Electronic Supplementary Material (ESI) for ChemComm.

Dual-function Pd/NHC catalysis: tandem allylation-isomerization-conjugate addition that allows access to pyrroles, thiophenes and furans

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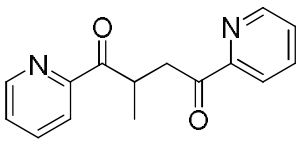
General information

General: All the reactions were carried out in a flame or oven dried glassware with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Organic solutions were concentrated under reduced pressure by rotary evaporation with a water bath (temperature below 40 °C). Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60–F254) using UV light at 254 nm as a visualizing agent and a $KMnO_4$ solution as stain. Product purification by flash column chromatography was accomplished using silica gel 60 (0.010–0.063 nm). Technical grade solvents were used for chromatography and were distilled prior to use. Optical rotations were measured in $CHCl_3$ or MeOH on a Schmidt + Haensdch polarimeter with a 1 cm cell (*c* given in g/100 mL). IR spectra were recorded using FTIR Restige-21 (Shimadzu). NMR spectra were recorded at room temperature on 400 MHz Bruker AVIII 400. The residual solvent signals were taken as the reference (7.26 ppm for 1H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$). Sometimes the TMS signal at 0.0 ppm was used an internal standard for ^1H NMR spectra. Chemical shift (δ) is reported in ppm, coupling constants (*J*) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal. HR-MS (ESI) spectra were recorded on a Waters Q-Tof premierTM mass spectrometer.

Material: Dimethyl sulfoxide (DMSO) and triethylamine (Et_3N) were purchased from commercial suppliers and used without further purification. NHC catalysts, tetrakis-triphenylphosphine palladium(0), Allyl acetate (**1a**), pyridine-2-carboxaldehyde (**2a**), 6-methylpyridine-2-carboxaldehyde (**2b**), 6-methoxylpyridine-2-carboxaldehyde (**2c**), 6-bromopyridine-2-carboxaldehyde (**2d**), 6-(2-Thienyl)pyridine-2-carboxaldehyde (**2f**), 5-bromopyridine-2-carboxaldehyde (**2h**), 2-quinolinecarboxaldehyde (**2j**) were purchased from commercial suppliers. 6-phenylpyridine-2-carboxaldehyde (**2e**),[1] 6-hydroxymethylpyridine-2-carboxaldehyde (**2f**),[2] 5-phenylpyridine-2-carboxaldehyde (**2i**),[1] 1-isoqunoline-carboxaldehyde[3] (**2k**) and 3-isoquinolinecarboxaldehyde[4] (**2l**) were prepared by reported methods.

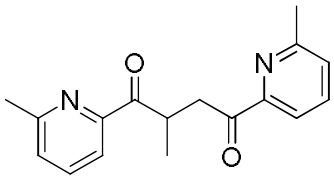
Experimental procedure

General experimental procedure of direct coupling by dual catalysis: To a solution of **1a** (0.4 mmol), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol) and triethylamine (1.2 mmol) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, (*o*-azaaryl)carboxaldehyde (0.8 mmol) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump within a 2-hour period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL) and dried over Na_2SO_4. The organic layer was evaporated and the residue was purified by flash column chromatography to afford the product.



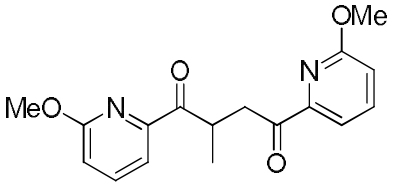
3a

2-methyl-1,4-di(pyridin-2-yl)butane-1,4-dione (3a) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, pyridine-2-carboxaldehyde (0.8 mmol, 76 μL) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 4:1) to afford the product as a brown solid (85 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34-1.36 (d, J = 7.2 Hz, 3H), 3.49–3.54 (dd, J = 4.4, 18.8 Hz, 1H), 3.91–3.99 (dd, J = 9.7, 18.8 Hz, 1H), 4.64–4.70 (m, 1H), 7.45–7.50 (m, 2H), 7.79-7.99 (m, 2H), 8.08-8.10 (m, 2H), 8.69-8.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4, 35.1, 41.9, 121.7, 122.5, 126.9, 127.1, 136.8, 136.9, 148.9, 149.0, 152.8, 153.1, 200.2, 204.4; IR (neat) 3055, 2972, 2933, 2358, 2330, 1693, 1680, 1583, 1435, 1348, 1219, 955, 746, 619 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_2$ $[M+H]^+$: 255.1134, found 255.1138.



3b

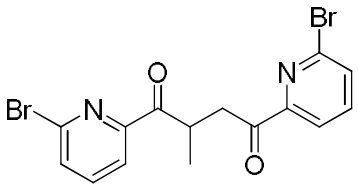
2-methyl-1,4-bis(6-methylpyridin-2-yl)butane-1,4-dione (3b) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 6-methylpyridine-2-carboxaldehyde (0.8 mmol, 96 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 4:1) to afford the product as a dark brown solid (91 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30-1.32 (d, J = 7.2 Hz, 3H), 2.61 (s, 6H), 3.45–3.51 (dd, J = 4.9, 18.7 Hz, 1H), 3.83–3.90 (dd, J = 9.2, 18.7 Hz, 1H), 4.62–4.71 (m, 1H), 7.28–7.30 (m, 2H), 7.63-7.69 (m, 2H), 7.71-7.77 (m, 1H), 7.85-7.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.5, 24.4, 24.5, 35.2, 41.7, 118.7, 119.4, 126.4, 126.6, 136.7, 136.8, 152.3, 152.8, 157.9, 157.9, 200.7, 204.8; IR (neat) 3020, 2358, 2341, 1693, 1591, 1456, 1344, 1215, 975, 756, 667 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}N_2O_2$ $[M+H]^+$: 283.1447, found 283.1443



3c

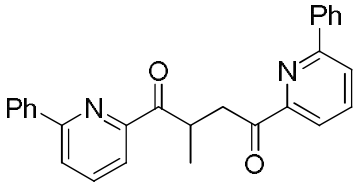
1,4-bis(6-methoxypyridin-2-yl)-2-methylbutane-1,4-dione (3c) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 6-methoxylpyridine-2-carboxaldehyde (0.8 mmol, 109 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 4:1) to afford the product as a white solid (77 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33-1.35 (d, J = 7.1 Hz, 3H), 3.37–3.43 (dd, J = 5.2, 18.6 Hz, 1H), 3.79–3.86 (dd, J = 8.7, 18.6 Hz, 1H), 3.98 (s, 3H), 4.00 (s, 3H), 4.54–4.63 (m, 1H), 6.91-6.94 (m, 2H), 7.56-7.58 (m, 1H), 7.64-7.70 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.3, 35.5, 41.7, 53.4, 53.5, 114.9, 115.1, 115.2, 115.7, 139.0, 139.1, 150.1, 150.7, 163.2, 163.3, 200.1, 204.0;

IR (neat) 2976, 2953, 1693, 1591, 1573, 1433, 1338, 1274, 1230, 1035, 812 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}N_2O_4$ $[M+H]^+$: 315.1345, found 315.1339



3d

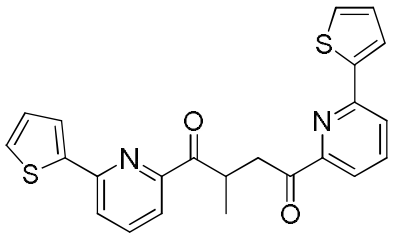
1,4-bis(6-bromopyridin-2-yl)-2-methylbutane-1,4-dione (3d) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine) palladium (0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 6-bromopyridine-2-carboxaldehyde (0.8 mmol, 149 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 2:1) to afford the product as a yellow solid (126 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32-1.34 (d, J = 7.2 Hz, 3H), 3.43–3.49 (dd, J = 4.2, 19.1 Hz, 1H), 3.81–3.88 (dd, J = 9.9, 19.1 Hz, 1H), 4.47–4.56 (m, 1H), 7.64-7.72 (m, 4H), 7.89-7.91 (m, 1H), 8.00-8.03 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4, 35.3, 41.8, 120.6, 121.3, 131.7, 131.9, 139.1, 139.2, 141.4, 153.4, 153.8, 198.7, 202.7; IR (neat) 2929, 1697, 1556, 1431, 1396, 1338, 1273, 1217, 985, 754 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2Br_2$ $[M+H]^+$: 410.9344, found 410.9349



3e

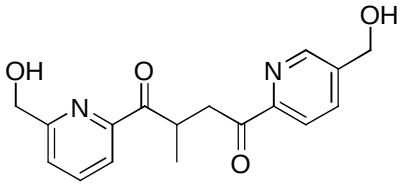
2-methyl-1,4-bis(6-phenylpyridin-2-yl)butane-1,4-dione (3e) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 6-phenylpyridine-2-carboxaldehyde (0.8 mmol, 146 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 4:1) to afford the product as a yellow solid (137 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44-1.46 (d, J = 7.2 Hz, 3H), 3.66–3.72 (dd, J = 4.9, 18.5 Hz, 1H), 4.00–4.07 (dd, J = 9.0, 18.5 Hz, 1H), 4.83–4.92 (m, 1H), 7.43-7.53 (m, 6H), 7.82-7.85 (m, 1H), 7.87-7.94

(m, 4H), 8.00-8.02 (m, 1H), 8.10-8.11 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.6, 35.6, 41.9, 119.9, 120.7, 123.2, 123.6, 126.9, 126.9, 128.8, 128.8, 129.3, 129.4, 137.6, 137.7, 138.4, 138.5, 152.5, 153.0, 156.2, 156.4, 200.7, 204.7; IR (neat) 3064, 2972, 1693, 1579, 1448, 1392, 1348, 1217, 1028, 985, 754 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{23}N_2O_2$ $[M+H]^+$: 407.1760, found 407.1756



3f

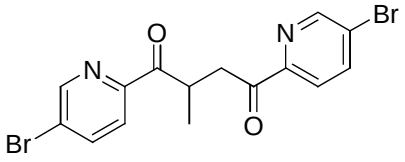
2-methyl-1,4-bis(6-(thiophen-2-yl)pyridin-2-yl)butane-1,4-dione (3f) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 6-(2-Thienyl)pyridine-2-carboxaldehyde (0.8 mmol, 151 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 4:1) to afford the product as a pale yellow solid (132 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41-1.43 (d, J = 7.1 Hz, 3H), 3.59–3.65 (dd, J = 5.2, 18.4 Hz, 1H), 3.93–4.00 (dd, J = 8.7, 18.4 Hz, 1H), 4.79–4.84 (m, 1H), 7.37-7.42 (m, 2H), 7.75-7.85 (m, 7H), 7.96-7.99 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.5, 35.7, 41.7, 119.6, 120.3, 123.0, 123.3, 124.1, 124.2, 126.2, 126.3, 126.5, 137.5, 137.6, 141.5, 141.6, 152.4, 152.5, 152.6, 153.0, 200.5, 204.5; IR (neat) 3018, 2972, 1693, 1587, 1465, 1392, 1342, 1215, 989, 756 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}N_2O_2S_2$ $[M+H]^+$: 419.0888, found 419.0883



3g

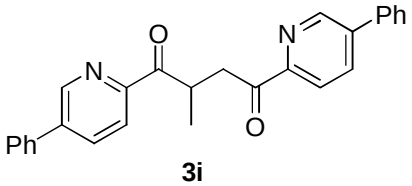
4-(5-(hydroxymethyl)pyridin-2-yl)-1-(6-(hydroxymethyl)pyridin-2-yl)-2-methylbutane-1,4-dione (3g) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis-(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 6-hydroxymethylpyridine-2-carboxaldehyde (0.8 mmol, 110 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature

for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 1:2) to afford the product as a white solid (29 mg, 23%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32-1.34 (d, J = 7.2 Hz, 3H), 3.37–3.43 (dd, J = 5.1, 18.2 Hz, 1H), 3.78-3.82 (m, 2H), 3.91–3.98 (dd, J = 9.0, 18.2 Hz, 1H), 4.67–4.72 (m, 1H), 4.84 (s, 4H), 7.42-7.44 (m, 2H), 7.80-7.91 (m, 3H), 7.99-8.01 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.2, 35.4, 42.0, 63.9, 64.0, 120.6, 121.4, 124.0, 124.1, 137.6, 137.7, 151.4, 151.9, 158.55, 158.5, 199.6, 203.5; IR (neat) 3012, 2931, 2854, 1942, 1681, 1589, 1446, 1373, 1338, 1219, 995, 753 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}N_2O_4$ $[M+H]^+$: 315.1345, found 315.1354



3h

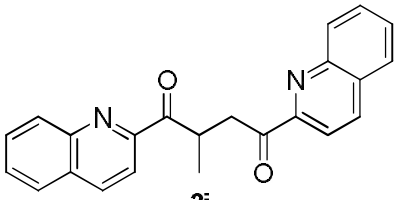
1,4-bis(5-bromopyridin-2-yl)-2-methylbutane-1,4-dione (3h) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 5-bromopyridine-2-carboxaldehyde (0.8 mmol, 149 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 2:1) to afford the product as a white solid (124 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31-1.33 (d, J = 7.2 Hz, 3H), 3.42–3.48 (dd, J = 4.3, 18.9 Hz, 1H), 3.84-3.91 (dd, J = 9.8, 18.9 Hz, 1H), 4.53–4.62 (m, 1H), 7.84-7.86 (m, 1H), 7.94-8.01 (m, 3H), 8.74-8.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.3, 35.1, 41.8, 123.0, 123.8, 125.1, 125.4, 139.6, 139.6, 150.1, 150.1, 150.9, 151.3, 199.3, 203.3; IR (neat) 3093, 2088, 1953, 1693, 1566, 1454, 1317, 1209, 981, 756 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2Br_2$ $[M+H]^+$: 410.9344, found 410.9342



3i

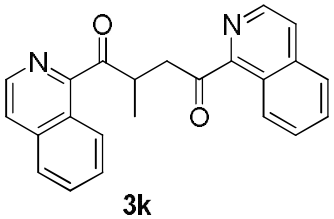
2-methyl-1,4-bis(5-phenylpyridin-2-yl)butane-1,4-dione (3i) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 5-phenylpyridine-2-carboxaldehyde (0.8 mmol, 146 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at

room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 4:1) to afford the product as a yellow solid (115 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37-1.39 (d, J = 7.2 Hz, 3H), 3.53–3.59 (dd, J = 4.4, 18.8 Hz, 1H), 3.97-4.04 (dd, J = 9.7, 18.7 Hz, 1H), 4.68–4.77 (m, 1H), 7.43-7.53 (m, 6H), 7.60-7.65 (m, 4H), 7.96-8.06 (m, 3H), 8.16-8.18 (m, 1H), 8.91-8.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.5, 35.2, 42.1, 121.9, 122.6, 127.3, 127.3, 128.7, 128.8, 129.2, 129.2, 135.0, 135.1, 136.9, 137.1, 139.6, 139.9, 147.4, 147.5, 151.4, 151.8, 199.9, 204.0; IR (neat) 3018, 2399, 1689, 1587, 1471, 1379, 1340, 1215, 927, 756 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{23}N_2O_2$ $[M+H]^+$: 407.1760, found 407.1763



3j

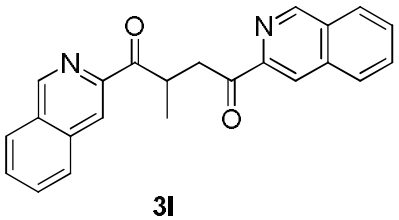
2-methyl-1,4-di(quinolin-2-yl)butane-1,4-dione (3j) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, quinoline-2-carboxaldehyde (0.8 mmol, 126 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 6:1) to afford the product as a brown solid (110 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45-1.47 (d, J = 7.1 Hz, 3H), 3.77–3.82 (dd, J = 5.0, 18.6 Hz, 1H), 4.08-4.15 (dd, J = 9.1, 18.6 Hz, 1H), 4.95–5.00 (m, 1H), 7.61-7.65 (m, 2H), 7.74-7.79 (m, 2H), 7.83-7.87 (m, 2H), 8.04-8.06 (m, 1H), 8.16-8.28 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.6, 35.3, 41.7, 118.1, 118.8, 127.5, 127.6, 128.3, 128.5, 129.6, 129.6, 129.9, 130.6, 130.8, 136.8, 136.8, 147.2, 147.3, 152.4, 152.8, 200.8, 204.9; IR (neat) 3018, 2974, 1693, 1593, 1456, 1375, 1215, 987, 835, 710 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}N_2O_2$ $[M+H]^+$: 355.1447, found 355.1448



3k

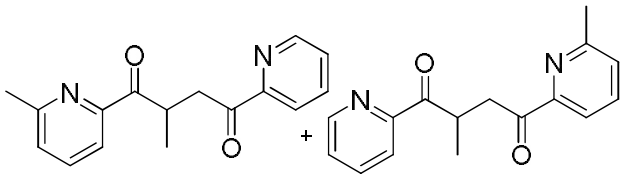
1,4-di(isoquinolin-1-yl)-2-methylbutane-1,4-dione (3k) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-

Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, isoquinoline-1-carboxaldehyde (0.8 mmol, 126 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 6:1) to afford the product as a dark brown solid (88 mg, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41-1.43 (d, J = 7.2 Hz, 3H), 3.65–3.71 (dd, J = 4.8, 18.4 Hz, 1H), 3.99-4.06 (dd, J = 9.0, 18.4 Hz, 1H), 4.69–4.74 (m, 1H), 7.56-7.73 (m, 4H), 7.79-7.88 (m, 4H), 8.57-8.62 (m, 2H), 8.77-8.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.3, 38.5, 44.2, 124.0, 124.5, 125.7, 126.3, 126.8, 126.8, 126.9, 126.9, 128.7, 128.9, 130.2, 130.3, 137.0, 137.0, 141.0, 141.2, 152.8, 153.4, 202.8, 206.6; IR (neat) 2958, 2852, 1732, 1683, 1456, 1361, 1215, 1091, 943, 755 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}N_2O_2$ $[M+H]^+$: 355.1447, found 355.1450



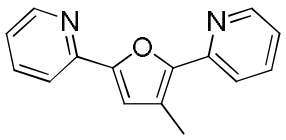
3l

1,4-di(isoquinolin-3-yl)-2-methylbutane-1,4-dione (3l) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, isoquinoline-3-carboxaldehyde (0.8 mmol, 126 mg) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 6:1) to afford the product as a yellow solid (102 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41-1.43 (d, J = 7.2 Hz, 3H), 3.61–3.67 (dd, J = 4.6, 18.7 Hz, 1H), 4.07-4.14 (dd, J = 9.5, 18.6 Hz, 1H), 4.79–4.88 (m, 1H), 7.70-7.78 (m, 4H), 7.93-8.00 (m, 2H), 8.04-8.07 (m, 2H), 8.42 (s, 1H), 8.54 (s, 1H), 9.30-9.34 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.5, 35.8, 42.8, 120.3, 121.0, 127.5, 127.5, 128.6, 128.6, 129.2, 129.3, 130.1, 130.2, 130.7, 130.9, 135.5, 135.7, 147.0, 147.4, 151.8, 151.9, 200.4, 204.6; IR (neat) 3018, 1685, 1624, 1492, 1388, 1215, 1170, 1128, 933, 904, 810 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}N_2O_2$ $[M+H]^+$: 355.1447, found 355.1443



