Supporting Information

Tandem reaction of 1,2-allenic ketone with α-halo ketone or α-halo ester in water: an efficient and sustainable synthesis of 1,3,4'-tricarbonyl compounds

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1. General details

Flash chromatographic purification of products was performed on silica gel (200-300 mesh). Thin-layer chromatography was visualized with UV light (254 and 365 nm). ^{1}H and ^{13}C NMR spectra were determined on a Bruker AC 400 spectrometer as $CDCl_3$ solutions. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane and were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants *J* were given in Hz. Mass spectra were obtained in API mode using a Waters Acquity SQ HPLC-mass spectrometer. The HRMS (High-Resolution Mass Spectra) were performed on a JEOL HX 110A spectrometer.

2. A typical procedure for the synthesis of 3a

To a flask containing 1-phenylbuta-2,3-dien-1-one (**1a**, 1 mmol) and bromoacetophenone (**2a**, 1 mmol) were added water (4 mL) and TBAF·$3H_2O$ (2 mmol). The mixture was stirred at 80 °C for 2 h. It was then cooled to room temperature and extracted with diethyl ether (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (5-10%) to give 2-aceto-1,4-diphenylbutane-1,4-dione (**3a**). **3b-3x** were obtained in a similar manner.

3. Procedures for the synthesis of 8-14

3.1 Procedure for the synthesis of 8

To a flask containing 2-aceto-1-(4-methylphenyl)-4-phenylbutane-1,4-dione (0.5 mmol) and hydrazine hydrate (0.5 mmol) were added ethanol (8 mL) and diluted hydrogen chloride (2%, 2 mL). The mixture was stirred at 80 °C overnight. Upon completion, the mixture was added with water (5 mL) and then extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (25%) to give 2-(3-methyl-5-(4-methylphenyl)-1*H*-pyrazol-4-yl)-1-phenylethanone (**8**) with a yield of 68%.

3.2 Procedure for the synthesis of 9

To a flask containing 2-aceto-1-(4-methylphenyl)-4-phenylbutane-1,4-dione (0.4 mmol) and hydroxylamine hydrochloride (0.8 mmol) were added ethanol (4 mL) and water (4 mL). The mixture was stirred at 80 °C for 2 h. Upon completion, the mixture was added with water (5 mL) and then extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (20%) to give 2-(3-methyl-5-(4-methylphenyl)-isoxazol-4-yl)-1-phenylethanone (**9**) with a yield of 82%.

3.3 Procedure for the synthesis of 10

To a flask containing 2-aceto-1-(4-methylphenyl)-4-phenylbutane-1,4-dione (0.5 mmol) were added toluene (5 mL) and 4-methylbenzenesulfonic acid (0.5 mmol). The mixture was stirred at 100 °C for 1.5 h. Upon completion, the mixture was added with water (5 mL) and then extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (10%) to give 1-(5-phenyl-2-(4-methylphenyl)-furan-3-yl)ethanone (**10**) with a yield of 74%.

3.4 Procedure for the synthesis of 11

To a flask containing 2-aceto-1-(4-methoxyphenyl)-4-phenylbutane-1,4-dione (0.4 mmol) were added toluene (6 mL) and P_2S_5 (0.8 mmol). The mixture was stirred at 110 °C overnight. Upon completion, the mixture was added with water (5 mL) and then extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (5%) to give 1-(2-(4-methoxyphenyl)-5-phenylthiophen-3-yl)ethanone (**11**) with a yield of 37%.

3.5 Procedure for the synthesis of 12

To a flask containing 2-aceto-1-(4-methylphenyl)-4-phenylbutane-1,4-dione (0.5 mmol) were added water (5 mL) and TBAF·3H_2O (2 mmol). The mixture was stirred at 90 °C for 12 h. Upon completion, the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic phases were washed with water, dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (20%) to give 1-phenyl-4-(4-methylphenyl)butane-1,4-dione (**12**) with a yield of 75%.

3.6 Procedure for the synthesis of 13

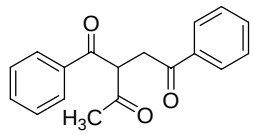
To a flask containing 1-phenyl-4-(4-methylphenyl)butane-1,4-dione (0.2 mmol) were added toluene (5 mL) and 4-methylbenzenesulfonic acid (0.2 mmol). The mixture was stirred at 100 °C for 2 h. Upon completion, the mixture was added with water (5 mL) and then extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (10%) to give 2-phenyl-5-(4-methylphenyl)furan (**13**) with a yield of 61%.

3.7 Procedure for the synthesis of 14

To a tube containing 1-phenyl-4-(4-methylphenyl)butane-1,4-dione (0.2 mmol) were added methanol (5 mL) and ammonium hydroxide (25%, 6 mL). The tube was then sealed and the mixture was stirred at 50 °C overnight. Upon completion, the mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (10%) to give 2-phenyl-5-(4-methylphenyl)-1*H*-pyrrole (**14**) with a yield of 82%.

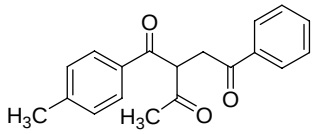
4. Spectroscopic characterization data

2-Aceto-1,4-diphenylbutane-1,4-dione (**3a**)[15a]



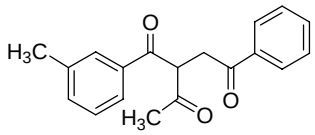
Colorless solid, mp 64-65°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 3.60 (dd, J_1 = 18.0 Hz, J_2 = 6.4 Hz, 1H), 3.78 (dd, J_1 = 18.0 Hz, J_2 = 6.4 Hz, 1H), 5.29 (t, J = 6.4 Hz, 1H), 7.42-7.63 (m, 6H), 7.96 (d, J = 7.6 Hz, 2H), 8.07 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.53, 38.02, 56.81, 128.18, 128.65, 128.86, 128.98, 133.53, 133.84, 136.00, 136.09, 196.23, 196.87, 202.29. MS: *m/z* 281 $(MH)^+$.

2-Aceto-1-(4-methylphenyl)-4-phenylbutane-1,4-dione (**3b**)



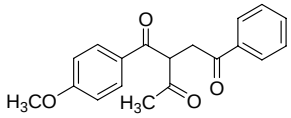
Colorless solid, mp 54-55°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22 (s, 3H), 2.40 (s, 3H), 3.56 (dd, J_1 = 18.0 Hz, J_2 = 6.4 Hz, 1H), 3.78 (dd, J_1 = 18.0 Hz, J_2 = 6.4 Hz, 1H), 5.27 (t, J = 6.4 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.94-7.98 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.66, 29.47, 38.02, 56.67, 128.16, 128.62, 129.02, 129.66, 133.47, 133.60, 136.06, 144.89, 195.78, 196.93, 202.39. MS: *m/z* 295 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{19}O_3$: 295.1335 [M+H], found: 295.1336.

2-Aceto-1-(3-methylphenyl)-4-phenylbutane-1,4-dione (**3c**)



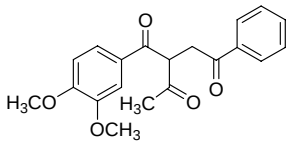
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.43 (s, 3H), 3.59 (dd, J_1 = 18.4 Hz, J_2 = 6.8 Hz, 1H), 3.79 (dd, J_1 = 18.4 Hz, J_2 = 6.8 Hz, 1H), 5.29 (t, J = 6.8 Hz, 1H), 7.38-7.47 (m, 3H), 7.52-7.58 (m, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.88-7.96 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.41, 29.62, 38.05, 56.75, 126.14, 128.21, 128.66, 128.87, 129.31, 133.57, 134.72, 135.96, 136.06, 138.92, 196.48, 196.95, 202.46. MS: *m/z* 295 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{19}O_3$: 295.1335 [M+H], found: 295.1338.

2-Aceto-1-(4-methoxylphenyl)-4-phenylbutane-1,4-dione (**3d**)



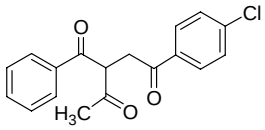
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 3.60 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.78 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.84 (s, 3H), 5.29 (t, J = 6.4 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.42, 38.03, 55.57, 56.39, 114.16, 128.18, 128.62, 128.91, 131.33, 133.52, 135.99, 164.14, 194.59, 197.05, 202.63. MS: *m/z* 311 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{19}O_4$: 311.1284 [M+H], found: 311.1295.

2-Aceto-1-(3,4-dimethoxylphenyl)-4-phenylbutane-1,4-dione (**3e**)



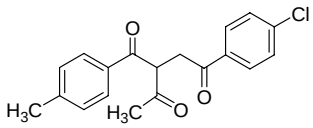
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.19 (s, 3H), 3.54 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.74 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.87 (s, 3H), 3.89 (s, 3H), 5.22 (t, J = 6.4 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.49-7.53 (m, 2H), 7.73 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.23, 38.04, 55.92, 56.12, 56.31, 110.20, 110.54, 123.91, 128.14, 128.61, 129.06, 133.50, 135.96, 149.24, 153.93, 194.56, 197.01, 202.61. MS: *m/z* 341 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{21}O_5$: 341.139 [M+H], found: 341.1381.

2-Aceto-4-(4-chlorophenyl)-1-phenylbutane-1,4-dione (**3f**)



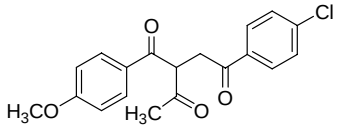
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 3.56 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.75 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.28 (t, J = 6.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.64, 37.94, 56.68, 128.88, 129.00, 129.05, 129.62, 134.00, 134.27, 135.94, 140.04, 195.81, 196.12, 202.18. MS: *m/z* 315 $(MH)^+$. HRMS (FAB) calcd for $C_{18}H_{16}ClO_3$: 315.0789 [M+H], found: 315.0773.

2-Aceto-4-(4-chlorophenyl)-1-(4-methylphenyl)butane-1,4-dione (**3g**)



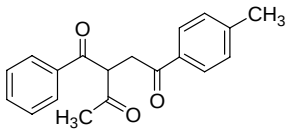
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.44 (s, 3H), 3.52 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.75 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.26 (t, J = 6.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.74, 29.59, 37.93, 56.54, 128.98, 129.04, 129.62, 129.74, 133.42, 134.33, 140.00, 145.12, 195.69, 195.90, 202.30. MS: *m/z* 329 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}ClO_3$: 329.0945 [M+H], found: 329.0932.

2-Aceto-4-(4-chlorophenyl)-1-(4-methoxyphenyl)butane-1,4-dione (**3h**)



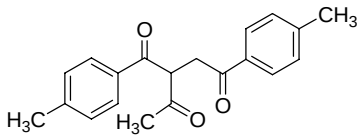
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 3.50 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.73 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5,22 (t, J = 6.4 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.43, 37.93, 55.59, 56.34, 114.19, 128.83, 128.95, 129.60, 131.34, 134.35, 139.92, 164.20, 194.42, 195.96, 202.43. MS: *m/z* 345 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}ClO_4$: 345.0894 [M+H], found: 345.0888.

2-Aceto-4-(4-methylphenyl)-1-phenylbutane-1,4-dione (**3i**)



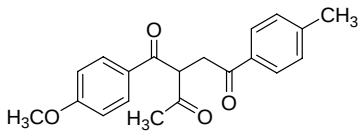
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.24 (s, 3H), 2.42 (s, 3H), 3.58 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.77 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.30 (t, J = 6.4 Hz, 1H), 7.24-7.29 (m, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 8.08 (J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.70, 29.62, 37.95, 56.75, 128.32, 128.89, 128.99, 129.34, 133.46, 133.87, 136.03, 144.48, 196.36, 196.48, 202.49. MS: *m/z* 295 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{19}O_3$: 295.1335 [M+H], found: 295.1331.

2-Aceto-1,4-di(4-methylphenyl)butane-1,4-dione (**3j**)



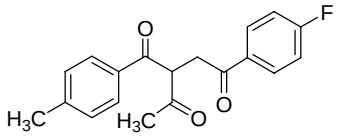
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.24 (s, 3H), 2.40 (s, 3H), 2.45 (s, 3H), 3.54 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.78 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.27 (t, J = 6.4 Hz, 1H), 7.25-7.33 (m, 4H), 7.88 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.71, 21.74, 29.59, 37.94, 56.60, 127.77, 128.32, 129.05, 129.33, 129.69, 133.51, 144.43, 144.96, 195.94, 196.57, 202.61. MS: *m/z* 309 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{21}O_3$: 309.1491 [M+H], found: 309.1482.

2-Aceto-1-(4-methoxyphenyl)-4-(4-methylphenyl)butane-1,4-dione (**3k**)



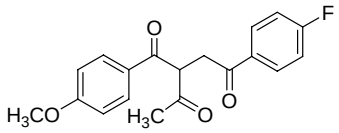
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22 (s, 3H), 2.38 (s, 3H), 3.53 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.77 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.86 (s, 3H), 5.23 (t, J = 6.4 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.68, 29.41, 37.93, 55.58, 56.43, 114.14, 128.30, 128.95, 129.31, 131.33, 133.55, 144.39, 164.11, 194.68, 196.63, 202.70. MS: *m/z* 325 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{21}O_4$: 325.1441 [M+H], found: 325.1452.

