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Supporting Information for:

Synthesis of Tetrasubstituted Allenes via a 1,4-Palladium Migration/Carbene Insertion/*β*-H Elimination Sequence

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1. General Information

Commercially available reagents were used without further purification unless specified. Tetrahydrofuran was distilled from sodium/benzophenone before use. Unless otherwise stated, reactions were performed with freshly dried solvents utilizing standard Schlenk techniques under pre-dried argon. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 365 nm) and were dipped into a solution of $KMnO_4$. Flash chromatography was performed on silica gel 60 (40-63 μm) under a positive pressure of air. NMR-spectra were recorded on a Bruker Avance II 400 spectrometer. Chemicals shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for **^{1}H NMR** and **^{13}C NMR** spectra ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm;). **^{19}F NMR** spectra are not calibrated by an internal reference. The multiplicity of all signals was described with standard abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quintet = quint, heptet = hept, m = multiplet, br = broad resonance. Coupling constants (*J*) are quoted in Hz.

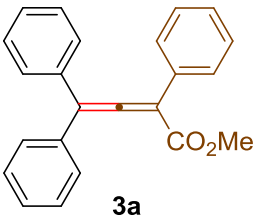
GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, film: 0.25 μm). High-resolution mass spectrometry was measured using an Agilent 6210 TOF LC/MS spectrometer or a Waters Quattro micro GC/MS/MS spectrometer.

The synthesis method and data of aryl bromides (**1**) and diazo compounds (**2**) were reported following the related references.[1-4]

2. General Procedure for Synthesis of Allenes

To a 25 mL Schlenk tube charged with a stir bar, aryl bromides (**1**) (0.2 mmol), diazoesters (**2**) (0.3 mmol), $Pd(OAc)_2$ (4.48 mg, 0.02 mmol), DPEPhos (16.2 mg, 0.03 mmol) and CsOAc (58 mg, 0.3 mmol) were added. After filled with argon, anhydrous THF (2 mL) were added *via* a syringe. The mixture was stirred at 80 ℃ in an oil bath for 2 h. Upon completion, the reaction mixture was washed with brine (15 mL) and extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After that the organic phase was filtered, and concentrated under reduced pressure. The crude products were purified by silica gel chromatography (PE/EA = 20:1 ~ 5:1) to afford pure products (**3**).

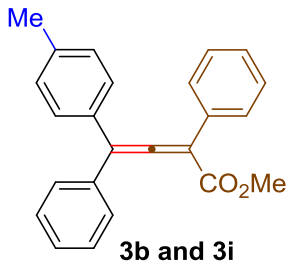
Methyl 2,4,4-triphenylbuta-2,3-dienoate (3a)



3a

White solid, 73-75 °C **m.p.**; 54.1 mg, 83% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64-7.58 (m, 2H), 7.47-7.26 (m, 13H), 3.86 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.62, 166.39, 134.75, 132.44, 128.83, 128.78, 128.58, 128.39, 128.33, 128.05, 114.82, 105.30, 52.64; **EI-MS** (m/z, %): 326 (M^+, 5.63), 91 (100), 167 (37.23), 150 (36.03); **HRMS** (EI): m/z calcd for $C_{23}H_{18}O_2$ $[M]^+$: 326.1307; found: 326.1315.

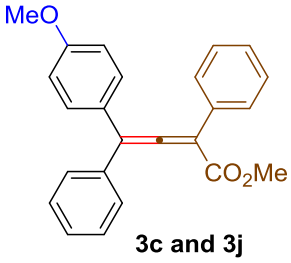
Methyl 2,4-diphenyl-4-(p-tolyl)buta-2,3-dienoate (3b and 3i)



3b and 3i

White solid, 73-76 °C **m.p.**; 49.6 mg, 73% yield for **3b** and 44.2 mg, 65% yield for **3i**; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62 (d, *J* = 7.1 Hz, 2H), 7.39-7.23 (m, 10H), 7.20-7.15 (m, 2H), 3.83 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.64, 166.48, 138.36, 134.90, 132.58, 131.71, 129.56, 128.79, 128.67, 128.55, 128.34, 127.97, 114.70, 105.15, 52.61, 21.37; **EI-MS** (m/z, %): 340 (M^+, 80.37), 281 (100), 325 (70.52), 265 (59.67); **HRMS** (EI): m/z calcd for $C_{24}H_{20}O_2$ $[M]^+$: 340.1463; found: 340.1457.

Methyl 4-(4-methoxyphenyl)-2,4-diphenylbuta-2,3-dienoate (3c and 3j)

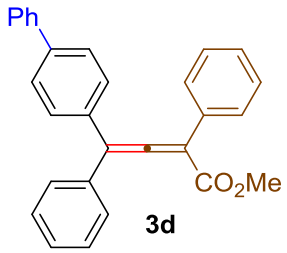


3c and 3j

White solid, 77-80 °C **m.p.**; 47.7 mg, 67% yield for **3c** and 55.5 mg, 78% yield for **3j**; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.46-7.23 (m, 10H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.60, 166.53, 159.84, 135.05, 132.68, 130.01, 128.81, 128.80, 128.57, 128.36, 128.33, 127.96, 126.78, 114.31, 105.08, 55.49, 52.64; **EI-MS** (m/z, %): 356

(M^+, 60.00), 297 (100), 252 (57.94), 105 (57.59); **HRMS** (EI): m/z calcd for $C_{24}H_{20}O_3$ $[M]^+$: 356.1412; found: 356.1408.

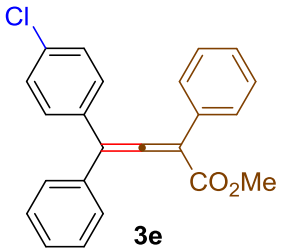
Methyl 4-([1,1'-biphenyl]-4-yl)-2,4-diphenylbuta-2,3-dienoate (**3d**)



3d

White solid, 93-97 °C **m.p.**; 60.3 mg, 75% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.69-7.55 (m, 6H), 7.53-7.24 (m, 13H), 3.85 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.84, 166.43, 141.30, 140.64, 134.72, 133.65, 132.42, 129.17, 128.99, 128.90, 128.63, 128.49, 128.38, 128.11, 127.67, 127.58, 127.19, 114.60, 105.41, 52.75; **EI-MS** (m/z, %): 402 (M^+,1.17), 84 (100), 86 (66.50), 47 (19.14); **HRMS** (EI): m/z calcd for $C_{29}H_{22}O_2$: 402.1620; found: 402.1625.

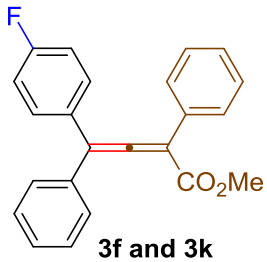
Methyl 4-(4-chlorophenyl)-2,4-diphenylbuta-2,3-dienoate (**3e**)



3e

White solid, 81-87 °C **m.p.**; 55.4 mg, 77% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.61-7.57 (m, 2H), 7.44-7.23 (m, 12H), 3.86 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.44, 166.22, 134.38, 134.34, 133.33, 132.18, 130.05, 129.08, 128.97, 128.72, 128.66, 128.62, 128.34, 128.23, 114.02, 105.63, 52.76; **EI-MS** (m/z, %): 360 (M^+, 58.27), 301 (100), 265 (92.01), 345 (56.13); **HRMS** (EI): m/z calcd for $C_{23}H_{17}O_2Cl$ [M]+: 360.0917; found: 360.0912.

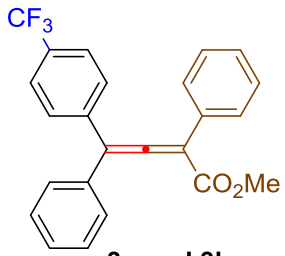
Methyl 4-(4-fluorophenyl)-2,4-diphenylbuta-2,3-dienoate (**3f and 3k**)



3f and 3k

White solid, 78-81 °C **m.p.**; 57.1 mg, 83% yield for **3f** and 51.6 mg, 75% yield for **3k**; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62-7.56 (m, 2H), 7.38 (m, 10H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ214.38, 166.32, 162.85 (d, *J* = 247.6 Hz), 134.65, 132.32, 130.51(d, *J* = 9.1 Hz), 128.93, 128.66 (d, *J* = 6 Hz),128.56, 128.33, 128.16, 115.87 (d, *J* = 21.1 Hz), 114.02, 105.44, 52.71; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.94; **EI-MS** (m/z, %): 344 (M^+,65.95), 285 (100), 105 (96.07), 283 (63.95); **HRMS** (EI): m/z calcd for $C_{23}H_{17}FO_2$: 344.1213; found: 344.1208.

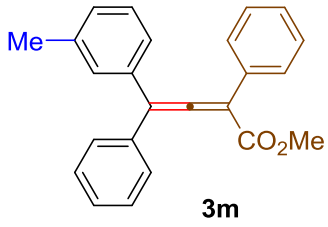
Methyl 2,4-diphenyl-4-(4-(trifluoromethyl)phenyl)buta-2,3-dienoate (3g and 3l)



3g and 3l

White solid, 87-88 °C **m.p.**; 63.0 mg, 80% yield for 3g and 57.5 mg, 73% yield for **3l**; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.67-7.60 (m, 4H), 7.55-7.52 (m, 2H), 7.45-7.22 (m, 8H), 3.87 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.69, 166.08, 138.77, 134.08, 131.91, 130.40 (q, *J* = 33 Hz), 129.06, 128.77, 128.72, 128.36, 125.87, 125.84, 125.80, 125.77 (q, *J* = 3.3 Hz), 124.17 (q, *J* = 271 Hz), 114.03, 105.96, 52.82. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.63; **EI-MS** (m/z, %): 394 (M^+, 67.16), 335 (100), 105 (66.43), 173 (52.34); **HRMS** (EI): m/z calcd for $C_{24}H_{17}O_2F_3$ $[M]^+$: 394.1181; found: 394.1175.

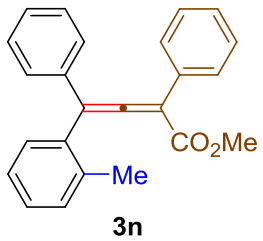
Methyl 2,4-diphenyl-4-(m-tolyl)buta-2,3-dienoate (3m)



3m

White solid, 73-75 °C **m.p.**; 53.0 mg, 78% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.67-7.57 (m, 2H), 7.50-7.19 (m, 11H), 7.15 (d, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.63, 166.49, 138.53, 134.89, 134.62, 132.52, 129.32, 129.22, 128.81, 128.73, 128.70, 128.58, 128.35, 128.01, 125.95, 114.86, 105.17, 52.65, 21.61; **EI-MS** (m/z, %): 340 (M^+,53.26), 281 (100), 105 (69.33), 165 (41.22); **HRMS** (EI): m/z calcd for $C_{24}H_{20}O_2$ $[M]^+$: 340.1463; found: 340.1467.

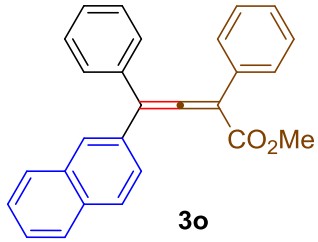
Methyl 2,4-diphenyl-4-(o-tolyl)buta-2,3-dienoate (3n)



3n

White solid, 77-79 °C **m.p.**; 44.2 mg, 65% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.39-7.22 (m, 12H), 3.84 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 213.19, 166.44, 137.36, 134.44, 133.96, 132.56, 130.69, 130.38, 128.95, 128.56, 128.52, 128.11, 128.01, 127.18, 126.29, 112.89, 104.88, 52.51, 20.16; **EI-MS** (m/z, %): 340 (M^+, 6.62), 84 (100), 86 (64.45), 47 (16.97); **HRMS** (EI): m/z calcd for $C_{24}H_{20}O_2$ $[M]^+$: 340.1463; found: 340.1470.

Methyl 4-(naphthalen-2-yl)-2,4-diphenylbuta-2,3-dienoate (3o)

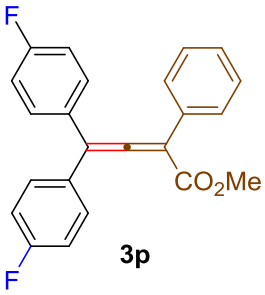


3o

White solid, 102-104 °C **m.p.**; 53.4 mg, 71% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.85 (d, *J* = 10.2 Hz, 3H), 7.81-7.76 (m, 1H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.56 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.50-7.47 (m, 3H), 7.39 (dd, *J* = 13.6, 7.3 Hz, 4H), 7.31 (d, *J* = 5.7 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.04, 166.44, 134.82, 133.54, 133.25, 132.43, 132.12, 128.98, 128.93, 128.74, 128.63, 128.57, 128.51, 128.40, 128.30, 128.11, 127.81, 126.57, 126.54, 126.50, 115.00, 105.46, 52.73; **EI-MS** (m/z, %): 376

(M^+,1.13), 105 (100), 77 (61.86), 167 (42.22); **HRMS** (EI): m/z calcd for $C_{27}H_{20}O_2$: 376.1463; found: 376.1463.

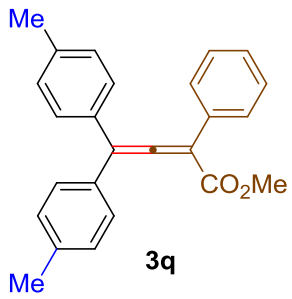
Methyl 4,4-bis(4-fluorophenyl)-2-phenylbuta-2,3-dienoate (**3p**)



3p

White solid, 83-85 °C **m.p.**; 54.3 mg, 75% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.61-7.55 (m, 2H), 7.35 (m, 7H), 7.07 (t, *J* = 8.7 Hz, 4H), 3.86 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.11, 166.21, 162.91 (d, *J* = 247.1 Hz), 132.18, 130.64, 130.61, 130.41 (d, *J* = 8.2 Hz), 128.49 (d, *J* = 37.6 Hz), 128.26, 116.09, 115.87, 113.21, 105.57, 77.48, 77.16, 76.84, 52.79; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.01; **EI-MS** (m/z, %): 362 (M^+,6.75), 84 (100), 86 (84.65); **HRMS** (EI): m/z calcd for $C_{23}H_{16}F_2O_2$: 362.1118; found: 362.1115.

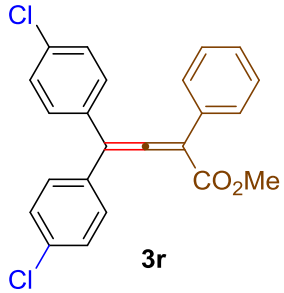
Methyl 2-phenyl-4,4-di-p-tolylbuta-2,3-dienoate (**3q**)



3q

White solid, 87-89 °C **m.p.**; 46.0 mg, 65% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64-7.57 (m, 2H), 7.34-7.26 (m, 7H), 7.18 (d, *J* = 8.0 Hz, 4H), 3.83 (s, 3H), 2.36 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.65, 166.55, 138.29, 132.71, 131.85, 129.52, 128.67, 128.53, 128.33, 127.90, 114.57, 104.98, 52.59, 21.38; **EI-MS** (m/z, %): 354 (M^+, 0.71), 84 (100), 167 (63.96), 86 (63.93); **HRMS** (EI): m/z calcd for $C_{25}H_{22}O_2$ $[M]^+$: 354.1620; found: 354.1619.

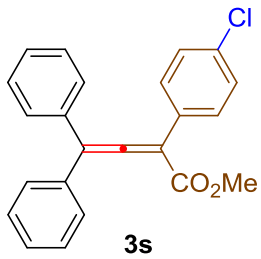
Methyl 4,4-bis(4-chlorophenyl)-2-phenylbuta-2,3-dienoate (**3r**)



3r

White solid, 92-95 °C **m.p.**; 61.4 mg, 78% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.56 (d, *J* = 7.1 Hz, 2H), 7.41-7.27 (m, 11H), 3.86 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.27, 166.01, 134.58, 132.91, 131.88, 129.96, 129.21, 128.73, 128.39, 128.33, 113.20, 105.94, 52.86; **EI-MS** (m/z, %): 394 (M^+, 60.64), 335 (100), 139 (71.71), 265 (68.23); **HRMS** (EI): m/z calcd for $C_{23}H_{16}O_2Cl_2$ $[M]^+$: 394.0527; found: 394.0522.

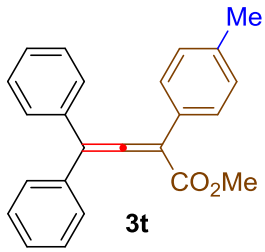
Methyl 2-(4-chlorophenyl)-4,4-diphenylbuta-2,3-dienoate (**3s**)



3s

White solid, 87-89 °C **m.p.**; 57.6 mg, 80% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.46-7.27 (m, 12H), 3.85 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.77, 166.16, 134.49, 133.96, 130.94, 129.65, 128.92, 128.80, 128.78, 128.58, 115.24, 104.36, 52.76; **EI-MS** (m/z, %): 360 (M^+, 52.19), 105 (100), 301 (71.32), 265 (68.21); **HRMS** (EI): m/z calcd for $C_{23}H_{17}ClO_2$ $[M]^+$: 360.0917; found: 360.0910.

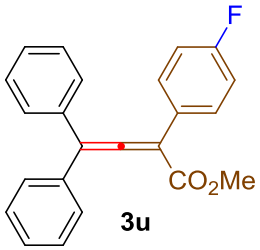
Methyl 4,4-diphenyl-2-(p-tolyl)buta-2,3-dienoate (**3t**)



3t

White solid, 84-90 °C **m.p.**; 53.7 mg, 79% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.46-7.30 (m, 10H), 7.16 (d, *J* = 8.1 Hz, 2H), 3.84 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.47, 166.58, 137.96, 134.88, 129.40, 129.32, 128.82, 128.81, 128.34, 128.22, 114.68, 105.21, 52.67, 21.36; **EI-MS** (m/z, %): 340 (M^+, 2.83), 84 (100), 86 (65.17), 47 (18.68); **HRMS** (EI): m/z calcd for $C_{24}H_{20}O_2$ $[M]^+$: 340.1463; found: 340.1467.

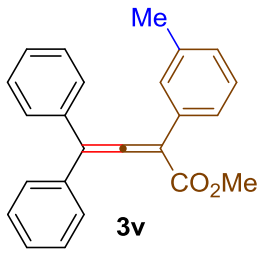
Methyl 2-(4-fluorophenyl)-4,4-diphenylbuta-2,3-dienoate (**3u**)



3u

White solid, 79-81 °C **m.p.**; 44.7 mg, 65% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62-7.56 (m, 2H), 7.44-7.32 (m, 10H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ δ 214.58, 166.36, 162.60 (d, *J* = 246.4 Hz), 134.63, 130.12 (d, *J* = 8.0 Hz), 128.90, 128.78, 128.51, 115.65 (d, J = 21.5 Hz), 114.99, 104.36, 52.73; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.94; **EI-MS** (m/z, %): 344 (M^+, 65.95), 285 (100), 105 (96.07), 283 (63.95); **HRMS** (EI): m/z calcd for $C_{23}H_{17}FO_2$ $[M]^+$: 344.1213; found: 344.1208.

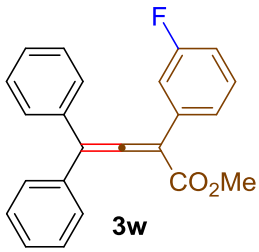
Methyl 4,4-diphenyl-2-(m-tolyl)buta-2,3-dienoate (**3v**)



3v

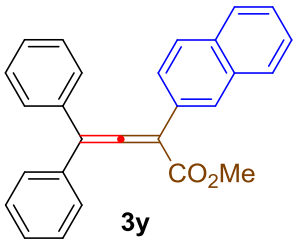
White solid, 79-81 °C **m.p.**; 55.0 mg, 81% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.30-7.45 (m, 12H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 3.84 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.49, 166.51, 138.18, 134.85, 132.33, 128.94, 128.88, 128.82, 128.81, 128.48, 128.35, 125.47, 114.67, 105.38, 52.63, 21.67; **EI-MS** (m/z, %): 340 (M^+, 2.83), 84 (100), 86 (65.17), 47 (18.68); **HRMS** (EI): m/z calcd for $C_{24}H_{20}O_2$ $[M]^+$: 340.1463; found: 340.1459.