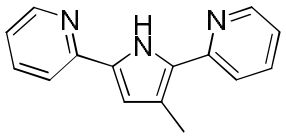
3ab & 3ba

2-methyl-1-(6-methylpyridin-2-yl)-4-(pyridin-2-yl)butane-1,4-dione (3ab) & 2-methyl-4-(6-methylpyridin-2-yl)-1-(pyridin-2-yl)butane-1,4-dione (3ba) To a solution of **1a** (0.4 mmol, 44 μL), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol, 23 mg), 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide (0.04 mmol, 12 mg) and triethylamine (1.2 mmol, 165 μL) in dimethyl sulfoxide (1.2 mL) under argon at room temperature, 6-methylpyridine-2-carboxaldehyde (0.4 mmol, 48 mg) and pyridine-2-carboxaldehyde (0.4 mmol, 47.5 μL) in dimethyl sulfoxide (0.8 mL) was added by a syringe pump with a 2 hours period. The mixture was allowed to stir at room temperature for another 1 hour. Then the mixture was diluted with ethyl acetate (10 mL), filtered, washed with water (20 mL) and brine (15 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane:EA = 6:1) to afford the product as a yellow solid (102 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29-1.31 (m, 3H), 2.58-2.59 (m, 3H), 3.41-3.53 (m, 1H), 3.85-3.93 (m, 1H), 4.64-4.65 (m, 1H), 7.27-7.29 (m, 1H), 7.42-7.45 (m, 1H), 7.61-7.69 (m, 1H), 7.72-7.85 (m, 2H), 7.96-8.06 (m, 1H), 8.65-8.71 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4, 17.5, 24.4, 24.5, 35.1, 35.1, 41.7, 41.9, 118.7, 119.5, 121.7, 122.4, 126.5, 126.7, 126.8, 127.1, 136.8, 136.8, 136.8, 148.9, 148.9, 152.2, 152.2, 152.8, 153.2, 157.9, 157.9, 200.2, 200.6, 204.5, 204.6; HRMS (ESI) calcd for $C_{16}H_{17}N_2O_2$ $[M+H]^+$: 269.1290, found 269.1289



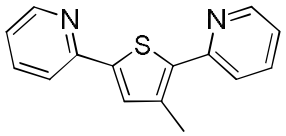
4a

2,2'-(3-methylfuran-2,5-diyl)dipyridine (4a) A solution of 2-methyl-1,4-di(pyridin-2-yl)butane-1,4-dione (**3a**) (51mg, 0.2mmol) and *p*-toluenesulfonic acid monohydrate (8mg, 0.04mmol) in toluene (10 mL) was heated to reflux for 5 hours under nitrogen. Then the solvent was removed under reduce pressure and the residue was purified by column chromatography (Hexane:EA = 6:1) to afford the product as white solid (36 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.55 (s, 3H), 7.06 (s, 1H), 7.11-7.18 (m, 2H), 7.70-7.75 (m, 2H), 7.78-7.83 (m, 2H), 8.59-8.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.1, 114.6, 118.7, 119.7, 121.1, 122.0, 123.6, 136.2, 136.5, 148.4, 149.1, 149.3, 149.7, 151.0, 152.1; IR (neat) 2926, 2852, 1620, 1589, 1556, 1471, 1429, 1273, 1151, 937, 752 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O$ $[M+H]^+$: 237.1028, found 237.1031



4b

2,2'-(3-methyl-1H-pyrrole-2,5-diyl)dipyridine (4b) A solution of 2-methyl-1,4-di(pyridin-2-yl)butane-1,4-dione (**3a**) (51mg, 0.2mmol) and ammonium acetate (770mg, 10 mmol) in acetic acid (8 mL) was heated to 100 ^{o}C under nitrogen for 12 hours. Then EA (20 mL) was added and the reaction mixture was washed with water (20 mL) and saturated sodium bicarbonate solution (20 mL) and dried over sodium sulfate. The solvent of organic layer was removed under reduce pressure and the residue was purified by column chromatography (Hexane:EA = 1:1) to afford the product as pale yellow solid (43 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 6.60-6.61 (d, J = 2.8 Hz), 7.02-7.07 (m, 2H), 7.51-7.54 (m, 2H), 7.61-7.68 (m, 2H), 8.51-8.57 (m, 2H), 10.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 111.6, 118.3, 119.1, 120.1, 120.4, 120.6, 129.1, 131.1, 136.2, 136.2, 149.2, 149.3, 150.1, 150.8; IR (neat) 3001, 1642, 1566, 1473, 1288, 1269, 1511, 1072, 948, 756 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{14}N_3$ $[M+H]^+$: 236.1188, found 236.1185



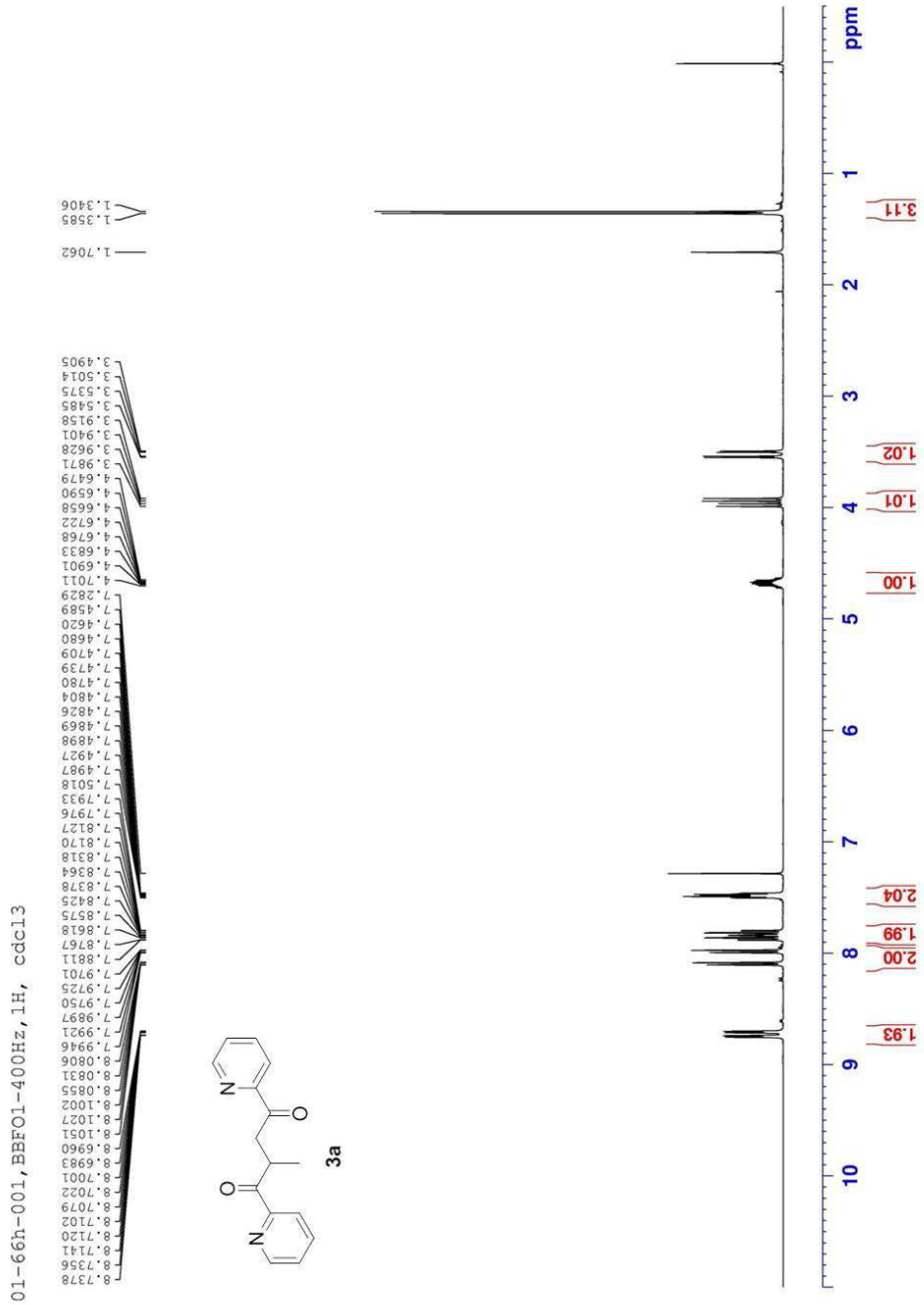
4c

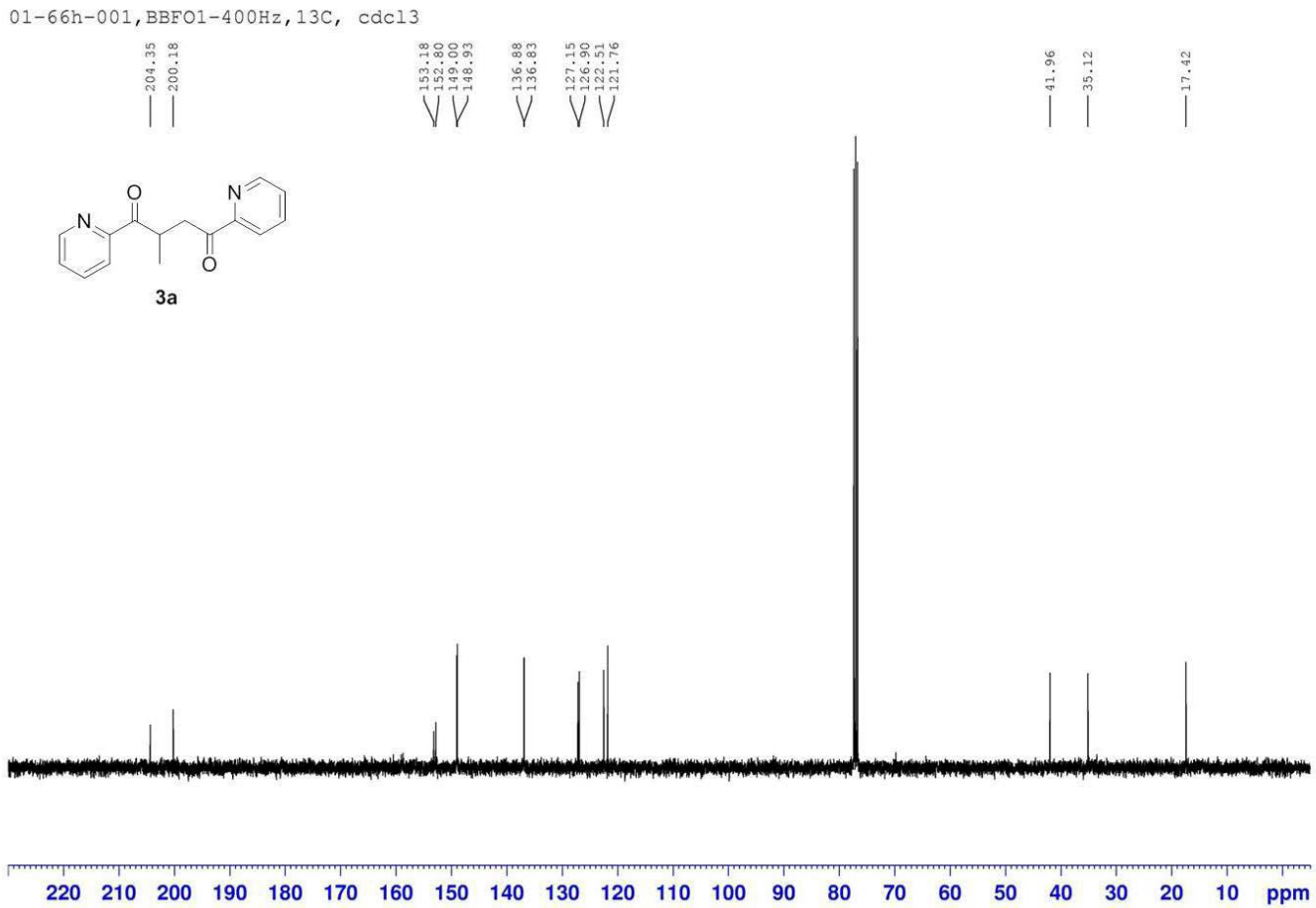
2,2'-(3-methylthiophene-2,5-diyl)dipyridine (4c) A solution of 2-methyl-1,4-di(pyridin-2-yl)butane-1,4-dione (**3a**) (51mg, 0.2mmol) and Lawesson's Reagent (89 mg, 0.22 mmol) in dichloromethane (3 mL) was stirred at 40 ^{o}C under nitrogen for 6 hours. Then EA (20 mL) was added and the reaction mixture was washed with water (10 mL) and saturated sodium bicarbonate solution (10 mL) and dried over sodium sulfate. The solvent of organic layer was removed under reduce pressure and the residue was purified by column chromatography (Hexane:EA = 4:1) to afford the product as yellow solid (32 mg, 64%).^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.55 (s, 3H), 7.13-7.18 (m, 2H), 7.48 (s, 1H), 7.60-7.74 (m, 4H), 8.57-8.59 (m, 1H), 8.63-8.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.4, 188.9, 121.4, 121.5, 121.9, 136.4, 136.6, 139.7, 143.4, 149.6, 149.6, 152.4, 153.5; IR (neat) 2960, 1747, 1681, 1581, 1471, 1259, 1153, 1004, 781 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2S$ $[M+H]^+$: 252.0799, found 252.0799

Reference

(1) Catherine A, F. *Tetrahedron Lett.* 2010, *51*, 5621.
(2) Ziessel, R.; Nguyen, P.; Douce, L.; Cesario, M.; Estournes, C. *Org. Lett.* 2004, *6*, 2865.
(3) Barrows, R. S.; Lindwall, H. G. *J. Am. Chem. Soc.* 1942, *64*, 2430.
(4) Jones, S. W.; Palmer, C. F.; Paul, J. M.; Tiffin, P. D. *Tetrahedron Lett.* 1999, *40*, 1211.

