Supporting Information

Blue Light-promoted Cross-Coupling of Aryldiazoacetates and Diazocarbonyl Compounds

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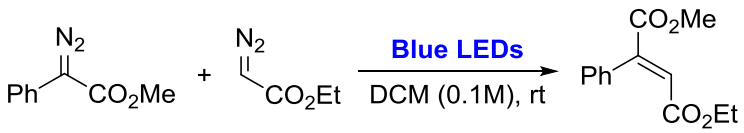
General Unless otherwise noted, all reactions were performed in a 10 mL test tube at room temperature. Photo-irradiation was carried out with 5 W blue LEDs. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. MS and HRMS were performed on Thermo MAT95XP mass spectrometer, or LTQ Orbitrap Elite mass spectrometer at analytical center of Sun Yat-Sen University. UV-Vis absorbance spectra were recorded on Shimadzu UV-2700 UV-Vis spectrophotometer. Bule LEDs' emission spectrum was recorded on Shimadzu RF-5301 fluorescence spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Brucker ARX 400 or Varian INOVA 500NB spectrometer. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, s referred to multiplet, quartet, triplet, doublet, singlet. Materials obtained from commercial suppliers were used without further purification. Diazo compounds were synthesized through reported methods.[1-2]

Typical procedure for the synthesis of 4a:



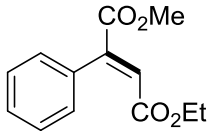
1a **2a** **4a**

To a 10 mL test tube equipped with a magnetic stir bar was charged with methyl phenyldiazoacetate **1a** (0.2 mmol, 35.2 mg), ethyl diazoacetate **2a** (0.2 mmol, 22.8 mg, 1 equiv), and 2 mL of DCM. The solution was stirred at room temperature with the irradiation of 5 W blue LEDs under argon for 12 h. Upon completion of the reaction, the solvent was evaporated under vacuum; the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (80/1) as the eluent, giving the pure product **4a** as a colorless liquid (38.5 mg, 88% yield).

The trisubstituted alkenes **4b-q**, **6b-r** and tetrasubstituted alkene **8** were prepared following the same procedure for the synthesis of **4a**.

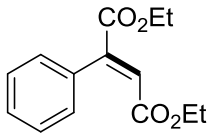
Characterization data

(*E*)-4-Ethyl 1-methyl 2-phenylfumarate (**4a**):[1]



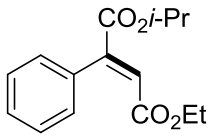
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 3H), 7.25 – 7.20 (m, 2H), 7.02 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.89, 165.35, 143.76, 134.08, 129.52, 128.91, 128.62, 127.89, 60.97, 53.00, 13.88; ESI-MS m/z 235.1 $(M+H)^+$.

(*E*)-Diethyl 2-phenylfumarate (**4b**):[3]



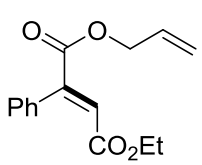
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 3H), 7.27 – 7.23 (m, 2H), 7.00 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.40, 165.52, 144.13, 134.19, 129.09, 128.99, 128.59, 127.85, 62.04, 60.95, 14.23, 13.91; ESI-MS m/z 249.1 $(M+H)^+$.

(*E*)-4-Ethyl 1-isopropyl 2-phenylfumarate (**4c**):



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 3H), 7.23 – 7.20 (m, 2H), 6.93 (s, 1H), 5.09 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 1.25 (d, *J* = 6.3 Hz, 6H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.87, 165.63, 144.47, 134.24, 129.01, 128.67, 128.54, 127.79, 69.74, 60.92, 21.80, 13.90; HRMS (ESI) calcd. for $C_{15}H_{19}O_4$ $[M+H]^+$ 263.12779, found: 263.12723.

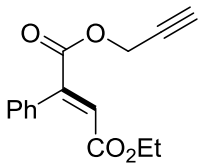
(*E*)-1-Allyl 4-ethyl 2-phenylfumarate (**4d**):



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 3H), 7.24 (dt, *J* = 5.4, 3.8 Hz, 2H), 7.02 (s, 1H), 5.91 (ddd, *J* = 22.7, 10.8, 5.6 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.23 (dd, *J* = 10.5, 1.0 Hz, 1H), 4.69 (d, *J* = 5.6 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126

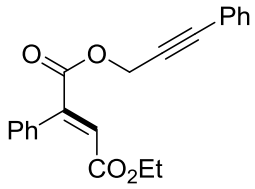
MHz, $CDCl_3$) δ 166.04, 165.40, 143.84, 134.06, 131.62, 129.48, 128.96, 128.64, 127.88, 118.74, 66.45, 60.99, 13.90; HRMS (ESI) calcd. for $C_{15}H_{17}O_4$ $[M+H]^+$ 261.11214, found: 261.11139.

(*E*)-4-Ethyl 1-(prop-2-yn-1-yl) 2-phenylfumarate (**4e**):



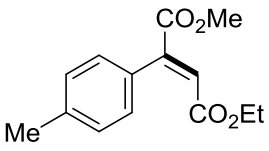
The product was isolated as a 10: 1 mixture of *E/Z*-isomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 0.2H'), 7.45 – 7.40 (m, 0.3H'), 7.37 (m, 3H), 7.27 – 7.24 (m, 2H), 7.07 (s, 1H), 6.35 (s, 0.1H'), 4.96 (d, *J* = 2.5 Hz, 0.2H'), 4.80 (d, *J* = 2.5 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 0.2H'), 4.05 (q, *J* = 7.1 Hz, 2H), 2.54 (t, *J* = 2.5 Hz, 0.1H'), 2.50 (t, *J* = 2.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 0.3H'), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.22, 165.64, 165.24, 164.94, 147.73, 142.95, 133.65, 133.11, 130.80, 130.22, 129.18, 129.04, 128.97, 128.82, 127.96, 126.89, 118.21, 81.77, 75.71, 75.53, 61.24, 61.09, 53.32, 14.29, 13.90; HRMS (ESI) calcd. for $C_{11}H_{13}O_4S$ $[M+H]^+$ 245.08084, found: 245.08014.

(*E*)-4-Ethyl 1-(3-phenylprop-2-yn-1-yl) 2-phenylfumarate (**4f**):



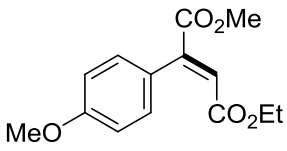
The product was isolated as a 6: 1 mixture of *E/Z*-isomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.1, 1.5 Hz, 0.33H'), 7.49 – 7.43 (m, 2H, 0.33H'), 7.42 – 7.35 (m, 3H, 0.5H'), 7.35 – 7.26 (m, 5H, 0.67H'), 7.09 (s, 1H), 6.36 (s, 0.14H'), 5.19 (s, 0.33H'), 5.04 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 0.33H'), 4.05 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 0.56H'), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.38, 165.78, 165.32, 164.98, 147.88, 143.15, 133.76, 133.20, 132.07, 132.00, 130.77, 130.06, 129.98, 129.18, 129.08, 129.01, 128.93, 128.80, 128.71, 128.45, 128.33, 127.95, 126.94, 122.13, 118.04, 87.30, 87.05, 82.59, 82.51, 61.23, 61.06, 54.24, 53.62, 14.29, 13.91; HRMS (ESI) calcd. for $C_{18}H_{17}O_4$ $[M+H]^+$ 321.11214, found: 321.11133.

(*E*)-4-Ethyl 1-methyl 2-(4- methylphenyl)fumarate (**4g**):[4]



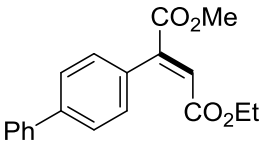
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.99 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.37 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.09, 165.43, 143.96, 138.60, 131.03, 129.00, 128.90, 128.65, 60.92, 52.96, 21.48, 13.96; ESI-MS m/z 249.1 $(M+H)^+$.

(*E*)-4-Ethyl 1-methyl 2-(4-methoxyphenyl)fumarate (**4h**):[1]



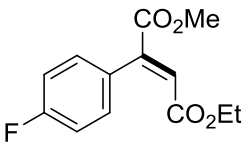
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.95 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.23, 165.58, 160.00, 143.45, 130.58, 128.51, 126.05, 113.35, 60.93, 55.32, 52.97, 14.03; ESI-MS m/z 265.1 $(M+H)^+$.

(*E*)-4-Ethyl 1-methyl 2-([1,1'-biphenyl]-4-yl)fumarate (**4i**):



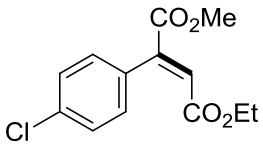
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.1 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 10.4, 7.9 Hz, 3H), 7.07 (s, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.89, 165.38, 143.47, 141.49, 140.68, 132.95, 129.51, 129.43, 128.86, 127.59, 127.23, 126.59, 61.01, 53.02, 13.91; HRMS (ESI) calcd. for $C_{13}H_{14}O_4Cl$ $[M+H]^+$ 311.12779, found: 311.12689.

(*E*)-4-Ethyl 1-methyl 2-(4-fluorophenyl)fumarate (**4j**):



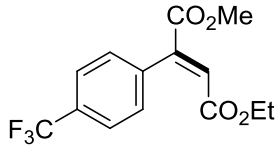
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.05 (t, *J* = 8.7 Hz, 2H), 7.02 (s, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.68, 165.18, 162.97 (d, *J* = 248.1 Hz), 142.79, 130.95 (d, *J* = 8.3 Hz), 129.87 (d, *J* = 3.3 Hz), 129.73, 114.99 (d, *J* = 21.7 Hz), 61.06, 53.03, 13.93; HRMS (ESI) calcd. for $C_{13}H_{14}O_4F$ $[M+H]^+$ 253.08706, found: 253.08643.

(*E*)-4-Ethyl 1-methyl 2-(4-chlorophenyl)fumarate (**4k**):



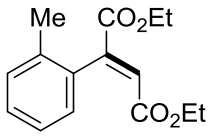
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.20 – 7.16 (m, 2H), 7.03 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.48, 165.05, 142.78, 134.78, 132.43, 130.44, 129.92, 128.19, 61.14, 53.10, 13.96; HRMS (ESI) calcd. for $C_{13}H_{14}O_4Cl$ $[M+H]^+$ 269.0575, found: 269.0568.

(*E*)-4-Ethyl 1-methyl 2-(4-(trifluoromethyl)phenyl)fumarate (**4l**):[1]



The product was isolated as a 4.5: 1 mixture of *E/Z*-isomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 0.47H'), 7.63 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 6.35 (s, 0.19H'), 4.26 (q, *J* = 7.1 Hz, 0.50H'), 4.05 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 0.71H'), 3.81 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 0.91H'), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.29, 167.81, 166.19, 164.83, 147.05, 142.78, 137.88, 137.03, 130.89, 130.57, 129.41, 128.54, 127.30, 126.07 (dd, *J* = 15.1, 3.3 Hz), 124.91 (d, *J* = 3.4 Hz), 124.04 (d, *J* = 2.9 Hz), 120.35, 77.41, 77.16, 76.91, 61.45, 61.25, 53.21, 53.01, 14.26, 13.86; ESI-MS m/z 303.1 $(M+H)^+$.

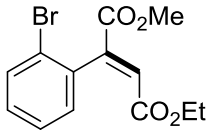
(*E*)-4-Ethyl 1-ethyl 2-(2- methylphenyl)maleate (**4m**):



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 5.7, 3.0 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.06 (s, 1H), 7.04 – 7.00 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.17 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.20, 165.12, 144.88, 135.85, 134.42, 129.73, 129.69, 128.50, 128.43, 125.38, 61.97, 60.84, 19.77, 14.21, 13.85; HRMS (ESI) calcd. for $C_{13}H_{14}O_4Cl$ $[M+H]^+$ 263.12779, found: 263.12739.

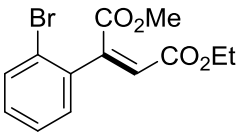
(*E*)-4-Ethyl 1-methyl 2-(2-bromophenyl)maleate (**4n**):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.32 (td, *J* = 7.5, 1.0 Hz,



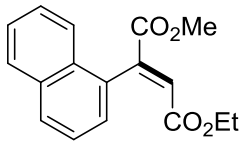
1H), 7.23 (td, *J* = 7.8, 1.7 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.10 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.81, 164.52, 143.88, 135.92, 132.33, 130.69, 130.38, 129.90, 127.00, 122.65, 61.07, 53.18, 13.89; HRMS (ESI) calcd. for $C_{13}H_{14}O_4Cl$ $[M+H]^+$ 313.00700, found: 313.00617.

(*Z*)-4-Ethyl 1-methyl 2-(2-bromophenyl)maleate (**4n'**):



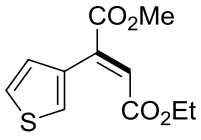
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.38 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.34 (dd, *J* = 10.7, 4.0 Hz, 1H), 7.23 (td, *J* = 7.8, 1.7 Hz, 1H), 6.23 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46, 165.03, 144.24, 136.47, 133.50, 130.67, 127.70, 122.60, 61.50, 52.83, 14.24; HRMS (ESI) calcd. for $C_{13}H_{14}O_4Cl$ $[M+H]^+$ 313.00700, found: 313.00722.

(*E*)-4-Ethyl 1-methyl 2-(naphthalen-1-yl)fumarate (**4o**):[1]



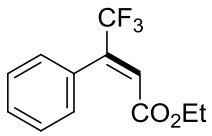
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.50 – 7.45 (m, 3H), 7.33 – 7.28 (m, 2H), 3.86 (dd, *J* = 6.9, 3.7 Hz, 2H), 3.74 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.07, 164.85, 143.31, 133.32, 132.30, 131.60, 131.52, 128.82, 128.54, 126.46, 126.39, 125.97, 125.05, 124.85, 60.79, 53.07, 13.56; ESI-MS m/z 285.1 $(M+H)^+$.

(*E*)-4-Ethyl 1-methyl 2-(thiophen-3-yl)fumarate (**4p**):



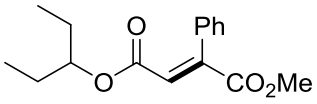
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.27 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.08 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.93 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.78, 165.67, 137.84, 133.19, 128.90, 128.72, 126.70, 124.61, 61.14, 53.00, 14.05; HRMS (ESI) calcd. for $C_{11}H_{13}O_4S$ $[M+H]^+$ 241.05291, found: 241.05246.

Ethyl (*E*)-4,4,4-trifluoro-3-phenylbut-2-enoate (**4q**):[5]



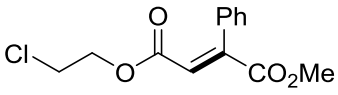
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.31 (dd, *J* = 7.5, 1.5 Hz, 2H), 6.66 – 6.61 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.23, 142.44 (q, *J* = 30.9 Hz), 131.17, 129.39, 128.75, 128.28, 124.69 (q, *J* = 5.4 Hz), 61.17, 13.78; ESI-MS m/z 245.1 $(M+H)^+$.

(*E*)-1-Methyl 4-(pentan-3-yl) 2-phenylfumarate (**6b**):



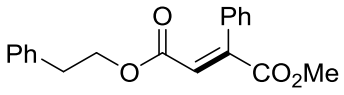
The product was isolated as a 10: 1 mixture of *E/Z*-isomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.7, 1.9 Hz, 0.28H'), 7.41 (dd, *J* = 7.0, 5.2 Hz, 0.55H'), 7.37 – 7.34 (m, 3H), 7.26 – 7.22 (m, 2H), 7.06 (s, 1H), 6.33 (s, 0.10H'), 4.72 – 4.64 (m, 1H), 3.94 (s, 0.32H'), 3.80 (s, 3H), 1.63 (dd, *J* = 7.4, 5.2 Hz, 0.41H'), 1.46 – 1.34 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 0.76H'), 0.72 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.51, 167.01, 165.28, 164.88, 148.34, 143.04, 134.20, 133.52, 130.19, 129.10, 128.98, 128.56, 128.08, 127.91, 126.83, 118.31, 77.82, 52.96, 52.72, 26.43, 26.03, 9.64, 9.43; HRMS (ESI) calcd. for $C_{16}H_{21}O_4$ $[M+H]^+$ 277.14344, found: 277.14272.

4-(2-Chloroethyl) (*E*)-1-methyl 2-phenylfumarate (**6c**):



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.25 (dd, *J* = 6.8, 3.2 Hz, 2H), 7.04 (s, 1H), 4.26 – 4.21 (m, 2H), 3.81 (s, 3H), 3.48 – 3.43 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.68, 164.82, 145.05, 133.90, 128.88, 128.85, 128.39, 128.01, 64.43, 53.11, 41.06; HRMS (ESI) calcd. for $C_{13}H_{14}O_4Cl$ $[M+H]^+$ 269.0575, found: 269.0571.

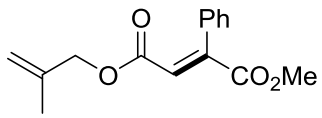
(*E*)-1-Methyl 4-phenethyl 2-phenylfumarate (**6d**):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.31 – 7.26 (m, 2H), 7.25 – 7.20 (m, 3H), 7.11 (d, *J* = 6.9 Hz, 2H), 7.02 (s, 1H), 4.22 (t, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.74 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.84, 165.24, 144.02, 137.54, 133.99, 129.21, 128.92, 128.71, 128.59, 127.93, 126.69, 65.42, 53.02, 34.80; HRMS (ESI) calcd. for

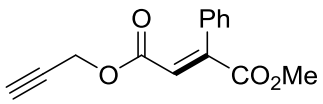
$C_{19}H_{18}O_4Na$ $[M+Na]^+$ 333.10973, found: 333.10978.

(*E*)-1-Methyl 4-(2-methylallyl) 2-phenylfumarate (**6e**):



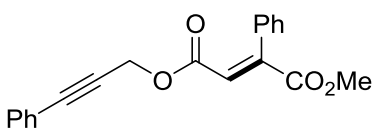
The product was isolated as a 10: 1 mixture of *E/Z*-isomers; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 0.19H'), 7.44 (m, 0.46H'), 7.41 – 7.36 (m, 3H), 7.31 – 7.24 (m, 2H), 7.09 (s, 1H), 6.39 (s, 0.08H'), 5.03 (d, *J* = 23.3 Hz, 0.20H'), 4.84 (d, *J* = 14.1 Hz, 2H), 4.64 (s, 0.19H'), 4.44 (s, 2H), 3.96 (s, 0.28H'), 3.83 (s, 3H), 1.82 (s, 0.28H'), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.28, 166.75, 164.93, 164.63, 149.01, 144.03, 139.56, 139.20, 133.86, 133.19, 130.66, 129.05, 128.95, 128.82, 128.62, 128.50, 127.89, 127.16, 126.78, 117.23, 113.66, 113.55, 68.39, 68.33, 52.94, 52.71, 19.56, 19.32; HRMS (ESI) calcd. for $C_{15}H_{17}O_4$ $[M+H]^+$ 261.11214, found: 261.11139.

(*E*)-1-Methyl 4-(prop-2-yn-1-yl) 2-phenylfumarate (**6f**):



The product was isolated as a 10: 1 mixture of *E/Z*-isomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 6.5, 1.6 Hz, 0.25H'), 7.46 – 7.42 (m, 0.40H'), 7.39 (dd, *J* = 6.4, 3.8 Hz, 3H), 7.25 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.04 (s, 1H), 6.35 (s, 0.08H'), 4.79 (d, *J* = 2.5 Hz, 0.19H'), 4.61 (d, *J* = 2.5 Hz, 2H), 3.96 (s, 0.3H'), 3.81 (s, 3H), 2.52 (t, *J* = 2.5 Hz, 0.09H'), 2.43 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.67, 165.84, 164.30, 164.16, 149.98, 145.49, 133.61, 132.25, 131.00, 129.23, 128.94, 128.90, 128.15, 128.01, 127.88, 126.96, 116.36, 77.08, 75.50, 75.30, 53.12, 52.93, 52.60, 52.35; HRMS (ESI) calcd. for $C_{15}H_{15}O_4$ $[M+H]^+$ 259.09649, found: 259.09604.

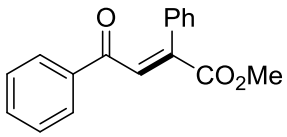
(*E*)-1-Methyl 4-(3-phenylprop-2-yn-1-yl) 2-phenylfumarate (**6g**):



Only *E*-isomer was isolated. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.38 – 7.35 (m, 3H), 7.35 – 7.31 (m, 3H), 7.29 – 7.25 (m, 2H), 7.08 (s, 1H), 4.85 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.73, 164.50, 145.19,

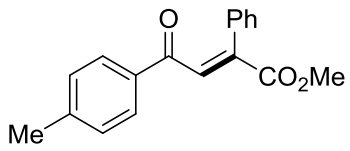
133.66, 132.00, 128.97, 128.87, 128.43, 128.18, 128.00, 122.17, 86.87, 82.37, 53.27, 53.10; HRMS (ESI) calcd. for $C_{21}H_{19}O_4$ $[M+H]^+$ 335.12779, found: 335.12698.

Methyl *(E)*-4-phenyl-4-oxo-2-phenylbut-2-enoate (**6h**):[1]



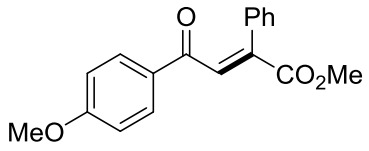
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.71 (s, 1H), 7.52 – 7.48 (m, 1H), 7.37 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.24 – 7.18 (m, 5H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.66, 167.13, 140.57, 136.55, 136.35, 133.84, 133.76, 129.51, 129.07, 128.71, 128.68, 128.05, 53.00; ESI-MS m/z 267.1 $(M+H)^+$.

Methyl *(E)*-4-(4- methylphenyl)-4-oxo-2-phenylbut-2-enoate (**6i**):



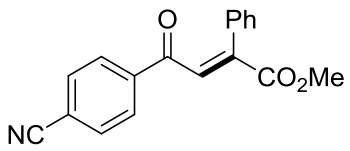
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.70 (s, 1H), 7.24 – 7.20 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.00, 167.29, 139.69, 137.81, 134.07, 129.40, 129.03, 128.33, 52.98, 41.23, 32.47, 27.53, 22.25; HRMS (ESI) calcd. for $C_{15}H_{17}O_4$ $[M+H]^+$ 281.11722, found: 281.11670.

Methyl *(E)*-4-(4-methoxyphenyl)-4-oxo-2-phenylbut-2-enoate (**6j**):[1]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.68 (s, 1H), 7.22 (s, 5H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.15, 167.22, 164.08, 139.65, 137.02, 133.96, 131.50, 129.46, 129.41, 128.60, 128.01, 113.93, 55.58, 52.92; ESI-MS m/z 297.1 $(M+H)^+$.

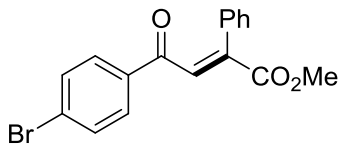
Methyl *(E)*-4-(4-cyanophenyl)-4-oxo-2-phenylbut-2-enoate (**6k**):



The product was isolated as a 6: 1 mixture of *E/Z*-isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 0.36H'), 7.83-7.78 (m, 2H, 0.52H'), 7.61-7.58 (m, 3H, 0.52H'), 7.45 (d, *J* = 7.4 Hz, 0.55H'), 7.30 (s, 0.22H'), 7.23 – 7.12 (m, 5H), 3.93 (s,

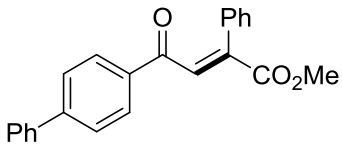
0.52H'), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.65, 187.59, 168.62, 166.67, 149.19, 142.04, 140.51, 139.23, 134.87, 133.39, 132.70, 132.37, 131.26, 129.53, 129.25, 129.19, 128.95, 128.17, 127.37, 121.12, 117.96, 117.87, 116.60, 116.56, 53.16, 52.95; HRMS (ESI) calcd. for $C_{18}H_{13}O_3NNa$ $[M+Na]^+$ 314.07876, found: 314.07800.

Methyl *(E)*-4-(4-bromophenyl)-4-oxo-2-phenylbut-2-enoate (**6l**):[1]



The product was isolated as a 7: 1 mixture of *E/Z*-isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H'), 7.65 (m, 2H, 2H'), 7.63 (s, 1H), 7.58 (m, 2H'), 7.48 (d, *J* = 8.5 Hz, 2H), 7.44 (m, 3H'), 7.30 (s, 1H'), 7.26 – 7.14 (m, 5H), 3.93 (s, 3H'), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.73, 187.91, 168.92, 166.92, 148.19, 140.93, 136.18, 135.80, 134.99, 133.94, 133.62, 132.19, 131.99, 130.93, 130.47, 130.11, 129.45, 129.19, 129.02, 128.90, 128.11, 127.30, 121.78, 53.05, 52.88; ESI-MS m/z 345.1 $(M(^{79}Br)+H)^+$; ESI-MS m/z 347.1 $(M(^{81}Br)+H)^+$.

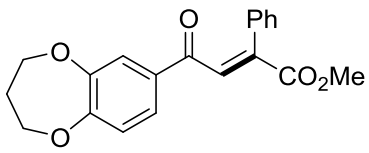
Methyl (*E*)-4-([1,1'-biphenyl]-4-yl)-4-oxo-2-phenylbut-2-enoate (**6m**):



The product was isolated as a 6: 1 mixture of *E/Z*-isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 0.39H'), 7.91 (d, *J* = 8.5 Hz, 2H), 7.81 – 7.77 (m, 0.24H'), 7.76 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 0.42H'), 7.65 (m, 0.58H'), 7.59 (m, 4H), 7.51 – 7.36 (m, 3H, 1.52H'), 7.25 (d, *J* = 4.9 Hz, 5H), 3.96 (s, 0.51H'), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.14, 188.46, 169.16, 167.15, 147.62, 146.37, 146.20, 140.50, 139.86, 139.76, 136.59, 136.17, 135.05, 134.19, 133.86, 132.25, 130.77, 129.67, 129.51, 129.27, 129.18, 129.10, 129.07, 128.95, 128.73, 128.49, 128.13, 128.07, 127.51, 127.41, 127.36, 127.31, 122.46, 53.01, 52.87; HRMS (ESI) calcd. for $C_{28}H_{19}O_3$ $[M+H]^+$ 343.13287, found: 343.13220.

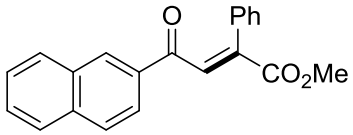
Methyl (*E*)-4-(3,4-dihydro-2H-benzo[*b*][1,4]dioxepin-7-yl)-4-oxo-2-phenylbut-2-enoate (**6n**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.46 – 7.39 (m, 2H), 7.27 – 7.16 (m, 5H),



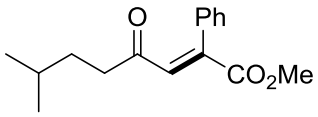
6.88 (d, *J* = 8.5 Hz, 1H), 4.27 (t, *J* = 5.7 Hz, 2H), 4.20 (t, *J* = 5.9 Hz, 2H), 3.84 (s, 3H), 2.23 – 2.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.21, 169.16, 155.75, 150.72, 147.22, 136.65, 134.21, 130.63, 129.80, 129.11, 127.21, 124.40, 122.43, 121.64, 70.49, 70.34, 52.79, 31.03; HRMS (ESI) calcd. for $C_{20}H_{19}O_5$ $[M+H]^+$ 3339.12270, found: 339.12184.

Methyl (*E*)-4-(naphthalen-2-yl)-4-oxo-2-phenylbut-2-enoate (**6o**):



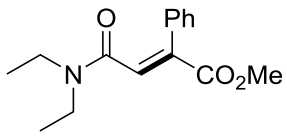
The product was isolated as a 14: 1 mixture of *E/Z*-isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 0.08H'), 8.36 (s, 1H), 8.09 (dd, *J* = 8.6, 1.6 Hz, 0.10H'), 7.98 (d, *J* = 8.2 Hz, 0.12H'), 7.95 – 7.87 (m, 2H, 0.24H'), 7.85 (s, 1H), 7.81 (t, *J* = 7.8 Hz, 2H), 7.65 (m, 0.24H'), 7.63 – 7.50 (m, 2H), 7.49 – 7.43 (m, 0.49H'), 7.29 – 7.23 (m, 2H), 7.23 – 7.17 (m, 3H, 0.24H'), 3.96 (s, 0.22H'), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.47, 188.82, 169.18, 167.18, 140.55, 136.76, 135.88, 135.80, 134.83, 134.22, 133.90, 133.70, 132.57, 132.40, 132.23, 131.71, 130.76, 130.45, 129.71, 129.42, 129.18, 128.96, 128.94, 128.70, 128.67, 128.11, 128.05, 127.96, 127.91, 127.32, 127.03, 126.96, 124.20, 123.87, 53.03, 52.86; HRMS (ESI) calcd. for $C_{21}H_{16}O_3Na$ $[M+Na]^+$ 339.09917, found: 339.09833.

Methyl (*E*)-7-methyl-4-oxo-2-phenyloct-2-enoate (**6p**):



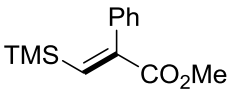
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.23 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.17 (s, 1H), 3.81 (s, 3H), 2.19 – 2.12 (m, 2H), 1.34 – 1.24 (m, 3H), 0.71 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.00, 167.29, 139.69, 137.81, 134.07, 129.40, 129.03, 128.33, 52.98, 41.23, 32.47, 27.53, 22.25; HRMS (ESI) calcd. for $C_{16}H_{21}O_3$ $[M+H]^+$ 261.14852, found: 261.14783.

Methyl (*E*)-4-(diethylamino)-4-oxo-2-phenylbut-2-enoate (**6q**):



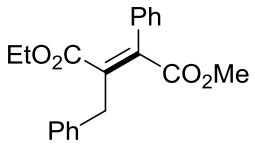
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 5H), 7.22 (s, 1H), 3.79 (s, 3H), 3.27 (q, *J* = 7.1 Hz, 2H), 3.06 (q, *J* = 7.2 Hz, 2H), 0.87 (dt, *J* = 11.0, 7.2 Hz, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.03, 166.09, 135.85, 134.21, 133.86, 129.26, 128.63, 128.07, 52.69, 42.25, 38.53, 13.93, 12.21; HRMS (ESI) calcd. for $C_{15}H_{20}O_3N$ $[M+H]^+$ 262.14377, found: 262.14349.

Methyl (*E*)-2-phenyl-3-(trimethylsilyl)acrylate (**6r**): [6]



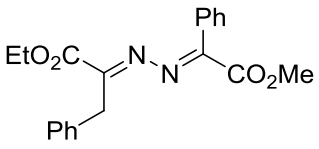
The product was isolated as a 3: 1 mixture of *E/Z*-isomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 3H, 0.59H'), 7.25 (s, 1H), 7.20 (m, 2H, 0.84H'), 6.47 (s, 0.31H'), 3.81 (s, 3H'), 3.74 (s, 3H), 0.21 (s, 2.87H'), -0.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.89, 167.39, 147.56, 145.78, 139.22, 138.37, 129.48, 129.06, 128.28, 127.87, 127.81, 127.33, 125.96, 124.09, 52.44, 51.91, -0.51, -0.64; ESI-MS m/z 235.2 $(M+H)^+$

(*E*)-1-Ethyl 4-methyl 2-benzyl-3-phenylfumarate (**8**):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 9H), 7.21 (t, *J* = 7.0 Hz, 1H), 3.94 (s, 2H), 3.77 (s, 3H), 3.77 – 3.72 (m, 2H), 0.71 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.36, 168.24, 138.89, 137.21, 136.96, 136.21, 129.14, 128.57, 128.43, 128.39, 128.28, 126.79, 60.90, 52.53, 37.81, 13.49; EI-MS (m/z, relative intensity): 324 (M^+, 1), 292 (32), 219 (24), 191 (100); HRMS (EI) calcd. for $C_{20}H_{20}O_4$ $[M]^+$ 324.1356, found: 324.1355.

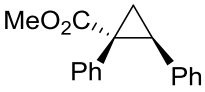
Ethyl (*E*)-2-(((*E*)-2-methoxy-2-oxo-1-phenylethylidene)hydrazono)-3-phenyl propanoate (**9**):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.25 (s, 1H), 7.19 (t, *J* = 6.2 Hz, 3H), 7.12 – 7.07 (m, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 2H), 3.83 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.50,

164.78, 163.97, 157.02, 135.50, 132.03, 129.81, 129.44, 129.02, 128.71, 128.28, 128.01, 62.06, 52.86, 34.33, 14.15; EI-MS (m/z, relative intensity): 352 (M^+, 5), 296 (52), 268 (44), 237 (47), 194 (62), 178 (94), 91 (100); HRMS (EI) calcd. for $C_{20}H_{20}O_4N_2$ $[M]^+$ 352.1418, found: 352.1418.

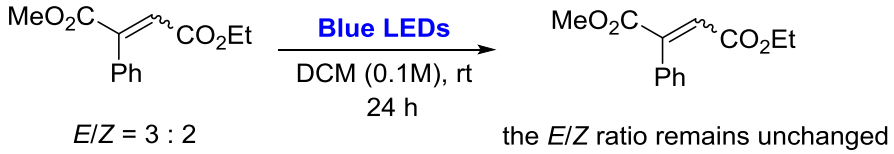
Methyl 1,2-diphenylcyclopropane-1-carboxylate (**10**):[7]



^{1}H NMR (400 MHz, CDCl3) δ 7.30 (t, J = 7.8 Hz, 1H), 7.15 – 7.12 (m, 2H), 7.09 – 6.98 (m, 5H), 6.77 (dd, J = 6.6, 2.8 Hz, 2H), 3.67 (s, 3H), 3.12 (dd, J = 9.2, 7.4 Hz, 1H), 2.14 (dd, J = 9.3, 4.9 Hz, 1H), 1.89 (dd, J = 7.3, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32, 136.30, 134.68, 131.89, 129.22, 128.55, 128.00, 127.64, 126.98, 126.26, 52.60, 37.36, 33.10, 20.45; ESI-MS m/z 253.1 $(M+H)^+$.

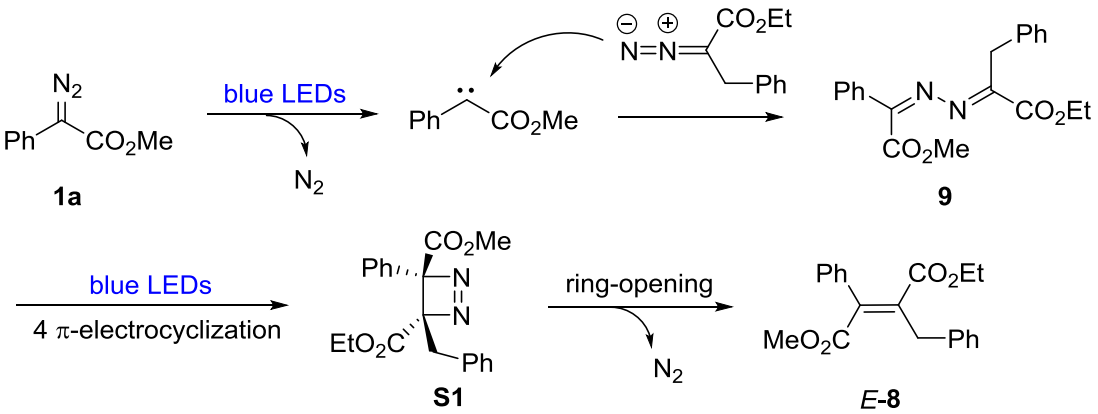
Control experiments and mechanism study

Visible light promoted photocatalytic *E* → *Z* isomerization of alkenes has been extensively studied.[8] In this work, only *E*-trisubstituted alkenes were obtained. To exclude that the high *E*/*Z* selectivity was produced by the photocatalytic isomerization of alkenes, a 3:2 mixture of *E*-**4a** and *Z*-**4a** was subjected to the same blue LEDs irradiation. We found that the ratio of two isomers remained unchanged after 24 hours. Based on this result, we concluded that the conversion of *Z*-isomers to *E*-isomers upon blue light irradiation is less likely.



Scheme S1 Photocatalytic isomerization reaction.

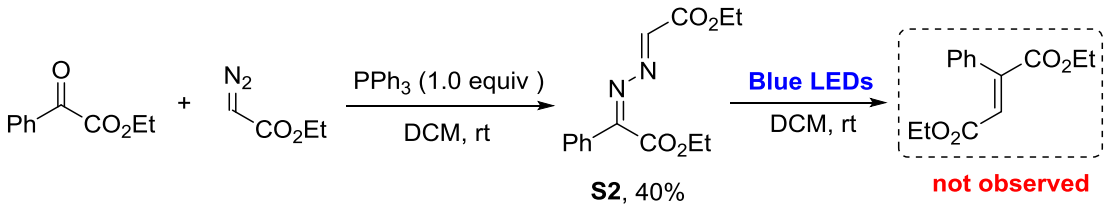
In the dimerization of phenyldiazoacetate **1a** with donor/acceptor diazo compound **7**, except the desired tetrasubstituted alkene **8**, azine **9** was isolated as a side product in 32% yield. Therefore, an alternative mechanism involves blue light-promoted 4π electrocyclization of azine **9** into diazacyclobutene **S1** and subsequent ring-opening of **SA** with the extrusion of N_2 was proposed.



Scheme S2 An alternative pathway.

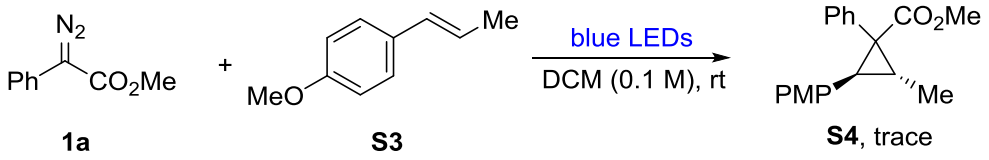
However, a literature survey by Scifinder indicates that the 4π electrocyclization of azine into diazacyclobutene has never been reported. To rule out this mechanism,

azine **S2** were prepared according to the reported method (^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 –7.83 (m, 2H), 7.79 (s, 1H), 7.55 – 7.53 (m, 1H), 7.50 – 7.46 (m, 2H), 4,48 (q, *J* = 8.0 Hz, 2H), 4,38 (q, *J* = 8.0 Hz, 2H), 1,43 (t, *J* = 8.0 Hz, 3H), 1.39 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ164.15, 162.56, 161.55, 150.31, 132.37, 130.82, 128.92, 128.04, 62.01, 61.83, 14.24, 14.07).[9] Subsequently, the isolated azine **S2** was irradiated with blue light for 24 hours; none of desired alkene product was observed and 95% NMR yield of **S2** was remained unreactive(Scheme S3).