Methyl 2-(3-fluorophenyl)-4,4-diphenylbuta-2,3-dienoate (3w)



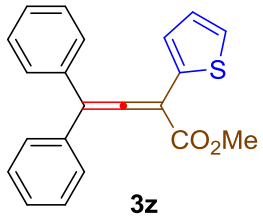
White solid, 69-74 °C **m.p.**; 48.1 mg, 71% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.68-7.21 (m, 13H), 6.98 (s, 1H), 3.85 (d, *J* = 3.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.86, 166.03, 163.0 (d, *J* = 236 Hz), 134.58, 134.42, 129.99, 128.87 (d, *J* = 8 Hz), 128.61, 123.97, 115.37, 114.93 (d, *J* = 21.1 Hz), 104.41, 52.82; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.85; **EI-MS** (m/z, %): 344 (M^+,65.95), 285 (100), 105 (96.07), 283 (63.95); **HRMS** (EI): m/z calcd for $C_{23}H_{17}FO_2$: 344.1213; found: 344.1208.

Methyl 2-(naphthalen-2-yl)-4,4-diphenylbuta-2,3-dienoate (**3y**)



White solid, 101-105 °C **m.p.**; 54.1 mg, 72% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.23 (s, 1H), 7.86-7.77 (m, 3H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.48-7.44 (m, 6H), 7.42-7.34 (m, 6H), 3.90 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.18, 166.52, 134.75, 133.54, 132.98, 129.57, 128.89, 128.86, 128.57, 128.48, 128.17, 127.67, 127.46, 126.40, 126.33, 126.05, 115.15, 105.39, 52.76; **EI-MS** (m/z, %): 376 (M^+, 10.01), 84 (100), 86 (63.29), 57 (49.28); **HRMS** (EI): m/z calcd for $C_{27}H_{20}O_2$ $[M]^+$: 376.1463; found: 376.1466.

Methyl 4,4-diphenyl-2-(thiophen-3-yl)buta-2,3-dienoate (**3z**)



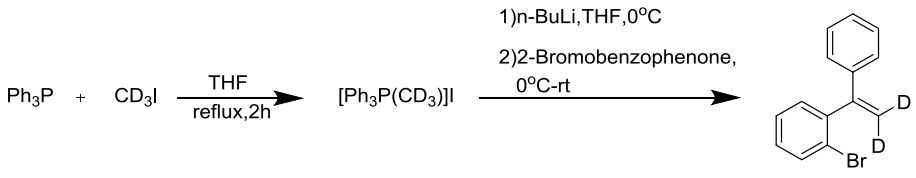
White solid, 71-75 °C **m.p.**; 55.1 mg, 83% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.89 (dd, *J* = 2.7, 1.3 Hz, 1H), 7.44-7.32 (m, 9H), 7.28-7.22 (m, 3H), 3.85 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.05, 166.28, 134.76, 131.77, 128.87, 128.46, 127.36, 125.32, 123.81, 115.08, 101.11, 52.66; **EI-MS** (m/z, %): 332 (M^+, 8.98), 84 (100), 86 (62.13), 47 (32.21); **HRMS** (EI): m/z calcd for $C_{21}H_{26}SO_2$ $[M]^+$: 332.0871; found: 332.0876.

2. Gram-Scale Synthesis

To a 250 mL Schlenk tube charged with a stir bar, aryl bromides (**1a**) (4.5 mmol), diazoesters (**2a**) (6.75 mmol), $Pd(OAc)_2$ (101.1 mg, 0.45 mmol), DPEPhos (363.5 mg, 0.675 mmol) and CsOAc (1.3 g, 6.75 mmol) were added. After filled with argon, anhydrous THF (45 mL) were added via a syringe. The mixture was stirred at 80 ℃ in an oil bath for 2 h. Upon completion, the reaction mixture was washed with brine (30 mL) and extracted with EA (3×25 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After that the organic phase was filtered, and concentrated under reduced pressure. The crude products were purified by silica gel chromatography (PE/EA = 20:1) to afford pure products (**3a**), as a white solid (79%,1.16 g).

3. Parallel Experiments and KIE Studies

(1) Synthesis of ***d*$_2$-1a:**

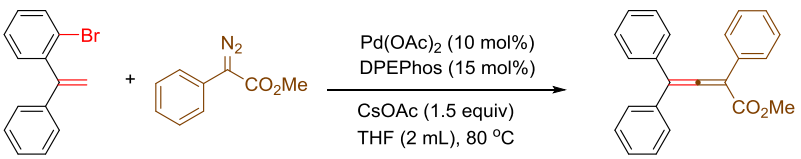


In a J-Young Schlenk tube, PPh_3 (2.5 mmol, 656 mg, 1.0 equiv) in 3.5 mL THF was added, and CD_3I (2.5 mmol, 0.16 ml, 1.0 equiv) was then added dropwise into the solution, which resulted in the immediate appearance of a white suspension. After the addition was complete, the reaction mixture was refluxed for 2 h. During the cooling of the reaction mixture to room temperature, a large amount of a white precipitate was formed, and the resulting white solid was isolated on a filter, washed with EA (3 x 10 ml) and dried under vacuum to give 998 mg of $[PPh_3(CD_3)]I$ (98% yield). 96% D atom incorporation (^{1}H NMR analysis).

An oven dried flask charged with $[PPh_3(CD_3)]I$ (2.4 mmol, 998 mg, 1.1 equiv.)and THF (7.0 mL) was cooled to 0 ^{o}C. Then 2.5 M n-BuLi (2.43 mmol, 0.97 mL, 1.2 equiv) was added dropwise and the resulting yellow suspension was stirred for 30 minutes. To this suspension, a solution of aryl bromides (1a) (2.25 mmol, 587.5 mg, 1.0 equiv) was added in one portion and the resulting mixture was warmed to room temperature and further stirred at room temperature for 5 h. Water and EA were added to the reaction mixture, separated and the aqueous phase was extracted with EA (3 x 10 mL).The combined organic phases were washed with brine, dried over Na_2SO_4 and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography using hexanes as eluent to obtain the product **1a-D$_2$** as a colorless oil,431 mg, 74% (two steps), 94% D atom incorporation (^{1}H NMR analysis).

(2) Parallel Experiments:

The parallel reactions of aryl bromides (**1a**) were carried out under the reaction conditions which were described in Figures S1 and S2, stopped at arbitrary reaction times, and analyzed by ^{1}H NMR spectroscopy (Figures S1 and S2). As a result, the slope values of two graphs were 0.0094 mM/min and 0.002 mM/min, respectively, and thus the KIE value was 4.7.



1a 0.2 mmol **2a** 0.3 mmol **3a**

entry	time（min）	^{1}H NMR（%）	product（mmol）
1	10	0.15	0.30
2	20	0.23	0.46
3	30	0.33	0.66
4	40	0.43	0.86

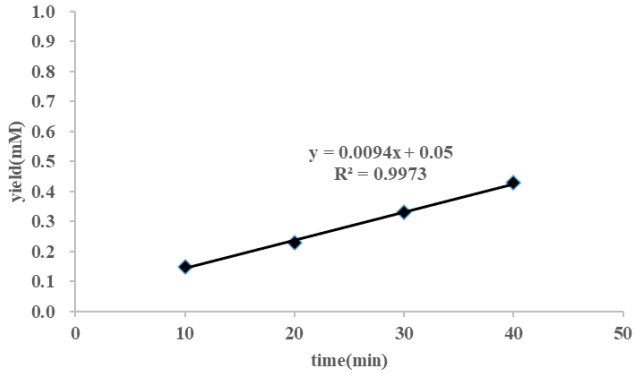
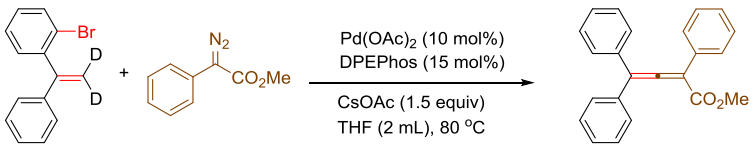


Figure S1. Determination of a reaction rate when **1a** was used as a substrate.



1a 0.2 mmol **2a** 0.3 mmol **3a**

entry	time（min）	^{1}H NMR（%）	product（mmol）
1	10	0.10	0.19
2	20	0.12	0.23
3	30	0.14	0.28
4	40	0.15	0.31

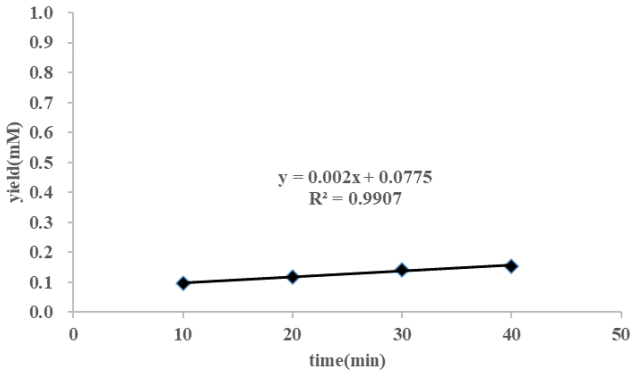


Figure S2. Determination of a reaction rate when **1a-D$_2$** was used as a substrate.

5. References

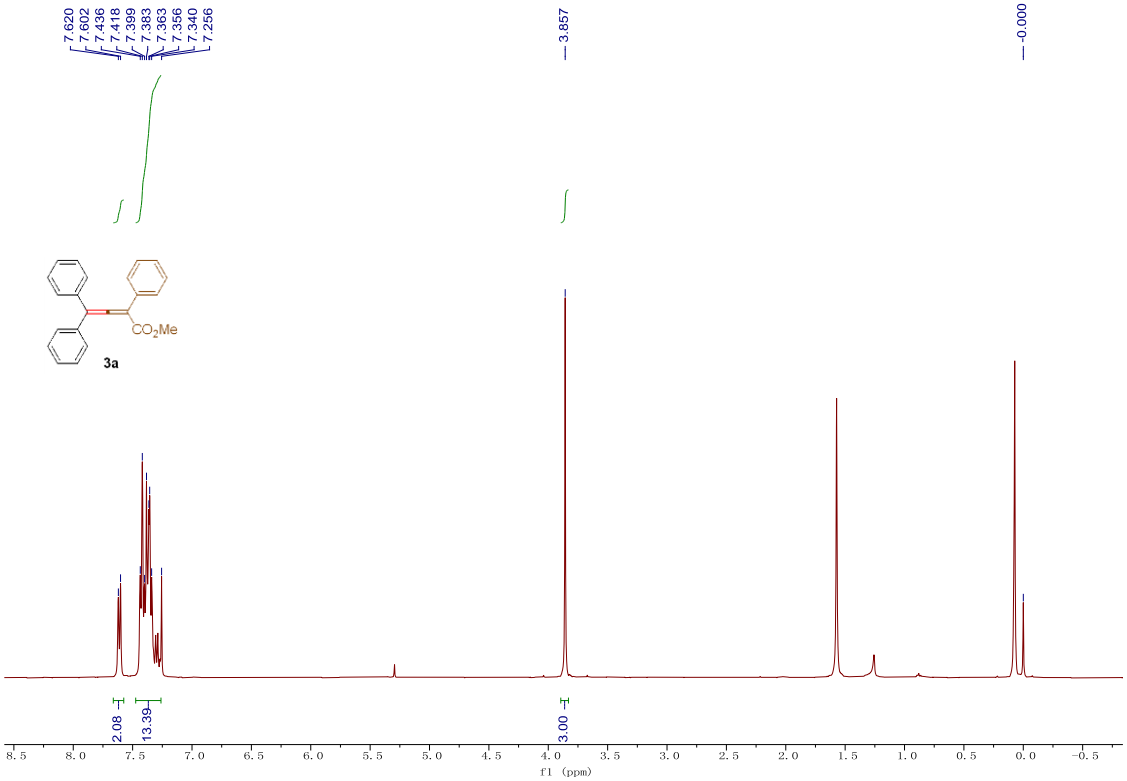
[1] T.-J. Hu, G. Zhang, Y.-H. Chen, C.-G. Feng and G.-Q. Lin. *J. Am. Chem. Soc.*, **2016**, *138*, 2897.

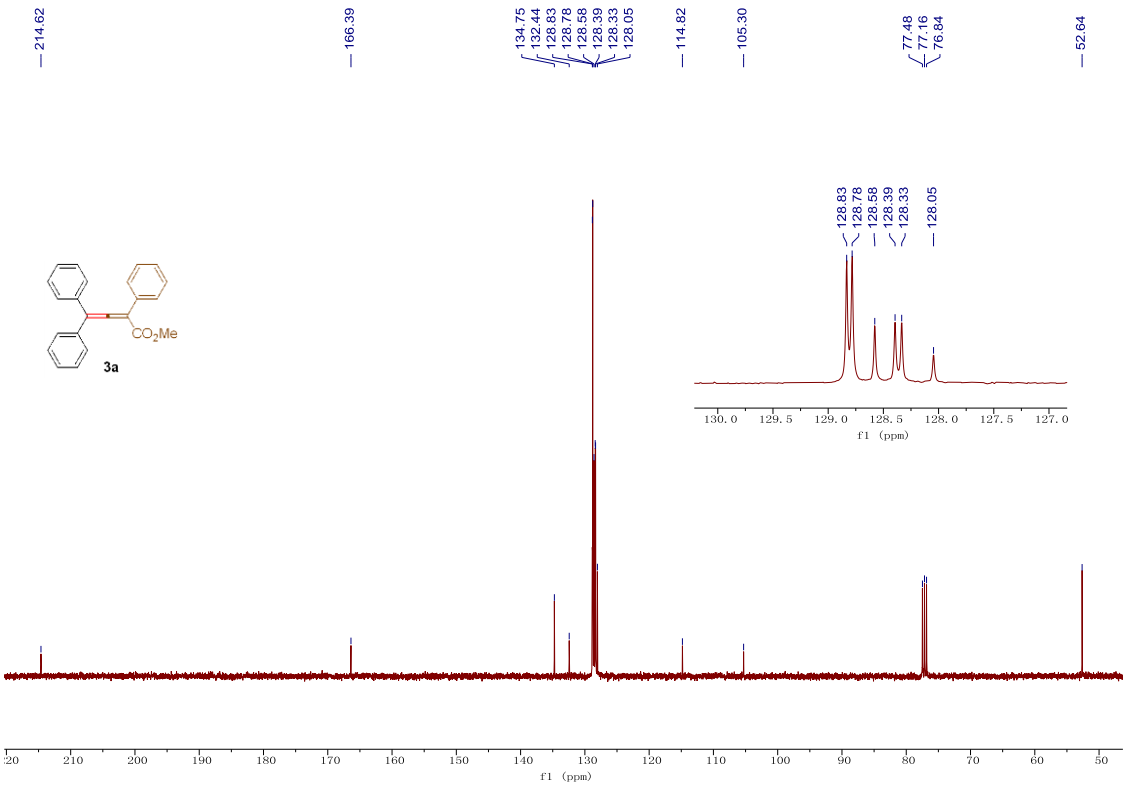
[2] D. Wei, T.-J. Hu, C.-G. Feng, G.-Q. Lin. *Chin. J. Chem.*, **2018**, *36*, 743.

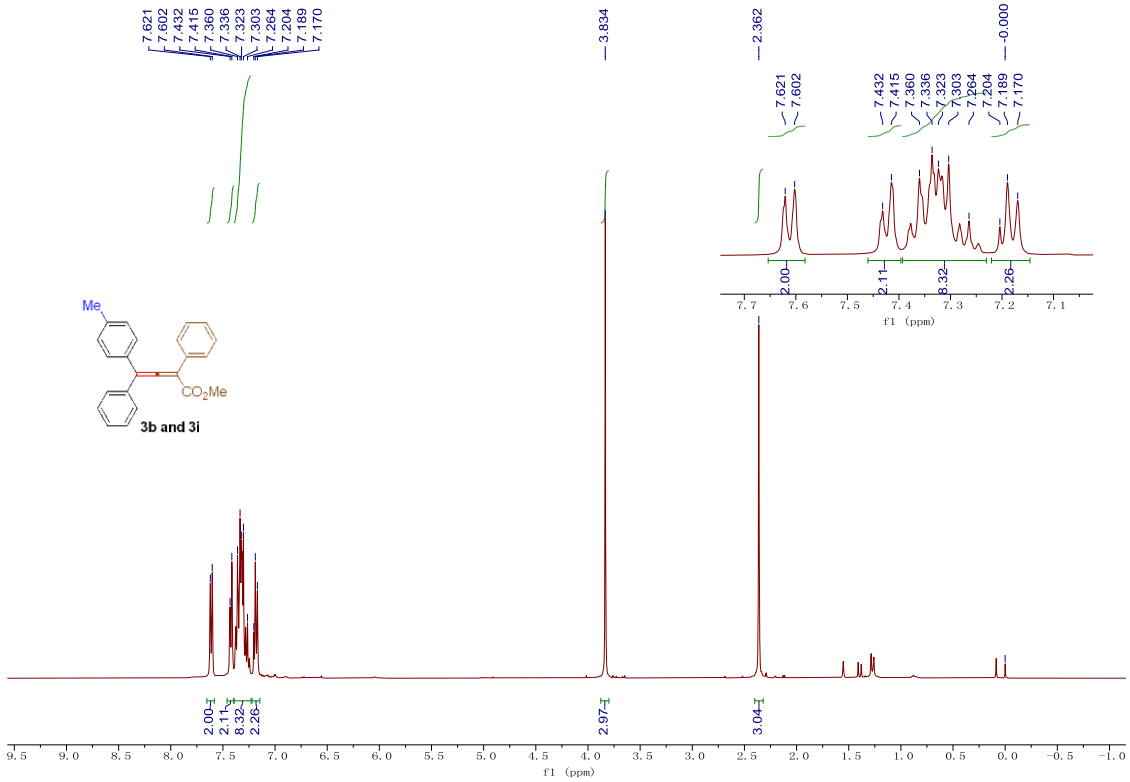
[3] M.-Y. Li, P. Han, T.-J. Hu, D. Wei, G. Zhang, A. Qin, C.-G. Feng, B. Z. Tang, G.-Q. Lin. *iScience*, **2020**, *23*, 100966.

