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Supporting Information

For the article entitled

Ruthenium-catalyzed olefinic C–H alkenylation of enol-carbamates: highly stereo-selective synthesis of (*Z*,*Z*) and (*Z*,*E*)-butadienes

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Supporting Information

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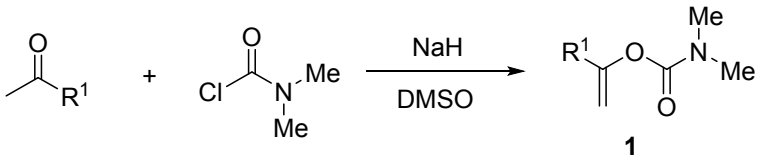
General methods

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 and 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 acetic anhydride were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from Alfa Aesar (China) Chemical Co., Ltd. and used without further purification.

General Procedure for the Preparation of N,N-dimethyl Enol-Carbamates



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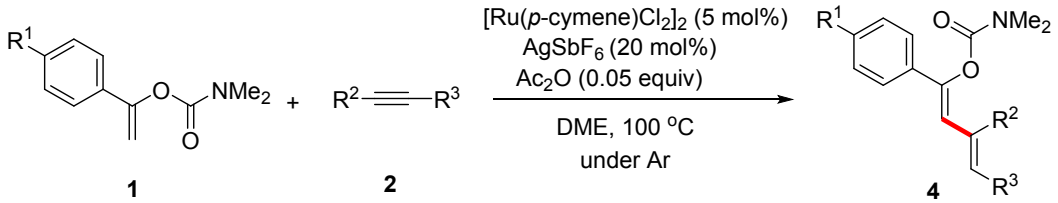
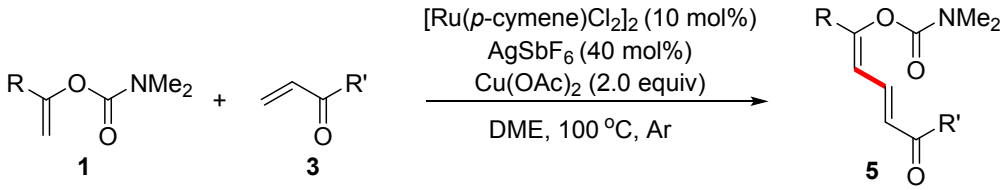
Typical procedure: Sodium hydride (264 mg, 10.0 mmol, 1.1 equiv, 60 % suspension in oil) was added in portions to dry DMSO (20 mL). After stirring for 2 h at 50°C the mixture was cooled to room temperature. A grey solution acetophenone (1.2 g, 10.0 mmol, 1.0 equiv) in 1 mL dry DMSO was added in dropwise in 15 minutes, the reaction was slightly exothermic and the color of the solution changed to yellow. This solution was allowed to stir for an additional 15 min. , then dimethylcarbamoyl chloride (1.8 mL, 11.0 mmol, 1.1 equiv) in 1 mL DMSO was added in dropwise in 15 min. After stirring for overnight, the reaction was quenched by water (30 mL), and the mixture was extracted with Et_2O (3 × 30 mL) and the combined extracts were washed with brine and dried over magnesium sulfate. Purification by flash chromatography (pentane/ethyl acetate mixtures) afforded the desired enol carbamate **1**.

General Procedure for Ru-Catalyzed Cross-Coupling of Enol Carbamates with Alkynes



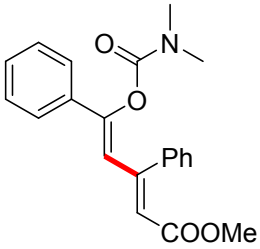
An oven-dried screw-cap vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol%, 0.01 mmol), $AgSbF_6$ (20.0 mol%, 0.04 mmol) and DME (1.0 mL). Then, enol carbamate **1** (1.0 eq, 0.20 mmol), alkyne **2** (2.0 eq, 0.4 mmol) and acetic anhydride (0.05 eq, 0.01mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 ℃ with stirring for 16 hours. After cooling down, the mixture was concentrated to give the crude product which was directly applied to a flash column chromatography (EtOAc/Petroleum ether mixtures) for separation.

General Procedure for Ru-Catalyzed Cross-Coupling of Enol Carbamates with Alkenes



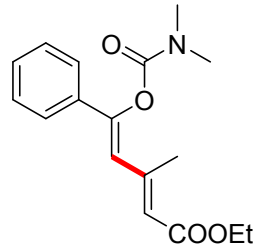
An oven-dried screw-cap vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (10.0 mol%, 0.02 mmol), $AgSbF_6$ (40.0 mol%, 0.08 mmol) and DME (1.0 mL). Then, enol carbamate (1.0 eq, 0.20 mmol), alkene **3** (2.0 eq, 0.4 mmol) and copper acetate (2.0 eq, 0.4 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 ℃ with stirring for 16 hours. After cooling down, the mixture was concentrated to give the crude product which was directly applied to a flash column chromatography (EtOAc/Petroleum ether mixtures) for purification.

Characterization of Products



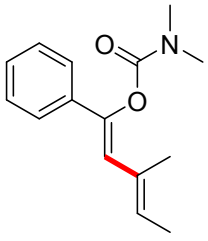
Methyl (2*Z*,4*Z*)-5-(dimethylcarbamoyl)oxy)-3,5-diphenylpenta-2,4-dienoate (**4aa**)

White solid, m.p.: 143.9 °C, yield = 86%. ^{1}H NMR ($CDCl_3$): δ = 7.44 (d, 2H, *J* = 7.0 Hz), 7.36-7.28 (m, 8H), 6.79 (s, 1H), 6.39 (s, 1H), 3.75 (s, 3H), 3.13 (s, 3H), 2.96 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 169.39, 153.27, 147.31, 135.51, 135.30, 134.56, 129.94, 128.81, 128.66, 128.51, 128.41, 128.21, 124.82, 115.83, 51.83, 36.74, 36.50. HRMS (ESI): m/z calculated for C_{21} H_{21} NO_4 $[M+H]^+$: 352.1543, found: 352.1546. FTIR (KBr, cm^{-1}): 3794.42, 3345.69, 3251.45, 3207.74, 3160.44, 2357.33, 1667.57, 1505.11, 1470.67, 1020.66.



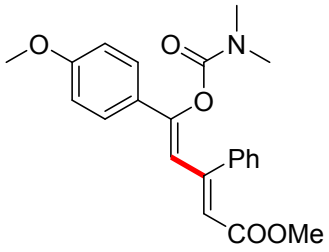
Ethyl (2*E*, 4*Z*)-5-((dimethylcarbamoyl)oxy)-3-methyl-5-phenylpenta-2,4-dienoate(**4ab**)

Yellow oil, yield = 47%. ^{1}H NMR ($CDCl_3$): δ = 7.41 (d, 2H, *J* = 3.8 Hz), 7.34-7.31 (m, 3H), 6.27 (s, 1H), 6.15 (q, 1H, *J* = 7.0 Hz), 4.22 (q, 2H, *J* = 7.0 Hz), 3.11 (s, 3H), 2.95 (s, 3H), 1.93 (d, 3H, *J* = 7.0 Hz), 1.33 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ = 167.96, 153.53, 145.93, 135.81, 135.47, 130.42, 128.53, 128.41, 124.70, 114.68, 60.63, 36.70, 36.42, 15.45, 14.21. HRMS (ESI): m/z calculated for $C_{17}H_{21}NO_4$ $[M+H]^+$: 304.1543, found: 304.1544. FTIR (KBr, cm^{-1}): 3897.52, 3542.56, 3417.76, 3332.02, 3226.01, 1732.20, 1633.87, 1515.16, 1455.31, 1012.27.



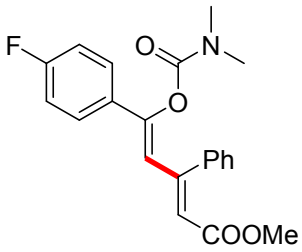
(1*Z*, 3*E*)-3-methyl-1-phenylpenta-1, 3-dien-1-yl dimethylcarbamate (**4ac**)

Brown oil, yield = 55%. ^{1}H NMR (CDCl3): δ =7.42 (d, 2H, *J* = 7.0 Hz), 7.32-7.29 (m, 3H), 6.25 (s, 1H), 5.73 (q, 1H, *J* = 7.0 Hz), 3.16 (s, 3H), 2.98 (s, 3H), 1.91 (s, 3H), 1.74 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 154.45, 143.20, 136.96, 132.11, 128.98, 128.46, 127.74, 124.46, 121.49, 36.78, 26.43, 14.42, 13.87. HRMS (ESI): m/z calculated for $C_{15}H_{19}NO_2$ $[M+H]^+$: 246.1489, found: 246.1482. FTIR (KBr, cm-1): 3355.18, 3299.42, 3251.21, 2354.54, 1732.22, 1667.57, 1621.55, 1360.57, 1246.90.



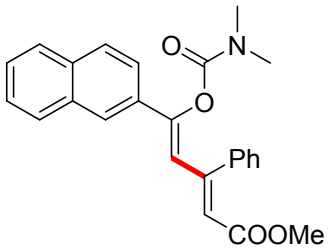
Methyl (2*Z*, 4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(4-methoxyphenyl)-3-phenylpenta-2,4-dienoate (**4ca**)

Yellow solid, m.p.: 125.1 °C, yield = 71%. ^{1}H NMR ($CDCl_3$): δ = 7.38 (d, 2H, *J* = 9.0 Hz), 7.30-7.26 (m, 5H), 6.88 (s, 1H), 6.87 (s, 1H), 6.11 (s, 1H), 6.75 (s, 1H), 6.29 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.12 (s, 3H), 2.96 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 169.52, 160.14, 153.32, 147.21, 135.44, 133.68, 130.10, 128.48, 128.23, 128.14, 126.27, 114.19, 114.15, 55.33, 51.80, 36.73, 36.48. HRMS (ESI): m/z calculated for $C_{22}H_{23}NO_5$ $[M+H]^+$: 382.1649, found: 382.1644. FTIR (KBr, cm^{-1}): 3819.03, 3445.14, 3332.19, 3262.67, 1614.70, 1574.30, 1455.27, 1434.73, 1416.86, 1293.01.



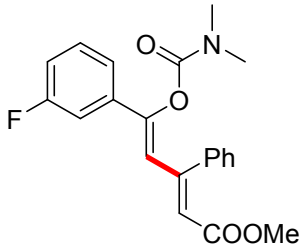
Methyl (2*Z*, 4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(4-fluorophenyl)-3-phenylpenta-2,4-dienoate (**4da**)

Yellow solid, m.p.: 204.1 °C, yield = 67%. ^{1}H NMR ($CDCl_3$): δ = 7.44-7.41 (m, 2H), 7.34-7.28 (m, 5H), 7.06-7.02 (m, 2H), 6.79 (s, 1H), 6.31 (s, 1H), 3.75 (s, 3H), 3.12 (s, 3H), 2.96 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 169.29, 161.00 ($J_{C\text{-}F}$ = 252.5 Hz), 153.17, 146.39, 135.22, 134.72, 131.83 ($J_{C\text{-}F}$ = 3.4 Hz), 129.74, 128.52, 128.47, 128.20, 126.76 ($J_{C\text{-}F}$ = 8.3 Hz), 126.70 ($J_{C\text{-}F}$ = 21.3 Hz), 115.74 ($J_{C\text{-}F}$ = 1.4 Hz), 51.85, 36.76, 36.49. HRMS (ESI): m/z calculated for $C_{21}H_{20}FNO_4$ $[M+H]^+$: 370.1449, found: 370.1458. FTIR (KBr, cm^{-1}): 3262.26, 3285.95, 1732.15, 1651.55, 1505.17, 1428.03, 1372.40, 1337.26, 1025.71.



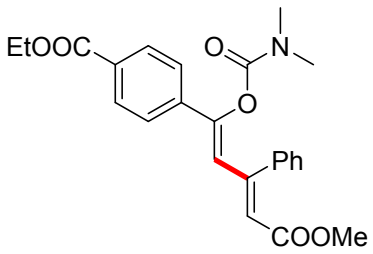
Methyl (2*Z*, 4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(naphthalen-2-yl)-3-phenylpenta-2,4-dienoate (**4ba**)

White oil, yield = 63%. ^{1}H NMR ($CDCl_3$): δ = 7.79-7.72 (m, 4H), 7.52-7.59 (m, 1H), 7.42-7.38 (m, 2H), 7.27-7.26 (s, 2H), 7.19 (s, 3H), 6.77 (s, 1H), 6.46 (s, 1H), 3.71 (s, 3H), 3.13 (s, 3H), 2.91 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 168.39, 152.32, 146.33, 134.29, 133.68, 132.43, 132.18, 131.90, 128.96, 127.50, 127.45, 127.44, 127.41, 127.21, 126.63, 125.49, 125.43, 123.13, 121.54, 115.35, 50.84, 35.76, 35.55. HRMS (ESI): m/z calculated for $C_{25}H_{23}NO_4$ $[M+H]^+$: 402.1701, found: 402.1698. FTIR (KBr, cm^{-1}): 3542.47, 3331.87, 1866.36, 1790.05, 1694.20, 1557.25, 1416.79, 1385.11, 1360.27, 1027.45.



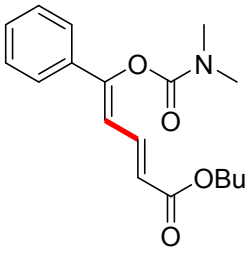
Methyl (2*Z*, 4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(3-fluorophenyl)-3-phenylpenta-2,4-dienoate (**4la**)

Brown oil, yield = 64%, ^{1}H NMR ($CDCl_3$): δ = 7.25 – 7.20 (m, 6H), 7.18 – 7.15 (m, 1H), 7.05 – 7.02 (m, 1H), 6.94 – 6.90 (m, 1H), 6.74 (s, 1H), 6.32 (d, 1H, *J* = 1.0 Hz), 3.68 (s, 3H), 3.05 (s, 3H), 2.89 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 169.19, 163.94, 161.98, 153.13, 145.94, 137.91 (d, J_{C-F} = 7.8 Hz), 135.40, 135.10, 130.26 (d, J_{C-F} = 8.4 Hz), 129.57, 128.58 (d, J_{C-F} = 7.3 Hz), 128.26, 120.53 (d, J_{C-F} = 2.6 Hz), 116.86, 115.65 (d, J_{C-F} = 21.3 Hz), 111.79 (d, J_{C-F} = 23.3 Hz), 51.89, 36.77, 36.50. HRMS (ESI): m/z calculated for $C_{21}H_{20}FNO_4$ $[M+H]^+$: 370.1449, found: 370.1439. FTIR (KBr, cm^{-1}): 3261.39, 3238.83, 1732.14, 1644.86, 1574.34, 1515.16, 1494.94, 1360.49, 1157.49, 1047.28.



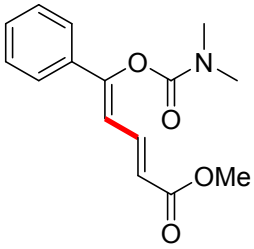
Ethyl-4-((1Z,3Z)-1-((dimethylcarbamoyl)oxy)-5-methoxy-5-oxo-3-phenylpenta-1,3-dien-yl)benzoate(**4ja**)

Brown solid, yield = 18%, m.p.: 114.0 °C, ^{1}H NMR ($CDCl_3$): δ = 7.96 (d, 2H, *J* = 8.5 Hz), 7.43 (d, 2H, *J* = 8.5 Hz), 7.27 – 7.25 (m, 5H), 6.77 (s, 1H), 6.41 (s, 1H), 4.32 (q, 2H, J = 7.5 Hz), 3.69 (s, 3H), 3.07 (s, 3H), 2.89 (s, 3H), 1.33 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 168.14, 165.07, 152.08, 145.23, 138.72, 134.76, 134.04, 129.38, 128.94, 128.59, 127.66, 127.54, 127.27, 123.58, 116.63, 60.01, 50.88, 35.76, 35.50, 13.31. HRMS (ESI): m/z calculated for $C_{24}H_{25}NO_6$ $[M+H]^+$: 424.1755, found: 424.1750. FTIR (KBr, cm^{-1}): 3851.07, 3742.89, 3646.42, 3626.79, 2340.55, 1651.68, 1557.49, 1538.62, 1505.40, 668.10.



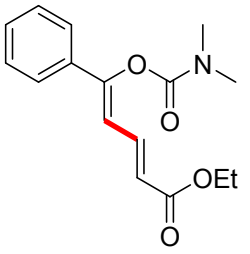
Butyl (2*E*, 4*Z*)-5-((dimethylcarbamoyl)oxy)-5-phenylpenta-2,4-dienoate (**5ad**)

Brown oil, yield = 63%. ^{1}H NMR ($CDCl_3$): δ = 7.50 (dd, 1H, *J* = 11.5, 15.0 Hz), 7.44-7.42 (m, 2H), 7.30-7.28 (m, 3H), 6.46 (d, 1H, *J* = 11.5 Hz), 5.95 (d, 1H, *J* = 15.0 Hz, 4.10 (t, 2H, *J* = 7.0 Hz), 3.15 (s, 3H), 2.93 (s, 3H), 1.62-1.56 (m, 2H), 1.37-1.32 (m, 2H), 0.88 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ = 166.06, 152.61, 151.65, 136.55, 133.51, 128.59, 127.72, 124.12, 120.99, 113.82, 63.28, 35.84, 35.57, 29.73, 18.17, 12.73. HRMS (ESI): m/z calculated for $C_{18}H_{23}NO_4$ $[M+H]^+$: 318.1730, found: 318.1738. FTIR (KBr, cm^{-1}): 3654.39, 3317.35, 3286.21, 3225.41, 2358.00, 2338.67, 1651.65, 1621.58, 1403.29, 1029.50.



Methyl (2E, 4Z)-5-((dimethylcarbamoyl)oxy)-5-phenylpenta-2,4-dienoate (**5ae**)

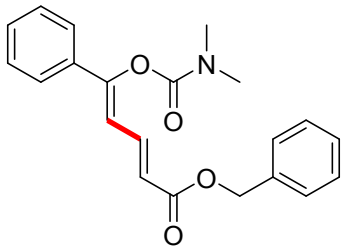
White solid, m.p.: 111.1 °C, yield = 69%. ^{1}H NMR ($CDCl_3$): δ = 7.52 (dd, 1H, *J* = 11.5, 15.5 Hz), 7.44-7.42 (m, 2H), 7.30-7.29 (m, 3H), 6.46 (d, 1H, *J* = 11.5 Hz), 5.97 (d, 1H, *J* = 15.5 Hz), 3.70 (s, 3H), 3.15 (s, 3H), 2.93 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 167.42, 153.60, 152.80, 137.86, 134.51, 129.66, 128.76, 125.16, 121.51, 114.87, 51.61, 36.88, 36.64. HRMS (ESI): m/z calculated for $C_{15}H_{17}NO_4$ $[M+H]^+$: 276.1243, found: 276.1252. FTIR (KBr, cm^{-1}): 3550.55, 3260.30, 3240.09, 1714.37, 1667.49, 1574.35, 1434.77, 1392.99, 1246.76, 1011.28.



Ethyl (2E, 4Z)-5-((dimethylcarbamoyl)oxy)-5-phenylpenta-2,4-dienoate (**5af**)

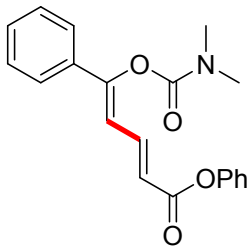
White solid, m.p.: 63.2 °C, yield = 69%. ^{1}H NMR ($CDCl_3$) : δ = 7.52 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.44-7.42 (m, 2H), 7.33 – 7.26 (m, 3H), 6.46 (d, 1H, *J* = 11.5 Hz), 5.96 (d, 1H, *J* = 15.5 Hz), 4.15 (q, 2H , *J* = 7.5 Hz), 3.15 (s, 3H), 2.93 (s, 3H), 1.24 (t, 3H, *J* = 7.0 Hz,). ^{13}C NMR ($CDCl_3$): δ = 165.98, 152.60, 151.66, 136.58, 133.52, 128.59, 127.73, 124.12, 120.98, 113.85, 59.37, 35.85, 35.60, 13.29. HRMS (ESI): m/z calculated for $C_{16}H_{19}NO_4$ $[M+H]^+$:

290.1389, found: 290.1398. FTIR (KBr, cm^{-1}): 3331.91, 3299.11, 2352.40, 1841.88, 1660.54, 1567.65, 1422.83, 1360.18, 1336.71, 1029.36.



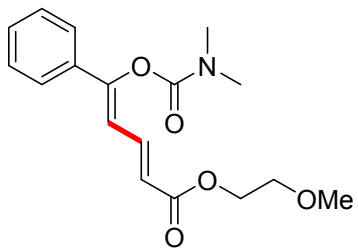
Benzyl (2E, 4Z)-5-((1-(dimethylamino)vinyl)oxy)-5-phenylpenta-2,4-dienoate (**5ag**)

Yellow solid, m.p.: 95.7 °C, yield = 49%. ^{1}H NMR ($CDCl_3$): δ = 7.56 (dd, 1H, *J* = 11.5, 15.5 Hz), 7.44-7.42 (m, 2H), 7.34-7.27 (m, 8H), 6.46 (d, 1H, *J* = 11.5 Hz), 6.01 (d, 1H, *J* = 15.5 Hz), 5.14 (s, 2H), 3.12 (s, 3H), 2.91 (s, 3H). ^{13}C NMR ($CDCl_3$):δ = 165.77, 152.56, 151.96, 137.21, 135.12, 133.44, 128.67, 127.73, 127.52, 127.15, 127.13, 124.16, 120.45, 113.74, 65.19, 35.83, 35.57. HRMS (ESI): m/z calculated for $C_{22}H_{23}NO_3$ $[M+H]^+$: 350.1751, found: 350.1760. FTIR (KBr, cm^{-1}): 3896.79, 3538.64, 3451.86, 1738.08, 1660.00, 1574.16, 1494.81, 1360.32, 1030.14, 666.25.



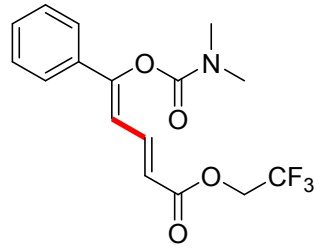
Phenyl (2E, 4Z)-5-((dimethylcarbamoyl)oxy)-5-phenylpenta-2,4-dienoate (**5ah**)

Yellow solid, m.p.: 149.7 °C, yield = 60%. ^{1}H NMR ($CDCl_3$) : δ = 7.67 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.48 – 7.44(m, 2H), 7.34 – 7.30 (m, 5H), 7.17 (d, 1H, *J* = 8.0 Hz), 7.07 (d, 2H, *J* = 8.0 Hz), 6.54 (d, 1H, *J* = 11.5 Hz), 6.15 (d, 1H, *J* = 15.5 Hz), 3.14 (s, 3H), 2.92 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 164.38, 152.55, 149.81, 138.51, 133.36, 128.86, 128.38, 127.80, 127.62, 124.70, 124.26, 120.65, 119.85, 113.71, 35.87, 35.61. HRMS (ESI): m/z calculated for $C_{20}H_{19}NO_4$ $[M+H]^+$: 338.1387, found: 338.1388. FTIR (KBr, m^{-1}): 3417.70, 3299.37, 2357.91, 1694.29, 1667.59, 1574.42, 1434.81, 1372.54, 1030.37, 667.89.



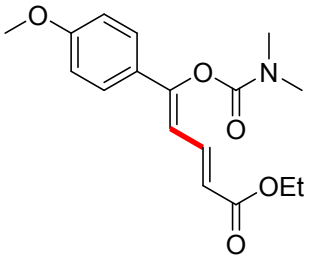
2-Methoxyethyl (2*E*, 4*Z*)-5-((dimethylcarbamoyl)oxy)-5-phenylpenta-2,4-dienoate (**5ai**)

Brown oil, yield = 43%. ^{1}H NMR ($CDCl_3$): δ = 7.55 (dd, 1H, *J* = 11.5, 15.5 Hz), 7.44-7.42 (m, 2H), 7.30-7.29 (m, 3H), 6.46 (d, 1H, *J* = 11.5 Hz), 6.01 (d, 1H, *J* = 15.0 Hz), 4.26 (t, 2H, *J* = 4.5 Hz), 4.57 (t, 2H, *J* = 5.0 Hz), 3.34 (s, 3H), 3.15 (s, 3H), 2.92 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 165.94, 152.58, 151.91, 137.16, 133.47, 128.66, 127.14, 124.16, 120.46, 113.81, 69.56, 62.48, 58.02, 35.84, 35.60. HRMS (ESI): m/z calculated for $C_{17}H_{21}NO_5$ $[M+H]^+$: 320.1492, found: 320.1500. FTIR (KBr, cm^{-1}): 3417.44, 3331.89, 1746.89, 1667.39, 1644.75, 1557.11, 1494.84, 1392.89, 1336.93, 1030.67.



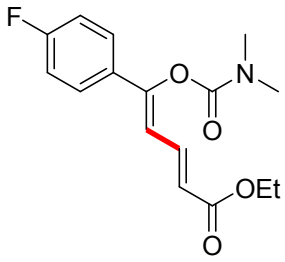
2, 2, 2-Trifluoroethyl (2E, 4Z)-5-((dimethylcarbamoyl)oxy)-5-phenylpenta-2,4-dienoate (**5aj**)

Yellow solid, m.p.: 74.9 °C, yield = 60%. ^{1}H NMR ($CDCl_3$): δ = 7.61 (dd, 1H, *J* = 11.5, 15.5 Hz), 7.46-7.44 (m, 2H), 7.32-7.30 (m, 3H), 6.48 (d, 1H, *J* = 11.5 Hz), 6.00 (d, 1H, *J* = 15.5 Hz), 4.50 (q, 2H, *J* = 8.5 Hz), 3.15 (s, 3H), 2.93 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 165.15, 154.05, 153.51, 140.13, 134.27, 130.00, 128.83, 125.33, 121.10 (q, J_{C-F} = 275.0 Hz), 119.30, 114.41, 60.32 (q, J_{C-F} = 36.3 Hz), 36.88, 36.60. HRMS (ESI): m/z calculated for $C_{16}H_{16}F_3NO_4$ $[M+H]^+$: 344.1104, found: 344.1110. FTIR (KBr, cm^{-1}): 3896.81, 3353.99, 1731.97, 1660.53, 1557.06, 1470.61, 1403.07, 1360.31, 1336.87, 1027.40.



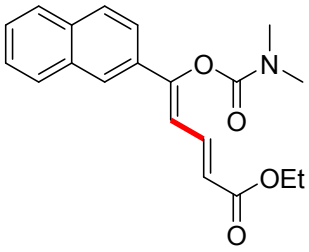
(2E, 4Z)-Ethyl-5-(dimethylcarbamoyloxy)-5-(4-methoxyphenyl)penta-2,4-dienoate (**5cf**)

Yellow solid, m.p.: 101.3 °C, yield = 68%. ^{1}H NMR ($CDCl_3$) δ = 7.48 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.37 (d, 2H, *J* = 9.0 Hz), 6.81 (d, 2H, *J* = 9.0 Hz), 6.36 (d, 1H, *J* = 11.5 Hz), 5.91 (d, 1H, *J* = 15.4 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 3.74 (s, 3H), 3.14 (s, 3H), 2.93 (s, 3H), 1.23 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ = 166.16, 159.79, 152.70, 151.6, 136.90, 126.07, 125.70, 119.92, 113.22, 112.12, 59.28, 54.35, 35.84, 35.58, 13.30. HRMS (ESI): m/z calculated for $C_{17}H_{21}NO_5$ $[M+H]^+$: 320.1492, found: 320.1496. FTIR (KBr, cm^{-1}): 3417.57, 3332.17, 1682.25, 1557.15, 1515.04, 1455.93, 1403.12, 1372.74, 1336.82, 1030.07.