Scheme 3 Synthesis of azine **S2** and its subsequent reaction under the blue light irradiation.

The photolysis of phenyl diazoacetate **1a** would generate highly reactive singlet free carbene. However, inter system crossing (ISC) converting singlet free carbene to triplet free carbene is generally a fast process. To examine whether singlet or triplet free carbene was involved in the present cross-coupling reaction of diazo compounds, we attempted to trap the free carbene using anethole **S3**. Although the cyclopropanation of **1a** with styrene under blue light irradiation is effective (Scheme 2, Eq. 4 in the main text), the similar reaction of **1a** and **S3** only gave trace amount of desired cyclopropane **S4** (Scheme S4).



Scheme S4 Blue light-promoted cyclopropanation of **1a** and anethole **S3**.

Triplet free carbene possesses the property of diradical. Styrene is a well-known radical acceptor, while the radical addition to diazo compounds is difficult, especially

in the absence of transition metal. As shown in the Scheme 2 in the main text, when 1:1:1 mixture of **1a**, **2a** and styrene was subjected to the optimized conditions, *E*-alkene **4a** as the major product along with 21% yield of cyclopropanation product **10**. If a triplet carbene is the key intermediate, cyclopropane **10** should be the major product. Moreover, the competitive reaction (Scheme 1, Eq. 3 in the main text) suggested that the nucleophilicity of diazo compounds affected the efficiency of the cross-coupling. These experimental results support that the reaction proceeds through singlet free carbene. We speculated that the inter system crossing converting singlet carbene to triplet carbene might be a reversible event, as demonstrated by Davies in his recent report.[10]

DFT calculations

Computational details All the calculations were carried out with the Gaussian 09 package.[11] The geometry were optimized using B3LYP[12]/6-311++G(d,p)[13] level using SMD[14] salvation model (solvent= dichloromethane). The frequnecy analysis was conducted at the same level of theory to verify the stationary points to be real minima or saddle points and to obtain the thermodynamic energy corrections. All transition states had a single imaginary frequency in the optimization in solvent phase. The connectivity between the reactant/product and transition state were confirmed by intrinsic reaction coordinate (IRC)[15] calculation.

Initially, we calculated the optimal structure of singlet free carbene **A** and found that the plane of carbonyl group is almost vertical to the phenyl group (Figure S1).

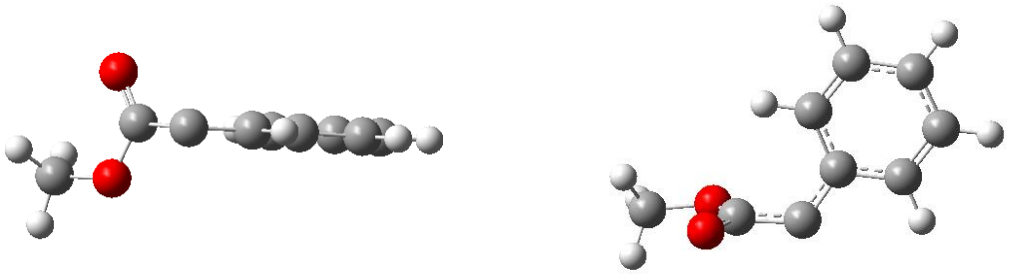


Figure S1. The optimal of structure of singlet free carbene **A**

Next, we scanned the transition structures for the reaction of singlet free carbene **A** with methyl diazoacetate. Eight transition structures for the formation of *E*-configured alkene **4a'** and four for *Z*-alkene **4a'** were obtained, and their corresponding Gibbs free energies were given in the Figure S2. We attempted to find other transition structures leading to *Z*-**4a'**. However, we found that they would be automatically optimized to the corresponding transition structures for the formation of *E*-**4a'**. The four most stable structures (**TS-E1**, **TS-E1b**, **TS-E2**, **TS-E2b**) indicated that the largest substituent (methyl ester) prefers to be oriented adjacent to the diazonium moiety (medium bulk) and hydrogen (small), while the conformations with two ester groups close to each other are less stable.

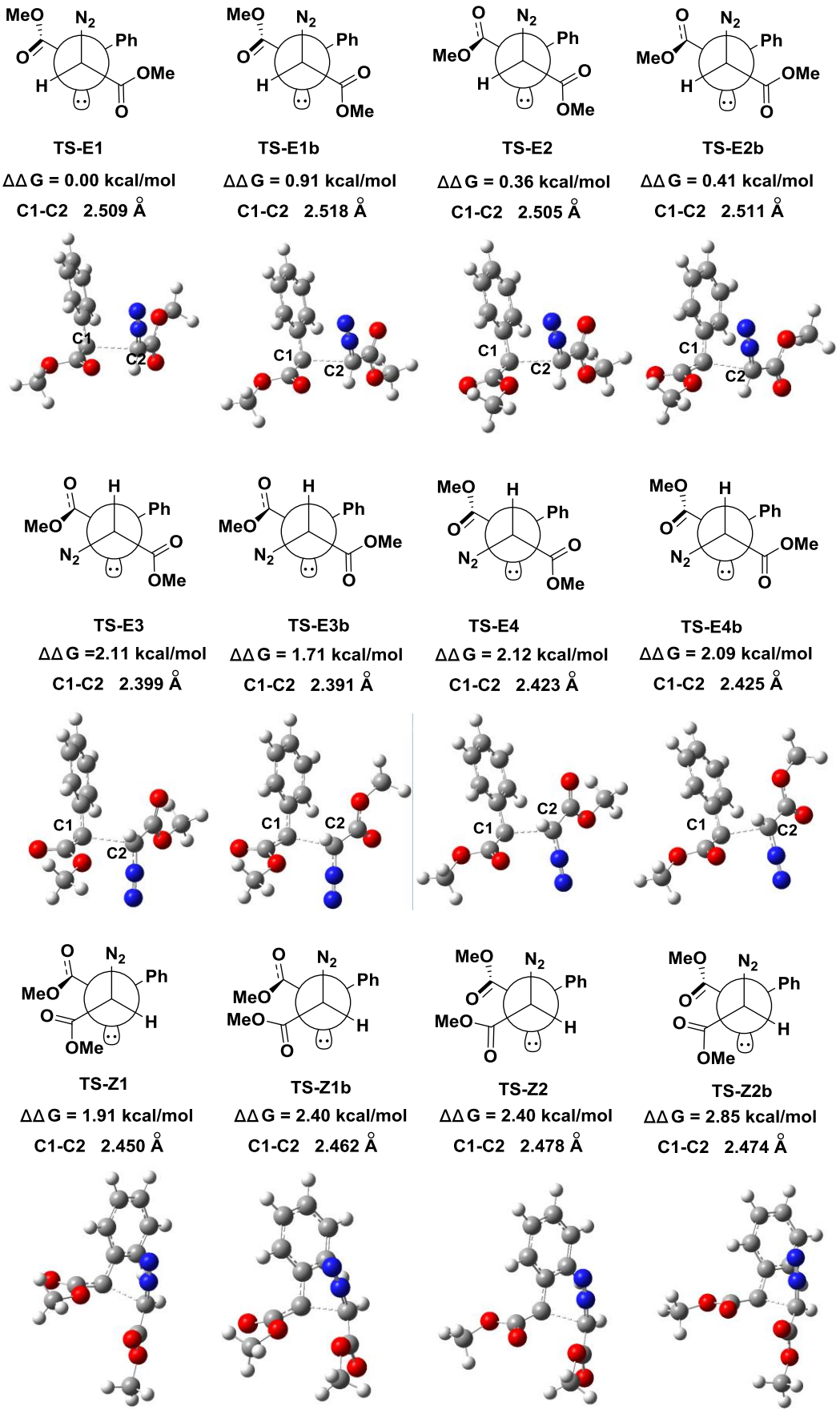


Figure S2. The structures and Gibbs free energies of transition structures

Table S1. The prediction of the ***E/Z*** selectivity by the calculation of distribution ratio of transition structures using Boltzmann formula.[a]

$$p_i = \frac{e^{-\Delta E_i / RT}}{\sum_j e^{-\Delta E_j / RT}} = \frac{Q_{i\,(\mathrm{Relat})}}{Q_{(\mathrm{Relat})}}$$

Index	DeltaG	Qi(Relat)	Distribution ratio
E1	0.00	1	0.402643643
E1b	0.91	0.215043897	0.086586058
E2	0.36	0.544433444	0.219212665
E2b	0.41	0.500346034	0.20146115
E3	2.11	0.028336298	0.01140943
E3b	1.71	0.055684943	0.022421188
E4	2.12	0.02786174	0.011218353
E4b	2.09	0.029309799	0.011801404
Z1	1.91	0.039722854	0.015994155
Z1b	2.40	0.017363288	0.006991218
Z2	2.40	0.017363288	0.006991218
Z2b	2.85	0.00812013	0.003269519

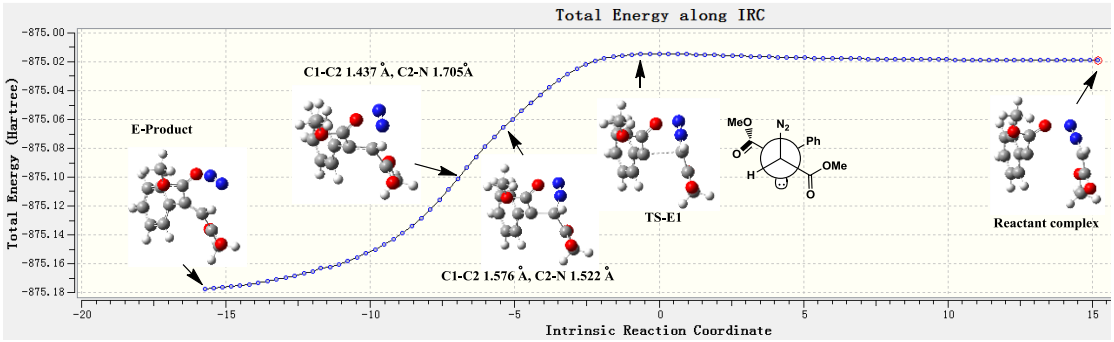
[a] Temperature: 298.15 K; Q(Relat): 2.483585714.

The predicted stereoselection of trisubstituted alkene **4a'** is 29.1:1, which is close to the experimental result of > 20:1.

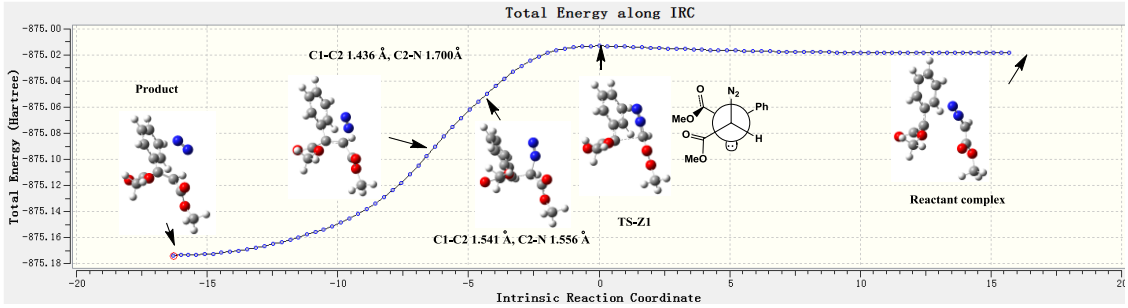
Intrinsic reaction coordinate (IRC) calculation

The connectivity between the reactant/product and transition state were confirmed by IRC calculation. We found the energy barrier for the extrusion of N_2 is almost zero no matter which conformational isomerism was assigned to intermediate **B**. The IRC calculations of three representative transition structures **TS-E1**, **TS-Z1**, and **TS-E3** were given in the Figure S3.

a) IRC of **TS-E1**



b) IRC of **TS-Z1**



c) IRC of **TS-E3**

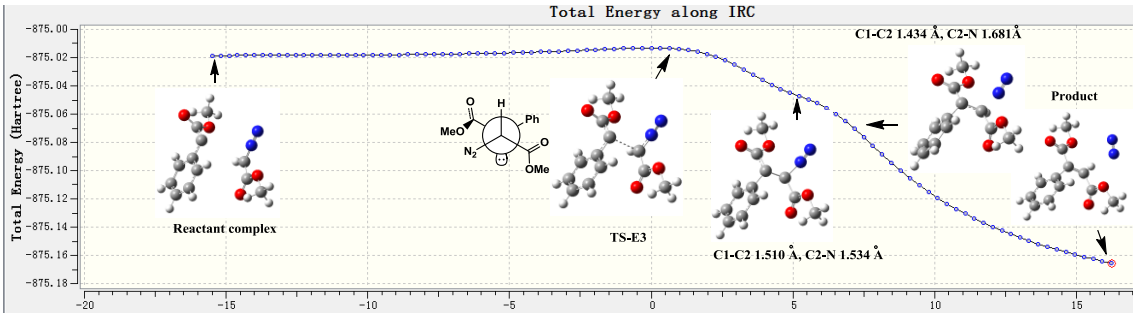
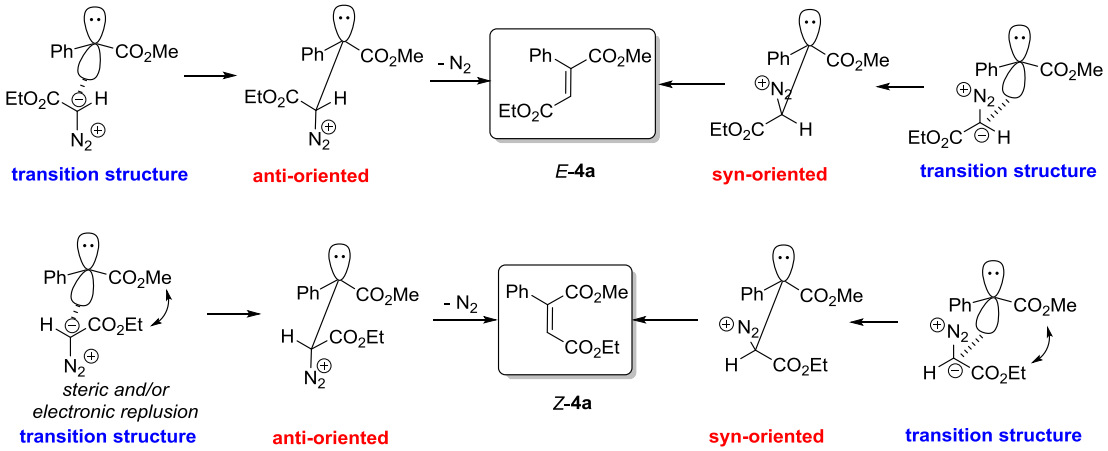


Figure S3. The IRC calculations of three representative transition structures

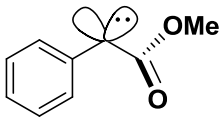
Therefore, the *E/Z* selectivity is determined by the energy barrier for the formation of transition structures TS-1 or TS-2, while the rotation of σ-bond of intermediate **B** has limited effects. Although we are not sure that the elimination of intermediate **B** was occurred through anti-periplanar conformation or syn-periplanar conformation, *E*-isomer is the major product from both conformations (Scheme S5).



Scheme S5. The formation of *E*-**4a** from anti-periplanar conformation or syn-periplanar conformation.

Energies and Thermal correction (in Hartrees) and Coordinate of the structures:

1. Carbene



Sum of electronic and thermal Free Energies = - 498.164729

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.537713	-1.109324	0.034343
2	6	0	-1.746577	-0.378940	0.295497
3	8	0	-2.172588	-0.250293	1.439176
4	8	0	-2.408108	0.016002	-0.807913
5	6	0	0.721694	-0.471833	0.014695
6	6	0	0.906392	0.932848	0.190527
7	6	0	1.874377	-1.277558	-0.211087
8	6	0	2.170576	1.488698	0.143445
9	1	0	0.043900	1.565032	0.368487
10	6	0	3.137332	-0.713035	-0.267076
11	1	0	1.733561	-2.344054	-0.340609
12	6	0	3.282298	0.666310	-0.087671
13	1	0	2.307102	2.554956	0.280204
14	1	0	4.009326	-1.331064	-0.444530
15	1	0	4.271825	1.108748	-0.126722
16	6	0	-3.733197	0.565943	-0.615716
17	1	0	-3.688565	1.486618	-0.032596

18	1	0	-4.103486	0.774372	-1.617436
19	1	0	-4.379194	-0.158936	-0.118640

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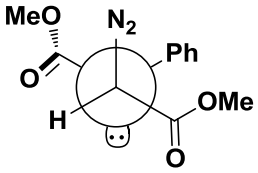
2. TS-E1



Sum of electronic and thermal Free Energies = - 874.841162

Imaginary frequency: -161.9681

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1	6	0	-0.878168	-0.328747	-0.792511
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3	8	0	-2.143275	-1.791560	0.632690
4	8	0	-3.167583	-0.466106	-0.897279
5	6	0	-0.490244	0.995970	-0.421200
6	6	0	-1.105391	1.726029	0.633343
7	6	0	0.542386	1.633611	-1.159248
8	6	0	-0.720740	3.028803	0.914777
9	1	0	-1.892414	1.260739	1.216217
10	6	0	0.922061	2.934953	-0.875401
11	1	0	1.013325	1.081571	-1.964237
12	6	0	0.289789	3.631759	0.161051
13	1	0	-1.202260	3.578854	1.715106
14	1	0	1.701729	3.416564	-1.454194
15	1	0	0.585632	4.652014	0.380377
16	6	0	-4.421179	-1.123766	-0.612778
17	1	0	-4.703632	-0.985974	0.432156

18	1	0	-5.150290	-0.644449	-1.263631
19	1	0	-4.358854	-2.189176	-0.840977
20	6	0	0.782752	-1.754621	0.433303
21	1	0	0.130638	-2.592794	0.246349
22	7	0	0.643686	-1.171955	1.607010
23	7	0	0.489286	-0.602482	2.564644
24	6	0	2.044535	-1.589444	-0.293167
25	8	0	2.323386	-2.228350	-1.285283
26	8	0	2.829918	-0.648143	0.257707
27	6	0	4.103542	-0.409753	-0.385170
28	1	0	3.956095	-0.102052	-1.420575
29	1	0	4.566708	0.391454	0.186479
30	1	0	4.720591	-1.308331	-0.345987

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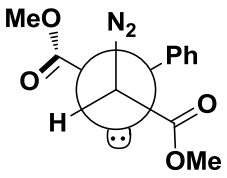
3. TS-E1b



Sum of electronic and thermal Free Energies = - 874.839727

Imaginary frequency: -149.4524

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3	8	0	-1.410042	-2.252327	0.789526
4	8	0	-2.616583	-1.572910	-1.007302
5	6	0	-0.771861	0.845920	-0.481835

6	6	0	-1.773403	1.379165	0.377277
7	6	0	0.064496	1.760591	-1.177135
8	6	0	-1.943026	2.749467	0.507963
9	1	0	-2.420313	0.702935	0.924679
10	6	0	-0.106395	3.128016	-1.040138
11	1	0	0.830186	1.361639	-1.831478
12	6	0	-1.110772	3.621302	-0.199456
13	1	0	-2.715864	3.144135	1.157518
14	1	0	0.531181	3.816263	-1.582785
15	1	0	-1.245312	4.692640	-0.096150
16	6	0	-3.561197	-2.637104	-0.761888
17	1	0	-4.024834	-2.527382	0.219724
18	1	0	-4.312895	-2.540314	-1.543355
19	1	0	-3.071686	-3.609840	-0.832614
20	6	0	1.282357	-1.077239	0.914341
21	1	0	0.996685	-2.115761	0.857782
22	7	0	0.781365	-0.397235	1.923812
23	7	0	0.305794	0.237385	2.721092
24	6	0	2.470582	-0.504811	0.276336
25	8	0	2.908891	0.608043	0.491141
26	8	0	2.994669	-1.382332	-0.590012
27	6	0	4.157220	-0.944184	-1.329480
28	1	0	4.977457	-0.713446	-0.648551
29	1	0	4.421419	-1.783745	-1.968865
30	1	0	3.916057	-0.069730	-1.935055

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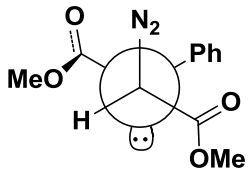
4. TS-E2



Sum of electronic and thermal Free Energies = - 874.840584

Imaginary frequency: -145.4618

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3	8	0	-2.741874	-0.844572	-1.671643
4	8	0	-1.892270	-1.992540	0.089982
5	6	0	-0.585195	1.094972	-0.559970
6	6	0	-1.575023	1.675925	0.278915
7	6	0	0.480067	1.920526	-1.002722
8	6	0	-1.506457	3.013530	0.638939
9	1	0	-2.401376	1.066510	0.627852
10	6	0	0.544493	3.257103	-0.641121
11	1	0	1.235847	1.484882	-1.645308
12	6	0	-0.448028	3.802792	0.179408
13	1	0	-2.270654	3.447127	1.273929
14	1	0	1.358502	3.879815	-0.993940
15	1	0	-0.397604	4.849290	0.460158
16	6	0	-3.062023	-2.843585	0.079808
17	1	0	-3.129636	-3.393210	-0.860139
18	1	0	-2.920247	-3.534190	0.909054
19	1	0	-3.968146	-2.255842	0.231258
20	6	0	0.874560	-1.377765	0.689332
21	1	0	0.509498	-2.339276	0.365129

22	7	0	0.311100	-0.877852	1.770368
23	7	0	-0.193278	-0.376649	2.641133
24	6	0	2.202947	-0.851390	0.360032
25	8	0	2.715421	0.118171	0.882712
26	8	0	2.763417	-1.588547	-0.607705
27	6	0	4.074695	-1.174182	-1.055868
28	1	0	4.787364	-1.208799	-0.230790
29	1	0	4.351720	-1.889961	-1.826554
30	1	0	4.033778	-0.166866	-1.471493

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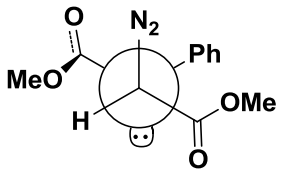
5. TS-E2b



Sum of electronic and thermal Free Energies = - 874.840509

Imaginary frequency: -154.2541

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.874049	0.133802	-1.008781
2	6	0	-2.280015	0.061319	-0.706824
3	8	0	-3.049719	0.810017	-1.306485
4	8	0	-2.704262	-0.917298	0.122465
5	6	0	-0.081185	1.217114	-0.506952
6	6	0	-0.497677	2.068607	0.551840
7	6	0	1.178659	1.469304	-1.108133
8	6	0	0.299562	3.124083	0.970602

9	1	0	-1.457429	1.898423	1.027051
10	6	0	1.971063	2.526153	-0.688592
11	1	0	1.497824	0.826073	-1.919834
12	6	0	1.531161	3.353071	0.350496
13	1	0	-0.031430	3.771665	1.774519
14	1	0	2.924711	2.717422	-1.167109
15	1	0	2.149954	4.182485	0.675755
16	6	0	-4.135575	-1.096840	0.226052
17	1	0	-4.558874	-1.362251	-0.743779
18	1	0	-4.271237	-1.915380	0.930550
19	1	0	-4.613400	-0.192642	0.604809
20	6	0	0.042740	-1.821345	0.273119
21	1	0	-0.797495	-2.407443	-0.063141
22	7	0	-0.067004	-1.293895	1.476194
23	7	0	-0.161222	-0.766035	2.465119
24	6	0	1.381782	-2.020830	-0.289441
25	8	0	1.585673	-2.660133	-1.299064
26	8	0	2.331624	-1.403023	0.432122
27	6	0	3.691916	-1.528943	-0.042335
28	1	0	3.779004	-1.148262	-1.060070
29	1	0	4.289882	-0.928188	0.639388
30	1	0	4.009249	-2.571864	-0.005936

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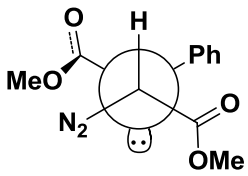
6. TS-E3



Sum of electronic and thermal Free Energies= - 874.837793

Imaginary frequency: -176.7793

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.675245	-0.509594	-0.740449
2	6	0	1.986649	-1.002952	-0.414200
3	8	0	2.408609	-2.003389	-0.994227
4	8	0	2.766253	-0.254326	0.403493
5	6	0	-0.498686	-1.264897	-0.383054
6	6	0	-0.505558	-2.274032	0.613244
7	6	0	-1.702988	-1.014552	-1.082752
8	6	0	-1.655576	-2.999996	0.883462
9	1	0	0.404494	-2.479851	1.166114
10	6	0	-2.853765	-1.742933	-0.811763
11	1	0	-1.703437	-0.249570	-1.850784
12	6	0	-2.830178	-2.735172	0.170788
13	1	0	-1.646841	-3.771226	1.645594
14	1	0	-3.766511	-1.546269	-1.362653
15	1	0	-3.728272	-3.305135	0.383263
16	6	0	4.151889	-0.649156	0.507468
17	1	0	4.645947	-0.577343	-0.462804
18	1	0	4.598628	0.054101	1.208200
19	1	0	4.237960	-1.666097	0.892322
20	6	0	0.499446	1.426323	0.664628
21	1	0	0.928372	0.924884	1.518986
22	7	0	1.349408	2.172315	-0.029776
23	7	0	2.055687	2.744380	-0.682273
24	6	0	-0.911519	1.833596	0.678193
25	8	0	-1.714040	1.386502	1.469074

26	8	0	-1.195517	2.720666	-0.287368
27	6	0	-2.565007	3.181820	-0.366181
28	1	0	-2.862831	3.648452	0.573207
29	1	0	-2.573521	3.913288	-1.171164
30	1	0	-3.231806	2.351557	-0.600009

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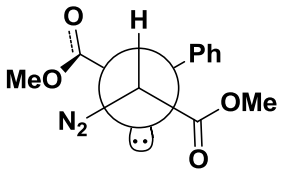
7. TS-E3b



Sum of electronic and thermal Free Energies = - 874.838439

Imaginary frequency: -187.9395

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.729478	-0.580035	-0.753652
2	6	0	1.925303	-1.189024	-0.236243
3	8	0	2.262593	-2.295276	-0.657751
4	8	0	2.715115	-0.450454	0.581192
5	6	0	-0.564784	-1.136130	-0.448254
6	6	0	-0.793334	-2.041386	0.618790
7	6	0	-1.661019	-0.795512	-1.276231
8	6	0	-2.050202	-2.586733	0.833545
9	1	0	0.029747	-2.316130	1.269062
10	6	0	-2.920548	-1.337071	-1.055565
11	1	0	-1.492854	-0.110959	-2.099714
12	6	0	-3.115213	-2.233732	-0.002141

13	1	0	-2.209018	-3.284023	1.648477
14	1	0	-3.748440	-1.072908	-1.703662
15	1	0	-4.097220	-2.662114	0.167318
16	6	0	4.016321	-0.999707	0.884816
17	1	0	4.602829	-1.127759	-0.026251
18	1	0	4.490882	-0.268504	1.537007
19	1	0	3.922182	-1.955759	1.401707
20	6	0	0.696121	1.525540	0.378855
21	1	0	0.993483	1.109086	1.329913
22	7	0	1.684457	2.057856	-0.329346
23	7	0	2.497360	2.442351	-0.993468
24	6	0	-0.622028	2.136968	0.152789
25	8	0	-0.901642	2.869800	-0.773654
26	8	0	-1.473967	1.748078	1.109748
27	6	0	-2.826047	2.254668	1.011318
28	1	0	-3.368666	1.780431	1.825911
29	1	0	-2.830143	3.338671	1.133396
30	1	0	-3.266573	1.984259	0.052081

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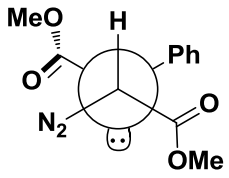
8. TS-E4



Sum of electronic and thermal Free Energies = - 874.837785

Imaginary frequency: -177.2610

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.792618	-0.287708	-0.564084
2	6	0	-1.934012	-0.984340	-0.003995
3	8	0	-1.939217	-1.916032	0.793033
4	8	0	-3.068981	-0.551493	-0.623503
5	6	0	-0.573956	1.103816	-0.287424
6	6	0	-1.278951	1.824231	0.712239
7	6	0	0.357153	1.814229	-1.085832
8	6	0	-1.076185	3.184423	0.885909
9	1	0	-1.988616	1.300663	1.343301
10	6	0	0.558794	3.175600	-0.910084
11	1	0	0.898097	1.271149	-1.852383
12	6	0	-0.158156	3.860368	0.074719
13	1	0	-1.625163	3.724663	1.648841
14	1	0	1.266490	3.708197	-1.534975
15	1	0	-0.001899	4.924882	0.212127
16	6	0	-4.263002	-1.329238	-0.396418
17	1	0	-4.526844	-1.336509	0.662153
18	1	0	-5.042137	-0.833494	-0.973115
19	1	0	-4.131166	-2.353670	-0.749850
20	6	0	0.906453	-1.389837	0.766714
21	1	0	0.305499	-1.308349	1.659042
22	7	0	0.804503	-2.546130	0.126585
23	7	0	0.680662	-3.479008	-0.479088
24	6	0	2.151775	-0.630794	0.622658
25	8	0	2.432607	0.308752	1.336509
26	8	0	2.909237	-1.077232	-0.392124
27	6	0	4.164392	-0.392859	-0.615804
28	1	0	4.804756	-0.481077	0.262630
29	1	0	4.617790	-0.897577	-1.466075

30	1	0	3.987749	0.657790	-0.847079

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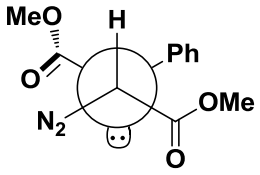
9. TS-E4b



Sum of electronic and thermal Free Energies = - 874.837840

Imaginary frequency: -181.6798

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.941374	0.041045	0.592005
2	6	0	2.188242	-0.073535	-0.135237
3	8	0	2.532995	-0.948535	-0.922259
4	8	0	3.050910	0.884963	0.309489
5	6	0	0.048321	1.143085	0.371543
6	6	0	0.159701	2.037763	-0.724746
7	6	0	-0.974218	1.380796	1.323853
8	6	0	-0.698040	3.119837	-0.848982
9	1	0	0.928737	1.870757	-1.470956
10	6	0	-1.829736	2.465922	1.198742
11	1	0	-1.062180	0.701971	2.164199
12	6	0	-1.691960	3.334302	0.112507
13	1	0	-0.600964	3.799962	-1.687598
14	1	0	-2.599371	2.642591	1.941236
15	1	0	-2.359725	4.183353	0.014280
16	6	0	4.438717	0.715893	-0.047032
17	1	0	4.571157	0.761082	-1.129031

18	1	0	4.961283	1.543765	0.429301
19	1	0	4.821120	-0.234417	0.330440
20	6	0	-0.195323	-1.815596	-0.475185
21	1	0	0.194690	-1.540292	-1.443090
22	7	0	0.505968	-2.735432	0.170832
23	7	0	1.111126	-3.452323	0.779781
24	6	0	-1.618046	-1.750986	-0.122201
25	8	0	-2.126108	-2.291601	0.839434
26	8	0	-2.272162	-0.986370	-1.007680
27	6	0	-3.693519	-0.824446	-0.792625
28	1	0	-3.887207	-0.401621	0.193077
29	1	0	-4.023996	-0.140311	-1.570964
30	1	0	-4.201365	-1.784700	-0.892914

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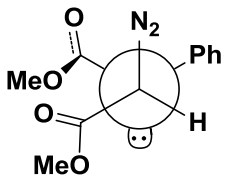
10. TS-Z1



Sum of electronic and thermal Free Energies = - 874.838114

Imaginary frequency: -189.3233

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.380093	0.262333	-0.978108
2	6	0	-0.128401	1.586010	-0.720003
3	8	0	0.226290	2.509608	-1.451301
4	8	0	-1.058882	1.720435	0.242608

5	6	0	1.723257	-0.071068	-0.581430
6	6	0	2.501516	0.734281	0.290642
7	6	0	2.310575	-1.255637	-1.092928
8	6	0	3.802781	0.377933	0.618451
9	1	0	2.077659	1.646998	0.694430
10	6	0	3.606270	-1.614472	-0.755417
11	1	0	1.724609	-1.873314	-1.764273
12	6	0	4.353529	-0.796419	0.099268
13	1	0	4.389650	1.006923	1.278242
14	1	0	4.044660	-2.520253	-1.158558
15	1	0	5.369422	-1.074510	0.358315
16	6	0	-1.692619	3.013528	0.357546
17	1	0	-2.215564	3.268493	-0.565599
18	1	0	-2.403775	2.912530	1.175041
19	1	0	-0.957784	3.785313	0.590976
20	6	0	-0.886467	-1.237555	0.487646
21	1	0	-0.359925	-2.047281	0.005629
22	7	0	-0.396197	-0.868092	1.658243
23	7	0	0.064934	-0.480319	2.606377
24	6	0	-2.335495	-1.036493	0.310311
25	8	0	-3.073112	-0.496937	1.107410
26	8	0	-2.721610	-1.553656	-0.863644
27	6	0	-4.126128	-1.437075	-1.186707
28	1	0	-4.419738	-0.387934	-1.231836
29	1	0	-4.233997	-1.902958	-2.163855
30	1	0	-4.731343	-1.962919	-0.447056

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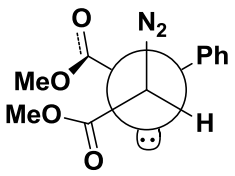
11. TS-Z1b



Sum of electronic and thermal Free Energies = - 874.837344

Imaginary frequency: -178.0855

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.521138	0.487232	-1.023493
2	6	0	-0.153995	1.660281	-0.531330
3	8	0	0.199488	2.764407	-0.942790
4	8	0	-1.221976	1.476874	0.269219
5	6	0	1.821025	0.143186	-0.514271
6	6	0	2.385488	0.734397	0.646548
7	6	0	2.588236	-0.828907	-1.205237
8	6	0	3.657220	0.383101	1.078835
9	1	0	1.820194	1.481687	1.192114
10	6	0	3.852918	-1.185691	-0.764651
11	1	0	2.165316	-1.282604	-2.094501
12	6	0	4.388703	-0.577711	0.376446
13	1	0	4.081107	0.849750	1.960818
14	1	0	4.430841	-1.926407	-1.305370
15	1	0	5.381244	-0.853143	0.716293
16	6	0	-2.003396	2.649934	0.584911
17	1	0	-2.473377	3.049919	-0.315295
18	1	0	-2.763411	2.309532	1.285663
19	1	0	-1.382989	3.416922	1.050012
20	6	0	-0.770554	-1.441648	-0.203334

21	1	0	-0.147532	-2.034414	-0.855003
22	7	0	-0.404297	-1.426376	1.065725
23	7	0	-0.036121	-1.328403	2.123751
24	6	0	-2.189581	-1.235652	-0.530910
25	8	0	-2.613495	-1.296459	-1.664751
26	8	0	-2.937737	-0.993891	0.555386
27	6	0	-4.333479	-0.698480	0.325822
28	1	0	-4.834100	-1.553102	-0.131206
29	1	0	-4.750543	-0.501355	1.311074
30	1	0	-4.436389	0.178970	-0.313446

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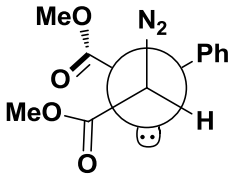
12. TS-Z2



Sum of electronic and thermal Free Energies = - 874.836766

Imaginary frequency: -179.1476

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.423421	0.593991	-0.905788
2	6	0	-0.286213	1.590734	-0.129025
3	8	0	-1.324512	1.449207	0.500450
4	8	0	0.307295	2.805083	-0.305349
5	6	0	1.676339	0.076057	-0.442489
6	6	0	2.201553	0.339120	0.851569

7	6	0	2.451102	-0.724759	-1.323097
8	6	0	3.447682	-0.144242	1.227786
9	1	0	1.626106	0.938447	1.548172
10	6	0	3.690229	-1.211693	-0.941271
11	1	0	2.057010	-0.933594	-2.311226
12	6	0	4.190085	-0.918188	0.333479
13	1	0	3.841933	0.075232	2.213422
14	1	0	4.277055	-1.811192	-1.627720
15	1	0	5.163270	-1.295240	0.628706
16	6	0	-0.426501	3.954570	0.167813
17	1	0	-0.594545	3.894832	1.244202
18	1	0	0.201852	4.812423	-0.065721
19	1	0	-1.383344	4.039768	-0.350871
20	6	0	-0.988946	-1.419667	-0.601768
21	1	0	-0.529216	-1.786588	-1.506575
22	7	0	-0.454226	-1.859876	0.521769
23	7	0	0.072486	-2.139621	1.475788
24	6	0	-2.409234	-1.030960	-0.600269
25	8	0	-2.992827	-0.686747	-1.605086
26	8	0	-2.964726	-1.138764	0.613725
27	6	0	-4.334998	-0.700274	0.738468
28	1	0	-4.985898	-1.297262	0.098295
29	1	0	-4.591570	-0.854258	1.784560
30	1	0	-4.419418	0.355540	0.479491

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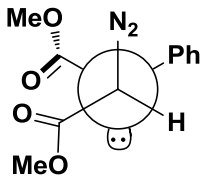
13. TS-Z2b



Sum of electronic and thermal Free Energies = - 874.836624

Imaginary frequency: -177.8264

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.283073	0.528022	0.797432
2	6	0	0.301715	1.572192	-0.021216
3	8	0	1.192850	1.461690	-0.850086
4	8	0	-0.202251	2.778629	0.363003
5	6	0	-1.604367	0.050839	0.514022
6	6	0	-2.333814	0.408140	-0.652050
7	6	0	-2.233713	-0.805821	1.455129
8	6	0	-3.633545	-0.040694	-0.845153
9	1	0	-1.871426	1.050804	-1.392961
10	6	0	-3.527822	-1.257062	1.255880
11	1	0	-1.682197	-1.085447	2.345615
12	6	0	-4.228908	-0.871397	0.106660
13	1	0	-4.184014	0.248683	-1.733051
14	1	0	-4.001709	-1.899936	1.988706
15	1	0	-5.244499	-1.220657	-0.045099
16	6	0	0.413368	3.948068	-0.216681
17	1	0	0.271026	3.965625	-1.298484
18	1	0	-0.094098	4.795830	0.240489
19	1	0	1.479416	3.980230	0.014217