[4] G. Zhang, Y.-K. Song, F. Zhang, Z.-J. Xue, M.-Y. Li, G.-S. Zhang, B.-B. Zhu, J. Wei, C. Li, C.-G. Feng, G.-Q. Lin. *Nat. Commun.* **2021**, *12*, 728.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectras of Products



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7.360
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7.303
7.264
7.204
7.189
7.170
3.834
2.362
-0.000
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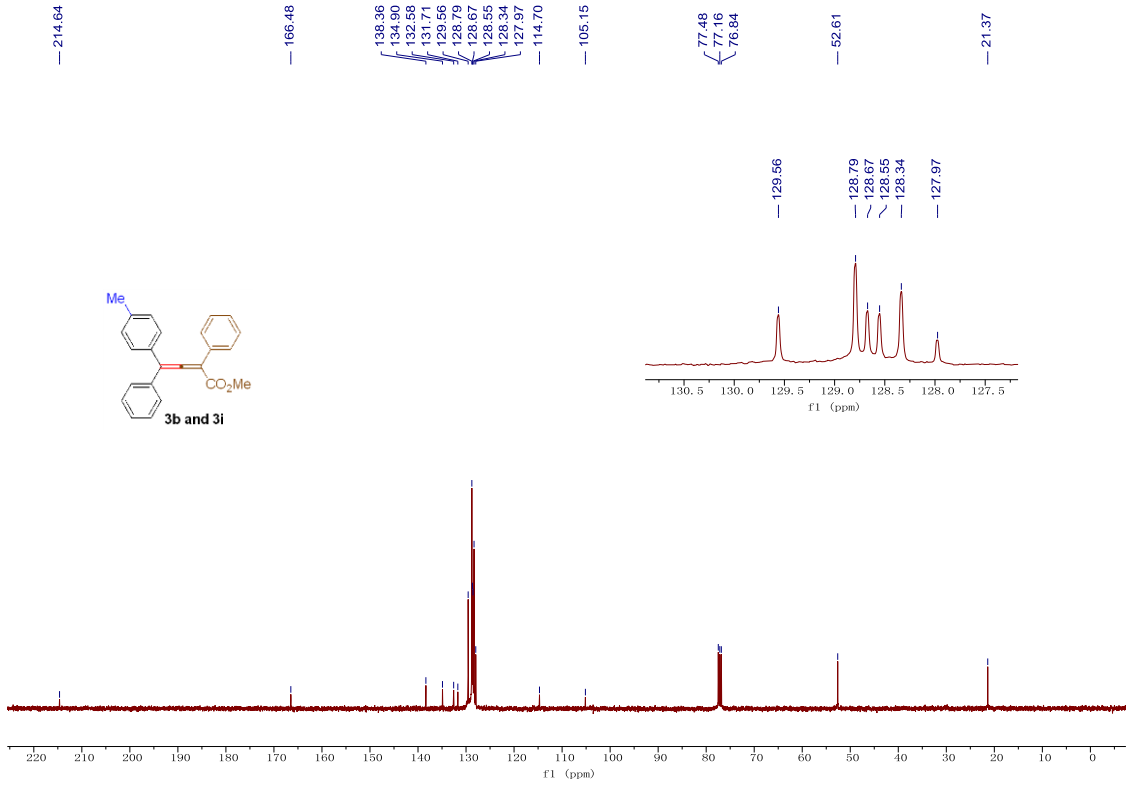
CO2Me
3b and 3i
2.00
2.11
8.32
2.26
2.97
3.04
f1 (ppm)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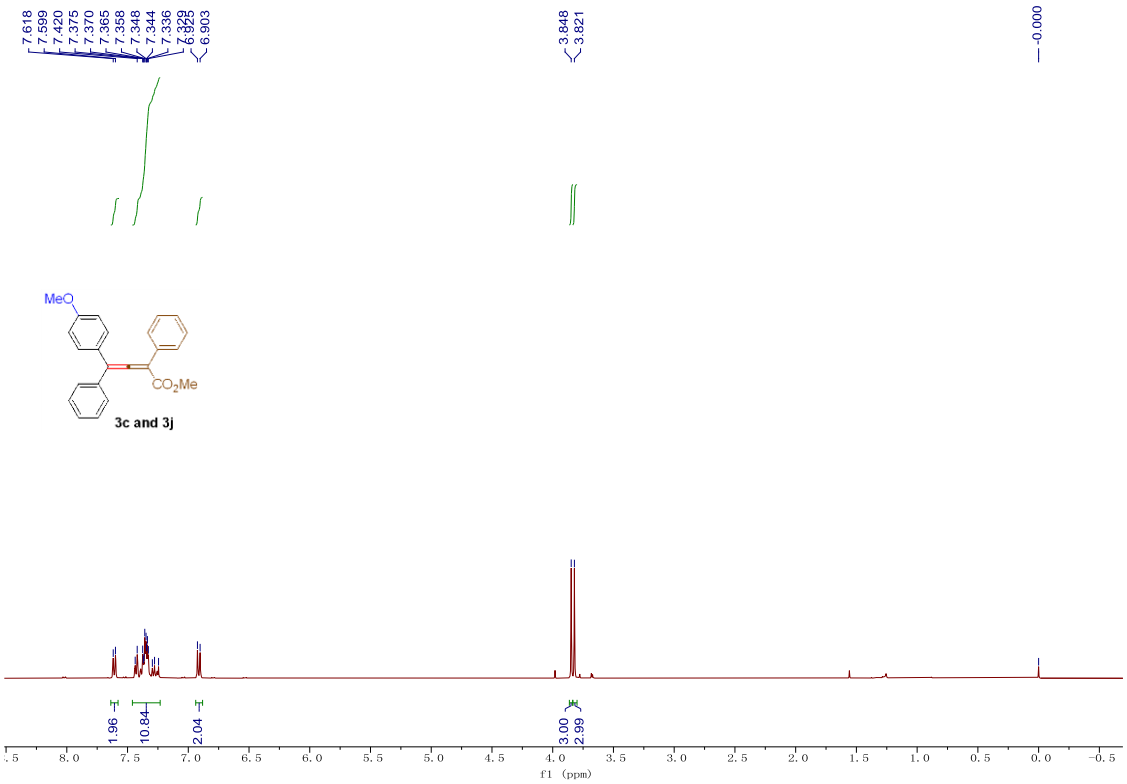
128.67
128.55
128.34
127.97
114.70
105.15
77.48
77.16
76.84
52.61
21.37
Me
CO2Me
3b and 3i
f1 (ppm)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7.348
7.344
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6.903
3.848
3.821
0.000
MeO
CO2Me
3c and 3j
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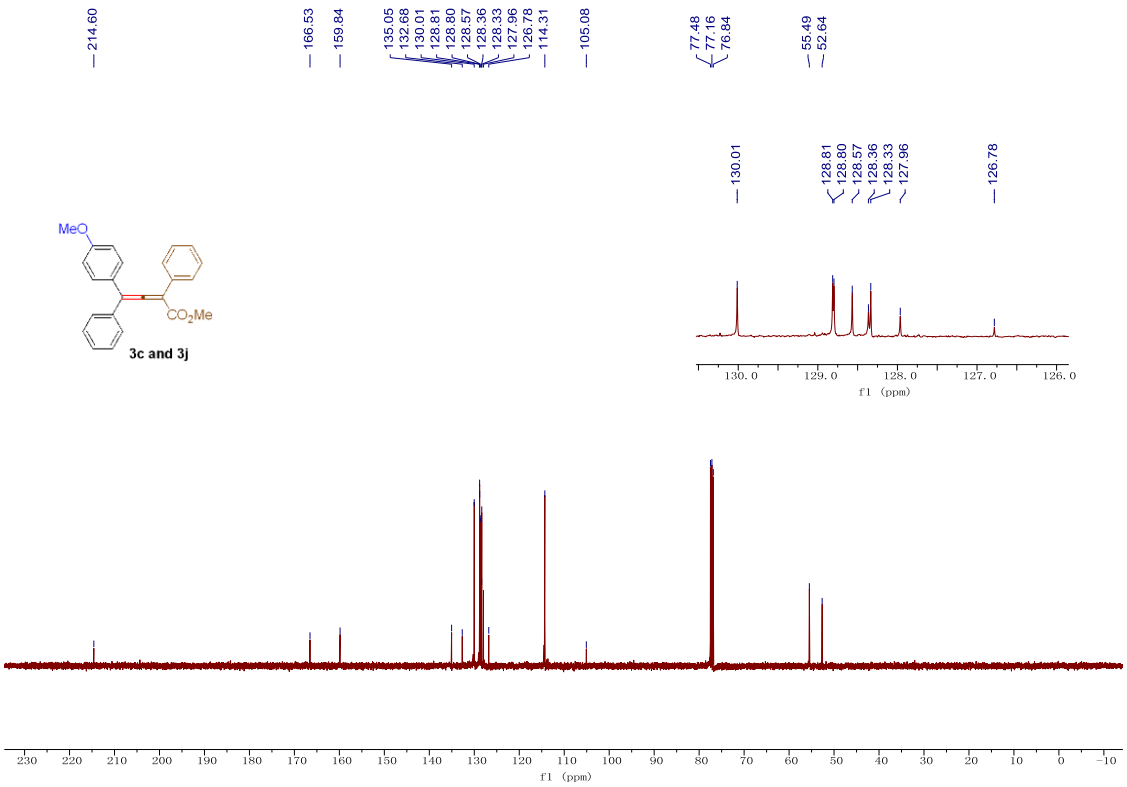
10.84
2.04
3.00
2.99
f1 (ppm)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126.78
114.31
105.08
77.48
77.16
76.84
55.49
52.64
MeO
CO2Me
3c and 3j
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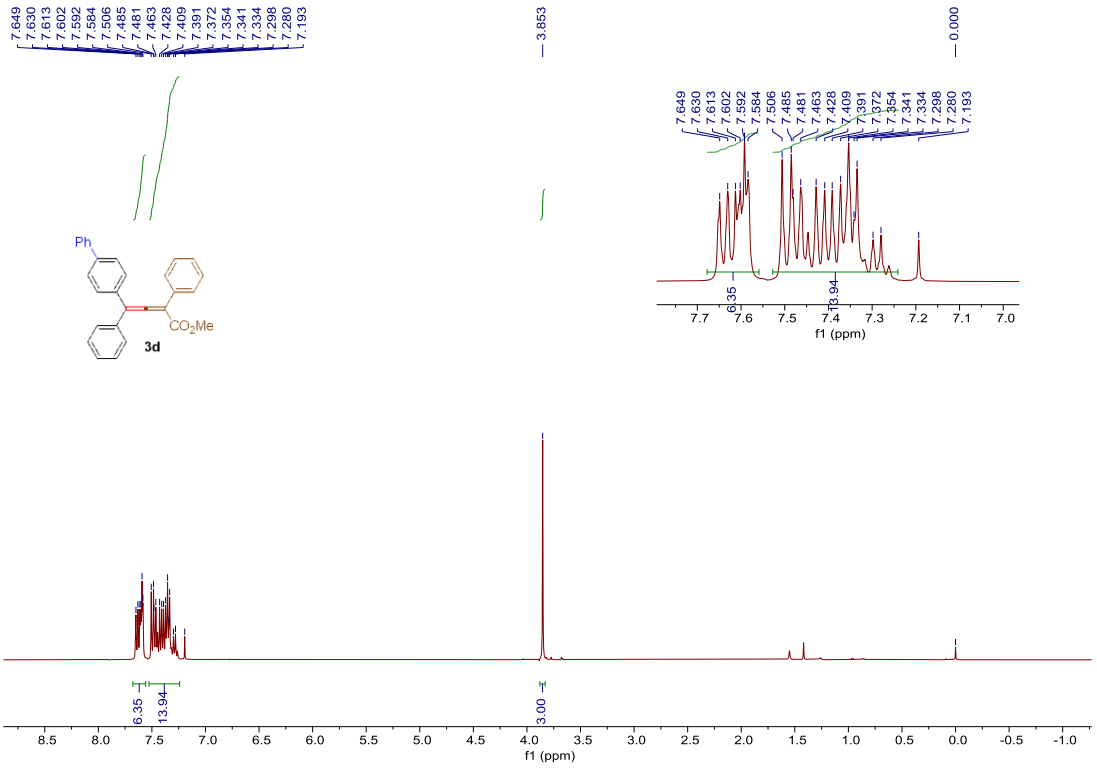
128.81
128.80
128.57
128.36
128.33
127.96
126.78
f1 (ppm)
f1 (ppm)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3d
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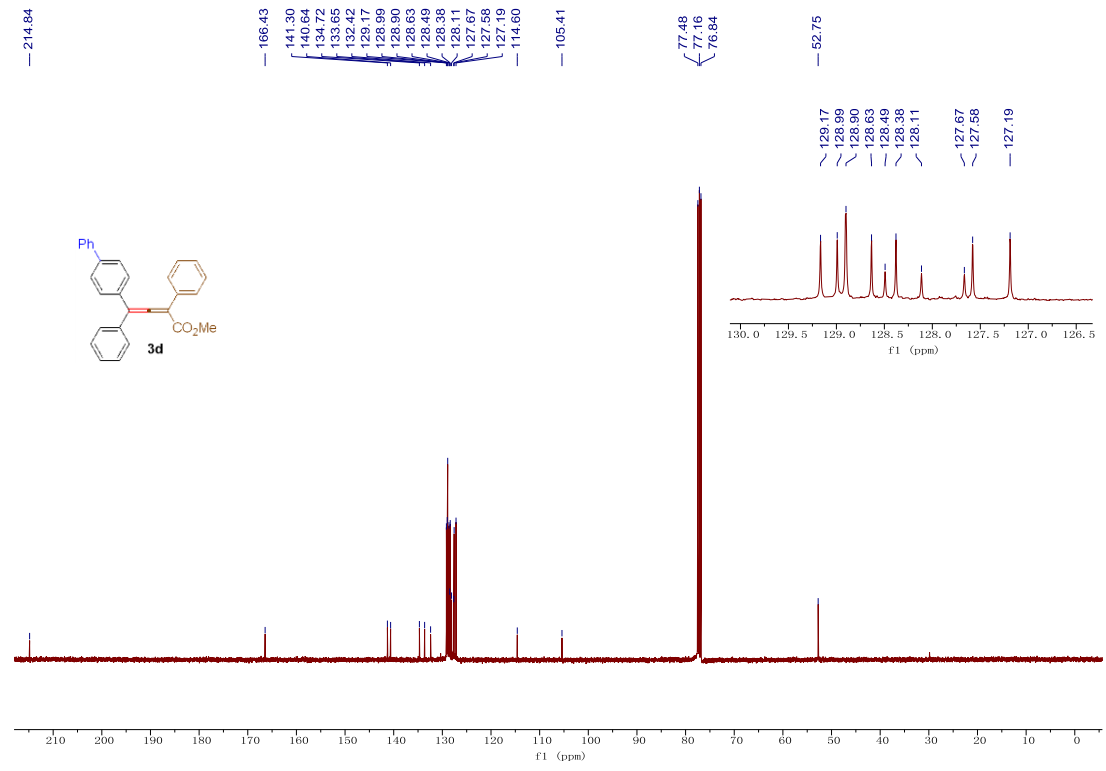
13.94
3.00
f1 (ppm)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52.75
Ph
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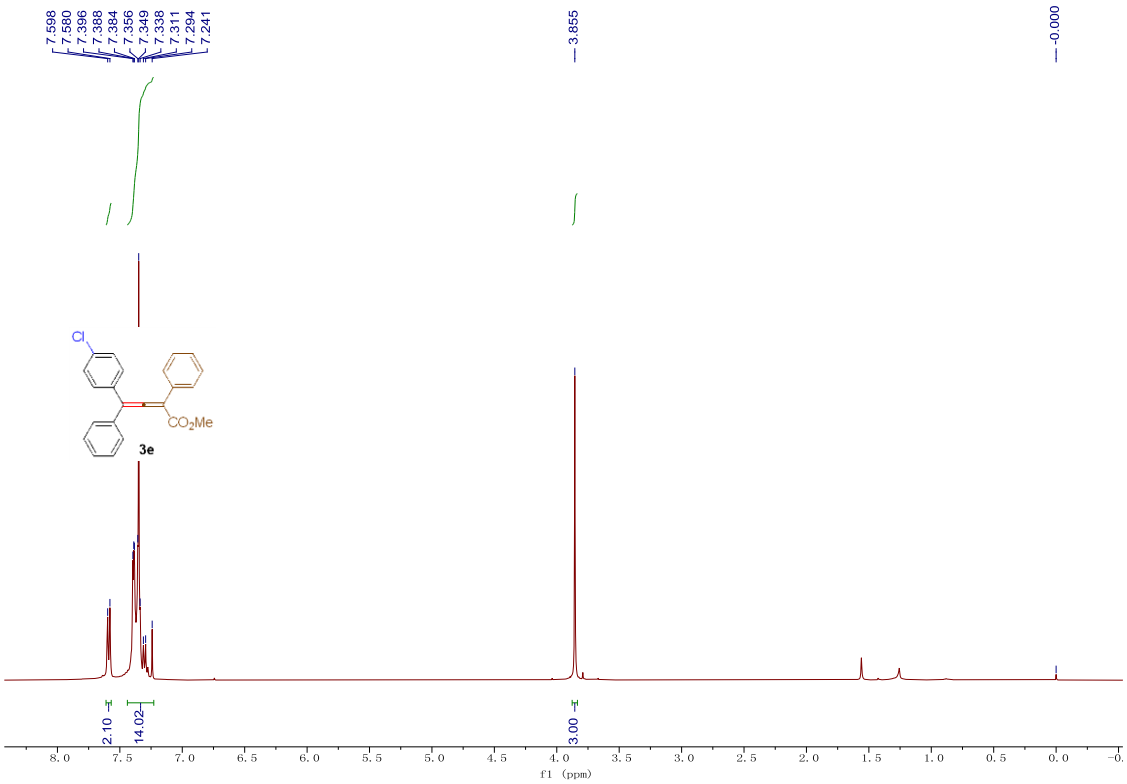
3d
f1 (ppm)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3e
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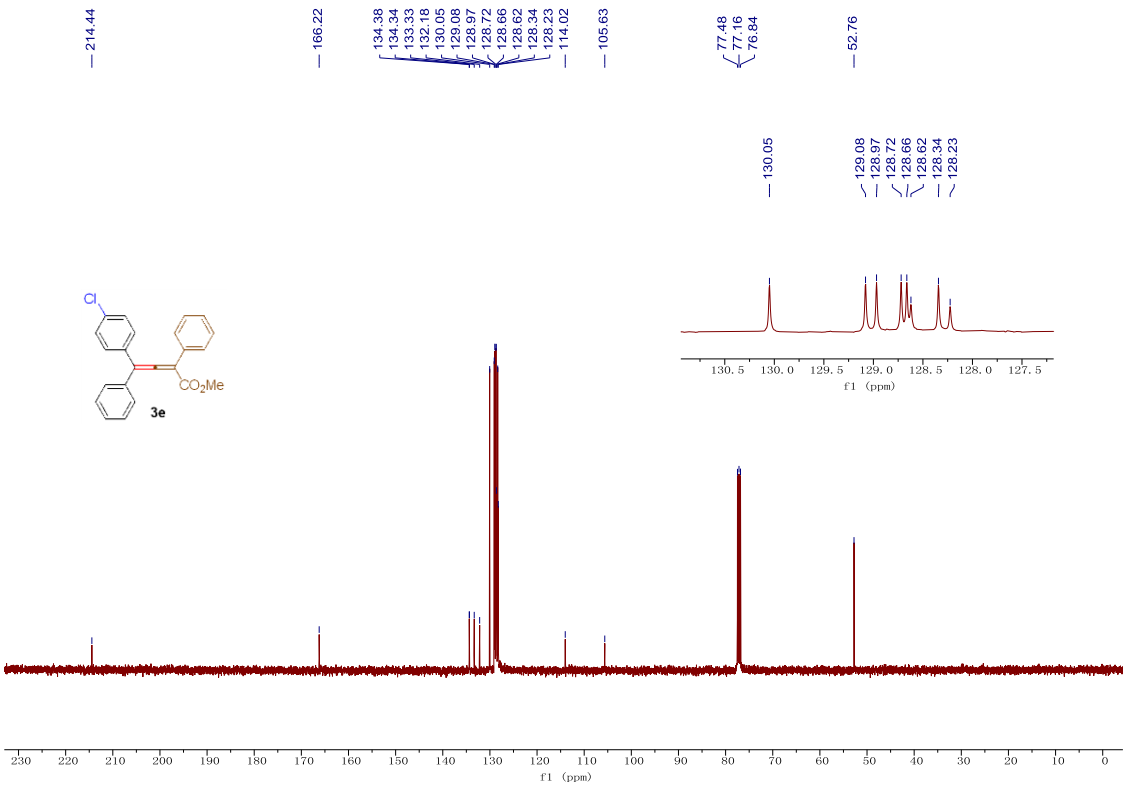
f1 (ppm)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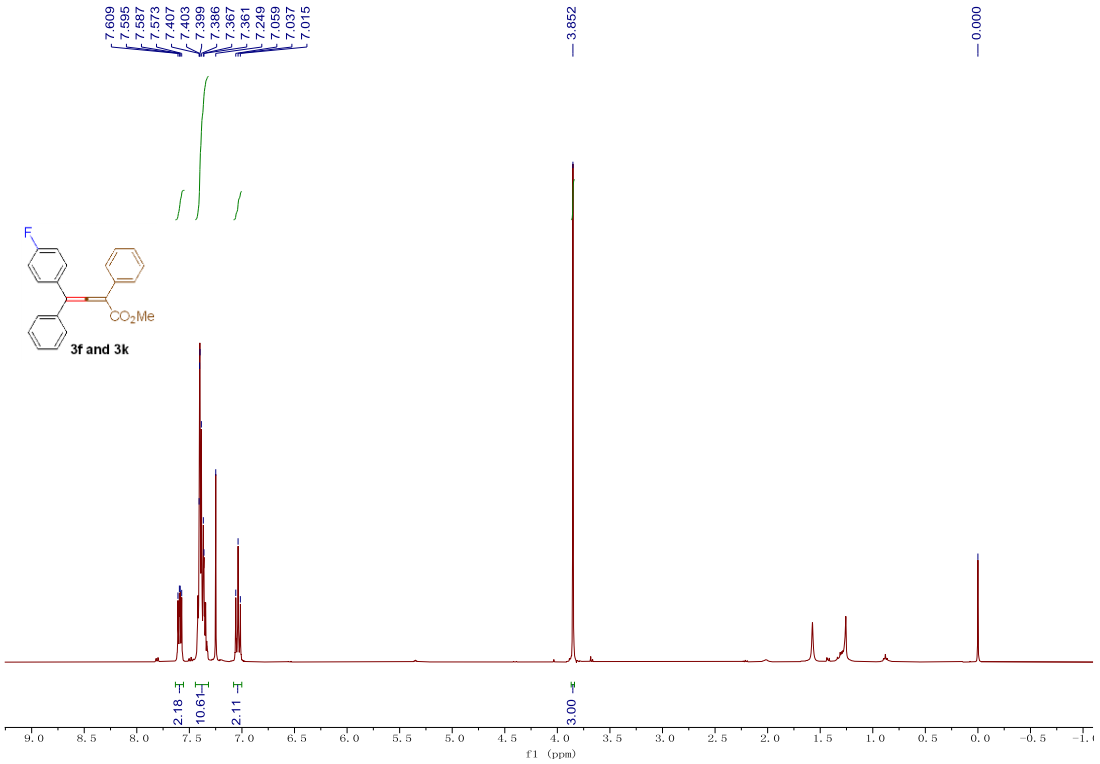
3e
f1 (ppm)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CO2Me
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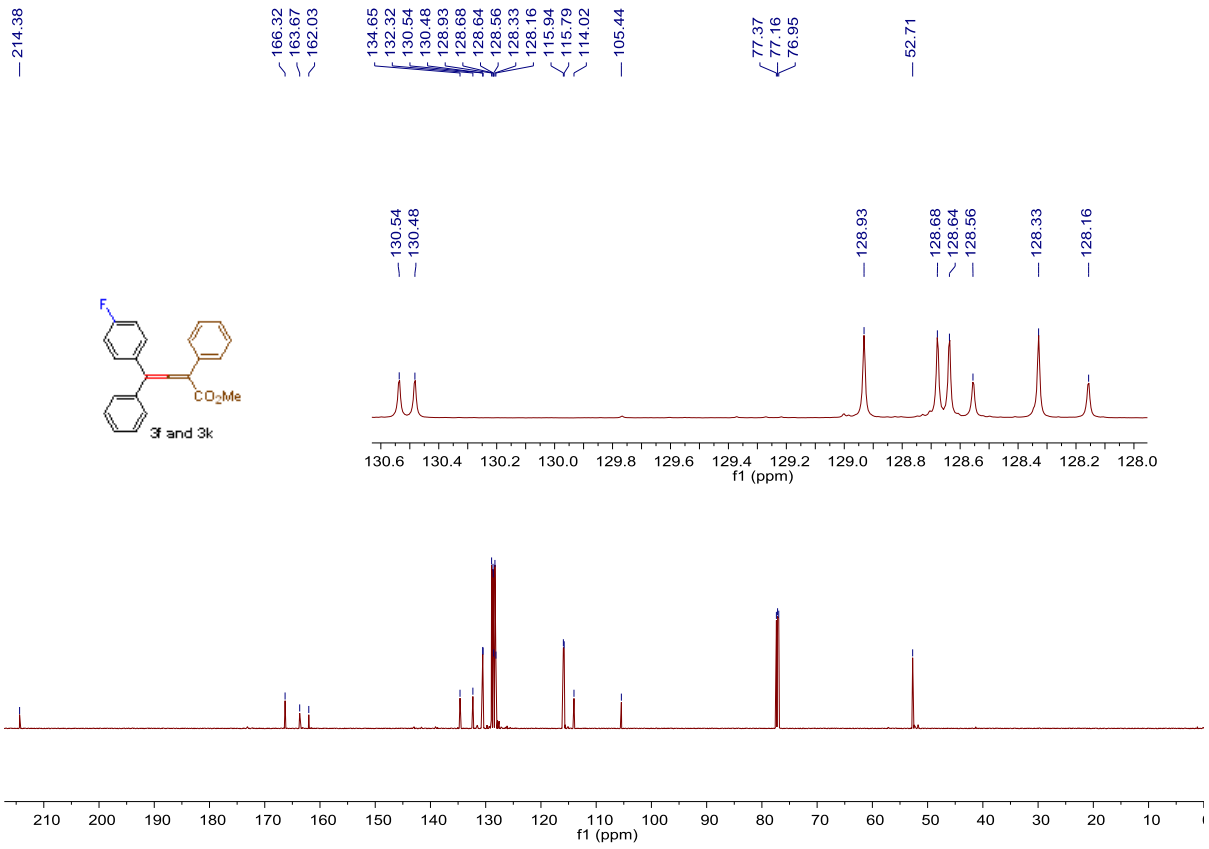
f1 (ppm)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F
CO2Me
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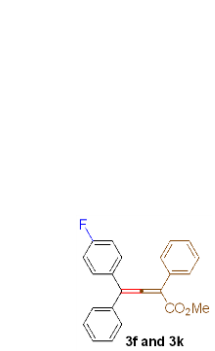
f1 (ppm)



