Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Informatio

Rhodium Catalyzed Oxidative Coupling of Salicylaldehydes with Diazabicyclic Olefins: A one pot strategy involving aldehyde C-H cleavage and π-allyl chemistry towards fused ring chromanones

Jijy E.[a], *Praveen Prakash*[a], *Shimi M.*[a], *Petri M. Pihko*[b,*], *Nayana Joseph*[a] *and*

K. V. Radhakrishnan[a,*]

[a]*Organic Chemistry Section, National Institute for Interdisciplinary Science and Technology (CSIR), Trivandrum 695 019, India*

[b] *University of Jyväskylä, Finland*

E-mail: radhu2005@gmail.com

Table of Contents

General Methods

All chemicals were of the best grade commercially available and are used without further purification. All solvents were purified according to standard procedure; dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulfate binder. Gravity column chromatography was performed using 60-120 or 100-200 mesh silica gel and mixtures of hexane-ethyl acetate were used for elution.

Melting points were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.25, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quadret); dd (double doublet); m (multiplet). Coupling constants are reported as *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03, triplet). Mass spectra were recorded under EI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer. IR spectra were recorded on Bruker FT-IR spectrometer.

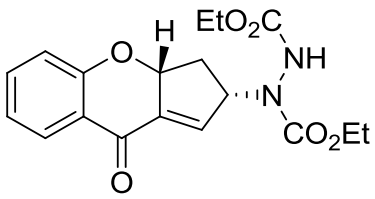
General Procedure for the Rh catalyzed oxidative coupling of salicylaldehydes with bicyclic hydrazines

A mixture of azabicyclic hydrazine (1.0 eqiuv.), salicylaldehyde (1.0 equiv.), $[RhCl_2Cp^*]_2$ (3 mol%) and $Cu(OAc)_2.H_2O$ (2.0 equiv.) were weighed in a schlenk tube and degassed for 10 minutes. Dry acetonitrile was added and the reaction mixture was purged with argon and allowed to stir at 80 ^{0}C for 16 hours. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography yielded cyclopentene fused chromanones.

Characterization of the Products

Diethyl 1-(9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3a)

Yield: 70% as yellow viscous liquid.
R_f: 0.35(5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3291, 2982, 2931, 1709, 1644, 1594, 1513, 1482, 1313, 1263, 1234, 1134, 1061, 1029, 865, 760 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 1H),

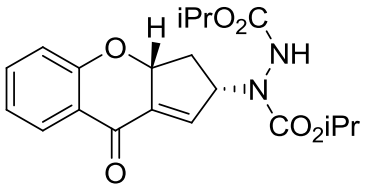


7.05 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.86 (brs, 1H), 6.56 (brs, 1H), 5.45 (brs, 1H), 5.21-5.32 (m, 1H), 4.24-4.18 (m, 4H), 3.04-3.00 (m, 1H), 2.33 (brs, 1H), 1.31-1.24 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 180.3, 160.9, 156.8, 155.5, 140.5, 138.8, 136.3, 127.7, 122.5, 118.4, 81.6, 63.0, 62.5, 62.4, 37.1, 14.5, 14.4.

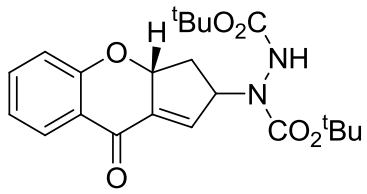
HRMS (ESI): Calcd for $C_{18}H_{20}N_2O_6$, (M+Na): 383.12191; Found: 383.12125.

diisopropyl 1-(9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3b)



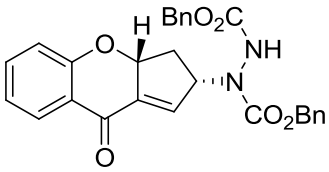
Yield: 65% as yellow viscous liquid.
R_f : 0.46 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3299, 2982, 2935, 2879, 1715, 1645, 1608, 1464, 1303, 1235, 1108, 1049, 858, 760 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.95 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 6.9 Hz, 1H), 7.04 (t, *J* = 7,5 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.84 (brs, 1H), 5.47 (brs, 1H), 6.35 (brs, 1H), 5.29 (m, 1H), 4.98-4.95 (m, 2H), 2.98 (m, 1H), 2.33-2.27 (brs, 1H), 1.28-1.26 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.1, 161.0, 156.3, 155.0, 140.5, 138.6, 136.0, 127.7, 122.6, 121.8, 118.3, 81.7, 70.8, 70.3, 61.4, 37.0, 21.9, 21.8.
HRMS (ESI): Calcd for $C_{20}H_{24}N_2O_6$, (M+Na): 411.15321; Found: 411.15286.

di-tert-butyl 1-(9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3c)



Yield: 60% as white solid.
Mp: 140-143 ^{o}C.
R_f : 0.53 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3329, 2978, 2929, 1707, 1673, 1642, 1607, 1464, 1306, 1246, 1156, 1126, 1051, 1019, 856, 758 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 1H), 7.07-6.97 (m, 2H), 6.88 (s, 1H), 6.26 (brs, 1H), 5.52-5.45 (m, 1H), 5.29 (m, 1H), 3.00-2.97 (m, 1H), 2.29-2.14 (brs, 1H), 1.52-1.43 (m, 18H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.4, 160.9, 155.6, 154.4, 139.4, 137.5, 136.7, 136.1, 127.7, 122.4, 121.8, 118.3, 82.0, 81.7, 60.2, 37.1, 28.2, 28.1, 27.8, 27.5.
HRMS (ESI): Calcd for $C_{22}H_{28}N_2O_6$, (M+Na): 439.18451; Found: 439.18413.

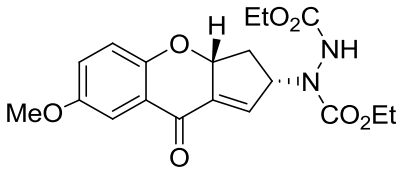
dibenzyl 1-(9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3d)



Yield: 50% as yellow viscous liquid.
R_f : 0.43 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3296, 2955, 2924, 2853, 1720, 1672, 1642, 1607, 1497, 1303, 1260, 1218, 1146, 1124, 1081, 1028, 857, 752 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.96 (d, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7 Hz, 1H), 7.32-7.27 (m, 10H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.84 (s, 1H), 5.51 (s, 1H), 5.26-5.17 (m, 5H), 3.01 (s, 1H), 2.31 (s, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.9, 156.4, 155.1, 140.6, 138.3, 136.0, 135.3, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 122.4, 121.7, 118.3, 112.9, 81.4, 68.4, 68.1, 62.1, 36.7.
HRMS (ESI): Calcd for $C_{28}H_{24}N_2O_6$,

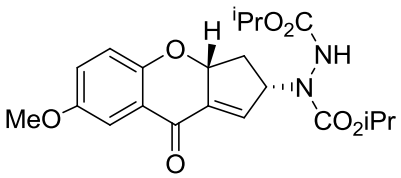
(M+Na): 507.15321; Found: 507.15317.

diethyl 1-(7-methoxy-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3e)



Yield: 67% as yellow viscous liquid.
R_f: 0.33 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3314, 2981, 2922, 2851, 1716, 1485, 1381, 1287, 1230, 1164, 1132, 1059, 1032, 870, 761 cm^{-1}.
^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.37 (s, 1H), 7.10 (dd, J_1 = 3.3 Hz, J_2 = 9 Hz, 1H), 6.92 (d, J = 9.0 Hz, 1H), 6.86 (s, 1H), 6.59 (brs, 1H), 5.49 (brs, 1H), 5.26-5.24 (m, 1H), 4.24-4.21 (m, 4H), 3.84 (s, 3H), 2.98 (m, 1H), 2.30 (brs, 1H), 1.31-1.28 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 179.9, 156.6, 155.6, 155.3, 154.4, 140.3, 138.5, 125.5, 122.3, 119.6, 107.7, 81.5, 62.9, 62.3, 60.8, 55.7, 36.9, 14.5, 14.4.
HRMS (ESI): Calcd for $C_{19}H_{22}N_2O_7$, (M+Na): 413.13247; Found: 413.13229.

diisopropyl 1-(7-methoxy-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3f)



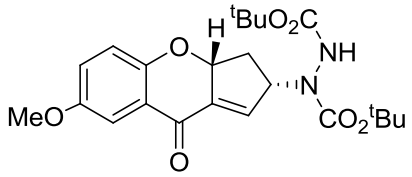
Yield: 51% as yellow solid.
Mp: 101-103 °C.
R_f: 0.41 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3404, 2979, 2926, 2854, 1709, 1665, 1484, 1381, 1286, 1233, 1205, 1107, 1031, 865, 771.

^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.35-7.34 (m, 1H), 7.07 (dd, J_1 = 3 Hz, J_2 = 9 Hz, 1H), 6.90-6.87 (m, 1H), 6.83 (s, 1H), 6.35 (brs, 1H), 5.46 (s, 1H), 5.24 (m, 1H), 4.97-4.95 (m, 2H), 3.81 (s, 3H), 2.95 (s, 1H), 2.31 (brs, 1H), 1.28-1.23 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.8, 155.5, 154.8, 154.3, 140.6, 138.6, 125.4, 122.4, 119.5, 107.7, 99.9, 81.5, 70.0, 62.1, 55.6, 37.3, 22.6, 22.0, 21.8.

HRMS (ESI): Calcd for $C_{21}H_{26}N_2O_7$, (M+Na): 441.16377; Found: 441.16327.

di-tert-butyl 1-(7-methoxy-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3g)



Yield: 54% as yellow solid.

Mp: 80-85 ^{o}C.

R_f : 0.48 (5:5 hexane/EtOAc).

IR (neat) ν_{max}: 3318, 2978, 2932, 1707, 1673, 1641, 1618, 1485, 1393, 1337, 1287, 1251, 1159, 1082, 1035, 882, 778.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.35 (m, 1H), 7.09-7.06 (m, 1H), 6.90-6.88 (m, 2H), 6.20 (s, 1H), 5.42 (s, 1H), 5.23 (m, 1H), 3.81 (s, 3H), 2.93 (brs, 1H), 2.30 (brs, 1H), 1.47-1.43 (m, 18H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 180.1, 155.7, 154.4, 140.1, 139.0, 124.7, 124.6, 122.6, 119.6, 108.6, 81.8, 61.1, 55.8, 37.0, 28.2, 28.1.

HRMS (ESI): Calcd for $C_{23}H_{30}N_2O_7$, (M+Na): 469.19507; Found: 469.19505.

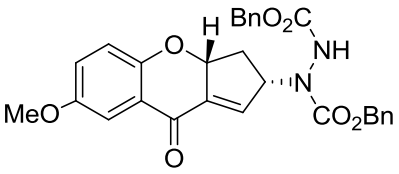
dibenzyl 1-(7-methoxy-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3h)

Yield: 56% as yellow viscous liquid.

R_f : 0.41 (5:5 hexane/EtOAc).

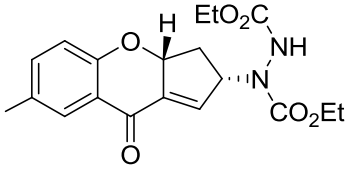
IR (neat) ν_{max}: 3336, 3034, 2924, 2853, 1715, 1666, 1590, 1485, 1356, 1287, 1227, 1124, 1039, 856, 754.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.36-7.33 (m, 11H), 7.10 (dd, J_1 = 3 Hz, J_2 = 9 Hz, 1H), 6.89 (d, J = 9 Hz, 1H), 6.80 (s, 1H), 6.55 (s, 1H), 5.52 (s, 1H), 5.18 (m, 5H), 3.83



(s, 3H), 2.99 (s, 1H), 2.26 (s, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.0, 155.6, 155.3, 154.6, 140.8, 137.9, 135.5, 135.4, 130.9, 128.5, 128.4, 128.3, 128.0, 128.0, 125.3, 122.5, 119.6, 108.2, 81.6, 68.6, 68.1, 61.7, 55.8, 36.8.
HRMS (ESI): Calcd for $C_{29}H_{26}N_2O_7$, (M+Na): 537.16377; Found: 537.16345.

diethyl 1-(7-methyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3i)

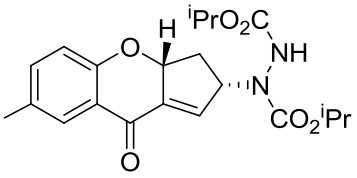


Yield: 58% as yellow viscous liquid.
R_f : 0.33 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3303, 2924, 2854, 1716, 1672, 1620, 1485, 1381, 1288, 1230, 1168, 1132, 1098, 1032, 828, 761.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.74 (s, 1H), 7.31-7.27 (m,1H), 6.88-6.85 (m, 2H), 6.47 (s, 1H), 5.48 (s, 1H), 5.26 (m, 1H), 4.25-4.20 (m, 4H), 2.98 (s, 1H), 2.37-2.34 (m, 4H), 1.32-1.26 (m, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.2, 159.0, 155.4, 140.8, 137.1, 131.3, 127.2, 122.2, 118.1, 81.6, 62.9, 62.3, 62.2, 61.5, 37.0, 20.2, 14.3, 14.2.
HRMS (ESI): Calcd for $C_{19}H_{22}N_2O_6$, (M+Na): 397.13756; Found: 397.13736.

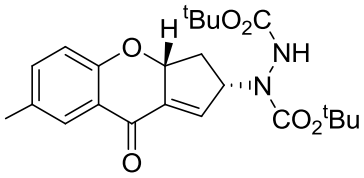
diisopropyl 1-(7-methyl-9-oxo 2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3j)

Yield: 50% as yellow viscous liquid.
R_f : 0.43 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3302, 2981, 2931, 2875, 1716, 1643, 1617, 1486, 1382, 1294, 1234, 1138, 1109, 1046, 826, 764.



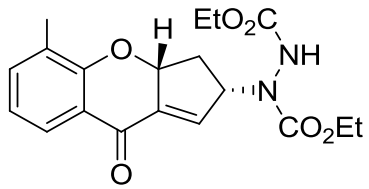
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.75 (s, 1H), 7.31-7.27 (m, 1H), 6.89-6.87 (m, 2H), 6.38-6.32 (s, 1H), 5.48 (s, 1H), 5.30-5.26 (m, 1H), 4.98-4.97 (m, 2H), 2.98 (s, 1H), 2.35-2.32 (m, 4H), 1.27-1.23 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.9, 159.0, 156.1, 154.9, 140.6, 138.2, 136.9, 131.1, 127.3, 122.3, 118.1, 81.6, 70.6, 70.1, 61.4, 37.0, 22.6, 22.0, 21.9, 21.8, 20.3.
LRMS (FAB): Calcd for $C_{21}H_{26}N_2O_6$, (M+Na): 425.16886; Found: 425.16834.

di-tert-butyl 1-(7-methyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3k)



Yield: 52% as yellow viscous liquid.
R_f : 0.51 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3325, 2978, 2927, 2856, 1709, 1644, 1619, 1485, 1394, 1295, 1249, 1158, 1083, 1052, 852, 761.
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.75 (s, 1H), 7.29 (m, 1H), 6.87 (d, J = 8.5 Hz, 2H), 6.23 (s, 1H), 5.44 (s, 1H), 5.25 (m, 1H), 2.96 (s, 1H), 2.31 (m, 4H), 1.48-1.42 (m, 18H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.4, 159.1, 155.6, 154.4, 140.3, 138.8, 137.0, 131.2, 127.2, 122.2, 118.2, 81.7, 61.2, 37.1, 28.2, 28.1, 20.2.
HRMS (ESI): Calcd for $C_{23}H_{30}N_2O_6$, (M+Na): 453.20016; Found: 453.20033.

diethyl 1-(5-methyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3l)

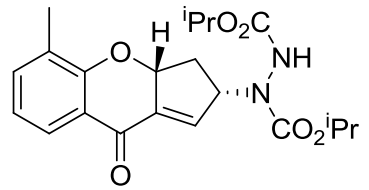


Yield: 40% as yellow viscous liquid.
R_f : 0.48 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3297, 2982, 2926, 2856, 1717, 1673, 1642, 1617, 1573, 1485, 1383, 1293, 1229, 1134, 1095, 1060, 879, 762.
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7 Hz, 1H), 6.94 (t, *J* = 8 Hz, 1H), 6.84 (s, 1H), 6.53 (s, 1H), 5.51 (s, 1H), 5.28 (t, *J* = 7 Hz, 1H), 4.23-4.18 (m, 4H), 3.04 (t, *J* = 6 Hz, 1H), 2.36 (s, 1H), 2.24 (s, 3H), 1.29-1.24 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 180.5, 159.1, 156.7, 155.4, 140.7, 137.8, 137.0, 127.6, 125.3, 122.2, 121.2, 81.5, 62.9, 62.3, 61.5, 37.1, 15.7, 14.3, 14.2.