2-Aceto-4-(4-fluorophenyl)-1-(4-methylphenyl)butane-1,4-dione (**3l**)



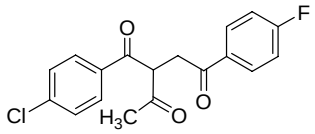
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.44 (s, 3H), 3.53 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.74 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.27 (t, J = 6.4 Hz, 1H), 7.06-7.15 (m, 3H), 7.33 (d, J = 8.0 Hz, 2H), 7.80-8.03 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.74, 29.59, 37.89, 56.57, 115.69, 115.91, 128.61, 129.04, 129.73, 130.84, 130.93, 133.45, 145.08, 195.45, 195.75, 202.34. MS: *m/z* 313 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}FO_3$: 313.1241 [M+H], found: 313.1255.

2-Aceto-4-(4-fluorophenyl)-1-(4-methoxyphenyl)butane-1,4-dione (**3m**)



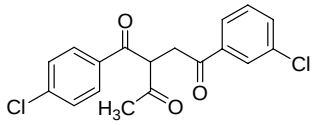
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22 (s, 3H), 3.51 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.75 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.23 (t, J = 6.4 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 6.99-7.14 (m, 2H), 7.98-8.02 (m, 2H), 8.06 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.44, 37.88, 55.60, 56.37, 114.19, 115.67, 115.89, 128.85, 130.83, 130.93, 131.35, 132.47, 164.20, 194.51, 195.54, 202.50. MS: *m/z* 329 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}FO_4$: 329.119 [M+H], found: 329.1198.

2-Aceto-1-(4-chlorophenyl)-4-(4-fluorophenyl)butane-1,4-dione (**3n**)



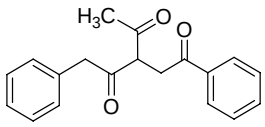
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 3.62 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.72 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.21 (t, J = 6.4 Hz, 1H), 7.13 (t, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.99-7.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.40, 37.93, 56.87, 115.74, 115.96, 129.34, 130.26, 130.84, 130.93, 134.43, 140.52, 194.95, 195.23, 201.84. MS: *m/z* 333 $(MH)^+$. HRMS (FAB) calcd for $C_{18}H_{15}ClFO_3$: 333.0695 [M+H], found: 333.0683.

2-Aceto-1-(4-chlorophenyl)-4-(3-chlorophenyl)butane-1,4-dione (**3o**)



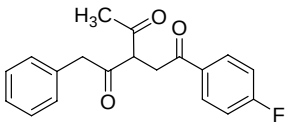
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 3.61 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 3.71 (dd, J_1 = 18.4 Hz, J_2 = 6.4 Hz, 1H), 5.20 (t, J = 6.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.50-7.56 (m, 2H), 7.85 (d, J = 7.6 Hz, 1H), 7.94 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.39, 38.08, 56.83, 126.27, 128.30, 129.36, 130.03, 130.26, 133.55, 134.38, 135.07, 137.39, 140.58, 194.82, 195.66, 201.68. MS: *m/z* 349 $(MH)^+$. HRMS (FAB) calcd for $C_{18}H_{15}Cl_2O_3$: 349.0399 [M+H], found: 349.0392.

3-Aceto-1,5-diphenylpentane-1,4-dione (**3p**)



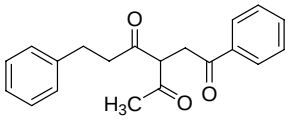
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.09 (s, 3H), 3.54-3.58 (m, 2H), 3.95 (s, 2H), 4.48 (t, J = 6.8 Hz, 1H), 7.25-7.61 (m, 8H), 7.95 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.53, 38.14, 50.09, 60.57, 127.43, 128.13, 128.69, 128.88, 129.92, 132.94, 133.64, 135.83, 196.86, 202.86. MS: *m/z* 295 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{19}O_3$: 295.1335 [M+H], found: 295.1345.

3-Aceto-1-(4-fluorophenyl)-5-phenylpentane-1,4-dione (**3q**)



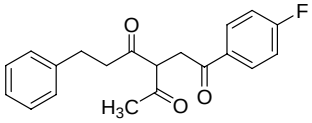
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.09 (s, 1H), 3.50-3.54 (m, 2H), 3.94 (s, 2H), 4.47 (t, J = 6.8 Hz, 1H), 7.11-7.16 (m, 3H), 7.24-7.38 (m, 4H), 7.96-7.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.56, 37.99, 50.12, 60.52, 115.75, 115.96, 127.47, 128.90, 129.90, 130.77, 130.87, 132.30, 132.86, 195.29, 202.72, 202.80. MS: *m/z* 313 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}FO_3$: 313.1241 [M+H], found: 313.1232.

3-Aceto-1,6-diphenylhexane-1,4-dione (**3r**)



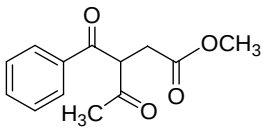
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.94-3.00 (m, 4H), 3.52-3.54 (m, 2H), 4.35 (t, J = 6.8 Hz, 1H), 7.18-7.31 (m, 5H), 7.47 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.94 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.49, 29.86, 37.53, 44.50, 62.08, 126.24, 128.12, 128.40, 128.54, 128.68, 133.62, 140.56, 196.92, 202.87, 204.40. MS: *m/z* 309 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{21}O_3$: 309.1491 [M+H], found: 309.1479.

3-Aceto-1-(4-fluorophenyl)-6-phenylhexane-1,4-dione (**3s**)



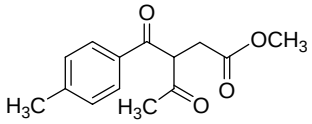
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.94-2.99 (m, 4H), 3.47-3.50 (m, 2H), 4.34 (t, J = 6.8 Hz, 1H), 7.11-7.22 (m, 5H), 7.27-7.31 (m, 2H), 7.95-7.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.49, 29.90, 37.37, 44.54, 62.04, 115.73, 115.94, 126.27, 128.39, 128.55, 130.77, 130.86, 140.52, 195.35, 202.71, 204.30. MS: *m/z* 327 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{20}FO_3$: 327.1397 [M+H], found: 327.1396.

Methyl 3-aceto-4-oxo-4-phenylbutanoate (**3t**)



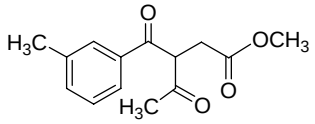
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.18 (s, 3H), 2.98 (dd, J_1 = 18.0 Hz, J_2 = 6.8 Hz, 1H), 3.04 (dd, J_1 = 18.0 Hz, J_2 = 6.8 Hz, 1H), 3.67 (s, 3H), 5.02 (t, J = 6.8 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 8.03 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.13, 32.81, 52.18, 57.68, 128.86, 129.01, 134.01, 135.82, 171.86, 195.52, 201.89. MS: *m/z* 235 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{15}O_4$: 235.0971 [M+H], found: 235.0956.

Methyl 3-aceto-4-oxo-4-(4-methylphenyl)butanoate (**3u**)



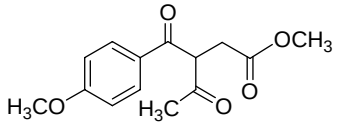
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.17 (s, 3H), 2.43 (s, 3H), 2.93 (dd, J_1 = 17.2 Hz, J_2 = 6.8 Hz, 1H), 3.04 (dd, J_1 = 17.2 Hz, J_2 = 6.8 Hz, 1H), 3.67 (s, 3H), 4.99 (t, J = 6.8 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.71, 29.05, 32.84, 52.13, 57.58, 129.02, 129.69, 133.34, 145.11, 171.91, 195.04, 202.00. MS: *m/z* 249 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{17}O_4$: 249.1128 [M+H], found: 249.1112.

Methyl 3-aceto--4-oxo-4-(3-methylphenyl)butanoate (**3v**)



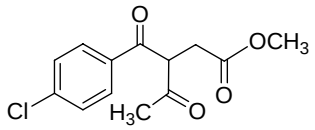
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.18 (s, 3H), 2.43 (s, 3H), 2.94 (dd, J_1 = 17.2 Hz, J_2 = 6.8 Hz, 1H), 3.04 (dd, J_1 = 17.2 Hz, J_2 = 6.8 Hz, 1H), 3.68 (s, 3H), 5.01 (t, J = 6.8 Hz, 1H), 7.40-7.43 (m, 2H), 7.81-7.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.34, 25.34, 29.09, 52.19, 57.71, 126.11, 128.85, 129.30, 134.83, 135.88, 138.94, 172.01, 195.77, 202.18. MS: *m/z* 249 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{17}O_4$: 249.1128 [M+H], found: 249.1122.

Methyl 3-aceto-4-oxo-4-(4-methoxyphenyl)butanoate (**3w**)



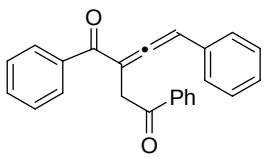
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.17 (s, 3H), 2.92 (dd, J_1 = 17.2 Hz, J_2 = 6.8 Hz, 1H), 3.05 (dd, J_1 = 17.2 Hz, J_2 = 6.8 Hz, 1H), 3.67 (s, 3H), 3.89 (s, 3H), 4.96 (t, J = 6.8 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.88, 32.85, 52.13, 55.59, 57.42, 114.16, 128.76, 131.34, 164.23, 171.97, 193.77, 202.17. MS: *m/z* 265 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{17}O_5$: 265.1077 [M+H], found: 265.1083.

Methyl 3-aceto-4-oxo-4-(4-chlorophenyl)butanoate (**3x**)



Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.17 (s, 3H), 3.00-3.02 (m, 2H), 3.67 (s, 3H), 4.94 (t, J = 6.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.89, 32.81, 52.18, 57.83, 129.31, 130.24, 134.24, 140.60, 171.70, 194.30, 201.49. MS: *m/z* 269 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{14}ClO_4$: 269.0581 [M+H], found: 269.0572.

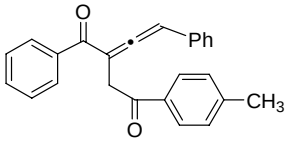
1,4-Diphenyl-2-(2-phenylvinylidene)butane-1,4-dione (**7a**)



Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.15 (dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 4.40 (dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz,

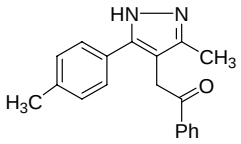
1H), 6.51 (s, 1H), 7.23-7.37 (m, 6H), 7.43-7.53 (m, 4H), 7.56-7.59 (m, 1H), 7.89 (d, J = 7.6 Hz, 2H), 8.05 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.54, 98.47, 105.08, 127.58, 127.95, 128.34, 128.47, 128.65, 128.91, 129.00, 131.71, 132.41, 133.29, 136.45, 137.61, 193.25, 196.47, 215.29. MS: *m/z* 339 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{19}O_2$: 339.1386 [M+H], found: 339.1388.

1-Phenyl-2-(2-phenylvinylidene)-4-p-tolylbutane-1,4-dione (**7b**)



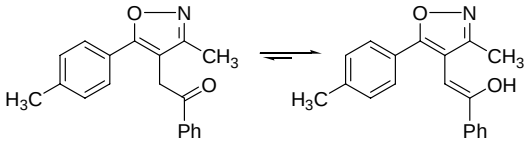
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.42 (s, 3H), 4.13 (dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 4.37 (dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 6.50 (s, 1H), 7.23-7.37 (m, 9H), 7.43-7.47 (m, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.94 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.68, 39.43, 98.40, 105.18, 127.43, 127.58, 127.94, 128.47, 128.89, 129.02, 129.34, 131.76, 132.39, 133.94, 137.64, 144.13, 193.33, 196.12, 215.22. MS: *m/z* 353 $(MH)^+$. HRMS (FAB) calcd for $C_{25}H_{21}O_2$: 353.1542 [M+H], found: 353.1539.

2-(3-Methyl-5-(4-methylphenyl)-1*H*-pyrazol-4-yl)-1-phenylethanone (**8**)



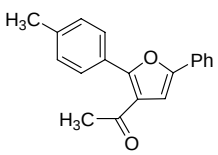
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.12 (s, 3H), 2.35 (s, 3H), 4.17 (s, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.93 (d, J = 7.6 Hz, 2H), 9.00 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.99, 21.21, 34.11, 108.29, 127.81, 128.29, 128.57, 128.99, 129.40, 133.10, 136.51, 137.88, 197.22. MS: *m/z* 291 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{19}N_2O$: 291.1498 [M+H], found: 291.1499.

2-(3-Methyl-5-(4-methylphenyl)isoxazol-4-yl)-1-phenylethanone (**9**)



Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.28 (s, 3H), 2.38 (s, 3H), 6.30 (s, 1H), 7.12 (d, J = 7.6 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 10.34 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.38, 21.61, 107.02, 115.05, 126.90, 127.18, 128.38, 128.80, 129.40, 129.67, 130.51, 136.06, 136.41, 142.55, 194.15. MS: *m/z* 292 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}NO_2$: 292.1338 [M+H], found: 292.1331.

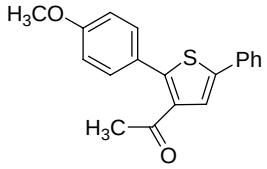
1-(5-Phenyl-2-(4-methylphenyl)furan-3-yl)ethanone (**10**)



Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 2.61 (s, 3H), 6.83 (s, 1H), 7.29-7.31 (m, 3H), 7.40 (t, J = 8.0

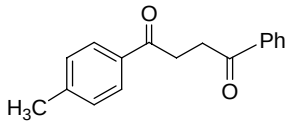
Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.33, 21.67, 106.61, 122.46, 123.67, 127.69, 128.75, 129.09, 129.23, 129.98, 136.38, 143.02, 151.44, 158.59, 191.01. MS: *m/z* 277 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{17}O_2$: 277.1229 [M+H], found: 277.1233.

1-(5-Phenyl-2-(4-methylphenyl)thiophene-3-yl)ethanone (**11**)



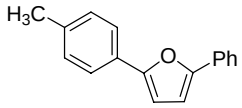
Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 3.79 (s, 3H), 6.40 (s, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.25, 55.26, 107.52, 113.79, 120.36, 123.15, 126.63, 128.52, 129.29, 131.03, 132.80, 147.57, 151.22, 157.87. MS: *m/z* 309 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{17}O_2S$: 309.095 [M+H], found: 309.0952.

1-Phenyl-4-(4-methylphenyl)butane-1,4-dione (**12**)[8c]



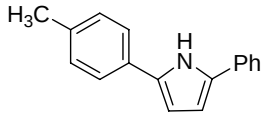
Colorless solid, mp 62-63°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.42 (s, 3H), 3.45 (s, 4H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 8.05 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.63, 32.45, 32.59, 128.10, 128.21, 128.56, 129.25, 133.09, 134.28, 136.79, 143.90, 198.29, 198.78. MS: *m/z* 253 $(MH)^+$.

2-Phenyl-5-(4-methylphenyl)furan (**13**)



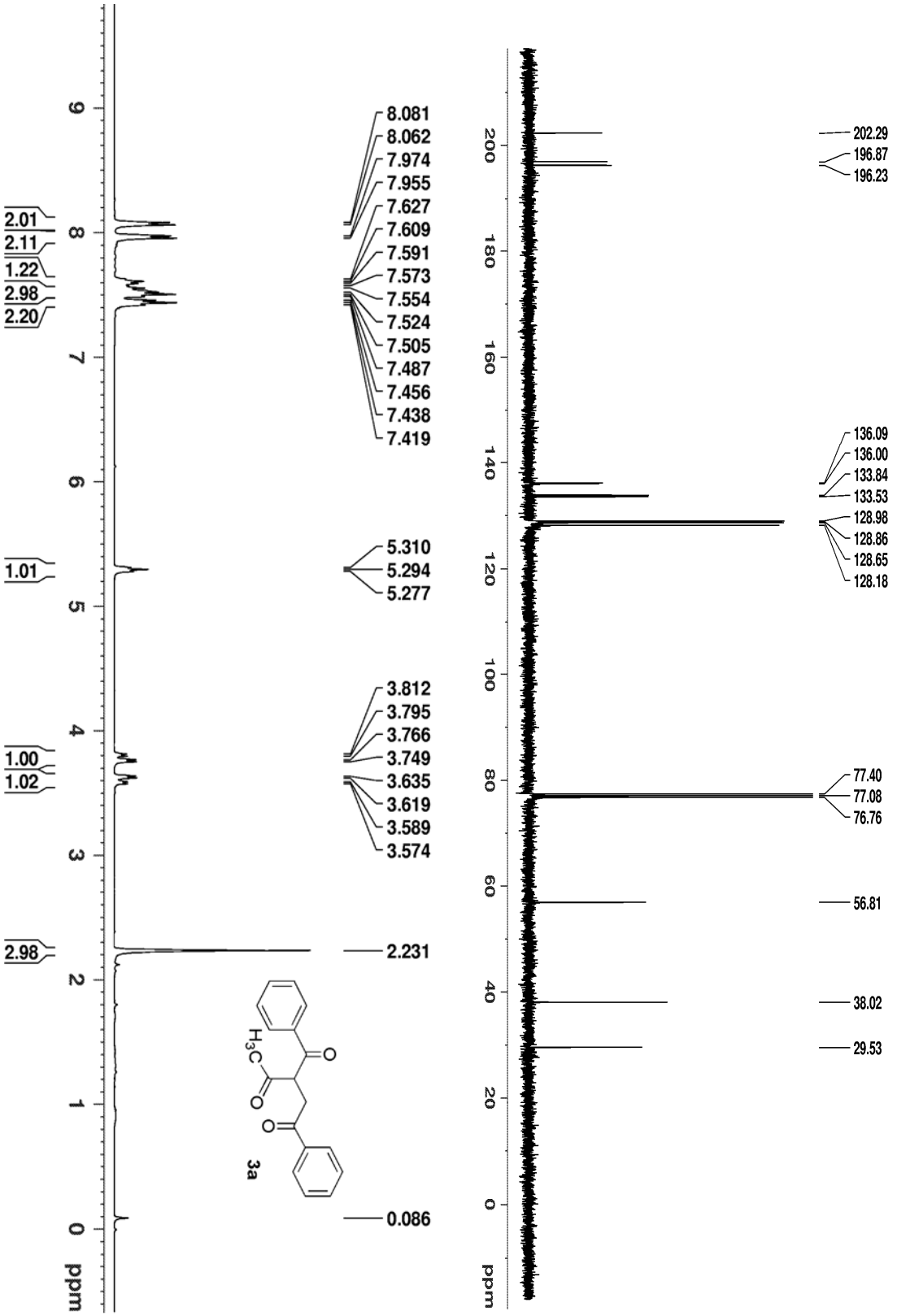
Colorless soild, mp 88-89°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 6.69 (d, *J* = 3.2 Hz, 1H), 6.74 (d, *J* = 3.6 Hz, 1H), 7.24-7.29 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.32, 106.49, 107.17, 123.61, 123.66, 127.18, 128.06, 128.68, 129.38, 130.82, 137.21, 152.90, 153.55. MS: *m/z* 235 $(MH)^+$. HRMS (FAB) calcd for $C_{17}H_{15}O$: 235.1124 [M+H], found: 235.1123.

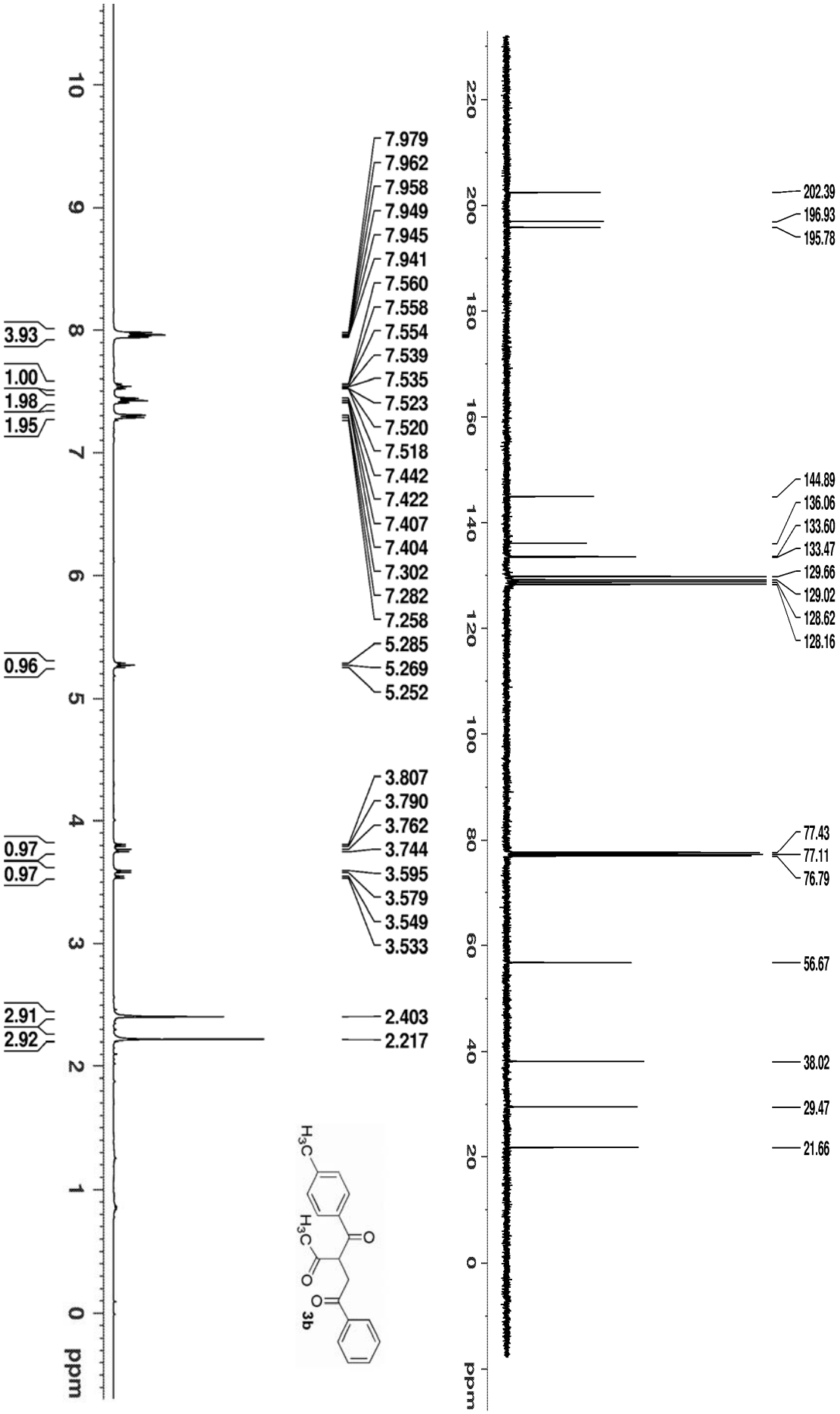
2-Phenyl-5-(4-methylphenyl)-1*H*-pyrrole (**14**)



Colorless soild, mp 140-141°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 6.56-6.61 (m, 2H), 7.21-7.26 (m, 3H), 7.39-7.46 (m, 4H), 7.55 (d, *J* = 8.0 Hz, 2H), 8.56 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.18, 107.37, 107.81, 123.72, 123.76, 126.26, 128.94, 129.63, 129.71, 132.53, 132.70, 133.29, 136.17. MS: *m/z* 234 $(MH)^+$. HRMS (FAB) calcd for $C_{17}H_{16}N$: 234.1283 [M+H], found: 234.1288.

5. Selected copies of ^{1}H and ^{13}C NMR spectra

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2.92
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7.958
7.949
7.945
7.941
7.560
7.558
7.554
7.539
7.535
7.523
7.520
7.518
7.442
7.422
7.407
7.404
7.302
7.282
7.258
5.285
5.269
5.252
3.807
3.790
3.762
3.744
3.595
3.579
3.549
3.533
2.403
2.217
H3C
H3C
O
O
O
O
3b
202.39
196.93
195.78
144.89
136.06
133.60
133.47
129.66
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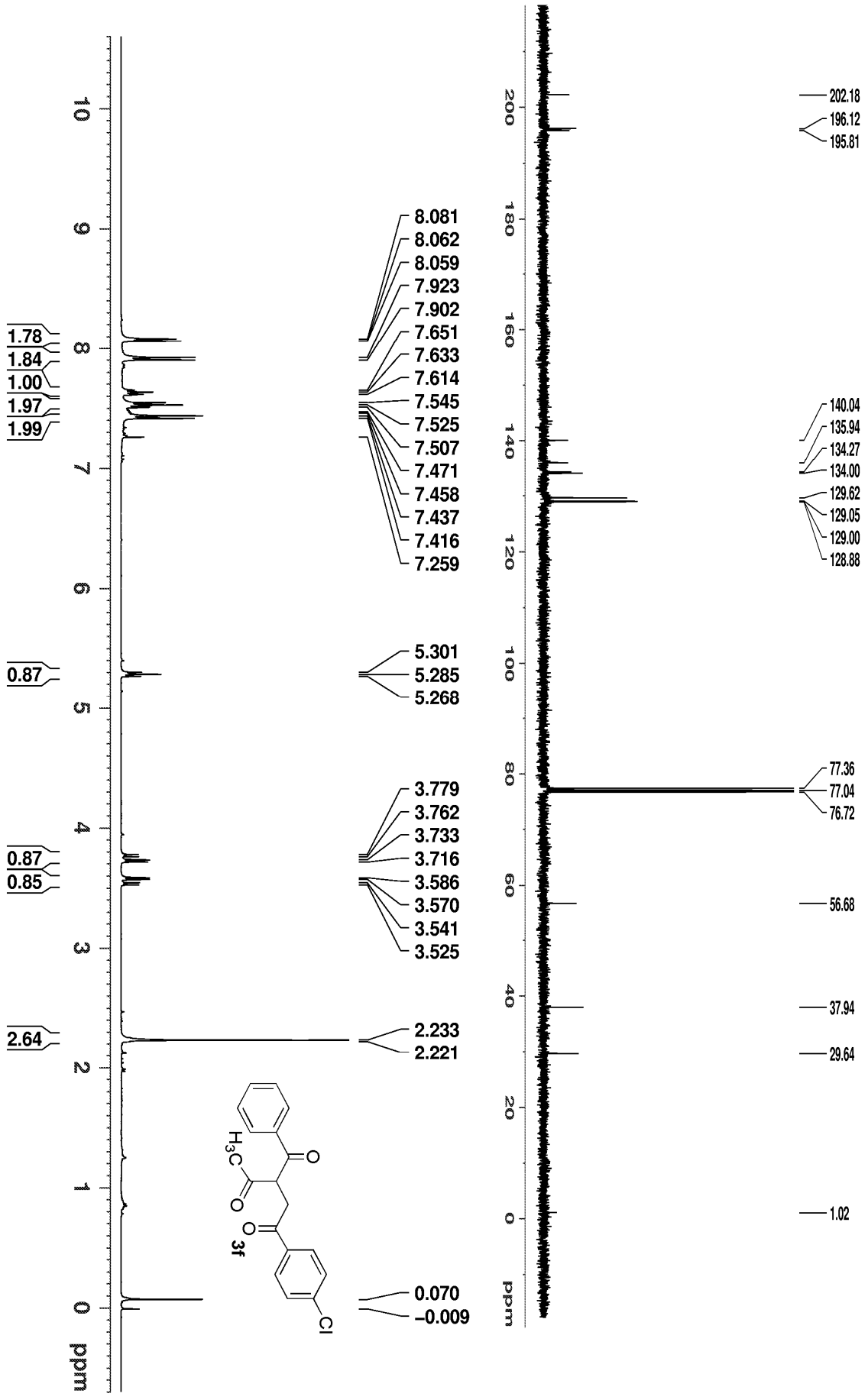
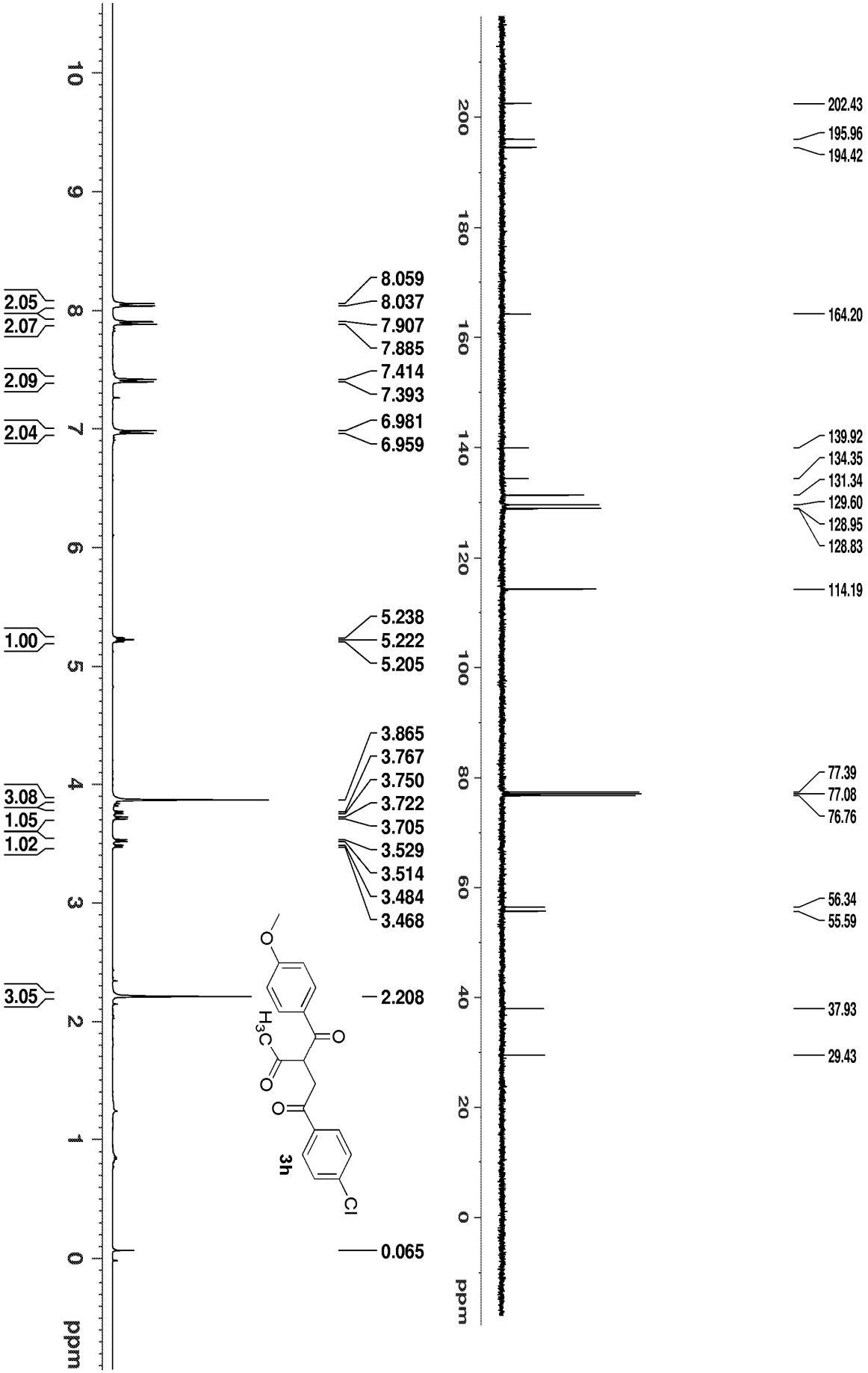
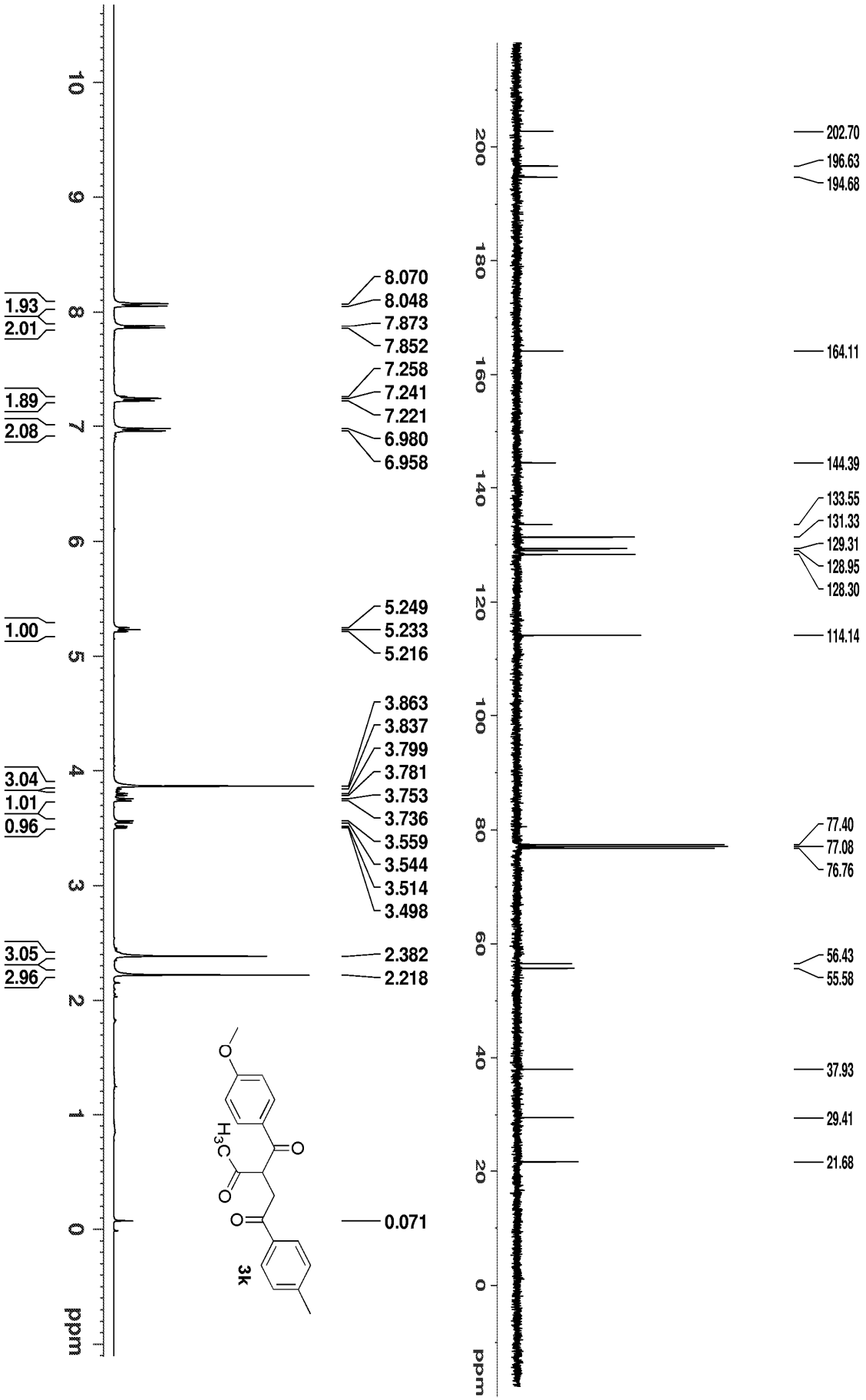
128.62
128.16
77.43
77.11
76.79
56.67
38.02
29.47
21.66
ppm



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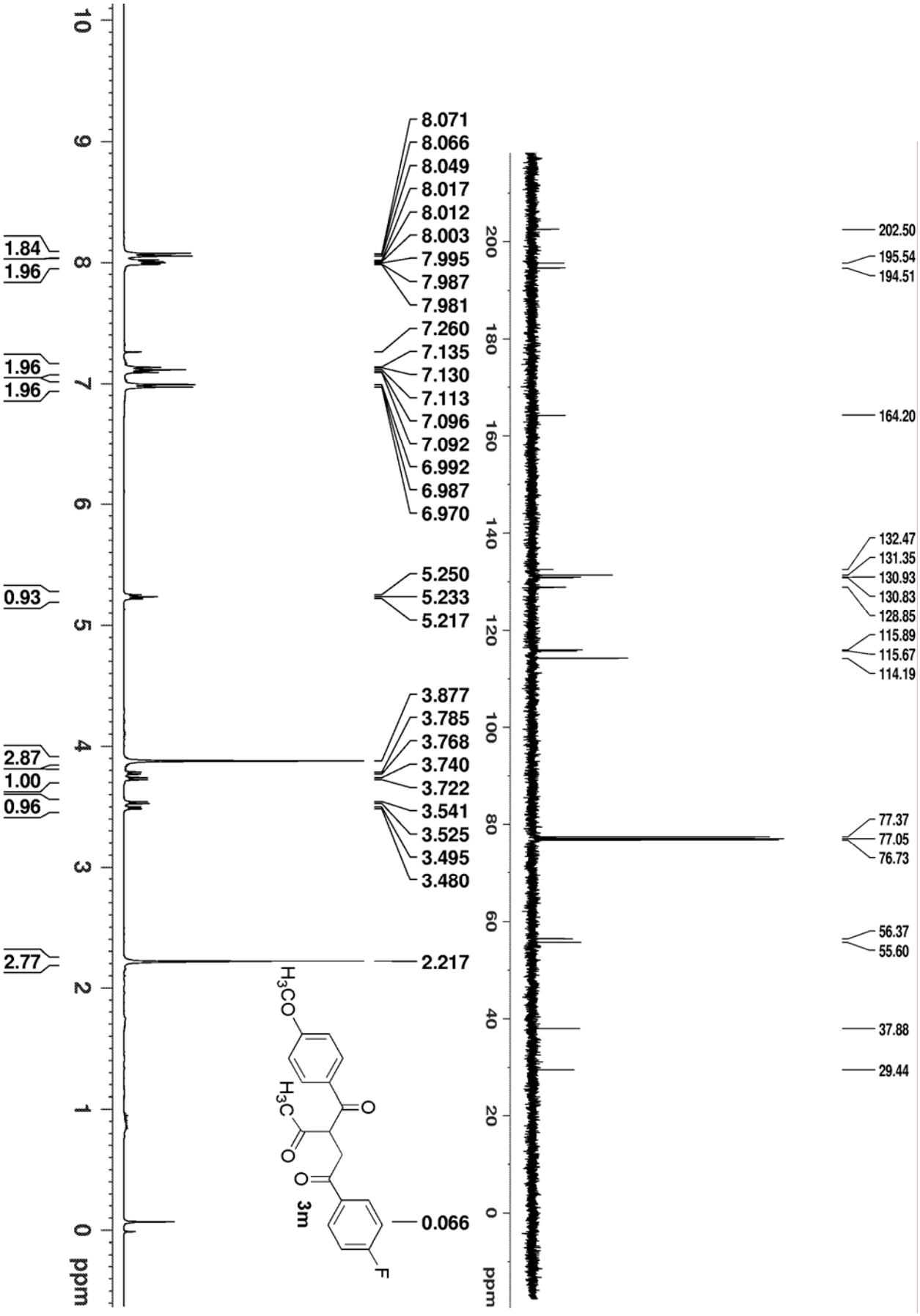
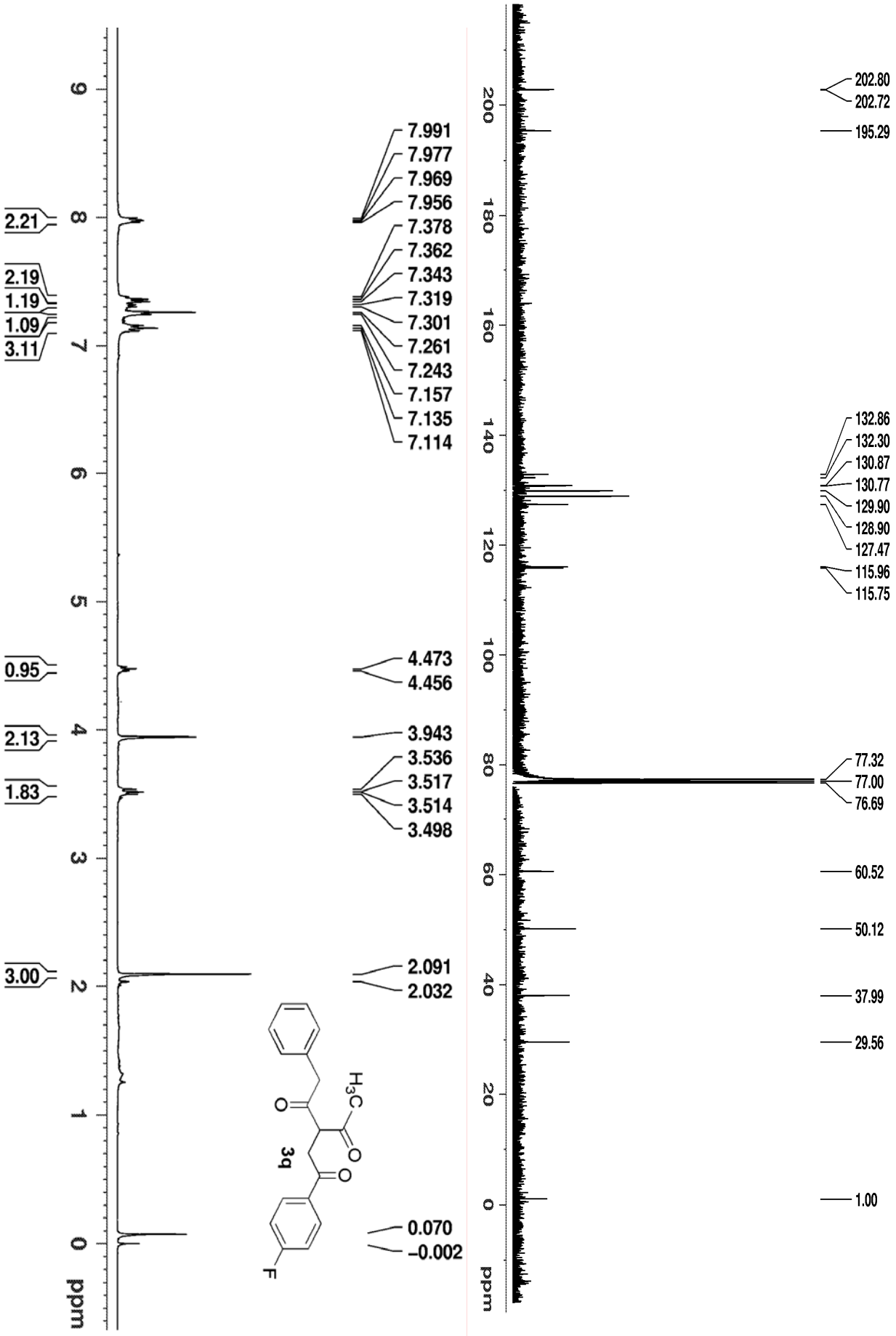
3.04
1.01
0.96
3.05
2.96
8.070
8.048
7.873
7.852
7.258
7.241
7.221
6.980
6.958
5.249
5.233
5.216
3.863
3.837
3.799
3.781
3.753
3.736
3.559
3.544
3.514
3.498
2.382
2.218
0.071
ppm
202.70
196.63
194.68
164.11
144.39
133.55
131.33
129.31
128.95
128.30
114.14
77.40
77.08
76.76
56.43
55.58
37.93
29.41
21.68
ppm
3k

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1.19
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3.11
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2.13
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7.969
7.956
7.378
7.362
7.343
7.319
7.301
7.261
7.243
7.157
7.135
7.114
4.473
4.456
3.943
3.536
3.517
3.514
3.498
2.091
2.032
0.070
−0.002
O
O
H3C
O
O
3q
F
ppm
202.80
202.72
195.29
132.86
132.30
130.87
130.77
129.90
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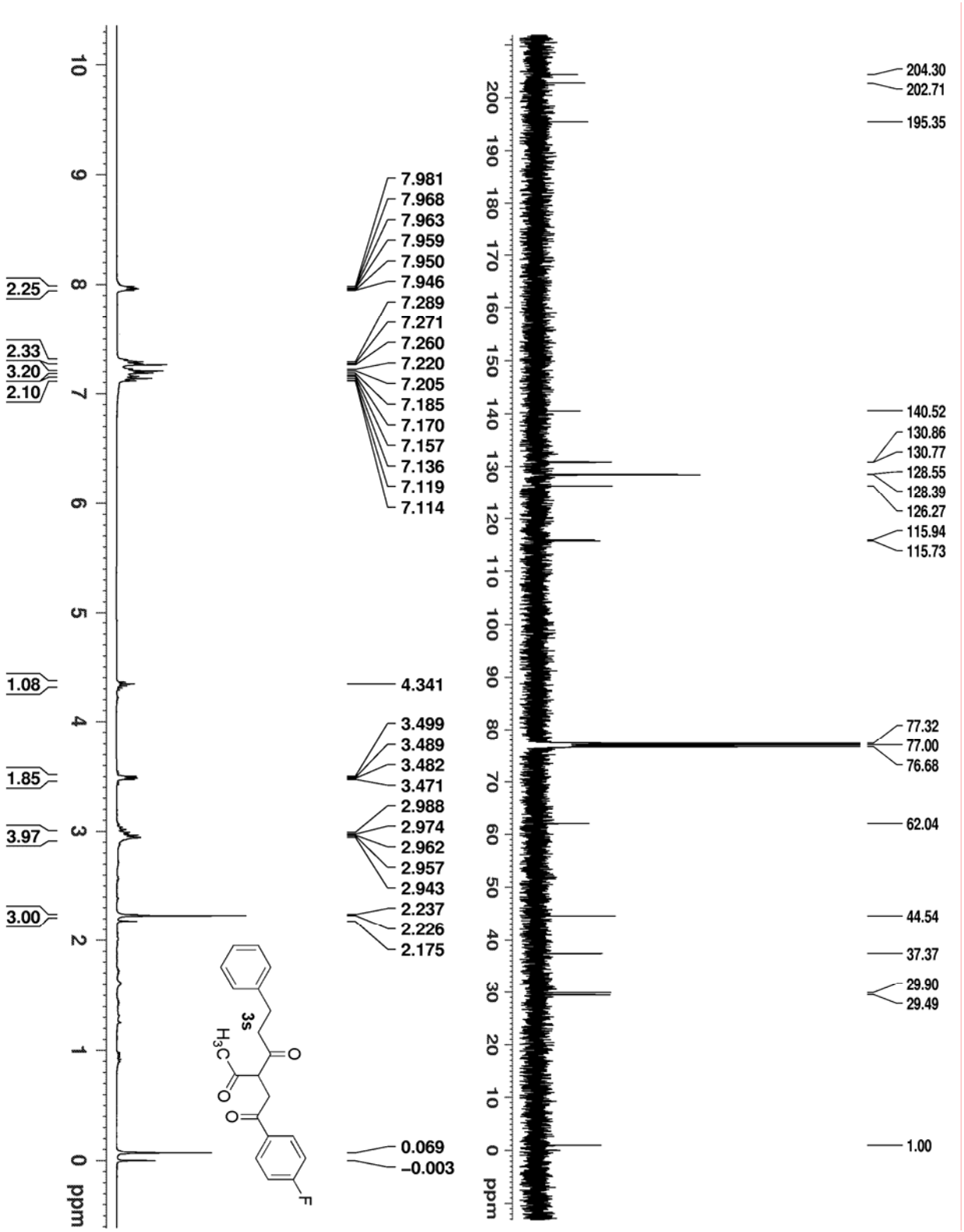
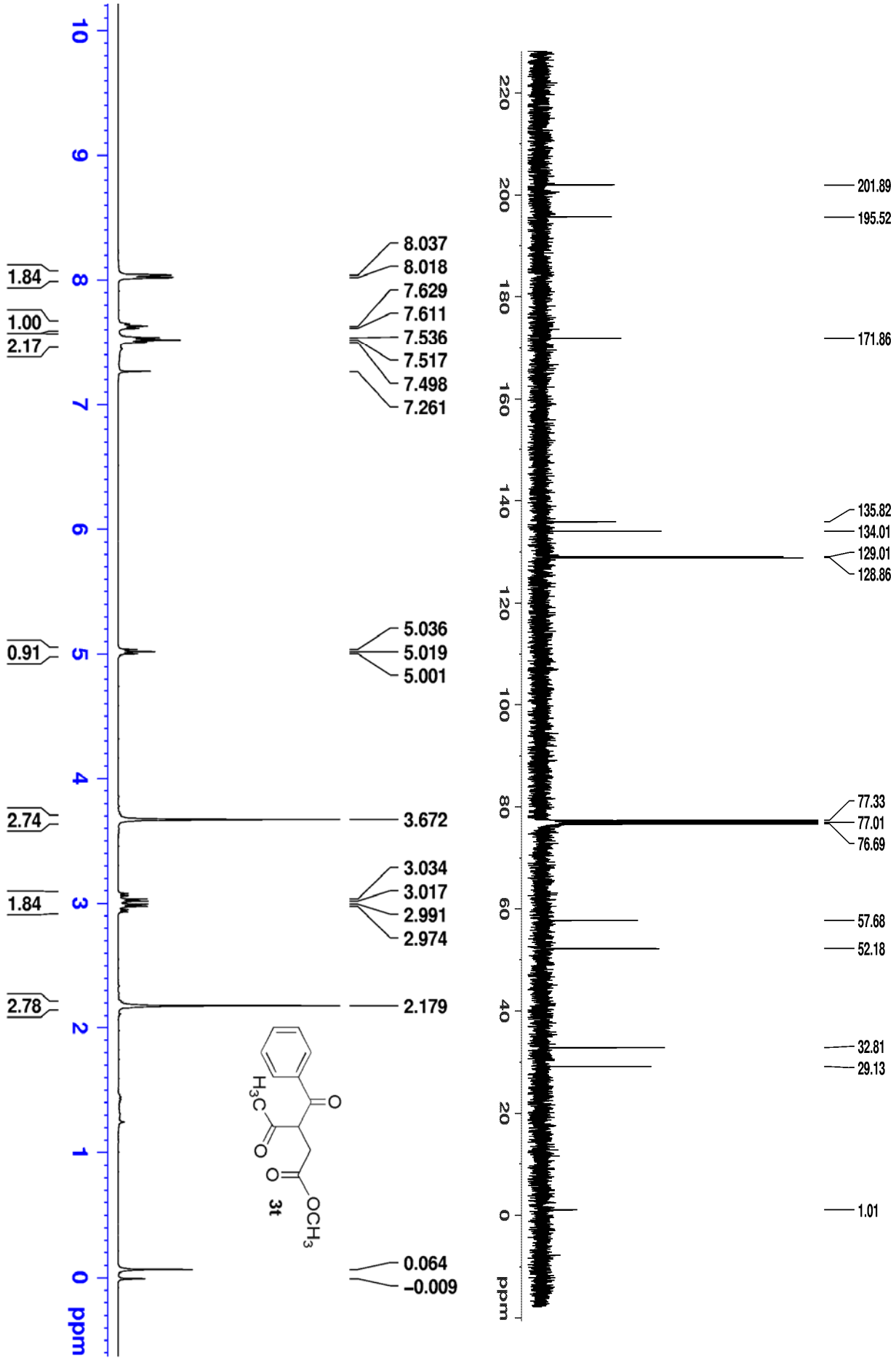
76.69
60.52
50.12
37.99
29.56
1.00

