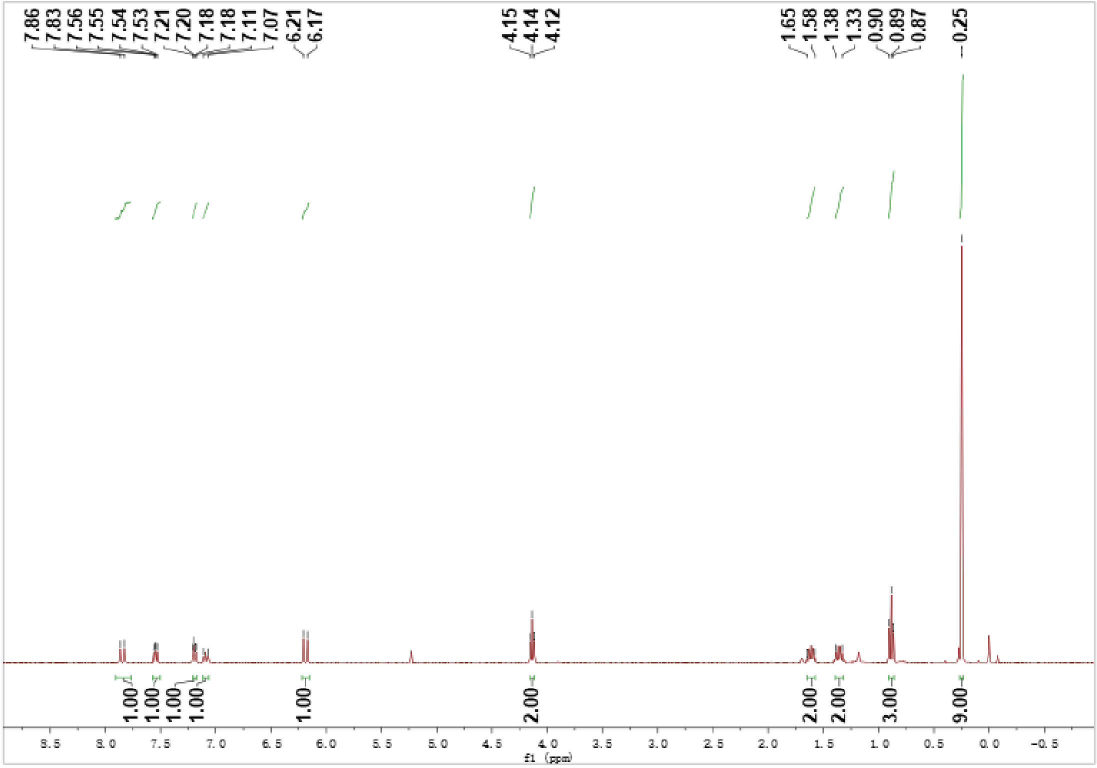
F
COOBu

(3ha)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7.20
7.18
7.18
7.11
7.07
6.21
6.17
4.15
4.14
4.12
1.65
1.58
1.38
1.33
0.90
0.89
0.87
0.25
1.00
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
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6.5
6.0
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5.0
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3.0
2.5
2.0
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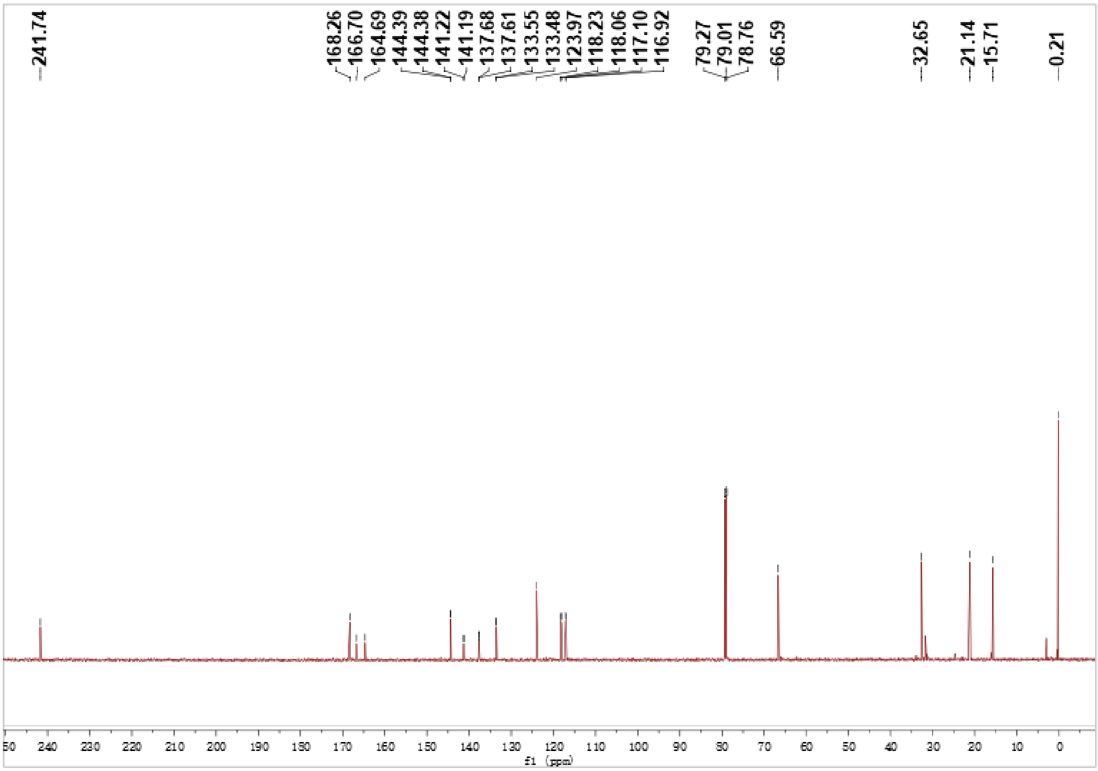
0.5
0.0
-0.5
f1 (ppm)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137.61
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133.48
123.97
118.23
118.06
117.10
116.92
79.27
79.01
78.76
66.59
32.65
21.14
15.71
-0.21
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
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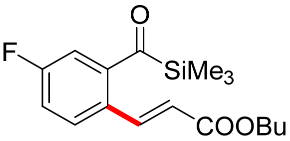
10
0
f1 (ppm)