HRMS (ESI): Calcd for $C_{19}H_{22}N_2O_6$, (M+Na): 397.13756; Found: 397.13746.

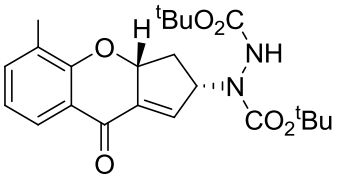
diisopropyl 1-(5-methyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3m)



Yield: 51% as yellow viscous liquid.
R_f : 0.58 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3319, 2981, 2927, 2856, 1714, 1668, 1643, 1598, 1470, 1299, 1237, 1109, 1039, 829, 759.
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.85-6.84 (m, 1H), 6.35 (s, 1H), 5.50 (s, 1H), 5.28 (t, *J* = 7 Hz, 1H), 5.00-4.93 (m, 2H), 3.04 (t, *J* = 6.5 Hz, 1H), 2.24 (m, 4H), 1.27-1.23 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.2, 159.0, 156.4, 154.8, 140.2, 138.2, 136.9, 127.4, 125.4, 122.1, 121.1, 81.3, 70.0, 69.9, 60.7, 37.1, 22.0, 15.9.

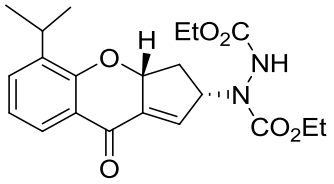
HRMS (ESI): Calcd for $C_{21}H_{26}N_2O_6$, (M+Na): 425.16886; Found: 425.16841.

di-tert-butyl 1-(5-methyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3n)



Yield: 51% as yellow solid.
Mp: 103-107 ^{o}C.
R_f : 0.68 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3315, 2978, 2929, 1710, 1670, 1599, 1477, 1368, 1344, 1301, 1251, 1157, 1053, 1019, 852, 757.
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.82 (d, *J* = 8 Hz, 1H), 7.35 (d, *J* = 7 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 6.23 (s, 1H), 5.45 (s, 1H), 5.27 (t, *J* = 6.5 Hz, 1H), 3.02 (s, 1H), 2.25-2.24 (m, 4H), 1.52-1.43 (m, 18H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.6, 159.2, 155.6, 154.4, 140.2, 138.5, 136.8, 127.5, 125.3, 122.3, 121.1, 82.0, 81.6, 61.0, 37.2, 28.2, 28.1, 15.6.
HRMS (ESI): Calcd for $C_{23}H_{30}N_2O_6$, (M+Na): 453.20016; Found: 453.20013.
.

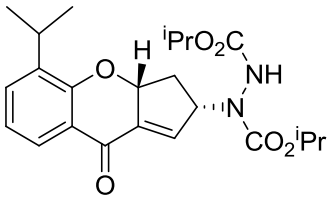
diethyl 1-(5-isopropyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3o)



Yield: 40% as yellow viscous liquid.
R_f : 0.41 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3299, 2967, 2928, 2870, 1717, 1670, 1646, 1595, 1472, 1383, 1292, 1230, 1123, 1060, 858, 760.
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.84-7.82 (m, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.85-6.83 (m, 1H), 6.51 (s, 1H), 5.50 (s, 1H), 5.26 (t, *J* = 7 Hz, 1H), 4.23-4.17 (m, 4H), 3.35-3.30 (m, 1H), 3.04 (t, *J* = 6.5 Hz, 1H), 2.38-2.30 (m, 1H), 1.29-1.20 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.4, 158.2, 156.6, 155.4, 140.8, 138.1, 138.0, 132.6, 122.6, 121.5, 120.8, 81.5, 62.8, 62.2, 61.6, 37.0, 26.9, 22.5, 22.3, 14.4, 14.2.

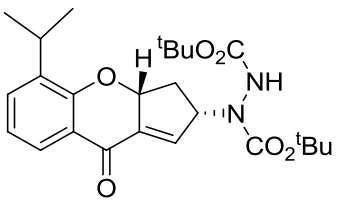
HRMS (ESI): Calcd for $C_{21}H_{26}N_2O_6$, (M+Na): 425.16886; Found: 425.16791.

diisopropyl 1-(5-isopropyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3p)



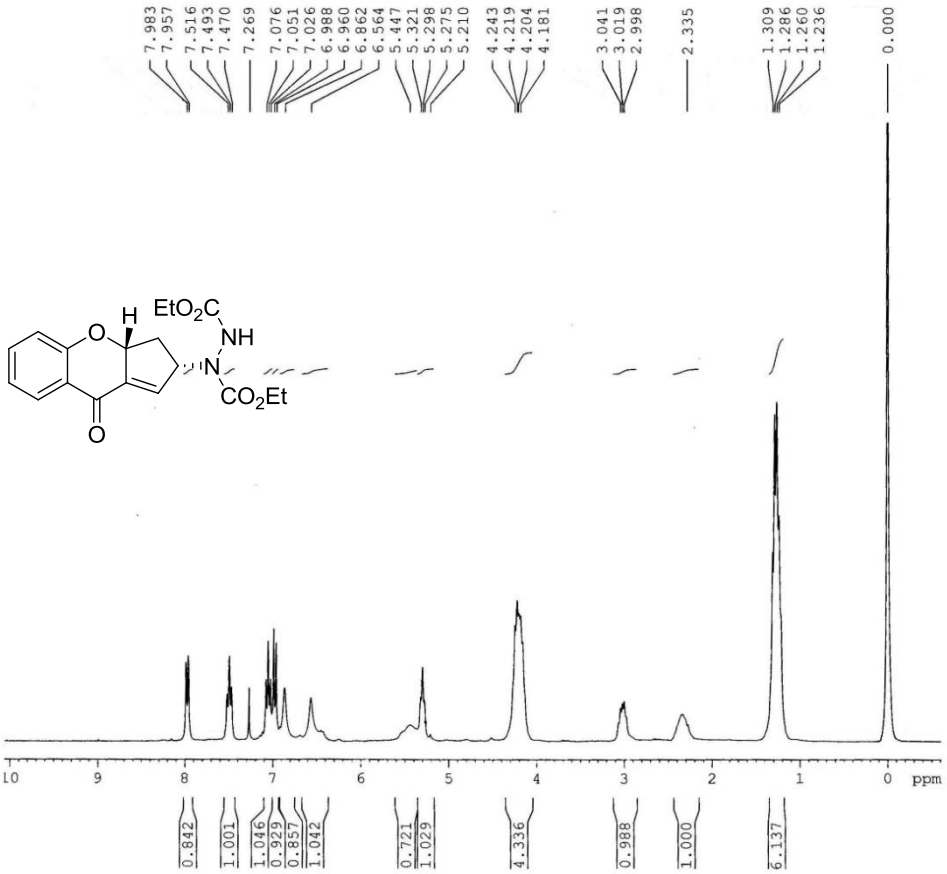
Yield: 50% as yellow viscous liquid.
R_f: 0.53 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3300, 2979, 2933, 2872, 1716, 1673, 1646, 1596, 1472, 1383, 1303, 1235, 1146, 1108, 1051, 855, 760.
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.83 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.85-6.83 (m, 1H), 6.34 (s, 1H), 5.49 (s, 1H), 5.26 (t, *J* = 7 Hz, 1H), 4.99-4.93 (m, 2H), 3.35-3.30 (m, 1H), 3.04-3.02 (m, 1H), 2.38-2.30 (m, 1H), 1.28-1.20 (m, 18H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.5, 158.2, 156.3, 155.0, 140.7, 138.0, 132.6, 125.2, 122.6, 121.5, 81.6, 70.7, 70.2, 61.7, 37.0, 26.9, 22.5, 22.3, 21.9, 21.8.
HRMS (ESI): Calcd for $C_{23}H_{30}N_2O_6$, (M+Na): 453.20016; Found: 453.19932.

di-tert-butyl 1-(5-isopropyl-9-oxo-2,3,3a,9-tetrahydrocyclopenta[b]chromen-2-yl)hydrazine-1,2-dicarboxylate (3q)

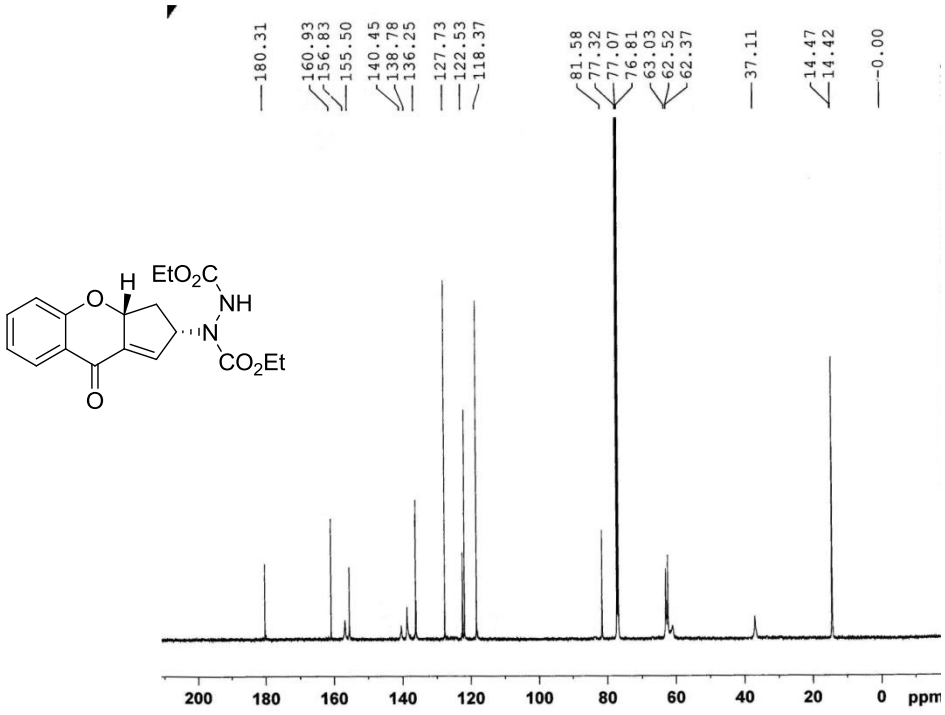


Yield: 52% as yellow viscous liquid.
R_f: 0.61 (5:5 hexane/EtOAc).
IR (neat) ν_{max}: 3327, 2972, 2928, 2871, 1707, 1670, 1594, 1473, 1369, 1253, 1157, 1048, 857, 757.
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.83 (d, *J* = 7 Hz, 1H), 7.43 (d, *J* = 6Hz, 1H), 7.02-6.99 (m, 1H), 6.86 (s, 1H), 6.24 (s, 1H), 5.46 (s, 1H), 5.26-5.24 (m, 1H), 3.36-3.30

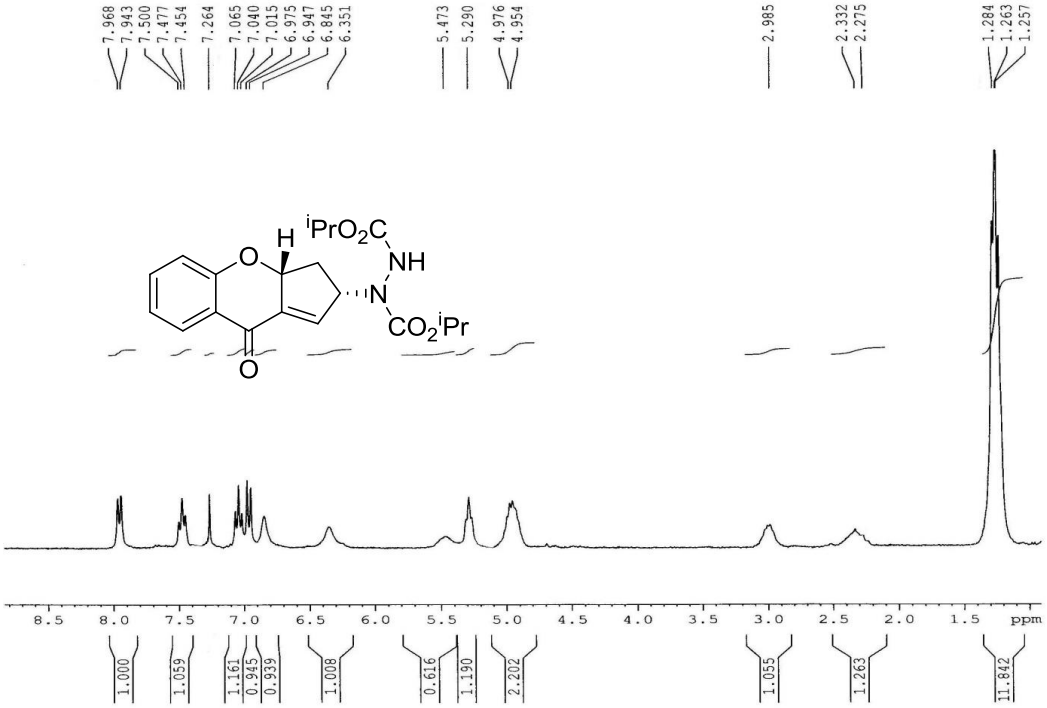
(m, 1H), 3.02-3.01 (m, 1H), 2.41-2.37 (m, 1H), 1.48-1.42 (m, 18H), 1.26-1.20 (m,6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.5. 158.3, 155.6, 154.3, 140.3, 138.4, 137.9, 132.5, 125.2, 122.6, 121.4, 81.9, 81.6, 61.2, 37.1, 28.2, 28.1, 27.1, 27.0, 22.5, 22.4.
HRMS (ESI): Calcd for $C_{25}H_{34}N_2O_6$, (M+Na): 489.23146; Found: 489.23146.



