Supporting Information

Structure-Activity Relationship Study of Xanthoxyline and Related Small Methyl Ketone Herbicides

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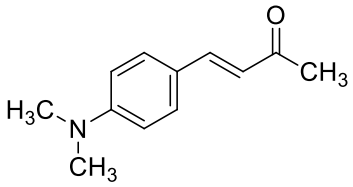
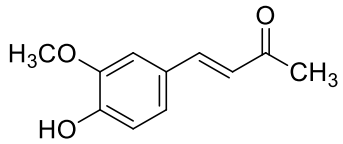
1. Spectroscopic data for some synthesized compounds in Figure 2

(*E*)-4-(4-(Dimethylamino)phenyl)but-3-en-2-one (52)



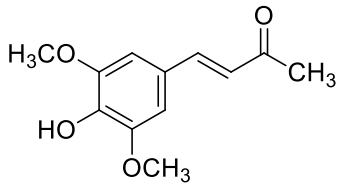
The title compound was prepared according to General Procedure from 4-(dimethylamino)benzaldehyde for a reaction time of 8 h and purified by recrystallization (MeOH) to afford an orange solid (158.5 mg, 83.75%).
m.p. 122-123 °C (MeOH);
R_f = 0.46 (70% EtOAc/hexane);
IR (film) 2912, 1670 (C=O), 1587, 1524, 1358, 1256, 1184, 972, 808, 735 cm^{-1};
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (3H, m, C**H**=CHCO and Ar**H**), 6.69 – 6.66 (2H, m, Ar**H**), 6.54 (1H, d, *J* = 16.1 Hz, CH=C**H**CO), 3.03 (6H, s, N(C**H**$_3$)$_2$), 2.34 (3H, s, C**H**$_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 198.54 (C=O), 151.93 (C), 144.38 (CH), 130.04 (2 × CH), 122.39 (CH), 121.95 (C), 111.83 (2 × CH), 40.11 (2 × CH_3), 27.14 (CH_3) (Figure S1).
HRMS (ESI) Exact mass calcd for $C_{12}H_{15}NNaO$ $[M+Na]^+$: 212.1051, found 212.1060.

(*E*)- 4-(4-hydroxy-3-methoxyphenyl)but-3-en-2-one (53)



The title compound was prepared according to General Procedure from vanillin for a reaction time of 8 h and purified by recrystallization (MeOH) to afford a yellow solid (185.3 mg, 96.40%).
m.p. 120-121 °C (MeOH);
R_f = 0.31 (30% EtOAc/hexane);
IR (film) 3296 (brd, OH), 3001, 1632 (C=O), 1580, 1516, 1257, 1163, 1024, 979, 823 cm^{-1};
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (1H, dd, *J* = 16.2, 2.6 Hz, C**H**=CHCO), 7.07 (1H, dd, *J* = 8.2, 2.0 Hz, Ar**H**), 7.04 (1H, d, *J* = 1.9 Hz, Ar**H**), 6.92 (1H, d, *J* = 8.2 Hz, Ar**H**), 6.57 (1H, d, *J* = 16.2 Hz, CH=C**H**CO), 6.23 (1H, s, O**H**), 3.91 (3H, s, OC**H**$_3$), 2.35 (3H, s, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 198.58 (C=O), 148.30 (C), 146.90 (C), 143.87 (CH), 126.76 (C), 124.81 (CH), 123.46 (CH), 114.82 (CH), 109.32 (CH), 55.87 (CH_3), 27.19 (CH_3) (Figure S2).
HRMS (ESI) Exact mass calcd for $C_{11}H_{12}NaO_3$ $[M+Na]^+$: 215.0684, found 215.0681.

(*E*)-4-(4-hydroxy-3,5-dimethoxyphenyl)but-3-en-2-one (54)



The title compound was prepared according to General Procedure from syringaldehyde for a reaction time of 6 h and purified by recrystallization (MeOH) to afford a pale-yellow solid (201.5 mg, 90.67%).
m.p. 130-131 °C (MeOH);
R_f = 0.47 (60% EtOAc/hexane);
IR (film) 3342 (brd, OH), 3005, 1638 (C=O), 1585, 1514, 1458, 1260, 1101, 968, 819 cm^{-1};
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (1H, d, *J* = 16.1 Hz, C**H**=CHCO), 6.79 (2H, s, Ar**H**), 6.59 (1H, d, *J* = 16.1 Hz, CH=C**H**CO), 5.84 (1H, s, O**H**), 3.92 (6H, s, OC**H**$_3$), 2.37 (3H, s, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 198.27 (C=O), 147.24 (C), 143.89 (CH), 137.33 (C), 125.81 (C), 125.26 (CH), 105.19 (2 × CH), 56.32 (2 × CH_3), 27.33 (CH_3) (Figure S3).
HRMS (ESI) Exact mass calcd for $C_{12}H_{14}NaO_4$ $[M+Na]^+$: 245.0790, found 245.0787.

2. ^{1}H NMR and ^{13}C NMR spectra for synthesized compounds

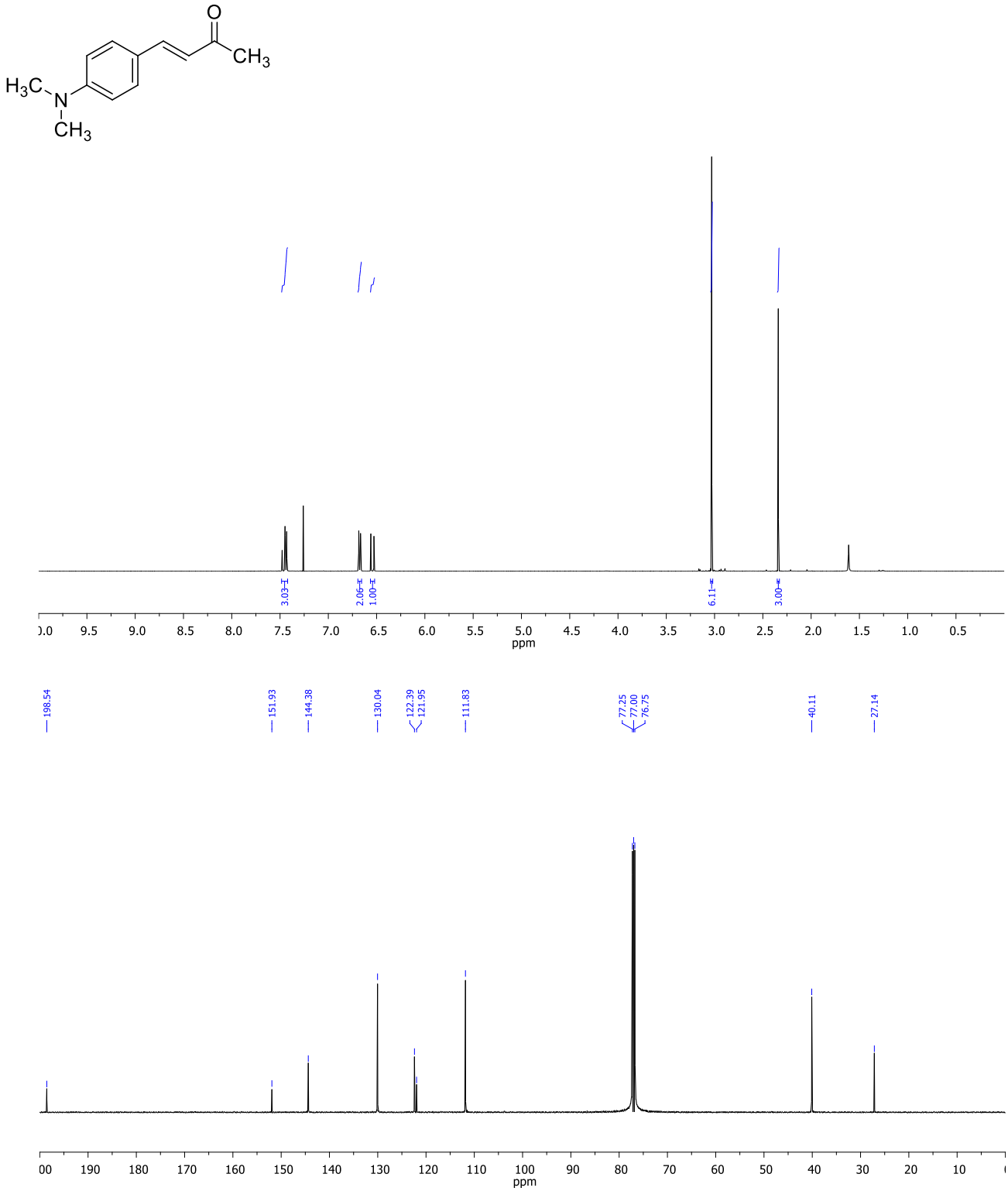


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of compound **52**

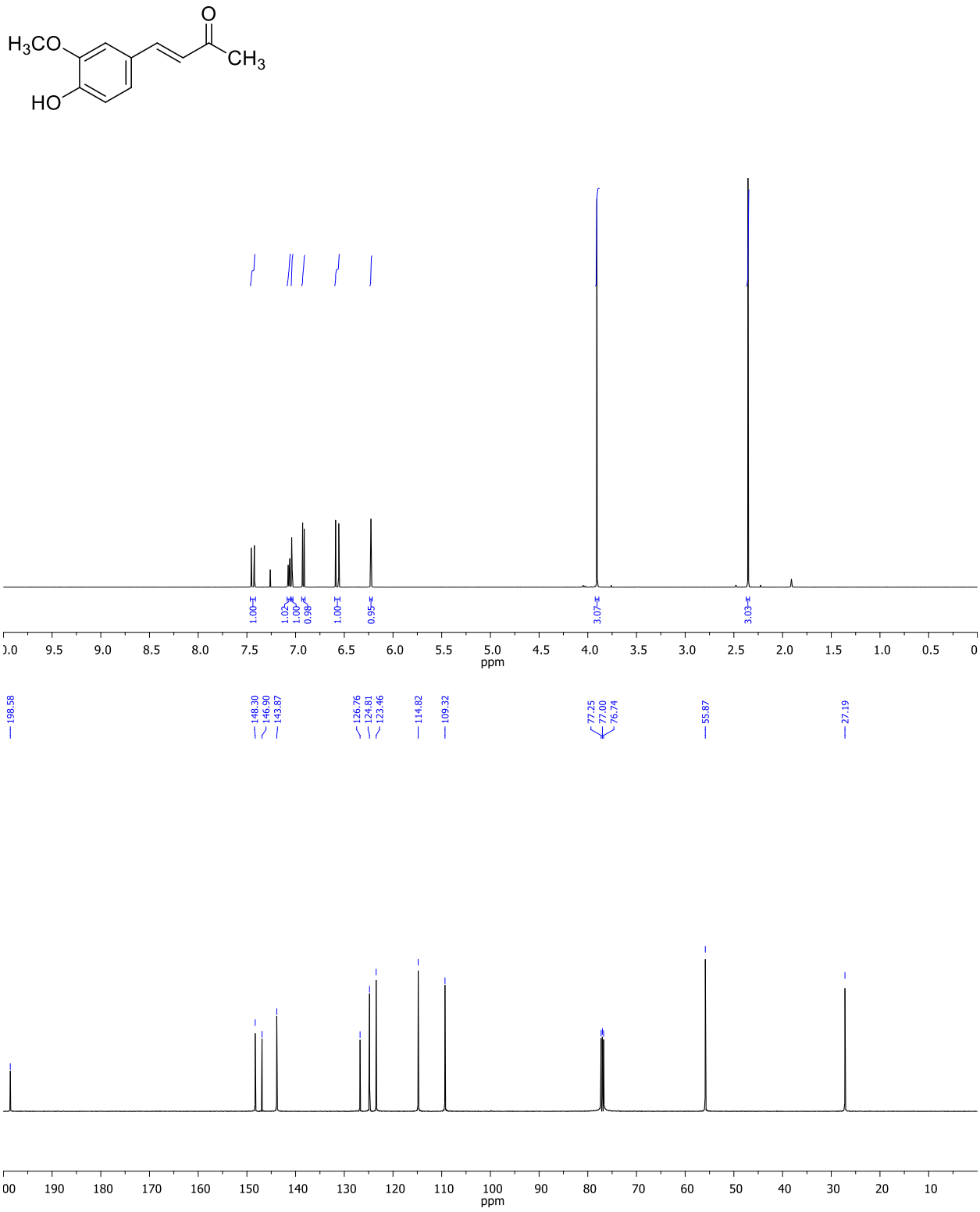


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of compound **53**

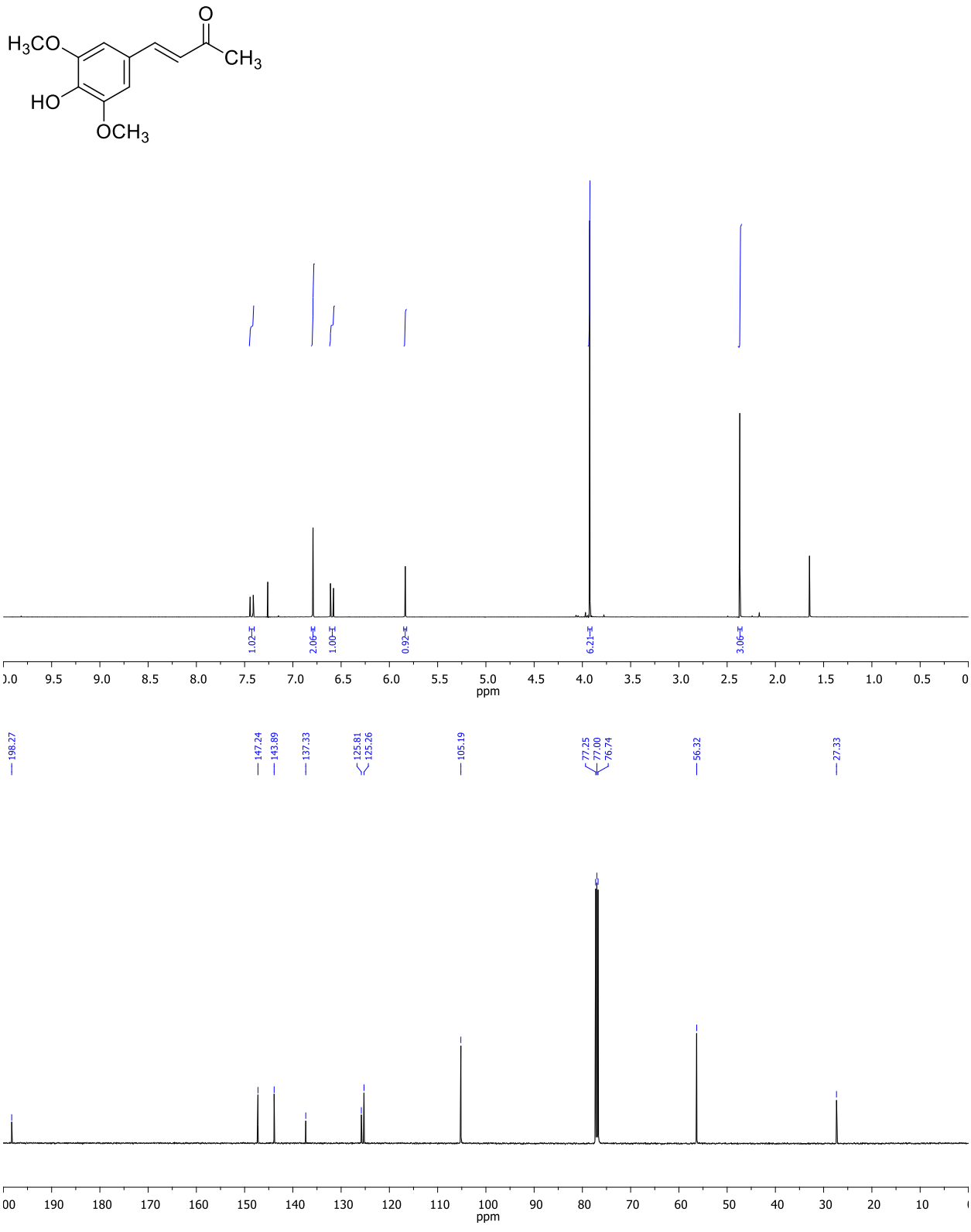


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of compound **54**