Supporting Information

C(sp^3)–H amination of 8-methylquinolines with azodicarboxylates under Rh(III) catalysis: cytotoxic evaluation of quinolin-8-ylmethanamines

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General methods

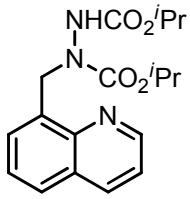
Commercially available reagents were used without additional purification, unless otherwise stated. Sealed tubes (13 × 100 mm^2) were purchased from Fischer Scientific and dried in oven for overnight and cooled at room temperature prior to use. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230–400 mesh) was used. Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Bruker Unity 400, 500 spectrometers in $CDCl_3$ solution and chemical shifts are reported as parts per million (ppm). Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet) and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

General procedure for the C(sp^3)–H amination of 8-methylquinolines with azodicarboxylates (3a–3u and 4b–4e)

To an oven-dried sealed tube charged with 8-methylquinoline (**1a**) (28.6 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), LiOAc (4.0 mg, 0.06 mmol, 30 mol %), Li_2CO_3 (14.8 mg, 0.2 mmol, 100 mol %), and $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol %) was added diisopropyl azodicarboxylate (**2a**) (80.9 mg, 0.4 mmol, 200 mol %) and DCE (1 mL) under air at room temperature. The reaction mixture was allowed to stir at 120 ^oC for 20 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 3:1) to afford 59.3mg of **3a** in 86% yield.

Characterization data for all products (3a–3u and 4b–4e)

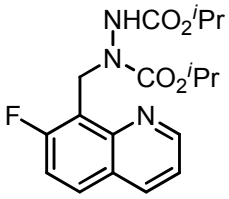
Diisopropyl 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (3a)



3a

59.3 mg (86%); white solid; mp = 105.0–107.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (br s, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.12 (br s, 1H), 5.24 (br s, 2H), 5.00–4.88 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 6H), 1.20 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.9, 146.9, 136.7, 135.5, 130.4, 129.8, 128.6, 128.0, 126.4, 121.3, 70.0, 69.7, 52.8, 22.3, 22.2; IR (KBr) υ 3298, 3044, 2979, 2936, 1699, 1498, 1406, 1374, 1263, 1214, 1179, 1105, 1033, 937, 822, 788, 761 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{23}N_3O_4$ $[M]^+$ 345.1689, found 345.1687.

Diisopropyl 1-((4-fluoroazecin-3-yl)methyl)hydrazine-1,2-dicarboxylate (3b)

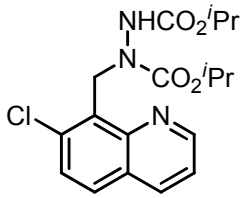


3b

66.0 mg (91%); white solid; mp = 86.9–88.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.76 (dd, *J* = 9.0, 5.9 Hz, 1H), 7.61 (br s, 1H), 7.39 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.33 (t, *J* = 9.1 Hz, 1H), 5.23–4.88 (m, 4H), 1.23 (d, *J* = 5.9 Hz, 6H), 1.18 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 268.1 Hz), 155.8, 150.9, 148.0, 143.3, 136.7, 129.6 (d, $J_{C\text{-}F}$ = 10.6 Hz), 129.0, 125.5, 120.5, 117.2 (d, $J_{C\text{-}F}$ = 14.4 Hz), 70.0, 69.5, 45.1, 22.2, 22.0; IR (KBr) υ 3303, 3057, 2980, 2937, 1701, 1622, 1582, 1504, 1467,

1406, 1374, 1312, 1257, 1223, 1179, 1105, 1053, 1033, 1010, 922, 834, 805, 761 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{22}FN_3O_4$ $[M]^+$ 363.1594, found 363.1593.

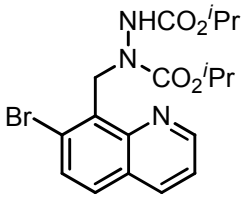
Diisopropyl 1-((7-chloroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3c)



3c

61.4 mg (81%); pale yellow sticky oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 2.7 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.41 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.55 (br s, 1H), 5.65–5.25 (m, 2H), 4.93 (br s, 2H), 1.21 (br s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 150.8, 147.9, 137.8, 136.6, 132.4, 128.8, 128.7, 128.5, 127.1, 121.3, 70.0, 69.5, 48.9, 22.2, 22.1; IR (KBr) υ 3296, 3064, 2979, 2936, 1702, 1607, 1489, 1404, 1373, 1253, 1177, 1105, 1037, 970, 834, 804, 759 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{18}H_{23}ClN_3O_4$ $[M+H]^+$ 380.1377, found 380.1374.

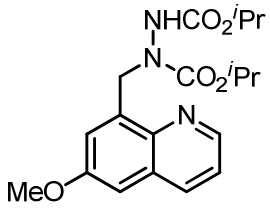
Diisopropyl 1-((7-bromoquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3d)



3d

59.4 mg (70%); pale yellow sticky oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 2.4 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.48 (br s, 1H), 5.63–5.43 (m, 2H), 4.94 (br s, 2H), 1.21 (br s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 150.6, 148.0, 136.6, 134.7, 134.0, 131.4, 129.0, 128.9 127.5, 121.5, 70.0, 69.5, 51.7, 22.2, 22.1; IR (KBr) υ 3302, 3055, 2979, 2935, 1702, 1605, 1590, 1487, 1404, 1373, 1308, 1256, 1224, 1177, 1105, 1034, 964, 833, 802, 761 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{18}H_{23}BrN_3O_4$ $[M+H]^+$ 424.0872, found 424.08624.

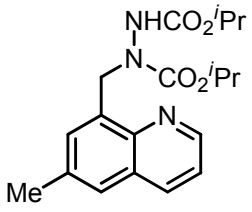
Diisopropyl 1-((6-methoxyquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3e)



3e

60.9 mg (81%); pale yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.36–7.33 (m, 3H), 6.98 (d, *J* = 2.6 Hz, 1H), 5.20 (br s, 2H), 5.00–4.88 (m, 2H), 3.90 (s, 3H), 1.24 (d, *J* = 6.2 Hz, 6H), 1.21 (d, *J* = 1.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 156.2, 147.3, 143.0, 137.2, 135.4, 129.8, 122.6, 122.5, 121.6, 104.9, 70.1, 70.0, 55.6, 51.9, 22.2, 22.1; IR (KBr) υ 3301, 2979, 2936, 1698, 1623, 1596, 1375, 1262, 1207, 1105, 1053, 1026, 946, 841, 781, 761 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{19}H_{26}N_3O_5$ $[M+H]^+$ 376.1872, found 376.18654.

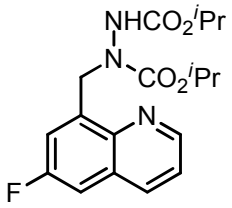
Diisopropyl 1-((6-methylquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3f)



3f

57.3 mg (80%); white solid; mp = 120.1−122.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.51 (s, 2H), 7.37 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.18 (br s, 2H), 5.01–4.87 (m, 2H), 2.51 (s, 3H), 1.25 (d, *J* = 6.2 Hz, 6H), 1.20 (d, *J* = 4.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.0, 145.5, 136.3, 136.0, 135.1, 132.7, 132.2, 128.8, 126.7, 121.3, 70.0, 69.6, 52.8, 22.3, 22.2, 21.8; IR (KBr) υ 3286, 2980, 2936, 1729, 1698, 1494, 1385, 1355, 1264, 1107, 1036, 979, 863, 784 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{19}H_{25}N_3O_4$ $[M]^+$ 359.1845, found 359.1844.

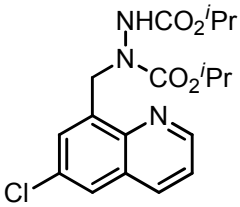
Diisopropyl 1-((6-fluoroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3g)



3g

46.6 mg (64%); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, J = 4.2, 1.6 Hz, 1H), 8.10 (dd, J = 8.3, 1.6 Hz, 1H), 7.52 (br s, 1H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H), 7.35 (dd, J = 8.5, 2.7 Hz, 1H), 7.20 (br s, 1H), 5.26 (br s, 2H), 5.00–4.90 (m, 2H), 1.24 (d, J = 6.2 Hz, 6H), 1.21 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, $J_{C\text{-}F}$ = 246.8 Hz), 156.2, 149.0, 143.9, 138.9, 136.1 (d, $J_{C\text{-}F}$ = 5.5 Hz), 130.9, 129.4 (d, $J_{C\text{-}F}$ = 10.0 Hz), 122.1, 119.9 (d, $J_{C\text{-}F}$ = 8.8 Hz), 110.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 70.5, 69.8, 51.6, 22.2, 22.1; IR (KBr) υ 3289, 2981, 2938, 1697, 1626, 1583, 1497, 1374, 1263, 1214, 1104, 1034, 980, 860, 782, 762 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{18}H_{23}FN_3O_4$ $[M+H]^+$ 364.1673, found 364.1668.

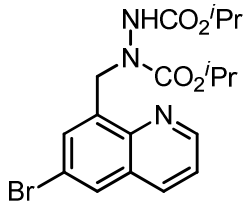
Diisopropyl 1-((6-chloroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3h)



3h

55.9 mg (74%); white solid; mp = 118.2−121.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, J = 4.2, 1.7 Hz, 1H), 8.06 (dd, J = 8.2, 1.0 Hz, 1H), 7.72–7.66 (m, 2H), 7.42 (dd, J = 8.2, 4.2 Hz, 1H), 7.20 (br s, 1H), 5.22 (br s, 2H), 5.00–4.89 (m, 2H), 1.25–1.21 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.0, 145.2, 137.7, 135.7, 132.2, 130.7, 130.5, 129.2, 126.3, 122.2, 70.4, 69.9, 51.5, 22.2, 22.1; IR (KBr) υ 3293, 3060, 2980, 2925, 1698, 1590, 1490, 1384, 1263, 1213, 1105, 1032, 864, 782, 760 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{22}ClN_3O_4$ $[M]^+$ 379.1299, found 379.1298.

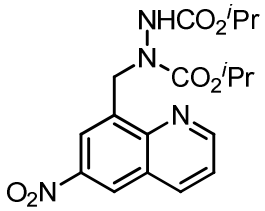
Diisopropyl 1-((6-bromoquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3i)



3i

64.2 mg (76%); white solid; mp = 127.5–128.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.91 (d, *J* = 1.8 Hz, 1H), 7.78 (br s, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28 (br s, 1H), 5.22 (br s, 2H), 5.00–4.89 (m, 2H), 1.25–1.22 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 150.2, 145.5, 137.8, 137.7, 135.7, 133.1, 133.0, 129.7, 122.2, 120.3, 70.5, 69.9, 51.4, 22.2, 22.1; IR (KBr) υ 3296, 3058, 2980, 2932, 1735, 1698, 1590, 1490, 1385, 1355, 1266, 1106, 1034, 866, 844, 783 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{22}BrN_3O_4$ $[M]^+$ 423.0794, found 423.0794.

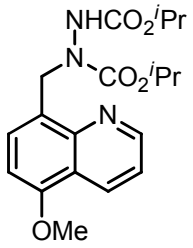
Diisopropyl 1-((6-nitroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3j)



3j

43.9 mg (56%); light yellow solid; mp = 148.6–149.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (br s, 1H), 8.48 (br s, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 8.1, 4.0 Hz, 1H), 6.99 (br s, 1H), 5.34 (br s, 2H), 5.00–4.93 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 153.2, 148.7, 145.4, 138.6, 138.5, 127.4, 124.2, 124.1, 123.1, 122.7, 70.7, 70.0, 52.2, 22.2, 22.1; IR (KBr) υ 3353, 3078, 2981, 2938, 1732, 1698, 1618, 1530, 1493, 1385, 1344, 1315, 1265, 1105, 1036, 906, 798 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{22}N_4O_6$ $[M]^+$ 390.1539, found 390.1541.

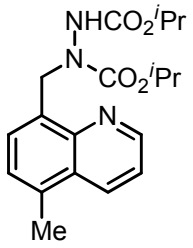
Diisopropyl 1-((5-methoxyquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3k)



3k

61.4 mg (82%); white solid; mp = 92.8–95.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.56 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.62 (br s, 1H), 7.47 (br s, 1H), 7.37 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.11 (br s, 2H), 5.00–4.86 (m, 2H), 3.97 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 6H), 1.20 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 155.1, 150.2, 147.5, 131.4, 131.0, 130.2, 127.1, 121.1, 120.3, 103.8, 69.9, 69.5, 55.9, 51.9, 22.2, 22.1; IR (KBr) υ 3296, 2979, 2935, 1730, 1698, 1590, 1466, 1384, 1268, 1206, 1105, 1088, 1034, 812, 783, 764 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{19}H_{25}N_3O_5$ $[M]^+$ 375.1794, found 375.1795.

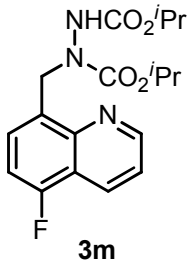
Diisopropyl 1-((5-methylquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3l)



3l

54.6 mg (76%); white solid; mp = 107.7–109.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.32 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.60 (br s, 1H), 7.45–7.42 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 5.19 (br s, 2H), 5.01–4.87 (m, 2H), 2.66 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 6H), 1.20 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 149.4, 147.1, 134.7, 133.4, 133.1, 130.3, 129.5, 128.0, 126.8, 120.8, 70.0, 69.6, 52.7, 22.3, 22.2, 18.8; IR (KBr) υ 3289, 3053, 2980, 2933, 1700, 1598, 1503, 1385, 1364, 1267, 1107, 1041, 826, 736 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{19}H_{25}N_3O_4$ $[M]^+$ 359.1845, found 359.1843.

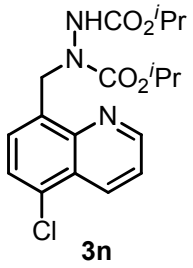
Diisopropyl 1-((5-fluoroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3m)



3m

62.6 mg (86%); white solid; mp = 130.8−131.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.42 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.67 (br s, 1H), 7.46 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.24 (br s, 1H), 7.16 (dd, *J* = 9.4, 8.0 Hz, 1H), 5.18 (br s, 2H), 4.98–4.87 (m, 2H), 1.21 (dd, *J* = 8.2, 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 (d, $J_{C\text{-}F}$ = 253.8 Hz), 156.1, 156.0, 150.7, 147.3, 131.4, 130.1, 129.9 (d, $J_{C\text{-}F}$ = 4.8 Hz), 121.3, 119.3 (d, $J_{C\text{-}F}$ = 16.3 Hz), 109.8 (d, $J_{C\text{-}F}$ = 14.6 Hz), 70.2, 69.7, 51.5, 22.2, 22.1; IR (KBr) υ 3301, 3073, 2981, 2938, 1735, 1690, 1631, 1597, 1474, 1385, 1255, 1204, 1104, 1056, 1007, 933, 839, 781, 765 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{26}H_{18}ClN_3O$ $[M]^+$ 363.1594, found 363.1592.

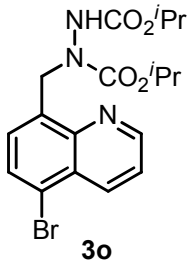
Diisopropyl 1-((5-chloroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3n)



3n

68.4 mg (90%); white solid; mp = 130.8−131.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.56 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.66–7.56 (m, 2H), 7.50 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.21 (br s, 1H), 5.22 (br s, 2H), 4.96–4.88 (m, 2H), 1.23–1.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 150.4, 147.3, 134.8, 133.4, 131.1, 130.0, 129.4, 126.5, 126.4, 122.0, 70.2, 69.7, 51.6, 22.2, 22.1; IR (KBr) υ 2997, 2955, 2900, 1765, 1695, 1613, 1576, 1499, 1466, 1394, 1358, 1321, 1194, 1067, 944, 928, 860, 804 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{18}H_{23}ClN_3O_4$ $[M+H]^+$ 380.1377, found 380.1371.

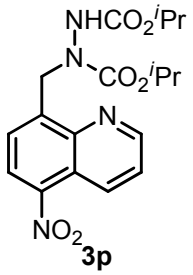
Diisopropyl 1-((5-bromoquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3o)



3o

71.9 mg (85%); white solid; mp = 150.8−152.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.53 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.58 (br s, 1H), 7.50 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.16 (br s, 1H), 5.21 (br s, 2H), 4.96–4.88 (m, 2H), 1.23–1.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.4, 147.4, 136.1, 135.6, 130.6, 130.2, 129.9, 127.8, 122.4, 121.7, 70.2, 69.8, 51.7, 22.2, 22.1; IR (KBr) υ 3297, 2980, 2938, 1787, 1703, 1631, 1567, 1492, 1408, 1384, 1260, 1213, 1106, 1037, 916, 827, 779 cm^{-1} HRMS (orbitrap, ESI) calcd for $C_{18}H_{23}BrN_3O_4$ $[M+H]^+$ 424.0872, found 424.0864.

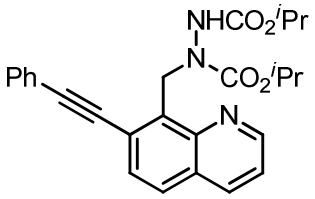
Diisopropyl 1-((5-nitroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3p)



3p

28.2 mg (36%); pale yellow sticky oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03–9.02 (m, 2H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.88 (br s, 1H), 7.67–7.64 (m, 1H), 6.90 (br s, 1H), 5.38 (br s, 2H), 4.96 (quint, *J* = 6.0 Hz, 2H), 1.24 (d, *J* = 6.3 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 150.8, 146.4, 145.2, 143.5, 132.6, 127.7, 124.6, 124.5, 124.0, 121.4, 70.7, 70.1, 52.2, 22.2, 22.1; IR (KBr) υ 3297, 3046, 2981, 2933, 1722, 1700, 1590, 1521, 1500, 1411, 1385, 1331, 1264, 1214, 1105, 1085, 1042, 985, 834, 805, 781 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{18}H_{23}N_4O_6$ $[M+H]^+$ 391.1618, found 391.1611.

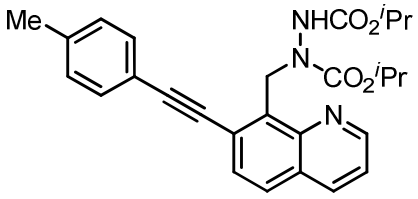
Diisopropyl 1-((7-(phenylethynyl)quinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3q)



3q

51.3 mg (58%); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (br s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.81 (br s, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.66–7.64 (m, 3H), 7.38–7.37 (m, 4H), 5.50 (br s, 2H), 4.94–4.87 (m, 2H), 1.25–1.07 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 150.6, 147.0, 136.6, 132.1, 132.0, 129.9, 128.9, 128.7, 128.6, 128.2, 127.8, 125.5, 123.1, 121.5, 96.2, 88.0, 69.9, 69.5, 51.5, 22.3, 22.2; IR (KBr) υ 3308, 2979, 2928, 1703, 1607, 1496, 1466, 1444, 1404, 1373, 1258, 1221, 1105, 1033, 997 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{26}H_{27}N_3O_4$ $[M]^+$ 445.2002, found 445.2005.

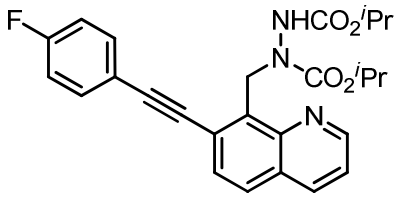
Diisopropyl 1-((7-(*p*-tolylethynyl)quinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3r)



3r

43.9 mg (48%); white sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.94 (br s, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.86 (br s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.65–7.64 (m, 1H), 7.52 (br s, 2H), 7.39 (br s, 1H), 7.18 (br s, 2H), 5.73–5.47 (m, 2H), 4.96–4.85 (m, 2H), 2.38 (s, 3H), 1.23–1.05 (m, 12H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.0, 155.4, 150.4, 146.8, 139.1, 137.5, 136.6, 131.8, 129.9, 129.3, 128.1, 127.6, 125.6, 121.3, 119.9, 96.4, 87.4, 69.8, 69.4, 51.6, 22.1, 21.7; IR (KBr) υ 3201, 2980, 2923, 1703, 1605, 1511, 1405, 1383, 1374, 1264, 1222, 1179, 1107, 1047, 949, 817 cm^{-1}; HRMS (quadrupole, ESI) calcd for $C_{27}H_{29}N_3NaO_4$ $[M+Na]^+$ 482.2050, found 482.2052.

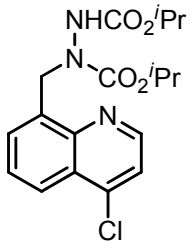
Diisopropyl 1-((7-((4-fluorophenyl)ethynyl)quinolin-8-yl)methyl)hydrazine-1,2-dicarboxylatee (3s)



3s

52.7 mg (57%); white sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.94 (br s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.64–7.62 (m, 3H), 7.40 (br s, 1H), 7.07 (br s, 2H), 5.69–5.48 (m, 2H), 4.94–4.86 (m, 2H), 1.21–1.07 (m, 12H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 248.6 Hz), 155.9, 155.4, 105.5, 146.7, 137.6, 136.5, 133.9 (d, $J_{C\text{-}F}$ = 30.3 Hz), 129.7, 128.2, 127.7, 125.2, 121.5, 119.1, 115.8 (d, $J_{C\text{-}F}$ = 22.0 Hz), 94.8, 87.7, 69.9, 69.4, 51.3, 22.1; IR (KBr) υ 3211, 2979, 2923, 1701, 1597, 1508, 1468, 1453, 1404, 1383, 1374, 1262, 1222, 1201, 1178, 1106, 1046, 1029, 950 cm^{-1}; HRMS (quadrupole, ESI) calcd for $C_{26}H_{26}FN_3NaO_4$ $[M+Na]^+$ 486.1800, found 486.1803.

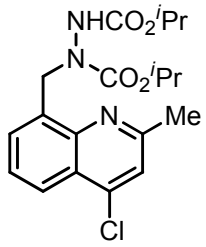
Diisopropyl 1-((4-chloroquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3t)



3t

48.2 mg (63%); white sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 4.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.76 (br s, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 4.8 Hz, 1H), 7.18 (br s, 1H), 5.25 (s, 2H), 4.96–4.89 (m, 2H), 1.23–1.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 155.7, 149.1, 147.7, 143.1, 135.7, 131.1, 127.2, 126.6, 123.9, 121.2, 69.9, 69.5, 51.6, 22.0, 21.9; IR (KBr) υ 3297, 2980, 2932, 1702, 1584, 1490, 1467, 1414, 1384, 1374, 1293, 1263, 1215, 1179, 1143, 1105, 1035, 983 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{22}ClN_3O_4$ $[M]^+$ 379.1299, found 379.1297.

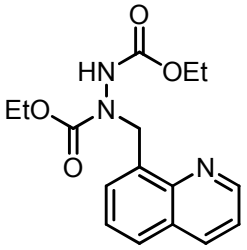
Diisopropyl 1-((4-chloro-2-methylquinolin-8-yl)methyl)hydrazine-1,2-dicarboxylate (3u)



3u

8.9 mg (11%); white solid; mp = 126.8−128.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.83–7.65 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.41 (s, 1H), 5.15 (s, 2H), 5.03–4.96 (m, 1H), 4.94–4.88 (m, 1H), 2.73 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 6H), 1.20 (d, *J* = 5.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 156.0, 155.9, 147.1, 143.1, 135.2, 131.5, 126.1, 124.9, 123.9, 121.9, 69.9, 69.5, 52.0, 25.2, 22.1, 22.0; IR (KBr) υ 3300, 2980, 2924, 2853, 1706, 1591, 1508, 1492, 1466, 1404, 1385, 1264, 1221, 1179, 1107, 1039, 997 cm^{-1}; HRMS (quadrupole, ESI) calcd for $C_{19}H_{24}ClN_3NaO_4$ $[M+Na]^+$ 416.1348, found 416.1351.

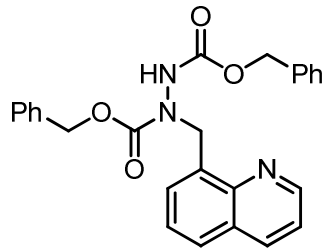
Diethyl 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (4b)



4b

53.3 mg (84%); white solid; mp = 103.9–105.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.77–7.68 (m, 3H), 7.50 (dd, *J* = 7.9, 7.4 Hz, 1H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 5.22 (br s, 2H), 4.22–4.12 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 149.9, 146.8, 136.8, 135.3, 130.9, 129.9, 128.7, 128.1, 126.4, 121.3, 62.5, 62.0, 52.9, 14.7 (two carbons overlap); IR (KBr) υ 3292, 3041, 2981, 2933, 1702, 1498, 1380, 1263, 1212, 1131, 1059, 918, 824, 788, 761 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{16}H_{19}N_3O_4$ $[M]^+$ 317.1376, found 317.1373.

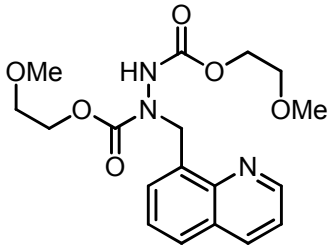
Dibenzyl 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (4c)



4c

65.9 mg (75%); pale yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (br s, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.87–7.75 (m, 3H), 7.50 (br s, 1H), 7.41 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.33–7.26 (m, 10H), 5.25–5.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.0, 146.9, 136.8, 136.1, 135.0, 131.0, 130.4, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 126.5, 121.3, 68.0, 67.7, 52.8; IR (KBr) υ 3294, 3063, 3033, 2954, 1708, 1498, 1455, 1408, 1263, 1211, 1131, 1050, 986, 823, 790 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{26}H_{23}N_3O_4$ $[M]^+$ 441.1689, found 441.1687.

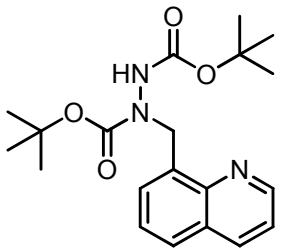
Bis(2-methoxyethyl) 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (4d)



4d

49.3 mg (65%); pale yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.78–7.10 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.24 (br s, 2H), 4.32–4.24 (m, 4H), 3.62–3.59 (m, 2H), 3.54 (br s, 2H), 3.38 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 150.0, 146.8, 142.8, 136.9, 135.1, 130.9, 128.7, 128.2, 126.5, 121.3, 70.8, 70.7, 65.5, 65.1, 59.2, 59.1, 52.6; IR (KBr) υ 2954, 2922, 2853, 1753, 1714, 1499, 1458, 1270, 1198, 1124, 1065, 923, 855, 824, 795 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{23}N_3O_6$ $[M]^+$ 377.1587, found 377.1585.

Di-*tert*-butyl 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (4e)



4e

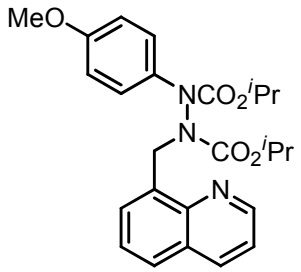
18.3 mg (10%); pale yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.76–7.65 (m, 3H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.08 (br s, 1H), 5.23 (br s, 2H), 1.44 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 149.8, 146.9, 136.7, 135.8, 130.1, 128.6, 127.8, 126.5, 126.3, 121.2, 81.1, 81.0, 53.0, 28.4, 28.3; IR (KBr) υ 3054, 2977, 2990, 1730, 1697, 1499, 1393, 1272, 1156, 1051, 737 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{27}N_3O_4$ $[M]^+$ 373.2002, found 373.2001.

Experimental procedure and characterization for transformation of hydrazine functionality (6a and 6b)

Synthetic procedure for the formation of compound 6a

To an oven-dried sealed tube charged with diisopropyl 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (**3a**) (51.8 mg, 0.15 mmol, 100 mol %), copper(I) iodide (28.6 mg, 0.15 mmol, 100 mol %), 1,10-phenanthroline (5.4 mg, 0.03 mmol, 20 mol %), and Cs_2CO_3 (97.7 mg, 0.3 mmol, 200 mol %) was added *p*-metoxy-phenyl iodide (**5a**) (55.1 mg, 0.221 mmol, 200 mol %), and DCE (0.75 mL) under air at room temperature. The reaction mixture was allowed to stir at 120 ^{o}C for 20 h, and cooled to room temperature, filtered through a plug of silica gel and washed with ethyl acetate. The filtrate was concentrated in vacuo and purified by silica-gel chromatography (*n*-hexanes/EtOAc = 2:1) to afford 66.3 mg of **6a** in 98% yield.

1-Methyl-3-((1,2,3,4-tetrahydroquinolin-8-yl)methyl)pyrrolidine-2,5-dione (6a)



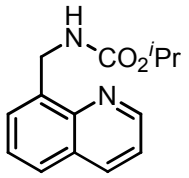
6a

66.3 mg (98%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (br s, 1H), 8.11–8.06 (m, 1H), 7.81–7.68 (m, 2H), 7.45–7.40 (m, 1H), 7.38–7.33 (m, 1H), 7.26–7.22 (m, 2H), 6.72 (br s, 2H), 5.59–5.44 (m, 1H), 5.26 (d, *J* = 14.8 Hz, 1H), 5.14–5.05 (m, 1H), 4.82–4.63 (m, 1H), 3.74 (s, 3H), 1.33 (d, *J* = 6.2 Hz, 3H), 1.27 (d, *J* = 6.2 Hz, 3H), 1.11–0.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.8, 156.3, 154.4, 149.7, 147.2, 136.1, 135.0, 133.9, 131.1, 128.2, 127.7, 126.3, 121.1, 113.7, 70.5, 70.3, 55.6, 48.0, 22.4, 22.3; IR (KBr) υ 3048, 2979, 2935, 1710, 1509, 1373, 1245, 1107, 1031, 828, 796 cm^{-1} HRMS (orbitrap, ESI) calcd for $C_{25}H_{30}N_3O_5$ $[M+H]^+$ 452.2185, found 452.2177.