20	6	0	1.013749	-1.470219	0.127884
21	1	0	0.664520	-1.880002	1.063457
22	7	0	0.315836	-1.818393	-0.936255
23	7	0	-0.337902	-2.018241	-1.828924
24	6	0	2.431834	-1.147457	-0.113435
25	8	0	2.979024	-1.162846	-1.194734
26	8	0	3.032733	-0.861786	1.049141
27	6	0	4.432641	-0.508464	0.975826
28	1	0	4.562939	0.395540	0.379881
29	1	0	4.736918	-0.329925	2.004872
30	1	0	5.010331	-1.326675	0.544227

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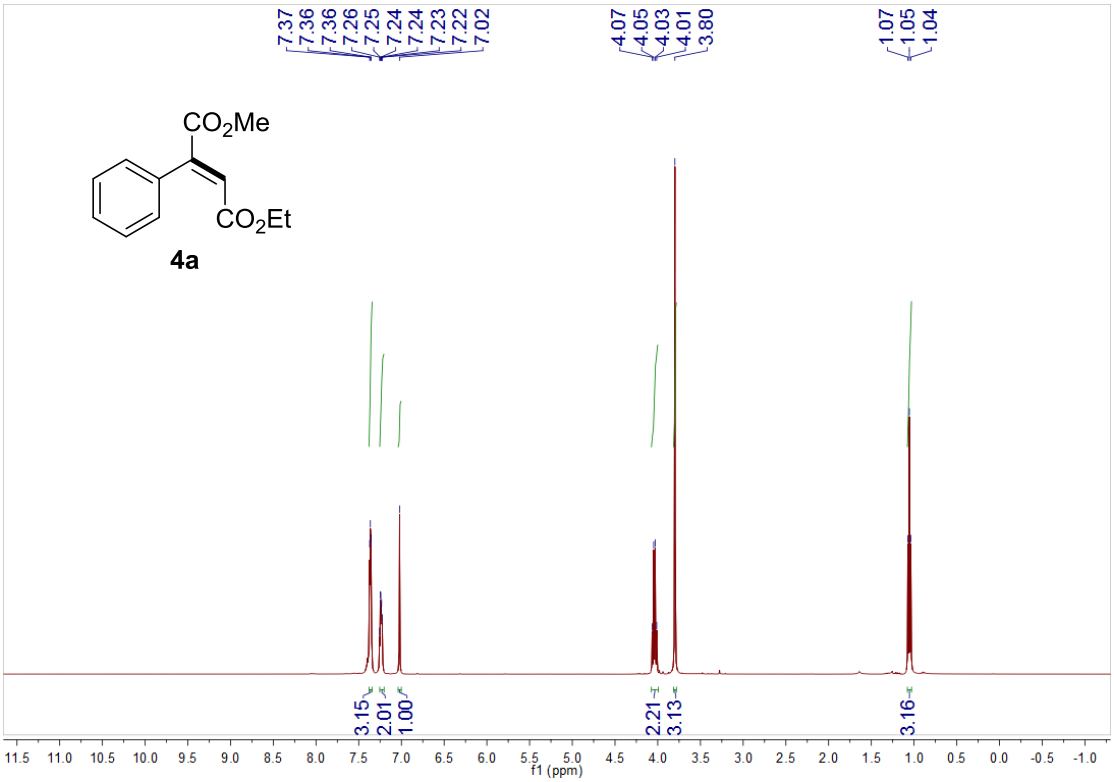
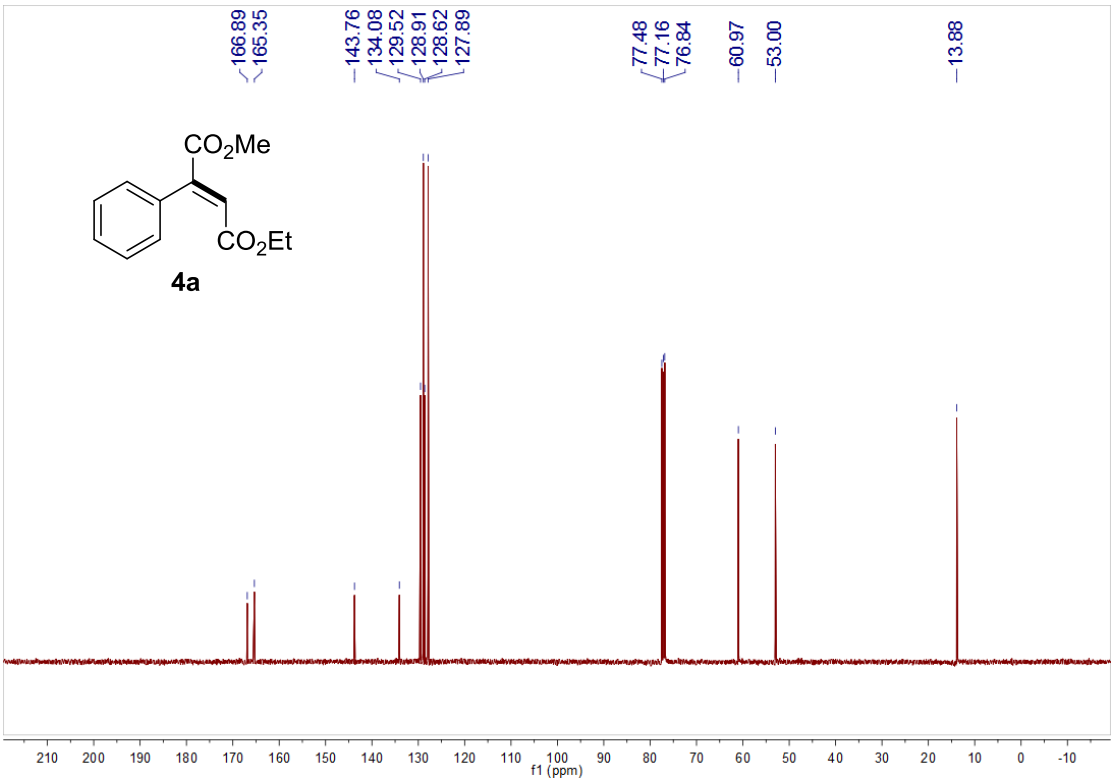
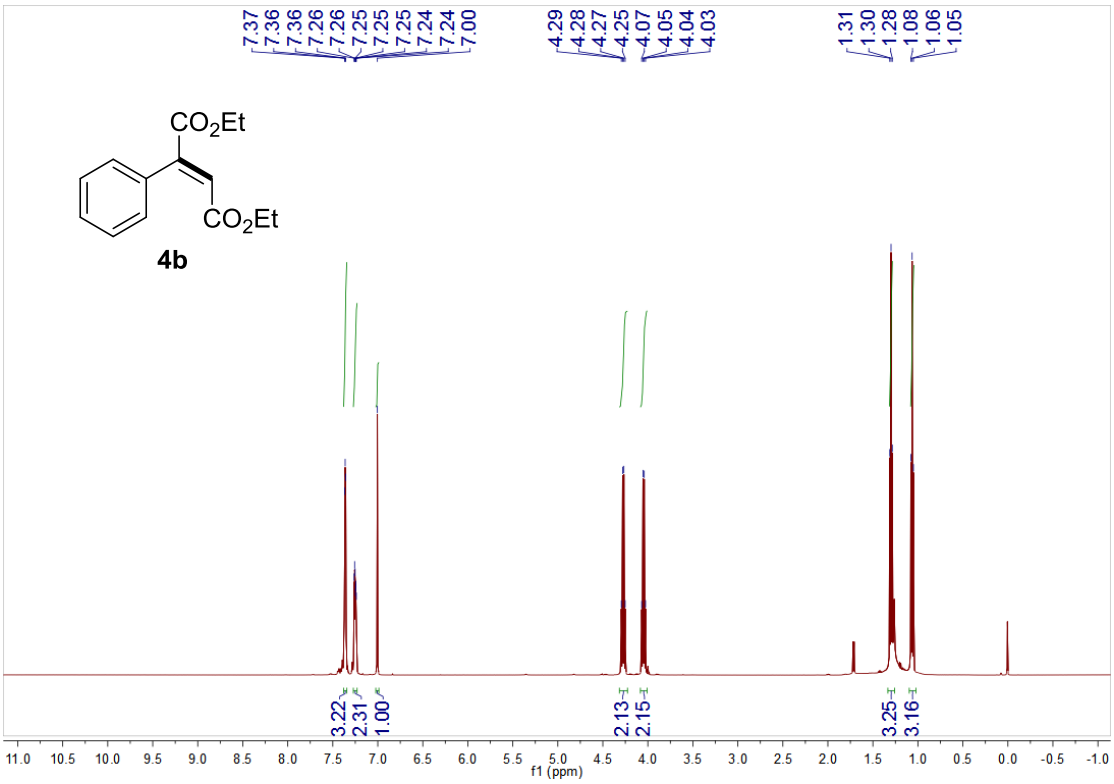
^{1}H NMR and ^{13}C NMR spectra



