Supporting Information

Exploring the growth inhibition potential of monoketone curcuminoids against *Spodoptera frugiperda*

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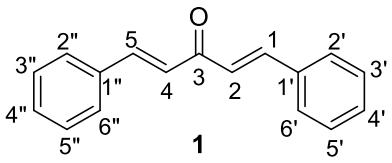
Experimental

^{1}H and ^{13}CNMR, and DEPT 135 experiments were performed on a Bruker Avance DRX400 spectrometer (Karlsruhe, Germany, 400.13 MHz for 1H and 100.61 MHz for ^{13}C). A direct 5-mm probe head (BBO) was used for ^{13}C{^{1}HNMR experiments, and an inverse 5-mm probe head (BBI) was used for other experiments. Experiments were performed at 300 K, and the concentrations for all samples were in the range of 10-15 mg mL^{-1}, in $CDCl_3$ using tetramethylsilane (TMS) as an internal reference.

ESI mass spectra were recorded on triple quadrupole MS equipment (QqQ) Xevo TQS (Waters, Milford, MA, USA) equipped with Z-spray operating in the positive ion mode and an Acquiti-H class UPLC system. The sample was dissolved in methanol/water (9:1, v/v) at a concentration of 0.5 mg mL^{-1} and infused directly into the ESI source by using a Harvard Apparatus system (model 1746, Houston, MA, USA) at a flow rate of 5 µL min^{-1}. The capillary voltage was 3.20 kV, and the gas flow was 700 L/h (0.15 V). The desolvation temperature was set at 250ºC.

EI-MS spectra were recorded on a gas chromatography-mass spectrometry (GC-MS) on a Shimadzu QP2010 Plus (Shimadzu Corporation, Kyoto, Japan) system equipped with an AOC-20i autosampler. The column consisted of Rtx-5MS (Restek Co., Bellefonte, PA, USA) fused silica capillary (30-m length x 0.25-mm i.d. x 0.25-µm film thickness). The electron ionization mode was used at 70 eV. Helium (99.999%) was employed as the carrier gas at a constant flow of 1.0 mL/min. The injection volume was 0.1 µL (split ratio of 1:10). The injector and the ion-source temperatures were set at 240 and 280 ºC, respectively. The oven temperature program was the same as the one used for GC. Mass spectra were taken with a scan interval of 0.5 s, in the mass range from 40 to 600 Da.



(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one (**1**). Yellowish solid, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. **S1a**): 7.10 (2H, *d*, $J_{4,5=2,1}$ = 16.0 Hz, H4=H2), 7.41 (6H, *m,* H3'=H3"=H5'=H5", and H6'=H6"), 7.62 (2H, *m*, H4'=H4"), 7.76 (2H, *d*, $J_{5,4=1,2}$ = 16.0 Hz, H1=H5). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. **S1b**): 125.6 (C2=C4), 128.5 (C2'=C2"=C6'=C6"), 129.1 (C3'=C5'=C3"=C5"), 130.6 (C4'=C4"), 134.9 (C1'=C1"), 143.5 (C1=C5), 189.1 (C3). EI-MS (*m/z*, relative intensity, Fig. **S1c**): 234 (100%, $M^{\bullet+}$), 131 (40%, $[M\text{-}C_8H_7^{\bullet}]^+$), 103 (62%, $[M\text{-}C_8H_7^{\bullet}\text{-CO}$), 77 (48%, $C_6H_5^+$).

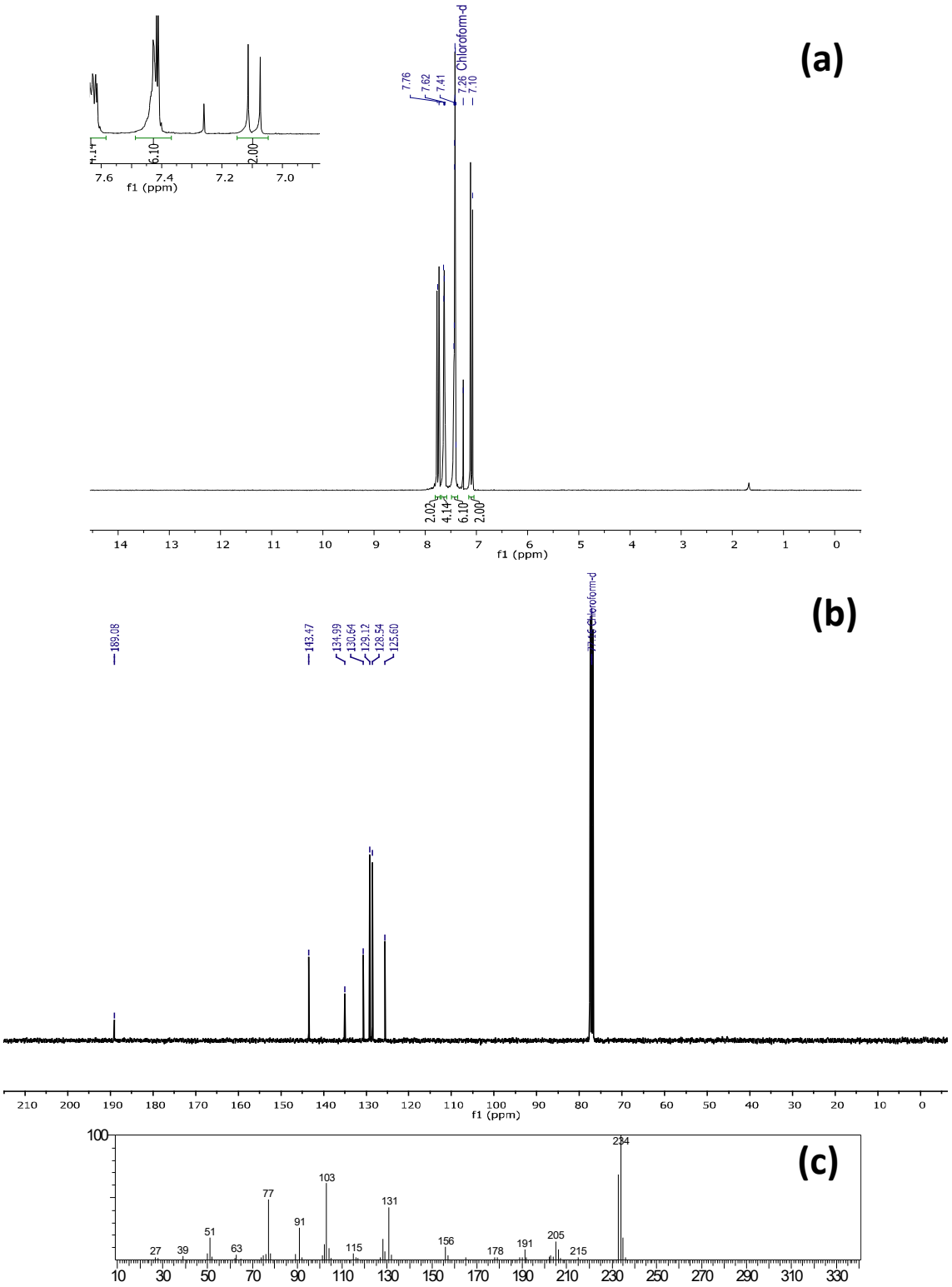
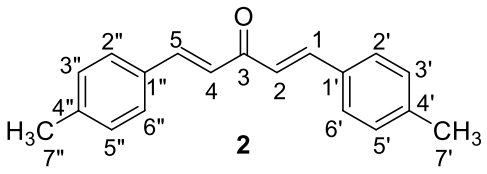


