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J. Serb. Chem. Soc. 83 (9) S257–S287 (2018) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Determination of the enol form of asymmetric 1,3-dicarbonyl compounds: 2D HMBC NMR data and DFT calculations

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EXPERIMENTAL

*Synthesis of 1-(2,6-dimethoxyphenyl)-3-phenylpropane-1,3-dione (**1**)*

1-(2,6-Dimethoxphenyl)ethanone (0.72 g, 4 mmol) and ethyl benzoate (2.8 mL, 20 mmol) were reacted according to the general procedure. Column chromatography with *n*-hexane/ethyl acetate (5:1) gave the product as white crystals. Yield: 1.113 g.[1]

*Synthesis of 1-phenyl-3-(2,4,6-trimethoxyphenyl)propane-1,3-dione (**2**)*

1-(2,4,6-Trimethoxyphenyl)ethanone (0.84 g, 4 mmol) and ethyl benzoate (2.8 mL, 20 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (5:1) gave the product as honey yellow crystals. Yield: 1.09 g.[2]

*Synthesis of 1-(2,6-dimethoxyphenyl)butane-1,3-dione (**3**)*

1-(2,6-Dimethoxyphenyl)ethanone (0.54 g, 3 mmol) and ethyl acetate (1,47 mL, 15 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (5:1) gave the product as a bright gel-like substance. Yield: 0.852 g.[3]

*Synthesis of 1-(2,4,6-trimethoxyphenyl)butane-1,3-dione (**4**)*

1-(2,4,6-Trimethoxyphenyl)ethanone (0.63 g, 3 mmol) and ethyl acetate (1.47 mL, 15 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (5:1) gave the product as a light yellow solid. Yield: 0.653 g.[4]

*Synthesis of 1,3-di(naphthalen-1-yl)propane-1,3-dione (**5**)*

1-Acetylnaphthalene (0.3 mL, 2 mmol) and ethyl 1-naphthoate (1,8 mL, 10 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (8:1) gave the product as light yellow crystals. Yield: 0.58 g.[5]

*Synthesis of 1-(naphthalen-1-yl)butane-1,3-dione (**6**)*

1-Acetylnaphthalene (0.75 mL, 5 mmol) and ethyl acetate (2.45 mL, 25 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (5:1) gave the product. Yield: 0.766 g.[6]

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*Synthesis of 1-(naphthalen-1-yl)-3-phenylpropane-1,3-dione (**7**)*

Acetophenone (0.58 mL, 5 mmol) and ethyl 1-naphthoate (4.5 mL, 25 mmol) was reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (8:1) gave the product as yellow crystals. Yield: 1 g.[7]

*Synthesis of 1-(3-bromothiophen-2-yl)butane-1,3-dione (**8**)*

3-Bromo-2-acetylthiophene (1.025 g, 5 mmol) and ethyl acetate (2.45 mL, 25 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (4:1) gave the product as a yellow solid. Yield: 0.65 g.

*Synthesis of 1,3-di(thiophen-2-yl)propane-1,3-dione (**9**)*

1-(Thiophen-2-yl)ethanone (0.43 mL, 4 mmol) and ethyl thiophene-2-carboxylate (2.7 mL, 20 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (5:1) gave the product as a lemon yellow solid. Yield: 0.736 g).[8]

Synthesis of 1-(thiophen-2-yl)butane-1,3-dione (10)

2-Acetylthiophene (0.54 mL, 5 mmol) and ethyl acetate (2.45 mL, 25 mmol) were reacted according to the general procedure. Column chromatography with hexane/ethyl acetate (5:1) gave the product as a brick red solid. Yield: 0.80 g.[9]

ANALYTICAL AND SPECTRAL DATA

*1-(2,6-Dimethoxyphenyl)-3-phenylpropane-1,3-dione (**1**)*. Yield: 95 %; white crystals; m.p.: 85–88 °C; IR (ATR, cm^{-1}): 2921, 2989, 1681, 1598, 1582, 1495, 1469, 1453, 1424, 1323, 1287, 1247, 1176, 1111, 1071; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 16.13 (1H, *bs*, OH), 7.92–7.90 (2H, *m*, Ar-H), 7.53–7.49 (1H, *m*, Ar-H), 7.47–7.42 (2H, *m*, Ar-H), 7.33 (1H, *t*, $J_{5,4}$ = 8.4 Hz, H-5), 6.61 (2H, *d*, $J_{4,5}$ = 8.4 Hz, H-4 & H-6), 6.4 (1H, *s*, H-13), 3.83 (6H, *s*, H-8 & H-12); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 189.4, 181.5, 157.7, 135.0, 132.1, 131.2, 128.5, 127.1, 117.2, 104.2, 100.6, 56.1; HR-MS (*m*/*z*, $(M+H)^+$): Calcd. for $C_{17}H_{17}O_4$: 285.1121. Found: 285.1119.

*1-Phenyl-3-(2,4,6-trimethoxyphenyl)propane-1,3-dione (**2**)*. Yield: 87 %; honey yellow crystals; m.p.: 95–98 °C; IR (ATR, cm^{-1}): 2969, 2940, 2838, 1698, 1682, 1585, 1490, 1452, 1411, 1331, 1274, 1226, 1203, 1185, 1154, 1123; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 16.23 (1H, *bs*, OH), 7.91–7.89 (2H, *m*, Ar-H), 7.52–7.48 (1H, *m*, Ar-H), 7.46–7.42 (2H, *m*, Ar-H), 6.41 (1H, *s*, H-15), 6.16 (2H, *s*, H-4 & H-6), 3.85 (3H, *s*, H-14), 3.82 (6H, *s*, H-8 & H-12); ^{13}C-NMR (100 MHz, CDCl3, δ / ppm): 188.7, 181.3, 162.8, 159.1, 135.3, 131.9, 128.5, 127.0, 110.3, 101.0, 90.8, 56.1, 55.5; HR-MS (*m*/*z*, $(M+H^+)$): Calcd. for $C_{18}H_{19}O_5$: 315.1227. Found: 315.1224.

*1-(2,6-Dimethoxyphenyl)butane-1,3-dione (**3**)*. Yield: 54 %; bright gel-like substance; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 15.54 (0.8 H, *bs*, OH), 7.32––7.27 (1.75 H, *m*, keto & enol H-5), 6.59–6.55 (3H, *m*, keto & enol H-4 & H-6), 5.71 (0.8 H, *s*, enol H-13), 3.88 (0.8 H, *s*, keto H-13), 3.81 (8.5 H, *s*, keto & enol H-8 & H-12), 2.29 (1H, *s*, keto H-16), 2.12 (3H, *s*, H-16); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 189.5, 186.8, 157.6, 131.1, 116.4, 104.1, 104.0, 56.0, 24.6 (enol

form), 201.8, 197.3, 157.0, 131.7, 119.2, 104.1, 60.1, 55.8, 30.2 (keto form); HR-MS (*m*/*z*, $(M+H^+)$): Calcd. for $C_{12}H_{15}O_4$: 223.0965. Found: 223.0964.

*1-(2,4,6-Trimethoxyphenyl)butane-1,3-dione (**4**)*. Yield: 86 %; light yellow solid; m.p.: 99–102 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 15.65 (1H, *bs*, OH), 6.12 (2H, *s*, enol H-4 & H-6), 6.09 (2H, *s*, keto H-4 & H-6), 5.71 (1H, *s*, enol H-15), 3.85 (1H, *s*, keto H-15), 3.83 (5H, *s*, keto & enol H-14), 3.80 (10H, *s*, keto & enol H-8 & H-12), 2.26 (1.5H, *s*, keto H-18), 2.10 (3H, *s*, enol H-18); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 189.5, 186.0, 162.6, 159.0, 104.3, 90.8, 90.6, 56.0, 55.8, 24.8 (enol form), 202.4, 195.9, 163.3, 159.1, 112.4, 109.6, 60.5, 55.5, 55.4, 30.1 (keto form); HRMS (*m*/*z*, $(M+H)^+$): Calcd. for $C_{13}H_{17}O_5$: 253.1071. Found: 253.1064.

*1,3-Di(naphthalen-1-yl)propane-1,3-dione (**5**)*. Yield: 89 %; light yellow crystals; m.p.: 104–108 °C; IR (ATR, cm^{-1}): 3041, 1708, 1673, 1593, 1574, 1527, 1506, 1459, 1423, 1384, 1364, 1338, 1290, 1278, 1243, 1194, 1123, 1065; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.61 (2H, *d*, Ar-H), 8.00 (2H, *d*, Ar-H), 7.92 (2H, *d*, Ar-H), 7.84 (2H, *dd*, Ar-H), 7.64–7.58 (3H, *m*, Ar-H), 7.56–7.53 (3H, *m*, Ar-H), 6.60 (1H, *s*, H-13); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 188.2, 133.4, 132.9, 130.9, 129.2, 127.6, 126.4, 126.3, 125.4, 124.6, 123.8, 102.1; HRMS (*m*/*z*, $(M+H)^+$): Calcd. for $C_{23}H_{17}O_2$: 325.1223. Found: 325.1219.

*1-(Naphthalen-1-yl)butane-1,3-dione (**6**)*. Yield: 81 %; IR (ATR, cm^{-1}): 3048, 1717, 1575, 1508, 1418, 1392, 1363, 1339, 1280, 1244, 1210, 1173, 1123, 1068; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 16.12 (1H, *bs*, OH), 8.46 (1H, *m*, Ar-H), 7.96 (1H, *m*, Ar-H), 7.89 (1H, *m*, Ar-H), 7.72 (1H, *m*, Ar-H), 7.59–7.48 (3H, *m*, Ar-H), 6.04 (1H, *s*, H-13), 2.22 (3H, *s*, H-16); ^{13}C-NMR (100 MHz, CDCl3, δ / ppm): 191.4, 187.3, 133.3, 132.8, 130.6, 129.1, 127.5, 126.2, 125,9, 125.3, 124.5, 123.7, 100.7, 24.4; HRMS (*m*/*z* $(M+H)^+$): Calcd. for $C_{14}H_{13}O_2$: 213.0910. Found: 213.0905.

*1-(Naphthalen-1-yl)-3-phenylpropane-1,3-dione (**7**)*. Yield: 80 %; yellow crystals; m.p.: 60–63 °C; IR (ATR, cm^{-1}): 3045, 2952, 2922, 2853, 1722, 1603, 1590, 1542, 1508, 1462, 1420, 1388, 1287, 1256, 1229, 1210, 1178, 1157, 1123, 1086, 1066; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.53 (1H, *m*, Naph-H), 8.01––7.98 (3H, *m*, Ar-H & Naph-H); 7.92 (1H, *m*, Naph-H), 7.83 (1H, *m*, Naph-H), 7.62–7.54 (4H, *m*, Ar-H & Naph-H), 7.52–7.48 (2H, *m*, Ar-H), 6.73 (1H, *s*, H-13); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 188.5, 182.4, 133.1, 133.0, 131.8, 130.5, 129.7, 128.1, 126.7, 126.5, 125.3, 125.2, 125.0, 124.4, 123.6, 122.8, 96.2; HRMS (*m*/*z* $(M+H)^+$): Calcd. for $C_{19}H_{15}O_2$: 275.1067. Found: 275. 1064.

*1-(3-Bromothiophen-2-yl)butane-1,3-dione (**8**)*. Yield: 53 %; yellow solid; m.p.: 55–58 °C; IR (ATR, cm^{-1}): 3101, 2915, 1716, 1698, 1559, 1540, 1499, 1458, 1398, 1363, 1350, 1255, 1179, 1151; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 15.88 (1H, *bs*, OH), 7.51 (1H, *d*, $J_{2,3}$ = 5.2 Hz, H-2), 7.10 (1H, *d*, $J_{3,2}$ = = 5.2 Hz, H-3), 6.56 (1H, *s*, H-9), 2.19 (3H, *s*, H-12); ^{13}C-NMR (100 MHz,

$CDCl_3$, δ / ppm): 190.9, 178.8, 135.4, 133.5, 130.8, 112.6, 97.9, 24.9; HRMS (m/z $(M+Na)^+$): Calcd. for $C_8H_7BrNaO_2S$: 268.9242. Found: 268.9242.

1,3-Di(thiophen-2-yl)propane-1,3-dione (***9***). Yield: 78 %; lemon yellow solid; m.p.: 99–101 °C; IR (ATR, cm^{-1}): 3102, 3080, 1526, 1406, 1336, 1276, 1228; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm); 16.18 (1H, *bs*, OH), 7.78 (2H, *dd*, $J_{4,2}$ = 1.2 Hz, $J_{4,3}$ = 3.8 Hz, H-4), 7.62 (2H, *dd*, $J_{2,3}$ = 4.9 Hz, $J_{2,4}$ = 1.2 Hz, H-2), 7.17 (2H, *dd*, $J_{3,2}$ = 4.9 Hz, $J_{3,4}$ = 3.8 Hz, H-3), 6.54 (1H, *s*, H-8); ^{13}C-NMR (100 MHz, $CHCl_3$, δ / ppm): 176.3, 138.2, 129.5, 127.5, 125.8, 90.2; HR-MS (m/z $(M+H)^+$): Calcd. for $C_{11}H_9O_2S_2$: 237.0038. Found: 237.0037.

1-(Thiophen-2-yl)butane-1,3-dione (***10***). Yield: 90 %; brick red solid; m.p.: 44–48 °C; IR (ATR, cm^{-1}): 3105, 1698, 1558, 1515, 1425, 1404, 1368, 1354, 1268, 1236; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 15.65 (1H, *bs*, OH), 7.69 (1H, *dd*, $J_{4,2}$ = 1.2 Hz, $J_{4,3}$ = 3.8 Hz, H-4), 7.60 (1H, *dd*, $J_{2,3}$ = 4.9 Hz, $J_{2,4}$ = 1.2 Hz, H-2), 7.13 (1H, *dd*, $J_{3,2}$ = 4.9 Hz, $J_{3,4}$ = 3.8 Hz, H-3), 6.03 (1H, *s*, H-8), 2.14 (3H, *s*, H-11); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 187.3, 181.7, 141.7, 132.3, 130.2, 128.2, 96.5, 23.9; HRMS (m/z $(M+Na)^+$): Calcd. for $C_8H_8NaO_2S$: 191.0137. Found: 191.0137.

^{1}H- AND ^{13}C-NMR SPECTRA OF **1**–**10**

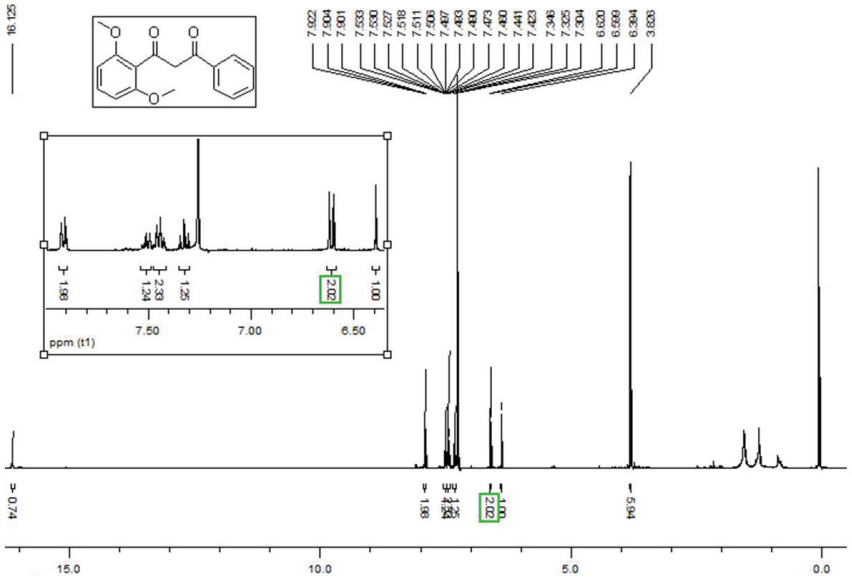


Fig. S-1. ^{1}H-NMR spectrum of **1** (400 MHz, $CDCl_3$).

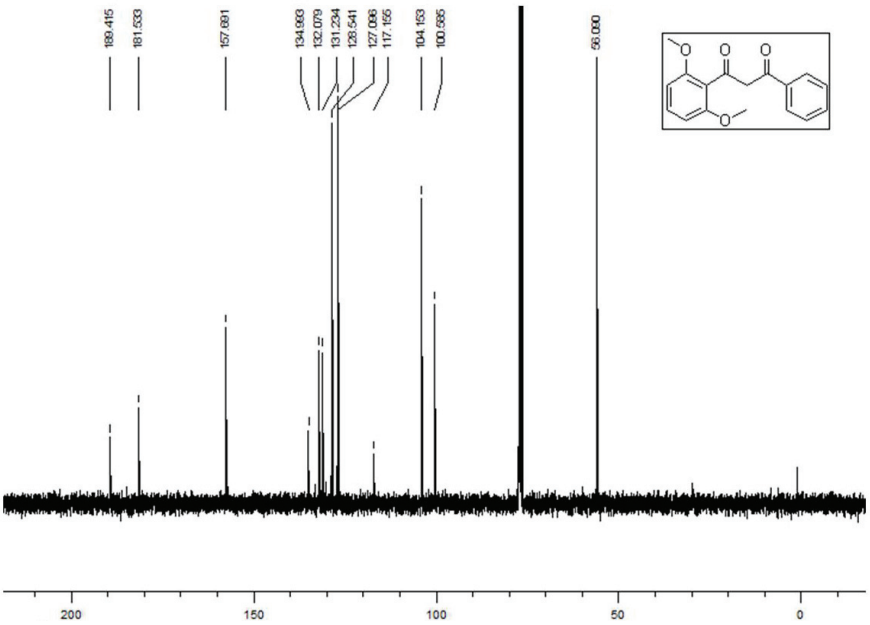


Fig. S-2. ^{13}C-NMR spectrum of **1** (100 MHz, $CDCl_3$).

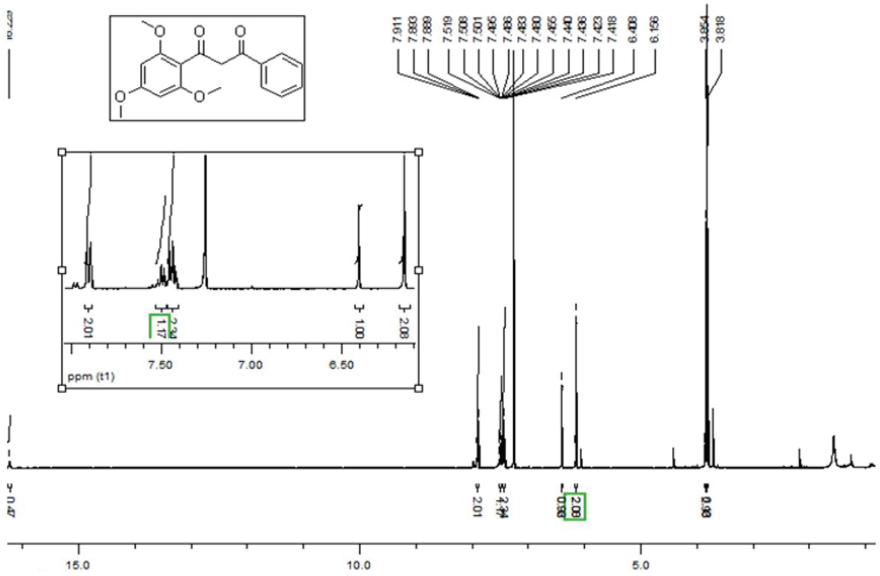


Fig. S-3. ^{1}H-NMR spectrum of **2** (400 MHz, $CDCl_3$).

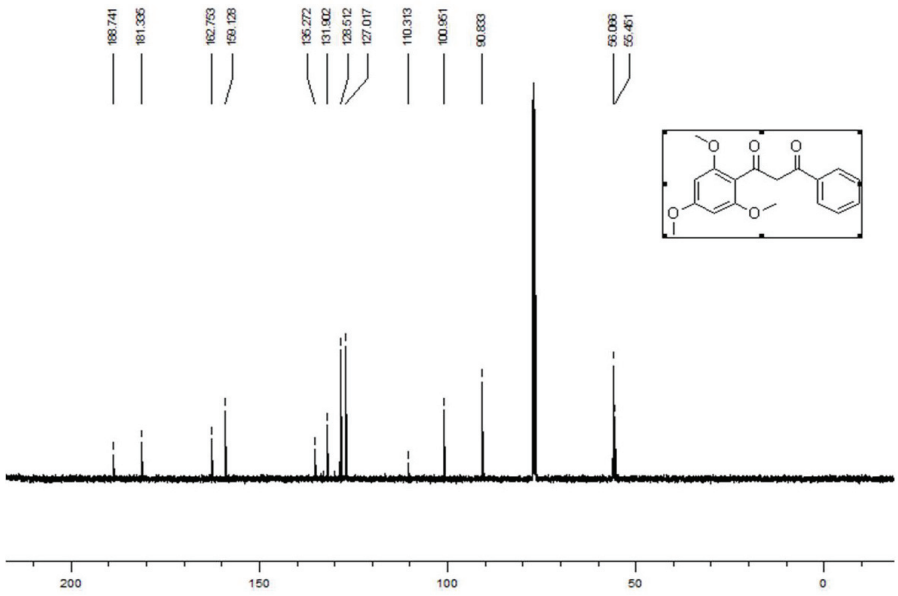


Fig. S-4. ^{13}C-NMR spectrum of **2** (400 MHz, $CDCl_3$).

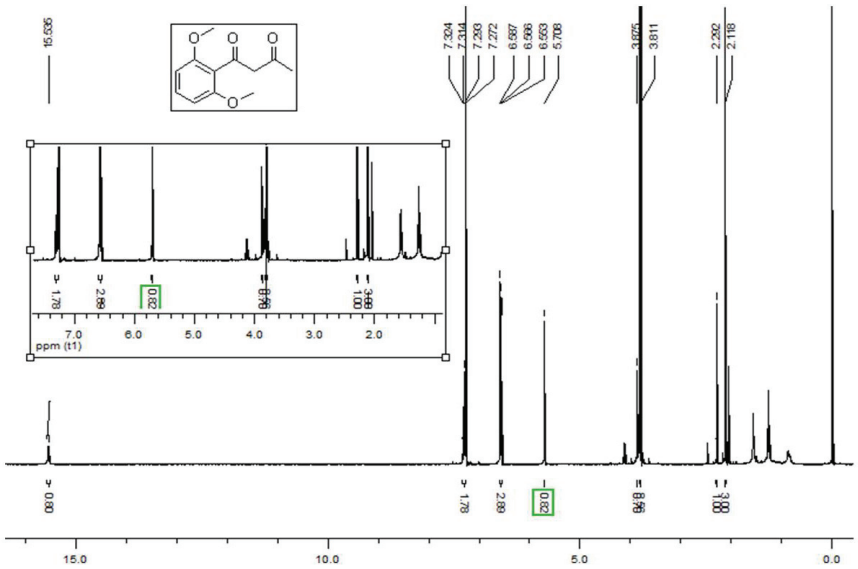


Fig. S-5. ^{1}H-NMR spectrum of **3** (400 MHz, $CDCl_3$).

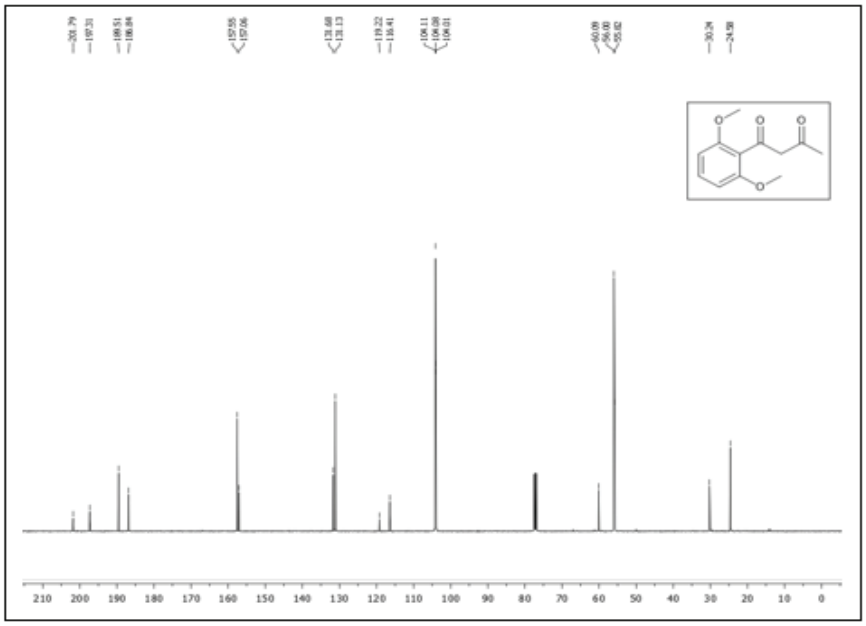


Fig. S-6. ^{13}C-NMR spectrum of **3** (100 MHz, $CDCl_3$).

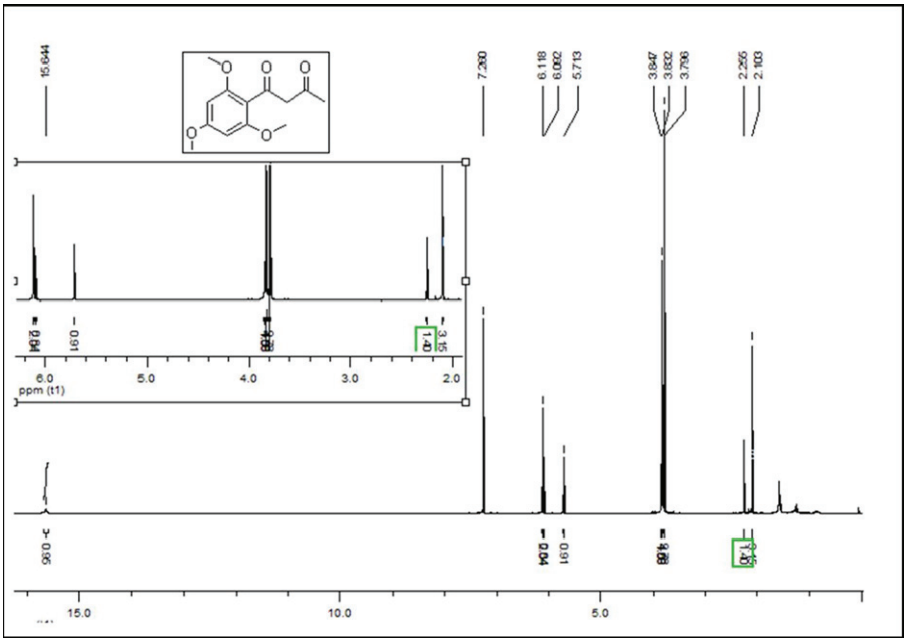


Fig. S-7. ^{1}H-NMR spectrum of **4** (400 MHz, $CDCl_3$).

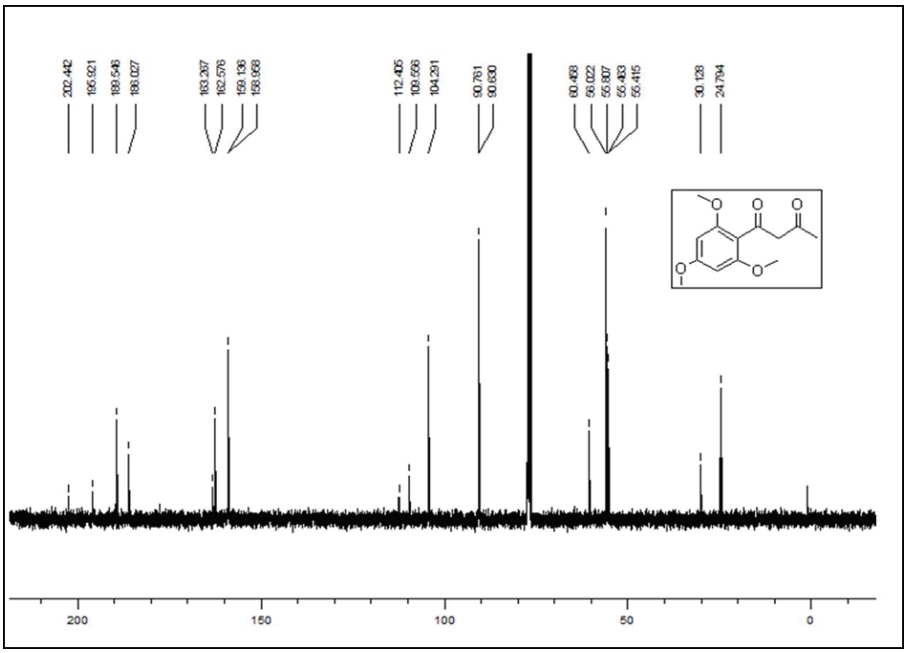


Fig. S-8. ^{13}C-NMR spectrum of **4** (100 MHz, $CDCl_3$).

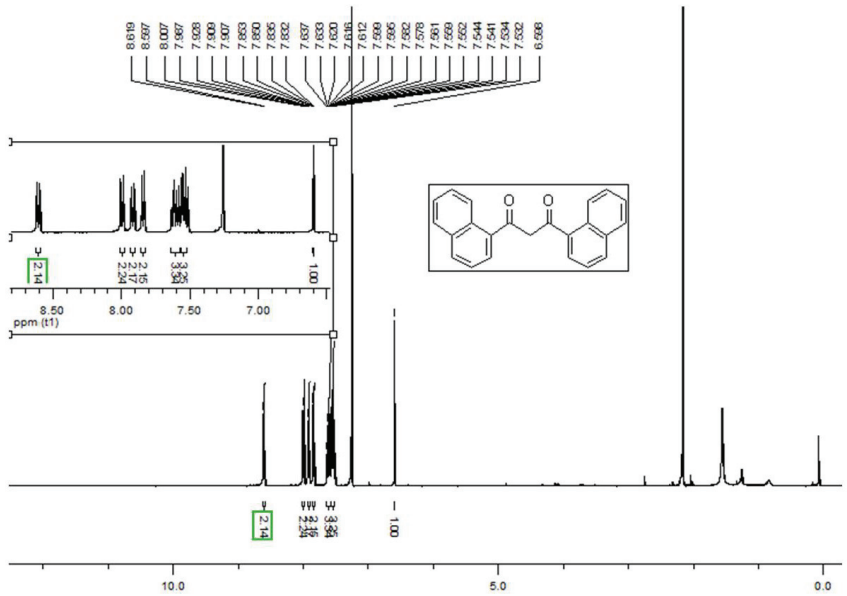


Fig. S-9. ^{1}H-NMR spectrum of **5** (400 MHz, $CDCl_3$).

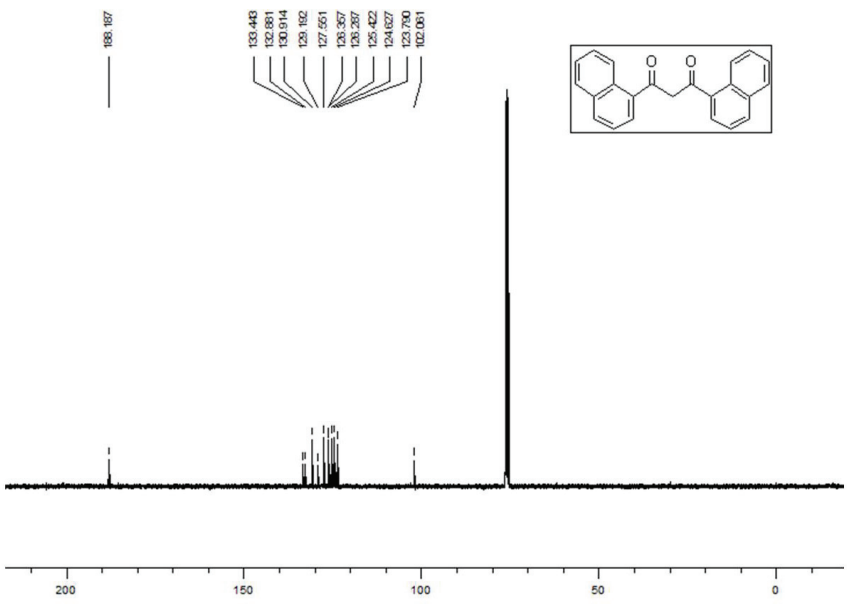


Fig. S-10. ^{13}C-NMR spectrum of **5** (100 MHz, $CDCl_3$).

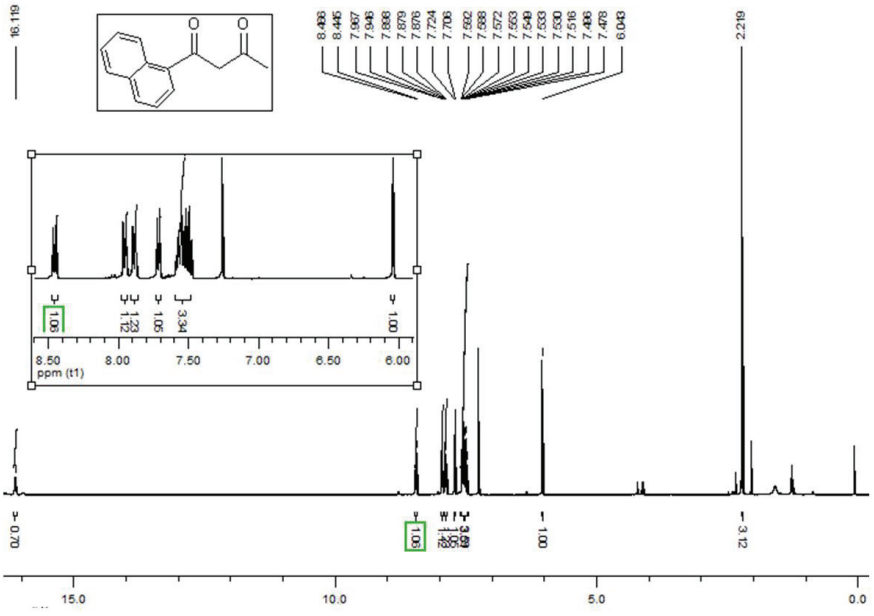


Fig. S-11. ^{1}H-NMR spectrum of **6** (400 MHz, $CDCl_3$).

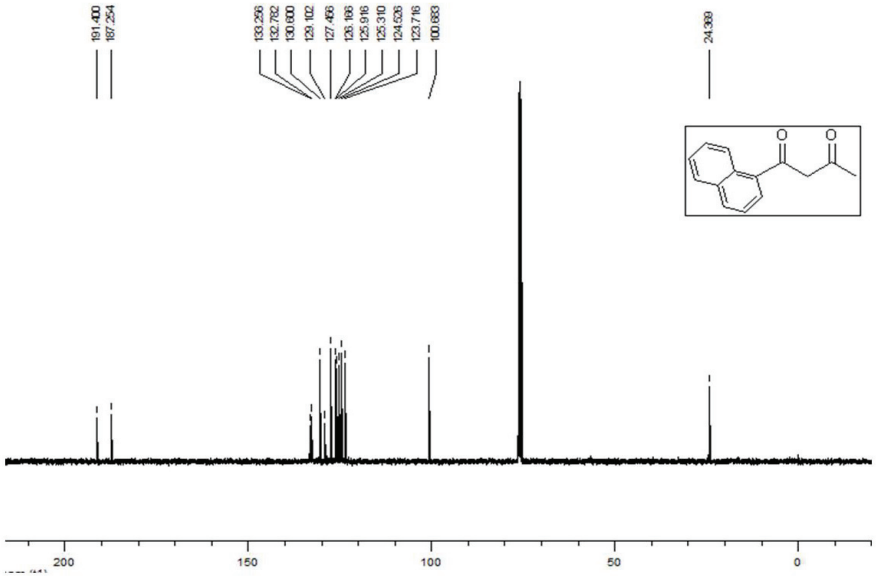


Fig. S-12. ^{13}C-NMR spectrum of **6** (100 MHz, $CDCl_3$).

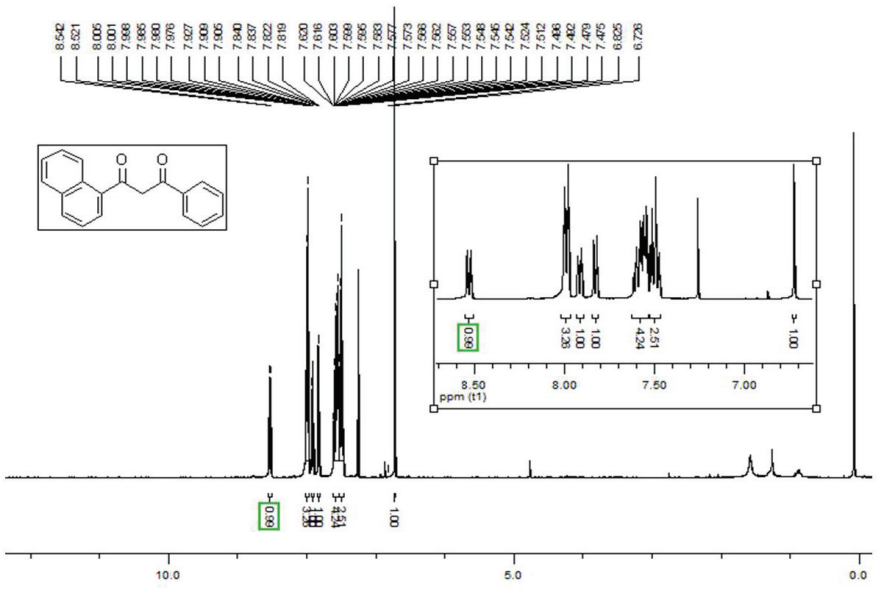


Fig. S-13. ^{1}H-NMR spectrum of **7** (400 MHz, $CDCl_3$).

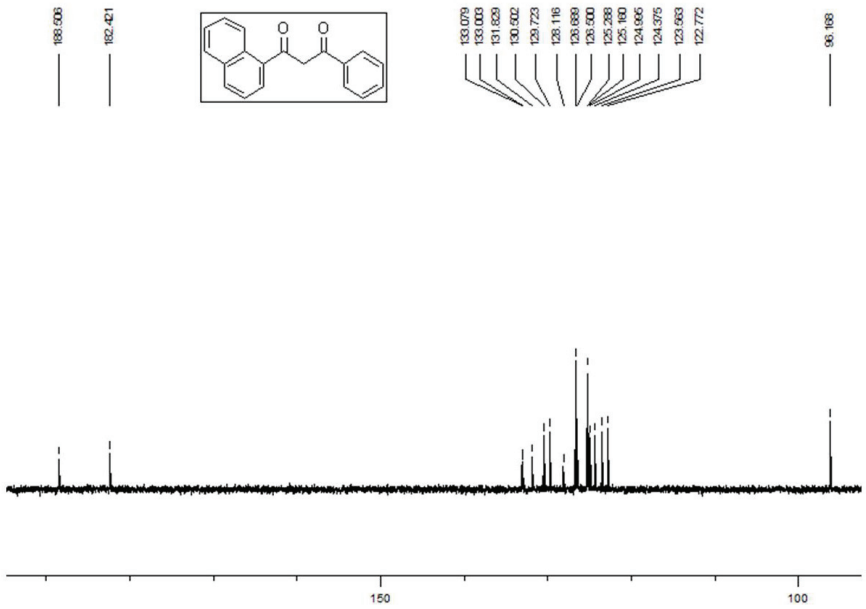


Fig. S-14. ^{13}C-NMR spectrum of **7** (100 MHz, $CDCl_3$).

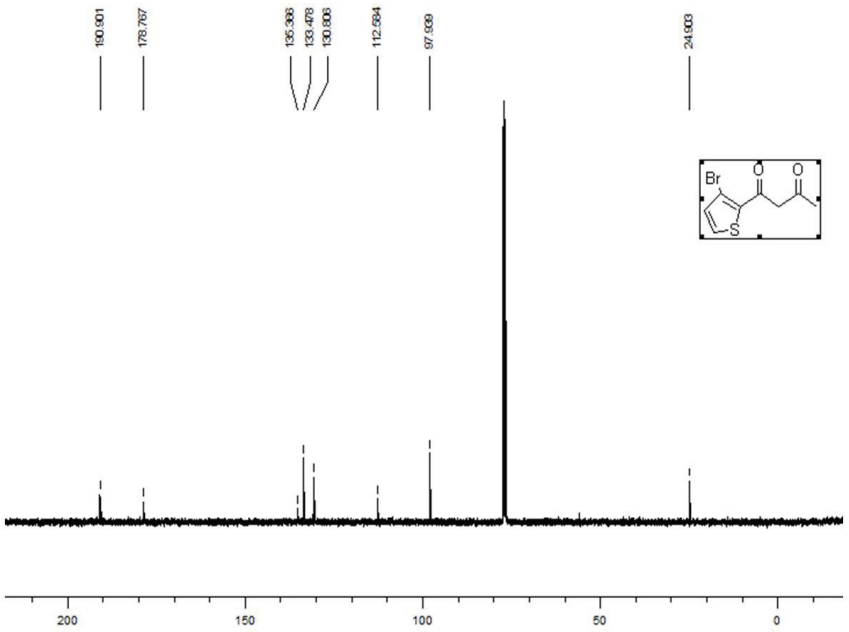


Fig. S-15. ^{1}H-NMR spectrum of **8** (400 MHz, $CDCl_3$).

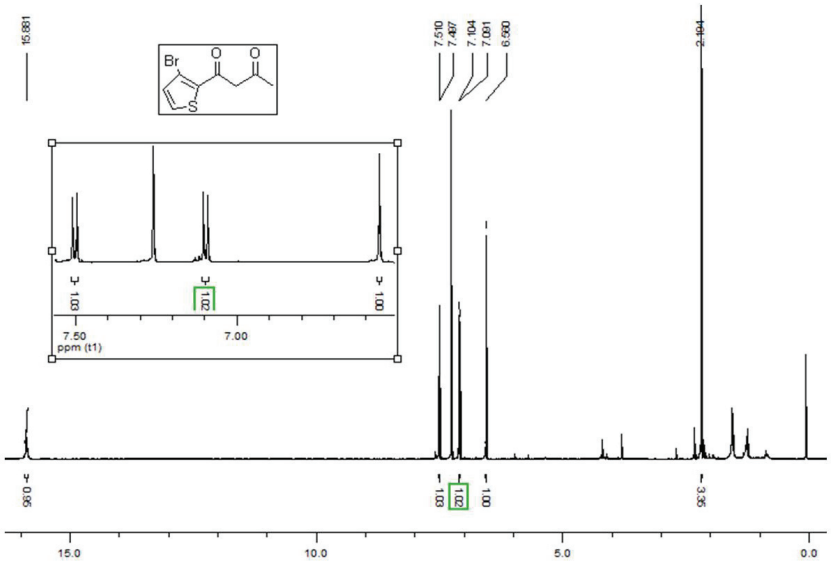


Fig. S-16. ^{13}C-NMR spectrum of **8** (100 MHz, $CDCl_3$).

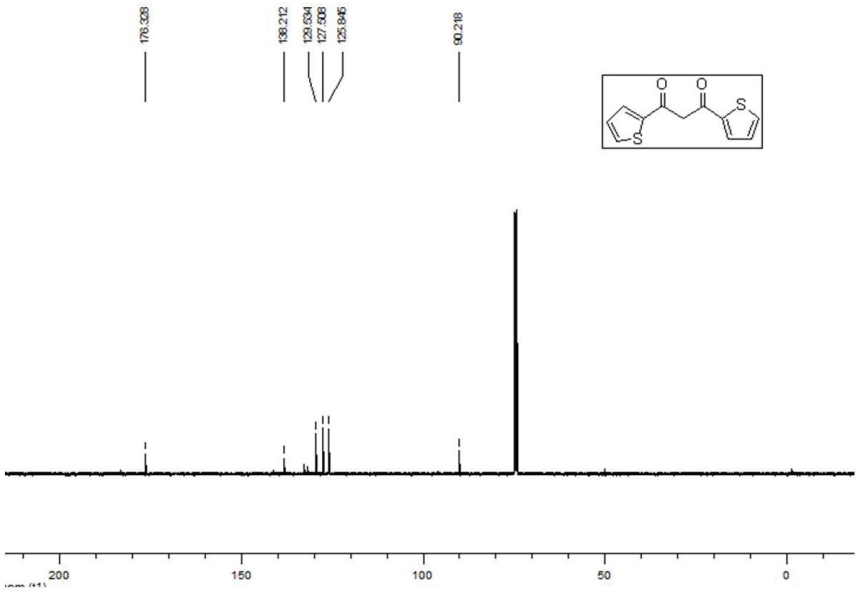


Fig. S-17. ^{1}H-NMR spectrum of **9** (400 MHz, $CDCl_3$).

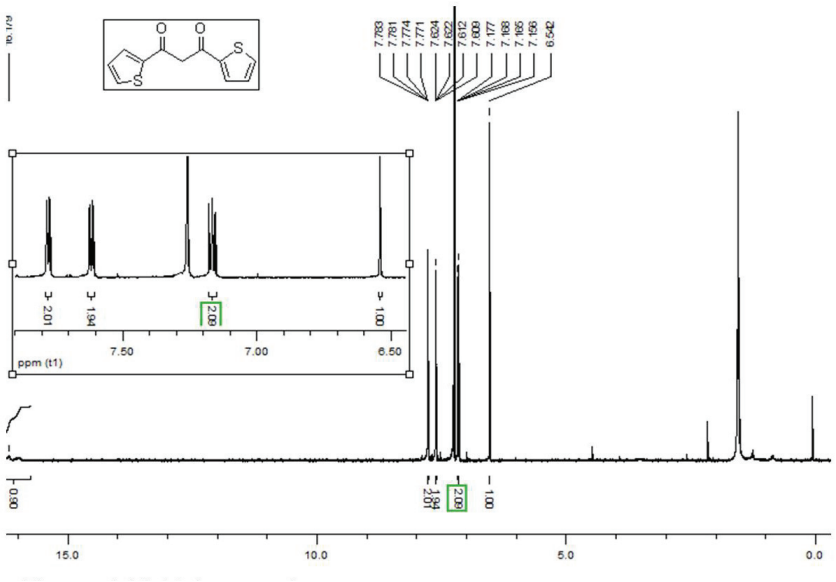


Fig. S-18. ^{13}C-NMR spectrum of **9** (100 MHz, $CDCl_3$).

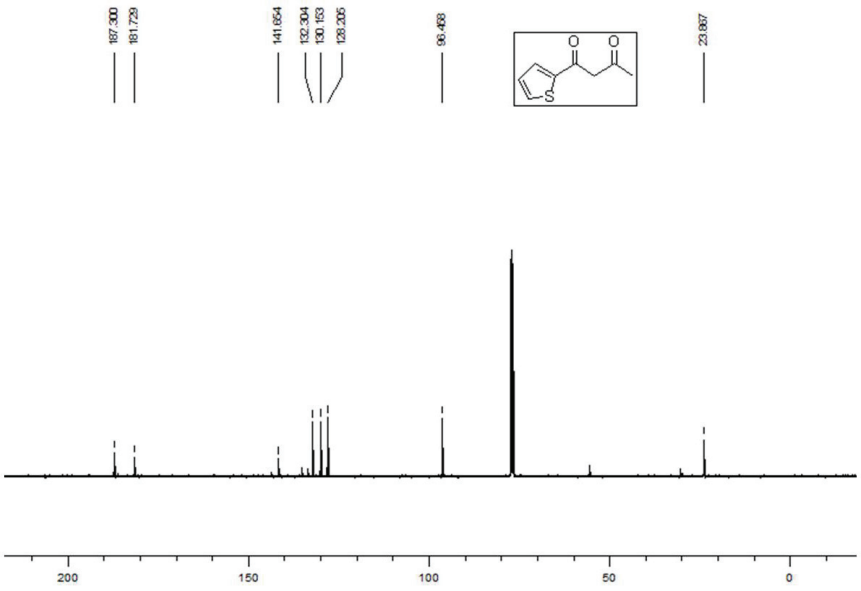


Fig. S-19. ^{1}H-NMR spectrum of **10** (400 MHz, $CDCl_3$).

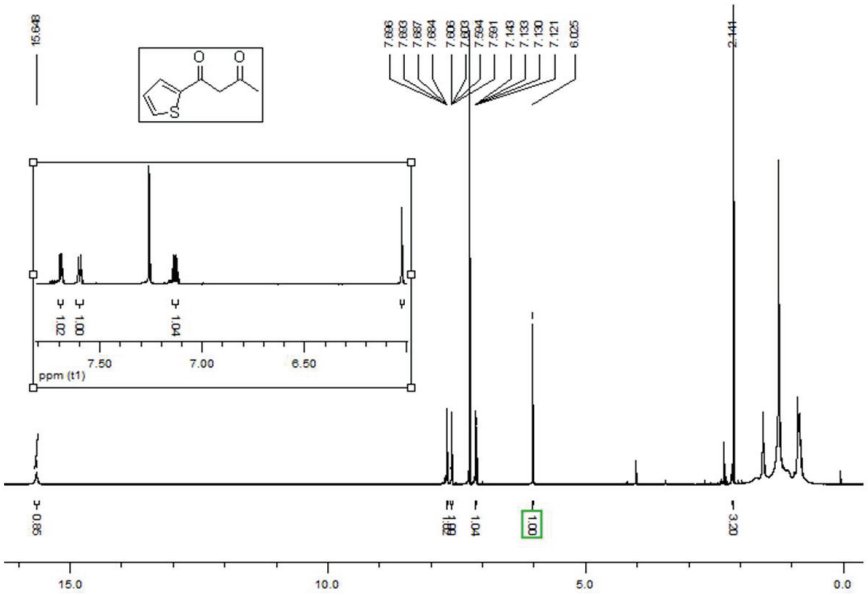


Fig. S-20. ^{13}C-NMR spectrum of **10** (100 MHz, $CDCl_3$).

FT-IR SPECTRA OF **1**–**10**

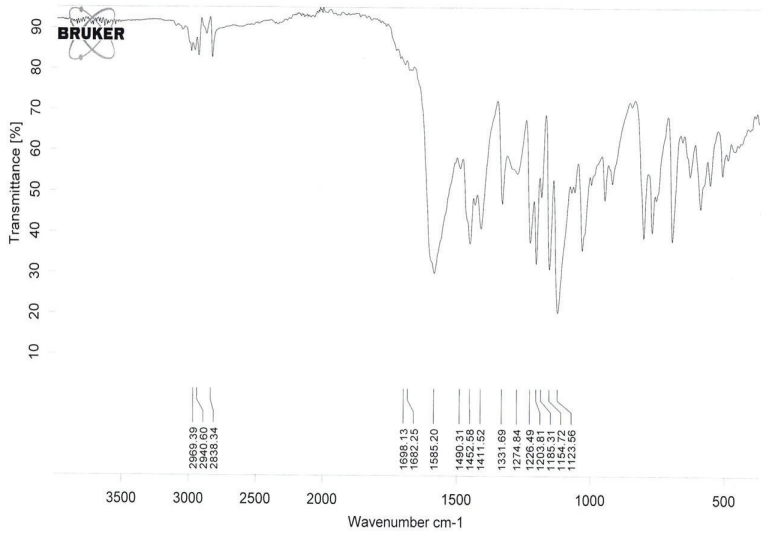


Fig. S-21. IR spectrum of **1** (ATR).

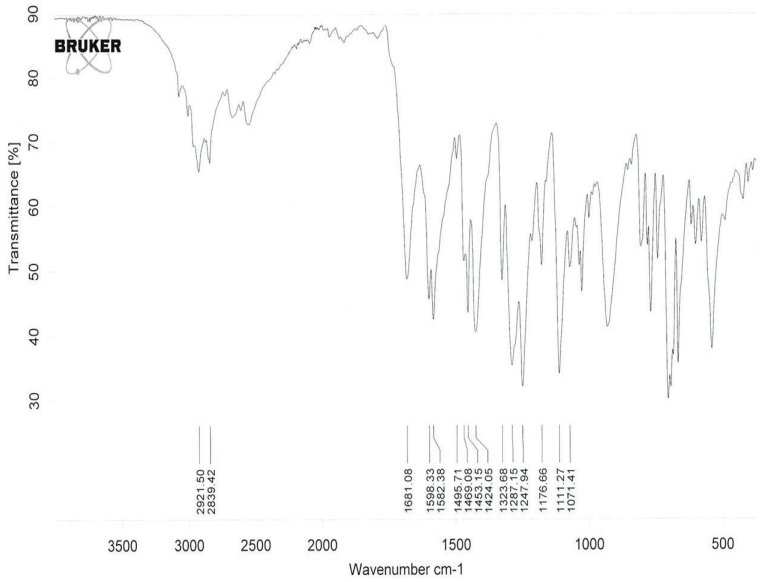


Fig. S-22. IR spectrum of **2** (ATR).

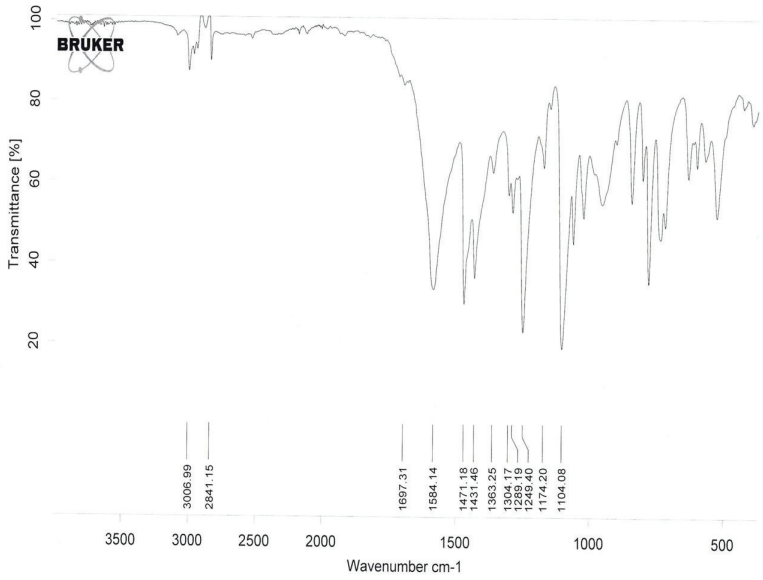


Fig. S-23. IR spectrum of **3** (ATR).

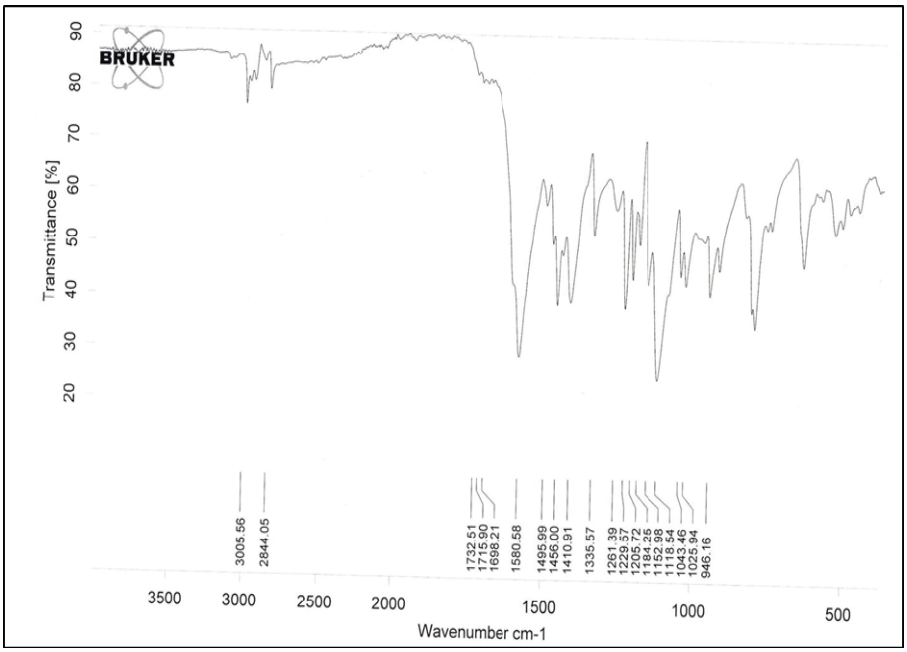


Fig. S-24. IR spectrum of **4** (ATR).

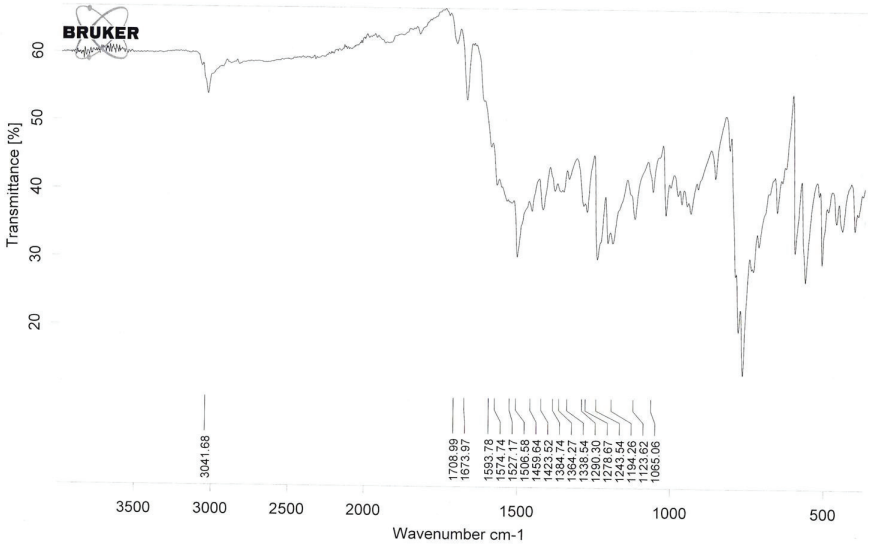


Fig. S-25. IR spectrum of **5** (ATR).

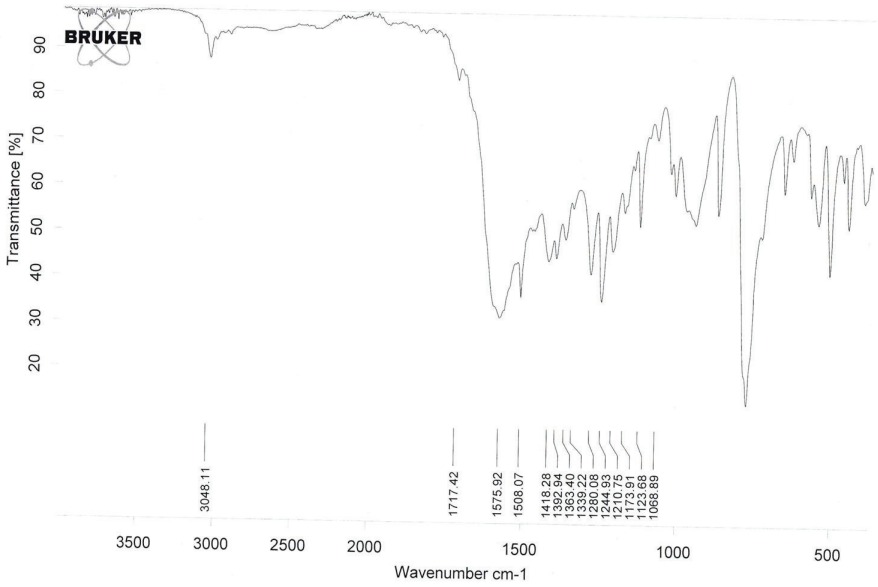


Fig. S-26. IR spectrum of **6** (ATR).

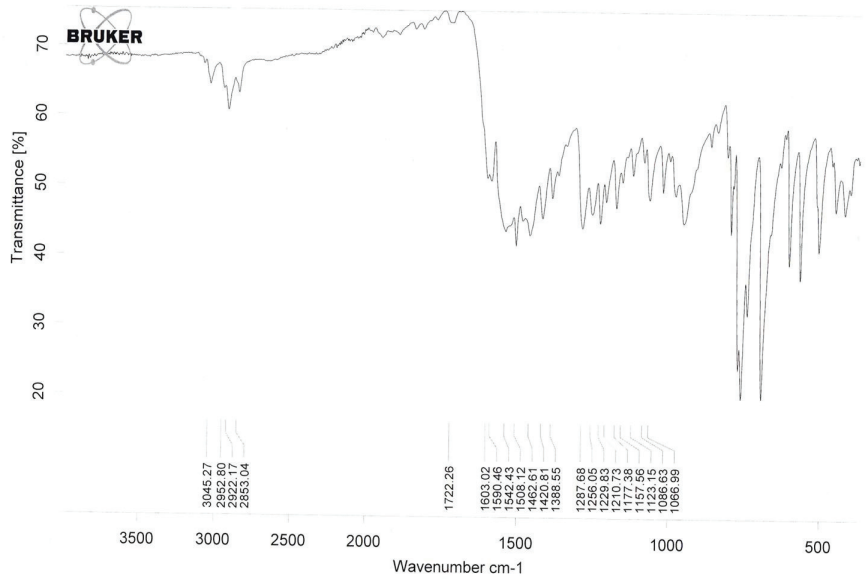


Fig. S-27. IR spectrum of **7** (ATR).

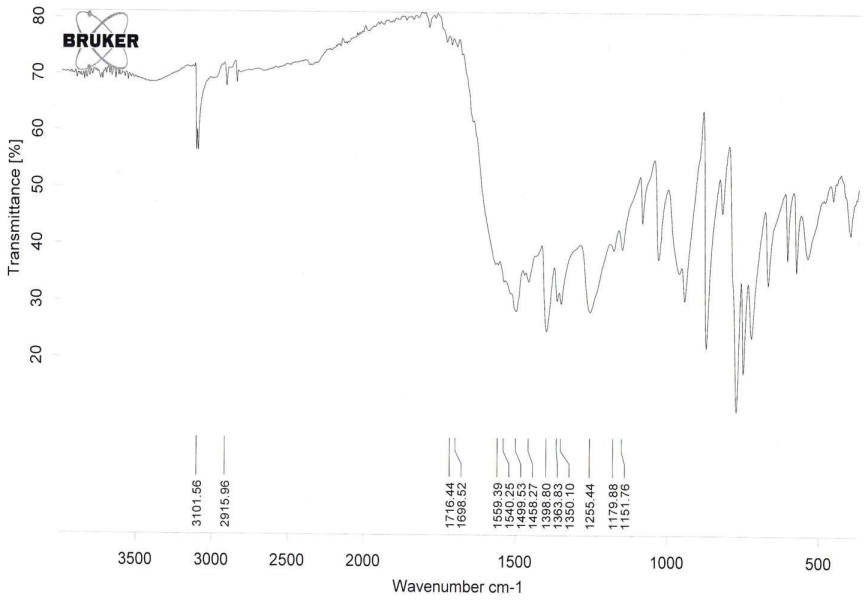


Fig. S-28. IR spectrum of **8** (ATR).

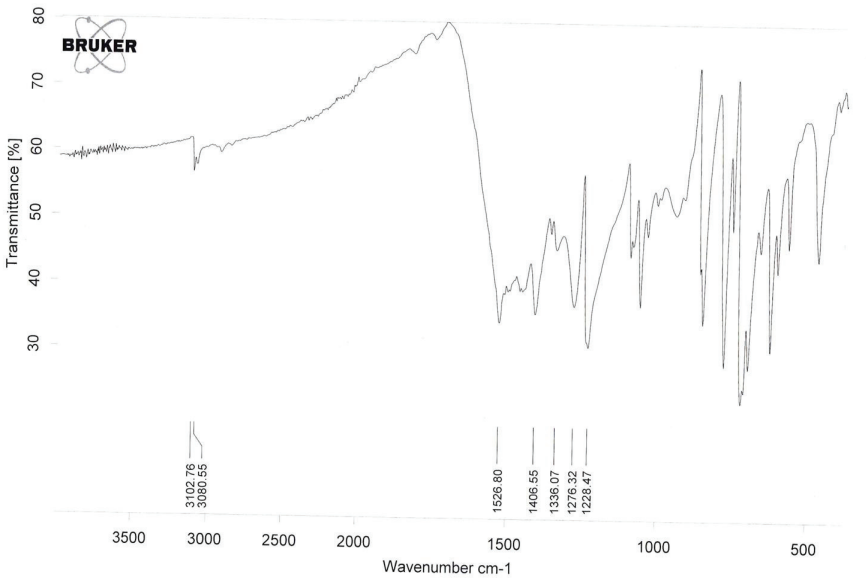


Fig. S-29. IR spectrum of **9** (ATR).

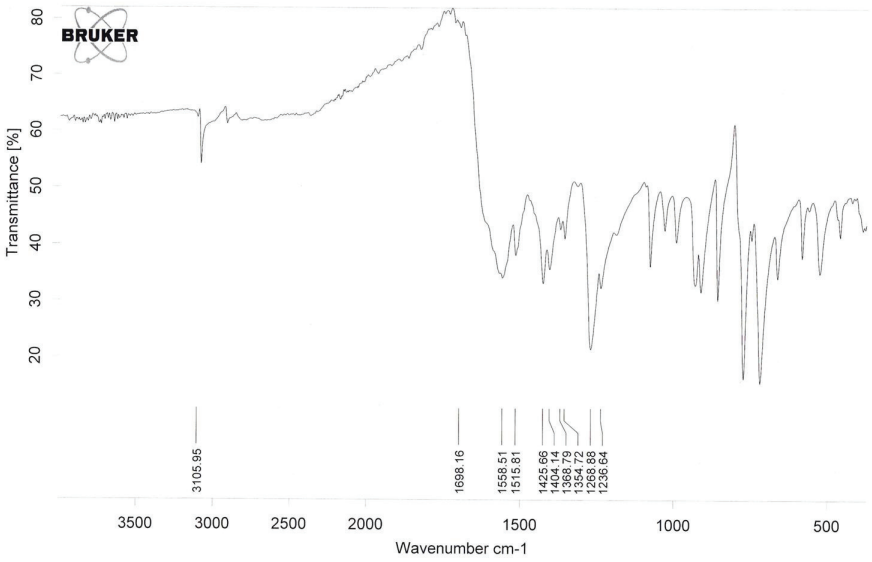


Fig. S-30. IR spectrum of 10 (ATR).

HR-MS SPECTRA OF **1**–**10**

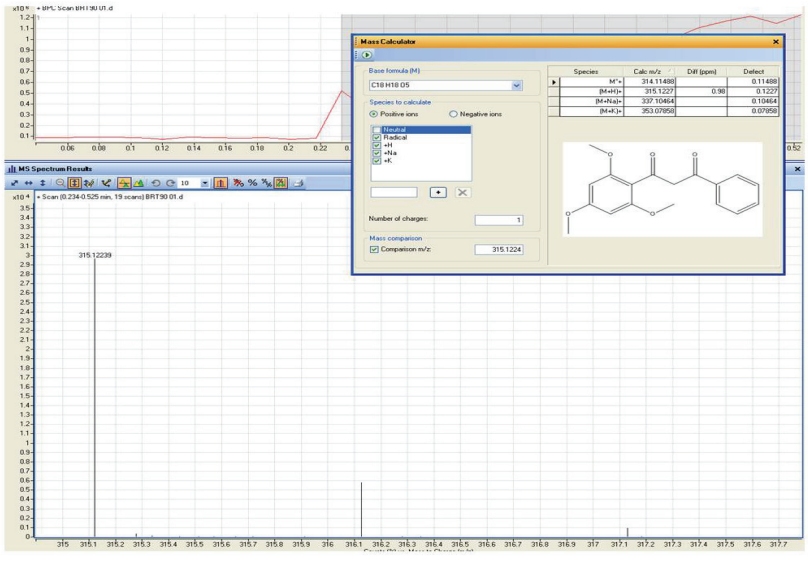


Fig. S-31. HR-MS (*m*/*z* $(M+H)^+$) spectrum of **1**.

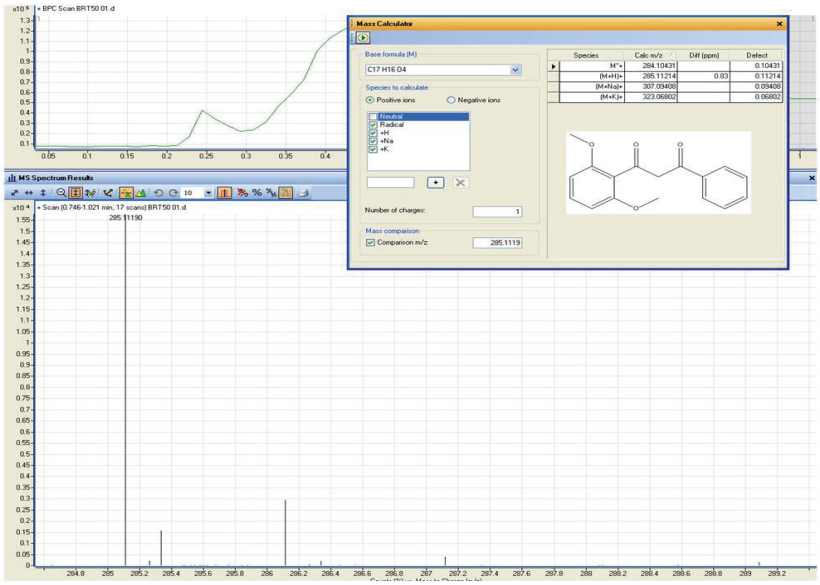


Fig. S-32. HR-MS (*m*/*z* $(M+H)^+$) spectrum of **2**.

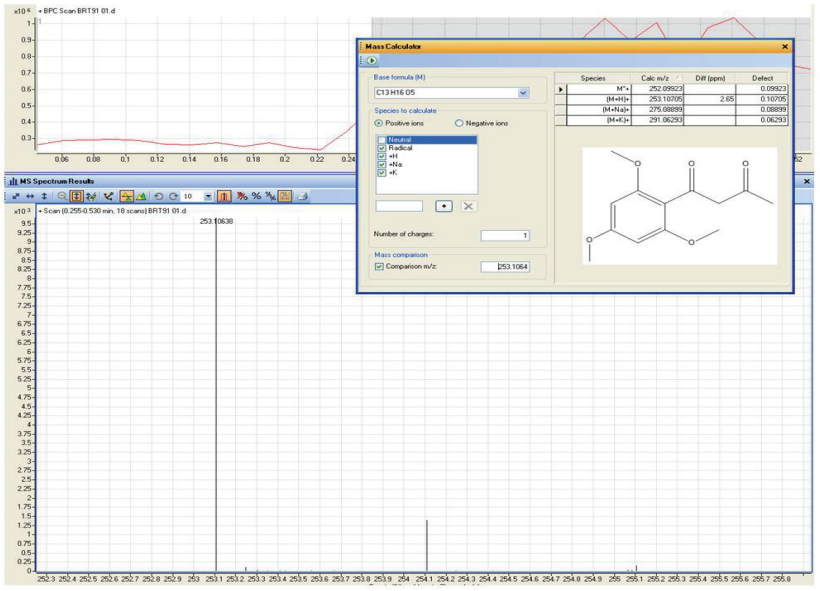


Fig. S-33. HR-MS (*m*/*z* $(M+H)^+$) spectrum of **3**.

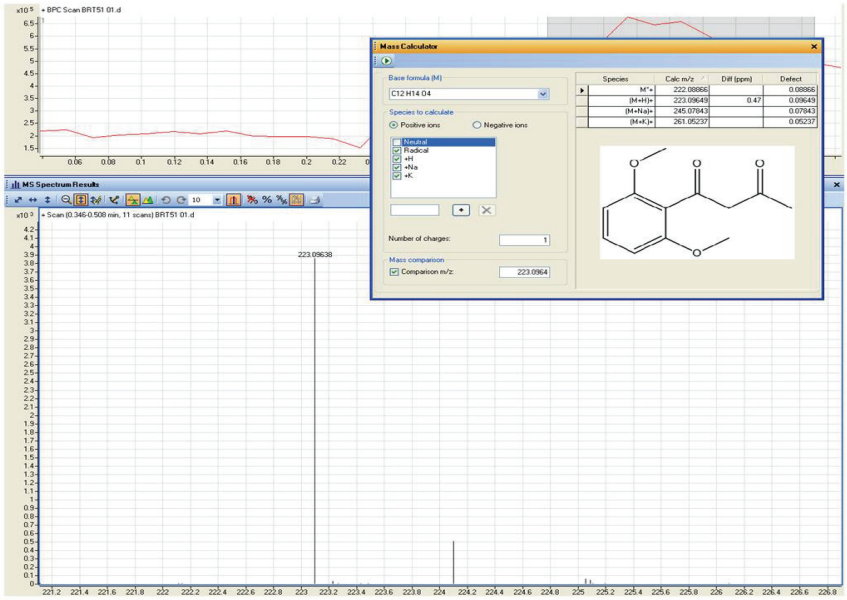


Fig. S-34. HR-MS (*m/z* $(M+H)^+$) spectrum of **4**.

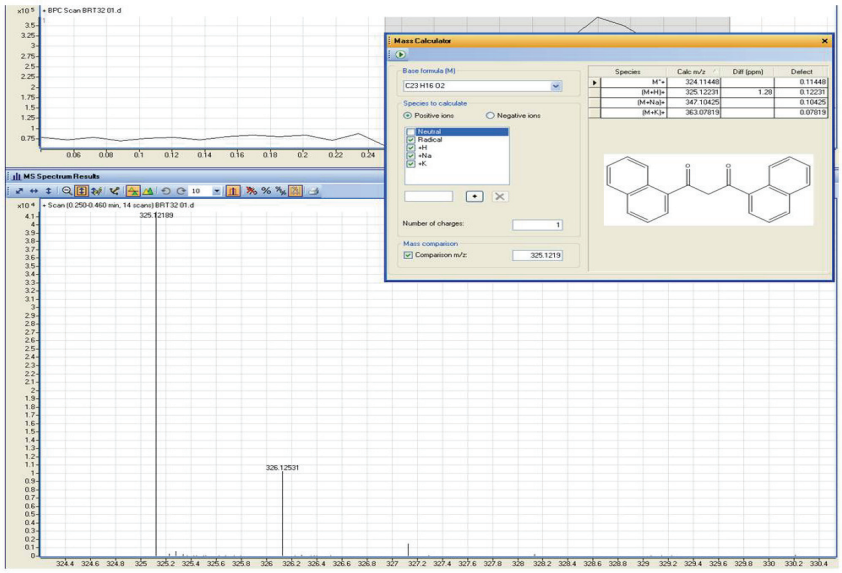


Fig. S-35. HR-MS (*m/z* $(M+H)^+$) spectrum of **5**.

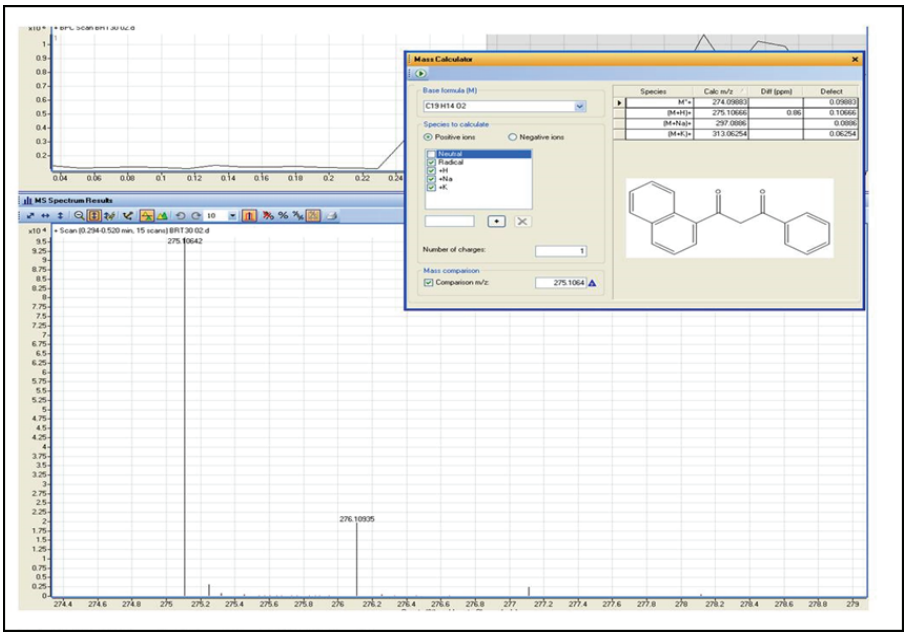


Fig. S-36. HR-MS (*m*/*z* $(M+H)^+$) spectrum of **6**.

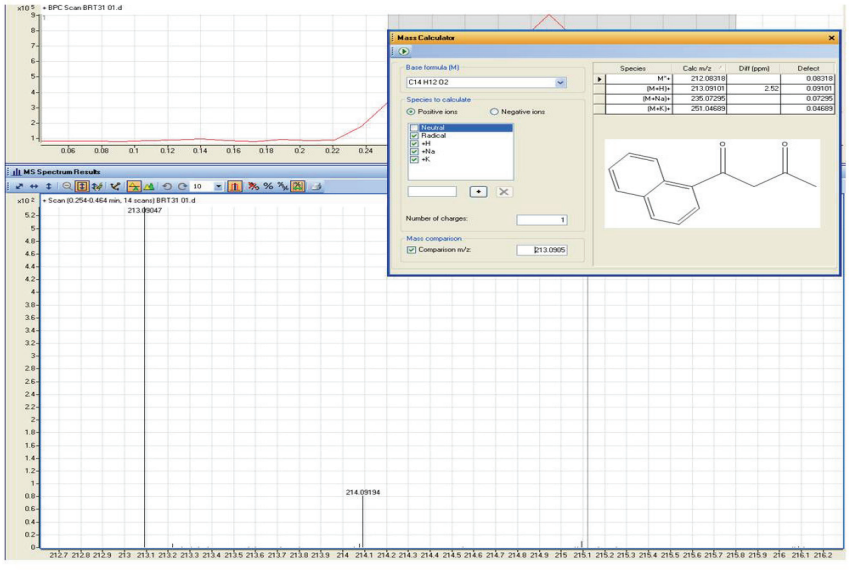


Fig. S-37. HR-MS (*m*/*z* $(M+H)^+$) spectrum of **7**.

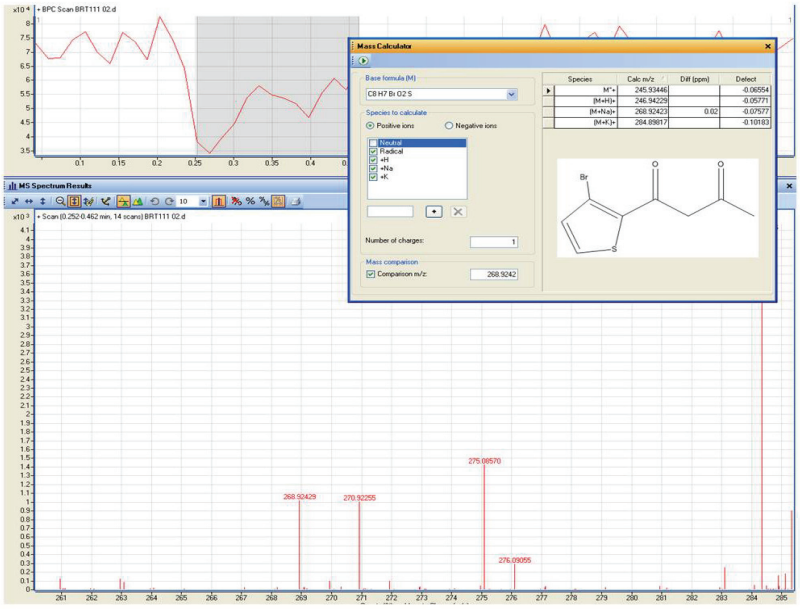


Fig. S-38. HR-MS (*m*/*z* $(M+Na)^+$) spectrum of **8**.

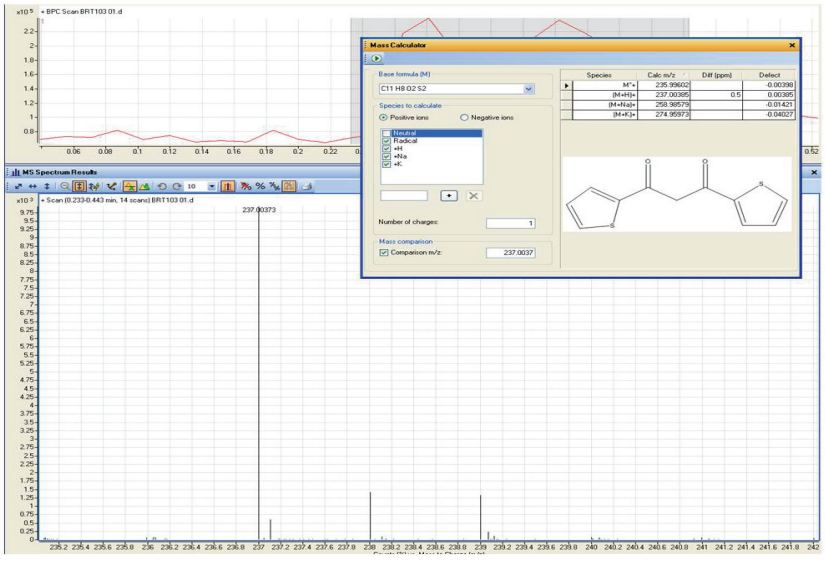


Fig. S-39. HR-MS (*m*/*z* $(M+H)^+$) spectrum of **9**.

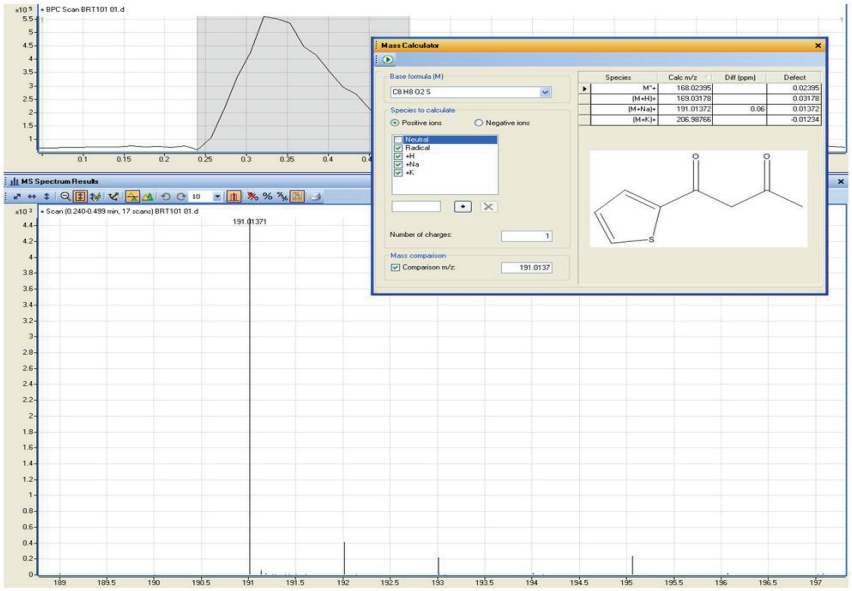
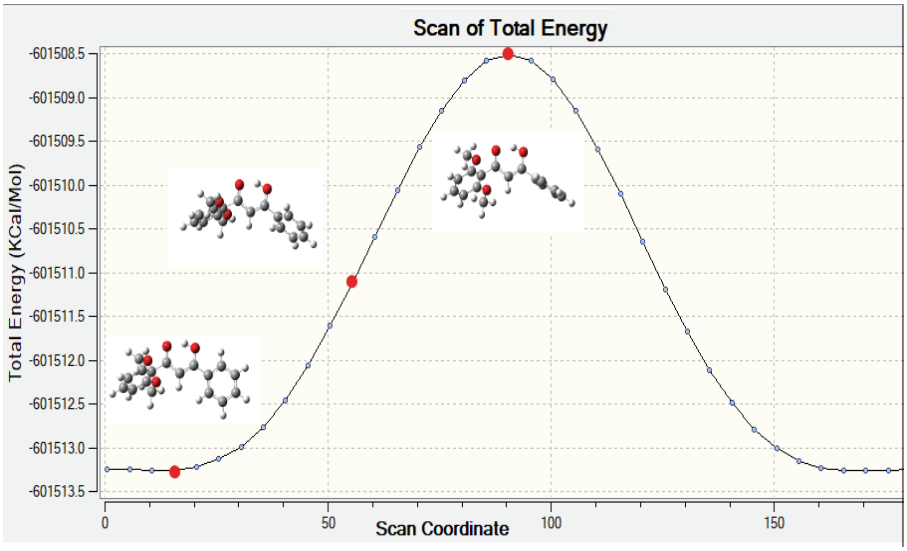


Fig. S-40. HR-MS (*m*/*z* $(M+Na)^+$) spectrum of **10**.

DIHEDRAL ANGLE SCANNING OF THE COMPOUNDS

a



b

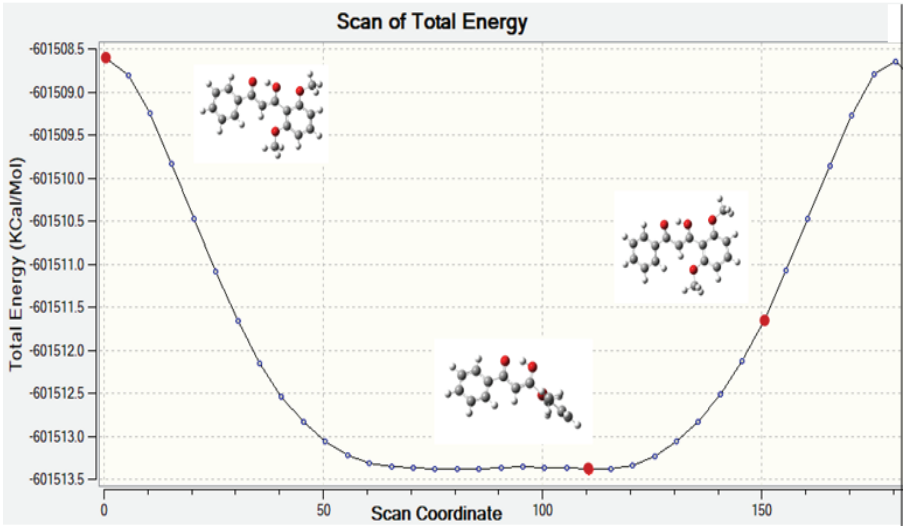
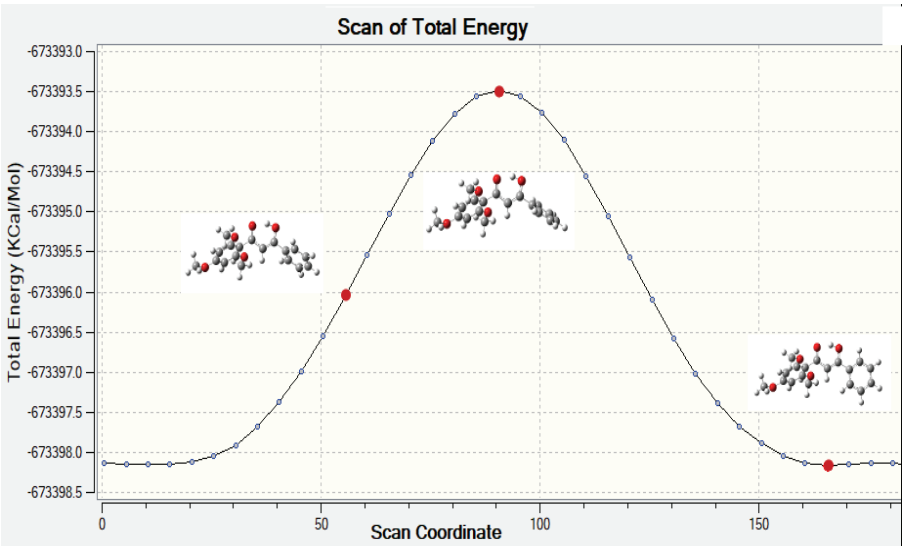


Fig. S-41. a) Dihedral angle scanning of the enol form **1a** (most and least stable conformers); b) Dihedral angle scanning of the enol form **1b** (most and least stable conformers).

a



b

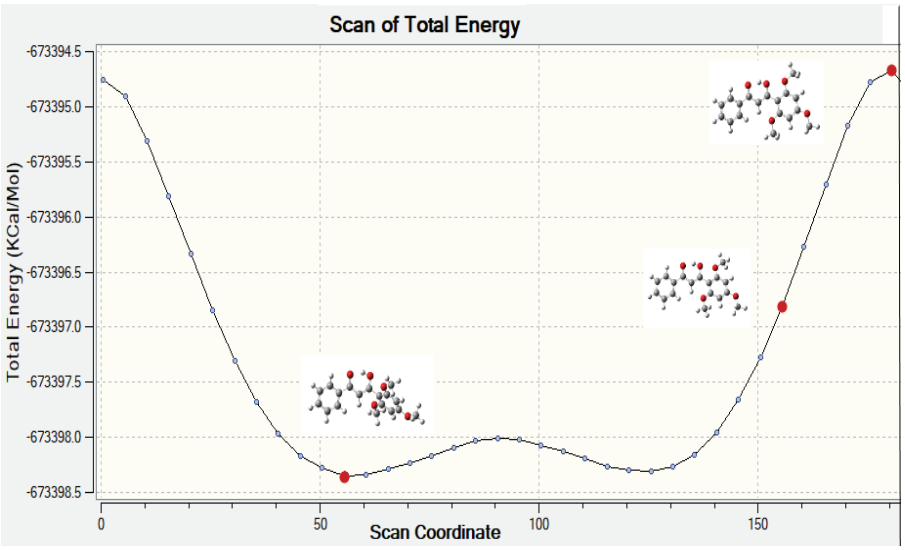
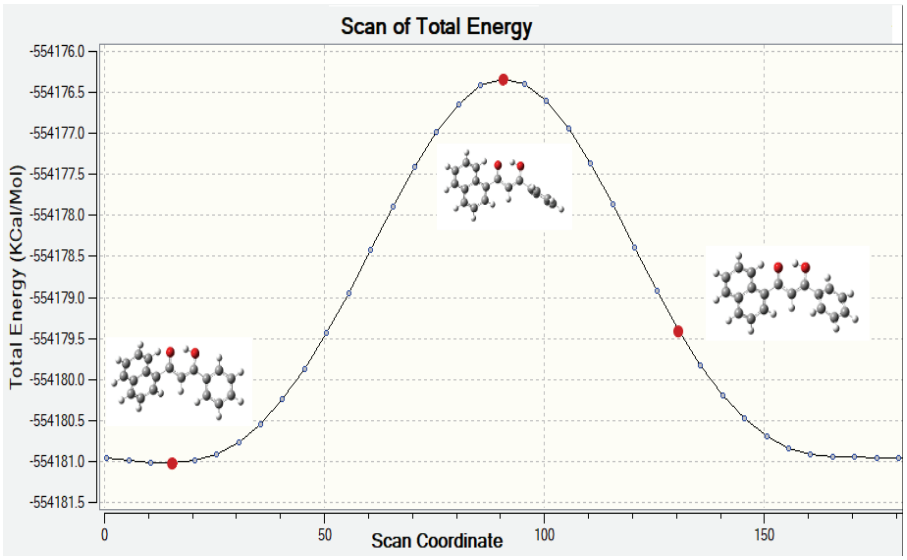


Fig. S-42. a) Dihedral angle scanning of the enol form **2a** (most and least stable conformers); b) Dihedral angle scanning of the enol form **2b** (most and least stable conformers).

a



b

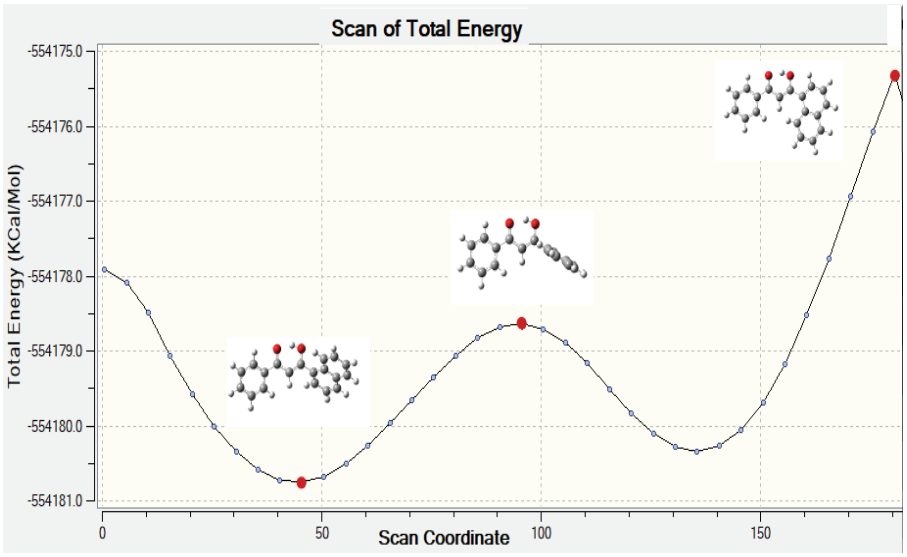


Fig. S-43. a) Dihedral angle scanning of the enol form **7a** (most and least stable conformers); b) Dihedral angle scanning of the enol form **7b** (most and least stable conformers).

HMBC SPECTRA

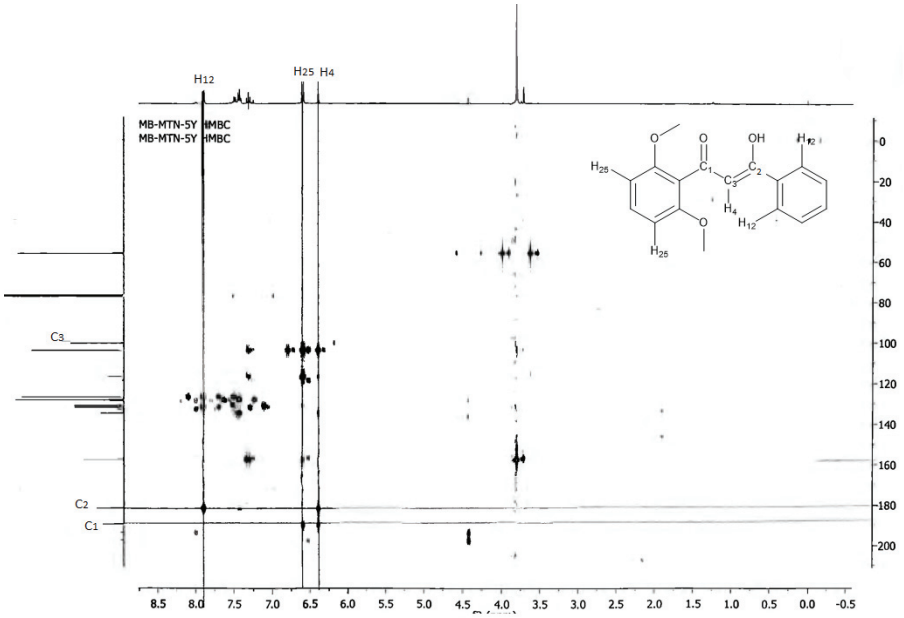


Fig. S-44. HMBC spectrum of compound **1**.

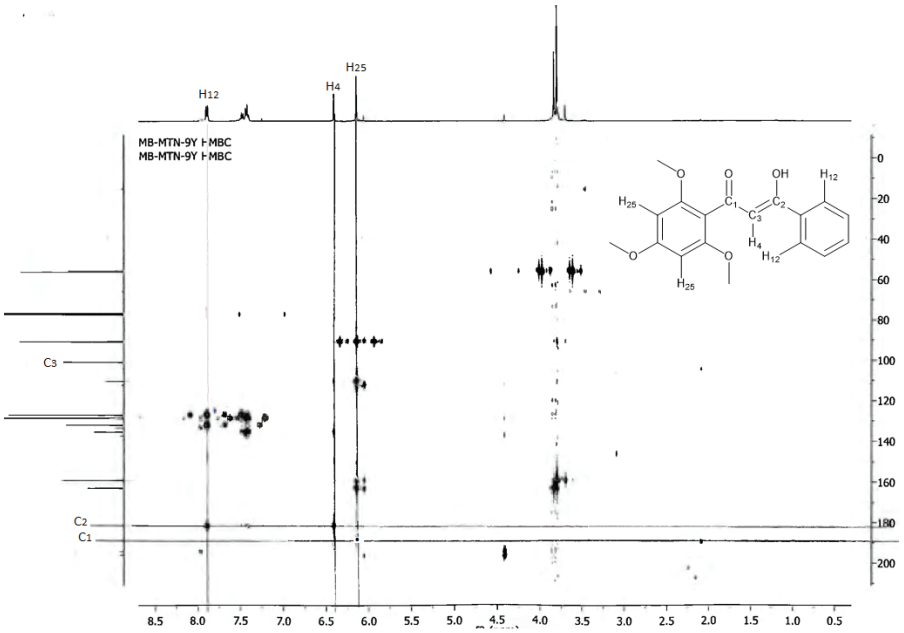


Fig. S-45. HMBC spectrum of compound **2**.

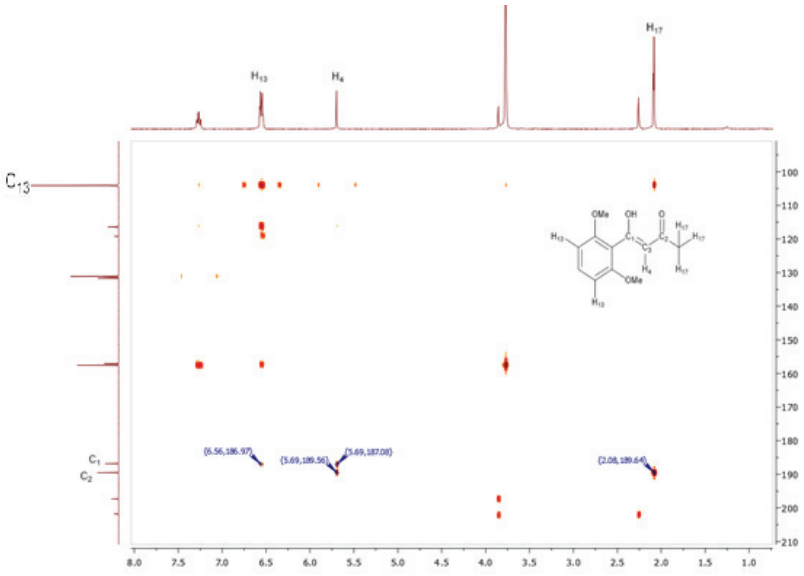


Fig. S-46. HMBC spectrum of compound **3**.

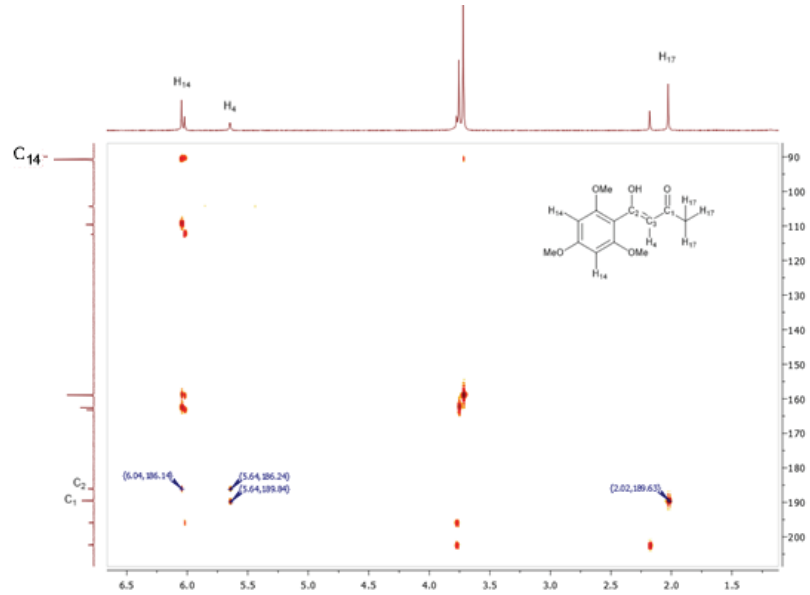


Fig. S-47. HMBC spectrum of compound **4**.

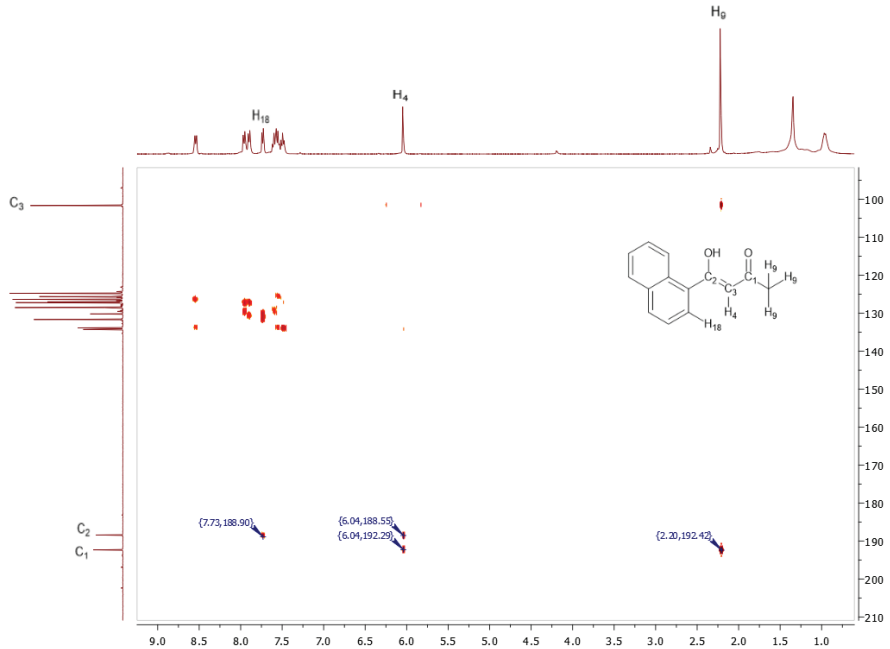


Fig. S-48. HMBC spectrum of compound **6**.

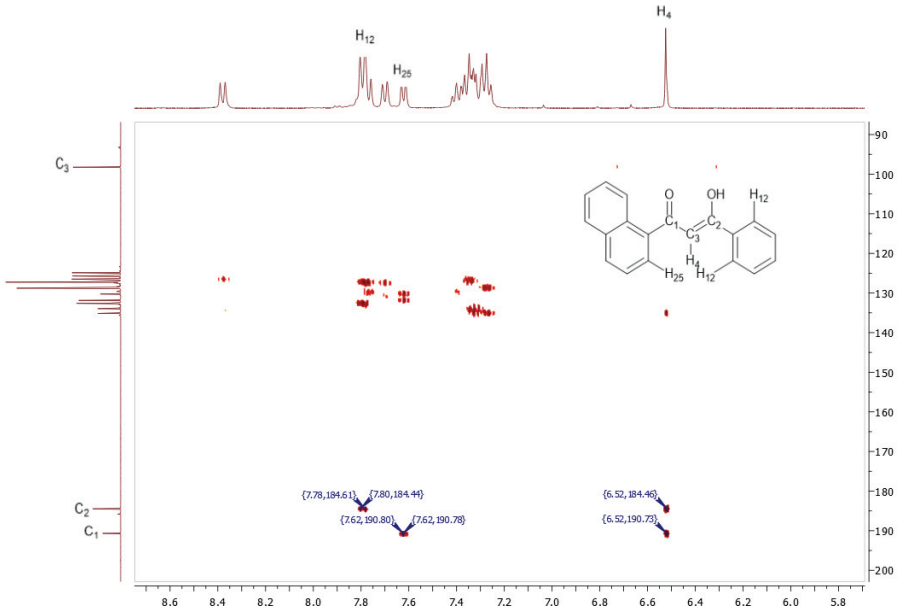


Fig. S-49. HMBC spectrum of the compound **7**.

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