F
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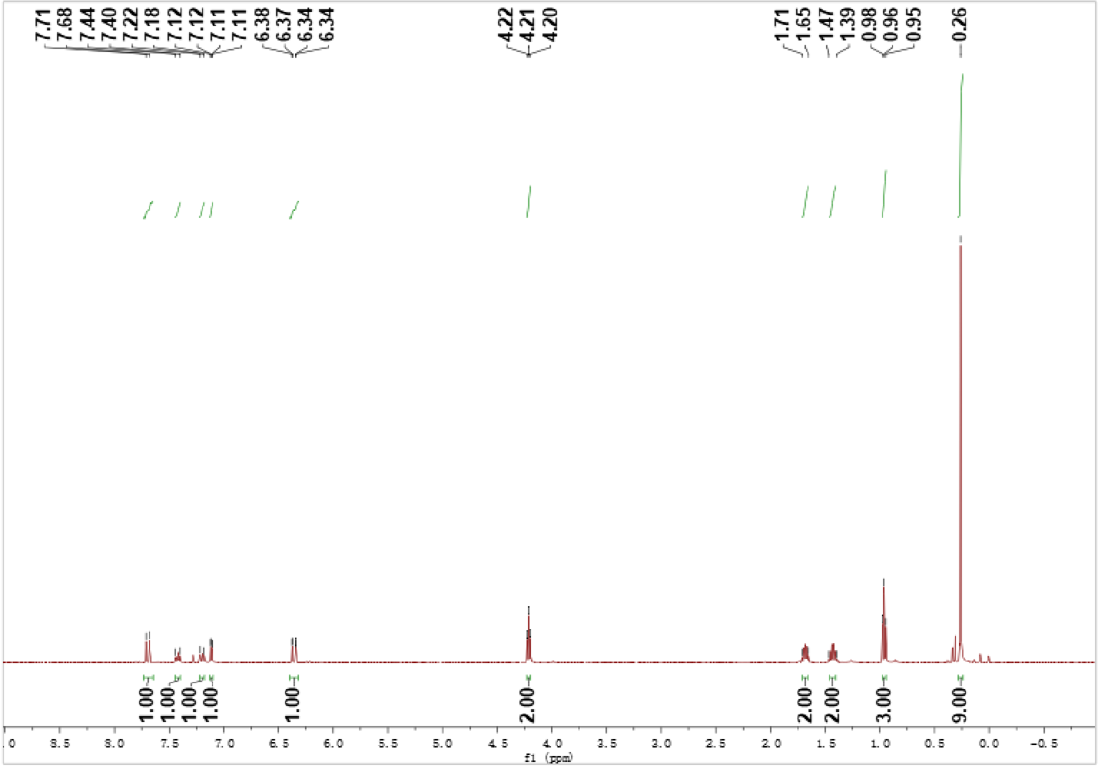
COOBu

(3ia)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7.18
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7.12
7.11
7.11
6.38
6.37
6.34
6.34
4.22
4.21
4.20
1.71
1.65
1.47
1.39
0.98
0.96
0.95
0.26
1.00
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
9.00
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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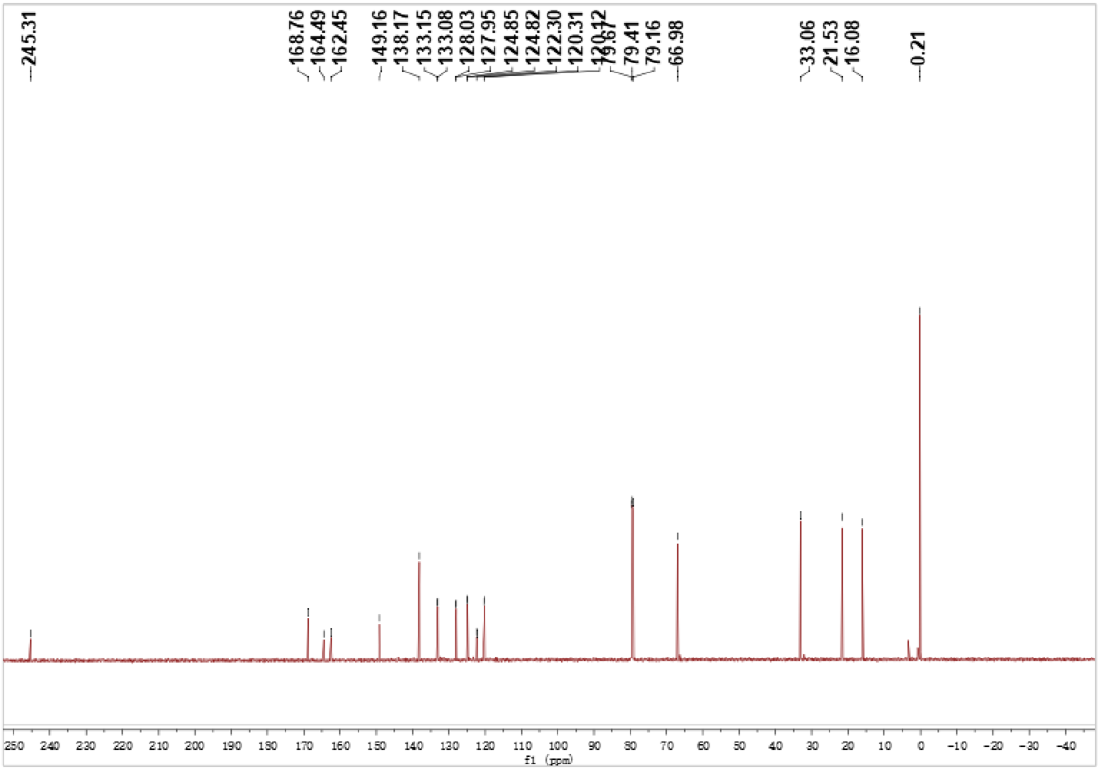
0.5
0.0
-0.5
f1 (ppm)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133.08
128.03
127.95
124.85
124.82
122.30
120.31
120.12
79.67
79.41
79.16
66.98
33.06
21.53
16.08
0.21
250
240
230
220
210
200
190
180
170
160
150
140
130
120
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100
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80
70
60
50
40
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20
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-10
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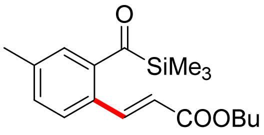
-30
-40
f1 (ppm)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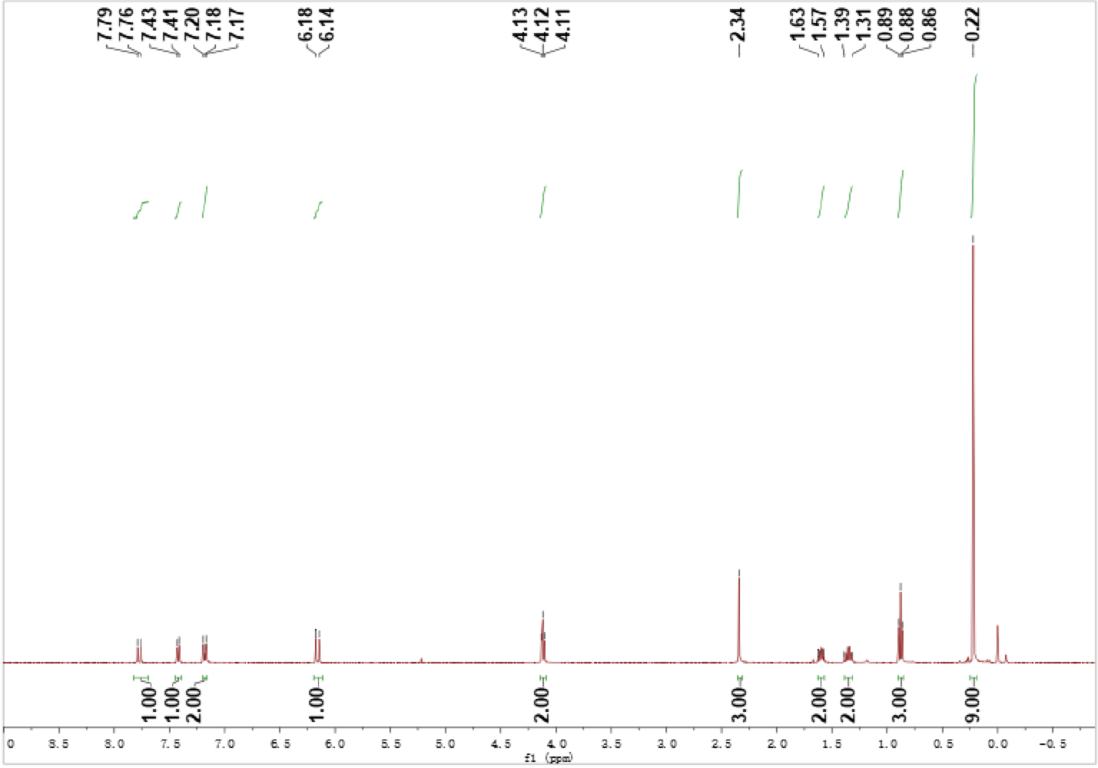
SiMe3
COOBu