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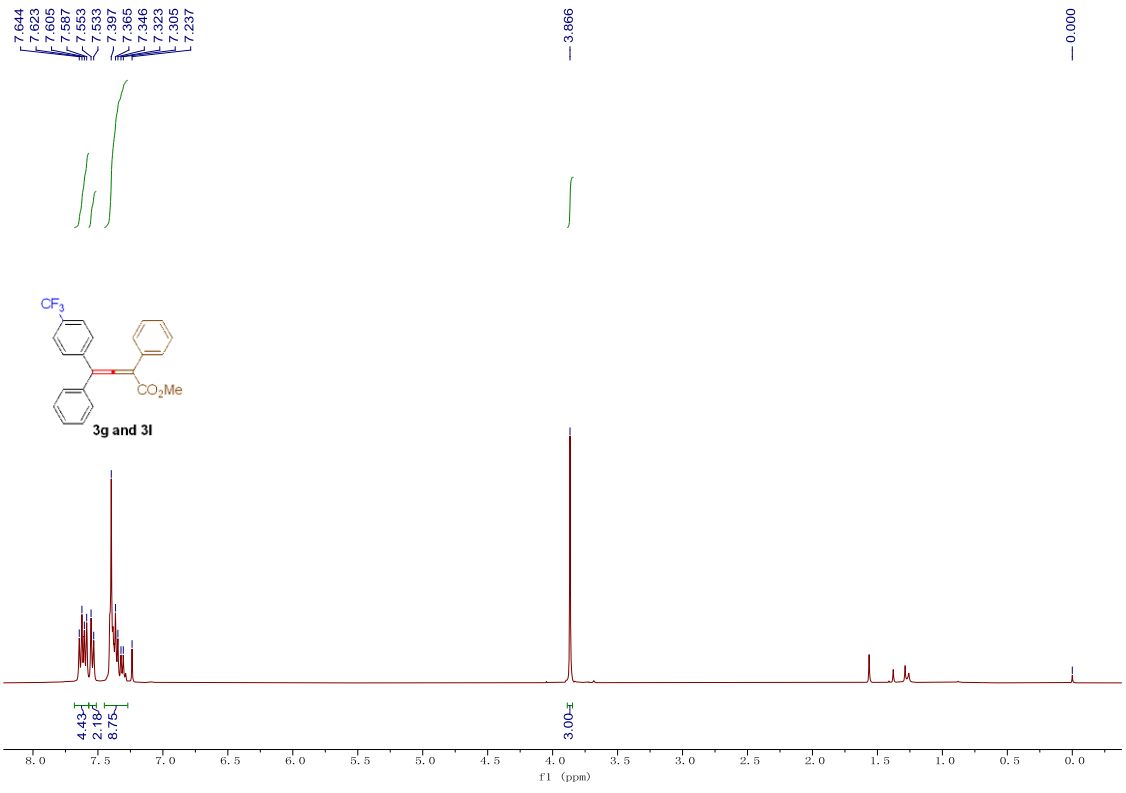

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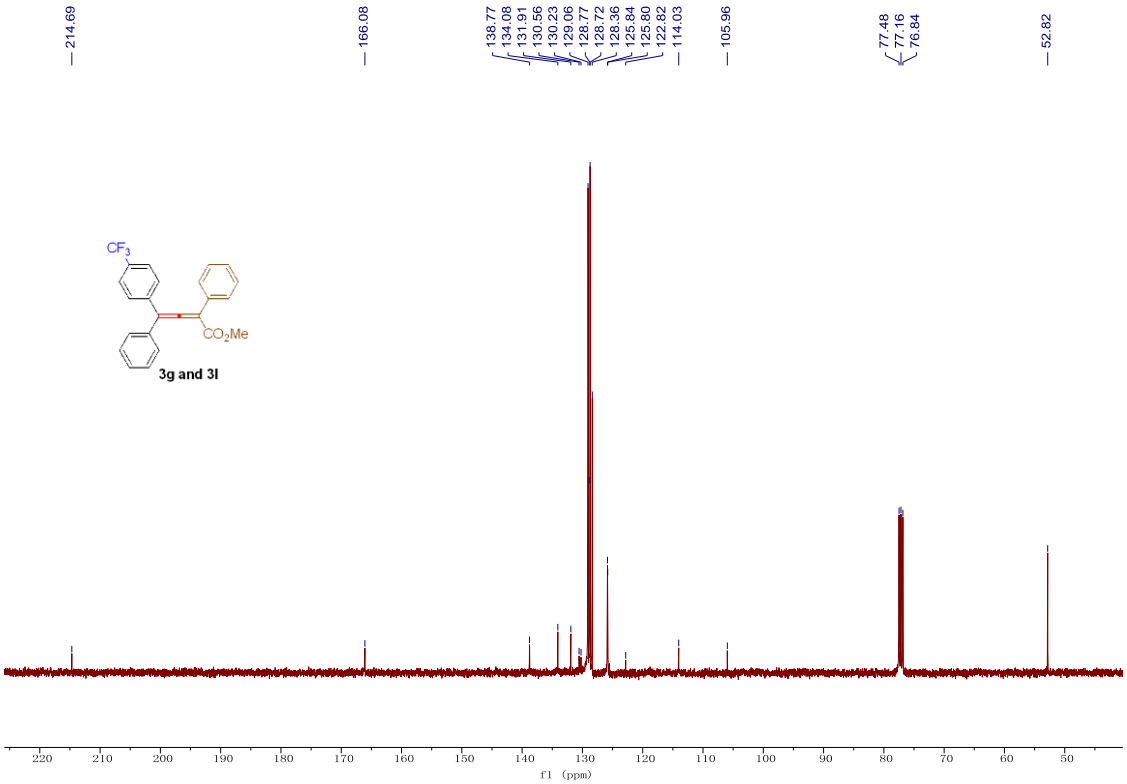
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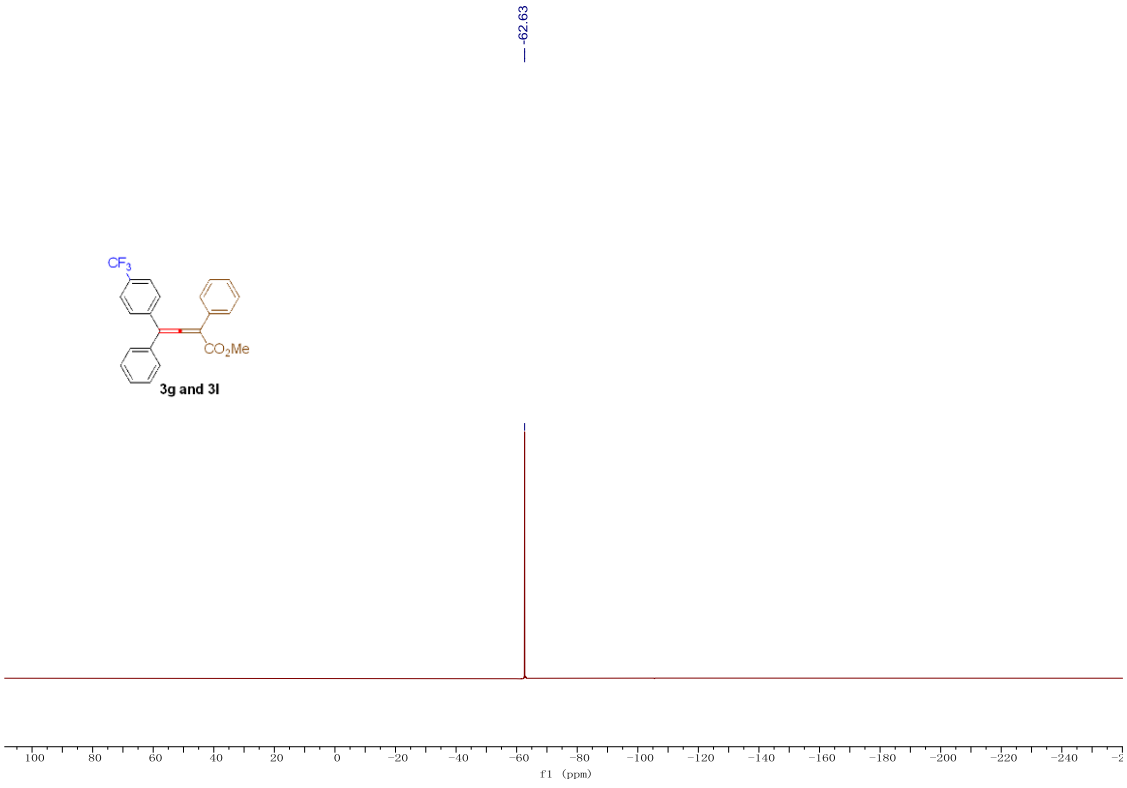
CF3
CO2Me
3g and 3l
f1 (ppm)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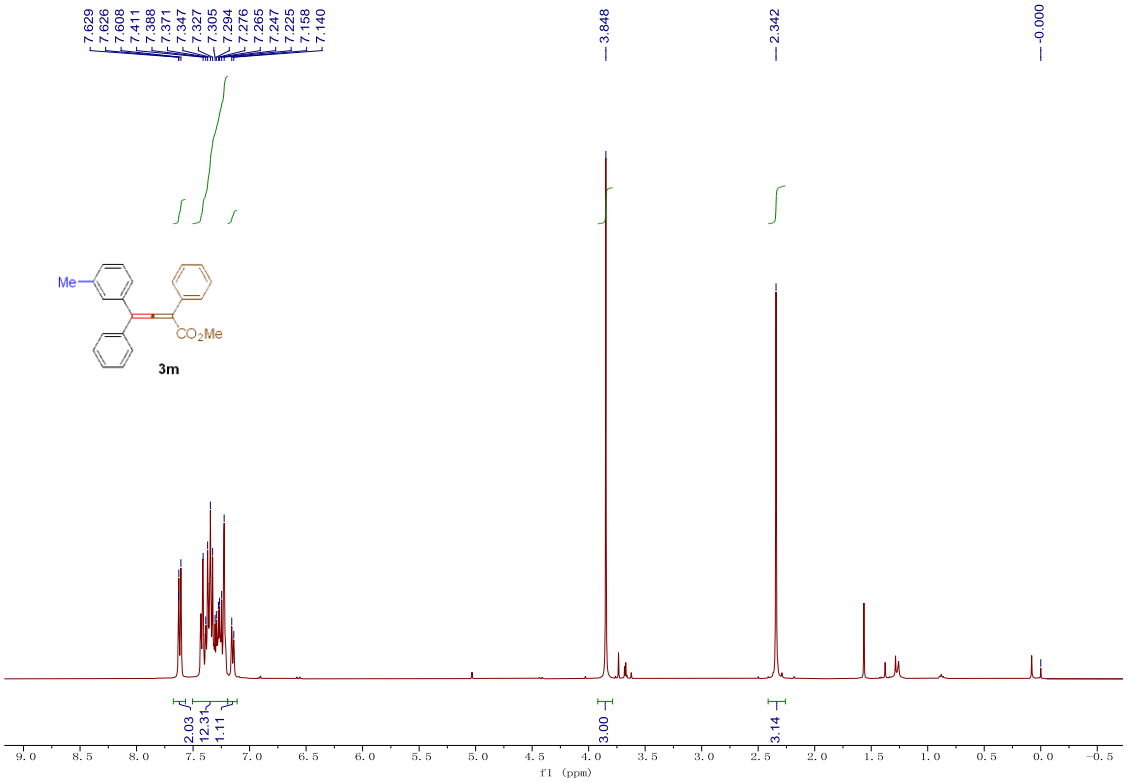
CO2Me
3g and 3l
f1 (ppm)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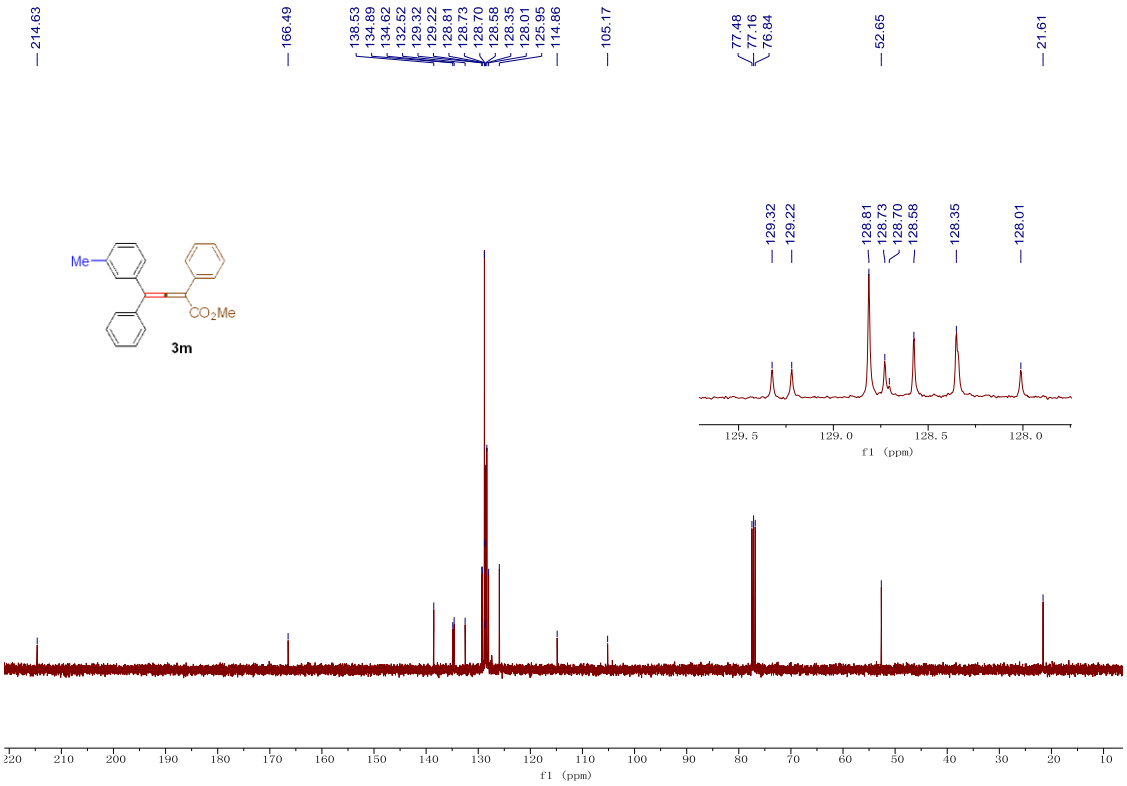
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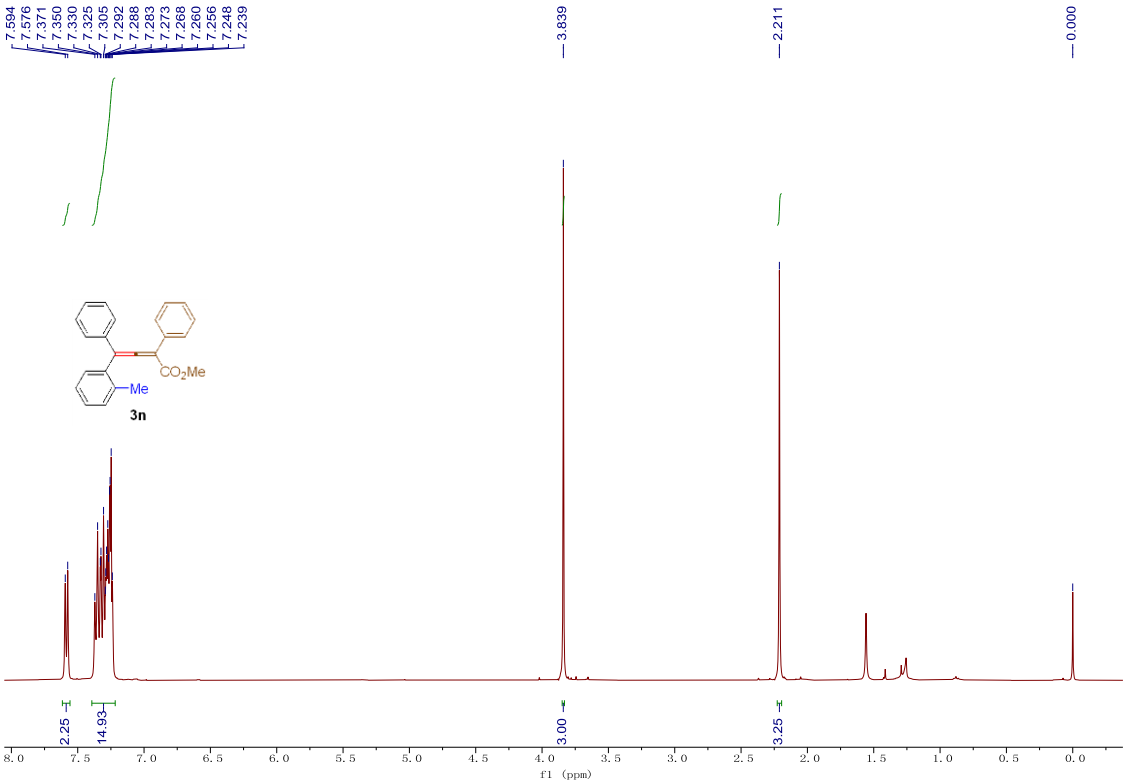
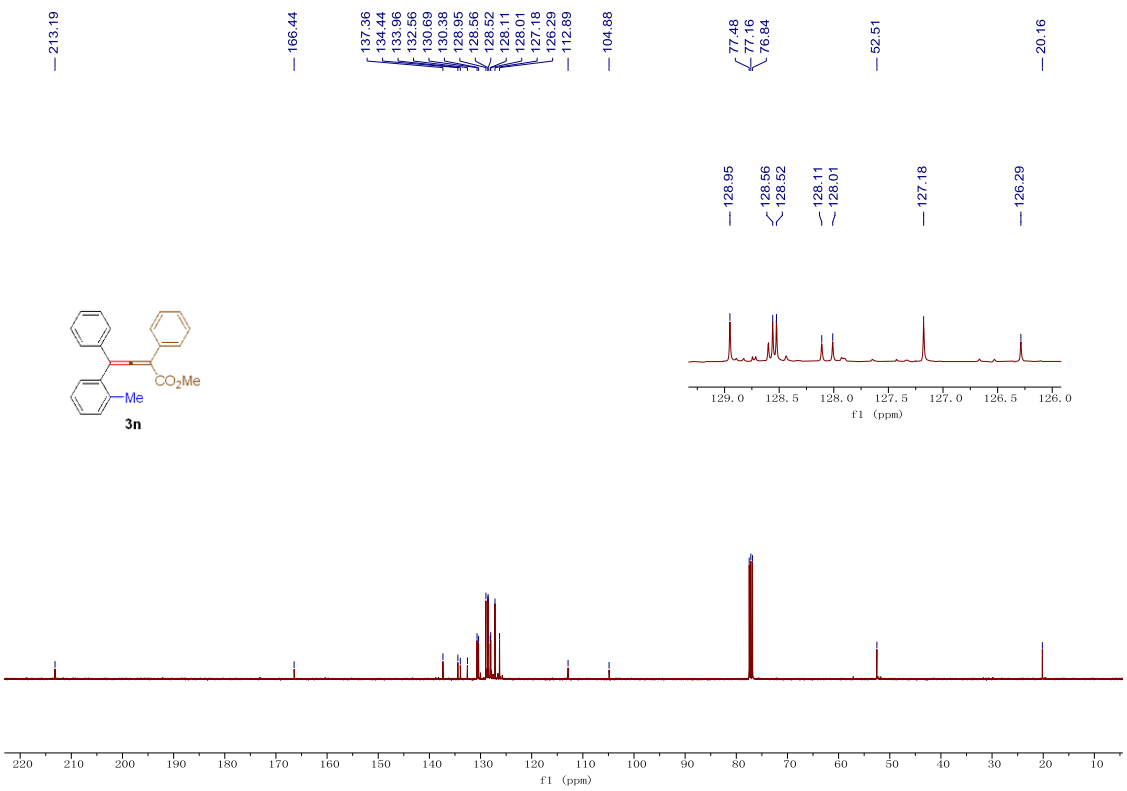
21.61
Me
CO2Me
3m
f1 (ppm)


