Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Diversified access to di- and trisubstituted allenes *via* nickel-catalysed reactions of 1,3-enynes with alkyl *N*-hydroxyphthalimide esters

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1 General Information

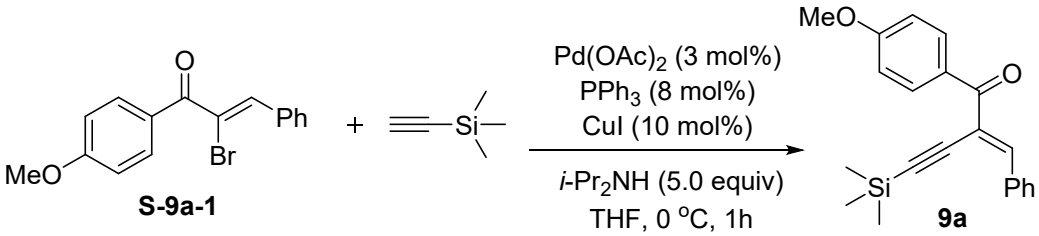
1.1 Solvents, Reagents, and Starting Materials

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. 2-(1-Alkynyl)-2-alken-1-ones **1** and **4** were reported in our previous work.[1] All alkyl *N*-hydroxyphthalimide esters are known compounds and prepared according to the reported procedures.[2] Dried solvents were obtained from commercial sources and used without further purification unless otherwise noted.

1.2 Instruments

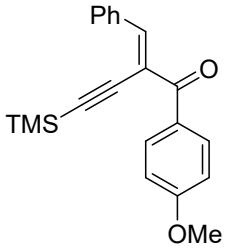
NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz) (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR, and 471 MHz for ^{19}F NMR). Chemical shifts were reported in ppm downfield from tetramethylsilaneand calibrated using residue undeuterated solvent ($CDCl_3$ at 7.26 ppm ^{1}H NMR; 77.0 ppm ^{13}C NMR). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Coupling constants are reported in Hertz where available. High resolution mass spectra (HRMS) were recorded on Waters Premier GC-TOF MS. Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions. Flash column chromatography was performed using silica gel (300-400 mesh) with solvents to use.

2 Synthesis of Various 1,3-Enynes Bearing TMS-Substituted Alkynes



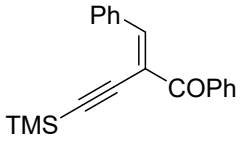
The preparation of (*Z*)-2-bromo-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one **S-9a-1** was reported in our previous work.[3] A solution of (*Z*)-2-bromo-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (1.6 g, 5.0 mmol) in THF (25 mL) was treated with $Pd(OAc)_2$ (33.7 mg, 0.15 mmol), PPh_3 (104.9 mg, 0.4 mmol) and CuI (95.2 mg, 0.5 mmol) and cooled down to 0°C in the dark. After 10 min of stirring,

ethynyltrimethylsilane (1.4 mL, 10.0 mmol) and diisopropylamine (3.5 mL, 25.0 mmol) were added, and the resulting dark brown solution was stirred at 0 °C for 1 h. The reaction mixture was partitioned between ethyl acetate and 0.5 N aqueous HCl solution. The aqueous layer was extracted with ethyl acetate (3 x 10 mL) and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to give **9a**.



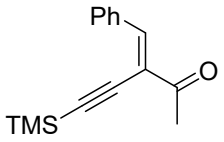
9a

(*E*)-2-Benzylidene-1-(4-methoxyphenyl)-4-(trimethylsilyl)but-3-yn-1-one (9a). Flash column chromatography to afford product **9a** as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.51 (s, 1H), 7.42-7.41 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 0.22 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 163.3, 145.3, 134.8, 132.4, 130.4, 130.3, 129.4, 128.4, 121.2, 113.2, 107.8, 102.4, 55.5, -0.5. These data are consistent with the published literature.[4]



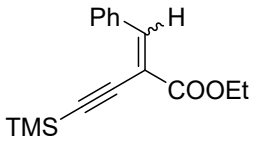
9b

(*E*)-2-Benzylidene-1-phenyl-4-(trimethylsilyl)but-3-yn-1-one (9b). Flash column chromatography to afford product **9b** as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.98-7.97 (m, 2H), 7.61 (s, 1H), 7.58-7.55 (m, 1H), 7.47-7.43 (m, 5H), 0.23 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 146.2, 136.8, 134.5, 132.4, 130.7, 130.4, 129.7, 128.3, 127.8, 120.8, 108.0, 102.1, -0.6. These data are consistent with the published literature.[4]



9c

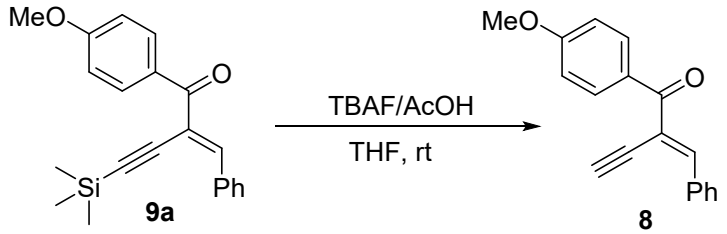
(*E*)-3-Benzylidene-5-(trimethylsilyl)pent-4-yn-2-one (9c). Flash column chromatography to afford product **9c** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.07 (m, 2H), 7.78 (s, 1H), 7.42-7.40 (m, 3H), 2.54 (s, 3H), 0.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 143.9, 134.3, 130.9, 130.8, 128.4, 119.9, 106.2, 102.5, 28.0, -0.4. These data are consistent with the published literature.[4]



9d

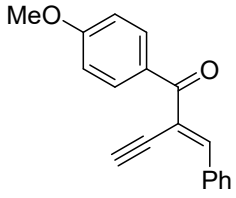
Ethyl 2-benzylidene-4-(trimethylsilyl)but-3-ynoate (9d). Flash column chromatography to afford product as yellow oil *Z*/*E* = 63:37). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09-8.07 (m, 1H), [7.90 (s, 0.37H), 7.22 (s, 0.63H)], 7.41-7.40 (m, 1H), 7.33-7.30 (m, 3H), [4.31 (q, *J* = 7.1 Hz, 0.74H), 4.22 (q, *J* = 7.1 Hz, 1.26H)], [1.37 (t, *J* = 7.1 Hz, 1.11H), 1.21 (t, *J* = 7.1 Hz, 1.89H)], [0.30 (s, 3.33H), 0.24 (s, 5.67H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4(1), 165.3(9), 146.3, 144.1, 134.4, 134.2, 130.7, 130.5, 129.1, 128.7, 128.3, 128.2, 116.9, 113.1, 104.9, 102.0, 100.4, 97.1, 61.6, 61.5, 14.1, 13.7, -0.3, -0.4. HRMS (ESI) $[M+H]^+$: calculated for $C_{16}H_{21}O_2Si$: 273.1311, found 273.1309.

3 Synthesis of Substrate 8



9a **8**

A solution of AcOH (6.6 mmol, 0.38 mL) and TBAF (8.7 mmol, 8.7 mL of 1.0 M solution in THF) in wet THF (28 mL) was stirred at room temperature for 30 min, and then a THF solution (7 mL) of (*E*)-2-Benzylidene-1-(4-methoxyphenyl)-4-(trimethylsilyl)but-3-yn-1-one **9a** (1.0 g, 3.0 mmol) was added slowly at room temperature and the mixture stirred at room temperature for 3 h. After this time, the aqueous layer was extracted with ethyl acetate (3x10 mL) and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to give **8**.

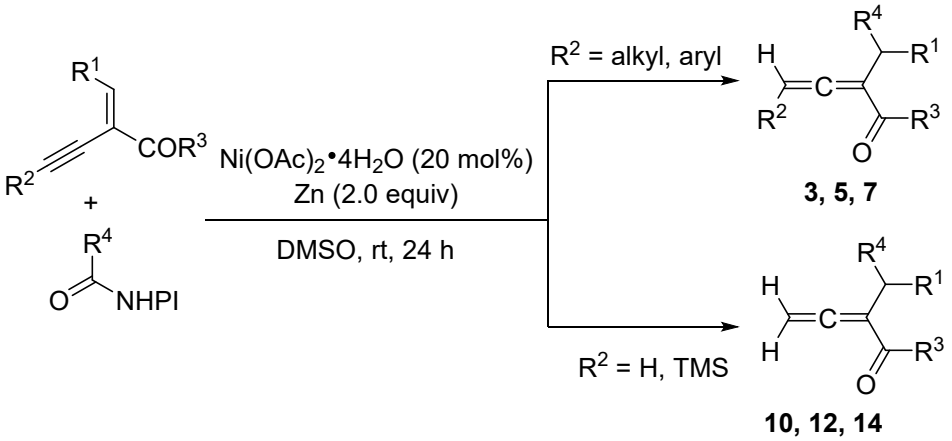


8

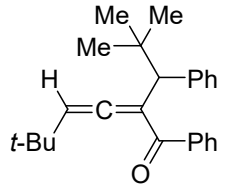
(*E*)-2-benzylidene-1-(4-methoxyphenyl)but-3-yn-1-one (8). Flash column chromatography to afford product **8** as a yellow solid solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.98 (d, *J* = 8.9 Hz, 2H), 7.54 (s, 1H), 7.44 – 7.42 (m,

3H), 6.95 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 3.68 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.9, 163.4, 146.4, 134.4, 132.3, 130.6, 130.2, 129.2, 128.5, 120.4, 113.4, 89.1, 80.8, 55.5. These data are consistent with the published literature.[4]

4 General Procedure of Nickel-Catalysed Reaction of 1,3-Enynes with Alkyl *N*-Hydroxyphthalimide Esters



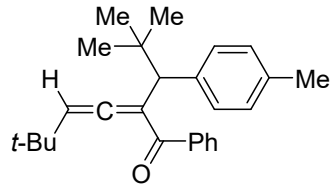
To an oven-dried Schlenk tube was charged with 1,3-enyne (0.2 mmol, 1.0 equiv), alkyl *N*-hydroxyphthalimide ester (0.4 mmol, 2.0 equiv), $Ni(OAc)_2$•$4H_2O$ (10.1 mg, 0.04 mmol), Zn (26.2 mg, 0.4 mmol) in DMSO (4 mL). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times. The reaction mixture was allowed to stir at room temperature for 24 h, H_2O (3 mL) and saturate NH_4Cl solution (3 mL) were added to quench the reaction and the mixture was extracted by ethyl acetate. The combined organic layer was dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography on silica gel. As the trisubsituted allenes, the dr value was determined by ^{1}H NMR analysis of the crude product.



3

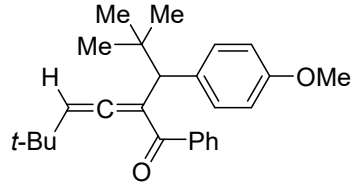
2-(2,2-Dimethyl-1-phenylpropyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (3). Flash column chromatography to afford product **3** as a white solid (66.5 mg, 96% yield, dr = 52:48). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 -7.43 (m, 2H), 7.37 -7.09 (m, 8H), [5.36 (d, J = 0.7 Hz, 0.52H), 5.33 (d, J = 0.9 Hz, 0.48H)], [4.06 (s, 0.52H), 4.01 (s, 0.48H)], [0.97 (s, 4.32H), 0.94 (s, 4.68H)], [0.87 (s, 4.32H), 0.60 (s, 4.68H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.3, 212.5, 196.4, 195.7, 141.9, 141.8,

138.8, 138.6, 131.1, 130.9, 130.3(3), 130.2(5), 128.7, 128.5, 127.5, 127.4(2), 127.3(9), 126.2(1), 126.2(0), 112.1, 111.9, 108.4, 108.1, 52.6, 52.0, 36.1, 34.9, 33.6, 33.2, 29.5, 29.1, 28.5, 28.4. HRMS (ESI) $[M+Na]^+$: calculated for $C_{25}H_{30}ONa$: 369.2194, found 369.2202.



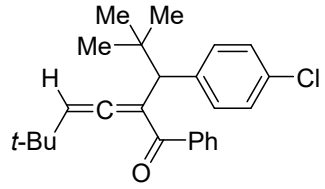
5a

2-(2,2-Dimethyl-1-(*p*-tolyl)propyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (5a). Flash column chromatography to afford product **5a** as a white solid (71.3 mg, 99% yield, dr = 48:52). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.45-7.39 (m, 1H), 7.31-7.29 (m, 4H), 7.10-7.06 (m, 2H), [5.44 (s, 0.44H), 5.41 (s, 0.56H)], [4.10 (s, 0.44H), 4.07 (s, 0.56H)], [2.33 (s, 1.68H), 2.32 (s, 1.32H)], [1.06 (s, 5.04H), 1.02 (s, 3.96H)], [0.96 (s, 5.04H), 0.72 (s, 3.96H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.3, 212.5, 196.4, 195.8, 138.8, 138.7(4), 138.7(2), 138.6(7), 135.6(2), 135.5(5), 131.1, 130.9, 130.2, 130.1, 128.7, 128.5, 128.2, 128.1, 127.5, 127.4, 112.2, 112.1, 108.3, 108.0, 52.2, 51.6, 36.0, 34.9, 33.6, 33.2, 29.5, 29.1, 28.4, 28.3, 20.9(7), 20.9(6). HRMS (ESI) $[M+H]^+$: calculated for $C_{26}H_{33}O$: 361.2531, found 361.2537.



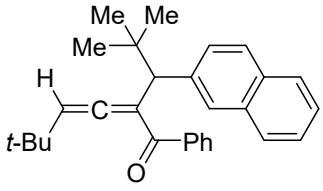
5b

2-(1-(4-Methoxyphenyl)-2,2-dimethylpropyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (5b). Flash column chromatography to afford product **5b** as a light yellow solid (61.7 mg, 82% yield, dr = 45:55). Two diastereoisomers are hard to be separated by column chromatography on silica gel.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.52 (m, 2H), 7.40-7.38 (m, 1H), 7.37-7.29 (m, 4H), 6.83-6.79 (m, 2H), [5.43 (s, 0.39H), 5.40 (s, 0.61H)], [4.09 (s, 0.39H), 4.04 (s, 0.61H)], [3.78 (s, 1.83H), 3.78 (s, 1.17H)], [1.04 (s, 5.49H), 1.00 (s, 3.51H)], [0.94 (s, 5.49H), 0.70 (s, 3.51H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.2, 212.4, 196.5, 195.8, 157.9(8), 157.9(6), 138.8, 138.7, 134.0, 133.9, 131.2, 131.1(1), 131.0(9), 130.9, 128.7, 128.5, 127.5, 127.4, 112.8, 112.7, 112.3, 112.2, 108.4, 108.1, 55.1(2), 55.1(0), 51.8, 51.2, 36.1, 34.9, 33.6, 33.2, 29.5, 29.1, 28.4, 28.3. These data are consistent with the published literature.[10]



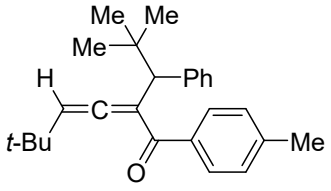
5c

2-(1-(4-Chlorophenyl)-2,2-dimethylpropyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (5c). Flash column chromatography to afford product **5c** as a white solid (53.2 mg, 70% yield, dr = 50:50). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.51 (m, 2H), 7.44-7.40 (m, 1H), 7.39-7.30 (m, 4H), 7.25-7.22 (m, 2H), [5.46 (d, *J* = 0.4 Hz, 0.50H), 5.41 (d, *J* = 0.8 Hz, 0.50H)], [4.12 (s, 0.50H), 4.07 (s, 0.50H)], [1.03 (s, 4.50H), 1.00 (s, 4.50H)], [0.95 (s, 4.50H), 0.69 (s, 4.50H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.1, 212.3, 196.2, 195.5, 140.3(8), 140.3(7), 138.6, 138.4, 132.1, 132.0, 131.6, 131.5, 131.3, 131.1, 128.7, 128.5, 127.6(2), 127.5(7), 127.5(3), 127.4(9), 111.7, 111.6, 108.8, 108.4, 52.0, 51.3, 36.1, 34.9, 33.7, 33.3, 29.5, 29.1, 28.3(1), 28.2(5). HRMS (ESI) $[M+H]^+$: calculated for $C_{25}H_{30}OCl$: 381.1985, found 381.1990.



5d

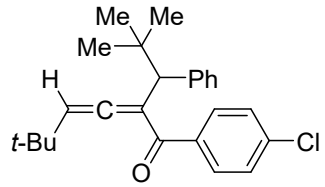
2-(2,2-Dimethyl-1-(naphthalen-2-yl)propyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (5d). Flash column chromatography to afford product **5d** as a light yellow solid (68.2 mg, 86% yield, dr = 53:47). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.74 (m, 4H), 7.66-7.59 (m, 2H), 7.55-7.53 (m, 1H), 7.47-7.40 (m, 3H), 7.39-7.29 (m, 2H), [5.52 (s, 0.53H), 5.47 (s, 0.47H)], [4.33 (s, 0.53H), 4.29 (s, 0.47H)], [1.12 (s, 4.23H), 1.08 (s, 4.77H)], [1.00 (s, 4.23H), 0.70 (s, 4.77H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.3, 212.5, 196.4, 195.8, 139.5(1), 139.4(8), 138.7, 138.6, 133.0, 132.9(9), 132.2(0), 132.1(9), 131.1(5), 130.9(7), 129.9, 129.1, 129.0, 128.7(3), 128.6(8), 128.5(5), 127.8(4), 127.7(6), 127.5(2), 127.4(4), 127.4(1), 126.8, 126.7, 125.7, 125.6, 125.3, 125.2, 112.1, 111.9, 108.6, 108.3, 52.8, 52.1, 36.4, 35.2, 33.7, 33.2, 29.6, 29.1, ^{2}8.5(2), 28.4(9). HRMS (ESI) $[M+H]^+$: calculated for $C_{29}H_{33}O$: 397.2531, found 397.2536.



5e

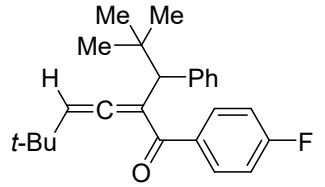
2-(2,2-Dimethyl-1-phenylpropyl)-5,5-dimethyl-1-(p-tolyl)hexa-2,3-dien-1-one (5e). Flash column chromatography to afford product **5e** as a white solid (54.0 mg, 75% yield, dr = 49:51). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.50 (m, 2H), 7.48-7.47 (m, 1H), 7.42-7.21 (m, 4H), 7.19-7.13 (m, 2H), [5.45 (s, 0.49H), 5.41 (s, 0.51H)], [4.13 (s, 0.49H), 4.07 (s, 0.51H)], [2.37 (s, 1.47H), 2.35 (s, 1.53H)], [1.05 (s, 4.59H), 1.02 (s, 4.41H)], [0.99 (s, 4.59H), 0.70 (s, 4.41H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.5, 211.7, 195.9, 195.2, 141.9(3), 141.8(7), 141.8(6), 141.6, 135.7, 135.6, 130.3(4), 130.2(6), 129.1, 129.0, 128.2, 128.1, 127.3(8), 127.3(6), 127.3, 126.2, 111.8, 111.6,

108.2, 107.9, 52.9, 52.3, 36.1, 34.9, 33.6, 33.2, 29.6, 29.1, 28.4(4), 28.3(6), 21.5(3), 21.5(0). HRMS (ESI) $[M+H]^+$: calculated for $C_{26}H_{33}O$: 361.2531, found 361.2536.



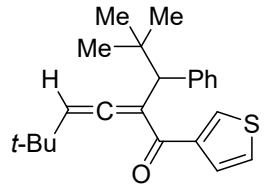
5f

1-(4-Chlorophenyl)-2-(2,2-dimethyl-1-phenylpropyl)-5,5-dimethylhexa-2,3-dien-1-one (5f). Flash column chromatography to afford product **5f** as a white solid (70.7 mg, 93% yield, dr = 47:53). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.48 (m, 2H), 7.44-7.42 (m, 1H), 7.38-7.27 (m, 4H), 7.25-7.17 (m, 2H), [5.48 (d, *J* = 0.4 Hz, 0.47H), 5.46 (d, *J* = 0.7 Hz, 0.53H)], [4.11 (s, 0.47H), 4.05 (s, 0.53H)], [1.04 (s, 4.77H), 1.01 (s, 4.23H)], [0.99 (s, 4.77H), 0.71 (s, 4.23H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.9, 212.2, 194.9, 194.3, 141.6(9), 141.6(6), 137.5, 137.2, 136.9, 136.8, 130.3, 130.2(4), 130.2(0), 130.1, 127.9, 127.8, 127.5(0), 127.4(6), 126.3(2), 126.3(0), 112.0, 111.8, 108.7, 108.4, 52.8, 52.2, 36.1, 34.9, 33.7, 33.3, 29.6, 29.1, 28.5, 28.3. HRMS (ESI) $[M+Na]^+$: calculated for $C_{20}H_{29}ONa$: 403.1805, found 403.1797.



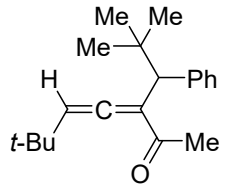
5g

2-(2,2-Dimethyl-1-phenylpropyl)-1-(4-fluorophenyl)-5,5-dimethylhexa-2,3-dien-1-one (5g). Flash column chromatography to afford product **5g** as a white solid (56.1 mg, 77% yield, dr = 49:51). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.56 (m, 2H), 7.44-7.42 (m, 1H), 7.38-7.19 (m, 4H), 7.06-6.97 (m, 2H), [5.47 (d, *J* = 0.7 Hz, 0.49H), 5.45 (d, *J* = 0.9 Hz, 0.51H)], [4.11 (s, 0.49H), 4.05 (s, 0.51H)], [1.04 (s, 4.59H), 1.01 (s, 4.41H)], [0.98 (s, 4.59H), 0.70 (s, 4.41H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.8, 212.0, 194.8, 194.1, 164.6 (d, *J* = 253.3 Hz), 164.5 (d, *J* = 252.0 Hz), 141.8, 141.7, 134.7 (d, *J* = 3.2 Hz), 134.6 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 8.9 Hz), 131.2 (d, *J* = 8.8 Hz), 130.3, 130.2, 127.5, 127.4, 126.3, 126.2(7), 114.6 (d, *J* = 21.8 Hz), 114.5 (d, *J* = 21.8 Hz), 112.0, 111.8, 108.6, 108.3, 52.9, 52.3, 36.1, 34.9, 33.7, 33.3, 29.6, 29.1, 28.5, 28.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.92, -108.21. HRMS (ESI) $[M+H]^+$: calculated for $C_{25}H_{30}OF$: 365.2281, found 365.2274.



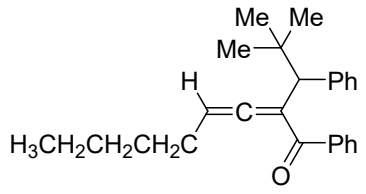
5h

2-(2,2-Dimethyl-1-phenylpropyl)-5,5-dimethyl-1-(thiophen-3-yl)hexa-2,3-dien-1-one (5h). Flash column chromatography to afford product **5h** as a white solid (61.3 mg, 87% yield, dr = 51:49). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.95-7.94 (m, 0.51H), 7.81-7.80 (m, 0.49H)], 7.45-7.17 (m, 7H), [5.56(4) (s, 0.51H), 5.55(8) (s, 0.49H)], [4.11 (s, 0.51H), 4.05 (s, 0.49H)], [1.07 (s, 4.41H), 1.04 (s, 4.59H)], [0.99 (s, 4.41H), 0.77 (s, 4.59H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.9, 211.2, 189.0, 188.3, 141.9, 141.8, 141.0, 140.9, 131.4, 131.2, 130.3, 130.2, 128.4, 128.3, 127.4(2), 127.4(1), 126.2(2), 126.2(0), 124.7, 124.6, 112.6, 112.4, 108.7, 108.3, 53.0, 52.4, 36.1, 34.9, 33.8, 33.3, 29.7, 29.2, 28.5, 28.4. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{29}OS$: 353.1939, found 353.1938.



5i

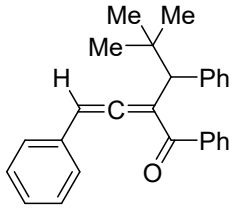
3-(2,2-Dimethyl-1-phenylpropyl)-6,6-dimethylhepta-3,4-dien-2-one (5i). Flash column chromatography to afford product **5i** as a yellow solid (49.5 mg, 87% yield, dr = 40:60). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.23 (m, 4H), 7.21-7.20 (m, 1H), [5.74 (s, 0.40H), 5.73 (s, 0.60H)], [4.0 (s, 0.40H), 3.96 (s, 0.60H)], [2.28 (s, 1.80H), 2.27 (s, 1.20H)], [1.29 (s, 3.60H), 1.11 (s, 5.40H)], [0.98 (s, 3.60H), 0.94 (s, 5.40H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.6, 211.5, 198.6, 198.5, 142.2, 141.8, 130.3, 130.1, 128.3, 127.4, 127.3, 126.1, 113.1, 112.9, 107.8, 107.5, 50.4(7), 50.4(6), 35.6, 34.6, 33.9, 33.6, 29.9, 29.5, 28.2, 28.1, 26.5, 26.4. HRMS (ESI) $[M+H]^+$: calculated for $C_{20}H_{29}O$: 285.2218, found 285.2216.



5j

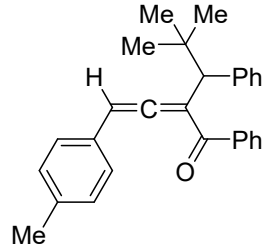
2-(2,2-Dimethyl-1-phenylpropyl)-1-phenylocta-2,3-dien-1-one (5j). Flash column chromatography to afford product **5j** as a white solid (63.0 mg, 91% yield, dr =46:54). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.64 (m, 2H), 7.46-7.41 (m, 3H), 7.36-7.33 (m, 2H), 7.29-7.26 (m, 2H), 7.23-7.20 (m, 1H), [5.48 (t, J = 7.4 Hz, 0.46H), 5.42 (t, J

= 7.5 Hz, 0.54H)], [4.06 (s, 0.46H), 4.05 (s, 0.54H)], 2.28-2.00 (m, 2H), 1.38-1.32 (m, 1H), 1.26-1.21 (m, 2H), 1.19-1.13 (m, 1H), 1.04 (s, 9H), [0.86 (t, *J* = 7.3 Hz, 1.62H), 0.79 (t, *J* = 7.2 Hz, 1.38H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.7, 214.5, 195.9, 195.8, 141.9, 141.7, 138.7, 131.4, 130.1(1), 130.0(9), 128.9(1), 128.8(9), 127.6, 127.4(7), 127.4(5), 126.2(1), 126.1(8), 109.4, 108.9, 96.9, 96.4, 52.5, 52.4, 35.6, 35.1, 30.9, 30.7, 28.6, 28.4, 28.3, 28.3, 22.1, 22.0, 13.8, 13.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{25}H_{31}O$: 347.2375, found 347.2368.



5k

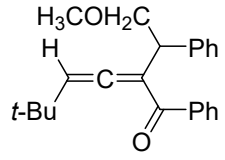
4,4-Dimethyl-1,3-diphenyl-2-(2-phenylvinylidene)pentan-1-one (5k). Flash column chromatography to afford product **5k** as a yellow solid (54.9 mg, 75% yield, dr = 51:49). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.46-7.43 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.19 (m, 8H), 7.14-7.12 (m, 1H), [6.59 (s, 0.51H), 6.54 (s, 0.49H)], 4.17 (s, 1H), [1.06 (s, 4.59H), 1.06 (s, 4.41H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.49, 215.27, 194.59, 194.42, 141.37, 141.34, 138.06, 138.00, 132.57, 132.29, 132.03, 131.98, 130.18, 130.16, 128.90, 128.86, 128.85, 128.73, 127.78, 127.76, 127.71, 127.61, 127.57, 127.37, 126.46, 126.42, 112.99, 112.50, 100.41, 99.99, 99.96, 54.28, 54.03, 35.90, 35.23, 28.47, 28.40. HRMS (ESI) $[M+H]^+$: calculated for $C_{27}H_{27}O$: 367.2062, found 367.2057.



5l

4,4-Dimethyl-1,3-diphenyl-2-(2-(p-tolyl)vinylidene)pentan-1-one (5l). Flash column chromatography to afford product **5l** as a yellow solid (56.3 mg, 74% yield, dr = 49:51). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.69 (m, 2H), 7.47-7.45 (m, 2H), 7.39-7.36 (m, 1H), 7.31-7.28 (m, 1H), 7.26-7.19 (m, 6H), 7.12-7.04 (m, 2H), [6.58 (s, 0.49H), 6.53 (s, 0.51H)],[4.19 (s, 0.49H), 4.18 (s, 0.51H)], [2.38 (s, 1.53H), 2.34 (s, 1.47H)], [1.07 (s, 4.41H), 1.06 (s, 4.59H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.47, 215.31, 194.66, 194.52, 141.43, 141.42, 138.12, 138.07, 137.71, 131.93, 131.88, 130.21, 130.16, 129.64, 129.52, 129.47, 129.26, 128.83, 128.82, 127.75, 127.72, 127.67, 127.57, 127.49, 127.30, 126.41, 126.37, 112.92, 112.45, 100.23, 99.80, 54.14,

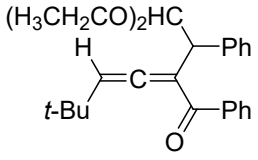
53.93, 35.86, 35.21, 28.46, 28.38, 21.24, 21.21. HRMS (ESI) $[M+Na]^+$: calculated for $C_{28}H_{28}ONa$: 403.2038, found 403.2033.



5m

2-(2-Methoxy-1-phenylethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (5m). Flash column chromatography to afford product **5m** (34.8 mg, 52% yield, dr = 38:62). The first fraction**:** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.46-7.43 (m, 1H), 7.36-7.28 (m, 6H), 7.22-7.19 (m, 1H), 5.46 (d, *J* = 1.9 Hz, 1H), 4.48-4.45 (m, 1H), 3.75-3.73 (m, 2H), 3.35 (s, 3H), 0.80 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.4, 194.5, 140.9, 138.7, 131.4, 128.7, 128.4, 128.3, 127.5, 126.7, 111.7, 108.62, 74.9, 58.7, 43.1, 33.0, 29.5. HRMS (ESI) $[M+Na]^+$: calculated for $C_{23}H_{26}O_2Na$: 357.1830, found 357.1836.

The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.63 (m, 2H), 7.44-7.41 (m, 1H), 7.35-7.28 (m, 6H), 7.22-7.19 (m, 1H), 5.50 (d, *J* = 1.7 Hz, 1H), 4.46-4.43 (m, 1H), 3.78-3.74 (m, 1H), 3.68-3.65 (m, 1H), 3.34 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.4, 141.1, 138.6, 131.4, 128.7, 128.3, 128.1, 127.5, 126.7, 111.2, 108.8, 75.5, 58.5, 42.9, 33.2, 29.7. HRMS (ESI) $[M+Na]^+$: calculated for $C_{23}H_{26}O_2Na$: 357.1830, found 357.1829.

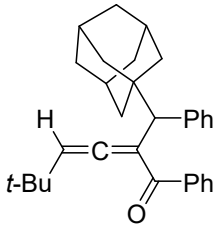


5n

2-(2,2-diethoxy-1-phenylethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (5n). Flash column chromatography to afford product **5n** (44.7 mg, 57 % yield, dr = 68:32).

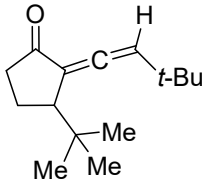
The first fraction**:** yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.45-7.42 (m, 1H), 7.41-7.27 (m, 6H), 7.21-7.18 (m, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 4.96 (d, *J* = 8.0 Hz, 1H), 4.46-4.44 (m, 1H), 3.73-3.70 (m, 1H), 3.57-3.51 (m, 2H), 3.40-3.37 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 0.95 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.8, 140.1, 138.9, 131.3, 129.1, 128.8, 127.9, 127.5, 126.5, 111.1, 108.4, 104.1, 61.6, 61.5, 47.3, 33.2, 29.7, 15.2, 15.0. HRMS (ESI) $[M+Na]^+$: calculated for $C_{26}H_{32}O_3Na$: 415.2249, found 415.2246.

The second fraction**:** yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.46-7.43 (m, 1H), 7.40-7.25 (m, 6H), 7.20-7.17 (m, 1H), 5.41 (d, *J* = 1.2 Hz, 1H), 4.97 (d, *J* = 8.2 Hz, 1H), 4.52 (d, *J* = 8.1 Hz, 1H), 3.73-3.70 (m, 1H), 3.56-3.52 (m, 2H), 3.48-3.44 (m, *J* = 9.3, 7.1 Hz, 1H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H), 0.68 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.5, 139.9, 138.7, 131.4, 129.1, 128.8, 128.0, 127.5, 126.5, 111.5, 108.7, 104.1, 62.2, 61.0, 46.6, 33.0, 29.3, 15.2, 15.1. HRMS (ESI) $[M+Na]^+$: calculated for $C_{26}H_{32}O_3Na$: 415.2249, found 415.2250.



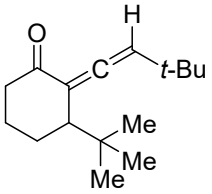
5o

2-((Adamantan-1-yl)(phenyl)methyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (5o). Flash column chromatography to afford product **5o** as a white solid (73.0 mg, 86% yield, dr = 55:45). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.51 (m, 2H), 7.44-7.20 (m, 8H), [5.45 (s, 0.55H), 5.39 (s, 0.45H)], [3.98 (s, 0.55H), 3.92 (s, 0.45H)], 1.95 (d, *J* = 2.2 Hz, 3H), 1.71-1.57 (m, 13H), [0.98 (s, 4.05H), 0.67 (s, 4.95H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.5, 212.8, 196.6, 195.7, 140.8, 140.7, 138.8, 138.6, 131.1, 130.9, 130.7, 130.5, 128.8, 128.6, 127.5, 127.4, 127.3(1), 127.2(8), 126.2, 110.8, 108.3, 107.7, 53.8, 53.0, 40.5, 40.0, 37.9, 36.9, 36.9, 36.6, 33.5, 33.2, 29.6, 29.0, 28.7. HRMS (ESI) $[M+Na]^+$: calculated for $C_{31}H_{36}ONa$: 447.2664, found 447.2662.