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1.84
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8.018
7.629
7.611
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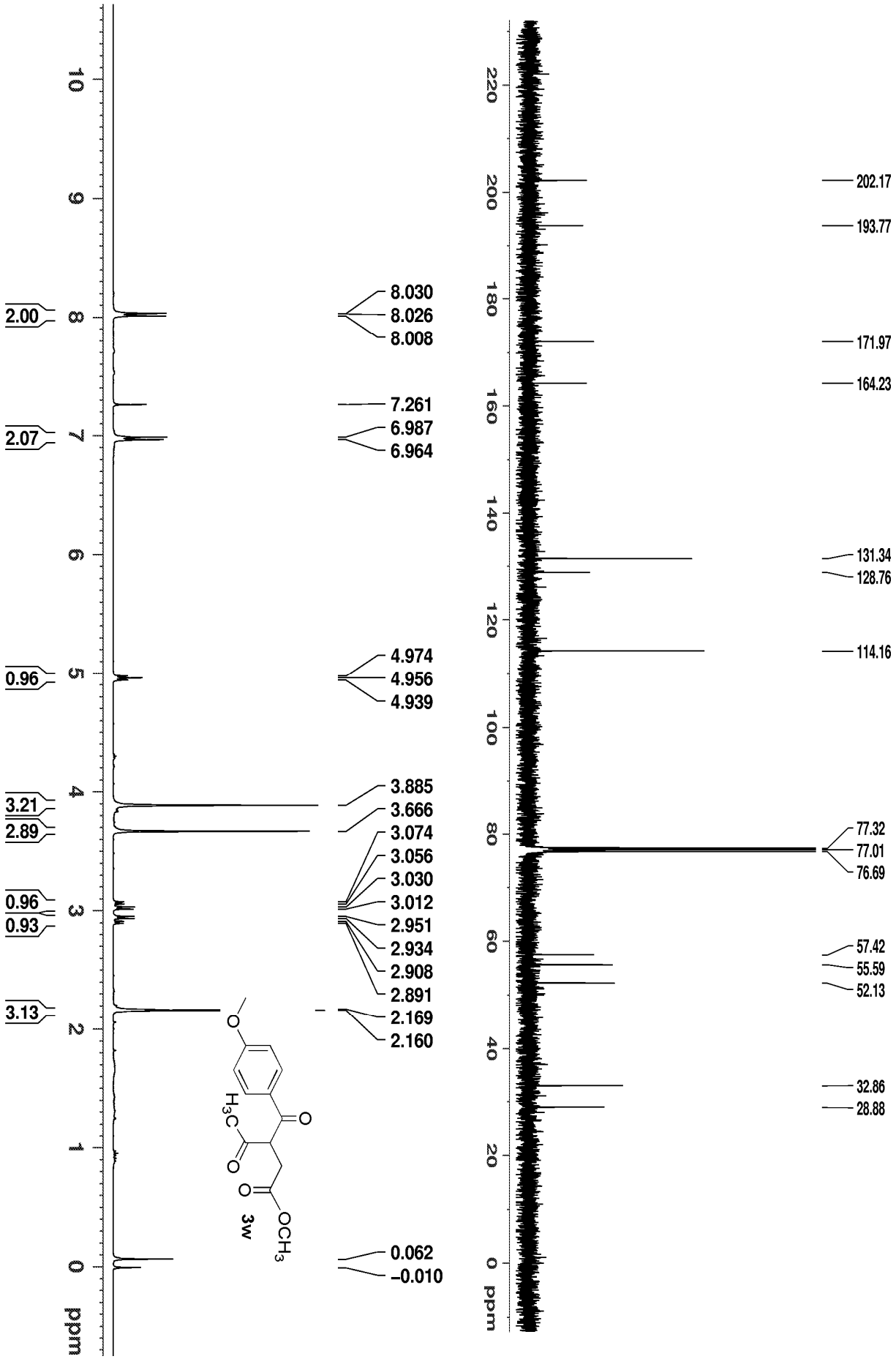
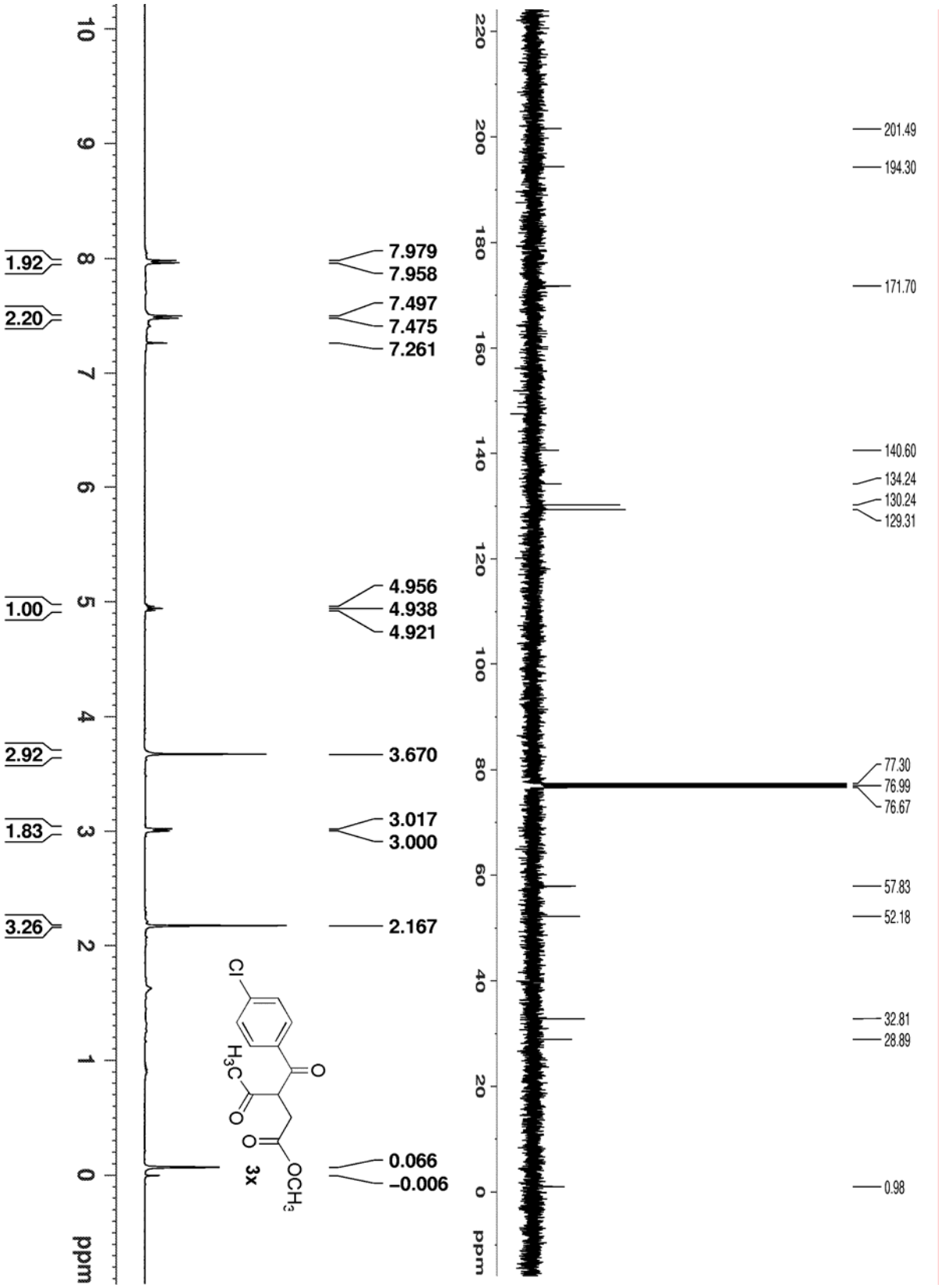
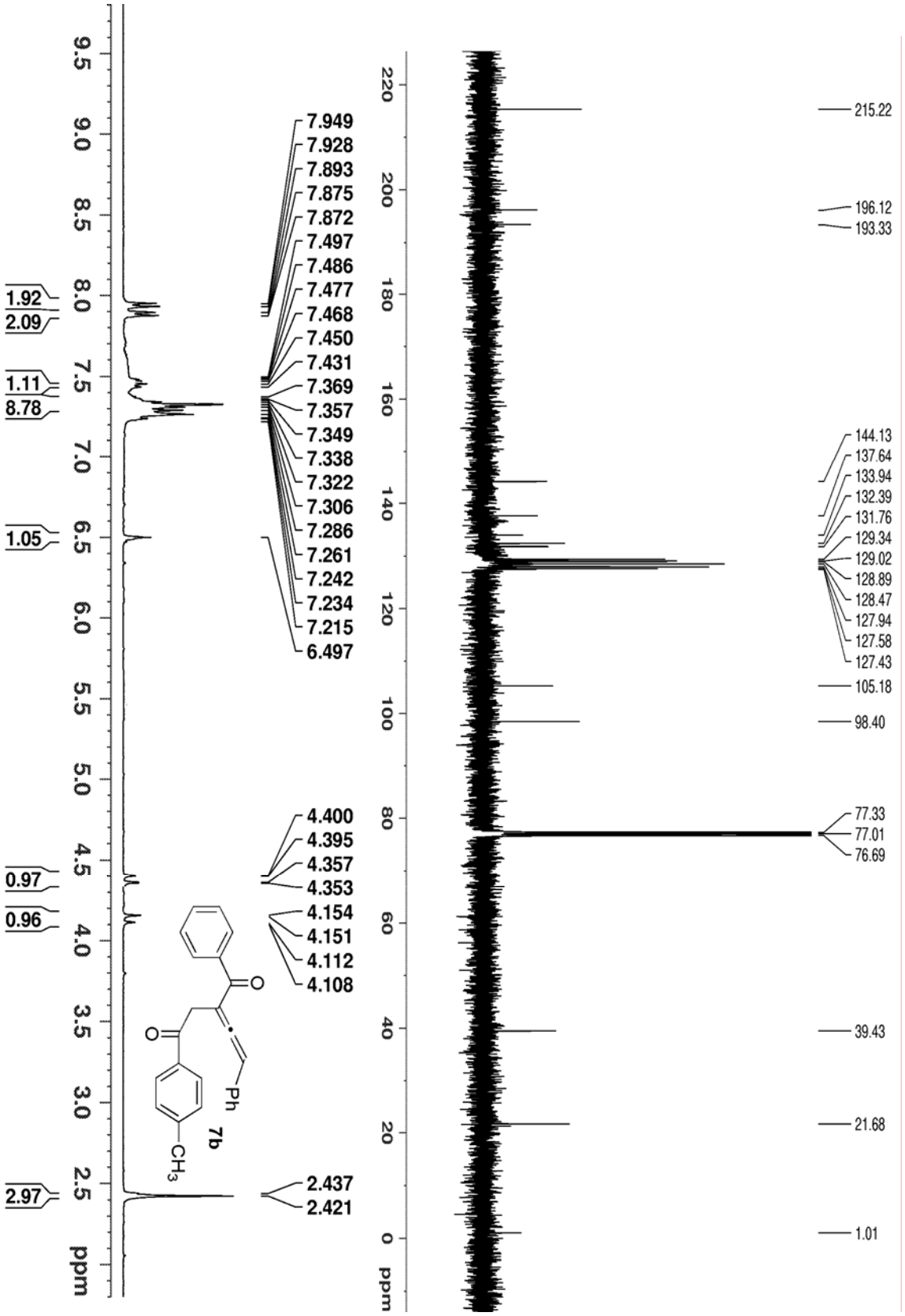
7.517
7.498
7.261
5.036
5.019
5.001
3.672
3.034
3.017
2.991
2.974
2.179
0.064
−0.009
ppm
3t
201.89
195.52
171.86
135.82
134.01
129.01
128.86
77.33
77.01
76.69
57.68
52.18
32.81
29.13
1.01
ppm



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0.96
2.97
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
7.949
7.928
7.893
7.875
7.872
7.497
7.486
7.477
7.468
7.450
7.431
7.369
7.357
7.349
7.338
7.322
7.306
7.286
7.261
7.242
7.234
7.215
6.497
4.400
4.395
4.357
4.353
4.154
4.151
4.112
4.108
2.437
2.421
O
O
Ph
CH3
7b
220
200
180
160
140
120
100
80
60
40
20
0
ppm
215.22
196.12
193.33
144.13
137.64
133.94
132.39
131.76
129.34
129.02
128.89
128.47
127.94
127.58
127.43
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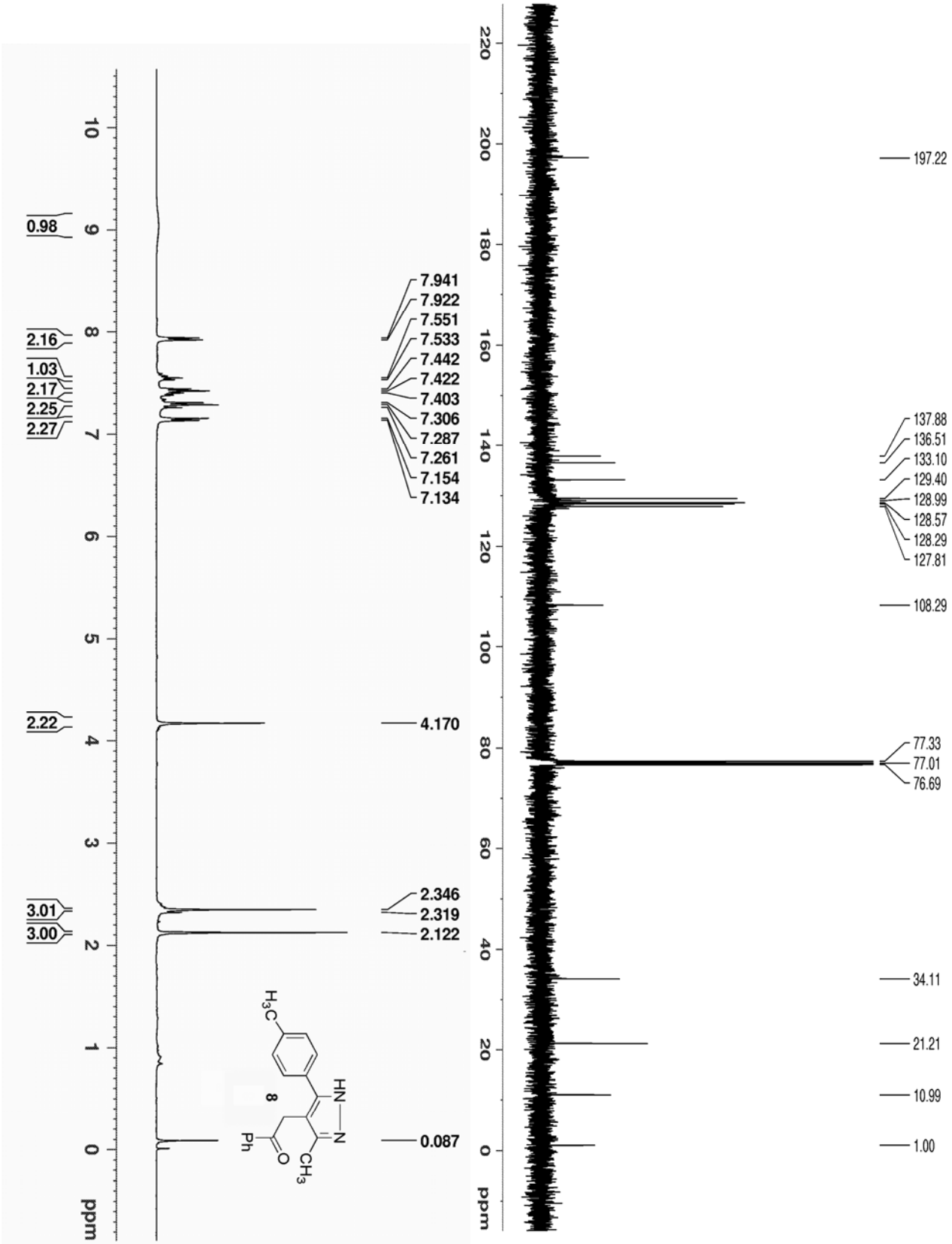
98.40
77.33
77.01
76.69
39.43
21.68
1.01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7.922
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7.533
7.442
7.422
7.403
7.306
7.287
7.261
7.154
7.134
4.170
2.346
2.319
2.122
0.087
ppm
197.22
137.88
136.51
133.10
129.40
128.99
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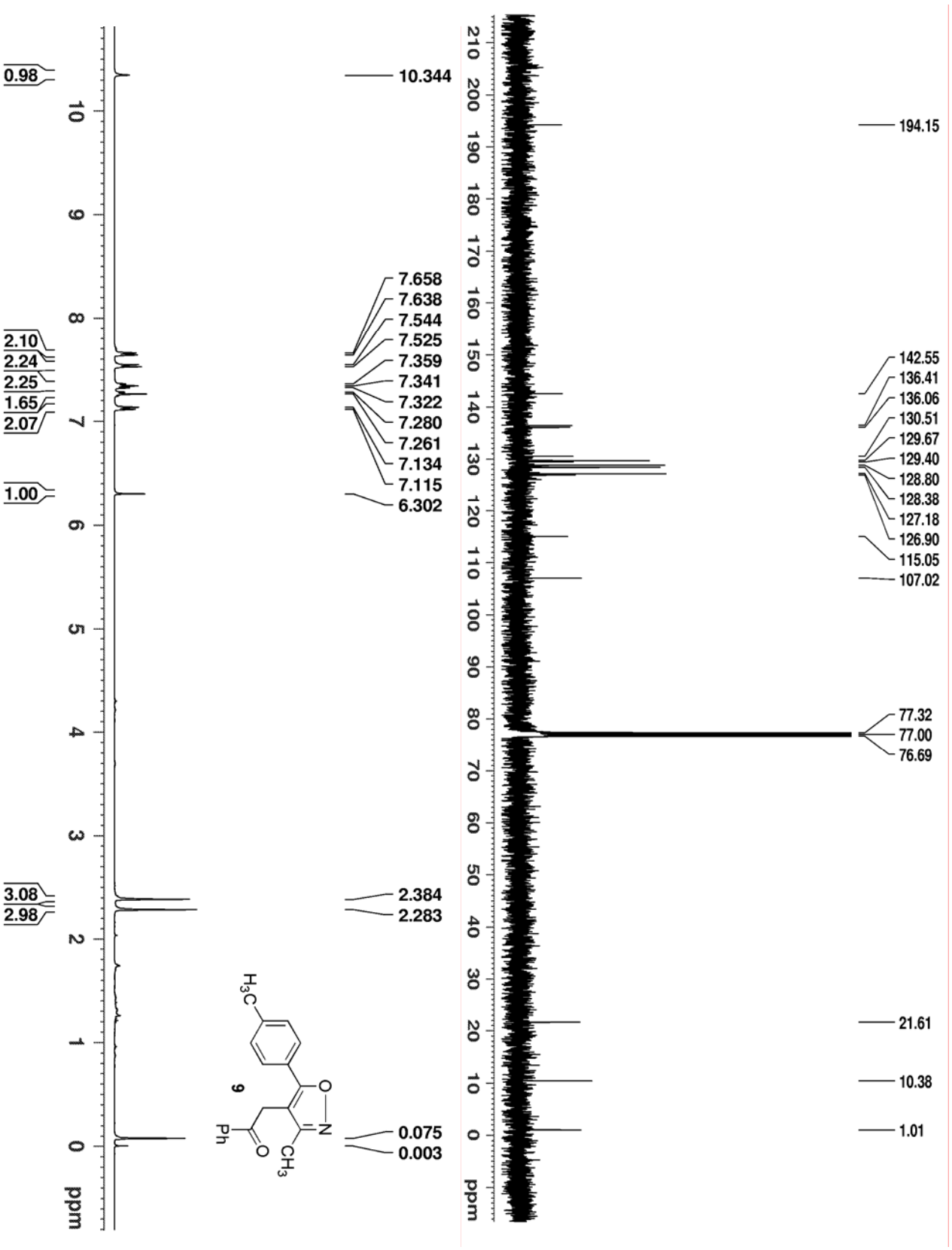
127.81
108.29
77.33
77.01
76.69
34.11
21.21
10.99
1.00
ppm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3.08
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7.544
7.525
7.359
7.341
7.322
7.280
7.261
7.134
7.115
6.302
2.384
2.283
0.075
0.003
H3C
O
N
CH3
O
Ph
9
ppm
194.15
142.55
136.41
136.06
130.51
129.67
129.40
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128.38
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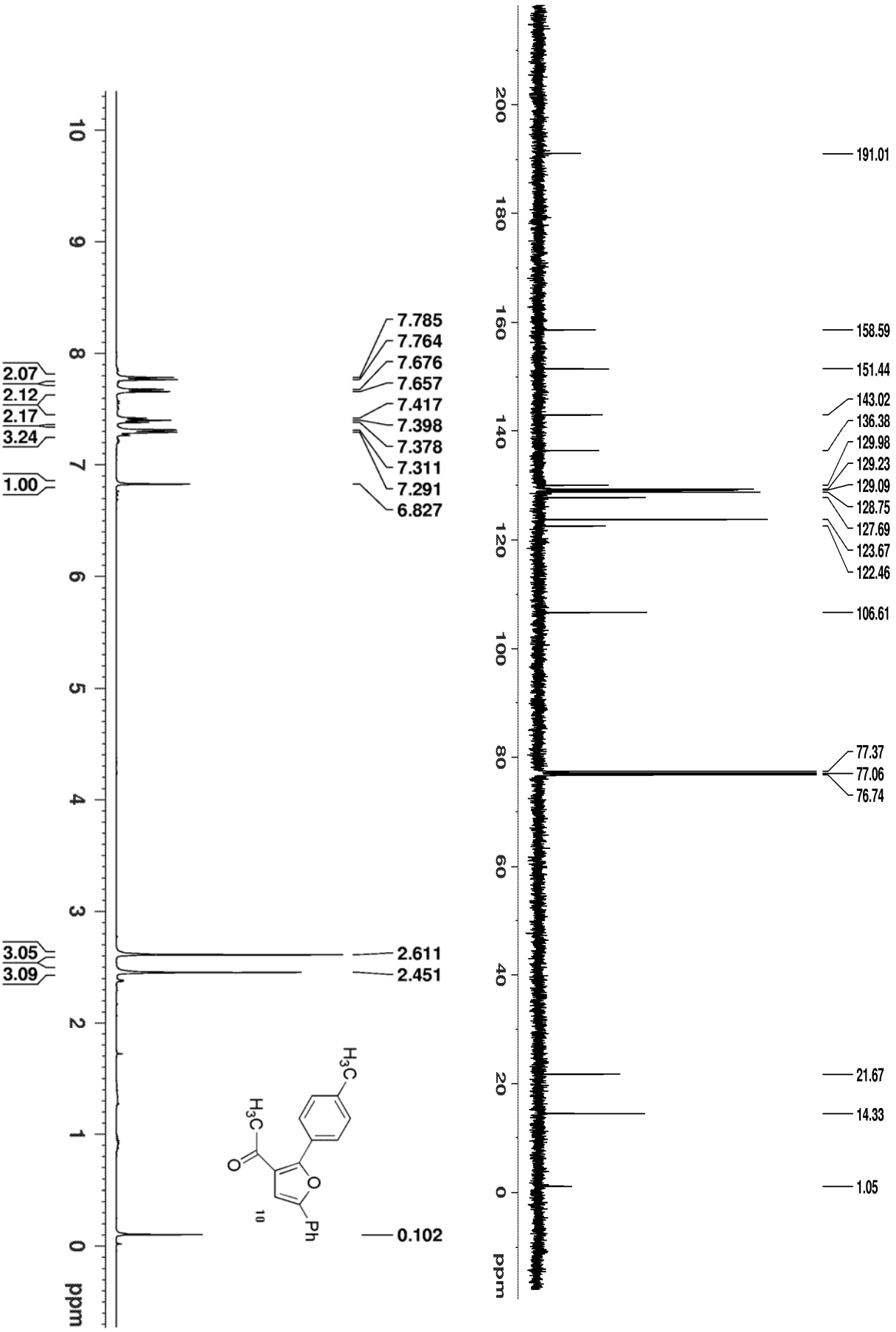
126.90
115.05
107.02
77.32
77.00
76.69
21.61
10.38
1.01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3.09
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7.676
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7.398
7.378
7.311
7.291
6.827
2.611
2.451
0.102
H3C
H3C
O
O
10
Ph
ppm
191.01
158.59
151.44
143.02
136.38
129.98
129.23
129.09
128.75
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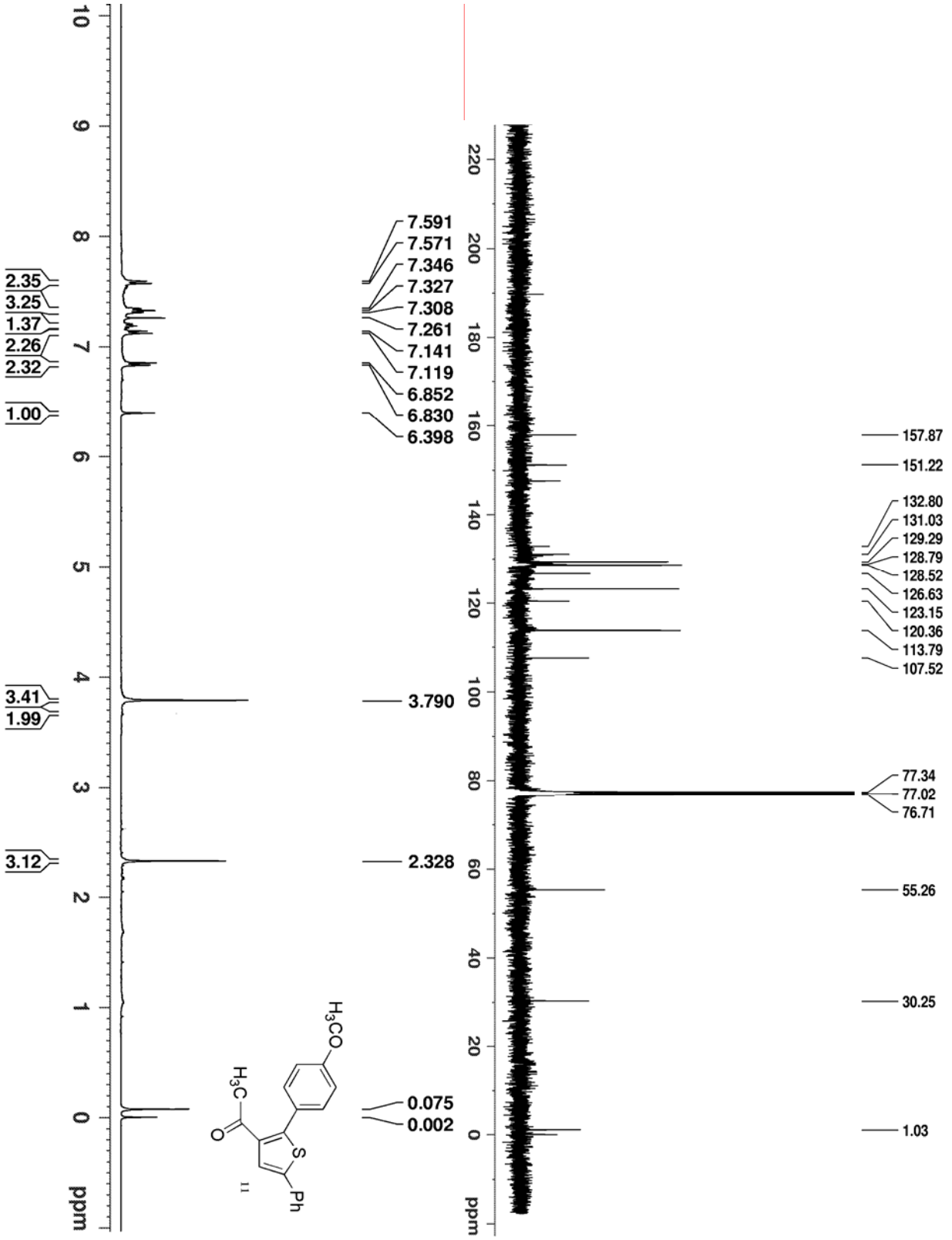
123.67
122.46
106.61
77.37
77.06
76.74
21.67
14.33
1.05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7.308
7.261
7.141
7.119
6.852
6.830
6.398
3.790
2.328
0.075
0.002
H3CO
H3C
O
S
Ph
157.87
151.22
132.80
131.03
129.29
128.79
128.52
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120.36
113.79
107.52
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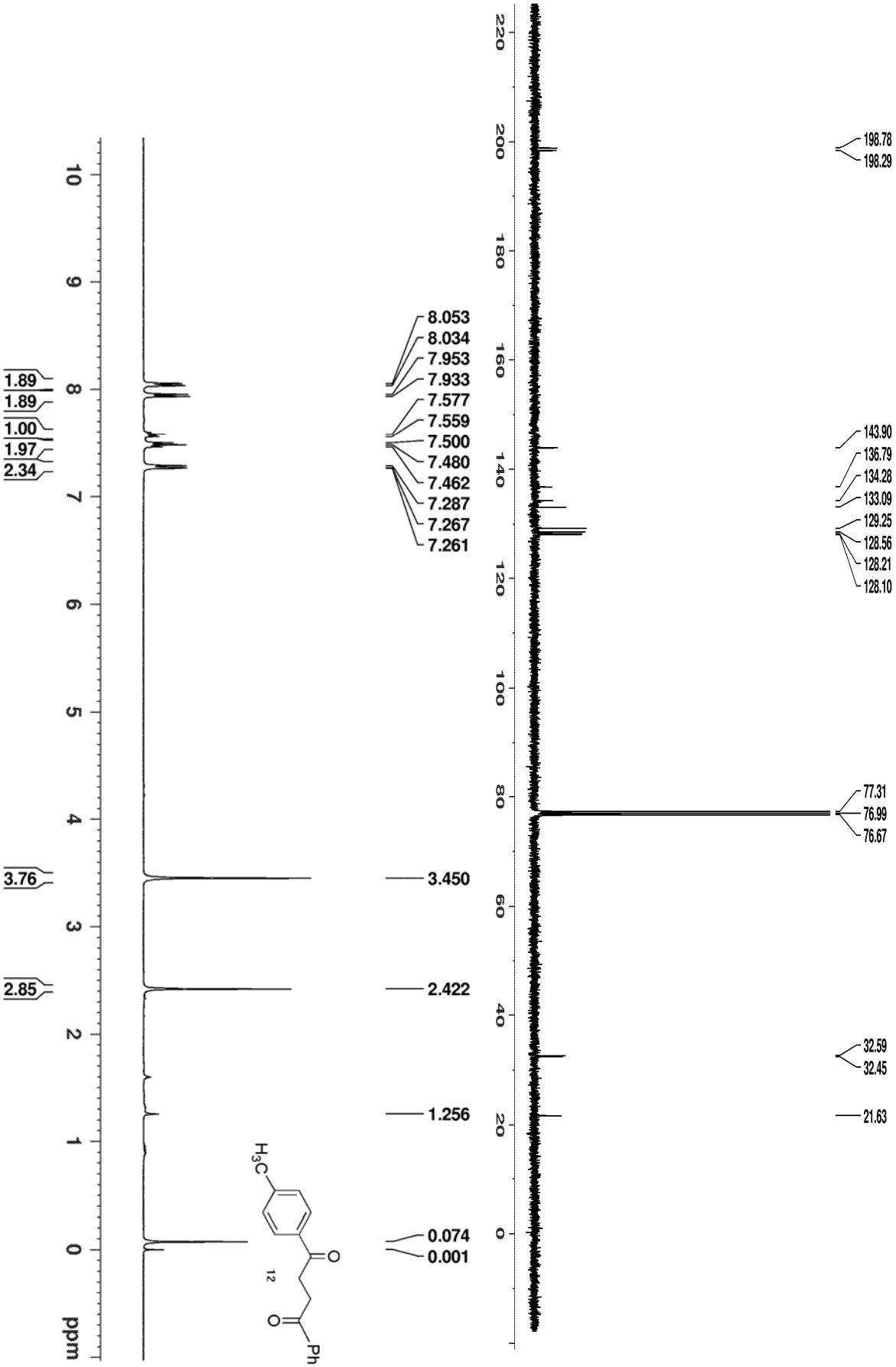
77.02
76.71
55.26
30.25
1.03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7.559
7.500
7.480
7.462
7.287
7.267
7.261
3.450
2.422
1.256
0.074
0.001
198.78
198.29
143.90
136.79
134.28
133.09
129.25
128.56
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76.99
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21.63
H3C
O
12
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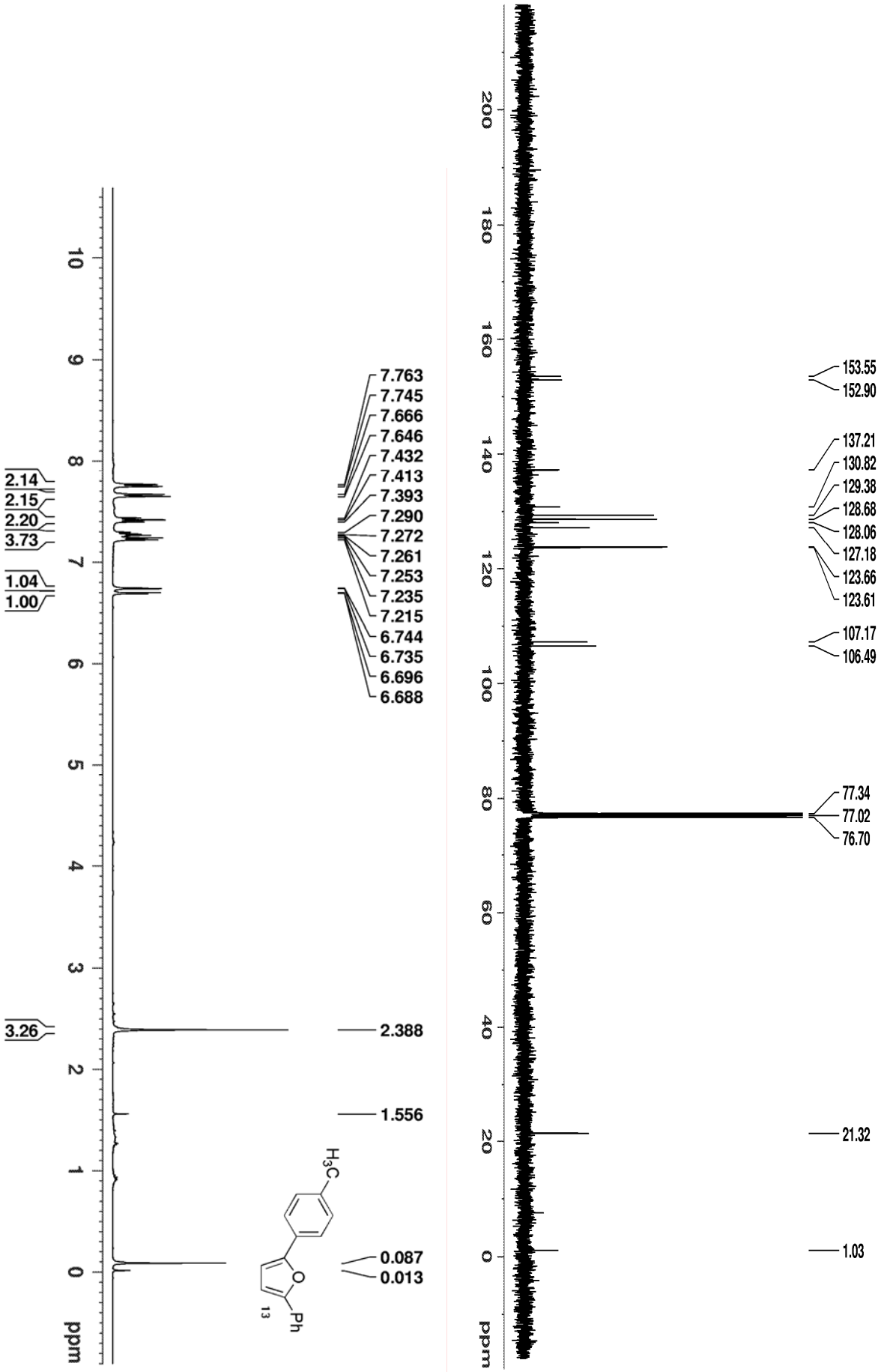
Ph
ppm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7.215
6.744
6.735
6.696
6.688
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1.556
0.087
0.013
2.14
2.15
2.20
3.73
1.04
1.00
3.26
ppm
153.55
152.90
137.21
130.82
129.38
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128.06
127.18
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107.17
106.49
77.34
77.02
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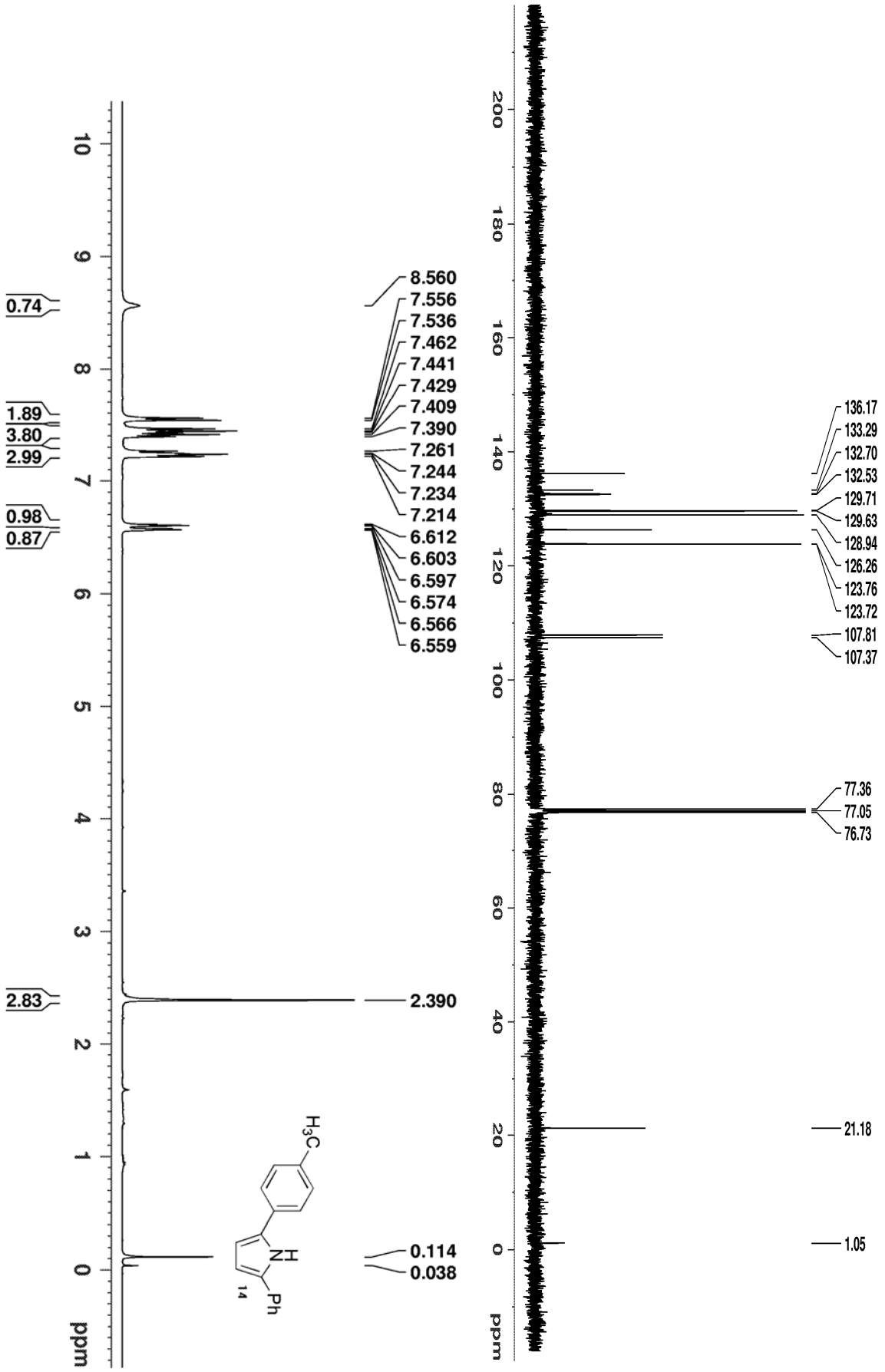
21.32
1.03
H3C
O
Ph
13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7.429
7.409
7.390
7.261
7.244
7.234
7.214
6.612
6.603
6.597
6.574
6.566
6.559
2.390
0.114
0.038
H3C
N
H
Ph
14
ppm
136.17
133.29
132.70
132.53
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129.63
128.94
126.26
123.76
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77.36
77.05
76.73
21.18
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ppm