7.594
7.576
7.371
7.350
7.330
7.325
7.305
7.292
7.288
7.283
7.273
7.268
7.260
7.256
7.248
7.239
3.839
2.211
0.000
CO2Me
Me
3n
2.25
14.93
3.00
3.25
f1 (ppm)


213.19
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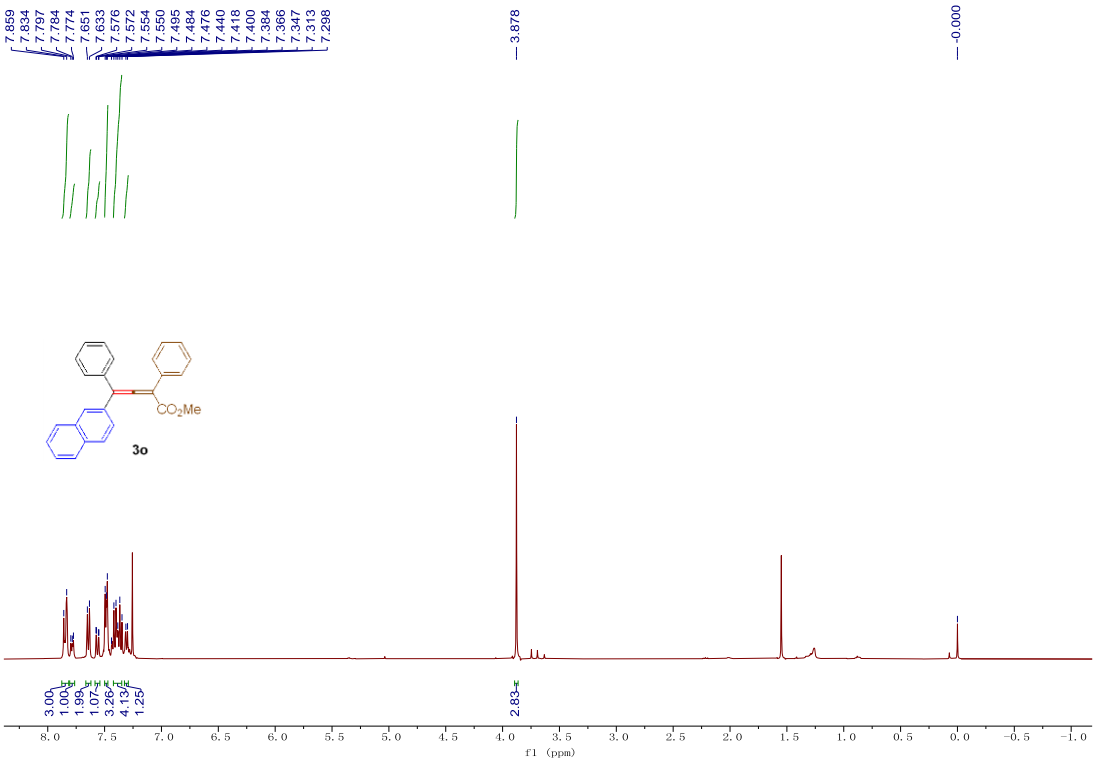
137.36
134.44
133.96
132.56
130.69
130.38
128.95
128.56
128.52
128.11
128.01
127.18
126.29
112.89
104.88
77.48
77.16
76.84
52.51
20.16
CO2Me
Me
3n
f1 (ppm)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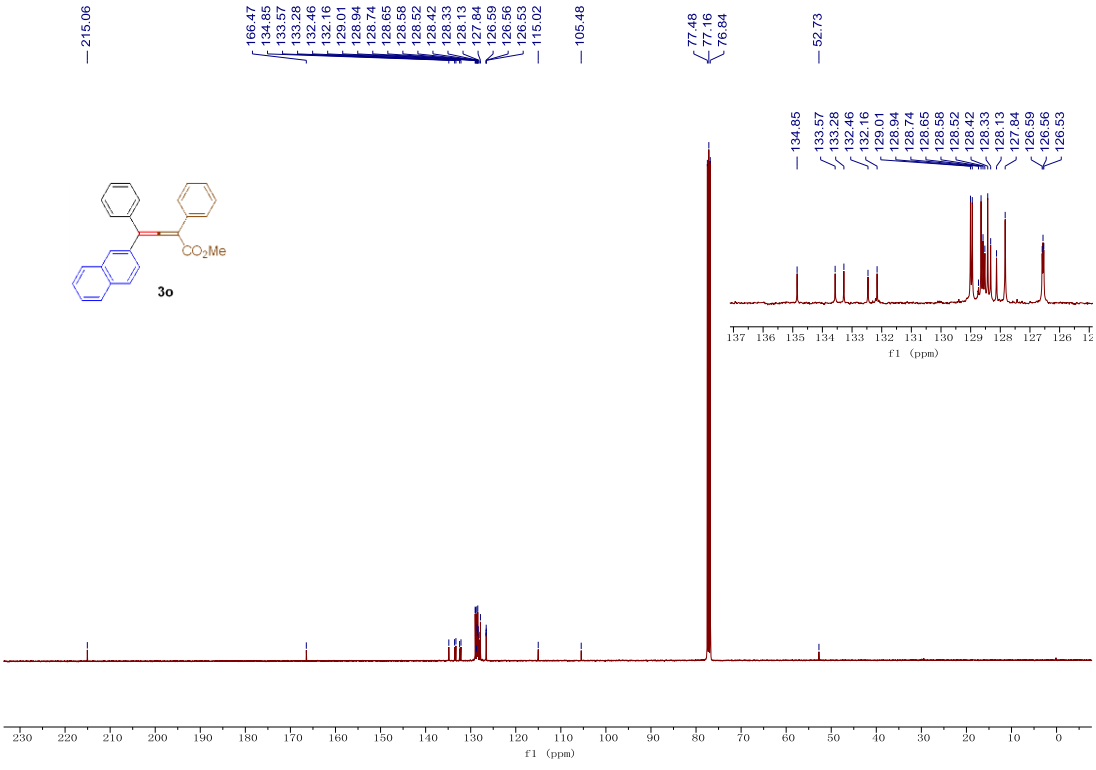
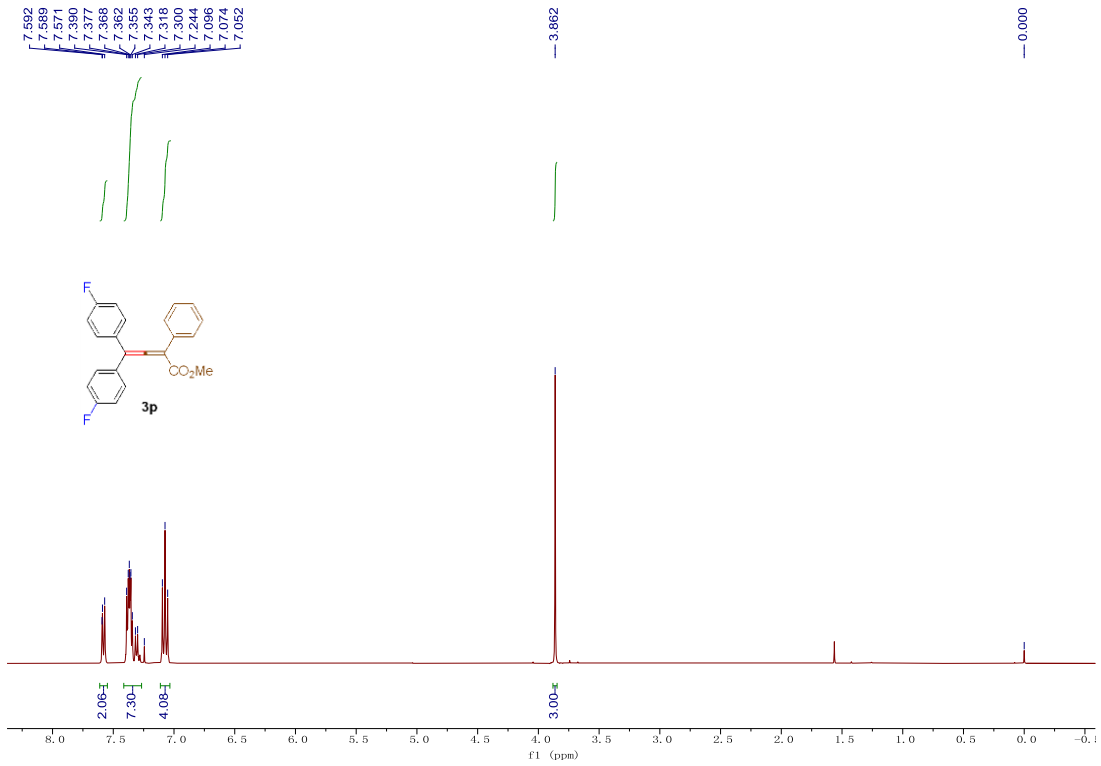
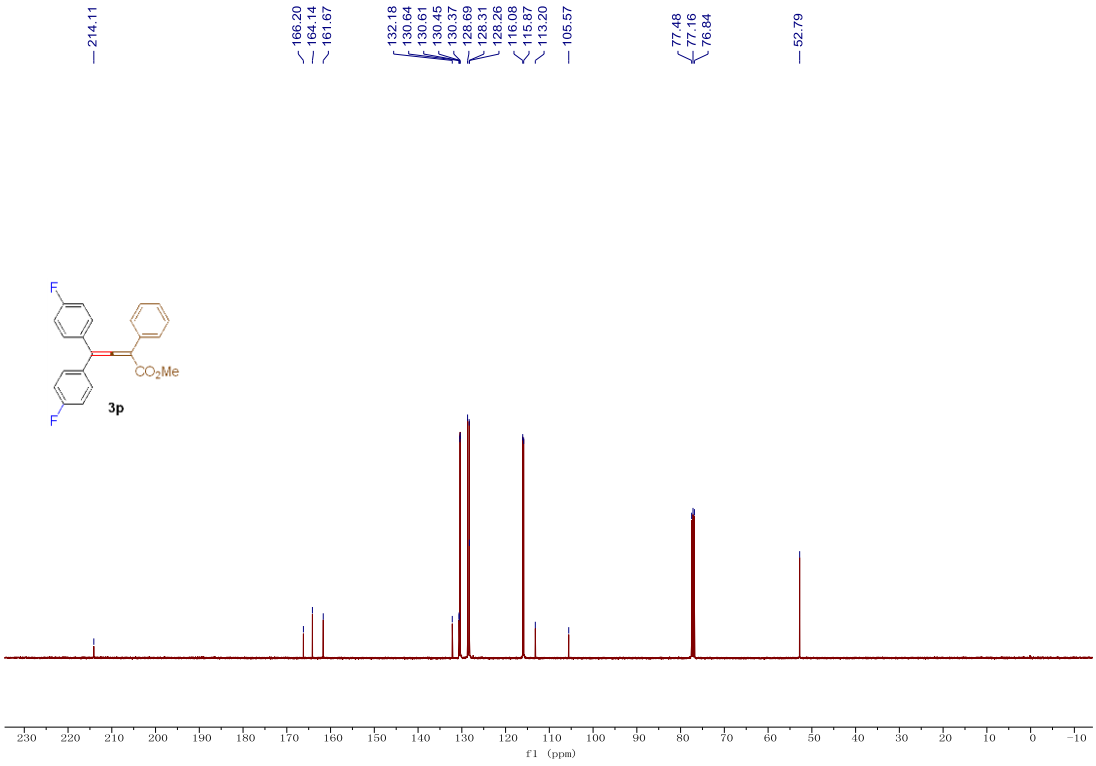
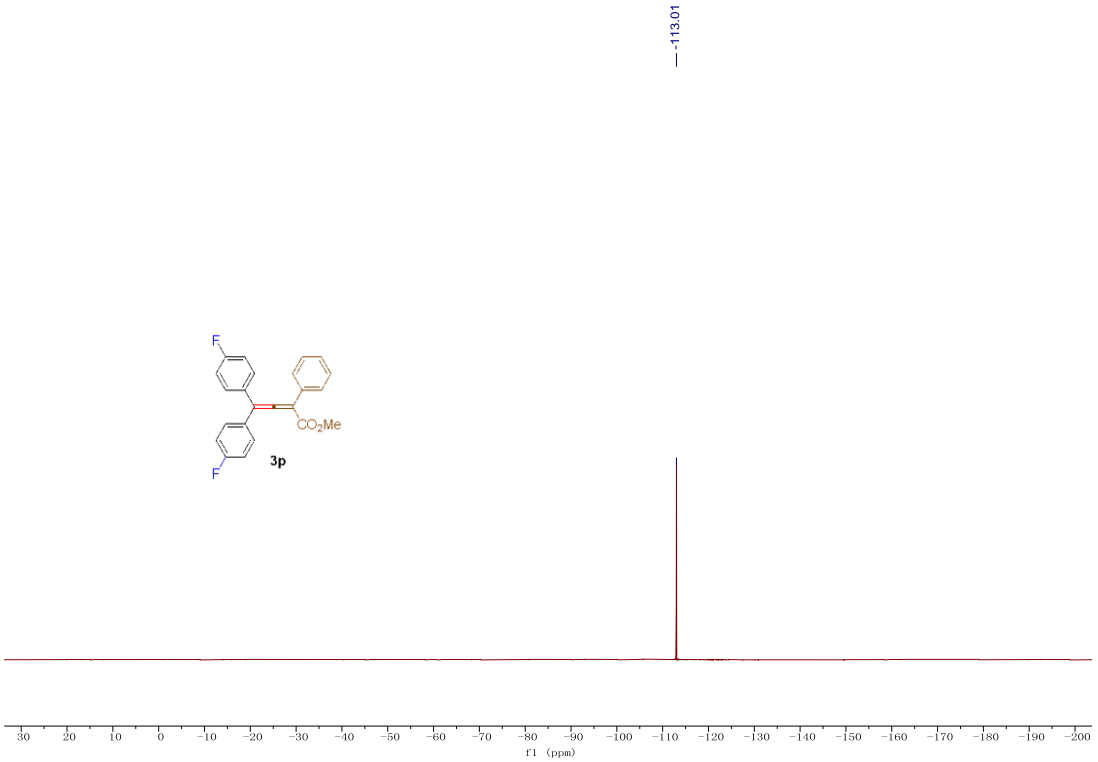
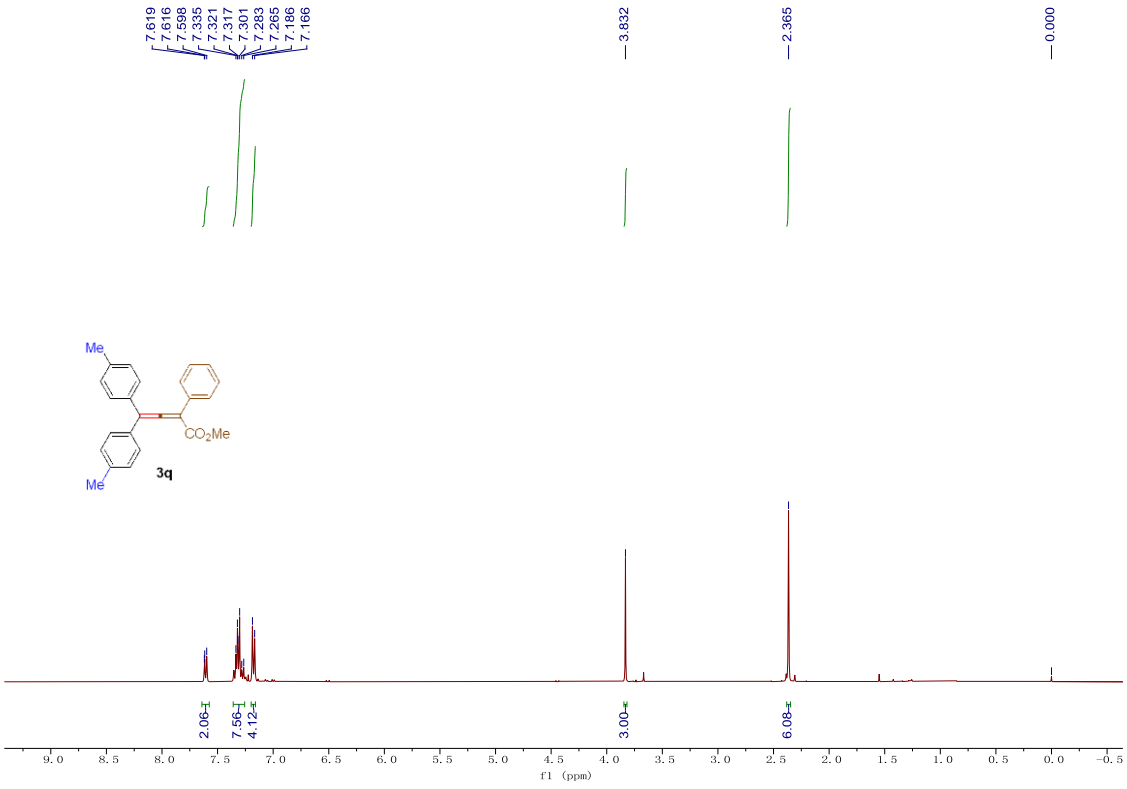
7.834
7.797
7.784
7.774
7.651
7.633
7.576
7.572
7.554
7.550
7.495
7.484
7.476
7.440
7.418
7.400
7.384
7.366
7.347
7.313
7.298
3.878
-0.000
CO2Me
3o
3.00
1.00
1.99
1.07
3.26
4.13
1.25
2.83
f1 (ppm)

