Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Regioselective C–H Alkylation and Alkenylation at C5 Position of 2-Amino-1,4-Naphthoquinones with Maleimides Under Rh(III) Catalysis

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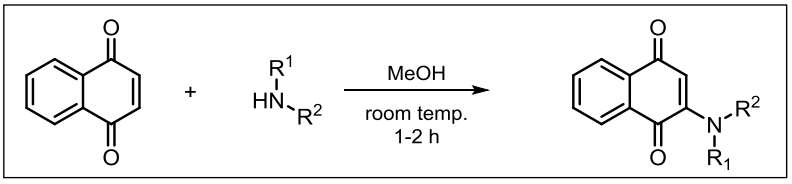
General Information. All the chemicals were purchased from Sigma-Aldrich. All the reactions were carried out under air using the sealed pressure tubes. NMR were recorded on Bruker (500 MHz) spectrometer with $CDCl_3$ or DMSO-d_6 as reference solvent. Chemical shifts of ^{1}H and ^{13}C NMR spectra were reported in parts per million (ppm). Chromatographic separations were performed using neutral aluminium oxide. IR spectra were recorded as KBr pellet on Bruker Alpha FT-IR spectrometer. High-resolution mass spectrometry (HRMS) were recorded on Agilent Q-TOF LC/MS. Melting points were uncorrected and were taken on Buchi M-560.

Synthesis of 2-Amino-1,4-Naphthoquinones (1a-1n, 1p). [1]



General Procedure for preparation of 2-Amino-1,4-naphthoquinones[1]: To a solution of naphthoquinone (5 mmol) in methanol (10 mL) were dropwise added amines (5 mmol) at room temperature. The reaction flask was tightly closed with stopper and the stirring was continued at 25 °C for 1 h. Completion of the reaction was monitored by TLC, the volatiles were removed under reduced pressure. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 4:1) to provide 2-Amino-1,4-naphthoquinones.

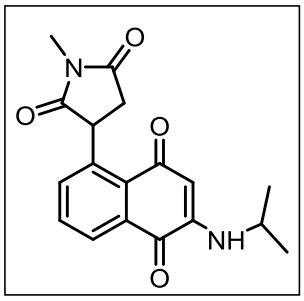
References:

1. M. Wang, C. Zhang, L. P. Sun, C. Ding and A. Zhang, *J. Org. Chem.*, 2014, **79**, 4553.

General procedure for regioselective C–H alkylation and spectral data (3aa-3ja, 3bb-3bf):

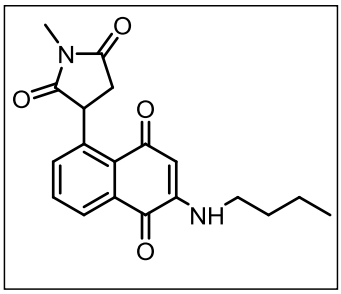
Typical procedure for regioselective C–H alkylation at C5 of 2-amino-1,4-naphthoquinone with N-substituted maleimide: To an oven-dried sealed tube with 2-(isoproylamino) naphthalene-1,4-dione (**1a**) (43 mg, 0.2 mmol, 100 mol %), *N*-Methylmaleimide (**2a**) (26.6 mg, 0.24 mmol, 120 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %) and AcOH (24.0 mg, 0.4 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 ºC for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 1:1) to provide **3aa** (59 mg) in 90% yield.

3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3aa):



59 mg (90 %); Orange solid; mp = 161.7–162.6 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.04 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.73–7.67 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.63 (s, 1H), 4.37 (bs, 1H), 3.68–3.59 (m, 1H), 3.00 (bs, 1H), 2.19 (s, 3H), 2.56 (dd, *J* = 17.0, 6.0 Hz, 1H), 1.19 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.4, 181.6, 177.3, 176.4, 146.5, 140.7, 136.6, 132.4, 131.9, 129.7, 126.9, 100.9, 47.1, 43.5, 36.6, 24.4, 21.1, 21.1; IR (KBr) υ 3336, 3064, 2970, 1761, 1691, 1607, 1565, 1506, 1438, 1347, 1280, 1234, 1162, 1114, 1033, 959, 870, 777, 674 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{19}N_2O_4$ $[M+H]^+$ 327.1339, found 327.1386.

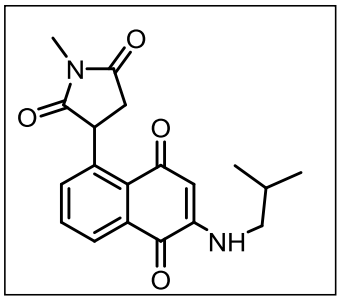
3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ba):



61 mg (89%); Orange solid; mp = 198.7–199.6 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.04 (d, *J* = 7.0 Hz, 1H), 7.72–7.67 (m, 2H), 7.57 (t, *J* = 6.5 Hz, 1H), 5.60 (s, 1H), 4.35 (bs, 1H) , 3.13 (q, *J* = 7.0 Hz, 2H), 3.00 (bs, 1H), 2.91 (s, 3H), 2.56 (dd, *J* = 17.0, 6.0 Hz, 1H), 1.54 (quint, *J* = 7.0, 2H), 1.31 (sextet, *J* = 7.5 Hz, 2H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.2, 181.5, 177.3, 176.5, 147.6, 140.9, 136.6, 132.4, 131.9, 129.8, 126.9, 100.5, 47.2, 41.5, 36.6, 29.4, 24.4,

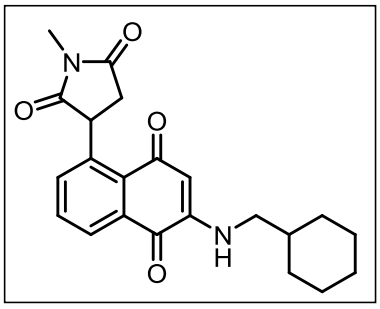
19.7, 13.7; IR (KBr) υ 3343, 2951, 2867, 1762, 1690, 1614, 1568, 1509, 1443, 1342, 1250, 1113, 1008, 958, 861, 778, 692 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{19}H_{21}N_2O_4$ $[M+H]^+$ 341.1496, found 341.1500.

3-(6-(Isobutylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ca):



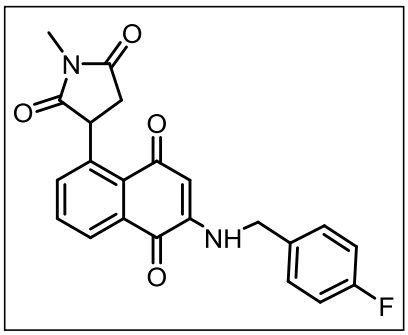
65 mg (96%); Yellow solid; mp = 217.0–218.3 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.05 (d, *J* = 7.0 Hz, 1H), 7.73–7.67 (m, 2H), 7.62 (t, *J* = 6.5 Hz, 1H), 5.62 (s, 1H), 4.35 (bs, 1H), 3.01 (bs, 1H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.91 (s, 3H), 2.56 (dd, *J* = 17.0, 6.0 Hz, 1H), 1.94 (septet, *J* = 6.5 Hz, 1H), 0.88 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.3, 181.5, 177.3, 176.5, 147.8, 140.9, 136.5, 132.4, 131.9, 129.7, 127.0, 100.7, 49.2, 47.1, 36.6, 26.8, 24.4, 20.1; IR (KBr) υ 3308, 2961, 2867, 1763, 1683, 1611, 1568, 1512, 1436, 1346, 1280, 1237, 1168, 1110, 1013, 955, 838, 772, 681 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{19}H_{21}N_2O_4$ $[M+H]^+$ 341.1496, found 341.1518.

3-(6-((Cyclohexylmethyl)amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1methylpyrrolidine-2,5-dione (3da):



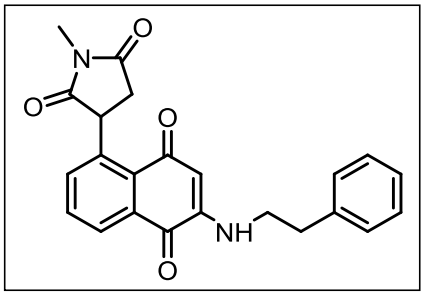
72 mg (94%); Yellow solid; mp = 207.0–208.6 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.05 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.73–7.67 (m, 2H), 7.63 (t, *J* = 6.5 Hz, 1H), 5.60 (s, 1H), 4.32 (bs, 1H), 3.04–2.97 (m, 3H), 2.91 (s, 3H), 2.55 (dd, *J* = 17.0, 6.0 Hz, 1H), 1.69–1.60 (m, 6H), 1.18–1.09 (m, 3H), 0.94–0.86 (m, 2H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.2, 181.5, 177.3, 176.5, 147.8, 140.9, 136.4, 132.4, 131.9, 129.7, 127.0, 100.6, 47.9, 47.2, 36.6, 36.1, 30.4, 26.0, 25.3, 24.4.; IR (KBr) υ 3365, 2923, 2851, 1764, 1687, 1610, 1567, 1501, 1438, 1339, 1243, 1113, 1050, 1003, 957, 863, 884, 779, 690 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{22}H_{25}N_2O_4$ $[M+H]^+$ 381.1809, found 381.1822.

3-(6-((4-Fluorobenzyl) amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ea):



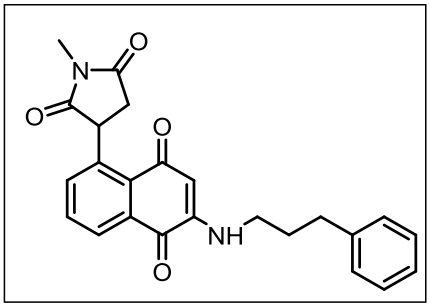
59 mg (75%); Yellow solid; mp = 228.0–230.0 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.19 (t, *J* = 6.5 Hz, 1H), 8.07–8.05 (m, 1H), 7.74–7.68 (m, 2H), 7.38 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 5.52 (s, 1H), 4.43–4.24 (m, 3H), 2.97 (bs, 1H), 2.88 (s, 3H), 2.52 (dd, *J* = 17.0, 6.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.4, 181.5, 177.2, 176.4, 161.3 (d, J_{C-F} = 241.2 Hz), 147.4, 140.8, 136.6, 133.6 (d, J_{C-F} = 3.1 Hz), 132.4, 132.1, 129.5, 129.1 (d, J_{C-F} = 8.0 Hz), 126.9, 115.2 (d, J_{C-F} = 21.2 Hz), 101.7, 47.1, 44.2, 36.5, 24.4; IR (KBr) υ 3390, 2869, 1785, 1695, 1621, 1577, 1438, 1385, 1277, 1236, 1119, 1067, 1008, 967, 879, 866, 775, 687, 665 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{22}H_{18}FN_2O_4$ $[M+H]^+$ 393.1245, found 393.1252.

3-(5,8-Dioxo-6-(phenethylamino)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3fa):



62 mg (80%); Orange solid; mp = 172.2–173.6 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.05 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.73–7.68 (m, 2H), 7.51 (t, *J* = 6.0 Hz, 1H), 7.30–7.26 (m, 4H), 7.22–7.18 (m, 1H), 5.67 (s, 1H), 4.37 (bs, 1H), 3.41–3.37 (m, 2H), 3.00 (bs, 1H), 2.91 (s, 3H), 2.87 (t, *J* = 7.0, 2H), 2.56 (dd, *J* = 17.0, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.4, 181.5, 177.3, 176.5, 147.3, 140.8, 138.9, 136.6, 132.3, 132.0, 129.7, 128.7, 128.4, 126.9, 126.2, 100.9, 47.3, 43.2, 36.6, 33.3, 24.4; IR (KBr) υ 3357, 2907, 1765, 1694, 1611, 1567, 1508, 1432, 1342, 1275, 1233, 1112, 1012, 953, 844, 770, 709, 680 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{23}H_{21}N_2O_4$ $[M+H]^+$ 389.1496, found 389.1512.

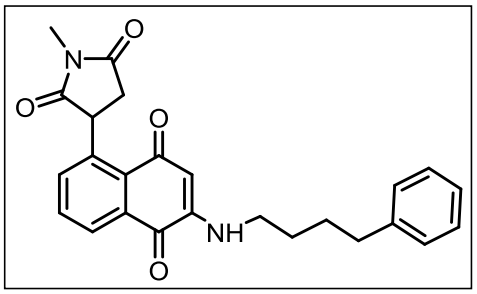
3-(5,8-Dioxo-6-((3-phenylpropyl) amino)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ga):



62 mg (78%); Orange solid; mp = 154.1–156.8 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.05 (d, *J* = 7.0 Hz, 1H), 7.73–7.67 (m, 2H), 7.62 (t, *J* = 6.0 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 6.5 Hz, 2H), 7.16 (t, *J* = 7.0 Hz, 1H), 5.59 (s,

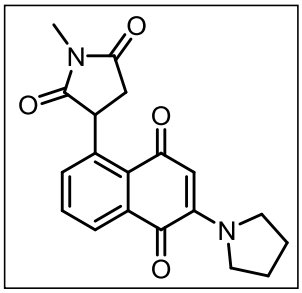
1H), 4.43 (bs, 1H), 3.16 (q, *J* = 6.5 Hz, 2H), 3.00 (bs, 1H), 2.91 (s, 3H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.54 (dd, *J* = 17.5, 6.5 Hz, 1H), 1.85 (quint, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.3, 181.5, 177.3, 176.5, 147.6, 141.5, 140.9, 136.6, 132.4, 131.9, 129.7, 128.3, 126.9, 125.8, 100.6, 47.1, 41.5, 36.6, 32.6, 29.2, 24.4; IR (KBr) υ 3323, 2923, 2860, 1689, 1615, 1566, 1512, 1436, 1341, 1243, 1113, 1041, 957, 837, 775, 689 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{24}H_{23}N_2O_4$ $[M+H]^+$ 403.1652, found 403.1658.

3-(5,8-Dioxo-6-((4-phenylbutyl)amino)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ha):



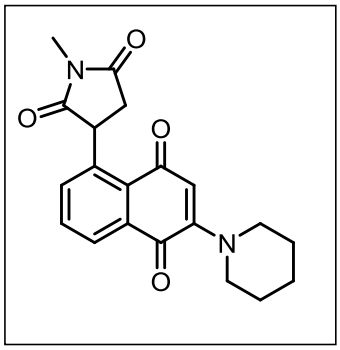
25 mg (30%); Yellow solid; mp = 136.3–137.0 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.04 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.72–7.67 (m, 2H), 7.58 (t, *J* = 6.0 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 6.5 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 5.62 (s, 1H), 4.36 (bs, 1H), 3.17 (q, *J* = 6.0 Hz, 2H), 3.01 (bs, 1H), 2.91 (s, 3H), 2.59 (t, *J* = 6.5 Hz, 2H), 2.55 (dd, *J* = 17.0, 6.0 Hz, 1H), 1.63–1.53 (m, 4H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.2, 181.5, 177.3, 176.4, 147.5, 142.0, 140.9, 136.6, 132.4, 131.9, 129.7, 128.3, 128.2, 126.9, 125.6, 100.5, 47.0, 41.6, 36.6, 34.7, 28.4, 26.9, 24.4; IR (KBr) υ 3293, 3026, 2942, 2904, 1766, 1698, 1612, 1571, 1518, 1441, 1377, 1350, 1286, 1249, 1036, 1001, 956, 841, 788, 752, 691 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{25}H_{25}N_2O_4$ $[M+H]^+$ 417.1809, found 417.1814.

3-(5,8-Dioxo-6-(pyrrolidin-1-yl)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ia):



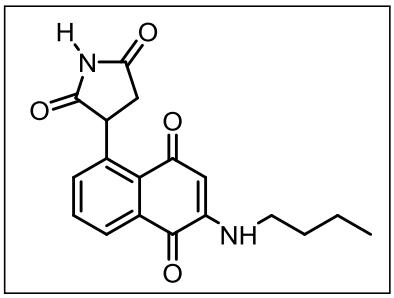
54 mg (80 %); Red solid; mp = 207.9–208.2 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.00–7.98 (m, 1H), 7.72–7.66 (m, 2H), 5.56 (s, 1H), 4.35 (bs, 1H), 3.85 (bs, 2H), 3.28 (bs, 2H), 3.01 (bs, 1H), 2.91 (s, 3H), 2.54 (dd, *J* = 17.5, 6.5 Hz, 1H), 1.91–1.86 (m, 4H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 182.6, 182.4, 177.3, 176.5, 148.4, 140.0, 136.0, 133.6, 131.7, 129.4, 127.1, 104.4, 50.8, 50.1, 46.9, 36.7, 26.1, 24.4, 23.5; IR (KBr) υ 2972, 2934, 1761, 1689, 1610, 1561, 1431, 1267, 1118, 1026, 955, 762, 684 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{19}H_{19}N_2O_4$ $[M+H]^+$ 339.1339, found 339.1359.

3-(5,8-Dioxo-6-(piperidin-1-yl)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ja):



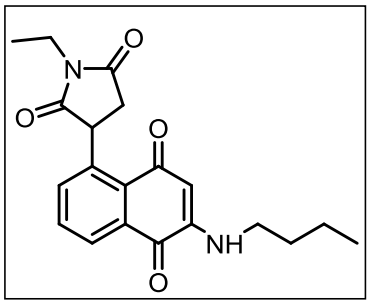
53 mg (75%); Red solid; mp = 148.2–150.0 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 7.94 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.71–7.66 (m, 2H), 5.91 (s, 1H), 4.40 (bs, 1H), 3.45 (s, 4H), 3.02 (bs, 1H), 2.91 (s, 3H), 2.55 (dd, *J* = 17.5, 6.0 Hz, 1H), 1.61 (s, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.7, 183.0, 177.3, 176.4, 153.0, 139.5, 136.1, 134.9, 132.2, 128.8, 127.3, 108.9, 49.4, 46.7, 36.5, 25.4, 24.4, 23.8; IR (KBr) υ 2948, 2842, 1767, 1686, 1615, 1561, 1431, 1377, 1334, 1275, 1235, 1114, 1040, 997, 951, 848, 775, 686 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{20}H_{21}N_2O_4$ $[M+H]^+$ 353.1496, found 353.1509.

3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)pyrrolidine-2,5-dione (3bb):



50 mg (76%); Orange solid; mp = 190.0–192.0 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 11.06 (s, 1H), 8.04–8.01 (m, 1H), 7.69–7.66 (m, 2H), 7.54 (t, *J* = 6.0 Hz, 1H), 5.59 (s, 1H), 4.36 (bs, 1H), 3.14 (q, *J* = 7.0 Hz, 2H), 2.91 (bs, 1H), 2.58 (dd, *J* = 17.0, 6.5 Hz, 1H), 1.54 (quint, *J* = 7.0 Hz, 2H), 1.32 (sextet, *J* = 7.5 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d6) δ 183.2, 181.6, 178.5, 177.8, 147.5, 140.8, 136.7, 132.4, 131.9, 129.8, 126.8, 100.5, 48.7, 41.5, 37.8, 29.4, 19.7, 13.7; IR (KBr) υ 3346, 3146, 2976, 2891, 1770, 1699, 1609, 1558, 1510, 1459, 1378, 1339, 1251, 1165, 1073, 954, 779, 677 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{19}N_2O_4$ $[M+H]^+$ 327.1339, found 327.1339.

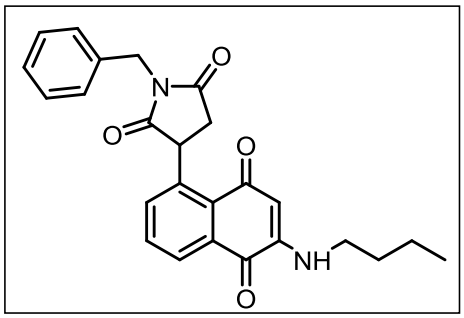
3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-ethylpyrrolidine-2,5-dione (3bc):



64 mg (90%); Red solid; mp = 182.0–183.4 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.05–8.03 (m, 1H), 7.71–7.66 (m, 2H), 7.54 (t, *J* = 6.0 Hz, 1H), 5.59 (s, 1H), 4.34 (bs, 1H), 3.52–3.44 (m, 2H), 3.13 (q, *J* = 6.5 Hz, 2H), 2.97 (bs, 1H), 2.56 (dd, *J* = 17.0, 6.0 Hz, 1H), 1.52 (quint, *J* = 7.5 Hz, 2H), 1.31 (sextet, *J* = 7.5 Hz, 2H),

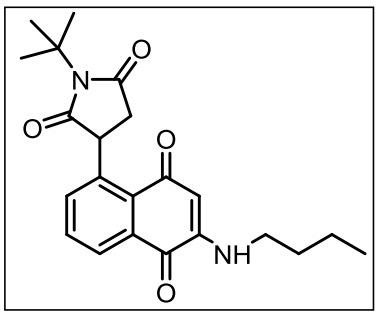
1.15 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.1, 181.5, 176.9, 176.1, 147.5, 141.0, 136.5, 132.4, 131.9, 129.7, 126.9, 100.5, 47.2, 41.5, 36.5, 33.0, 29.5, 19.7, 13.7, 12.8; IR (KBr) υ 3321, 2976, 2891, 1768, 1687, 1607, 1564, 1515, 1454, 1389, 1341, 1249, 1125, 1070, 954, 848, 786, 679 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{20}H_{23}N_2O_4$ $[M+H]^+$ 355.1652, found 355.1674.

1-Benzyl-3-(6-(butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)pyrrolidine-2,5-dione (3bd):



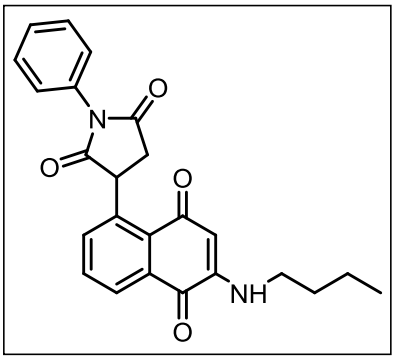
66 mg (79%); Orange solid; mp = 166.0–167.1 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06–8.04 (m, 1H), 7.73–7.67 (m, 2H), 7.59 (t, *J* = 6.0 Hz, 1H), 7.37–7.32 (m, 4H), 7.29–7.25 (m, 1H), 5.61 (s, 1H), 4.71 (d, *J* = 15.0 Hz, 1H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.49 (bs, 1H), 3.15 (q, *J* = 7.0 Hz, 2H), 3.07 (bs, 1H), 2.66 (dd, *J* = 17.5, 6.5 Hz, 1H), 1.54 (quint, *J* = 7.5 Hz, 2H), 1.32 (sextet, *J* = 7.5 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.2, 181.5, 176.9, 176.2, 147.6, 140.9, 136.6, 136.3, 132.4, 131.9, 129.8, 128.4, 127.5, 127.2, 127.0, 100.5, 47.3, 41.5, 41.4, 36.5, 29.4, 19.7, 13.7; IR (KBr) υ 3324, 2935, 2872, 1771, 1700, 1514, 1443, 1399, 1353, 1243, 1169, 997, 839, 777, 733, 687, 645 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{25}H_{25}N_2O_4$ $[M+H]^+$ 417.1809, found 417.1820.

1-(tert-butyl)-3-(6-(butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)pyrrolidine-2,5-dione (3be):



23 mg (30%); Orange solid; mp = 139.3–140.1 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.02 (t, *J* = 4.5 Hz, 1H), 7.70–7.64 (m, 2H), 7.50 (t, *J* = 6.0 Hz, 1H), 5.58 (s, 1H), 4.22 (bs, 1H), 3.14 (q, *J* = 7.0 Hz, 2H), 2.86 (bs, 1H), 2.46 (dd, *J* = 17.0, 6.5 Hz, 1H), 1.56 (s, 9H), 1.52 (quint, *J* = 7.5 Hz, 2H), 1.31 (sextet, *J* = 7.5 Hz, 2H), 0.88 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d6) δ 183.0, 181.6, 177.9, 177.1, 147.4, 140.9, 137.2, 132.4, 131.8, 129.6, 126.8, 100.6, 56.8, 47.1, 41.5, 36.6, 29.5, 28.1, 19.7, 13.7; IR (KBr) υ 3337, 2960, , 2873, 1769, 1697, 1624, 1571, 1521, 1456, 1352, 1257, 1213, 1160, 1119, 990, 777, 684 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{22}H_{27}N_2O_4$ $[M+H]^+$ 383.1965, found 383.1976.

3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-phenylpyrrolidine-2,5-dione (3bf):

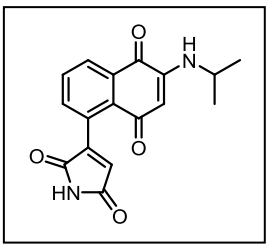


55 mg (69%); Yellow solid; mp = 190.4–191.0 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.08–8.07 (m, 1H), 7.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.72 (t, *J* = 7.5, Hz, 1H), 7.61 (t, *J* = 6.0, Hz, 1H), 7.53 (t, *J* = 7.5, Hz, 2H), 7.43 (t, *J* = 7.5, Hz, 1H), 7.40–7.38 (m, 2H), 5.67 (s, 1H), 4.56 (bs, 1H), 3.17–3.14 (m, 3H), 2.76 (dd, *J* = 17.5, 6.5 Hz, 1H), 1.54 (quint, *J* = 7.0 Hz, 2H), 1.32 (sextet, *J* = 7.5 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.3, 181.5, 176.2, 175.6, 147.7, 141.0, 136.3, 133.3, 132.5, 132.0, 129.7, 128.8, 128.1, 127.4, 127.1, 100.5, 47.3, 41.6, 36.7, 29.5, 19.7, 13.7; IR (KBr) υ 3293, 2977, 2896, 1774, 1700, 1605, 1563, 1499, 1385, 1345, 1246, 1164, 1068, 954, 961, 882, 828, 755, 692 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{24}H_{23}N_2O_4$ $[M+H]^+$ 403.1652, found 403.1658.

General procedure for regioselective C–H alkenylation and spectral data (4ab-4lb, 4aa-4af):

Typical procedure for regioselective C–H alkenylation at C5 of 2-amino-1,4-naphthoquinone with *N*-substituted maleimide: To an oven-dried sealed tube with 2-(isopropylamino)naphthalene-1,4-dione (**1a**) (43 mg, 0.2 mmol, 100 mol %), *N*-Methylmaleimide (**2a**) (33.3 mg, 0.3 mmol, 150 mol %), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and Ag_2CO_3 (110.3 mg, 0.4 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 ºC for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 5:1 to 1:10) provide **4aa** (43 mg) in 66% yield.

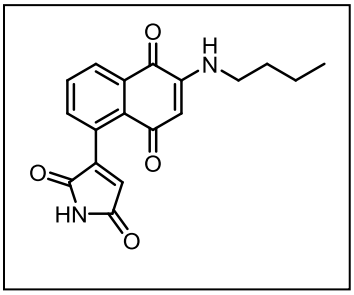
3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ab);



46 mg (74%); Orange solid; mp = 182.1–184.4 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 10.93 (s, 1H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 5.63 (s, 1H), 3.72–3.65 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.5, 181.1, 172.3, 170.5, 150.8, 148.2, 136.7,

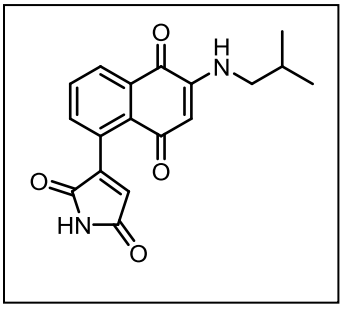
131.9, 131.7, 131.1, 128.8, 128.0, 124.3, 99.8, 49.3, 26.8, 20.2; IR (KBr) υ 3431, 3336, 3018, 2929, 2751, 1724, 1604, 1527, 1349, 1239, 1166, 1065, 890, 772 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{17}H_{15}N_2O_4$ $[M+H]^+$ 311.1026, found 311.1036.

3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4bb)



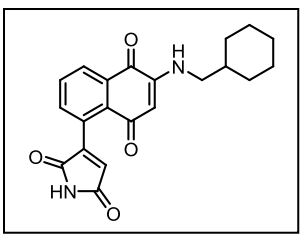
39 mg (60%); Orange solid; mp = 230.4–232.6 ^oC; ^1H NMR (500 MHz, DMSO–d_6) δ 10.92 (s, 1H), 8.13 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.65 (t, *J* = 6.0 Hz, 1H), 6.66 (s, 1H), 5.59 (s, 1H), 3.17 (q, *J* = 7.0 Hz, 2H), 1.55 (quint, *J* = 7.5 Hz, 2H), 1.33 (sextet, *J* = 7.5 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.4, 181.1, 172.3, 170.4, 150.8, 148.0, 136.6, 131.9, 131.7, 131.1, 128.8, 127.9, 124.3, 99.6, 41.6, 29.4, 19.7, 13.7; IR (KBr) υ 3440, 3360, 3150, 3049, 2926, 2742, 1731, 1663, 1609, 1557, 1520, 1343, 1238, 839, 767 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{17}N_2O_4$ $[M+H]^+$ 325.1183, found 325.1183.

3-(6-(Isobutylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4cb):



41 mg (63%); Orange solid; mp = 262.6–264.3 ^oC; ^1H NMR (500 MHz, DMSO–d_6) δ 10.92 (s, 1H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.72–7.68 (m, 2H), 6.67 (s, 1H), 5.61 (s, 1H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.01–1.93 (m, 1H), 0.90 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.9, 181.5, 172.7, 170.9, 151.2, 148.6, 137.1, 132.2, 132.3, 131.5, 129.2, 128.4, 124.8, 100.29, 49.7, 27.2, 20.6; IR (KBr) υ 3432, 3356, 3158, 3062, 2925, 2861, 2731, 1724, 1683, 1607, 1558, 1521, 1460, 1348, 1251, 1171, 1062, 979, 861, 771 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{17}N_2O_4$ $[M+H]^+$ 325.1183, found 325.1196.

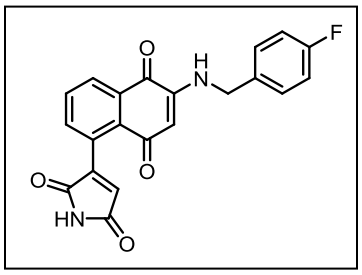
3-(6-((Cyclohexylmethyl)amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4db):



45 mg (62%); Red solid; mp = 228.0–230.2 ^oC; ^1H NMR (500 MHz, DMSO–d_6) δ 10.91 (s, 1H), 8.13 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.5 Hz, 2H), 6.66 (s, 1H), 5.59 (s, 1H),

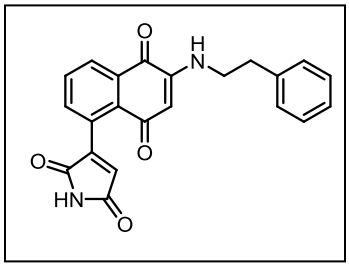
3.02 (t, *J* = 6.5 Hz, 2H), 1.71–1.59 (m, 6H), 1.22–1.11 (m, 3H), 0.94 (t, *J* = 12.0 Hz, 2H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.4, 181.1, 142.3, 170.5, 150.8, 148.2, 136.6, 135.3, 131.9, 131.1, 128.8, 128.0, 124.3, 99.8, 48.0, 36.1, 30.5, 26.0, 25.4; IR (KBr) υ 3413, 3281, 3145, 2925, 2854, 2747, 1724, 1681, 1600, 1556, 1457, 1332, 1250, 1183, 1132, 1057, 966, 882, 777 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{21}H_{21}N_2O_4$ $[M+H]^+$ 365.1496, found 365.1496.

3-(6-((4-Fluorobenzyl)amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4eb)



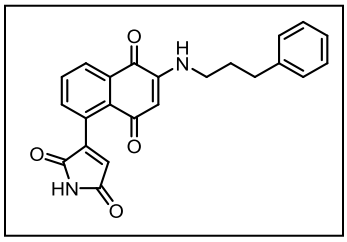
34 mg (47%); Light brown solid; mp = 291.7–292.5 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 10.91 (s, 1H), 8.29 (t, *J* = 6.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.40 (dd, *J* = 9.0, 1.0 Hz, 2H), 7.17 (t, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 1.5 Hz, 1H), 5.52 (s, 1H), 4.42 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.7, 181.1, 172.2, 170.4, 161.3 (d, J_{C-F} = 241.2 Hz), 150.7, 147.8, 136.7, 133.5 (d, J_{C-F} = 2.7 Hz), 132.1, 131.5, 131.2, 129.2 (d, J_{C-F} = 8.1 Hz), 128.8, 128.0, 124.5, 115.3 (d, J_{C-F} = 21.1 Hz), 100.9, 44.3; IR (KBr) υ 3442, 3270, 3069, 2924, 2860, 1713, 1610, 1513, 1415, 1344, 1234, 1168, 1105, 908, 836, 765 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{21}H_{14}FN_2O_4$ $[M+H]^+$ 377.0932, found 377.0926.

3-(5,8-Dioxo-6-(phenethylamino)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione(4fb)



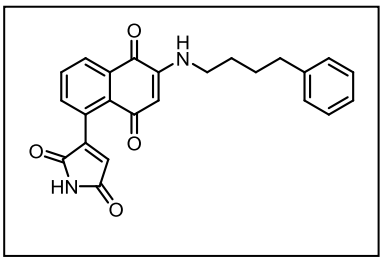
34 mg (45%); Light yellowish solid; mp = 208.8–209.4 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 10.94 (s, 1H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 (t, *J* = 6.0 Hz, 1H), 7.30–7.27 (m, 4H), 7.21 (t, *J* = 7.0 Hz, 1H), 6.68 (d, *J* = 1.5 Hz, 1H), 5.67 (s, 1H), 3.42 (q, *J* = 6.5 Hz, 2H), 2.90 (t, *J* = 12.0 Hz, 2H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.6, 181.1, 172.3, 170.5, 150.8, 147.8, 138.9, 136.7, 135.3, 132.0, 131.7, 131.0, 128.8, 128.4, 128.0, 126.3, 124.4, 100.1, 43.3, 33.4; IR (KBr) υ 3460, 3385, 3157, 3059, 2927, 2748, 1723, 1610, 1560, 1508, 1451, 1343, 1288, 1244, 1134, 982, 844, 753 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{22}H_{17}N_2O_4$ $[M+H]^+$ 373.1183, found 373.1188.

