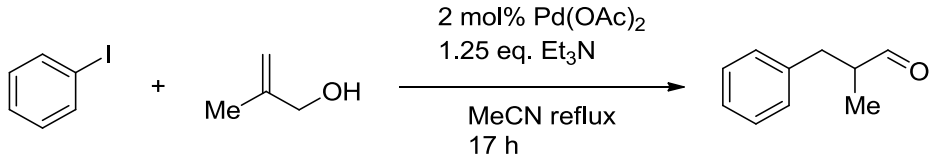
SUPPORTING INFORMATION

GENERAL

All reactions were carried out under an inert atmosphere of nitrogen using either two-manifold vacuum/inert gas lines or a M.Braun glove-box, unless otherwise noted. Solvents were dried over activated alumina columns or by distillation from metallic sodium and further degassed by three successive "freeze-pump-thaw" cycles if necessary.
NMR spectra were recorded on ARX-300 and AMX-400 Bruker Avance spectrometers at 298K unless otherwise noted. Deuterated solvents: from Cambridge Isotope Laboratories. Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t) and quartet (q) with coupling constants (J) given in Hz, or multiplet (m). Broad peaks are marked as "br". ^{1}H and ^{13}C resonances were assigned with the aid of additional information from 1-D & 2-D NMR spectra (H,H-COSY, DEPT 135, HSQC, HMBC and NOESY). ^{1}H and ^{13}C NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. $^{1}HNMR$ spectra were referenced to $CDCl_3$ (7.26 ppm) or C_6D_6 (7.15 ppm) and $^{13}CNMR$ spectra were referenced to $CDCl_3$ (77.36 ppm) or C_6D_6 (128.62 ppm) unless otherwise indicated. $^{31}P\{^{1}H\}NMR$ chemical shifts are reported in ppm relative to H_3PO_4. $^{19}F\{^{1}H\}NMR$ chemical shifts are reported in ppm with absolute reference to ^{1}H.
Infrared spectra were obtained on a Perkin-Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler.
The mass spectrometric data were obtained at the mass spectrometry facility of the University of Geneva (http://www.ms.unige.ch/sms).
Chiral HPLC analyses were performed on Shimadzu CTO-20AA. Retention times (R_t) are given in minutes.
Commercial reagents were purchased from Aldrich, Acros or Strem and used without further purification, unless otherwise noted. Liquid reagents were transferred with stainless steel syringes or cannula.
Thin layer chromatography (TLC) was performed on plates of silica pre-coated with 0.25 mm Kieselgel 60 F_{254}. Flash chromatography was performed using silica gel 60 (230–400 mesh ASTM) from Aldrich.
3-methylcyclohex-1-enecarbaldehyde **(1h)** was synthesized according to the literature.[1]
(E)-5-methyl-2-phenylhex-2-enal **(13)** was purchased from Sigma-Aldrich and used as received. (*E*)-4-methyl-2-phenylpent-2-enal **(1f)** was purchased from Alfa Aesar and used as received.

DMF = *N*,*N*'-dimethylformamide
DMA = *N*,*N*'-dimethyacetamide
DBU = 1,8-diazabicyclo[5.4.0]unde-7-ene
DIBALH = Diisobutylaluminum hydride
DMP = Dess-Martin periodinane
THF = Tetrahydrofuran

SYNTHESIS OF 2-METHYL-3-PHENYLPROPANAL[2]



In a 250 mL round bottomed flask under N_2, $Pd(OAc)_2$ (480 mg, 2.1 mmol, 0.02 eq.), Et_3N (18.7 mL, 133.8 mmol, 1.25 eq.), phenyl iodide (12.0 mL, 107.1 mmol, 1 eq.) and methallyl alcohol (11.35 mL, 133.82 mmol, 1.25 eq.) were solubilized in 48 mL of dry acetonitrile. The reaction was placed in a pre-heated oil bath (100°C) and refluxed for 17 h. The mixture was cooled to room temperature and then transferred in a 500 mL separatory funnel with 100 mL of Et_2O and 100 mL of distilled water. After separation the organic layer was washed with water (100 mL x 3) and the aqueous phases were extracted with Et_2O. The organic layers were dried over Na_2SO_4 and the solvent evaporated. The crude mixture was first distilled under reduced pressure (65-67°C at 5 mbar) and then purified by chromatography (pentane/Et_2O 20:1; R_f = 0.18) to afford 9.24 g of the aldehyde (58% yield - lit. 60% yield).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

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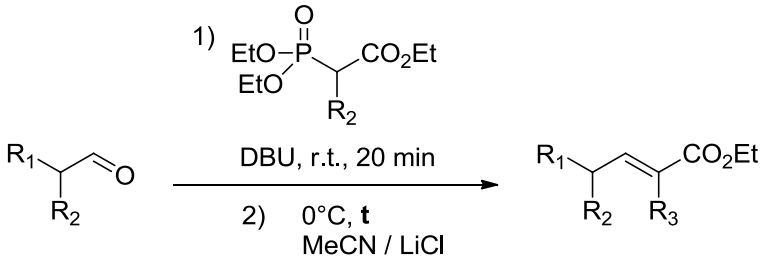
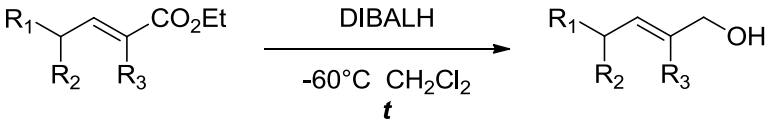
[1] a) S. P. Tanis, M. C. McMills, P. M. Herrinton, *J. Org. Chem.*, 1985, **50**, 5887; b) J. A. Marshall, B. E. Blough, *J. Org. Chem.*, 1990, **55**, 1540
[2] Adapted from S. A. Buntin, R. F. Heck, *Organic Syntheses*, 1990, **coll. Vol. 7**, 361

GENERAL PROCEDURE FOR OLEFINATION[3]



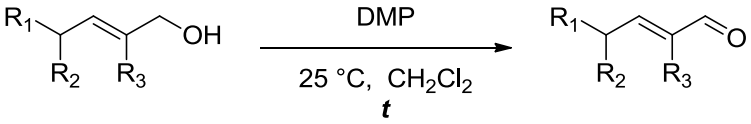
In a 100 mL round bottomed flask anhydrous LiCl (1.02 g, 24.1 mmol, 1.5 eq.) and the appropriate phosphopropionate (24.1 mmol, 1.5 eq.) were dissolved in 40 mL of dry acetonitrile. DBU (3.62 mL, 24.1 mmol, 1.5 eq.) was added drop-wise and the resulting solution was stirred at room temperature for 20 minutes. The system was cooled to 0°C and a solution of the appropriate aldehyde (16.0 mmol, 1 eq.) in 3 mL of dry acetonitrile was added. The reaction was monitored by TLC (pentane/Et_2O) until complete conversion of the starting material. The reaction was quenched with 100 mL of a saturated NH_4Cl. The aqueous phase was extracted with Et_2O (15 mL x 3). The organic layers were separated and dried over Na_2SO_4. After evaporation of the solvent, the crude mixture was purified by flash chromatography (pentane/Et_2O). Olefin isomers were separated at this stage (when applicable).

GENERAL PROCEDURE FOR REDUCTION WITH DIBALH[4]



In a 250 mL two-necked round bottomed flask the ester (7.1 mmol, 1 eq.) was dissolved in 70 mL of dry dichloromethane. The system was cooled to -60°C and DIBALH (14.3 mL, 1M solution in hexanes, 14.3 mmol, 2 eq.) was added drop-wise. The reaction was stirred at -78°C and monitored by TLC (pentane/Et_2O) until complete conversion of the starting material. The solution was quenched with 25 mL of a saturated aqueous solution of potassium sodium tartrate. The reaction was warmed to room temperature and the water phase was extracted with dichloromethane (25 mL x 3). The organic phases were separated, combined and dried over Na_2SO_4. After evaporation of the solvent the crude mixture was purified by flash chromatography (pentane/Et_2O) to afford the alcohol.

GENERAL PROCEDURE FOR OXIDATION WITH DESS-MARTIN PERIODINANE

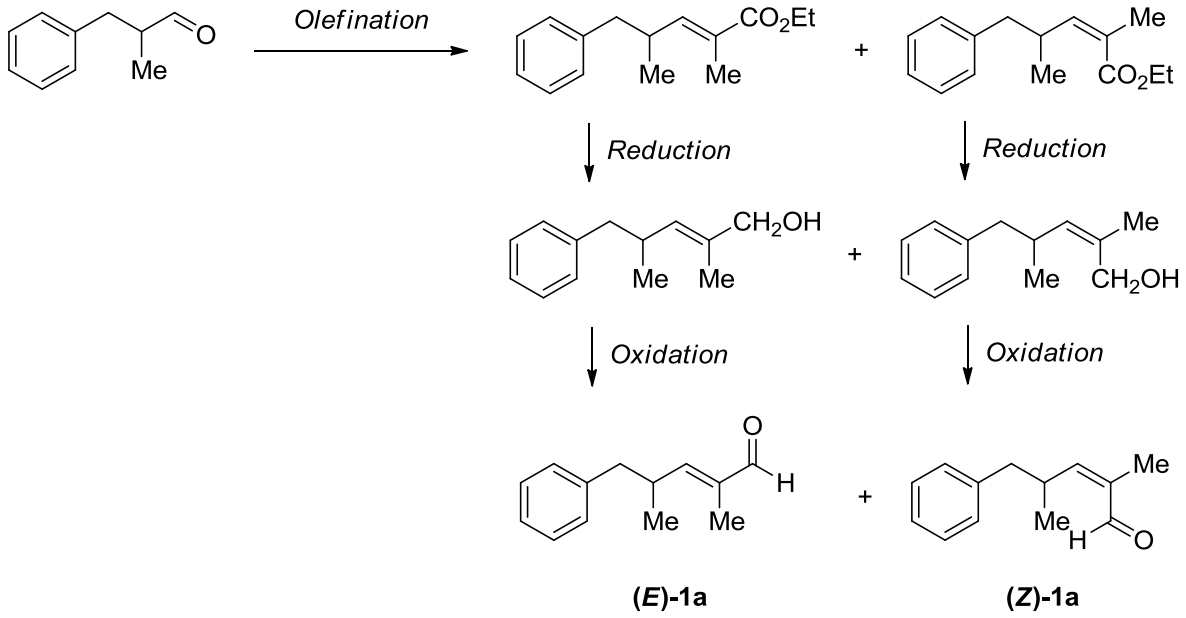


In a 250 mL, two-necked flask the alcohol (8.7 mmol, 1 eq.) was dissolved in 87 mL of dichloromethane. Dess-Martin periodinane[5] (6.27 g, 14.8 mmol, 1.7 eq.) was added in one portion and the reaction was stirred at room temperature while monitoring the reaction by TLC (pentane/Et_2O) until complete conversion of the starting material. The solution was quenched with 60 mL of a 1/1 (v/v) solution of saturated $NaHCO_3$ and saturated $Na_2S_2O_3$ for 15 minutes. The aqueous phase was extracted with dichloromethane (30 mL x 2), the combined organic layers were dried over Na_2SO_4 and the solvent evaporated. The crude mixture was purified by flash chromatography (pentane/Et_2O) to afford the aldehyde.

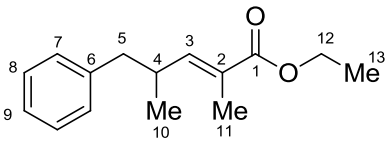
[3] Adapted from C. C. Browder, F. P. Marmsäter, F. G. West, *Org. Lett.*, 2001, **19**, 3033
[4] Adapted from C. C. Browder, F. P. Marmsäter, F. G. West, *Org. Lett.*, 2001, **19**, 3033
[5] Synthesized according to R. K. Boeckman, P. Shao, J. J. Mullins, *Organic Syntheses*, 2004, **coll. Vol. 10**, 696

SYNTHESIS OF 2,4-dimethyl-5-phenylpent-2-enal (1a)

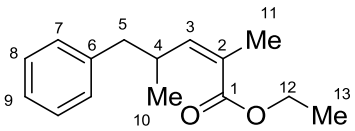
For the synthesis of 2,4-dimethyl-5-phenylpent-2-enal the previous general olefination, reduction and DMP oxidation procedures were used starting from 2-methyl-3-phenylpropanal.



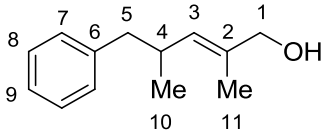
(*E*)-1a **(*Z*)-1a**



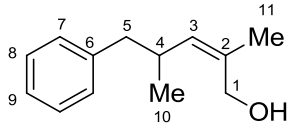
(*E*)-ethyl 2,4-dimethyl-5-phenylpent-2-enoate (56 % yield) Colorless oil (Pentane/Et_2O 25:1, R_f = 0.26). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ(ppm) = 1.03 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-10); 1.29 (t, $^3J_{HH}$ = 7.15 Hz, 3H, H-13); 1.67 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-11); 2.59-5.68 (m, $^3J_{HH}$ = 7.15 Hz, 2H, H-5); 2.74-2.79 (m, 1H, H-4); 4.17 (q, $^3J_{HH}$ = 7.15 Hz, 2H, H-12); 6.61 (dq, $^3J_{HH}$ = 9.90 Hz, $^4J_{HH}$ = 1.38 Hz, 1H, H-3); 7.13-7.14 (m, 2H, H-7); 7.17-7.20 (m, 1H, H-9) ; 7.24-7.27 (m, 2H, H-8). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ(ppm) = 12.61 (C-11) ; 14.60 (C-13) ; 19.92 (C-10) ; 35.73 (C-4) ; 43.17 (C-5) ; 60.73 (C-12) ; 126.33 (C-9) ; 127.17 (C-2) ; 128.53 (C-8) ; 129.42 (C-7) ; 140.23 (C-6) ; 146.95 (C-3) ; 168.61 (C-1). **HRMS** (ESI Positive) calculated for 255.1355 $[M+Na]^+$, found 255.1355. **IR spectrum (neat)** ν (cm^{-1}) = 2960, 1706, 1649, 1453, 1249, 1116, 742.



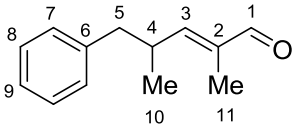
(*Z*)-ethyl 2,4-dimethyl-5-phenylpent-2-enoate (27 % yield) Pale yellow oil (Pentane/Et_2O 25:1, R_f = 0.34). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ(ppm) = 0.98 (d, $^3J_{HH}$ = 6.88 Hz, 3H, H-10) ; 1.30 (t, $^3J_{HH}$ = 7.01 Hz, 3H, H-13) ; 1.89 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-11) ; 2.52 (dd, $^2J_{HH}$ = 13.34 Hz, $^3J_{HH}$ = 7.84 Hz, 1H, H-5) ; 2.71 (dd, $^2J_{HH}$ = 13.34 Hz, $^3J_{HH}$ = 7.84 Hz, 1H, H-5') ; 3.46-3.52 (m, 1H, H-4) ; 4.18 (q, $^3J_{HH}$ = 7.01 Hz, 2H, H-12) ; 5.75 (dq, $^3J_{HH}$ = 9.90 Hz, $^4J_{HH}$ = 1.38 Hz, 1H, H-3) ; 7.17-7.20 (m, 3H, H-7 and H-9) ; 7.26-7.29 (m, 2H, H-8). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ(ppm) = 14.59 (C-13) ; 20.18 (C-10) ; 21.08 (C-11) ; 35.33 (C-5) ; 60.37 (C-12) ; 126.14 (C-9) ; 126.49 (C-6) ; 128.39 (C-8) ; 129.53 (C-7) ; 140.53 (C-2) ; 147.88 (C-3) ; 168.30 (C-1). **HRMS** (ESI Positive) calculated for 187.1118 $[M-C_2H_5O]^+$, found 118.1117. **IR spectrum (neat)** ν (cm^{-1}) = 2979, 1711, 1454, 1370, 1234, 1192, 1155, 1119, 1028, 772, 743, 699.



(*E*)-2,4-dimethyl-5-phenylpent-2-enol (96 % yield) Colorless oil (Pentane/Et_2O 9:1, R_f = 0.10). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.99 (d, $^3J_{HH}$ = 6.6Hz, 3H, H-10); 1.43 (br s, 1H, -OH); 1.50 (d, $^4J_{HH}$ = 1.3Hz, 3H, H-11); 2.58 (d, $^3J_{HH}$ = 7.2 Hz, 2H, H-5); 2.64-2.75 (m, 1H, H-4); 3.95 (d, $^4J_{HH}$ = 0.7Hz, 2H, H-1); 5.26 (dq, $^4J_{HH}$ = 1.2Hz, $^3J_{HH}$ = 9.3Hz, 1H, H-3); 7.14-7.17 (m, 2H, H-7); 7.18-7.21 (m, 1H, H-9); 7.25-7.29 (m, 2H, H-8). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 13.96 (C-11); 20.81 (C-10); 34.53 (C-4); 44.01 (C-5); 69.17 (C-1); 126.06 (C-9); 128.34 (C-8); 129.53 (C-7); 131.89 (C-3); 134.21 (C-2); 141.12 (C-6). **HRMS** (ESI Positive) calculated for 208.1695 $[M+NH_4]^+$, found 208.1688. **IR spectrum (neat)** ν (cm^{-1}) = 3357, 3026, 2955, 2921, 2866 1603, 1494, 1452, 1373, 1217, 1067, 1005, 848, 804, 743, 697, 595.

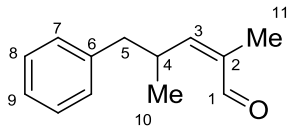


(*Z*)-2,4-dimethyl-5-phenylpent-2-enol (88 % yield) Pale yellow oil (Pentane/Et_2O 9:1, R_f = 0.13). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 0.37-0.39 (br m, 1H, -OH); 1.05 (d, $^3J_{HH}$ = 6.62 Hz, 3H, H-10) ; 1.72 (d, $^4J_{HH}$ = 1.58 Hz, 3H, H-11) ; 2.39-2.44 (m, 1H, H-5) ; 2.67-2.72 (m, 2H, H-4 and H-5') ; 3.66 (dd, $^2J_{HH}$ = 11.82 Hz, $^3J_{HH}$ = 8.04 Hz, 1H, H-1) ; 3.79 (dd, $^2J_{HH}$ = 11.82 Hz, $^3J_{HH}$ = 3.94 Hz, 1H, H-1') ; 5.06 (br d, $^4J_{HH}$ = 1.58 Hz, 1H, H-3) ; 7.13-7.15 (m, 2H, H-7) ; 7.20 (tt, $^3J_{HH}$ = 7.25 Hz, $^4J_{HH}$ = 1.26 Hz, 1H, H-9) ; 7.28-7.31 (m, 2H, H-8). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 21.48 (C-11); 21.92 (C-10); 35.34 (C-4); 44.55 (C-5); 62.00 (C-1); 126.27 (C-8); 128.40 (C-9); 129.62 (C-7); 133.60 (C-3); 134.22 (C-2); 141.41 (C-6). **HRMS** (ESI Positive) calculated for 190.1352 $[M]^+$, found 190.1355. **IR spectrum (neat)** ν (cm^{-1}) = 3319, 2956, 2922, 1494, 1452, 1374, 1003, 743, 698.



(*E*)-1a

(*E*)-2,4-dimethyl-5-phenylpent-2-enal (Table 1) (94 % yield) Colorless oil (Pentane/Et_2O 9:1, R_f = 0.28). **^{1}H NMR ($CDCl_3$, 400MHz MHz)** δ (ppm) = 1.13 (d, $^3J_{HH}$ = 6.6Hz, 3H, H-10); 1.56 (d, $^4J_{HH}$ = 1.3Hz, 3H, H-11); 2.65-2.78 (m, 2H, H-5); 2.95-3.06 (m, 1H, H-4); 6.31 (dd, $^4J_{HH}$ = 1.3Hz, $^3J_{HH}$ = 9.9Hz, 1H, H-3), 7.13-7.15 (m, 2H, H-7); 7.18-7.22 (m, 1H, H-9); 7.26-7.30 (m, 2H, H-8); 9.38 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 9.46 (C-11); 19.93 (C-10); 36.00 (C-4); 43.02 (C-5); 126.61 (C-9); 128.68 (C-8); 129.35 (C-7); 138.73 (C-2); 139.66 (C-6); 159.32 (C-3); 195.79 (C-1). **HRMS** (ESI Positive) calculated for 188.1196 $[M]^+$, found 188.1267. **IR spectrum (neat)** ν (cm^{-1}) = 3028, 2962, 2926, 2707, 1682, 1640, 1494, 1453, 1405, 1378, 1314, 1236, 1085, 1051, 1016, 812, 744, 699, 674, 596.



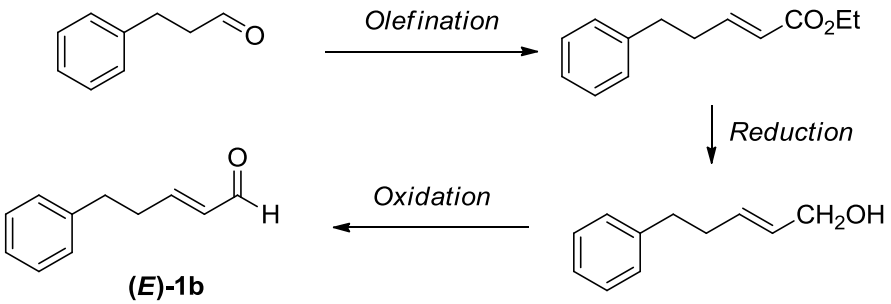
(*Z*)-1a

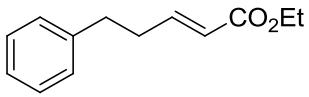
(*Z*)-2,4-dimethyl-5-phenylpent-2-enal (Scheme 2) (87 % yield) Colorless oil (Pentane/Et_2O 8:1, R_f = 0.37). **^{1}H NMR (C_6D_6 , 500 MHz)** δ (ppm) = 0.72 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-10); 1.65 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-11); 2.20 (dd, $^2J_{HH}$ = 13.34 Hz, $^3J_{HH}$ = 7.84 Hz, 1H, H-5); 2.27 (dd, $^2J_{HH}$ = 13.34 Hz, $^3J_{HH}$ = 7.84 Hz, 1H, H-5'); 2.99-3.05 (m, 1H, H-4); 5.74 (dq, $^3J_{HH}$ = 10.60 Hz, $^4J_{HH}$ = 1.38 Hz, 1H, H-3); 6.81-6.83 (m, 2H, H-7); 7.02-7.04 (m, 1H, H-9); 7.07-7.10 (m, 2H, H-8); 9.74 (s, 1H, H-1). **^{13}C{^{1}H} NMR (C_6D_6 , 125 MHz)** δ (ppm) = 17.18 (C-11);

21.38 (C-10); 33.54 (C-4); 44.28 (C-5); 127.20 (C-9); 129.16 (C-8); 129.97 (C-7); 136.05 (C-2); 140.08 (C-6); 152.72 (C-3); 190.36 (C-1). **HRMS** (ESI Positive) calculated for 188.1196 $[M]^+$, found 188.1195. **IR spectrum (neat)** ν (cm^{-1}) = 2925, 1673, 1453, 1023, 744, 699.

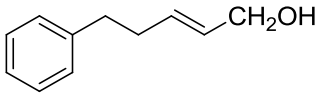
SYNTHESIS OF (2*E*)-5-phenylpent-2-enal (1b)

For the synthesis of (2*E*)-5-phenylpent-2-enal the previous general olefination, reduction and DMP oxidation procedures were used starting from commercial 3-phenylpropanal.

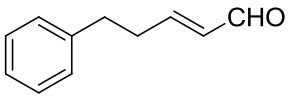




(*E*)-ethyl 5-phenylpent-2-enoate (72 % yield) Colorless oil (Pentane/Et_2O 20:1, R_f = 0.22).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.



(*E*)-5-phenylpent-2-enol (60 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.27).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

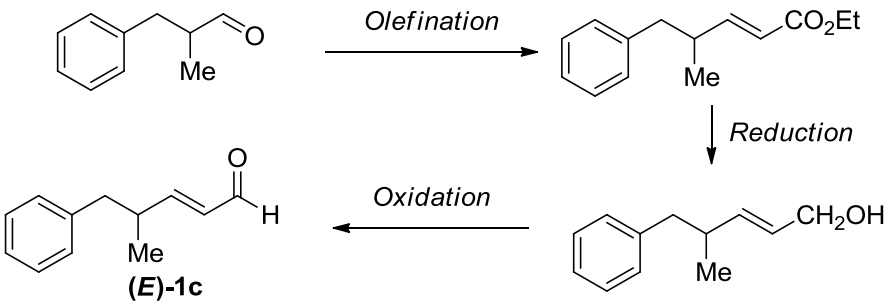


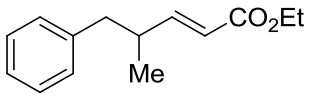
(*E*)-1b

(*E*)-5-phenylpent-2-enal (Scheme 1) (97 % yield) Brown oil (Pentane/Et_2O 1:1, R_f = 0.55).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

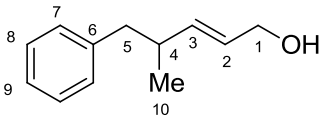
SYNTHESIS OF (2*E*)-4-methyl-5-phenylpent-2-enal (1c)

For the synthesis of (2*E*)-4-methyl-5-phenylpent-2-enal the previous general olefination, reduction and DMP oxidation procedures were used starting from 2-methyl-3-phenylpropanal.

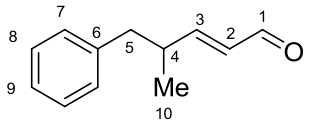




(*E*)-ethyl 4-methyl-5-phenylpent-2-enoate (86 % yield) Colorless oil (Pentane/Et_2O 9:1, R_f = 0.41).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.



(*E*)-4-methyl-5-phenylpent-2-enal (90 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.36).
^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) = 1.01 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-10); 2.46-2.57 (m, 2H, H-4 and H-5); 2.70 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, H-5'); 4.06 (d, $^3J_{HH}$ = 6.0 Hz, 2H, H-1); 5.57 (dtd, $^3J_{HH}$ = 5.7 Hz, $^3J_{HH}$ = 15.4 Hz, $^4J_{HH}$ = 0.95 Hz, 1H, H-2); 5.67 (ddt, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 15.4 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H-3); 7.14-7.15 (m, 2H, H-7); 7.19 (tt, $^3J_{HH}$ = 7.6 Hz, 1H, H-9); 7.26-7.29 (m, 2H, H-8). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 19.94 (C-10); 38.32 (C-4); 43.67 (C-5); 64.07 (C-1); 126.18 (C-9); 127.84 (C-2); 128.44 (C-8); 129.54 (C-7); 138.42 (C-3); 140.87 (C-6). **HRMS** (ESI Positive) calculated for 176.1196 $[M]^+$, found 176.1195. **IR spectrum (neat)** ν (cm^{-1}) = 3303, 3026, 2958, 2922, 2867, 1494, 1453, 1004, 969, 740, 697.

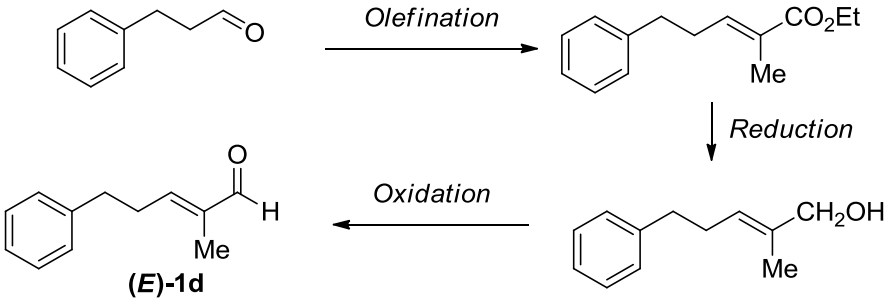


(*E*)-1c

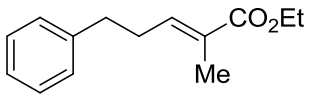
(*E*)-4-methyl-5-phenylpent-2-enal (Scheme 1) (91 % yield) Colorless oil (Pentane/Et_2O 7:1, R_f = 0.48).
^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) = 1.12 (d, $^3J_{HH}$ = 6.3 Hz, 3H, H-10); 2.66-2.71 (m, 1H, H-5); 2.74-2.79 (m, 2H, H-4 and H-5'); 6.06 (ddd, $^3J_{HH}$ = 7.88 Hz, $^3J_{HH}$ = 15.76 Hz, $^4J_{HH}$ = 0.95 Hz, 1H, H-2); 6.79 (dd, $^3J_{HH}$ = 6.62 Hz, $^3J_{HH}$ = 15.76 Hz, 1H, H-3); 7.14-7.16 (m, 2H, H-7); 7.20-7.24 (m, 1H, H-9); 7.28-7.31 (m, 2H, H-8); 9.48 (d, $^3J_{HH}$ = 7.88 Hz, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 18.95 (C-10); 38.88 (C-4); 42.54 (C-5); 126.70 (C-9); 128.73 (C-8); 129.35 (C-7); 131.73 (C-6); 139.37 (C-2); 163.02 (C-3); 194.41 (C-1). **HRMS** (ESI Positive) calculated for 174.1039 $[M]^+$, found 174.1038. **IR spectrum (neat)** ν (cm^{-1}) = 3028, 2966, 2927, 1686, 1633, 1454, 1144, 1120, 976, 742, 699.

SYNTHESIS OF (2*E*)-2-methyl-5-phenylpent-2-enal (1d)

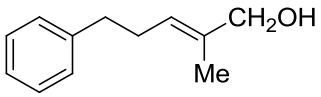
For the synthesis of (2*E*)-2-methyl-5-phenylpent-2-enal the previous general olefination, reduction and DMP oxidation procedures were used starting from commercial 3-phenylpropanal.



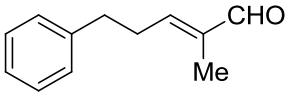
(*E*)-1d



(*E*)-ethyl 2-methyl-5-phenylpent-2-enoate (78 % yield) Colorless oil (Pentane/Et_2O 10:1, R_f = 0.32).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.



(*E*)-2-methyl-5-phenylpent-2-enol (90 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.31).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

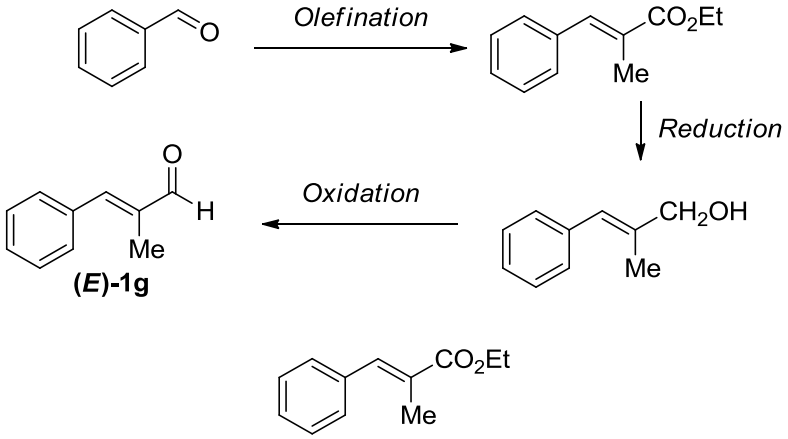


(*E*)-1d

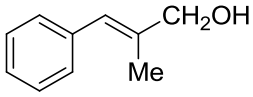
(*E*)-2-methyl-5-phenylpent-2-enal (Scheme 1) (81 % yield) Colorless oil (Pentane/Et_2O 7:1, R_f = 0.27).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

SYNTHESIS OF (*E*)-3-cyclohexyl-2-methylprop-2-enal (1g)

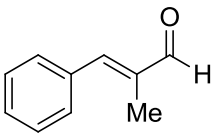
For the synthesis of (*E*)-3-cyclohexyl-2-methylprop-2-enal the previous general olefination, reduction and DMP oxidation procedures were used starting from commercial cyclohexane-carboxaldehyde.



(*E*)-ethyl 3-cyclohexyl-2-methylacrylate (67 % yield) Colorless oil (Pentane/Et_2O 5:1, R_f = 0.0.58).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.



(*E*)-3-cyclohexyl-2-methylprop-2-en-1-ol (75 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.41).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

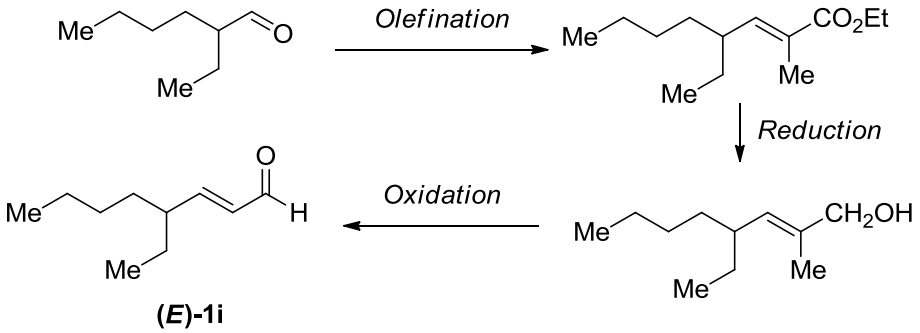


(*E*)-1g

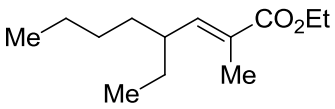
(*E*)-3-cyclohexyl-2-methylprop-2-enal (Scheme 3) (96 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.64).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

SYNTHESIS OF (*E*)-4-ethyl-2-methyloct-2-enal (1i)

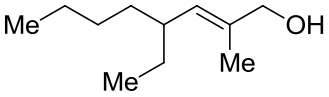
For the synthesis of (E)-4-ethyl-2-methyloct-2-enal the previous general olefination, reduction and DMP oxidation procedures were used starting from commercial 2-ethylexanal.



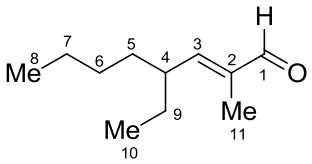
(*E*)-1i



(*E*)-ethyl 4-ethyl-2-methyloct-2-enoate (80 % yield) Colorless oil.
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.



(*E*)-4-ethyl-2-methyloct-2-en-1-ol (97 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.24).
All spectrometric and spectroscopic analyses are consistent with the data reported in literature.

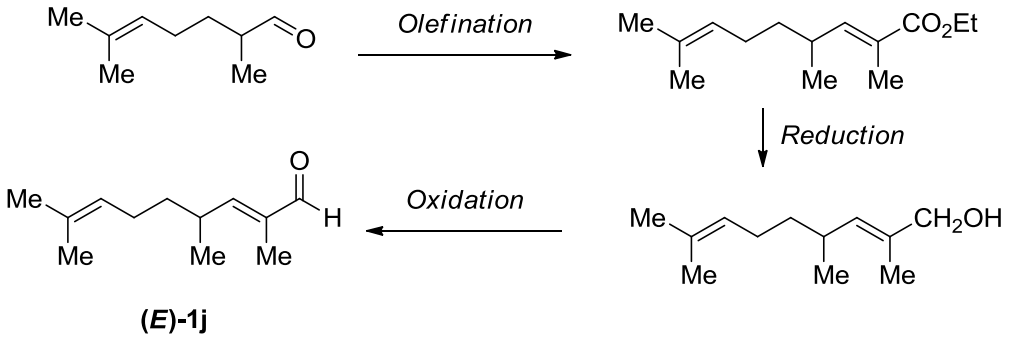


(*E*)-1i

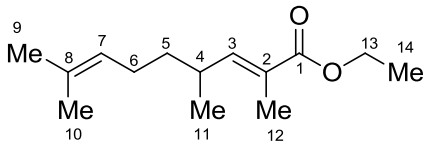
(*E*)-4-ethyl-2-methyloct-2-enal (Scheme 3) (98 % yield) Colorless oil (Pentane/Et_2O 7:1, R_f = 0.66).
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 0.82-0.88 (m, 6H, H-8 and H-10); 1.15-1.36 and 1.48-1.59 (2m, 6H and 2H, H-5, 6, 7 and H-9); 1.74 (d, $^4J_{HH}$ = 1.23 Hz, 3H, H-11); 2.44-2.54 (m, 1H, H-4); 6.20 (dq, $^3J_{HH}$ = 10.38 Hz, $^4J_{HH}$ = 1.23 Hz, 1H, H-3); 9.41 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 10.06 (C-11); 12.14 (C-10); 14.32 (C-8); 23.14 (C-7); 28.27 (C-9); 29.94 (C-6); 34.87 (C-5); 41.25 (C-4); 139.71 (C-2); 160.28 (C-3); 195.89 (C-1). **LRMS** (ESI Positive) calculated for 169.2 $[M+H]^+$, found 169.6. **IR spectrum (neat)** ν (cm^{-1}) = 2959, 2928, 2858, 1688, 1642, 1460, 1379, 1125, 1026, 832, 777, 730, 673.

SYNTHESIS OF (*E*)-2,4,8-trimethylnona-2,7-dienal (1j)

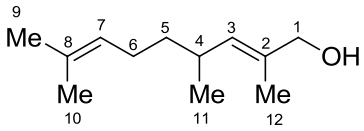
For the synthesis of (*E*)-2,4,8-trimethylnona-2,7-dienal the previous general olefination, reduction and DMP oxidation procedures were used starting from commercial 2,6-dimethylhept-5-enal.



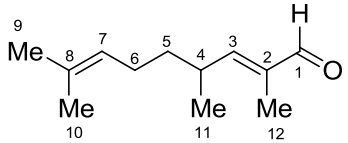
(*E*)-1j



(*E*)-ethyl 2,4,8-trimethylnona-2,7-dienoate (55 % yield) Colorless oil (Pentane/Et_2O 5:1, R_f = 0.57). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.97 (d, $^3J_{HH}$ = 6.69 Hz, 3H, H-11); 1.27 (t, $^3J_{HH}$ = 7.13 Hz, 3H, H-14); 1.30-1.42 (m, 2H, H-5); 1.54 (br s, 3H, H-9); 1.65 (br s, 3H, H-10); 1.80 (d, $^4J_{HH}$ = 1.34 Hz, 3H, H-12); 1.88-1.93 (m, 2H, H-6); 2.42-2.53 (m, 1H, H-4); 4.16 (q, $^3J_{HH}$ = 7.13 Hz, 2H, H-13); 5.04 (br t, $^3J_{HH}$ = 6.45 Hz, 1H, H-7); 6.51 (dq, $^3J_{HH}$ = 10.10 Hz, $^4J_{HH}$ = 1.34 Hz, 1H, H-3). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 13.06 (C-12); 14.89 (C-14); 18.24 (C-9); 20.57 (C-11); 26.28 (C-10); 26.54 (C-6); 33.41 (C-4); 37.54 (C-5); 60.96 (C-13); 124.83 (C-7); 127.08 (C-8); 132.26 (C-2); 148.48 (C-3); 169.01 (C-1). **LRMS** (ESI Positive) calculated for 151.1 [M-C_2H_5O]$^+$, found 151.3. **IR spectrum (neat)** ν (cm^{-1}) = 2927, 1709, 1650, 1449, 1368, 1256, 1176, 1120, 1076, 1033, 749.



(*E*)-2,4,8-trimethyloct-2,7-dien-1-ol (98 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.46). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.93 (d, $^3J_{HH}$ = 6.70 Hz, 3H, H-11); 1.20-1.38 (m, 3H, H-5 and –OH); 1.57 (br s, 3H, H-10); 1.65 (d, $^4J_{HH}$ = 1.37 Hz, 3H, H-12); 1.68 (br s, 3H, H-9); 1.89-1.95 (m, 2H, H-6); 2.34-2.42 (m, 1H, H-4); 3.99 (br s, 2H, H-1); 5.07 (tt, $^3J_{HH}$ = 7.08 Hz, $^4J_{HH}$ = 1.45 Hz, 1H, H-7); 5.17 (dq, $^3J_{HH}$ = 9.58 Hz, $^4J_{HH}$ = 1.37 Hz, 1H, H-3). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 14.16 (C-12); 17.99 (C-10); 21.28 (C-11); 26.04 (C-9); 26.30 (C-6); 32.01 (C-4); 37.94 (C-5); 69.42 (C-1); 125.05 (C-7); 131.60 (C-8); 133.08 (C-3); 133.77 (C-2). **LRMS** (ESI Positive) calculated for 205.2 [M+Na]$^+$, found 205.1. **IR spectrum (neat)** ν (cm^{-1}) = 3307, 2956, 2915, 2857, 1451, 1376, 1070, 1008, 860, 829.

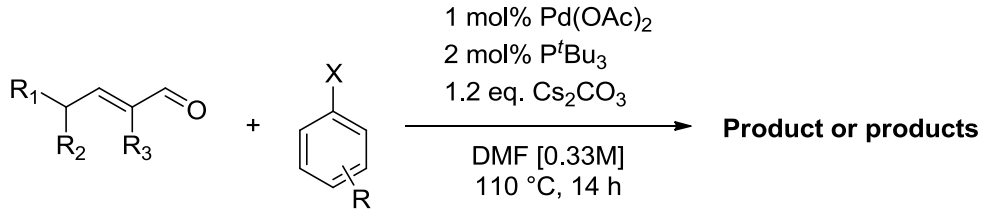


(*E*)-1j

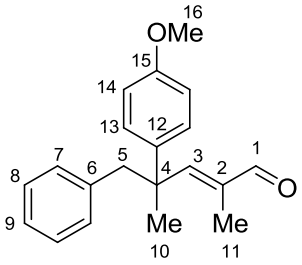
(*E*)-2,4,8-trimethylnona-2,7-dienal (Scheme 3) (76 % yield) Colorless oil (Pentane/Et_2O 1:1, R_f = 0.68). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.05 (d, $^3J_{HH}$ = 6.68 Hz, 3H, H-11); 1.34-1.51 (m, 2H, H-5); 1.54 (br s, 3H, H-10); 1.66 (br s, 3H, H-9); 1.72 (d, $^4J_{HH}$ = 1.39 Hz, 3H, H-12); 1.90-1.96 (m, 2H, H-6); 2.64-2.75 (m, 1H, H-4); 5.05 (br t, $^3J_{HH}$ = 7.10 Hz, 1H, H-7); 6.24 (dq, $^3J_{HH}$ = 9.98 Hz, $^4J_{HH}$ = 1.39 Hz, 1H, H-3); 9.38 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 9.62 (C-12); 17.98 (C-10); 20.12 (C-11); 25.99 (C-9); 26.21 (C-

6); 33.45 (C-4); 37.08 (C-5); 124.16 (C-7); 132.37 (C-8); 138.42 (C-2); 160.78 (C-3); 195.87 (C-1). **LRMS** (ESI Positive) calculated for 203.1 $[M+Na]^+$, found 203.3. **IR spectrum (neat)** ν (cm^{-1}) = 2924, 1686, 1641, 1453, 1378, 1237, 1025, 829, 736, 674.

GENERAL PROCEDURE FOR CATALYTIC REACTIONS

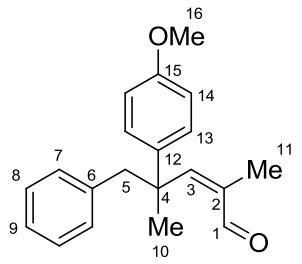


In the glove box, a 5 mL Schlenk tube was charged with the $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 0.01 eq.), tris-*tert*-butylphosphine (2.0 mg, 0.01 mmol, 0.02 eq.) and Cs_2CO_3 (195.5 mg, 0.6 mmol, 1.2 eq.). The Schlenk tube was taken out of the glove box, 1.5 mL of dry and degassed *N,N'*-dimethylformamide was added. Aryl halide was added (0.5 mmol, 1 eq.) and the resulting mixture was stirred for 5 minutes at room temperature. The appropriate aldehyde (0.5 mmol) was added and the reaction tube was immerged in a 110 °C pre-heated oil bath for 14 hours. The reaction was quenched by addition of 2.5 mL of deionized water and extracted with Et_2O (1.5 ml for four times).[6] The organic phases were separated and dried over Na_2SO_4. After evaporation of the solvent the crude mixture was purified by flash chromatography (pentane:Et_2O).



(*E*)-2aa

(*E*)-4-(4-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 1) White solid (Pentane/Et_2O 12:1, R_f = 0.10, Mp = 68-70 °C). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.30 (d, $^4J_{HH}$ = 1.3Hz, 3H, H-11); 1.47 (s, 3H. H-10); 3.05 (d, $^2J_{HH}$ = 12.9Hz, 1H, H-5); 3.19 (d, $^2J_{HH}$ = 12.9Hz, 1H, H-5); 3.81 (s, 3H, H-16); 6.77-6.83 (m, 4H, H-8 and H-14); 6.85 (d, $^4J_{HH}$ = 1.3Hz, 1H, H-3); 7.04-7.07 (m, 2H, H-13); 7.14-7.19 (m, 3H, H-9 and H-7); 9.42 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 10.68 (C-11); 24.44 (C-10); 44.85 (C-6); 51.02 (C-5); 55.44 (C-16); 113.74 (C-14); 126.68 (C-9); 127.88 (C-7); 128.31 (C-13); 131.00 (C-8); 137.09 (C-4); 138.03 (C-15); 140.26 (C-2); 158.19 (C-12); 163.30 (C-3); 196.45 (C-1). **HRMS** (ESI Positive) calculated for 295.1692 $[M+H]^+$, found 295.1692. **IR spectrum (neat)** ν (cm^{-1}) = 2942, 1674, 1511, 1455, 1253, 1182, 1023, 827, 705.

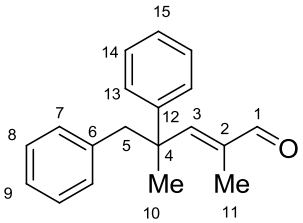


(*Z*)-2aa

(*Z*)-4-(4-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 1) White solid (Pentane/Et_2O 10:1, R_f = 0.31, Mp = 55-57 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.56 (s, 3H, H-10); 1.79 (d, $^4J_{HH}$ =

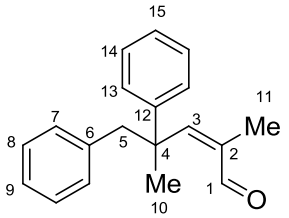
[6] In case of solvents not soluble in water, the solvent was evaporated under reduced pressure at 40°C and the residue was filtered through Celite® with Et_2O (5 mL x 4).

1.26 Hz, 3H, H-11); 2.98 (d, $^{2}J_{HH}$ = 12.6 Hz, 1H, H-5); 3.15 (d, $^{2}J_{HH}$ = 12.6 Hz, 1H, H-5'); 3.79 (s, 3H, H-16); 6.74-6.76 (m, 2H, H-7); 6.78-6.80 (m, $^{3}J_{HH}$ = 8.83 Hz, 2H, H-14); 6.91 (q, $^{4}J_{HH}$ = 1.26 Hz,, 1H, H-3); 7.09-7.11 (m, $^{3}J_{HH}$ = 8.83 Hz, 2H, H-13); 7.15-7.17 (m, 3H, H-8 and H-9); 9.44 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 17.51 (C-11); 28.92 (C-10); 44.89 (C-4); 52.87 (C-5); 55.58 (C-16); 114.08 (C-14); 126.79 (C-9); 127.97 (C-8); 128.35 (C-13); 131.20 (C-7); 135.52 (C-2); 137.18 (C-6); 140.80 (C-12); 157.17 (C-3); 158.35 (C-15); 193.15 (C-1). **HRMS** (ESI Positive) calculated for 295.1693 $[M+H]^+$, found 295.1692. **IR spectrum (neat)** ν (cm^{-1}) = 2925, 1668, 1607, 1510, 1454, 1252, 1183, 1029, 826, 760, 731, 706.



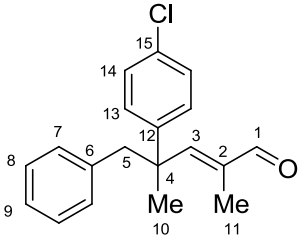
(*E*)-2ab

(*E*)-2,4-dimethyl-4,5-diphenylpent-2-enal (Table 2 Entry 2,3,4) White solid (Pentane/Et_2O 10:1, R_f = 0.23, Mp = 84-86 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.29 (d, $^{4}J_{HH}$ = 1.29 Hz, 3H, H-11); 1.51 (s, 3H, H-10); 3.10 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5); 3.22 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.78-6.80 (m, 2H, H-7); 6.86 (q, $^{4}J_{HH}$ = 1.29 Hz, 1H, H-3); 7.14-7.20 (m, 5H, H-(8, 9 and 13)); 7.21-7.24 (m, 1H, H-15); 7.27-7.30 (m, 2H, H-14); 9.43 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 10.86 (C-11); 24.47 (C-10); 45.60 (C-4); 51.01 (C-5); 126.79 (C-15); 126.85 (C-9); 127.39 (C-8); 128.02 (C-13); 128.62 (C-14); 131.09 (C-7); 137.10 (C-6); 140.48 (C-2); 146.13 (C-12); 162.99 (C-3); 196.45 (C-1). **HRMS** (ESI Positive) calculated for 287.1406 $[M+Na]^+$, found 287.1404. **IR spectrum (neat)** ν (cm^{-1}) = 3030, 2969, 2940, 2852, 1740, 1682, 1633, 1494, 1446, 1376, 1215, 1019, 853, 778, 681.



(*Z*)-2ab

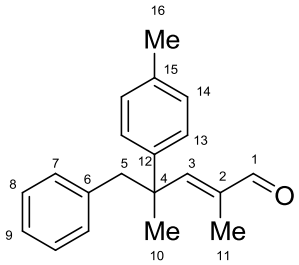
(*Z*)-2,4-dimethyl-4,5-diphenylpent-2-enal (Table 2 Entry 2,3,4) White solid (Pentane/Et_2O 10:1, R_f = 0.32, Mp = 52-54 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.59 (s, 3H, H-10); 1.80 (d, $^{4}J_{HH}$ = 1.26 Hz, 3H, H-11); 3.01 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5); 3.19 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.74-6.76 (m, 2H, H-7); 6.93 (q, $^{4}J_{HH}$ = 1.26 Hz, 1H, H-3); 7.13-7.17 (m, 3H, H-8 and H-9); 7.18-7.21 (m, 4H, H-13 and H-14); 7.25-7.27 (m, 1H, H-15); 9.41 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 17.47 (C-11); 28.81 (C-10); 45.48 (C-4); 52.81 (C-5); 126.85 (C-9); 127.31 (C-13 or 14); 127.98 (C-8); 128.79 (C-15); 131.17 (C-7 and C-13 or 14); 135.61 (C-2); 137.05 (C-6); 148.74 (C-12); 156.89 (C-3); 193.00 (C-1). **HRMS** (ESI Positive) calculated for 265.1592 $[M+H]^+$, found 265.1590. **IR spectrum (neat)** ν (cm^{-1}) = 3028, 2925, 1672, 1028.



(*E*)-2ac

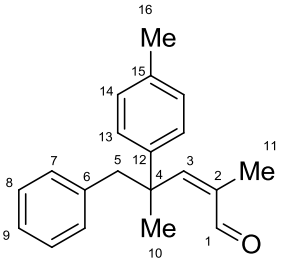
(*E*)-4-(4-chlorophenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 5) Oil (Pentane/Et_2O 10:1, R_f = 0.15). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.29 (d, $^{4}J_{HH}$ = 1.26 Hz, 3H, H-11); 1.50 (s, 3H, H-10); 3.05 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5); 3.18 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.76-6.78 (m, 2H, H-7); 6.84 (m, 1H, H-3); 7.07 (dt, $^{3}J_{HH}$ = 8.8 Hz, 2H, H-14); 7.17-7.19 (m, 3H, H-8 and H-9); 7.25 (dt, $^{2}J_{HH}$ = 8.8 Hz, 2H, H-13); 9.43 (s, 1H,

H-1). **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz)** δ (ppm) = 11.06 (C-11); 24.43 (C-10); 45.29 (C-4); 51.14 (C-5); 127.02 (C-9); 128.15 (C-8); 128.73 (C-13); 128.85 (C-14); 131.05 (C-7); 132.63 (C-15); 136.65 (C-6); 140.67 (C-2); 144.61 (C-12); 162.08 (C-3); 196.20 (C-1). **HRMS** (ESI Positive) calculated for 298.1119 $[M]^+$, found 298.1121. **IR spectrum (neat)** ν (cm^{-1}) = 3029, 2970, 2925, 2821, 2713, 1683, 1632, 1491, 1210, 1095, 1011, 828, 722, 701.



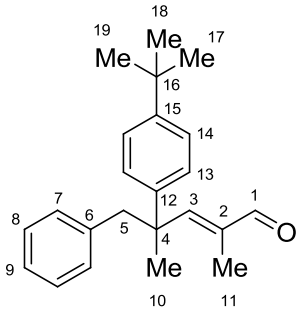
(*E*)-2ad

(*E*)-2,4-dimethyl-5-phenyl-4-(*p*-tolyl)pent-2-enal (Table 2 Entry 6) Yellow oil (Pentane/Et$_2$O 10:1, R_f = 0.22). **^{1}H NMR (CDCl$_3$, 500 MHz)** δ (ppm) = 1.30 (d, $^{4}J_{HH}$ = 1.3 Hz, 3H, H-11); 1.48 (s, 3H, H-10); 2.34 (s, 3H, H-16); 3.08 (d, $^{3}J_{HH}$ = 12.9 Hz, 1H, H-5); 3.19 (d, $^{3}J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.80-6.82 (m, 2H, H-7); 6.84 (q, $^{4}J_{HH}$ = 1.3 Hz, 1H, H-3); 7.04-7.05 (m, 2H, H-13); 7.08-7.09 (m, 2H, H-14); 7.15-7.19 (m, 3H, H-8 and H-9); 9.42 (s, 1H, H-1). **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz)** δ (ppm) = 10.60 (C-11); 21.08 (C-16); 24.46 (C-10); 45.01 (C-4); 50.60 (C-5); 126.54 (C-9); 126.95 (C-13); 127.76 (C-8); 129.05 (C-14); 130.87 (C-7); 136.02 (C-15); 137.03 (C-6); 140.12 (C-2); 142.91 (C-12); 162.98 (C-3); 196.29 (C-1). **HRMS** (ESI Positive) calculated for 301.1562 $[M+Na]^+$, found 301.1575. **IR spectrum (neat)** ν (cm^{-1}) = 3027, 2924, 2710, 1683, 1632, 1511, 1438, 1376, 1211, 1018, 817, 755, 724, 701, 575, 522.



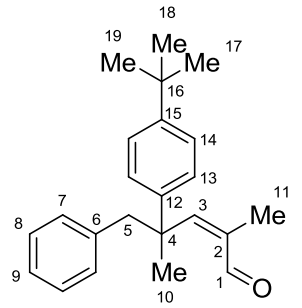
(*Z*)-2ad

(*Z*)-2,4-dimethyl-5-phenyl-4-(*p*-tolyl)pent-2-enal (Table 2 Entry 6) Yellow oil (Pentane/Et$_2$O 10:1, R_f = 0.33). **^{1}H NMR (CDCl$_3$, 500 MHz)** δ (ppm) = 1.56 (s, 3H, H-10); 1.79 (d, $^{4}J_{HH}$ = 1.3 Hz, 3H, H-11); 2.32 (s, 3H, H-16); 3.00 (d, $^{3}J_{HH}$ = 12.9 Hz, 1H, H-5); 3.17 (d, $^{3}J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.78 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 2.0 Hz, 2H, H-7); 6.90 (q, $^{4}J_{HH}$ = 1.3 Hz, 1H, H-3); 7.05-7.07 (m, 2H, H-14); 7.09-7.10 (m, 2H, H-13); 7.15-7.19 (m, 3H, H-8 and H-9); 9.41 (s, 1H, H-1). **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz)** δ (ppm) = 17.49 (C-11); 21.29 (C-16); 28.95 (C-10); 45.15 (C-4); 52.67 (C-5); 126.79 (C-9); 127.12 (C-13); 127.97 (C-8); 129.47 (C-14); 131.22 (C-7); 135.48 (C-2); 136.33 (C-15); 137.21 (C-6); 145.80 (C-12); 157.07 (C-3); 193.19 (C-1). **HRMS** (ESI Positive) calculated for 301.1562 $[M+Na]^+$, found 301.1561. **IR spectrum (neat)** ν (cm^{-1}) = 3028, 2970, 2922, 2870, 1672, 1511, 1453, 1376, 1216, 1191, 1100, 1081, 1029, 816, 754, 724, 632, 575.



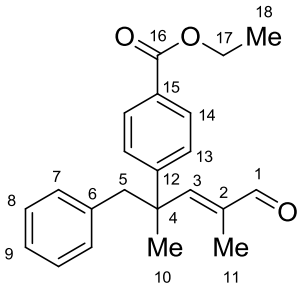
(*E*)-2ae

(*E*)-4-(4-(*tert*-butyl)phenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 7) Oil (Pentane/Et_2O 10:1, R_f = 0. 23). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.32 (m, 12H, H-(11, 17, 18, 19)); 1.50 (s, 3H, H-10); 3.11 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5); 3.19 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.82 (m, 1H, H-3); 6.83 (m, 2H, H-7); 7.09-7.11 (m, $^3J_{HH}$ = 8.5 Hz, 2H, H-14); 7.16-7.19 (m, 3H, H-8 and H-9); 7.28-7.30 (m, $^3J_{HH}$ = 8.5 Hz, 2H, H-13), 9.42 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 10.78 (C-11); 24.85 (C-10); 31.72 (C-17, C-18, C-19); 34.71 (C-16); 45.23 (C-4); 50.55 (C-5); 125.42 (C-13); 126.79 (C-9); 126.87 (C-14); 127.99 (C-8); 131.11 (C-7); 137.37 (C-6); 140.36 (C-2); 143.21 (C-12); 149.68 (C-3); 196.56)C-1). **HRMS** (ESI Positive) calculated for 321.2213 $[M+H]^+$, found 321.2252. **IR spectrum (neat)** ν (cm^{-1}) = 3028, 2962, 2868, 1684, 1510, 1494, 1454, 1362, 1207, 1017, 831, 739, 701.



(*Z*)-2ae

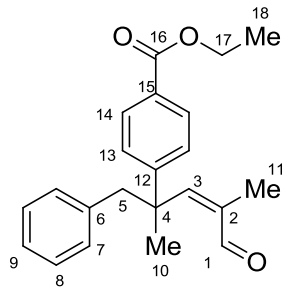
(*Z*)-4-(4-(*tert*-butyl)phenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 7) Oil (Pentane/Et_2O 10:1, R_f = 0. 37). **^{1}H NMR (C_6D_6 , 500 MHz)** δ (ppm) = 1.20 (s, 9H, -^{t}Bu); 1.29 (s, 3H, H-10); 1.79 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-11); 2.69 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5) ; 2.90 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5') ; 6.49 (m, $^4J_{HH}$ = 1.38 Hz, 1H, H-3) ; 6.62-6.64 (m, 2H, H-7) ; 6.96 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H-13) ; 7.00-7.01 (m, 3H, H-8 and H-9) ; 7.14 (H-14) ; 9.68 (s, 1H, H-1). **^{13}C{^{1}H} NMR (C_6D_6 , 125 MHz)** δ (ppm) = 18.08 (C-11); 29.00 (C-10); 31.96 (C-17/18/19); 34.90 (C-16); 45.22 (C-4); 52.82 (C-5); 126.00 (C-14); 127.34 (C-9); 127.49 (C-13); 128.53 (C-8); 131.75 (C-7); 136.18 (C-2); 137.89 (C-6);146.52 (C-12); 149.83 (C-15); 156.02 (C-3); 191.99 (C-1). **HRMS** (ESI Positive) calculated for 343.2022 $[M+Na]^+$, found 343.2032. **IR spectrum (neat)** ν (cm^{-1}) = 2962, 1672, 1454, 1029, 832, 701.



(*E*)-2af

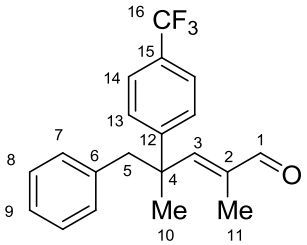
(*E*)-ethyl 4-(2,4-dimethyl-5-oxo-1-phenylpent-3-en-2-yl)benzoate (Table 2 Entry 8) White solid (Pentane/Et_2O 5:1, R_f = 0. 16, Mp = 56-58 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.25 (d, $^4J_{HH}$ = 1.3 Hz,

3H, H-11); 1.40 (t, $^{3}J_{HH}$ = 7.1 Hz, 4H, H-18); 1.54 (s, 3H, H-10); 3.09 (d, $^{3}J_{HH}$ = 12.9 Hz, 1H, H-5); 3.23 (d, $^{3}J_{HH}$ = 12.9 Hz, 1H, H-5'); 4.39 (q, $^{3}J_{HH}$ = 7.1 Hz, 2H, H-17); 6.75-6.76 (m, 2H, H-7); 6.87 (m, 1H, H-3); 7.15-7.18 (m, 3H, H-8 and H-9); 7.22 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, H-13); 7.96 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, H-14); 9.44 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 11.08 (C-11); 14.69 (C-18); 24.29 (C-10); 45.83 (C-4); 51.06 (C-5); 61.34 (C-17); 126.71 (C-9); 127.15 (C-13); 127.80 (C-8); 128.70 (C-15); 129.54 (C-14); 130.67 (C-7); 136.16 (C-6); 140.39 (C-2); 150.95 (C-12); 161.52 (C-3); 166.43 (C-16); 196.15 (C-1). **HRMS** (ESI Positive) calculated for 337.1798 $[M+H]^+$, found 337.1801. **IR spectrum (neat)** ν (cm^{-1}) = 2972, 2939, 2853, 1739, 1710, 1684, 1634, 1608, 1454, 1408, 1368, 1276, 1213, 1186, 1110, 1015, 855, 781, 706.



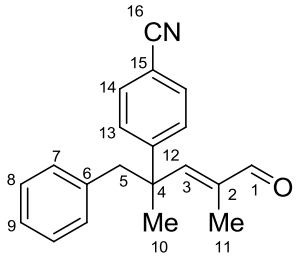
(*Z*)-2af

(*Z*)-ethyl 4-(2,4-dimethyl-5-oxo-1-phenylpent-3-en-2-yl)benzoate (Table 2 Entry 8) Oil (Pentane/Et_2O 5:1, R_f = 0.22). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.03 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, H-18); 1.18 (s, 3H, H-10); 1.75 (d, $^{4}J_{HH}$ = 1.3 Hz, 3H, H-11); 2.54 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5); 2.75 (d, $^{2}J_{HH}$ = 12.9 Hz, 1H, H-5'); 4.13 (q, $^{3}J_{HH}$ = 7.1 Hz, 2H, H-17); 6.40 (d, $^{4}J_{HH}$ = 1.3 Hz, 1H, H-3); 6.51-6.53 (m, 2H, H-7); 6.88 (d, , $^{3}J_{HH}$ = 8.2 Hz, 2H, H-13); 6.92-6.97 (m, 3H, H-8 and H-9); 8.01 (d, , $^{3}J_{HH}$ = 8.2 Hz, 2H, H-14); 9.52 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 14.88 (C-18); 17.92 (C-11); 28.52 (C-10); 45.70 (C-4); 52.81 (C-5); 61.42 (C-17); 127.52 (C-9); 127.89 (C-13); 128.55 (C-8); 128.72 (C-6); 128.91 (C-15); 129.84 (C-12); 130.57 (C-14); 131.57 (C-7); 154.26 (C-2); 155.23 (C-5); 166.53 (C-16); 191.40 (C-1). **HRMS** (ESI Positive) calculated for 337.1798 $[M+H]^+$, found 337.1803. **IR spectrum (neat)** ν (cm^{-1}) = 2979, 2928, 1714, 1674, 1607, 1453, 1366, 1185, 1105, 1019, 853, 777, 704.



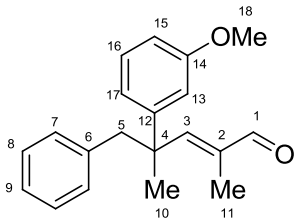
(*E*)-2ag

(*E*)-2,4-dimethyl-5-phenyl-4-(4-(trifluoromethyl)phenyl)pent-2-enal (Table 2 Entry 9) Yellow oil (Pentane/Et_2O 10:1, R_f=0.16). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.27 (d, $^{4}J_{HH}$ = 1.26 Hz, 3H, H-11); 1.55 (s, 3H, H-10); 3.10 (d, $^{2}J_{HH}$ = 13.2 Hz, 1H, H-5); 3.21 (d, $^{2}J_{HH}$ = 13.2 Hz, 1H, H-5'); 6.76-6.78 (m, 2H, H-7); 6.86 (q, $^{4}J_{HH}$ = 1.26 Hz, 1H, H-3); 7.15-7.20 (m, 3H, H-8 and H-9); 7.27 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, H-13); 7.54 (d, $^{2}J_{HH}$ = 8.2 Hz, 2H, H-14); 9.45 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 11.15 (C-11); 24.47 (C-10); 45.71 (C-4); 51.01 (C-5); 125.54 (q, $^{1}J_{CF}$ = 272 Hz, C-16); 125.54 (q, $^{4}J_{CF}$ = 3.6 Hz, C-14); 127.14 (C-9); 127.78 (C-13); 128.21 (C-8); 129.14 (q, $^{2}J_{CF}$ = 32 Hz, C-15); 131.00 (C-7); 136.39 (C-6); 140.83 (C-2); 150.28 (C-12); 161.38 (C-3); 196.03 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = -62.40 (s). **HRMS** (ESI Positive) calculated for 355.1280 $[M+Na]^+$, found 355.1284. **IR spectrum (neat)** ν (cm^{-1}) = 3031, 2975, 1686, 1617, 1409, 1324, 1164, 1117, 1069, 1014, 840, 702.



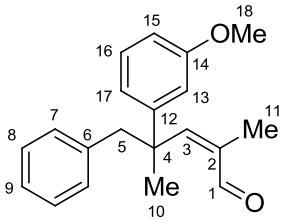
(*E*)-2ah

(*E*)-4-(2,4-dimethyl-5-oxo-1-phenylpent-3-en-2-yl)benzonitrile (Table 2 Entry 10) Oil (Pentane/Et_2O 5:3, R_f = 0. 27). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.26 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-11); 1.55 (s, 3H, H-10); 3.08 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5); 3.20 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.72-6.74 (m, 2H, H-7); 6.85 (q, $^4J_{HH}$ = 1.38 Hz, 1H, H-3); 7.15-7.20 (m, 3H, H-8 and H-9); 7.25 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H-13); 7.57 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H-14); 9.45 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 11.27 (C-11); 24.18 (C-10); 45.99 (C-4); 51.12 (C-5); 110.86 (C-15); 119.06 (C-16); 127.28 (C-9); 128.28 (C-8); 128.31 (C-13); 130.94 (C-7); 132.44 (C-14); 136.04 (C-6); 140.96 (C-2); 151.64 (C-12); 160.71 (C-3); 195.80 (C-1). **HRMS** (ESI Positive) calculated for 307.1804 $[M+NH_4]^+$, found 307.1808. **IR spectrum (neat)** ν (cm^{-1}) = 2923, 2227, 1683, 1605, 1454, 1208, 1017, 837, 735, 703.



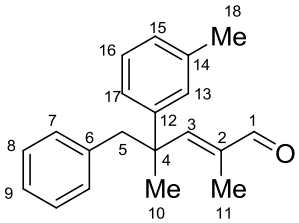
(*E*)-2ai

(*E*)-4-(3-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 11) Pale yellow oil (Pentane/Et_2O 12:1, R_f = 0.10). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.33 (d, $^4J_{HH}$ = 1.3 Hz, 3H, H-11); 1.49 (s, 3H, H-10); 3.08 (d, $^3J_{HH}$ = 12.9 Hz, 1H, H-5); 3.20 (d, $^3J_{HH}$ = 12.9 Hz, 1H, H-5'); 3.75 (s, 3H- H-18); 6.70 (t, $^4J_{HH}$ = 2.0 Hz, 1H, H-13); 6.77 (m, $^3J_{HH}$ = 8.1 Hz, 2H, H-15/17); 6.81-6.83 (m, 3H, H-3 and H-8); 7.15-7.19 (m, 3H, H-7 and H-9); 7.21 (t, $^3J_{HH}$ = 8.1 Hz, 1H, H-16); 9.42 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 10.89 (C-11); 24.65 (C-10); 45.64 (C-4); 50.88 (C-5); 55.58 (C-18); 111.52 (C-15/17); 114.00 (C-13); 119.97 (C-15/17); 126.90 (C-9); 128.05 (C-7); 129.55 (C-16); 131.09 (C-8); 137.13 (C-6); 140.58 (C-2); 147.89 (C-12); 159.89 (C-14); 162.62 (C-3); 196.39 (C-1). **HRMS** (ESI Positive) calculated for 317.1512 $[M+Na]^+$, found 317.1520. **IR spectrum (neat)** ν (cm^{-1}) = 2935, 2834, 2713, 1683, 1600, 1582, 1490, 1453, 1431, 1290, 1234, 1167, 1041, 1021, 862, 781, 702.



