Supporting Information

Palladium(II)-Catalyzed Tandem Oxidative Acetoxylation/*ortho* C-H Activation/Carbo-cyclization of Arylallenes

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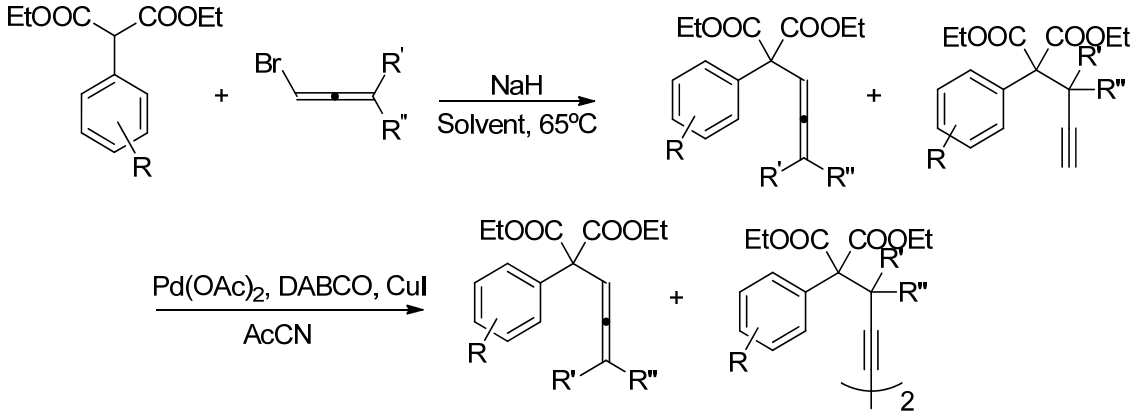
Index

General information

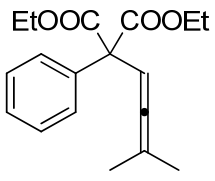
Unless otherwise noted, all reagents were used as received from the commercial suppliers. $Pd(OAc)_2$ was obtained from Pressure Chemicals and used without further purification. Commercially available benzoquinone was separated from insoluble impurities by dissolving it in refluxing cyclohexane and decanting. After evaporation, benzoquinone was obtained as yellow needles. The cyclization reactions described in this report were performed without any efforts to exclude moisture unless otherwise noted. AcOH (p.a. grade) were purchased from Sigma Aldrich. Dry THF and DMF for the preparation of starting materials were obtained from a VAC Solvent Purifier. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), vanillin stain or $KMnO_4$ stain. Flash chromatography was carried out with 60Å (particle size 35−70 μm) normal flash silica gel. NMR spectra were recorded at 400 MHz (^{1}H) or 500 MHz (^{1}H) and at 100 MHz (^{13}C) or 125 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δH = 7.26 and δC = 77.16 ppm) as internal standard, and coupling constants (J) are given in Hz. HRMS were recorded using ESI-TOF techniques.

Preparation of starting materials

All bromoallenes were prepared according to the procedure published by Landor with minor modifications.[1] Diethyl arylmalonates were prepared as described in literature.[2]



*Representative procedure for the synthesis of allenes **1**. Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-phenylmalonate (**1a**)*

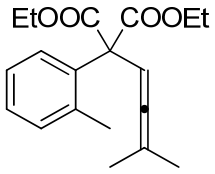


1a

To a suspension of NaH (60% in mineral oil, 840 mg, 20.1 mmol) in anhydrous THF (150 ml) was added a solution of diethyl phenylmalonate (3.8 g, 3.5 mL, 16.0 mmol) in anhydrous THF (10 ml) at 0 ºC. After the addition, the mixture was stirred for another 20 min at r.t. Then a solution of 1-bromo-3-methylbuta-1,2-diene (4.8 g, 32.0 mmol) in anhydrous THF (10 ml) was added at r.t. and the resulting mixture was stirred for 20h at 65 ºC. After the reaction was complete as monitored by TLC, it was cooled to room temperature. The reaction mixture was diluted with 50 mL of Et_2O and quenched with 30 mL of water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organic layers were dried over $MgSO_4$. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 25/1) afforded 4g of a 5:1 mixture of product **1a**:terminal alkyne. This mixture was dissolved in acetonitrile and $Pd(OAc)_2$ (12 mg, 0.053 mmols), CuI (11 mg, 0.053 mmols) and DABCO (892 mg, 7.95 mmols) were added. The resulting mixture was stirred overnight at room temperature. The reaction mixture was diluted with 50 mL of Et_2O and quenched with 30 mL of water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organic layers were dried over $MgSO_4$. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 25/1) afforded **1a** as a colorless oil (2.88 g, 60%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 7.38-7.28 (m, 3H), 5.83 (h, 1H, *J* = 2.8 Hz), 4.26 (m, 4H), 1.66 (d, 6H, *J* = 2.8 Hz), 1.28 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.3, 169.9, 137.5, 128.5, 127.9, 127.6, 99.7, 90.6, 64.5, 61.8, 19.8, 14.0; HRMS (ESI): calc. for $C_{18}H_{22}O_4$ [M+Na]+ : 325.1410; found: 325.1435.

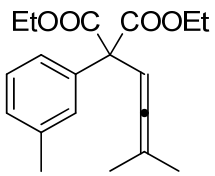
*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(o-tolyl)malonate (**1b**)*



1b

57% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.10 (m, 4H), 5.85 (h, 1H, *J* = 2.8 Hz), 4.28 (m, 4H), 2.25 (s, 3H), 1.50 (d, 6H, *J* = 2.8 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.9, 170.5, 137.3, 136.8, 131.5, 128.0, 127.3, 125.4, 99.3, 90.7, 65.2, 62.0, 21.2, 19.4, 14.0; HRMS (ESI): calc. for $C_{19}H_{24}O_4$ [M+Na]+ : 339.1567; found: 339.1579.

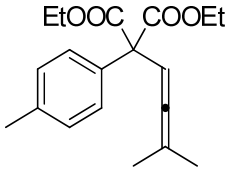
*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(m-tolyl)malonate (**1c**)*



1c

55% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.21 (m, 3H), 7.15-7.09 (m, 1H), 5.82 (h, 1H, *J* = 2.9 Hz), 4.26 (m, 4H), 2.37 (s, 3H), 1.67 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.4, 169.8, 137.3, 129.2, 128.3, 127.8, 125.5, 99.6, 90.6, 64.5, 61.8, 21.6, 19.9, 14.0; HRMS (ESI): calc. for $C_{19}H_{24}O_4$ $[M+Na]^+$: 339.1567; found: 339.1588.

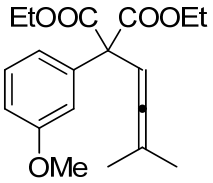
*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(p-tolyl)malonate (**1d**)*



1d

55% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.32 (m, 2H), 7.18-7.13 (m, 2H), 5.82 (h, 1H, *J* = 2.9 Hz), 4.25 (m, 4H), 2.35 (s, 3H), 1.67 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 170.0 ,137.3, 134.5, 128.6, 128.3, 99.5, 90.5, 64.1, 61.7, 21.0, 19.9, 14.0; HRMS (ESI): calc. for $C_{19}H_{24}O_4$ $[M+Na]^+$: 339.1567; found: 339.1586.

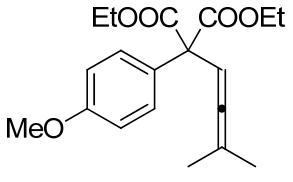
*Diethyl 2-(3-methoxyphenyl)-2-(3-methylbuta-1,2-dien-1-yl)malonate (**1e**)*



1e

64% Isolated yield, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.23 (m, 1H), 7.07-7.01 (m, 2H), 6.88-7.81 (m, 1H), 5.81 (h, 1H, *J* = 2.9 Hz), 4.25 (m, 4H), 3.81 (s, 3H), 1.68 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.2, 169.7, 159.1, 138.9, 128.8, 120.9, 114.7, 113.0, 99.6, 90.4, 64.4, 61.8, 55.2, 19.9, 14.0; HRMS (ESI): calc. for $C_{19}H_{24}O_5$ $[M+Na]^+$: 355.1516; found: 355.1545.

*Diethyl 2-(4-methoxyphenyl)-2-(3-methylbuta-1,2-dien-1-yl)malonate (**1f**)*

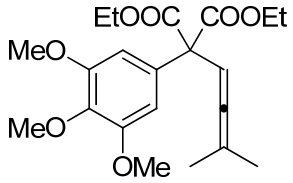


1f

68% Isolated yield, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.35 (m, 2H), 6.91-6.85 (m, 2H), 5.82 (h, 1H, *J* = 2.9 Hz), 4.24 (m, 4H), 3.82 (s, 3H), 1.67 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 170.1, 158.9,

129.7, 129.6, 113.3, 99.6, 90.6, 63.8, 61.7, 55.2, 19.9, 14.0; HRMS (ESI): calc. for $C_{19}H_{24}O_5$ $[M+Na]^+$: 355.1516; found: 355.1529.

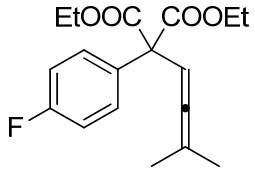
*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(3,4,5-trimethoxyphenyl)malonate (**1g**)*



1g

70% Isolated yield, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.74 (s, 2H), 5.83 (h, 1H, *J* = 2.8 Hz), 4.27 (m, 4H), 3.87 (s, 3H), 3.86 (s, 6H), 1.69 (d, 6H, *J* = 2.8 Hz), 1.31 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.2, 169.7, 152.5, 137.6, 132.8, 106.1, 99.7, 90.4, 64.3, 61.8, 60.8, 56.1, 19.9, 14.0; HRMS (ESI): calc. for $C_{21}H_{28}O_7$ $[M+Na]^+$: 415.1727; found: 415.1752.

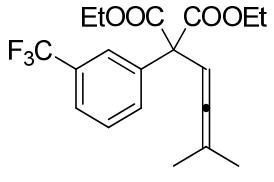
*Diethyl 2-(4-fluorophenyl)-2-(3-methylbuta-1,2-dien-1-yl)malonate (**1h**)*



1h

52% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.39 (m, 2H), 7.08-6.98 (m, 2H), 5.81 (h, 1H, *J* = 2.9 Hz), 4.26 (m, 4H), 1.65 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.4, 169.7, 163.4, 160.9, 133.3, 130.4, 114.6, 99.9, 90.5, 63.8, 61.9, 19.8, 14.0; HRMS (ESI): calc. for $C_{18}H_{21}FO_4$ $[M+Na]^+$: 343.1316; found: 343.1332.

*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(3-(trifluoromethyl)phenyl)malonate (**1i**)*

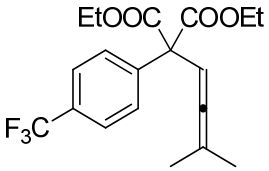


1i

Following the general procedure but using DMF as solvent instead of THF. 45% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.65-7.55 (m, 2H), 7.50-7.44 (m, 1H), 5.85 (h, 1H, *J* = 2.9 Hz), 4.28 (m, 4H), 1.63 (d, 6H, *J* = 2.9 Hz), 1.30 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.7, 169.8, 138.4, 132.0, 130.3, 130.0, 128.2, 125.8, 125.7, 125.5, 125.4, 124.4, 124.3, 122.8, 100.4, 90.3, 64.1,

61.2, 19.6, 14.0; HRMS (ESI): calc. for $C_{19}H_{21}F_3O_4$ $[M+Na]^+$: 393.1284; found: 393.1288.

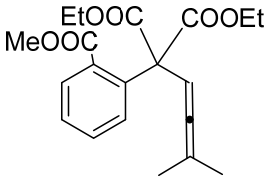
*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(4-(trifluoromethyl)phenyl)malonate (**1j**)*



1j

Following the general procedure but using DMF as solvent instead of THF. 47% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63-7.56 (m, 4H), 5.84 (h, 1H, *J* = 2.9 Hz), 4.28 (m, 4H), 1.64 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.6, 169.2, 141.5, 129.6, 129.1, 124.7, 122.7, 100.2, 90.2, 64.2, 62.1, 19.7, 14.0; HRMS (ESI): calc. for $C_{19}H_{21}F_3O_4$ $[M+Na]^+$: 393.1284; found: 393.1267.

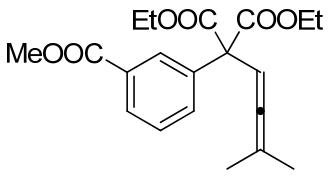
*Diethyl 2-(2-(methoxycarbonyl)phenyl)-2-(3-methylbuta-1,2-dien-1-yl)malonate (**1k**)*



1k

Following the general procedure but using DMF as solvent instead of THF. 43% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (dd, 1H, *J* = 7.8 Hz, *J* = 1.5 Hz), 7.47 (td, 1H, *J* = 7.8 Hz, 1.6 Hz), 7.37 (td, 1H, *J* = 7.8 Hz, 1.6 Hz), 7.26 (dd, 1H, *J* = 7.8 Hz, *J* = 1.5 Hz), 5.90 (h, 1H, *J* = 2.9 Hz), 4.25 (m, 4H), 3.81 (s, 3H), 1.50 (d, 6H, *J* = 2.9 Hz), 1.26 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.9, 169.8, 168.1, 139.5, 131.3, 130.9, 130.5, 129.8, 127.2, 92.1, 65.4, 61.9, 51.8, 21.6, 19.5, 13.9; HRMS (ESI): calc. for $C_{20}H_{24}O_6$ $[M+Na]^+$: 383.1465; found: 383.1468.

*Diethyl 2-(3-(methoxycarbonyl)phenyl)-2-(3-methylbuta-1,2-dien-1-yl)malonate (**1l**)*

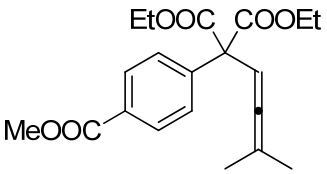


1l

Following the general procedure but using DMF as solvent instead of THF. 47% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18-8.15 (m, 1H), 8.02-7.97 (m, 1H), 7.68-7.63 (m, 1H), 7.43 (t, 1H, *J* = 7.8 Hz), 5.85 (h, 1H, *J* = 2.9 Hz), 4.27

(m, 4H), 3.92 (s, 3H), 1.65 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.6, 169.5, 166.9, 137.9, 133.3, 129.9, 129.8, 128.8, 127.9, 100.1 90.3, 64.2, 62.0, 52.1, 19.7, 14.0; HRMS (ESI): calc. for $C_{20}H_{24}O_6$ $[M+Na]^+$: 383.1465; found: 383.1479.

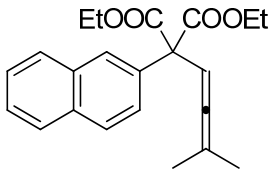
*Diethyl 2-(4-(methoxycarbonyl)phenyl)-2-(3-methylbuta-1,2-dien-1-yl)malonate (**1m**)*



1m

Following the general procedure but using DMF as solvent instead of THF. 40% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04-7.99 (m, 2H), 7.55-7.51 (m, 2H), 5.84 (d, 1H, *J* = 2.9 Hz), 4.26 (m, 4H), 3.94 (s, 3H), 1.63 (d, 6H, *J* = 2.9 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.6, 169.3, 166.8, 142.6, 129.1, 128.7, 100.1, 90.3, 64.4, 62.0, 52.1, 19.7, 14.0; HRMS (ESI): calc. for $C_{20}H_{24}O_6$ $[M+Na]^+$: 383.1465; found: 383.1477.

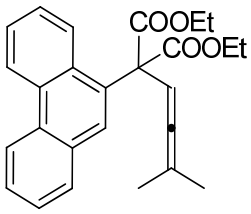
*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(naphthalen-2-yl)malonate (**1n**)*



1n

30% Isolated yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92-7.89 (m, 1H), 7.87-7.79 (m, 3H), 7.61-7.56 (m, 1H), 7.52-7.46 (m, 2H), 5.93 (h, 1H, *J* = 2.9 Hz), 4.29 (m, 4H), 1.67 (d, 6H, *J* = 2.9 Hz), 1.30 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.6, 169.9, 135.4, 132.9, 132.7, 128.3, 127.4, 127.3, 127.2, 126.9, 126.2, 125.9, 99.7, 90.5, 64.5, 61.9, 19.8, 14.0; HRMS (ESI): calc. for $C_{22}H_{24}O_4$ $[M+Na]^+$: 375.1567; found: 375.1568.

*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-(phenanthren-9-yl)malonate (**1o**)*

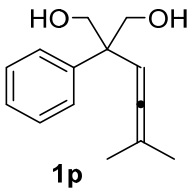


1o

25% Isolated yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (dd, 2H, *J* = 20.2, *J* = 8.7), 7.88 (dd, 2H, *J* = 20.2, *J* = 8.7), 7.70-7.64 (m, 2H), 7.63-7.57 (m, 2H), 7.55-

7.49 (m, 1H), 6.07 (h, 1H, J = 2.9 Hz), 4.30 (m, 4H), 1.23 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.9, 170.4, 133.1, 131.1, 130.4, 130.1, 129.1, 127.5, 127.1, 127.0, 162.6, 125.9, 125.6, 123.0, 122.3, 99.8, 90.9, 65.4, 62.1, 19.0, 13.9; HRMS (ESI): calc. for $C_{26}H_{26}O_4$ $[M+Na]^+$: 425.1723; found: 425.1738.

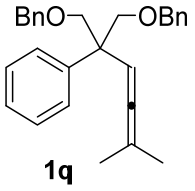
*2-(3-methylbuta-1,2-dien-1-yl)-2-phenylpropane-1,3-diol (**1p**)*



1p

To a suspension of $LiAlH_4$ (233 mg, 6.15 mmols) in 40 mL Et_2O at 0ºC, a solution of **1a** (600mg, 1.98 mmols) in 10 mL Et_2O were added. The mixture was stirred overnight at rt. The reaction mixture was quenched with 20 mL of water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were dried over $MgSO_4$. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) afforded 412 mg of product **1p** (95% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.44 (m, 2H), 7.42-7.36 (m, 2H), 7.32-7.26 (m, 1H), 5.20 (h, 1H, J = 2.9 Hz), 4.10-3.91 (m, 4H), 1.98 (b, 2H), 1.79 (d, 6H, J = 2.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.7, 141.6, 128.6, 127.4, 127.0, 98.4, 91.9, 68.2, 50.4, 20.6; HRMS (ESI): calc. for $C_{14}H_{18}O_2$ $[M+Na]^+$: 241.1199; found: 241.1205.

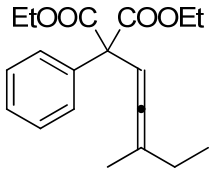
*(((2-(3-methylbuta-1,2-dien-1-yl)-2-phenylpropane-1,3-diyl)bis(oxy))bis(methylene))-dibenzene (**1q**)*



1q

To a suspension of NaH (190 mg in 60% oil, 4.67 mmols) in 4 mL DMF, **1p** (300 mg, 1.37 mmols) in 2mL DMF was added dropwise at 0 ºC and stirred for 1h at 0 ºC. BnBr (360 μL, 515mg, 3.01 mmols) was added dropwise at 0 ºC and the mixture was stirred overnight at rt. The reaction mixture was quenched with a mixture of 15 mL Et_2O and 5 mL water, extracted with Et_2O (3 x 20 mL) washed with water (25 mL). The combined organic layers were dried over $MgSO_4$. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded 497 mg of product **1q** (91% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.44 (m, 2H), 7.36-7.20 (m, 13H), 5.33 (h, 1H, J = 2.8 Hz), 4.54 (m, 4H), 3.88 (d, 2H, J = 9.1 Hz), 3.78 (d, 2H, J = 9.1 Hz), 1.69 (d, 6H, J = 2.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.9, 143.2, 138.8, 128.2, 127.8, 127.7, 127.3, 127.2, 126.3, 97.4, 93.0, 74.0, 73.3, 48.8, 20.4; HRMS (ESI): calc. for $C_{28}H_{30}O_2$ $[M+Na]^+$: 421.2138; found: 421.2140.

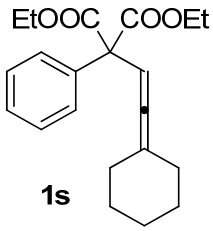
*Diethyl 2-(3-methylpenta-1,2-dien-1-yl)-2-phenylmalonate (**1r**)*



1r

Following the general procedure but using 1-bromo-3-methylpenta-1,2-diene instead of 1-bromo-3-methylbuta-1,2-diene. 62% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.44 (m, 2H), 7.38-7.27 (m, 3H), 5.91 (h, 1H, *J* = 2.9 Hz), 4.25 (m, 4H), 1.90 (m, 2H), 1.65 (d, 6H, *J* = 2.9 Hz), 1.28 (td, 3H, *J* = 7.2 Hz, *J* = 1.6 Hz), 0.93 (t, 3H, *J* = 7.4 Hz) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.4, 169.9, 169.8, 137.5, 128.5, 127.8, 127.5, 106.0, 92.4, 64.5, 61.7, 26.8, 18.3, 14.0, 12.0; HRMS (ESI): calc. for $C_{19}H_{24}O_4$ $[M+Na]^+$: 339.1567; found: 339.1581.

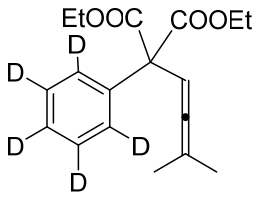
*Diethyl 2-(2-cyclohexylidenevinyl)-2-phenylmalonate (**1s**)*



1s

Following the general procedure but using (2-bromovinylidene)cyclohexane instead of 1-bromo-3-methylbuta-1,2-diene. 65% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-7.41 (m, 2H), 7.37-7.27 (m, 3H), 5.84 (h, 1H, *J* = 2.9 Hz), 4.27 (m, 4H), 2.09-2.02 (m, 4H), 1.60-1.32 (m, 6H), 1.28 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.1, 169.9, 137.6, 128.5, 127.8, 127.5, 106.7, 90.7, 64.7, 61.8, 30.7, 27.0, 25.9, 14.0; HRMS (ESI): calc. for $C_{21}H_{26}O_4$ $[M+Na]^+$: 365.1723; found: 365.1755.

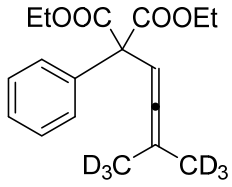
*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-phenylmalonate-d_5 (**1a**-d_5)*



1a-*d*$_5$

58% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.84 (h, 1H, *J* = 2.8 Hz), 4.26 (m, 4H), 1.66 (d, 6H, *J* = 2.8 Hz), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.3, 99.7, 90.6, 64.4, 61.8, 19.8, 14.0; HRMS (ESI): calc. for $C_{18}H_{17}D_5O_4$ [M+Na]+ : 330.1724; found: 330.1744.

*Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-phenylmalonate-d_6 (**1a-d_6**)*



1a-*d*$_6$

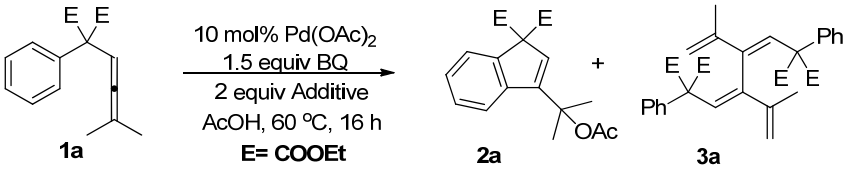
52% Isolated yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 7.38-7.28 (m, 3H), 5.83 (s, 1H), 4.26 (m, 4H), 1.29 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.3, 169.9, 137.5, 128.5, 127.9, 127.6, 90.6, 64.5, 61.8, 14.0; HRMS (ESI): calc. for $C_{18}H_{16}D_6O_4$ [M+Na]+ : 331.1787; found: 331.1801.

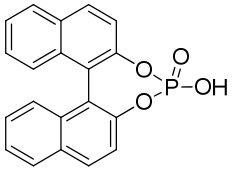
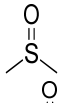
Typical Experimental Procedure for Carbocyclization of 1 to 2.

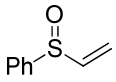
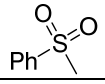
In a sealable microwave tube were placed 0.2 mmol of arylallene, 4.5 mg $Pd(OAc)_2$ (0.02 mmols) and 36.5 mg of benzoquinone (0.34 mmol). The mixture was dissolved in 2 mL of acetic acid and 32 μL DMSO-d6 (0.4 mmols) were added. The mixture was stirred for 16h at 60ºC. The resulting mixture was quenched with a 5 mL 1:1 mixture H_2O:AcOEt and extracted with AcOEt (3 x 3 mL). The combined organic layers were dried over $MgSO_4$. Evaporation and column chromatography on silica gel afforded the desired indene product.

Selected optimization results

Table S1. Optimization of additives

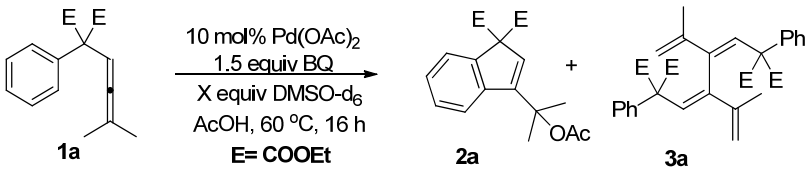


Entry[a]	Additive	**2a**, Yield [%]	**3a**, Yield [%]
1	No Add	34	18
2	PPh_3	<5	-
3	Acridine	<5	-
4	 *rac*	<5	-
5		60	6
6		43	10
7		33	11

8		<5	-
9		17	12

[a] Yields were determined by ^{1}H NMR using mesitylene as internal standard.

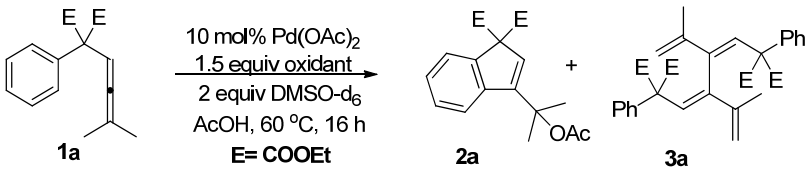
Table S2. Optimization amount of DMSO-d6

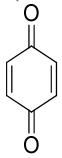
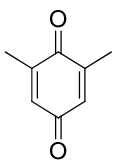


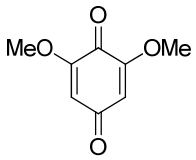
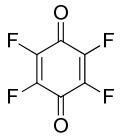
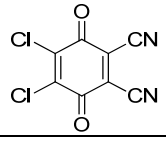
Entry[a]	Equiv. DMSO-d6	**2a**, Yield [%]	**3a**, Yield [%]
1	0	34	18
2	0.5	47	10
3	1	49	8
4	2	60	6
5	3	57	6
6	4	53	5
7	5	52	<5
8	10	47	<5
9	20	36	<5

[a] Yields were determined by ^{1}H NMR using mesitylene as internal standard.

Table S3. Optimization of oxidants

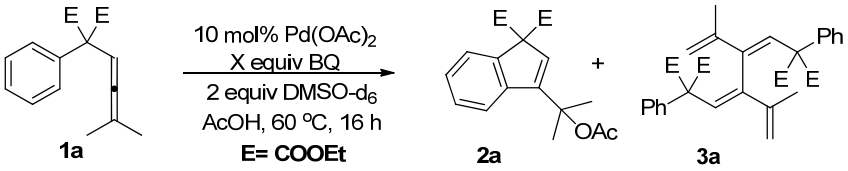


Entry[a]	Oxidant	**2a**, Yield [%]	**3a**, Yield [%]
1	$CuCl_2$	0	-
2	$Cu(OAc)_2$	0	-
3	AgOAc	0	-
4	Ag_2O	0	-
5	$PhI(OAc)_2$	0	-
6		60	6
7		25	5

8		<5	-
9		0	-
10		0	-

[a] Yields were determined by ^{1}H NMR using mesitylene as internal standard.

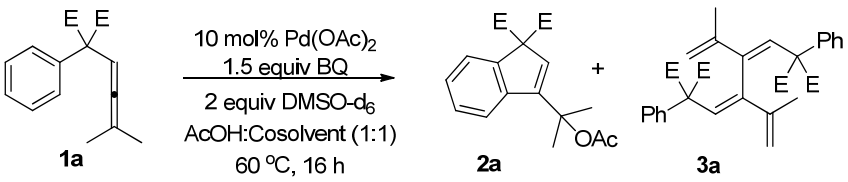
Table S4. Optimization of the amount of benzoquinone



Entry[a]	Equiv. BQ	**2a**, Yield [%]	**3a**, Yield [%]
1	1.1	49	5
2	1.3	56	6
3	1.5	60	6
4	1.7	65	6
5	2	61	6

[a] Yields were determined by ^{1}H NMR using mesitylene as internal standard.

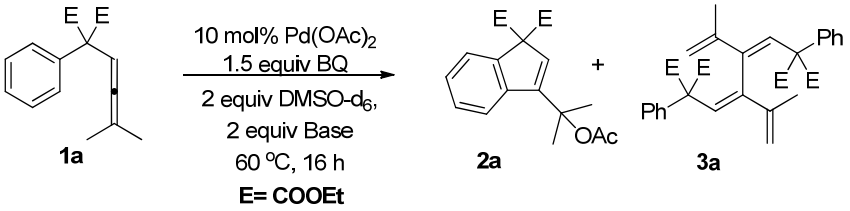
Table S5. Use of co-solvents



Entry[a]	Cosolvent	**2a**, Yield [%]	**3a**, Yield [%]
1	-	60	6
2	THF	33	<5
3	Dioxane	37	<5
4	DCE	26	<5
5	Toluene	32	<5
6	DMF	0	-
7	AcOEt	38	<5

[a] Yields were determined by ^{1}H NMR using mesitylene as internal standard.

Table S6. Use of bases

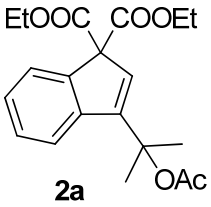


Entry[a]	Base	**2a**, Yield [%]	**3a**, Yield [%]
1	-	60	6
2	$LiOAc{\cdot}2H_2O$	50	8
3	KOAc	46	9
4	CsOAc	44	8
5	PivOLi	-	-

[a] Yields were determined by ^{1}H NMR using mesitylene as internal standard.

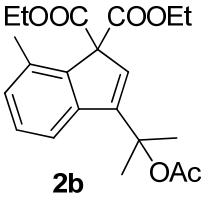
Characterization of products 2.

*Diethyl 3-(2-acetoxypropan-2-yl)-1H-indene-1,1-dicarboxylate (**2a**)*



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 1H, *J* = 7.4 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), 7.39-7.26 (m, 2H), 6.38 (s, 1H), 4.23 (m, 4H), 2.02 (s, 3H), 1.82 (s, 6H), 1.28 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 167.7, 150.9, 142.0, 140.8, 128.5, 126.7, 126.2, 125.9, 121.5, 79.1, 68.8, 62.1, 26.6, 21.9, 14.0; HRMS (ESI): calc. for $C_{20}H_{24}O_6$ $[M+Na]^+$: 383.1465; found: 383.1477.

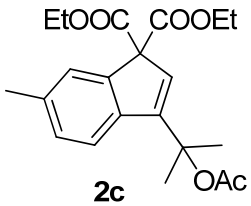
*Diethyl 3-(2-acetoxypropan-2-yl)-7-methyl-1H-indene-1,1-dicarboxylate (**2b**)*



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, 1H, *J* = 7.8 Hz), 7.26 (t, 1H, *J* = 7.8 Hz), 7.08 (d, 1H, *J* = 7.8 Hz), 6.30 (s, 1H), 4.22 (m, 4H), 2.45 (s, 3H), 2.02 (s, 3H), 1.80 (s, 6H), 1.26 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 167.8, 150.6, 142.8,

139.5, 136.2, 129.0, 128.5, 127.5, 119.2, 78.9, 69.2, 61.9, 26.7, 21.8, 19.5, 14.0; HRMS (ESI): calc. for $C_{21}H_{26}O_6$ $[M+Na]^+$: 397.1622; found:397.1634.

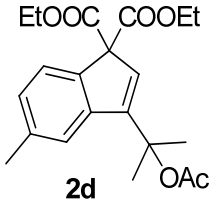
*Diethyl 3-(2-acetoxypropan-2-yl)-6-methyl-1H-indene-1,1-dicarboxylate (**2c**)*



2c

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.37 (d, 1H, *J* = 7.8 Hz), 7.16 (d, 1H, *J* = 7.8 Hz), 6.30 (s, 1H), 4.23 (m, 4H), 2.42 (s, 3H), 2.01 (s, 3H), 1.80 (s, 6H), 1.29 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 167.9, 150.9, 141.0, 139.3, 136.1, 129.2, 126.7, 125.7, 121.1, 79.1, 68.6, 62.1, 26.5, 21.9, 21.5, 14.0; HRMS (ESI): calc. for $C_{21}H_{26}O_6$ $[M+Na]^+$: 397.1622; found: 397.1644.

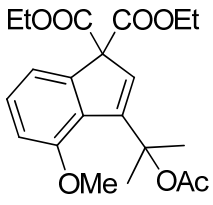
*Diethyl 3-(2-acetoxypropan-2-yl)-5-methyl-1H-indene-1,1-dicarboxylate (**2d**)*



2d

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, 1H, *J* = 7.8 Hz), 7.30 (s, 1H), 7.10 (d, 1H, *J* = 7.8 Hz), 6.36 (s, 1H), 4.23 (m, 4H), 2.41 (s, 3H), 2.03 (s, 3H), 1.82 (s, 6H), 1.28 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 167.9, 150.9, 142.1, 138.2, 138.0, 128.7, 127.0, 125.5, 122.3, 79.2, 68.5, 62.1, 26.6, 21.9, 21.8, 14.0; HRMS (ESI): calc. for $C_{21}H_{26}O_6$ $[M+Na]^+$: 397.1622; found: 397.1629.

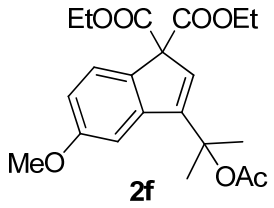
*Diethyl 3-(2-acetoxypropan-2-yl)-4-methoxy-1H-indene-1,1-dicarboxylate (**2e**)*



2e

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (s, 1H, *J* = 8.5 Hz), 7.33 (d, 1H, *J* = 2.5 Hz), 6.88 (dd, 1H, *J* = 8.5 Hz, *J* = 2.5 Hz), 6.25 (s, 1H), 4.22 (m, 4H), 3.86 (s, 3H), 2.02 (s, 3H), 1.80 (s, 6H), 1.29 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 167.8, 158.5, 150.7, 142.6, 134.8, 124.7, 121.9, 114.0, 112.3, 79.1, 68.7, 62.1, 55.6, 26.6, 21.9, 14.0; HRMS (ESI): calc. for $C_{21}H_{26}O_7$ $[M+Na]^+$: 413.1571; found: 413.1585.