Copies of ^{1}H NMR and ^{13}C NMR spectra

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126.90
122.51
121.76
41.96
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17.42
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N
N
O
O
3a
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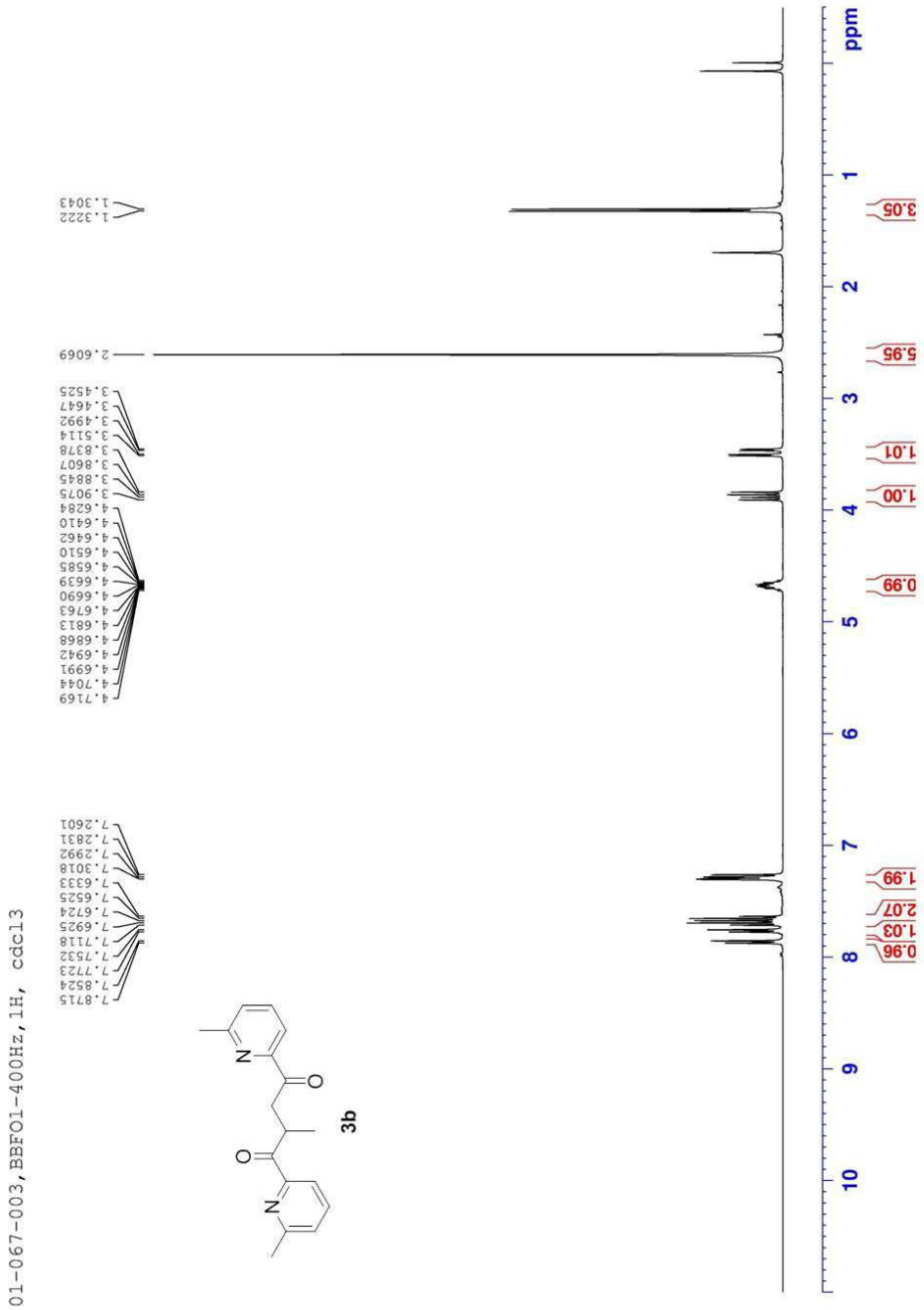
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3.8845
3.9075
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4.6462
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7.6925
7.7118
7.7532
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7.8524
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1.01
1.00
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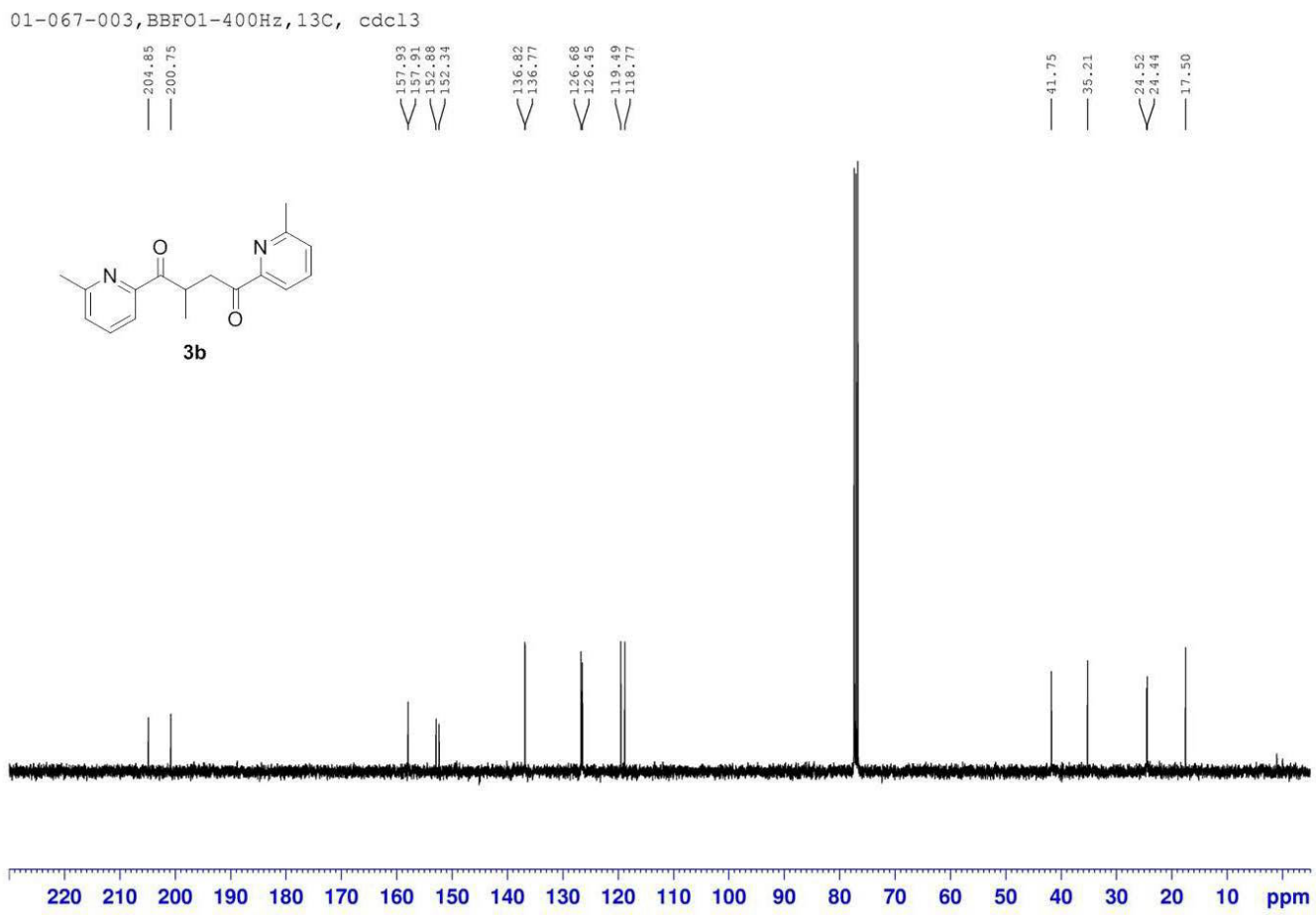
2.07
1.03
0.96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3b
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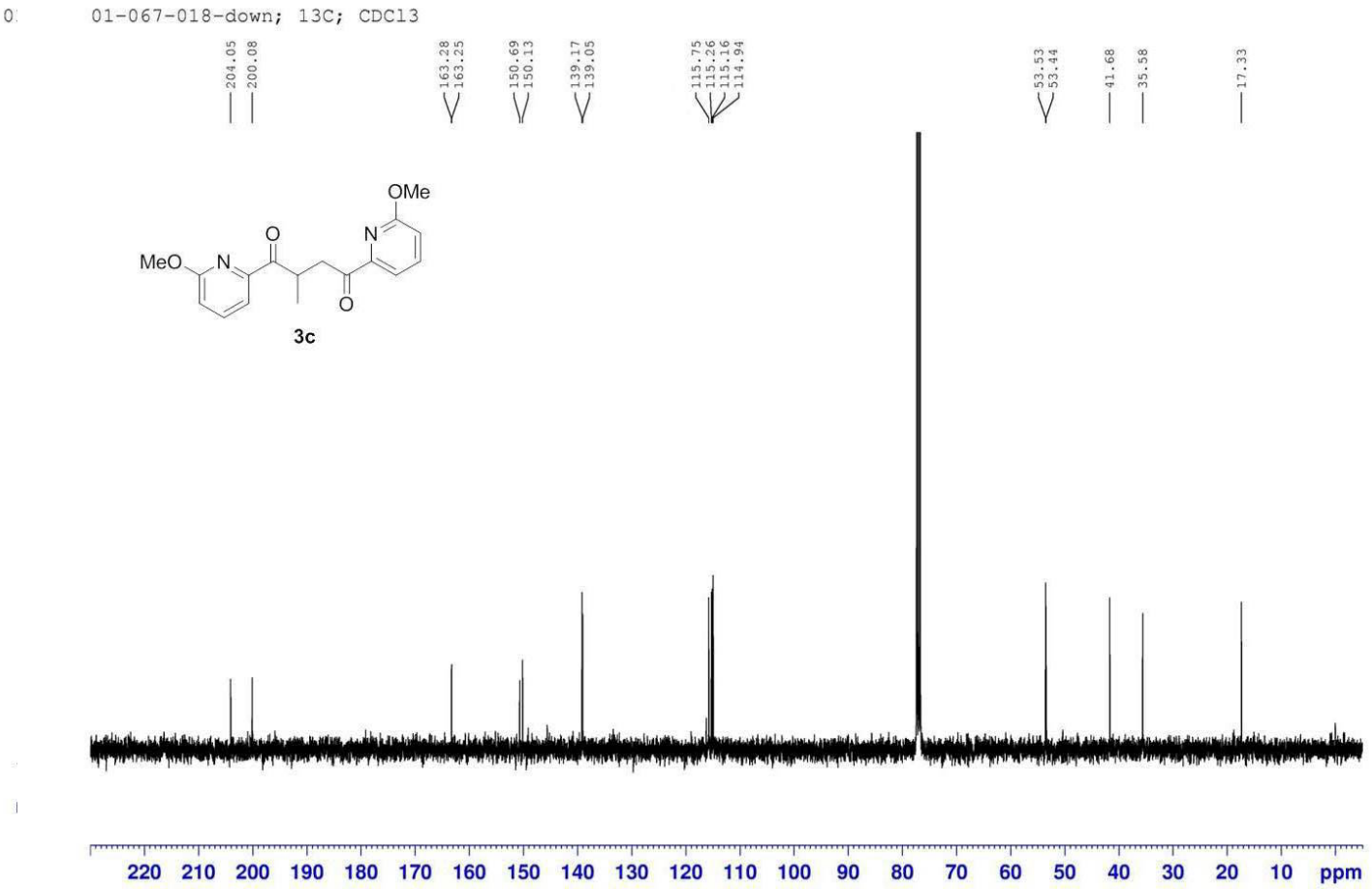
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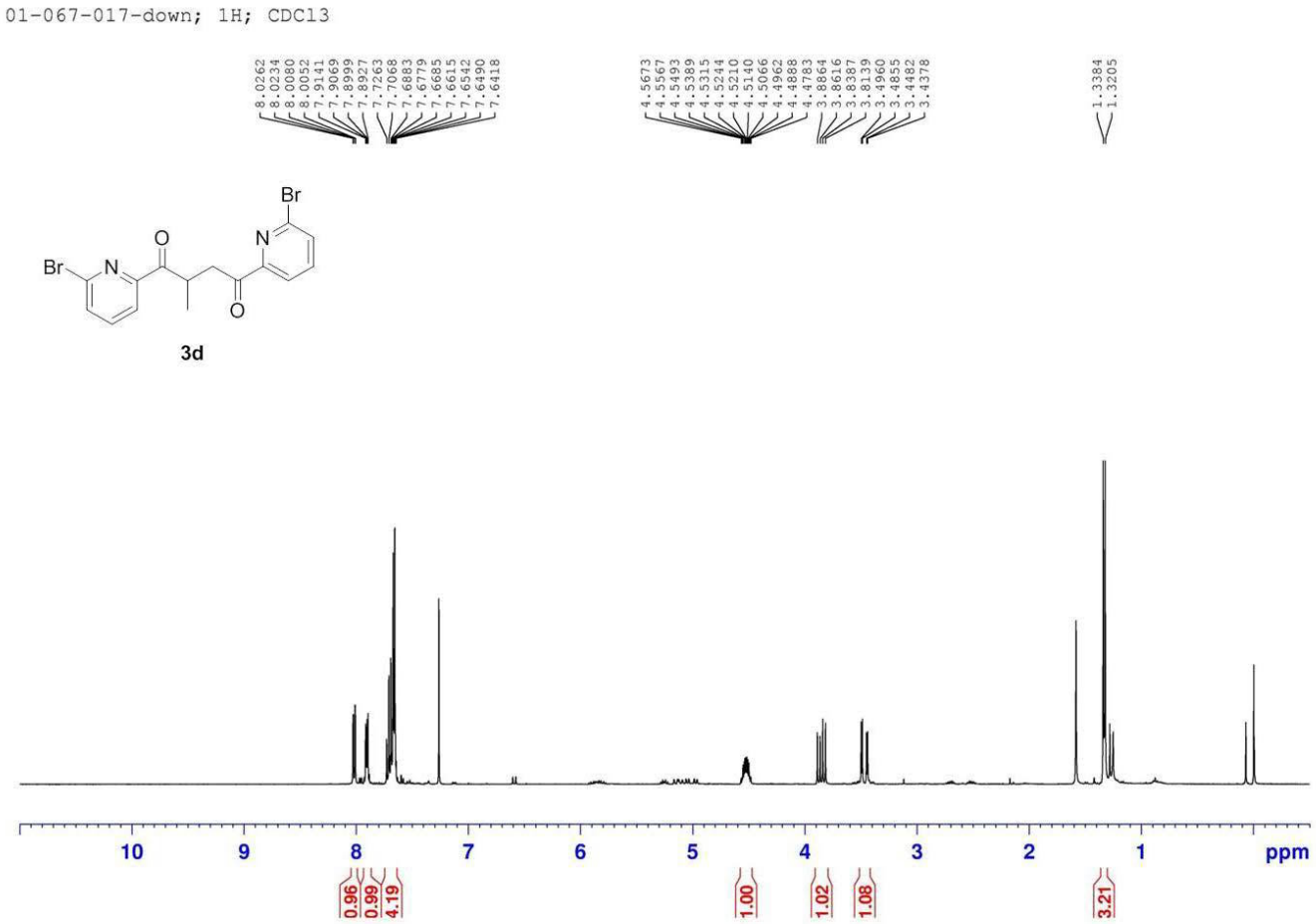
139.05
115.75
115.26
115.16
114.94
53.53
53.44
41.68
35.58
17.33
OMe
MeO
N
O
N
O
3c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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O
O
N
Br
3d
10
9
8
7
6
5
4
3
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ppm
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4.19
1.00
1.02
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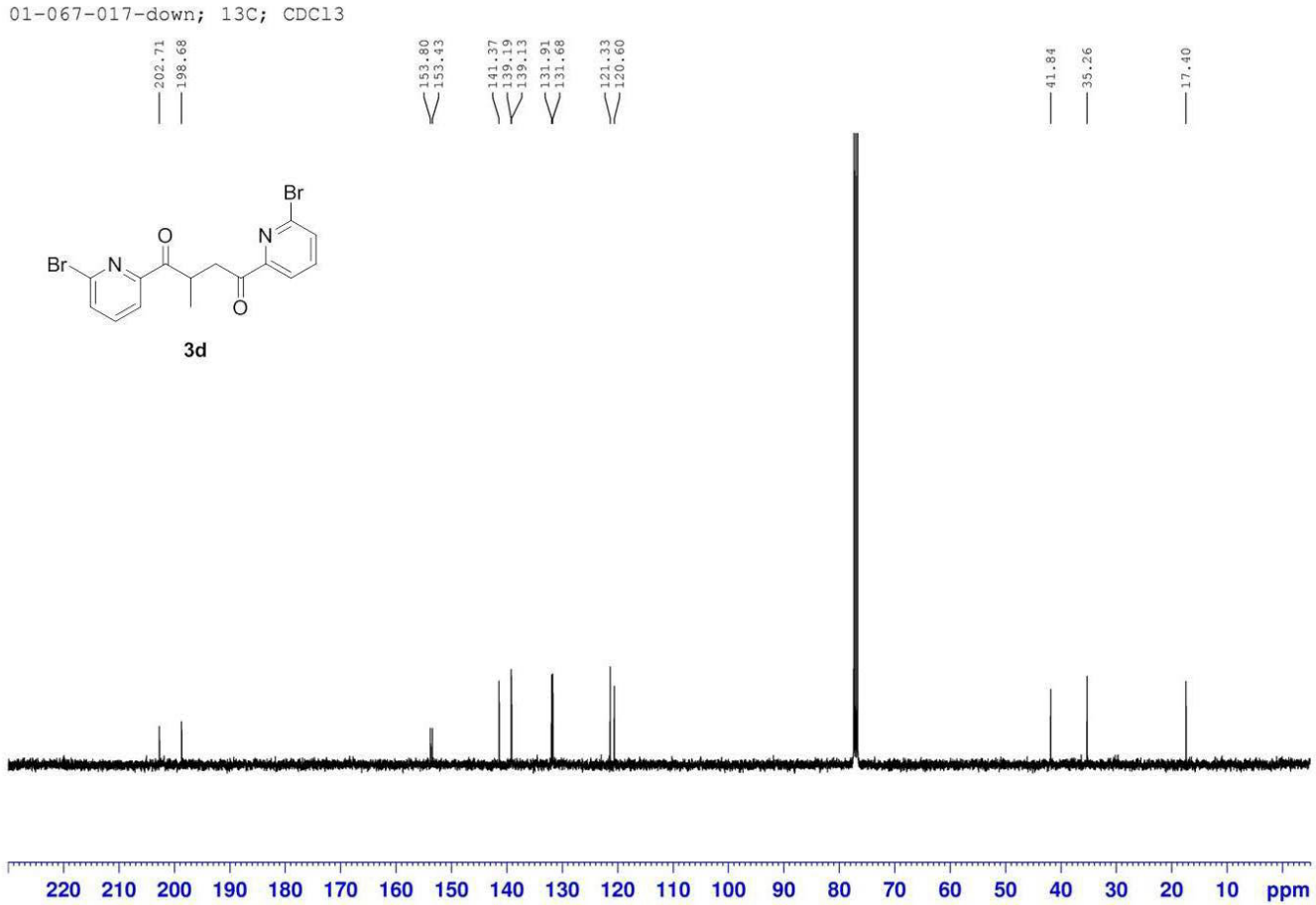
3.21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120.60
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Br
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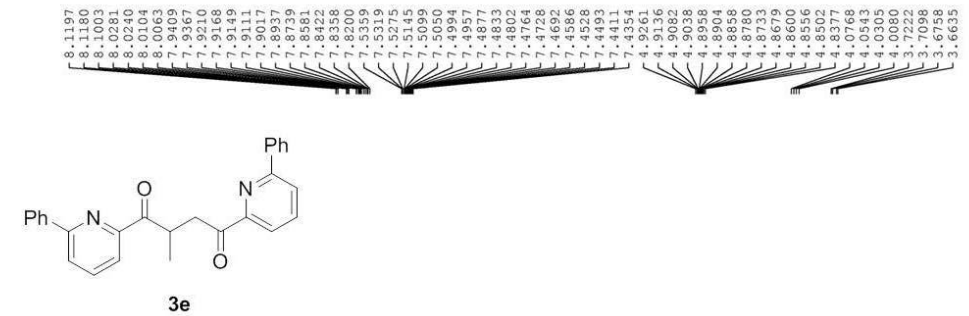
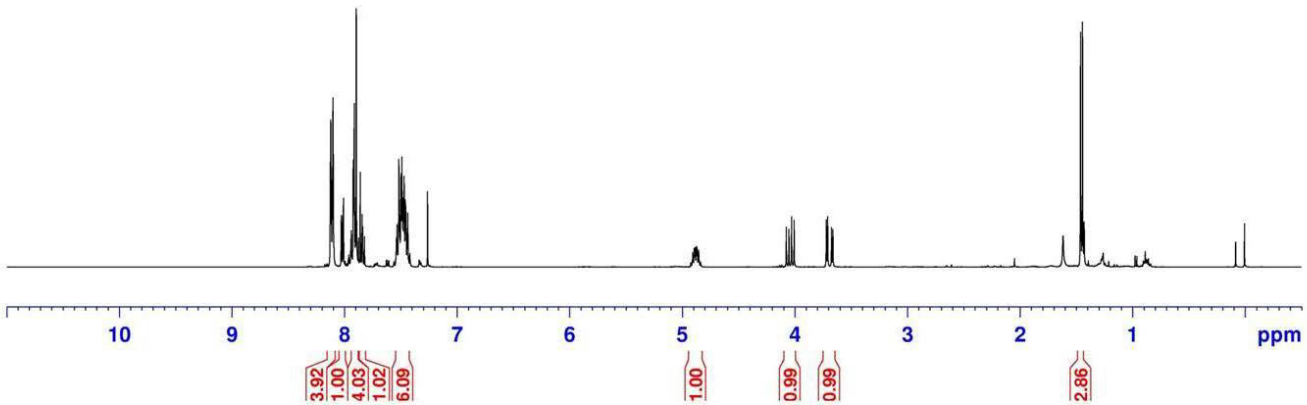
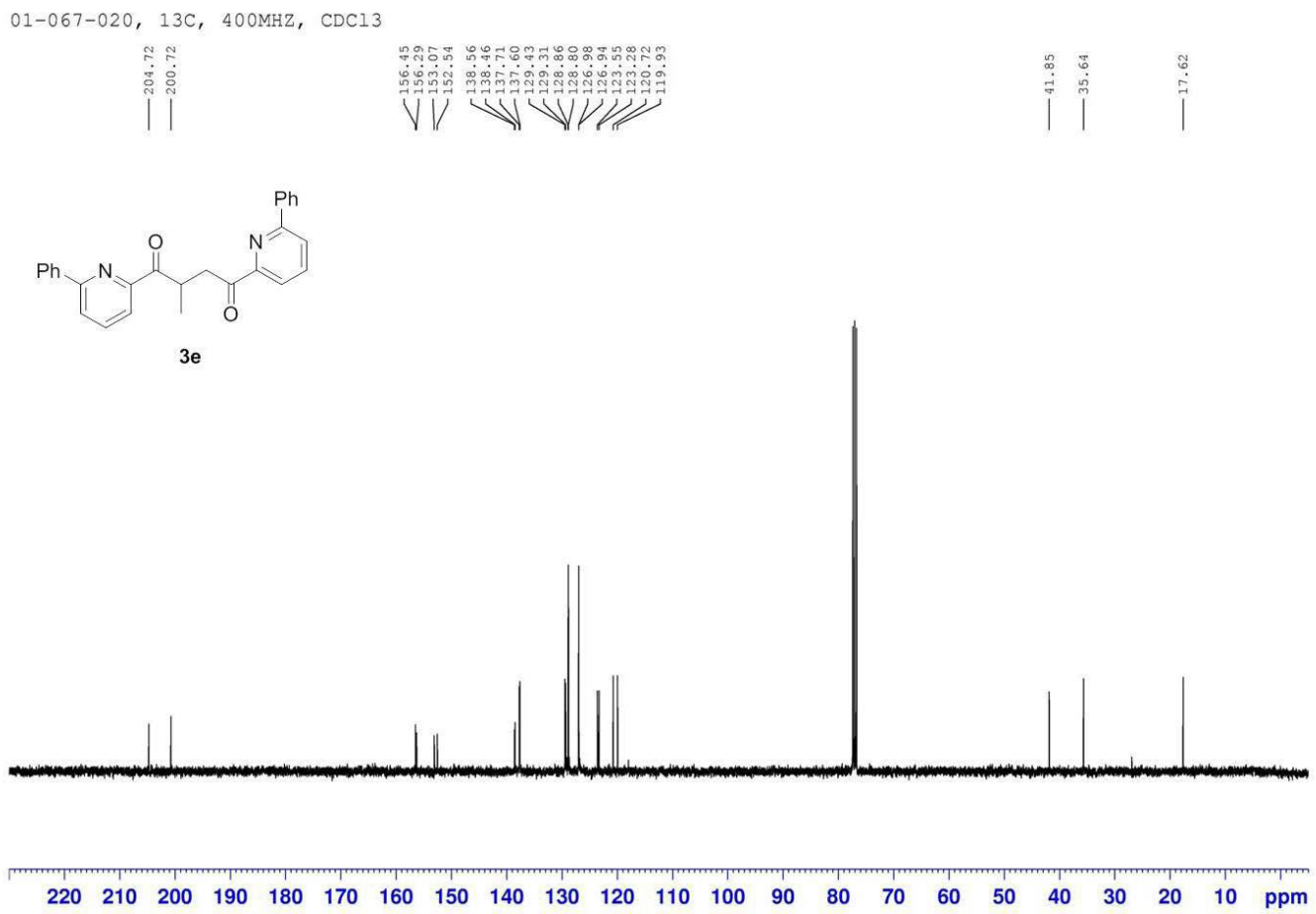