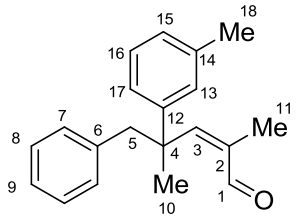
(*Z*)-2ai

(*Z*)-4-(3-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 11) Pale yellow oil (Pentane/Et_2O 12:1, R_f = 0.17). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.57 (s, 3H, H-10) ; 1.79 (d, $^4J_{HH}$ = 1.26 Hz, 3H, H-11); 2.99 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5) ; 3.17 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5') ; 3.74 (s, 3H, H-18) ; 6.73-6.75 (m, 2H, H-13 and H-15) ; 6.77-6.82 (m, 3H, H-7 and H-17) ; 6.89 (q, $^4J_{HH}$ = 1.26 Hz,, 1H, H-3) ; 7.16-7.20 (m, 4H, H-8,9 and H-16) ; 9.43 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 17.45 (C-11) ; 28.90 (C-10) ; 45.48 (C-4) ; 52.68 (C-5) ; 55.54 (C-18) ; 11.50 (C-15) ; 113.98 (C-13) ; 119.88 (C-17) ; 126.89 (C-9) ; 127.99 (C-8) ; 129.76 (C-16) ; 131.17 (C-7) ; 135.69 (C-2) ; 137.05 (C-6) ; 150.46 (C-12) ; 156.58 (C-3) ; 159.84 (C-14) ; 193.06 (C-1). **HRMS** (ESI Positive) calculated for 295.1703 $[M+H]^+$, found 295.1692. **IR spectrum (neat)** ν (cm^{-1}) = 2925, 1672, 1599, 1581, 1490, 1453, 1431, 1289, 1235, 1040, 781.



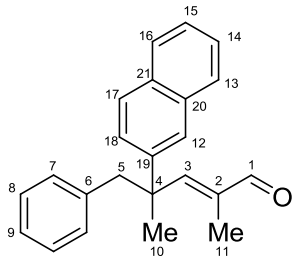
(*E*)-2aj

(*E*)-2,4-dimethyl-5-phenyl-4-(*m*-tolyl)pent-2-enal (Table 2 Entry 12) Pale yellow oil (Pentane/Et_2O 12:1, R_f = 0.24). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.31 (d, $^4J_{HH}$ = 1.26 Hz, 3H, H-11); 1.50 (s, 3H, H-10); 2.31 (s, 3H, H-18) ; 3.09 (d, $^2J_{HH}$ = 12.6 Hz, 1H, H-5) ; 3.20 (d, $^2J_{HH}$ = 12.6 Hz, 1H, H-5') ; 6.80-6.82 (m, 2H, H-7) ; 6.84 (q, $^4J_{HH}$ = 1.26 Hz, 1H, H-3) ; 6.96-6.97 (m, 2H, H-13 and 17) ; 7.05 (br d, 1H, H-15) ; 7.15-7.19 (m, 4H, H-8,9 and 16) ; 9.43 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 10.89 (C-11) ; 21.95 (C-18) ; 24.70 (C-10) ; 45.51 (C-4) ; 50.84 (C-5) ; 124.36 (C-17) ; 126.83 (C-9) ; 127.46 (C-15) ; 127.98 (C-8) ; 128.11 (C-13) ; 128.45 (C-16) ; 131.11 (C-7) ; 137.25 (C-6) ; 138.08 (C-14) ; 140.40 (C-2) ; 146.16 (C-12) ; 163.06 (C-3) ; 196.54 (C-1). **HRMS** (ESI Positive) calculated for 278.1665 $[M]^+$, found 278.1669. **IR spectrum (neat)** ν (cm^{-1}) = 3029, 2924, 1683, 1632, 1604, 1493, 1454, 1211, 1020, 786, 704.



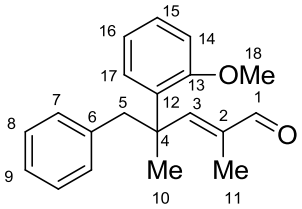
(*Z*)-2aj

(*Z*)-2,4-dimethyl-5-phenyl-4-(*m*-tolyl)pent-2-enal (Table 2 Entry 12) Oil (Pentane/Et_2O 12:1, R_f = 0.36). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.57 (s, 3H, H-10) ; 1.80 (d, $^4J_{HH}$ = 1.26 Hz, 3H, H-11); 2.29 (s, 3H, H-18), 3.00 (d, $^2J_{HH}$ = 12.6 Hz, 1H, H-5) ; 3.17 (d, $^2J_{HH}$ = 12.6 Hz, 1H, H-5') ; 6.76-6.78 (m, 2H, H-7) ; 6.90 (q, $^4J_{HH}$ = 1.26 Hz, 1H, H-3) ; 7.00-7.01 (m, 3H, H-13,15 and 17) ; 7.14-7.17 (m, 4H, H-8,9 and 16) ; 9.42 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 17.47 (C-11) ; 21.98 (C-18) ; 28.99 (C-10) ; 45.38 (C-4) ; 52.71 (C-5) ; 124.37 (C-13) ; 126.84 (C-9) ; 127.56 (C-17) ; 127.95 (C-8) ; 127.99 (C-15) ; 128.65 (C-16) ; 131.23 (C-7) ; 135.53 (C-2) ; 137.20 (C-6) ; 138.26 (C-14) ; 148.79 (C-12) ; 156.96 (C-3) ; 193.18 (C-1). **HRMS** (ESI Positive) calculated for 278.1665 $[M]^+$, found 278.1667. **IR spectrum (neat)** ν (cm^{-1}) = 2923, 2869, 1672, 1453, 1029, 786, 704.



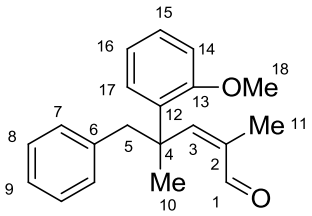
(*E*)-2ak

(*E*)-2,4-dimethyl-4-(naphtalen-2-yl)-5-phenylpent-2-enal (Table 2 Entry 13) Sticky gel (Pentane/Et_2O 10:1, R_f = 0.14). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.26 (d, $^4J_{HH}$ = 1.3 Hz, 3H, H-11); 1.62 (s, 3H, H-10); 3.19 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5); 3.31 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.79-6.80 (m, 2H, H-7); 6.92 (q, $^4J_{HH}$ = 1.3 Hz, 1H, H-3); 7.10-7.14 (m, 2H, H-8); 7.15-7.19 (m, 1H, H-9); 7.33 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.9 Hz , 1H, H-18); 7.45-7.49 (m, 2H, H-14 and H-15); 7.56 (d, $^4J_{HH}$ = 1.9 Hz, 1H, H-12); 7.72-7.76 (m, 1H, H-13); 7.78 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H-17); 7.82-7.85 (m, 1H, H-16); 9.47 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 10.83 (C-11); 24.64 (C-10); 45.74 (C-4); 50.67 (C-5); 125.39 (C-12); 126.18 (C-14); 126.42 (C-18); 126.46 (C-15); 126.89 (C-9); 127.83 (C-16); 128.07 (C-8); 128.36 (C-13); 128.40 (C-17); 131.09 (C-7-); 132.38 (C-21); 133.49 (C-20); 137.02 (C-6); 140.70 (C-2); 143.58 (C-19); 162.59 (C-3); 196.45 (C-1). **HRMS** (ESI Positive) calculated for 337.1562 $[M+Na]^+$, found 337.1558. **IR spectrum (neat)** ν (cm^{-1}) = 3056, 3027, 2926, 2708, 1682, 1630, 1599, 1453, 1376, 1212, 1019, 857, 817, 743, 702.



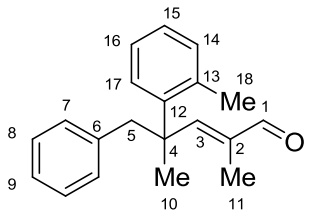
(*E*)-2al

(*E*)-4-(2-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 14) White solid (Pentane/Et_2O 12:1, R_f = 0.10, Mp = 84-86 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.24 (d, $^4J_{HH}$ = 1.3 Hz, 3H, H-11); 1.44 (s, 3H, H-10); 3.00 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5); 3.57 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5'); 3.77 (s, 3H, H-18); 6.76-6.78 (m, 2H, H-7); 6.85 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H-15); 6.89-6.91 (m, 2H, H-17 and H-3); 6.98 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H-14); 7.11-7.14 (m, 3H, H-8 and H-9); 7.23-7.27 (m, $^4J_{HH}$ = 1.7 Hz, 1H, H-16); 9.40 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 9.82 (C-11); 23.33 (C-10); 43.68 (C-4); 47.07 (C-5); 55.68 (C-18); 111.83 (C-17); 120.99 (C-15); 126.56 (C-9); 127.74 (C-14); 127.85 (C-8); 128.52 (C-16); 131.13 (C-7); 133.75 (C-12); 136.71 (C-2); 137.86 (C-6); 157.55 (C-13); 165.41 (C-3); 196.80 (C-1). **HRMS** (ESI Positive) calculated for 295.1692 $[M+H]^+$, found 295.1705. **IR spectrum (neat)** ν (cm^{-1}) = 3024, 2964, 2843, 2730, 1676, 1634, 1599, 1491, 1467, 1452, 1435, 1374, 1288, 1243, 1221, 1180, 1124, 1080, 1020, 848, 746, 695.



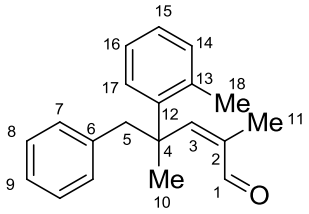
(*Z*)-2al

(*Z*)-4-(2-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enal (Table 2 Entry 14) White solid (Pentane/Et_2O 12:1, R_f = 0.17, Mp = 71-73 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.54 (s, 3H, H-10) ; 1.76 (d, $^4J_{HH}$ = 1.58 Hz, 3H, H-11); 2.80 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5) ; 3.55 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5') ; 3.80 (s, 3H, H-18) ; 6.72-6.74 (m, $^4J_{HH}$ = 1.89 Hz, 2H, H-7) ; 6.82 (td, $^4J_{HH}$ = 1.26 Hz, $^3J_{HH}$ = 7.57 Hz, 1H, H-16) ; 6.92 (dd, $^4J_{HH}$ = 1.26 Hz, $^3J_{HH}$ = 8.2 Hz, 1H, H-14) ; 6.99 (dd, $^4J_{HH}$ = 1.58 Hz, $^3J_{HH}$ = 7.57 Hz, 1H, H-17) ; 7.06 (m, 1H, H-3) ; 7.11-7.14 (m, 3H, H-8 and H-9) ; 7.20-7.25 (m, 1H, H-15) ; 9.55 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 17.09 (C-11); 28.18 (C-10); 43.22 (C-4); 48.43 (C-5); 55.80 (C-18); 112.85 (C-14); 121.19 (C-16); 126.52 (C-9); 126.75 (C-17); 127.78 (C-8); 128.78 (C-15); 131.14 (C-7); 132.46 (C-2); 136.47 (C-12) ; 137.77 (C-6). **HRMS** (ESI Positive) calculated for 295.1692 $[M+H]^+$, found 295.1699. **IR spectrum (neat)** ν (cm^{-1}) = 3028, 2965, 1663, 1599, 1491, 1454, 1244, 1025, 848, 754, 699.



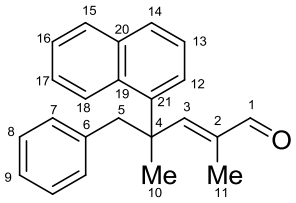
(*E*)-2am

(*E*)-2,4-dimethyl-5-phenyl-4-(*o*-tolyl)pent-2-enal (Table 2 Entry 15) White solid (Pentane/Et_2O 10:1, R_f = 0.17, Mp = 102-104 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.21 (d, $^4J_{HH}$ = 1.26 Hz, 3H, H-11); 1.50 (s, 3H, H-10); 2.33 (s, 3H, H-18); 3.03 (d, $^2J_{HH}$ = 13.2 Hz, 1H, H-5); 3.38 (d, $^2J_{HH}$ = 13.2 Hz, 1H, H-5'); 6.78 (dd, $^3J_{HH}$ = 7.57 Hz, $^4J_{HH}$ = 1.58 Hz, 2H, H-7); 6.89 (m, $^4J_{HH}$ = 1.26 Hz, 1H, H-3); 7.08-7.10 (m, 2H, H-15 and H-17); 7.15-7.18 (m, 5H, H-8,9,14 and H-16); 9.44 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 9.92 (C-11); 23.36 (C-18); 24.80 (C-10); 45.32 (C-4); 47.95 (C-5); 126.30 (C-15,16 or 17); 126.81 (C-9); 127.07 (C-15,16 or 17); 127.20 (C-15,16 or 17); 127.99 (C-8); 131.22 (C-7); 132.32 (C-14); 136.13 (C-13); 137.14 (C-6); 138.63 (C-2); 143.22 (C-12); 162.77 (C-3); 196.30 (C-1). **HRMS** (ESI Positive) calculated for 278.1665 $[M]^+$, found 278.1668. **IR spectrum (neat)** ν (cm^{-1}) = 3027, 2949, 1675, 1632, 1452, 1376, 1213, 1019, 773, 729, 703.



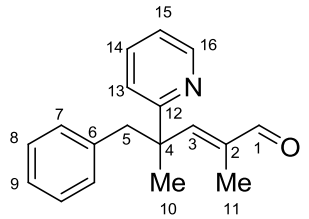
(*Z*)-2am

(*Z*)-2,4-dimethyl-5-phenyl-4-(*o*-tolyl)pent-2-enal (Table 2 Entry 15) White solid (Pentane/Et_2O 10:1, R_f = 0.28, Mp = 95-97 °C). **^{1}H NMR (C_6D_6 , 500 MHz)** δ (ppm) = 1.27 (s, 3H, H-10); 1.75 (s, 3H, H-11); 2.09 (s, 3H, H-18); 2.53 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5); 3.07 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.47 (s, 1H, H-3); 6.57-6.59 (m, 2H, H-7); 6.81 (br d, $^3J_{HH}$ = 7.7 Hz, 1H, H-17); 6.84-6.85 (m, 1H, H-16); 6.95-6.99 (m, 5H, H-8,9,14 and H-15); 9.64 (s, 1H, H-1). **^{13}C{^{1}H} NMR (C_6D_6 , 125 MHz)** δ (ppm) = 17.51 (C-11); 24.00 (C-18); 29.59 (C-10); 45.11 (C-4); 49.75 (C-5); 126.89 (C-16); 126.95 (C-17); 127.31 (C-9); 127.71 (C-14); 131.78 (C-7); 133.47 (C-15); 134.90 (C-2); 135.87 (C-13); 137.78 (C-6); 146.48 (C-12); 156.07 (C-3); 191.40 (C-1). **HRMS** (ESI Positive) calculated for 278.1665 $[M]^+$, found 278.1664. **IR spectrum (neat)** ν (cm^{-1}) = 3027, 2964, 2871, 1665, 1451, 1026, 775, 727, 701.



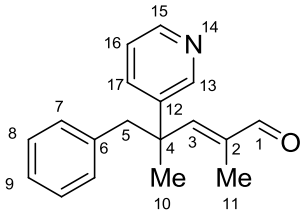
(*E*)-2an

(*E*)-2,4-dimethyl-4-(naphtalen-1-yl)-5-phenylpent-2-enal (Table 2 Entry 16) Sticky gel (Pentane/Et_2O 10:1, R_f = 0.10). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 0.98 (d, $^4J_{HH}$ = 1.3 Hz, 3H, H-11); 1.62 (s, 3H, H-10); 3.25 (d, $^3J_{HH}$ = 12.9 Hz, 1H, H-5); 0.73 (d, $^3J_{HH}$ = 12.9 Hz, 3H, H-5'); 6.61 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H-7); 7.07-7.10 (m, 2H, H-8); 7.12-7.15 (m, 1H, H-9); 7.18 (m, 1H, H-3); 7.24 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H-12); 7.42-7.46 (m, 1H, H-17); 7.47-7.50 (m, 1H, H-16); 7.79 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-14); 7.90-7.92 (m, 1H, H-15); 8.06 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H-18); 9.48 (s,1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 9.75 (C-11); 25.28 (C-10); 45.56 (C-4); 48.69 (C-5); 125.28 (C-12); 125.44 (C-13); 125.55 (C-17); 125.63 (C-16); 126.30 (C-18); 126.81 (C-9); 127.88 (C-8); 128.63 (C-14); 129.94 (C-15); 130.90 (C-21); 131.08 (C-7); 134.85 (C-20); 137.09 (C-6); 139.06 (C-2); 141.43 (C-19); 163.00 (C-3); 196.13 (C-1). **HRMS** (ESI Positive) calculated for 314.1665 $[M]^+$, found 314.1660. **IR spectrum (neat)** ν (cm^{-1}) = 3032, 2919, 1665, 1630, 1454, 1215, 1018, 799, 775, 752, 702.



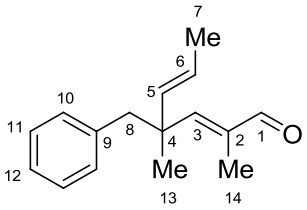
(*E*)-2ap

(*E*)-2,4-dimethyl-5-phenyl-4-(pyridin-2-yl)pent-2-enal (Table 2 Entry 18) Brown oil (Pentane/Et_2O 1:1, R_f = 0. 26). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.25 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-11); 1.58 (s, 3H, H-10); 3.21 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5); 3.47 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5'); 6.80-6.82 (m, 2H, H-7); 6.90 (m, 1H, H-3); 7.09 (br d, $^3J_{HH}$ = 7.98 Hz, 1H, H-13); 7.14-7.18 (m, 3H, H-8 and H-9); 7.19-7.21 (m, 1H, H-15); 7.60 (br t, $^3J_{HH}$ = 7.29 Hz, 1H, H-14); 8.64 (br d, $^3J_{HH}$ = 4.13 Hz, 1H, H-16); 9.44 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 10.61 (C-11); 23.98 (C-10); 48.17 (C-4); 49.19 (C-5); 122.07 (C-15); 122.38 (C-13); 124.45 (C-9); 126.91 (C-8); 130.90 (C-7); 137.00 (C-14); 137.14 (C-6); 140.03 (C-2); 149.07 (C-16); 161.68 (C-3); 164.84 (C-12); 196.32 (C-1). **HRMS** (ESI Positive) calculated for 266.1539 $[M+H]^+$, found 266.1539. **IR spectrum (neat)** ν (cm^{-1}) = 2924, 1682, 1585, 1454, 1207, 1020, 749.



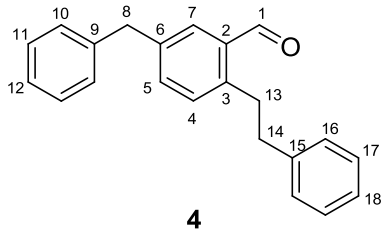
(*E*)-2aq

(*E*)-2,4-dimethyl-5-phenyl-4-(pyridin-3-yl)pent-2-enal (Table 2 Entry 19) Yellow oil (Pentane/Et_2O 1:1, R_f = 0. 15). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.30 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-11) ; 1.58 (s, 3H, H-10) ; 3.10 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5) ; 3.22 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5') ; 6.76-6.78 (m, 2H, H-7) ; 6.87 (q, $^4J_{HH}$ = 1.38 Hz, 1H, H-3) ; 7.15-7.20 (m, 3H, H-8 and H-9) ; 7.24 (ddd, $^3J_{HH}$ = 7.98 Hz, $^3J_{HH}$ = 4.81 Hz, $^5J_{HH}$ = 0.69 Hz, 1H, H-16) ; 7.44 (ddd, $^3J_{HH}$ = 7.98 Hz, $^4J_{HH}$ = 2.48 Hz, $^4J_{HH}$ = 1.51 Hz, 1H, H-17) ; 8.45 (m, 1H, H-13) ; 8.51 (dd, $^3J_{HH}$ = 4.81 Hz, $^4J_{HH}$ = 1.51 Hz, 1H, H-15) ; 9.45 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 11.26 (C-11) ; 24.27 (C-10) ; 44.31 (C-4) ; 51.01 (C-5) ; 123.59 (C-16) ; 127.27 (C-9) ; 128.32 (C-8) ; 131.04 (C-7) ; 135.48 (C-17) ; 136.12 (C-6) ; 140.88 (C-2) ; 141.87 (C-12) ; 147.61 (C-15) ; 148.55 (C-13) ; 160.59 (C-3) ; 199.84 (C-1). **HRMS** (ESI Positive) calculated for 266.1539 $[M+H]^+$, found 266.1539. **IR spectrum (neat)** ν (cm^{-1}) = 2971, 1683, 1415, 1207, 1019, 715.



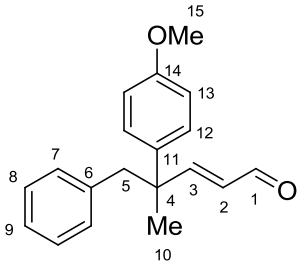
(*E*)-2ar

(2*E*,5*E*)-4-benzyl-2,4-dimethylhepta-2,5-dienal (Table 2 Entry 20) Pale yellow oil (Pentane/Et_2O 4:1, R_f = 0.47). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.26 (s, 3H, H-13); 1.72 (dd, $^3J_{HH}$ = 6.46 Hz, $^4J_{HH}$ = 1.51 Hz, 3H, H-7); 1.75 (d, $^4J_{HH}$ = 1.38 Hz, 3H, H-14); 2.82-2.89 (m, $^2J_{HH}$ = 13.20 Hz, 2H, H-8); 5.38 (dq, $^3J_{HH}$ = 6.46 Hz, $^3J_{HH}$ = 15.68 Hz, 1H, H-6); 5.57 (dq, $^3J_{HH}$ = 15.68 Hz, $^4J_{HH}$ = 1.51 Hz,, 1H, H-5); 6.45 (q, $^4J_{HH}$ = 1.38 Hz, 1H, H-3); 7.10-7.11 (m, 2H, H-10); 7.22-7.28 (m, 3H, H-11 and H-12); 9.33 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 10.67 (C-14); 18.33 (C-7); 24.99 (C-13); 43.64 (C-4); 48.71 (C-8); 124.08 (C-6); 126.75 (C-12); 128.12 (C-11); 131.03 (C-10); 136.83 (C-5); 137.62 (C-9); 139.69 (C-2); 161.50 (C-3); 196.70 (C-1). **HRMS** (ESI Positive) calculated for 228.1509 $[M]^+$, found 228.1510. **IR spectrum (neat)** ν (cm^{-1}) = 2924, 1685, 1634, 1452, 1021, 973, 741, 101.



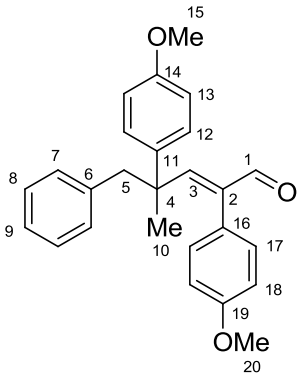
4

5-benzyl-2-phenethylbenzaldehyde (Scheme 1) White solid (Pentane/Et_2O 6:1, R_f = 0.37, Mp = 43-45°C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 2.88-2.91 (m, 2H, H-14); 3.28-3.31 (m, 2H, H-13); 4.04 (s, 2H, H-8); 7.17 (d, $^3J_{HH}$ = 7.57 Hz, 1H, H-4); 7.19-7.25 (m, 6H, H-10,11,12 and H-18); 7.28-7.34 (m, 5H, H-5, 16 and H-17); 7.67 (d, $^4J_{HH}$ = 1.89 Hz, 1H, H-7); 10.17 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 34.86 (C-13); 38.65 (C-14); 41.60 (C-8); 126.44 and 126.71 (C-12 and C-18); 128.73 (C-17); 128.78 (C-16); 128.97 and 129.21 (C-10 and C-11); 131.77 (C-4); 132.86 (C-7); 134.16 (C-3); 134.68 (C-5); 140.11 (C-6); 140.66 (C-2); 141.58 (C-15); 142.51 (C-2); 192.66 (C-1). **HRMS** (ESI Positive) calculated for 301.1586 $[M+H]^+$, found 301.1590. **IR spectrum (neat)** ν (cm^{-1}) = 3026, 2920, 2853, 1687, 1494, 1453, 1231, 743, 696.



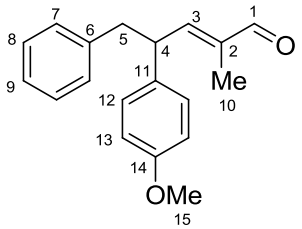
(*E*)-2ca

(*E*)-4-(4-methoxyphenyl)-4-methyl-5-phenylpent-2-enal (Scheme 1) Yellow oil (Pentane/Et_2O 4:1, R_f = 0.20). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.40 (s, 3H, H-10); 3.09 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5); 3.16 (d, $^2J_{HH}$ = 12.9 Hz, 1H, H-5'); 3.81 (s, 3H, H-15); 6.08 (dd, $^3J_{HH}$ = 7.57 Hz, $^3J_{HH}$ = 15.8 Hz, 1H, H-2); 6.81-6.82 (m, 2H, H-7); 6.86 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H-13); 7.06 (d, $^3J_{HH}$ = 15.8 Hz, 1H, H-3); 7.13-7.17 (m, 4H, H-8,9 and 12); 9.57 (d, $^3J_{HH}$ = 7.57 Hz, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 24.22 (C-10); 45.55 (C-4); 47.70 (C-5); 55.63 (C-15); 114.09 (C-13); 126.85 (C-9); 128.10 (C-8); 128.39 (C-12); 130.36 (C-2); 130.86 (C-7); 136.35 (C-11); 137.15 (C-6); 157.70 (C-14); 166.32 (C-3); 194.57 (C-1). **HRMS** (ESI Positive) calculated for 280.1458 $[M]^+$, found 280.1461. **IR spectrum (neat)** ν (cm^{-1}) = 2932, 2835, 1684, 1607, 1510, 1454, 1293, 1248, 1182, 1116, 1030, 829, 750, 700.



(*E*)-5

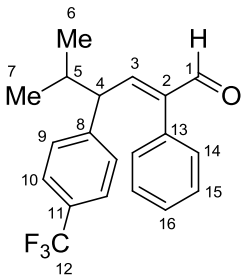
(*E*)-2,4-bis(4-methoxyphenyl)-4-methyl-5-phenylpent-2-enal (Scheme 1) Sticky solid (Pentane/Et_2O 4:1, R_f = 0. 13). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.17 (s, 3H, H-10); 3.09 (s, 2H, H-5); 3.74 (s, 3H, H-20); 3.81 (s, 3H, H-15); 6.54 (d, $^3J_{HH}$ = 8.83 Hz, 2H, H-18); 6.68 (d, $^3J_{HH}$ = 8.83 Hz, 2H, H-17); 6.79 (d, $^3J_{HH}$ = 8.83 Hz, 2H, H-13); 6.85-6.86 (m, 2H, H-7); 7.00 (s, 1H, H-3); 7.07 (d, $^3J_{HH}$ = 8.83 Hz, 2H, H-12); 7.17-7.19 (m, 3H, H-8 and H-9); 9.61 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 25.10 (C-10); 46.08 (C-4); 50.17 (C-5); 55.47 (C-20); 55.63 (C-15); 113.53 (C-17); 113.94 (C-13); 125.72 (C-16); 126.84 (C-9); 128.09 (C-8); 128.23 (C-12); 130.77 (C-18); 131.06 (C-7); 137.55 (C-6); 138.91 (C-11); 143.30 (C-2); 158.43 (C-14); 159.27 (C-19); 163.34 (C-3); 195.73 (C-1). **HRMS** (ESI Positive) calculated for 387.1954 $[M+H]^+$, found 387.1960. **IR spectrum (neat)** ν (cm^{-1}) = 2931, 2835, 1722, 1687, 1605, 1509, 1454, 1289, 1245, 1177, 1029, 829, 670.



(*E*)-2da

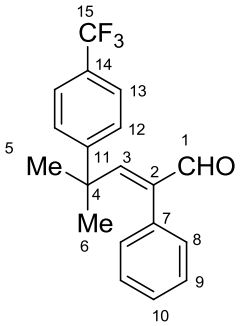
(*E*)-4-(4-methoxyphenyl)-2-methyl-5-phenylpent-2-enal (Scheme 1) White solid (Pentane/Et_2O 1:1, R_f = 0.47, Mp = 73-75 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.54 (d, $^4J_{HH}$ = 0.95 Hz, 3H, H-10); 3.00 (dd, $^3J_{HH}$ = 8.83 Hz, $^2J_{HH}$ = 13.6 Hz, 1H, H-5); 3.16 (dd, $^3J_{HH}$ = 6.31 Hz, $^2J_{HH}$ = 13.6 Hz, 1H, H-5'); 3.80 (s, 3H, H-15); 4.00-4.05 (m, 1H, H-4); 6.59-6.61 (m, $^3J_{HH}$ = 10.9 Hz, 1H, H-3); 6.86 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H-13); 7.07-7.08 (m, 2H, H-7); 7.14-7.16 (m, 2H, H-12); 7.17-7.19 (m, 1H, H-9); 7.23-7.26 (m, 2H, H-8); 9.38 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 9.58 (C-10); 42.96 (C-5); 46.72 (C-4); 55.64 (C-15); 114.62 (C-

13); 126.74 (C-9); 128.70 (C-12); 128.75 (C-8); 129.36 (C-7); 134.39 (C-11); 139.04 (C-2); 139.20 (C-6); 156.40 (C-3); 158.89 (C-14); 195.50 (C-1). **HRMS** (ESI Positive) calculated for 303.1355 $[M+Na]^+$, found 303.1361. **IR spectrum (neat)** ν (cm^{-1}) = 2917, 2835, 1685, 1511, 1455, 1263, 1244, 1177, 1032, 833, 748, 701.



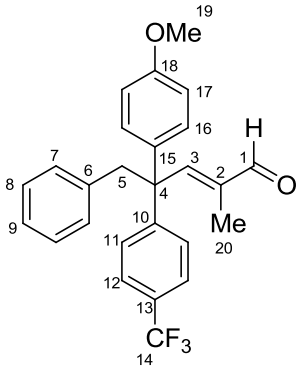
(*E*)-2eg

(*E*)-5-methyl-2-phenyl-4-(4-(trifluoromethyl)phenyl)hex-2-enal (Scheme 3) Wax solid (Pentane/Et_2O 1:1, R_f = 0.53). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.70 and 0.97 (2d, 2·3H, H-6 and H-7); 2.05-2.14 (m, 1H, H-5); 3.36 (dd, $^3J_{HH}$ = 9.41 Hz, $^3J_{HH}$ = 10.9 Hz, 1H, H-4); 6.86 (d, $^3J_{HH}$ = 10.9 Hz, 1H, H-3); 7.03-7.05 (m, 2H, H-14); 7.22 (d, $^3J_{HH}$ = 8.02 Hz, H-9); 7.39-7.45 (m, 3H, H-15 and H-16); 7.59 (d, $^3J_{HH}$ = 8.02 Hz, 2H, H-10); 9.67 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 20.84 and 21.17 (C-7 and C-6); 34.12 (C-5); 53.24 (C-4); 124.42 (q, $^1J_{CF}$ = 272 Hz, C-12); 126.20 (q, $^3J_{CF}$ = 3.82 Hz, C-10); 128.54 (C-9); 128.76 (C-15 and C-16); 129.50 (q, $^2J_{HH}$ = 32.4 Hz, C-11); 129.60 (C-14); 132.93 (C-13); 144.78 (C-8); 146.43 (C-2); 156.10 (C-3); 193.59 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = -62.47 (s). **LRMS** (ESI Positive) calculated for 333.2 $[M+H]^+$, found 333.5. **IR spectrum (neat)** ν (cm^{-1}) = 2926, 1690, 1616, 1323, 1163, 1117, 1067, 1017, 854, 831, 705.



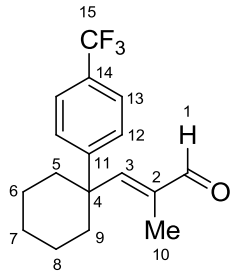
(*E*)-2fg

(*E*)-4-methyl-2-phenyl-4-(4-(trifluoromethyl)phenyl)pent-2-enal (Scheme 3) White solid (Pentane/Et_2O 1:1, R_f = 0.48, Mp = 50-52 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.46 (s, 6H, H-5 and H-6); 6.75-6.77 (m, 2H, H-8); 6.91 (s, 1H, H-3); 7.14-7.20 (m, 3H, H-9 and H-10); 7.27 (d, $^3J_{HH}$ = 8.22 Hz, 2H, H-12); 7.44 (d, $^3J_{HH}$ = 8.22 Hz, 2H, H-13); 9.61 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 30.15 (C-5 and C-6); 42.21 (C-4); 124.43 (q, $^1J_{CF}$ = 272 Hz, C-15); 125.48 (q, $^3J_{CF}$ = 3.66 Hz, C-13); 126.88 (C-2); 128.02 (C-10); 128.11 (C-9); 128.91 (q, $^2J_{CF}$ = 32.35 Hz, C-14); 129.56 (C-8); 133.14 (C-7), 143.98 (C-2); 151.76 (C-11); 162.75 (C-3); 194.96 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = -62.57 (s). **LRMS** (ESI Positive) calculated for 336.12 $[M+H]^+$, found 336.5. **IR spectrum (neat)** ν (cm^{-1}) = 2983, 2848, 1679, 1616, 1414, 1329, 1156, 1113, 1100, 1067, 1014, 838, 714, 605.



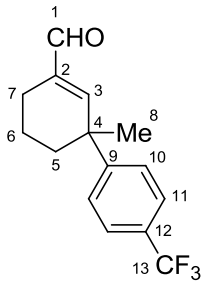
(*E*)-2dag

(*E*)-4-(4-methoxyphenyl)-2-methyl-5-phenyl-4-(4-(trifluoromethyl)phenyl)pent-2-enal (Scheme 3) Inseparable mixture of (*E*)-**2dag** from (*E*)-**2da** (Pentane/Et_2O 1:1, R_f = 0.52). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.30 (d, $^4J_{HH}$ = 1.41 Hz, 3H, H-20); 3.61 (d, $^1J_{HH}$ = 12.8 Hz, 1H, H-5); 3.69 (d, $^1J_{HH}$ = 12.8 Hz, 1H, H-5'); 3.82 (s, 3H, H-19); 6.61-6.64 (m, 2H, H-7); 7.25 (d, $^3J_{HH}$ = 8.36 Hz, 2H, H-11); 7.53 (d, $^3J_{HH}$ = 8.36 Hz, 2H, H-12); 9.45 (s, 1H, H-1). Protons 3, 8, 9, 16 and 17 cannot be assigned due to overlap of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ(ppm) = 11.04 (C-20); 47.23 (C-5); 53.99 (C-4); 55.63 (C-19); 125.40 (q, $^3J_{CF}$ = 3.65 Hz, C-12); 131.05 (C-7); 141.59 (C-2); 158.88 (C-3); 196.17 (C-1). Carbons 6, 8, 9, 10, 11, 13, 14, 15, 16, 17 and 18 cannot be assigned due to overlap of signals. **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = -62.44 (s). **LRMS** (ESI Positive) calculated for 425.2 $[M+H]^+$, found 425.6.



(*E*)-2gg

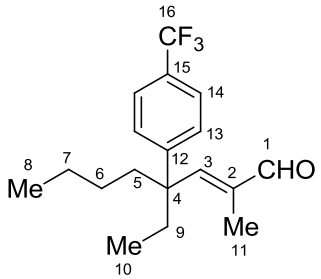
(*E*)-2-methyl-3-(1-(4-(trifluoromethyl)phenyl)cyclohexyl)acrylaldehyde (Scheme 3) Yellow oil (Pentane/Et_2O 1:1, R_f = 0.59). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.33 (d, $^4J_{HH}$ = 1.35 Hz, 3H, H-10); 1.30-1.40 (m, 1H, H-7); 1.47-1.62 (m, 2H, H-8); 1.69-1.74 (m, 3H, H-6 and H-7); 1.82-1.89 (m, 2H, H-5/9); 2.13-2.18 (H-5/9); 6.85 (br s, 1H, H-3); 7.42 (d, $^3J_{HH}$ = 8.24 Hz, 2H, H-12); 7.56 (d, $^3J_{HH}$ = 8.24 Hz, 2H, H-13); 9.46 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ(ppm) = 10.56 (C-10); 2308 (C-6 and C-8); 25.85 (C-7); 38.04 (C-5 and C-9); 44.96 (C-4); 124.47 (q, $^1J_{HH}$ = 272 Hz, C-15); 125.72 (q, $^3J_{HH}$ = 3.75 Hz, C-13); 127.12 (C-12); 128.81 (q, $^2J_{HH}$ = 33 Hz, C-14); 140.62 (C-11); 152.15 (C-2); 160.98 (C-3); 196.21 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ(ppm) = -62.45 (s). **LRMS** (ESI Positive) calculated for 297.2 $[M+H]^+$, found 297.5. **IR spectrum (neat)** ν(cm^{-1}) = 2933, 2859, 1687, 1618, 1451, 1409, 1324, 1223, 1163, 1114, 1069, 1013, 832, 606.



(*E*)-2hg

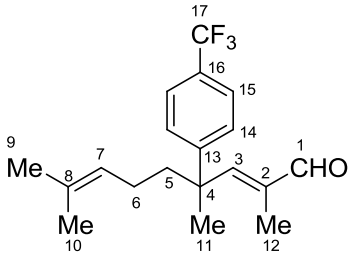
1-methyl-4'-(trifluoromethyl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-carbaldehyde (Scheme 3) Yellow oil (Pentane/Et_2O 1:1, R_f = 0.52). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ(ppm) = 1.46-1.52 (m, 1H, H-7); 1.54 (s, 3H, H-8); 1.66-1.73 (m, 1H, H-7'); 1.77 (ddd, $^3J_{HH}$ = 2.87 Hz, $^3J_{HH}$ = 9.72 Hz, $^2J_{HH}$ = 13.22 Hz, 1H, H-5); 1.95 (ddd, $^3J_{HH}$ = 2.87 Hz, $^3J_{HH}$ = 8.02 Hz, $^2J_{HH}$ = 13.22 Hz, 1H, H-5'); 2.25-2.28 (m, 2H, H-6); 6.73 (br s, 1H, H-3); 7.39

(d, $^{3}J_{HH}$ = 8.17 Hz, 2H, H-10); 7.59 (d, $^{3}J_{HH}$ = 8.17 Hz, 2H, H-11); 9.57 (s, 1H, H-1). **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz)** δ (ppm) = 18.58 (C-8); 21.77 (C-6); 28.12 (C-8); 39.98 (C-5); 41.41 (C-4); 124.47 (q, $^{1}J_{CF}$ = 272 Hz, C-13); 125.73 (q, $^{3}J_{CF}$ = 3.84 Hz, C-11); 127.02 (C-10); 128.98 (q, $^{2}J_{HH}$ = 32.5 Hz, C-12); 141.52 (C-2); 151.80 (C-9); 156.10 (C-3); 194.72 (C-1). **^{19}F{^{1}H} NMR (CDCl$_3$, 282 MHz)** δ (ppm) = -62.49 (s). **LRMS** (ESI Positive) calculated for 286.1 $[M+H_2O]^+$, found 286.1. **IR spectrum (neat)** ν (cm^{-1}) = 2937, 1685, 1642, 1617, 1457, 1409, 1324, 1163, 1114, 1087, 1065, 1014, 834, 697, 607.



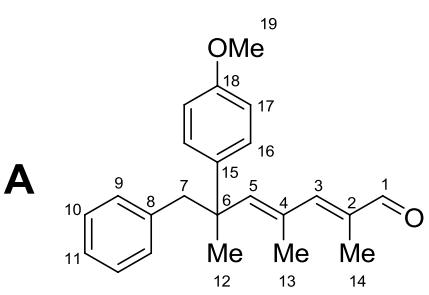
(*E*)-2ig

(*E*)-4-ethyl-2-methyl-4-(4-(trifluoromethyl)phenyl)oct-2-enal (Scheme 3) Yellow oil (Pentane/Et$_2$O 1:1, R$_f$ = 0.60). **^{1}H NMR (CDCl$_3$, 300 MHz)** δ (ppm) = 0.76 (t, $^{3}J_{HH}$ = 7.39 Hz, 3H, H-10); 0.87 (t, $^{3}J_{HH}$ = 7.22 Hz, 3H, H-8); 1.02-1.17 (m, 2H, H-6); 1.23-1.33 (m, 2H, H-7); 1.30 (s, 3H, H-11); 1.91-2.06 (m, 4H, H-5 and H-9); 6.64 (br s, 1H, H-3); 7.34 (d, $^{3}J_{HH}$ = 8.25 Hz, 2H, H-13); 7.56 (d, $^{3}J_{HH}$ = 8.25 Hz, 2H, H-14); 9.46 (s, 1H, H-1). **^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz)** δ (ppm) = 8.78 (C-10); 11.27 (C-11); 14.28 (C-8); 23.61 (C-7); 26.47 (C-6); 32.09 (C-9); 38.43 (C-5); 48.37 (C-4); 124.52 (q, $^{1}J_{CF}$ = 272 Hz, C-16); 125.48 (q, $^{3}J_{CF}$ = 3.74 Hz, C-14); 127.89 (C-13); 128.78 (q, $^{2}J_{CF}$ = 32.5 Hz, C-15); 140.87 (C-2); 150.12 (C-12); 162.09 (C-3); 196.21 (C-1). **^{19}F{^{1}H} NMR (CDCl$_3$, 282 MHz)** δ (ppm) = -62.41 (s). **LRMS** (ESI Positive) calculated for 313.2 $[M+H]^+$, found 313.0. **IR spectrum (neat)** ν (cm^{-1}) = 2961, 2935, 2869, 1689, 1618, 1461, 1409, 1324, 1164, 1120, 1068, 1016, 841, 792, 615.

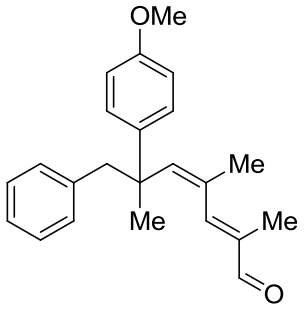


(*E*)-2jg

(*E*)-2,4,8-trimethyl-4-(4-(trifluoromethyl)phenyl)nona-2,7-dienal (Scheme 3) Yellow oil (Pentane/Et$_2$O 1:1, R$_f$ = 0.59). **^{1}H NMR (CDCl$_3$, 500 MHz)** δ (ppm) = 1.31 (d, $^{4}J_{HH}$ = 1.35 Hz, 3H, H-12); 1.50 (C-10); 1.58 (C-11); 1.65 (C-9); 1.73-1.92 (m, 4H, H-5 and H-6); 5.01-5.04 (m, 1H, H-7); 6.75 (q, $^{4}J_{HH}$ = 1.35 Hz, 1H, H-3); 7.38 (d, $^{3}J_{HH}$ = 8.15 Hz, 2H, H-14); 7.57 (d, $^{3}J_{HH}$ = 8.15 Hz, 2H, H-15); 9.44 (s, 1H, H-1). **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz)** δ (ppm) = 10.93 (C-12); 17.92 (C-10); 23.39 (C-6); 25.21 (C-11); 25.97 (C-9); 44.63 (C-5); 44.78 (C-4); 123.75 (C-7); 124.49 (q, $^{1}J_{CF}$ = 272 Hz, C-17); 125.68 (q, $^{3}J_{CF}$ = 3.79 Hz, C-15); 127.34 (C-14); 128.95 (q, $^{2}J_{CF}$ = 32.45 Hz, C-16); 132.71 (C-8); 140.58 (C-2); 150.82 (C-13); 161.95 (C-3); 196.15 (C-1). **^{19}F{^{1}H} NMR (CDCl$_3$, 282 MHz)** δ (ppm) = -62.45 (s). **LRMS** (ESI Positive) calculated for 325.2 $[M+H]^+$, found 325.5. **IR spectrum (neat)** ν (cm^{-1}) = 2925, 1688, 1618, 1451, 1409, 1379, 1325, 1165, 1121, 1076, 1014, 839, 612.



(2*E*,4*E*)-11aa



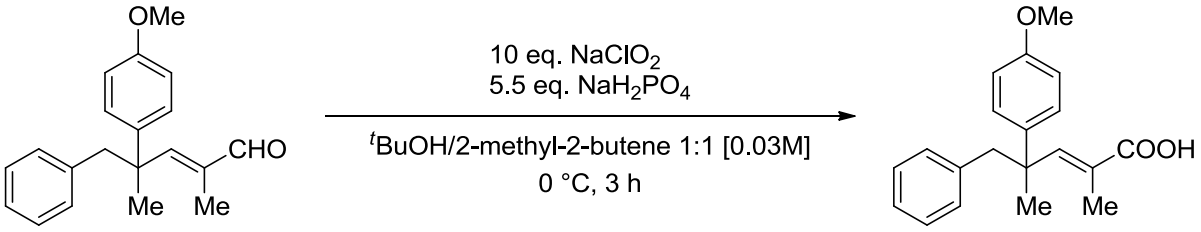
(2*E*,4*Z*)-11aa

The two isomers were not separable by chromatography

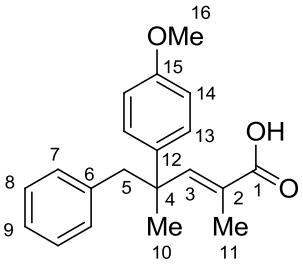
A) **(2*E*,4*E*)-6-(4-methoxyphenyl)-2,4,6-trimethyl-7-phenylhepta-2,4-dienal (Scheme 4)** (Pentane/Et_2O 5:1, R_f = 0.22). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.20 (d, $^4J_{HH}$ = 1.23 Hz, 3H, H-13); 1.41 (s, 3H, H-12); 1.70 (d, $^4J_{HH}$ = 1.27 Hz, 3H, H-14); 3.13 (br s, 2H, H-7); 3.31 (s, 3H, H-19); 5.63 (q, $^4J_{HH}$ = 1.23 Hz, 1H, H-5); 6.58 (q, $^4J_{HH}$ = 1.27 Hz, 1H, H-3); 6.75-6.77 (m, 2H, H-17); 9.29 (s, 1H, H-1), Protons H-9, 10, 11 and 16 cannot be assigned due to overlap of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 11.61 (C-14); 18.94 (C-13); 31.09 (C-12); 46.12 (C-6); 47.75 (C-7); 55.37 (C-19); 114.74 (C-17); 134.87 (C-5); 138.39 (C-4); 139.88 (C-2); 140.56 (C-6); 140.73 (C-8); 159.13 (C-18); 162.96 (C-3); 195.47 (C-1); Carbons C-9, 10, 11, 15 and 16 cannot be assigned due to overlap of signals. **HRMS** (ESI Positive) calculated for 335.2005 $[M+H]^+$, found 335.2003.

B) **(2*E*,4*Z*)-6-(4-methoxyphenyl)-2,4,6-trimethyl-7-phenylhepta-2,4-dienal (Scheme 4)** (Pentane/Et_2O 5:1, R_f = 0.22). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.45 (s, 3H, H-12); 1.53 (d, $^4J_{HH}$ = 1.40 Hz, 3H, H-13); 1.71 (d, $^4J_{HH}$ = 1.28 Hz, 3H, H-14); 3.02 (d, $^2J_{HH}$ = 15.4 Hz, 1H, H-7); 3.10 (d, $^2J_{HH}$ = 15.4 Hz, 1H, H-7'); 3.34 (s, 3H, H-19); 5.72 (q, $^4J_{HH}$ = 1.40 Hz, 1H, H-5); 6.67 (q, $^4J_{HH}$ = 1.28 Hz, 1H, H-3); 9.27 (s, 1H, H-1), Protons H-9, 10, 11, 16 and 17 cannot be assigned due to overlap of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 11.69 (C-14); 24.33 (C-13); 31.62 (C-12); 40.50 (C-7); 46.09 (C-6); 55.42 (C-19); 114.78 (C-17); 135.81 (C-5); 137.08 (C-4); 140.05 (C-2); 159.19 (C-18); 162.77 (C-3); 195.43 (C-1); Carbons C-8, 9, 10, 11, 15 and 16 cannot be assigned due to overlap of signals. **HRMS** (ESI Positive) calculated for 335.2005 $[M+H]^+$, found 335.2003.

SYNTHESIS OF (*E*)-4-(4-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enoic acid ((*E*)-6)



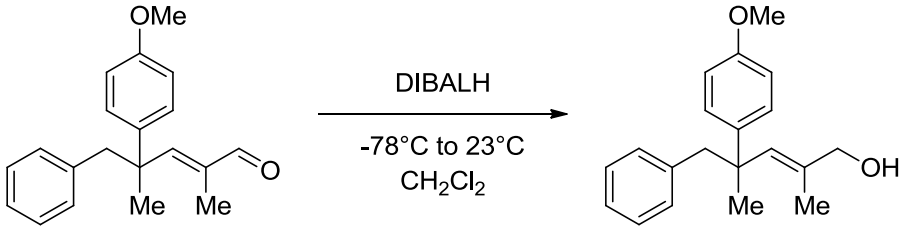
In a 50 mL, two-necked, round bottomed flask, (*E*)-**2aa** (0.51 mmol, 1 eq.) was dissolved in 17 mL of a 1:1 solution of *tert*-butanol and 2-methyl-2-butene at 0°C. NaH_2PO_4 (2.80 mmol., 5.5 eq.) was added as a solution in 1 mL of water followed by the dropwise addition of a solution of $NaClO_2$ (5.09 mmol., 10 eq.) in 1 mL of water. The reaction was stirred at 0°C for 3h. The solution was diluited with 10 mL of water and quenched with few drops of a solution of HCl 0.25N. The aqueous phase was extracted with Et_2O (7 mL x 3), the combined organic layers dried over Na_2SO_4. After evaporation of the solvent the crude mixture was purified by flash chromatography (pentane/Et_2O 2:1) to afford (*E*)-**6**.



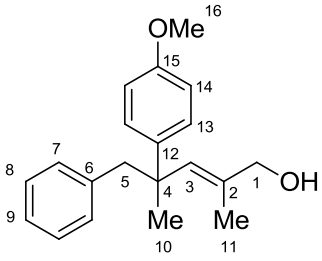
(*E*)-6

(Scheme 4) White soft solid (Pentane/Et_2O 1:2, R_f = 0.38, Mp = 127-129°C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.39 (d, $^4J_{HH}$ = 1.37 Hz, 3H, H-11); 1.44 (s, 3H, H-10); 2.99 (d, $^2J_{HH}$ = 12.39 Hz, 1H, H-5); 3.12 (d, $^2J_{HH}$ = 12.39 Hz, 1H, H-5'); 3.81 (s, 3H, H-16); 6.75-6.77 (m, 2H, H-7); 6.79-6.81 (m, $^3J_{HH}$ = 8.81 Hz, 2H, H-14); 7.03-7.06 (m, 2H, H-13); 7.13-7.16 (m, 3H, H-8 and H-9); 7.40 (q, $^4J_{HH}$ = 1.37 Hz, 1H, H-3); 11.26 (br s, 1H, -COOH). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 13.94 (C-11); 24.21 (C-10); 44.48 (C-4); 51.98 (C-5); 55.56 (C-16); 113.75 (C-14); 126.62 (C-9); 127.88 (C-8); 128.49 (C-13); 128.60 (C-2); 131.16 (C-7); 137.48 (C-6); 138.60 (C-12); 153.28 (C-3); 158.16 (C-15); 178.95 (C-1). **HRMS** (ESI Positive) calculated for 333.1461 $[M+Na]^+$, found 333.1466. **IR spectrum (neat)** ν (cm^{-1}) = 2923, 1696, 1679, 1630, 1607, 1510, 1283, 1244, 1033, 831, 733, 703.

SYNTHESIS OF (*E*)-4-(4-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-enol ((*E*)-7)



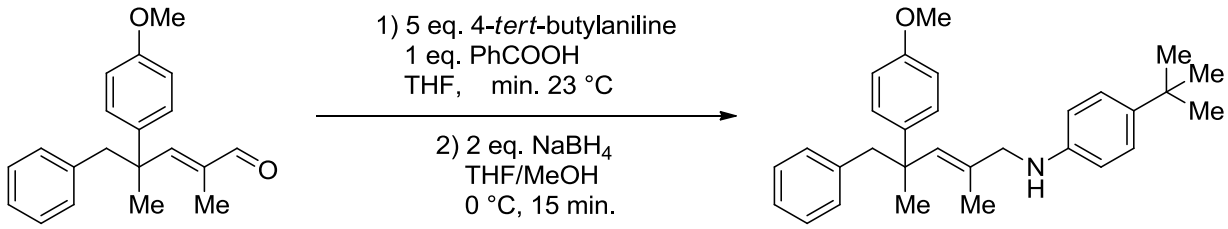
In a 10 mL, two-necked, round bottomed flask, (*E*)-**2aa** (0.51 mmol, 1 eq.) was dissolved in 4 mL of dry dichloromethane. The system was cooled to -78°C and DIBALH (0.82 mL 1M solution in hexane, 0.81 mmol, 2 eq.) was added drop-wise. The reaction was slowly warmed to 23°C and monitored by TLC (pentane/Et_2O) until complete conversion of the starting material. The solution was quenched with 2 mL of a saturated aqueous solution of potassium sodium tartrate and the aqueous phase was extracted with dichloromethane (3 mL x 3). The organic phases were separated, combined and dried over Na_2SO_4. After evaporation of the solvent the crude mixture was purified by flash chromatography (pentane/Et_2O 4:1 then 1:1) to afford (*E*)-**7**.



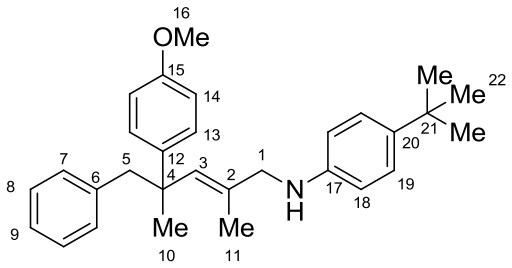
(*E*)-7

(Scheme 3) Colorless liquid (Pentane/Et_2O 1:1, R_f = 0.27). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.21 (d, $^4J_{HH}$ = 1.36 Hz, 3H, H-11); 1.35 (br t, $^3J_{HH}$ = 5.88 Hz, 1H, -OH); 1.39 (s, 3H, H-10); 2.91 (d, $^2J_{HH}$ = 12.7 Hz, 1H, H-5); 3.04 (d, $^2J_{HH}$ = 12.7 Hz, 1H, H-5'); 3.81 (s, 3H, H-16); 3.98 (br d, $^3J_{HH}$ = 5.88 Hz, 2H, H-1); 5.85 (q, $^4J_{HH}$ = 1.36 Hz, 1H, H-3); 6.74-6.76 (m, 2H, H-7); 6.78-6.80 (m, $^3J_{HH}$ = 8.83 Hz, 2H, H-14); 7.10-7.11 (m, $^3J_{HH}$ = 8.83 Hz, 2H, H-13); 7.12-7.14 (m, 3H, H-8 and H-9). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 15.57 (C-11); 25.72 (C-10); 43.23 (C-4); 52.20 (C-5); 55.51 (C-16); 70.15 (C-1); 113.43 (C-14); 126.30 (C-9); 127.67 (C-8); 128.51 (C-13); 131.20 (C-7); 135.31 (C-3); 136.48 (C-2); 138.32 (C-6); 140.47 (C-12); 157.69 (C-15). **HRMS** (ESI Positive) calculated for 319.1668 $[M+Na]^+$, found 319.1669. **IR spectrum (neat)** ν (cm^{-1}) = 3322, 1607, 1509, 1455, 1241, 1178, 1035, 828, 732, 702.

SYNTHESIS OF (*E*)-4-(*tert*-butyl)-N-(4-(4-methoxyphenyl)-2,4-dimethyl-5-phenylpent-2-en-1-yl)aniline ((*E*)-8)



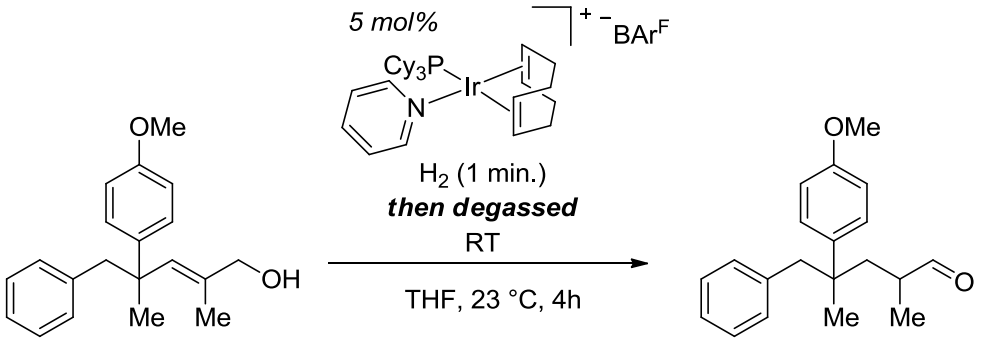
In a dry 5 mL Schlenk tube under nitrogen atmosphere, (*E*)-**2aa** (0.2 mmol., 1 eq.) and benzoic acid (0.2 mmo., 1 eq.) were dissolved in 1.0 mL of dry THF. 4-*tert*-butylaniline (1.02 mmol., 5 eq.) was added and the solution was stirred at 23 °C for 5 hours. The reaction was diluted with 1 mL of methanol and cooled to 0 °C. $NaBH_4$ (0.41 mmol., 8 eq.) was added and the mixture was stirred at 0°C for 40 minutes. The reaction was quenched with 0.5 mL of saturated NH_4Cl solution and the aqueous phase was extracted with Et_2O (1 mL x 3). The combined organic layers were dried over Na_2SO_4 and then the solvent was evaporated. The crude mixture was purified by flash chromatography (pentane/Et_2O 4:1).



(*E*)-8

(Scheme 3) White solid (Pentane/Et_2O 1:1, R_f = 0.64, Mp = 76-78 °C). **^{1}H NMR ($CDCl_3$, 300 MHz)** δ (ppm) = 1.21 (d, $^4J_{HH}$ = 1.30 Hz, 3H, H-11); 1.31 (s, 9H, H-22); 1.39 (s, 3H, H-10); 2.88 (d, $^2J_{HH}$ = 12.7 Hz, 1H, H-5); 2.98 (d, $^2J_{HH}$ = 12.7 Hz, 1H, H-5'); 3.62 (br s, 2H, H-1); 3.80 (s, 3H, H-18); 5.87 (q, $^4J_{HH}$ = 1.30 Hz, 1H, H-3); 6.58 (m, $^3J_{HH}$ = 8.68 Hz, 2H, H-18); 6.72-6.74 (m, 2H, H-7); 6.75-6.78 (m, $^3J_{HH}$ = 8.84 Hz, 2H, H-14); 7.05-7.07 (m, $^3J_{HH}$ = 8.84 Hz, 2H, H-13); 7.08-7.16 (m, 3H, H-8 and H-9); 7.20-7.23 (m, $^3J_{HH}$ = 8.68 Hz, 2H, H-19). **^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz)** δ (ppm) = 16.63 (C-11); 25.95 (C-10); 31.94 (C-22); 34.21 (C-21); 43.44 (C-4); 52.34 (C-5); 53.66 (C-1); 55.50 (C-18); 113.24 (C-18); 113.39 (C-14); 126.20 (C-19); 126.23 (C-9); 127.65 (C-8); 128.51 (C-13); 131.22 (C-7); 134.35 (C-2); 135.68 (C-3); 138.44 (C-6); 140.41 (C-20); 140.77 (C-12); 146.40 (C-17); 157.66 (C-15). **HRMS** (ESI Positive) calculated for 428.2947 $[M+H]^+$, found 428.2950. **IR spectrum (neat)** ν (cm^{-1}) = 2958, 1612, 1511, 1460, 1299, 1246, 1180, 1032, 908, 821, 730, 701.

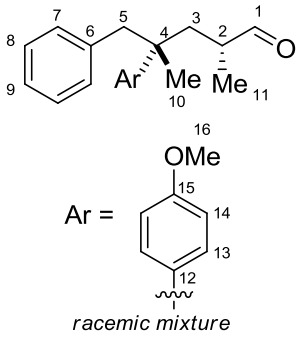
SYNTHESIS OF 4-(4-methoxyphenyl)-2,4-dimethyl-5-phenylpentanal (9)



Activation of the catalyst: Crabtree catalyst (0.005 mmol, 0.05 eq.) was dissolved in 1.5 mL of dry and degassed THF. Hydrogen was bubbled in the solution under vigorous stirring for 1 minute. Next, the solution was degassed by two successive "freeze-pump-thaw" cycles. Allylic alcohol (*E*)-**7** (0.1 mmol. 1 eq.) was added to the cold solution of the activated catalyst and the reaction was stirred at 23 °C for 4 hours. The solvent was

evaporated and the residue was purified by flash chromatography (pentane/Et_2O 8:1) and the pure diastereoisomers were separated.

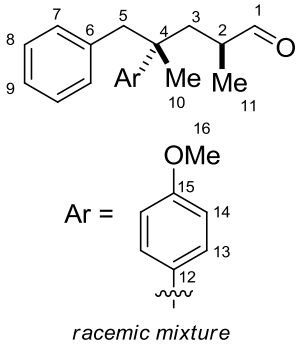
The relative configuration of the two diastereoisomers was determined by single crystal X-ray diffraction study.



racemic mixture

***Syn* product [*syn*-9]**

(Scheme 4) White solid (pentane/Et_2O 1:1, R_f = 0.54, Mp = 51-53 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ(ppm) = 0.88 (d, $^3J_{HH}$ = 6.68 Hz, 3H, H-11); 1.17 (s, 3H, H-10); 1.84-1.88 (m, 1H, H-3); 2.15-2.21 (m, 2H, H-2 and H-3'); 2.78 (d, $^2J_{HH}$ = 13.13 Hz, 1H, H-5); 2.97 (d, $^2J_{HH}$ = 13.13 Hz, 1H, H-5'); 3.81 (s, 3H, H-16); 6.74-6.76 (m, 2H, H-7); 6.83-6.84 (m, $^3J_{HH}$ = 8.77 Hz, 2H, H-14); 7.11-7.14 (m, 5H, H-8,9 and H-13); 9.49 (d, $^3J_{HH}$ = 2.04 Hz, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ(ppm) = 16.52 (C-11); 23.86 (C-10); 42.12 (C-4); 43.41 (C-3); 43.62 (C-2); 51.47 (C-5); 55.55 (C-16); 113.74 (C-14); 126.37 (C-9); 127.85 (C-8); 128.23 (C-13); 130.88 (C-7); 138.17 (C-12); 138.35 (C-6); 158.09 (C-15), 205.24 (C-1). **HRMS** (ESI Positive) calculated for 314.2114 $[M+NH_4]^+$, found 314.2114. **IR spectrum (neat)** ν(cm^{-1}) = 2929, 1722, 1610, 1511, 1454, 1295, 1249, 1185, 1031, 829, 752, 701.



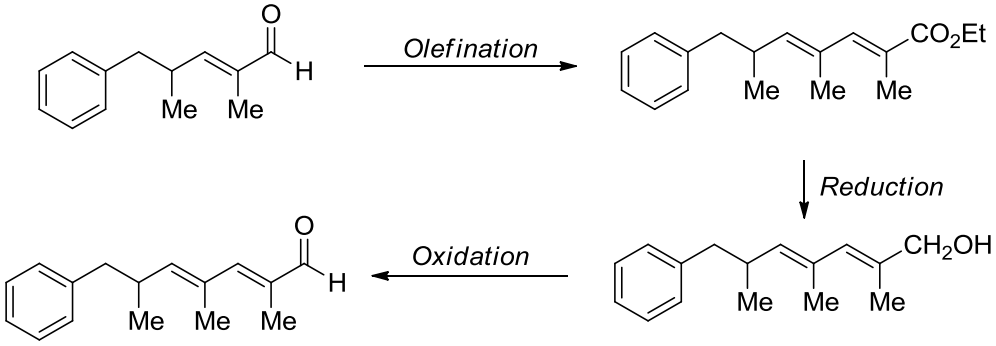
racemic mixture

***Anti* product [*anti*-9]**

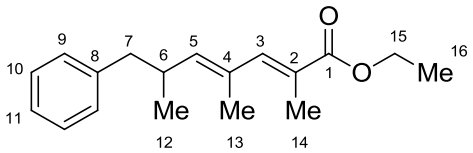
(Scheme 4) White solid (pentane/Et_2O 1:1, R_f = 0.42, Mp = 41-43 °C). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ(ppm) = 1.04 (d, $^3J_{HH}$ = 7.02 Hz, 3H, H-11); 1.27 (s, 3H, H-10); 1.48 (dd, $^2J_{HH}$ = 14.35 Hz, $^3J_{HH}$ = 4.39 Hz, 1H, H-3); 2.21-2.25 (m, 1H, H-2); 2.57 (dd, $^2J_{HH}$ = 14.35 Hz, $^3J_{HH}$ = 7.03 Hz, 1H, H-3'); 2.77 (d, $^2J_{HH}$ = 13.21 Hz, 1H, H-5); 3.01 (d, $^2J_{HH}$ = 13.21 Hz, 1H, H-5'); 3.80 (s, 3H, H-16); 6.76-6.78 (m, 2H, H-7); 6.81-6.83 (m, $^3J_{HH}$ = 8.81 Hz, 2H, H-14); 7.11-7.16 (m, 5H, H-8,9 and H-13); 9.07 (d, $^3J_{HH}$ = 2.59 Hz, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ(ppm) = 16.67 (C-11); 23.49 (C-10); 42.03 (C-4); 43.55 (C-2); 44.66 (C-3); 51.60 (C-5); 55.51 (C-16); 113.79 (C-14); 126.38 (C-9); 127.87 (C-8); 128.48 (C-13); 130.83 (C-7); 137.88 (C-12); 138.39 (C-6); 158.25 (C-15); 204.31 (C-1). **HRMS** (ESI Positive) calculated for 319.1668 $[M+Na]^+$, found 319.1666. **IR spectrum (neat)** ν(cm^{-1}) = 2929, 1721, 1610, 1512, 1454, 1249, 1185, 1031, 829, 701.

SYNTHESIS OF (2*E*, 4*E*)-2,4,6-trimethyl-7-phenylhepta-2,4-dienal (10a)

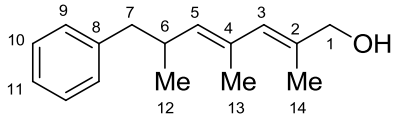
For the synthesis of (2*E*, 4*E*)-2,4,6-trimethyl-7-phenylhepta-2,4-dienal the previous general olefination, reduction and DMP oxidation procedures were used starting from (*E*)-2,4-dimethyl-5-phenylpent-2-enal.



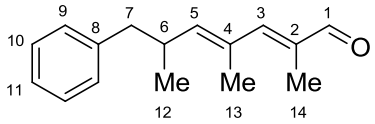
(*E*,*E*)-10a



(2*E*, 4*E*)-ethyl 2,4,6-trimethyl-7-phenylhepta-2,4-dienoate (72 % yield) Colorless oil (Pentane/Et_2O 10:1, R_f = 0.41). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.02 (d, $^3J_{HH}$ = 6.62 Hz, 3H, H-12); 1.30 (t, $^3J_{HH}$ = 7.13 Hz, 3H, H-16); 1.64 (d, $^4J_{HH}$ = 1.21 Hz, 3H, H-13); 1.92 (d, $^4J_{HH}$ = 1.37 Hz, 3H, H-14); 2.56-2.66 (m, 2H, H-7); 2.72-2.83 (m, 1H, H-6); 4.19 (q, $^3J_{HH}$ = 7.13 Hz, 2H, H-15); 5.41 (br d, $^3J_{HH}$ = 9.52 Hz, 1H, H-5); 7.06 (br s, 1H, H-3); 7.13-7.19 (m, 3H, H-9 and H-11); 7.24-7.27 (m, 2H, H-10). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 14.28 (C-14); 14.67 (C-16); 16.60 (C-13); 20.75 (C-12); 35.39 (C-6); 43.80 (C-7); 60.90 (C-15); 125.79 (C-2); 126.20 (C-9); 128.46 (C-10); 129.48 (C-11); 131.51 (C-4); 140.76 (C-8); 141.54 (C-5); 143.22 (C-3); 169.51 (C-1). **HRMS** (ESI Positive) calculated for 273.1849 $[M+H]^+$, found 273.1846. **IR spectrum (neat)** ν (cm^{-1}) = 2959, 1702, 1452, 1247, 1110, 1030, 745, 699.



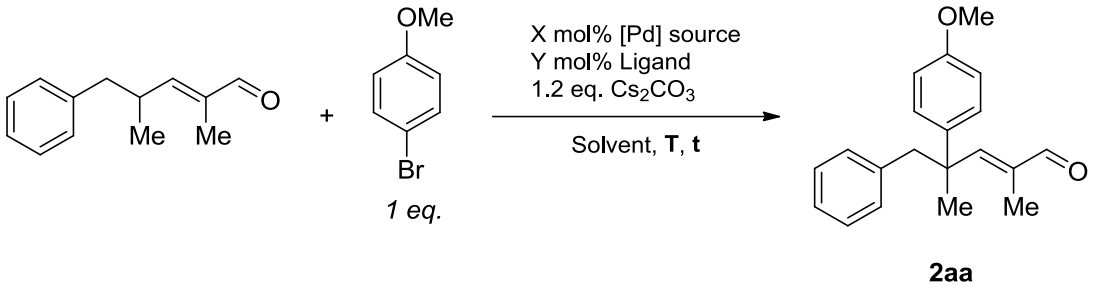
(2*E*, 4*E*)-2,4,6-trimethyl-7-phenylhepta-2,4-dien-1-ol (92 % yield) Colorless oil (Pentane/Et_2O 2:1, R_f = 0.22). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.01 (d, $^3J_{HH}$ = 6.59 Hz, 3H, H-12); 1.47 (br s, 1H, -OH); 1.59 (d, $^4J_{HH}$ = 1.17 Hz, 3H, H-13); 1.75 (d, $^4J_{HH}$ = 1.14 Hz, 3H, H-14); 2.60 (d, $^3J_{HH}$ = 7.17 Hz, 2H, H-7); 2.69-2.80 (m, 1H, H-6); 4.03 (br s, 2H, H-1); 5.17 (br d, $^3J_{HH}$ = 9.37 Hz, 1H, H-5); 5.84 (br s, 1H, H-3); 7.15-7.20 (m, 3H, H-9 and H-11); 7.25-7.28 (m, 2H, H-10). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.60 (C-14); 17.16 (C-13); 21.01 (C-12); 35.13 (C-6); 44.09 (C-7); 69.80 (C-1); 126.04 (C-11); 128.38 (C-10); 129.51 (C-9); 129.74 (C-3); 131.40 (C-4); 134.59 (C-2); 136.28 (C-5); 141.18 (C-8). **LRMS** (ESI Positive) calculated for 253.1563 $[M+Na]^+$, found 253.1561. **IR spectrum (neat)** ν (cm^{-1}) = 3307, 2955, 2919, 1494, 1451, 1375, 1004, 8845, 743, 698.



(2*E*,4*E*)-10a

(2*E*, 4*E*)-2,4,6-trimethyl-7-phenylhepta-2,4-dienal (Scheme 4) (45 % yield) Colorless oil (Pentane/Et_2O 4:1, R_f = 0.38). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 1.05 (d, $^3J_{HH}$ = 6.62 Hz, 3H, H-12); 1.76 (d, $^4J_{HH}$ = 1.26 Hz, 3H, H-13); 1.88 (d, $^4J_{HH}$ = 1.12 Hz, 3H, H-14); 2.59-2.68 (m, 2H, H-7); 2.78-2.87 (m, 1H, H-6); 5.68 (br d, $^3J_{HH}$ = 9.59 Hz, 1H, H-5); 6.67 (br s, 1H, H-3); 7.13-7.14 (m, 2H, H-9); 7.17-7.20 (m, 1H, H-11); 7.24-7.28 (m, 2H, H-10); 9.36 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 11.00 (C-14); 16.30 (C-13); 20.57 (C-12); 35.60 (C-6); 43.65 (C-7); 126.37 (C-11); 128.55 (C-10); 129.47 (C-9); 132.44 (C-4); 135.97 (C-2); 140.41 (C-8); 145.97 (C-5); 155.34 (C-3); 196.49 (C-1). **HRMS** (ESI Positive) calculated for 251.1406 $[M+Na]^+$, found 251.1408. **IR spectrum (neat)** ν (cm^{-1}) = 2960, 2925, 1675, 1609, 1452, 1194, 1021, 909, 744, 682.

REACTION OPTIMIZATION TABLE[a]

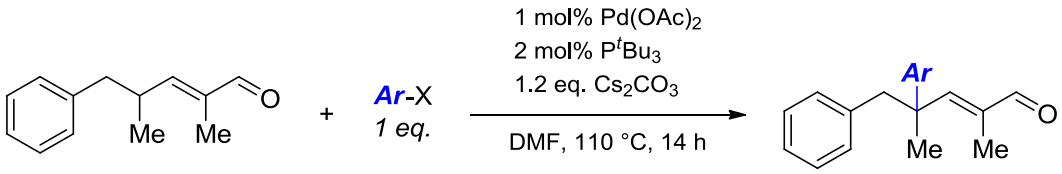


2aa

Entry	Solvent	Ligand	L mol%	Pd source	[Pd] mol%	T (°C)	t (h)	NMR conversion (E:Z)[b]
1	DMF	PPh_3	10	$Pd(OAc)_2$	5	80	14	24 % (>99:1)
2	DMF	*rac*-BINAP	6	$Pd(OAc)_2$	5	80	14	82 % (12:1)
3	DMF	$Cy_3PH{\cdot}BF_4$	10	$Pd(OAc)_2$	5	80	14	47% (>99:1)
4	DMF	$^tBu_3PH{\cdot}BF_4$	10	$Pd(OAc)_2$	5	80	14	86 % (6:1)
5	DMF	PCy_3	10	$Pd(OAc)_2$	5	80	14	55 % (29:1)
6	DMF	Xantphos	10	$Pd(OAc)_2$	5	80	14	69 % (3.6:1)
7	DMF	Q-Phos	10	$Pd(OAc)_2$	5	80	14	51% (6:1)
8	DMF	P^tBu_3	10	$Pd(OAc)_2$	5	80	14	96 % (6.5:1)
9	DMF	rac-BINAP	6	$Pd(OAc)_2$	5	110	14	52 % (7.7:1)
10	DMF	P^tBu_3	15	$Pd(OAc)_2$	5	110	14	>99 % (7.5:1)
11	DMF	P^tBu_3	10	$Pd(OAc)_2$	5	110	14	>99 % (8:1)
12	DMF	P^tBu_3	10	$Pd(dba)_2$	5	110	14	81 % (6.3:1)
13	DMF	P^tBu_3	10	$PdCl_2(CH_3CN)_2$	5	110	14	90 % (6.1:1)
14	DMF	P^tBu_3	10	$Pd(OAc)_2$	5	110	6	98 % (6.6:1)
15	*t*-amyl alcohol	P^tBu_3	10	$Pd(OAc)_2$	5	110	6	No reaction
16	Dioxane	P^tBu_3	10	$Pd(OAc)_2$	5	110	6	No reaction
17	Toluene	P^tBu_3	10	$Pd(OAc)_2$	5	110	6	No reaction
18	TBME	P^tBu_3	10	$Pd(OAc)_2$	5	110	6	No reaction
19	DMSO	P^tBu_3	2	$Pd(OAc)_2$	1	110	14	80% (>99/1)
20	MEK	P^tBu_3	2	$Pd(OAc)_2$	1	110	14	15% (>99/1)
21	DMA	P^tBu_3	2	$Pd(OAc)_2$	1	110	14	94% (7.6/1)
22	NMP	P^tBu_3	2	$Pd(OAc)_2$	1	110	14	84% (8/1)
23	DMF	-	-	$Pd(P^tBu_3)_2$	5	110	6	82 % (6:1)
24	DMF	-	-	$Pd(P^tBu_3)_2$	1	110	14	95 % (6:1)
25	DMF	P^tBu_3	5	$Pd(OAc)_2$	2.5	110	14	>99 % (8:1)
26	DMF	P^tBu_3	2	$Pd(OAc)_2$	1	110	14	99 % (8:1)
27	DMF	P^tBu_3	1	$Pd(OAc)_2$	0.5	110	14	92% (10/1)
28	DMF	P^tBu_3	0.2	$Pd(OAc)_2$	0.1	110	14	38% (>99/1)
29[c]	DMF	P^tBu_3	2	$Pd(OAc)_2$	1	110	14	98 % (7:1)

[a] (*E*)-**1a** (0.5 mmol), 4-bromoanisole (0.5 mmol). Average of at least two experiments.
[b] Determined by ^1H NMR.
[c] Reaction performed in presence of a 10 mmol% of (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (TEMPO)

SUBSTRATE SCOPE (ARYL HALIDE)[a]



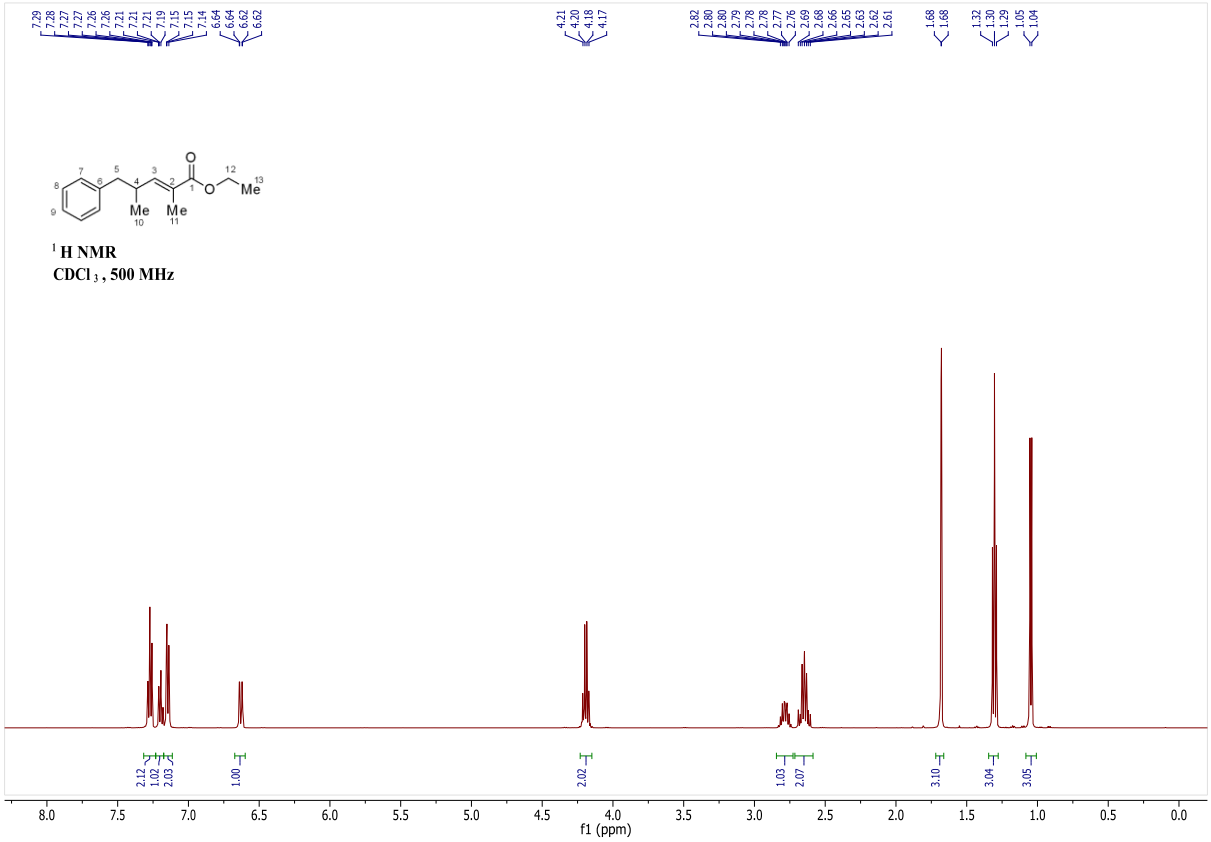
Entry	Ar-X	Product	Conv. (%)[b]	Yield (%)[c]	*E*/*Z*[b]
1	4-MeO-C_6H_4-Br	**2aa**	99	84	8:1
2	C_6H_5-I	**2ab**	82	73	12:1
3	C_6H_5-Br	**2ab**	95	85	9:1
4	C_6H_5-Cl	**2ab**	7	*nd*	*nd*
5	4-Cl-C_6H_4-Br	**2ac**	92	66	10:1
6	4-Me-C_6H_4-Br	**2ad**	95	83	8:1
7	4-*t*-Bu-C_6H_4-Br	**2ae**	94	87	10:1
8	4-CO_2Et-C_6H_4-Br	**2af**	89	74	10:1
9	4-CF_3-C_6H_4-Br	**2ag**	91	78	19:1
10	4-CN-C_6H_4-Br	**2ah**	68	48	>50:1
11	3-MeO-C_6H_4-Br	**2ai**	95	79	8:1
12	3-Me-C_6H_4-Br	**2aj**	96	79	8:1
13	2-bromonaphthalene	**2ak**	94	80	11:1
14	2-MeO-C_6H_4-Br	**2al**	74	62	4:1
15	2-Me-C_6H_4-Br	**2am**	84	63	7:1
16	1-bromonaphthalene	**2an**	74	66	7:1
17	2,6-$(Me)_2$-C_6H_3-Br	**2ao**	<5	*nd*	*nd*
18	2-bromopyridine	**2ap**	25	23[d]	>50:1
19	3-bromopyridine	**2aq**	79	63	>50:1
20	(*E*)-1-bromopropene	**2ar**	46	39[e]	10:1

[a] (*E*)-**1a** (0.5 mmol), aryl halide (0.5 mmol). Average of at least two experiments.
[b] Based on product formation. Determined by ^{1}H NMR.
[c] Isolated yield after chromatography.
[d] Isolated along with 6% of 2,2'-dipyridil.
[e] At 60°C for 24 h.

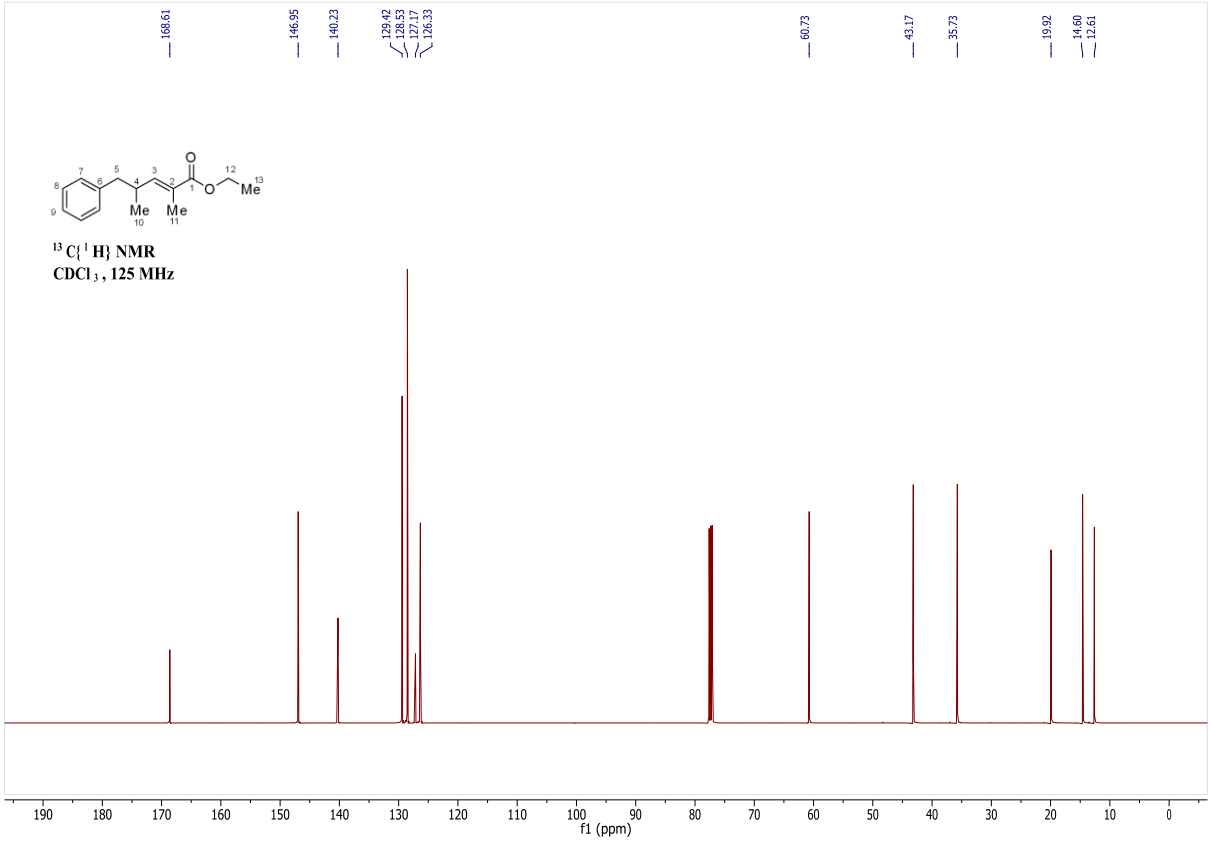
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR COMPOUNDS 4 AND *ANTI*-9

Compound	**4**	*Anti*-**9**
Empirical formula	C22 H20 O	C20 H24 O2
Formula weight	300.38	296.39
Temperature (K)	180(2)	180(2)
Wavelength	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Orthorhombic
Space group	*P* $2_1/c$	*P b c a*
Unit cell dimensions	*a* = 16.0527(3) Å	*a* = 9.79459(15) Å
	b = 5.53030(10) Å	*b* = 10.18235(18) Å
	c = 20.7663(7) Å	*c* = 34.1007(7) Å
	α = 90°	α = 90°.
	β = 115.425(2)°	β = 90°.
	γ = 90°	γ = 90°.
Volume ($Å^3$)	1665.00(7)	3400.93(10)
Z	4	8
Density (calculated) (Mg/m^3)	1.198	1.158
Absorption coefficient	0.551 mm^{-1}	0.570 mm^{-1}
F(000)	640	1280
Crystal size (mm^3)	0.4297 x 0.1639 x 0.0755	0.3199 x 0.2088 x 0.1123
Theta range for data collection	3.05 to 73.27°.	2.59 to 73.36°.
Index ranges	-18≤h≤19, -6≤k≤4, -20≤l≤25	-5≤*h*≤11, -12≤*k*≤11, -41≤*l*≤41
Reflections collected	6464	10550
Independent reflections	3240 [R(int) = 0.0109]	3356 [R(int) = 0.0142]
Completeness to theta = 67.50°	99.9 %	99.8 %
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.959 and 0.878	0.939 and 0.872
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3240 / 0 / 208	3356 / 0 / 202
Goodness-of-fit on F^2	1.043	1.035
Final *R* indices [I>2σ(I)]	R_1 = 0.0365, wR_2 = 0.0990	R_1 = 0.0481, wR_2 = 0.1294
R indices (all data)	R_1 = 0.0401, wR_2 = 0.1022	R_1 = 0.0510, wR_2 = 0.1320
Largest diff. peak and hole ($e.Å^{-3}$)	0.208 and -0.153	0.434 and -0.344

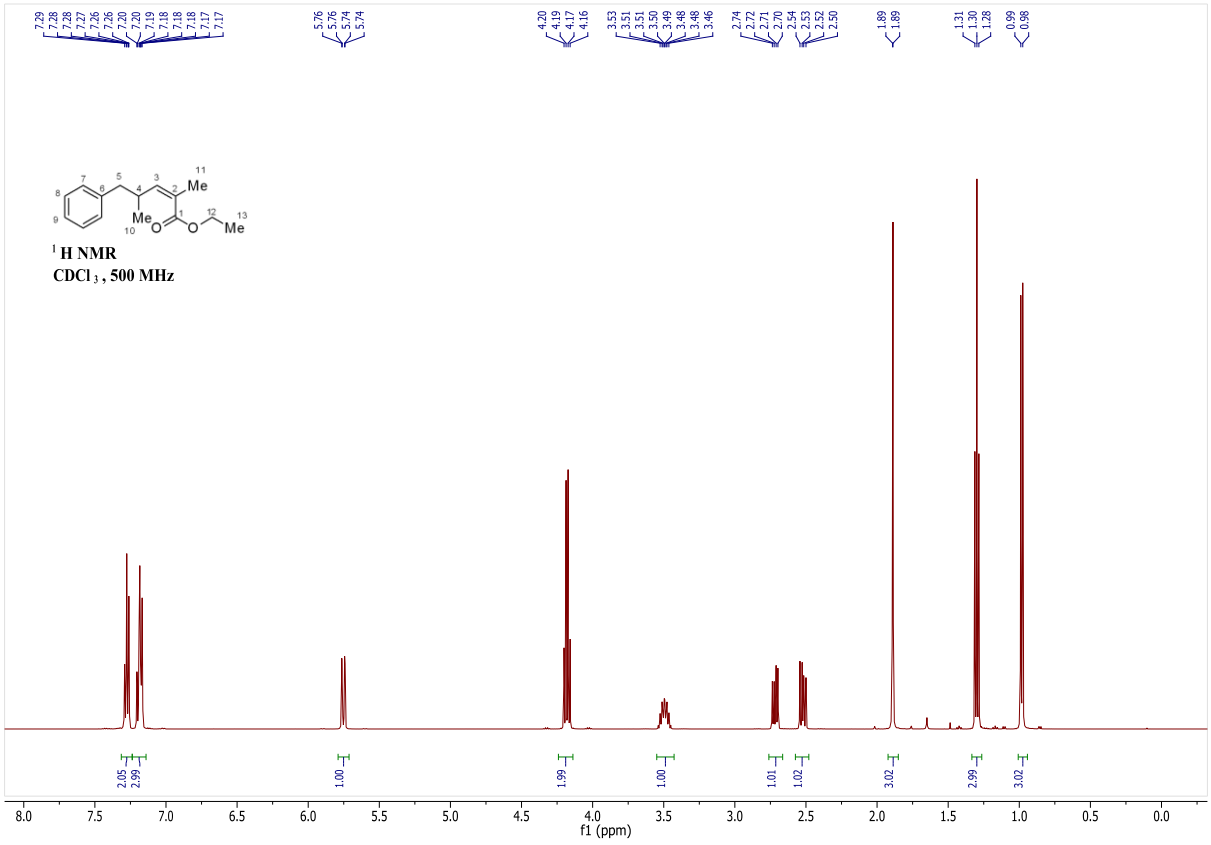
NMR SPECTRA



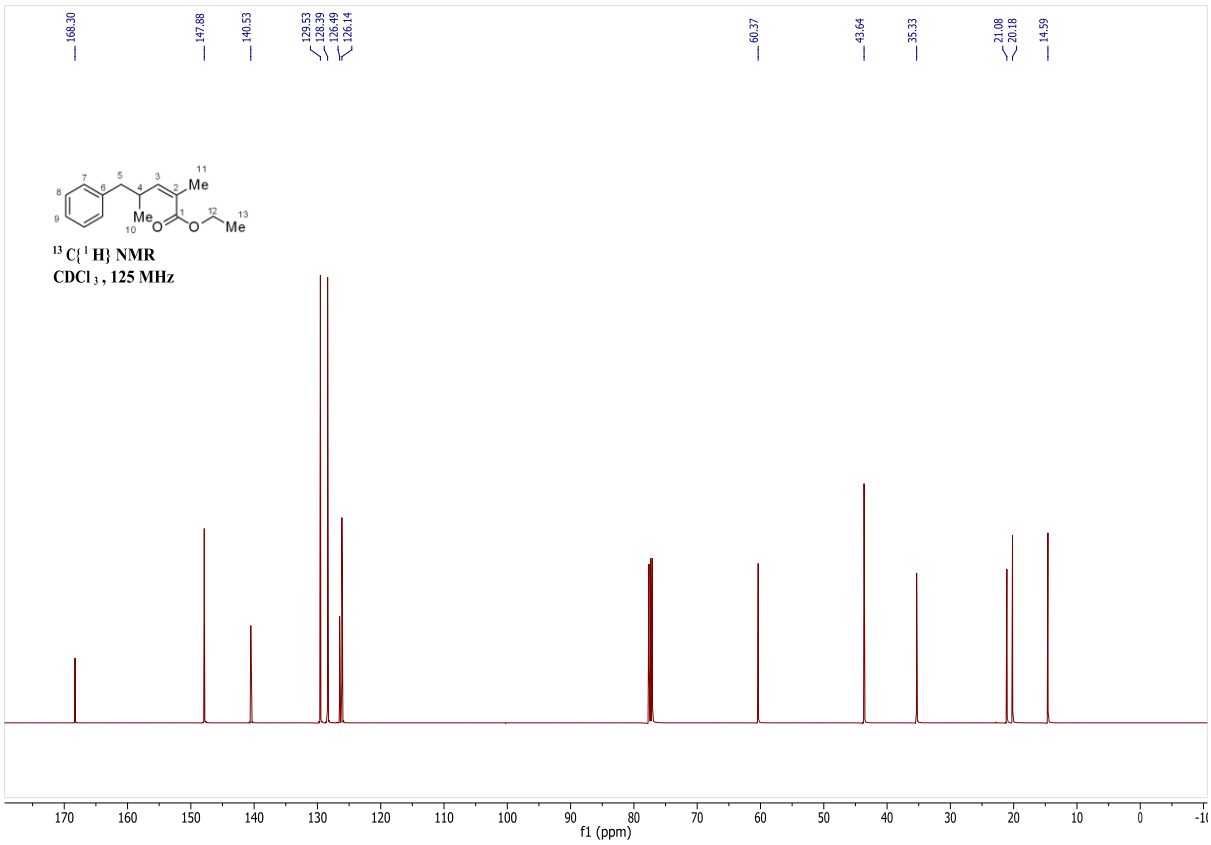
^{1}H NMR
$CDCl_3$, 500 MHz



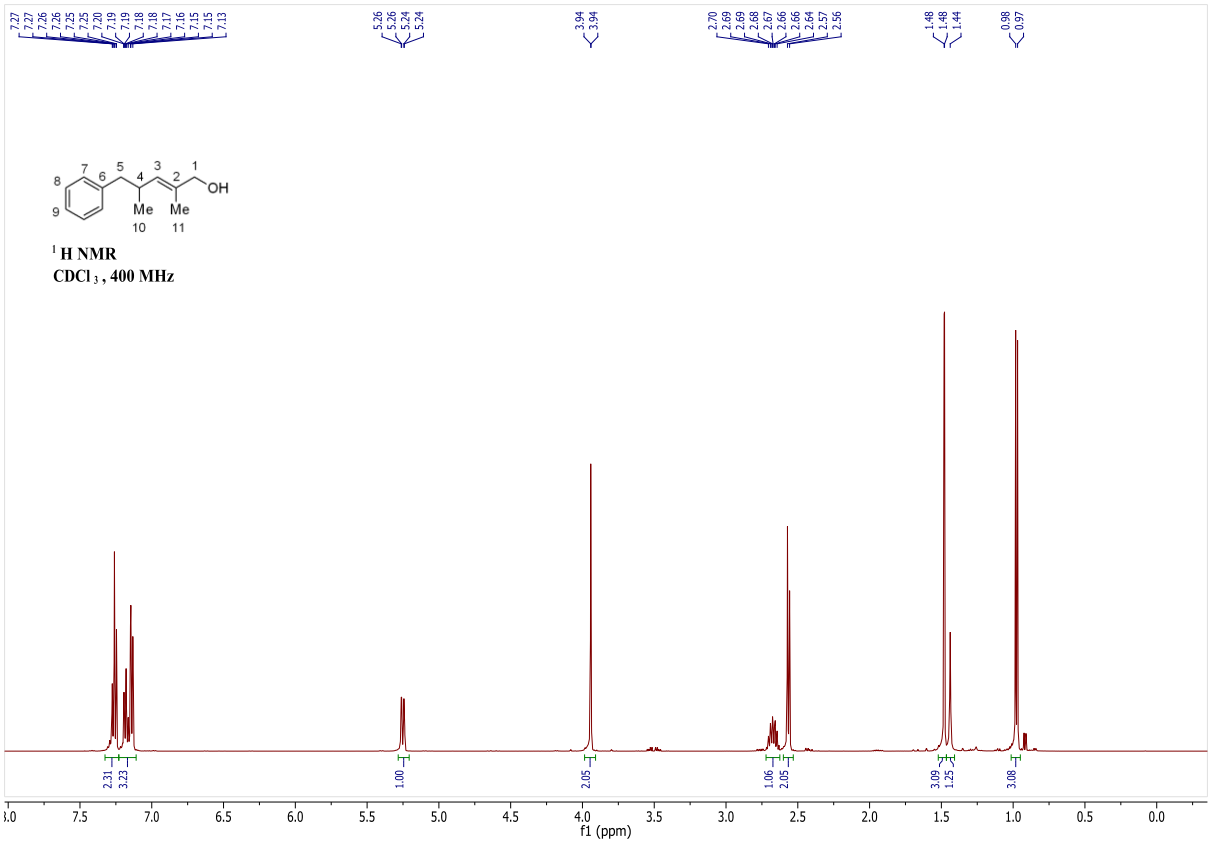
$^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 125 MHz



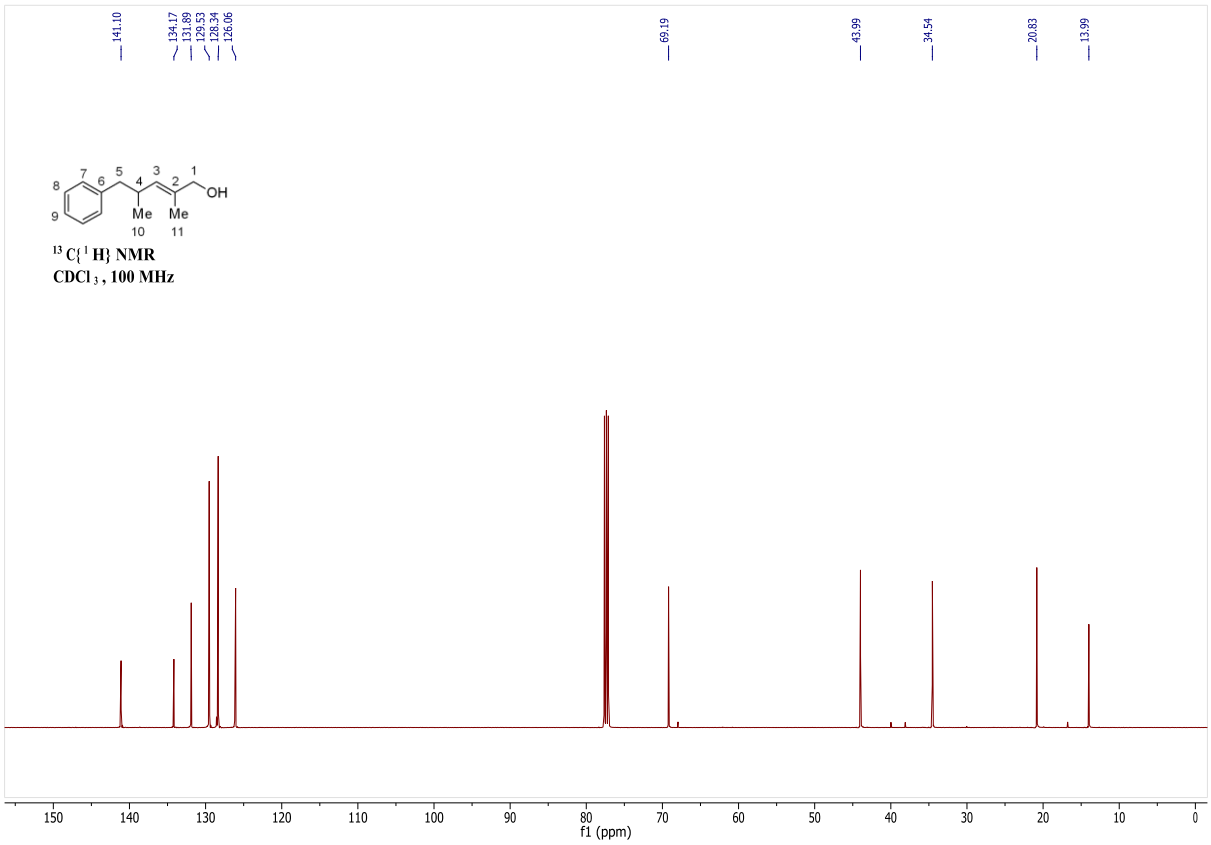
^{1}H NMR
$CDCl_3$, 500 MHz



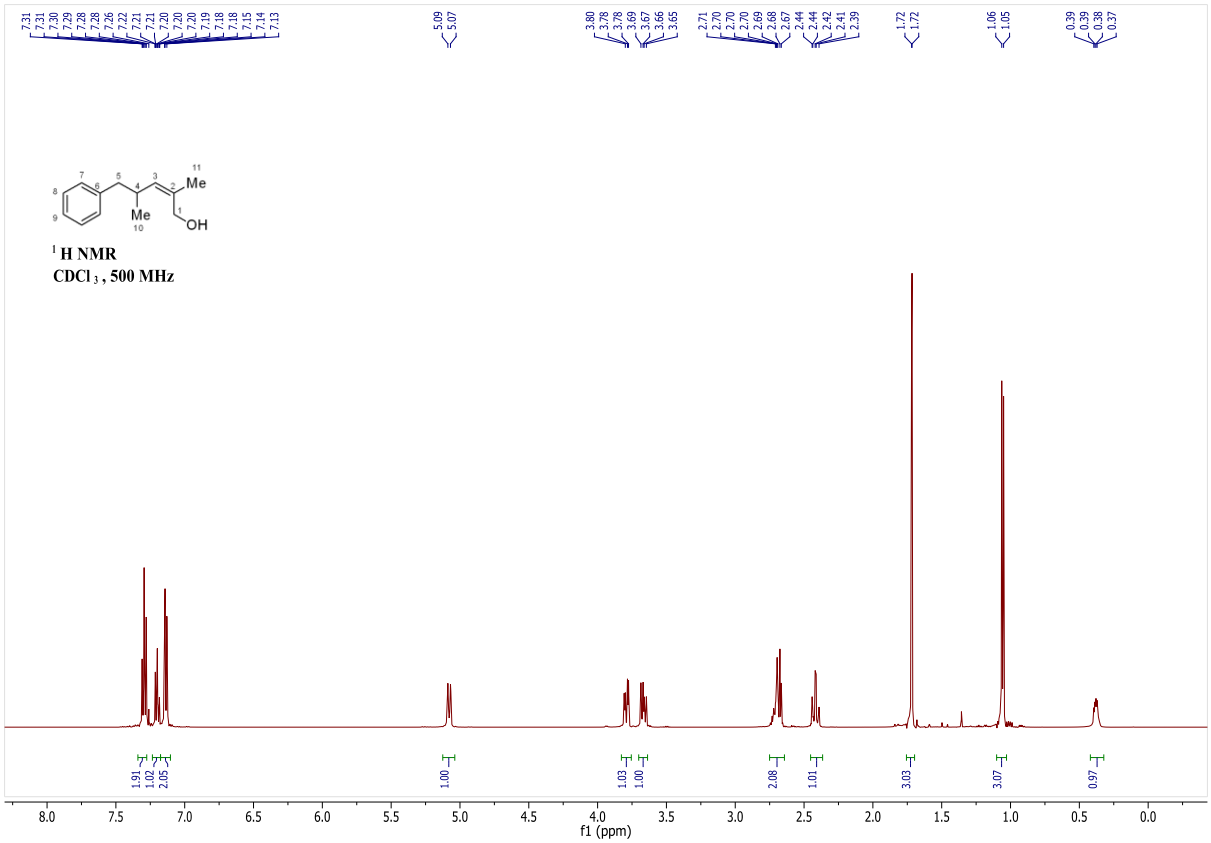
$^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 125 MHz



^{1}H NMR
CDCl$_3$, 400 MHz



^{13}C{^{1}H} NMR
CDCl$_3$, 100 MHz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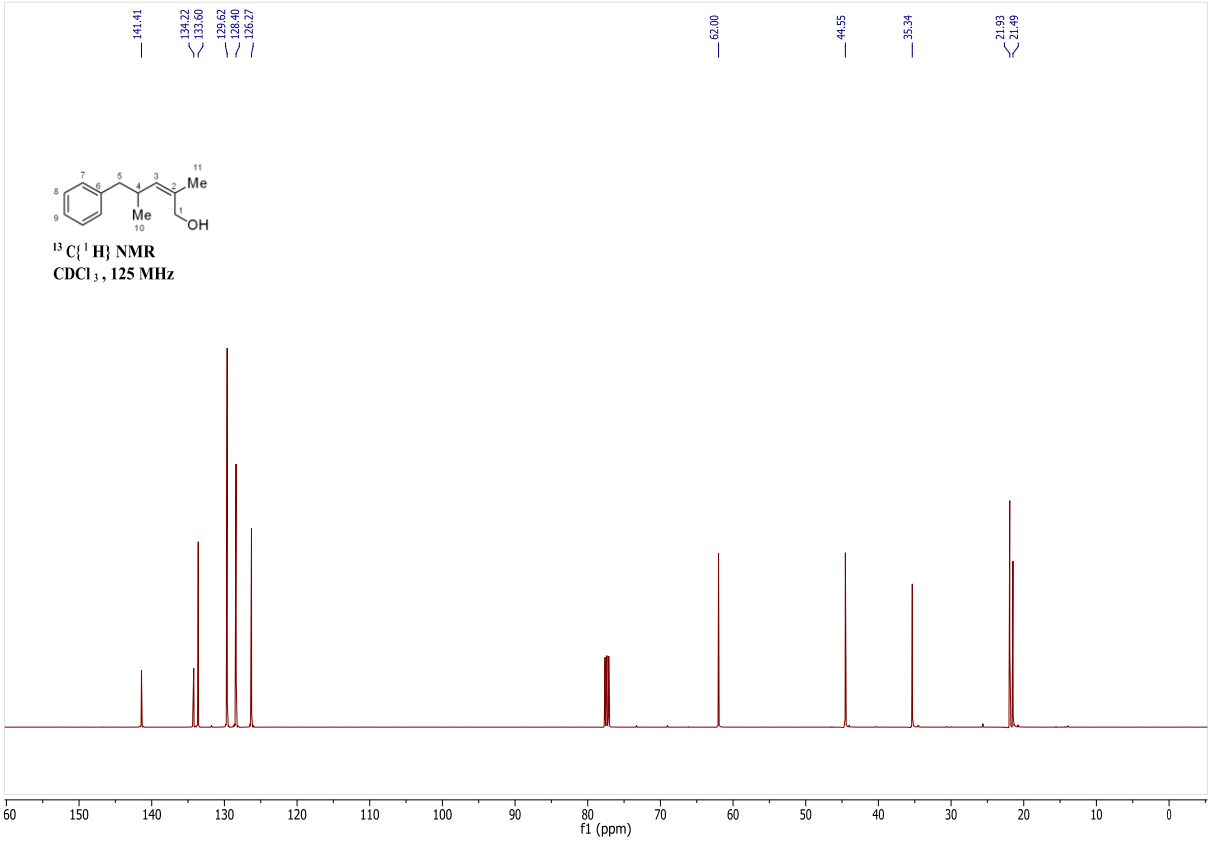
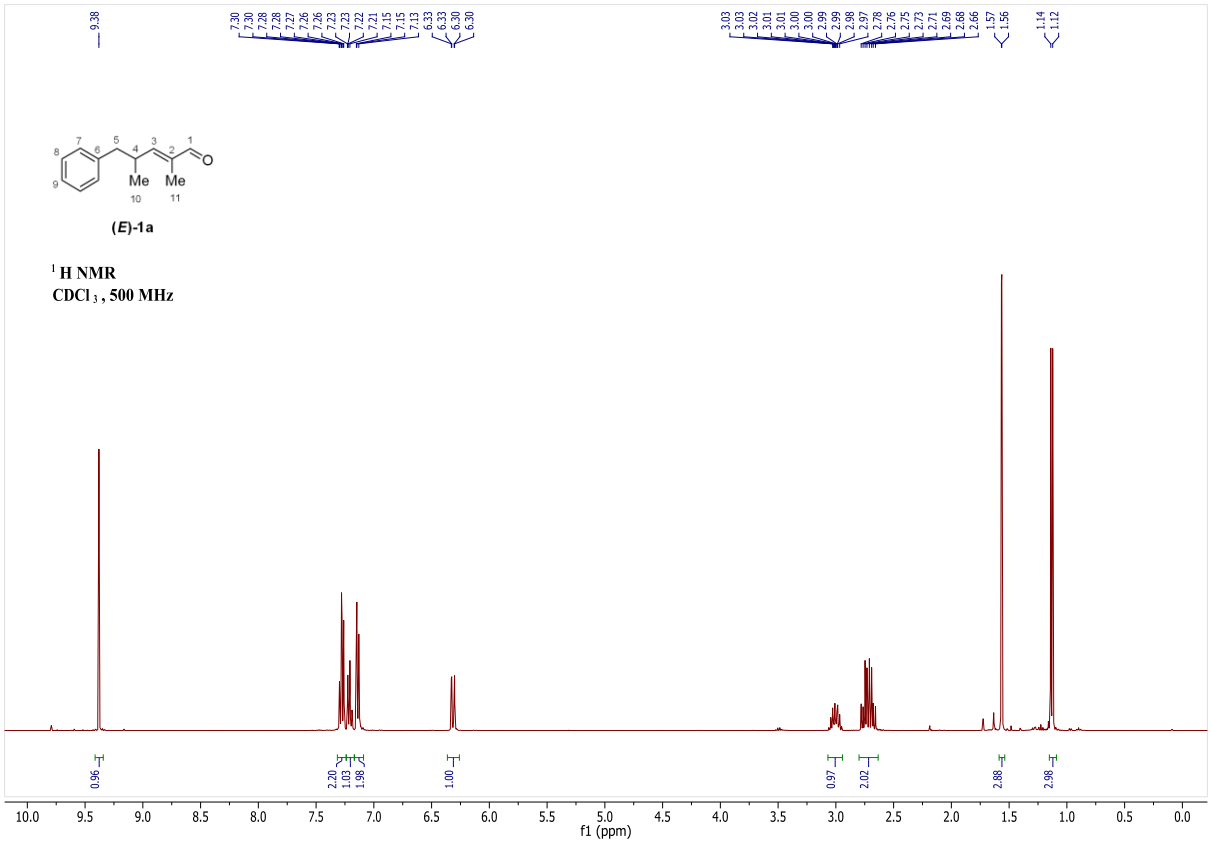
5.09 5.07
3.80 3.78 3.78 3.69 3.67 3.66 3.65
2.71 2.70 2.70 2.70 2.69 2.68 2.67 2.44 2.44 2.42 2.41 2.39
1.72 1.72
1.06 1.05
0.39 0.39 0.38 0.37
Me
Me
OH
1 H NMR
CDCl 3 , 500 MHz
1.91 1.02 2.05 1.00 1.03 1.00 2.08 1.01 3.03 3.07 0.97
f1 (ppm)


141.41
134.22 133.60
129.62 128.40 126.27
62.00
44.55
35.34
21.93 21.49
Me
Me
OH
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)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2.75
2.73
2.71
2.69
2.68
2.66
1.57
1.56
1.14
1.12
Me
Me
10
11
(E)-1a
1 H NMR
CDCl 3 , 500 MHz
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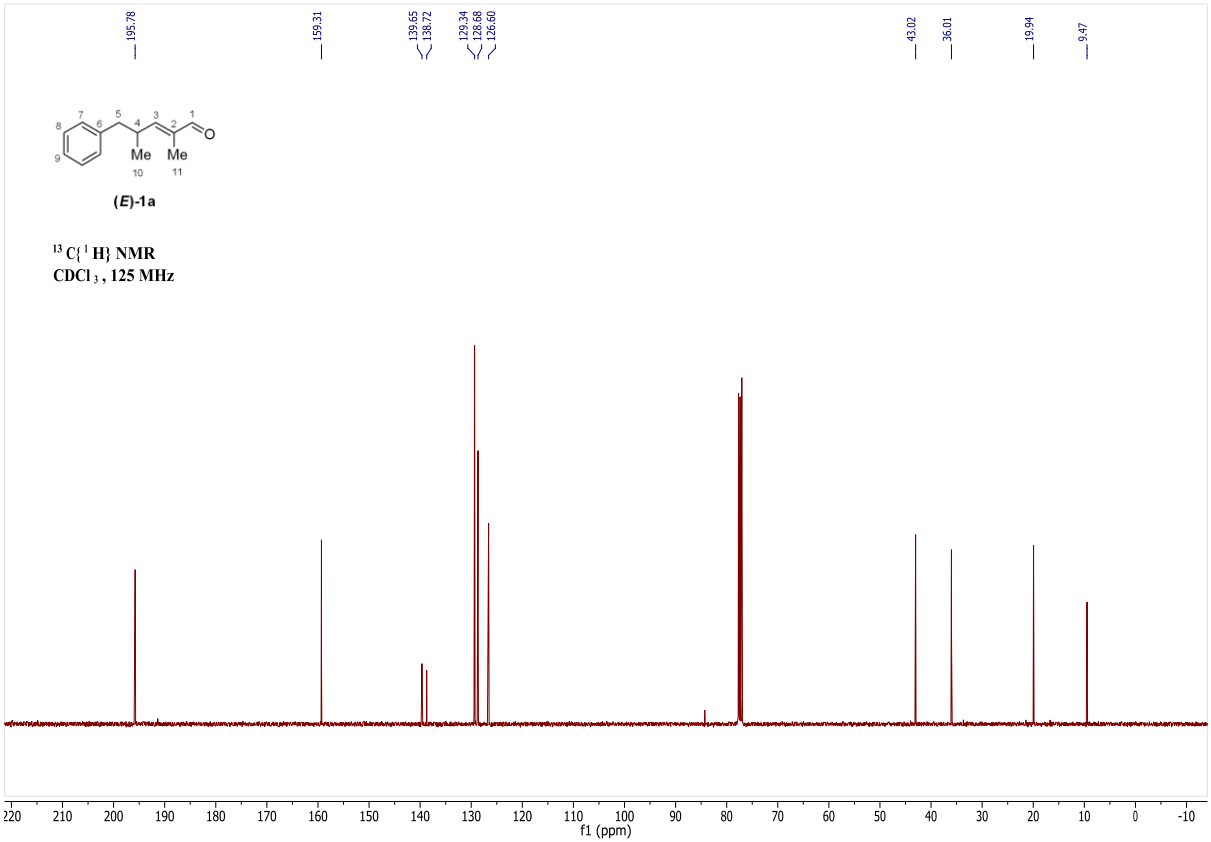
2.20
1.03
1.98
1.00
0.97
2.02
2.88
2.98
f1 (ppm)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126.60
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36.01
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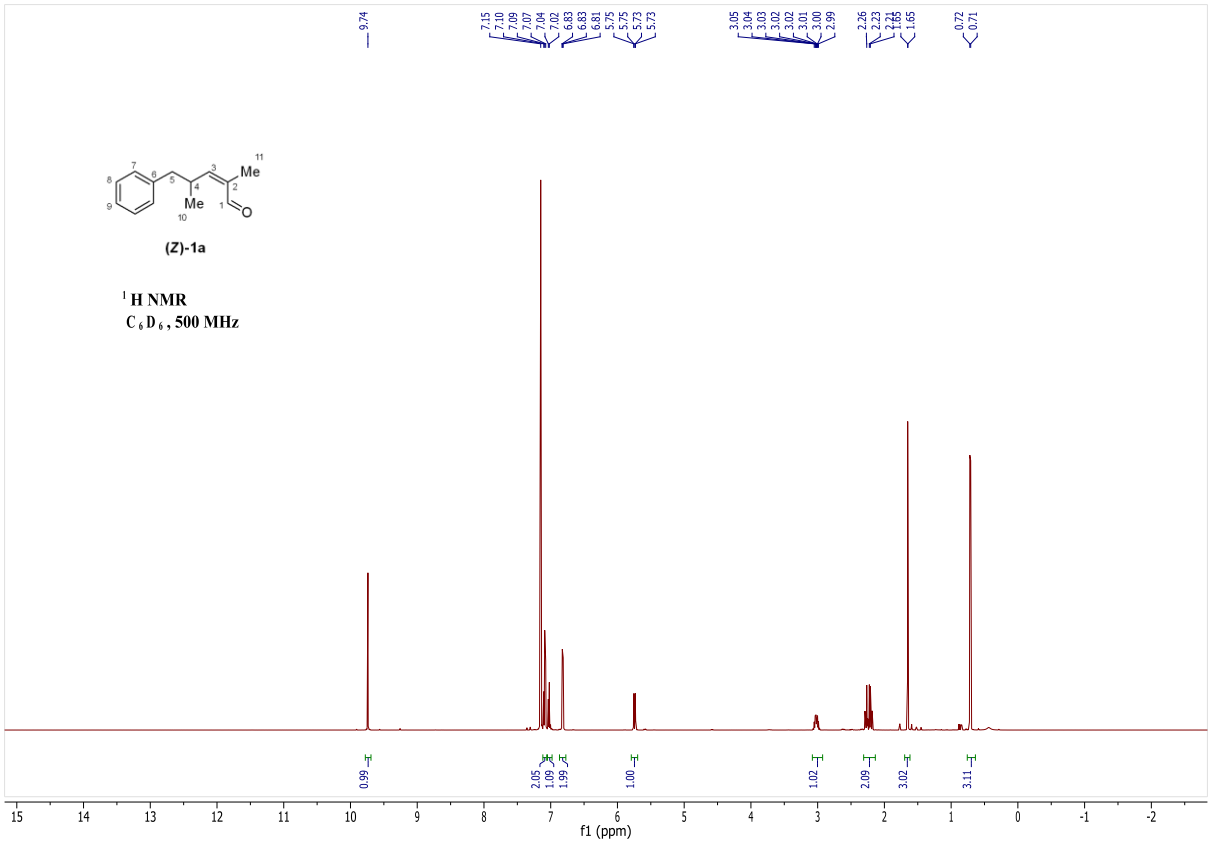
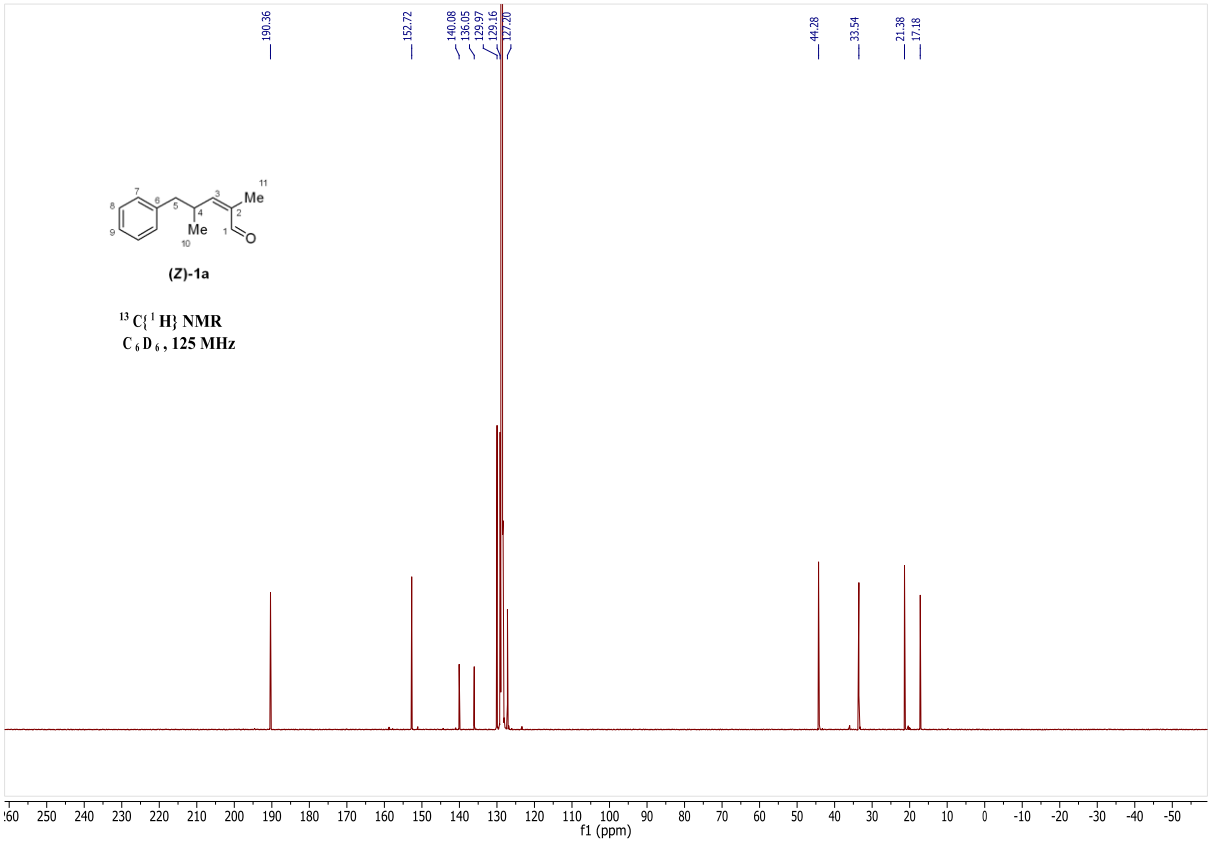
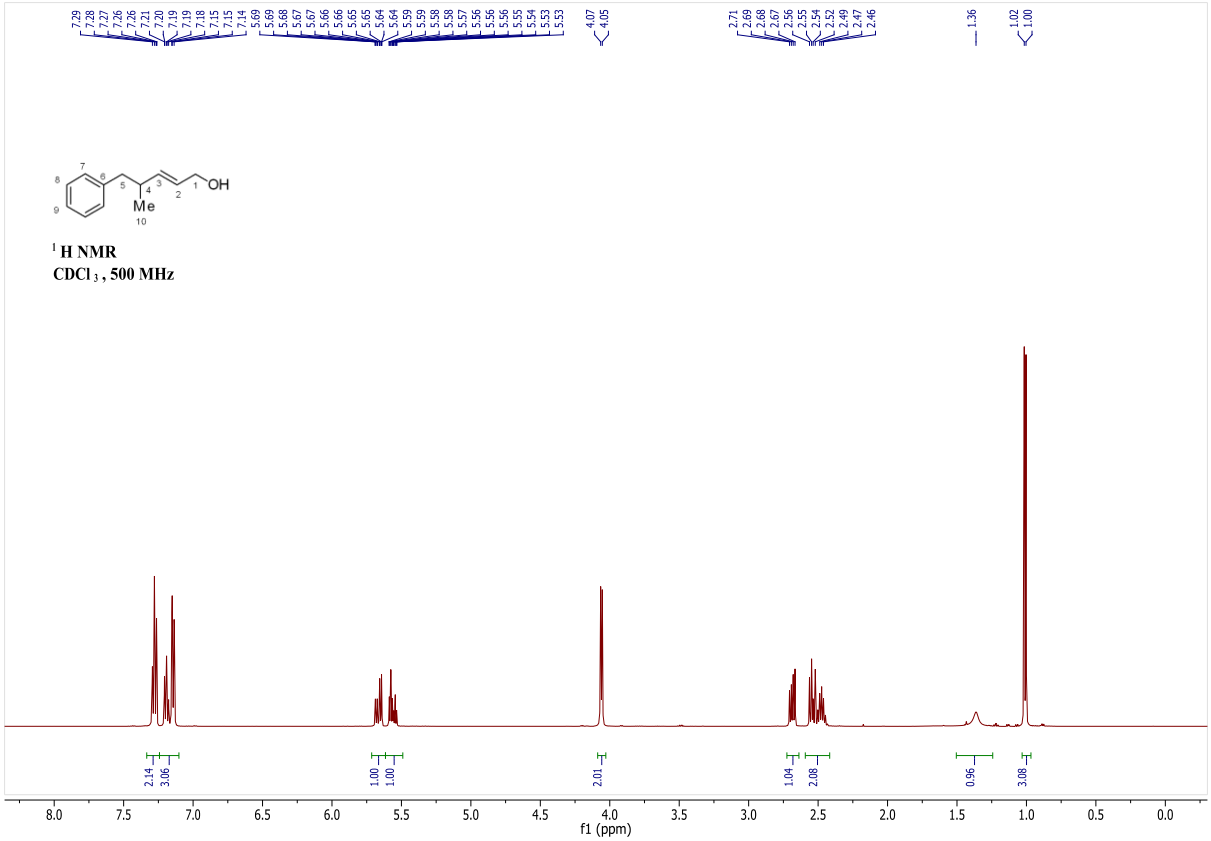
9.47
Me
Me
10
11
(E)-1a
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)



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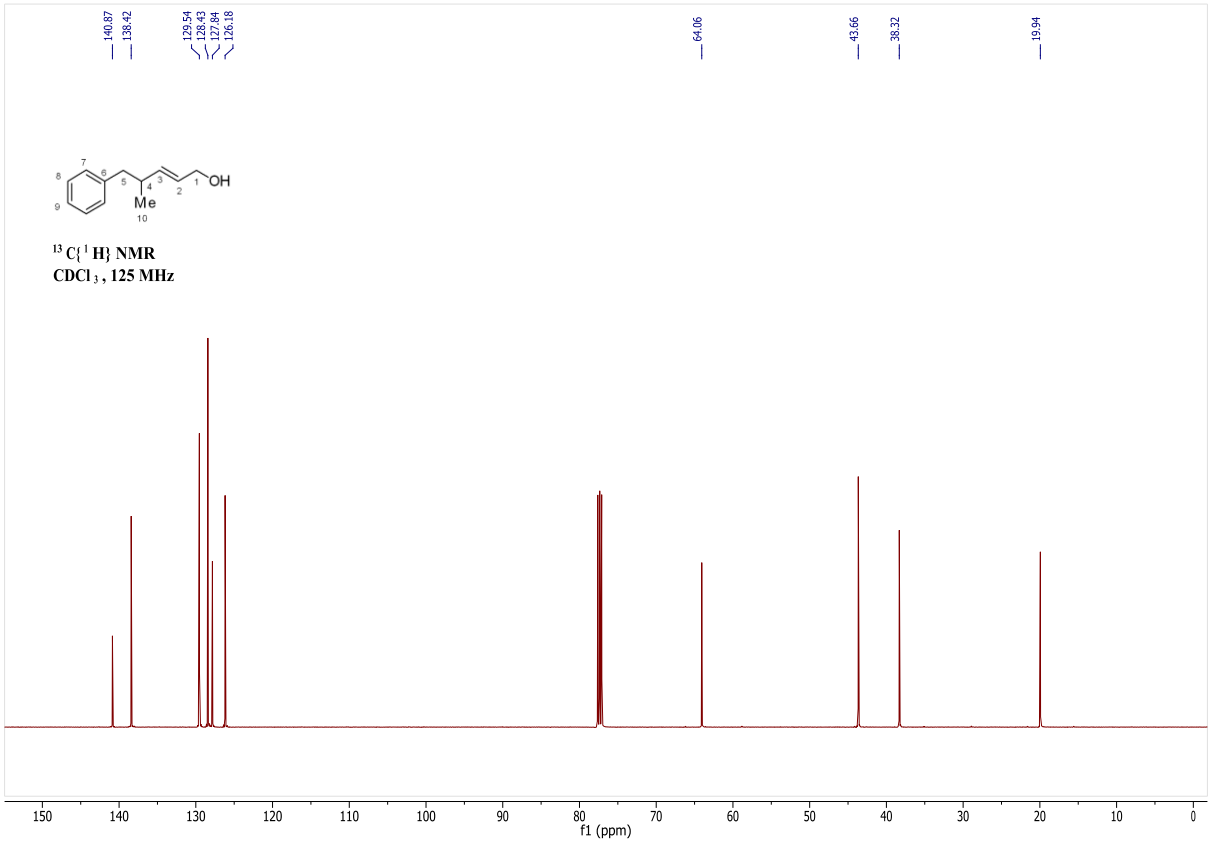
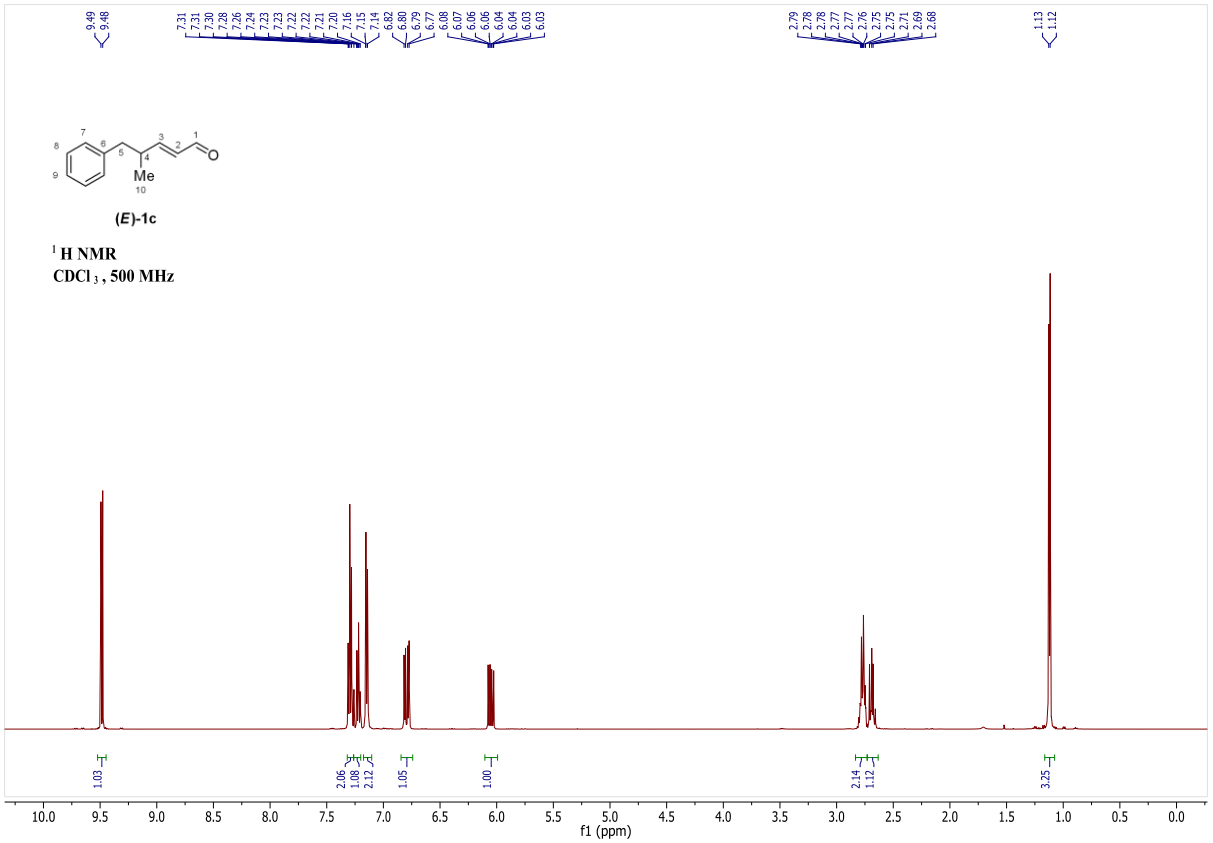
5.69 5.69 5.68 5.67 5.67 5.66 5.66 5.65 5.65 5.64 5.64 5.59 5.59 5.58 5.58 5.57 5.56 5.56 5.56 5.55 5.54 5.53 5.53
4.07 4.05
2.71 2.69 2.68 2.67 2.56 2.55 2.54 2.52 2.49 2.47 2.46
1.36
1.02 1.00
OH
Me
1H NMR
CDCl3, 500 MHz
2.14 3.06 1.00 1.00 2.01 1.04 2.08 0.96 3.08
f1 (ppm)


140.87 138.42 129.54 128.43 127.84 126.18
64.06
43.66 38.32
19.94
OH
Me
13C{1H} NMR
CDCl3, 125 MHz
f1 (ppm)