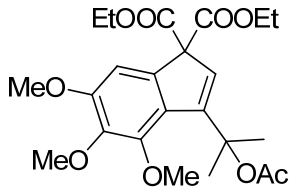
*Diethyl 3-(2-acetoxypropan-2-yl)-5-methoxy-1H-indene-1,1-dicarboxylate (**2f**)*



2f

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.05 (d, 1H, *J* = 2.4 Hz), 6.81 (d, 1H, *J* = 8.6 Hz, *J* = 2.4 Hz), 6.39 (s, 1H), 4.23 (m, 4H), 3.85 (s, 3H), 2.03 (s, 3H), 1.80 (s, 6H), 1.28 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 167.9, 160.2, 150.7, 143.4, 132.9, 127.9, 126.3, 110.8, 108.4, 79.0, 68.1, 62.0, 55.5, 26.6, 21.9, 14.0; HRMS (ESI): calc. for $C_{21}H_{26}O_7$ $[M+Na]^+$: 413.1571 found: 413.1546.

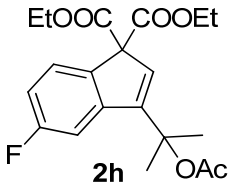
*Diethyl 3-(2-acetoxypropan-2-yl)-4,5,6-trimethoxy-1H-indene-1,1-dicarboxylate (**2g**)*



2g

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (s, 1H), 6.29 (s, 1H), 4.25 (m, 4H), 3.98 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H), 2.05 (s, 3H), 1.85 (s, 6H), 1.28 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 167.9, 152.8, 151.4, 147.3, 142.7, 137.1, 126.7, 125.4, 105.8, 79.6, 38.0, 62.1, 60.5, 56.3, 26.3, 22.5, 14.0; HRMS (ESI): calc. for $C_{23}H_{30}O_9$ $[M+Na]^+$: 473.1782; found: 473.1807.

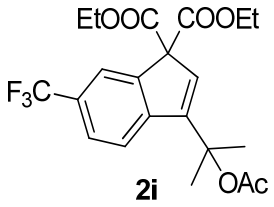
*Diethyl 3-(2-acetoxypropan-2-yl)-5-fluoro-1H-indene-1,1-dicarboxylate (**2h**)*



2h

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (dd, 1H, *J* = 8.4 Hz, *J* = 5.5 Hz), 7.17 (dd, 1H, *J* = 9.0 Hz, *J* = 2.5 Hz), 7.00-6.94 (m, 1H), 6.44 (s, 1H), 4.23 (m, 4H), 2.04 (s, 3H), 1.80 (s, 6H), 1.28 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 167.3, 150.3, 143.9, 136.2, 128.6, 126.9, 113.0, 112.7, 109.1, 108.9, 78.8, 68.3, 62.3, 26.5, 21.8, 13.9; HRMS (ESI): calc. for $C_{20}H_{23}FO_6$ $[M+Na]^+$: 401.1371; found: 401.1366.

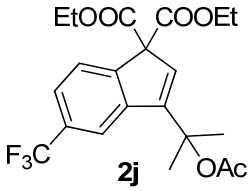
*Diethyl 3-(2-acetoxypropan-2-yl)-6-(trifluoromethyl)-1H-indene-1,1-dicarboxylate (**2i**)*



2i

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.66-7.56 (m, 2H), 6.52 (s, 1H), 4.25 (m, 4H), 2.03 (s, 3H), 1.81 (s, 6H), 1.30 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 166.8, 150.3, 145.4, 141.3, 129.3, 128.2, 125.9, 122.9, 121.5, 78.7, 68.9, 62.5, 26.6, 21.8, 13.9; HRMS (ESI): calc. for $C_{21}H_{23}F_3O_6$ $[M+Na]^+$: 451.1339; found: 451.1379.

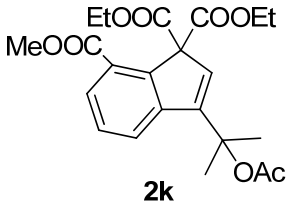
*Diethyl 3-(2-acetoxypropan-2-yl)-5-(trifluoromethyl)-1H-indene-1,1-dicarboxylate (**2j**)*



2j

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, 1H, *J* = 8.1 Hz), 7.72 (s, 1H), 7.57 (d, 1H, *J* = 8.4 Hz), 6.48 (s, 1H), 4.25 (m, 4H), 2.02 (s, 3H), 1.82 (s, 6H), 1.29 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 166.8, 150.2, 144.2, 142.7, 130.8, 128.3, 126.2, 125.6, 123.3, 122.9, 118.2, 78.8, 69.0, 62.5, 26.7, 21.6, 14.0; HRMS (ESI): calc. for $C_{21}H_{23}F_3O_6$ $[M+Na]^+$: 451.1339; found: 451.1364.

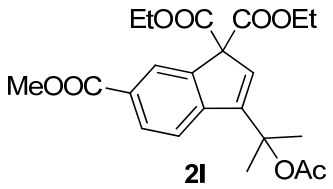
*1,1-Diethyl 7-methyl 3-(2-acetoxypropan-2-yl)-1H-indene-1,1,7-tricarboxylate (**2k**)*



2k

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, 1H, *J* = 7.9 Hz), 7.71 (dd, 1H, *J* = 7.9 Hz, *J* = 1.1 Hz), 7.45 (t, 1H, *J* = 7.9 Hz), 6.39 (s, 1H), 4.16 (m, 4H), 3.85 (s, 1H), 2.02 (s, 3H), 1.80 (s, 6H), 1.18 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 167.3, 166.7, 149.4, 143.8, 142.7, 128.5, 128.4, 128.3, 127.5, 125.3, 78.7, 69.7, 61.8, 51.7, 26.6, 21.8, 13.9; HRMS (ESI): calc. for $C_{22}H_{26}O_8$ $[M+Na]^+$: 441.1520; found: 441.1528.

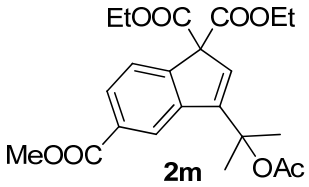
*1,1-Diethyl 7-methyl 3-(2-acetoxypropan-2-yl)-1H-indene-1,1,6-tricarboxylate (**2l**)*



2l

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, 1H, *J* = 1.4 Hz), 8.08 (dd, 1H, *J* = 8.4 Hz, *J* = 1.4 Hz), 7.56 (d, 1H, *J* = 8.4 Hz), 6.52 (s, 1H), 4.25 (m, 4H), 3.94 (s, 1H), 2.02 (s, 3H), 1.81 (s, 6H), 1.29 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 167.0, 166.9, 150.6, 146.6, 141.0, 130.5, 129.7, 128.1, 126.8, 121.2, 78.8, 68.8, 62.4, 52.1, 26.6, 21.8, 14.0; HRMS (ESI): calc. for $C_{22}H_{26}O_8$ $[M+Na]^+$: 441.1520; found: 441.1536.

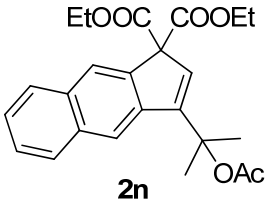
*1,1-Diethyl 7-methyl 3-(2-acetoxypropan-2-yl)-1H-indene-1,1,5-tricarboxylate (**2m**)*



2m

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 8.00 (d, 1H, *J* = 8.0 Hz), 7.80 (d, 1H, *J* = 8.0 Hz), 6.43 (s, 1H), 4.24 (m, 4H), 3.95 (s, 1H), 2.05 (s, 3H), 1.83 (s, 6H), 1.28 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 167.1, 167.0, 150.6, 145.4, 142.4, 130.6, 127.9, 127.6, 125.8, 122.5, 78.9, 69.0, 62.4, 52.2, 26.7, 21.8, 13.9; HRMS (ESI): calc. for $C_{22}H_{26}O_8$ $[M+Na]^+$: 441.1520; found: 441.1539.

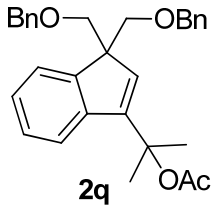
*Diethyl 3-(2-acetoxypropan-2-yl)-1H-cyclopenta[b]naphthalene-1,1-dicarboxylatedi-carboxylate (**2n**)*



2n

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.92-7.81 (m, 3H), 7.53-7.45 (m, 2H), 6.47 (s, 1H), 4.26 (m, 4H), 2.05 (s, 3H), 1.88 (s, 6H), 1.30 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 167.9, 160.2, 150.7, 143.4, 132.9, 127.9, 126.3, 110.8, 108.4, 79.0, 68.1, 62.0, 55.5, 26.6, 21.9, 14.0; HRMS (ESI): calc. for $C_{24}H_{26}O_6$ $[M+Na]^+$: 433.1622; found: 433.1634.

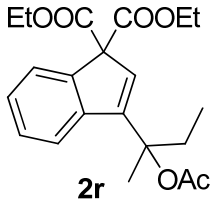
*2-(1,1-bis((benzyloxy)methyl)-1H-inden-3-yl)propan-2-yl acetate (**2q**)*



2q

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, 1H, *J* = 7.6 Hz), 7.51 (d, 1H, *J* = 7.6 Hz), 7.38-7.26 (m, 11H), 7.17 (t, 1H, *J* = 7.6 Hz), 6.35 (s, 1H), 4.56 (m, 4H), 3.69 (d, 1H, *J* = 8.7 Hz), 3.64 (d, 1H, *J* = 8.7 Hz), 2.02 (s, 3H), 1.78 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 148.1, 142.0, 138.8, 132.6, 128.3, 127.4, 127.3, 127.2, 125.0, 124.6, 121.3, 79.6, 73.4, 71.1, 57.1, 26.9, 22.0; HRMS (ESI): calc. for $C_{30}H_{32}O_4$ $[M+Na]^+$: 479.2193; found: 479.2221.

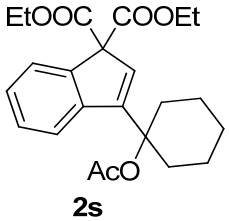
*Diethyl 3-(2-acetoxybutan-2-yl)-1H-indene-1,1-dicarboxylate (**2r**)*



2r

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, 1H, *J* = 7.4 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), 7.37-7.25 (m, 2H), 6.37 (s, 1H), 4.22 (m, 4H), 2.25-2.07 (m, 2H), 2.05 (s, 3H), 1.83 (s, 3H), 1.31-1.14 (m, 6H), 0.87 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 168.0, 167.6, 149.7, 142.0, 140.8, 128.4, 128.0, 126.2, 125.8, 121.5, 82.4, 68.8, 62.1, 31.4, 22.7, 21.9, 14.0, 8.0; HRMS (ESI): calc. for $C_{21}H_{26}O_6$ $[M+Na]^+$: 397.1622; found: 397.1611.

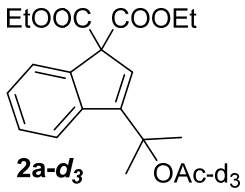
*Diethyl 3-(1-acetoxycyclohexyl)-1H-indene-1,1-dicarboxylate (**2s**)*



2s

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, 1H, *J* = 7.4 Hz), 7.52 (d, 1H, *J* = 7.9 Hz), 7.36-7.23 (m, 2H), 6.38 (s, 1H), 4.22 (m, 4H), 2.70-2.55 (m, 2H), 2.04 (s, 3H), 1.81-1.64 (m, 8H), 1.28 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 167.8, 150.7, 142.2, 140.7, 128.3, 127.0, 126.1, 125.9, 121.4, 80.1, 69.0, 62.1, 34.5, 25.5, 21.6, 14.0; HRMS (ESI): calc. for $C_{23}H_{28}O_6$ $[M+Na]^+$: 423.1756; found: 423.1778.

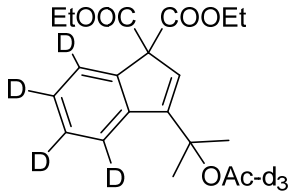
*Diethyl 3-(2-acetoxypropan-2-yl)-1H-indene-1,1-dicarboxylate-d_3 (**2a-d_3**)*



2a-*d_3*

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 1H, *J* = 7.4 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), 7.39-7.26 (m, 2H), 6.38 (s, 1H), 4.23 (m, 4H), 1.82 (s, 6H), 1.29 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 167.7, 151.0, 142.0, 140.8, 128.5, 126.7, 126.2, 125.9, 121.5, 79.1, 68.8, 62.1, 26.6, 21.6, 14.0; HRMS (ESI): calc. for $C_{20}H_{21}D_3O_6$ $[M+Na]^+$: 386.1653; found: 386.1637.

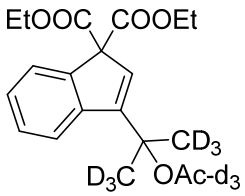
*Diethyl 3-(2-acetoxypropan-2-yl)-1H-indene-1,1-dicarboxylate-d_7 (**2a-d_7**)*



2a-*d_7*

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.38 (s, 1H), 4.23 (m, 4H), 1.82 (s, 6H), 1.29 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9, 151.0, 162.7, 79.1, 68.8, 62.1, 26.6, 14.0; HRMS (ESI): calc. for $C_{20}H_{17}D_7O_6$ $[M+Na]^+$: 390.1904; found: 390.1888.

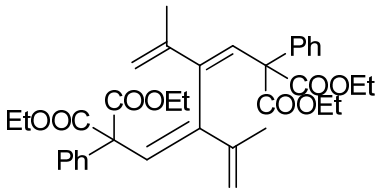
*Diethyl 3-(2-acetoxypropan-2-yl)-1H-indene-1,1-dicarboxylate-d_9 (**2a-d_9**)*



2a-*d_9*

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 1H, *J* = 7.4 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), 7.39-7.26 (m, 2H), 6.38 (s, 1H), 4.23 (m, 4H), 1.29 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 167.7, 150.9, 142.0, 140.8, 128.5, 126.7, 126.2, 125.9, 121.5, 78.8, 68.8, 62.1, 29.7, 14.0; HRMS (ESI): calc. for $C_{20}H_{15}D_9O_6$ $[M+Na]^+$: 392.2030; found: 392.2050.

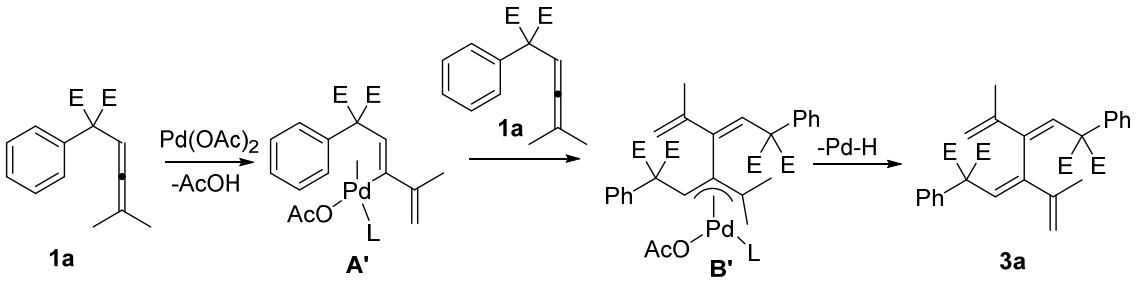
Characterization of side product



3a

Dimer **3a** was formed during the reaction and was isolated and fully characterized by ^{1}H and ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (m, 4H), 7.39-7.26 (m, 6H), 6.52 (s, 2H), 4.93 (s, 2H), 4.67 (s, 2H), 4.20 (m, 8H), 2.70 (s, 6H), 1.26 (t, 12H, J = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 145.8, 140.4, 137.9, 128.0, 127.7, 126.6, 118.1, 63.8, 61.8, 21.6, 13.9; HRMS (ESI): calc. for $C_{36}H_{42}O_8$ $[M+Na]^+$: 625.2772; found: 625.2738.

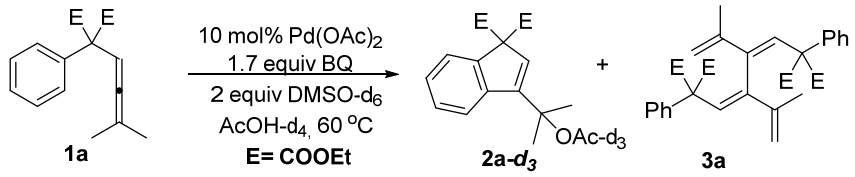
The formation of the dimer could be explained by the following pathway (Scheme S1):

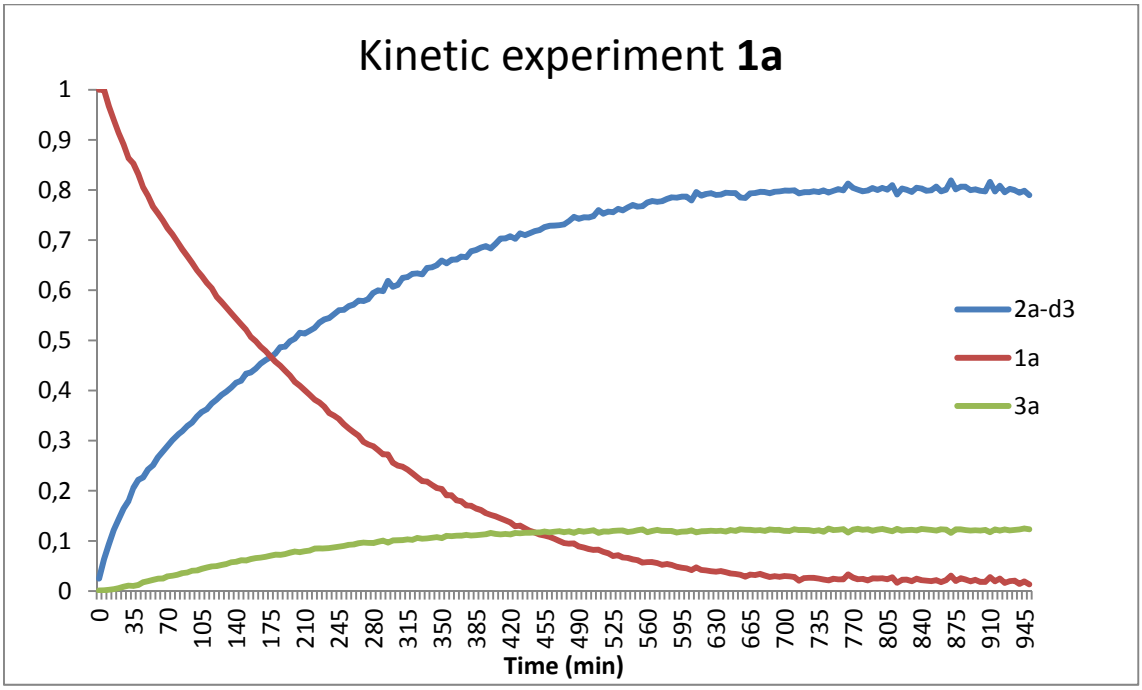


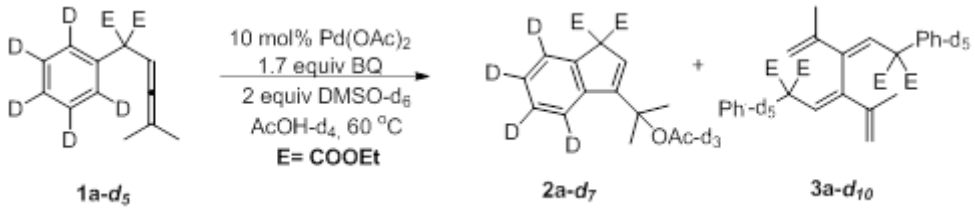
Scheme S1. Mechanism for formation of dimer **3a**.

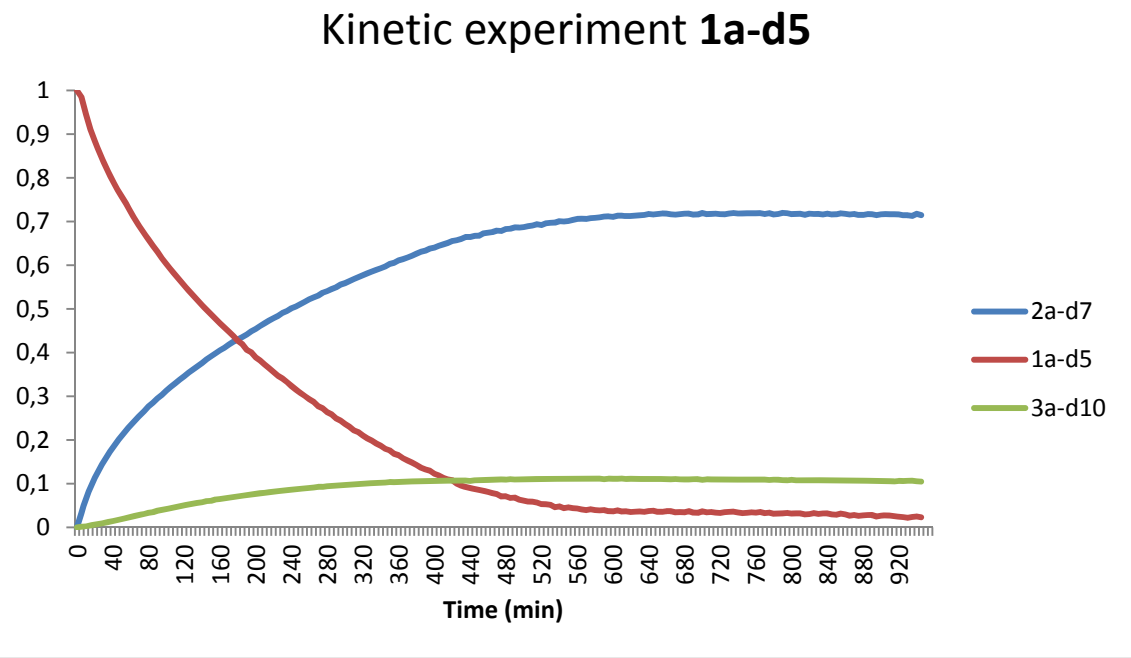
The reaction starts with a C-H activation of the allene moiety to form the Pd-vinyl complex **A'**. Insertion into the allene moiety of a new aryl-allene molecule leads to the formation of the (π-allyl)palladium species **B'**. Final β-hydride elimination releases a Pd-H species (which is reoxidazed by BQ) under the formation of dimer **3a**.

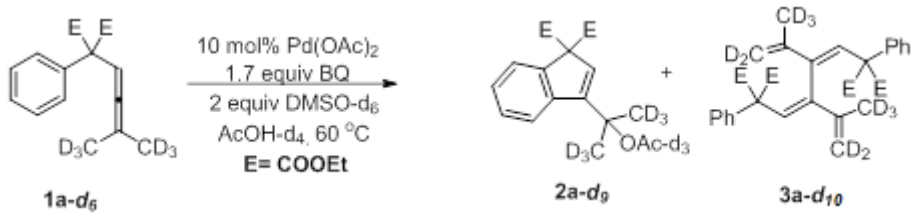
Kinetic Experiments

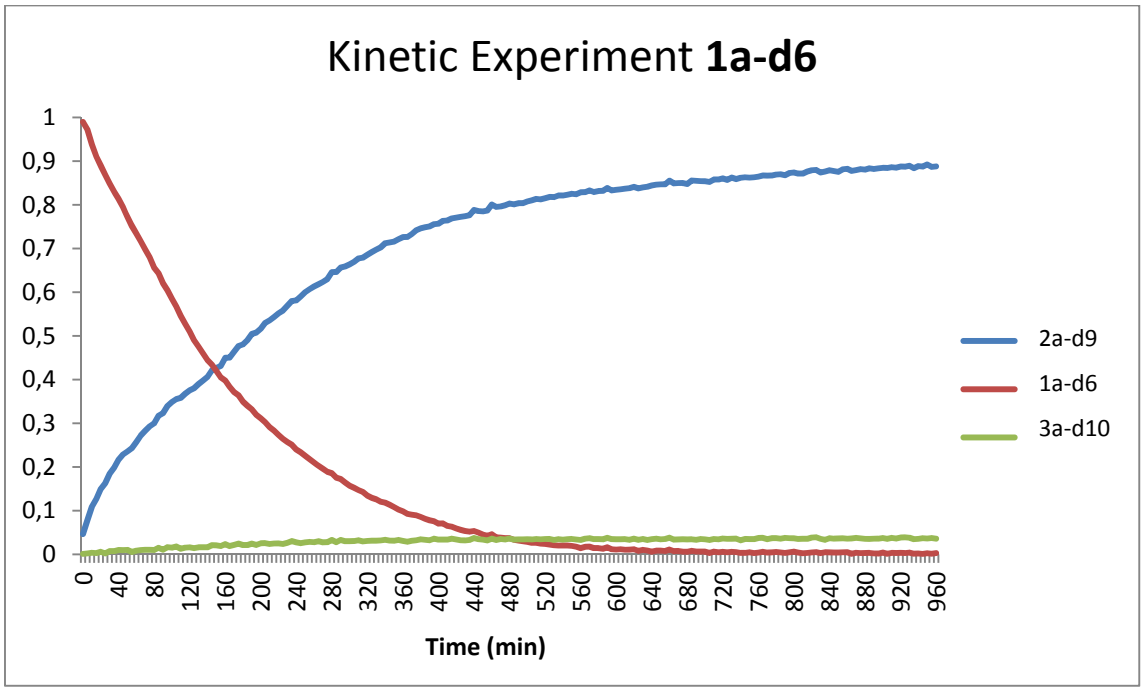




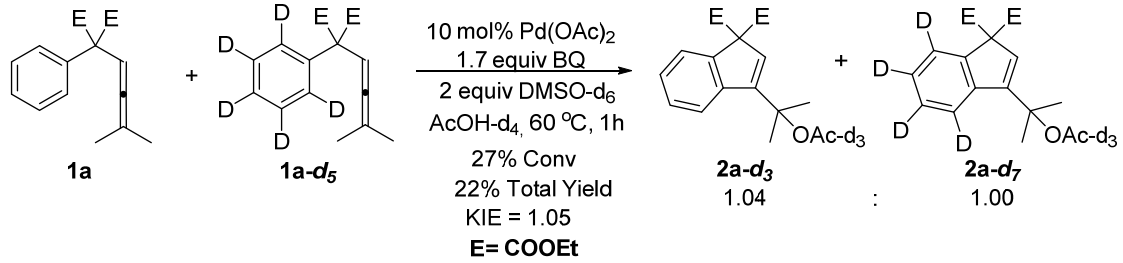

10 mol% Pd(OAc)2
1.7 equiv BQ
2 equiv DMSO-d6
AcOH-d4, 60 °C
E= COOEt
1a-d5
2a-d7
3a-d10


Kinetic experiment 1a-d5
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
40
80
120
160
200
240
280
320
360
400
440
480
520
560
600
640
680
720
760
800
840
880
920
Time (min)
2a-d7
1a-d5
3a-d10

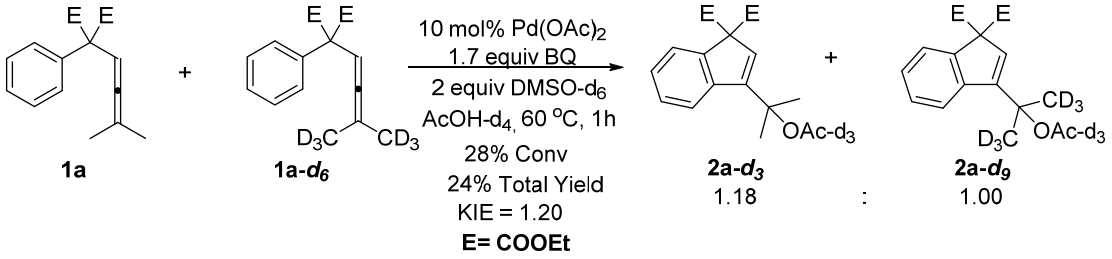

E E
D3C CD3
10 mol% Pd(OAc)2
1.7 equiv BQ
2 equiv DMSO-d6
AcOH-d4, 60 °C
E= COOEt
1a-d6
E E
CD3
D3C OAc-d3
2a-d9
CD3
D2C
Ph
E E
Ph
E E
CD3
CD2
3a-d10


Kinetic Experiment 1a-d6
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
40
80
120
160
200
240
280
320
360
400
440
480
520
560
600
640
680
720
760
800
840
880
920
960
Time (min)
2a-d9
1a-d6
3a-d10

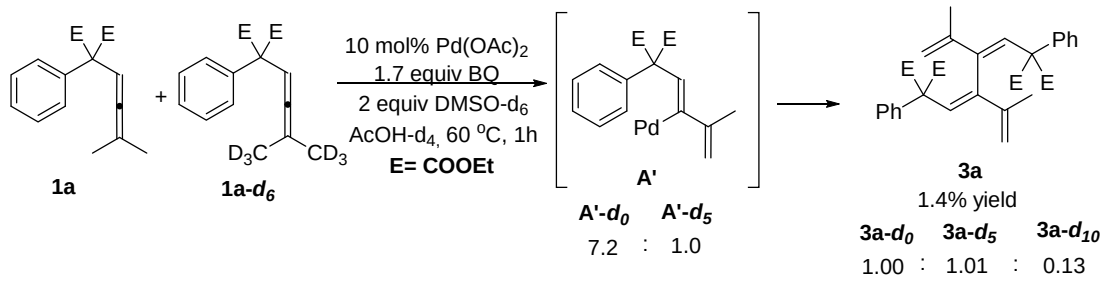
Calculations Kinetic Isotopic Effect (KIE)



The kinetic isotopic effect value was calculated from the conversion (c = 27%) and the excess of **2a-*d*$_3$** (e**2a-*d*$_3$** = ([**2a-*d*$_3$**]-[**2a-*d*$_7$**])/ ([**2a-*d*$_3$**]+[**2a-*d*$_7$**])) using the equation k_H/k_D= ln(1-(c(1+e**2a-*d*$_3$**)))/ ln(1-(c(1-e**2a-*d*$_3$**))), which gave a value of 1.05.

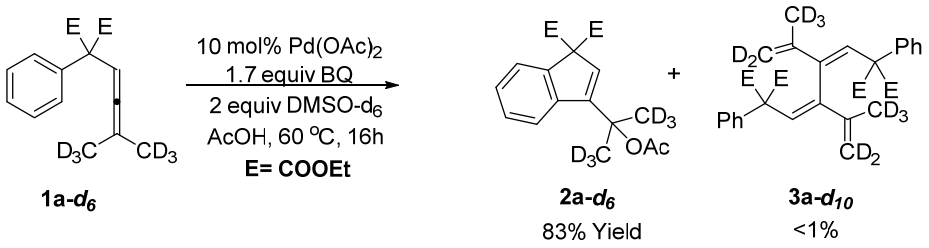


The kinetic isotopic effect value was calculated from the conversion (c = 28%) and the excess of **2a-*d*$_3$** (e**2a-*d*$_3$** = ([**2a-*d*$_3$**]-[**2a-*d*$_9$**])/ ([**2a-*d*$_3$**]+[**2a-*d*$_9$**])) using the equation k_H/k_D= ln(1-(c(1+e**2a-*d*$_3$**)))/ ln(1-(c(1-e**2a-*d*$_3$**))), which gave a value of 1.20.



The ratio of the formation of products **3a-*d*$_0$** vs **3a-*d*$_5$** vs **3a-*d*$_{10}$** was determined by HRMS. It was assumed that formation of **A'** is irreversible and that once the intermediates **A'-*d*$_0$** or **A'-*d*$_5$** were formed, they react with the same rate with either **1a** or **1a-*d*$_6$** (see mechanism in Scheme S1 on p. S24). According to this assumption the KIE was calculated to k_H/k_D = 7.2 (k_H/k_D = ([**3a-*d*$_0$**]+[**3a-*d*$_5$**]-[**3a-*d*$_{10}$**])/2[**3a-*d*$_{10}$**]).