3e

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128.80
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126.94
123.55
123.28
120.72
119.93
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Ph
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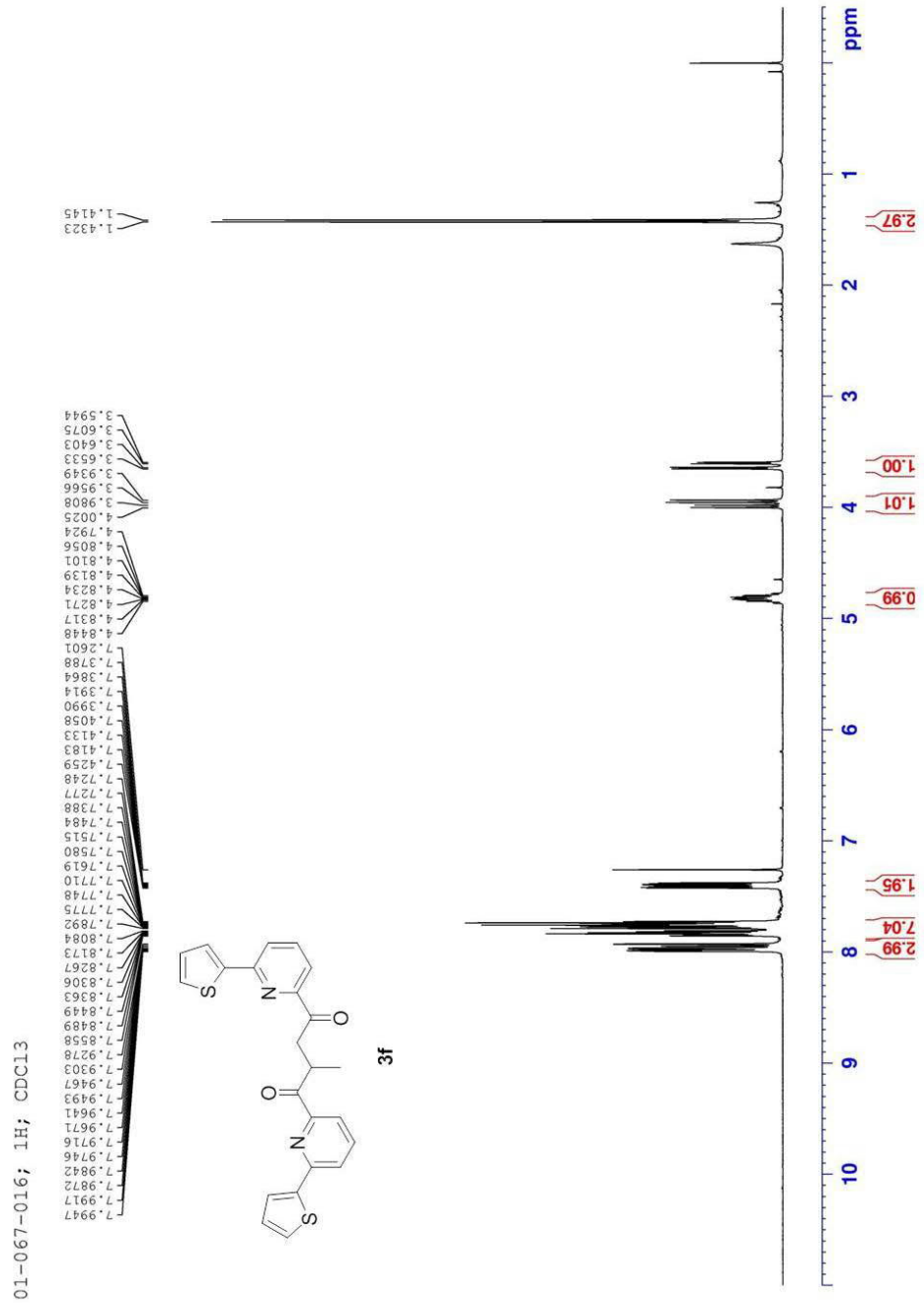
Ph
3e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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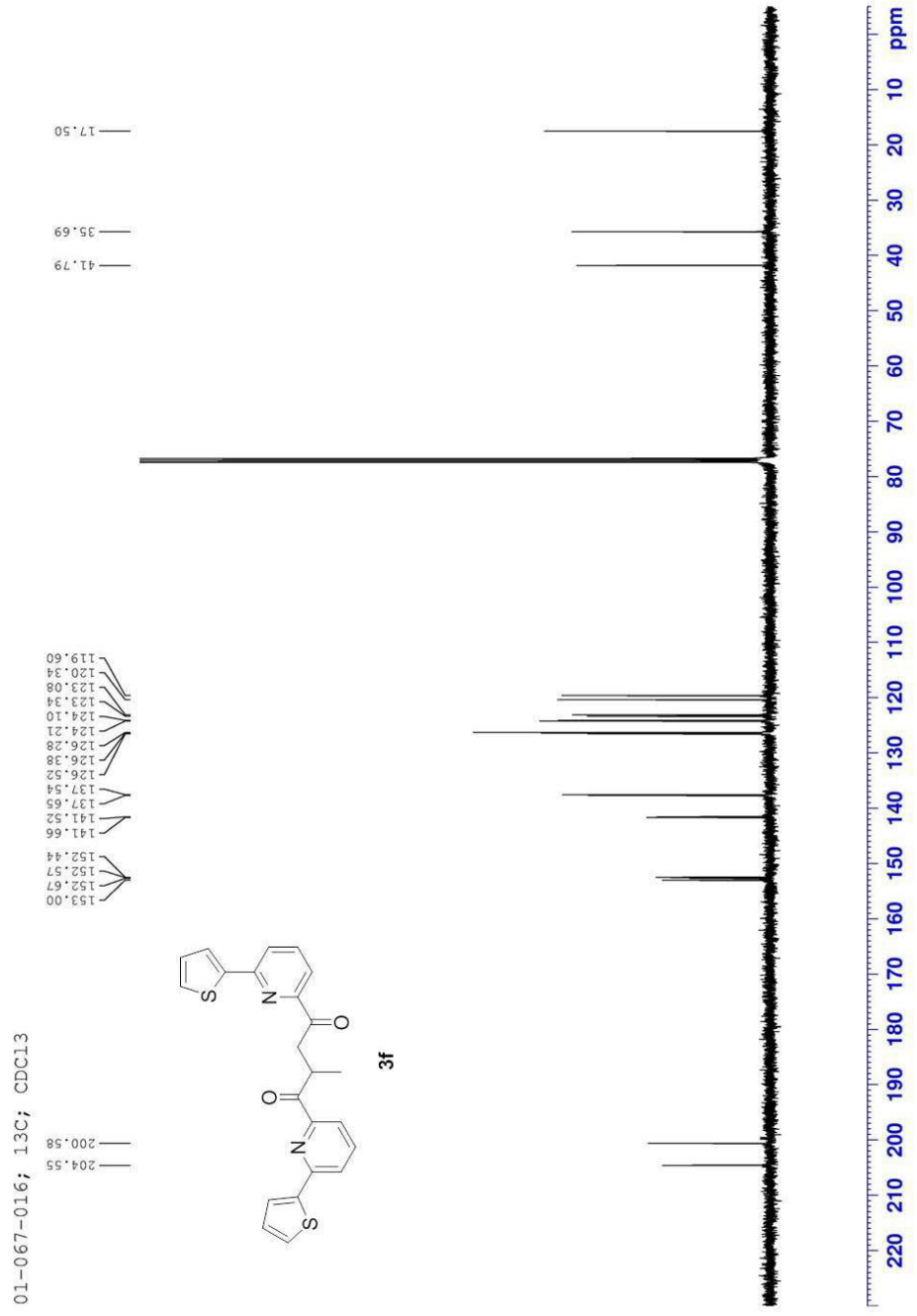
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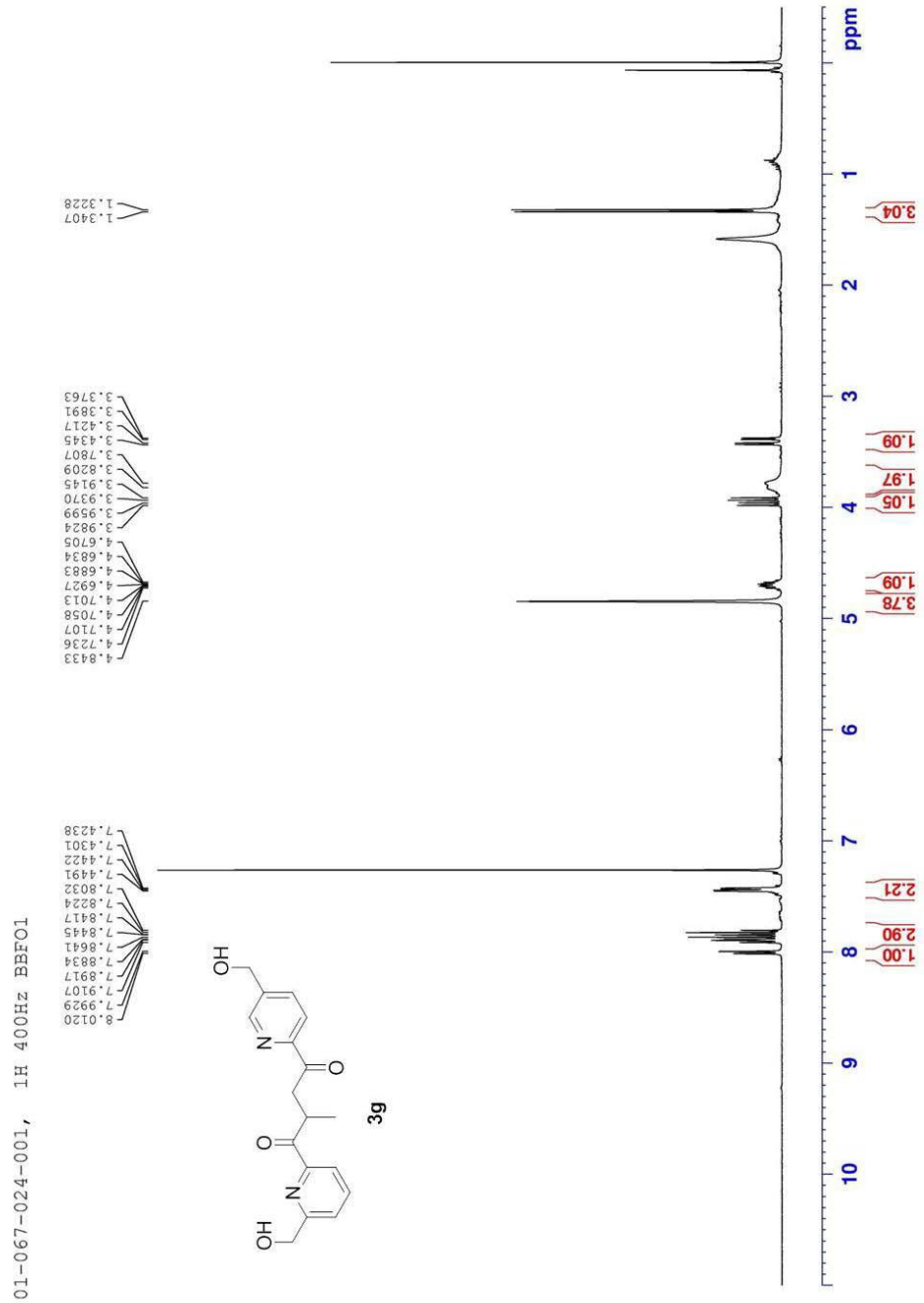
ppm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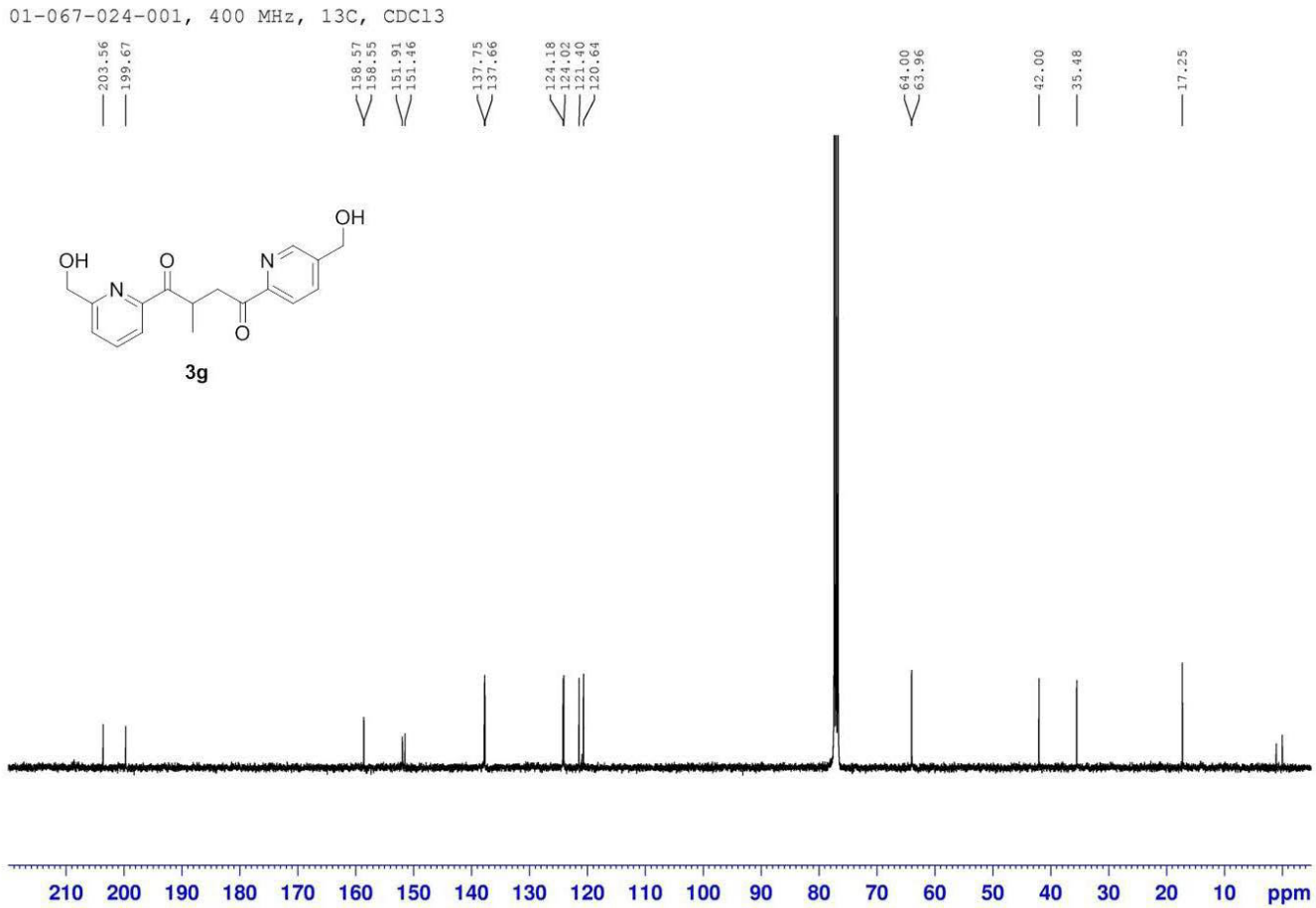
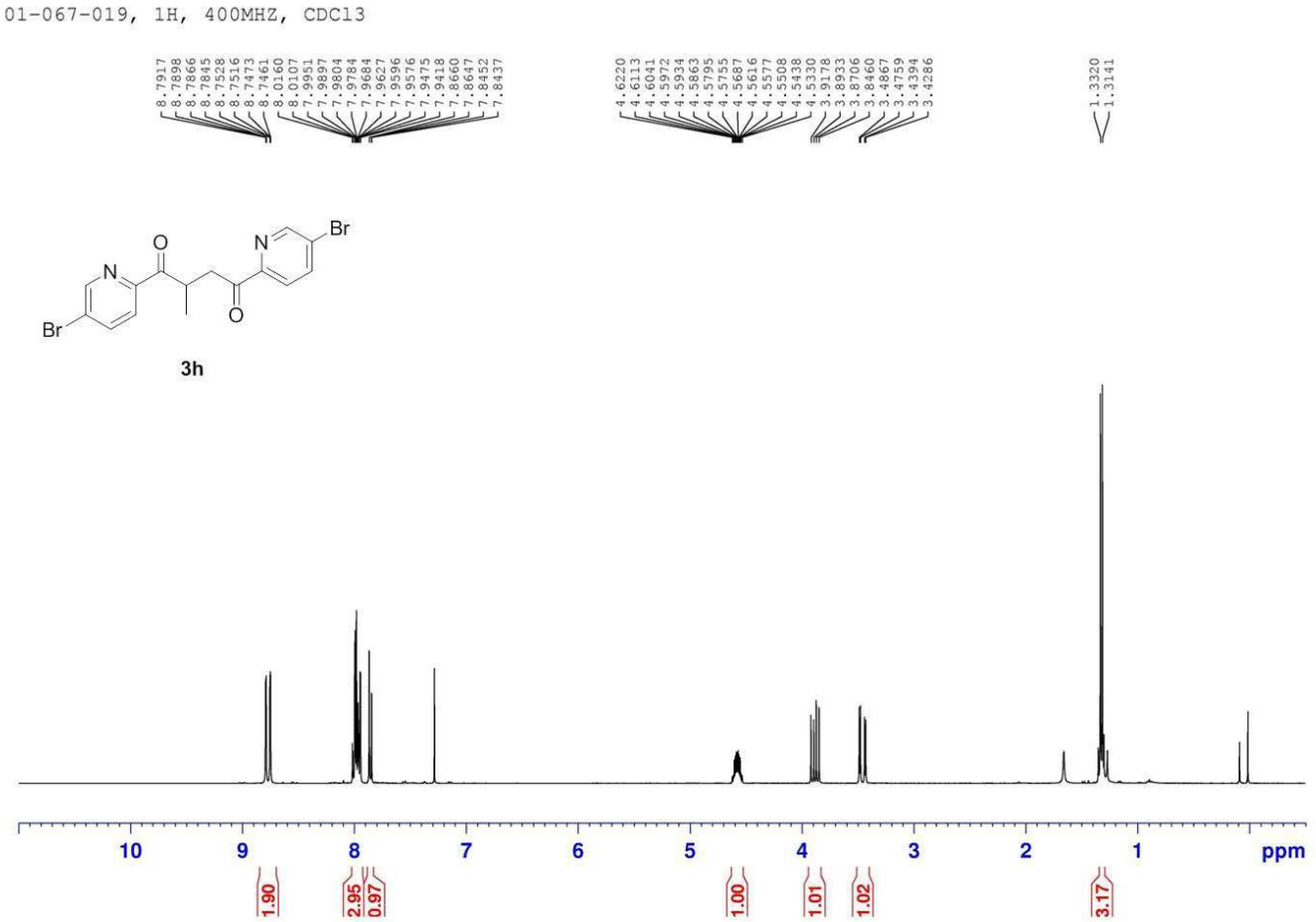
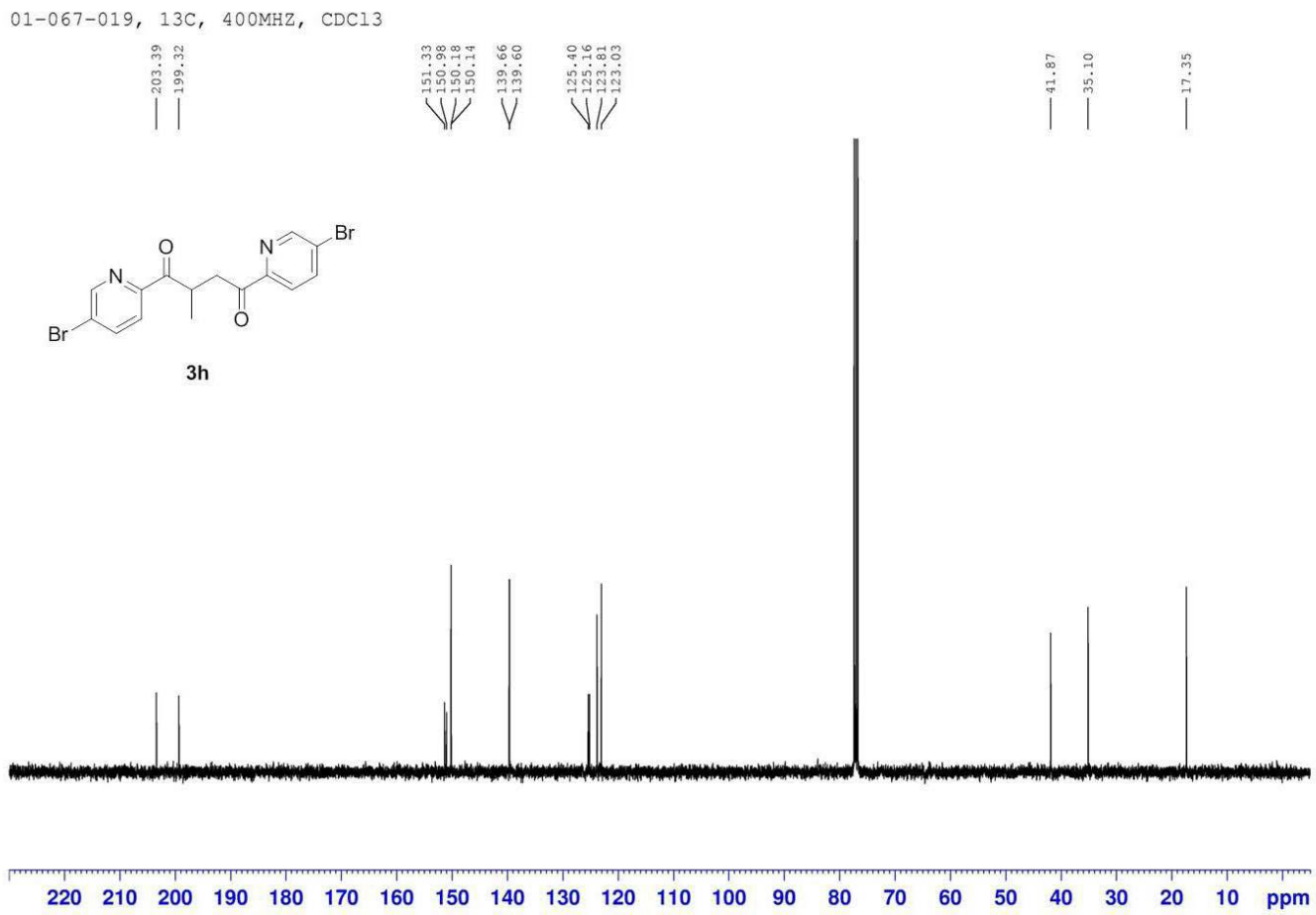
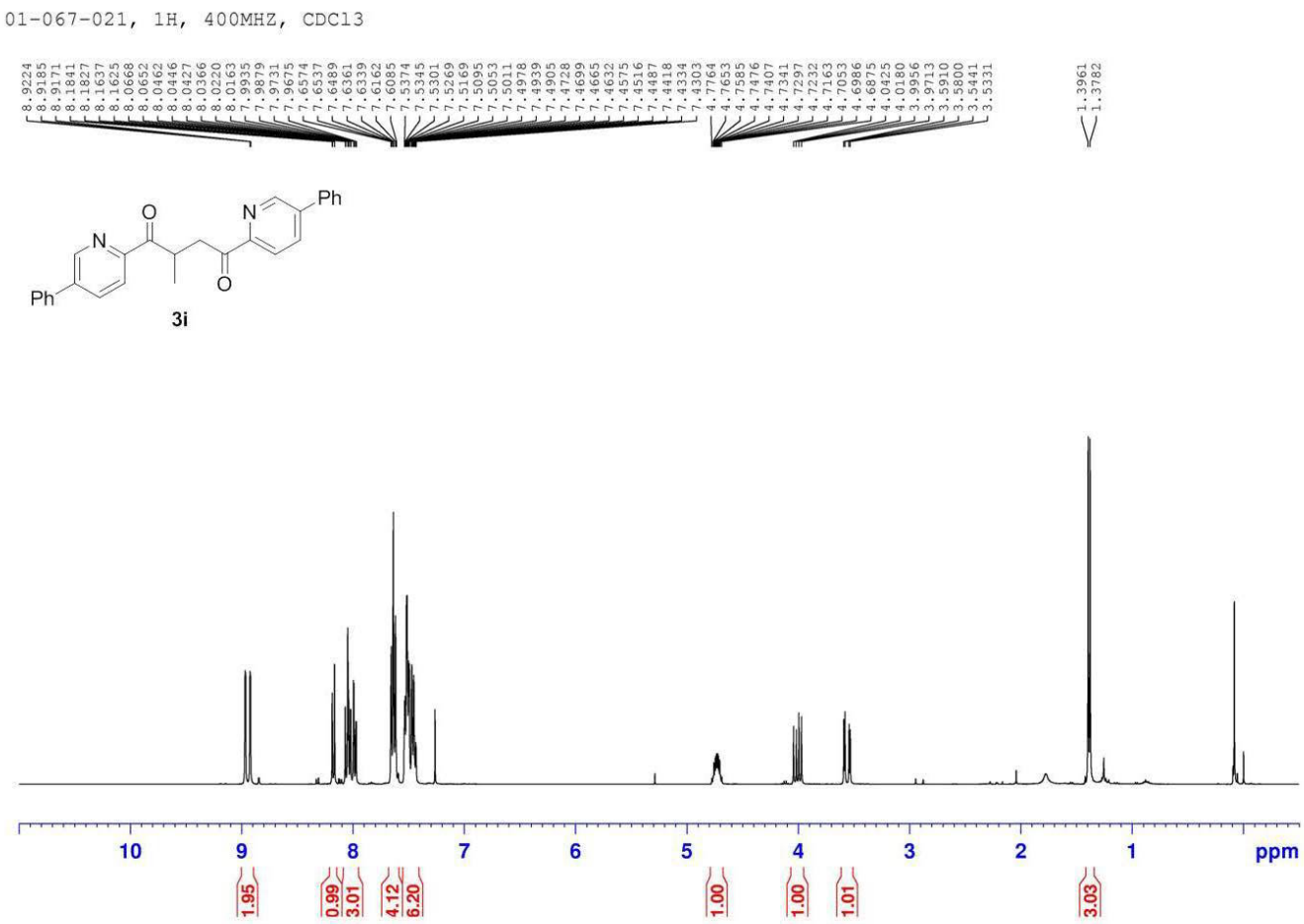
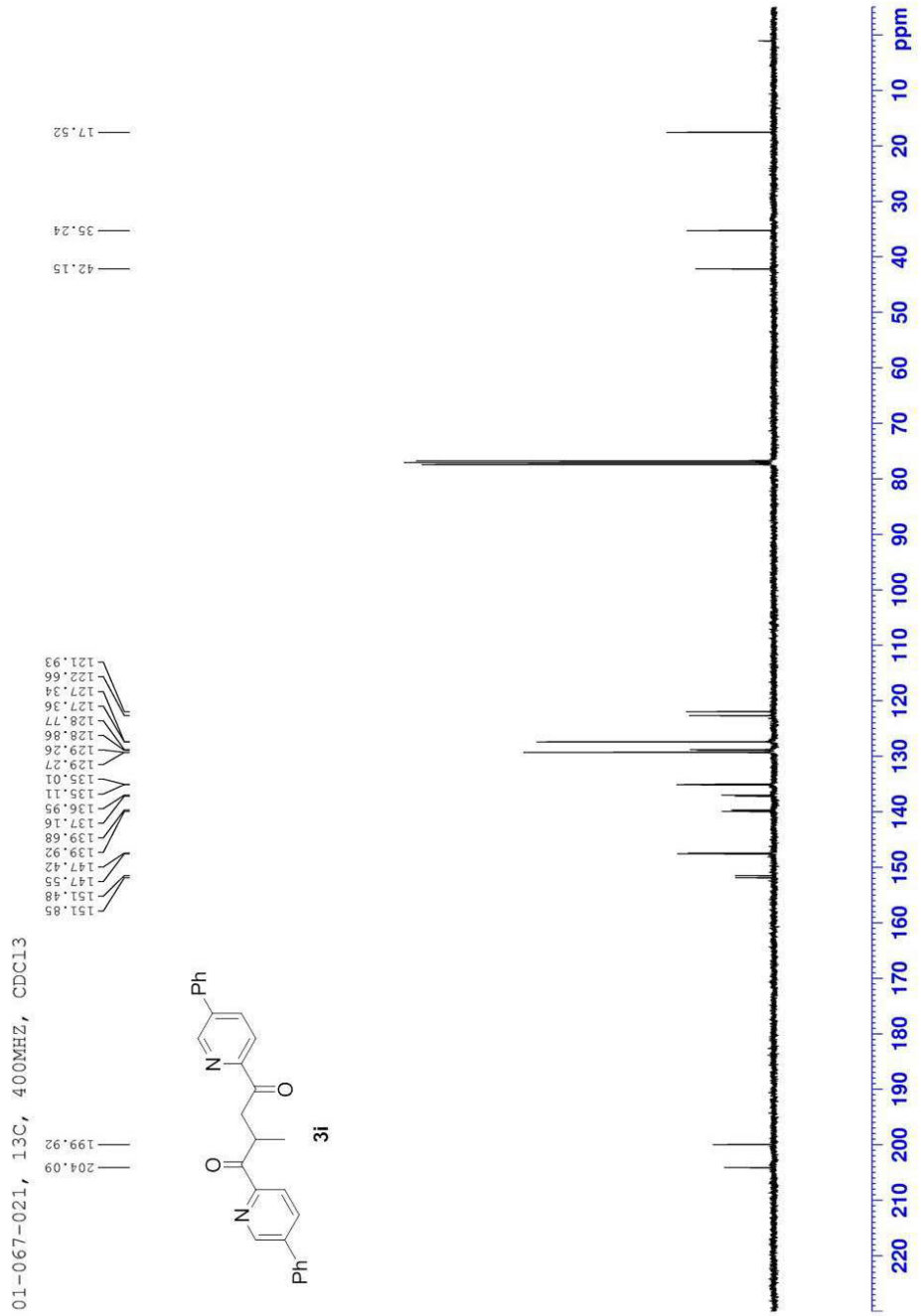
3.7807
3.4345
3.4217
3.3891
3.3763
1.3407
1.3228
OH
N
O
O
N
OH
3g
ppm
1.00
2.90
2.21
3.78
1.09
1.05
1.97
1.09
3.04