7a

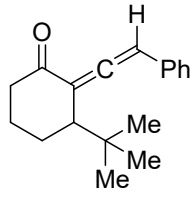
3-(*tert*-Butyl)-2-(3,3-dimethylbut-1-en-1-ylidene)cyclopentan-1-one (7a). Flash column chromatography to afford product **7a** as a pale yellow oil (25.5 mg, 58% yield, dr = 76:24). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ [5.65 (d, *J* = 5.2 Hz, 0.76H), 5.64 (d, *J* = 5.0 Hz, 0.24H)], 2.79-2.75 (m, 1H), 2.42-2.34 (m, 1H), 2.31-2.24 (m, 1H), 2.04-1.97 (m, 1H), 1.78-1.70 (m, 1H), [1.13 (s, 6.84H), 1.09 (s, 2.16H)], [0.99 (s, 6.84H), 0.95 (s, 2.16H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.7, 207.6, 204.2, 203.7, 107.9, 107.8(4), 107.7(6), 107.5, 51.5(2), 51.2(0), 38.2(3), 38.2(0), 34.2, 33.6(0), 33.5(7), 33.3, 30.2(0), 30.1(5), 27.5, 27.3, 22.9, 22.8. These data are consistent with the published literature.[1]



7b

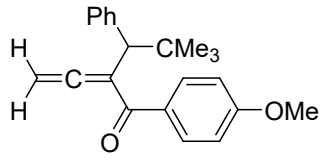
3-(*tert*-Butyl)-2-(3,3-dimethylbut-1-en-1-ylidene)cyclohexan-1-one (7b). Flash column chromatography to afford product **7b** as a pale yellow oil (22.0 mg, 47% yield, dr = 71:29). Two diastereoisomers are hard to be separated by column

chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ [5.45 (d, *J* = 3.0 Hz, 0.71H), 5.42 (d, *J* = 2.5 Hz, 0.29H)], 2.52-2.45 (m, 2H), 2.30-2.18 (m, 1H), 2.02-1.96 (m, 1H), 1.94-1.88 (m, 1H), 1.74-1.62 (m, 1H), 1.55-1.41 (m, 1H), [1.12 (s, 6.39H), 1.06 (s, 2.61H)], [0.96 (s, 6.39H), 0.89 (s, 2.61H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.8, 205.1, 203.6, 203.5, 109.2, 108.9, 105.4, 105.0, 48.9, 48.5, 40.0, 35.8, 34.2, 33.0, 32.9, 31.5, 30.1, 30.0, 27.8, 27.4, 25.6, 25.0, 21.4, 21.1. These data are consistent with the published literature.[1]



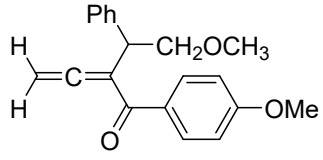
7c

3-(*tert*-Butyl)-2-(2-phenylvinylidene)cyclohexan-1-one (7c). Flash column chromatography to afford product **7c** as a pale yellow oil (10.2 mg, 20% yield, dr = 75:25). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.30 (m, 3H), 7.24-7.21 (m, 2H), [6.53 (d, *J* = 3.1 Hz, 0.75H), 6.45 (d, *J* = 2.7 Hz, 0.25H)], 2.61-2.53 (m, 3.0 Hz, 2H), 2.37-2.29 (m, 1H), 2.10-1.97 (m, 2H), 1.83-1.72 (m, 1H), 1.58-1.52 (m, 1H), [0.95 (s, 2.25H), 0.94 (s, 6.75H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3, 209.4, 202.6, 202.3, 132.8, 132.6, 128.7(3), 128.6(8), 127.5, 127.4, 127.3, 127.0, 110.9, 110.8, 97.7, 97.2, 49.7, 48.5, 40.3(2), 40.2(9), 35.5, 34.4, 27.5, 27.4, 25.5, 25.1, 21.5, 21.4. These data are consistent with the published literature.[1]



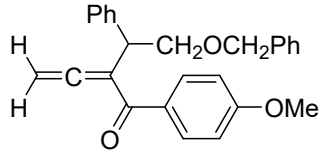
10a

1-(4-Methoxyphenyl)-4,4-dimethyl-3-phenyl-2-vinylidenepentan-1-one (10a). Flash column chromatography to afford product **10a** as a white solid (41.6 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.45-7.42 (m, 2H), 7.29-7.26 (m, 2H), 7.22-7.19 (m, 1H), 6.87-6.85 (m, 2H), 5.21 (s, 2H), 3.95 (s, 1H), 3.83 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.3, 193.5, 162.8, 141.5, 132.3, 132.2, 131.7, 131.5(3), 131.5(0), 130.4, 130.1, 128.5, 128.4, 127.5, 126.3, 113.0, 108.4, 81.4, 55.3, 53.2, 35.7, 28.4. HRMS (ESI) $[M+H]^+$: calculated for $C_{22}H_{25}O_2$: 321.1855, found 321.1850.



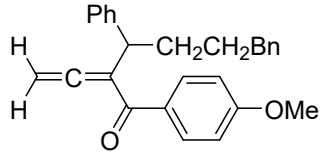
10b

2-(2-Methoxy-1-phenylethyl)-1-(4-methoxyphenyl)buta-2,3-dien-1-one (10b). Flash column chromatography to afford product **10b** as a pale yellow oil (43.8 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.36-7.34 (m, 2H), 7.31-7.28 (m, 2H), 7.22-7.19 (m, 1H), 6.87-6.84 (m, 2H), 5.24-5.16 (m, 2H), 4.38-4.35 (m, 1H), 3.83 (s, 3H), 3.78-3.75 (m, 1H), 3.71-3.68 (m, 1H), 3.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.5, 192.0, 162.9, 140.6, 131.5, 130.7, 128.4, 128.1, 126.8, 113.1, 107.8, 81.0, 75.1, 58.7, 55.3, 43.3. HRMS (ESI) $[M+H]^+$: calculated for $C_{20}H_{21}O_3$: 309.1491, found 309.1495.



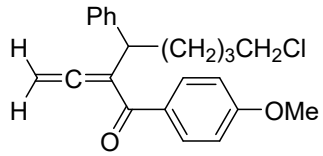
10c

2-(2-(Benzyloxy)-1-phenylethyl)-1-(4-methoxyphenyl)buta-2,3-dien-1-one (10c). Flash column chromatography to afford product **10c** as a white solid (36.1 mg, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.37-7.35 (m, 2H), 7.33-7.26 (m, 7H), 7.23-7.20 (m, 1H), 6.88-6.85 (m, 2H), 5.15 (d, *J* = 2.1 Hz, 2H), 4.54 (s, 2H), 4.44-4.41 (m, 1H), 3.88-3.86 (m, 1H), 3.84 (s, 3H), 3.79-3.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.5, 192.1, 162.9, 140.7, 138.3, 131.5, 130.8, 128.3, 128.2(6), 128.2, 127.6, 127.5, 126.8, 113.1, 107.9, 81.0, 72.9, 72.7, 55.4, 43.7. HRMS (ESI) $[M+Na]^+$: calculated for $C_{26}H_{24}O_3Na$: 407.1623, found 407.1626



10d

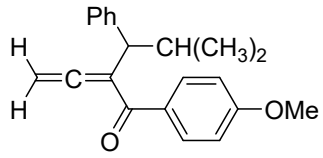
1-(4-methoxyphenyl)-3,6-diphenyl-2-vinylidenehexan-1-one (10d). Flash column chromatography to afford product **10d** as a pale yellow oil (16.8 mg, 22% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.32-7.31 (m, 2H), 7.30-7.26 (m, 4H), 7.20-7.15 (m, 4H), 6.87-6.85 (m, 2H), 5.16 (d, *J* = 2.1 Hz, 2H), 4.05 (t, *J* = 7.7 Hz, 1H), 3.85 (s, 3H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.96-1.90 (m, 1H), 1.88-1.80 (m, 1H), 1.71-1.61 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 192.4, 162.9, 143.6, 142.4, 131.5, 130.9, 128.4, 128.3, 128.2, 127.8, 126.4, 125.6, 113.1, 110.7, 80.9, 55.4, 43.0, 35.7, 34.6, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{27}H_{27}O_2$: 383.2011, found 383.2014.



10e

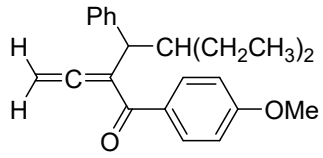
7-Chloro-1-(4-methoxyphenyl)-3-phenyl-2-vinylideneheptan-1-one (10e). Flash column chromatography to afford product **10e** as a white solid (19.1 mg, 27 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.31-7.26 (m, 4H), 7.19-7.17 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.25-5.17 (m, 2H), 4.01-3.98 (m, 1H), 3.83 (s, 3H), 3.52-3.49 (m, 2H), 1.91-1.85 (m, 1H), 1.82-1.75 (m, 3H), 1.53-1.44 (m, 1H), 1.41-1.34 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.0, 192.4, 162.9, 143.3, 131.5, 130.7, 128.3, 127.8, 126.5, 113.1, 110.6, 81.1, 55.4, 44.9, 43.0, 34.2, 32.4, 25.0. HRMS (ESI) $[M+H]^+$: calculated for $C_{22}H_{24}ClO_2$: 355.1465, found 355.1463.



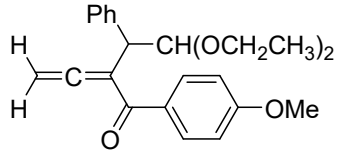
10f

1-(4-Methoxyphenyl)-4-methyl-3-phenyl-2-vinylidenepentan-1-one (10f). Flash column chromatography to afford product **10f** as a white oil (19.6 mg, 32% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.32-7.28 (m, 4H), 7.20-7.17 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.25-5.17 (m, 2H), 3.84 (s, 3H), 3.63 (d, *J* = 10.6 Hz, 1H), 2.23-2.16 (m, 1H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.6, 192.8, 162.9, 143.4, 131.5, 130.9, 128.3, 128.1, 126.3, 113.0, 110.5, 80.8, 55.4, 51.2, 32.0, 21.7, 21.2. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{23}O_2$: 307.1698, found 307.1701.



10g

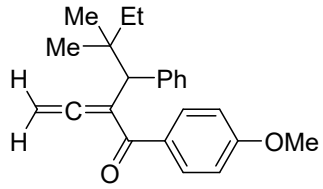
Ethyl-1-(4-methoxyphenyl)-3-phenyl-2-vinylidenehexan-1-one (10g). Flash column chromatography to afford product **10g** as a yellow oil (24.7 mg, 37% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 2H), 7.34-7.26 (m, 4H), 7.20-7.17 (m, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.23-5.16 (m, 2H), 3.91 (d, *J* = 10.9 Hz, 1H), 3.84 (s, 3H), 1.97-1.93 (m, 1H), 1.64-1.61 (m, 1H), 1.54-1.49 (m, 1H), 1.34-1.27 (m, 1H), 1.14-1.08 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.8, 192.8, 162.8, 143.3, 131.4, 130.9, 128.4, 128.1, 126.2, 113.0, 110.5, 80.8, 55.3, 46.6, 42.9, 22.3, 21.9, 10.3, 9.9. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{27}O_2$: 335.2011, found 335.2015.



10h

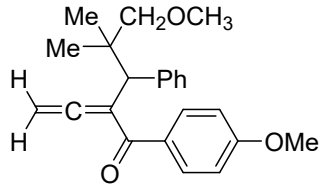
2-(2,2-Diethoxy-1-phenylethyl)-1-(4-methoxyphenyl)buta-2,3-dien-1-one (10h). Flash column chromatography to afford product **10h** as a colorless clear liquid (27.8 mg, 38% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.41-7.26 (m, 4H), 7.21-7.18 (m,, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.17-5.09 (m, 2H), 4.93 (d, *J* = 8.2

Hz, 1H), 4.35 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 3.73-3.67 (m, 1H), 3.58-3.52 (m, 2H), 3.38-3.32 (m, 1H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 192.2, 162.9, 139.7, 131.6, 130.8, 128.9, 128.1, 126.6, 113.1, 107.6, 104.0, 80.7, 61.9, 61.7, 55.4, 47.4, 15.2, 15.0. HRMS (ESI) $[M+Na]^+$: calculated for $C_{23}H_{26}O_4Na$: 389.1729, found 389.1724.



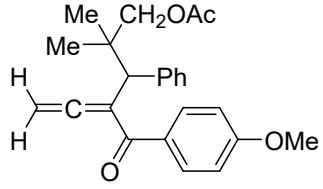
10i

1-(4-Methoxyphenyl)-4,4-dimethyl-3-phenyl-2-vinylidenehexan-1-one (10i). Flash column chromatography to afford product **10i** as a white solid (47.5 mg, 71 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.45-7.43 (m, 2H), 7.29-7.19 (m, 3H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.20 (d, *J* = 0.5 Hz, 2H), 4.03 (s, 1H), 3.83 (s, 3H), 1.50-1.46 (m, 1H), 1.39-1.30 (m, 1H), 1.03 (s, 3H), 0.96 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.5, 193.5, 162.8, 141.4, 131.7, 130.4, 130.3, 127.4, 126.3, 113.0, 108.2, 81.2, 55.3, 51.8, 38.2, 33.4, 24.7, 24.4, 8.4. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{27}O_2$: 335.2011, found 335.2014.



10j

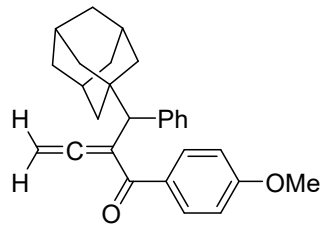
2-Methoxy-1-(4-methoxyphenyl)-4,4-dimethyl-3-phenyl-2-vinylidenepentan-1-one (10j). Flash column chromatography to afford product **10j** as a white solid (19.6 mg, 28 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.45-7.26 (m, 4H), 7.22-7.19 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.22-5.16 (m, 2H), 4.21 (s, 1H), 3.83 (s, 3H), 3.22 (s, 3H), 3.10 (d, *J* = 8.8 Hz, 1H), 3.02 (d, *J* = 8.8 Hz, 1H), 1.14 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.3, 193.1, 162.8, 141.1, 131.7, 130.4, 130.1, 127.6, 126.4, 113.0, 108.1, 81.3, 81.2, 58.8, 55.3, 48.9, 39.7, 22.7(9), 22.7(8). HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{27}O_3$: 351.1960, found 351.1960.



10k

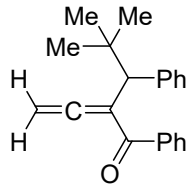
2-(4-Methoxybenzoyl)-2,2-dimethyl-3-phenylhexa-4,5-dien-1-yl acetate (10k). Flash column chromatography to afford product **10k** as a yellow solid (15.1 mg, 20%

yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.41-7.26 (m, 4H), 7.23-7.20 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.25 (s, 2H), 4.20 (s, 1H), 4.05 (d, *J* = 10.9 Hz, 1H), 3.83 (s, 3H), 3.74 (d, *J* = 10.9 Hz, 1H), 2.04 (s, 3H), 1.11 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.3, 193.0, 171.2, 162.9, 140.2, 131.6, 130.2, 130.1, 127.8, 126.7, 113.1, 107.4, 81.7, 71.4, 55.4, 48.7, 38.6, 23.1, 22.7, 20.9. HRMS (ESI) $[M+Na]^+$: calculated for $C_{24}H_{26}O_4Na$: 401.1729, found 401.1727.



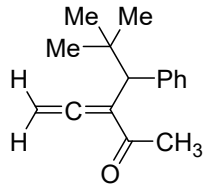
10l

2-((Adamantan-1-yl)(phenyl)methyl)-1-(4-methoxyphenyl)buta-2,3-dien-1-one (10l). Flash column chromatography to afford product **10l** as a white solid (72.5 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.7 Hz, 2H), 7.42-7.26 (m, 4H), 7.23-7.20 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.20 (q, *J* = 13.5 Hz, 2H), 3.83 (s, 3H), 3.78 (s, 1H), 1.95 (s, 3H), 1.68 (d, *J* = 2.0 Hz, 6H), 1.67-1.56 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.6, 193.6, 162.8, 140.5, 131.7, 130.4, 130.3, 127.4, 126.3, 113.0, 107.3, 81.2, 55.3, 54.2, 40.4, 37.5, 36.9, 28.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{28}H_{31}O_2$: 399.2324, found 399.2327.



10m

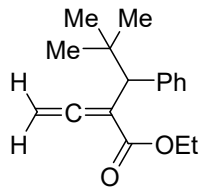
4,4-Dimethyl-1,3-diphenyl-2-vinylidenepentan-1-one (10m). Flash column chromatography to afford product **10m** as a yellow solid (25.5 mg, 44% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.49-7.43 (m, 3H), 7.38-7.35 (m, 2H), 7.30-7.27 (m, 2H), 7.23-7.21 (m, 1H), 5.22 (s, 2H), 4.01 (s, 1H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.6, 195.0, 141.5, 137.9, 131.9, 130.1, 129.2, 127.7, 127.6, 126.4, 108.9, 81.8, 52.7, 35.7, 28.4. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{23}O$: 291.1749, found 291.1747.



10n

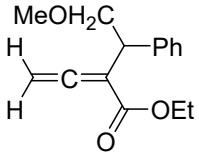
5,5-Dimethyl-4-phenyl-3-vinylidenehexan-2-one (10n). Flash column chromatography to afford product **10n** as a yellow solid (31.5 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.23 (m, 4H), 7.21-7.18 (m, 1H), 5.42 (s, 2H), 3.87 (s, 1H), 2.28 (s, 3H), 0.93 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.9, 197.8, 141.7,

130.0, 127.5, 126.3, 110.8, 81.5, 50.1, 35.3, 28.2, 26.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{16}H_{21}O$: 229.1590, found 229.1592



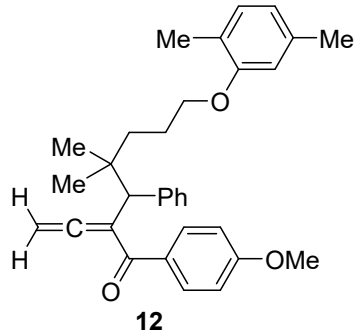
10o

Ethyl 4,4-dimethyl-3-phenyl-2-vinylidenepentanoate (10o). Flash column chromatography to afford product **10o** as a colorless clear liquid (30.5 mg, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.34 (m, 2H), 7.27-7.24 (m, 2H), 7.22-7.19 (m, 1H), 5.37-5.31 (m, 2H), 4.18-4.07 (m, 2H), 3.73 (s, 1H), 1.21 (t, J = 7.1 Hz, 3H), 0.97 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.7, 167.7, 141.5, 130.0, 127.5, 126.3, 102.4, 80.9, 61.2, 53.1, 35.4, 28.2, 14.1. HRMS (ESI) $[M+H]^+$: calculated for $C_{17}H_{23}O_2$: 259.1698, found 259.1695.



10p

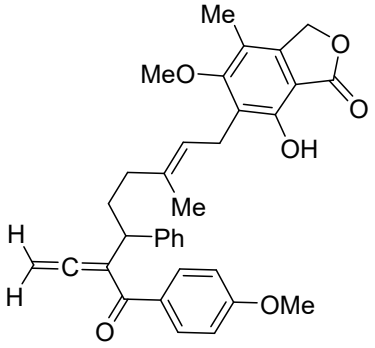
Ethyl 2-(2-methoxy-1-phenylethyl)buta-2,3-dienoate (10p). Flash column chromatography to afford product **10p** as a colorless clear liquid (12.8 mg, 26% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 4H), 7.21-7.18 (m, 1H), 5.34-5.27 (m, 2H), 4.16-4.03 (m, 3H), 3.65-3.62 (m, 1H), 3.57-3.54 (m, 1H), 3.30 (s, 3H), 1.20-1.17 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.8, 166.3, 140.5, 128.3, 128.0, 126.9, 101.8, 80.8, 75.2, 61.1, 58.7, 43.6, 14.1. HRMS (ESI) $[M+Na]^+$: calculated for $C_{15}H_{18}O_3Na$: 269.1154, found 269.1158.



12

7-(2,5-Dimethylphenoxy)-1-(4-methoxyphenyl)-4,4-dimethyl-3-phenyl-2-vinylideneheptan-1-one (12). Flash column chromatography to afford product **12** as a yellow solid (77.7 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.9 Hz, 2H), 7.44-7.26 (m, 4H), 7.22-7.19 (m, 1H), 7.00 (d, J = 7.4 Hz, 1H), 6.85 (d, J = 8.9 Hz, 2H), 6.65 (d, J = 7.5 Hz, 1H), 6.60 (s, 1H), 5.20 (s, 2H), 4.06 (s, 1H), 3.90-3.87 (m, 2H), 3.83 (s, 3H), 2.30 (s, 3H), 2.14 (s, 3H), 1.90-1.77 (m, 2H), 1.66-1.60 (m, 1H), 1.52-1.46 (m, 1H), 1.09 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

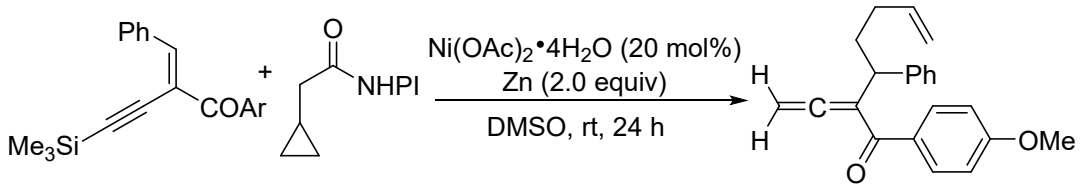
217.4, 193.4, 162.8, 157.1, 141.1, 136.4, 131.7, 130.4, 130.3, 130.2, 127.6, 126.4, 123.5, 120.5, 113.0, 111.9, 108.1, 81.4, 68.5, 55.4, 52.0, 37.9, 37.3, 25.4, 25.1, 24.2, 21.4, 15.8. HRMS (ESI) $[M+Na]^+$: calculated for $C_{32}H_{36}O_3Na$: 491.2562, found 491.2565.



14

(*E*)-7-Hydroxy-5-methoxy-6-(7-(4-methoxybenzoyl)-3-methyl-6-phenylnona-2,7,8-trien-1-yl)-4-methylisobenzofuran-1(3H)-one (14). Flash column chromatography to afford product 14 as a white solid (46.4 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 (s, 1H), 7.24-7.21 (m, 3H), 7.15-7.13 (m, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.20-5.12 (m, 5H), 3.90-3.87 (m, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.38 (d, *J* = 6.9 Hz, 2H), 2.13 (s, 3H), 2.02-1.83 (m, 4H), 1.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.2, 192.3, 172.9, 163.6, 162.8, 153.6, 143.8, 143.6, 135.3, 131.4, 130.8, 128.2, 127.8, 126.3, 122.4, 122.3, 116.7, 112.9, 110.4, 106.3, 81.0, 70.0, 61.0, 55.4, 42.7, 37.7, 33.3, 22.6, 16.1, 11.5. HRMS (ESI) $[M+Na]^+$: calculated for $C_{34}H_{34}O_6Na$: 561.2253, found 561.2252.

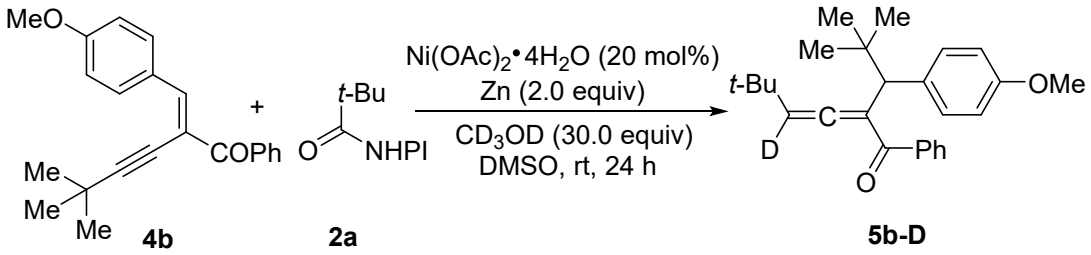
5 Mechanism Studies



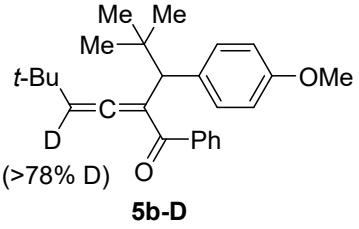
9a, Ar = 4-MeOC$_6$H$_4$ **15** **16**

To an oven-dried Schlenk tube was charged with (*E*)-2-benzylidene-1-(4-methoxyphenyl)-4-(trimethylsilyl)but-3-yn-1-one **9a** (66.9 mg, 0.2 mmol), redox-active ester **15** (100 mg, 0.4 mmol), $Ni(OAc)_2$•$4H_2O$ (10.1 mg, 0.04 mmol), Zn (26.2 mg, 0.4 mmol) in DMSO (4 mL). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times. The reaction mixture was allowed to stir at room temperature for 24 h, H_2O (3 mL) and saturate NH_4Cl solution (3 mL) were added to quench the reaction and the mixture was extracted by ethyl acetate. The combined organic layer was dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography on silica gel to

give 3-(4-methoxyphenyl)-1-phenyl-2-vinylidenehept-6-en-1-one **16** as a orange clear liquid (10.2 mg, 16% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 2H), 7.32-7.25 (m, 4H), 7.18-7.15 (m, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 5.85-5.78 (m, 1H), 5.23-5.15 (m, 2H), 5.00-4.95 (m, 2H), 4.03-4.00 (m, 1H), 3.83 (s, 3H), 2.06-1.99 (m, 2H), 1.98-1.94 (m, 1H), 1.89-1.84 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 192.4, 163.0, 143.3, 138.3, 131.5, 130.9, 128.3, 127.9, 126.4, 114.8, 113.1, 110.7, 81.0, 55.4, 42.7, 34.3, 31.9. HRMS (ESI) $[M+H]^+$: calculated for $C_{20}H_{21}O_3$: 319.1698, found 319.1707.

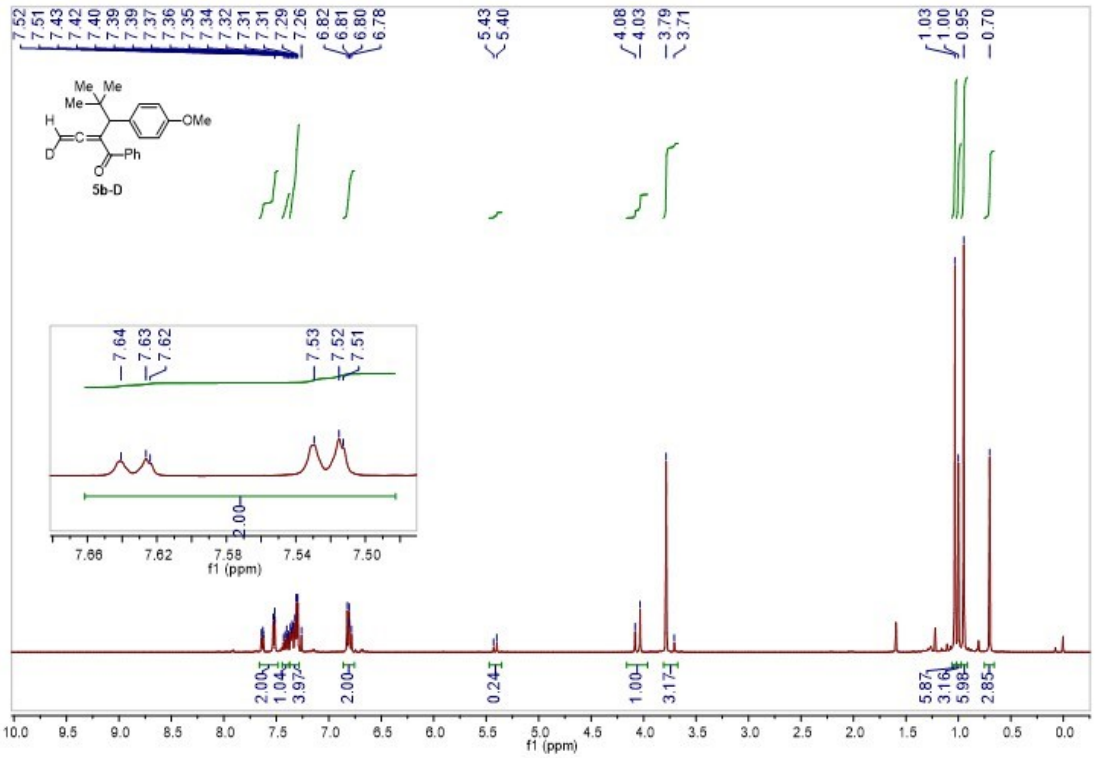


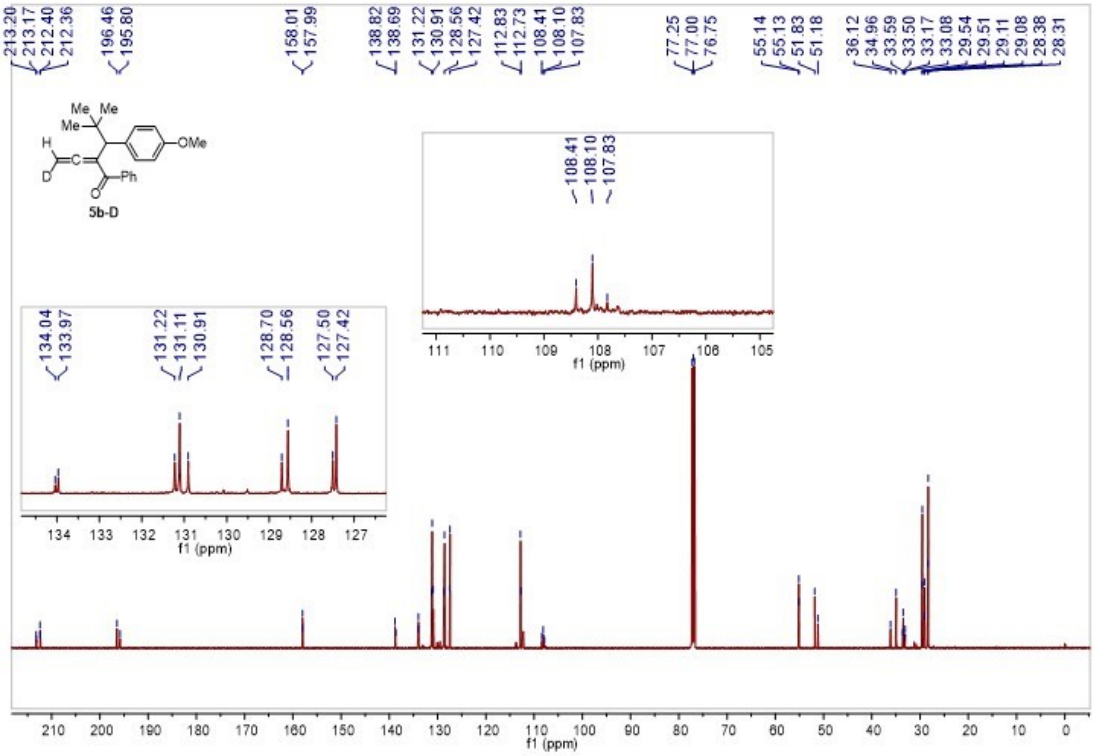
To an oven-dried Schlenk tube was charged with 2-(1-alkynyl)-2-alken-1-one **4b** (66.3 mg, 0.2 mmol), redox-active ester **2a** (98.8 mg, 0.4 mmol), $Ni(OAc)_2$•$4H_2O$ (10.1 mg, 0.04 mmol), Zn (26.2 mg, 0.4 mmol) in DMSO (4 mL). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point CD_3OD (244 μL, 30 equiv) was added via a syringe prior. The reaction mixture was allowed to stir at room temperature for 24 h, H_2O (3 mL) and saturate NH_4Cl solution (3 mL) were added to quench the reaction and the mixture was extracted by ethyl acetate. The combined organic layer was dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography on silica gel.

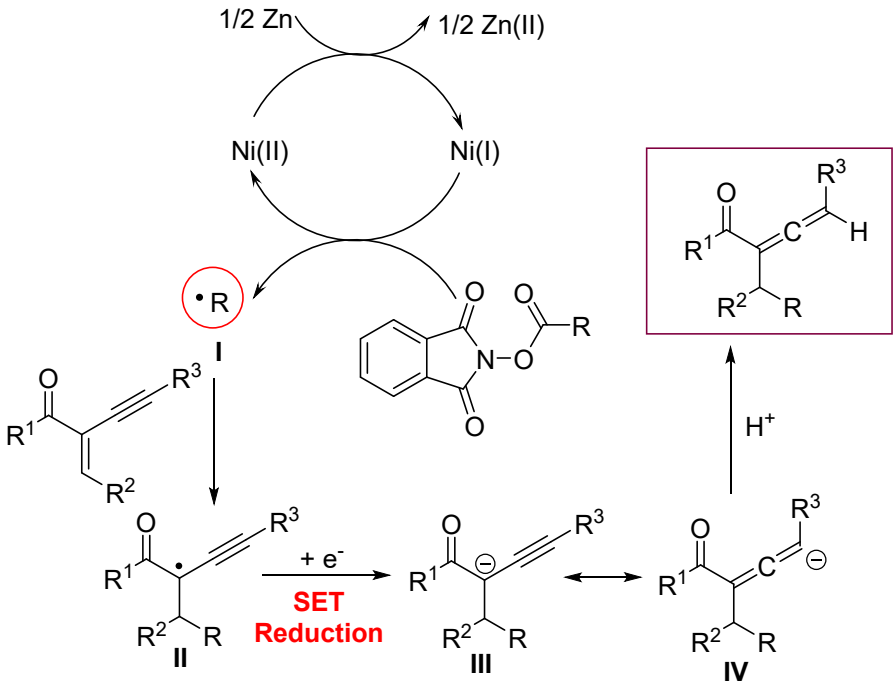


2-(1-(4-Methoxyphenyl)-2,2-dimethylpropyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one-4-D (5b-D). The product **5b-D** was obtained in 63% yield (62.2 mg, with over 78% D-incorporation, dr = 52:48) as a white solid after column chromatography. Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.51 (m, 2H), 7.43-7.39 (m, 1H), 7.37-7.29 (m, 4H), 6.82-6.78 (m, 2H), [5.43 (s, 0.08H), 5.40 (s, 0.16H)], [4.08 (s, 0.33H), 4.03 (s, 0.67H)], [3.79 (s, 2.01H), 3.71 (s, 0.99H)], [1.03 (s, 6.03H), 1.00 (s, 2.97H)], [0.95 (s, 6.03H), 0.70 (s, 2.97H)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.2(0), 213.1(7), 212.4(0), 212.3(6), 196.5, 195.8, 158.0(1), 157.9(9), 138.8, 138.7, 134.0(4), 133.9(7), 131.2, 131.1, 130.9, 128.7, 128.6, 127.5, 127.4, 112.8, 112.7, 108.4, 108.1, 107.8, 55.1(4), 55.1(3), 51.8, 51.2, 36.1, 35.0, 33.6, 33.5, 33.2, 33.1, 29.5(4), 29.5(1), 29.1(1),

29.0(8), 28.4, 28.3. HRMS (ESI) $[M+H]^+$: calculated for $C_{26}H_{32}DO_2$: 378.2538, found 378.2534.

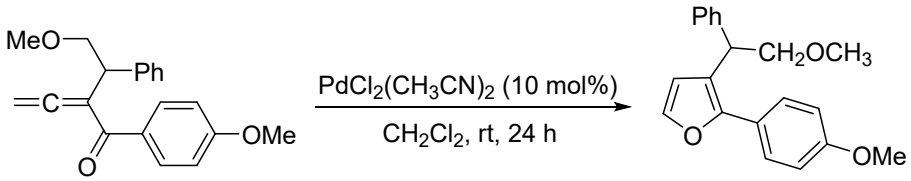






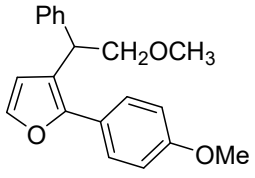
Scheme 1 Proposed mechanism.

6 Transformation of 1,2-Allenyl Ketone



10b **17**

To a solution of 2-(2-methoxy-1-phenylethyl)-1-(4-methoxyphenyl)buta-2,3-dien-1-one **10b** (61.6 mg, 0.20 mmol) in dried DCM (3 mL), $PdCl_2(CH_3CN)_2$ (5.2 mg, 0.02 mmol) was added. Then the mixture was stirred at room temperature, **10b** was consumed completely after 24 h by TLC analysis. H_2O (3 mL) was added to quench the reaction and the mixture was extracted by ethyl acetate. The combined organic layer was dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography on silica gel to give **17** (23.4 mg, 38% yield).