Synthetic procedure for the formation of compound 6b

To an oven-dried sealed tube charged with diisopropyl 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (**3a**) (69.1 mg, 0.2 mmol, 100 mol %), and Cs_2CO_3 (162.9 mg, 0.5 mmol, 250 mol %) was added methyl bromoacetate (**5b**) (61.2 mg, 0.4 mmol, 200 mol %) and CH_3CN (1.0 mL) under air at room temperature. The reaction mixture was allowed to stir at 50 ^oC for 20 h, and cooled to room temperature. The reaction mixture was quenched with saturated NH_4Cl(aq), extracted with EtOAc, and the combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude oil was purified by column chromatography to give pale yellow oil. Then a solution of pale yellow oil in acetonitrile (1.0 mL) was added cesium carbonate (195.5 mg, 0.6 mmol, 300 mol %), and mixture was heated at reflux for 20 h. The reaction mixture was quenched with saturated NH_4Cl(aq), and extracted with EtOAc. The combined extracts were washed with brine, and dried over Na_2SO_4. The filtrate was concentrated in vacuo and purified by silica-gel chromatography (*n*-hexanes/EtOAc = 2:1) to afford 29.5 mg of **6b** in 60% yield.

1-Methyl-3-((1,2,3,4-tetrahydroquinolin-8-yl)methyl)pyrrolidine-2,5-dione (6b)



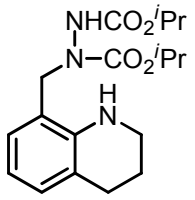
6b

29.5 mg (60%); pale yellow sticky oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.17 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.77–7.72 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 5.95 (br s, 1H), 4.95–4.86 (m, 3H), 1.20 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 149.8, 136.8, 129.3, 128.7, 127.8 (two carbons overlap), 126.7, 121.4 (two carbons overlap), 68.1, 42.8, 22.4; IR (KBr) υ 3335, 3044, 2977, 2932, 1695, 1497, 1373, 1244, 1109, 948, 827, 789 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{14}H_{16}N_2O_2$ $[M]^+$ 244.1212, found 244.1212.

Experimental procedure and characterization for reduction of quinoline moiety (7a)

To an oven-dried 50 mL round bottom flask charged with diisopropyl 1-(quinolin-8-ylmethyl)hydrazine-1,2-dicarboxylate (**3a**) (138.2 mg, 0.4 mmol, 100 mol %), and $NiCl_2 \cdot 6H_2O$ (9.5 mg, 0.04 mmol, 10 mol %) was added MeOH (4 mL) and CH_2Cl_2 (2 mL). $NaBH_4$ (121.0 mg, 3.2 mmol) was added in portions with stirring under cooling for 1 h, then the stirring was continued for another 1 h. After the removal of the solvents, the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (*n*-hexanes/EtOAc = 6:1) to afford 74.0 mg of **7a** in 53% yield.

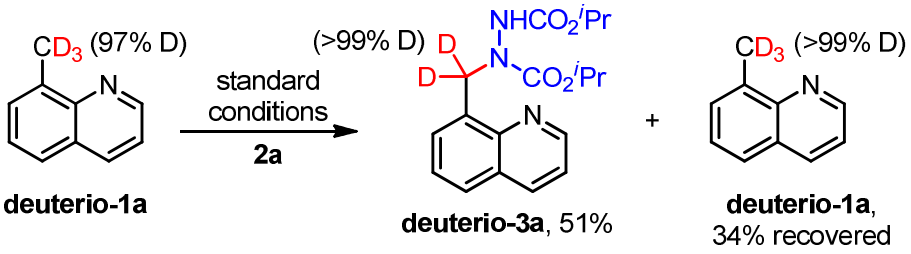
1-Methyl-3-((1,2,3,4-tetrahydroquinolin-8-yl)methyl)pyrrolidine-2,5-dione (7a)



7a

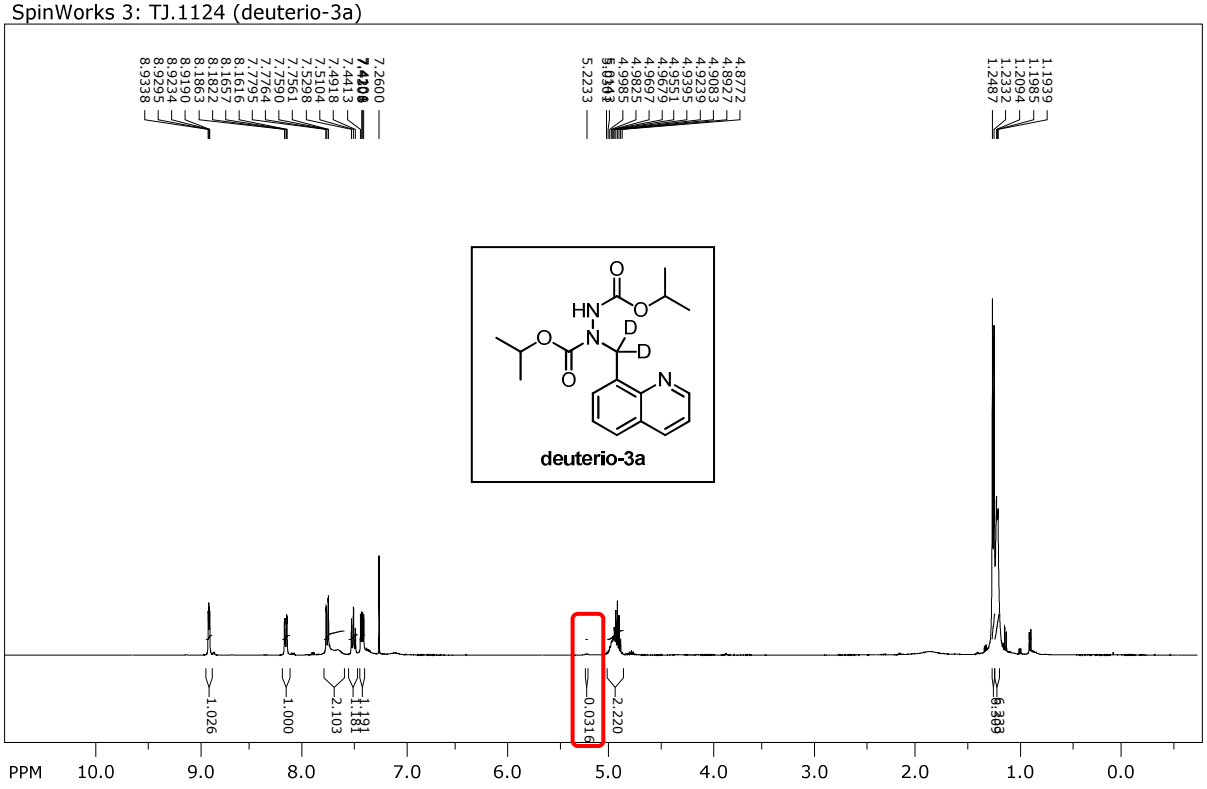
74.0 mg (53%); red sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.54 (br s, 1H), 6.36 (br s, 1H), 6.19 (br s, 1H), 4.99–4.93 (m, 2H), 4.56 (br s, 2H), 3.34 (t, *J* = 5.5 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 1.91 (quint, *J* = 6.3 Hz, 2H), 1.24 (d, *J* = 6.2 Hz, 6H), 1.23 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 155.5, 143.1, 129.9, 129.8, 121.7, 119.1, 116.1, 70.8, 69.9, 50.7, 42.1, 27.6, 22.2, 22.1, 21.7; IR (KBr) υ 3360, 2978, 2929, 2849, 1733, 1683, 1601, 1512, 1465, 1419, 1384, 1307, 1278, 1206, 1179, 1105, 1043, 931, 760 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{27}N_3O_4$ $[M]^+$ 349.2002, found 349.2006.

Mechanistic investigation (deuterium incorporation)

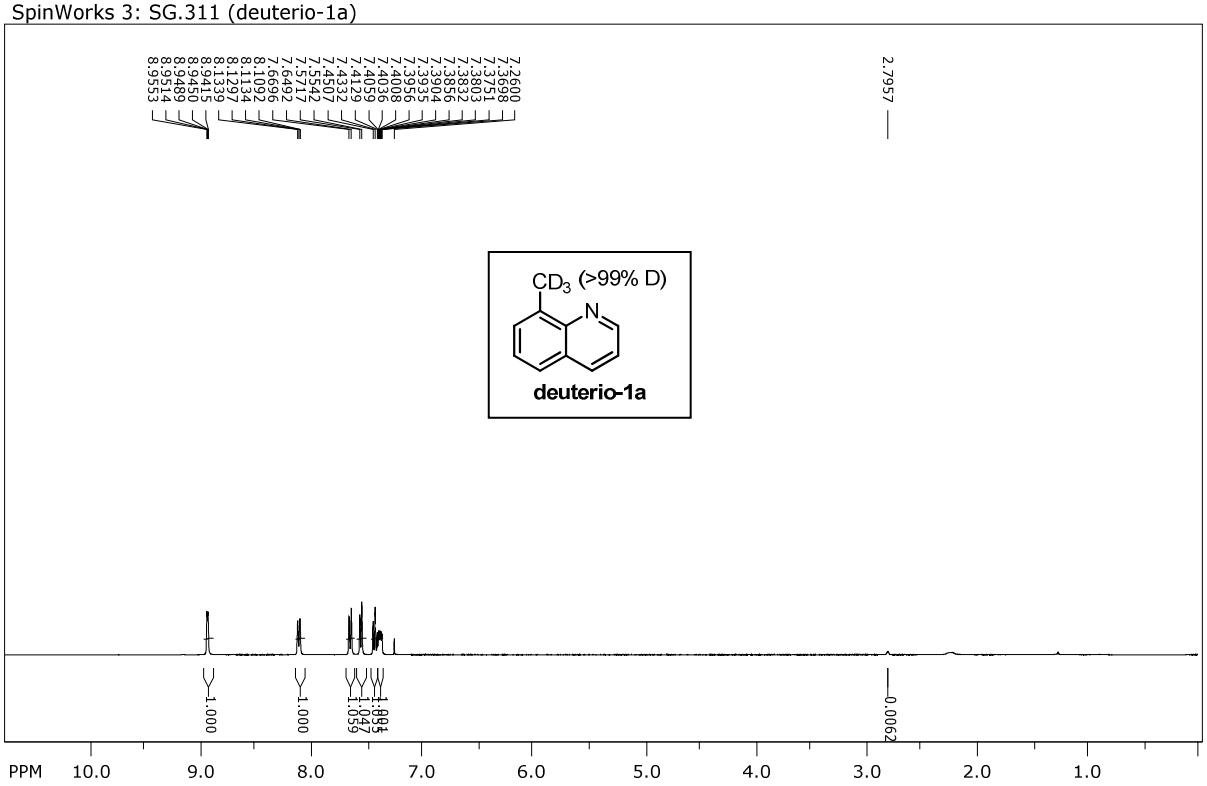


To an oven-dried sealed tube charged with 8-methylquinoline (**deuterio-1a**) (29.2 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), LiOAc (4.0 mg, 0.06 mmol, 30 mol %), Li_2CO_3 (14.8 mg, 0.2 mmol, 100 mol %), and $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol %) was added diisopropyl azodicarboxylate (**2a**) (80.9 mg, 0.4 mmol, 200 mol %) and DCE (1 mL) under air at room temperature. The reaction mixture was allowed to stir at 120 ^oC for 20 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 3:1) to afford **deuterio-3a** (35.4 mg, 51% yield) and **deuterio-1a** (9.9 mg, 34% recovered yield), respectively.

SpinWorks 3: TJ.1124 (deuterio-3a)



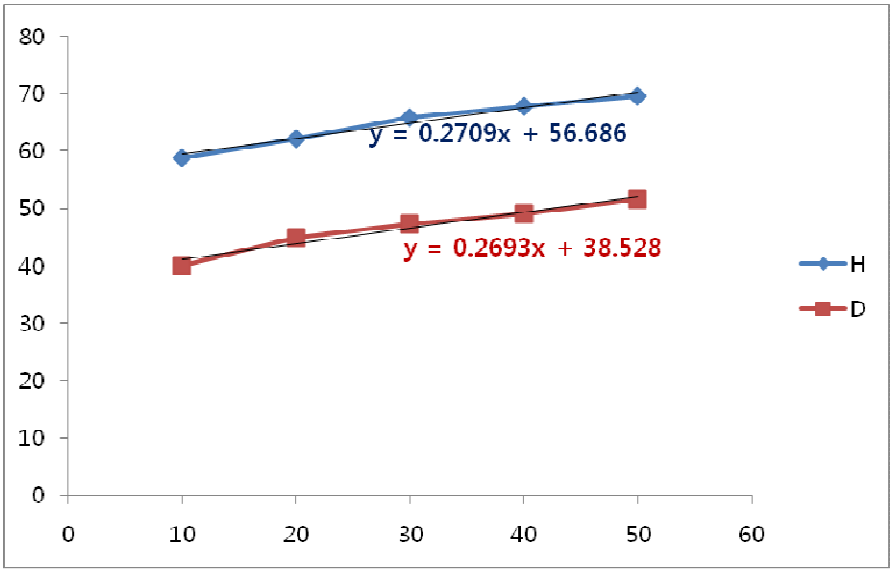
SpinWorks 3: SG.311 (deuterio-1a)



Kinetic Isotope Effect (KIE) experiment

To an oven-dried sealed tube charged with 8-methylquinoline (**1a**) (28.6 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), LiOAc (4.0 mg, 0.06 mmol, 30 mol %), Li_2CO_3 (14.8 mg, 0.2 mmol, 100 mol %), and $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol %) was added diisopropyl azodicarboxylate (**2a**) (80.9 mg, 0.4 mmol, 200 mol %) and DCE (1 mL) was added bromobenzene (157.0 mg, 1.0 mmol, 500 mol %) as an internal standard. In another reaction tube, **deutrio-1a** (29.2 mg, 0.2 mmol, 100 mol %, >99% D) was used instead of **1a**. The two reactions were allowed to stir at 120 °C. An aliquot of each reaction mixture was taken at the time of 10 min, 20 min, 30 min, 40 min, and 50 min. The corresponding yield of each product was determined by GC-MS (bromobenzene as an internal standard). A kinetic isotope effect value (k_H/k_D) of 1.05 was observed.

	Relative yield (%) based on bromobenzene				
	10	20	30	40	50
3a (H)	58.76401886	62.21125524	65.80200801	67.73416775	69.54528331
deuterio-3a (D)	40.14361019	44.99798715	47.27139252	49.02250629	51.5944754

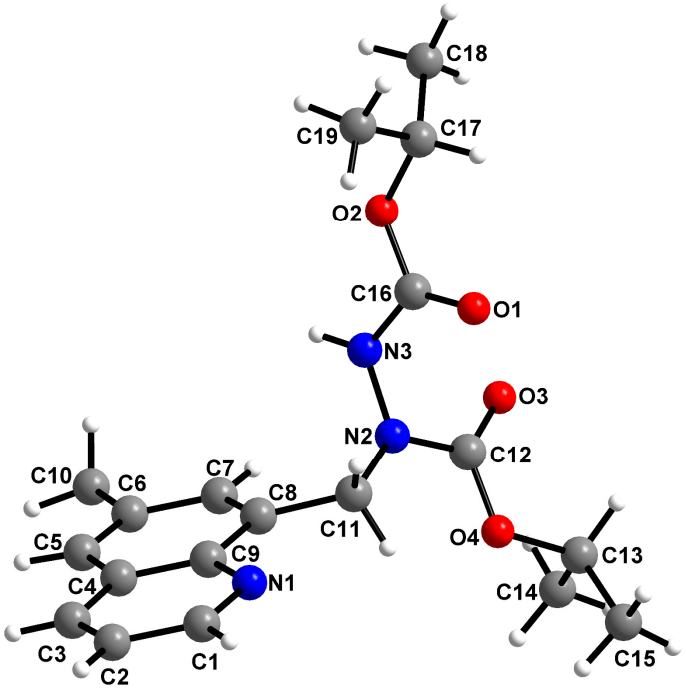


Cancer cell growth inhibition assay (MTT assay)

Human breast adenocarcinoma cells (MCF-7) and human prostate adenocarcinoma cells (LNCaP) were grown in DMEM medium supplemented with 1% of penicillin/streptomycin, and 10% fetal bovine serum (all from Life Technologies, Grand Island, NY). Cells were seeded in 96-well plates (5×10^3 cells/well) containing 50 μL of growth medium for 24 h. After medium removal, 100 μL of fresh medium containing individual analogue compounds at different concentrations was added to each well and incubated at 37 ^{o}C for 72 h. After 24 h of culture, the cells were supplemented with 10 μL of test compounds dissolved in DMSO (less than 0.25% in each preparation). After 24 h of incubation, 15 μL of the MTT reagent was added to each well. After 4 h incubation at 37 ^{o}C, the supernatant was aspirated, and the formazan crystals were dissolved in 100 μL DMSO at 37 ^{o}C for 10 min with gentle agitation. The absorbance per well was measured at 540 nm using a VERSA max Microplate Reader (Molecular Devices Corp., USA). The IC_{50} was defined as the compound concentration required inhibiting cell proliferation by 50% in comparison with cells treated with the maximum amount of DMSO (0.25%) and considered as 100% viability.

X-ray crystallographic data of compound 3f (CCDC 1570778)

A colorless block-like specimen of $C_{19}H_{25}N_3O_4$, approximate dimensions 0.050 mm x 0.100 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.



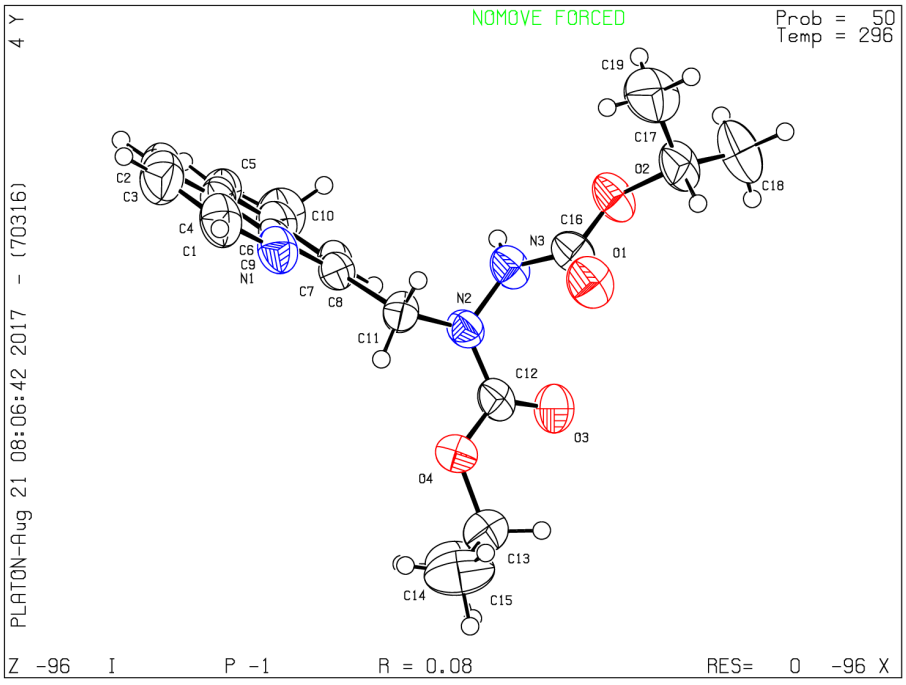


Table 1: Data collection details for compound 3f.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	62.244	31.91	-160.09	80.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	-120.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	-40.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	160.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	0.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	-160.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	120.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	40.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	31.91	-160.09	-80.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Omega	62.244	-17.38	-209.38	51.00	54.74	0.50	408	10.00	0.71073	50	30.0	n/a
Phi	62.244	-7.38	5.62	0.00	54.74	0.50	720	10.00	0.71073	50	30.0	n/a
Phi	62.244	0.00	0.00	0.00	54.74	360.00	1	60.00	0.71073	50	30.0	n/a

A total of 4801 frames were collected. The total exposure time was 13.35 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 16561 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 3321 were independent (average redundancy 4.987, completeness = 98.4%, R_{int} = 16.42%, R_{sig} = 16.71%) and 1331 (40.08%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.916(3) Å, b = 9.462(3) Å, c = 12.490(4) Å, α = 71.60(2)°, β = 82.91(2)°, γ = 73.48(2)°, volume = 957.9(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 1780 reflections above 20 σ(I) with 4.768° < 2θ < 38.99°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.682. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9880 and 0.9960.

The final anisotropic full-matrix least-squares refinement on F^2 with 241 variables converged at R1 = 8.18%, for the observed data and wR2 = 22.15% for all data. The goodness-of-fit was 0.953. The largest peak in the final difference electron density synthesis was 0.249 $e^-/Å^3$ and the largest hole was -0.208 $e^-/Å^3$ with an RMS deviation of 0.059 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.246 g/cm^3 and F(000), 384 e^-.

Table 2. Sample and crystal data for compound 3f.

Identification code	TJ-998	
Chemical formula	$C_{19}H_{25}N_3O_4$	
Formula weight	359.42	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.100 x 0.140 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.916(3) Å	α = 71.60(2)°

	b = 9.462(3) Å	β = 82.91(2)°
	c = 12.490(4) Å	γ = 73.48(2)°
Volume	957.9(6) $Å^3$	
Z	2	
Density (calculated)	1.246 g/cm^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	384	

Table 3. Data collection and structure refinement for compound 3f.

Theta range for data collection	1.72 to 25.00°	
Index ranges	-10<=h<=10, -11<=k<=11, -14<=l<=14	
Reflections collected	16561	
Independent reflections	3321 [R(int) = 0.1642]	
Coverage of independent reflections	98.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9960 and 0.9880	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3321 / 0 / 241	
Goodness-of-fit on F^2	0.953	
Final R indices	1331 data; I>2σ(I)	R1 = 0.0818, wR2 = 0.1634
	all data	R1 = 0.2111, wR2 = 0.2215
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0842P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0410(70)	
Largest diff. peak and hole	0.249 and -0.208 $eÅ^{-3}$	
R.M.S. deviation from mean	0.059 $eÅ^{-3}$	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for compound 3f.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.6489(7)	0.1447(7)	0.5287(5)	0.0715(16)
C2	0.7681(7)	0.0940(8)	0.4551(5)	0.0827(18)

	x/a	y/b	z/c	U(eq)
C3	0.8208(7)	0.9426(8)	0.4676(4)	0.0731(17)
C4	0.7597(6)	0.8365(7)	0.5542(4)	0.0558(13)
C5	0.8081(6)	0.6761(7)	0.5733(4)	0.0636(15)
C6	0.7425(6)	0.5763(6)	0.6560(4)	0.0580(14)
C7	0.6259(6)	0.6391(6)	0.7281(4)	0.0533(13)
C8	0.5770(5)	0.7939(6)	0.7164(4)	0.0450(12)
C9	0.6429(6)	0.8967(6)	0.6268(4)	0.0480(12)
C10	0.7927(6)	0.4030(6)	0.6771(5)	0.0802(18)
C11	0.4558(5)	0.8609(5)	0.7963(3)	0.0477(12)
C12	0.2748(6)	0.7229(6)	0.9312(4)	0.0468(13)
C13	0.0068(6)	0.8012(6)	0.8894(4)	0.0672(15)
C14	0.9800(7)	0.6725(7)	0.8530(6)	0.100(2)
C15	0.9047(7)	0.9574(8)	0.8323(6)	0.118(3)
C16	0.5254(6)	0.7334(6)	0.0622(4)	0.0535(13)
C17	0.6553(7)	0.6931(6)	0.2310(4)	0.0668(16)
C18	0.6879(7)	0.5500(7)	0.3318(4)	0.092(2)
C19	0.7874(7)	0.7709(7)	0.1956(5)	0.091(2)
N1	0.5875(5)	0.0515(5)	0.6134(3)	0.0596(12)
N2	0.4208(5)	0.7430(4)	0.8959(3)	0.0473(10)
N3	0.5353(4)	0.6772(4)	0.9745(3)	0.0514(11)
O1	0.4345(4)	0.8500(4)	0.0725(3)	0.0702(11)
O2	0.6345(4)	0.6390(4)	0.1368(3)	0.0610(10)
O3	0.2532(4)	0.6281(4)	0.0203(3)	0.0604(10)
O4	0.1681(4)	0.8121(4)	0.8584(3)	0.0560(9)

Table 5. Bond lengths (Å) for compound 3f.

C1-N1	1.319(6)	C1-C2	1.398(7)
C1-H1	0.93	C2-C3	1.338(8)
C2-H2	0.93	C3-C4	1.398(7)
C3-H3	0.93	C4-C5	1.404(7)
C4-C9	1.409(6)	C5-C6	1.361(7)
C5-H5	0.93	C6-C7	1.415(6)
C6-C10	1.516(7)	C7-C8	1.369(6)
C7-H7	0.93	C8-C9	1.422(6)
C8-C11	1.519(6)	C9-N1	1.368(6)
C10-H10A	0.96	C10-H10B	0.96
C10-H10C	0.96	C11-N2	1.454(5)

C11-H11A	0.97	C11-H11B	0.97
C12-O3	1.223(5)	C12-O4	1.311(5)
C12-N2	1.368(6)	C13-O4	1.466(6)
C13-C15	1.501(7)	C13-C14	1.513(7)
C13-H13	0.98	C14-H14A	0.96
C14-H14B	0.96	C14-H14C	0.96
C15-H15A	0.96	C15-H15B	0.96
C15-H15C	0.96	C16-O1	1.203(5)
C16-N3	1.344(6)	C16-O2	1.348(5)
C17-O2	1.473(5)	C17-C19	1.512(7)
C17-C18	1.514(7)	C17-H17	0.98
C18-H18A	0.96	C18-H18B	0.96
C18-H18C	0.96	C19-H19A	0.96
C19-H19B	0.96	C19-H19C	0.96
N2-N3	1.376(4)	N3-H3A	0.86

Table 6. Bond angles (°) for compound 3f.

N1-C1-C2	123.8(6)	N1-C1-H1	118.1
C2-C1-H1	118.1	C3-C2-C1	119.0(6)
C3-C2-H2	120.5	C1-C2-H2	120.5
C2-C3-C4	120.6(6)	C2-C3-H3	119.7
C4-C3-H3	119.7	C3-C4-C5	124.3(5)
C3-C4-C9	116.9(5)	C5-C4-C9	118.8(5)
C6-C5-C4	122.8(5)	C6-C5-H5	118.6
C4-C5-H5	118.6	C5-C6-C7	117.4(5)
C5-C6-C10	123.5(5)	C7-C6-C10	119.1(5)
C8-C7-C6	122.6(5)	C8-C7-H7	118.7
C6-C7-H7	118.7	C7-C8-C9	119.0(4)
C7-C8-C11	122.7(4)	C9-C8-C11	118.3(4)
N1-C9-C4	122.6(5)	N1-C9-C8	118.1(4)
C4-C9-C8	119.3(5)	C6-C10-H10A	109.5
C6-C10-H10B	109.5	H10A-C10-H10B	109.5
C6-C10-H10C	109.5	H10A-C10-H10C	109.5
H10B-C10-H10C	109.5	N2-C11-C8	112.6(4)
N2-C11-H11A	109.1	C8-C11-H11A	109.1
N2-C11-H11B	109.1	C8-C11-H11B	109.1
H11A-C11-H11B	107.8	O3-C12-O4	126.1(5)
O3-C12-N2	121.5(4)	O4-C12-N2	112.4(5)

O4-C13-C15	105.5(4)	O4-C13-C14	109.3(4)
C15-C13-C14	113.6(5)	O4-C13-H13	109.4
C15-C13-H13	109.4	C14-C13-H13	109.4
C13-C14-H14A	109.5	C13-C14-H14B	109.5
H14A-C14-H14B	109.5	C13-C14-H14C	109.5
H14A-C14-H14C	109.5	H14B-C14-H14C	109.5
C13-C15-H15A	109.5	C13-C15-H15B	109.5
H15A-C15-H15B	109.5	C13-C15-H15C	109.5
H15A-C15-H15C	109.5	H15B-C15-H15C	109.5
O1-C16-N3	125.6(5)	O1-C16-O2	125.0(5)
N3-C16-O2	109.3(4)	O2-C17-C19	106.9(4)
O2-C17-C18	105.2(4)	C19-C17-C18	114.7(5)
O2-C17-H17	110.0	C19-C17-H17	110.0
C18-C17-H17	110.0	C17-C18-H18A	109.5
C17-C18-H18B	109.5	H18A-C18-H18B	109.5
C17-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C17-C19-H19A	109.5
C17-C19-H19B	109.5	H19A-C19-H19B	109.5
C17-C19-H19C	109.5	H19A-C19-H19C	109.5
H19B-C19-H19C	109.5	C1-N1-C9	117.0(5)
C12-N2-N3	116.8(4)	C12-N2-C11	125.3(4)
N3-N2-C11	115.3(4)	C16-N3-N2	119.2(4)
C16-N3-H3A	120.4	N2-N3-H3A	120.4
C16-O2-C17	116.9(4)	C12-O4-C13	116.6(4)

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 3f.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.105(5)	0.068(4)	0.056(3)	-0.020(3)	-0.001(3)	-0.043(4)
C2	0.102(5)	0.095(5)	0.063(4)	-0.022(4)	0.009(4)	-0.051(4)
C3	0.085(4)	0.095(5)	0.056(3)	-0.035(4)	0.008(3)	-0.040(4)
C4	0.065(4)	0.073(4)	0.043(3)	-0.026(3)	0.003(3)	-0.030(3)
C5	0.059(4)	0.086(4)	0.059(3)	-0.043(3)	0.008(3)	-0.019(3)
C6	0.065(4)	0.069(4)	0.058(3)	-0.042(3)	-0.002(3)	-0.019(3)
C7	0.073(4)	0.056(3)	0.044(3)	-0.029(3)	0.001(3)	-0.024(3)
C8	0.049(3)	0.054(3)	0.046(3)	-0.031(3)	0.001(2)	-0.017(2)
C9	0.061(3)	0.055(3)	0.042(3)	-0.024(3)	-0.012(3)	-0.021(3)

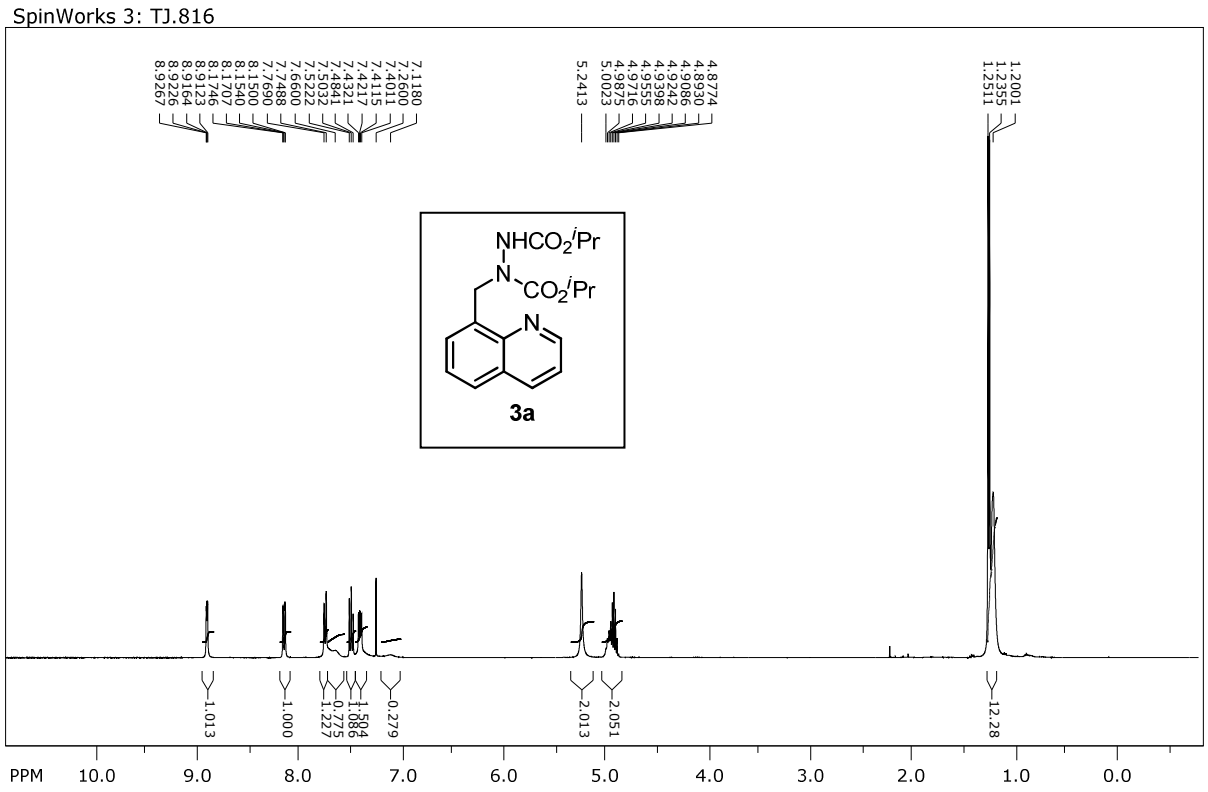
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	0.093(5)	0.070(4)	0.085(4)	-0.044(3)	0.004(3)	-0.012(3)
C11	0.056(3)	0.049(3)	0.042(3)	-0.015(2)	0.004(2)	-0.020(2)
C12	0.057(4)	0.043(3)	0.048(3)	-0.031(3)	-0.006(3)	-0.003(3)
C13	0.059(4)	0.074(4)	0.067(4)	-0.021(3)	0.003(3)	-0.017(3)
C14	0.092(5)	0.100(5)	0.129(6)	-0.047(4)	-0.011(4)	-0.039(4)
C15	0.056(4)	0.125(6)	0.162(7)	-0.044(5)	-0.007(4)	-0.003(4)
C16	0.058(3)	0.044(3)	0.058(3)	-0.016(3)	-0.014(3)	-0.006(3)
C17	0.086(4)	0.074(4)	0.057(3)	-0.045(3)	-0.008(3)	-0.017(3)
C18	0.136(6)	0.086(5)	0.060(4)	-0.027(3)	-0.029(4)	-0.021(4)
C19	0.106(5)	0.092(5)	0.104(5)	-0.061(4)	-0.009(4)	-0.033(4)
N1	0.078(3)	0.058(3)	0.052(3)	-0.021(2)	-0.004(2)	-0.026(2)
N2	0.047(3)	0.049(3)	0.043(2)	-0.0109(19)	-0.009(2)	-0.007(2)
N3	0.058(3)	0.048(2)	0.052(2)	-0.030(2)	-0.008(2)	0.000(2)
O1	0.084(3)	0.058(2)	0.073(3)	-0.035(2)	-0.008(2)	-0.006(2)
O2	0.081(2)	0.053(2)	0.059(2)	-0.0360(18)	-0.018(2)	-0.0045(19)
O3	0.075(3)	0.055(2)	0.053(2)	-0.0217(18)	0.0021(19)	-0.0151(19)
O4	0.048(2)	0.064(2)	0.056(2)	-0.0167(17)	-0.0073(18)	-0.0129(17)

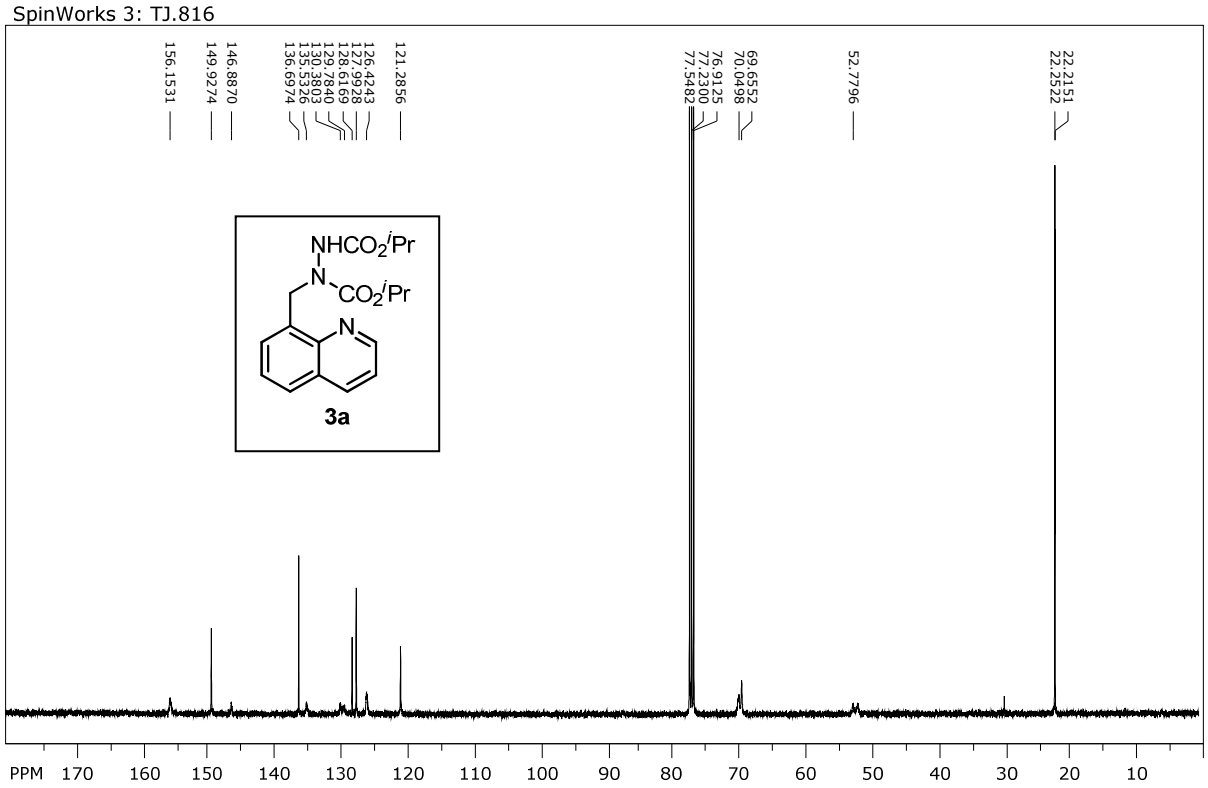
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 3f.

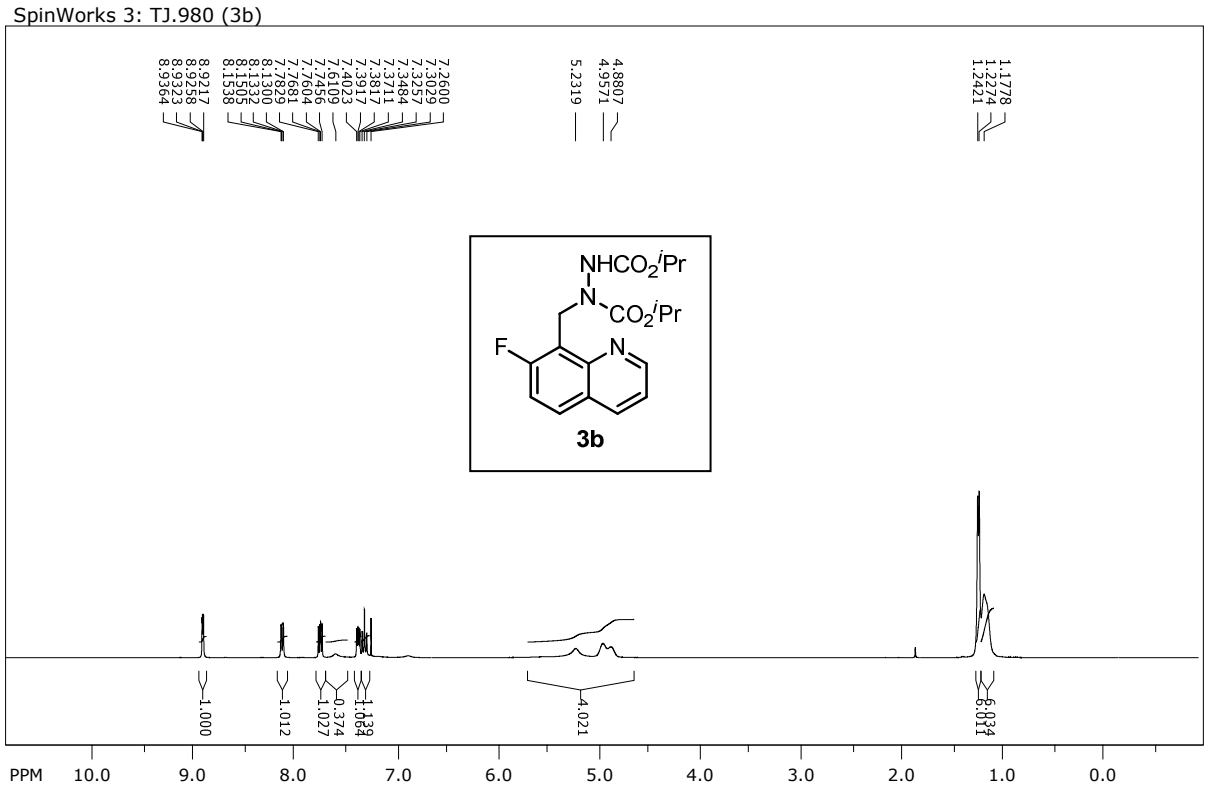
	x/a	y/b	z/c	U(eq)
H1	0.6106	1.2504	0.5173	0.086
H2	0.8102	1.1643	0.3983	0.099
H3	0.8988	0.9077	0.4182	0.088
H5	0.8885	0.6364	0.5274	0.076
H7	0.5806	0.5725	0.7858	0.064
H10A	0.8642	0.3787	0.6175	0.12
H10B	0.7024	0.3659	0.6792	0.12
H10C	0.8432	0.3546	0.7480	0.12
H11A	0.4941	0.9323	0.8198	0.057
H11B	0.3602	0.9184	0.7564	0.057
H13	-0.0102	0.7790	0.9714	0.081
H14A	0.0037	0.6905	0.7735	0.151
H14B	-0.1274	0.6696	0.8686	0.151
H14C	0.0468	0.5758	0.8937	0.151
H15A	-0.0841	1.0311	0.8667	0.177
H15B	-0.2026	0.9533	0.8398	0.177

	x/a	y/b	z/c	U(eq)
H15C	-0.0646	0.9878	0.7537	0.177
H17	0.5589	0.7671	1.2455	0.08
H18A	0.6014	0.5043	1.3459	0.138
H18B	0.7016	0.5776	1.3969	0.138
H18C	0.7814	0.4775	1.3164	0.138
H19A	0.8838	0.6953	1.1898	0.137
H19B	0.7961	0.8192	1.2507	0.137
H19C	0.7664	0.8475	1.1236	0.137
H3A	0.6122	0.6012	0.9676	0.062

^{1}H and ^{13}C NMR spectra of all compounds



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8.1502
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7.7681
7.7604
7.7456
7.6109
7.4023
7.3917
7.3817
7.3711
7.3484
7.3257
7.3029
7.2600
5.2319
4.9571
4.8807
1.2421
1.2274
1.1778
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CO2iPr
F
N
3b
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0.374
1.027
1.139
1.084
4.021
6.011
6.034
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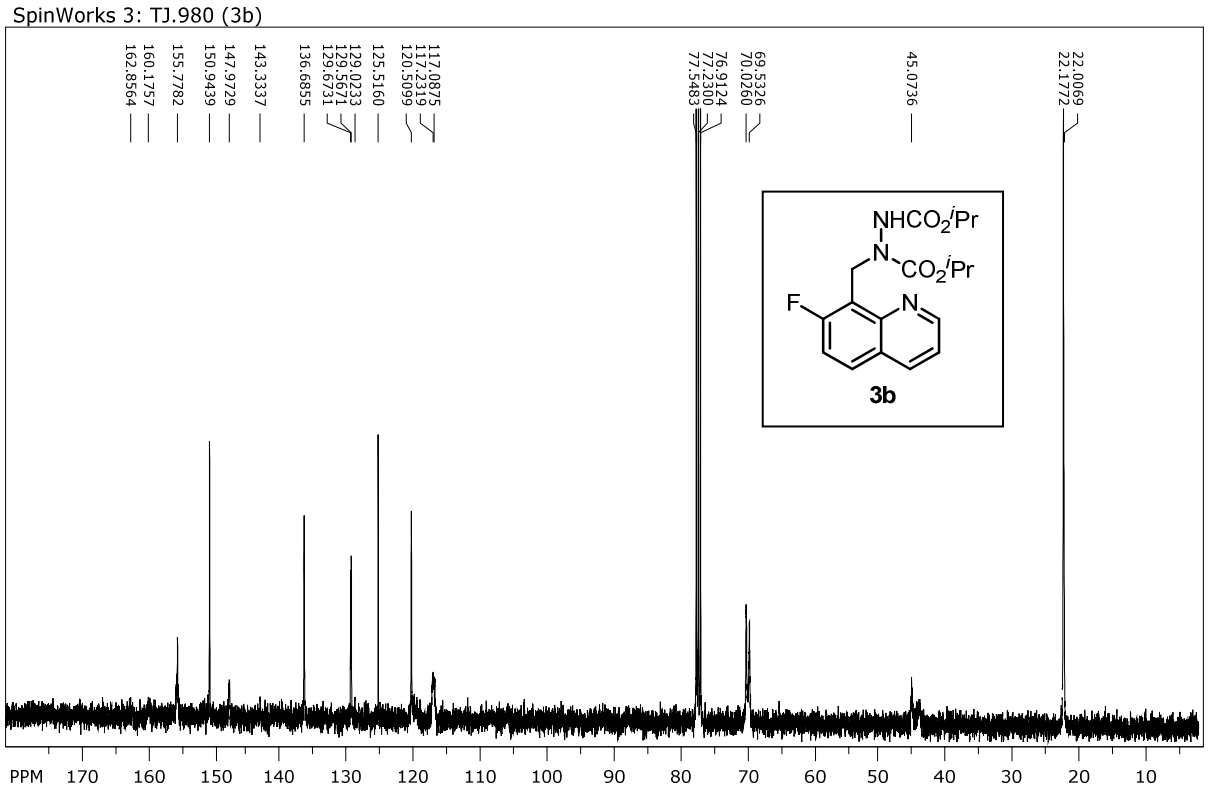
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136.6855
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129.0233
125.5160
120.5099
117.2319
117.0875
77.5483
77.2300
76.9124
70.0260
69.5326
45.0736
22.1772
22.0069
NHCO2iPr
N
CO2iPr
F
N
3b
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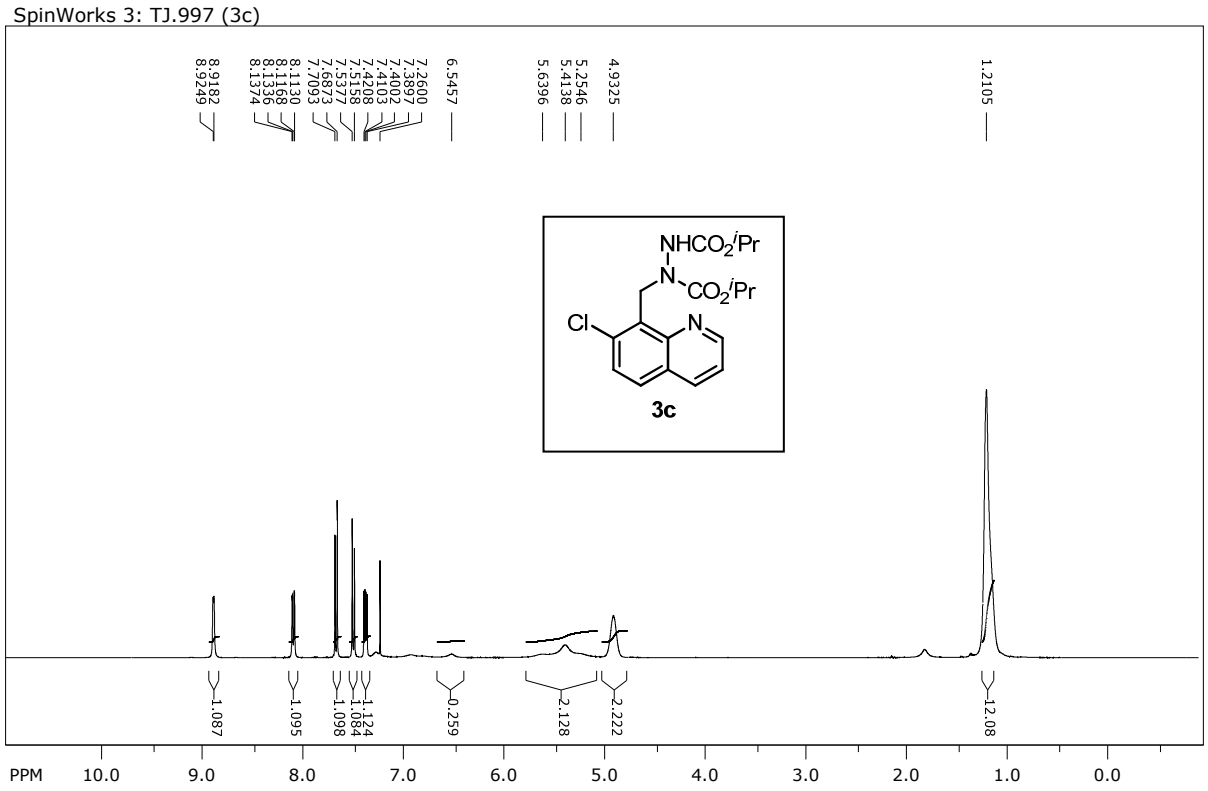
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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8.1130
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7.6873
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7.5158
7.4308
7.4103
7.3897
7.2600
6.5457
5.6396
5.4138
5.2546
4.9325
1.2105
NHCO2iPr
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CO2iPr
Cl
N
3c
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1.095
1.098
1.124
1.084
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2.128
2.222
12.08
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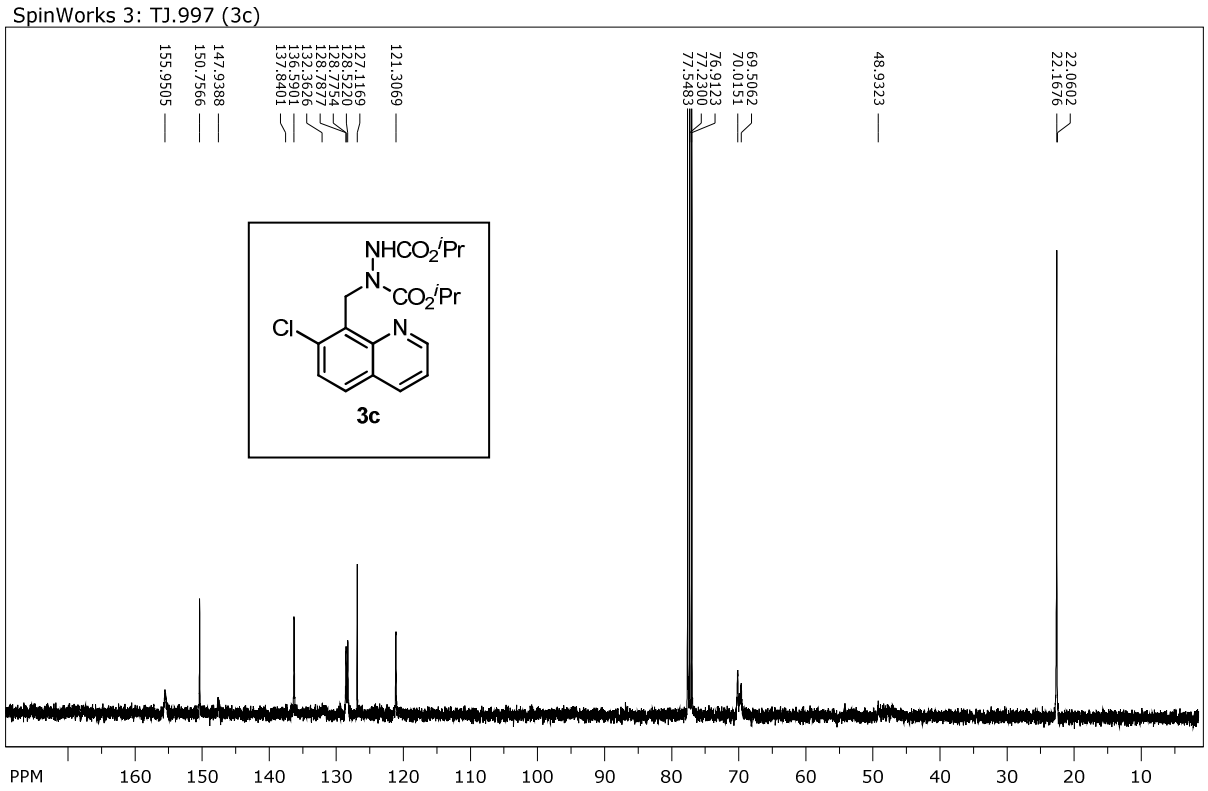
1.0
0.0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128.5220
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121.3069
77.5483
77.2300
76.9123
70.0151
69.5062
48.9323
22.1676
22.0602
NHCO2iPr
N
CO2iPr
Cl
N
3c
PPM
160
150
140
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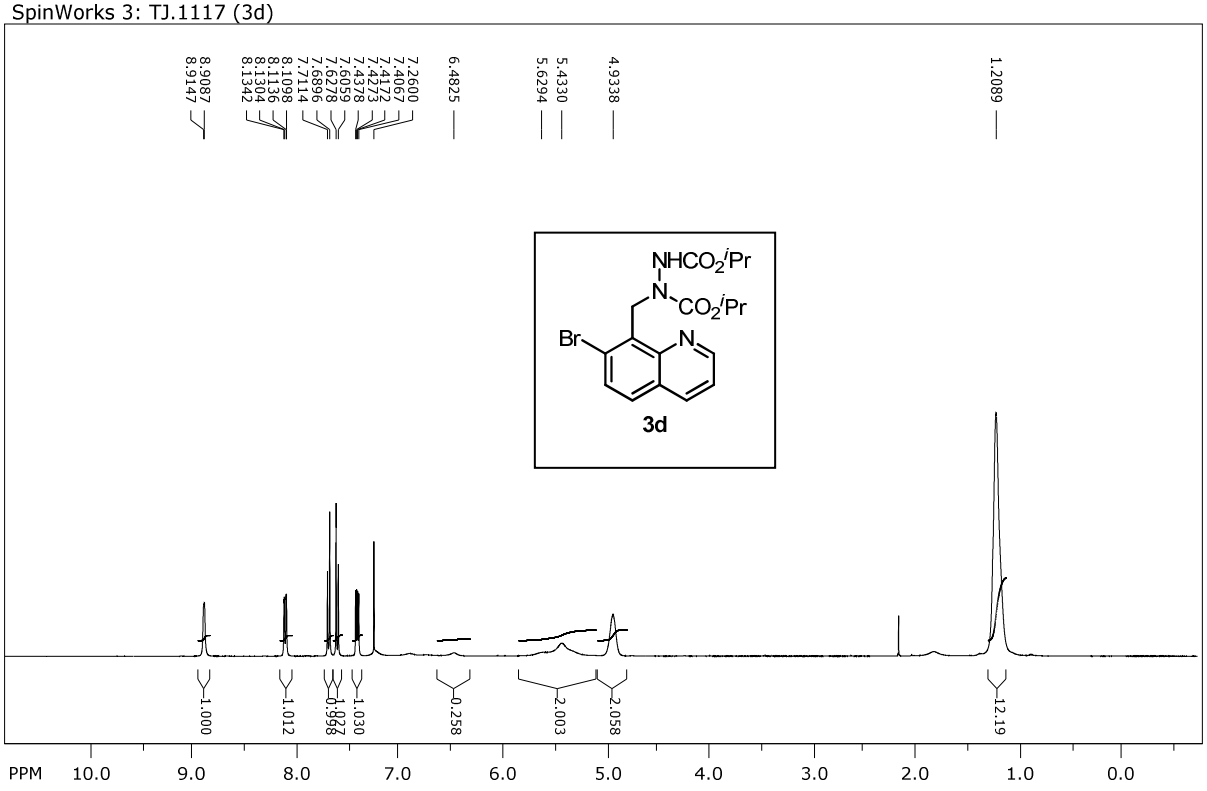
120
110
100
90
80
70
60
50
40
30
20
10

SpinWorks 3: TJ.1117 (3d)



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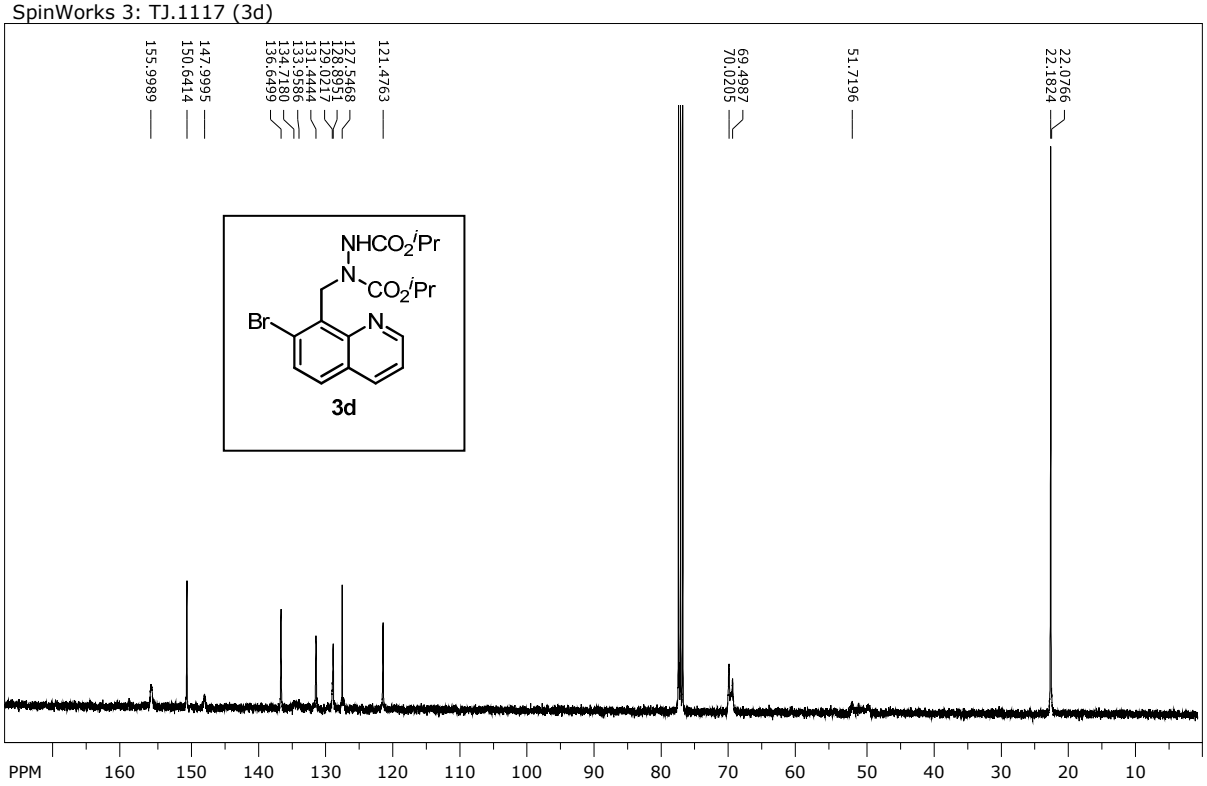

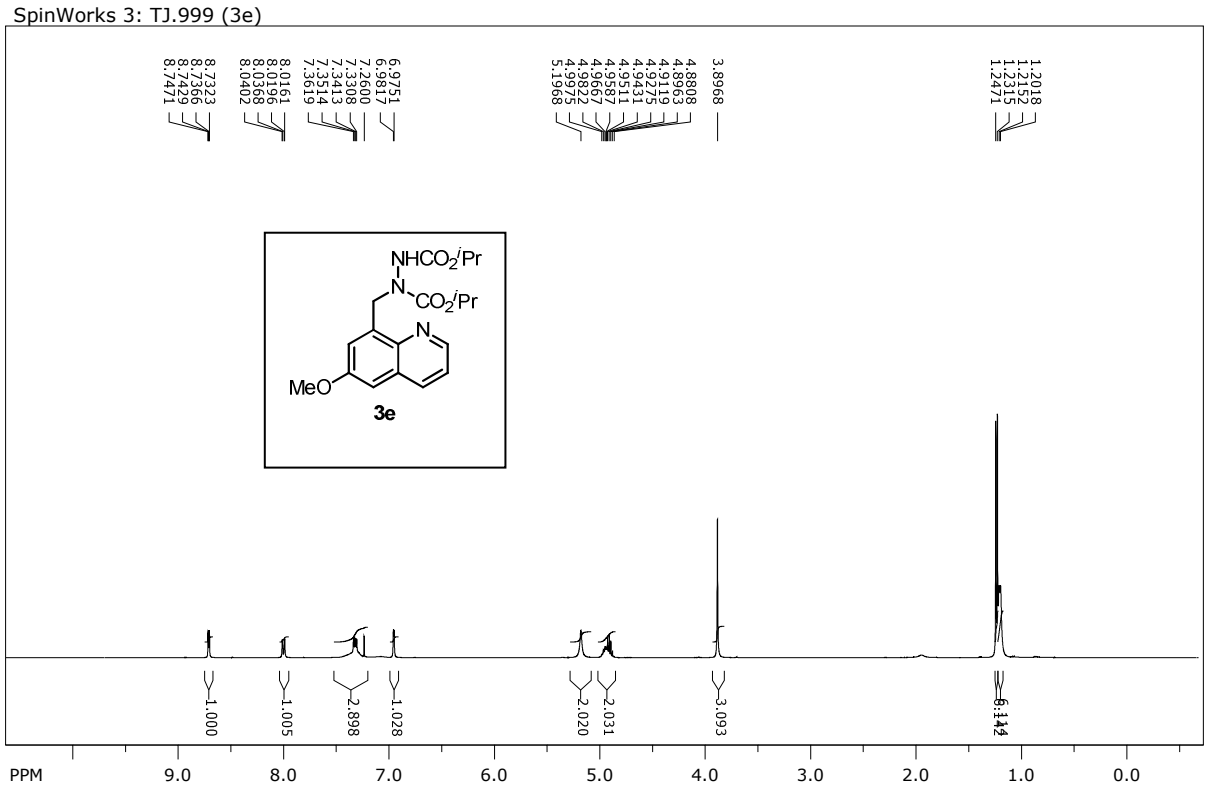
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8.0402
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7.3514
7.3413
7.3308
7.2600
6.9751
6.9617
5.1968
4.9975
4.9822
4.9667
4.9587
4.9511
4.9431
4.9275
4.9119
4.8963
4.8808
3.8968
1.2018
1.2152
1.2315
1.2471
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CO2iPr
N
MeO
3e
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3.093
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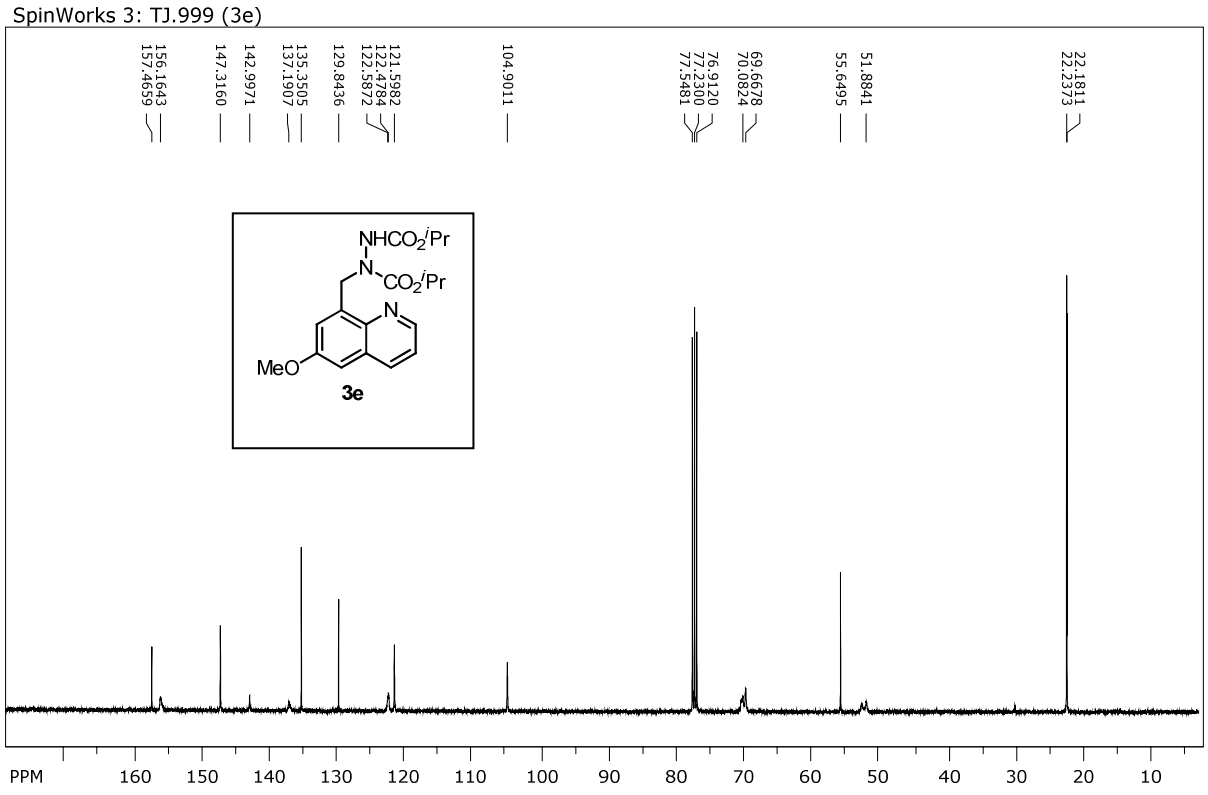
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77.5481
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22.1811
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CO2iPr
N
MeO
3e
PPM
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80
70
60
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20
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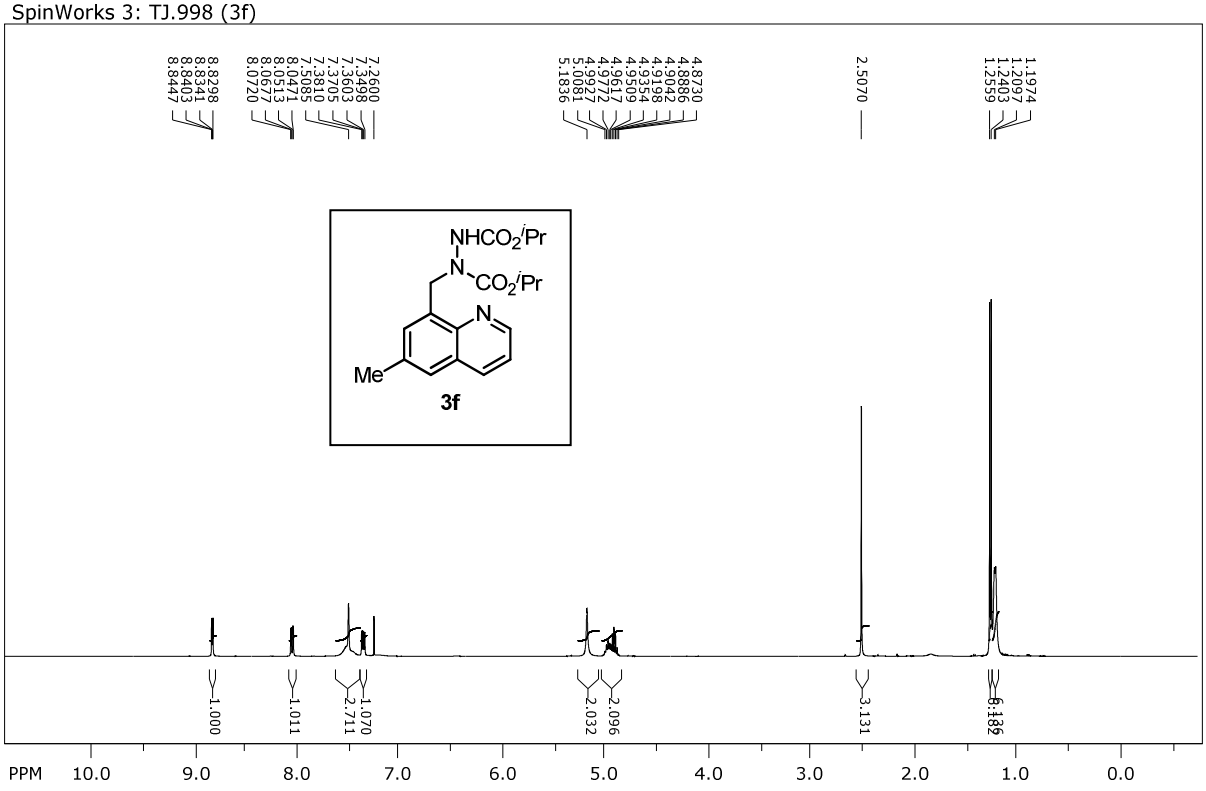
SpinWorks 3: TJ.998 (3f)



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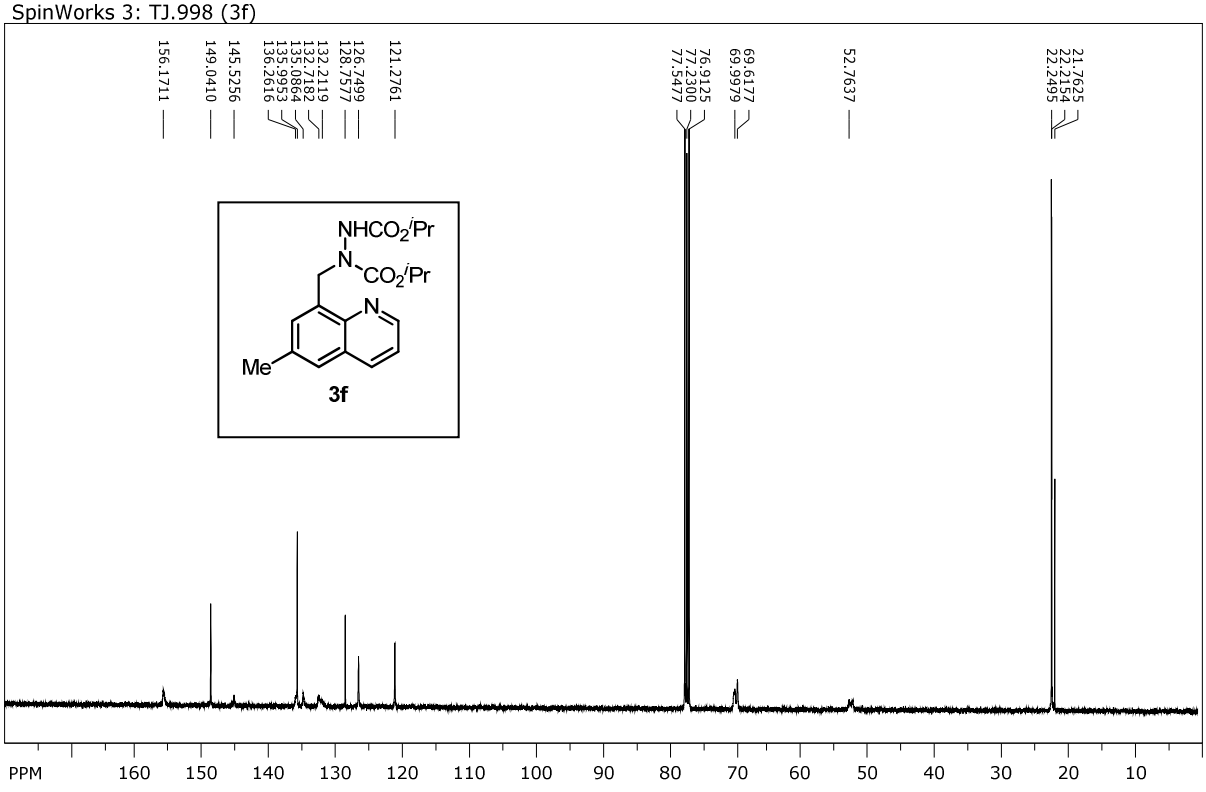

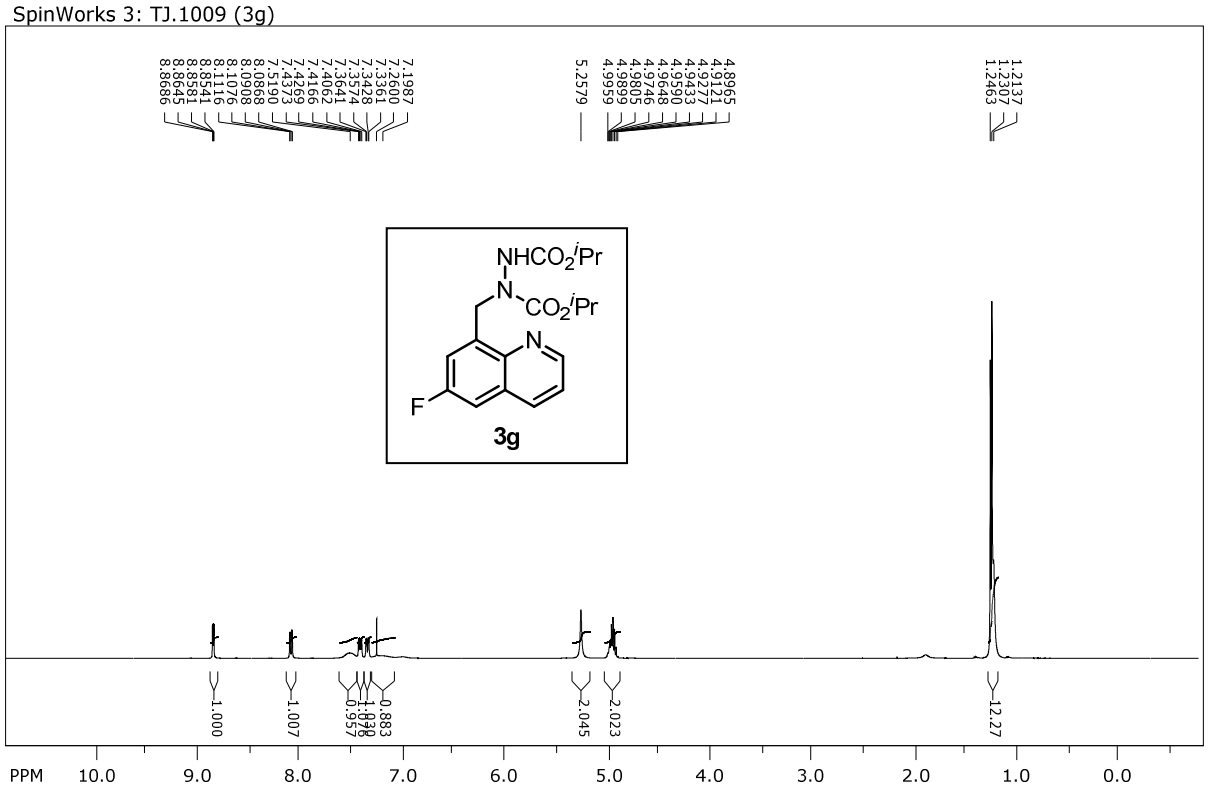
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8.0868
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7.4373
7.4269
7.4166
7.4062
7.3641
7.3578
7.3361
7.2600
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4.9648
4.9590
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1.2307
1.2137
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N
CO2iPr
N
F
3g
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1.007
0.957
1.030
1.018
0.883
2.045
2.023
12.27
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4.0
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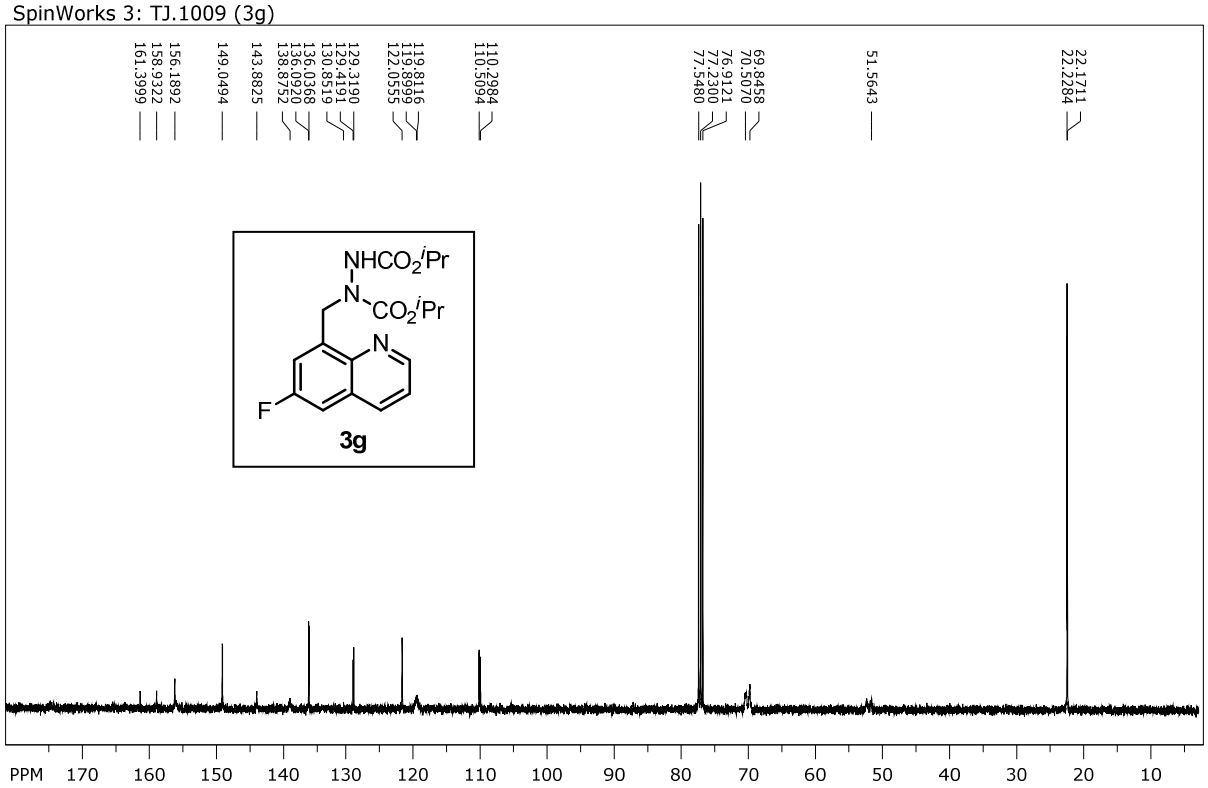
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129.4191
129.3190
119.8999
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22.1711
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CO2iPr
N
F
3g
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130
120
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80
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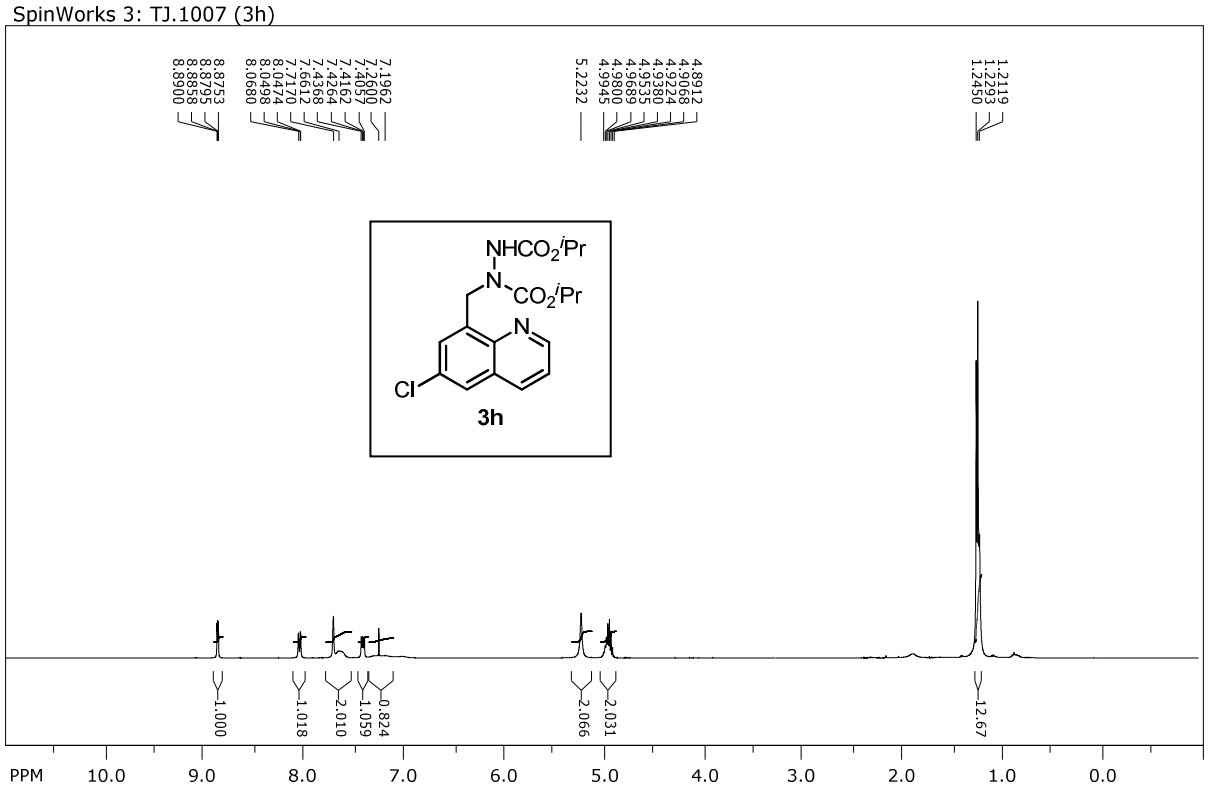
50
40
30
20
10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4.9945
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4.9068
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CO2iPr
N
Cl
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0.824
2.066
2.031
12.67
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4.0
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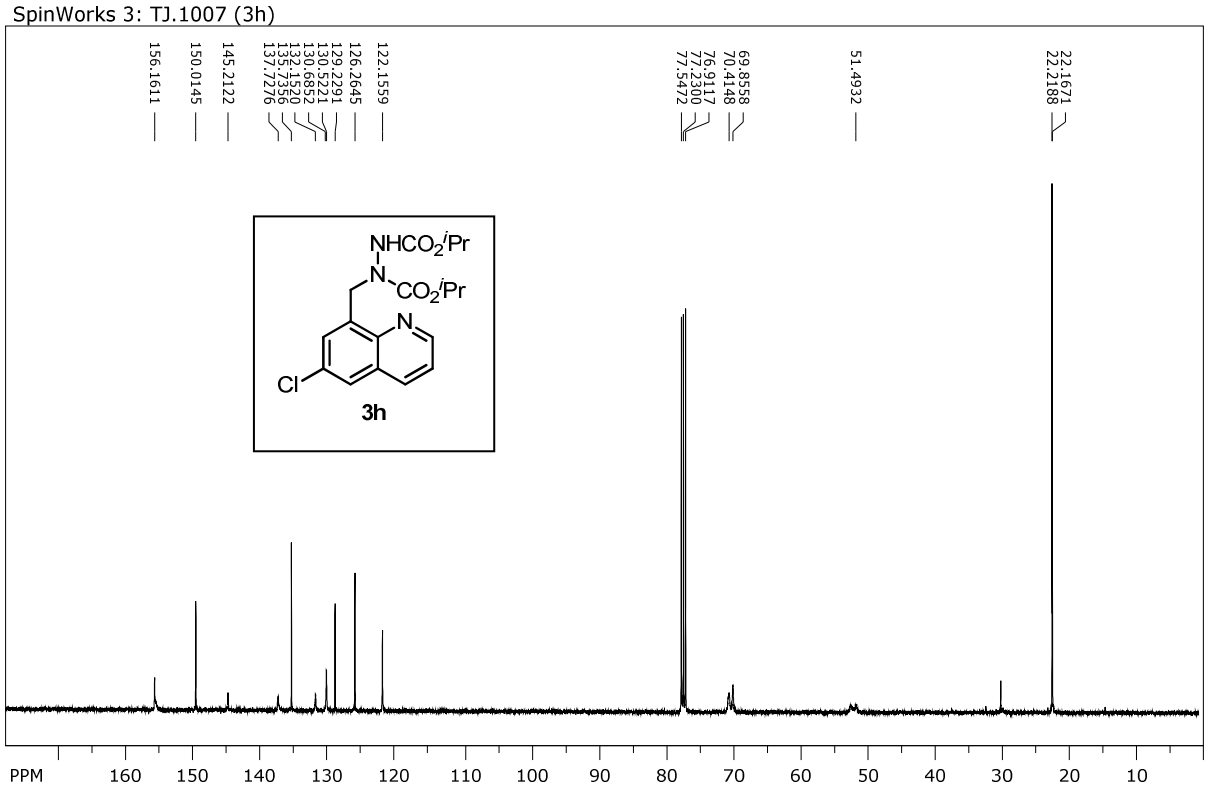
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126.2645
122.1559
77.5472
77.2300
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CO2iPr
N
Cl
3h
PPM
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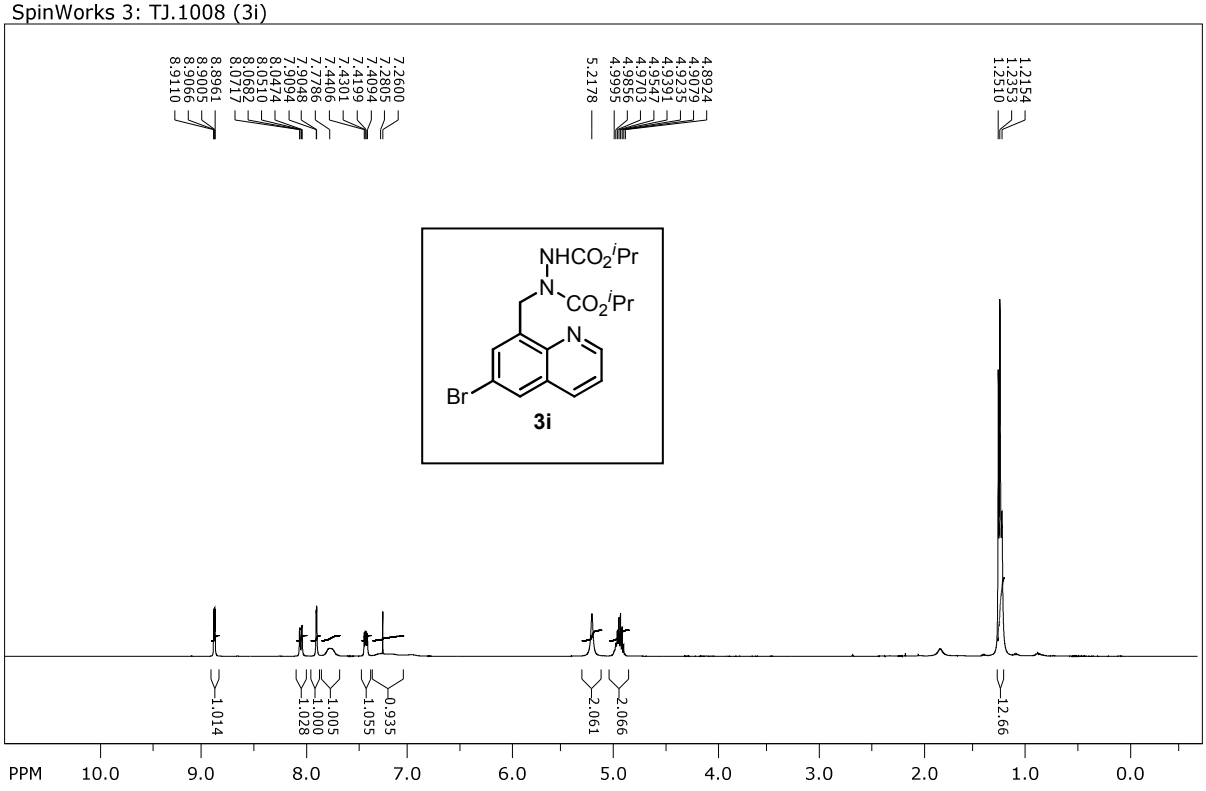
140
130
120
110
100
90
80
70
60
50
40
30
20
10

SpinWorks 3: TJ.1008 (3i)



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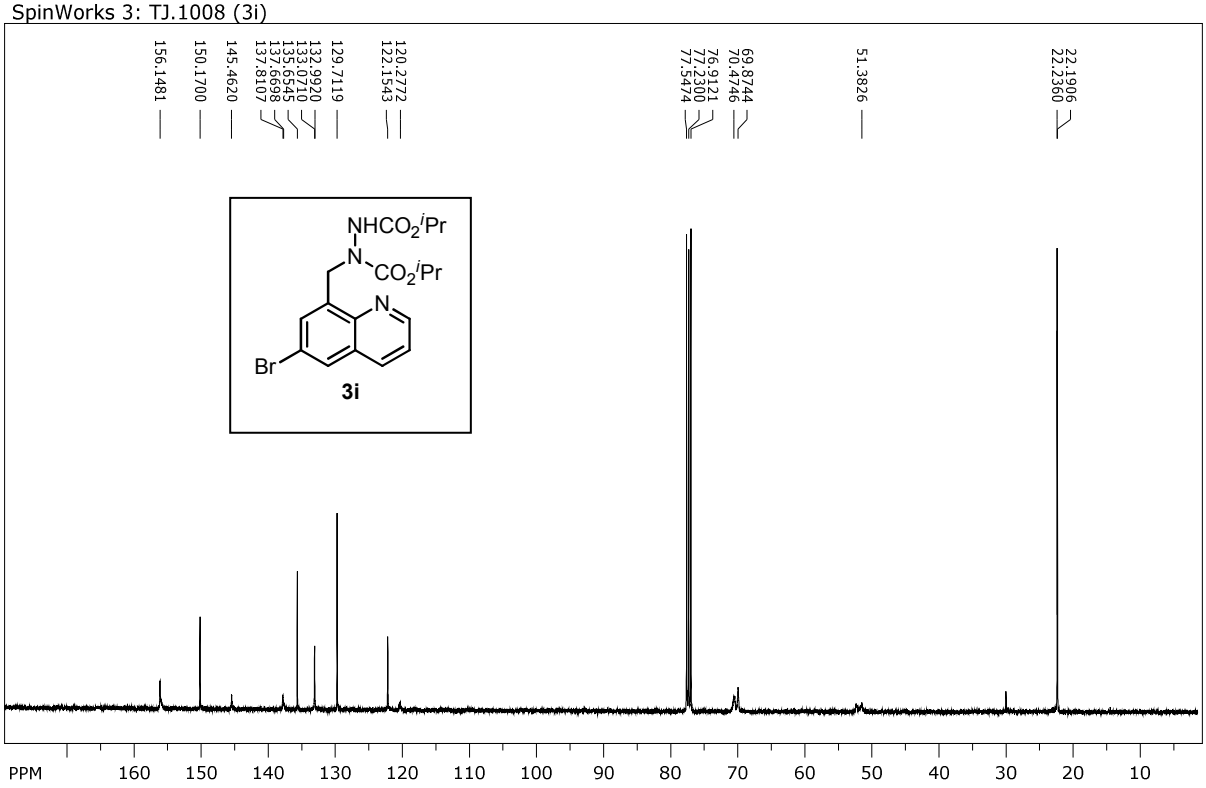

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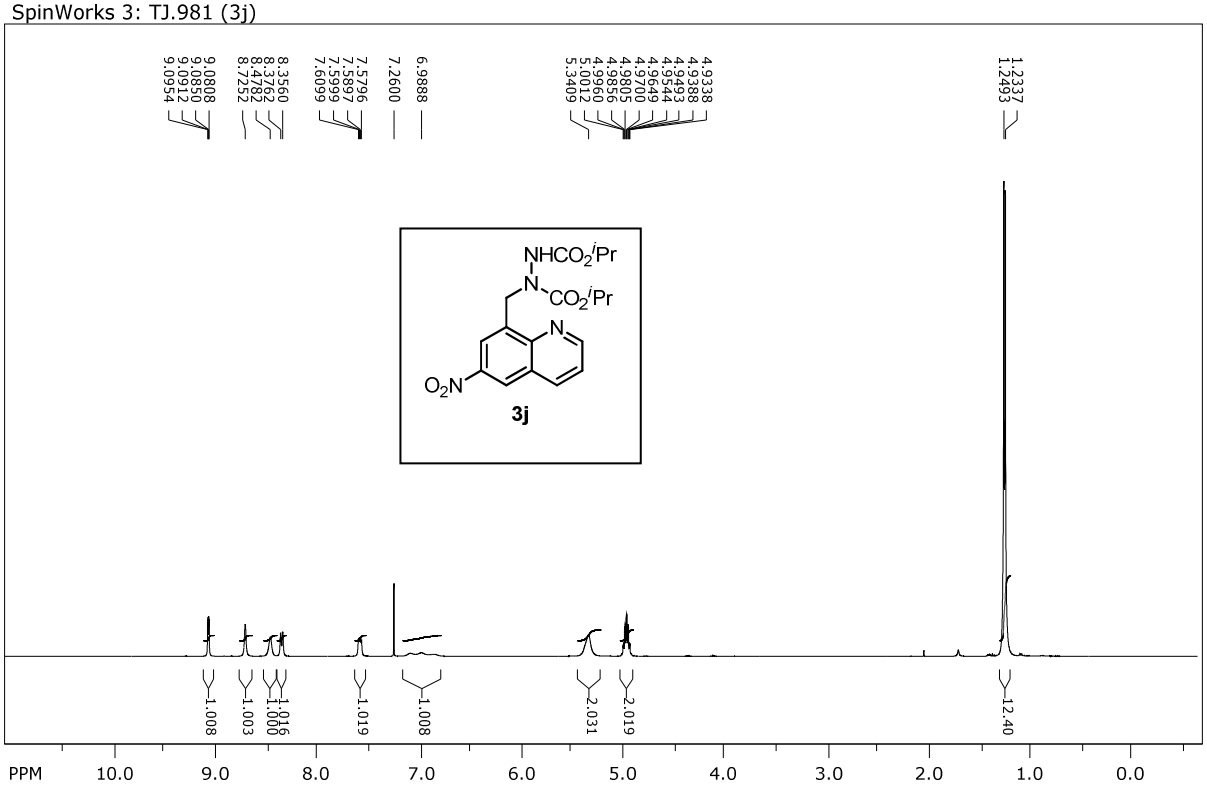
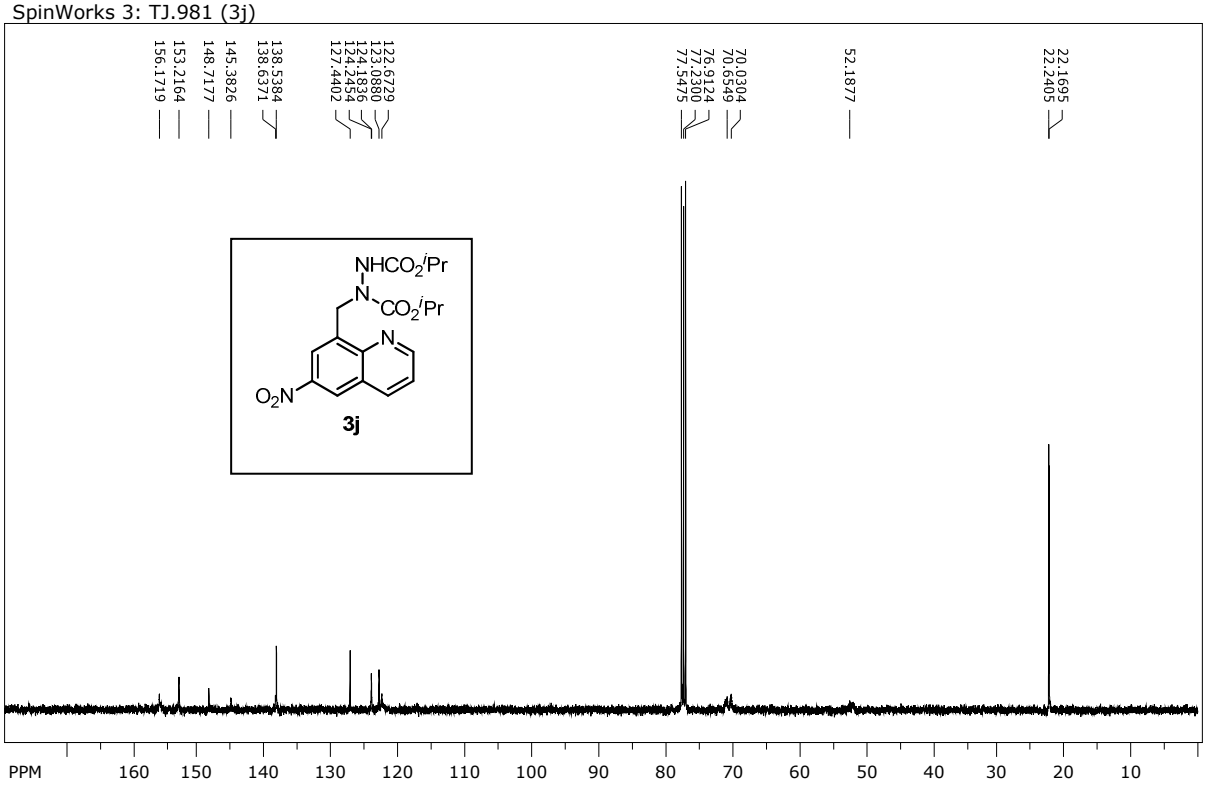
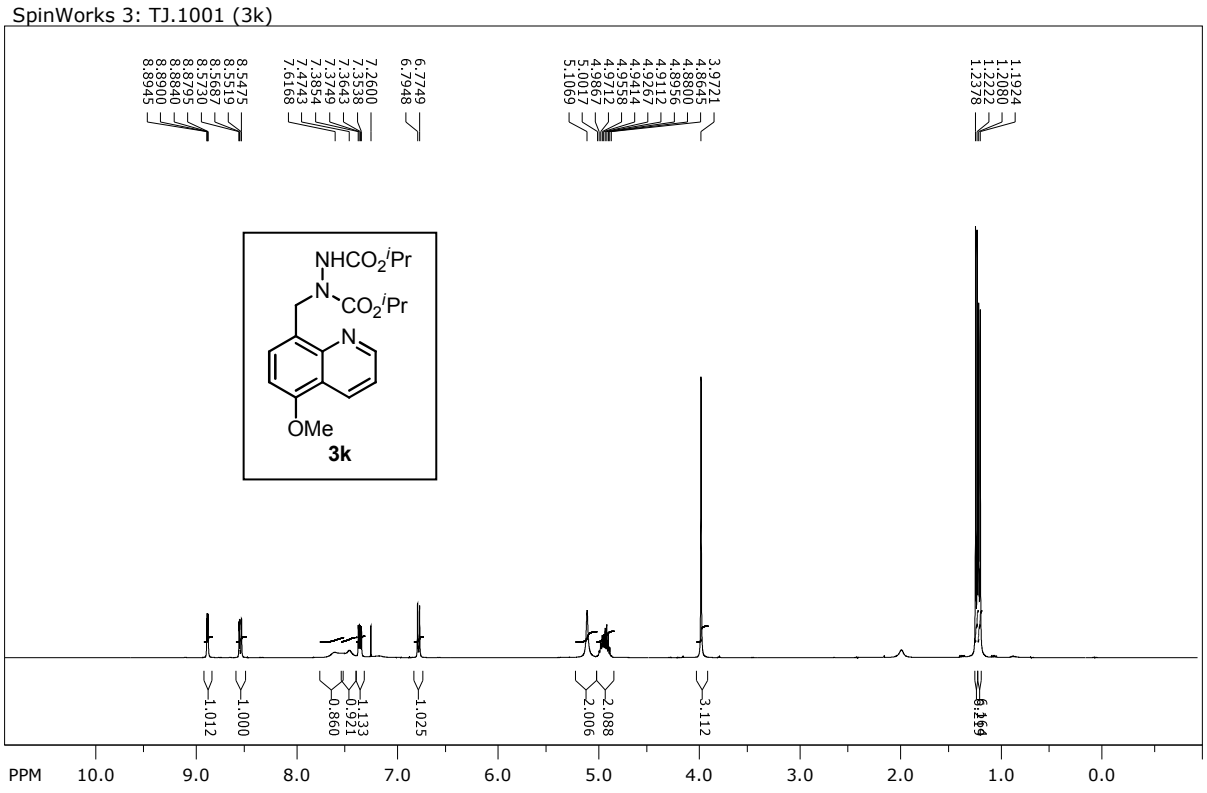
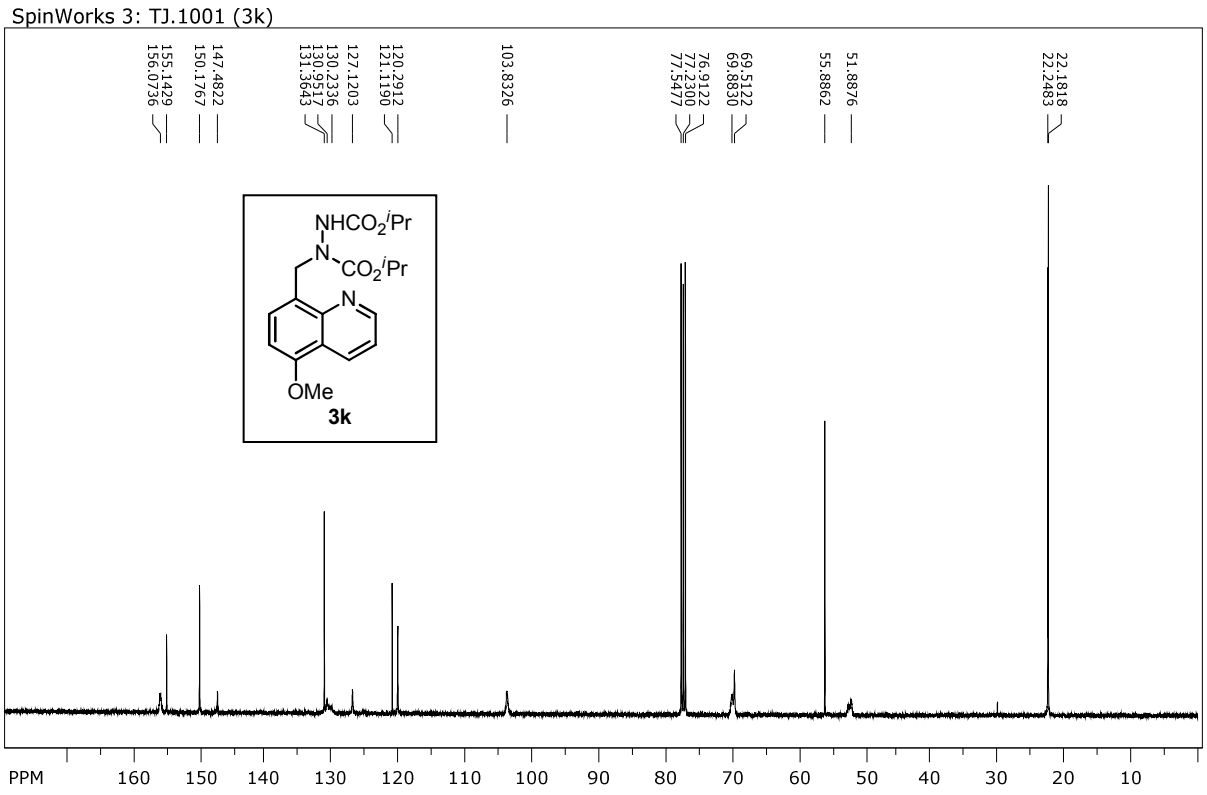


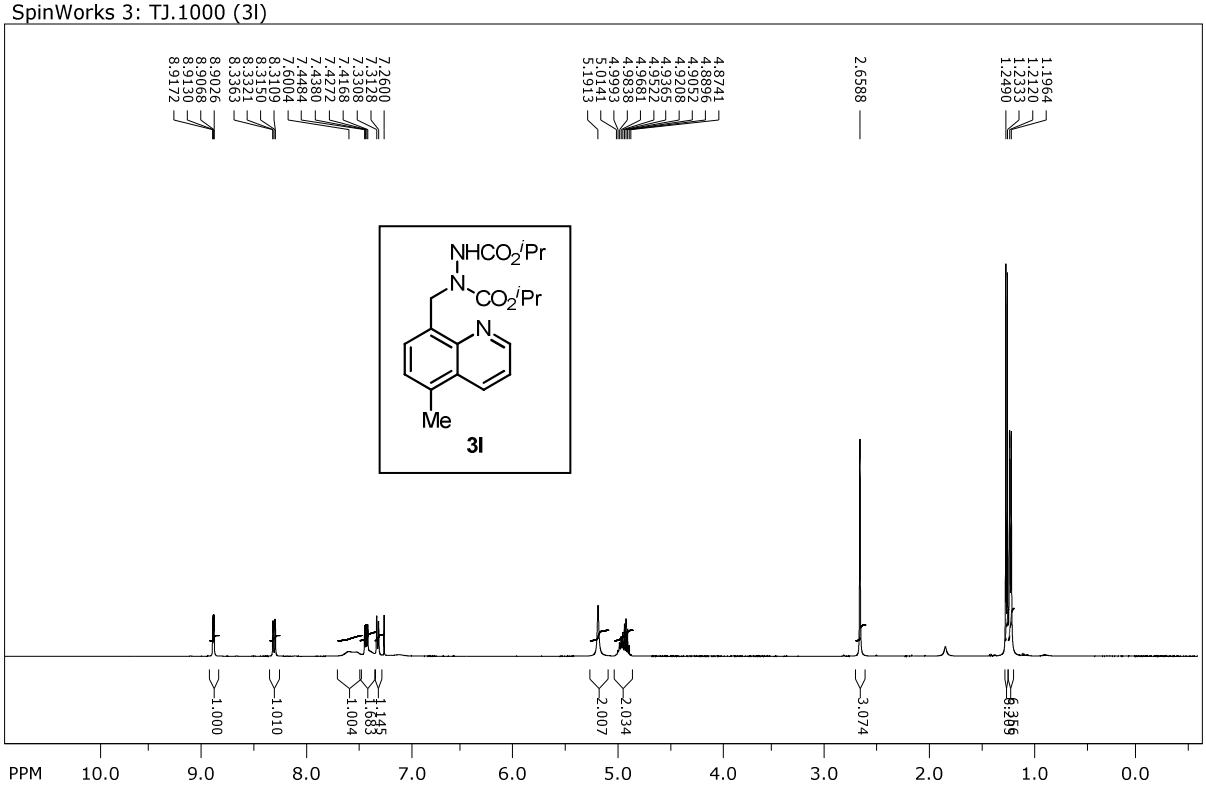
SpinWorks 3: TJ.981 (3j)



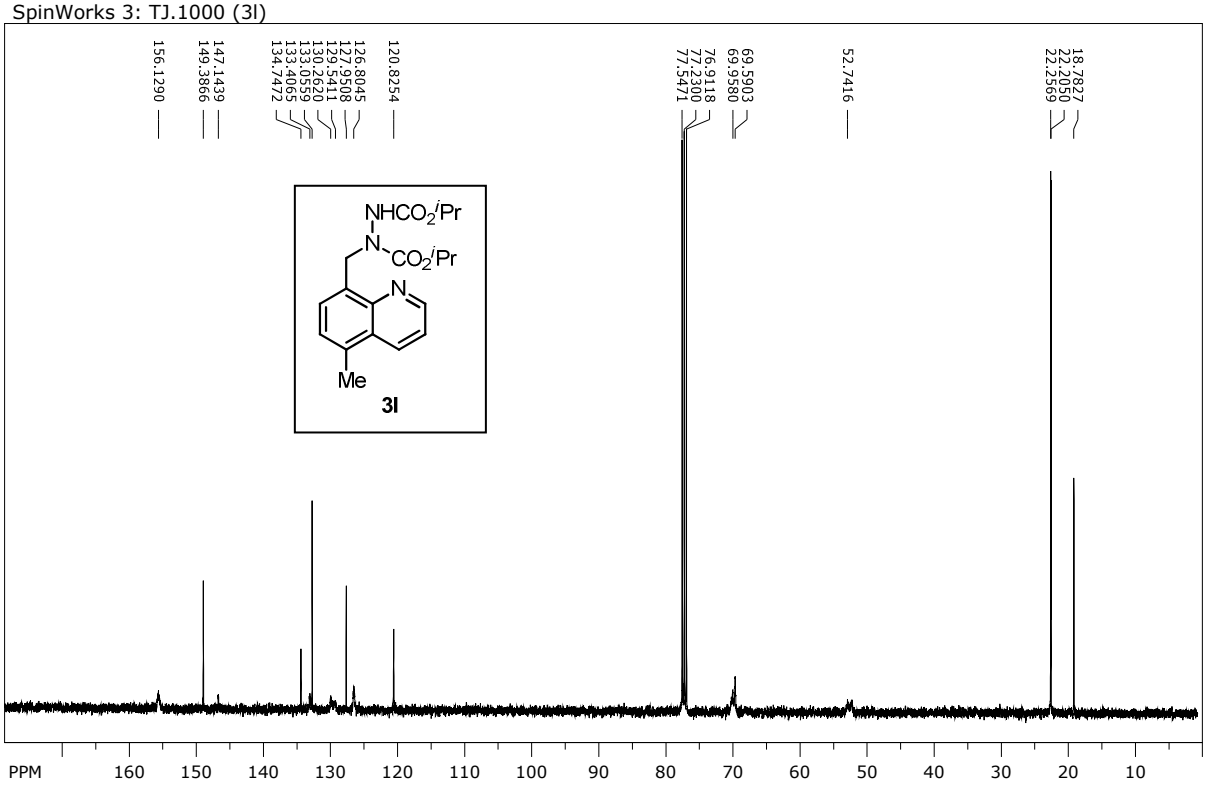

SpinWorks 3: TJ.1001 (3k)
NHCO2iPr
N
CO2iPr
N
OMe
3k
PPM

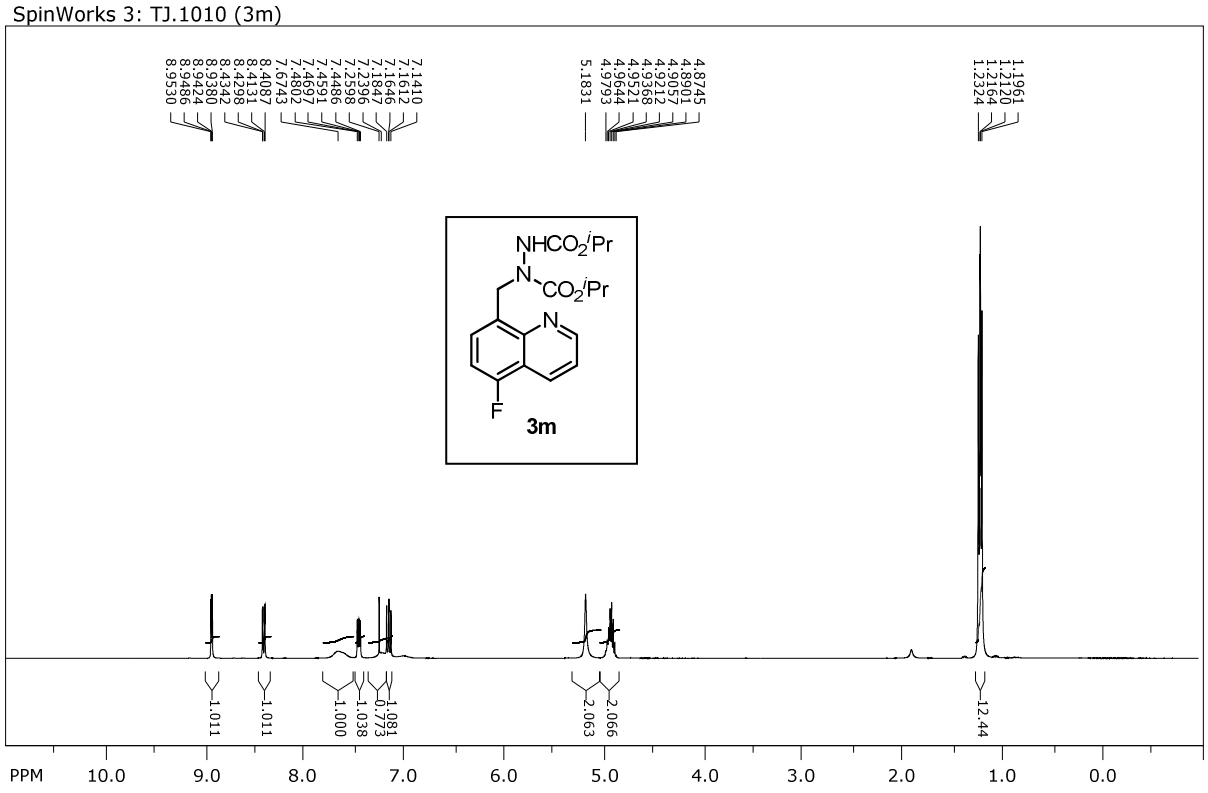

SpinWorks 3: TJ.1001 (3k)
NHCO2iPr
N
CO2iPr
N
OMe
3k
PPM

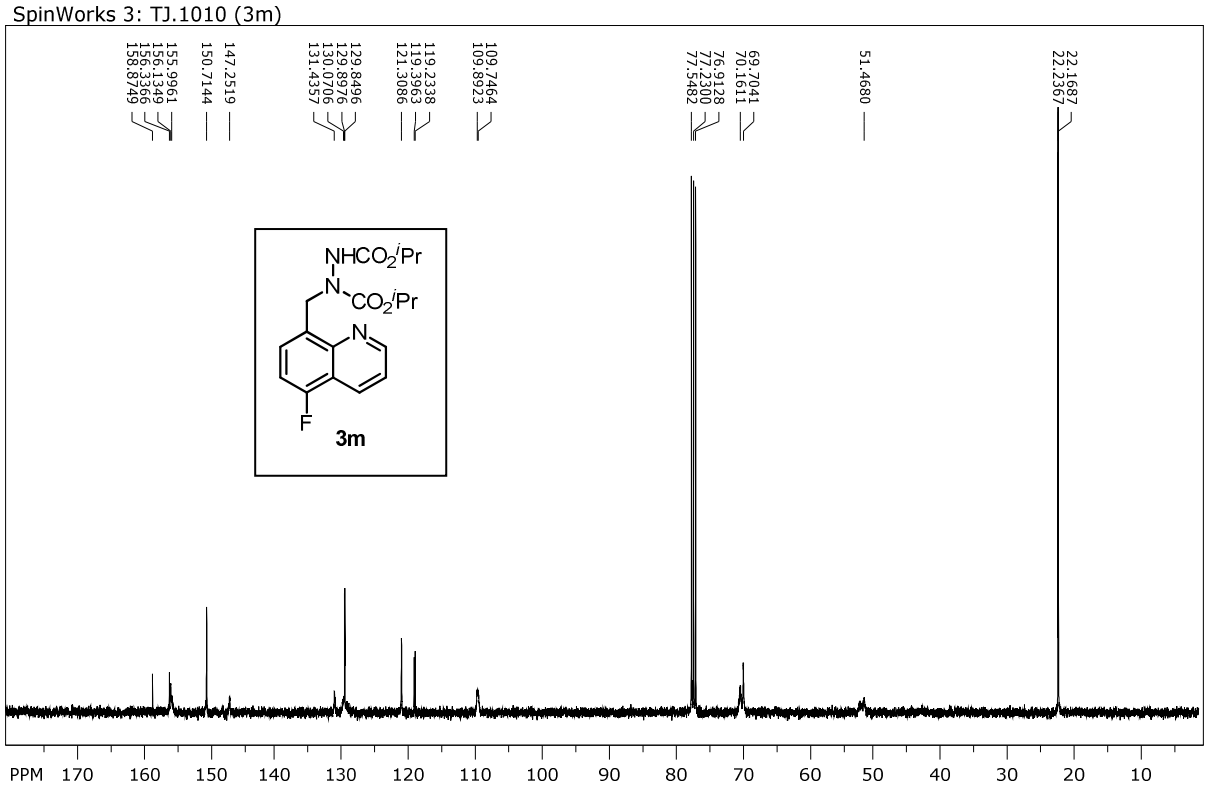
SpinWorks 3: TJ.1000 (3l)

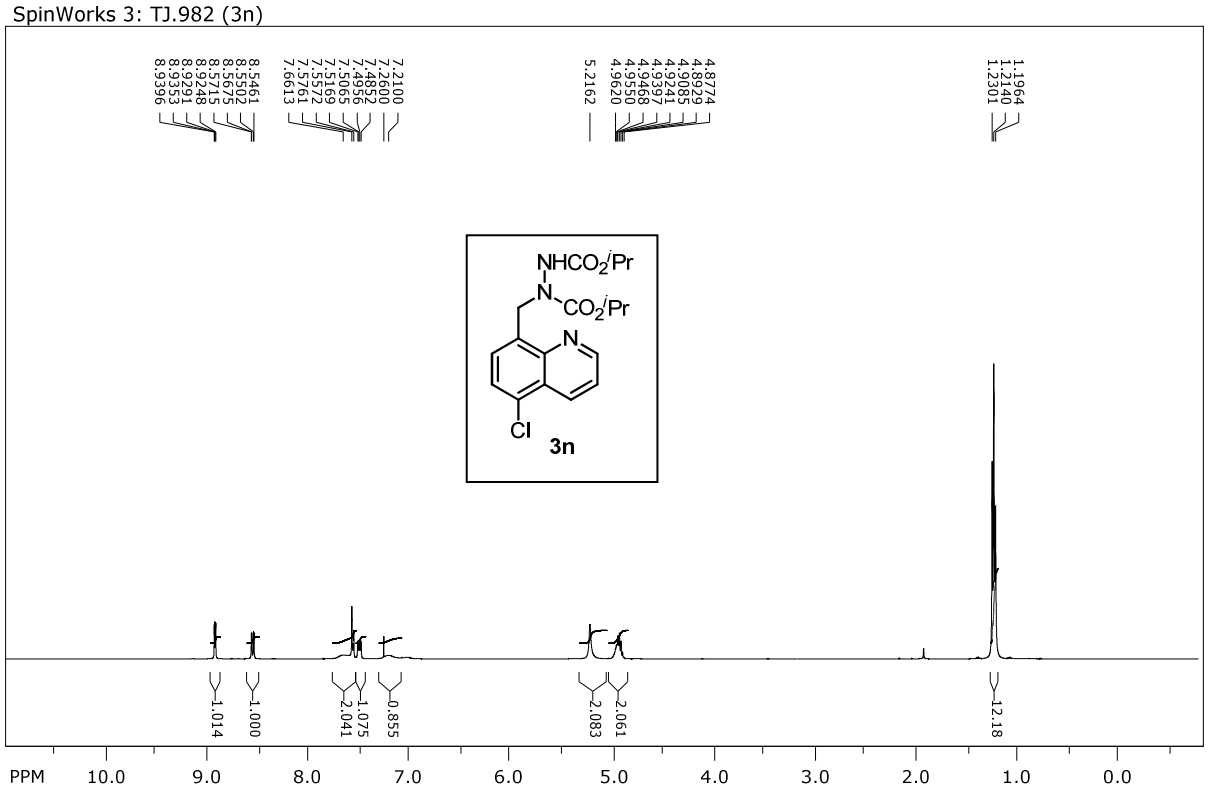


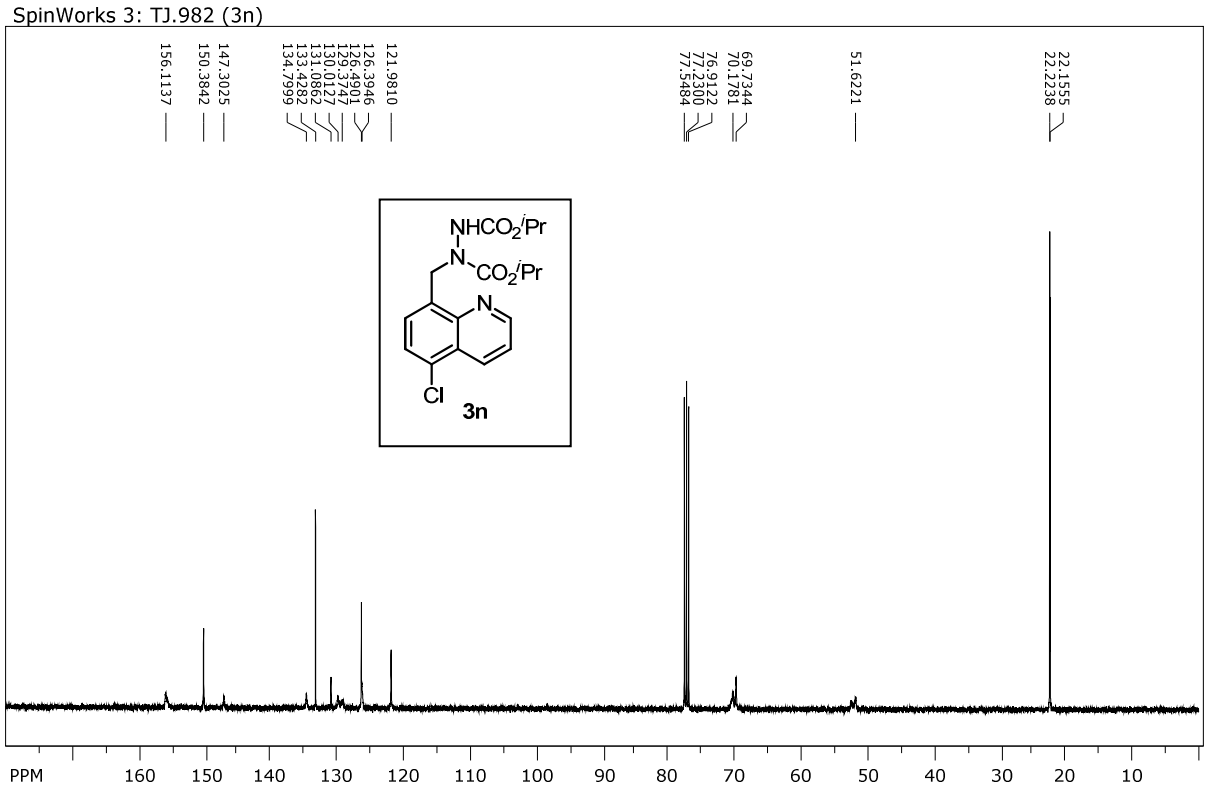
SpinWorks 3: TJ.1000 (3l)



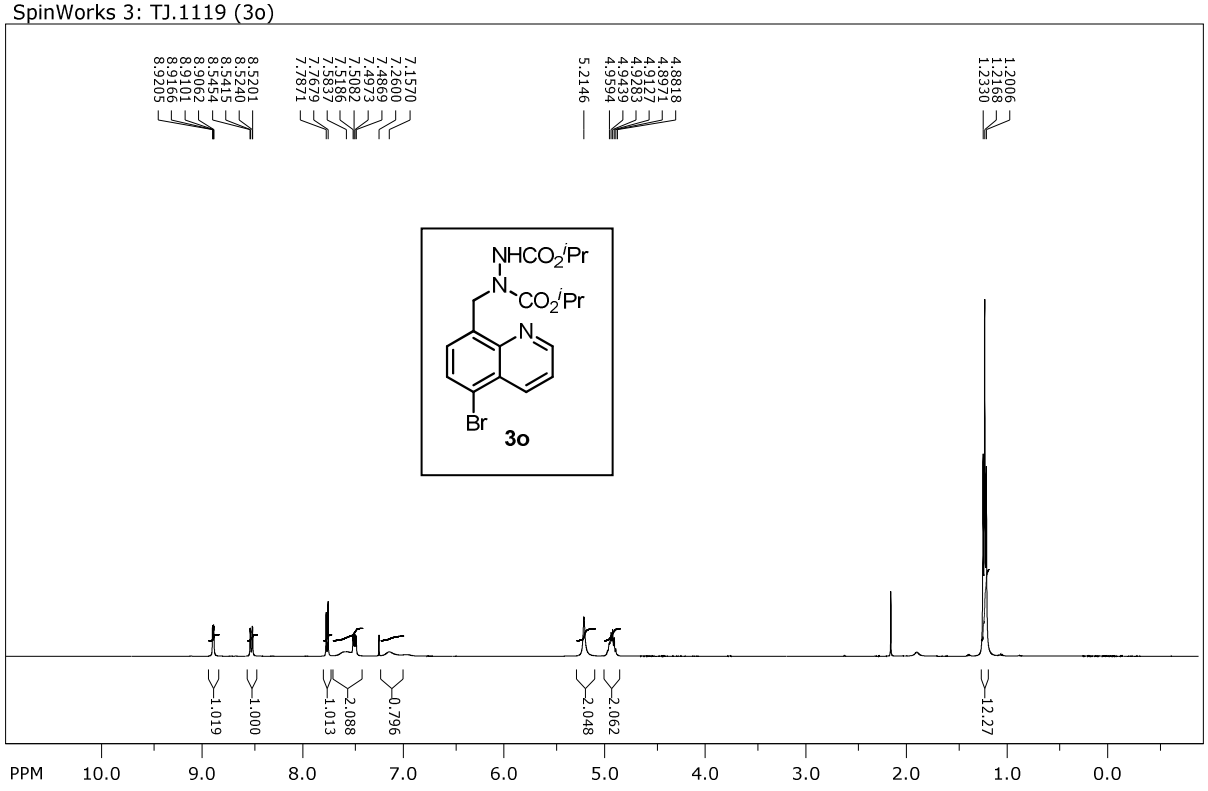

SpinWorks 3: TJ.1010 (3m)
NHCO2iPr
N
CO2iPr
N
F
3m
PPM


SpinWorks 3: TJ.1010 (3m)
NHCO2iPr
N
CO2iPr
N
F
3m
PPM

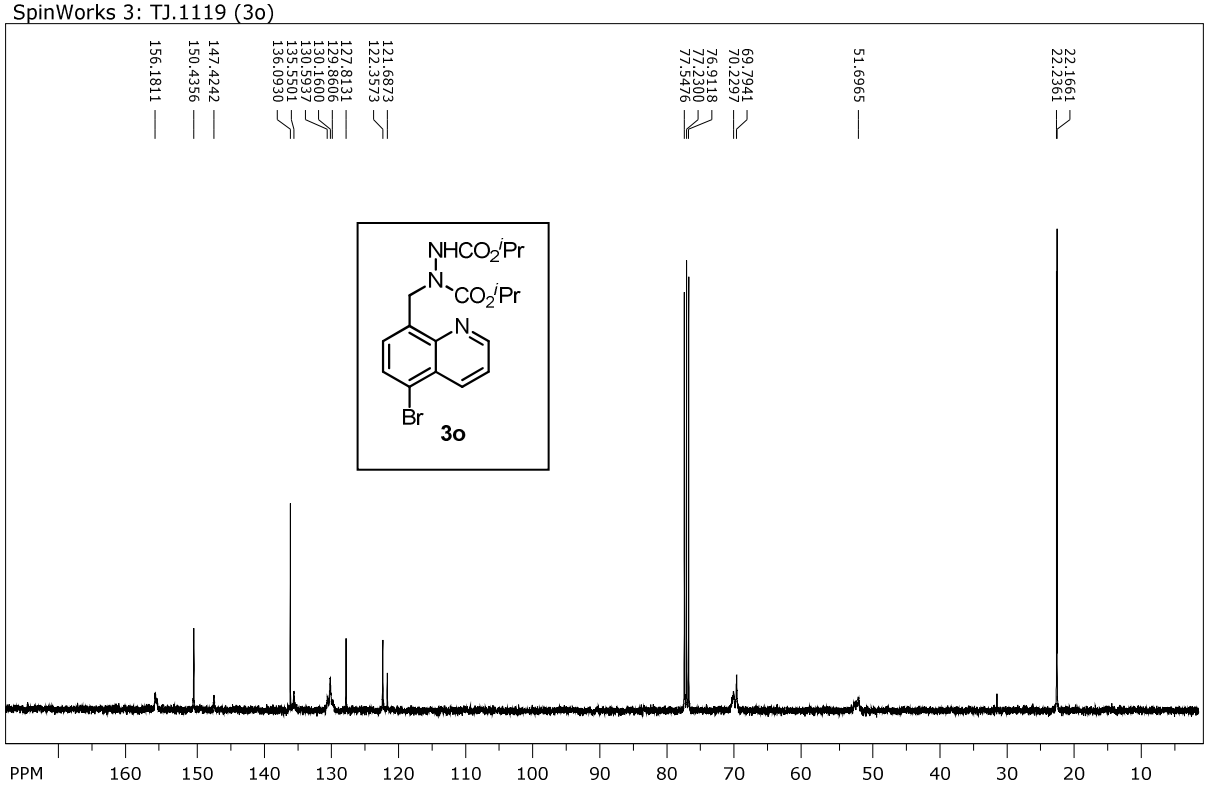

SpinWorks 3: TJ.982 (3n)
8.9396
8.9353
8.9291
8.9248
8.5715
8.5607
8.5461
7.6613
7.5761
7.5572
7.5169
7.5065
7.4956
7.4852
7.2600
7.2100
5.2162
4.9620
4.9550
4.9468
4.9397
4.9241
4.9085
4.8929
4.8774
1.2301
1.2140
1.1964
NHCO2iPr
N
CO2iPr
N
Cl
3n
1.014
1.000
2.041
1.075
0.855
2.083
2.061
12.18
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


SpinWorks 3: TJ.982 (3n)
156.1137
150.3842
147.3025
134.7999
133.4282
131.0862
130.0127
129.3747
126.4901
126.3946
121.9810
77.5484
77.2300
76.9122
70.1781
69.7344
51.6221
22.2238
22.1555
NHCO2iPr
N
CO2iPr
N
Cl
3n
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

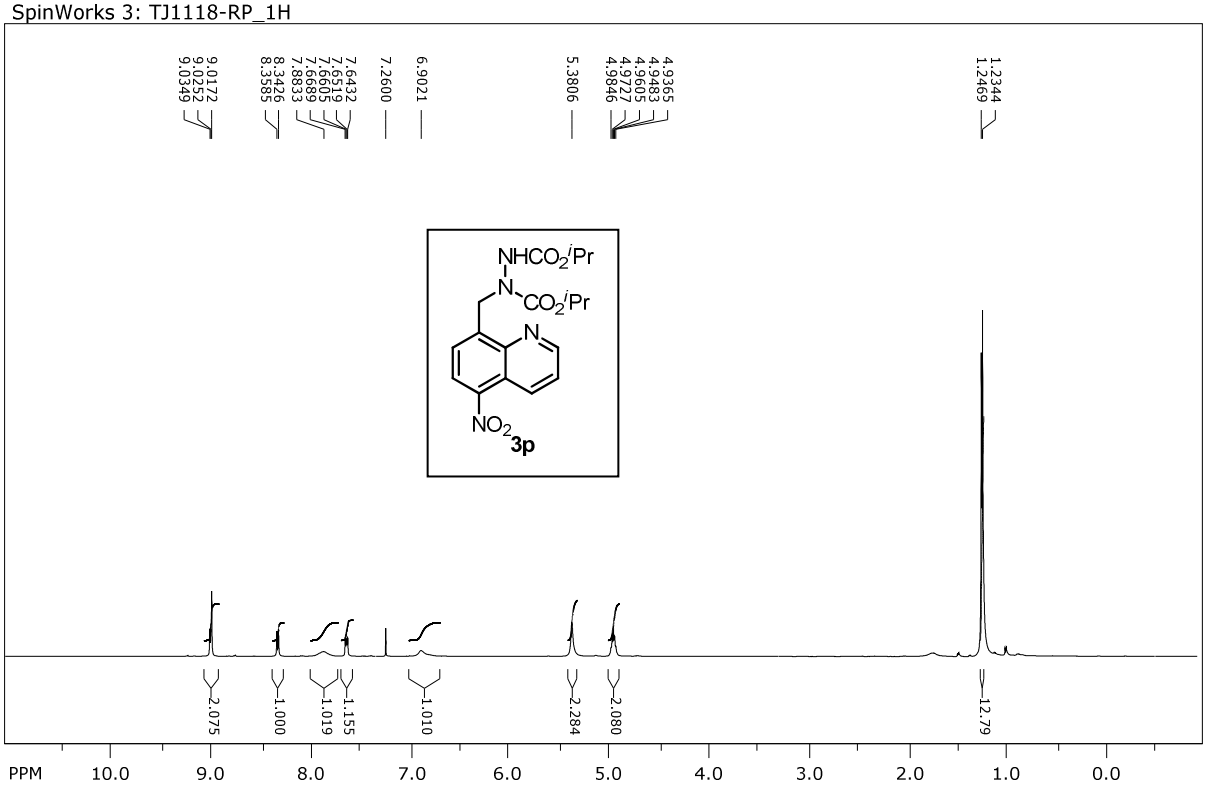
SpinWorks 3: TJ.1119 (3o)



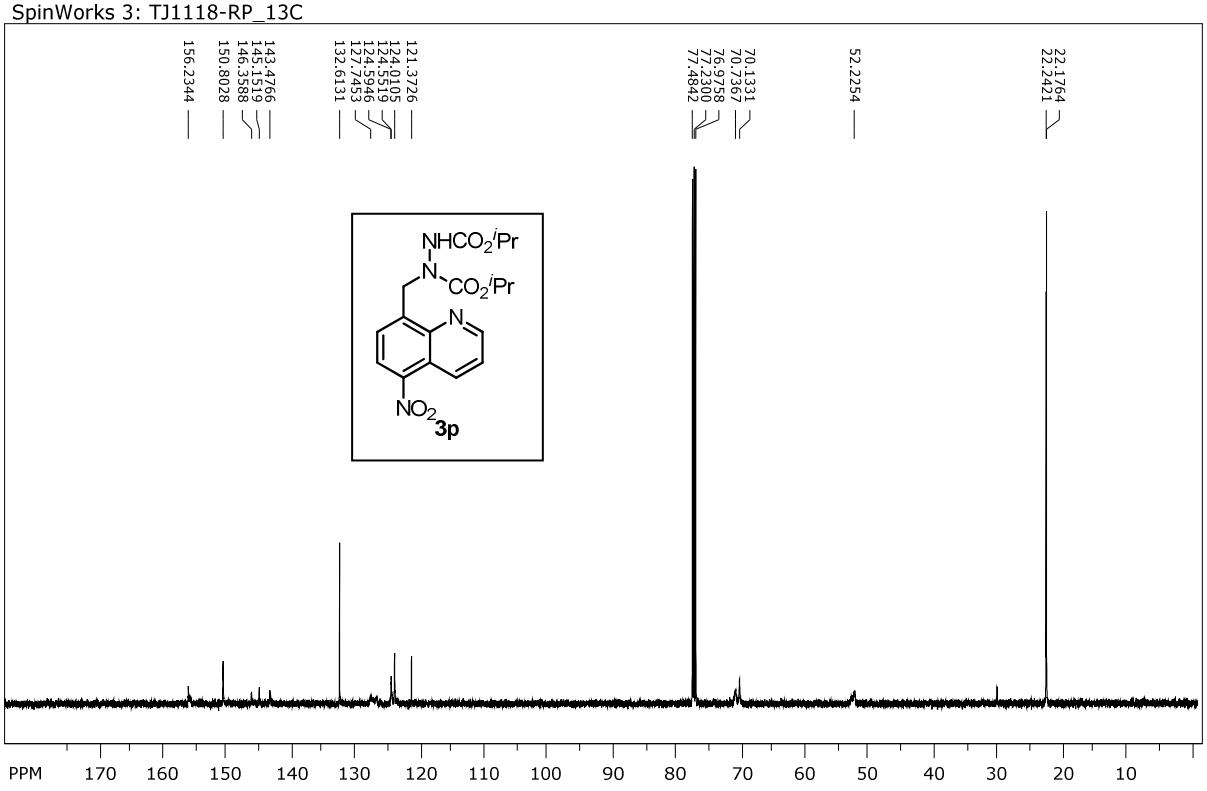
SpinWorks 3: TJ.1119 (3o)



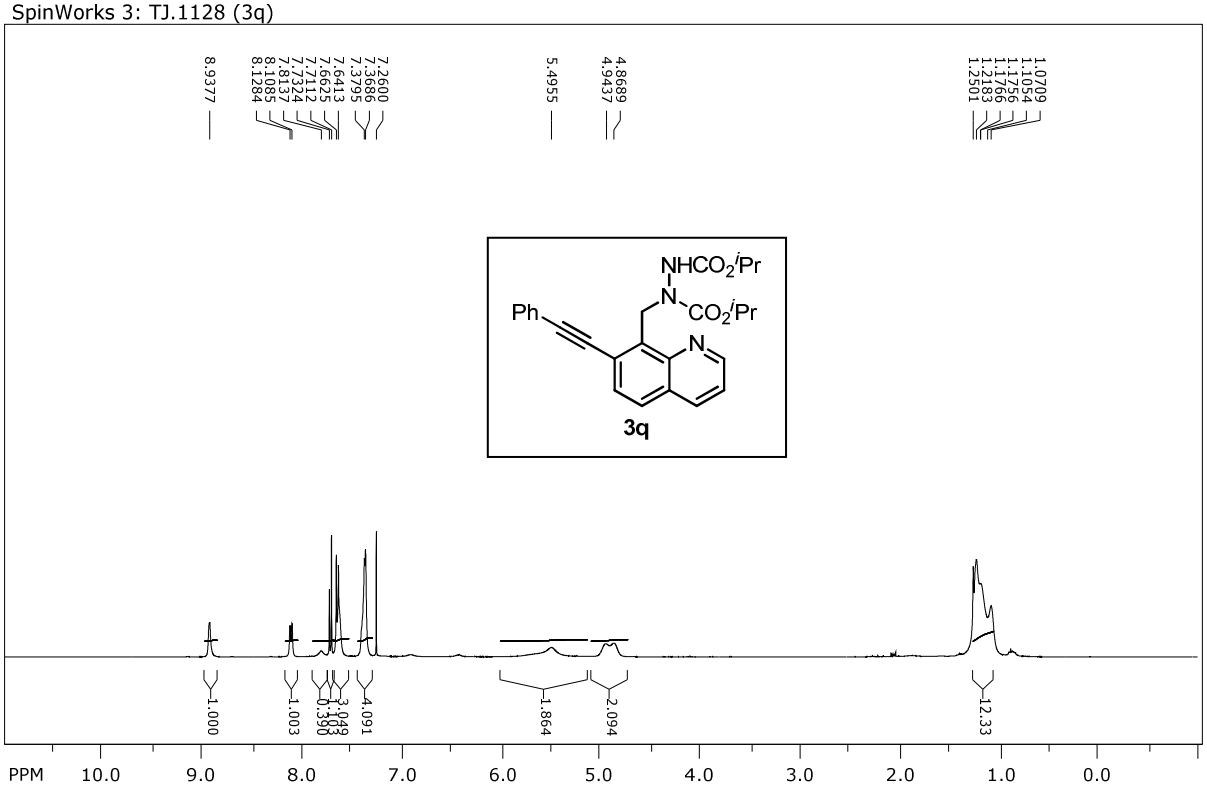
SpinWorks 3: TJ1118-RP_1H



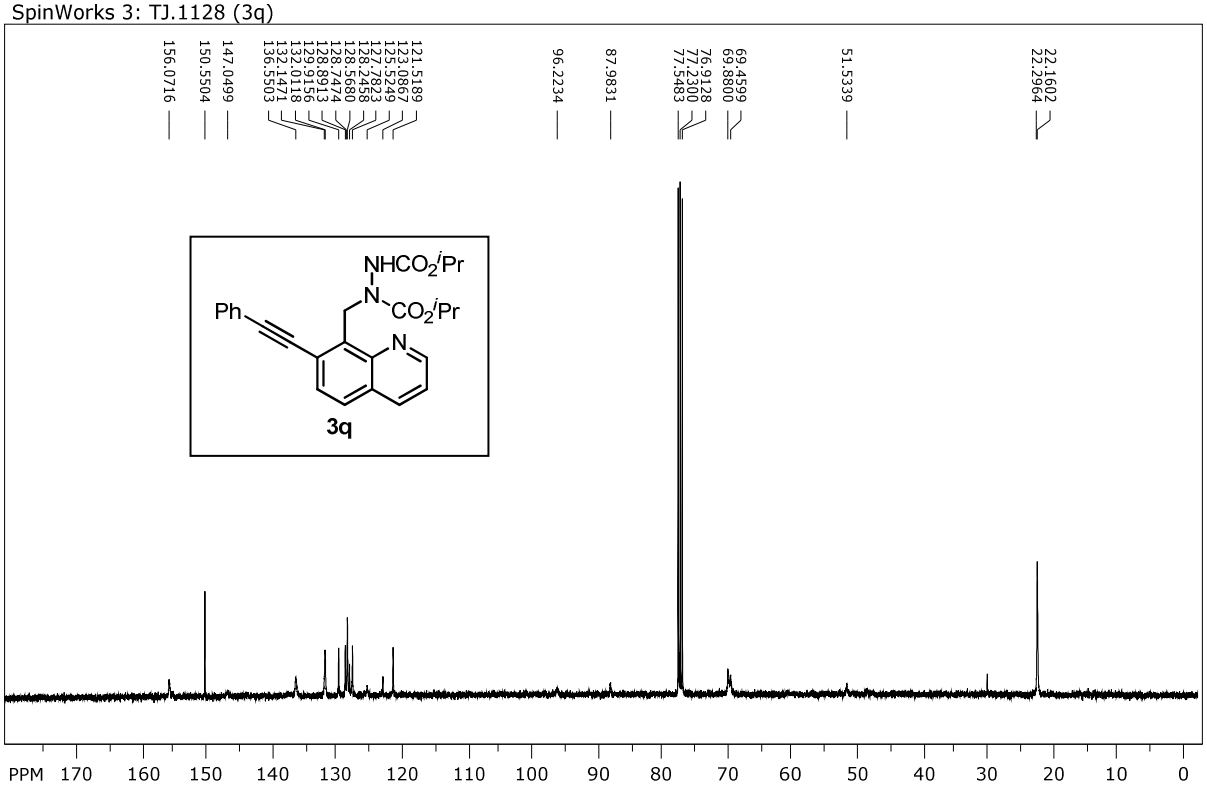
SpinWorks 3: TJ1118-RP_13C



SpinWorks 3: TJ.1128 (3q)

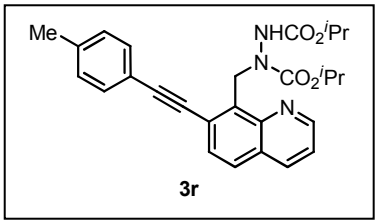


SpinWorks 3: TJ.1128 (3q)

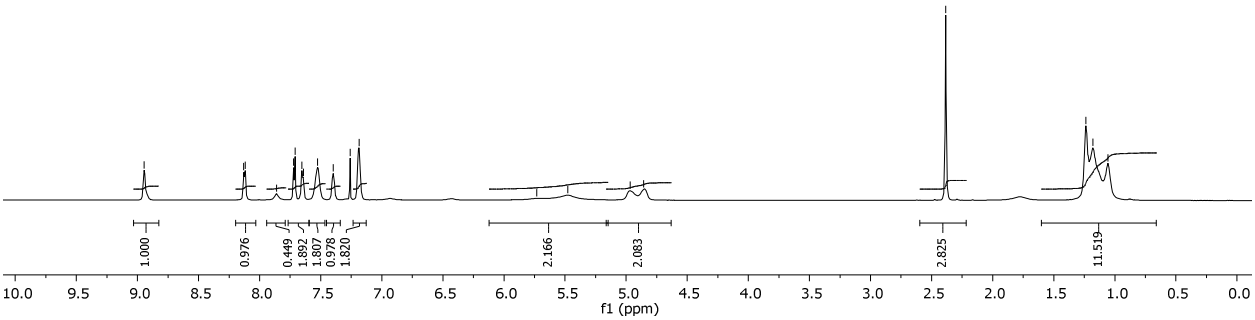


TJ-1147

8.945
8.130
8.119
7.862
7.722
7.710
7.654
7.642
7.526
7.398
7.260
7.185
5.732
5.478
4.967
4.856
2.384
1.236
1.180
1.056

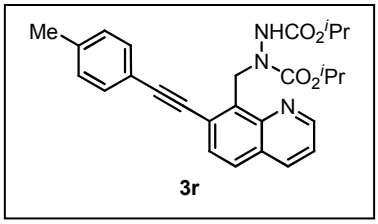


3r

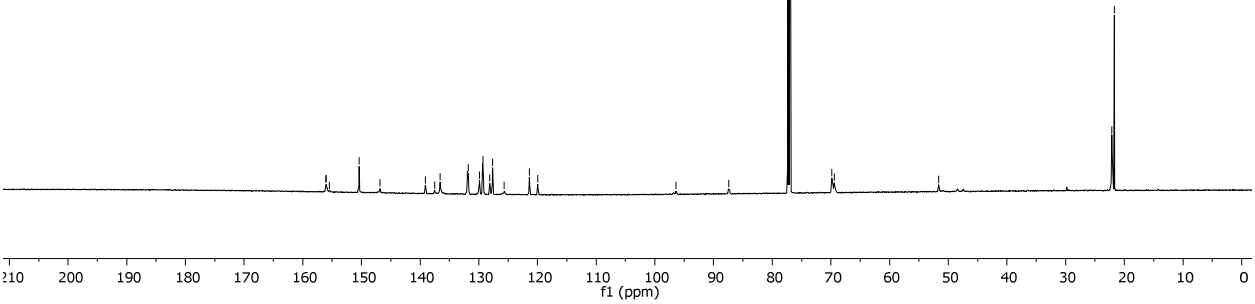


TJ-1147

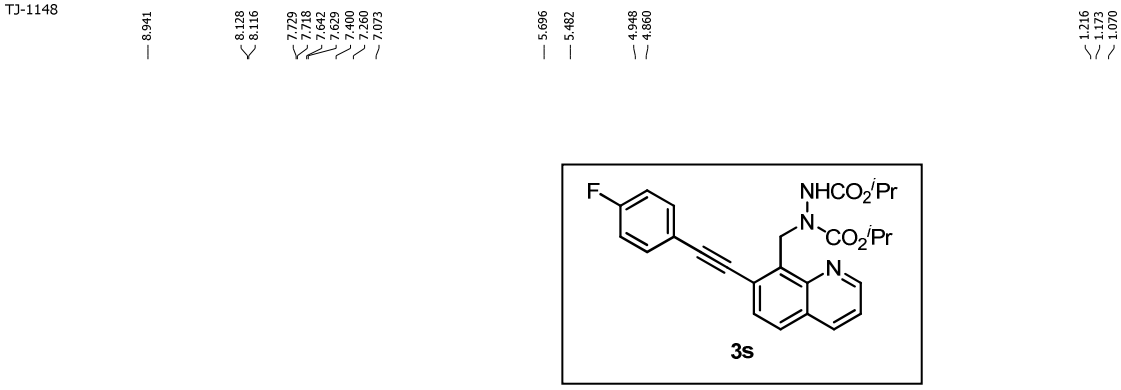
156.042
156.018
155.447
150.414
146.831
139.081
137.530
136.587
131.954
131.808
129.878
129.301
128.116
127.656
125.663
121.359
119.948
96.389
87.422
77.341
77.161
76.979
69.872
69.417
51.629
22.149
21.712



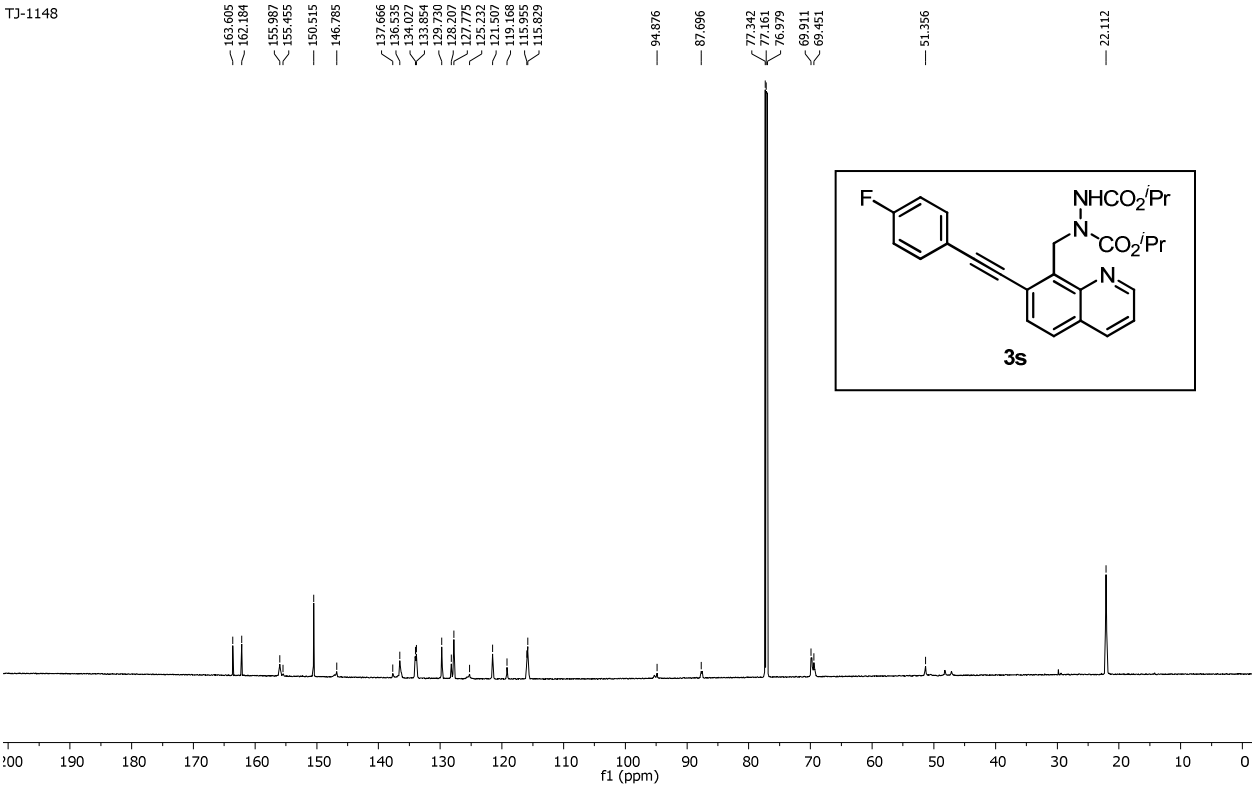
3r



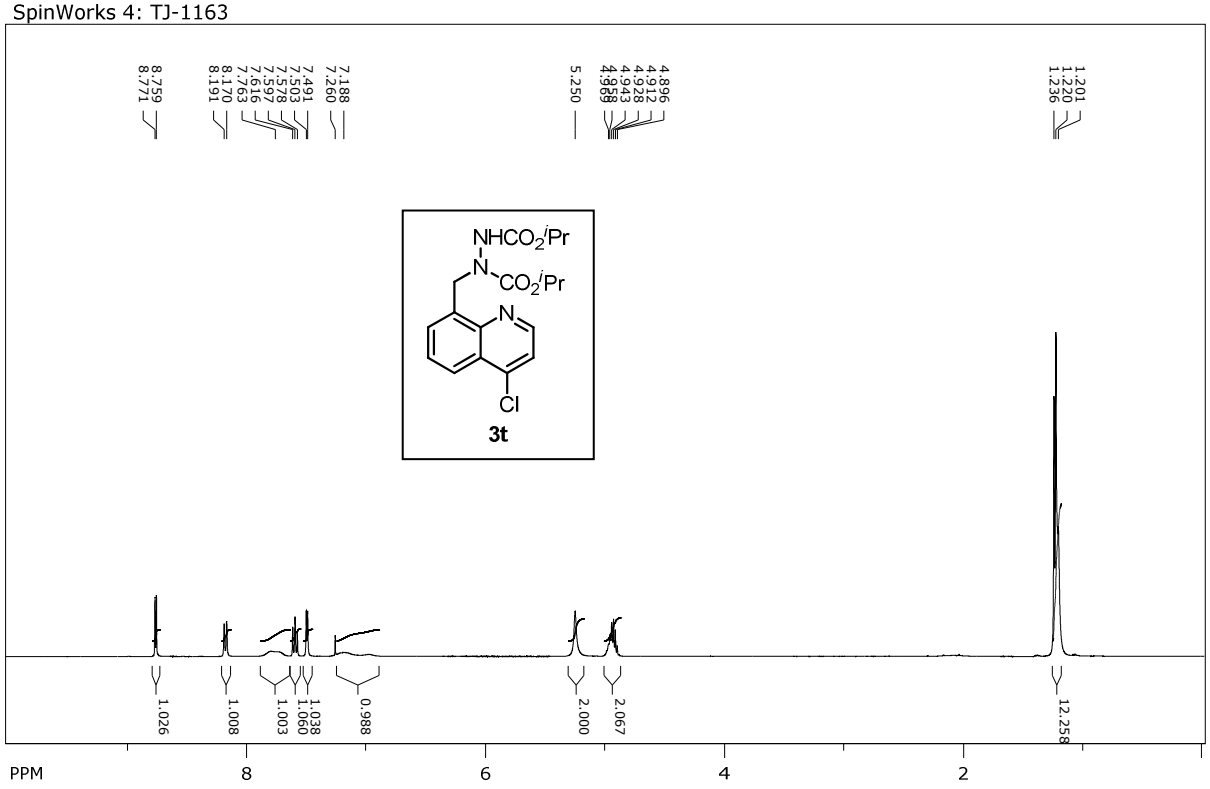
TJ-1148



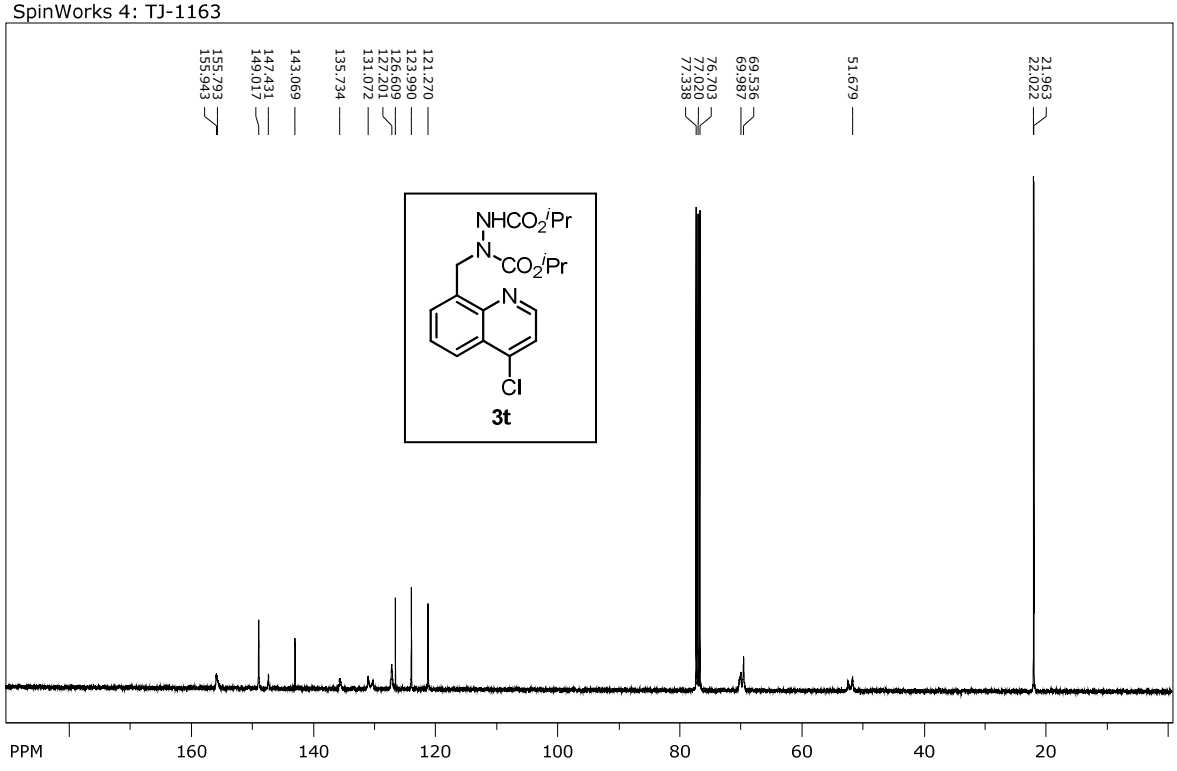
TJ-1148



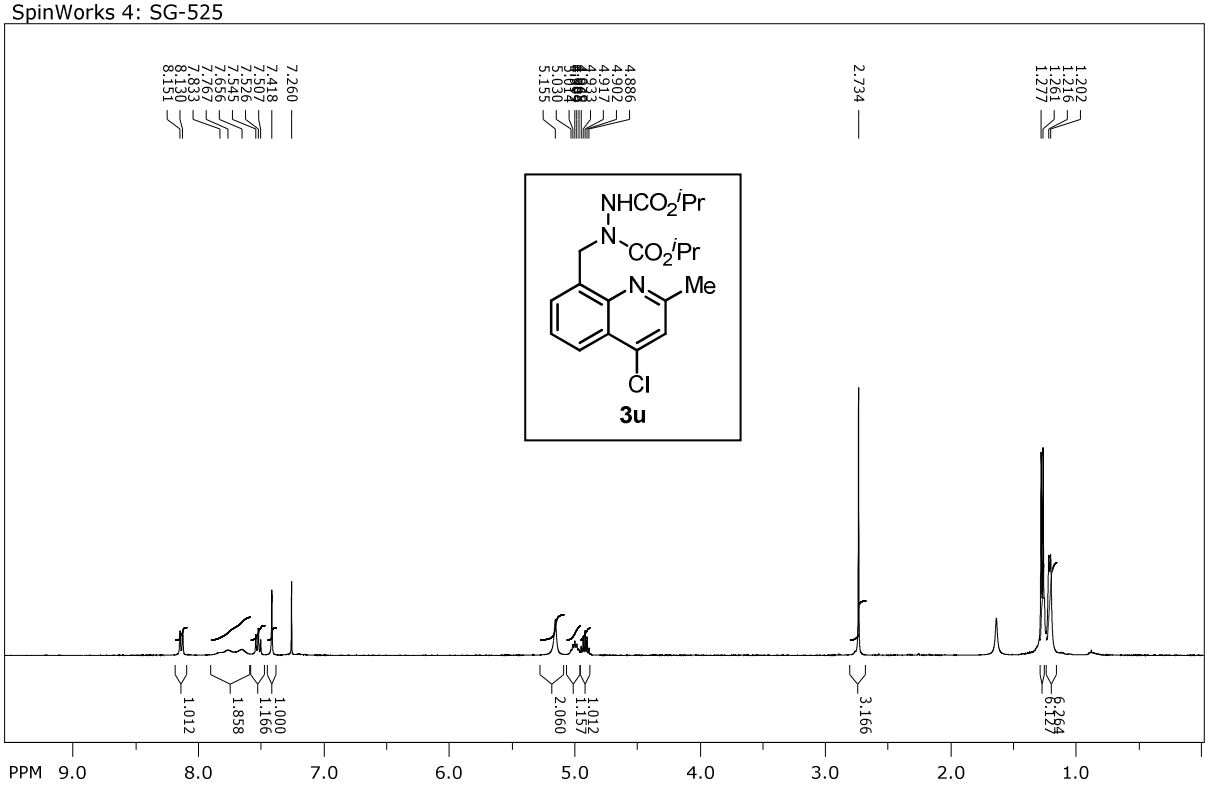
SpinWorks 4: TJ-1163



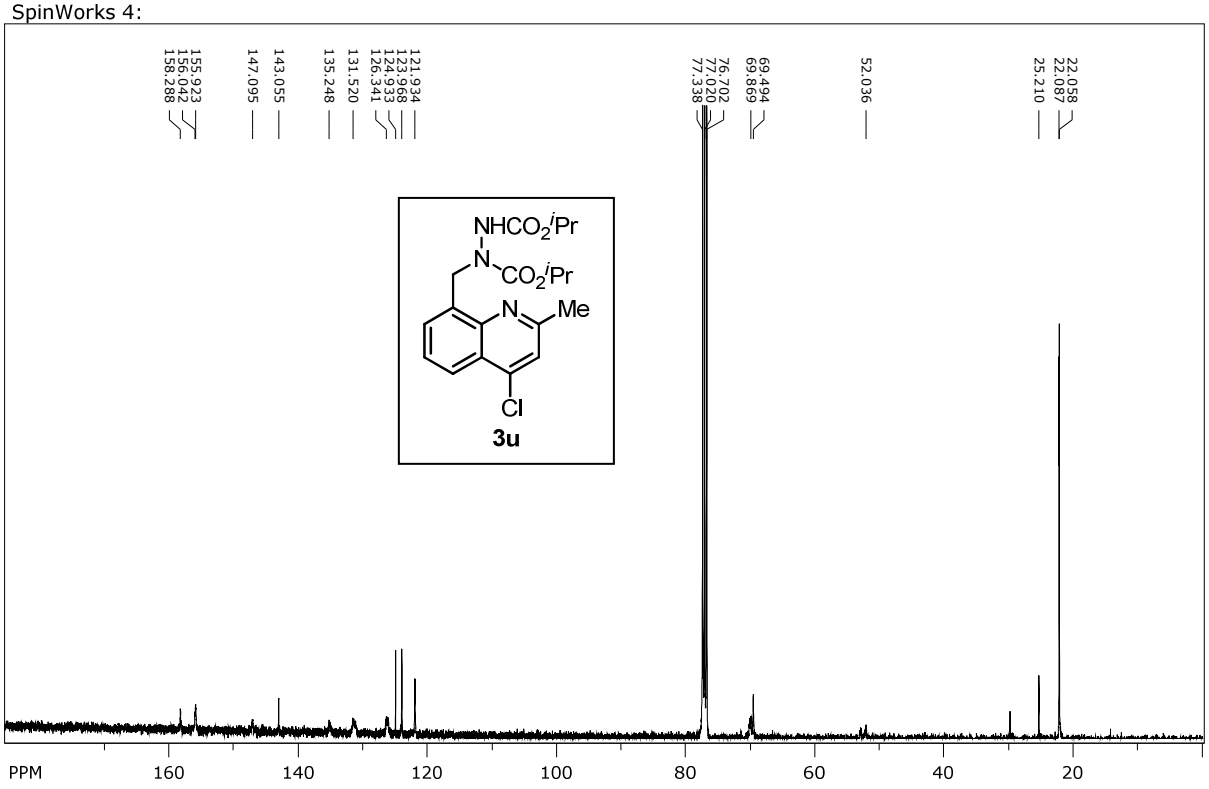
SpinWorks 4: TJ-1163



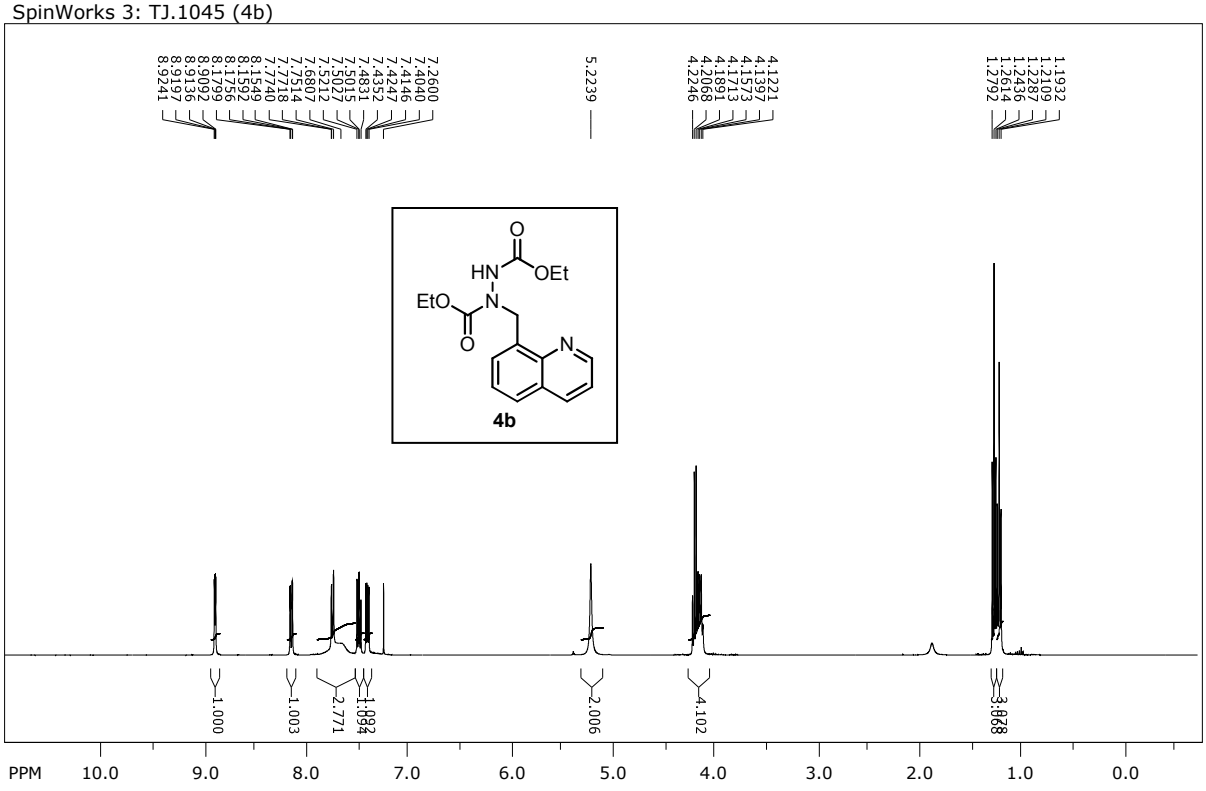
SpinWorks 4: SG-525



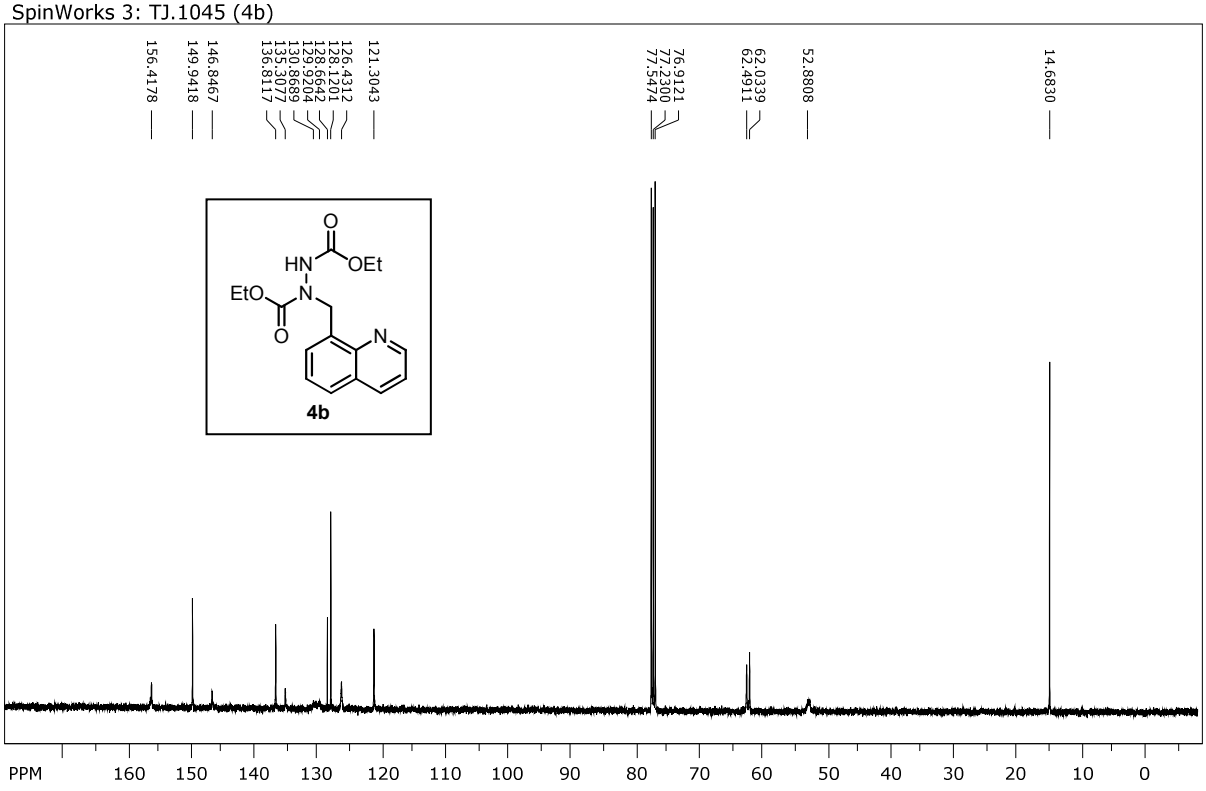
SpinWorks 4:



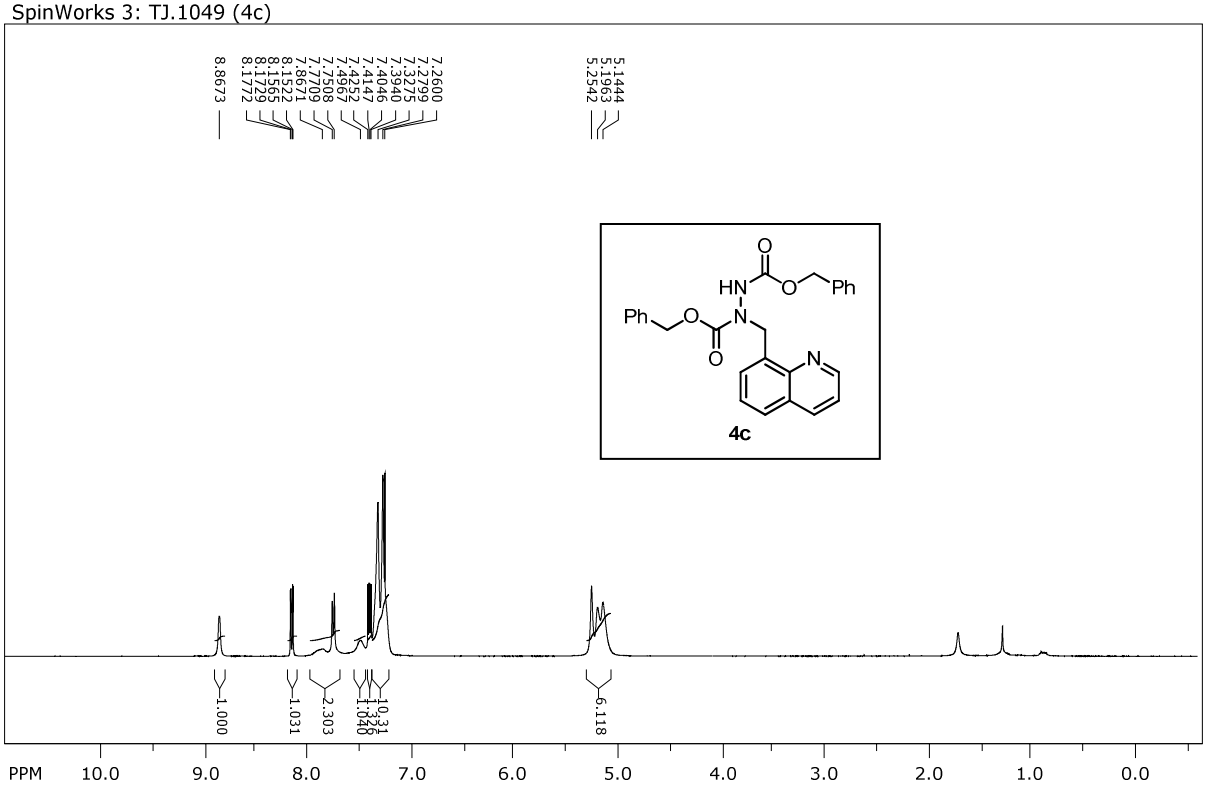
SpinWorks 3: TJ.1045 (4b)



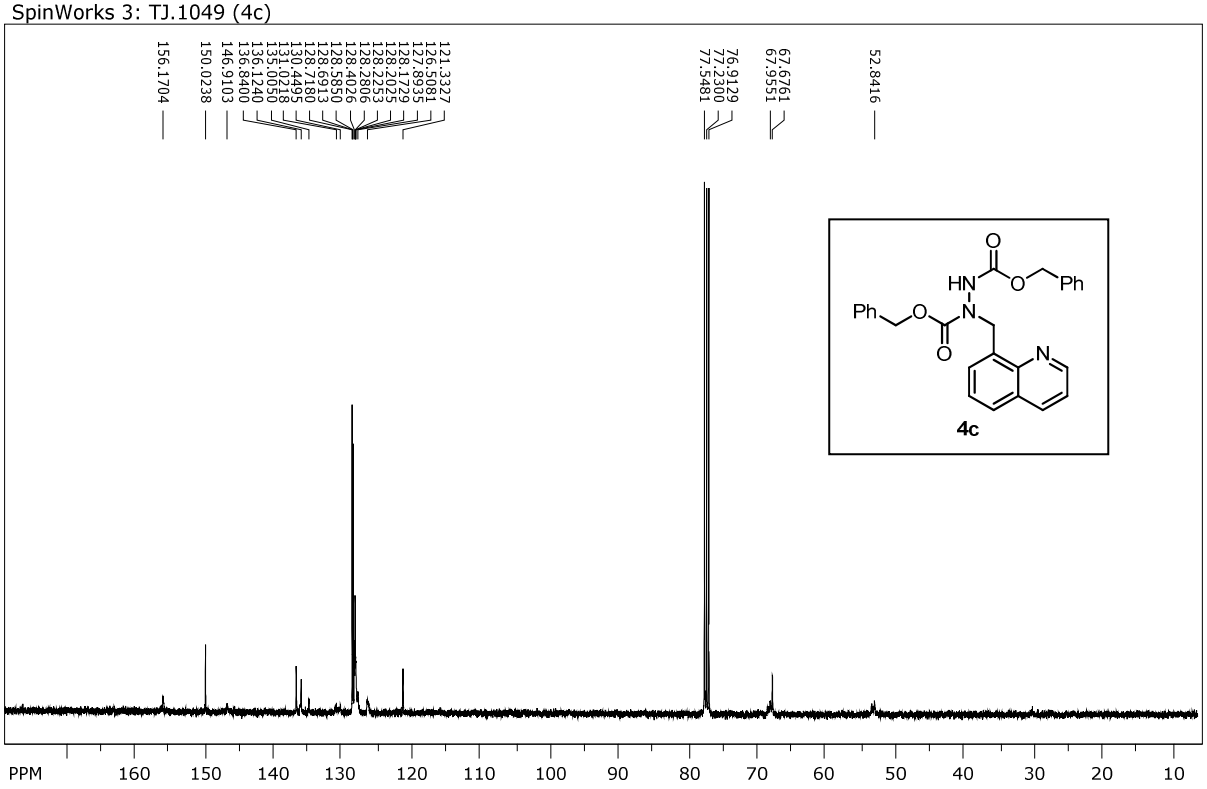
SpinWorks 3: TJ.1045 (4b)



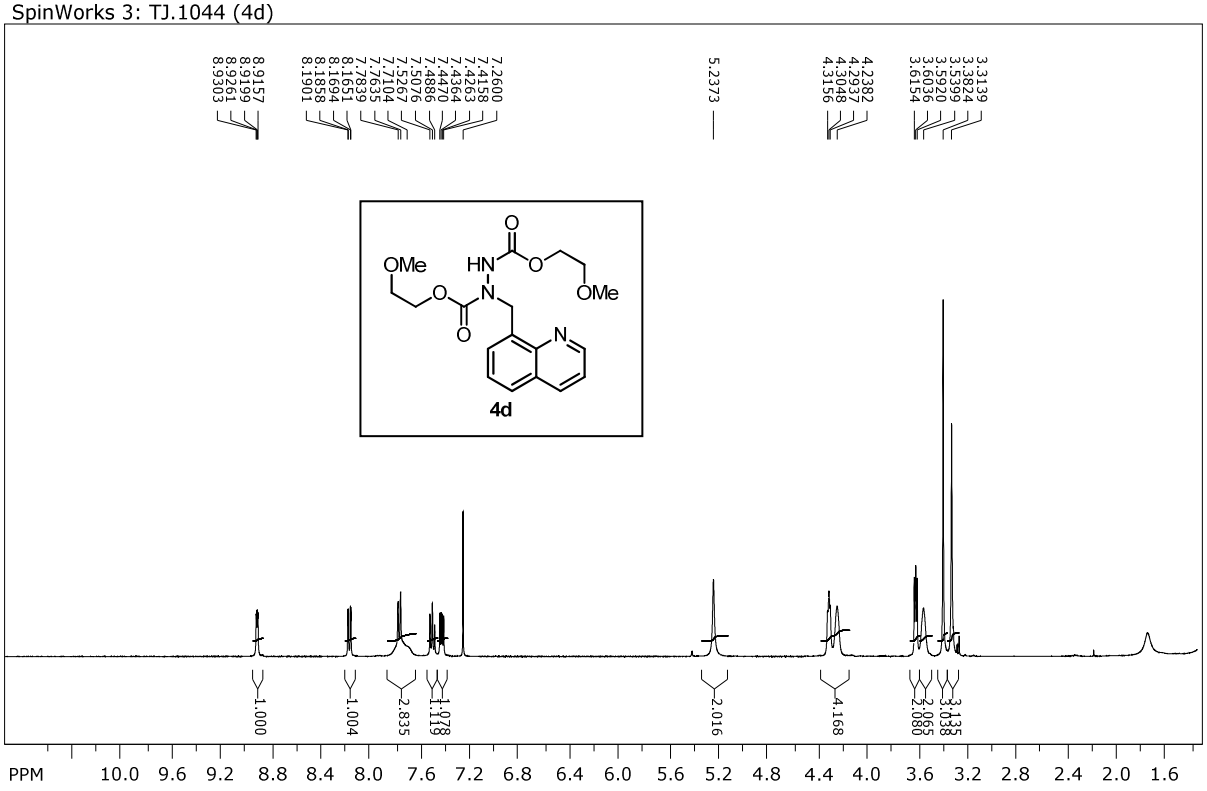
SpinWorks 3: TJ.1049 (4c)



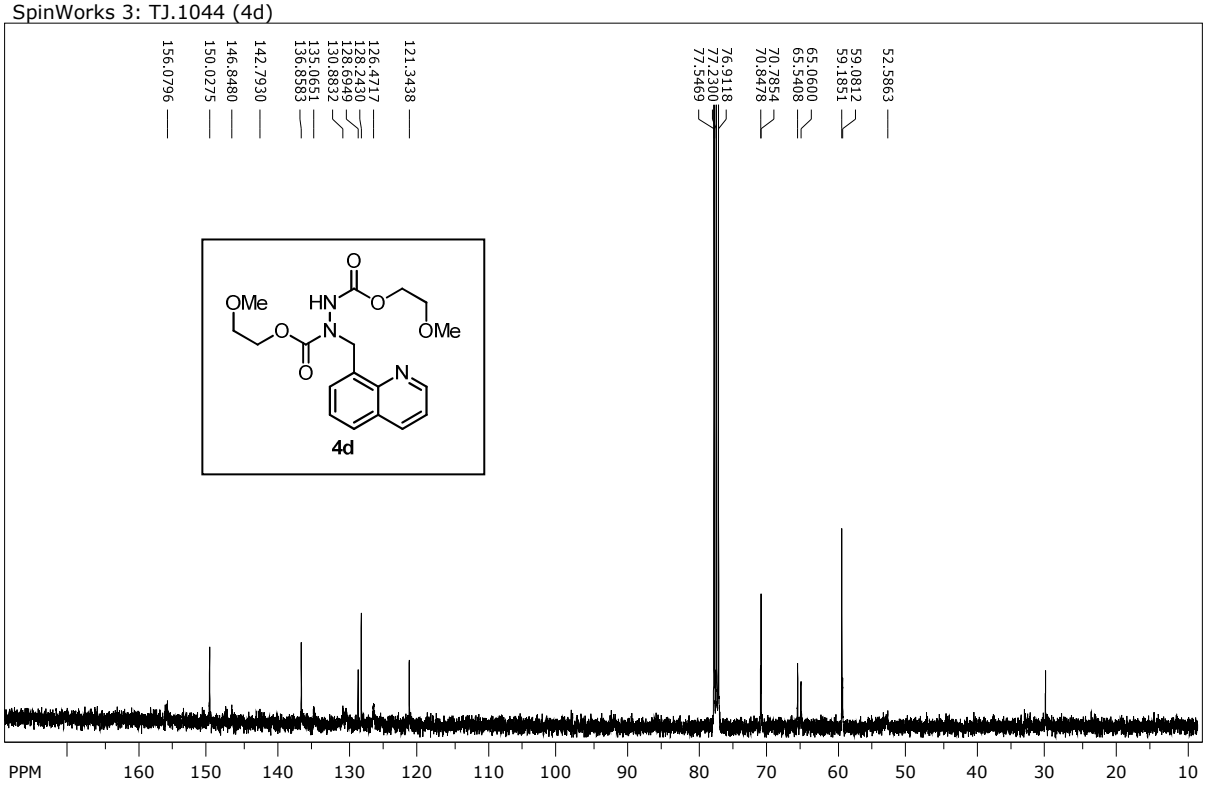
SpinWorks 3: TJ.1049 (4c)



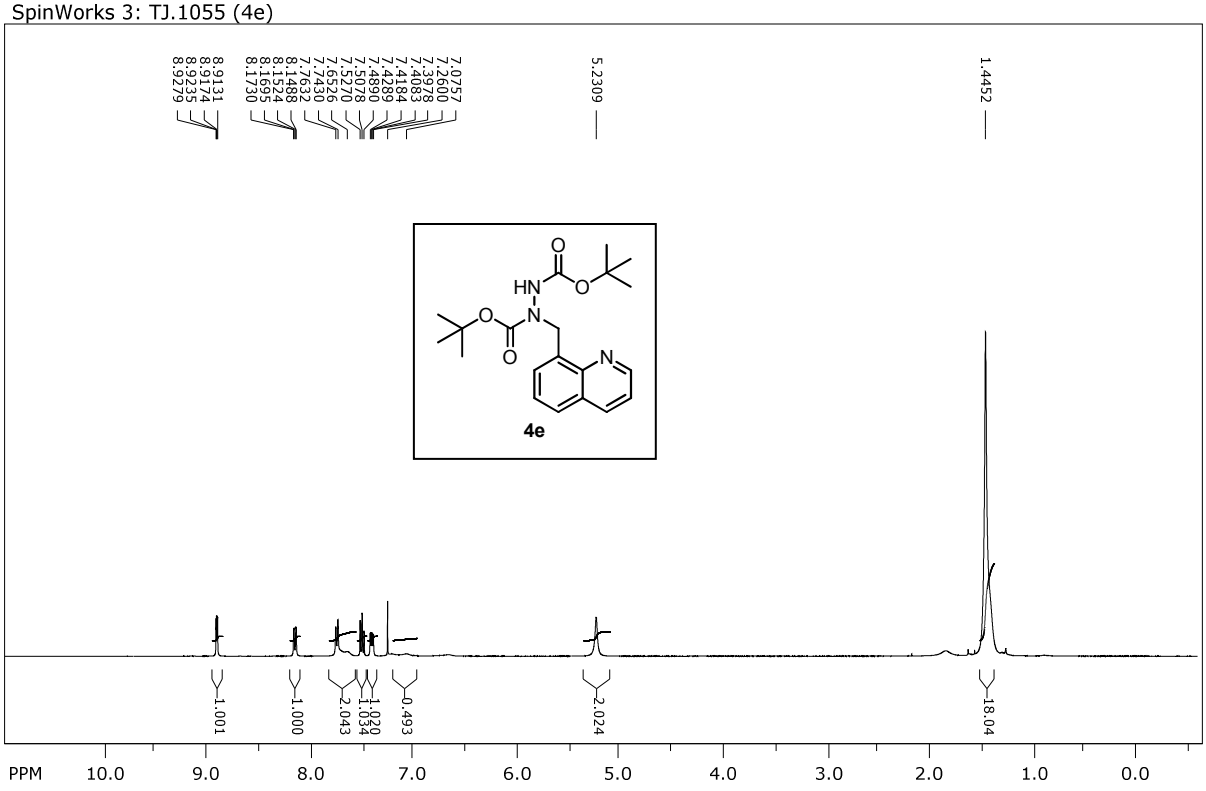
SpinWorks 3: TJ.1044 (4d)



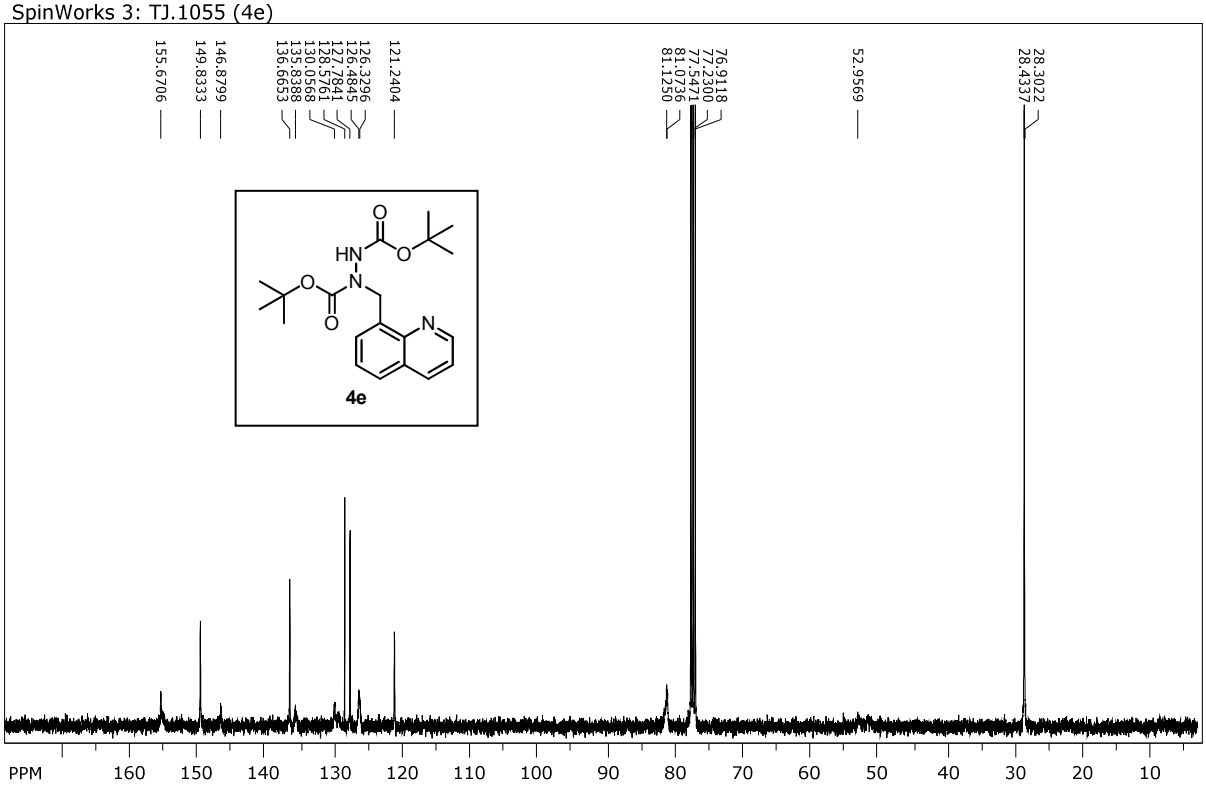
SpinWorks 3: TJ.1044 (4d)



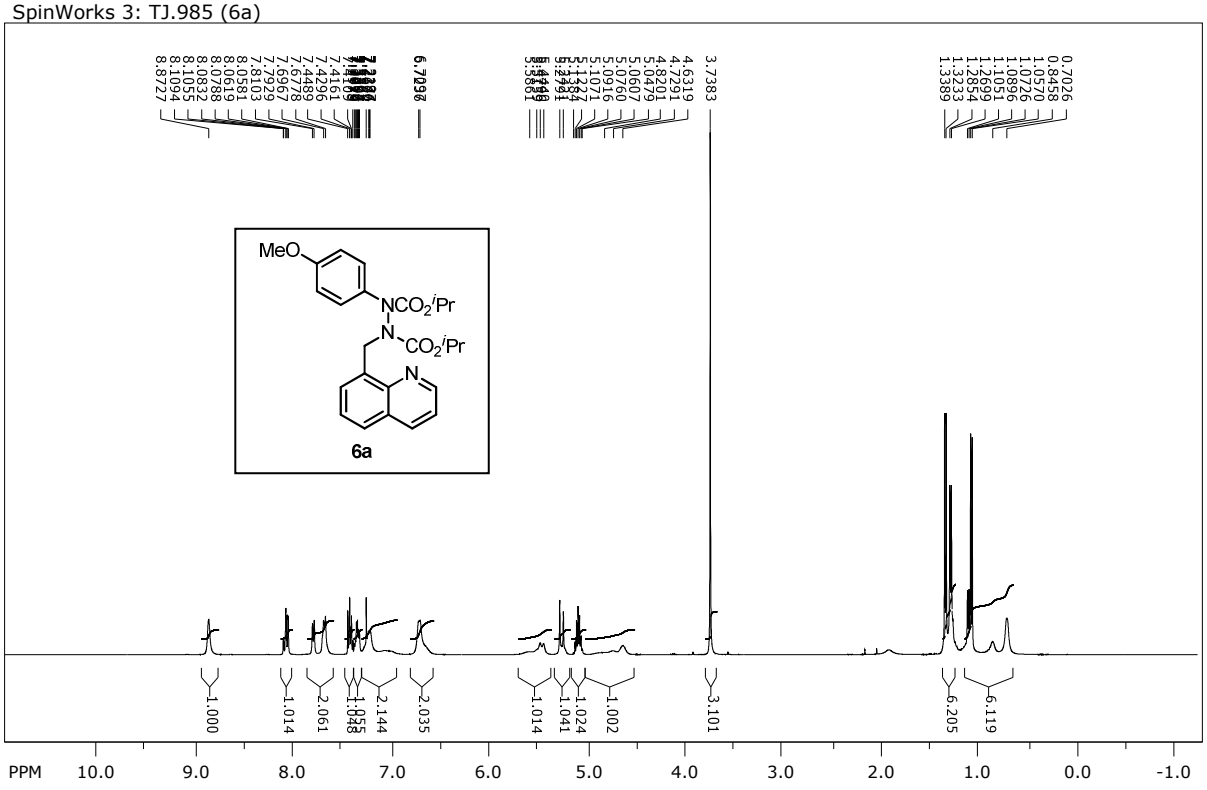
SpinWorks 3: TJ.1055 (4e)



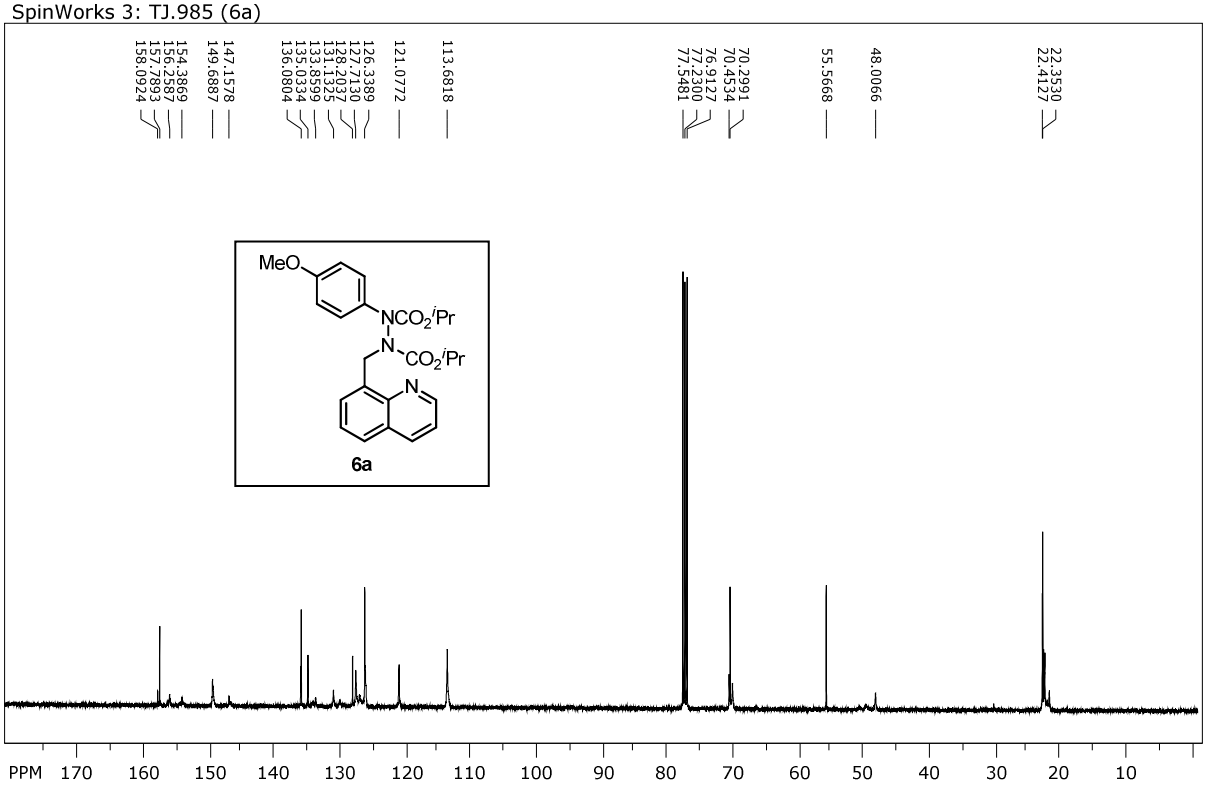
SpinWorks 3: TJ.1055 (4e)



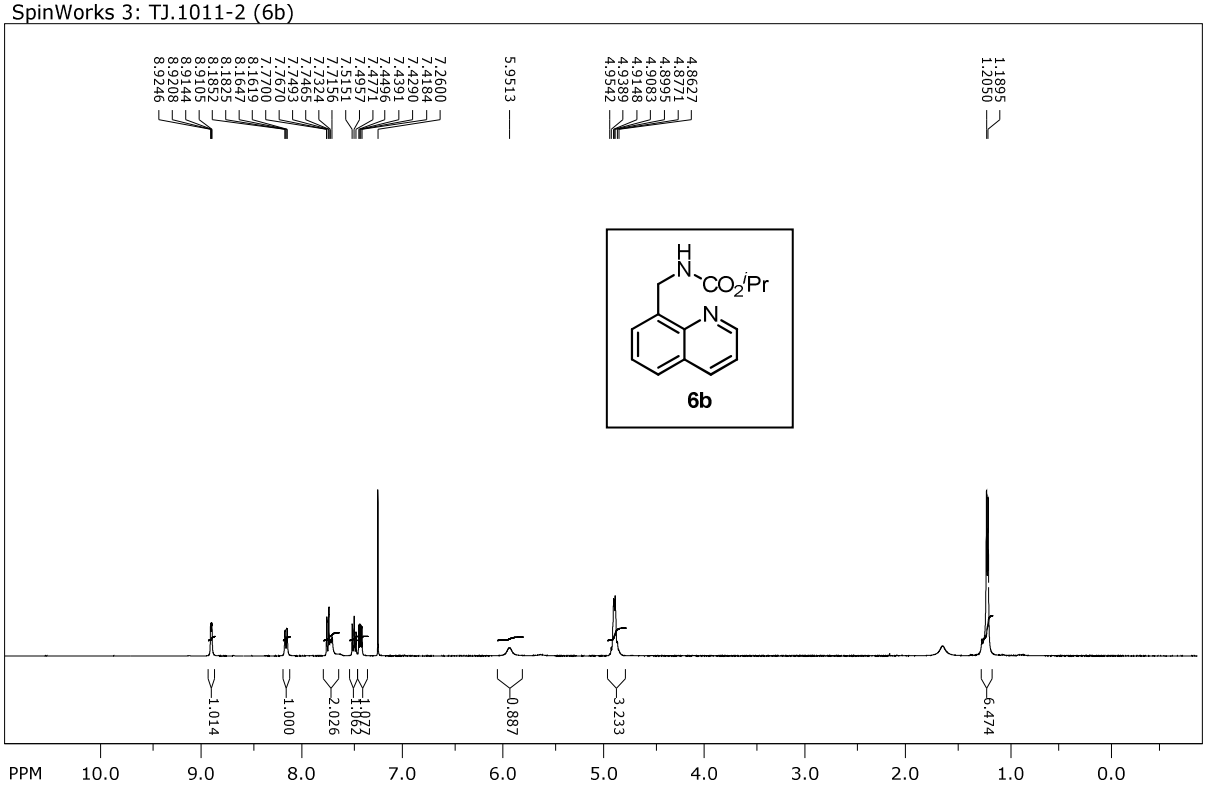
SpinWorks 3: TJ.985 (6a)



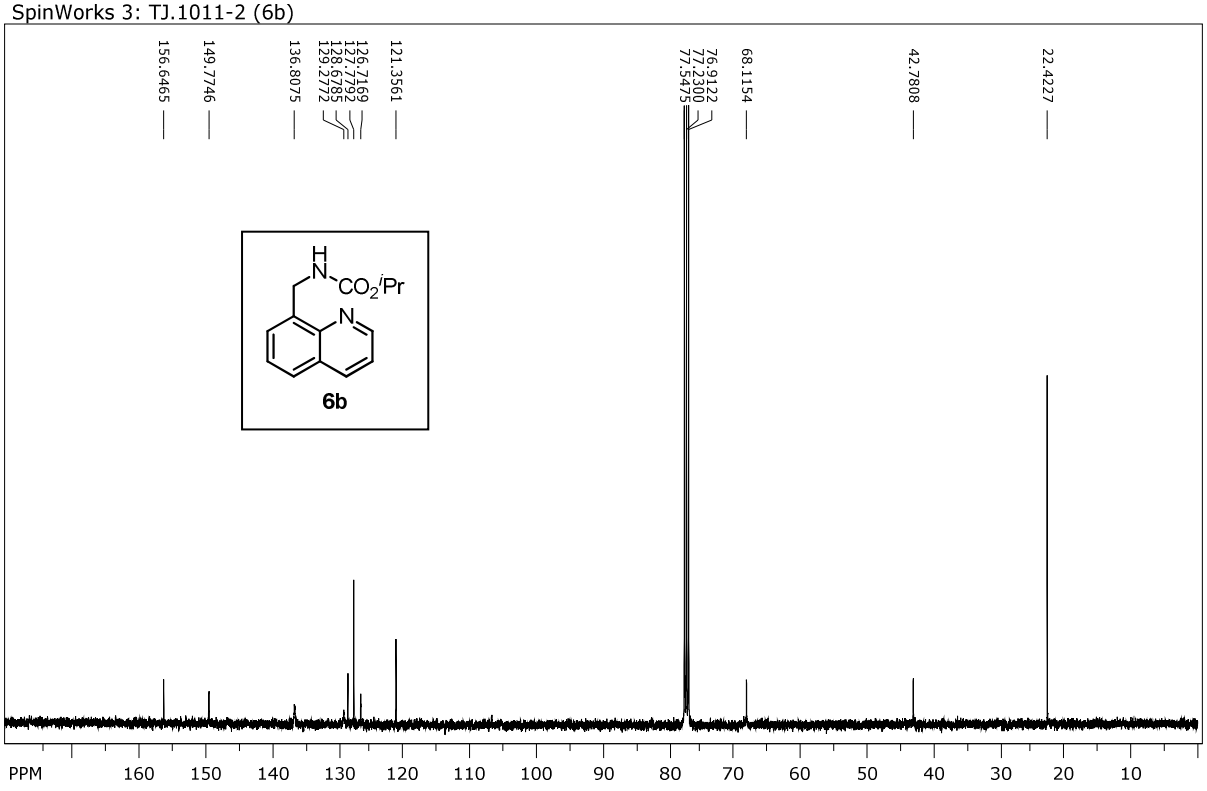
SpinWorks 3: TJ.985 (6a)



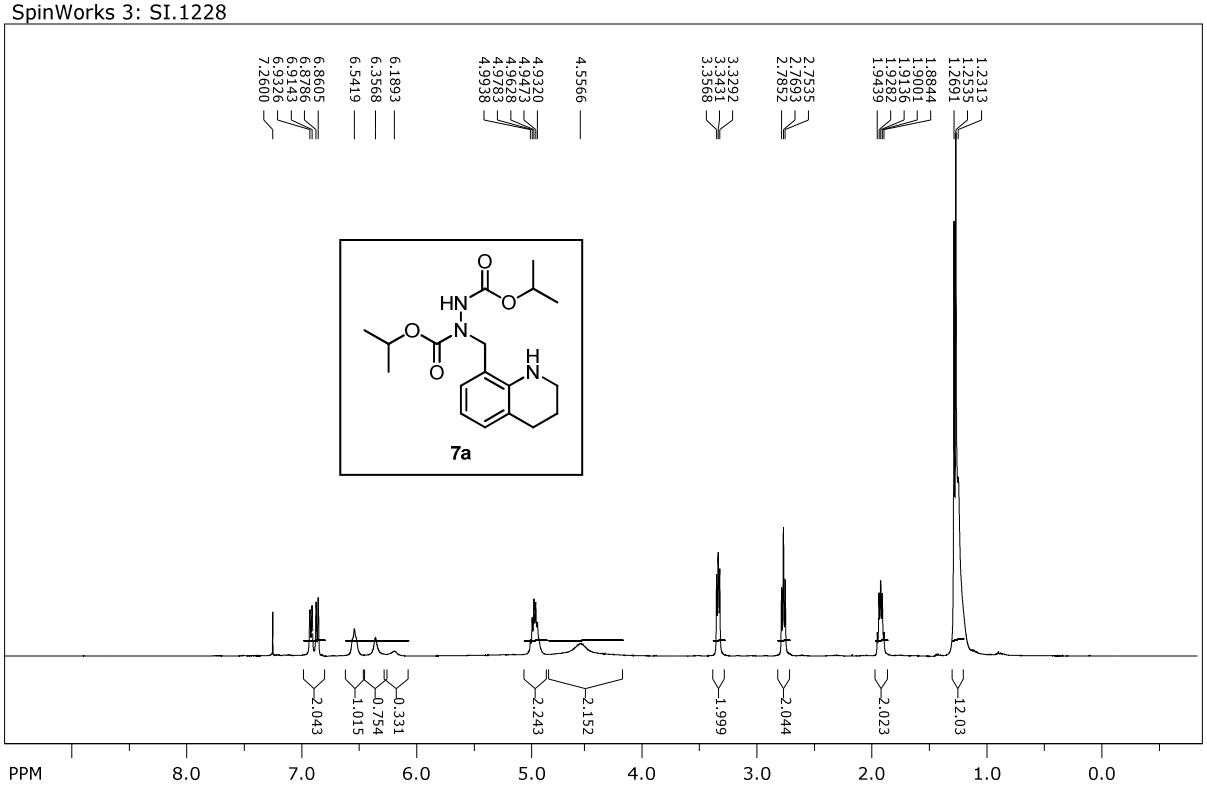
SpinWorks 3: TJ.1011-2 (6b)



SpinWorks 3: TJ.1011-2 (6b)



SpinWorks 3: SI.1228



SpinWorks 3: SI.1228