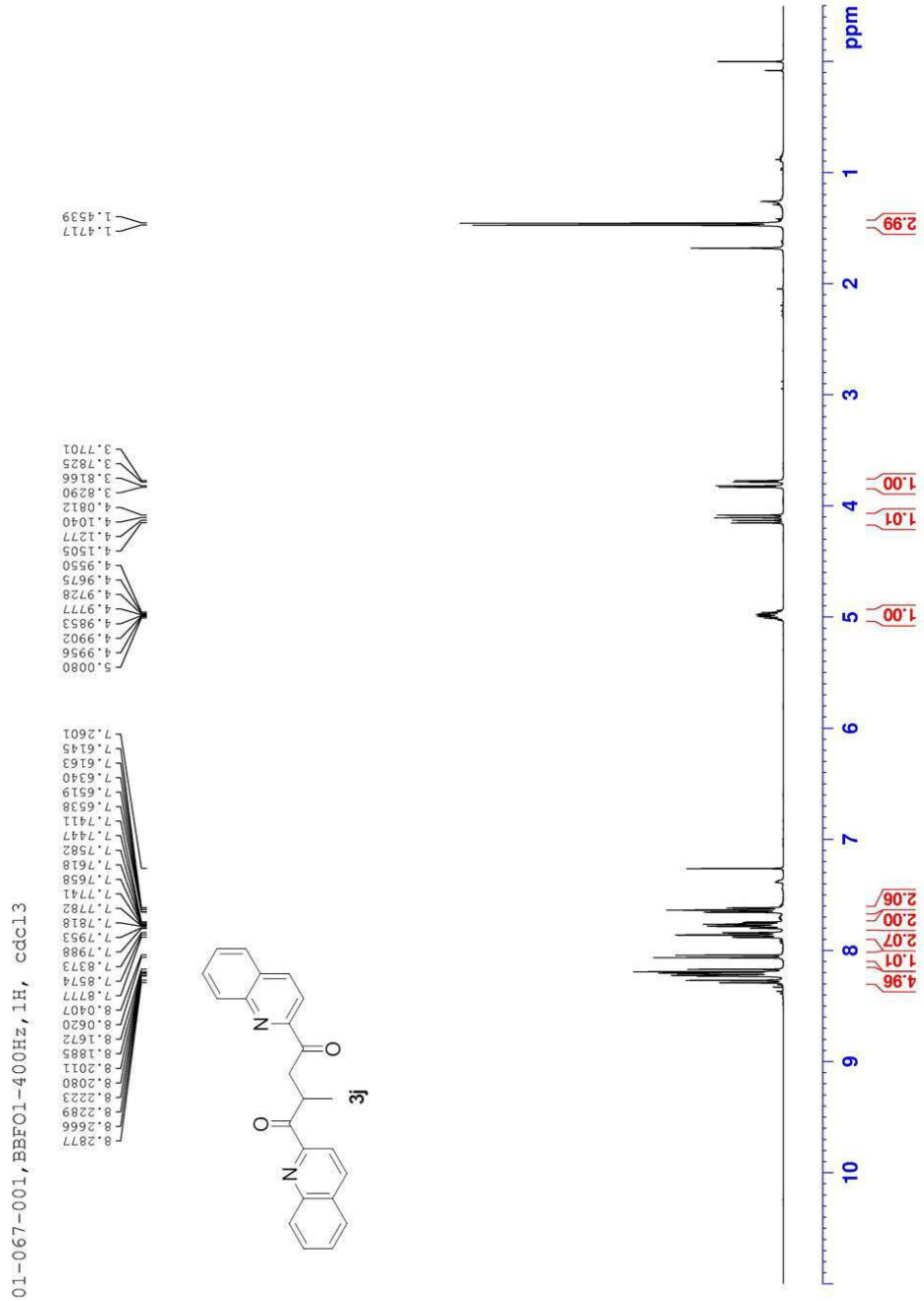

01-067-024-001, 400 MHz, 13C, CDCl3
203.56
199.67
158.57
158.55
151.91
151.46
137.75
137.66
124.18
124.02
121.40
120.64
64.00
63.96
42.00
35.48
17.25
OH
OH
O
N
N
O
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