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4.27
4.25
4.07
4.05
4.04
4.03
1.31
1.30
1.28
1.08
1.06
1.05
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CO2Et
4b
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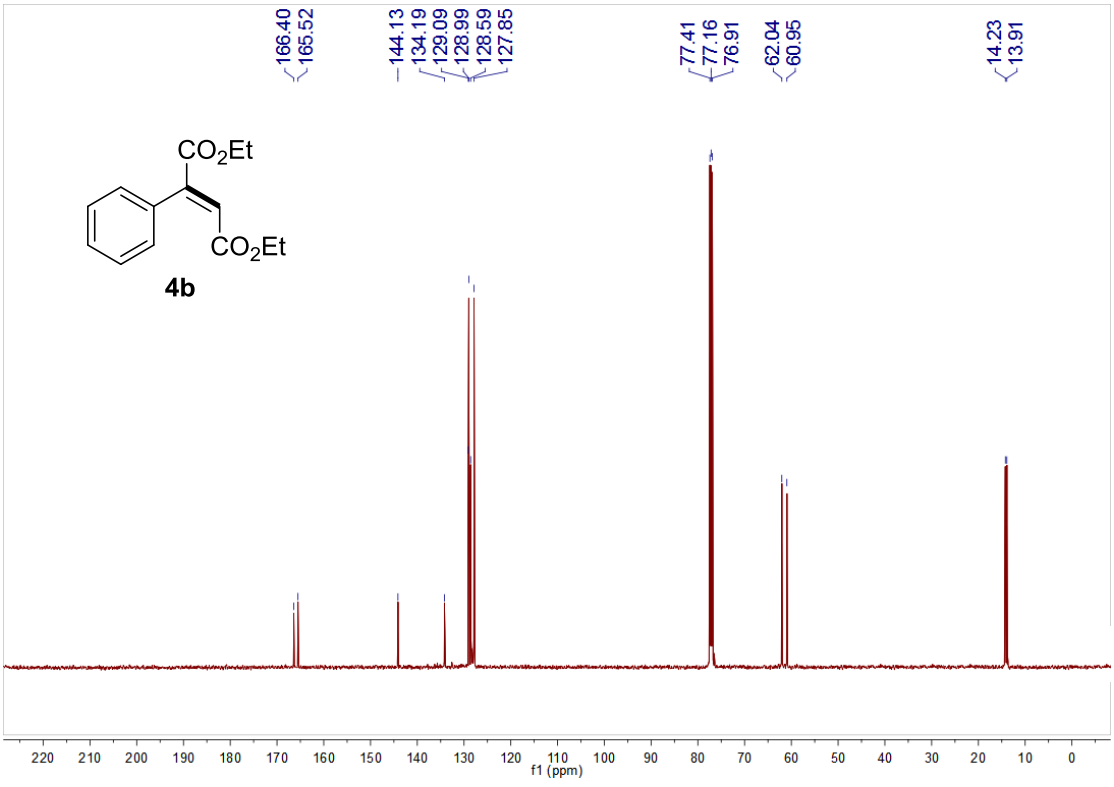
2.15
3.25
3.16
f1 (ppm)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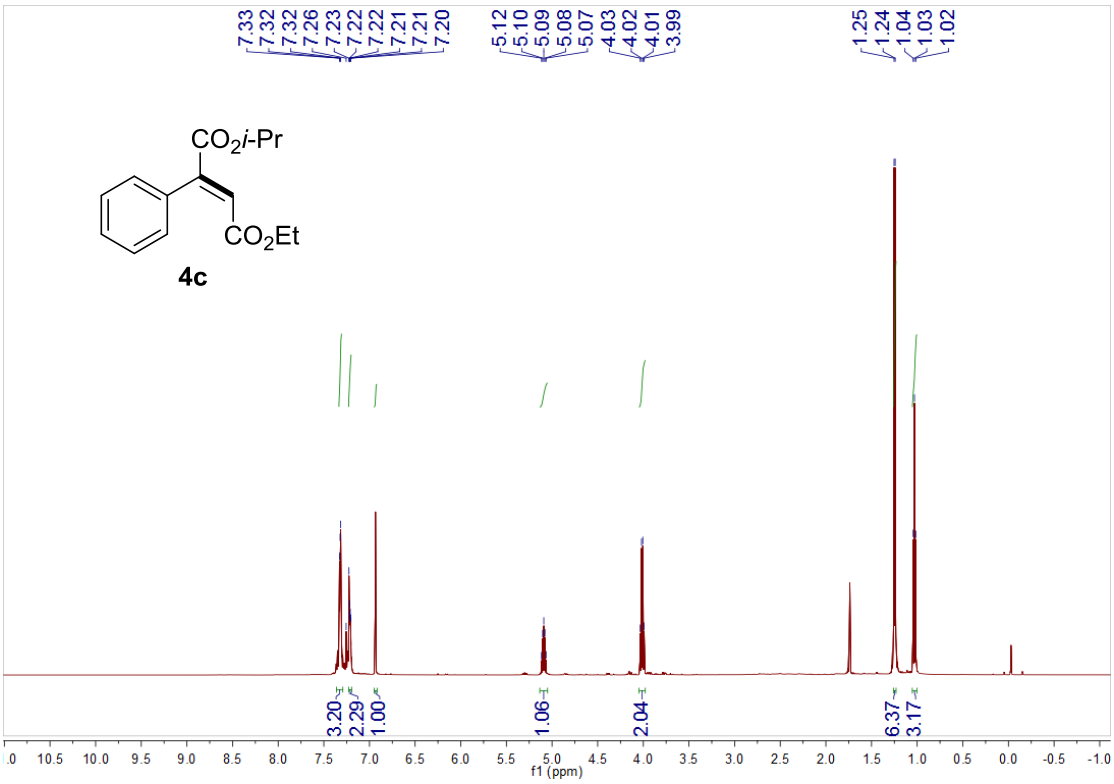
13.91
CO2Et
CO2Et
4b
f1 (ppm)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5.09
5.08
5.07
4.03
4.02
4.01
3.99
1.25
1.24
1.04
1.03
1.02
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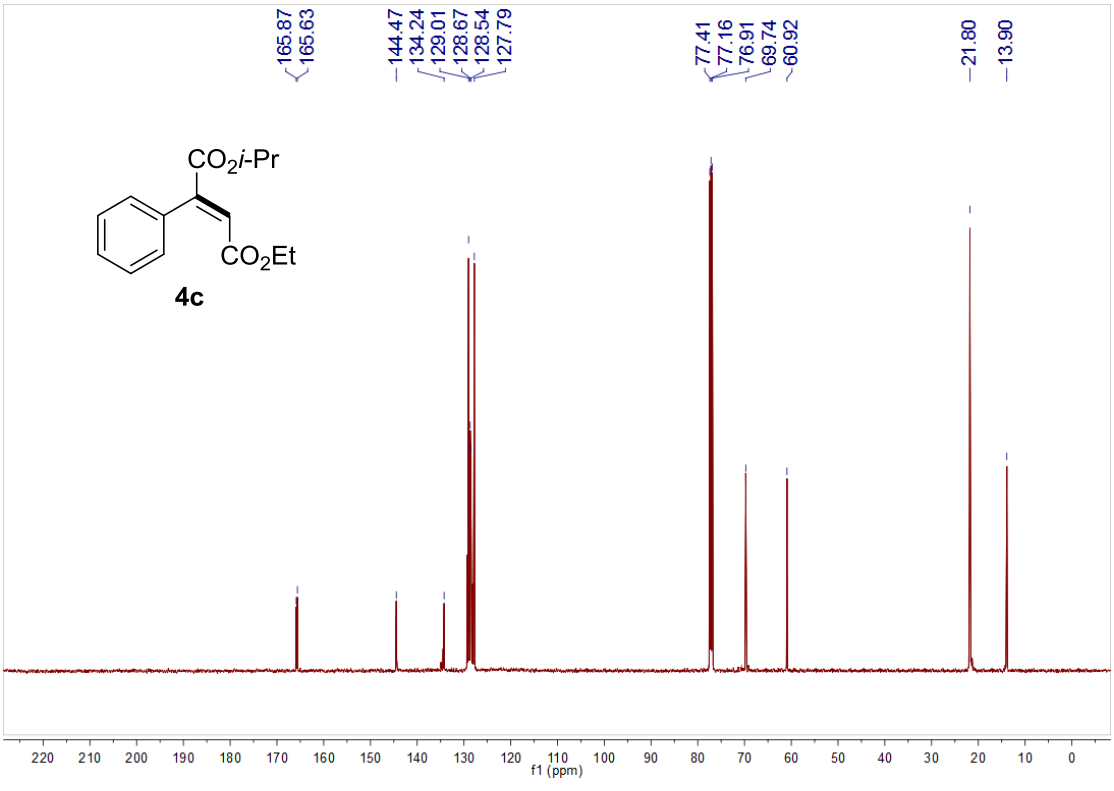
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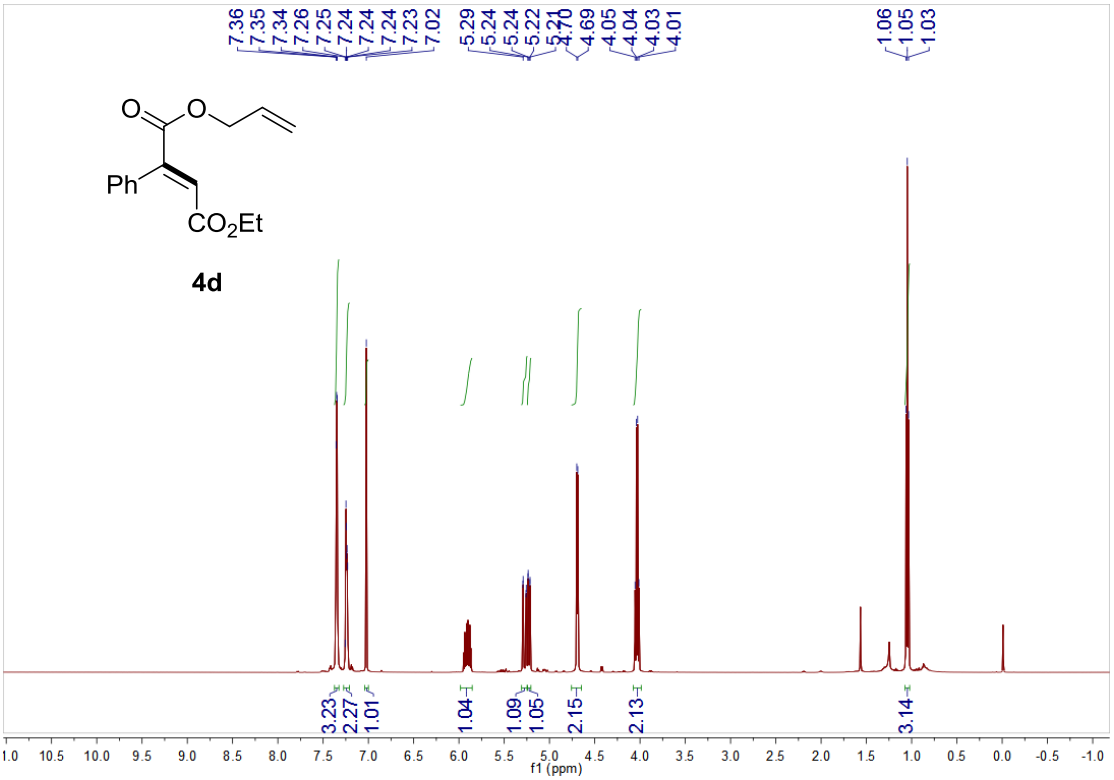
4c
f1 (ppm)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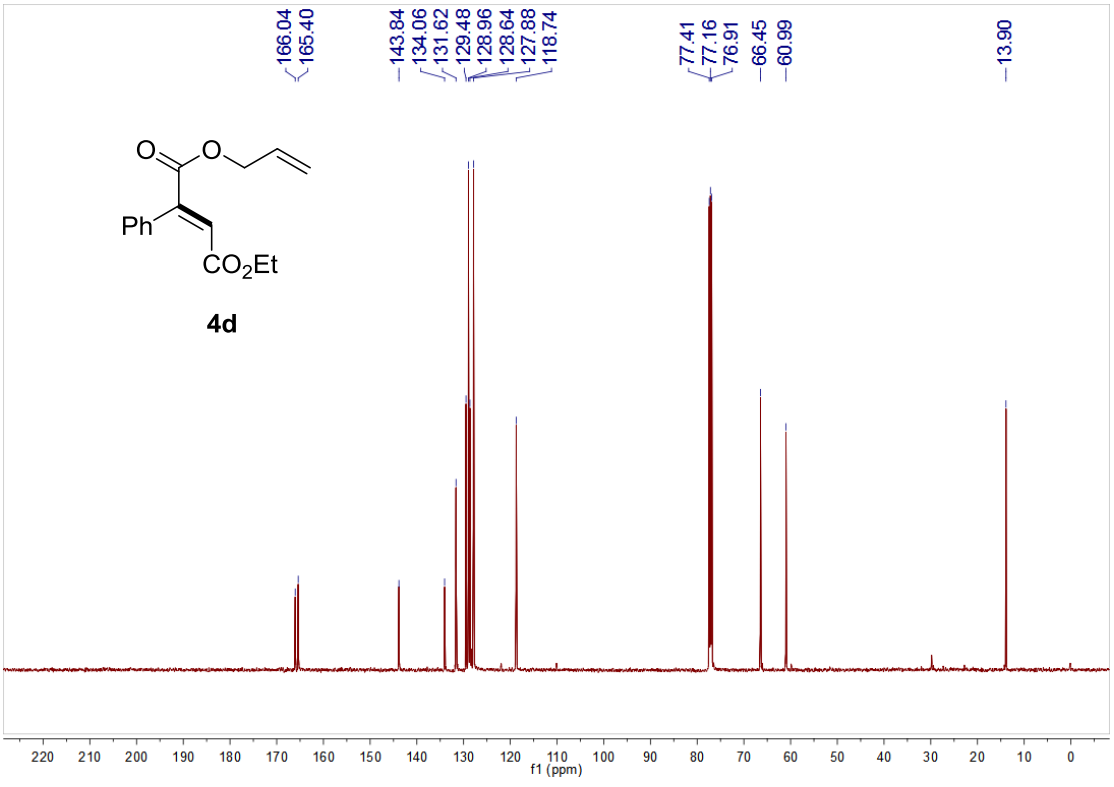
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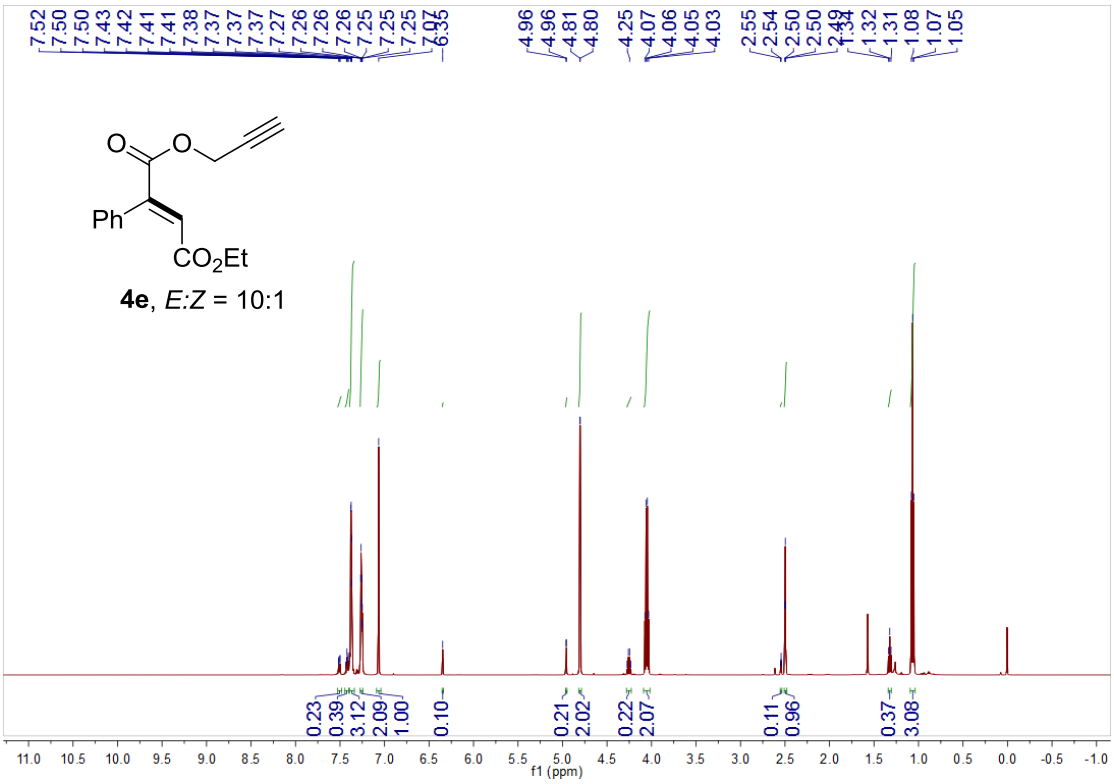
4d
f1 (ppm)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Ph
CO2Et
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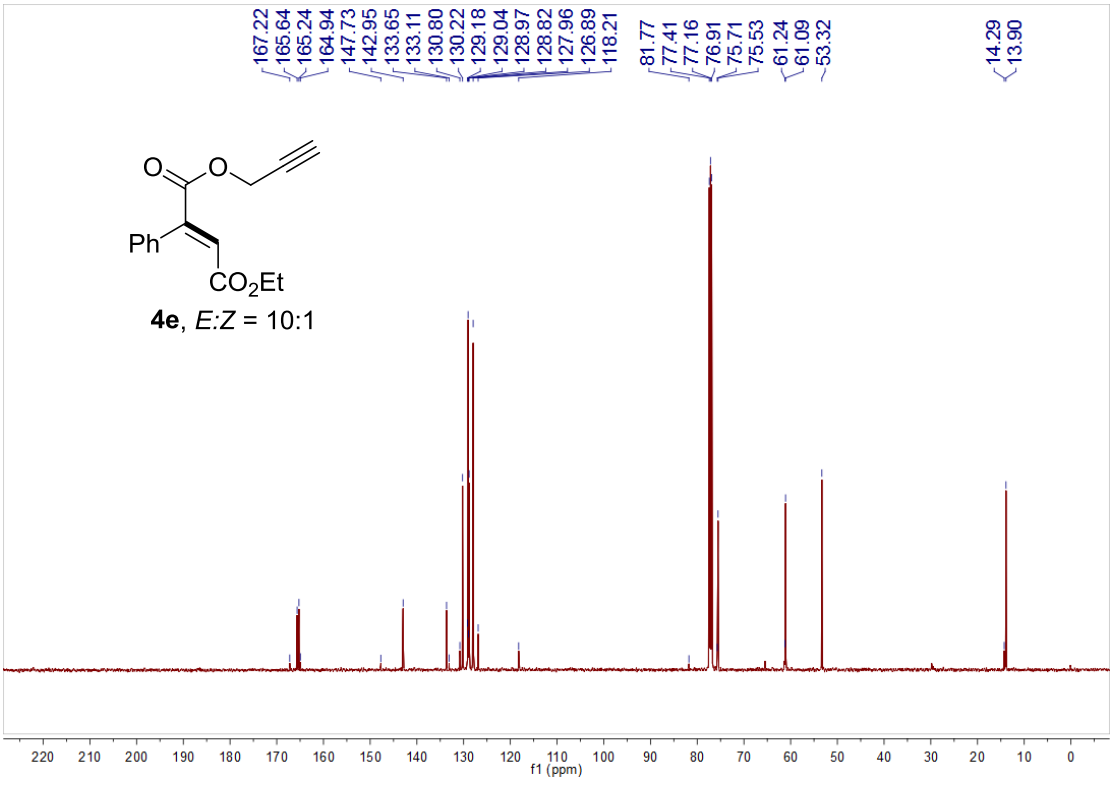
f1 (ppm)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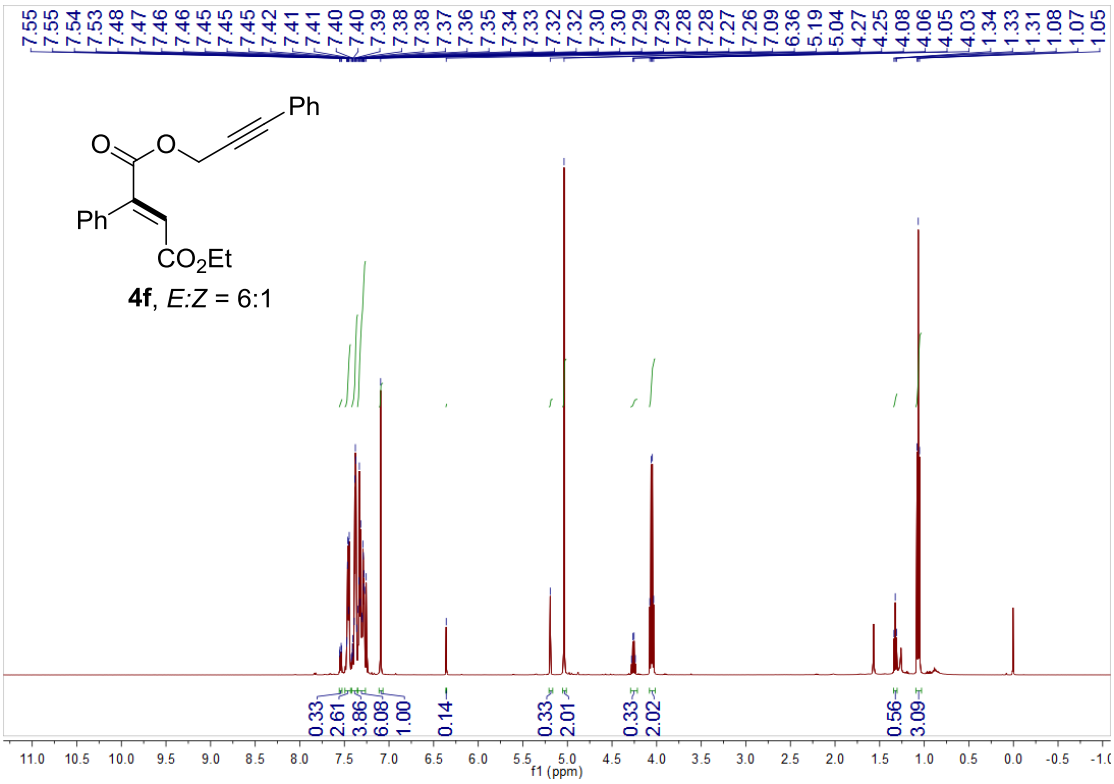
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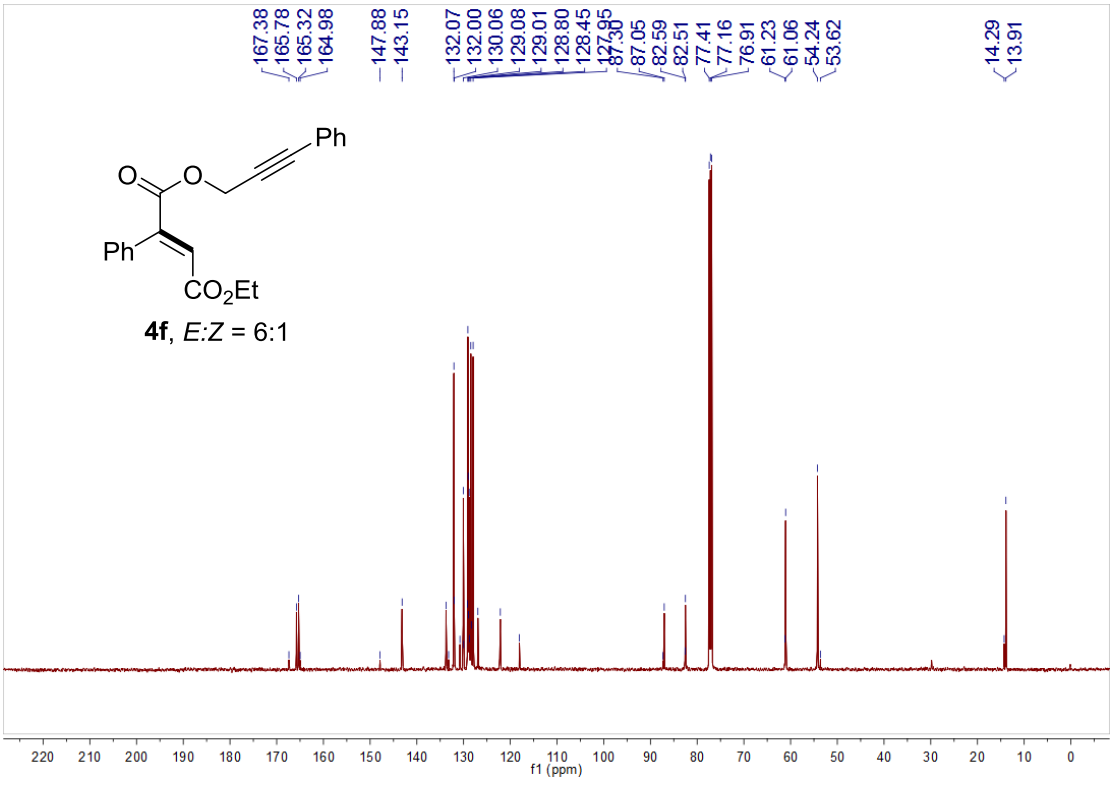
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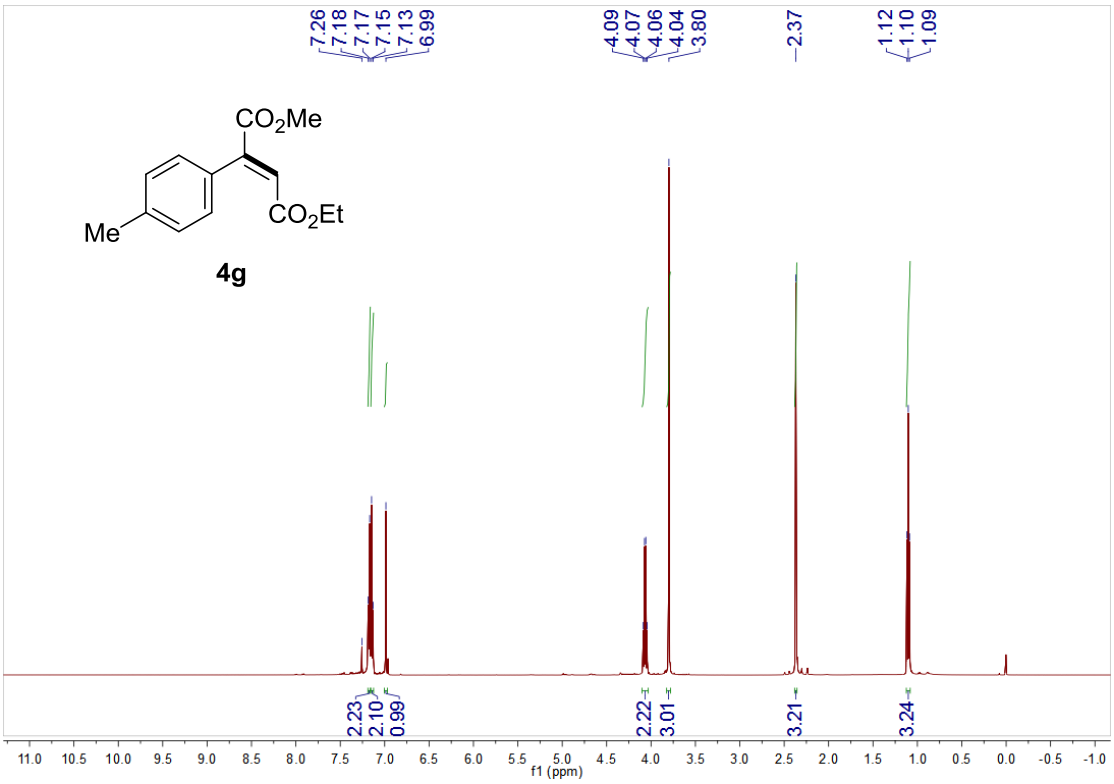
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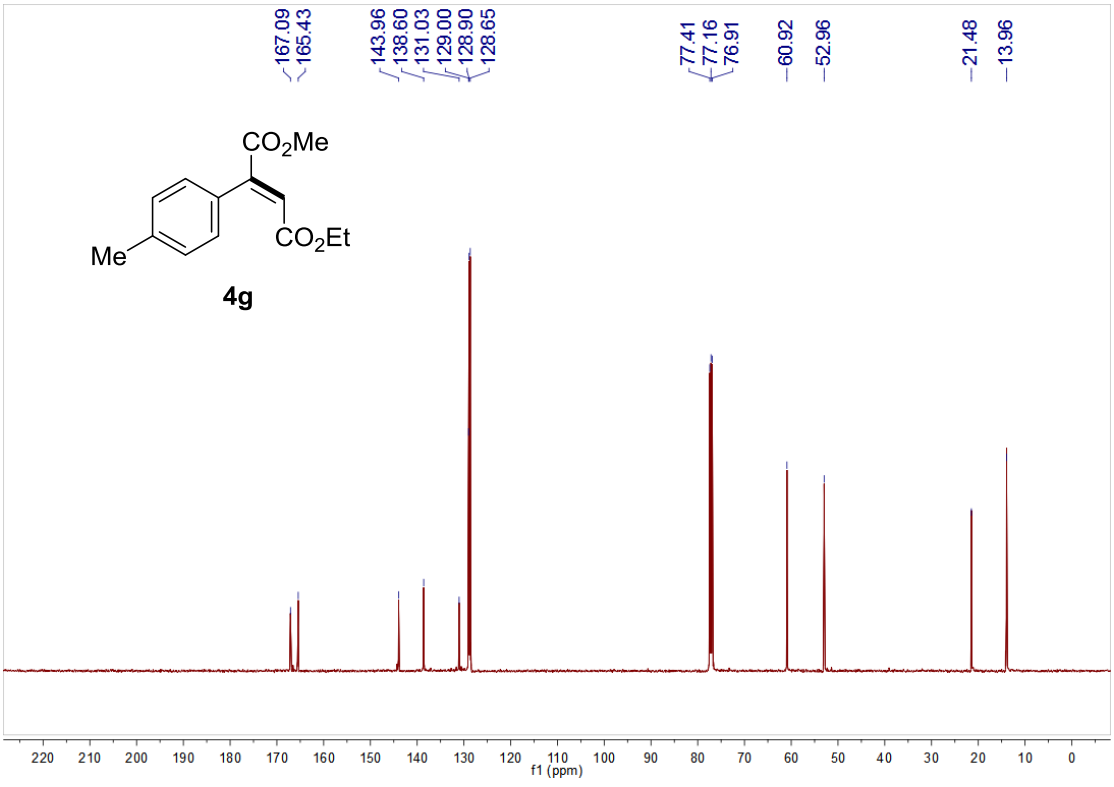
f1 (ppm)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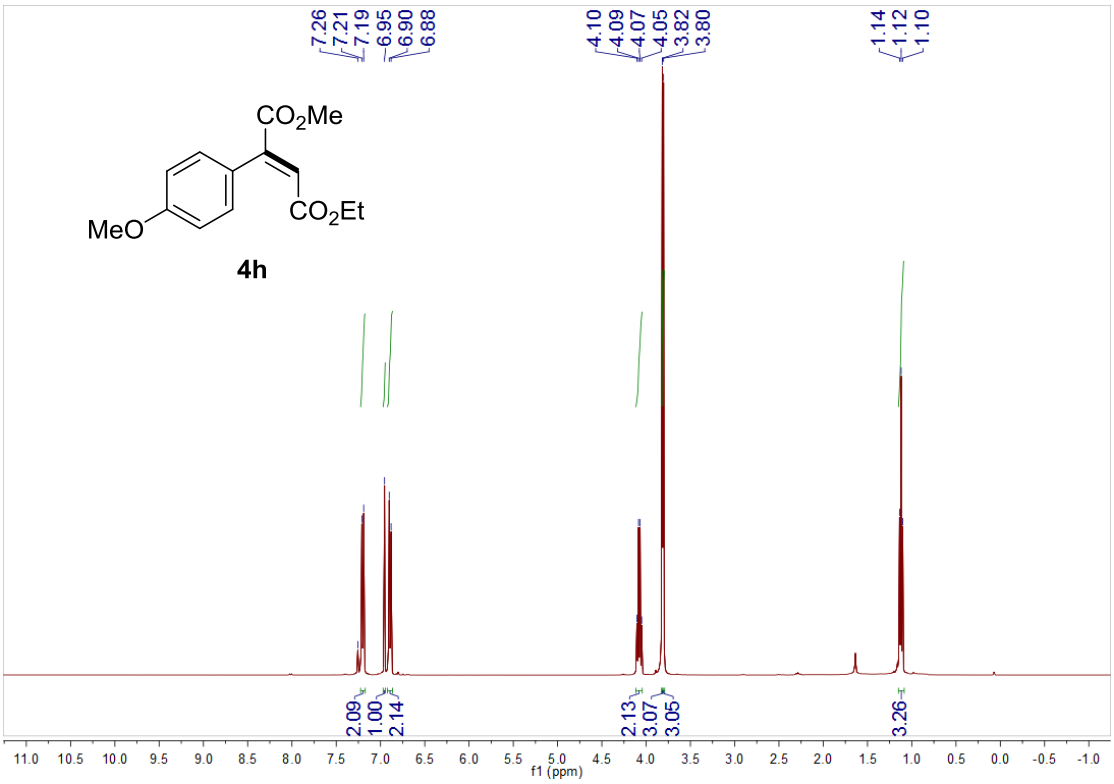
CO2Et
Me
4g
f1 (ppm)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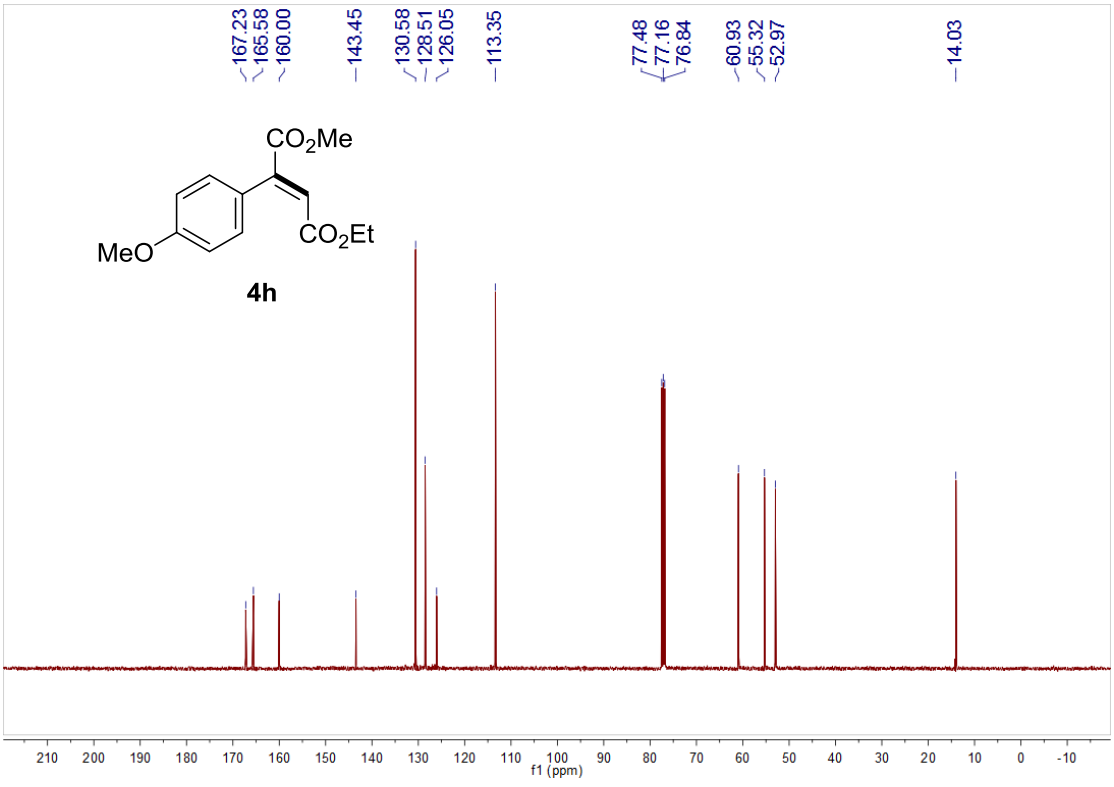
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4h
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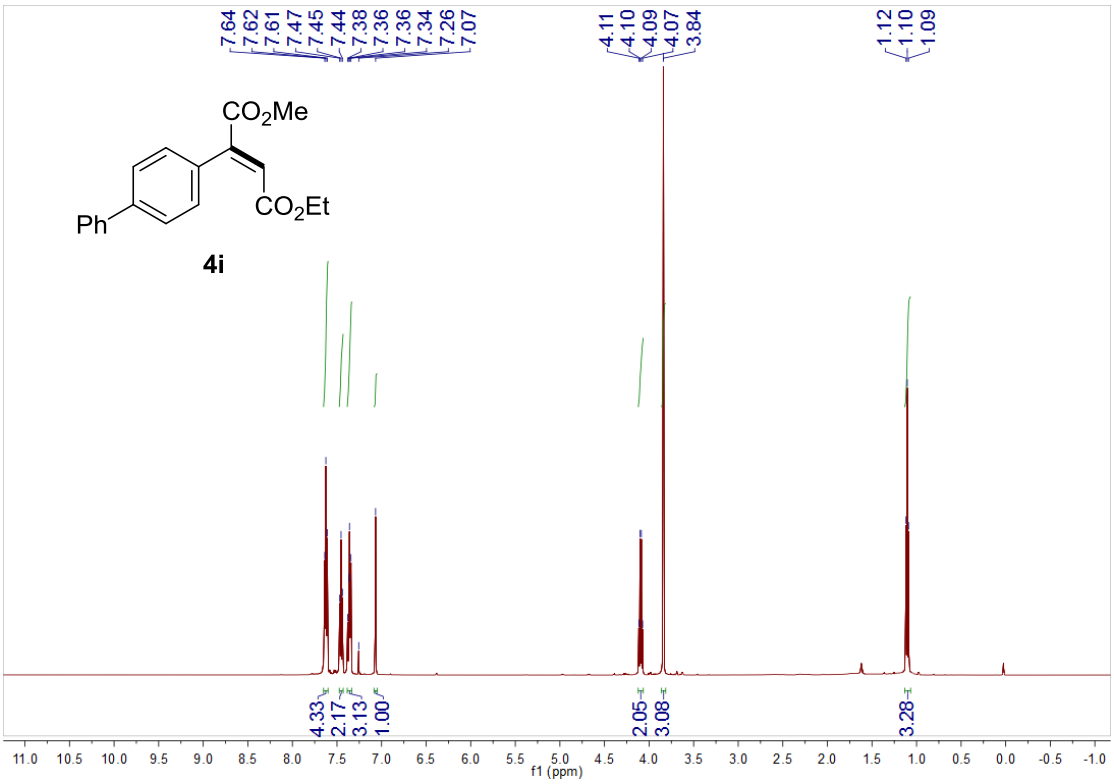
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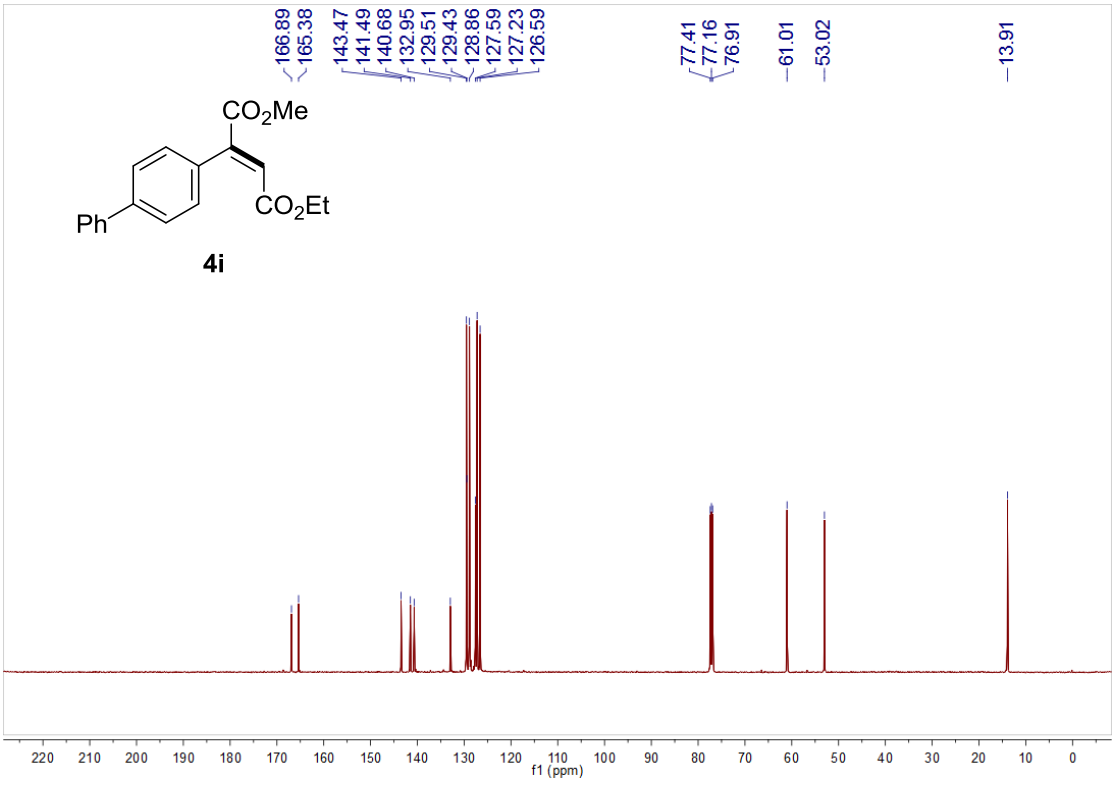
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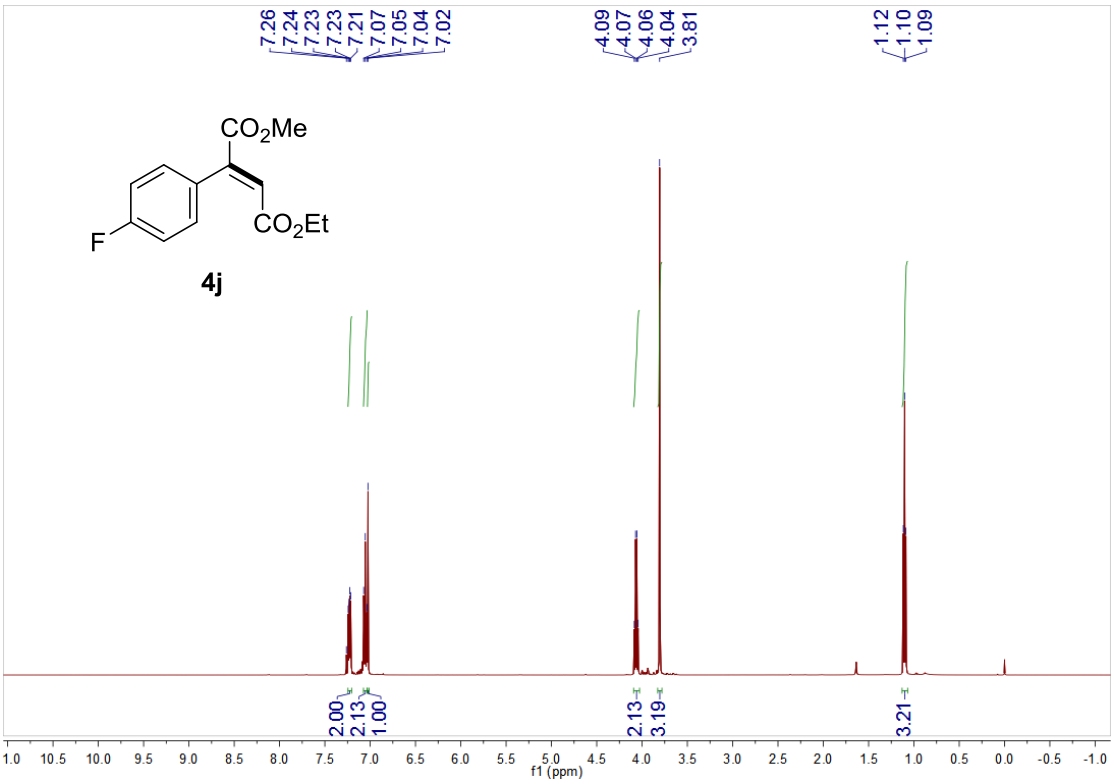
Ph
4i
f1 (ppm)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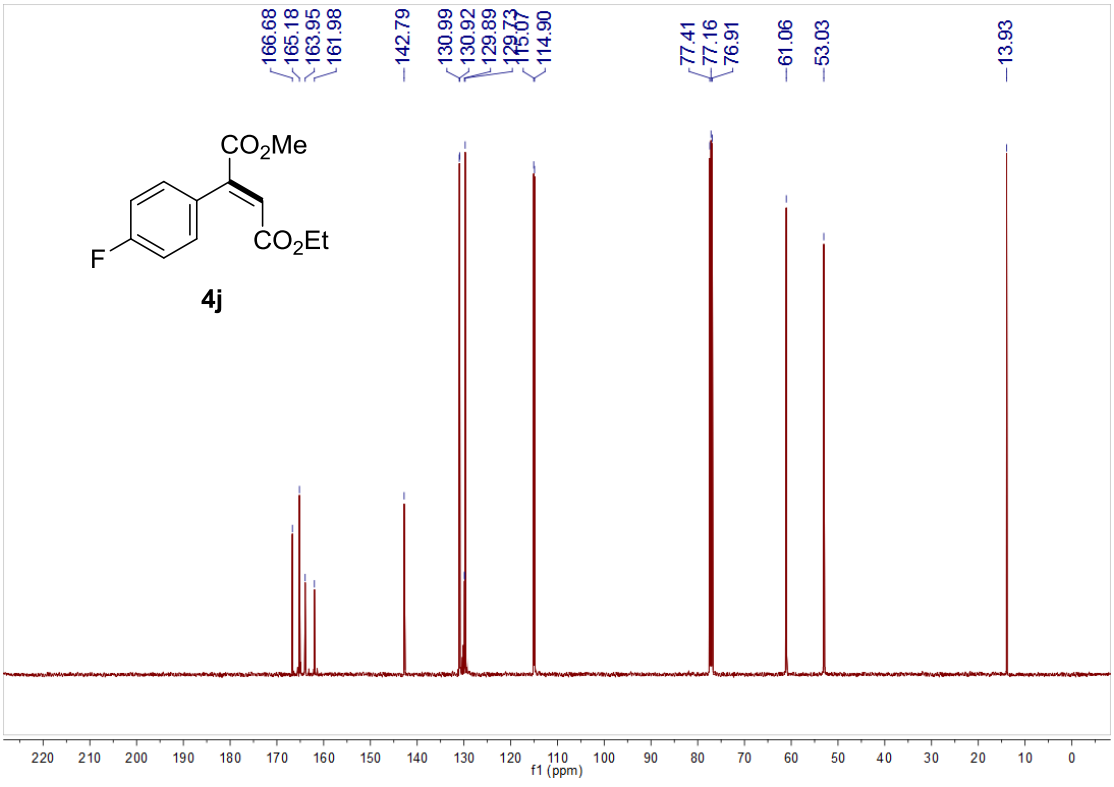
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F
4j
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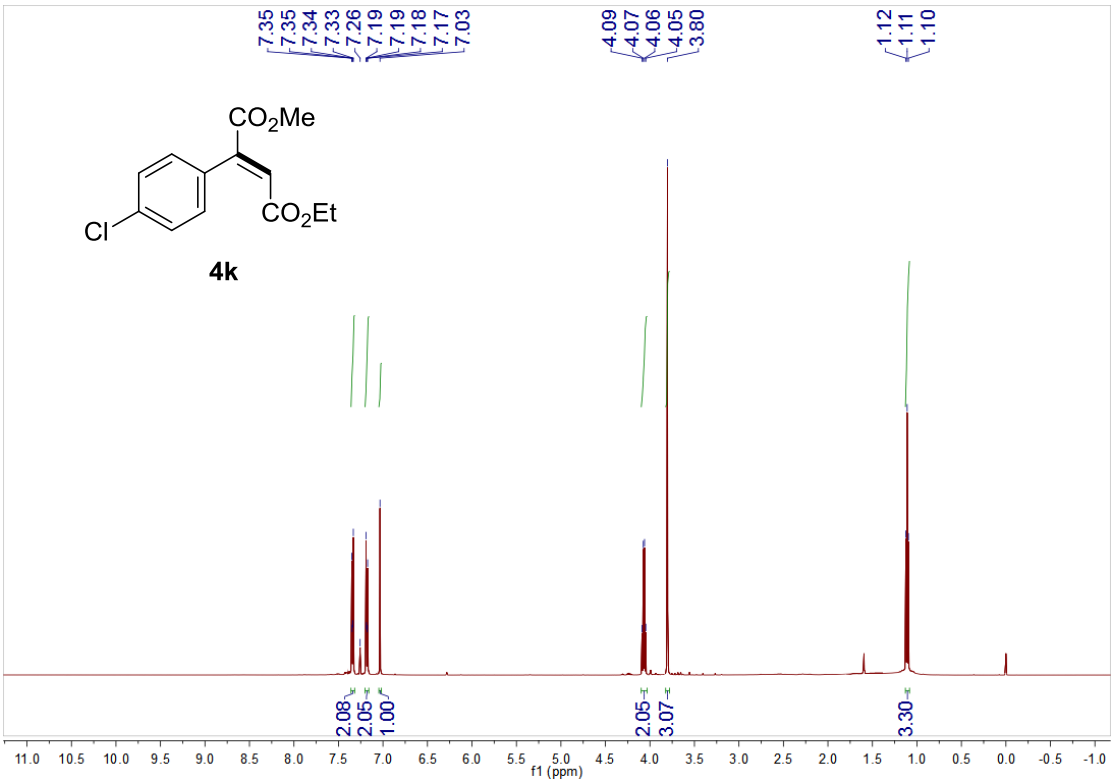
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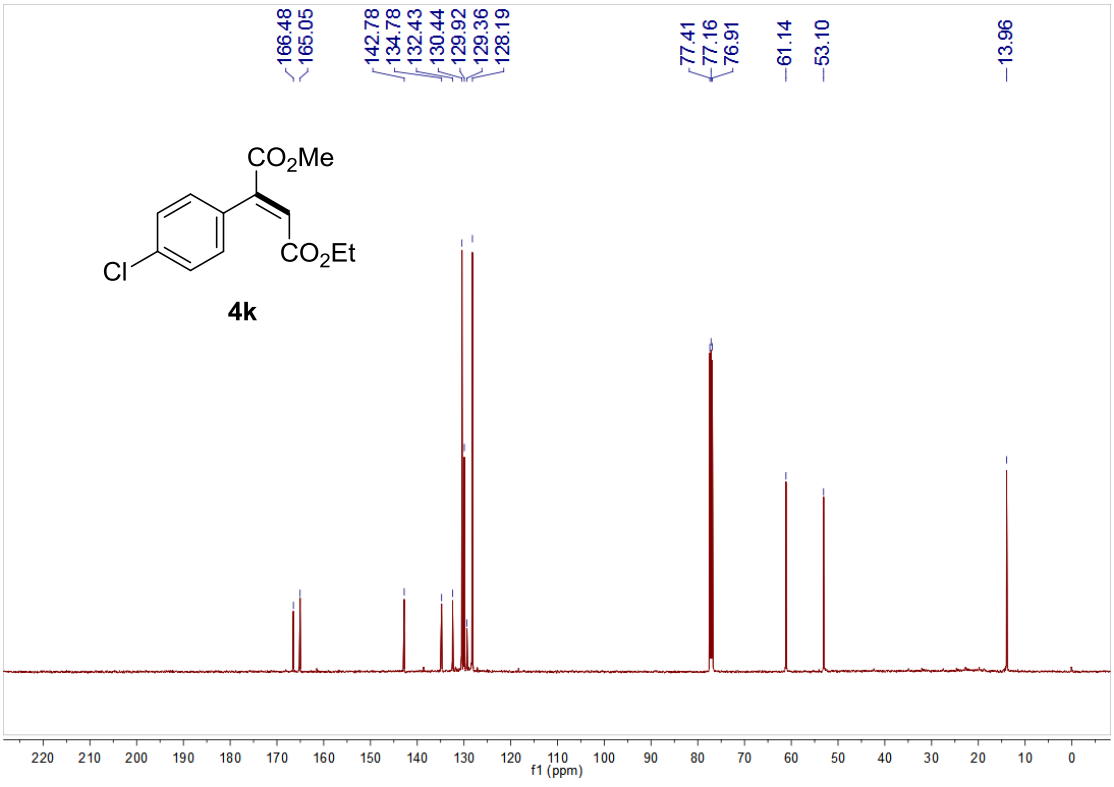
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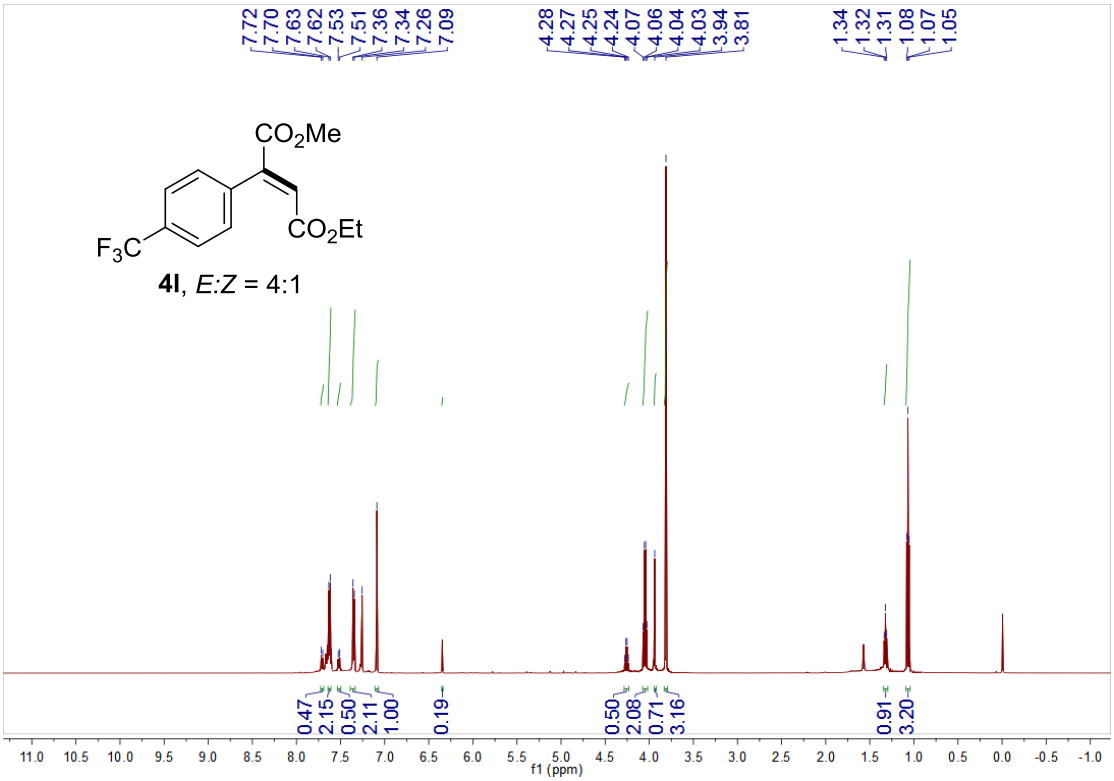
4k
f1 (ppm)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1.32
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CO2Et
F3C
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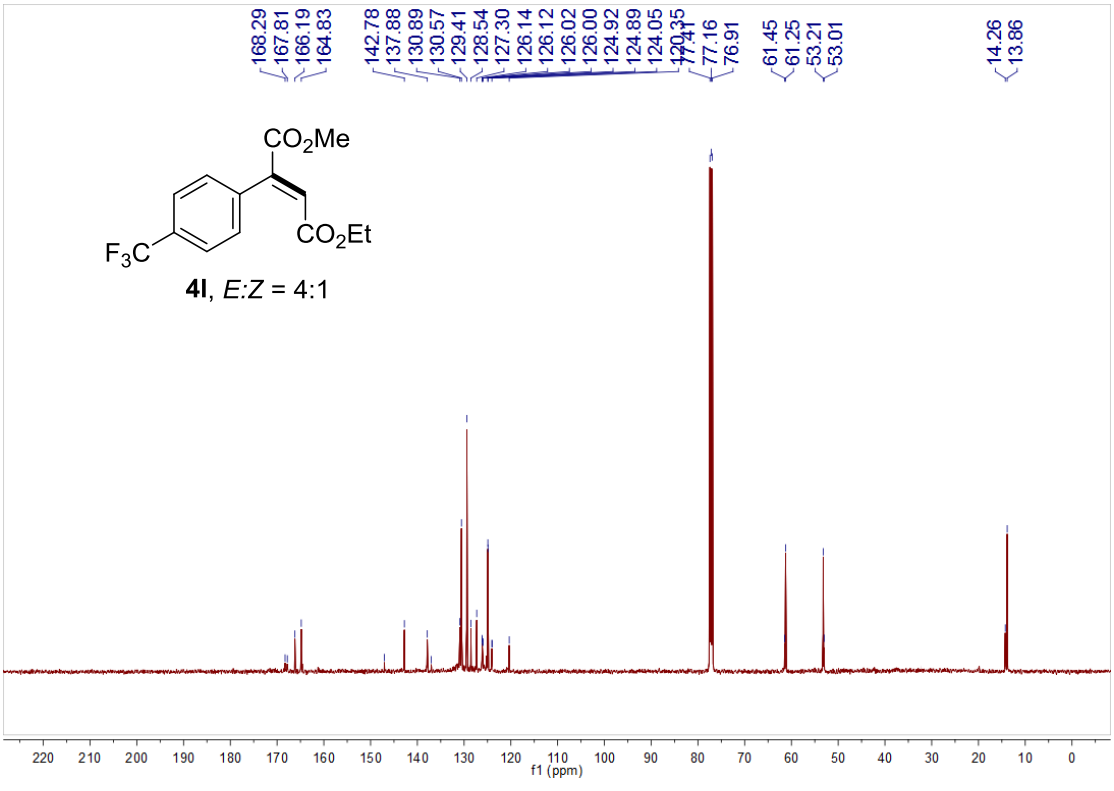
3.20
f1 (ppm)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166.19
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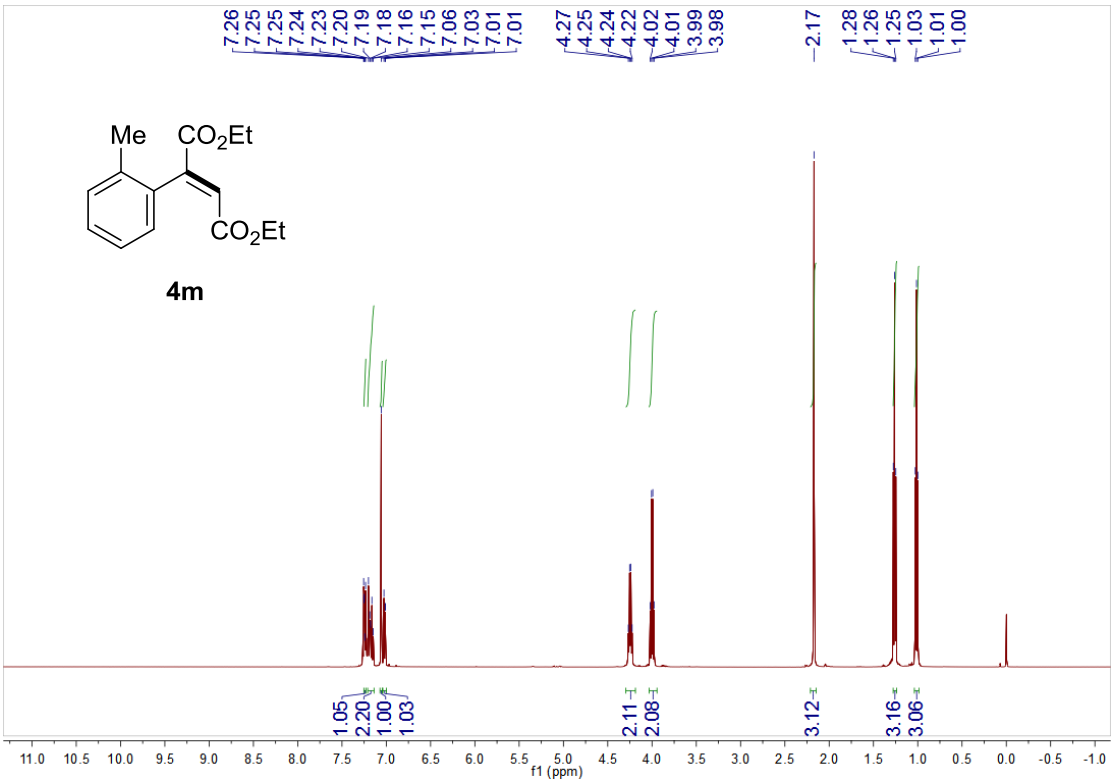
137.88
130.89
130.57
129.41
128.54
127.30
126.14
126.12
126.02
126.00
124.92
124.89
124.05
120.35
77.41
77.16
76.91
61.45
61.25
53.21
53.01
14.26
13.86
CO2Me
CO2Et
F3C
4l, E:Z = 4:1
f1 (ppm)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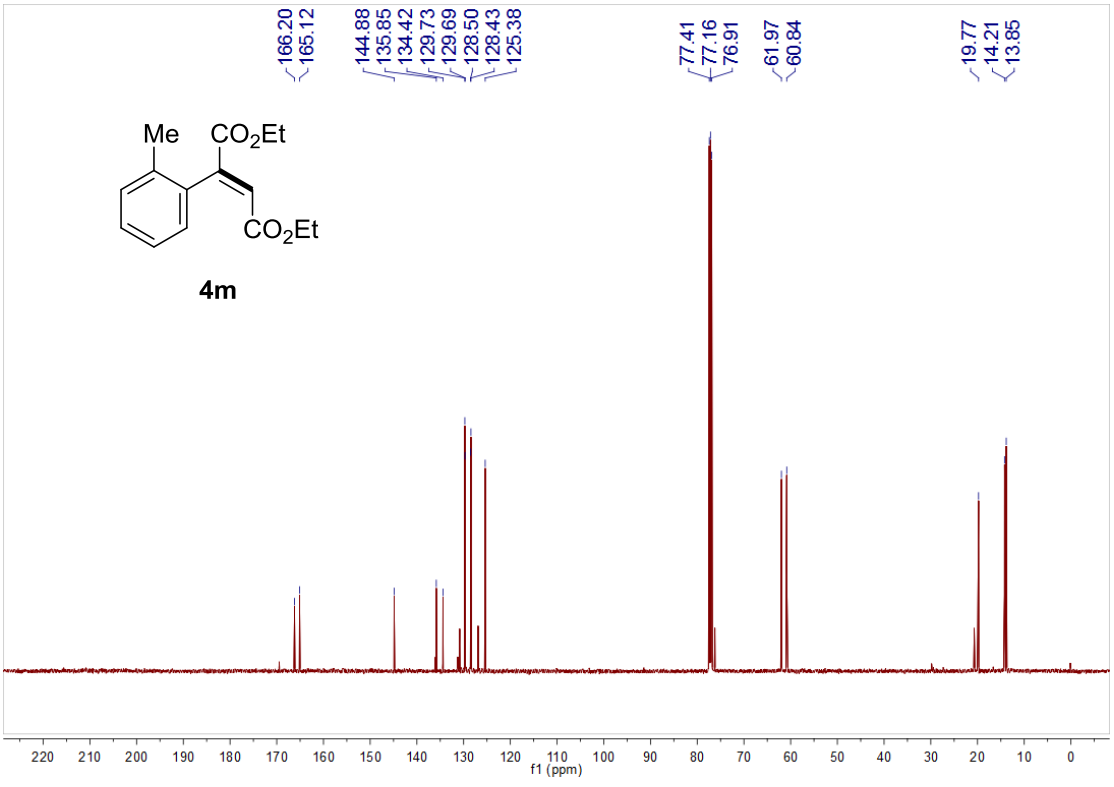
7.06
7.03
7.01
7.01
4.27
4.25
4.24
4.22
4.02
4.01
3.99
3.98
2.17
1.28
1.26
1.25
1.03
1.01
1.00
Me
CO2Et
CO2Et
4m
1.05
2.20
1.00
1.03
2.11
2.08
3.12
3.16
3.06
f1 (ppm)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128.50
128.43
125.38
77.41