(3ja)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4.13
4.12
4.11
2.34
1.63
1.57
1.39
1.31
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0.88
0.86
0.22
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1.00
2.00
3.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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3.0
2.5
2.0
1.5
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0.5
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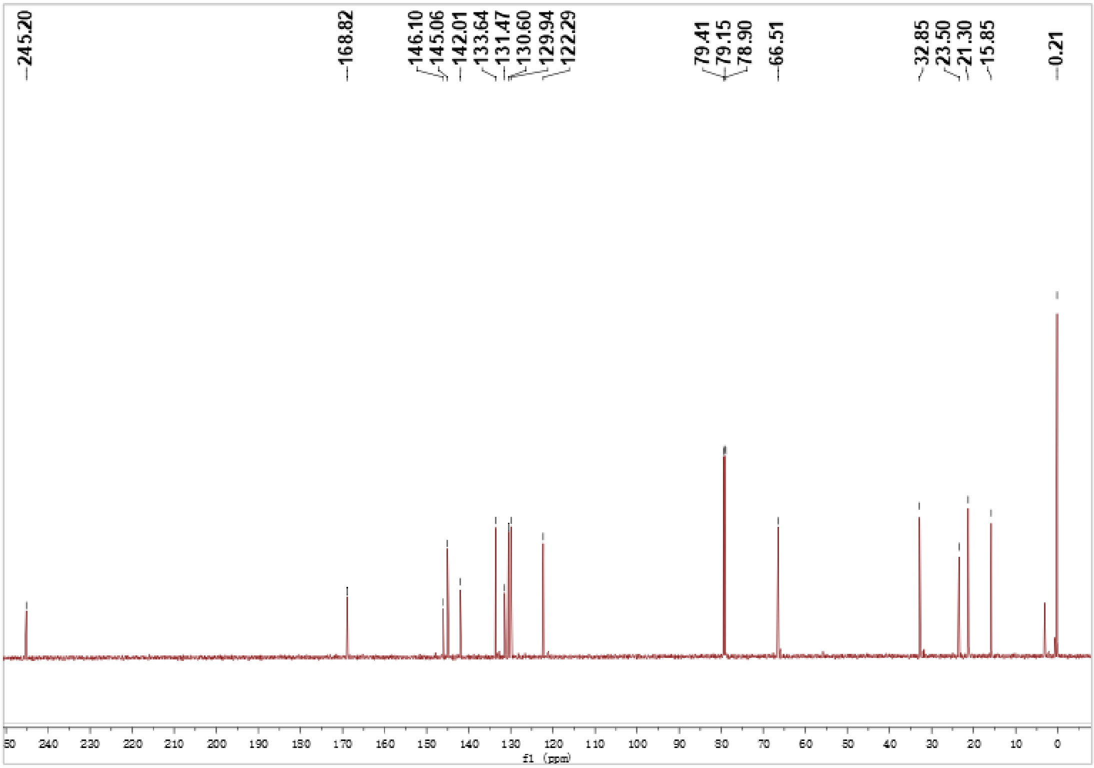
-0.5
f1 (ppm)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122.29
79.41
79.15
78.90
66.51
32.85
23.50
21.30
15.85
0.21
240
230
220
210
200
190
180
170
160
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130
120
110
100
90
80
70
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40
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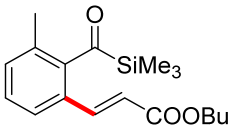
0
f1 (ppm)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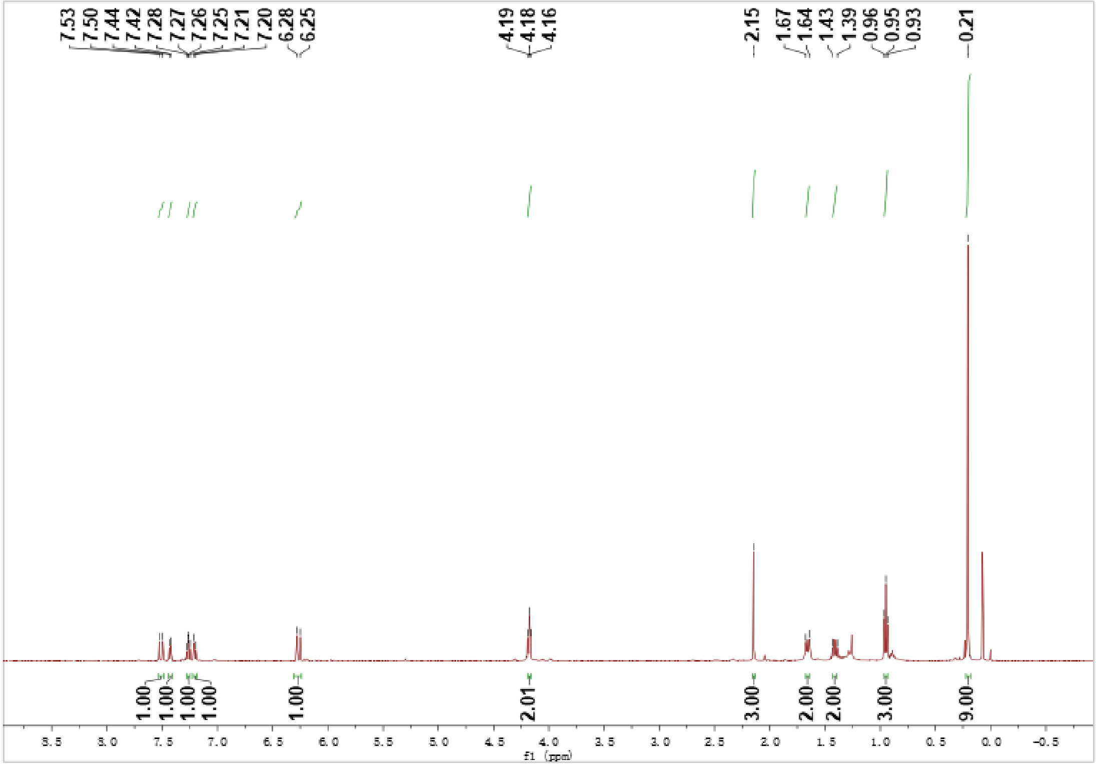
COOBu

(3ka)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7.20
6.28
6.25
4.19
4.18
4.16
2.15
1.67
1.64
1.43
1.39
0.96
0.95
0.93
0.21
1.00
1.00
1.00
1.00
1.00
2.01
3.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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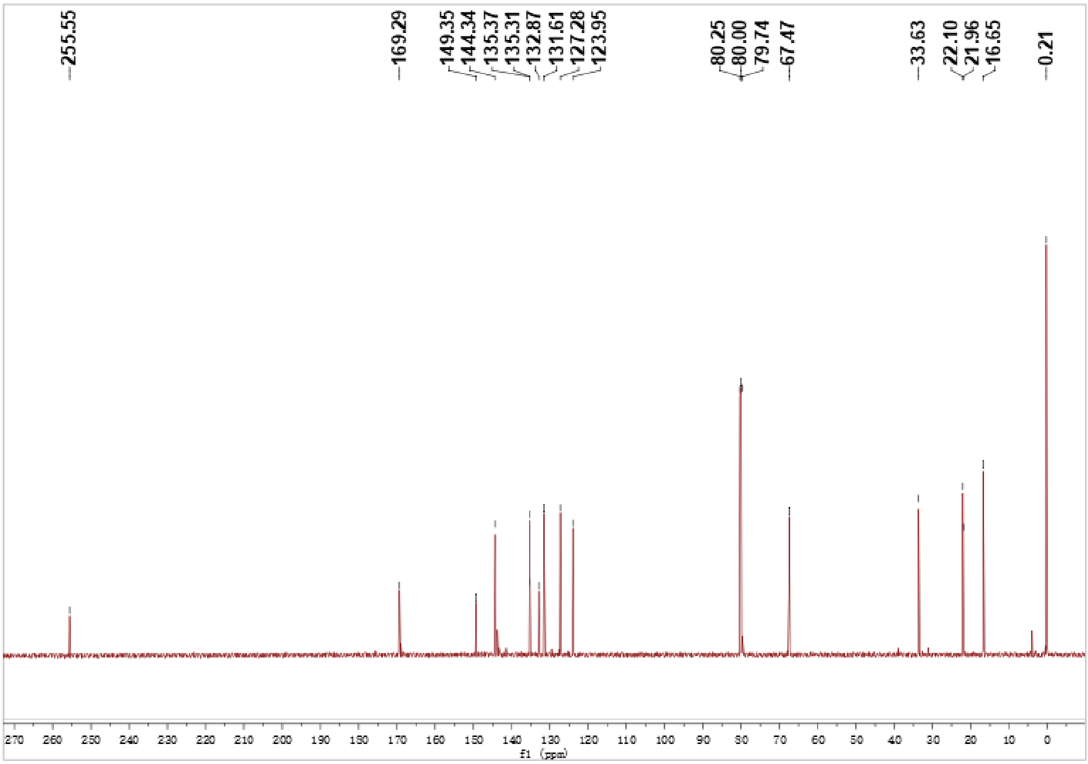
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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131.61
127.28
123.95
80.25
80.00
79.74
67.47
33.63
22.10
21.96
16.65
0.21
270
260
250
240
230
220
210
200
190
180
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130
120
110
100
90
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70
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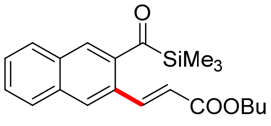
10
0
f1 (ppm)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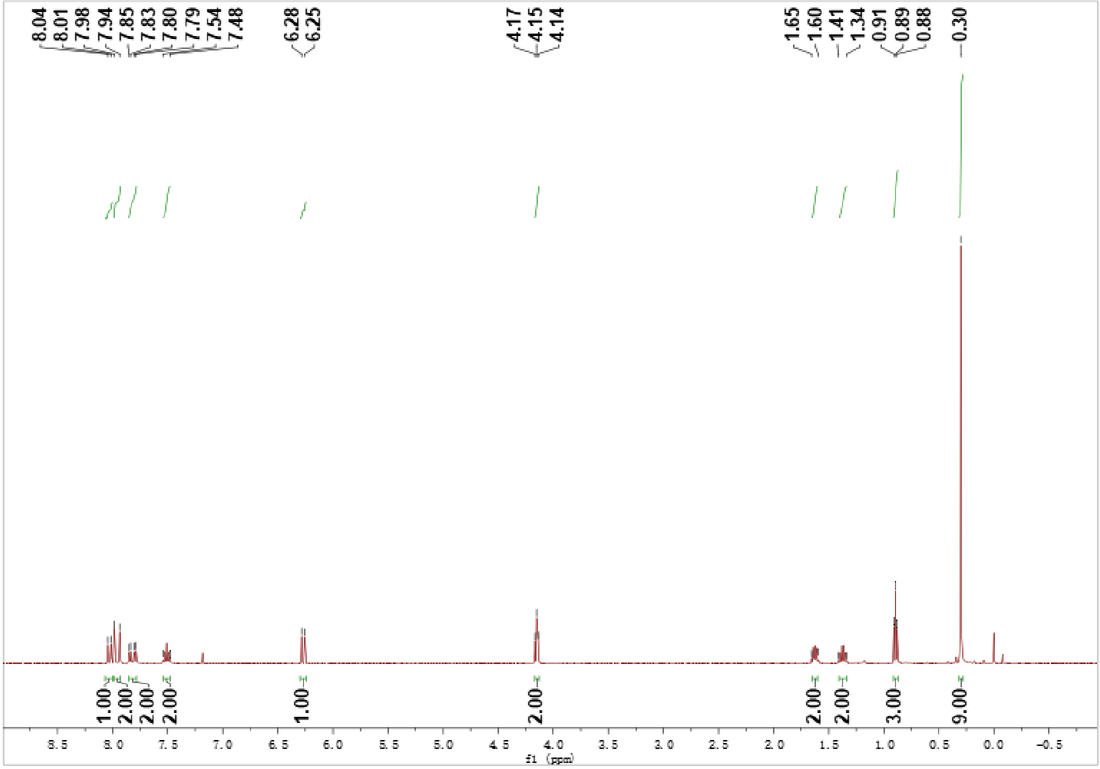
COOBu

(3la)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7.54
7.48
6.28
6.25
4.17
4.15
4.14
1.65
1.60
1.41
1.34
0.91
0.89
0.88
0.30
1.00
2.00
2.00
2.00
1.00
2.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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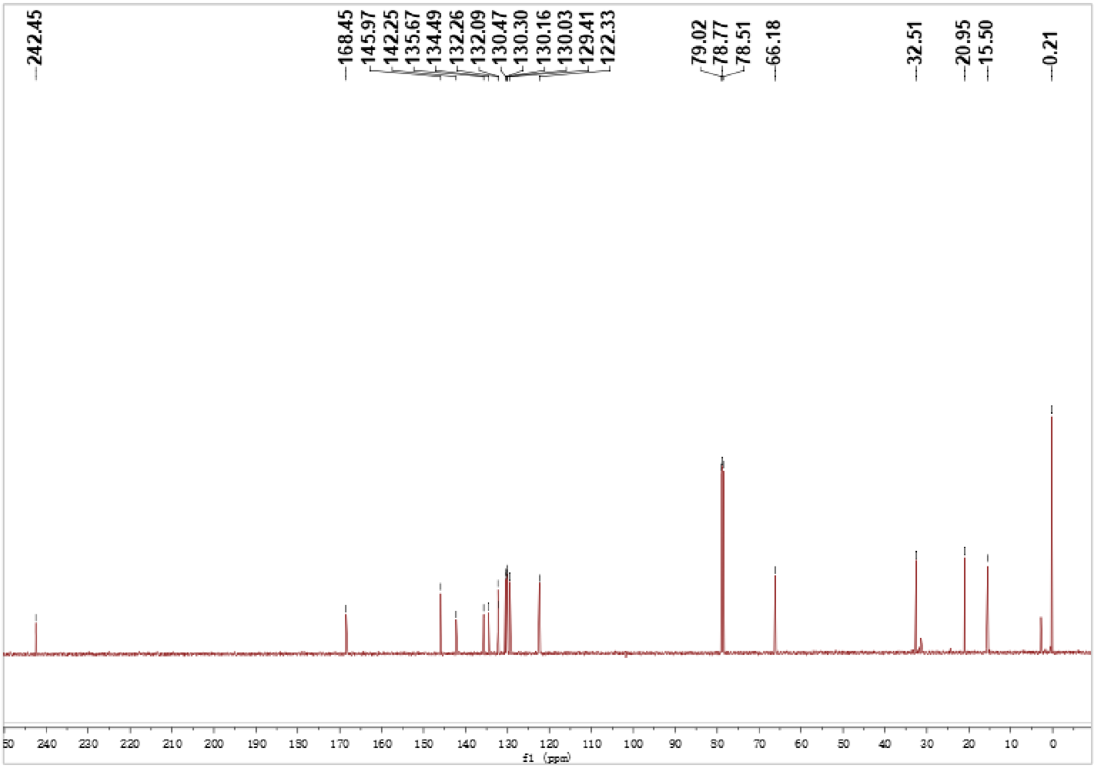
0.5
0.0
-0.5
f1 (ppm)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134.49
132.26
132.09
130.47
130.30
130.16
130.03
129.41
122.33
79.02
78.77
78.51
66.18
32.51
20.95
15.50
-0.21
50
240
230
220
210
200
190
180
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130
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100
90
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70
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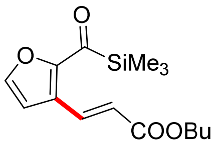
0
f1 (ppm)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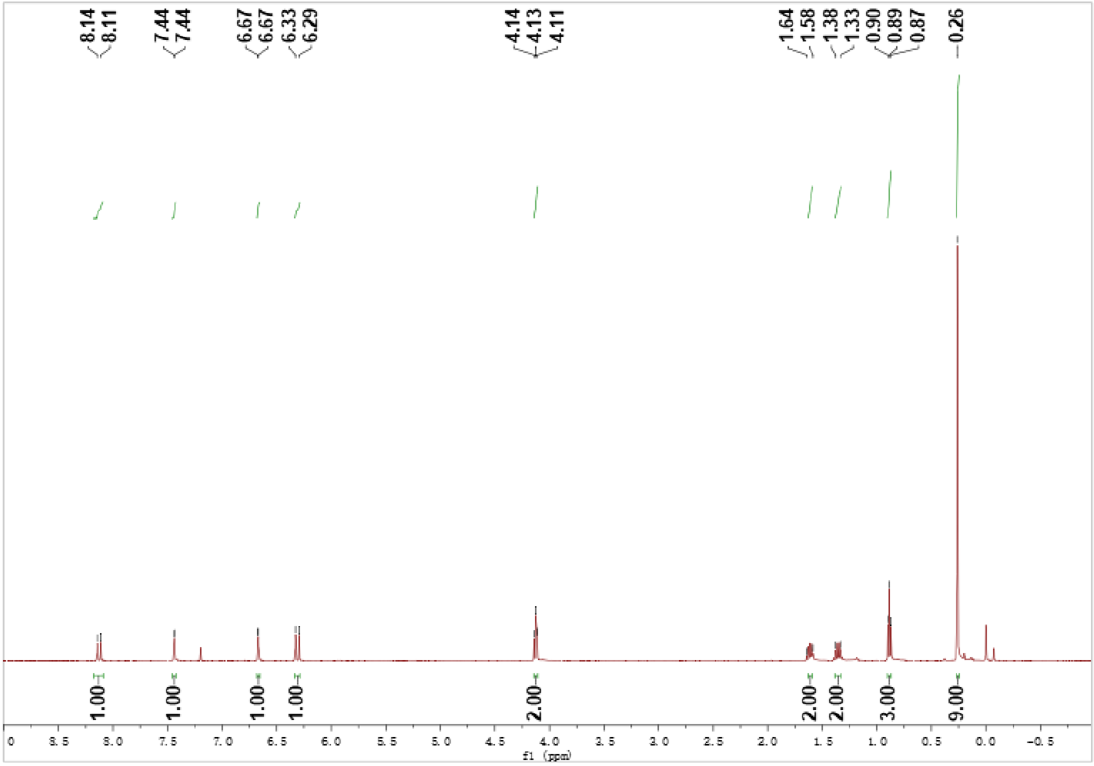
O
COOBu

(3ma)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6.29
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4.13
4.11
1.64
1.58
1.38
1.33
0.90
0.89
0.87
0.26
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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0.5
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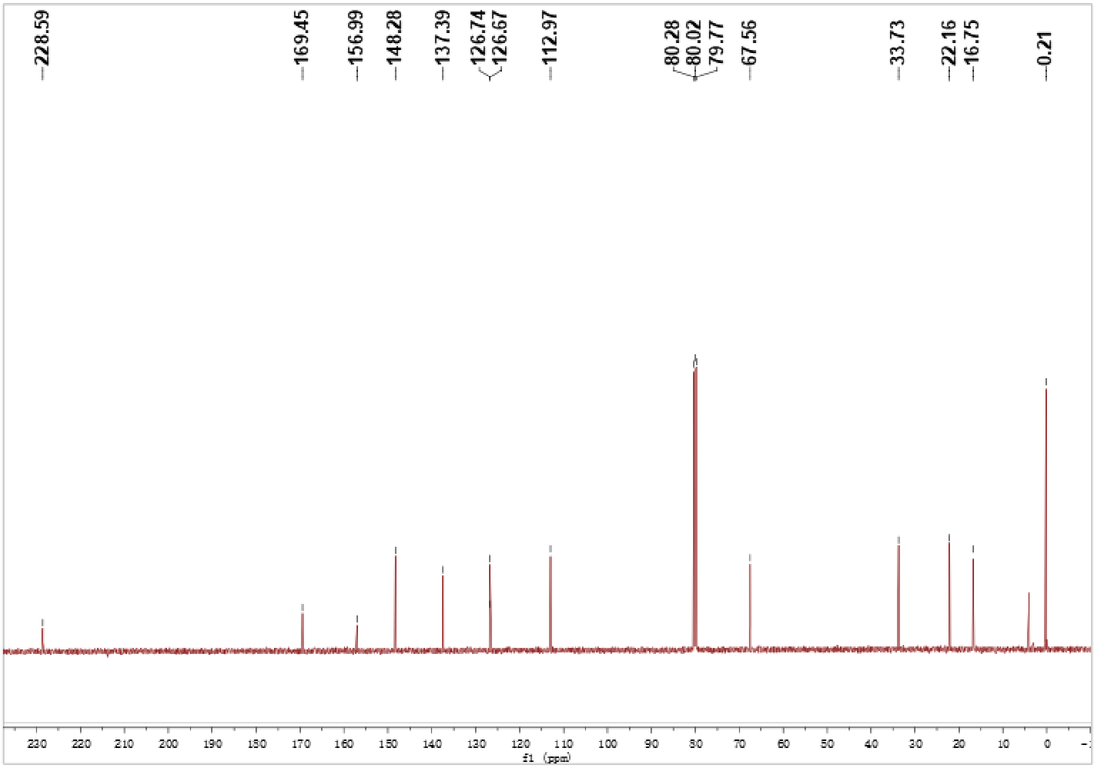
-0.5
f1 (ppm)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80.02
79.77
67.56
33.73
22.16
16.75
0.21
230
220
210
200
190
180
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150
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130
120
110
100
90
80
70
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40
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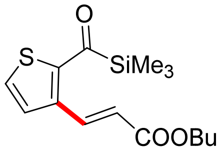
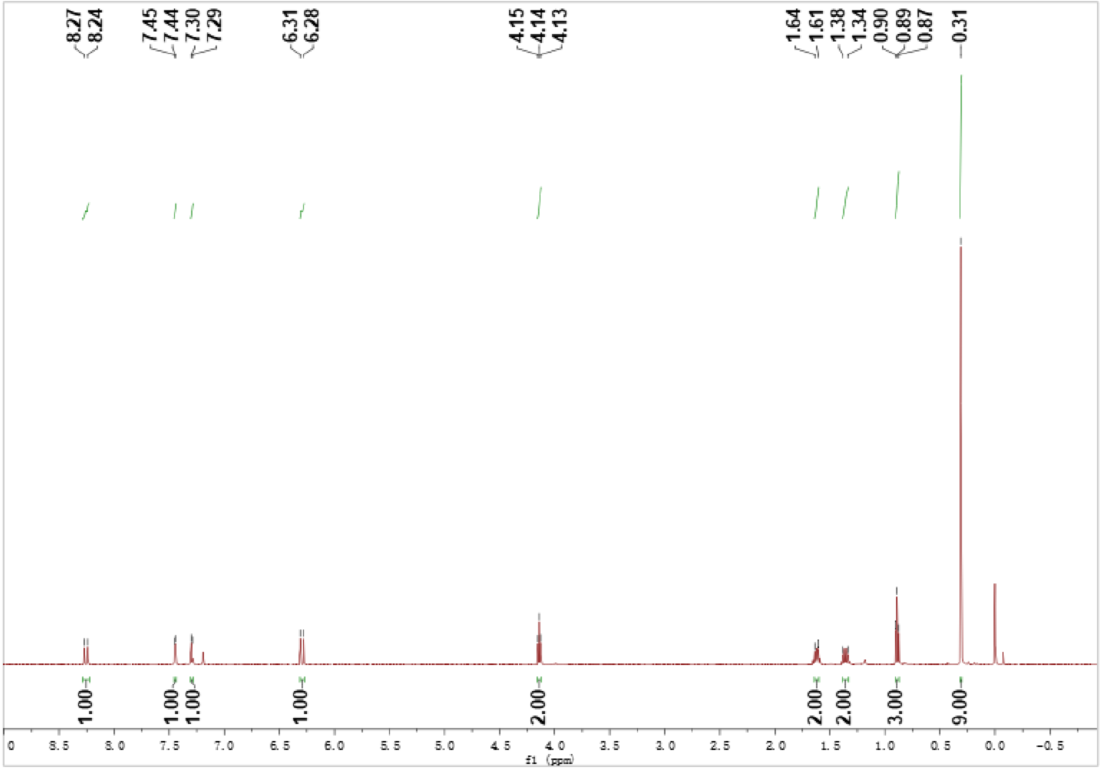
20
10
0
f1 (ppm)


O
S
SiMe3
COOBu

(3na)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6.31
6.28
4.15
4.14
4.13
1.64
1.61
1.38
1.34
0.90
0.89
0.87
0.31
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
9.00
8.5
8.0
7.5
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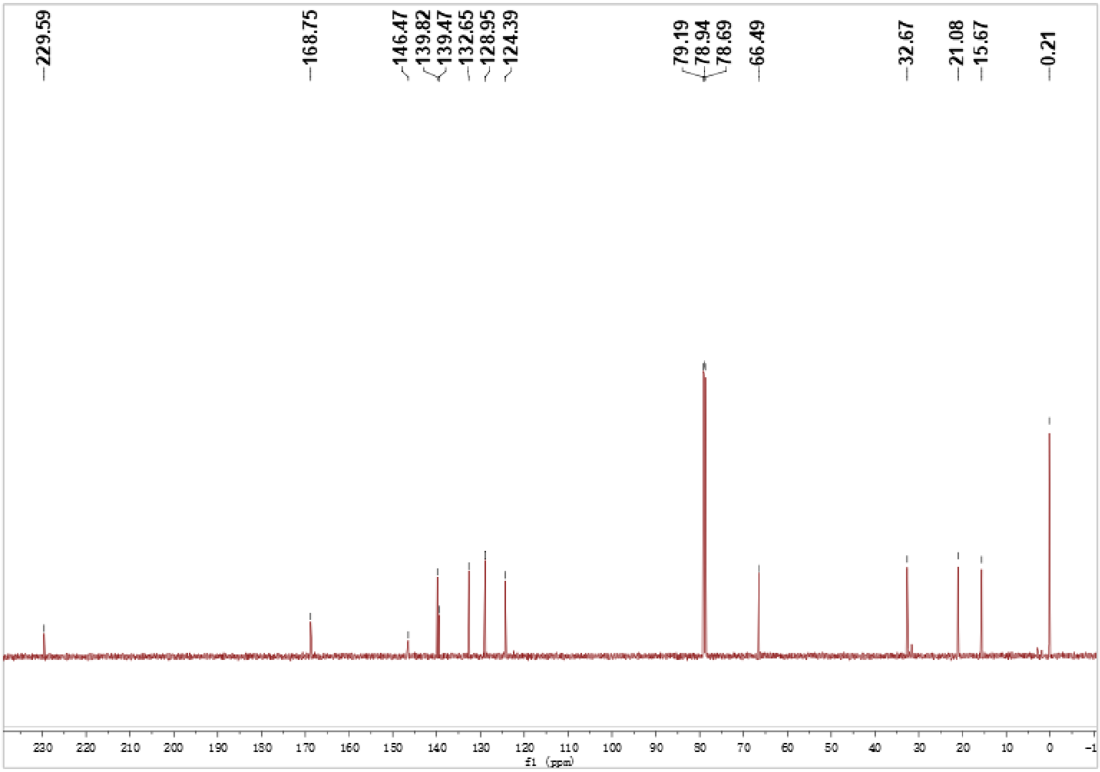
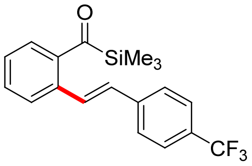
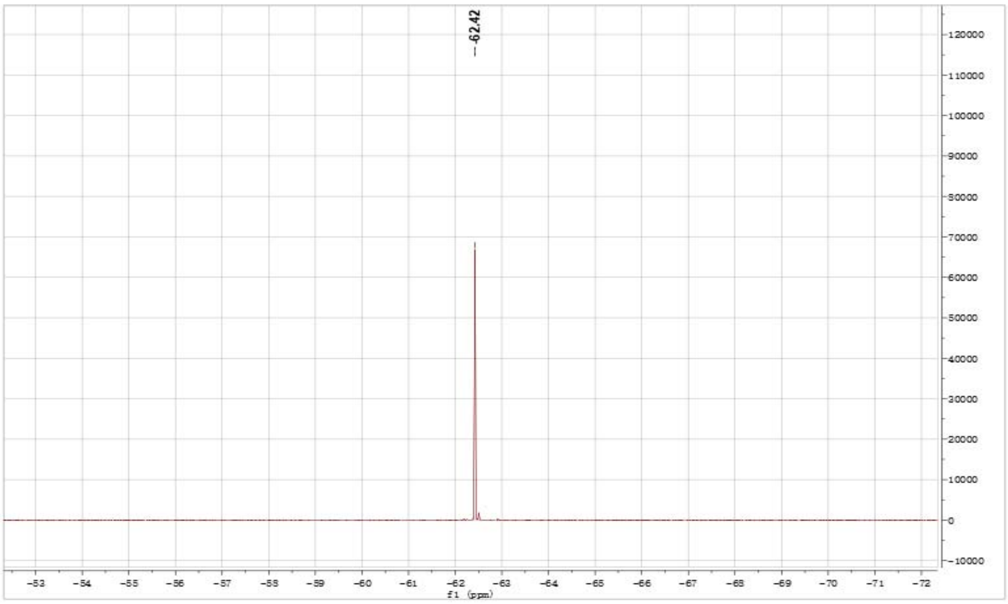
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

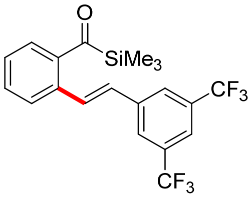

229.59
168.75
146.47
139.82
139.47
132.65
128.95
124.39
79.19
78.94
78.69
66.49
32.67
21.08
15.67
0.21
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR charts

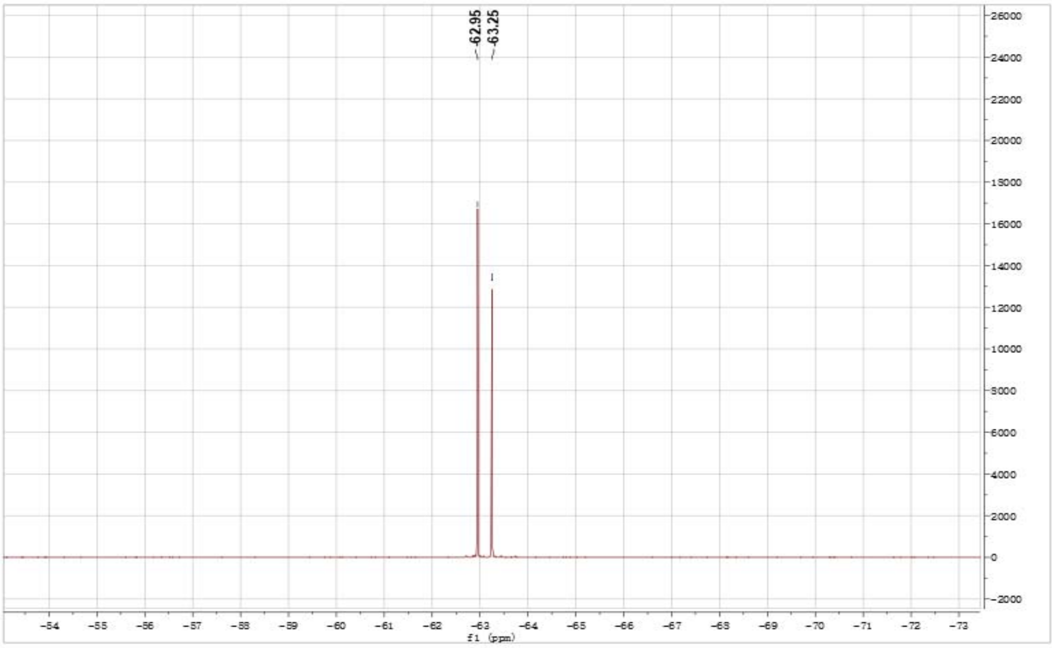


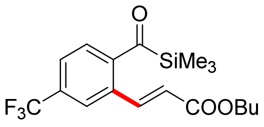
(3aj)



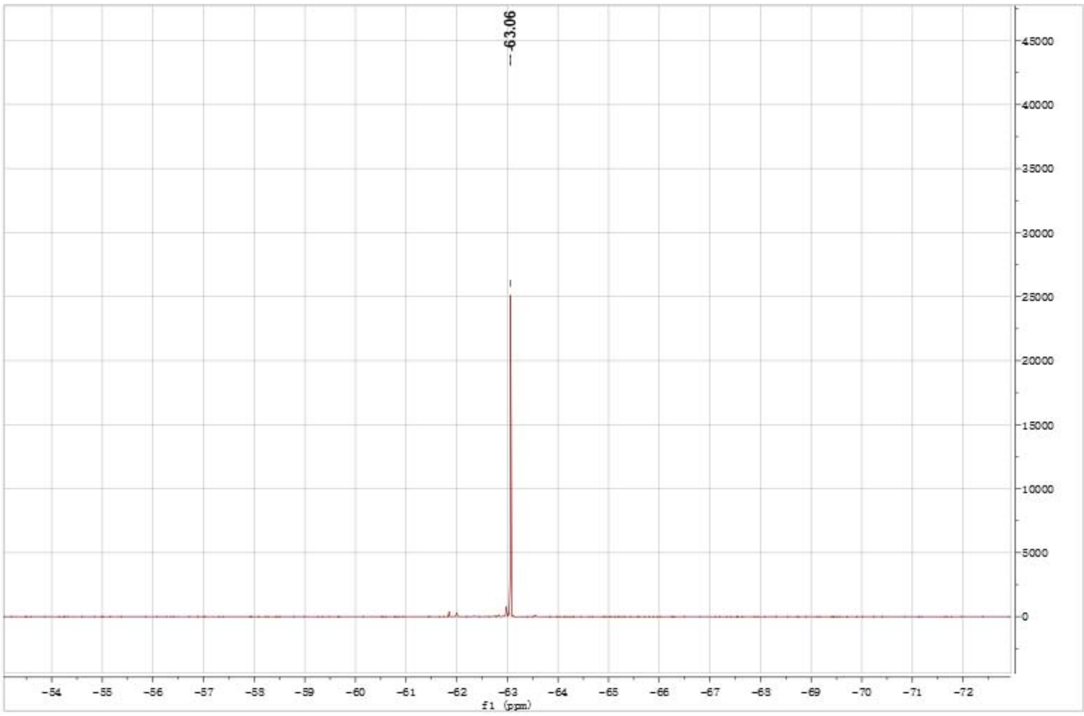


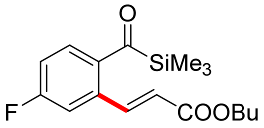
(3ak)



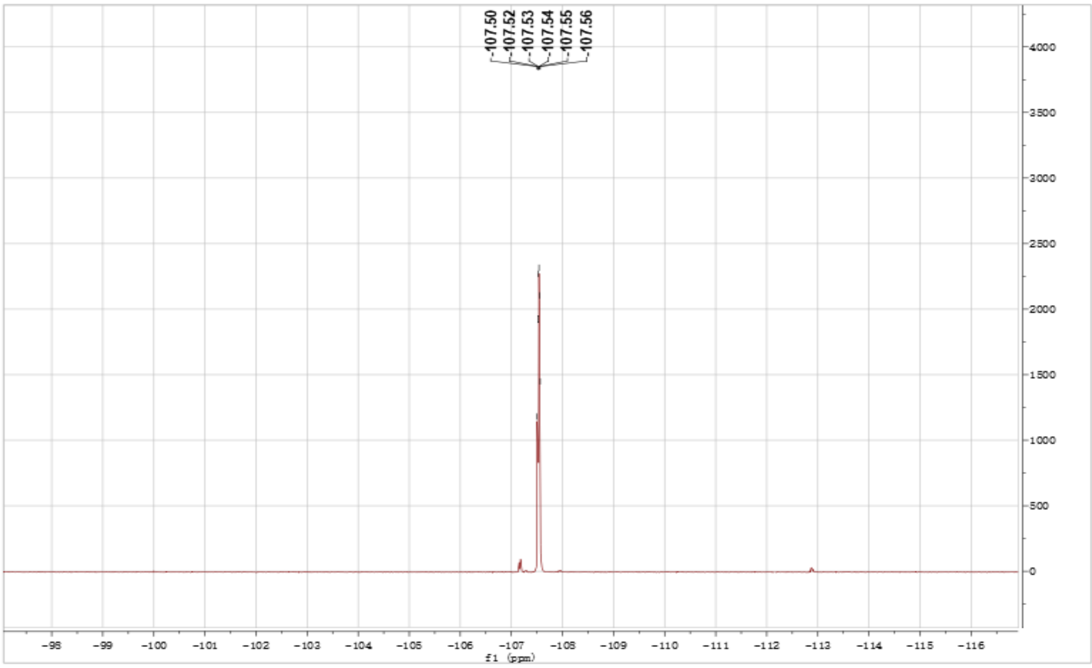

O
SiMe3
F3C
COOBu

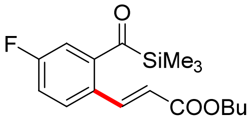
(3ea)


-63.06
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
f1 (ppm)

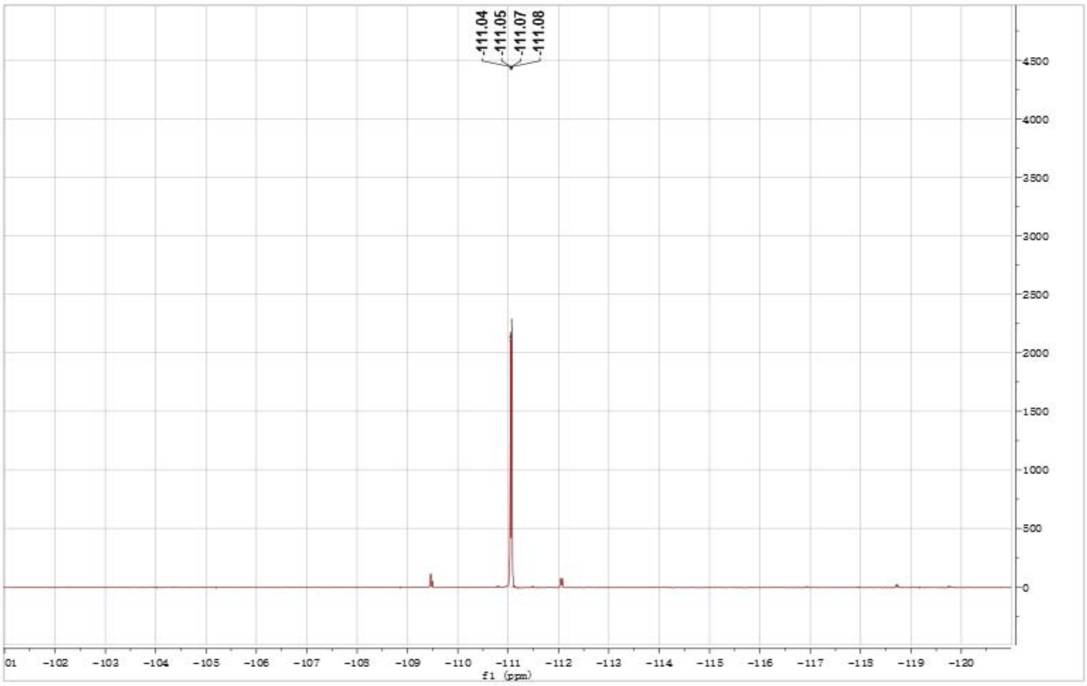

O
SiMe3
F
COOBu

(3ha)


-107.50
-107.52
-107.53
-107.54
-107.55
-107.56
4000
3500
3000
2500
2000
1500
1000
500
0
-98
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
f1 (ppm)


F
O
SiMe3
COOBu

(3ia)


-111.04
-111.05
-111.07
-111.08
4500
4000
3500
3000
2500
2000
1500
1000
500
0
01
−102
−103
−104
−105
−106
−107
−108
−109
−110
−111
−112
−113
−114
−115
−116
−117
−118
−119
−120
f1 (ppm)