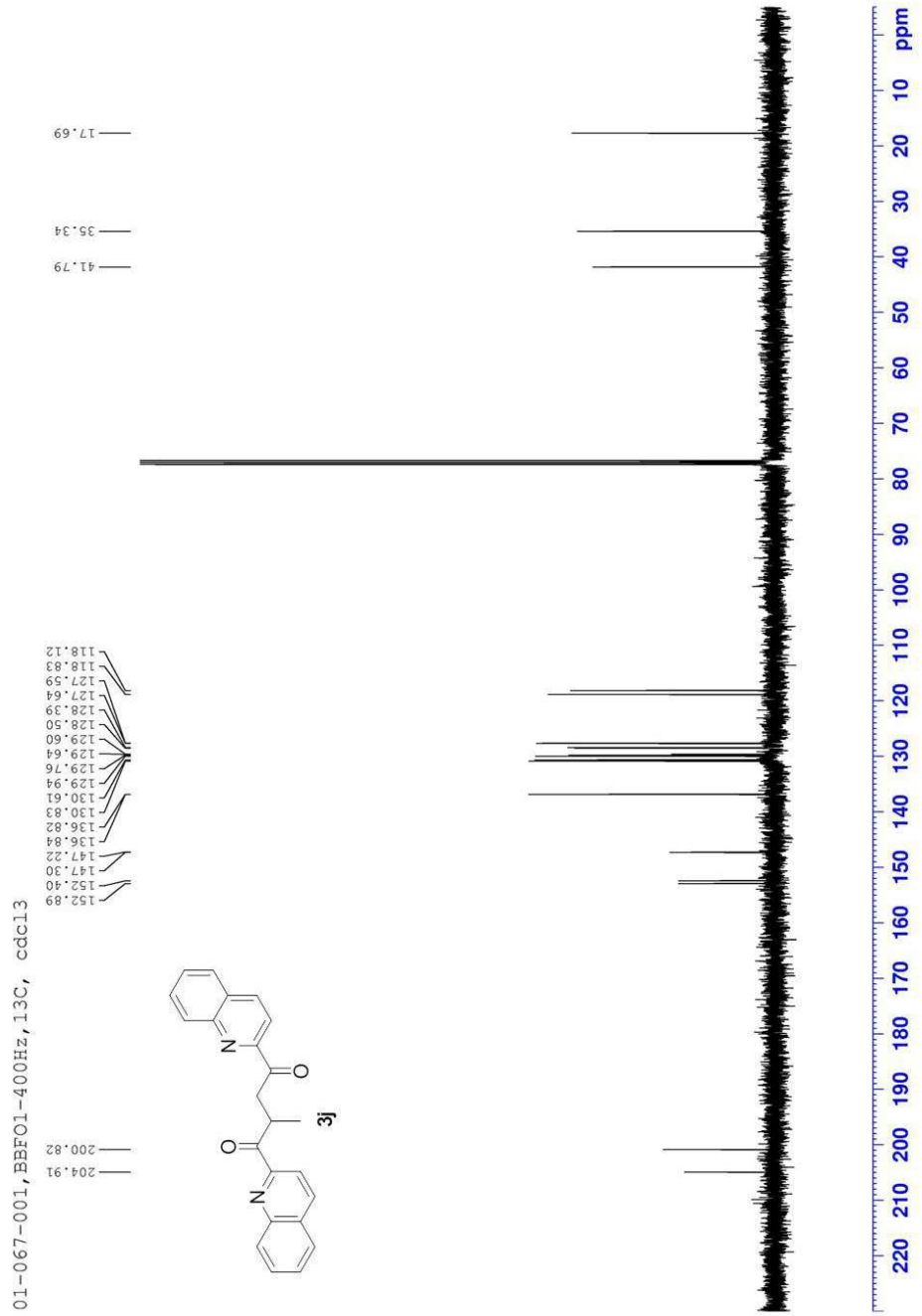

01-067-019, 1H, 400MHZ, CDCl3
8.7917
8.7898
8.7866
8.7845
8.7528
8.7516
8.7473
8.7461
8.0160
8.0107
7.9951
7.9897
7.9804
7.9784
7.9684
7.9627
7.9596
7.9576
7.9475
7.9418
7.8660
7.8647
7.8452
7.8437
4.6220
4.6113
4.6041
4.5972
4.5934
4.5863
4.5795
4.5755
4.5687
4.5616
4.5577
4.5508
4.5438
4.5330
3.9178
3.8933
3.8706
3.8460
3.4867
3.4759
3.4394
3.4286
1.3320
1.3141
Br
N
O
O
N
Br
3h
10
9
8
7
6
5
4
3
2
1
ppm
1.90
2.95
0.97
1.00
1.01
1.02
3.17

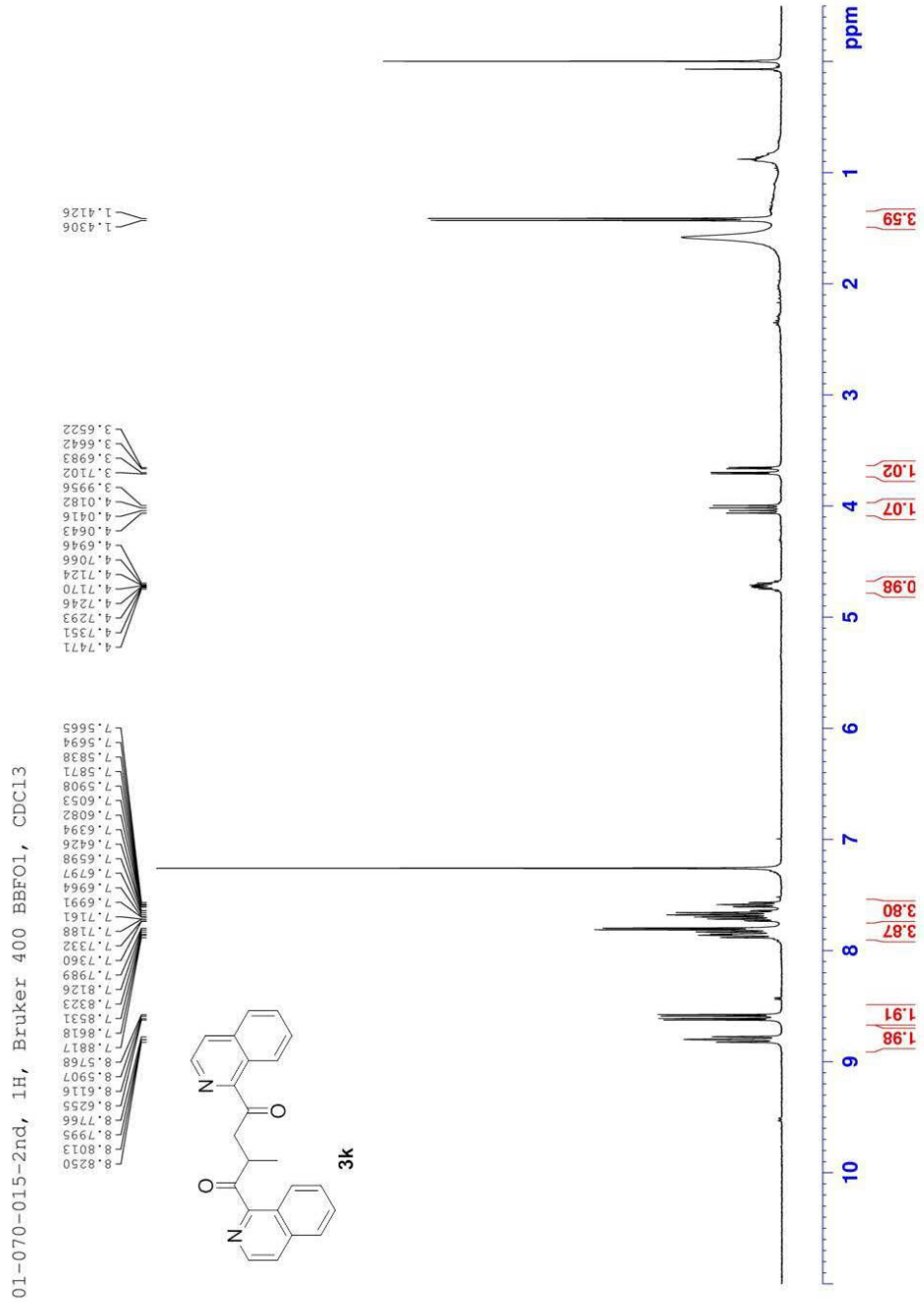

01-067-019, 13C, 400MHZ, CDCl3
203.39
199.32
151.33
150.98
150.18
150.14
139.66
139.60
125.40
125.16
123.81
123.03
41.87
35.10
17.35
Br
Br
3h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

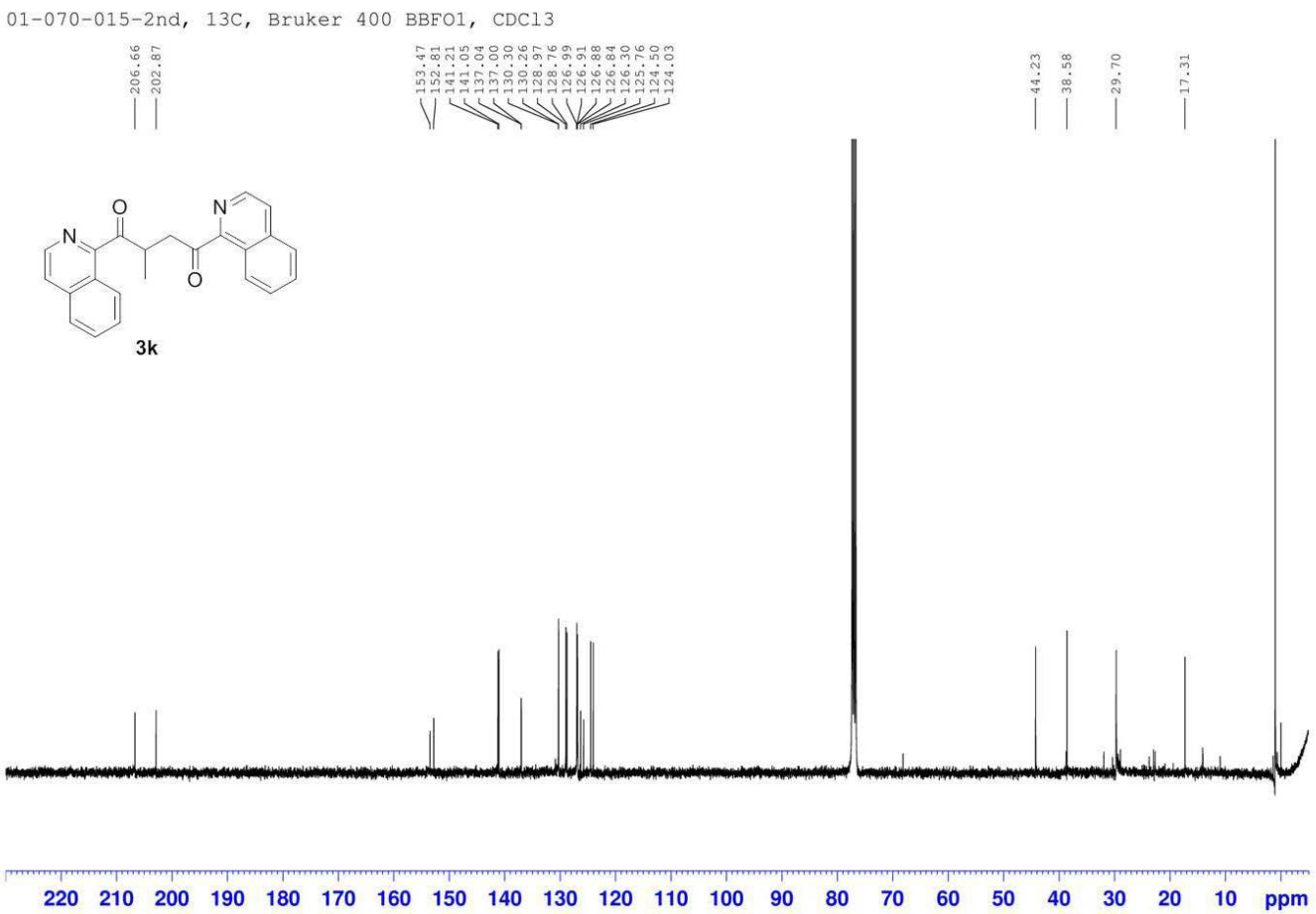

01-067-021, 1H, 400MHZ, CDCl3
8.9224
8.9185
8.9171
8.1841
8.1827
8.1637
8.1625
8.0668
8.0652
8.0462
8.0446
8.0427
8.0366
8.0220
8.0163
7.9935
7.9879
7.9731
7.9675
7.6574
7.6537
7.6489
7.6361
7.6339
7.6162
7.6085
7.5374
7.5345
7.5301
7.5269
7.5169
7.5095
7.5053
7.5011
7.4978
7.4939
7.4905
7.4728
7.4699
7.4665
7.4632
7.4575
7.4516
7.4487
7.4418
7.4334
7.4303
4.7764
4.7653
4.7585
4.7476
4.7407
4.7341
4.7297
4.7232
4.7163
4.7053
4.6986
4.6875
4.0425
4.0180
3.9956
3.9713
3.5910
3.5800
3.5441
3.5331
1.3961
1.3782
N
O
N
Ph
Ph
O
3i
10
9
8
7
6
5
4
3
2
1
ppm
1.95
0.99
3.01
4.12
6.20
1.00
1.00
1.01
3.03


01-067-021, 13C, 400MHZ, CDCl3
204.09
199.92
151.85
151.48
147.55
147.42
139.92
139.68
137.16
136.95
135.11
135.01
129.27
129.26
128.86
128.77
127.36
127.34
122.66
121.93
42.15
35.24
17.52
Ph
N
O
O
N
Ph
3i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

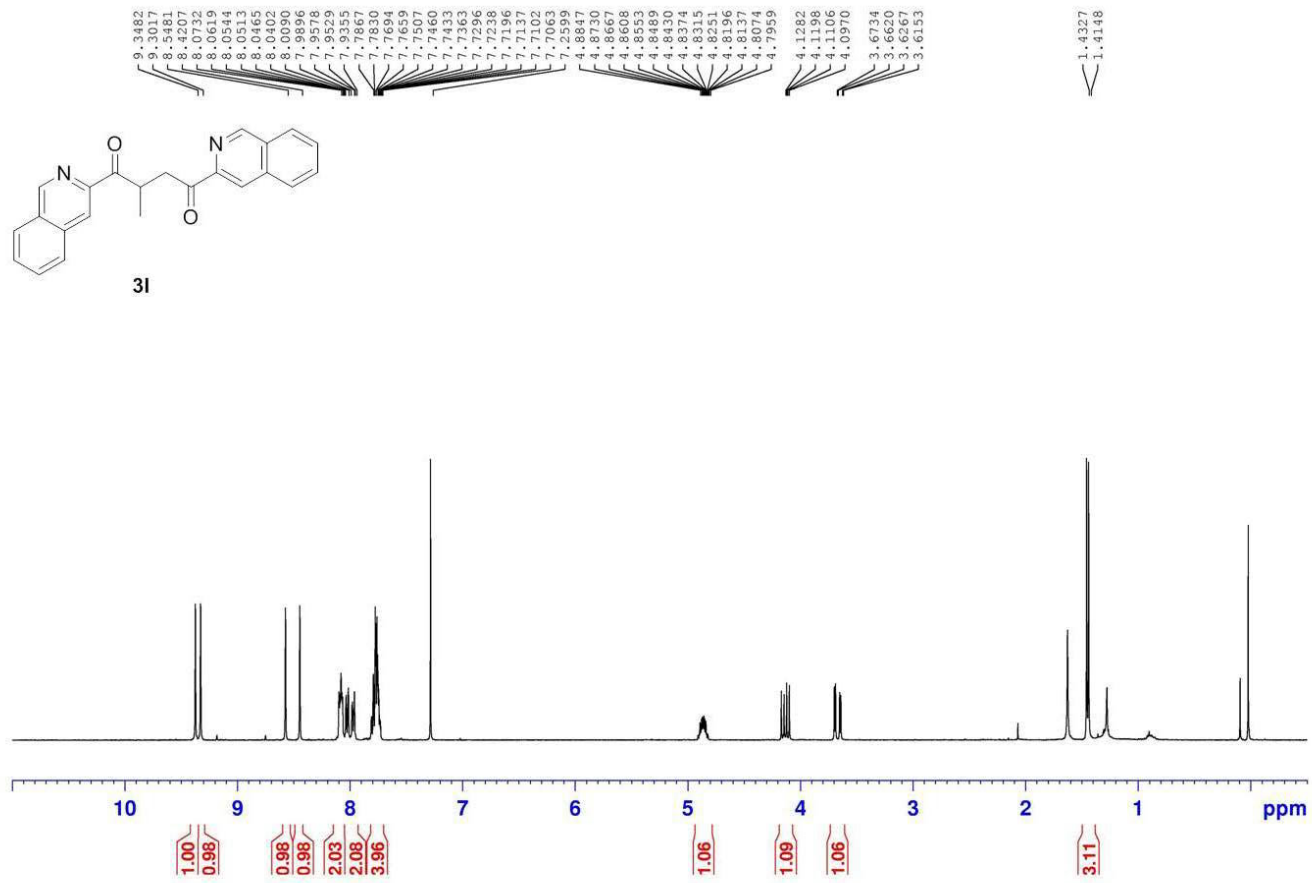

01-067-001,BBFO1-400Hz,1H, cdcl3
8.2877
8.2666
8.2289
8.2223
8.2080
8.2011
8.1885
8.1672
8.0620
8.0407
7.8777
7.8574
7.8373
7.7988
7.7953
7.7818
7.7782
7.7741
7.7658
7.7618
7.7582
7.7447
7.7411
7.6538
7.6519
7.6340
7.6163
7.6145
7.2601
5.0080
4.9956
4.9902
4.9853
4.9777
4.9728
4.9675
4.9550
4.1505
4.1277
4.1040
4.0812
3.8290
3.8166
3.7825
3.7701
1.4717
1.4539
3j
4.96
1.01
2.07
2.00
2.06
1.00
1.01
1.00
2.99
ppm