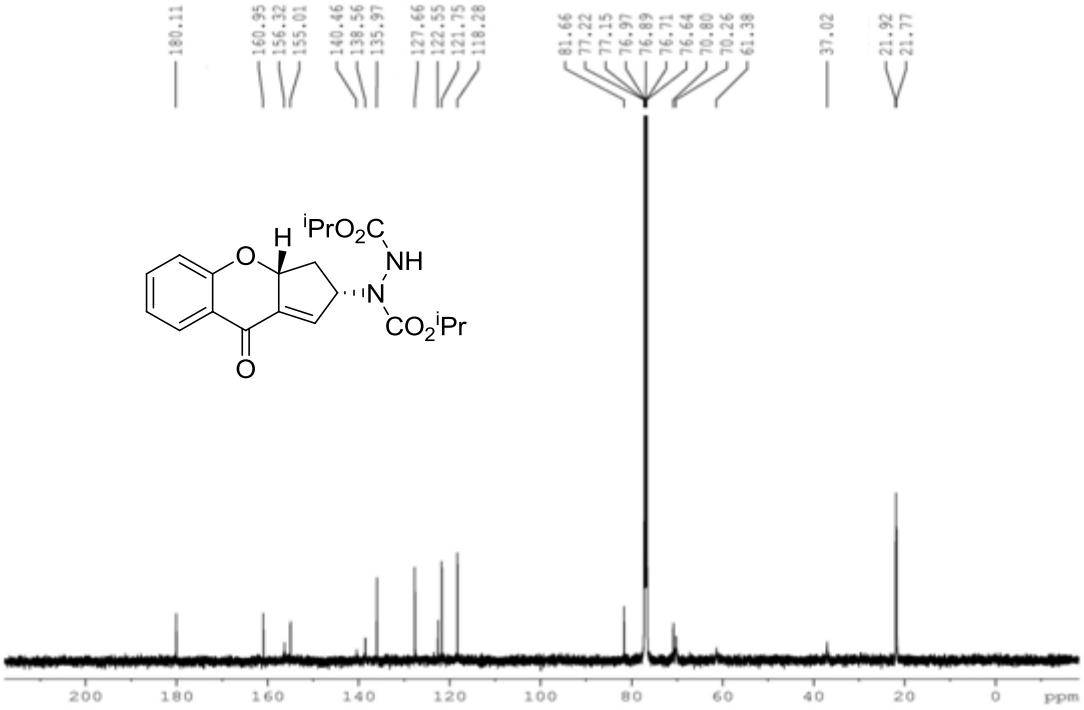
^{1}H NMR of 3a



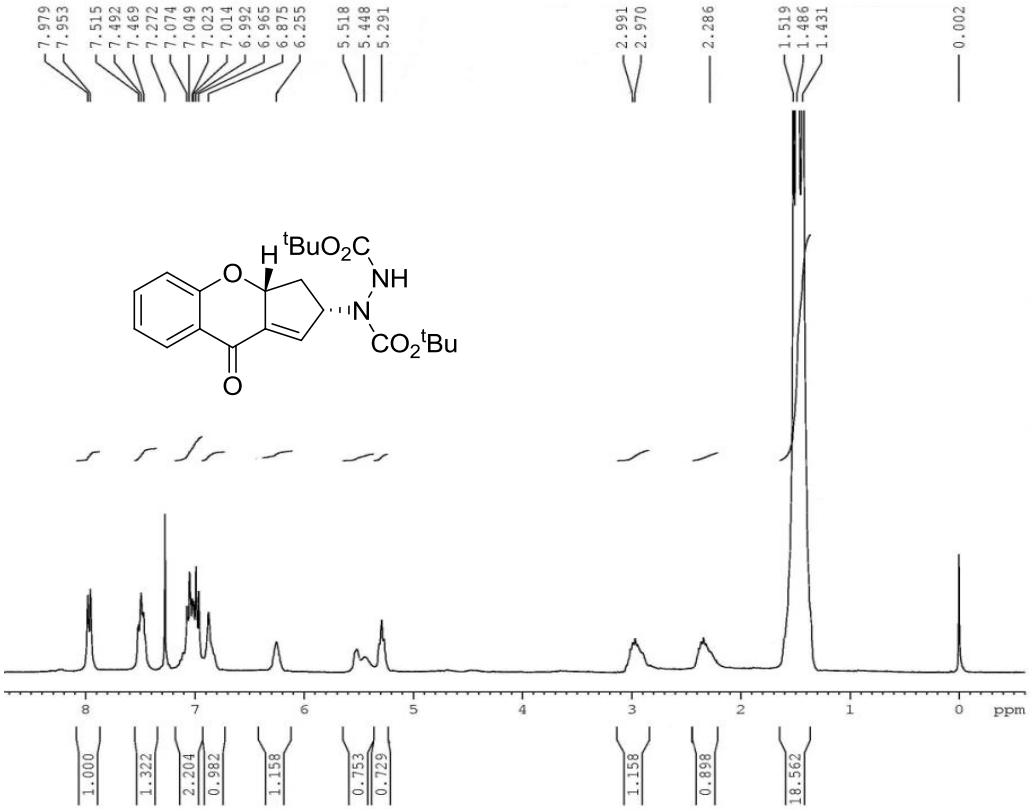
^{13}C NMR of 3a



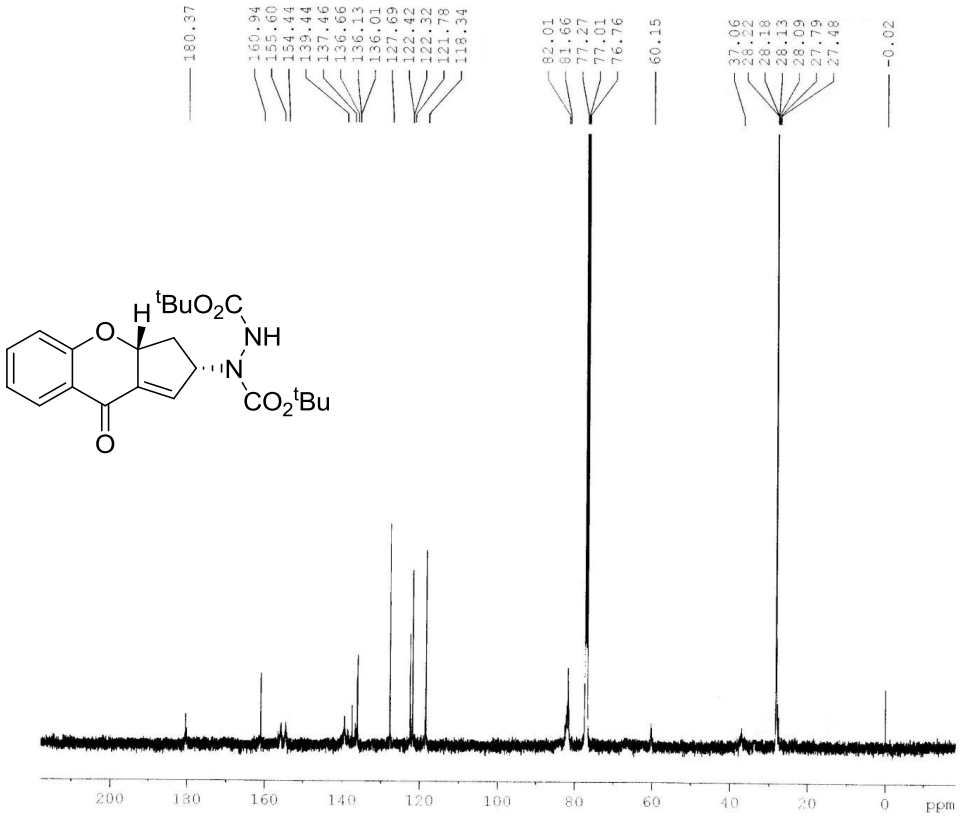
^{1}H NMR of 3b



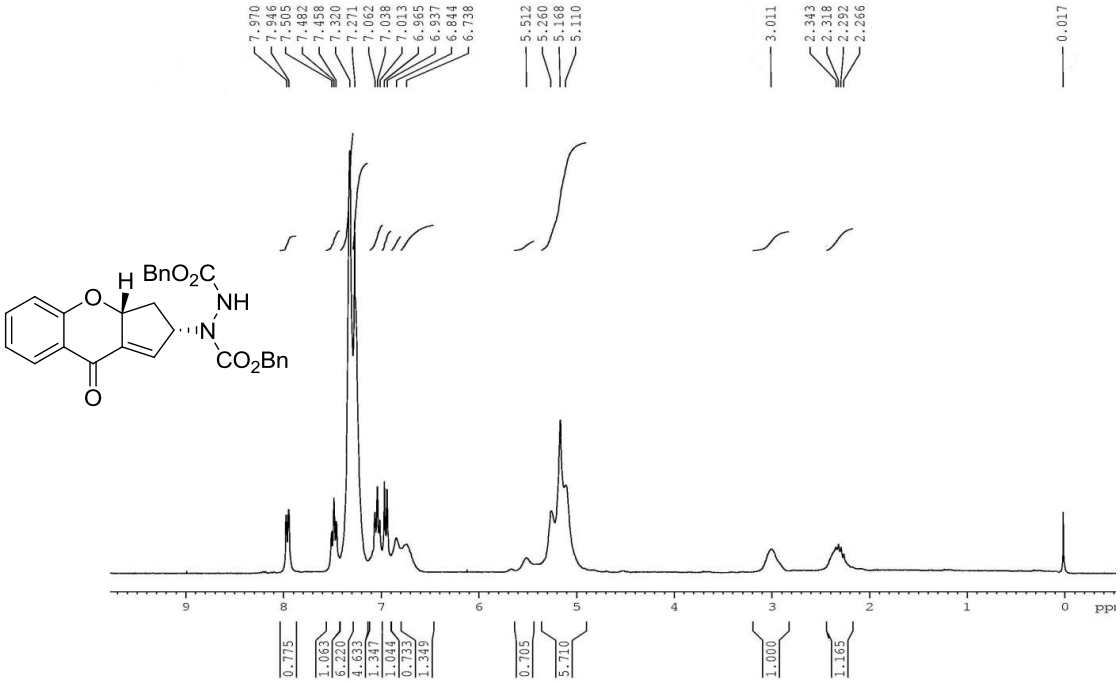
^{13}C NMR of 3b



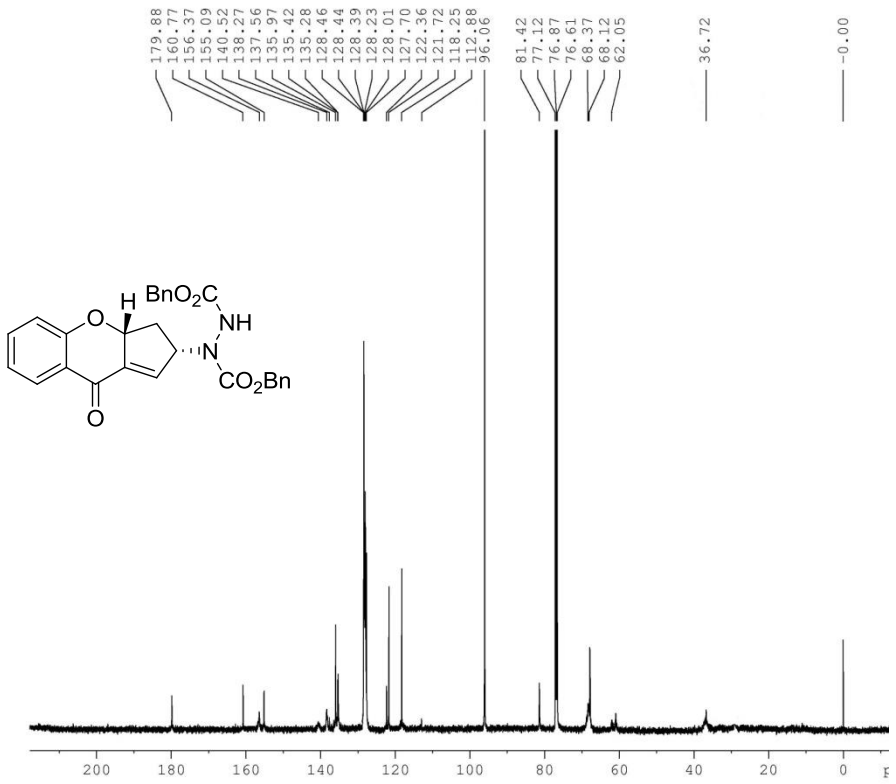
^{1}H NMR of 3c



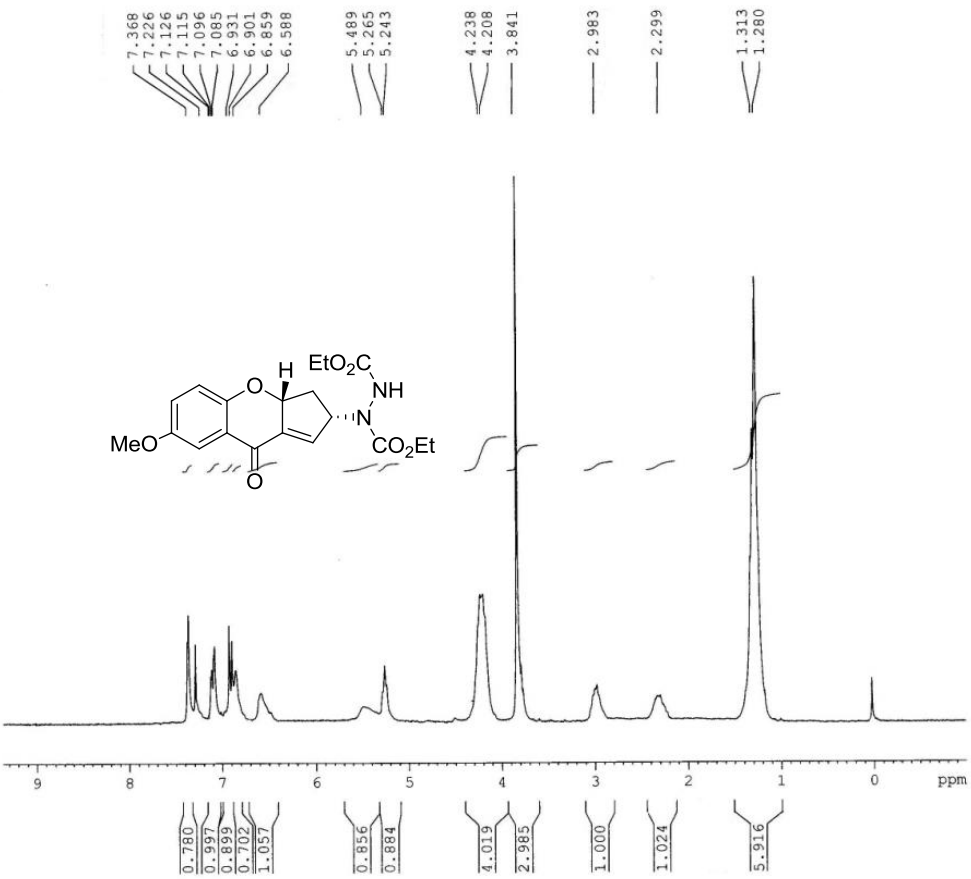
^{13}C NMR of 3c



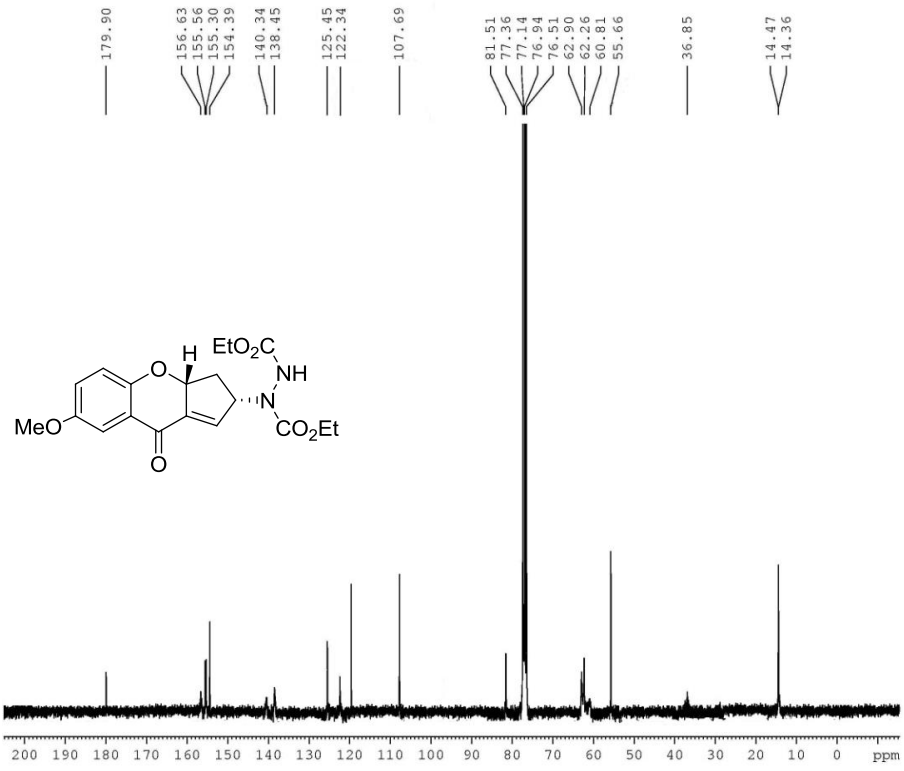
^{1}H NMR of 3d



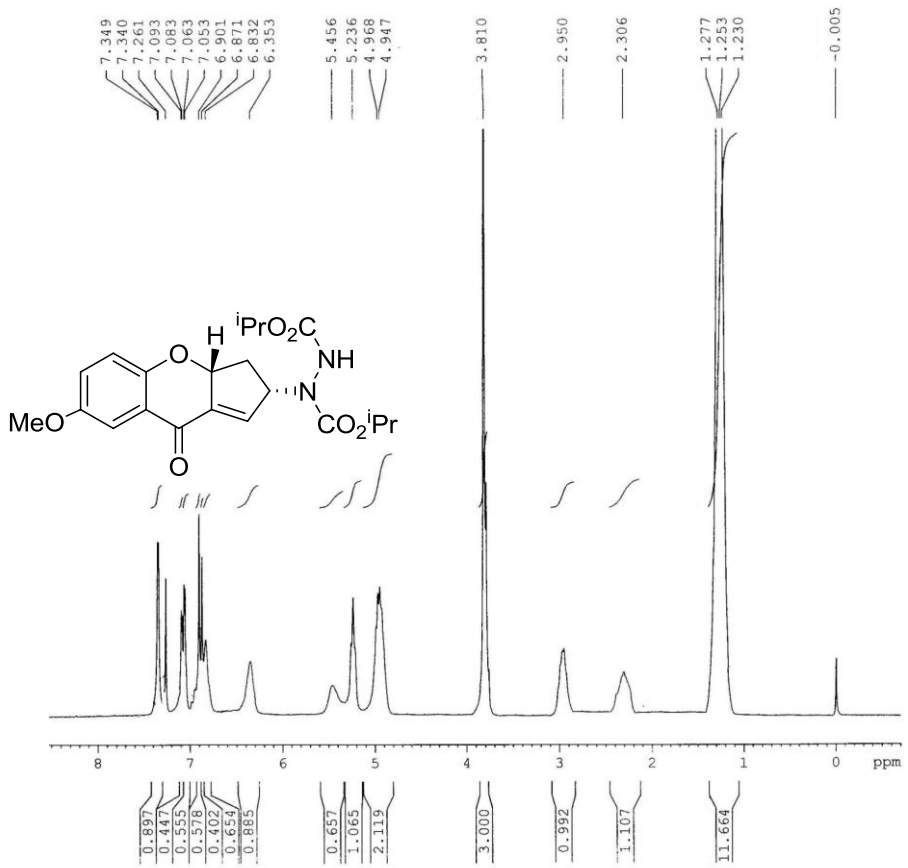
^{13}C NMR of 3d



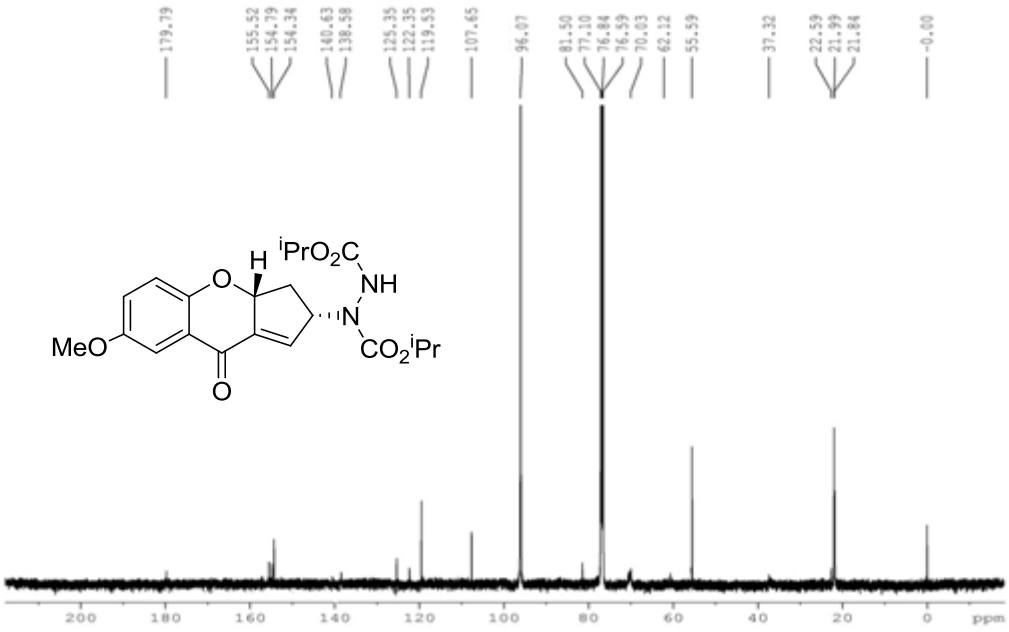
^{1}H NMR of 3e



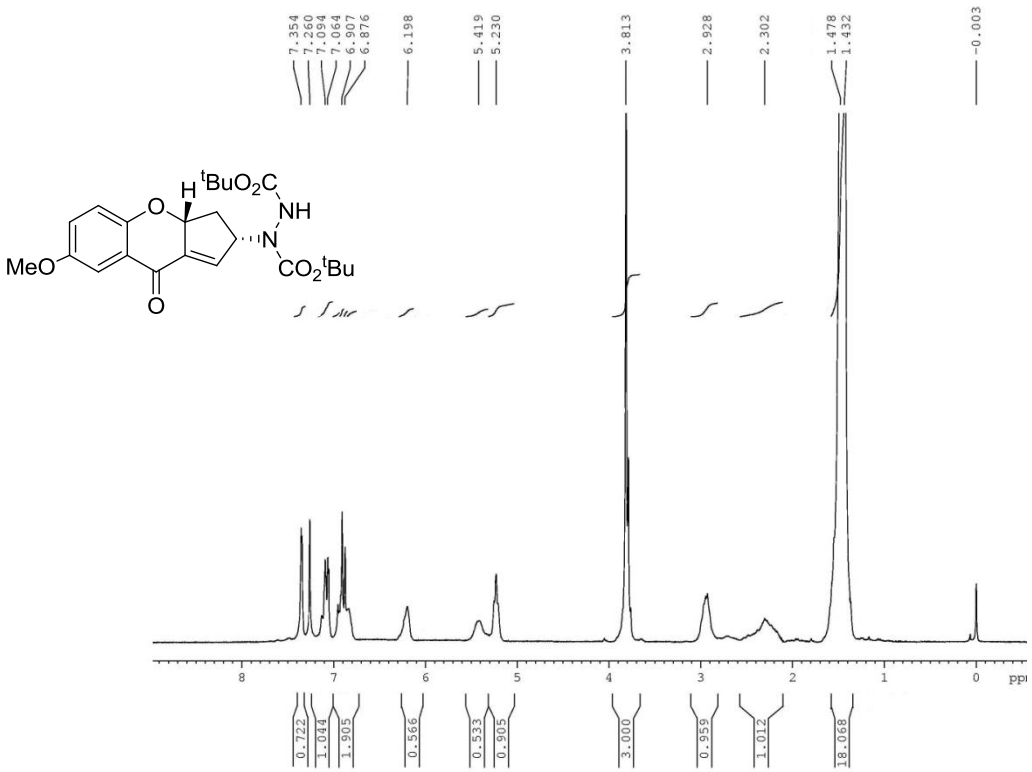
^{13}C NMR of 3e



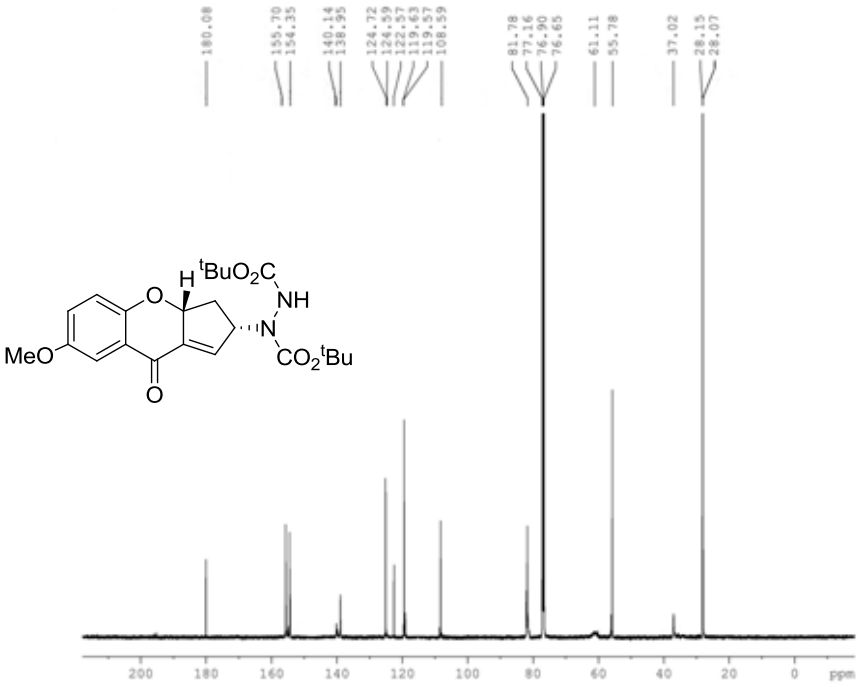
^{1}H NMR of 3f



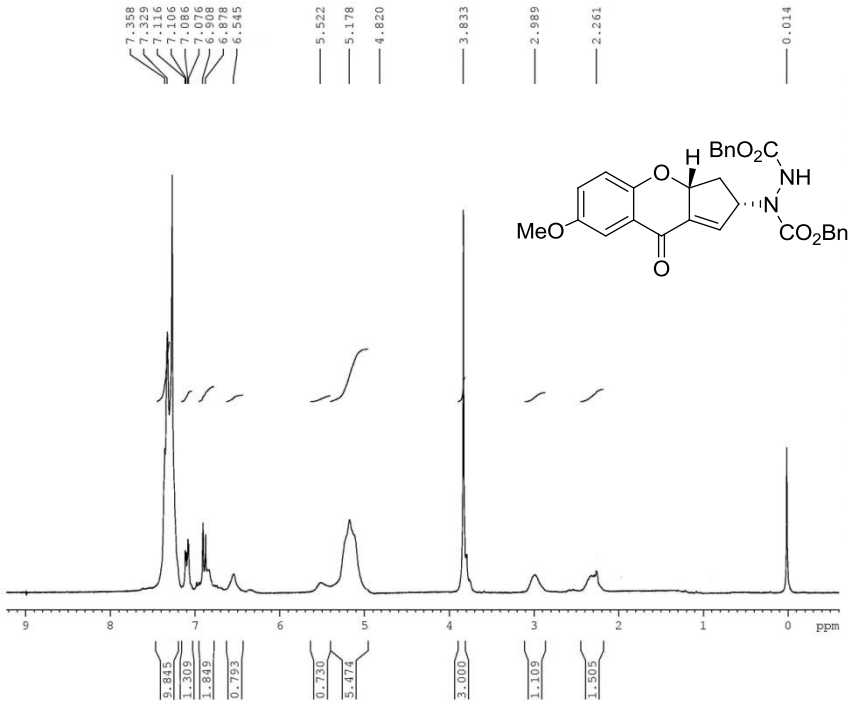
^{13}C NMR of 3f



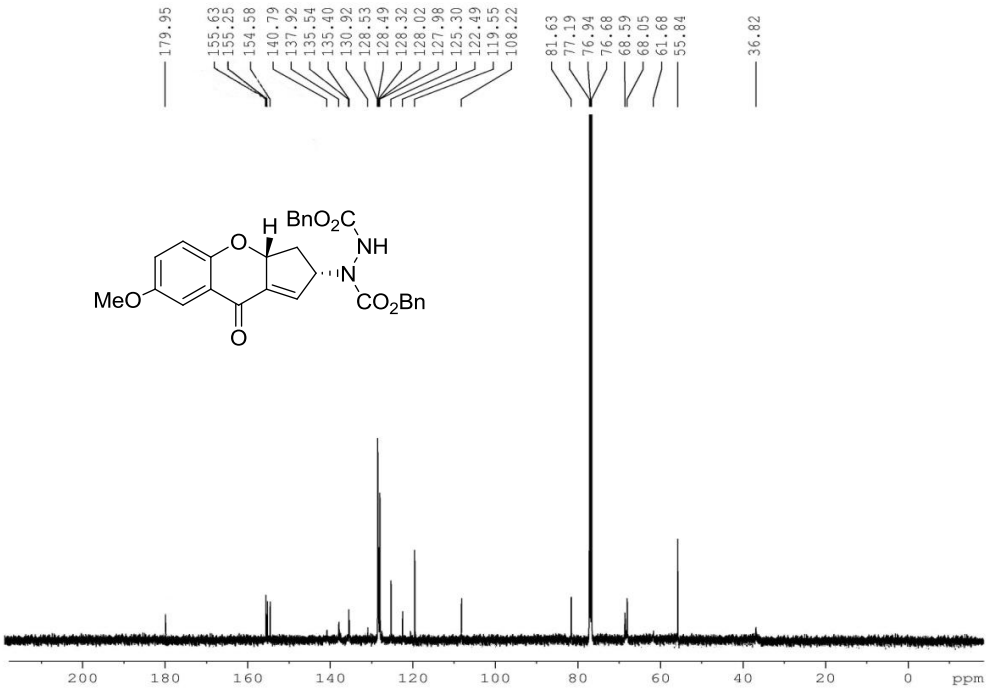
^{1}H NMR of 3g



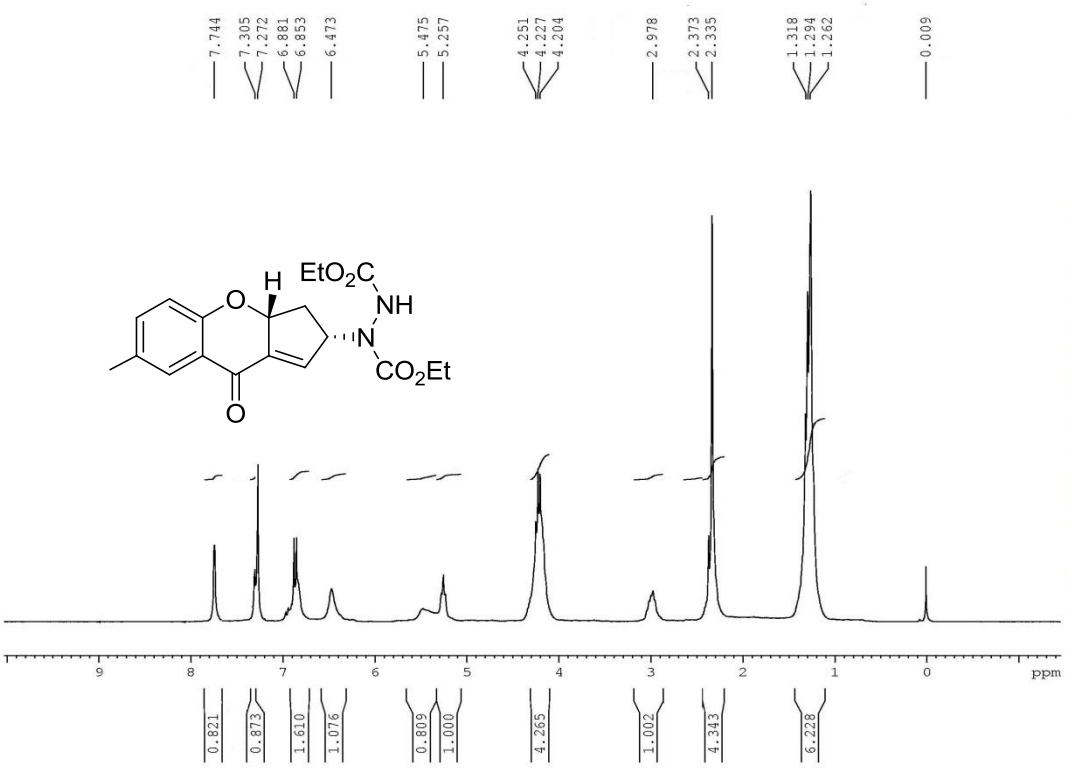
^{13}C NMR of 3g



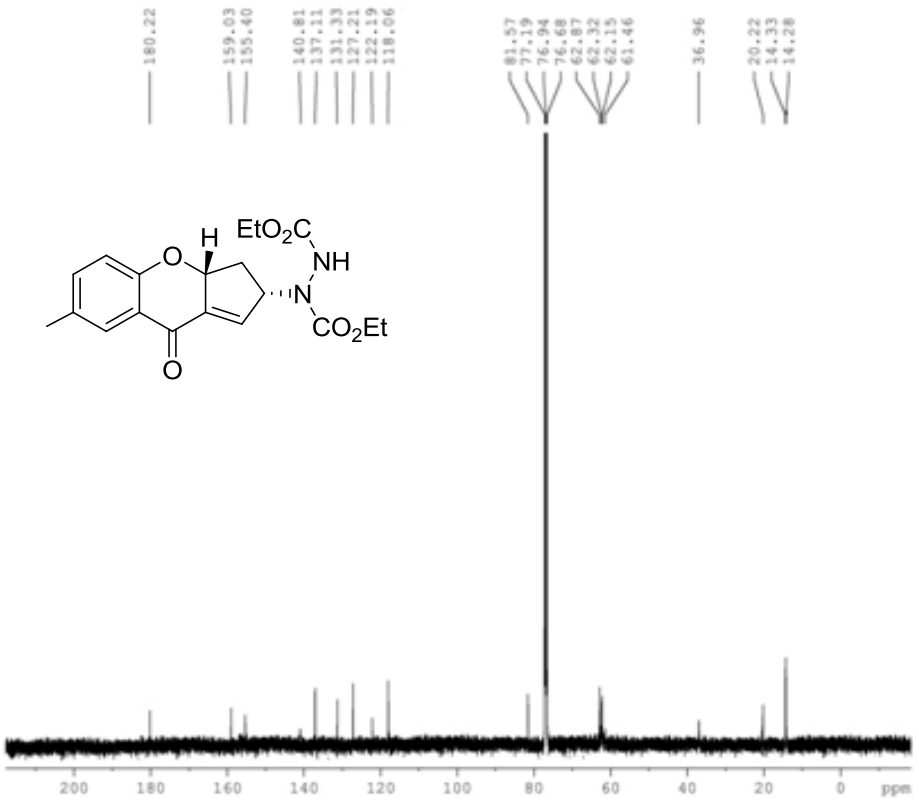
^{1}H NMR of 3h



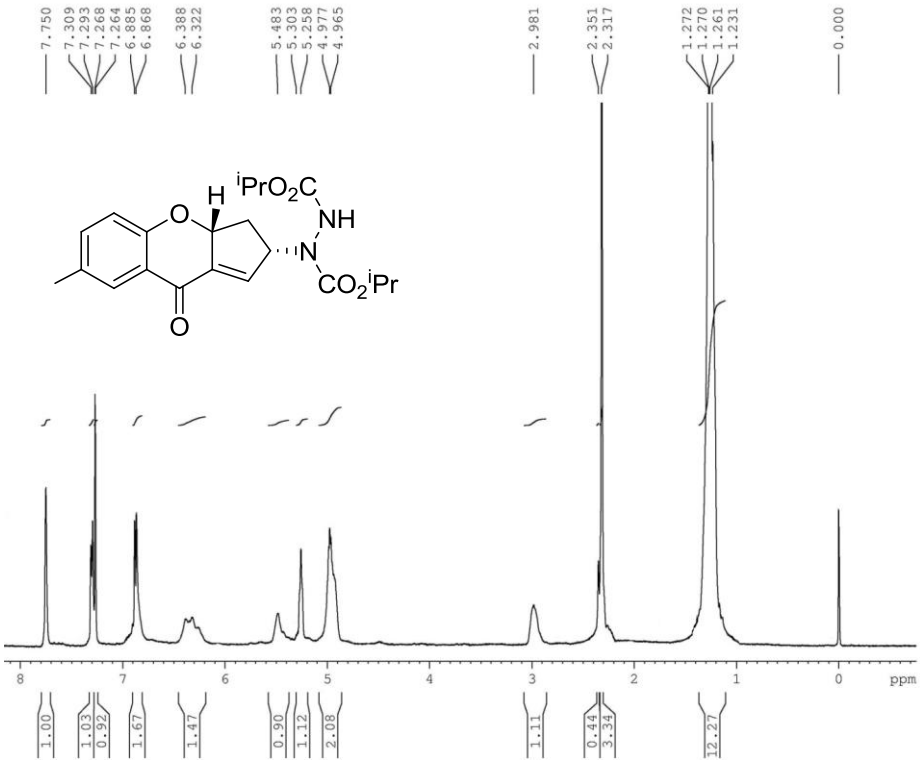
^{13}C NMR of 3h



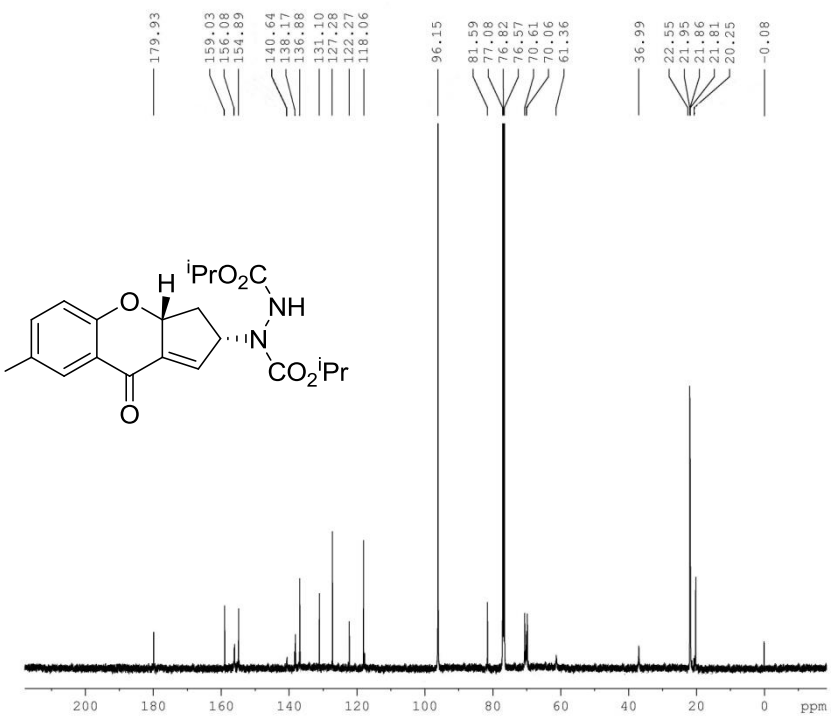
^{1}H NMR of 3i



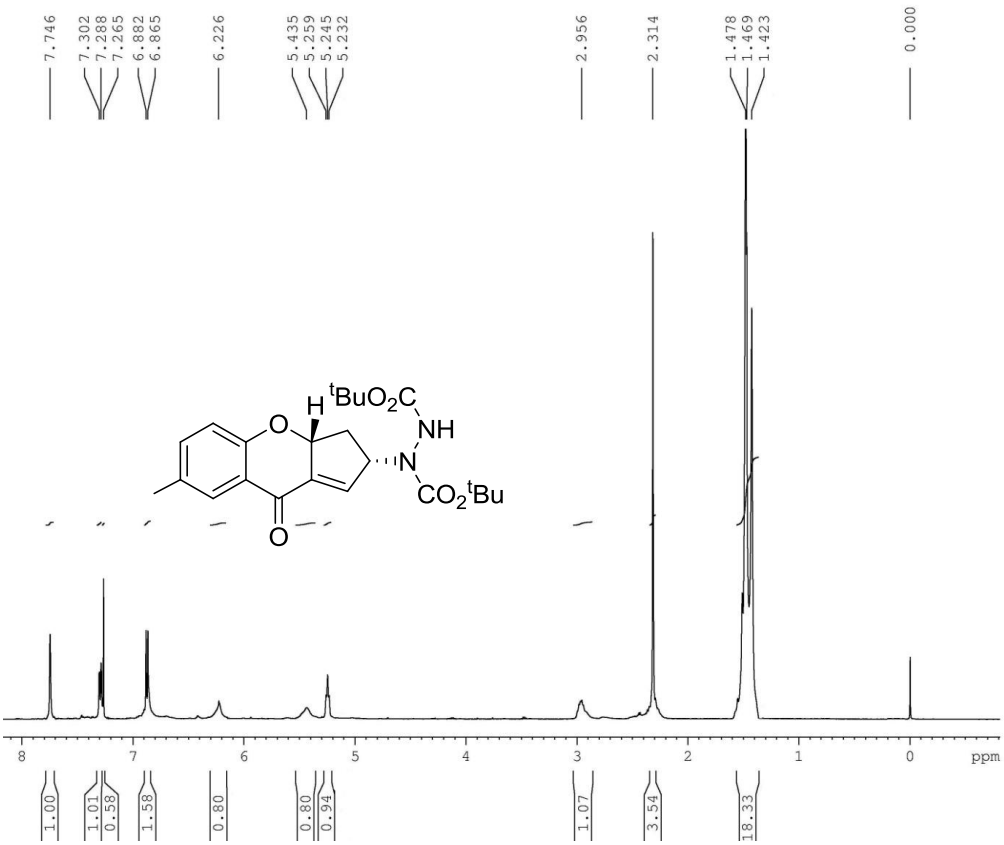
^{13}C NMR of 3i



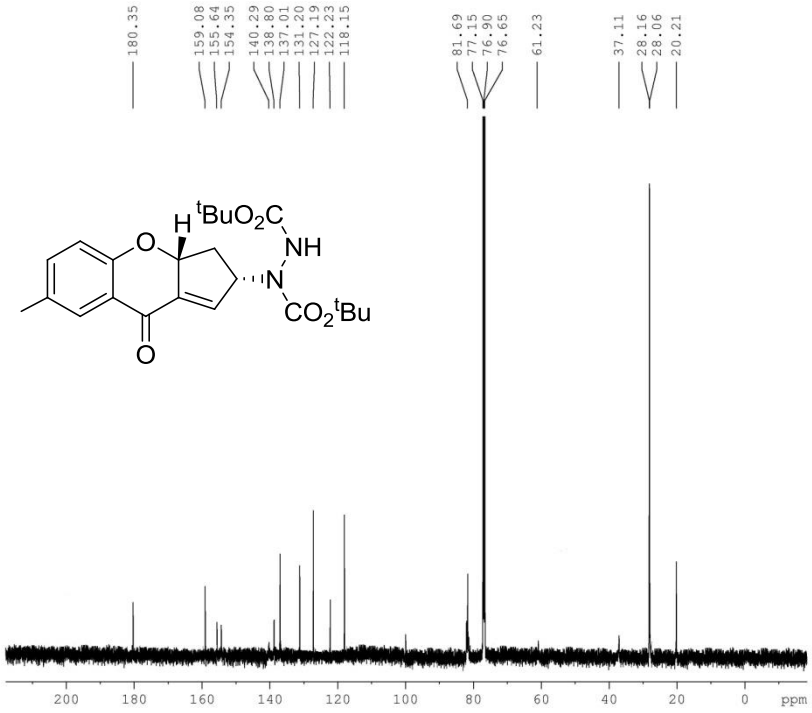
^{1}H NMR of 3j



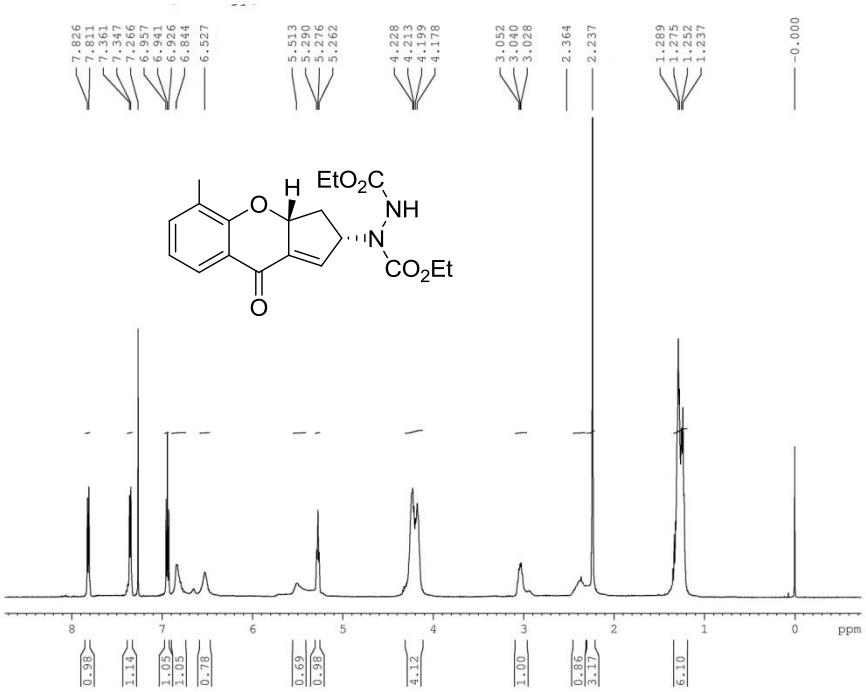
^{13}C NMR of 3j



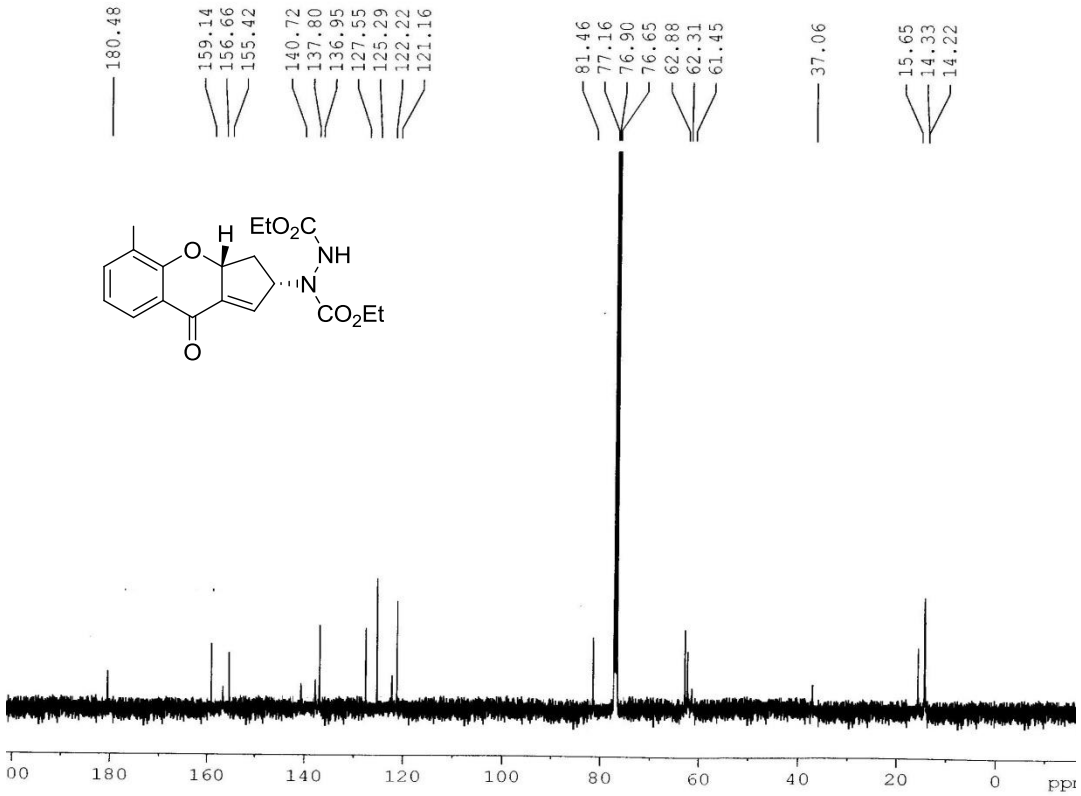
^{1}H NMR of 3k



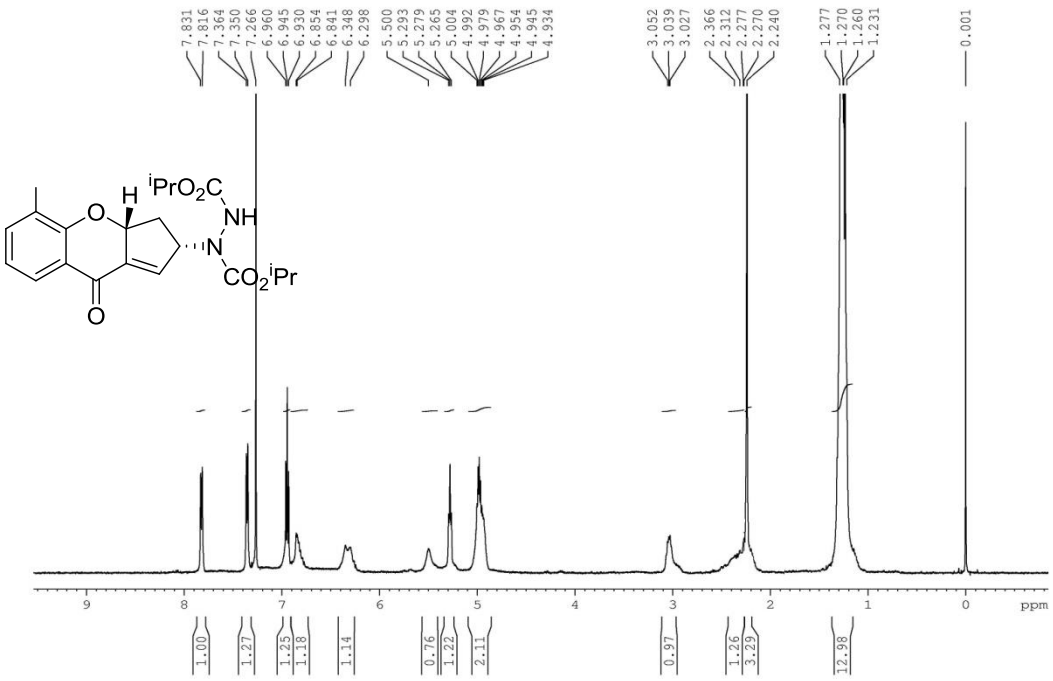
^{13}C NMR of 3k



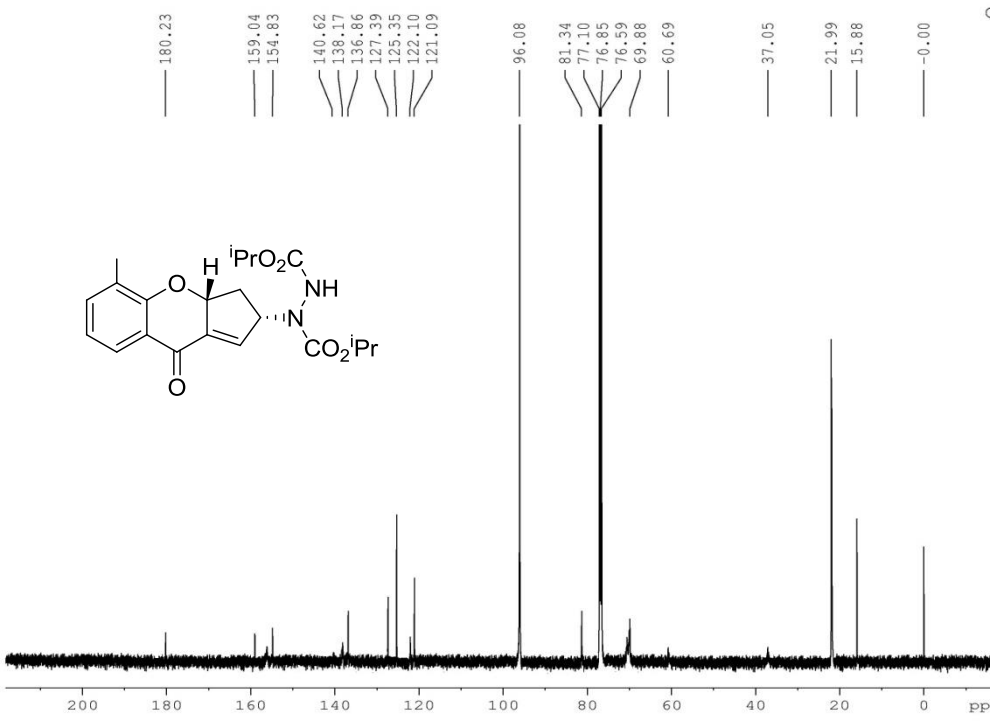
^{1}H NMR of 3l



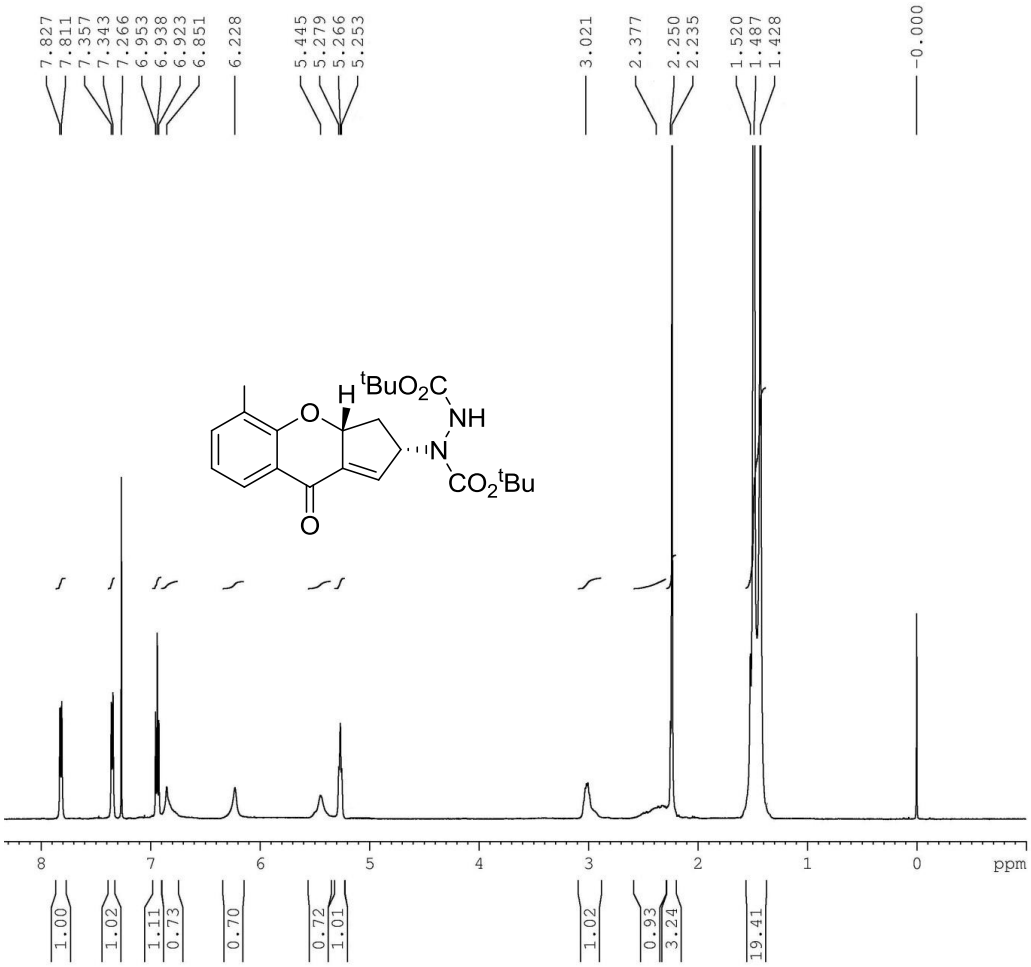
^{13}C NMR of 3l



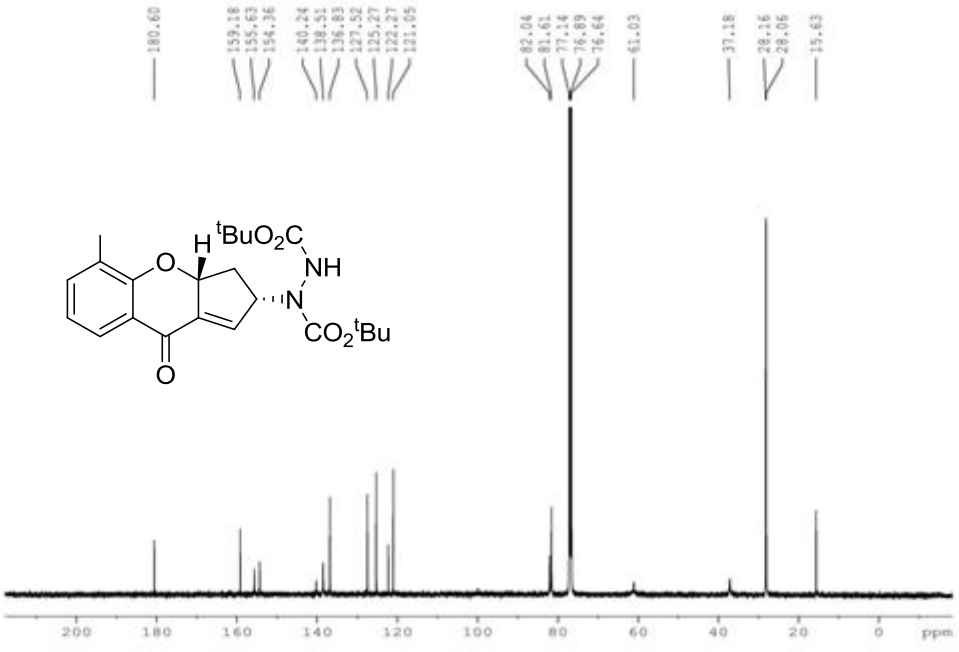
^{1}H NMR of 3m



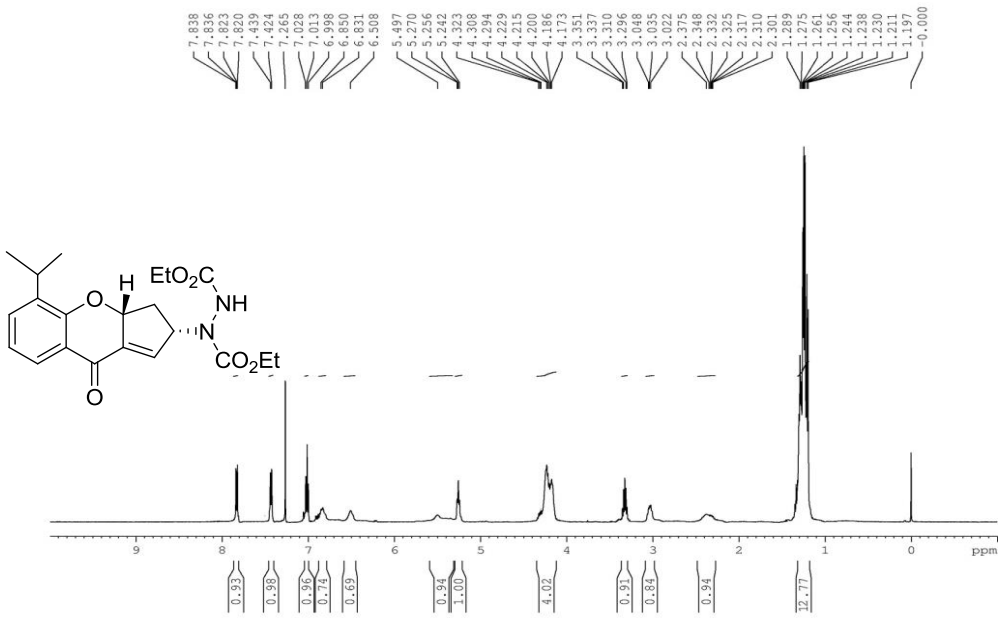
^{13}C NMR of 3m



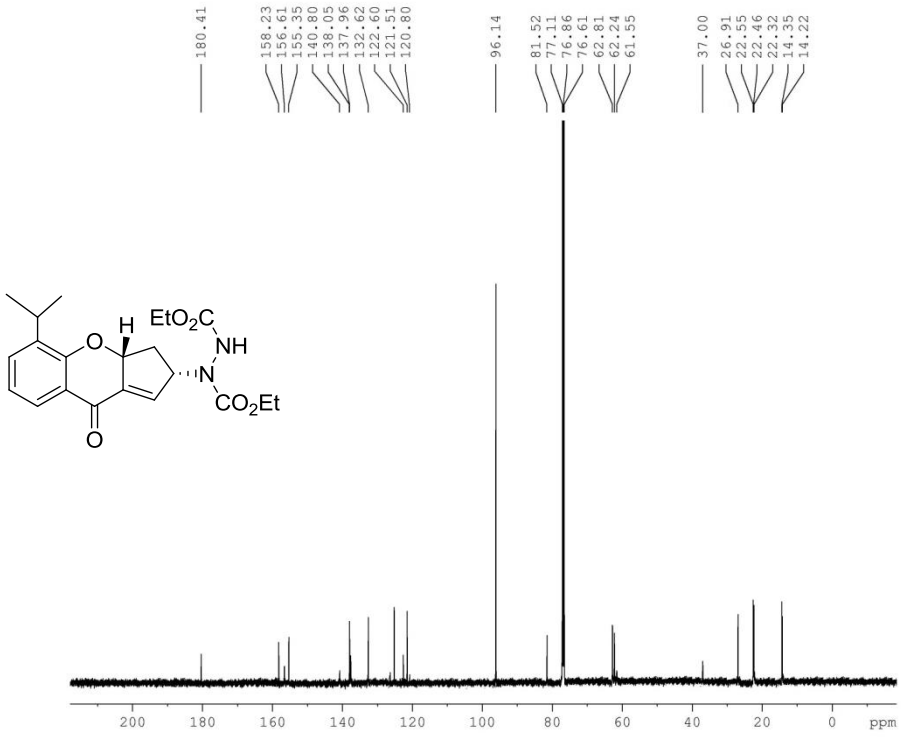
^{1}H NMR of 3n



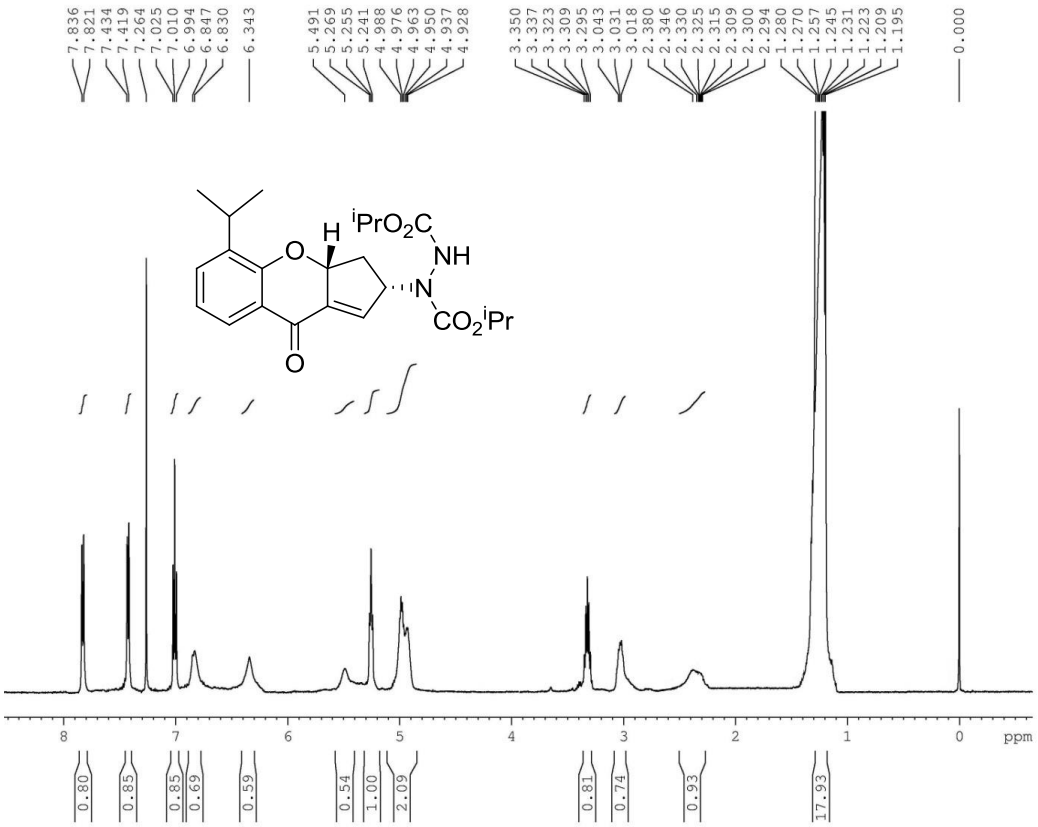
^{13}C NMR of 3n



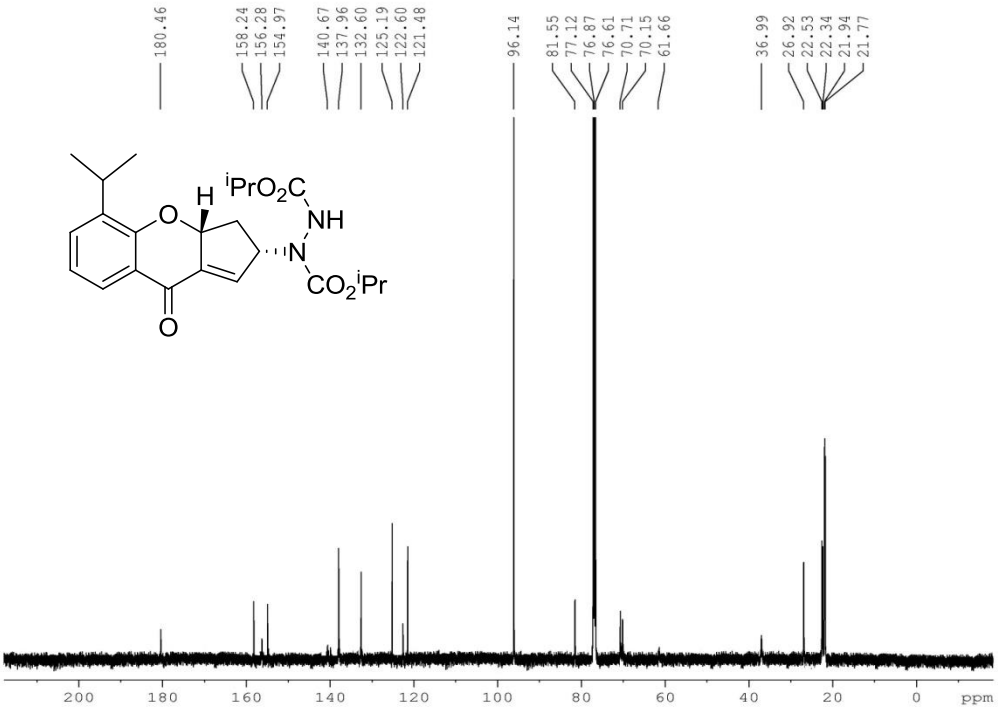
^{1}H NMR of 3o



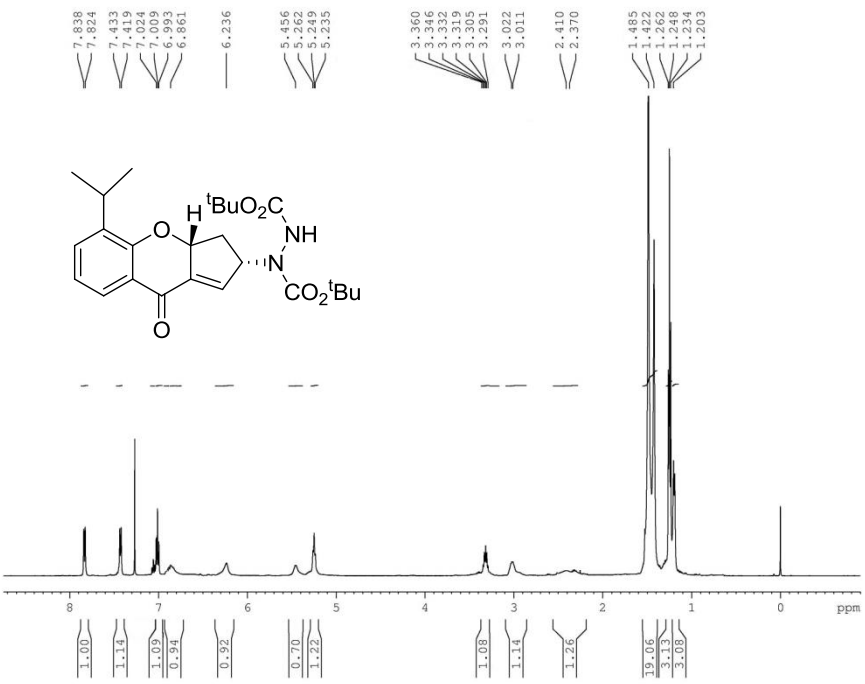
^{13}C NMR of 3o



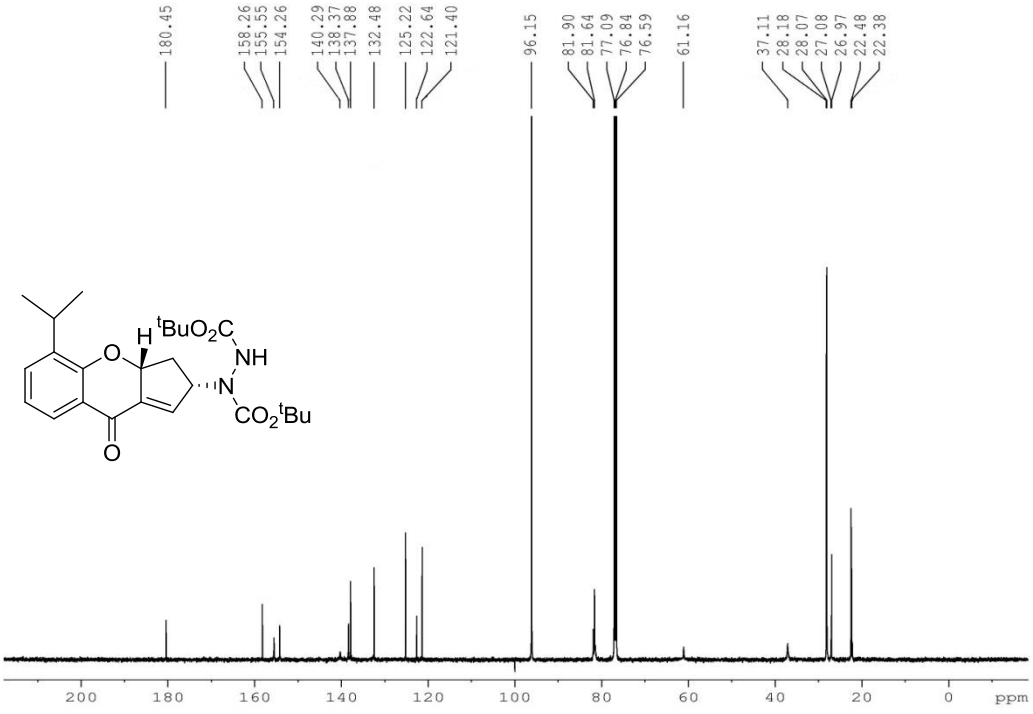
^{1}H NMR of 3p



^{13}C NMR of 3p



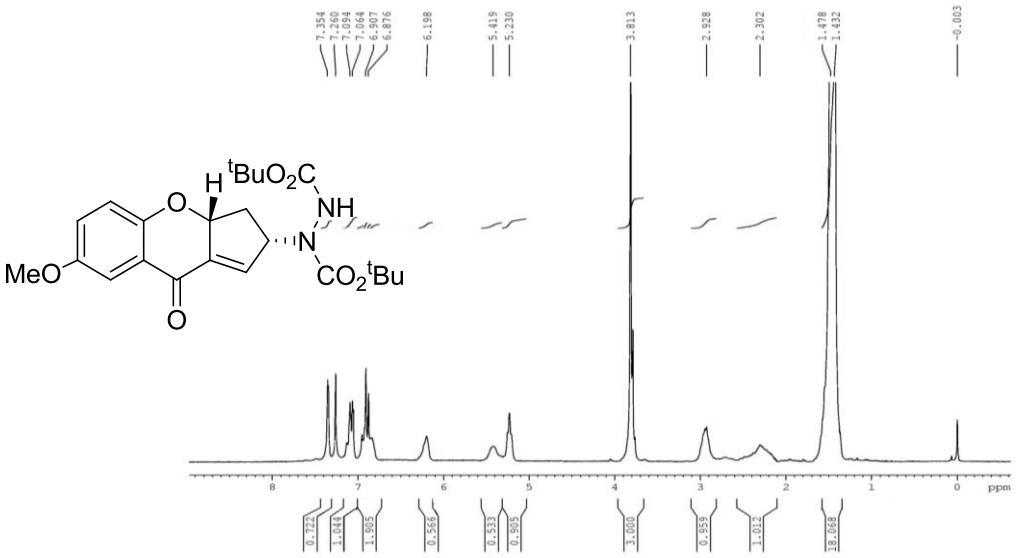
^{1}H NMR of 3q



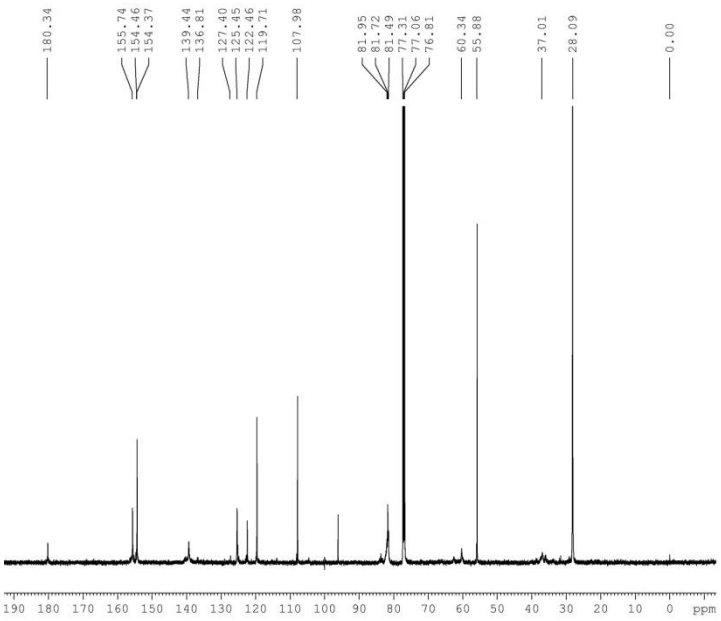
^{13}C NMR of 3q

Assignment of Stereochemistry

Spectral Details of Compound 3g

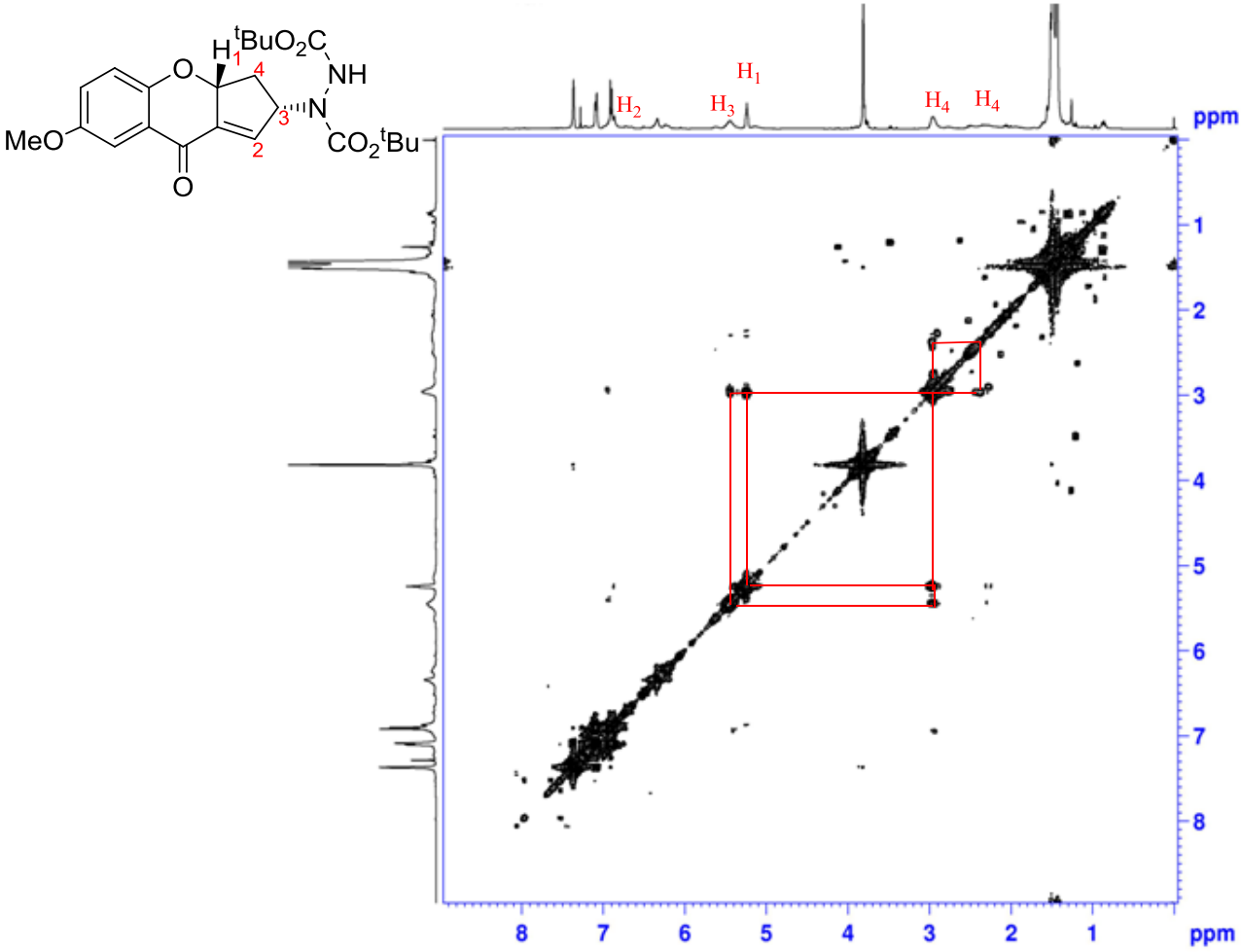


^{1}H NMR of 3g

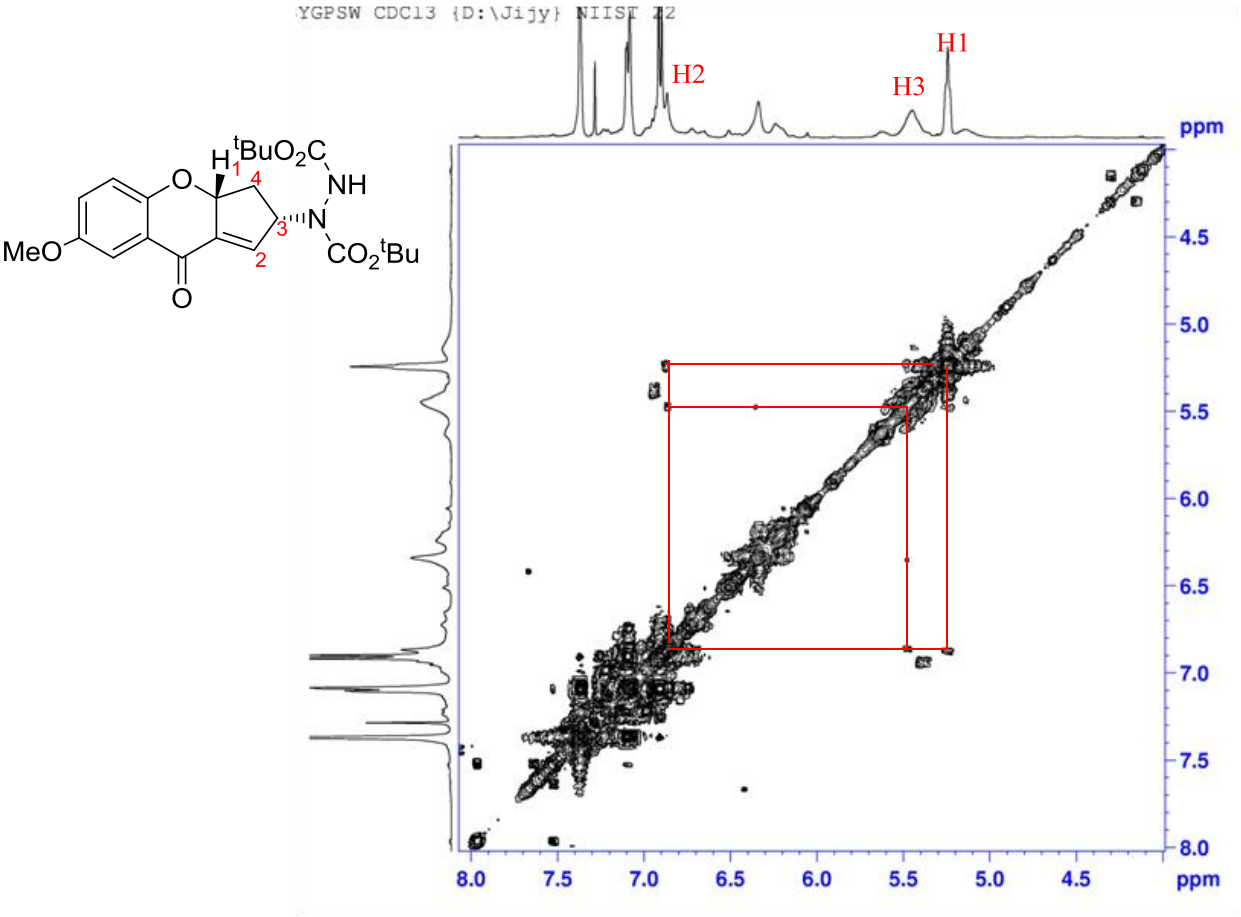


^{13}C NMR of 3g

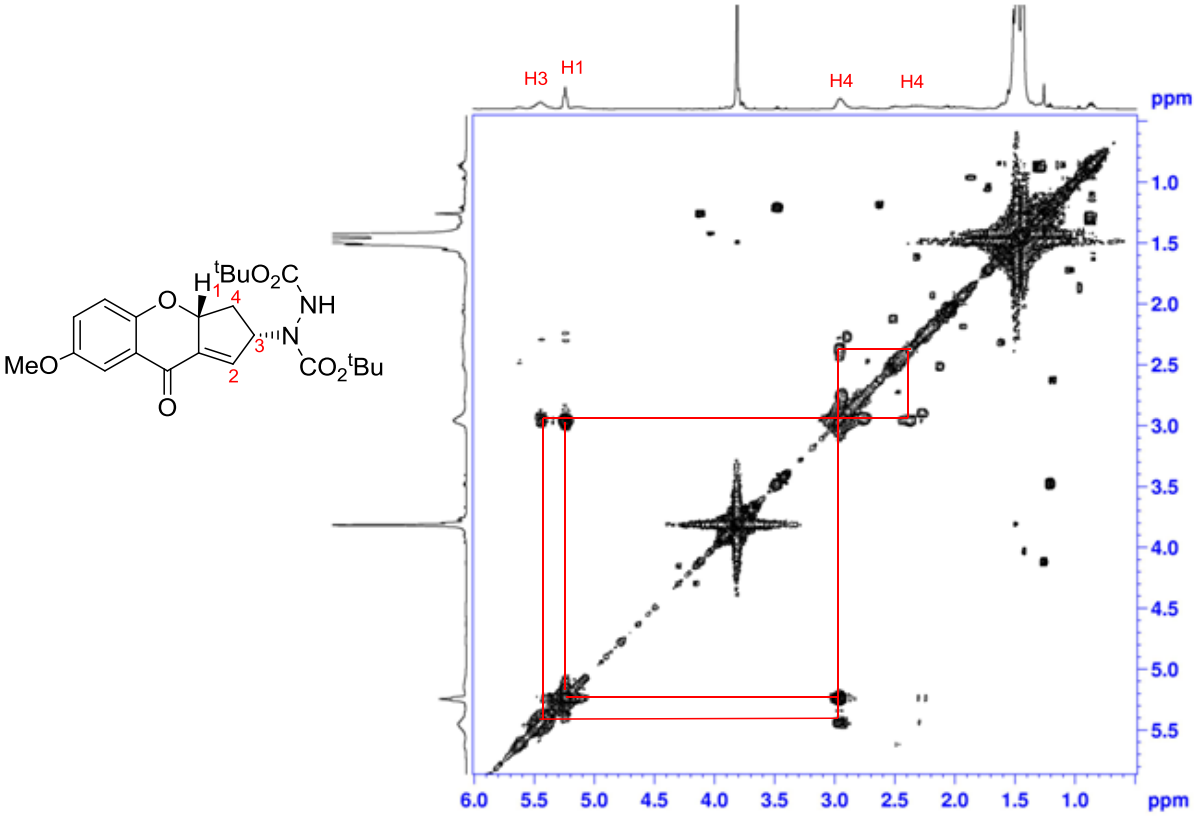
^{1}H-^{1}H COSY NMR of 3g



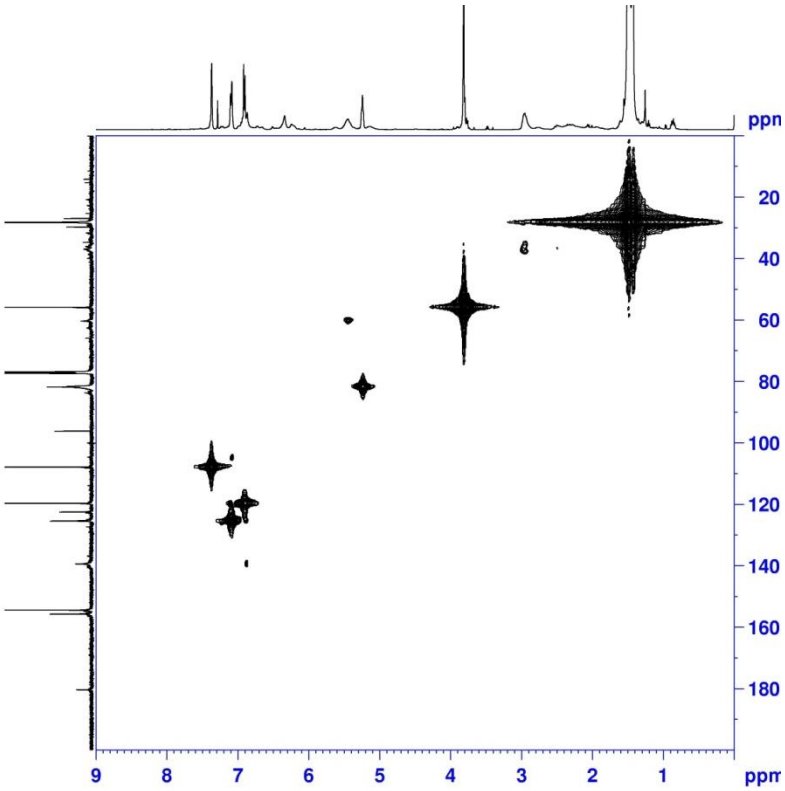
COSY NMR of 3g showing correlation between (i) H_3 and H_4 (ii) H_1 and H_4 (iii) H_4 and H_4 (iv) H_2 and H_1 (v) H_2 and H_3



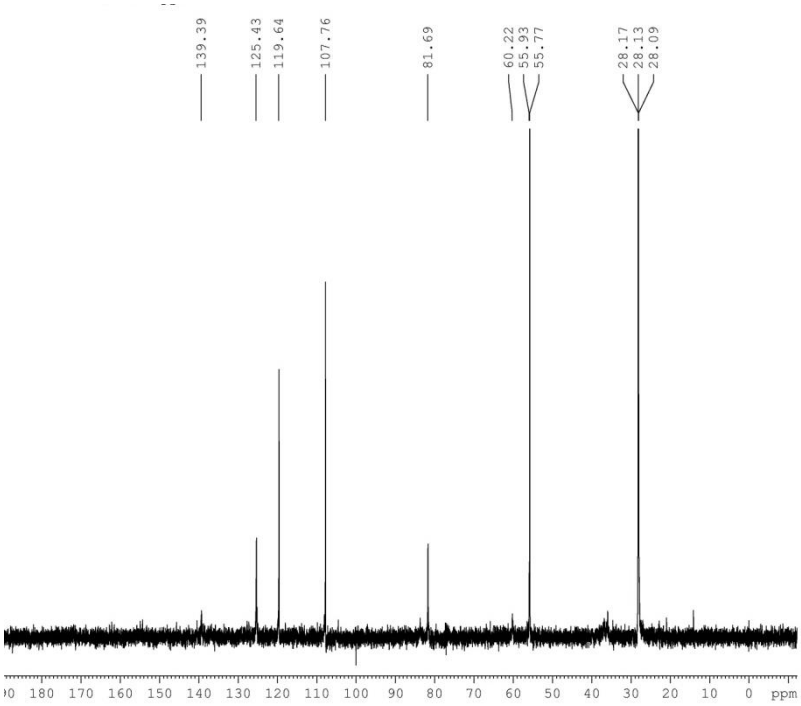
Expansion of COSY NMR of 3g showing correlation between (i) H_2 and H_3 (ii) H_2 and H_1



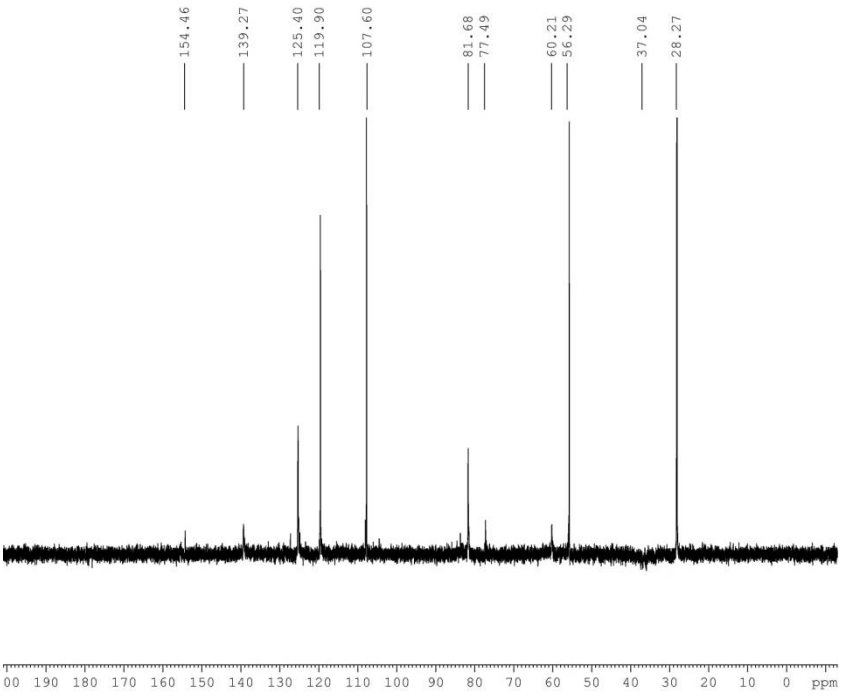
Expansion of COSY NMR of 3g showing correlation between (i) H_1 and H_4 (ii) H_3 and H_4 (iii) H_1 and H_4 (Two methylene protons)



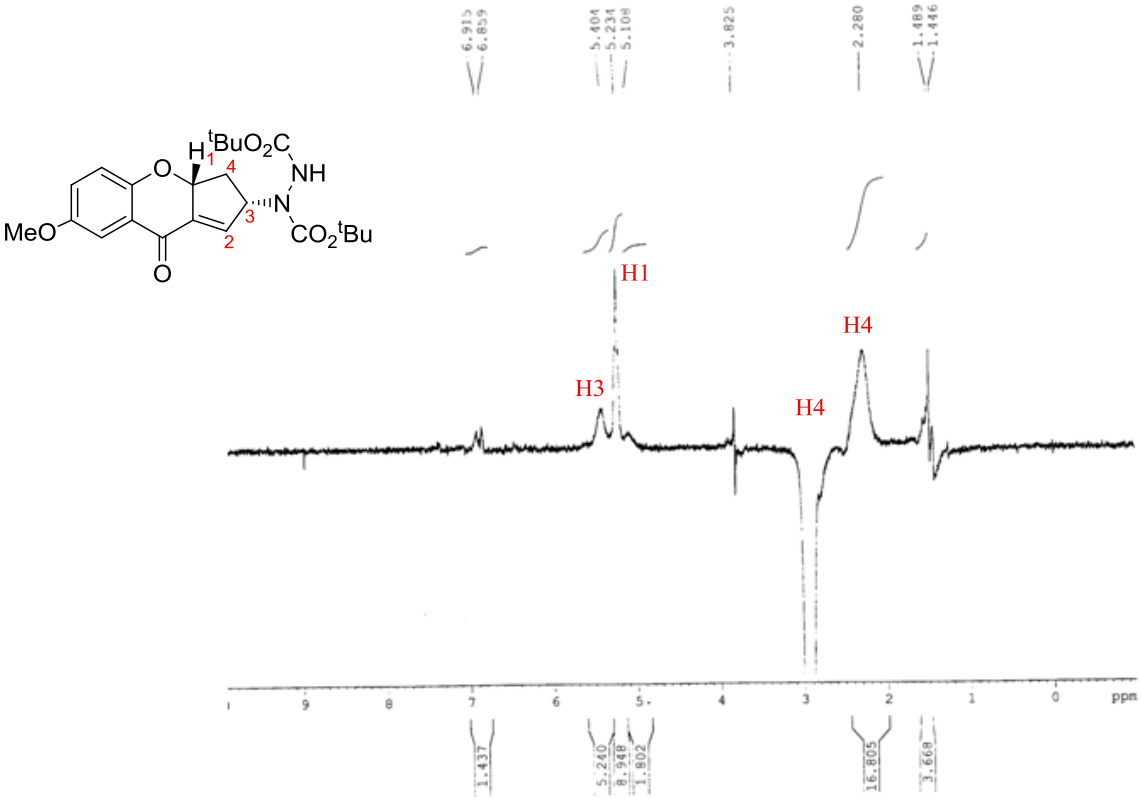
HMQC of 3g



DEPT 45 of 3g

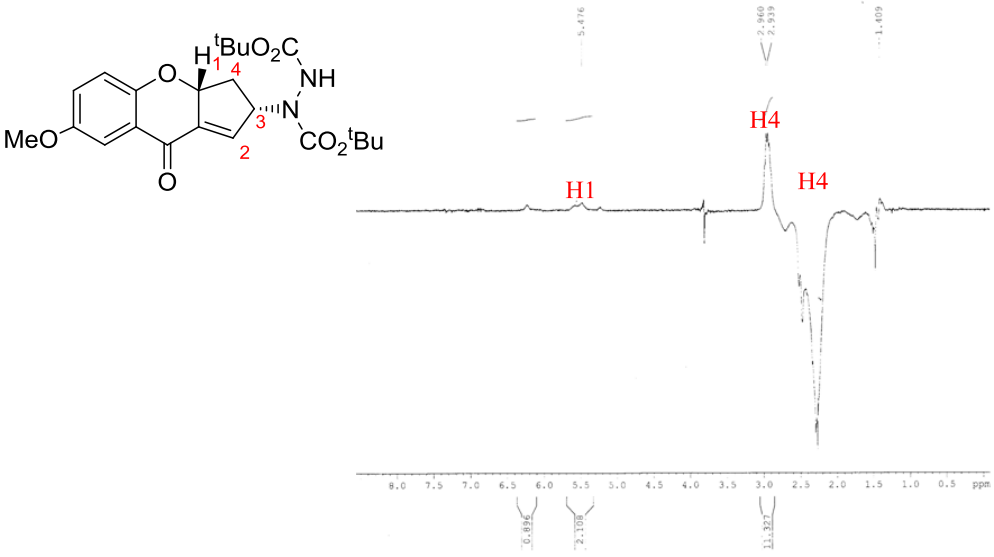


DEPT 135 of 3g



NOE spectrum of 3g

On irradiation of one of the methylene protons, both H_1 and H_3 signals were enhanced.



NOE spectrum of 3g

Irradiation of the other methylene proton did not produce enhancement on H_1 and H_3 signals.