3-(5,8-Dioxo-6-((3-phenylpropyl)amino)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4gb)



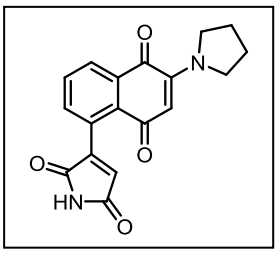
40 mg (52%); Yellow solid; mp = 236.5–238.6 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 10.93 (s, 1H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.74 (t, *J* = 6 Hz, 1H), 7.69 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.19–7.16 (m, 1H), 6.66 (d, *J* = 1.5 Hz, 1H), 5.55 (s, 1H), 3.19 (q, J = 7.0 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.88 (quint, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.5, 181.1, 172.3, 170.5, 150.8, 148.0, 141.5, 136.6, 135.3, 131.9, 131.7, 131.1, 128.8, 128.3, 128.0, 125.9, 124.4, 99.7, 41.6, 32.6, 29.1; IR (KBr) υ 3392, 3158, 3064, 2933, 2744, 1721, 1677, 1609, 1563, 1511, 1462, 1346, 1285, 1238, 1131, 1054, 976, 875, 769 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{23}H_{19}N_2O_4$ $[M+H]^+$ 387.1339, found 387.1363.

3-(5,8-Dioxo-6-((4-phenylbutyl)amino)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4hb)



37 mg (46%); Light yellow solid; mp = 224.1–227.8 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 10.93 (s, 1H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.72–7.68 (m, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.21–7.14 (m, 3H), 6.67 (d, *J* = 1.5 Hz, 1H), 5.61 (s, 1H), 3.20 (q, *J* = 6.5 Hz, 2H), 2.60 (t, *J* = 7.0 Hz, 2H), 1.61 (quint, *J* = 3.5 Hz, 4H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.5, 181.1, 172.3, 170.5, 150.8, 148.0, 142.0, 136.7, 131.9, 131.7, 131.1, 128.8, 128.3, 128.2, 128.0, 125.7, 124.3, 99.7, 41.7, 34.8, 28.4, 27.0; IR (KBr) υ 3397, 3211, 2934, 2863, 1727, 1683, 1609, 1563, 1511, 1349, 1238, 1135, 1100, 1032, 933, 867, 820, 758 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{24}H_{21}N_2O_4$ $[M+H]^+$ 401.1496, found 401.1499.

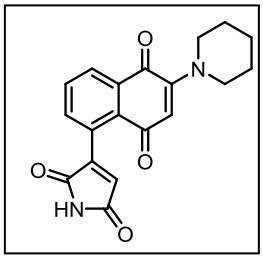
3-(5,8-Dioxo-6-(pyrrolidin-1-yl)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dion (4ib)



40 mg (63%); Light orange solid; mp = 278.8–280.9 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 10.90 (s, 1H), 8.09 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.66 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.67 (s, 1H), 5.56 (s, 1H), 3.90 (s, 2H), 3.33 (s, 2H), 1.92 (quint, *J* = 4.0 Hz, 4H); ^{13}C NMR

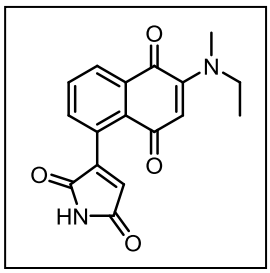
(125 MHz, DMSO–d_6) δ 182.2, 180.7, 172.3, 170.4, 150.8, 148.8, 136.0, 132.2, 131.7, 131.4, 128.1, 124.3, 103.6, 51.1, 50.2, 26.2, 23.4; IR (KBr) υ 3127, 2984, 2749, 2383, 2311, 1722, 1596, 1552, 1432, 1329, 1283, 882, 828, 755 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{15}N_2O_4$ $[M+H]^+$ 323.1026, found 323.1033.

3-(5,8-Dioxo-6-(piperidin-1-yl)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione(4jb):



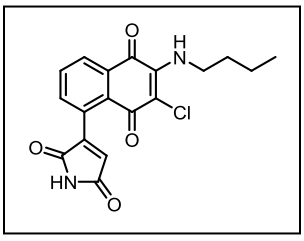
35 mg (52%); Brick red solid; mp = 250.1–251.9 ^oC; ^1H NMR (500 MHz, DMSO–d_6) δ 10.95 (s, 1H), 8.05 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 5.91 (s, 1H), 3.49 (s, 4H), 1.64 (s, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 182.4, 182.0, 172.2, 170.4, 153.4, 150.3, 135.7, 133.5, 132.1, 130.6, 128.4, 128.1, 125.0, 108.1, 49.6, 25.5, 23.7; IR (KBr) υ 3422, 2927, 1724, 1683, 1604, 1553, 1437, 1341, 1283, 977, 884, 760 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{19}H_{17}N_2O_4$ $[M+H]^+$ 337.1183, found 337.1185.

3-(6-(Ethyl(methyl)amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4kb):



35 mg (57%); Light orange solid; mp = 228.7–229.9 ^oC; ^1H NMR (500 MHz, DMSO–d_6) δ 10.92 (s, 1H), 8.05 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.66 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.69 (d, *J* = 1.5 Hz, 1H), 5.68 (s, 1H), 3.59 (q, *J* = 7.0 Hz, 2H), 3.05 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 182.5, 181.2, 172.2, 170.4, 151.9, 150.5, 135.7, 133.1, 131.9, 131.0, 128.3, 128.0, 124.7, 104.9, 48.5, 39.2, 12.8; IR (KBr) υ 3400, 2926, 2312, 1723, 1599, 1450, 1450, 1333, 1237, 1217, 1059, 926, 848, 770 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{17}H_{15}N_2O_4$ $[M+H]^+$ 311.1026, found 311.1035.

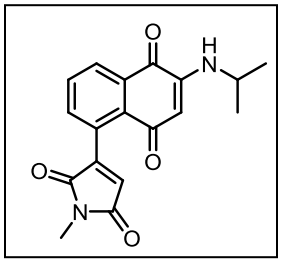
3-(6-(Butylamino)-7-chloro-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4lb)



45 mg (62%); Orange solid; mp = 239.7–241.2 ^oC; ^1H NMR (500 MHz, DMSO–d_6) δ 10.97 (s, 1H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.62 (s, 1H), 6.71 (d,

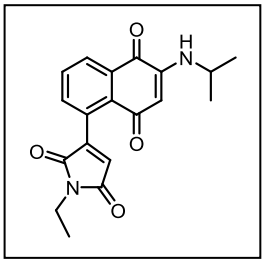
J = 1.5 Hz, 1H), 3.71 (q, *J* = 7.0 Hz, 2H), 1.60 (quint, *J* = 7.5 Hz, 2H), 1.33 (sextet, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 179.7, 175.3, 172.1, 170.4, 150.2, 144.8, 144.6, 136.7, 132.4, 130.7, 130.5, 129.1, 128.5, 124.9, 43.7, 32.9, 19.3, 13.7; IR (KBr) υ 3274, 3212, 3088, 2950, 2871, 2697, 1728, 1690, 1528, 1591, 1335, 1138, 1062, 931, 843, 754 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{16}N_2O_4$ $[M+H]^+$ 359.0793, found 359.0801.

3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methyl-1H-pyrrole-2,5-dione (4aa)



43 mg (66%); Orange solid; mp = 175.2–178.7 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.15 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.69 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.81 (s, 1H), 5.63 (s, 1H), 3.71–3.65 (m, 1H), 2.65 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.6, 181.2, 170.9, 169.2, 150.3, 147.0, 136.6, 132.0, 131.7, 131.1, 128.6, 128.1, 123.6, 99.9, 43.6, 23.7, 21.1; IR (KBr) υ 3446, 3342, 2926, 2859, 1708, 1609, 1566, 1512, 1447, 1350, 1241, 1169, 1128, 1044, 972, 860, 778 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{17}N_2O_4$ $[M+H]^+$ 325.1183, found 325.1227.

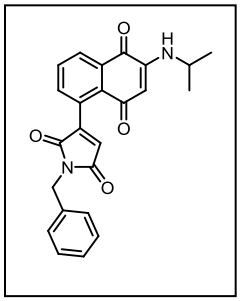
1-Ethyl-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ac)



46 mg (68%); Reddish orange solid; mp = 208.1–210.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 6.43 (s, 1H), 5.77 (d, *J* = 7.5 Hz, 1H), 5.68 (s, 1H), 3.69–3.58 (m, 3H), 1.30–1.28 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.6, 181.5, 170.7, 169.1, 150.4, 146.2, 136.3, 132.4, 131.7, 131.5, 129.2, 128.6, 123.5, 101.4, 44.1, 33.1, 21.7, 14.0; IR (KBr) υ 3338, 2923, 2859, 1707, 1620, 1566, 1520, 1449, 1405, 1318, 1250, 1120, 1166, 1097, 1012, 960, 886, 839, 762 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{19}H_{19}N_2O_4$ $[M+H]^+$ 339.1339, found 339.1348.

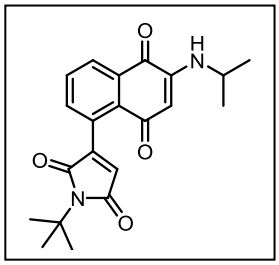
1-Benzyl-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ad)

58 mg (73%); Light orange solid; mp = 198.4–200.2 °C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.16 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.74 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.39–7.33 (m,



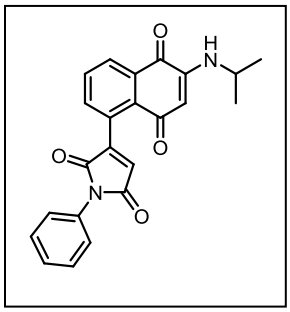
6H), 6.88 (s, 1H), 5.66 (s, 1H), 4.68 (s, 2H), 3.74–3.67 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.5, 181.2, 170.6, 168.8, 150.4, 147.0, 136.9, 136.7, 132.0, 131.7, 131.2, 128.6, 128.2, 127.3, 127.0, 123.7, 99.9, 43.6, 40.7, 21.1; IR (KBr) υ 3338, 2924, 2859, 1764, 1706, 1611, 1566, 1512, 1428, 1348, 1237, 1139, 1099, 960, 849, 767 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{24}H_{21}N_2O_4$ $[M+H]^+$ 401.1496, found 401.1523.

1-(tert-butyl)-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ae)



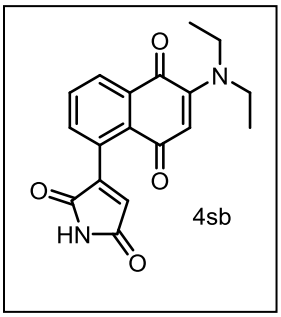
33 mg (46%); Light red solid; mp = 176.5–178.4 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 6.63 (s, 1H), 5.68 (s, 1H), 3.73–3.66 (m, 1H), 1.55 (s, 9H), 1.21 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 181.6, 181.2, 171.9, 167.0, 149.5, 146.9, 136.6, 131.9, 131.7, 131.1, 128.8, 128.0, 123.6, 100.0, 56.4, 43.5, 28.6, 21.1; IR (KBr) υ 3349, 2983, 1700, 1623, 1565, 1517, 1450, 1352, 1237,1133, 1063, 958, 852, 771 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{21}H_{23}N_2O_4$ $[M+H]^+$ 367.1652, found 367.1676.

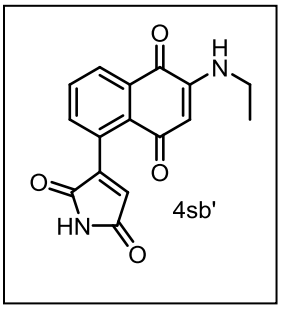
3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-phenyl-1H-pyrrole-2,5-dione (4af)



52 mg (67%); Orange solid; mp = 214.5–216.3 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.18 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.86 (t, *J* = 7.5 Hz, 1H), 7.79 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 3H), 7.01 (s, 1H), 5.69 (s, 1H), 3.73–3.66 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 182.1, 181.6, 170.0, 168.4, 150.7, 147.5, 137.1, 132.5, 132.4, 132.3, 131.7, 129.5, 128.9, 128.8, 128.2, 127.0, 124.1, 100.3, 44.1, 21.6; IR (KBr) υ 3346, 2923, 2859, 1712, 1619, 1564, 1506, 1382, 1237, 1133, 1096, 1016, 961, 884, 840, 763 cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{23}H_{19}N_2O_4$ $[M+H]^+$ 387.1339, found 387.1346.

3-(6-(Diethylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4sb) and 3-(6-(ethylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4sb′):





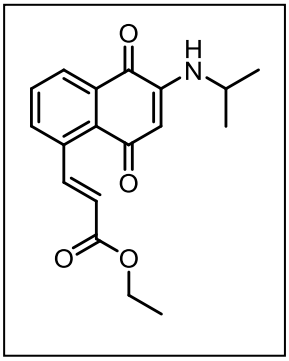
Mixture of **4sb & 4sb′** (40mg); Brick red solid; ^{1}H NMR (500 MHz, DMSO–d_6) (**4sb**; 47%);^{1}H NMR (500 MHz, DMSO–d_6) δ 10.90 (s, 1H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.78 (t, *J* = 7.5, 1H), 7.65 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.67 (d, *J* = 1.5 Hz, 1H), 5.70 (s, 1H), 3.33 (s, 4H), 1.21 (t, *J* = 7.0 Hz, 6H); **(4sb′,**16%); ^{1}H NMR (500 MHz, DMSO–d_6) δ 10.90 (s, 1H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.79 (t, *J* = 7.5, 1H), 7.69 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.62 (d, *J* = 6.0 Hz, 1H), 6.67 (d, *J* = 1.5 Hz, 1H), 5.60 (s, 1H), 3.50 (q, *J* = 7 Hz, 2H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO–d_6) for the mixture **4sb & 4sb′** δ 182.8, 181.5, 181.1, 181.1, 172.2, 170.4, 151.0, 150.8, 150.5, 147.8, 136.7, 135.6, 133.3, 131.9, 131.8, 131.7, 131.1, 130.9, 128.8, 128.3, 127.9, 124.6, 124.3, 104.2, 99.6, 46.0, 45.1, 36.7, 13.0, 12.5; IR (KBr) for the mixture **4sb & 4sb′**υ 3437, 3390, 3280, 3061, 2925, 2853, 1718, 1611, 1561, 1517, 1448, 1345, 1236, 1063, 936, 847, 770 cm^{-1}; HRMS (Q-TOF, ESI) of **(4sb)** calcd for $C_{18}H_{17}N_2O_4$ $[M+H]^+$ 325.1183, found 325.1263.

Procedure for competitive reaction between 2-amino-1,4-naphthoquinone and acetophenone with maleimide: To an oven-dried sealed tube with 2-(isopropylamino)naphthalene-1,4-dione (**1a**) (21.5 mg, 0.1 mmol, 100 mol %), acetophenone (**5**) (12.0 mg, 0.1 mmol, 100 mol %), *N*-Methylmaleimide (**2a**) (11.1 mg, 0.1 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 5 mol %), $AgSbF_6$ (6.8 mg, 0.02 mmol, 20 mol %) and Ag_2CO_3 (55.1 mg, 0.2 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 ºC for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 5:1 to 1:10) to provide **4aa** (21 mg) in 65% yield.

Procedure for competitive reaction between maleimide and acrylate with 2-amino-1,4-naphthaquinone: To an oven-dried sealed tube with 2-(isopropylamino)naphthalene-1,4-dione (**1a**) (21.5 mg, 0.1 mmol, 100 mol %), *N*-Methylmaleimide (**2a**) (11.1 mg, 0.1 mmol, 100 mol %), ethyl acrylate (**7**) (10.0 mg, 0.1 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 5 mol

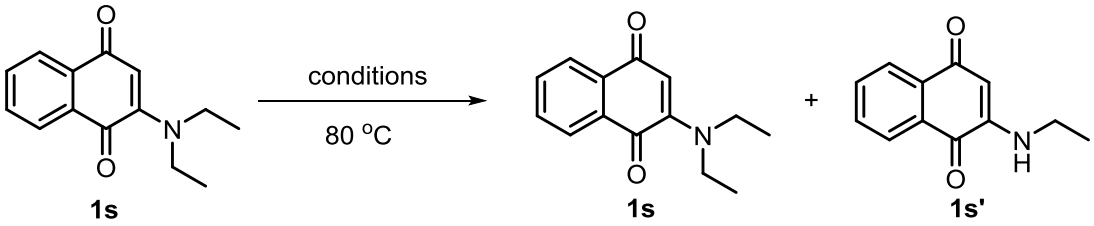
%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 20 mol %) and Ag_2CO_3 (55.1 mg, 0.2 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 ºC for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 1:1) to provide **8** (20.1 mg) in 64% and **4aa** (2.7 mg) in 8% yield.

Ethyl (E)-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)acrylate (8)



40 mg (64%); Orange solid; mp = 141.5–144.6 ^{o}C; ^{1}H NMR (500 MHz, DMSO–d_6) δ 8.72 (d, *J* = 16.0 Hz, 1H), 8.07 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 5.68 (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.72–3.63 (m, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.21 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO–d_6) δ 183.6, 181.5, 166.0, 146.5, 146.3, 135.2, 131.9, 131.7, 129.9, 127.9, 120.4, 101.2, 60.1, 45.1, 43.5, 21.1, 14.2; IR (KBr) υ 3420, 2979, 2354, 2252, 2124, 1664, 1618, 1247, 1175, 1094, 1011, 821, cm^{-1}; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{19}NO_4$ $[M+H]^+$ 314.1387, found 314.1396.

Control experiment for dealkylation



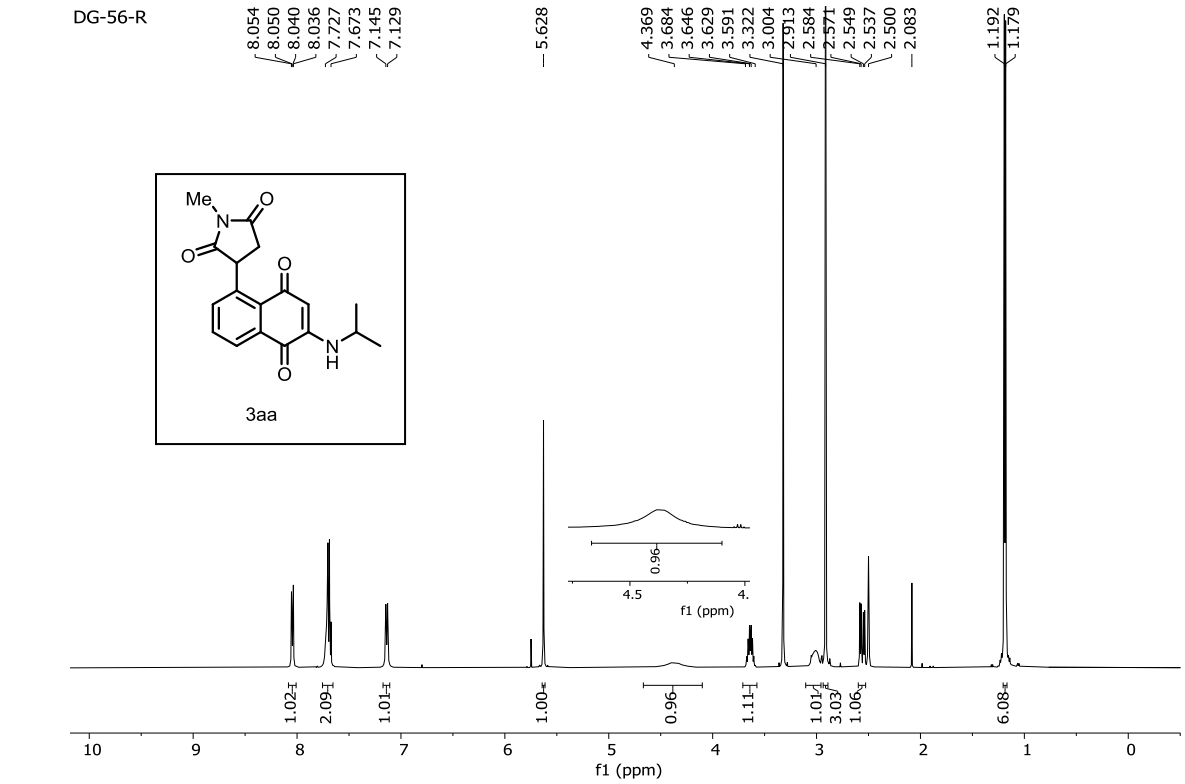
entry	conditions	ratio (1s:1s') [a]
1	$RhCp^*Cl_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), Ag_2CO_3 (200 mol %), DCE	3:1
2	Ag_2CO_3 (200 mol %), DCE	4:1
3	Ag_2CO_3 (200 mol %), TEMPO (100 mol %), DCE	4:1
4	DCE	100:0

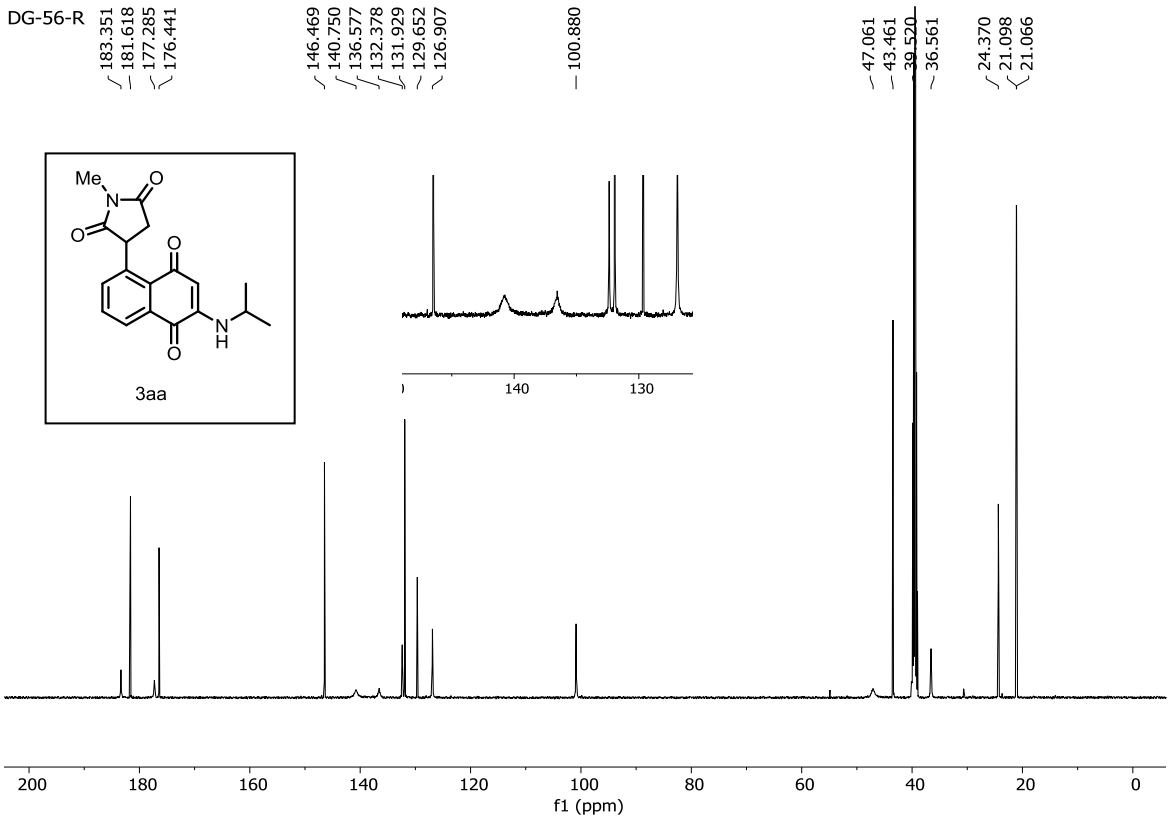
General Procedure for dealkylation reaction:

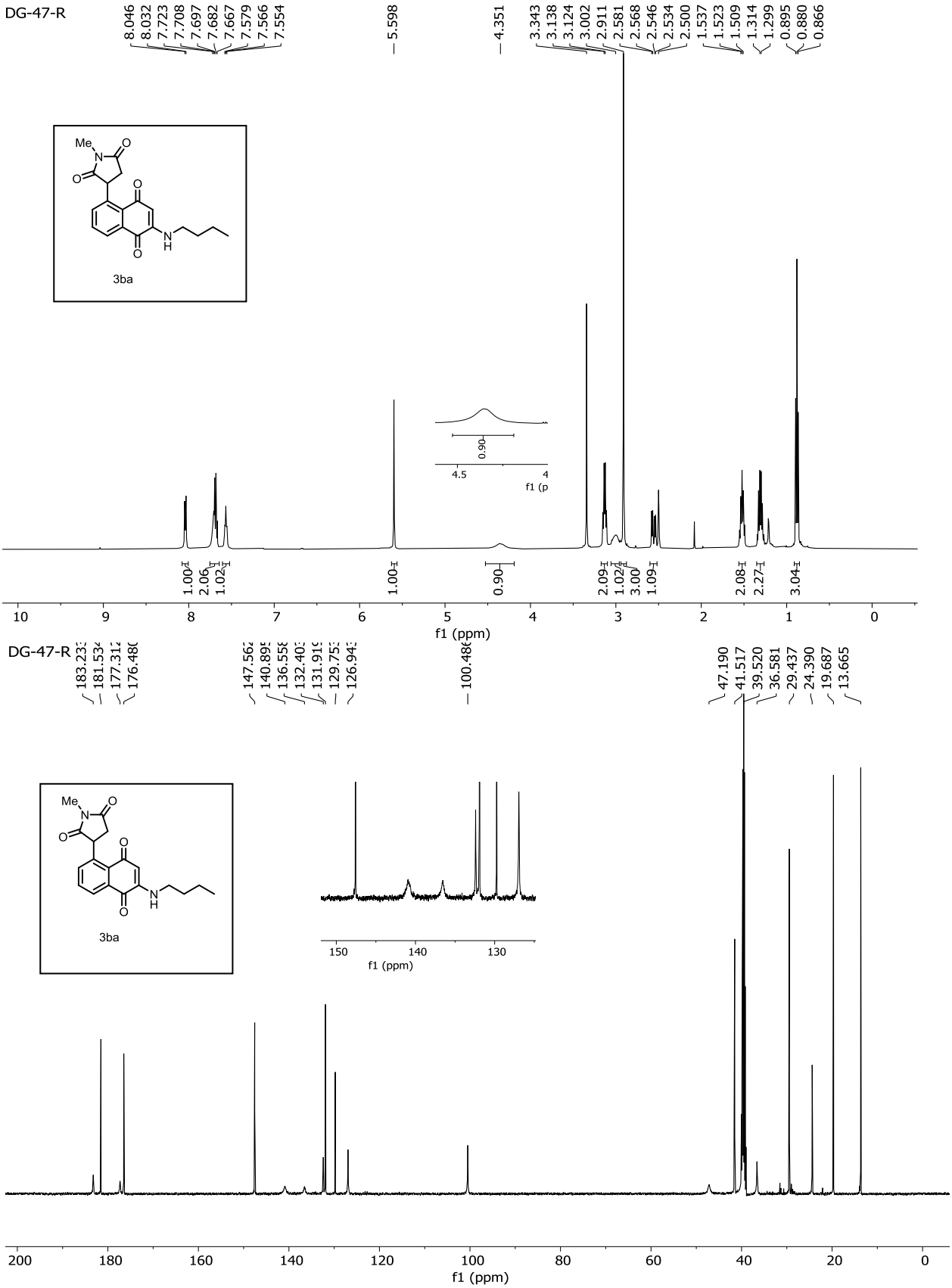
To an oven-dried sealed tube with 2-(diethylamino)naphthalene-1,4-dione (**1s**) (22.9 mg, 0.1 mmol, 100 mol %) in DCE (1 mL) was added catalyst and additives as per the above table. The reaction mixture was allowed to stir at 80 ºC for 16 h. After cooling at room temperature, the reaction mixture was evaporated and the residue was passed through neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 4:1) to provide inseparable mixture of **1s and 1s'.**

The ratio of 1s:1s' was determined by ^{1}H NMR

^{1}H NMR and ^{13}C NMR Copies of all products



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7.723
7.708
7.697
7.682
7.667
7.579
7.566
7.554
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4.351
3.343
3.138
3.124
3.002
2.911
2.581
2.568
2.546
2.534
2.500
1.537
1.523
1.509
1.314
1.299
0.895
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Me
N
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O
O
O
N
H
3ba
0.90
4.5
4
f1 (p
1.00
2.06
1.02
1.00
0.90
2.09
1.02
3.00
1.09
2.08
2.27
3.04
10
9
8
7
6
5
4
3
2
1
0
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181.53
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136.55
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129.75
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H
3ba
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130
f1 (ppm)
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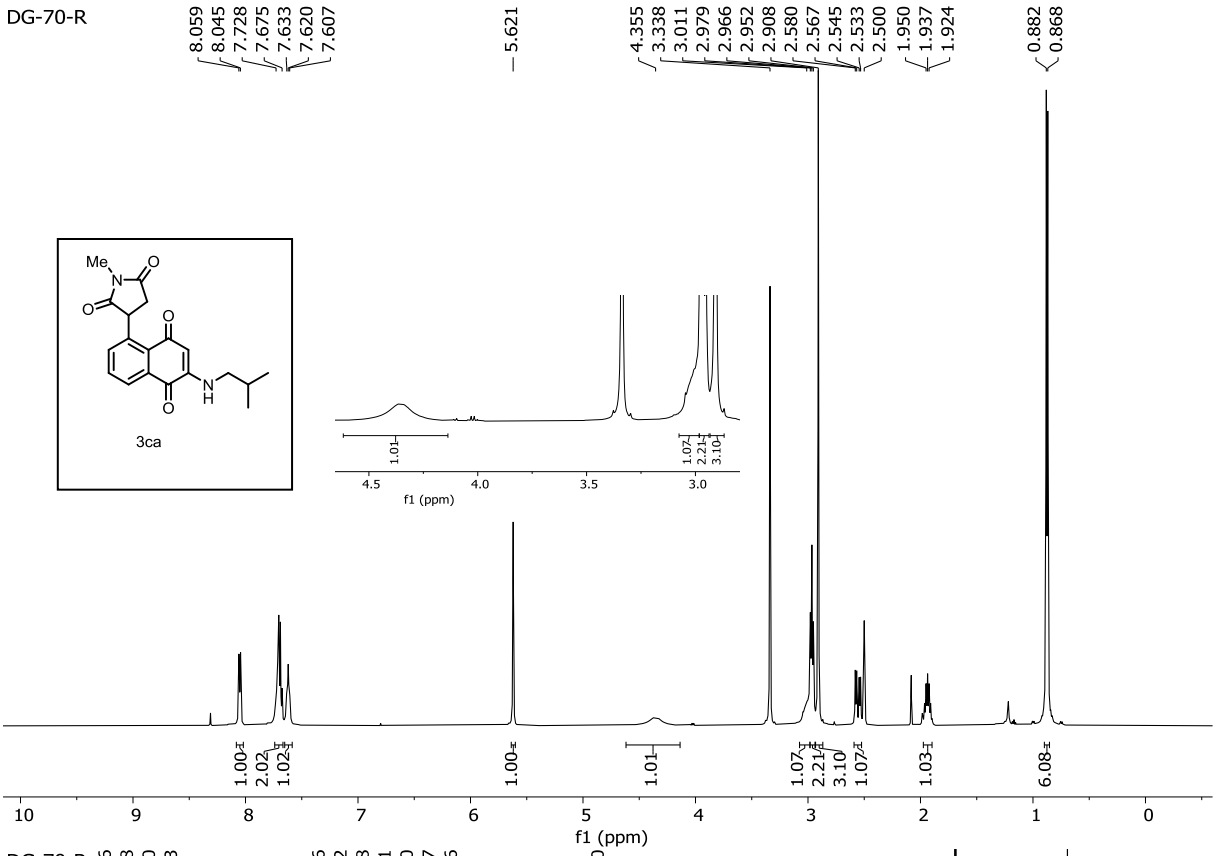
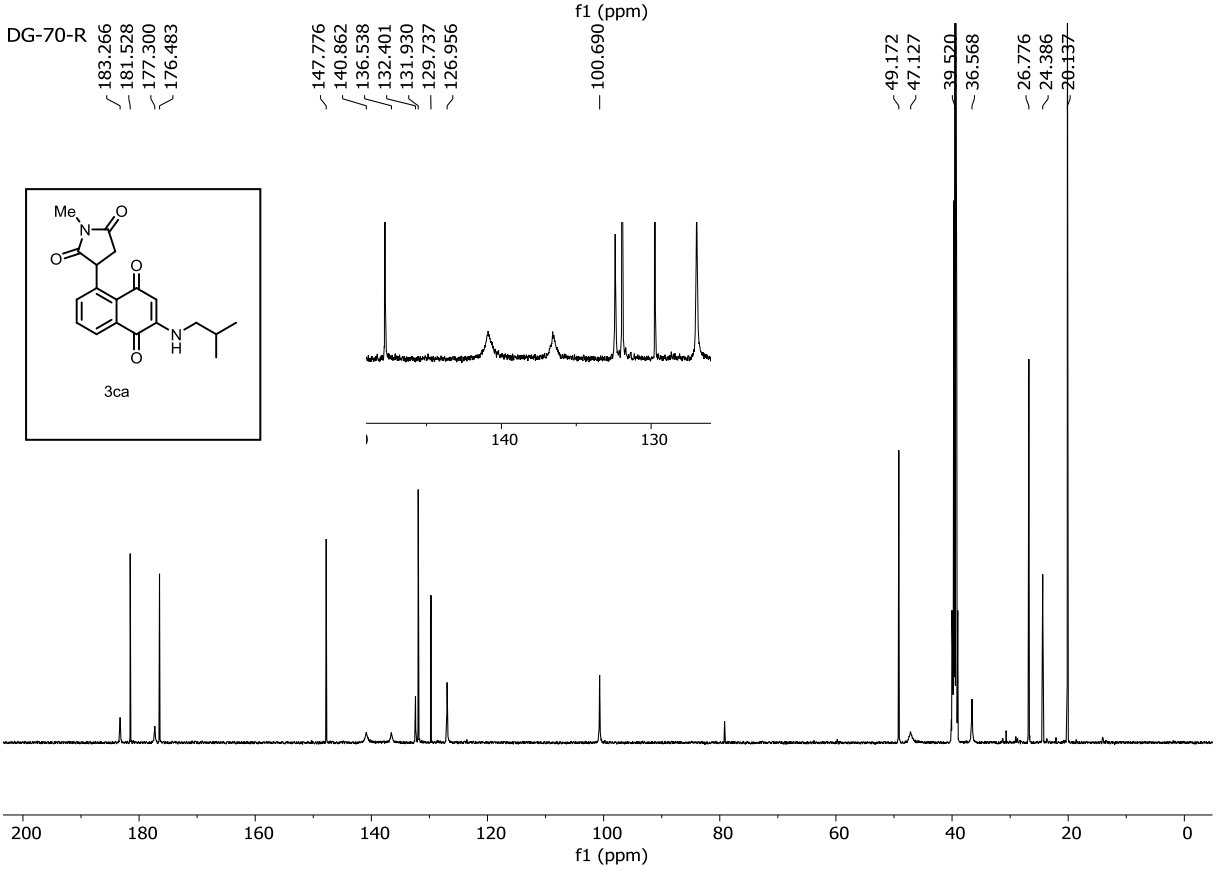
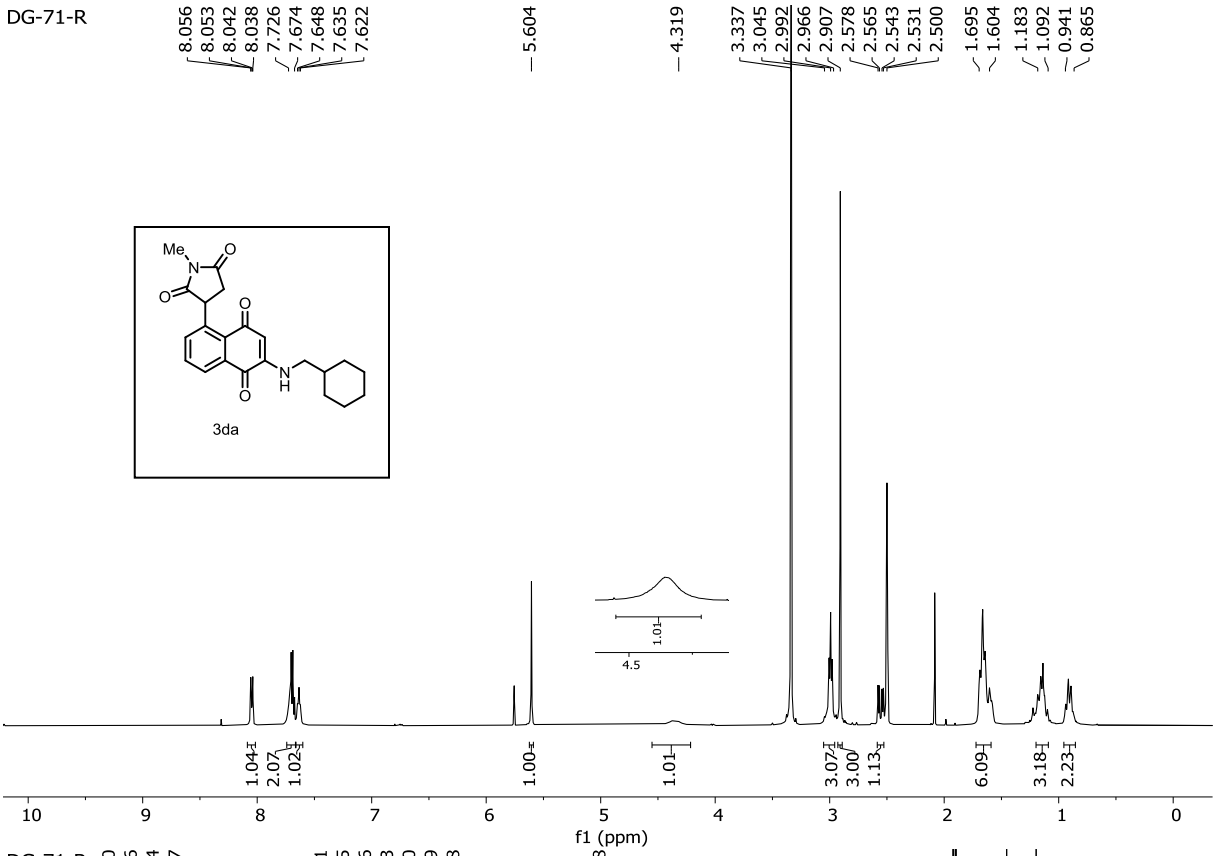
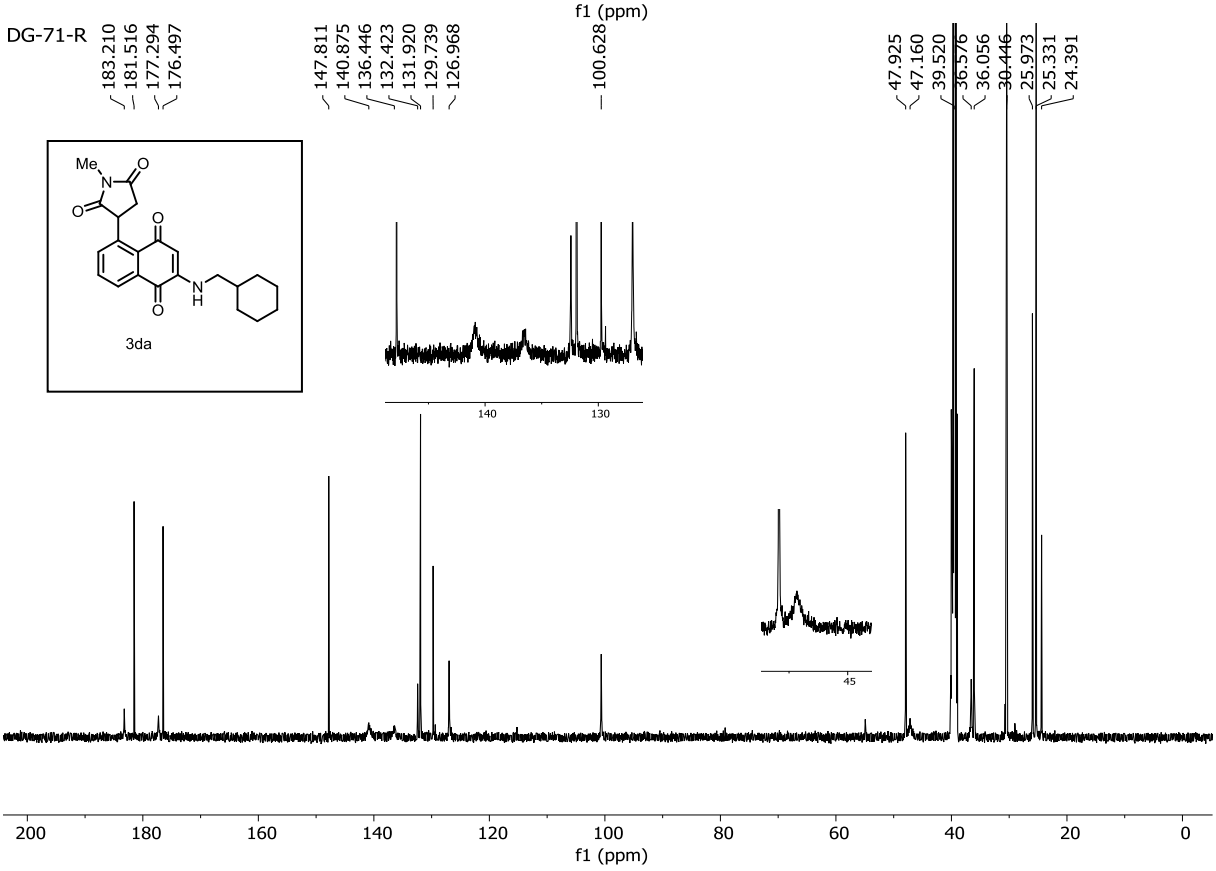
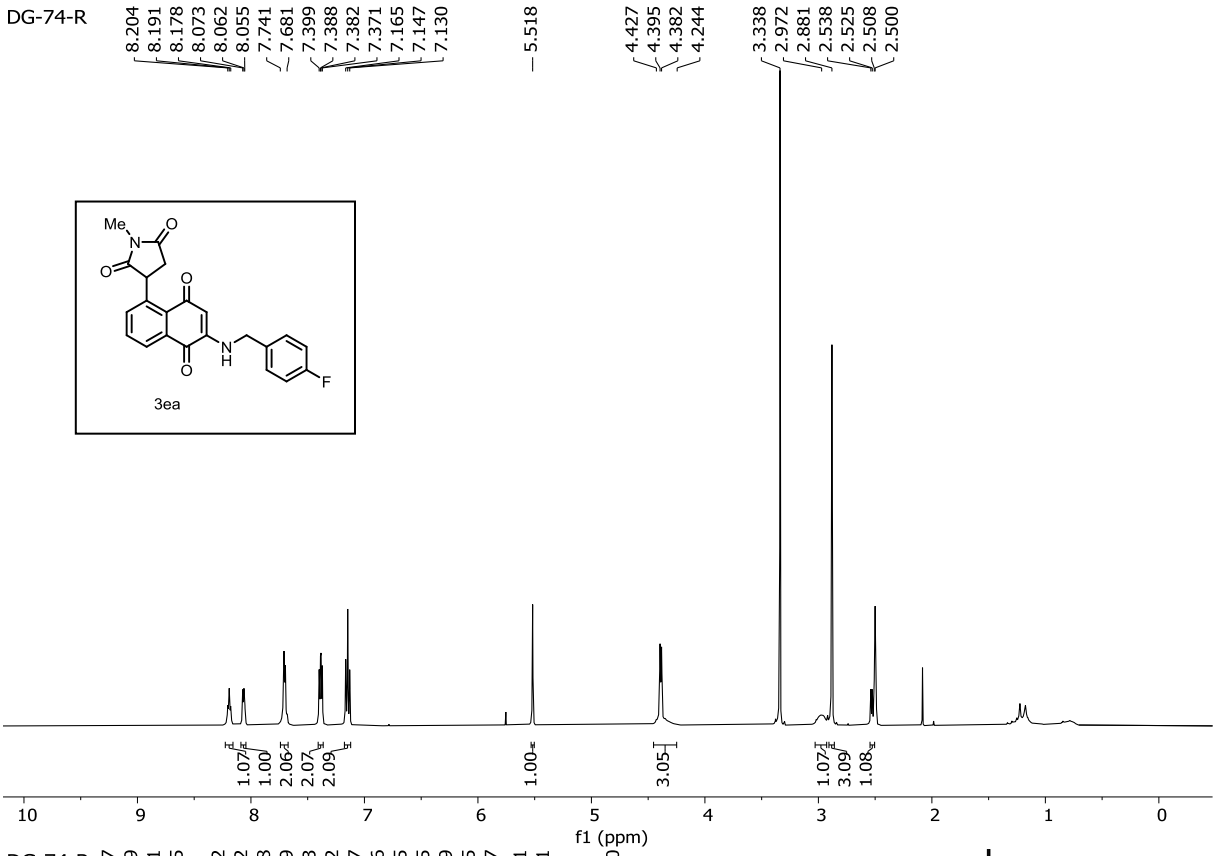
140
120
100
80
60
40
20
0
f1 (ppm)

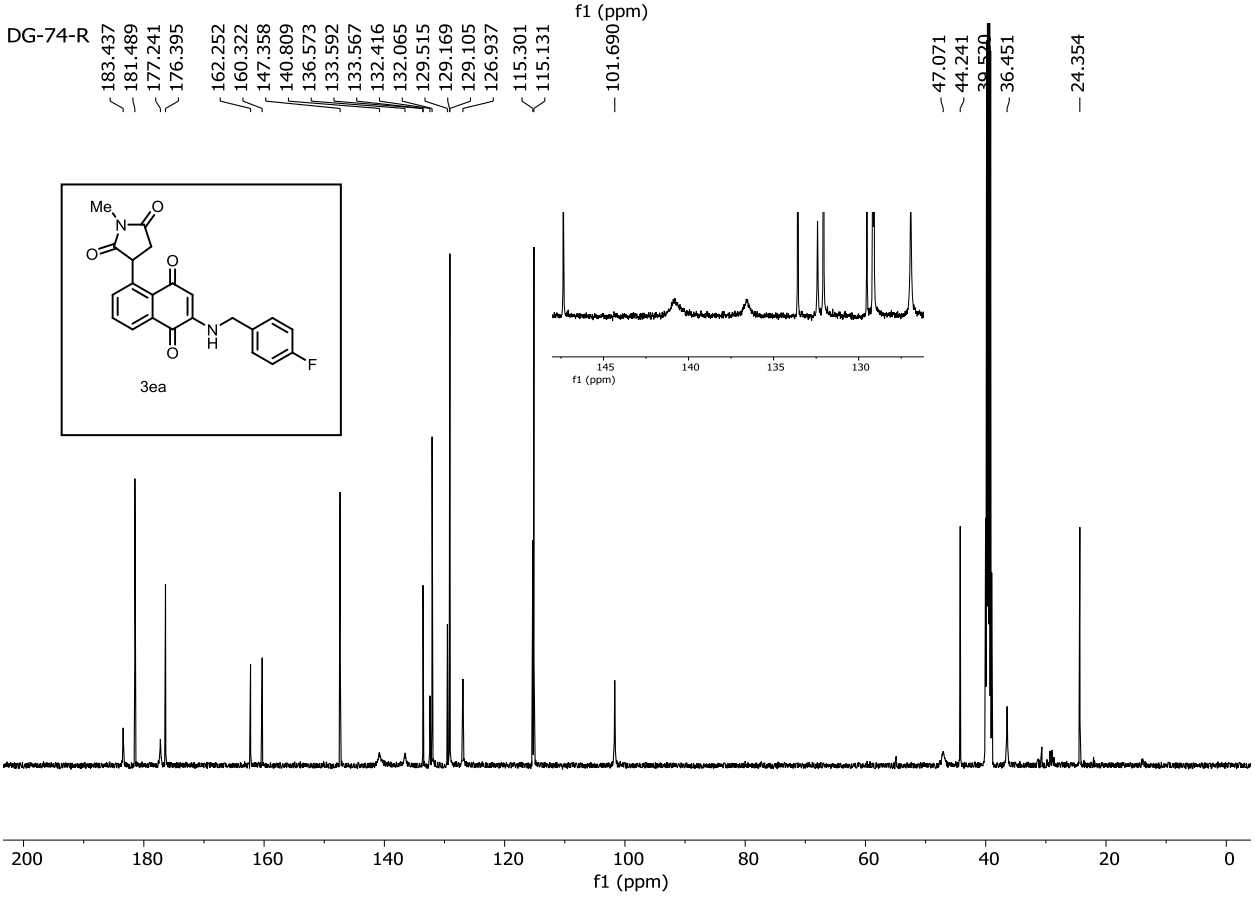

DG-70-R
8.059
8.045
7.728
7.675
7.633
7.620
7.607
5.621
4.355
3.338
3.011
2.979
2.966
2.952
2.908
2.580
2.567
2.545
2.533
2.500
1.950
1.937
1.924
0.882
0.868
Me
N
O
O
O
O
N
H
3ca
1.01
1.07
2.21
3.10
4.5
4.0
3.5
3.0
f1 (ppm)
1.00
2.02
1.02
1.00
1.01
1.07
2.21
3.10
1.07
1.03
6.08
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

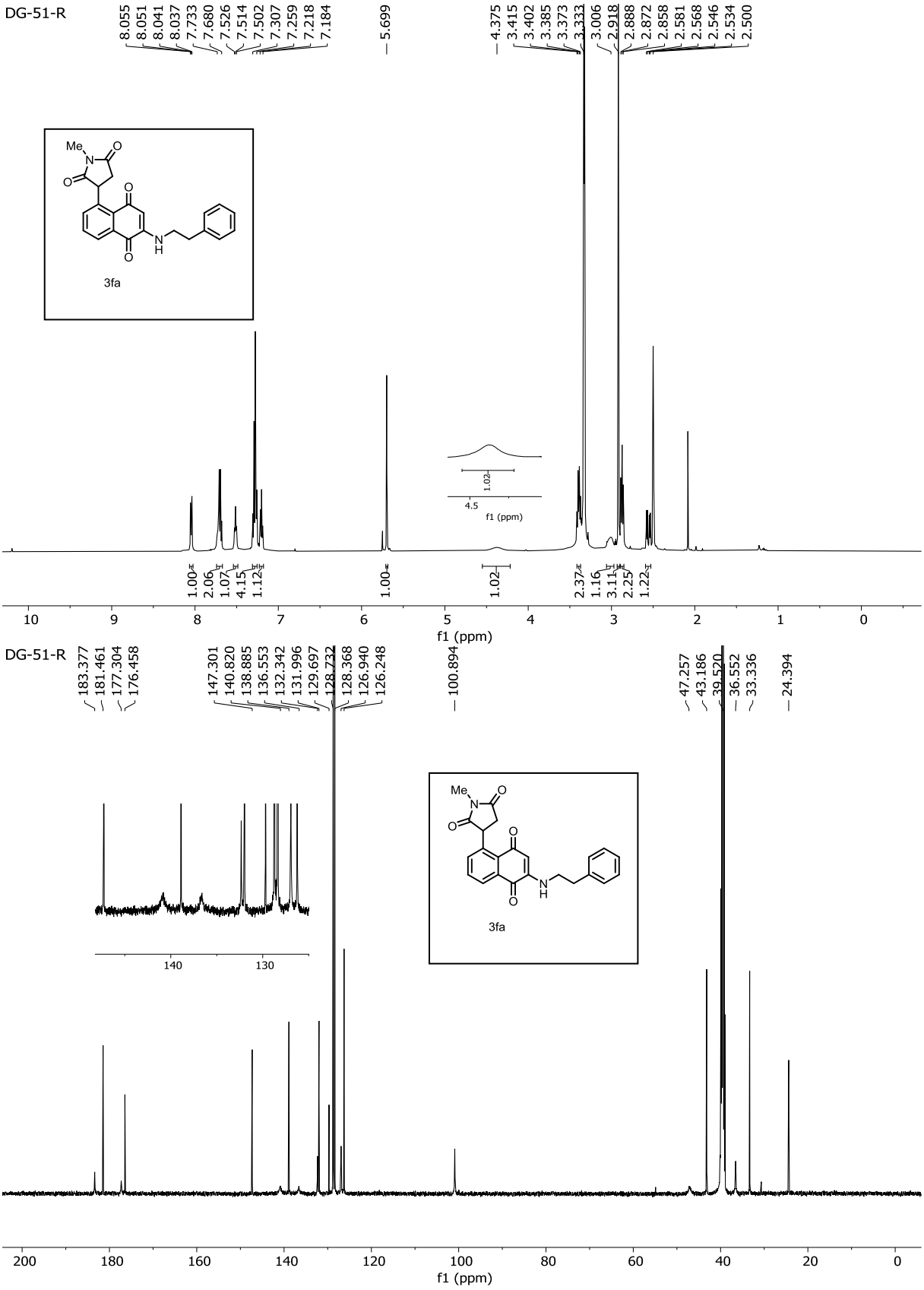

DG-70-R
183.266
181.528
177.300
176.483
147.776
140.862
136.538
132.401
131.930
129.737
126.956
100.690
49.172
47.127
39.520
36.568
26.776
24.386
20.137
Me
N
O
O
O
O
N
H
3ca
140
130
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

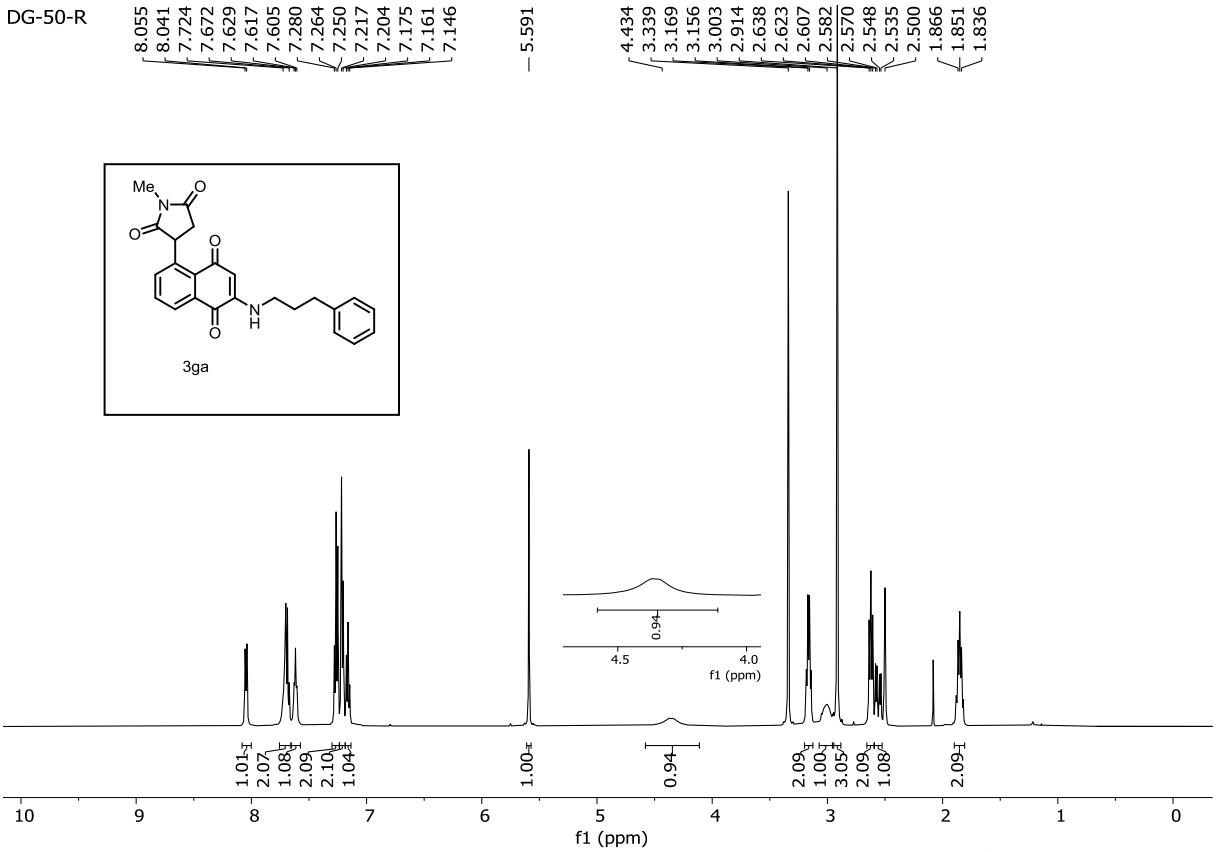

DG-71-R
8.056
8.053
8.042
8.038
7.726
7.674
7.648
7.635
7.622
5.604
4.319
3.337
3.045
2.992
2.966
2.907
2.578
2.565
2.543
2.531
2.500
1.695
1.604
1.183
1.092
0.941
0.865
Me
3da
1.01
4.5
1.04
2.07
1.02
1.00
1.01
3.07
3.00
1.13
6.09
3.18
2.23
f1 (ppm)

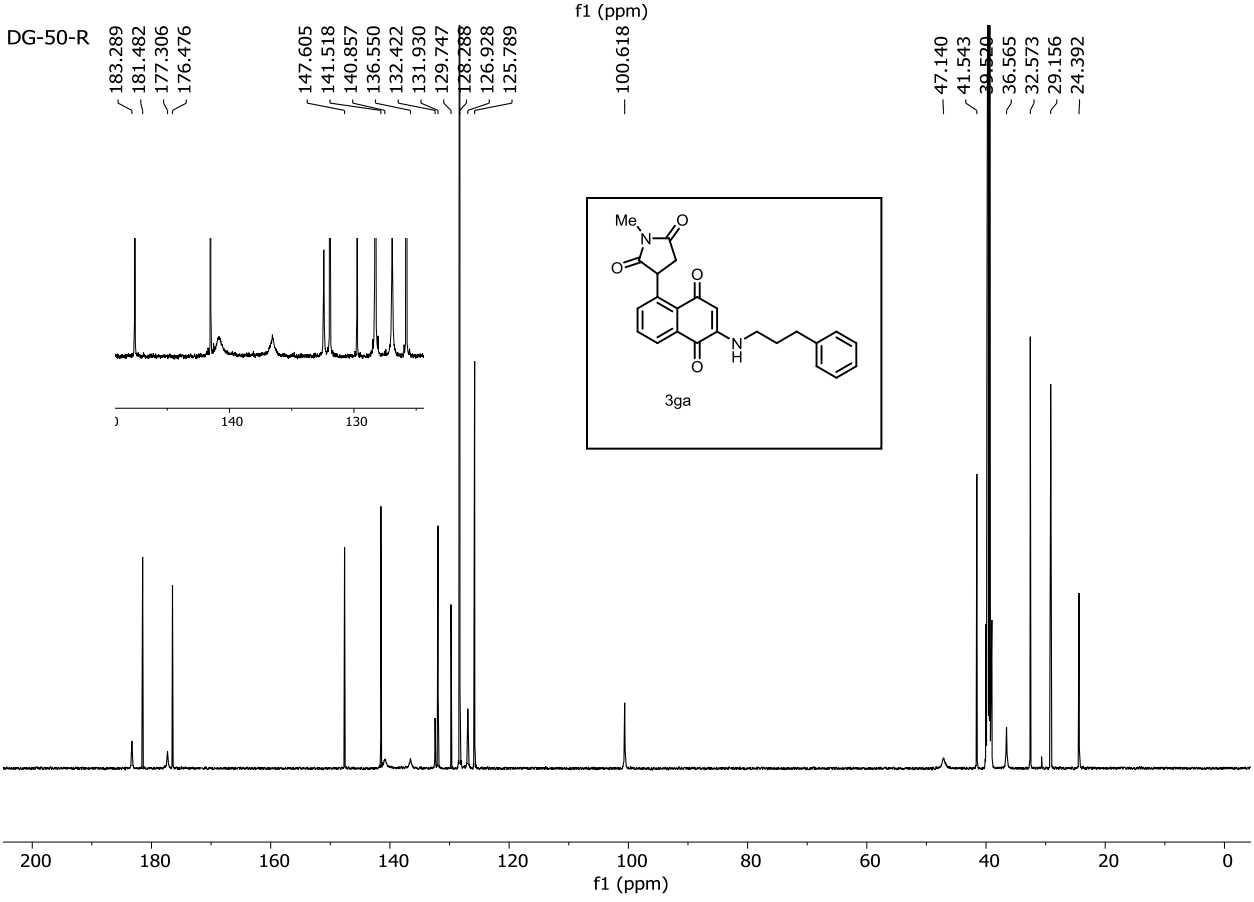

DG-71-R
183.210
181.516
177.294
176.497
147.811
140.875
136.446
132.423
131.920
129.739
126.968
100.628
47.925
47.160
39.520
36.576
36.056
30.446
25.973
25.331
24.391
Me
3da
140
130
45
f1 (ppm)

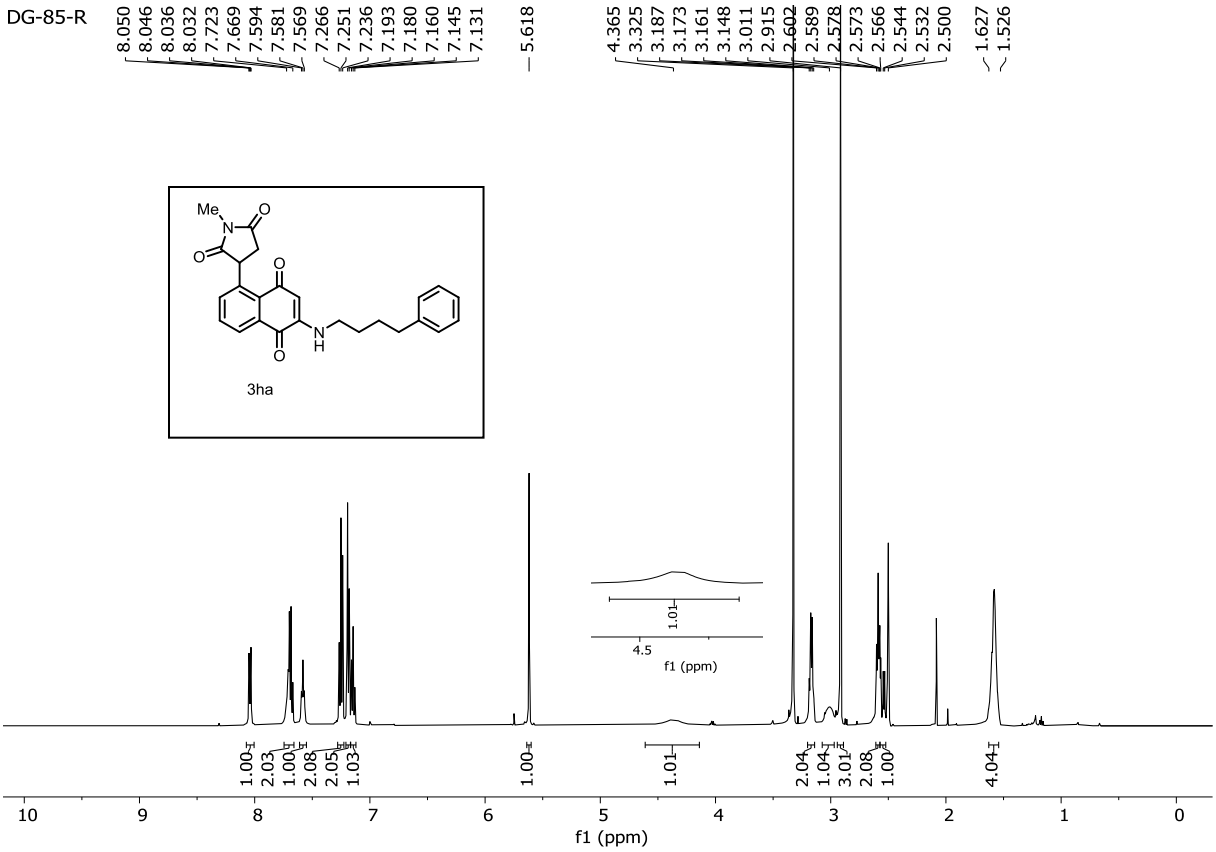

DG-74-R
8.204
8.191
8.178
8.073
8.062
8.055
7.741
7.681
7.399
7.388
7.382
7.371
7.165
7.147
7.130
5.518
4.427
4.395
4.382
4.244
3.338
2.972
2.881
2.538
2.525
2.508
2.500
Me
N
O
O
O
O
N
H
F
3ea
1.07
1.00
2.06
2.07
2.09
1.00
3.05
1.07
3.09
1.08
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

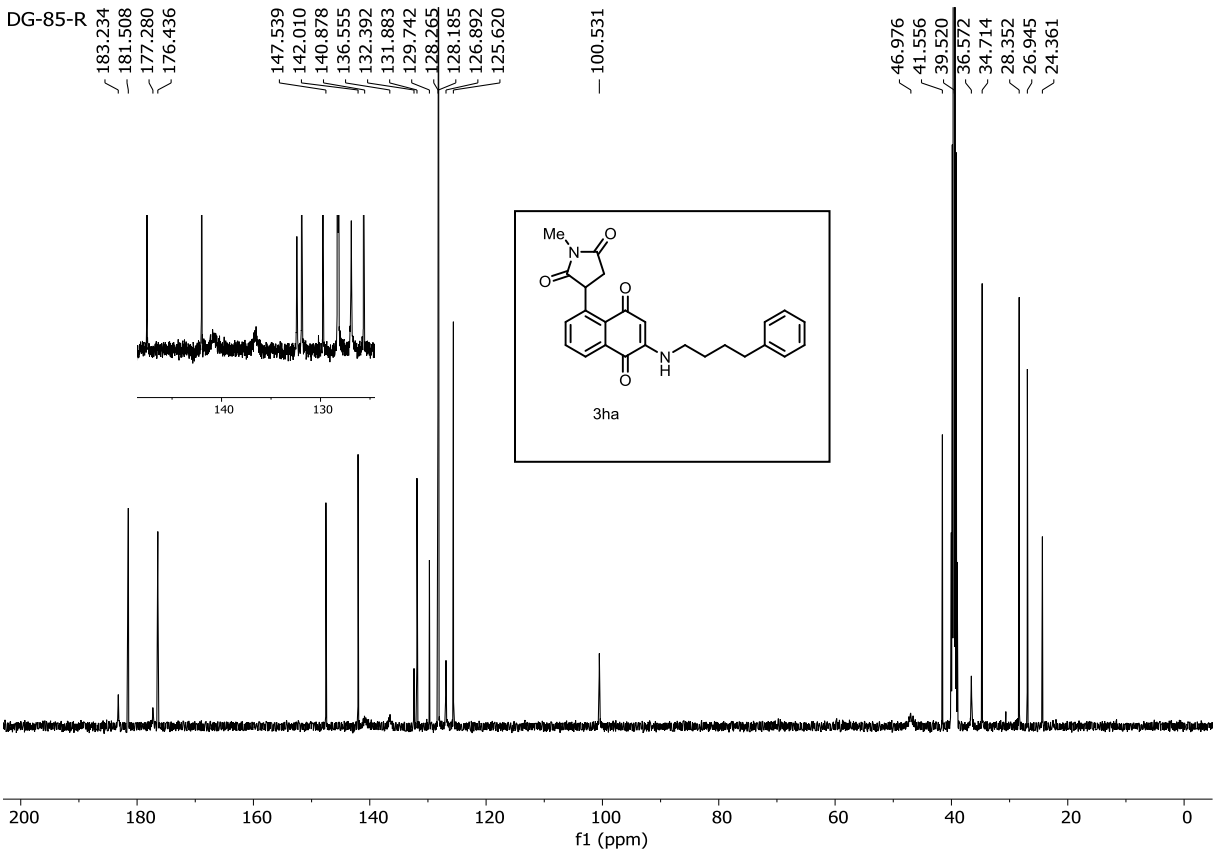

DG-74-R
183.437
181.489
177.241
176.395
162.252
160.322
147.358
140.809
136.573
133.592
133.567
132.416
132.065
129.515
129.169
129.105
126.937
115.301
115.131
101.690
47.071
44.241
39.520
36.451
24.354
Me
N
O
O
O
O
N
H
F
3ea
145
140
135
130
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

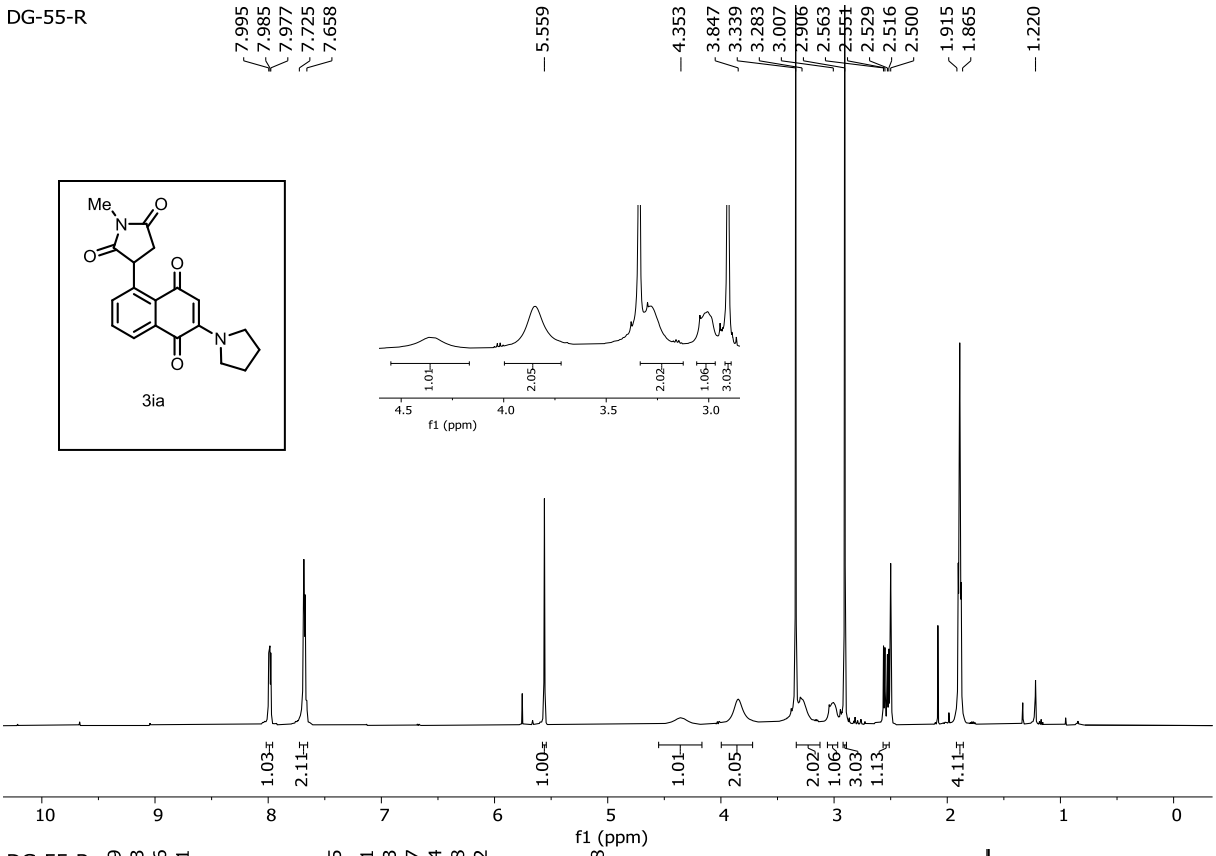

DG-51-R
8.055
8.051
8.041
8.037
7.733
7.680
7.526
7.514
7.502
7.307
7.259
7.218
7.184
5.699
4.375
3.415
3.402
3.385
3.373
3.333
3.006
2.918
2.888
2.872
2.858
2.581
2.568
2.546
2.534
2.500
Me
N
O
O
O
O
N
H
O
3fa
1.02
4.5
f1 (ppm)
1.00
2.06
1.07
4.15
1.12
1.00
1.02
2.37
1.16
3.11
2.25
1.22
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
DG-51-R
183.377
181.461
177.304
176.458
147.301
140.820
138.885
136.553
132.342
131.996
129.697
128.732
128.368
126.940
126.248
100.894
47.257
43.186
39.520
36.552
33.336
24.394
140
130
Me
N
O
O
O
O
N
H
O
3fa
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

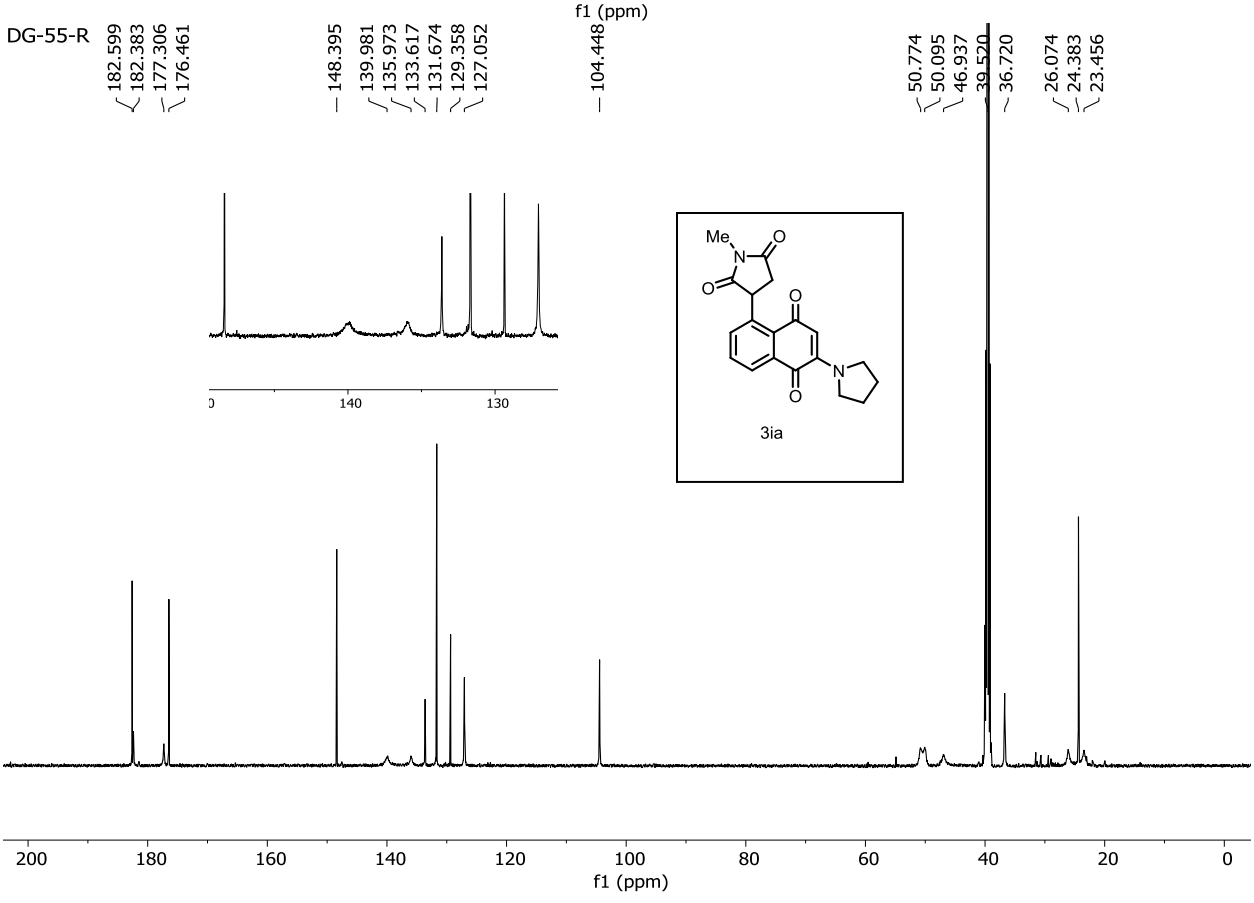

DG-50-R
8.055
8.041
7.724
7.672
7.629
7.617
7.605
7.280
7.264
7.250
7.217
7.204
7.175
7.161
7.146
5.591
4.434
3.339
3.169
3.156
3.003
2.914
2.638
2.623
2.607
2.582
2.570
2.548
2.535
2.500
1.866
1.851
1.836
Me
N
O
O
O
O
N
H
3ga
0.94
4.5
4.0
f1 (ppm)
1.01
2.07
1.08
2.09
2.10
1.04
1.00
0.94
2.09
1.00
3.05
2.09
1.08
2.09
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

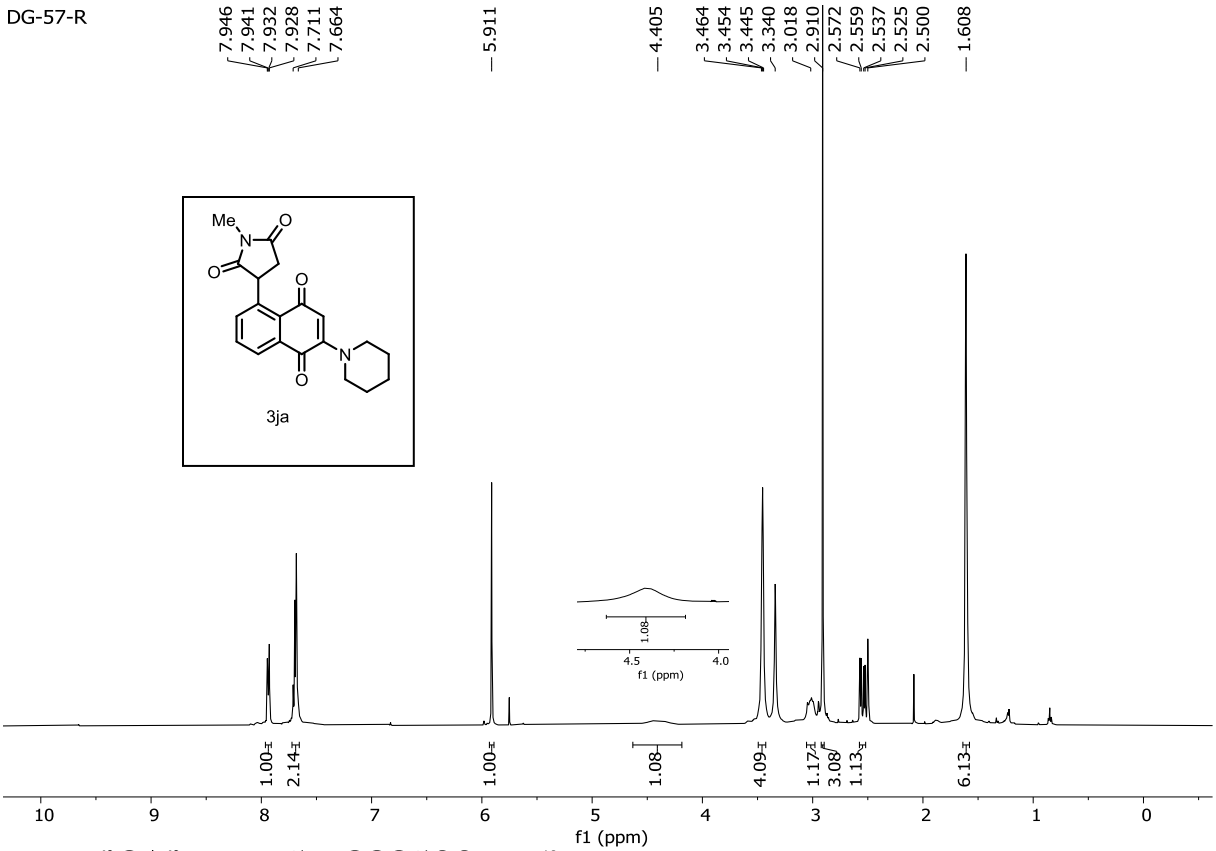

DG-50-R
183.289
181.482
177.306
176.476
147.605
141.518
140.857
136.550
132.422
131.930
129.747
128.288
126.928
125.789
100.618
47.140
41.543
39.520
36.565
32.573
29.156
24.392
Me
N
O
O
O
O
N
H
3ga
140
130
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

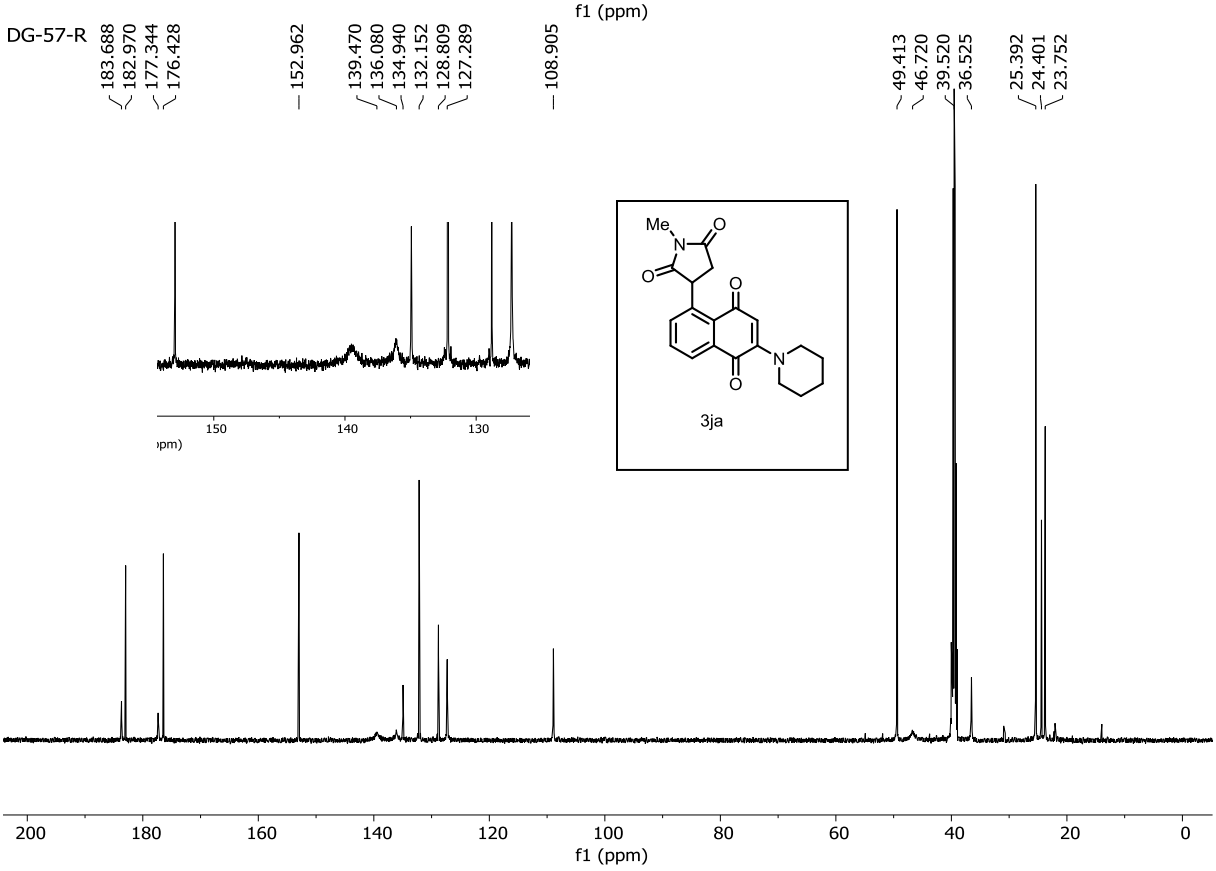

DG-85-R
8.050
8.046
8.036
8.032
7.723
7.669
7.594
7.581
7.569
7.266
7.251
7.236
7.193
7.180
7.160
7.145
7.131
5.618
4.365
3.325
3.187
3.173
3.161
3.148
3.011
2.915
2.602
2.589
2.578
2.573
2.566
2.544
2.532
2.500
1.627
1.526
Me
N
O
O
O
O
N
H
3ha
1.01
4.5
f1 (ppm)
1.00
2.03
1.00
2.08
2.05
1.03
1.00
1.01
2.04
1.04
3.01
2.08
1.00
4.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

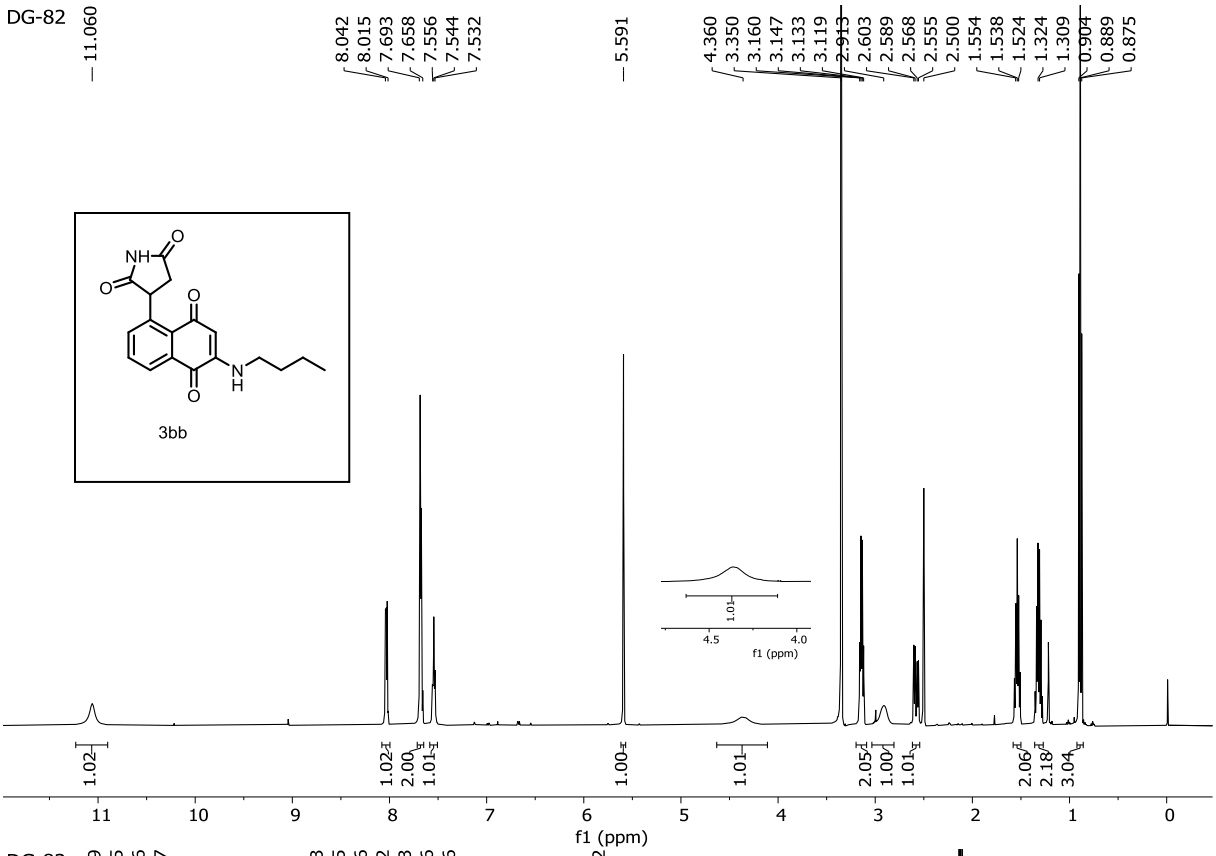

DG-85-R
183.234
181.508
177.280
176.436
147.539
142.010
140.878
136.555
132.392
131.883
129.742
128.265
128.185
126.892
125.620
100.531
46.976
41.556
39.520
36.572
34.714
28.352
26.945
24.361
140
130
Me
N
O
O
O
O
N
H
3ha
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

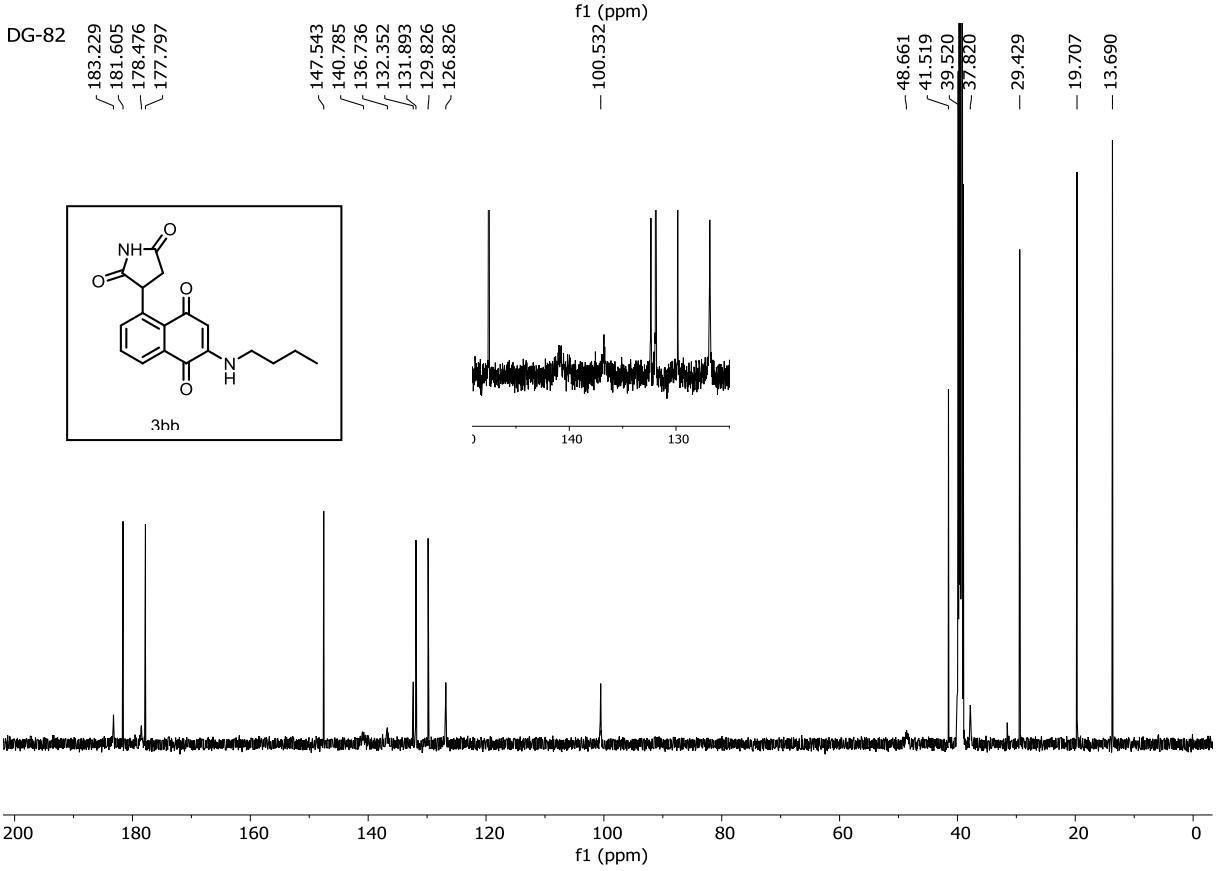

DG-55-R
7.995
7.985
7.977
7.725
7.658
5.559
4.353
3.847
3.339
3.283
3.007
2.906
2.563
2.551
2.529
2.516
2.500
1.915
1.865
1.220
Me
O
N
O
O
O
N
O
3ia
1.01
2.05
2.02
1.06
3.03
4.5
4.0
3.5
3.0
f1 (ppm)
1.03
2.11
1.00
1.01
2.05
2.02
1.06
3.03
1.13
4.11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

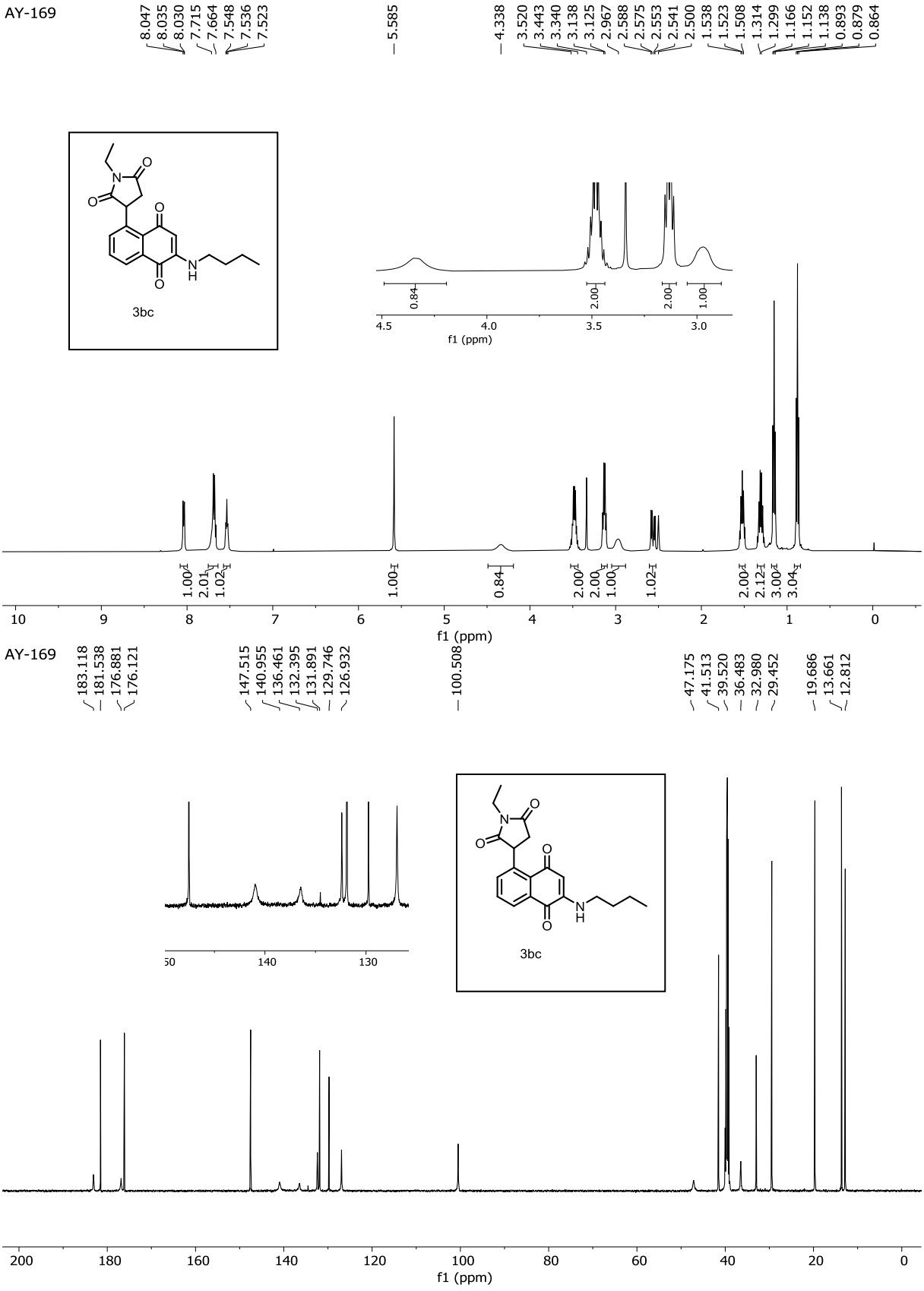

DG-55-R
182.599
182.383
177.306
176.461
148.395
139.981
135.973
133.617
131.674
129.358
127.052
104.448
50.774
50.095
46.937
39.520
36.720
26.074
24.383
23.456
140
130
Me
O
N
O
O
O
N
O
3ia
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

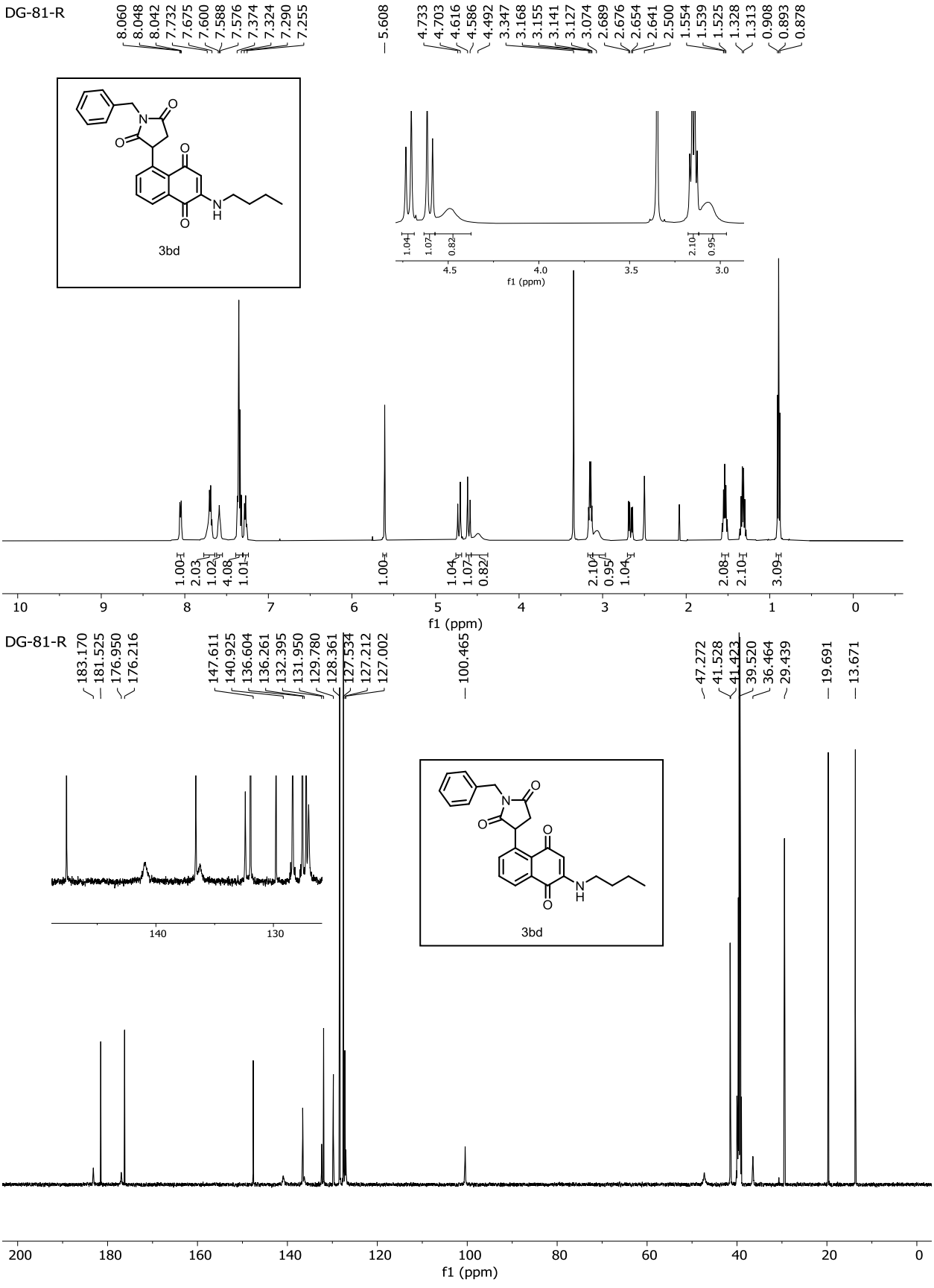

DG-57-R
7.946
7.941
7.932
7.928
7.711
7.664
5.911
4.405
3.464
3.454
3.445
3.340
3.018
2.910
2.572
2.559
2.537
2.525
2.500
1.608
Me
O
N
O
O
O
N
O
3ja
1.08
4.5
4.0
f1 (ppm)
1.00
2.14
1.00
1.08
4.09
1.17
3.08
1.13
6.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

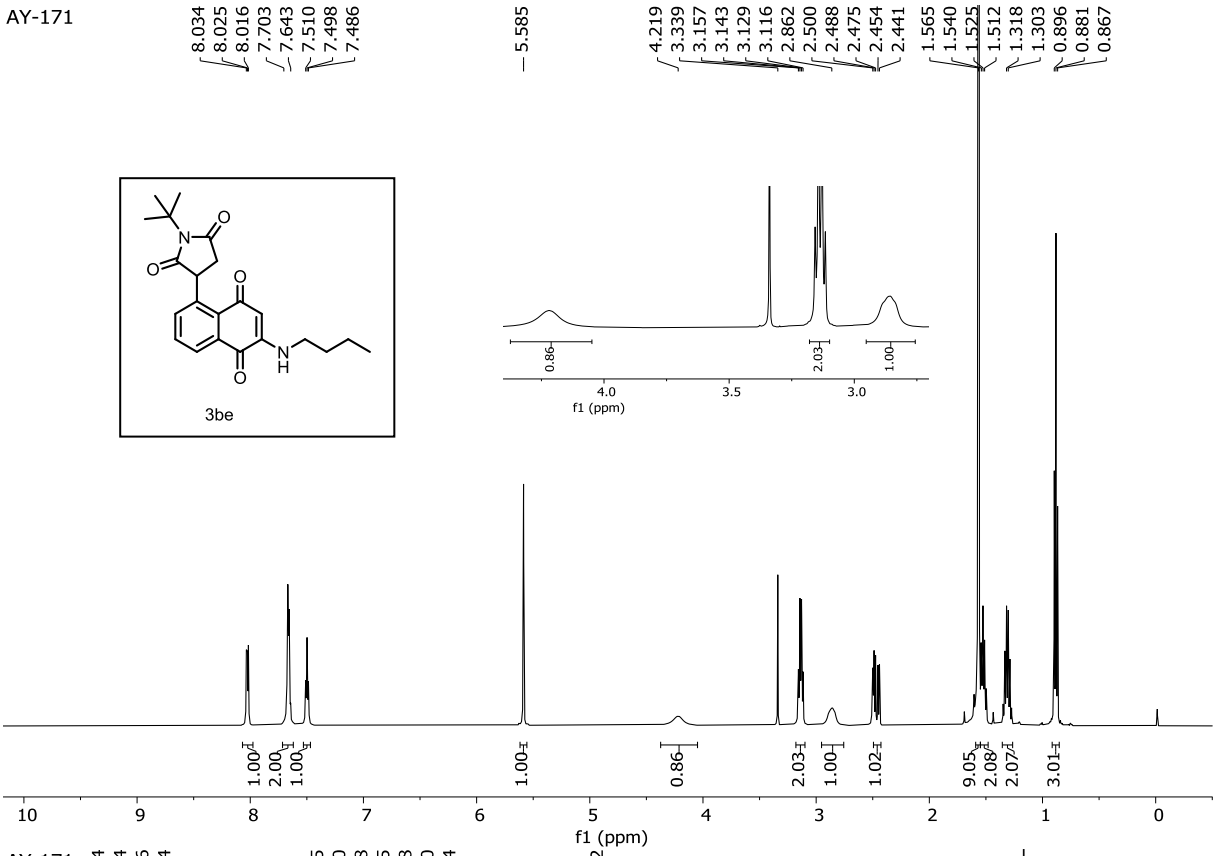

DG-57-R
183.688
182.970
177.344
176.428
152.962
139.470
136.080
134.940
132.152
128.809
127.289
108.905
49.413
46.720
39.520
36.525
25.392
24.401
23.752
150
140
130
Me
O
N
O
O
O
N
O
3ja
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

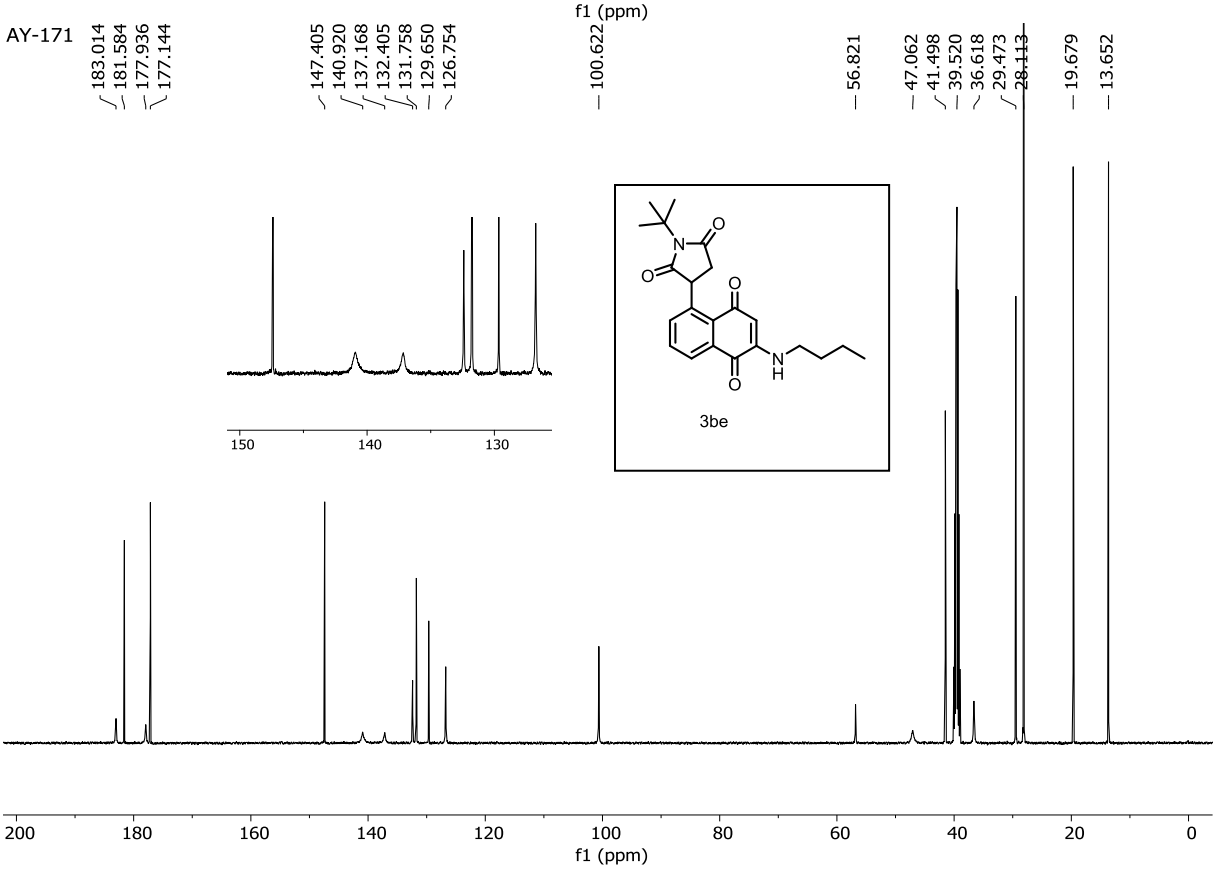

DG-82
11.060
8.042
8.015
7.693
7.658
7.556
7.544
7.532
5.591
4.360
3.350
3.160
3.147
3.133
3.119
2.913
2.603
2.589
2.568
2.555
2.500
1.554
1.538
1.524
1.324
1.309
0.904
0.889
0.875
3bb
1.02
1.02
2.00
1.01
1.00
1.01
2.05
1.00
1.01
2.06
2.18
3.04
f1 (ppm)

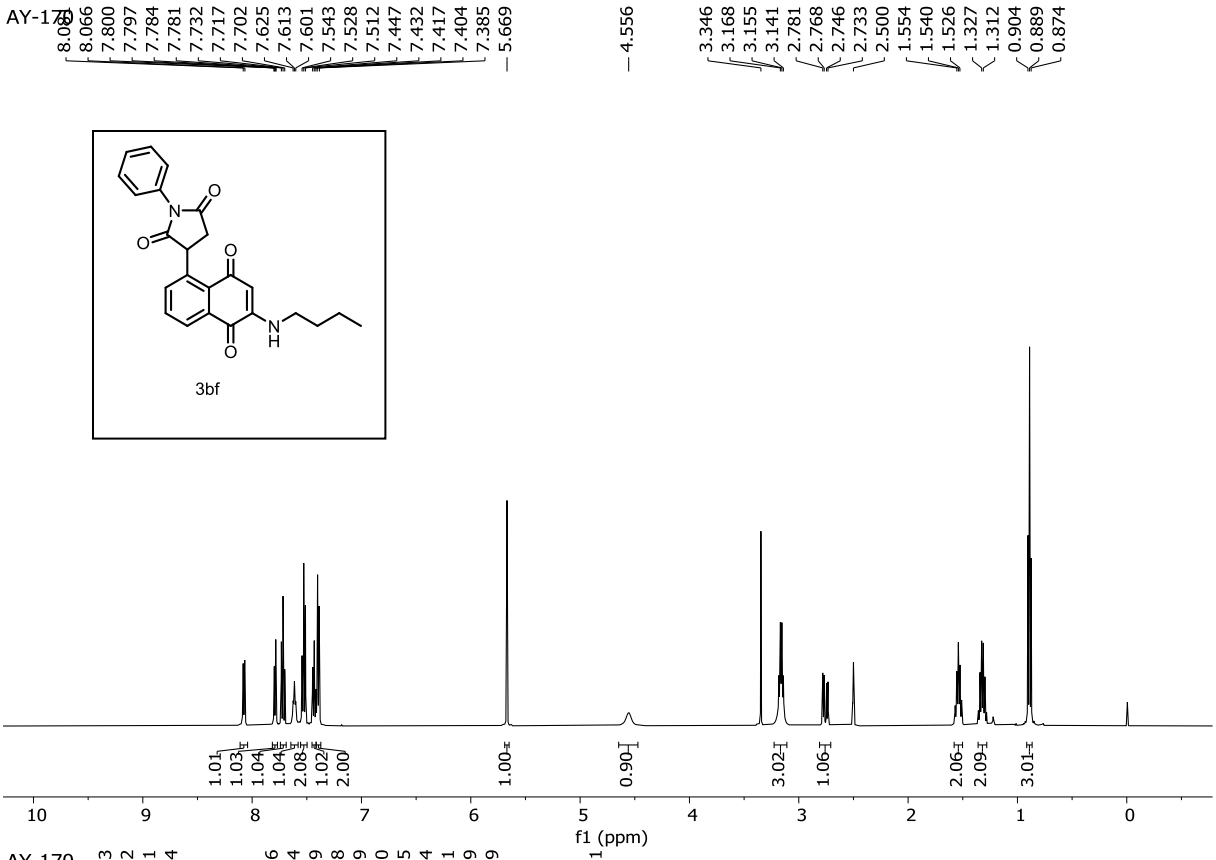

DG-82
183.229
181.605
178.476
177.797
147.543
140.785
136.736
132.352
131.893
129.826
126.826
100.532
48.661
41.519
39.520
37.820
29.429
19.707
13.690
3bb
f1 (ppm)

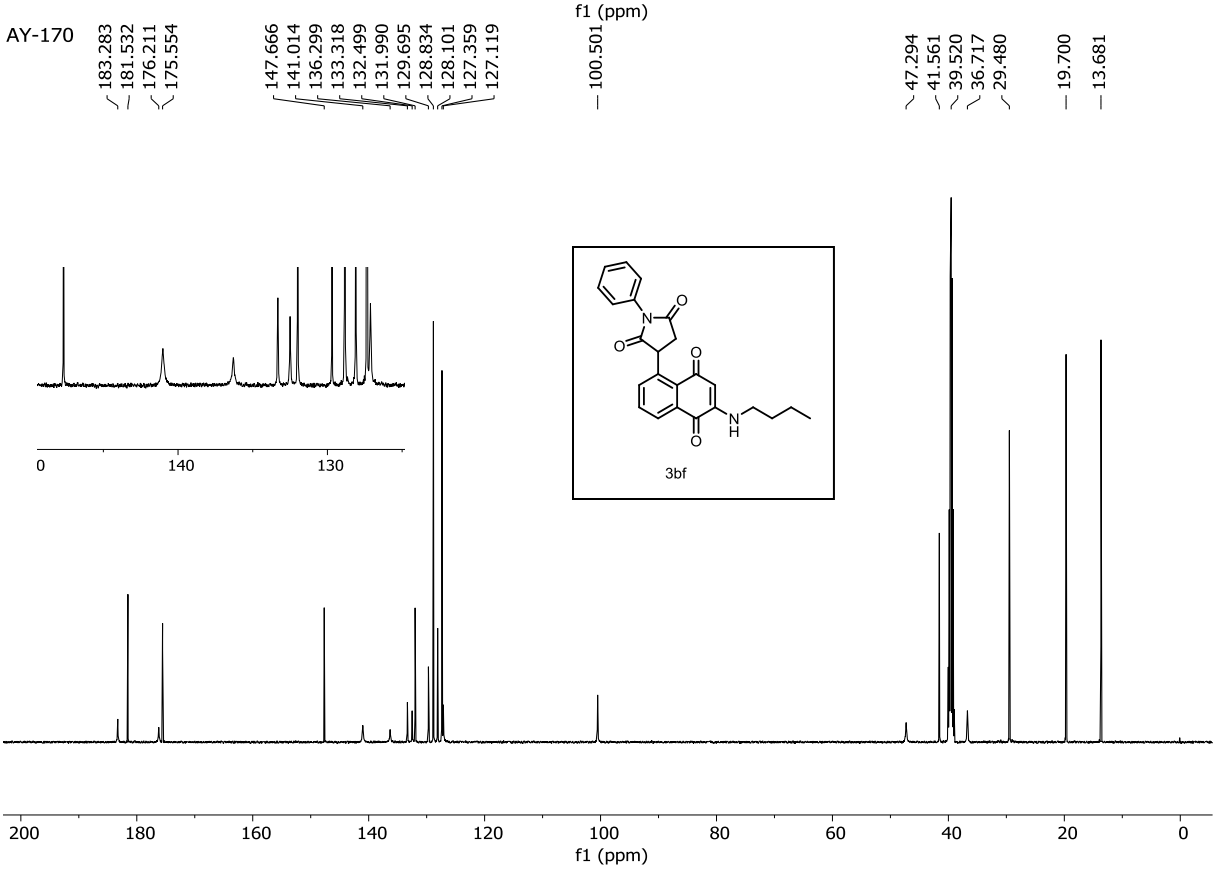

AY-169
8.047
8.035
8.030
7.715
7.664
7.548
7.536
7.523
5.585
4.338
3.520
3.443
3.340
3.138
3.125
2.967
2.588
2.575
2.553
2.541
2.500
1.538
1.523
1.508
1.314
1.299
1.166
1.152
1.138
0.893
0.879
0.864
3bc
0.84
2.00
2.00
1.00
4.5
4.0
3.5
3.0
f1 (ppm)
1.00
2.01
1.02
1.00
0.84
2.00
2.00
1.00
1.02
2.00
2.12
3.00
3.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
AY-169
183.118
181.538
176.881
176.121
147.515
140.955
136.461
132.395
131.891
129.746
126.932
100.508
47.175
41.513
39.520
36.483
32.980
29.452
19.686
13.661
12.812
3bc
50
140
130
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

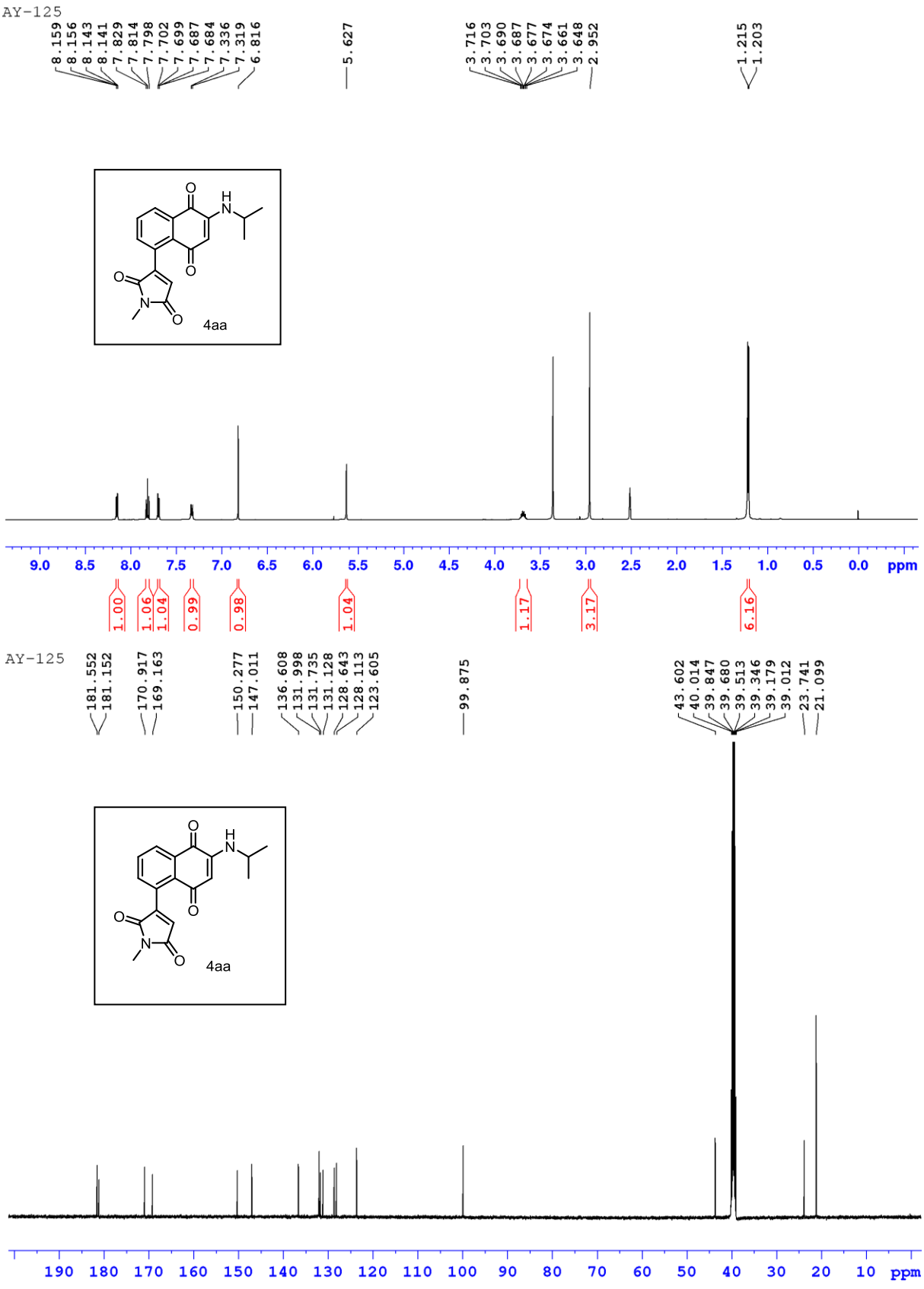

DG-81-R
8.060
8.048
8.042
7.732
7.675
7.600
7.588
7.576
7.374
7.324
7.290
7.255
5.608
4.733
4.703
4.616
4.586
4.492
3.347
3.168
3.155
3.141
3.127
3.074
2.689
2.676
2.654
2.641
2.500
1.554
1.539
1.525
1.328
1.313
0.908
0.893
0.878
3bd
1.04
1.07
0.82
2.10
0.95
4.5
4.0
3.5
3.0
f1 (ppm)
1.00
2.03
1.02
4.08
1.01
1.00
1.04
1.07
0.82
2.10
0.95
1.04
2.08
2.10
3.09
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
DG-81-R
183.170
181.525
176.950
176.216
147.611
140.925
136.604
136.261
132.395
131.950
129.780
128.361
127.534
127.212
127.002
100.465
47.272
41.528
41.423
39.520
36.464
29.439
19.691
13.671
3bd
140
130
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

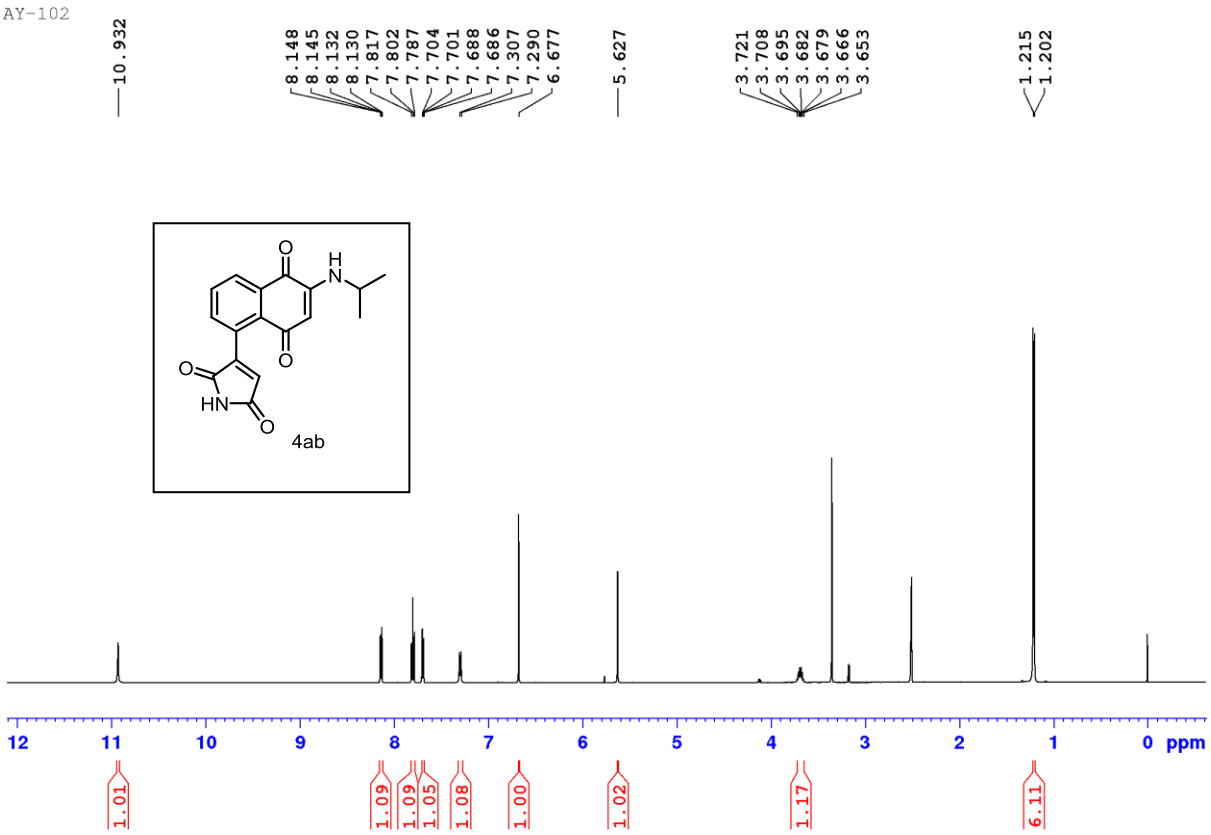

AY-171
8.034
8.025
8.016
7.703
7.643
7.510
7.498
7.486
5.585
4.219
3.339
3.157
3.143
3.129
3.116
2.862
2.500
2.488
2.475
2.454
2.441
1.565
1.540
1.525
1.512
1.318
1.303
0.896
0.881
0.867
3be
0.86
2.03
1.00
4.0
3.5
3.0
f1 (ppm)
1.00
2.00
1.00
1.00
0.86
2.03
1.00
1.02
9.05
2.08
2.07
3.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

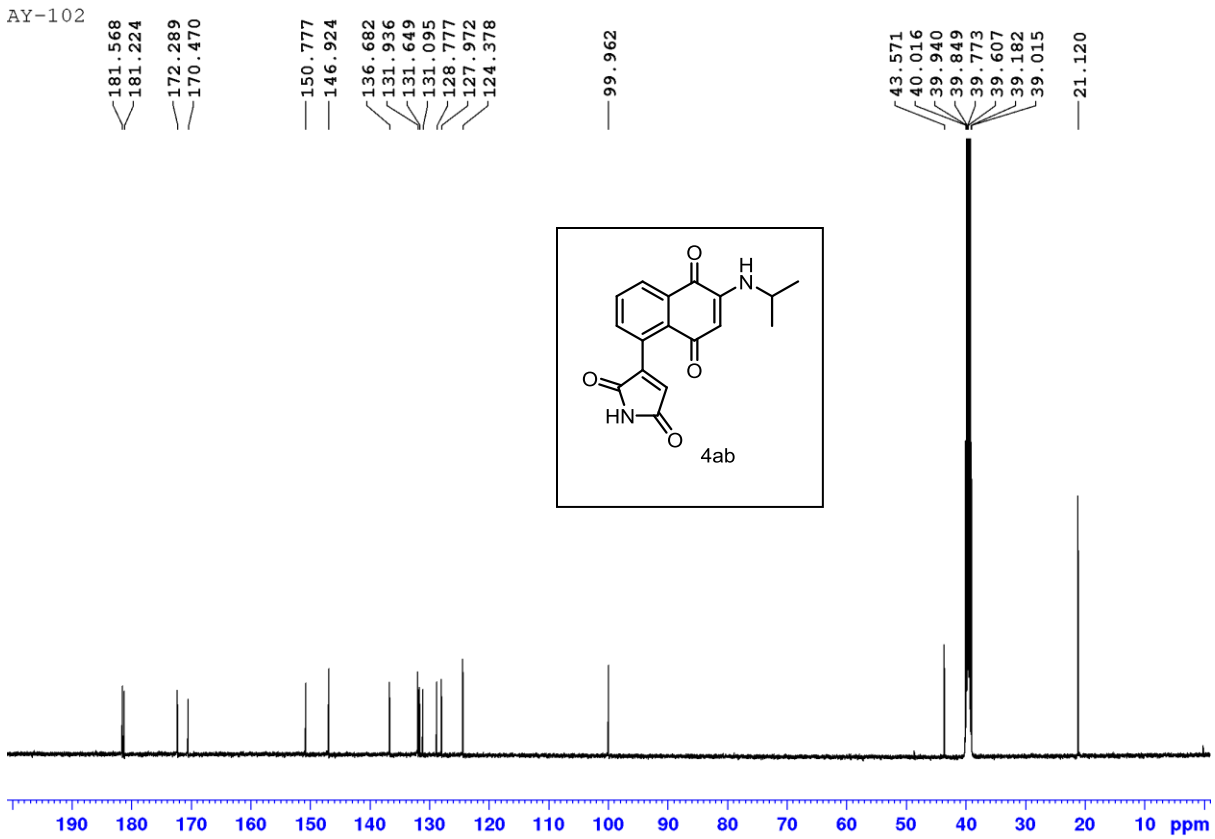

AY-171
183.014
181.584
177.936
177.144
147.405
140.920
137.168
132.405
131.758
129.650
126.754
100.622
56.821
47.062
41.498
39.520
36.618
29.473
28.113
19.679
13.652
3be
150
140
130
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

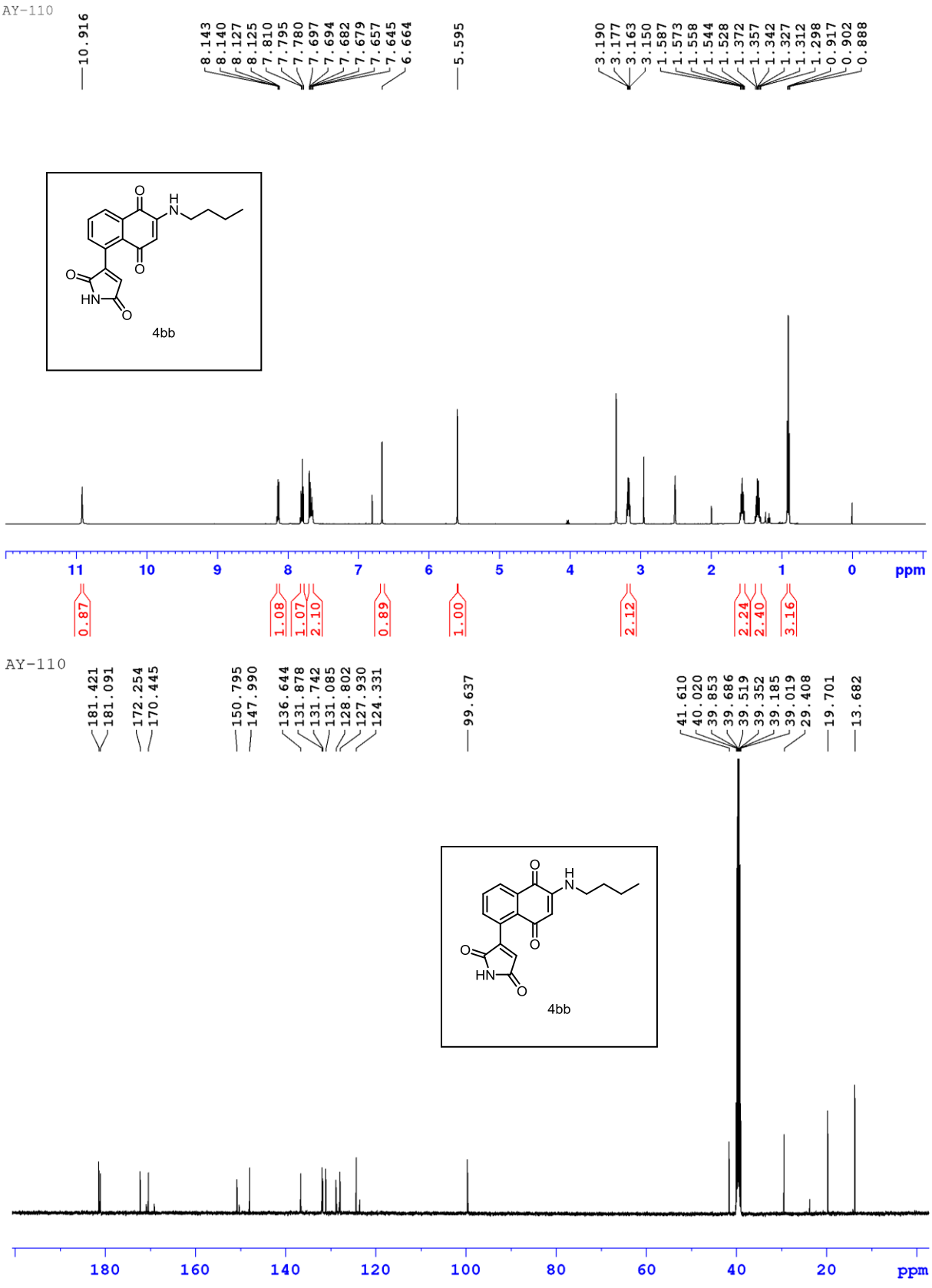

AY-170
8.080
8.066
7.800
7.797
7.784
7.781
7.732
7.717
7.702
7.625
7.613
7.601
7.543
7.528
7.512
7.447
7.432
7.417
7.404
7.385
5.669
4.556
3.346
3.168
3.155
3.141
2.781
2.768
2.746
2.733
2.500
1.554
1.540
1.526
1.327
1.312
0.904
0.889
0.874
3bf
1.01
1.03
1.04
1.04
2.08
1.02
2.00
1.00
0.90
3.02
1.06
2.06
2.09
3.01
f1 (ppm)

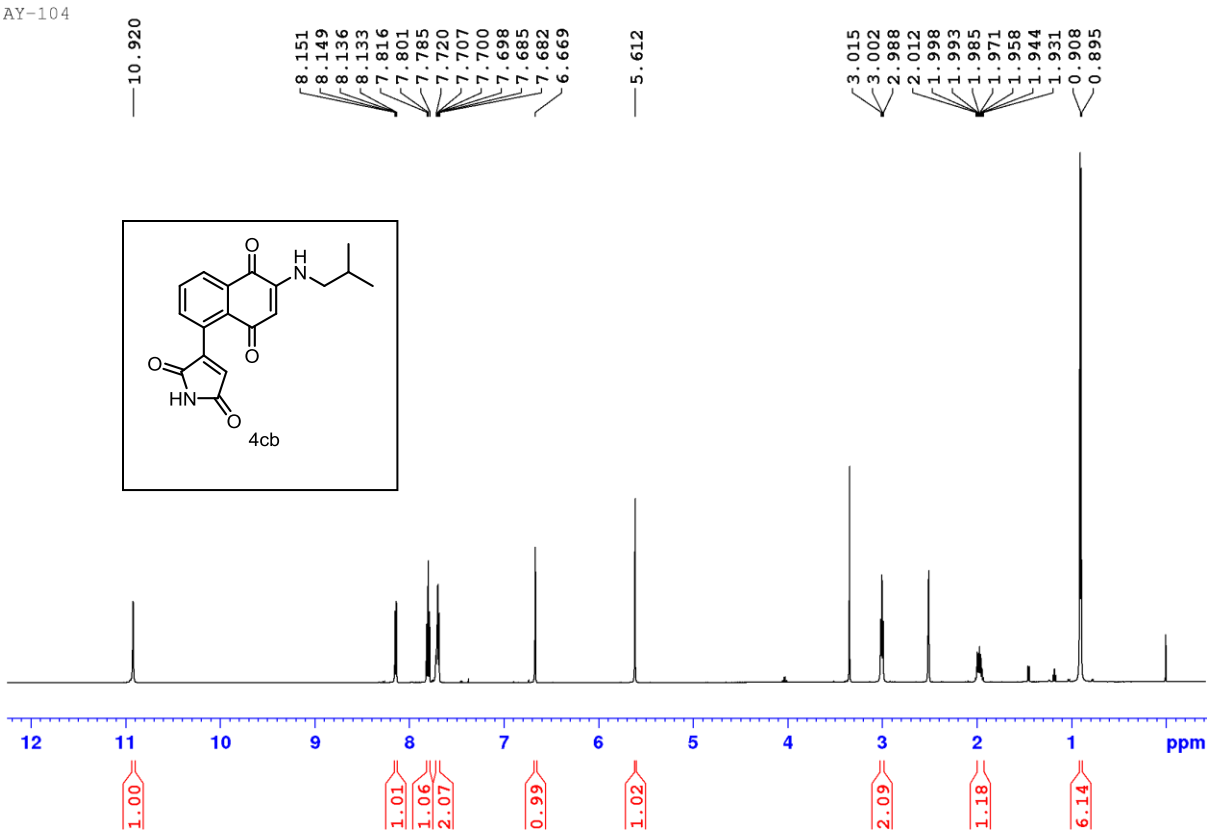

AY-170
183.283
181.532
176.211
175.554
147.666
141.014
136.299
133.318
132.499
131.990
129.695
128.834
128.101
127.359
127.119
100.501
47.294
41.561
39.520
36.717
29.480
19.700
13.681
0
140
130
3bf
f1 (ppm)

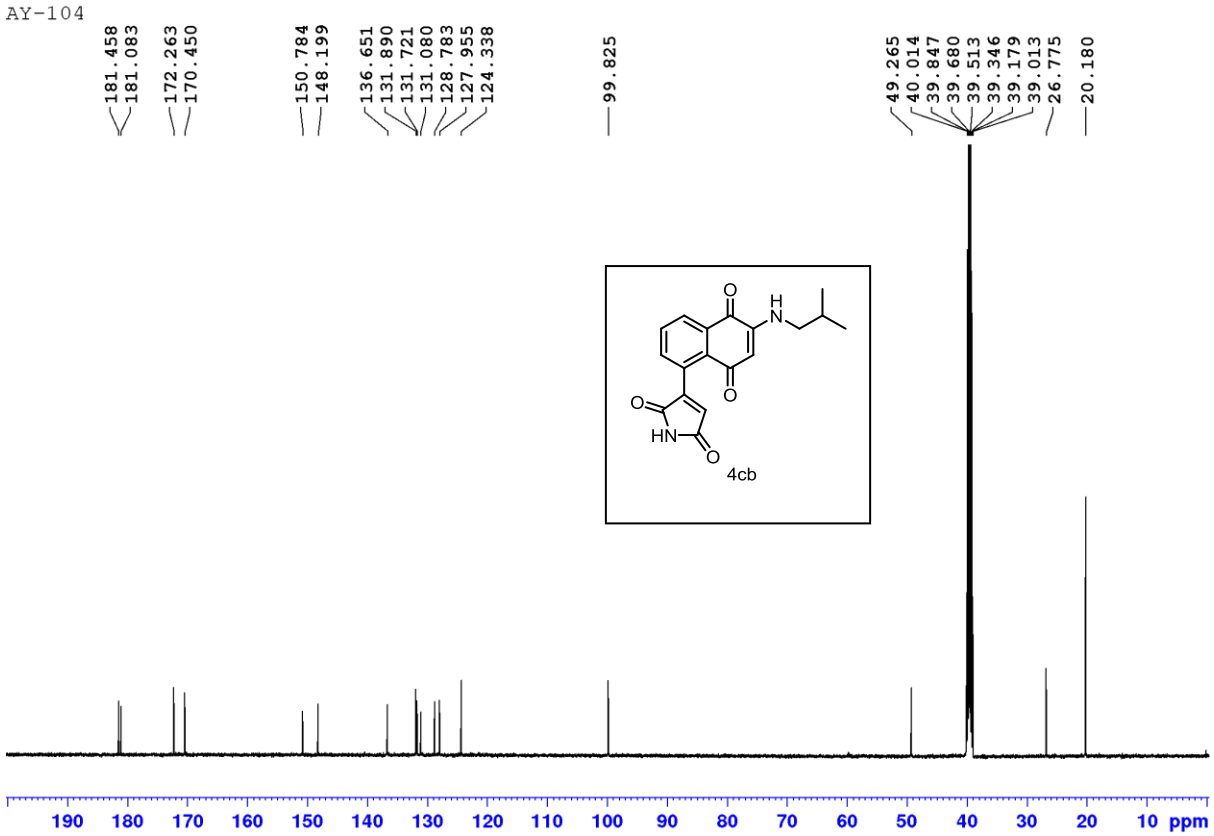

AY-125
8.159
8.156
8.143
8.141
7.829
7.814
7.798
7.702
7.699
7.687
7.684
7.336
7.319
6.816
5.627
3.716
3.703
3.690
3.687
3.677
3.674
3.661
3.648
2.952
1.215
1.203
4aa
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.06
1.04
0.99
0.98
1.04
1.17
3.17
6.16
AY-125
181.552
181.152
170.917
169.163
150.277
147.011
136.608
131.998
131.735
131.128
128.643
128.113
123.605
99.875
43.602
40.014
39.847
39.680
39.513
39.346
39.179
39.012
23.741
21.099
4aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


AY-102
10.932
8.148
8.145
8.132
8.130
7.817
7.802
7.787
7.704
7.701
7.688
7.686
7.307
7.290
6.677
5.627
3.721
3.708
3.695
3.682
3.679
3.666
3.653
1.215
1.202
4ab
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.01
1.09
1.09
1.05
1.08
1.00
1.02
1.17
6.11


AY-102
181.568
181.224
172.289
170.470
150.777
146.924
136.682
131.936
131.649
131.095
128.777
127.972
124.378
99.962
43.571
40.016
39.940
39.849
39.773
39.607
39.182
39.015
21.120
4ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

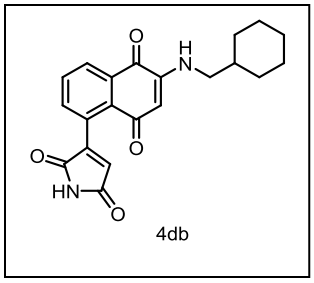

AY-110
10.916
8.143
8.140
8.127
8.125
7.810
7.795
7.780
7.697
7.694
7.682
7.679
7.657
7.645
6.664
5.595
3.190
3.177
3.163
3.150
1.587
1.573
1.558
1.544
1.528
1.372
1.357
1.342
1.327
1.312
1.298
0.917
0.902
0.888
4bb
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.87
1.08
1.07
2.10
0.89
1.00
2.12
2.24
2.40
3.16
AY-110
181.421
181.091
172.254
170.445
150.795
147.990
136.644
131.878
131.742
131.085
128.802
127.930
124.331
99.637
41.610
40.020
39.853
39.686
39.519
39.352
39.185
39.019
29.408
19.701
13.682
4bb
180
160
140
120
100
80
60
40
20
ppm


AY-104
10.920
8.151
8.149
8.136
8.133
7.816
7.801
7.785
7.720
7.707
7.700
7.698
7.685
7.682
6.669
5.612
3.015
3.002
2.988
2.012
1.998
1.993
1.985
1.971
1.958
1.944
1.931
0.908
0.895
4cb
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.06
2.07
0.99
1.02
2.09
1.18
6.14

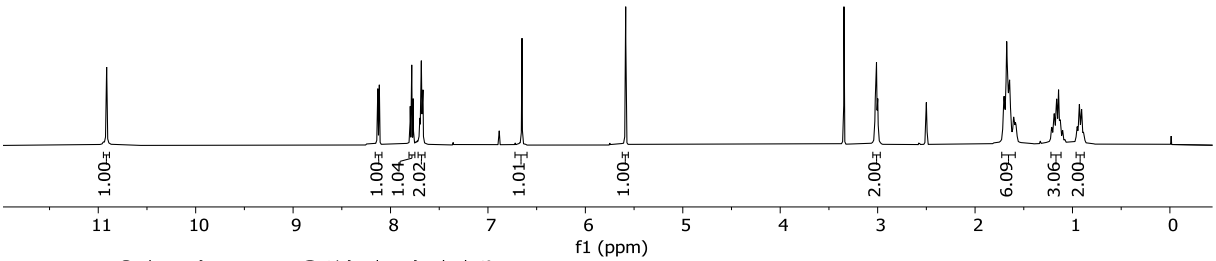

AY-104
181.458
181.083
172.263
170.450
150.784
148.199
136.651
131.890
131.721
131.080
128.783
127.955
124.338
99.825
49.265
40.014
39.847
39.680
39.513
39.346
39.179
39.013
26.775
20.180
4cb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

AY-124-R1

10.914
8.130
8.114
7.797
7.782
7.767
7.700
7.666
6.649
5.586
3.346
3.025
3.012
2.999
2.500
1.708
1.604
1.210
1.101
0.951
0.885

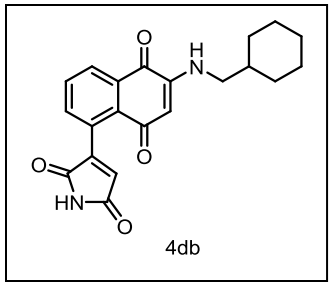


4db

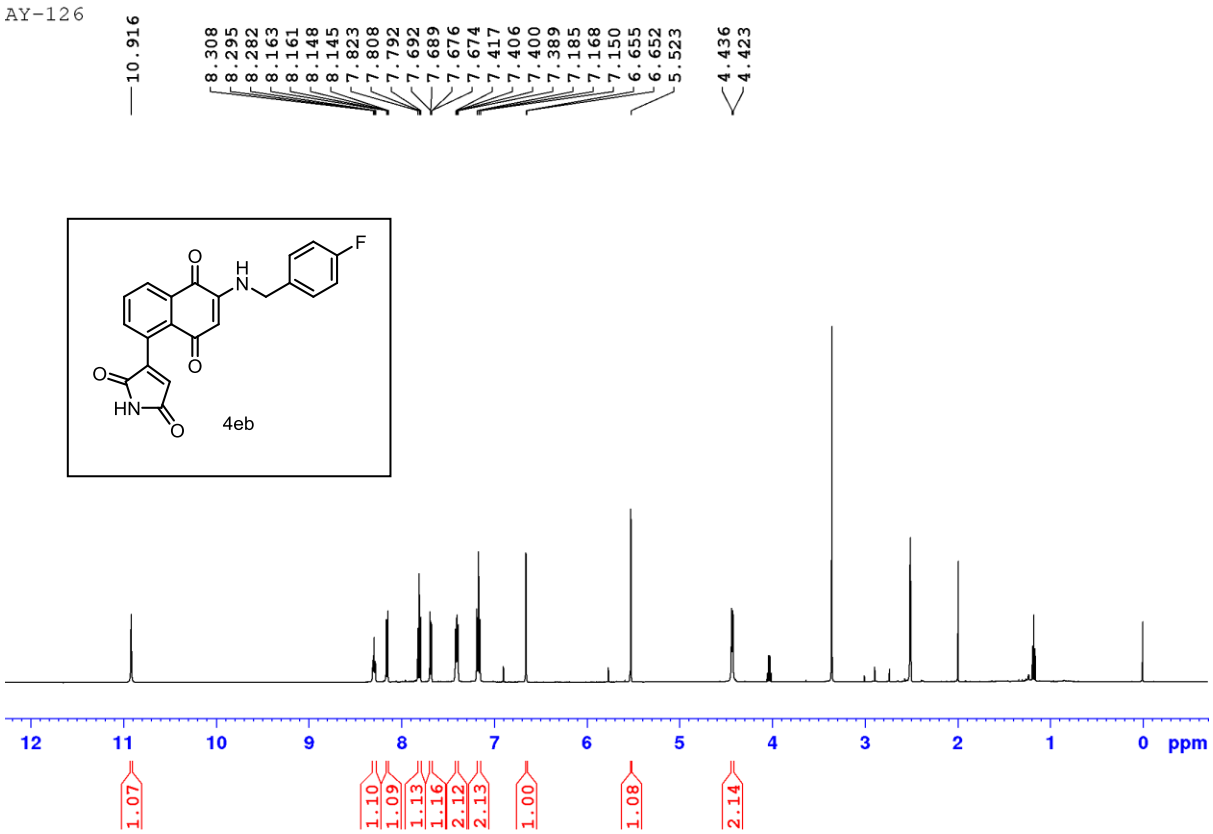


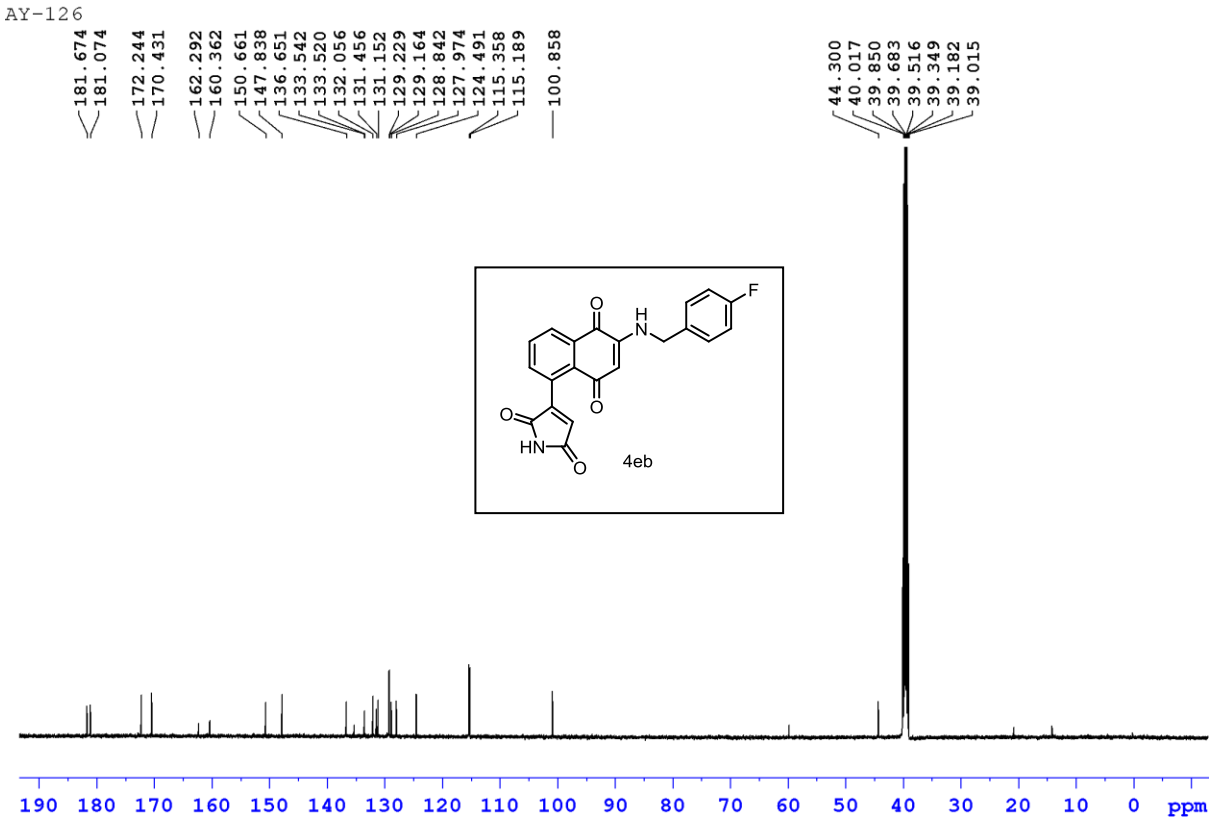
AY-124

181.409
181.054
172.261
170.467
150.820
148.222
136.627
135.254
131.861
131.737
131.094
128.794
127.943
124.311
99.785
48.030
39.520
36.091
30.480
25.968
25.352

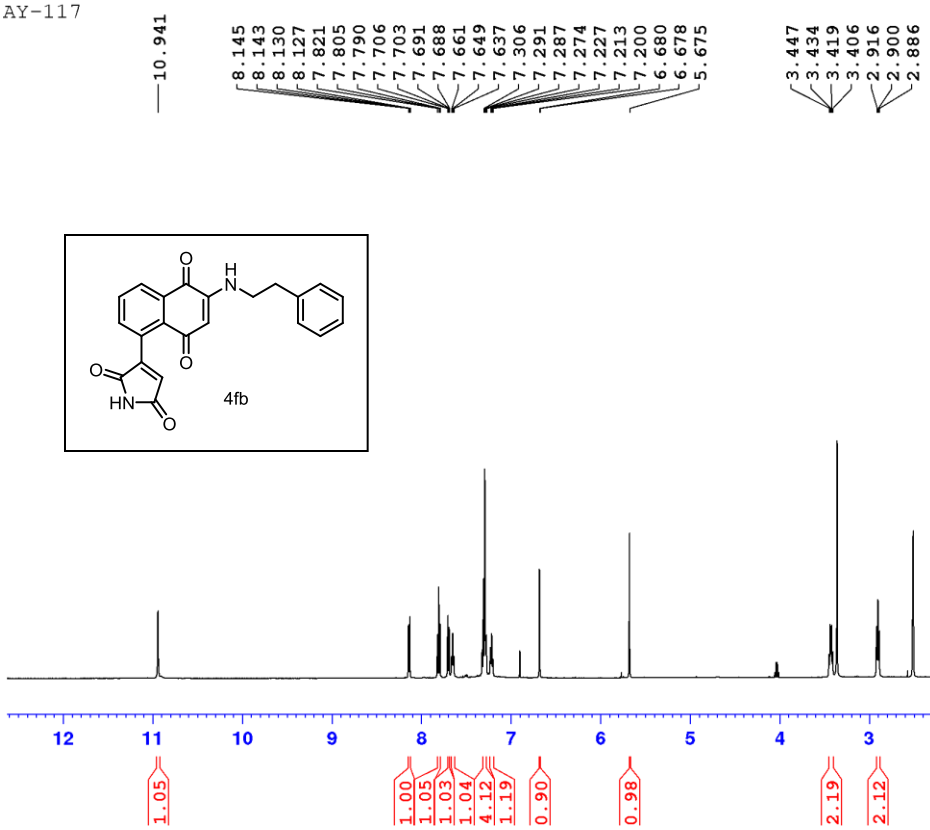


4db

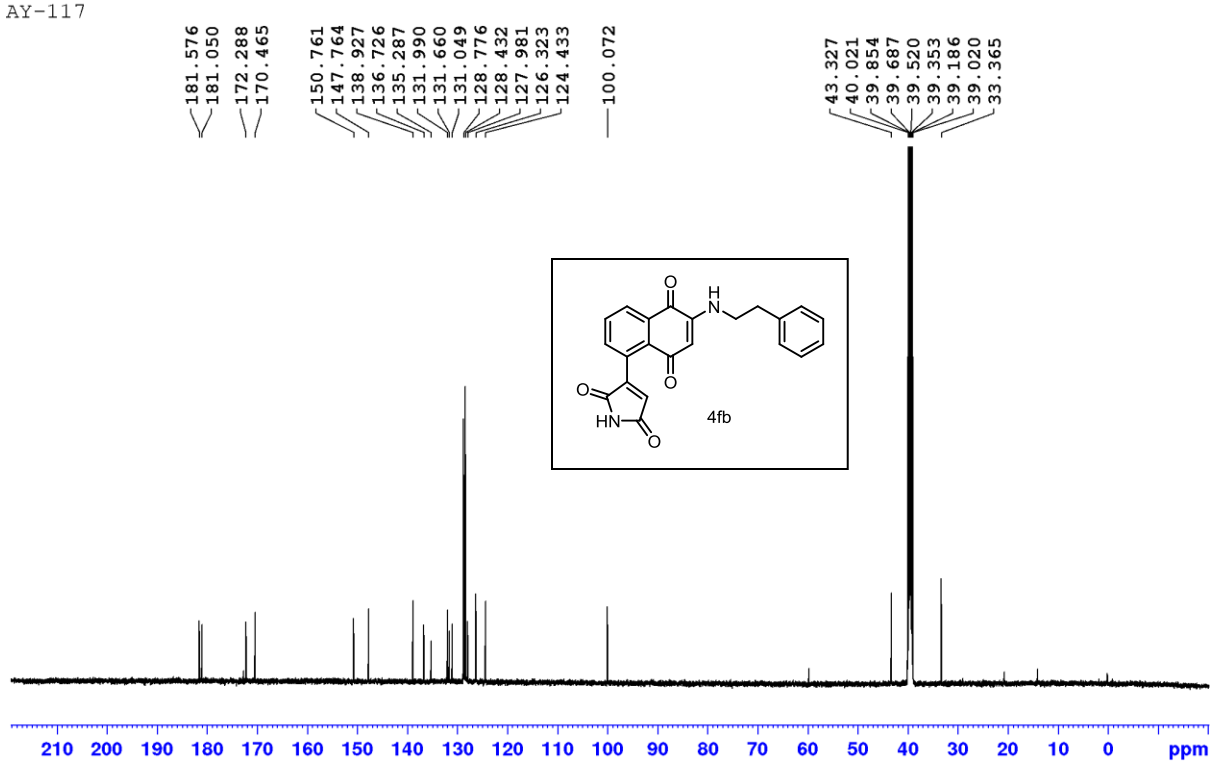

AY-126
10.916
8.308
8.295
8.282
8.163
8.161
8.148
8.145
7.823
7.808
7.792
7.692
7.689
7.676
7.674
7.417
7.406
7.400
7.389
7.185
7.168
7.150
6.655
6.652
5.523
4.436
4.423
4eb
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.07
1.10
1.09
1.13
1.16
2.12
2.13
1.00
1.08
2.14

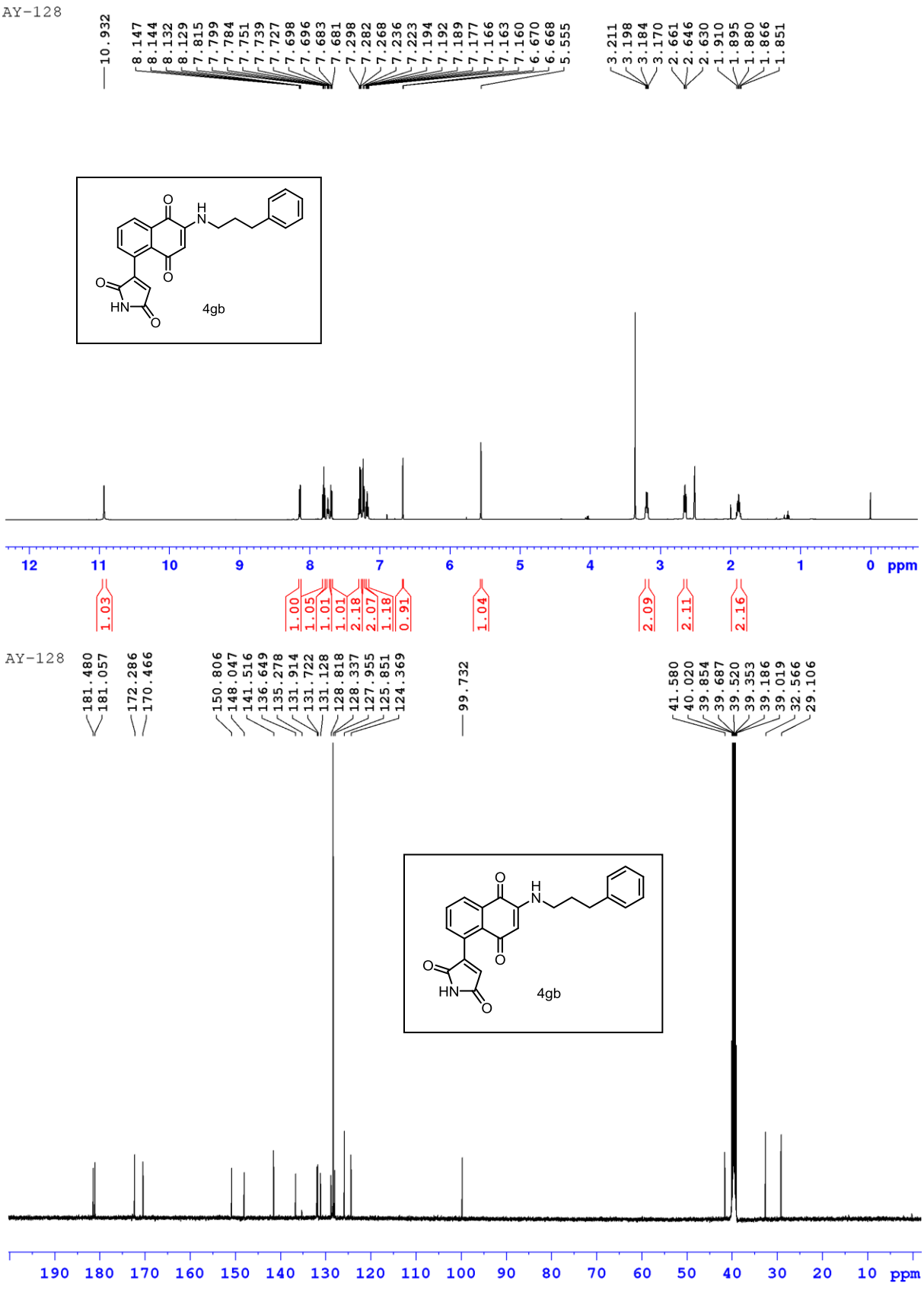

AY-126
181.674
181.074
172.244
170.431
162.292
160.362
150.661
147.838
136.651
133.542
133.520
132.056
131.456
131.152
129.229
129.164
128.842
127.974
124.491
115.358
115.189
100.858
44.300
40.017
39.850
39.683
39.516
39.349
39.182
39.015
4eb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

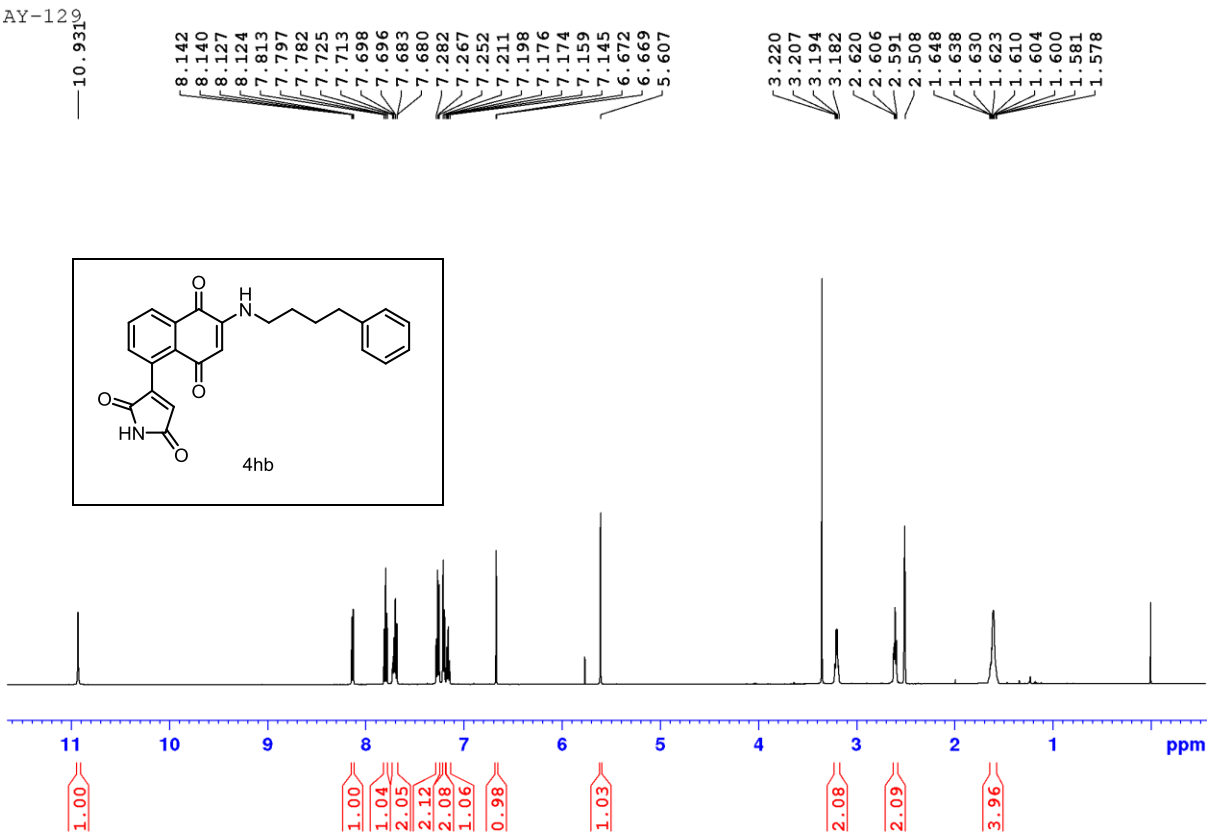
AY-117

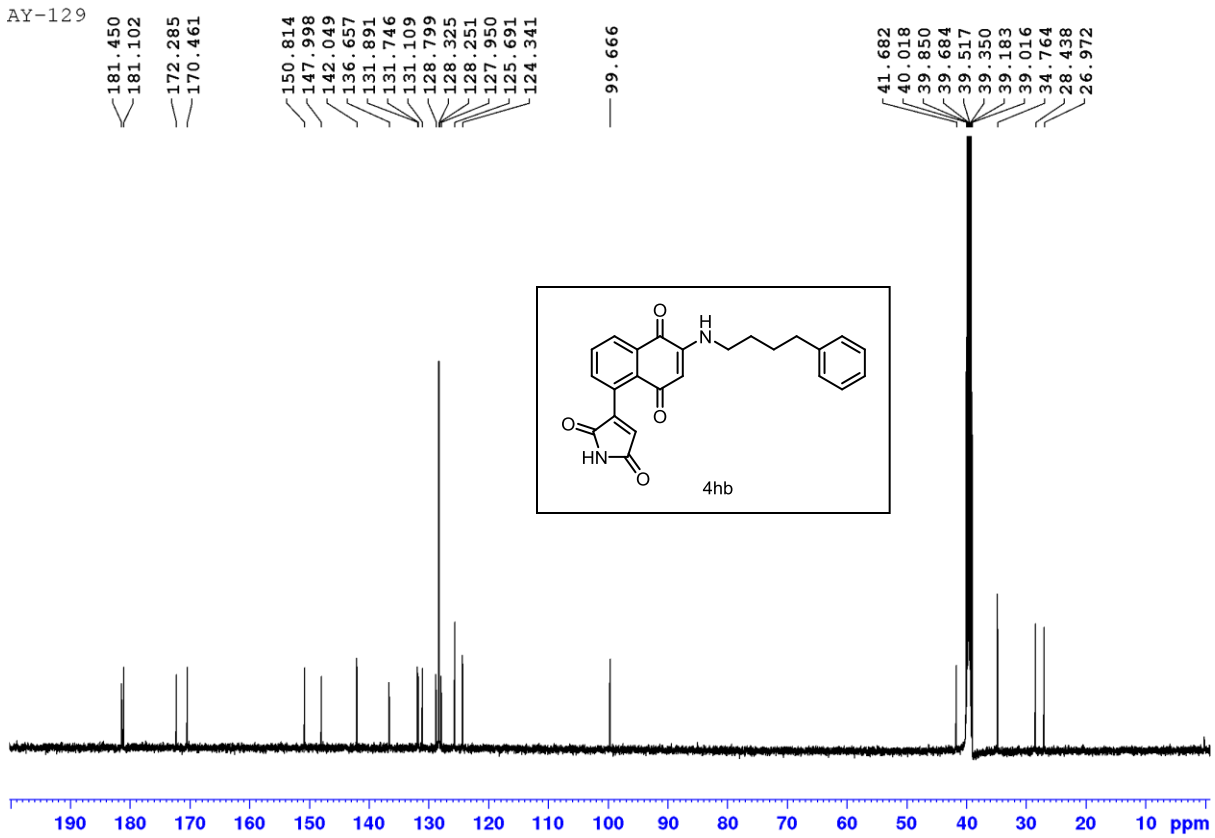

10.941
8.145
8.143
8.130
8.127
7.821
7.805
7.790
7.706
7.703
7.691
7.688
7.661
7.649
7.637
7.306
7.291
7.287
7.274
7.227
7.213
7.200
6.680
6.678
5.675
3.447
3.434
3.419
3.406
2.916
2.900
2.886
4fb
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.00
1.05
1.03
1.04
4.12
1.19
0.90
0.98
2.19
2.12

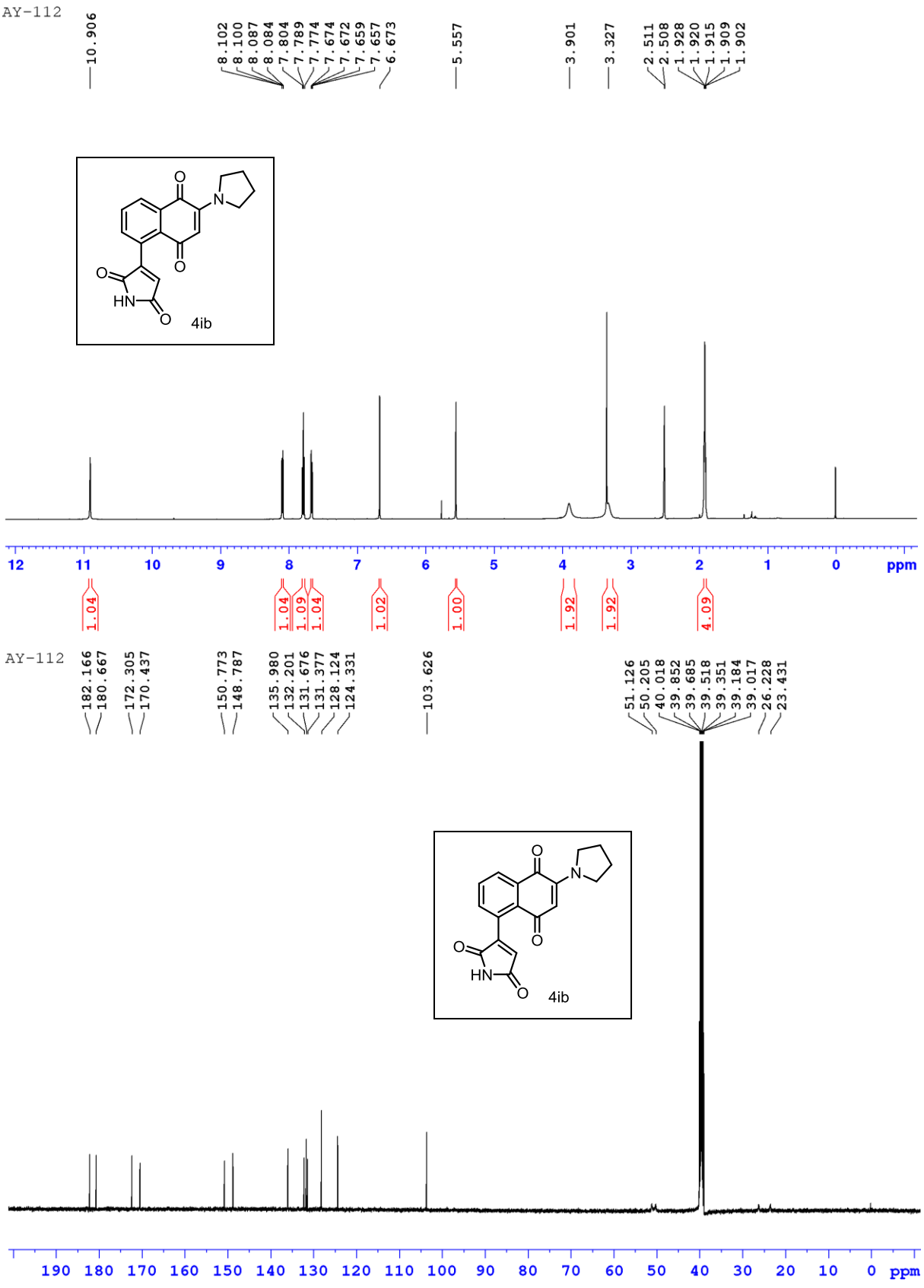
AY-117

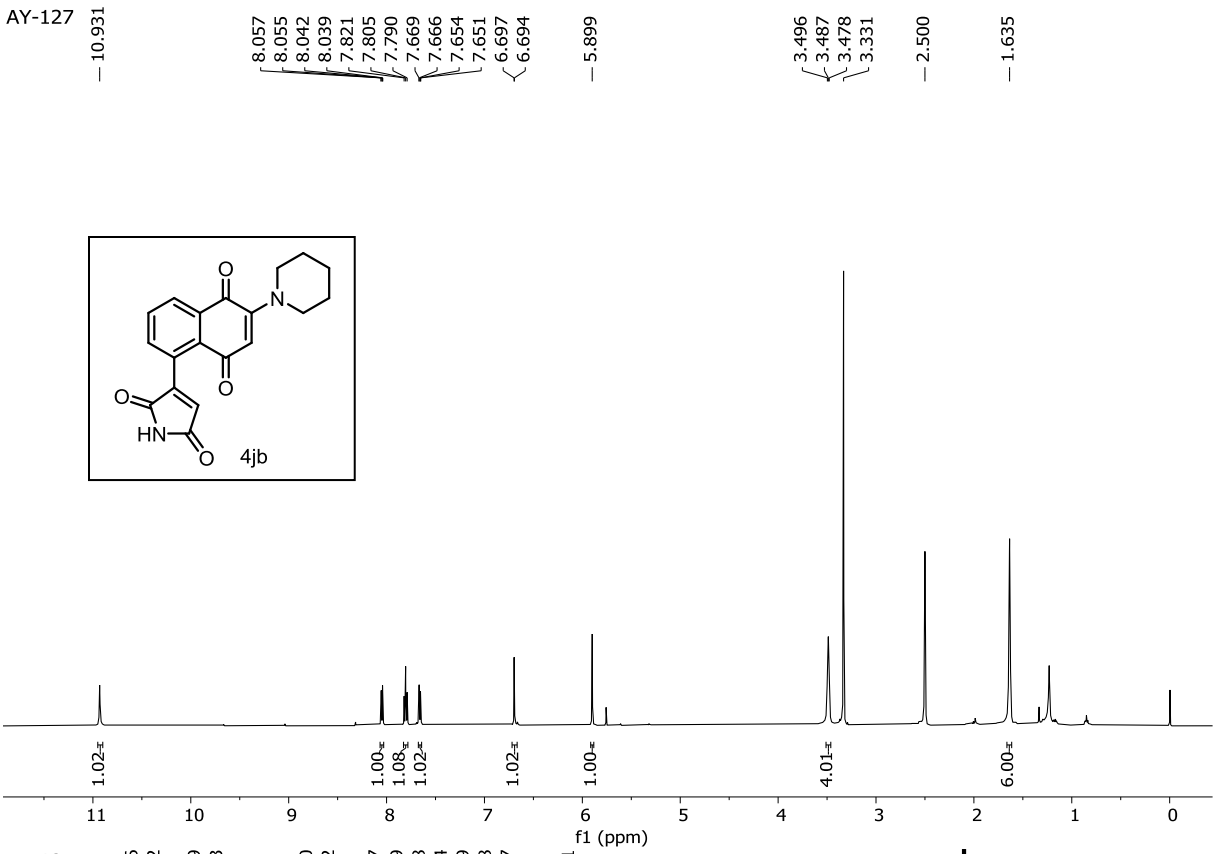

181.576
181.050
172.288
170.465
150.761
147.764
138.927
136.726
135.287
131.990
131.660
131.049
128.776
128.432
127.981
126.323
124.433
100.072
43.327
40.021
39.854
39.687
39.520
39.353
39.186
39.020
33.365
4fb
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

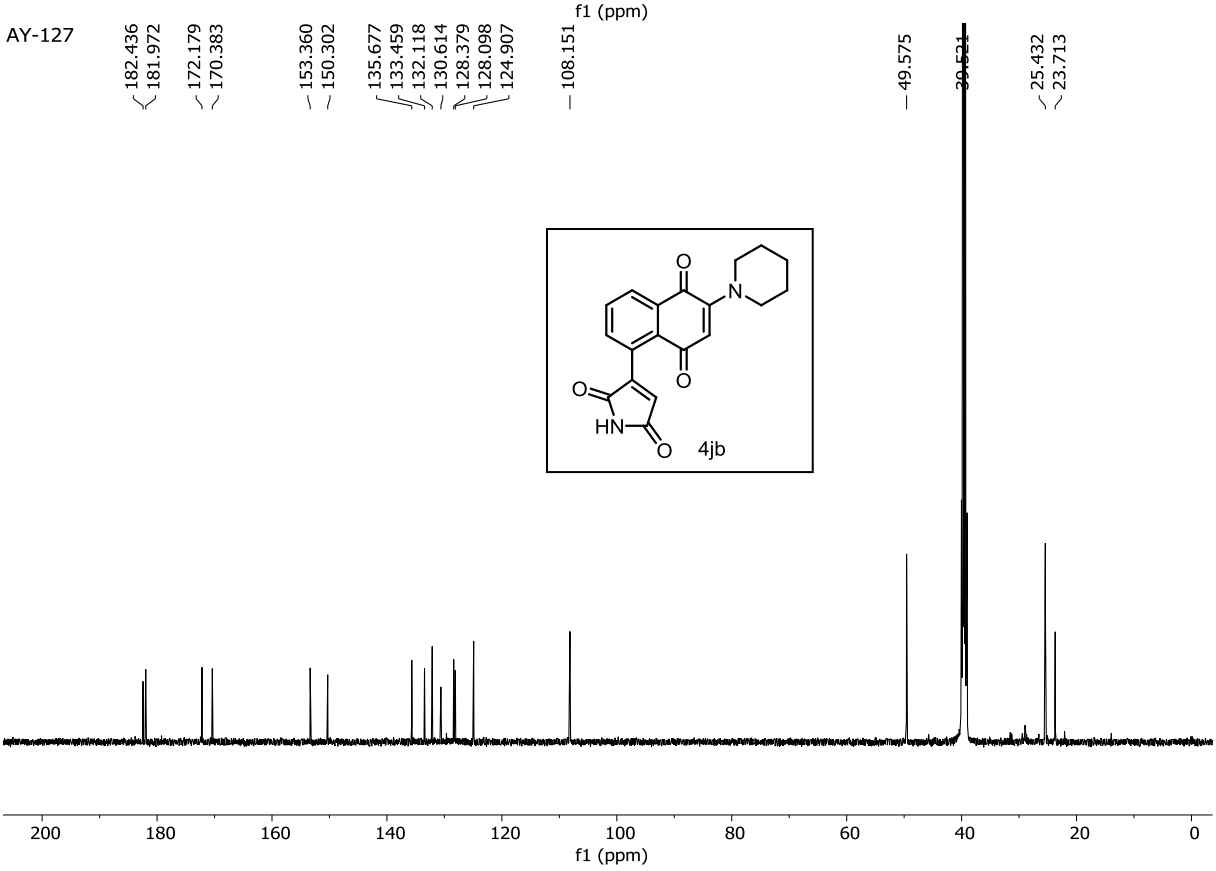

AY-128
10.932
8.147
8.144
8.132
8.129
7.815
7.799
7.784
7.751
7.739
7.727
7.698
7.696
7.683
7.681
7.298
7.282
7.268
7.236
7.223
7.194
7.192
7.189
7.177
7.166
7.163
7.160
6.670
6.668
5.555
3.211
3.198
3.184
3.170
2.661
2.646
2.630
1.910
1.895
1.880
1.866
1.851
4gb
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.00
1.05
1.01
1.01
2.18
2.07
1.18
0.91
1.04
2.09
2.11
2.16
AY-128
181.480
181.057
172.286
170.466
150.806
148.047
141.516
136.649
135.278
131.914
131.722
131.128
128.818
128.337
127.955
125.851
124.369
99.732
41.580
40.020
39.854
39.687
39.520
39.353
39.186
39.019
32.566
29.106
4gb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

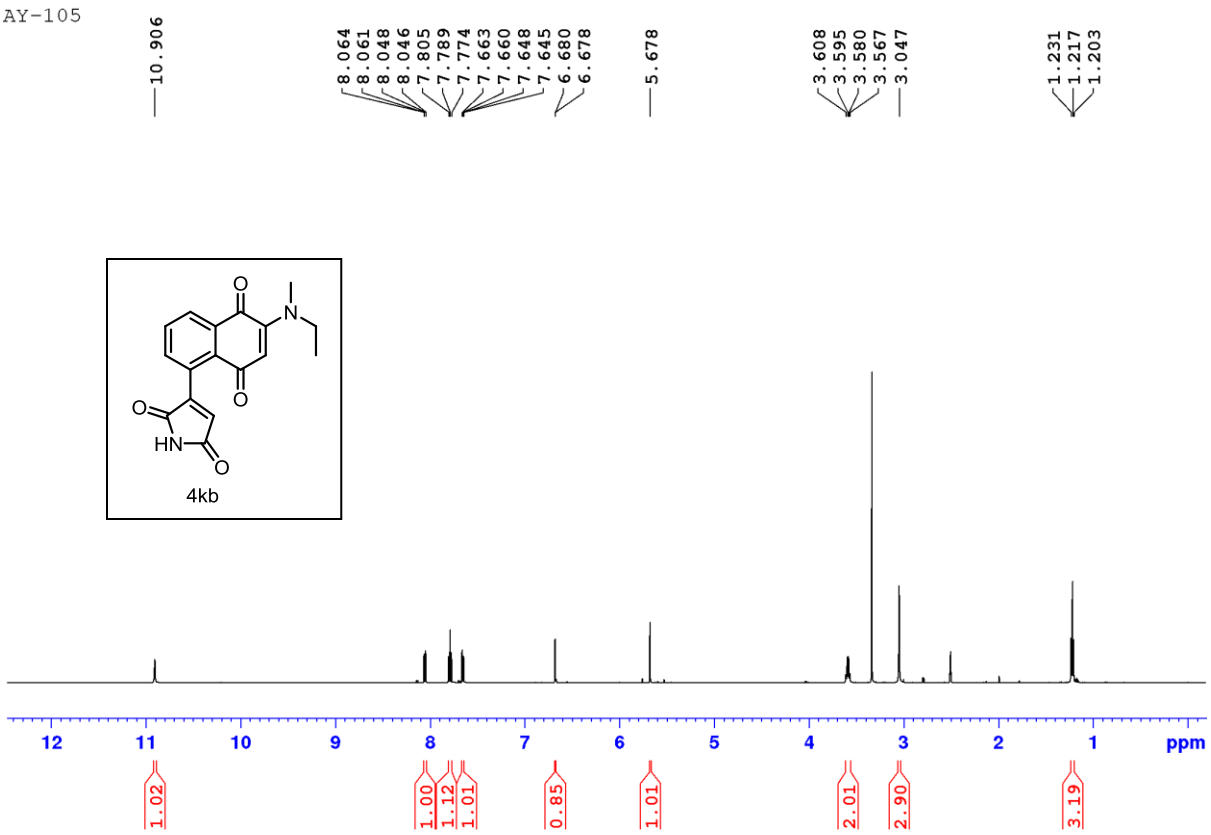

AY-129
10.931
8.142
8.140
8.127
8.124
7.813
7.797
7.782
7.725
7.713
7.698
7.696
7.683
7.680
7.282
7.267
7.252
7.211
7.198
7.176
7.174
7.159
7.145
6.672
6.669
5.607
3.220
3.207
3.194
3.182
2.620
2.606
2.591
2.508
1.648
1.638
1.630
1.623
1.610
1.604
1.600
1.581
1.578
4hb
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.04
2.05
2.12
2.08
1.06
0.98
1.03
2.08
2.09
3.96

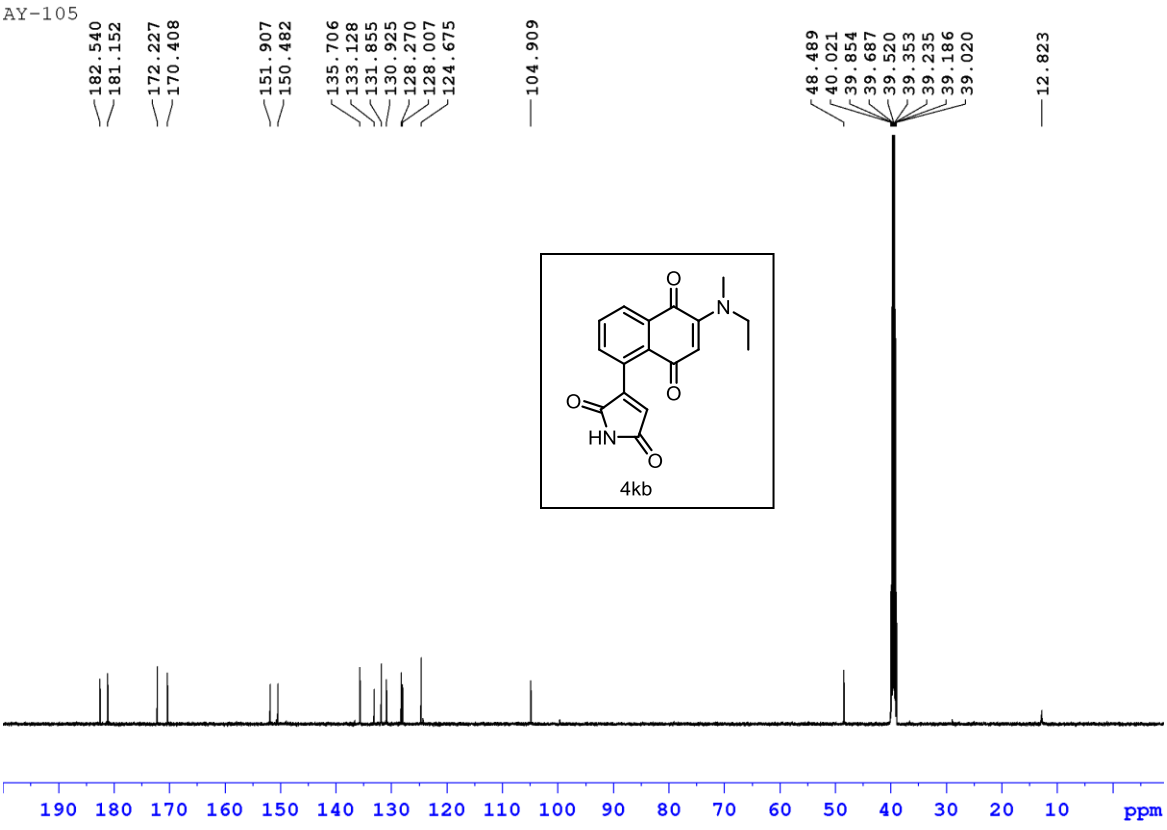

AY-129
181.450
181.102
172.285
170.461
150.814
147.998
142.049
136.657
131.891
131.746
131.109
128.799
128.325
128.251
127.950
125.691
124.341
99.666
41.682
40.018
39.850
39.684
39.517
39.350
39.183
39.016
34.764
28.438
26.972
4hb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

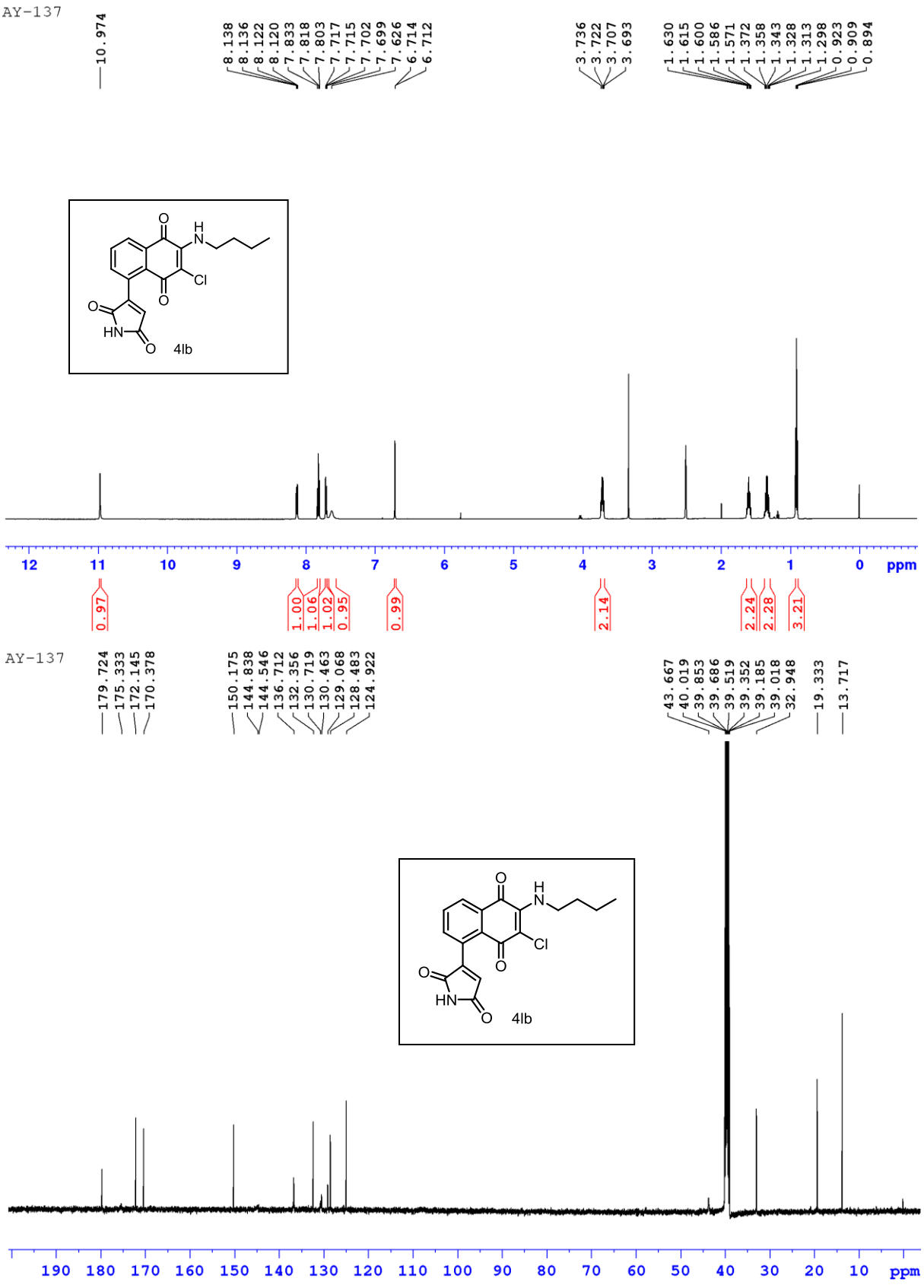

AY-112
10.906
8.102
8.100
8.087
8.084
7.804
7.789
7.774
7.674
7.672
7.659
7.657
6.673
5.557
3.901
3.327
2.511
2.508
1.928
1.920
1.915
1.909
1.902
4ib
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.04
1.09
1.04
1.02
1.00
1.92
1.92
4.09
AY-112
182.166
180.667
172.305
170.437
150.773
148.787
135.980
132.201
131.676
131.377
128.124
124.331
103.626
51.126
50.205
40.018
39.852
39.685
39.518
39.351
39.184
39.017
26.228
23.431
4ib
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

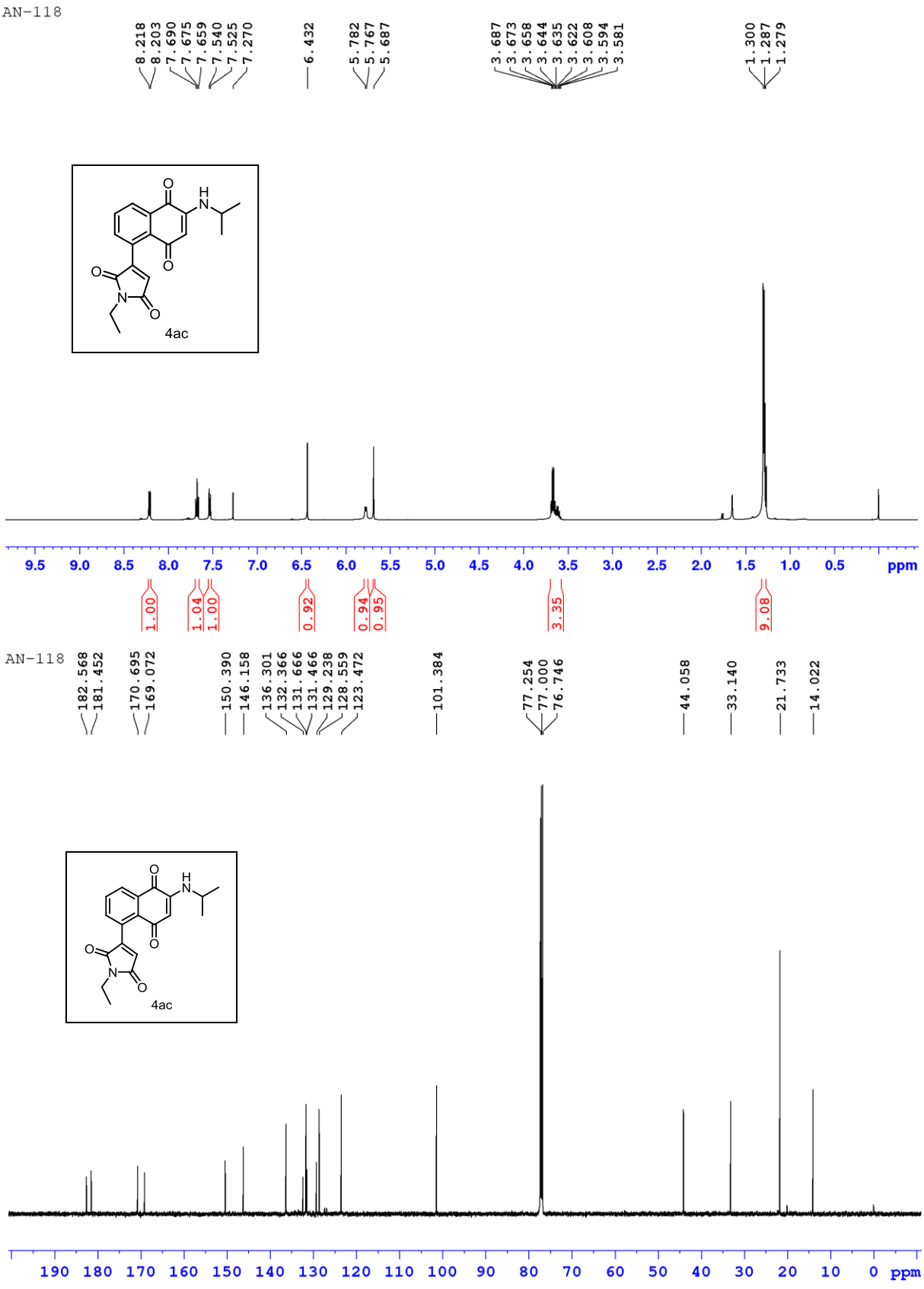

AY-127
10.931
8.057
8.055
8.042
8.039
7.821
7.805
7.790
7.669
7.666
7.654
7.651
6.697
6.694
5.899
3.496
3.487
3.478
3.331
2.500
1.635
4jb
1.02
1.00
1.08
1.02
1.02
1.00
4.01
6.00
f1 (ppm)

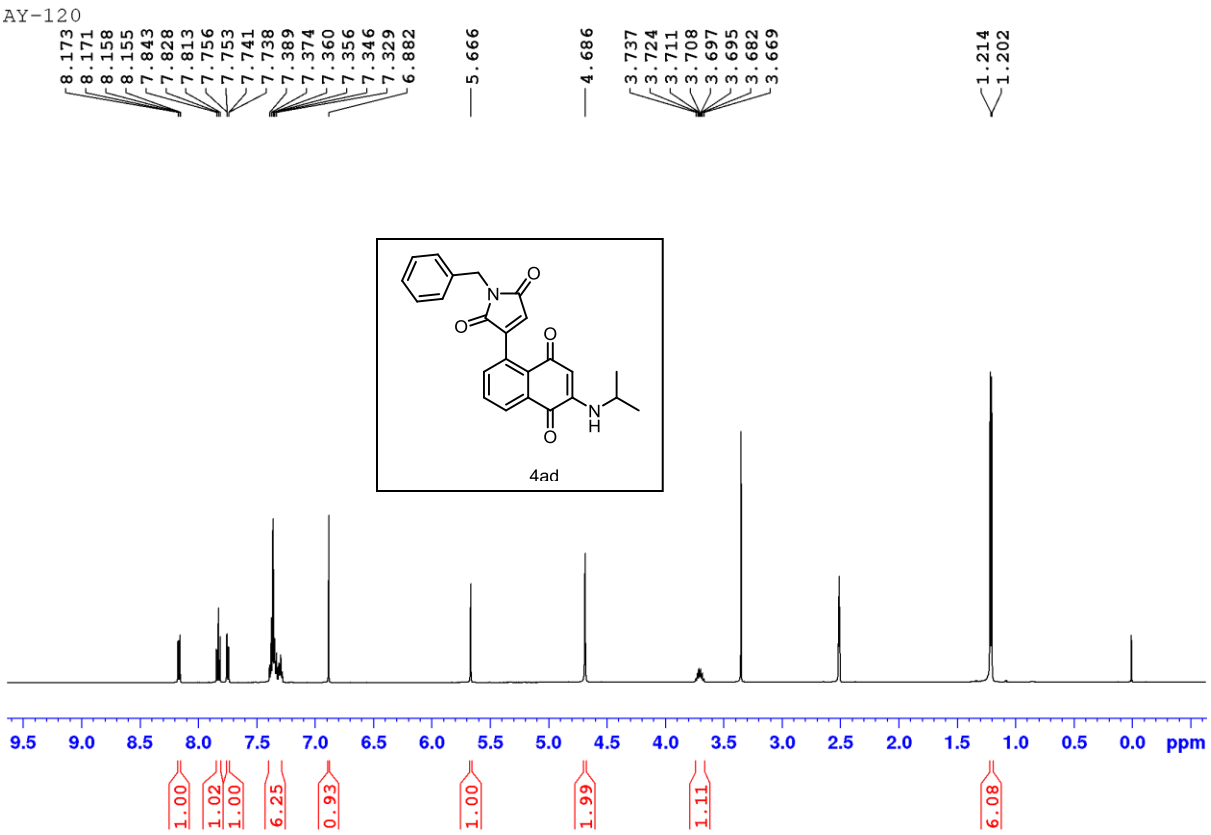

AY-127
182.436
181.972
172.179
170.383
153.360
150.302
135.677
133.459
132.118
130.614
128.379
128.098
124.907
108.151
49.575
39.521
25.432
23.713
4jb
f1 (ppm)

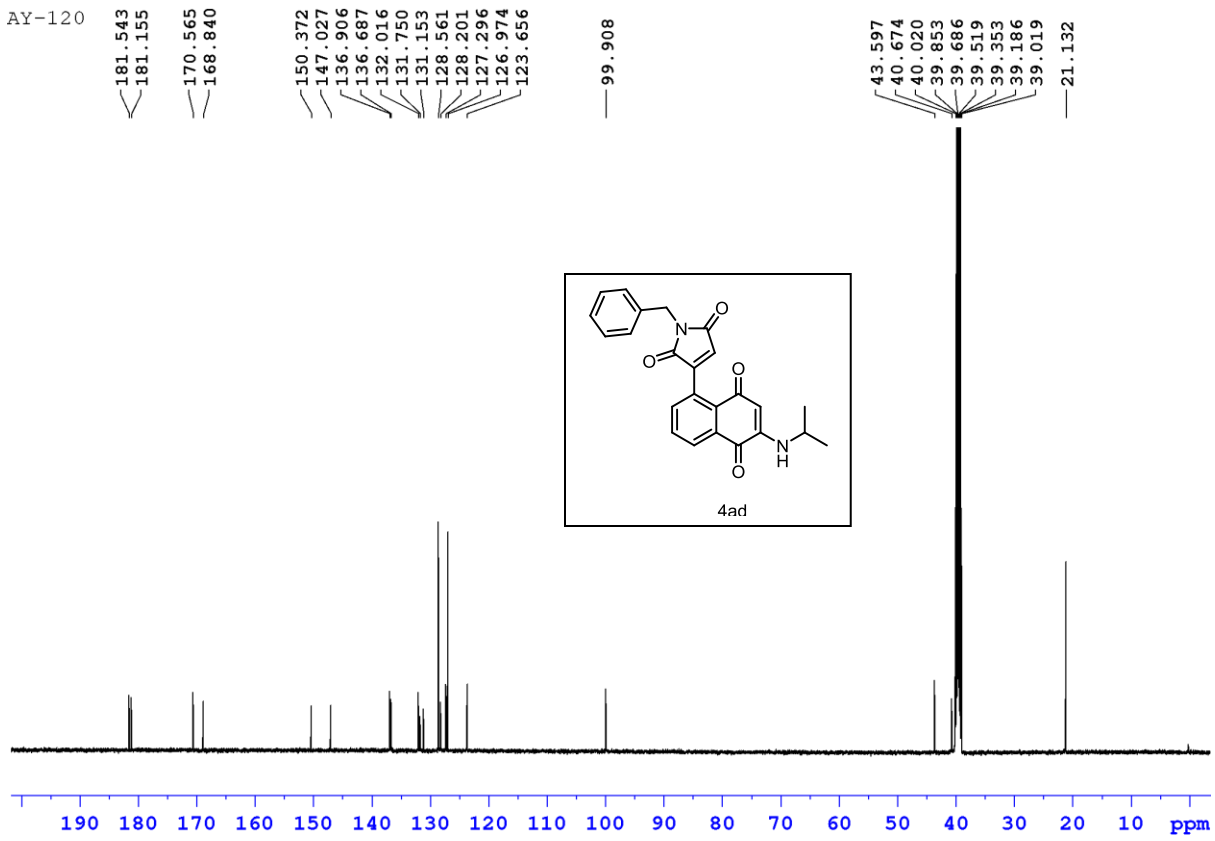

AY-105
10.906
8.064
8.061
8.048
8.046
7.805
7.789
7.774
7.663
7.660
7.648
7.645
6.680
6.678
5.678
3.608
3.595
3.580
3.567
3.047
1.231
1.217
1.203
4kb
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.00
1.12
1.01
0.85
1.01
2.01
2.90
3.19

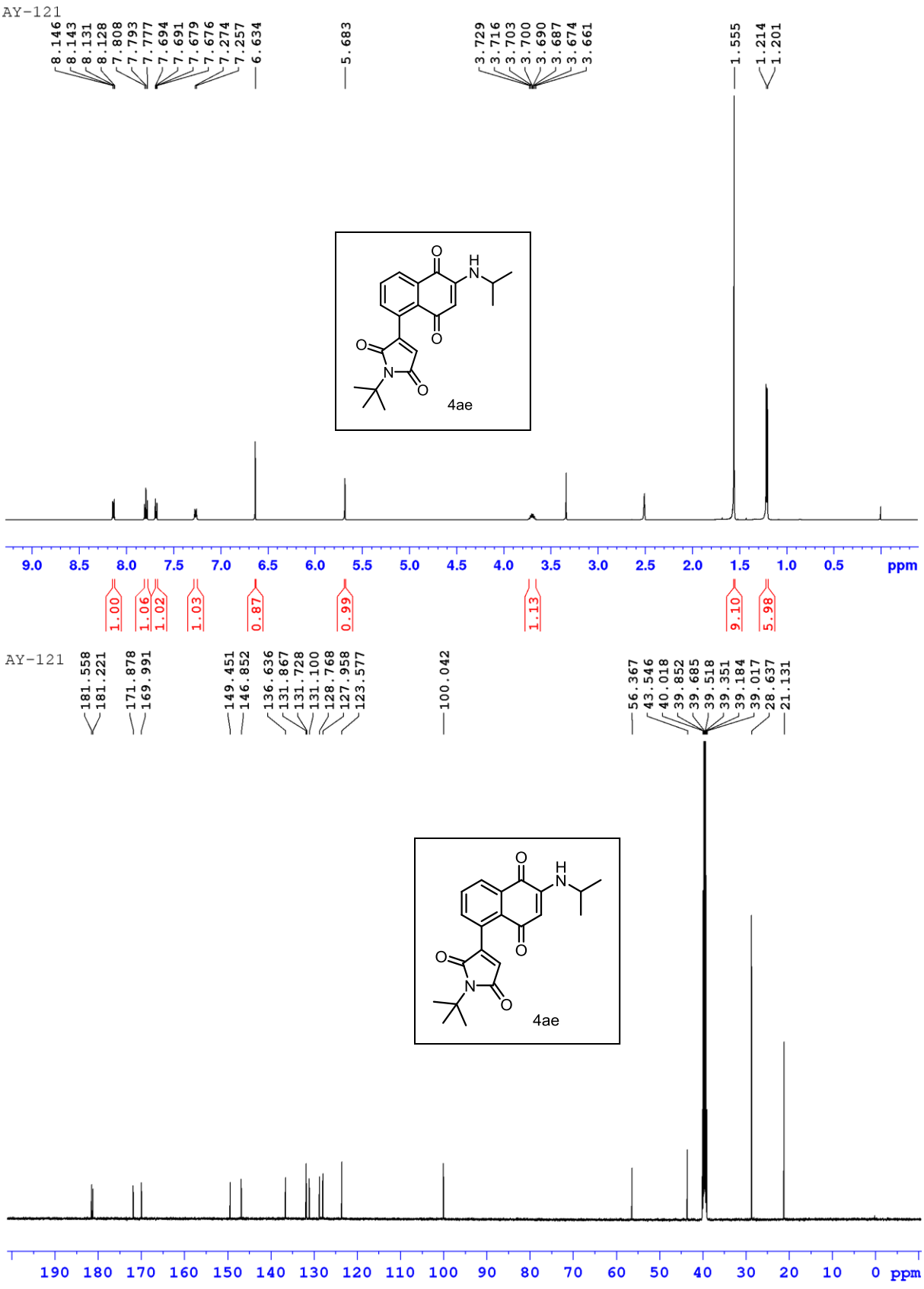

AY-105
182.540
181.152
172.227
170.408
151.907
150.482
135.706
133.128
131.855
130.925
128.270
128.007
124.675
104.909
48.489
40.021
39.854
39.687
39.520
39.353
39.235
39.186
39.020
12.823
4kb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

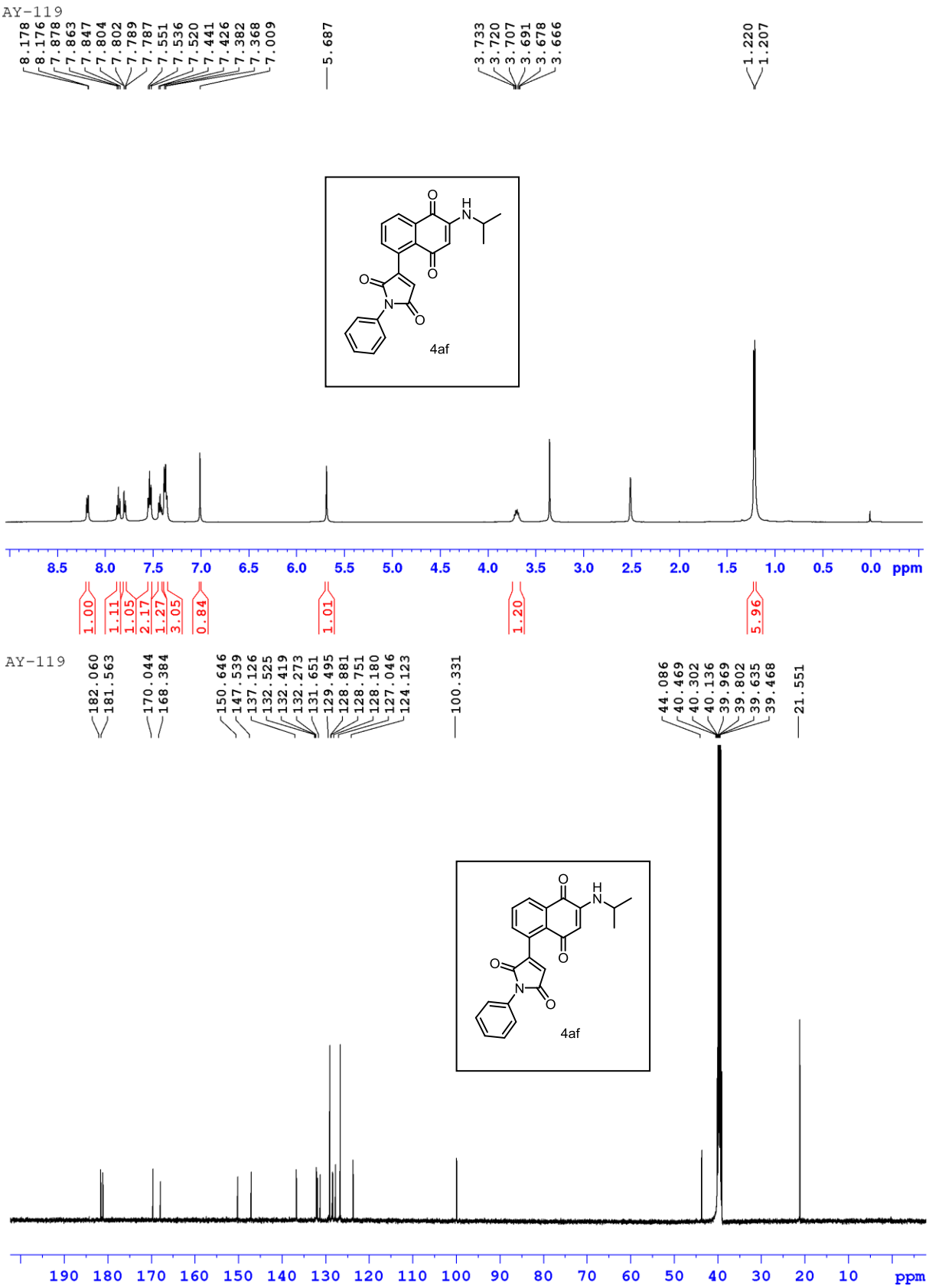

AY-137
10.974
8.138
8.136
8.122
8.120
7.833
7.818
7.803
7.717
7.715
7.702
7.699
7.626
6.714
6.712
3.736
3.722
3.707
3.693
1.630
1.615
1.600
1.586
1.571
1.372
1.358
1.343
1.328
1.313
1.298
0.923
0.909
0.894
4lb
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
1.00
1.06
1.02
0.95
0.99
2.14
2.24
2.28
3.21
AY-137
179.724
175.333
172.145
170.378
150.175
144.838
144.546
136.712
132.356
130.719
130.463
129.068
128.483
124.922
43.667
40.019
39.853
39.686
39.519
39.352
39.185
39.018
32.948
19.333
13.717
4lb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

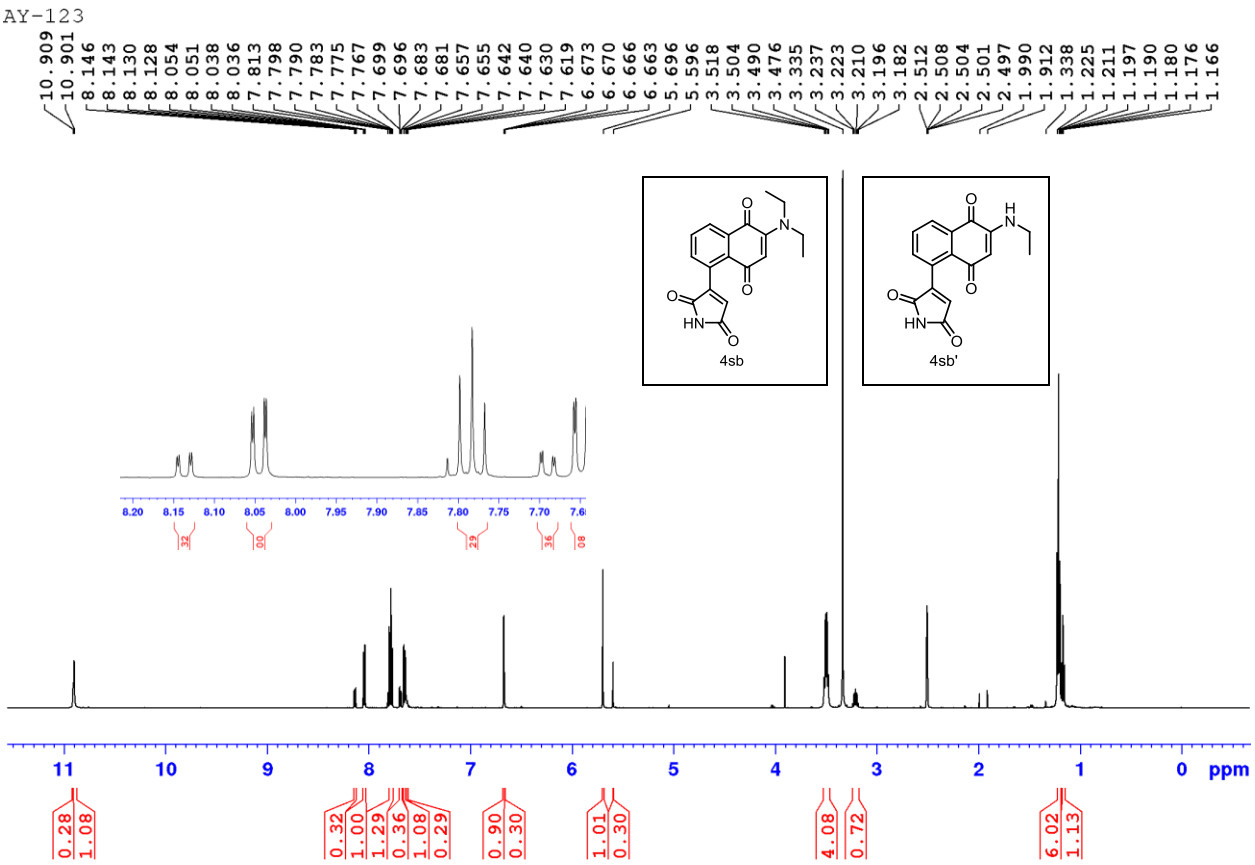

AN-118
8.218
8.203
7.690
7.675
7.659
7.540
7.525
7.270
6.432
5.782
5.767
5.687
3.687
3.673
3.658
3.644
3.635
3.622
3.608
3.594
3.581
1.300
1.287
1.279
4ac
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.04
1.00
0.92
0.94
0.95
3.35
9.08
AN-118
182.568
181.452
170.695
169.072
150.390
146.158
136.301
132.366
131.666
131.466
129.238
128.559
123.472
101.384
77.254
77.000
76.746
44.058
33.140
21.733
14.022
4ac
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

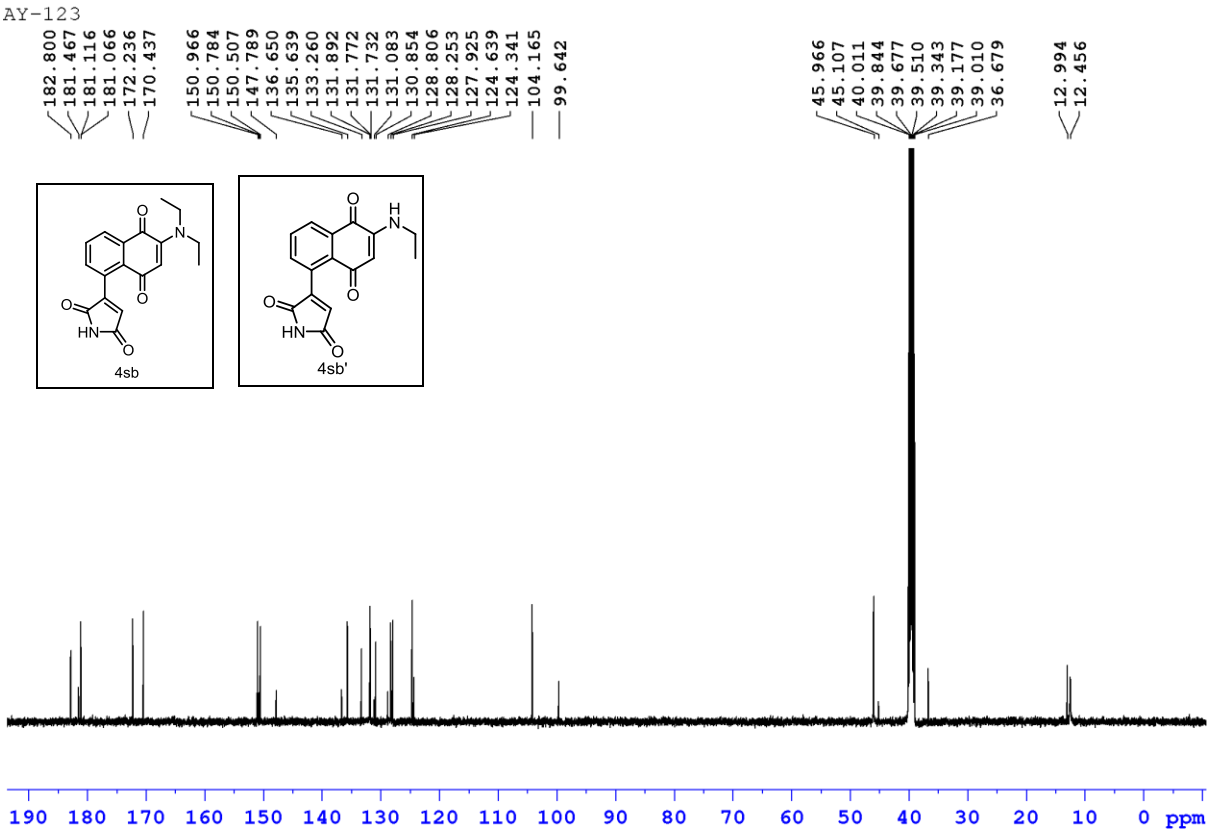

AY-120
8.173
8.171
8.158
8.155
7.843
7.828
7.813
7.756
7.753
7.741
7.738
7.389
7.374
7.360
7.356
7.346
7.329
6.882
5.666
4.686
3.737
3.724
3.711
3.708
3.697
3.695
3.682
3.669
1.214
1.202
4ad
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.00
6.25
0.93
1.00
1.99
1.11
6.08


AY-120
181.543
181.155
170.565
168.840
150.372
147.027
136.906
136.687
132.016
131.750
131.153
128.561
128.201
127.296
126.974
123.656
99.908
43.597
40.674
40.020
39.853
39.686
39.519
39.353
39.186
39.019
21.132
4ad
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

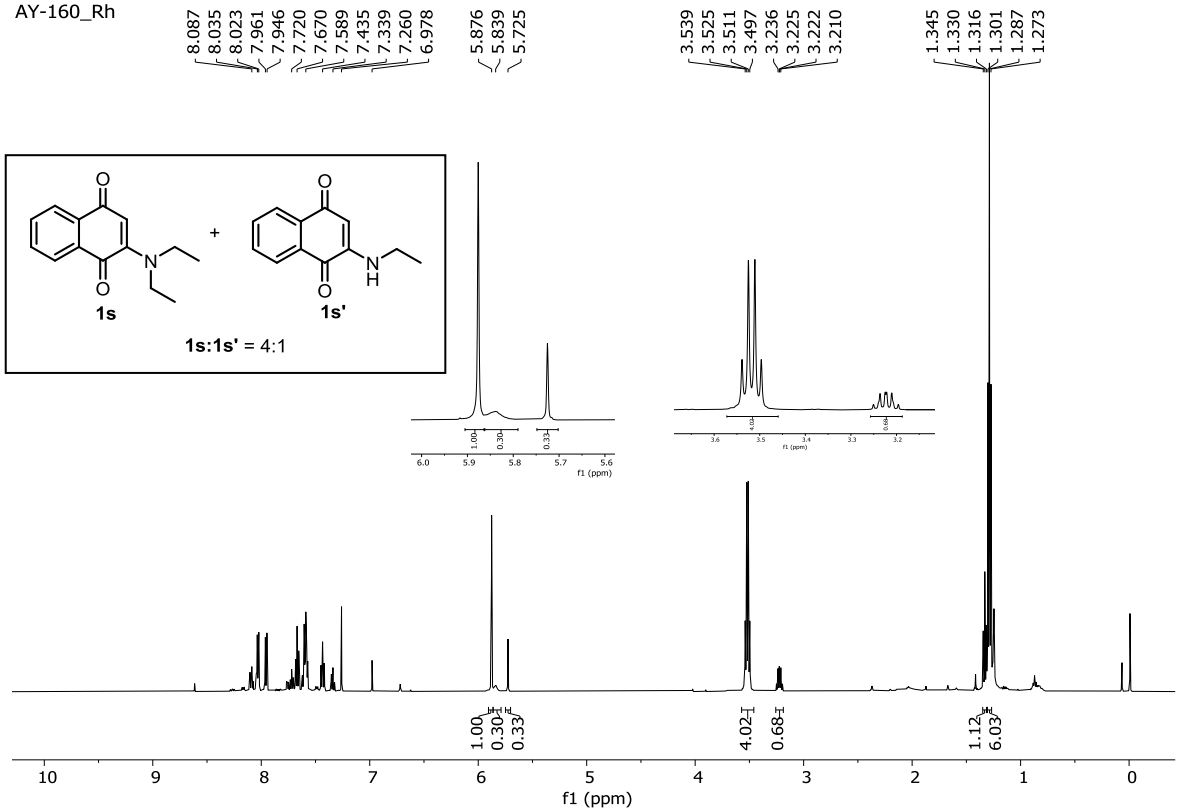

AY-121
8.146
8.143
8.131
8.128
7.808
7.793
7.777
7.694
7.691
7.679
7.676
7.274
7.257
6.634
5.683
3.729
3.716
3.703
3.700
3.690
3.687
3.674
3.661
1.555
1.214
1.201
4ae
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.06
1.02
1.03
0.87
0.99
1.13
9.10
5.98
AY-121
181.558
181.221
171.878
169.991
149.451
146.852
136.636
131.867
131.728
131.100
128.768
127.958
123.577
100.042
56.367
43.546
40.018
39.852
39.685
39.518
39.351
39.184
39.017
28.637
21.131
4ae
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


AY-119
8.178
8.176
7.878
7.863
7.847
7.804
7.802
7.789
7.787
7.551
7.536
7.520
7.441
7.426
7.382
7.368
7.009
5.687
3.733
3.720
3.707
3.691
3.678
3.666
1.220
1.207
4af
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 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.11
1.05
2.17
1.27
3.05
0.84
1.01
1.20
5.96
AY-119
182.060
181.563
170.044
168.384
150.646
147.539
137.126
132.525
132.419
132.273
131.651
129.495
128.881
128.751
128.180
127.046
124.123
100.331
44.086
40.469
40.302
40.136
39.969
39.802
39.635
39.468
21.551
4af
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

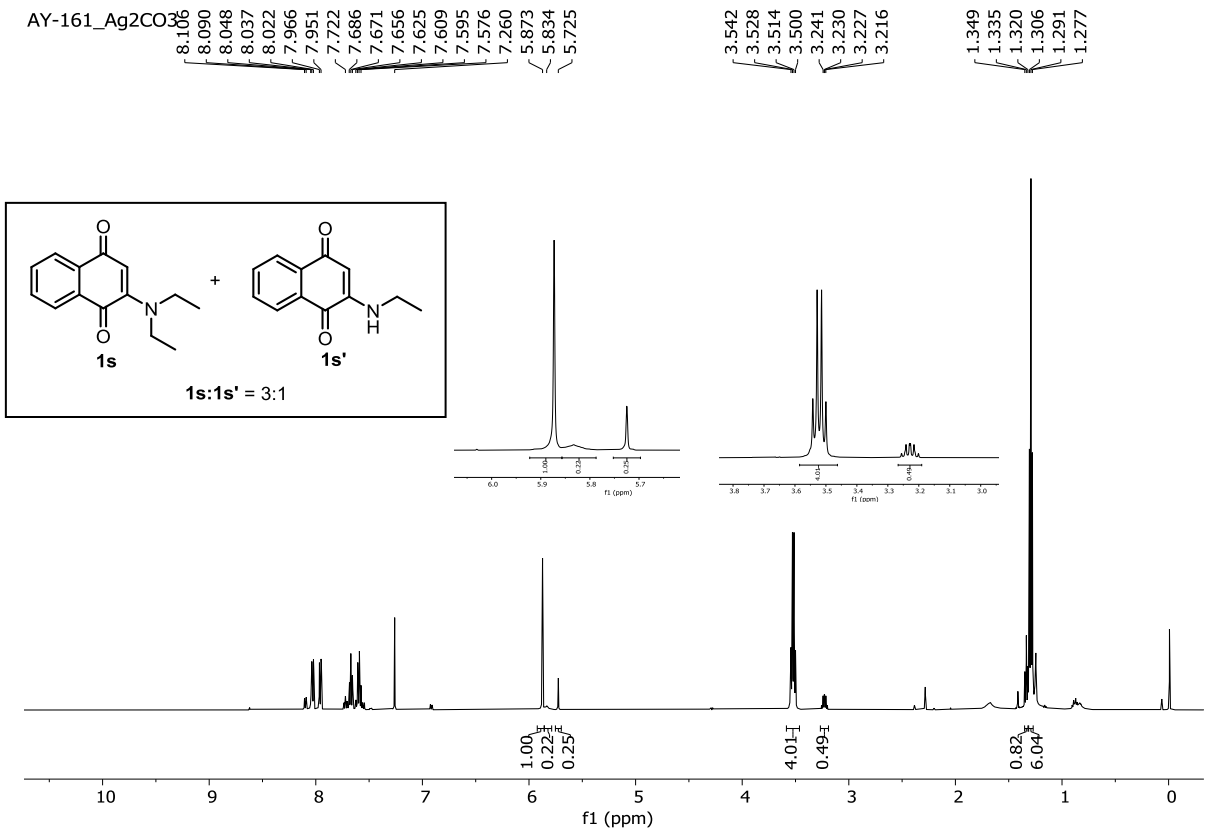

AY-123
10.909
10.901
8.146
8.143
8.130
8.128
8.054
8.051
8.038
8.036
7.813
7.798
7.790
7.783
7.775
7.767
7.699
7.696
7.683
7.681
7.657
7.655
7.642
7.640
7.630
7.619
6.673
6.670
6.666
6.663
5.696
5.596
3.518
3.504
3.490
3.476
3.335
3.237
3.223
3.210
3.196
3.182
2.512
2.508
2.504
2.501
2.497
1.990
1.912
1.338
1.225
1.211
1.197
1.190
1.180
1.176
1.166
4sb
4sb'
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.28
1.08
0.32
1.00
1.29
0.36
1.08
0.29
0.90
0.30
1.01
0.30
4.08
0.72
6.02
1.13

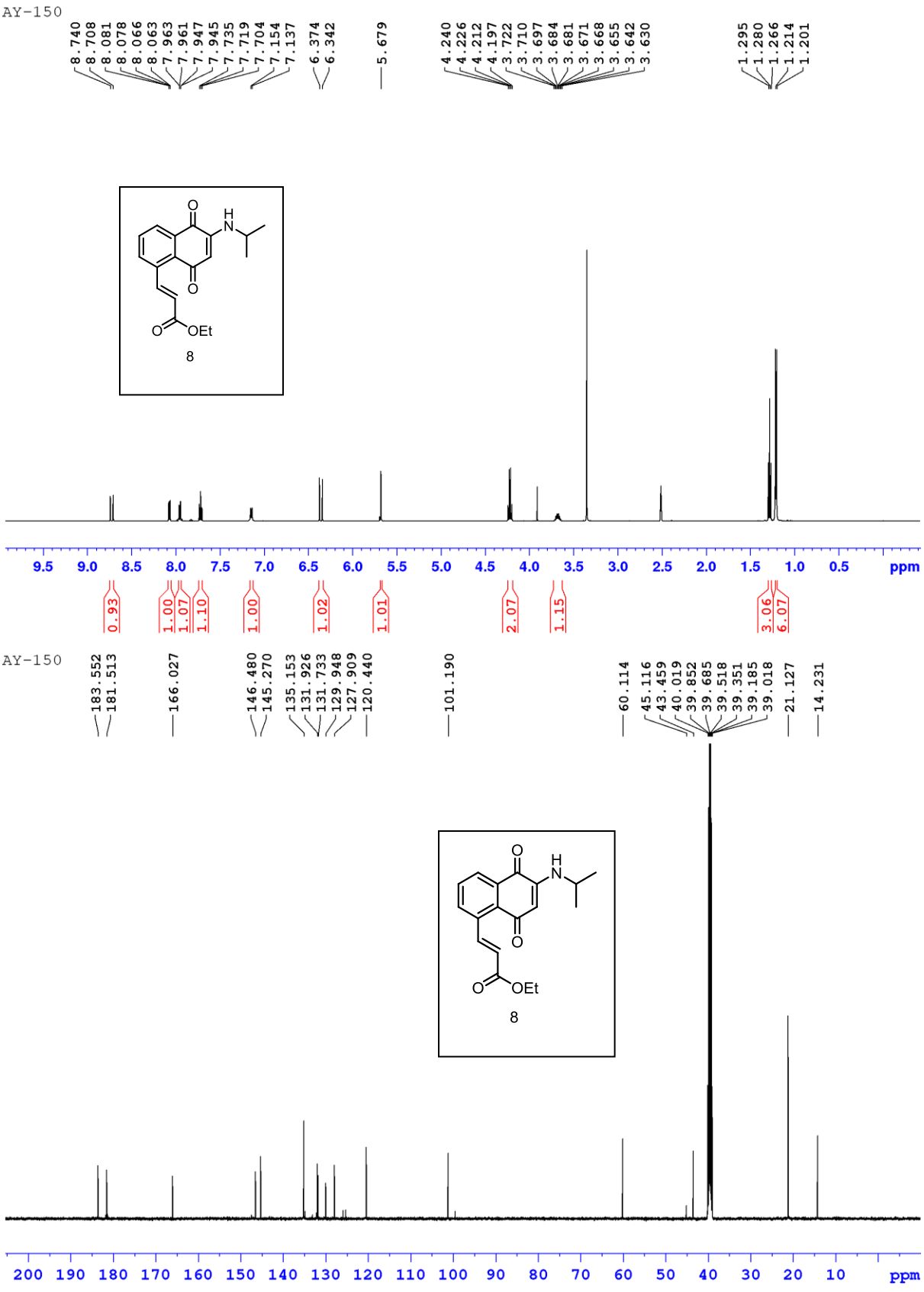

AY-123
182.800
181.467
181.116
181.066
172.236
170.437
150.966
150.784
150.507
147.789
136.650
135.639
133.260
131.892
131.772
131.732
131.083
130.854
128.806
128.253
127.925
124.639
124.341
104.165
99.642
45.966
45.107
40.011
39.844
39.677
39.510
39.343
39.177
39.010
36.679
12.994
12.456
4sb
4sb'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

AY-160_Rh



AY-161_Ag2CO3




AY-150
8.740
8.708
8.081
8.078
8.066
8.063
7.963
7.961
7.947
7.945
7.735
7.719
7.704
7.154
7.137
6.374
6.342
5.679
4.240
4.226
4.212
4.197
3.722
3.710
3.697
3.684
3.681
3.671
3.668
3.655
3.642
3.630
1.295
1.280
1.266
1.214
1.201
O
H
N
O
O
OEt
8
9.5 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 2.0 1.5 1.0 0.5 ppm
0.93
1.00
1.07
1.10
1.00
1.02
1.01
2.07
1.15
3.06
6.07
AY-150
183.552
181.513
166.027
146.480
145.270
135.153
131.926
131.733
129.948
127.909
120.440
101.190
60.114
45.116
43.459
40.019
39.852
39.685
39.518
39.351
39.185
39.018
21.127
14.231
O
H
N
O
O
OEt
8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Single Crystal X-ray data of 3bc

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: DG83R

Bond precision:	C-C = 0.0012 A	Wavelength=0.71073 Cell: a=10.5905(2) b=16.0282(4) c=11.3851(3)
alpha=90	beta=116.637(1) gamma=90	
Temperature: 135 K		
Calculated	Reported	
Volume	1727.47(7)	1727.47(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C20 H22 N2 O4	?
Sum formula	C20 H22 N2 O4	C20 H22 N2 O4
Mr	354.40	354.39
Dx,g cm-3	1.363	1.363
Z	4	4
Mu (mm-1)	0.096	0.096
F000	752.0	752.0
F000'	752.36	
h,k,lmax	16,24,17	16,24,17
Nref	6628	6609
Tmin,Tmax	0.974,0.982	0.964,0.982
Tmin'	0.964	

Correction method= # Reported T Limits: Tmin=0.964 Tmax=0.982 AbsCorr = MULTI SCAN

Data completeness= 0.997	Theta(max)= 33.210
R(reflections)= 0.0397(5586)	wR2(reflections)= 0.1129(6609)
S = 1.051	Npar= 323

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094 ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.62 Report PLAT911 ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 15 Report PLAT913 ALERT_3_C Missing # of Very Strong Reflections in FCF .... 6 Note

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Alert level G

PLAT066 ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT333 ALERT_2_G Large Aver C6-Ring C-C Dist C9 -C14 . 1.45 Ang.
PLAT793 ALERT_4_G Model has Chirality at C4 (Centro SPGR) S Verify
PLAT883 ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do ! PLAT910 ALERT_3_G
Missing # of FCF Reflection(s) Below Theta(Min). 1 Note PLAT912 ALERT_4_G Missing
# of FCF Reflections Above STh/L= 0.600 4 Note PLAT978 ALERT_2_G Number
C-C Bonds with Positive Residual Density. 19 Info

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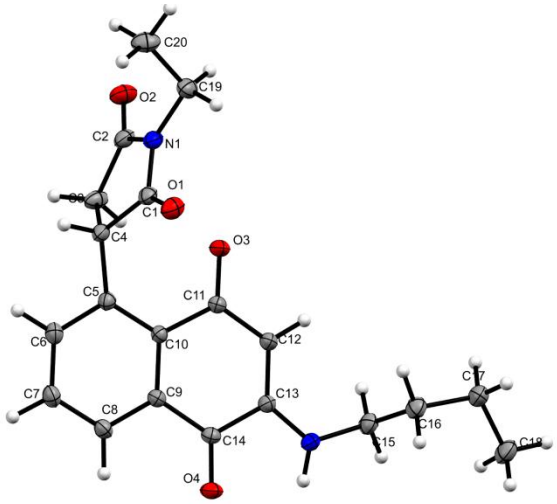
0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

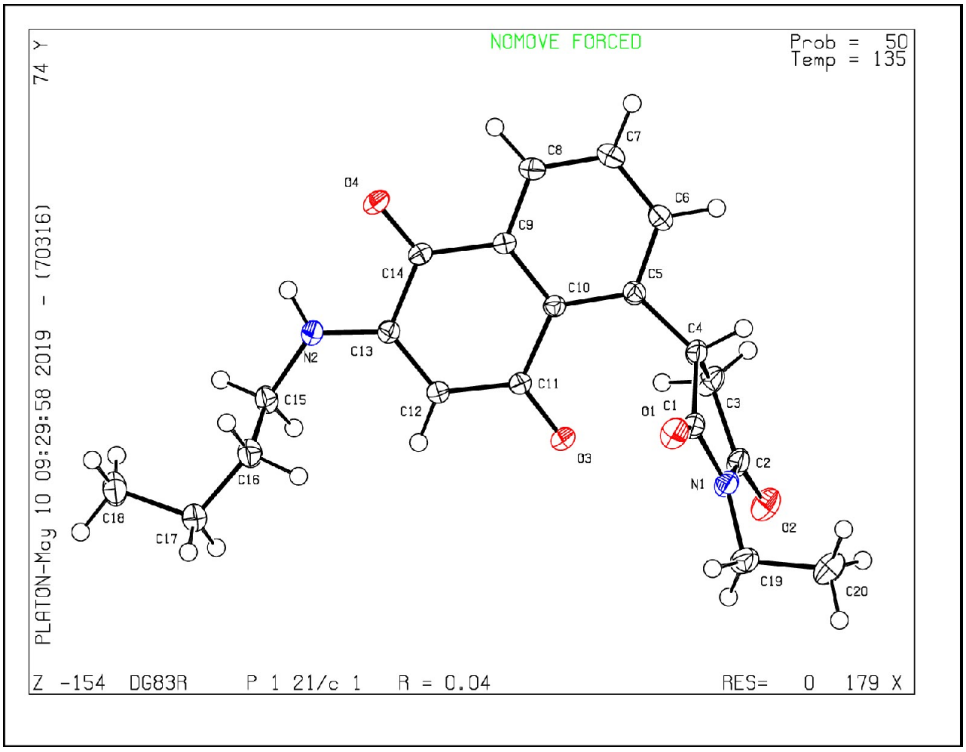
2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low

```
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
```



Thermal ellipsoid plot of the organic compound with atom numbering scheme(50% probability factor for the thermal ellipsoids)

PLATON version of 03/05/2019; check.def file version of 29/04/2019
Datablock DG83R - ellipsoid plot



HMBC Spectra of **4bb**