Figure S1. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, $CDCl_3$, TMS) and mass spectrum (**c**) (EI-MS, 70 eV) of compound **1**.



(1*E*,4*E*)-1,5-di-*p*-tolylpenta-1,4-dien-3-one (2). Yellow solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. **S2a**): 2.55 (6 H, *s*, H7'=H7"), 7.07 (2 H, *d*, $J_{4,5=2,1}$= 16.0 Hz, H2=H4), 7.25 (4 H, *d*, $J_{5'6'=5",6"=3',2'=3",2"}$=8.0 Hz, H3'=H3"=H5'=H5"), 7.54 (4 H, *d,* $J_{6',5'=6",5"=2',3'=2",3"}$= 8.0 Hz, H6'=H6"=H2'=H2"), 7.75 (2 H, *d*, $J_{5,4=1,2}$ = 16.0 Hz, H1=H5). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. **S2b**): 21.6 (C7'=C7"), 124.8 (C2=C4), 128.5 (C2'=C2"=C6'=C6"), 129.8 (C3'=C3"=C5'=C5"), 132.3 (C1'=C1"), 141.0 (C4'=C4"), 143.3 (C1=C5), 189.2 (C3). EI-MS (*m/z*, relative intensity, Fig. **S2c**): 262 (65%, $M^{\bullet+}$), 261 (45%, $[M\text{-}H^{\bullet}]^{+}$), 247 (100%, $[M\text{-}CH_3^{\bullet}]^{+}$), 115 (50%, $C_9H_7^{+}$).

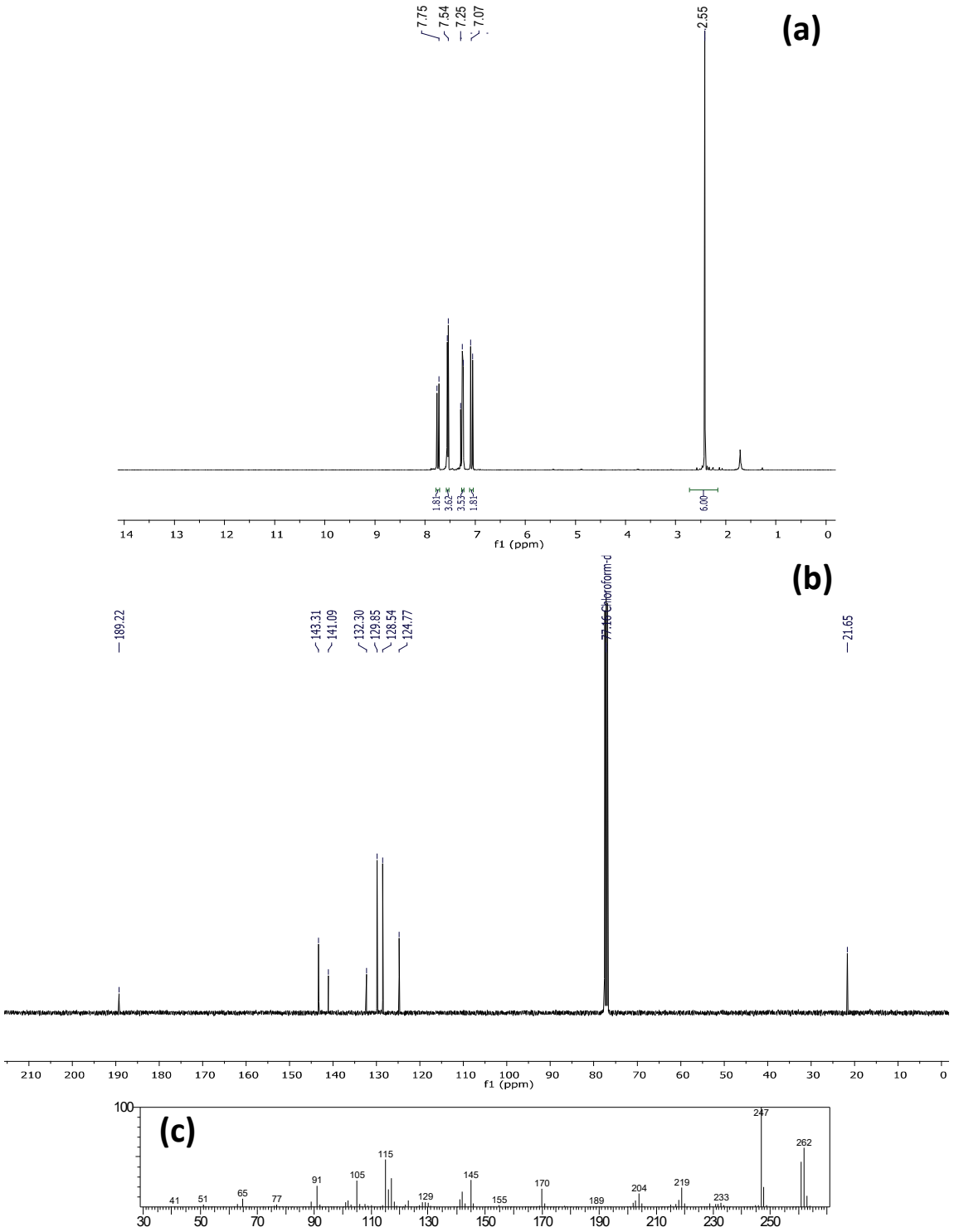
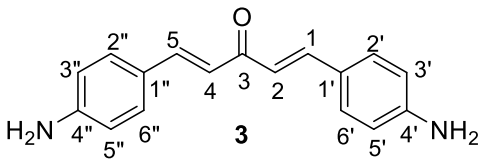


Figure 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, $CDCl_3$, TMS) and mass spectrum (**c**) (EI-MS, 70 eV) of compound **2.**



(1*E*,4*E*)-1,5-*bis*(4-aminophenyl)penta-1,4-dien-3-one (3). Orange solid, 67 % yield. ^{1}H NMR (400 MHz, CD_2Cl_2, Fig. **S3a**): 6.68 (4 H, *d*, $J_{3',2'=5',6'}$= 8.0 Hz, H3'=H3"=H5'=H5",), 6.88 (2 H, *d*, $J_{4,5=2,1}$= 16.0 Hz, H2=H4), 7.66 (4 H, *d,* $J_{2',3'=6',5'}$ = 8.0 Hz, H2'=H2"=H6'=H6"), 7.82 (2 H, *d*, $J_{5,4=1,2}$ = 16.0 Hz, H1=H5). ^{13}C NMR (100 MHz, CD_2Cl_2, Fig. **S3b**): 112.1 (C3'=C3"=C5'=C5"), 121.5 (C2=C4), 123.2 (C1'=C1"), 130.2 (C2'=C2"=C6'=C6"), 143.0 (C1=C5), 151.9 (C4'=C4"), 189.0 (C3). ESI(+)-MS (*m/z*, relative intensity, **Fig. S3c**): 297 (25 %, $[M+Na]^+$), 265 (100 %, $[M+H]]^+$)

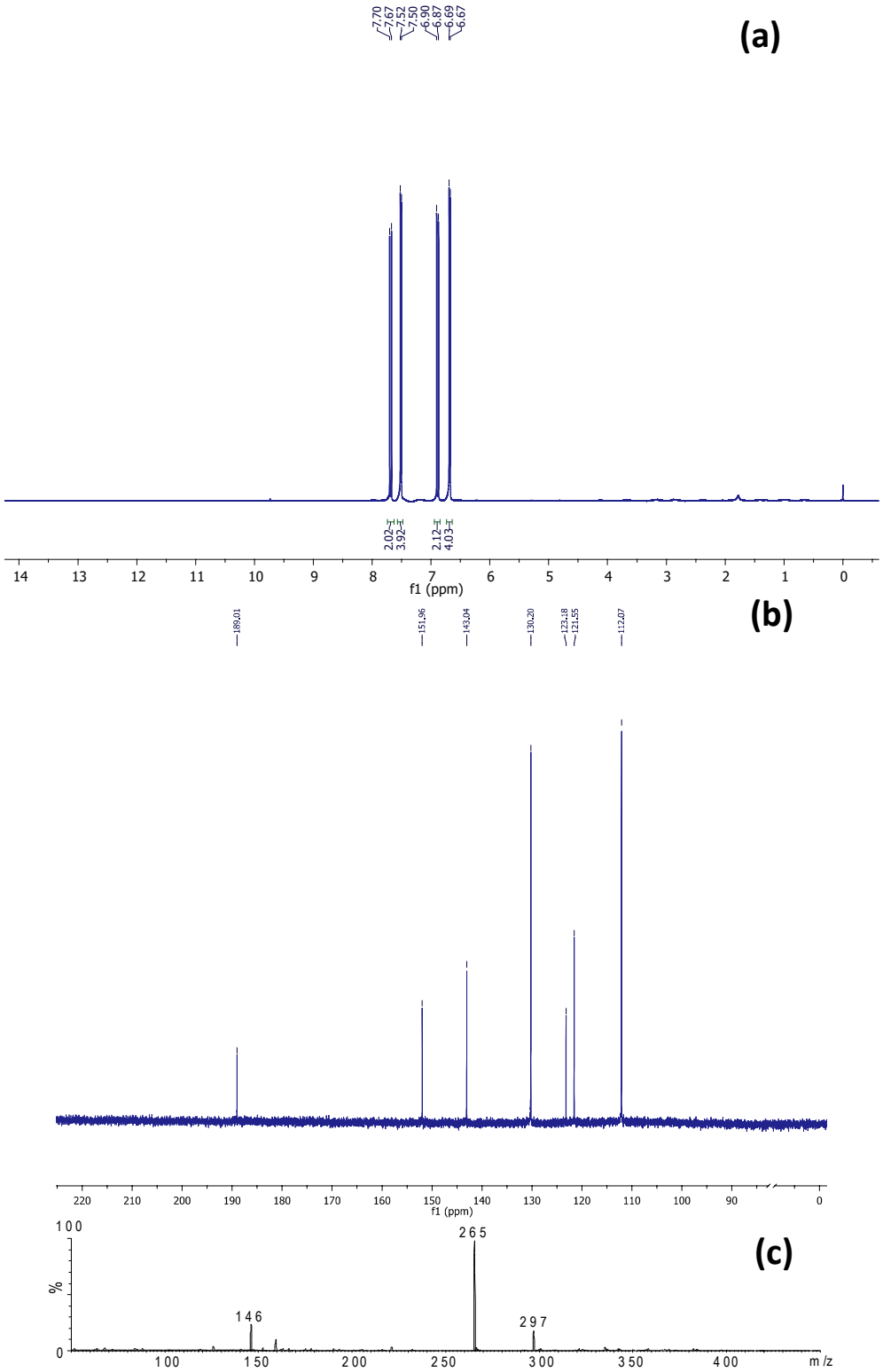
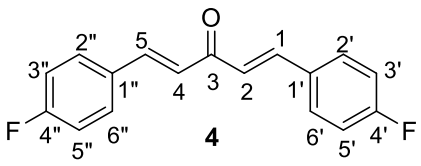


Figure S3. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, CD_2Cl_2, TMS) and mass spectrum (**c**) (ESI(+)-MS, full scan) of compound **3.**



(1*E*,4*E*)-1,5-*bis*(4-fluorophenyl)penta-1,4-dien-3-one (4). White solid, 55% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, Fig. **S4a**): 7.05 (2 H, *d*, $J_{4,5=2,1}$= 16.0 Hz, H2=H4), 7.32 (4 H, *d*, $J_{3',2'=5',6'}$= 8.0 Hz, H3'=H3"=H5'=H5",), 7.39 (4 H, *d*, $J_{2',3'=6',5'}$ = 8.0 Hz, H2'=H2"=H6'=H6"), 7.69 (2 H, *d*, $J_{5,4=1,2}$ = 16.0 Hz, H1=H5). ^{13}C NMR (100 MHz, CD_2Cl_2, Fig. **S4b**): 114.7 (C3'=C3"=C5'=C5"), 126.5 (C2=C4), 130.6 (C2'C2"=C6'=C6"), 137.7 (C1'=C1"), 142.3 (C1=C5), 164.2 (C4'=C4"), 188.4 (C3). EI-MS (*m/z*, relative intensity, Fig. **S4c**): 270 (100%, $M^{\bullet+}$), 149 (30%, $M^{\bullet+}$-$C_8H_6F^{\bullet}$), 121 (55%, $M^{\bullet+}$-$C_8H_6F^{\bullet}$-CO), 101 ($C_8H_5^{+}$, 100%).

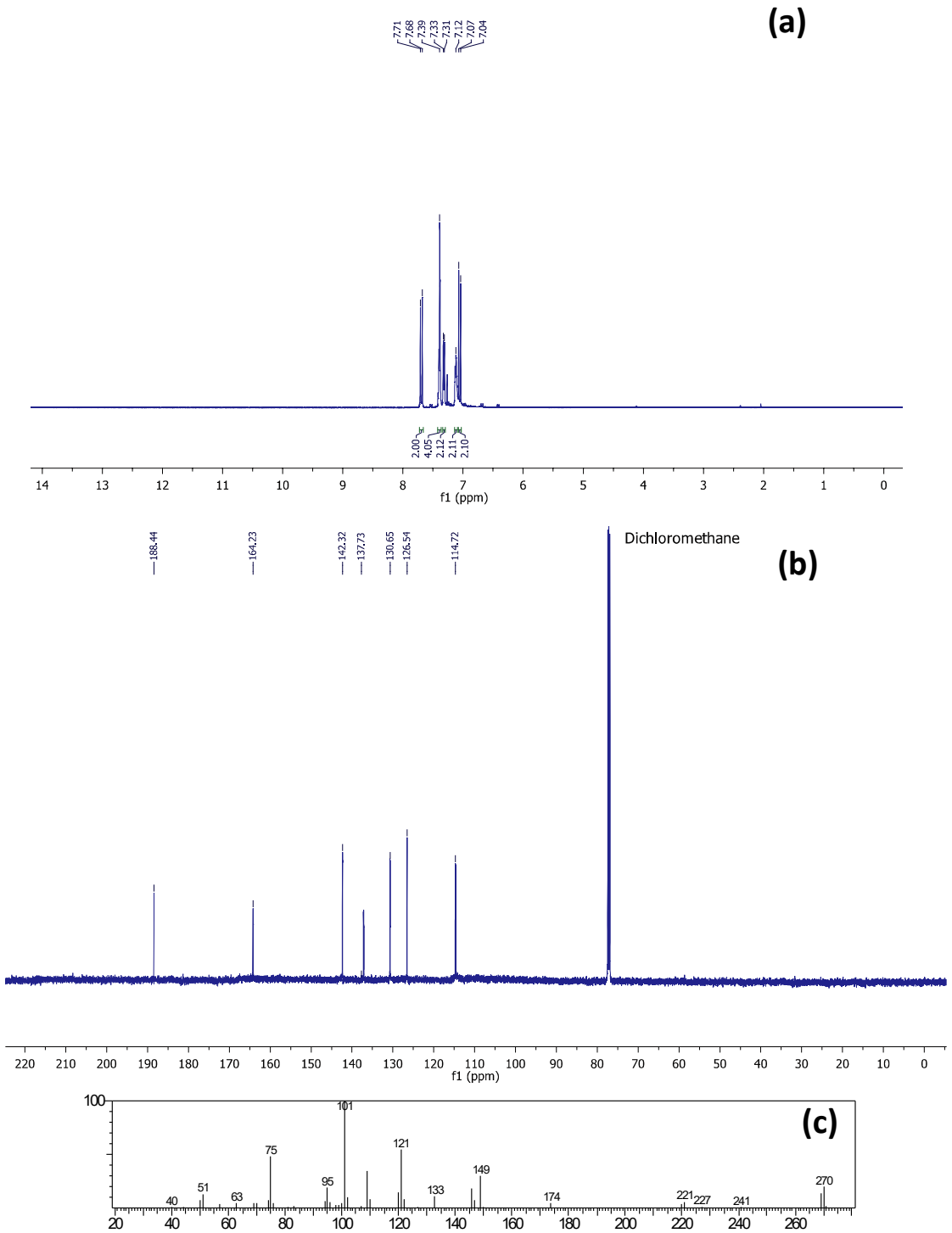
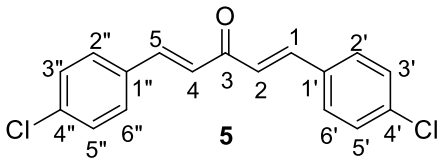


Figure S4. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, CD_2Cl_2, TMS) and mass spectrum (**c**) (EI-MS, 70 eV) of compound **2.**



(1*E*,4*E*)-1,5-*bis*(4-chlorophenyl)penta-1,4-dien-3-one (5). Yellowish solid, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. **S5a**): 7.05 (2 H, *d*, $J_{4,5=2,1}$= 16.0 Hz, H2=H4), 7.40 (4 H, *d*, $J_{3',2'=5',6'}$= 8.0 Hz, H3'=H3"=H5'=H5"), 7.55 (4 H, *d,* $J_{2',3'=6',5'}$ = 8.0 Hz, H2'=H2"=H6'=H6"), 7.68 (2 H, *d*, $J_{5,4=1,2}$ = 16.0 Hz, H1=H5). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. **S5b**): 126.1 (C2=C4), 129.4 (C3'=C3"=C5'=C5"), 129.7 (C2'=C2"=C6'=C6"), 133.4 (C1'=C1"), 136.7 (C4'=C4"), 142.2 (C1=C5), 188.7 (C3). EI-MS (*m/z*, relative intensity, Fig. **S5c**): 302/304/306 (75 %, 9:6:1, $M^{\bullet+}$, $M^{\bullet+}$+1, $M^{\bullet+}$+2), 267 (80 %, $[M–Cl^{\bullet}]^{+}$), 101 (100 %, $C_8H_5^{+}$)

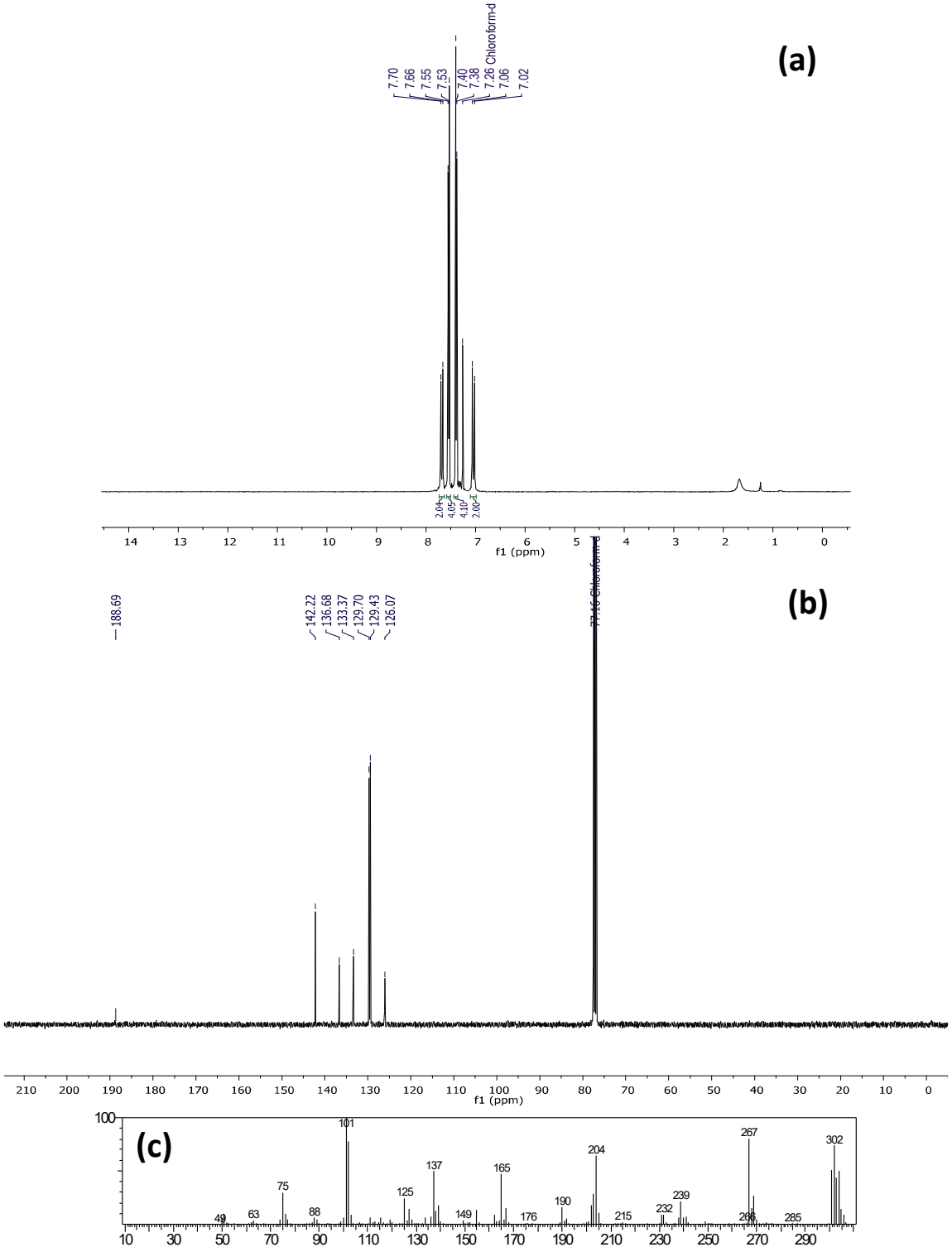
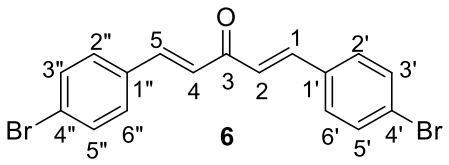


Figure S5. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, $CDCl_3$, TMS) and mass spectrum (**c**) (EI-MS, 70 eV) of compound **5.**



(1*E*,4*E*)-1,5-*bis*(4-bromophenyl)penta-1,4-dien-3-one (6). Yellowish solid, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. **S6a**): 7.05 (2H, *d*, $J_{2,1=4,5}$= 16.0 Hz, H2=H4), 7.48 (4H, *d*, $J_{2',3'=5',6'}$ = 8.4 Hz, H2'=H2"=H6'=H6"), 7.56 (4 H, *d*, $J_{3',2'}$=8.4 Hz, H3'=H3"=H5'=H5"), 7.67 (2H, *d*, $J_{1,2=5,4}$ = 16.0 Hz, H1=H5). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. **S6b**): 125.1 (C4'=C4"), 126.0 (C2=C4), 129.9 (C3'=C3"=C5'=C5"), 132.4 (C2'=C2"=C6'=C6"), 133.8 (C1'=C1"), 142.3 (C1=C5), 188.5 (C3). EI-MS (*m/z*, relative intensity, Fig. **S6c**): 392/394/396 (1:2:1, $M^{\bullet+}$, $M^{\bullet+}$+2, $M^{\bullet+}$+4), 311/313 (30%, 1:1, $[M - {\bullet}Br]^+$), 102 (100 %, $C_8H_6^{\bullet+}$).

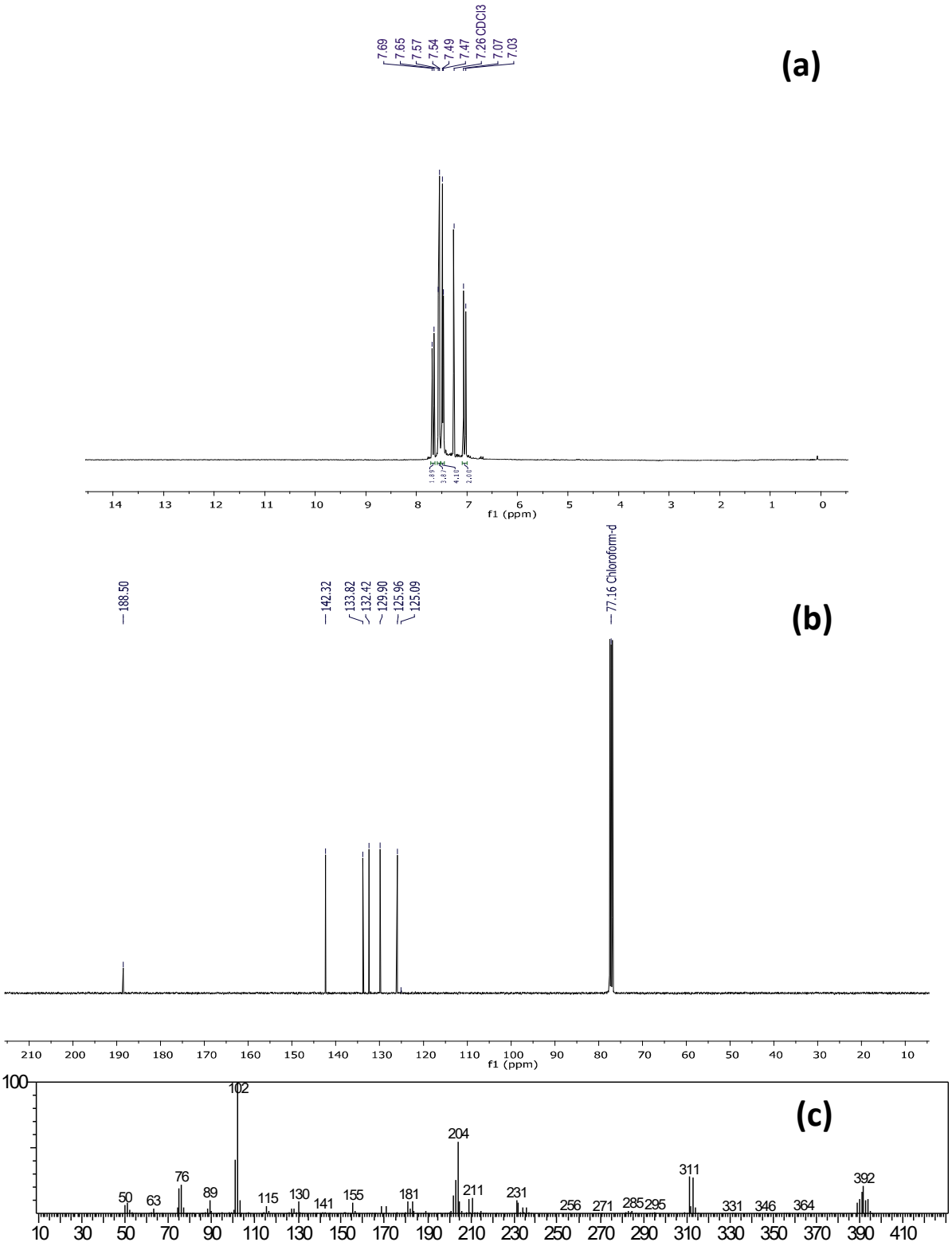
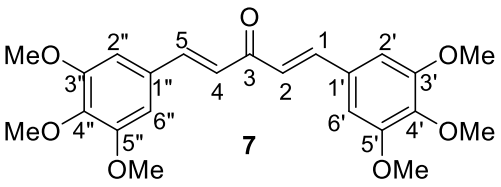


Figure S6. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, $CDCl_3$, TMS) and mass spectrum (**c**) (EI-MS, 70 eV) of compound **6.**



(1*E*,4*E*)-1,5-*bis*(3,4,5-trimethoxyphenyl)penta-1,4-dien-3-one (**7**). Yellow solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. **S7a**): 3.84 (18 H, *s*, 9 OMe), 6.84 (4 H, *s*, H2'=H2"=H6'=H6"), 6.97 (2H, *d*, $J_{2,1=4,5}$=15.8 Hz, H2=H4), 7.66 (2 H, *d*, $J_{1,2=5,4}$ = 15.8 Hz, H1=H5). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. **S7b**): 56.5 (3'=3"=5'=5"-OCH_3), 60.9 (4=4"-OCH_3), 106.1 (C2'=C2"=C6'=C6"), 125.2 (C2=C4), 130.6 (C1'=C1"), 140.9 (C4'=C4"), 143.8 (C1=C5), 153.9 (C3'=C3"=C5'=C5"), 188.9 (C3). ESI(+)-MS (*m/z*, relative intensity, **Fig. S7c**): 437 (100 %, $[M+Na]^+$), 415 (40 %, $[M+H]^+$)

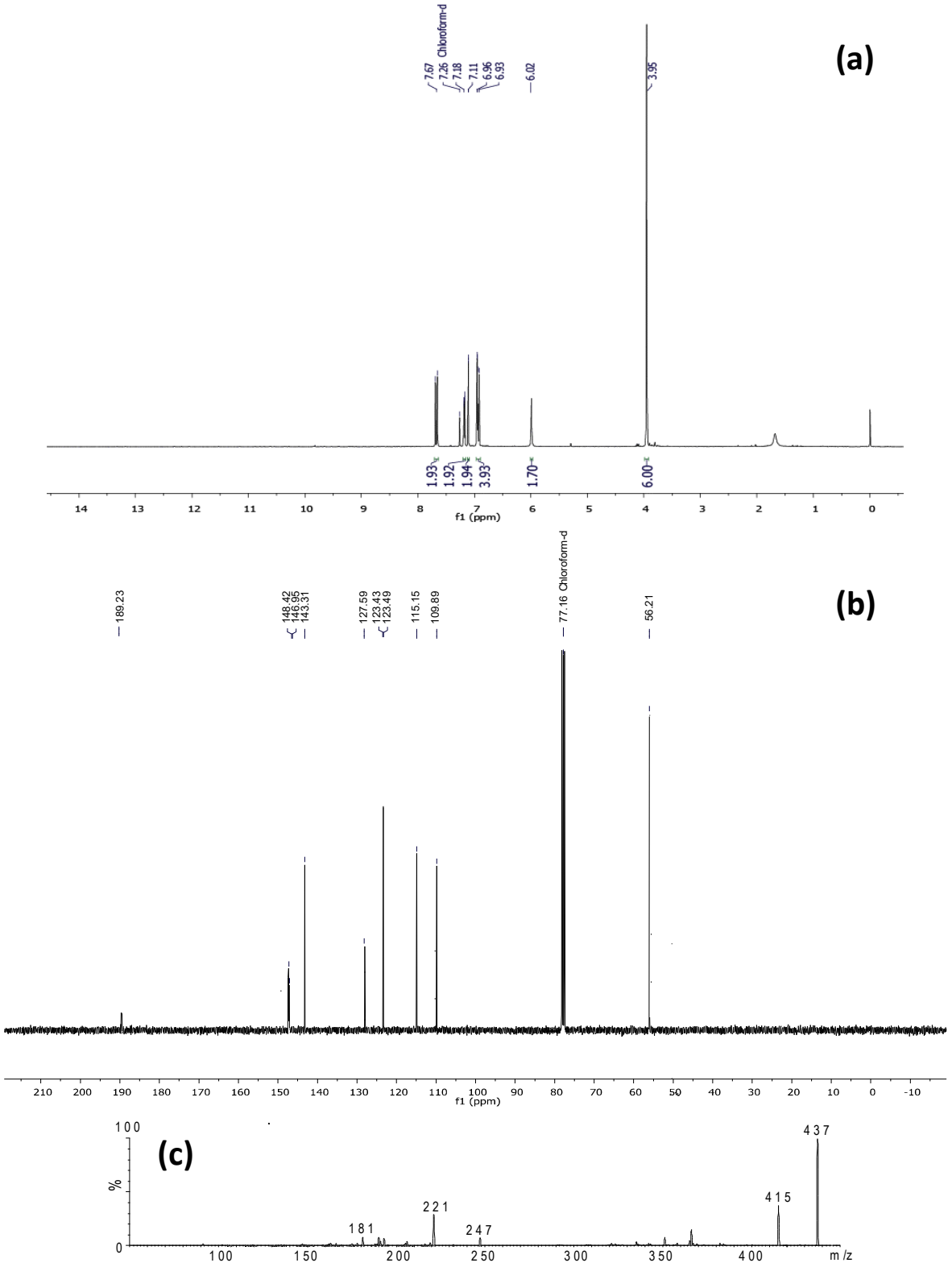
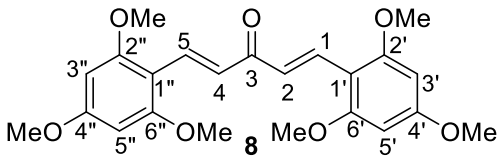


Figure S7. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, $CDCl_3$, TMS) and mass spectrum (**c**) (ESI(+)-MS, full scan) of compound **7.**



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(1*E*,4*E*)-1,5-*bis*(2,4,6-trimethoxyphenyl)penta-1,4-dien-3-one (**8**). Yellow solid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. **S8a**): 3.81 (6 H, s, H8'), 3.84 (12 H, *s*, H7'=H9'), 6.12 (4 H, *s*, H3'=H3"=H5'=H5"), 7.08 (2H, *d*, $J_{2,1=4,5}$=16.5 Hz, H2=H4), 7.96 (2 H, *d*, $J_{1,2=5,4}$ = 16.5 Hz, H1=H5). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. **S8b**): 55.8 (C8'=C8"), 56.2 (C7'= C7"=C9'=C9"), 90.9 (C3'=C3"=C5'=C5"), 106.2 (C1'=C1"), 128.0 (C2=C4), 135.4 (C1=C5), 161.9 (C2'=C2"=C6'=C6"), 163.5 (C4'=C4"), 201.1 (C3). ESI(+)-MS (*m/z*, relative intensity, **Fig. S8c**): 437 (50 %, $[M+Na]^+$), 415 (100 %, $[M+H]]^+$)

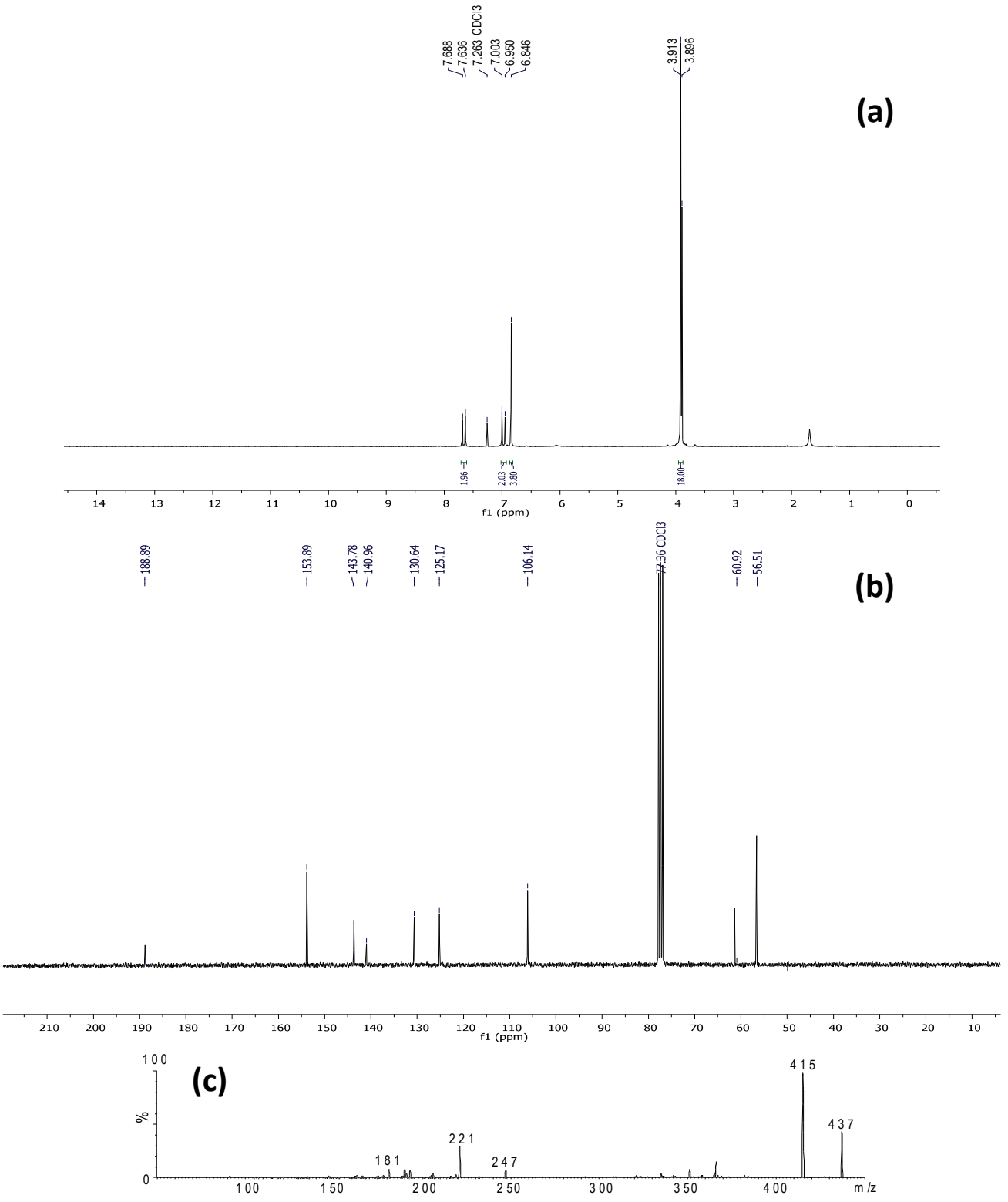

Figure S8. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectrum (**a** and **b**, respectively, $CDCl_3$, TMS) and mass spectrum (**c**) (ESI(+)-MS, full scan) of compound **8.**