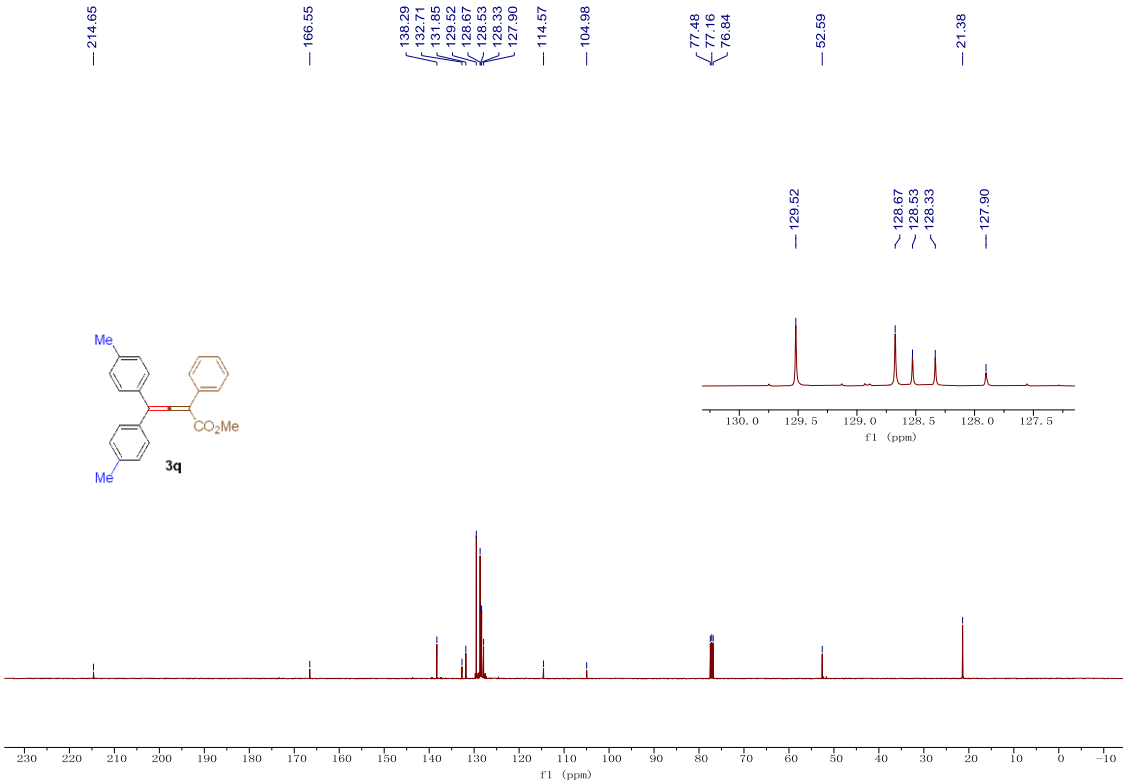

215.06
166.47
134.85
133.57
133.28
132.46
132.16
129.01
128.94
128.74
128.65
128.58
128.52
128.42
128.33
128.13
127.84
126.59
126.56
126.53
115.02
105.48
77.48
77.16
76.84
52.73
CO2Me
3o
f1 (ppm)


7.592
7.589
7.571
7.390
7.377
7.368
7.362
7.355
7.343
7.318
7.300
7.244
7.096
7.074
7.052
3.862
0.000
F
CO2Me
F
3p
2.06
7.30
4.08
3.00
f1 (ppm)


214.11
166.20
164.14
161.67
132.18
130.64
130.61
130.45
130.37
128.69
128.31
128.26
116.08
115.87
113.20
105.57
77.48
77.16
76.84
52.79
F
CO2Me
F
3p
f1 (ppm)


-113.01
F
CO2Me
F
3p
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


7.619
7.616
7.598
7.335
7.321
7.317
7.301
7.283
7.265
7.186
7.166
3.832
2.365
0.000
Me
CO2Me
Me
3q
2.06
7.56
4.12
3.00
6.08
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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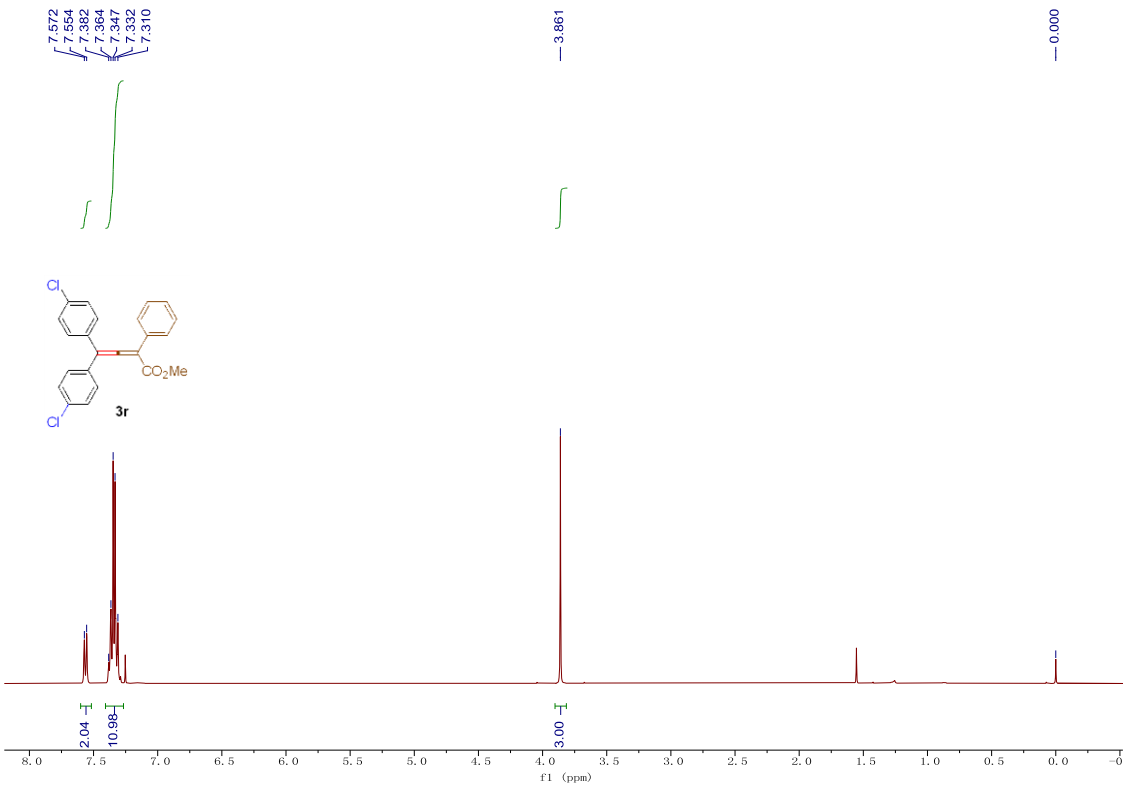
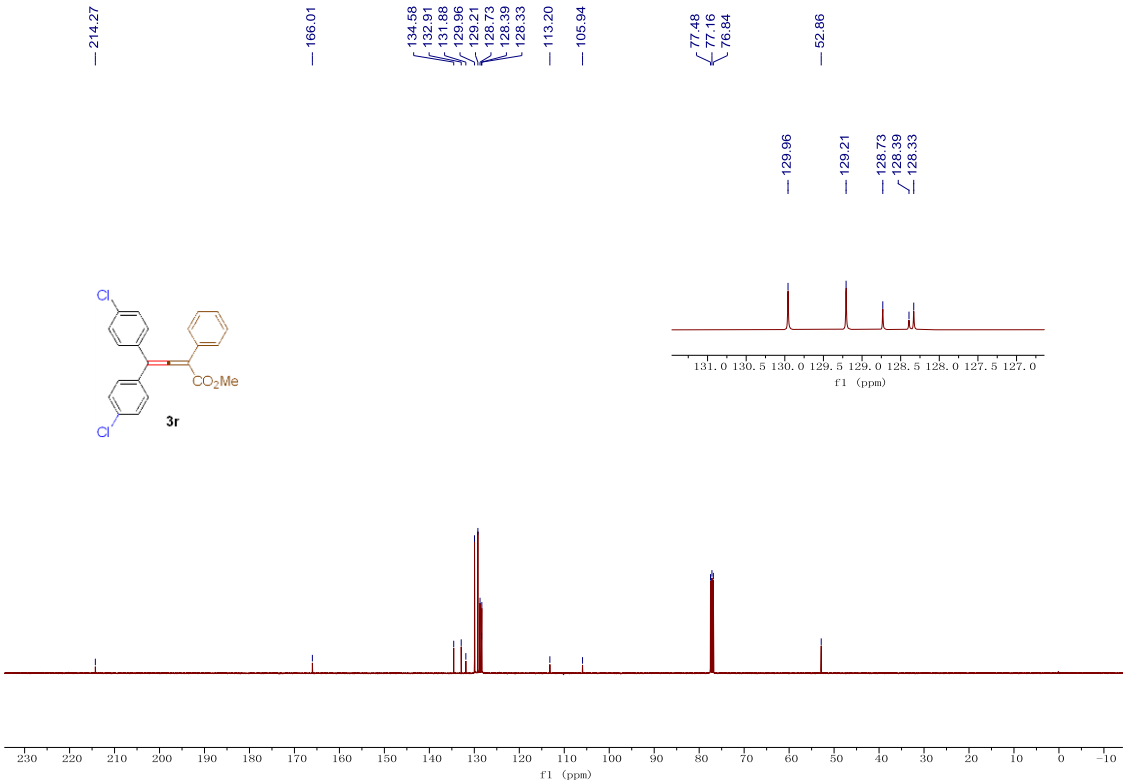
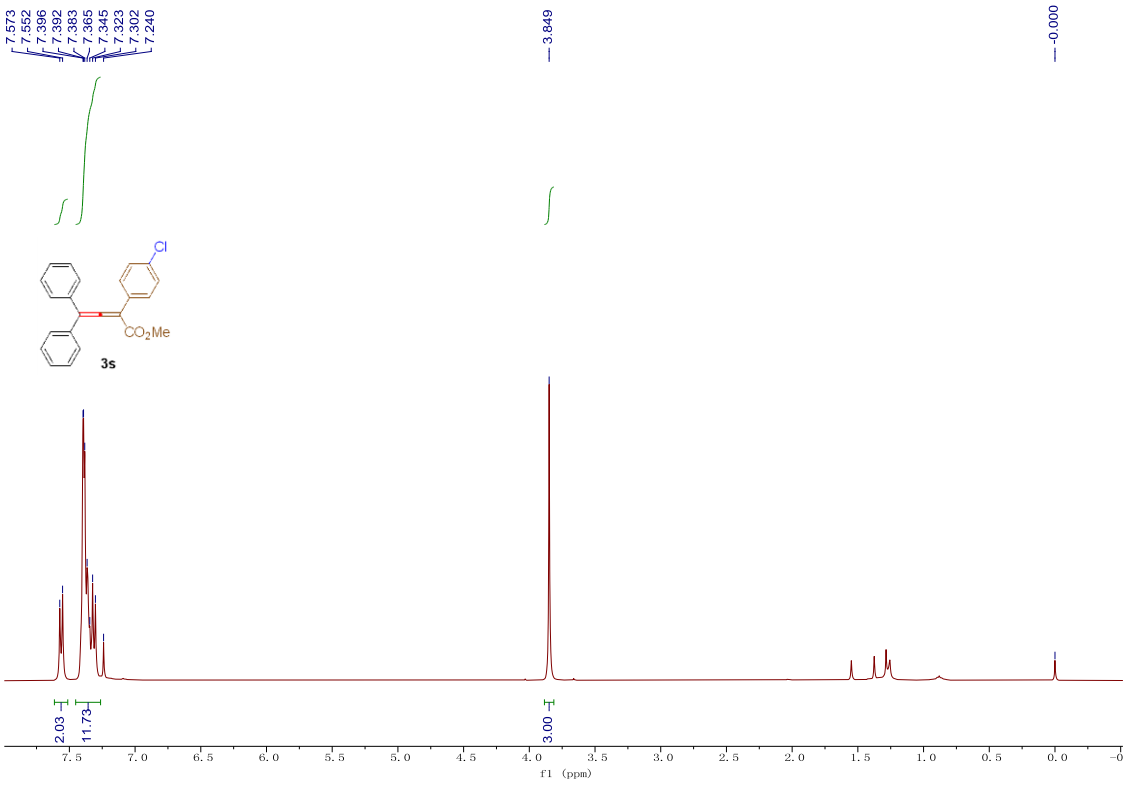
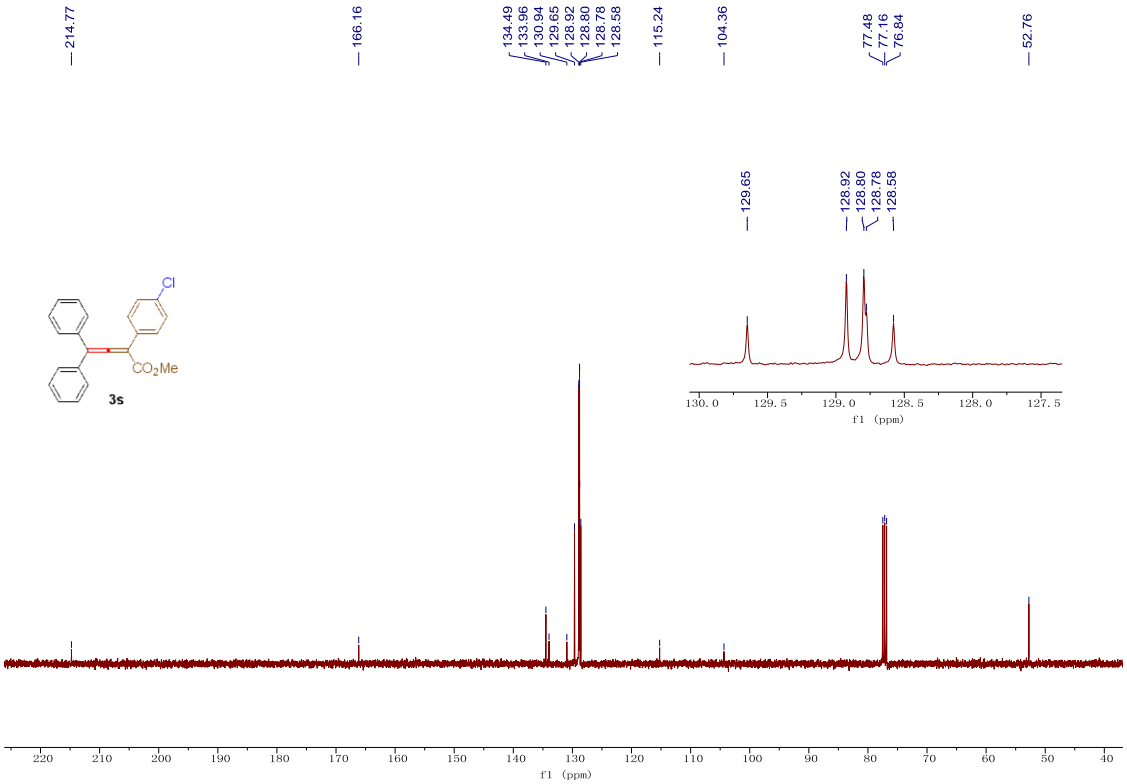
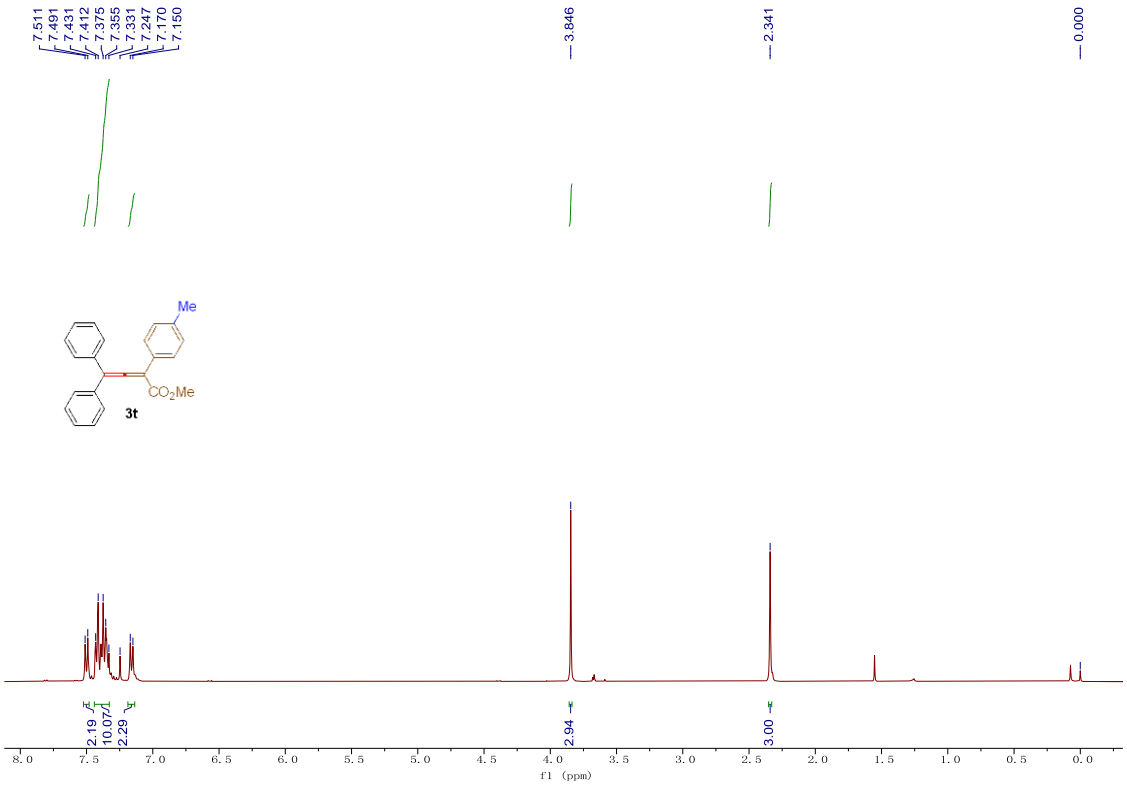
132.71
131.85
129.52
128.67
128.53
128.33
127.90
114.57
104.98
77.48
77.16
76.84
52.59
21.38
129.52
128.67
128.53
128.33
127.90
Me
CO2Me
Me
3q
f1 (ppm)

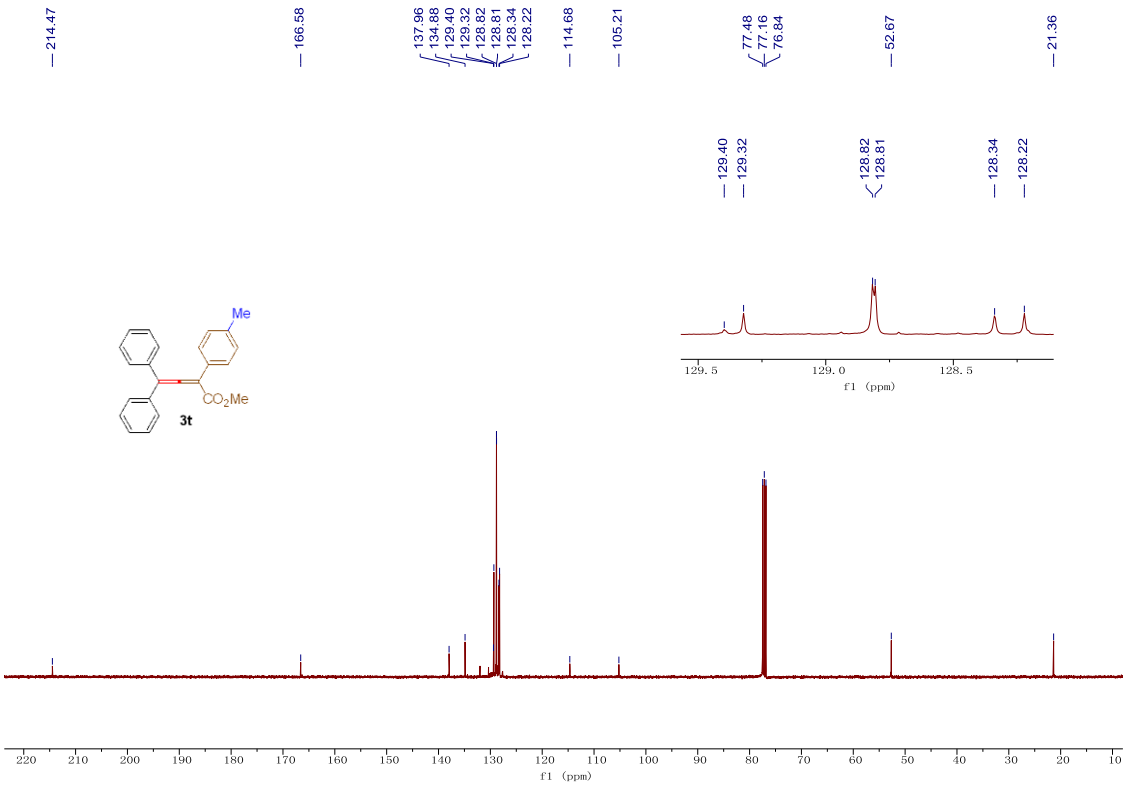

7.572
7.554
7.382
7.364
7.347
7.332
7.310
3.861
0.000
Cl
CO2Me
Cl
3r
2.04
10.98
3.00
f1 (ppm)


214.27
166.01
134.58
132.91
131.88
129.96
129.21
128.73
128.39
128.33
113.20
105.94
77.48
77.16
76.84
52.86
129.96
129.21
128.73
128.39
128.33
Cl
CO2Me
Cl
3r
131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0
f1 (ppm)
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
f1 (ppm)


7.573
7.552
7.396
7.392
7.383
7.365
7.345
7.323
7.302
7.240
3.849
0.000
Cl
CO2Me
3s
2.03
11.73
3.00
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)


214.77
166.16
134.49
133.96
130.94
129.65
128.92
128.80
128.78
128.58
115.24
104.36
77.48
77.16
76.84
52.76
129.65
128.92
128.80
128.78
128.58
Cl
CO2Me
3s
f1 (ppm)
f1 (ppm)


7.511
7.491
7.431
7.412
7.375
7.355
7.331
7.247
7.170
7.150
3.846
2.341
0.000
Me
CO2Me
3t
2.19
10.07
2.29
2.94
3.00
f1 (ppm)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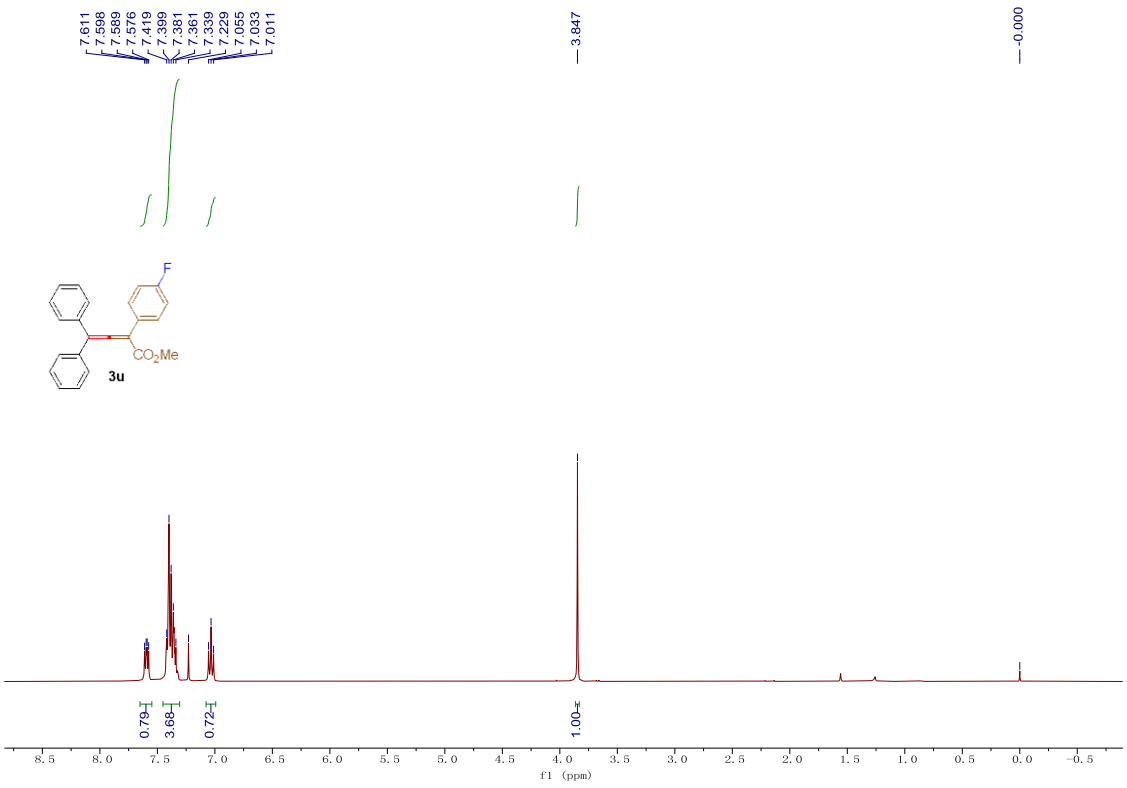
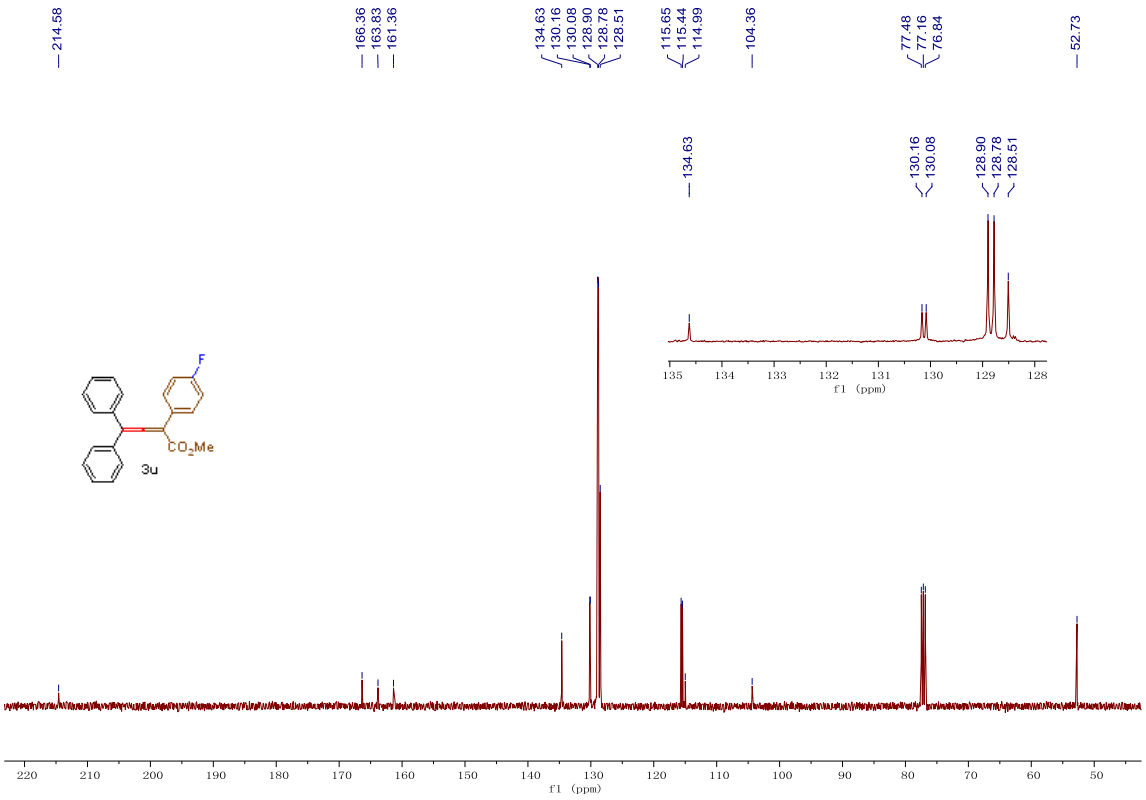
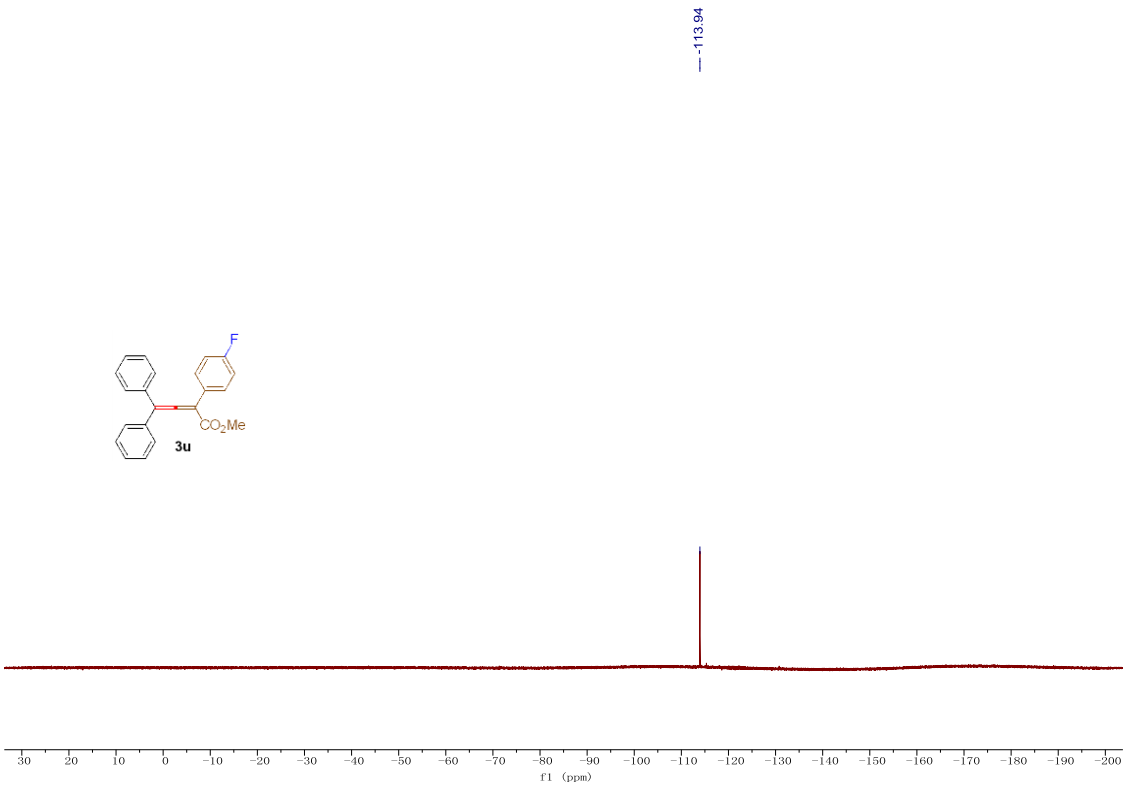
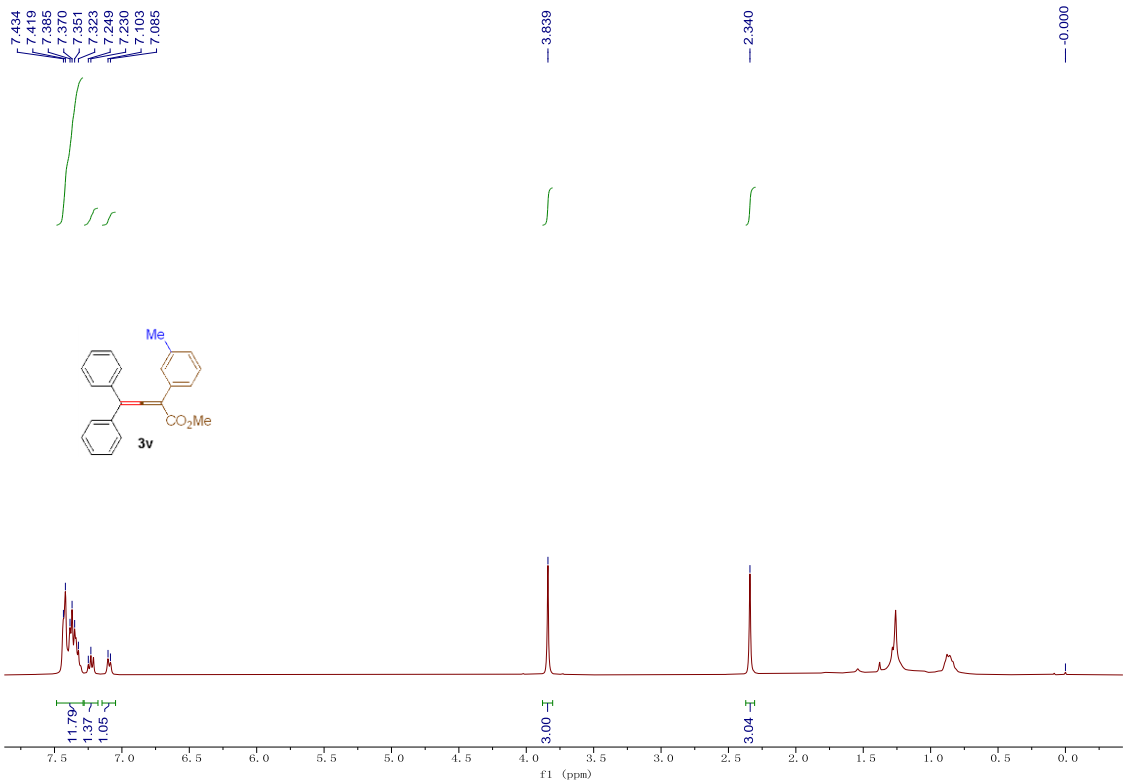
166.58
137.96
134.88
129.40
129.32
128.82
128.81
128.34
128.22
114.68
105.21
77.48
77.16
76.84
52.67
21.36
129.40
129.32
128.82
128.81
128.34
128.22
Me
CO2Me
3t
129.5
129.0
128.5
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.611
7.598
7.589
7.576
7.419
7.399
7.381
7.361
7.339
7.229
7.055
7.033
7.011
3.847
-0.000
F
CO2Me
3u
0.79
3.68
0.72
1.00
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)


214.58
166.36
163.83
161.36
134.63
130.16
130.08
128.90
128.78
128.51
115.65
115.44
114.99
104.36
77.48
77.16
76.84
52.73
F
CO2Me
3u
f1 (ppm)