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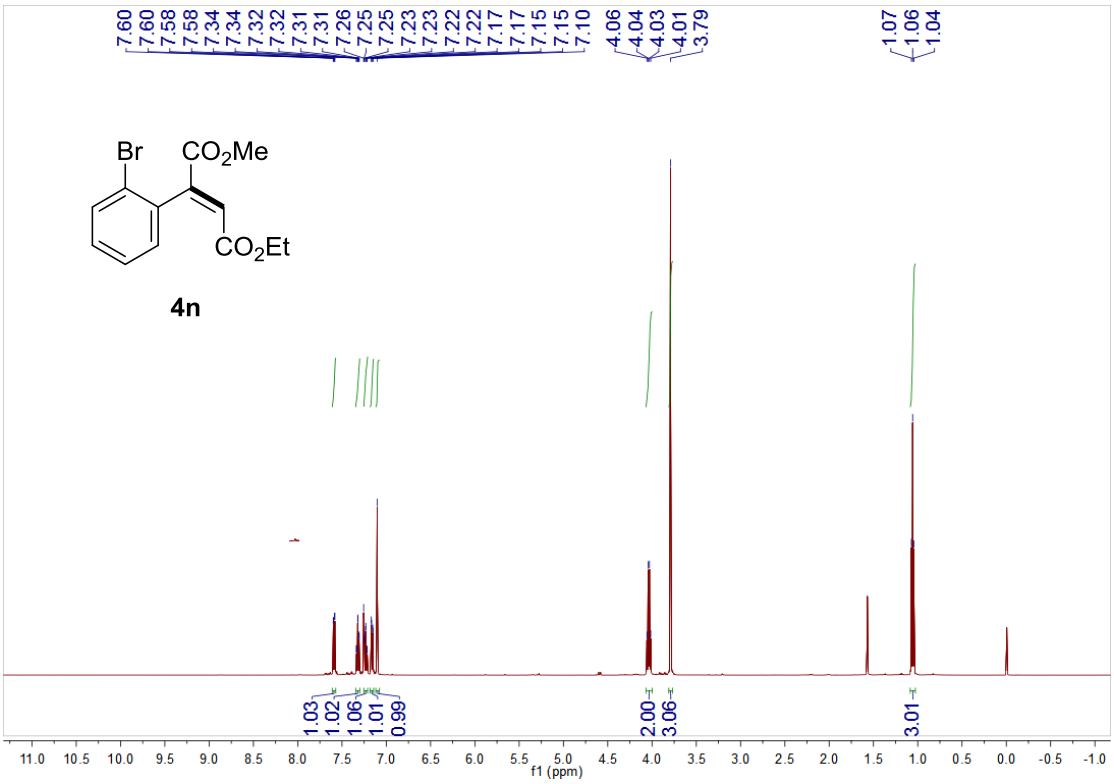
76.91
61.97
60.84
19.77
14.21
13.85
Me
CO2Et
CO2Et
4m
f1 (ppm)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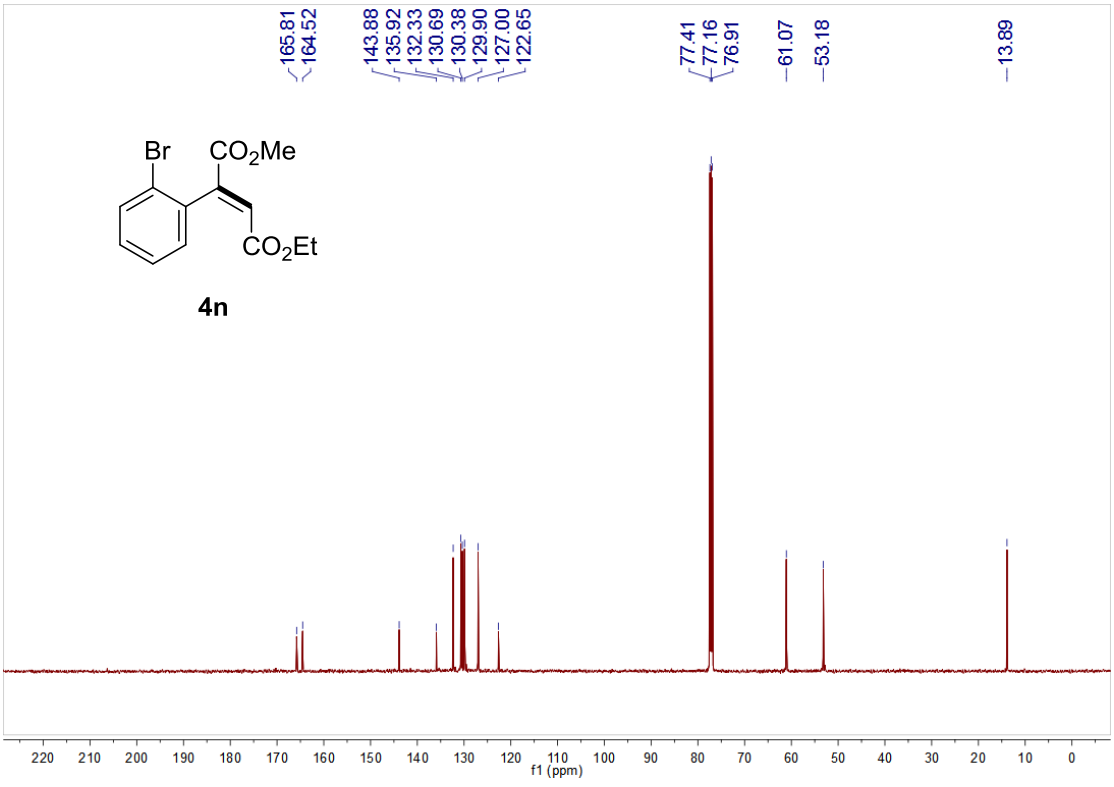
7.25
7.23
7.23
7.22
7.22
7.17
7.17
7.15
7.15
7.10
4.06
4.04
4.03
4.01
3.79
1.07
1.06
1.04
Br
CO2Me
CO2Et
4n
1.03
1.02
1.06
1.01
0.99
2.00
3.06
3.01
f1 (ppm)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129.90
127.00
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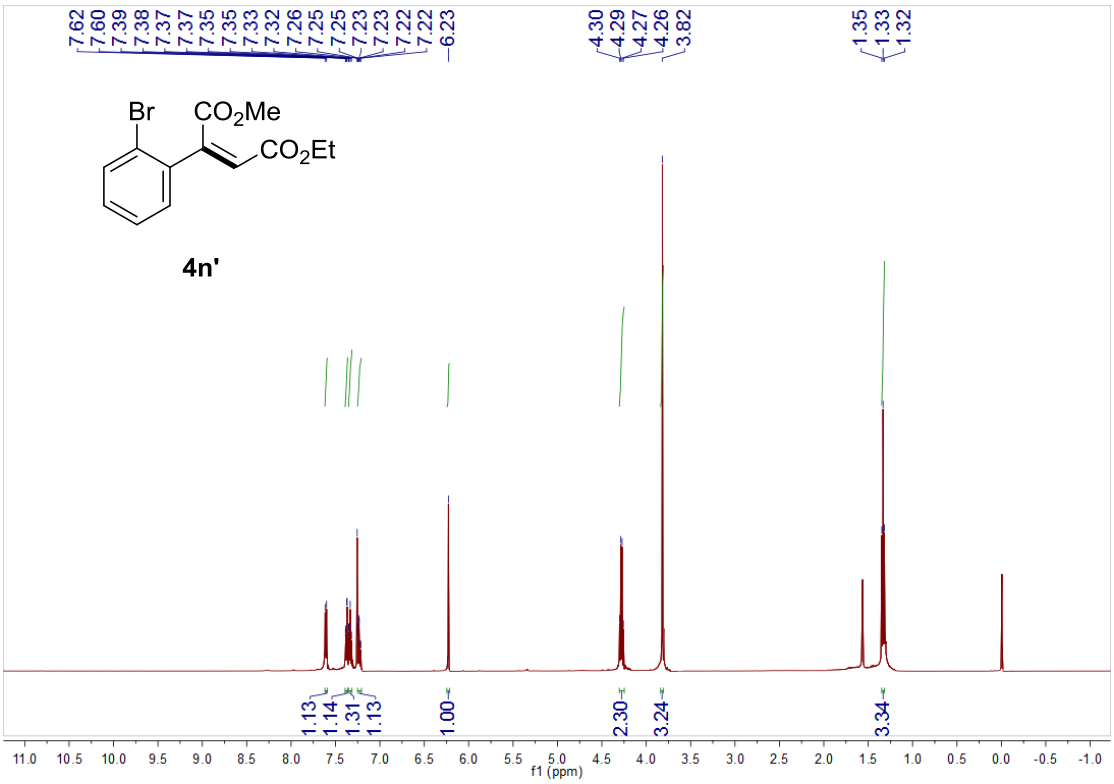
77.16
76.91
61.07
53.18
13.89
Br
CO2Me
CO2Et
4n
f1 (ppm)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7.32
7.26
7.25
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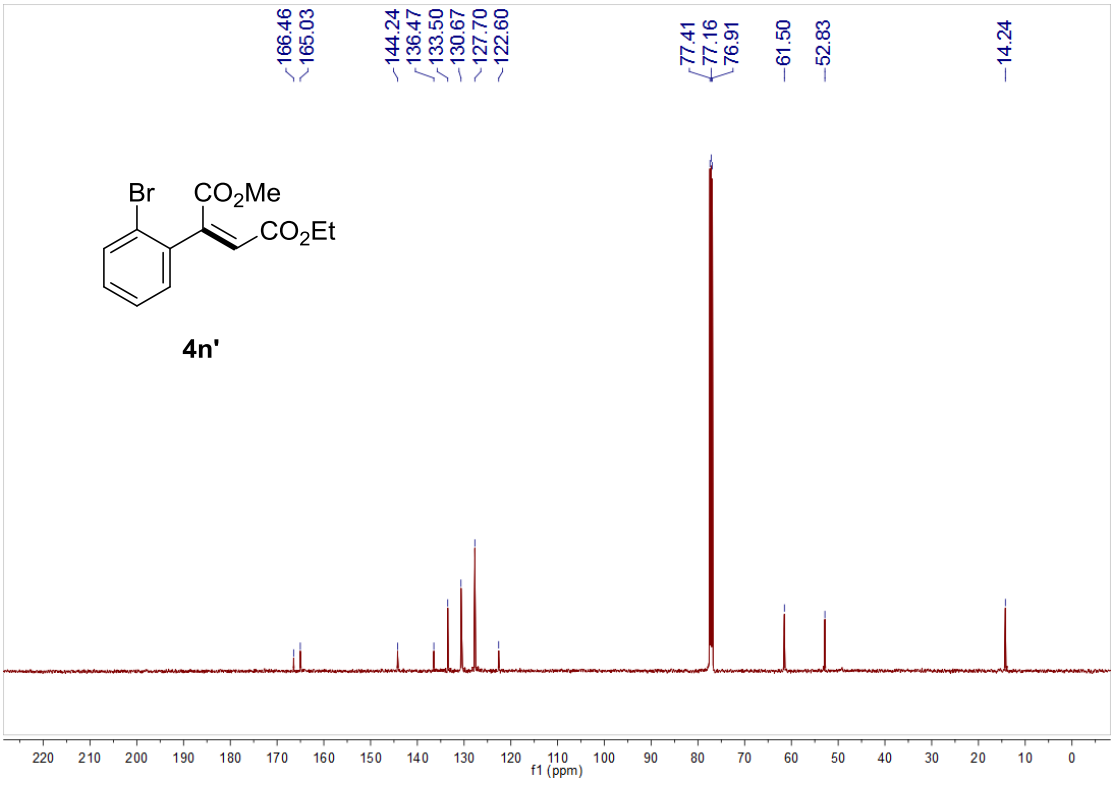
7.23
7.23
7.22
7.22
6.23
4.30
4.29
4.27
4.26
3.82
1.35
1.33
1.32
Br
CO2Me
CO2Et
4n'
1.13
1.14
1.31
1.13
1.00
2.30
3.24
3.34
f1 (ppm)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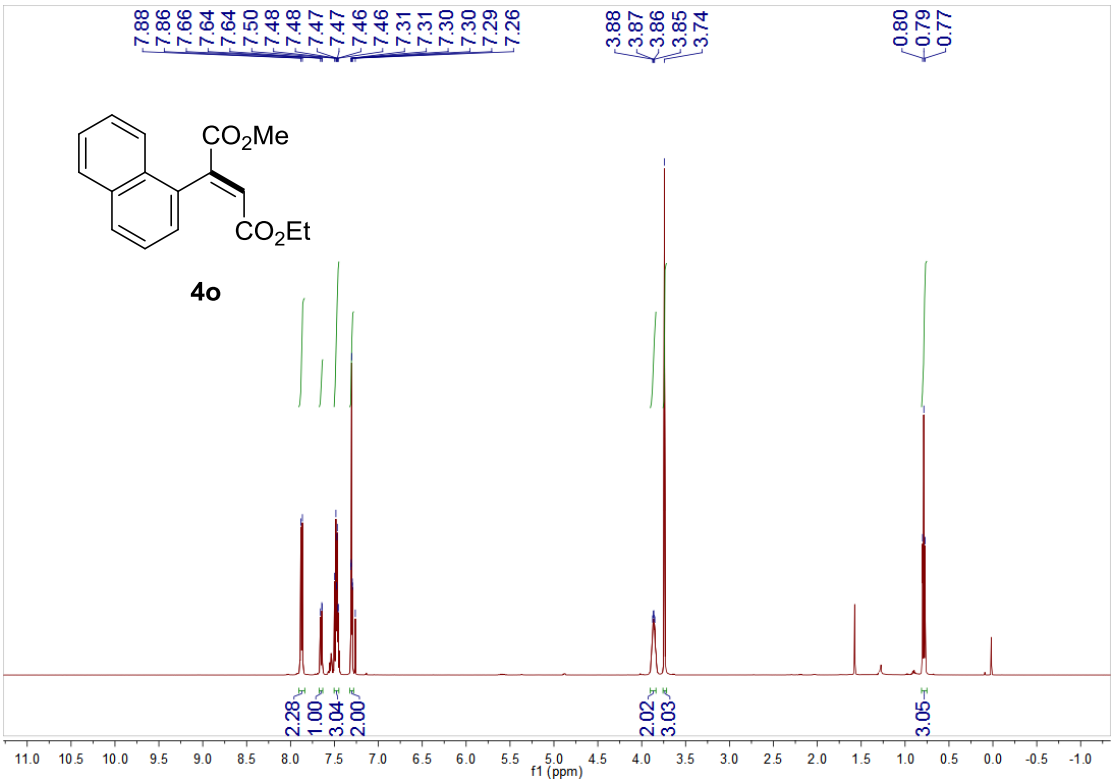
76.91
61.50
52.83
14.24
Br
CO2Me
CO2Et
4n'
f1 (ppm)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7.86
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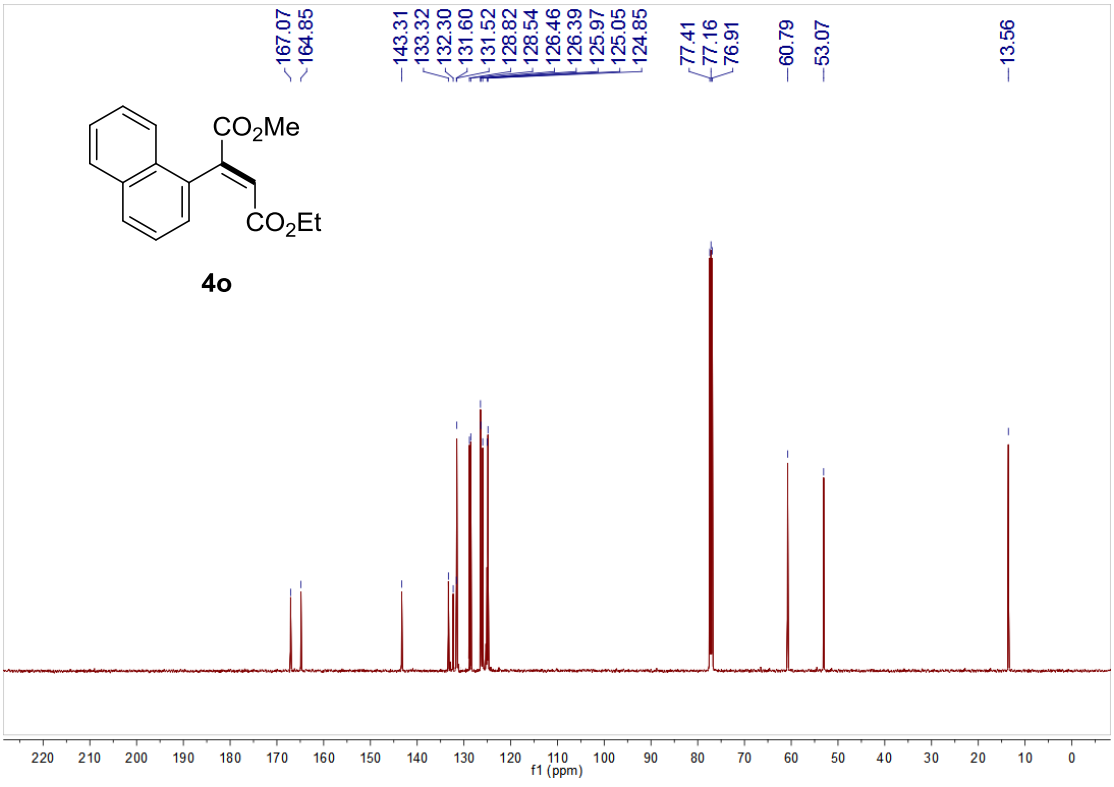
7.48
7.48
7.47
7.47
7.46
7.46
7.31
7.31
7.30
7.30
7.29
7.26
3.88
3.87
3.86
3.85
3.74
0.80
0.79
0.77
CO2Me
CO2Et
4o
2.28
1.00
3.04
2.00
2.02
3.03
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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143.31
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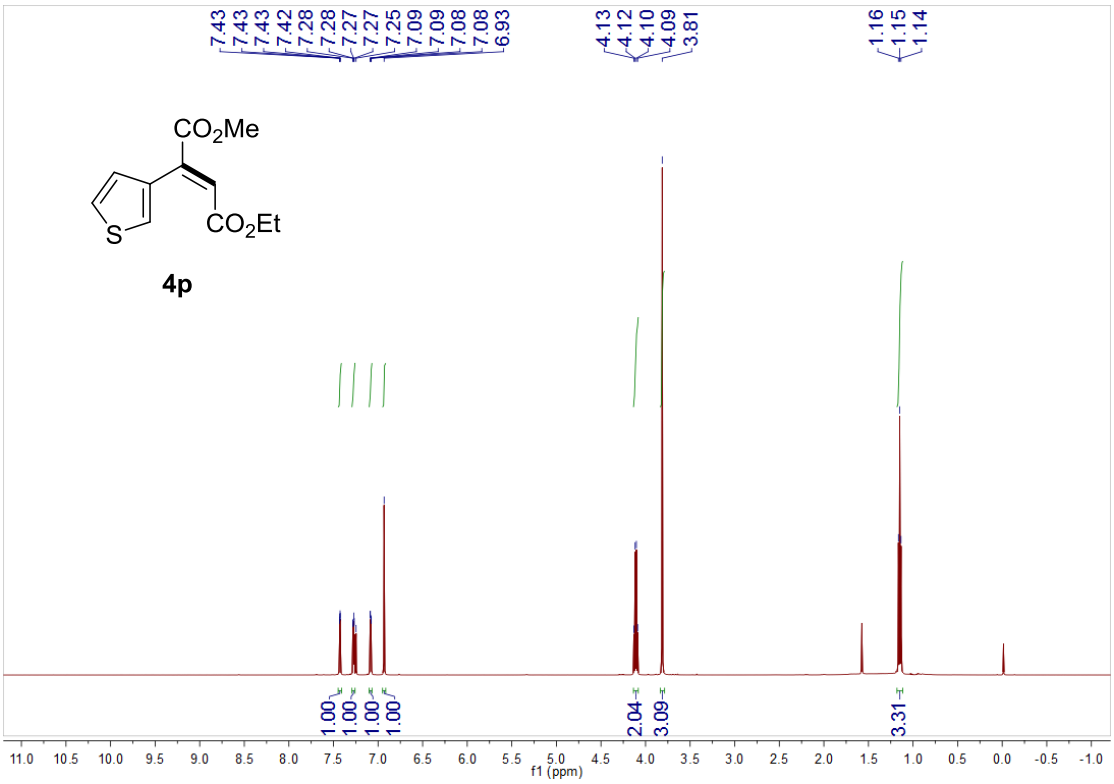
132.30
131.60
131.52
128.82
128.54
126.46
126.39
125.97
125.05
124.85
77.41
77.16
76.91
60.79
53.07
13.56
CO2Me
CO2Et
4o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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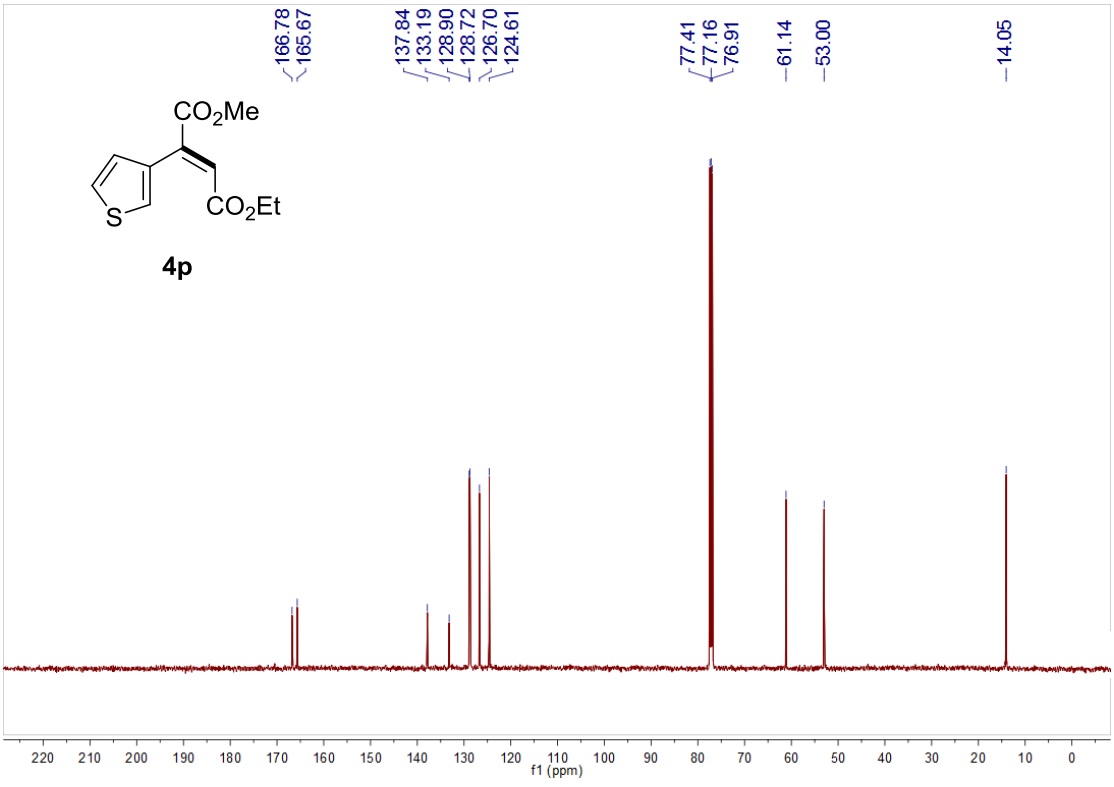
7.27
7.27
7.25
7.09
7.09
7.08
7.08
6.93
4.13
4.12
4.10
4.09
3.81
1.16
1.15
1.14
CO2Me
CO2Et
S
4p
1.00
1.00
1.00
1.00
2.04
3.09
3.31
f1 (ppm)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126.70
124.61
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77.16
76.91
61.14
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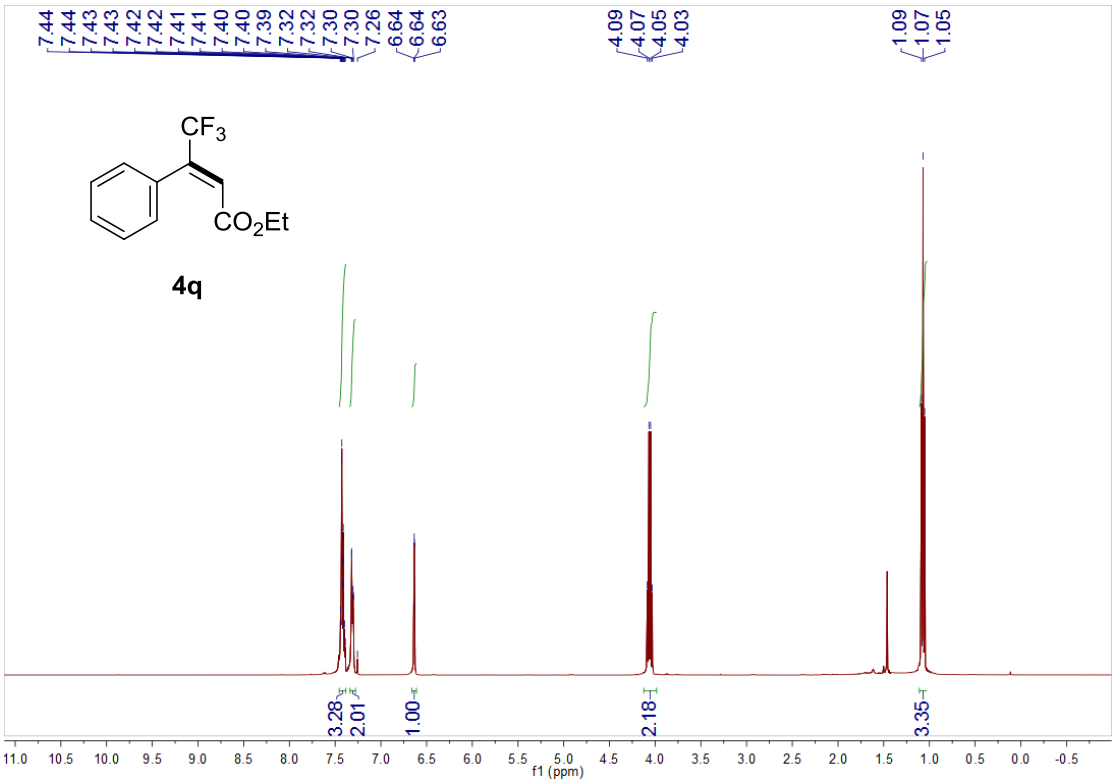
14.05
CO2Me
CO2Et
S
4p
f1 (ppm)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7.41
7.40
7.40
7.39
7.32
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7.30
7.30
7.26
6.64
6.64
6.63
4.09
4.07
4.05
4.03
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CF3
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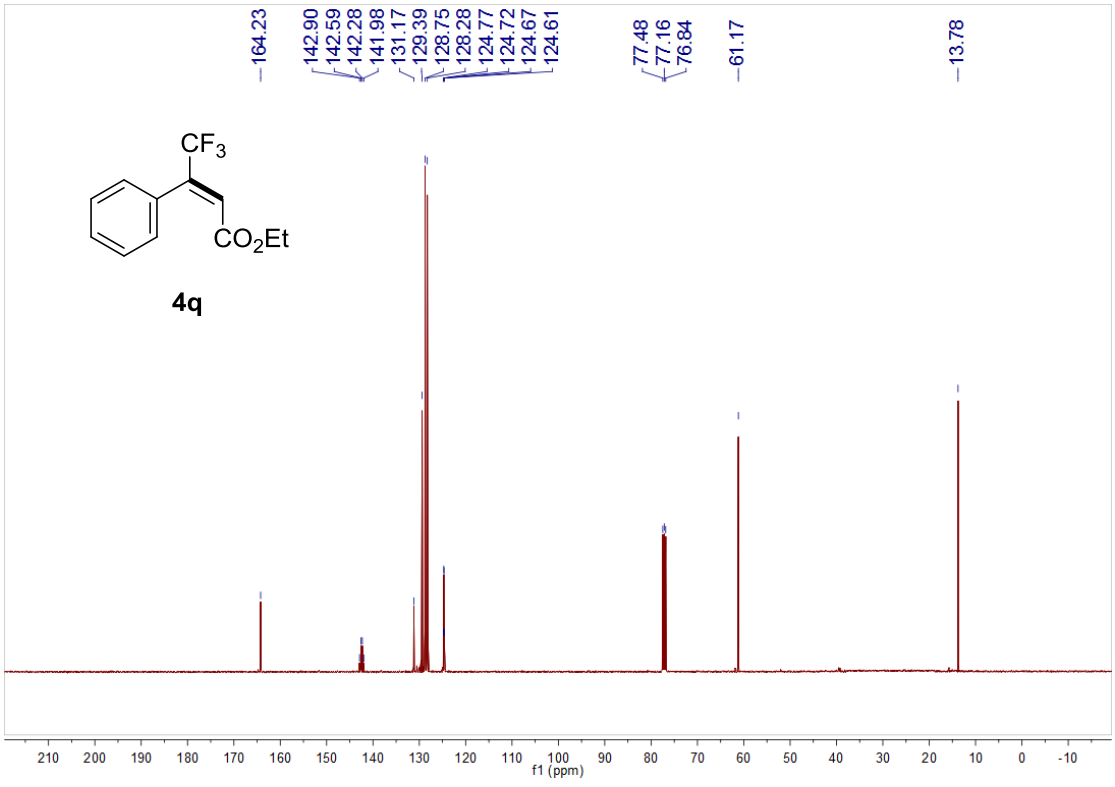
2.01
1.00
2.18
3.35
f1 (ppm)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129.39
128.75
128.28
124.77
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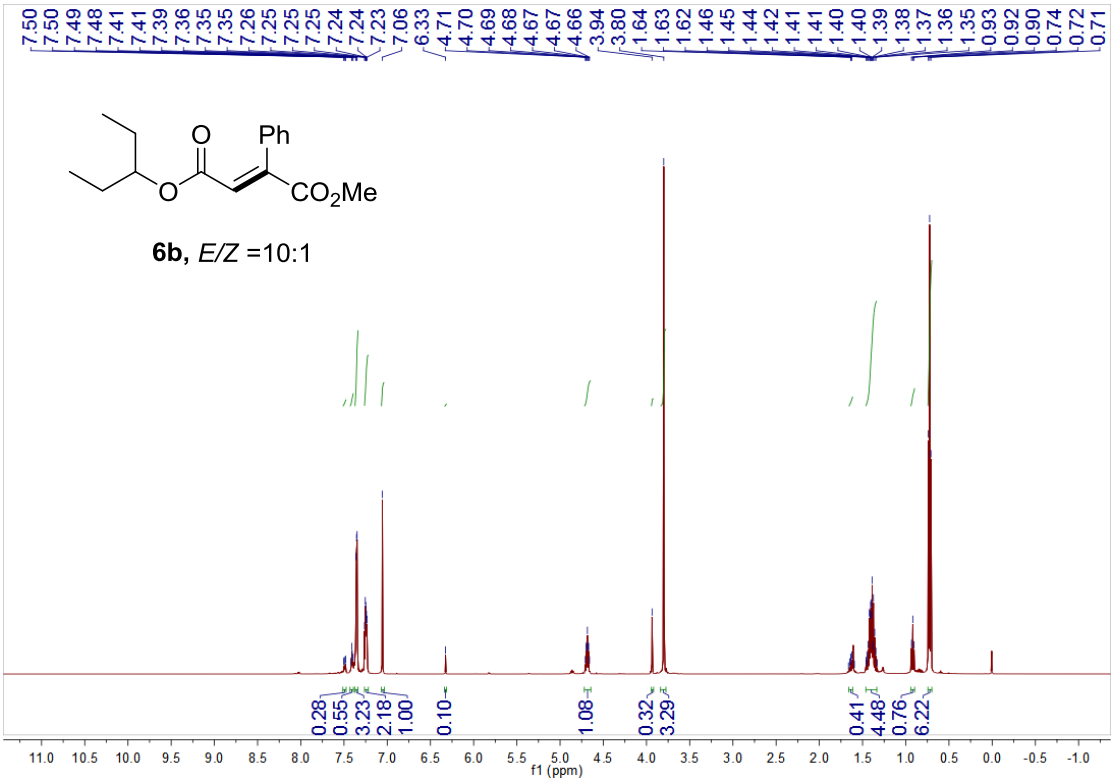
124.61
77.48
77.16
76.84
61.17
13.78
CF3
CO2Et
4q
f1 (ppm)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7.41
7.41
7.39
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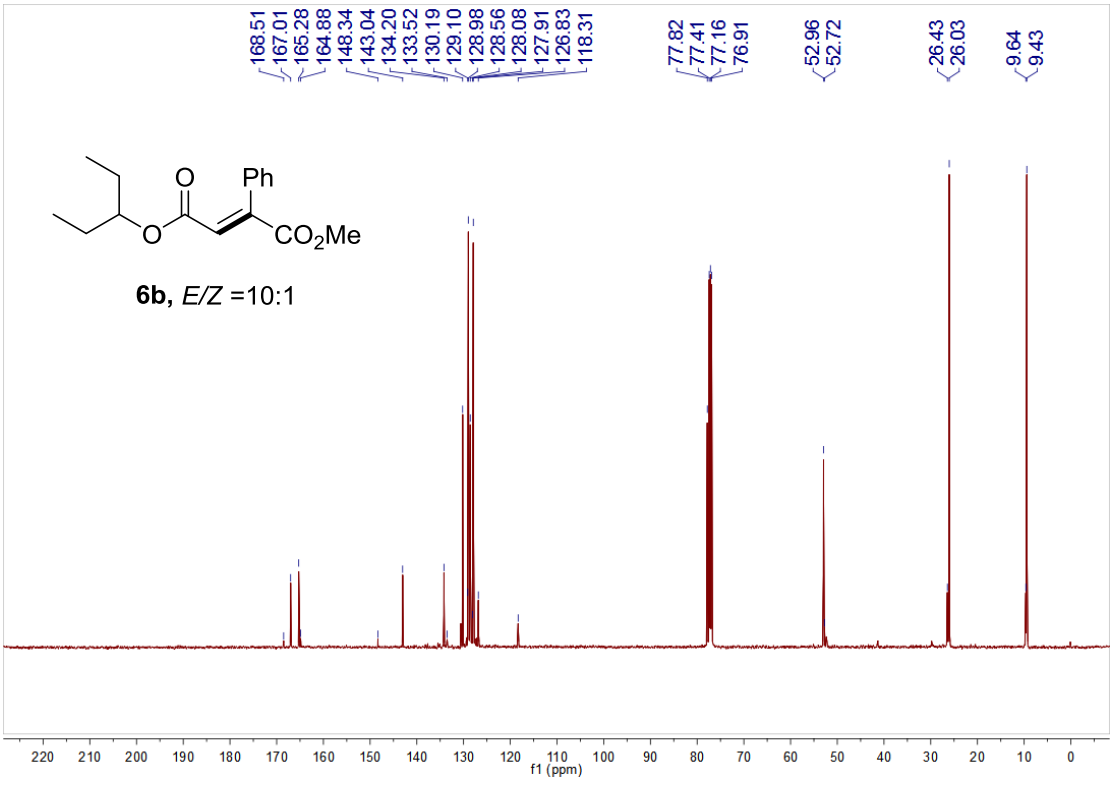
7.35
7.35
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.06
6.33
4.71
4.70
4.69
4.68
4.67
4.67
4.66
3.94
3.80
1.64
1.63
1.62
1.46
1.45
1.44
1.42
1.41
1.41
1.40
1.40
1.39
1.38
1.37
1.36
1.35
0.93
0.92
0.90
0.74
0.72
0.71
O
Ph
O
CO2Me
6b, E/Z =10:1
0.28
0.55
3.23
2.18
1.00
0.10
1.08
0.32
3.29
0.41
4.48
0.76
6.22
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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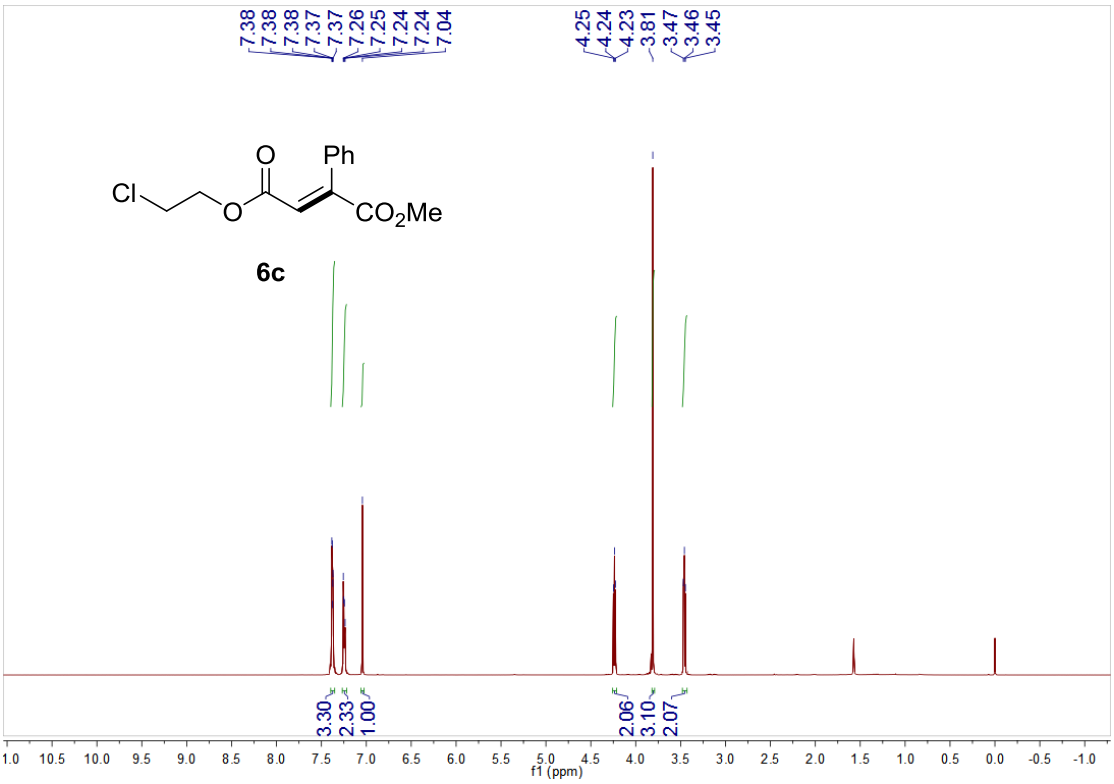