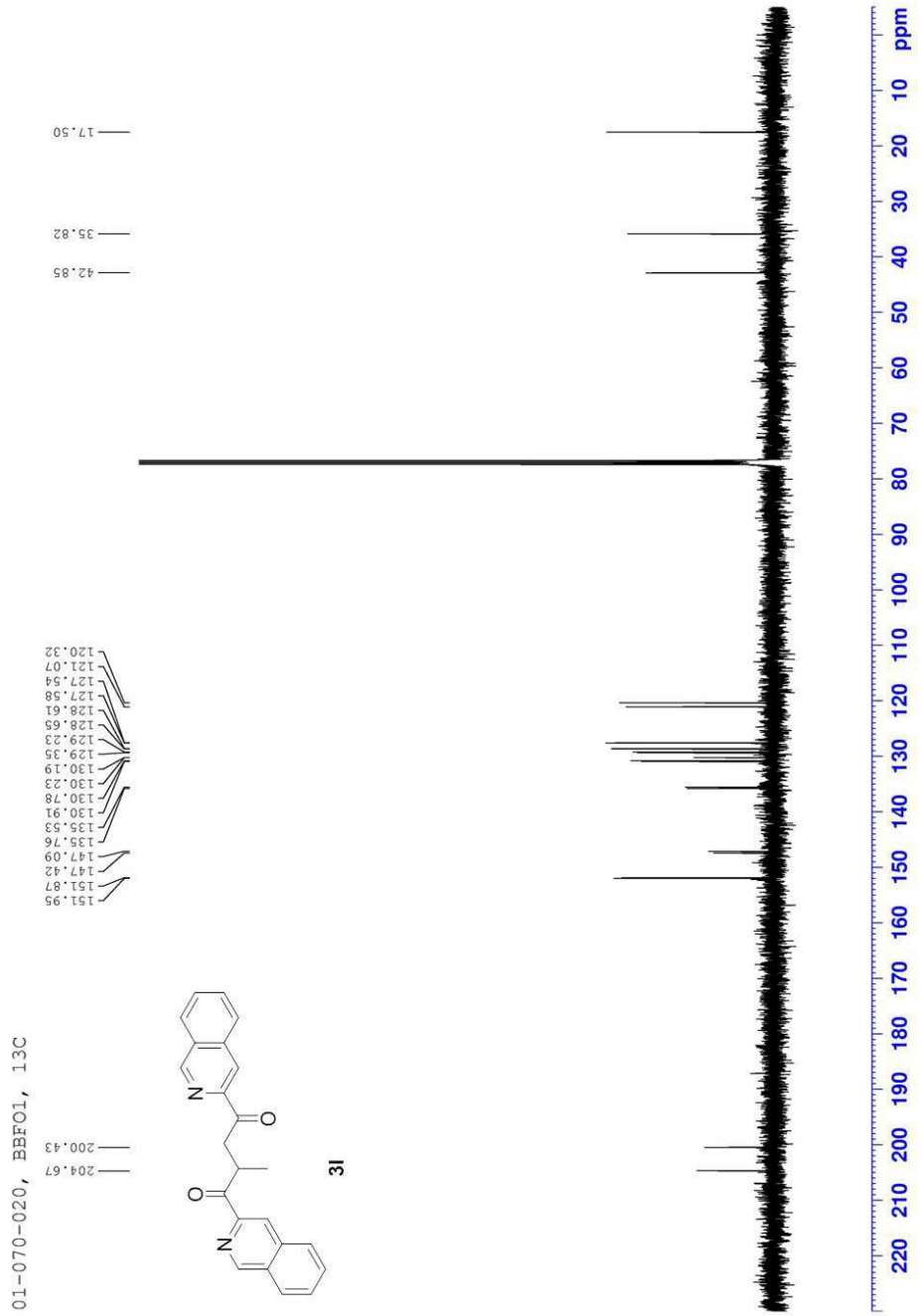

01-067-001,BBFO1-400Hz,13C, cdcl3
3j
17.69
35.34
41.79
118.12
118.83
127.59
127.64
128.39
128.50
129.60
129.64
129.76
129.94
130.61
130.83
136.82
136.84
147.22
147.30
152.40
152.89
200.82
204.91
ppm

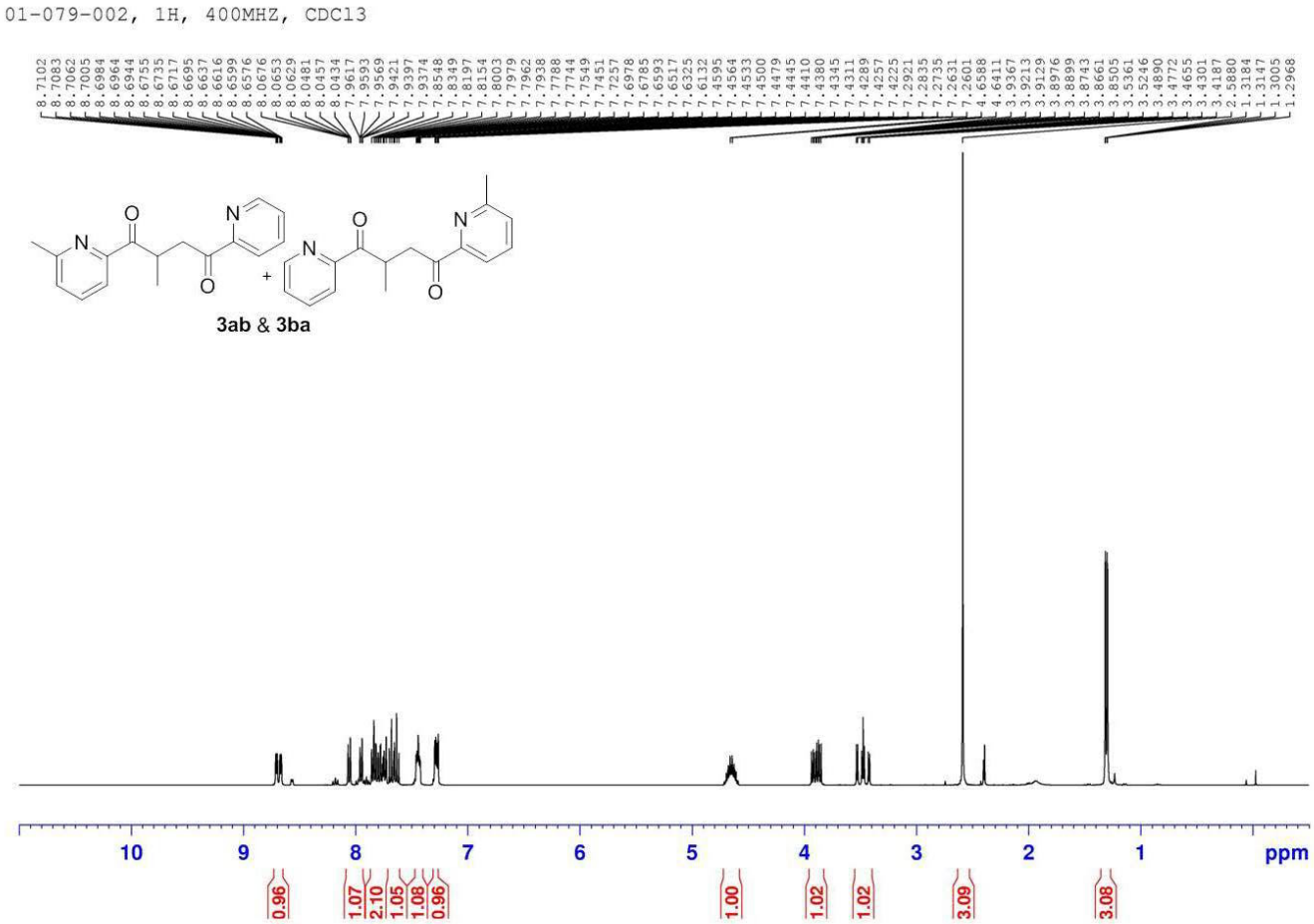

01-070-015-2nd, 1H, Bruker 400 BBFO1, CDC13
8.8250
8.8013
8.7995
8.7766
8.6255
8.6116
8.5907
8.5768
7.8817
7.8618
7.8531
7.8323
7.8126
7.7989
7.7360
7.7332
7.7188
7.7161
7.6991
7.6964
7.6797
7.6598
7.6426
7.6394
7.6082
7.6053
7.5908
7.5871
7.5838
7.5694
7.5665
4.7471
4.7351
4.7293
4.7246
4.7170
4.7124
4.7066
4.6946
4.6643
4.6416
4.6182
3.9956
3.7102
3.6983
3.6642
3.6522
1.4306
1.4126
3k
ppm
1.98
1.91
3.87
3.80
0.98
1.07
1.02
3.59

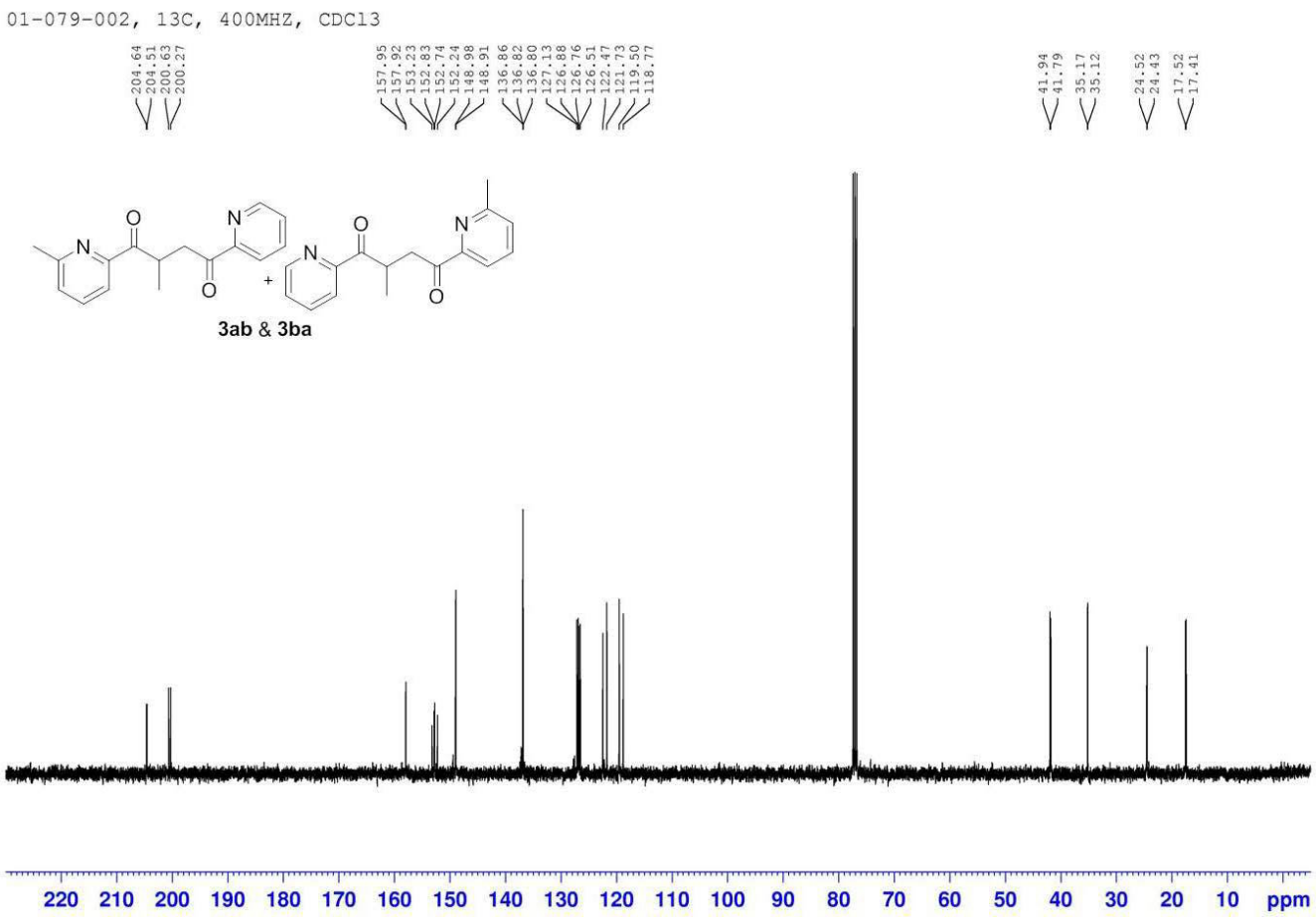

01-070-015-2nd, 13C, Bruker 400 BBFO1, CDCl3
206.66
202.87
153.47
152.81
141.21
141.05
137.04
137.00
130.30
130.26
128.97
128.76
126.99
126.91
126.88
126.84
126.30
125.76
124.50
124.03
44.23
38.58
29.70
17.31
O
N
N
O
3k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