-113.94
F
CO2Me
3u
f1 (ppm)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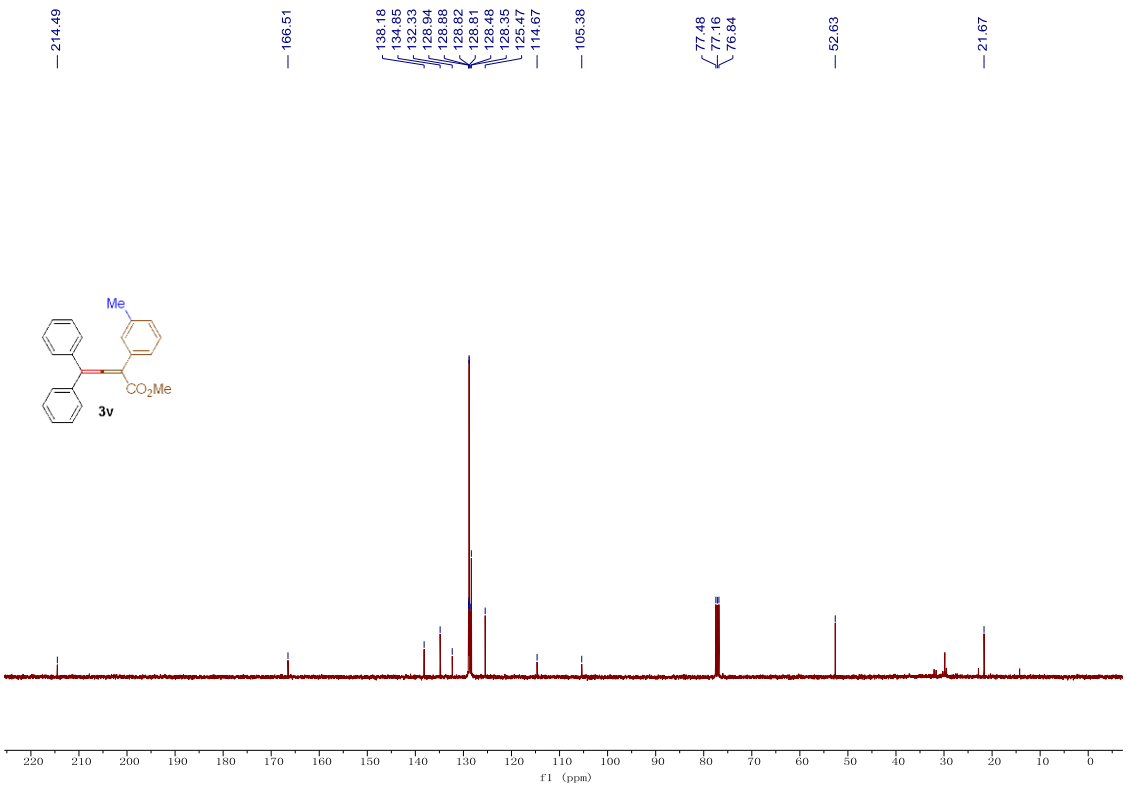
7.419
7.385
7.370
7.351
7.323
7.249
7.230
7.103
7.085
3.839
2.340
-0.000
Me
CO2Me
3v
11.79
1.37
1.05
3.00
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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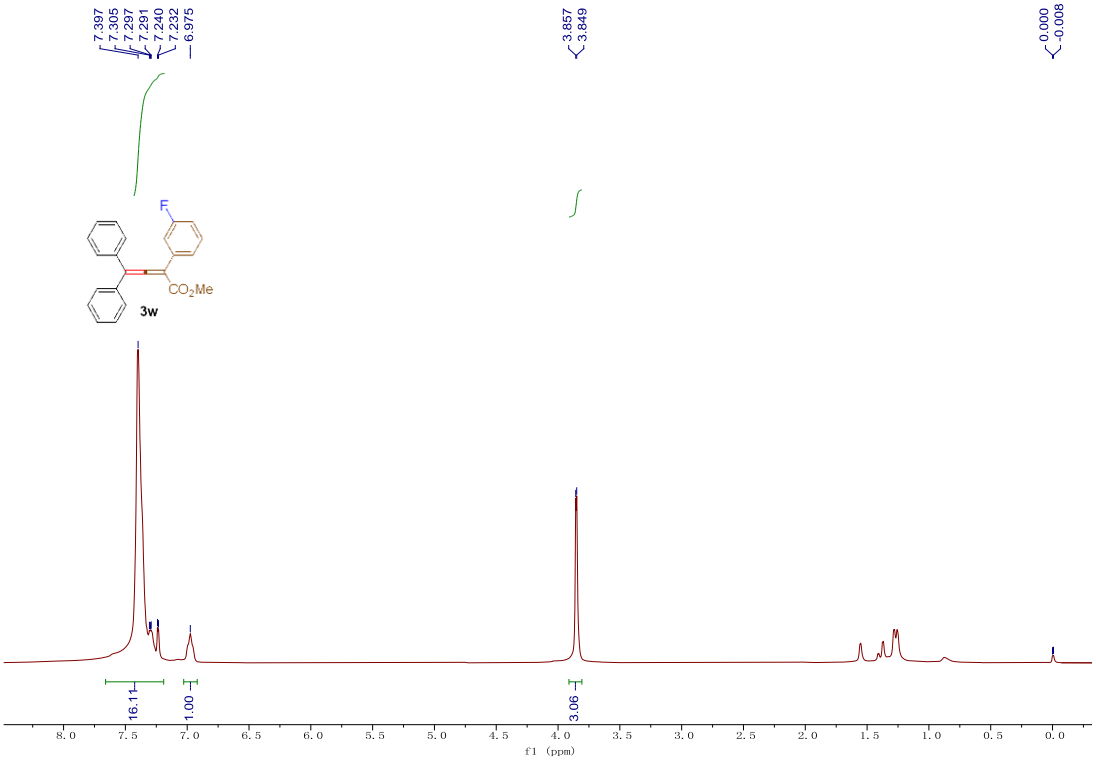
128.88
128.82
128.81
128.48
128.35
125.47
114.67
105.38
77.48
77.16
76.84
52.63
21.67
Me
CO2Me
3v
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.240
7.232
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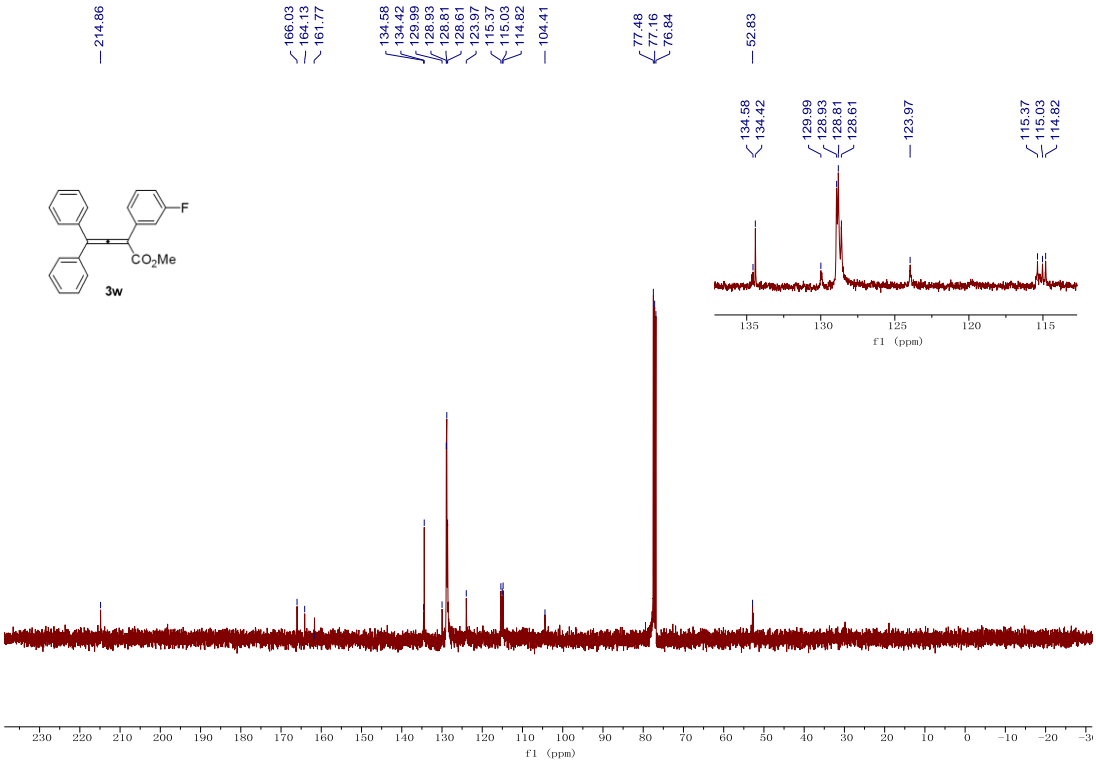
3.849
0.000
-0.008
F
CO2Me
3w
16.11
1.00
3.06
f1 (ppm)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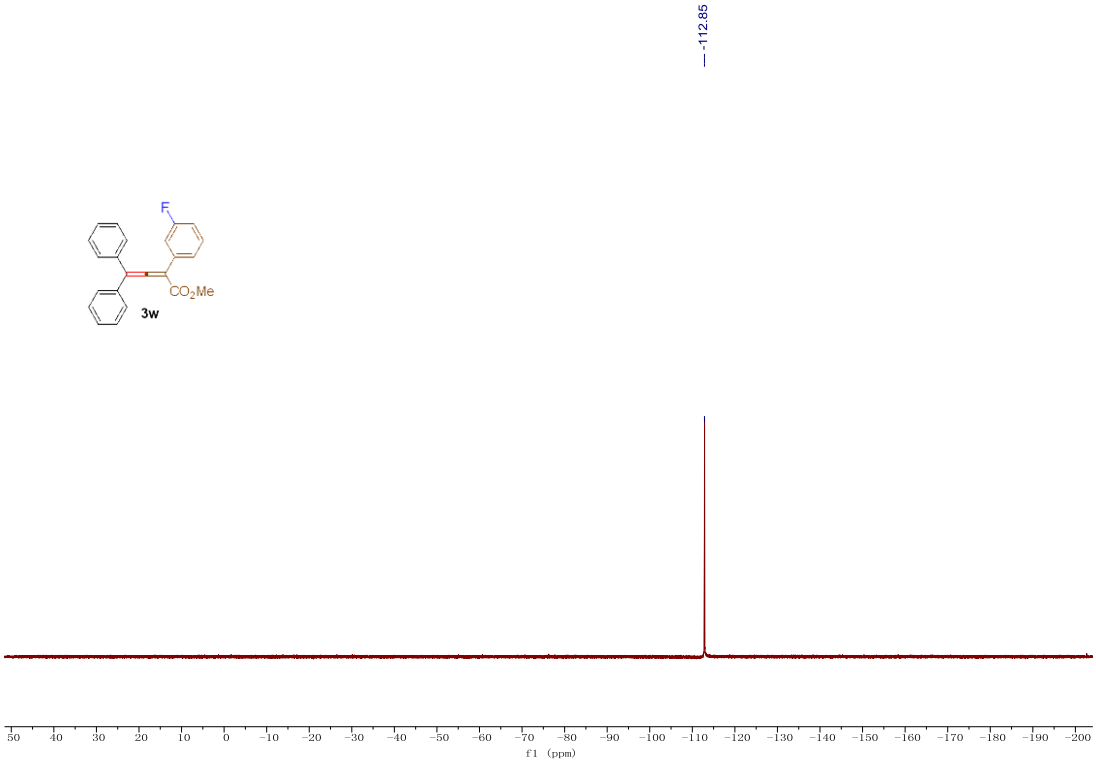
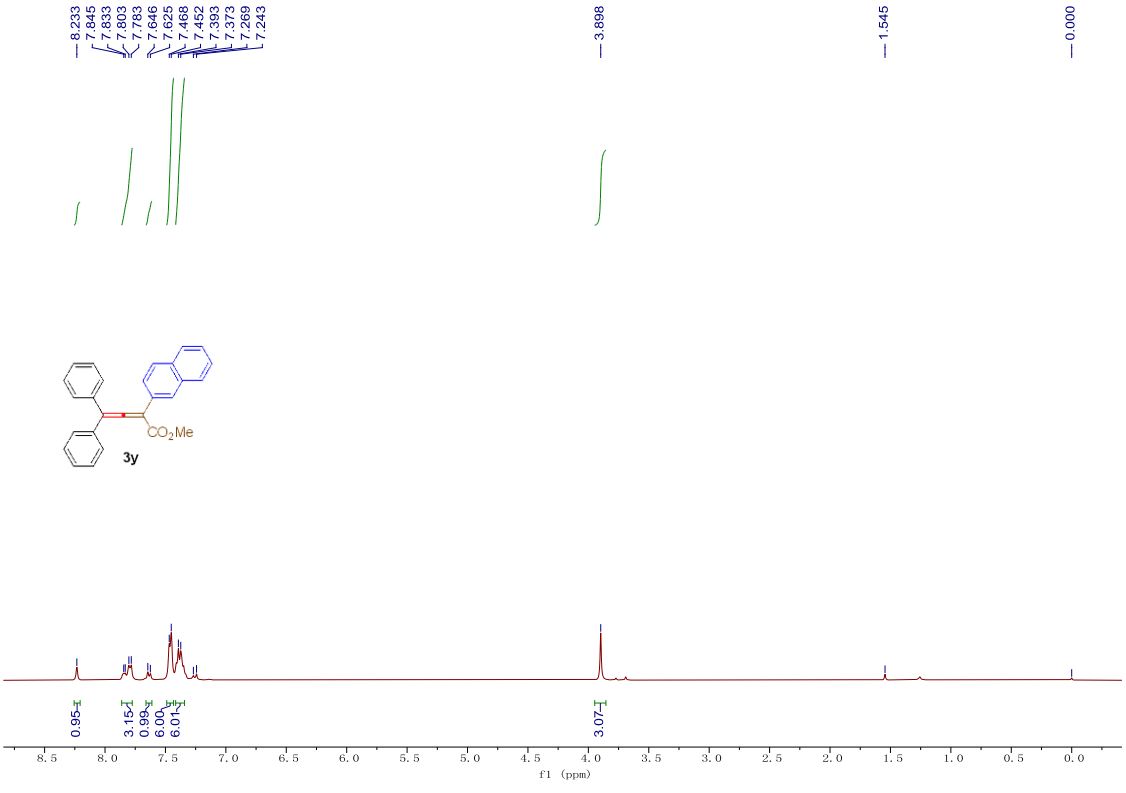
164.13
161.77
134.58
134.42
129.99
128.93
128.81
128.61
123.97
115.37
115.03
114.82
104.41
77.48
77.16
76.84
52.83
F
CO2Me
3w
f1 (ppm)


-112.85
F
CO2Me
3w
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


8.233
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7.833
7.803
7.783
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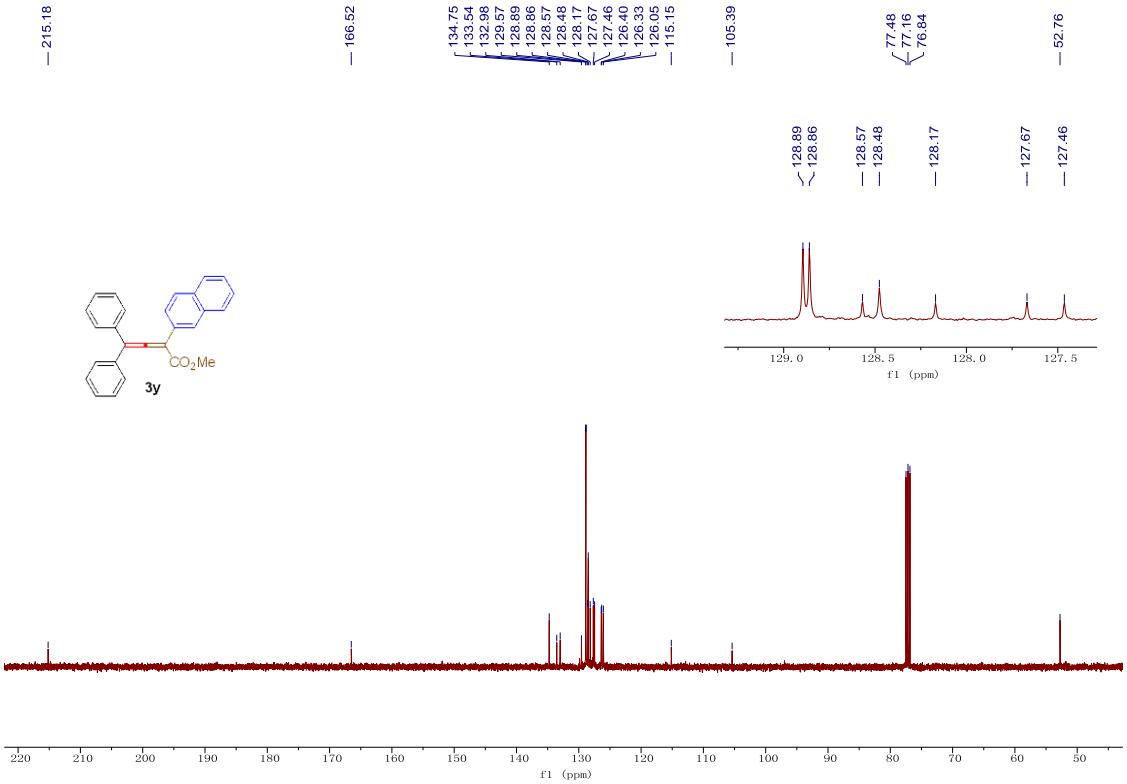
7.625
7.468
7.452
7.393
7.373
7.269
7.243
3.898
1.545
0.000
CO2Me
3y
0.95
3.15
0.99
6.00
6.01
3.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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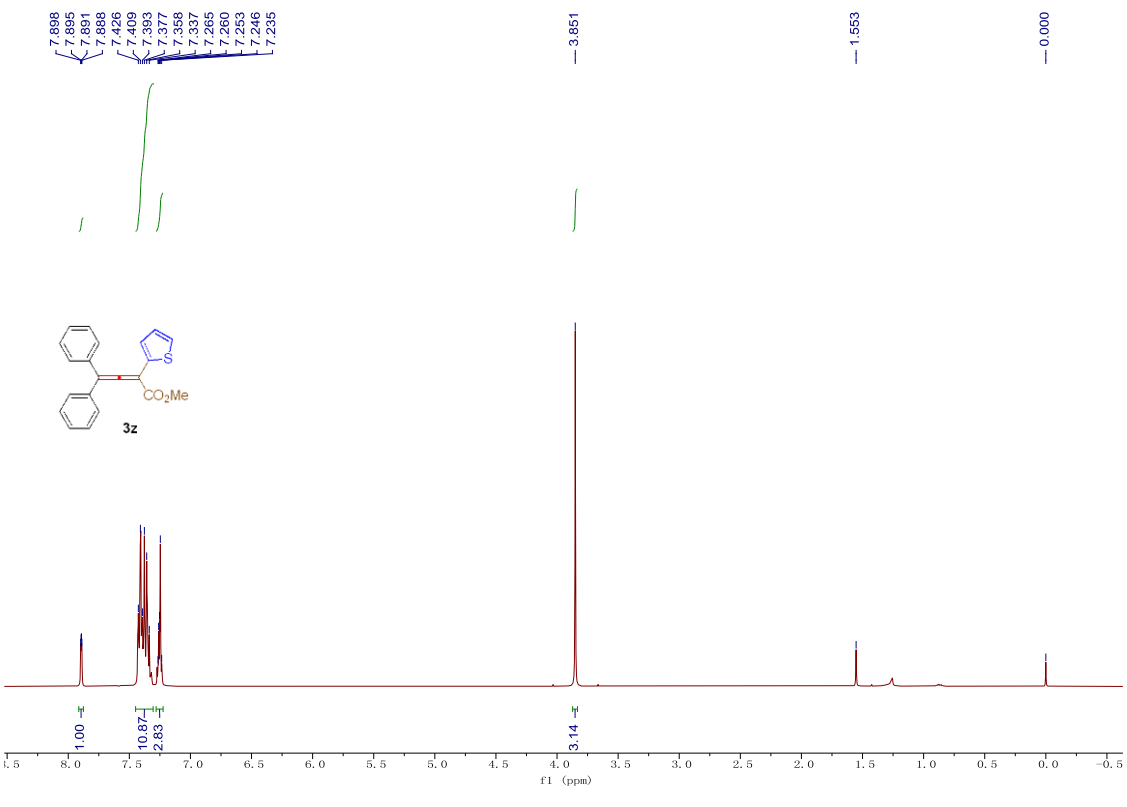
128.89
128.86
128.57
128.48
128.17
127.67
127.46
126.40
126.33
126.05
115.15
105.39
77.48
77.16
76.84
52.76
128.89
128.86
128.57
128.48
128.17
127.67
127.46
CO2Me
3y
f1 (ppm)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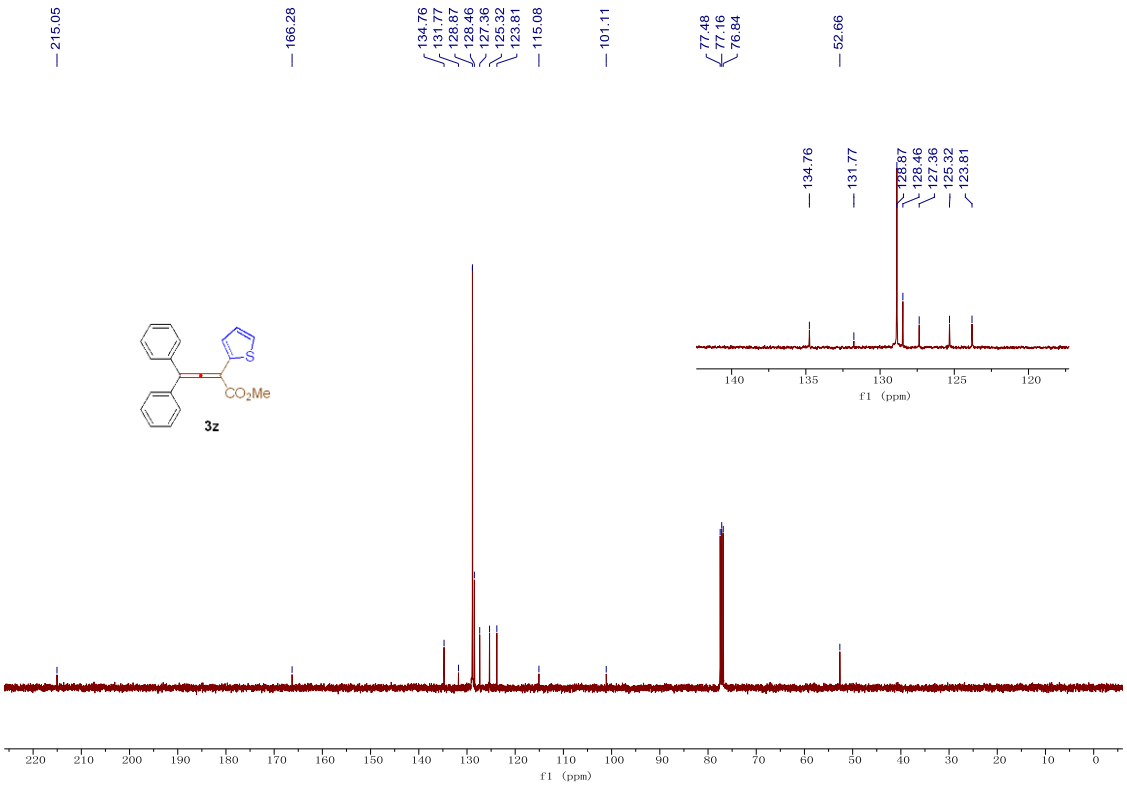
7.377
7.358
7.337
7.265
7.260
7.253
7.246
7.235
3.851
1.553
0.000
S
CO2Me
3z
1.00
10.87
2.83
3.14
f1 (ppm)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128.87
128.46
127.36
125.32
123.81
115.08
101.11
77.48
77.16
76.84
52.66
CO2Me
S
3z
f1 (ppm)