9.49
9.48
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7.28
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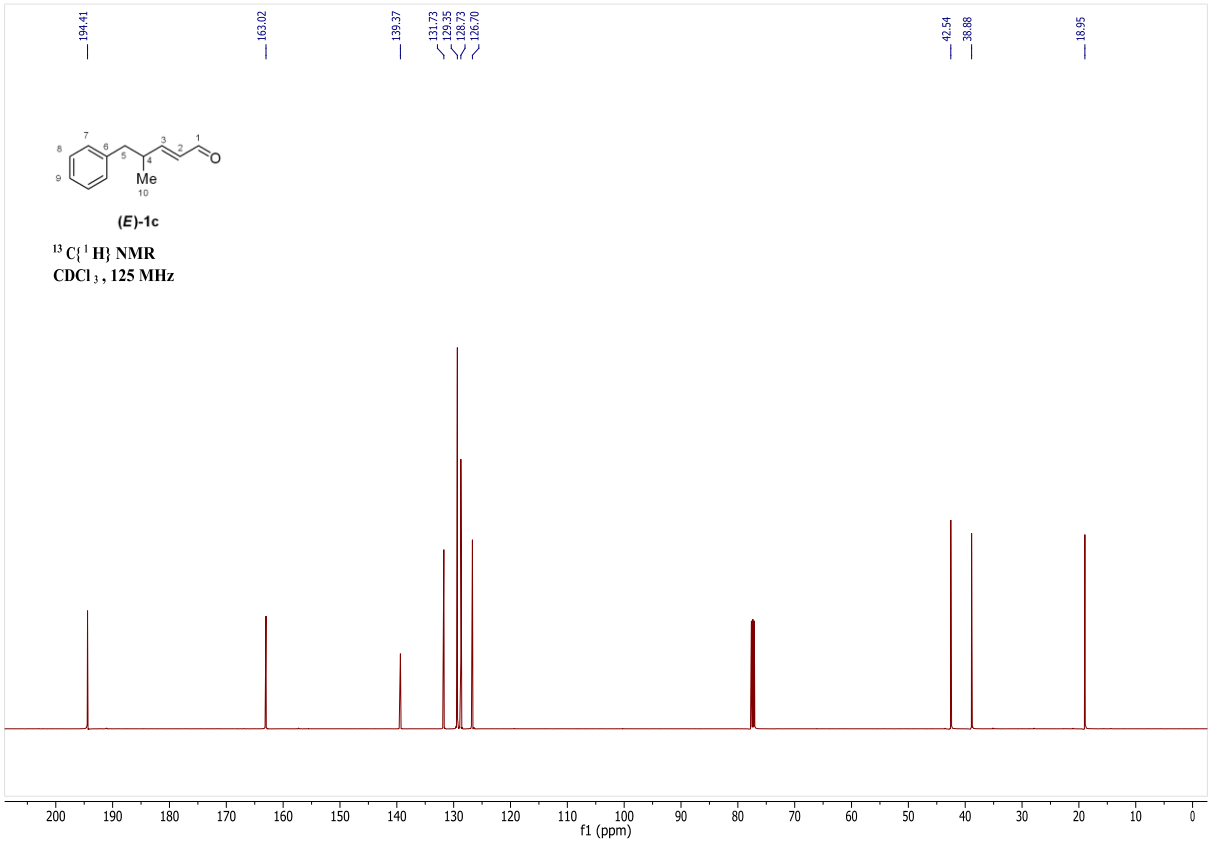
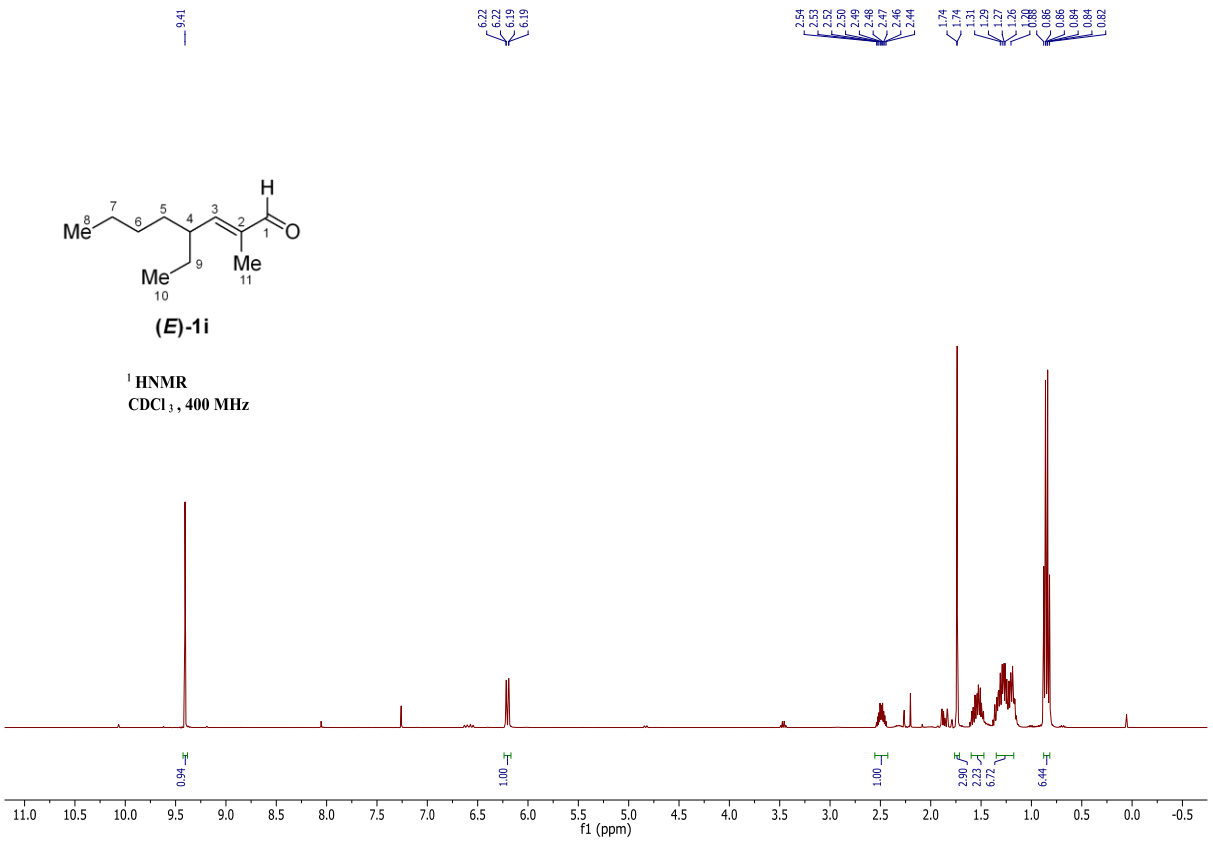
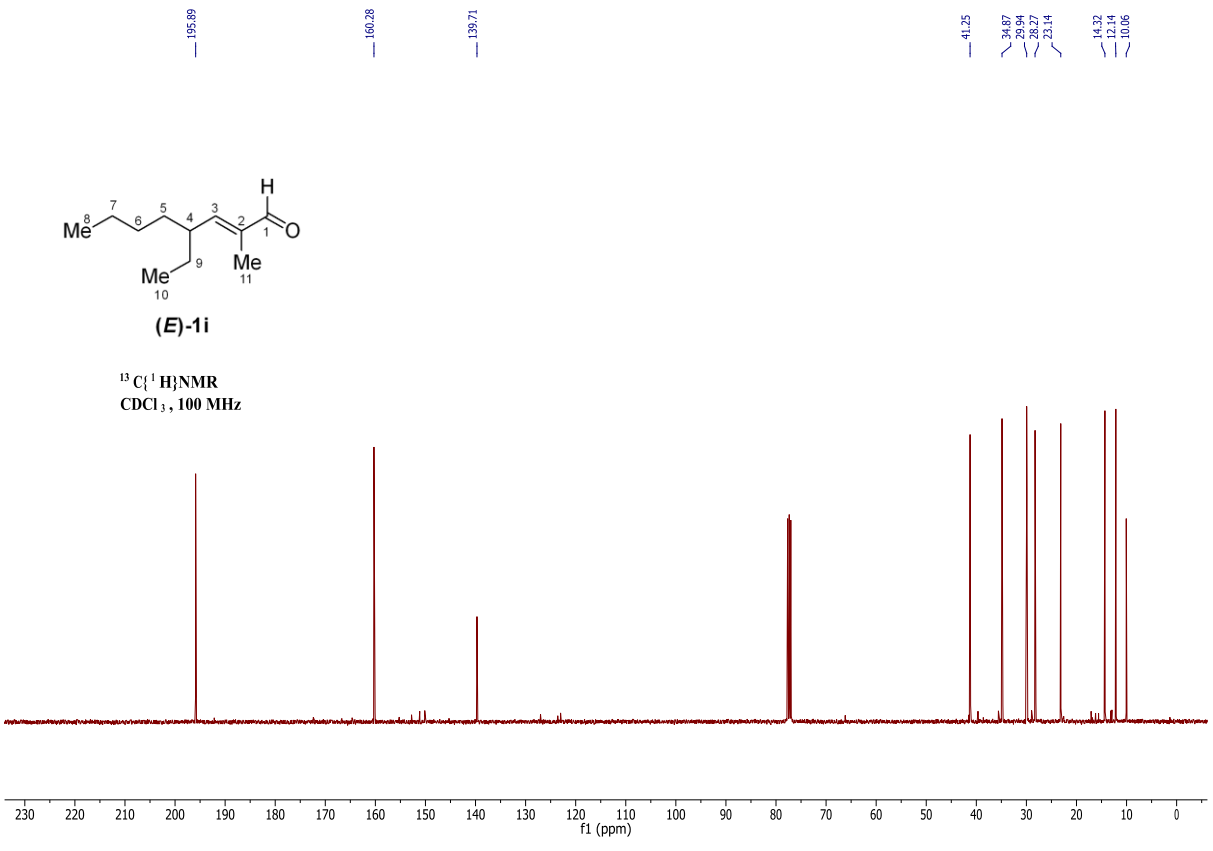
7.23
7.23
7.22
7.22
7.21
7.20
7.16
7.15
7.14
6.82
6.80
6.79
6.77
6.08
6.07
6.06
6.06
6.04
6.04
6.03
6.03
2.79
2.78
2.78
2.77
2.77
2.76
2.75
2.75
2.71
2.69
2.68
1.13
1.12
Me
(E)-1c
1 H NMR
CDCl 3 , 500 MHz
1.03
2.06
1.08
2.12
1.05
1.00
2.14
1.12
3.25
f1 (ppm)


194.41
163.02
139.37
131.73
129.35
128.73
126.70
42.54
38.88
18.95
Me
(E)-1c
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)



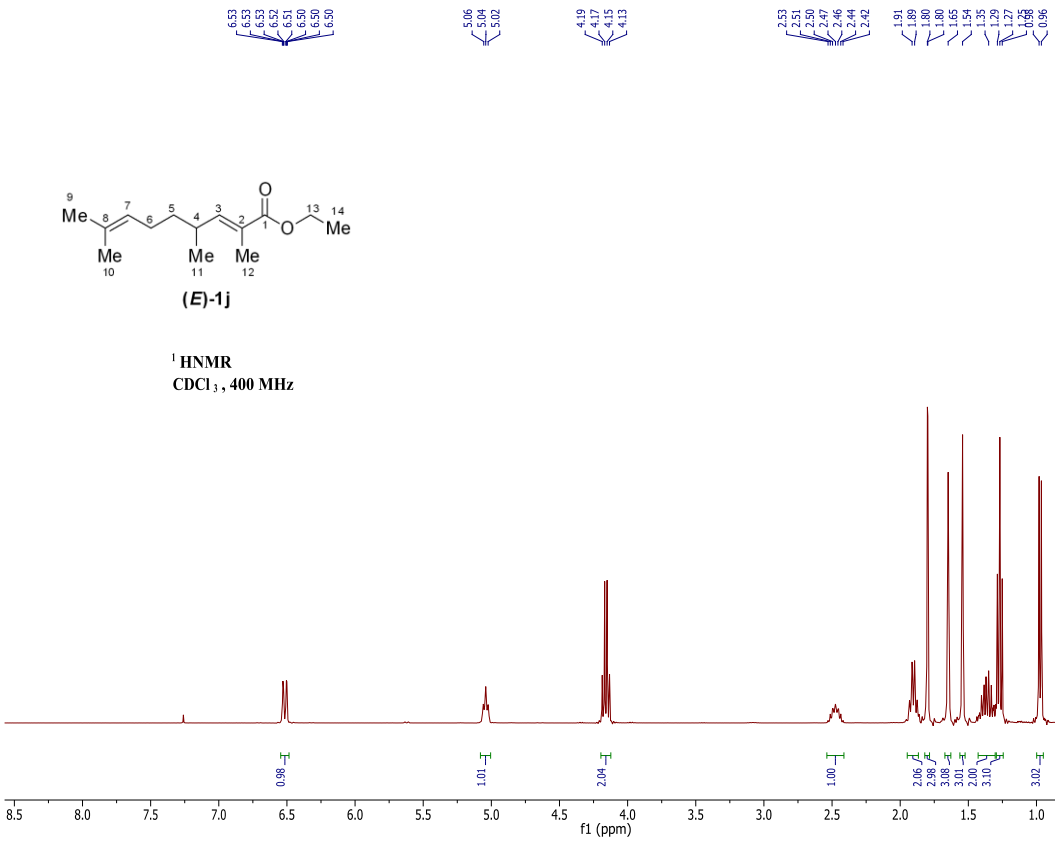
(*E*)-1i

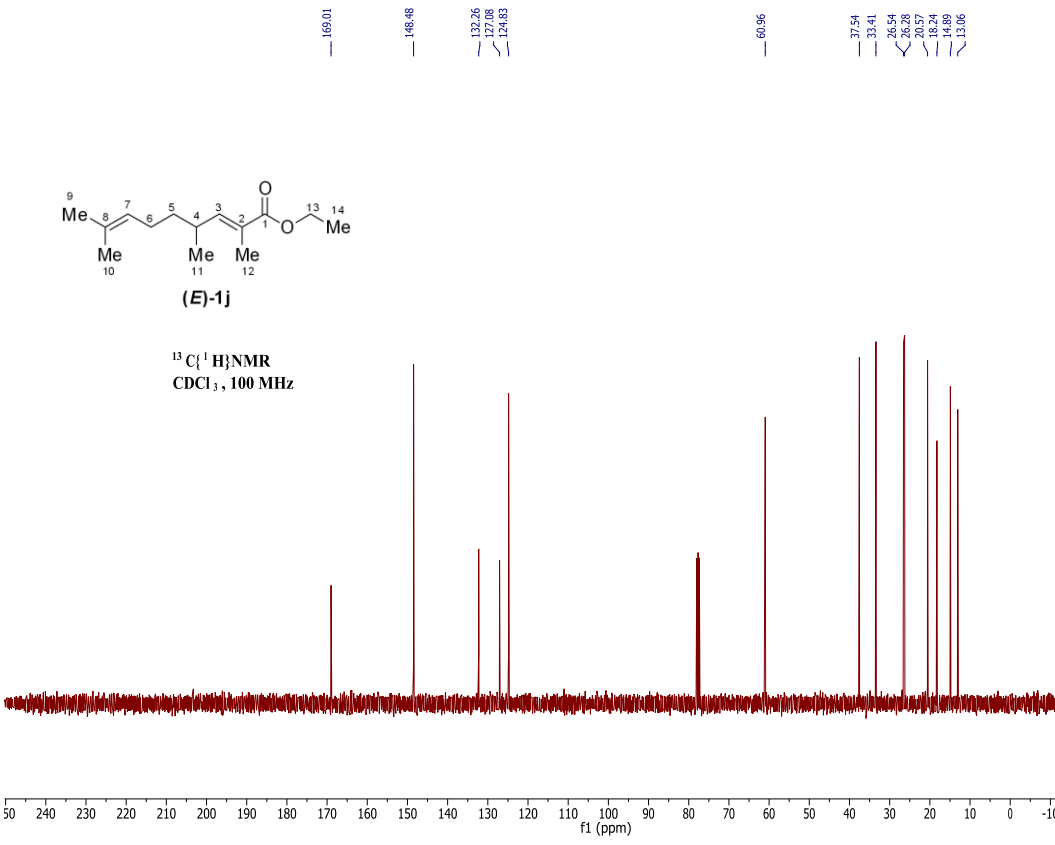
^{1}HNMR
$CDCl_3$, 400 MHz



(*E*)-1i

$^{13}C\{^{1}H\}$NMR
$CDCl_3$, 100 MHz


6.53
6.53
6.53
6.52
6.51
6.50
6.50
6.50
5.06
5.04
5.02
4.19
4.17
4.15
4.13
2.53
2.51
2.50
2.47
2.46
2.44
2.42
1.91
1.89
1.80
1.80
1.65
1.54
1.35
1.29
1.27
0.98
0.96
Me
Me
Me
Me
Me
O
O
(E)-1j
1 HNMR
CDCl 3 , 400 MHz
0.98
1.01
2.04
1.00
2.06
2.98
3.08
3.01
2.00
3.10
3.02
f1 (ppm)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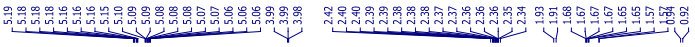
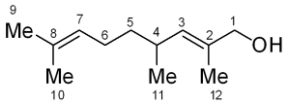
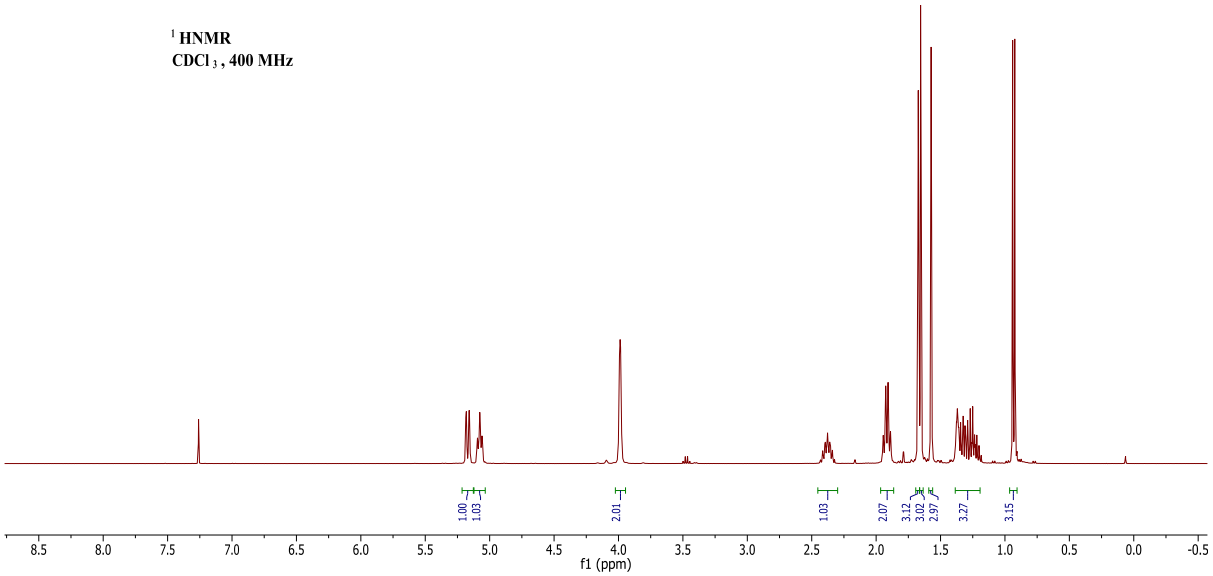
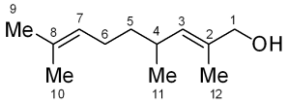
148.48
132.26
127.08
124.83
60.96
37.54
33.41
26.54
26.28
20.57
18.24
14.89
13.06
Me
Me
Me
Me
Me
O
O
(E)-1j
13 C{ 1 H}NMR
CDCl 3 , 100 MHz
f1 (ppm)



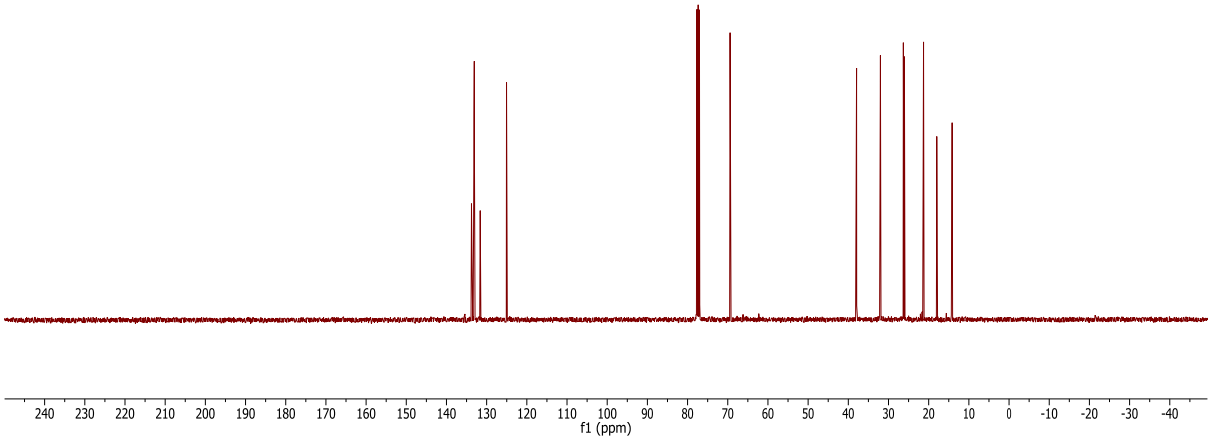


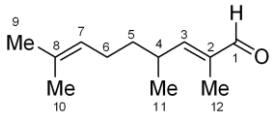
^{1}HNMR
$CDCl_3$, 400 MHz





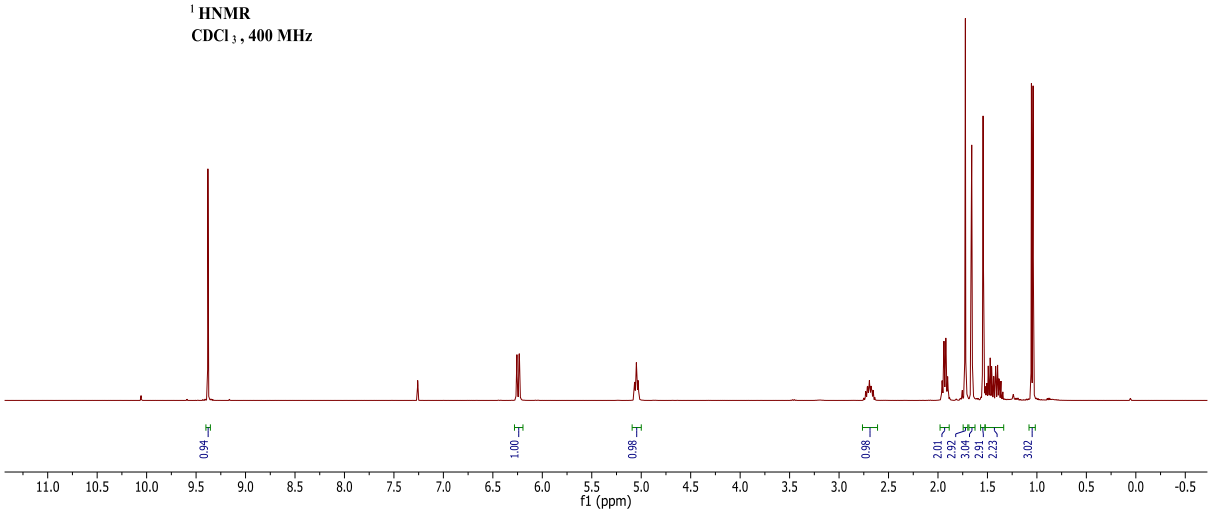
$^{13}C\{^{1}H\}$NMR
$CDCl_3$, 100 MHz

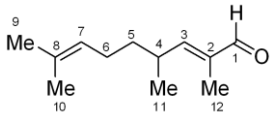




(*E*)-1j

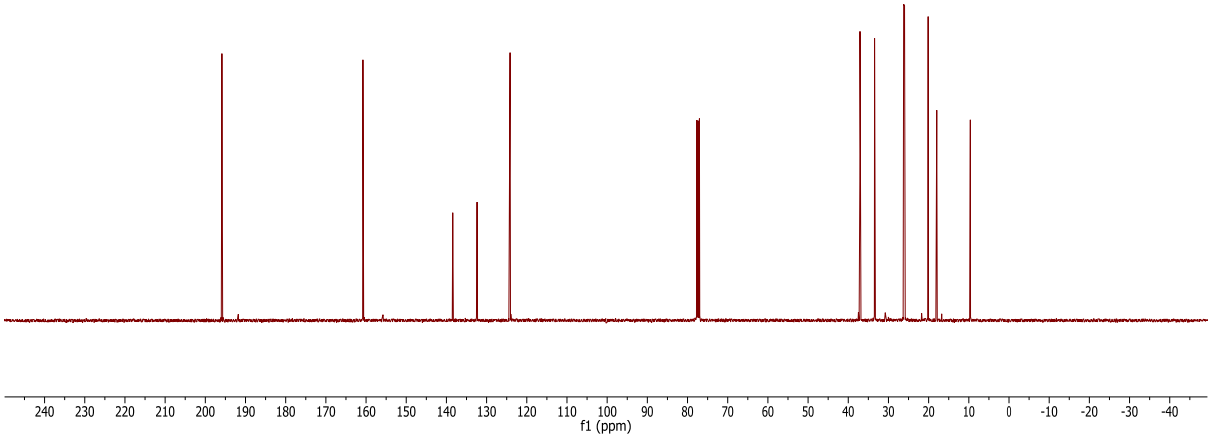
^{1}HNMR
$CDCl_3$, 400 MHz

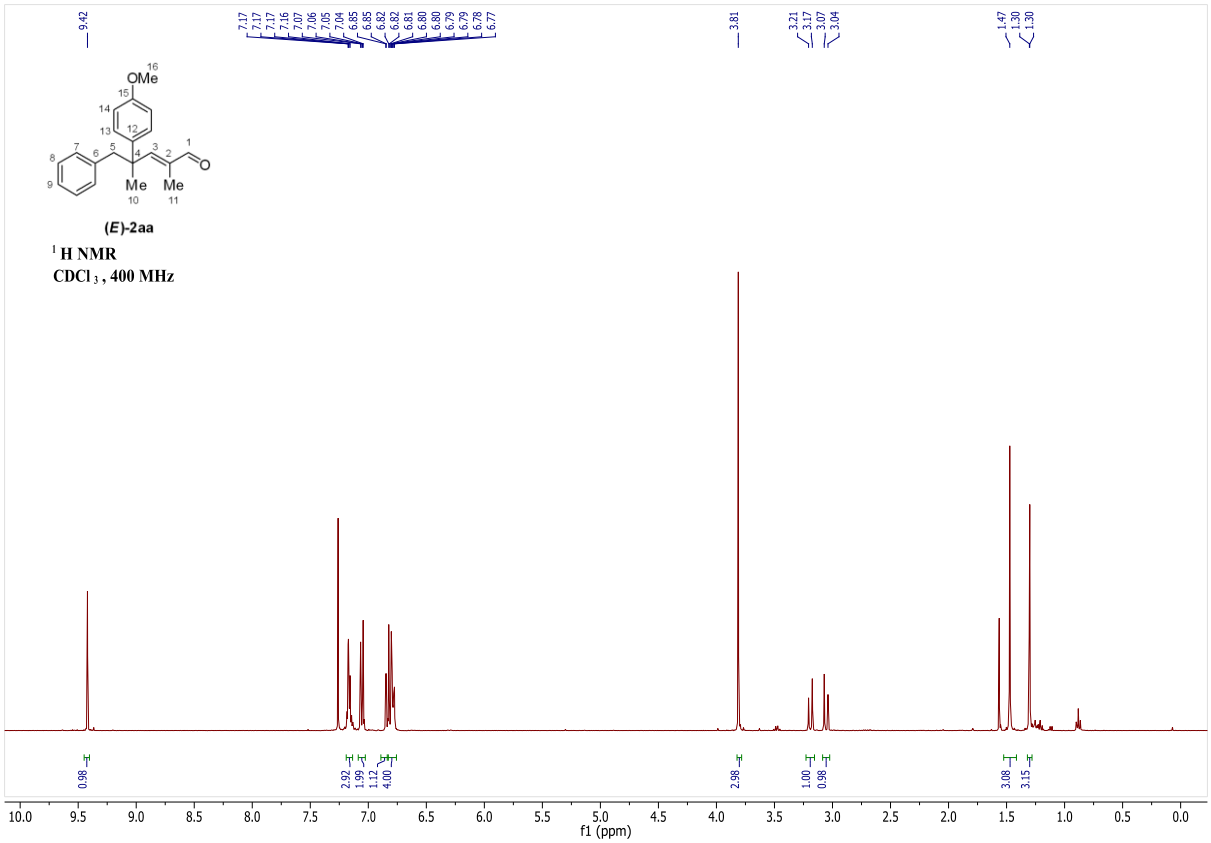


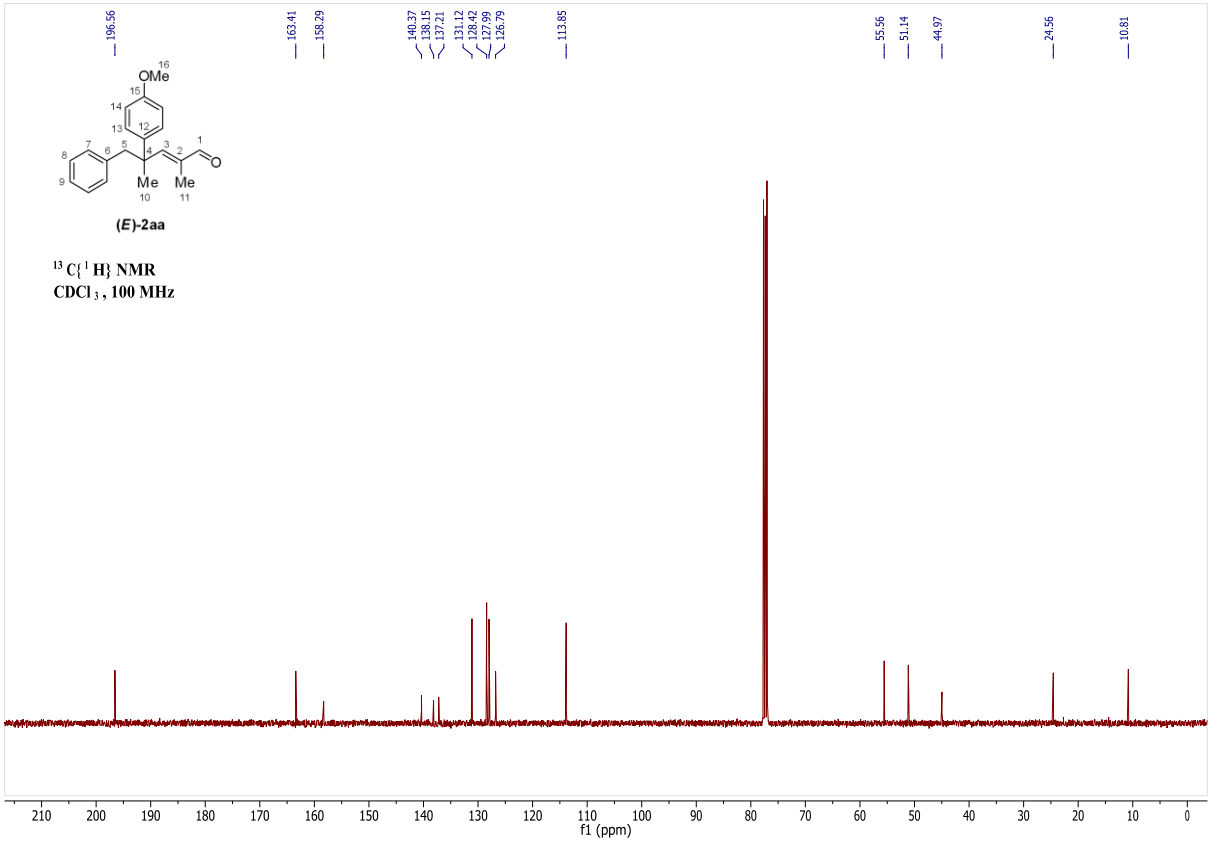


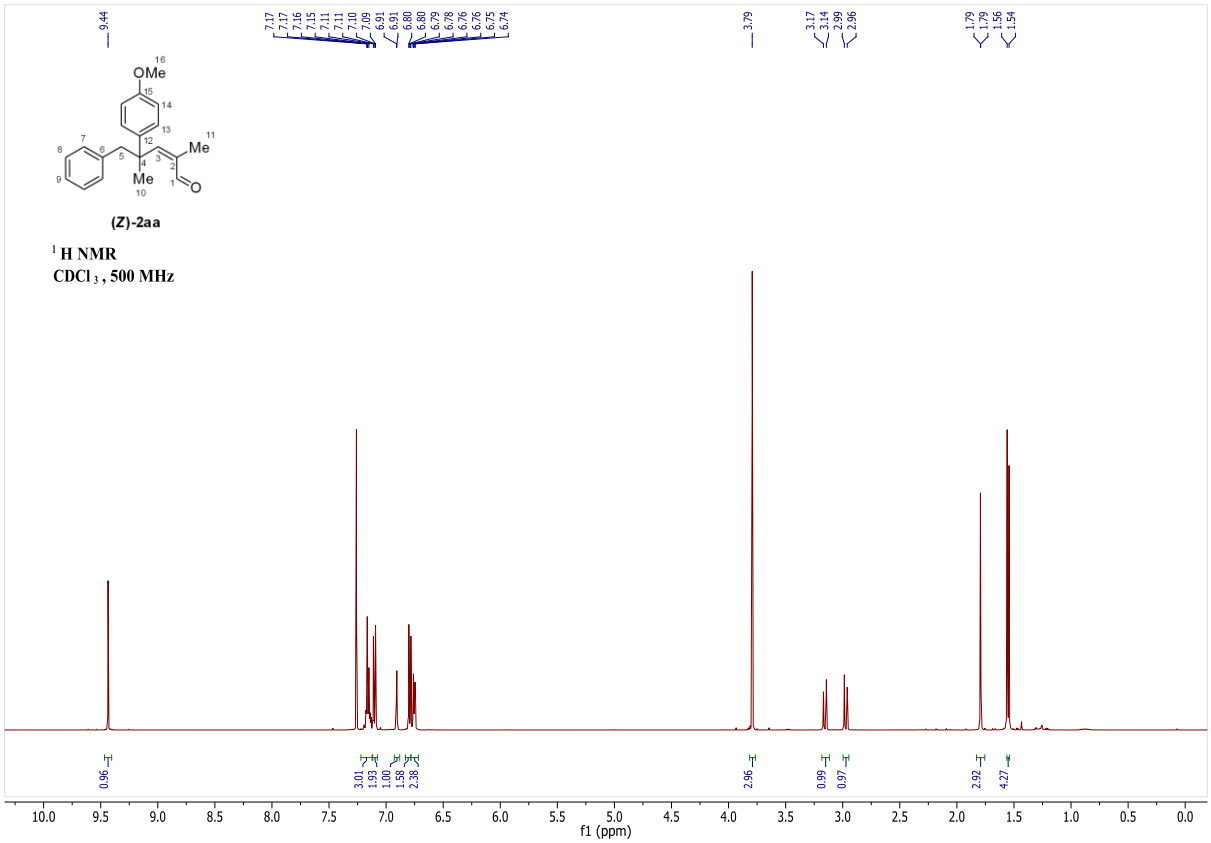
(*E*)-1j

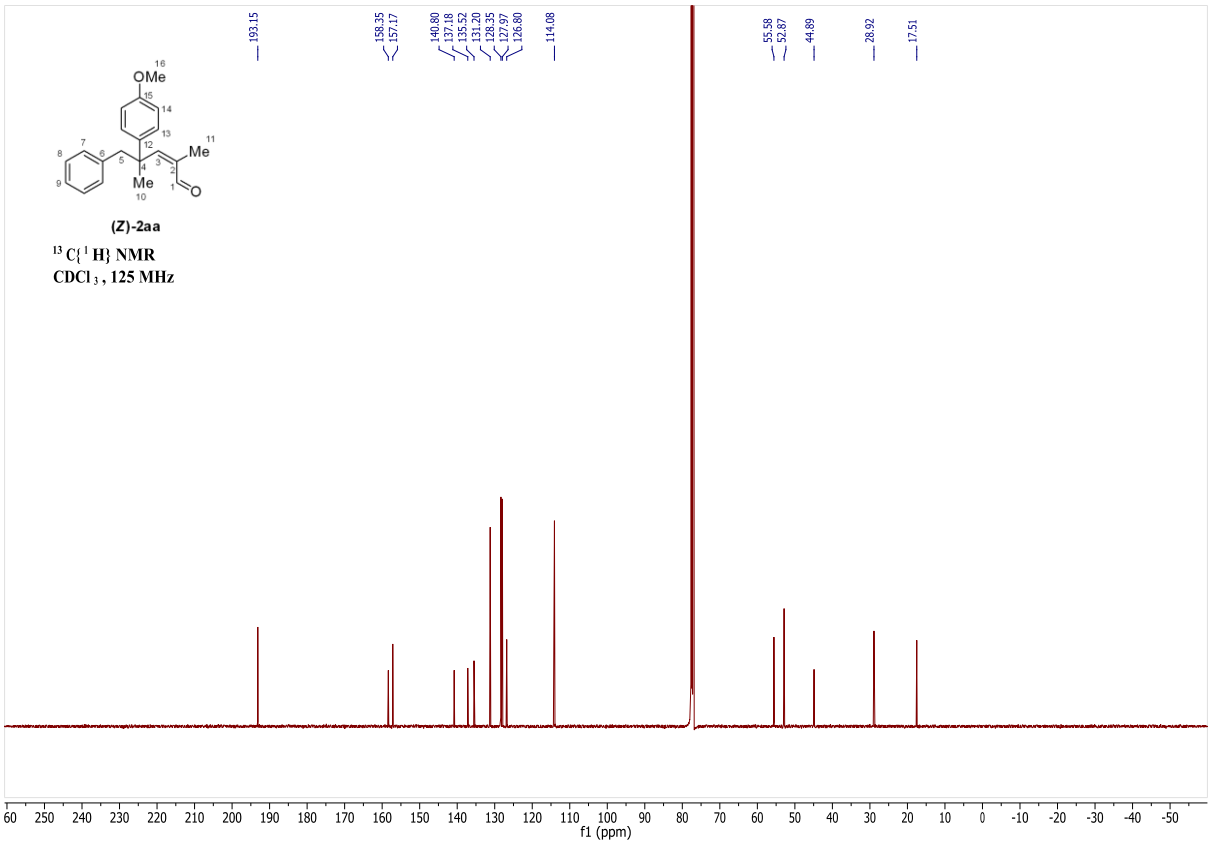
$^{13}C\{^{1}H\}$NMR
$CDCl_3$, 100 MHz

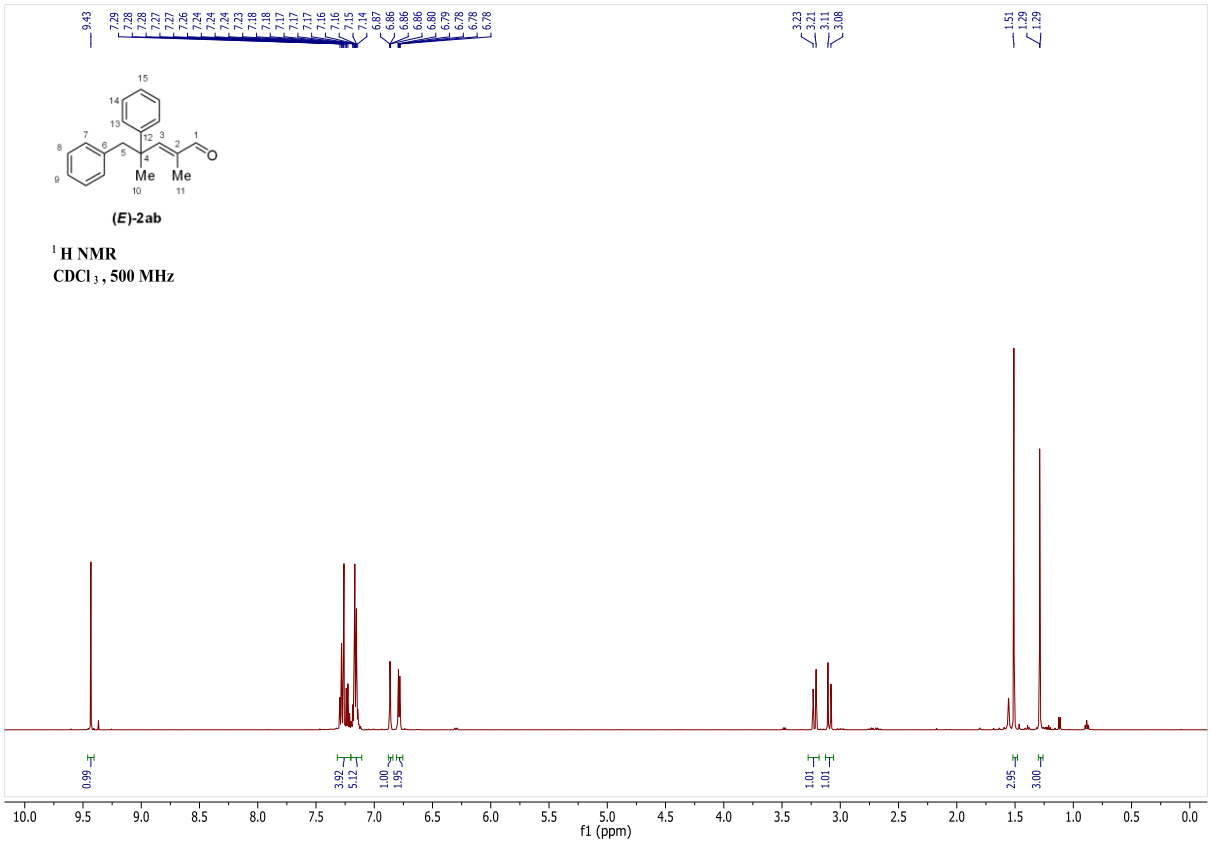


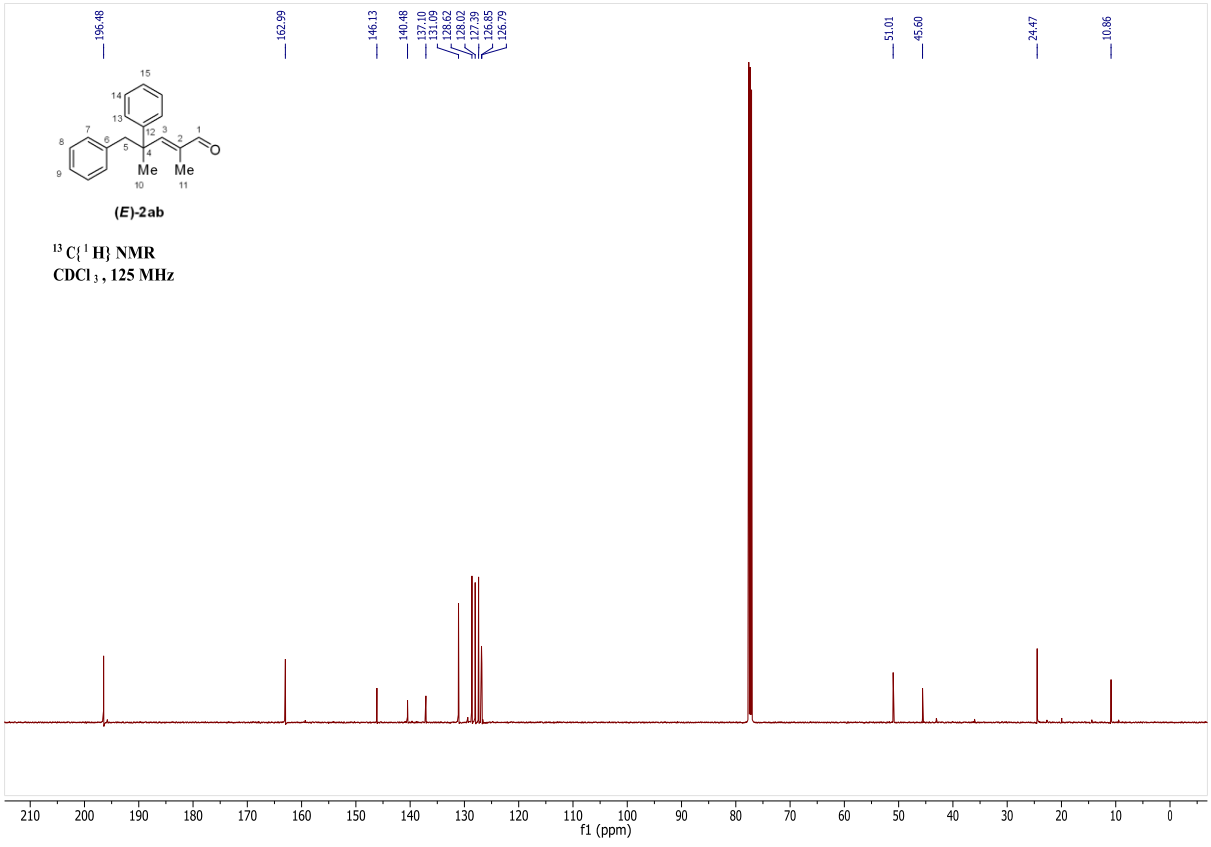

9.42
7.17
7.17
7.17
7.16
7.07
7.06
7.05
7.04
6.85
6.85
6.82
6.82
6.81
6.80
6.80
6.79
6.79
6.78
6.77
3.81
3.21
3.17
3.07
3.04
1.47
1.30
1.30
OMe
Me
Me
(E)-2aa
1 H NMR
CDCl 3 , 400 MHz
0.98
2.92
1.99
1.12
4.00
2.98
1.00
0.98
3.08
3.15
f1 (ppm)

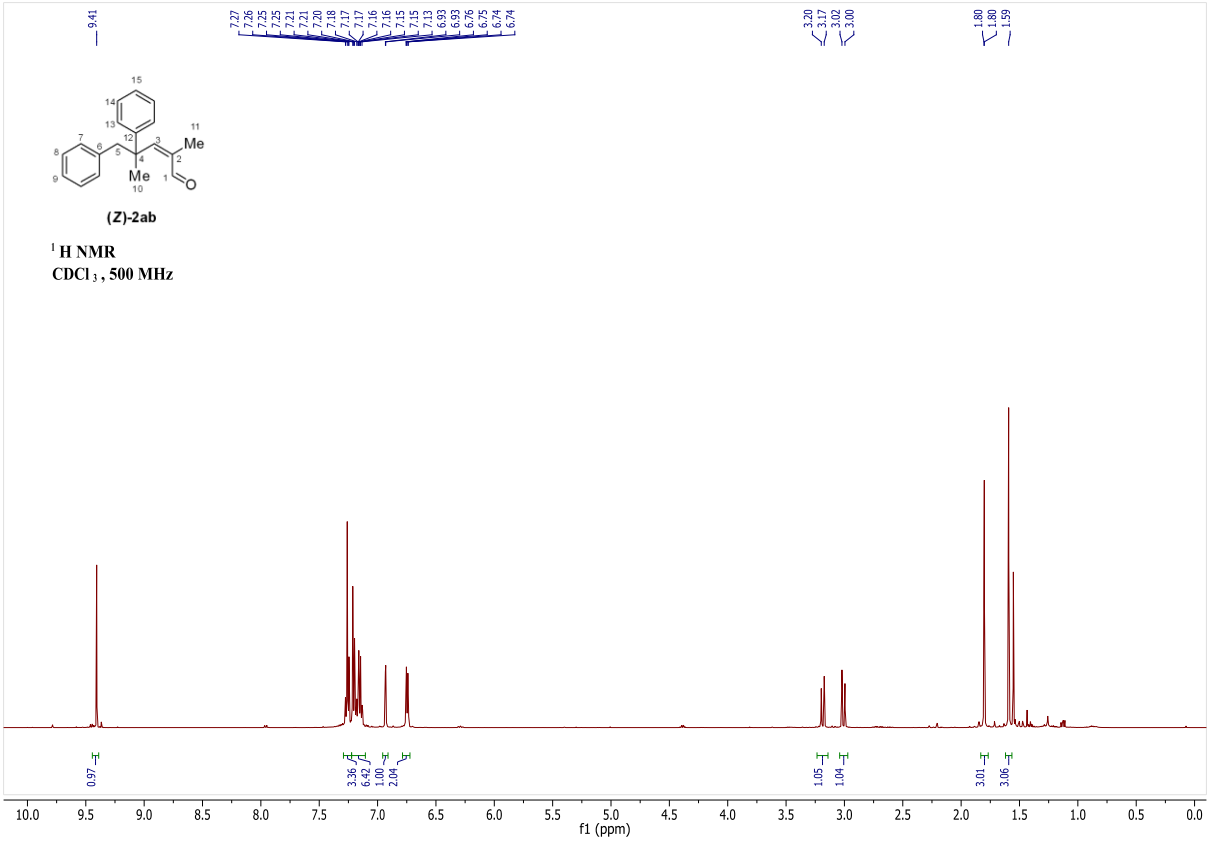

196.56
163.41
158.29
140.37
138.15
137.21
131.12
128.42
127.99
126.79
113.85
55.56
51.14
44.97
24.56
10.81
OMe
Me
Me
(E)-2aa
13 C{ 1 H} NMR
CDCl 3 , 100 MHz
f1 (ppm)

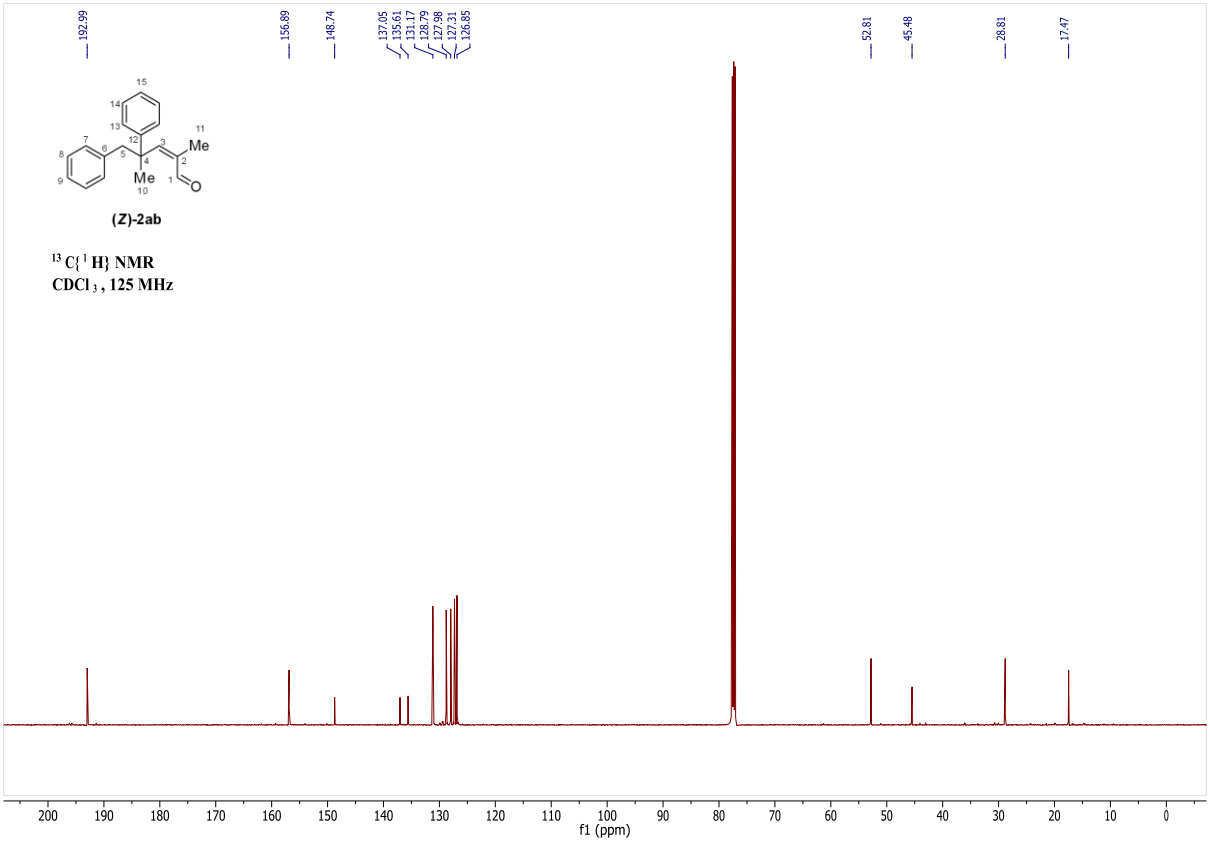

(Z)-2aa
^{1}H NMR
CDCl$_3$, 500 MHz
f1 (ppm)


(Z)-2aa
^{13}C{^{1}H} NMR
CDCl$_3$, 125 MHz
f1 (ppm)


(E)-2ab
^{1}H NMR
CDCl$_3$, 500 MHz
f1 (ppm)


(E)-2ab
^{13}C{^{1}H} NMR
CDCl$_3$, 125 MHz
f1 (ppm)


9.41
7.27
7.26
7.25
7.25
7.21
7.21
7.20
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.13
6.93
6.93
6.76
6.75
6.74
6.74
3.20
3.17
3.02
3.00
1.80
1.80
1.59
Me
Me
(Z)-2ab
1 H NMR
CDCl 3 , 500 MHz
0.97
3.36
6.42
1.00
2.04
1.05
1.04
3.01
3.06
f1 (ppm)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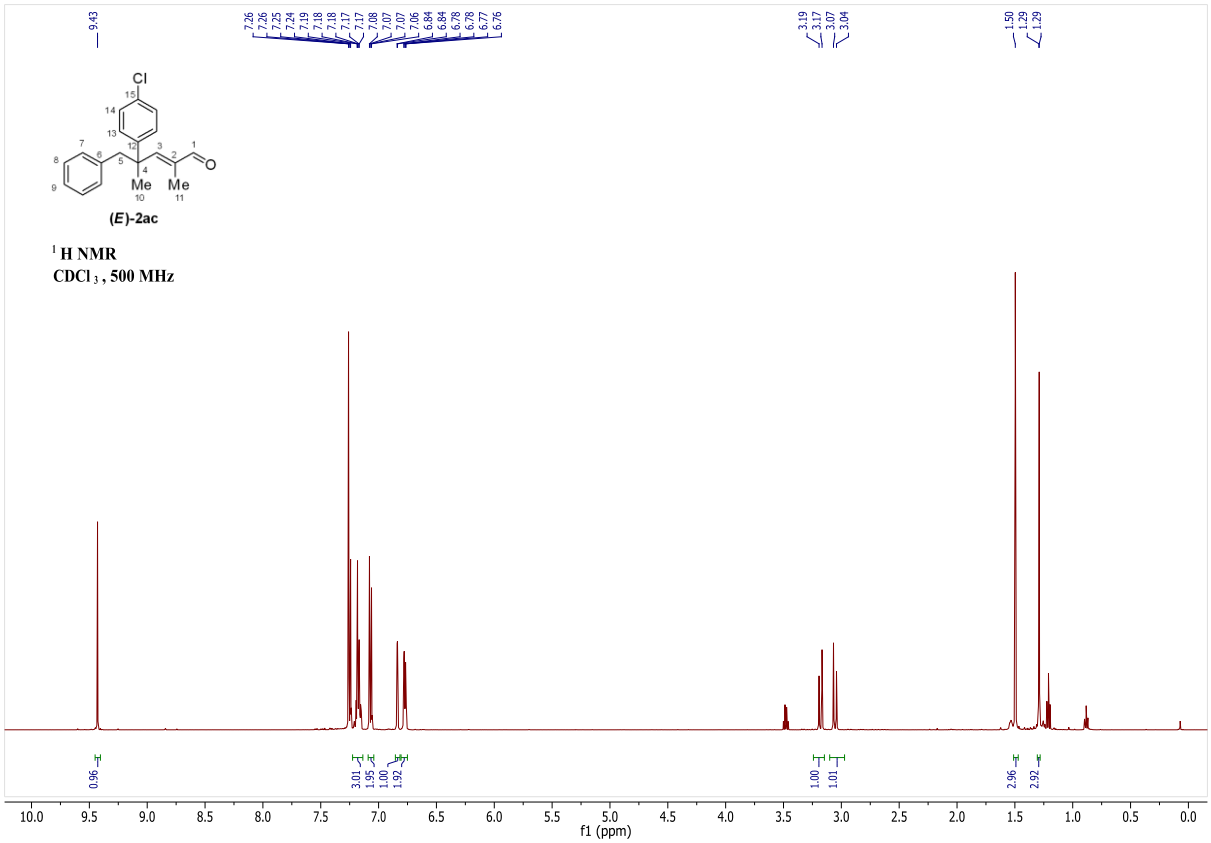
156.89
148.74
137.05
135.61
131.17
128.79
127.98
127.31
126.85
52.81
45.48
28.81
17.47
Me
Me
(Z)-2ab
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)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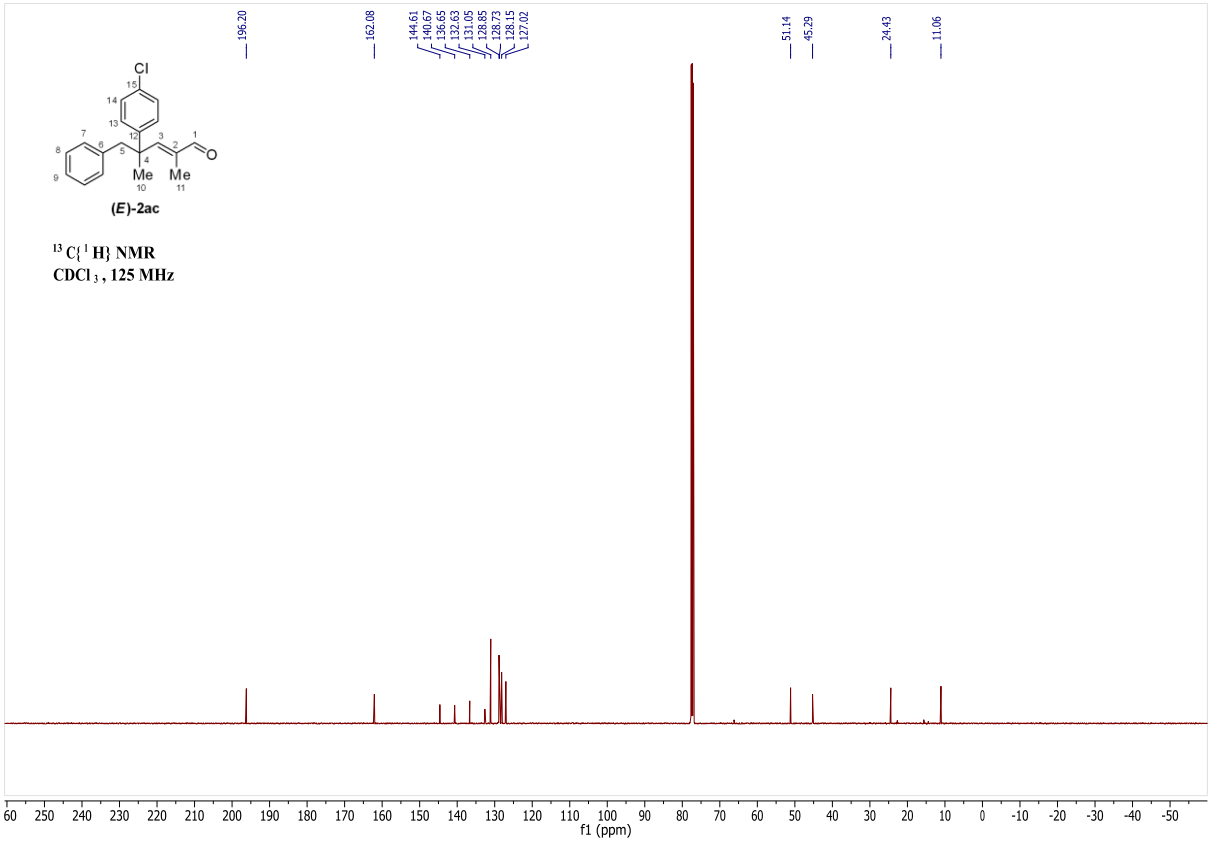
7.26
7.25
7.24
7.19
7.18
7.17
7.08
7.07
7.06
6.84
6.78
6.77
6.76
3.19
3.17
3.07
3.04
1.50
1.29
Cl
Me
Me
O
(E)-2ac
1H NMR
CDCl3, 500 MHz
0.96
3.01
1.95
1.00
1.92
1.00
1.01
2.96
2.92
f1 (ppm)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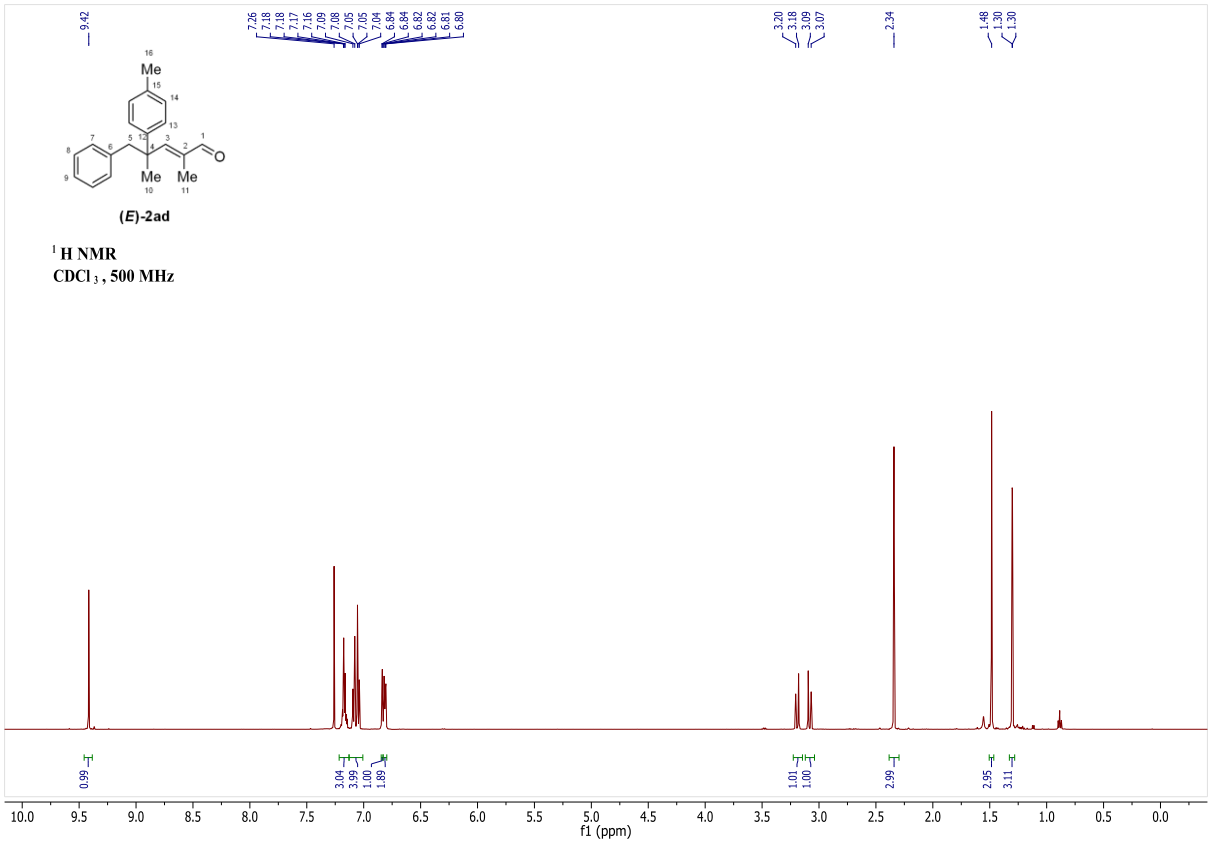
131.05
128.85
128.73
128.15
127.02
51.14
45.29
24.43
11.06
Cl
Me
Me
O
(E)-2ac
13C{1H} NMR
CDCl3, 125 MHz
f1 (ppm)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7.26
7.18
7.18
7.17
7.16
7.09
7.08
7.05
7.05
7.04
6.84
6.84
6.82
6.82
6.81
6.80
3.20
3.18
3.09
3.07
2.34
1.48
1.30
1.30
Me
Me
Me
(E)-2ad
1 H NMR
CDCl 3 , 500 MHz
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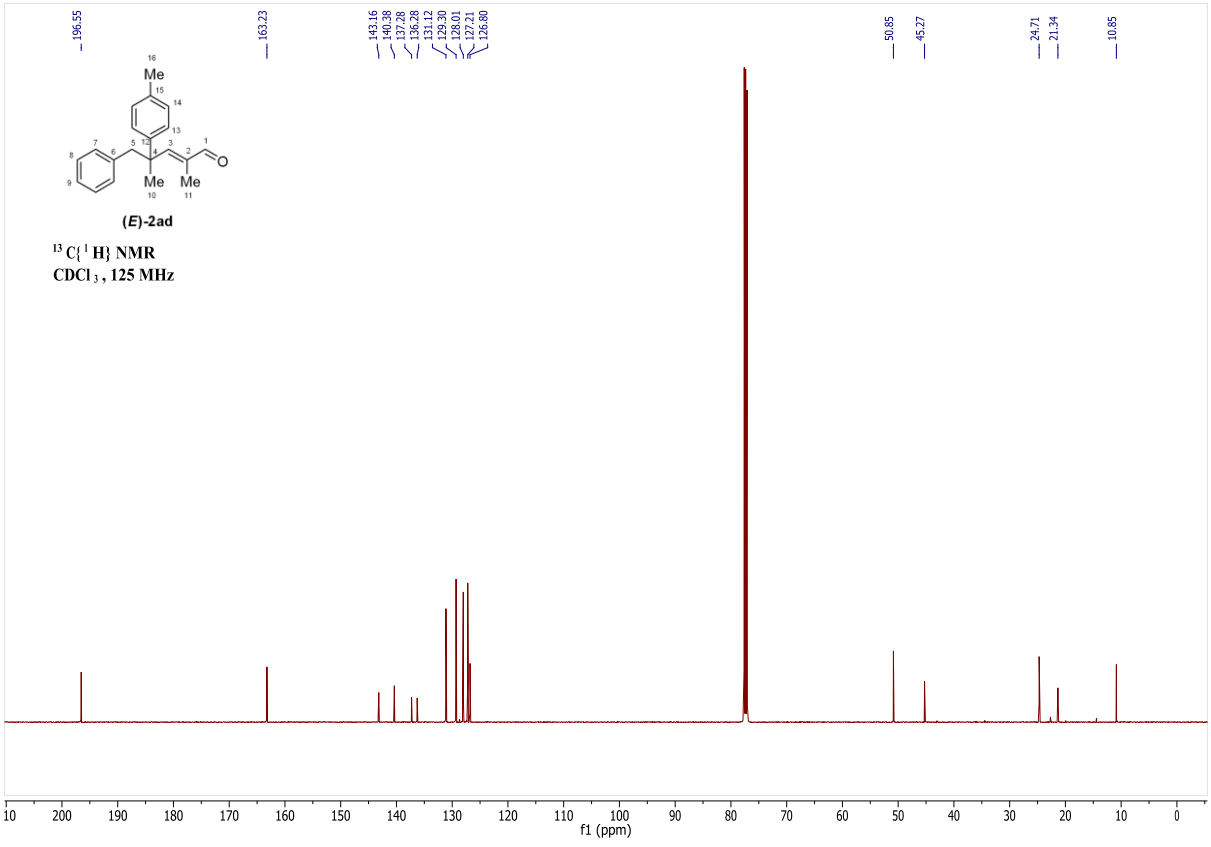
3.04
3.99
1.00
1.89
1.01
1.00
2.99
2.95
3.11
f1 (ppm)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136.28
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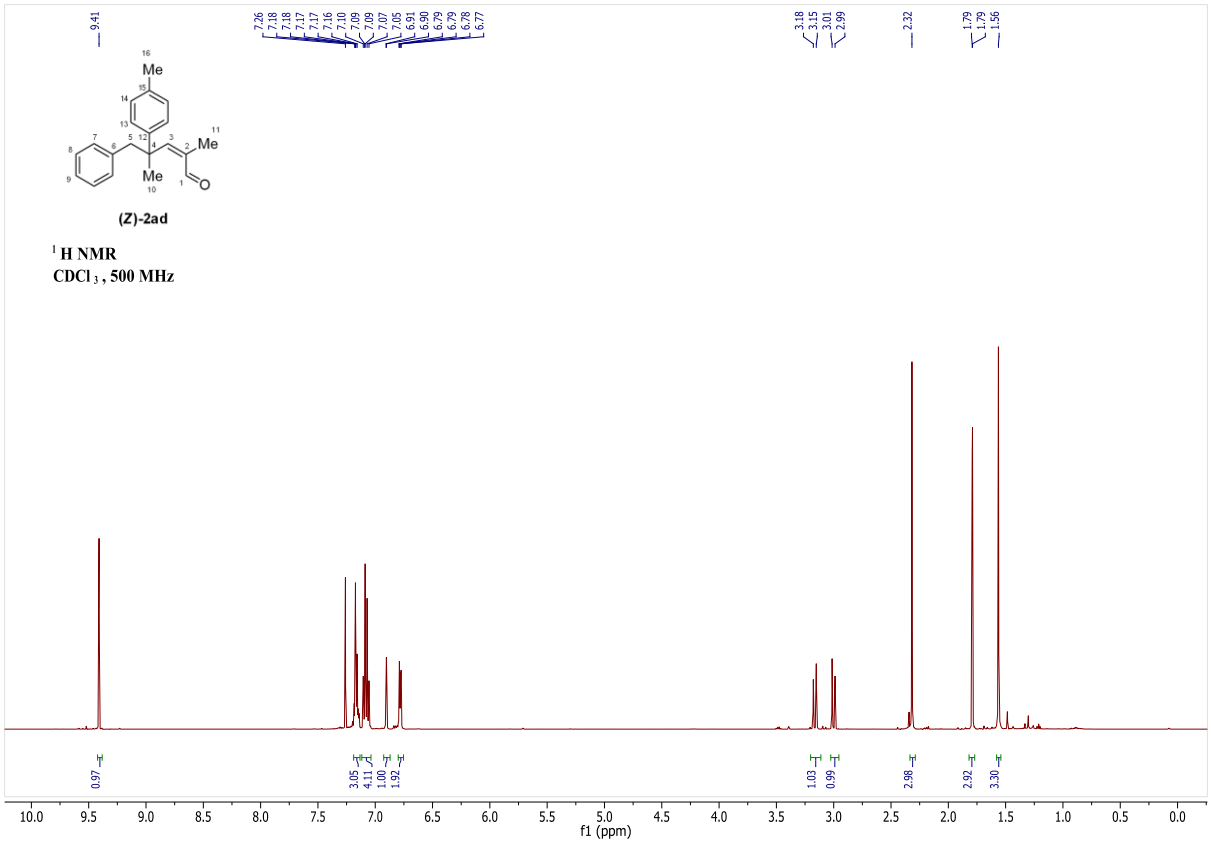
129.30
129.01
127.21
126.80
50.85
45.27
24.71
21.34
10.85
Me
Me
Me
(E)-2ad
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)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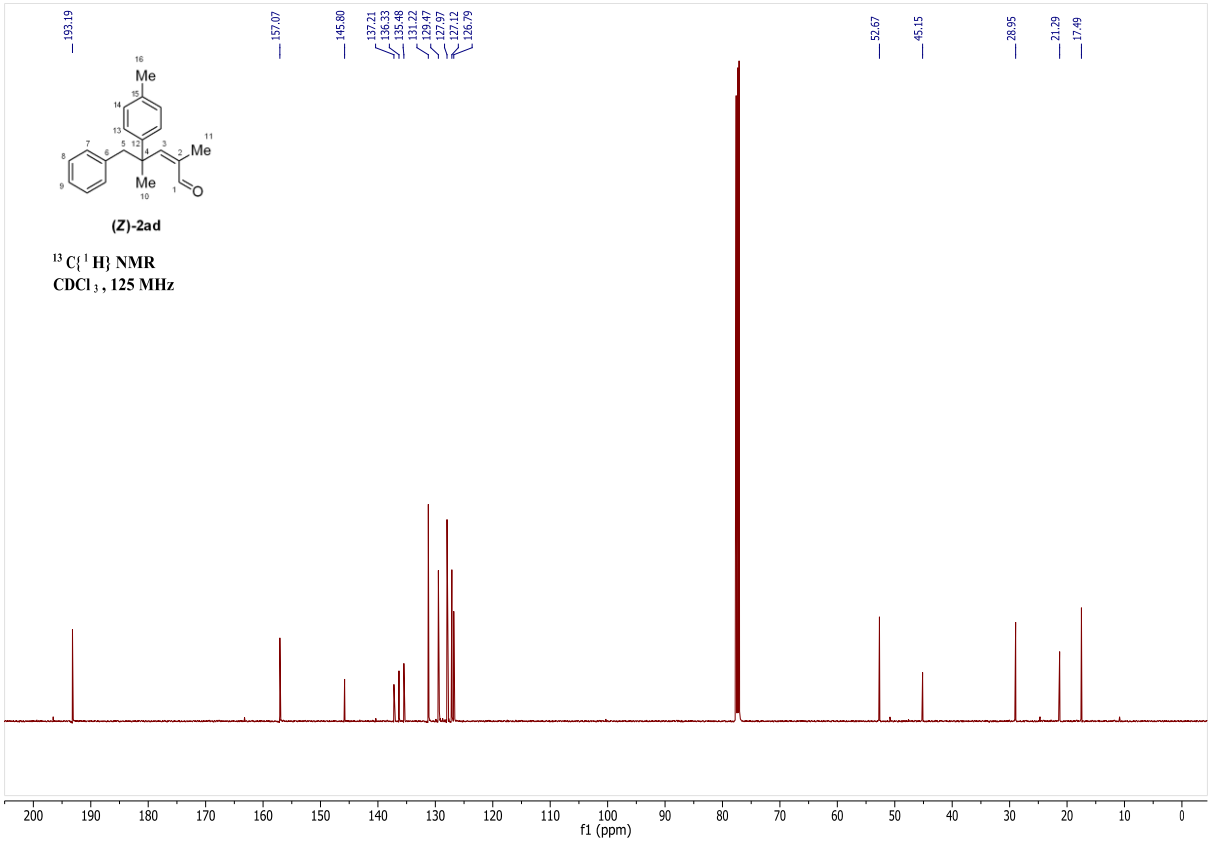
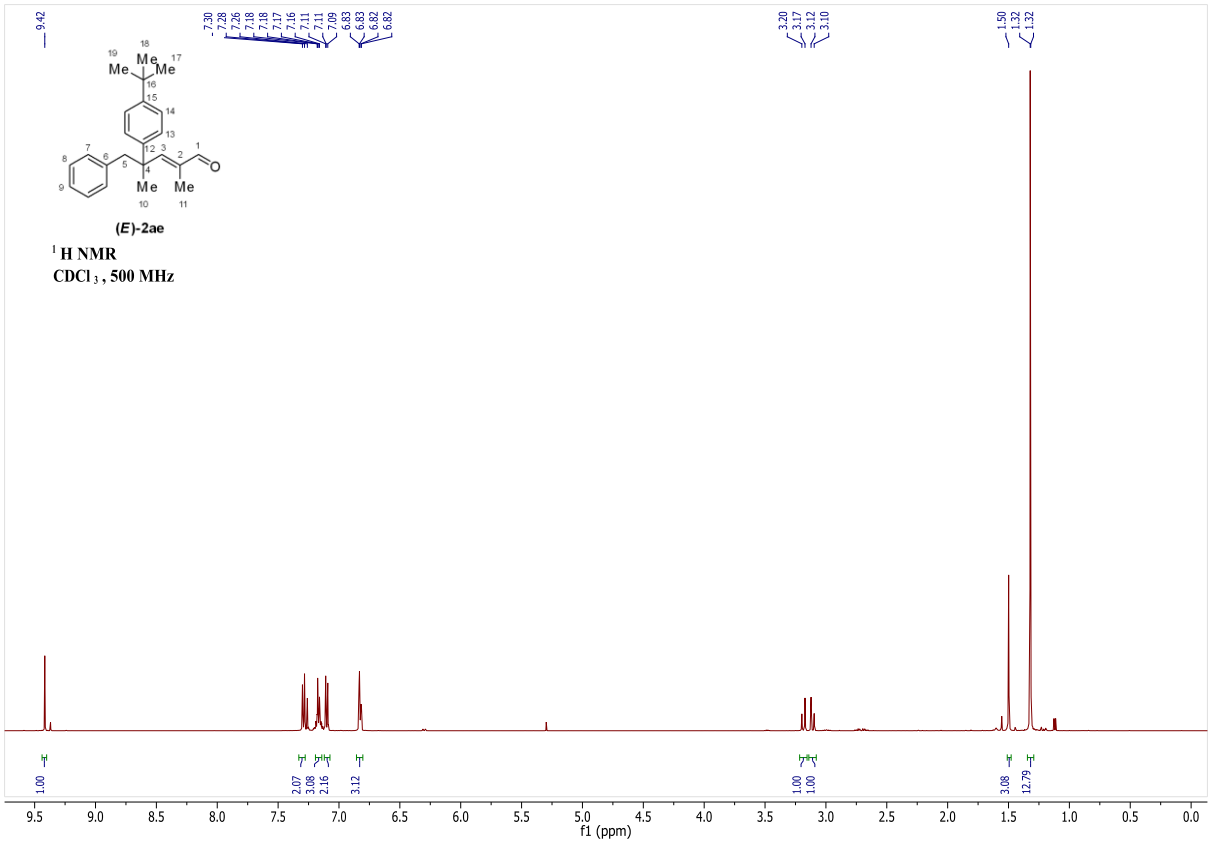
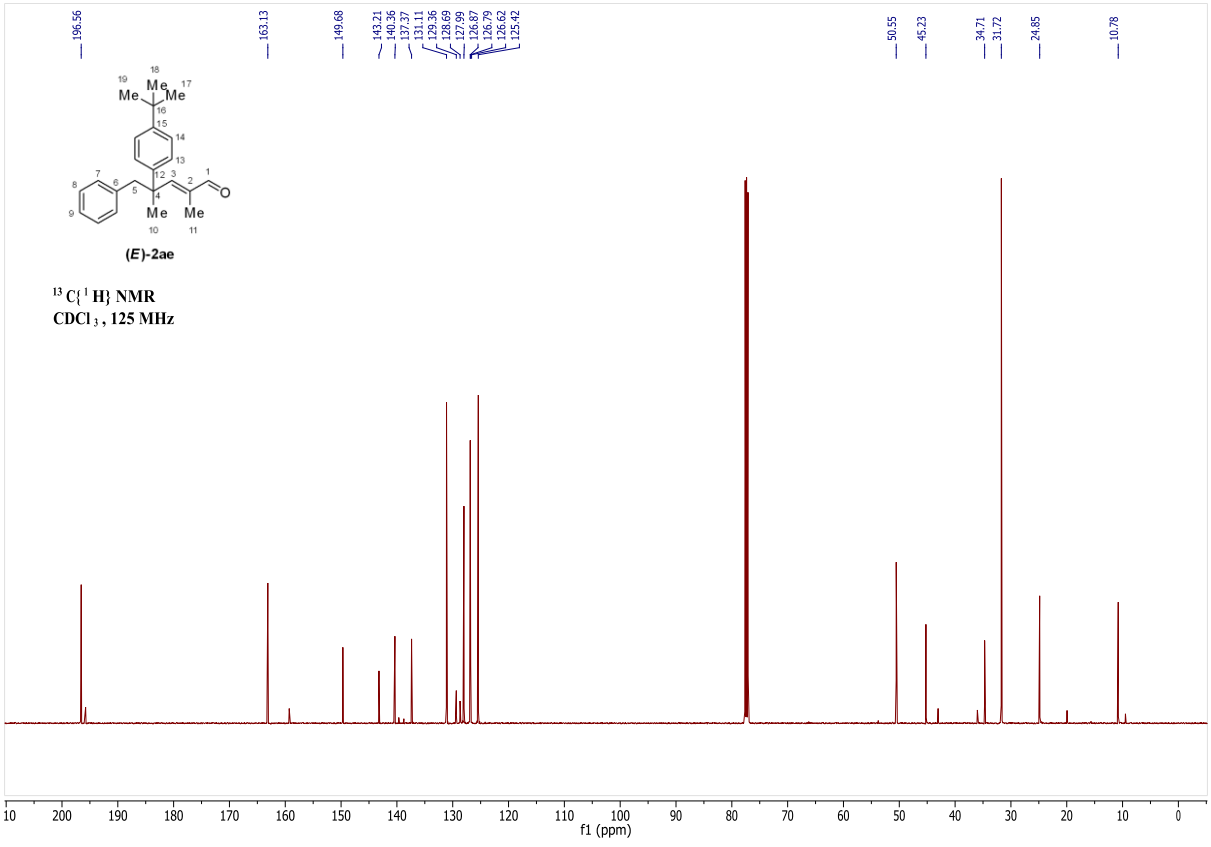
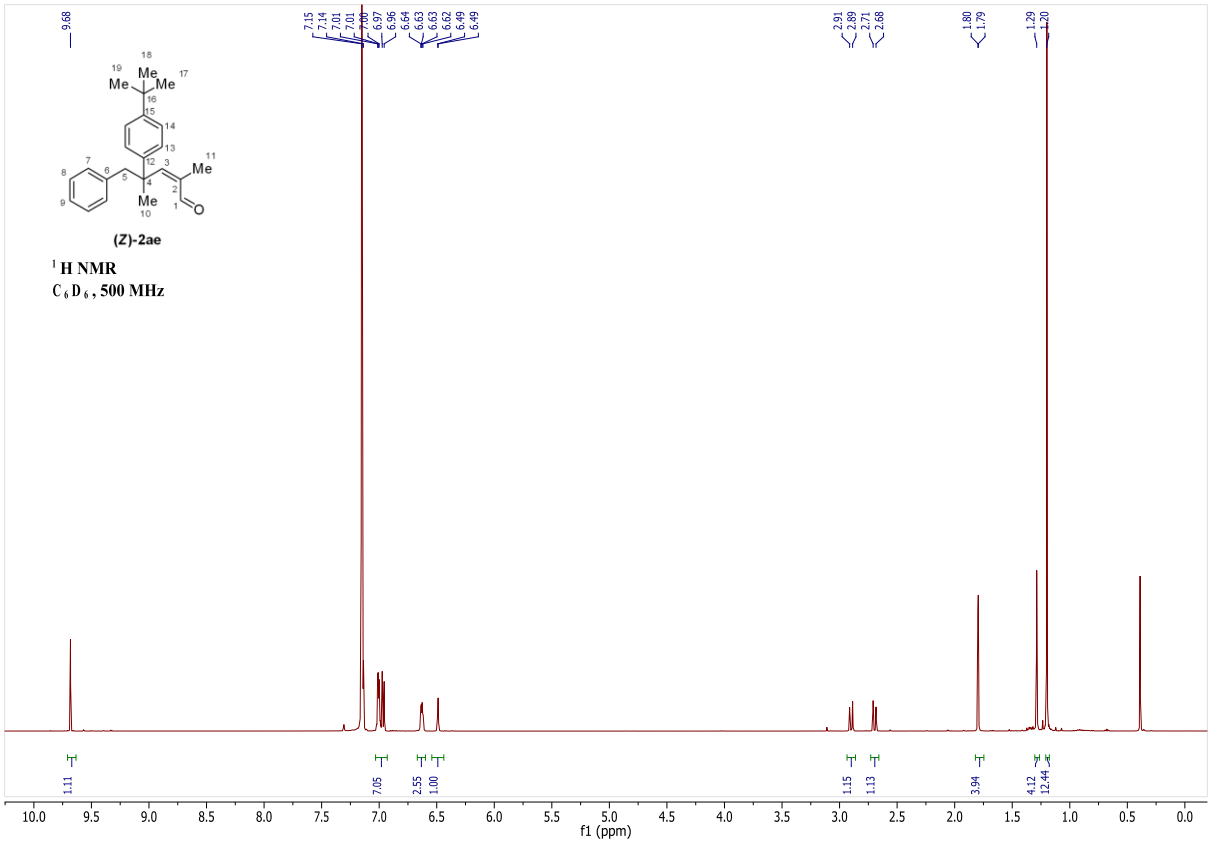
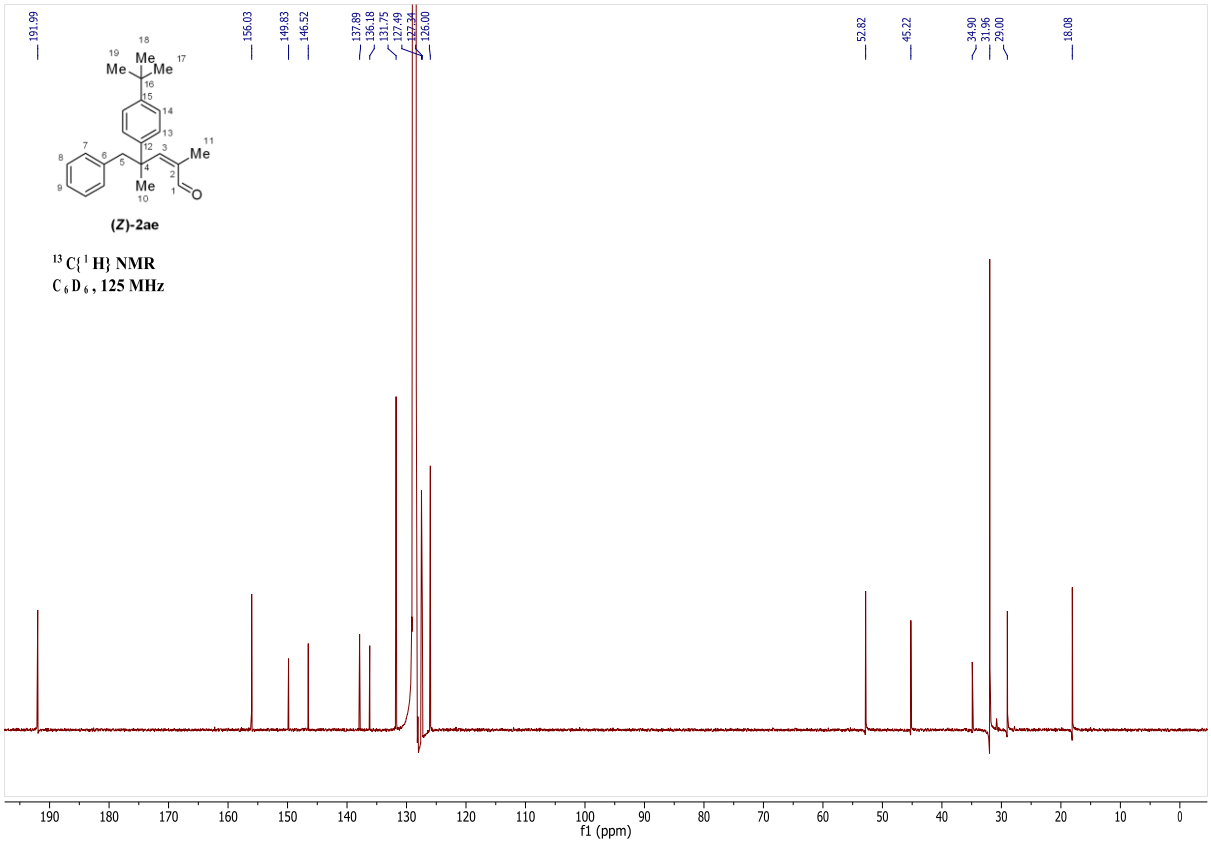
^{1}H NMR
CDCl$_3$, 500 MHz
f1 (ppm)

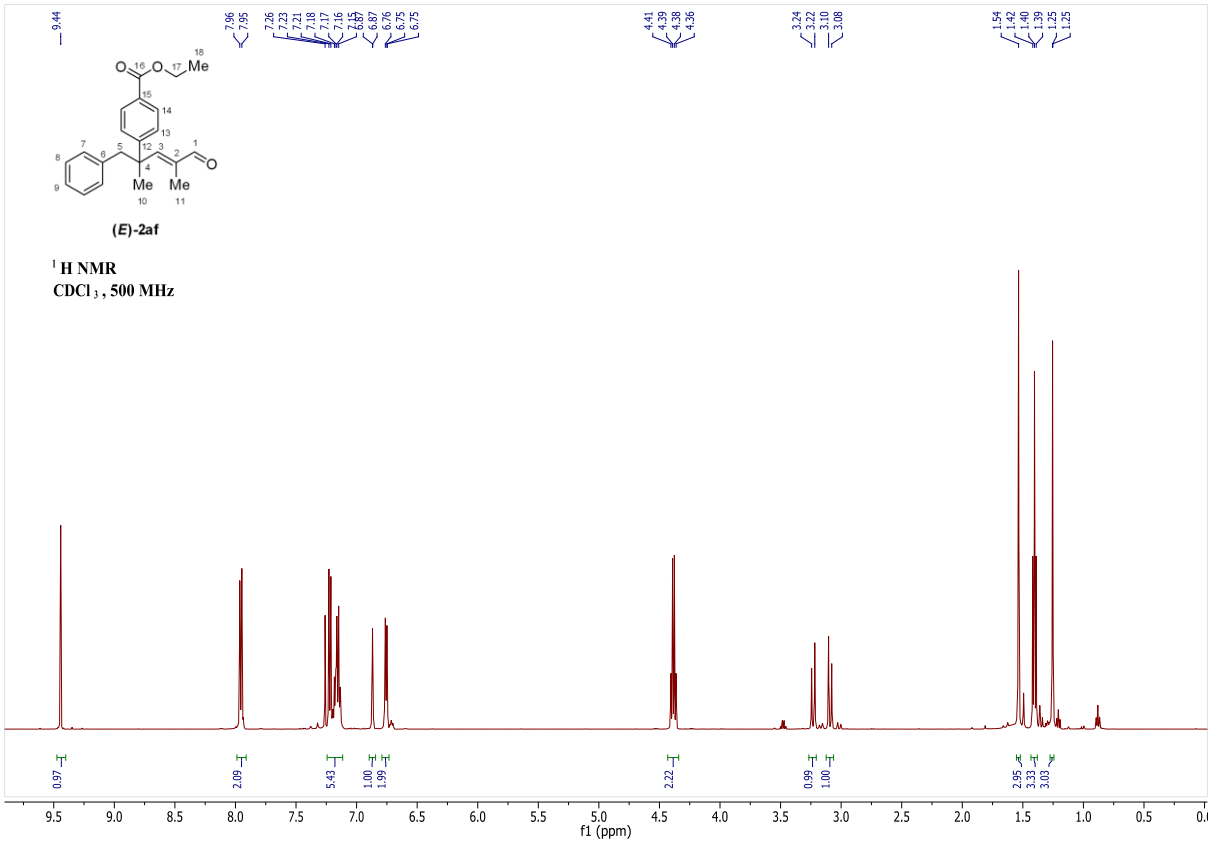

(Z)-2ad
^{13}C{^{1}H} NMR
CDCl$_3$, 125 MHz
f1 (ppm)


(E)-2ae
1 H NMR
CDCl 3 , 500 MHz
f1 (ppm)


(E)-2ae
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)


(Z)-2ae
^{1}H NMR
C_6D_6, 500 MHz
f1 (ppm)


(Z)-2ae
$^{13}C\{^{1}H\}$ NMR
C_6D_6, 125 MHz
f1 (ppm)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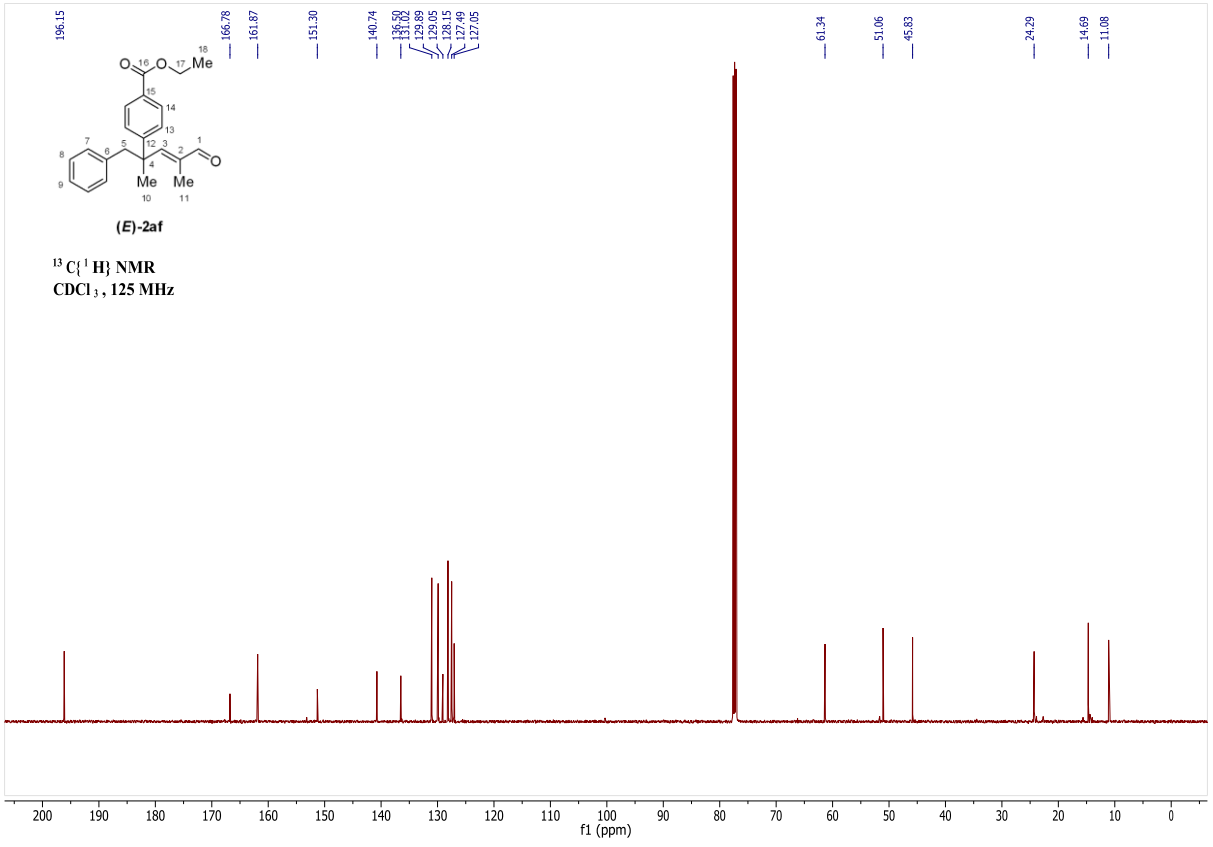
7.26
7.23
7.21
7.18
7.17
7.16
6.87
6.76
6.75
6.75
4.41
4.39
4.38
4.36
3.24
3.22
3.10
3.08
1.54
1.42
1.40
1.39
1.25
1.25
Me
Me
Me
(E)-2af
1 H NMR
CDCl 3 , 500 MHz
0.97
2.09
5.43
1.00
1.99
2.22
0.99
1.00
2.95
3.33
3.03
f1 (ppm)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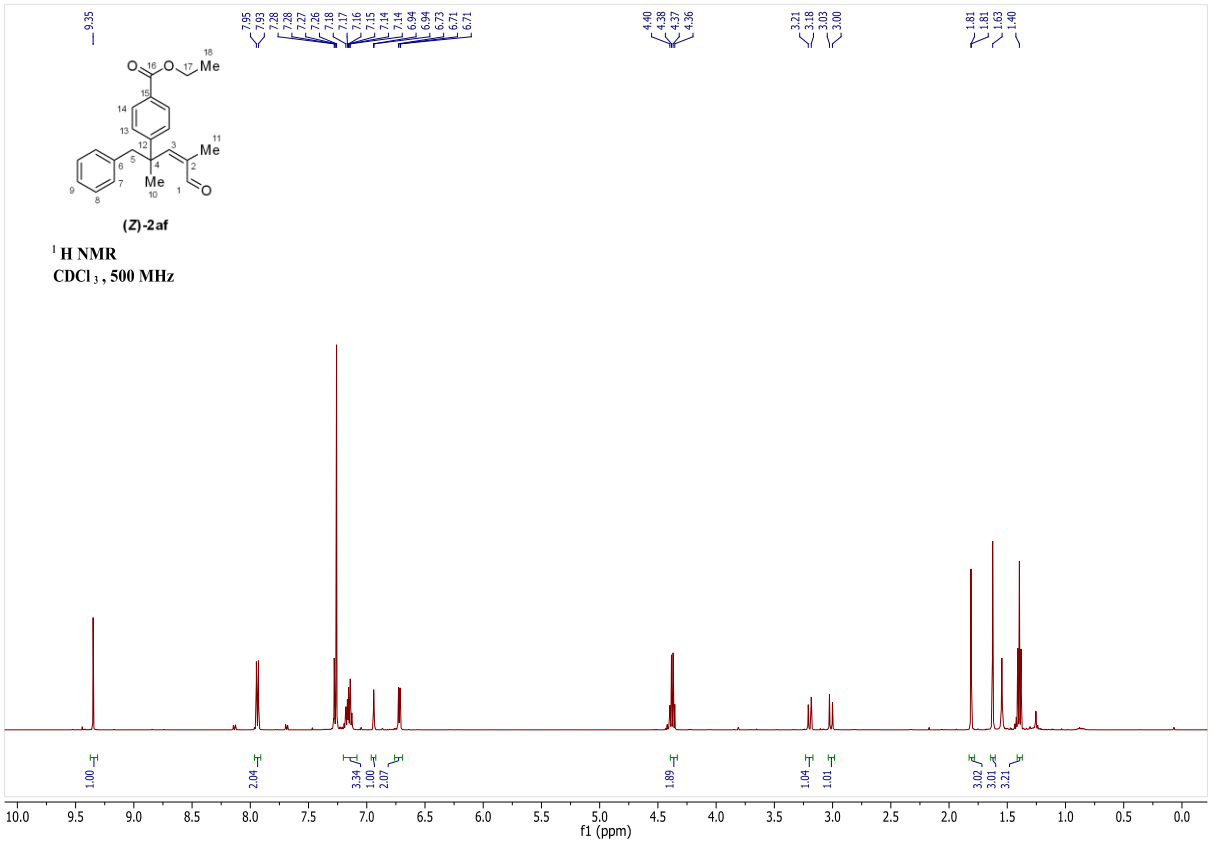
136.50
131.02
129.89
129.05
128.15
127.49
127.05
61.34
51.06
45.83
24.29
14.69
11.08
Me
Me
Me
(E)-2af
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)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7.28
7.27
7.26
7.18
7.17
7.16
7.15
7.14
7.14
6.94
6.94
6.73
6.71
6.71
4.40
4.38
4.37
4.36
3.21
3.18
3.03
3.00
1.81
1.81
1.63
1.40
(Z)-2af
1 H NMR
CDCl 3 , 500 MHz
1.00
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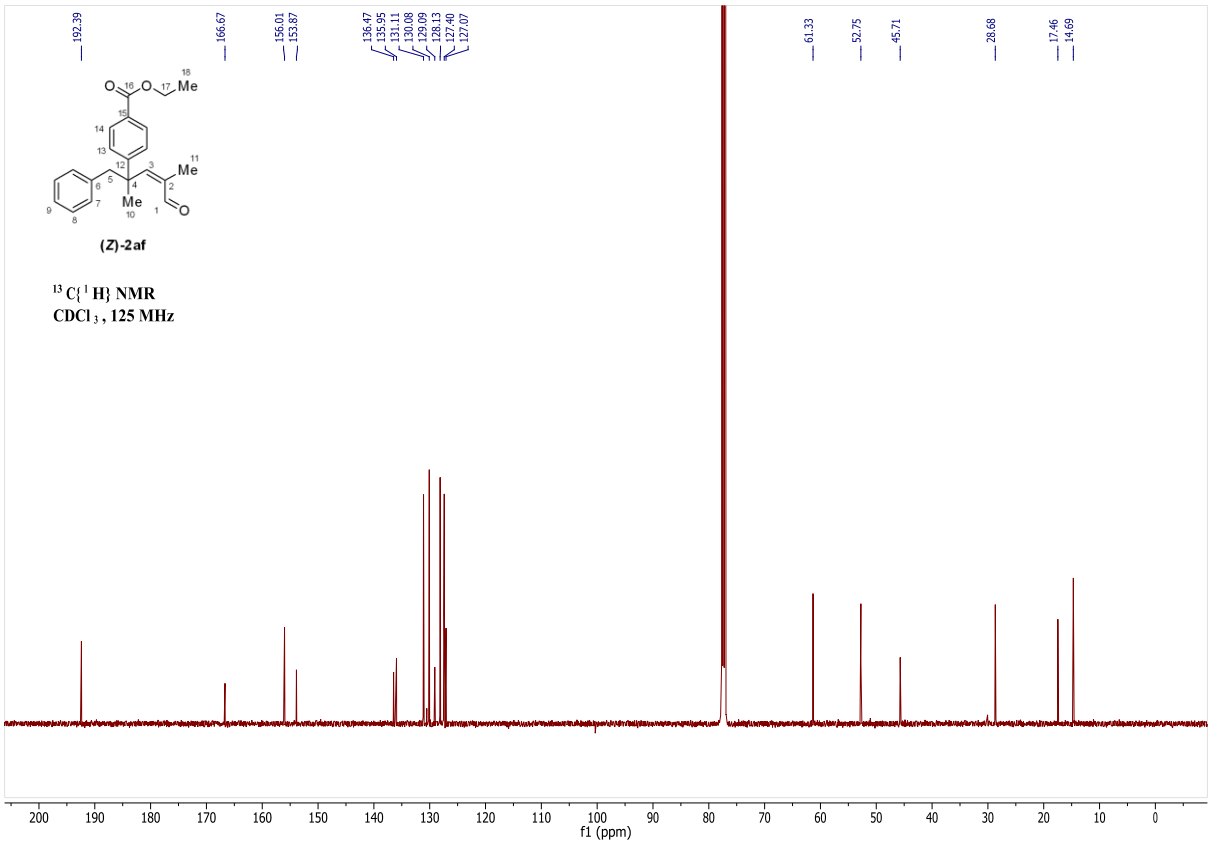
3.34
1.00
2.07
1.89
1.04
1.01
3.02
3.01
3.21
f1 (ppm)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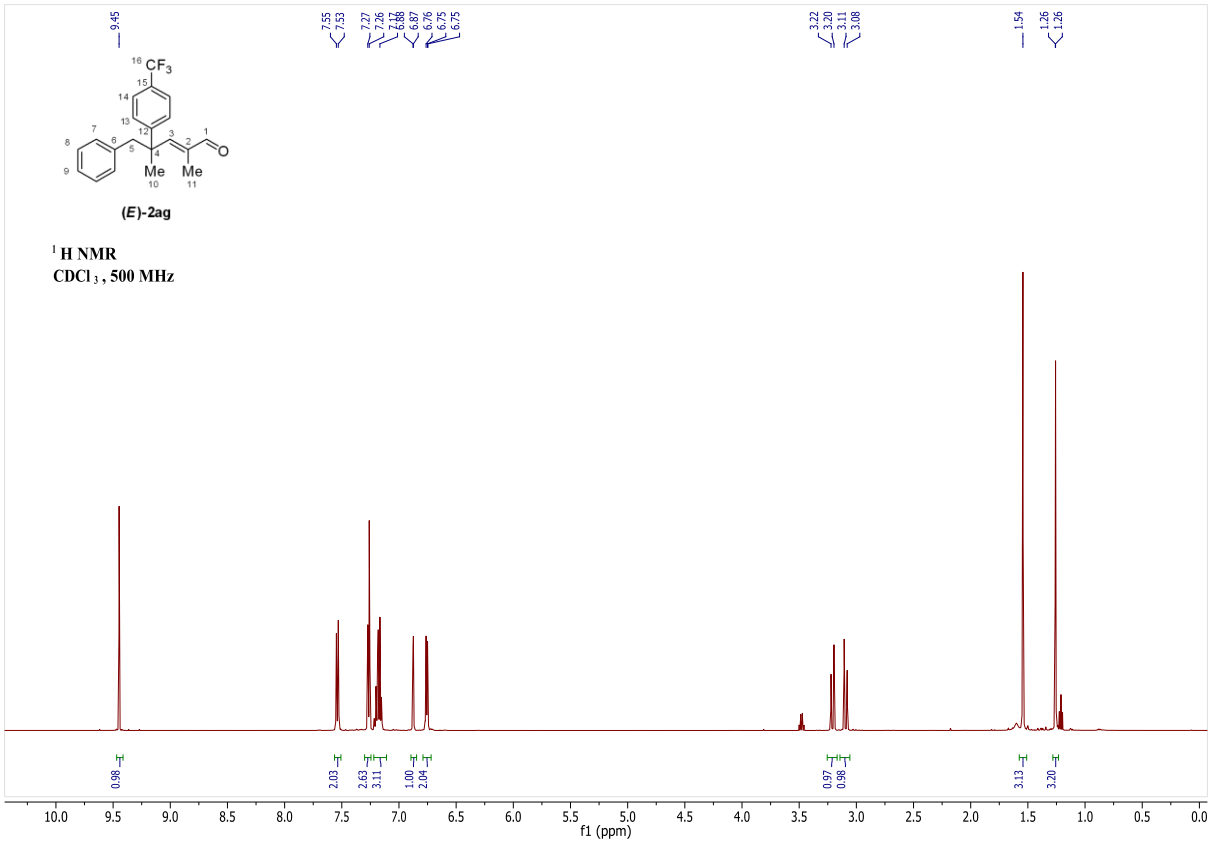
128.13
127.40
127.07
61.33
52.75
45.71
28.68
17.46
14.69
(Z)-2af
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)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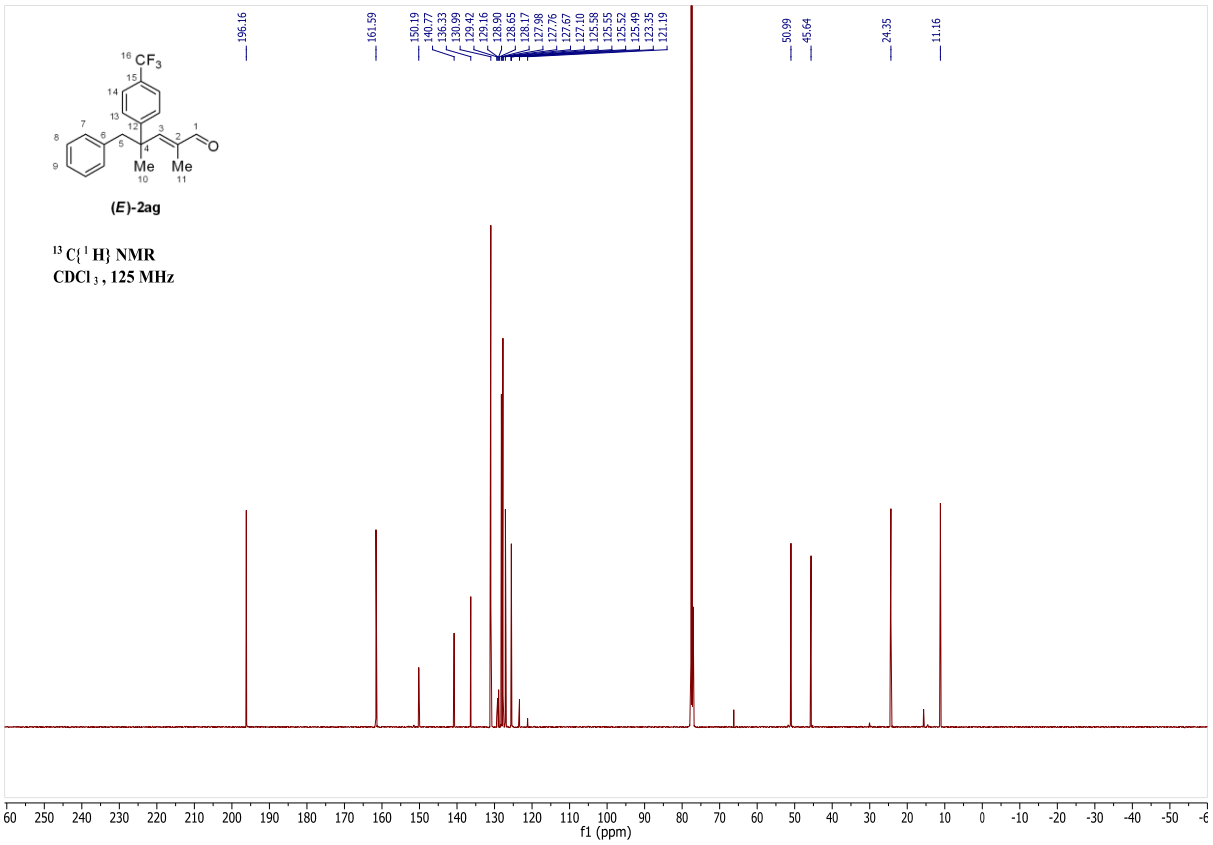
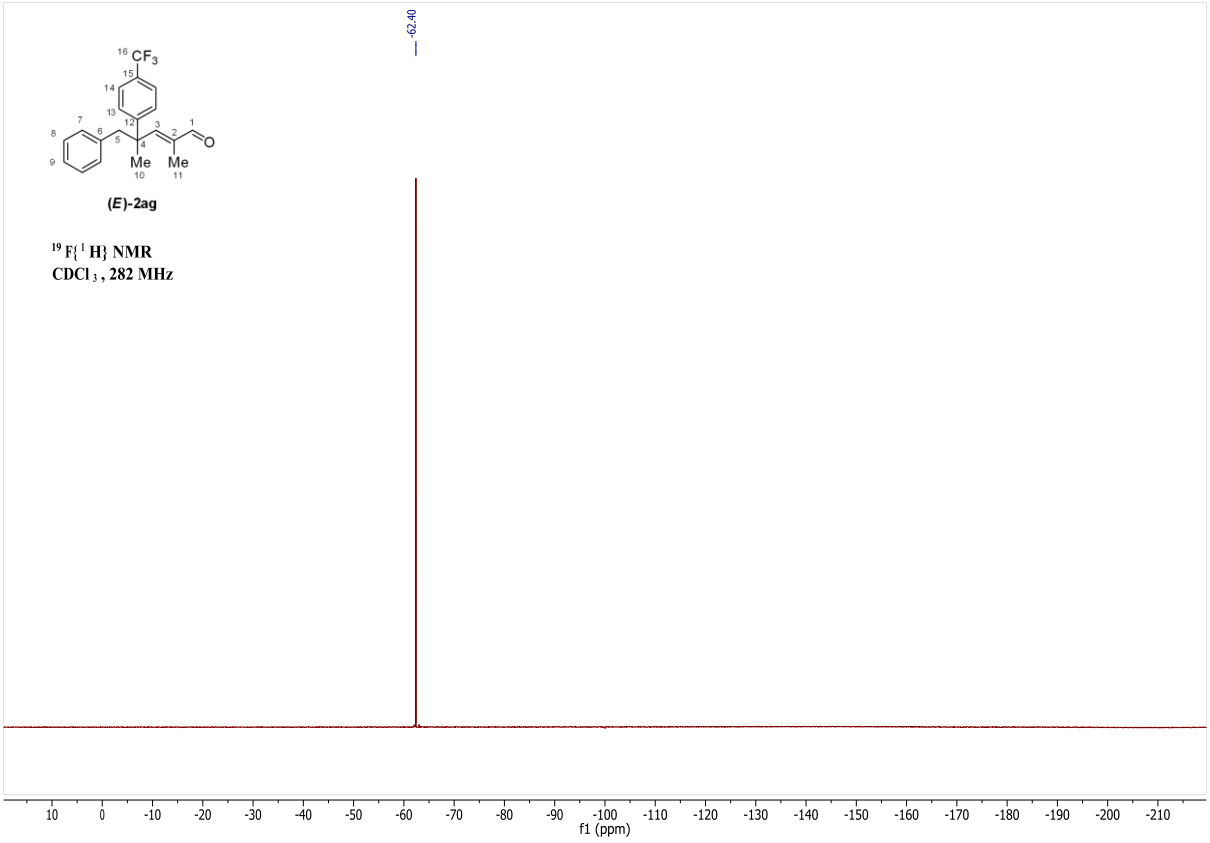
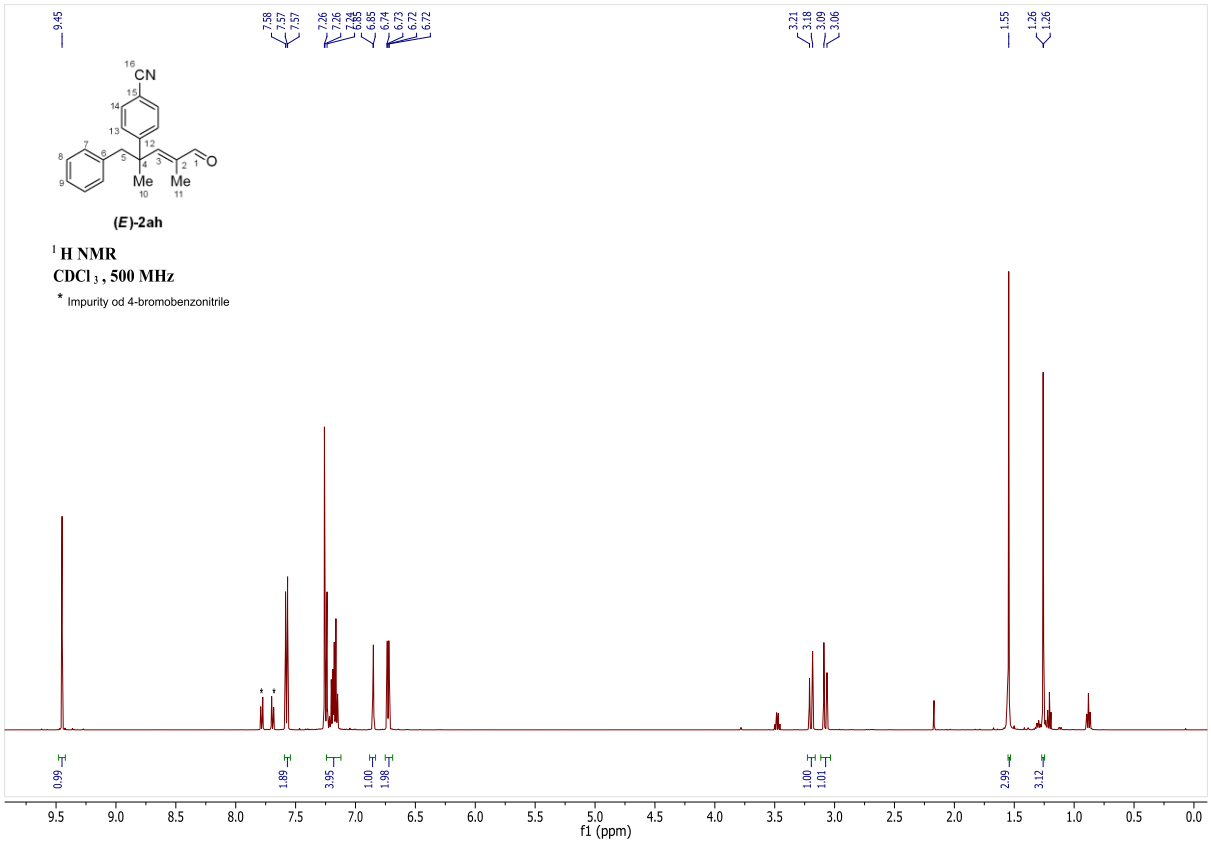
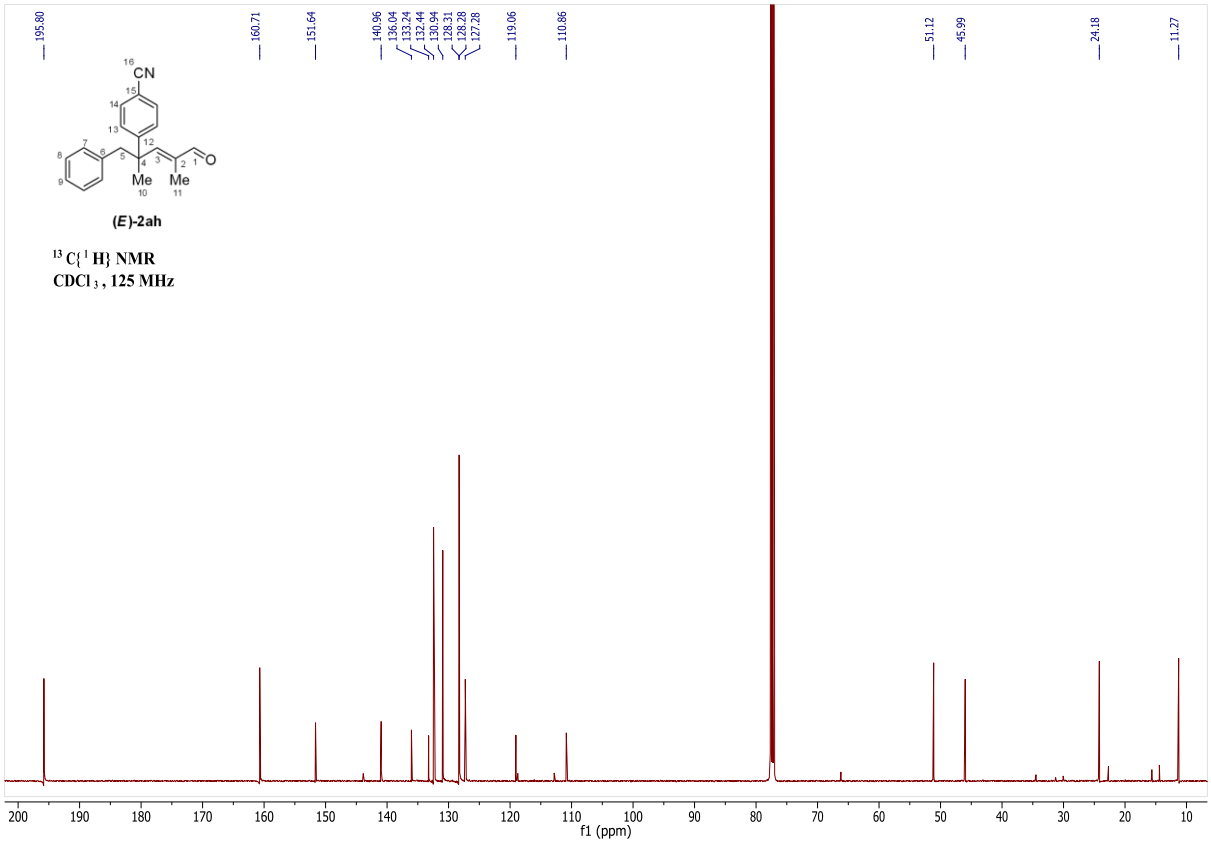
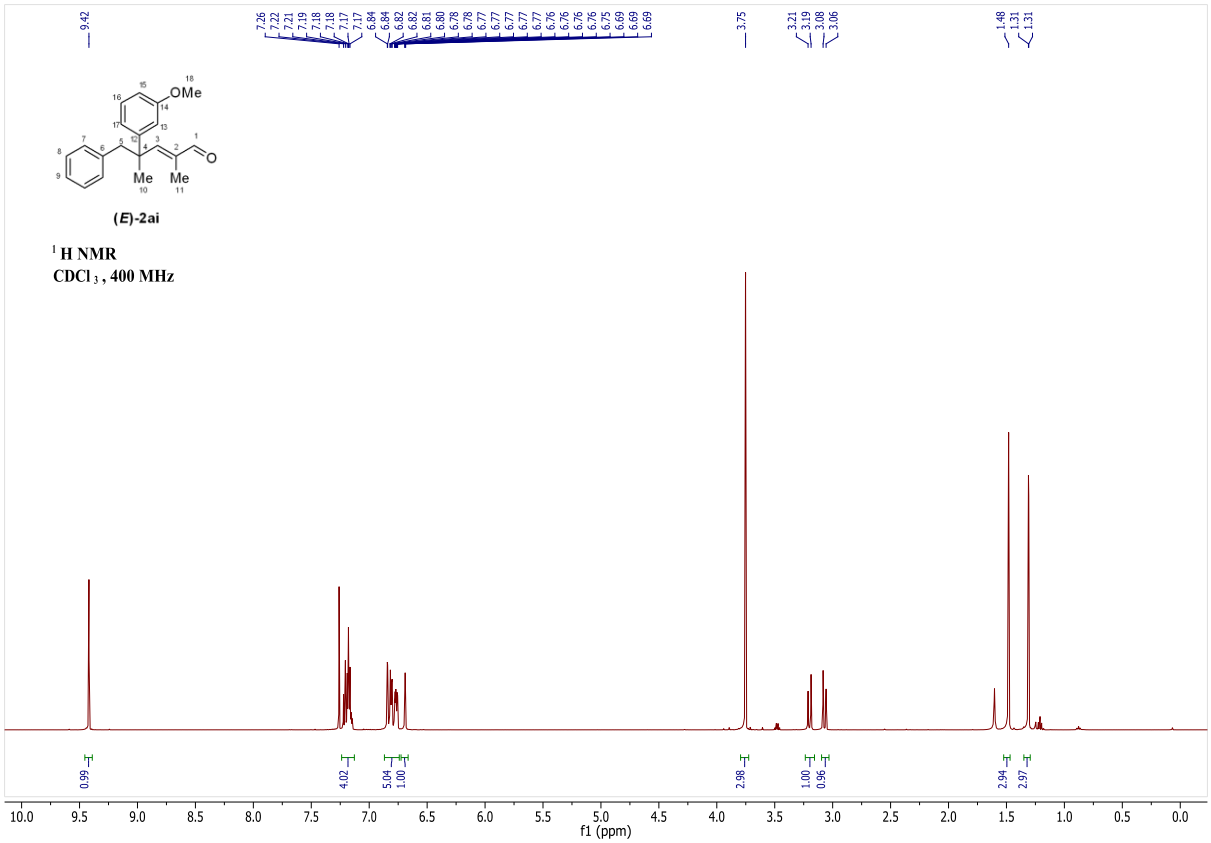
7.26
7.17
6.88
6.87
6.76
6.75
6.75
3.22
3.20
3.11
3.08
1.54
1.26
1.26
CF3
Me
Me
O
(E)-2ag
1H NMR
CDCl3, 500 MHz
0.98
2.03
2.63
3.11
1.00
2.04
0.97
0.98
3.13
3.20
f1 (ppm)

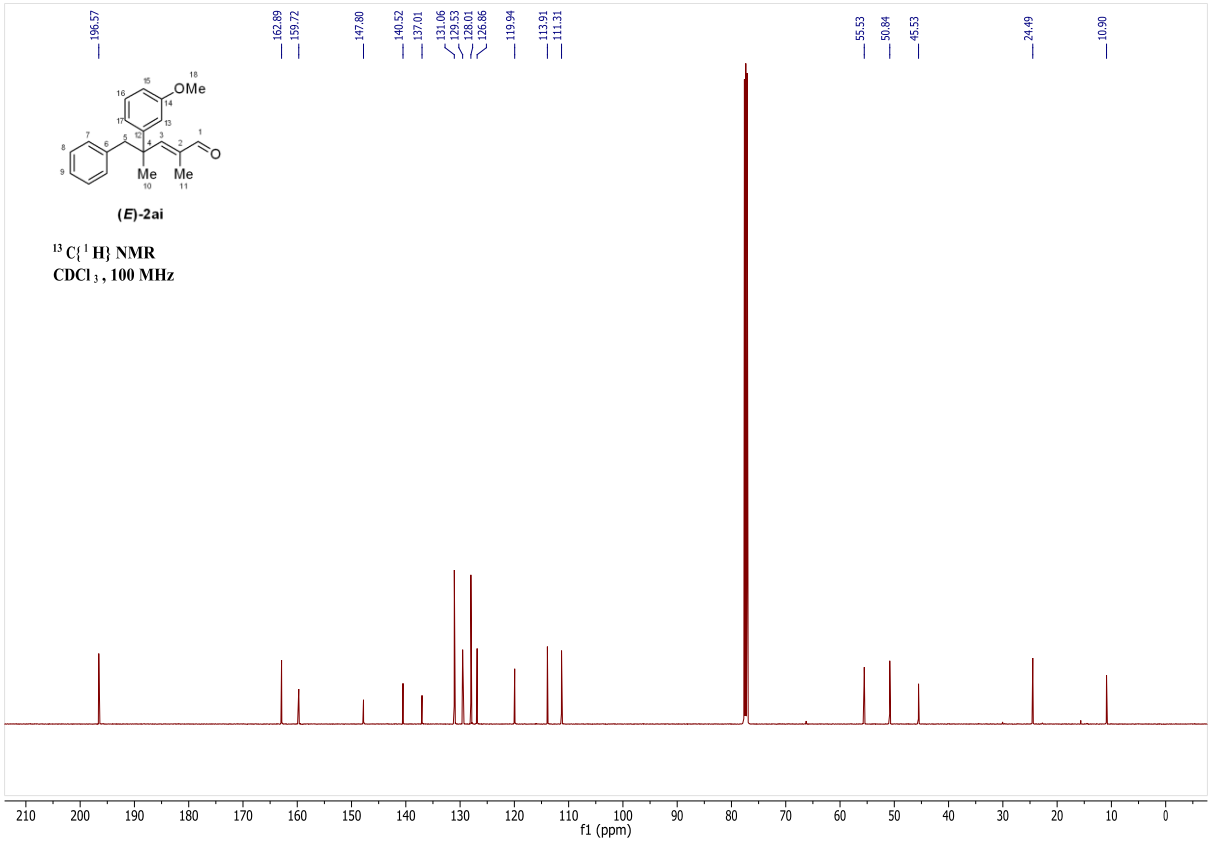

196.16
161.59
150.19
140.77
136.33
130.99
129.42
129.16
128.90
128.65
128.17
127.98
127.76
127.67
127.10
125.58
125.55
125.52
125.49
123.35
121.19
50.99
45.64
24.35
11.16
CF3
Me
Me
O
(E)-2ag
13C{1H} NMR
CDCl3, 125 MHz
f1 (ppm)

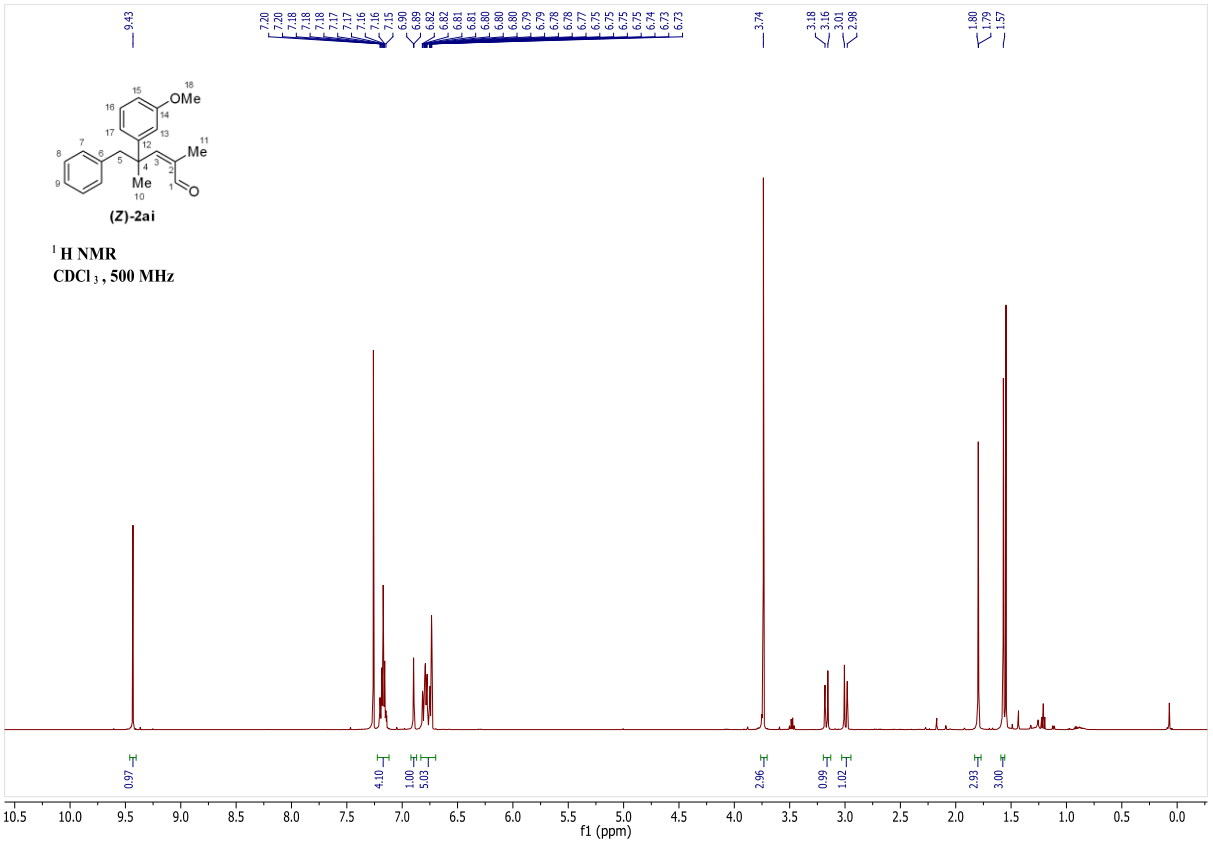

-62.40
16 CF3
15
14
13
12
3
2
1
O
7
6
5
4
8
9
Me
10
Me
11
(E)-2ag
19F{1H} NMR
CDCl3, 282 MHz
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

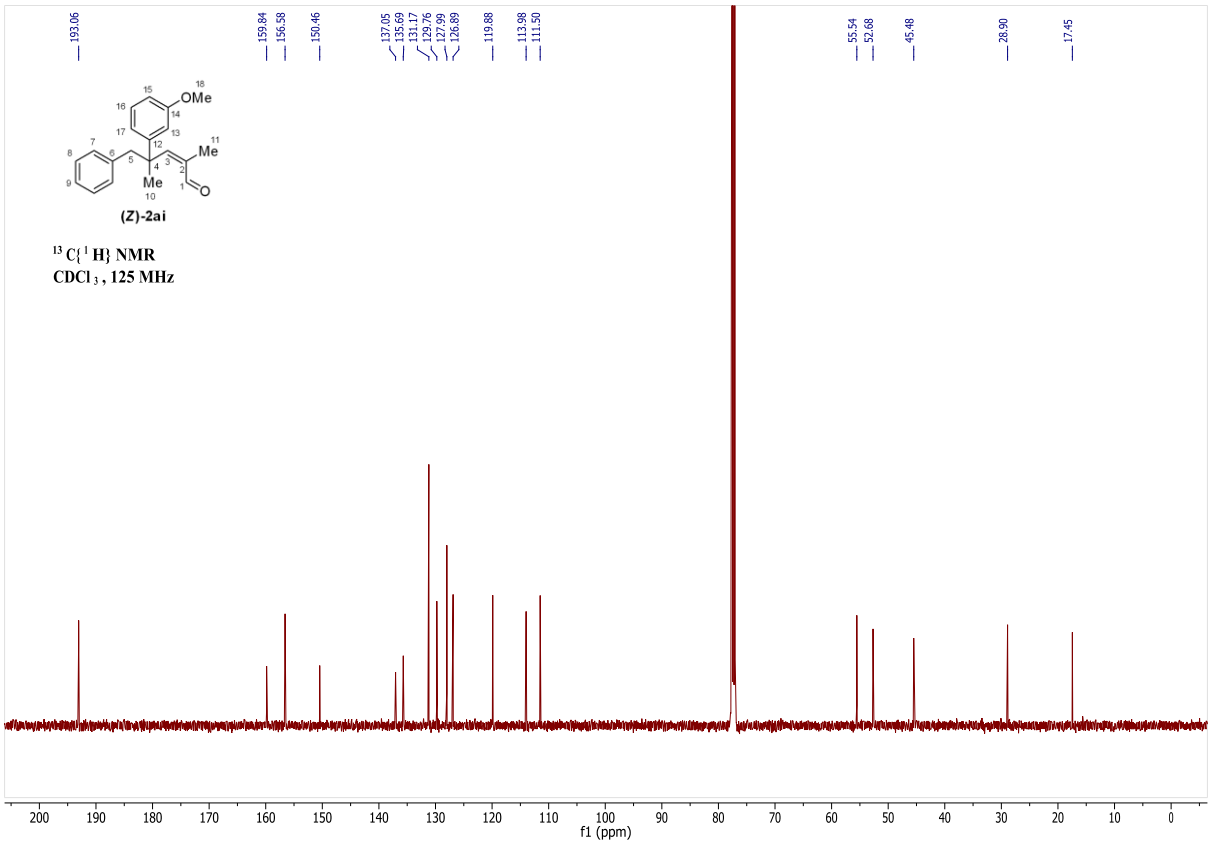

9.45
7.58
7.57
7.57
7.26
7.26
7.24
6.85
6.74
6.73
6.72
6.72
3.21
3.18
3.09
3.06
1.55
1.26
1.26
CN
Me
Me
(E)-2ah
1 H NMR
CDCl 3 , 500 MHz
* Impurity od 4-bromobenzonitrile
0.99
1.89
3.95
1.00
1.98
1.00
1.01
2.99
3.12
f1 (ppm)

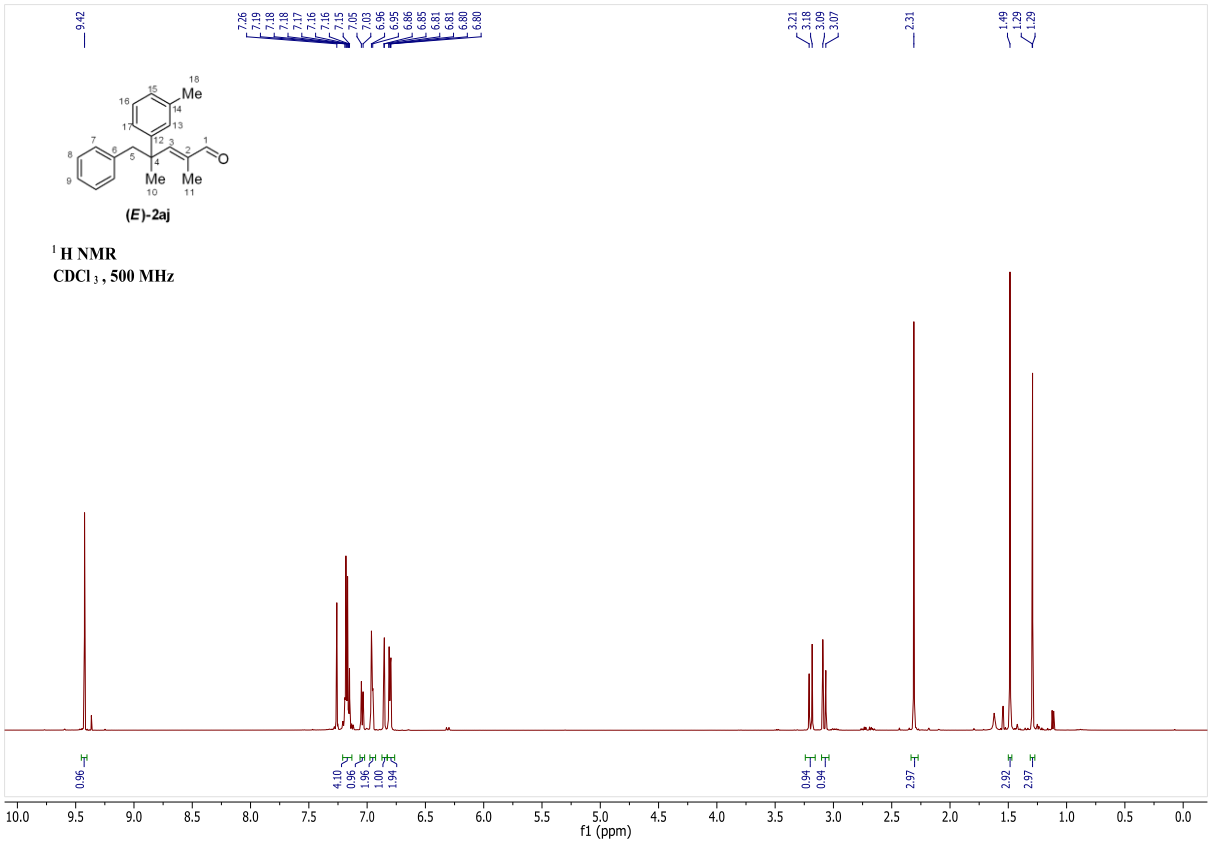

195.80
160.71
151.64
140.96
136.04
133.24
132.44
130.94
128.31
128.28
127.28
119.06
110.86
51.12
45.99
24.18
11.27
CN
Me
Me
(E)-2ah
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

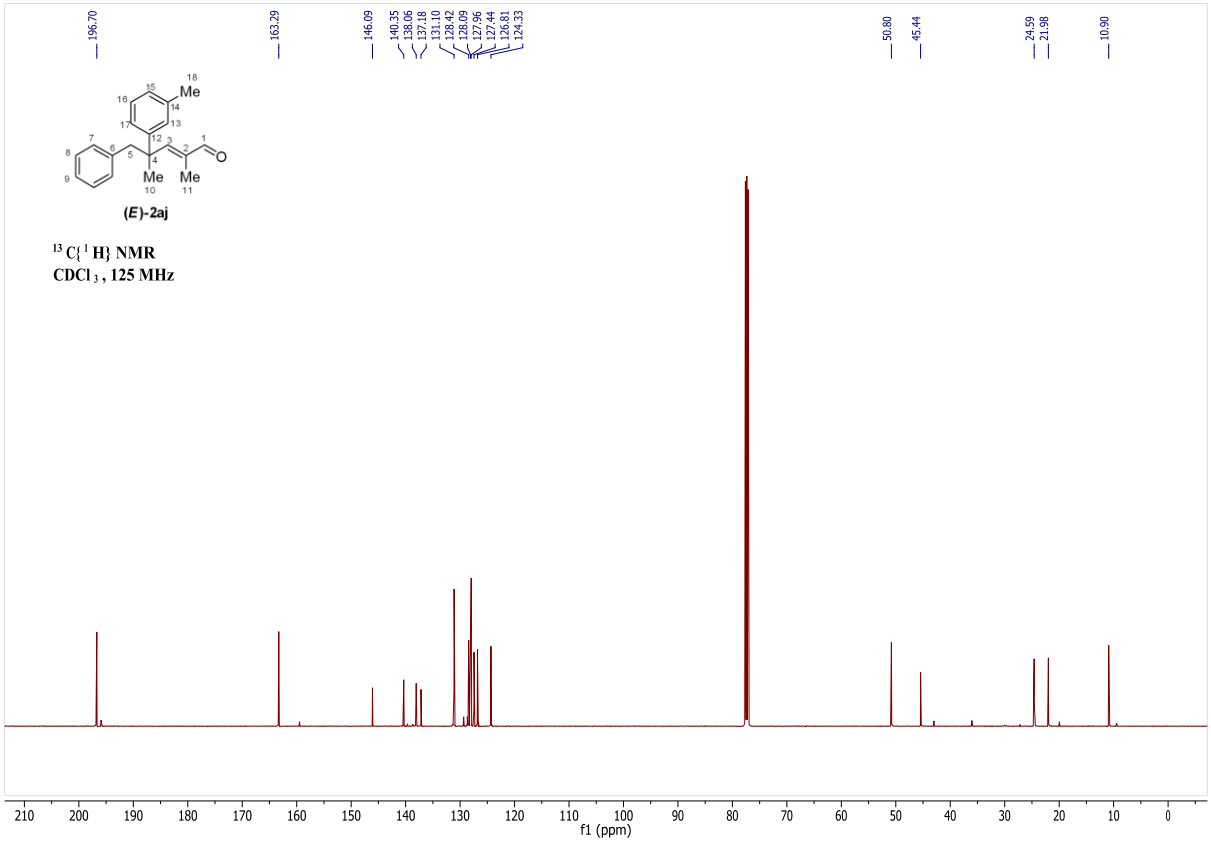

9.42
7.26
7.22
7.21
7.19
7.18
7.18
7.17
7.17
6.84
6.82
6.82
6.81
6.80
6.78
6.78
6.77
6.77
6.77
6.77
6.76
6.76
6.76
6.76
6.75
6.69
6.69
6.69
3.75
3.21
3.19
3.08
3.06
1.48
1.31
1.31
OMe
Me
Me
(E)-2ai
1 H NMR
CDCl 3 , 400 MHz
0.99
4.02
5.04
1.00
2.98
1.00
0.96
2.94
2.97
f1 (ppm)

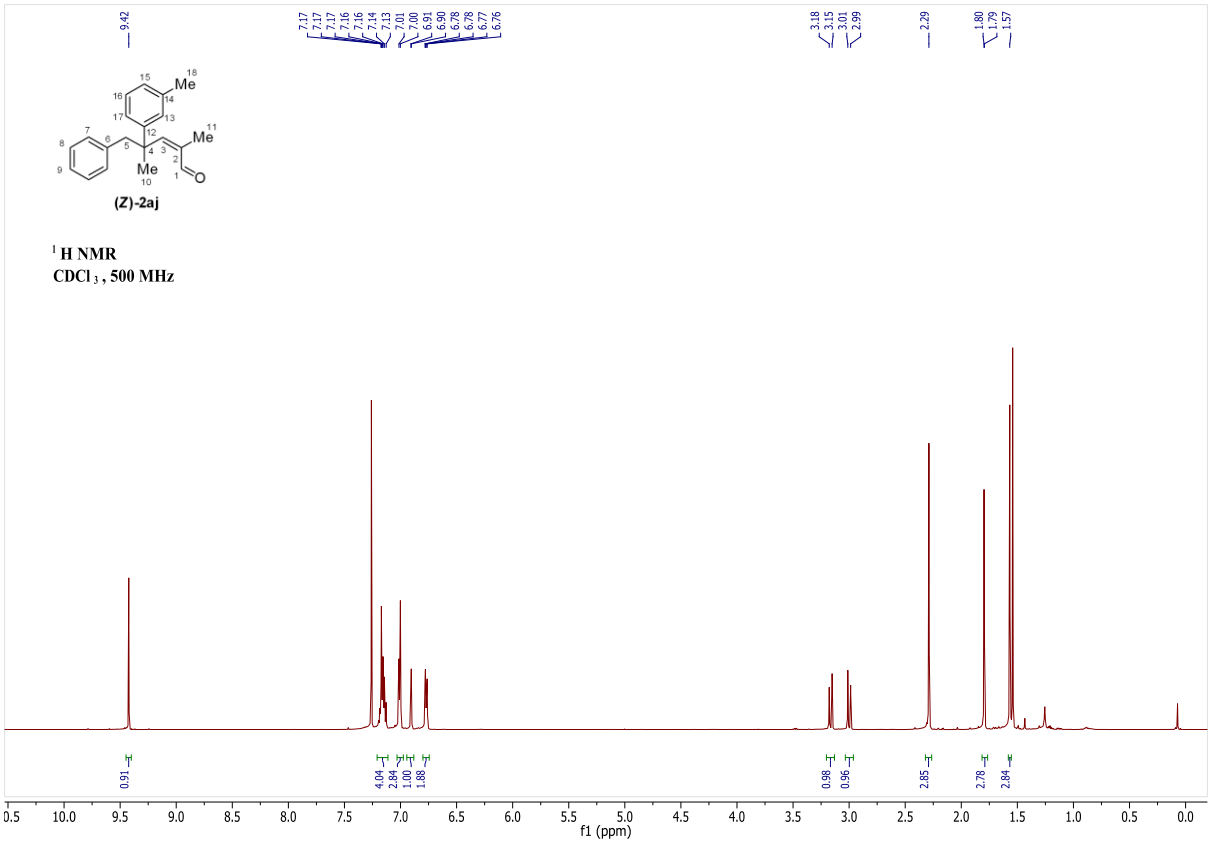

196.57
162.89
159.72
147.80
140.52
137.01
131.06
129.53
128.01
126.86
119.94
113.91
111.31
55.53
50.84
45.53
24.49
10.90
OMe
Me
Me
(E)-2ai
13 C{ 1 H} NMR
CDCl 3 , 100 MHz
f1 (ppm)

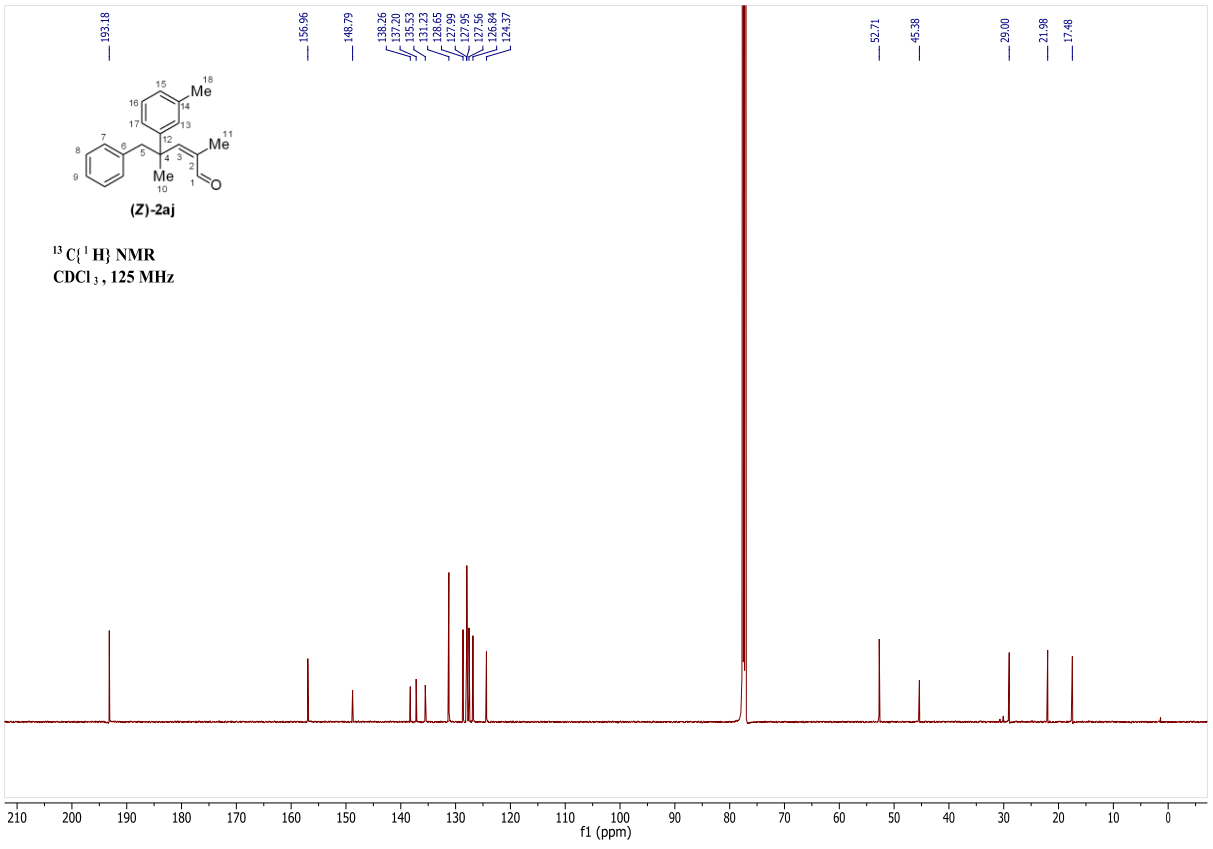

9.43
7.20
7.18
7.17
7.16
7.15
6.90
6.89
6.82
6.81
6.80
6.79
6.78
6.77
6.75
6.74
6.73
3.74
3.18
3.16
3.01
2.98
1.80
1.79
1.57
OMe
Me
Me
(Z)-2ai
1 H NMR
CDCl 3 , 500 MHz
0.97
4.10
1.00
5.03
2.96
0.99
1.02
2.93
3.00
f1 (ppm)

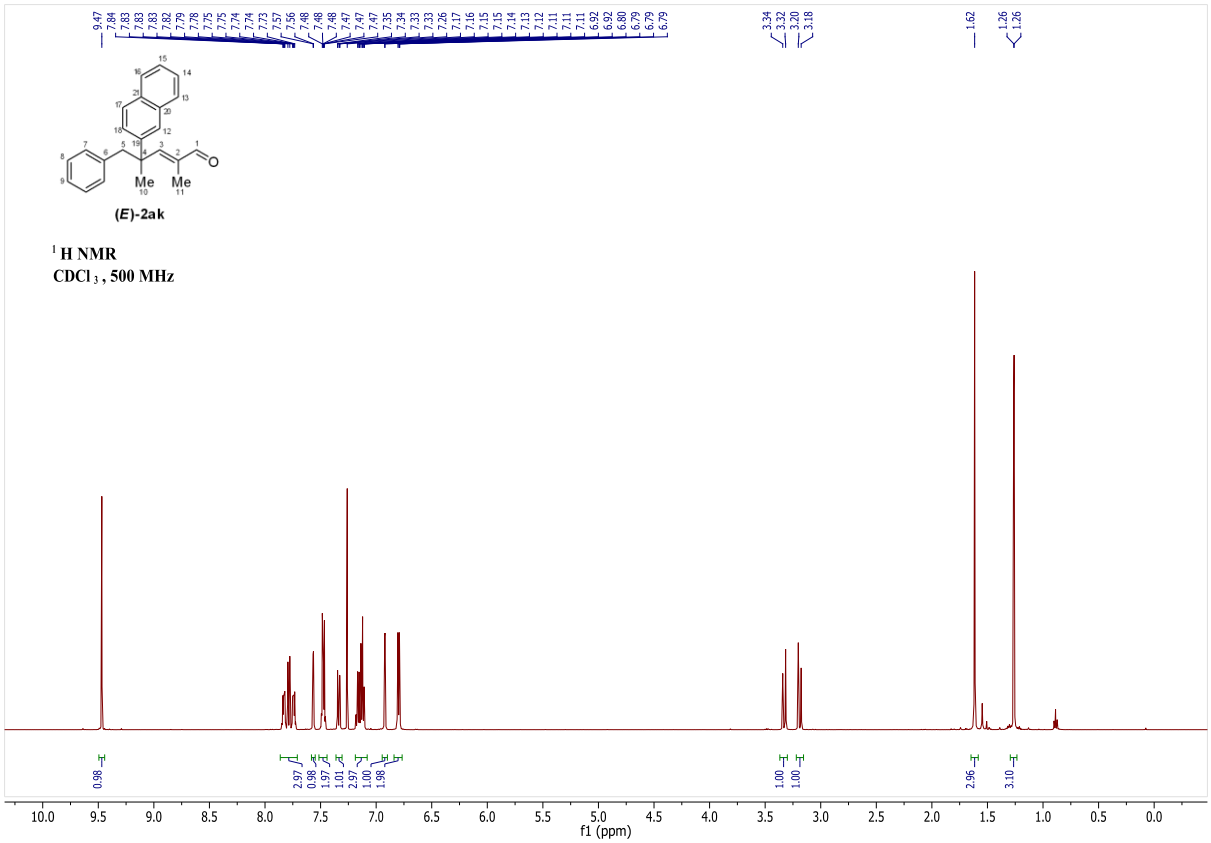

193.06
159.84
156.58
150.46
137.05
135.69
131.17
129.76
127.99
126.89
119.88
113.98
111.50
55.54
52.68
45.48
28.90
17.45
OMe
Me
Me
(Z)-2ai
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

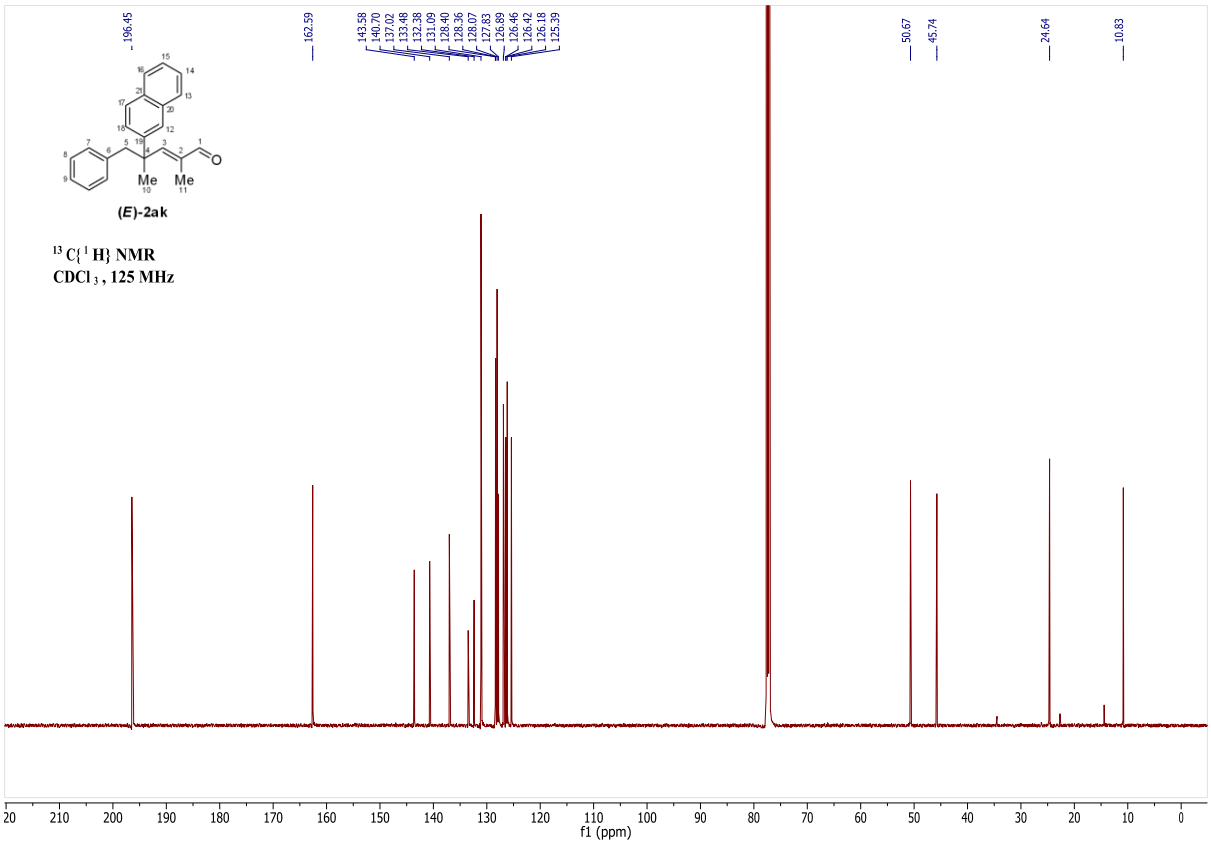

9.42
7.26
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.05
7.03
6.96
6.95
6.86
6.85
6.81
6.81
6.80
6.80
3.21
3.18
3.09
3.07
2.31
1.49
1.29
1.29
Me
Me
Me
(E)-2aj
1 H NMR
CDCl 3 , 500 MHz
0.96
4.10
0.96
1.96
1.00
1.94
0.94
0.94
2.97
2.92
2.97
f1 (ppm)

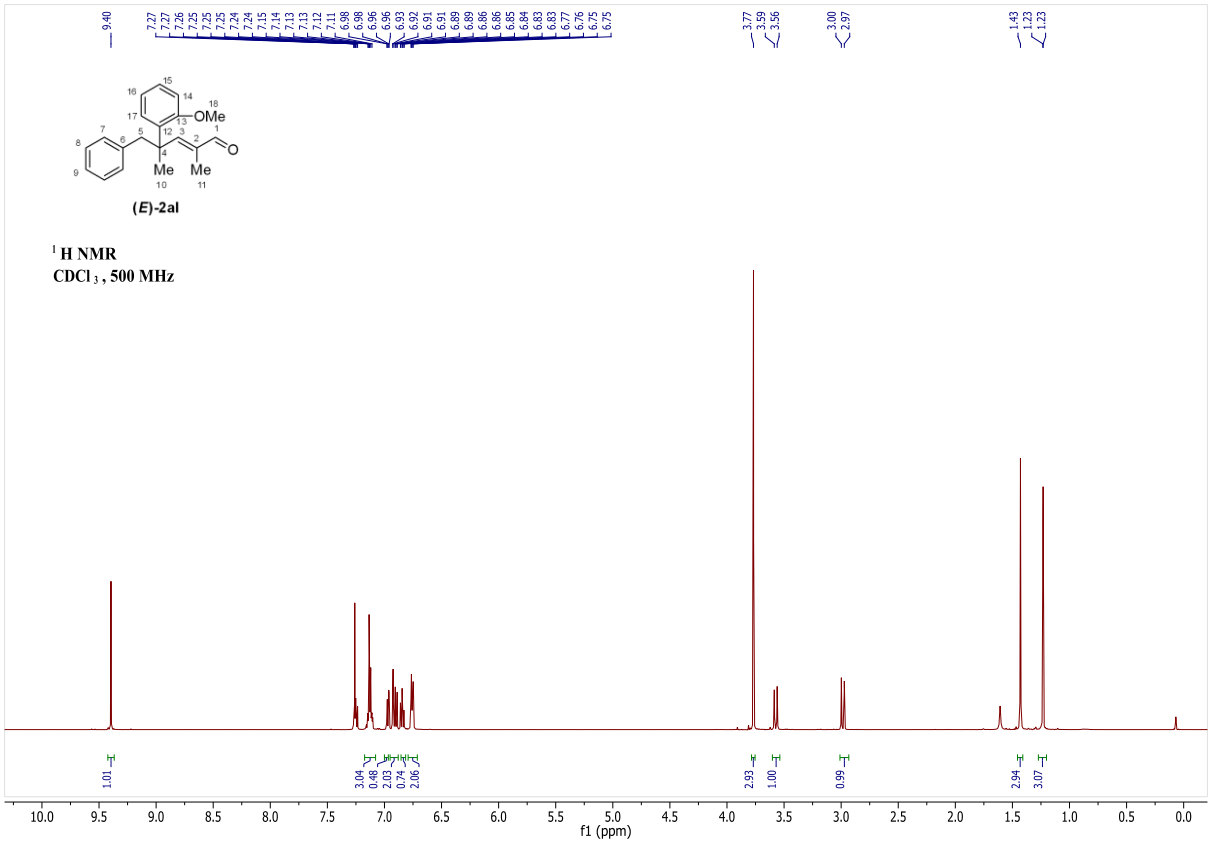

196.70
163.29
146.09
140.35
138.06
137.18
131.10
128.42
128.09
127.96
127.44
126.81
124.33
50.80
45.44
24.59
21.98
10.90
Me
Me
Me
(E)-2aj
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

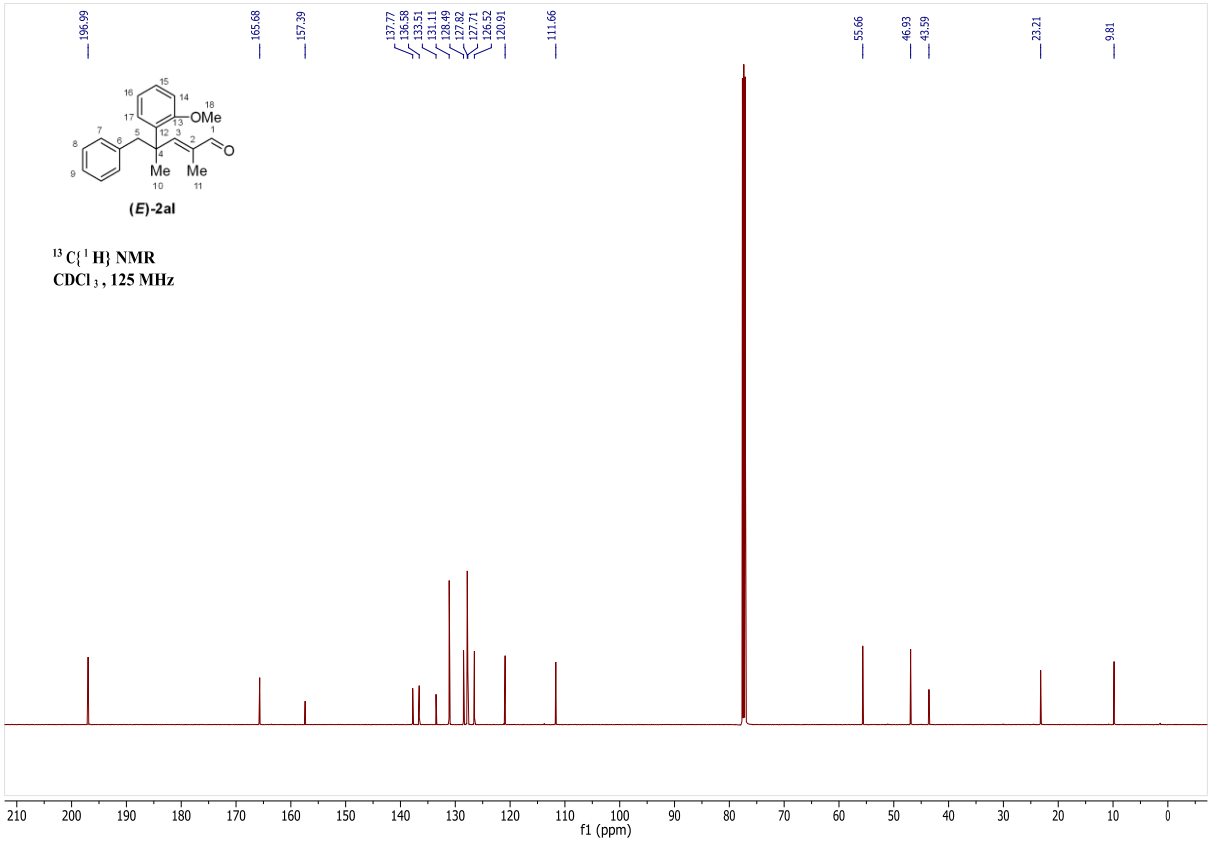


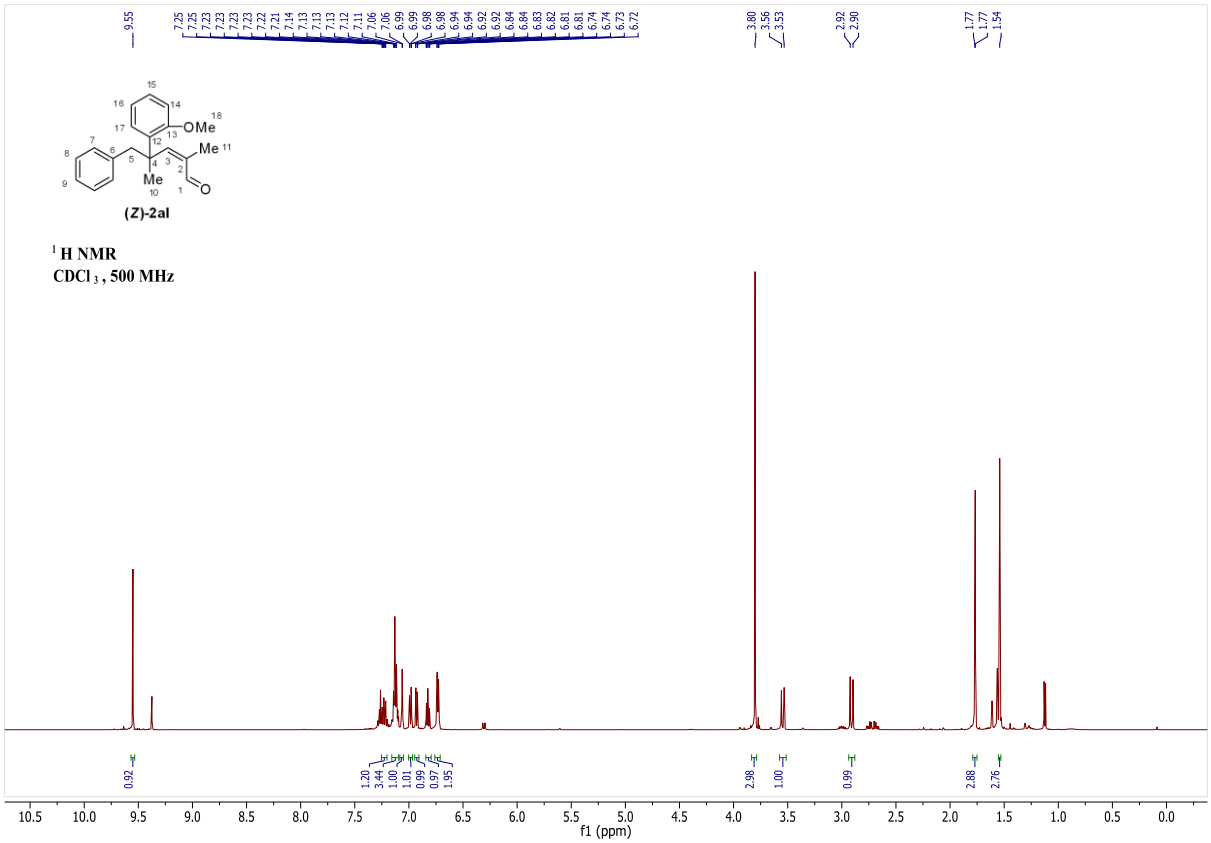


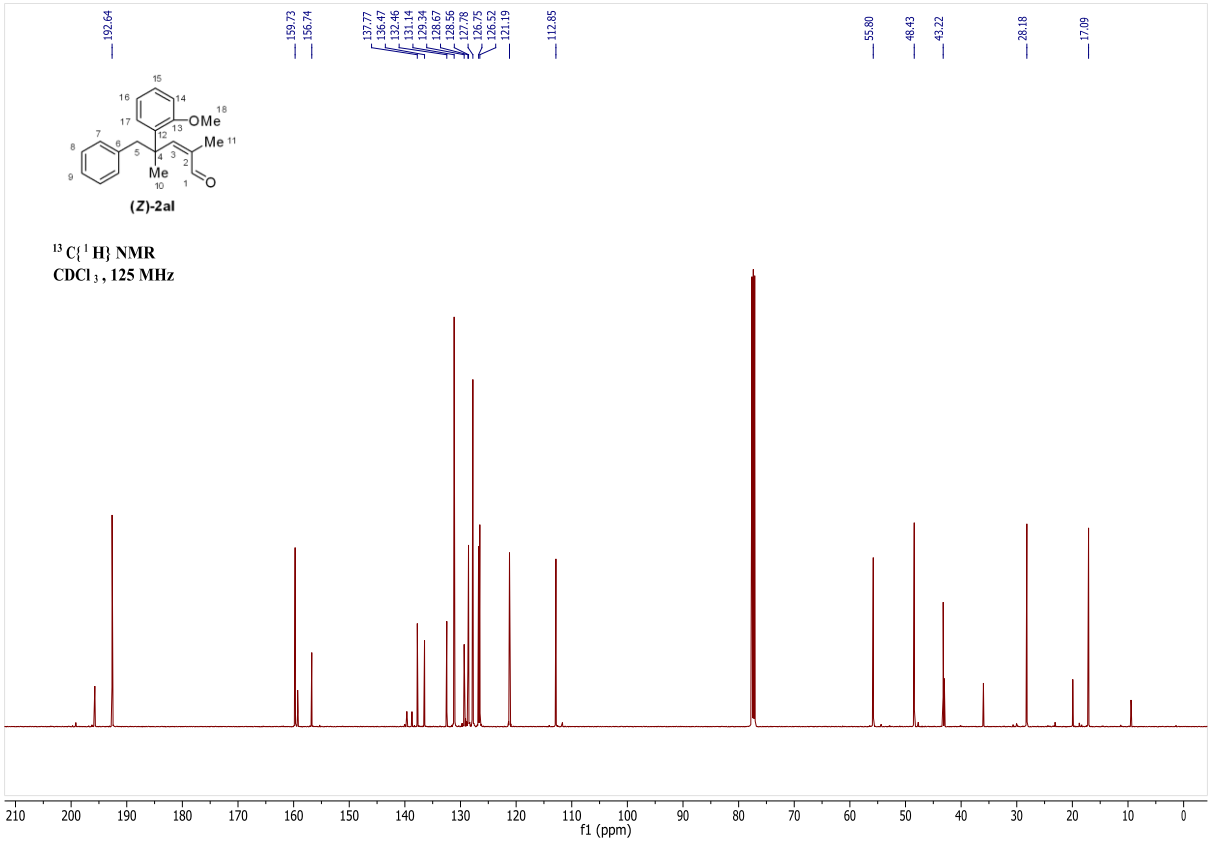

(E)-2ak
^{1}H NMR
CDCl$_3$, 500 MHz
f1 (ppm)

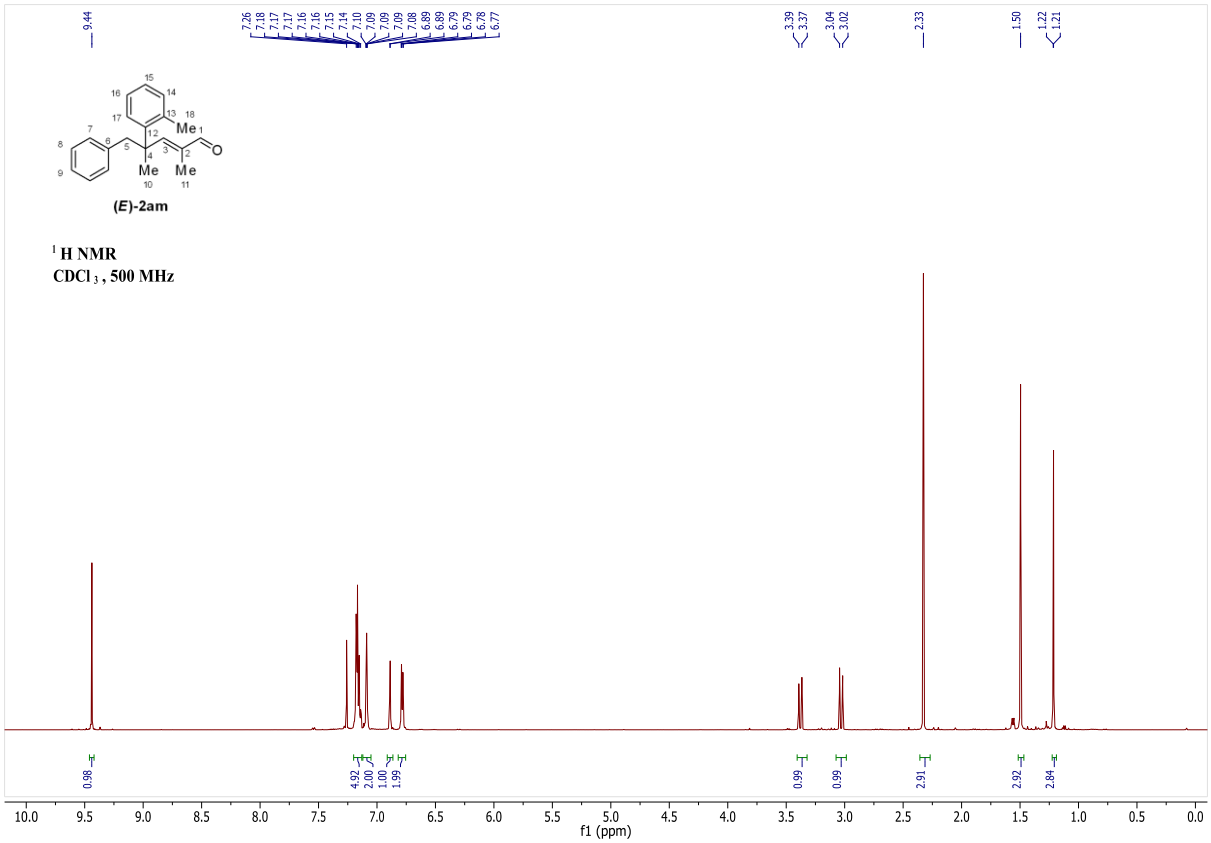

(E)-2ak
^{13}C{^{1}H} NMR
CDCl$_3$, 125 MHz
f1 (ppm)

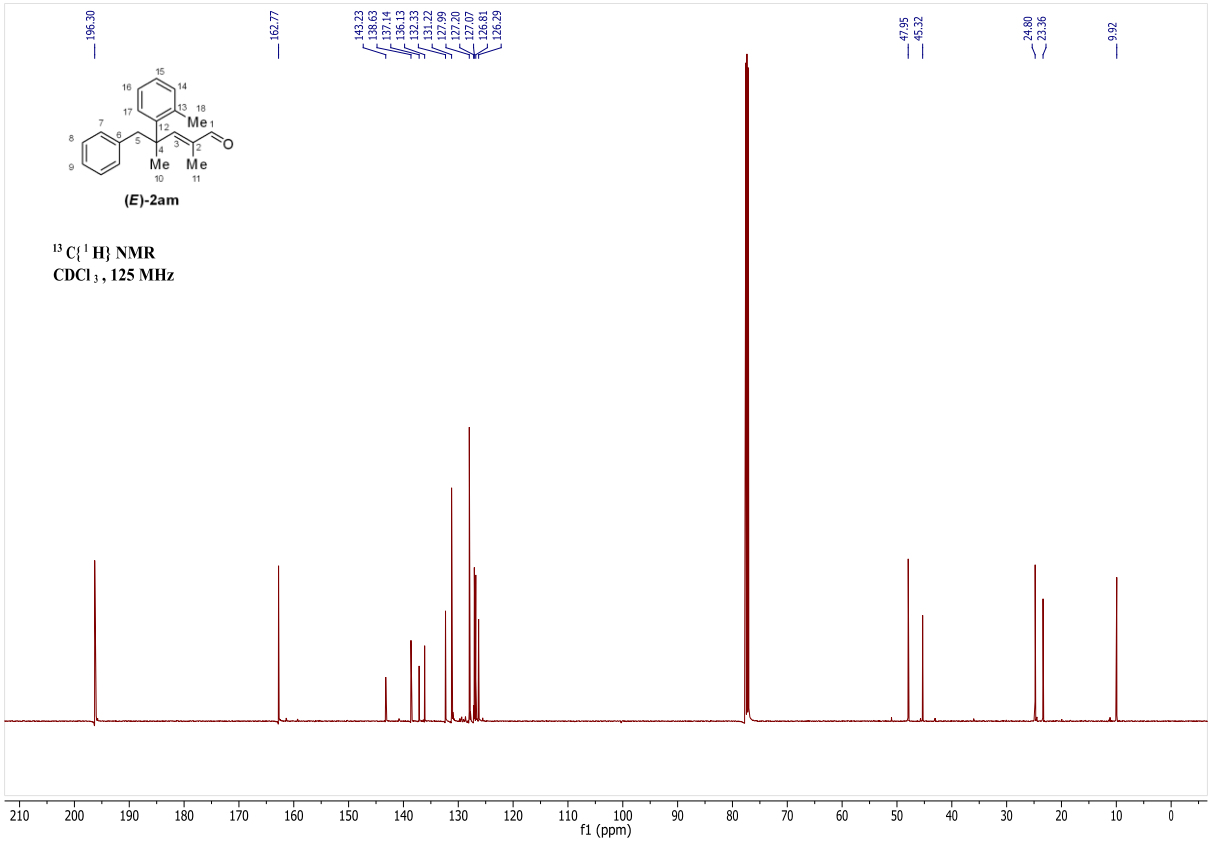

(E)-2al
1H NMR
CDCl3, 500 MHz
f1 (ppm)

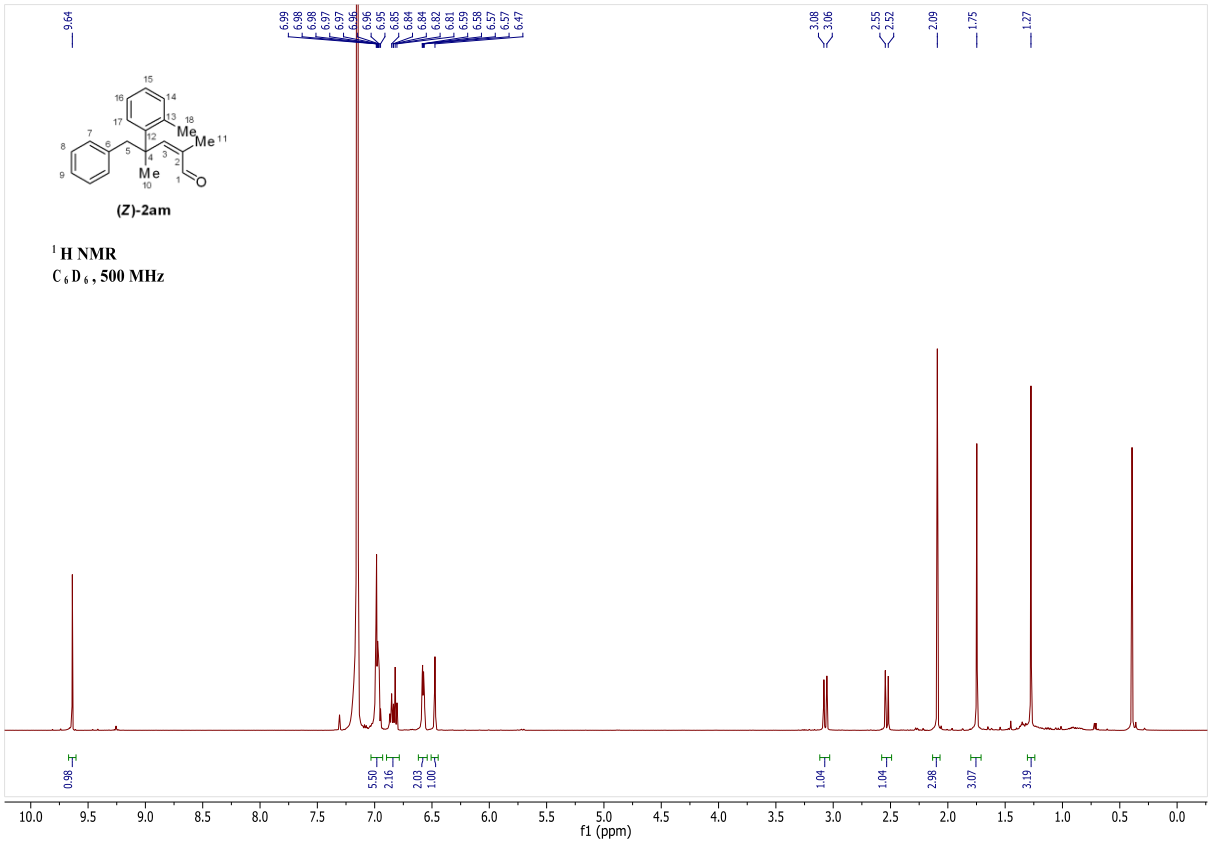

(E)-2al
13C{1H} NMR
CDCl3, 125 MHz
f1 (ppm)

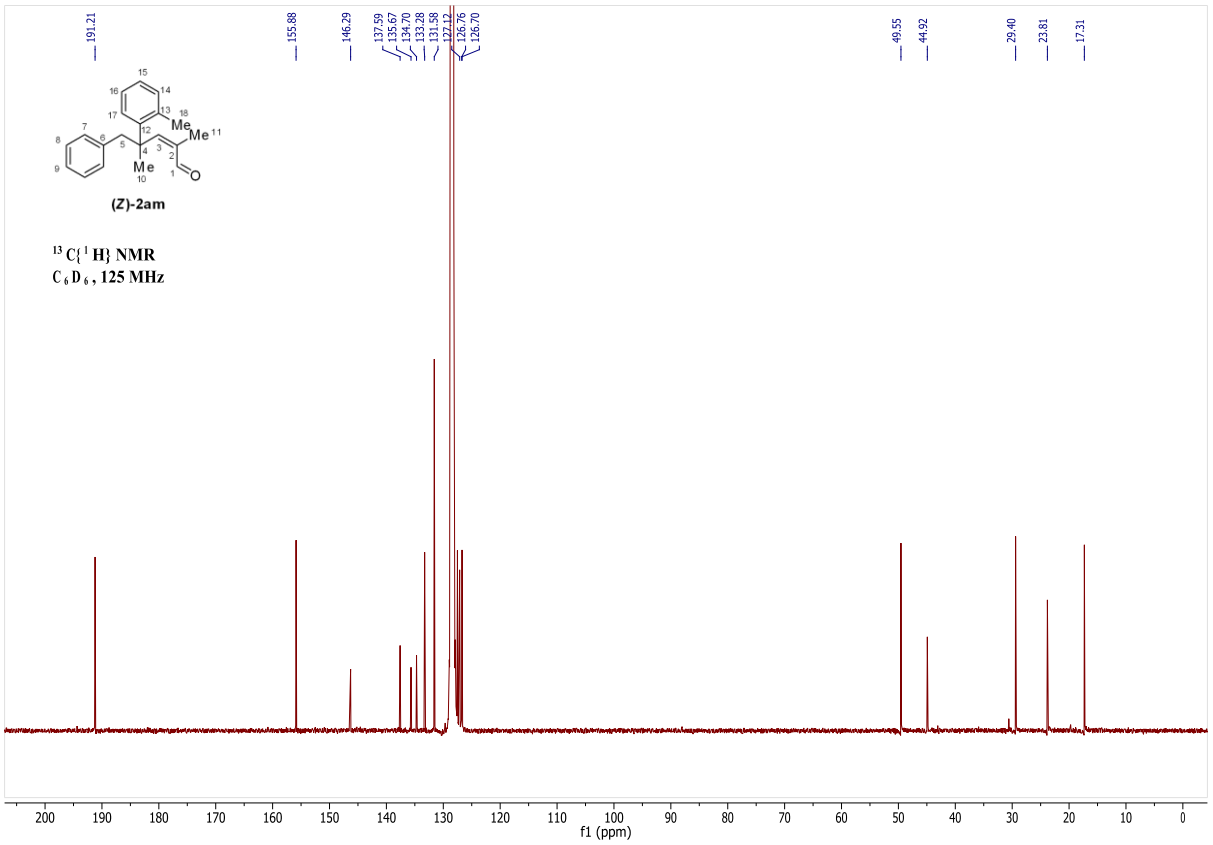

(Z)-2al
^{1}H NMR
CDCl$_3$, 500 MHz
f1 (ppm)

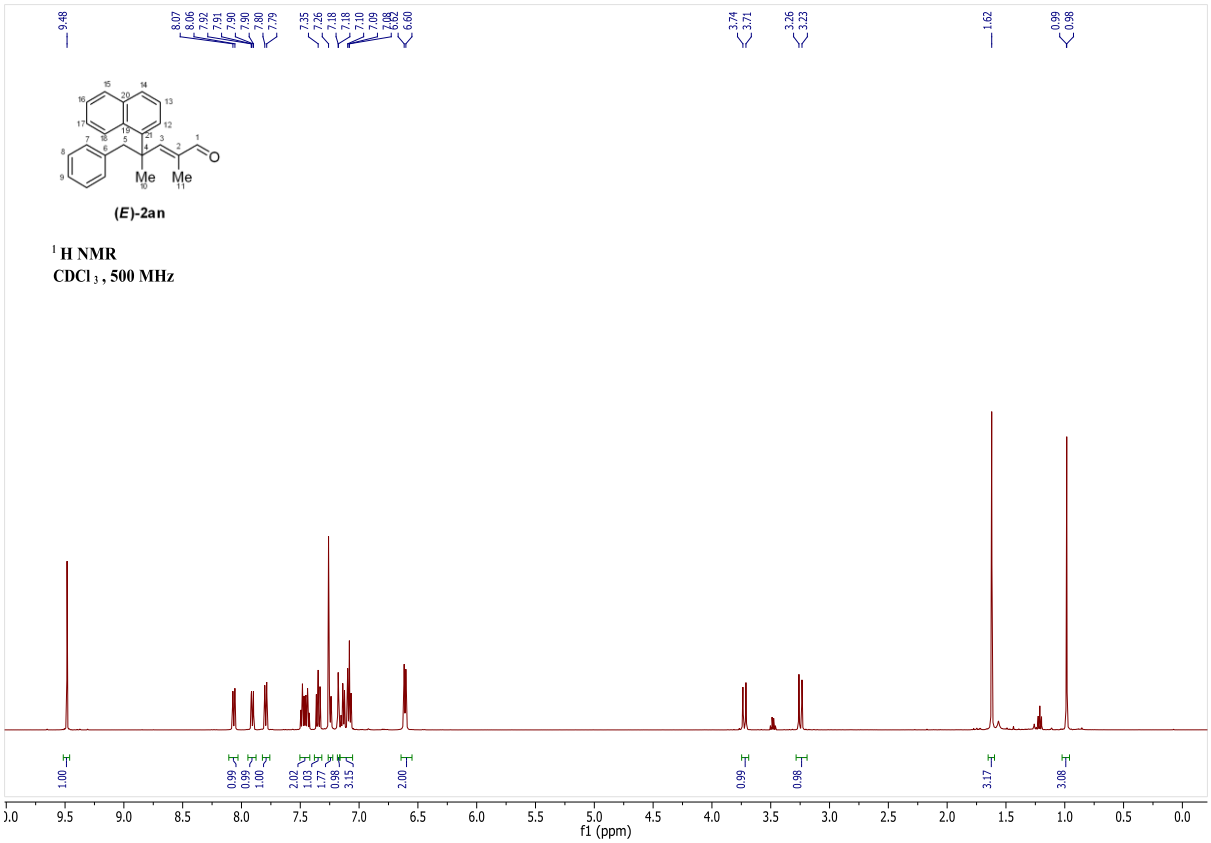

(Z)-2al
^{13}C{^{1}H} NMR
CDCl$_3$, 125 MHz
f1 (ppm)

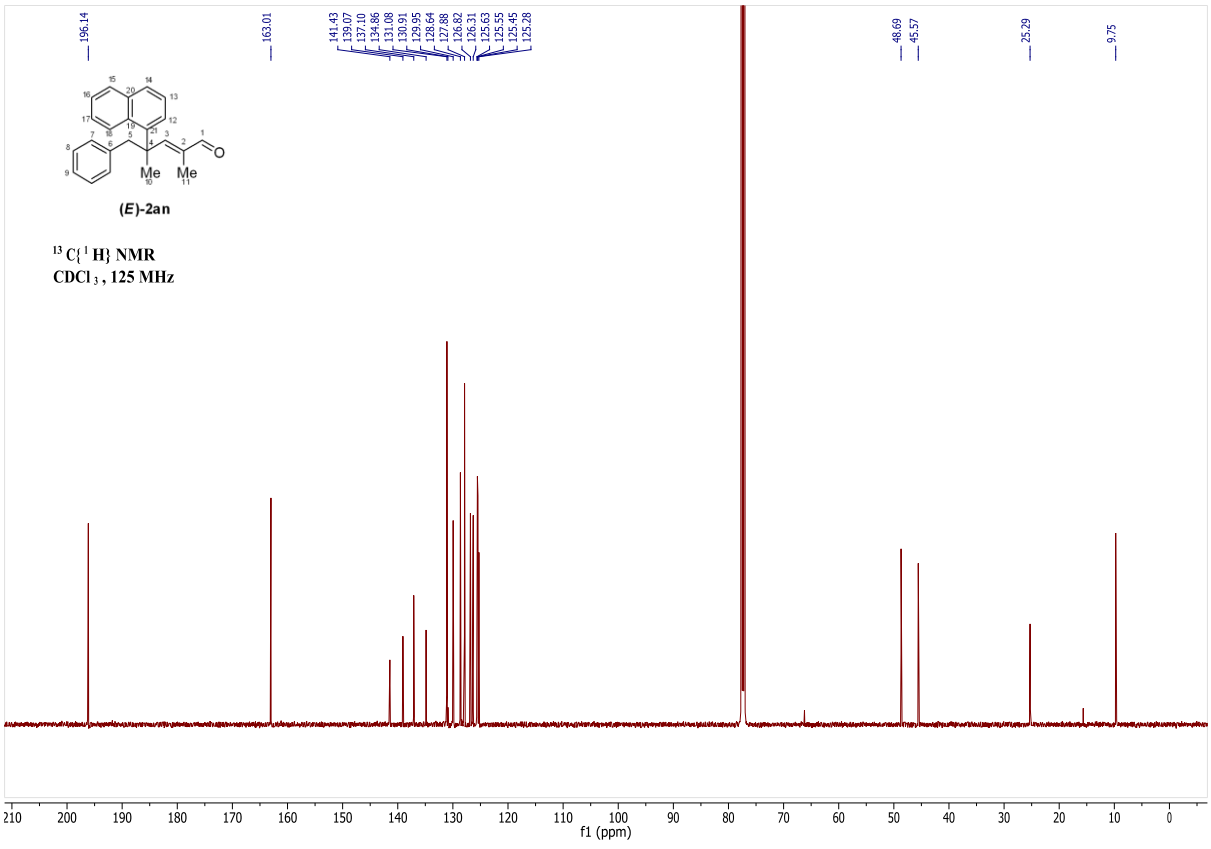

9.44
7.26
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.10
7.09
7.09
7.09
7.08
6.89
6.89
6.79
6.79
6.78
6.77
3.39
3.37
3.04
3.02
2.33
1.50
1.22
1.21
(E)-2am
1 H NMR
CDCl 3 , 500 MHz
0.98
4.92
2.00
1.00
1.99
0.99
0.99
2.91
2.92
2.84
f1 (ppm)

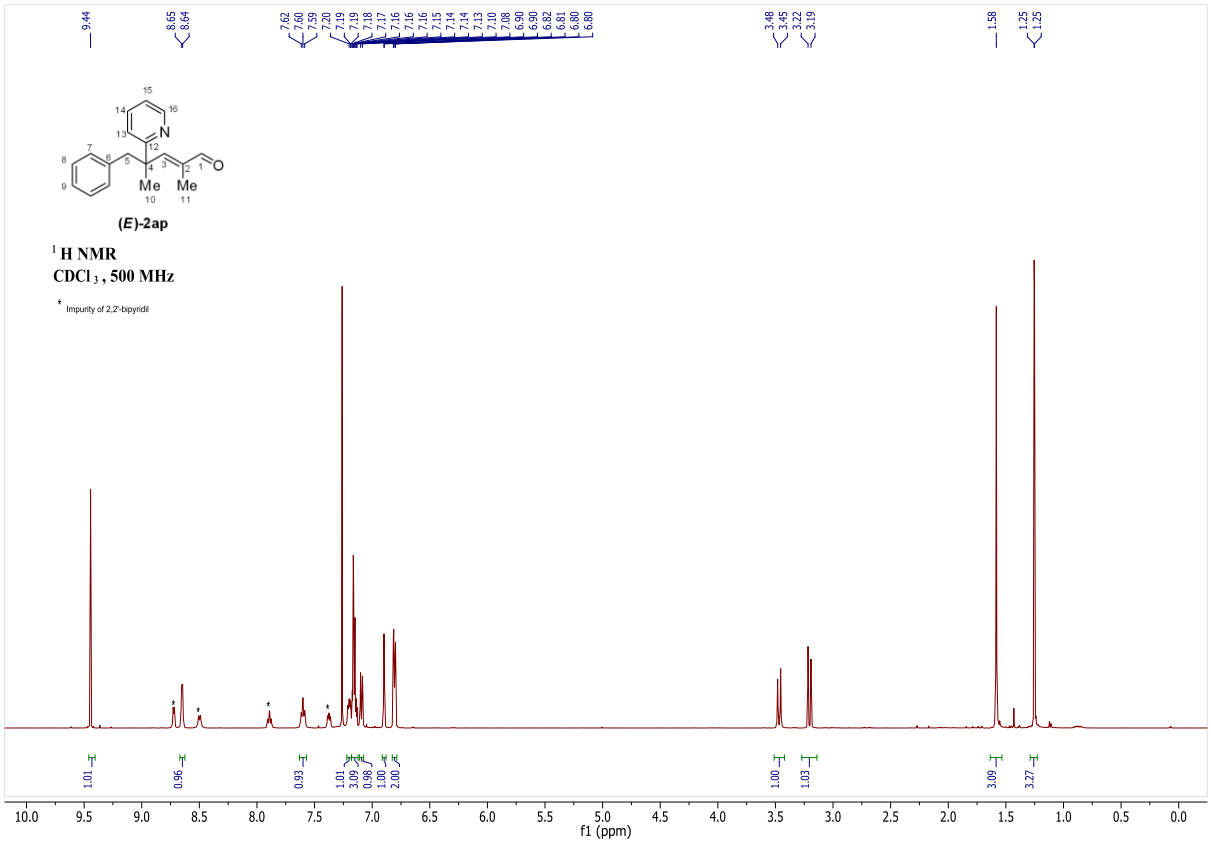

196.30
162.77
143.23
138.63
137.14
136.13
132.33
131.22
127.99
127.20
127.07
126.81
126.29
47.95
45.32
24.80
23.36
9.92
(E)-2am
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

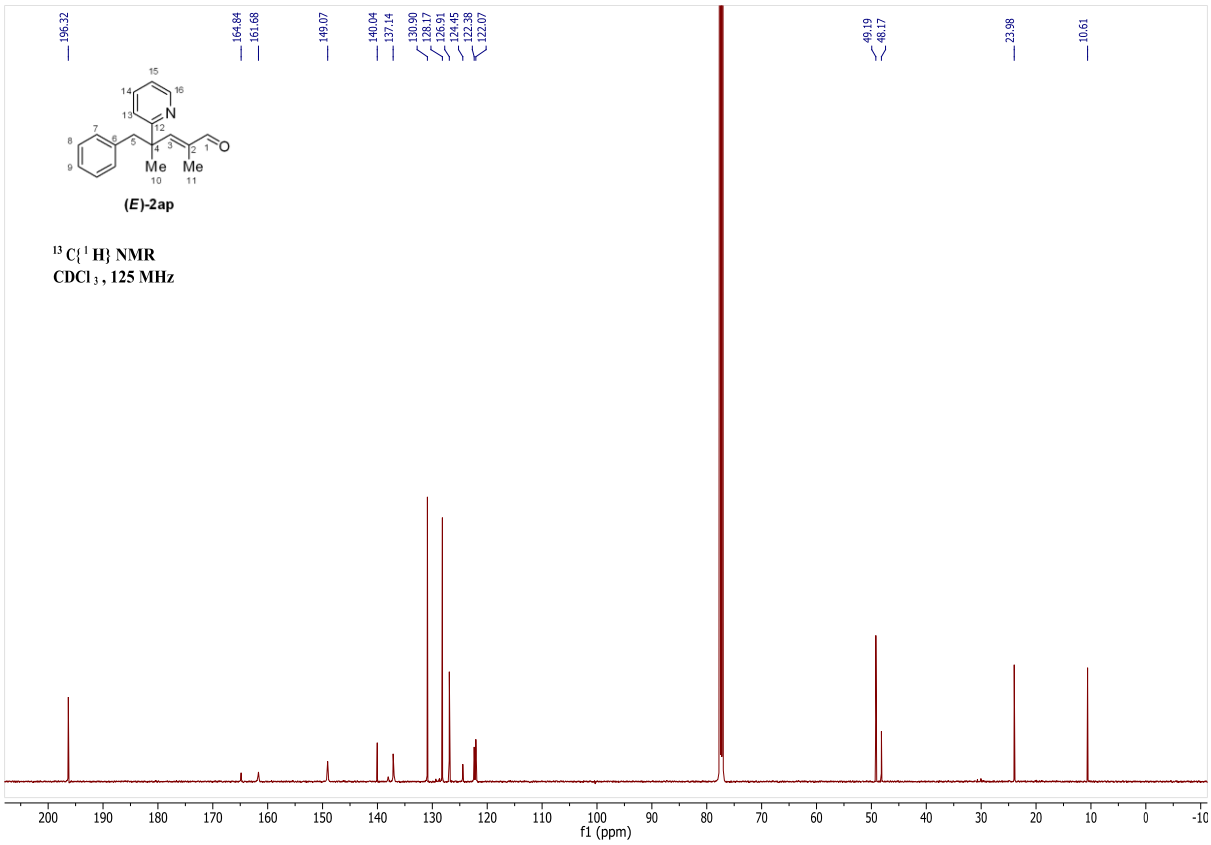


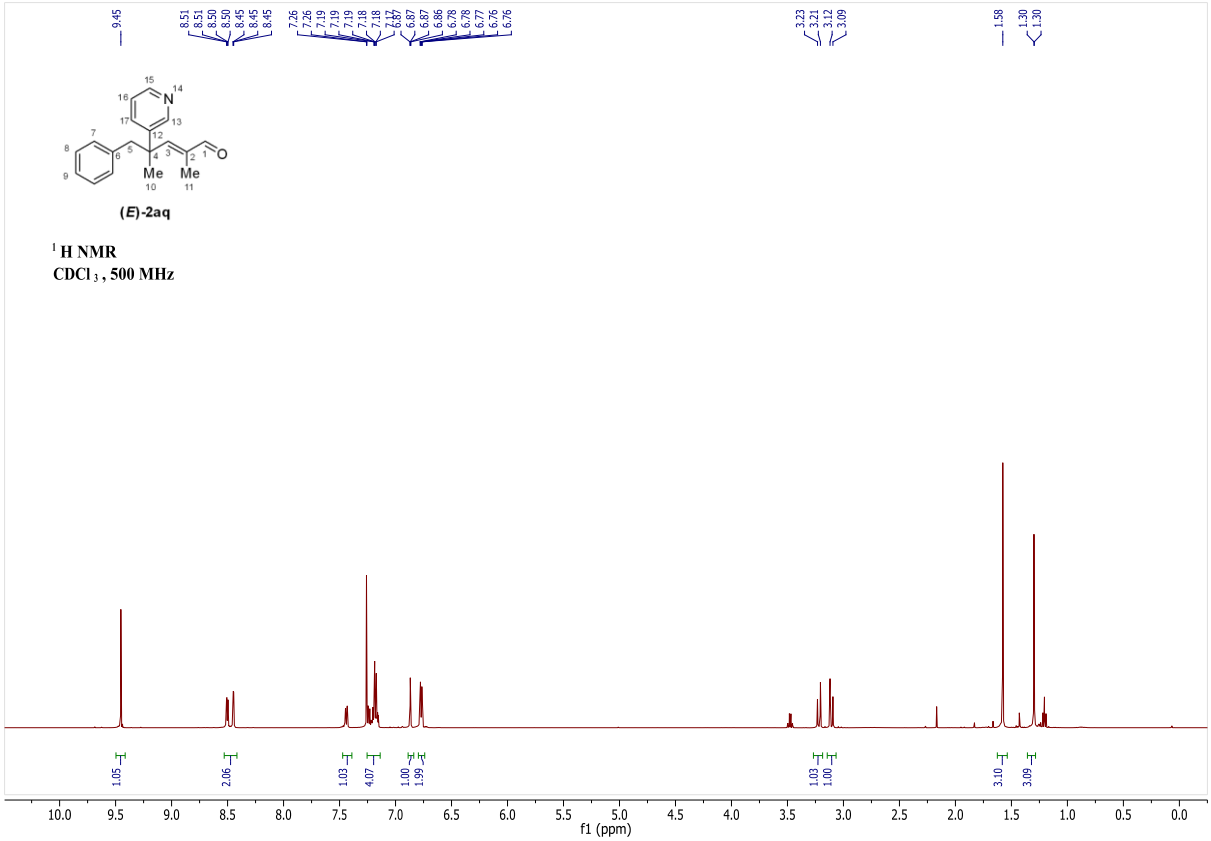


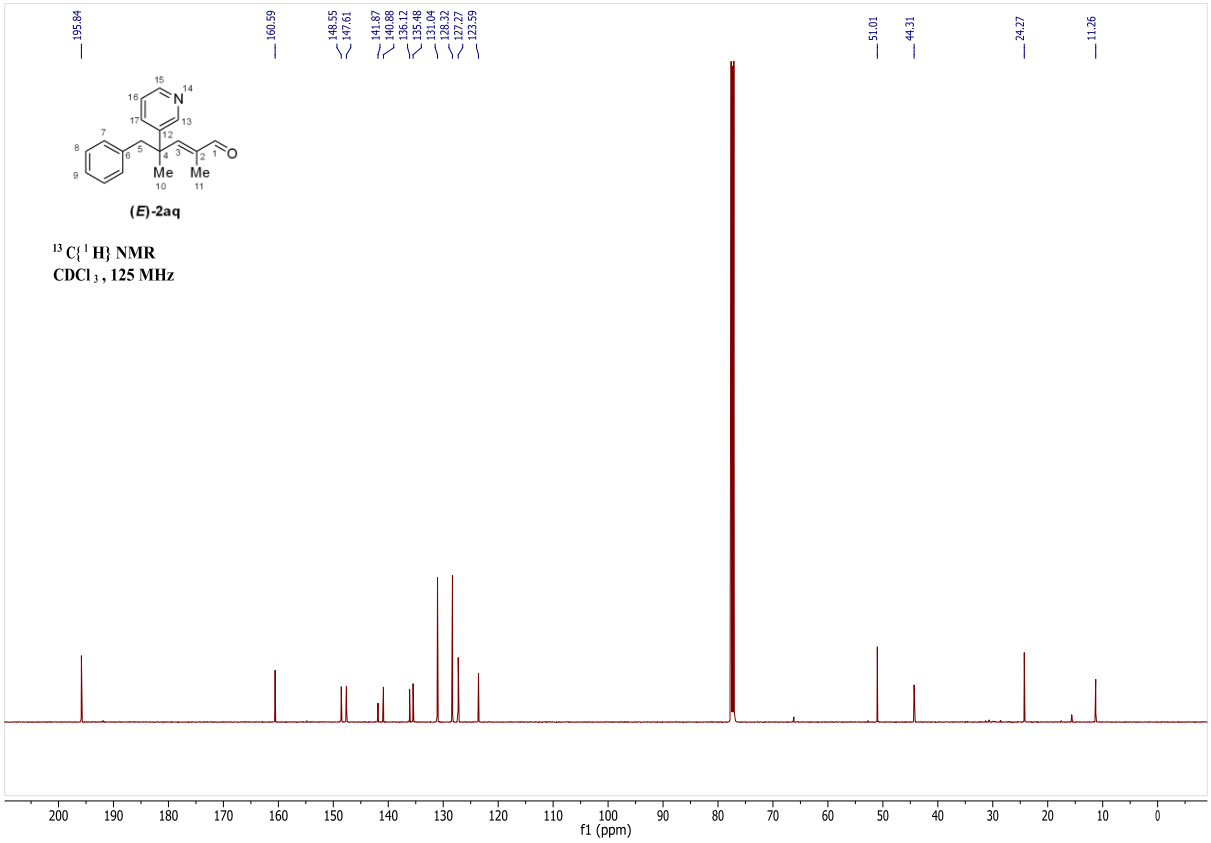

9.48
8.07
8.06
7.92
7.91
7.90
7.80
7.79
7.35
7.26
7.18
7.10
7.09
6.62
6.60
3.74
3.71
3.26
3.23
1.62
0.99
0.98
Me
Me
(E)-2an
1H NMR
CDCl3, 500 MHz
1.00
0.99
0.99
1.00
2.02
1.03
1.77
0.98
3.15
2.00
0.99
0.98
3.17
3.08
f1 (ppm)

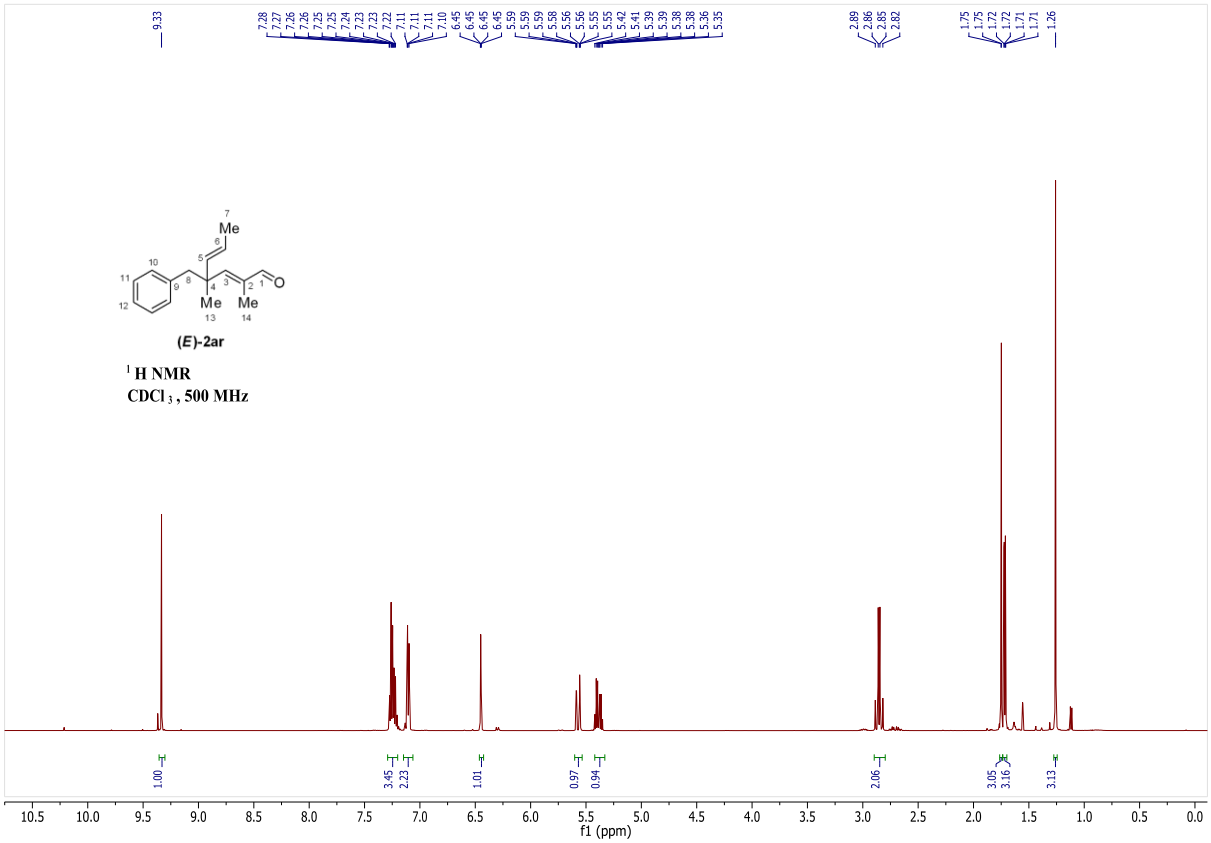

196.14
163.01
141.43
139.07
137.10
134.86
131.08
130.91
129.95
128.64
127.88
126.82
126.31
125.63
125.55
125.45
125.28
48.69
45.57
25.29
9.75
Me
Me
(E)-2an
13C{1H} NMR
CDCl3, 125 MHz
f1 (ppm)

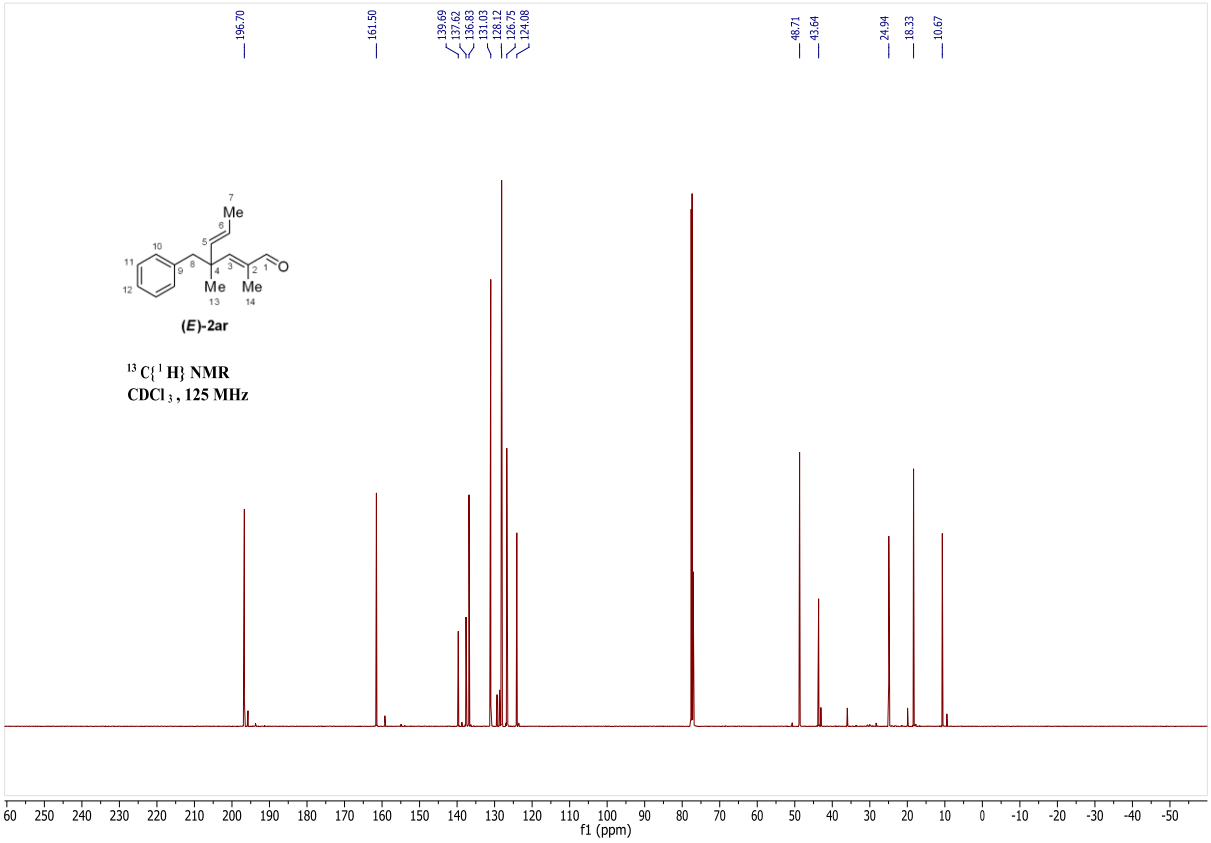

9.44
8.65
8.64
7.62
7.60
7.59
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.16
7.15
7.14
7.14
7.13
7.10
7.08
6.90
6.90
6.82
6.81
6.80
6.80
3.48
3.45
3.22
3.19
1.58
1.25
1.25
(E)-2ap
1 H NMR
CDCl 3 , 500 MHz
* Impurity of 2,2'-bipyridil
1.01
0.96
0.93
1.01
3.09
0.98
1.00
2.00
1.00
1.03
3.09
3.27
f1 (ppm)

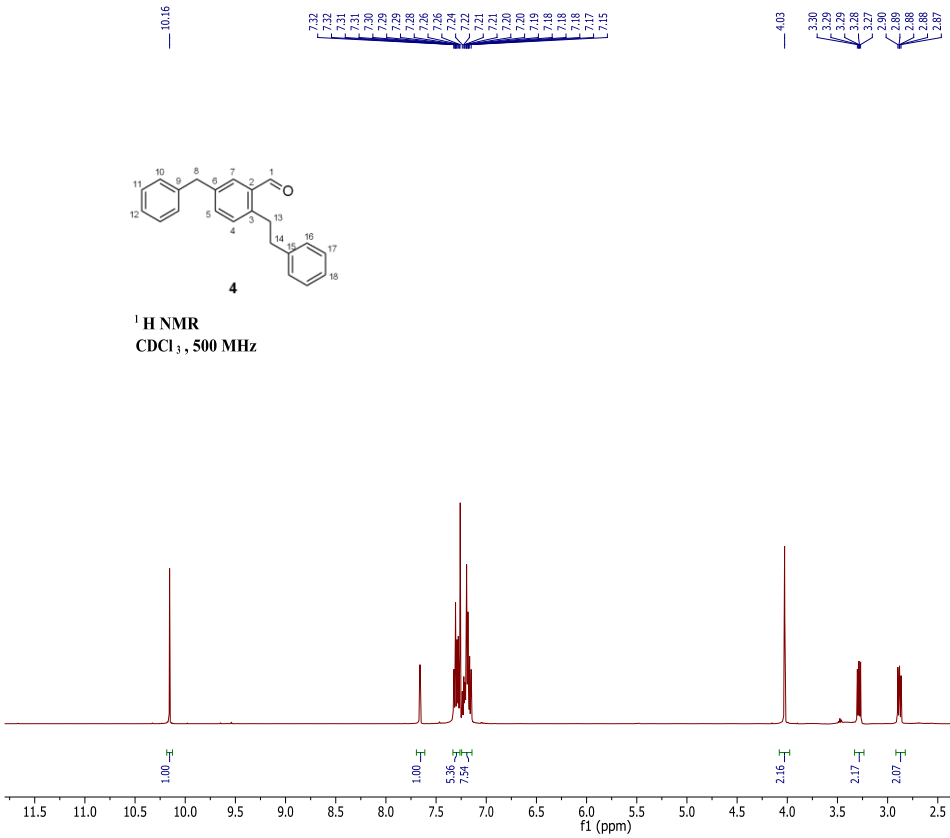

196.32
164.84
161.68
149.07
140.04
137.14
130.90
128.17
126.91
124.45
122.38
122.07
49.19
48.17
23.98
10.61
(E)-2ap
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)


9.45
8.51
8.51
8.50
8.50
8.45
8.45
8.45
7.26
7.26
7.19
7.19
7.19
7.18
7.18
6.87
6.87
6.87
6.86
6.78
6.78
6.77
6.76
6.76
3.23
3.21
3.12
3.09
1.58
1.30
1.30
(E)-2aq
1 H NMR
CDCl 3 , 500 MHz
1.05
2.06
1.03
4.07
1.00
1.99
1.03
1.00
3.10
3.09
f1 (ppm)


195.84
160.59
148.55
147.61
141.87
140.88
136.12
135.48
131.04
128.32
127.27
123.59
51.01
44.31
24.27
11.26
(E)-2aq
13 C{1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

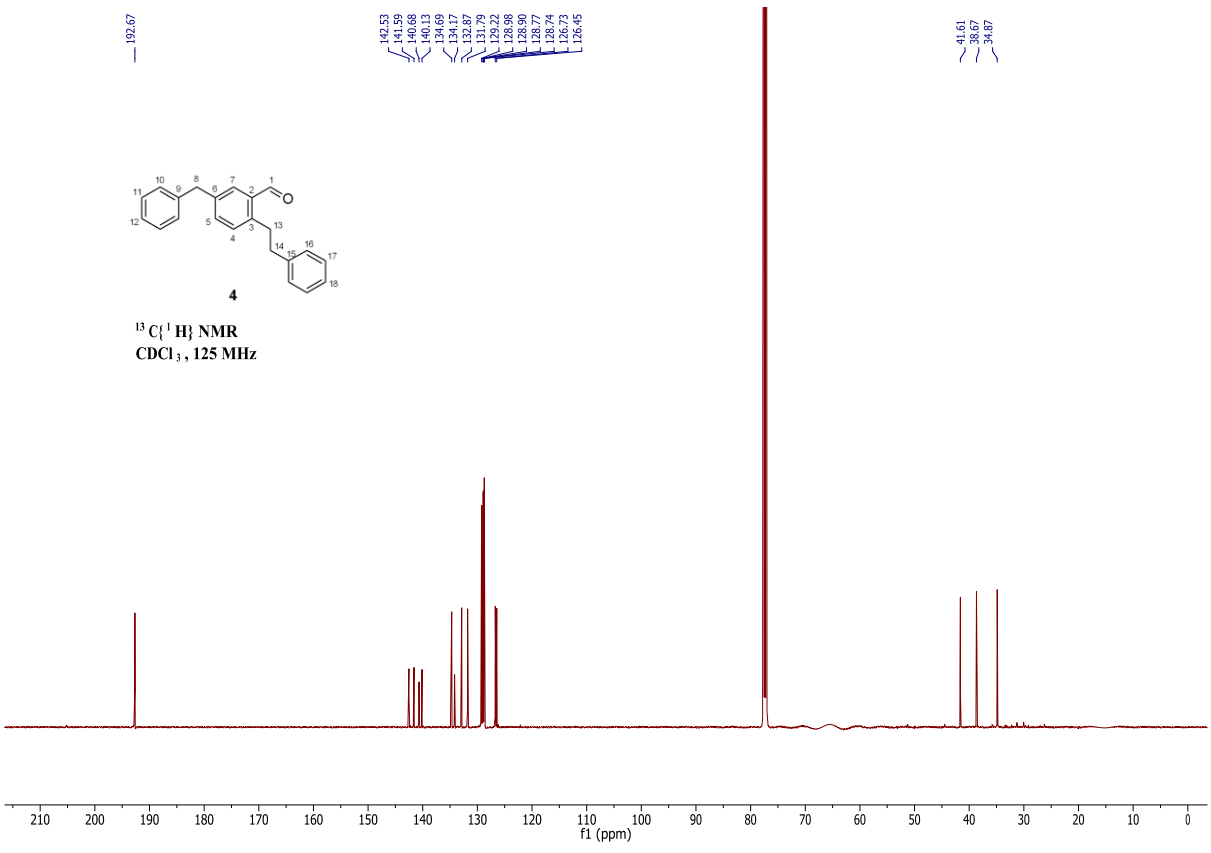

(E)-2ar
1H NMR
CDCl3, 500 MHz
f1 (ppm)


(E)-2ar
13C{1H} NMR
CDCl3, 125 MHz
f1 (ppm)



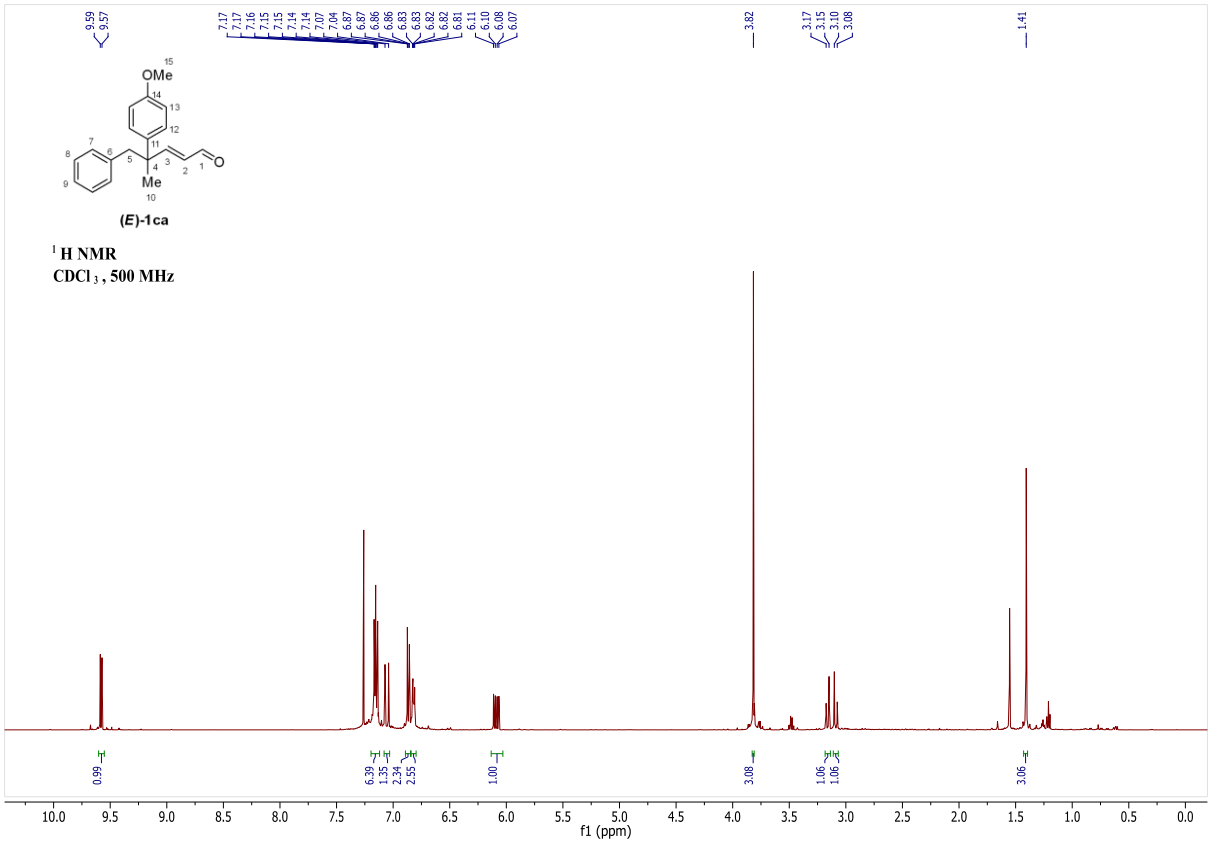
4

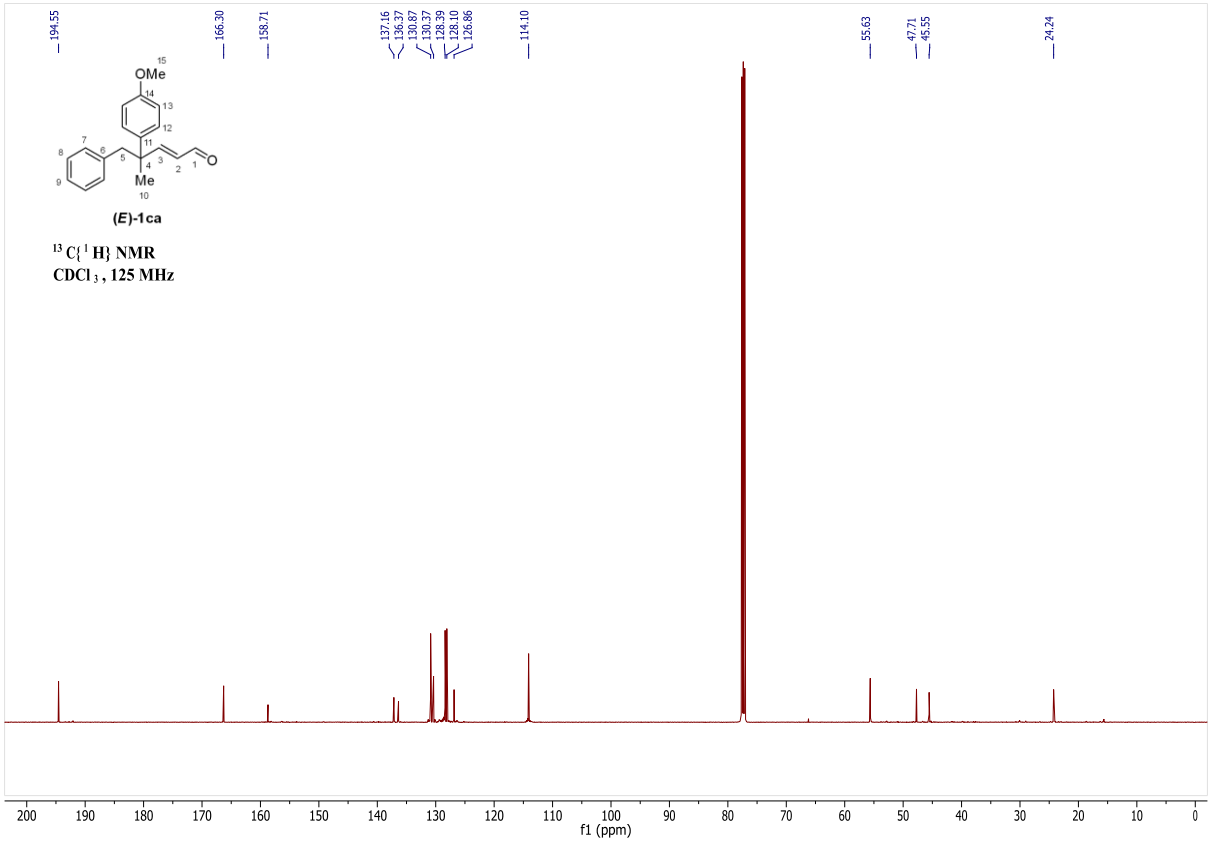
^{1}H NMR
$CDCl_3$, 500 MHz

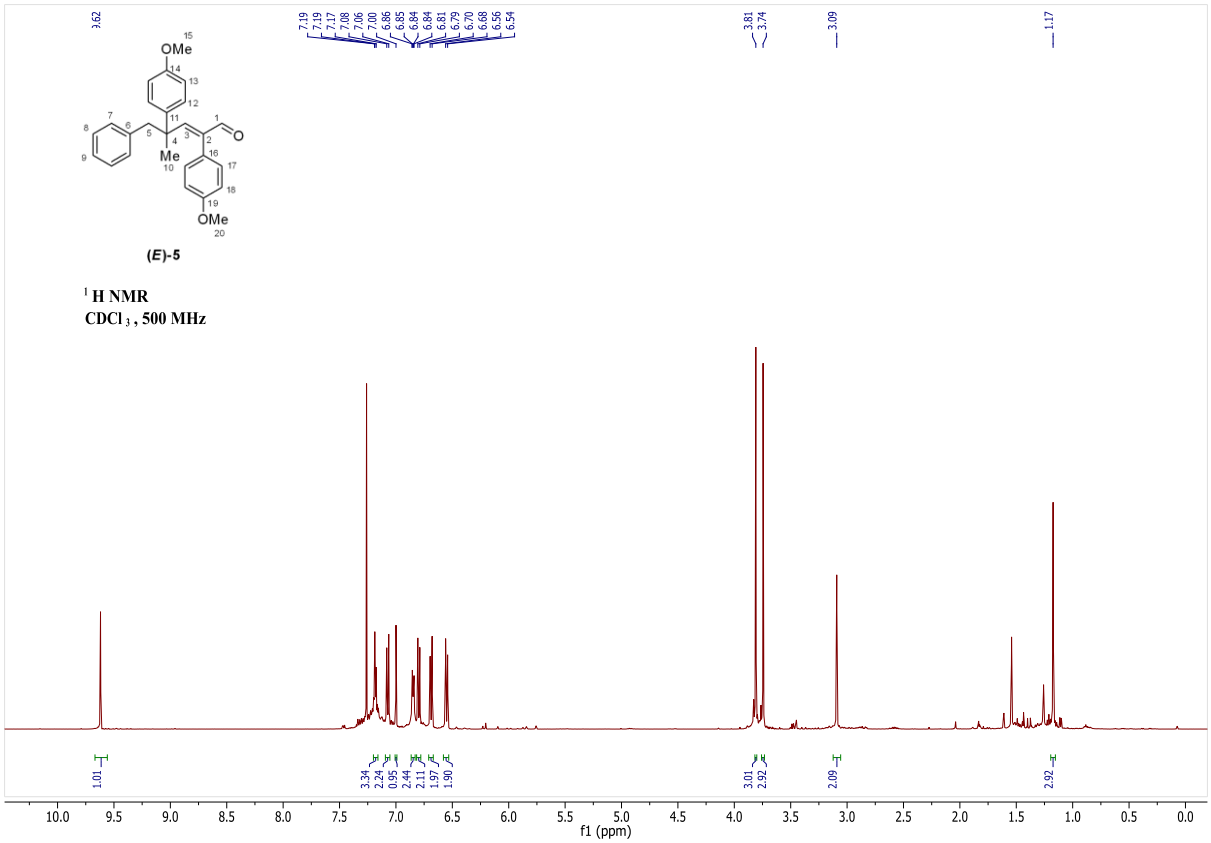


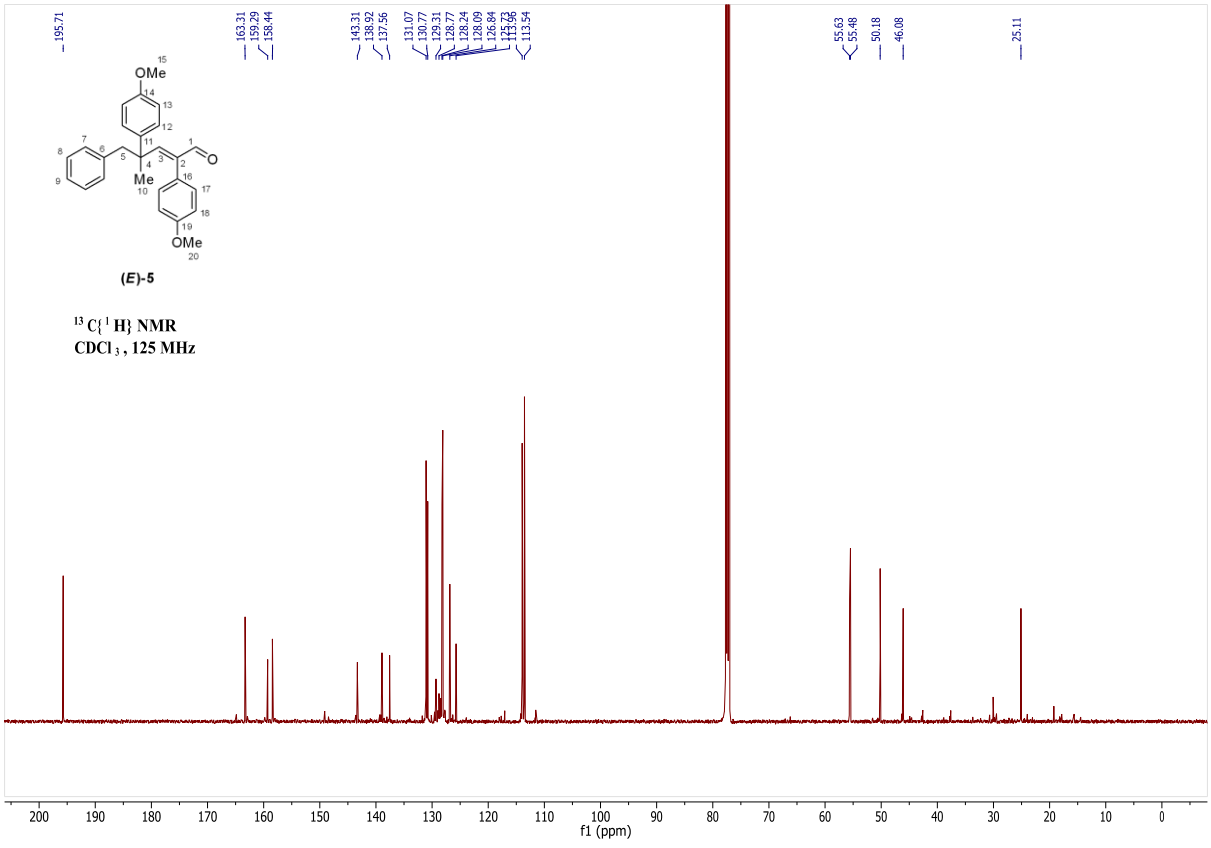
4

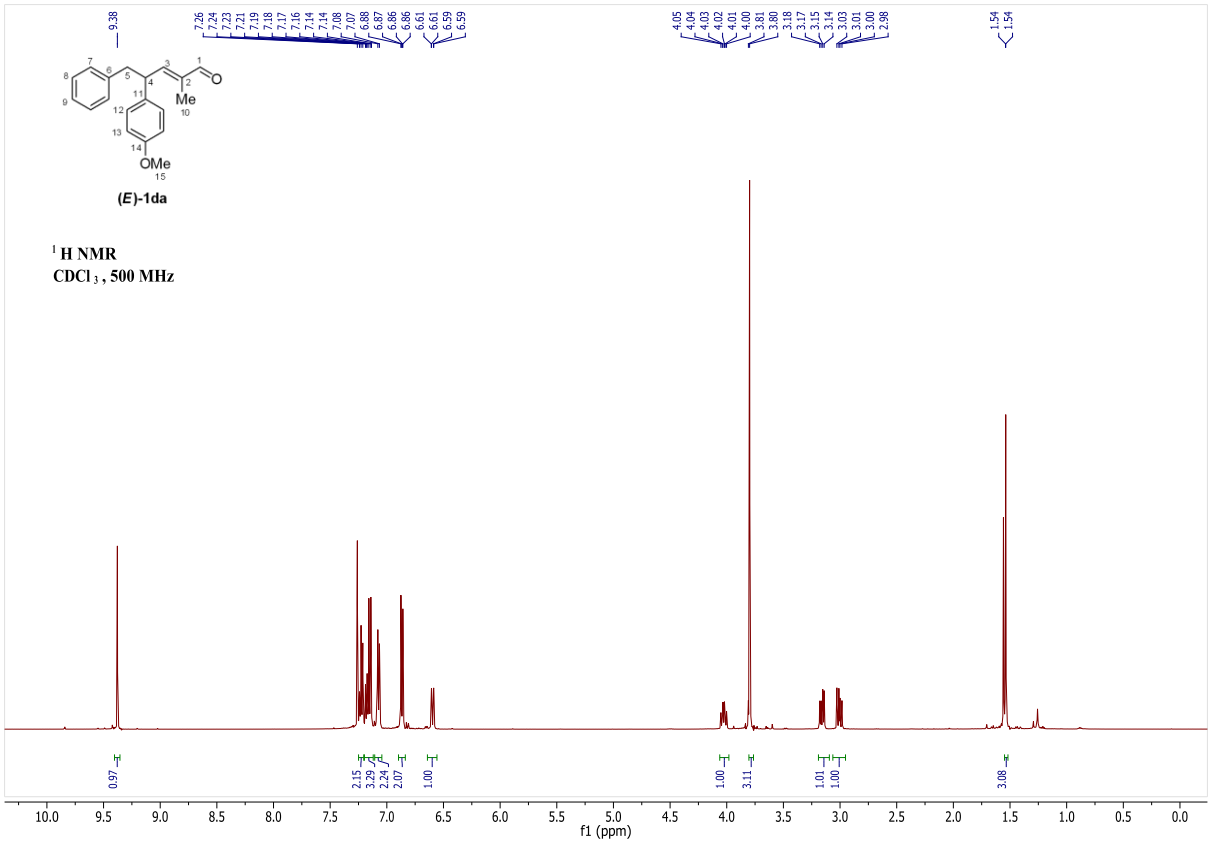
$^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 125 MHz

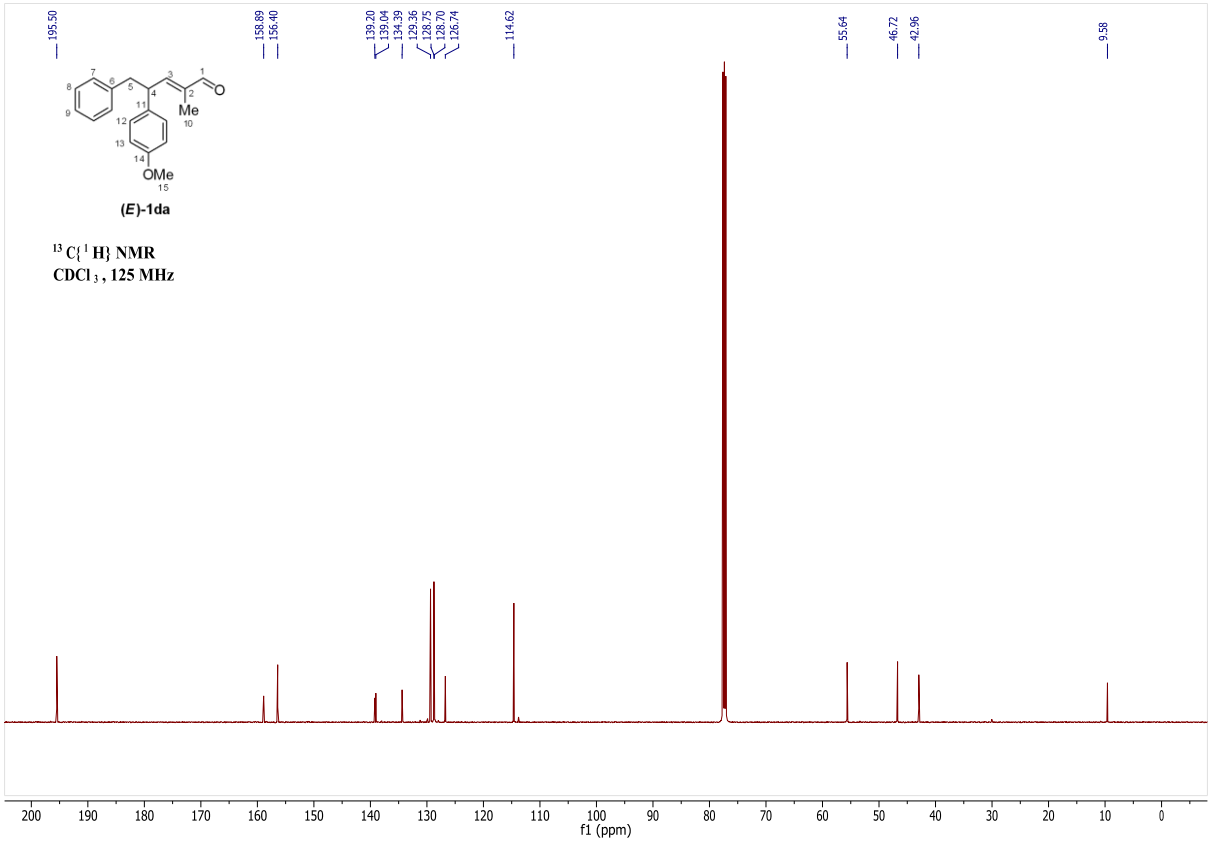

9.59
9.57
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.07
7.04
6.87
6.87
6.86
6.86
6.83
6.83
6.82
6.82
6.81
6.11
6.10
6.08
6.07
3.82
3.17
3.15
3.10
3.08
1.41
OMe
Me
(E)-1ca
1 H NMR
CDCl 3 , 500 MHz
0.99
6.39
1.35
2.34
2.55
1.00
3.08
1.06
1.06
3.06
f1 (ppm)

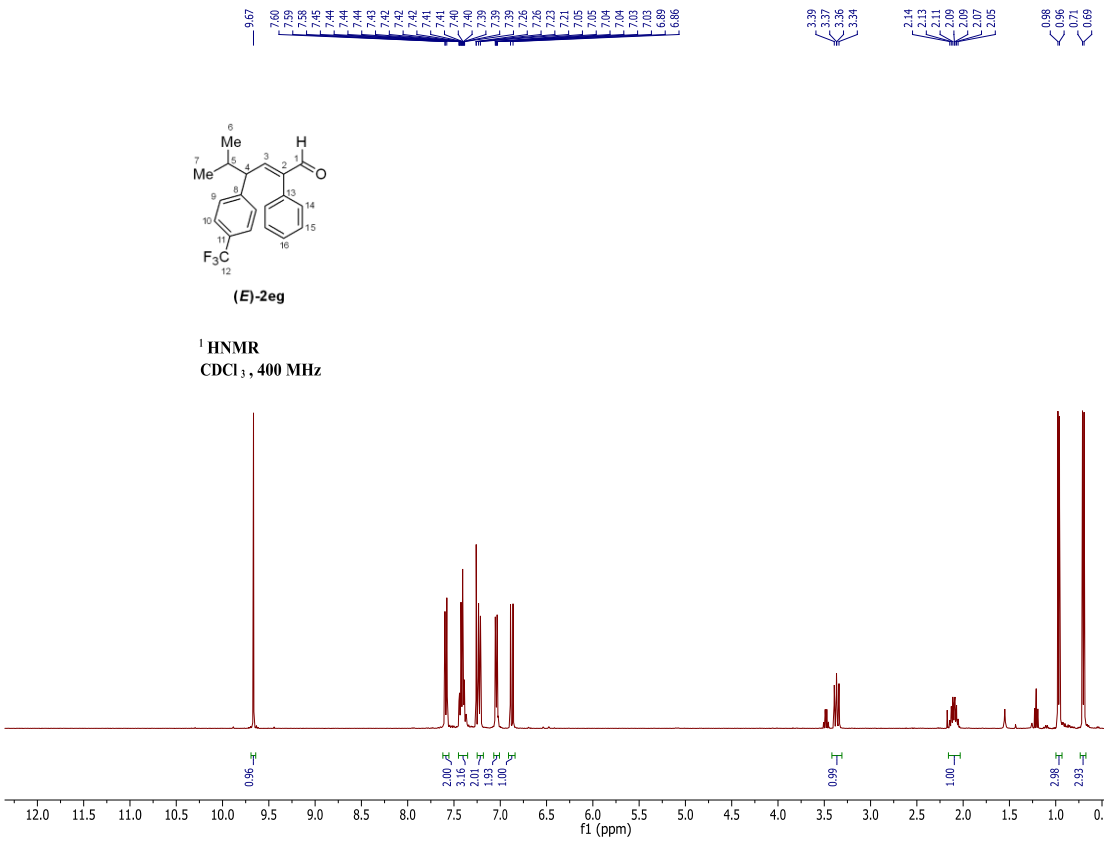

194.55
166.30
158.71
137.16
136.37
130.87
130.37
128.39
128.10
126.86
114.10
55.63
47.71
45.55
24.24
OMe
Me
(E)-1ca
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

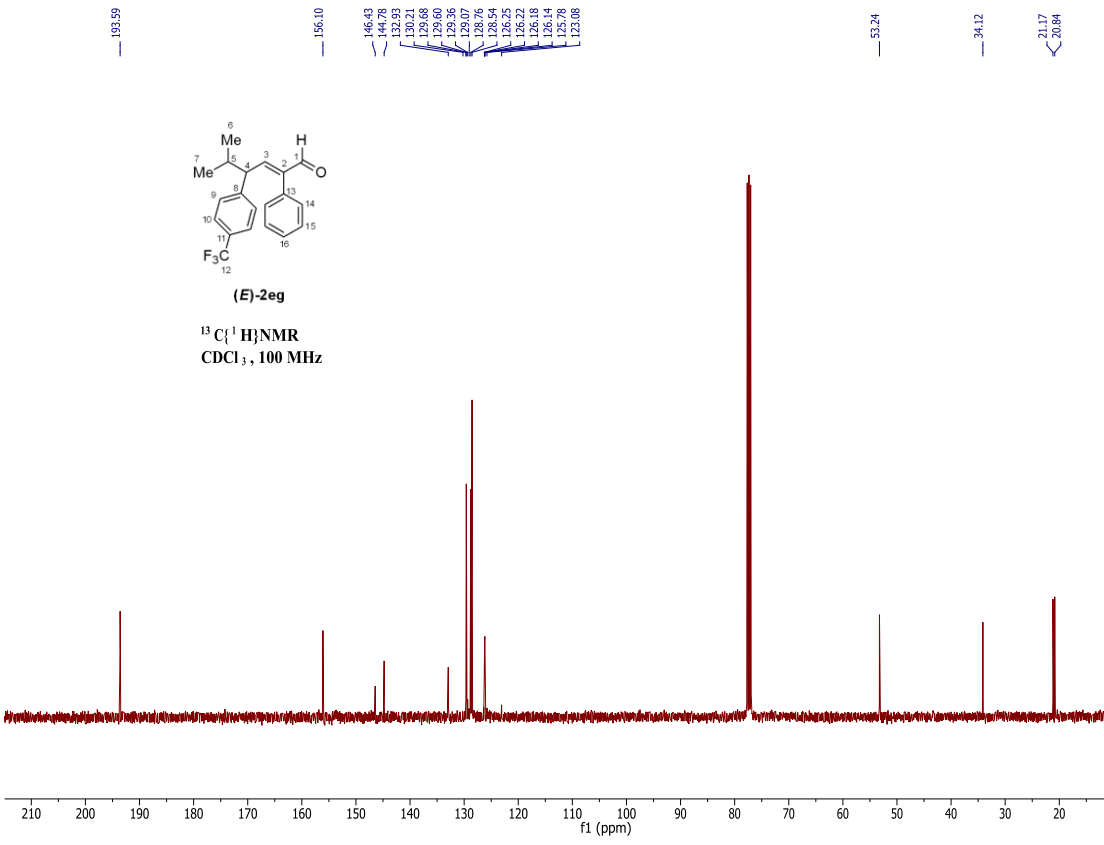

(E)-5
^{1}H NMR
CDCl$_3$, 500 MHz
f1 (ppm)

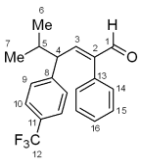

(E)-5
^{13}C{^{1}H} NMR
CDCl$_3$, 125 MHz
f1 (ppm)


9.38
7.26
7.24
7.23
7.21
7.19
7.18
7.17
7.16
7.14
7.14
7.08
7.07
6.88
6.87
6.86
6.86
6.61
6.61
6.59
6.59
4.05
4.04
4.03
4.02
4.01
4.00
3.81
3.80
3.18
3.17
3.15
3.14
3.03
3.01
3.00
2.98
1.54
1.54
Me
OMe
(E)-1da
1 H NMR
CDCl 3 , 500 MHz
0.97
2.15
3.29
2.24
2.07
1.00
1.00
3.11
1.01
1.00
3.08
f1 (ppm)


195.50
158.89
156.40
139.20
139.04
134.39
129.36
128.75
128.70
126.74
114.62
55.64
46.72
42.96
9.58
Me
OMe
(E)-1da
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

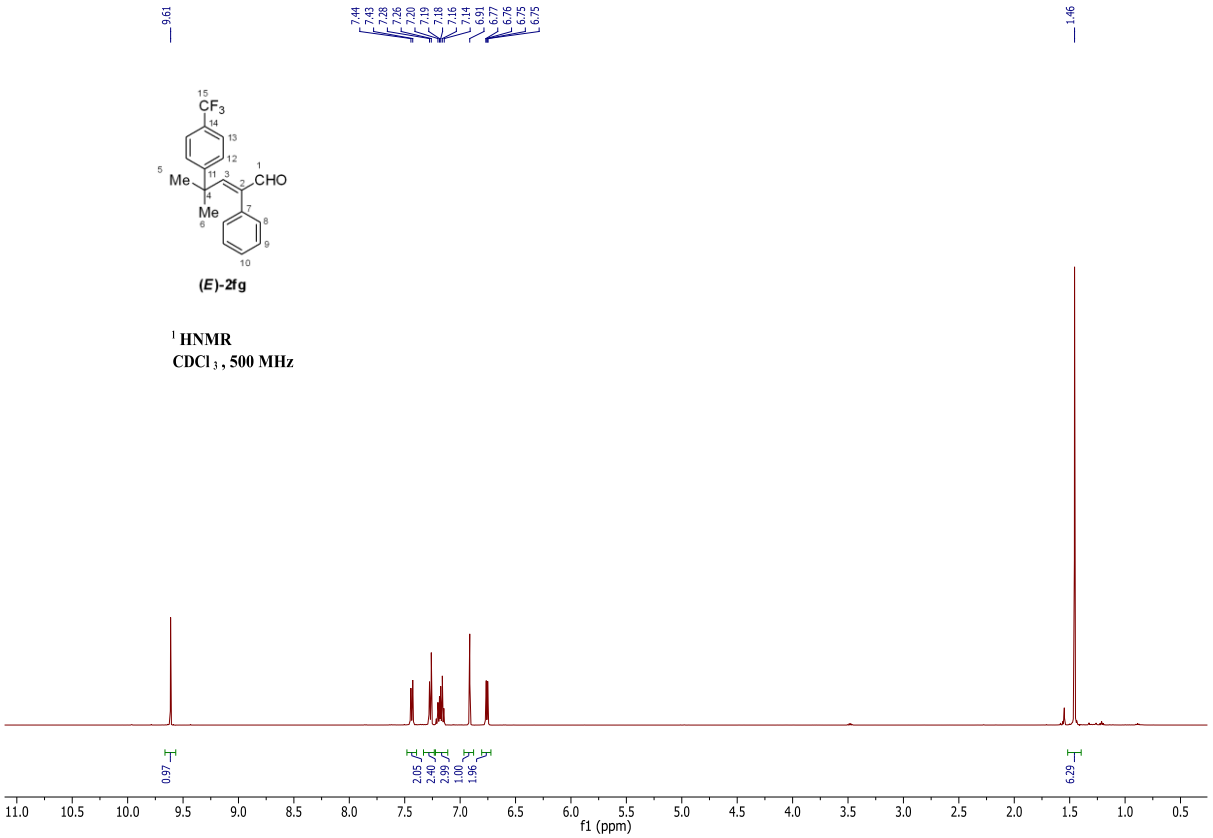

9.67
7.60
7.59
7.58
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.26
7.26
7.23
7.21
7.05
7.05
7.04
7.04
7.03
7.03
6.89
6.86
3.39
3.37
3.36
3.34
2.14
2.13
2.11
2.09
2.09
2.09
2.07
2.05
0.98
0.96
0.71
0.69
Me
H
O
Me
F3C
(E)-2eg
1HNMR
CDCl3, 400 MHz
0.96
2.00
3.16
2.01
1.93
1.00
0.99
1.00
2.98
2.93
f1 (ppm)

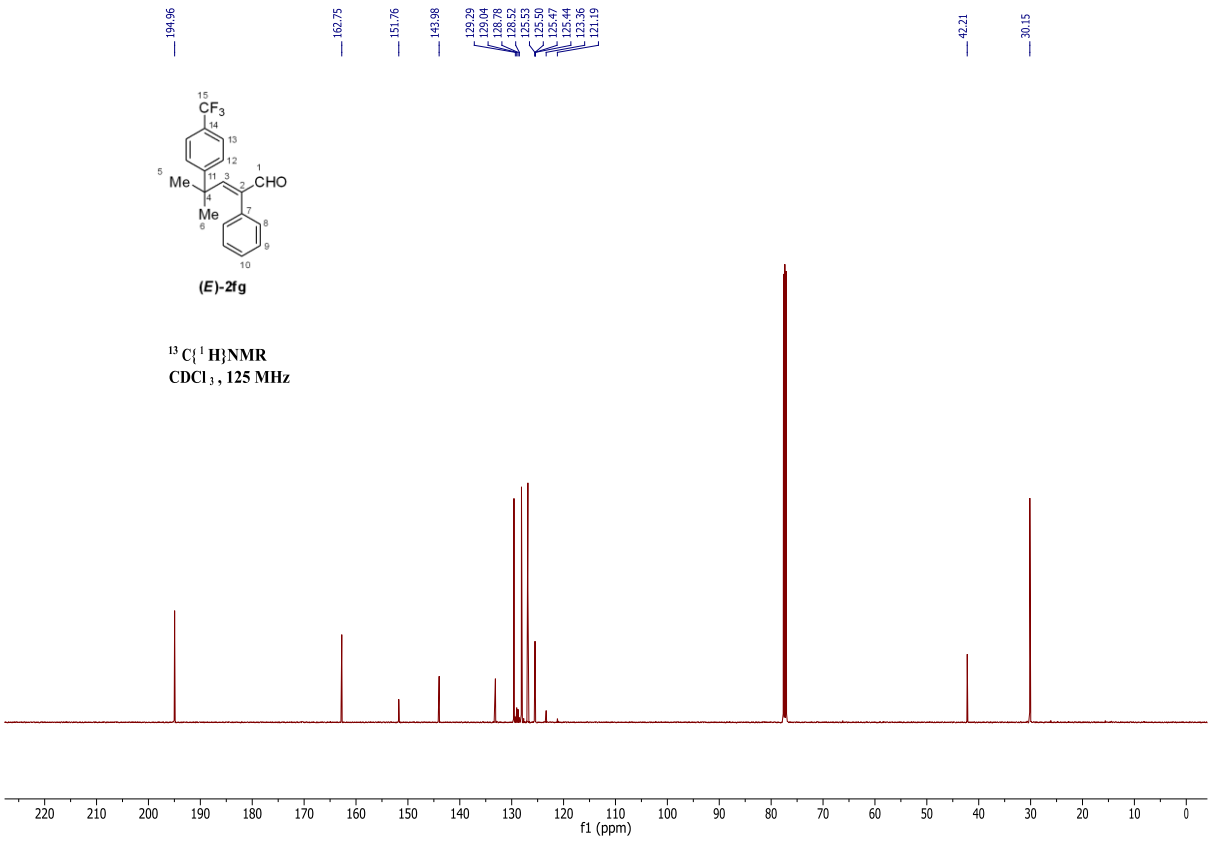

193.59
156.10
146.43
144.78
132.93
130.21
129.68
129.60
129.36
129.07
128.76
128.54
126.25
126.22
126.18
126.14
125.78
123.08
53.24
34.12
21.17
20.84
Me
H
O
Me
F3C
(E)-2eg
13C{1H}NMR
CDCl3, 100 MHz
f1 (ppm)

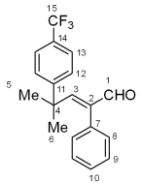


(*E*)-2eg

$^{19}F\{^{1}H\}$NMR
$CDCl_3$, 282 MHz

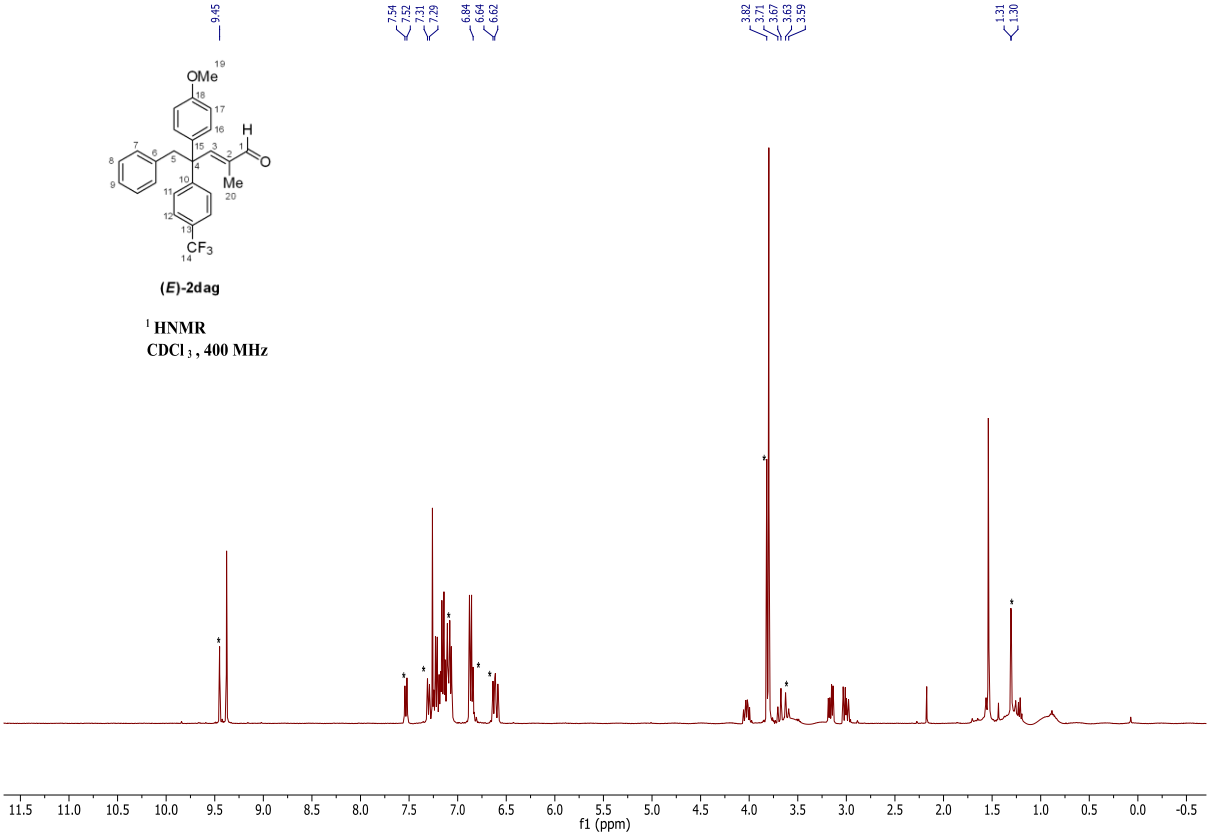

9.61
7.44
7.43
7.28
7.26
7.20
7.19
7.18
7.16
7.14
6.91
6.77
6.76
6.75
6.75
1.46
CF3
CHO
Me
Me
(E)-2fg
1 HNMR
CDCl 3 , 500 MHz
0.97
2.05
2.40
2.99
1.00
1.96
6.29
f1 (ppm)


194.96
162.75
151.76
143.98
129.29
129.04
128.78
128.52
125.53
125.50
125.47
125.44
123.36
121.19
42.21
30.15
CF3
CHO
Me
Me
(E)-2fg
13 C{ 1 H}NMR
CDCl 3 , 125 MHz
f1 (ppm)



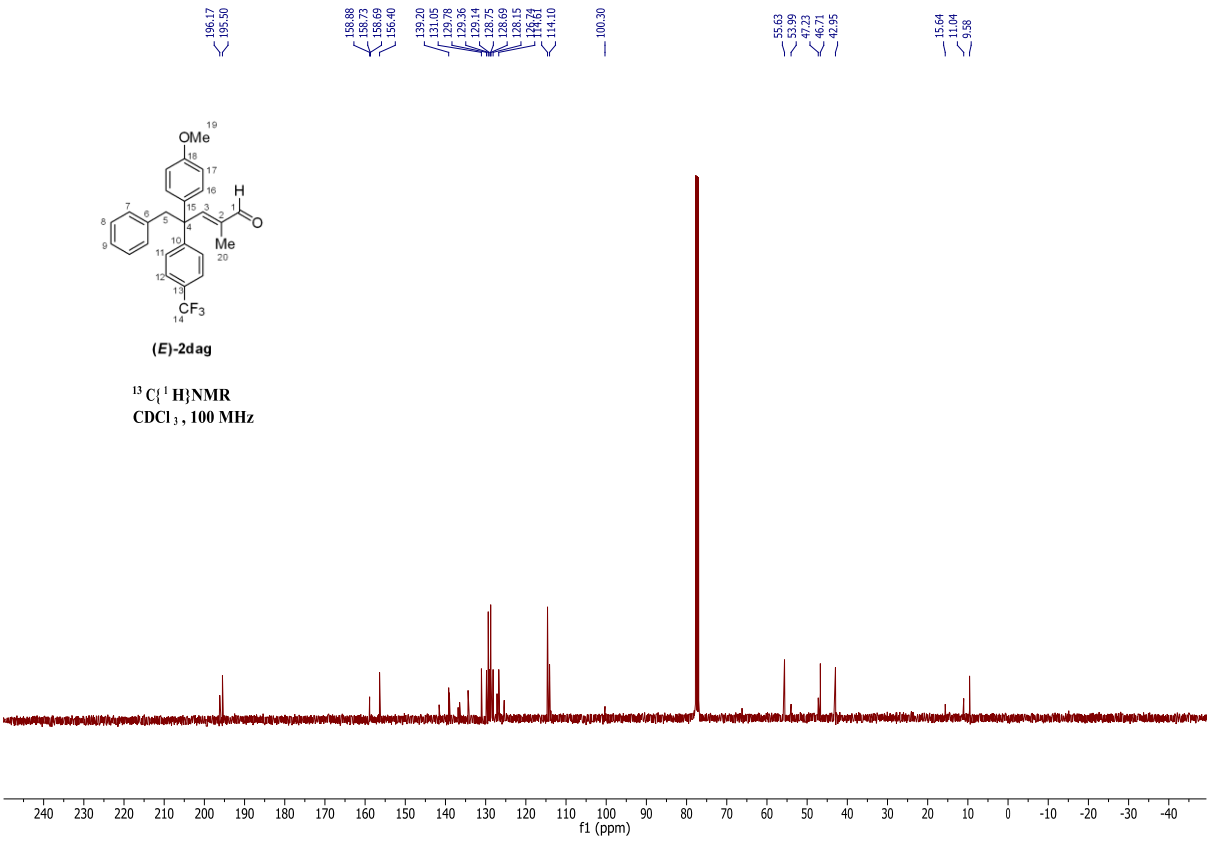
(*E*)-2fg

$^{19}F\{^{1}H\}$NMR
$CDCl_3$, 282 MHz



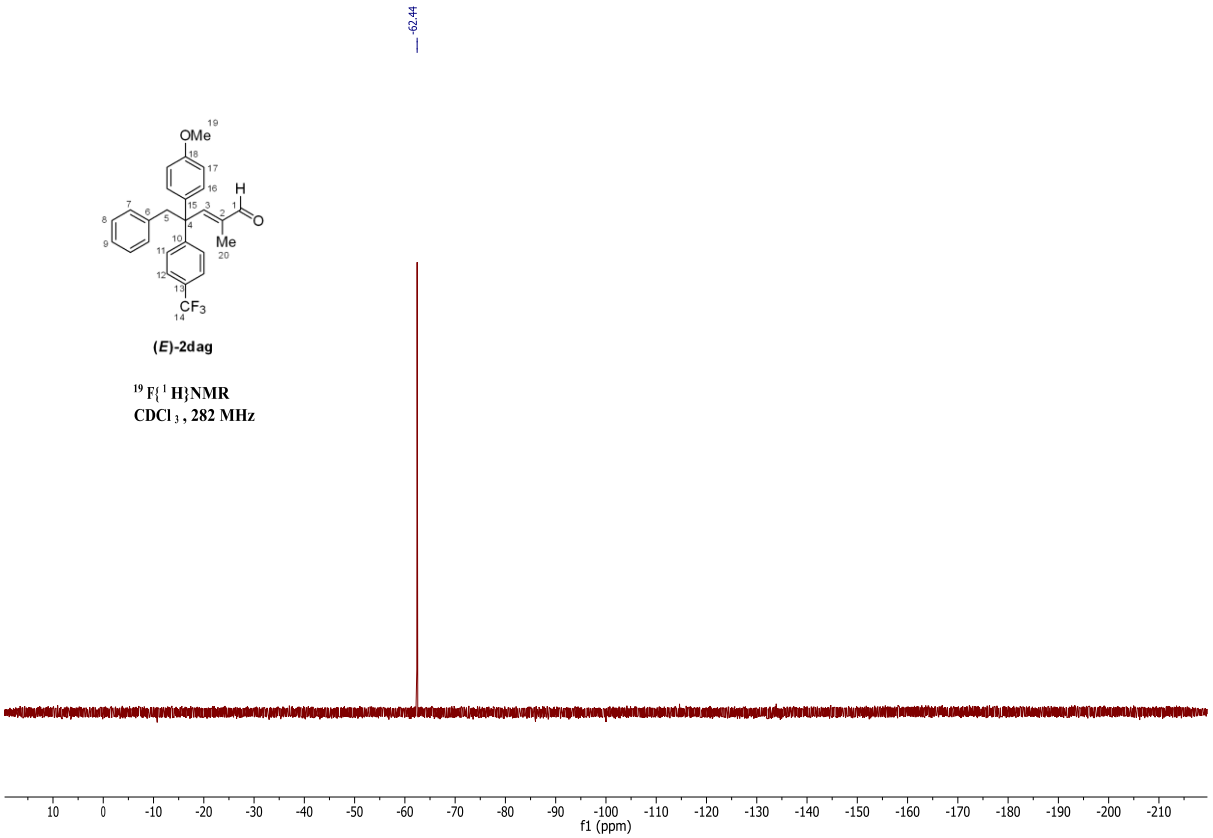
(*E*)-2dag

^{1}HNMR
$CDCl_3$, 400 MHz



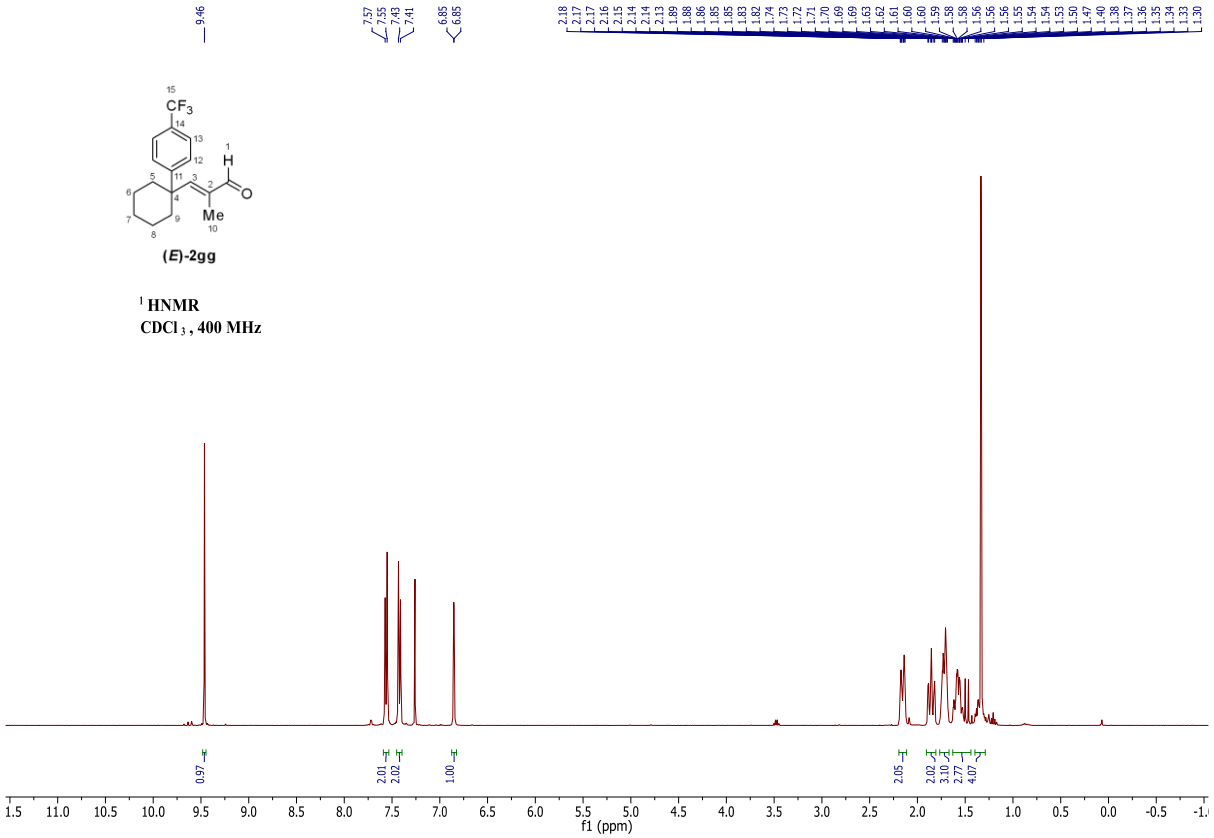
(*E*)-2dag

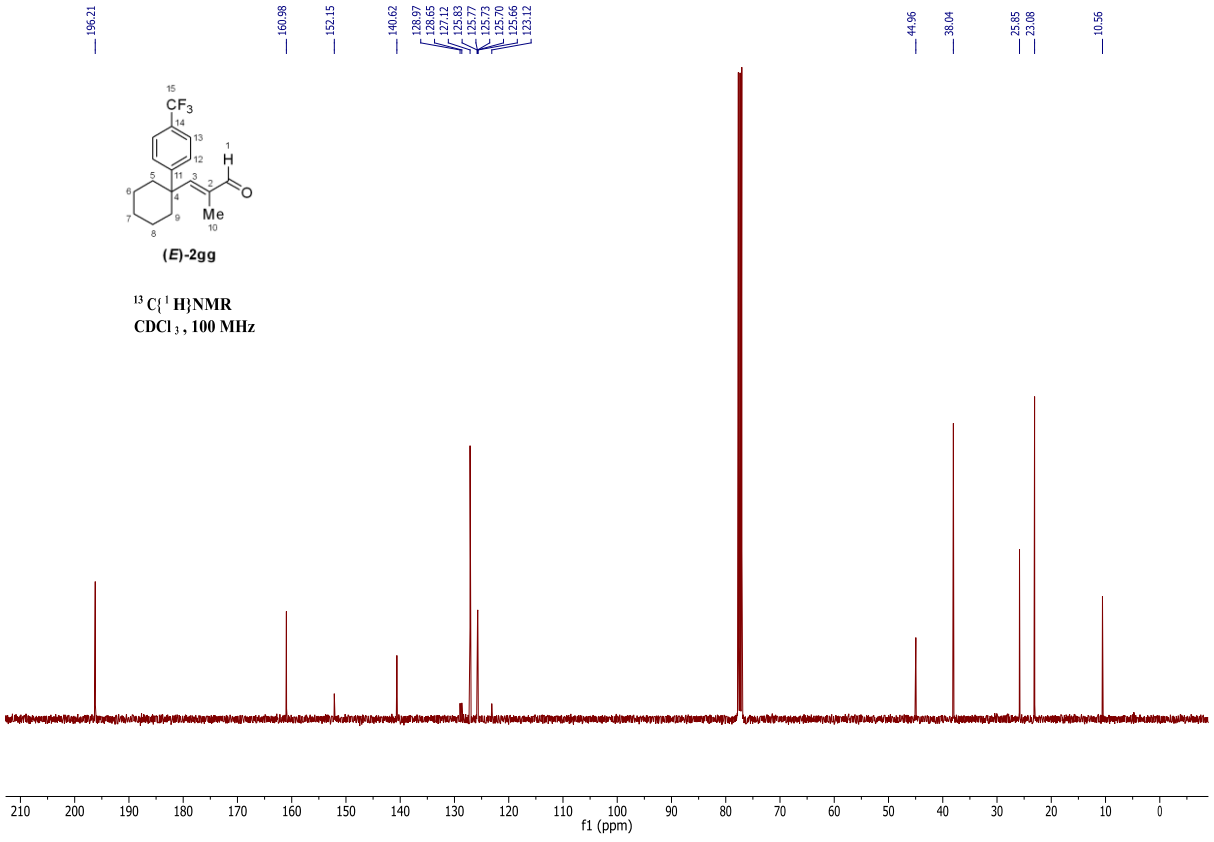
$^{13}C\{^{1}H\}$NMR
$CDCl_3$, 100 MHz



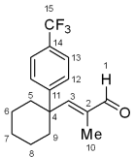
(*E*)-2dag

$^{19}F\{^{1}H\}$NMR
$CDCl_3$, 282 MHz


9.46
7.57
7.55
7.43
7.41
6.85
6.85
CF3
H
O
Me
(E)-2gg
1 HNMR
CDCl 3 , 400 MHz
0.97
2.01
2.02
1.00
2.05
2.02
3.10
2.77
4.07
f1 (ppm)

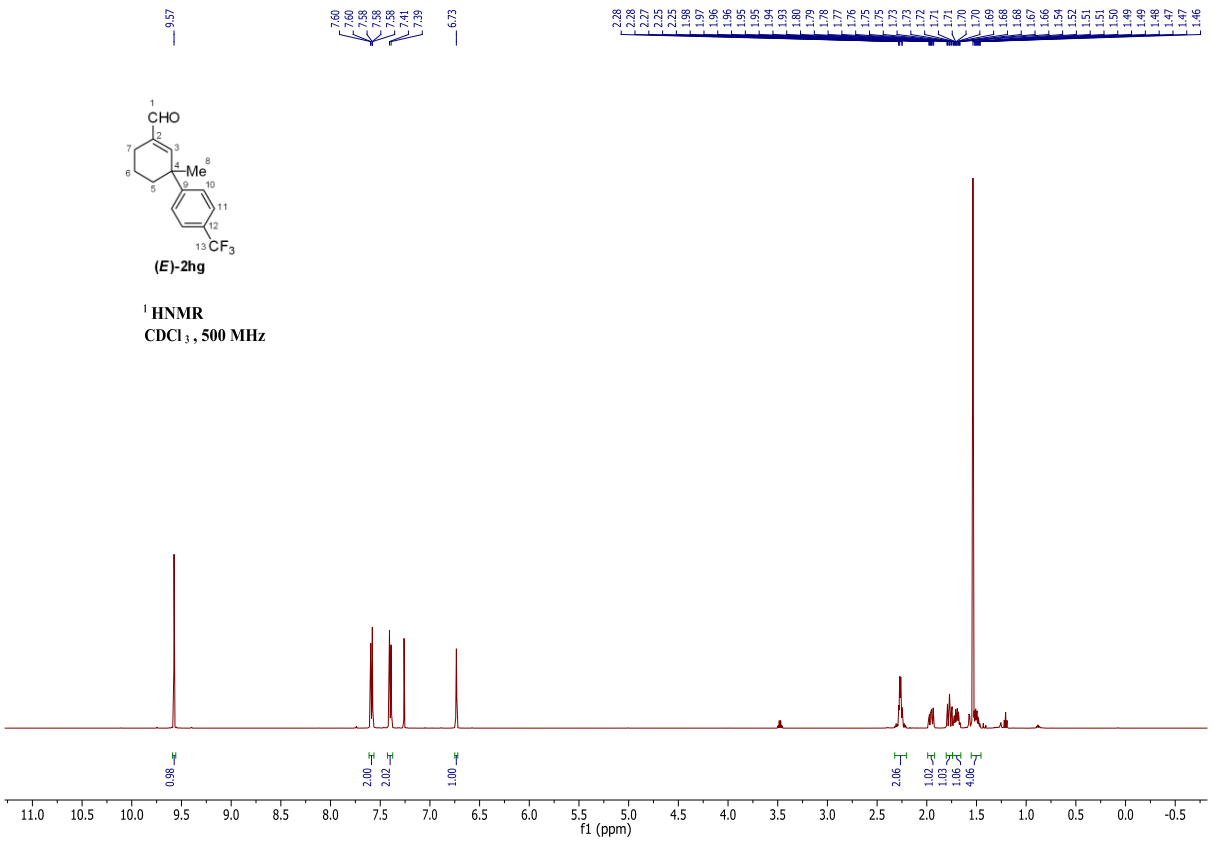

196.21
160.98
152.15
140.62
128.97
128.65
127.12
125.83
125.77
125.73
125.70
125.66
123.12
44.96
38.04
25.85
23.08
10.56
CF3
H
O
Me
(E)-2gg
13 C{ 1 H}NMR
CDCl 3 , 100 MHz
f1 (ppm)

IF297/30
F19CPD



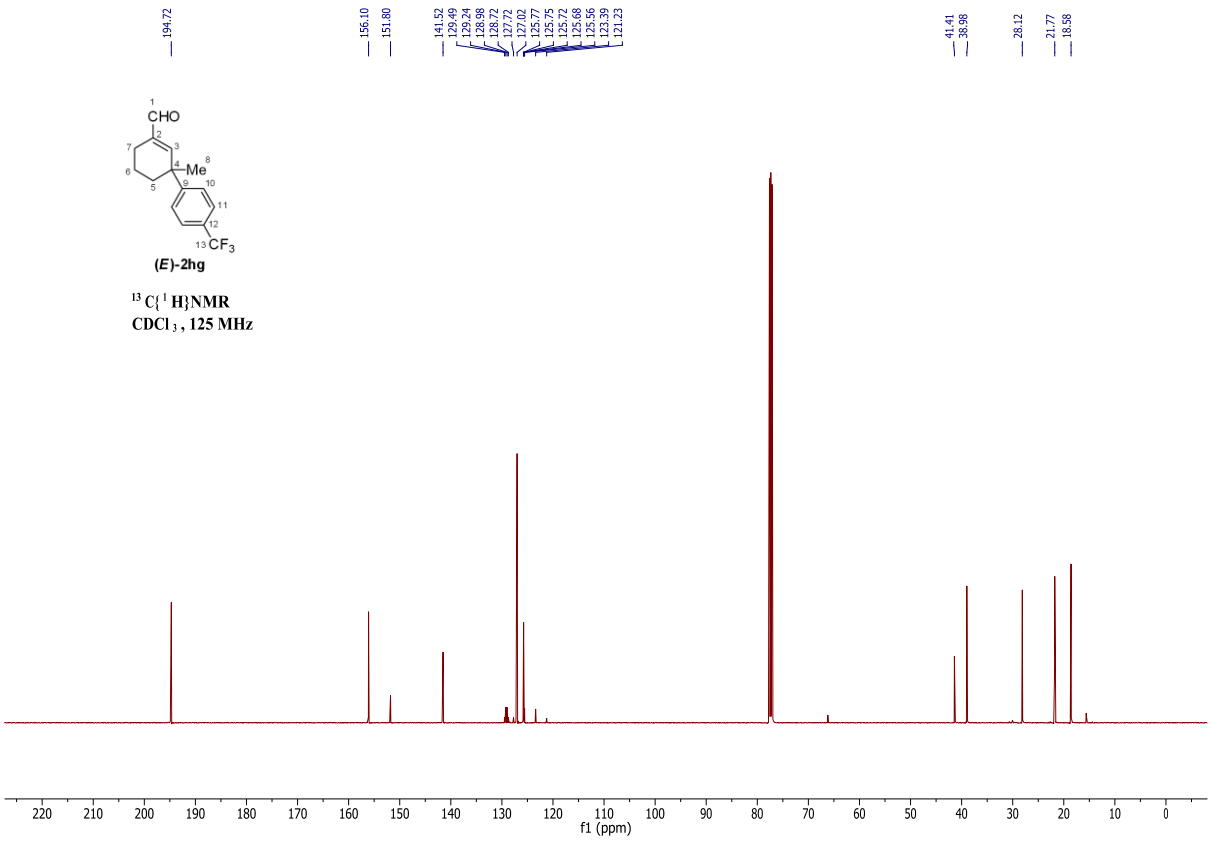
(*E*)-2gg

$^{19}F\{^{1}H\}$NMR
$CDCl_3$, 282 MHz



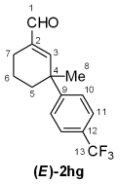
(*E*)-2hg

^{1}HNMR
$CDCl_3$, 500 MHz



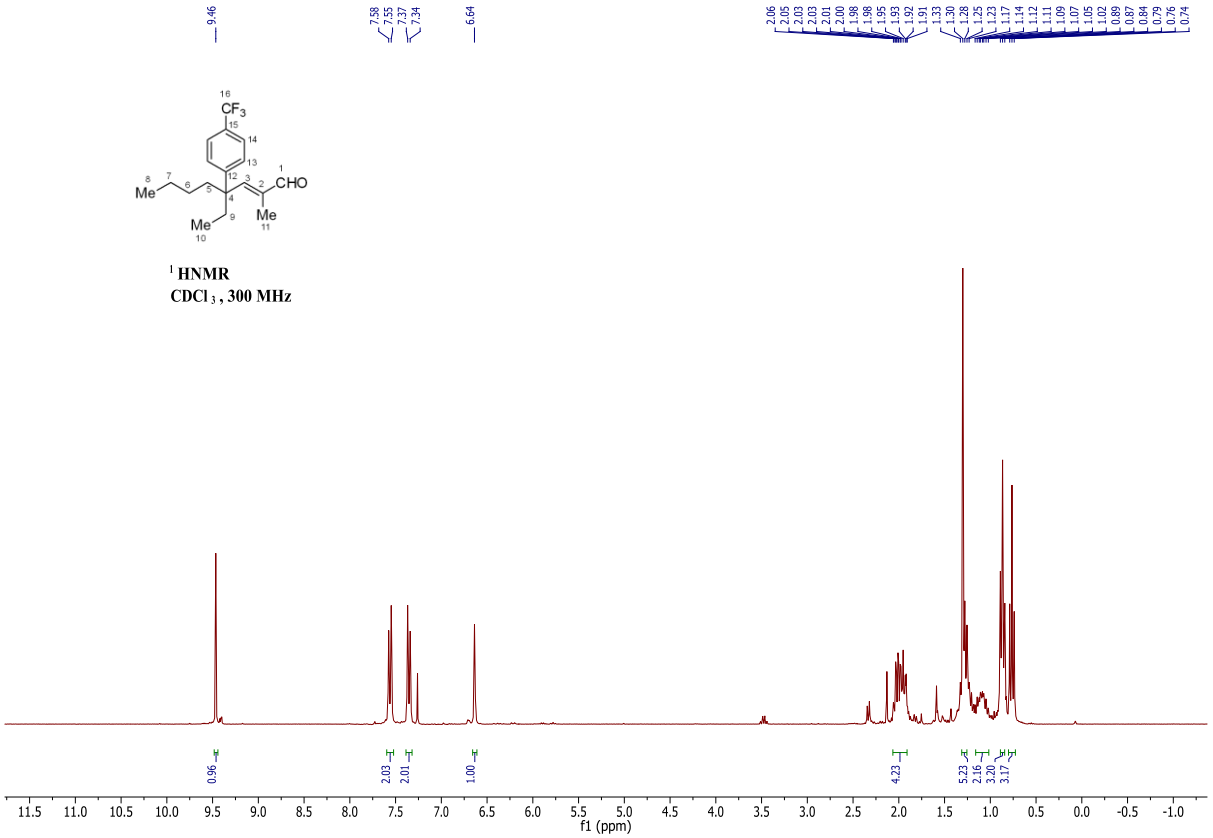
(*E*)-2hg

$^{13}C\{^{1}H\}$NMR
$CDCl_3$, 125 MHz

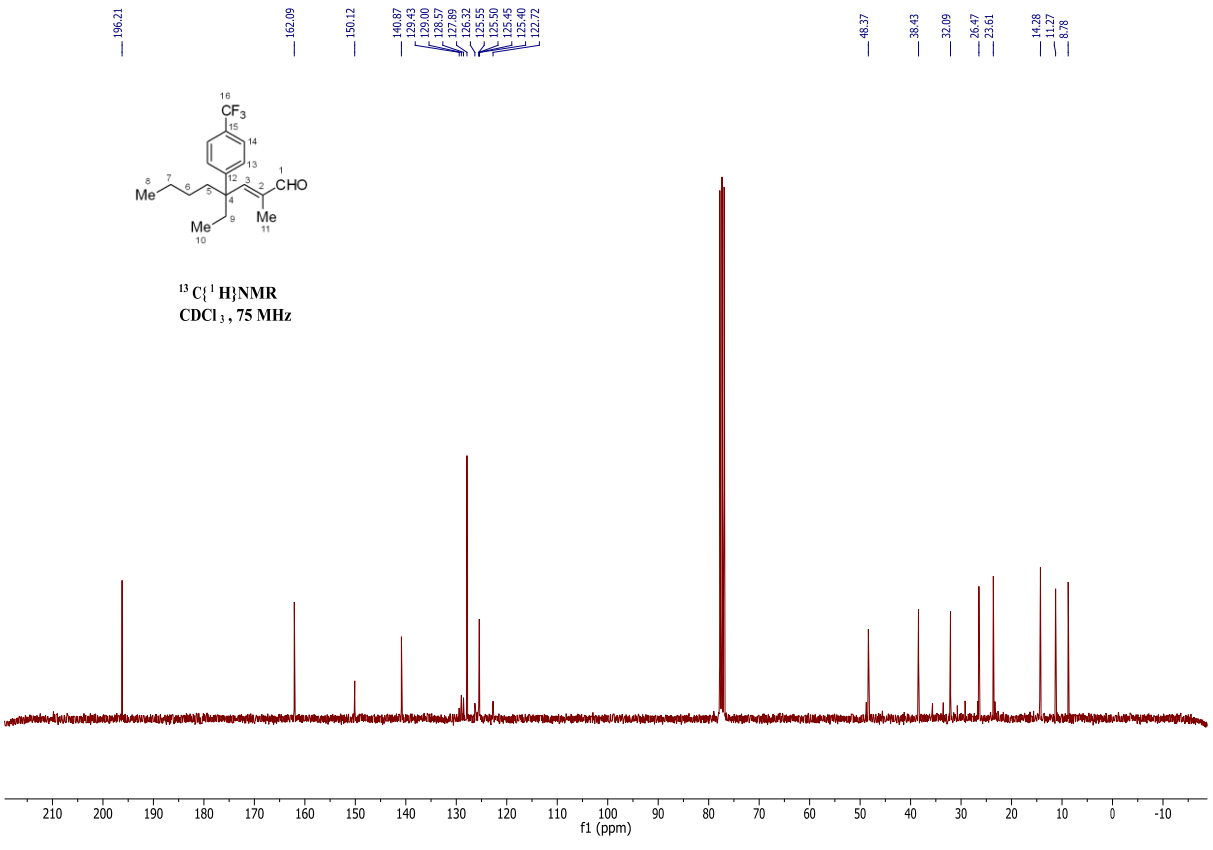


(*E*)-2hg

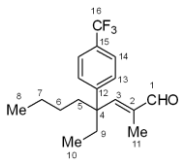
$^{19}F\{^{1}H\}$NMR
$CDCl_3$, 282 MHz



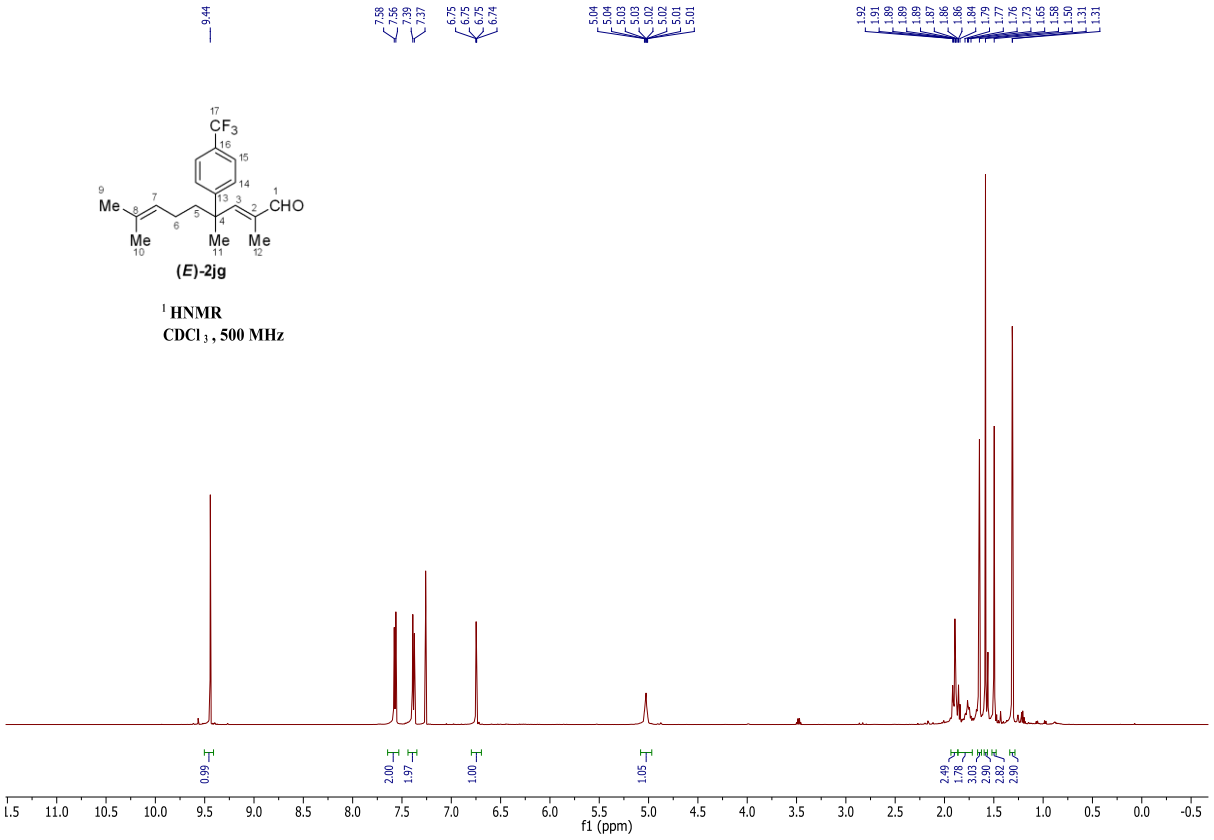
^{1}HNMR
$CDCl_3$, 300 MHz



$^{13}C\{^{1}H\}$NMR
$CDCl_3$, 75 MHz

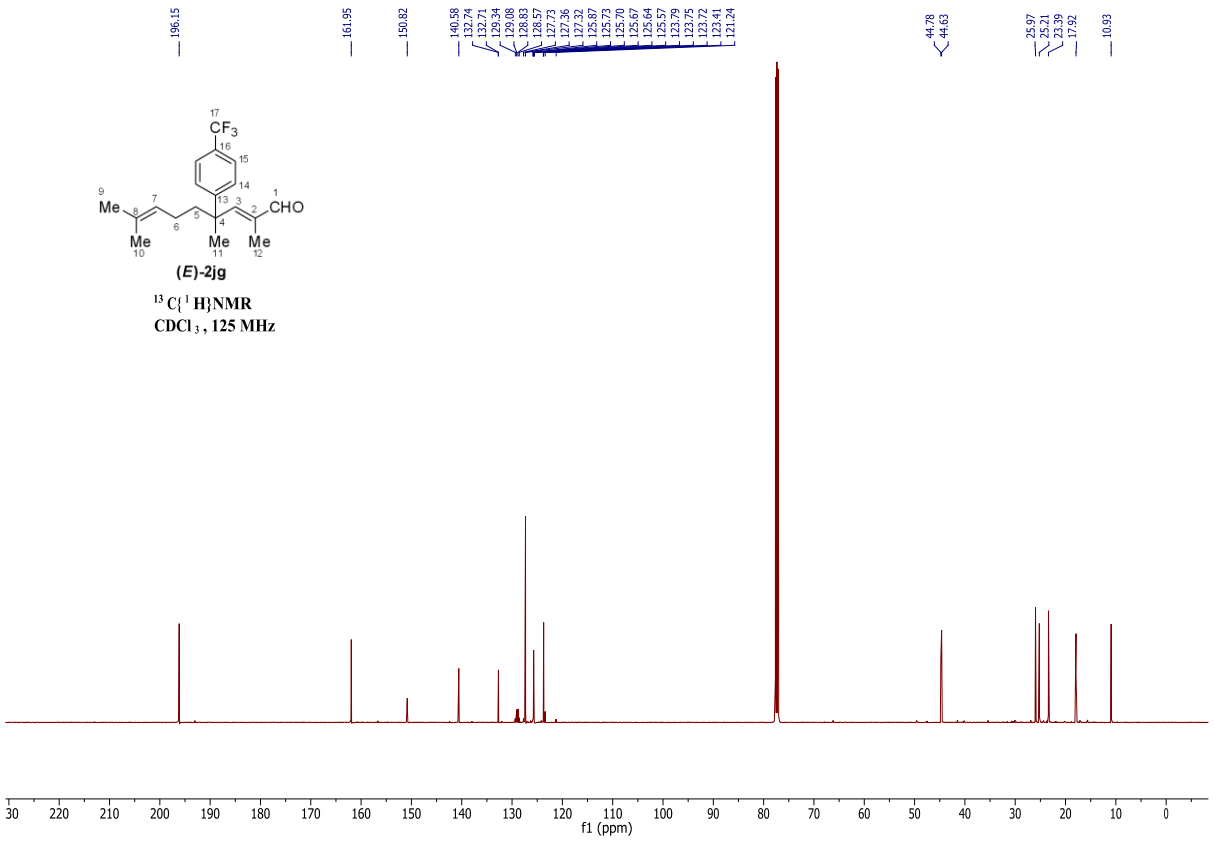


$^{19}F\{^{1}H\}$NMR
$CDCl_3$, 282 MHz



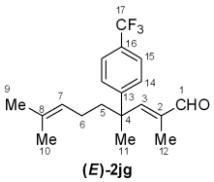
(*E*)-2jg

^{1}HNMR
$CDCl_3$, 500 MHz



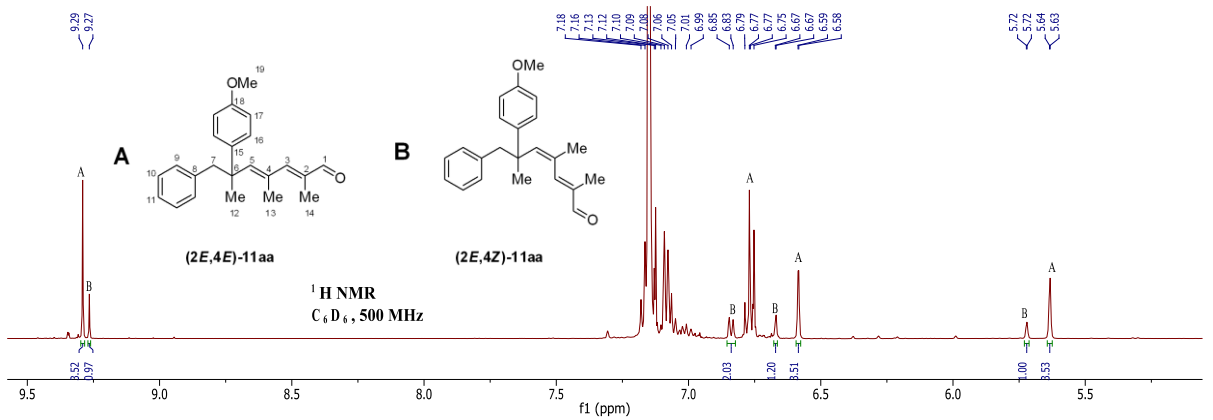
(*E*)-2jg

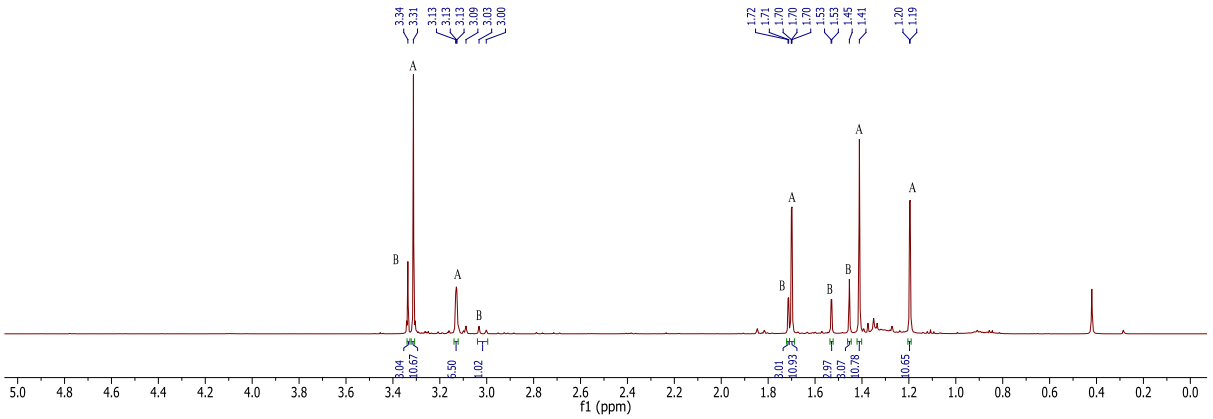
$^{13}C\{^{1}H\}$NMR
$CDCl_3$, 125 MHz

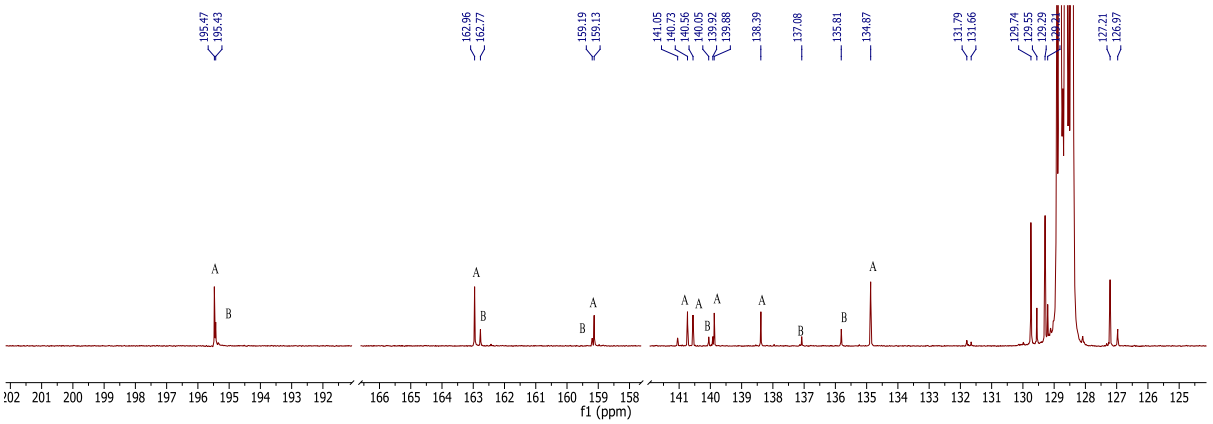


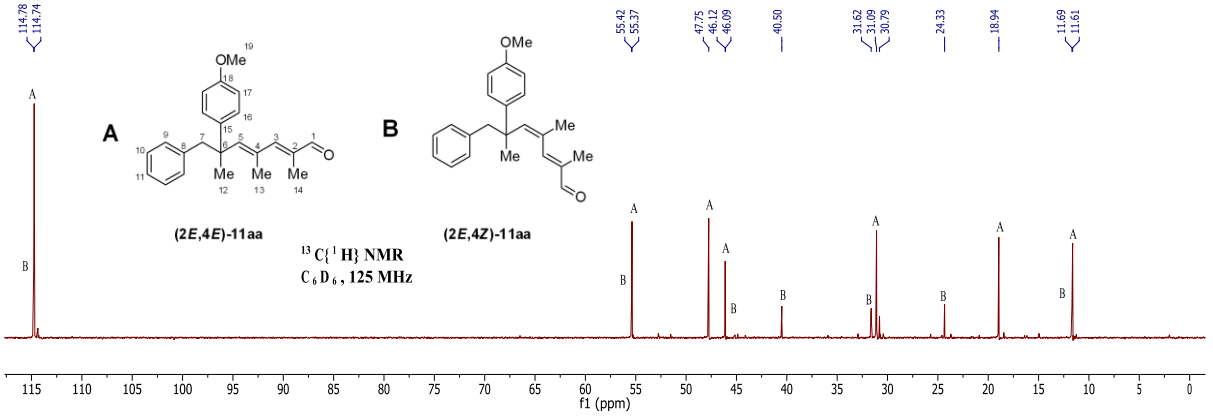
(*E*)-2jg

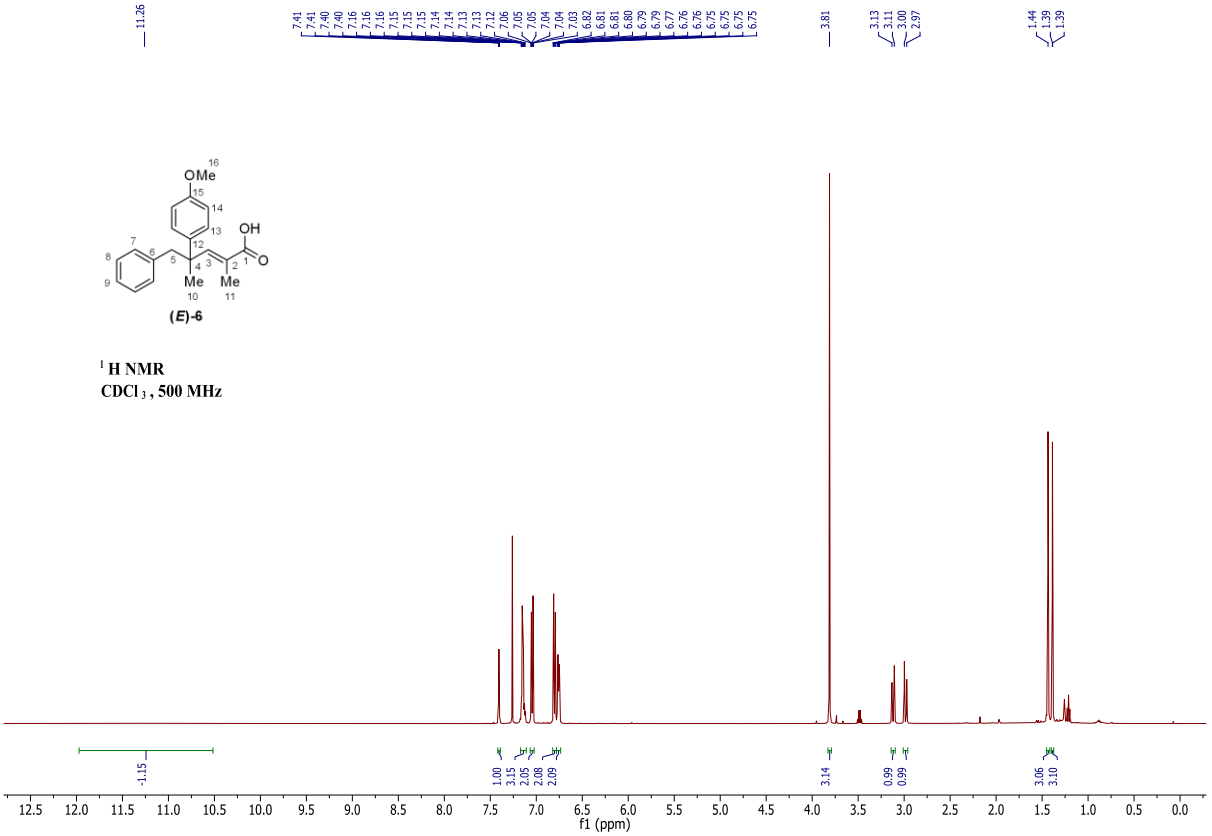
$^{19}F\{^{1}H\}$NMR
$CDCl_3$, 282 MHz

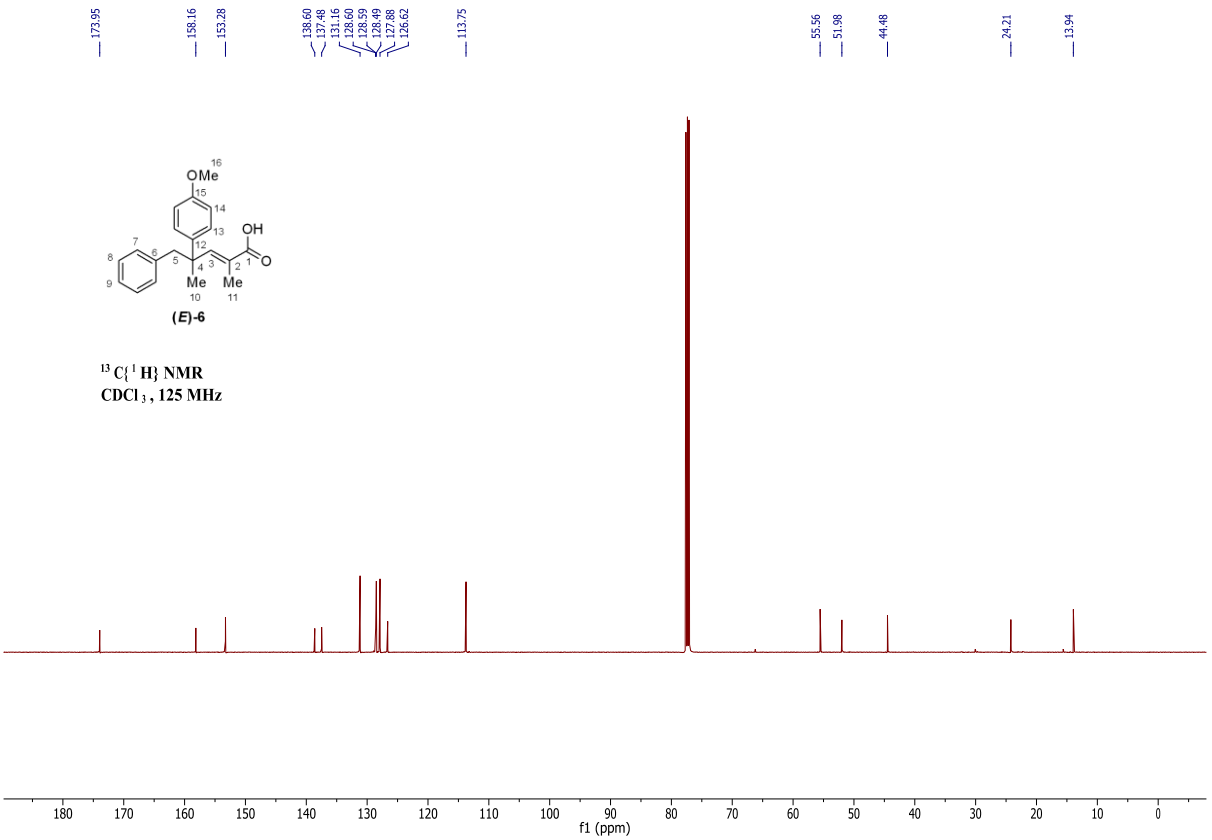

A
B
(2E,4E)-11aa
(2E,4Z)-11aa
^{1}H NMR
C$_6$D$_6$, 500 MHz
f1 (ppm)

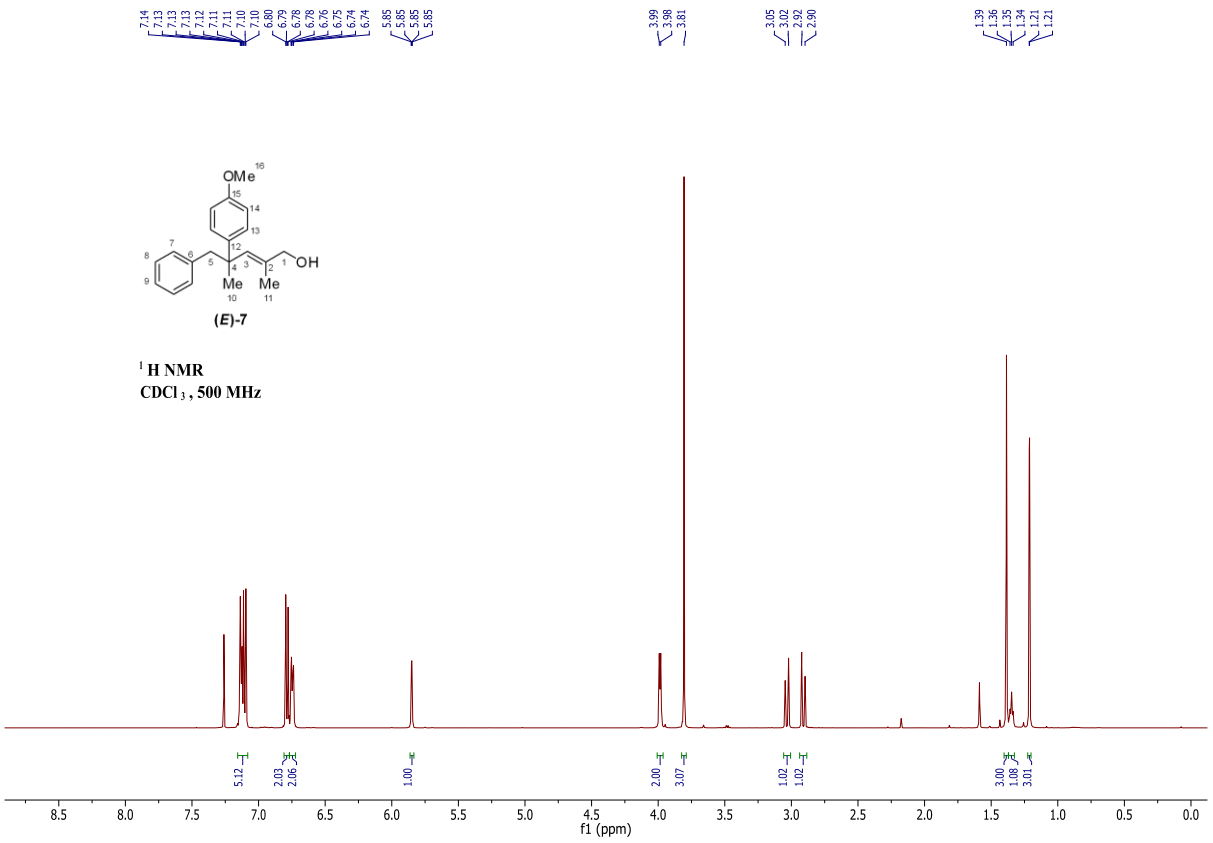

f1 (ppm)


f1 (ppm)


A
B
(2E,4E)-11aa
(2E,4Z)-11aa
^{13}C{^{1}H} NMR
C$_6$D$_6$, 125 MHz
f1 (ppm)

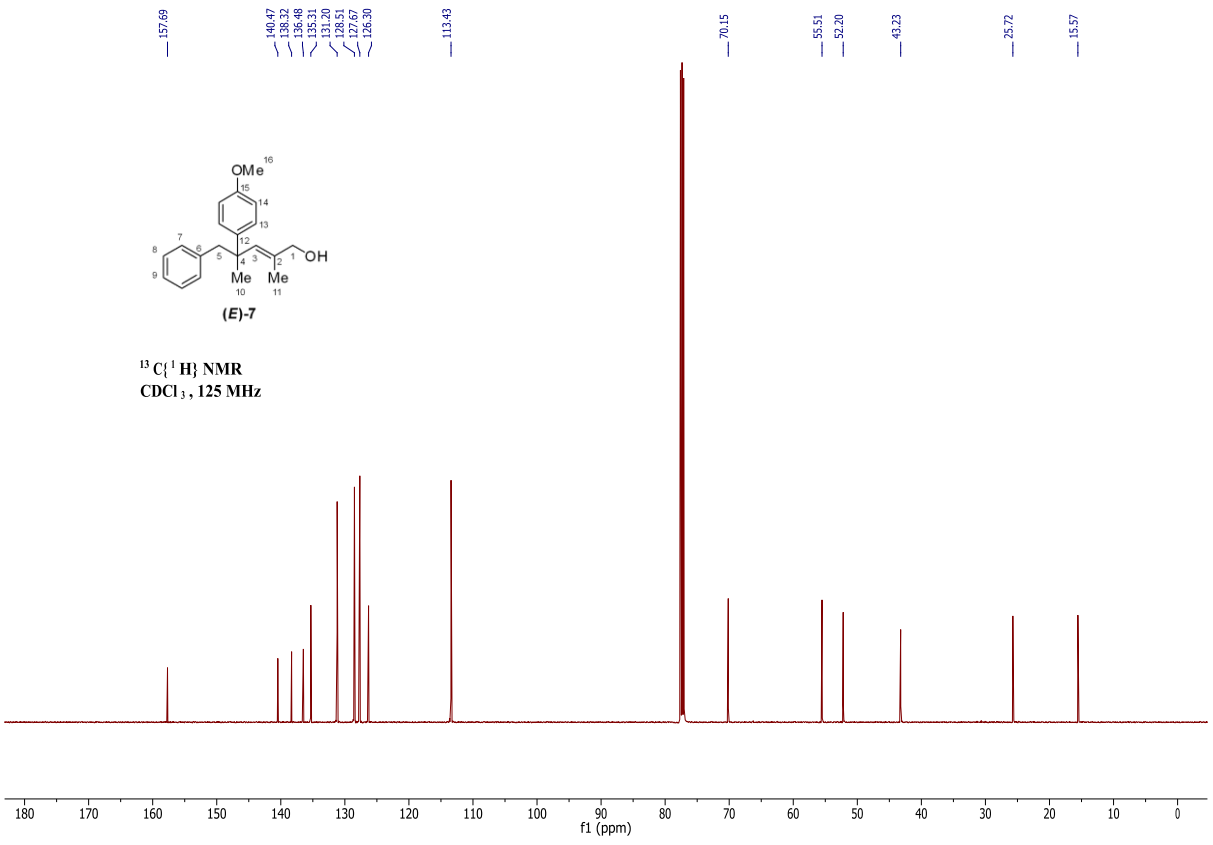

OMe
OH
Me
Me
(E)-6
1 H NMR
CDCl 3 , 500 MHz
f1 (ppm)


OMe
OH
Me
Me
(E)-6
13 C{1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)



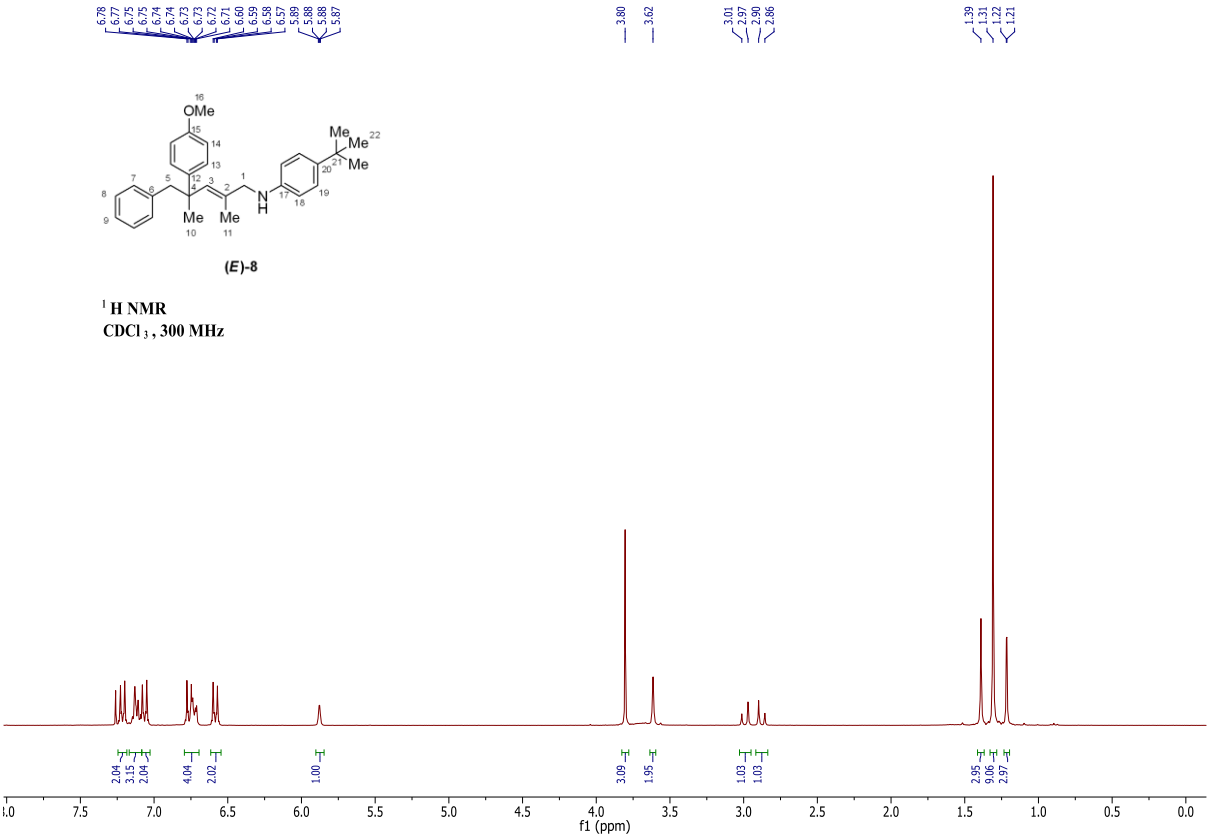
(*E*)-7

^{1}H NMR
CDCl$_3$, 500 MHz



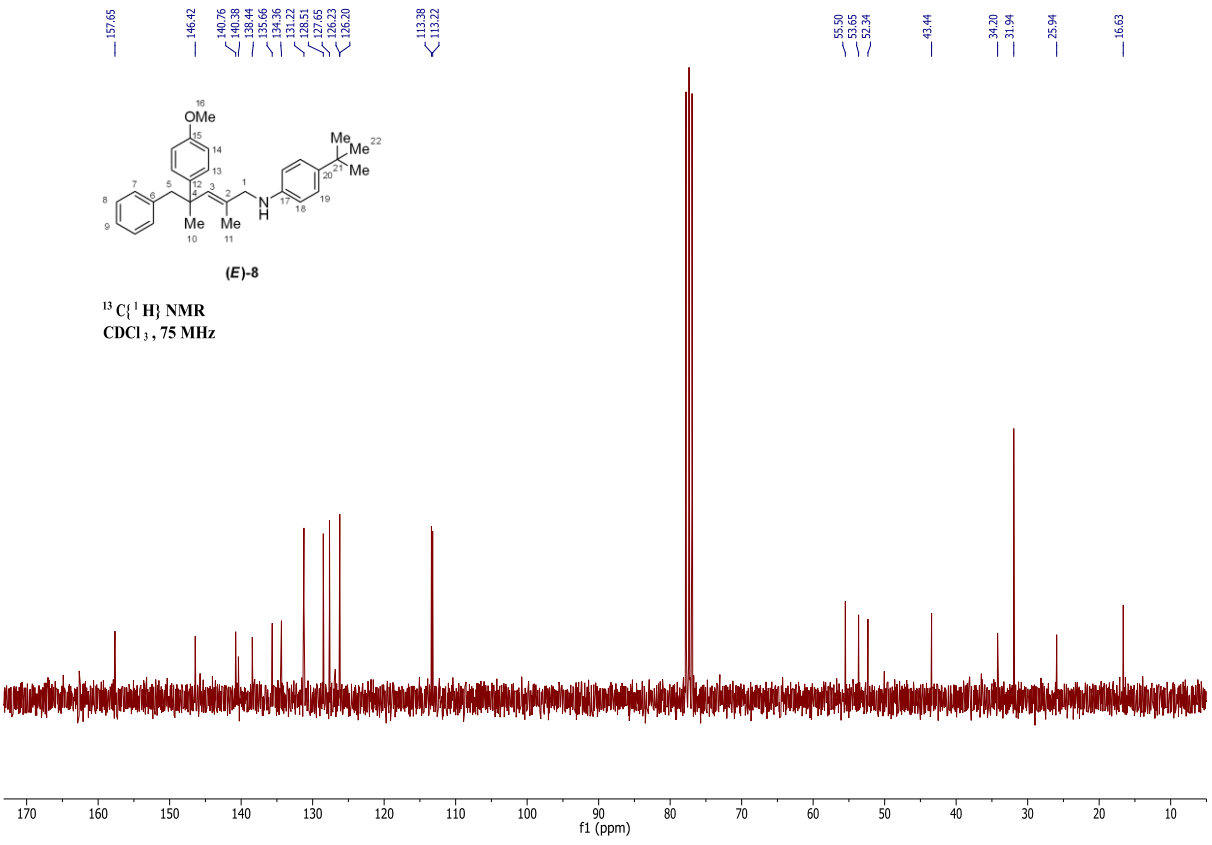
(*E*)-7

^{13}C{^{1}H} NMR
CDCl$_3$, 125 MHz



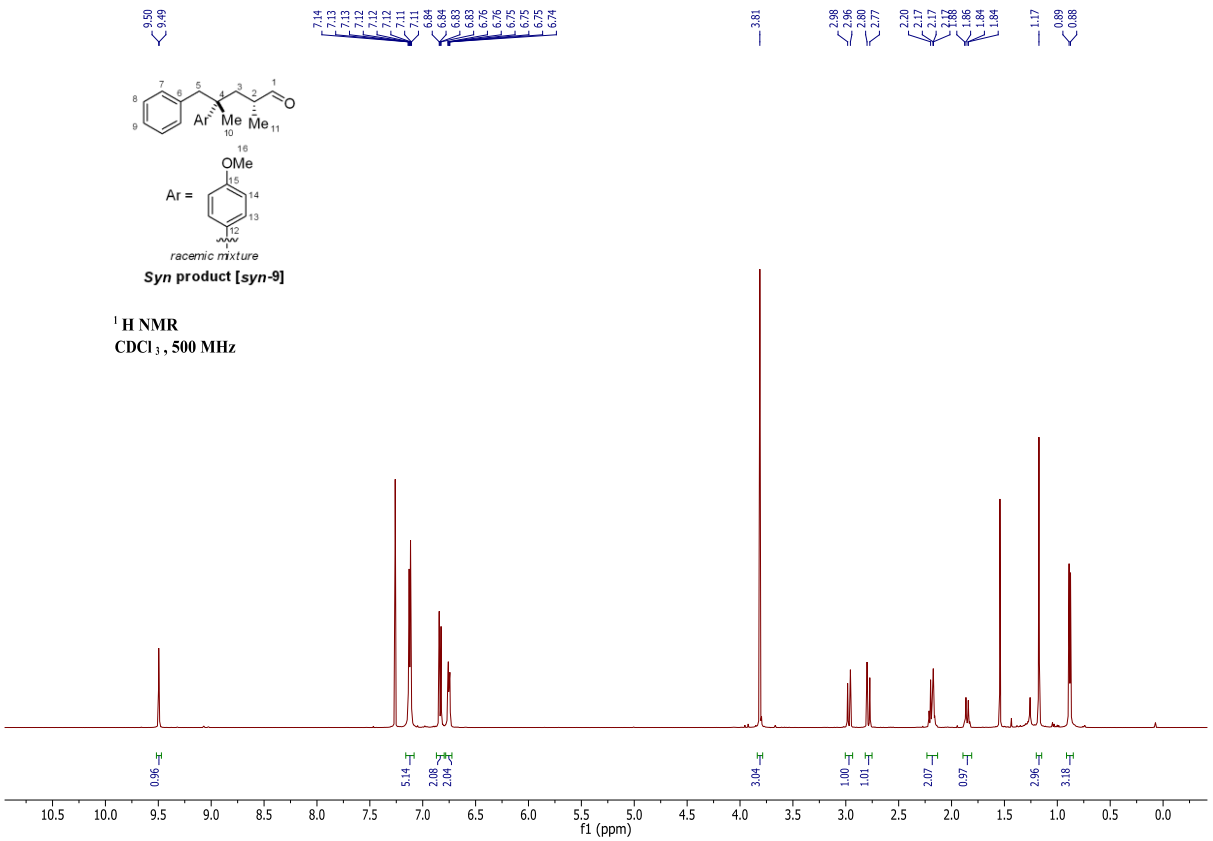
(*E*)-8

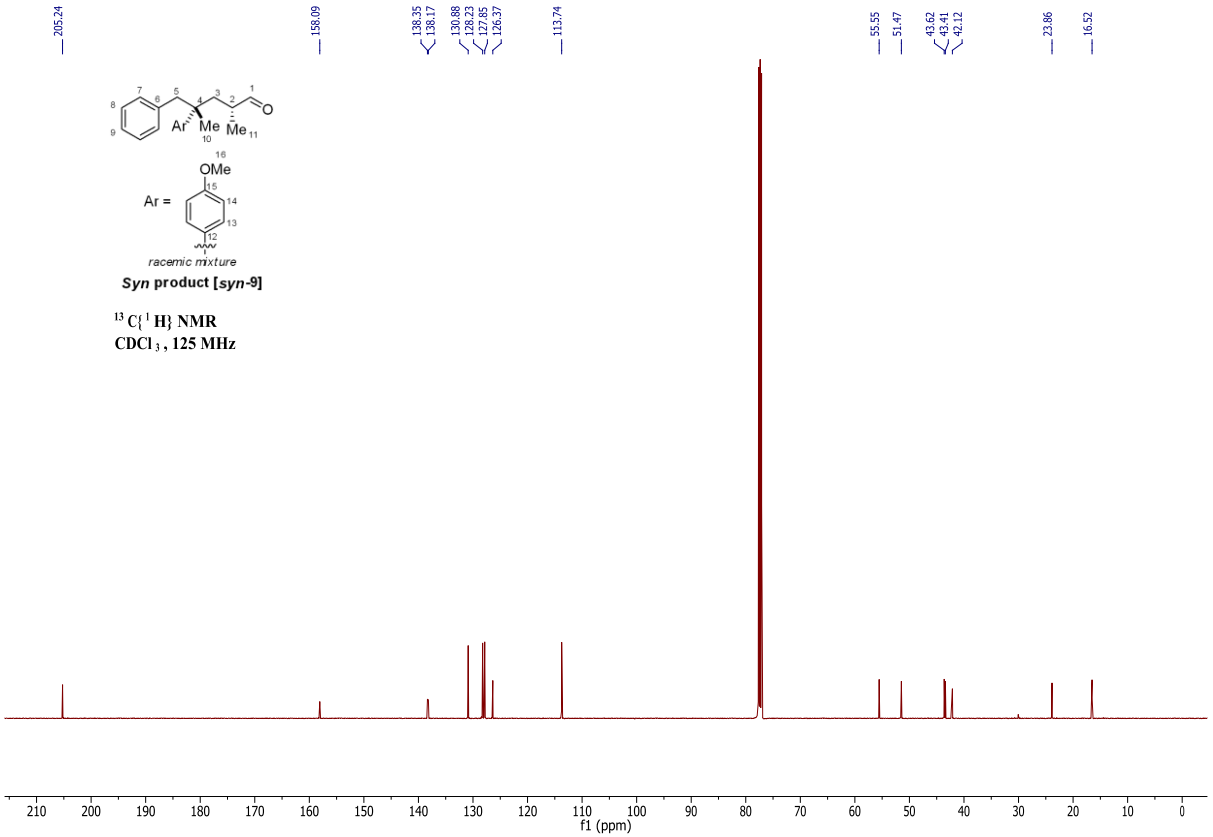
^{1}H NMR
$CDCl_3$, 300 MHz

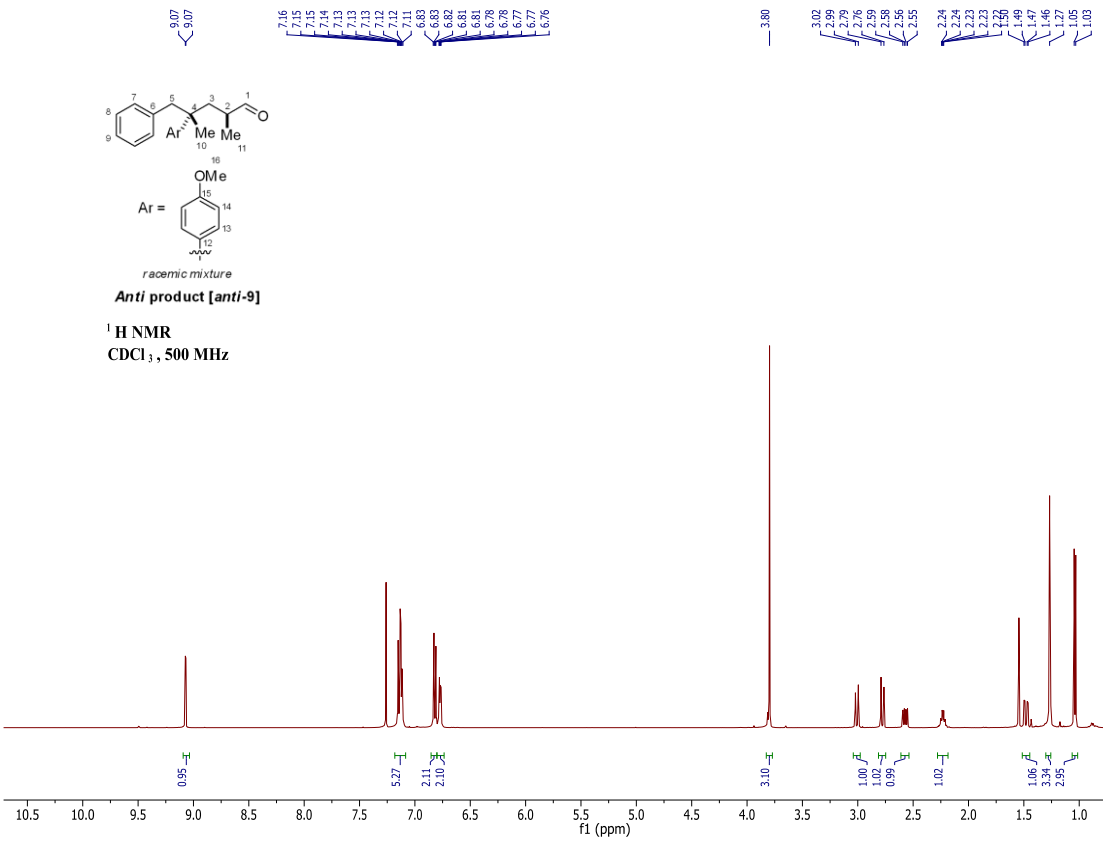


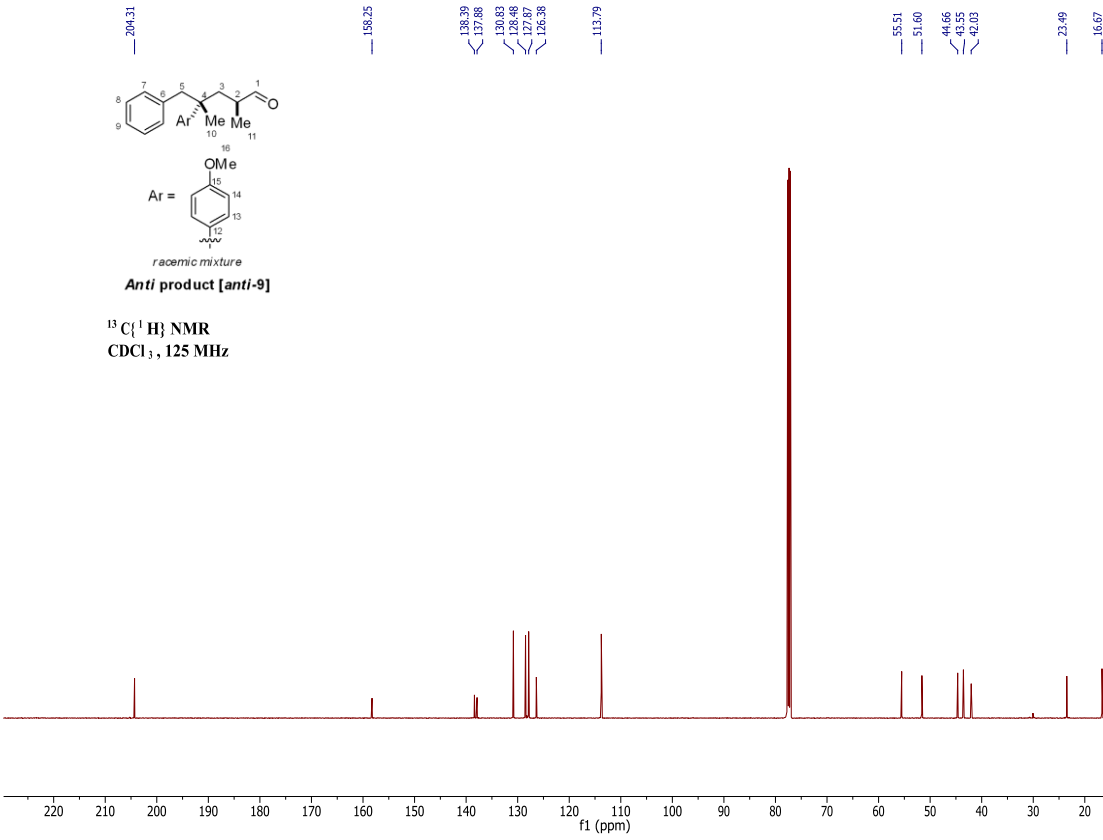
(*E*)-8

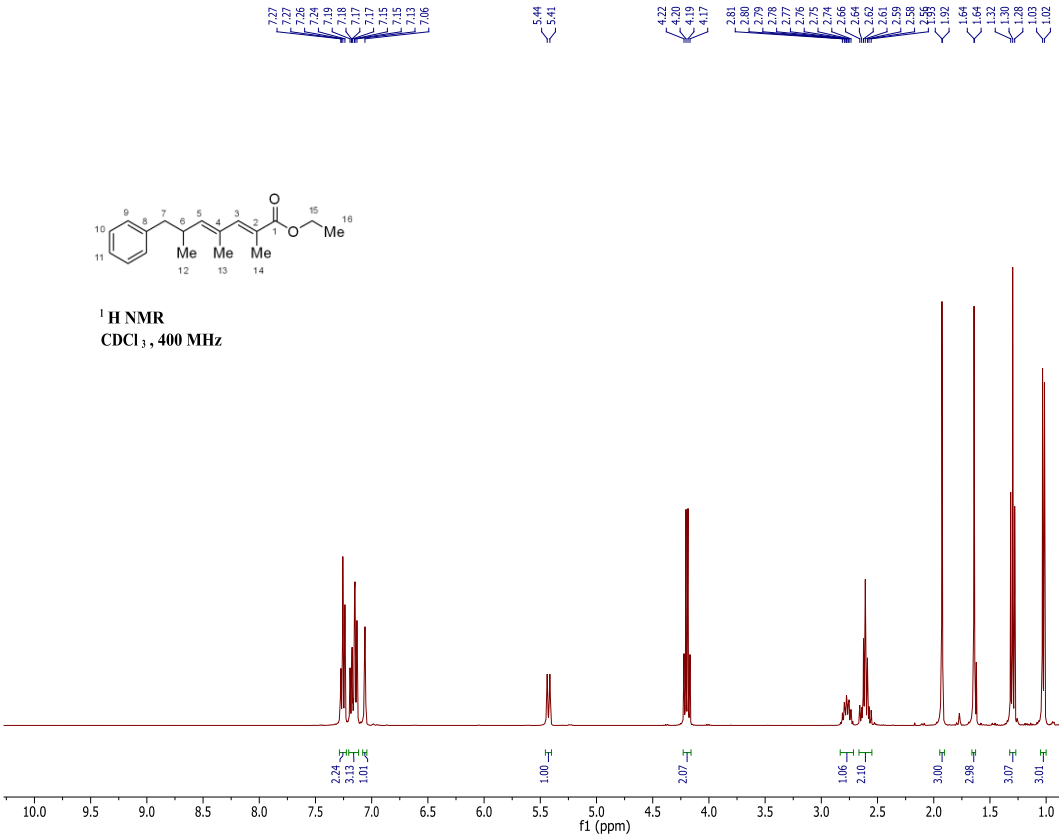
$^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 75 MHz

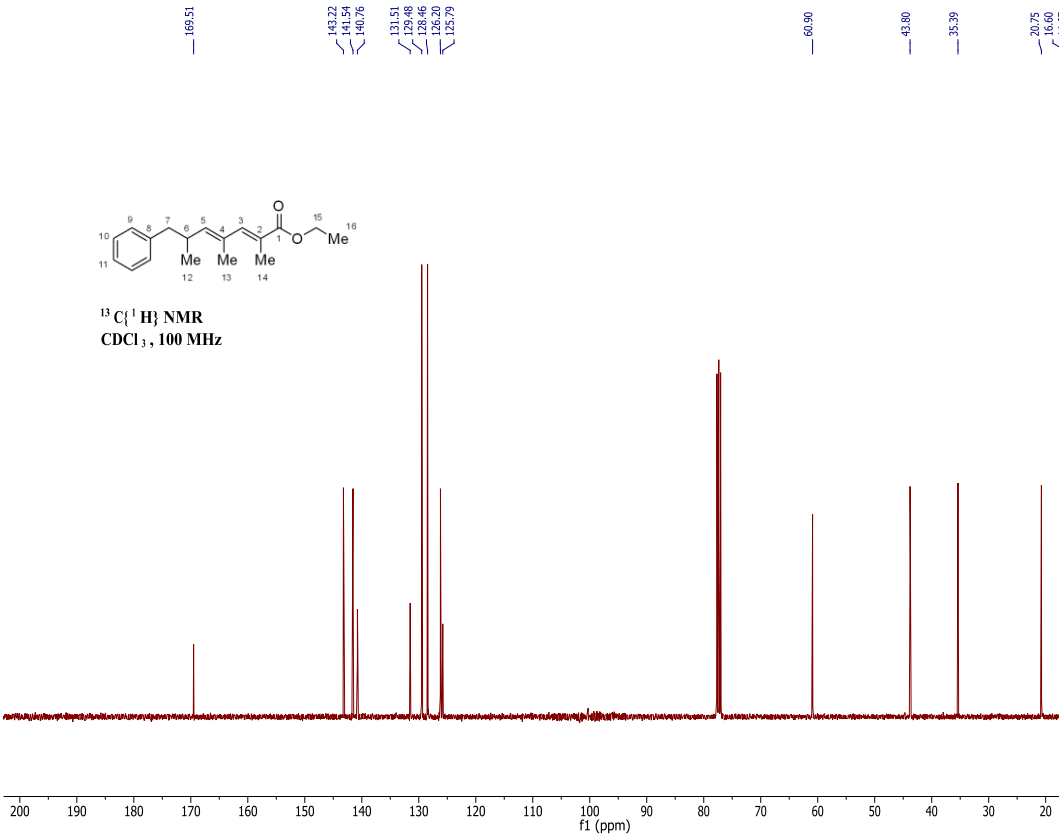

racemic mixture
Syn product [syn-9]
1 H NMR
CDCl 3 , 500 MHz
f1 (ppm)

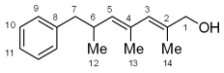

racemic mixture
Syn product [syn-9]
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)


racemic mixture
Anti product [anti-9]
1 H NMR
CDCl 3 , 500 MHz
f1 (ppm)

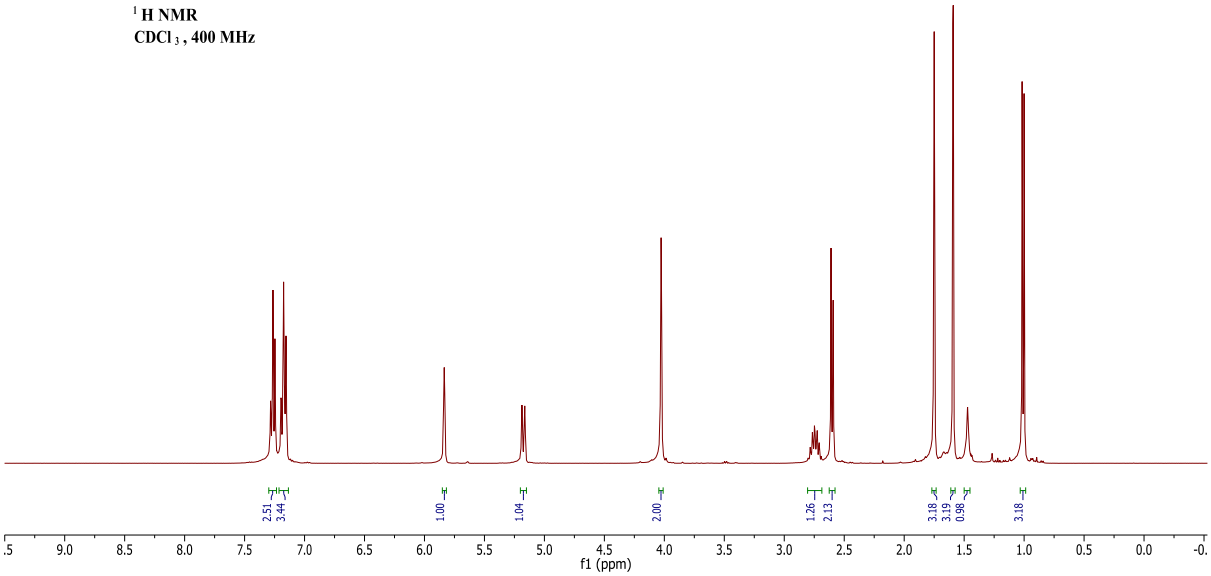

racemic mixture
Anti product [anti-9]
13 C{ 1 H} NMR
CDCl 3 , 125 MHz
f1 (ppm)

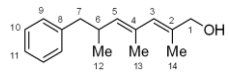

7.27
7.27
7.26
7.24
7.19
7.18
7.17
7.17
7.15
7.15
7.13
7.06
5.44
5.41
4.22
4.20
4.19
4.17
2.81
2.80
2.79
2.78
2.77
2.76
2.75
2.74
2.66
2.64
2.62
2.61
2.59
2.58
1.92
1.64
1.64
1.32
1.30
1.28
1.03
1.02
Me
Me
Me
Me
Me
1H NMR
CDCl3, 400 MHz
2.24
3.13
1.01
1.00
2.07
1.06
2.10
3.00
2.98
3.07
3.01
f1 (ppm)


169.51
143.22
141.54
140.76
131.51
129.48
128.46
126.20
125.79
60.90
43.80
35.39
20.75
16.60
14.67
14.28
Me
Me
Me
Me
Me
13C{1H} NMR
CDCl3, 100 MHz
f1 (ppm)

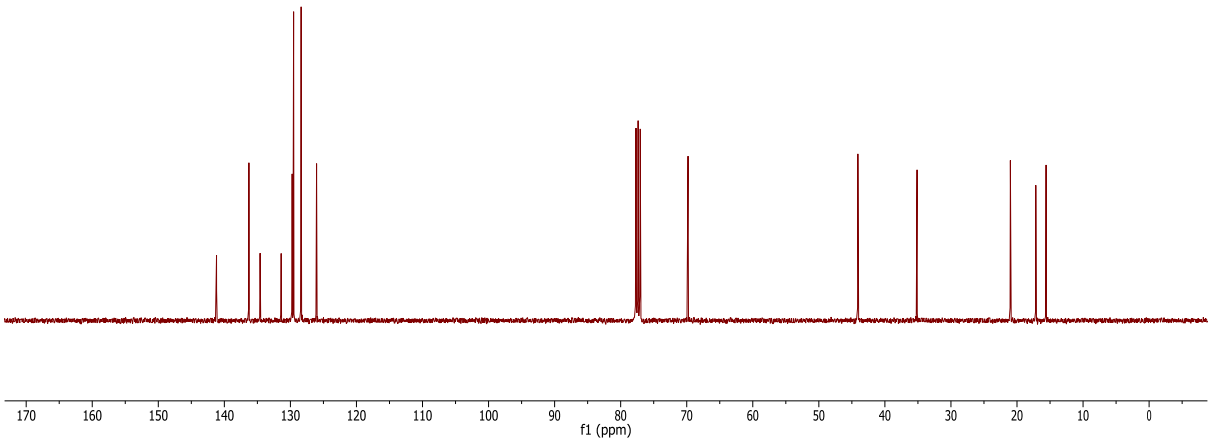


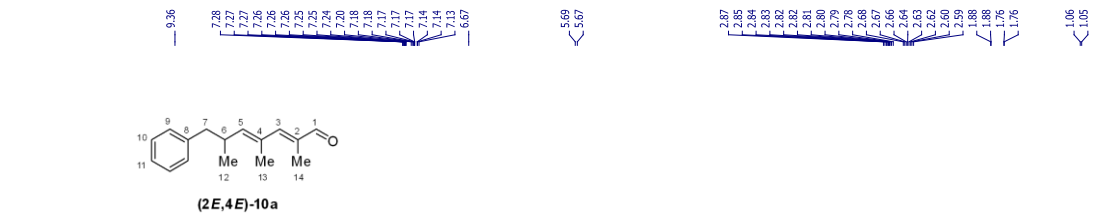
^{1}H NMR
CDCl$_3$, 400 MHz





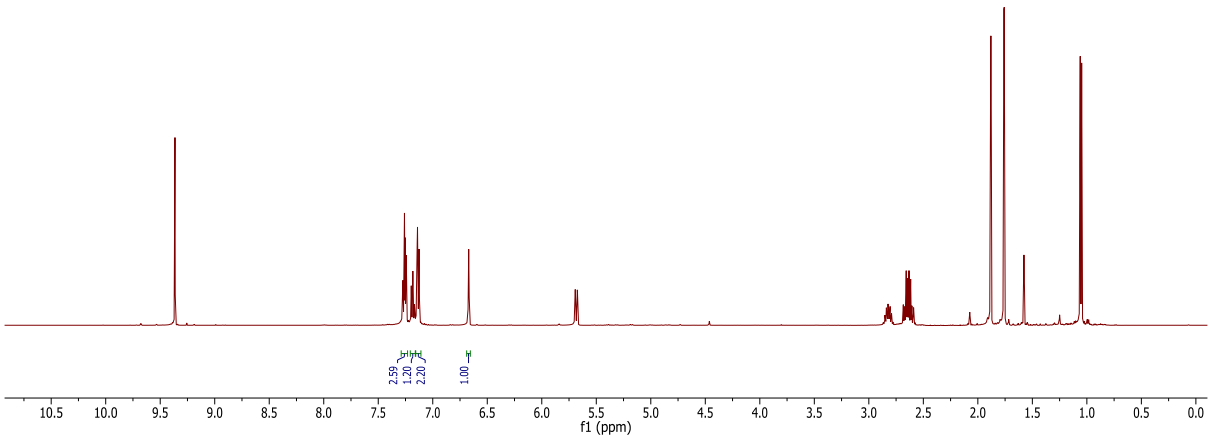
^{13}C{^{1}H} NMR
CDCl$_3$, 400 MHz





(2*E*,4*E*)-10a

^{1}H NMR
$CDCl_3$, 500 MHz



(2*E*,4*E*)-10a

$^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 500 MHz