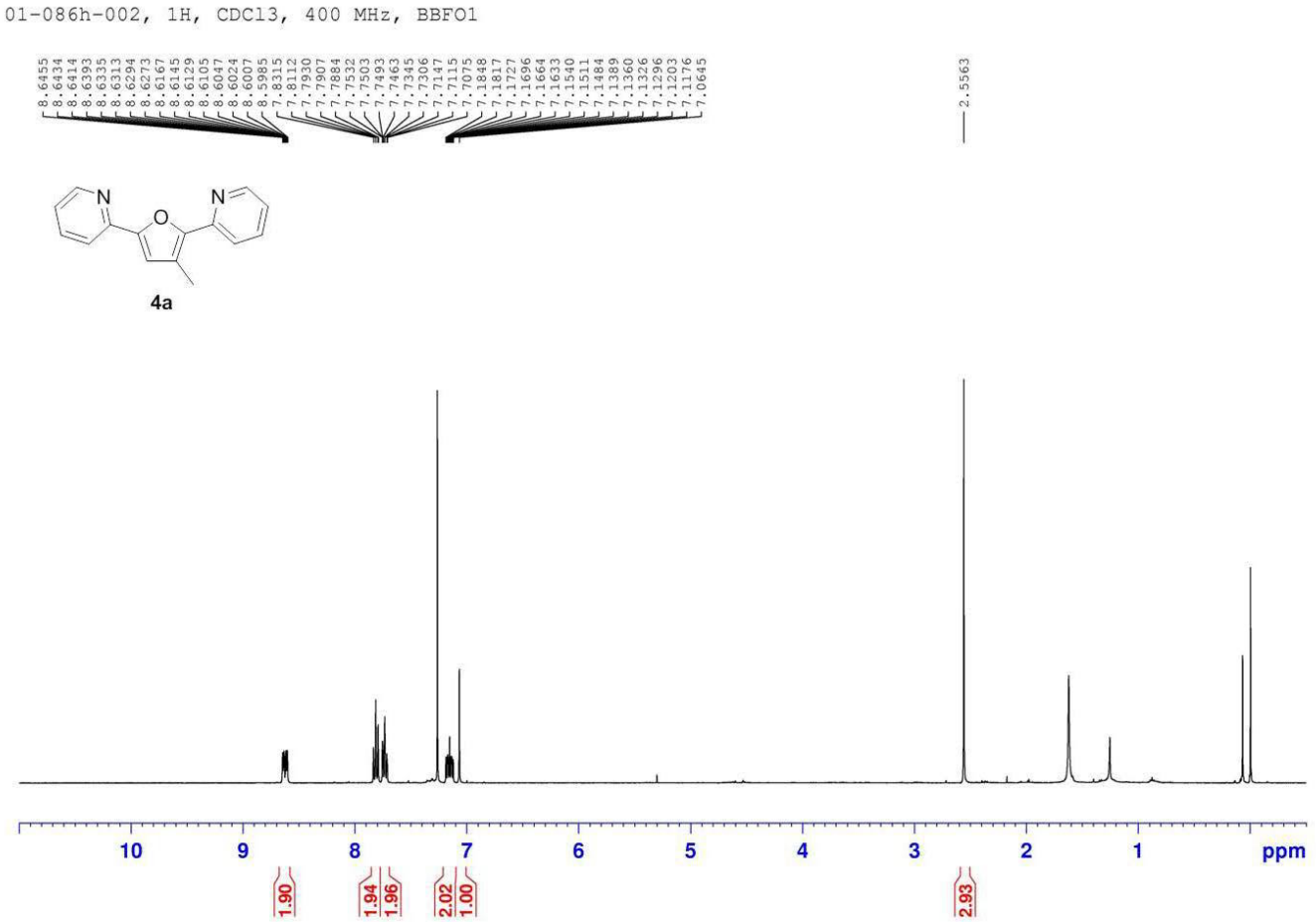
01-070-020, BBFO1, 1H

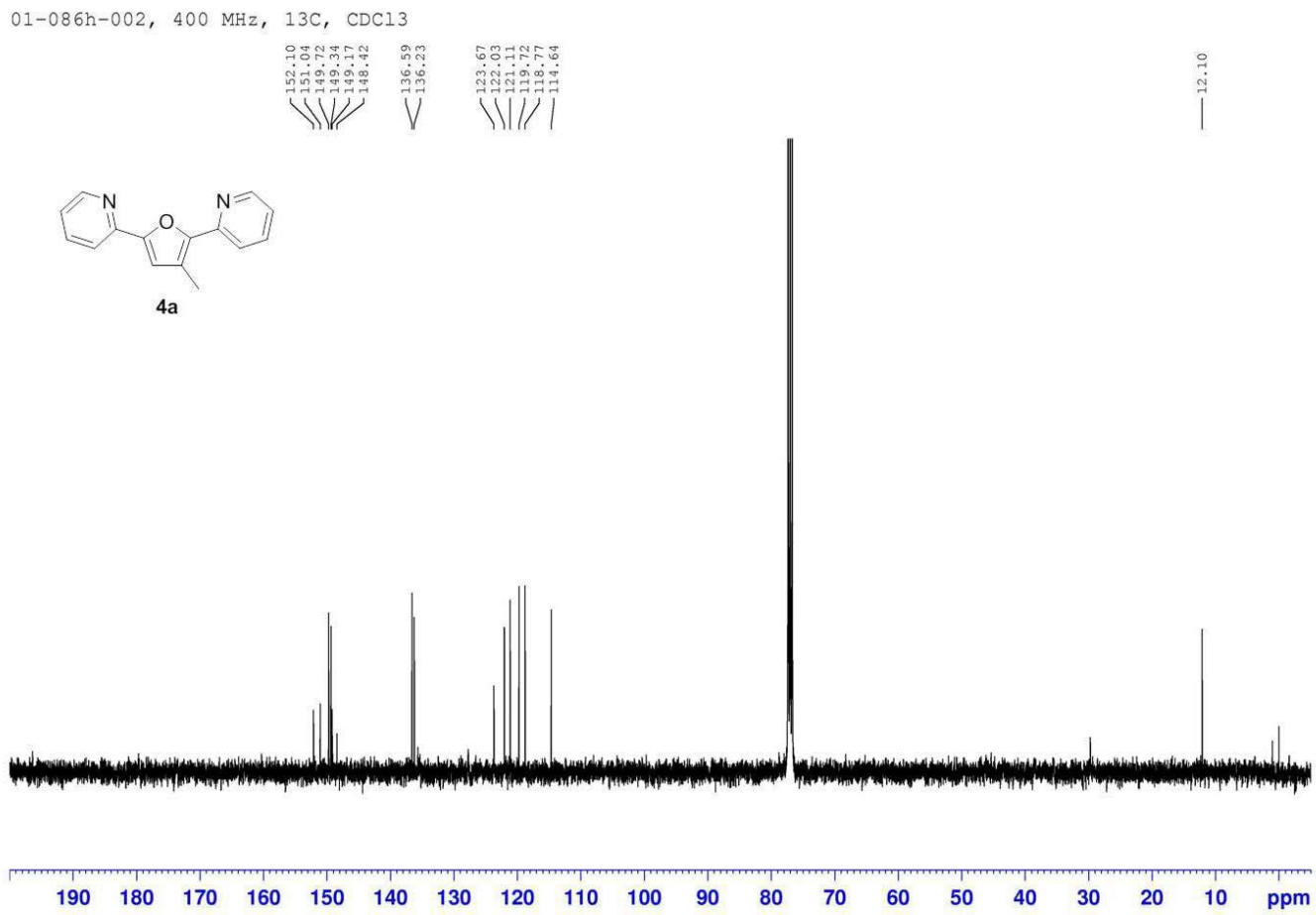


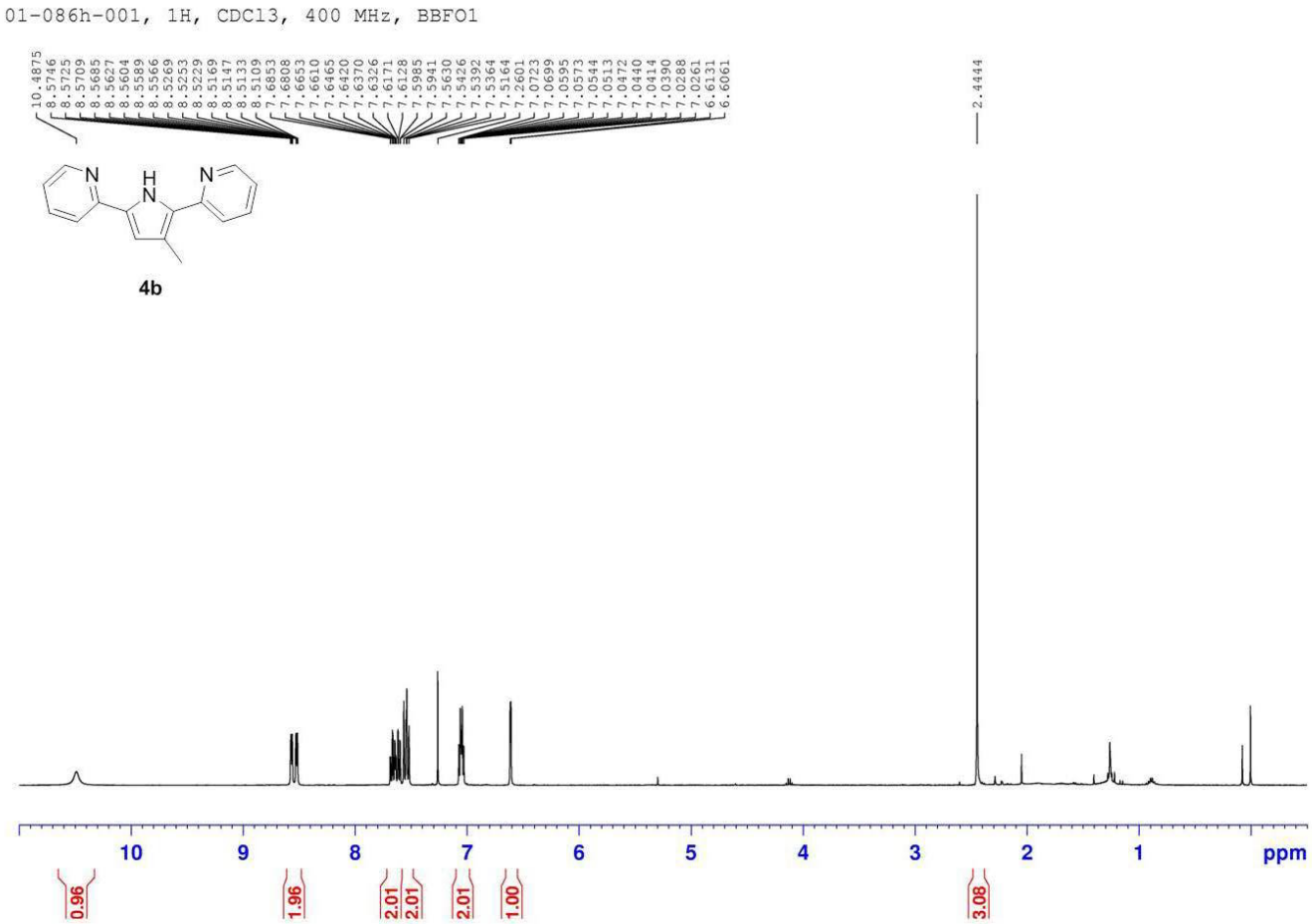

01-070-020, BBFO1, 13C
204.67
200.43
151.95
151.87
147.42
147.09
135.76
135.53
130.91
130.78
130.23
130.19
129.35
129.23
128.65
128.61
127.58
127.54
121.07
120.32
42.85
35.82
17.50
3l
ppm

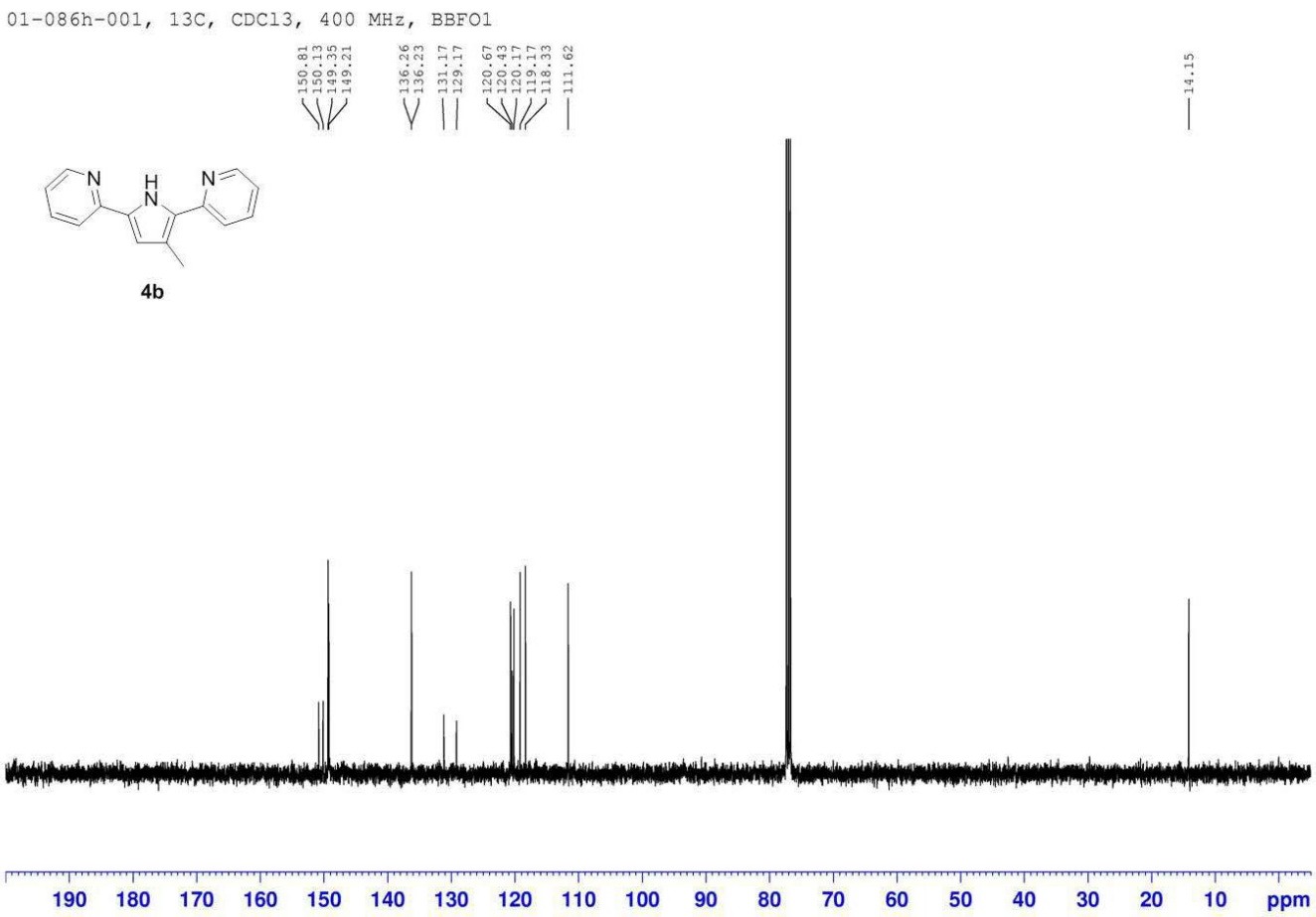

01-079-002, 1H, 400MHZ, CDCl3
3ab & 3ba
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.07
2.10
1.05
1.08
0.96
1.00
1.02
1.02
3.09
3.08

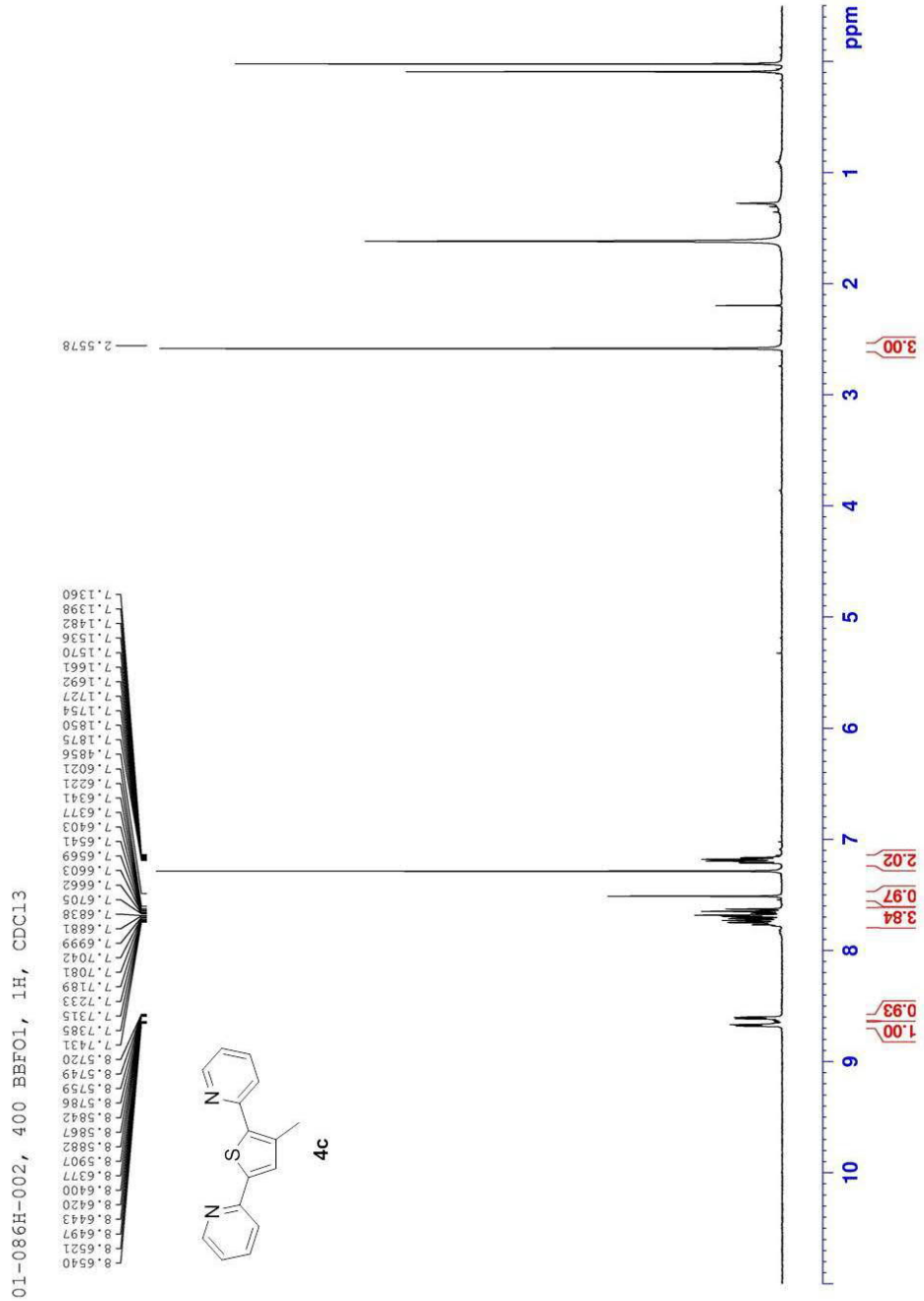

01-079-002, 13C, 400MHZ, CDCl3
204.64
204.51
200.63
200.27
157.95
157.92
153.23
152.83
152.74
152.24
148.98
148.91
136.86
136.82
136.80
127.13
126.88
126.76
126.51
122.47
121.73
119.50
118.77
41.94
41.79
35.17
35.12
24.52
24.43
17.52
17.41
3ab & 3ba
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

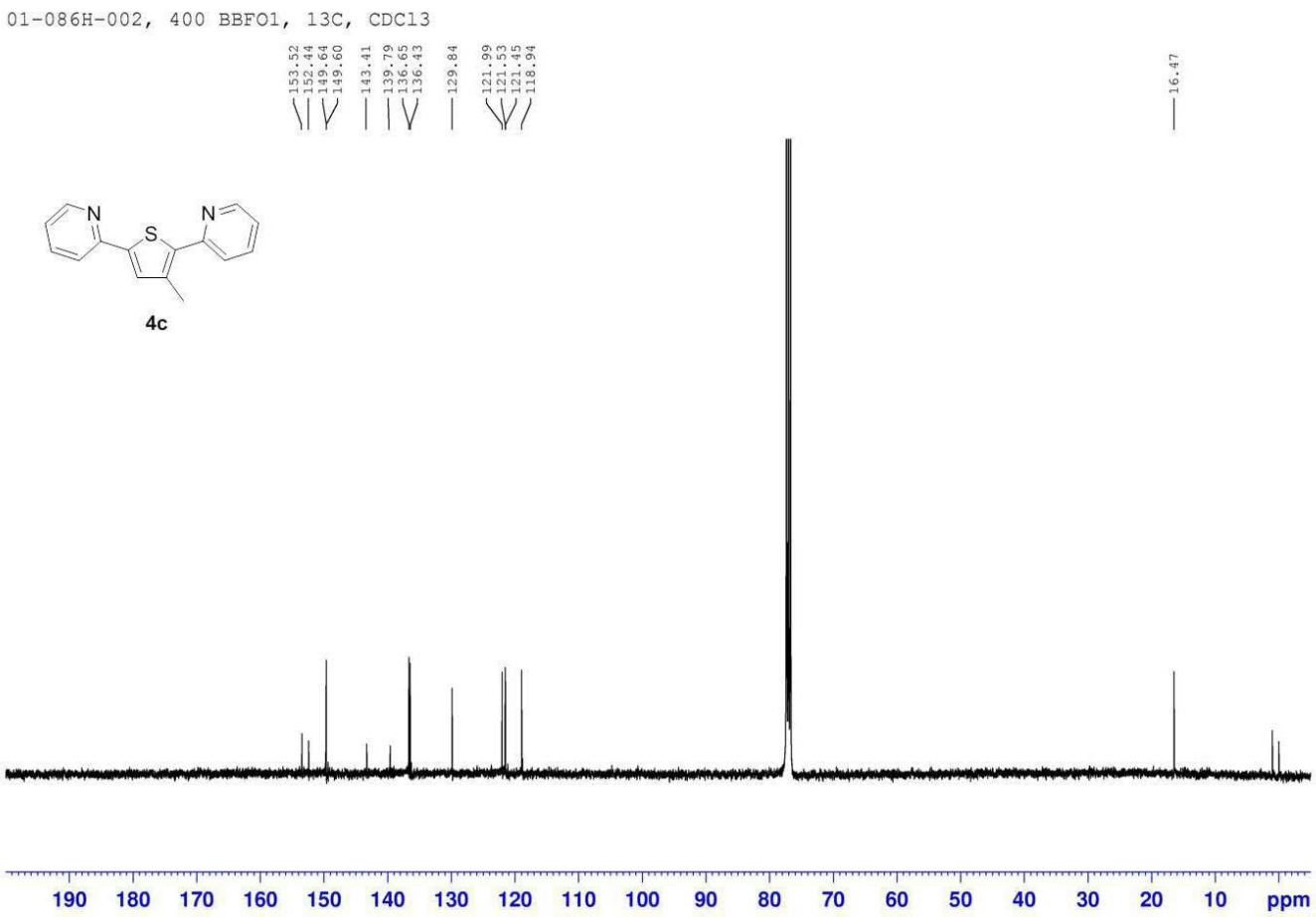

01-086h-002, 1H, CDCl3, 400 MHz, BBFO1
8.6455
8.6434
8.6414
8.6393
8.6335
8.6313
8.6294
8.6273
8.6167
8.6145
8.6129
8.6105
8.6047
8.6024
8.6007
8.5985
7.8315
7.8112
7.7930
7.7907
7.7884
7.7532
7.7503
7.7493
7.7463
7.7345
7.7306
7.7147
7.7115
7.7075
7.1848
7.1817
7.1727
7.1696
7.1664
7.1633
7.1540
7.1511
7.1484
7.1389
7.1360
7.1326
7.1296
7.1203
7.1176
7.0645
2.5563
N
O
N
4a
10
9
8
7
6
5
4
3
2
1
ppm
1.90
1.94
1.96
2.02
1.00
2.93


01-086h-002, 400 MHz, 13C, CDCl3
152.10
151.04
149.72
149.34
149.17
148.42
136.59
136.23
123.67
122.03
121.11
119.72
118.77
114.64
12.10
N
O
N
4a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


01-086h-001, 1H, CDCl3, 400 MHz, BBFO1
10.4875
8.5746
8.5725
8.5709
8.5685
8.5627
8.5604
8.5589
8.5566
8.5269
8.5253
8.5229
8.5169
8.5147
8.5133
8.5109
7.6853
7.6808
7.6653
7.6610
7.6465
7.6420
7.6370
7.6326
7.6171
7.6128
7.5985
7.5941
7.5630
7.5426
7.5392
7.5364
7.5164
7.2601
7.0723
7.0699
7.0595
7.0573
7.0544
7.0513
7.0472
7.0440
7.0414
7.0390
7.0288
7.0261
6.6131
6.6061
2.4444
N
H
N
N
4b
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.96
2.01
2.01
2.01
1.00
3.08


01-086h-001, 13C, CDCl3, 400 MHz, BBFO1
150.81
150.13
149.35
149.21
136.26
136.23
131.17
129.17
120.67
120.43
120.17
119.17
118.33
111.62
14.15
N
H
N
N
4b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


01-086H-002, 400 BBFO1, 1H, CDC13
8.6540
8.6521
8.6497
8.6443
8.6420
8.6400
8.6377
8.5907
8.5882
8.5867
8.5842
8.5786
8.5759
8.5749
8.5720
7.7431
7.7385
7.7315
7.7233
7.7189
7.7081
7.7042
7.6999
7.6881
7.6838
7.6705
7.6662
7.6603
7.6569
7.6541
7.6403
7.6377
7.6341
7.6221
7.6021
7.4856
7.1875
7.1850
7.1754
7.1727
7.1692
7.1661
7.1570
7.1536
7.1482
7.1398
7.1360
2.5578
4c
ppm
1.00
0.93
3.84
0.97
2.02
3.00


01-086H-002, 400 BBFO1, 13C, CDCl3
153.52
152.44
149.64
149.60
143.41
139.79
136.65
136.43
129.84
121.99
121.53
121.45
118.94
16.47
N
S
N
4c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm