Electronic Supplementary Information for

Substituent Effects on the Regioselectivity of the Paternò-Büchi Reaction of 5- or/and 6-Methyl Substituted Uracils with 4,4'-Disubstituted Benzophenones

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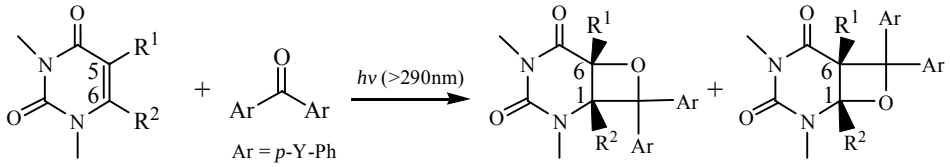
Scheme 1S.



1A: R^1=CH_3, R^2=H
1B: R^1=R^2=H
1C: R^1=H, R^2=CH_3
1D: R^1=R^2=CH_3

2a: Y = CH_3O
2b: Y = CH_3
2c: Y = *t*-Bu
2d: Y = H
2e: Y = F
2f: Y= Cl

3A(a–f)
3B(a–f)
3C(a–f)
3D(a–f)

4A(a–f)
4B(a–f)
4C(a–f)
4D(a–f)

Characterization data of compounds 3C, 4C, 3D and 4D

Z-8,8-bis(4-methoxyphenyl)-1,2,4-trimethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Ca):

R_f = 0.17 (EtOAc/n-hexane, 1:2); m.p. 146–147℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.37 (m, 4H, H_{Ar}), 6.87 (m, 4H, H_{Ar}), 4.65 (s, 1H, CH), 3.79 (s, 3H, CH_3O), 3.75 (s, 3H, CH_3O), 2.97 (s,3H, NCH_3), 2.95 (s, 3H, NCH_3), 1.56 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, $CDCl_3$) δ 167.1, 159.3, 158.9, 152.2, 133.5, 132.6, 126.9, 126.2, 113.9, 113.8, 97.3 , 77.1, 62.6, 55.4, 55.3, 31.2, 27.6, 23.3 ppm; IR (KBr) 1716s, 1667s, 1249s, 1176s, 826s, 747m cm$^-$; TOFMS (CI) calcd for $(M+1)^+$ $C_{22}H_{25}N_2O_5$: 397.1763, found: 397.1758.

Z-7,7-bis(4-methoxyphenyl)-1,2,4-trimethyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Ca):

R_f = 0.34 (EtOAc/n-hexane, 1:2); m.p. >85 ℃（decompose）; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.40–6.81(m, 8H, H_{Ar}), 4.49 (s, 1H, CH), 3.81 (s, 3H, CH_3O), 3. 74 (s, 3H, CH_3O), 3.09 (s, 3H, NCH_3), 2.73 (s, 3H, NCH_3), 1.74 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 166.0, 159.9, 152.0, 139.0, 134.3, 132.7, 127.6, 127.3, 114.4, 114.0, 87.3, 86.3, 55.9, 55.6, 55.5, 55.0, 29.1, 28.2, 27.4 ppm; IR (KBr) 1704s, 1668s, 1251s, 1173m, 841m, 747m cm$^-$; TOFMS (CI) calcd for $(M+1)^+$ $C_{22}H_{25}N_2O_5$:397.1763, found: 397.1757.

Z-1,2,4-trimethyl-8,8-dip-tolyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Cb):

R_f = 0.42 (EtOAc/n-hexane, 1:2); m.p. 181–182℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.34 (m, 4H, H_{Ar}), 7.13 (m, 4H, H_{Ar}), 4.62 (s, 1H, CH), 3.02 (s, 3H, NCH_3), 2.89 (s, 3H, NCH_3), 2.31 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 1.57 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, $CDCl_3$): δ 167.1, 152.2, 138.5, 137.7, 137.1, 129.1, 129.0, 125.3, 124.7, 97.7, 77.2, 62.4, 31.2, 27.4, 23.3, 21.1, 21.0 ppm; IR (KBr) 1712s, 1670s, 1270m, 1167m, 821s, 748m cm$^-$; TOFMS (CI) calcd for $(M+1)^+$ $C_{22}H_{25}N_2O_3$: 365.1854, found: 365.1860.

Z-1,2,4-trimethyl-7,7-dip-tolyl-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Cb):

R_f = 0.60 (EtOAc/n-hexane, 1:2); m.p. >65℃（decompose）; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.37–7.05 (m, 8H, H_{Ar}), 4.49 (s, 1H, CH), 3.08 (s, 3H, NCH_3), 2.71 (s, 3H, NCH_3), 2.31 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 1.72 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 165.9, 151.9, 144.1, 139.4, 137.9，129.9,

129.7, 129.3, 126.1, 125.7, 87.5, 86.4, 55.1, 28.1, 27.4, 21.1, 21.0 ppm; IR (KBr) 1708s, 1666s, 1277m, 1177m, 818m, 751m cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{22}H_{25}N_2O_3$: 365.1854, found: 365.1862.

Z-8,8-bis(4-tert-butylphenyl)-1,2,4-trimethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Cc):

R_f = 0.55 (EtOAc/n-hexane, 1:2); m p. 215–216℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.37 (m, 8H, H_{Ar}), 4.62 (s, 1H, CH), 3.06 (s, 3H, NCH_3); 2.81(s, 3H, NCH_3), 1.59 (s, 3H, CH_3), 1.29 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$) ppm; ^{13}C NMR (75MHz, $CDCl_3$): δ 167.3, 152.3, 150.9, 150.3, 138.3, 137.7, 125.4, 125.2, 124.5, 97.8, 77.4, 62.5, 34.6, 31.4, 31.3, 31.2, 23.3 ppm; IR (KBr) 1715s, 1677s, 1271m, 1168m, 832m, 750m cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{28}H_{37}N_2O_3$: 449.2804, found: 449.2798.

Z-7,7-bis(4-tert-butylphenyl)-1,2,4-trimethyl-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Cc):

R_f = 0.72 (EtOAc/n-hexane, 1:2); m.p. >80℃（decompose）; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.34 (m, 8H, H_{Ar}), 4.51 (s, 1H, CH), 3.10 (s, 3H, NCH_3); 2.66 (s, 3H, NCH_3), 1.74 (s, 3H, CH_3), 1.31 (s, 9H, $C(CH_3)_3$), 1.24 (s, 9H, $C(CH_3)_3$) ppm; ^{13}C NMR (75MHz, Acetone-d_6) δ 165.9, 151.9, 151.1, 144.0, 139.3, 126.0, 125.6, 125.5, 87.5, 86.3, 55.3, 35.1, 34.9, 31.6, 31.5, 28.2, 27.5, 27.3 ppm; IR (KBr) 1716s, 1667s, 1269m, 1162m, 842m, 750m cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{28}H_{37}N_2O_3$: 449.2804, found: 449.2797.

Z-1,2,4-trimethyl-8,8-diphenyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Cd):

R_f = 0.33 (EtOAc/n-hexane, 1:2); m.p. 177–178℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.31 (m, 10H, H_{Ar}), 4.64 (s, 1H, CH), 3.08 (s, 3H, NCH_3); 2.85 (s, 3H, NCH_3), 1.61 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, $CDCl_3$): δ 167.1, 152.2, 141.2, 140.5, 128.5, 128.4, 128.0, 127.5, 125.4, 124.7, 97.6, 77.3, 62.4, 31.2, 27.4, 23.3 ppm; IR (KBr) 1710s, 1677s, 1268m, 1164m, 748s, 712s cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{20}H_{21}N_2O_3$: 337.1552, found: 337.1549.

Z-1,2,4-trimethyl-7,7-diphenyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Cd):

R_f = 0.57 (EtOAc/n-hexane, 1:2); m.p. 139–140℃; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.30 (m, 10H, H_{Ar}), 4.55 (s, 1H,CH), 3.10 (s, 3H, NCH_3); 2.70 (s, 3H, NCH_3), 1.73 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 165.7, 151.7, 146.7, 142.1, 129.2, 128.7, 128.3, 126.1, 125.7, 87.7, 86.3, 55.1, 28.2, 27.3 ppm; IR (KBr) 1706s, 1667s, 1266m, 1173m, 747s, 701s cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{20}H_{21}N_2O_3$: 337.1552, found: 337.1554.

Z-8,8-bis(4-fluorophenyl)-1,2,4-trimethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Ce):

R_f = 0.28 (EtOAc/n-hexane, 1:2); m.p.145–146℃; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.41 (m, 4H, H_{Ar}), 7.06 (m, 4H, H_{Ar}), 4.66 (s, 1H,CH), 3.05 (s, 3H, NCH_3); 2.91 (s, 3H, NCH_3), 1.59 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 166.8, 164.1, 160.8, 152.1, 136.9, 136.2, 127.4, 127.3, 126.7, 126.6, 115.8, 115.7, 115.5, 115.4, 97.0, 77.3, 62.4, 31.2, 27.6, 23.3 ppm; IR (KBr) 1712s, 1674s, 1225s, 1162m, 844m, 749m cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{20}H_{19}N_2O_3F_2$: 373.1364, found: 373.1363.

Z-7,7-bis(4-fluorophenyl)-1,2,4-trimethyl-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Ce):

R_f = 0.48 (EtOAc/n-hexane, 1:2); m.p. 128–129℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.27 (m, 8H, H_{Ar}), 4.58 (s, 1H, CH), 3.11 (s, 3H, NCH_3), 2.75 (s, 3H, NCH_3), 1.76 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, $CDCl_3$): δ 165.7, 164.5, 161.3, 151.7, 142.6, 138.1, 128.5, 128.4, 128.1, 128.0, 116.2, 115.9, 115.7, 115.5, 87.8, 85.6, 55.0, 28.2, 27.4, 27.3 ppm; IR (KBr) 1711s, 1675s, 1224s, 1157m, 844m, 749m cm$^-$; TOFMS (CI) calcd for $(M+1)^+$ $C_{20}H_{19}N_2O_3F_2$: 373.1364, found: 373.1371.

Z-8,8-bis(4-chlorophenyl)-1,2,4-trimethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione(3Cf):

R_f = 0.30 (EtOAc/n-hexane, 1:2); m.p. 157–158℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.35 (m, 8H, H_{Ar}), 4.65 (s, 1H, CH), 3.06 (s, 3H, NCH_3), 2.90 (s, 3H, NCH_3), 1.60 (s, 3H, CH_3); ^{13}C NMR (75MHz, $CDCl_3$) δ 166.6, 152.0, 139.3, 138.7, 134.4, 133.8, 128.9, 128.8, 126.8, 126.2, 96.9, 77.3, 62.3, 31.2, 27.6, 23.3 ppm; IR (KBr) 1711s, 1678s, 1272s, 1170m, 826s, 747m cm^{-1}; TOFMS (CI) calcd for $(M+1)^+$ $C_{20}H_{19}N_2O_3Cl_2$: 405.0773, found: 405.0767.

Z-8,8-bis(4-methoxyphenyl)-1,2,4,6-tetramethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Da):

R_f = 0.30 (EtOAc/n-hexane, 1:2); m.p. 195–196℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.35–7.26 (m, 4H, H_{Ar}), 6.86–6.83 (m, 4H, H_{Ar}), 3.77 (s, 3H, CH_3O), 3.74 (s, 3H, CH_3O), 3.18 (s, 3H, NCH_3), 2.75 (s, 3H, NCH_3); 1.59 (s, 3H, CH_3), 1.42 (s, 3H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 75MHz): δ 171.0, 159.0, 158.7, 152.5, 134.3, 133.0, 126.5, 126.0, 113.9, 95.0, 80.2, 64.9, 55.4, 55.3, 31.5, 27.8, 19.7, 19.4 ppm; IR (KBr) 1711s, 1663s, 1287m, 1114m, 827m, 746m cm^{-1}; TOFMS (CI) calcd for $(M+1)^+$ $C_{23}H_{27}N_2O_5$: 411.1920, found: 411.1925.

Z-7,7-bis(4-methoxyphenyl)-1,2,4,6-tetramethyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Da):

R_f = 0.43 (EtOAc/n-hexane, 1:2); m.p. 130–131℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.80–7.77 (m, 4H, H_{Ar}), 6.98–6.95 (m, 4H, H_{Ar}), 3.89 (s, 6H, CH_3O), 3.44 (s, 3H, NCH_3), 3.37 (s,3H, NCH_3), 2.25 (s, 3H, CH_3), 2.00 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 169.8, 159.7, 159.6, 151.1, 136.3, 135.4, 132.7, 127.1, 126.7, 114.3, 114.0, 92.1, 90.2, 55.5, 55.4, 54.1, 28.6, 28.0, 22.1, 18.4ppm; IR (KBr) 1703s, 1661s, 1298m, 1112m, 834s, 745m cm$^-$; TOFMS (CI) calcd for $(M+1)^+$ $C_{23}H_{27}N_2O_5$: 411.1920, found: 411.1913.

Z-1,2,4,6-tetramethyl-8,8-dip-tolyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Db):

R_f = 0.44 (EtOAc/n-hexane, 1:2); m.p. 190–191℃; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.42–7.33 (m, 4H, H_{Ar}), 7.17–7.08 (m, 4H, H_{Ar}), 3.19 (s, 3H, NCH_3), 2.60 (s, 3H, NCH_3), 2.25 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.49 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 170.8, 152.5, 140.3, 139.2, 137.3, 136.9, 129.3, 129.0, 125.8, 125.2, 95.5, 80.8, 65.3, 31.3, 27.3, 20.6, 20.5, 19.5, 19.2 ppm; IR (KBr) 1709s, 1671s, 1277m, 1112m, 817m, 748m cm$^-$; TOFMS (CI) calcd for $(M+1)^+$ $C_{23}H_{27}N_2O_3$: 379.2022, found: 379.2021.

Z-1,2,4,6-tetramethyl-7,7-diphenyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Db):

R_f = 0.59 (EtOAc/n-hexane, 1:2); m.p. 137–138℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.69 (d, 4H, H_{Ar}), 7.27

(d, 4H, H_{Ar}), 3.43 (s, 3H, NCH_3), 3.36 (s,3H, NCH_3), 2.43 (s, 6H, CH_3), 2.25 (s, 3H, CH_3), 2.00 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 169.7, 151.0, 143.7, 141.4, 140.4, 137.5, 137.4, 130.7, 129.8, 129.5, 129.2, 125.7, 125.4, 92.1, 90.4, 54.0, 22.1, 21.5, 21.0, 20.9, 18.5, 16.5 ppm; IR (KBr) 1704s, 1661s, 1294m, 1117m, 824m, 755m cm^{-}; TOFMS (CI) calcd for $(M+1)^+$ $C_{23}H_{27}N_2O_3$: 379.2022, found: 379.2029.

Z-8,8-bis(4-tert-butylphenyl)-1,2,4,6-tetramethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Dc):

R_f = 0.39 (EtOAc/n-hexane, 1:3); m.p. 242–243℃; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.48–7.35 (m, 8H, H_{Ar}), 3.25 (s, 3H, NCH_3), 2.54 (s, 3H, NCH_3), 1.58 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.27 (d, 18H, t-$C(CH_3)_3$) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 171.1, 152.8, 150.76, 150.4, 140.4, 139.5, 125.9, 125.6, 125.3, 95.9, 81.3, 65.6, 34.9, 31.5, 31.4, 27.5, 19.8, 19.3 ppm; IR (KBr) 1714, 1672, 1275, 1111, 748 cm^{-}; TOFMS (CI) calcd for $(M+1)^+$ $C_{29}H_{39}N_2O_3$: 463.2961, found: 463.2963.

Z-7,7-bis(4-tert-butylphenyl)-1,2,4,6-tetramethyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Dc):

R_f = 0.50 (EtOAc/n-hexane, 1:3); m.p. 162–163℃; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.36 (m, 8H, H_{Ar}), 3.02 (s, 3H, NCH_3); 2.77 (s, 3H, NCH_3), 1.66 (s, 3H, CH_3); 1.44 (s, 3H, CH_3), 1.26 (d, 18H, t-$C(CH_3)_3$) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 169.7, 151.1, 150.7, 141.1, 140.3, 125.8, 125.6, 125.4, 125.3, 92.0, 90.2, 54.4, 35.0, 34.9, 31.564, 31.5, 28.7, 27.9, 22.3, 18.4 ppm. IR (KBr): 1707s, 1666s, 1269m, 1113m, 835m, 747m cm^{-}; TOFMS (CI) calcd for $(M+1)^+$ $C_{29}H_{39}N_2O_3$: 463.2961, found: 463.2953.

Z-1,2,4,6-tetramethyl-8,8-diphenyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Dd):

R_f = 0.41 (EtOAc/n-hexane, 1:2); m.p. 207–208℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.32 (m, 10H, H_{Ar}), 3.24 (s, 3H, NCH_3), 2.67 (s, 3H, NCH_3), 1.61 (s, 3H, CH_3), 1.46 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, $CDCl_3$): δ 170.8, 152.5, 141.8, 140.7, 130.2, 128.5, 128.4, 127.8, 127.3, 125.2, 124.7, 95.3, 80.4, 64.9, 31.5, 27.7, 19.8, 19.3 ppm; IR (KBr) 1706s, 1674s, 1274m, 1117m, 747m, 711m cm^{-}; TOFMS (EI) calcd for (M^+) $C_{21}H_{22}N_2O_3$: 350.1630, found: 350.1623.

Z-1,2,4,6-tetramethyl-7,7-diphenyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Dd):

R_f = 0.59 (EtOAc/n-hexane, 1:2); m.p. 149–150℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.64 (m, 10H, H_{Ar}), 3.44 (s, 3H, NCH_3), 3.37 (s, 3H, NCH_3), 2.25 (s, 3H, CH_3), 2.00 (s, 3H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 75MHz): δ 169.5, 150.9, 144.1, 143.1, 129.0, 128.7, 128.0, 125.8, 125.5, 92.3, 90.3, 54.2, 28.6, 28.0, 22.0, 18.5 ppm; IR (KBr) 1701s, 1663s, 1293m, 1125m, 750s, 713s cm^{-}; TOFMS (CI) calcd for $(M+1)^+$ $C_{21}H_{23}N_2O_3$: 351.1705, found: 351.1709.

Z-8,8-bis(4-fluorophenyl)-1,2,4,6-tetramethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3De):

R_f = 0.41 (EtOAc/n-hexane, 1:2); m. p. 199–200℃; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.51 (m, 4H, H_{Ar}), 7.11 (m, 4H, H_{Ar}), 3.23 (s, 3H, NCH_3); 2.66 (s, 3H, NCH_3), 1.62 (s, 3H, CH_3), 1.53 (s, 3H, CH_3) ppm; ^{13}C

NMR (75MHz, Acetone-d_6): δ 170.9, 164.3, 161.1, 152.7, 139.2, 138.2, 128.5, 128.4, 127.8, 127.7, 116.1, 115.8, 115.8, 115.6, 95.3, 81.6, 65.7, 31.6, 27.7, 19.7, 19.5 ppm. IR (KBr) 1708s, 1671s, 1276, 1116m, 835m, 743m cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{21}H_{21}N_2O_3F_2$: 387.1520, found: 387.1521.

Z-7,7-bis(4-fluorophenyl)-1,2,4,6-tetramethyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4De):
R_f = 0.63 (EtOAc/n-hexane, 1:2); m.p. 116–118℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.82 (m, 4H, H_{Ar}), 7.17 (m, 4H, H_{Ar}), 3.44 (s, 3H, NCH_3), 3.37 (s, 3H, NCH_3), 2.26 (s, 3H, CH_3), 2.00 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 169.4, 164.3, 161.1, 150.9, 139.9, 138.9, 127.9, 127.7, 116.0, 115.7, 115.4, 92.4, 89.6, 54.2, 28.7, 28.0, 22.0, 18.4 ppm; IR (KBr) 1708s, 1668s, 1291m, 1123m, 836s, 748m cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{21}H_{21}N_2O_3F_2$: 387.1520, found: 387.1523.

Z-8,8-bis(4-chlorophenyl)-1,2,4,6-tetramethyl-7-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3Df):
R_f = 0.38 (EtOAc/n-hexane, 1:2); m.p. 192–193℃; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.32 (m, 8H, H_{Ar}), 3.21 (s, 3H, NCH_3), 2.73 (s, 3H, NCH_3), 1.60 (s, 3H, CH_3), 1.44 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, $CDCl_3$): δ 170.5, 152.3, 139.9, 138.9, 134.2, 133.6, 128.9, 128.9, 126.6, 126.1, 94.6, 80.6, 76.7, 64.9, 31.5, 27.9, 19.8, 19.3 ppm; IR (KBr) 1708s, 1672s, 1276m, 1092s, 824m, 748m cm^{-}; TOFMS(EI) calcd for (M^{+}) $C_{21}H_{20}N_2O_3Cl_2$: 418.0851, found: 418.0853.

Z-7,7-bis(4-chlorophenyl)-1,2,4,6-tetramethyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (4Df):
R_f = 0.55 (EtOAc/n-hexane, 1:2); m.p. 69–70℃; ^{1}H NMR (300MHz, Acetone-d_6): δ 7.42 (m, 8H, H_{Ar}), 3.01 (s, 3H, NCH_3), 2.85 (s, 3H, NCH_3), 1.69 (s, 3H, CH_3), 1.45 (s, 3H, CH_3) ppm; ^{13}C NMR (75MHz, Acetone-d_6): δ 169.3, 150.9, 142.6, 141.5, 133.8, 129.3, 129.0, 128.7, 127.635, 127.3, 92.6, 89.5, 54.2, 28.7, 28.0, 22.0, 18.4 ppm; IR (KBr) 1708s,1672s, 1291m, 1092s, 828m, 746m cm^{-}; TOFMS (CI) calcd for $(M+1)^{+}$ $C_{21}H_{21}N_2O_3Cl_2$: 419.0929, found:419.0926.

Figure S1. ^{1}H NMR and ^{13}C NMR spectra of **3Ca**

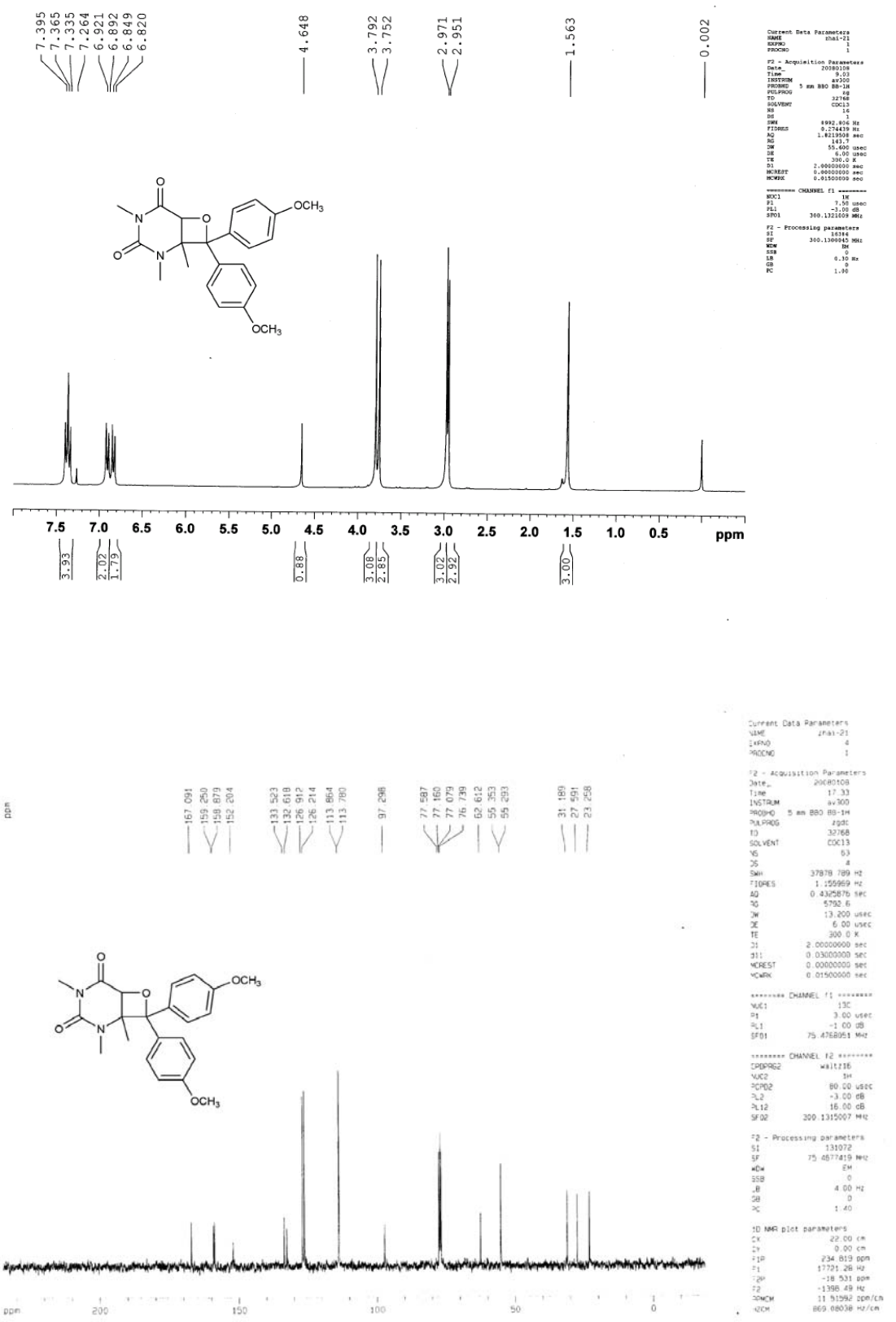


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of **4Ca**

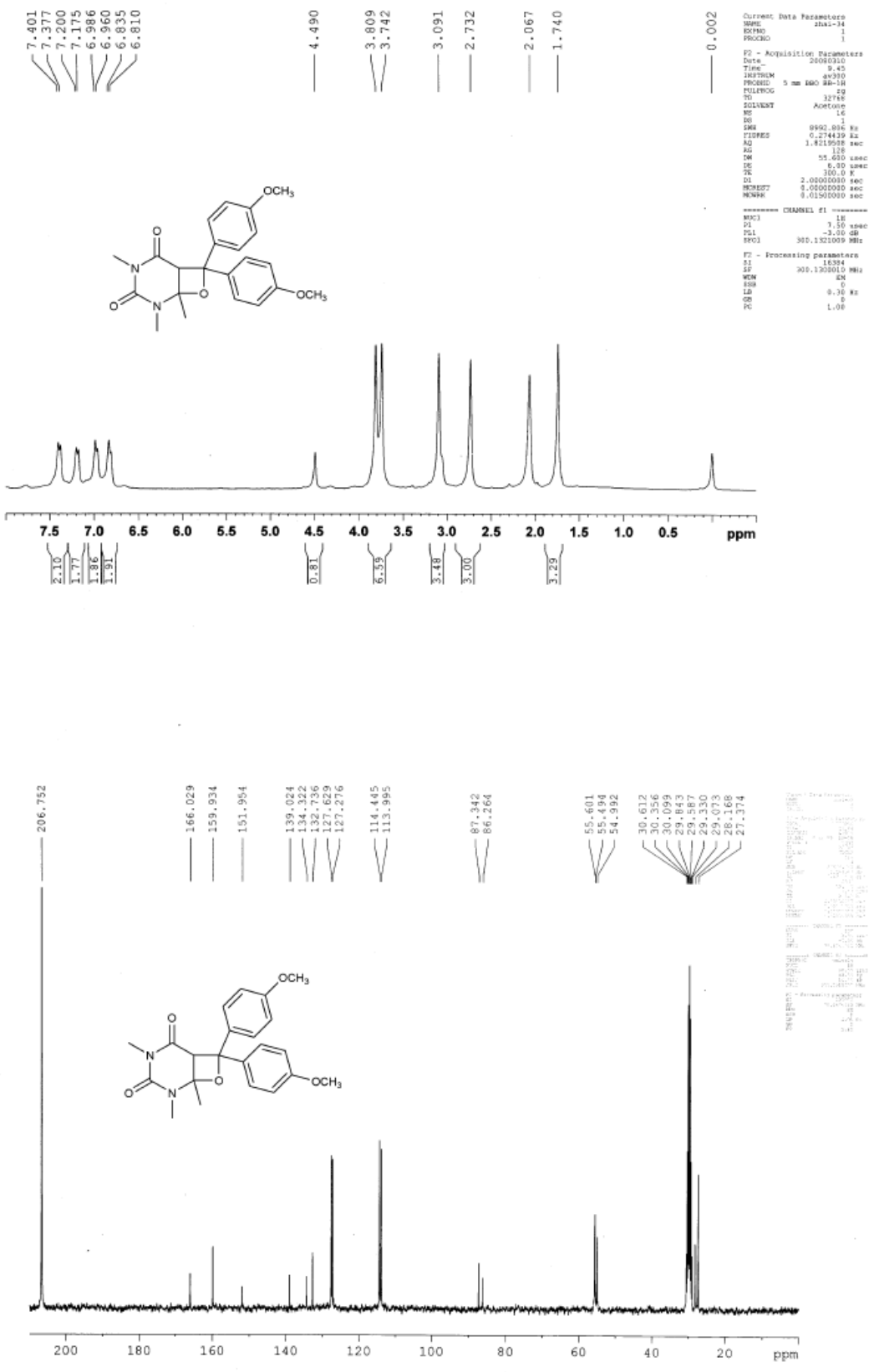


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of **3Cb**

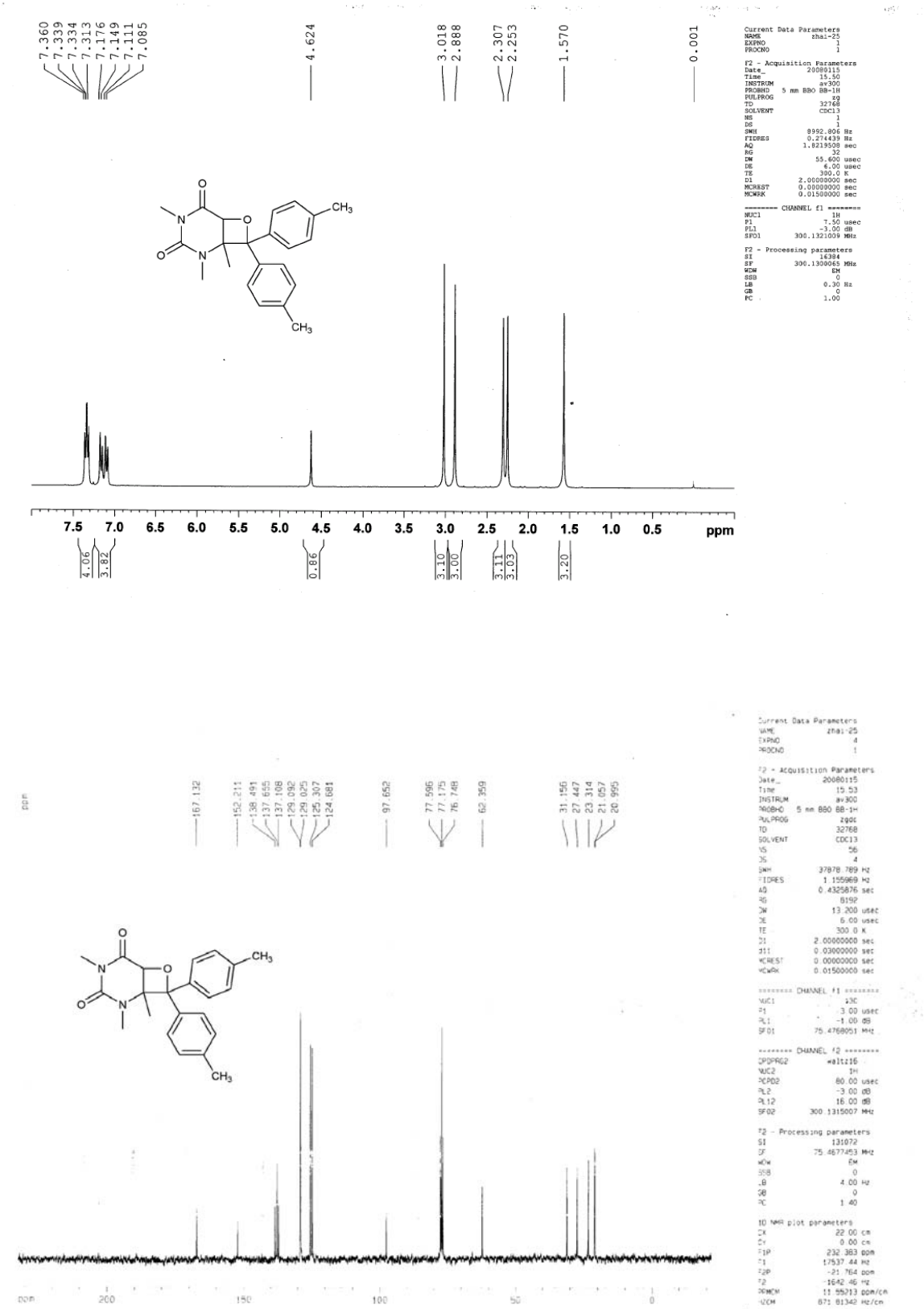


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **4Cb**

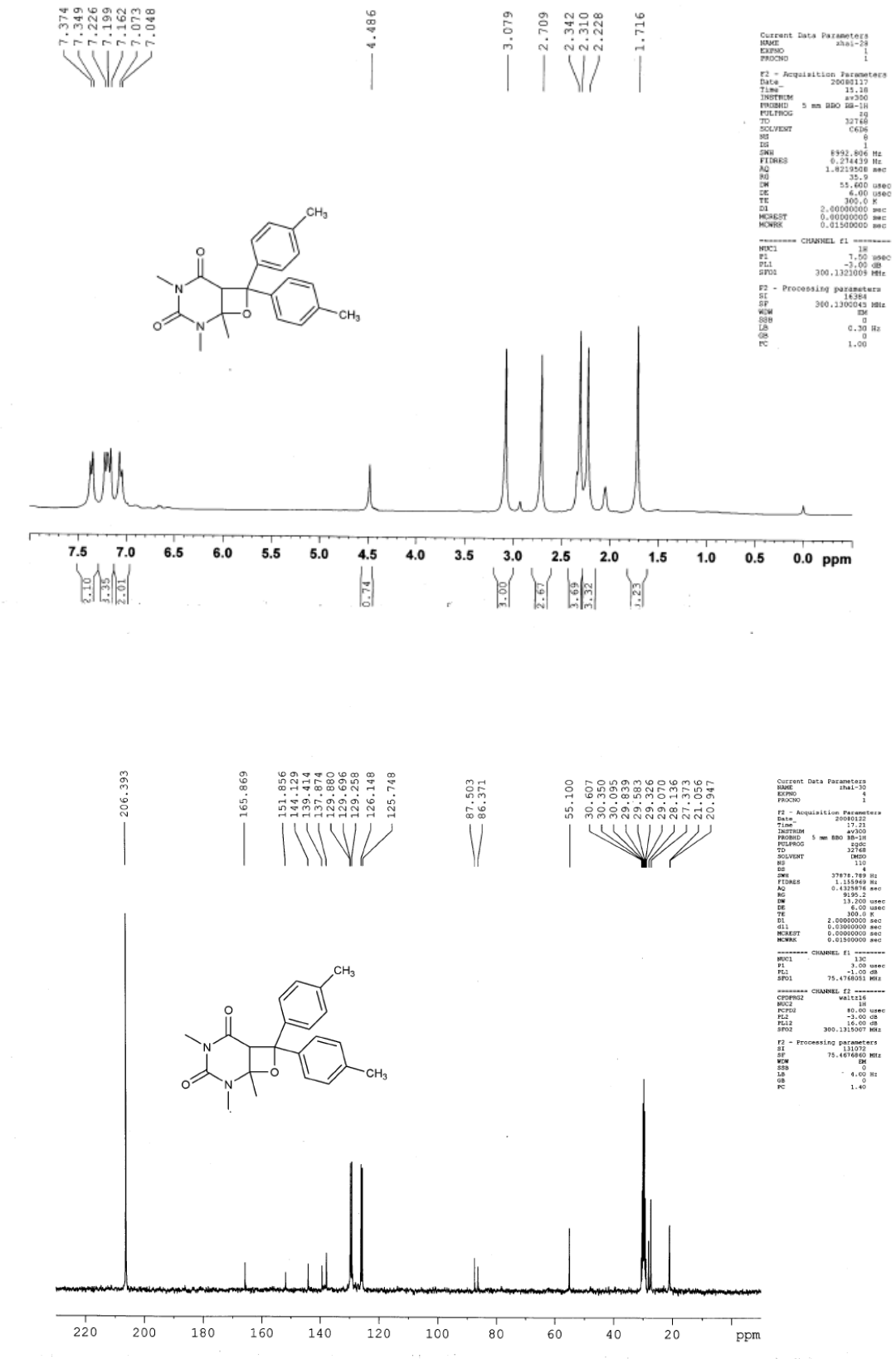


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of **3Cc**

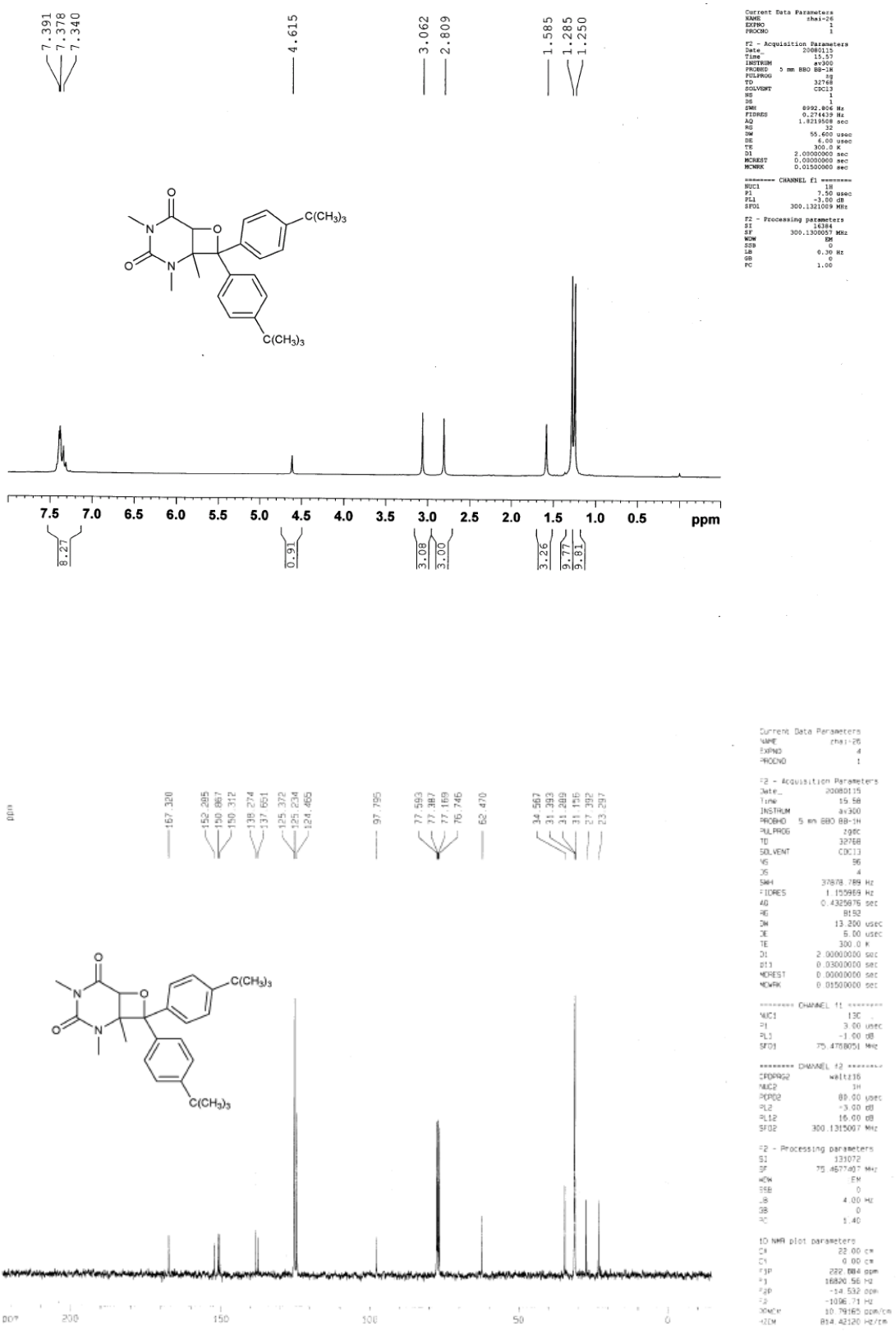


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of **4Cc**

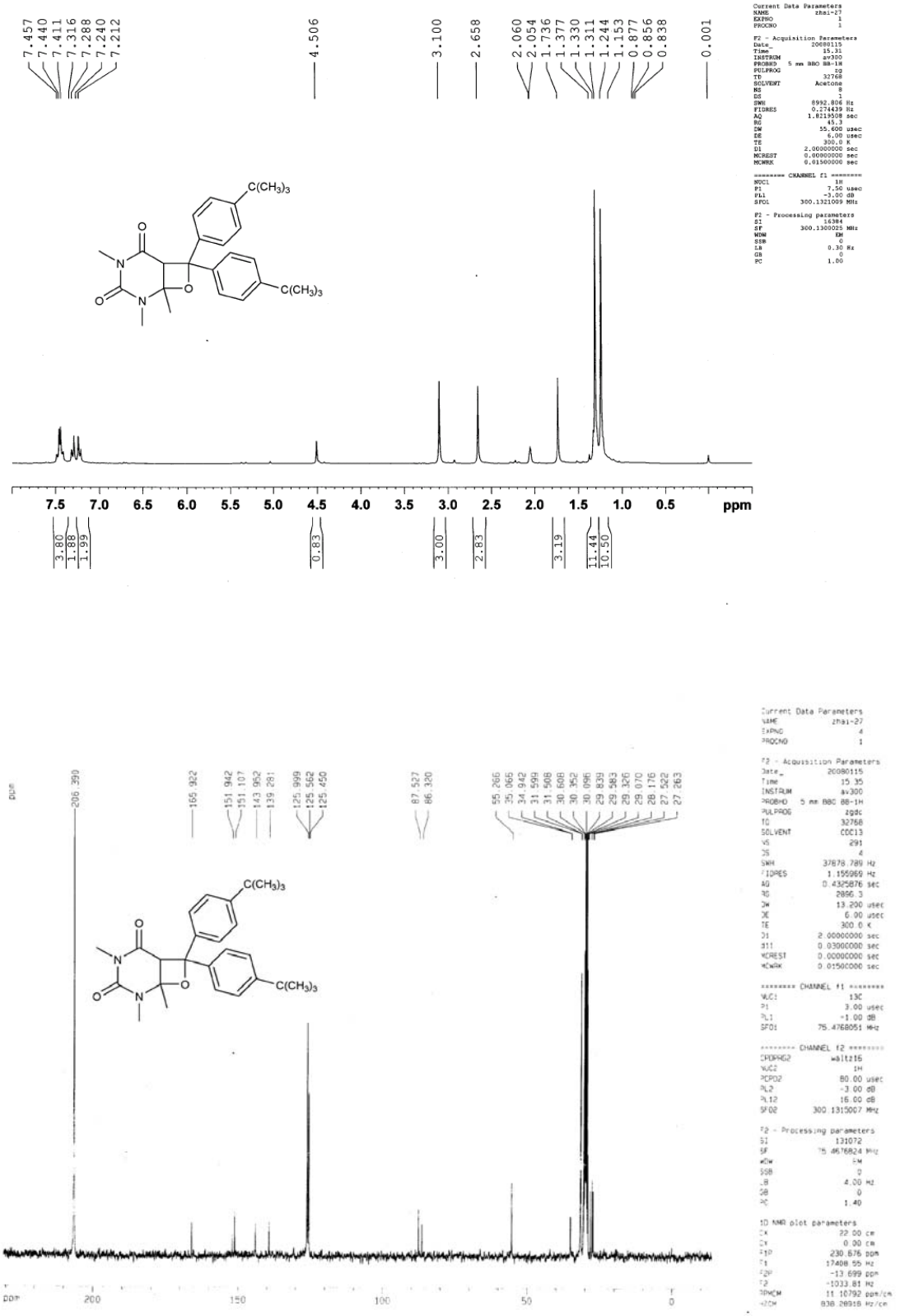


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of **3Cd**

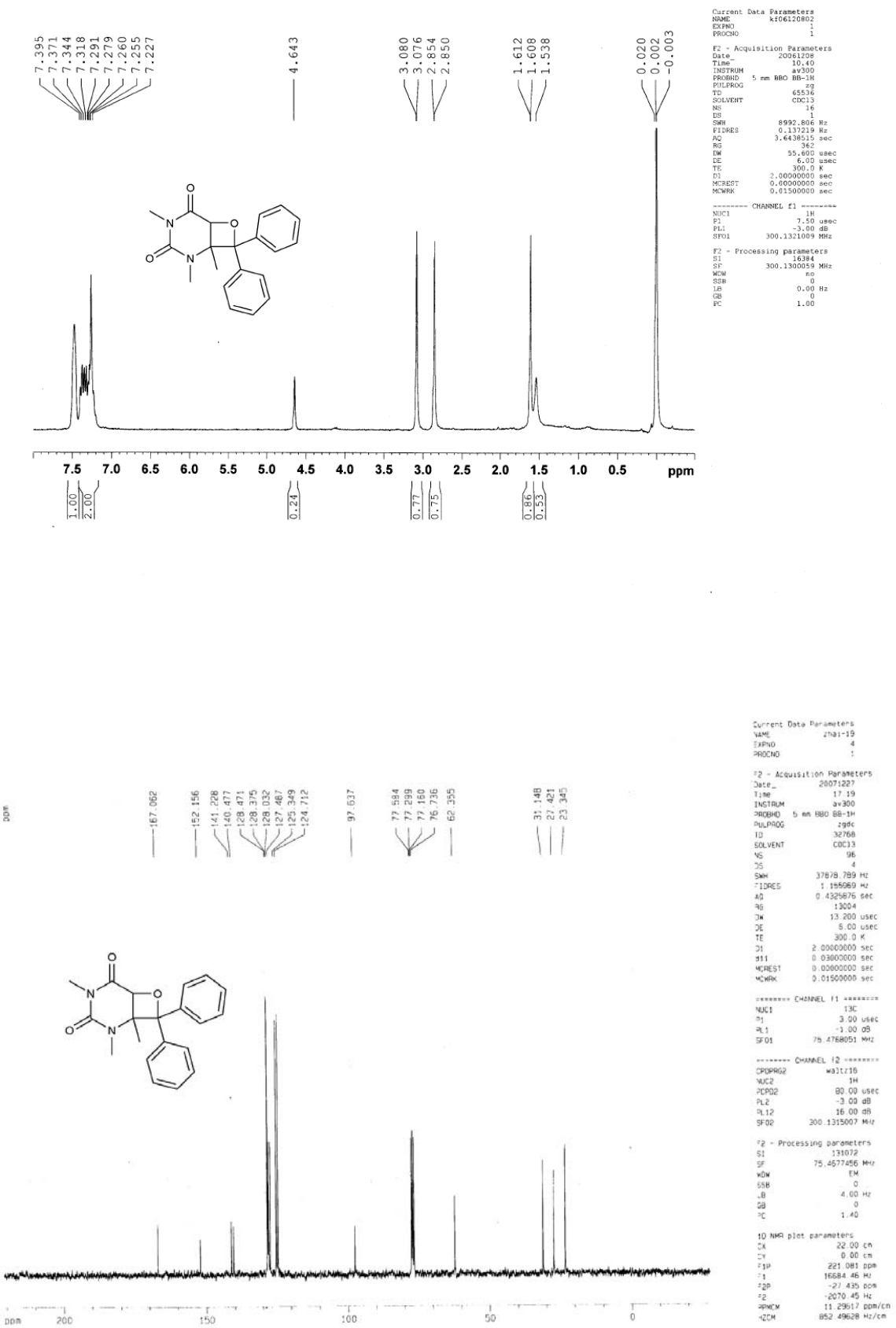


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of **4Cd**

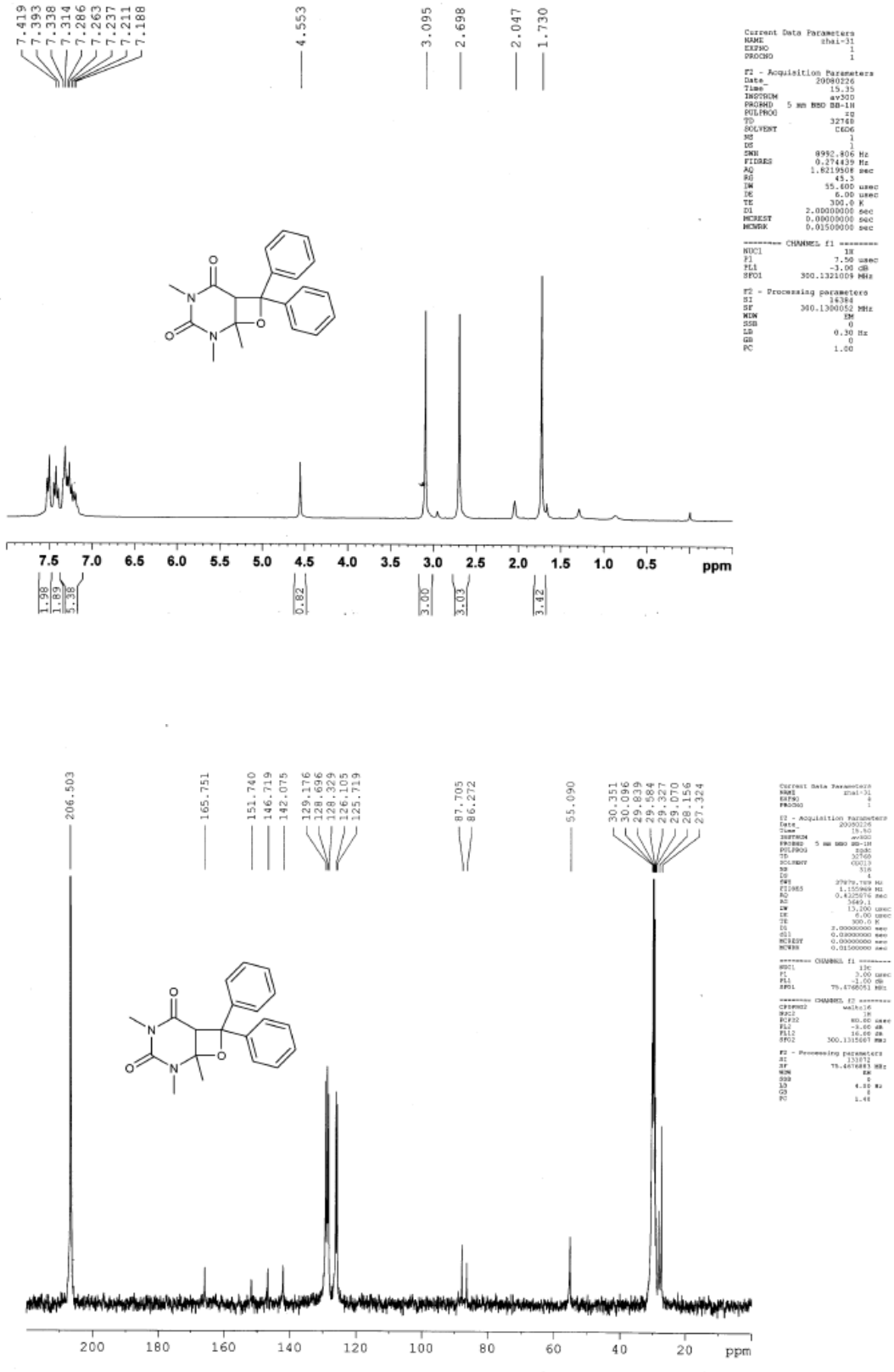


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of **3Ce**

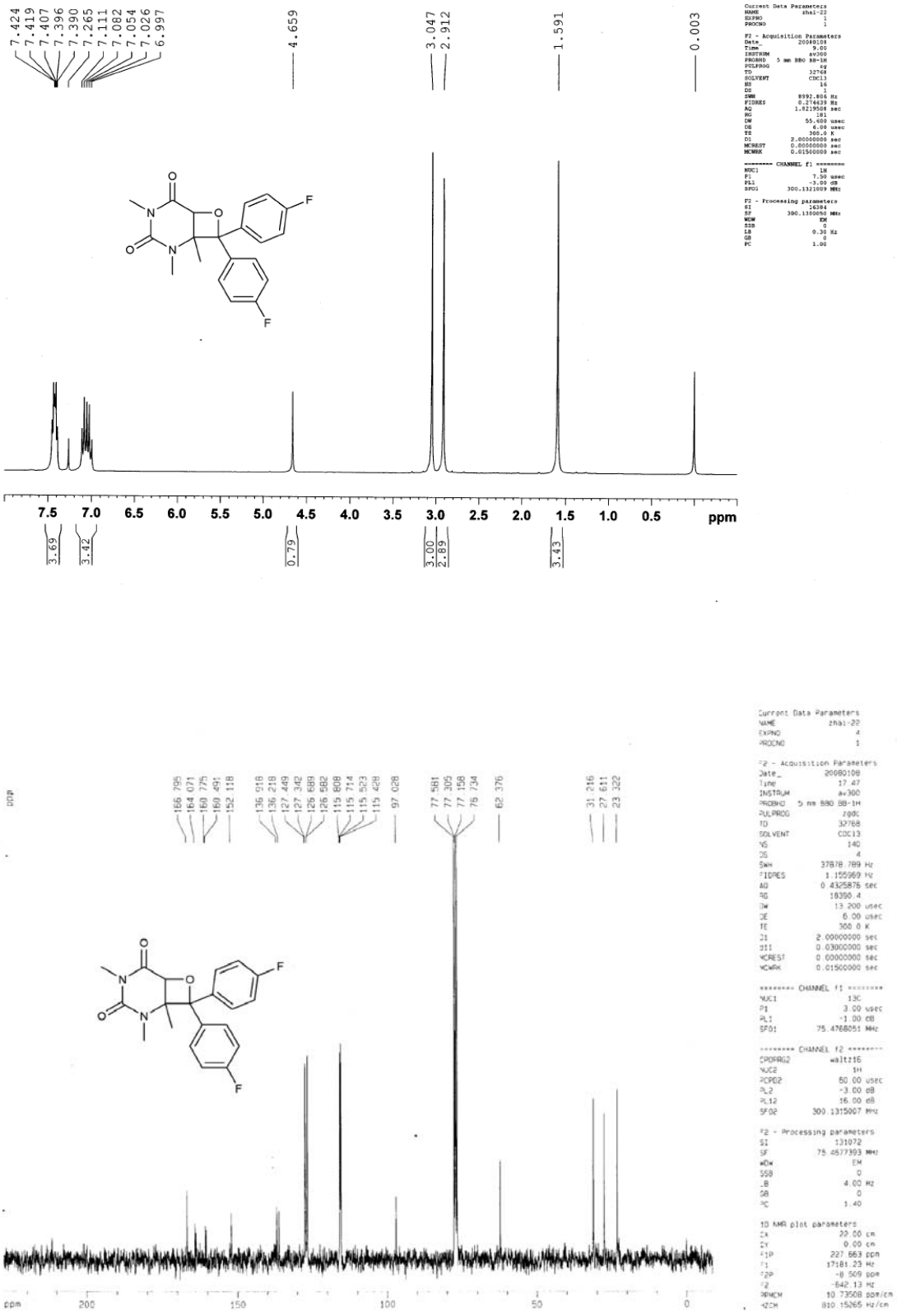
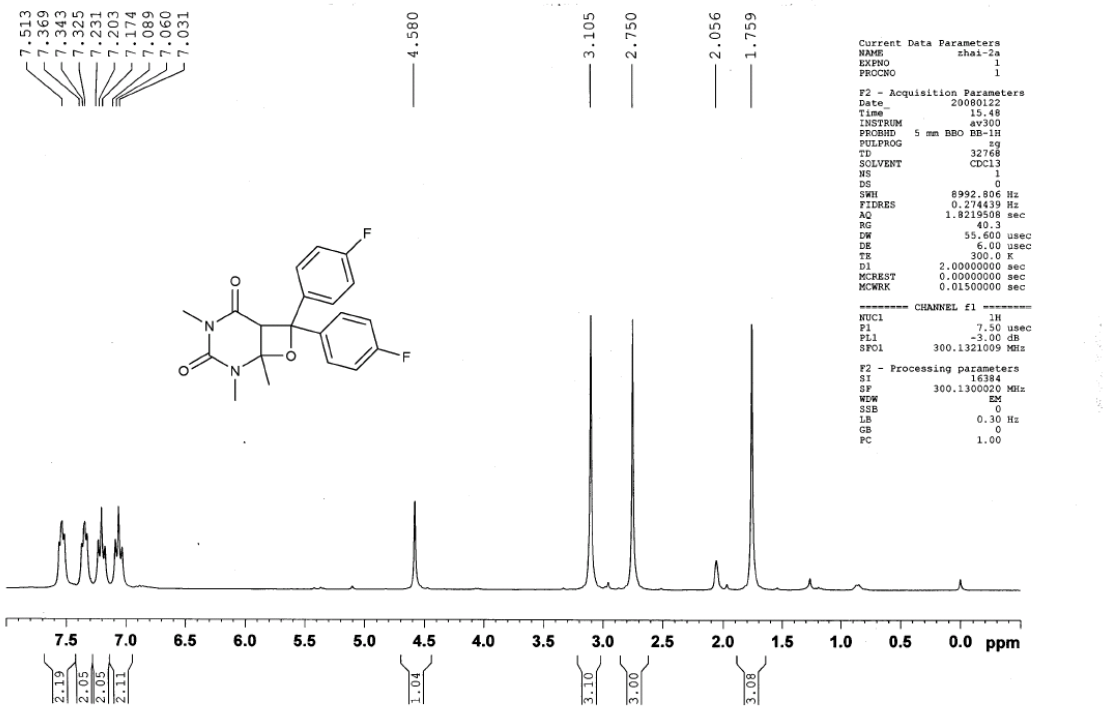


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of **4Ce**



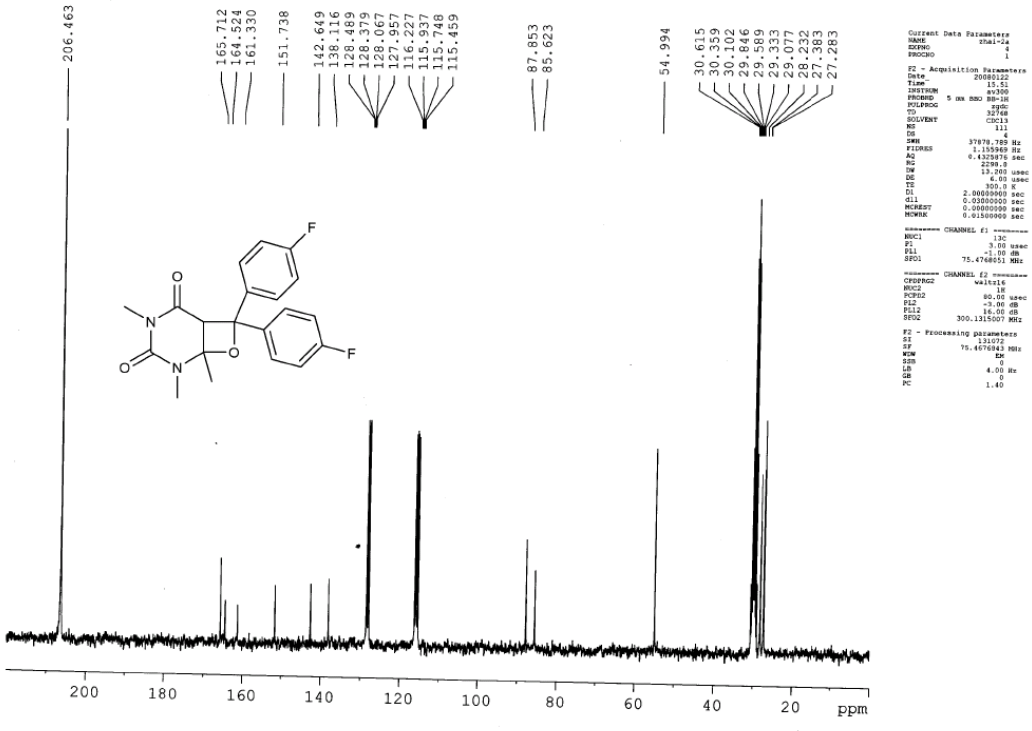


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of **3Cf**

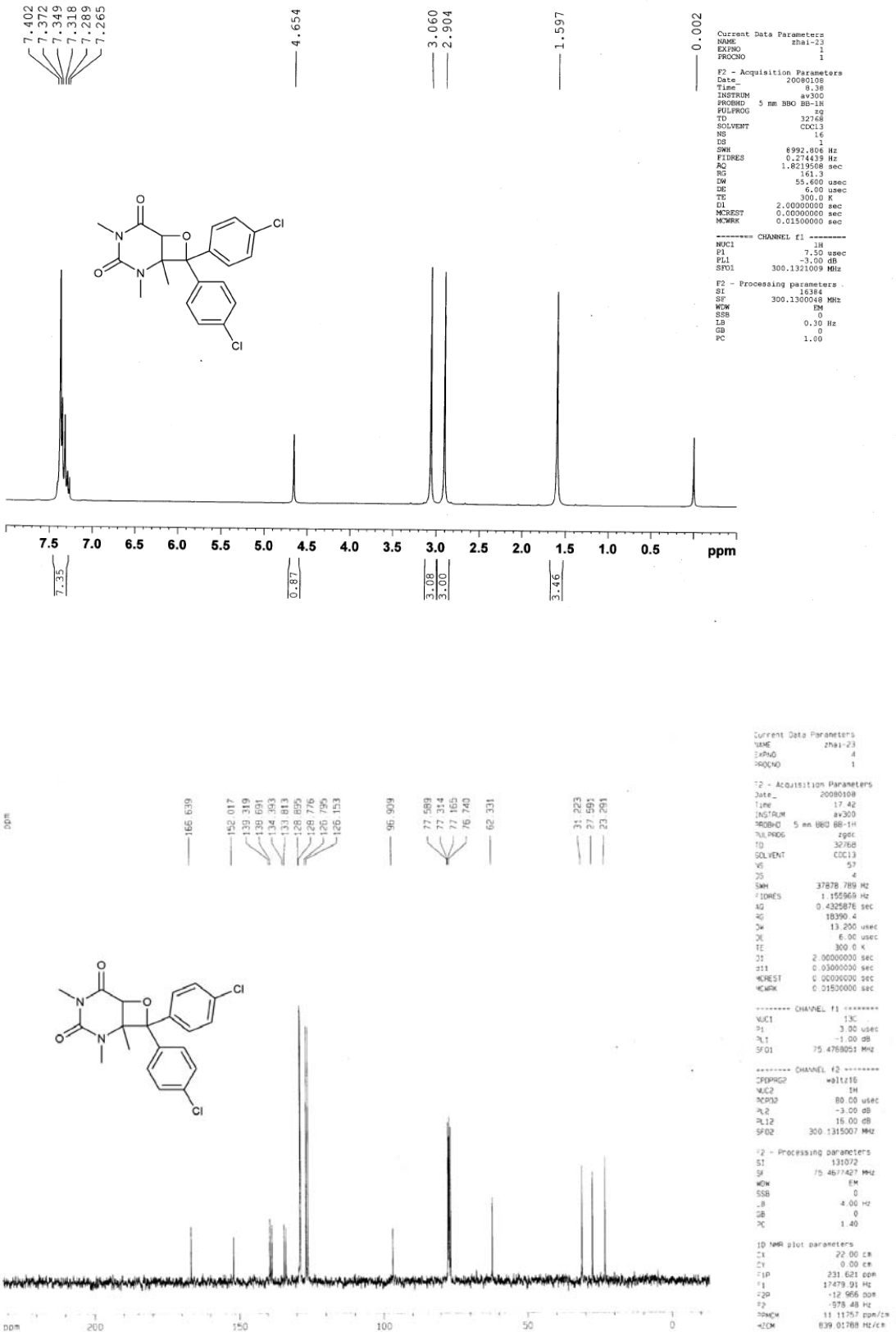


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of **3Da**

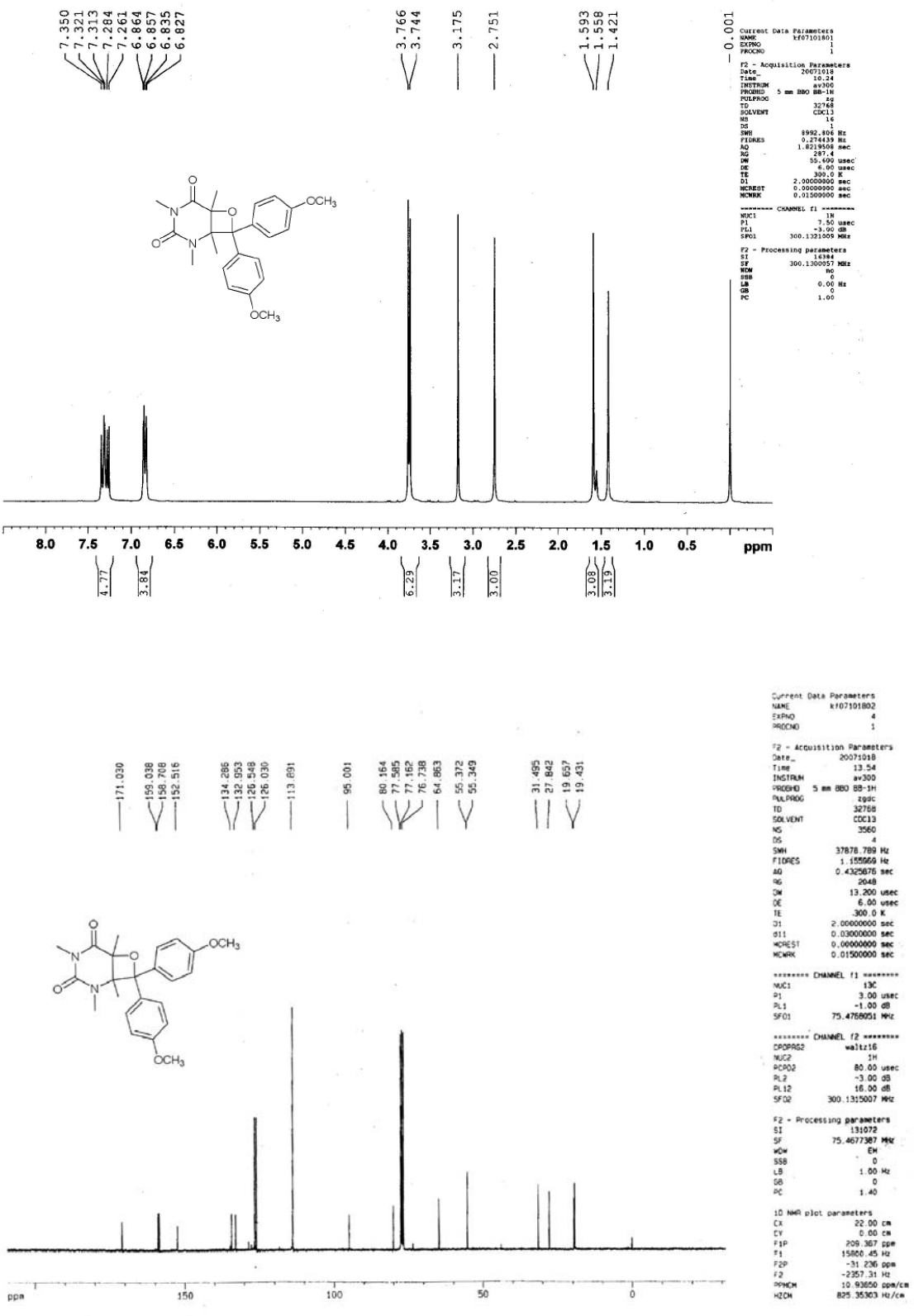


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of **4Da**

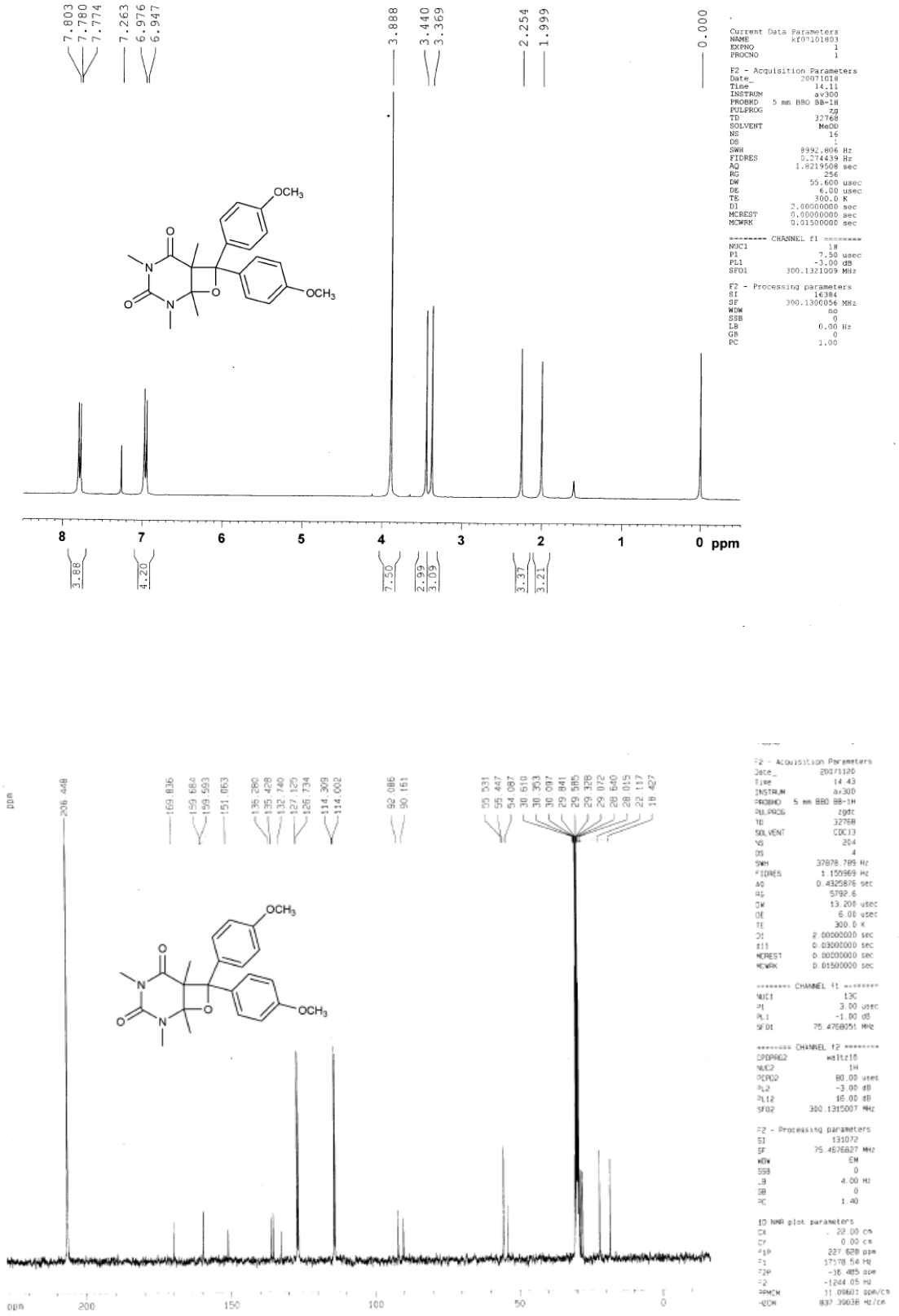
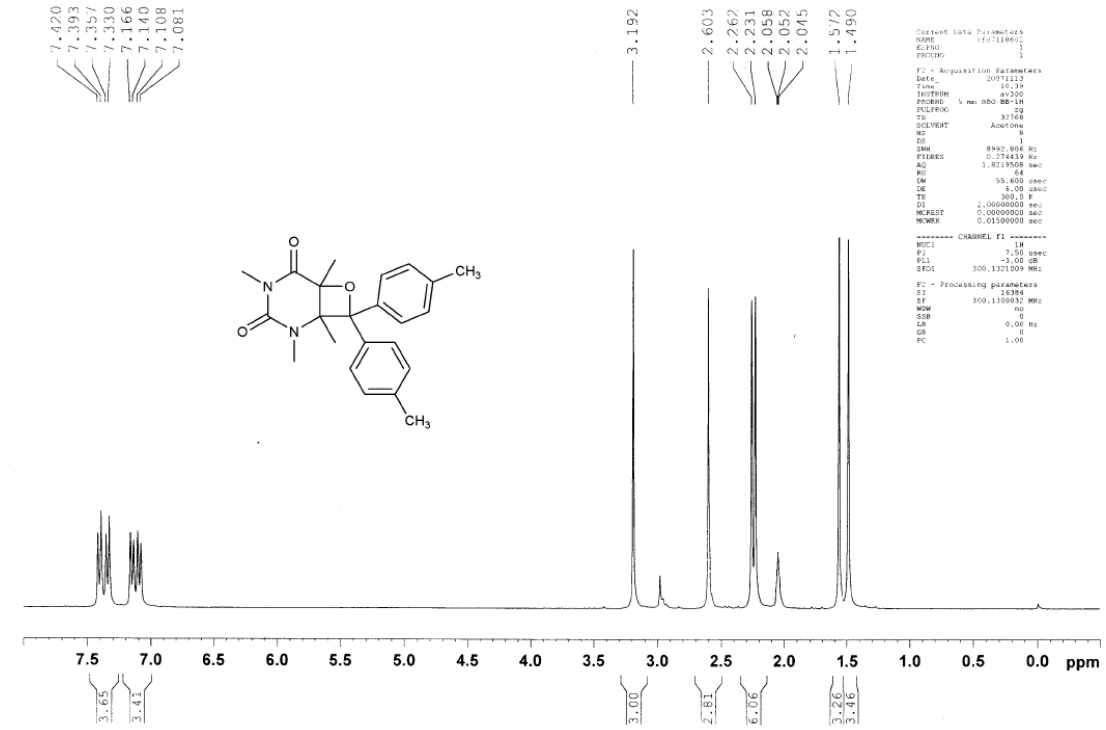
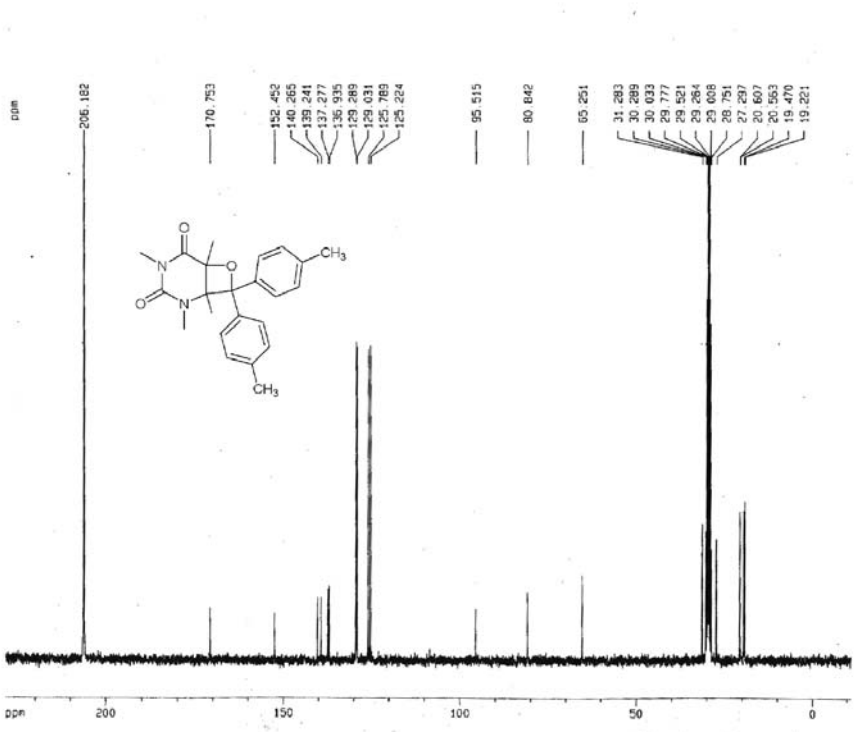


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of **3Db**





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PROCNO 1

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Figure S15. ^{1}H NMR and ^{13}C NMR spectra of **4Db**

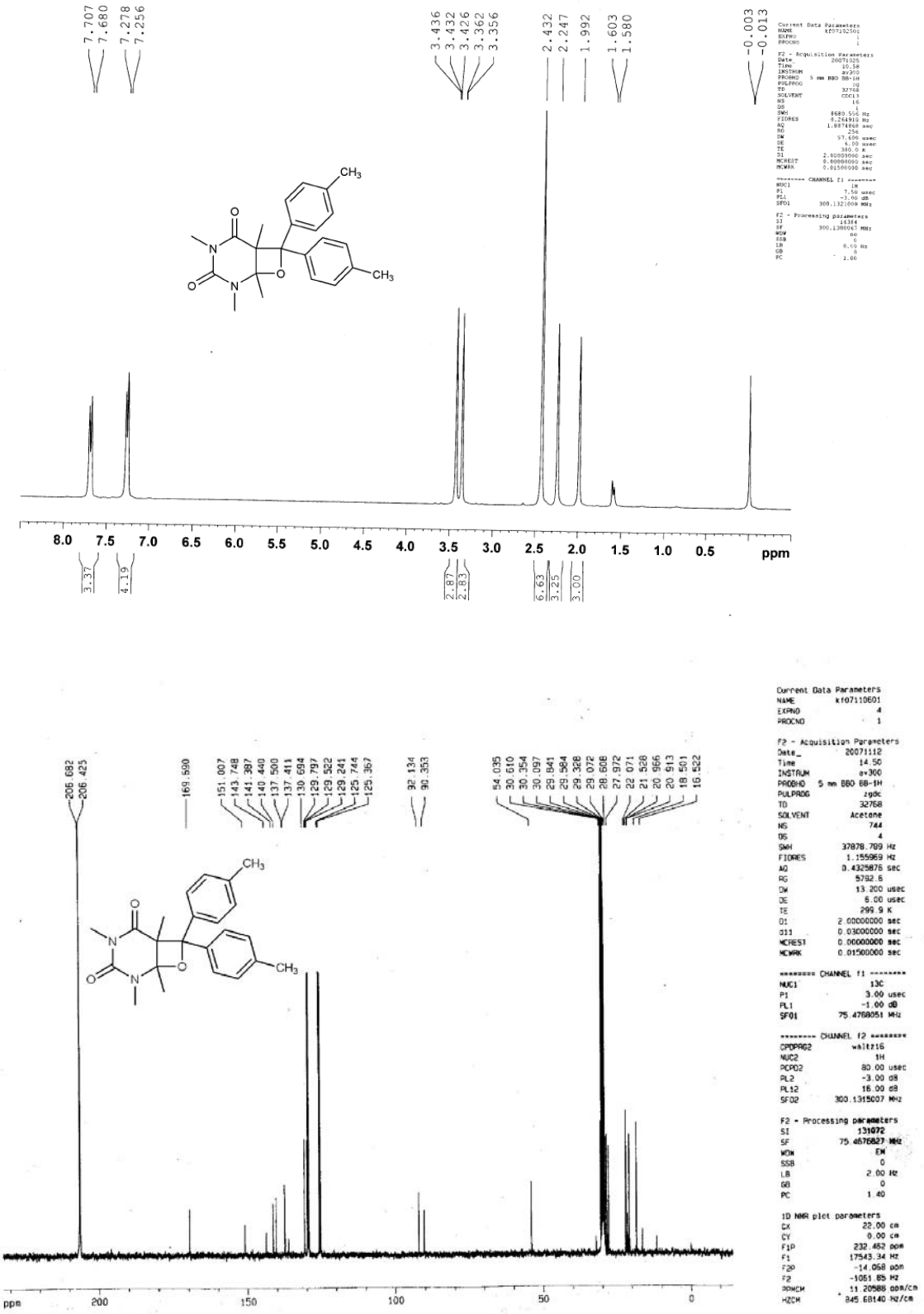

Figure S16. ^{1}H NMR and ^{13}C NMR spectra of **3Dc**

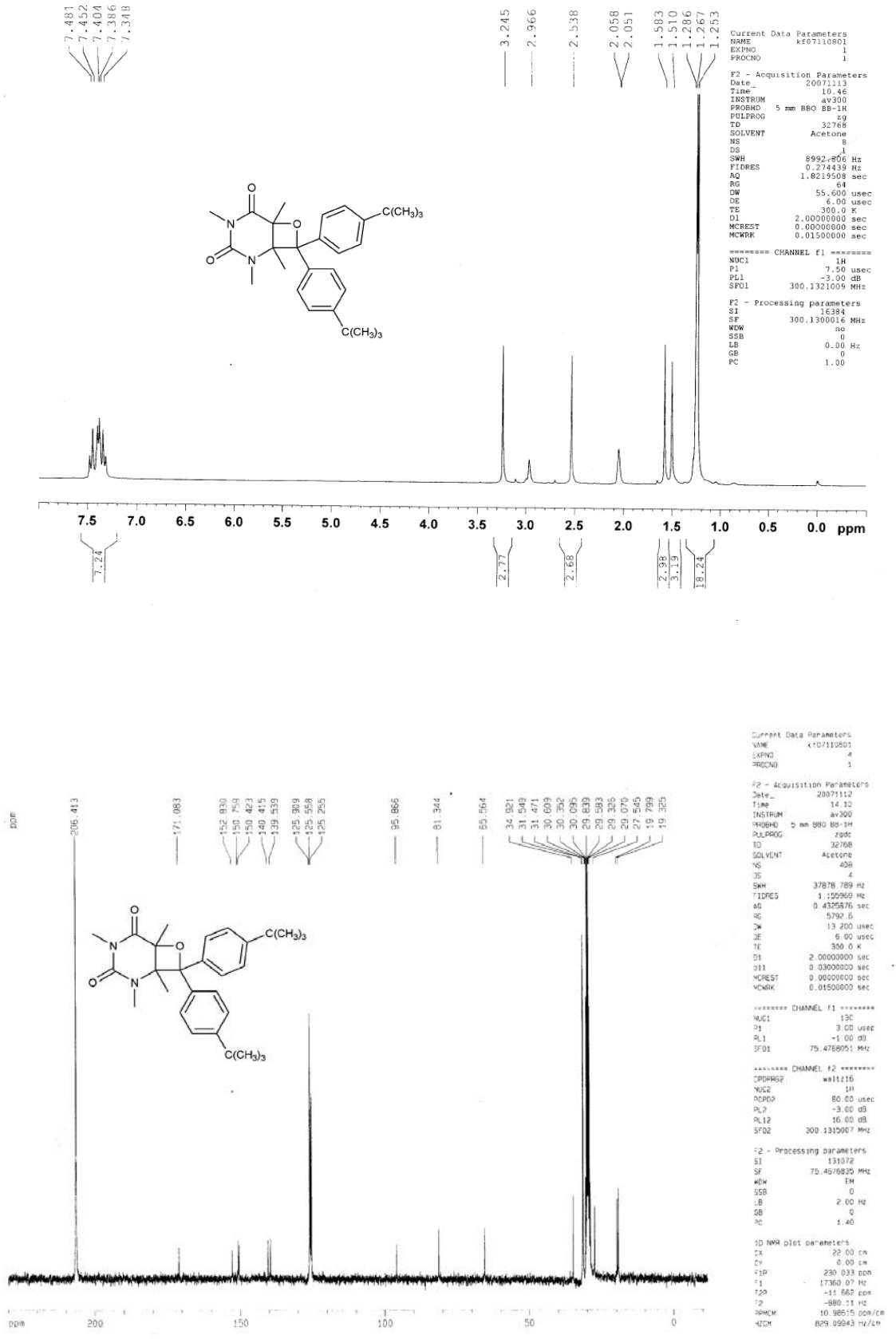

Figure S17. ^{1}H NMR and ^{13}C NMR spectra of **4Dc**

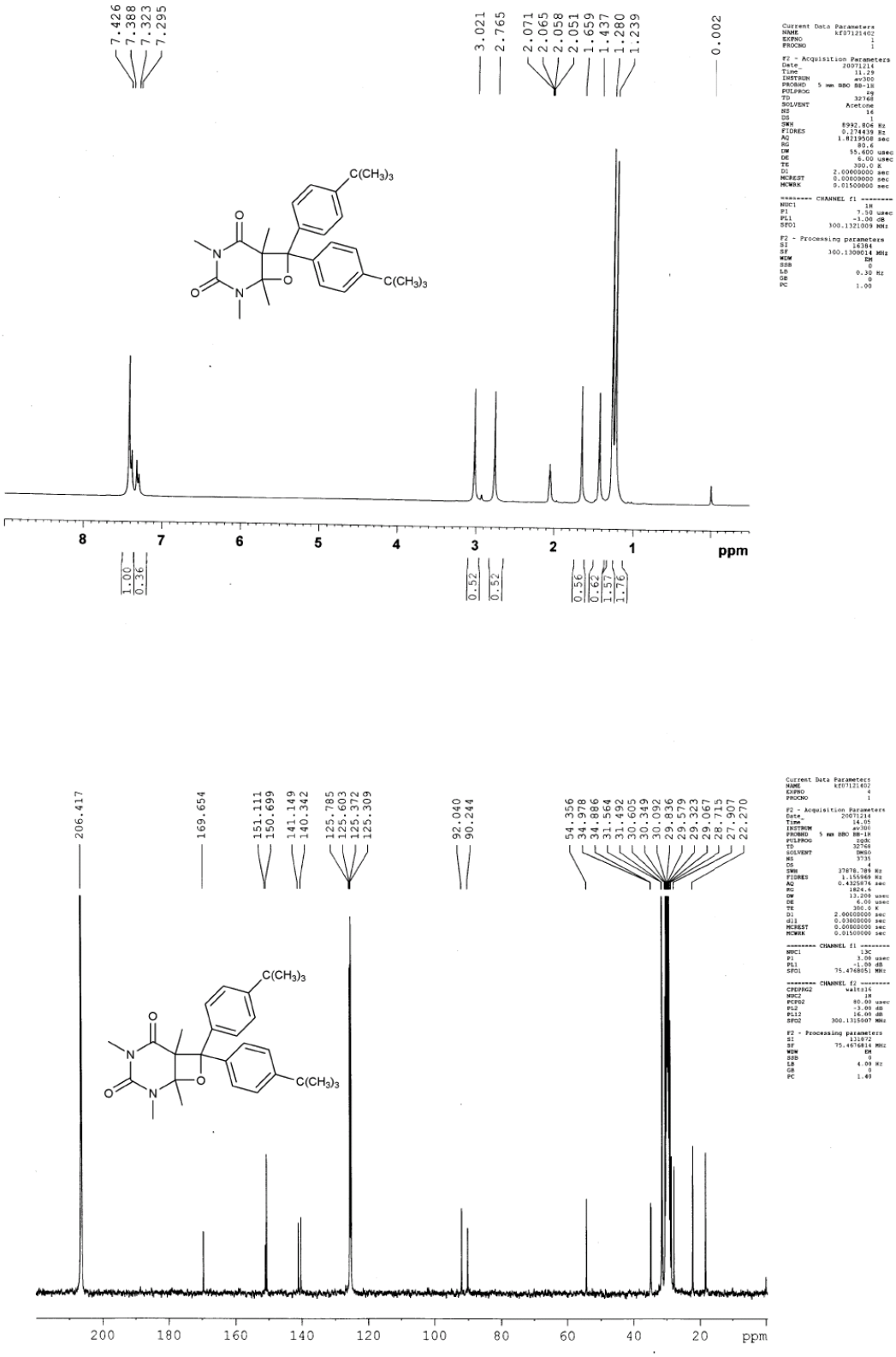

Figure S18. ^{1}H NMR and ^{13}C NMR spectra of **3Dd**

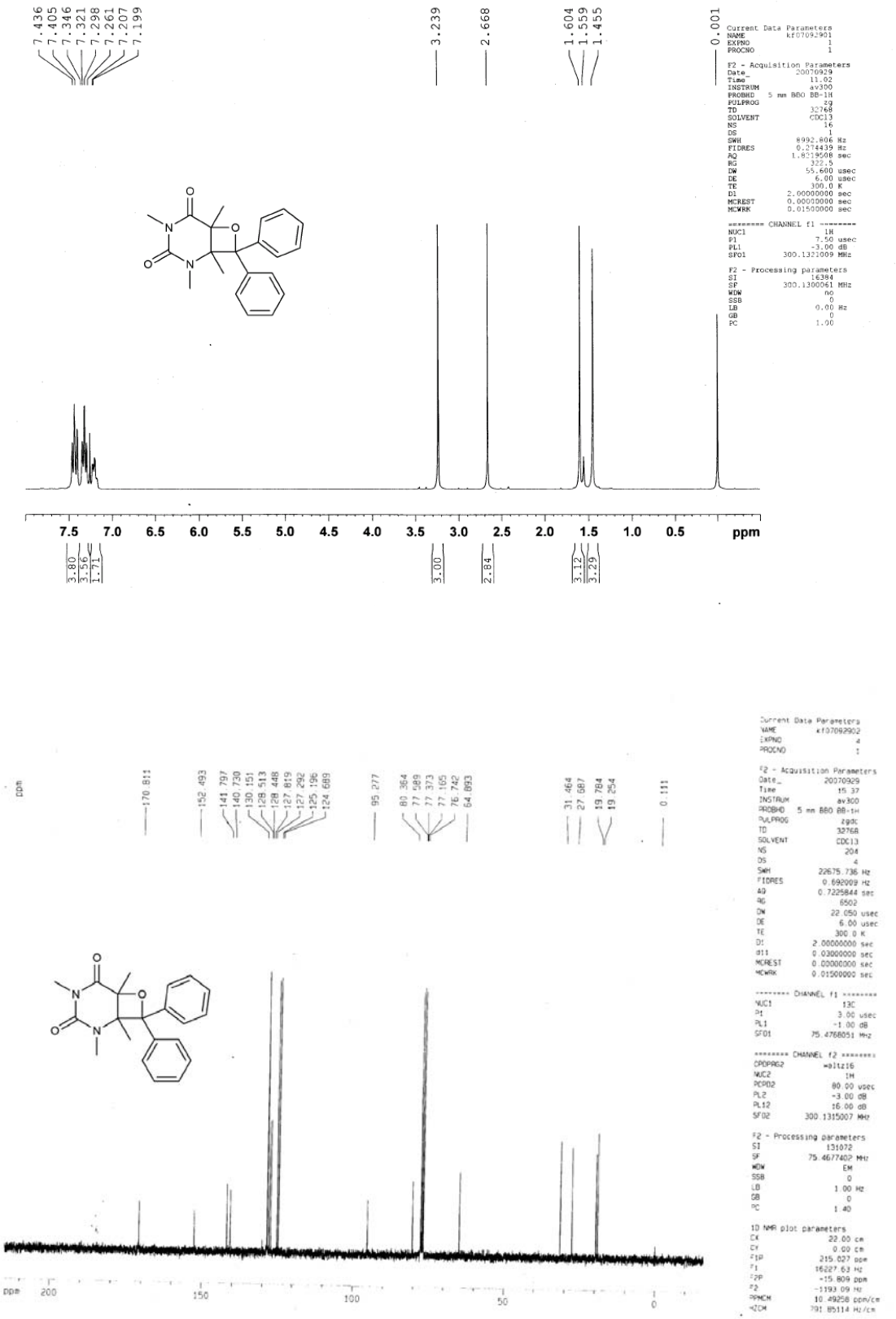

Figure S19. ^{1}H NMR and ^{13}C NMR spectra of **4Dd**

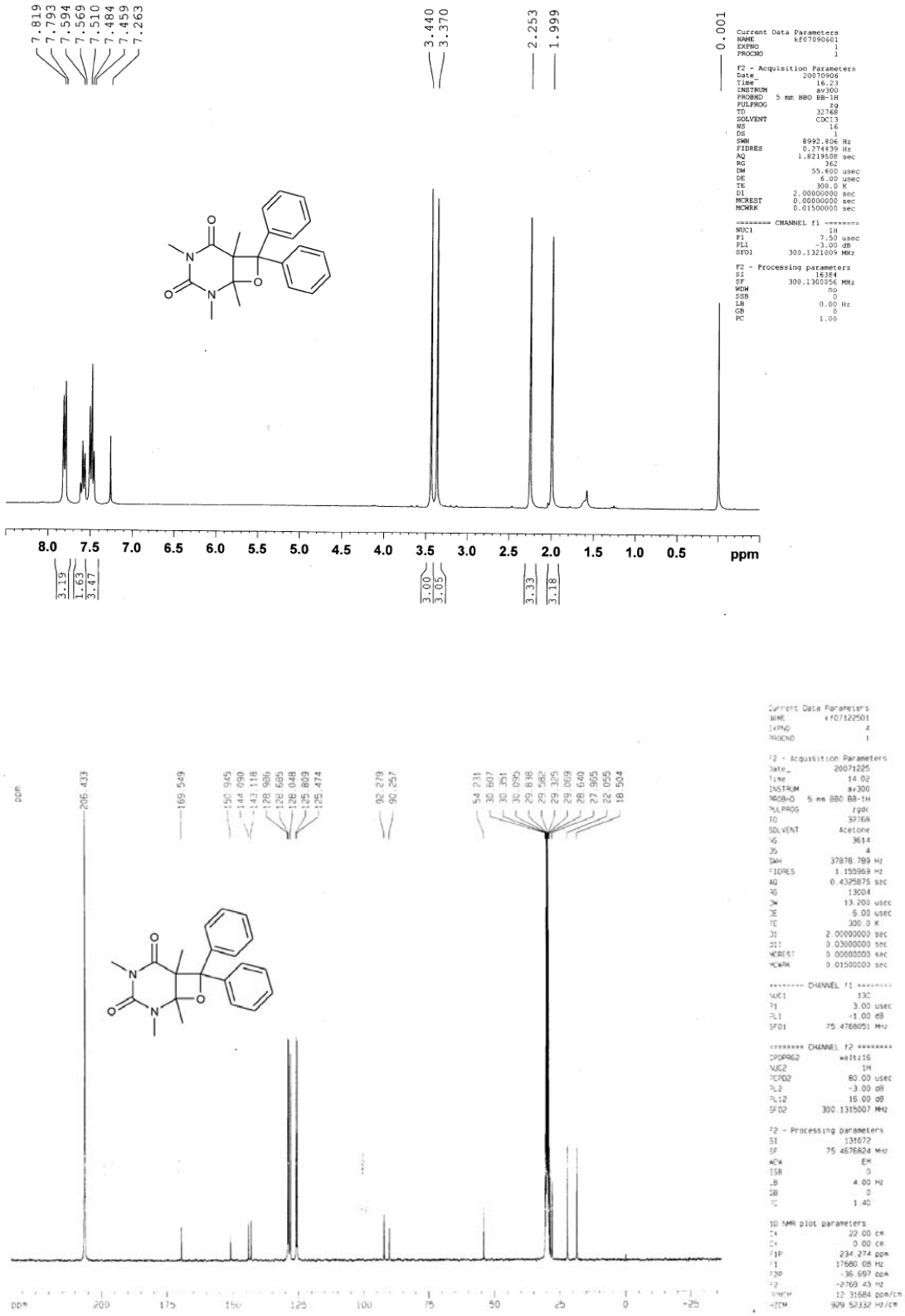

Figure S20. ^{1}H NMR and ^{13}C NMR spectra of **3De**

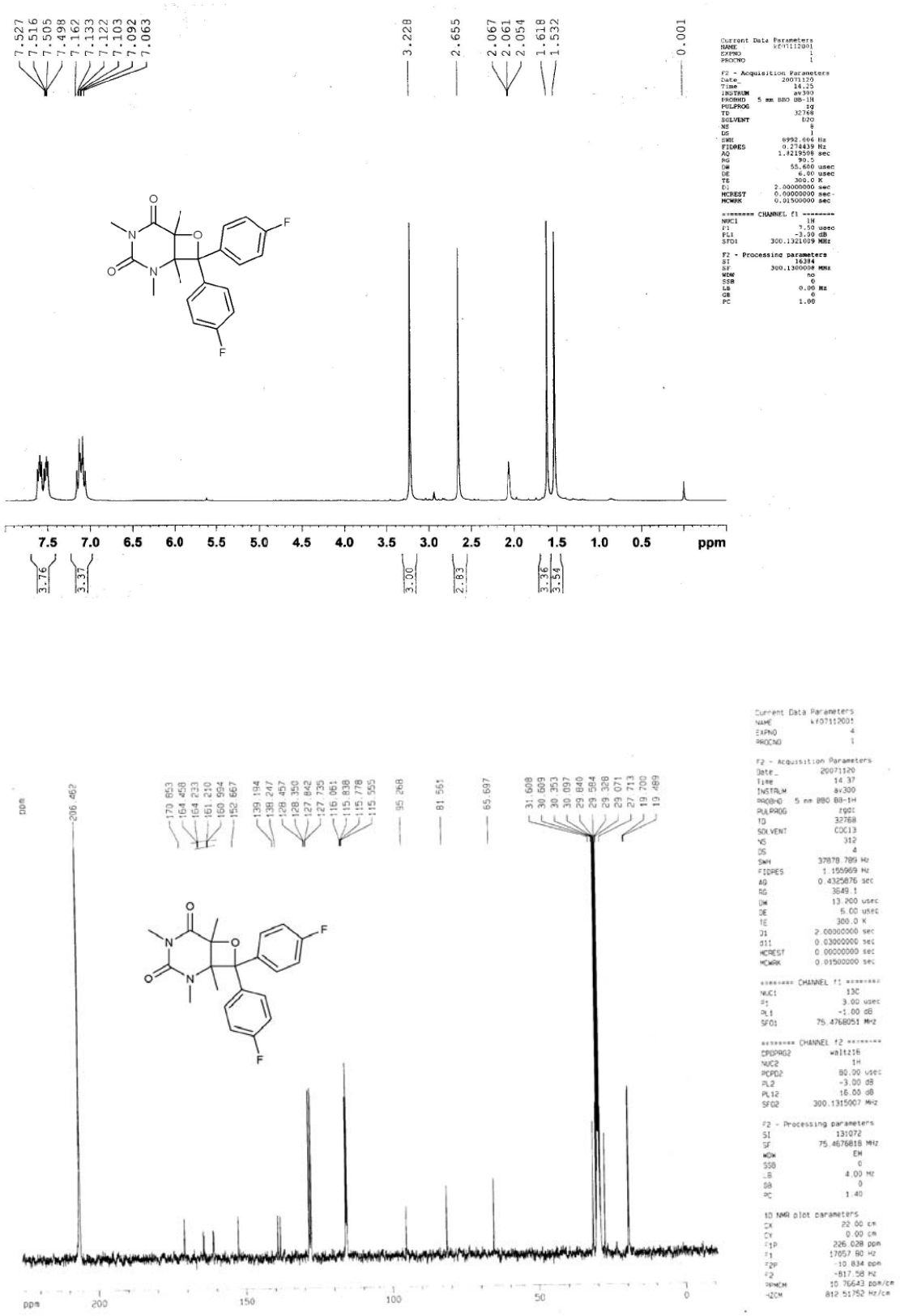

Figure S21. ^{1}H NMR and ^{13}C NMR spectra of **4De**

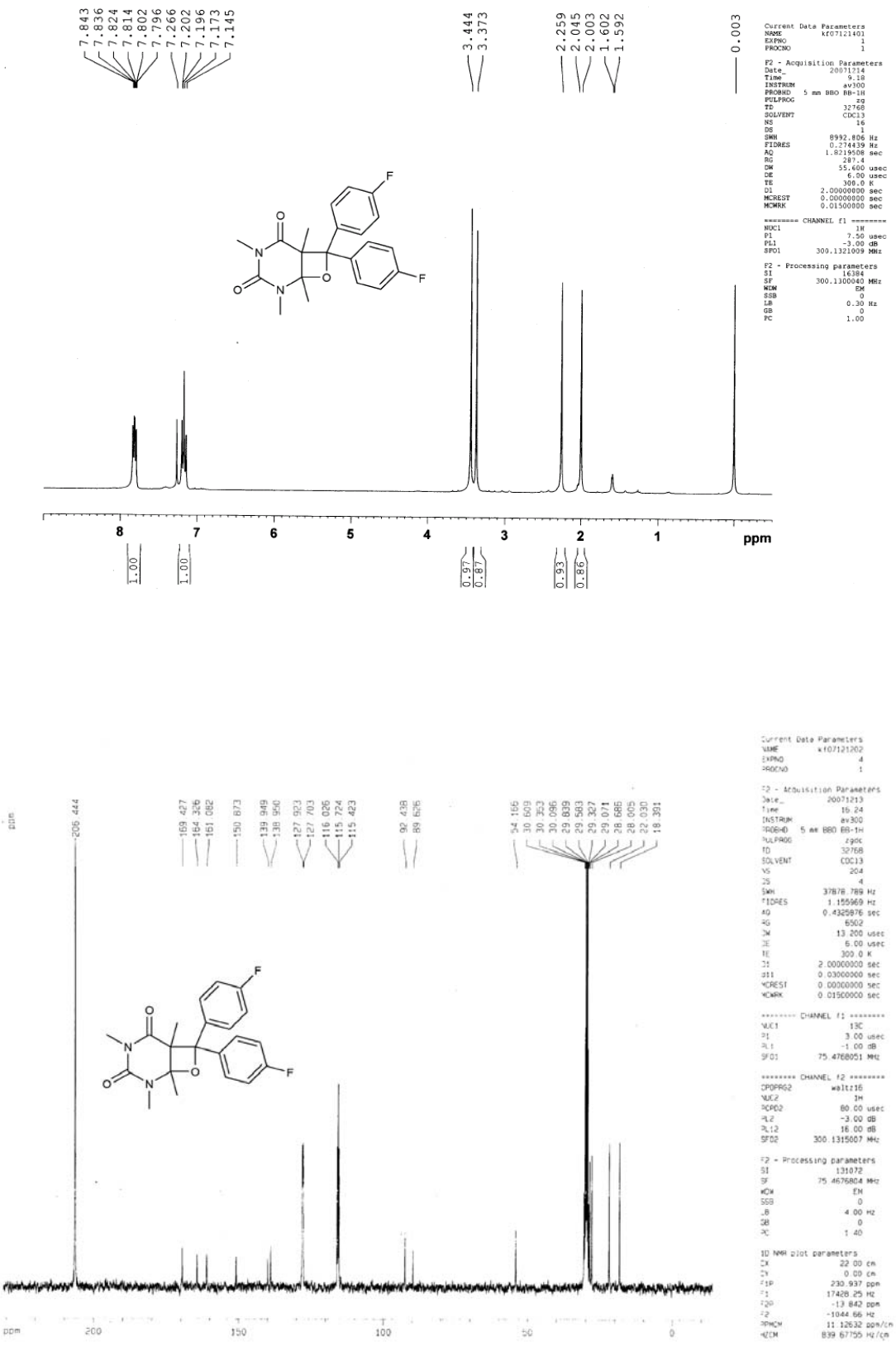

Figure S22. ^{1}H NMR and ^{13}C NMR spectra of **3Df**

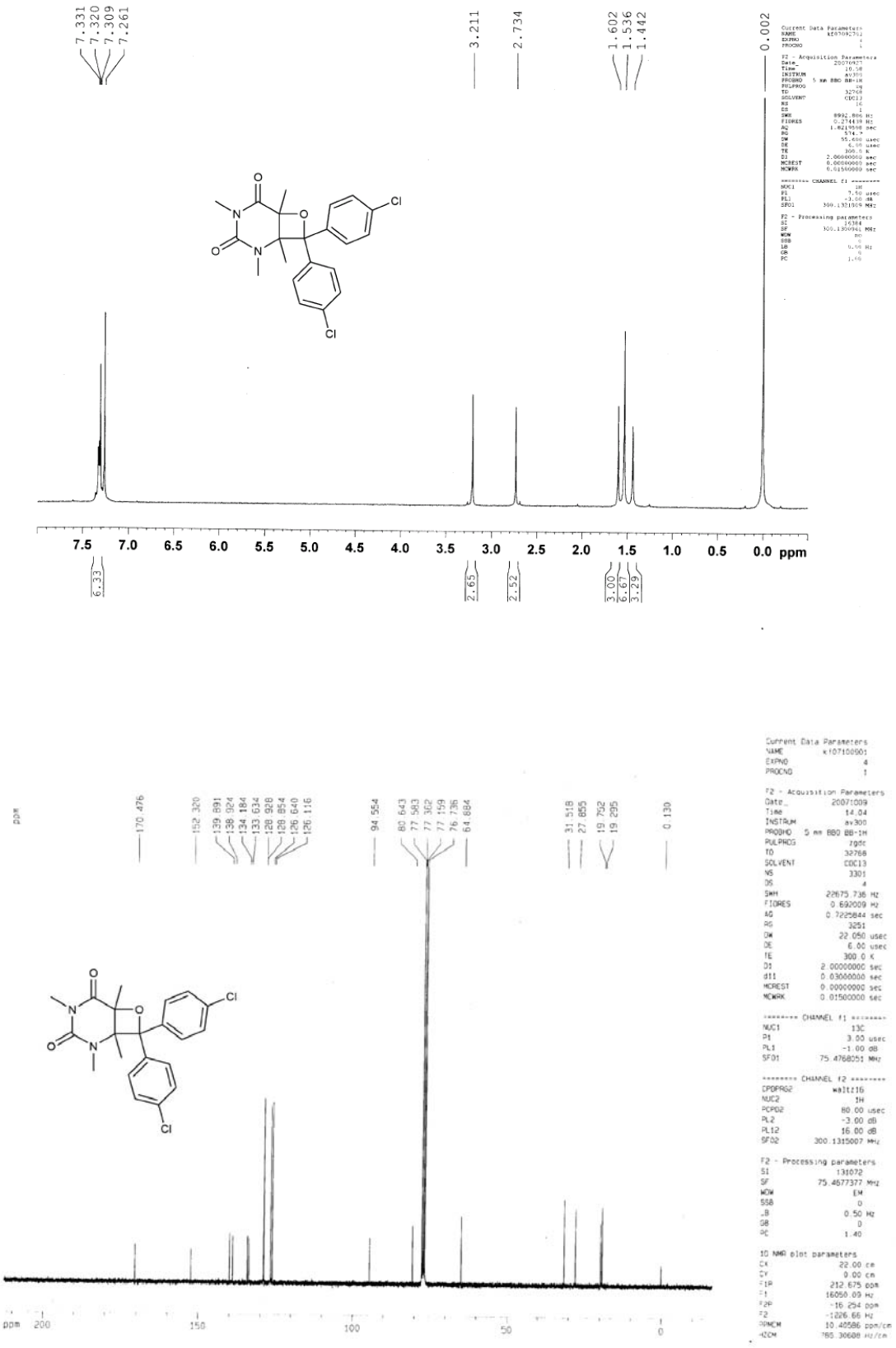

Figure S23. ^{1}H NMR and ^{13}C NMR spectra of **4Df**