Carbocyclization using *[D_6]-Diethyl 2-(3-methylbuta-1,2-dien-1-yl)-2-phenyl-malonate (1a-d_6)*



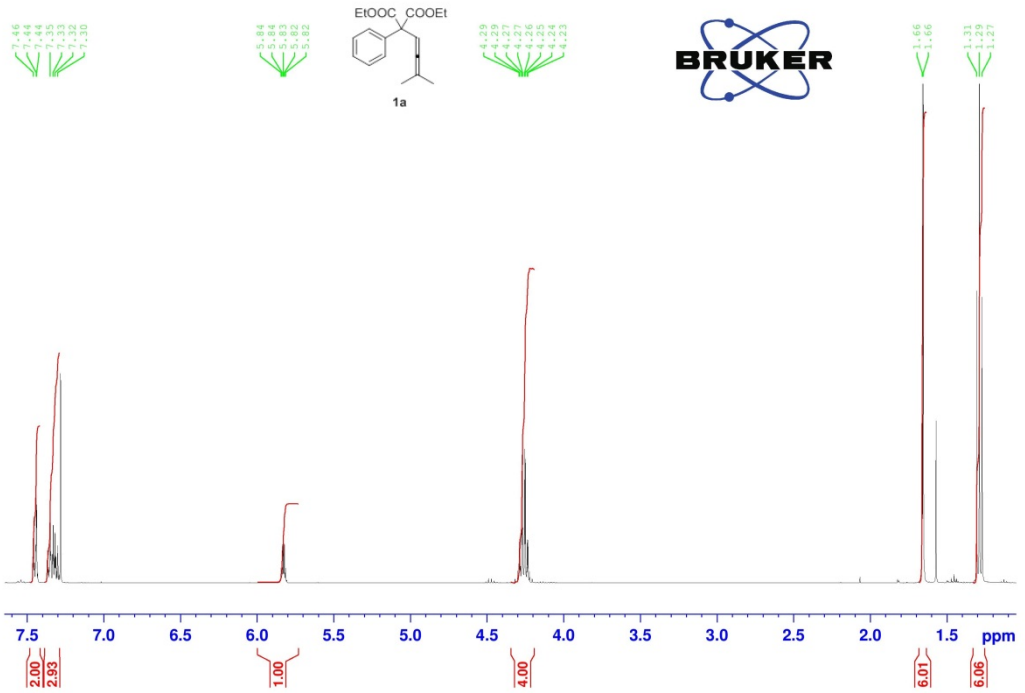
1a-*d*$_6$ **2a-*d*$_6$** 83% Yield **3a-*d*$_{10}$** <1%

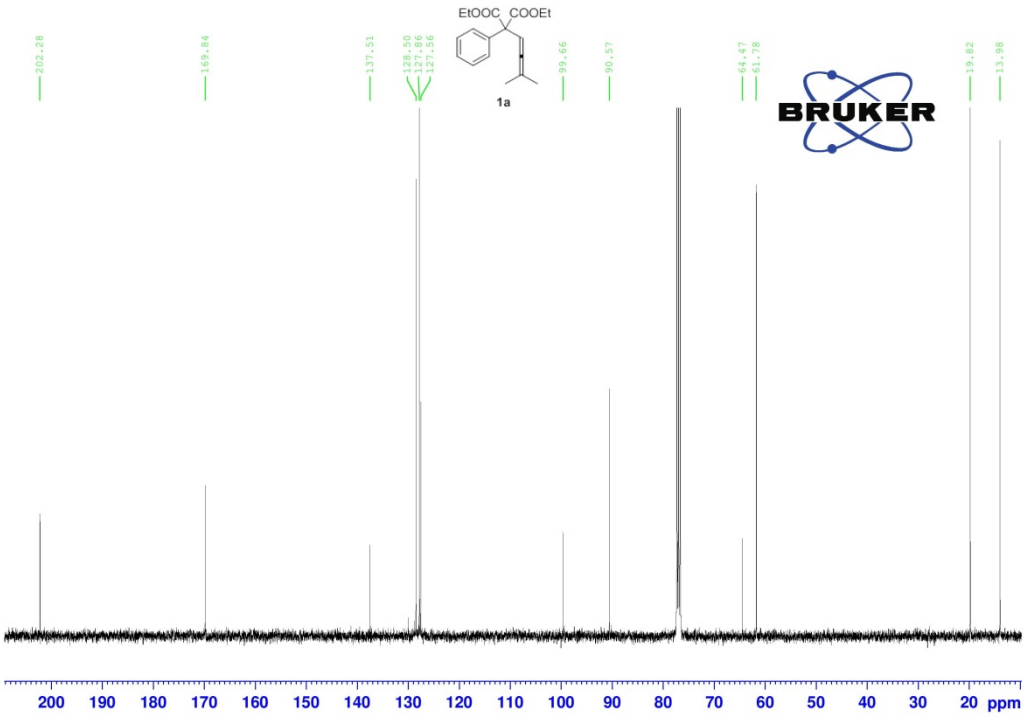
References

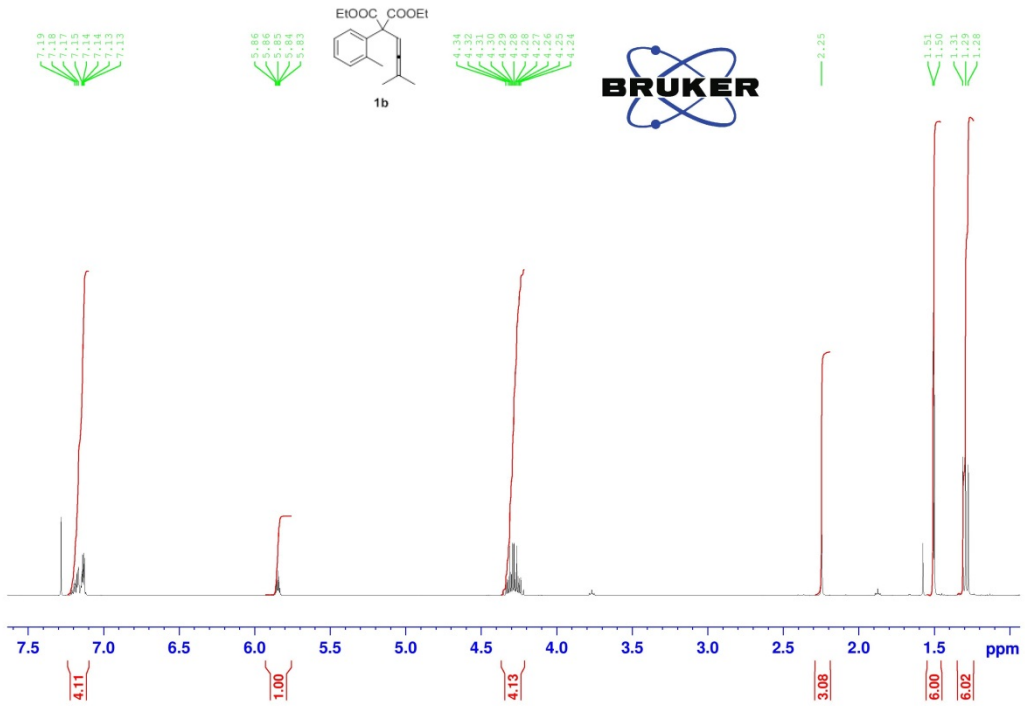
[1]Landor, S. R.; Patel, A. N.; Whiter, P. F.; Greaves, P. M. *J. Chem. Soc*. (C) **1966**, 1223.

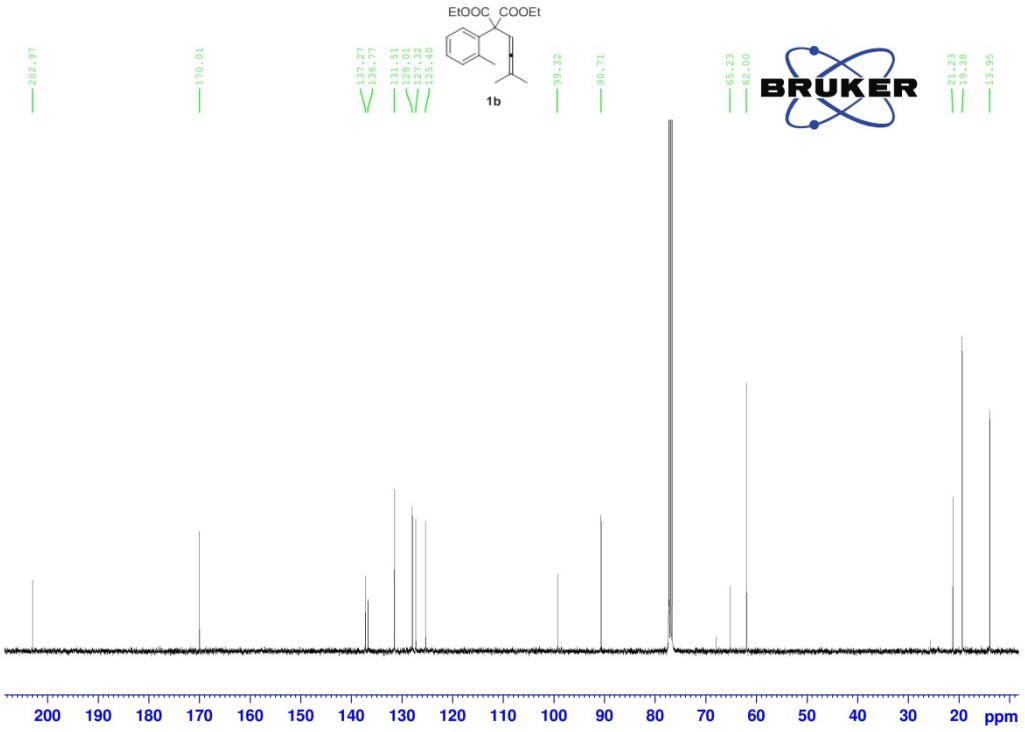
[2]Yip, S.F.; Cheung, H.Y.; Zhou, Z.; Kwong, F. Y. *Org. Lett.* **2007**, *17*, 3469.

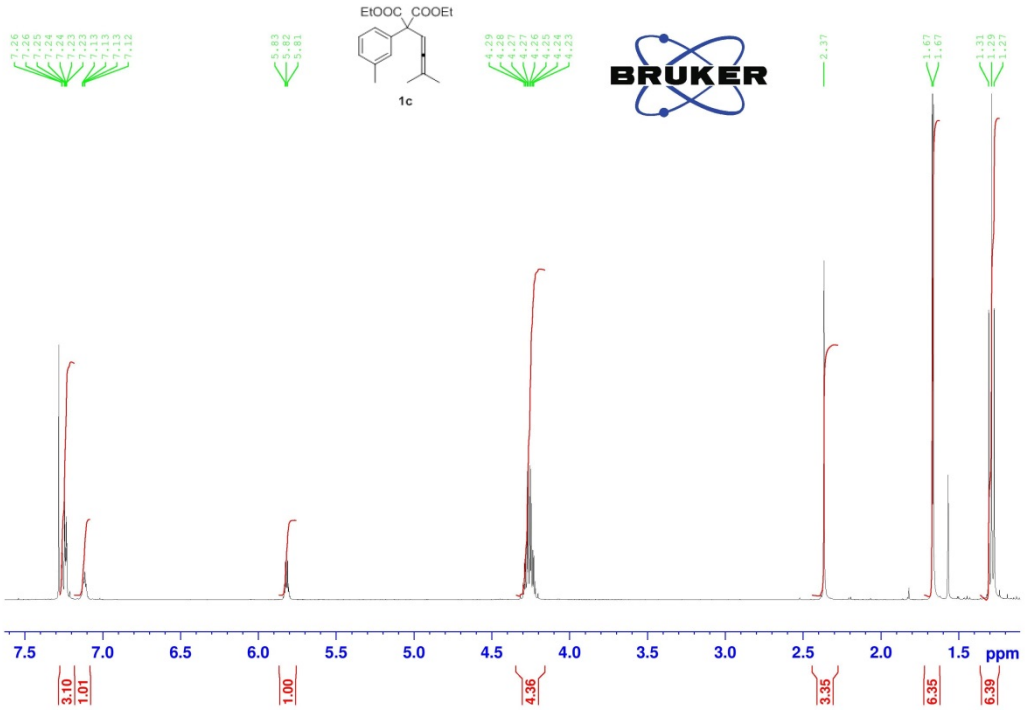
NMR Spectra

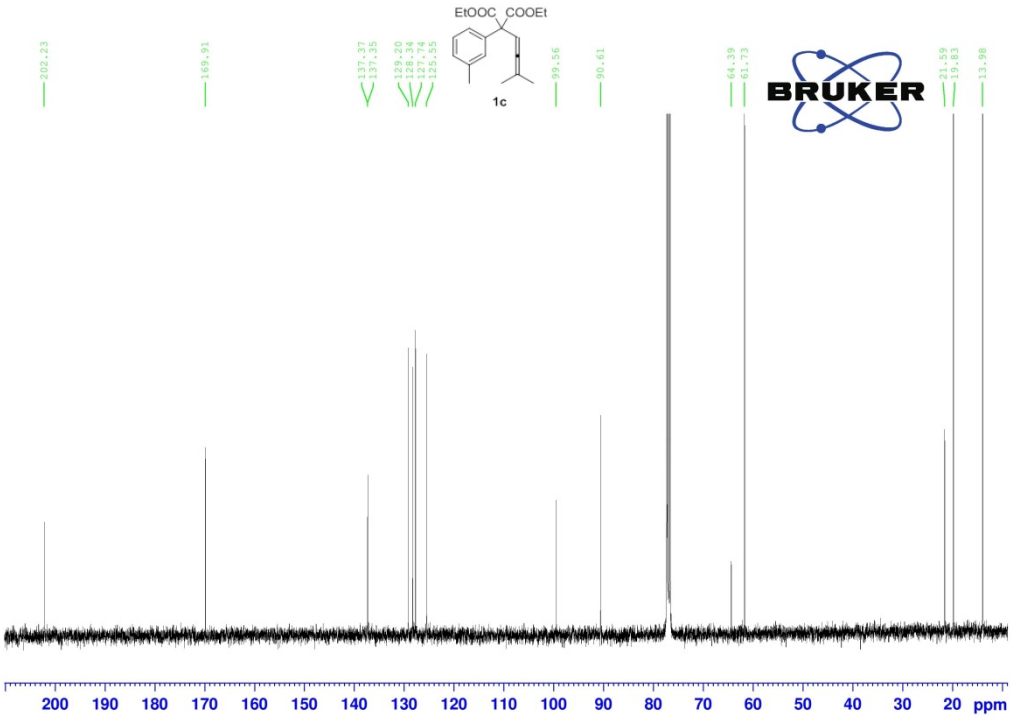

EtOOC COOEt
1a
BRUKER
7.46
7.44
7.35
7.33
7.32
7.30
5.84
5.84
5.83
5.82
5.82
4.29
4.29
4.27
4.27
4.26
4.25
4.24
4.23
1.66
1.66
1.31
1.29
1.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.00
2.93
1.00
4.00
6.01
6.06

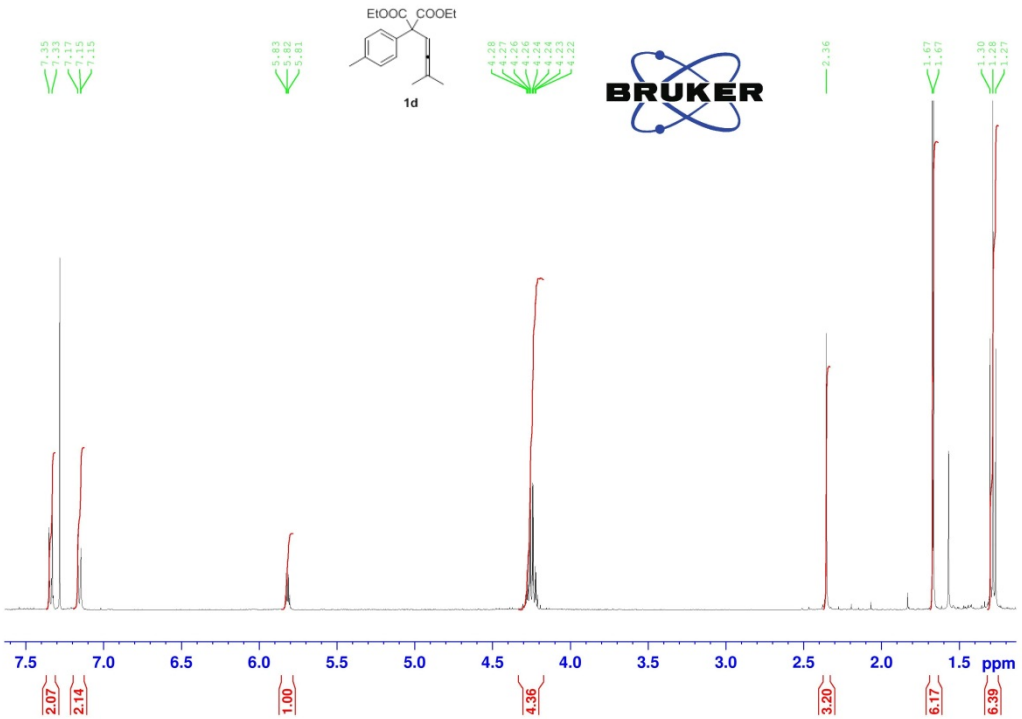

EtOOC COOEt
1a
BRUKER
202.28
169.84
137.51
128.50
127.86
127.56
99.66
90.57
64.47
61.78
19.82
13.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
1b
BRUKER
7.19
7.18
7.17
7.15
7.14
7.14
7.13
7.13
5.86
5.86
5.85
5.84
5.83
4.34
4.32
4.31
4.30
4.29
4.28
4.28
4.27
4.26
4.25
4.24
2.25
1.51
1.50
1.31
1.29
1.28
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
ppm
4.11
1.00
4.13
3.08
6.00
6.02


EtOOC COOEt
1b
BRUKER
202.97
170.01
137.27
136.77
131.51
128.01
127.32
125.40
99.32
90.71
65.23
62.00
21.23
19.38
13.95
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
1c
BRUKER
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.13
7.13
7.12
5.83
5.82
5.81
4.29
4.28
4.27
4.27
4.26
4.25
4.24
4.23
2.37
1.67
1.67
1.31
1.29
1.27
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
ppm
3.10
1.01
1.00
4.36
3.35
6.35
6.39


EtOOC COOEt
1c
BRUKER
202.23
169.91
137.37
137.35
129.20
128.34
127.74
125.55
99.56
90.61
64.39
61.73
21.59
19.83
13.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
1d
BRUKER
7.35
7.33
7.17
7.15
7.15
5.83
5.82
5.81
4.28
4.27
4.26
4.26
4.24
4.24
4.23
4.22
2.36
1.67
1.67
1.30
1.28
1.27
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
ppm
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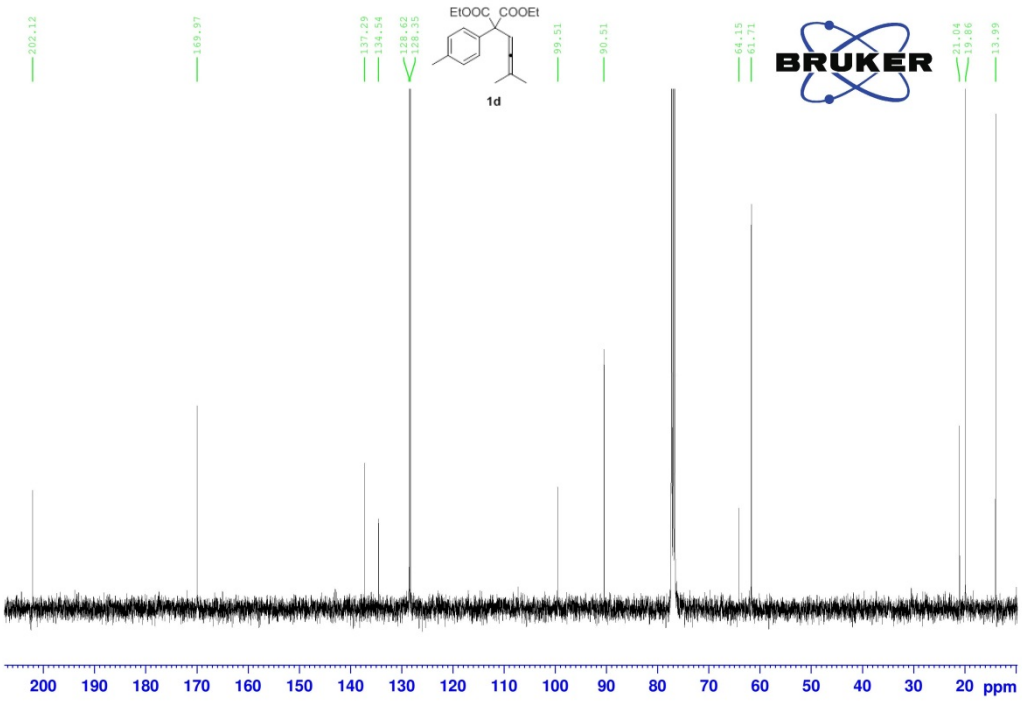
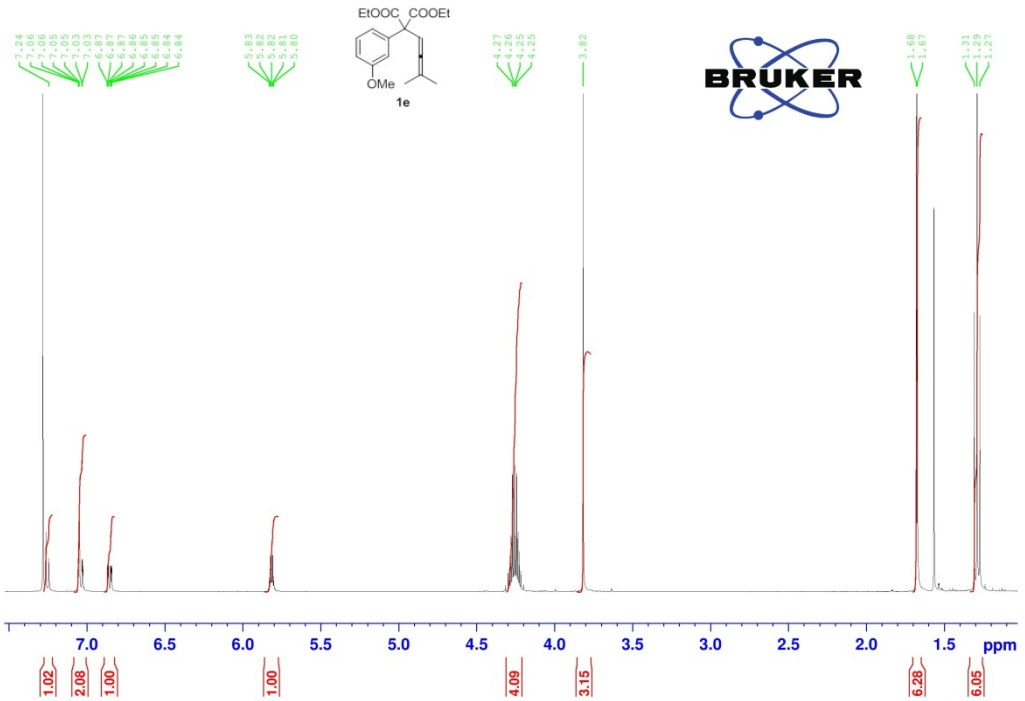
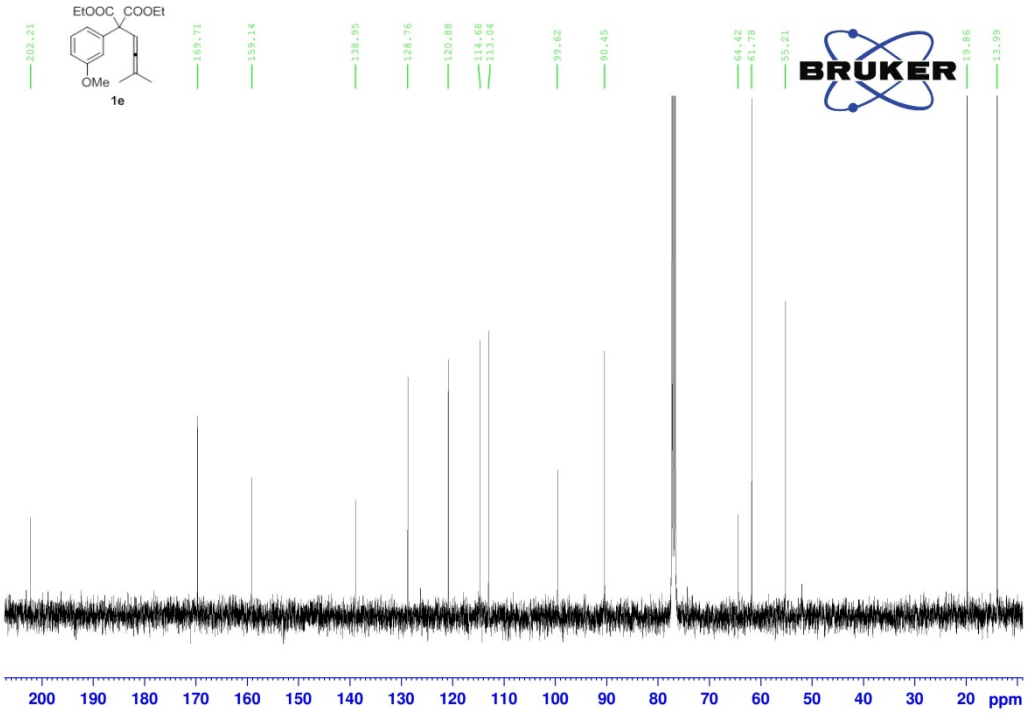
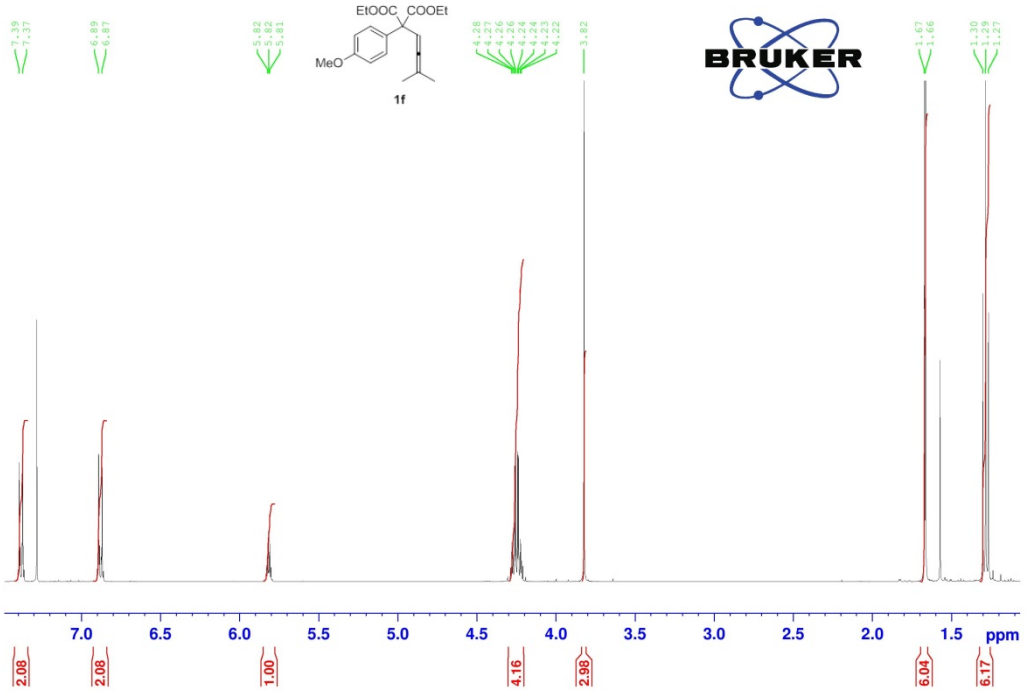
2.14
1.00
4.36
3.20
6.17
6.39


EtOOC COOEt
1d
BRUKER
202.12
169.97
137.29
134.54
128.62
128.35
99.51
90.51
64.15
61.71
21.04
19.86
13.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
OMe
1e
BRUKER
7.24
7.06
7.05
7.03
6.87
6.86
6.85
6.84
5.83
5.82
5.81
5.80
4.27
4.26
4.25
4.25
3.82
1.68
1.67
1.31
1.29
1.27
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.02
2.08
1.00
1.00
4.09
3.15
6.28
6.05


EtOOC COOEt
OMe
1e
BRUKER
202.21
169.71
159.14
138.95
128.76
120.88
114.68
113.04
99.62
90.45
64.42
61.78
55.21
19.86
13.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
MeO
1f
BRUKER
7.39
7.37
6.89
6.87
5.82
5.82
5.81
4.28
4.27
4.26
4.26
4.24
4.24
4.23
4.22
3.82
1.67
1.66
1.30
1.29
1.27
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
ppm
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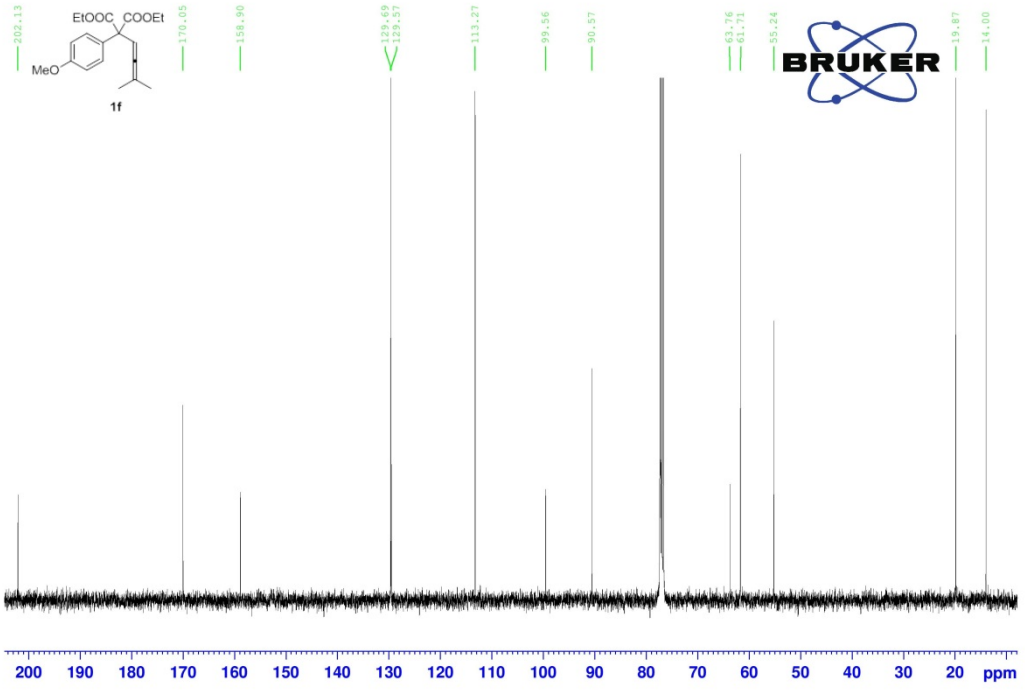
2.08
1.00
4.16
2.98
6.04
6.17


EtOOC COOEt
MeO
1f
BRUKER
202.13
170.05
158.90
129.69
129.57
113.27
99.56
90.57
63.76
61.71
55.24
19.87
14.00
200
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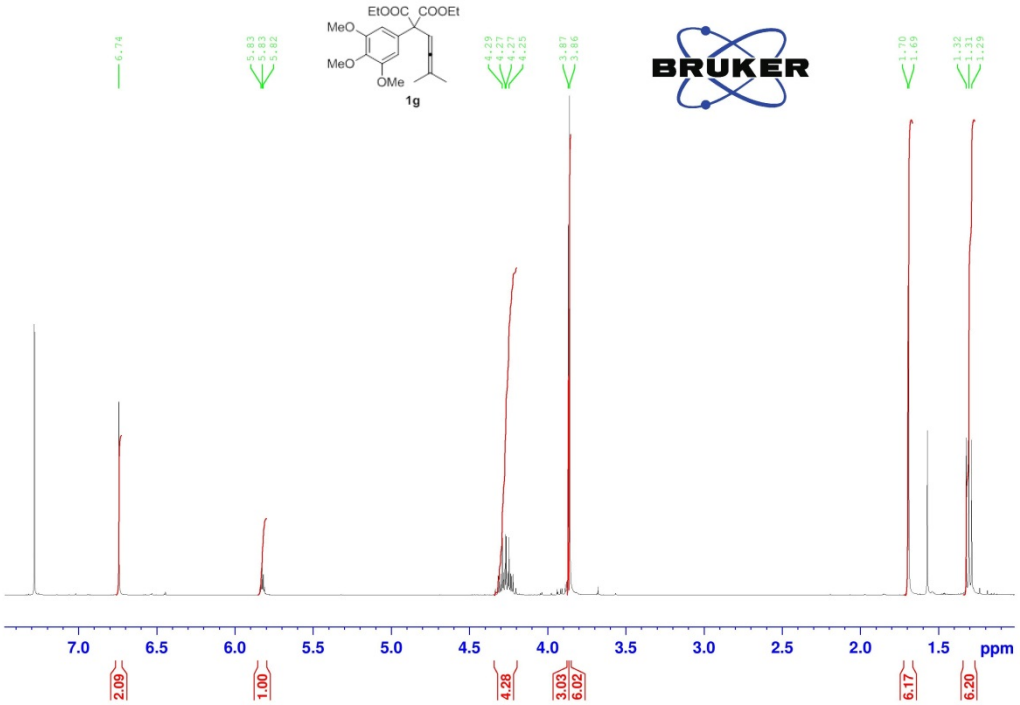
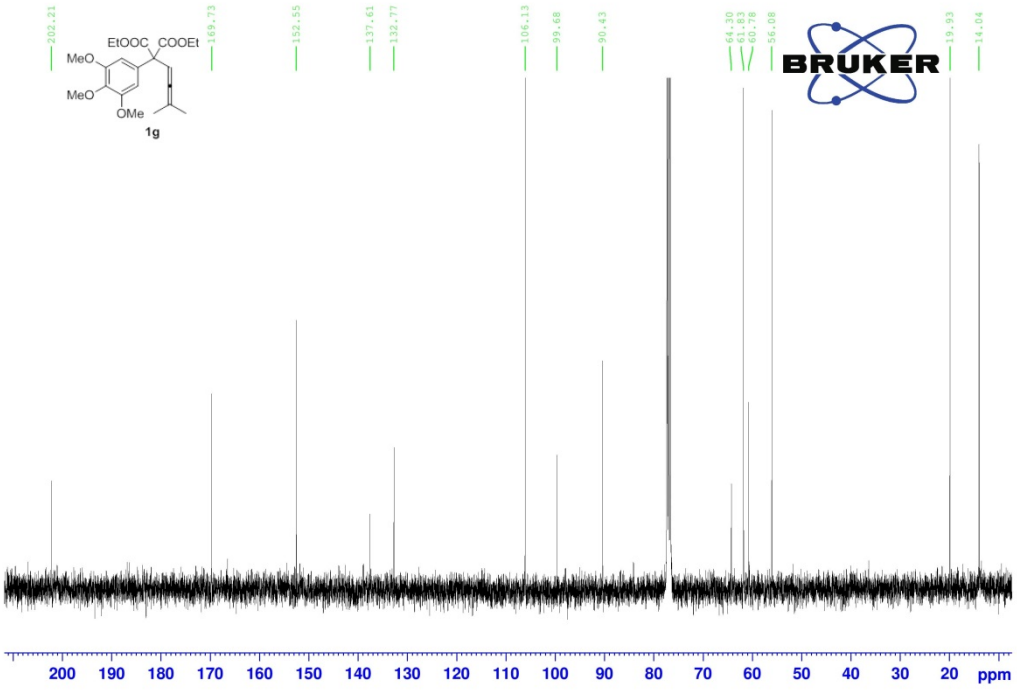
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
MeO
MeO
OMe
1g
6.74
5.83
5.83
5.82
4.29
4.27
4.27
4.25
3.87
3.86
1.70
1.69
1.32
1.31
1.29
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.09
1.00
4.28
3.03
6.02
6.17
6.20


EtOOC COOEt
MeO
MeO
OMe
1g
202.21
169.73
152.55
137.61
132.77
106.13
99.68
90.43
64.30
61.83
60.78
56.08
19.93
14.04
200
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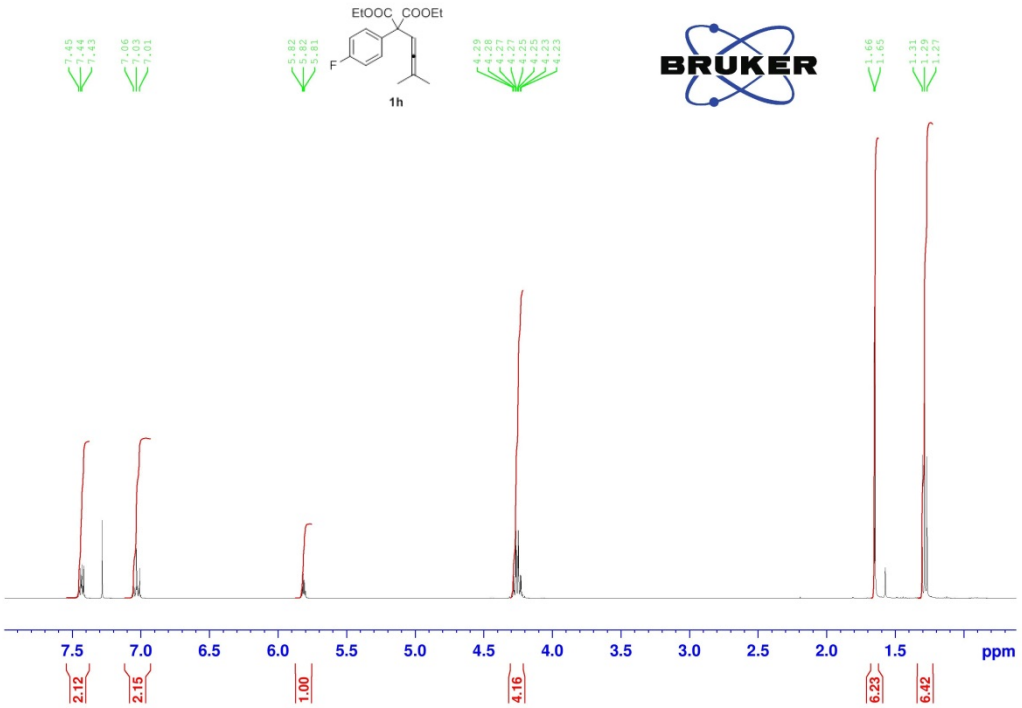
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
F
1h
BRUKER
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
ppm
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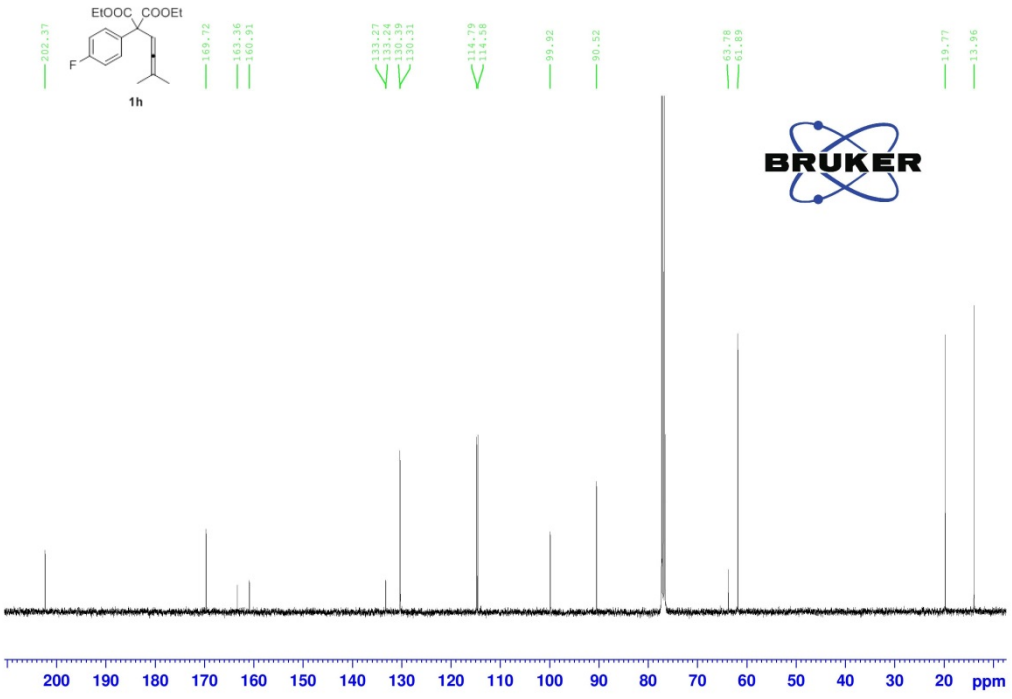
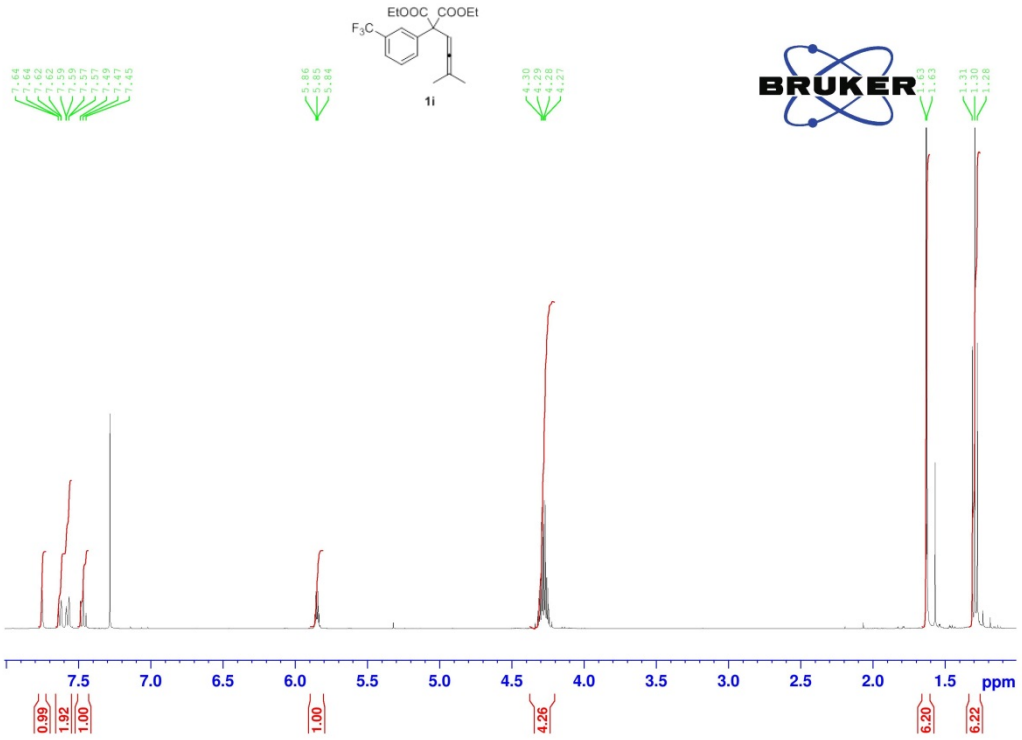
1.00
4.16
6.23
6.42


EtOOC COOEt
F
1h
BRUKER
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
F3C
1i
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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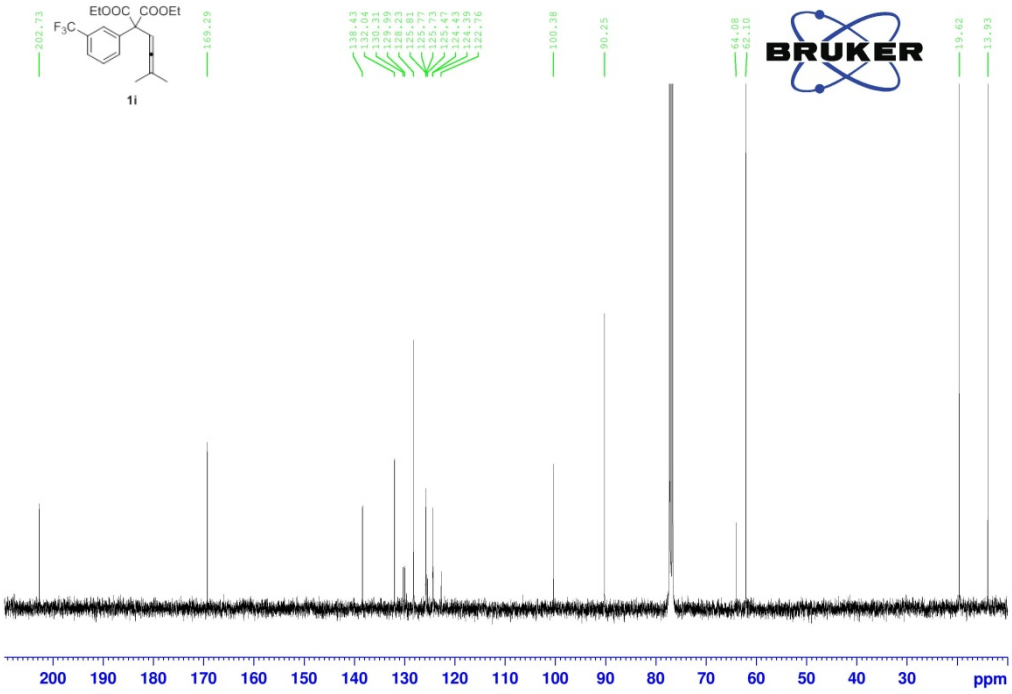
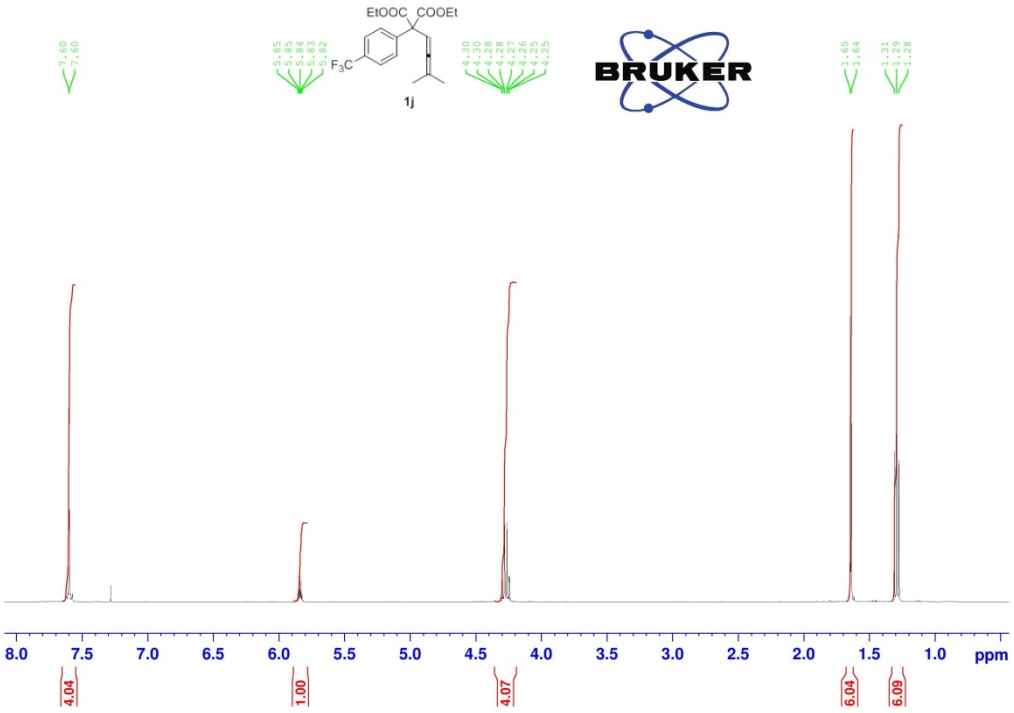
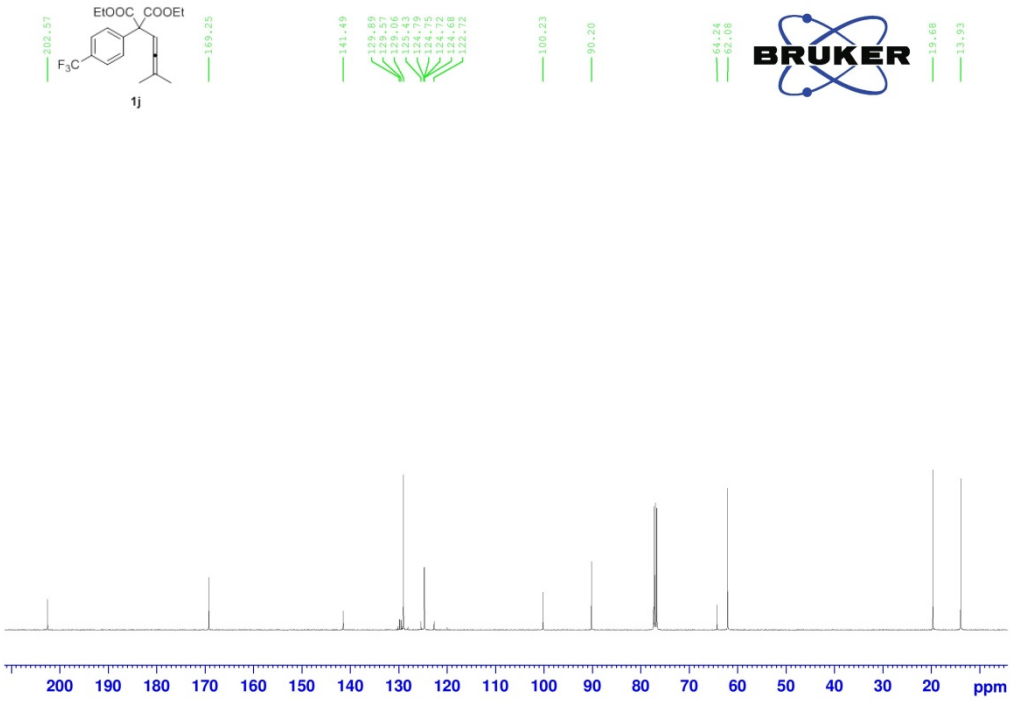
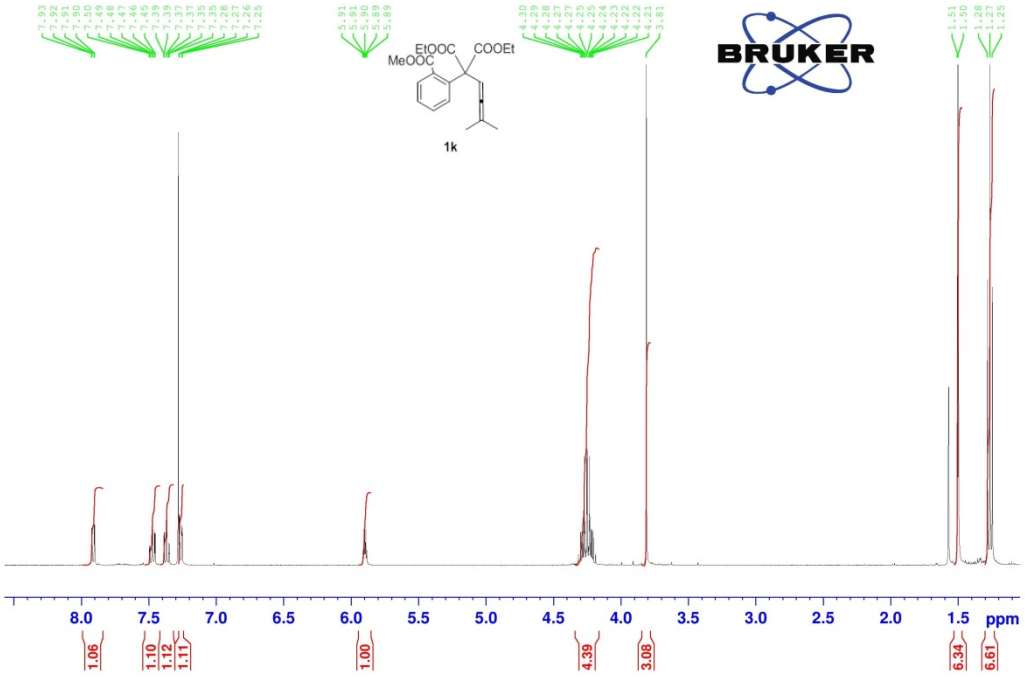
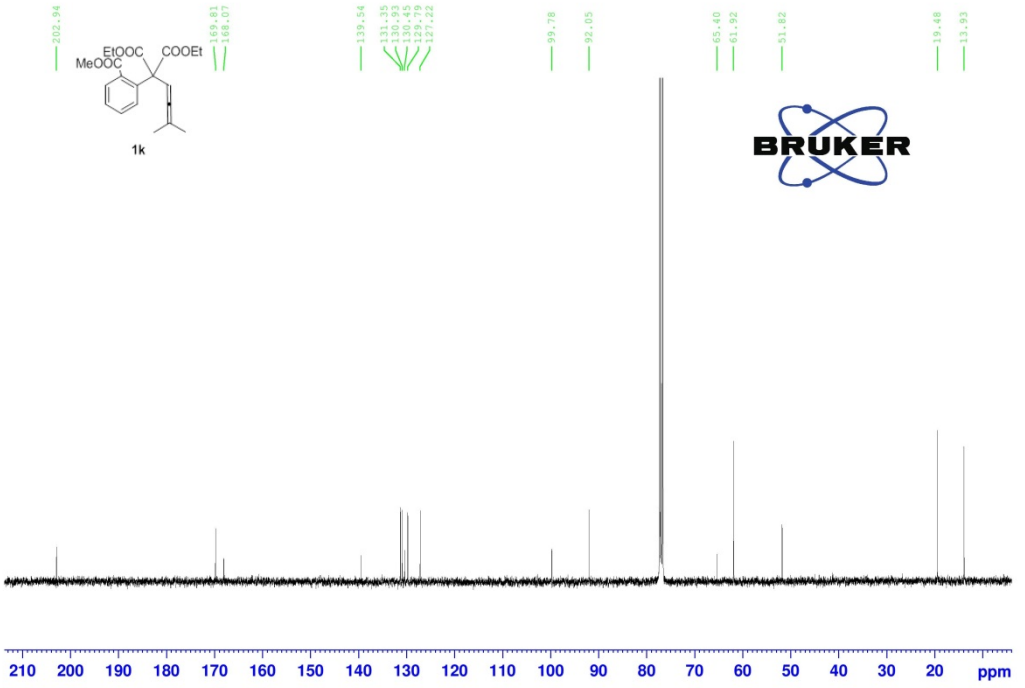
3.5
3.0
2.5
2.0
1.5
ppm

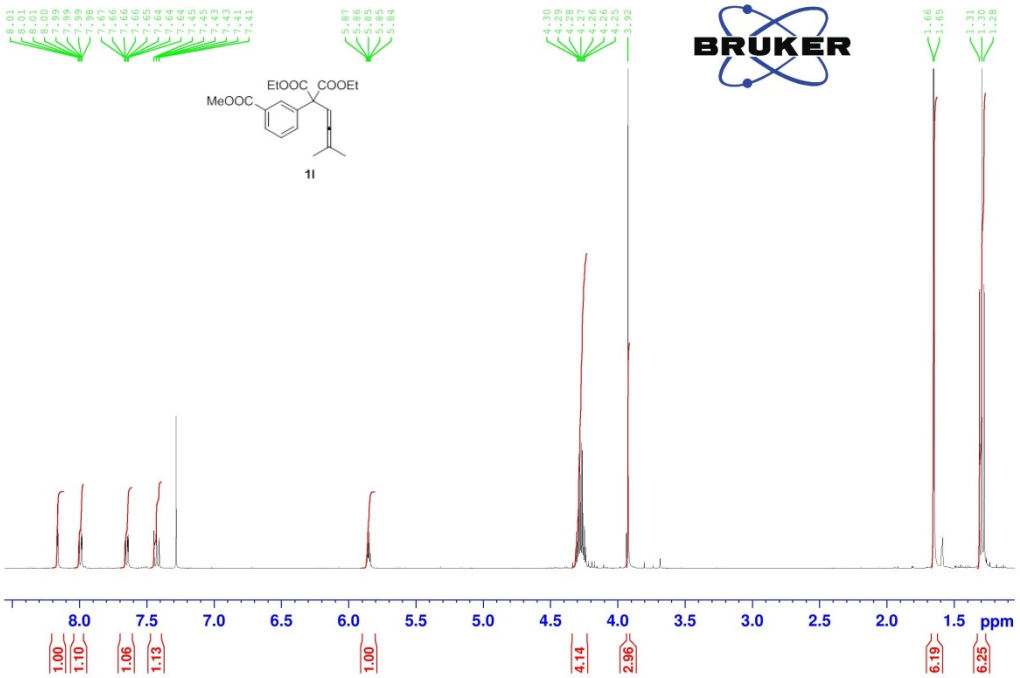

EtOOC COOEt
F3C
1i
BRUKER
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

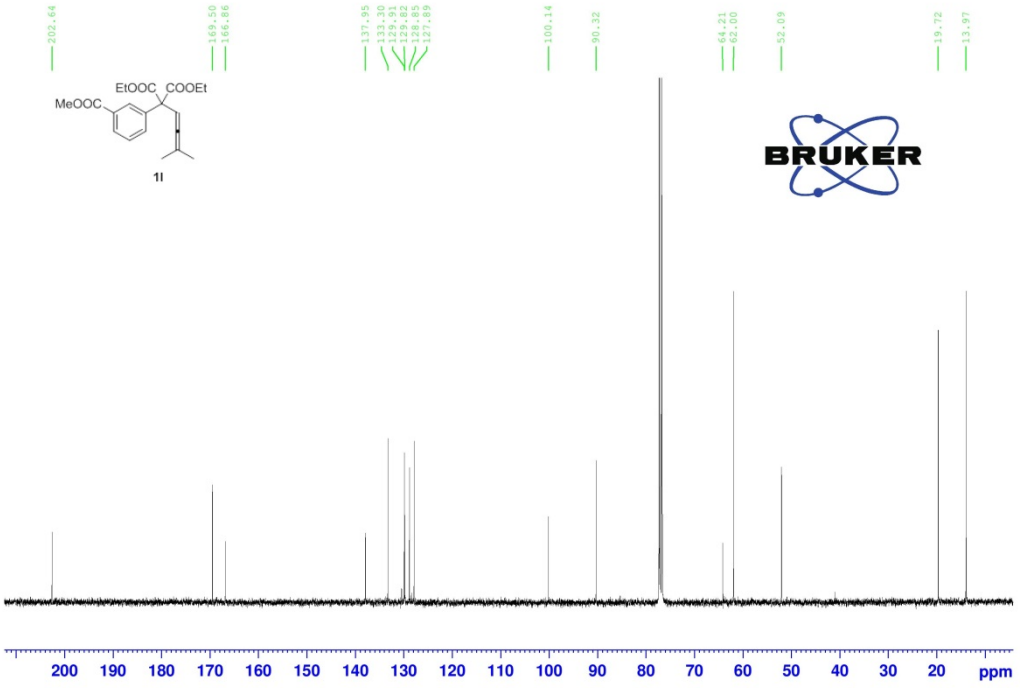

EtOOC COOEt
F3C
1j
BRUKER
7.60
7.60
5.85
5.85
5.84
5.83
5.82
4.30
4.28
4.28
4.28
4.27
4.26
4.25
4.25
4.25
1.65
1.64
1.31
1.29
1.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.04
1.00
4.07
6.04
6.09


EtOOC COOEt
F3C
1j
BRUKER
202.57
169.25
141.49
129.89
129.57
129.06
125.43
124.79
124.75
124.72
124.68
122.72
100.23
90.20
64.24
62.08
19.68
13.93
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC
COOEt
MeOOC
1k
BRUKER
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
ppm
1.06
1.10
1.12
1.11
1.00
4.39
3.08
6.34
6.61


EtOOC
COOEt
MeOOC
1k
BRUKER
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
MeOOC
1l
BRUKER
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
ppm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MeOOC
1l
BRUKER
200
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180
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160
150
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120
110
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90
80
70
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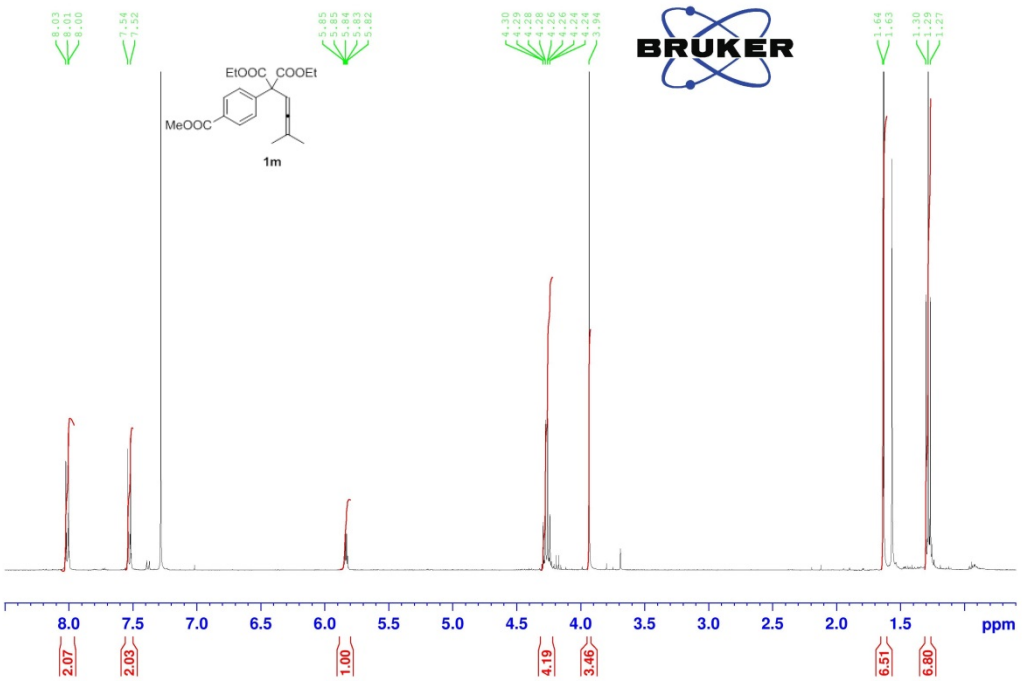
50
40
30
20
ppm


8.03
8.01
8.00
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7.52
5.85
5.85
5.84
5.83
5.82
4.30
4.29
4.28
4.28
4.26
4.26
4.24
4.24
3.94
1.64
1.63
1.30
1.29
1.27
EtOOC COOEt
MeOOC
1m
BRUKER
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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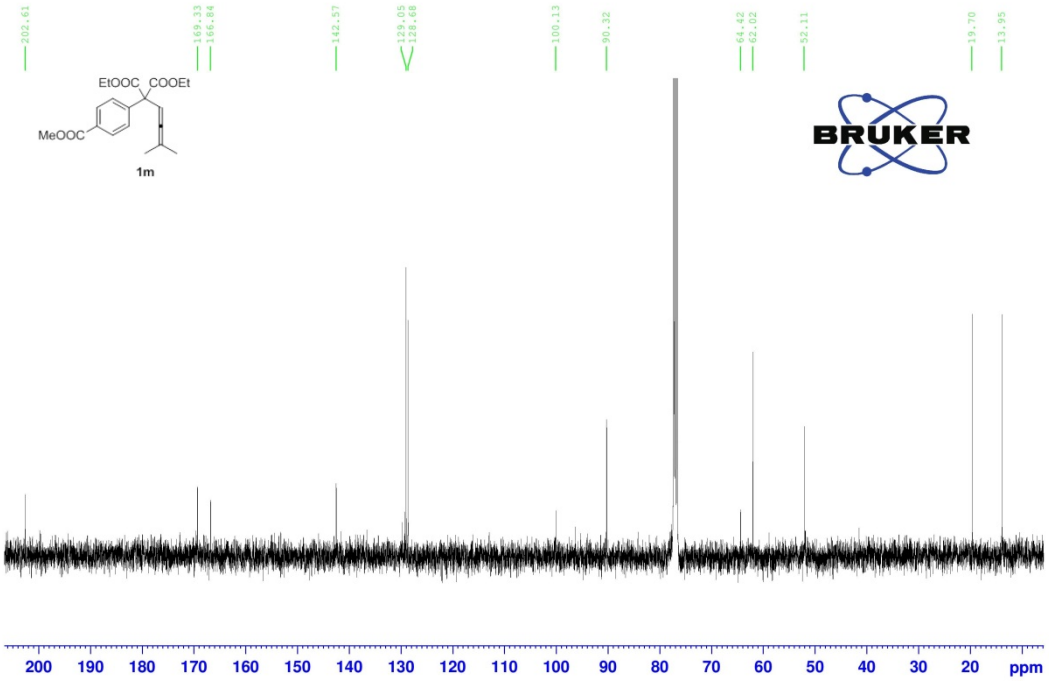
2.0
1.5
ppm
2.07
2.03
1.00
4.19
3.46
6.51
6.80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166.84
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129.05
128.68
100.13
90.32
64.42
62.02
52.11
19.70
13.95
EtOOC COOEt
MeOOC
1m
BRUKER
200
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160
150
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130
120
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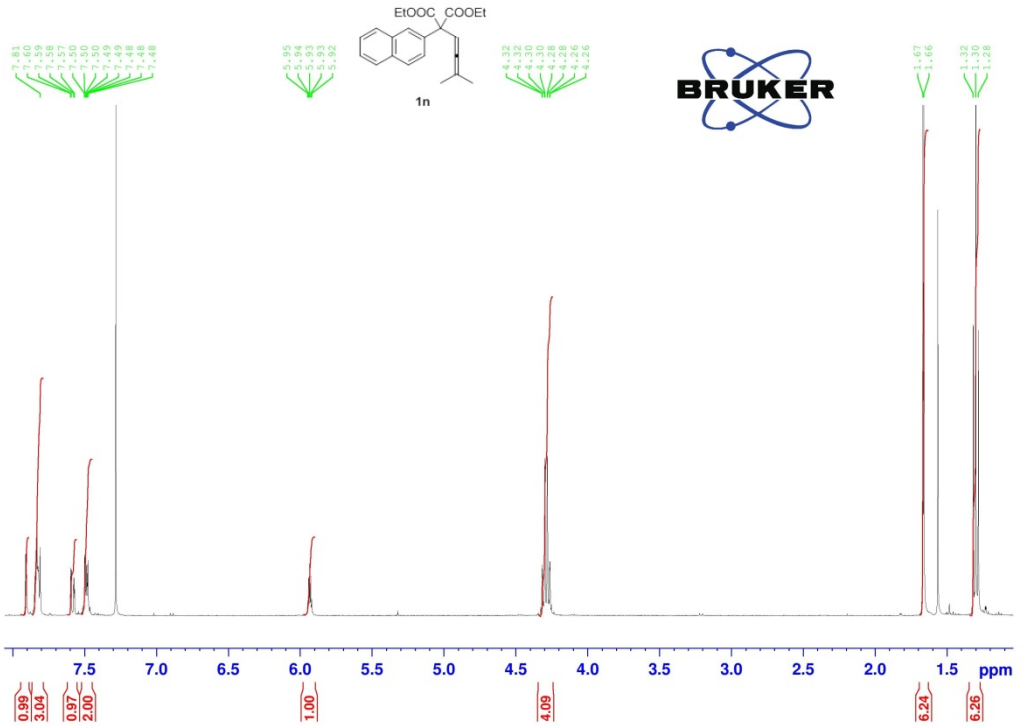
20
ppm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BRUKER
7.5
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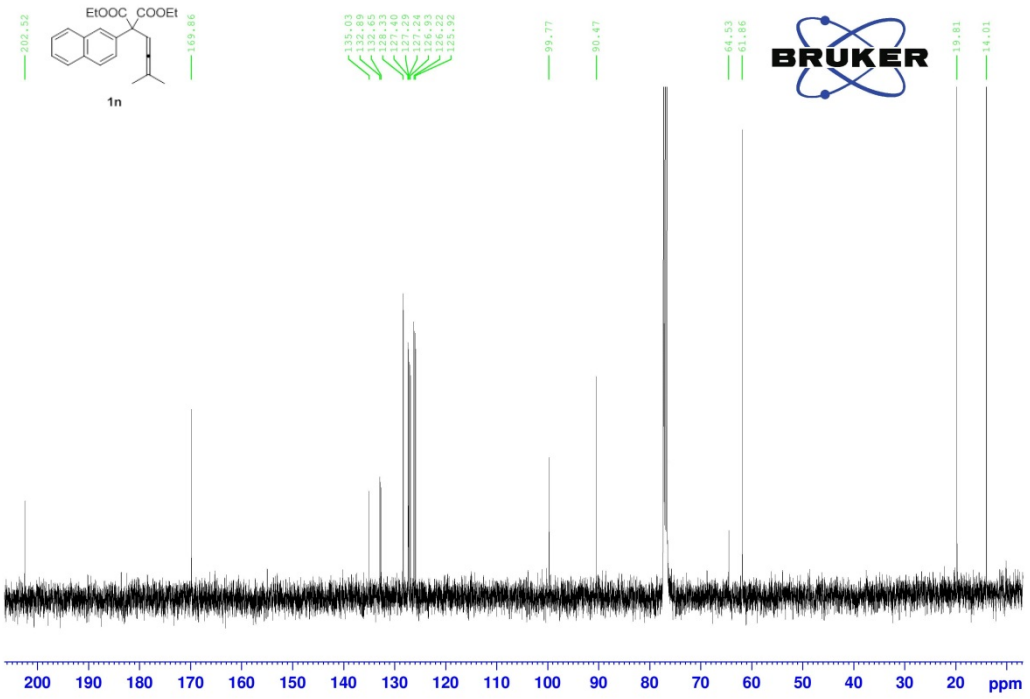
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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1n
BRUKER
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190
180
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160
150
140
130
120
110
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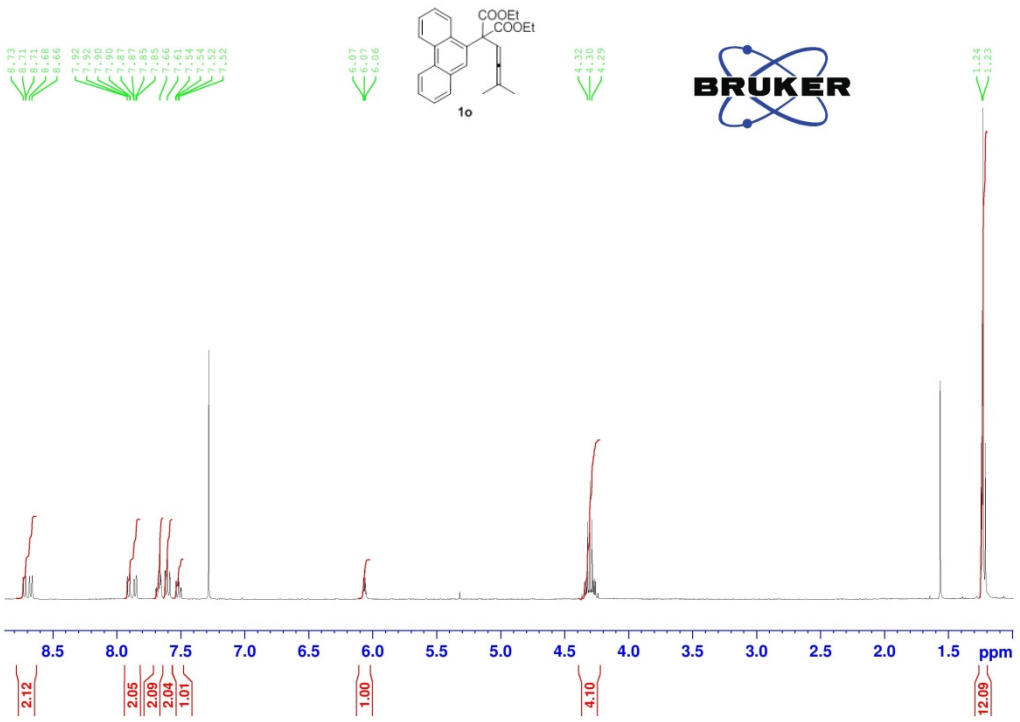
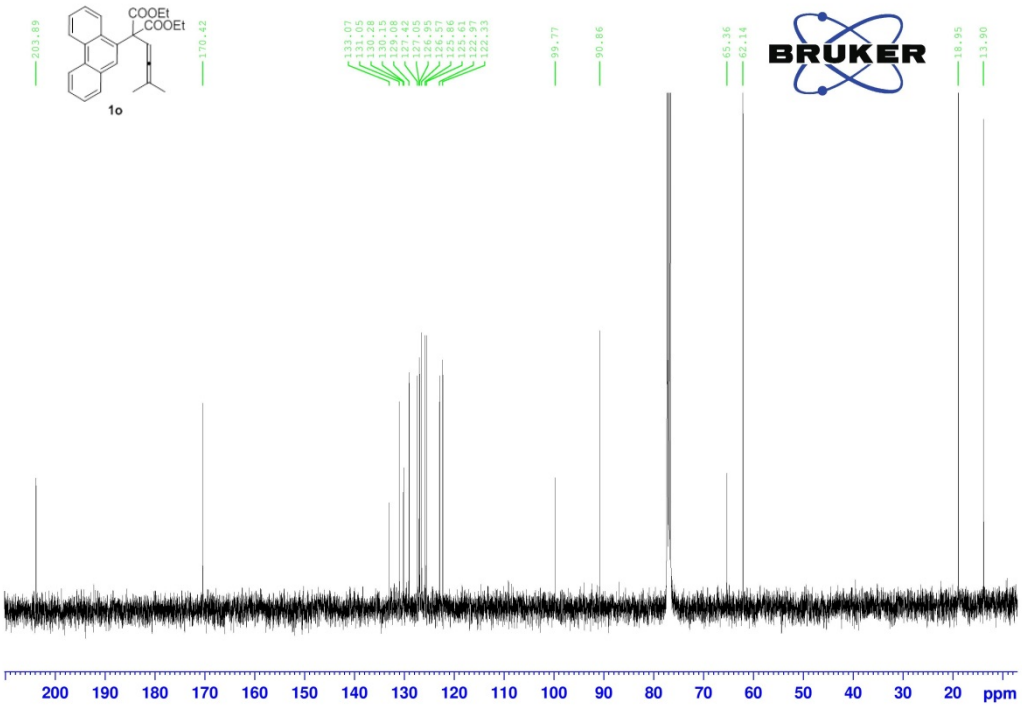
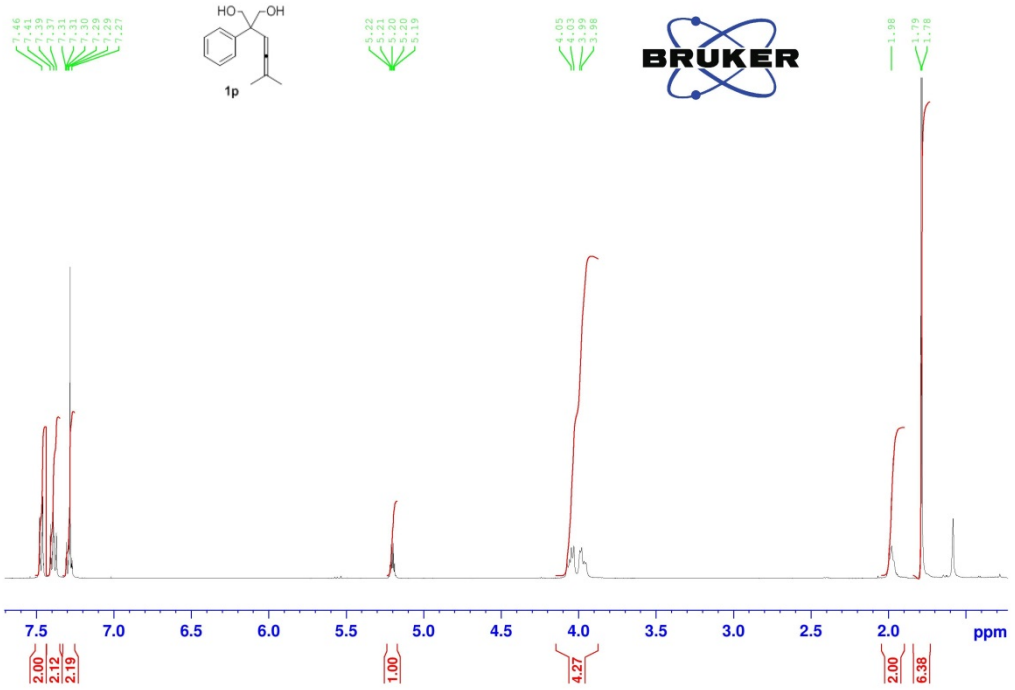
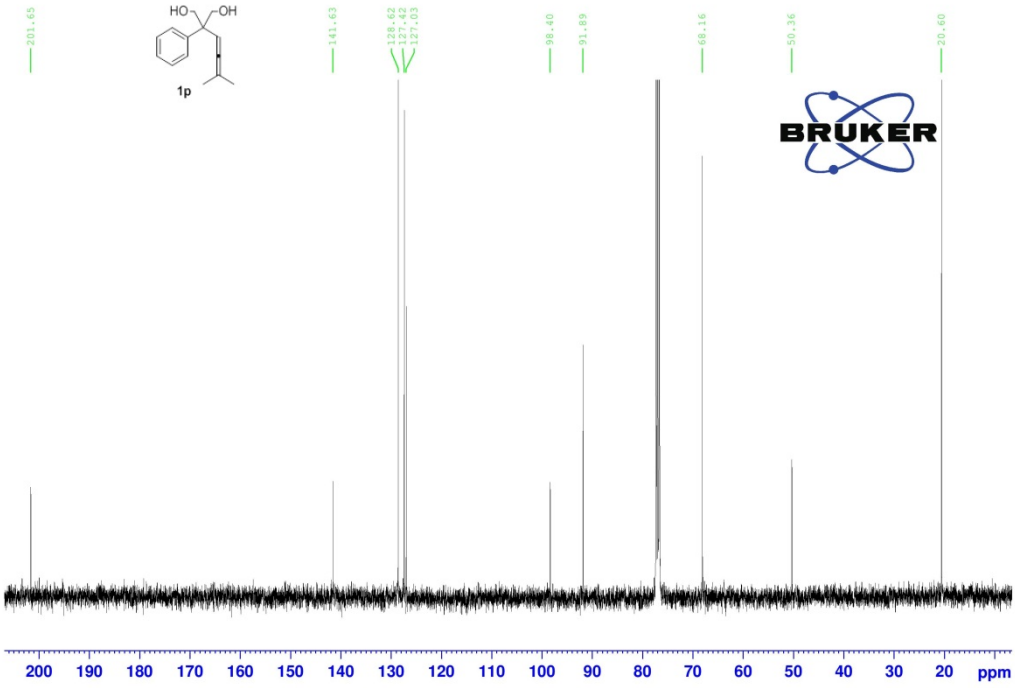
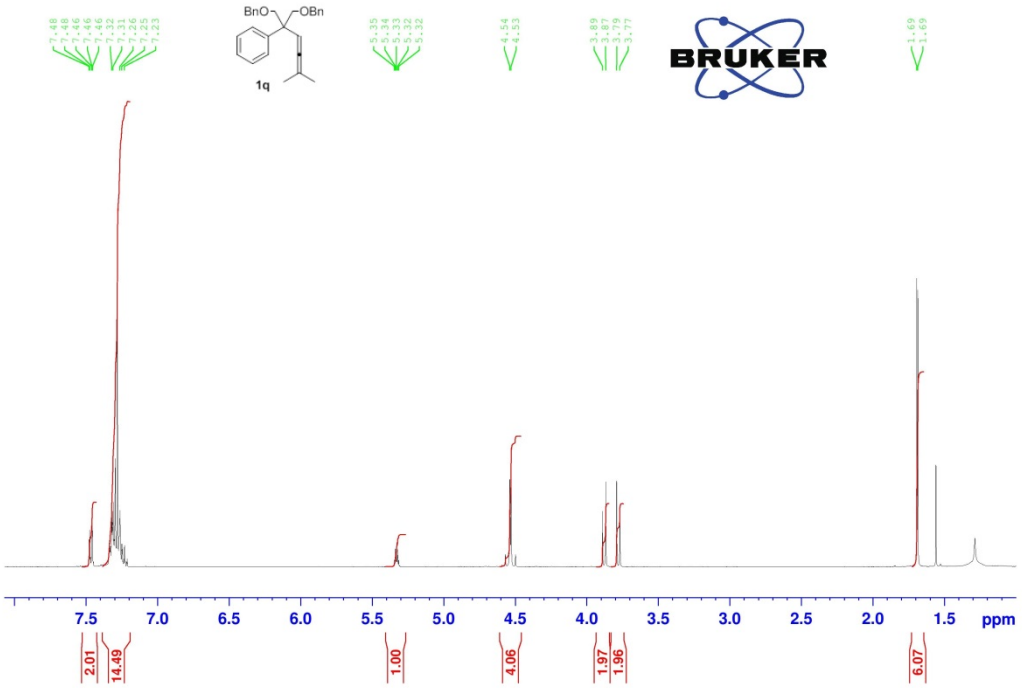
90
80
70
60
50
40
30
20
ppm


COOEt
COOEt
1o
BRUKER
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
ppm
2.12
2.05
2.09
2.04
1.01
1.00
4.10
12.09


COOEt
COOEt
1o
BRUKER
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


HO
OH
1p
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.00
2.12
2.19
1.00
4.27
2.00
6.38


HO
OH
1p
BRUKER
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


BnO
OBn
1q
BRUKER
7.48
7.46
7.32
7.31
7.26
7.25
7.23
5.35
5.34
5.33
5.32
4.54
4.53
3.89
3.87
3.79
3.77
1.69
1.69
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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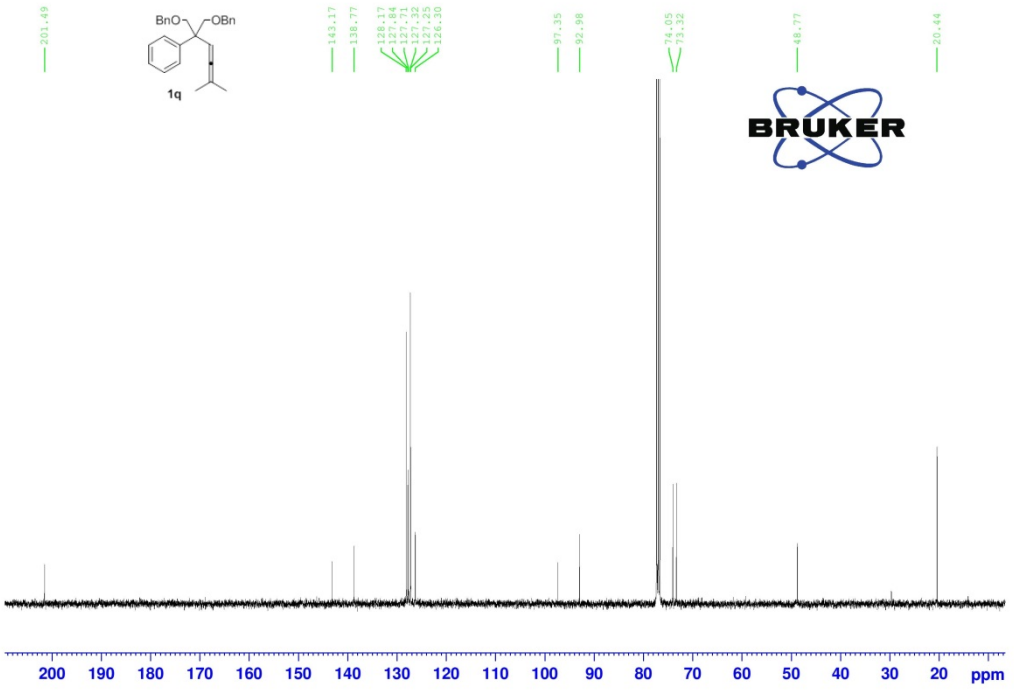
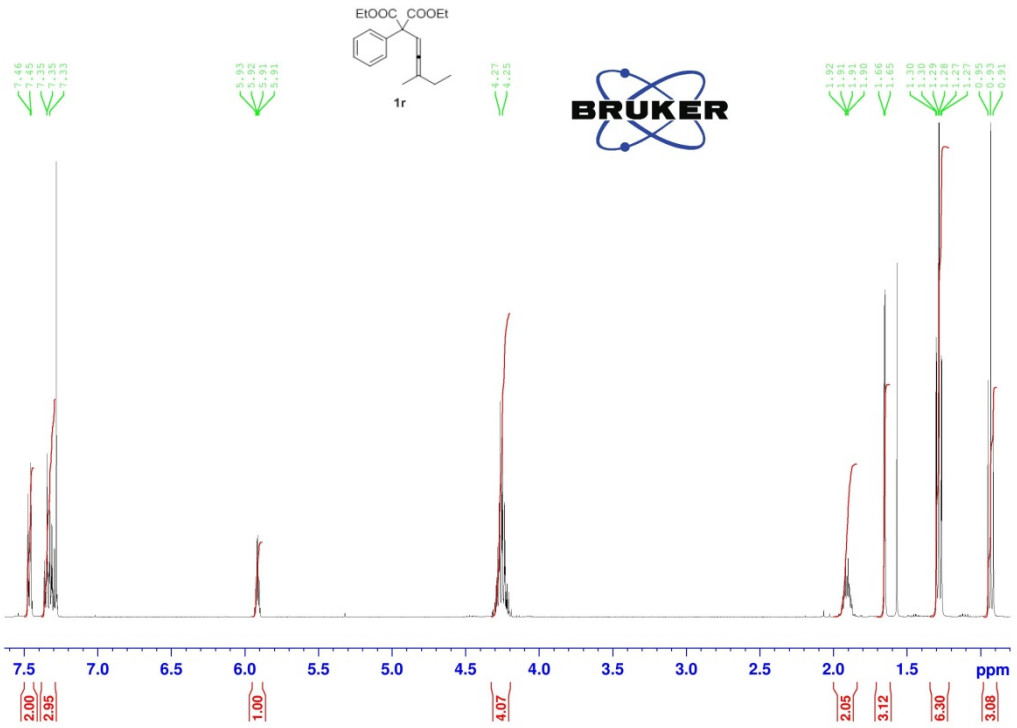
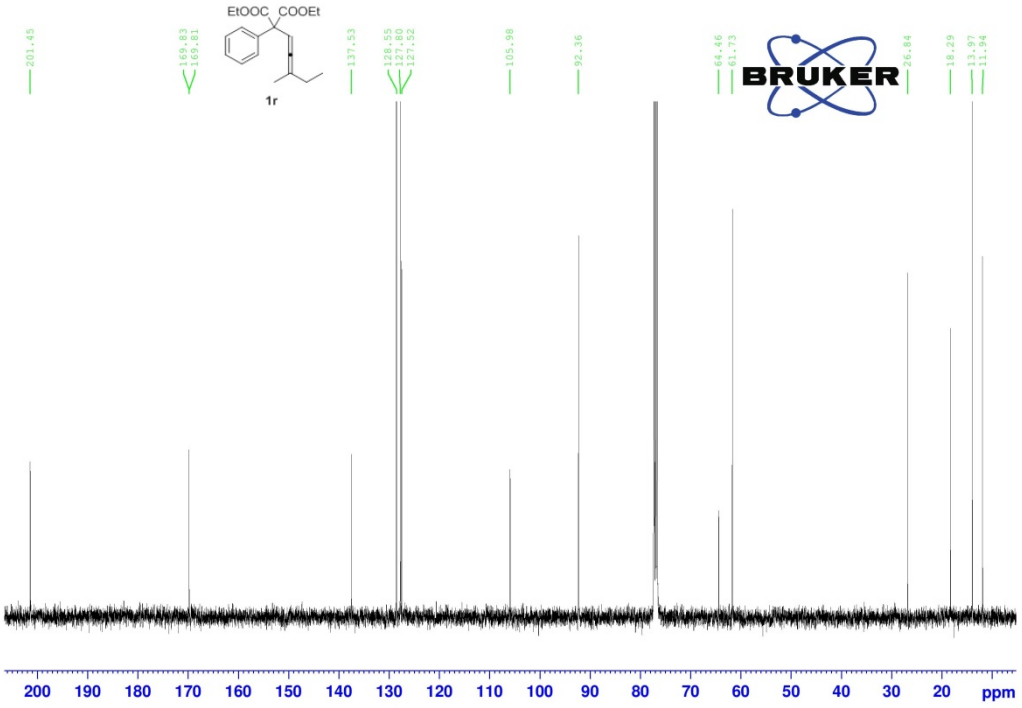
14.49
1.00
4.06
1.97
1.96
6.07


BnO
OBn
1q
BRUKER
201.49
143.17
138.77
128.17
127.84
127.71
127.32
127.25
126.90
97.35
92.98
74.05
73.32
48.77
20.44
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
1r
BRUKER
7.46
7.45
7.35
7.35
7.33
5.93
5.92
5.91
5.91
4.27
4.25
1.92
1.91
1.91
1.90
1.66
1.65
1.30
1.30
1.29
1.28
1.27
1.27
0.95
0.93
0.91
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
ppm
2.00
2.95
1.00
4.07
2.05
3.12
6.30
3.08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1r
BRUKER
201.45
169.83
169.81
137.53
128.55
127.80
127.52
105.98
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64.46
61.73
26.84
18.29
13.97
11.94
200
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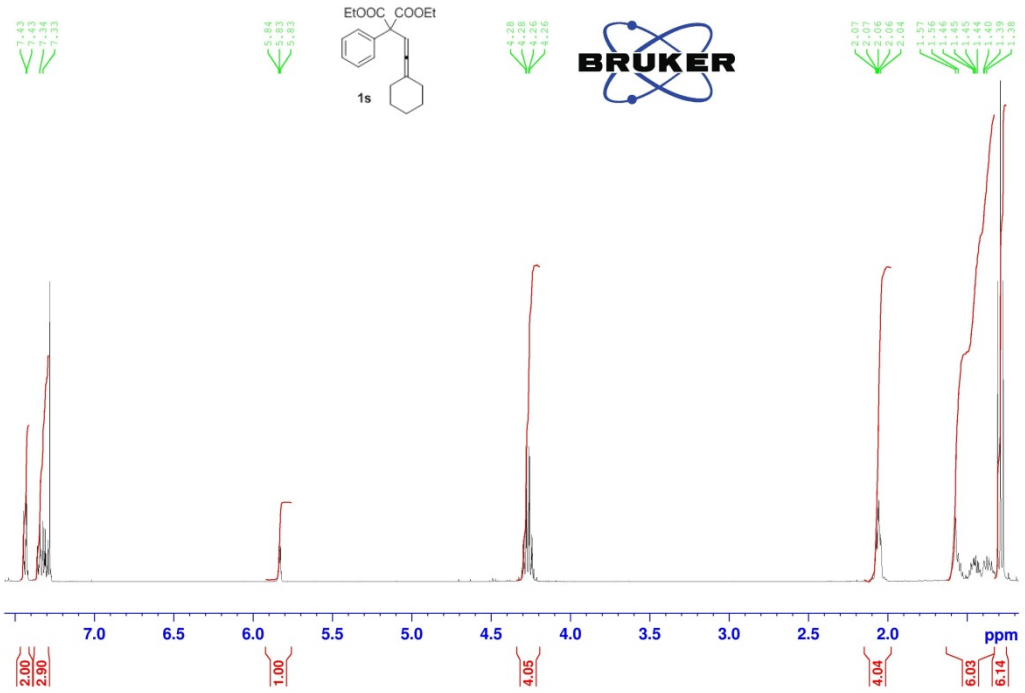
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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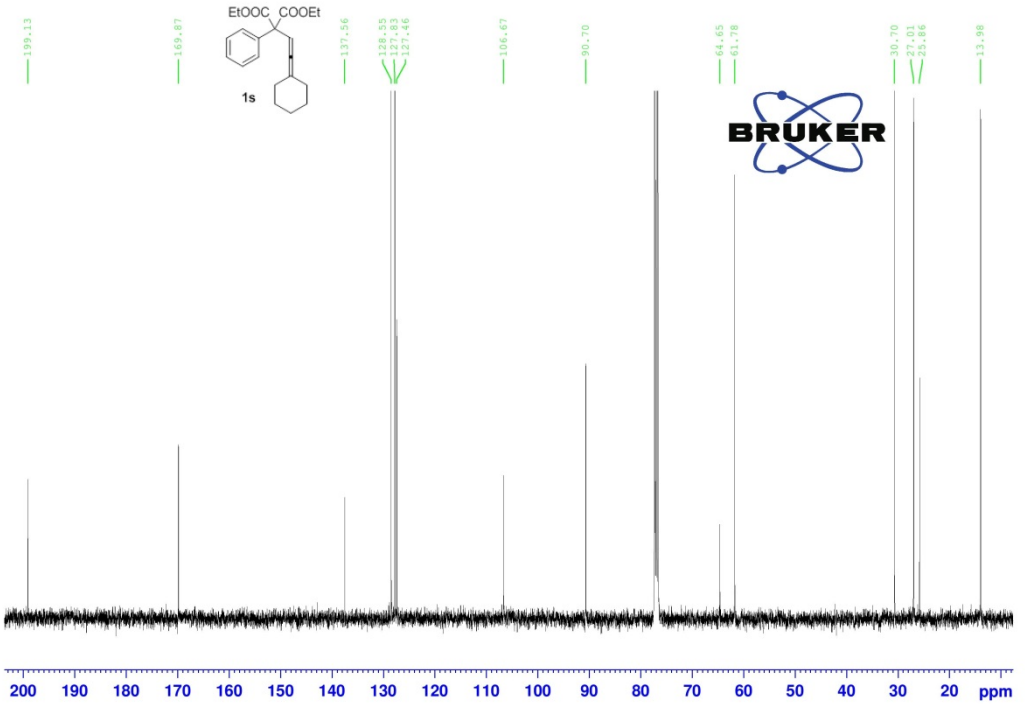
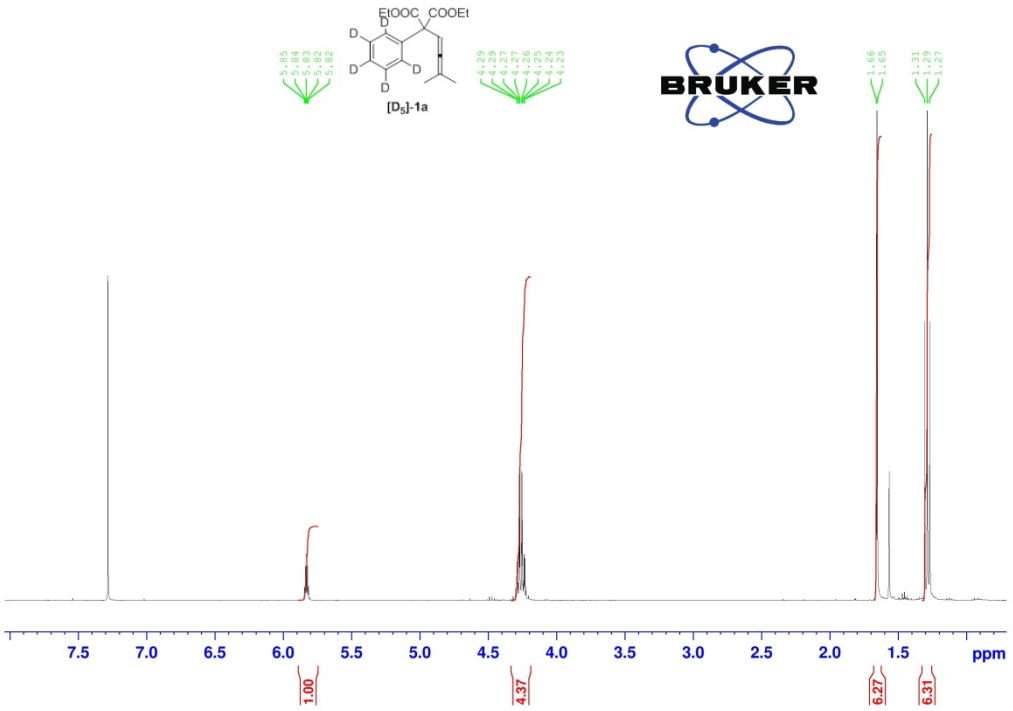
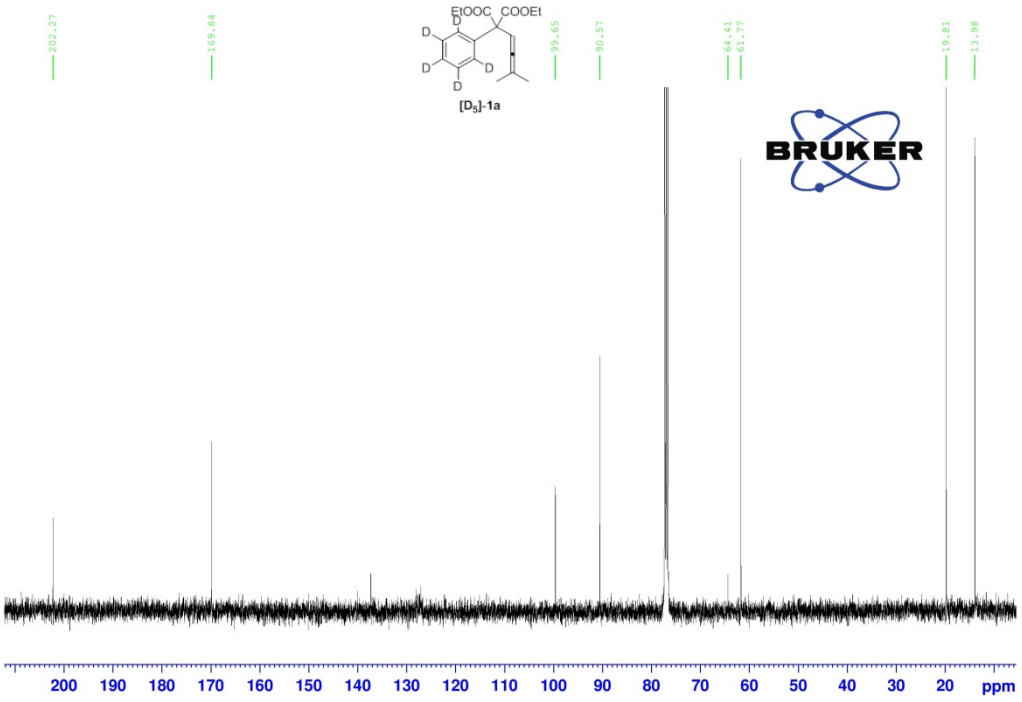
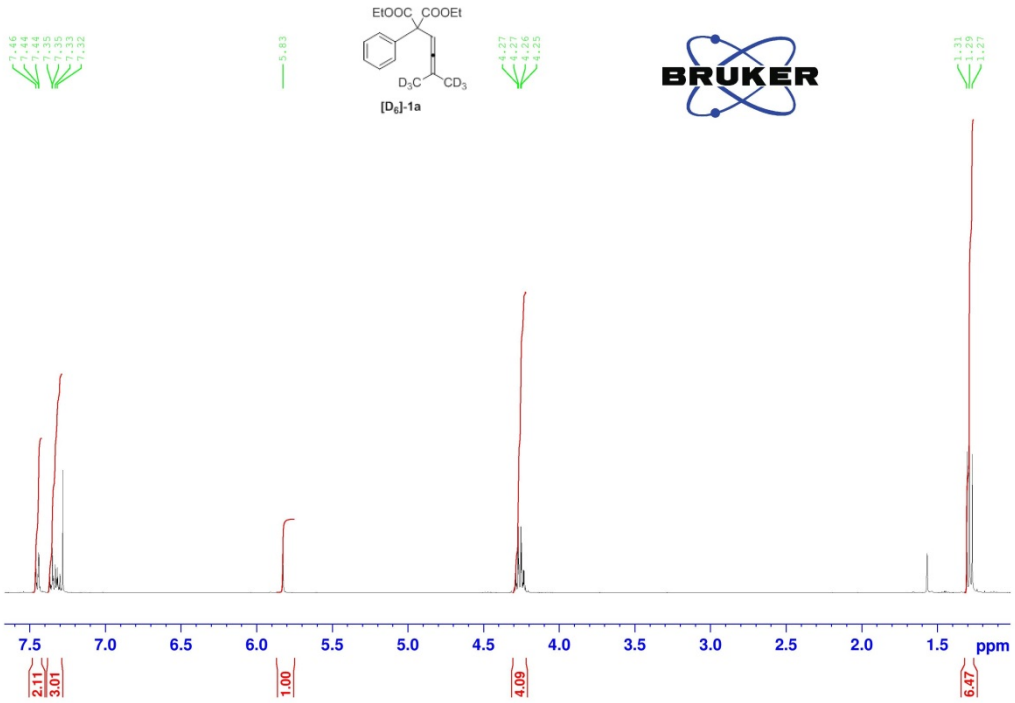
1s
BRUKER
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.00
2.90
1.00
4.05
4.04
6.03
6.14


EtOOC COOEt
1s
BRUKER
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
D
D
D
D
D
[D5]-1a
5.85
5.84
5.83
5.82
5.82
4.29
4.28
4.27
4.27
4.26
4.25
4.24
4.23
1.66
1.65
1.31
1.29
1.27
BRUKER
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
ppm
1.00
4.37
6.27
6.31