134.20
133.52
130.19
129.10
128.98
128.56
128.08
127.91
126.83
118.31
77.82
77.41
77.16
76.91
52.96
52.72
26.43
26.03
9.64
9.43
O
Ph
O
CO2Me
6b, E/Z =10:1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.38
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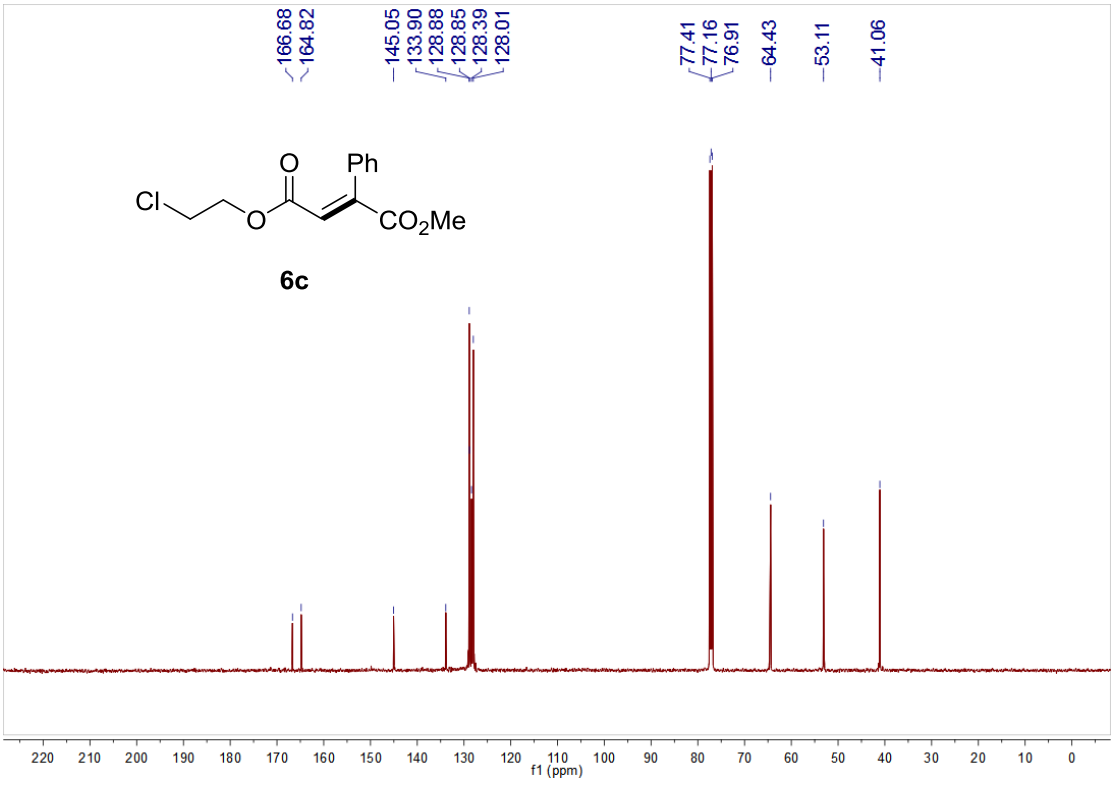
7.37
7.26
7.25
7.24
7.24
7.04
4.25
4.24
4.23
3.81
3.47
3.46
3.45
O
Ph
Cl
O
CO2Me
6c
3.30
2.33
1.00
2.06
3.10
2.07
f1 (ppm)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164.82
145.05
133.90
128.88
128.85
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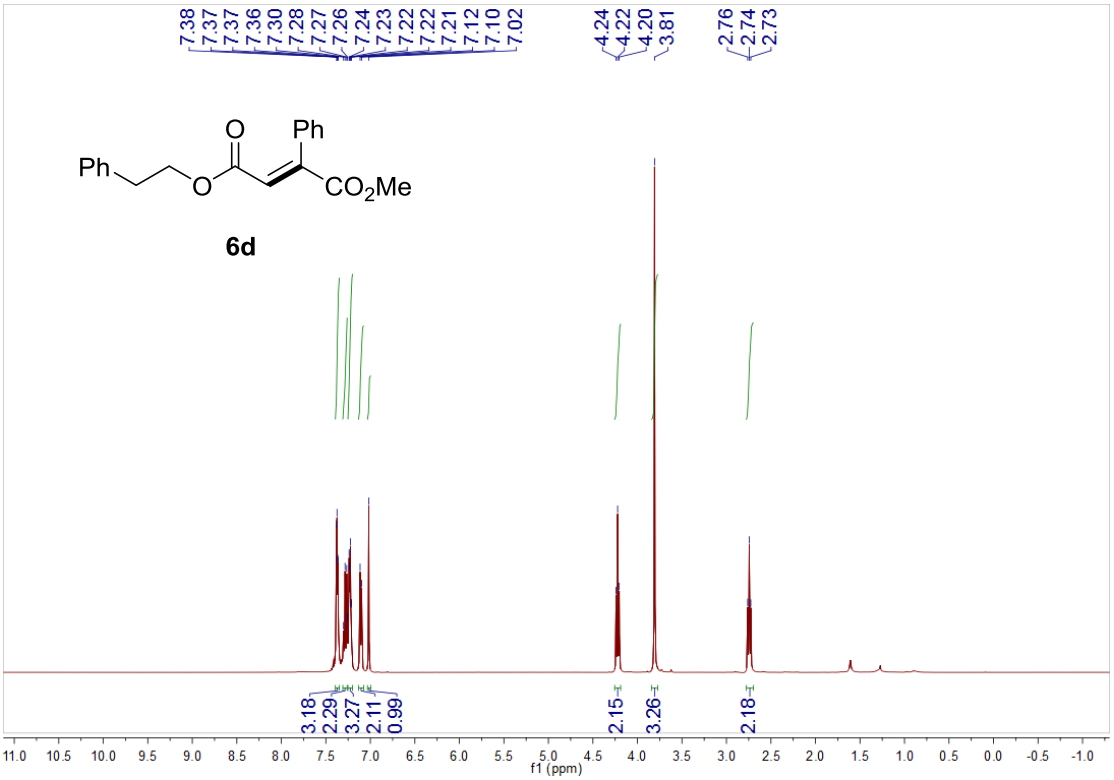
77.41
77.16
76.91
64.43
53.11
41.06
O
Ph
Cl
O
CO2Me
6c
f1 (ppm)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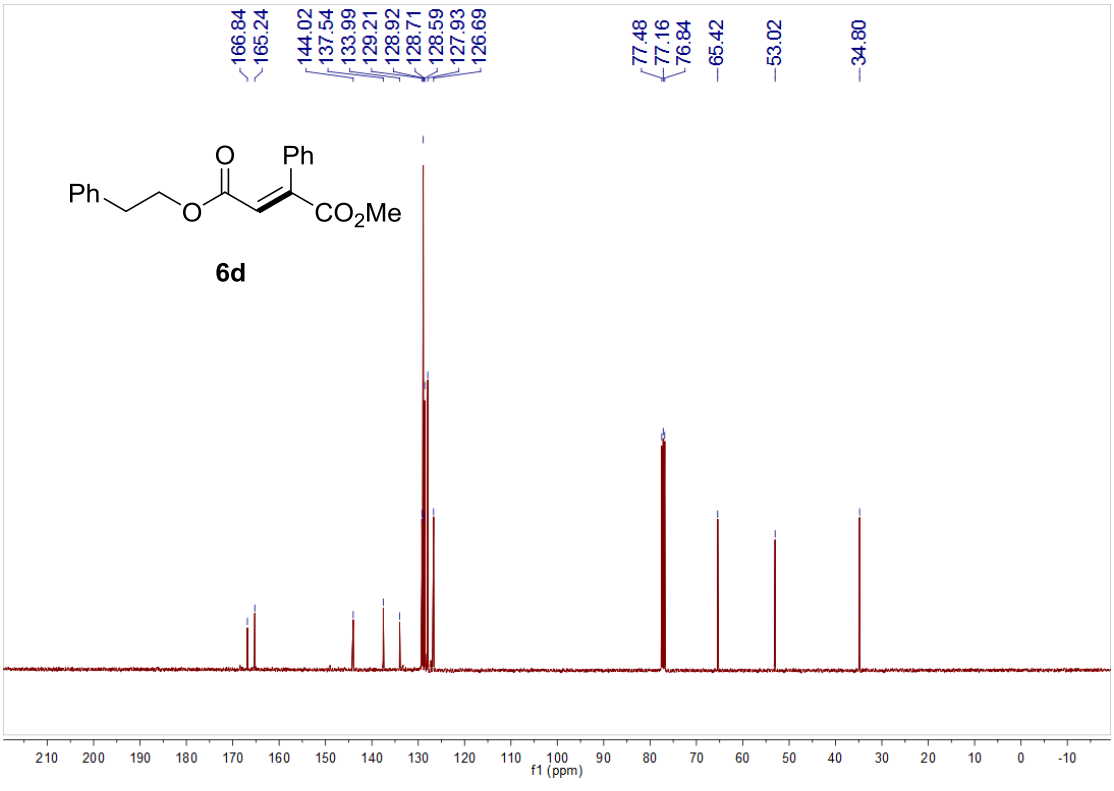
7.26
7.24
7.23
7.22
7.22
7.21
7.12
7.10
7.02
4.24
4.22
4.20
3.81
2.76
2.74
2.73
O
Ph
Ph
O
CO2Me
6d
3.18
2.29
3.27
2.11
0.99
2.15
3.26
2.18
f1 (ppm)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127.93
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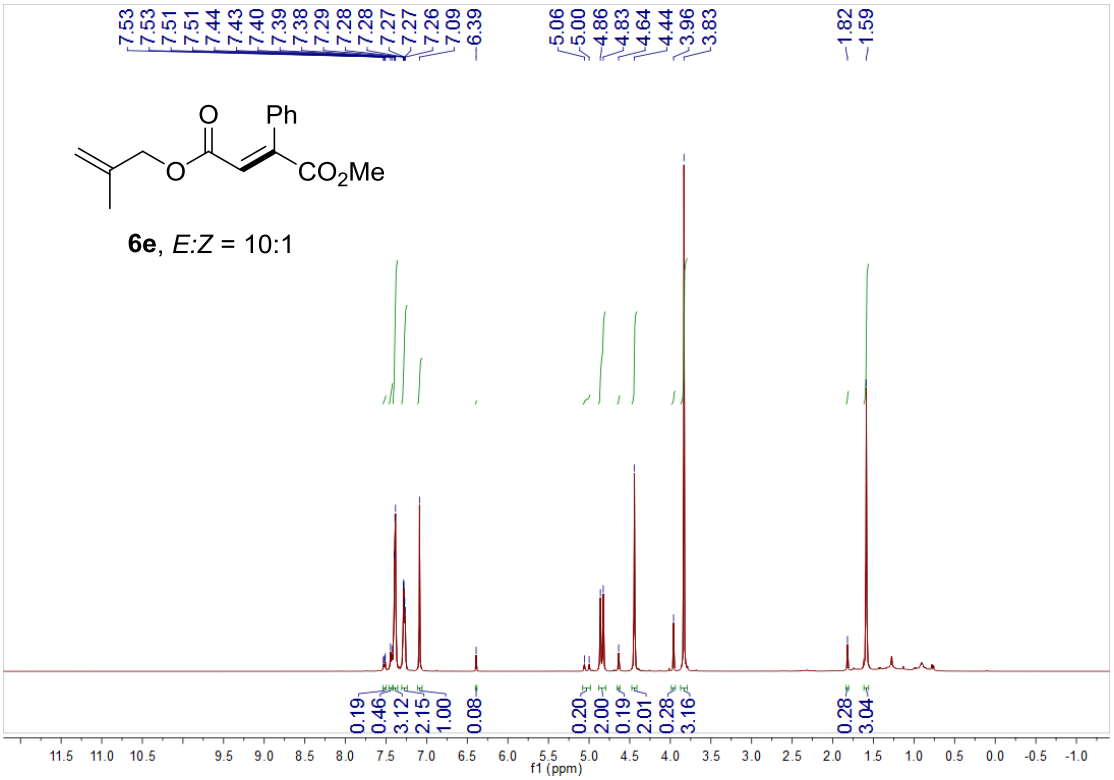
76.84
65.42
53.02
34.80
O
Ph
Ph
O
CO2Me
6d
f1 (ppm)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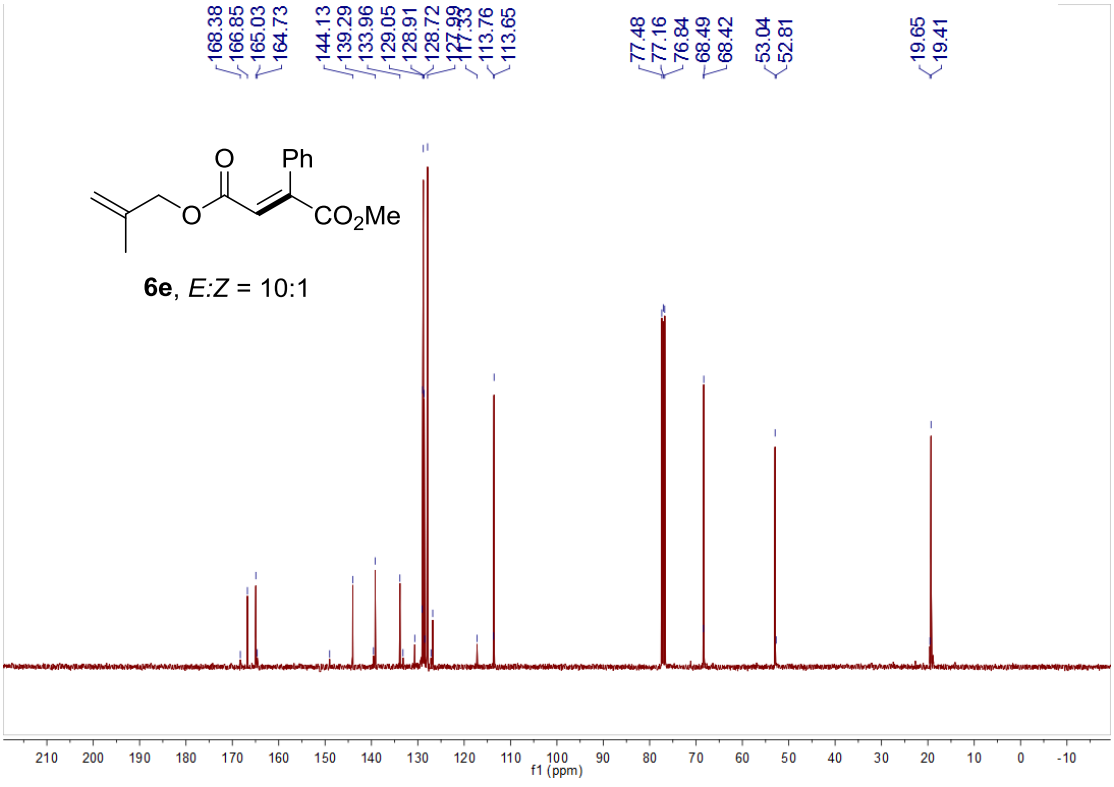
7.39
7.38
7.29
7.28
7.28
7.27
7.27
7.26
7.09
6.39
5.06
5.00
4.86
4.83
4.64
4.44
3.96
3.83
1.82
1.59
O
Ph
O
CO2Me
6e, E:Z = 10:1
0.19
0.46
3.12
2.15
1.00
0.08
0.20
2.00
0.19
2.01
0.28
3.16
0.28
3.04
f1 (ppm)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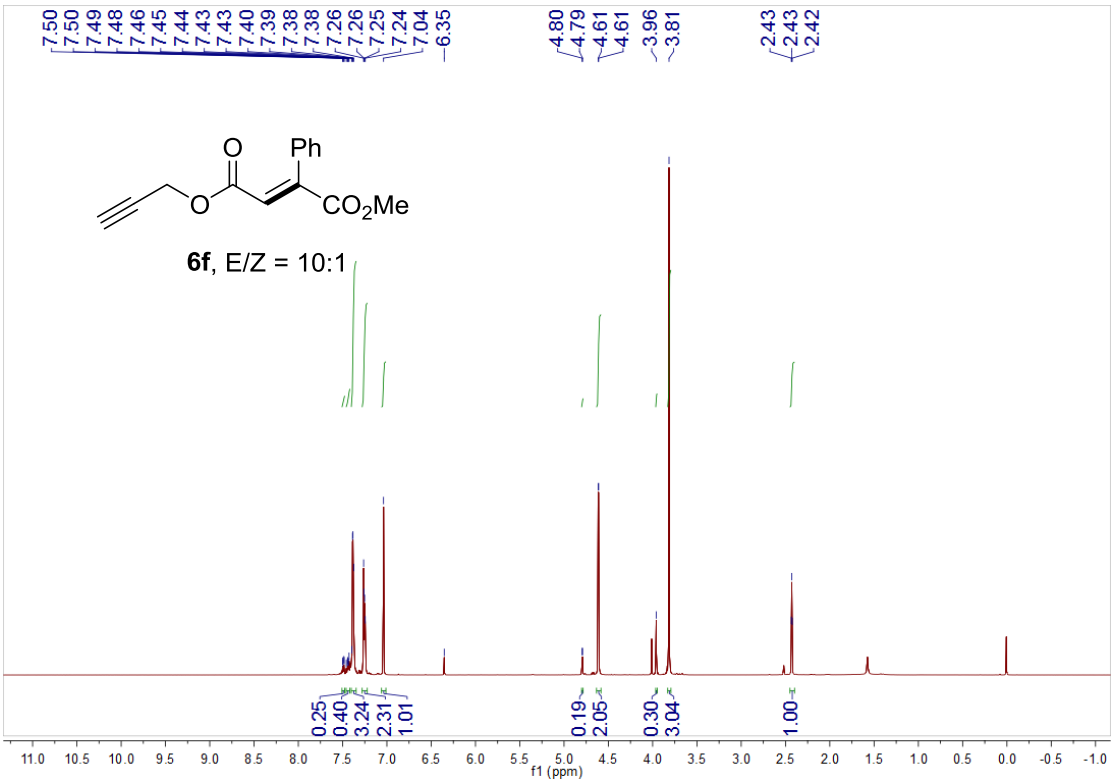
129.05
128.91
128.72
113.76
113.65
77.48
77.16
76.84
68.49
68.42
53.04
52.81
19.65
19.41
O
Ph
O
CO2Me
6e, E:Z = 10:1
f1 (ppm)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7.40
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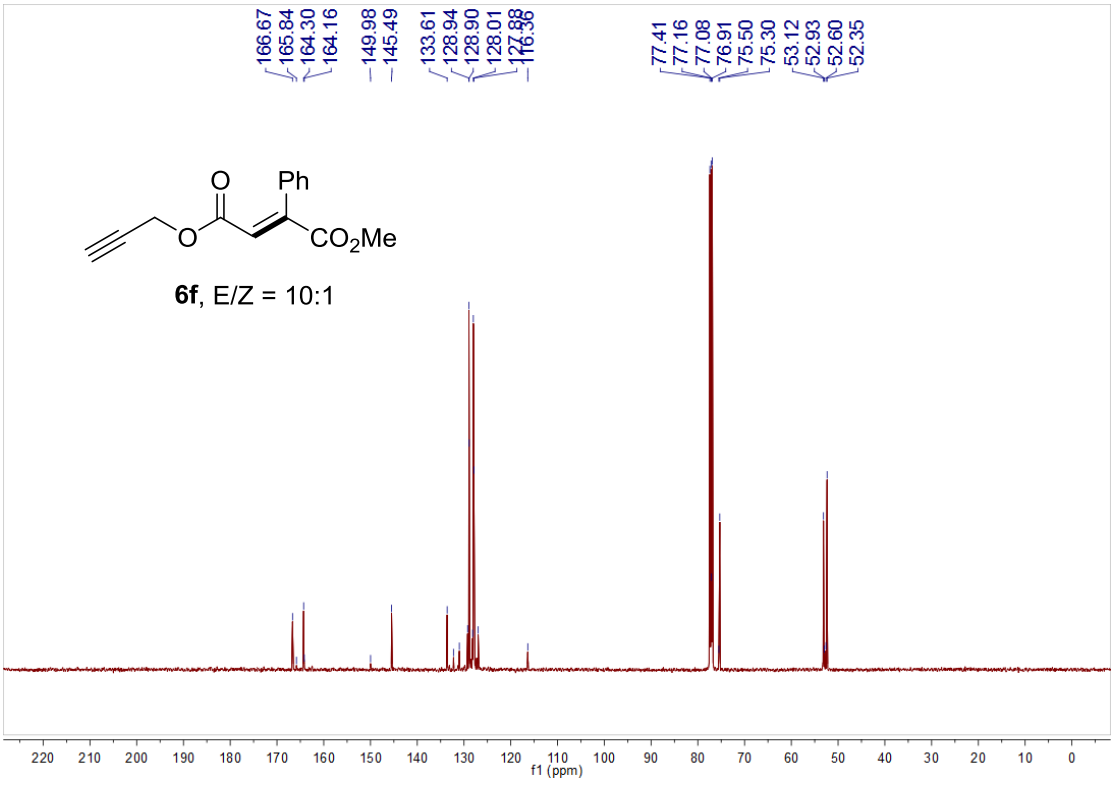
7.38
7.38
7.26
7.26
7.25
7.24
7.04
6.35
4.80
4.79
4.61
4.61
3.96
3.81
2.43
2.43
2.42
O
Ph
O
CO2Me
6f, E/Z = 10:1
0.25
0.40
3.24
2.31
1.01
0.19
2.05
0.30
3.04
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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164.16
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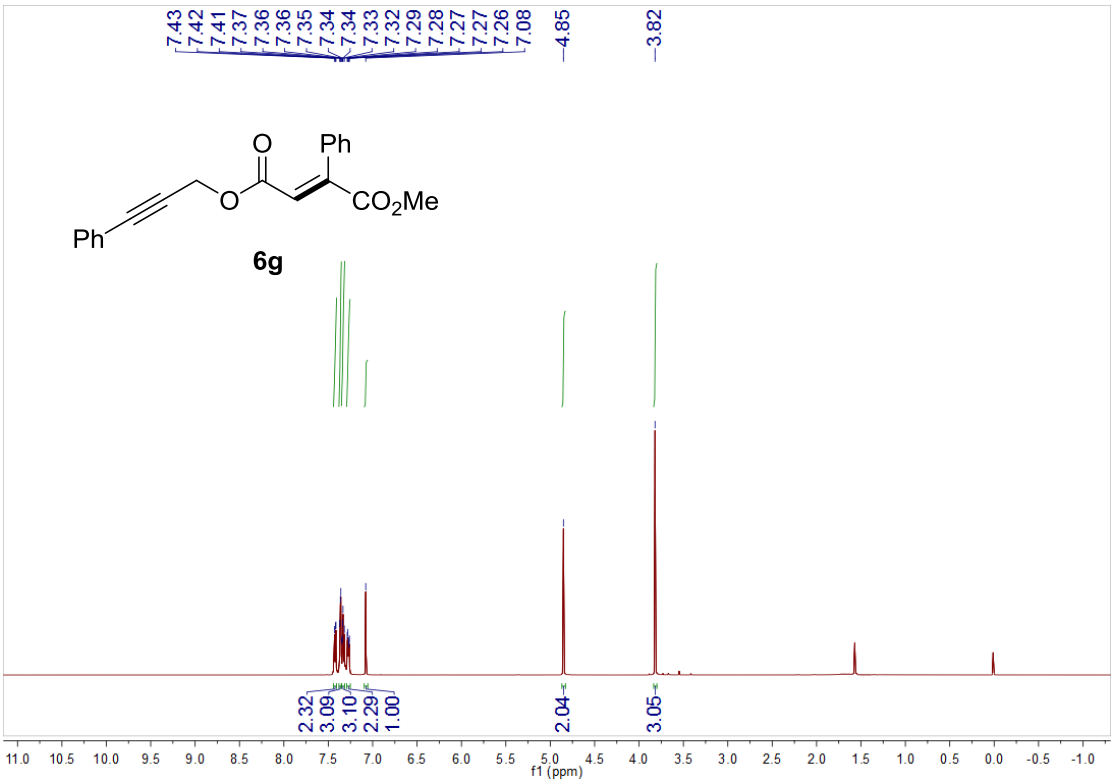
145.49
133.61
128.94
128.90
128.01
77.41
77.16
77.08
76.91
75.50
75.30
53.12
52.93
52.60
52.35
O
Ph
O
CO2Me
6f, E/Z = 10:1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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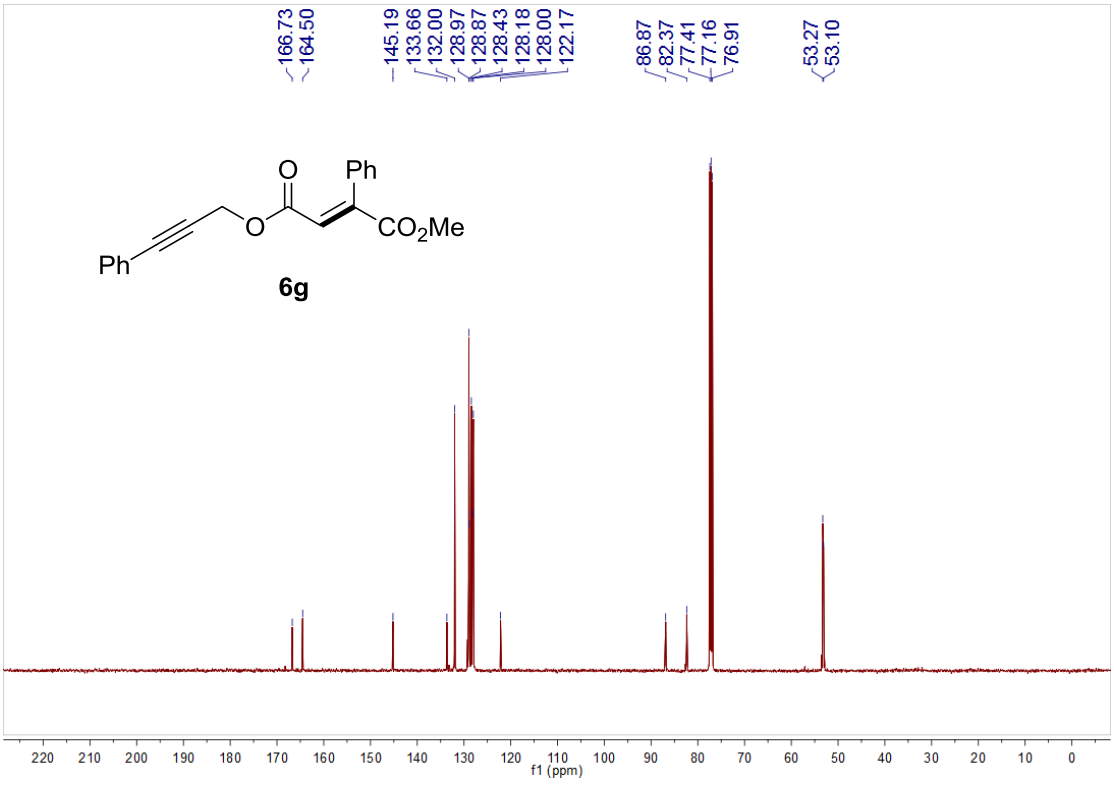
7.32
7.29
7.28
7.27
7.27
7.26
7.08
4.85
3.82
O
Ph
O
CO2Me
Ph
6g
2.32
3.09
3.10
2.29
1.00
2.04
3.05
f1 (ppm)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128.43
128.18
128.00
122.17
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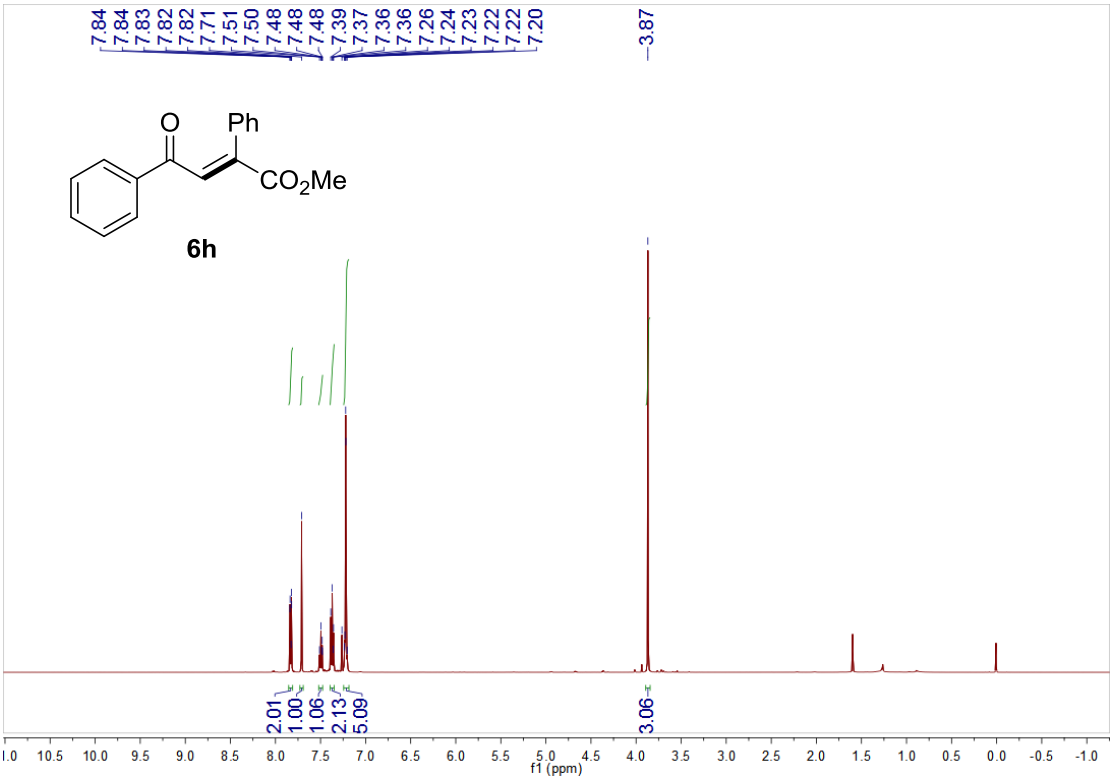
82.37
77.41
77.16
76.91
53.27
53.10
O
Ph
O
CO2Me
Ph
6g
f1 (ppm)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7.36
7.36
7.26
7.24
7.23
7.22
7.22
7.20
3.87
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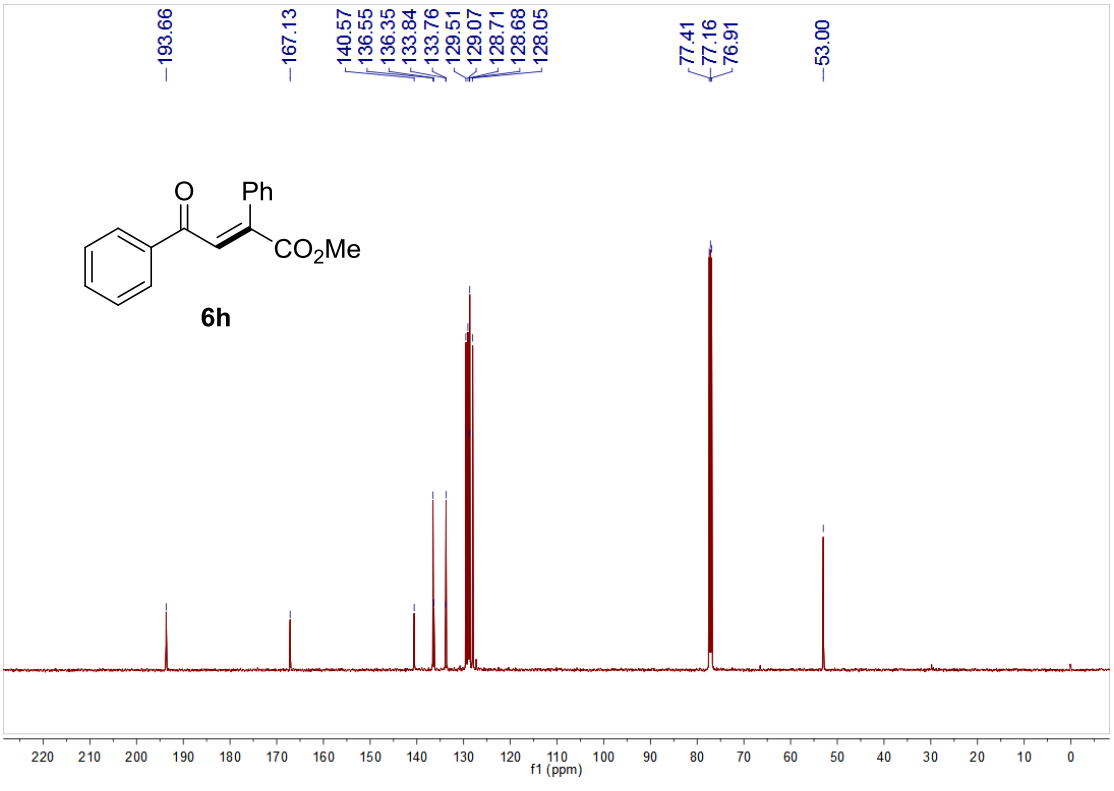
Ph
CO2Me
6h
2.01
1.00
1.06
2.13
5.09
3.06
f1 (ppm)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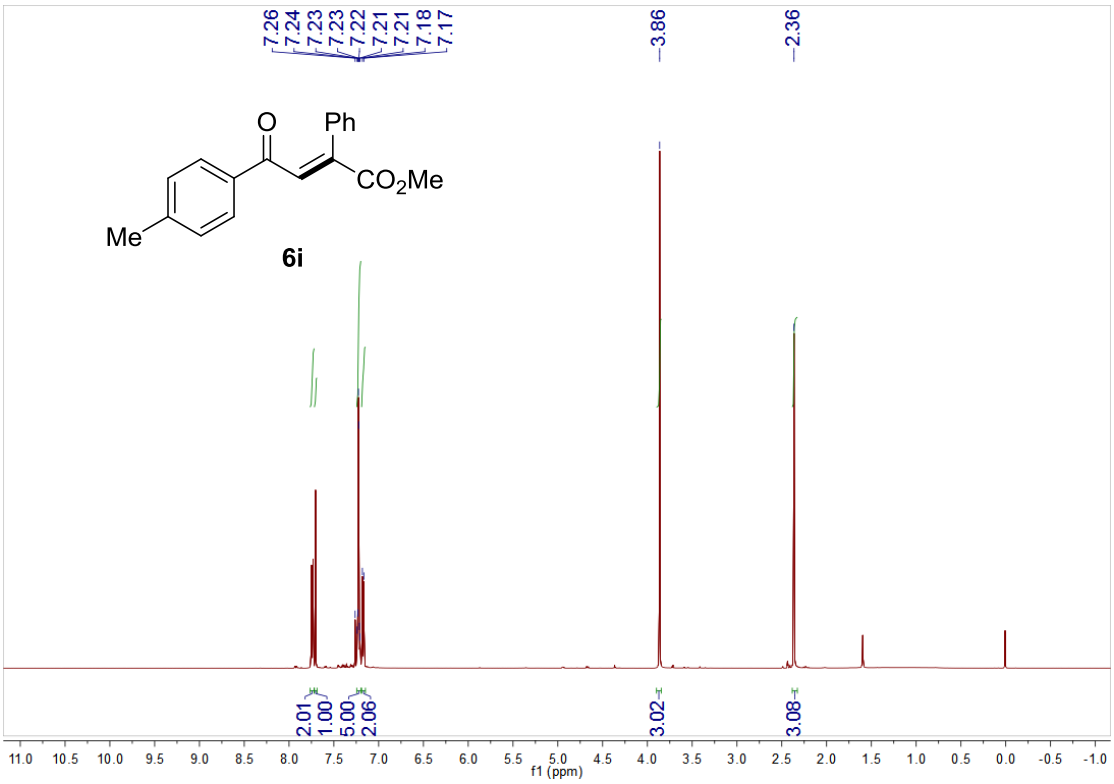
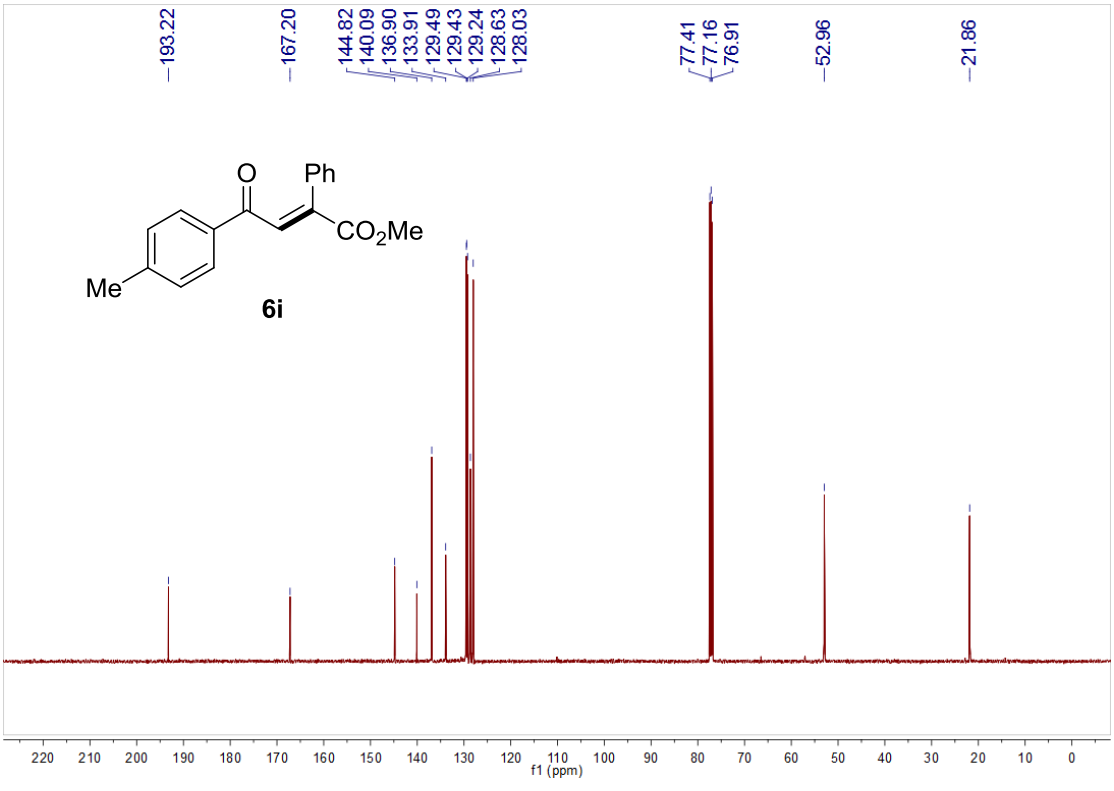
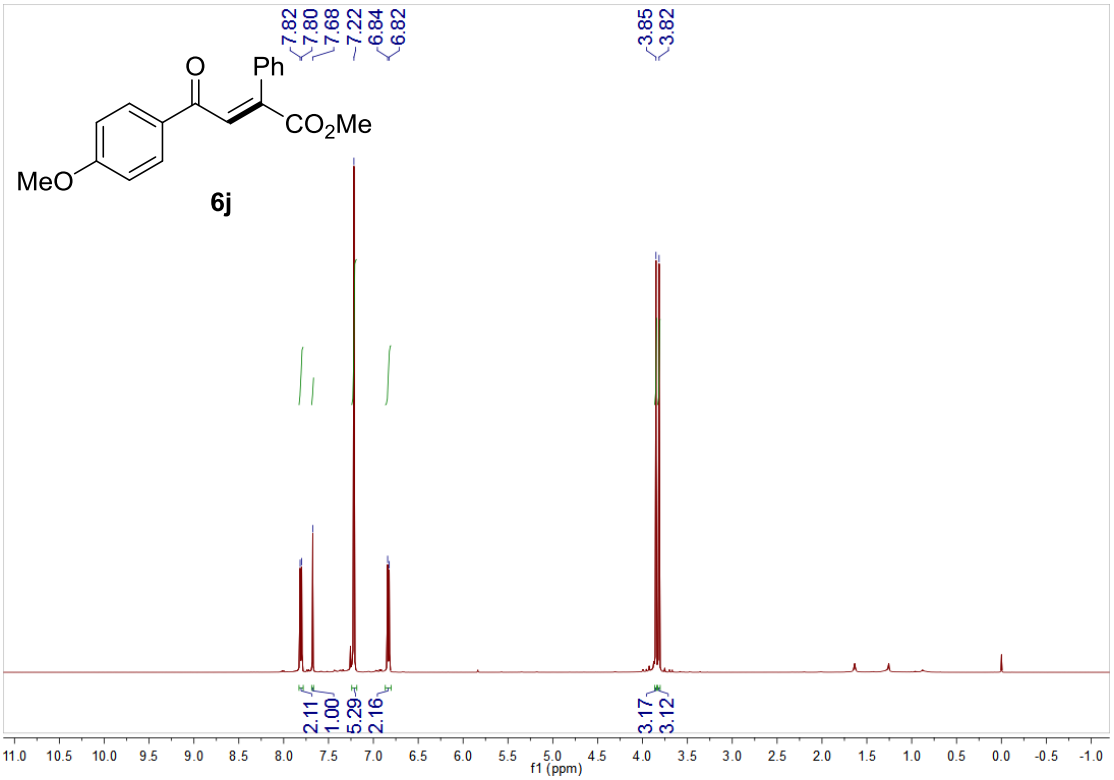
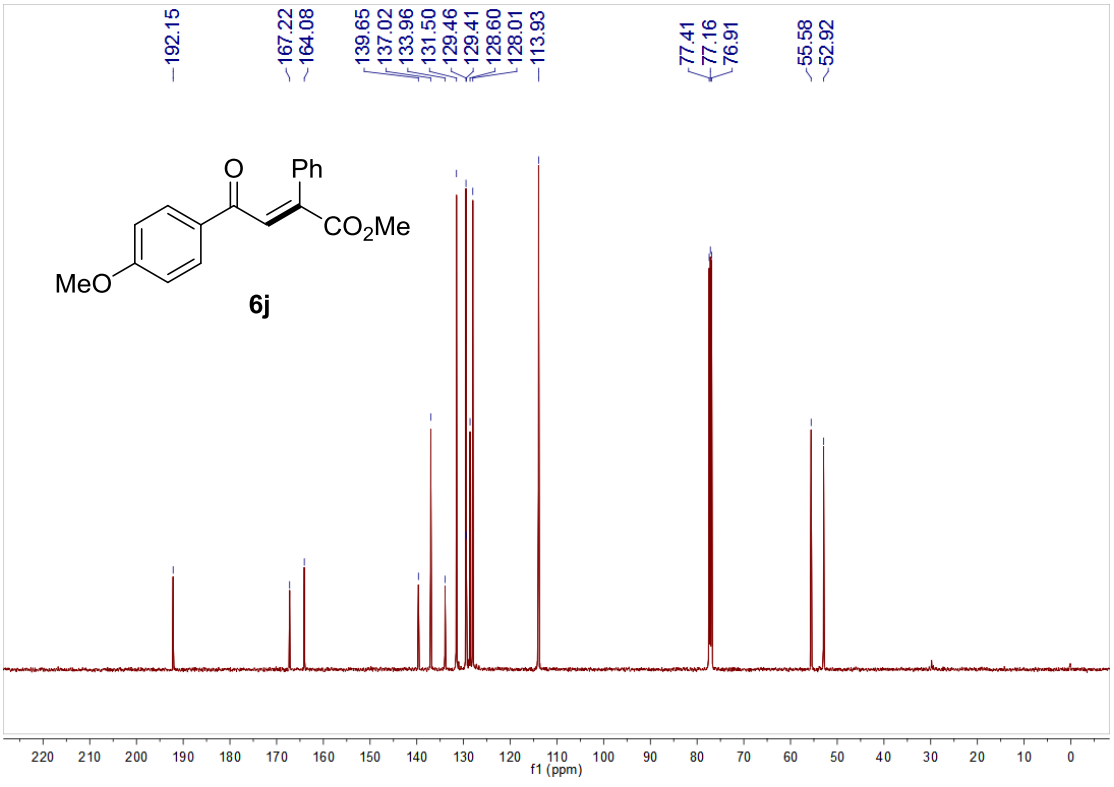
136.35
133.84
133.76
129.51
129.07
128.71
128.68
128.05
77.41
77.16
76.91
53.00
O
Ph
CO2Me
6h
f1 (ppm)


