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**First Synthesis of 1-Chlorovinyl Allenes via Palladium-Catalyzed
Allenation of Alkynoates with Propargyl Alcohols****

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Guangzhou 510640, China.

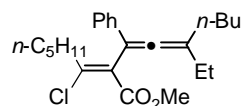
[**] We are grateful to the National Natural Science Foundation of China for financial support
(Grants: 20332030, 20572027, 20625205 and 20772034) and Guangdong Natural Science
Foundation (Grant. 07118070).

Experimental Section

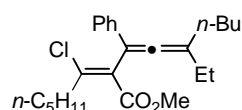
General. All reactions were performed at RT under air atmosphere in a round bottom flask equipped with magnetic stir bar. ^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer (100 MHz for carbon) and respectively referenced to 7.27 and 77.0 ppm for chloroform-d solvent with TMS as internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A at an ionization voltage of 70eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF₂₅₄), and visualization was effected at 254 nm. Compounds **2d-2m** were produced according to literature by Sonogashira coupling. All the other chemicals were purchased from Aldrich Chemicals.

General procedure for the preparation of methyl 2-(1-chlorohexylidene)-5-ethyl-3-phenylnona-3,4-dienoate (**3ac**):

A test tube (10 mL) was charged with palladium chloride (10 mg, 0.056 mmol), LiCl (20 mg, 0.5 mmol), propargyl alcohol **2c** (108 mg, 0.5 mmol) and 0.5 mL 3N HCl. After the mixture was stirred for 2 min, alkynoate **1a** (77 mg, 0.25 mmol) was added, followed by the addition of PBU_3 (12 mg, 0.075 mmol). The reaction was carried out at RT for 12 h (monitored by TLC). The reaction mixture was taken up by in ether (10 mL) and washed with brine (10 mL). The organic layer was dried (MgSO_4), concentrated in vacuo and purified by flash silica gel chromatography using petroleum ether : ethyl acetate = 10:1 as eluant to give *Z*-**3ac** (33 mg in sum, 0.08 mmol, 32 %) and *E*-**3ac** (33 mg in sum, 0.08 mmol, 32 %) as yellow oils.

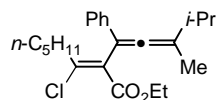


(*Z*)-Methyl 2-(1-chlorohexylidene)-5-ethyl-3-phenylnona-3,4-dienoate (*Z*-**3ac**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.298–7.254 (m, 4H), 7.190–7.156 (m, 1H), 3.660 (s, 3H), 2.890 (d, 2H, J =7.6 Hz), 2.167–2.106 (m, 4H), 1.725–1.752 (m, 2H), 1.377–1.250 (m, 8H), 1.066 (t, 3H, J =7.2 Hz), 0.923 (t, 3H, J =6.8 Hz), 0.865 (t, 3H, J =7.2 Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 201.0, 166.8, 151.2, 136.2, 128.3, 126.7, 126.3, 125.5, 111.7, 105.2, 51.9, 37.3, 32.4, 31.1, 29.8, 29.8, 29.6, 27.7, 26.0, 22.5, 22.3, 139, 13.9, 12.3; IR (neat): ν =3061, 2963, 1946, 1718, 1025, 767, 694; MS (70 eV): m/z (%): 390 [$\text{M}^+(\text{Cl})$], 388 [$\text{M}^+(\text{Cl})$], 331 (M^+-Cl), 251(100), 165, 90, 55; $\text{C}_{24}\text{H}_{33}\text{ClO}_2$: Calcd. C, 74.11; H, 8.55; Found: C, 74.42; H, 8.49.

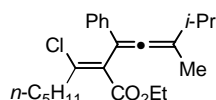


(*E*)-Methyl 2-(1-chlorohexylidene)-5-ethyl-3-phenylnona-3,4-dienoate (*E*-**3ac**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.377–7.358 (m, 2H), 7.316–7.254 (m, 2H), 7.206–7.170 (m, 1H), 3.705 (s, 3H), 2.388 (t, 2H, J =8 Hz), 2.140–2.101 (m, 4H), 1.455–1.065 (m, 10H), 1.047 (t, 3H, J =7.2 Hz), 0.859 (t, 3H, J =7.2 Hz), 0.800 (t, 3H, J =6.8 Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 201.2,

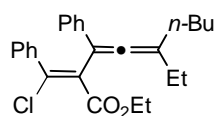
167.1, 141.6, 136.2, 128.4, 128.0, 127.0, 126.8, 126.0, 111.7, 103.7, 52.0, 36.7, 32.65, 31.2, 30.0, 27.0, 26.1, 22.7, 22.4, 13.9, 13.8, 12.2; IR(neat): ν =3064, 2963, 1946, 1720, 1027, 768, 694; MS (70 eV): m/z (%): 390 [$M^+(^{37}\text{Cl})$], 388 [$M^+(^{35}\text{Cl})$], 331 ($M^+-\text{Cl}$), 251(100), 165, 90, 55; $\text{C}_{24}\text{H}_{33}\text{ClO}_2$: Calcd. C, 74.11; H, 8.55; Found: C, 74.02; H, 8.47.



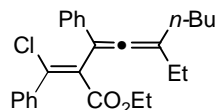
(*Z*)-Ethyl 3-chloro-2-(3,4-dimethyl-1-phenylpenta-1,2-dienyl)oct-2-enoate (**Z-3ad**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.270–7.259 (m, 4H), 7.170–7.138 (m, 1H), 4.083 (q, 2H, $J=7.2$ Hz), 2.912–2.822 (m, 2H), 2.296–2.262 (m, 1H), 1.807 (s, 3H), 1.728–1.693 (m, 2H), 1.355–1.338 (m, 4H), 1.167–1.078 (m, 8H), 0.905 (t, 3H, $J=6.8$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 201.1, 166.3, 150.6, 126.3, 128.3, 127.3, 126.7, 126.3, 126.1, 125.6, 110.7, 104.2, 61.0, 37.3, 33.1, 31.2, 27.7, 22.4, 21.6, 16.0, 14.0; IR (neat): ν =3059, 2964, 1946, 1720, 1023, 768, 694; MS (70 eV): m/z (%): 376 [$M^+(^{37}\text{Cl})$], 374 [$M^+(^{35}\text{Cl})$], 339 ($M^+-\text{Cl}$), 317 (100), 207, 193, 129, 105, 75, 43; $\text{C}_{23}\text{H}_{31}\text{ClO}_2$ Calcd. C, 73.68; H, 8.33; Found: C, 73.51; H, 8.28.



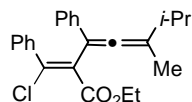
(*E*)-Ethyl 3-chloro-2-(3,4-dimethyl-1-phenylpenta-1,2-dienyl)oct-2-enoate (**E-3ad**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.352–7.329 (m, 2H), 7.295–7.257 (m, 2H), 7.188–7.152 (m, 1H), 4.152 (q, 2H, $J=7.2$ Hz), 2.412–2.359 (m, 2H), 2.295–2.261 (m, 1H), 1.788 (s, 3H), 1.552–1.425 (m, 2H), 1.204–1.079 (m, 13H), 0.802 (t, 3H, $J=6.8$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 201.1, 166.5, 141.3, 136.2, 128.4, 127.4, 126.7, 126.1, 110.3, 102.8, 61.0, 36.7, 33.1, 31.4, 31.2, 27.0, 22.4, 16.5, 14.0, 13.9; IR (neat): ν =3059, 2964, 1946, 1719, 1023, 769, 694; MS (70 eV): m/z (%): 376 [$M^+(^{37}\text{Cl})$], 374 [$M^+(^{35}\text{Cl})$], 339 ($M^+-\text{Cl}$), 317 (100), 207, 193, 129, 105, 75, 43; $\text{C}_{23}\text{H}_{31}\text{ClO}_2$ Calcd. C, 73.68; H, 8.33; Found: C, 73.49; H, 8.19.



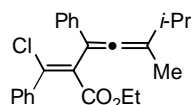
(*Z*)-Methyl 2-(chloro(phenyl)methylene)-5-ethyl-3-phenylnona-3,4-dienoate (**Z-3bc**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.406–7.357 (m, 4H), 7.286–7.240 (m, 2H), 7.203–7.160 (m, 4H), 4.220 (q, 2H, $J=7.2$ Hz), 1.799–1.744 (d, 2H, $J=7.2$ Hz), 1.654–1.596 (m, 2H), 1.382–1.346 (m, 2H), 1.232–1.125 (m, 5H), 0.842 (t, 3H, $J=7.2$ Hz), 0.781 (t, 3H, $J=7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 203.2, 166.8, 137.7, 136.6, 136.4, 129.0, 128.5, 128.4, 127.9, 126.6, 126.1, 111.1, 104.9, 61.3, 31.7, 29.6, 25.4, 22.6, 13.9, 13.8, 12.0; IR (neat): ν =3061, 2963, 1946, 1723, 1025, 765, 695; MS (70 eV): m/z (%): 410 [$M^+(^{37}\text{Cl})$], 408 [$M^+(^{35}\text{Cl})$], 373 ($M^+-\text{Cl}$), 327, 333, 257, 228, 105 (100), 77, 57; $\text{C}_{26}\text{H}_{29}\text{ClO}_2$ Calcd. C, 76.36; H, 7.15; Found: C, 76.56; H, 7.21.



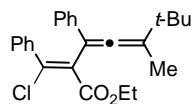
(*E*)-Methyl 2-(chloro(phenyl)methylene)-5-ethyl-3-phenylnona-3,4-dienoate (***E*-3bc**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.494–7.488 (m, 2H), 7.450–7.430 (m, 2H), 7.362–7.302 (m, 5H), 7.255–7.201 (m, 1H), 3.935 (q, 2H, *J*=7.2 Hz), 2.196–2.159 (m, 4H), 1.555–1.519 (m, 2H), 1.382–1.346 (m, 2H), 1.138 (t, 3H, *J*=7.2 Hz), 0.925–0.846 (m, 6H); ¹³C NMR (CDCl₃, 100 Hz): 201.4, 166.8, 141.5, 138.5, 135.7, 129.3, 128.5, 128.4, 128.2, 128.1, 126.6, 125.8, 112.3, 105.2, 61.1, 32.4, 29.8, 26.0, 22.5, 13.9, 13.6, 12.3; IR (neat): ν =3062, 2963, 1946, 1718, 1027, 765, 695; MS (70 eV): *m/z* (%): 410 [M⁺(³⁷Cl)], 408 [M⁺(³⁵Cl)], 373 (M⁺-Cl), 327, 333, 257, 228, 105 (100), 77, 57; C₂₆H₂₉ClO₂ Calcd. C, 76.36; H, 7.15; Found: C, 76.21; H, 7.09.



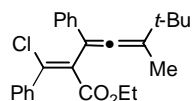
(*Z*)-Ethyl 2-(chloro(phenyl)methylene)-5,6-dimethyl-3-phenylhepta-3,4-dienoate (***Z*-3bd**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.391–7.335 (m, 4H), 7.282–7.239 (m, 2H), 7.210–7.140 (m, 4H), 4.182 (q, 2H, *J*=7.2 Hz), 2.040 (tt, 1H, *J*=6.8 Hz), 1.162 (t, 3H, *J*=7.2 Hz), 1.129 (s, 3H), 0.909 (d, 6H, *J*=7.2 Hz); ¹³C NMR (CDCl₃, 100 Hz): 203.2, 166.7, 138.0, 136.5, 129.0, 128.5, 128.4, 128.0, 126.7, 126.1, 110.3, 104.3, 61.3, 32.7, 21.2, 14.9, 13.9; IR (neat): ν =3059, 2963, 1947, 1721, 1021, 762, 695; MS (70 eV): *m/z* (%): 382 [M⁺(³⁷Cl)], 380 [M⁺(³⁵Cl)], 100], 345 (M⁺-Cl), 299, 271, 229, 104, 77; C₂₄H₂₅ClO₂ Calcd. C, 75.68; H, 6.62; Found: C, 75.53; H, 6.64.



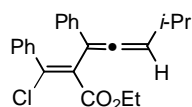
(*E*)-Ethyl 2-(chloro(phenyl)methylene)-5,6-dimethyl-3-phenylhepta-3,4-dienoate (***E*-3bd**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.495–7.471 (m, 2H), 7.416–7.286 (m, 7H), 7.206–7.188 (m, 1H), 3.944 (q, 2H, *J*=7.2 Hz), 2.349 (tt, 1H, *J*=7.2 Hz), 1.866 (s, 3H), 1.181 (dd, 6H, *J*=6.8 Hz), 0.894 (t, 3H, *J*=7.2 Hz); ¹³C-NMR (CDCl₃, 100 Hz): 201.4, 166.8, 141.5, 138.6, 135.8, 129.7, 129.3, 128.4, 128.3, 128.1, 126.6, 125.9, 111.4, 104.3, 31.1, 33.1, 21.5, 16.1, 13.6; IR (neat): ν =3060, 2964, 1947, 1721, 1021, 764, 695; MS (70 eV): *m/z* (%): 382 [M⁺(³⁷Cl)], 380 [M⁺(³⁵Cl)], 100], 345 (M⁺-Cl), 299, 271, 229, 104, 77; C₂₄H₂₅ClO₂ Calcd. C, 75.68; H, 6.62; Found: C, 75.45; H, 6.68.



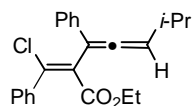
(*Z*)-Ethyl 2-(chloro(phenyl)methylene)-5,6,6-trimethyl-3-phenylhepta-3,4-dienoate (***Z*-3be**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.375–7.342 (m, 4H), 7.256–7.207 (m, 2H), 7.204–7.148 (m, 4H), 4.202 (q, 2H, *J*=7.2 Hz), 1.181 (t, 3H, *J*=7.2 Hz), 1.051 (s, 3H), 1.012 (s, 9H); ¹³C NMR (CDCl₃, 100 Hz): 203.1, 166.7, 138.0, 136.6, 136.5, 128.9, 128.5, 128.4, 128.0, 126.6, 126.0, 113.2, 103.7, 113.2, 103.7, 61.2, 34.9, 28.8, 13.9, 12.3; IR (neat): ν =3060, 2963, 1946, 1723, 1587, 1110, 761, 695; MS (70 eV): *m/z* (%): 396 [M⁺(³⁷Cl)], 394 [M⁺(³⁵Cl)], 359 (M⁺-Cl), 337 [M⁺-(*n*-butyl)], 229 (100), 104, 77, 57; C₂₅H₂₇ClO₂ Calcd. C, 76.03; H, 6.89; Found: C, 76.13; H, 6.85.



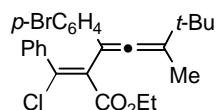
(*E*)-Ethyl 2-(chloro(phenyl)methylene)-5,6,6-trimethyl-3-phenylhepta-3,4-dienoate (***E*-3be**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.477–7.470 (m, 2H), 7.412–7.237 (m, 7H), 7.201–7.166 (m, 1H), 3.927 (q, 2H, J =7.9 Hz), 1.855 (s, 3H), 1.180 (s, 9H), 0.898 (t, 3H, J =7.9 Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 201.4, 166.8, 141.5, 138.6, 135.8, 129.3, 128.4, 128.3, 128.1, 126.5, 125.8, 114.3, 103.6, 61.1, 35.2, 29.1, 13.7, 13.5; IR (neat): ν =3059, 2963, 1946, 1718, 1587, 1098, 764, 695; MS (70 eV): m/z (%): 396 [$\text{M}^+(\text{}^{37}\text{Cl})$], 394 [$\text{M}^+(\text{}^{35}\text{Cl})$], 359 (M^+-Cl), 337 [$\text{M}^+-(n\text{-butyl})$], 229 (100), 104, 77, 57; $\text{C}_{25}\text{H}_{27}\text{ClO}_2$ Calcd. C, 76.03; H, 6.89; Found: C, 75.69; H, 6.71.



(*Z*)-Ethyl 2-(chloro(phenyl)methylene)-6-methyl-3-phenylhepta-3,4-dienoate (***Z*-3bf**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.380–7.333 (m, 4H), 7.269–7.192 (m, 6H), 5.175 (d, 1H, J =6.0 Hz), 4.229 (q, 2H, J =7.2 Hz), 2.068 (tt, 1H, J =6.8 Hz), 1.190 (t, 3H, J =7.2 Hz), 0.903–0.881 (m, 6H), ^{13}C NMR (CDCl_3 , 100 Hz): 205.0, 166.5, 137.7, 137.0, 135.6, 129.2, 128.9, 128.5, 128.0, 126.9, 126.3, 105.3, 102.2, 61.3, 28.3, 22.5, 22.3, 13.9; IR (neat): ν =3063, 2961, 1720, 1023, 761, 695; MS (70 eV): m/z (%): 368 [$\text{M}^+(\text{}^{37}\text{Cl})$], 366 [$\text{M}^+(\text{}^{35}\text{Cl})$], 331 [M^+-Cl], 100, 289, 257, 215, 165, 105, 91, 77; $\text{C}_{23}\text{H}_{23}\text{ClO}_2$ Calcd. C, 75.30; H, 6.32; Found: C, 75.78; H, 6.21.

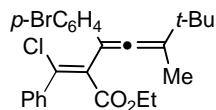


(*E*)-Ethyl 2-(chloro(phenyl)methylene)-6-methyl-3-phenylhepta-3,4-dienoate (***E*-3bf**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.477–4.440 (m, 2H), 4.437–4.418 (m, 2H), 7.367–7.294 (m, 5H), 7.239–7.201 (m, 1H), 5.755 (d, 1H, J =6.0 Hz), 3.944 (q, 2H, J =7.2 Hz), 2.579 (tt, 1H, J =6.4 Hz), 1.153–1.126 (m, 6H), 0.876 (t, 3H, J =7.2 Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 203.1, 166.6, 142.2, 138.6, 135.0, 133.0, 129.6, 128.7, 128.5, 126.9, 126.0, 105.6, 103.4, 61.2, 28.7, 22.7, 22.5, 13.5; IR (neat): ν =3063, 2962, 1721, 1023, 761, 695; MS (70 eV): m/z (%): 368 [$\text{M}^+(\text{}^{37}\text{Cl})$], 366 [$\text{M}^+(\text{}^{35}\text{Cl})$], 331 [M^+-Cl], 100, 289, 257, 215, 165, 105, 91, 77; $\text{C}_{23}\text{H}_{23}\text{ClO}_2$ Calcd. C, 75.30; H, 6.32; Found: C, 75.75; H, 6.27.

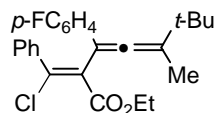


(*Z*)-Ethyl 3-(4-bromophenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (***Z*-3bg**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): δ =7.377–7.315 (m, 5H), 7.216–7.176 (m, 4H), 4.199 (q, 2H, J =7.2 Hz), 1.183 (t, 3H, J =7.2 Hz), 1.080 (s, 3H), 0.998 (s, 9H), ^{13}C NMR (CDCl_3 , 100 Hz): 203.0, 166.6, 137.8, 136.9, 135.7, 131.5, 129.1, 128.2, 128.1, 127.6, 120.4, 113.8, 103.0, 61.3, 35.0, 29.8, 13.9, 13.4; IR (neat): ν =3061, 2964, 1944, 1718, 1096, 762, 695; MS (70 eV): m/z (%): 474 [$\text{M}^+(\text{}^{81}\text{Br})$], 472 [$\text{M}^+(\text{}^{79}\text{Br})$], 393 [$\text{M}^+(\text{}^{35}\text{Cl})-\text{Br}$], 337 [$\text{M}^+-(n\text{-butyl})-\text{Br}$], 229 (100),

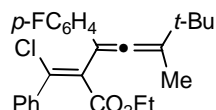
104, 77, 57; C₂₅H₂₆ClBrO₂ Calcd. C, 63.37; H, 5.53; Found: C, 63.77; H, 5.39.



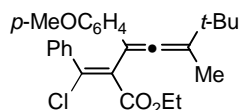
(*E*)-Ethyl 3-(4-bromophenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (***E*-3bg**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.459–7.450 (m, 2H), 7.425–7.403 (m, 2H), 7.364–7.265 (m, 3H), 7.265–7.240 (m, 2H), 3.929 (q, 2H, *J*=7.2 Hz), 1.846 (s, 3H), 1.158 (s, 9H), 0.904 (t, 3H, *J*=7.2 Hz); ¹³C NMR (CDCl₃, 100 Hz): 201.3, 166.6, 141.8, 138.3, 135.0, 132.9, 131.5, 129.4, 128.4, 127.4, 120.3, 114.9, 102.9, 61.2, 35.2, 29.0, 13.7, 13.6; IR (neat): ν =3061, 2963, 1944, 1718, 1096, 761, 695; MS (70 eV): *m/z* (%): 474 [M⁺(⁸¹Br)], 472 [M⁺(⁷⁹Br)], 415 [M⁺(*n*-butyl)], 393 [M⁺(³⁵Cl)-Br], 308, 229 (100), 105, 77, 57; C₂₅H₂₆ClBrO₂ Calcd. C, 63.37; H, 5.53; Found: C, 63.83; H, 5.46.



(*Z*)-Ethyl 3-(4-fluorophenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (***Z*-3bh**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.362–7.327 (m, 3H), 7.291–7.256 (m, 2H), 7.212–7.194 (m, 2H), 6.933–6.911 (m, 2H), 4.198 (q, 2H, *J*=7.2 Hz), 1.085 (s, 3H), 1.006 (s, 9H), 1.176 (t, 3H, *J*=7.2 Hz); ¹³C NMR (CDCl₃, 100 Hz): 202.8, 166.7, 163.0, 160.5, 137.9, 136.4, 132.5, 129.0, 128.4, 128.0, 127.7, 115.4, 115.1, 113.5, 102.8, 61.3, 34.9, 28.8, 13.7, 12.5; IR (neat): ν =3063, 2964, 1946, 1724, 1600, 1232, 1097, 762, 695; MS (70 eV): *m/z* (%): 474 [M⁺(⁸¹Br)], 472 [M⁺(⁷⁹Br)], 415 [M⁺(*n*-butyl)], 393 [M⁺(³⁵Cl)-Br], 308, 229 (100), 105, 77, 57; C₂₅H₂₆ClFO₂ Calcd. C, 72.72; H, 6.35; Found: C, 72.54; H, 6.41.

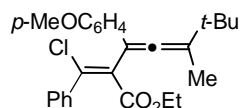


(*E*)-Ethyl 3-(4-fluorophenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (***E*-3bh**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.478–7.454 (m, 2H), 7.363–7.328 (m, 5H), 7.011–6.967 (m, 2H), 3.924 (q, 2H, *J*=7.2 Hz), 1.846 (s, 3H), 1.163 (s, 9H), 0.897 (t, 3H, *J*=7.2 Hz); ¹³C NMR (CDCl₃, 100 Hz): 201.1, 166.7, 163.0, 160.6, 141.5, 138.4, 131.8, 129.6, 129.4, 128.5, 127.3, 115.4, 115.2, 114.6, 102.8, 61.1, 35.2, 29.1, 13.9, 13.7; IR (neat): ν =3063, 2963, 1947, 1721, 1232, 1027, 764, 695; MS (70 eV): *m/z* (%): 414 [M⁺(³⁷Cl)], 412 [M⁺(³⁵Cl)], 377 (M⁺-Cl), 355 [M⁺(*n*-butyl)], 247 (100), 123, 105, 57; C₂₅H₂₆ClFO₂ Calcd. C, 72.72; H, 6.35; Found: C, 72.60; H, 6.38.

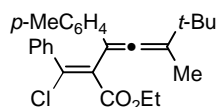


(*Z*)-Ethyl 3-(4-methoxyphenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (***Z*-3bk**): yellow oil; ¹H NMR (CDCl₃, 400 Hz): *d*=7.379–7.355 (m, 2H), 7.269–7.192 (m, 5H), 6.817–6.795 (m, 2H), 4.187 (q, 2H, *J*=7.2 Hz), 3.781 (s, 3H), 1.039 (s, 3H), 0.996 (s, 9H), 1.169 (t,

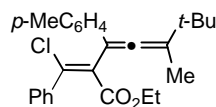
3H, $J=7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 202.3, 116.9, 158.6, 138.0, 136.0, 130.5, 128.9, 128.5, 128.1, 127.2, 113.9, 113.0, 103.2, 61.2, 55.2, 34.9, 28.8, 13.9, 12.4; IR (neat): $\nu=3060, 2960, 1946, 1716, 1605, 1249, 1097, 762, 695$; MS (70 eV): m/z (%): 426 [$\text{M}^+(\text{}^{37}\text{Cl})$], 424 [$\text{M}^+(\text{}^{35}\text{Cl})$], 389 (M^+-Cl), 367 [$\text{M}^+-(n\text{-butyl})$], 331, 287, 259, 215, 105 (100), 77, 57; $\text{C}_{26}\text{H}_{29}\text{ClO}_3$ Calcd. C, 73.48; H, 6.88; Found: C, 73.69; H, 6.78.



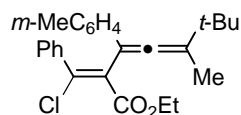
(*E*)-Ethyl 3-(4-methoxyphenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (**E-3bk**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): $\delta=7.477\text{--}7.462$ (m, 2H), 7.357–7.309 (m, 5H), 6.866–6.844 (m, 2H), 3.823 (q, 2H, $J=7.2$ Hz), 3.783 (s, 3H), 1.840 (s, 3H), 1.165 (s, 9H), 0.902 (t, 3H, $J=7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 200.6, 166.8, 158.5, 141.1, 138.6, 130.0, 129.3, 128.5, 128.1, 127.3, 127.0, 114.0, 113.6, 103.1, 61.0 55.3, 35.2, 29.1, 13.8, 13.6; IR (neat): $\nu=3061, 2963, 1946, 1716, 1605, 1249, 1097, 763, 694$; MS (70 eV): m/z (%): 426 [$\text{M}^+(\text{}^{37}\text{Cl})$], 424 [$\text{M}^+(\text{}^{35}\text{Cl})$], 389 (M^+-Cl), 367 [$\text{M}^+-(n\text{-butyl})$], 331, 287, 259, 215, 105 (100), 77, 57; $\text{C}_{26}\text{H}_{29}\text{ClO}_3$ Calcd. C, 73.48; H, 6.88; Found: C, 73.76; H, 6.82.



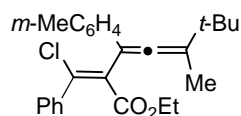
(*Z*)-Ethyl 3-(4-methylphenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (**Z-3bl**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): $\delta=7.379\text{--}7.356$ (m, 2H), 7.223–7.190 (m, 5H), 7.084–7.064 (m, 2H), 4.181 (q, 2H, $J=7.2$ Hz), 2.298 (s, 3H), 1.163 (t, 3H, $J=7.2$ Hz), 1.021 (s, 3H), 0.998 (s, 9H); ^{13}C NMR (CDCl_3 , 100 Hz): 202.7, 166.8, 138.1, 136.4, 133.6, 130.4, 129.1, 128.9, 128.5, 127.9, 126.0, 112.9, 103.5, 61.2, 34.9, 30.8, 28.8, 21.5, 13.9, 12.3; IR (neat): $\nu=3074, 3059, 2957, 1945, 1784, 1603, 1247, 1094, 767, 693$; MS (70 eV): m/z (%): 410 [$\text{M}^+(\text{}^{37}\text{Cl})$], 408 [$\text{M}^+(\text{}^{35}\text{Cl})$], 374 (M^+-Cl), 351 [$\text{M}^+-(n\text{-butyl})$], 243 (100), 228, 119, 91, 57; $\text{C}_{26}\text{H}_{29}\text{ClO}_2$ Calcd. C, 76.36; H, 7.15; Found: C, 76.10; H, 7.20.



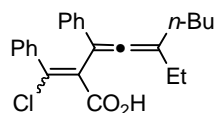
(*E*)-Ethyl 3-(4-methylphenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (**E-3bl**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): $\delta=7.497\text{--}7.473$ (m, 2H), 7.363–7.347 (m, 3H), 7.311–7.291 (m, 2H), 7.132–7.112 (m, 2H), 3.949 (m, 2H), 2.322 (s, 3H), 1.850 (s, 3H), 1.177 (s, 9H), 0.910 (t, 3H, $J=7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 200.9, 166.8, 141.2, 138.7, 136.3, 132.8, 129.2, 128.1, 128.0, 125.7, 114.1, 103.5, 61.2, 35.2, 29.1, 21.1, 13.8, 13.6; IR (neat): $\nu=3064, 2963, 1945, 1723, 1603, 1246, 1022, 767, 693$; MS (70 eV): m/z (%): 410 [$\text{M}^+(\text{}^{37}\text{Cl})$], 408 [$\text{M}^+(\text{}^{35}\text{Cl})$], 374 (M^+-Cl), 351 [$\text{M}^+-(n\text{-butyl})$], 243 (100), 228, 119, 91, 57; $\text{C}_{26}\text{H}_{29}\text{ClO}_2$ Calcd. C, 76.36; H, 7.15; Found: C, 76.19; H, 7.07.



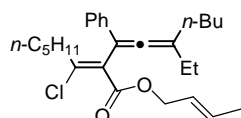
(*Z*)-Ethyl 3-(3-methylphenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (**Z-3bm**): yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 Hz): δ =7.378–7.354 (m, 2H), 7.217–7.182 (m, 3H), 7.151–7.137 (m, 3H), 6.967–6.959 (m, 1H), 4.185 (q, 2H, J =7.2 Hz), 2.229 (s, 3H), 1.161 (t, 3H, J =7.2 Hz), 1.025 (s, 3H), 1.009 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 100 Hz): 203.1, 166.8, 138.1, 137.9, 136.4, 136.3, 130.4, 128.9, 128.5, 128.3, 127.9, 127.4, 126.7, 123.3, 112.9, 103.5, 61.2, 34.9, 30.8, 28.8, 21.0, 13.9, 12.3; IR (neat): ν =3059, 2957, 1945, 1725, 1603, 1247, 1094, 765, 693; MS (70 eV): m/z (%): 410 [$\text{M}^+(\text{}^{37}\text{Cl})$], 408 [$\text{M}^+(\text{}^{35}\text{Cl})$], 374 (M^+-Cl), 351 [$\text{M}^-(n\text{-butyl})$], 324, 243 (100), 228, 207, 105, 91, 77, 57; $\text{C}_{26}\text{H}_{29}\text{ClO}_2$ Calcd. C, 76.36; H, 7.15; Found: C, 76.73; H, 7.11.



(*E*)-Ethyl 3-(3-methylphenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (**E-3bm**): yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 Hz): δ =7.493–7.469 (m, 2H), 7.368–7.346 (m, 3H), 7.213–7.190 (m, 3H), 7.022–6.962 (m, 1H), 3.919–3.901 (m, 2H), 2.328 (s, 3H), 1.850 (s, 3H), 1.179 (s, 9H), 0.90 (t, 3H, J =7.2 Hz); $^{13}\text{C NMR}$ (CDCl_3 , 100 Hz): 201.4, 166.8, 141.3, 138.7, 137.9, 135.7, 129.3, 128.3, 128.3, 127.4, 126.4, 123.0, 114.1, 103.7, 61.2, 35.2, 29.1, 21.1, 13.8, 13.6; IR (neat): ν =3059, 2966, 1717, 1652, 1247, 1094, 765, 693; MS (70 eV): m/z (%): 410 [$\text{M}^+(\text{}^{37}\text{Cl})$], 408 [$\text{M}^+(\text{}^{35}\text{Cl})$], 374 (M^+-Cl), 351 [$\text{M}^-(n\text{-butyl})$], 324, 243 (100), 228, 207, 105, 91, 77, 57; $\text{C}_{26}\text{H}_{29}\text{ClO}_2$ Calcd. C, 76.36; H, 7.15; Found: C, 76.73; H, 7.11.

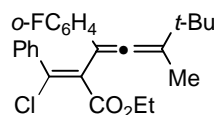


2-(Chloro(phenyl)methylene)-5-ethyl-3-phenylnona-3,4-dienoic acid: a mixture of *Z* and *E* isomers (**3cc**: Z/E =45:55): deep yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 Hz): δ =7.493–7.479 (m), 7.397–7.316 (m), 7.291–7.240 (m), 7.224–7.167 (m), 2.156–2.149 (m), 1.778–1.759 (m), 1.744–1.586 (m), 1.534–1.522 (m), 1.125–1.079 (m), 0.848–0.735 (m); $^{13}\text{C NMR}$ (CDCl_3 , 100 Hz): 203.4, 201.4, 170.8, 169.5, 142.4, 138.0, 137.8, 136.5, 135.6, 135.1, 133.4, 130.1, 129.5, 129.2, 128.4, 128.0, 126.7, 126.0, 125.7, 31.6, 29.8, 26.5, 25.4, 22.5, 13.7, 13.5, 12.1; IR (neat): ν =3059, 2960, 2930, 1946, 1700, 1263, 1027, 762, 696; MS (70 eV): m/z (%): 382 [$\text{M}^+(\text{}^{37}\text{Cl})$], 380 [$\text{M}^+(\text{}^{35}\text{Cl})$], 345 (M^+-Cl), 228 (100), 191, 77, 55; $\text{C}_{24}\text{H}_{25}\text{ClO}_2$ Calcd. C, 75.68; H, 6.62; Found: C, 75.22; H, 6.68.

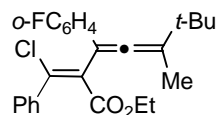


(*Z*)-(But-2-enyl) 2-(1-chlorohexylidene)-5-ethyl-3-phenylnona-3,4-dienoate (**Z-3dc**): yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 Hz): δ =7.294–7.259 (m, 4H), 7.165–7.123 (m, 1H), 5.656–5.602 (m, 1H), 5.457–5.415 (m, 1H), 4.620 (d, 2H, J =6.4 Hz), 2.831 (t, 2H, J =7.8 Hz), 2.126–2.089 (m, 4H), 1.765–1.723 (m, 2H), 1.640–1.606 (m, 2H), 1.550 (m, 2H), 1.352–1.238 (m, 7H), 1.052 (t, 3H,

$J=7.6$ Hz), 0.904 (t, 3H, $J=7.2$ Hz), 0.848 (t, 3H, $J=7.6$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 201.2, 166.14, 150.2, 136.3, 131.1, 130.0, 128.2, 127.2, 125.6, 124.8, 124.0, 111.5, 105.1, 65.5, 60.6, 37.2, 32.3, 31.1, 29.9, 27.7, 26.0, 22.5, 22.4, 17.6, 14.0, 12.9, 12.4; IR (neat): $\nu=3027$, 2960, 2860, 1947, 1715, 1603, 1027, 765, 694; MS (70 eV): m/z (%): 373 [$\text{M}^+(\text{}^{37}\text{Cl})\text{-crotyl}$], 370 [$\text{M}^+(\text{}^{35}\text{Cl})\text{-crotyl}$, 100], 337($\text{M}^+\text{-Cl-crotyl}$), 319, 164, 55; $\text{C}_{27}\text{H}_{37}\text{ClO}_2$ Calcd. C, 75.59; H, 8.69; Found: C, 75.21; H, 8.61.



(*Z*)-Ethyl 3-(2-fluorophenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (***Z*-3bq**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): $\delta=7.453\text{--}7.436$ (m, 2H), 7.371–7.327 (m, 4H), 7.191–7.172 (m, 1H), 7.091–7.055 (m, 1H), 7.053–6.954 (m, 1H), 3.915 (q, 2H, $J=7.2$ Hz), 1.819 (s, 3H), 1.145 (s, 9H), 0.889 (t, 3H, $J=7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 Hz): 203.8, 166.6, 161.5, 159.0, 140.5, 130.1, 129.2, 128.8, 128.2, 123.9, 116.0, 115.8, 112.5, 98.3, 61.0, 34.7, 28.8, 13.9, 13.8; IR (neat): $\nu=3062$, 2964, 1946, 1717, 1265, 1095, 758, 697; MS (70 eV): m/z (%): 414 [$\text{M}^+(\text{}^{37}\text{Cl})$], 412 [$\text{M}^+(\text{}^{35}\text{Cl})$], 377 ($\text{M}^+\text{-Cl}$), 355 [$\text{M}^+\text{-(}n\text{-butyl)}$], 326, 247, 105, 77, 57; $\text{C}_{25}\text{H}_{26}\text{ClFO}_2$ Calcd. C, 72.72; H, 6.35; Found: C, 72.55; H, 6.42.



(*E*)-Ethyl 3-(2-fluorophenyl)-2-(chloro(phenyl)methylene)-5,6,6-trimethylhepta-3,4-dienoate (***E*-3bq**): yellow oil; ^1H NMR (CDCl_3 , 400 Hz): $\delta=7.363\text{--}7.339$ (m, 2H), 7.240–7.200 (m, 1H), 7.176–7.160 (m, 3H), 7.023–6.975 (m, 1H), 6.950–6.891 (m, 1H), 6.831–6.798 (m, 1H), 4.208 (q, 2H, $J=7.2$ Hz), 1.194 (t, 3H, $J=7.2$ Hz), 1.027 (s, 9H), 1.169 (s, 3H); ^{13}C NMR (CDCl_3 , 100 Hz): 205.2, 166.6, 161.1, 158.6, 137.8, 134.5, 130.8, 129.5, 129.2, 128.5, 128.1, 124.4, 123.7, 123.6, 115.8, 111.7, 98.1, 61.2, 34.6, 28.6, 14.0, 12.7; IR (neat): $\nu=3066$, 2964, 1946, 1720, 1265, 1092, 761, 697; MS (70 eV): m/z (%): 414 [$\text{M}^+(\text{}^{37}\text{Cl})$], 412 [$\text{M}^+(\text{}^{35}\text{Cl})$], 377 ($\text{M}^+\text{-Cl}$), 355 [$\text{M}^+\text{-(}n\text{-butyl)}$], 326, 247, 105, 77, 57; $\text{C}_{25}\text{H}_{26}\text{ClFO}_2$ Calcd. C, 72.72; H, 6.35; Found: C, 72.83; H, 6.39.