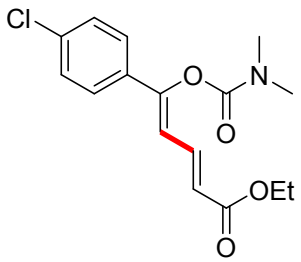
(2E, 4Z)-Ethyl-5-(4-fluorophenyl)-5-(dimethylcarbamoyloxy)penta-2,4-dienoate (**5df**)

Yellow solid, m.p.: 67.3 °C, yield = 70%. ^{1}H NMR ($CDCl_3$): δ = 7.47 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.44-7.40 (m, 2H), 7.00-6.97 (m, 2H), 6.38 (d, 1H, *J* = 11.5 Hz), 5.95 (d, 1H, *J* = 15.5 Hz), 4.15 (q, 2H, *J* = 7.0 Hz), 3.14 (s, 3H), 2.92 (s, 3H), 1.24 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.94, 162.01 (d, J_{C-F} = 249.0 Hz), 152.51, 150.70, 136.38, 129.86 (d, J_{C-F} = 3.8 Hz), 125.13 (d, J_{C-F} = 8.3 Hz), 121.09, 114.85 (d, J_{C-F} = 21.9 Hz), 113.70 (d, J_{C-F} = 1.3 Hz), 59.41, 35.86, 35.59, 13.28. HRMS (ESI): m/z calculated for $C_{16}H_{18}FNO_4$ $[M+H]^+$: 308.1293, found: 308.1297. FTIR (KBr, cm^{-1}): 3860.59, 3144.84, 2935.90, 2351.47, 1789.78, 1651.36, 1427.82, 1385.05, 1311.22, 1027.80.



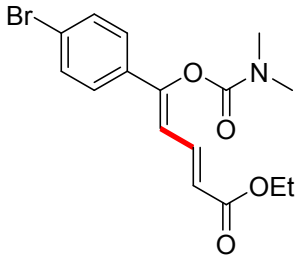
Ethyl (2E, 4Z)-5-((dimethylcarbamoyl)oxy)-5-(naphthalen-2-yl)penta-2,4-dienoate (**5bf**)

Brown solid, m.p.: 118.5 °C, yield = 60%. ^{1}H NMR ($CDCl_3$): δ = 7.86 (s, 1H), 7.78 – 7.72 (m, 3H), 7.55 (ddd, 2H, *J* = 11.4, 10.1, 8.2 Hz), 7.42 (dd, 2H, *J* = 6.2, 3.2 Hz), 6.60 (d, 1H, *J* = 11.5 Hz), 6.00 (d, 1H, *J* = 15.5 Hz), 4.17 (q, 2H, *J* = 7.0 Hz), 3.22(s, 3H), 2.95 (s, 3H), 1.25 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 166.01, 152.70, 151.72, 136.60, 132.78, 132.08, 130.87, 127.62, 127.57, 126.66, 125.95, 125.60, 123.89, 121.44, 121.05, 114.34, 59.40, 35.91, 35.68, 13.30. HRMS (ESI): m/z calculated for $C_{20}H_{21}NO_4$ $[M+H]^+$: 340.1543, found: 340.1538. FTIR (KBr, cm^{-1}): 3286.15, 3262.62, 1732.18, 1698.66, 1557.36, 1486.99, 1403.26, 1360.55, 1253.93, 1030.37.



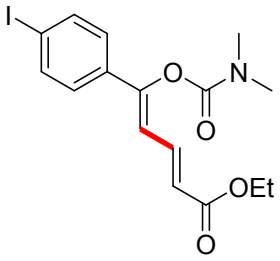
(2E, 4Z)-ethyl-5-(4-chlorophenyl)-5-(dimethylcarbamoyloxy)penta-2,4-dienoate (**5ef**)

Yellow solid, m.p.: 101.8 °C, yield = 60%. ^{1}H NMR ($CDCl_3$): δ = 7.47 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 7.26 (d, 2H, *J* = 8.5 Hz), 6.42 (d, 1H, *J* = 11.5 Hz), 5.96 (d, 1H, *J* = 15.5 Hz), 4.15 (q, 2H, *J* = 7.0 Hz), 3.13 (s, 3H), 2.92 (s, 3H), 1.23 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.87, 152.46, 150.55, 136.18, 134.51, 132.14, 127.99, 125.40, 121.47, 114.24, 59.45, 35.87, 35.60, 13.28. HRMS (ESI): m/z calculated for $C_{16}H_{18}ClNO_4$ $[M+H]^+$: 324.0997, found: 324.0996. FTIR (KBr, cm^{-1}): 3741.89, 3509.10, 1714.38, 1667.39, 1633.74, 1557.13, 1434.67, 1422.84, 1337.02, 1029.62.



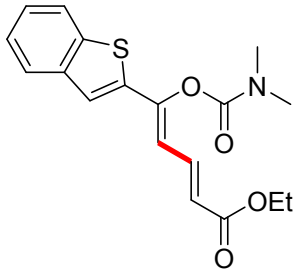
(2E, 4Z)-ethyl-5-(4-bromophenyl)-5-(dimethylcarbamoyloxy)penta-2,4-dienoate (**5ff**)

Yellow solid, m.p.: 105.5 °C, yield = 41%. ^{1}H NMR ($CDCl_3$): δ = 7.47 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.44 – 7.39 (m, 2H), 7.31 – 7.26 (m, 2H), 6.43 (d, 1H, *J* = 11.5 Hz), 5.96(d, 1H, *J* = 15.5 Hz), 4.15 (q, 2H, *J* = 7.0 Hz), 3.13 (s, 3H), 2.92 (s, 3H), 1.24 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.86, 152.44, 150.62, 136.20, 132.61, 130.93, 125.63, 122.81, 121.53, 114.30, 59.45, 35.87, 35.60, 13.28. HRMS (ESI): m/z calculated for $C_{16}H_{18}NO_4Br$ $[M+H]^+$: 368.0492, found: 368.0487. FTIR (KBr, cm^{-1}): 3741.71, 3591.87, 1713.99, 1651.29, 1621.27, 1557.01, 1403.06, 1360.17, 1336.17, 1030.52.



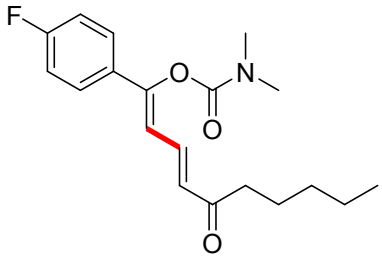
(2E, 4Z)-ethyl-5-(4-iodophenyl)-5-(dimethylcarbamoyloxy)penta-2,4-dienoate (**5gf**)

Brown solid, m.p.: 116.9 °C, yield = 37%. ^{1}H NMR ($CDCl_3$): δ = 7.63 (d, 2H, *J* = 8.5 Hz), 7.47 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.19 – 7.14 (m, 2H), 6.43 (d, 1H, *J* = 11.5 Hz), 5.97 (d, 1H, *J* = 15.5 Hz), 4.15 (q, 2H, *J* = 7.0 Hz), 3.13 (s, 3H), 2.92 (s, 3H), 1.24 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.86, 152.44, 150.75, 136.88, 136.17, 133.20, 125.69, 121.58, 114.33, 94.67, 59.45, 35.87, 35.60, 13.28. HRMS (ESI): m/z calculated for $C_{16}H_{18}NO_4I$ $[M+H]^+$: 416.0353, found: 416.0343. FTIR (KBr, cm^{-1}): 3500.16, 3262.64, 1789.88, 1667.41, 1633.74, 1567.72, 1434.67, 1360.37, 1336.89, 1026.91.



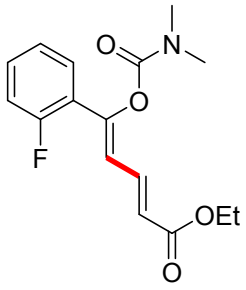
Ethyl (2E, 4E)-5-(benzo[b]thiophen-2-yl)-5-((dimethylcarbamoyl)oxy)penta-2,4-dienoate (**5mf**)

Brown solid, m.p.: 111.3 °C, yield = 44%. ^{1}H NMR ($CDCl_3$): δ = 7.71 – 7.64 (m, 2H), 7.43 (dd, 1H, *J* = 15.5, 11.5 Hz), 7.31 (s, 1H), 7.26 (dd, 2H, *J* = 6.0, 3.0 Hz), 6.47 (d, 1H, *J* = 11.5 Hz), 5.99 (d, 1H, *J* = 15.5 Hz), 4.16 (q, 2H, *J* = 7.1 Hz), 3.17 (s, 3H), 2.98 (s, 3H), 1.23 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.83, 152.35, 146.39, 138.79, 138.63, 137.27, 135.75, 124.66, 123.81, 123.27, 121.73, 121.61, 121.19, 115.40, 59.46, 36.02, 35.69, 13.28. HRMS (ESI): m/z calculated for $C_{18}H_{19}NO_4S$ $[M+H]^+$: 346.1108, found: 346.1101. FTIR (KBr, cm^{-1}): 3382.59, 3286.25, 1746.88, 1660.60, 1574.23, 1505.06, 1403.16, 1385.21, 1337.05, 1028.49.



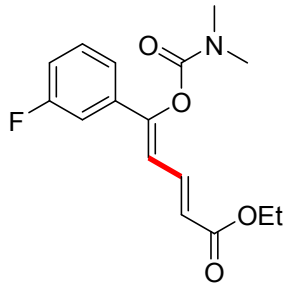
(1*Z*, 3*E*)-1-(4-Fluorophenyl)-5-oxodeca-1, 3-dien-1-yl dimethylcarbamate (**5dk**)

Brown oil, yield = 67%. ^{1}H NMR ($CDCl_3$): δ = 7.44 – 7.39 (m, 2H), 7.35 (dd, 1H, *J* = 15.5, 11.5 Hz), 6.99 (t, 2H, *J* = 8.5 Hz), 6.38 (d, 1H, *J* = 11.5 Hz), 6.26 (d, 1H, *J* = 15.5 Hz), 3.14 (s, 3H), 2.93 (s, 3H), 2.48 (t, 2H, *J* = 7.5 Hz), 1.58 (dd, 2H, *J* = 14.8, 7.5 Hz), 1.24 (dt, 4H, *J* = 8.1, 3.4 Hz), 0.83 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 199.52, 170.06, 162.00 (d, J_{C-F} = 248.8 Hz), 152.49, 151.46, 133.87, 128.81, 126.12 (d, J_{C-F} = 8.3 Hz), 114.89 (d, J_{C-F} = 22.0 Hz), 114.17 (d, J_{C-F} = 1.6 Hz), 40.47, 35.87, 35.61, 30.47, 23.04, 21.47, 12.92. HRMS (ESI): m/z calculated for $C_{19}H_{24}NO_3FI$ $[M+H]^+$: 334.1863, found: 334.1873. FTIR (KBr, cm^{-1}): 3793.69, 3686.00, 1789.75, 1738.06, 1651.33, 1606.39, 1557.09, 1494.76, 1360.21, 1029.41.



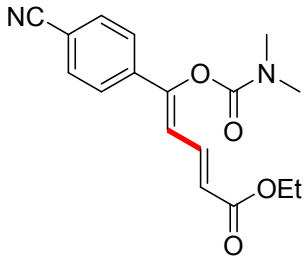
Ethyl-(2E, 4Z)-5-((dimethylcarbamoyl)oxy)-5-(2-fluorophenyl)penta-2,4-dienoate (**5kf**)

Yellow oil, yield = 54%, ^{1}H NMR ($CDCl_3$): δ = 7.54 (dd, 1H, *J* = 11.0, 15.0 Hz), 7.35 –7.32 (m, 1H), 7.25 – 7.19 (m, 1H), 7.09 –6.99 (m, 2H), 6.52 (d, 1H, *J* = 11.0 Hz), 5.97 (d, 1H, *J* = 15.0 Hz), 4.17 (q, 2H, *J* = 7.0 Hz), 3.11 (s, 3H), 2.91 (s, 3H), 1.25 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.92, 158.86 (d, J_{C-F} = 251.3 Hz), 152.48, 146.68 (d, J_{C-F} = 4.0 Hz), 136.36, 129.77 (d, J_{C-F} = 8.8 Hz), 127.10, 123.34, 121.91 (d, J_{C-F} = 10.8 Hz), 121.71, 118.19 (d, J_{C-F} = 9.9 Hz), 115.48 (d, J_{C-F} = 22.6 Hz), 59.41, 35.81, 35.55, 13.28. HRMS (ESI): m/z calculated for $C_{16}H_{18}FNO_4$ $[M+H]^+$: 308.1293, found: 308.1285. FTIR (KBr, cm^{-1}): 3332.58, 3286.74, 1732.11, 1714.42, 1644.85, 1519.36, 1470.68, 1360.38, 1336.95, 1048.86.



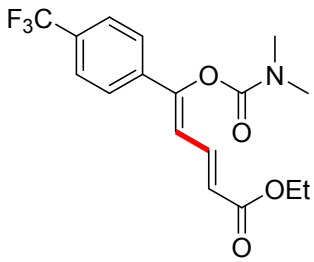
Ethyl-(2E, 4Z)-5-((dimethylcarbamoyl)oxy)-5-(3-fluorophenyl)penta-2,4-dienoate (**5lf**)

Yellow solid, yield = 54%, m.p.: 79.0 °C, ^{1}H NMR ($CDCl_3$): δ = 7.49 (dd, 1H, *J* = 11.5, 15.5 Hz), 7.27 – 7.22 (m, 2H), 7.11–7.08 (m, 1H), 6.98 – 6.97 (m, 1H), 6.45 (d, 1H, *J* = 11.5 Hz), 5.98 (d, 1H, *J* = 15.5 Hz), 4.18 (q, 2H, *J* = 7.5 Hz), 3.15 (s, 3H), 2.93 (s, 3H), 1.25 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.82, 161.94 (d, J_{C-F} = 244.9 Hz), 152.43, 150.26 (d, J_{C-F} = 2.9 Hz), 136.09, 135.91 (d, J_{C-F} = 7.8 Hz), 129.34 (d, J_{C-F} = 8.3 Hz), 121.84, 119.84, 115.44 (d, J_{C-F} = 21.3 Hz), 114.85, 111.12 (d, J_{C-F} = 23.4 Hz), 59.47, 35.88, 35.61, 13.27. HRMS (ESI): m/z calculated for $C_{16}H_{18}FNO_4$ $[M+H]^+$: 308.1293, found: 308.1291. FTIR (KBr, cm^{-1}): 3500.27, 3417.27, 1738.19, 1633.78, 1538.29, 1455.22, 1403.13, 1360.43, 1336.57, 1047.22.



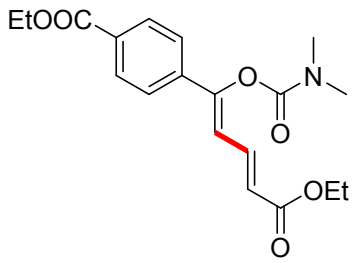
Ethyl-(2E, 4Z)-5-(4-cyanophenyl)-5-((dimethylcarbamoyl)oxy)penta-2,4-dienoate (**5hf**)

Brown solid, yield = 40%, m.p.: 135.0 °C, ^{1}H NMR ($CDCl_3$): 7.60 – 7.58 (m, 2H), 7.52 – 7.51(m, 2H), 7.49 (dd, 1H, *J* = 11.5, 15.5 Hz), 6.53 (d, 1H, *J* = 11.5 Hz), 6.03 (d, 1H, *J* = 15.5Hz), 4.18 (q, 2H, *J* = 7.5 Hz), 3.15 (s, 3H), 2.93 (s, 3H), 1.26 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.58, 152.25, 149.48, 137.97, 135.54, 131.50, 124.58, 123.08, 117.40, 116.60, 111.69, 59.63, 35.92, 35.64, 13.26. HRMS (ESI): m/z calculated for $C_{17}H_{18}N_2O_4$ $[M+H]^+$: 315.1339, found: 315.1338. FTIR (KBr, cm^{-1}): 3914.73, 1747.01, 1694.29, 1651.66, 1567.92, 1470.80, 1403.00, 1360.56, 1336.95, 983.83.



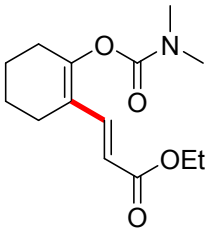
Ethyl-(2E,4Z)-5-((dimethylcarbamoyl)oxy)-5-(4-(trifluoromethyl)phenyl)penta-2,4-dienoate (**5if**)

Yellow solid, yield = 51%, m.p.: 98.6 °C, ^{1}H NMR ($CDCl_3$): 7.56 – 7.52 (m, 4H), 7.51 (dd, 1H, *J* = 11.5, 15.5 Hz), 6.50 (d, 1H, *J* = 11.5 Hz), 6.01 (d, 1H, *J* = 15.5 Hz), 4.18 (q, 2H, *J* = 7.0 Hz), 3.15 (s, 3H), 2.92 (s, 3H),1.25 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.72, 152.37, 150.08, 137.10, 135.86, 130.18 (q, J_{C-F} = 23.8 Hz), 124.78 (q, J_{C-F} = 3.8 Hz), 124.37, 122.83 (q, J_{C-F} = 272.5 Hz), 122.41, 115.70, 59.54, 35.88, 35.62, 13.26. HRMS (ESI): m/z calculated for $C_{17}H_{18}F_3NO_4$ $[M+H]^+$:358.1261, found: 358.1256. FTIR (KBr, cm^{-1}): 3813.85, 3418.03, 1714.84, 1694.33, 1557.39, 1446.02, 1360.43, 1239.20, 1090.63, 992.54.



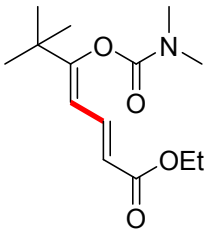
Ethyl-4-((1Z,3E)-1-((dimethylcarbamoyl)oxy)-5-ethoxy-5-oxopenta-1,3-dien-1-yl)benzoate(**5jf**)

Brown solid, yield = 53%, m.p.: 95.0 °C, ^{1}H NMR ($CDCl_3$): 7.96 (d, 2H, *J* = 8.5 Hz), 7.52 – 7.47 (m, 3H), 6.54 (d, 1H, *J* = 11.0 Hz), 6.01 (d, 1H, *J* = 15.5 Hz), 4.32 (q, 2H, *J* = 7.0 Hz), 4.18 (q, 2H, *J* = 7.0 Hz), 3.15 (s, 3H), 2.93 (s, 3H), 1.32 (t, 3H, *J* = 7.0 Hz), 1.25 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ = 165.77, 164.92, 152.41, 150.55, 137.68, 136.05, 130.08, 128.95, 123.96, 122.19, 115.63, 60.11, 59.50, 35.88, 35.62, 13.28, 13.27. HRMS (ESI): m/z calculated for $C_{19}H_{23}NO_6$ $[M+H]^+$: 362.1598, found: 362.1595. FTIR (KBr, cm^{-1}): 3699.61, 3417.82, 1715.07, 1645.12, 1538.62, 1495.15, 1372.53, 1276.75, 1142.58, 449.95.



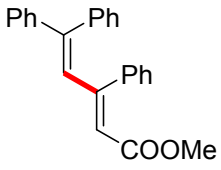
Ethyl (E)-3-(2-((dimethylcarbamoyl)oxy)cyclohex-1-en-1-yl)acrylate (**5nf**)

Yellow oil, yield = 45%. ^{1}H NMR ($CDCl_3$): δ = 7.63 (d, 1H, *J* = 16.0 Hz), 5.73 (d, 1H, *J* = 16.0 Hz), 4.13 (q, 2H, *J* = 7.0 Hz), 2.98 (s, 3H), 2.89 (s, 3H), 2.29 (t, 2H, *J* = 5.8 Hz), 2.18 (d, 2H, *J* = 6.2 Hz), 1.71 – 1.62 (m, 4H), 1.22 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ = 166.57, 152.88, 151.97, 138.27, 119.90, 115.21, 59.17, 35.57, 35.44, 27.74, 23.03, 21.37, 20.75, 13.29. HRMS (ESI): m/z calculated for $C_{14}H_{21}NO_4$ $[M+H]^+$: 268.1543, found: 268.1541. FTIR (KBr, cm^{-1}): 3584.83, 3500.39, 1842.06, 1714.61, 1667.52, 1644.84, 1557.24, 1434.77, 1258.16, 1014.40.



Ethyl (2E, 4Z)-5-((dimethylcarbamoyl)oxy)-6,6-dimethylhepta-2,4-dienoate (**5of**)

Yellow oil, yield = 47%. ^{1}H NMR ($CDCl_3$): δ = 7.20 – 7.11 (m, 1H), 5.88 (d, 1H, *J* = 11.3 Hz), 5.80 (d, 1H, *J* = 15.5 Hz), 4.11 (q, 2H, *J* = 7.0 Hz), 3.01 (s, 3H), 2.92 (s, 3H), 1.20 (t, 3H, *J* = 7.0 Hz), 1.07 (s, 9H). ^{13}C NMR ($CDCl_3$): δ = 166.09, 162.38, 152.81, 137.33, 119.68, 111.36, 59.15, 36.06, 35.88, 35.39, 26.87, 13.27. HRMS (ESI): m/z calculated for $C_{14}H_{23}NO_4$ $[M+H]^+$: 270.1700, found: 270.1702. FTIR (KBr, cm^{-1}): 3654.26, 1828.02, 1704.25, 1694.16, 1667.47, 1531.75, 1470.65, 1246.52, 1142.63, 1069.92.

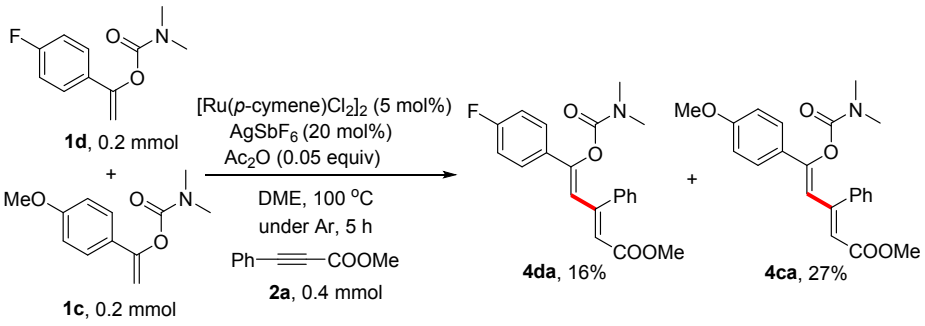


Methyl (Z)-3, 5, 5-triphenylpenta-2,4-dienoate (**6**)

Yellow oil, yield = 58%. ^{1}H NMR ($CDCl_3$): δ = 7.44 – 7.42 (m, 2H), 7.35 (s, 1H), 7.26 – 7.16 (m, 11H), 7.07 (dd, 2H, *J* = 7.7, 1.8 Hz), 6.63 (d, 1H, *J* = 1.7 Hz), 3.23 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 167.64, 145.99, 141.13, 139.27, 138.91, 134.62, 129.73, 129.03, 128.75, 127.94, 127.44, 127.30, 127.17, 126.97, 126.92, 126.69, 121.25, 50.65.

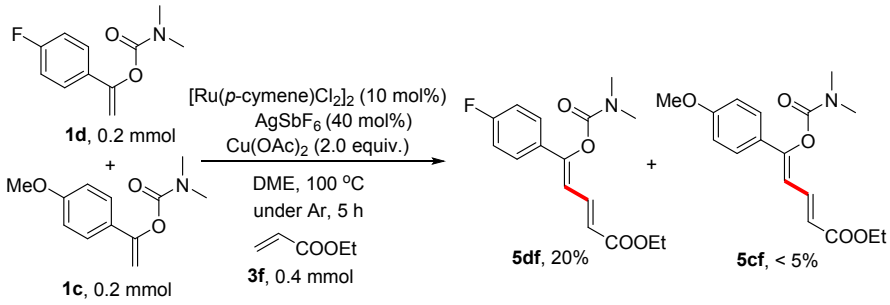
HRMS (ESI): m/z calculated for $C_{24}H_{20}NO_2$ $[M+H]^+$: 341.1536, found: 341.1528. FTIR (KBr, cm^{-1}): 3550.18, 1841.93, 1770.12, 1698.43, 1644.70, 1557.10, 1486.49, 1392.79, 1360.27, 1257.81.

Competitive reaction of different enol-carbamates with alkyne 2a



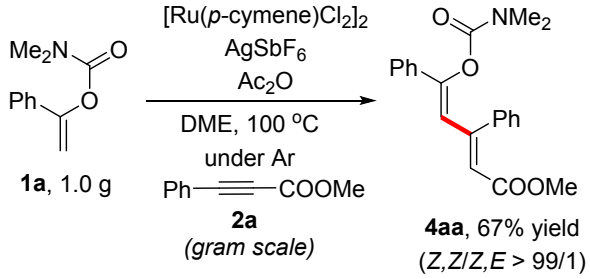
A 10 mL vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 5.0 mol %), $AgSbF_6$ (13.7 mg, 20 mol %) and DME (1.0 mL). Then, enol carbamate **1d** (43.8mg, 0.2 mmol), enol carbamate **1c** (46.2 mg, 0.2 mmol), acetic anhydride (1.0 mg, 5.0 mol %) and methyl phenylpropiolate (**2a**) (64.1 mg, 0.4 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 100℃ with stirring for 5 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **4da** (10.0 mg, 16 %) and **4ca** (17.0 mg, 27%).

Competitive reaction of different enol-carbamates with alkene 3f

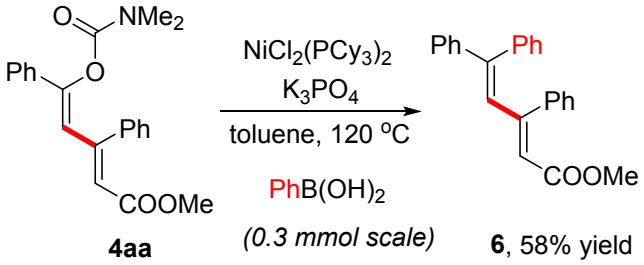


A 10 mL vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (12.2 mg, 10.0 mol %), $AgSbF_6$ (27.5 mg, 40 mol %) and DME (1.0 mL). Then, enol carbamate **1d** (43.8mg, 0.2 mmol), enol carbamate **1c** (46.2 mg, 0.2 mmol), $Cu(OAc)_2$ (2.0 equiv,0.4 mmol) and alkene **3f** (20.0 mg, 0.4 mmol**)** were added into the solution in sequence. The vial was sealed under Ar and heated to 100℃ with stirring for 5 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **5df** (12.0 mg, 20 %) and 5**cf** (yield < 5%).

Synthetic Applications

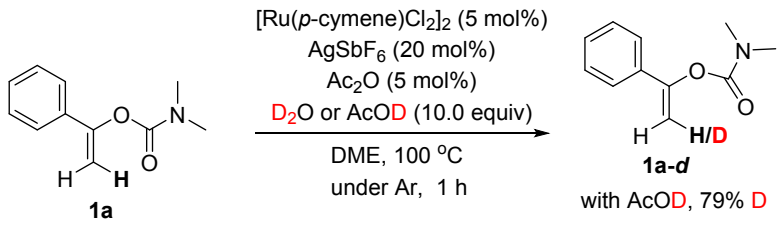


An oven-dried screw-cap vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol%, 0.26 mmol), $AgSbF_6$ (20.0 mol%, 1.04 mmol) and DME (1.0 ml). Then, vinyl carbamate **1a** (1.0 g, 1.0 eq, 5.23 mmol), Alkyne **2a** (2.0 eq, 10.46 mmol) and acetic anhydride (0.05 eq, 0.26 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 ℃ with stirring for 16 hours. After cooling down, the mixture was concentrated to give the crude product which was directly applied to a flash column chromatography (EtOAc/Petroleum ether mixtures) for separation, finally delivering product **3aa** as a white solid (1.23 g, 67%).

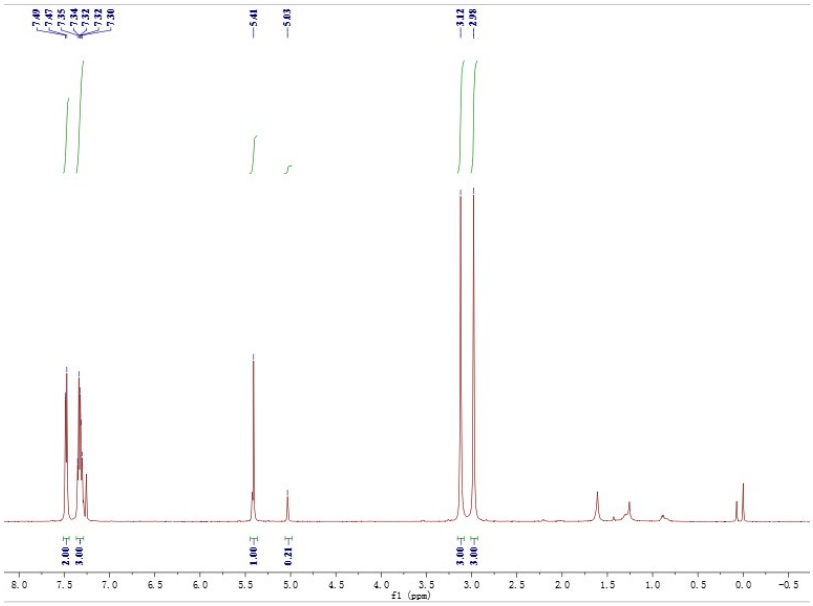


A flame-dried Schlenk tube (8 mL) equipped with a magnetic stirring bar was charged with anhydrous K_3PO_4 (1.44 mmol, 30.6 mg, 7.2 equiv). Phenylboronic acid (0.6 mmol, 73.2 mg, 4.0 equiv), $NiCl_2(PCy_3)_2$ (38.2 mg, 10 mol %), enol carbamate **4aa** (0.2 mmol, 70.2 mg, 1.0 equiv) and toluene (1.4 mL) were then added under a stream of argon. The reaction vessel was sealed with a Teflon-lined screw cap and the heterogeneous mixture was allowed to stir at 23 °C for 1 h before heating up to 120 °C for 24 h. After cooling down, the reaction mixture was transferred to a round bottom flask and rinsed with dichloromethane. Silica was then added and the solvent was removed under vacuo. The obtained powder was dry-loaded onto a silica gel column and purification by column chromatography (EtOAc/petroleum ether mixtures 1:20) afforded the desired arylated product **6** as a yellow oil (39.4 mg, 58%).

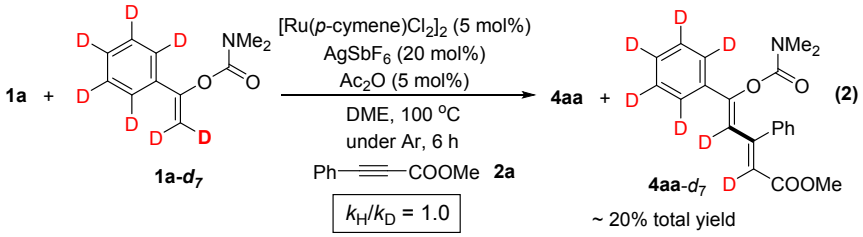
Ru-Catalyzed H/D Exchange in 1a and KIE study



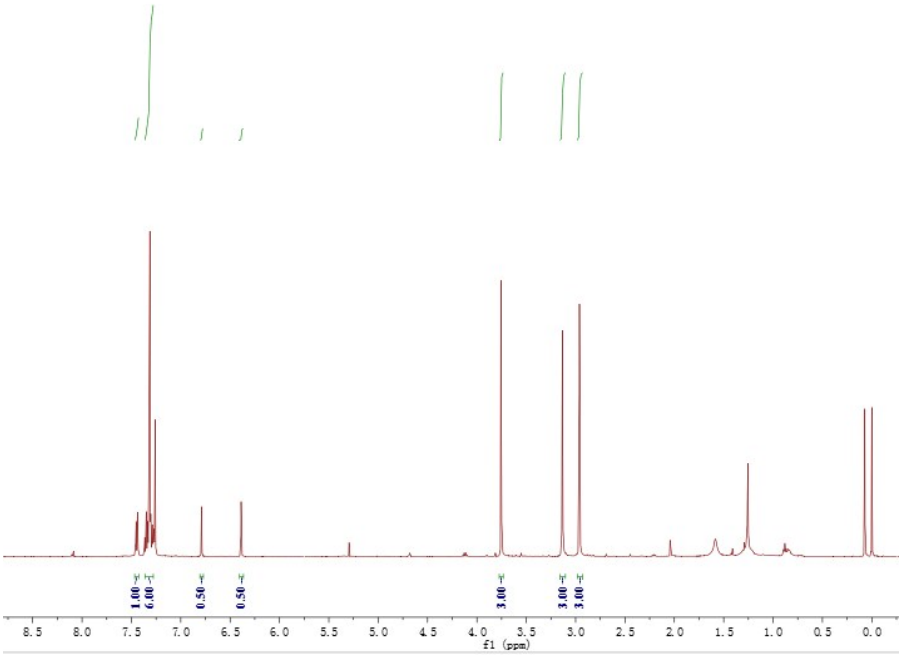
An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol %, 0.01 mmol), $AgSbF_6$ (20 mol %, 0.04 mmol), acetic anhydride (5.0 mol%, 0.01 mmol), DME (1.0 mL) and AcOD (10.0 eq, 2.0 mmol). Then, enol carbamate (0.2 mmol) was added into the solution. The vial was sealed under argon and heated to 100℃ with stirring for 1 hour. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures) on silica gel (26 mg, 68% recovered). The D % of **1a-*d*** was estimated by ^{1}HNMR.



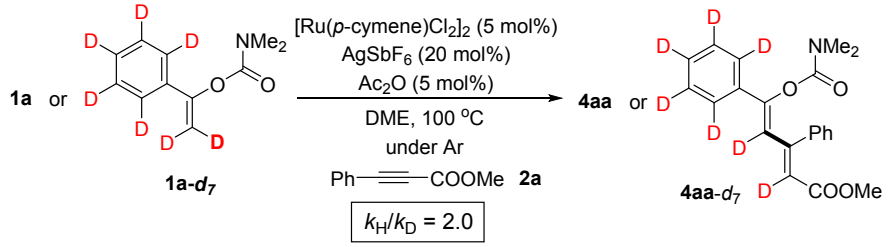
Competitive reactions in 1 vessel



A 10 mL vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (3.1 mg, 5.0 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and DME (1.0 mL). Then, alkyne **2a** (32.0 mg, 0.2 mmol**)**, enol carbamate **1a** (19.1 mg, 0.1 mmol), acetic anhydride (0.5 mg, 5.0 mol %) and **1a-*d*$_7$** (19.8 mg, 0.1 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 100℃ with stirring for 6 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product (14.0 mg, ~ 20% yield) as a white solid. The ratio of **4aa**/**4a-*d*$_7$** was determined by ^{1}H NMR (500 MHz, $CDCl_3$) to be 1.0.

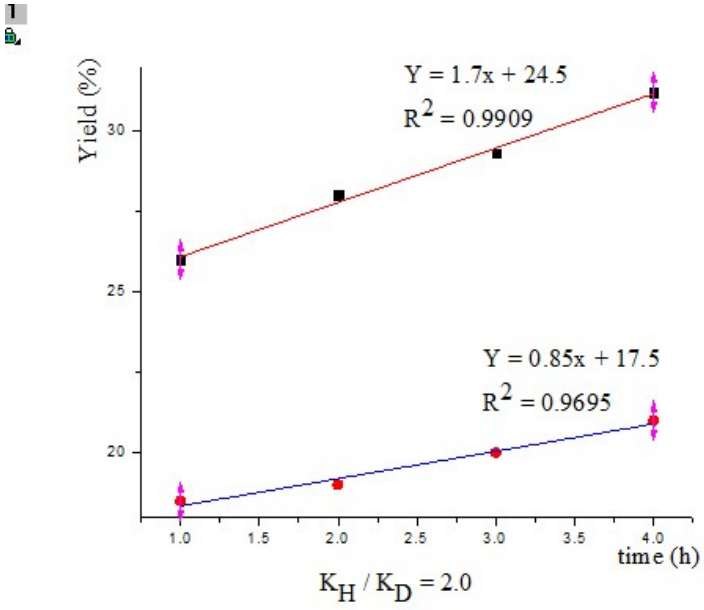


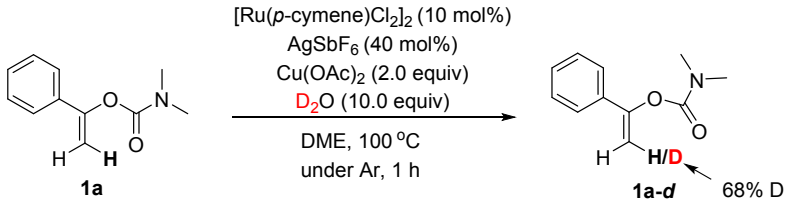
Parallel reactions in 2 vessels



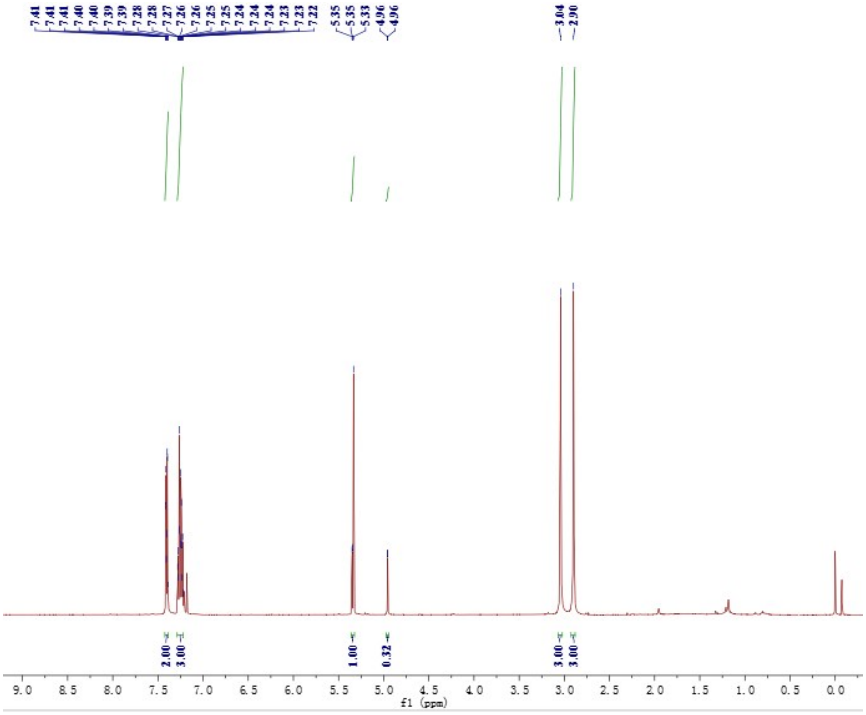
Four parallel independent reactions of **1a**/**1a-*d*$_7$** with **2a**, were performed to determine the corresponding KIE value. A 10 mL vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (3.1 mg, 5.0 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and DME (1.0 mL). Then, alkyne **2a** (32.0 mg, 0.2 mmol**)**, enol carbamate **1a** (19.1 mg, 0.1 mmol) or **1a-d$_7$** (19.8 mg, 0.1 mmol) and acetic anhydride (0.5 mg, 5.0 mol %) were added into the solution in sequence. The vial was sealed under Ar and heated to 100℃ with stirring for 1-4 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **4aa**/**4aa-*d*$_7$**.

t/h / yield	1	2	3	4
4aa	26%	28%	29%	31%
4aa-d$_7$	18.5%	19%	20%	21%

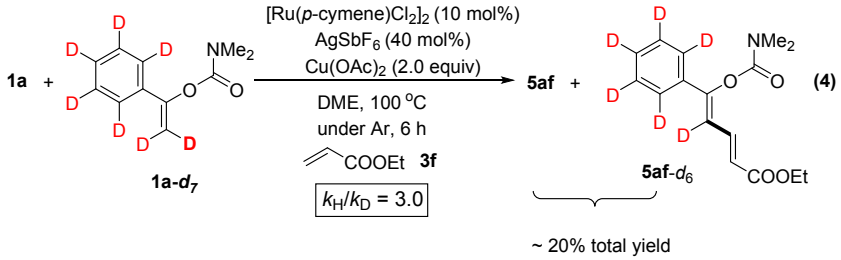




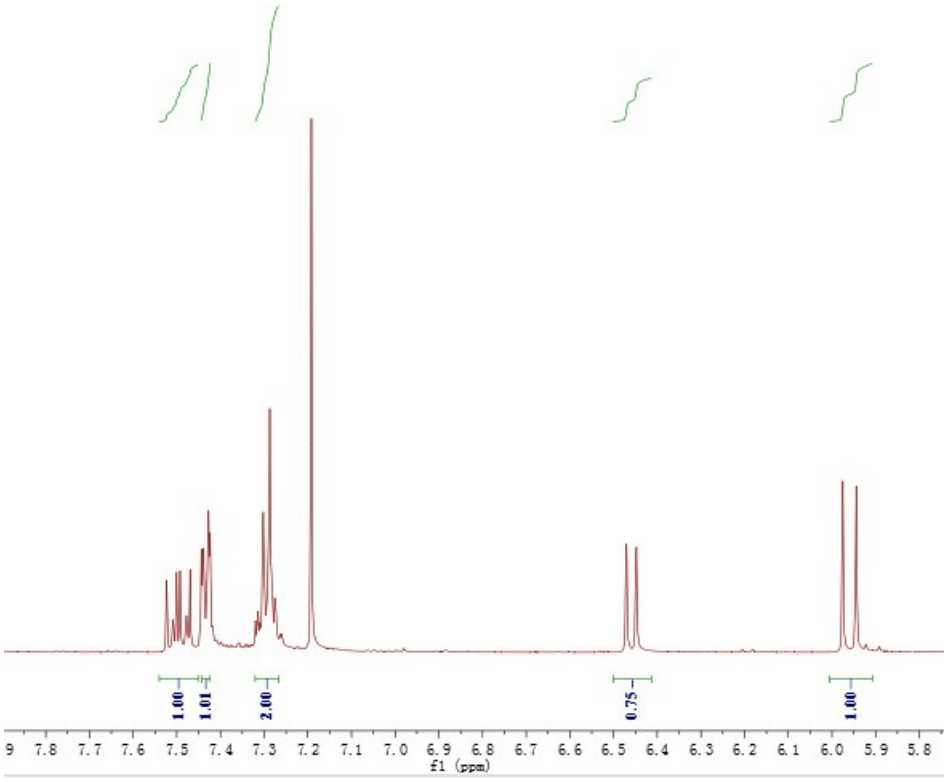
An oven-dried vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (10.0 mol %, 0.02 mmol), $AgSbF_6$ (40 mol %, 0.08 mmol), $Cu(OAc)_2$ (2.0 equiv,0.4 mmol), DME (1.0 mL) and D_2O (10.0 eq, 2.0 mmol). Then, enol carbamate **1a** (0.2 mmol) was added into the solution. The vial was sealed under argon and heated to 100℃ with stirring for 1 hour. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures) on silica gel (29 mg, 76% recovered). The D % of **1a-*d*** was estimated by ^{1}HNMR.



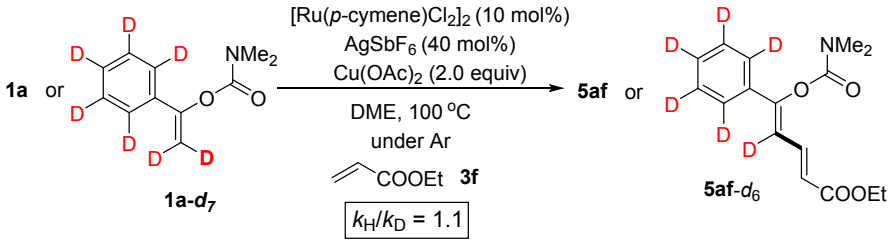
Competitive reactions in 1 vessel



A 10 mL vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (6.12 mg, 10.0 mol %), $AgSbF_6$ (13.74 mg, 40 mol %) and DME (1.0 mL). Then, alkene **3f** (20.0 mg, 0.2 mmol**)**, enol carbamate **1a** (19.1 mg, 0.1 mmol), $Cu(OAc)_2$ (2.0 equiv,0.2 mmol) and **1a-*d*$_7$** (19.8 mg, 0.1 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 100℃ with stirring for 6 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product (15.0 mg, ~ 20% yield) as brown oil. The ratio of **5af**/**5af-*d*$_6$** was determined by ^{1}H NMR (500 MHz, $CDCl_3$) to be 3.0.

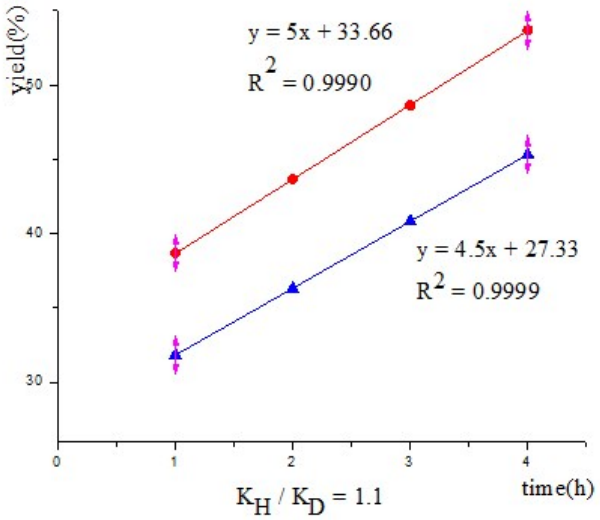


Parallel reactions in 2 vessels



Four parallel independent reactions of **1a**/**1a-d**$_7$ with **3f** were performed to determine the corresponding KIE value. A 10 mL vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (6.12 mg, 10.0 mol %), $AgSbF_6$ (13.74 mg, 40 mol %) and DME (1.0 mL). Then, alkene **3f** (20.0 mg, 0.2 mmol**)**, enol carbamate **1a** (19.1 mg, 0.1 mmol) or **1a-*d*$_7$** (19.8 mg, 0.1 mmol) and $Cu(OAc)_2$ (2.0 equiv,0.2 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 100℃ with stirring for 1-4 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **5af**/**5af-*d*$_6$**.

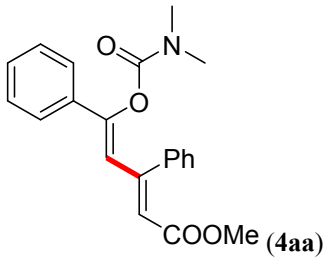
t/h / yield	1	2	3	4
5af	38.7%	43.7%	48.7%	53.6%
5af-d$_6$	31.8%	36.3%	40.8%	45.3%



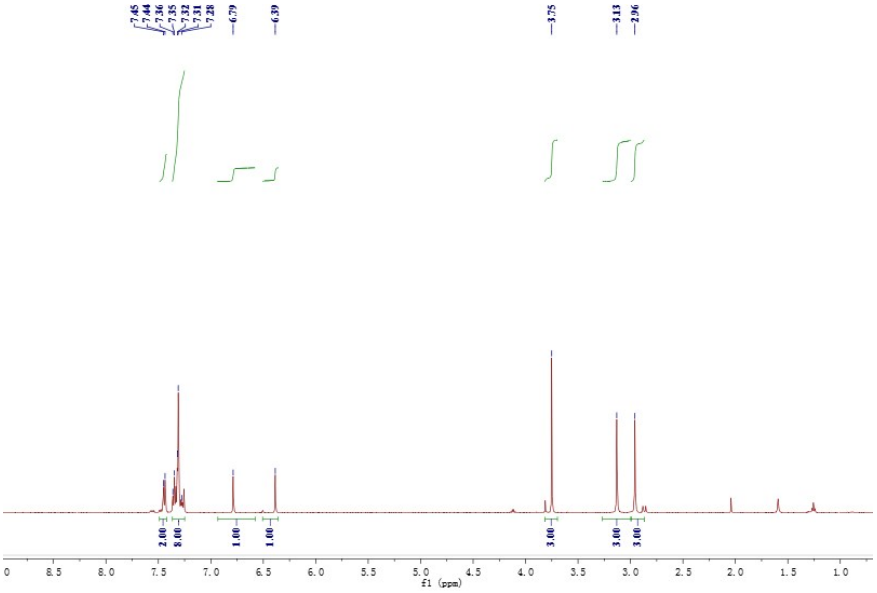
References:

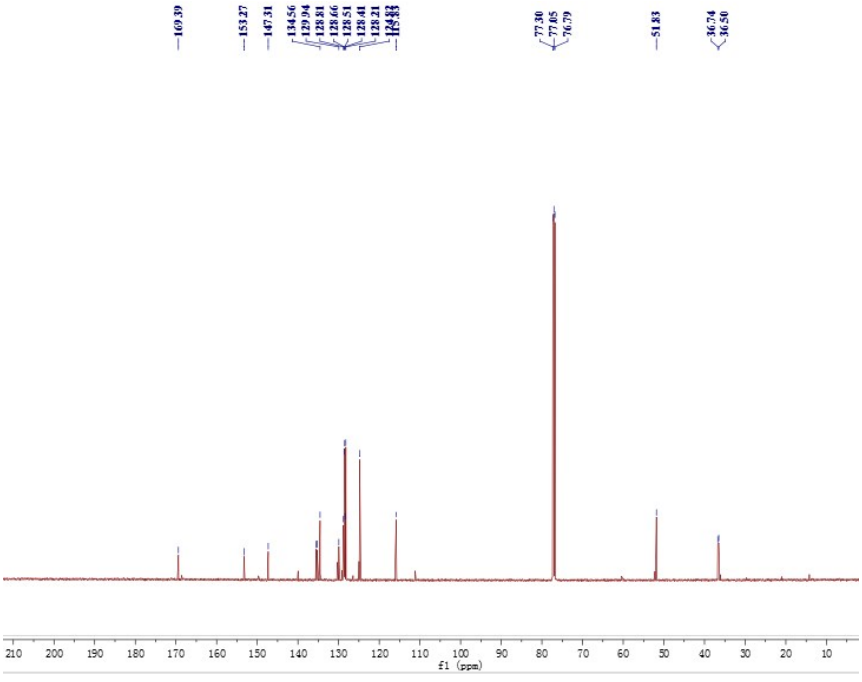
1. M. Boultadakis-Arapinis, M. N. Hopkinson and F. Glorius, *Org. Lett*. 2014, **16**, 1630-1633.

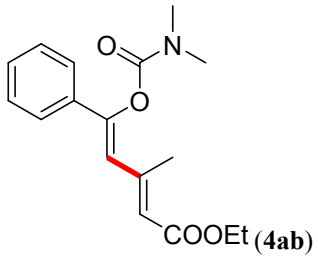
NMR Spectra



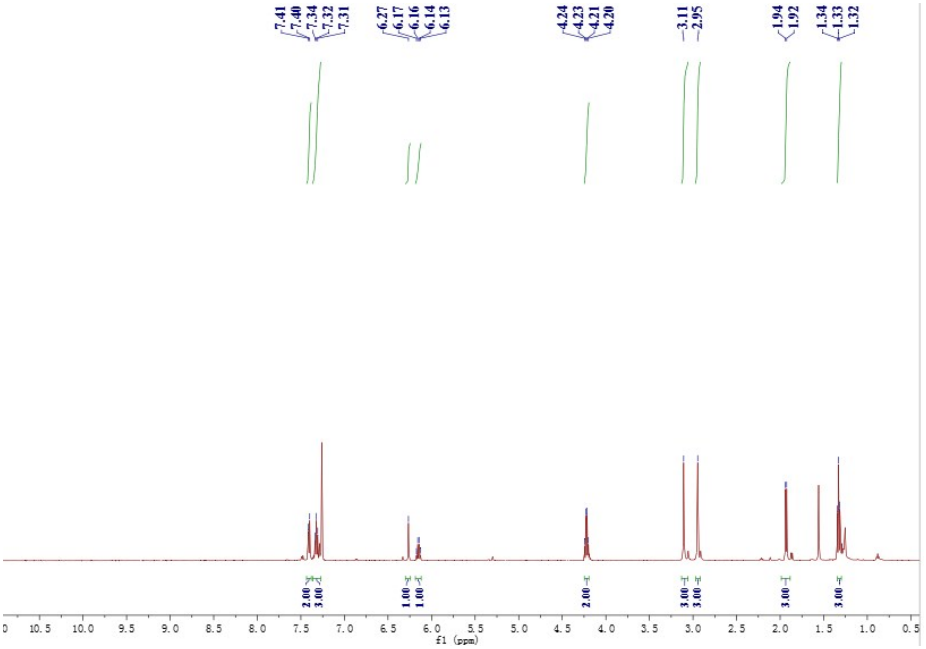
(4aa)






O
N
O
COOEt

(4ab)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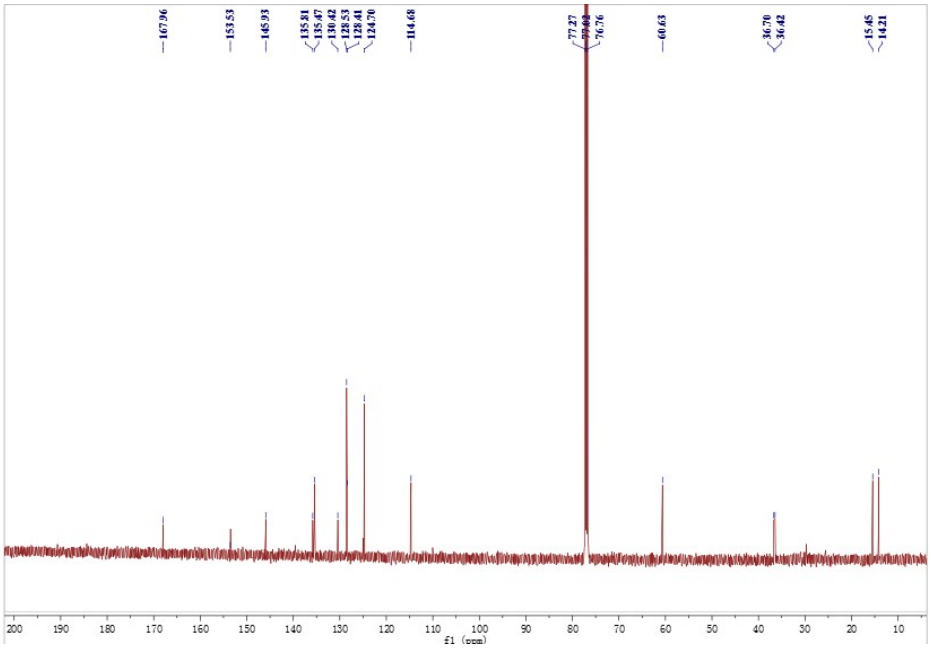
f1 (ppm)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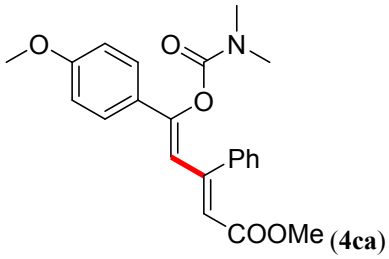
77.03
76.76
60.63
36.70
36.42
15.45
14.21
f1 (ppm)


O
O
N
O
O
Ph
COOMe

(4ca)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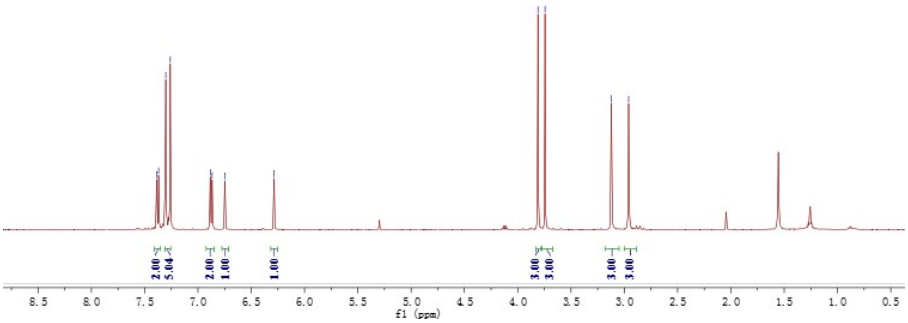
6.87
6.75
6.29
3.81
3.74
3.12
2.96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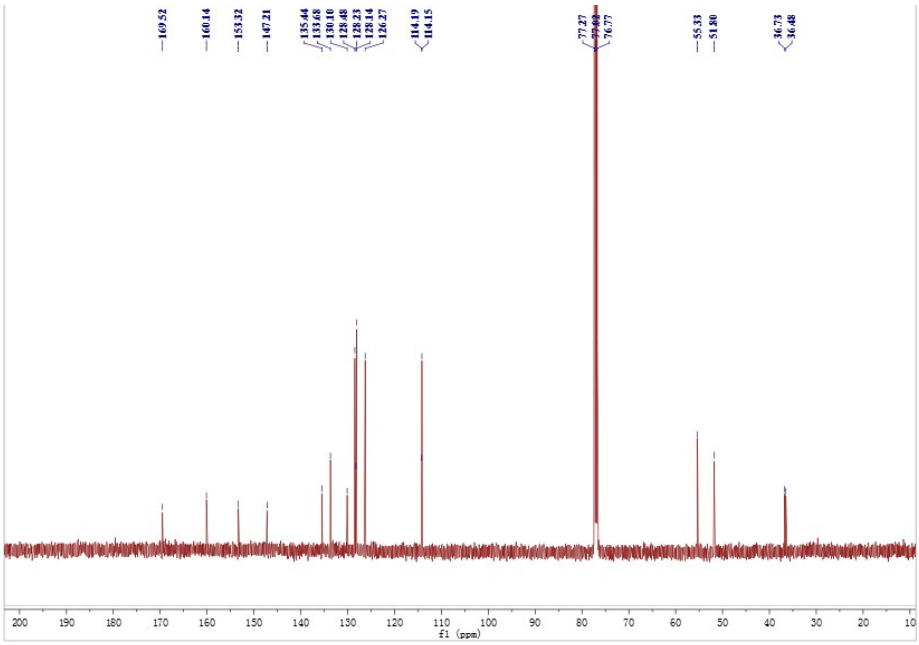
5.04
2.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)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153.32
147.21
135.44
133.68
130.10
128.48
128.23
128.14
126.27
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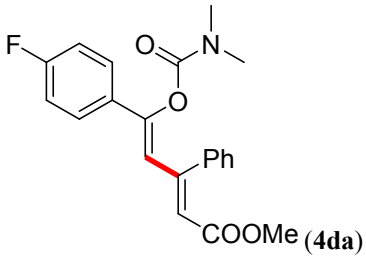
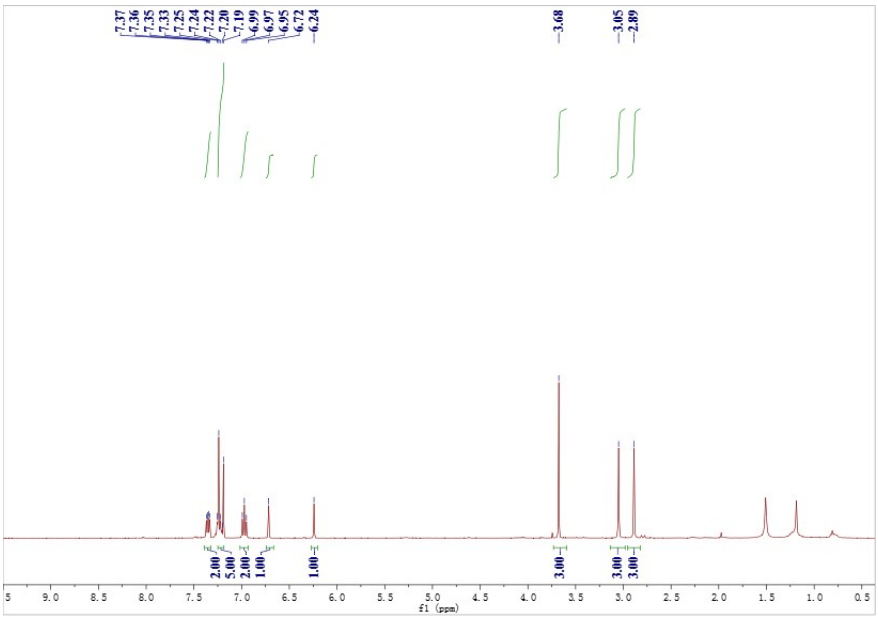
114.15
77.27
77.00
76.77
55.33
51.80
36.73
36.48
f1 (ppm)


F
O
N
O
Ph
COOMe
(**4da**)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7.36
7.35
7.33
7.25
7.24
7.22
7.20
7.19
6.99
6.97
6.95
6.72
6.24
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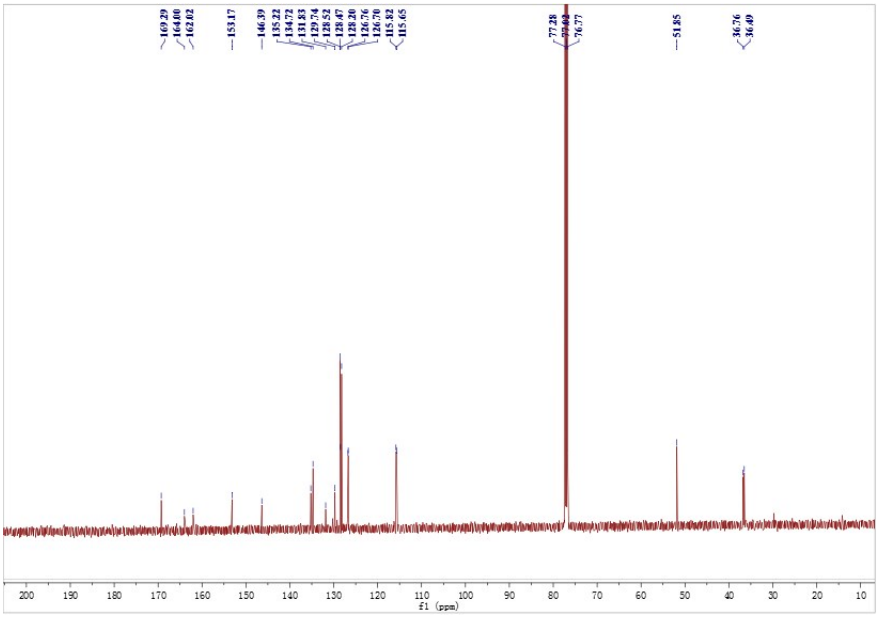
1.00
3.00
3.00
3.00
f1 (ppm)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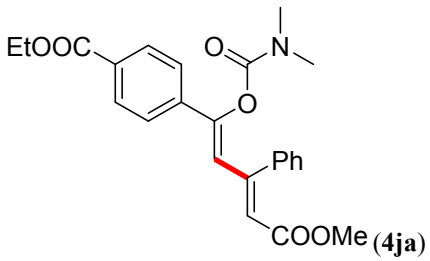
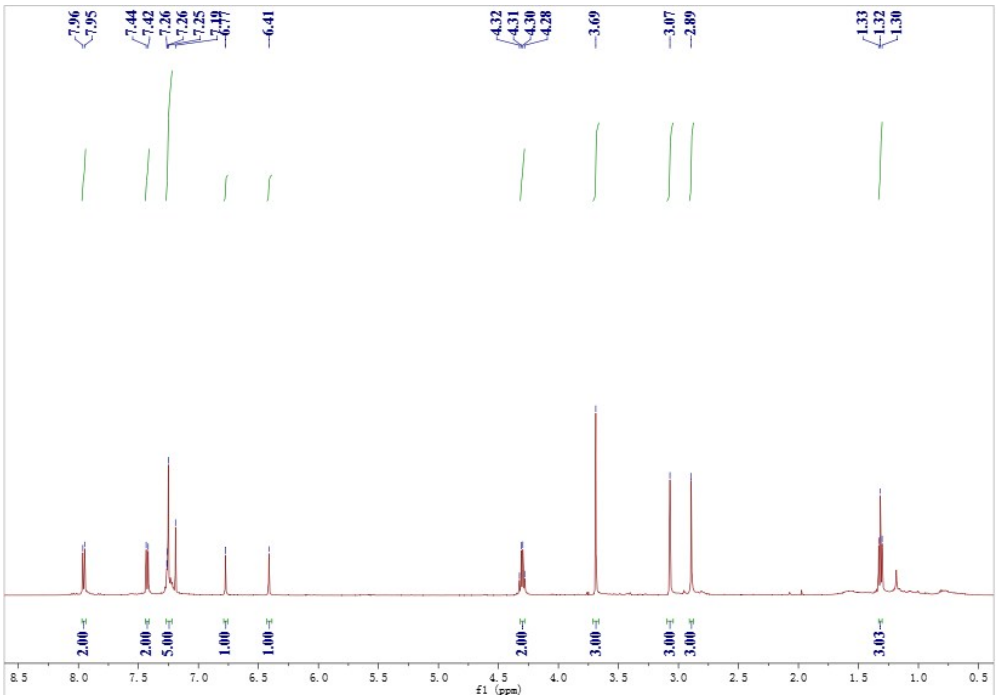
164.00
162.02
153.17
146.39
135.22
134.72
131.85
131.74
128.52
128.47
128.20
126.76
126.70
115.82
115.65
77.38
77.06
76.77
51.85
36.76
36.49
f1 (ppm)


EtOOC
O
N
O
Ph
COOMe

(**4ja**)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7.95
7.44
7.42
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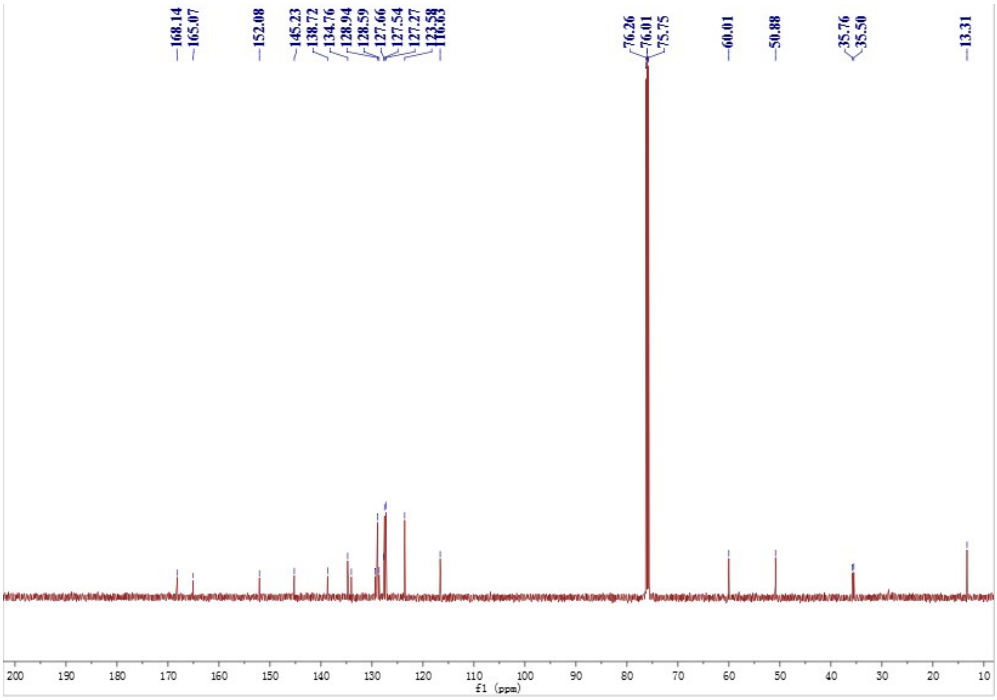
7.26
7.25
7.19
6.77
6.41
4.32
4.31
4.30
4.28
3.69
3.07
2.89
1.33
1.32
1.30
2.00
2.00
5.00
1.00
1.00
2.00
3.00
3.00
3.00
3.03
f1 (ppm)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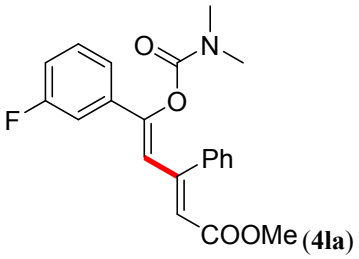
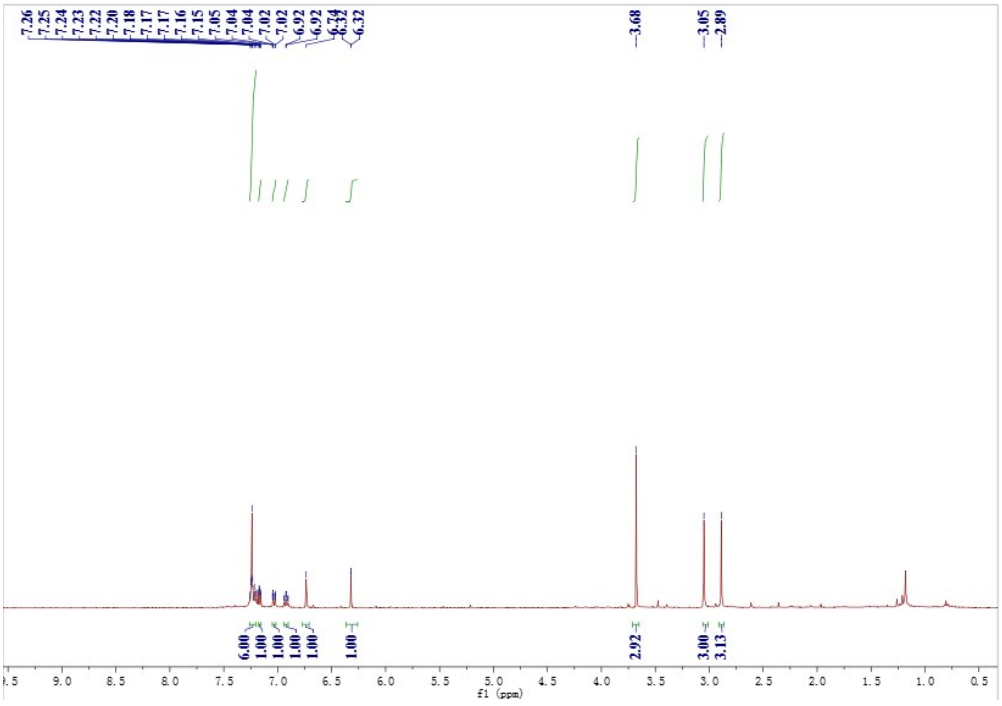
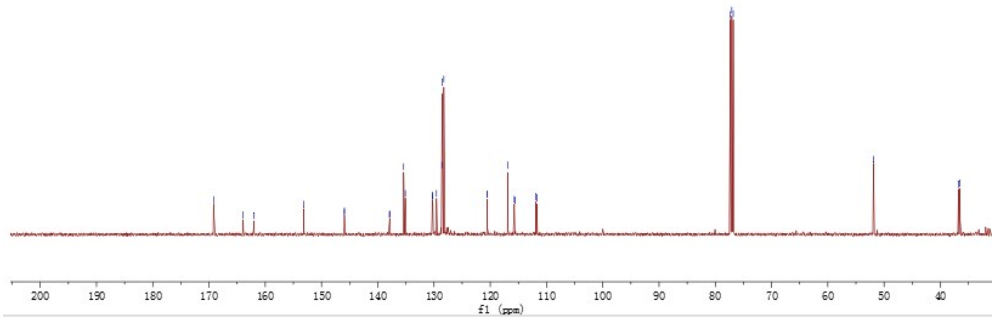
165.07
152.08
145.23
138.72
134.76
128.94
128.59
127.66
127.54
127.27
123.58
116.83
76.26
76.01
75.75
60.01
50.88
35.76
35.50
13.31
f1 (ppm)

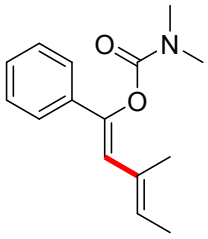

O
N
O
F
Ph
COOMe

(**4la**)

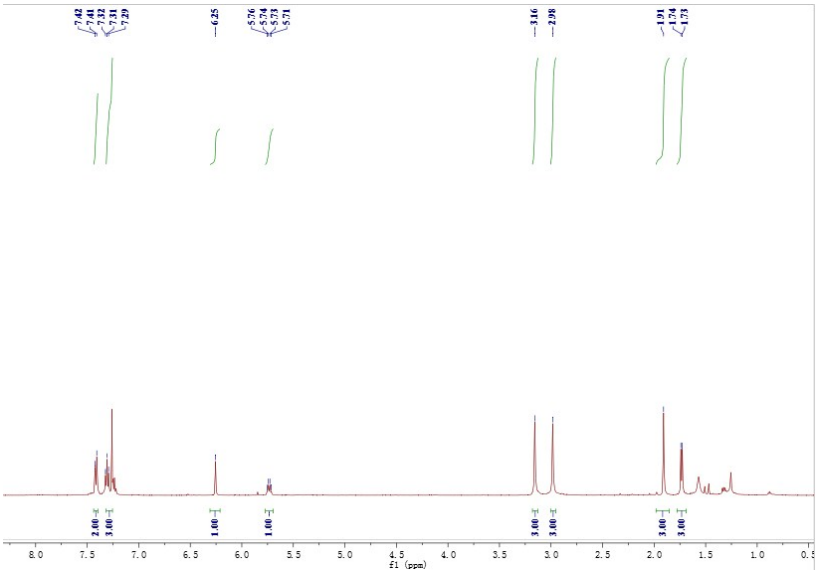

7.26
7.25
7.24
7.23
7.22
7.20
7.18
7.17
7.17
7.16
7.15
7.05
7.04
7.04
7.02
7.02
6.92
6.92
6.34
6.32
3.68
3.05
2.89
6.00
1.00
1.00
1.00
1.00
1.00
2.92
3.00
3.13
f1 (ppm)

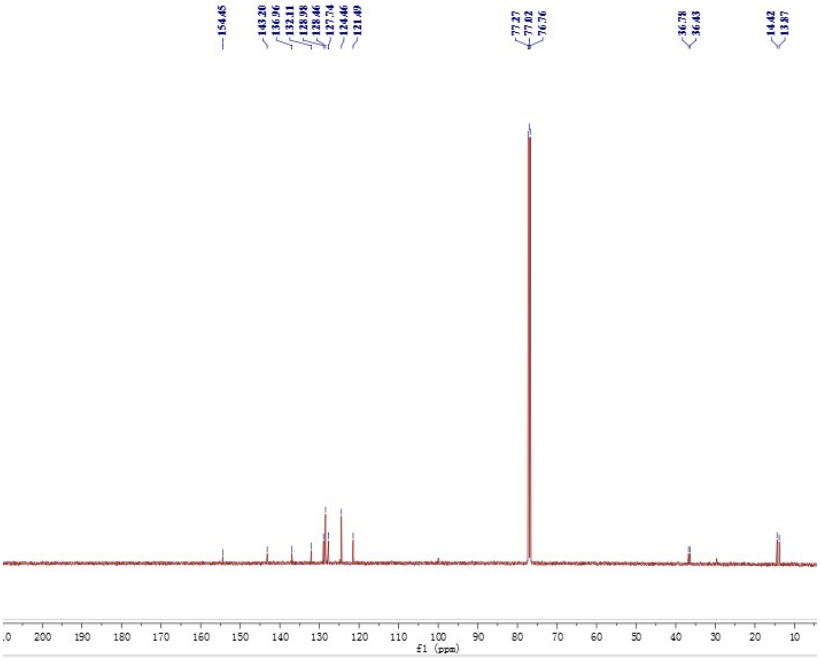

169.19
163.94
161.98
153.13
145.95
145.93
135.40
135.10
129.57
128.61
128.55
120.52
116.86
115.73
115.56
111.88
111.70
77.32
77.07
76.81
51.89
36.77
36.50

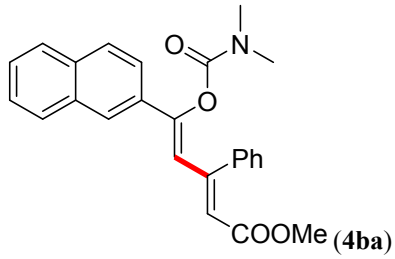

f1 (ppm)



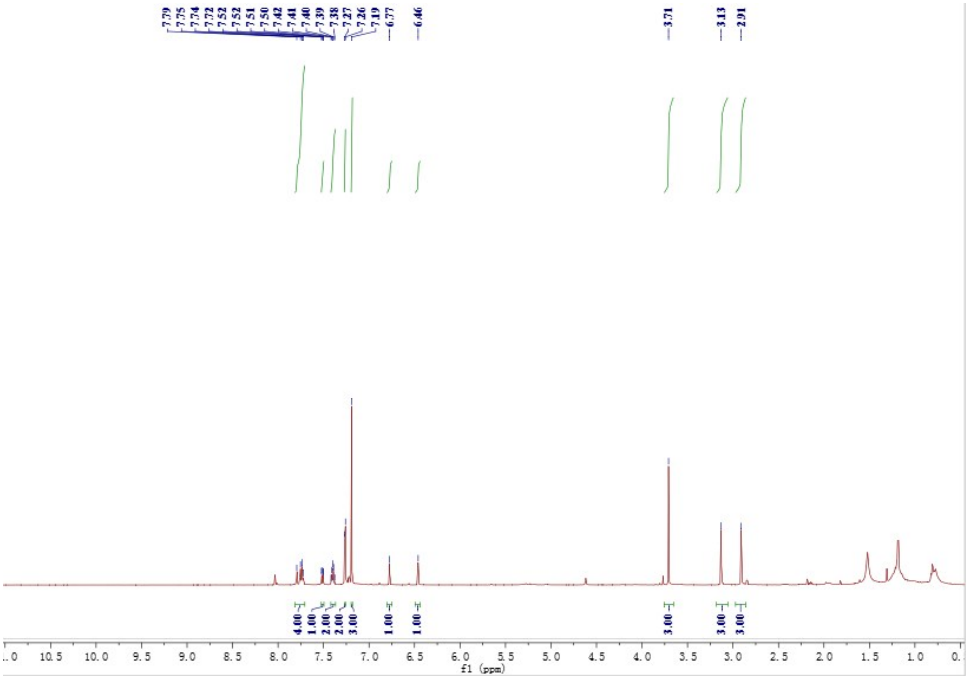
(4ac)

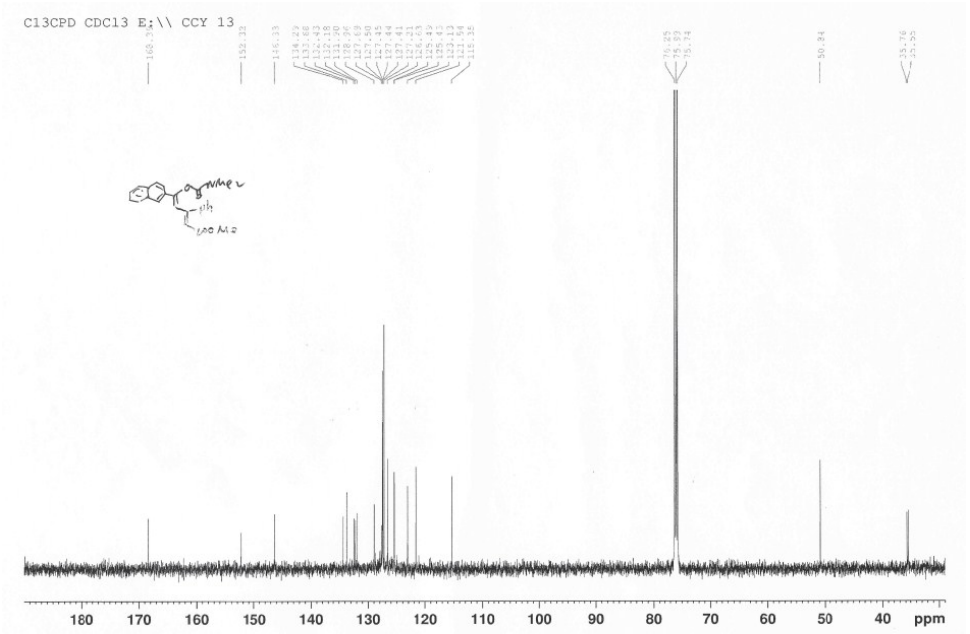

7.42
7.41
7.32
7.31
7.29
6.25
5.76
5.74
5.73
5.71
3.46
2.98
1.91
1.74
1.73
2.00
3.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)

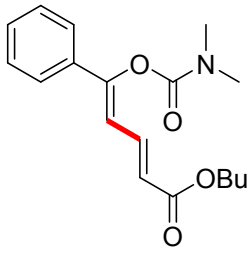

154.45
145.20
136.96
132.11
128.98
128.46
127.74
124.46
121.49
77.27
77.02
76.76
36.78
36.43
14.42
13.87
f1 (ppm)


O
N
O
Ph
COOMe

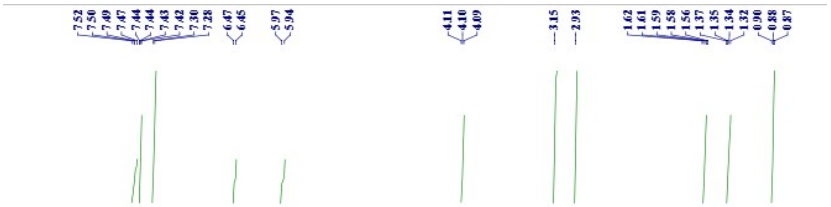
(4ba)


7.79
7.75
7.74
7.72
7.52
7.52
7.51
7.50
7.42
7.41
7.40
7.39
7.38
7.27
7.26
7.19
6.77
6.46
3.71
3.13
2.91
4.00
1.00
2.00
2.00
3.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)


C13CPD CDCl3 E:\\ CCY 13
168.39
132.31
146.33
134.22
133.66
132.43
132.10
131.90
128.96
128.60
127.50
127.45
127.44
127.41
127.11
126.63
125.43
125.13
123.13
121.54
110.38
79.95
79.69
79.43
75.34
50.84
35.76
35.55
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


O
N
O
OBu
O

(**5ad**)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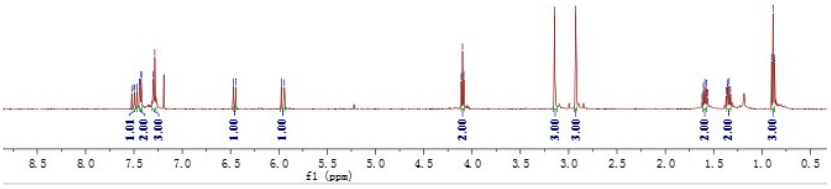
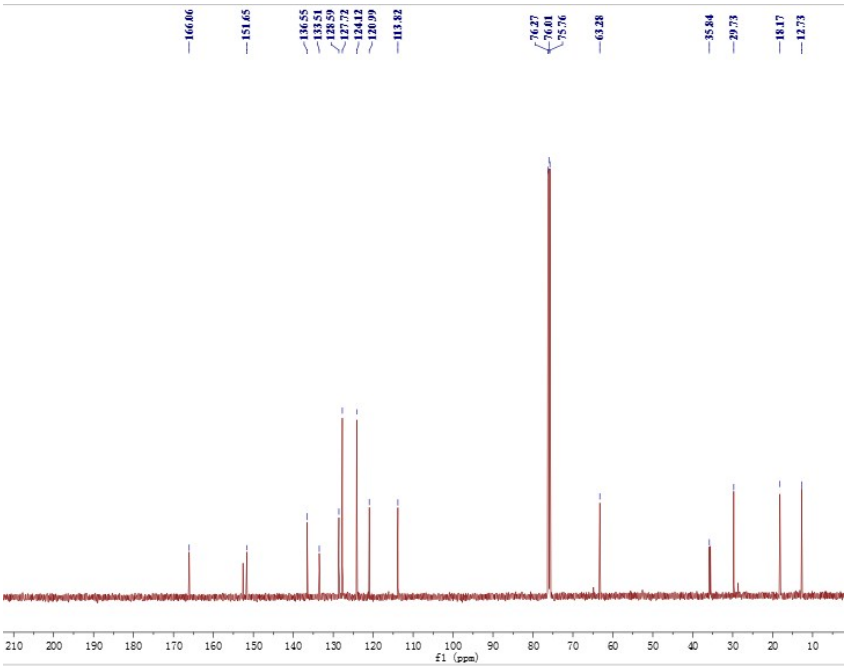
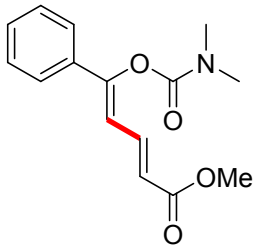
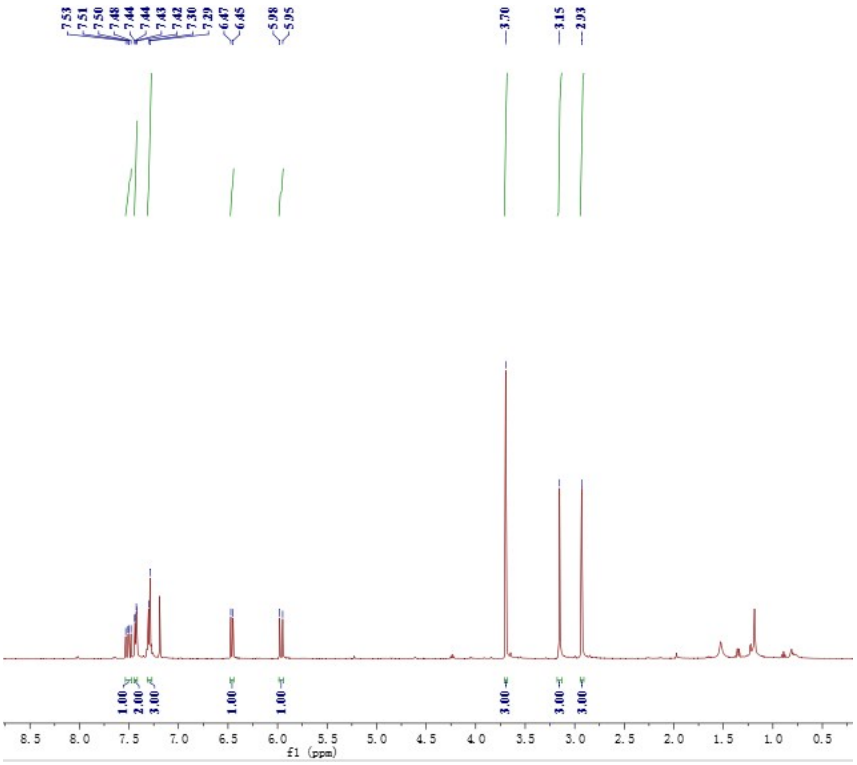
7.50
7.49
7.47
7.44
7.44
7.43
7.42
7.30
7.28
6.47
6.45
5.97
5.94
4.11
4.10
4.09
3.15
2.93
1.62
1.61
1.59
1.58
1.56
1.37
1.35
1.34
1.32
0.90
0.88
0.87


1.01
2.00
3.00
1.00
1.00
2.00
3.00
3.00
2.00
2.00
3.00
f1 (ppm)


166.06
151.65
136.55
133.51
128.59
127.72
124.12
120.99
115.82
76.27
76.01
75.76
63.28
35.84
29.73
18.17
12.73
f1 (ppm)


O
N
O
OMe
O

(**5ae**)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7.44
7.43
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7.30
7.29
6.47
6.45
5.98
5.95
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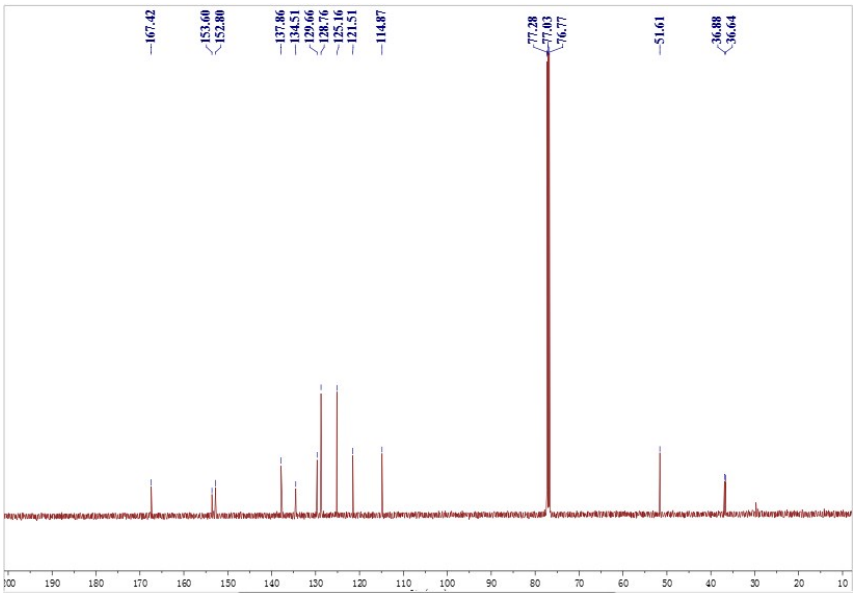
1.00
3.00
3.00
3.00
f1 (ppm)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137.86
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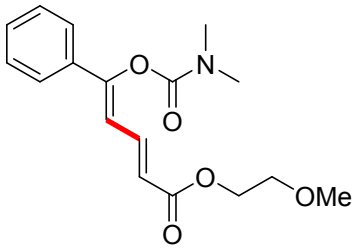
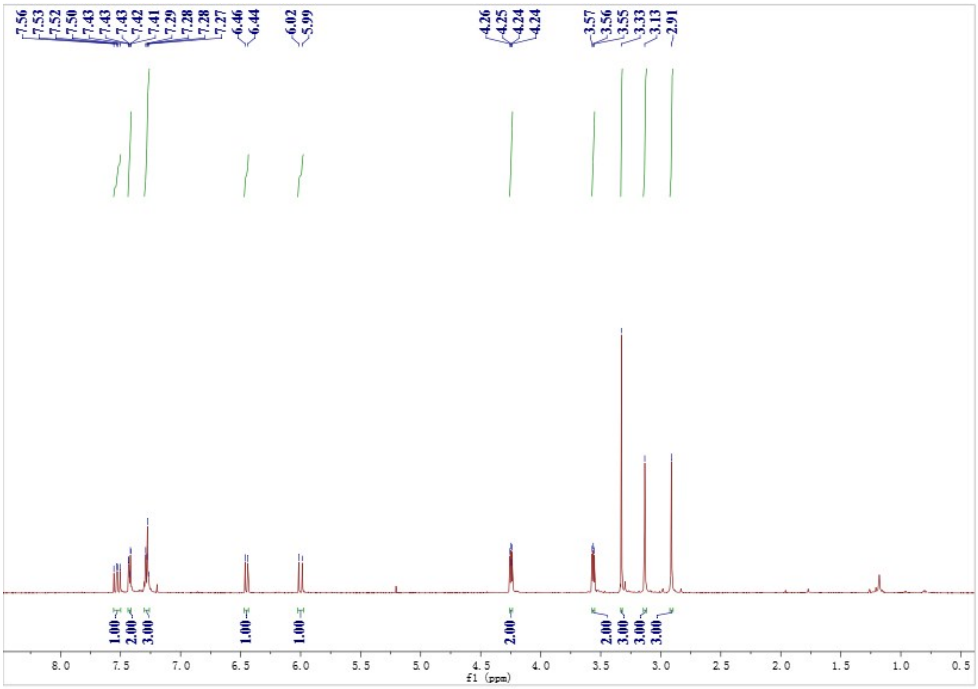
125.16
121.51
114.87
77.28
77.03
76.77
51.61
36.88
36.64



(**5ai**)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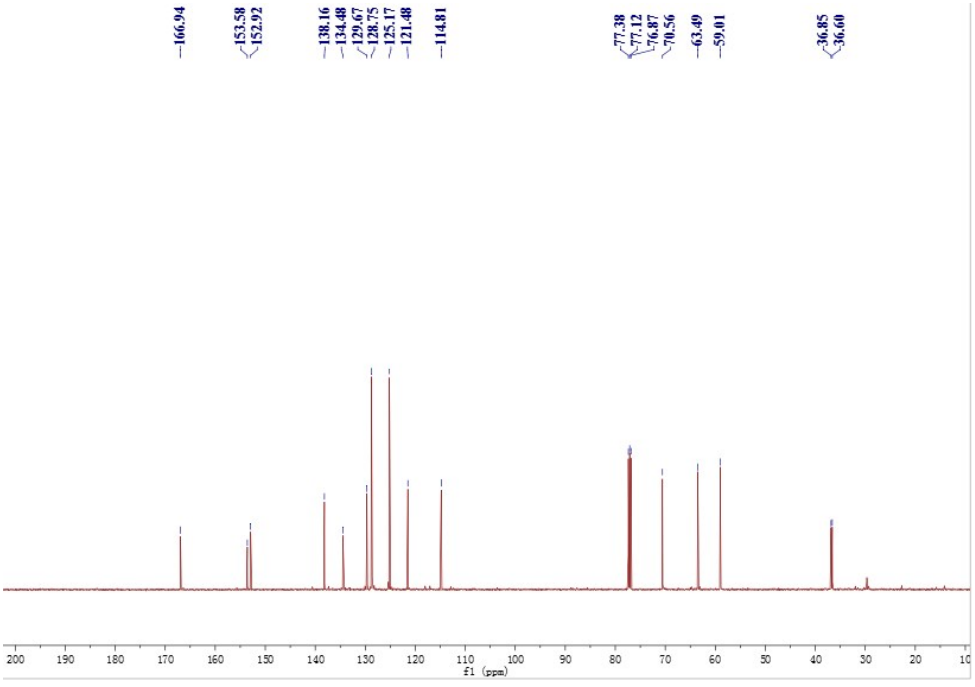
7.28
7.28
7.27
6.46
6.44
6.02
5.99
4.26
4.25
4.24
4.24
3.57
3.56
3.55
3.33
3.13
2.91
1.00
2.00
3.00
1.00
1.00
2.00
2.00
3.00
3.00
3.00
f1 (ppm)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129.67
128.75
125.17
121.48
114.81
77.38
77.12
76.87
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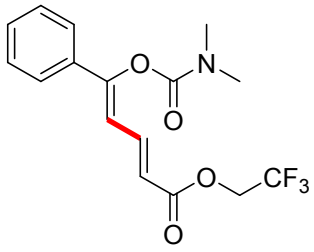
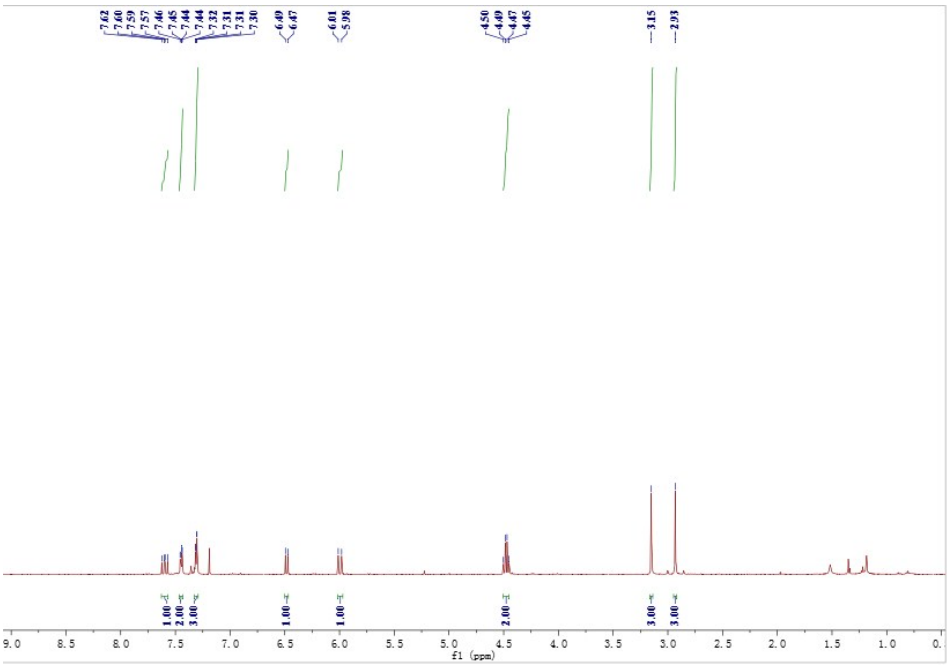
63.49
59.01
36.85
36.60
f1 (ppm)



(**5aj**)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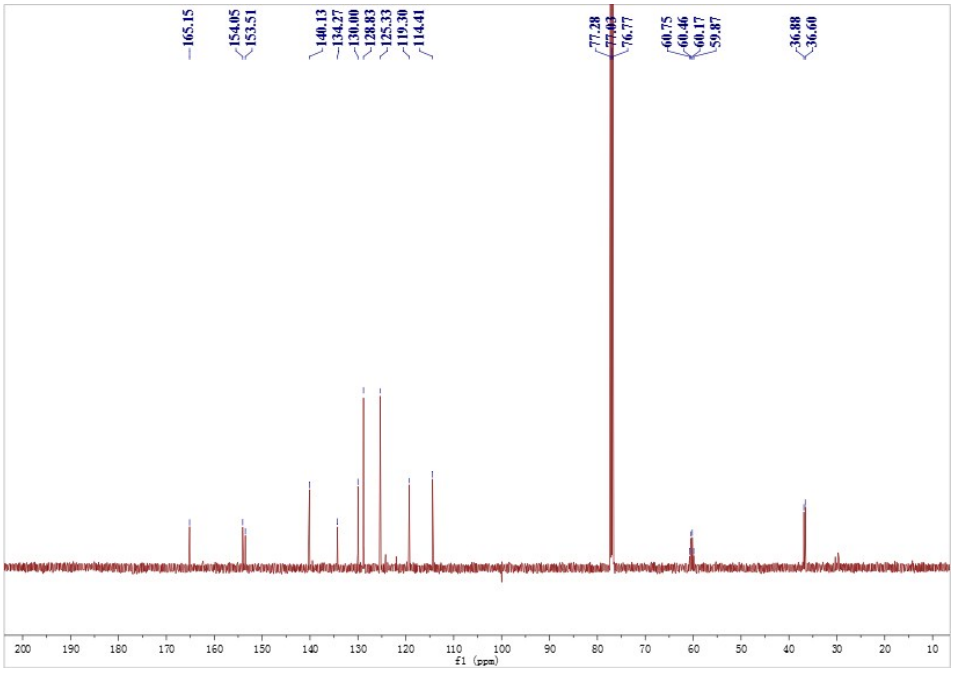
7.31
7.30
6.49
6.47
6.01
5.98
4.50
4.49
4.47
4.45
3.15
2.93
1.00
2.00
3.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)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154.05
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140.13
134.27
130.00
128.83
125.33
119.30
114.41
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77.03
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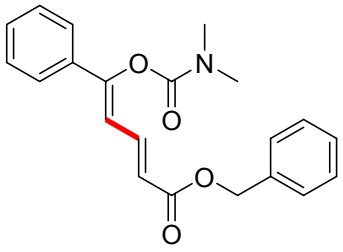
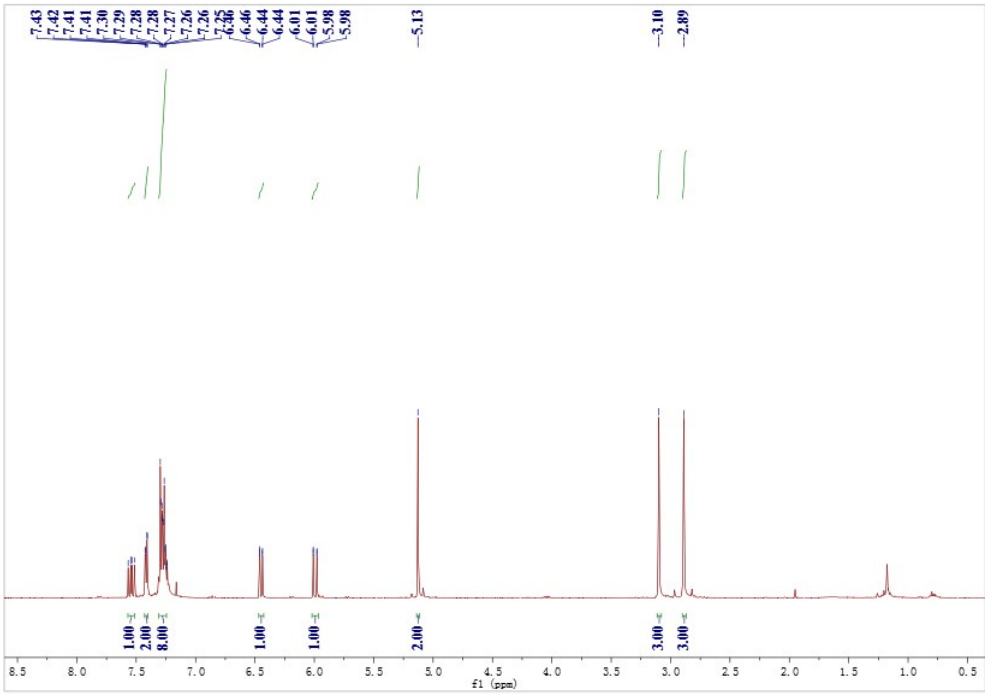
60.17
59.87
36.88
36.60
f1 (ppm)



(**5ag**)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7.27
7.26
7.26
6.46
6.44
6.44
6.01
6.01
5.98
5.98
5.13
3.10
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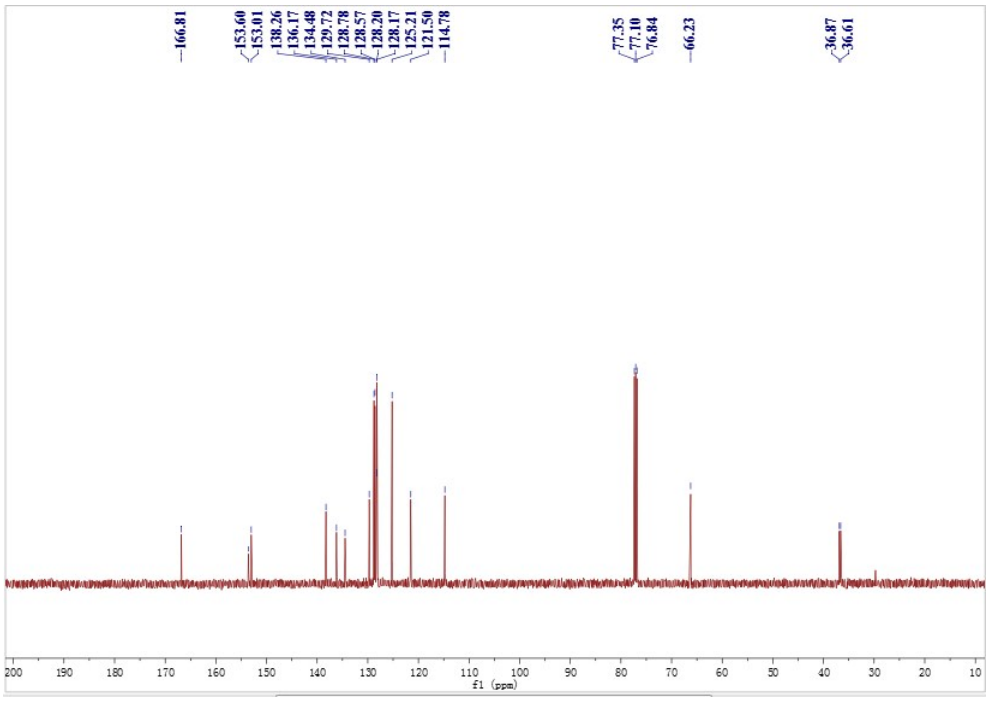
1.00
2.00
8.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)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153.01
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136.17
134.48
129.72
128.78
128.57
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128.17
125.21
121.50
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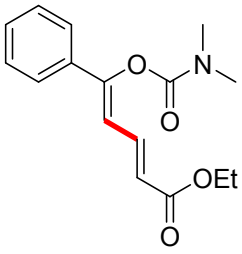
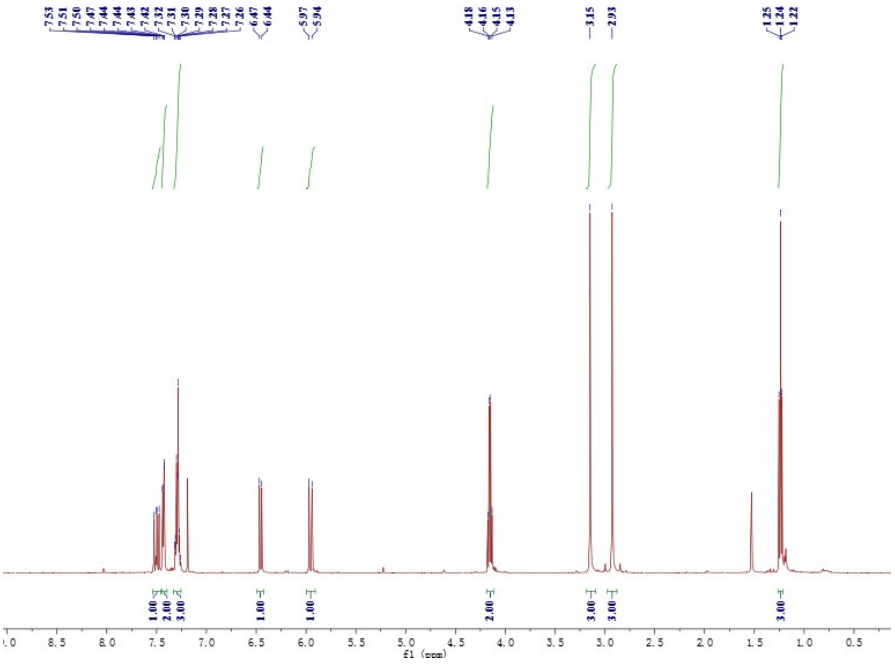
77.10
76.84
66.23
36.87
36.61
f1 (ppm)


O
N
O
OEt
O

(**5af**)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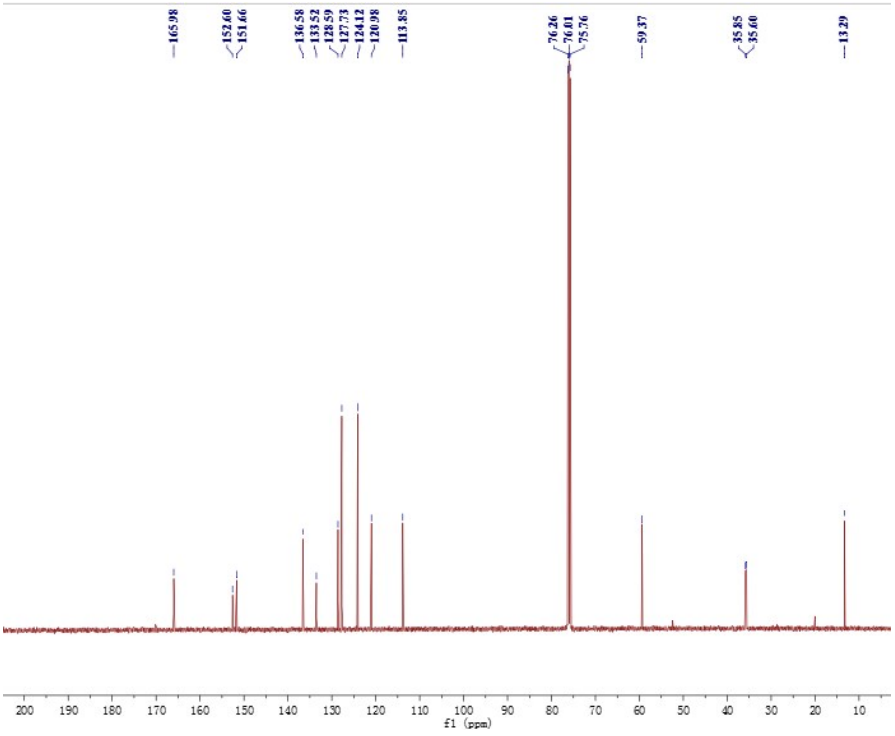
7.32
7.31
7.30
7.29
7.28
7.27
7.26
6.47
6.44
5.97
5.94
4.18
4.16
4.15
4.13
3.15
2.93
1.25
1.24
1.22
1.00
2.00
3.00
1.00
1.00
2.00
3.00
3.00
3.00
f1 (ppm)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151.66
136.58
133.52
128.59
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124.12
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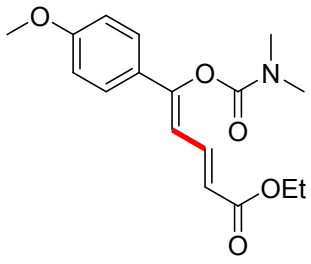
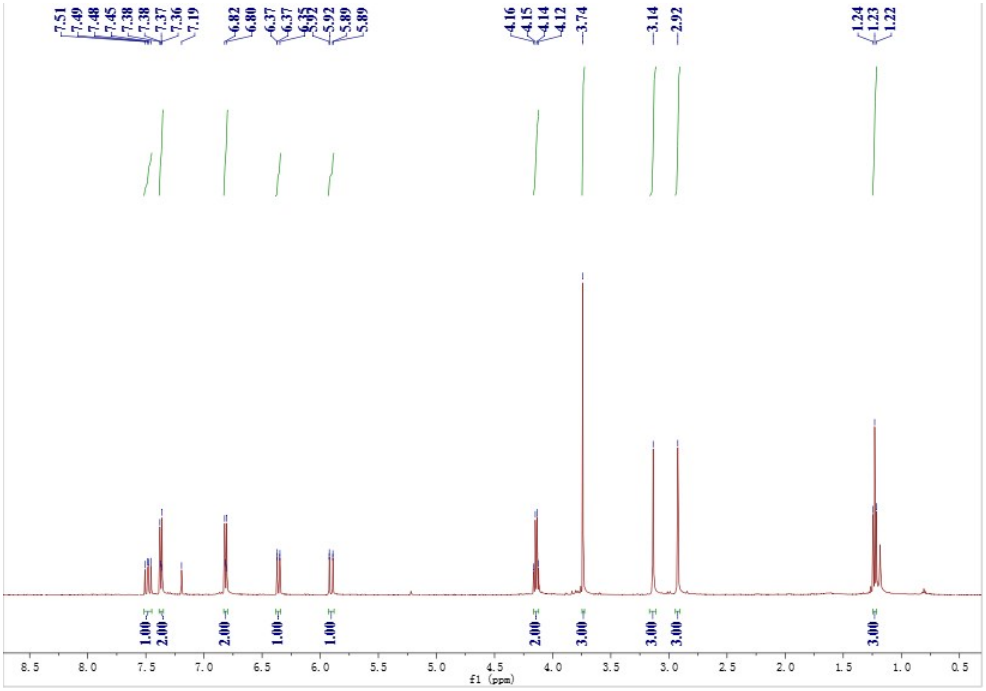
113.85
76.26
76.01
75.76
59.37
35.85
35.60
13.29
f1 (ppm)



(**5cf**)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7.49
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7.38
7.38
7.37
7.36
7.19
6.82
6.80
6.37
6.37
5.92
5.89
5.89
4.16
4.15
4.14
4.12
3.74
3.14
2.92
1.24
1.23
1.22
1.00
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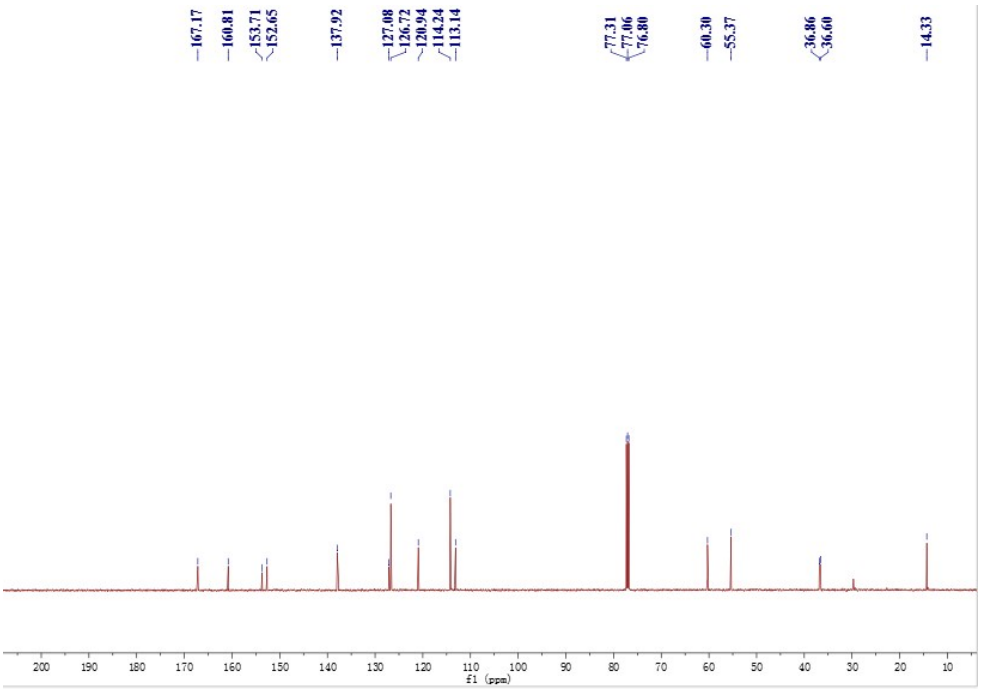
2.00
1.00
1.00
2.00
3.00
3.00
3.00
3.00
f1 (ppm)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127.08
126.72
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76.80
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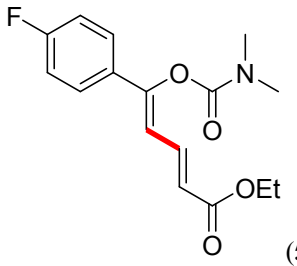
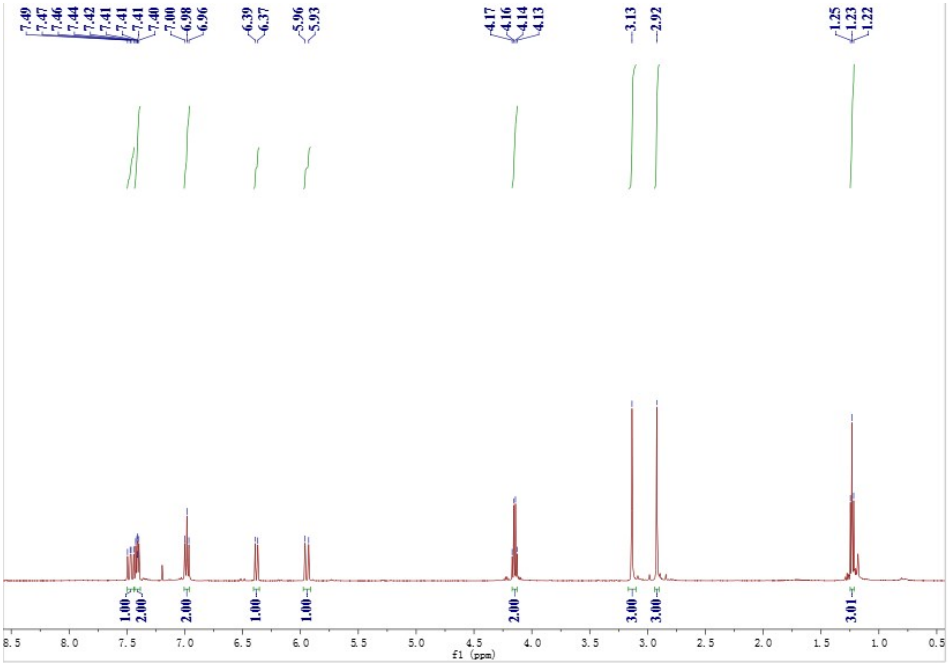
55.37
36.86
36.60
14.33
f1 (ppm)


F
O
N
O
OEt
O

(**5df**)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6.39
6.37
5.96
5.93
4.17
4.16
4.14
4.13
3.13
2.92
1.25
1.23
1.22
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2.00
2.00
1.00
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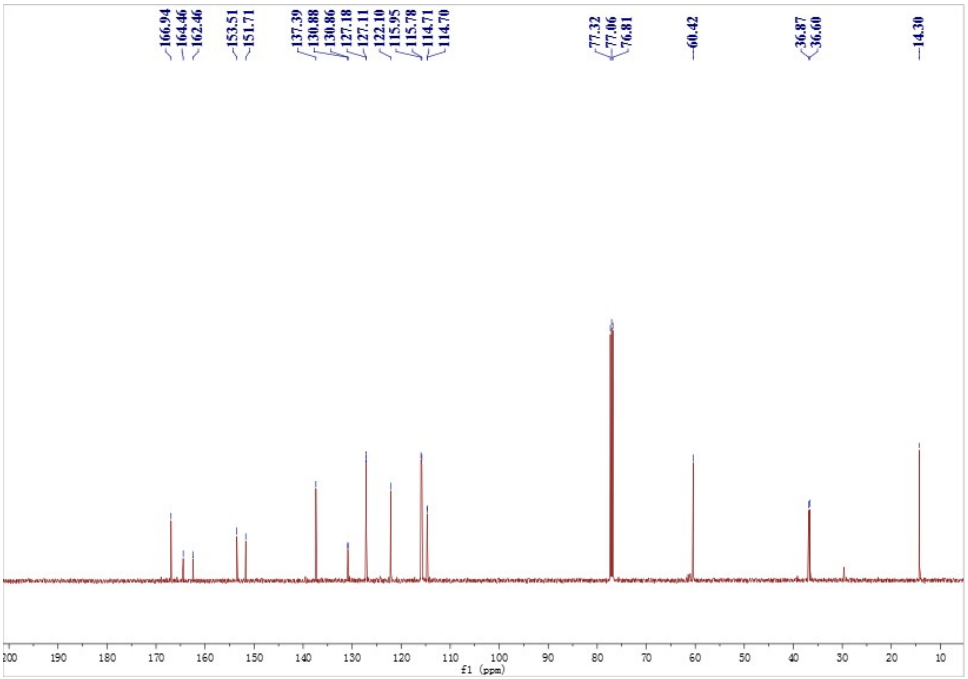
2.00
3.00
3.00
3.01
f1 (ppm)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153.51
151.71
137.39
130.88
130.86
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127.11
122.10
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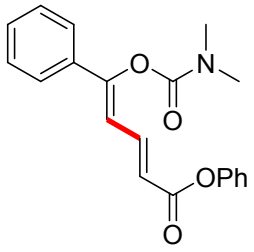
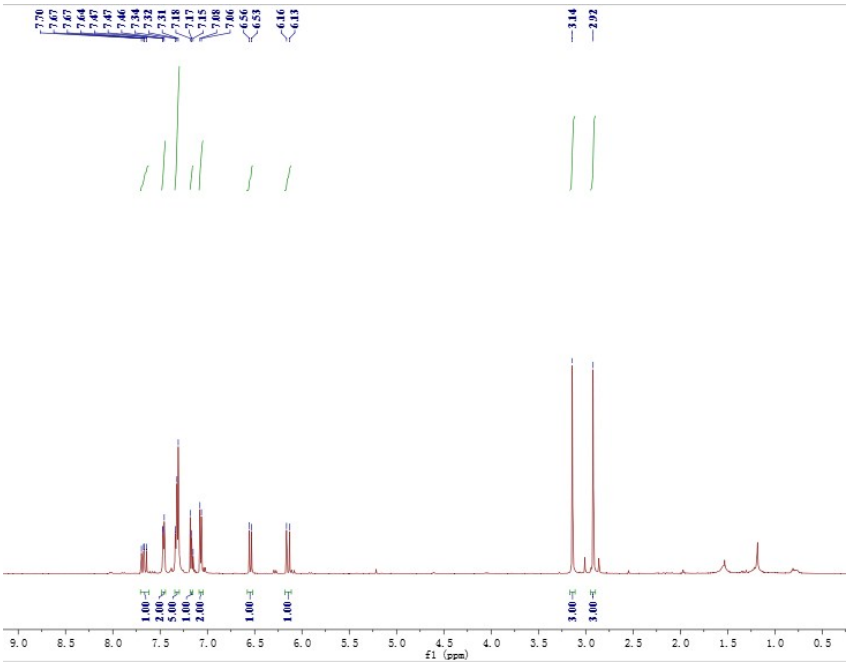
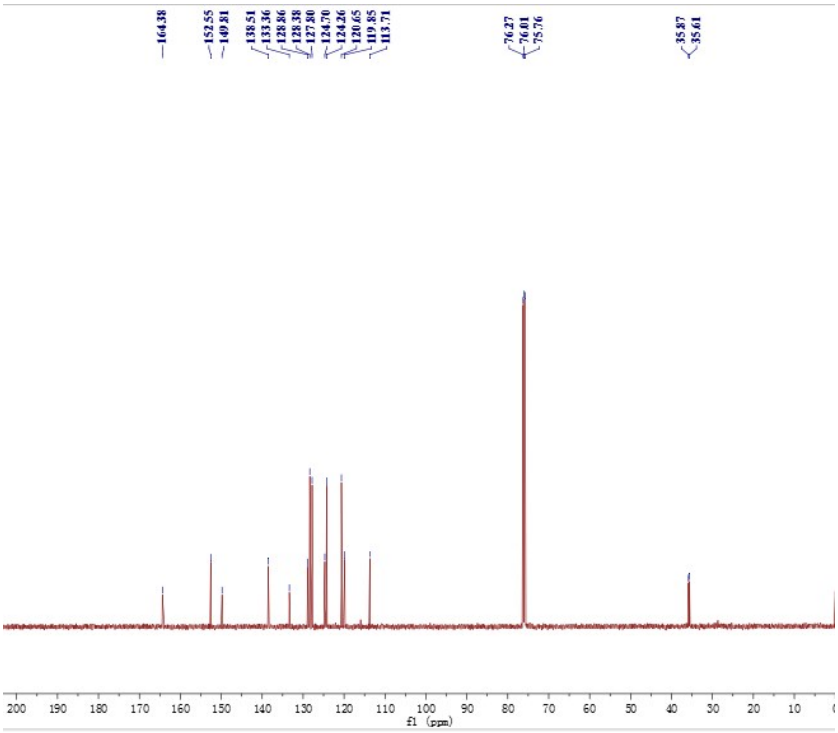
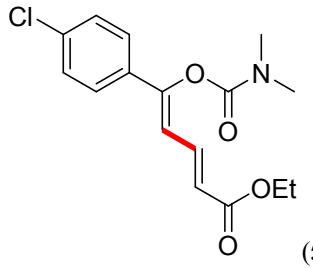
60.42
36.87
36.60
14.30
f1 (ppm)



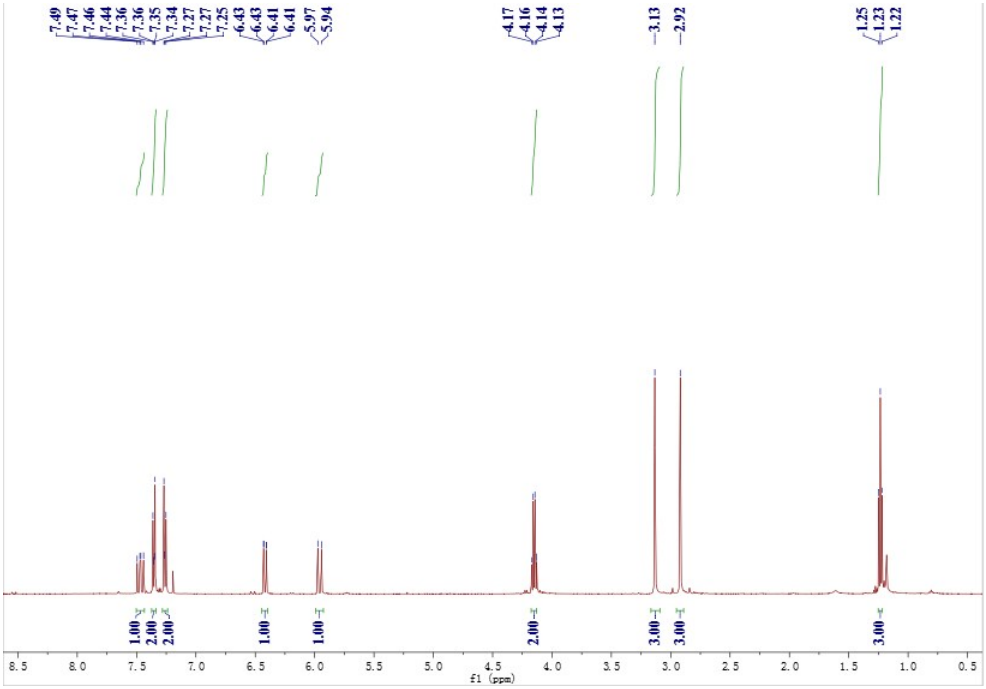
(**5ah**)






Cl
O
N
O
OEt
O

(**5ef**)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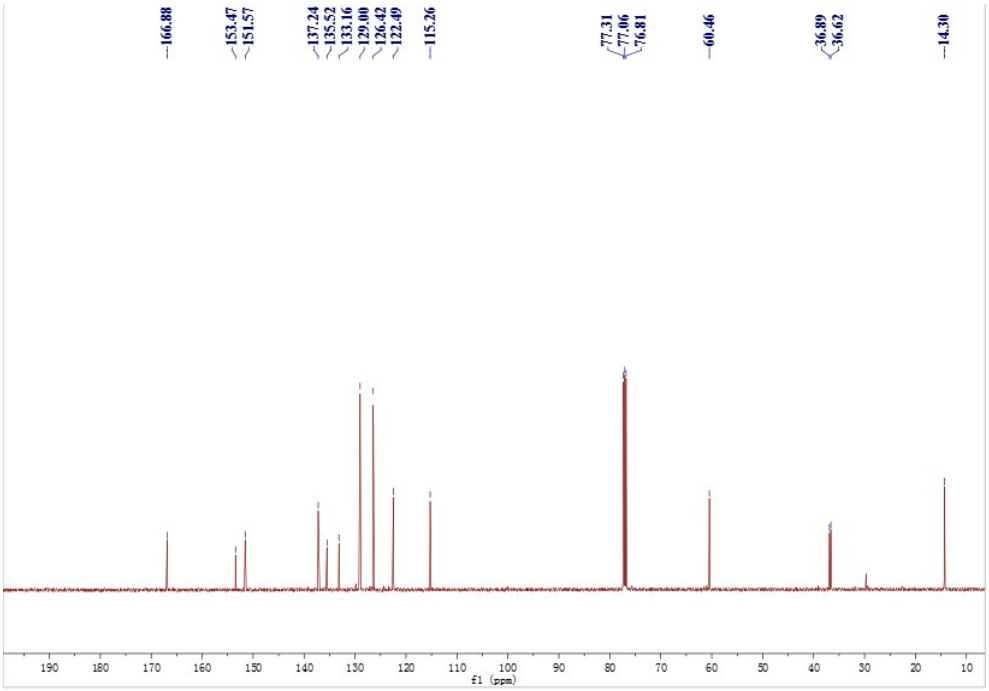
7.25
6.43
6.41
6.41
5.97
5.94
4.17
4.16
4.14
4.13
3.13
2.92
1.25
1.23
1.22
1.00
2.00
2.00
1.00
1.00
2.00
3.00
3.00
3.00
f1 (ppm)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122.49
115.26
77.31
77.06
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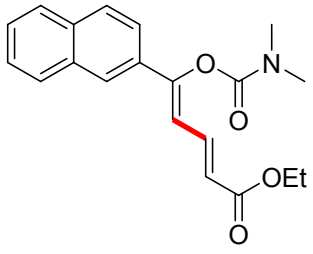
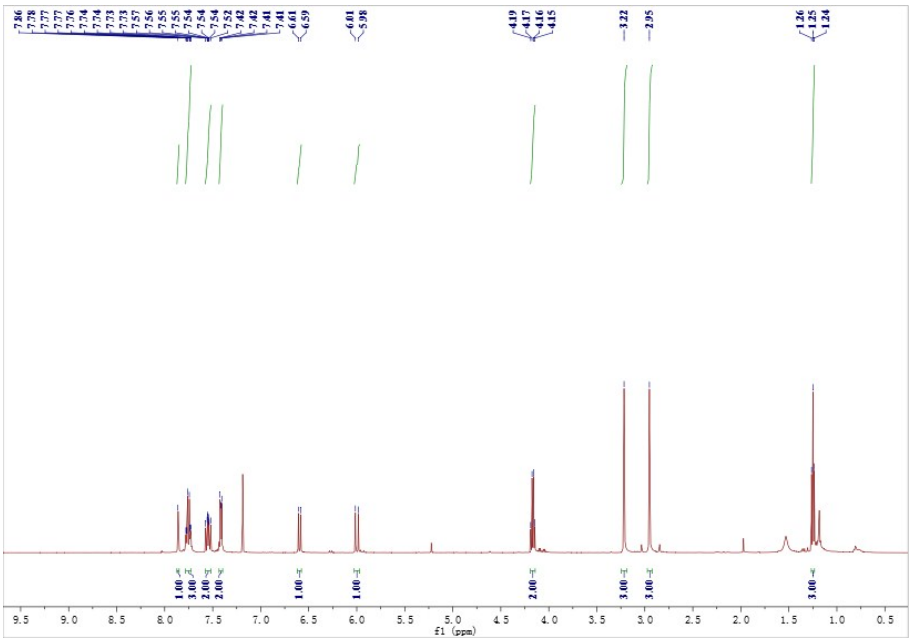
60.46
36.89
36.62
14.30
f1 (ppm)


O
N
O
OEt
O

(**5bf**)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7.73
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7.55
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7.41
6.61
6.59
6.01
5.98
4.19
4.17
4.16
4.15
3.22
2.95
1.26
1.25
1.24
1.00
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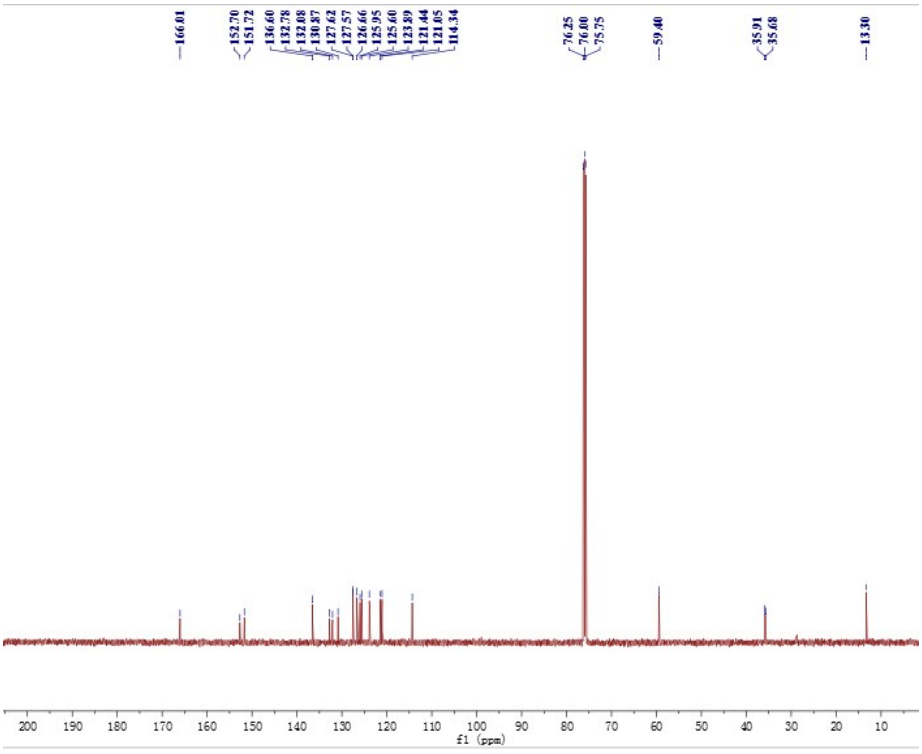
2.00
1.00
1.00
2.00
3.00
3.00
3.00
f1 (ppm)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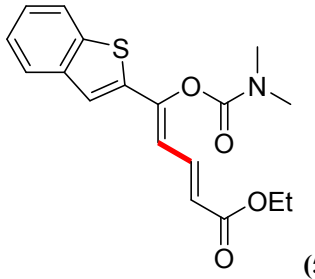
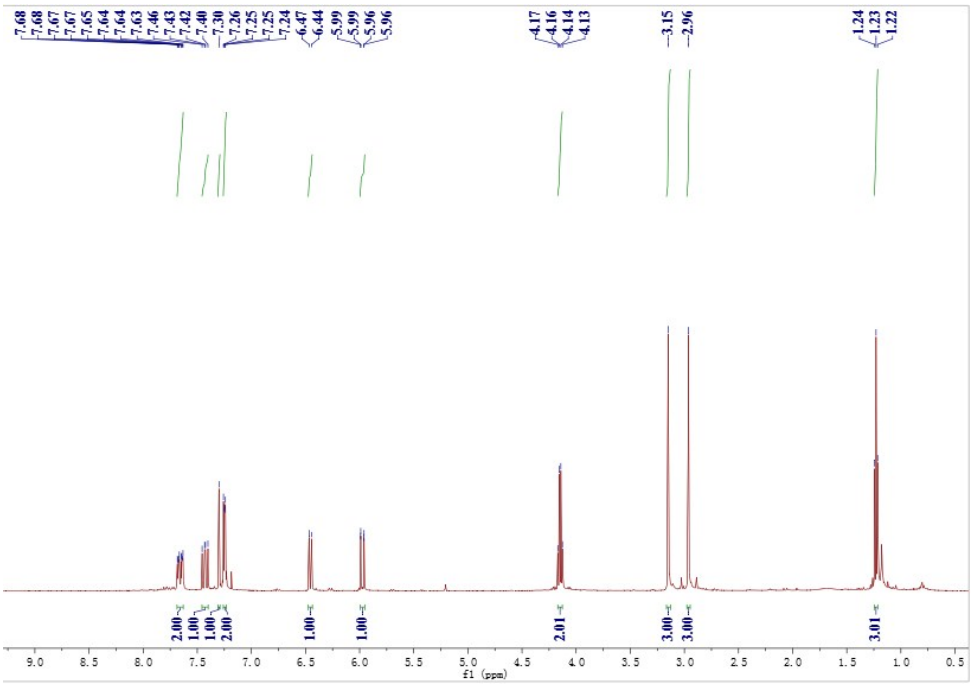
132.78
132.08
130.87
127.62
127.57
126.66
125.95
125.60
123.89
121.44
121.05
114.34
76.25
76.00
75.75
59.40
35.91
35.68
13.30
f1 (ppm)


S
O
N
O
OEt
O

(5mf)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7.25
7.25
7.24
6.47
6.44
5.99
5.99
5.96
5.96
4.17
4.16
4.14
4.13
3.15
2.96
1.24
1.23
1.22
2.00
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1.00
2.01
3.00
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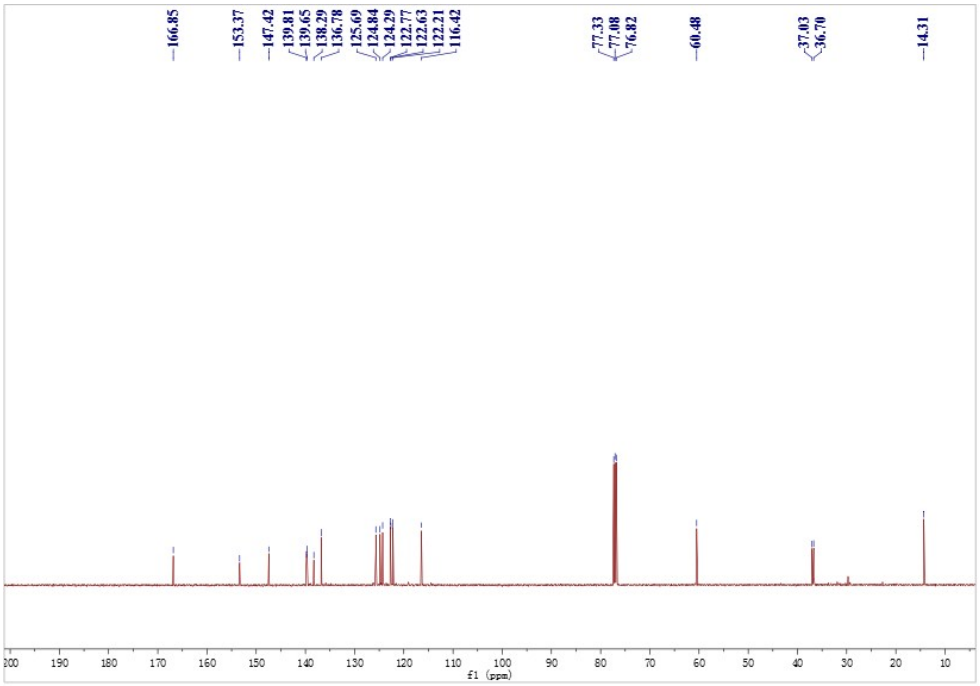
3.01
f1 (ppm)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77.08
76.82
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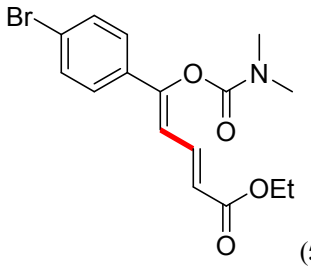
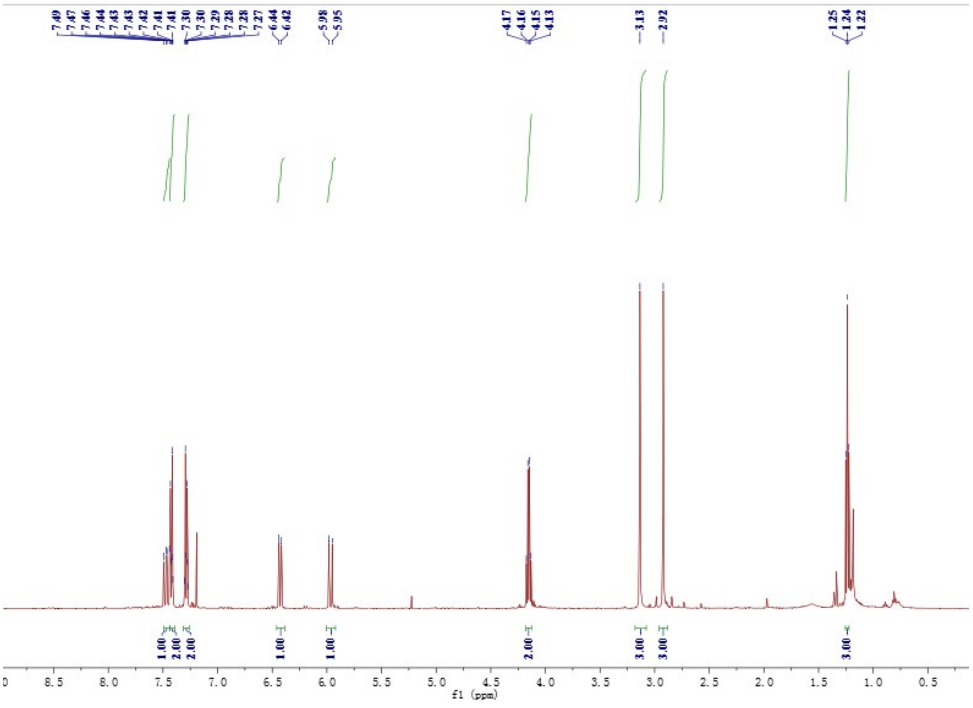
37.03
36.70
14.31
f1 (ppm)


Br
O
N
O
OEt
O

(**5ff**)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7.28
7.28
7.27
6.44
6.42
5.98
5.95
4.17
4.16
4.15
4.13
3.13
2.92
1.25
1.24
1.22
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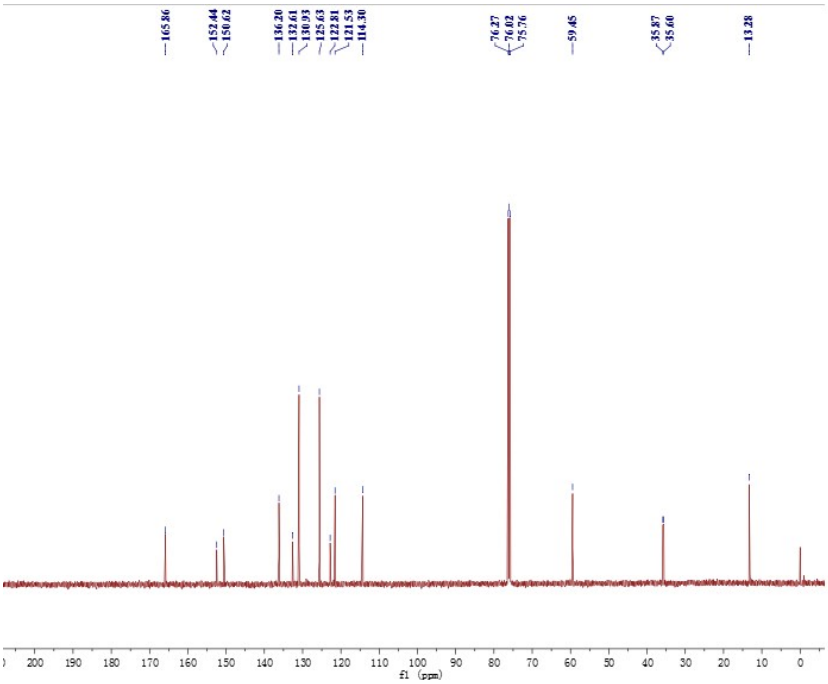
2.00
2.00
1.00
1.00
2.00
3.00
3.00
3.00
f1 (ppm)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76.02
75.76
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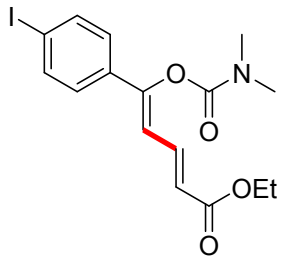
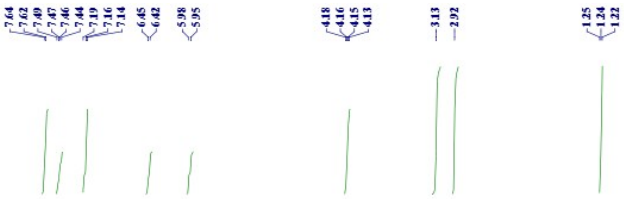
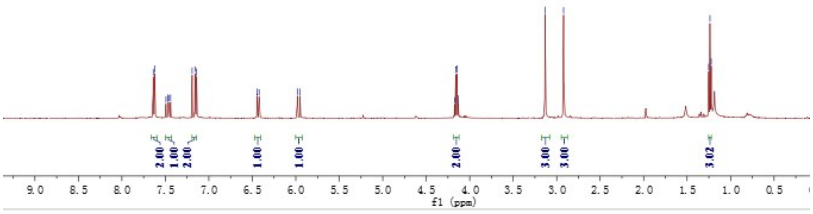
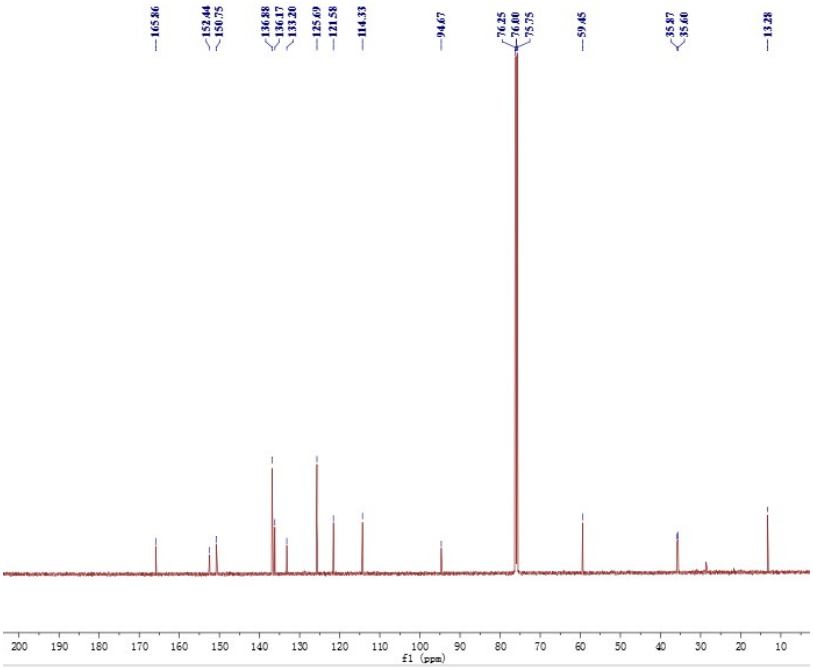
35.87
35.60
13.28
f1 (ppm)

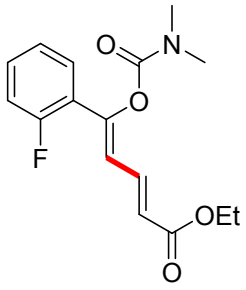


(5gf)

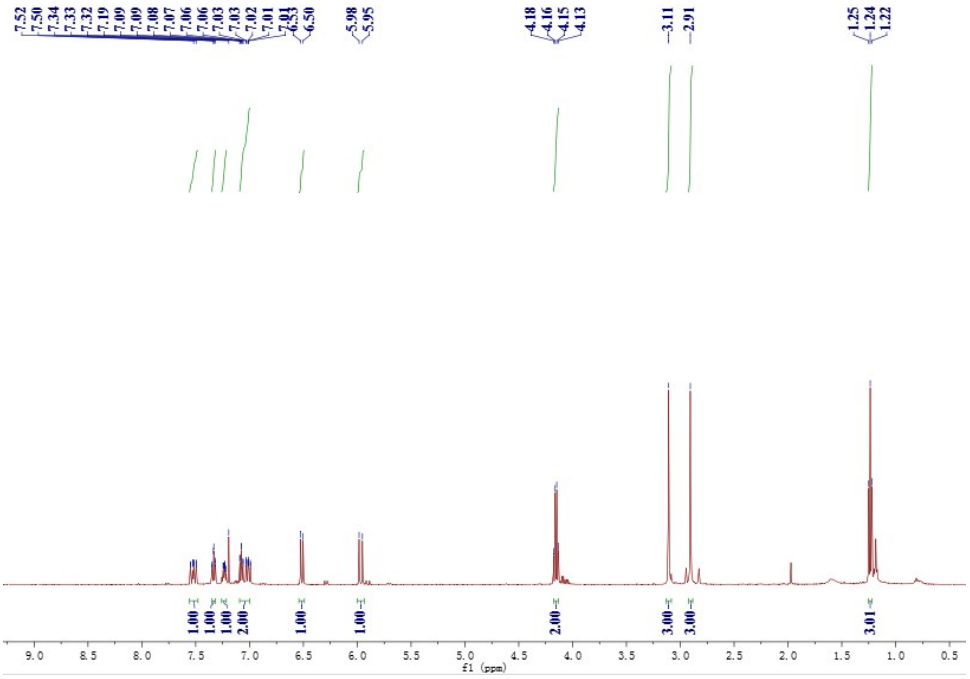







O
N
O
F
OEt
O

(**5kf**)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7.03
7.03
7.02
7.01
7.01
6.53
6.50
5.98
5.95
4.18
4.16
4.15
4.13
3.11
2.91
1.25
1.24
1.22
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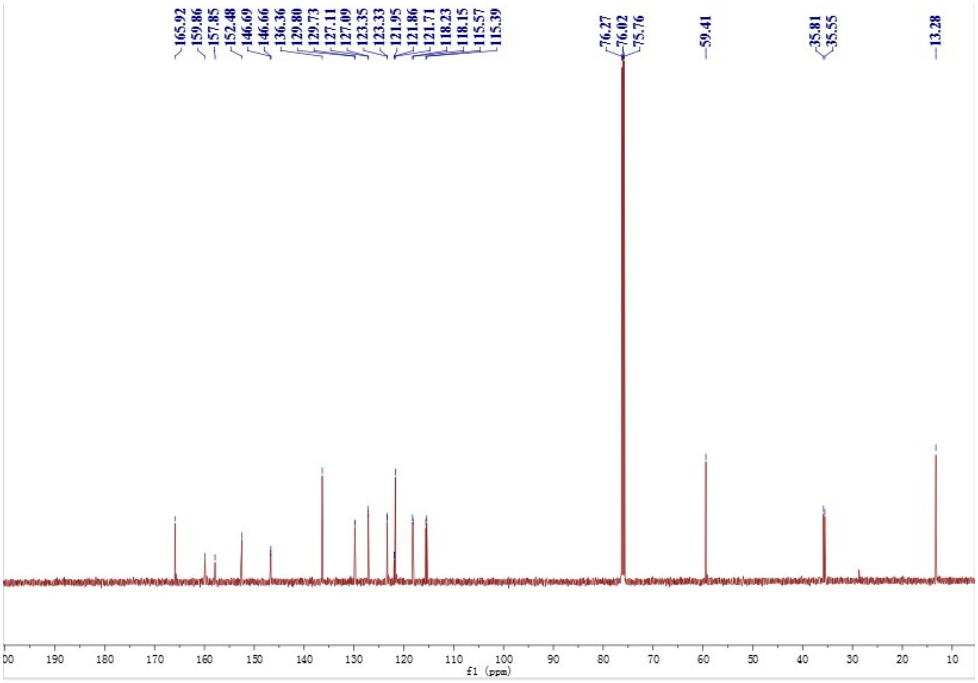
2.00
3.00
3.00
3.01
f1 (ppm)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127.09
123.35
123.33
121.95
121.86
121.71
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118.15
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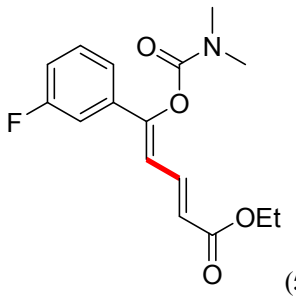
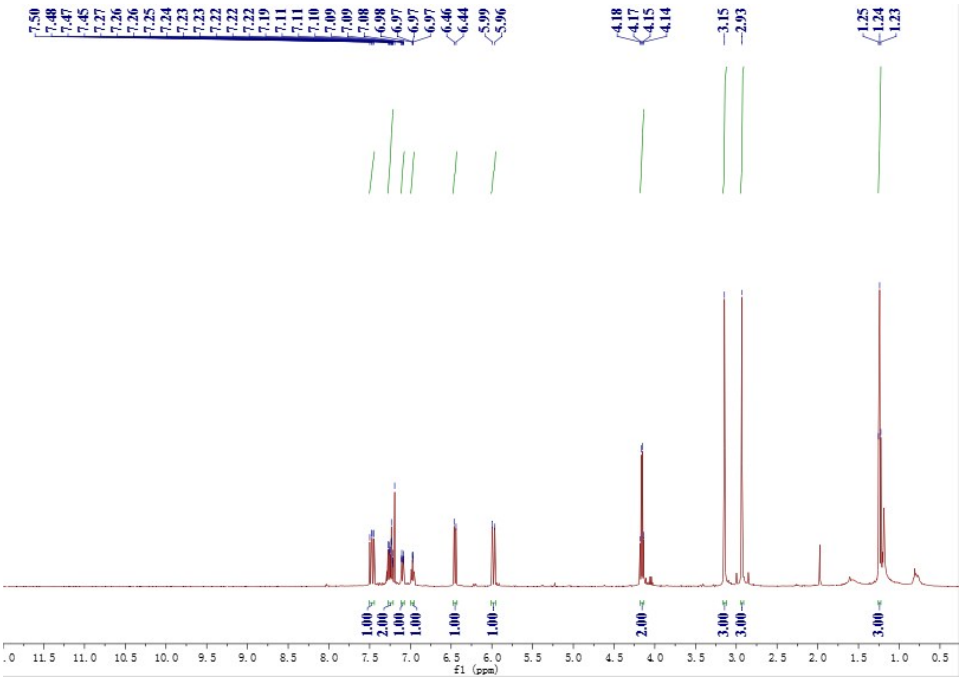
115.39
76.27
76.02
75.76
59.41
35.81
35.55
13.28
f1 (ppm)


O
N
O
F
OEt
O

(**5lf**)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7.23
7.23
7.22
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7.11
7.10
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7.08
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6.46
6.44
5.99
5.96
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4.17
4.15
4.14
3.15
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1.24
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3.00
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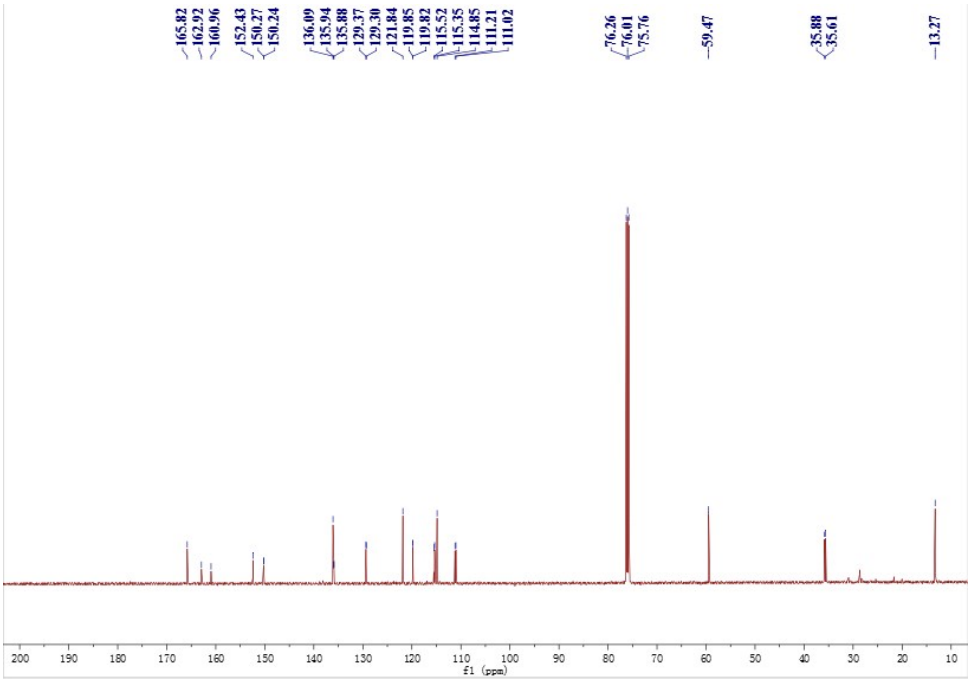
3.00
f1 (ppm)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150.24
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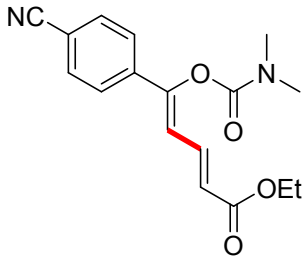
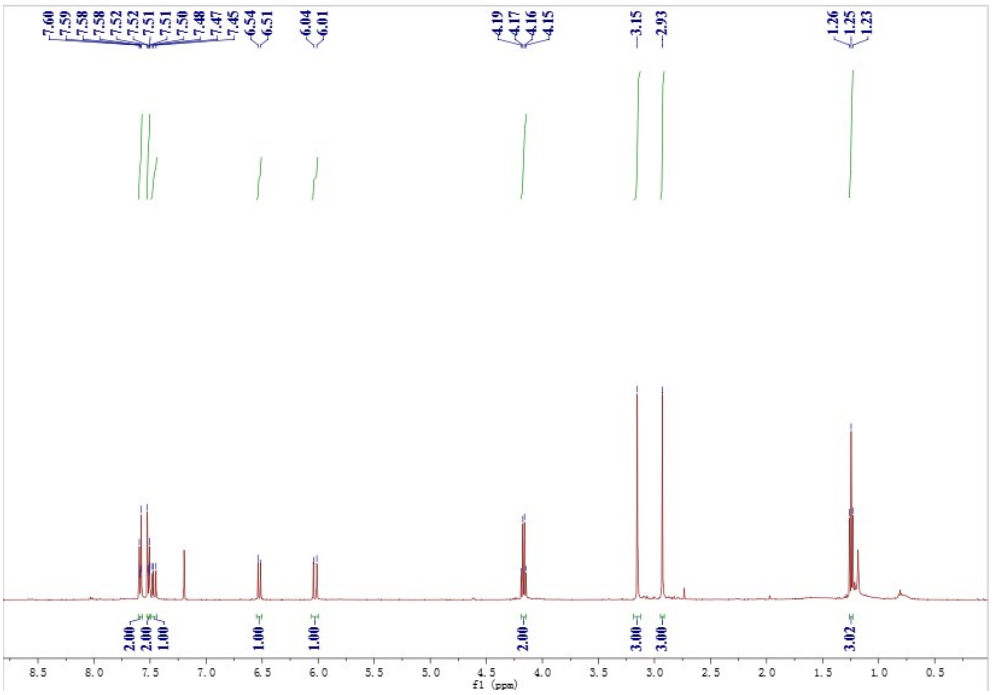
135.94
135.88
129.37
129.30
121.84
119.85
119.82
115.52
115.35
114.85
111.21
111.02
76.26
76.01
75.76
59.47
35.88
35.61
13.27
f1 (ppm)


NC
O
N
O
OEt
O

(**5hf**)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7.45
6.54
6.51
6.04
6.01
4.19
4.17
4.16
4.15
3.15
2.93
1.26
1.25
1.23
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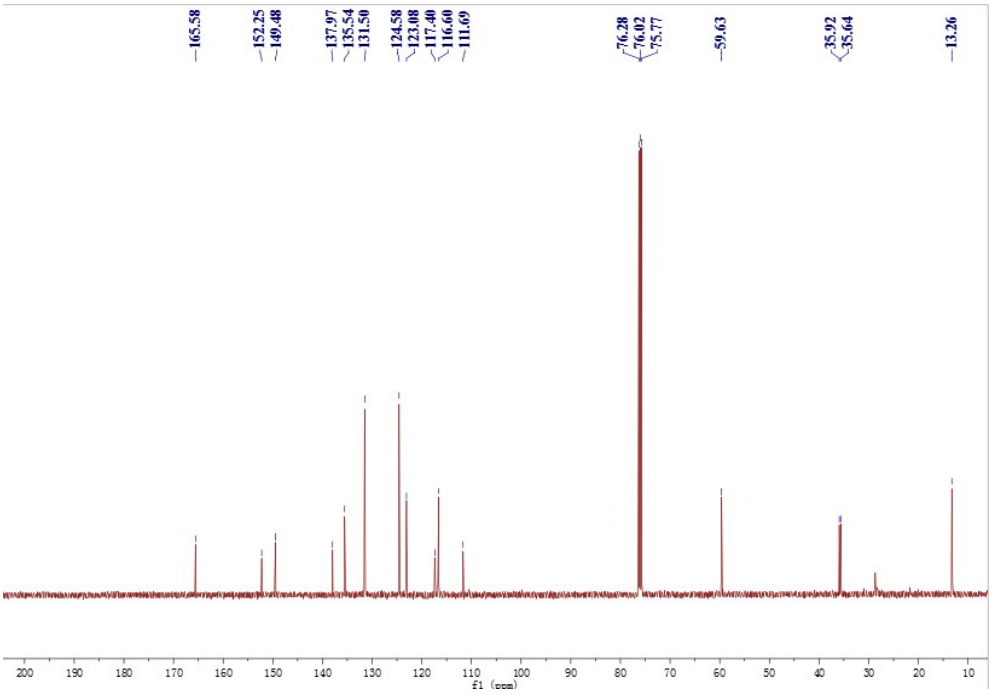
1.00
1.00
1.00
2.00
3.00
3.00
3.02
f1 (ppm)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137.97
135.54
131.50
124.58
123.08
117.40
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111.69
76.28
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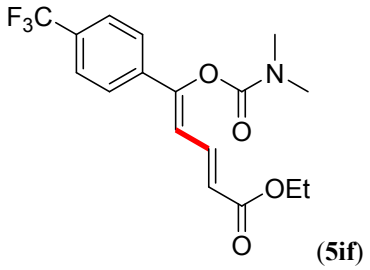
59.63
35.92
35.64
13.26
f1 (ppm)



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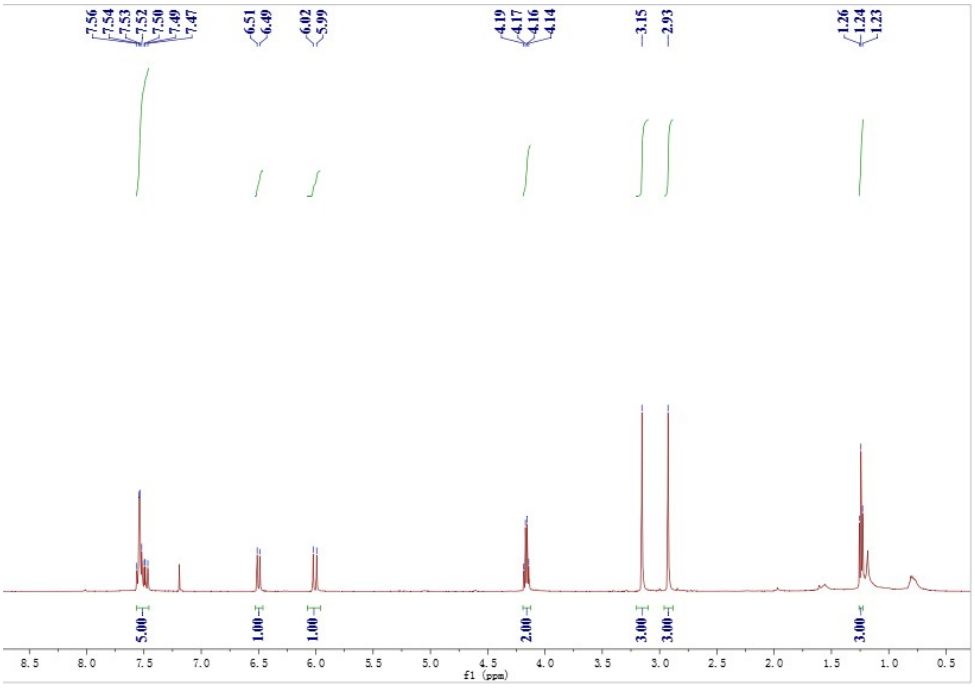
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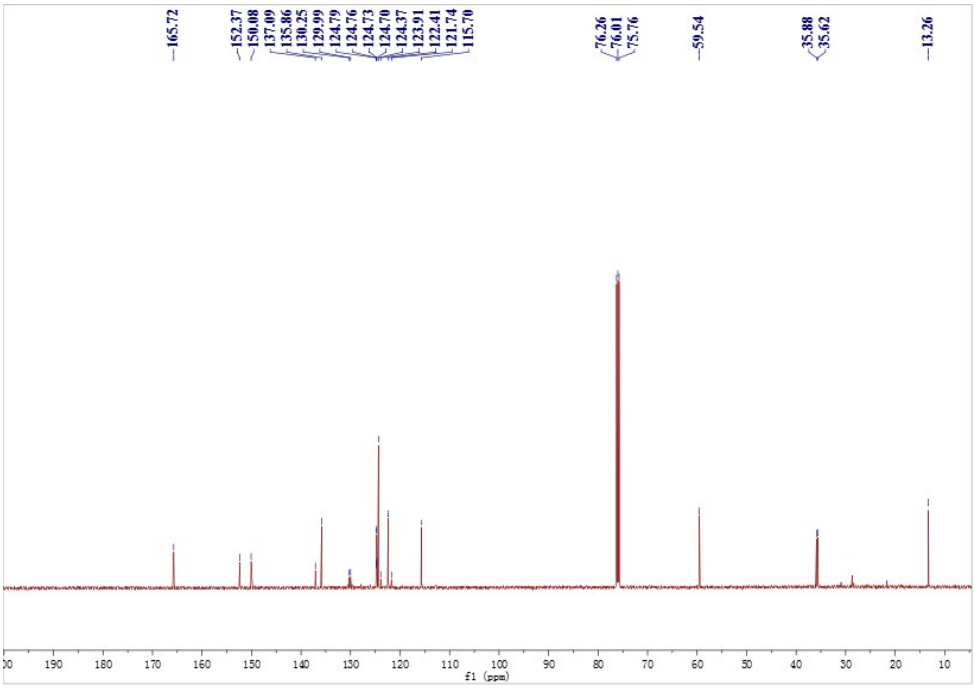
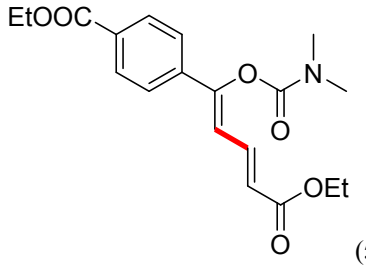
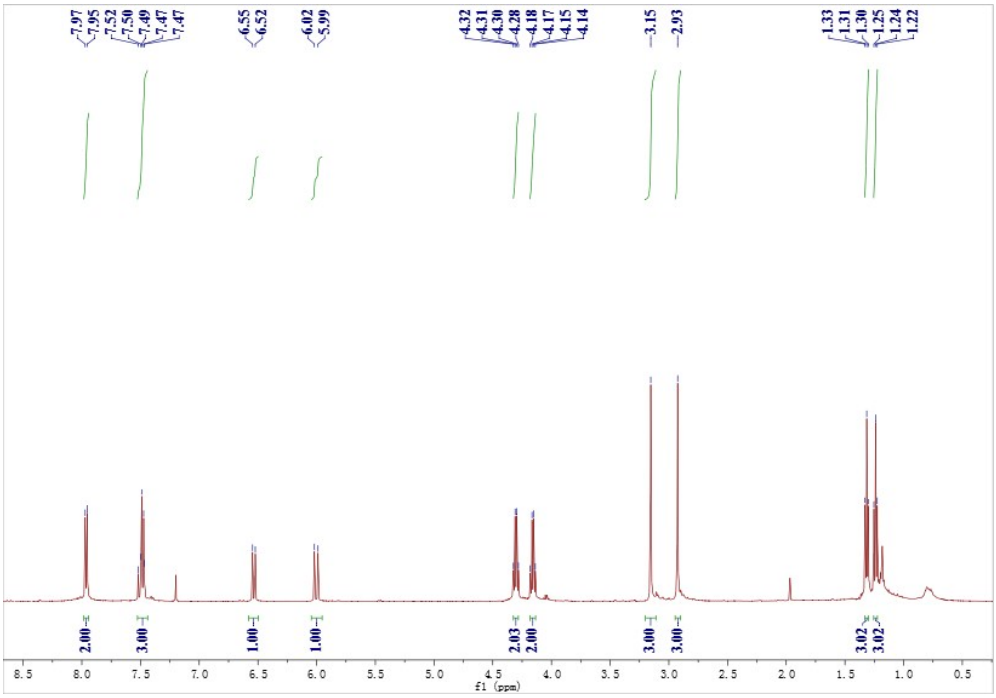
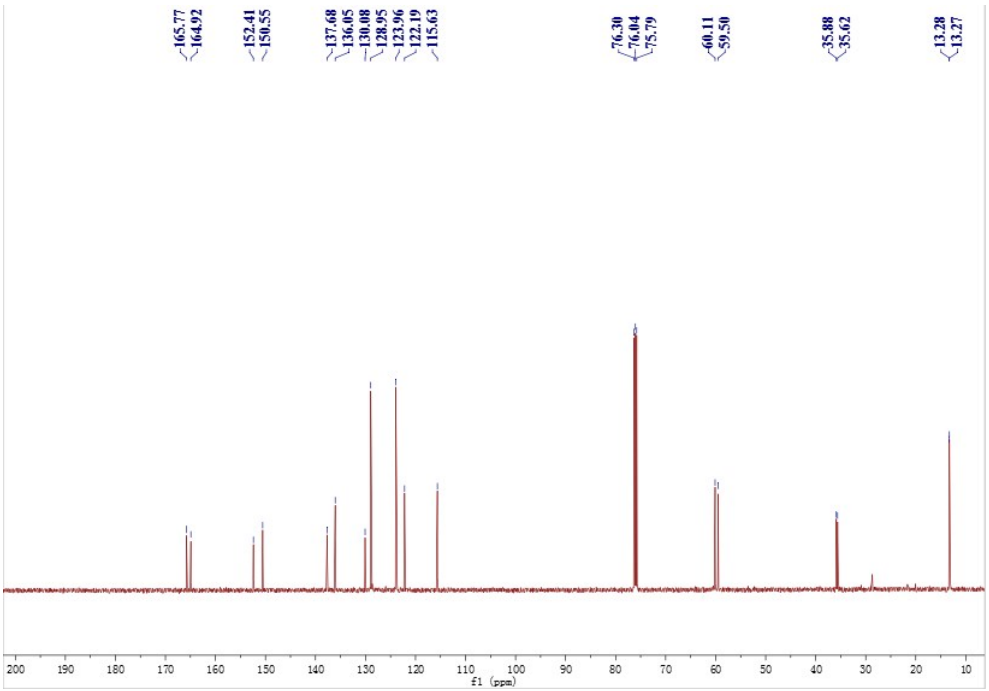
7.47
6.51
6.49
6.02
5.99
4.19
4.17
4.16
4.14
3.15
2.93
1.26
1.24
1.23
5.00
1.00
1.00
2.00
3.00
3.00
3.00
f1 (ppm)

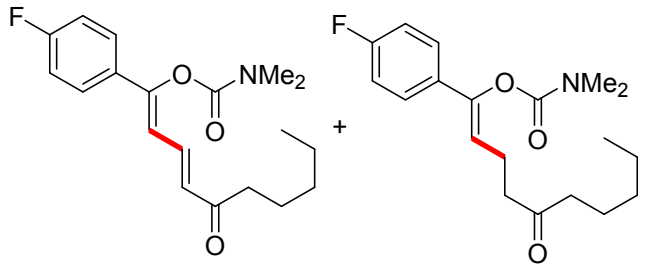

165.72
152.37
150.08
137.09
135.86
130.25
129.99
124.79
124.76
124.73
124.70
124.37
123.91
122.41
121.74
115.70
76.26
76.01
75.76
59.54
35.88
35.62
13.26
f1 (ppm)


EtOOC
O
N
O
OEt
O

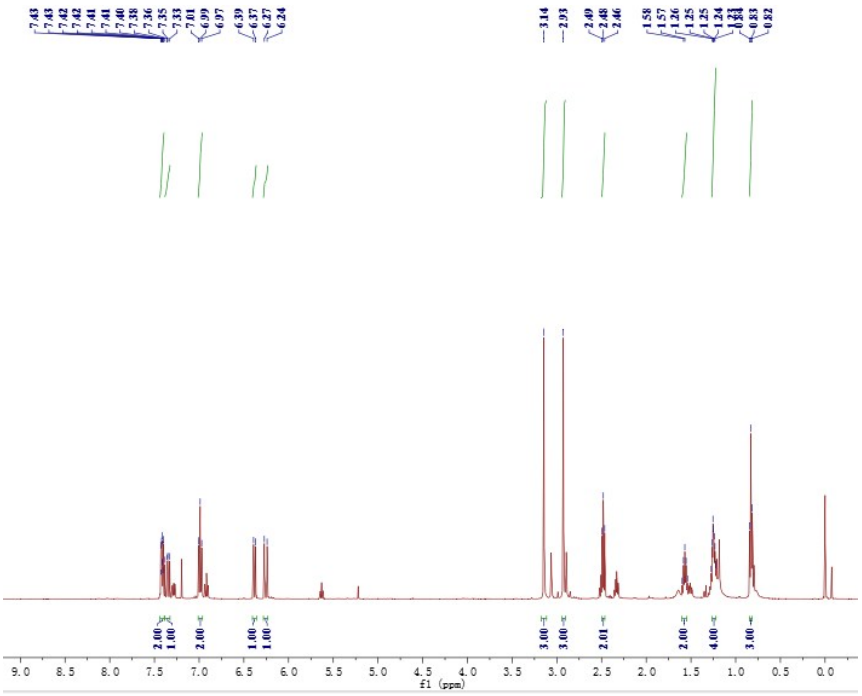
(**5jf**)

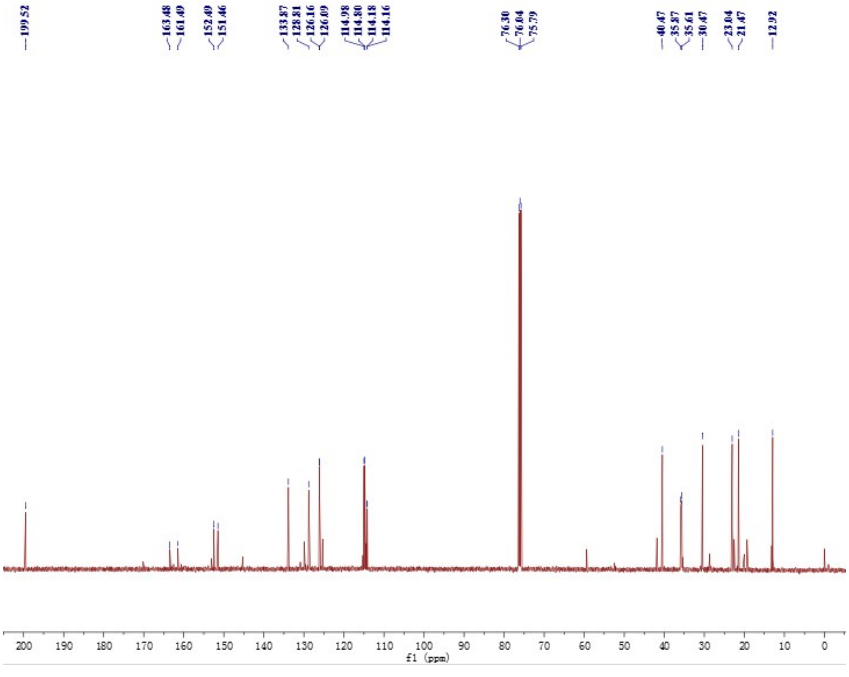

7.97
7.95
7.52
7.50
7.49
7.47
7.47
6.55
6.52
6.02
5.99
4.32
4.31
4.30
4.28
4.18
4.17
4.15
4.14
3.15
2.93
1.33
1.31
1.30
1.25
1.24
1.22
2.00
3.00
1.00
1.00
2.03
2.00
3.00
3.00
3.02
3.02
f1 (ppm)

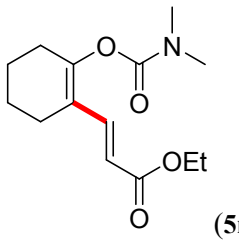

165.77
164.92
152.41
150.55
137.68
136.05
130.08
128.95
123.96
122.19
115.63
76.30
76.04
75.79
60.11
59.50
35.88
35.62
13.28
13.27
f1 (ppm)



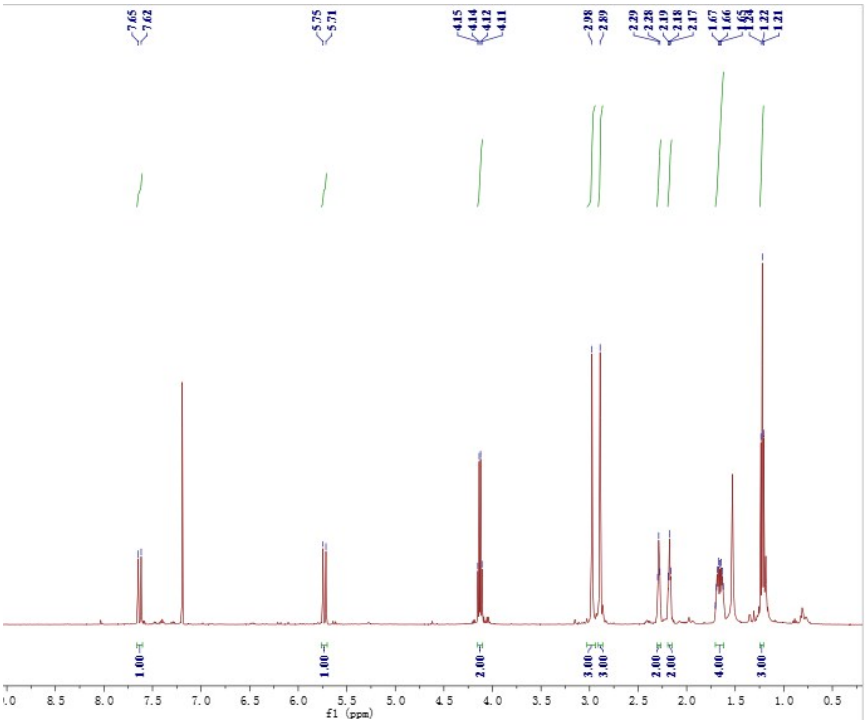
(5dk + 5dk'= 4/1)

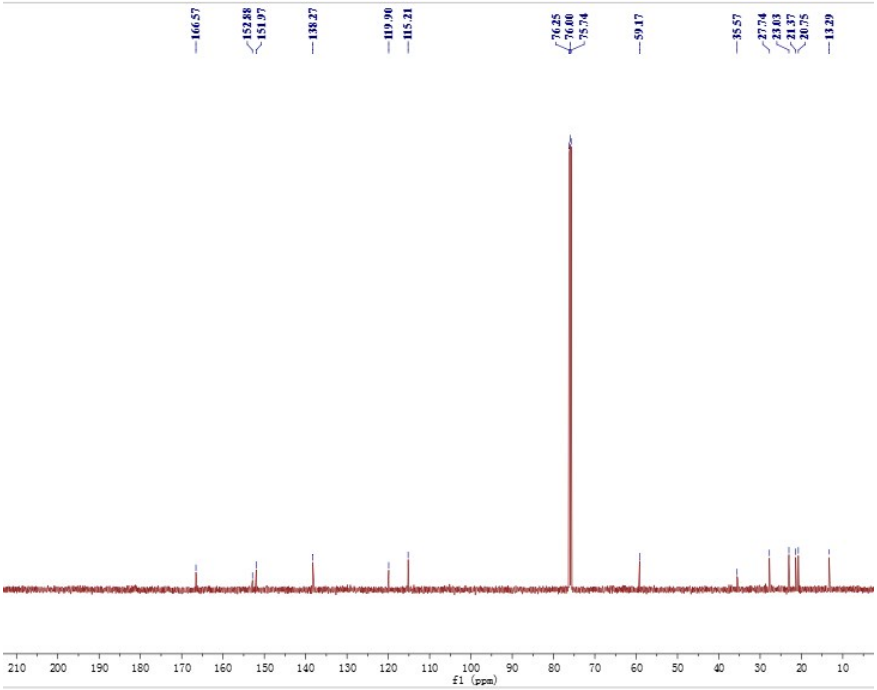


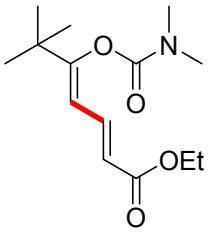




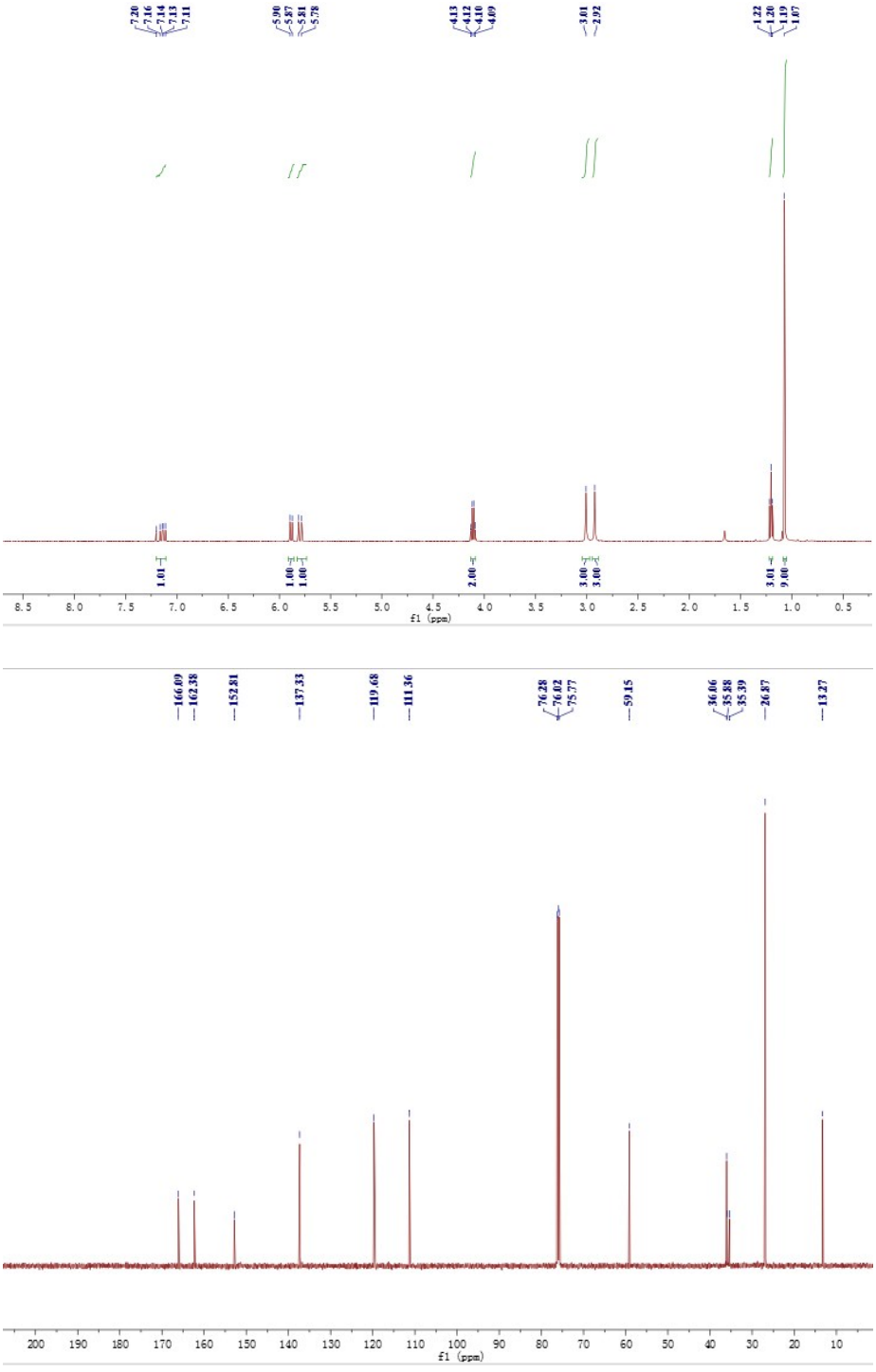
(**5nf**)






O
N
O
OEt
O

(**5of**)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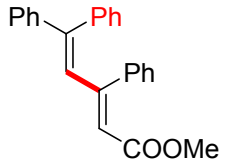
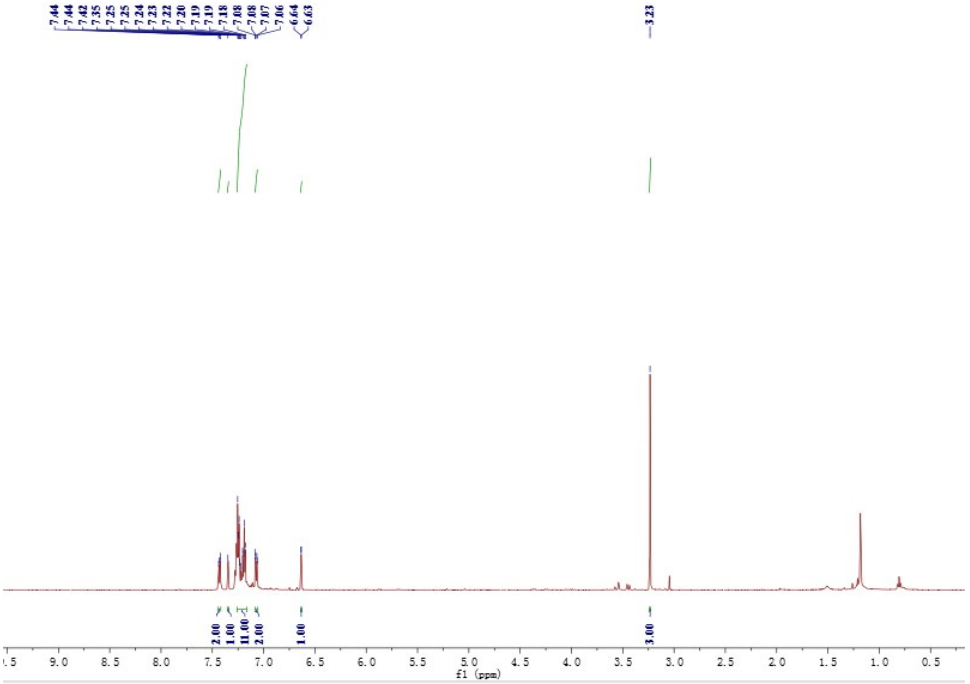
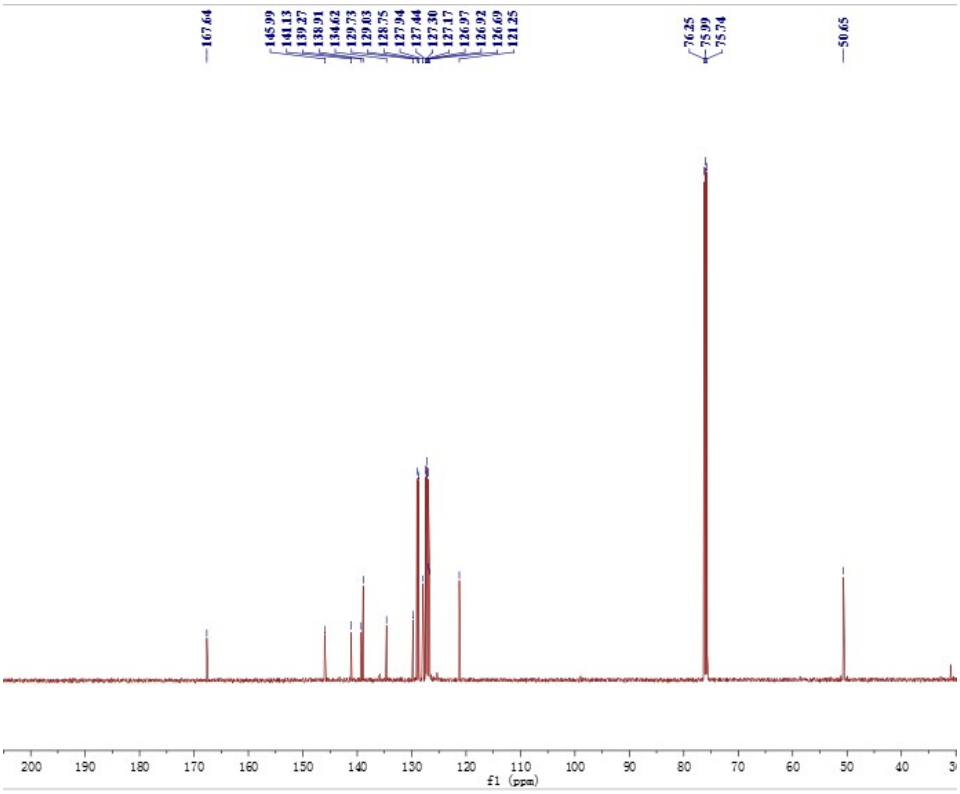
7.14
7.13
7.11
5.90
5.87
5.81
5.78
4.13
4.12
4.10
4.09
3.01
2.92
1.22
1.20
1.19
1.07
1.01
1.00
1.00
2.00
3.00
3.00
3.01
9.00
f1 (ppm)
166.09
162.38
152.81
137.33
119.68
111.56
76.28
76.02
75.77
59.15
36.06
35.88
35.39
26.87
13.27
f1 (ppm)


Ph
Ph
Ph
COOMe


7.44
7.44
7.42
7.35
7.25
7.25
7.24
7.23
7.22
7.20
7.19
7.19
7.18
7.08
7.08
7.07
7.06
6.64
6.63
3.23
2.60
1.60
11.00
2.00
1.60
3.60
f1 (ppm)


167.64
145.99
141.13
139.27
138.91
134.62
129.73
129.03
128.75
127.94
127.44
127.30
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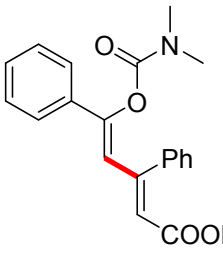
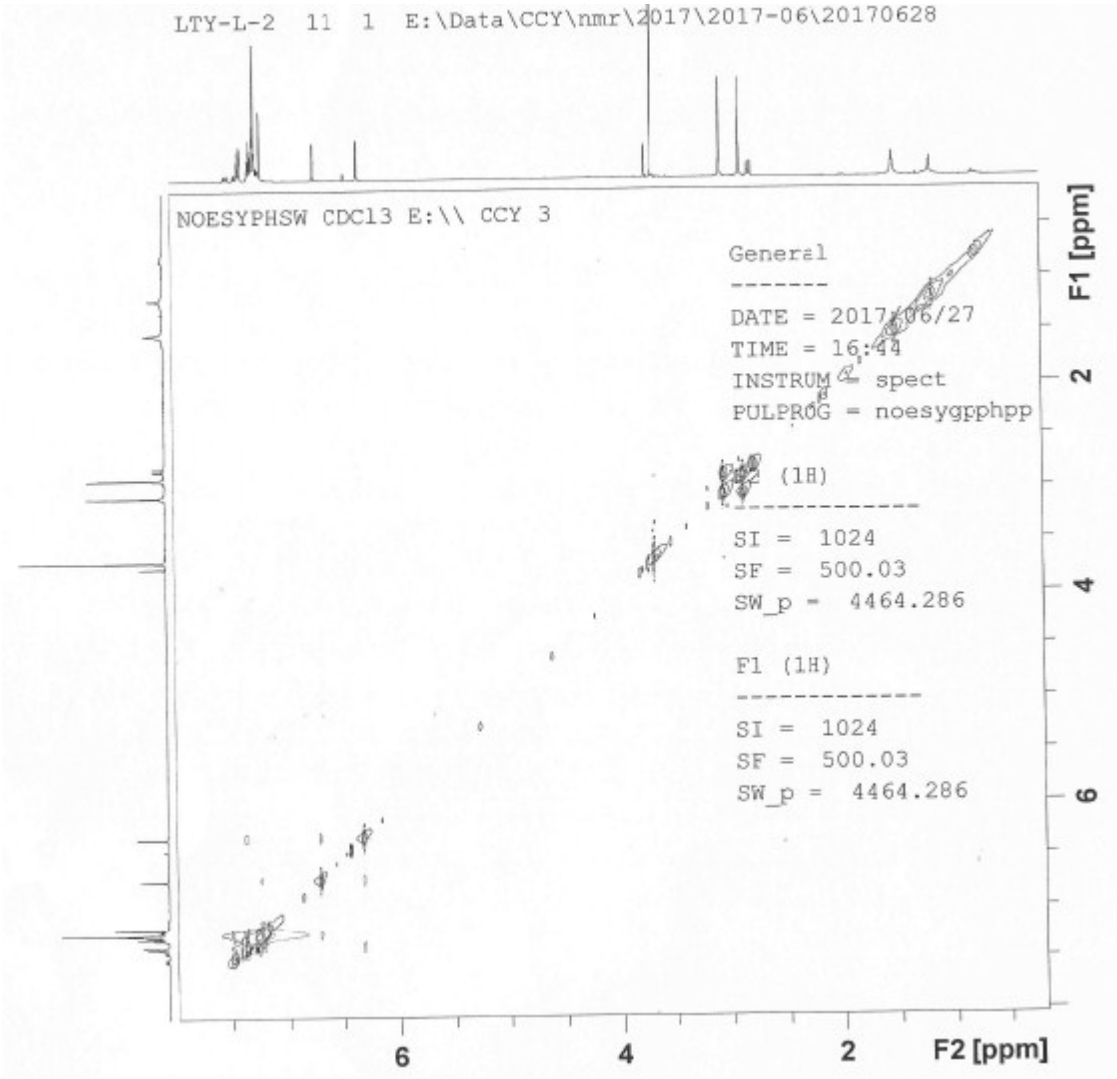
121.25
76.25
75.99
75.74
50.65
f1 (ppm)


O
N
O
Ph
COOMe

(4aa) NOE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PULPROG = noesygpphpp
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SI = 1024
SF = 500.03
SW_p = 4464.286
F1 (1H)
SI = 1024
SF = 500.03
SW_p = 4464.286
F1 [ppm]
F2 [ppm]
2
4
6
6
4
2