17

3-(2-Methoxy-1-phenylethyl)-2-(4-methoxyphenyl)furan (17). Flash column chromatography to afford product **17** as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.47-7.44 (m, 3H), 7.32-7.31 (m, 4H), 7.24-7.21 (m, 1H), 6.91-6.89 (m, 2H), 6.54 (d,

J = 1.8 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 1H), 3.83-3.81 (m, 5H), 3.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.9, 141.9, 140.9, 128.5, 128.0, 127.8, 126.6, 124.0, 119.7, 113.9, 111.6, 76.8, 58.9, 55.3, 41.9. HRMS (ESI) $[M+H]^+$: calculated for $C_{20}H_{21}O_3$: 309.1491, found 309.1490.

7 Reference

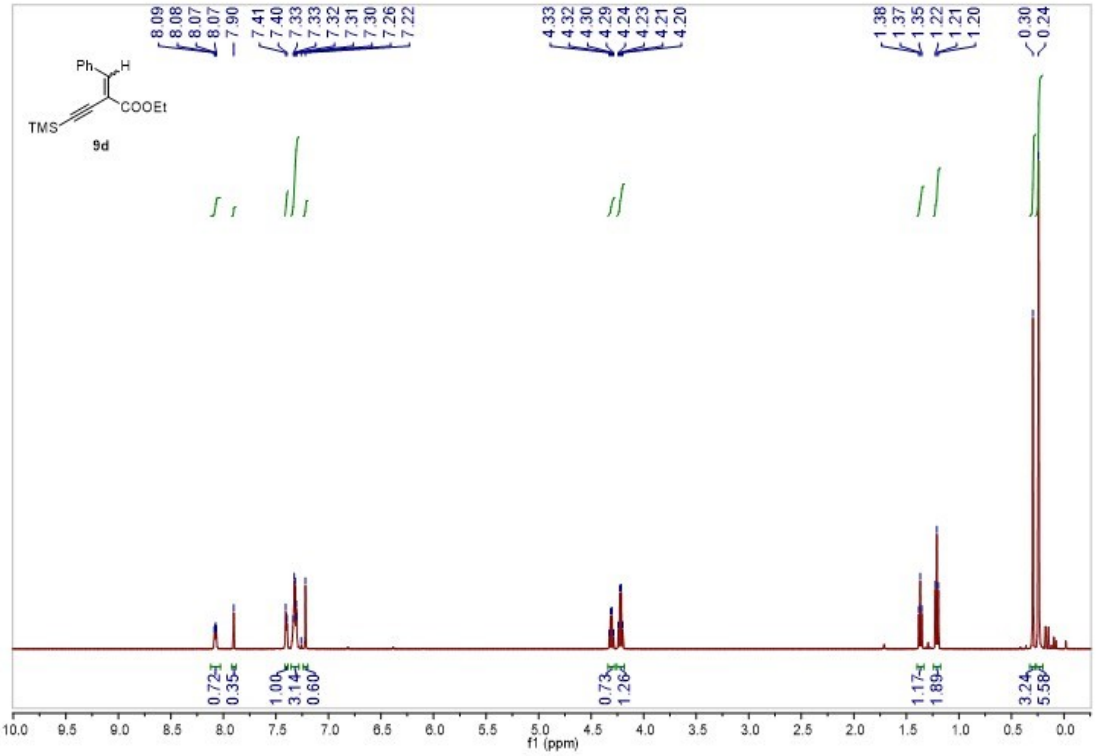
[1] W. Lei, H. Liu, Y. Li and Y. Fang, Nickel-catalysed SET-reduction-based access to functionalized allenes via 1,4-carbohydrogenation of 1,3-enynes with alkyl bromides, *Org. Chem. Front.*, 2022, **9**, 3862-3868.

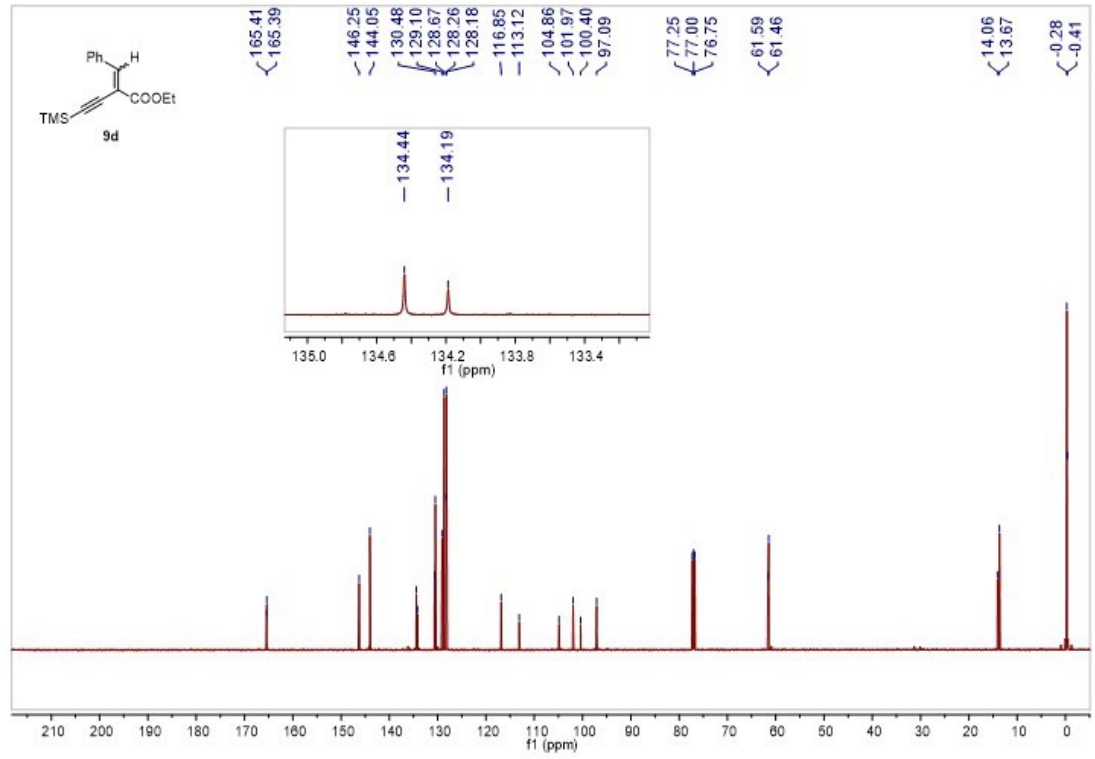
[2] (*a*) C. Zheng, Y. Wang, Y. Xu, Z. Chen, G. Chen and S. H. Liang, Ru-Photoredox-Catalyzed Decarboxylative Oxygenation of Aliphatic Carboxylic Acids through *N*-(acyloxy)phthalimide, *Org. Lett*., 2018, **20**, 4824-4827; (*b*) Z. Zhou, Z. S. Sales, D. J. Pippel, M. Qian and C. L. Martin, Blue Light-Mediated, Photocatalyst-Free Decarboxylative Alkylation of Heteroaryl Sulfinimines, *J. Org. Chem.,* 2022, **87**, 14948–14952; (*c*) M. Luo, S. Zhu, C. Shi, Y, Du, C. Yang, L. Guo and W. Xia, Photoinduced Remote C(sp3)−H Cyanation and Oxidation Enabled by a Vinyl Radical-Mediated 1,5-HAT Strategy, *Org. Lett.,* 2022, **24**, 6560−6565; (*d*) H.-Y. Liu, Y. Lu, Y. Li and J.-H. Li, Photocatalytic Decarboxylative [2 + 2 + *m*] Cyclization of 1,7-Enynes Mediated by Tricyclohexylphosphine and Potassium Iodide, *Org. Lett.,* 2020, **22**, 8819−8823; (*e*) J. Dong, X. Wang, H. Song, Y. Liu and Q. Wang, Photoredox-Catalyzed Redox-Neutral Minisci C−H Formylation of N-Heteroarenes, *Adv. Synth. Catal*., 2020, **362**, 2155-2159; (*f*) X. Xi, Y. Chen and W. Yuan, Nickel-Catalyzed Three-Component Alkylacylation of Alkenes Enabled by a Photoactive Electron Donor−Acceptor Complex, *Org. Lett*., 2022, **24**, 3938−3943; (*g*) K. K. Ghosh, A. Uttry, A. Koldemir, M. Ong and M. van Gemmeren, Direct β-C(sp3)−H Acetoxylation of Aliphatic Carboxylic Acids, *Org. Lett*., 2019, **21**, 7154−7157; (*h*) V. Maharaj, P. P. Chandrachud, W. Che, L. Wojtas and J. M. Lopchuk, Photodecarboxylative Amination of Redox-Active Esters with Diazirines, *Org. Lett*., 2021, **23**, 8838−8842.

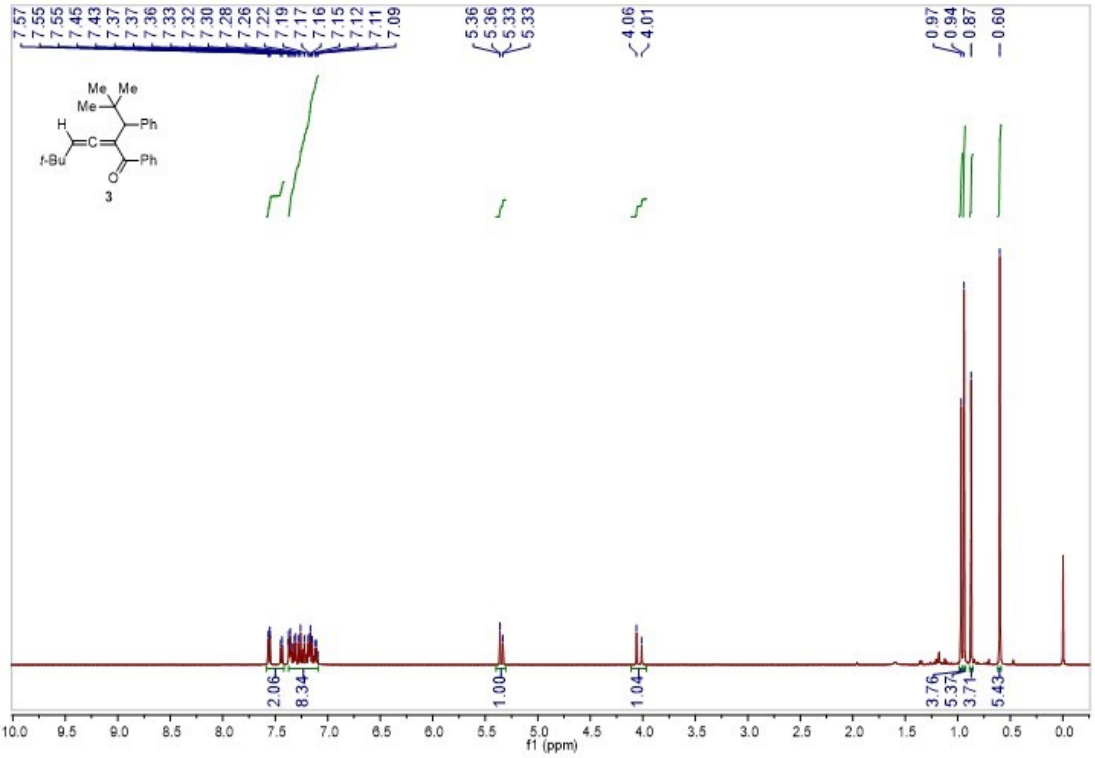
[3] W. Lei, Y. Liu, Y. Fang, Y. Li, C. Du and J. Fang, Modular access to 1,2-allenyl ketones based on a photoredox-catalysed radical-polar crossover process, *Org. Biomol. Chem.*, 2021, **19**, 8502-8506.

[4] W. Li, L. Gao, Z. Yue and J. Zhang, Phosphine-Catalyzed Regioselective and Stereoselective Hydrohalogenation Reaction of 2-(1-Alkynyl)-2-alken-1-ones: Synthesis of 2-Halo-1,3-dienes, *Adv. Synth. Catal*., 2015, **357**, 2651-2655.

8 NMR spectra of new compound



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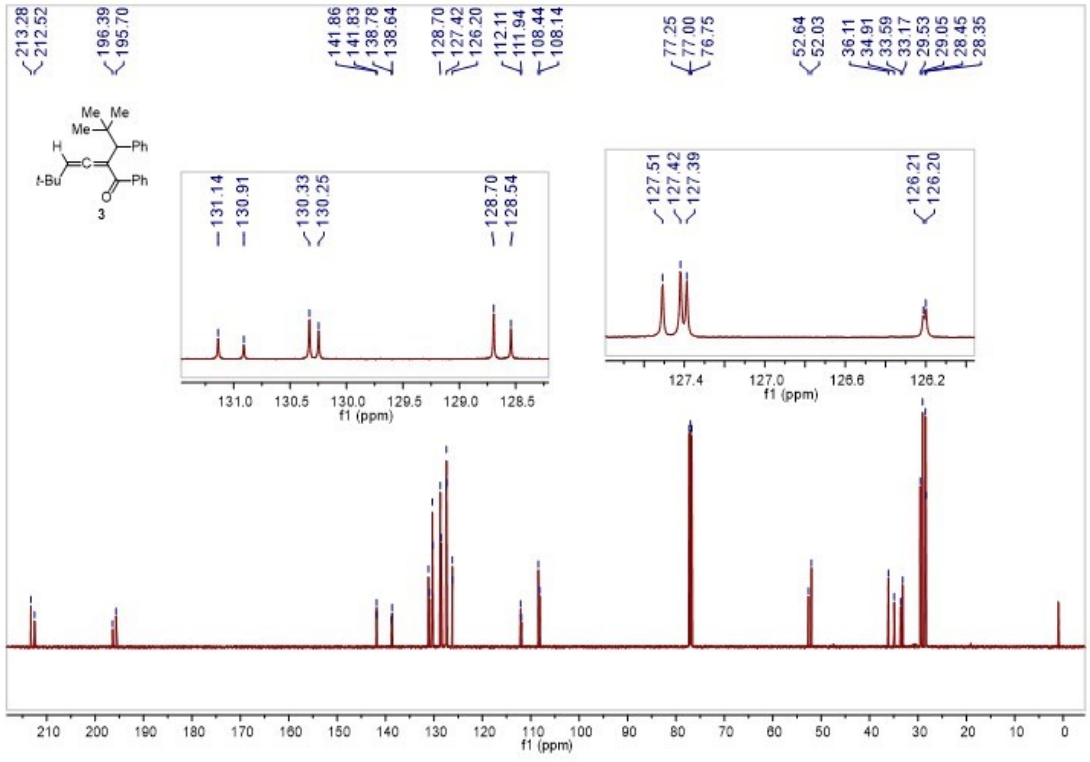
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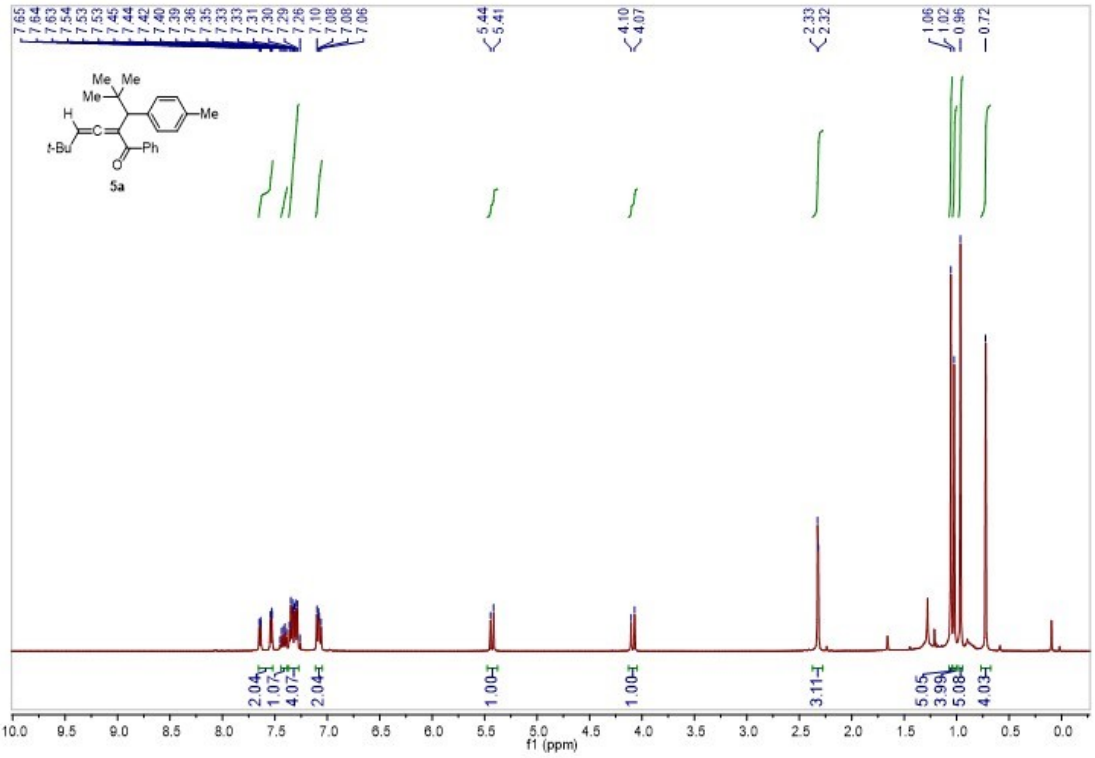
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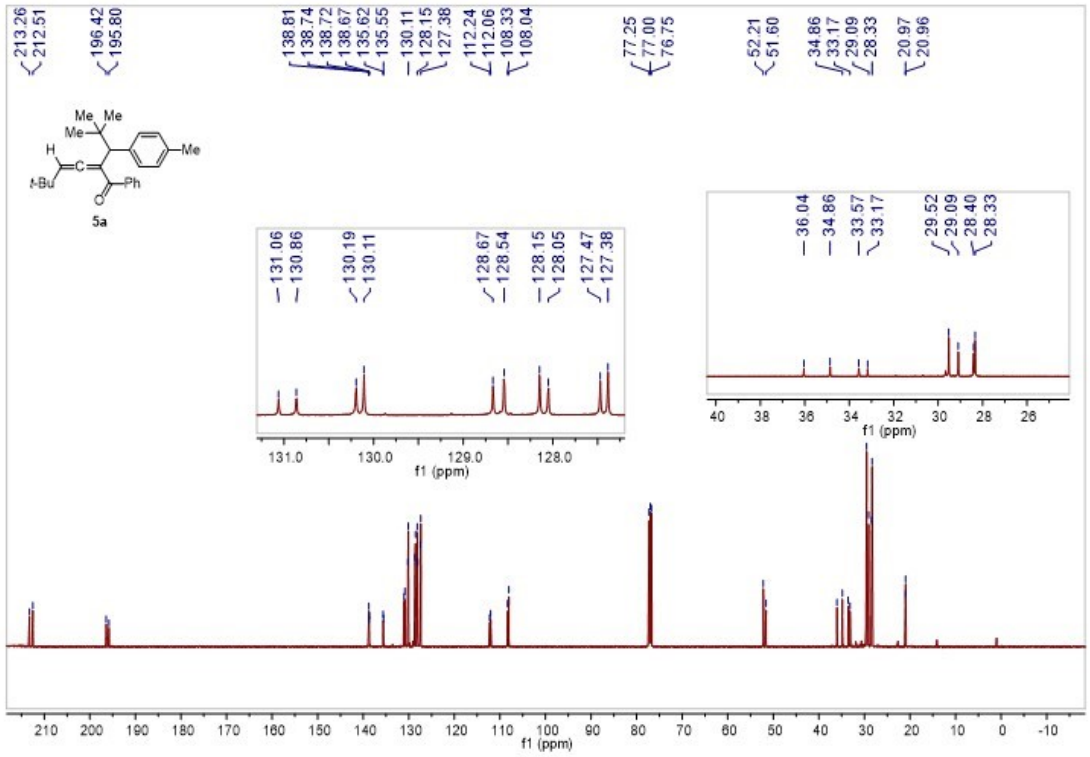
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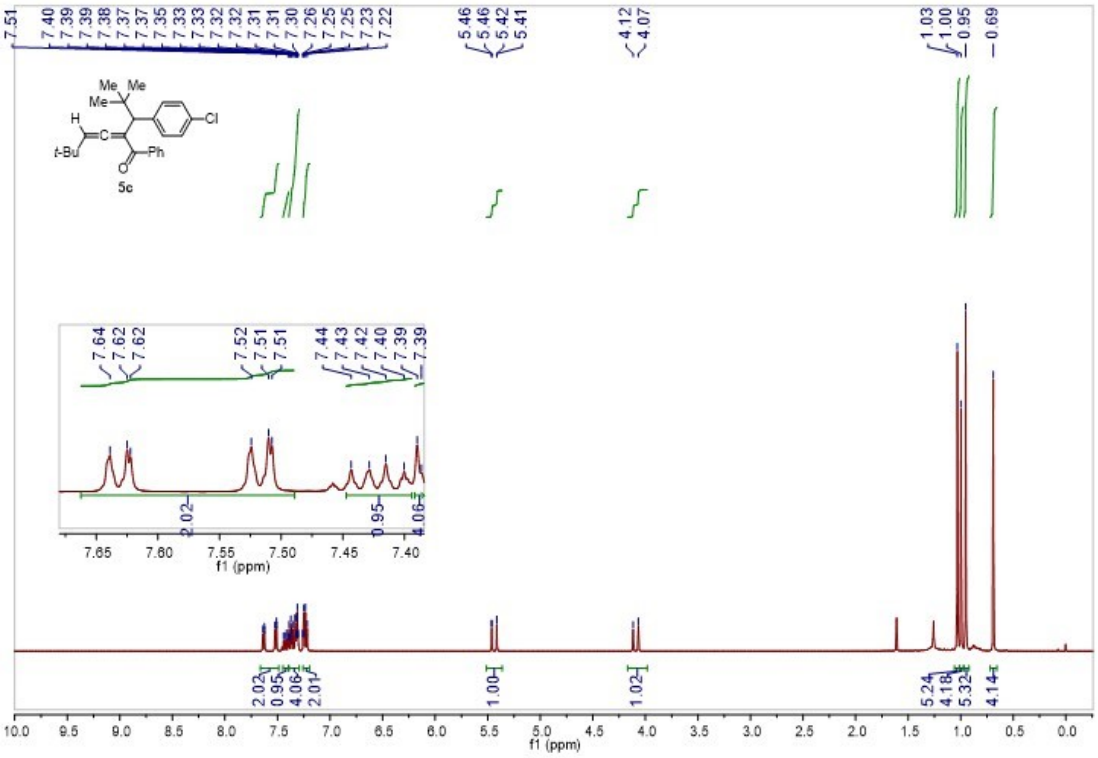
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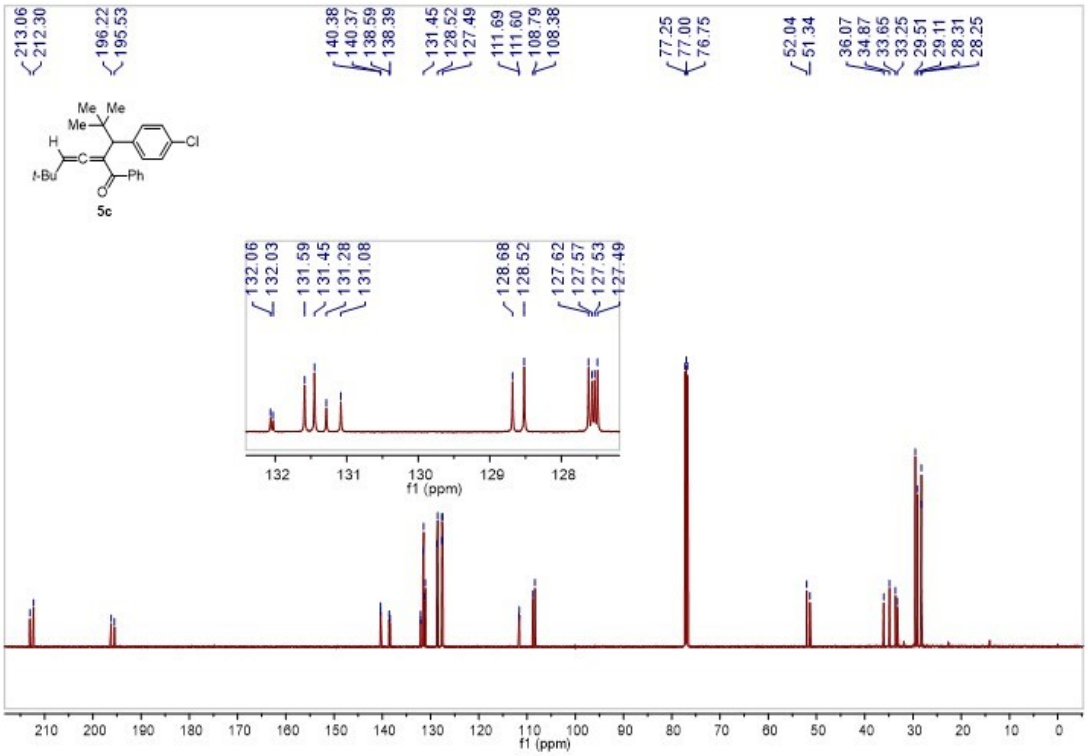
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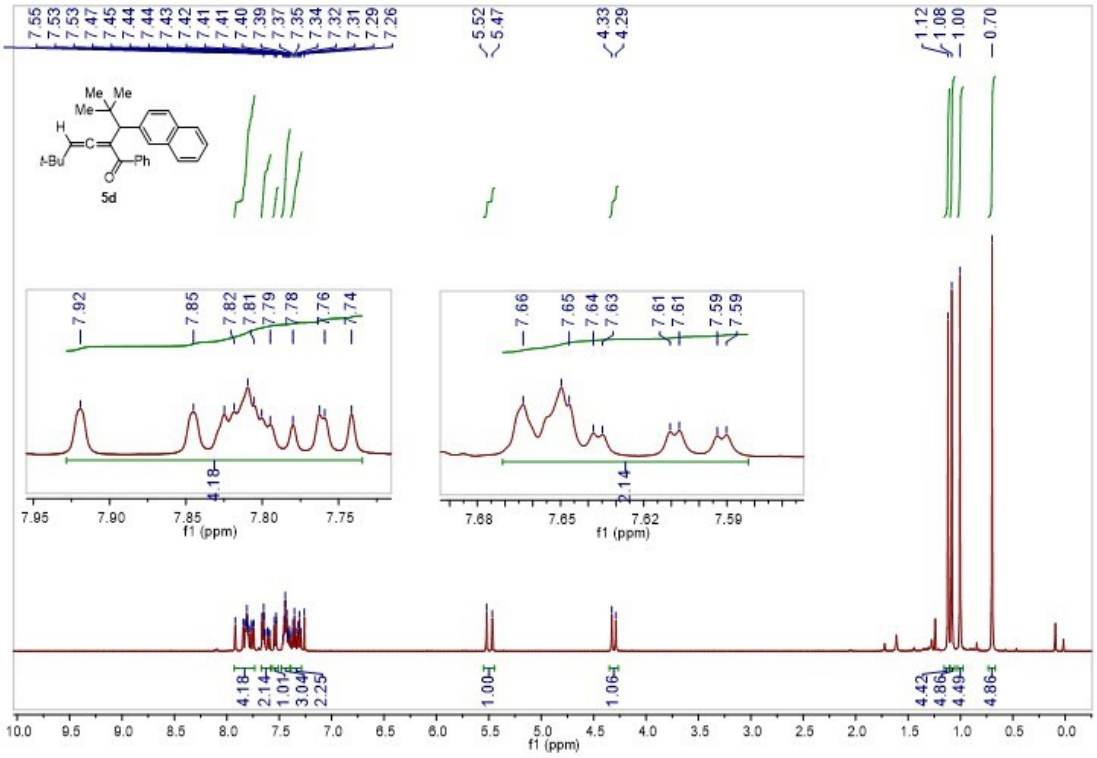
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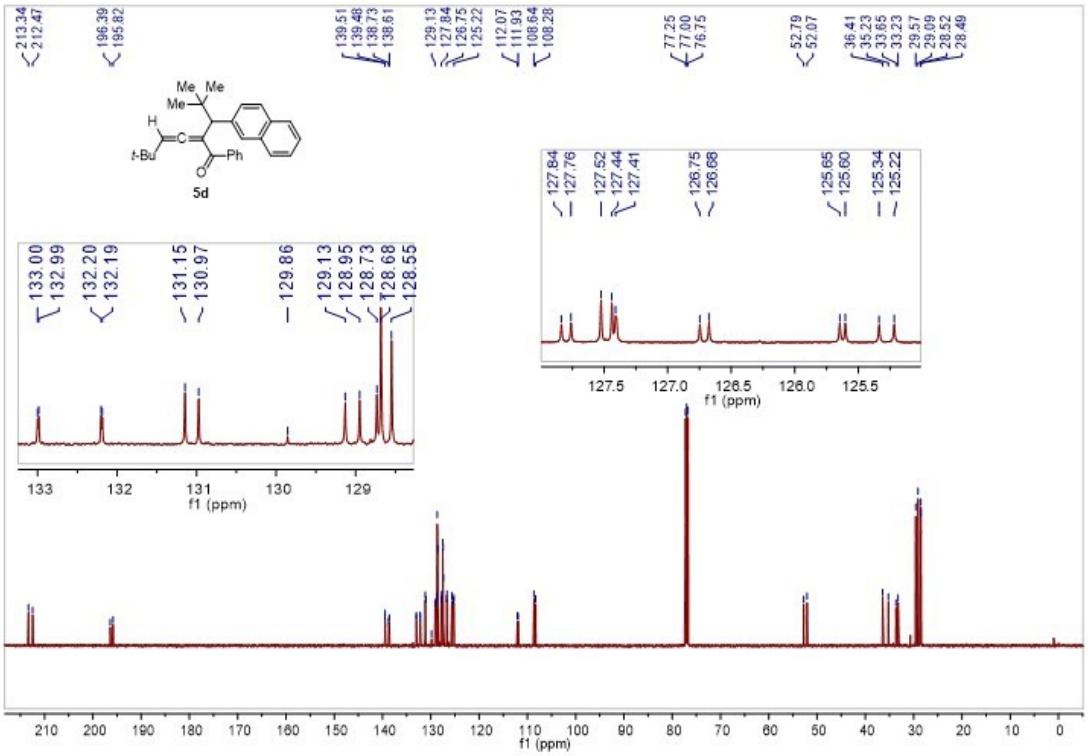
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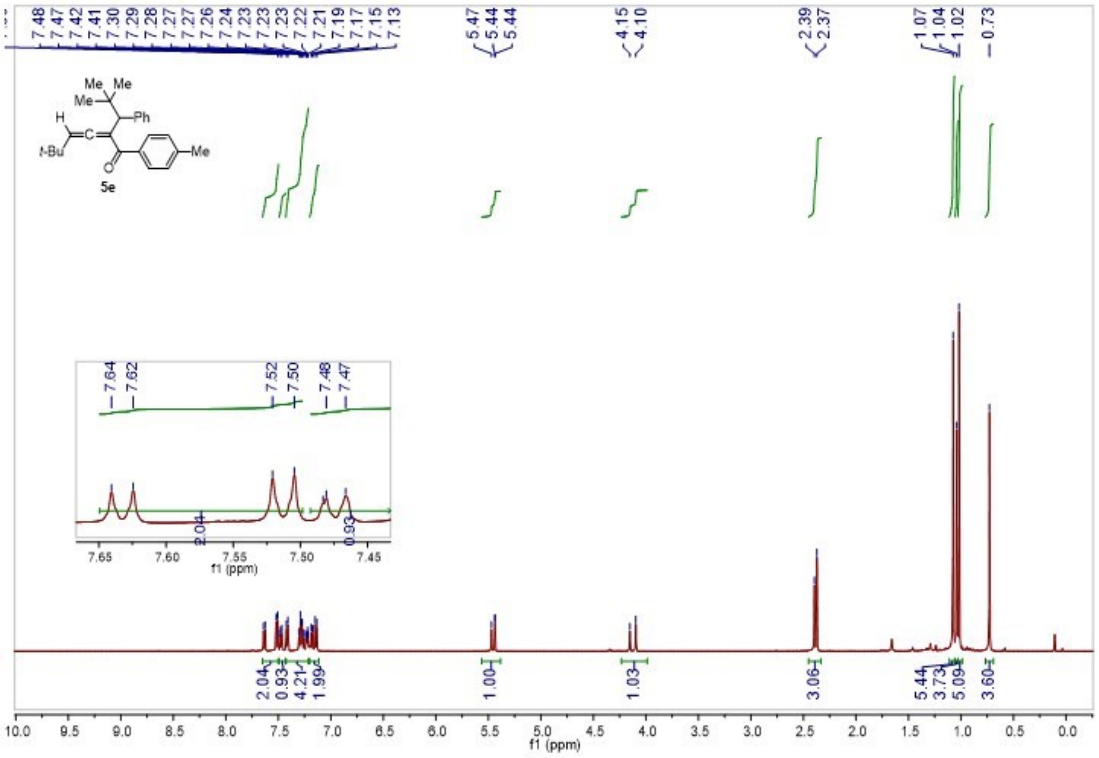
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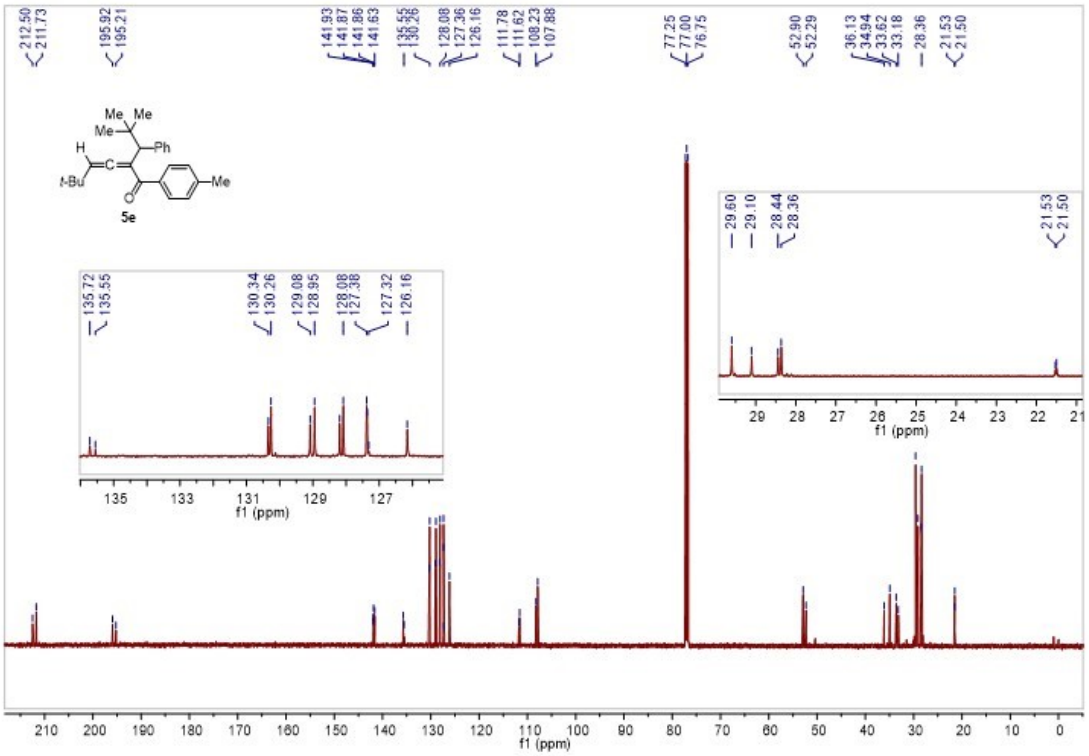
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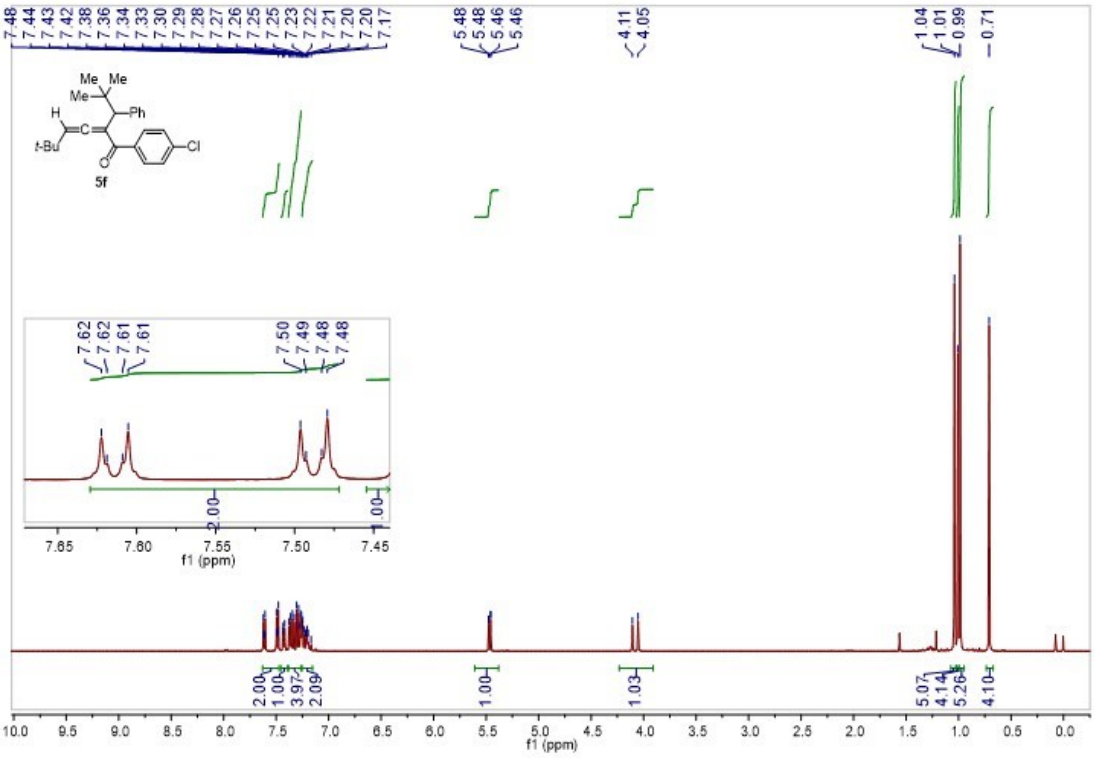
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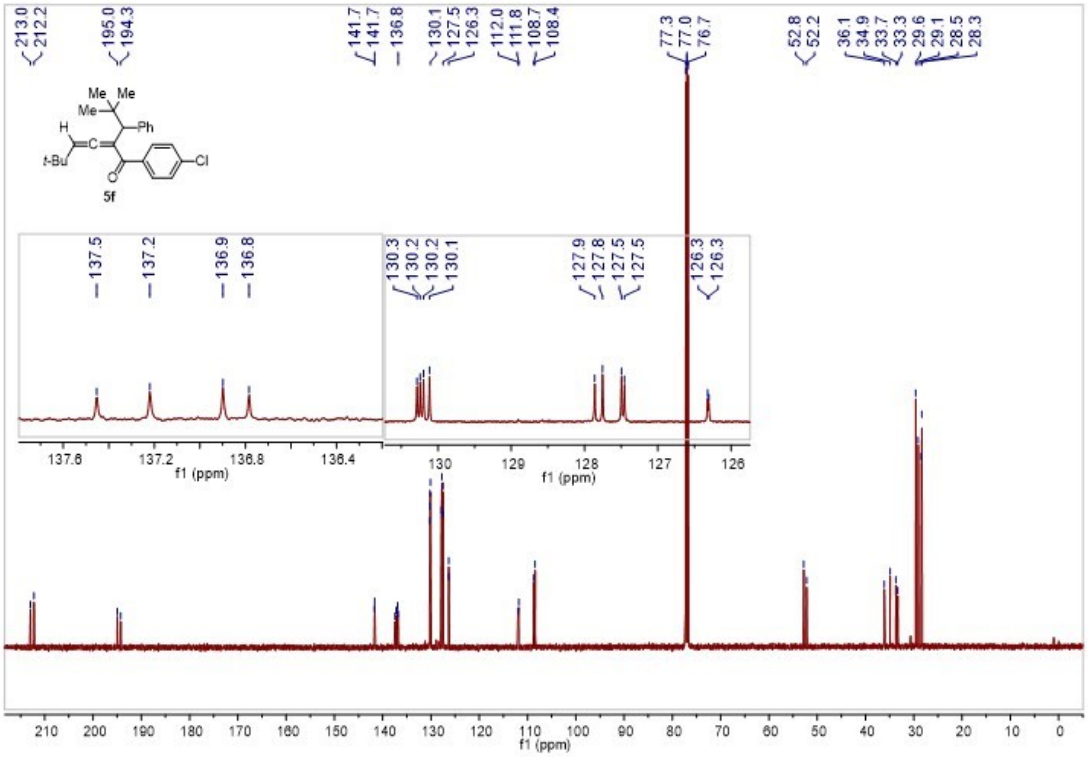
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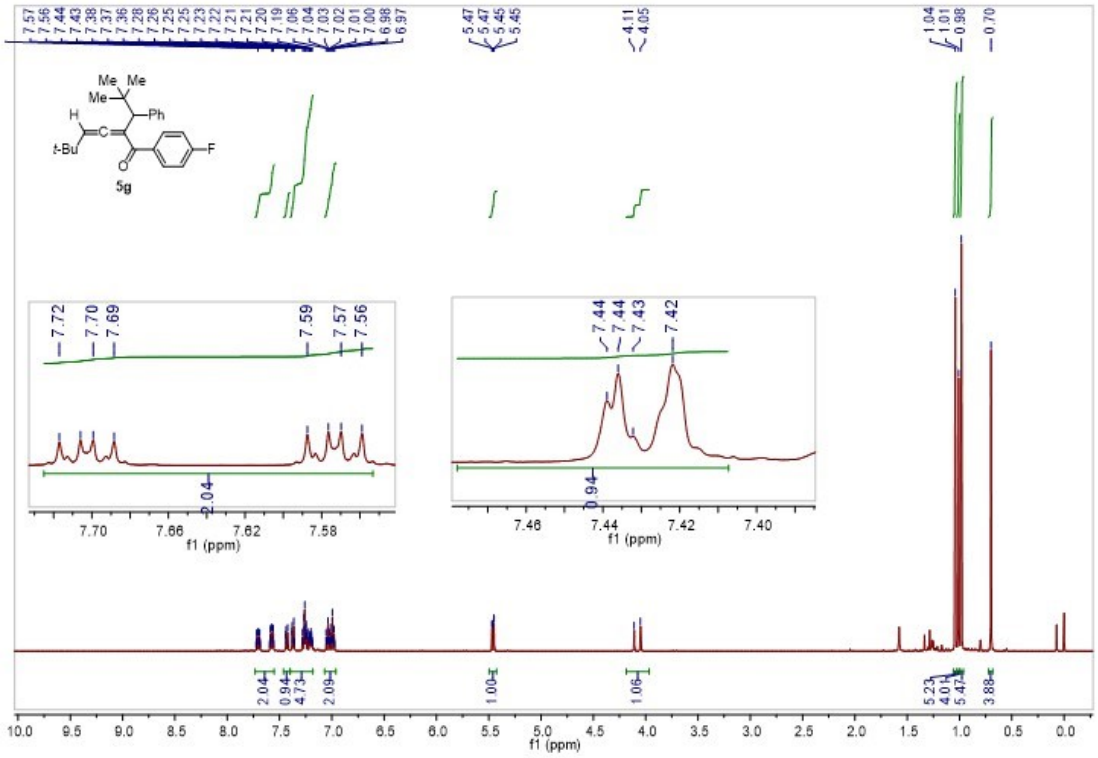
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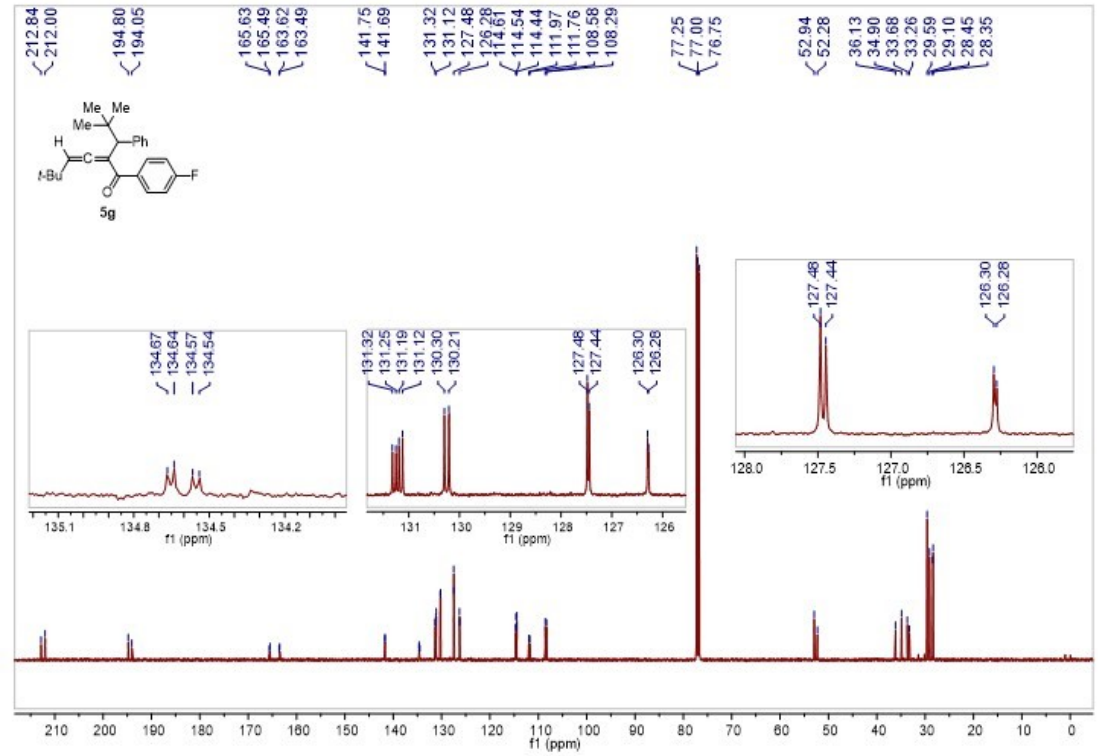
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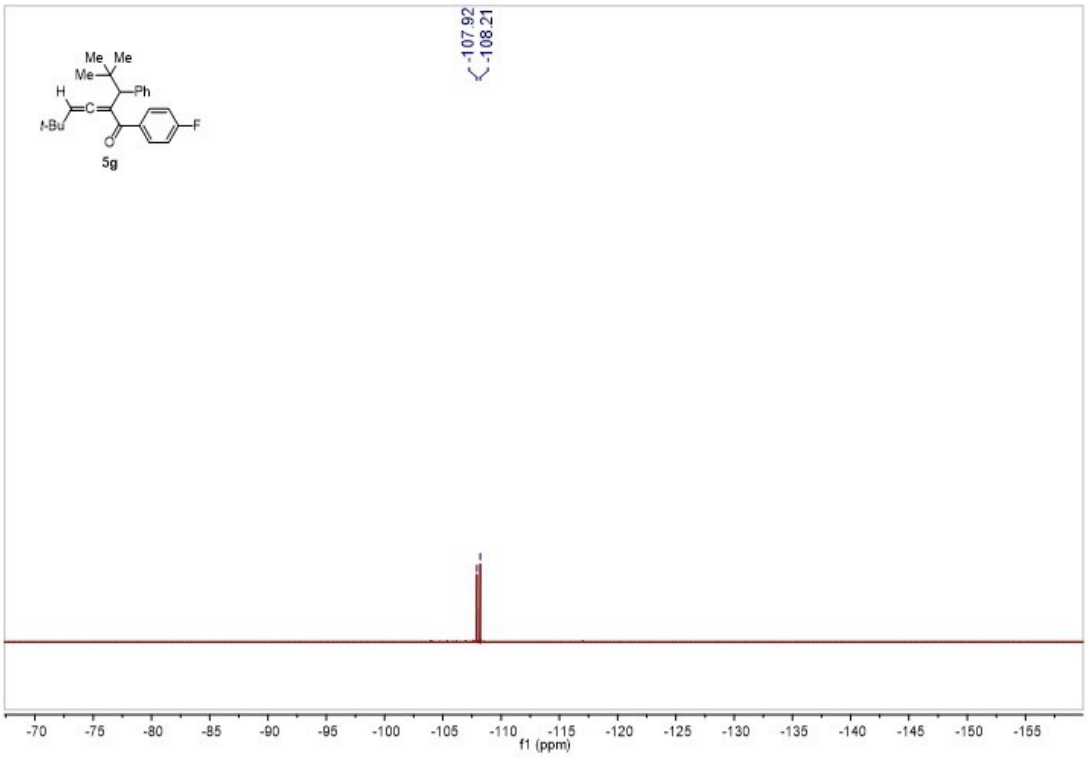
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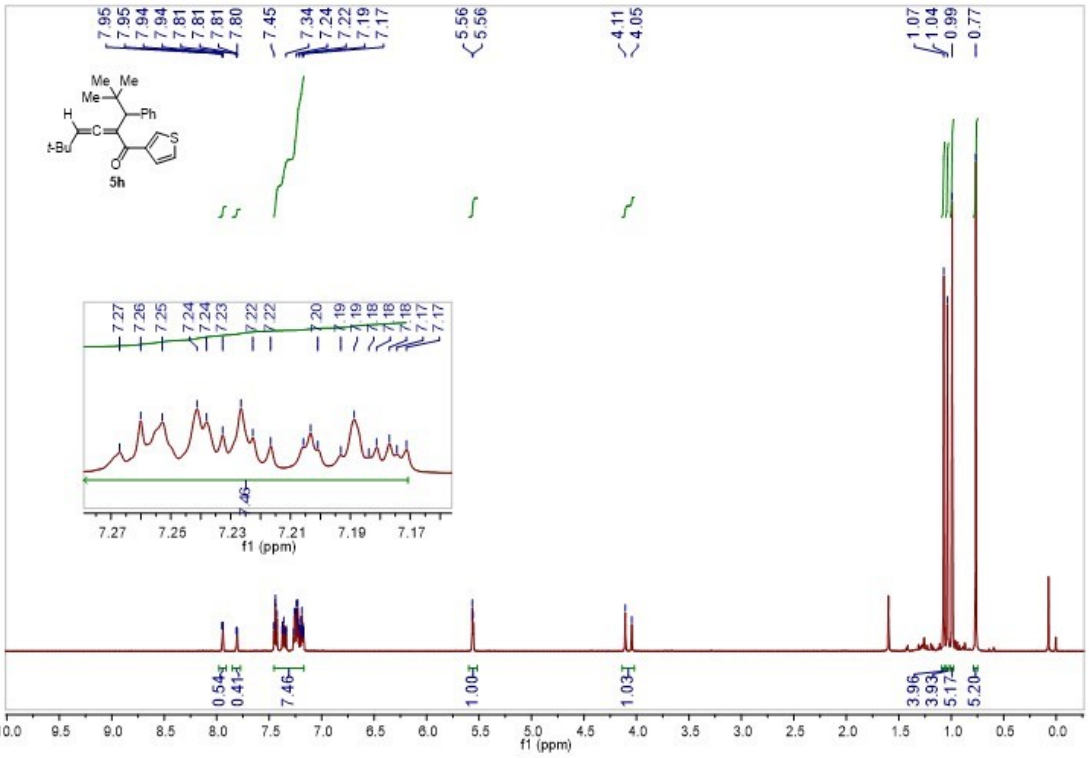
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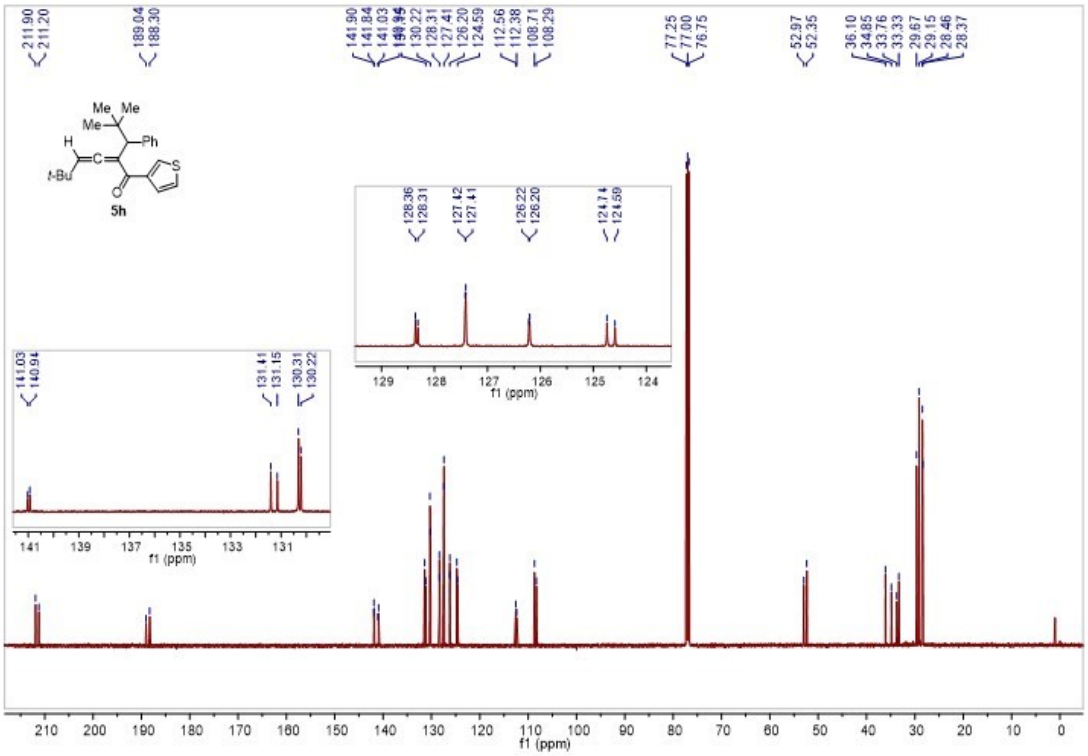
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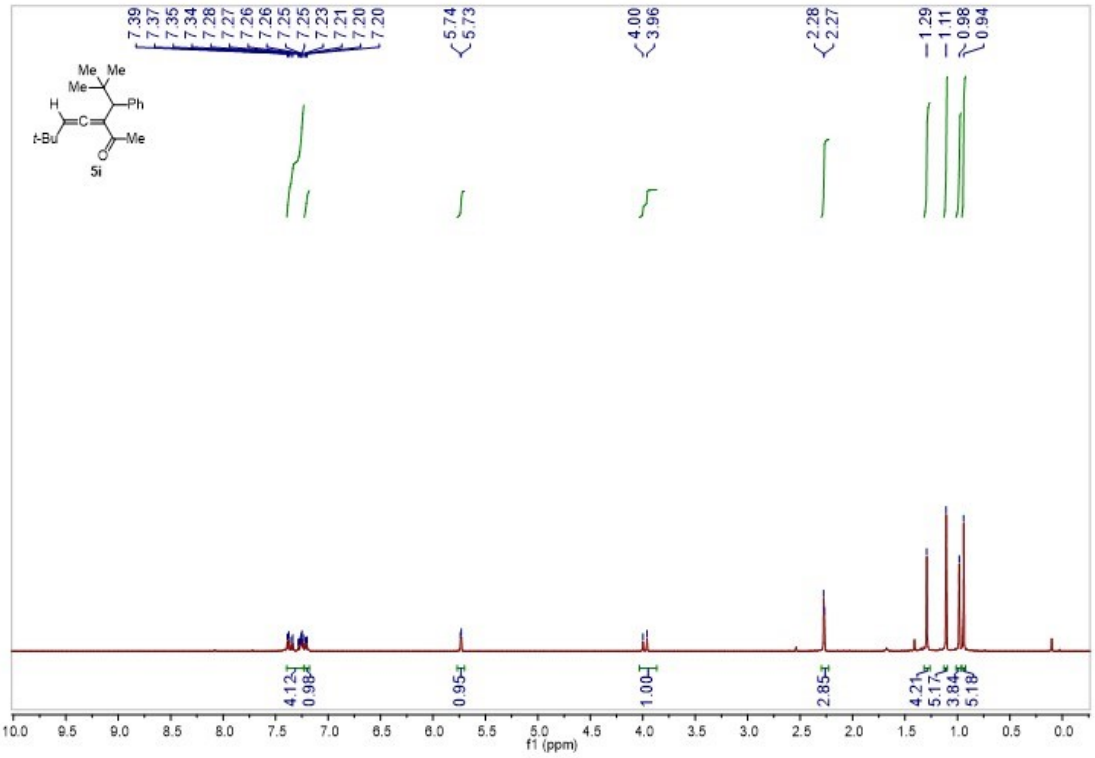
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7.23
7.21
7.20
7.20
5.74
5.73
4.00
3.96
2.28
2.27
1.29
1.11
0.98
0.94
Me
Me
Me
Ph
H
t-Bu
Me
O
5i
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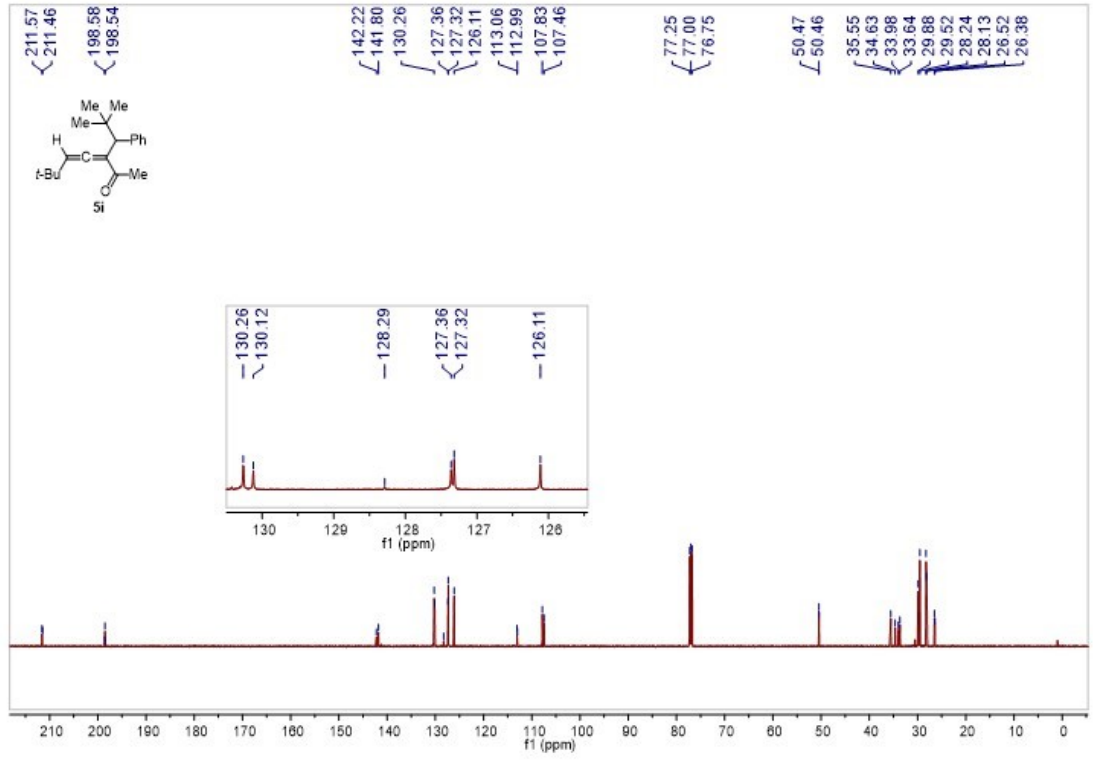
0.95
1.00
2.85
4.21
5.17
3.84
5.18
f1 (ppm)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112.99
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107.46
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77.00
76.75
50.47
50.46
35.55
34.63
33.98
33.64
29.88
29.52
28.24
28.13
26.52
26.38
Me
Me
Me
Ph
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Me
O
5i
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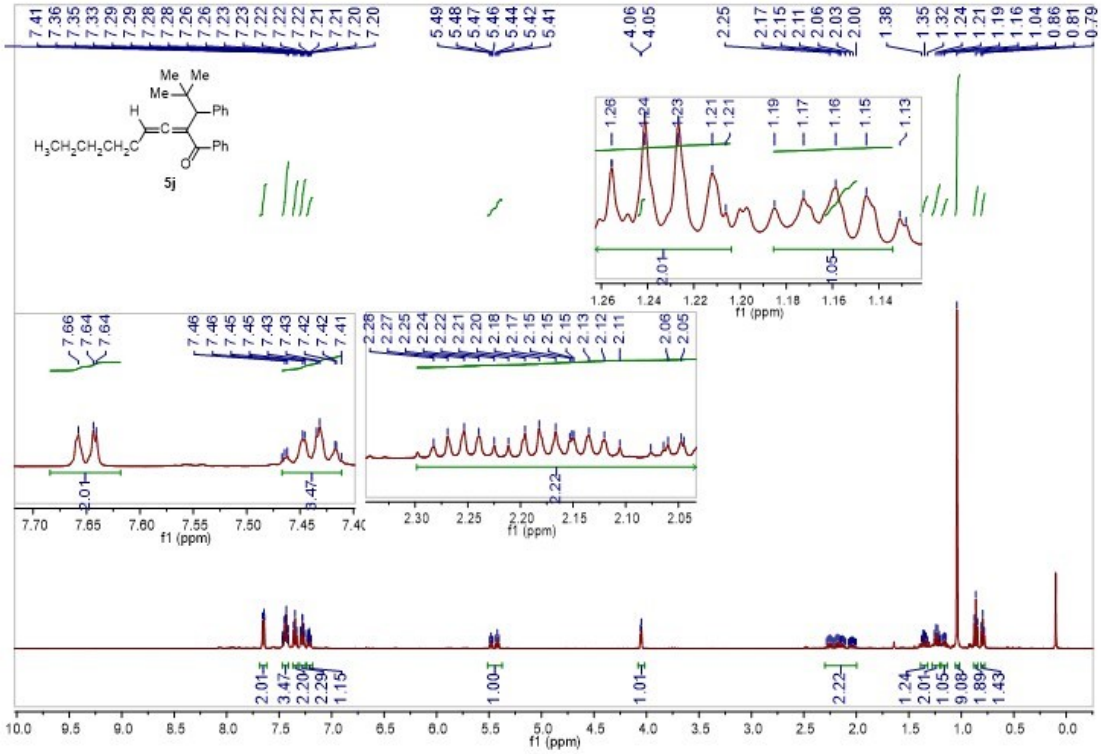
130.12
128.29
127.36
127.32
126.11
f1 (ppm)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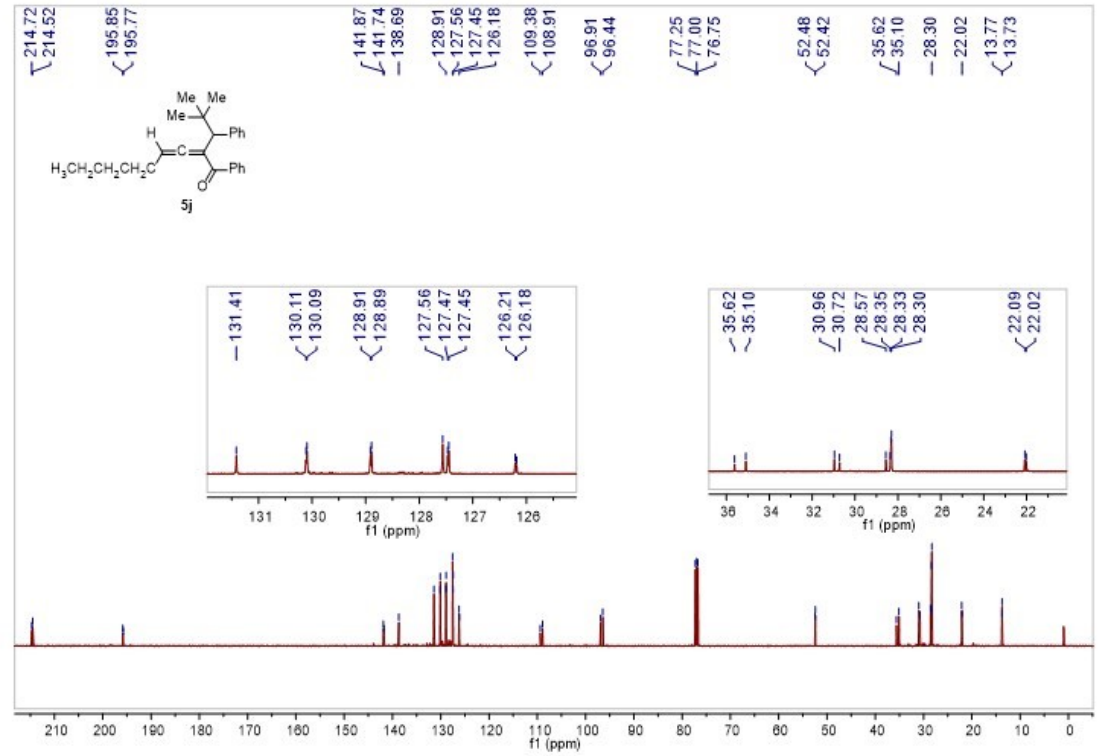
f1 (ppm)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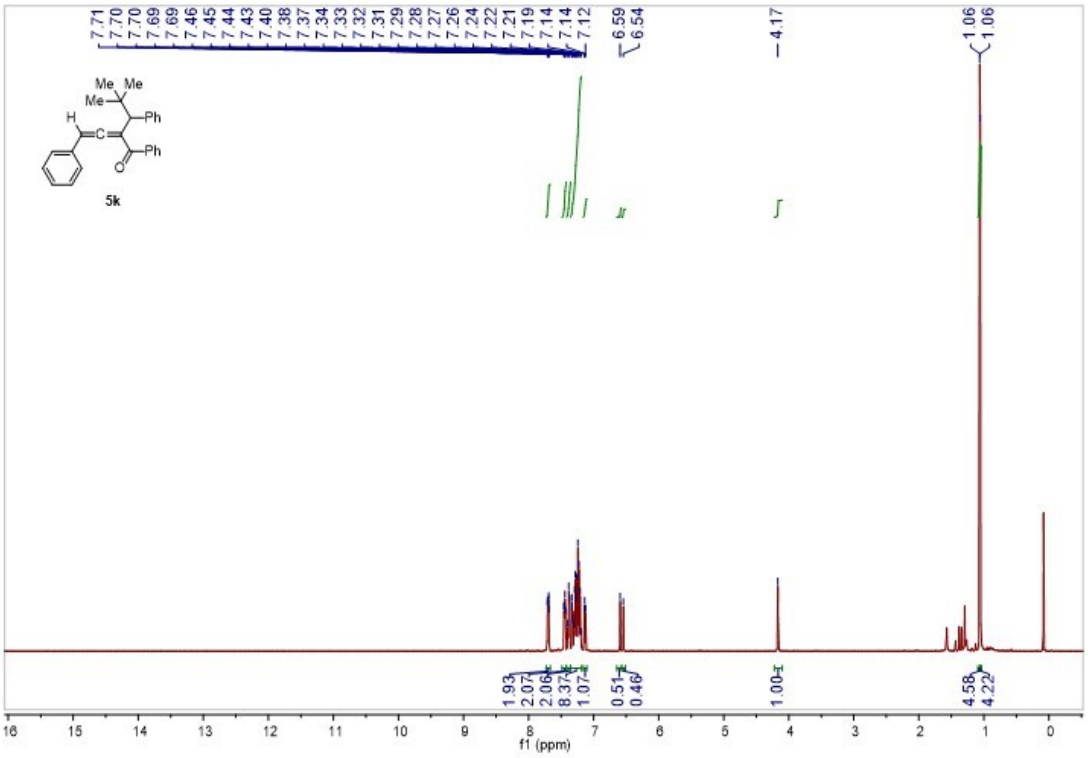
f1 (ppm)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7.33
7.32
7.31
7.29
7.28
7.27
7.26
7.24
7.22
7.21
7.19
7.14
7.12
6.59
6.54
4.17
1.06
1.06
Me
Me
Me
H
Ph
Ph
O
5k
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8.37
1.07
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0.46
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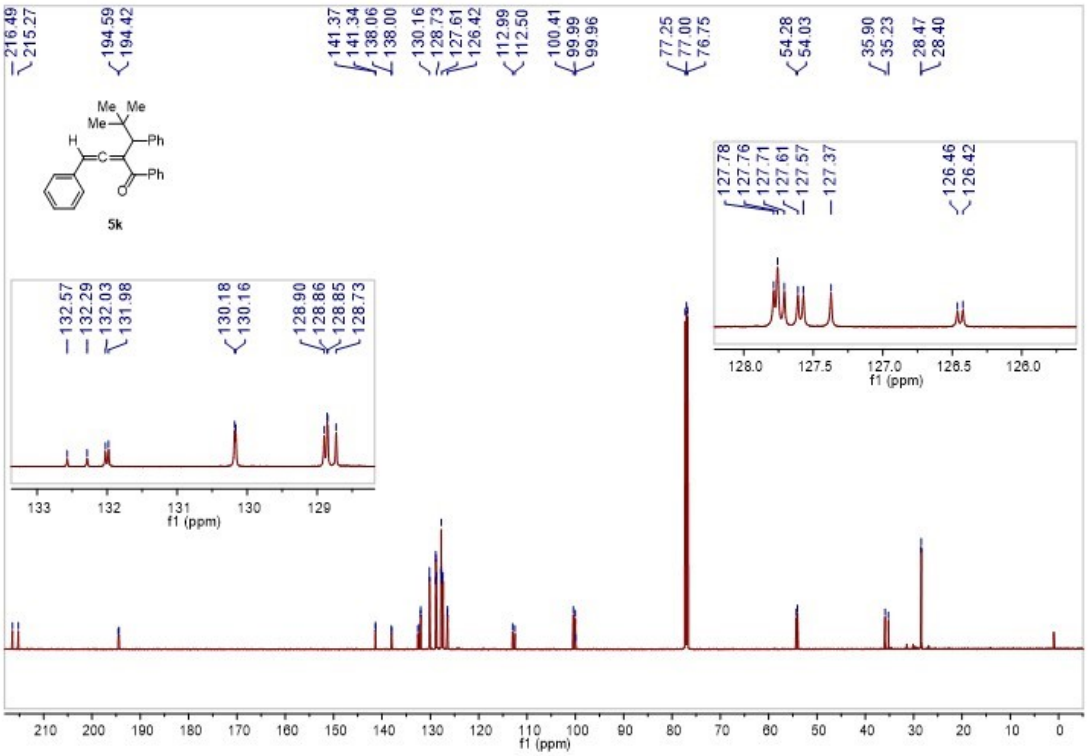
4.58
4.22
f1 (ppm)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99.99
99.96
77.25
77.00
76.75
54.28
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35.90
35.23
28.47
28.40
Me
Me
Me
H
Ph
Ph
O
5k
132.57
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132.03
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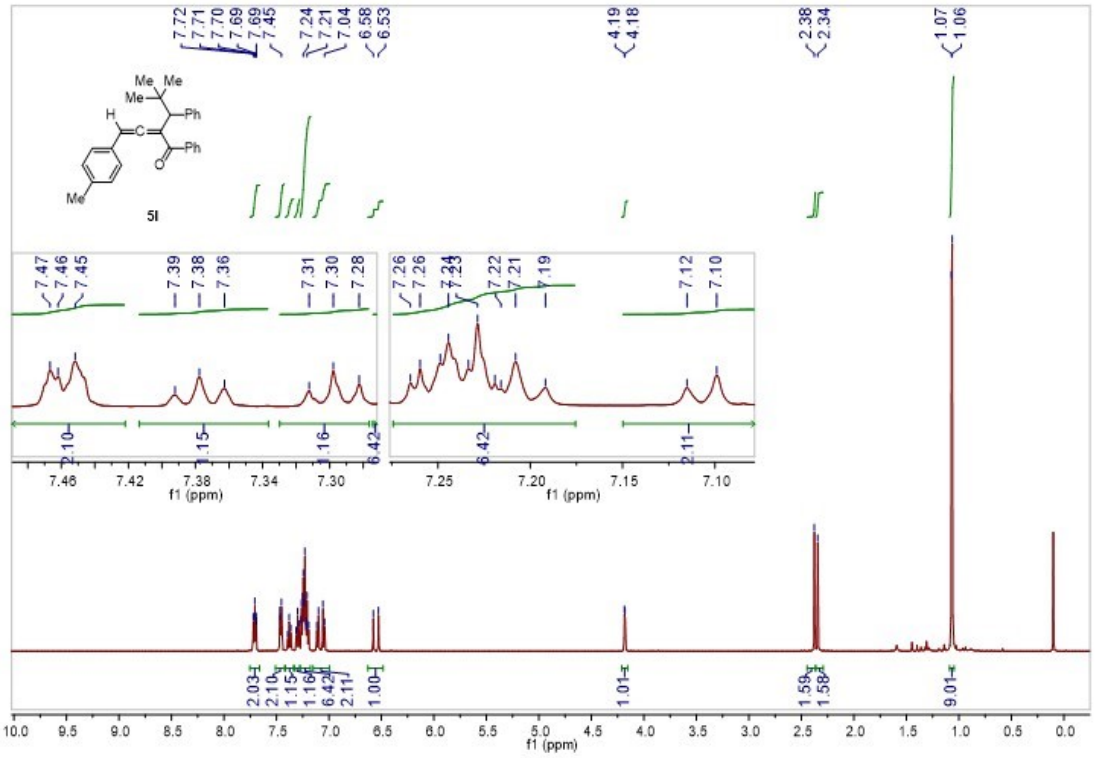
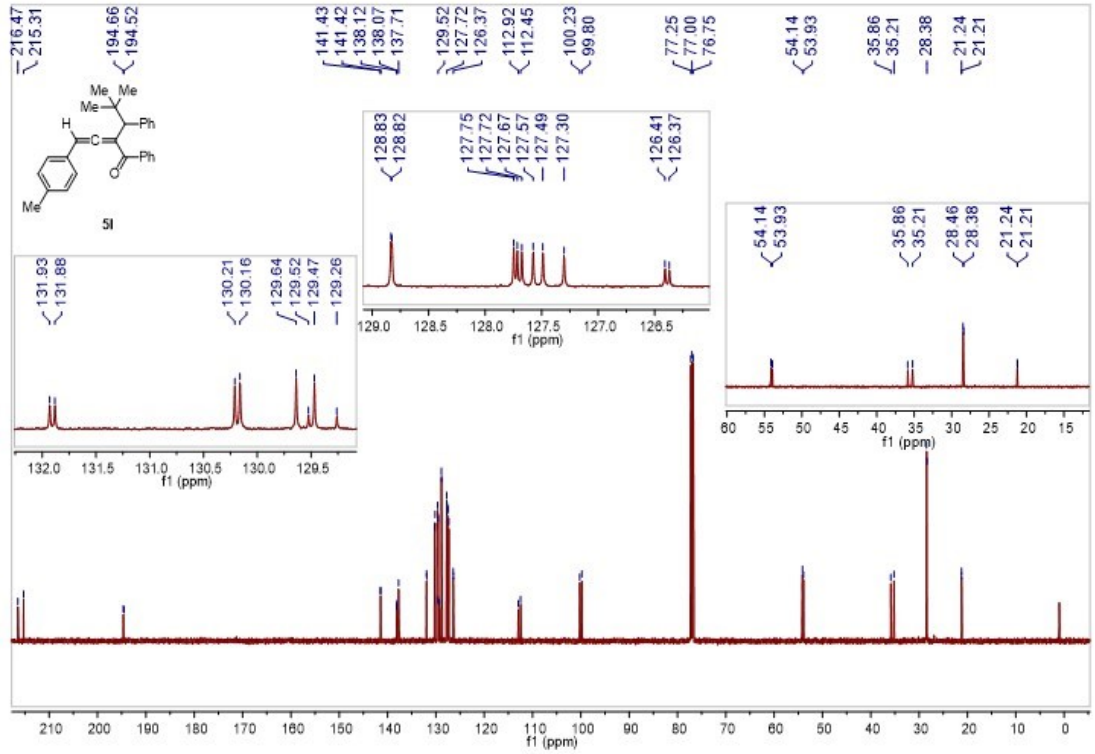
126.42
f1 (ppm)