EtOOC COOEt
D
D
D
D
D
[D5]-1a
202.27
169.84
99.65
90.57
64.41
61.77
19.61
13.98
BRUKER
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
D3C CD3
[D6]-1a
BRUKER
7.46
7.44
7.44
7.35
7.35
7.33
7.32
5.83
4.27
4.27
4.26
4.25
1.31
1.29
1.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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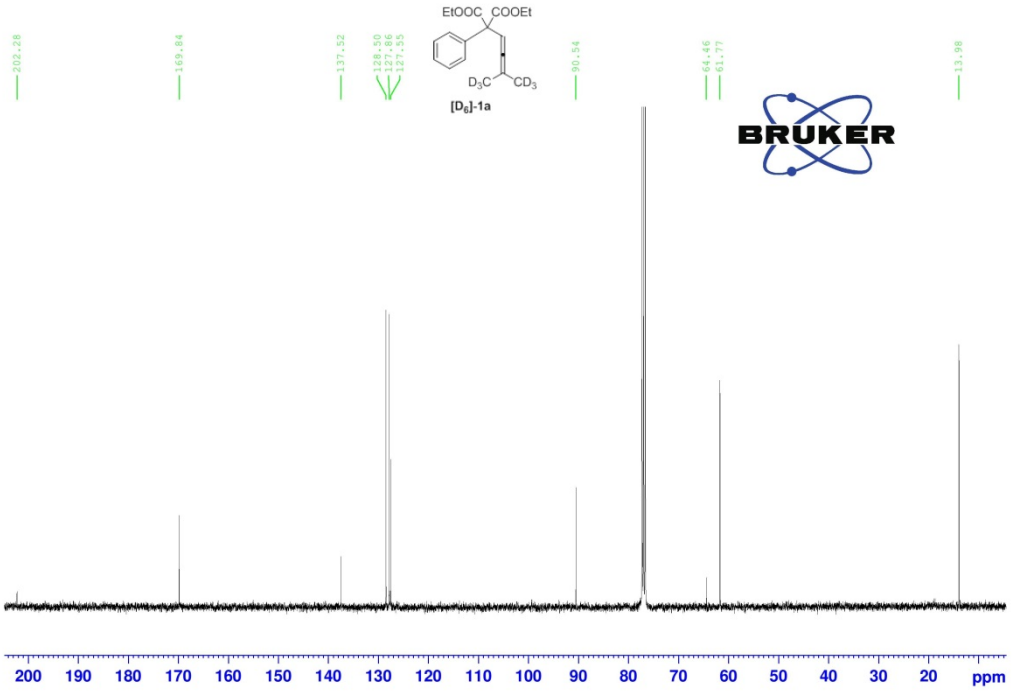
1.00
4.09
6.47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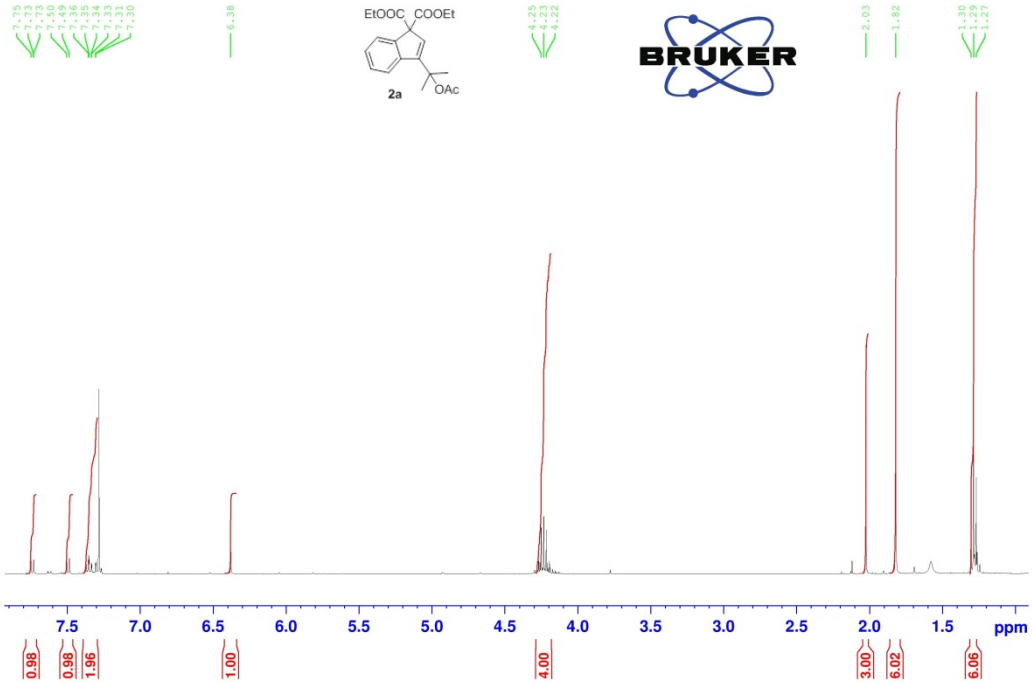
D3C CD3
[D6]-1a
BRUKER
202.28
169.84
137.52
128.50
127.86
127.55
90.54
64.46
61.77
13.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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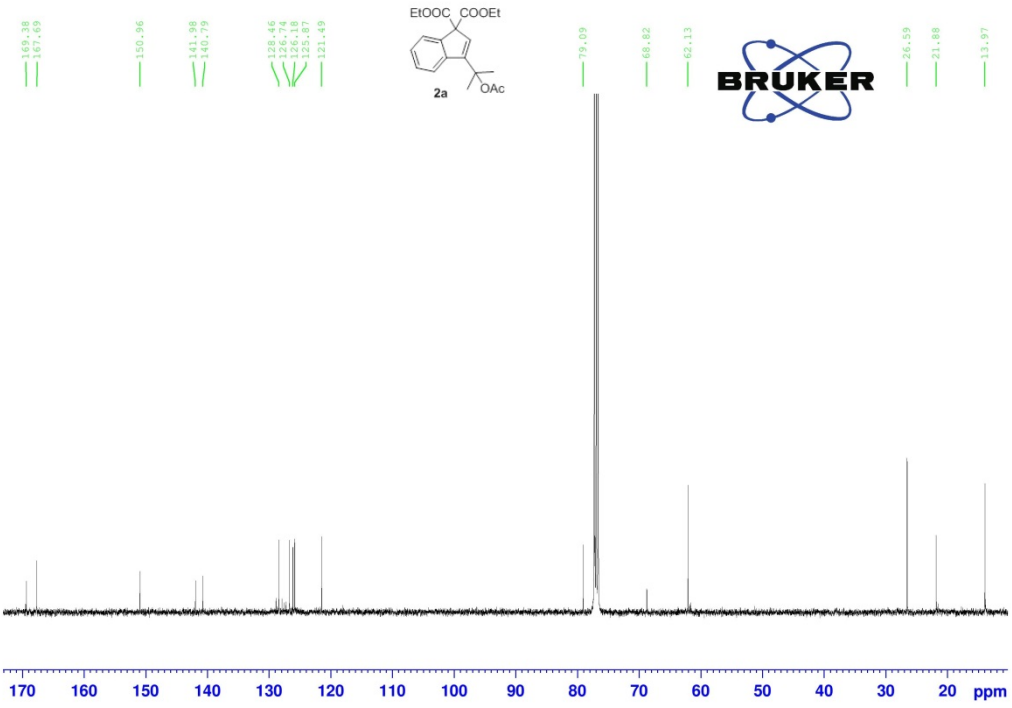
7.35
7.34
7.33
7.31
7.30
6.38
EtOOC COOEt
OAc
2a
4.25
4.23
4.22
BRUKER
2.03
1.82
1.30
1.29
1.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.99
0.98
1.96
1.00
4.00
3.00
6.02
6.06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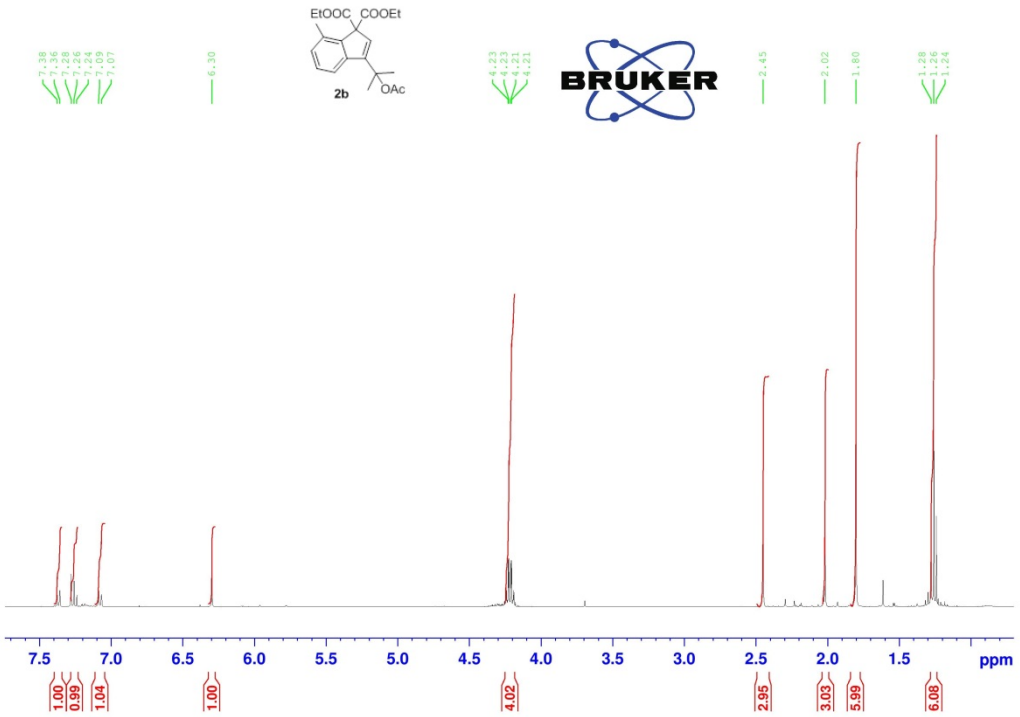
167.69
150.96
141.98
140.79
128.46
126.74
126.18
125.87
121.49
EtOOC COOEt
OAc
2a
79.09
68.82
62.13
BRUKER
26.59
21.88
13.97
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
OAc
2b
BRUKER
7.38
7.36
7.28
7.26
7.24
7.09
7.07
6.30
4.23
4.23
4.21
4.21
2.45
2.02
1.80
1.28
1.26
1.24
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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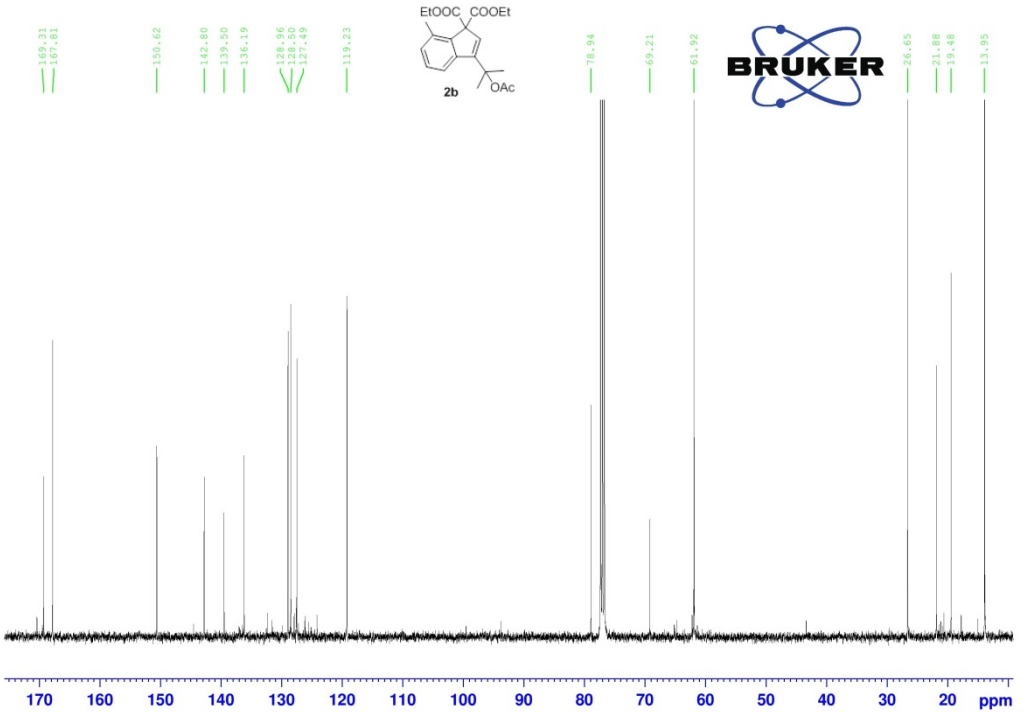
0.99
1.04
1.00
4.02
2.95
3.03
5.99
6.08


EtOOC COOEt
OAc
2b
BRUKER
169.31
167.81
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142.80
139.50
136.19
128.96
128.50
127.49
119.23
78.94
69.21
61.92
26.65
21.88
19.48
13.95
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160
150
140
130
120
110
100
90
80
70
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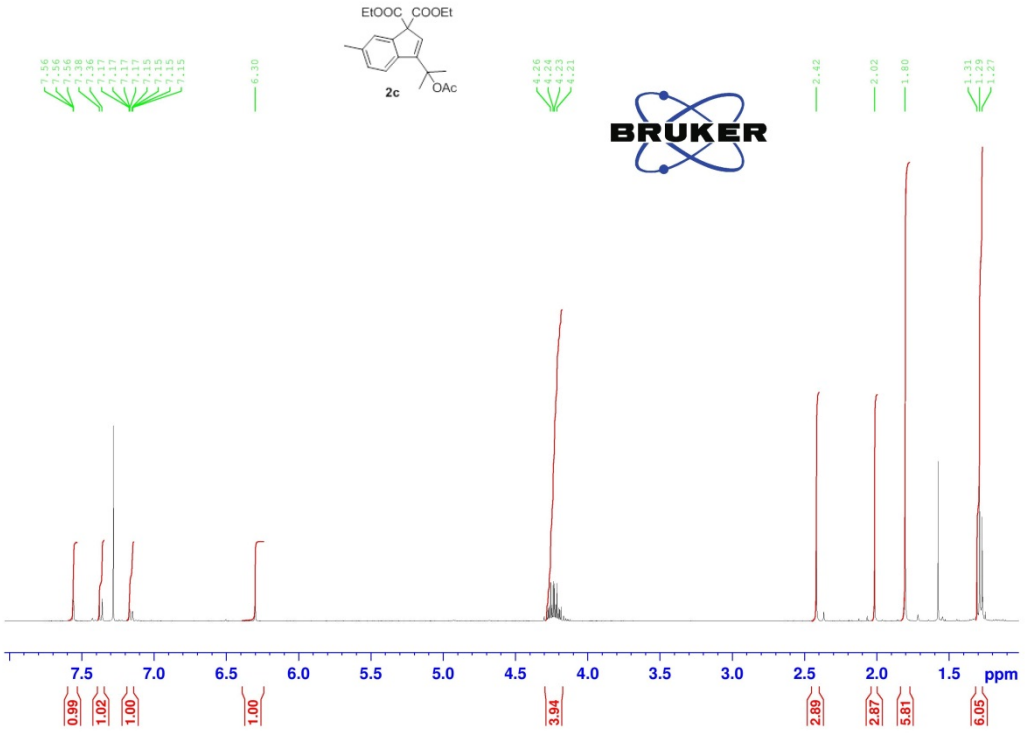
50
40
30
20
ppm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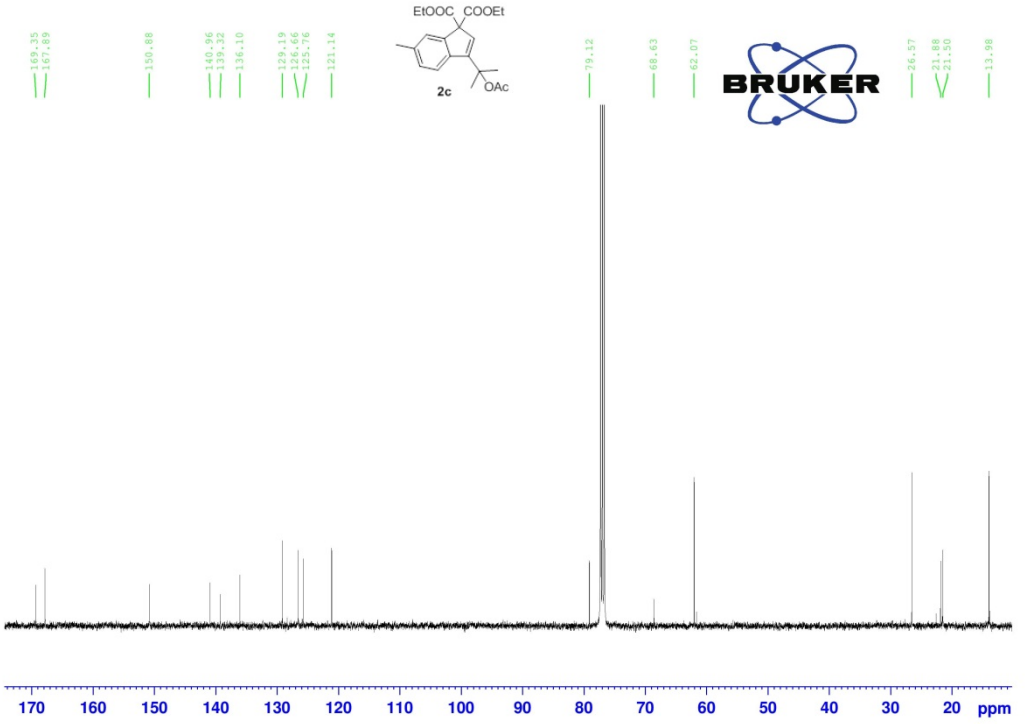
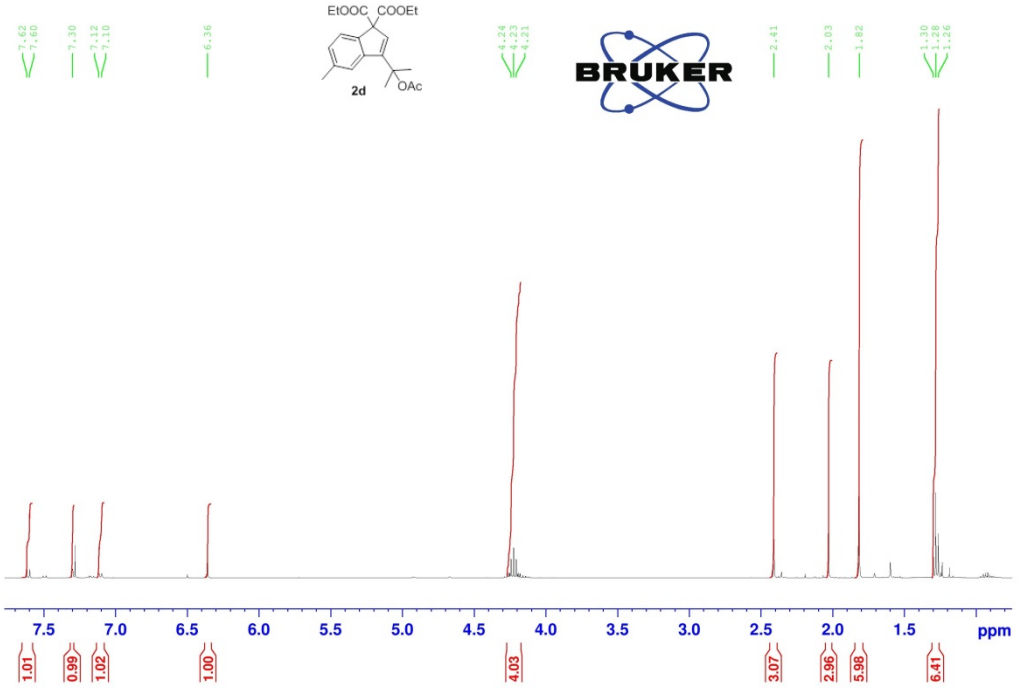
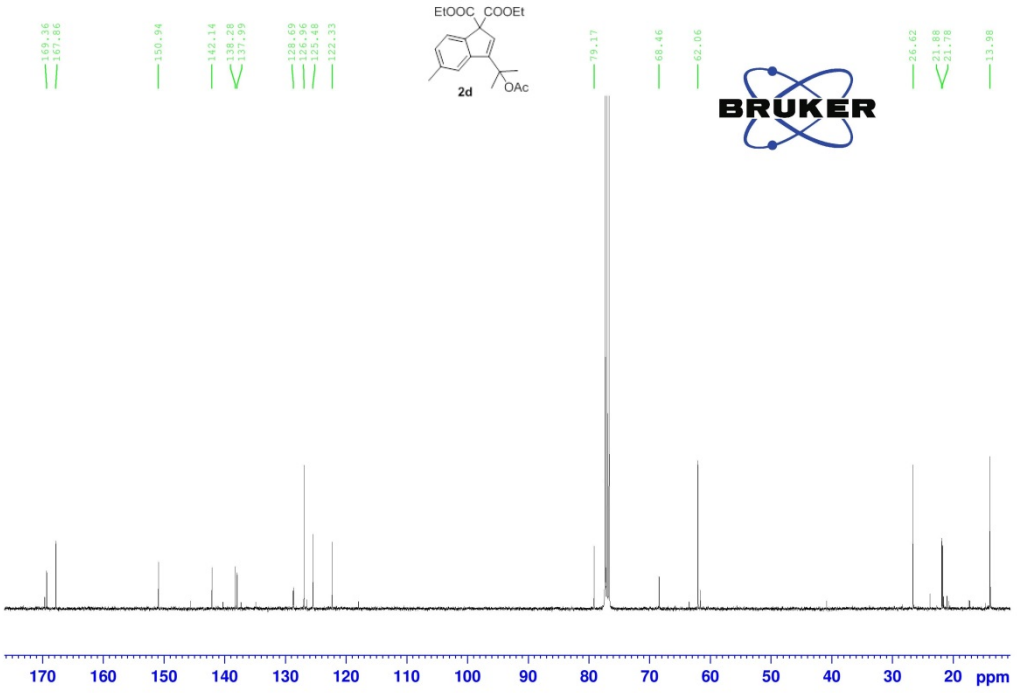
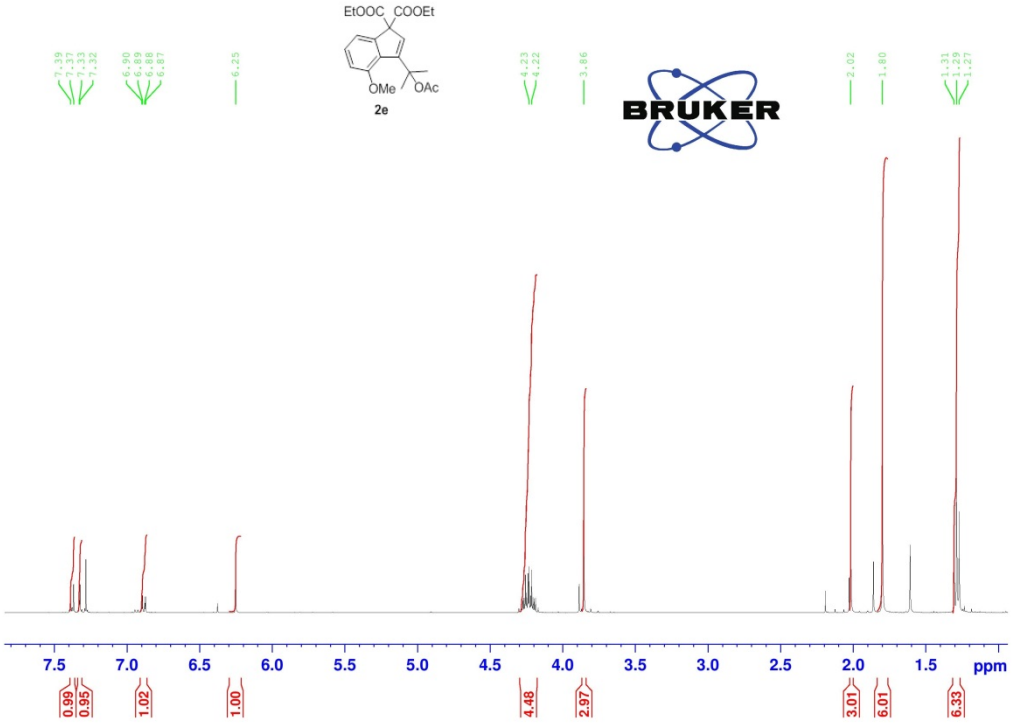
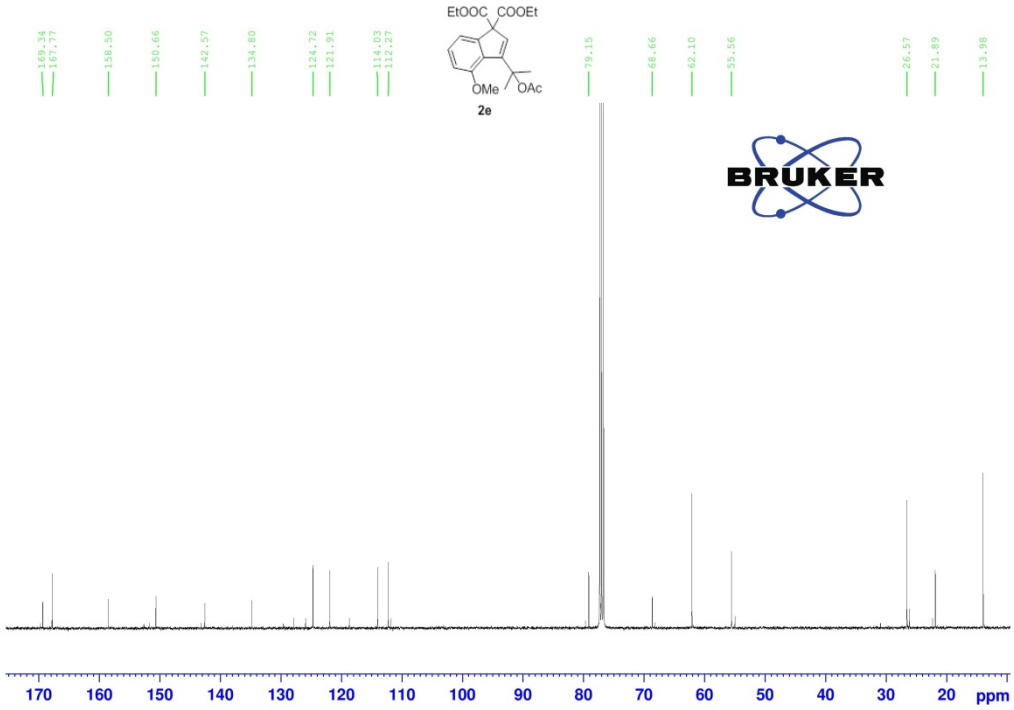
OAc
2c
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.99
1.02
1.00
1.00
3.94
2.89
2.87
5.81
6.05


EtOOC COOEt
OAc
2c
BRUKER
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
OAc
2d
BRUKER
7.62
7.60
7.30
7.12
7.10
6.36
4.24
4.23
4.21
2.41
2.03
1.82
1.30
1.28
1.26
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
ppm
1.01
0.99
1.02
1.00
4.03
3.07
2.96
5.98
6.41


EtOOC COOEt
OAc
2d
BRUKER
169.36
167.66
150.94
142.14
138.28
137.99
128.69
126.96
125.48
122.33
79.17
68.46
62.06
26.62
21.88
21.78
13.98
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
OMe OAc
2e
BRUKER
7.39
7.37
7.33
7.32
6.90
6.89
6.88
6.87
6.25
4.23
4.22
3.86
2.02
1.80
1.31
1.29
1.27
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 ppm
0.99
0.95
1.02
1.00
4.48
2.97
3.01
6.01
6.33


