Supporting Information for

Resettable Multiple-Mode Molecular Arithmetic Systems Based on Spectral Properties of 2-Quinolin-2-ylmethylene-malonic Acids

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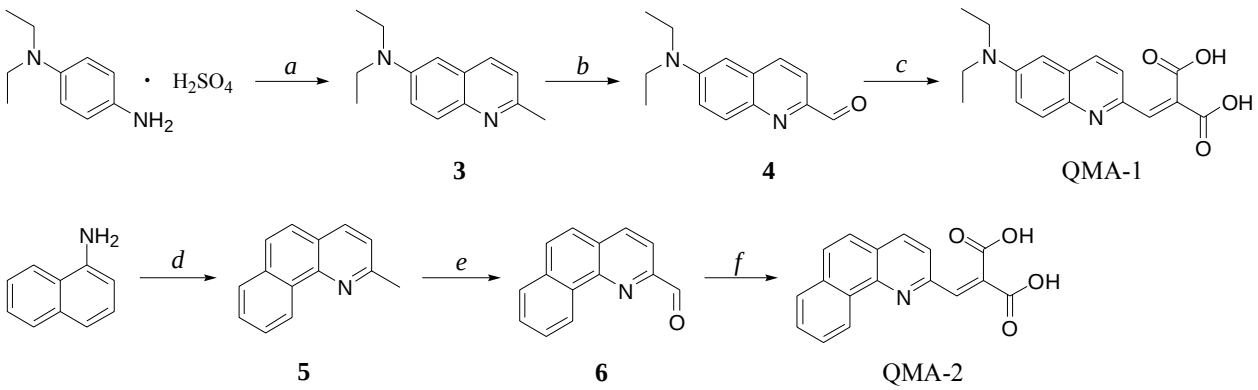
I. General methods.

All the chemicals for the preparation of QMAs were purchased from commercial suppliers and were used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ or d_6-DMSO with a Bruker AV spectrometer operating at 300 and 75 MHz, respectively and chemical shifts were reported in ppm using tetramethylsilane (TMS) as the internal standard. FT-IR spectra were measured with a Bruker Vector22 Infrared Spectrometer. Mass spectra were obtained with a Micromass GCF TOF mass spectrometer.

II. Synthesis and characterization of 2-quinolin-2-ylmethylene-malonic acids (QMAs)

QMAs were synthesized from a convenient three-step synthetic route using aniline derivatives as starting materials. For QMA-1, N, N-diethylbenzene-1, 4-diamine sulfate was dissolved in a mixture of concentrated HCl solution and n-butanol and then refluxed in the presence of chloranil serving as oxidant to yield 2-methyl quinoline **3**.[1] The quinoline **3** was oxidized by SeO_2 on the methyl position in dioxane solution under N_2 atmosphere to give corresponding aldehyde compound **4**,[2] which was further modified through Knoevenagel condensation reaction with malonic acid in the presence of piperidine of catalytic amount in refluxed ethanol to afford target product QMA-1.[3] For QMA-2, the same procedure was carried out and shown in Scheme S1.



Scheme S1 Reagents and conditions: (a) crotonaldehyde, concentrated hydrochloric acid, reflux, 90 min; (b) SeO_2, dioxane, reflux, 24 h; (c) malonic acid, ethanol, reflux, 4 h; (d) crotonaldehyde, concentrated hydrochloric acid, reflux, 40 min; (e) SeO_2, dioxane, reflux, 24 h; (f) malonic acid, ethanol, reflux, 4 h.

N,N-diethyl-2-methylquinolin-6-amine (3). *N, N*-diethylbenzene-1, 4-diamine sulfate (1.0 g, 3.8 mmol) and chloranil (1.7 g, 6.9 mmol) was added to 3 mL n-butanol with following addition of 2 mL concentrated HCl solution. The mixture was stirred at 105 ˚C and crotonaldehyde (0.6 mL) in 0.5 mL n-butanol was dropwise added within 20 min. After complete addition, another 90 min was consumed for further reaction. The reaction solution was washed with 30 mL ether. The aqueous layer was neutralized with 30% NaOH solution and extracted with 20 mL ethyl acetate three times. Purification from column chromatography (silica gel-H, ethyl acetate / petroleum ether 1:3) gave **3** (0.42 g, 51.7%) as dark-red oil. R_f= 0.62 (ethyl acetate / petroleum ether 1:3). IR (KBr): nu(tilde) = 2971m, 1719s, 1621s, 1506s, 1357s, 1258s cm^{-1}. ^1H NMR (300Hz, $DCCl_3$): δ = 1.19-1.24 (m, 6H, CH_2CH_3), 3.42-3.49 (m, 4H, CH_2CH_3), 2.70 (s, 3H, CH_3),6.73-6.74 (d, J=2.4Hz, 1H, quinoline-H), 7.14-7.16 (d, J=8.4Hz, 1H, quinoline-H), 7.26-7.30 (m, 1H, quinoline-H), 7.85-7.88 (d, J=8.4Hz, 1H, quinoline-H), 7.94-7.97 (d, J=9.0Hz, 1H, quinoline-H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 153.9, 145.5, 141.4, 134.2, 129.3, 128.2, 122.0, 119.0, 104.4, 44.6, 24.8, 12.6. TOFMS (EI) calcd for (M^+) $C_{14}H_{18}N_2$: 214.1470, found 214.1463.

6-(diethylamino)quinoline-2-carbaldehyde (4). A portion of 2 mL dioxane solution dissolved with **3** (0.42 g, 2.0 mmol) was added to 3 mL dioxane suspended with 0.33 g SeO_2. The reaction proceeded at 80 ˚C for 24 h under N_2 atmosphere. After reaction, 30 mL ethyl acetate was added for dilution followed by water-washing once. Solvent was removed and **4** (0.31 g, 69.4%) was obtained as orange solid via column chromatography (silica gel-H, ethyl acetate / petroleum ether 1:3). R_f=

0.69 (ethyl acetate / petroleum ether 1:3). IR (KBr): nu(tilde) = 2970s, 1688s, 1613s, 1577s, 1508s, 1237s cm^{-1}. ^{1}H NMR (300Hz, $DCCl_3$): δ = 1.26-1.30 (m, 6H, CH_2CH_3), 3.50-3.57 (m, 4H, CH_2CH_3), 6.77 (s, 1H, quinoline-H), 7.35-7.39 (m, 1H, quinoline-H), 7.87-7.90 (d, J = 8.4Hz, 1H, quinoline-H), 7.95-7.98 (m, J = 8.7Hz, 1H, quinoline-H), 8.02-8.06 (d, J=9.6Hz, 1H, quinoline-H), 10.12 (s, 1H, CO). ^{13}C NMR (100MHz, $CDCl_3$): δ = 193.3, 148.4, 147.9, 141.3, 133.9, 132.7, 131.5, 119.6, 118.2, 102.9, 44.8, 12.6. TOFMS (EI) calcd for (M^+) $C_{14}H_{16}N_2O$: 228.1263, found 228.1270.

2-((6-(diethylamino)quinolin-2-yl)methylene)malonic acid (QMA-1). To a portion of 8 ml ethanol solution was added **4** (0.20 g, 0.88 mmol) and malonic acid (0.094 g, 0.90 mmol). The mixture was refluxed for 4 h in the presence of piperidine of catalytic amount (10 mmol%) and then cooled to the room temperature. Solid precipitated out was collected by filtration, washed with ethanol twice (2 × 10 mL) and crystallized in ethanol / H_2O (4:1) to give **1** (0.12 g, 43.5%) as dark brown powder. IR (KBr): nu(tilde) = 3445s, 2969m, 1713s, 1619s, 1597s, 1508s, 1392s cm^{-1}. ^{1}H NMR (300Hz, d_6-DMSO): δ = 1.15-1.20 (m, 6H, CH_2CH_3), 3.47-3.51 (m, 4H, CH_2CH_3), 6.91 (s, 1H, quinoline-H), 7.46-7.49 (d, J = 9.3Hz, 1H, quinoline-H), 7.59-7.62 (d, J = 8.4Hz, 1H, quinoline-H), 7.66 (s, 1H, double bond-H), 7.73-7.76 (d, J = 9.3Hz, 1H, quinoline-H), 8.11-8.14 (d, J = 8.4Hz, 1H, quinoline-H), 13.65 (s, 1H, COOH). ^{13}C NMR (100MHz, d_6-DMSO): δ = 167.9, 165.6, 146.7, 145.0, 139.6, 137.9, 134.4, 130.1, 129.3, 129.0, 123.4, 120.3, 102.8, 44.0, 12.5. TOFMS (EI) calcd for (M^+) $C_{17}H_{18}N_2O_4$: 314.1267, found 314.1282.

2-methylbenzo[h]quinoline (5). Naphthalen-1-amine (1.0 g, 7.0 mmol) and chloranil (1.8 g, 7.4 mmol) was added to 3 mL n-butanol with following addition of 2 mL concentrated HCl solution. The mixture was stirred at 105 ˚C and crotonaldehyde (0.8 mL) in 0.5 mL n-butanol was dropwise added within 20 min. After complete addition, another 40 min was consumed for further reaction. The

reaction solution was washed with 30 mL ether. The aqueous layer was neutralized with 30% NaOH solution and extracted with 20 mL ethyl acetate three times. Purification from column chromatography (silica gel-H, ethyl acetate / petroleum ether 1:4) gave **5** (0.57 g, 42.2%) as light-yellow oil. R_f= 0.75 (ethyl acetate / petroleum ether 1:3). IR (KBr): nu(tilde) = 3050m, 1598s, 1506s, 1449s, 841s, 749s cm^{-1}. ^1H NMR (300Hz, $DCCl_3$): δ = 2.83 (s, 3H, CH_3), 7.36-7.39 (d, J = 8.1Hz, 1H, phenyl-H), 7.62-7.76 (m, 4H, phenyl-H), 7.86-7.89 (m, 1H, phenyl-H), 8.03-8.05 (d, J = 8.1Hz, 1H, phenyl-H), 9.32-9.34 (d, J = 7.8Hz, 1H, phenyl-H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 157.6, 145.9, 135.8, 133.6, 131.3, 127.8, 127.6, 126.7, 126.5, 125.1, 124.4, 124.1, 122.1, 25.4. TOFMS (EI) calcd for (M^+) $C_{14}H_{11}N$: 193.0891, found 193.0858.

benzo[h]quinoline-2-carbaldehyde (6). A portion of 2 mL dioxane solution dissolved with **5** (0.57 g, 3.0 mmol) was added to 3 mL dioxane suspended with 0.33 g SeO_2. The reaction proceeded at 80 ˚C for 24 h under N_2 atmosphere. After reaction, 30 mL ethyl acetate was added for dilution followed by water-washing once. Solvent was removed and **6** (0.39 g, 63.9%) was obtained as white solid via column chromatography (silica gel-H, ethyl acetate / petroleum ether 1:4). R_f= 0.77 (ethyl acetate / petroleum ether 1:3). IR (KBr): nu(tilde) = 1708s, 1507s, 1398s, 849s, 758s cm^{-1}. ^1H NMR (300Hz, $DCCl_3$): δ = 7.72-7.83 (m, 3H, phenyl-H), 7.93-7.95 (m, 2H, phenyl-H), 8.14-8.17 (d, J=8.1Hz, 1H, phenyl-H), 8.29-8.32 (d, J=8.1Hz, 1H, phenyl-H), 9.40-9.43 (m, 1H, phenyl-H), 10.4 (s, 1H, CO). ^{13}C NMR (100MHz, $CDCl_3$): δ = 194.0, 151.1, 146.4, 136.7, 133.7, 131.4, 130.6, 128.9, 128.0, 127.7, 124.9, 124.5, 118.4. TOFMS (EI) calcd for (M^+) $C_{14}H_9NO$: 207.0684, found 207.0685.

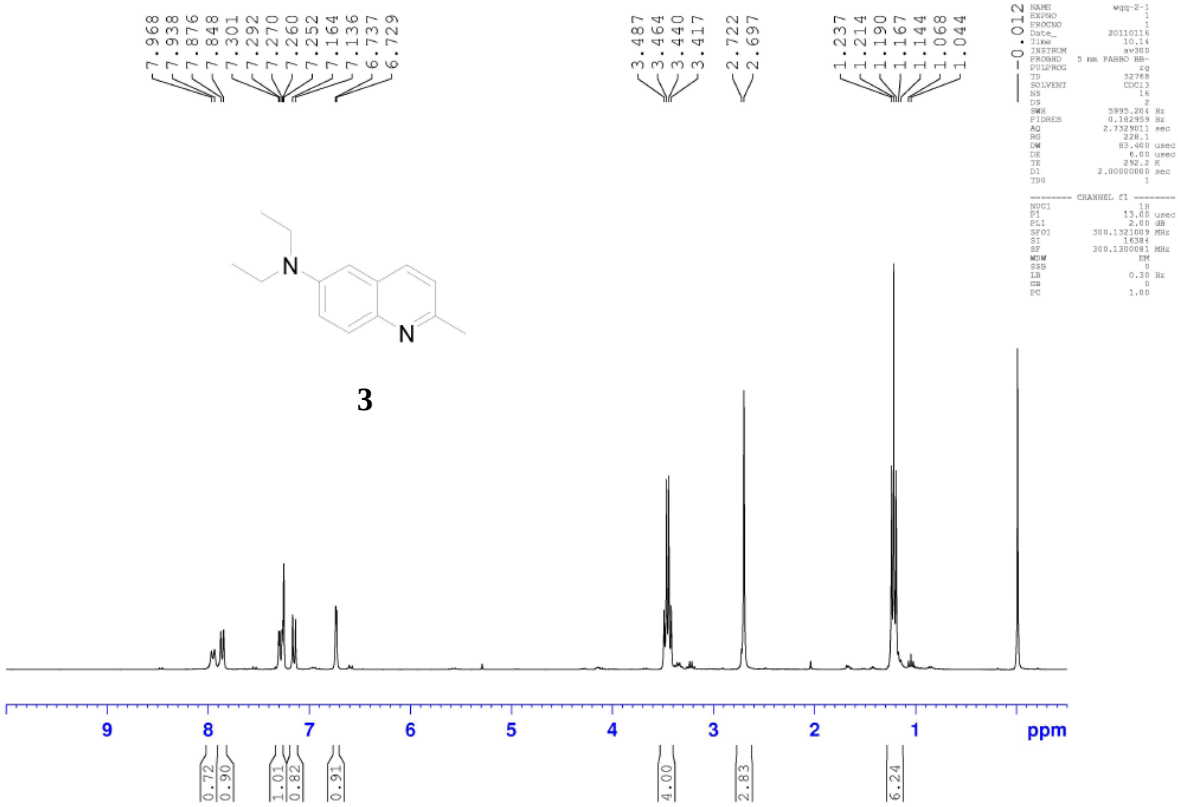
2-(benzo[h]quinolin-2-ylmethylene)malonic acid (QMA-2). To a portion of 8 ml ethanol solution was added **6** (0.20 g, 0.97 mmol) and malonic acid (0.11 g, 1.0 mmol). The mixture was refluxed for 4 h in the presence of piperidine of catalytic amount (10 mmol%) and then cooled to the room

temperature. Solid precipitated out was collected by filtration, washed with ethanol twice (10 mL × 2) and crystallized in ethanol / H_2O (4:1) to give **2** (0.18 g, 63.4%) as bright yellow powder. IR (KBr): nu(tilde) = 3441s, 3059s, 1721s, 1625s, 1603s, 1396s, 822s, 750s cm^{-1}. ^1H NMR (300Hz, d_6-DMSO): δ = 7.74-8.00 (m, 7H, phenyl-H), 8.43-8.45 (m, 1H, phenyl-H), 9.21-9.23 (m, 1H, phenyl-H), 13.15 (s, 2H, COOH). ^{13}C NMR (100MHz, d_6-DMSO): δ = 167.6, 165.3, 149.9, 145.6, 136.9, 133.5, 131.4, 130.9, 128.7, 127.9, 127.5, 126.2, 125.2, 125.1, 124.4. TOFMS (EI) calcd for (M^+) $C_{17}H_{11}NO_4$: 293.0688, found 293.0702.

References

1. Chen, X. Y.; Shi, J.; Li, Y. M.; Wang, F. L.; Wu, X.; Guo, Q. X.; Liu, L. *Org. Lett*. **2009**, 11, 4426-4429.
2. Davis, M. J.; Kragor, C. H.; Reddie, K. G.; Wilson, H. C.; Zhu, Y.; Dore, T. M.; *J. Org. Chem*. **2009**, 74, 1721–1729.
3. Phillips, A. P. *J. Am. Chem. Soc*. **1948**, 70, 452-454.

III. Copies of ^{1}H and ^{13}C NMR spectra of new compounds



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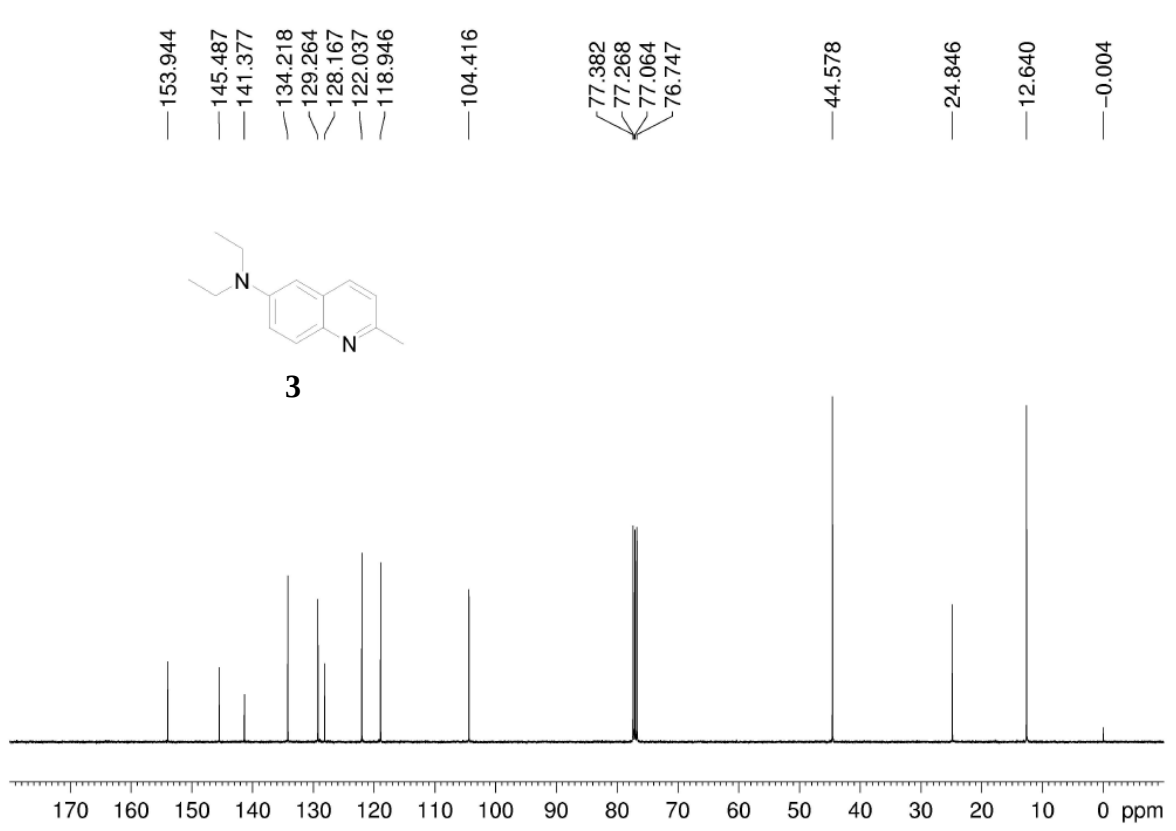

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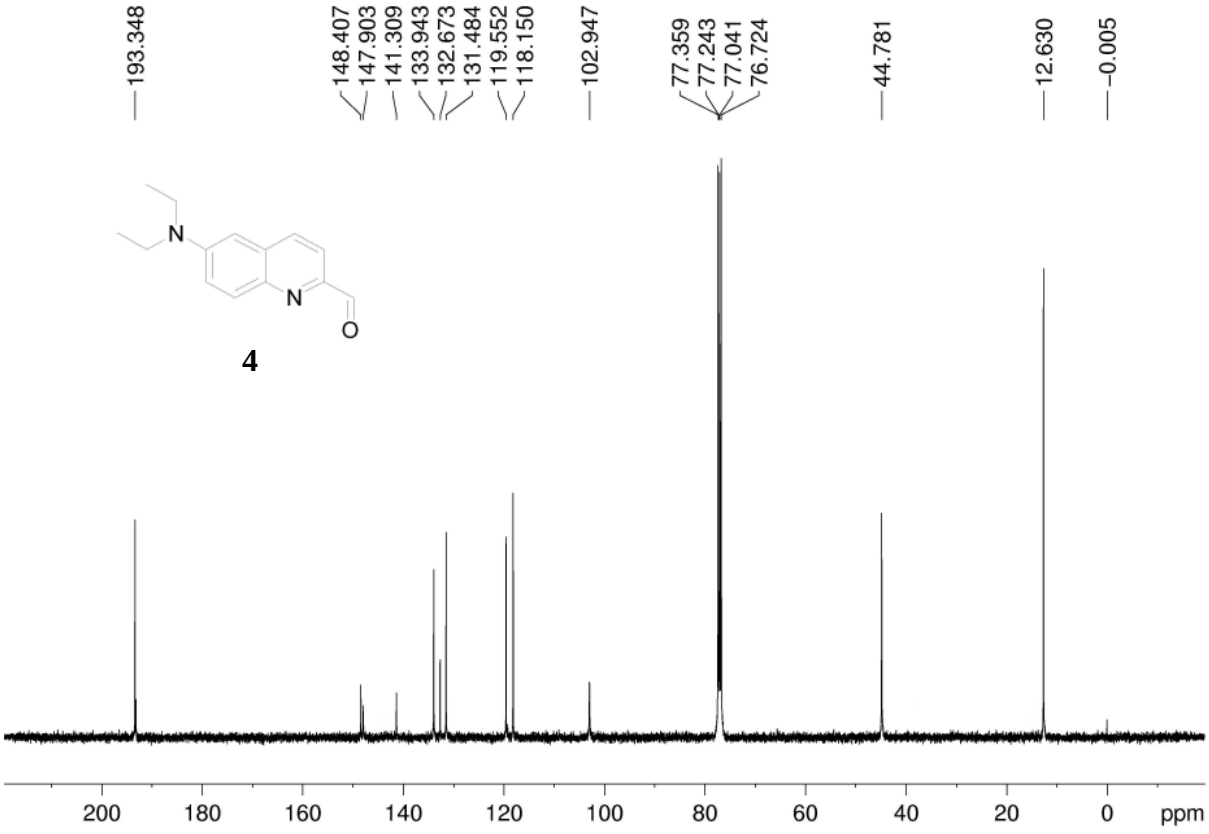

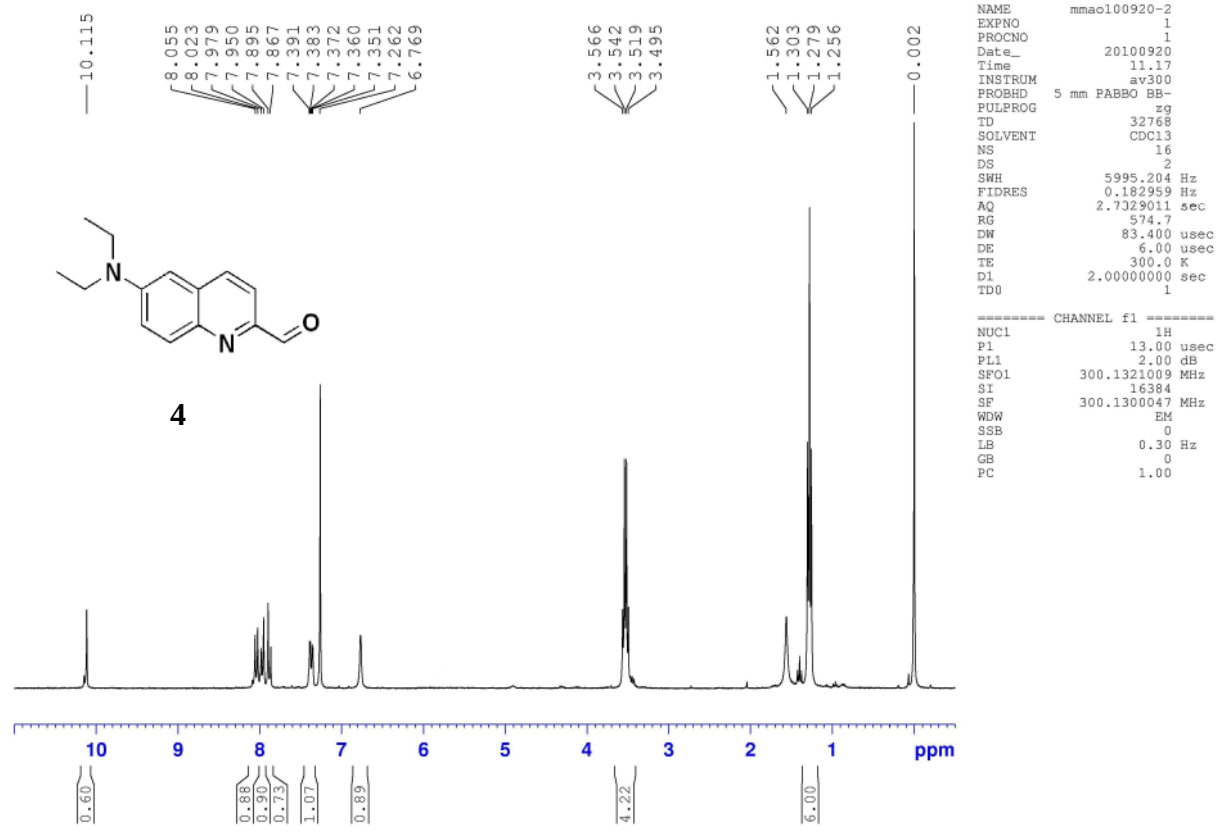


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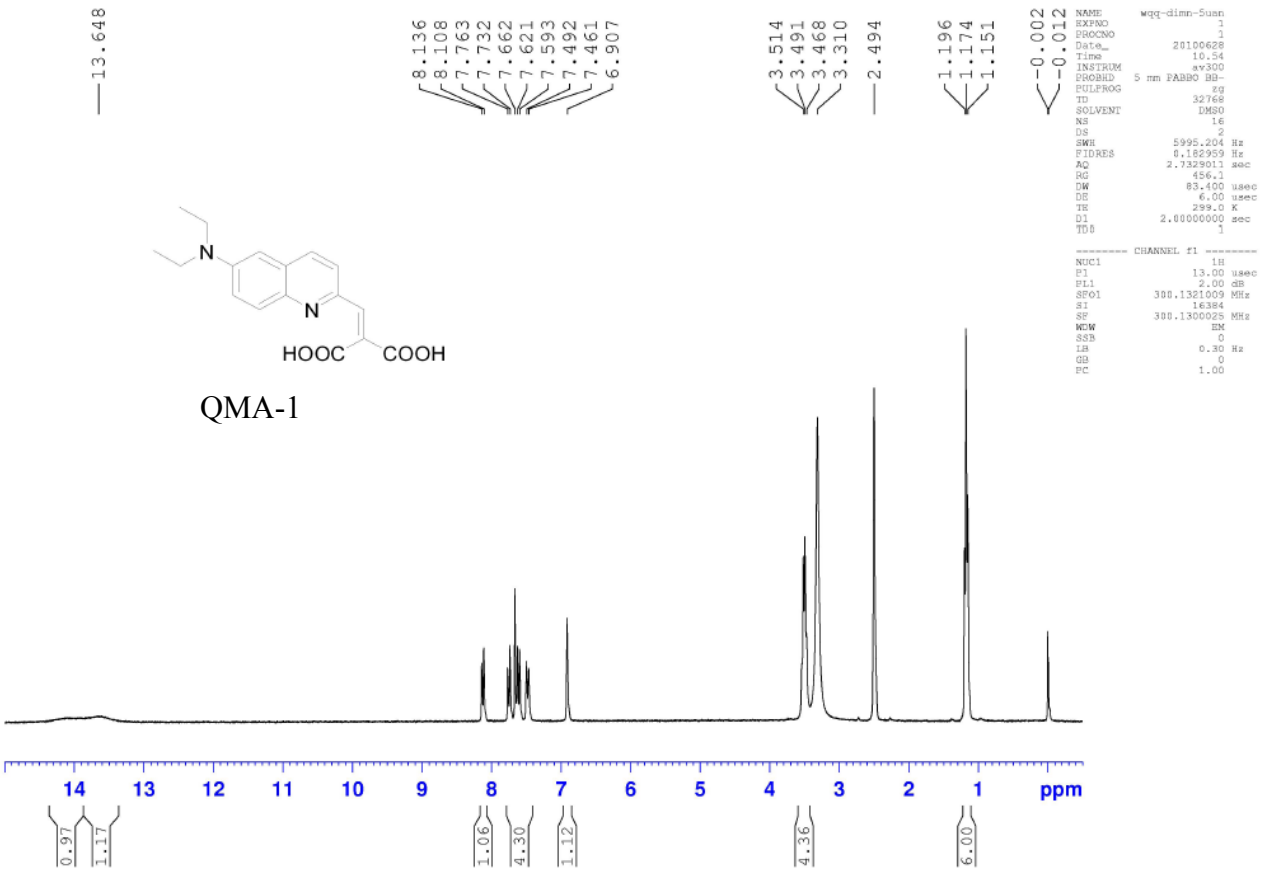
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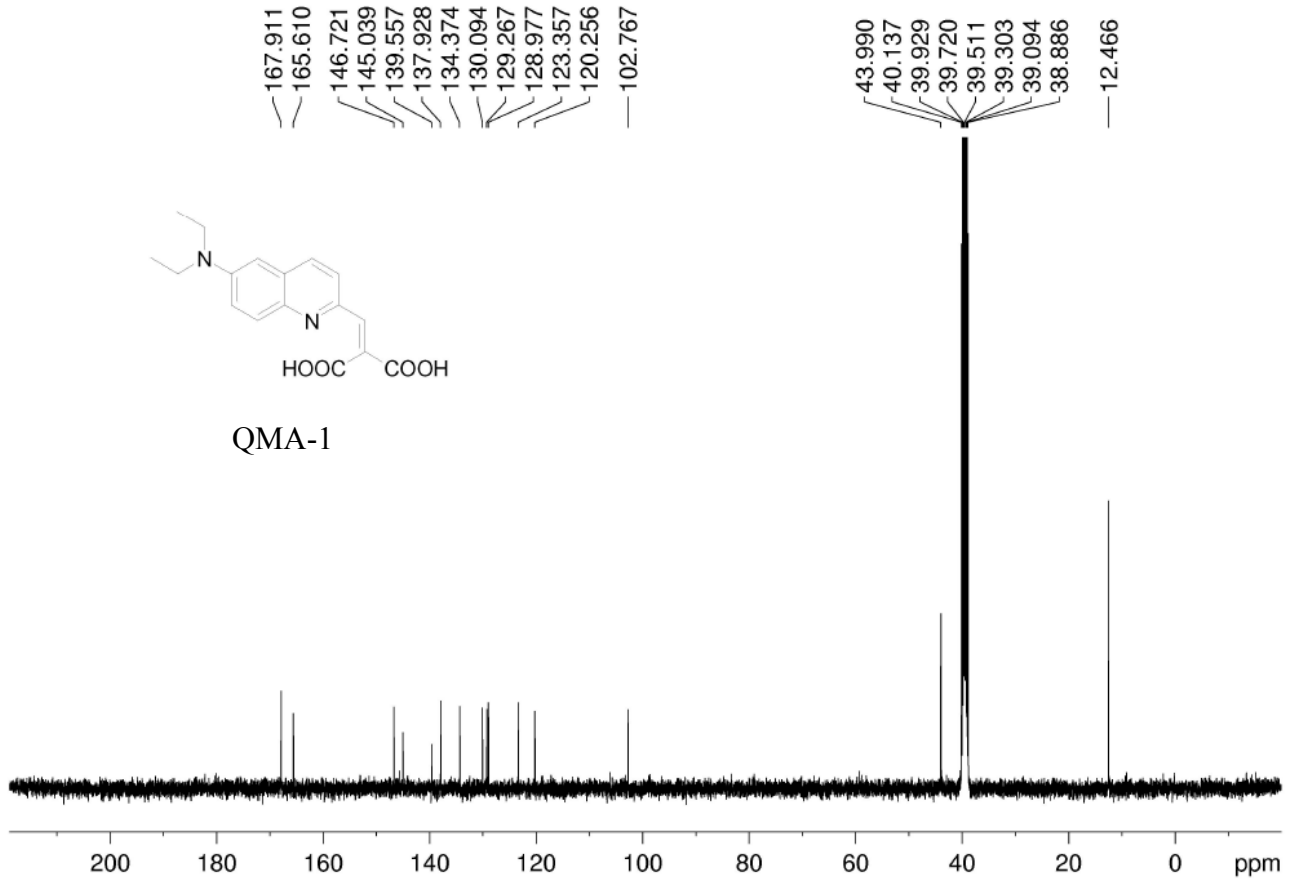
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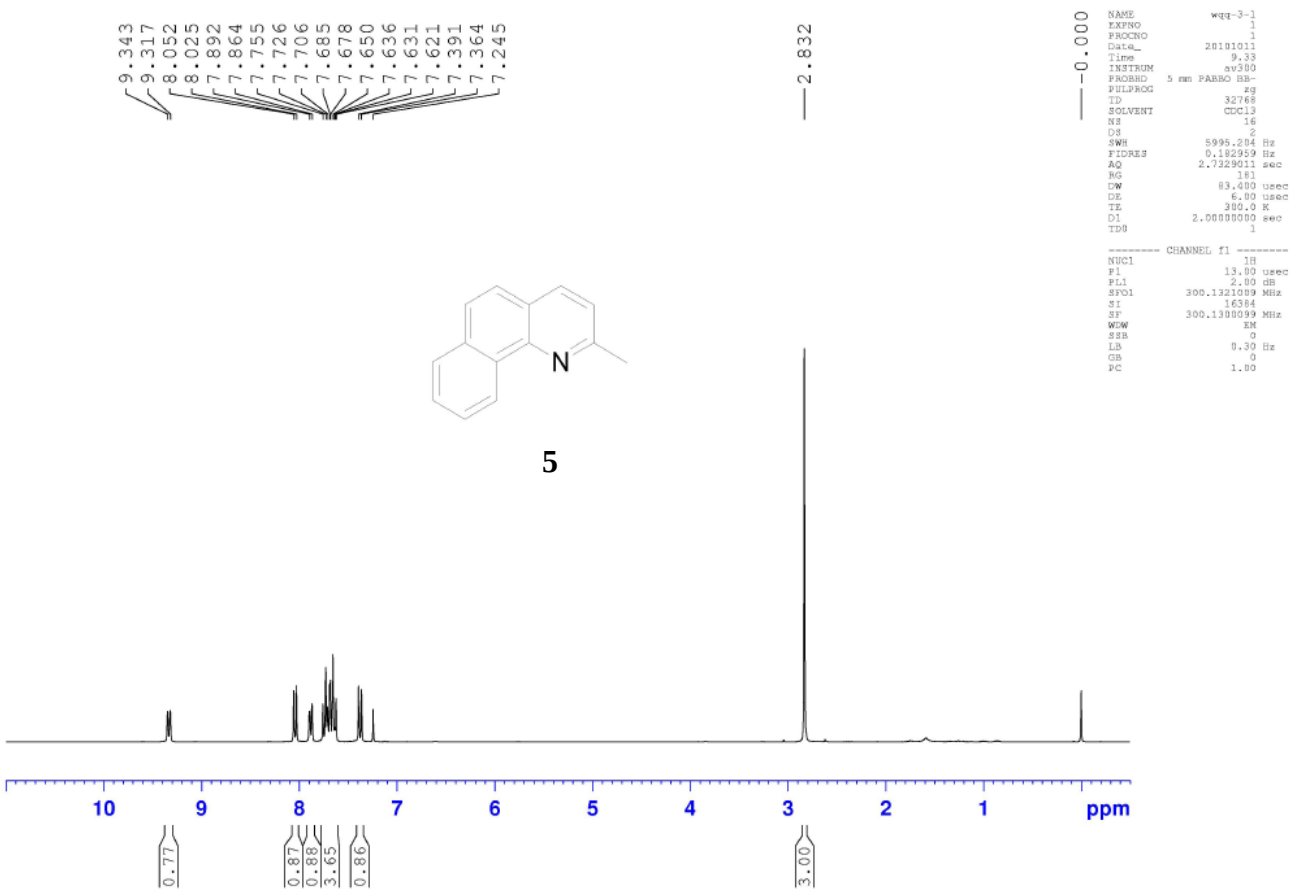
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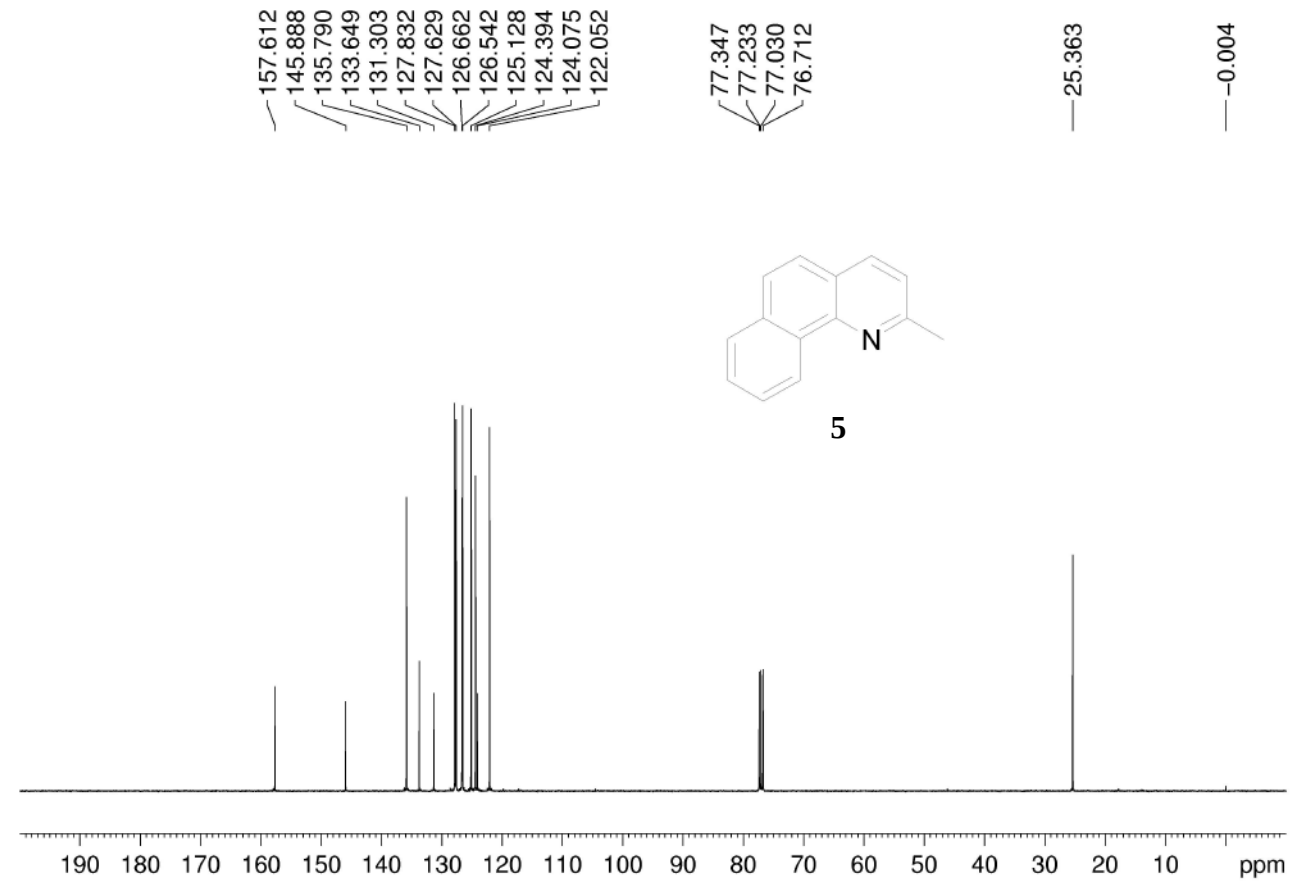
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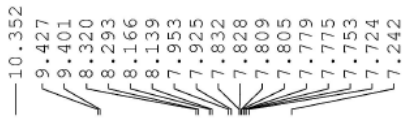


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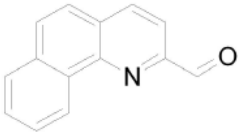

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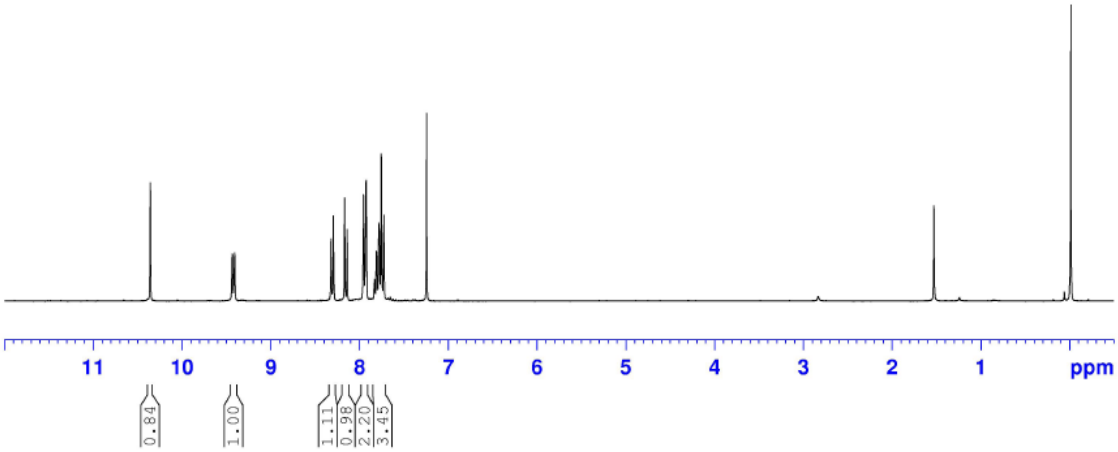

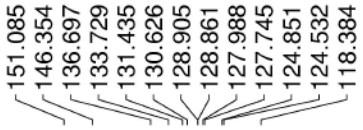

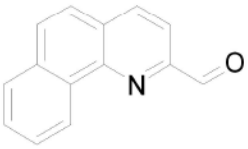

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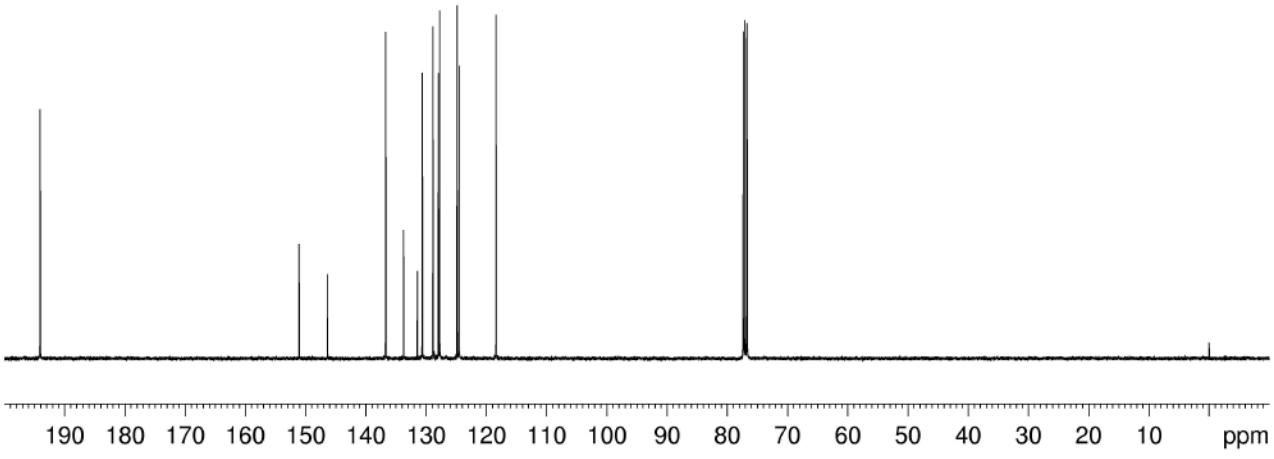

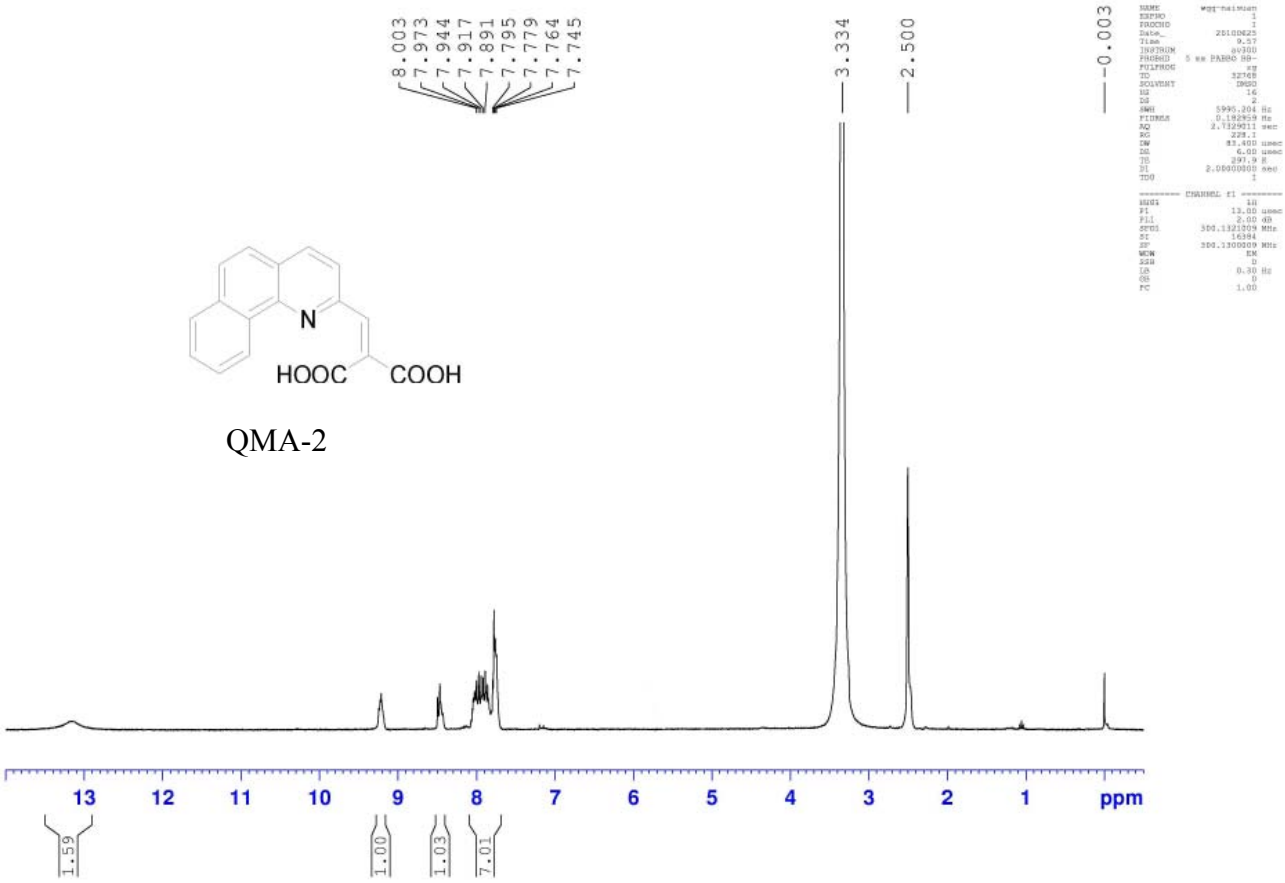
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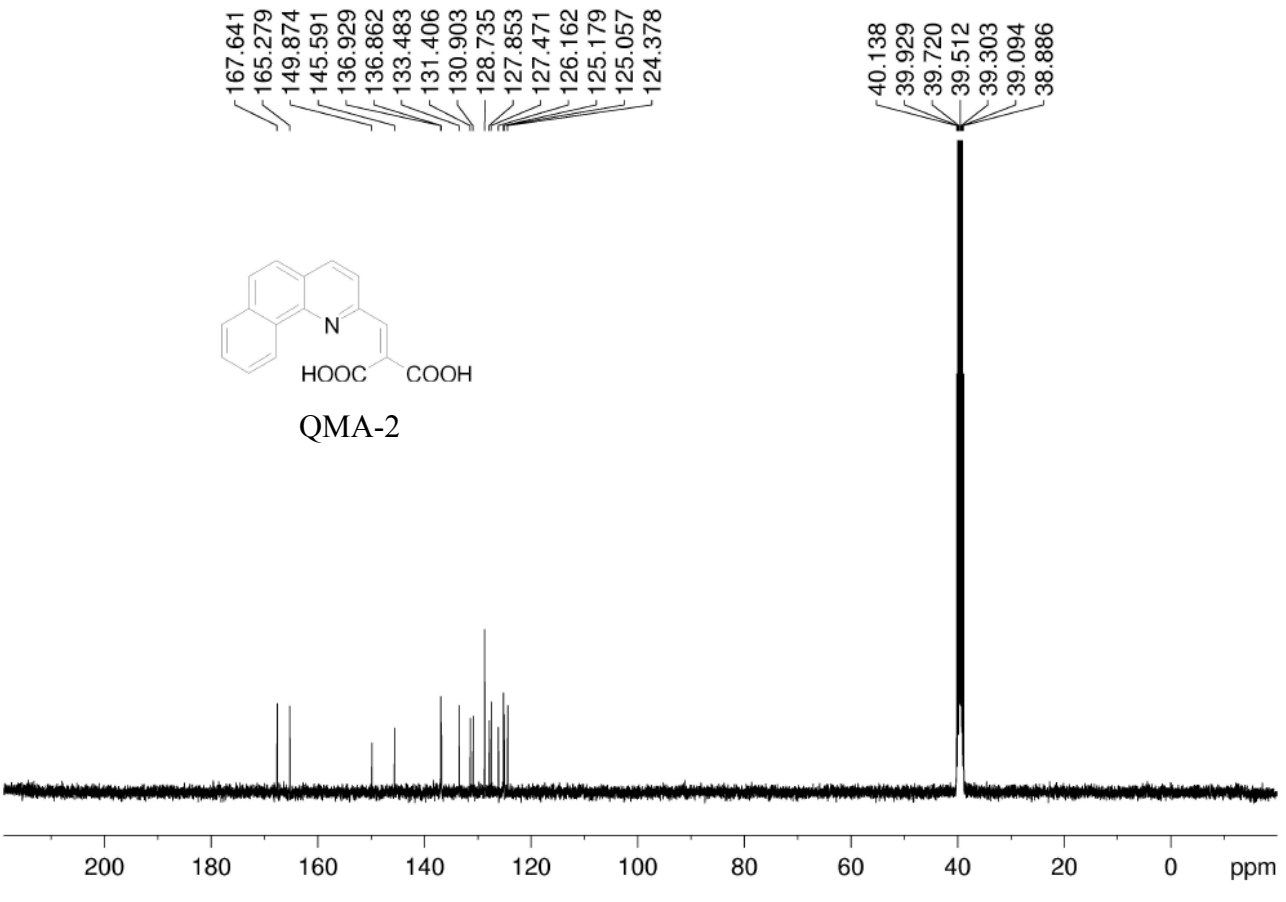
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