5l
f1 (ppm)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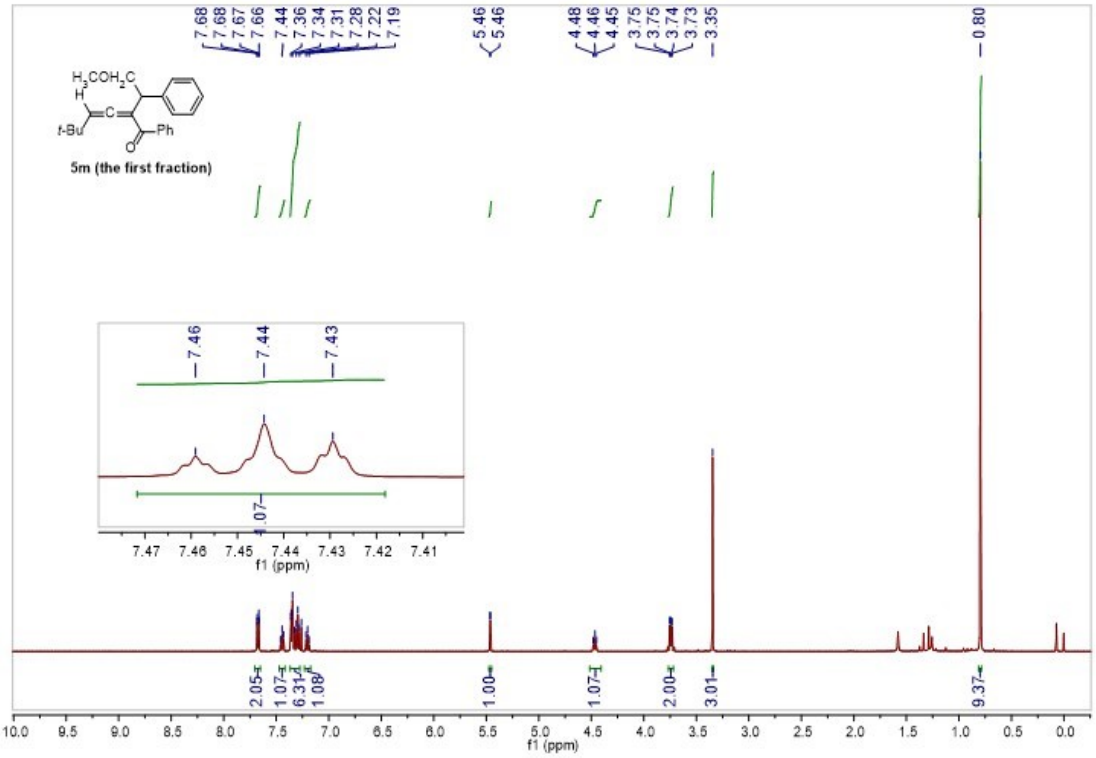
f1 (ppm)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7.36
7.34
7.31
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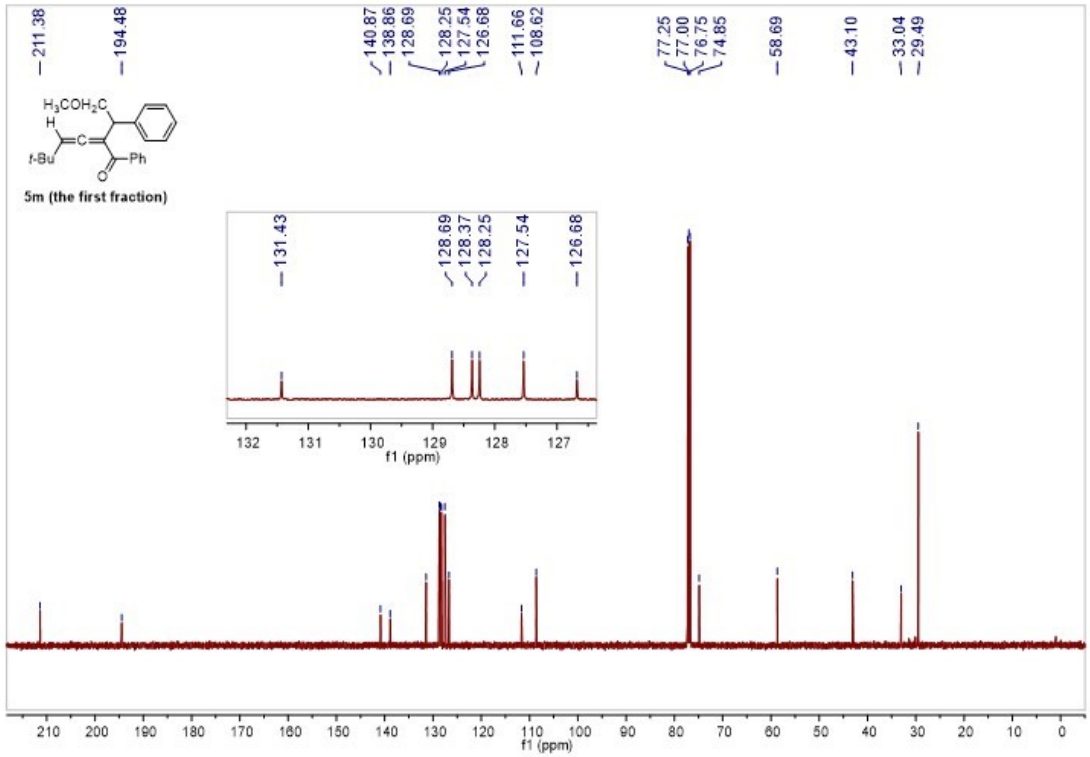
7.22
7.19
5.46
5.46
4.48
4.46
4.45
3.75
3.75
3.74
3.73
3.35
0.80
5m (the first fraction)
7.46
7.44
7.43
1.07
7.47 7.46 7.45 7.44 7.43 7.42 7.41
f1 (ppm)
2.05
1.07
6.31
1.08
1.00
1.07
2.00
3.01
9.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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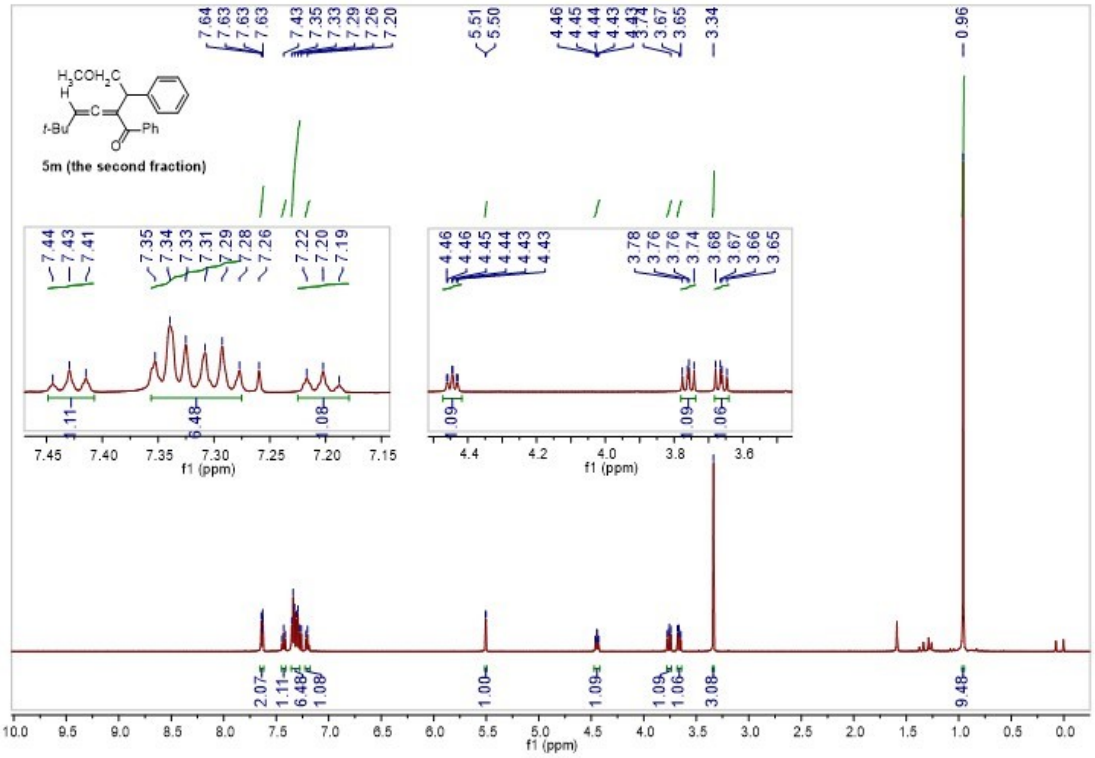
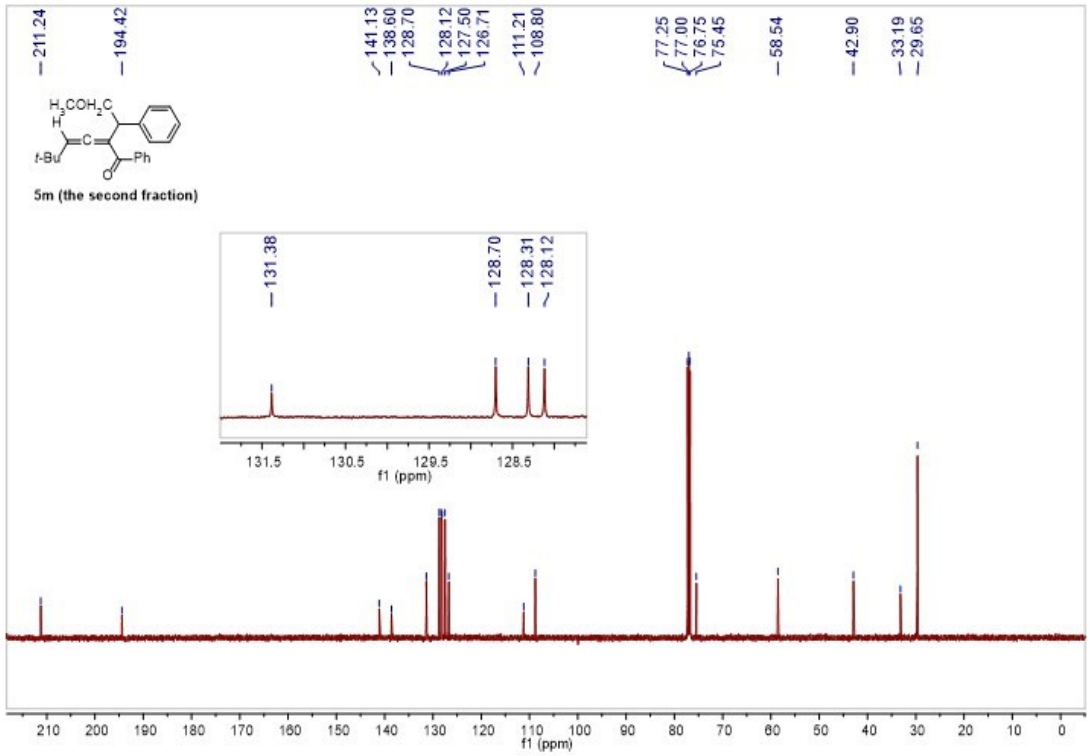
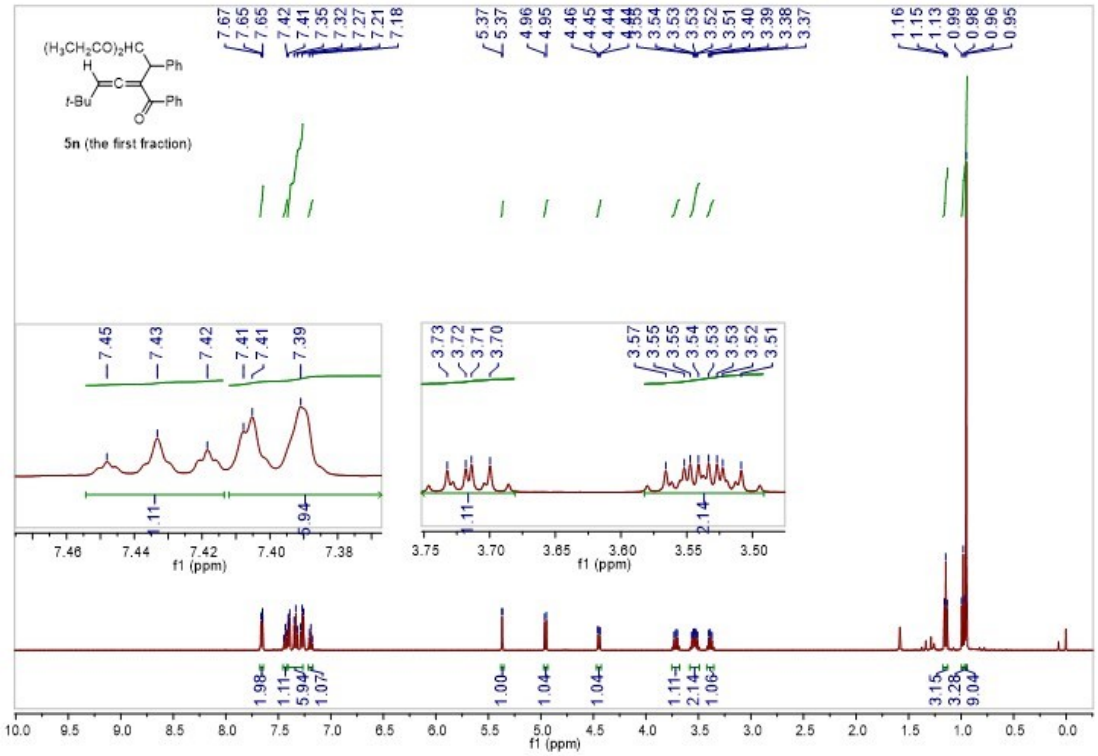
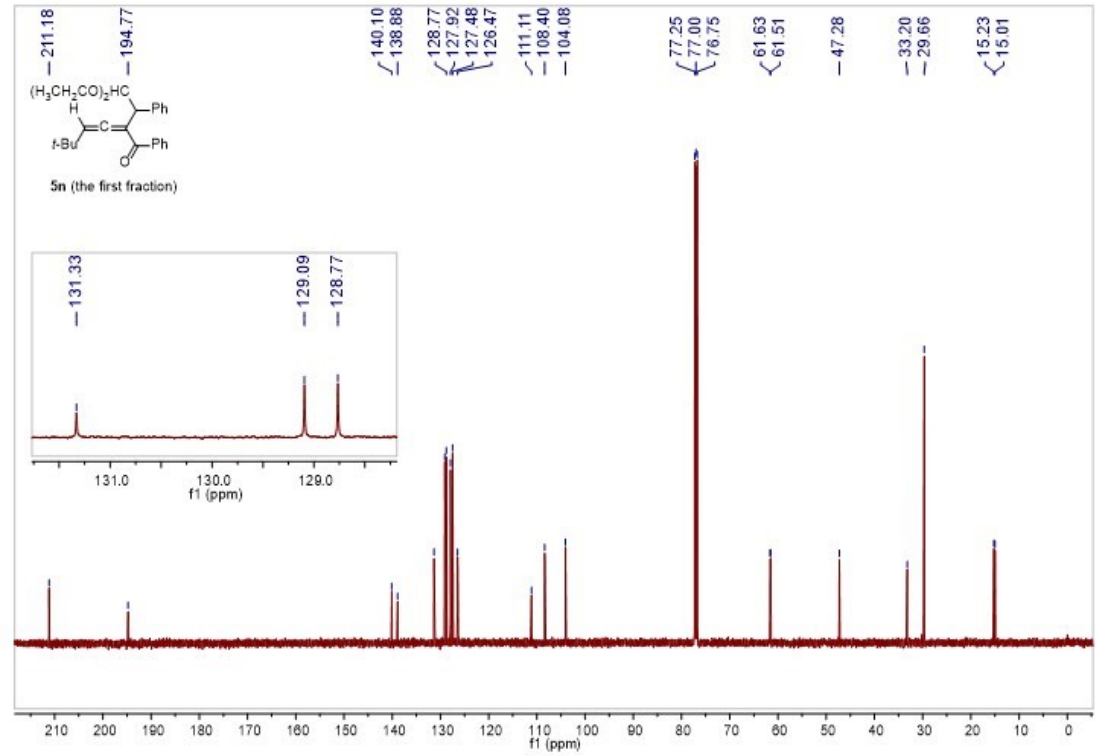
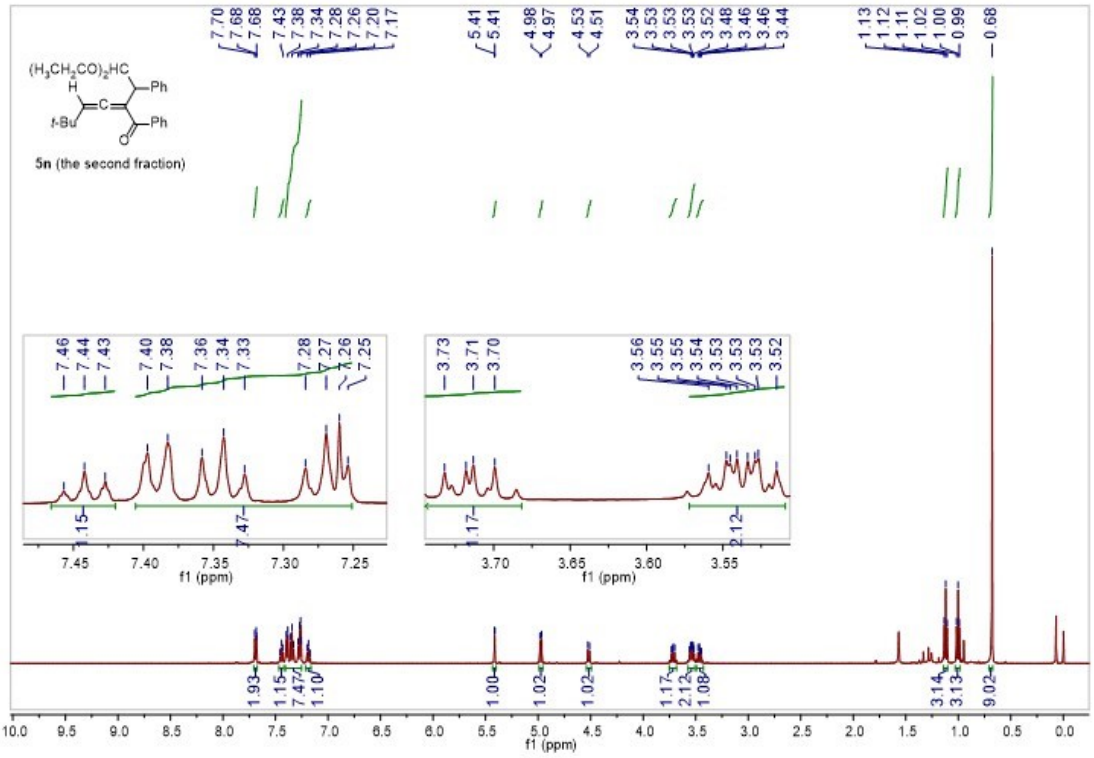
126.68
111.66
108.62
77.25
77.00
76.75
74.85
58.69
43.10
33.04
29.49
5m (the first fraction)
131.43
128.69
128.37
128.25
127.54
126.68
132 131 130 129 128 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

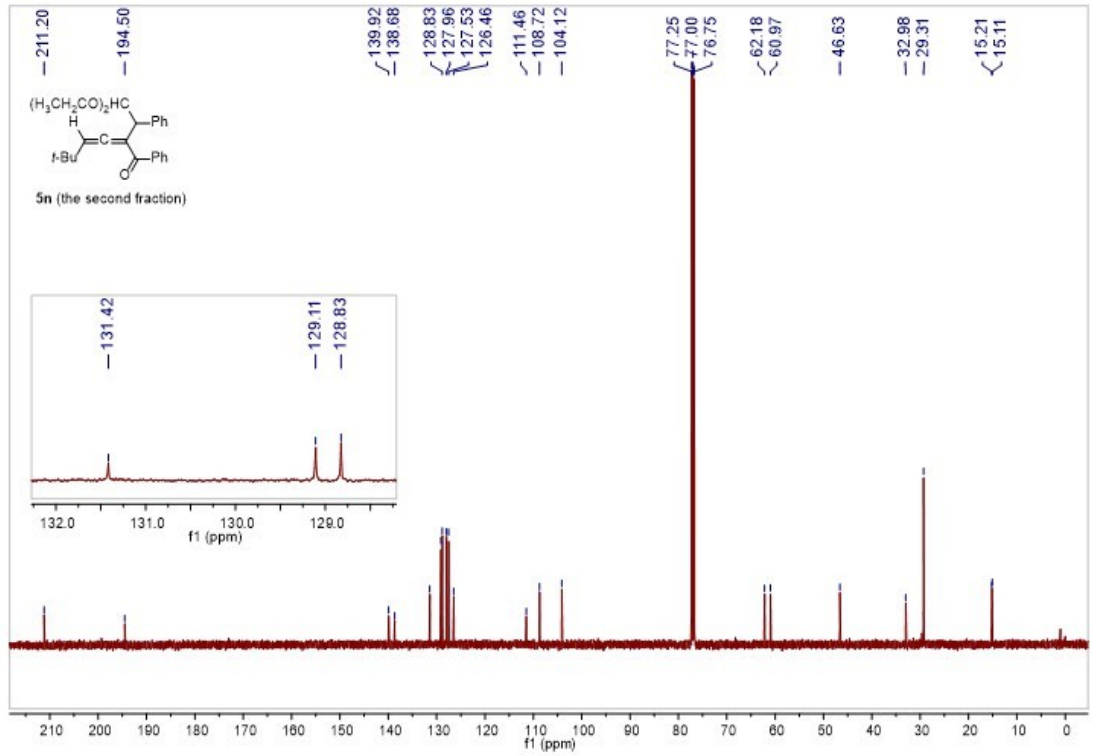

5m (the second fraction)
f1 (ppm)

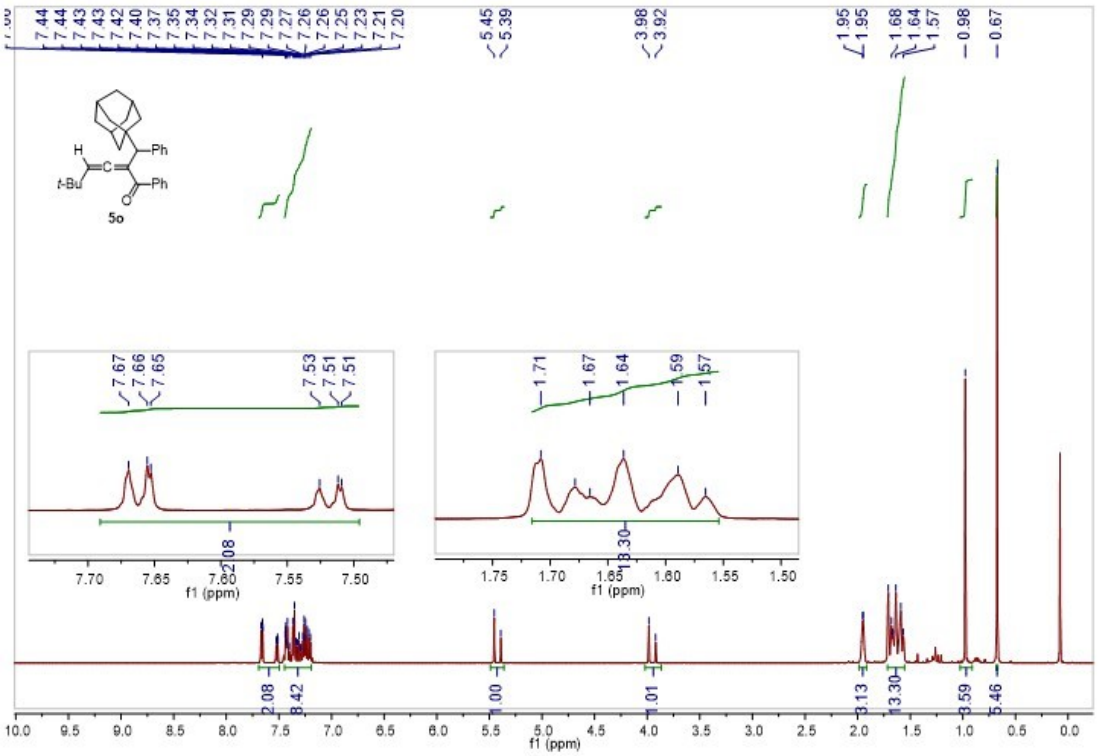

5m (the second fraction)
f1 (ppm)


5n (the first fraction)
f1 (ppm)


5n (the first fraction)
f1 (ppm)


5n (the second fraction)
f1 (ppm)


5n (the second fraction)
f1 (ppm)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7.27
7.26
7.26
7.25
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7.21
7.20
5.45
5.39
3.98
3.92
1.95
1.95
1.68
1.64
1.57
0.98
0.67
H
Ph
t-Bu
Ph
O
5o
7.67
7.66
7.65
7.53
7.51
7.51
2.08
1.71
1.67
1.64
1.59
1.57
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f1 (ppm)
2.08
8.42
1.00
1.01
3.13
13.30
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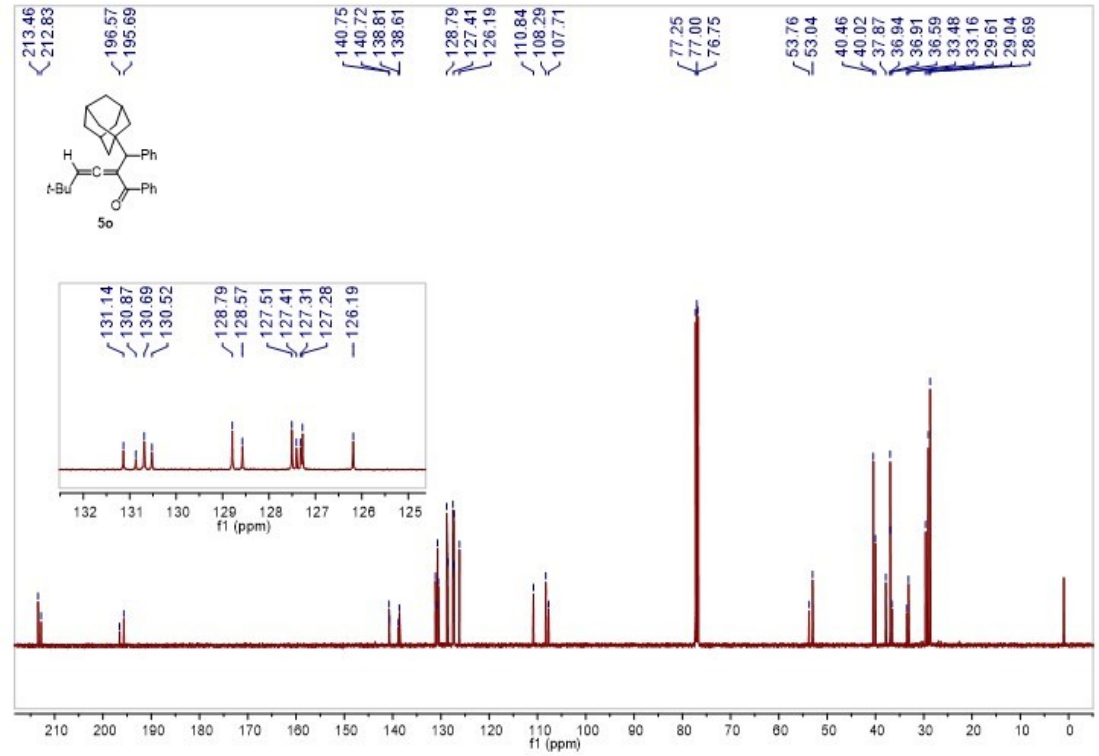
5.46
f1 (ppm)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126.19
110.84
108.29
107.71
77.25
77.00
76.75
53.76
53.04
40.46
40.02
37.87
36.94
36.91
36.59
33.48
33.16
29.61
29.04
28.69
H
Ph
t-Bu
Ph
O
5o
131.14
130.87
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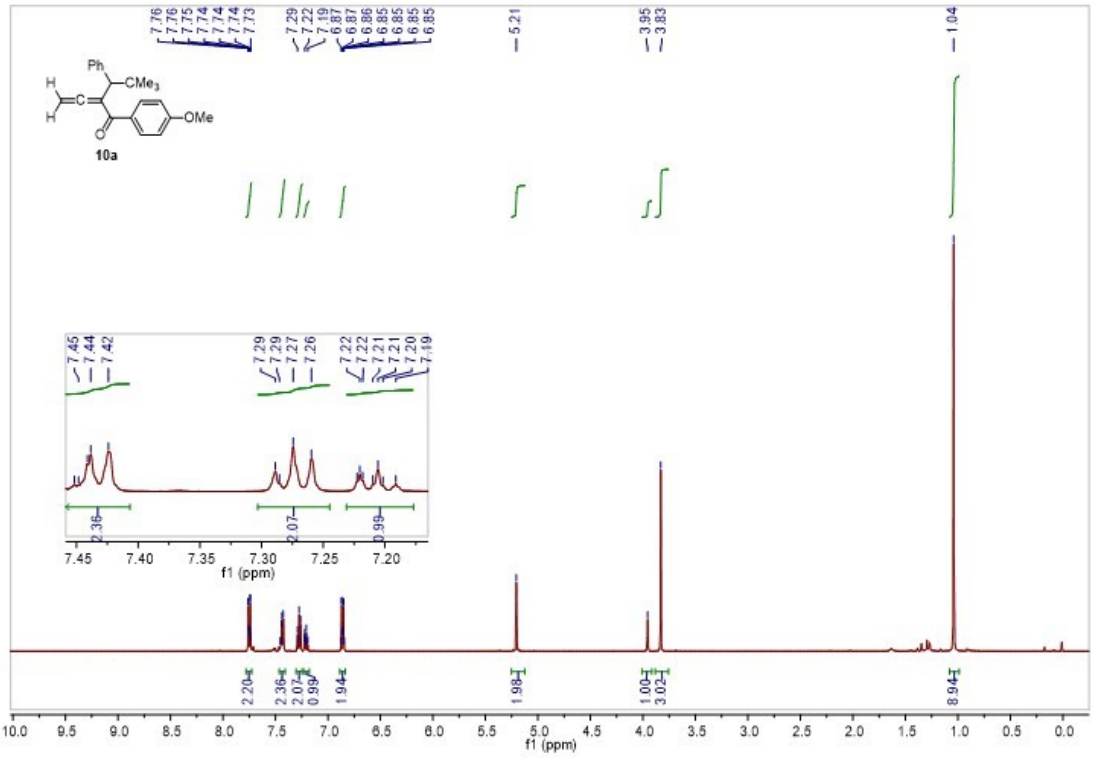
128.79
128.57
127.51
127.41
127.31
127.28
126.19
f1 (ppm)
f1 (ppm)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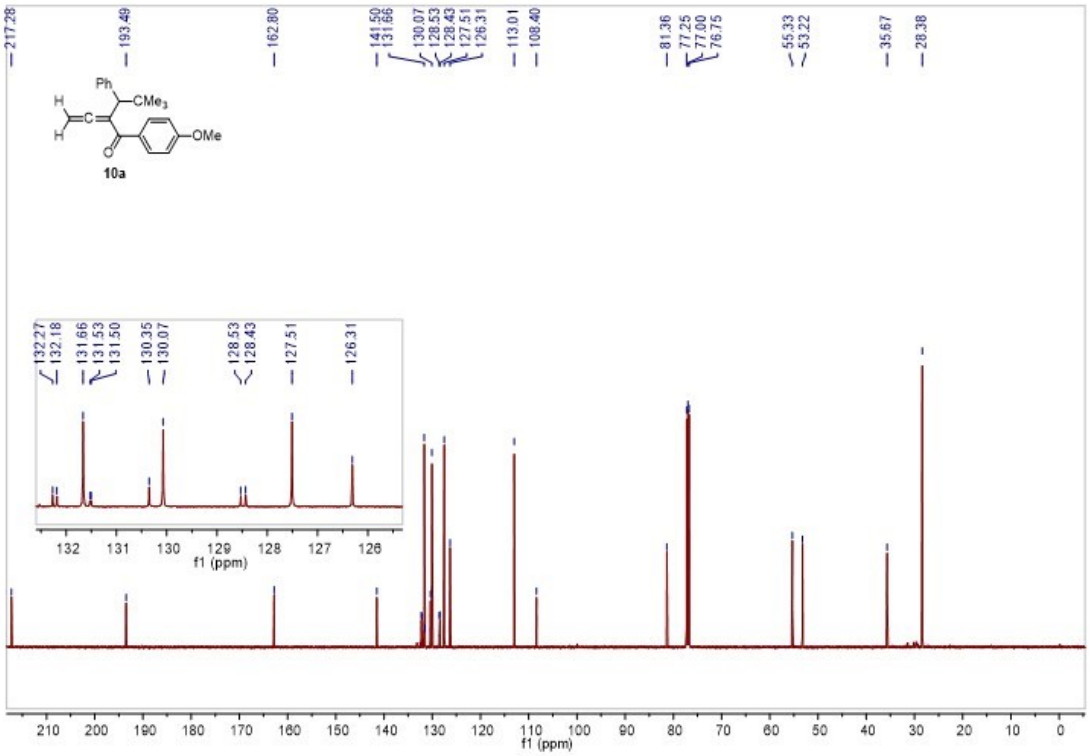
f1 (ppm)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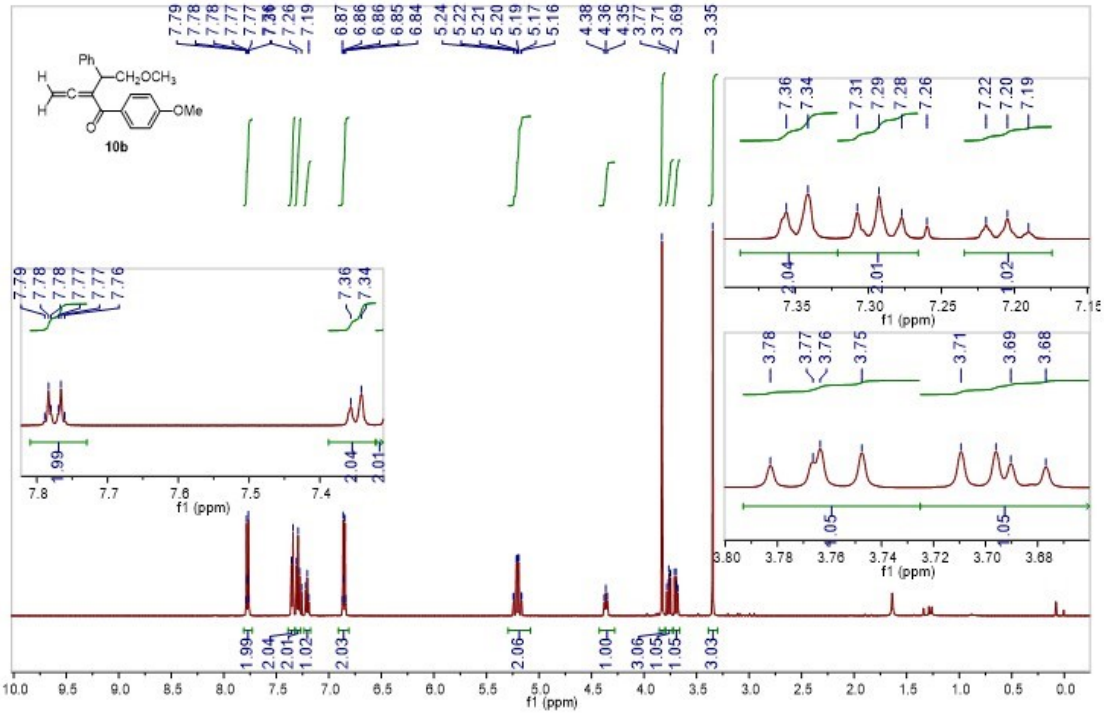
f1 (ppm)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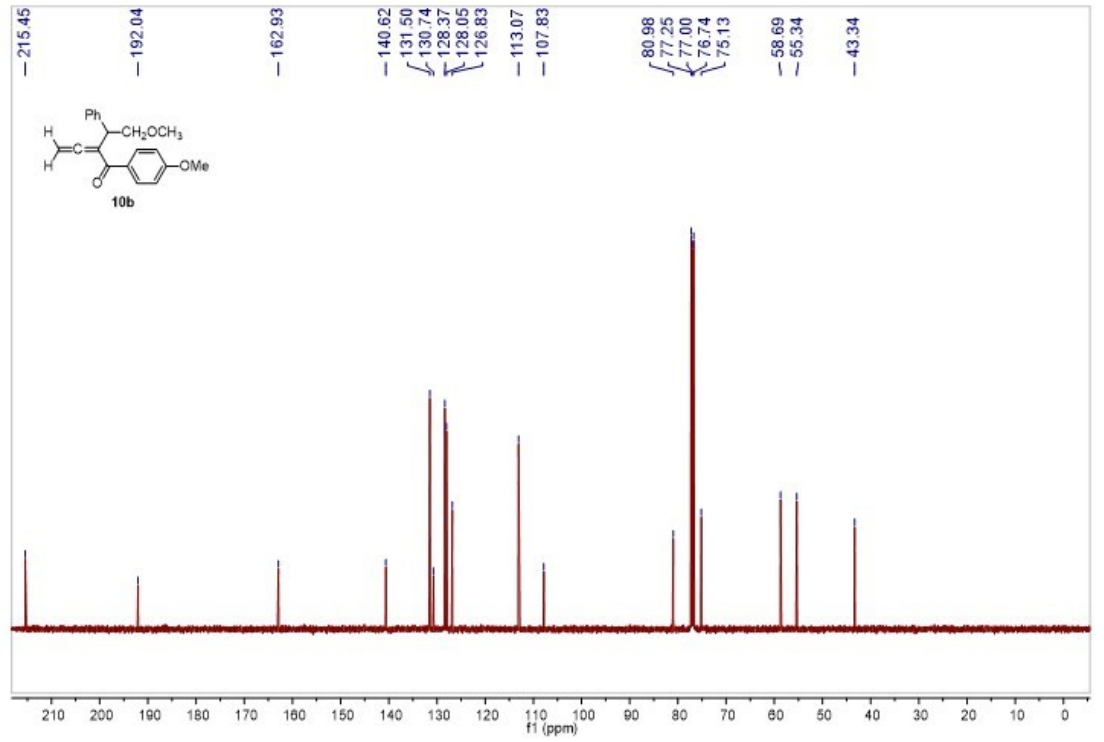
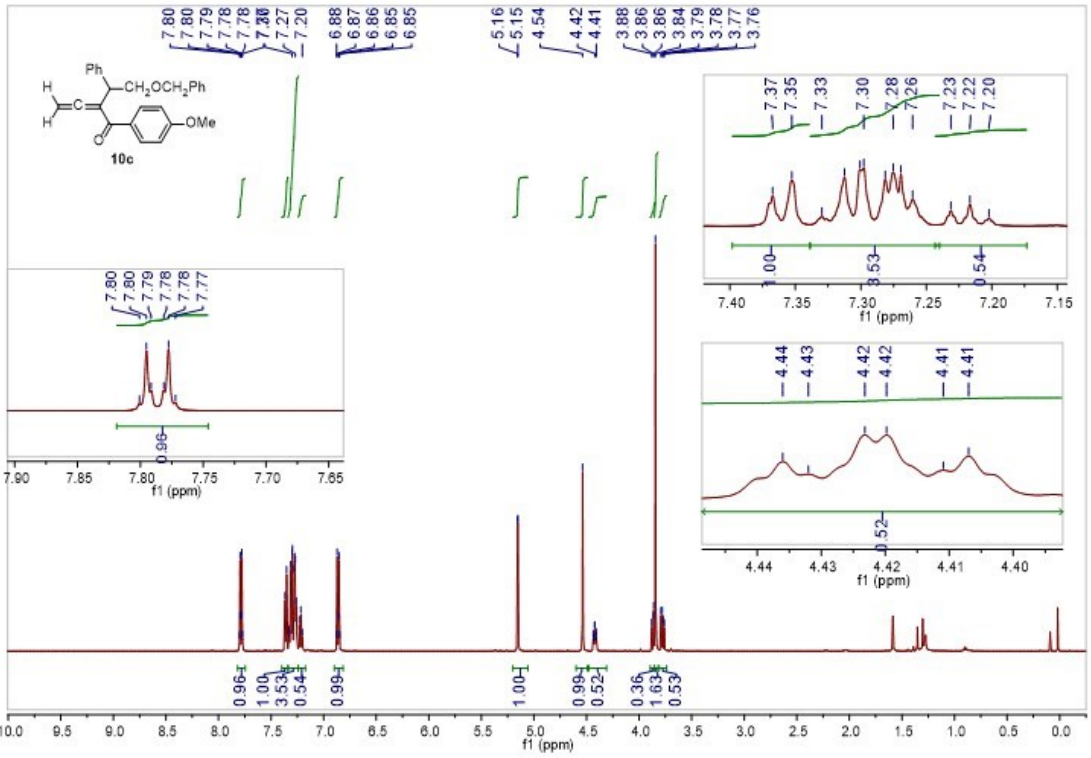
f1 (ppm)


10b
f1 (ppm)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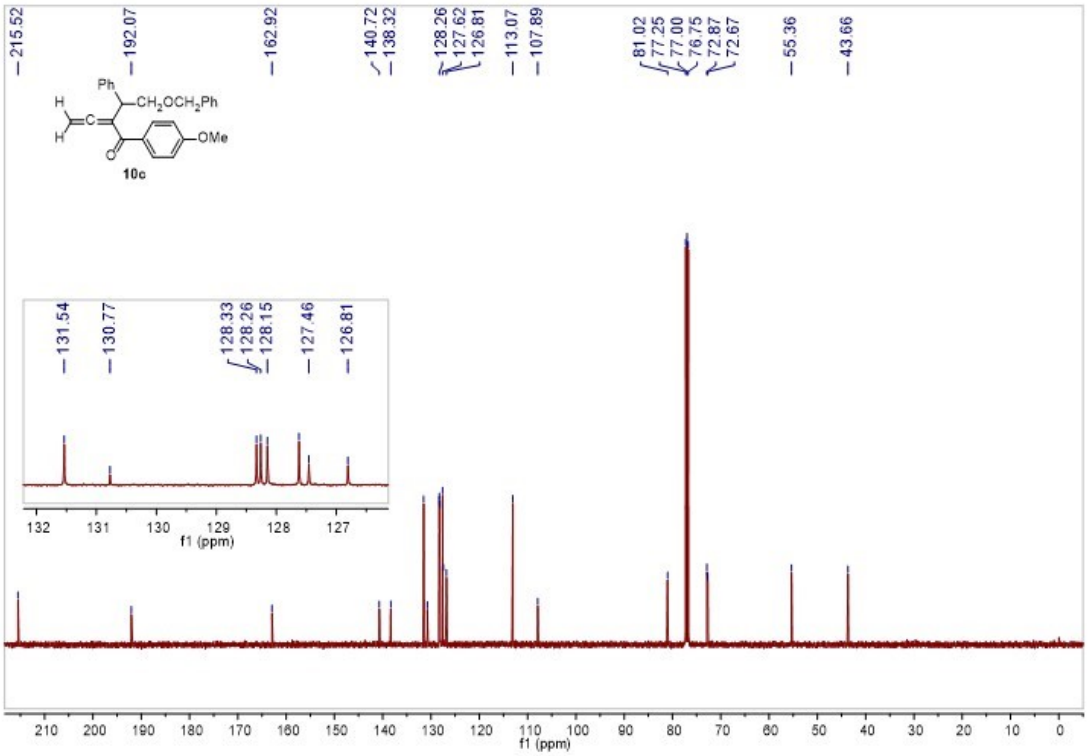
f1 (ppm)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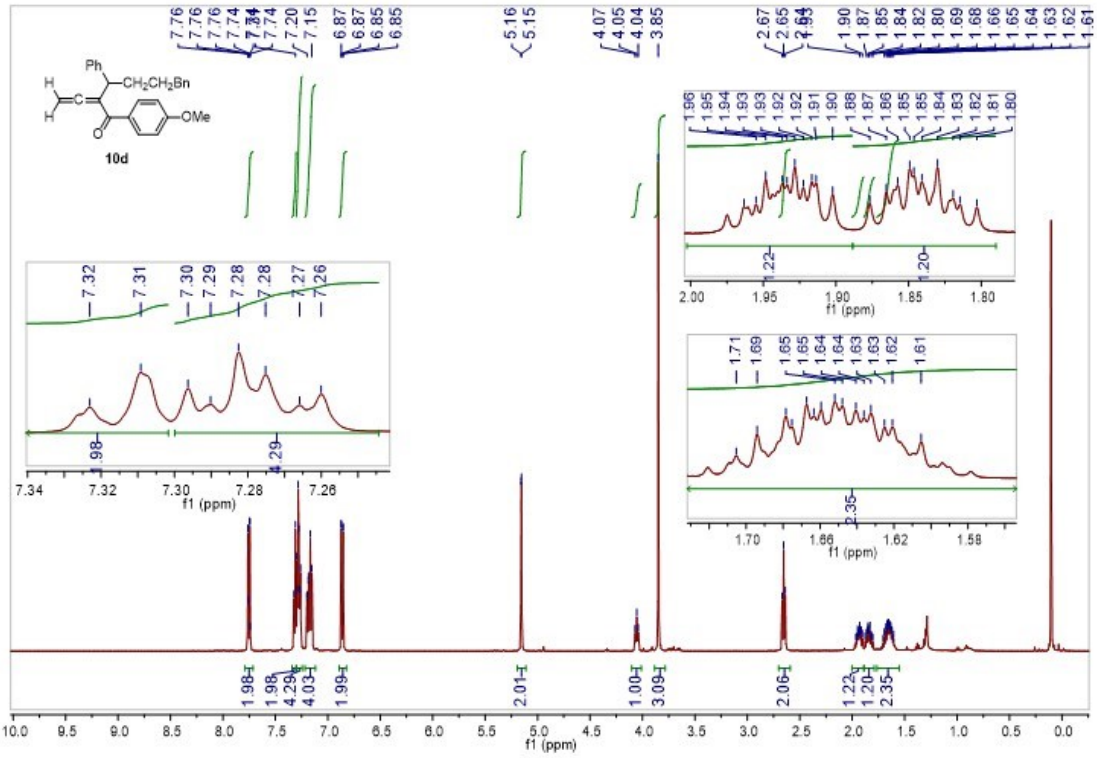
f1 (ppm)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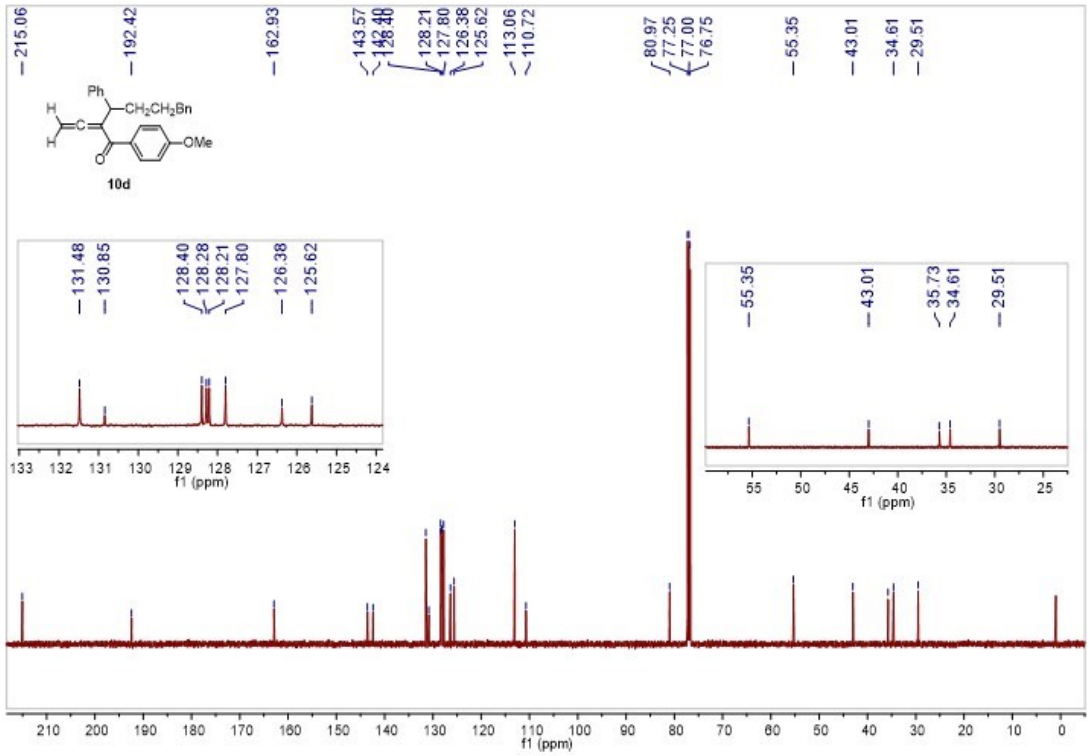
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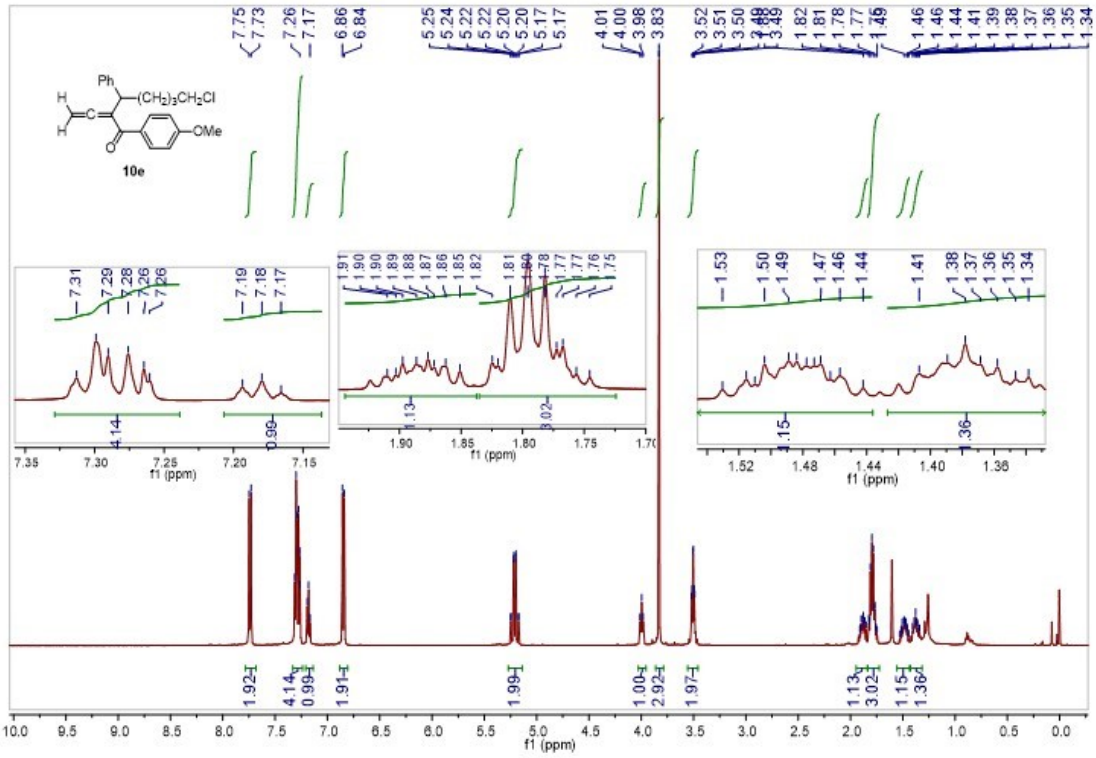
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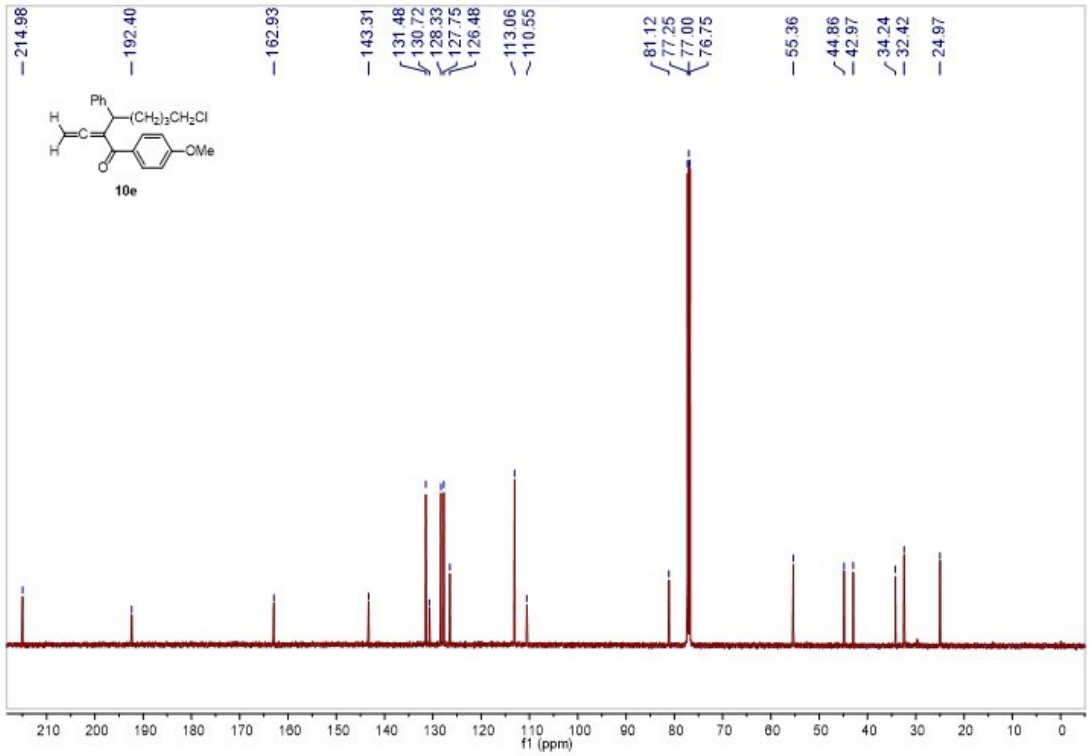
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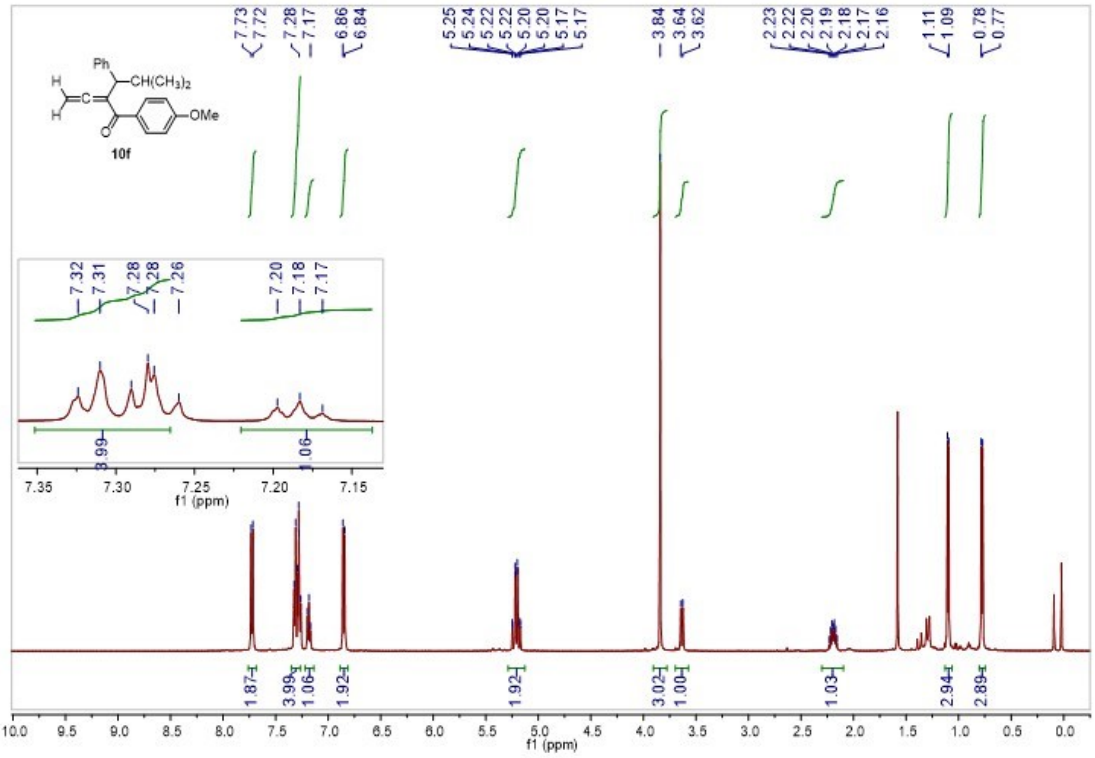
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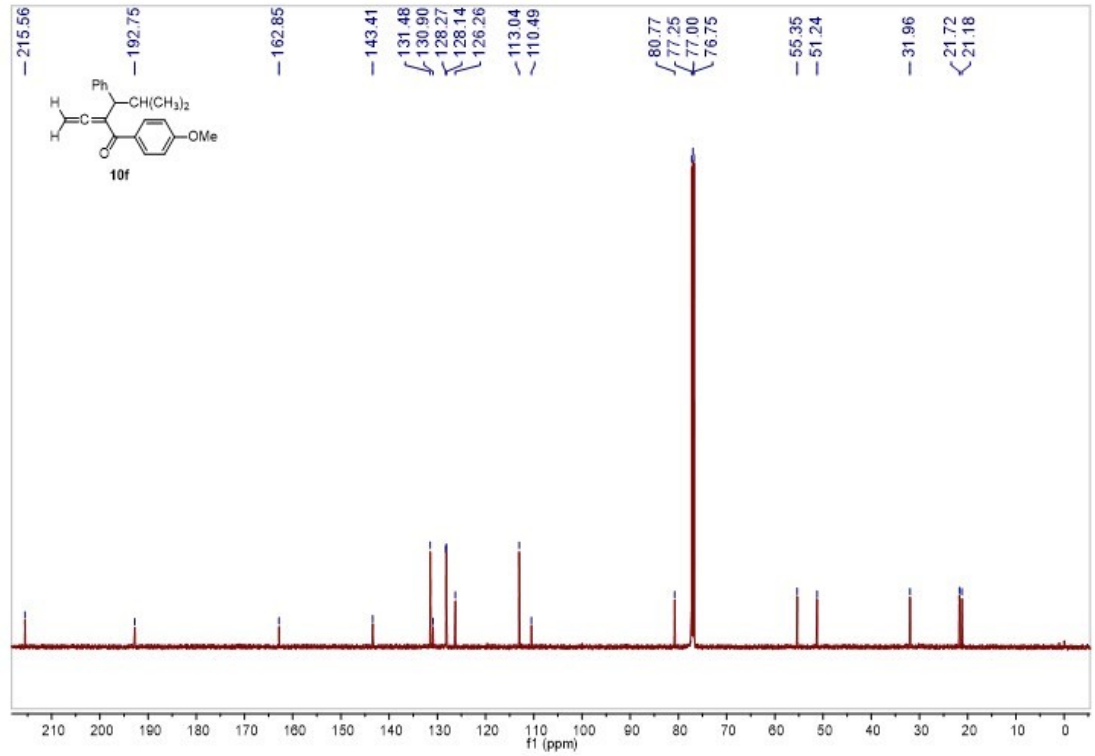
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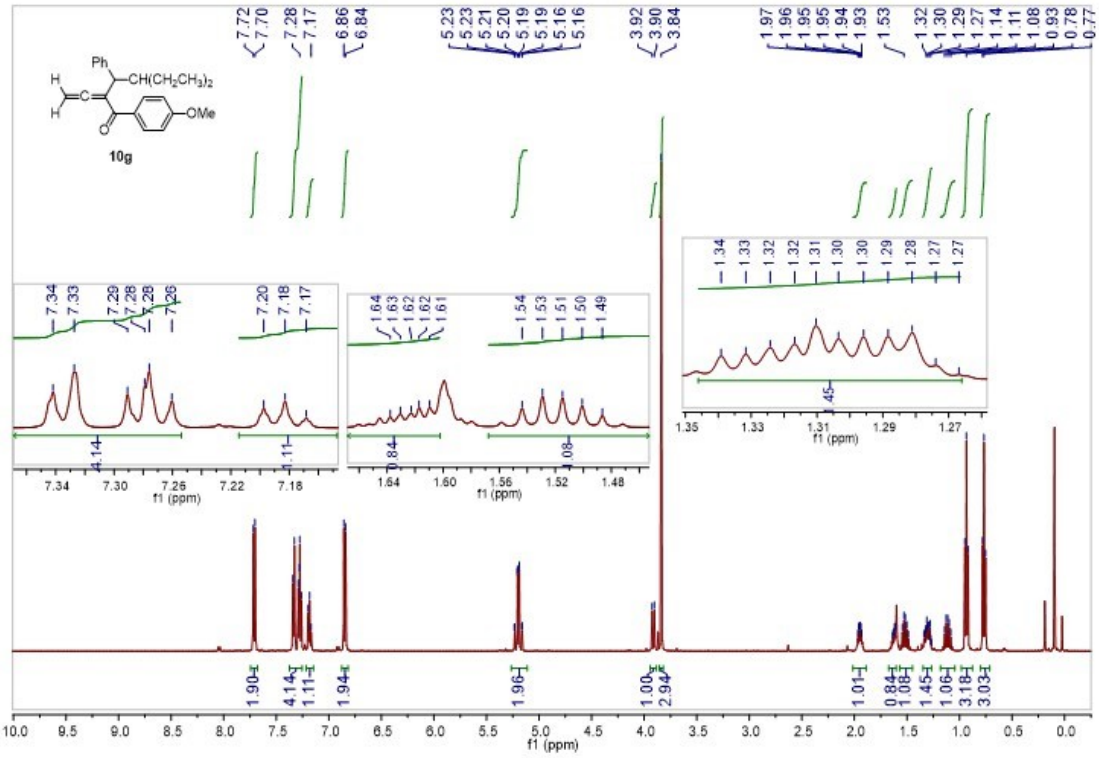
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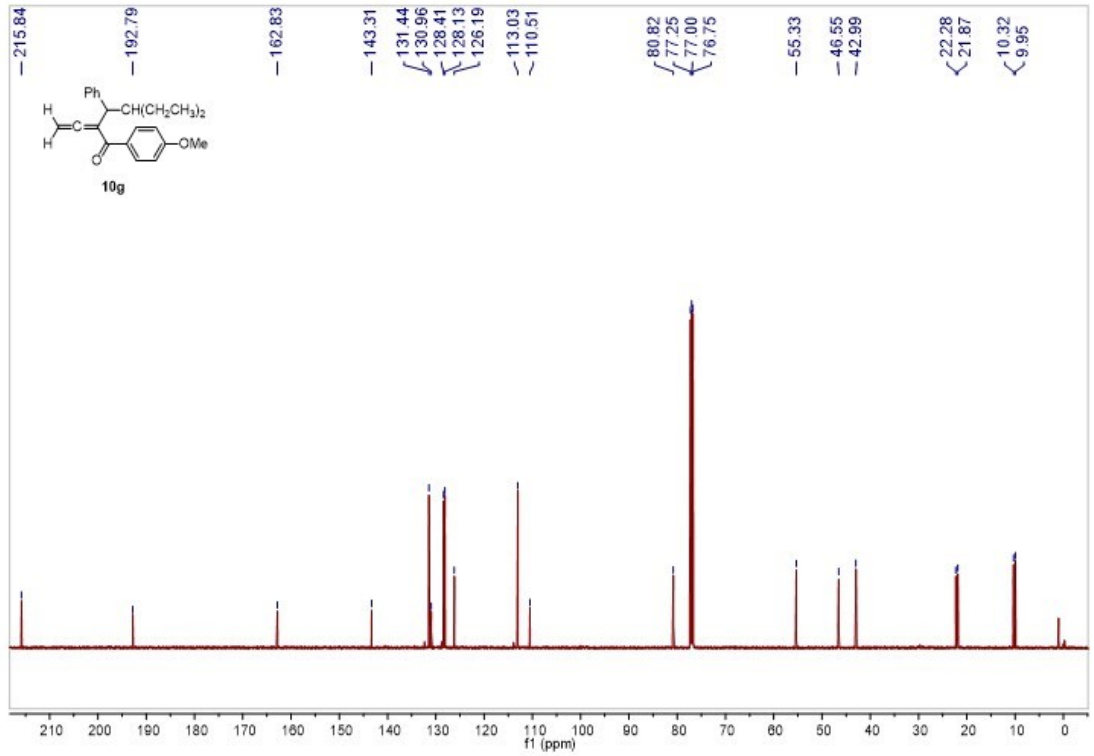
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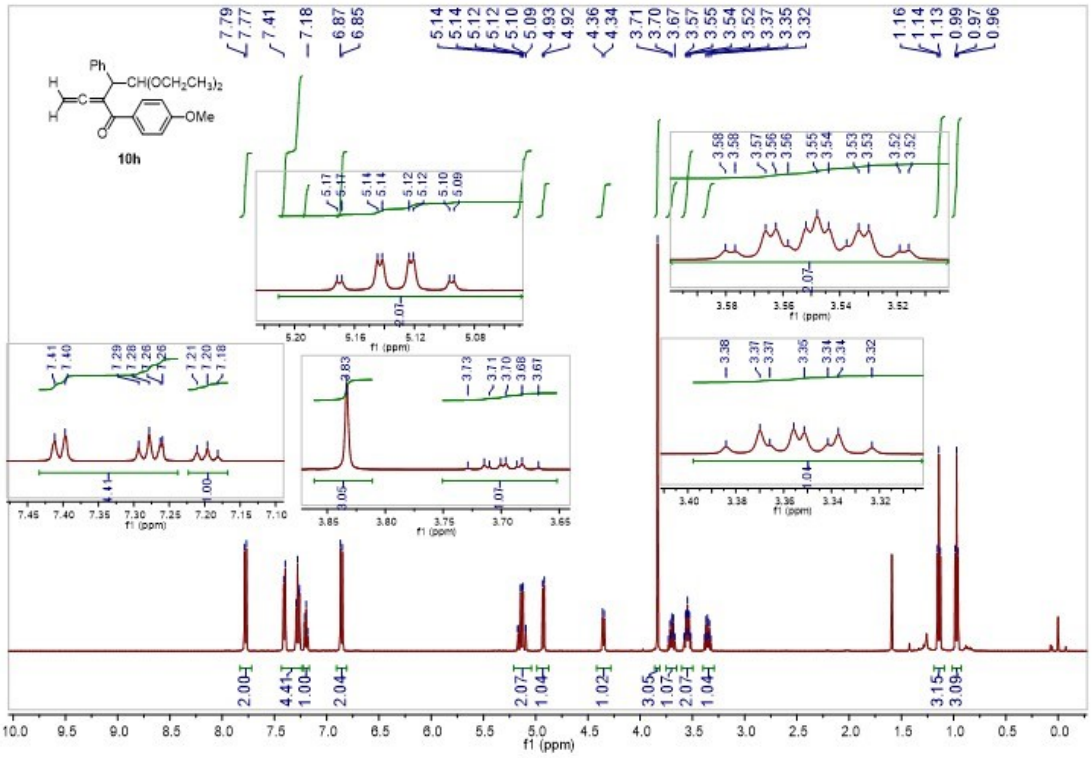
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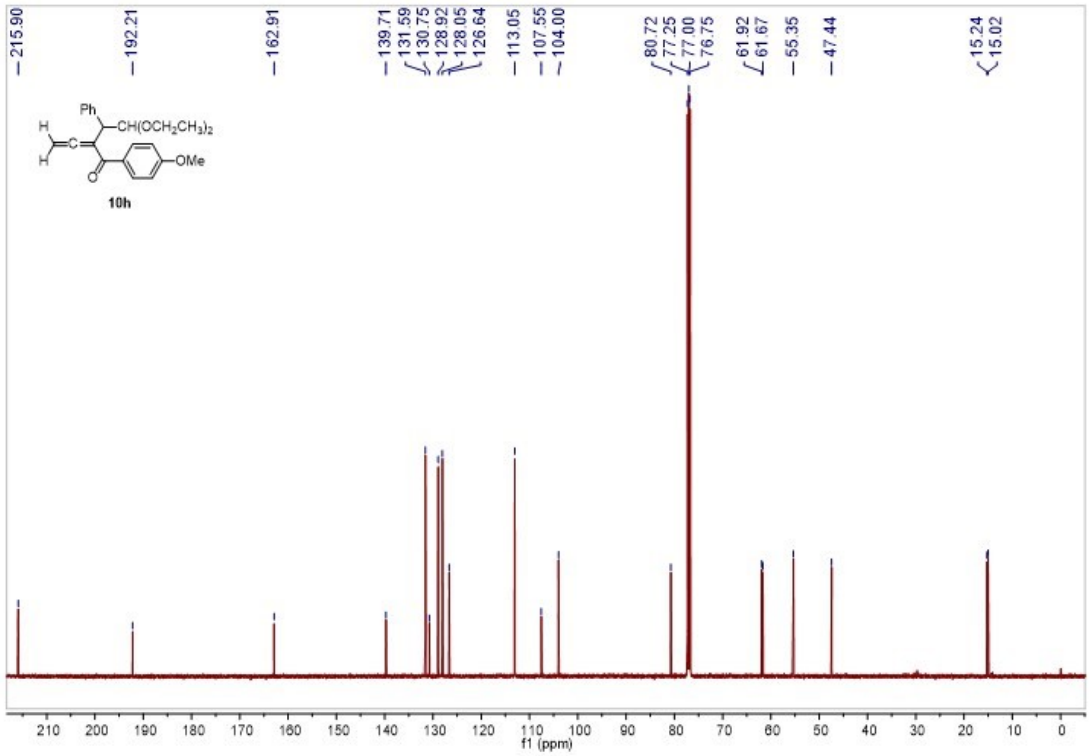
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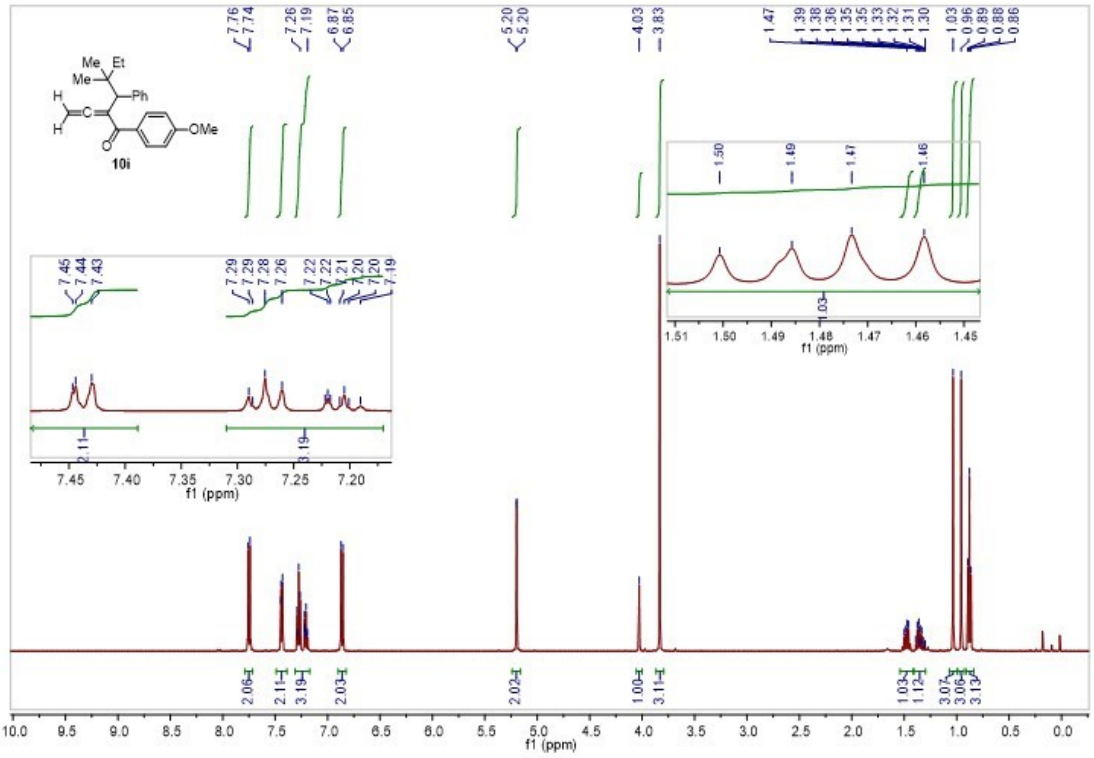
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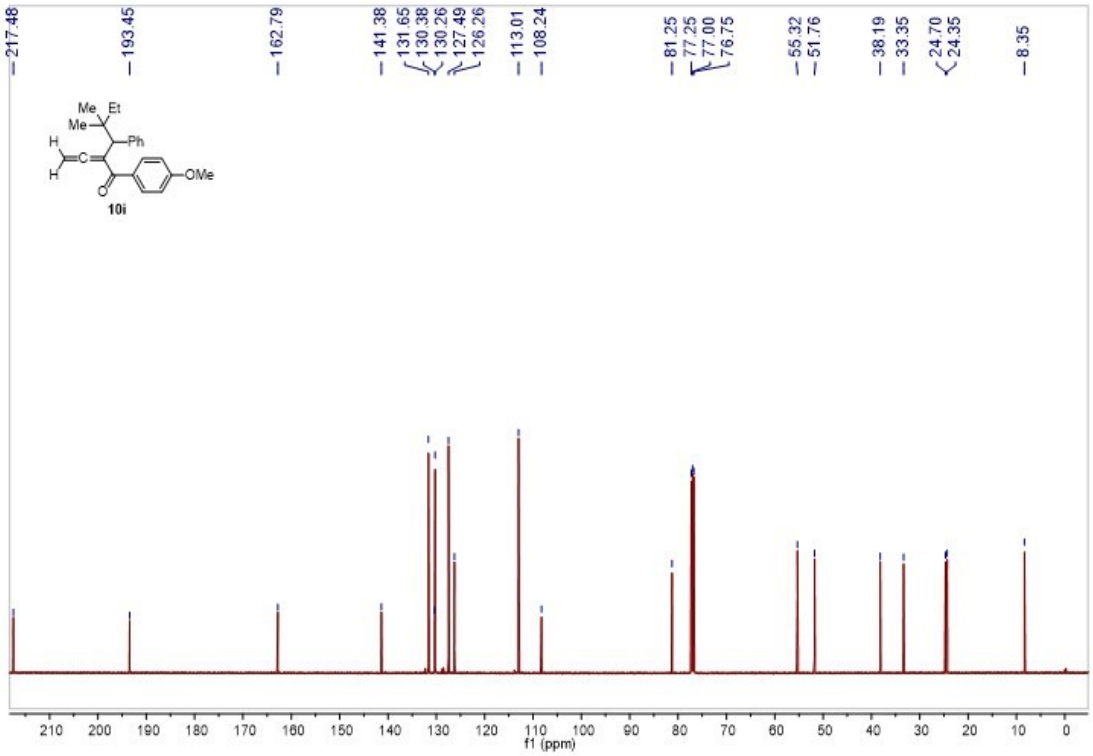
f1 (ppm)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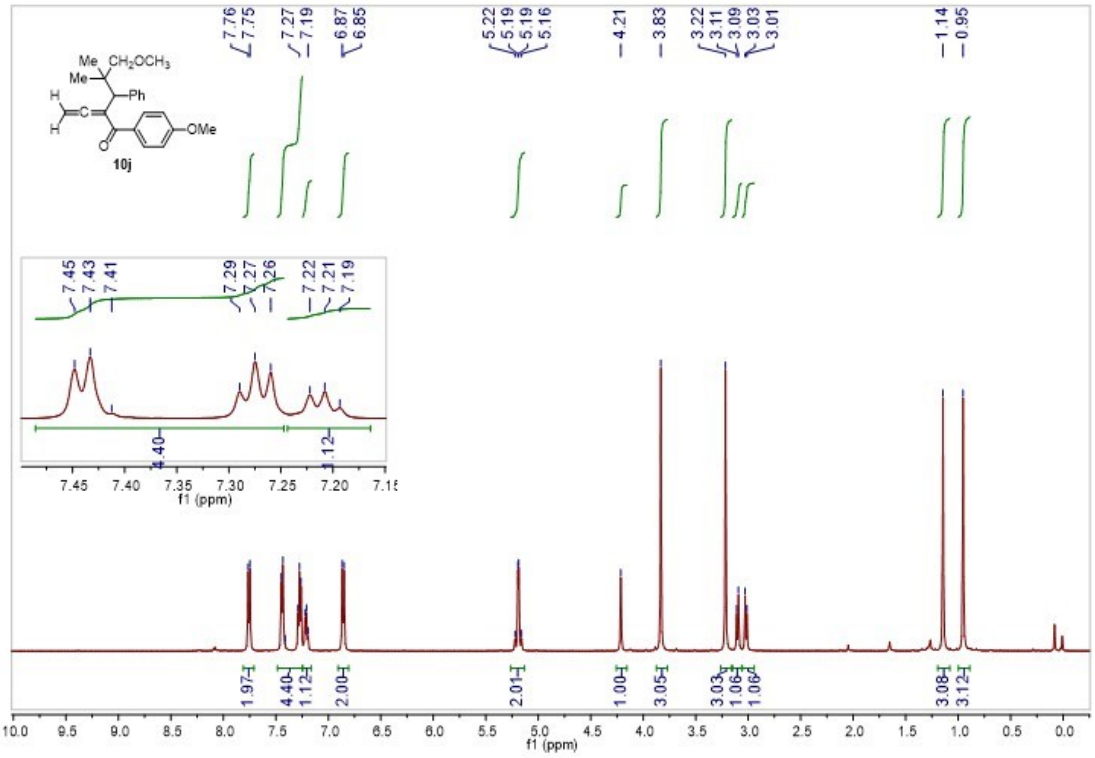
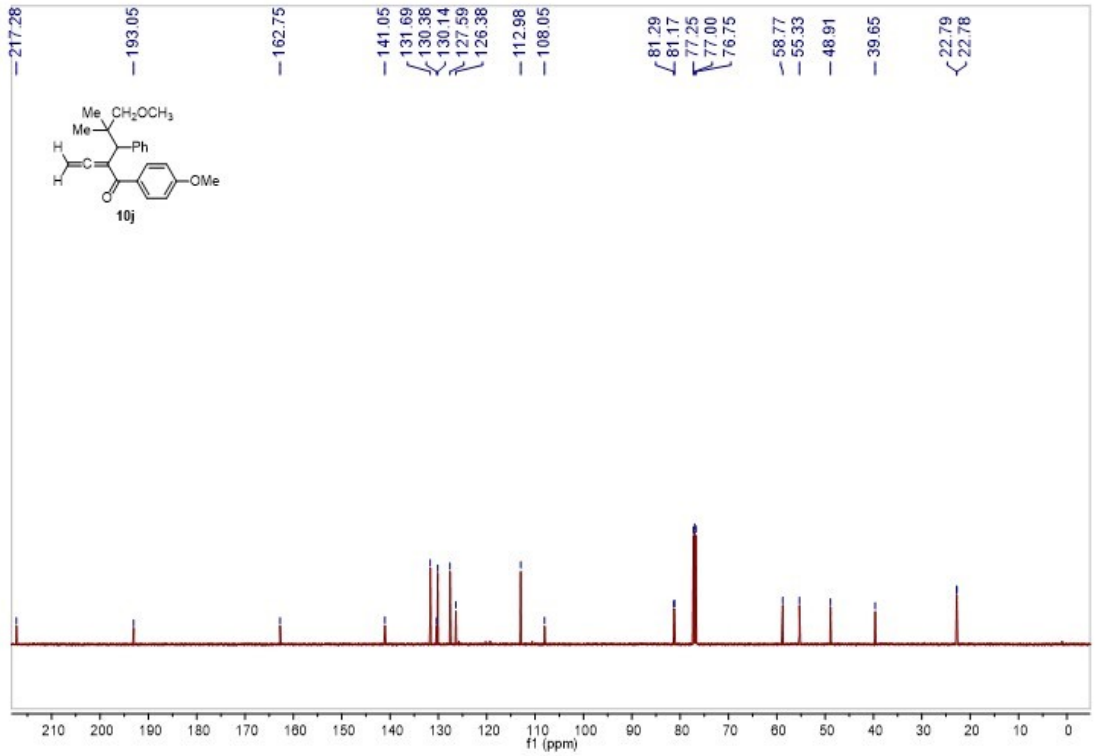
f1 (ppm)


10j
f1 (ppm)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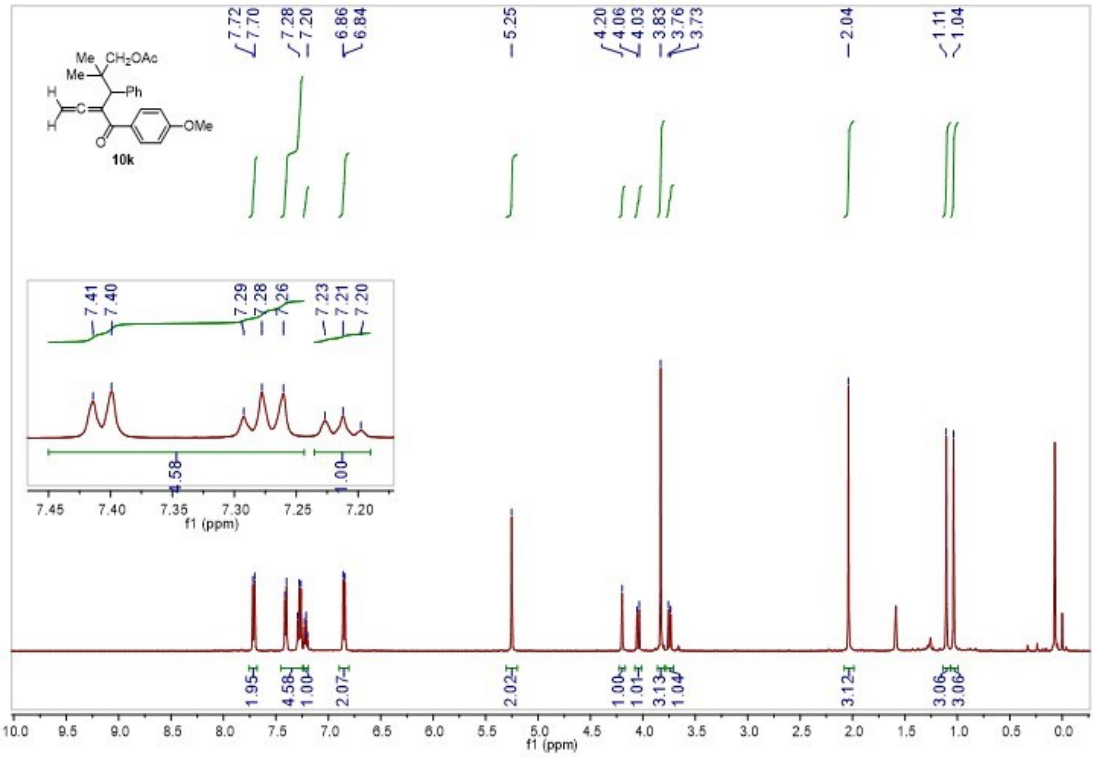
f1 (ppm)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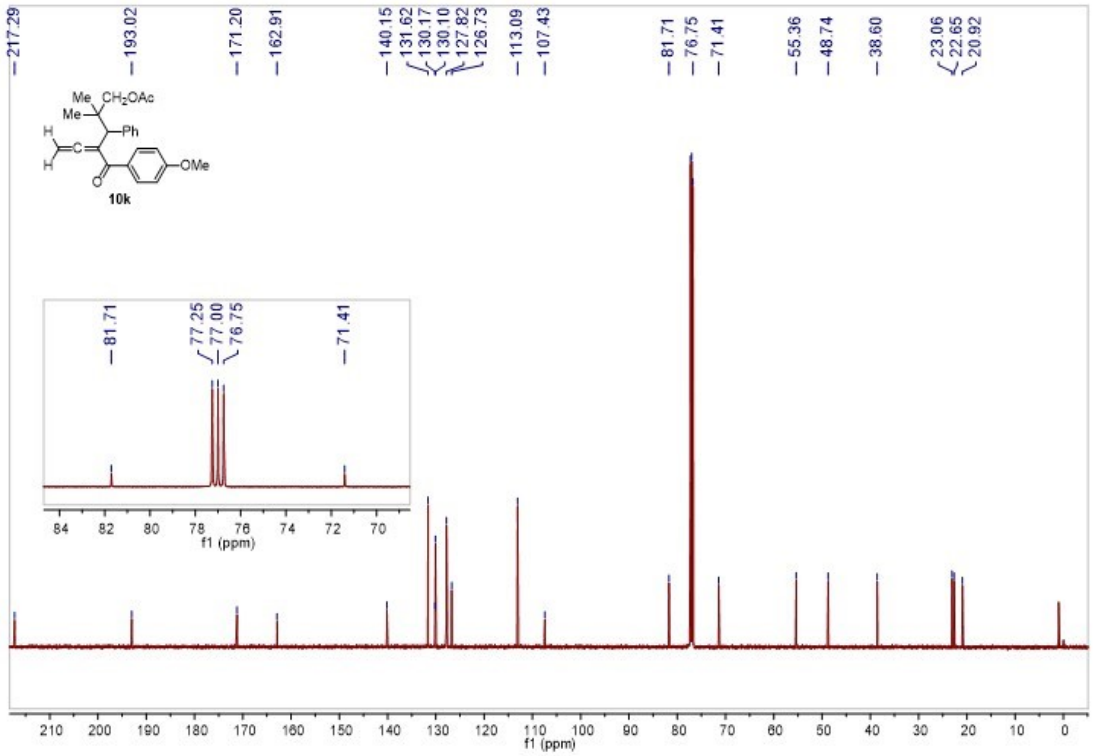
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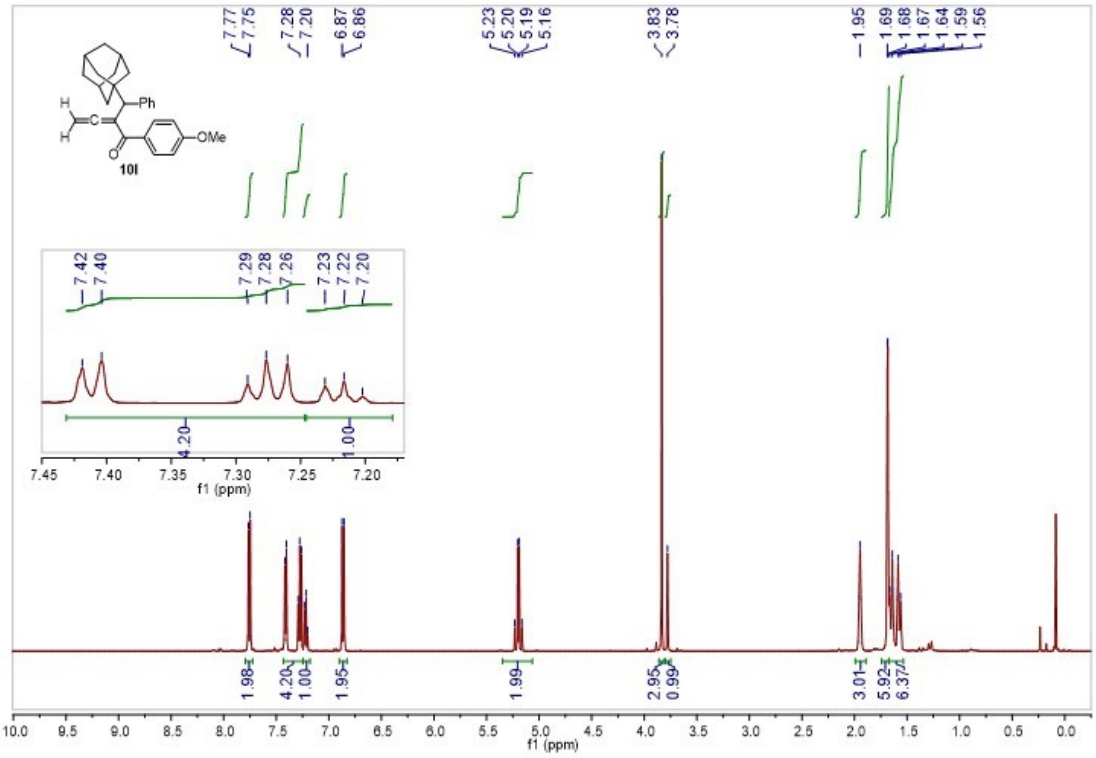
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1.68
1.67
1.64
1.59
1.56
Ph
OMe
10l
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7.40
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7.28
7.26
7.23
7.22
7.20
4.20
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7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
1.98
4.20
1.00
1.95
1.99
2.95
0.99
3.01
5.92
6.37
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
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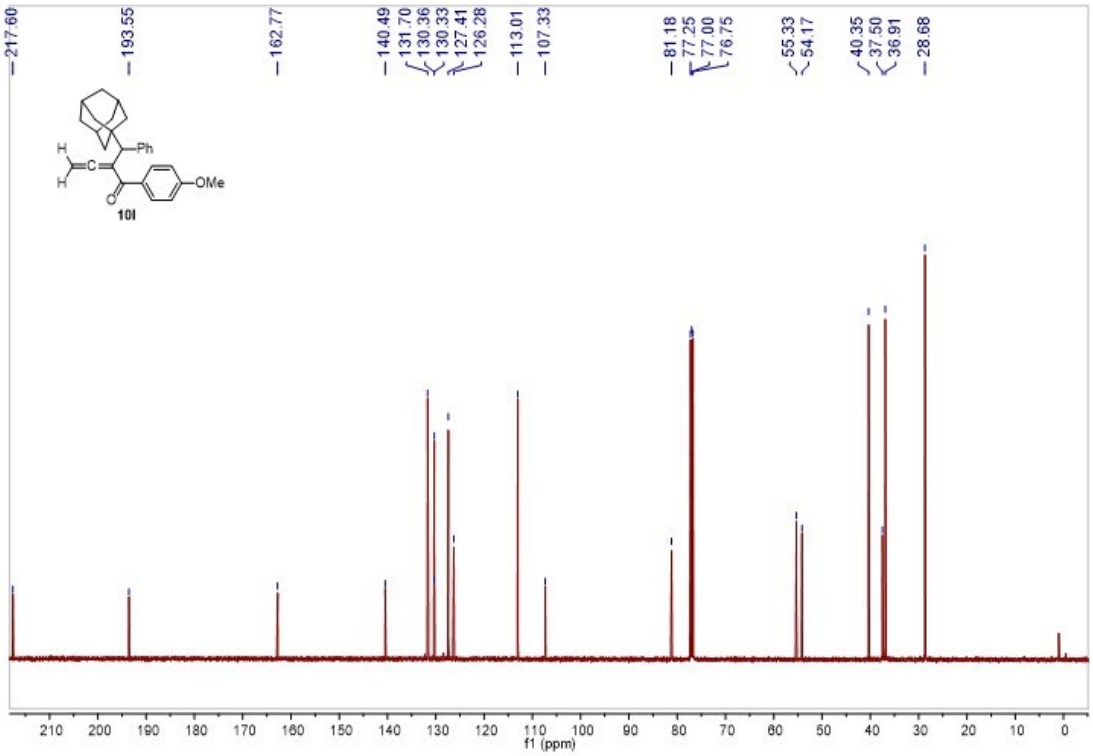
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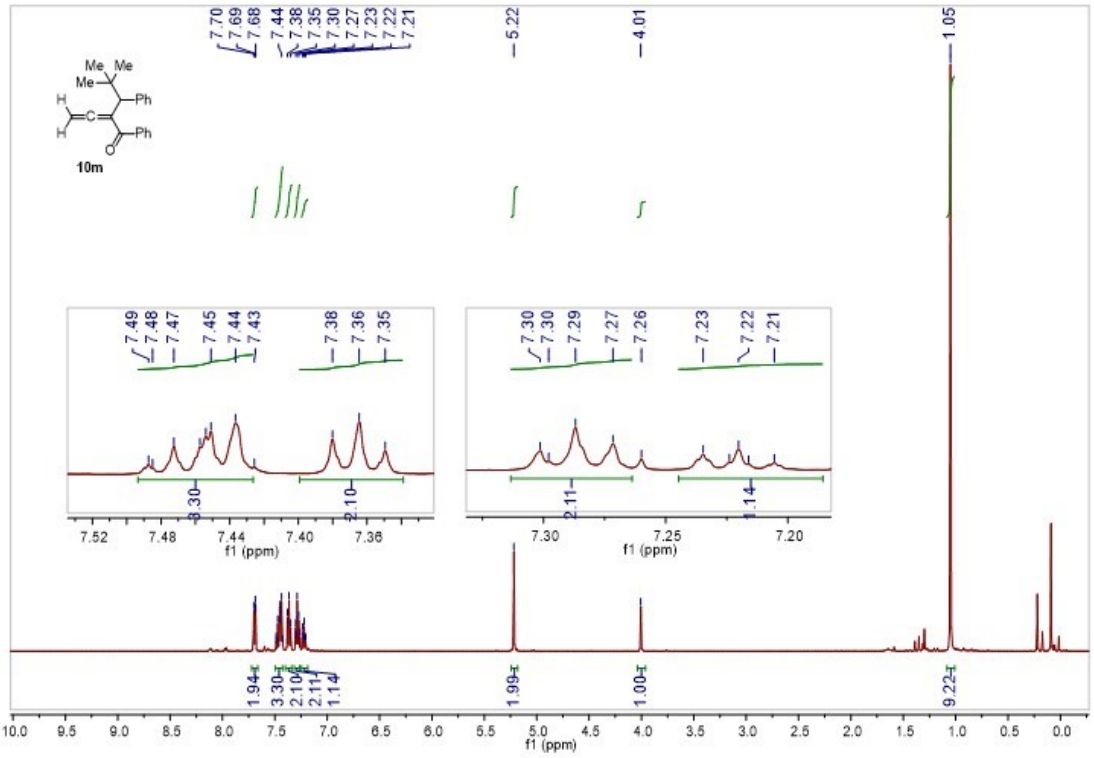
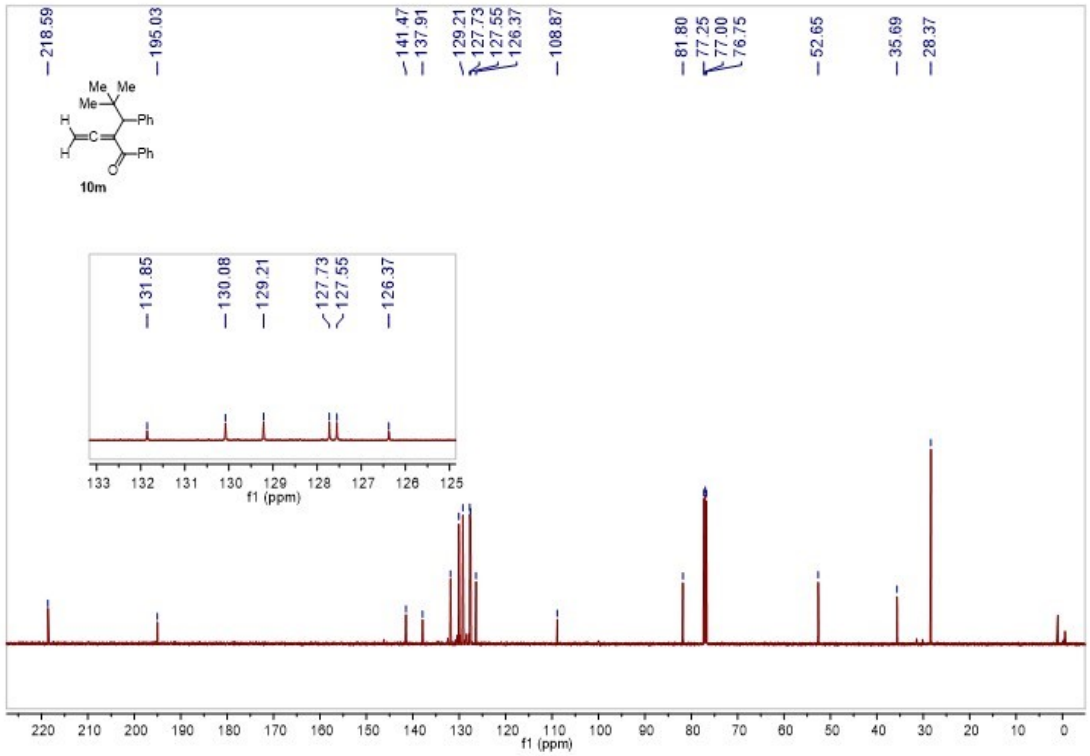
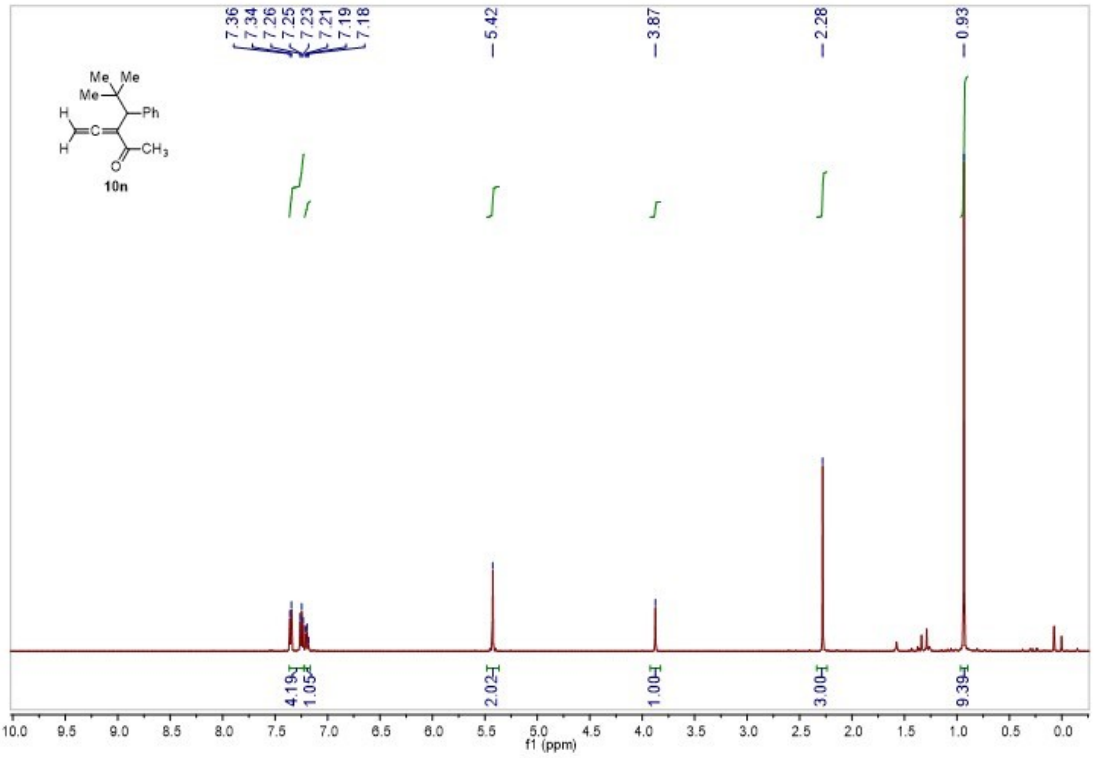
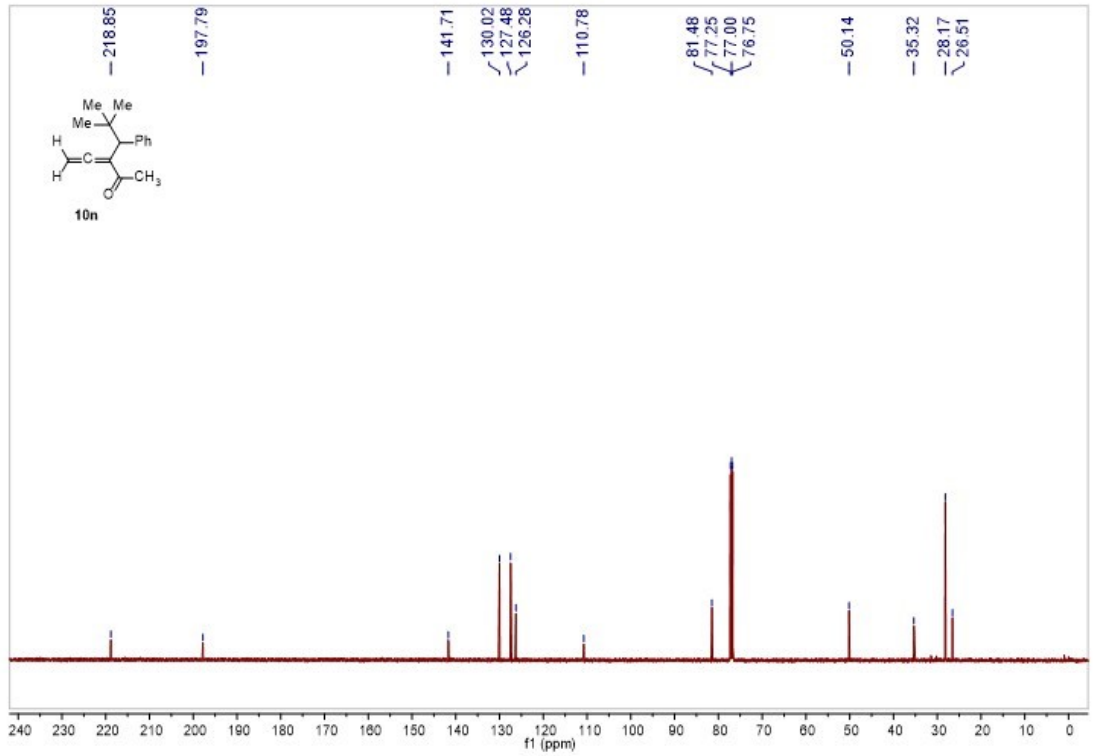
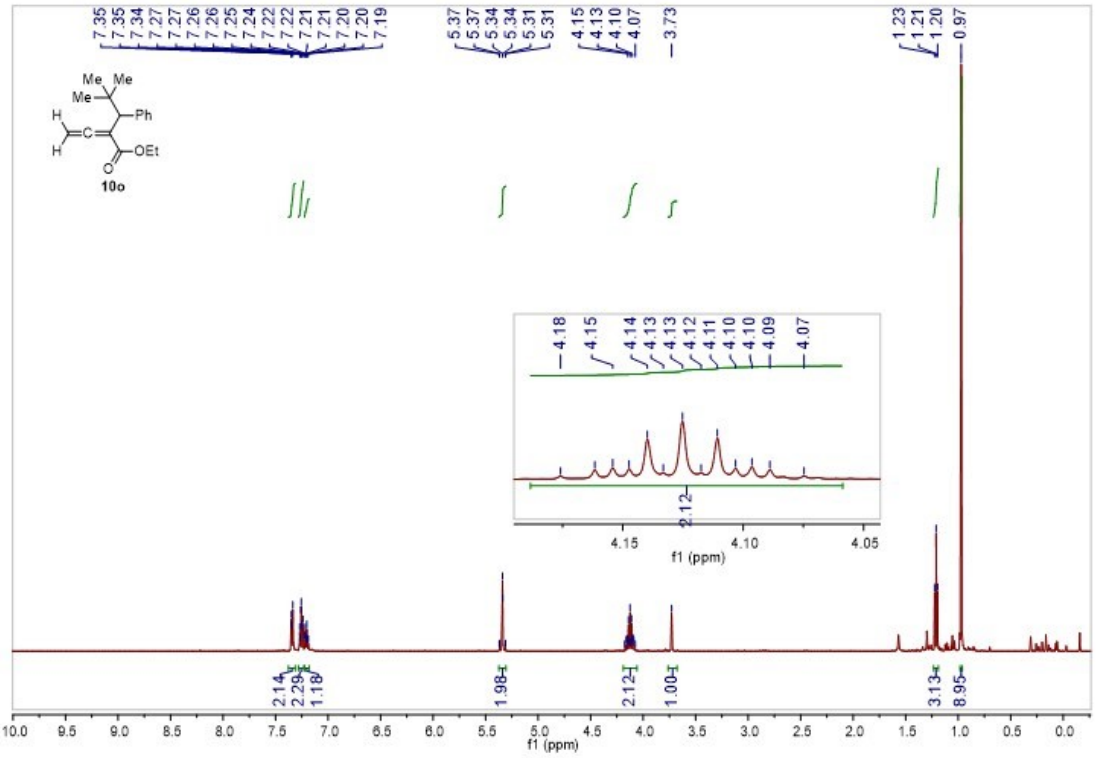
126.28
113.01
107.33
81.18
77.25
77.00
76.75
55.33
54.17
40.35
37.50
36.91
28.68
Ph
OMe
10l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

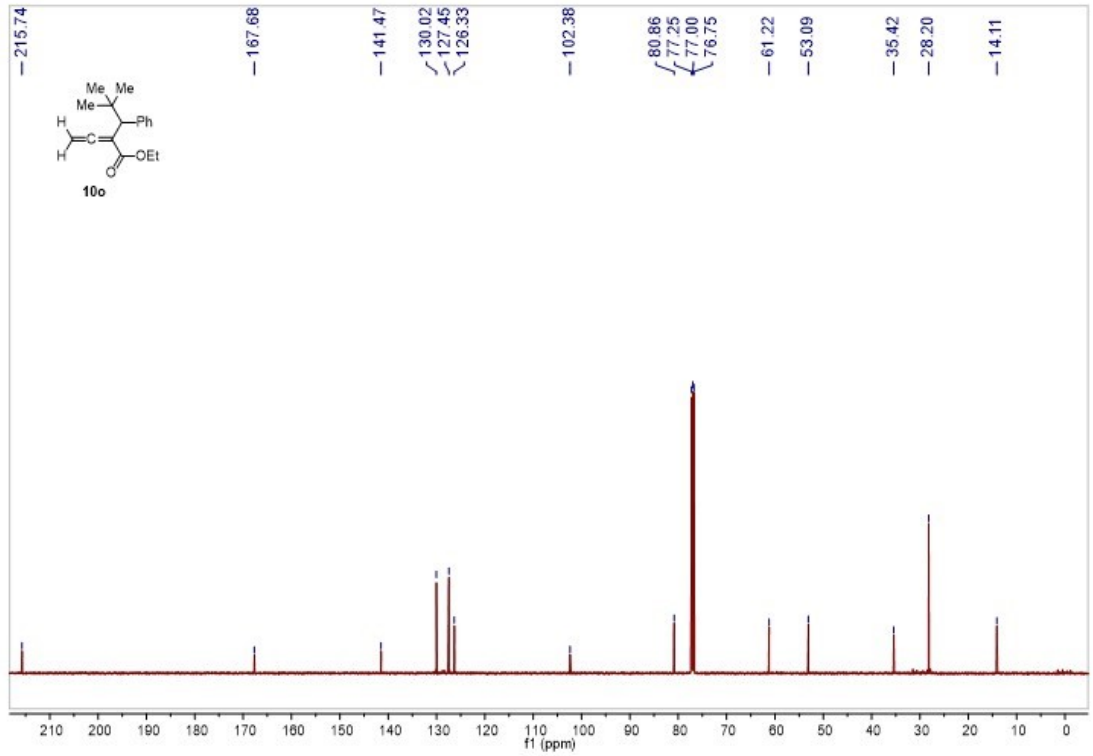

10m
f1 (ppm)

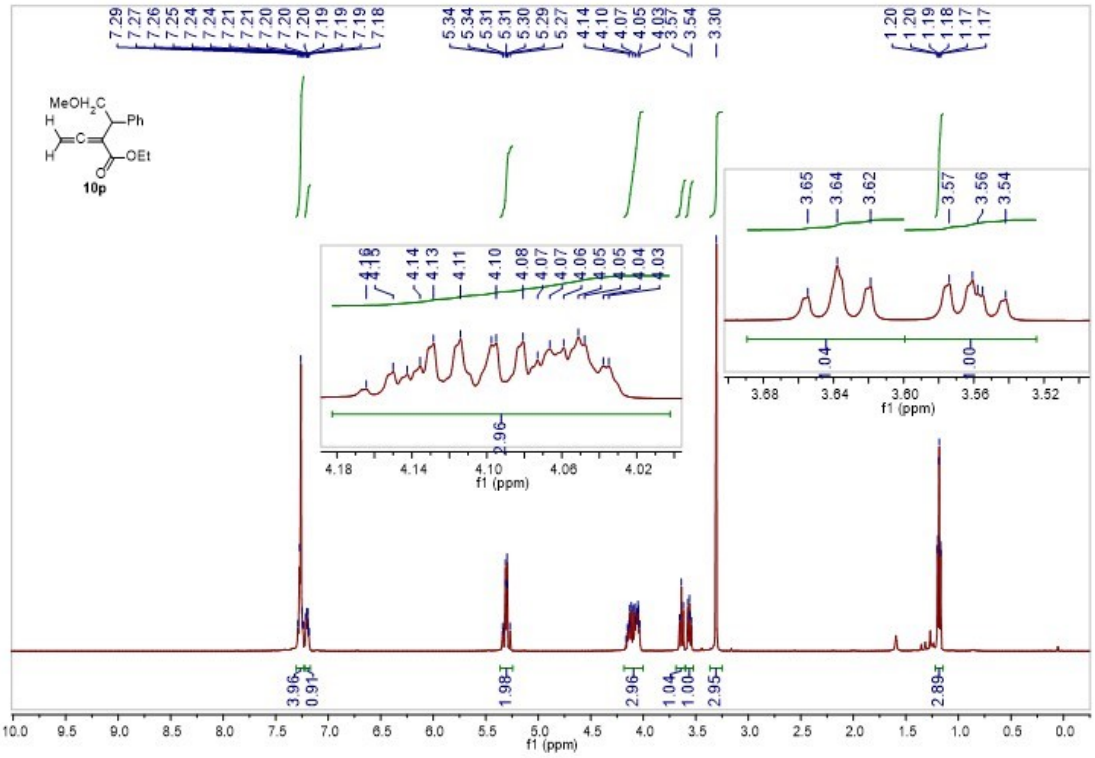

10m
f1 (ppm)

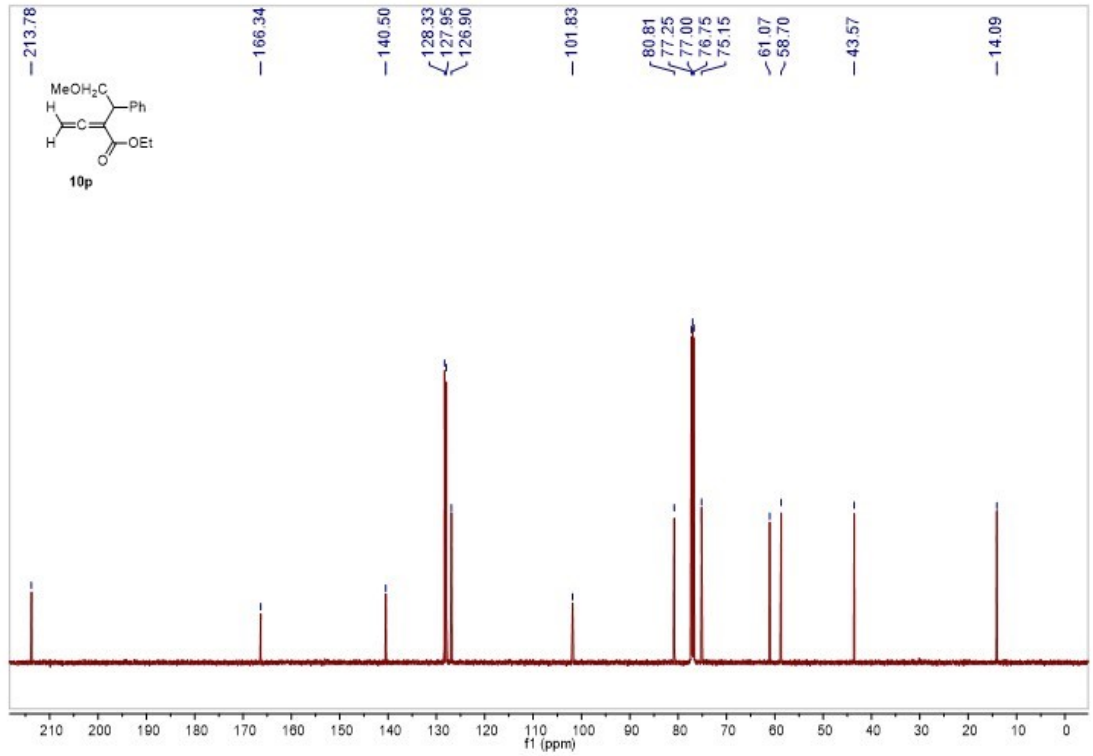

7.36
7.34
7.26
7.25
7.23
7.21
7.19
7.18
5.42
3.87
2.28
0.93
Me Me
Me
Ph
H
H
CH3
O
10n
4.19
1.05
2.02
1.00
3.00
9.39
f1 (ppm)

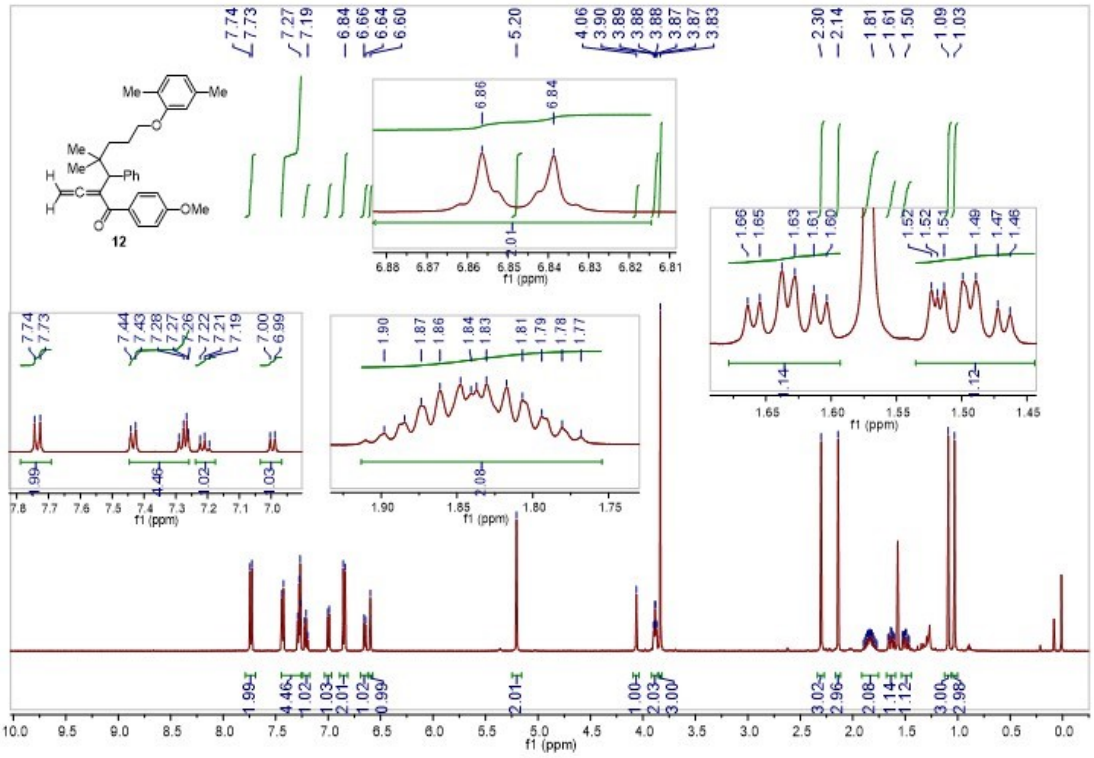

218.85
197.79
141.71
130.02
127.48
126.28
110.78
81.48
77.25
77.00
76.75
50.14
35.32
28.17
26.51
Me Me
Me
Ph
H
H
CH3
O
10n
f1 (ppm)

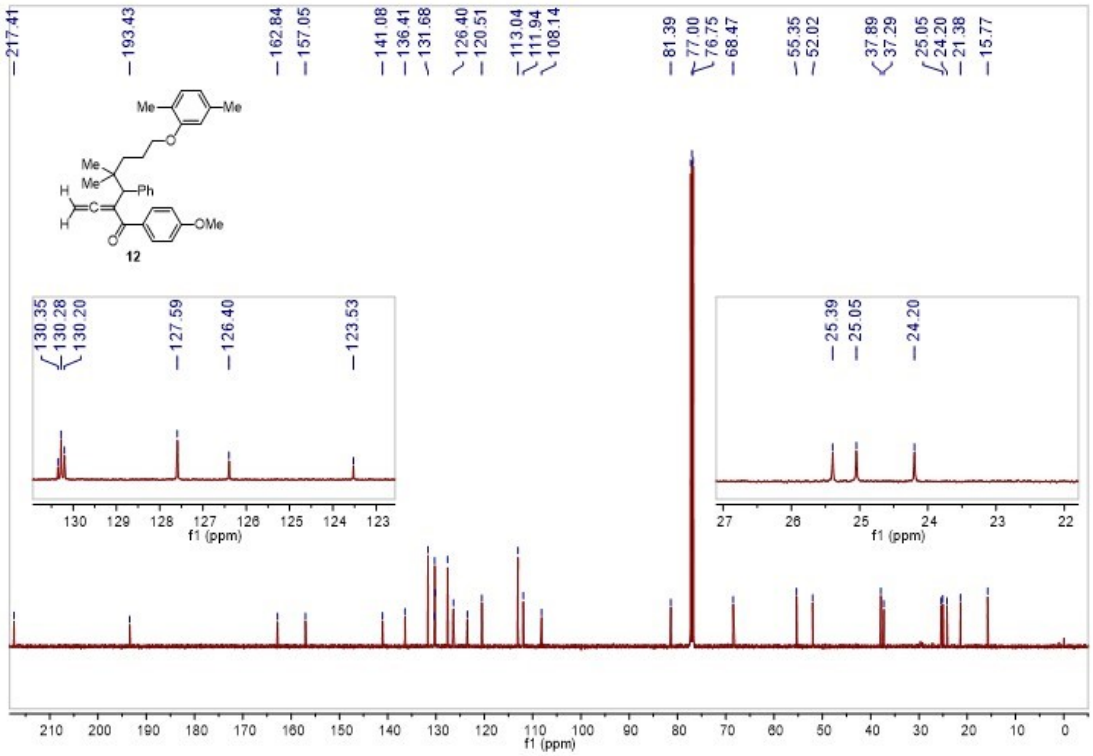

10o
f1 (ppm)

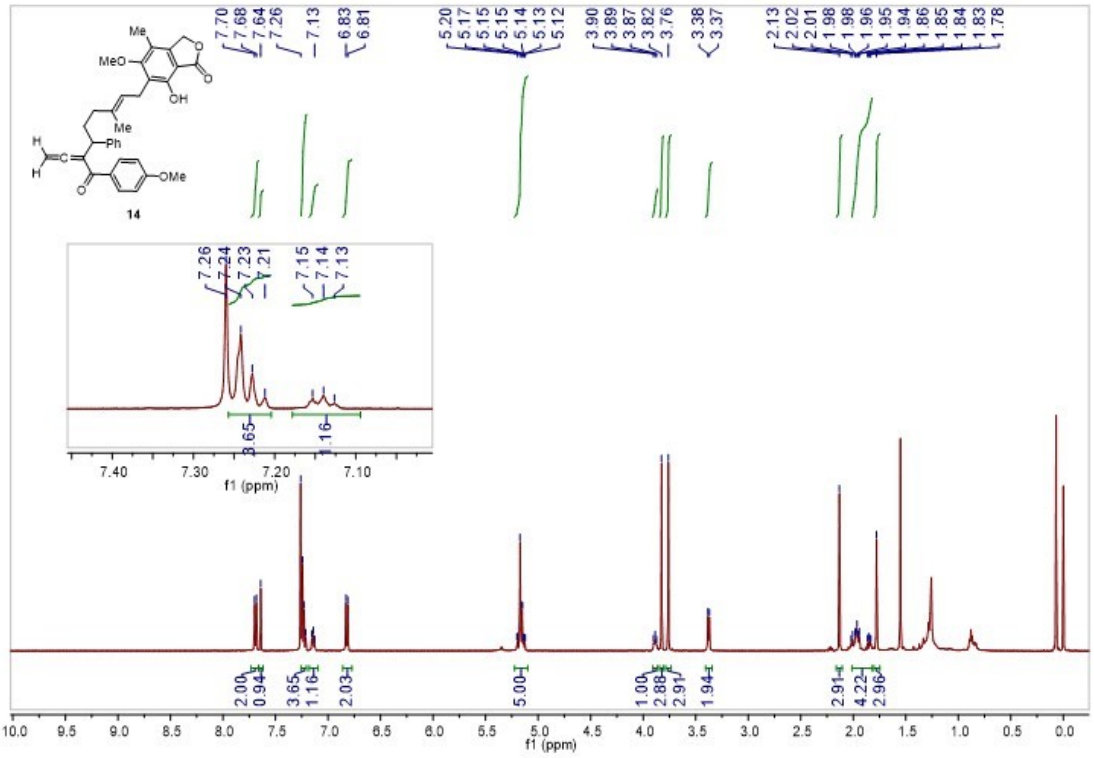

10o
f1 (ppm)

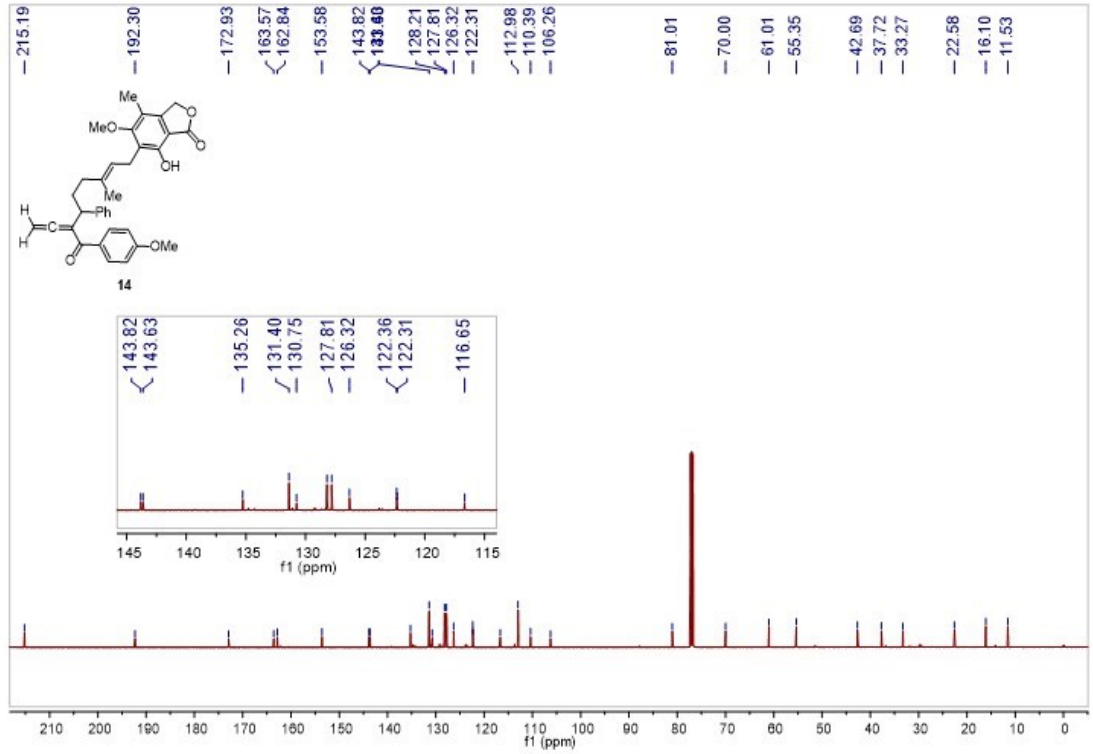

10p
f1 (ppm)

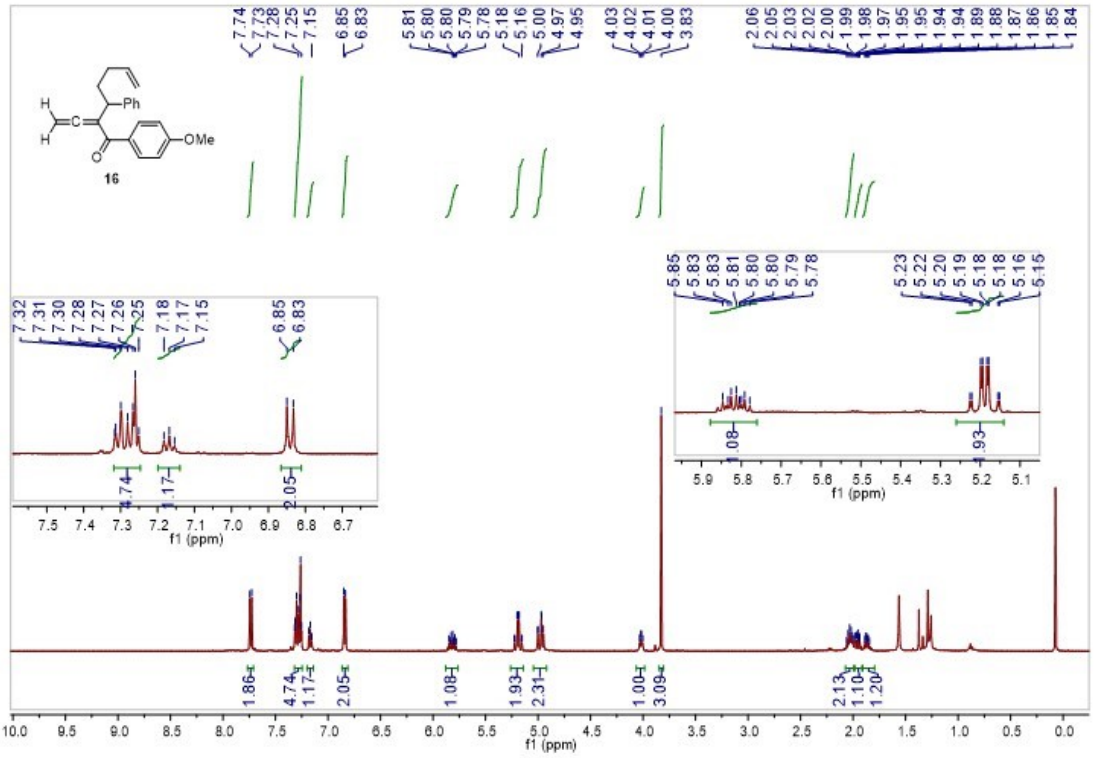

10p
f1 (ppm)

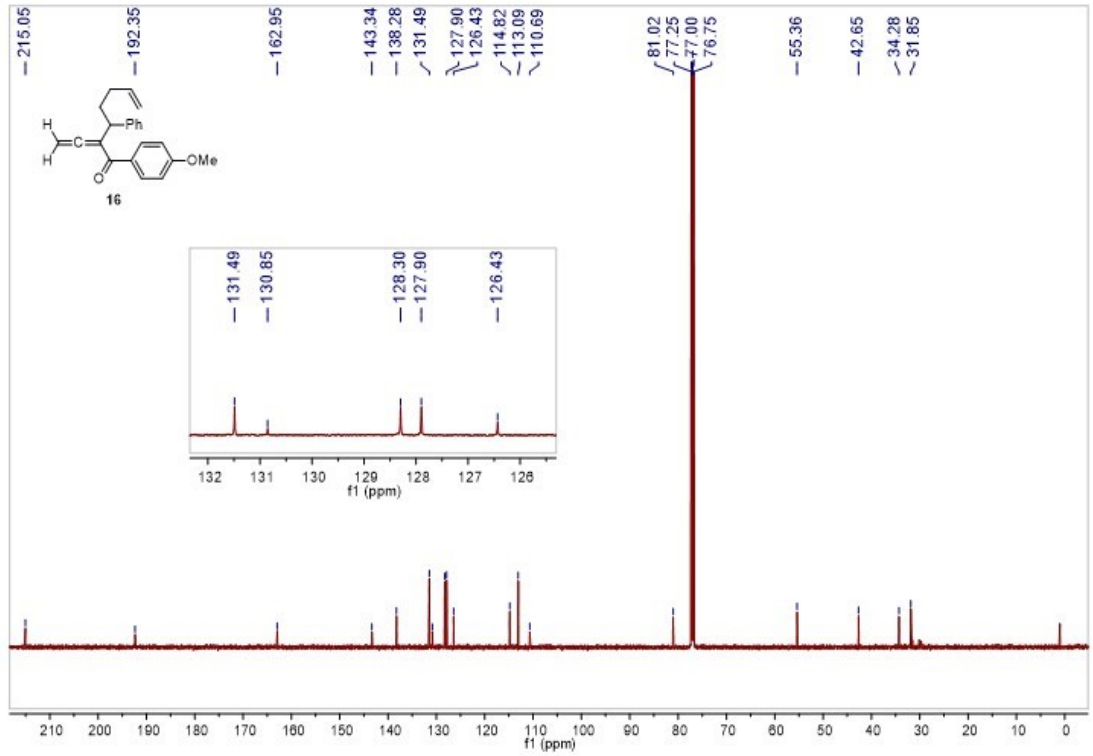

12
f1 (ppm)

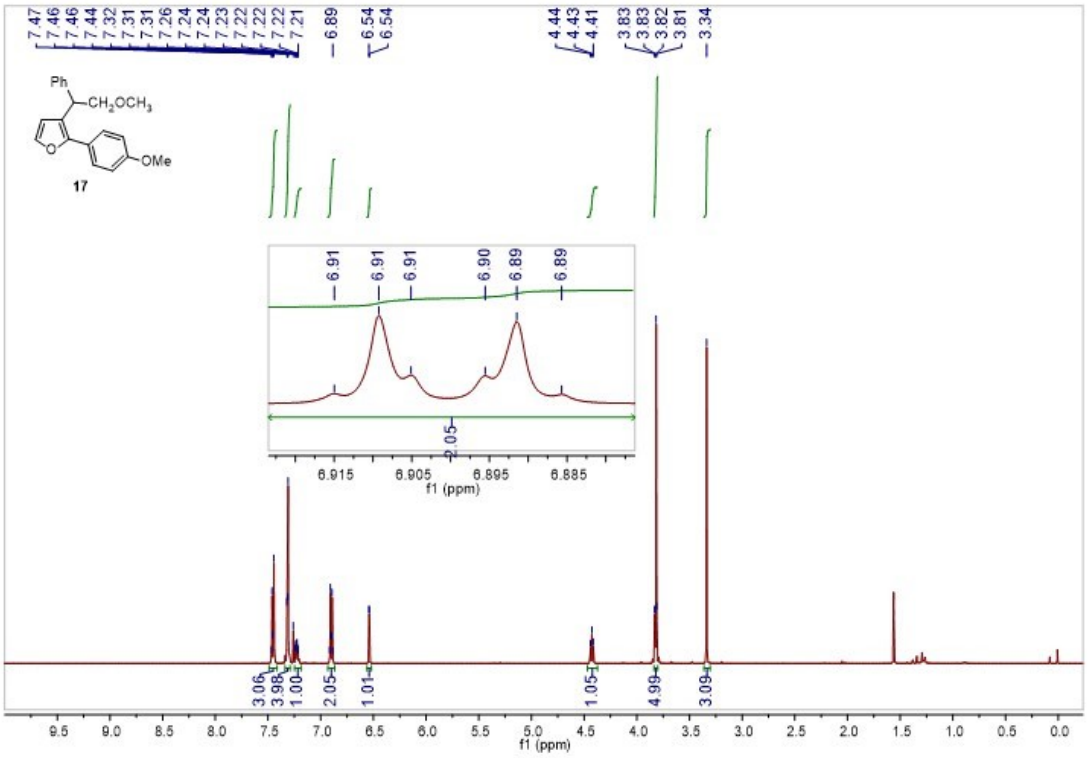

12
f1 (ppm)

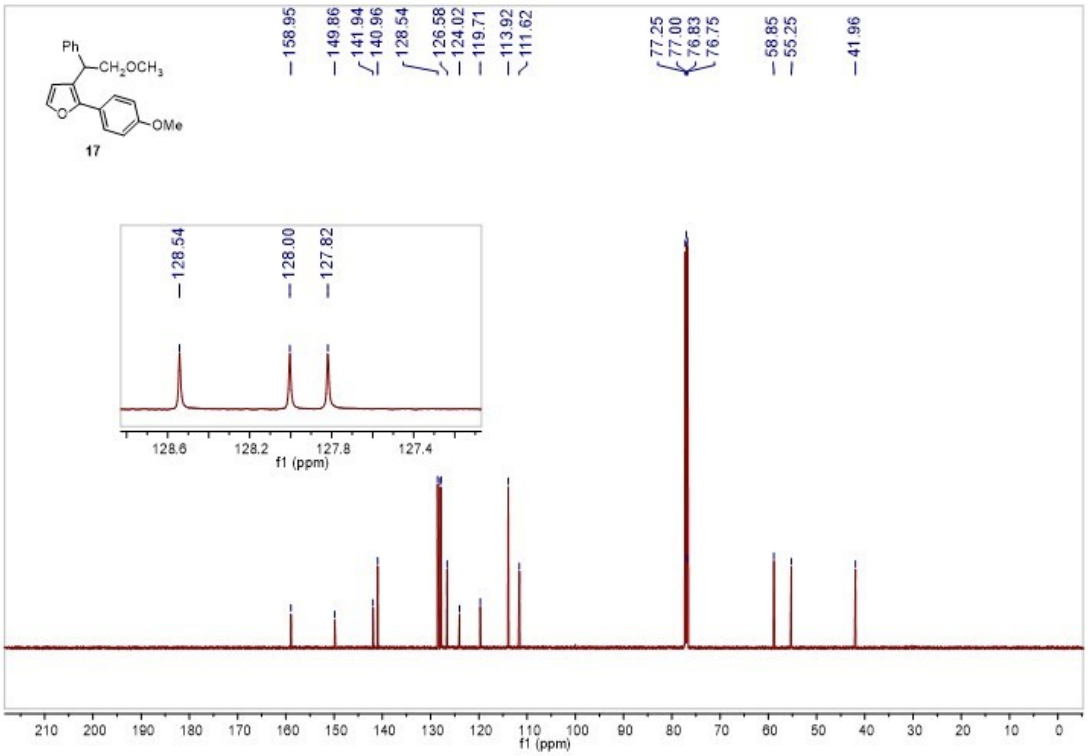

14
f1 (ppm)


14
f1 (ppm)


16
f1 (ppm)


16
f1 (ppm)


7.47
7.46
7.46
7.44
7.32
7.31
7.31
7.26
7.24
7.24
7.23
7.22
7.22
7.22
7.21
6.89
6.54
6.54
4.44
4.43
4.41
3.83
3.83
3.82
3.81
3.34
Ph
CH2OCH3
OMe
17
6.91
6.91
6.91
6.90
6.89
6.89
2.05
6.915
6.905
6.895
6.885
f1 (ppm)
3.06
3.98
1.00
2.05
1.01
1.05
4.99
3.09
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
f1 (ppm)


158.95
149.86
141.94
140.96
128.54
126.58
124.02
119.71
113.92
111.62
77.25
77.00
76.83
76.75
58.85
55.25
41.96
Ph
CH2OCH3
OMe
17
128.54
128.00
127.82
128.6
128.2
127.8
127.4
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)