EtOOC COOEt
OMe OAc
2e
BRUKER
169.34
167.77
158.50
150.66
142.57
134.80
124.72
121.91
114.03
112.27
79.15
68.66
62.10
55.56
26.57
21.89
13.98
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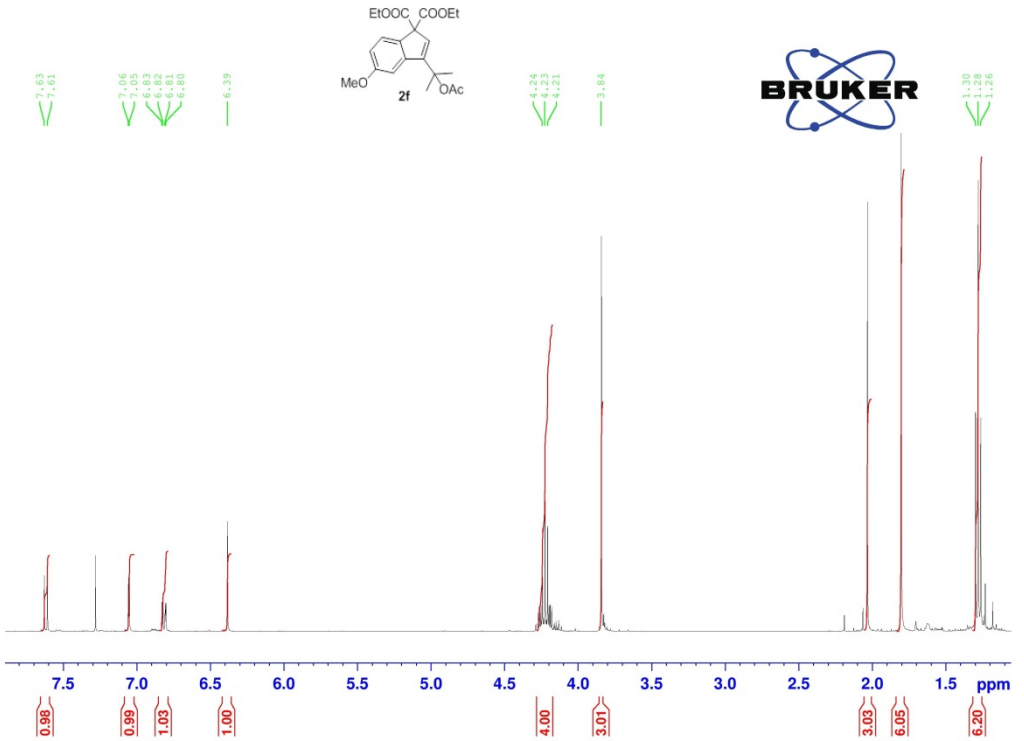
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MeO
OAc
2f
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7.06
7.05
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6.82
6.81
6.80
6.39
4.24
4.23
4.21
3.84
1.30
1.28
1.26
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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ppm
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4.00
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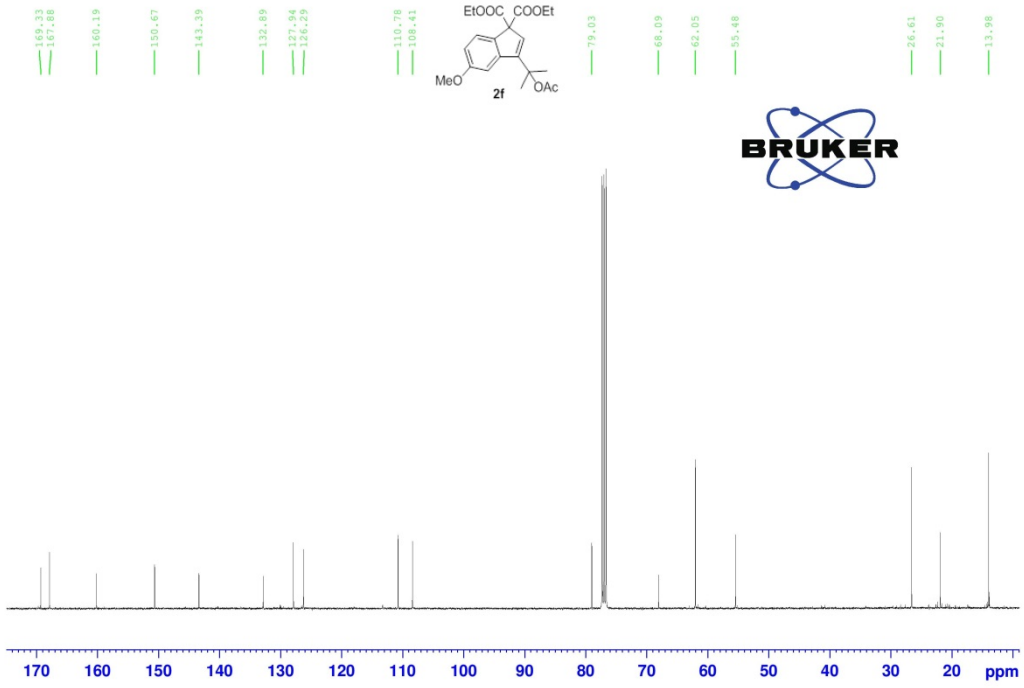
3.03
6.05
6.20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OAc
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132.89
127.94
126.29
110.78
108.41
79.03
68.09
62.05
55.48
26.61
21.90
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160
150
140
130
120
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80
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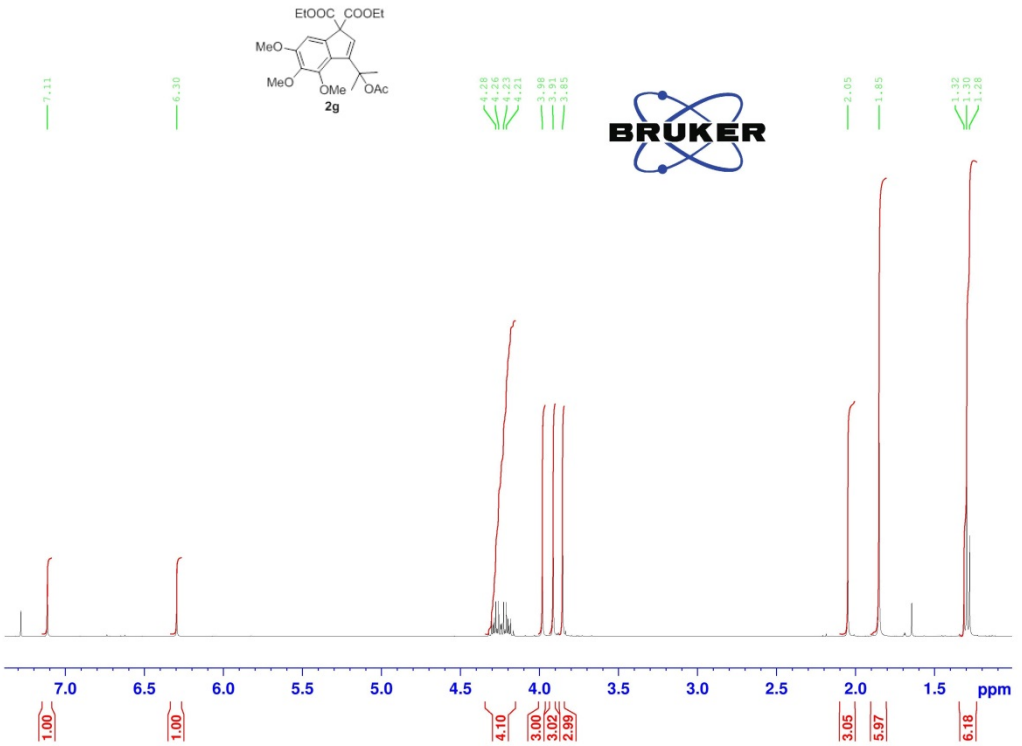
20
ppm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MeO
MeO
OMe
OAc
2g
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6.30
4.28
4.26
4.23
4.21
3.98
3.91
3.85
2.05
1.85
1.32
1.30
1.28
BRUKER
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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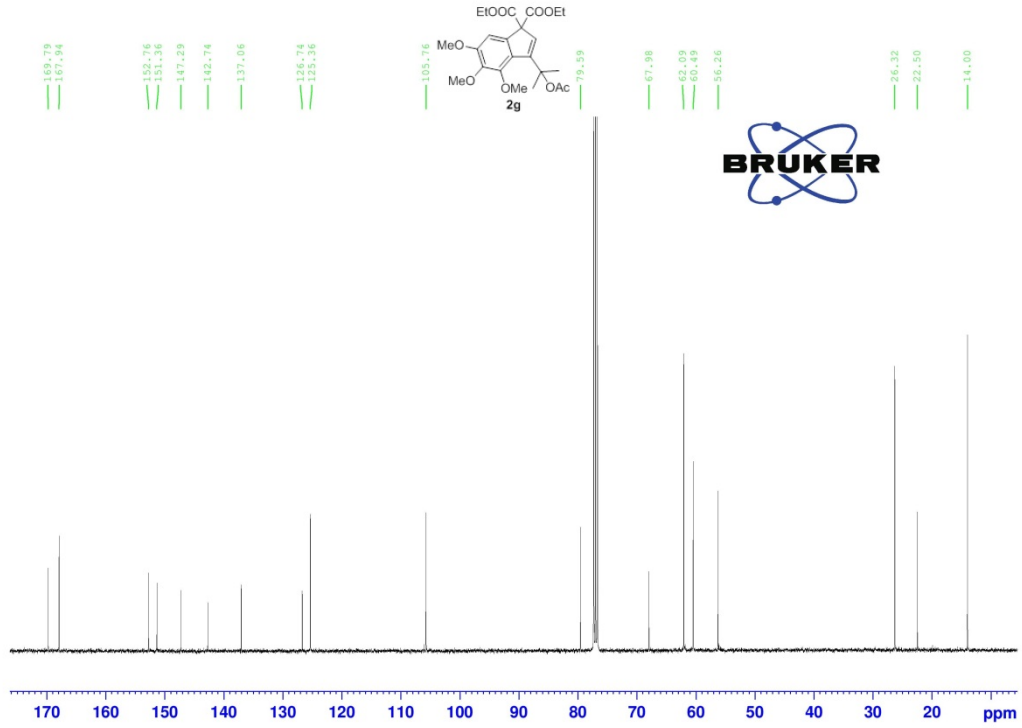
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MeO
OMe
OAc
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147.29
142.74
137.06
126.74
125.36
105.76
79.59
67.98
62.09
60.49
56.26
26.32
22.50
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150
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130
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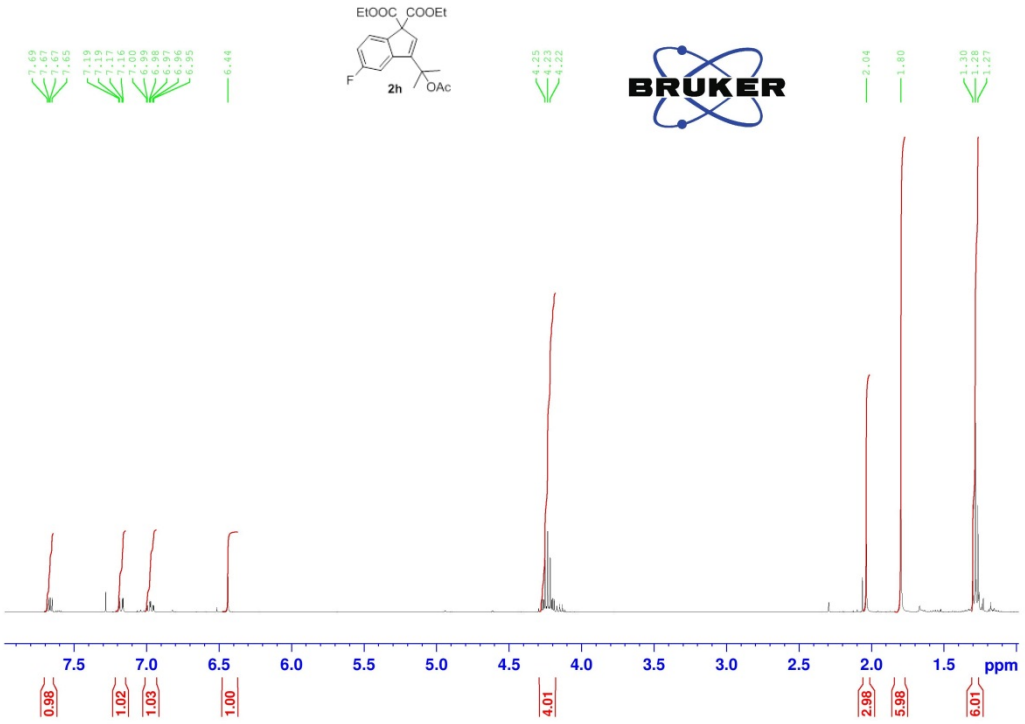
ppm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F
2h
OAc
BRUKER
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7.67
7.67
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7.19
7.19
7.17
7.16
7.00
6.99
6.98
6.97
6.96
6.95
6.44
4.25
4.23
4.22
2.04
1.80
1.30
1.28
1.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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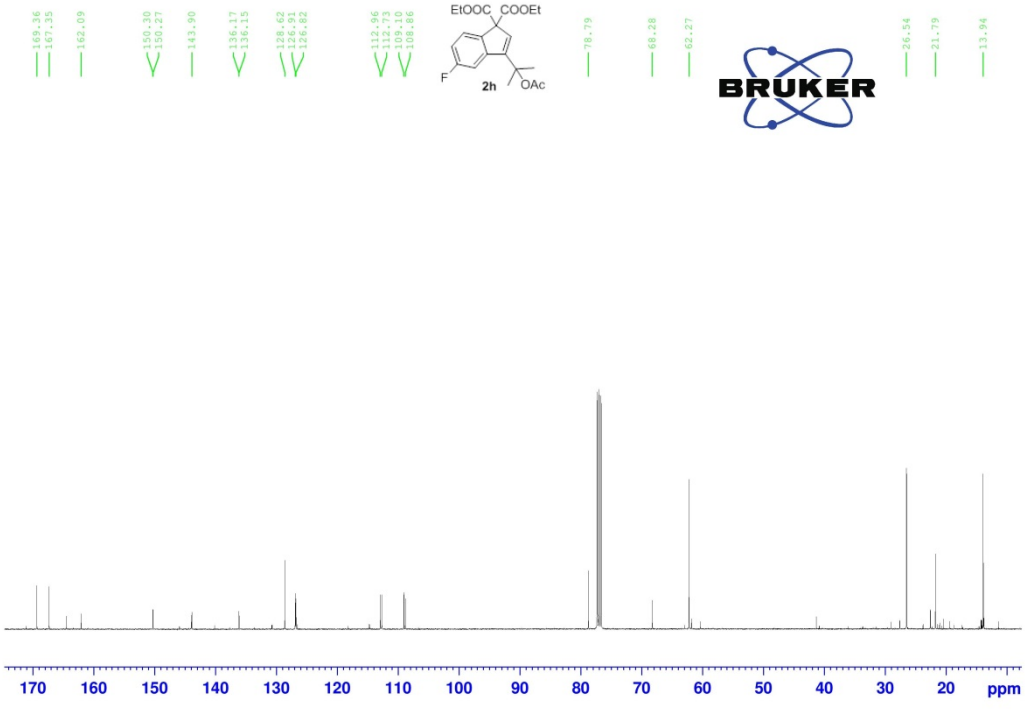
6.01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126.91
126.82
112.96
112.73
109.10
108.86
EtOOC COOEt
F
2h
OAc
78.79
68.28
62.27
BRUKER
26.54
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160
150
140
130
120
110
100
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80
70
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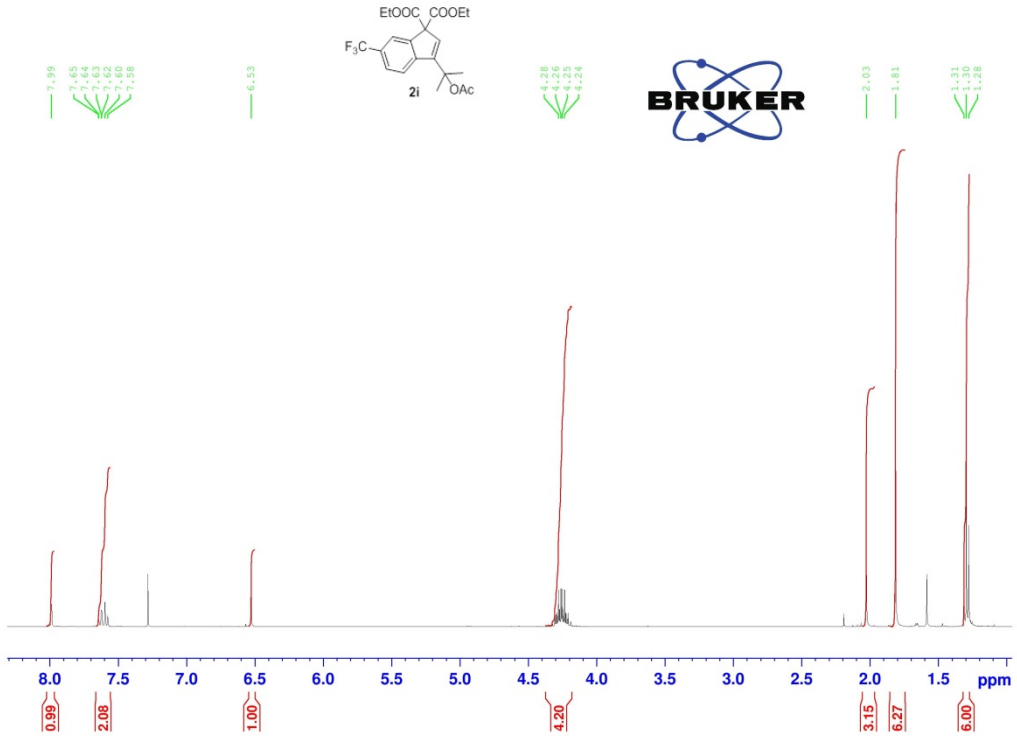
50
40
30
20
ppm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OAc
2i
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7.62
7.60
7.58
6.53
4.28
4.26
4.25
4.24
2.03
1.81
1.31
1.30
1.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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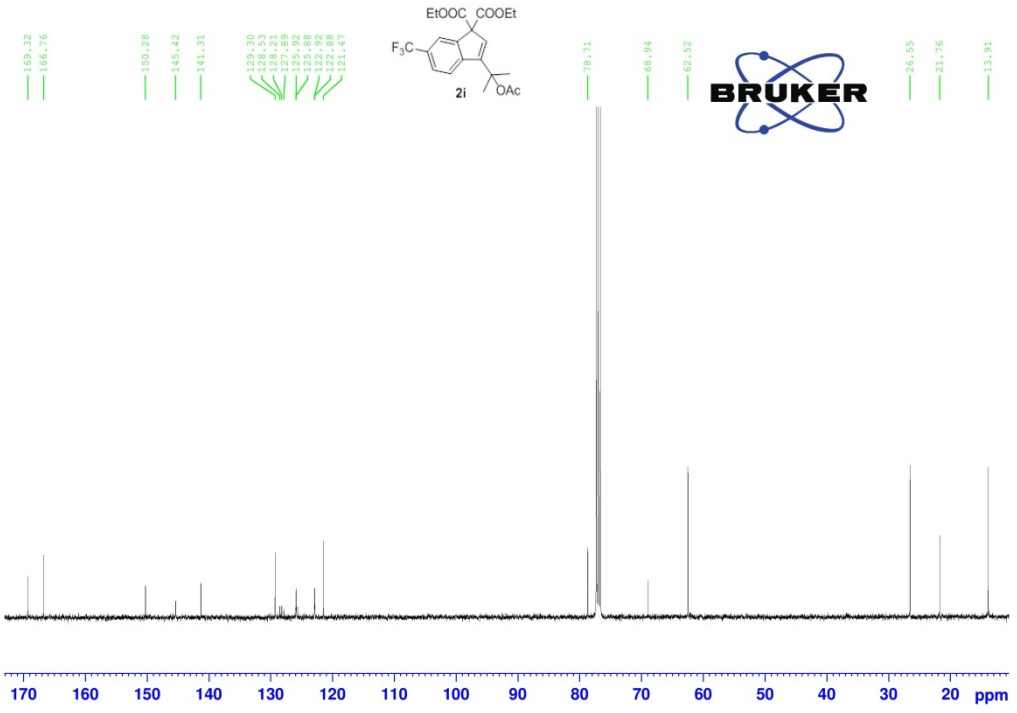
2.08
1.00
4.20
3.15
6.27
6.00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F3C
OAc
2i
BRUKER
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150.28
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129.30
128.53
128.21
127.69
125.92
125.88
122.92
122.88
121.47
78.71
68.94
62.52
26.55
21.76
13.91
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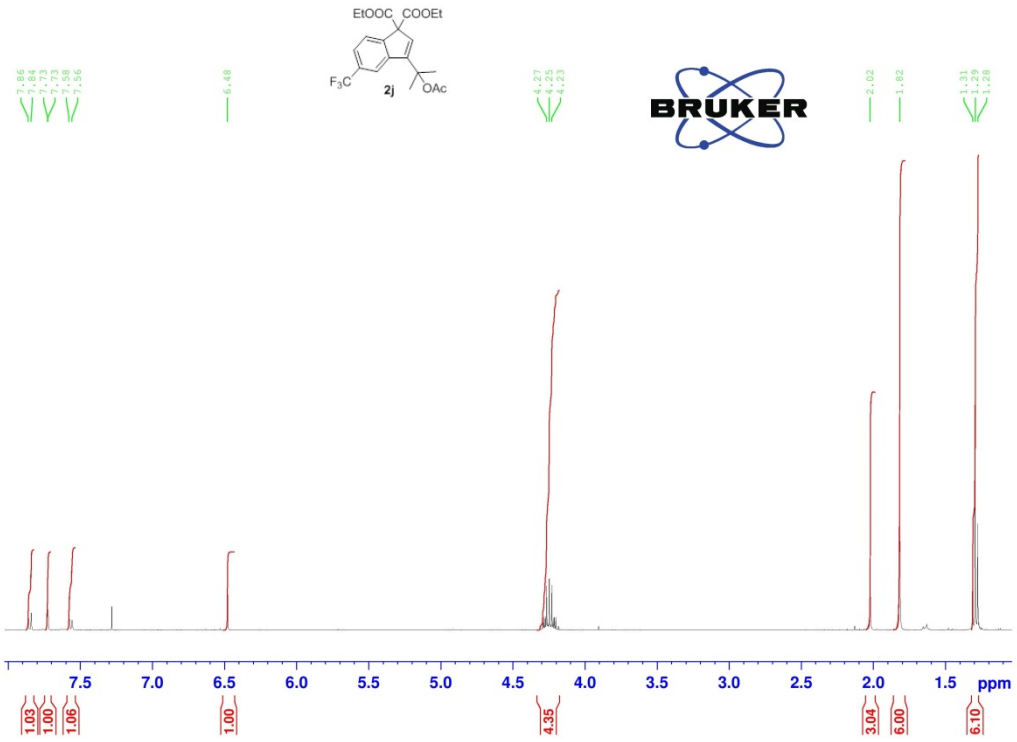
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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F3C
OAc
2j
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7.84
7.73
7.58
7.56
6.48
4.27
4.25
4.23
2.02
1.82
1.31
1.29
1.28
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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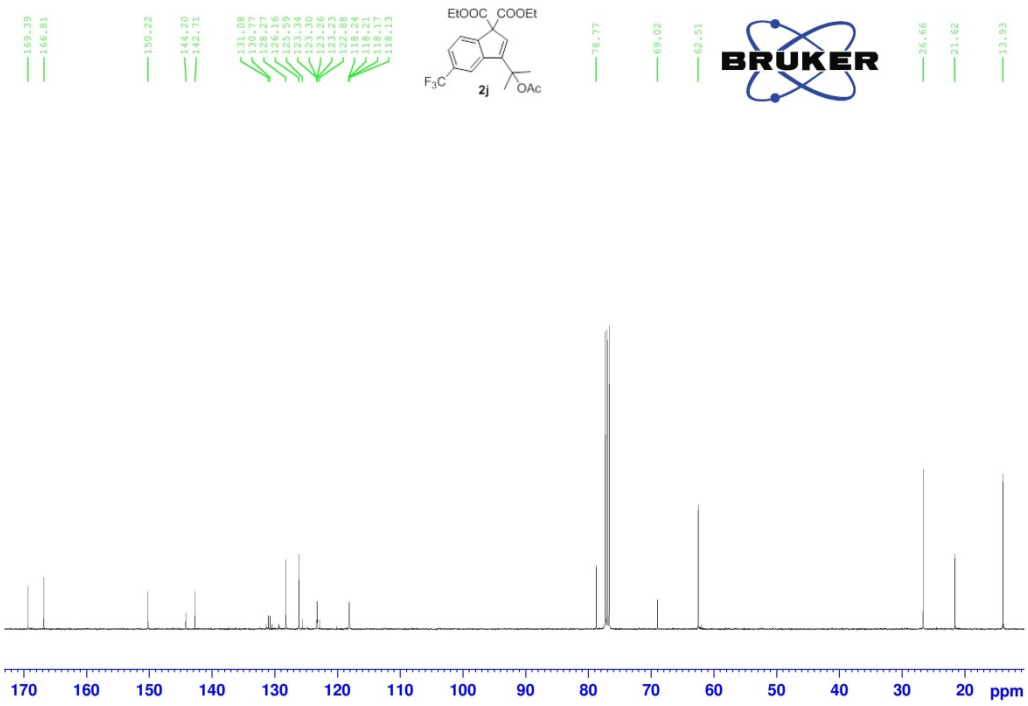
1.06
1.00
4.35
3.04
6.00
6.10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142.71
131.08
130.77
128.27
126.16
125.59
123.34
123.30
123.26
123.23
122.88
118.24
118.21
118.17
118.13
EtOOC COOEt
F3C
OAc
2j
78.77
69.02
62.51
BRUKER
26.66
21.62
13.93
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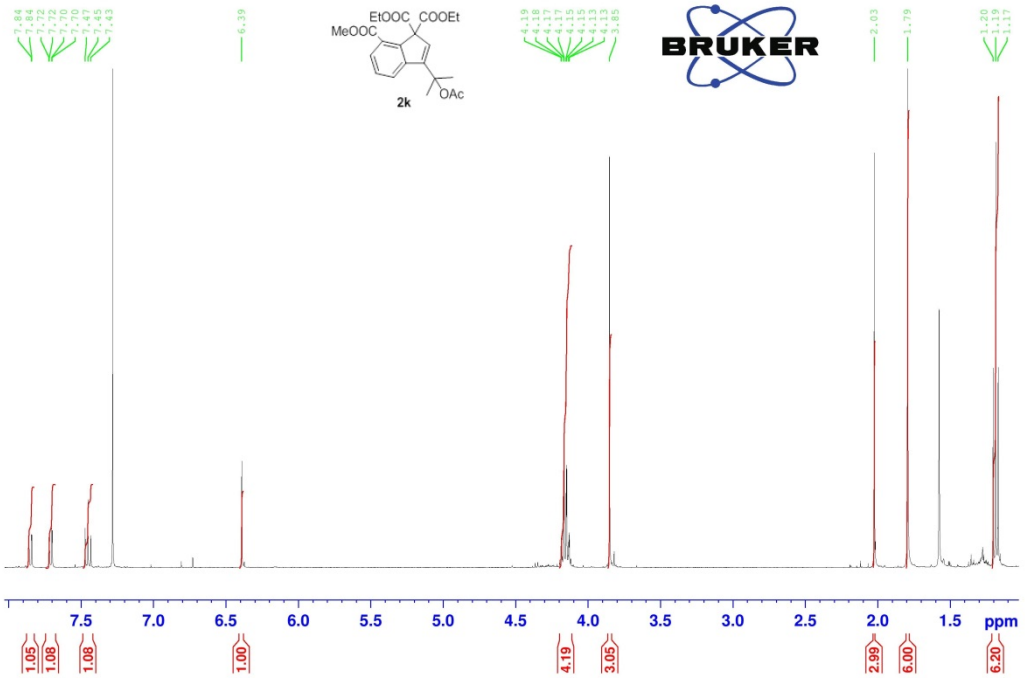
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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MeOOC
OAc
2k
BRUKER
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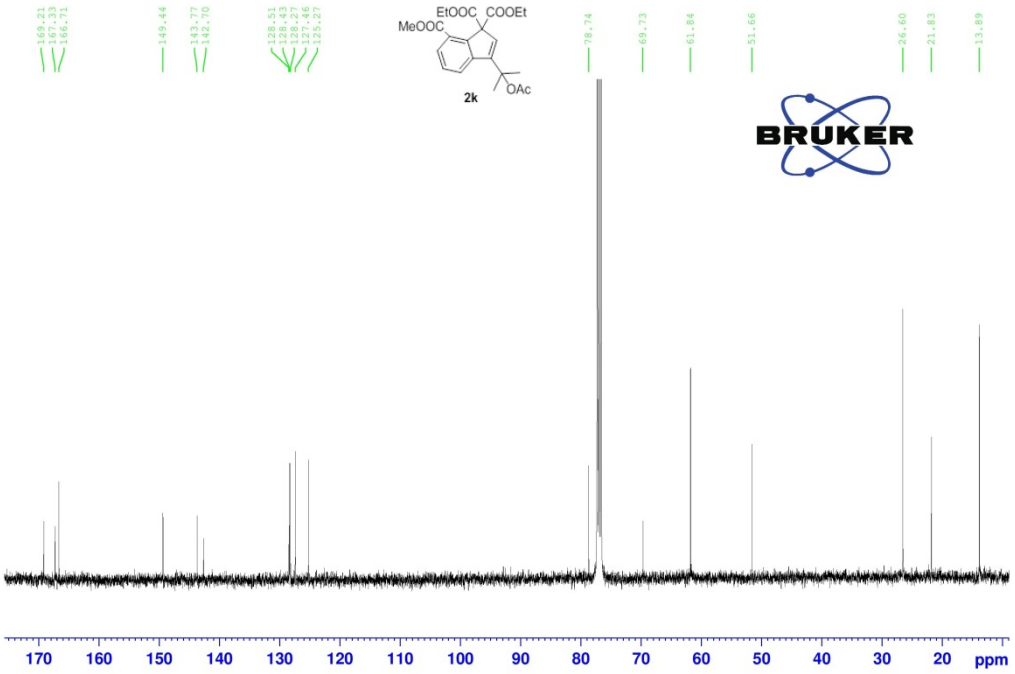
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


EtOOC COOEt
MeOOC
OAc
2k
BRUKER
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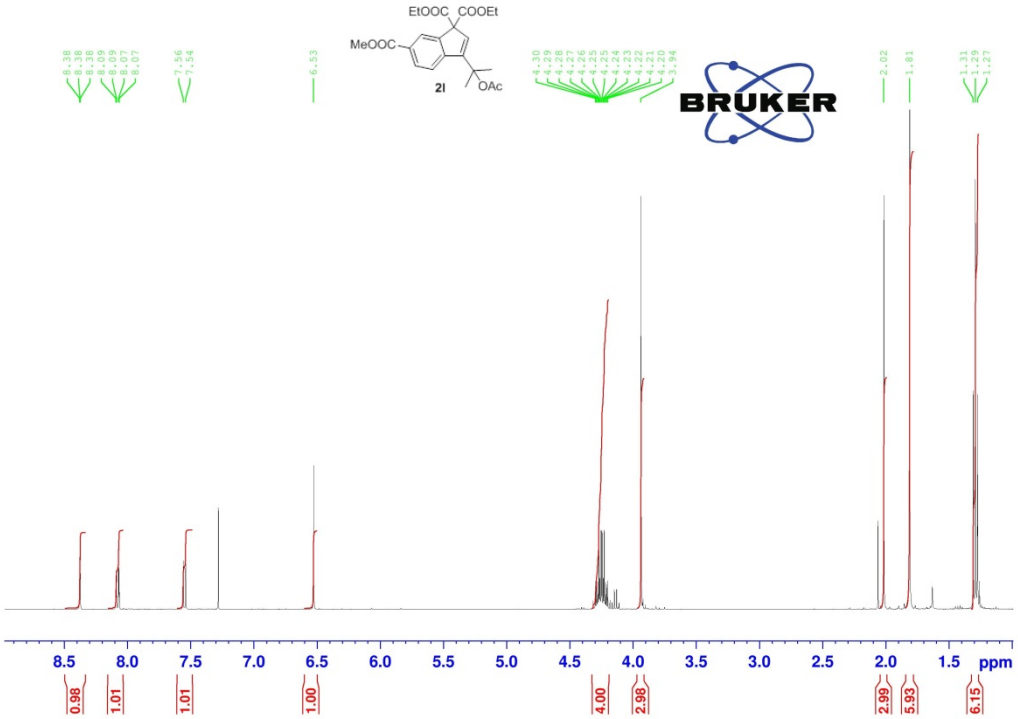
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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MeOOC
OAc
2l
BRUKER
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8.38
8.09
8.09
8.07
8.07
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7.54
6.53
4.30
4.28
4.27
4.26
4.25
4.25
4.24
4.23
4.22
4.21
4.20
3.94
2.02
1.81
1.31
1.29
1.27
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
ppm
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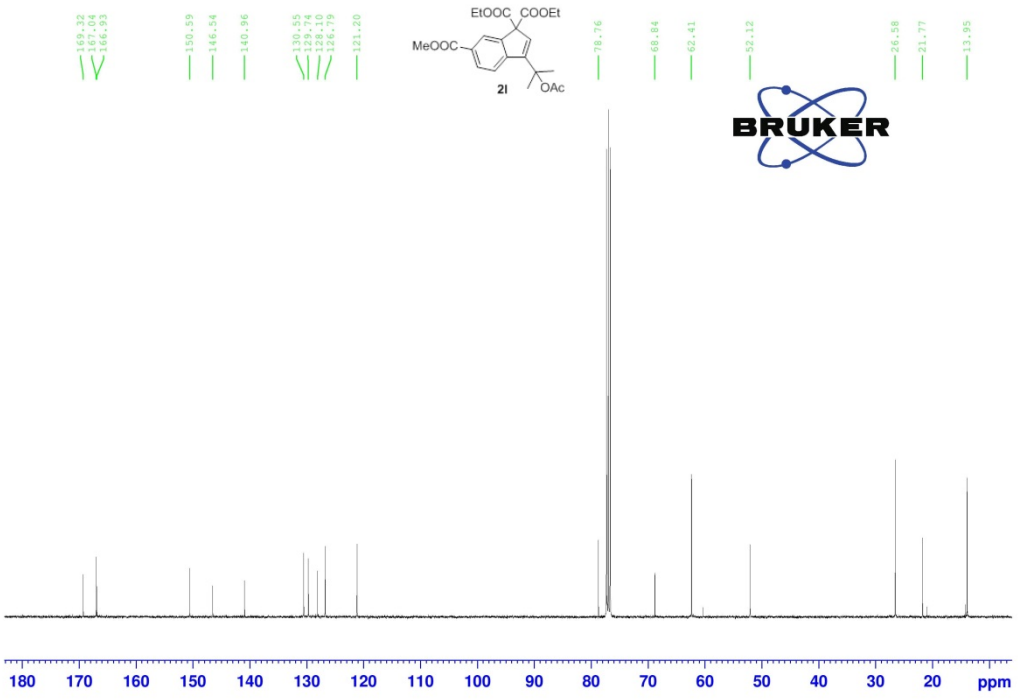
1.01
1.01
1.00
4.00
2.98
2.99
5.93
6.15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MeOOC
OAc
2l
BRUKER
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146.54
140.96
130.55
129.74
128.10
126.79
121.20
78.76
68.84
62.41
52.12
26.58
21.77
13.95
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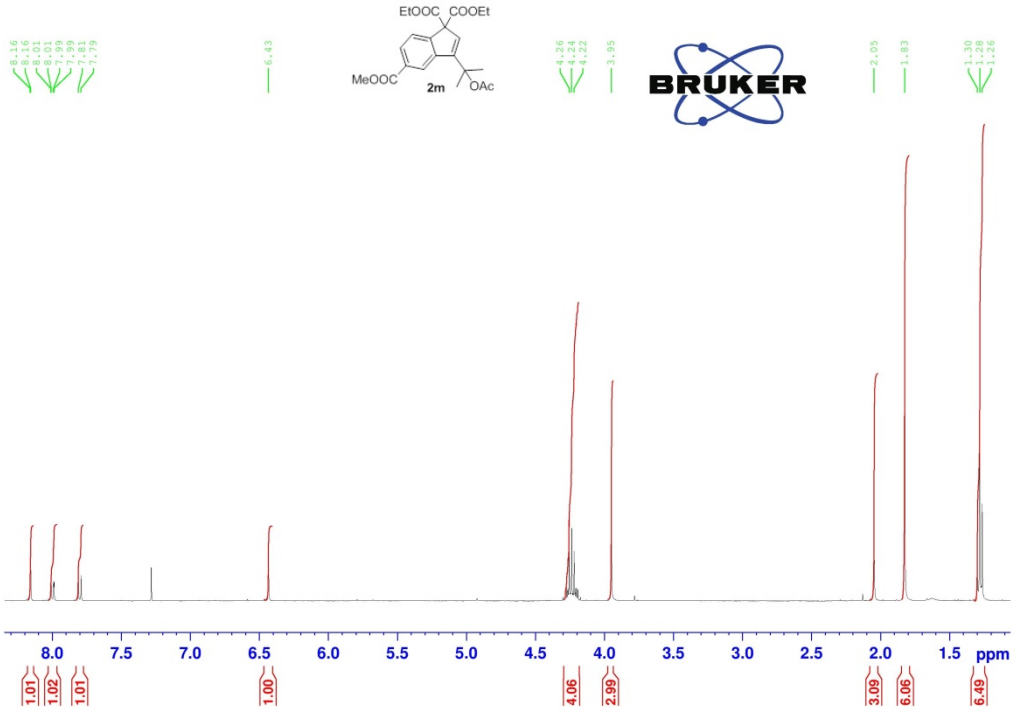
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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MeOOC
2m
OAc
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8.16
8.01
8.01
7.99
7.99
7.81
7.79
6.43
4.26
4.24
4.22
3.95
2.05
1.83
1.30
1.28
1.26
BRUKER
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.01
1.02
1.01
1.00
4.06
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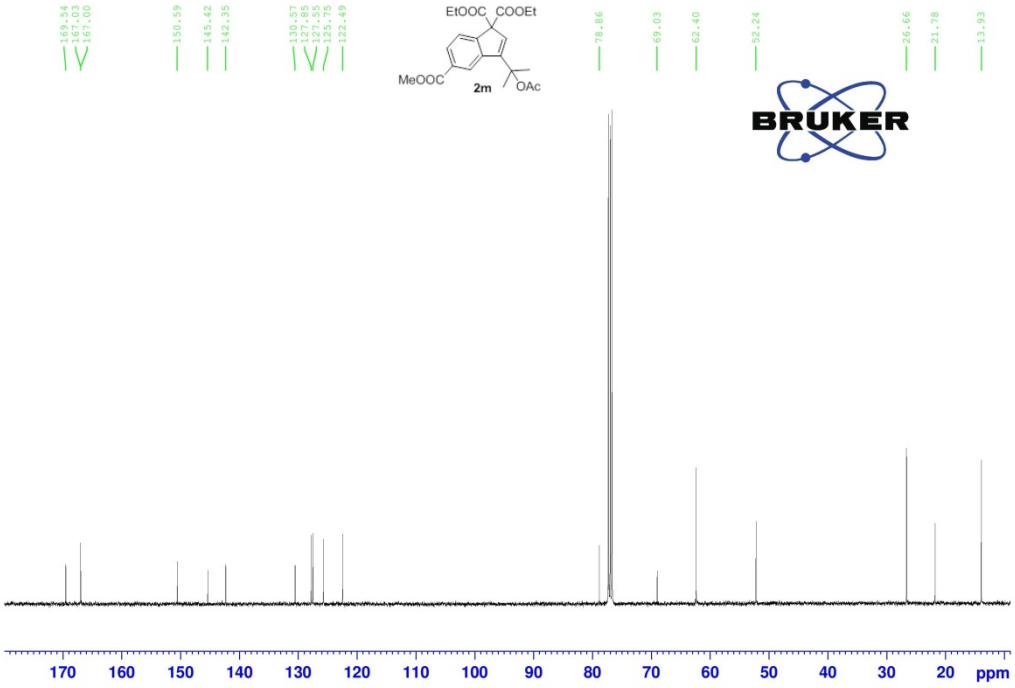
3.09
6.06
6.49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127.85
127.55
125.75
122.49
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MeOOC
2m
OAc
78.86
69.03
62.40
52.24
26.66
21.78
13.93
BRUKER
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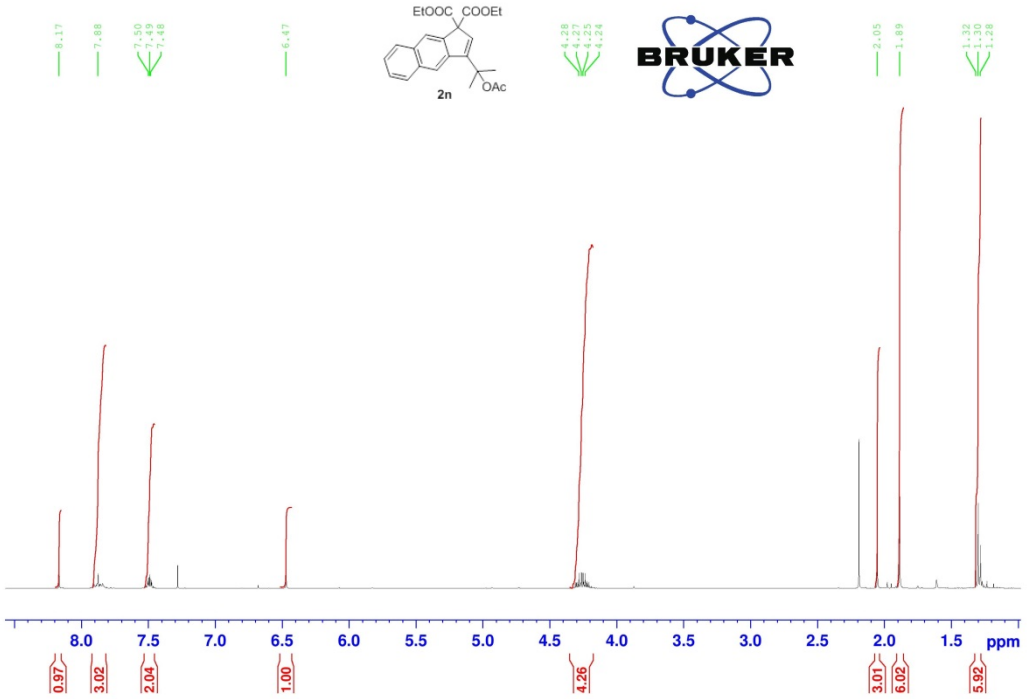
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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OAc
2n
BRUKER
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7.49
7.48
6.47
4.28
4.27
4.25
4.24
2.05
1.89
1.32
1.30
1.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
ppm
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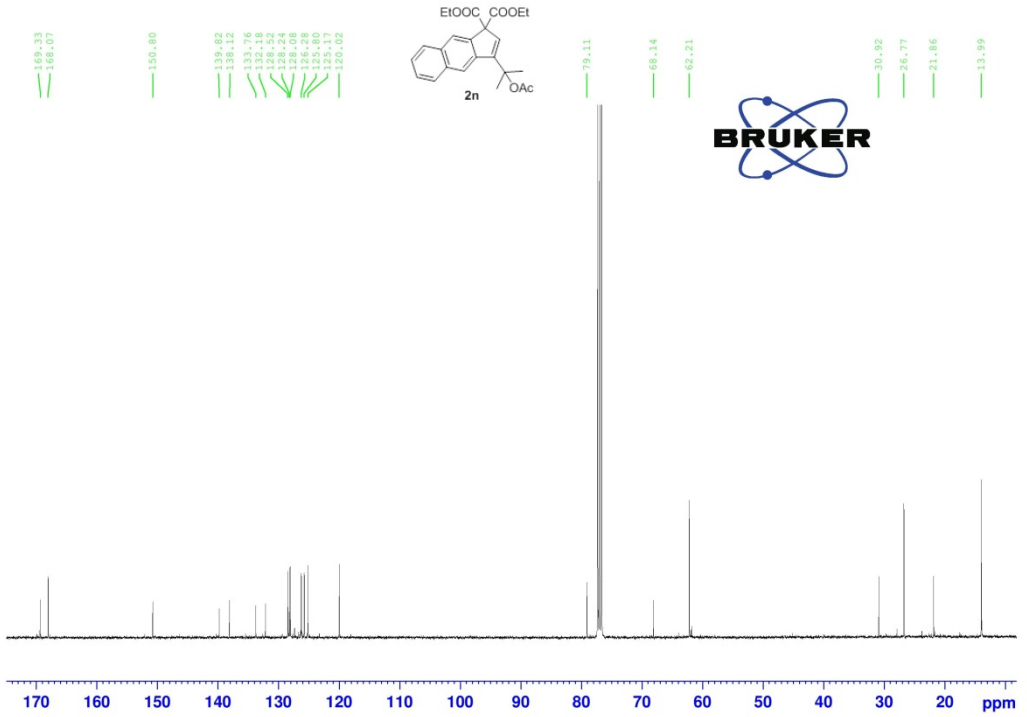
3.01
6.02
5.92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OAc
2n
BRUKER
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138.12
133.76
132.18
128.52
128.34
128.08
126.28
125.80
125.17
120.02
79.11
68.14
62.21
30.92
26.77
21.86
13.99
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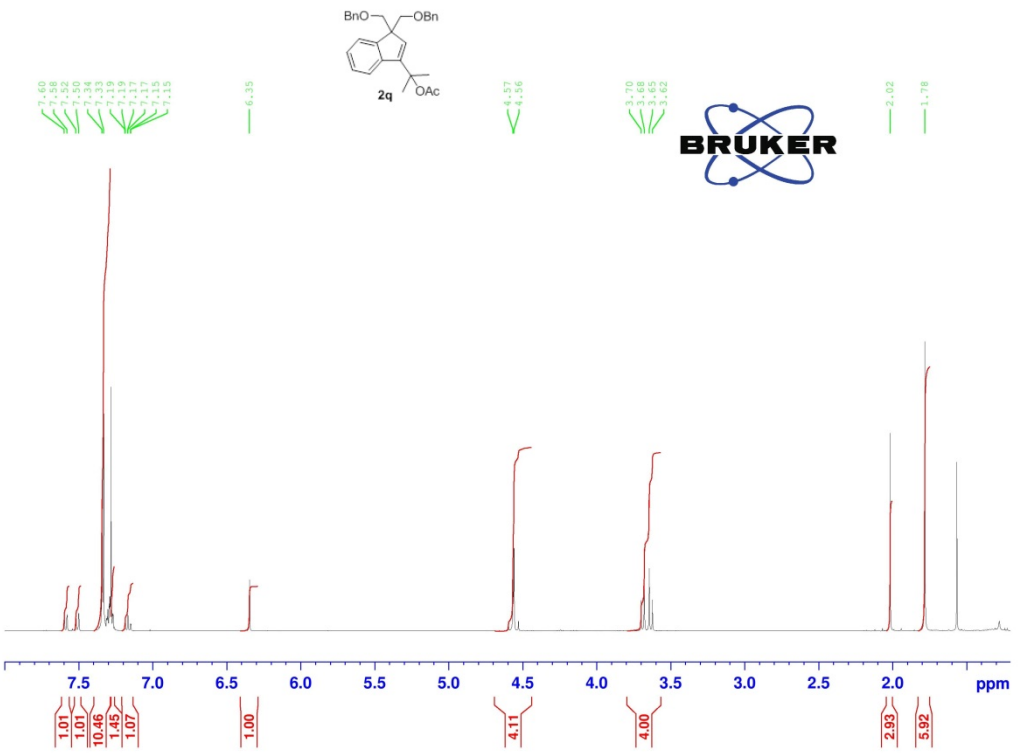
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