7.26
7.24
7.23
7.23
7.22
7.21
7.21
7.18
7.17
3.86
2.36
O
Ph
CO2Me
Me
6i
2.01
1.00
5.00
2.06
3.02
3.08
f1 (ppm)


193.22
167.20
144.82
140.09
136.90
133.91
129.49
129.43
129.24
128.63
128.03
77.41
77.16
76.91
52.96
21.86
O
Ph
CO2Me
Me
6i
f1 (ppm)


7.82
7.80
7.68
7.22
6.84
6.82
3.85
3.82
O
Ph
CO2Me
MeO
6j
2.11
1.00
5.29
2.16
3.17
3.12
f1 (ppm)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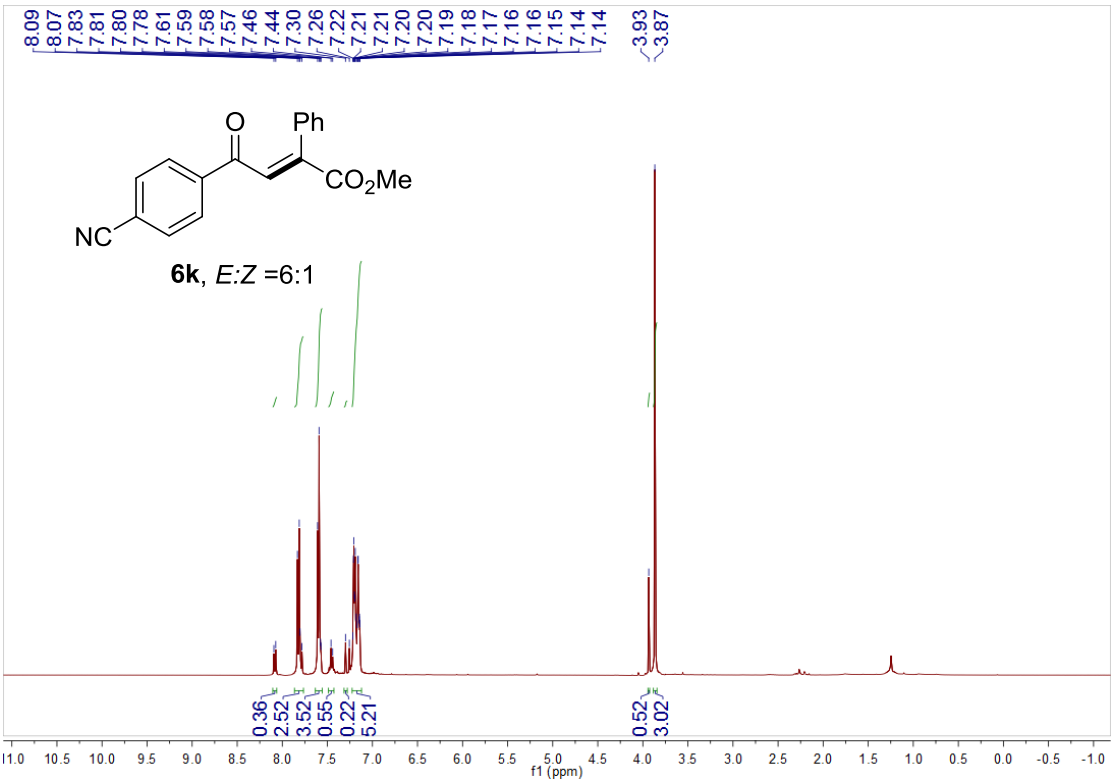
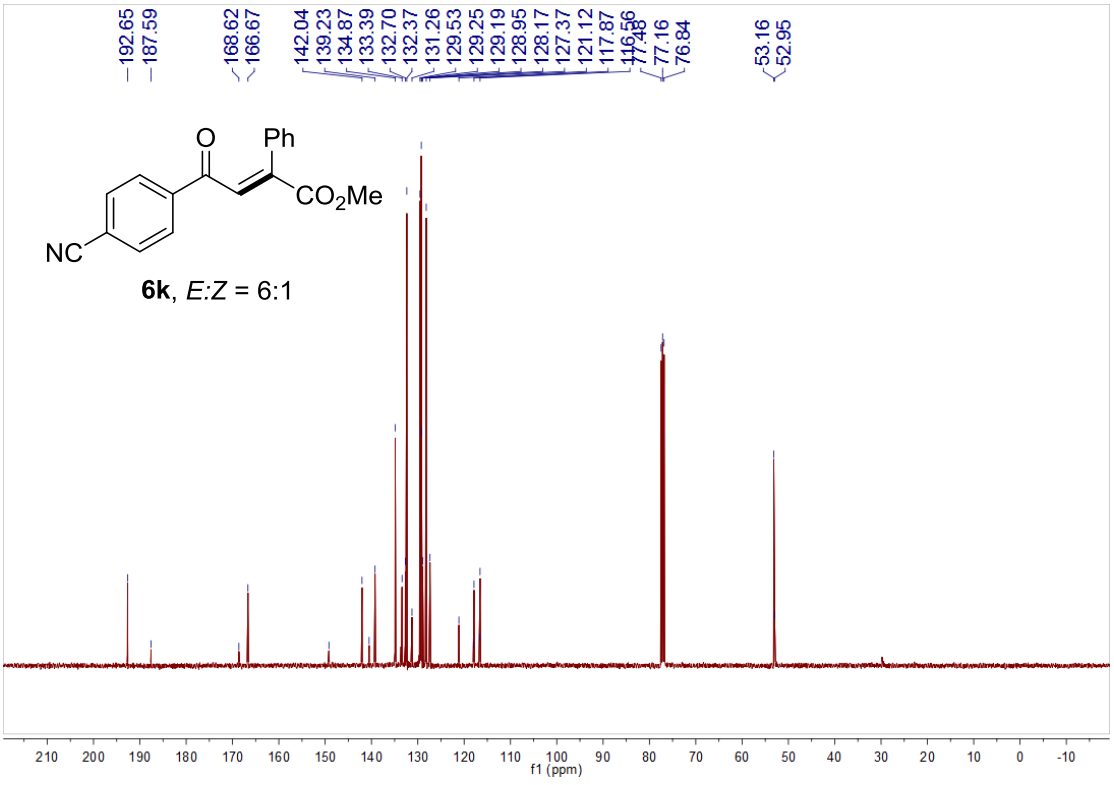
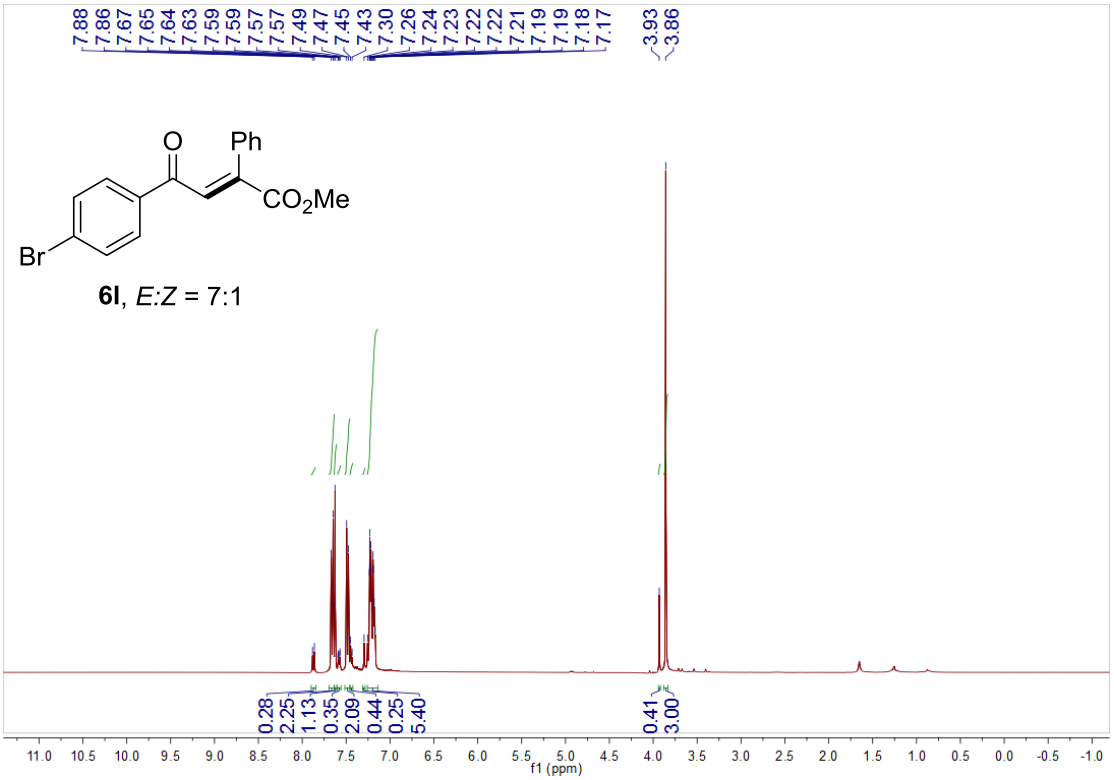
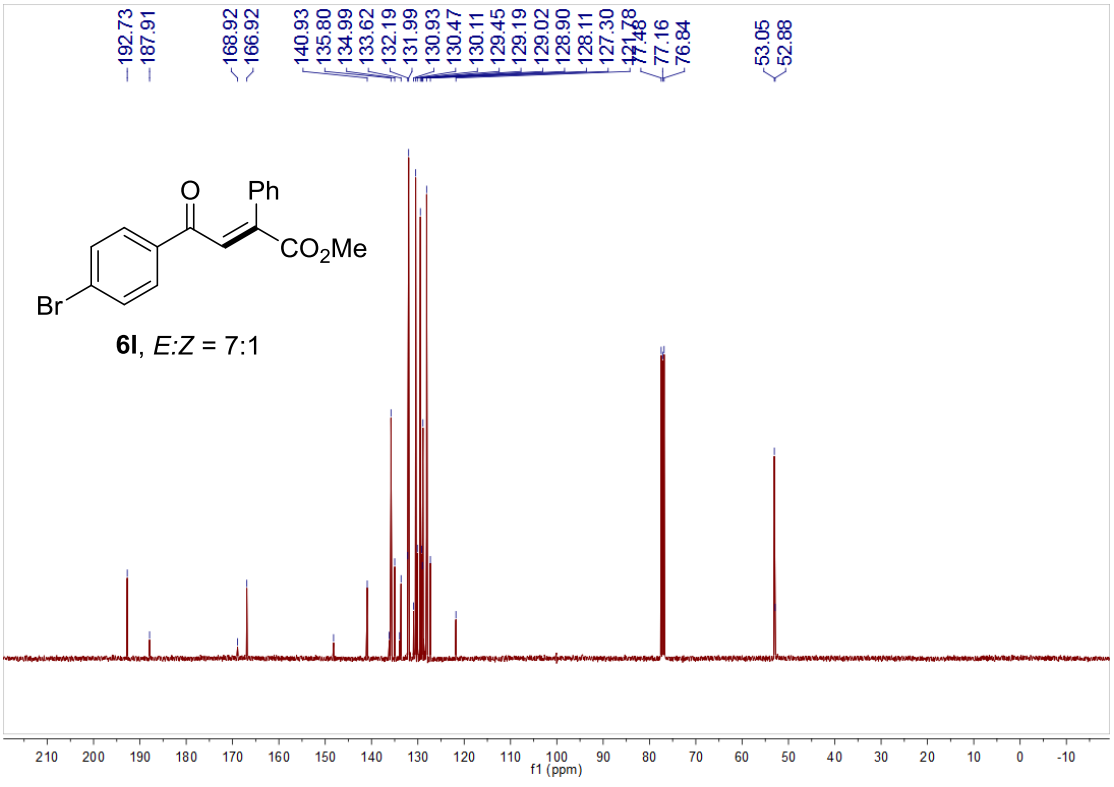
167.22
164.08
139.65
137.02
133.96
131.50
129.46
129.41
128.60
128.01
113.93
77.41
77.16
76.91
55.58
52.92
O
Ph
CO2Me
MeO
6j
f1 (ppm)


8.09
8.07
7.83
7.81
7.80
7.78
7.61
7.59
7.58
7.57
7.46
7.44
7.30
7.26
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.16
7.15
7.14
7.14
3.93
3.87
O
Ph
CO2Me
NC
6k, E:Z =6:1
0.36
2.52
3.52
0.55
0.22
5.21
0.52
3.02
f1 (ppm)


192.65
187.59
168.62
166.67
142.04
139.23
134.87
133.39
132.70
132.37
131.26
129.53
129.25
129.19
128.95
128.17
127.37
121.12
117.87
116.56
77.48
77.16
76.84
53.16
52.95
O
Ph
CO2Me
NC
6k, E:Z = 6:1
f1 (ppm)


7.88
7.86
7.67
7.65
7.64
7.63
7.59
7.59
7.57
7.57
7.49
7.47
7.45
7.43
7.30
7.26
7.24
7.23
7.22
7.22
7.21
7.19
7.19
7.18
7.17
3.93
3.86
O
Ph
CO2Me
Br
6l, E:Z = 7:1
0.28
2.25
1.13
0.35
2.09
0.44
0.25
5.40
0.41
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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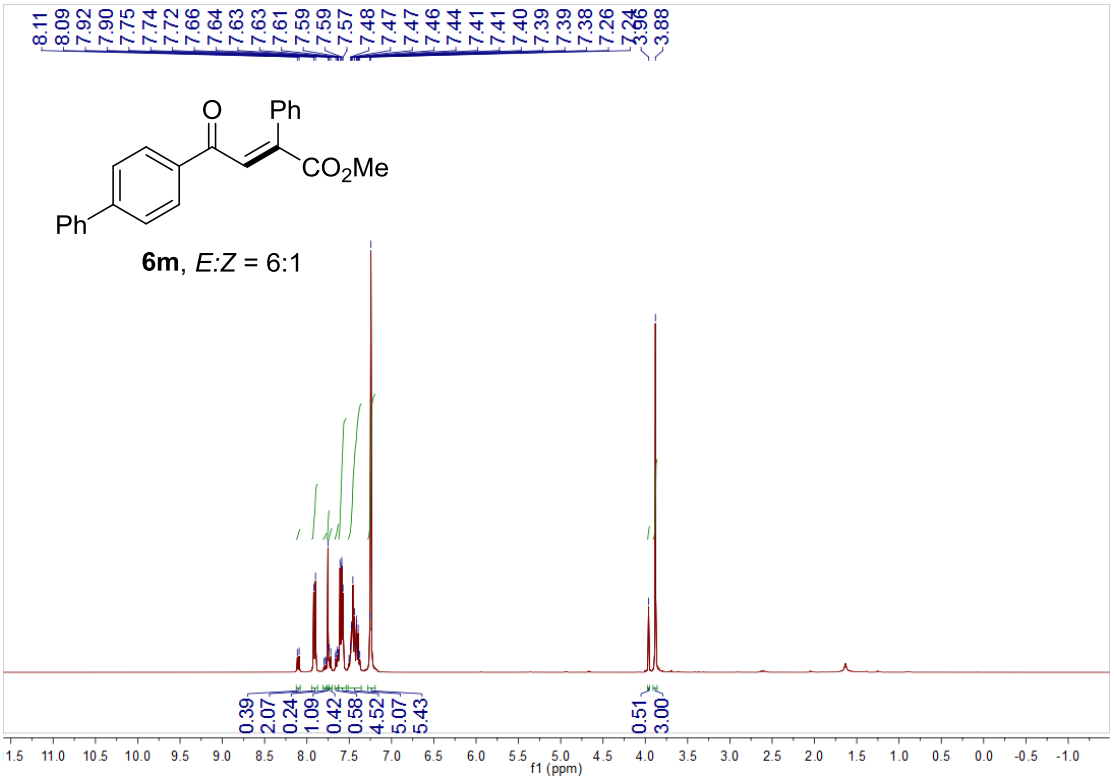
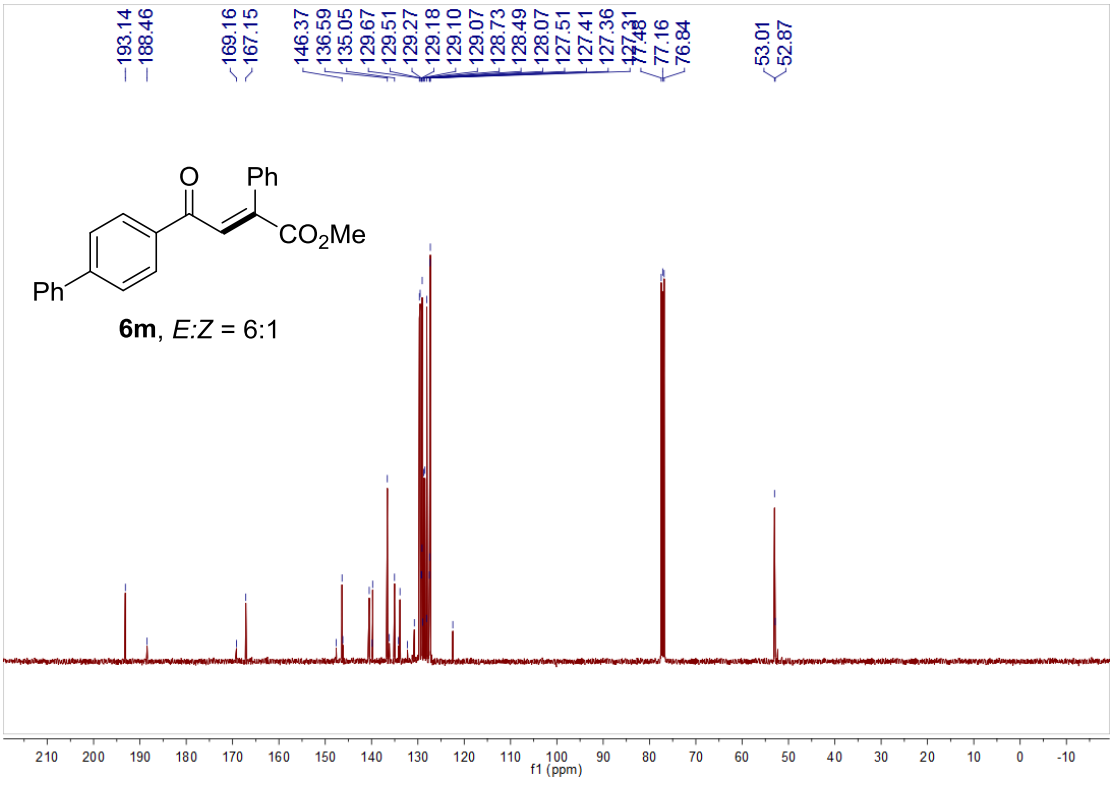
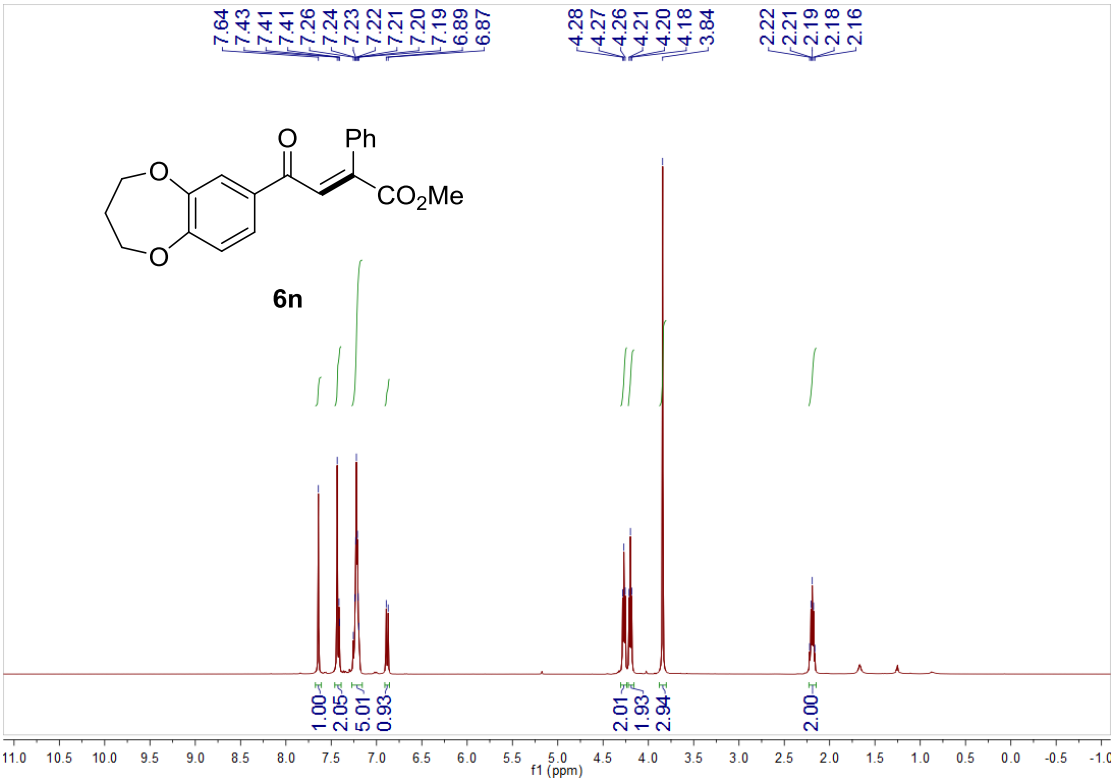
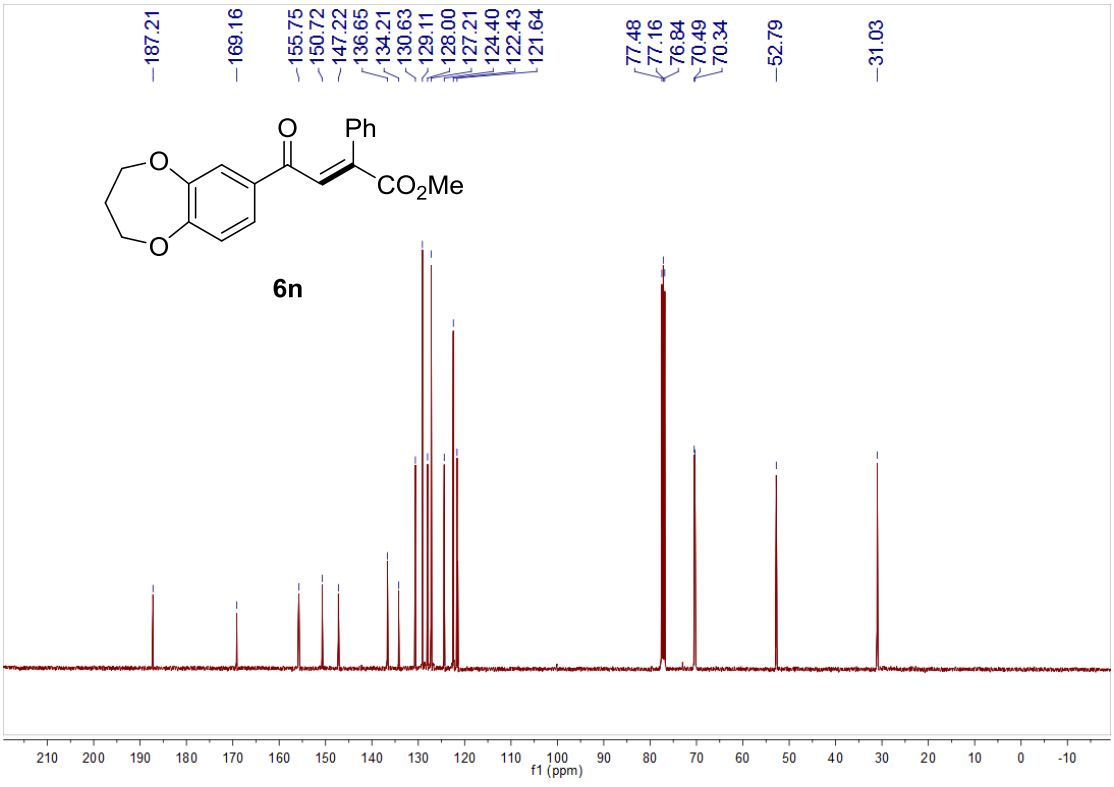
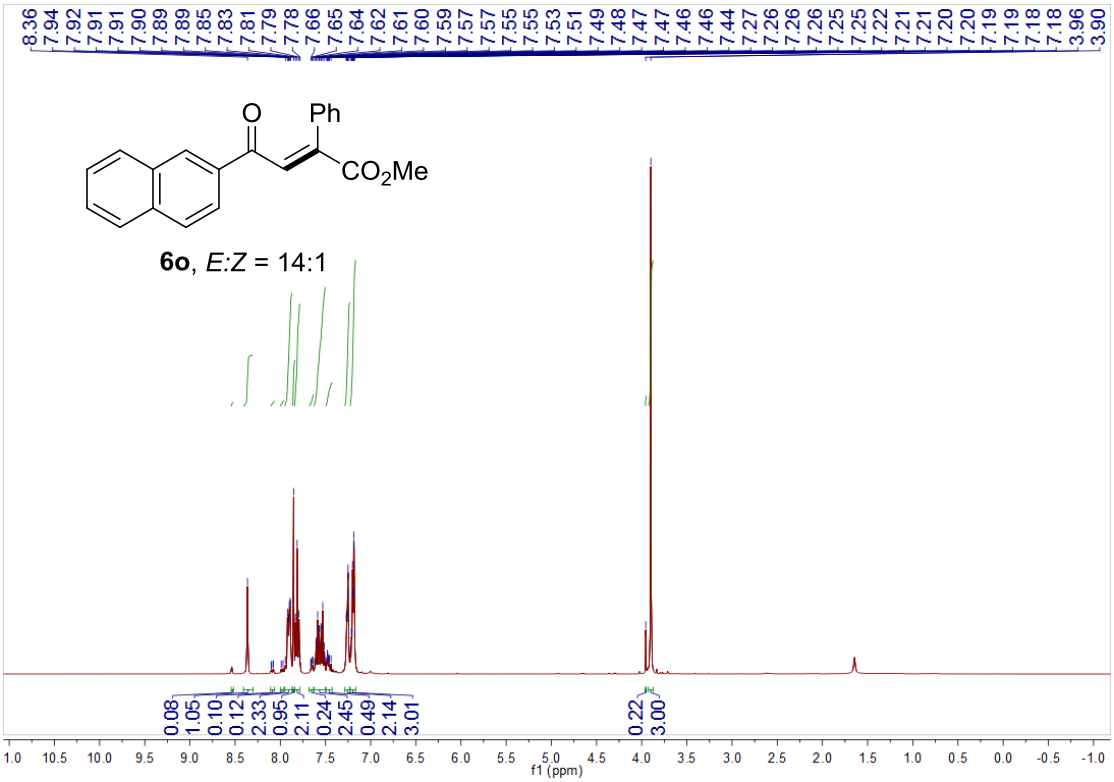
187.91
168.92
166.92
140.93
135.80
134.99
133.62
132.19
131.99
130.93
130.47
130.11
129.45
129.19
129.02
128.90
128.11
127.30
121.78
77.48
77.16
76.84
53.05
52.88
O
Ph
CO2Me
Br
6l, E:Z = 7:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

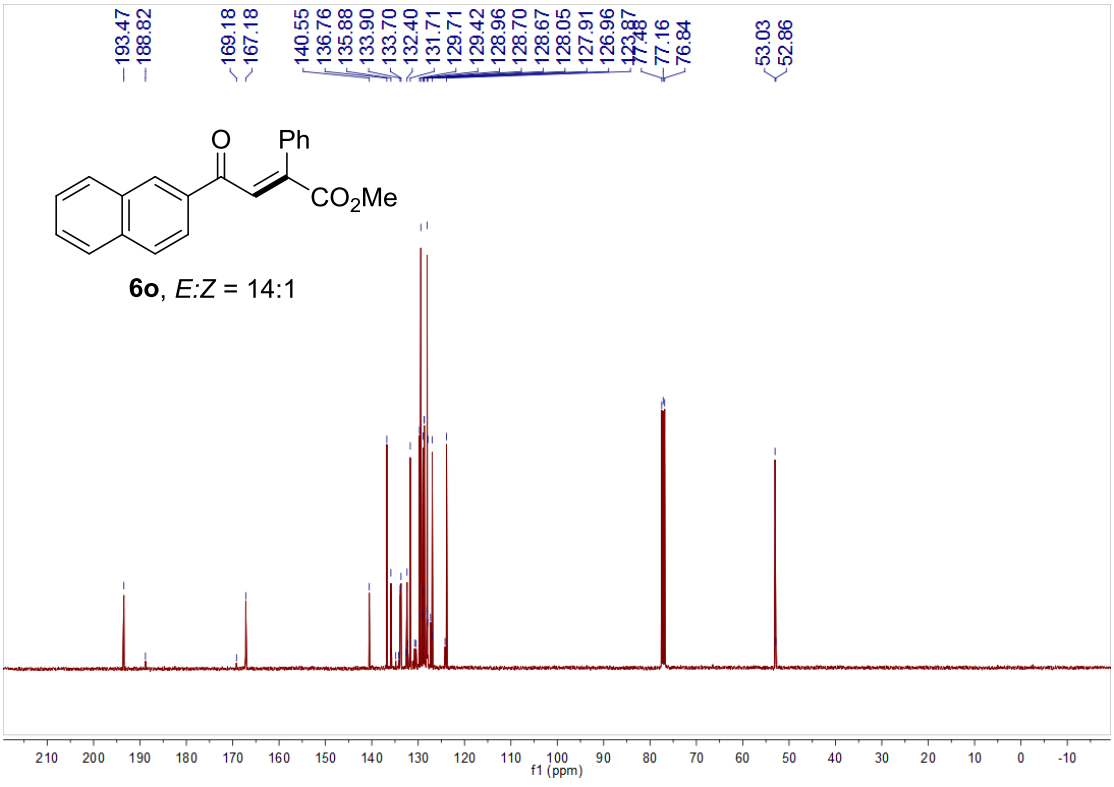

8.11
8.09
7.92
7.90
7.75
7.74
7.72
7.66
7.64
7.63
7.63
7.61
7.59
7.59
7.57
7.48
7.47
7.47
7.46
7.44
7.41
7.41
7.40
7.39
7.39
7.38
7.26
3.96
3.88
O
Ph
CO2Me
Ph
6m, E:Z = 6:1
0.39
2.07
0.24
1.09
0.42
0.58
4.52
5.07
5.43
0.51
3.00
f1 (ppm)

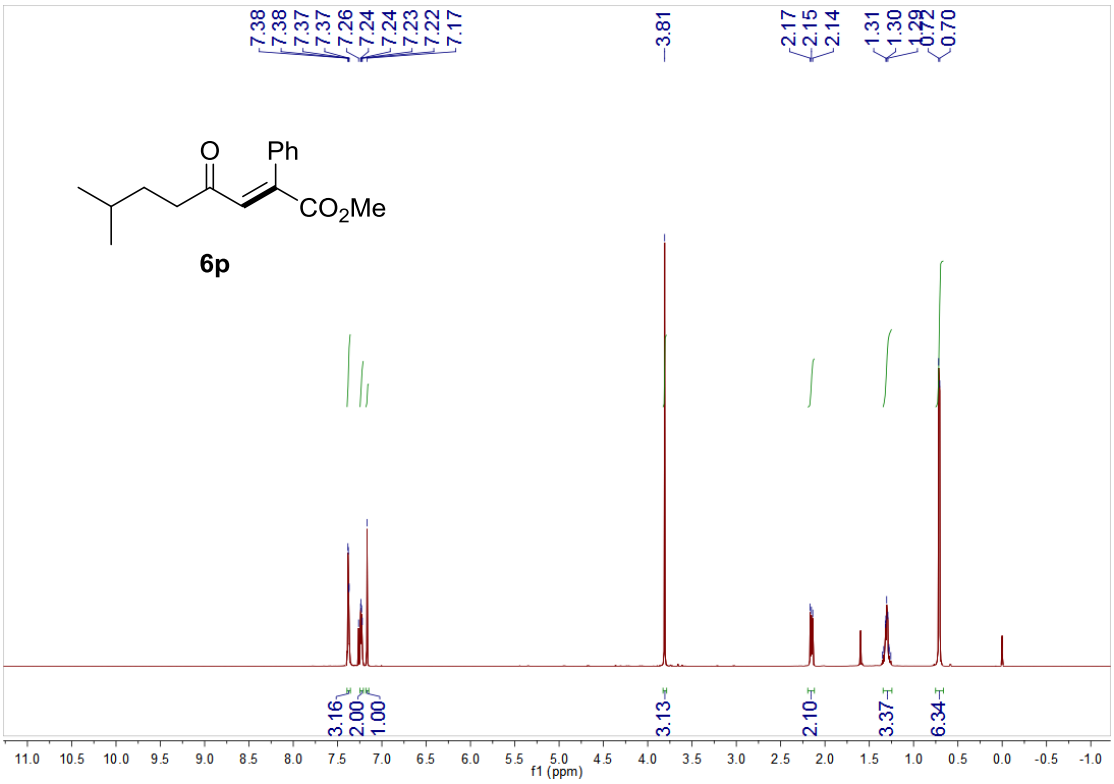

193.14
188.46
169.16
167.15
146.37
136.59
135.05
129.67
129.51
129.27
129.18
129.10
129.07
128.73
128.49
128.07
127.51
127.41
127.36
77.16
76.84
53.01
52.87
O
Ph
CO2Me
Ph
6m, E:Z = 6:1
f1 (ppm)

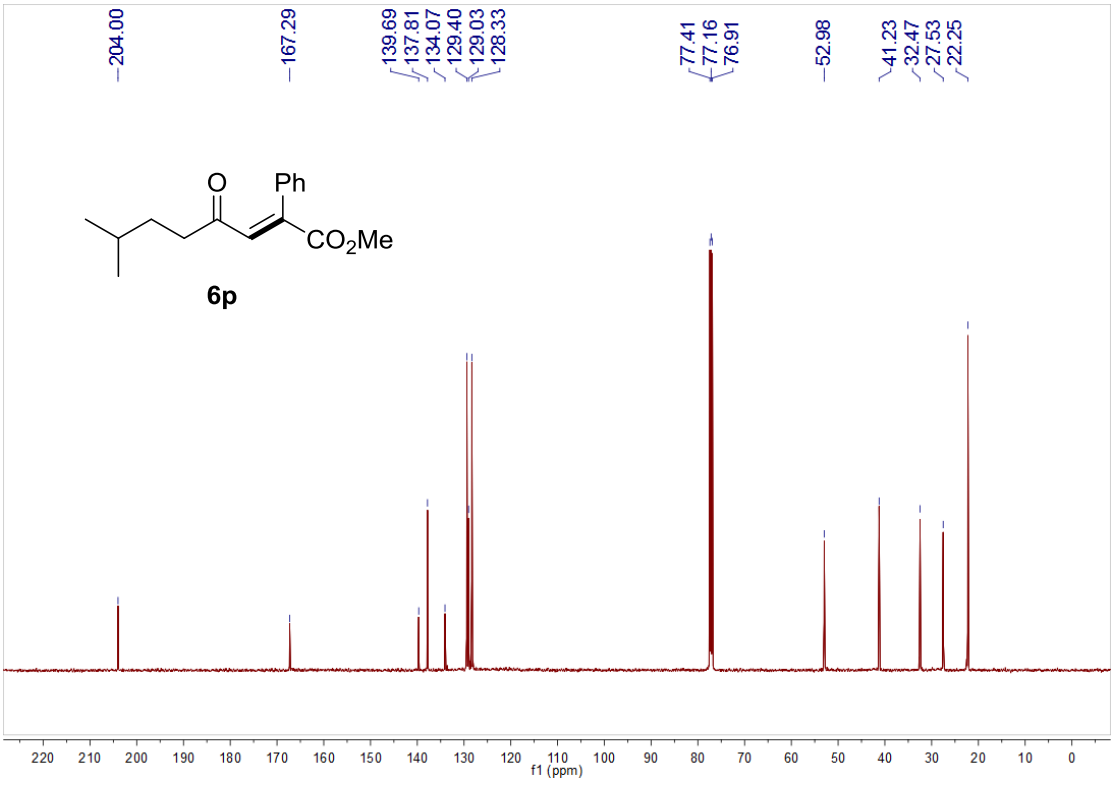

7.64
7.43
7.41
7.41
7.26
7.24
7.23
7.22
7.21
7.20
7.19
6.89
6.87
4.28
4.27
4.26
4.21
4.20
4.18
3.84
2.22
2.21
2.19
2.18
2.16
O
Ph
O
O
CO2Me
6n
1.00
2.05
5.01
0.93
2.01
1.93
2.94
2.00
f1 (ppm)

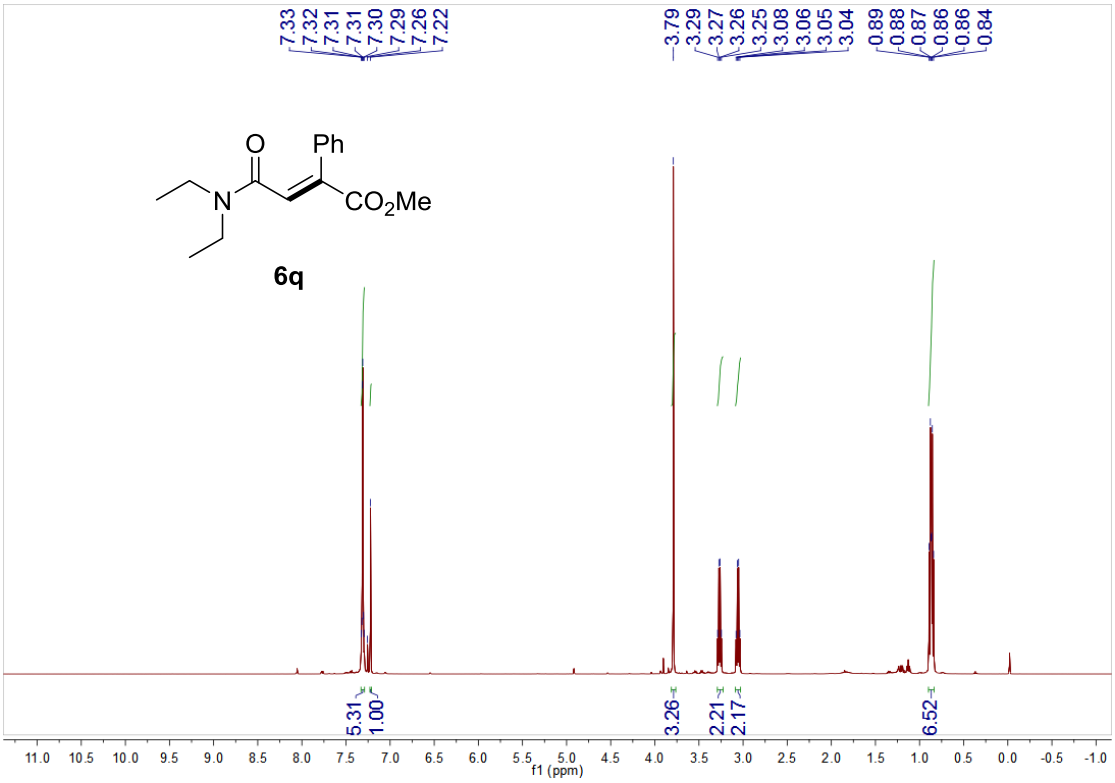

187.21
169.16
155.75
150.72
147.22
136.65
134.21
130.63
129.11
128.00
127.21
124.40
122.43
121.64
77.48
77.16
76.84
70.49
70.34
52.79
31.03
O
Ph
O
O
CO2Me
6n
f1 (ppm)

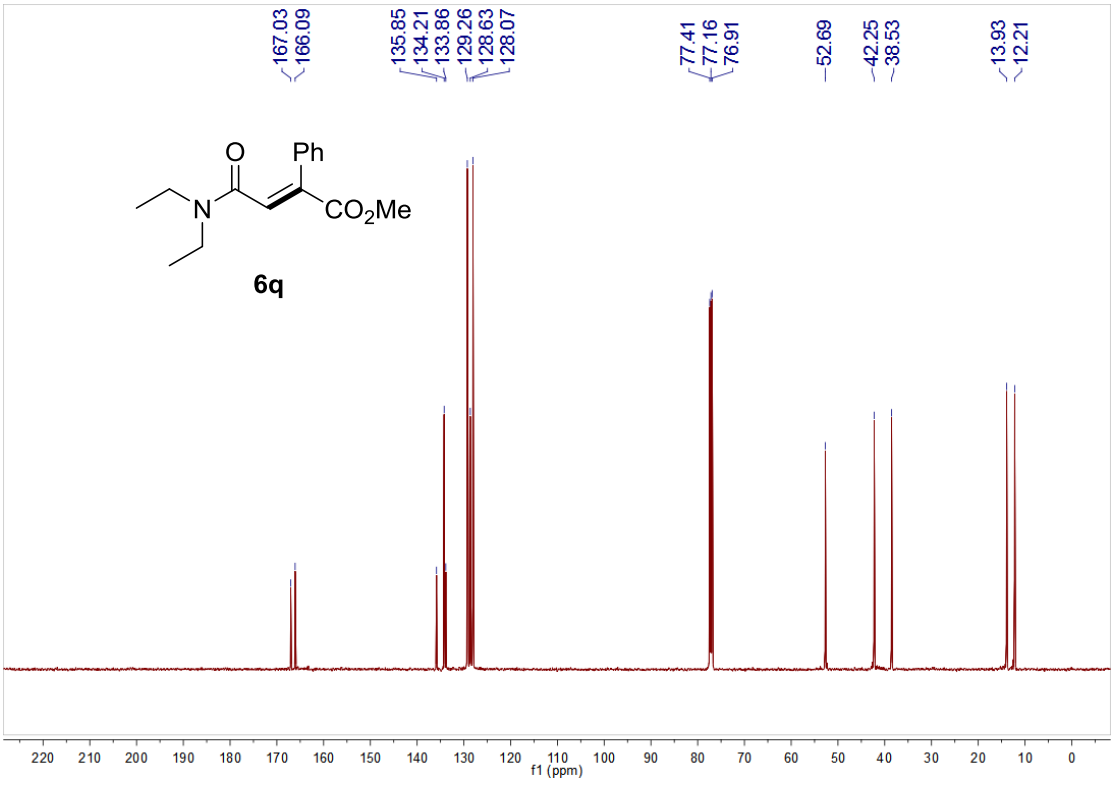

8.36 7.94 7.92 7.91 7.91 7.90 7.89 7.89 7.85 7.83 7.81 7.79 7.78 7.66 7.65 7.64 7.62 7.61 7.60 7.59 7.57 7.57 7.55 7.55 7.53 7.51 7.49 7.48 7.47 7.47 7.46 7.46 7.44 7.27 7.26 7.26 7.26 7.25 7.25 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 3.96 3.90
O
Ph
CO2Me
6o, E:Z = 14:1
0.08 1.05 0.10 0.12 2.33 0.95 2.11 0.24 2.45 0.49 2.14 3.01 0.22 3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

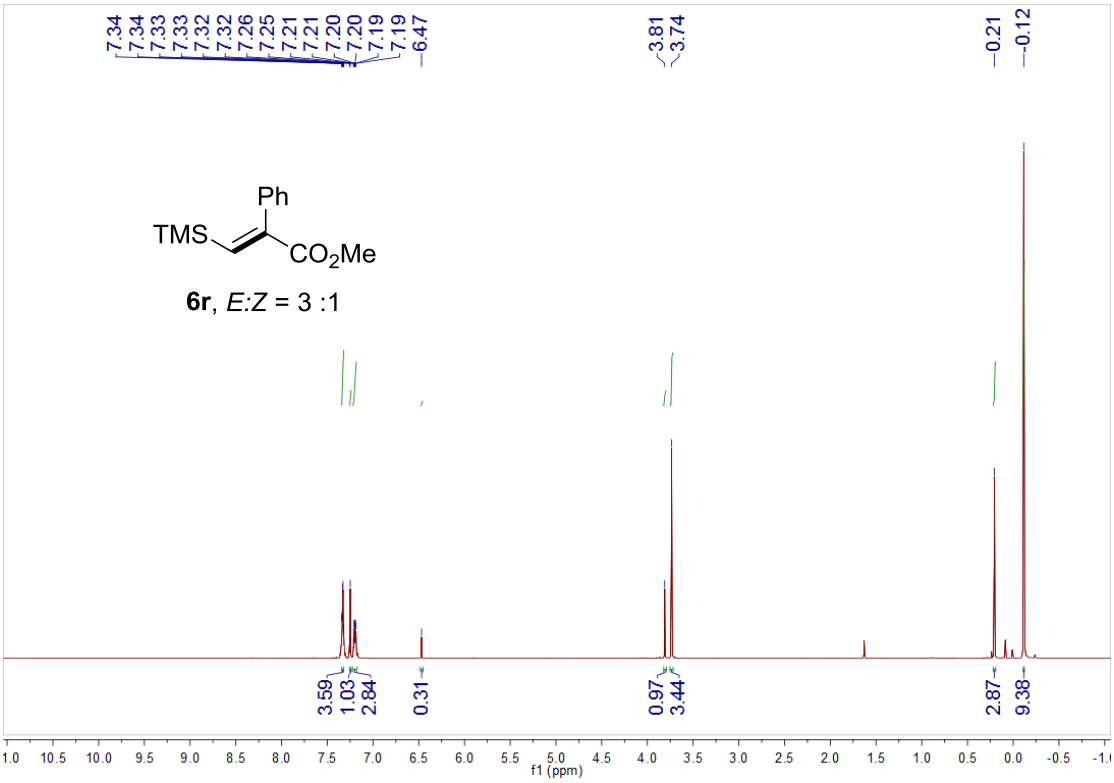

193.47 188.82 169.18 167.18 140.55 136.76 135.88 133.90 133.70 132.40 131.71 129.71 129.42 128.96 128.70 128.67 128.05 127.91 126.96 123.87 77.48 77.16 76.84 53.03 52.86
O
Ph
CO2Me
6o, E:Z = 14:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

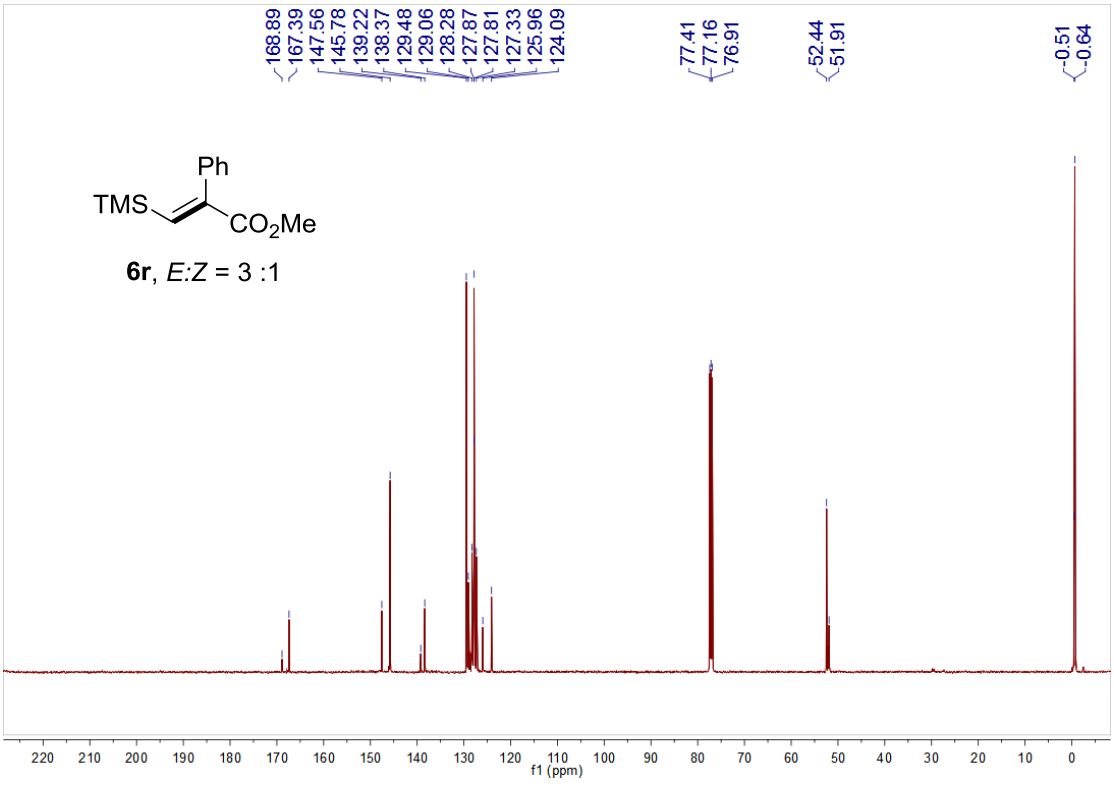

7.38
7.38
7.37
7.37
7.26
7.24
7.24
7.23
7.22
7.17
3.81
2.17
2.15
2.14
1.31
1.30
0.72
0.70
O
Ph
CO2Me
6p
3.16
2.00
1.00
3.13
2.10
3.37
6.34
f1 (ppm)


204.00
167.29
139.69
137.81
134.07
129.40
129.03
128.33
77.41
77.16
76.91
52.98
41.23
32.47
27.53
22.25
O
Ph
CO2Me
6p
f1 (ppm)


7.33
7.32
7.31
7.31
7.30
7.29
7.26
7.22
3.79
3.29
3.27
3.26
3.25
3.08
3.06
3.05
3.04
0.89
0.88
0.87
0.86
0.86
0.84
O
Ph
N
CO2Me
6q
5.31
1.00
3.26
2.21
2.17
6.52
f1 (ppm)


167.03
166.09
135.85
134.21
133.86
129.26
128.63
128.07
77.41
77.16
76.91
52.69
42.25
38.53
13.93
12.21
O
Ph
N
CO2Me
6q
f1 (ppm)


7.34
7.34
7.33
7.33
7.32
7.32
7.26
7.25
7.21
7.21
7.20
7.20
7.19
7.19
6.47
3.81
3.74
0.21
0.12
Ph
TMS
CO2Me
6r, E:Z = 3 :1
3.59
1.03
2.84
0.31
0.97
3.44
2.87
9.38
f1 (ppm)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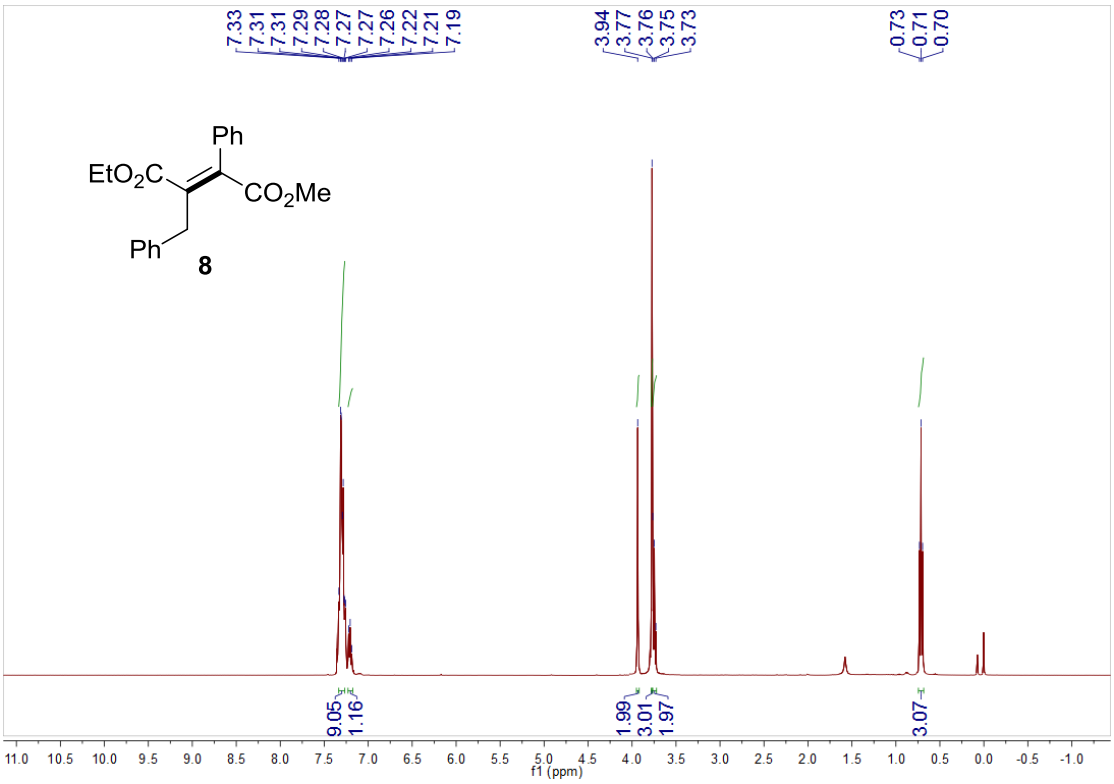
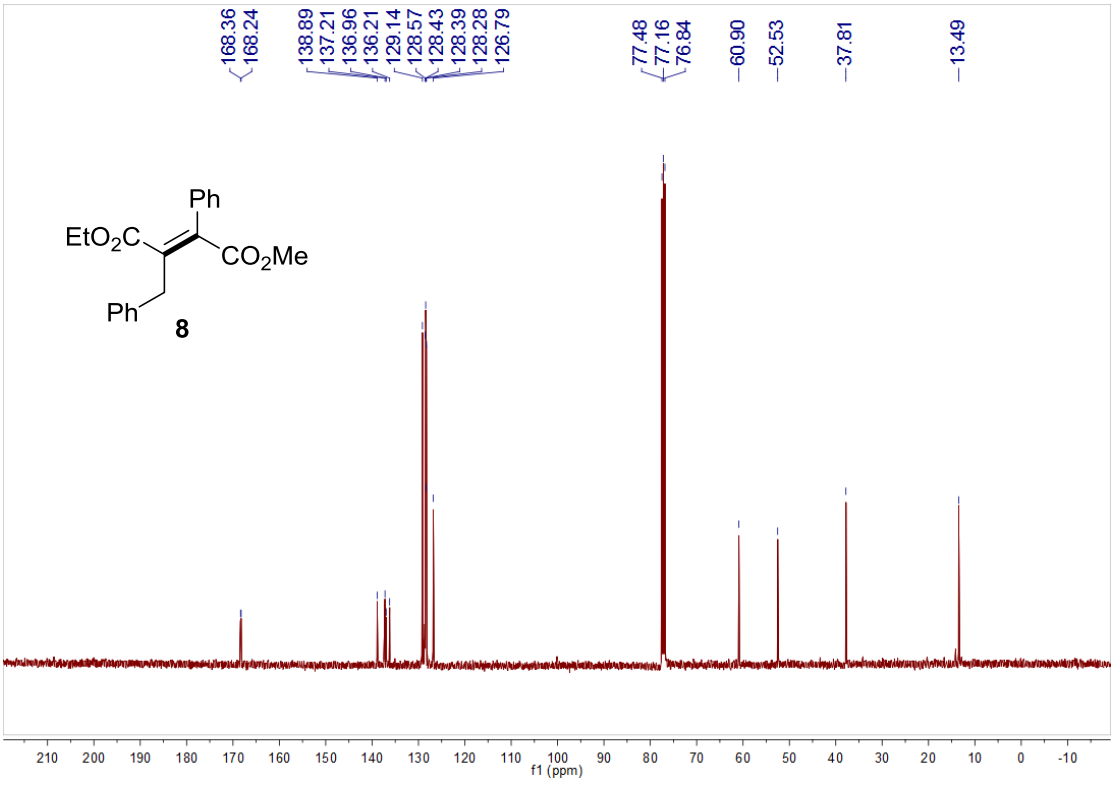
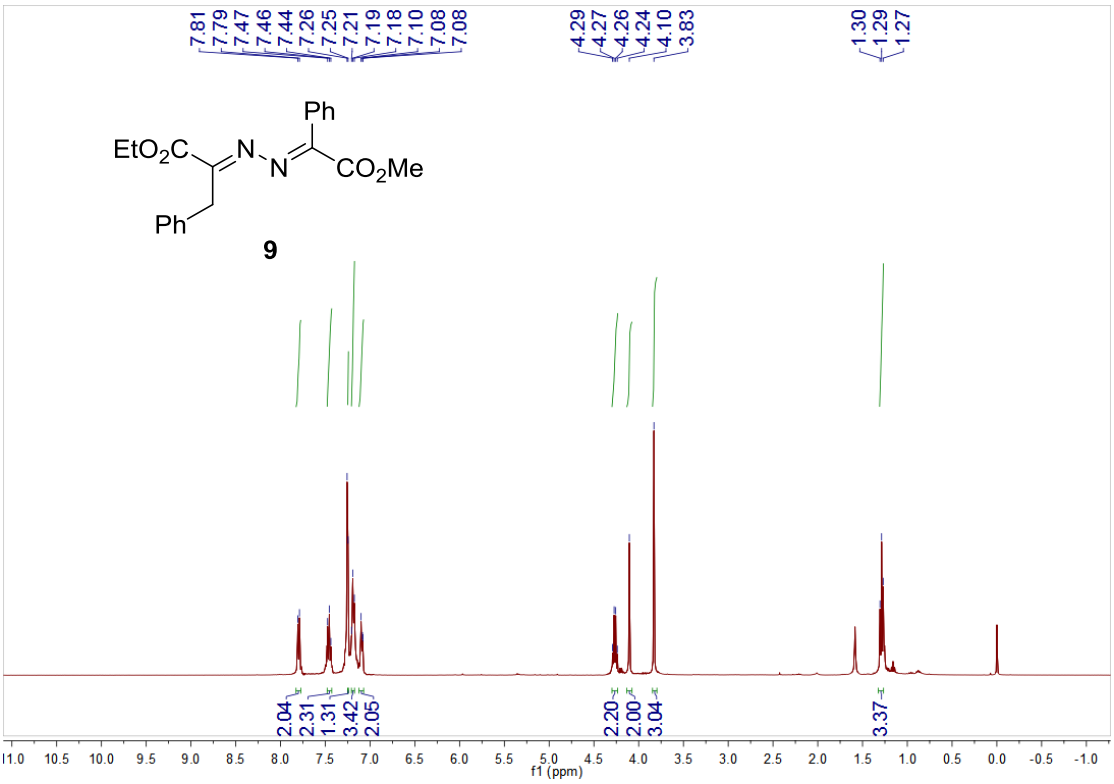
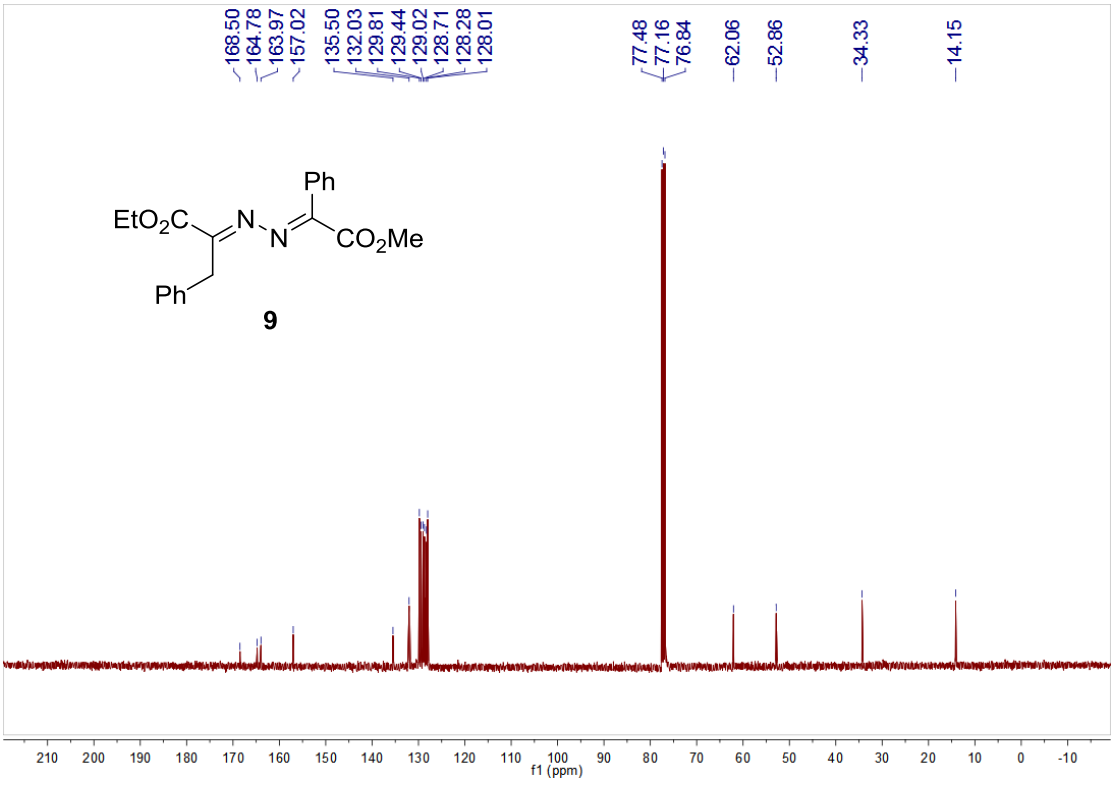
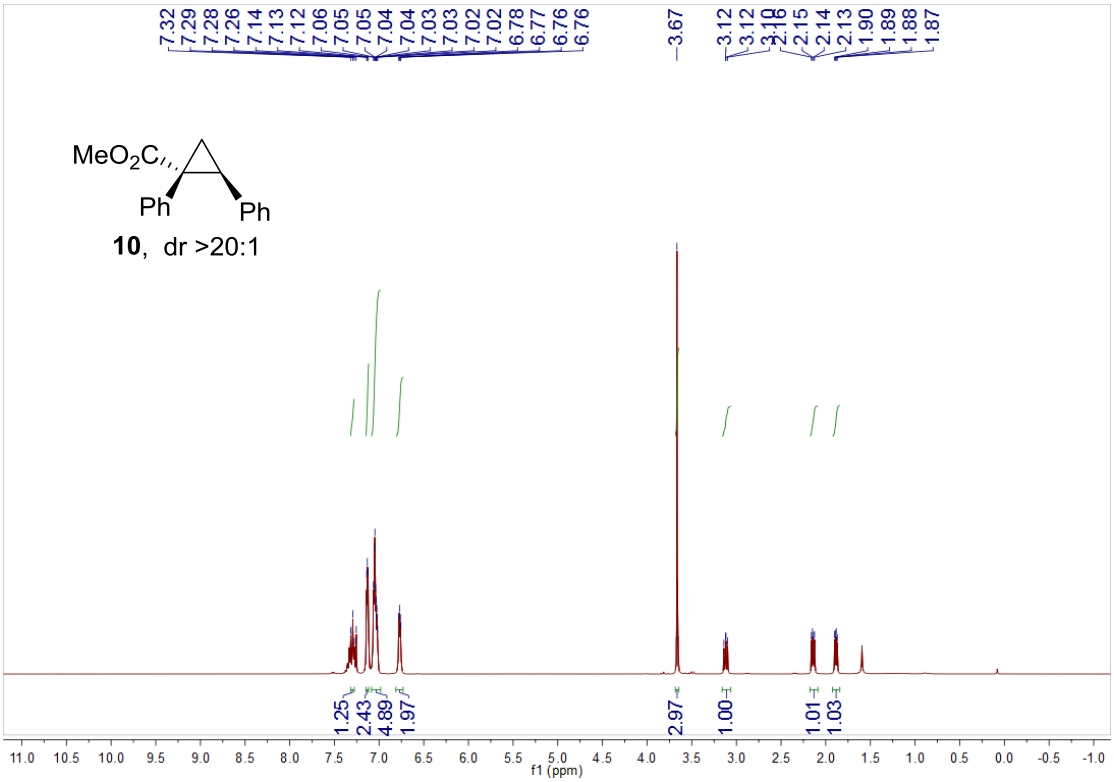
167.39
147.56
145.78
139.22
138.37
129.48
129.06
128.28
127.87
127.81
127.33
125.96
124.09
77.41
77.16
76.91
52.44
51.91
0.51
0.64
Ph
TMS
CO2Me
6r, E:Z = 3 :1
f1 (ppm)

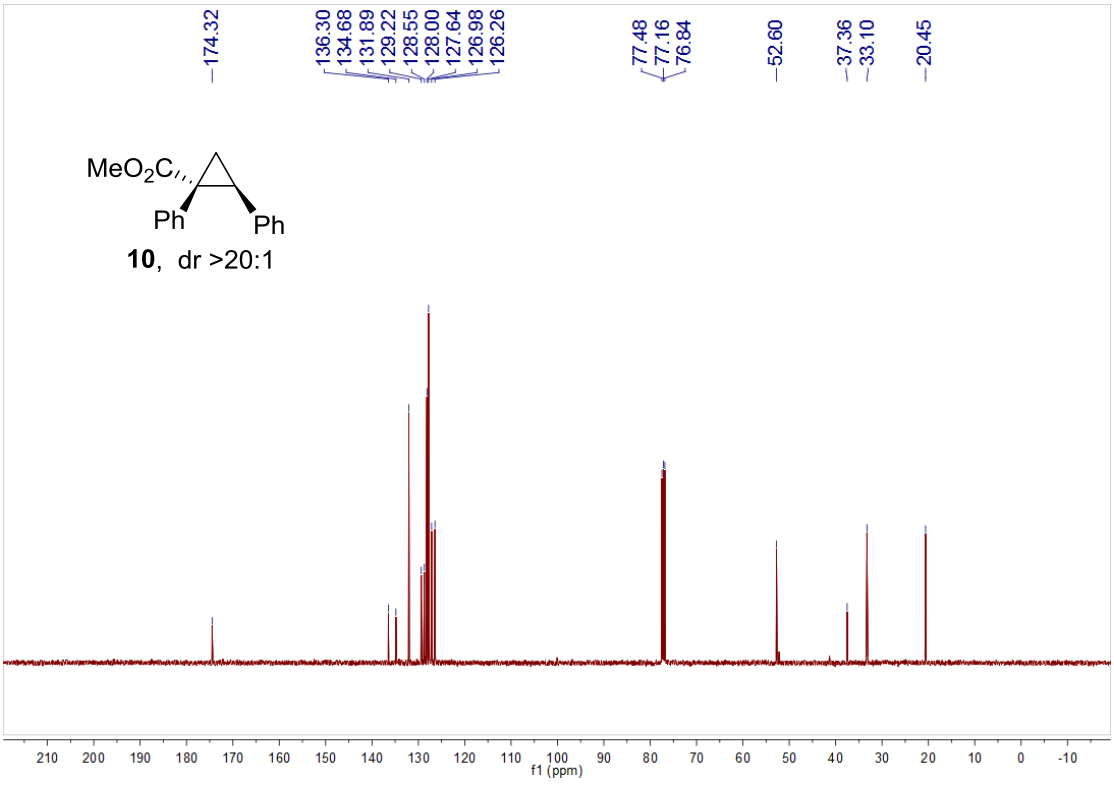

7.33
7.31
7.31
7.29
7.28
7.27
7.27
7.26
7.22
7.21
7.19
3.94
3.77
3.76
3.75
3.73
0.73
0.71
0.70
Ph
EtO2C
CO2Me
Ph
8
9.05
1.16
1.99
3.01
1.97
3.07
f1 (ppm)

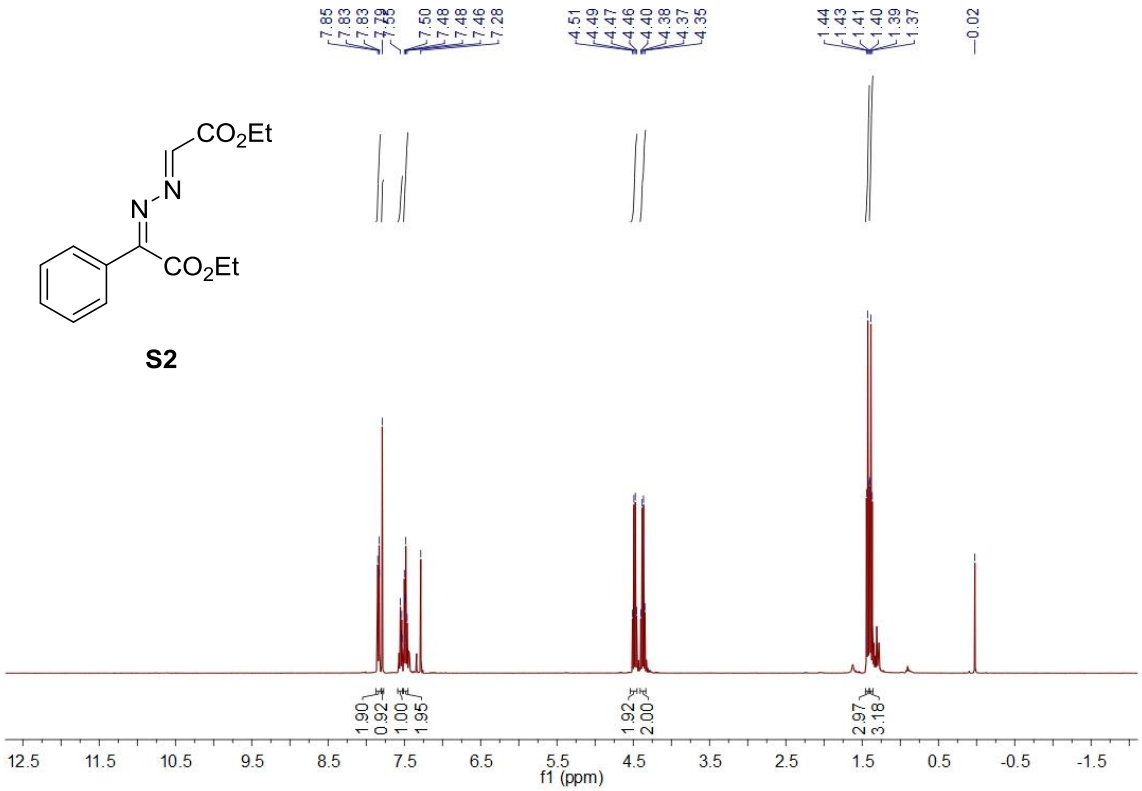

168.36
168.24
138.89
137.21
136.96
136.21
129.14
128.57
128.43
128.39
128.28
126.79
77.48
77.16
76.84
60.90
52.53
37.81
13.49
Ph
EtO2C
CO2Me
Ph
8
f1 (ppm)


7.81
7.79
7.47
7.46
7.44
7.26
7.25
7.21
7.19
7.18
7.10
7.08
7.08
4.29
4.27
4.26
4.24
4.10
3.83
1.30
1.29
1.27
Ph
EtO2C
N
N
CO2Me
Ph
9
2.04
2.31
1.31
3.42
2.05
2.20
2.00
3.04
3.37
f1 (ppm)

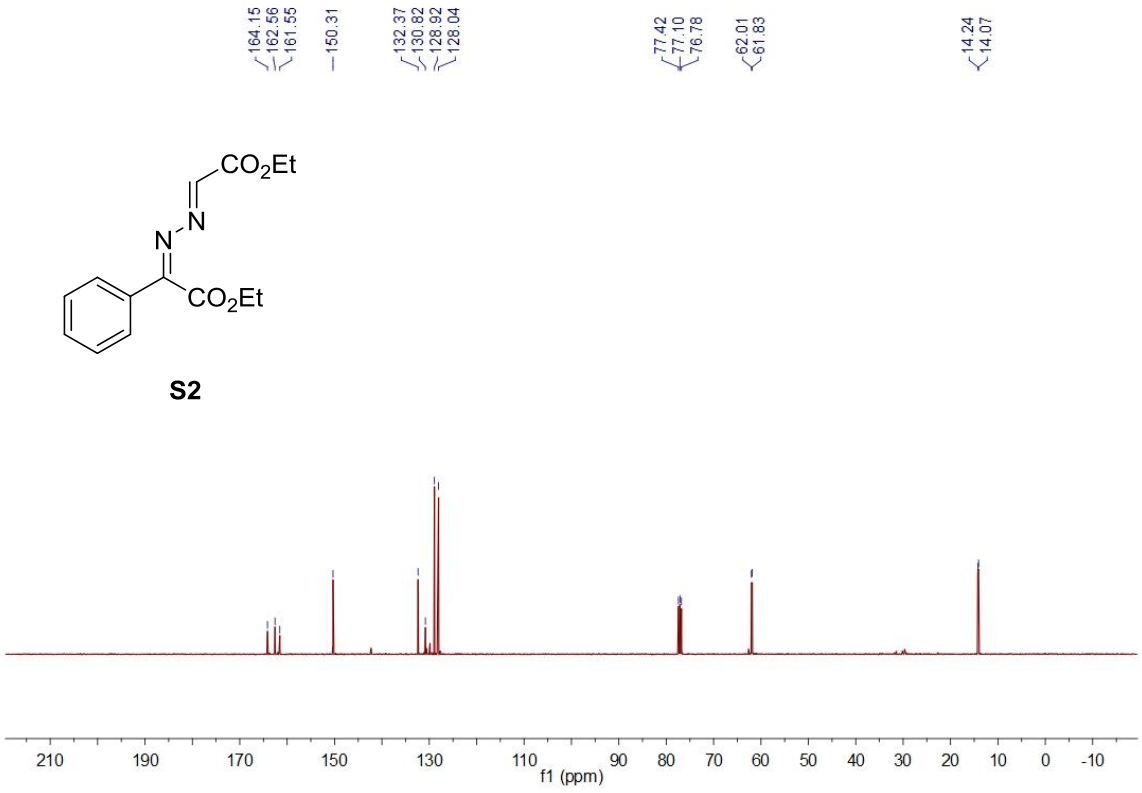

168.50
164.78
163.97
157.02
135.50
132.03
129.81
129.44
129.02
128.71
128.28
128.01
77.48
77.16
76.84
62.06
52.86
34.33
14.15
Ph
EtO2C
N
N
CO2Me
Ph
9
f1 (ppm)


7.32
7.29
7.28
7.26
7.14
7.13
7.12
7.06
7.05
7.05
7.04
7.04
7.03
7.03
7.02
7.02
6.78
6.77
6.76
6.76
3.67
3.12
3.12
3.10
2.15
2.14
2.13
1.90
1.89
1.88
1.87
MeO2C
Ph
Ph
10, dr >20:1
1.25
2.43
4.89
1.97
2.97
1.00
1.01
1.03
f1 (ppm)


174.32
136.30
134.68
131.89
129.22
128.55
128.00
127.64
126.98
126.26
77.48
77.16
76.84
52.60
37.36
33.10
20.45
MeO2C
Ph
Ph
10, dr >20:1
f1 (ppm)


7.85
7.83
7.83
7.79
7.55
7.50
7.48
7.48
7.46
7.28
4.51
4.49
4.47
4.46
4.40
4.38
4.37
4.35
1.44
1.43
1.41
1.40
1.39
1.37
0.02
CO2Et
N
N
CO2Et
1.90
0.92
1.00
1.95
1.92
2.00
2.97
3.18
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

S2


164.15
162.56
161.55
150.31
132.37
130.82
128.92
128.04
77.42
77.10
76.78
62.01
61.83
14.24
14.07
CO2Et
N
N
CO2Et
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S2