BnO
OBn
OAc
2q
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7.52
7.50
7.34
7.33
7.19
7.18
7.17
7.17
7.15
7.15
6.35
4.57
4.56
3.70
3.68
3.65
3.62
2.02
1.78
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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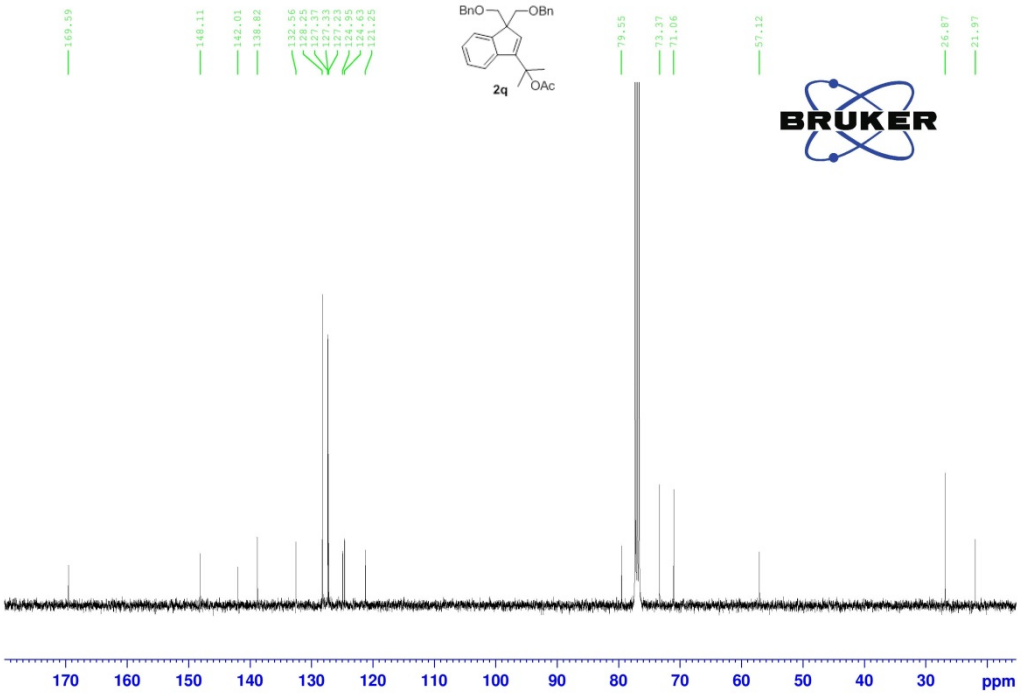
1.01
10.46
1.45
1.07
1.00
4.11
4.00
2.93
5.92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148.11
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132.56
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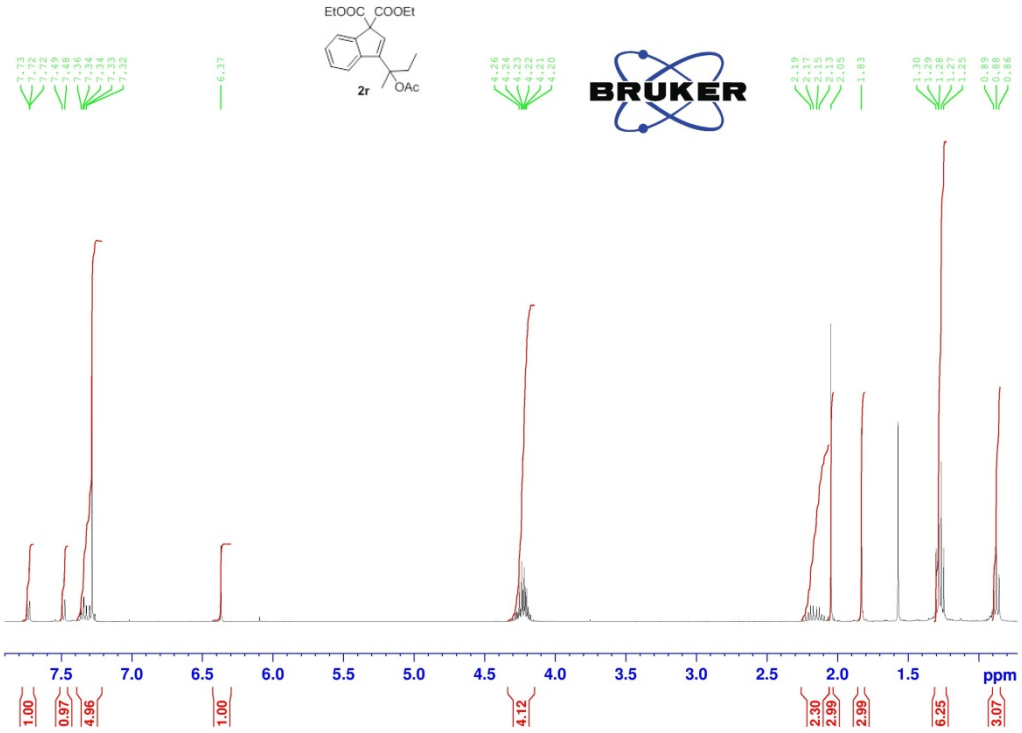
127.37
127.33
127.23
124.95
124.63
121.25
BnO
OBn
OAc
2q
79.55
73.37
71.06
57.12
26.87
21.97
BRUKER
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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2r
OAc
BRUKER
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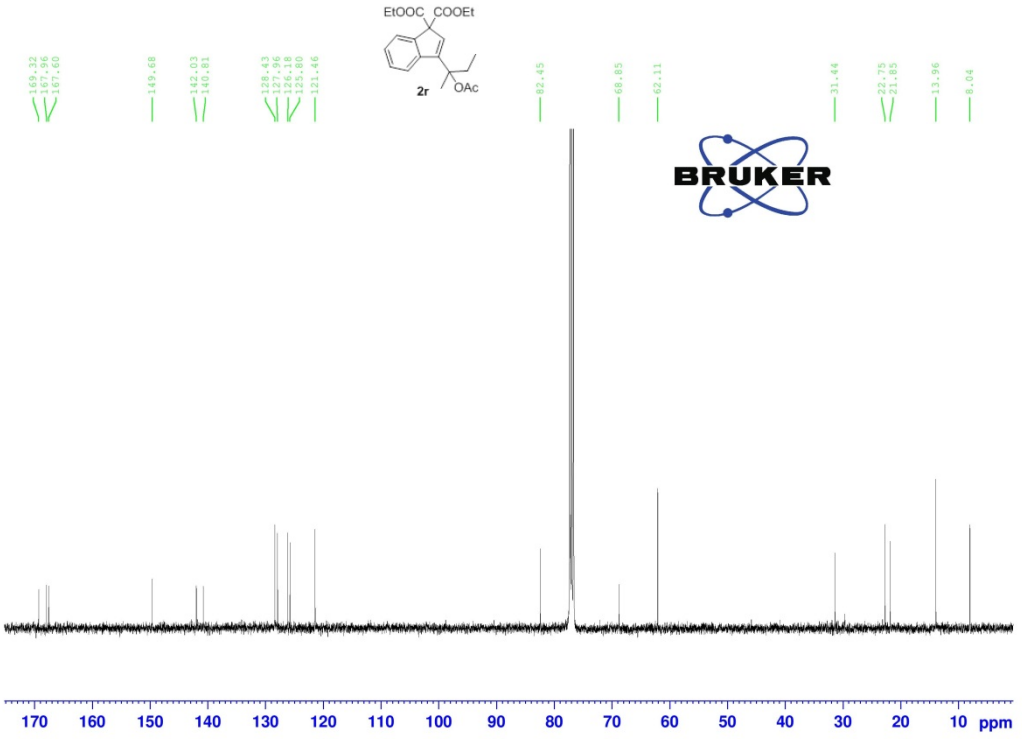
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


EtOOC COOEt
2r
OAc
BRUKER
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150
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70
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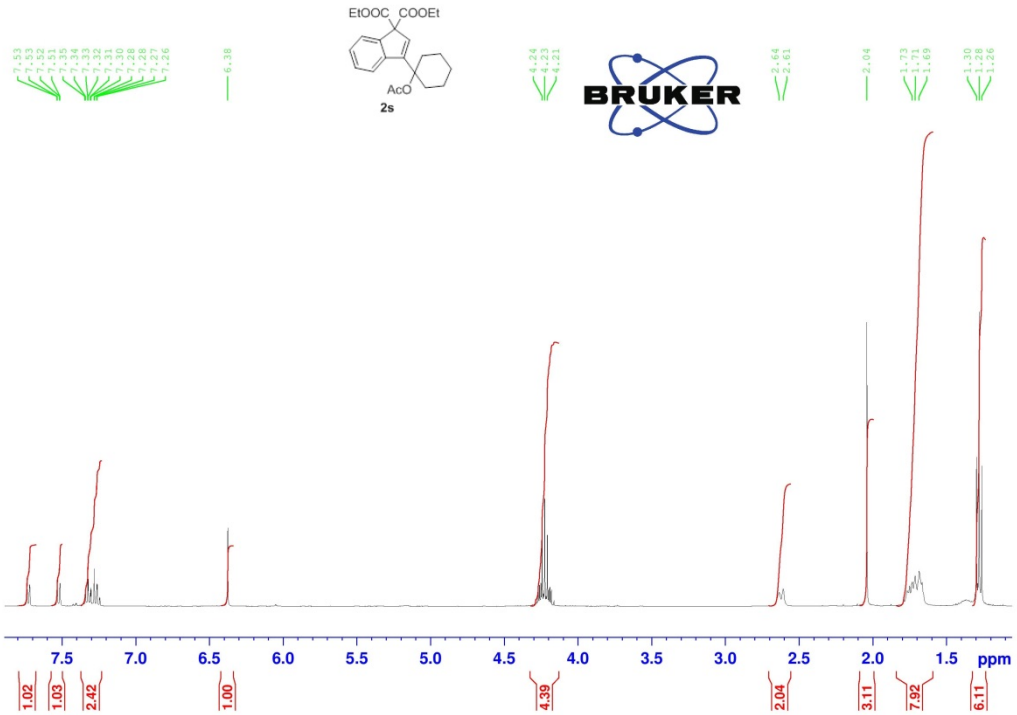
40
30
20
10
ppm


EtOOC COOEt
AcO
2s
BRUKER
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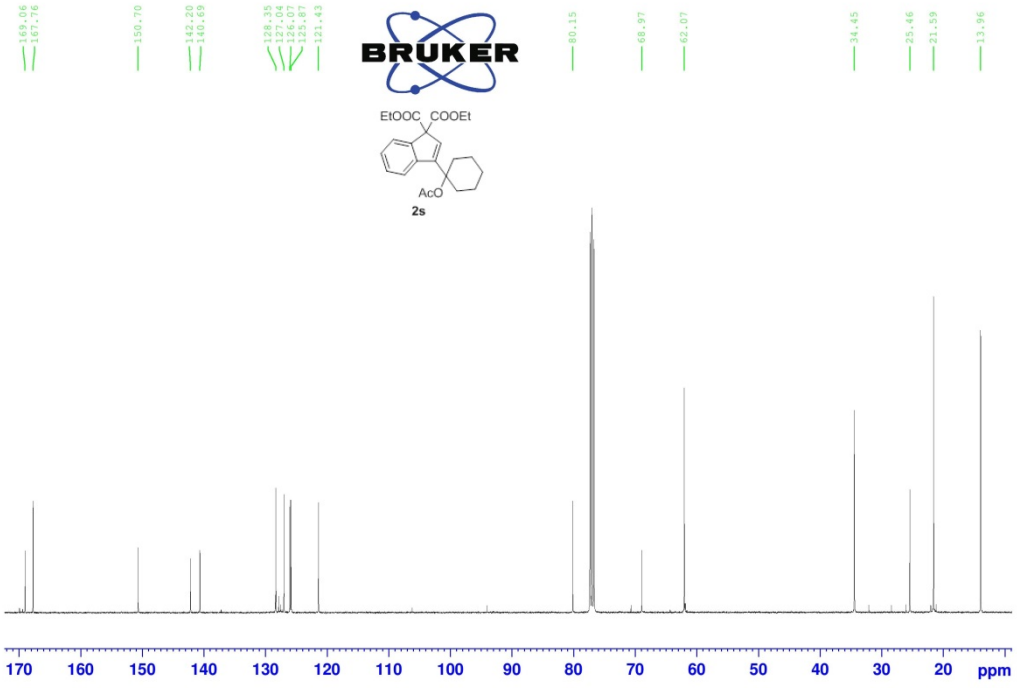
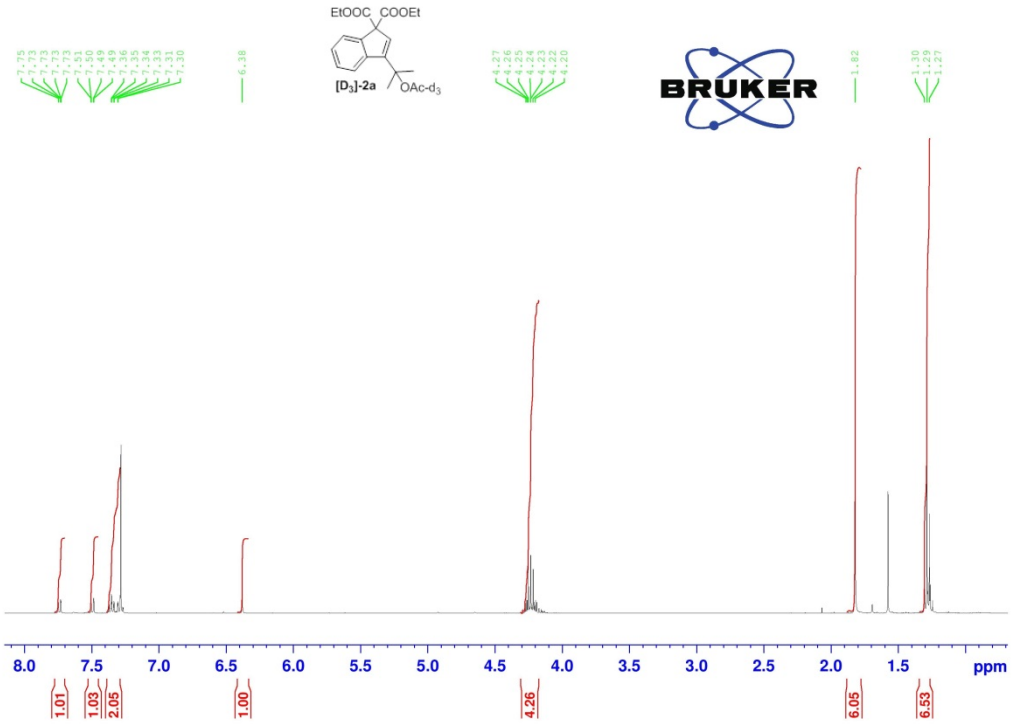
7.53
7.52
7.51
7.35
7.34
7.33
7.32
7.31
7.30
7.28
7.28
7.27
7.26
6.38
4.24
4.23
4.21
2.64
2.61
2.04
1.73
1.71
1.69
1.30
1.28
1.26
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.02
1.03
2.42
1.00
4.39
2.04
3.11
7.92
6.11


169.06
167.76
150.70
142.20
140.69
128.35
127.04
126.07
125.87
121.43
BRUKER
80.15
68.97
62.07
34.45
25.46
21.59
13.96
EtOOC COOEt
AcO
2s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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OAc-d3
BRUKER
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
ppm
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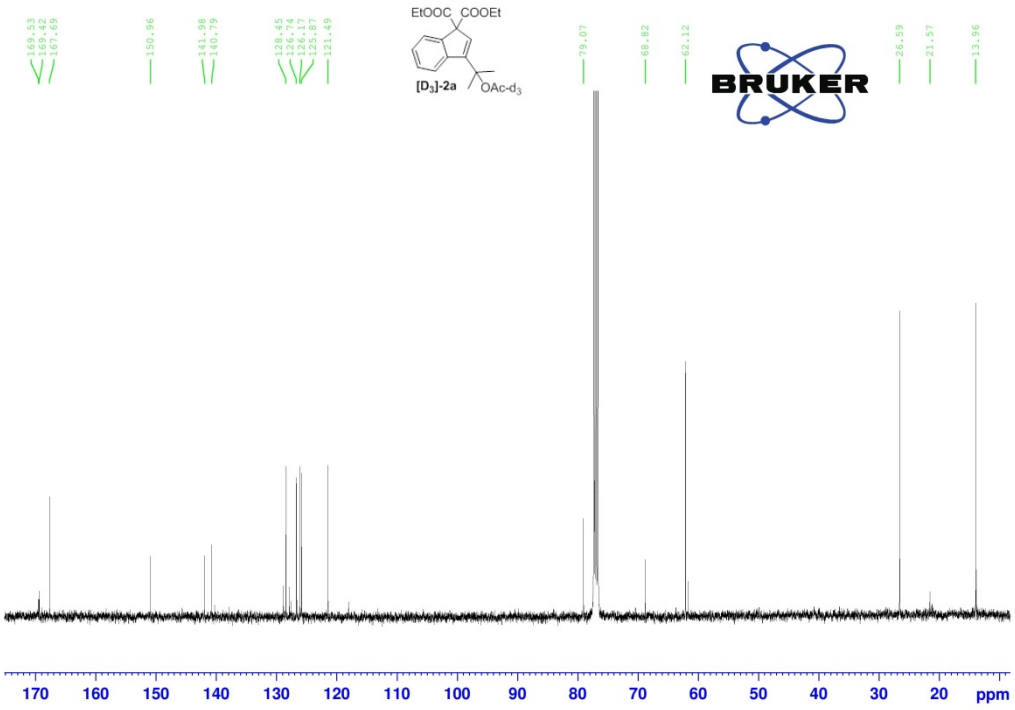
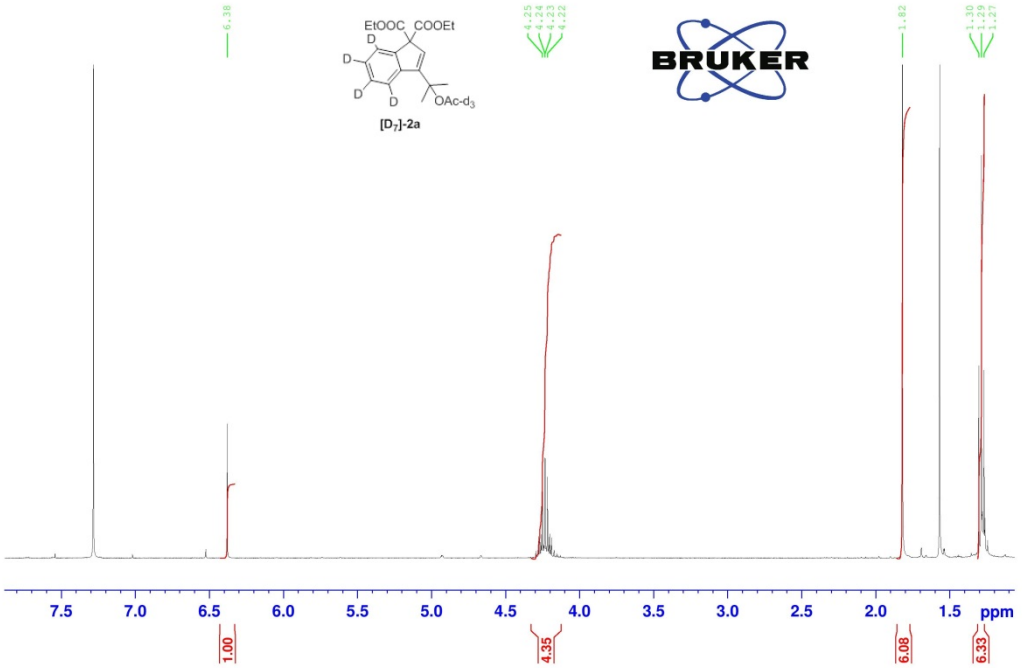
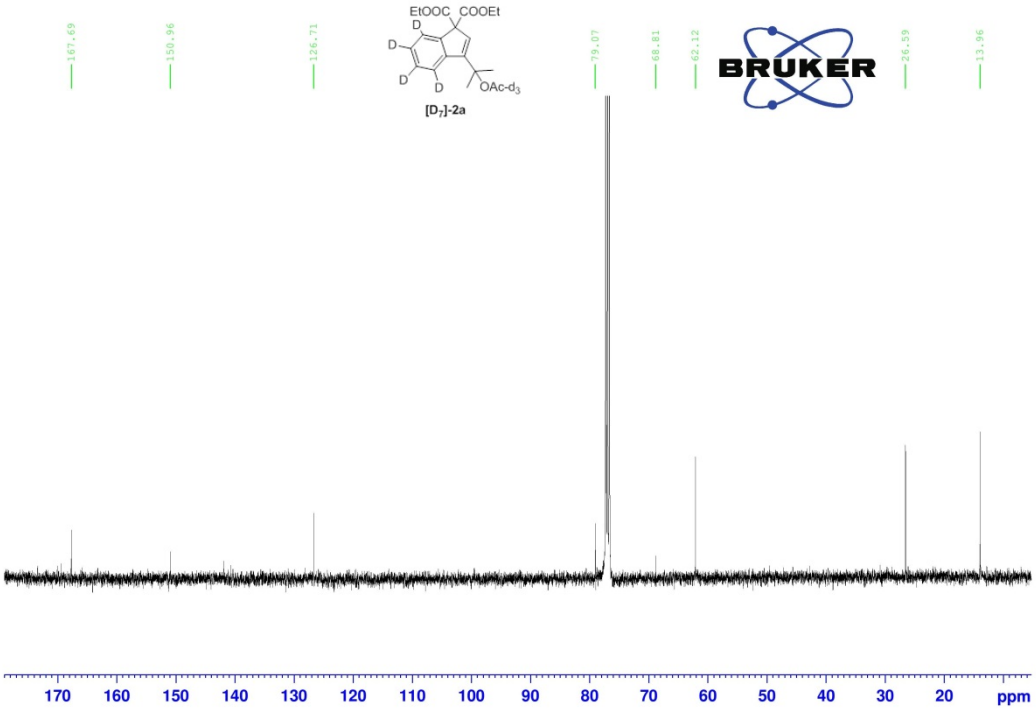
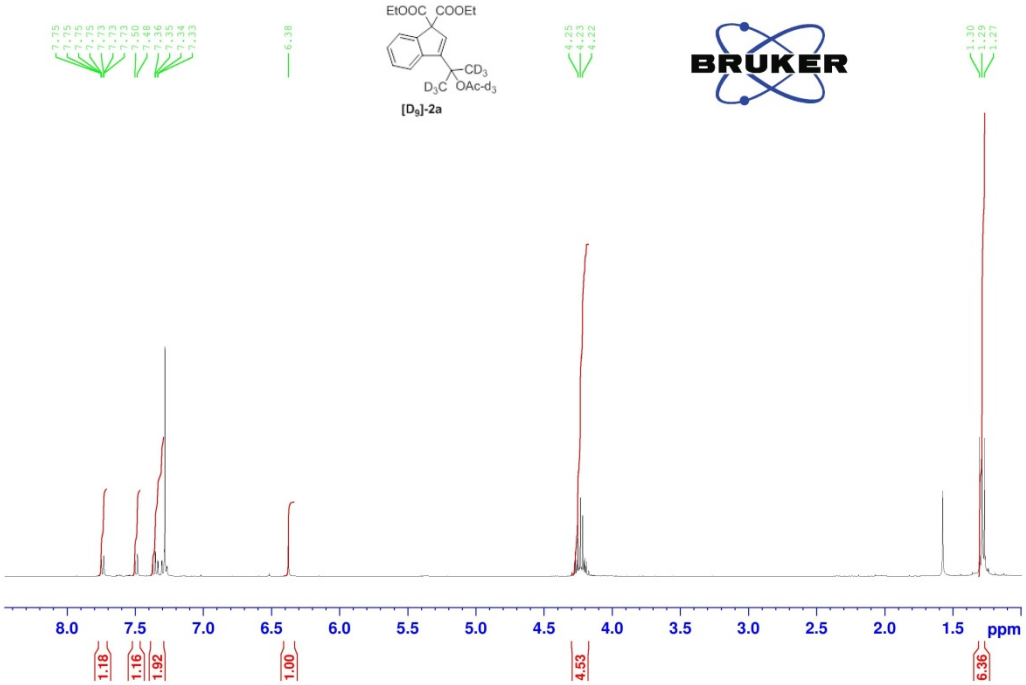
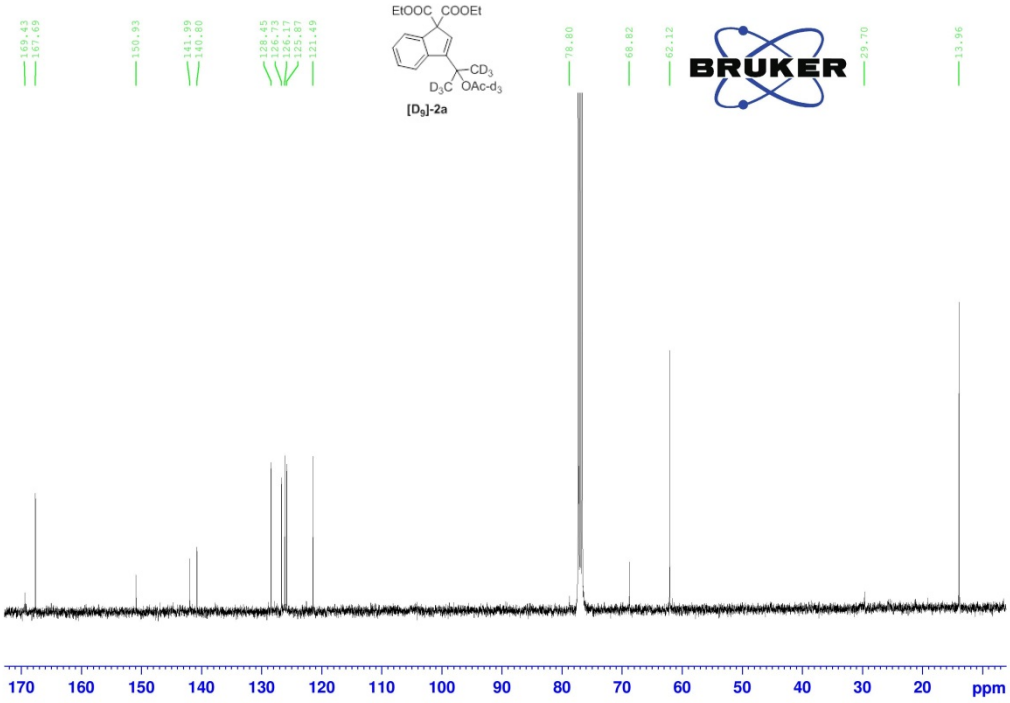
1.03
2.05
1.00
4.26
6.05
6.53

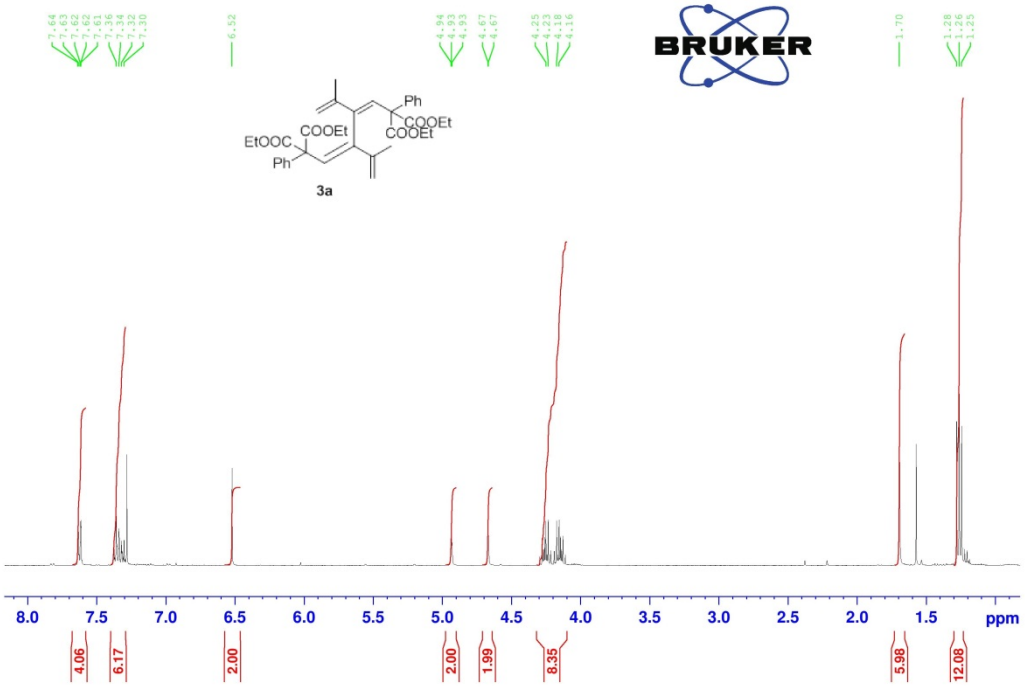

EtOOC COOEt
[D3]-2a
OAc-d3
BRUKER
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

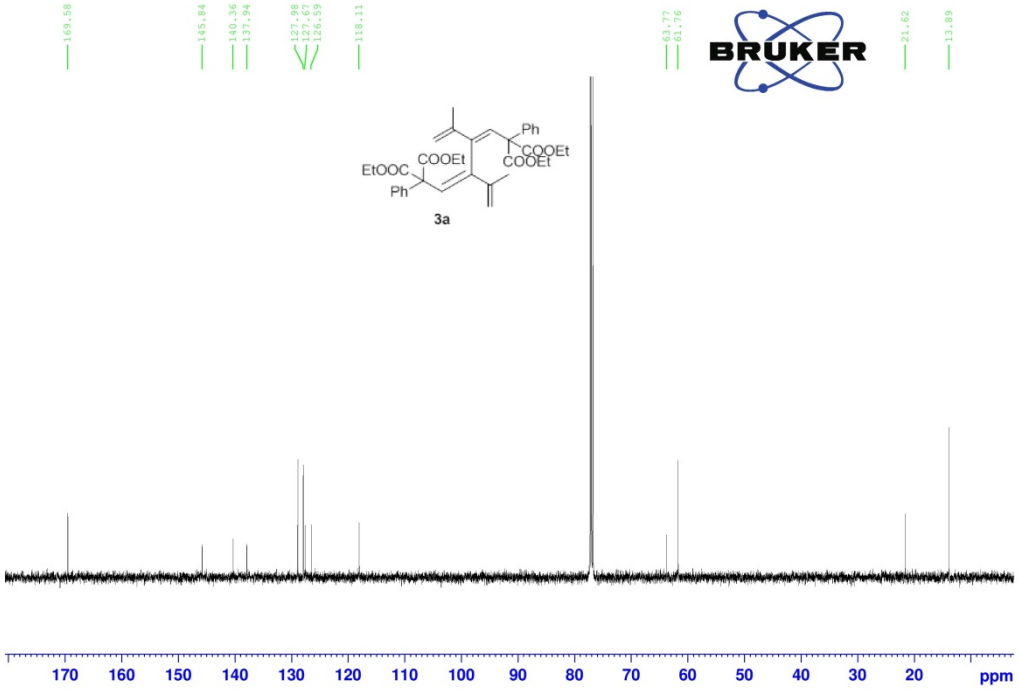

6.38
4.25
4.24
4.23
4.22
1.82
1.30
1.29
1.27
EtOOC COOEt
D
D
D
D
OAc-d3
[D7]-2a
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
4.35
6.08
6.33


167.69
150.96
126.71
79.07
68.81
62.12
26.59
13.96
EtOOC COOEt
D
D
D
D
OAc-d3
[D7]-2a
BRUKER
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


EtOOC COOEt
CD3
D3C OAc-d3
[D8]-2a
BRUKER
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
ppm
1.18
1.16
1.92
1.00
4.53
6.36


EtOOC COOEt
CD3
D3C OAc-d3
[D8]-2a
BRUKER
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.64
7.63
7.62
7.62
7.61
7.36
7.34
7.32
7.30
6.52
4.94
4.93
4.93
4.67
4.67
4.25
4.23
4.18
4.16
1.70
1.28
1.26
1.25
Ph
COOEt
COOEt
EtOOC
COOEt
Ph
3a
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
ppm
4.06
6.17
2.00
2.00
1.99
8.35
5.98
12.08


169.58
145.84
140.36
137.94
127.98
127.67
126.59
118.11
63.77
61.76
21.62
13.89
Ph
COOEt
COOEt
EtOOC
COOEt
Ph
3a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm