Supporting Information

Diastereoselective Construction of Carbo-Bridged Polyheterocycles by a Three-component Tandem Annulation Reaction

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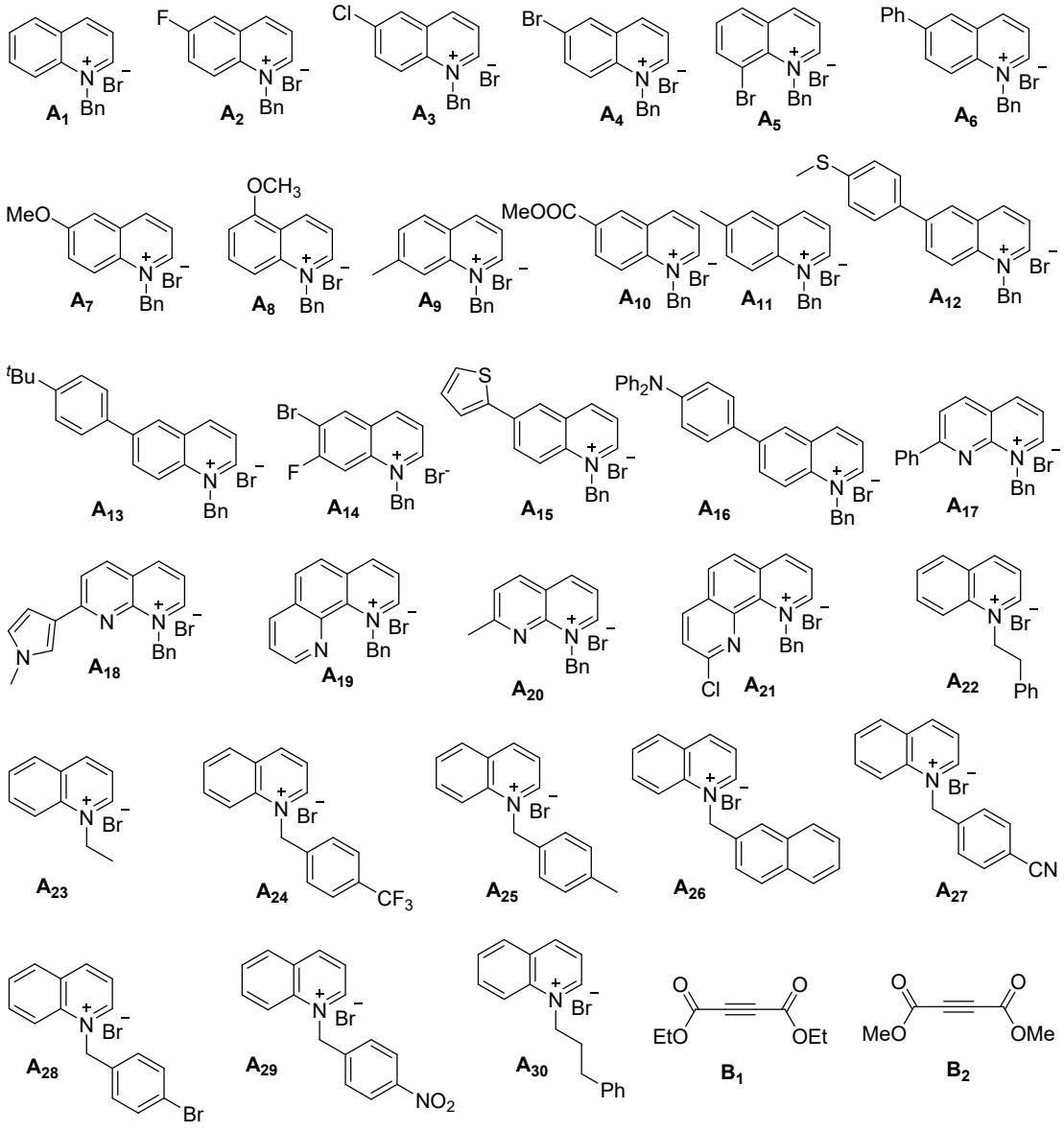
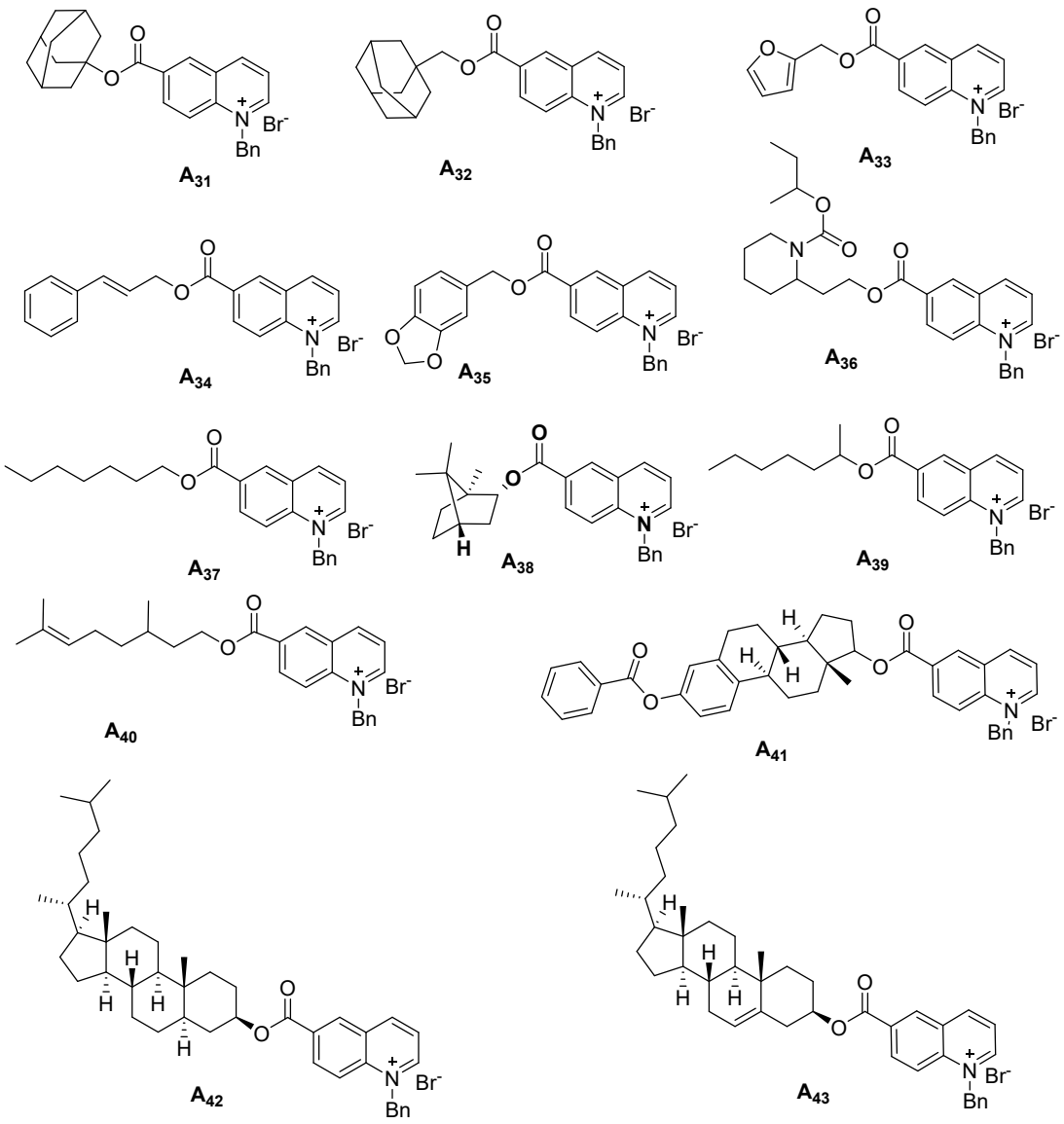
General information

All the obtained products were characterized by melting points (m.p.), ^{1}H NMR, and ^{13}C NMR. Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected. ^{1}H-NMR, ^{13}C-NMR and NOESY spectra were obtained on Bruker-400 or Bruker-500 and referenced to 7.26 ppm for chloroform solvent or 2.54 ppm for dimethyl sulfoxide solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 600 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Analytical HPLC was run with an Agilent 1260 Infinity, equipped with a Daicel CHIRALPAK IA (4.6 mm × 250 mm) and an Agilent LC1260 II DAD-G7115A detector. Unless otherwise stated, all the reagents were purchased from commercial sources, used without further purification.





Scheme S1. Substrates employed for the reaction

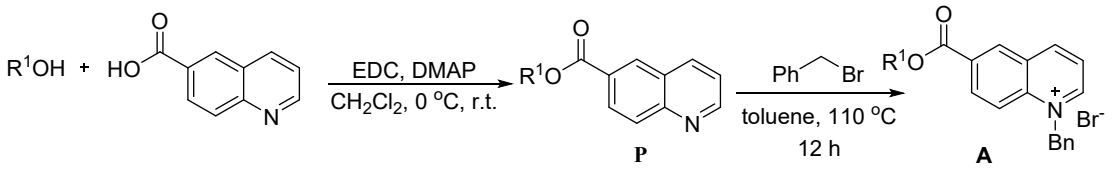
Substrate preparation

Synthesis of N-heteroarenium Salts Method: N-heteroarenes (3 mmol), halogenated compound (3 mmol) and toluene (3 mL) were introduced in a flask (25 mL), and the resulting mixture was stirred at 110 °C for 24 hours. After that, the solvent was removed. The reaction mixture was washed with small amount of diethyl ether and finally dried under vacuum to afford quinolinium salts $\mathbf{A_1}$-$\mathbf{A_{30}}$.

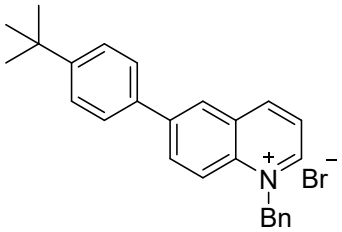
To a suspension of quinoline-6-carboxylic acid (5.0 mmol) in CH_2Cl_2 was added DMAP (4-(dimethylamino)-pyridine, 10.0 mmol) in one portion at room temperature. The reaction mixture was stirred for 10 min at room temperature. Then, N-(3-(Dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride (EDC, 5.0 mmol) was added at 0 ºC， the resultant suspension was stirred for 10 min at 0 ºC, and a solution of alcohol (4.0 mmol) in CH_2Cl_2 was added at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 16 h. The solution was diluted by addition of saturated aqueous NH_4Cl solution and CH_2Cl_2 at room temperature. The organic phase was dried with anhydrous sodium sulfate, and then concentrated

by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give 6-ester substituted quinolines.

Then**,** 6-ester substituted quinolines (3 mmol), benzyl bromide (3 mmol) and toluene (3 mL) were introduced in a flask (25 mL), and the resulting mixture was stirred at 110 °C for 24 hours. After removing the solvent, the reaction mixture was washed with small amount of diethyl ether and finally dried under vacuum to get reactants $\mathbf{A_{31}}$-$\mathbf{A_{43}}$.

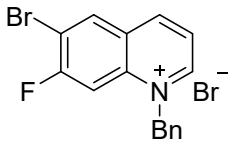


(1) 1-benzyl-6-(4-(tert-butyl)phenyl)quinolin-1-ium bromide ($\mathbf{A_{13}}$)



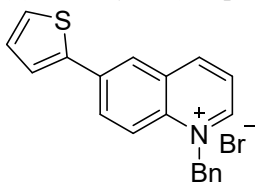
Yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.82 (d, J = 16.1 Hz, 1H), 9.42 (d, J = 9.0 Hz, 1H), 8.85 (s, 1H), 8.64 – 8.50 (m, 2H), 8.33 (t, J = 7.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.56 – 7.32 (m, 1H), 7.31 – 7.10 (m, 2H), 6.47 (d, J = 8.2 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, DMSO) δ 150.4, 148.5, 141.4, 134.9, 134.5, 131.0, 129.6, 129.4, 129.3, 128.7, 127.8, 127.6, 127.6, 126.7, 125.8, 123.3, 120.4, 60.4, 34.9, 31.5. HRMS (ESI): Calcd. for $C_{26}H_{26}N$ $[M–Br]^+$: 352.2060; found: 352.2065.

(2) 1-benzyl-6-bromo-7-fluoroquinolin-1-ium bromide ($\mathbf{A_{14}}$)



Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.92 (dd, J = 6.0, 1.4 Hz, 1H), 9.41 (d, J = 8.3 Hz, 1H), 9.16 (d, J = 7.5 Hz, 1H), 8.75 (d, J = 10.4 Hz, 1H), 8.37 (dd, J = 8.4, 5.8 Hz, 1H), 7.55 – 7.32 (m, 5H), 6.45 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 161.5 (d, J = 256.3 Hz), 151.9, 147.6, 138.8 (d, J = 12.1 Hz), 136.5 (d, J = 2.6 Hz), 133.8, 129.6, 129.4, 128.7, 128.2, 123.6 (d, J = 2.2 Hz), 113.7 (d, J = 24.1 Hz), 107.1 (d, J = 29.2 Hz), 60.4. HRMS (ESI): Calcd. for $C_{16}H_{12}NFBr$ $[M–Br]^+$: 316.0132; found: 316.0137.

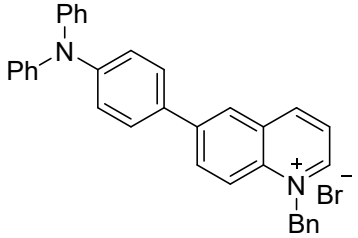
(3) 1-benzyl-6-(thiophen-2-yl)quinolin-1-ium ($\mathbf{A_{15}}$)



Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.78 (dd, J = 5.8, 1.4 Hz, 1H), 9.39 (d, J = 8.3 Hz, 1H), 8.76 (d, J = 2.1 Hz, 1H), 8.59 – 8.51 (m, 2H), 8.31 (dd, J = 8.4, 5.7 Hz, 1H), 7.89 (dd,

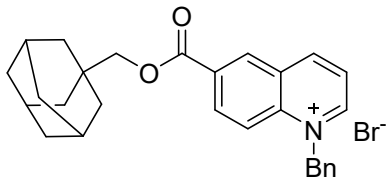
J = 3.7, 1.2 Hz, 1H), 7.79 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.47 – 7.37 (m, 5H), 7.26 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.46 (s, 2H).^{13}C NMR (126 MHz, DMSO) δ 150.1, 148.2, 140.6, 137.2, 135.3, 134.4, 133.6, 131.2, 129.6, 129.6, 129.4, 129.3, 127.8, 127.6, 125.5, 123.6, 120.7, 60.4. HRMS (ESI): Calcd. for $C_{20}H_{16}NS$ $[M–Br]^+$: 302.0998; found: 302.1003.

(4) 1-benzyl-6-(4-(diphenylamino)phenyl)quinolin-1-ium bromide (**A$_{16}$**)



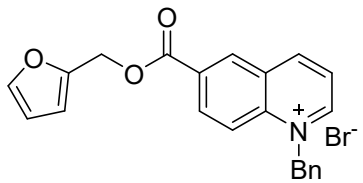
Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.84 – 9.62 (m, 1H), 9.36 (t, *J* = 8.9 Hz, 1H), 8.78 (q, *J* = 2.6 Hz, 1H), 7.86 – 7.81 (m, 2H), 8.29 (dd, *J* = 8.4, 5.7 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.40 (dt, *J* = 31.2, 6.5 Hz, 9H), 7.10 (dp, *J* = 14.6, 6.7, 6.2 Hz, 8H), 6.57 – 6.30 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.0, 148.8, 148.3, 147.1, 141.0, 141.0, 137.1, 134.5, 134.5, 131.1, 130.2, 129.6, 129.3, 128.9, 127.8, 126.7, 125.3, 124.4, 123.3, 122.6, 120.4, 60.3. HRMS (ESI): Calcd. for $C_{34}H_{27}N_2$ $[M–Br]^+$: 463.2169; found: 463.2174.

(5) 6-((adamantan-1-ylmethoxy)carbonyl)-1-benzylquinolin-1-ium bromide (**A$_{32}$**)



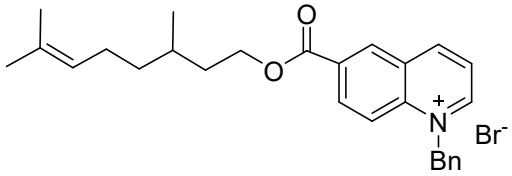
Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.01 (s, 1H), 9.67 (d, *J* = 8.4 Hz, 1H), 9.16 (s, 1H), 8.63 (dd, *J* = 61.0, 9.3 Hz, 2H), 8.43 (t, *J* = 7.3 Hz, 1H), 7.53 – 7.29 (m, 3H), 7.25 – 7.04 (m, 2H), 6.49 (s, 2H), 3.97 (s, 2H), 1.95 (s, 3H), 1.73 – 1.54 (m, 12H). ^{13}C NMR (126 MHz, DMSO) δ 163.98, 152.30, 149.59, 139.34, 134.03, 133.62, 132.69, 130.40, 129.70, 129.03, 128.78, 127.41, 123.44, 120.44, 74.58, 60.11, 38.52, 36.28, 33.06, 27.37. HRMS (ESI): Calcd. for $C_{28}H_{30}NO_2$ $[M–Br]^+$: 412.2271; found: 412.2277.

(6) 1-benzyl-6-((furan-2-ylmethoxy)carbonyl)quinolin-1-ium bromide (**A$_{33}$**)



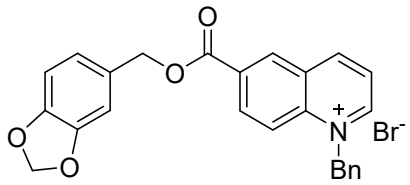
Brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.12 (d, *J* = 6.0 Hz, 1H), 9.67 (d, *J* = 8.6 Hz, 1H), 9.17 (s, 1H), 8.78 (d, *J* = 9.2 Hz, 1H), 8.55 (dd, *J* = 9.3, 2.0 Hz, 1H), 8.50 – 8.45 (m, 1H), 7.79 (s, 1H), 7.55 – 7.49 (m, 2H), 7.45 – 7.37 (m, 3H), 6.72 (d, *J* = 3.3 Hz, 1H), 6.61 – 6.50 (m, 3H), 5.47 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 164.1, 152.8, 150.0, 149.2, 144.6, 139.9, 134.5, 134.1, 133.3, 130.4, 130.1, 129.5, 129.3, 128.1, 124.0, 121.0, 112.1, 111.4, 60.5, 59.7. HRMS (ESI): Calcd. for $C_{22}H_{18}NO_3$ $[M–Br]^+$: 344.1281; found: 344.1287.

(7) 1-benzyl-6-(((3,7-dimethyloct-6-en-1-yl)oxy)carbonyl)quinolin-1-ium bromide (**A_{34}**)



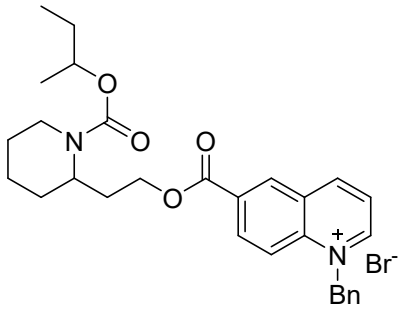
Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.95 (dd, J = 5.9, 1.5 Hz, 1H), 9.62 (d, J = 8.4 Hz, 1H), 9.15 (d, J = 2.0 Hz, 1H), 8.68 (d, J = 9.4 Hz, 1H), 8.56 (dd, J = 9.3, 2.1 Hz, 1H), 8.43 (dd, J = 8.4, 5.8 Hz, 1H), 7.62 – 7.21 (m, 5H), 6.47 (s, 2H), 5.12 – 5.03 (m, 1H), 4.51 – 4.35 (m, 2H), 3.79 (s, 1H), 2.05 – 1.97 (m, 2H), 1.87 – 1.76 (m, 1H), 1.68 – 1.51 (m, 7H), 1.43 – 1.32 (m, 1H), 1.25 – 1.15 (m, 1H), 0.95 (d, J = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 164.5, 152.8, 150.0, 139.9, 134.5, 134.1, 133.2, 131.1, 131.0, 130.2, 129.6, 129.3, 128.0, 124.9, 124.0, 120.9, 64.6, 60.7, 36.9, 35.3, 29.4, 25.9, 25.3, 19.8, 18.0. HRMS (ESI): Calcd. for $C_{27}H_{32}NO_2$ $[M–Br]^+$: 402.2428; found: 402.2433.

(8) 6-((benzo[d][1,3]dioxol-5-ylmethoxy)carbonyl)-1-benzylquinolin-1-ium bromide (**A_{35}**)



Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.99 (d, J = 5.8 Hz, 1H), 9.63 (d, J = 8.5 Hz, 1H), 9.17 (s, 1H), 8.70 (d, J = 9.3 Hz, 1H), 8.63 – 8.56 (m, 1H), 8.43 (dd, J = 8.4, 5.7 Hz, 1H), 7.52 – 7.32 (m, 5H), 7.13 (s, 1H), 6.99 (dd, J = 44.8, 7.9 Hz, 2H), 6.49 (s, 2H), 6.05 (s, 2H), 5.36 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 164.4, 152.8, 150.0, 147.9, 147.9, 139.9, 134.7, 134.1, 133.3, 130.8, 130.2, 129.6, 129.6, 129.3, 128.0, 124.0, 122.9, 120.9, 109.5, 108.7, 101.7, 67.7, 60.6. HRMS (ESI): Calcd. for $C_{25}H_{20}NO_4$ $[M–Br]^+$: 398.1387; found: 398.1392.

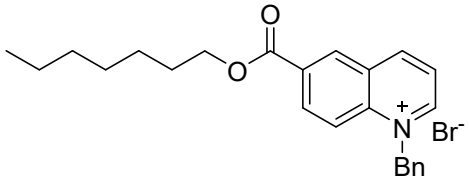
(9)1-benzyl-6-((2-(1-(sec-butoxycarbonyl)piperidin-2-yl)ethoxy)carbonyl)quinolin-1-ium bromide (**A_{36}**)



Pink solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.98 (d, J = 5.8 Hz, 1H), 9.61 (d, J = 8.3 Hz, 1H), 9.27 – 9.07 (m, 1H), 8.70 (d, J = 9.3 Hz, 1H), 8.57 (dt, J = 9.3, 2.5 Hz, 1H), 8.44 (dd, J = 8.4, 5.8 Hz, 1H), 7.50 – 7.35 (m, 5H), 6.49 (s, 2H), 4.55 – 4.41 (m, 2H), 4.39 – 4.28 (m, 2H), 3.92 (d, J = 13.4 Hz, 1H), 2.90 (t, J = 13.2 Hz, 1H), 2.34 – 2.23 (m, 1H), 1.97 – 1.85 (m, 1H), 1.68 – 1.51 (m, 5H), 1.45 – 1.21 (m, 3H), 1.00 (d, J = 6.3 Hz, 3H), 0.70 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 164.4, 155.1, 155.0, 152.8, 149.9, 139.8, 134.5, 134.1, 133.2, 130.1, 129.6, 129.3, 128.0,

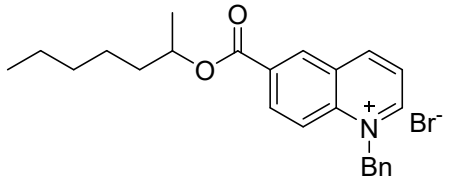
124.1, 120.8, 72.5, 72.4, 63.9, 60.6, 28.8, 28.5, 25.7, 19.9, 19.1, 9.9, 9.9. HRMS (ESI): Calcd. for $C_{29}H_{35}N_2O_4$ $[M–Br]^+$: 475.2591; found: 475.2597.

(10) 1-benzyl-6-((heptyloxy)carbonyl)quinolin-1-ium bromide (**A_{37}**)



Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.17 (d, J = 5.6 Hz, 1H), 9.71 (d, J = 8.4 Hz, 1H), 9.19 (d, J = 1.9 Hz, 1H), 8.81 (d, J = 9.3 Hz, 1H), 8.57 (dd, J = 9.3, 2.0 Hz, 1H), 8.49 (dd, J = 8.4, 5.8 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.46 – 7.35 (m, 3H), 6.60 (s, 2H), 4.39 (t, J = 6.5 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.47 – 1.39 (m, 2H), 1.38 – 1.22 (m, 6H), 0.89 – 0.82 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 163.91, 152.23, 149.39, 139.24, 133.88, 133.60, 132.58, 130.37, 129.58, 128.94, 128.71, 127.51, 123.47, 120.45, 65.65, 59.96, 31.05, 28.25, 28.02, 25.26, 21.93, 13.79. HRMS (ESI): Calcd. for $C_{24}H_{28}NO_2$ $[M–Br]^+$: 362.2115; found: 362.2120.

(11) 1-benzyl-6-((heptan-2-yloxy)carbonyl)quinolin-1-ium bromide (**A_{39}**)

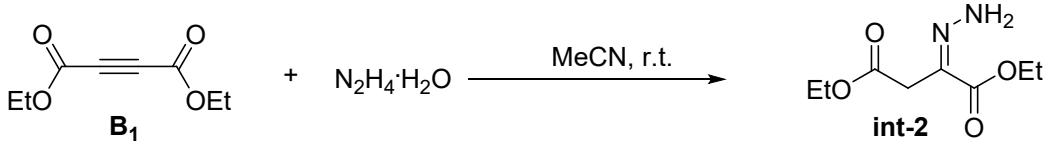


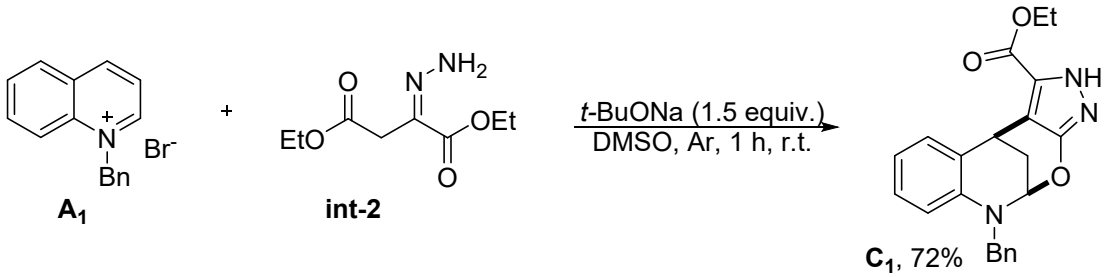
White solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.96 (dd, J = 5.8, 1.4 Hz, 1H), 9.63 (d, J = 8.3 Hz, 1H), 9.15 (d, J = 1.9 Hz, 1H), 8.69 (d, J = 9.3 Hz, 1H), 8.57 (dd, J = 9.3, 1.9 Hz, 1H), 8.43 (dd, J = 8.4, 5.8 Hz, 1H), 7.52 – 7.29 (m, 5H), 6.47 (s, 2H), 5.26 – 5.11 (m, 1H), 4.39 (s, 1H), 1.89 – 1.57 (m, 2H), 1.47 – 1.16 (m, 8H), 0.99 – 0.53 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 164.1, 152.7, 150.0, 139.9, 134.6, 134.1, 133.1, 131.3, 130.2, 129.6, 129.3, 127.9, 124.0, 120.8, 73.3, 60.6, 35.7, 31.5, 24.9, 22.4, 20.2, 14.3. HRMS (ESI): Calcd. for $C_{24}H_{28}NO_2$ $[M–Br]^+$: 362.2115; found: 362.2120.

Control experiments

Synthesis of diethyl-2-hydrazineylidenesuccinate (int-2)

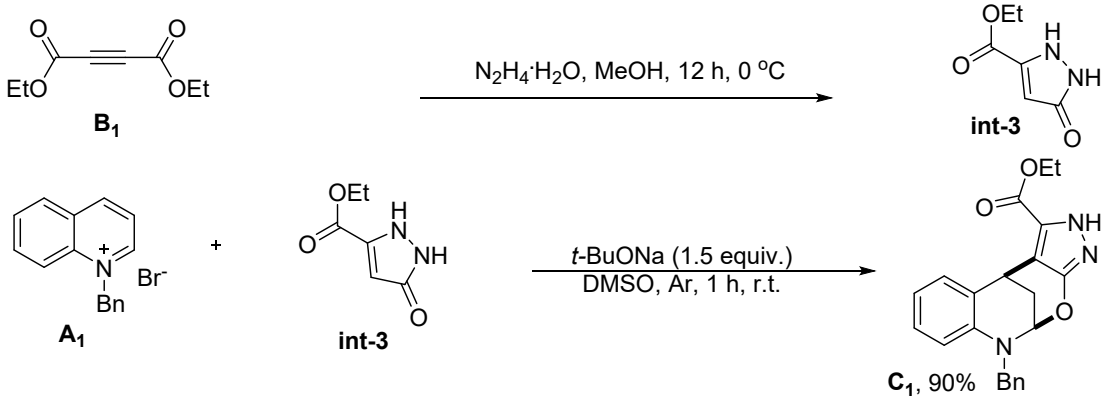
To a solution of 2-butynedioic acid diethyl ester **B_1** (3.0 mmol) in 6 mL of MeCN was slowly added $N_2H_4{\cdot}H_2O$ (3 mmol) at room temperature. The reaction was stirred at room temperature, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **int-2**. ^{1}H NMR (500 MHz, Chloroform-d) δ 6.68 (s, 2H), 4.25 (q, J = 7.2 Hz, 2H), 4.11 (q, J = 7.2, 6.8 Hz, 2H), 3.56 (s, 2H), 1.29 (td, J = 7.1, 1.8 Hz, 3H), 1.21 (td, J = 7.1, 1.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 164.3, 131.6, 61.5, 61.4, 31.2, 14.1, 13.9.



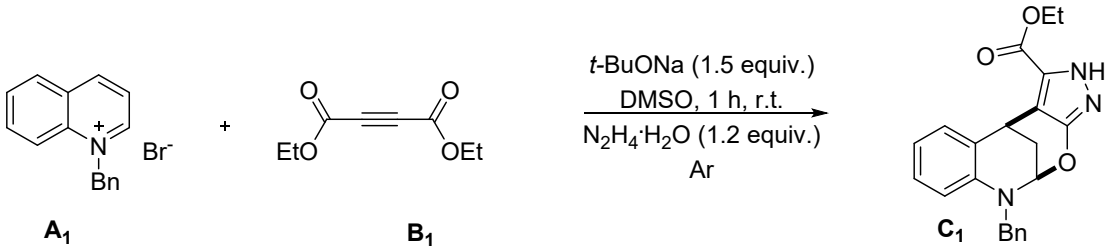


Synthesis of ethyl 5-oxo-2,5-dihydro-1H-pyrazole-3-carboxylate (int-3)

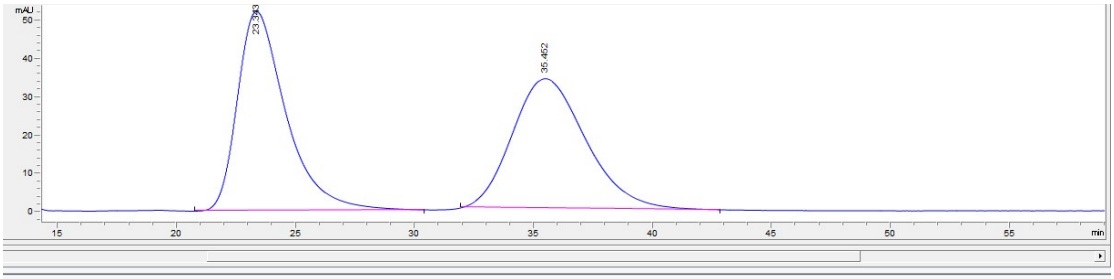
To a solution of 2-butynedioic acid diethyl ester $\mathbf{B_1}$ (3.0 mmol) in 6 mL of MeOH was slowly added $N_2H_4{\cdot}H_2O$ (3 mmol) at 0 °C. The reaction was stirred at 0 °C for 12 h. After cooling down to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **int-3**. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.20 (s, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 161.4, 134.3, 92.9, 62.3, 14.1.



Typical procedure for the synthesis of C_1



Under argon atmosphere, 2-butynedioic acid diethyl ester $\mathbf{B_1}$ (0.17 mmol), DMSO (1 mL) were introduced in a Schlenk flask **I**, 0.2 mmol of $N_2H_4{\cdot}H_2O$ dissolved in 1.5 ml of DMSO was added dropwise at room temperature. Then, *t*-BuONa (0.26 mmol) was added in a Schlenk flask **I**, and it was stirred at room temperature for 5 min. Next, 1-benzylquinolin-1-ium bromide $\mathbf{A_1}$ (0.2 mmol) was added in the mixture at room temperature. After stirring for 1 h, the reaction was quenched with brine (10 mL) and extracted with EtOAc (3 × 5 mL), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Finally, the residue was purified by preparative TLC on silica to give $\mathbf{C_1}$.

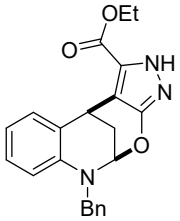


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	23.343	7432.9	52.4	1.9059	0.607	50.330	BB
2	35.452	7335.5	34.1	2.532	0.774	49.670	BB

For **C_1**, conditions: CHIRALCEL OJ (4.6 mm × 250 mm), hexane : IPA = 80 : 20, Flow: 1 mL/min, UV: 250 nm.

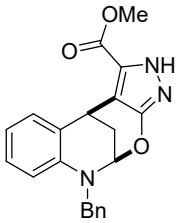
Analytic data of the obtained compounds

(1) Ethyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3] oxazocine-1 -carboxylate (**C_1**)



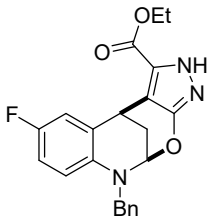
Red solid; M.p. 107-109 ºC, (54.9 mg, 86% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.76 (s, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.15 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 5.64 (q, *J* = 2.1 Hz, 1H), 4.90 (d, *J* = 17.6 Hz, 1H), 4.64 (d, *J* = 17.6 Hz, 1H), 4.49 – 4.31 (m, 3H), 2.32 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.11 (dt, *J* = 13.1, 2.7 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 158.5, 141.3, 137.7, 128.9, 128.6, 127.6, 126.9, 126.9, 126.6, 126.1, 117.7, 111.2, 108.1, 84.3, 61.1, 51.8, 27.8, 27.1, 14.3. HRMS (ESI): Calcd. for $C_{22}H_{22}N_3O_3$ $[M+H]^+$: 376.1656; found: 376.1647.

(2) Methyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3] oxazocine-1-carboxylate (**C_2**)



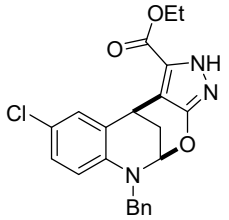
Red solid; M.p. 147-149 ºC, (51.0 mg, 83% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.41 – 7.31 (m, 3H), 7.28 (d, *J* = 4.3 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.08 – 6.99 (m, 1H), 6.75 (td, *J* = 7.4, 1.1 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 5.72 (q, *J* = 2.6 Hz, 1H), 4.97 (d, *J* = 17.6 Hz, 1H), 4.71 (d, *J* = 17.6 Hz, 1H), 4.48 (d, *J* = 3.2 Hz, 1H), 4.00 (s, 3H), 2.41 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.19 (dt, *J* = 13.1, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 158.7, 141.4, 137.7, 128.7, 127.7, 127.0, 126.6, 126.2, 117.9, 111.3, 108.5, 84.5, 51.9, 27.9, 27.2. HRMS (ESI): Calcd. for $C_{21}H_{20}N_3O_3$ $[M+H]^+$: 362.1499; found: 362.1490.

(3) Methyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3] oxazocine-1-carboxylate (**C_3**)



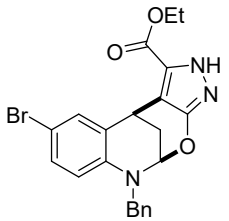
White solid; M.p. 116-118 ºC, (60.1 mg, 90% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.61 (s, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.10 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.67 (td, *J* = 8.7, 3.1 Hz, 1H), 6.42 (dd, *J* = 9.0, 4.5 Hz, 1H), 5.68 (q, *J* = 2.1 Hz, 1H), 4.92 (d, *J* = 17.6 Hz, 1H), 4.62 (d, *J* = 17.6 Hz, 1H), 4.54 – 4.36 (m, 3H), 2.37 (dt, *J* = 13.2, 3.0 Hz, 1H), 2.14 (dt, *J* = 13.2, 2.6 Hz, 1H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 157.9 (d, *J* = 237.5 Hz), 154.3, 137.6, 137.6, 129.0, 128.8, 127.8 (d, *J* = 6.8 Hz), 127.1, 126.1, 113.8 (d, *J* = 43.2 Hz), 113.8 (d, *J* = 1.5 Hz), 111.9 (d, *J* = 7.6 Hz), 107.8, 84.5, 61.4, 52.3, 28.0, 27.2, 14.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -127.25. HRMS (ESI): Calcd. for $C_{22}H_{21}N_3O_3F$ $[M+H]^+$: 394.1561; found: 394.1562.

(4) Ethyl-6-benzyl-9-chloro-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*] [1,3]oxazocine-1-carboxylate (**C_4**)



Red solid; M.p. 147-149 ºC, (56.3 mg, 81% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.05 (s, 1H), 7.33 (d, *J* = 2.6 Hz, 1H), 7.28 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 6.89 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.42 (d, *J* = 8.7 Hz, 1H), 5.63 (q, *J* = 2.1 Hz, 1H), 4.88 (d, *J* = 17.6 Hz, 1H), 4.60 (d, *J* = 17.6 Hz, 1H), 4.54 – 4.47 (m, 1H), 4.44 – 4.33 (m, 2H), 2.34 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.09 (dt, *J* = 13.2, 2.6 Hz, 1H), 1.48 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 158.5, 139.9, 137.2, 129.0, 128.7, 128.0, 127.1, 127.0, 126.7, 126.0, 122.3, 112.3, 107.3, 84.2, 61.4, 52.1, 27.8, 27.0, 14.3. HRMS (ESI): Calcd. for $C_{22}H_{21}N_3O_3Cl$ $[M+H]^+$: 410.1266; found: 410.1260.

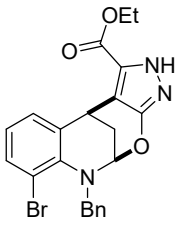
(5) Ethyl-6-benzyl-9-bromo-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*] [1,3]oxazocine-1-carboxylate (**C_5**)



White solid; M.p. 148-150 ºC, (61.6 mg, 80% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.30

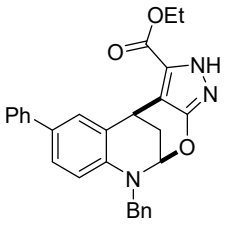
(s, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.06 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.40 (d, *J* = 8.7 Hz, 1H), 5.66 (q, *J* = 2.2 Hz, 1H),4.91 (d, *J* = 17.5 Hz, 1H), 4.63 (d, *J* = 17.6 Hz, 1H), 4.54 (dq, *J* = 10.9, 7.2 Hz, 1H), 4.47 – 4.36 (m, 2H), 2.38 (dt, *J* = 13.2, 3.0 Hz, 1H), 2.12 (dt, *J* = 13.2, 2.7 Hz, 1H), 1.52 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 158.7, 140.5, 137.2, 130.2, 129.6, 129.1, 128.8, 128.5, 127.2, 126.1, 113.0, 109.7, 107.4, 84.2, 61.5, 52.1, 27.8, 27.1, 14.5. HRMS (ESI): Calcd. for $C_{22}H_{21}N_3O_3Br$ $[M+H]^+$: 454.0761; found: 454.0750.

(6) Ethyl-6-benzyl-7-bromo-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*] [1,3]oxazocine-1-carboxylate (**C_6**)



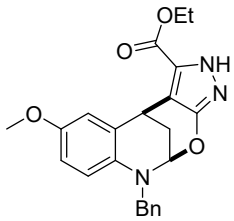
White solid; M.p. 149-151ºC, (33.1 mg, 43% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 1H), 7.11 – 7.01 (m, 3H), 6.35 (d, *J* = 8.7 Hz, 1H), 5.64 (q, *J* = 1.9 Hz, 1H), 4.86 (d, *J* = 17.6 Hz, 1H), 4.63 – 4.49 (m, 2H), 4.48 – 4.35 (m, 2H), 2.39 (dt, *J* = 13.2, 2.9 Hz, 1H), 2.11 (dt, *J* = 13.3, 2.6 Hz, 1H), 1.52 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 158.7, 140.2, 136.3, 131.9, 131.8, 130.3, 129.7, 128.6, 128.0, 121.0, 112.9, 110.0, 107.4, 84.4, 61.6, 52.0, 27.7, 27.1, 14.5. HRMS (ESI): Calcd. for $C_{22}H_{21}N_3O_3Br$ $[M+H]^+$: 454.0761; found: 454.0753.

(7) Ethyl-6-benzyl-9-phenyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_7**)



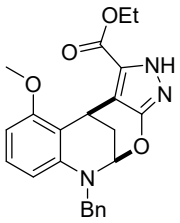
Red solid; M.p. 126-128 ºC, (52.9 mg, 69% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.75 (s, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 5H), 6.60 (d, *J* = 8.5 Hz, 1H), 5.67 (q, *J* = 2.1 Hz, 1H), 4.93 (d, *J* = 17.5 Hz, 1H), 4.68 (d, *J* = 17.6 Hz, 1H), 4.50 (d, *J* = 3.1 Hz, 1H), 4.42 – 4.33 (m, 2H), 2.37 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.16 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 158.7, 140.9, 140.7, 137.6, 130.8, 128.9, 128.7, 128.5, 127.0, 126.2, 126.2, 126.2, 125.7, 111.6, 108.1, 84.3, 61.3, 52.0, 28.0, 27.2, 14.3 HRMS (ESI): Calcd. for $C_{28}H_{26}N_3O_3$ $[M+H]^+$: 452.1969; found: 452.1965.

(8) Ethyl-6-benzyl-9-methoxy-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_8**)



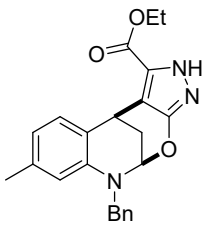
Red solid; M.p. 100-102 ºC, (55.1 mg, 80% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.17 (m, 3H), 7.00 (d, *J* = 2.9 Hz, 1H), 6.56 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.45 (d, *J* = 8.8 Hz, 1H), 5.69 (q, *J* = 2.1 Hz, 1H), 4.92 (d, *J* = 17.5 Hz, 1H), 4.62 (d, *J* = 17.6 Hz, 1H), 4.49 – 4.37 (m, 3H), 3.72 (s, 3H), 2.37 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.16 (dt, *J* = 13.2, 2.6 Hz, 1H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 159.2, 151.9, 138.1, 135.4, 128.9, 128.7, 127.7, 127.0, 126.2, 113.4, 112.3, 111.9, 108.3, 84.9, 61.3, 55.7, 52.3, 28.2, 27.4, 14.5. HRMS (ESI): Calcd. for $C_{23}H_{24}N_3O_4$ $[M+H]^+$: 406.1761; found: 406.1757.

(9) Ethyl-6-benzyl-10-methoxy-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C$_9$**)



Red solid; M.p. 140-142 ºC, (25.5 mg, 37% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.22 (s, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.17 (m, 3H), 6.93 (t, *J* = 8.3 Hz, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 6.24 (d, *J* = 8.3 Hz, 1H), 5.61 (q, *J* = 2.1 Hz, 1H), 5.01 (d, *J* = 3.2 Hz, 1H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.69 (d, *J* = 17.6 Hz, 1H), 4.53 – 4.47 (m, 1H), 4.34 – 4.27 (m, 1H), 3.86 (s, 3H), 2.34 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.04 (dt, *J* = 13.2, 2.7 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 159.35, 155.6, 142.8, 138.0, 129.2, 128.7, 127.5, 126.9, 126.2, 114.3, 107.6, 104.9, 101.1, 83.7, 60.9, 55.5, 52.2, 27.5, 20.3, 14.4. HRMS (ESI): Calcd. for $C_{23}H_{24}N_3O_4$ $[M+H]^+$: 406.1761; found: 406.1760.

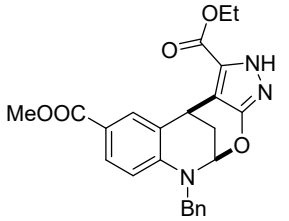
(10) Ethyl-6-benzyl-8-methyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C$_{10}$**)



Red solid; M.p. 117-119 ºC, (58.2 mg, 88% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.19 (m, 4H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.41 (s, 1H), 5.64 (q, *J* = 2.1 Hz, 1H), 4.91 (d, *J* = 17.6 Hz, 1H), 4.68 (d, *J* = 17.6 Hz, 1H), 4.48 – 4.36 (m, 3H), 2.35 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.20 – 2.08 (m, 4H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 159.0, 141.5, 137.9, 137.7, 128.8, 128.6, 127.0, 126.9, 126.3, 123.9, 118.7, 112.0, 108.8,

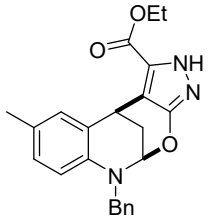
84.2, 61.2, 51.7, 27.6, 27.5, 21.6, 14.5. HRMS (ESI): Calcd. for $C_{23}H_{24}N_3O_3$ $[M+H]^+$: 390.1812; found: 390.1809.

(11) 1-ethyl 9-methyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{11}**)



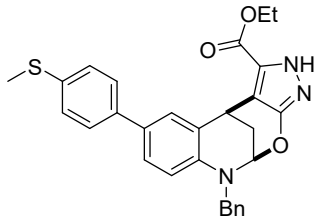
White solid; M.p. 157-159 ºC, (65.5 mg, 89% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.05 (s, 1H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 1H), 5.65 (q, *J* = 2.4 Hz, 1H), 4.93 (d, *J* = 17.5 Hz, 1H), 4.72 (d, *J* = 17.5 Hz, 1H), 4.59 – 4.39 (m, 3H), 3.83 (s, 3H), 2.39 (dt, *J* = 13.2, 3.0 Hz, 1H), 2.11 (dt, *J* = 13.3, 2.7 Hz, 1H), 1.57 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 159.6, 158.3, 145.5, 136.7, 129.9, 129.0, 128.8, 128.5, 127.2, 126.1, 126.1, 119.2, 110.7, 107.2, 83.7, 61.6, 52.0, 51.5, 27.8, 26.9, 14.1. HRMS (ESI): Calcd. for $C_{24}H_{24}N_3O_5$ $[M+H]^+$: 434.1710; found: 434.1710.

(12) Ethyl-6-benzyl-9-methyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{12}**)



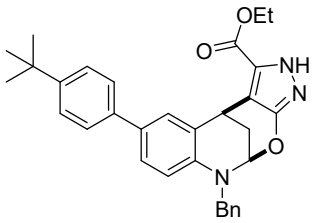
Red solid; M.p. 132-134 ºC, (54.9 mg, 83% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.35 (s, 1H), 7.30 (dd, *J* = 7.9, 6.5 Hz, 2H), 7.20 (dd, *J* = 7.4, 1.9 Hz, 4H), 6.80 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 5.66 (q, *J* = 2.1 Hz, 1H), 4.91 (d, *J* = 17.6 Hz, 1H), 4.64 (d, *J* = 17.6 Hz, 1H), 4.54 – 4.38 (m, 3H), 2.35 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.22 (s, 3H), 2.13 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 159.0, 139.1, 138.0, 128.9, 128.7, 128.1, 127.7, 127.0, 126.9, 126.5, 126.2, 111.2, 108.3, 84.6, 61.2, 52.0, 27.9, 27.4, 20.2, 14.5. HRMS (ESI): Calcd. for $C_{23}H_{24}N_3O_3$ $[M+H]^+$: 390.1812; found: 390.1808.

(13) Ethyl-6-benzyl-9-(4-(methylthio)phenyl)-2,5,6,11-tetrahydro-5,11-methanobenzo [*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{13}**)



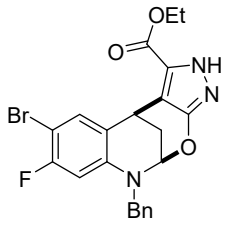
Red solid; M.p. 149-151 ºC, (53.3 mg, 63% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 7.64 – 7.58 (m, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.19 (m, 8H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.68 (s, 1H), 4.93 (d, *J* = 17.6 Hz, 1H), 4.68 (d, *J* = 17.6 Hz, 1H), 4.50 (s, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 2.42 – 2.32 (m, 1H), 2.17 (d, *J* = 13.2 Hz, 1H), 1.40 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 158.8, 140.9, 137.8, 137.6, 136.1, 130.2, 128.9, 128.8, 128.4, 127.1, 127.0, 126.6, 126.2, 126.0, 125.4, 111.7, 108.2, 84.4, 61.3, 52.1, 28.0, 27.3, 16.0, 14.4. HRMS (ESI): Calcd. for $C_{29}H_{28}N_3O_3S$ $[M+H]^+$: 498.1846; found: 498.1840.

(14) Ethyl-6-benzyl-9-(4-(tert-butyl)phenyl)-2,5,6,11-tetrahydro-5,11-methanobenzo [*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{14}**)



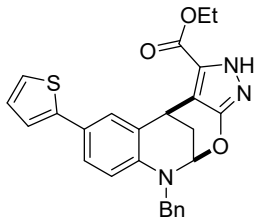
Red solid; M.p. 138-140 ºC, (70.7 mg, 82% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.73 (s, 1H), 7.63 (s, 1H), 7.49 – 7.22 (m, 10H), 6.59 (d, *J* = 8.4 Hz, 1H), 5.67 (s, 1H), 4.93 (d, *J* = 17.6 Hz, 1H), 4.67 (d, *J* = 17.5 Hz, 1H), 4.53 – 4.33 (m, 3H), 2.36 (d, *J* = 13.2 Hz, 1H), 2.17 (d, *J* = 13.1 Hz, 1H), 1.41 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 158.7, 149.0, 140.7, 137.9, 137.7, 130.8, 128.9, 128.7, 127.0, 127.0, 126.2, 126.1, 125.9, 125.6, 125.5, 111.6, 108.2, 84.4, 61.3, 52.0, 34.3, 31.3, 28.1, 27.3, 14.3. HRMS (ESI): Calcd. for $C_{32}H_{34}N_3O_3$ $[M+H]^+$: 508.2595; found: 508.2592.

(15) Ethyl-6-benzyl-9-bromo-8-fluoro-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*] pyrazolo[4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{15}**)



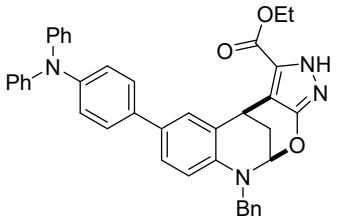
Red solid; M.p. 139-141 ºC, (42.4 mg, 53% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.58 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.32 (d, *J* = 11.2 Hz, 1H), 5.67 – 5.61 (m, 1H), 4.90 (d, *J* = 17.6 Hz, 1H), 4.66 – 4.49 (m, 2H), 4.45 – 4.37 (m, 2H), 2.37 (dt, *J* = 13.4, 3.0 Hz, 1H), 2.10 (dt, *J* = 13.2, 2.8 Hz, 1H), 1.51 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 159.3, 158.0 (d, *J* = 131.0 Hz), 142.2 (d, *J* = 9.7 Hz), 136.5, 130.6 (d, *J* = 1.6 Hz), 128.9, 128.9 (d, *J* = 14.6 Hz), 127.4, 126.1, 123.9 (d, *J* = 2.9 Hz), 107.4, 100.1(d, *J* = 27.6 Hz), 95.3 (d, *J* = 21.5 Hz), 83.7, 61.6, 52.4, 27.1, 27.1, 14.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.78. HRMS (ESI): Calcd. for $C_{22}H_{20}N_3O_3BrF$ $[M+H]^+$:472.0667; found: 472.0663.

(16) Ethyl-6-benzyl-9-(thiophen-2-yl)-2,5,6,11-tetrahydro-5,11-methanobenzo [*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{16}**)



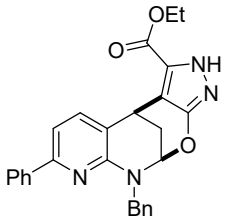
Red solid; M.p. 115-117 ºC, (26.4 mg, 34% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.42 (s, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 5.1 Hz, 1H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.01 (t, *J* = 4.3 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 1H), 5.70 (s, 1H), 4.95 (d, *J* = 17.6 Hz, 1H), 4.70 (d, *J* = 17.6 Hz, 1H), 4.47 (dq, *J* = 14.9, 7.4 Hz, 3H), 2.41 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.18 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.50 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 158.8, 144.6, 141.0, 137.5, 129.0, 128.8, 127.8, 127.1, 127.0, 126.2, 125.5, 124.9, 124.6, 123.2, 121.3, 111.7, 107.9, 84.4, 61.5, 52.1, 28.0, 27.3, 14.5. HRMS (ESI): Calcd. for $C_{26}H_{24}N_3O_3S$ $[M+H]^+$: 458.1533; found: 458.1527.

(17) Ethyl-6-benzyl-9-(4-(diphenylamino)phenyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{17}**)



Red solid; M.p. 156-158 ºC, (55.7 mg, 53% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.46 (s, 1H), 7.61 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.16 (m, 10H), 7.09 (t, *J* = 7.5 Hz, 6H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.68 (s, 1H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.69 (d, *J* = 17.5 Hz, 1H), 4.50 (s, 1H), 4.46 – 4.28 (m, 2H), 2.38 (d, *J* = 13.1 Hz, 1H), 2.18 (d, *J* = 13.1 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 158.8, 147.7, 146.1, 140.5, 137.7, 135.1, 130.4, 129.1, 128.9, 128.7, 127.0, 127.0, 126.9, 126.2, 125.8, 125.4, 124.2, 124.1, 122.6, 111.7, 108.3, 84.4, 61.3, 52.0, 28.0, 27.3, 14.4. HRMS (ESI): Calcd. for $C_{40}H_{35}N_4O_3$ $[M+H]^+$:619.2704; found: 619.2696.

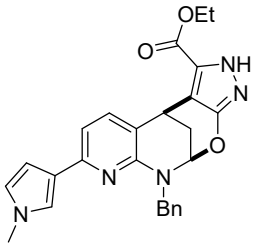
(18) Ethyl-6-benzyl-8-phenyl-2,5,6,11-tetrahydro-5,11-methanopyrazolo[4,3-*g*] pyrido[2,3-*d*][1,3]oxazocine-1-carboxylate (**C_{18}**)



Red solid; M.p. 117-119 ºC, (39.2 mg, 51% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.34 (s, 1H), 7.97 – 7.83 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.38 – 7.21 (m, 6H), 7.11

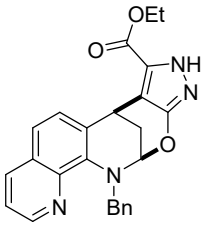
(d, *J* = 7.5 Hz, 1H), 5.79 (d, *J* = 15.4 Hz, 1H), 5.70 (q, *J* = 2.3 Hz, 1H), 4.62 (d, *J* = 15.4 Hz, 1H), 4.56 – 4.32 (m, 3H), 2.33 (dt, *J* = 13.2, 3.0 Hz, 1H), 2.03 (dt, *J* = 13.2, 2.6 Hz, 1H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 158.7, 153.4, 152.5, 139.4, 139.0, 134.5, 128.9, 128.4, 128.3, 128.3, 128.0, 127.0, 126.5, 119.6, 110.3, 108.1, 82.8, 61.3, 48.7, 27.6, 26.8, 14.4. HRMS (ESI): Calcd. for $C_{27}H_{25}N_4O_3$ $[M+H]^+$: 453.1921; found: 453.1917.

(19) Ethyl-6-benzyl-8-(1-methyl-1H-pyrrol-3-yl)-2,5,6,11-tetrahydro-5,11-methano pyrazolo[4,3-*g*]pyrido[2,3-*d*][1,3]oxazocine-1-carboxylate (**C_{19}**)



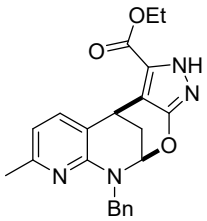
Red solid; M.p. 162-164 ºC, (34.0 mg, 44% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 7.75 – 7.44 (m, 1H), 7.37 – 7.17 (m, 5H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.51 (d, *J* = 35.2 Hz, 2H), 6.07 (s, 1H), 5.80 – 5.43 (m, 2H), 4.66 (d, *J* = 16.1 Hz, 1H), 4.52 – 4.32 (m, 3H), 3.59 (s, 3H), 2.35 (d, *J* = 12.9 Hz, 1H), 2.10 (d, *J* = 13.2 Hz, 1H), 1.60 – 1.37 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 158.9, 151.9, 149.3, 145.5, 138.7, 134.5, 132.4, 128.9, 128.5, 127.1, 126.9, 125.7, 117.3, 111.6, 110.0, 108.4, 107.2, 83.2, 61.3, 48.9, 36.9, 27.6, 26.9, 14.5. HRMS (ESI): Calcd. for $C_{26}H_{26}N_5O_3$ $[M+H]^+$: 456.2030; found: 456.2018.

(20) Ethyl-11-benzyl-2,4,11,12-tetrahydro-4,12-methanopyrazolo[4',3':7,8][1,3] oxazocino[5,4-*h*]quinoline-3-carboxylate (**C_{20}**)



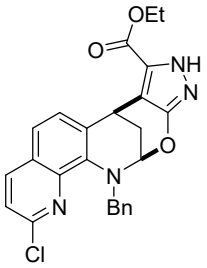
Yellowish brown solid; M.p. 114-116 ºC, (26.8 mg, 37% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.24 (s, 1H), 8.64 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.19 (m, 3H), 6.21 (d, *J* = 14.7 Hz, 1H), 5.62 (d, *J* = 2.6 Hz, 1H), 4.88 (d, *J* = 14.8 Hz, 1H), 4.53 – 4.41 (m, 3H), 2.35 (dt, *J* = 13.2, 2.8 Hz, 1H), 2.02 (dt, *J* = 13.2, 2.6 Hz, 1H), 1.49 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 158.6, 146.4, 139.9, 139.8, 138.8, 136.1, 129.1, 128.9, 128.9, 128.0, 127.8, 126.7, 126.7, 120.1, 118.2, 108.1, 82.8, 61.3, 53.1, 28.7, 27.4, 14.5. HRMS (ESI): Calcd. for $C_{25}H_{23}N_4O_3$ $[M+H]^+$: 427.1765; found: 427.1764.

(21) Ethyl-6-benzyl-8-methyl-2,5,6,11-tetrahydro-5,11-methanopyrazolo[4,3-*g*]pyrido [2,3-*d*][1,3]oxazocine-1-carboxylate (**C_{21}**)



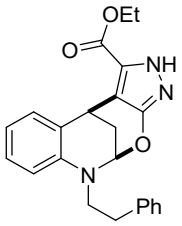
Red solid; M.p. 113-115 ºC, (26.5 mg, 40% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.39 (dd, *J* = 7.5, 4.9 Hz, 3H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 7.3 Hz, 1H), 5.67 (d, *J* = 15.4 Hz, 2H), 4.53 (d, *J* = 15.3 Hz, 1H), 4.42 (p, *J* = 7.1 Hz, 2H), 4.34 (s, 1H), 2.33 (s, 3H), 2.29 (dt, *J* = 13.1, 3.0 Hz, 1H), 1.97 (dd, *J* = 13.3, 2.6 Hz, 1H), 1.44 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 158.7, 155.0, 152.3, 139.0, 134.1, 128.8, 128.3, 128.2, 126.9, 117.6, 112.9, 108.4, 82.7, 61.2, 48.3, 27.5, 26.8, 24.2, 14.4. HRMS (ESI): Calcd. for $C_{22}H_{23}N_4O_3$ $[M+H]^+$: 391.1765; found: 391.1757.

(22) Ethyl-11-benzyl-9-chloro-2,4,11,12-tetrahydro-4,12-methanopyrazolo[4',3':7,8] [1,3]oxazocino[5,4-*h*]quinoline-3-carboxylate (**C_{22}**)



Red solid; M.p. 101-103 ºC, (21.1 mg, 27% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.29 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.64 (dd, *J* = 15.5, 7.8 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.16 (m, 3H), 5.89 (d, *J* = 14.8 Hz, 1H), 5.73 – 5.55 (m, 1H), 4.94 (d, *J* = 14.8 Hz, 1H), 4.61 – 4.36 (m, 3H), 2.36 (dt, *J* = 13.6, 2.9 Hz, 1H), 2.00 (dt, *J* = 13.4, 2.7 Hz, 1H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 158.5, 146.3, 139.1, 139.1, 138.6, 138.0, 129.2, 129.1, 128.8, 128.0, 127.7, 127.0, 126.7, 121.3, 117.8, 107.6, 82.9, 61.4, 53.2, 28.6, 27.4, 14.5. HRMS (ESI): Calcd. for $C_{25}H_{22}N_4O_3Cl$ $[M+H]^+$: 461.1375; found: 461.1369.

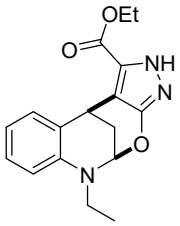
(23) Ethyl-6-phenethyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*] [1,3]oxazocine-1-carboxylate (**C_{23}**)



Red solid; M.p. 121-123 ºC, (56.9 mg, 86% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 (s, 1H), 7.39 – 7.27 (m, 3H), 7.28 – 7.19 (m, 3H), 7.19 – 7.11 (m, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.73 (td, *J* = 7.4, 1.1 Hz, 1H), 5.43 (dt, *J* = 3.6, 1.7 Hz, 1H), 4.56 – 4.29 (m, 3H), 3.96 – 3.83 (m, 1H), 3.71 – 3.61 (m, 1H), 3.04 – 2.87 (m, 2H), 2.21 (dt, *J* = 13.1, 3.0 Hz, 1H), 1.96 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 159.1, 140.7, 139.2, 129.4,

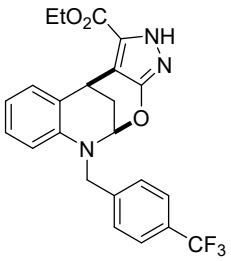
128.8, 128.6, 127.8, 127.4, 126.8, 126.4, 117.7, 110.5, 108.8, 85.1, 61.2, 50.8, 33.9, 27.8, 26.8, 14.5. HRMS (ESI): Calcd. for $C_{23}H_{24}N_3O_3$ $[M+H]^+$: 390.1812; found: 390.1802.

(24) Ethyl-6-ethyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*] [1,3]oxazocine-1-carboxylate (**C_{24}**)



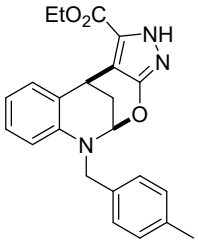
Red solid; M.p. 132-134 ºC, (38.3 mg, 72% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 7.33 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.14 – 7.06 (m, 1H), 7.14 – 7.06 (m, 2H), 5.64 (q, *J* = 2.2 Hz, 1H), 4.52 – 4.31 (m, 3H), 3.84 – 3.71 (m, 1H), 3.52 – 3.41 (m, 1H), 2.29 (dt, *J* = 13.1, 3.0 Hz, 1H), 1.99 (dt, *J* = 13.0, 2.6 Hz, 1H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 159.1, 140.6, 128.8, 127.7, 127.2, 126.7, 117.3, 110.5, 108.6, 84.7, 61.2, 43.4, 28.0, 27.1, 14.4, 12.7. HRMS (ESI): Calcd. for $C_{17}H_{20}N_3O_3$ $[M+H]^+$: 314.1499; found: 314.1491.

(25) Ethyl-6-(4-(trifluoromethyl)benzyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*] pyrazolo[4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{25}**)



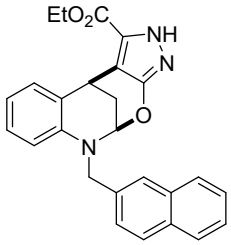
Red solid; M.p. 103-105 ºC, (48.2 mg, 64% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.38 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.99 (td, *J* = 7.7, 1.7 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 5.66 (q, *J* = 2.2 Hz, 1H), 4.99 (d, *J* = 17.8 Hz, 1H), 4.71 (d, *J* = 17.8 Hz, 1H), 4.55 – 4.34 (m, 3H), 2.39 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.16 (dt, *J* = 13.2, 2.6 Hz, 1H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 158.7, 142.1, 141.0, 129.4 (d, *J* = 32.3 Hz), 129.0, 127.8, 127.2, 126.8, 126.6, 125.7 (d, *J* = 4.0 Hz), 124.1 (d, *J* = 272.0 Hz), 118.3, 111.2, 108.3, 84.6, 61.3, 52.1, 27.9, 27.3, 14.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.40. HRMS (ESI): Calcd. for $C_{23}H_{21}N_3O_3F_3$ $[M+H]^+$: 444.1530; found: 444.1528.

(26) Ethyl-6-(4-methylbenzyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{26}**)



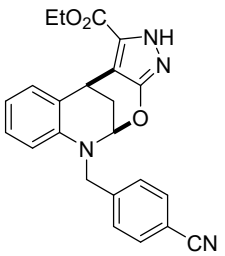
Red solid; M.p. 102-104 ºC, (36.4 mg, 55% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 7.36 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.10 (s, 4H), 6.98 (td, *J* = 7.8, 1.7 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 5.65 (q, *J* = 2.1 Hz, 1H), 4.87 (d, *J* = 17.5 Hz, 1H), 4.62 (d, *J* = 17.5 Hz, 1H), 4.48 – 4.36 (m, 3H), 2.40 – 2.27 (m, 4H), 2.11 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 158.8, 141.5, 136.5, 134.6, 129.4, 128.9, 127.7, 127.0, 126.6, 126.2, 117.7, 111.3, 108.3, 84.3, 61.2, 51.6, 27.9, 27.2, 20.9, 14.4. HRMS (ESI): Calcd. for $C_{23}H_{24}N_3O_3$ $[M+H]^+$: 390.1812; found: 390.1803.

(27) Ethyl-6-(naphthalen-2-ylmethyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*] pyrazolo[4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{27}**)



White solid; M.p. 139-141 ºC, (53.5 mg, 74% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.57 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.74 – 7.67 (m, 1H), 7.60 (s, 1H), 7.46 – 7.30 (m, 4H), 7.02 – 6.92 (m, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 5.72 (s, 1H), 5.07 (d, *J* = 17.5 Hz, 1H), 4.80 (d, *J* = 17.6 Hz, 1H), 4.51 – 4.35 (m, 3H), 2.38 (dt, *J* = 13.2, 2.9 Hz, 1H), 2.20 (dt, *J* = 13.2, 2.7 Hz, 1H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 158.8, 141.5, 135.3, 133.4, 132.6, 128.5, 127.8, 127.6, 127.6, 127.1, 126.7, 126.1, 125.6, 124.7, 124.6, 117.9, 111.4, 108.4, 84.4, 61.2, 52.2, 27.9, 27.3, 14.4. HRMS (ESI): Calcd. for $C_{26}H_{24}N_3O_3$ $[M+H]^+$: 426.1812; found: 426.1809.

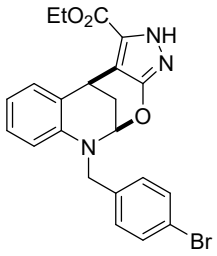
(28) Ethyl-6-(4-cyanobenzyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{28}**)



Red solid; M.p. 151-153 ºC, (28.6 mg, 42% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.39 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.02 – 6.96 (m, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 8.2 Hz, 1H), 5.66 (d, *J* = 2.9 Hz, 1H), 5.01 (d, *J* = 18.1 Hz, 1H), 4.71 (d, *J* = 18.1 Hz, 1H), 4.60 – 4.31 (m, 3H), 2.41 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.17

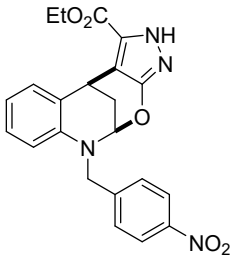
(dt, *J* = 13.2, 2.7 Hz, 1H), 1.48 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 158.8, 143.7, 140.8, 132.6, 129.0, 127.8, 127.3, 127.1, 126.9, 118.7, 118.5, 111.1, 111.0, 108.3, 84.8, 61.4, 52.4, 27.8, 27.3, 14.5. HRMS (ESI): Calcd. for $C_{23}H_{21}N_4O_3$ $[M+H]^+$: 401.1608; found: 401.1608.

(29) Ethyl-6-(4-bromobenzyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{29}**)



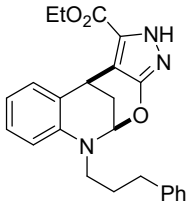
Red solid; M.p. 111-113 ºC, (39.3 mg, 51% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.39 (s, 1H), 7.49 – 7.36 (m, 3H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.06 – 7.01 (m, 1H), 6.75 (td, *J* = 7.4, 1.1 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 5.68 (q, *J* = 2.6 Hz, 1H), 4.91 (d, *J* = 17.6 Hz, 1H), 4.65 (d, *J* = 17.6 Hz, 1H), 4.54 – 4.40 (m, 3H), 2.41 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.17 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 158.8, 141.1, 136.9, 131.8, 128.9, 128.1, 127.7, 127.2, 126.7, 120.8, 118.2, 111.2, 108.3, 84.5, 61.3, 51.7, 27.9, 27.3, 14.4. HRMS (ESI): Calcd. for $C_{22}H_{21}N_3O_3Br$ $[M+H]^+$: 454.0760; found: 454.0748.

(30) Ethyl-6-(4-nitrobenzyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{30}**)



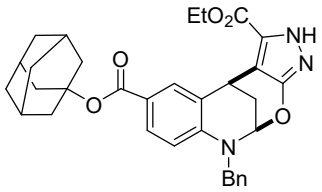
Yellow solid; M.p. 165-167 ºC, (22.1 mg, 31% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 8.17 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 20.3, 7.9 Hz, 3H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 5.70 (s, 1H), 5.08 (d, *J* = 18.1 Hz, 1H), 4.79 (s, 1H), 4.53 – 4.44 (m, 3H), 2.45 (dt, *J* = 13.2, 3.1 Hz, 1H), 2.28 – 2.11 (m, 1H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 158.8, 147.2, 145.9, 140.7, 129.0, 127.9, 127.4, 127.2, 127.0, 124.1, 118.7, 111.2, 108.4, 85.0, 61.4, 52.4, 27.9, 27.4, 14.5. HRMS (ESI): Calcd. for $C_{22}H_{21}N_4O_5$ $[M+H]^+$: 421.1506; found: 421.1501.

(31) Ethyl-6-(4-phenylbutyl)-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1-carboxylate (**C_{31}**)



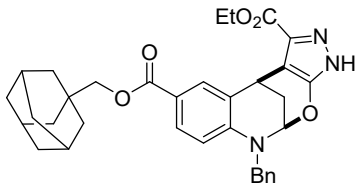
Red solid; M.p. 113-115 ºC, (45.9 mg, 67% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.22 (s, 1H), 7.37 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 7.12 (td, *J* = 7.8, 1.7 Hz, 1H), 6.73 (td, *J* = 7.3, 1.0 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 5.66 (q, *J* = 2.2 Hz, 1H), 4.56 – 4.33 (m, 3H), 3.82 – 3.68 (m, 1H), 3.46 – 3.37 (m, 1H), 2.69 (td, *J* = 7.3, 2.8 Hz, 2H), 2.31 (dt, *J* = 13.0, 3.0 Hz, 1H), 2.03 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.74 (dq, *J* = 8.7, 5.7, 4.5 Hz, 4H), 1.49 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 159.0, 142.2, 140.9, 128.8, 128.3, 128.3, 127.6, 127.2, 126.6, 125.8, 117.4, 110.6, 108.6, 84.9, 61.2, 49.0, 35.6, 28.8, 27.9, 27.0, 26.9, 14.4. HRMS (ESI): Calcd. for $C_{25}H_{28}N_3O_3$ $[M+H]^+$: 418.2125; found: 418.2120.

(32) 9-(adamantan-1-yl) 1-ethyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*] pyrazolo[4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{32}**)



Red solid; M.p. 125-127 ºC, (61.1 mg, 65% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.88 (s, 1H), 7.96 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.53 (d, *J* = 8.7 Hz, 1H), 5.65 (s, 1H), 4.94 (d, *J* = 17.5 Hz, 1H), 4.72 (d, *J* = 17.5 Hz, 1H), 4.59 – 4.39 (m, 3H), 2.39 (d, *J* = 13.1 Hz, 1H), 2.19 (d, *J* = 14.9 Hz, 8H), 2.10 (d, *J* = 13.2 Hz, 1H), 1.73 – 1.63 (m, 7H), 1.55 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 159.6, 158.4, 145.0, 136.9, 129.8, 129.1, 128.8, 128.2, 127.1, 126.1, 125.9, 121.4, 110.6, 107.3, 83.9, 80.0, 61.5, 52.1, 41.4, 36.2, 31.5, 30.8, 27.9, 27.1, 22.5, 14.6, 14.0. HRMS (ESI): Calcd. for $C_{33}H_{36}N_3O_5$ $[M+H]^+$: 554.2649; found: 554.2643.

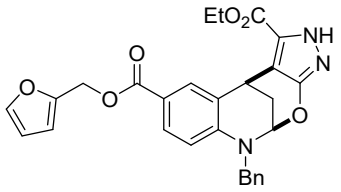
(33) 9-(adamantan-1-ylmethyl) 1-ethyl-6-benzyl-3,5,6,11-tetrahydro-5,11-methanobenzo[*d*] pyrazolo[4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{33}**)



Red solid; M.p. 118-120 ºC, (39.5 mg, 41% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.74 (s, 1H), 8.08 (d, *J* = 2.1 Hz, 1H), 7.71 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 1H), 5.67 (s, 1H), 4.96 (d, *J* = 17.5 Hz, 1H), 4.73 (d, *J* = 17.5 Hz, 1H), 4.56 – 4.39 (m, 3H), 3.86 (q, *J* = 10.7 Hz, 2H), 2.41 (dt, *J* = 13.2, 2.9 Hz, 1H), 2.14 (dt, *J* = 13.2, 2.7 Hz, 1H), 2.00 – 1.87 (m, 3H), 1.76 – 1.63 (m, 7H), 1.60 (s, 5H), 1.54 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 159.4, 158.4, 145.4, 136.8, 129.8,

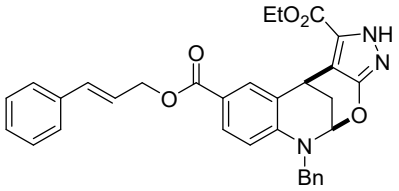
129.1, 128.8, 128.6, 127.2, 126.2, 126.1, 119.8, 110.7, 107.4, 83.9, 73.8, 61.6, 52.2, 39.3, 36.9, 33.5, 31.5, 28.0, 27.9, 27.0, 22.6, 14.4, 14.1. HRMS (ESI): Calcd. for $C_{34}H_{38}N_3O_5$ $[M+H]^+$: 568.2806; found: 568.2801.

(34) 1-ethyl 9-(furan-2-ylmethyl)-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{34}**)



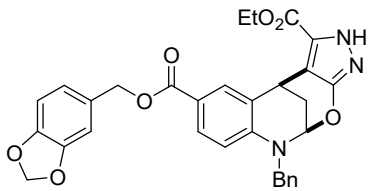
Light yellow solid; M.p. 143-145 ºC, (39.0 mg, 46% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.90 (s, 1H), 8.01 (s, 1H), 7.71 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.40 (s, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.54 (d, *J* = 8.6 Hz, 1H), 6.43 (d, *J* = 3.3 Hz, 1H), 6.35 (t, *J* = 2.5 Hz, 1H), 5.64 (s, 1H), 5.27 (d, *J* = 13.1 Hz, 1H), 5.19 (d, *J* = 13.1 Hz, 1H), 4.93 (d, *J* = 17.5 Hz, 1H), 4.72 (d, *J* = 17.5 Hz, 1H), 4.51 – 4.38 (m, 3H), 2.38 (dt, *J* = 13.2, 2.9 Hz, 1H), 2.09 (dt, *J* = 13.1, 2.7 Hz, 1H), 1.47 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 159.6, 158.4, 149.8, 145.6, 143.0, 136.7, 130.2, 129.1, 128.8, 128.5, 127.2, 126.1, 118.9, 110.8, 110.5, 110.4, 107.1, 83.8, 61.6, 57.9, 52.1, 27.9, 26.9, 14.1. HRMS (ESI): Calcd. for $C_{28}H_{26}N_3O_6$ $[M+H]^+$: 500.1816; found: 500.1810.

(35) 9-cinnamyl 1-ethyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{35}**)



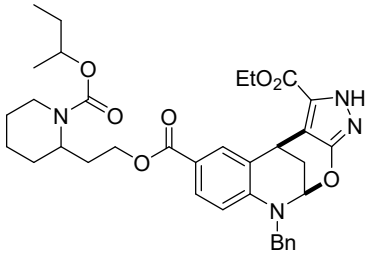
Red solid; M.p. 122-124 ºC, (47.3 mg, 52% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.92 (s, 1H), 8.07 (d, *J* = 2.3 Hz, 1H), 7.74 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.24 (q, *J* = 7.6, 6.7 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 6.42 – 6.26 (m, 1H), 5.65 (d, *J* = 3.4 Hz, 1H), 5.00 – 4.88 (m, 3H), 4.73 (d, *J* = 17.5 Hz, 1H), 4.51 – 4.35 (m, 3H), 2.39 (dt, *J* = 13.2, 2.9 Hz, 1H), 2.20 – 2.08 (m, 1H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 159.6, 158.4, 145.6, 136.7, 136.2, 133.8, 130.1, 128.8, 128.6, 128.5, 128.3, 127.9, 127.2, 126.5, 126.1, 126.1, 123.6, 119.2, 110.8, 107.2, 83.8, 64.9, 61.7, 52.1, 27.9, 27.0, 14.3. HRMS (ESI): Calcd. for $C_{32}H_{30}N_3O_5$ $[M+H]^+$: 536.2180; found: 536.2175.

(36) 9-(benzo[d][1,3]dioxol-5-ylmethyl) 1-ethyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo [*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{36}**)



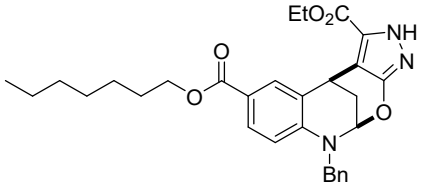
Red solid; M.p. 121-123 ºC, (63.9 mg, 68% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.98 (s, 1H), 8.02 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.93 – 6.83 (m, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 5.92 (s, 2H), 5.64 (s, 1H), 5.30 – 5.10 (m, 2H), 4.92 (d, *J* = 17.5 Hz, 1H), 4.71 (d, *J* = 17.5 Hz, 1H), 4.50 – 4.32 (m, 3H), 2.38 (d, *J* = 13.2 Hz, 1H), 2.09 (d, *J* = 13.2 Hz, 1H), 1.44 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 159.6, 158.3, 147.6, 147.4, 145.5, 136.7, 130.1, 130.1, 129.1, 128.8, 128.5, 127.2, 126.1, 126.1, 122.0, 119.1, 110.8, 108.9, 108.1, 107.2, 101.0, 83.8, 66.0, 61.6, 52.1, 27.8, 26.9, 14.2. HRMS (ESI): Calcd. for $C_{31}H_{26}N_3O_7$ [M-H]$^-$: 552.1776; found: 552.1773.

(37) 9-(2-(1-(sec-butoxycarbonyl)piperidin-2-yl)ethyl) 1-ethyl -6-benzyl-2,5,6,11-tetrahydro-5,11 -methanobenzo[*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{37}**)



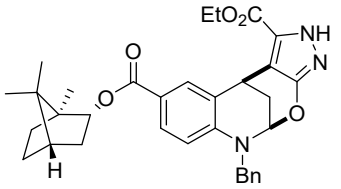
Red solid; M.p. 98 -100 ºC, (66.4 mg, 62% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.90 (s, 1H), 8.04 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.25 (q, *J* = 7.4, 6.6 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 1H), 5.67 (s, 1H), 4.95 (d, *J* = 17.5 Hz, 1H), 4.80 – 4.66 (m, 2H), 4.56 – 4.40 (m, 4H), 4.31 – 4.21 (m, 2H), 4.06 (s, 1H), 2.85 (t, *J* = 13.4 Hz, 1H), 2.51 – 2.32 (m, 1H), 2.17 – 2.01 (m, 3H), 1.92 – 1.79 (m, 1H),1.65 – 1.39 (m, 7H), 1.42 (dt, *J* = 13.5, 6.6 Hz, 2H), 1.14 (t, *J* = 5.5 Hz, 3H), 0.90 – 0.77 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 159.5, 158.3, 155.4, 145.4, 136.8, 129.8, 129.1, 128.8, 128.6, 127.2, 126.1, 126.1, 119.4, 110.7, 107.2, 83.8, 72.9, 62.0, 61.6, 52.1, 47.9, 47.9, 28.9, 27.9, 27.0, 25.4, 19.6, 19.6, 18.9, 14.3, 9.6, 9.6. HRMS (ESI): Calcd. for $C_{35}H_{41}N_4O_7$ [M-H]$^-$: 629.2981; found:629.2979.

(38) 1-ethyl 9-heptyl -6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*] [1,3]oxazocine-1,9-dicarboxylate (**C_{38}**)



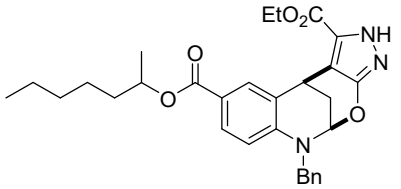
Red solid; M.p. 107 -109 ºC, (47.5 mg, 54% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.89 (s, 1H), 8.04 (d, *J* = 2.1 Hz, 1H), 7.70 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 1H), 5.67 (s, 1H), 4.95 (d, *J* = 17.5 Hz, 1H), 4.74 (d, *J* = 17.5 Hz, 1H), 4.59 – 4.42 (m, 3H), 4.25 (t, *J* = 6.7 Hz, 2H), 2.41 (dt, *J* = 13.2, 2.9 Hz, 1H), 2.12 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.75 – 1.67 (m, 2H), 1.57 (t, *J* = 7.1 Hz, 3H), 1.45 – 1.23 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 159.6, 158.4, 145.4, 136.8, 129.9, 128.8, 128.5, 127.2, 126.1, 119.7, 110.8, 107.3, 83.9, 64.5, 61.7, 52.1, 31.7, 28.9, 28.8, 27.9, 27.0, 25.9, 22.5, 14.3, 14.0. HRMS (ESI): Calcd. for $C_{30}H_{36}N_3O_5$ [M+H]$^+$: 518.2649; found: 518.2647.

(39) 1-ethyl 9-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{39}**)



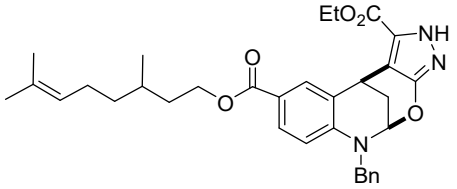
Red solid; M.p. 117 - 119 ºC, (52.9 mg, 56% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.58 (s, 1H), 8.06 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.57 (d, *J* = 8.6 Hz, 1H), 5.68 (s, 1H), 5.06 (td, *J* = 9.5, 4.8 Hz, 1H), 4.96 (d, *J* = 17.5 Hz, 1H), 4.74 (d, *J* = 17.5 Hz, 1H), 4.59 – 4.42 (m, 3H), 2.57 – 2.33 (m, 2H), 2.25 – 1.98 (m, 2H), 1.89 – 1.64 (m, 2H), 1.57 – 1.51 (m, 3H), 1.41 – 1.20 (m, 2H), 1.06 (dt, *J* = 13.7, 3.4 Hz, 1H), 0.94 (s, 3H), 0.90 – 0.84 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 166.7, 159.4, 159.4, 158.5, 145.3, 145.3, 136.8, 129.8, 129.2, 128.9, 128.5, 127.3, 126.2, 126.1, 120.2, 120.2, 110.7, 107.6, 107.5, 84.0, 83.9, 79.7, 79.6, 61.6, 61.6, 52.2, 52.2, 49.0, 49.0, 47.8, 47.7, 44.9, 44.9, 36.9, 36.9, 28.0, 27.9, 27.9, 27.4, 27.3, 27.1, 27.1, 19.7, 18.9, 14.5, 14.5, 13.5, 13.5. HRMS (ESI): Calcd. for $C_{33}H_{38}N_3O_5$ $[M+H]^+$: 556.2806; found: 556.2801.

(40) 1-ethyl 9-(heptan-2-yl)-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo [4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{40}**)



Red solid; M.p. 95 - 97 ºC, (44.8 mg, 51% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.27 (s, 1H), 8.04 (d, *J* = 6.4 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (q, *J* = 7.4, 6.1 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 1H), 5.66 (s, 1H), 5.12 (p, *J* = 6.3 Hz, 1H), 4.94 (d, *J* = 17.5 Hz, 1H), 4.72 (d, *J* = 17.5 Hz, 1H), 4.61 – 4.35 (m, 3H), 2.40 (d, *J* = 13.1 Hz, 1H), 2.11 (d, *J* = 13.2 Hz, 1H), 1.80 – 1.48 (m, 5H), 1.44 – 1.17 (m, 9H), 0.87 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 166.0, 159.7, 159.6, 158.3, 145.3, 145.2, 136.8, 136.8, 129.8, 129.8, 129.1, 128.7, 128.4, 128.3, 127.1, 126.1, 126.0, 120.0, 120.0, 110.7, 110.7, 107.2, 107.1, 83.8, 83.8, 70.8, 70.7, 61.6, 61.5, 52.1, 52.1, 36.0, 36.0, 31.6, 31.5, 27.9, 27.9, 27.0, 25.0, 22.4, 20.1, 20.1, 14.4, 14.4, 13.9, 13.9. HRMS (ESI): Calcd. for $C_{30}H_{36}N_3O_5$ $[M+H]^+$: 518.2649; found: 518.2644.

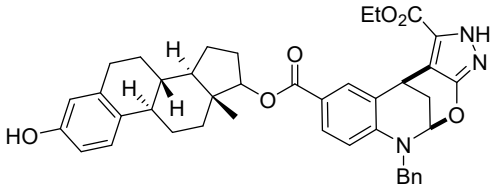
(41) 9-(3,7-dimethyloct-6-en-1-yl) 1-ethyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo [*d*]pyrazolo[4,3-g][1,3]oxazocine-1,9-dicarboxylate (**C_{41}**)



Red solid; M.p. 97 - 99 ºC, (64.4 mg, 68% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.78 (s,

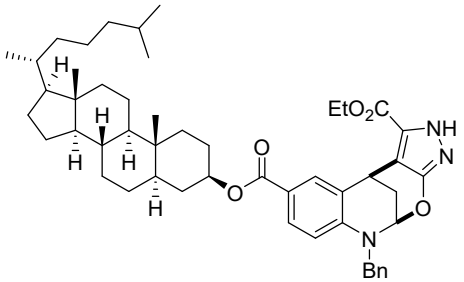
1H), 8.04 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 1H), 5.67 (s, 1H), 5.08 (t, *J* = 7.3 Hz, 1H), 4.95 (d, *J* = 17.5 Hz, 1H), 4.74 (d, *J* = 17.5 Hz, 1H), 4.56 – 4.40 (m, 3H), 4.77 – 4.43 (m, 2H), 2.41 (dt, *J* = 13.5, 3.1 Hz, 1H), 2.13 (d, *J* = 13.2 Hz, 1H), 2.05 – 1.92 (m, 3H), 1.84 – 1.72 (m, 2H), 1.67 – 1.47 (m, 9H), 1.42 – 1.31 (m, 1H), 1.21 (dt, *J* = 14.3, 7.4 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 159.6, 158.5, 145.4, 136.8, 131.2, 129.9, 129.1, 128.8, 128.5, 127.2, 126.1, 124.5, 119.7, 110.8, 109.7, 107.3, 83.8, 62.9, 61.7, 52.1, 37.0, 35.6, 29.5, 27.9, 27.1, 25.6, 25.3, 19.4, 17.6, 14.4. HRMS (ESI): Calcd. for $C_{33}H_{40}N_3O_5$ $[M+H]^+$: 558.2962; found: 558.2959.

(42) 1-ethyl 9-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a] phenanthren-17-yl) -6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3] oxazocine-1,9-dicarboxylate (**C_{42}**)



Light yellow solid; M.p. 128 - 130 ºC, (73.3 mg, 64% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.64 (s, 1H), 8.06 (dd, *J* = 11.3, 2.0 Hz, 1H), 7.84 – 7.60 (m, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.73 – 6.62 (m, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 6.55 (dd, *J* = 8.9, 2.1 Hz, 1H), 5.66 (s, 1H), 5.06 – 4.83 (m, 2H), 4.71 (d, *J* = 17.6 Hz, 1H), 4.60 – 4.36 (m, 3H), 2.87 – 2.63 (m, 2H), 2.48 – 2.37 (m, 1H), 2.33 – 2.19 (m, 2H), 2.20 – 2.09 (m, 2H), 1.93 – 1.81 (m, 2H), 1.75 (dd, *J* = 13.5, 5.9 Hz, 1H), 1.68 – 1.61 (m, 1H), 1.52 (dt, *J* = 9.2, 7.2 Hz, 3H), 1.48 – 1.37 (m, 4H), 1.33 – 1.22 (m, 3H), 0.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 159.5, 159.4, 158.4, 153.8, 145.4, 145.4, 137.9, 137.9, 136.8, 136.8, 131.9, 129.9, 129.9, 129.3, 129.2, 128.8, 128.6, 128.5, 127.3, 126.3, 126.2, 126.2, 126.1, 119.9, 119.9, 115.3, 112.8, 110.8, 107.6, 107.4, 84.0, 84.0, 82.6, 82.6, 61.7, 61.7, 52.2, 52.2, 49.7, 49.7, 43.7, 43.3, 43.2, 38.5, 36.9, 36.8, 29.5, 27.9, 27.8, 27.7, 27.6, 27.1, 27.0, 27.0, 26.2, 23.3, 23.3, 14.5, 14.4, 12.2, 12.2. HRMS (ESI): Calcd. for $C_{41}H_{42}N_3O_6$ $[M-H]^-$: 672.3079; found: 672.3078.

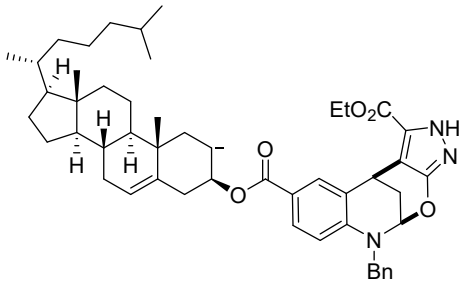
(43) 9-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[a] phenanthrene-3-yl)1-ethyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3]Oxazocine-1,9-dicarboxylate (**C_{43}**)



Red solid; M.p. 141 - 143 ºC, (33.6 mg, 25% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.50 (s, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.70 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 1H), 5.66 (s, 1H), 5.12 – 4.85 (m, 2H), 4.74 (d, *J* = 17.5 Hz, 1H), 4.58 – 4.33 (m, 3H), 2.41 (dt, *J* = 13.2, 3.0 Hz, 1H), 2.12 (dt, *J* = 13.2,

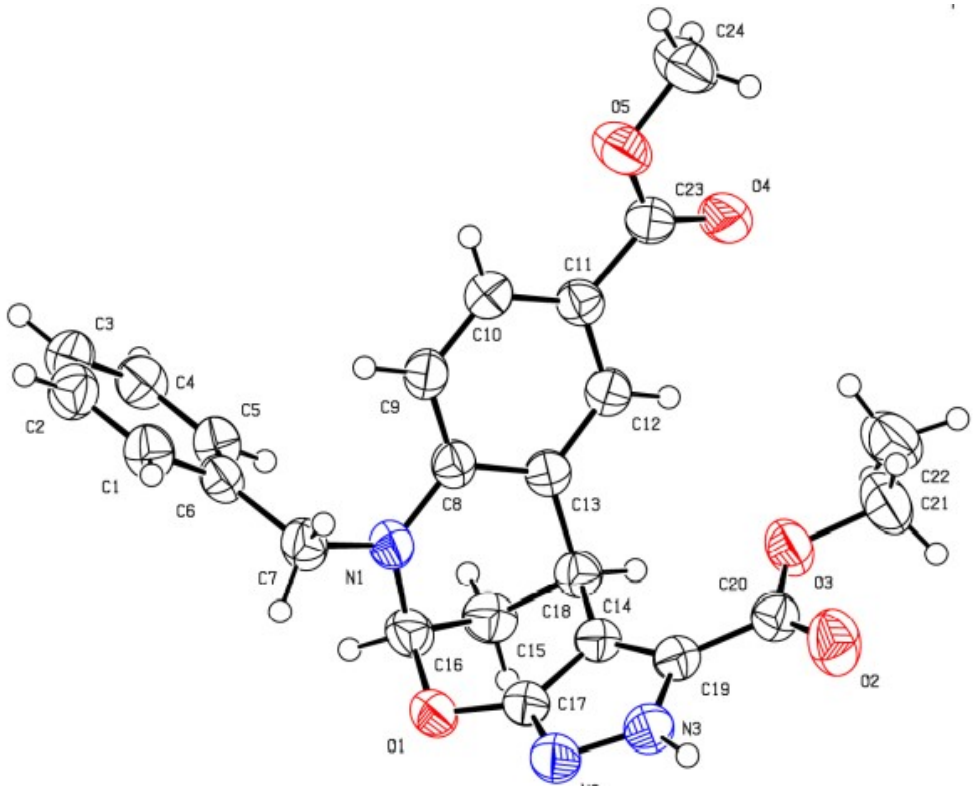
2.8 Hz, 1H), 1.97 (dt, *J* = 12.6, 3.5 Hz, 1H), 1.89 (dt, *J* = 13.3, 4.3 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.75 (dt, *J* = 13.6, 4.0 Hz, 1H), 1.66 (dt, *J* = 11.9, 5.1 Hz, 2H), 1.63 – 1.47 (m, 7H), 1.40 – 1.19 (m, 10H), 1.17 – 0.96 (m, 10H), 0.92 – 0.82 (m, 13H), 0.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 159.6, 158.6, 145.3, 136.9, 130.0, 129.1, 128.9, 128.4, 127.3, 126.2, 126.0, 120.2, 110.8, 107.3, 83.9, 73.6, 61.7, 56.4, 56.2, 54.2, 52.2, 44.7, 44.6, 42.6, 40.0, 39.5, 36.8, 36.1, 35.8, 35.5, 34.2, 34.2, 32.0, 28.6, 28.2, 28.0, 27.7, 27.6, 27.1, 24.2, 23.8, 22.8, 22.5, 21.2, 18.6, 14.6, 12.2, 12.0. HRMS (ESI): Calcd. for $C_{50}H_{66}N_3O_5$ [M-H]$^-$: 788.5008; found: 788.5005.

(44) 9-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)1-ethyl-6-benzyl-2,5,6,11-tetrahydro-5,11-methanobenzo[*d*]pyrazolo[4,3-*g*][1,3]oxazocine-1,9-dicarboxylate (**C_{44}**)



Red solid; M.p. 137 - 139 ºC, (41.4 mg, 31% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.02 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 5.3 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 1H), 5.67 (s, 1H), 5.40 (s, 1H), 4.96 (d, *J* = 17.6 Hz, 1H), 4.86 – 4.69 (m, 2H), 4.59 – 4.39 (m, 3H), 2.42 (d, *J* = 10.5 Hz, 3H), 2.13 (d, *J* = 13.2 Hz, 1H), 2.06 – 1.92 (m, 4H), 1.91 – 1.79 (m, 3H), 1.74 – 1.65 (m, 3H), 1.60 (t, *J* = 7.1 Hz, 3H), 1.56 – 1.43 (m, 6H), 1.37 – 1.31 (m, 4H), 1.29 – 1.24 (m, 1H), 1.22 – 1.07 (m, 5H), 1.04 (s, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.88 – 0.87 (m, 3H), 0.86 (s, 3H), 0.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 159.529, 158.7, 145.4, 139.7, 136.9, 130.0, 129.1, 128.9, 128.5, 127.3, 126.2, 126.0, 122.7, 120.1, 110.8, 107.4, 83.9, 73.8, 61.7, 56.7, 56.1, 52.2, 50.0, 42.3, 39.7, 39.5, 38.3, 37.0, 36.6, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 28.0, 27.1, 24.3, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 14.6, 11.8. HRMS (ESI): Calcd. for $C_{50}H_{64}N_3O_5$ [M-H]$^-$: 786.4851; found: 786.4847.

Crystallographic data of compound C_{11}



Crystal data and structure refinement for C_{11}(CCDC 2099592).

Identification code	WRJ-210125WYM
Empirical formula	$C_{24}H_{23}N_3O_5$
Formula weight	433.45
Temperature/K	299(1)
Crystal system	monoclinic
Space group	C2/c
a/Å	19.1728(5)
b/Å	12.7276(3)
c/Å	19.2357(6)
α/°	90.00
β/°	117.121(4)
γ/°	90.00
Volume/Å^3	4177.8(2)
Z	8
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	0.806
F(000)	1824.0
Crystal size/mm^3	0.25 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	8.66 to 155.56
Index ranges	$-23 \le h \le 23$, $-15 \le k \le 15$, $-23 \le l \le 18$
Reflections collected	13079
Independent reflections	4302 [R_{int} = 0.0156, R_{sigma} = 0.0179]
Data/restraints/parameters	4302/0/295
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1203
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.1249
Largest diff. peak/hole / e $Å^{-3}$	0.37/-0.25

Crystal structure determination of [WRJ-210125WYM] (C_{11})

Crystal Data for $C_{24}H_{23}N_3O_5$ (M =433.45 g/mol): monoclinic, space group C2/c (no. 15), a = 19.1728(5) Å, b = 12.7276(3) Å, c = 19.2357(6) Å, β = 117.121(4)°, V = 4177.8(2) $Å^3$, Z = 8, T = 299(1) K, μ(CuKα) = 0.806 mm^{-1}, *Dcalc* = 1.378 g/cm^3, 13079 reflections measured (8.66° ≤ 2Θ ≤ 155.56°), 4302 unique (R_{int} = 0.0156, R_{sigma} = 0.0179) which were used in all calculations. The final R_1 was 0.0447 (>2sigma(I)) and wR_2 was 0.1249 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for WRJ-210125WYM. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5456.4(8)	6261.6(9)	338.1(7)	53.7(3)
O2	6316.4(9)	10680.7(11)	434.4(9)	72.2(4)
O3	5788.6(8)	10304.3(9)	1230.5(8)	59.1(3)
O4	6535.6(8)	10119.2(10)	3907.5(7)	63.2(4)
O5	7620.4(8)	9171.2(11)	4579.3(8)	66.7(4)
N1	6019.0(8)	6072.5(10)	1719.9(8)	47.8(3)
N2	5994.1(9)	7527.7(11)	-149.3(8)	52.6(3)
N3	6119.3(9)	8571.9(12)	-29.3(8)	50.6(3)
C1	7198.1(10)	3680.6(13)	2736.7(11)	51.2(4)
C2	7266.8(11)	2957.5(14)	3301.4(11)	56.1(4)
C3	6723.0(11)	2941.2(14)	3581.9(11)	55.0(4)
C4	6106.6(10)	3636.7(14)	3292.7(10)	51.7(4)
C5	6033.5(10)	4354.5(13)	2721.1(10)	47.1(4)
C6	6581.4(9)	4384.6(11)	2439.4(9)	42.7(3)
C7	6531.3(11)	5172.9(13)	1827.0(10)	51.0(4)
C8	6246.0(9)	6862.5(11)	2281.4(9)	41.5(3)
C9	6874.3(9)	6724.4(12)	3026.0(10)	45.7(4)
C10	7092.7(10)	7515.5(13)	3576.3(10)	46.5(4)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for WRJ-210125WYM. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C11	6679.2(9)	8460.3(12)	3409.2(9)	42.8(3)
C12	6052.7(9)	8601.3(12)	2668.6(9)	41.8(3)
C13	5844.6(9)	7835.4(12)	2099.1(9)	40.0(3)
C14	5217.8(9)	7987.2(12)	1268.8(9)	42.8(3)
C15	4751.3(10)	6955.9(14)	1025.5(11)	52.6(4)
C16	5296.8(10)	6107.8(13)	1004.6(10)	50.2(4)
C17	5671.5(10)	7273.5(12)	308.2(9)	45.2(3)
C18	5580.1(9)	8121.9(12)	723.6(9)	41.6(3)
C19	5888.0(9)	8955.4(13)	488.9(9)	43.8(3)
C20	6025.8(10)	10069.8(13)	704.8(10)	48.1(4)
C21	5865.1(14)	11406.8(15)	1465.6(14)	69.4(5)
C22	5460.3(15)	11526.8(19)	1948.2(14)	81.7(7)
C23	6916.3(10)	9333.6(13)	3978.1(9)	46.9(4)
C24	7925.1(13)	9985.3(18)	5161.2(13)	74.3(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for WRJ-210125WYM. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	76.8(8)	42.1(6)	46.6(6)	-6.3(5)	31.9(6)	-6.4(5)
O2	88.4(10)	52.6(8)	91.6(11)	-0.9(7)	55.0(9)	-12.7(7)
O3	74.7(8)	43.2(6)	66.3(8)	-9.0(6)	38.2(7)	-2.4(6)
O4	79.1(9)	56.0(7)	50.3(7)	-6.9(6)	25.9(6)	15.3(6)
O5	59.3(7)	64.2(8)	60.2(8)	-19.1(6)	13.0(6)	4.9(6)
N1	61.2(8)	38.3(7)	47.3(7)	-1.4(6)	27.7(6)	1.2(6)
N2	70.1(9)	48.9(8)	46.0(7)	-2.3(6)	32.7(7)	0.9(7)
N3	64.3(9)	48.9(8)	46.8(8)	1.1(6)	32.4(7)	-1.7(6)
C1	52.2(9)	49.5(9)	61.5(10)	-1.5(8)	34.2(8)	3.0(7)
C2	55.3(10)	50.6(9)	59.9(10)	3.8(8)	24.1(8)	6.5(8)
C3	67.0(11)	48.0(9)	51.2(9)	3.3(7)	27.9(9)	-7.7(8)
C4	56.8(9)	51.5(9)	56.7(10)	-4.3(8)	34.5(8)	-10.2(7)
C5	47.4(8)	42.6(8)	58.0(9)	-1.9(7)	29.9(8)	-1.0(6)
C6	50.7(8)	36.2(7)	47.7(8)	-6.0(6)	28.1(7)	-3.9(6)
C7	69.3(10)	41.7(8)	55.2(10)	-1.3(7)	39.9(9)	2.2(7)
C8	48.1(8)	38.3(7)	45.9(8)	1.4(6)	28.2(7)	-1.0(6)
C9	50.4(8)	38.9(8)	49.0(9)	3.8(6)	23.7(7)	3.1(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for WRJ-210125WYM. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	49.1(8)	46.3(8)	43.7(8)	2.7(7)	20.7(7)	0.6(7)
C11	47.6(8)	44.4(8)	42.8(8)	-2.1(6)	26.1(7)	-1.6(6)
C12	46.3(8)	42.3(8)	44.7(8)	1.5(6)	27.7(7)	4.3(6)
C13	42.9(7)	41.1(8)	42.2(8)	0.3(6)	24.9(7)	-0.6(6)
C14	42.5(8)	44.5(8)	43.0(8)	-1.3(6)	21.0(7)	1.8(6)
C15	47.2(9)	58.2(10)	52.4(9)	-4.1(8)	22.8(8)	-8.5(7)
C16	60.7(10)	43.8(8)	49.0(9)	-5.1(7)	27.5(8)	-11.9(7)
C17	55.3(9)	42.1(8)	39.1(8)	-1.5(6)	22.3(7)	0.0(7)
C18	44.8(8)	42.2(8)	37.0(7)	-0.6(6)	17.8(6)	1.2(6)
C19	47.4(8)	44.3(8)	39.1(8)	1.3(6)	19.2(7)	2.0(6)
C20	48.4(8)	45.6(8)	48.8(9)	1.5(7)	20.7(7)	2.1(7)
C21	77.5(13)	48.6(10)	78.1(14)	-16.3(9)	32.2(11)	-2.7(9)
C22	89.7(16)	70.4(14)	72.9(14)	-20.6(11)	26.4(12)	13.1(12)
C23	55.0(9)	48.1(9)	42.6(8)	-1.6(7)	26.5(7)	1.4(7)
C24	66.6(12)	74.5(14)	66.7(13)	-25.3(11)	17.3(10)	-3.2(10)

Table 4 Bond Lengths for WRJ-210125WYM.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C16	1.4606(19)	C4	C5	1.386(2)
O1	C17	1.3615(19)	C5	C6	1.385(2)
O2	C20	1.204(2)	C6	C7	1.517(2)
O3	C20	1.318(2)	C8	C9	1.400(2)
O3	C21	1.461(2)	C8	C13	1.415(2)
O4	C23	1.209(2)	C9	C10	1.380(2)
O5	C23	1.334(2)	C10	C11	1.395(2)
O5	C24	1.439(2)	C11	C12	1.394(2)
N1	C7	1.461(2)	C11	C23	1.479(2)
N1	C8	1.392(2)	C12	C13	1.382(2)
N1	C16	1.441(2)	C13	C14	1.511(2)
N2	N3	1.352(2)	C14	C15	1.536(2)
N2	C17	1.326(2)	C14	C18	1.509(2)
N3	C19	1.353(2)	C15	C16	1.516(2)
C1	C2	1.383(2)	C17	C18	1.401(2)
C1	C6	1.383(2)	C18	C19	1.386(2)
C2	C3	1.375(3)	C19	C20	1.468(2)
C3	C4	1.375(3)	C21	C22	1.464(3)

Table 5 Bond Angles for WRJ-210125WYM.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	O1	C16	110.65(12)	C8	C13	C14	117.03(13)
C20	O3	C21	115.71(15)	C12	C13	C8	119.53(14)
C23	O5	C24	117.02(15)	C12	C13	C14	123.41(14)
C8	N1	C7	120.29(14)	C13	C14	C15	106.55(13)
C8	N1	C16	122.88(13)	C18	C14	C13	110.67(12)
C16	N1	C7	116.80(14)	C18	C14	C15	105.89(13)
C17	N2	N3	103.11(13)	C16	C15	C14	107.67(13)
N2	N3	C19	112.84(14)	O1	C16	C15	110.54(14)
C6	C1	C2	120.88(15)	N1	C16	O1	110.35(13)
C3	C2	C1	120.02(17)	N1	C16	C15	111.79(14)
C4	C3	C2	119.80(16)	O1	C17	C18	125.87(14)
C3	C4	C5	120.17(15)	N2	C17	O1	120.05(14)
C6	C5	C4	120.53(16)	N2	C17	C18	114.08(14)
C1	C6	C5	118.59(15)	C17	C18	C14	121.73(14)
C1	C6	C7	119.30(14)	C19	C18	C14	135.47(14)
C5	C6	C7	122.10(15)	C19	C18	C17	102.81(13)
N1	C7	C6	115.38(13)	N3	C19	C18	107.16(14)
N1	C8	C9	121.46(14)	N3	C19	C20	118.68(14)
N1	C8	C13	119.82(14)	C18	C19	C20	134.11(15)
C9	C8	C13	118.71(14)	O2	C20	O3	125.07(16)
C10	C9	C8	120.77(15)	O2	C20	C19	124.11(16)
C9	C10	C11	120.68(15)	O3	C20	C19	110.82(14)
C10	C11	C23	121.79(15)	O3	C21	C22	106.79(18)
C12	C11	C10	118.74(14)	O4	C23	O5	123.12(15)
C12	C11	C23	119.37(14)	O4	C23	C11	124.93(15)
C13	C12	C11	121.45(14)	O5	C23	C11	111.93(14)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for WRJ-210125WYM.

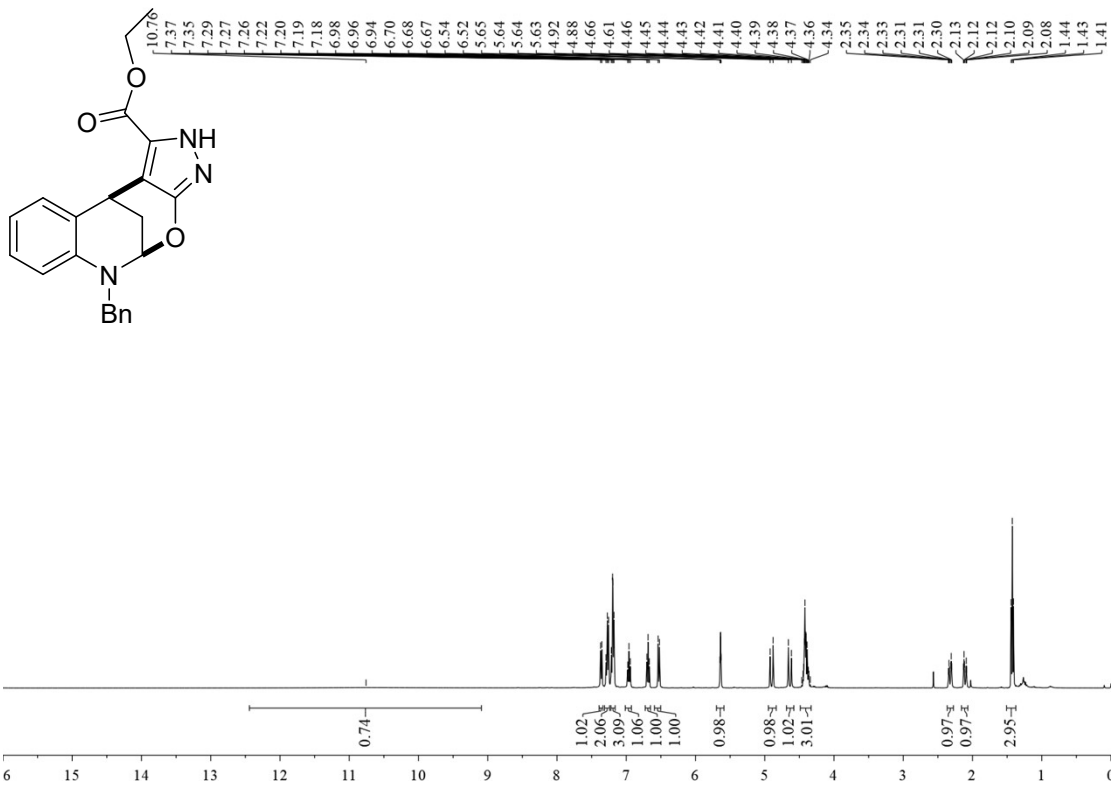
Atom	*x*	*y*	*z*	U(eq)
H1	7572	3693	2555	61
H2	7681	2482	3491	67
H3A	6772	2461	3966	66
H4	5738	3626	3481	62
H5	5613	4819	2525	57

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for WRJ-210125WYM.

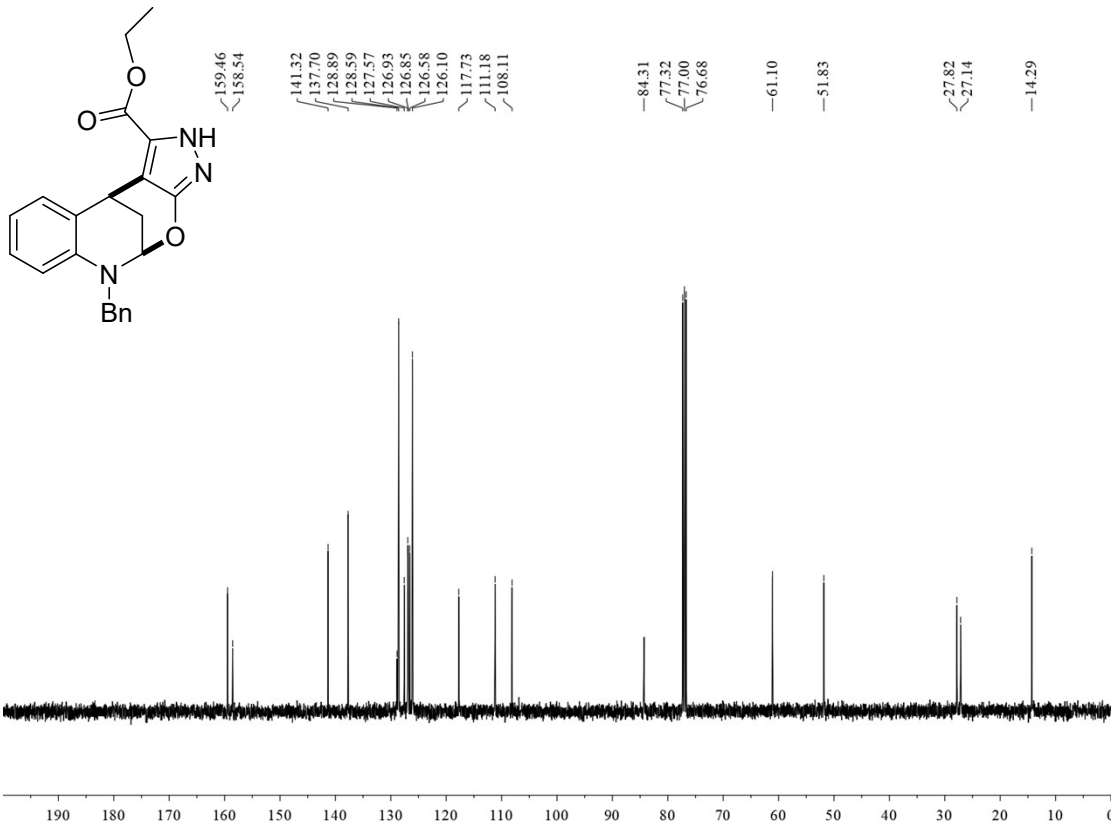
Atom	*x*	*y*	*z*	U(eq)
H7A	7055	5432	1968	61
H7B	6349	4811	1331	61
H9	7148	6092	3151	55
H10	7520	7418	4063	56
H12	5768	9224	2555	50
H14	4877	8582	1230	51
H15A	4560	6772	1398	63
H15B	4305	7032	514	63
H16	5033	5429	940	60
H21A	5629	11857	1010	83
H21B	6413	11595	1761	83
H22A	4944	11232	1680	123
H22B	5422	12259	2045	123
H22C	5749	11168	2436	123
H24A	7953	10633	4919	111
H24B	8440	9793	5552	111
H24C	7586	10073	5401	111
H3	6336(12)	8959(17)	-281(12)	67(6)

NMR spectra of the obtained compounds

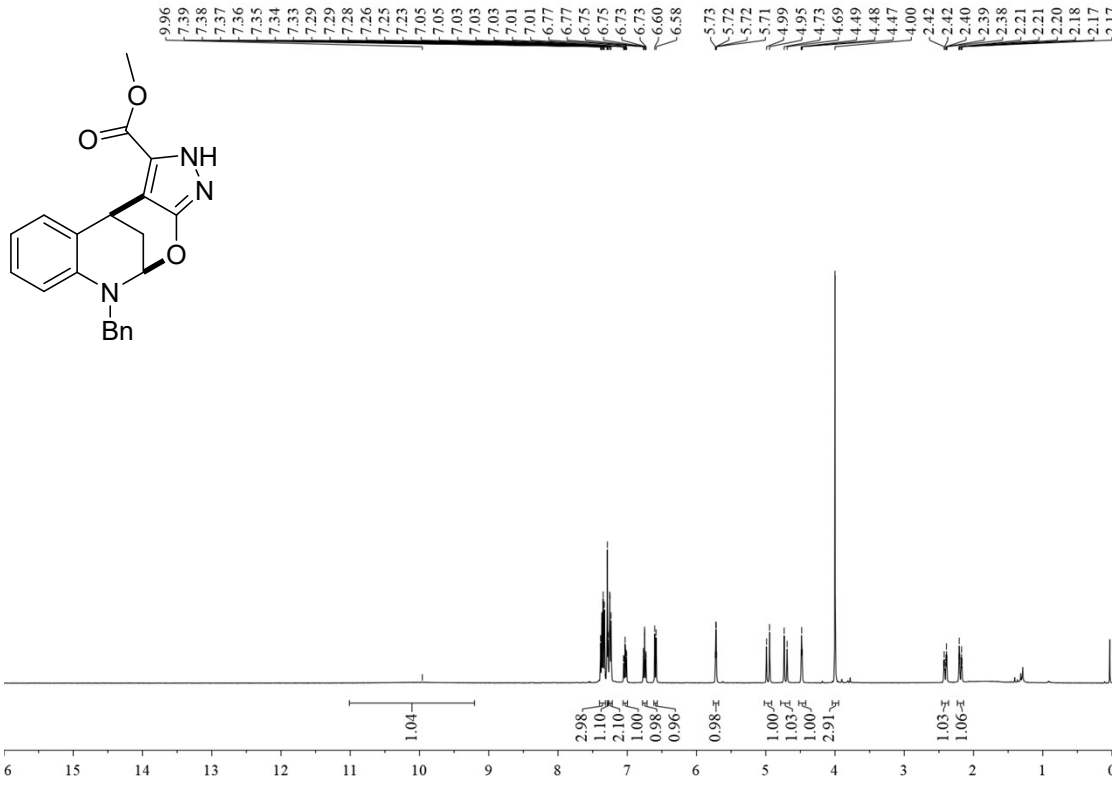
^{1}H-NMR spectrum of C_1



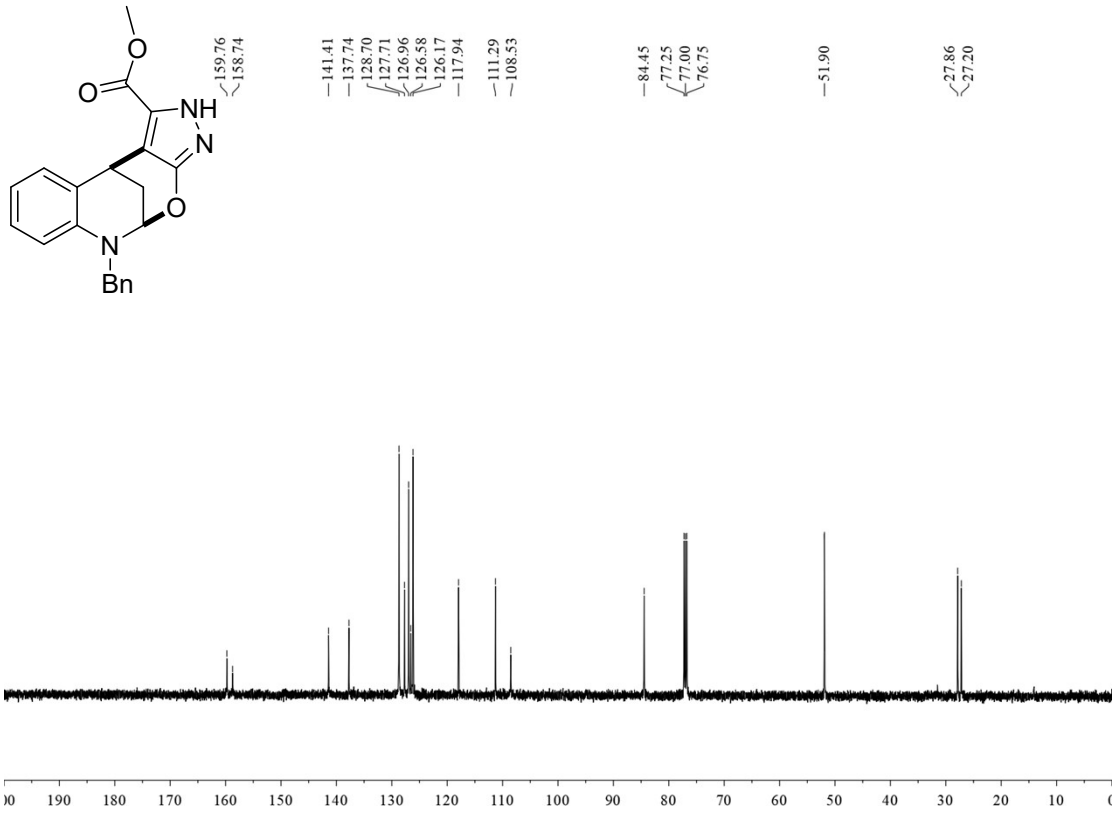
^{13}C-NMR spectrum of C_1



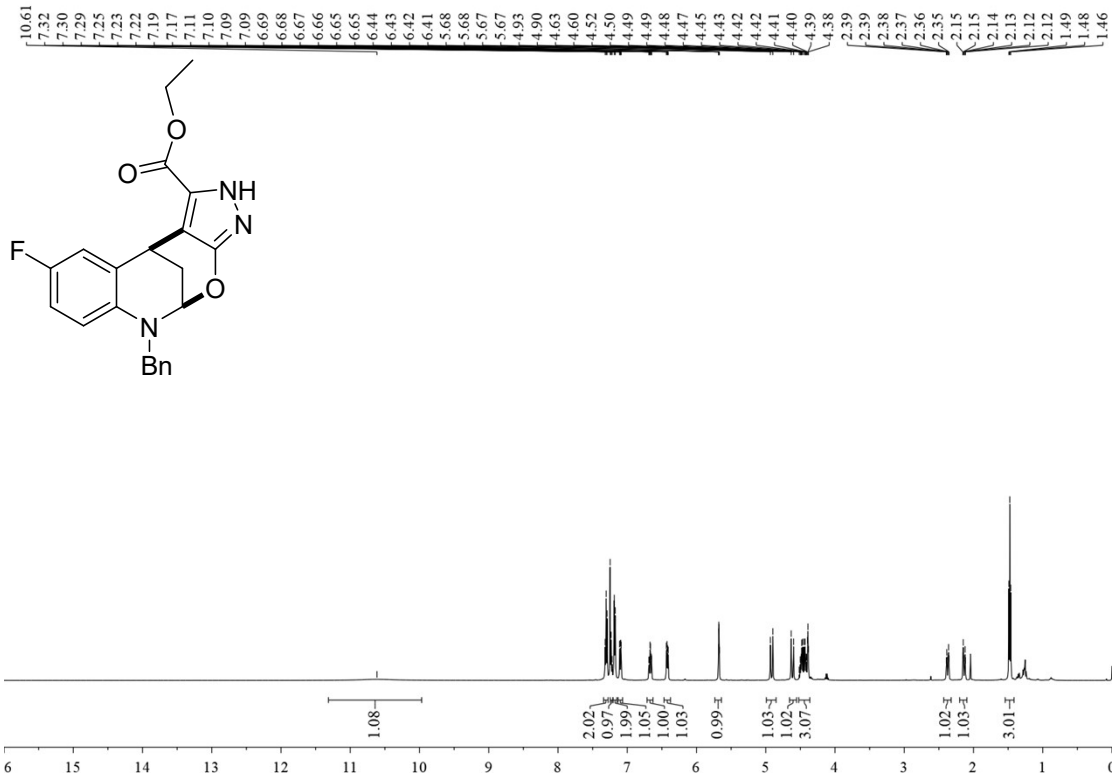
^{1}H-NMR spectrum of C_2



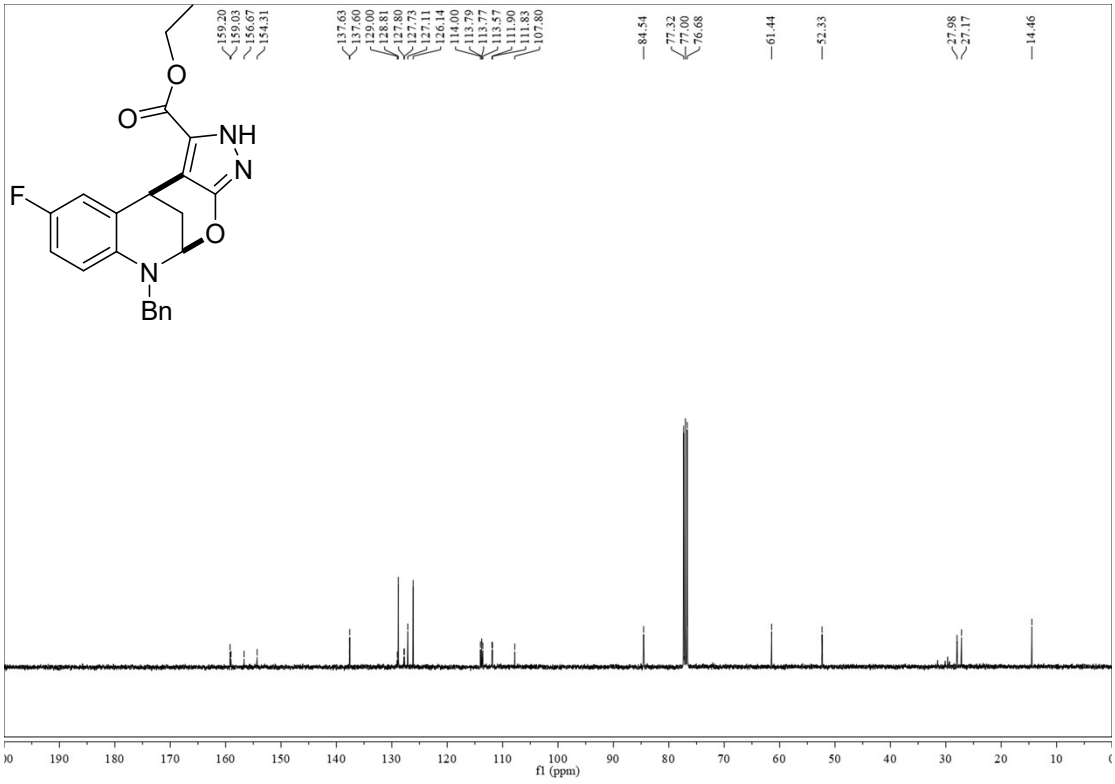
^{13}C-NMR spectrum of C_2



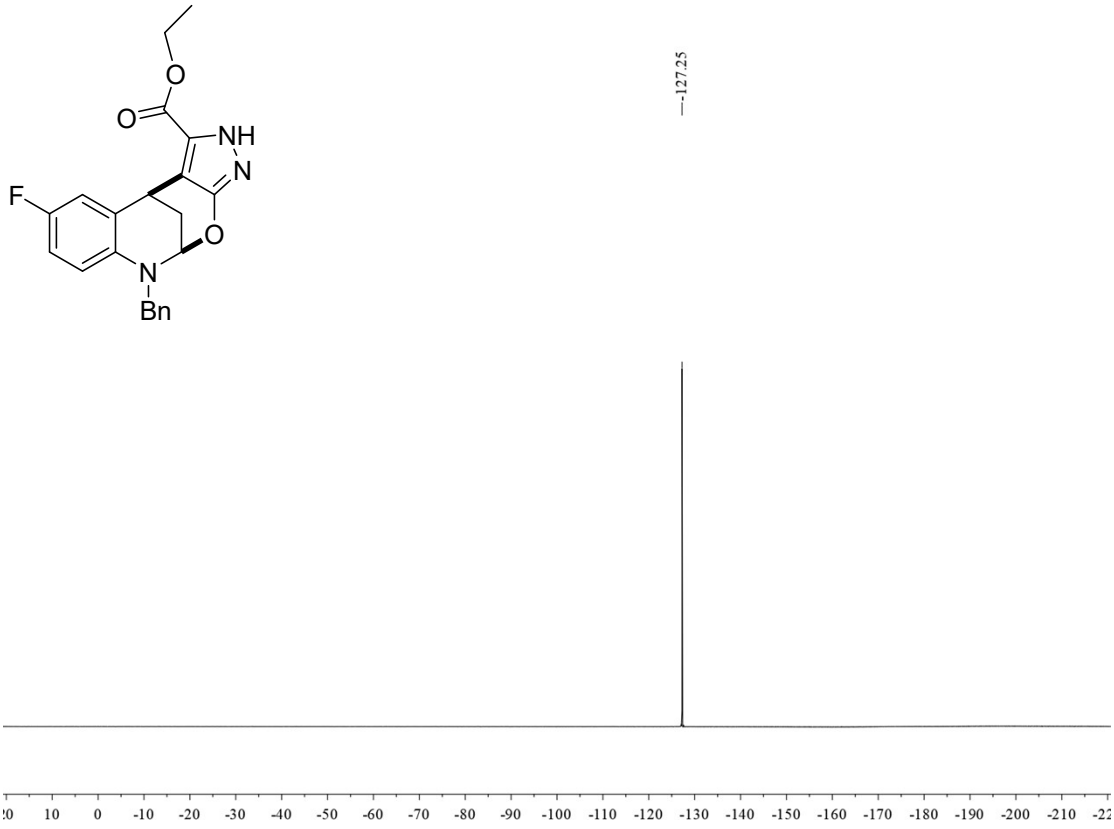
^{1}H-NMR spectrum of C_3



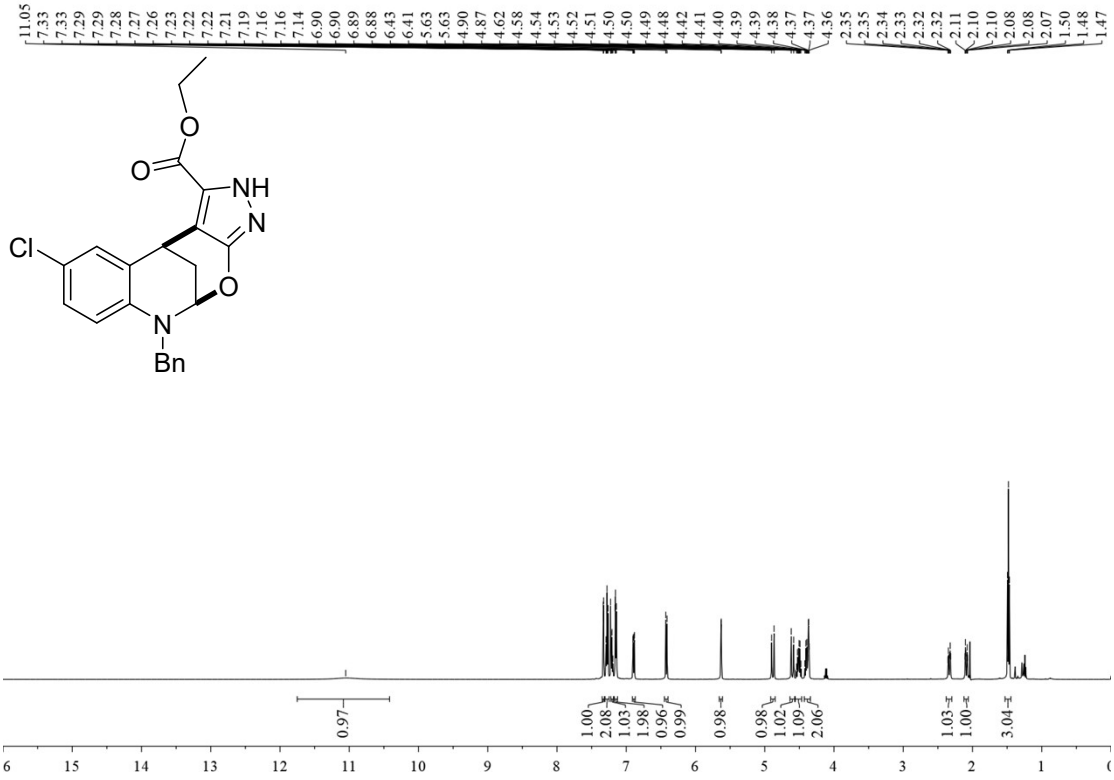
^{13}C-NMR spectrum of C_3



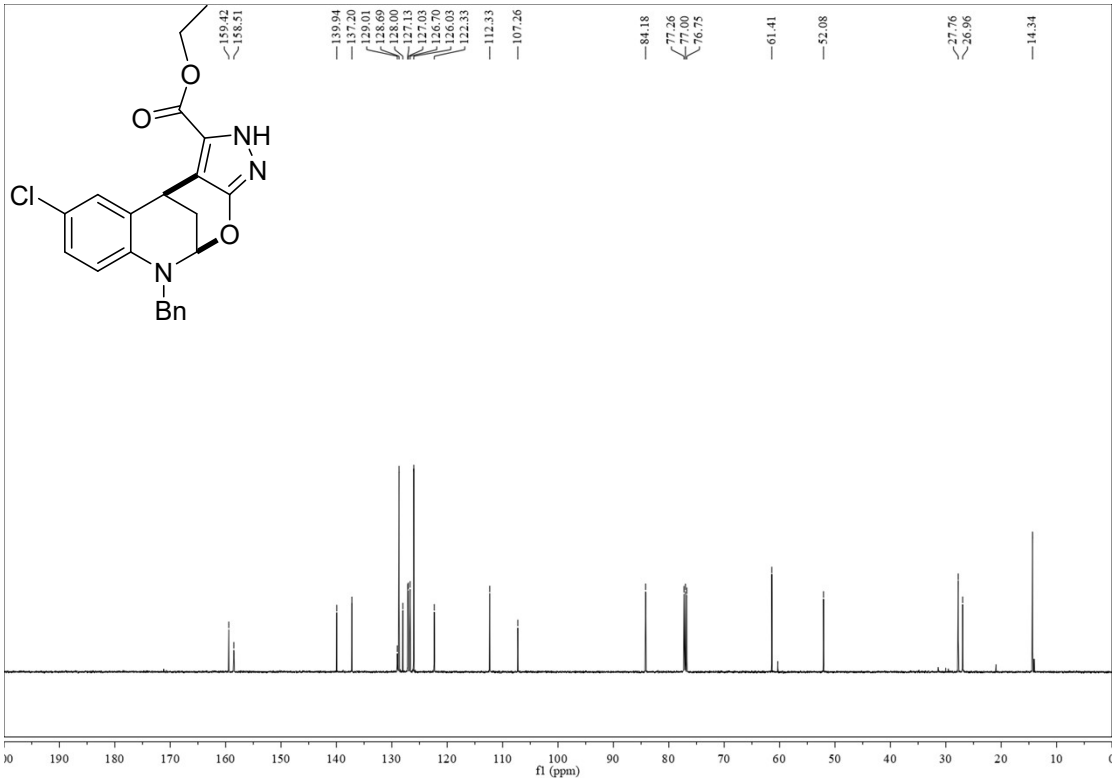
^{19}F-NMR spectrum of C_3



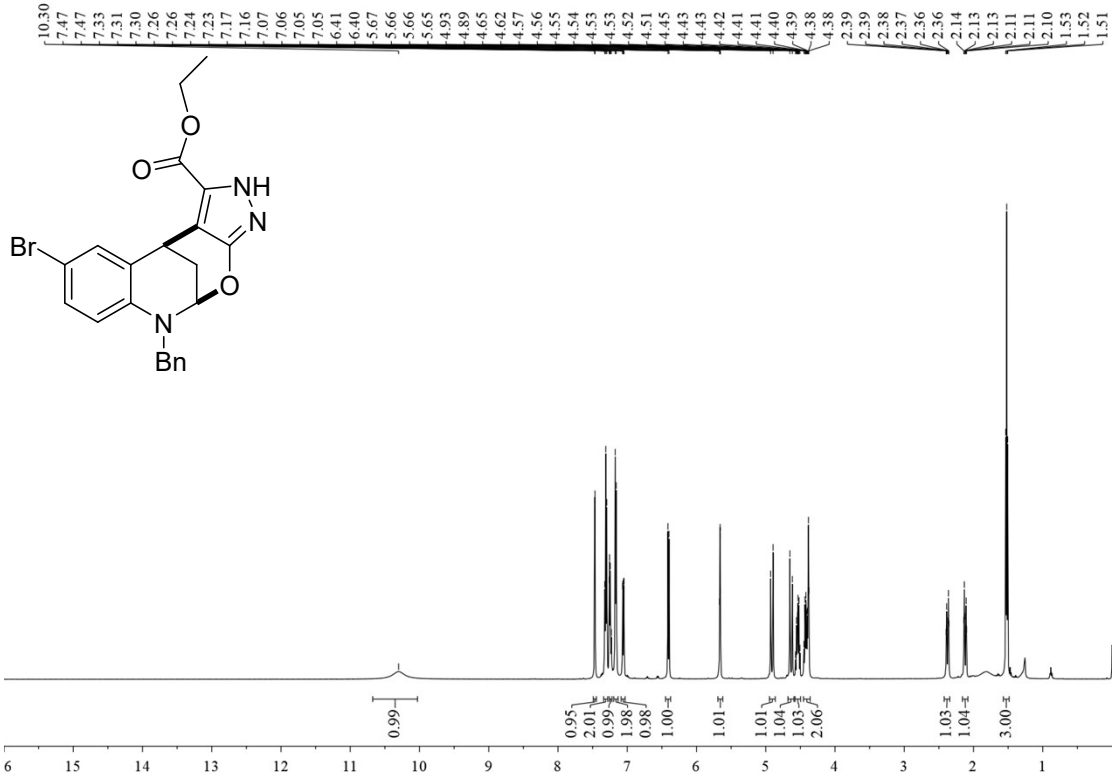
^{1}H-NMR spectrum of C_4



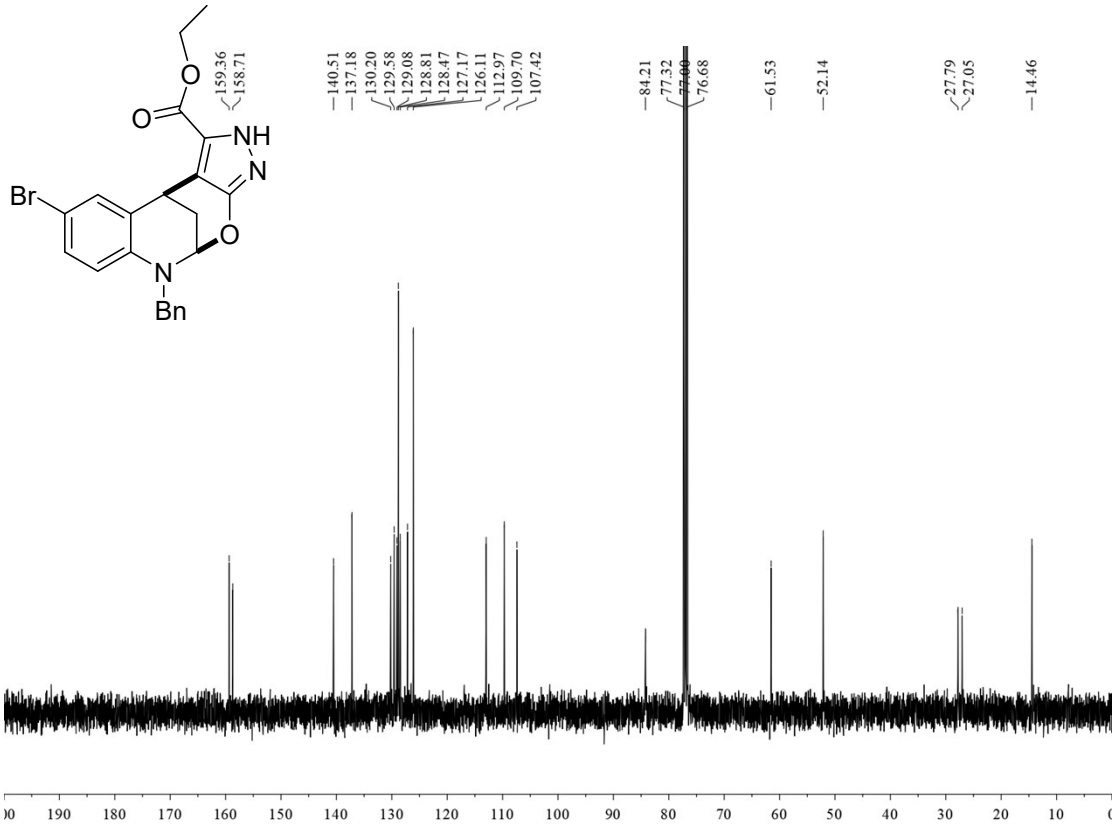
^{13}C-NMR spectrum of C_4



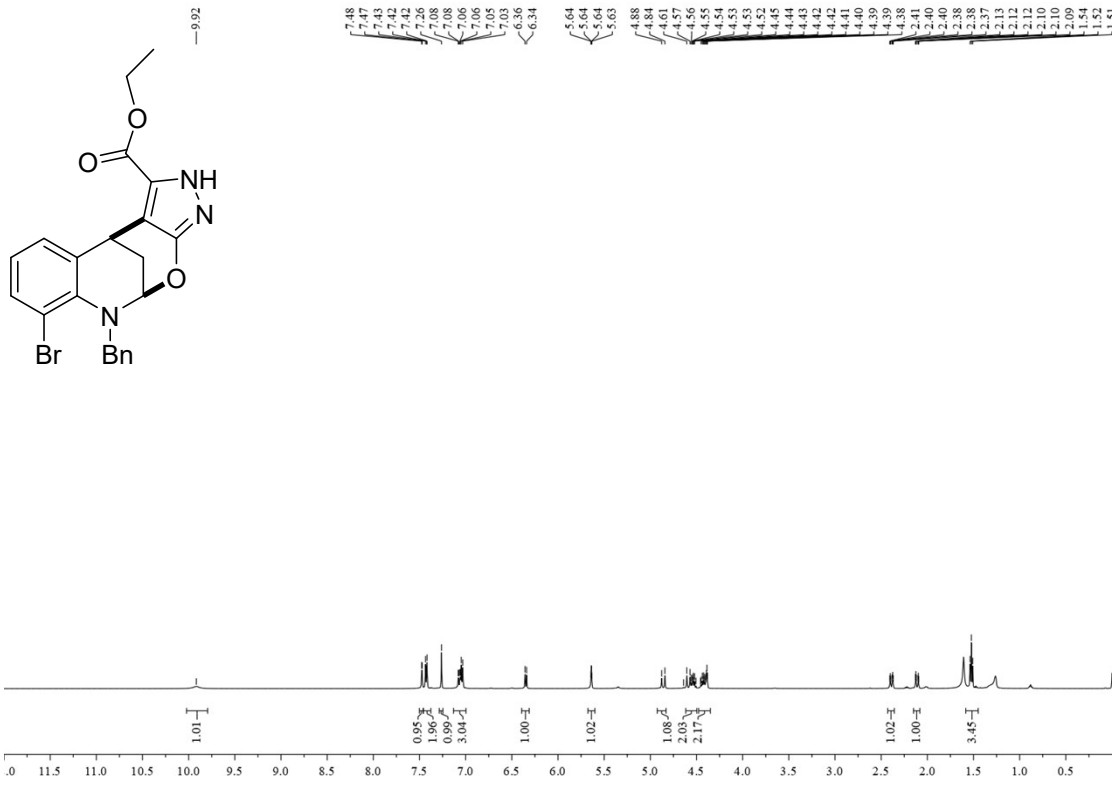
^{1}H-NMR spectrum of C_5



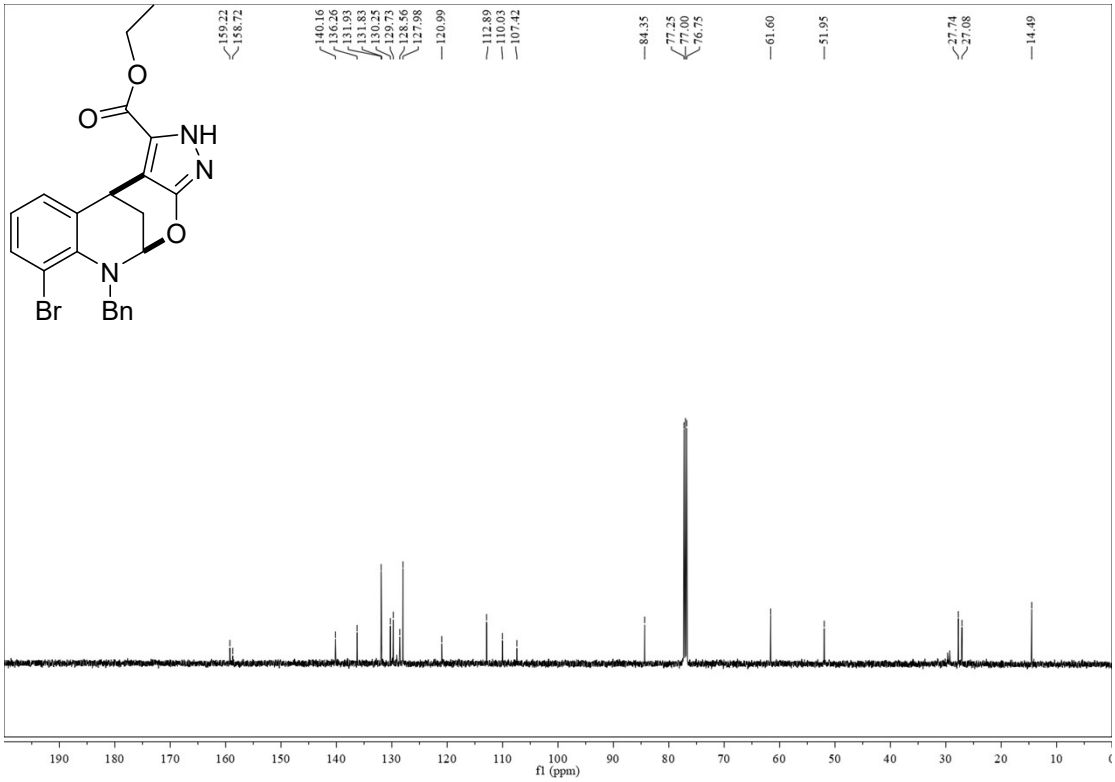
^{13}C-NMR spectrum of C_5



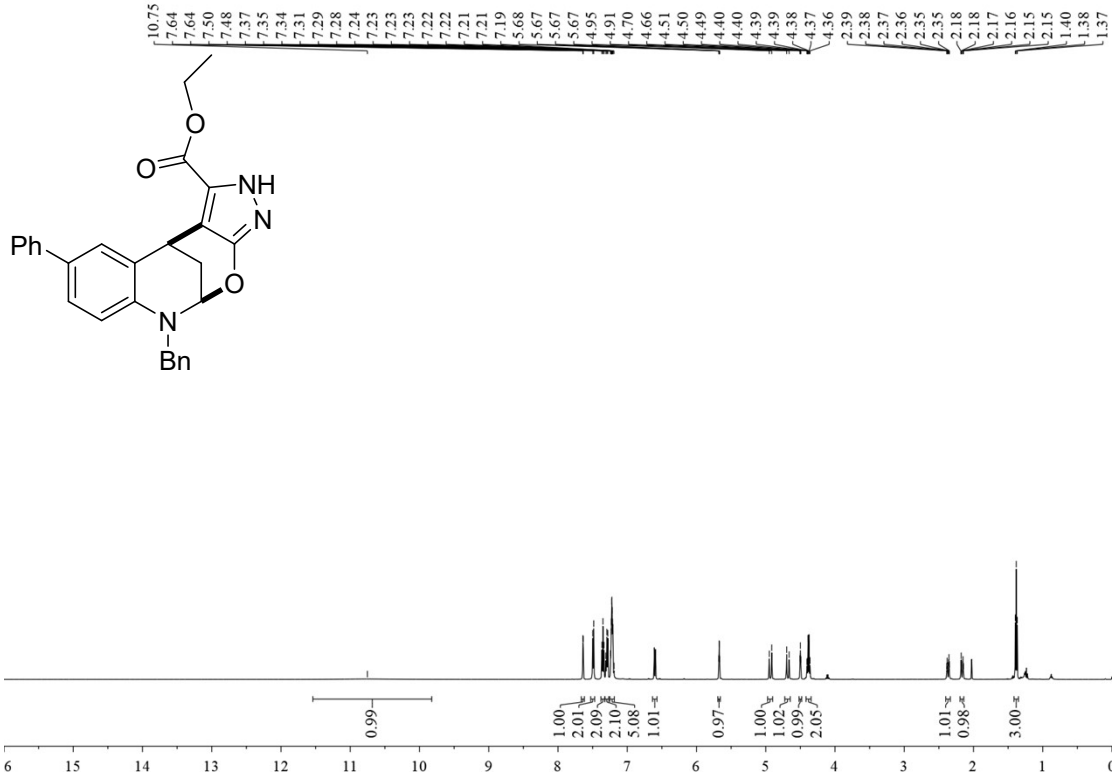
^{1}H-NMR spectrum of C_6



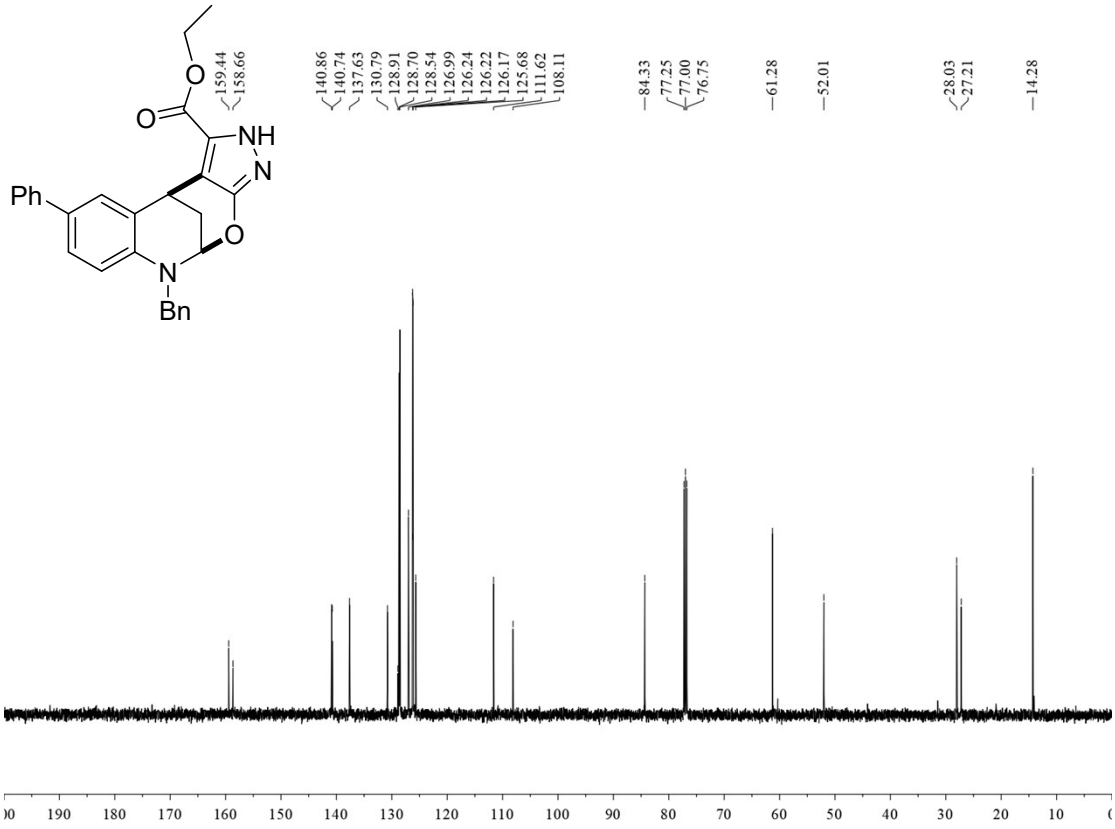
^{13}C-NMR spectrum of C_6



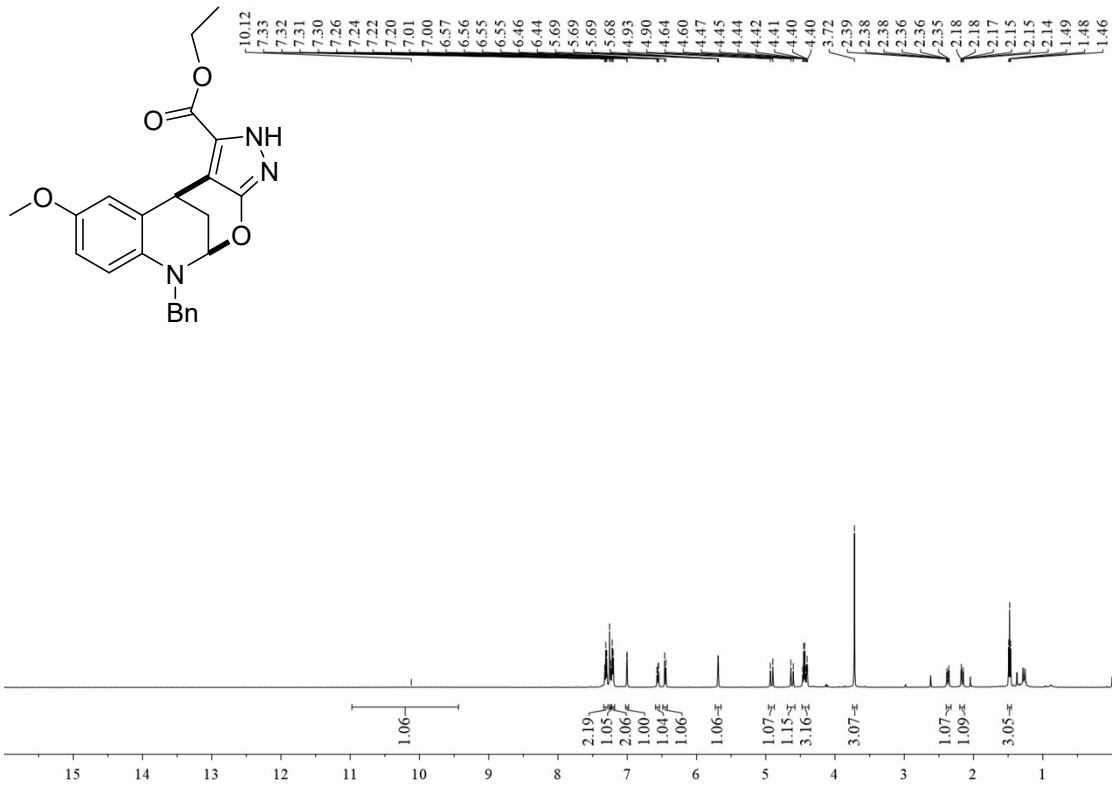
^{1}H-NMR spectrum of C_7



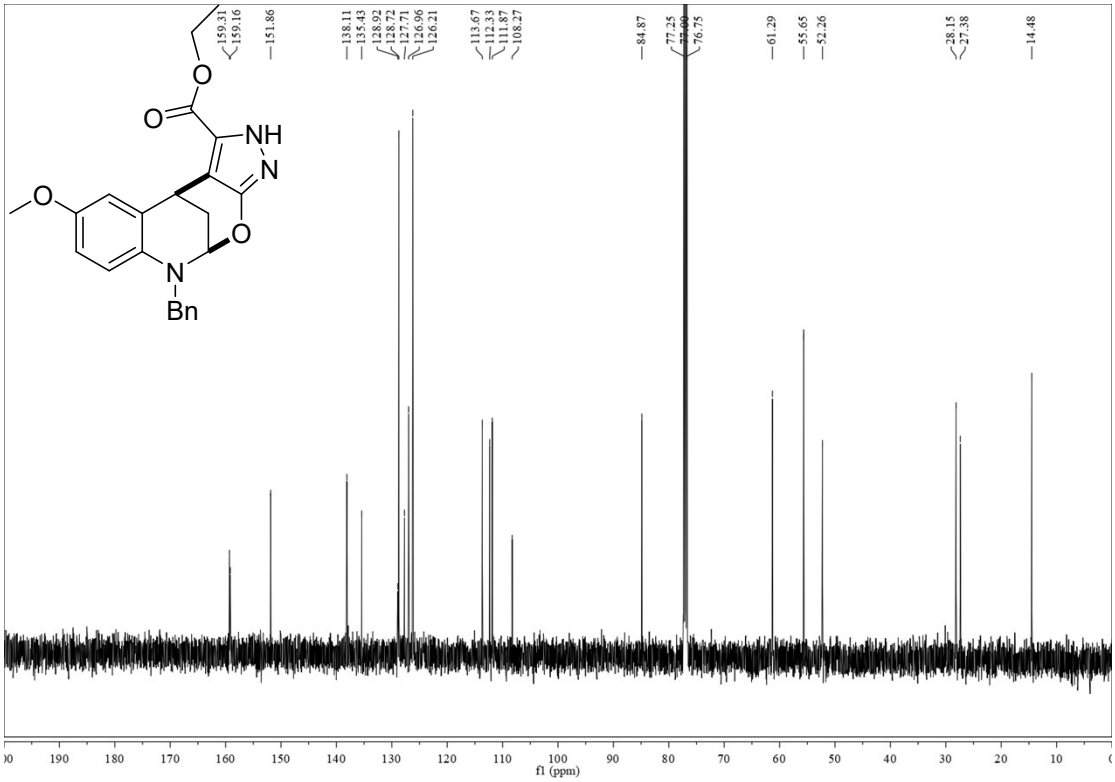
^{13}C-NMR spectrum of C_7



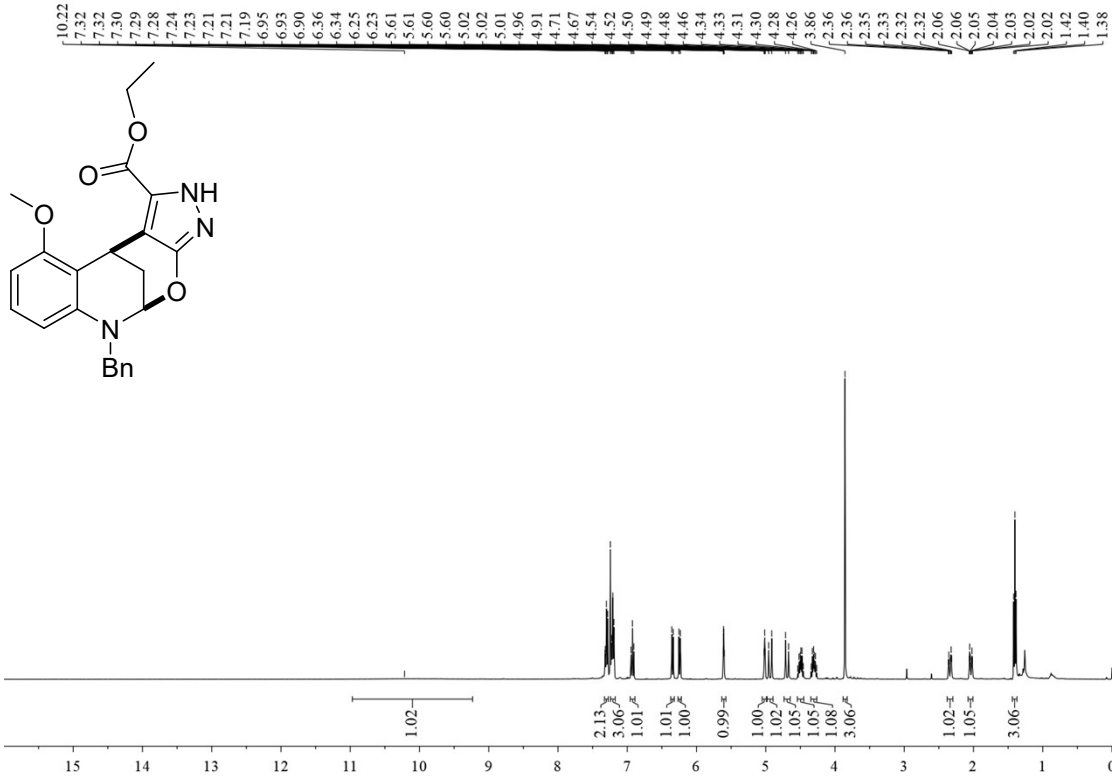
^{1}H-NMR spectrum of C_8



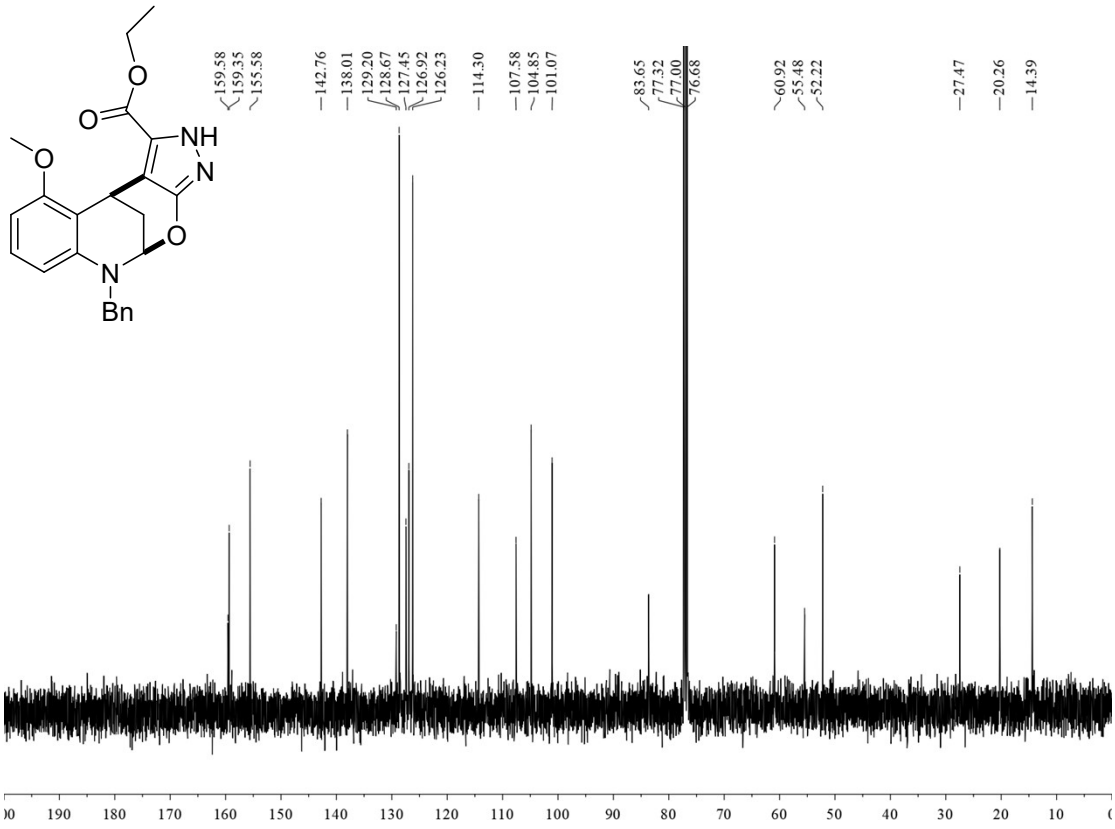
^{13}C-NMR spectrum of C_8



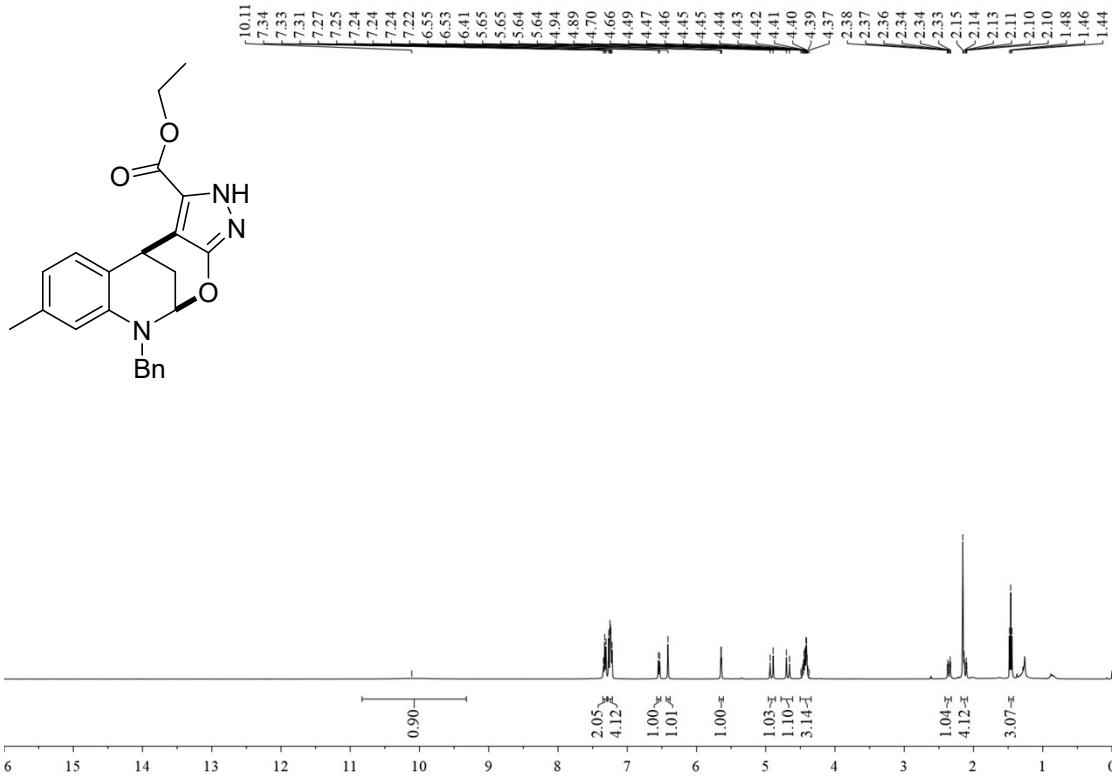
^{1}H-NMR spectrum of C_9



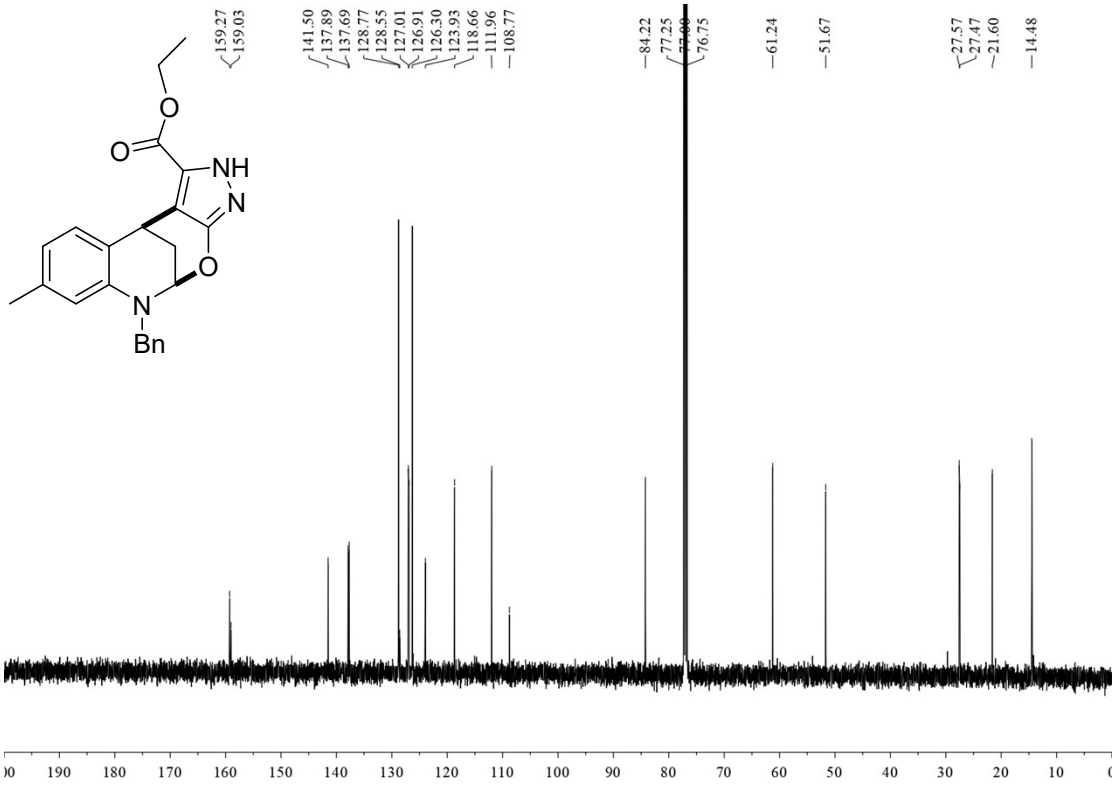
^{13}C-NMR spectrum of C_9



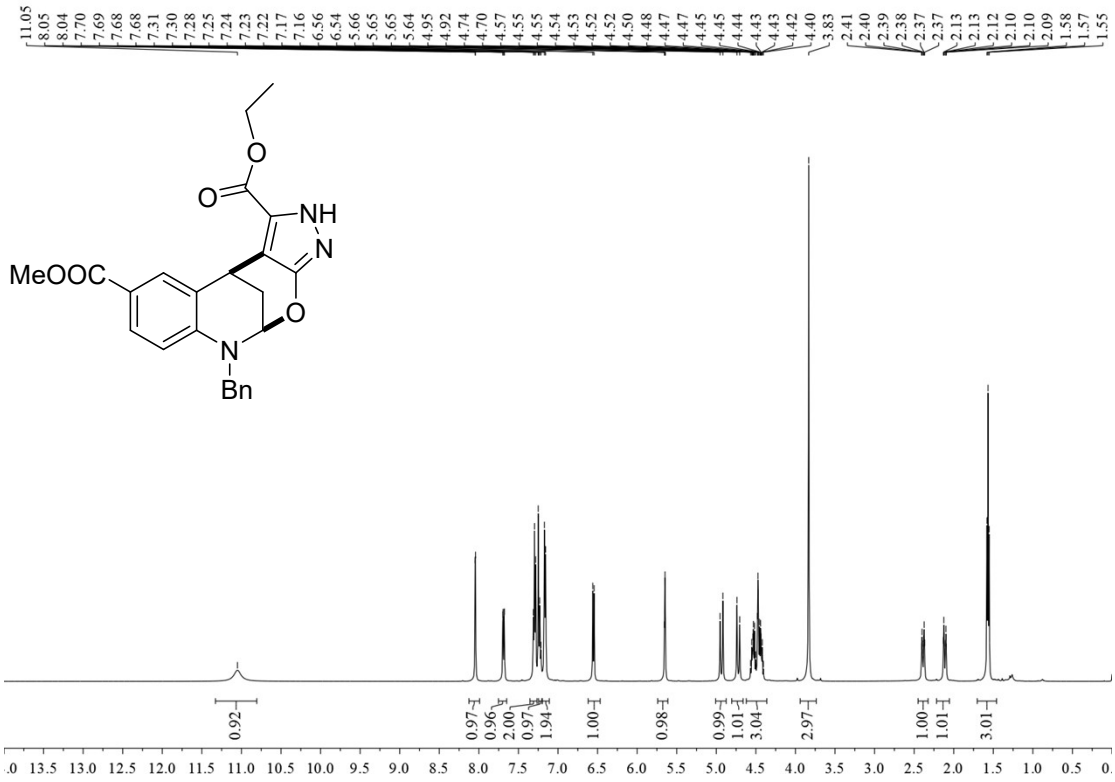
^{1}H-NMR spectrum of C_{10}



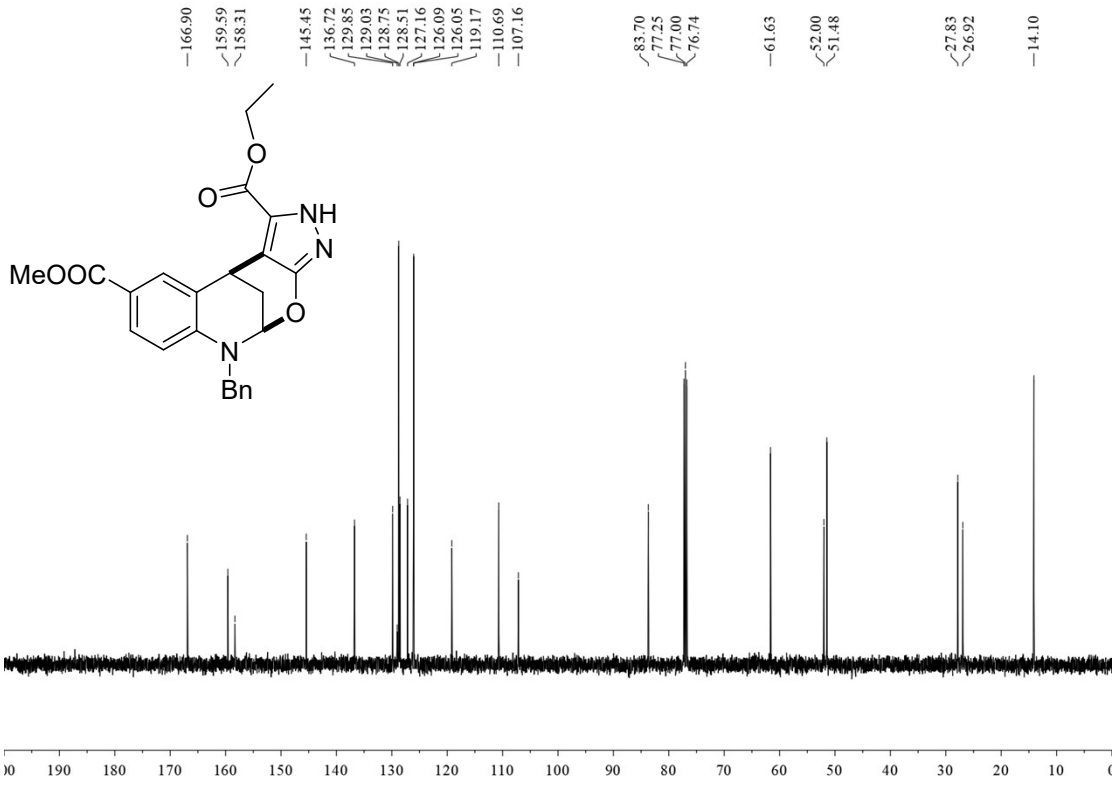
^{13}C-NMR spectrum of C_{10}



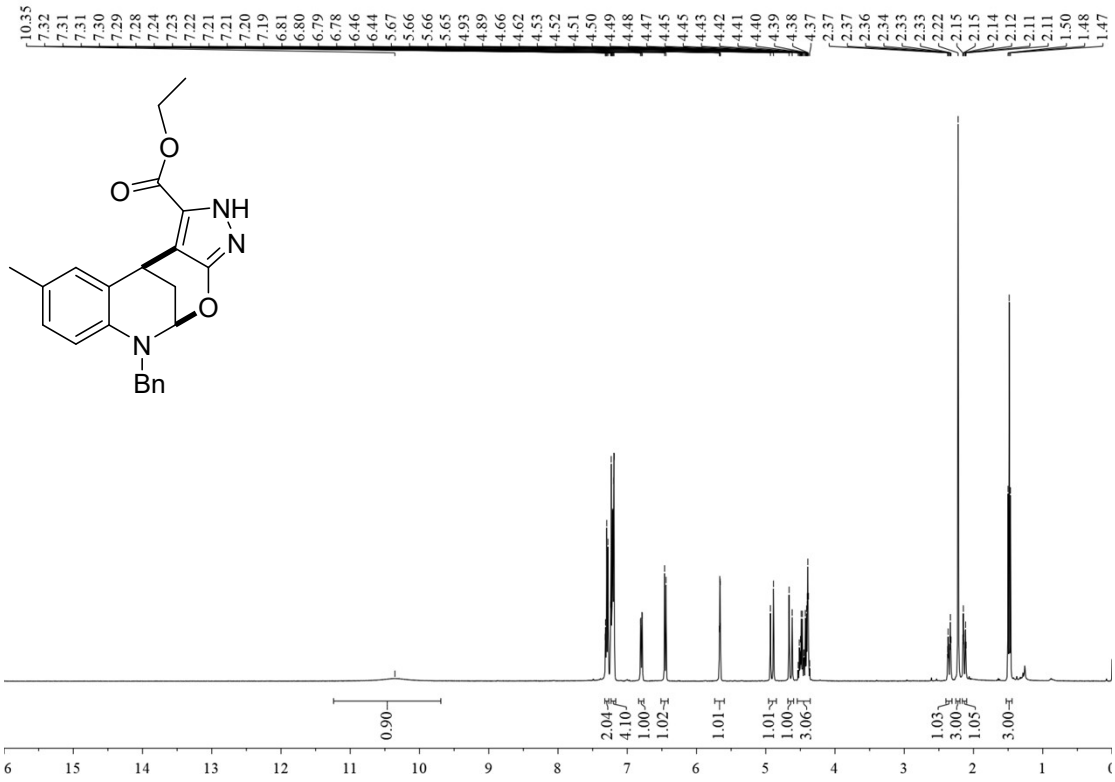
^{1}H-NMR spectrum of C_{11}



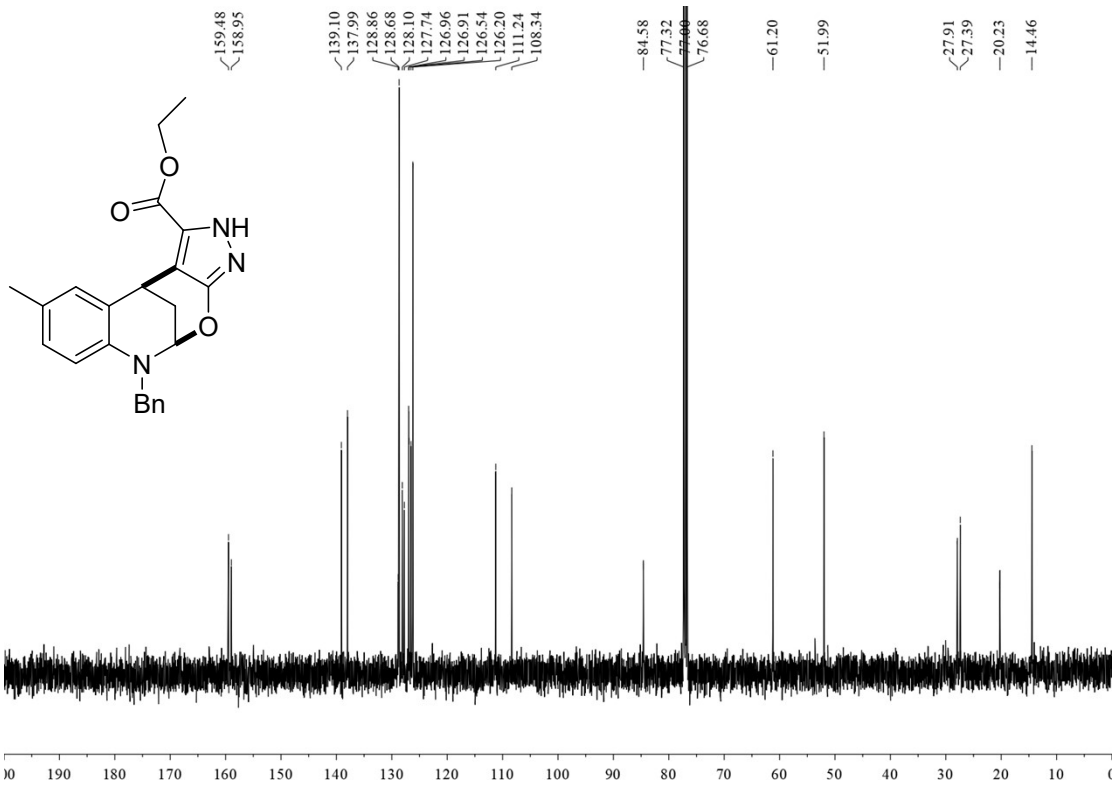
^{13}C-NMR spectrum of C_{11}



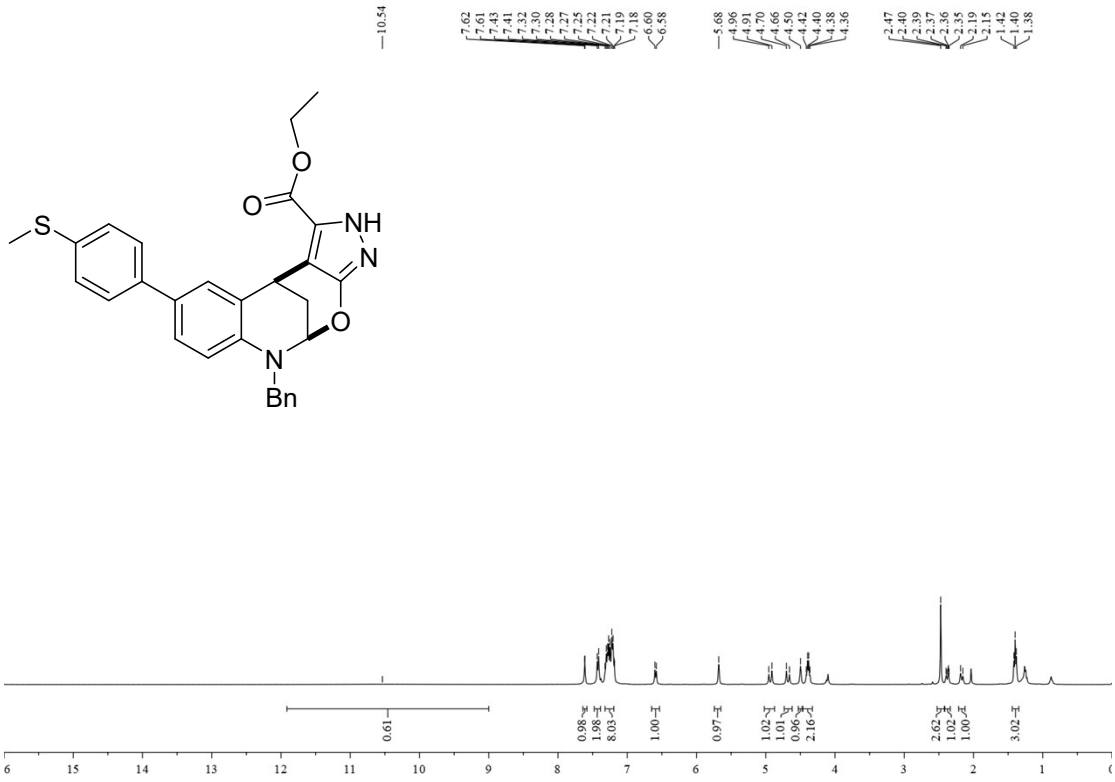
^{1}H-NMR spectrum of C_{12}



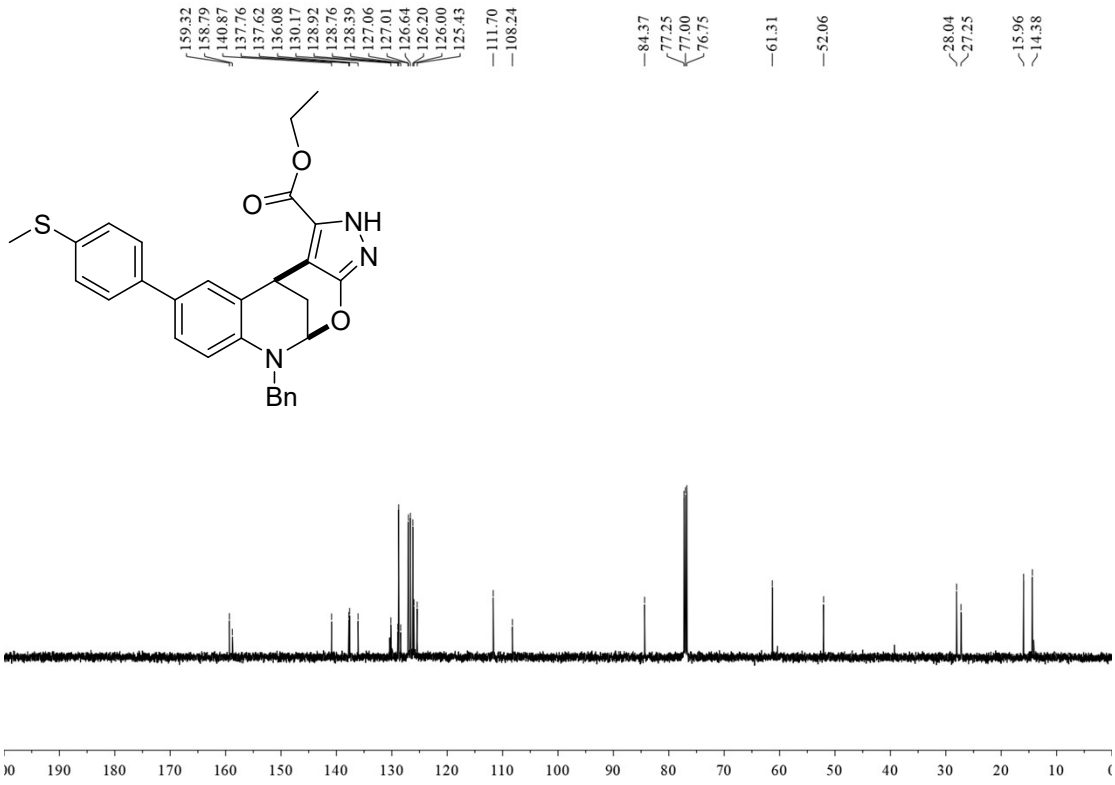
^{13}C-NMR spectrum of C_{12}



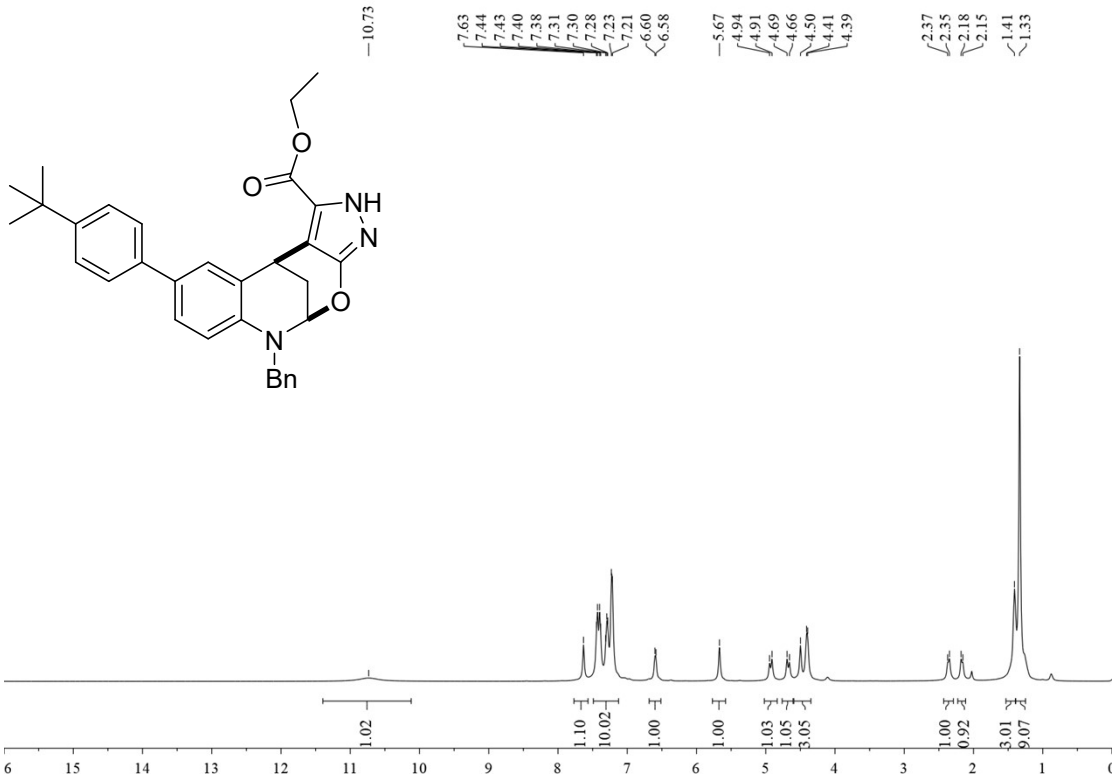
^{1}H-NMR spectrum of C_{13}



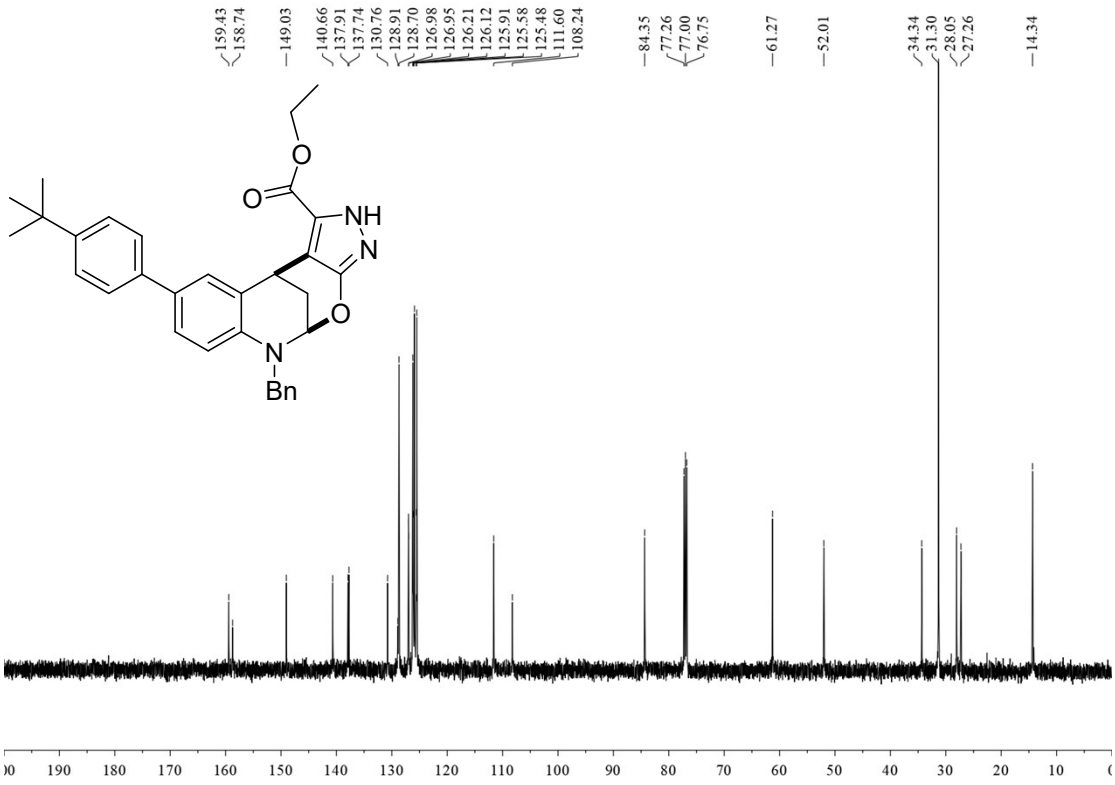
^{13}C-NMR spectrum of C_{13}



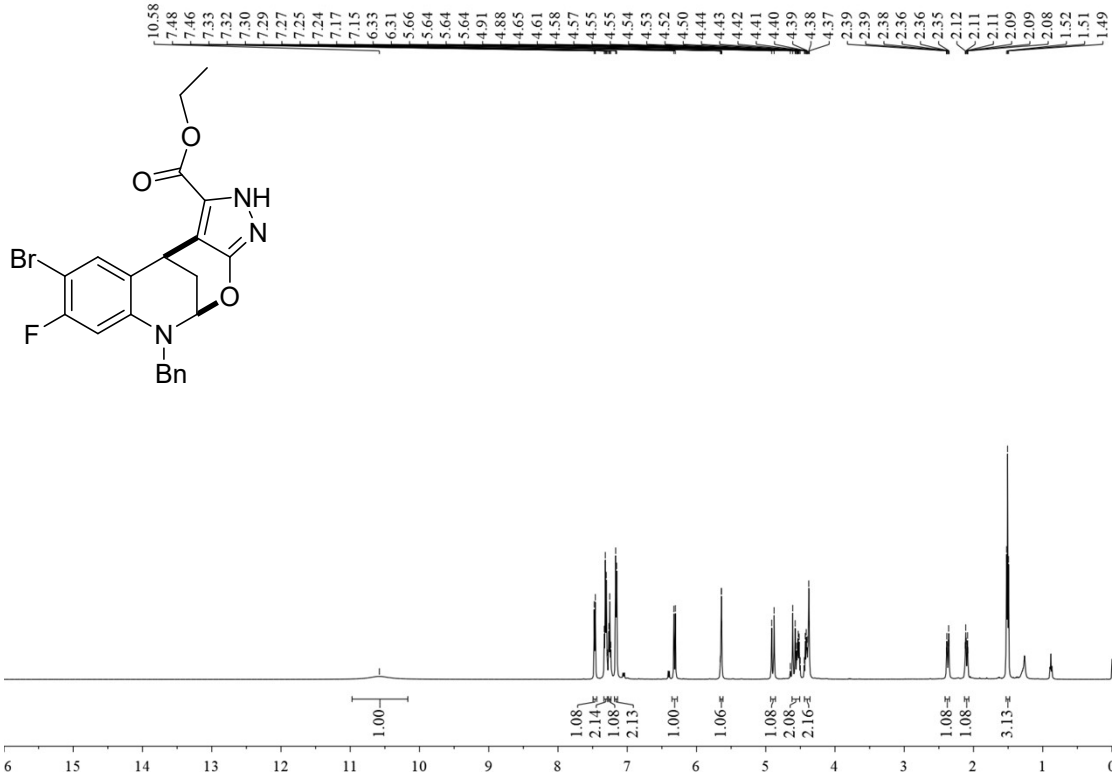
^{1}H-NMR spectrum of C_{14}



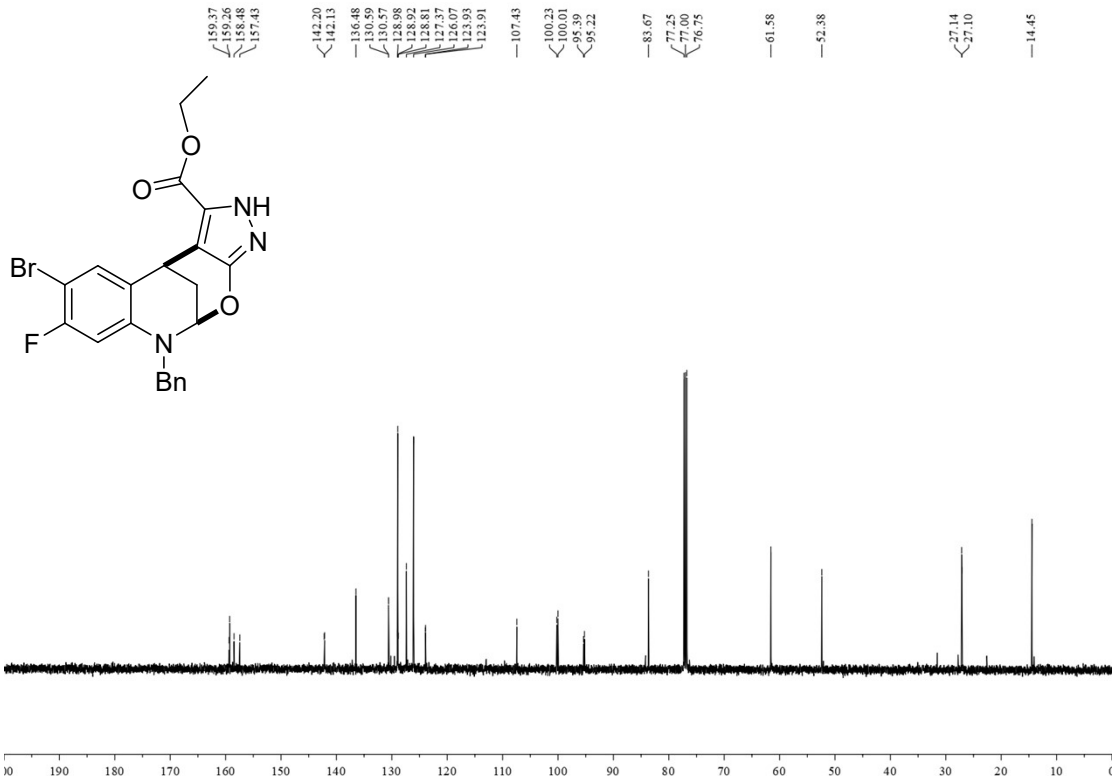
^{13}C-NMR spectrum of C_{14}



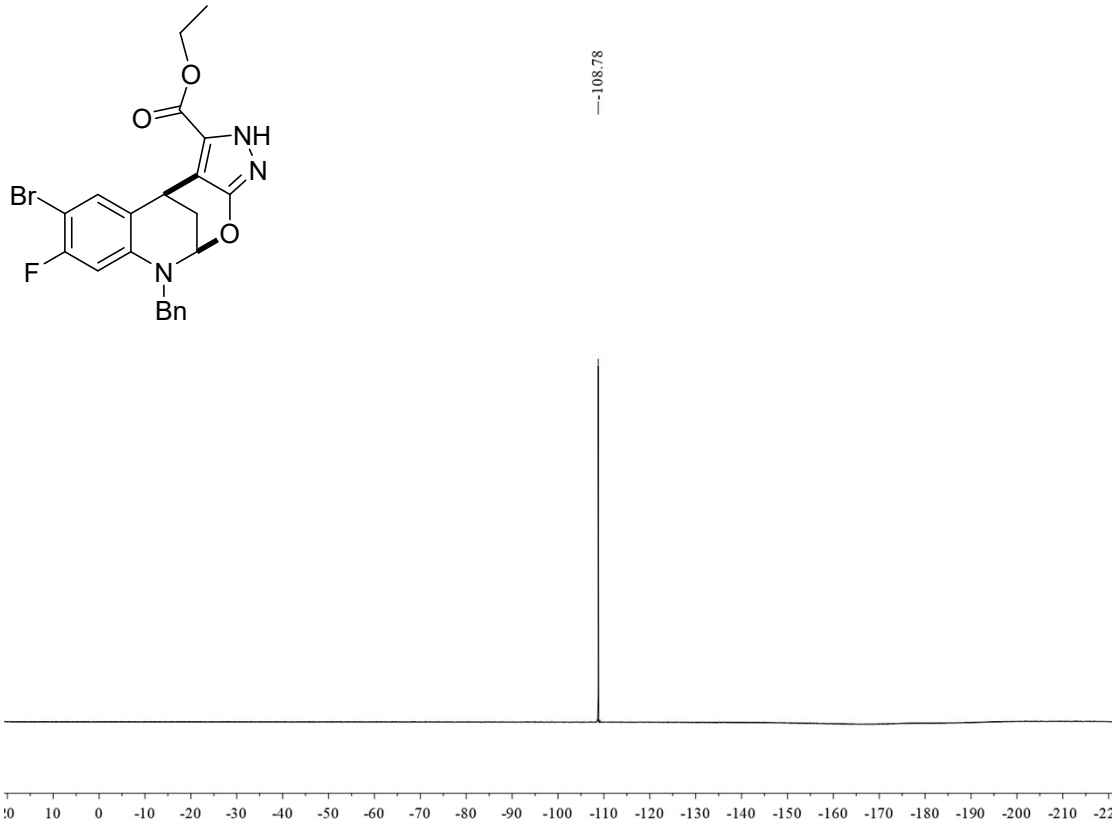
^{1}H-NMR spectrum of C_{15}



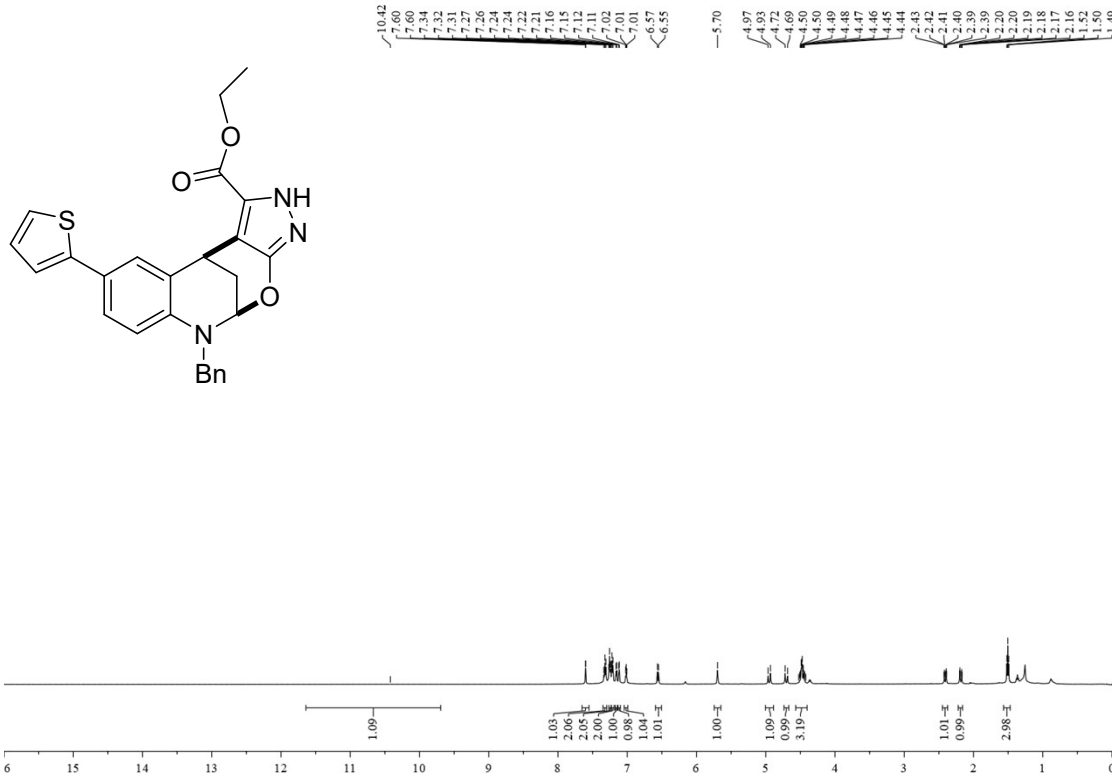
^{13}C-NMR spectrum of C_{15}



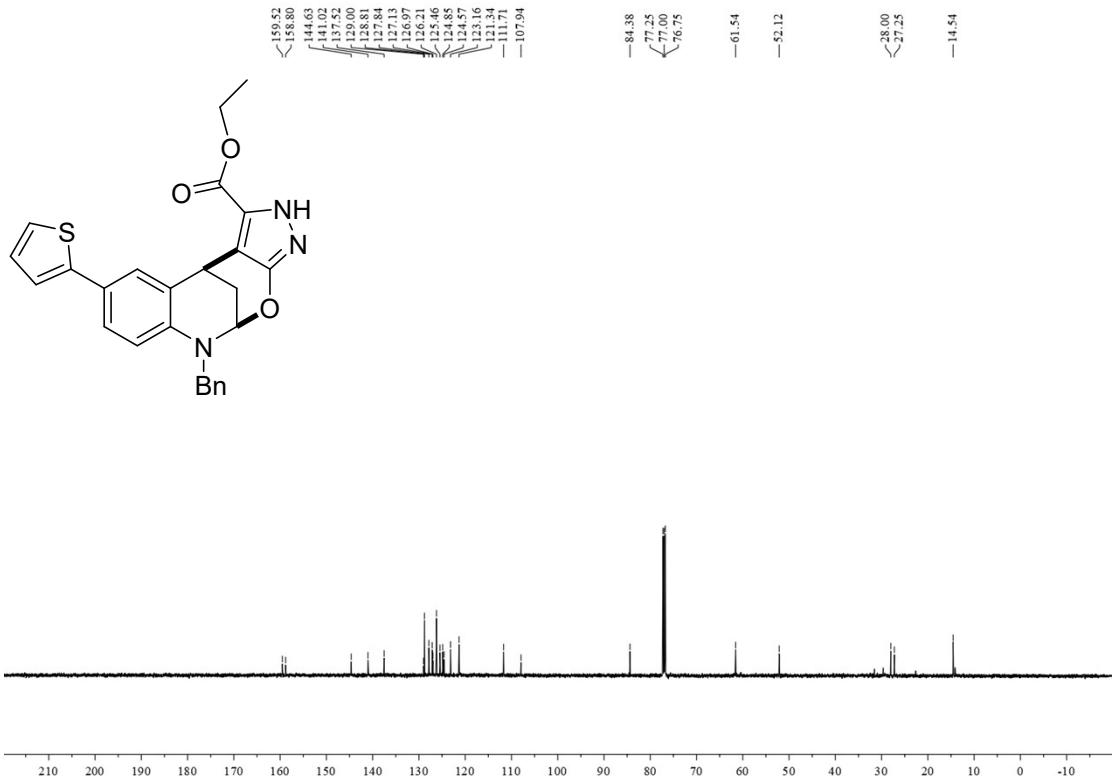
^{19}F-NMR spectrum of C_{15}



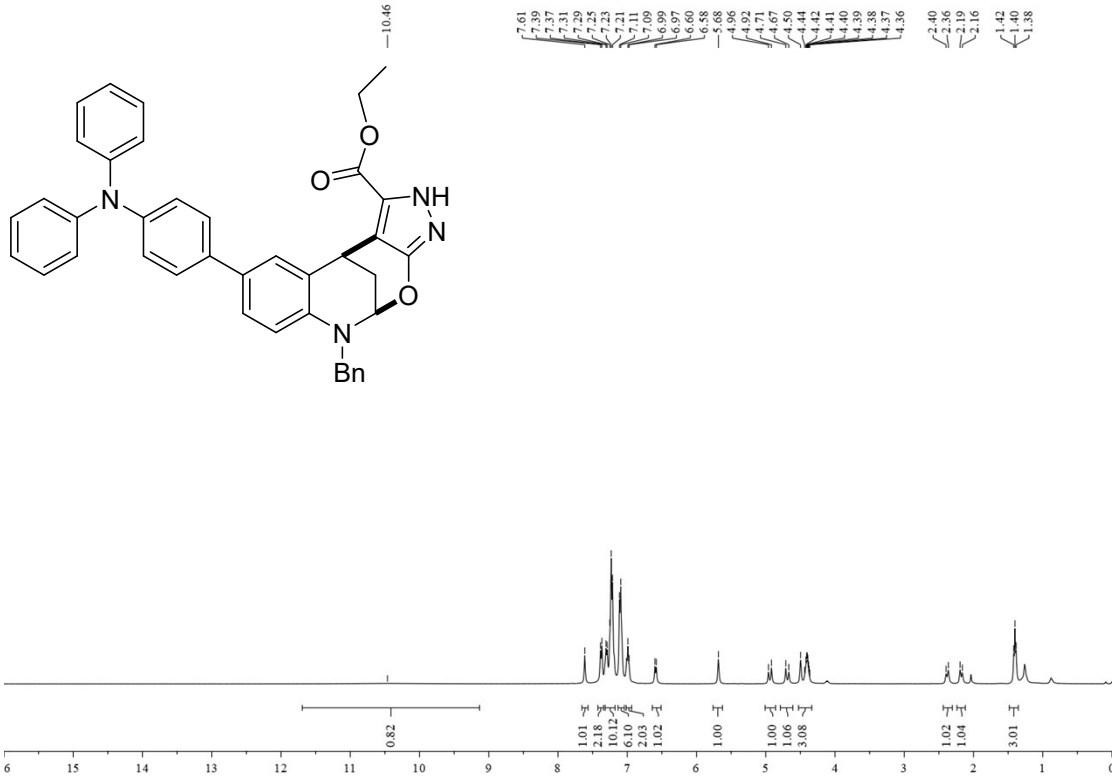
^{1}H-NMR spectrum of C_{16}



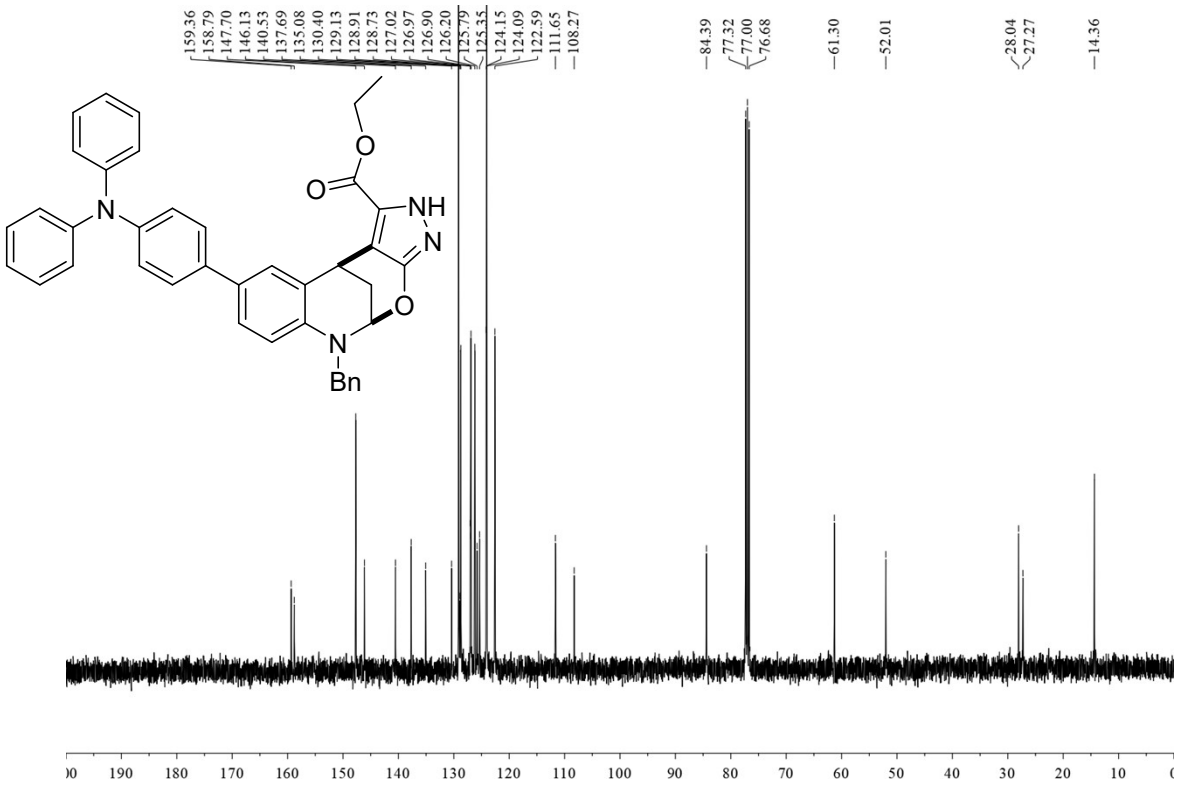
^{13}C-NMR spectrum of C_{16}



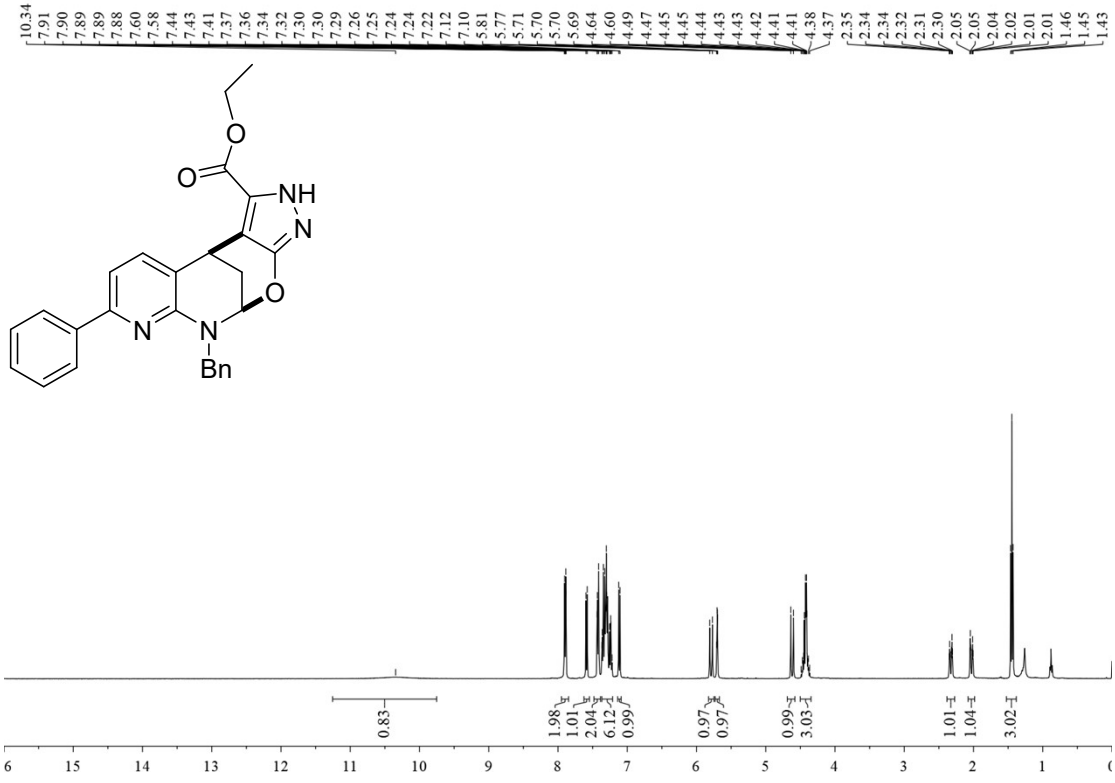
^{1}H-NMR spectrum of C_{17}



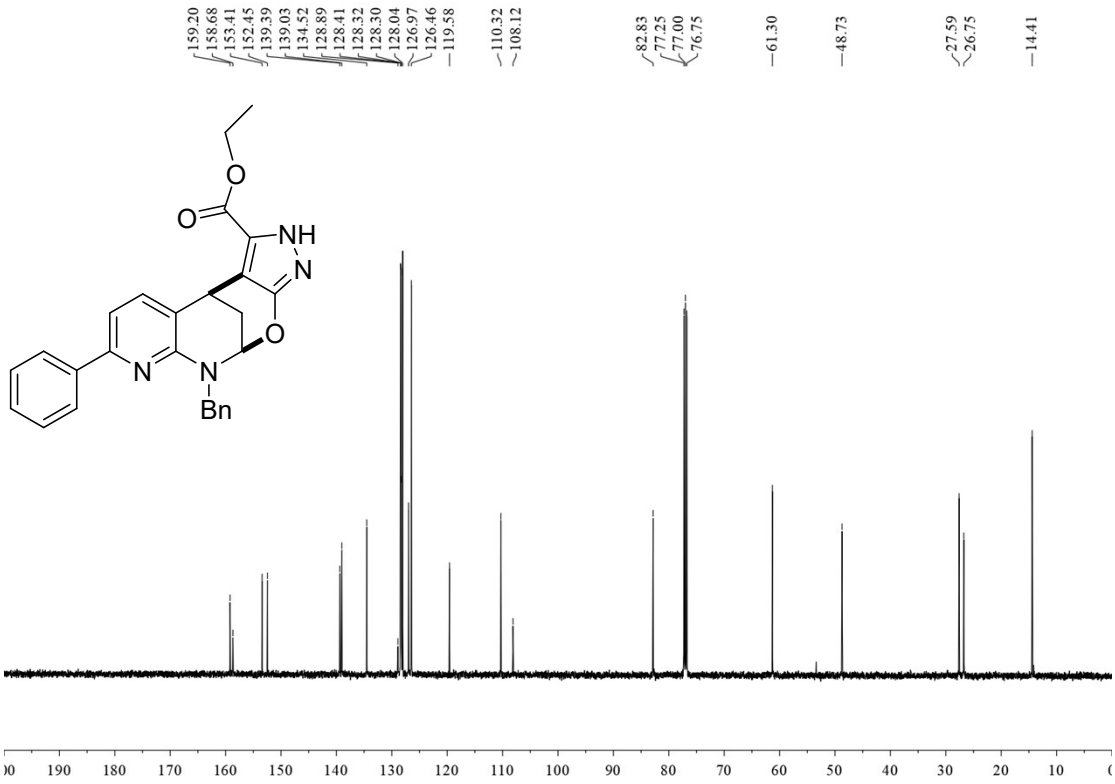
^{13}C-NMR spectrum of C_{17}



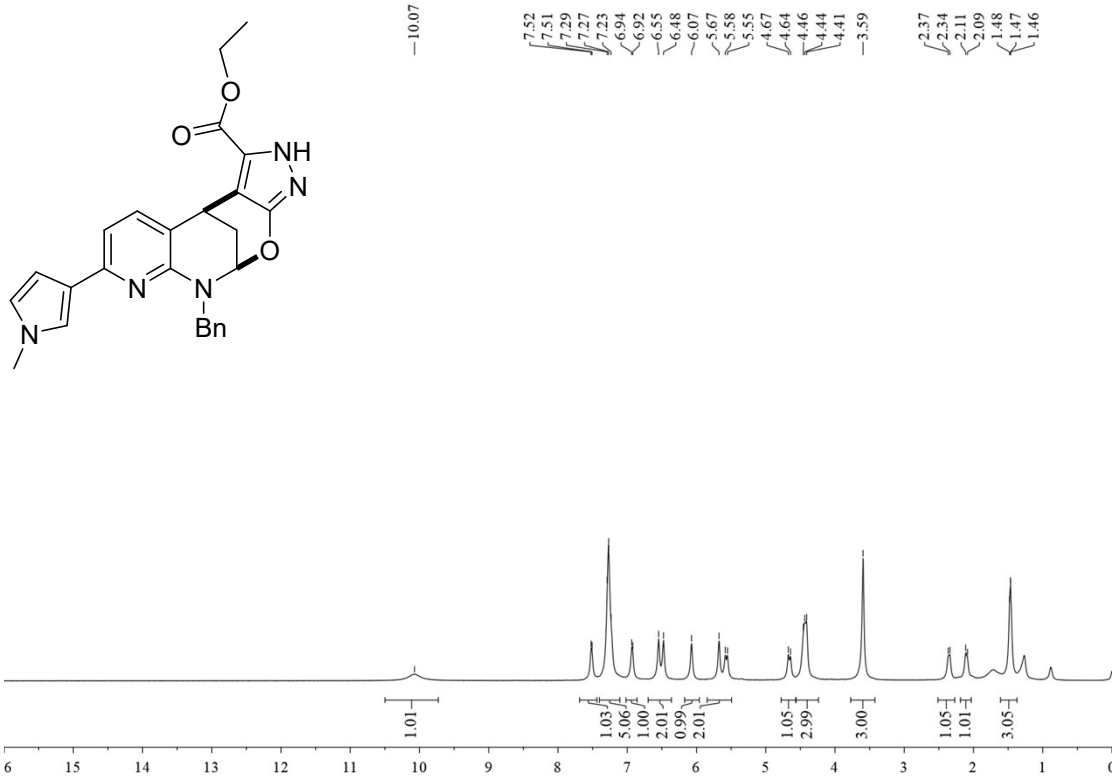
^{1}H-NMR spectrum of C_{18}



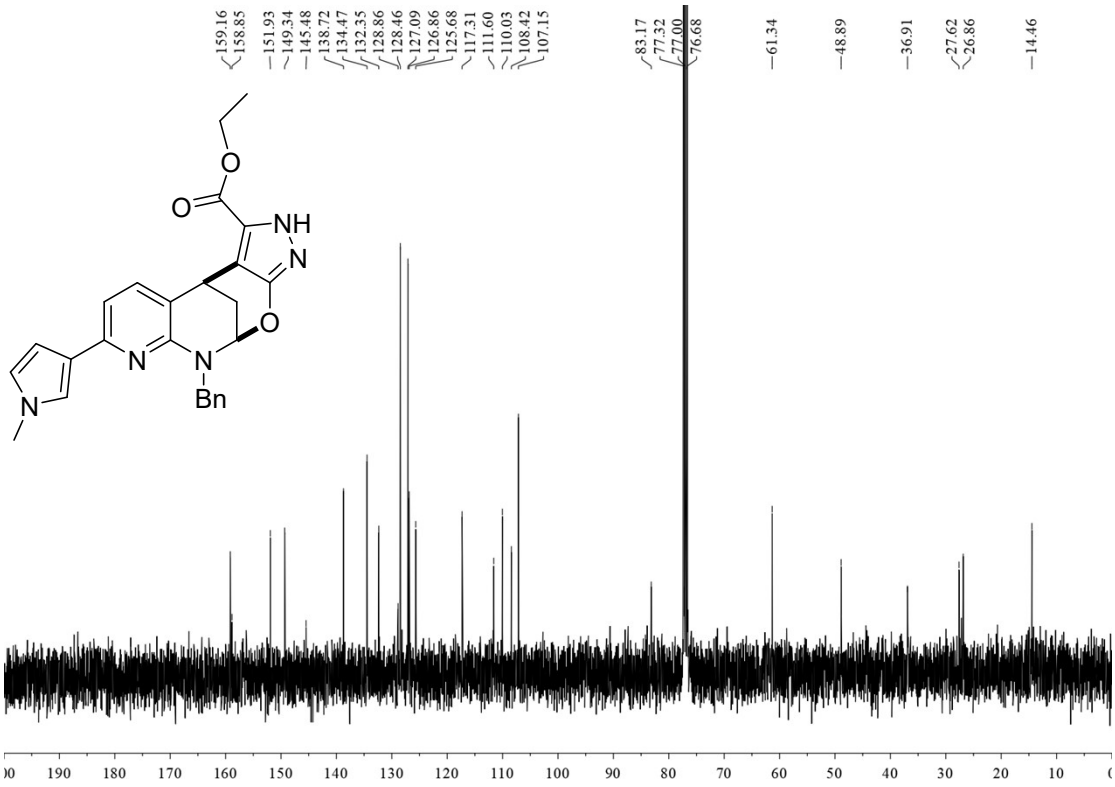
^{13}C-NMR spectrum of C_{18}



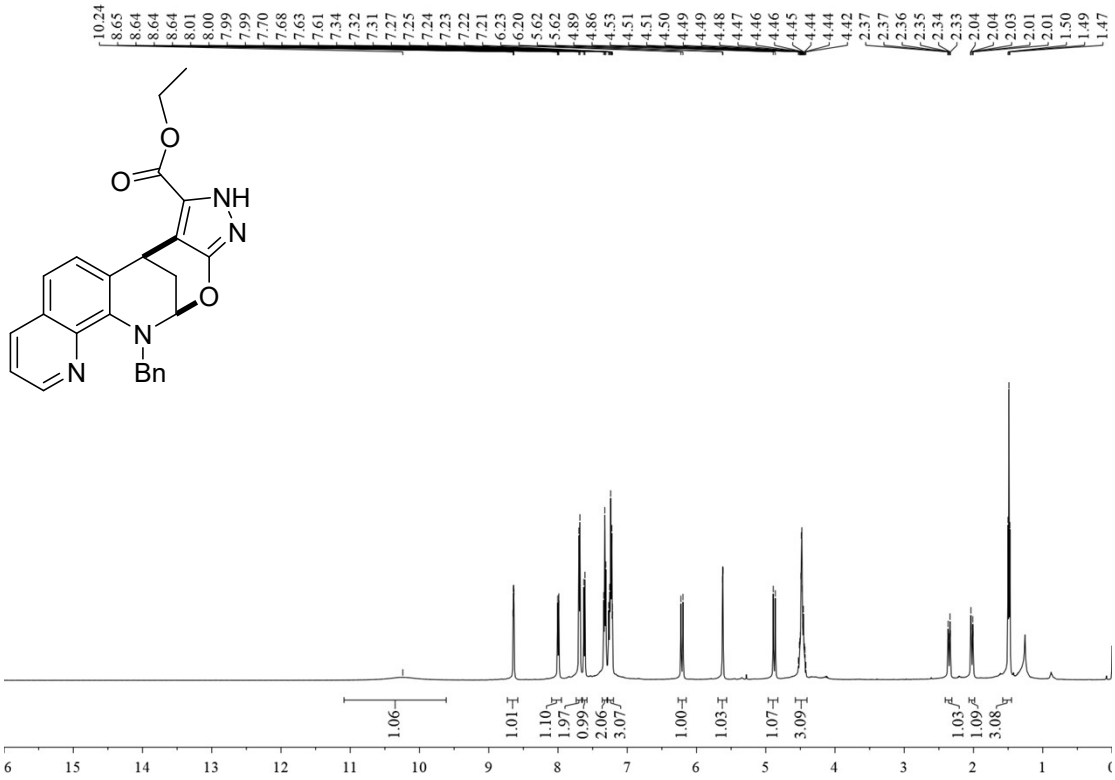
^{1}H-NMR spectrum of C_{19}



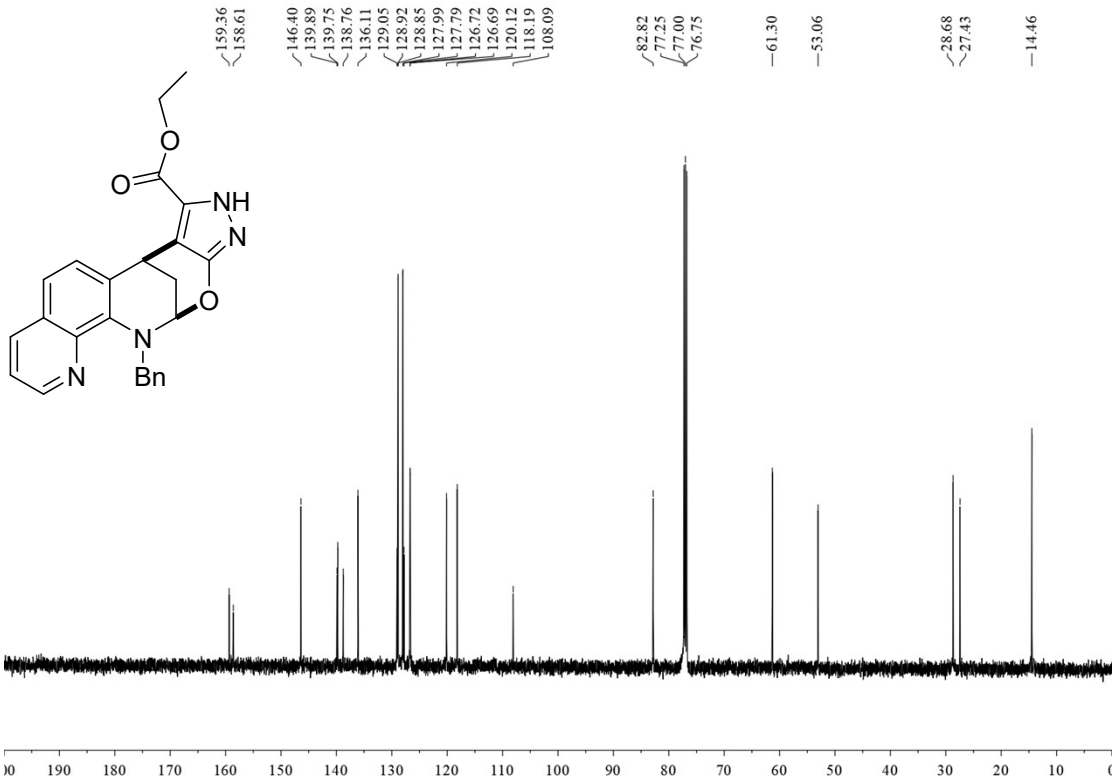
^{13}C-NMR spectrum of C_{19}



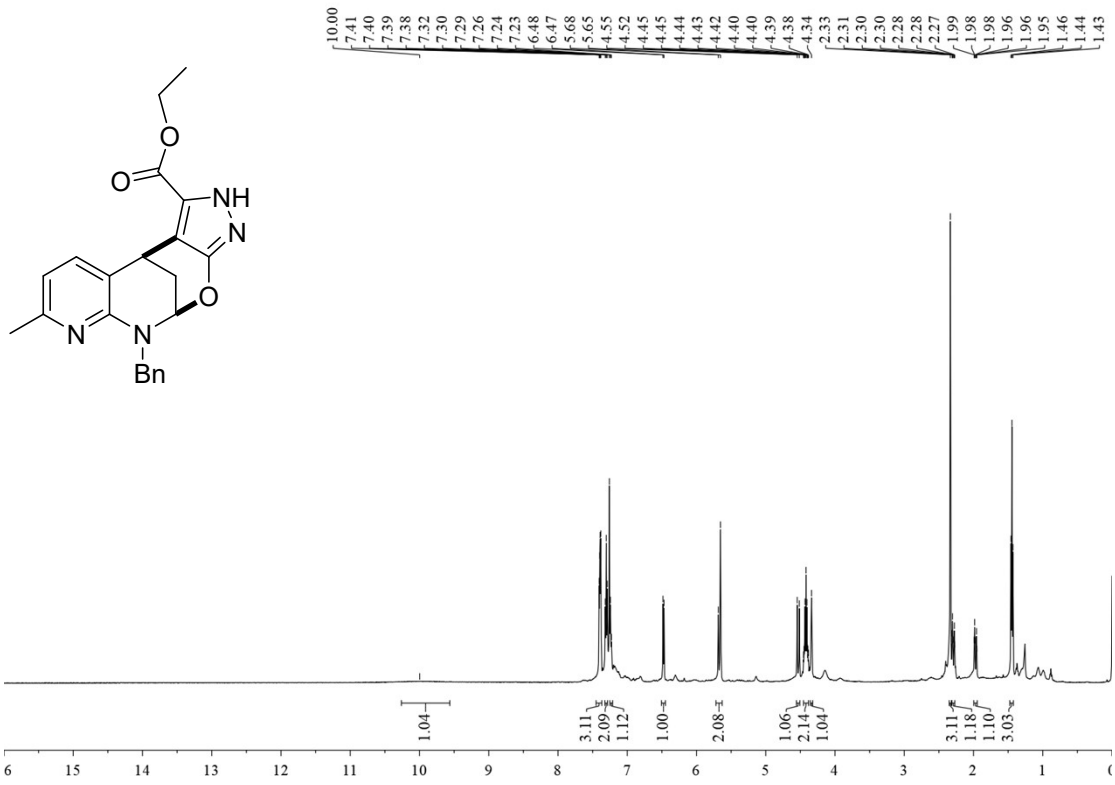
^{1}H-NMR spectrum of C_{20}



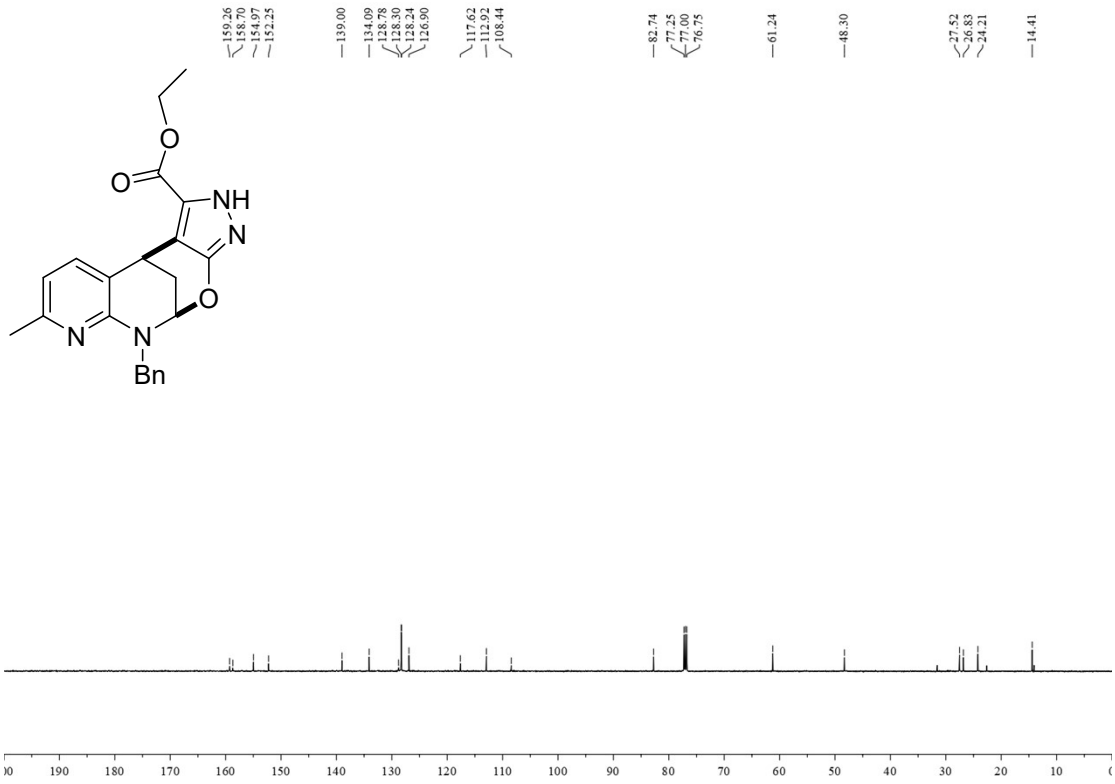
^{13}C-NMR spectrum of C_{20}



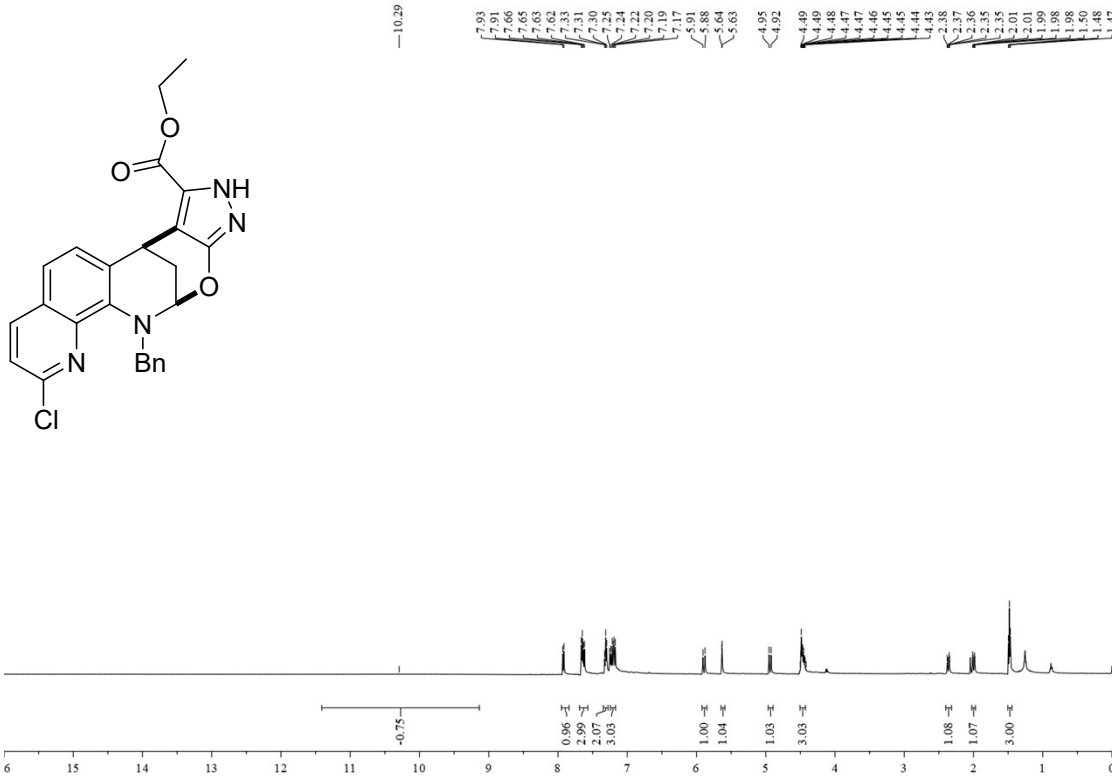
^{1}H-NMR spectrum of C_{21}



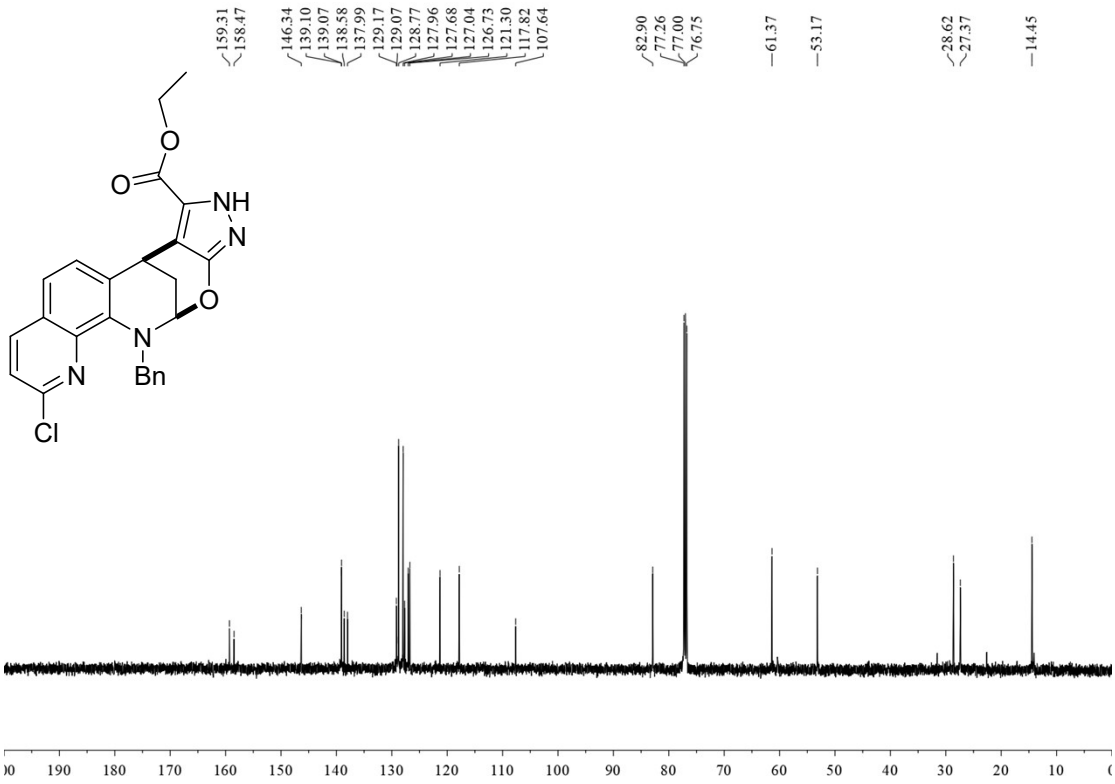
^{13}C-NMR spectrum of C_{21}



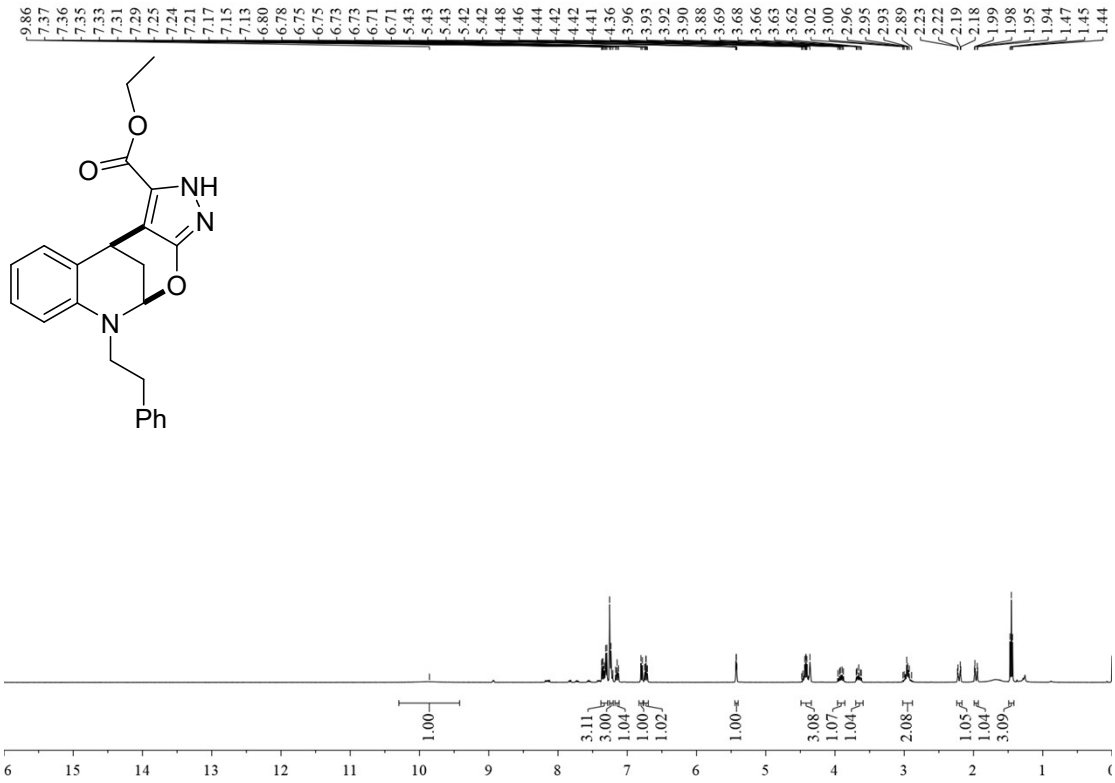
^{1}H-NMR spectrum of C_{22}



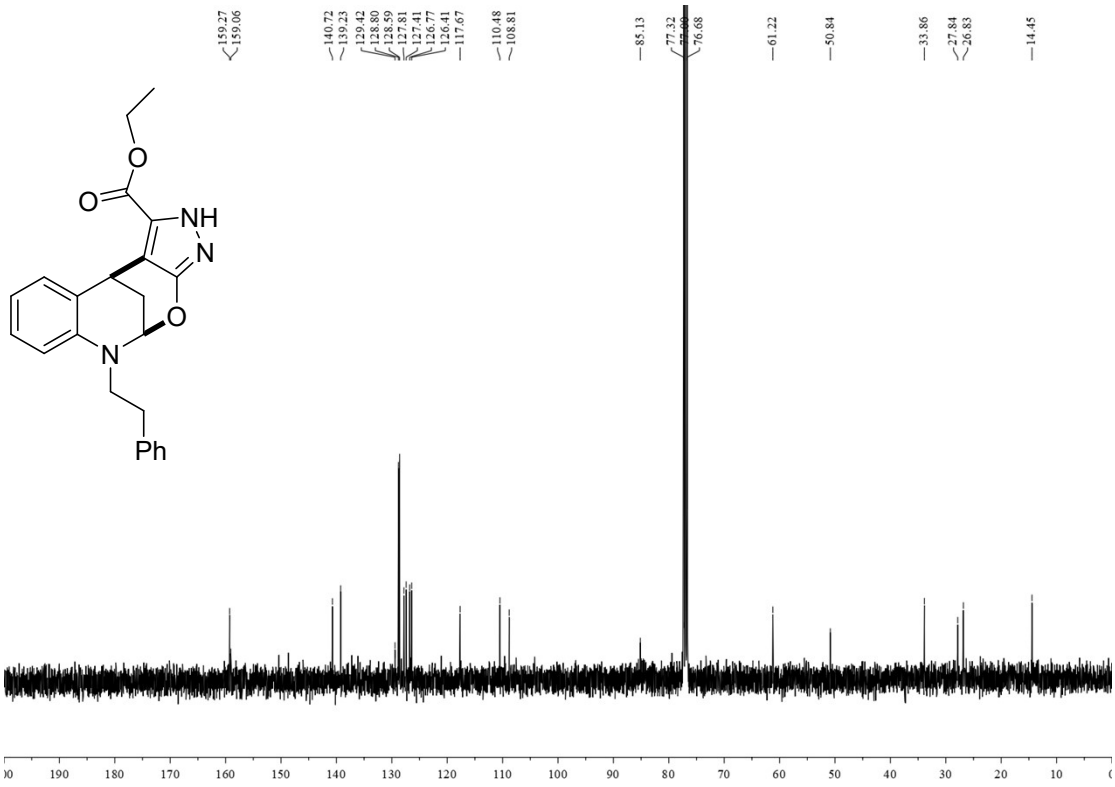
^{13}C-NMR spectrum of C_{22}



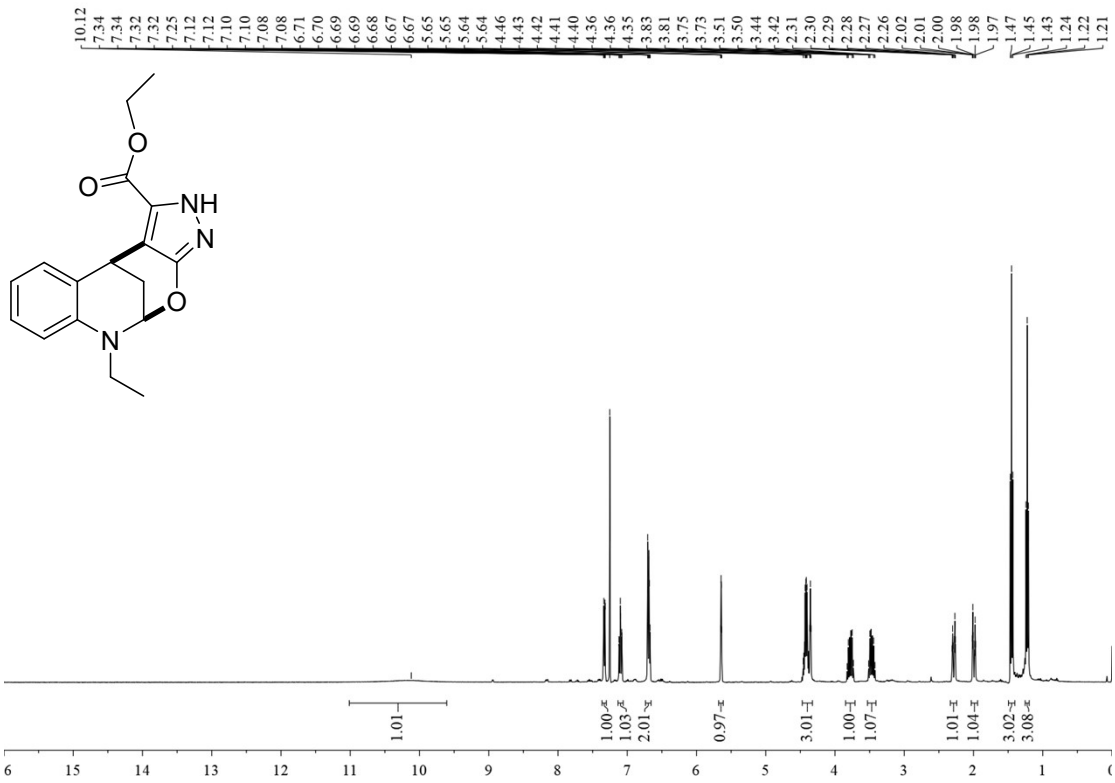
^{1}H-NMR spectrum of C_{23}



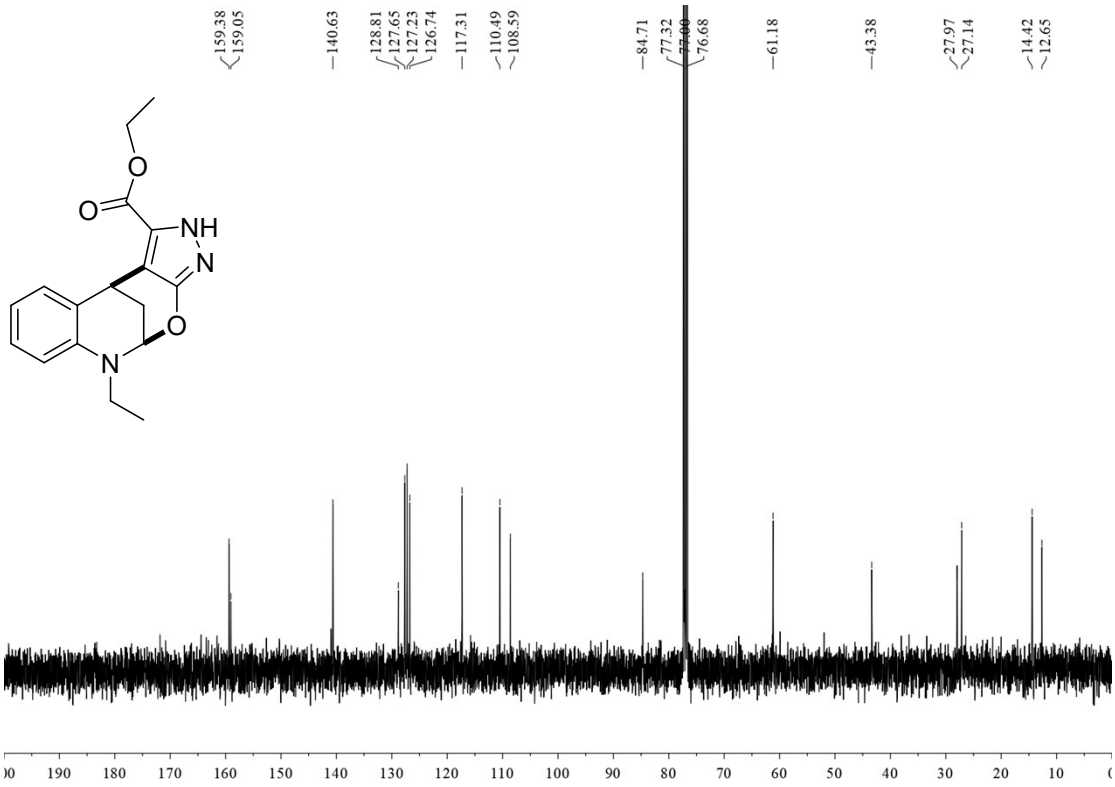
^{13}C-NMR spectrum of C_{23}



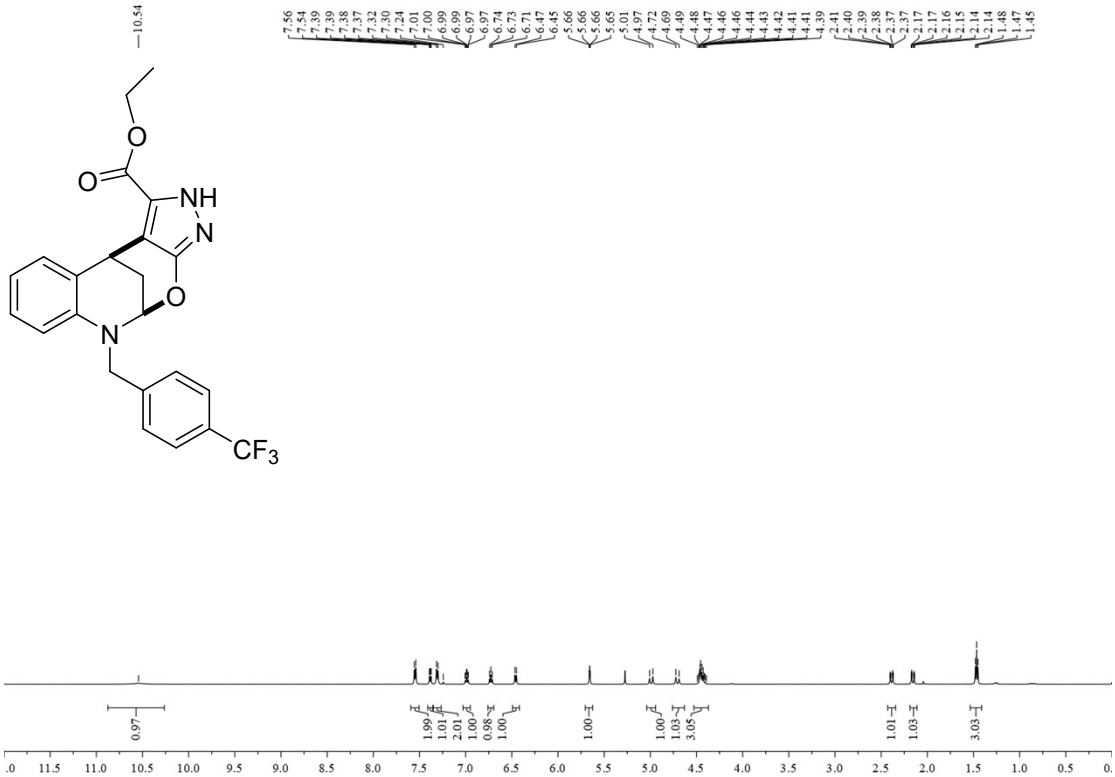
^{1}H-NMR spectrum of C_{24}



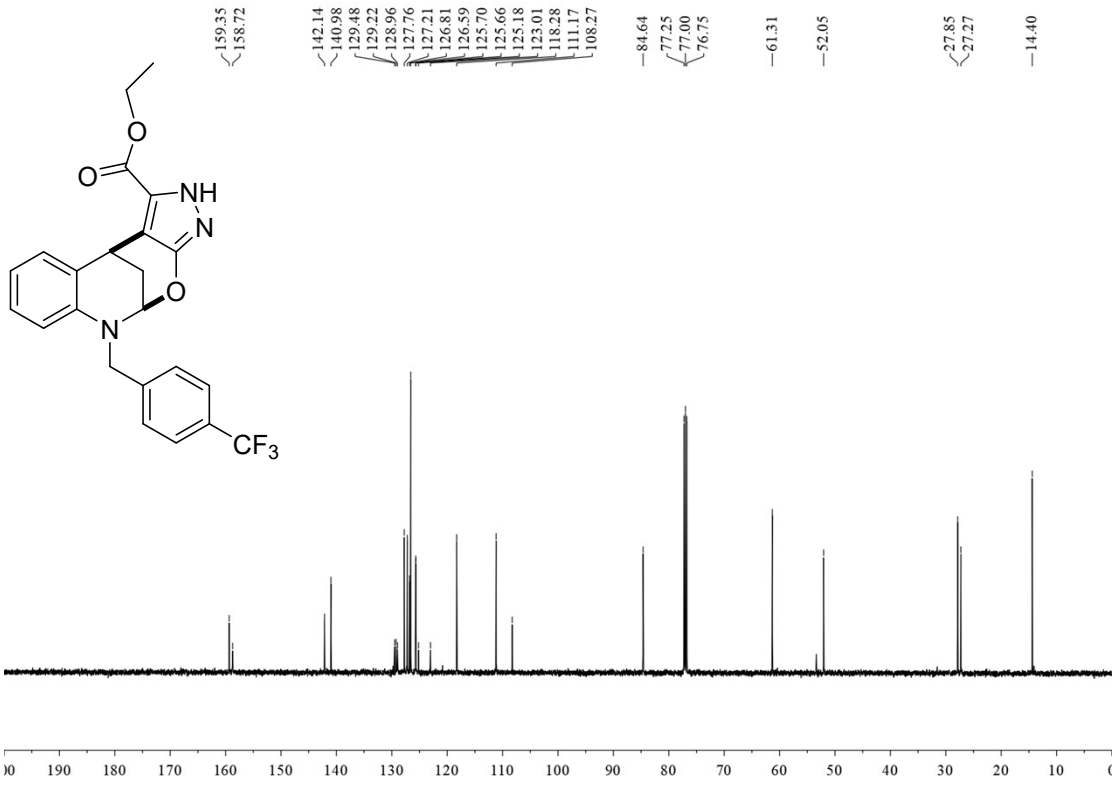
^{13}C-NMR spectrum of C_{24}



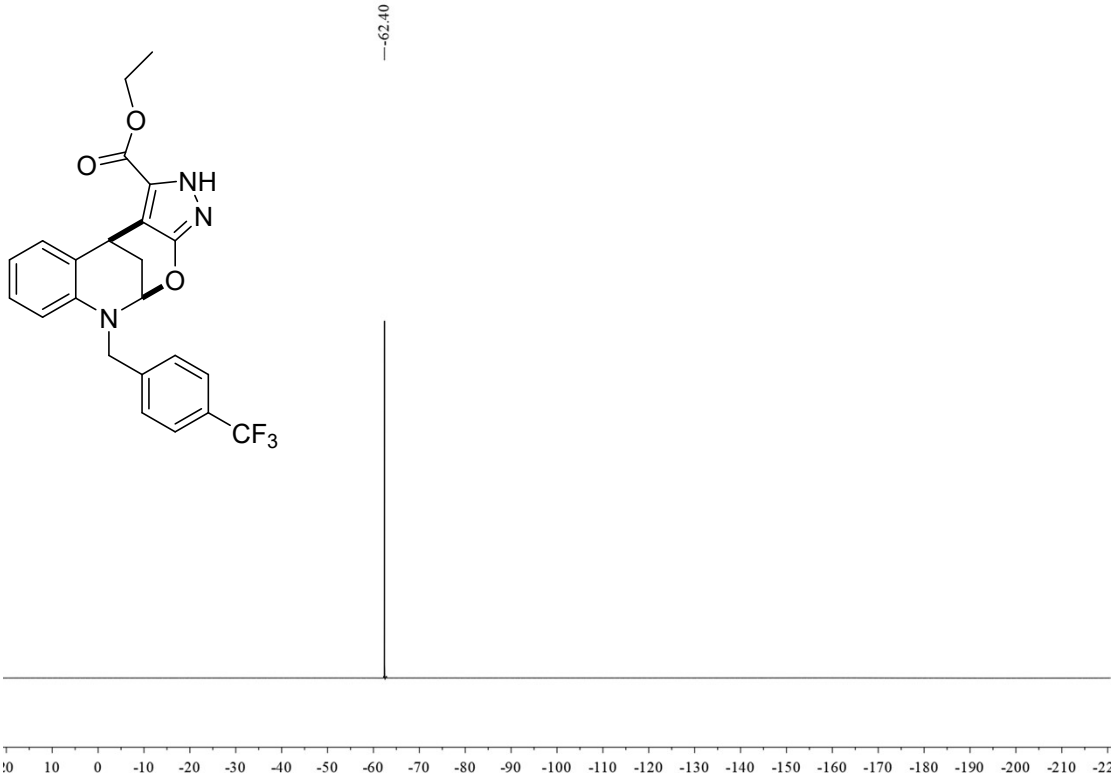
^{1}H-NMR spectrum of C_{25}



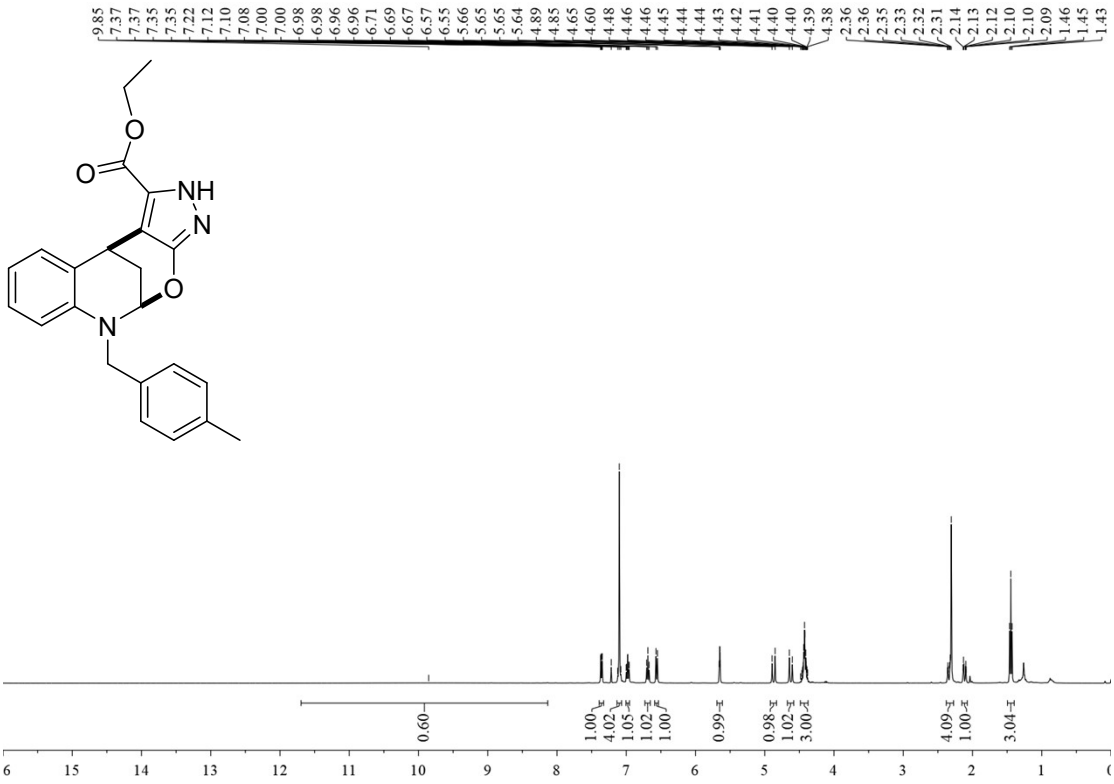
^{13}C-NMR spectrum of C_{25}



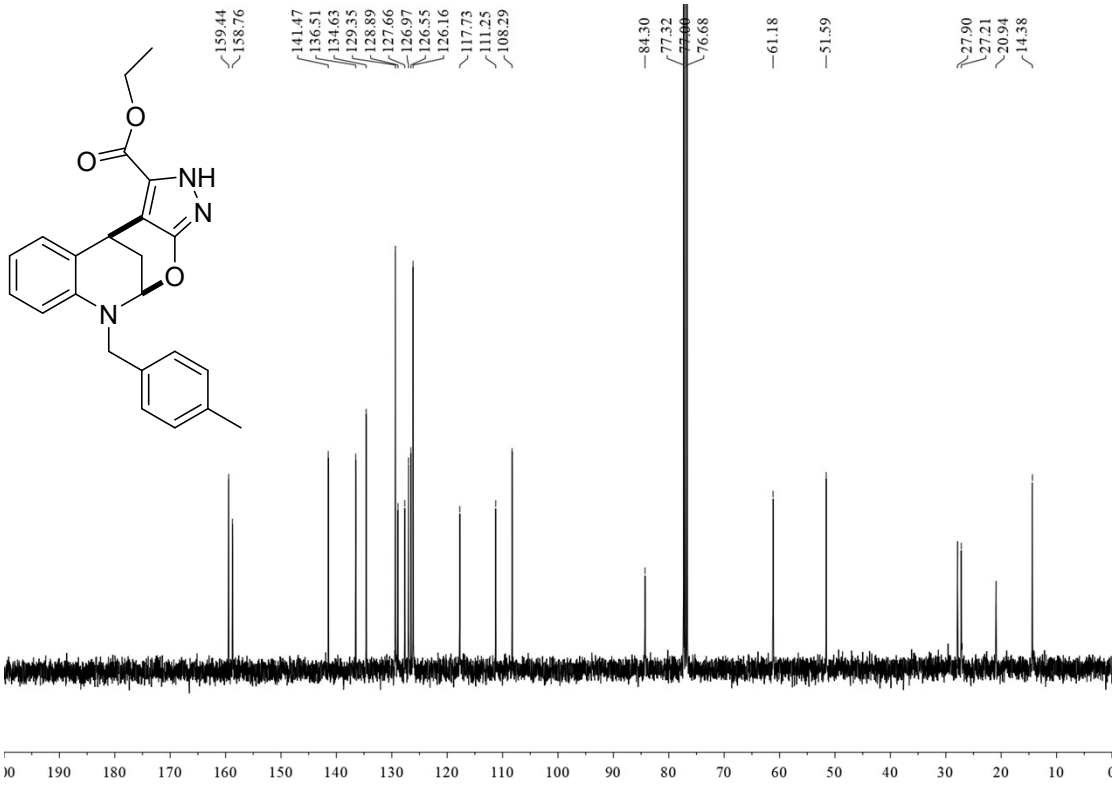
^{19}F-NMR spectrum of C_{25}



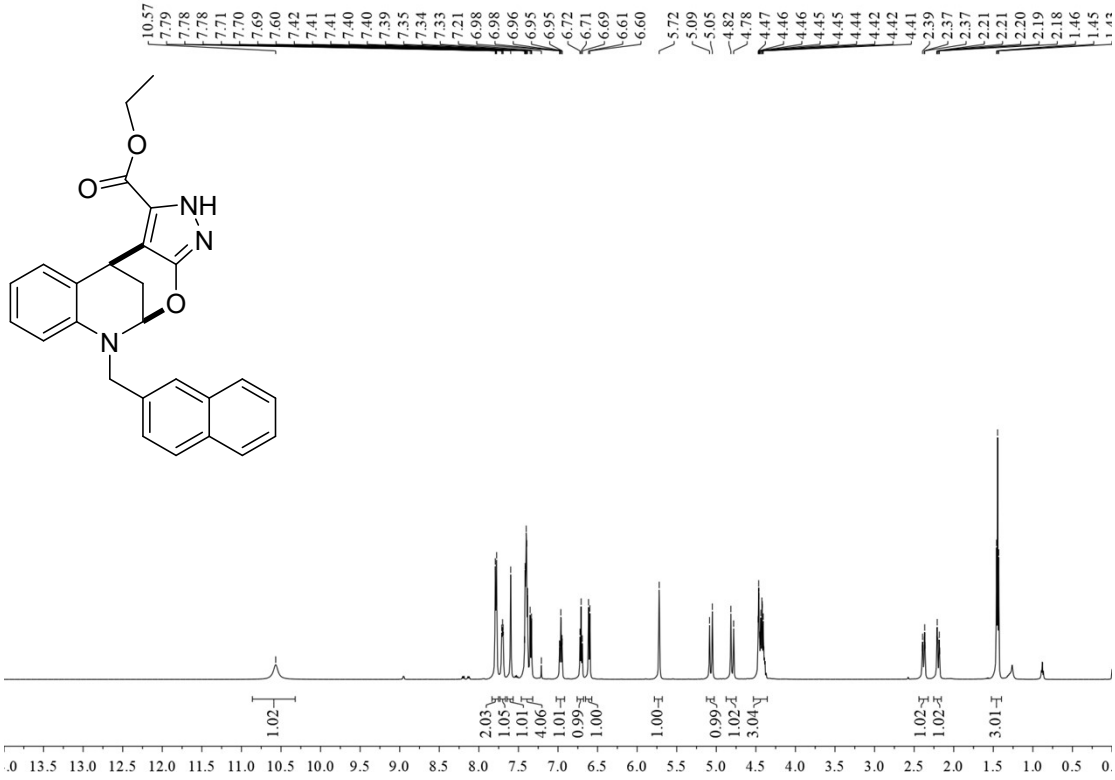
^{1}H-NMR spectrum of C_{26}



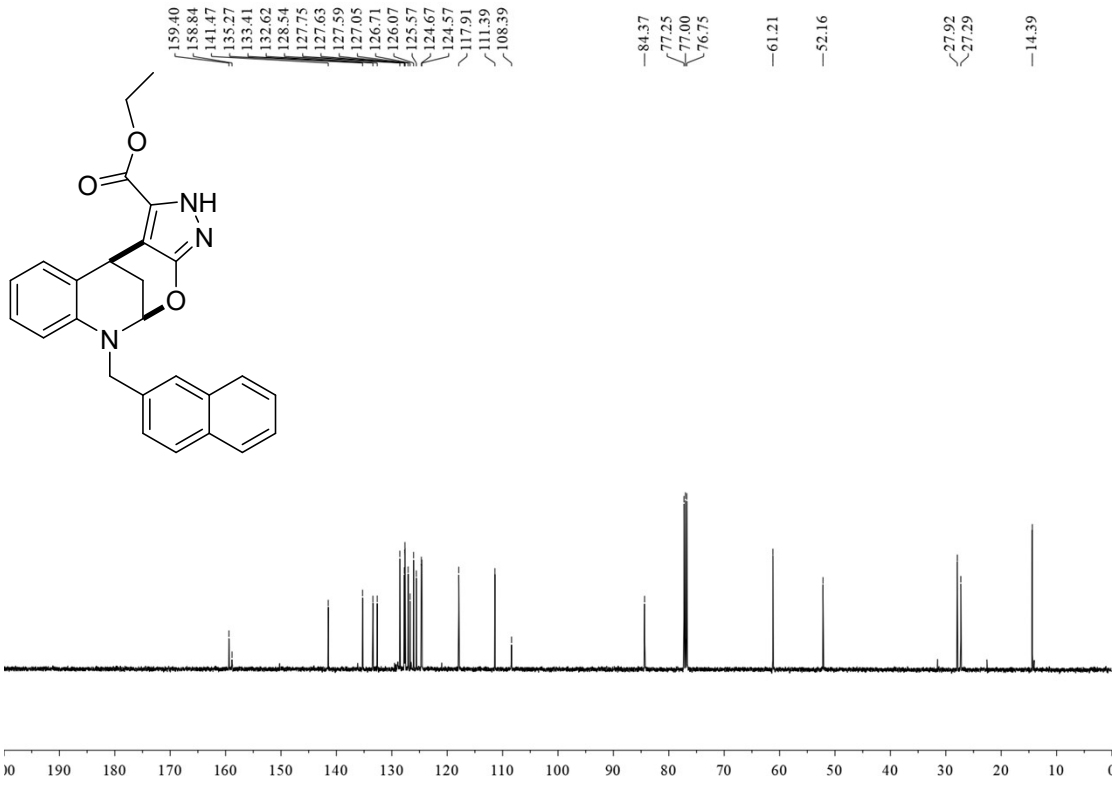
^{13}C-NMR spectrum of C_{26}



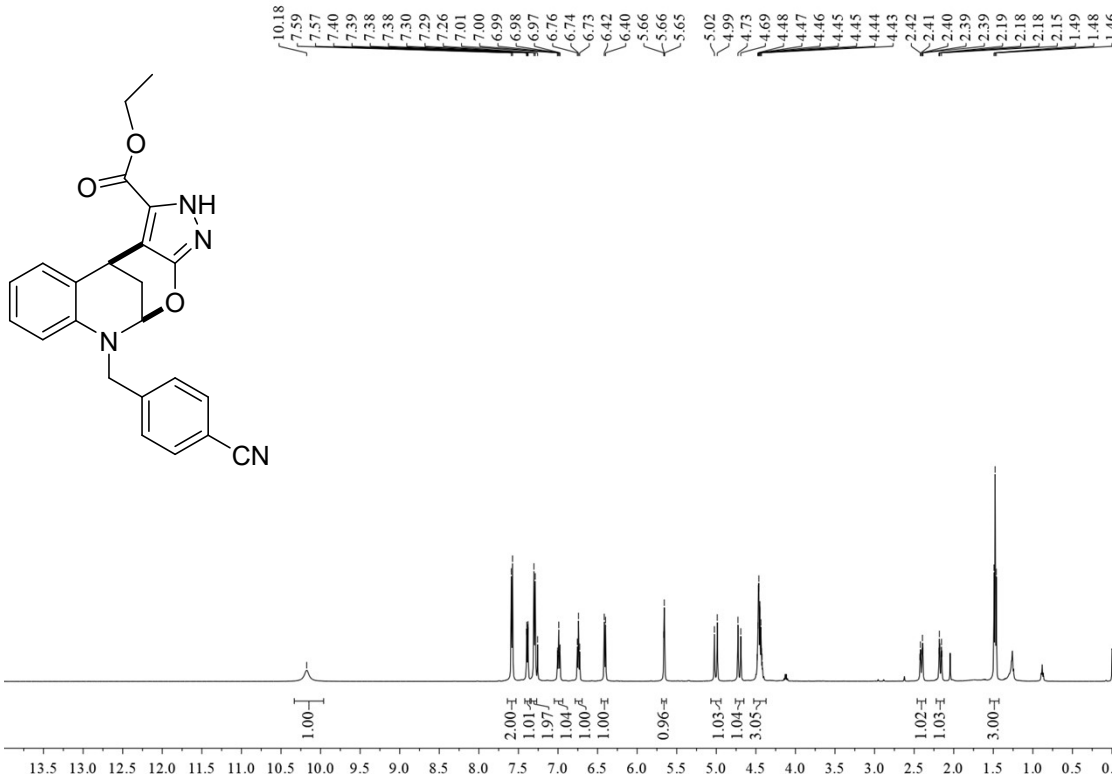
^{1}H-NMR spectrum of C_{27}



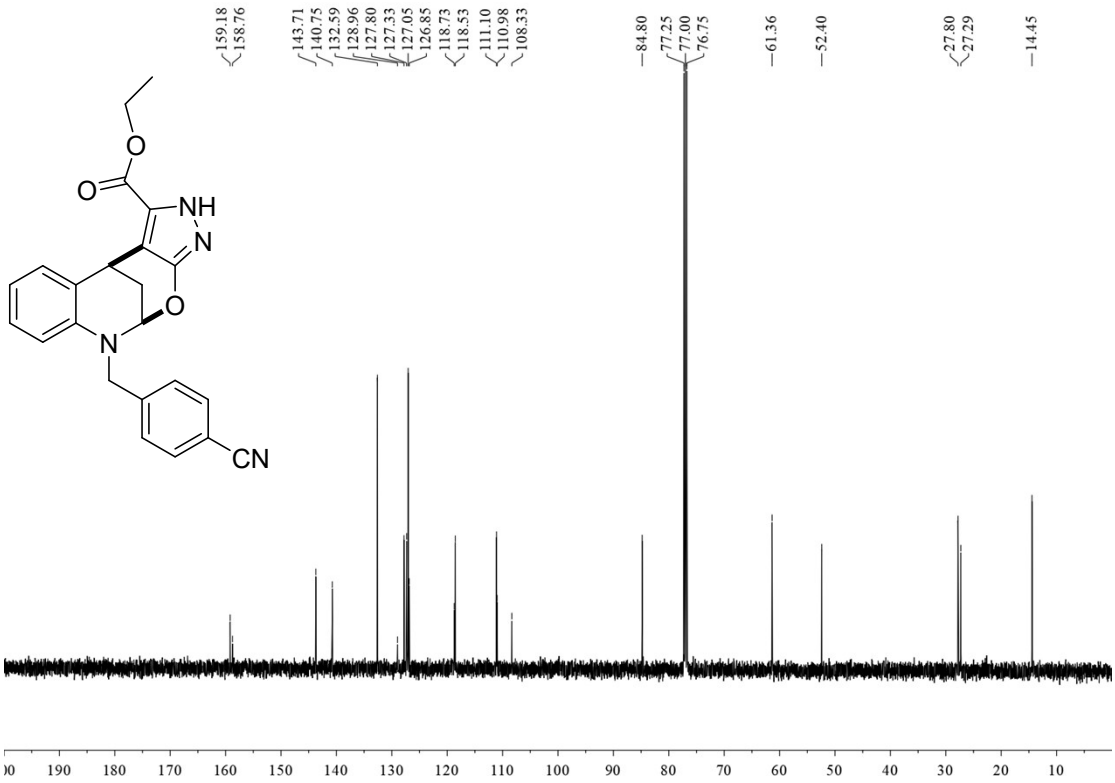
^{13}C-NMR spectrum of C_{27}



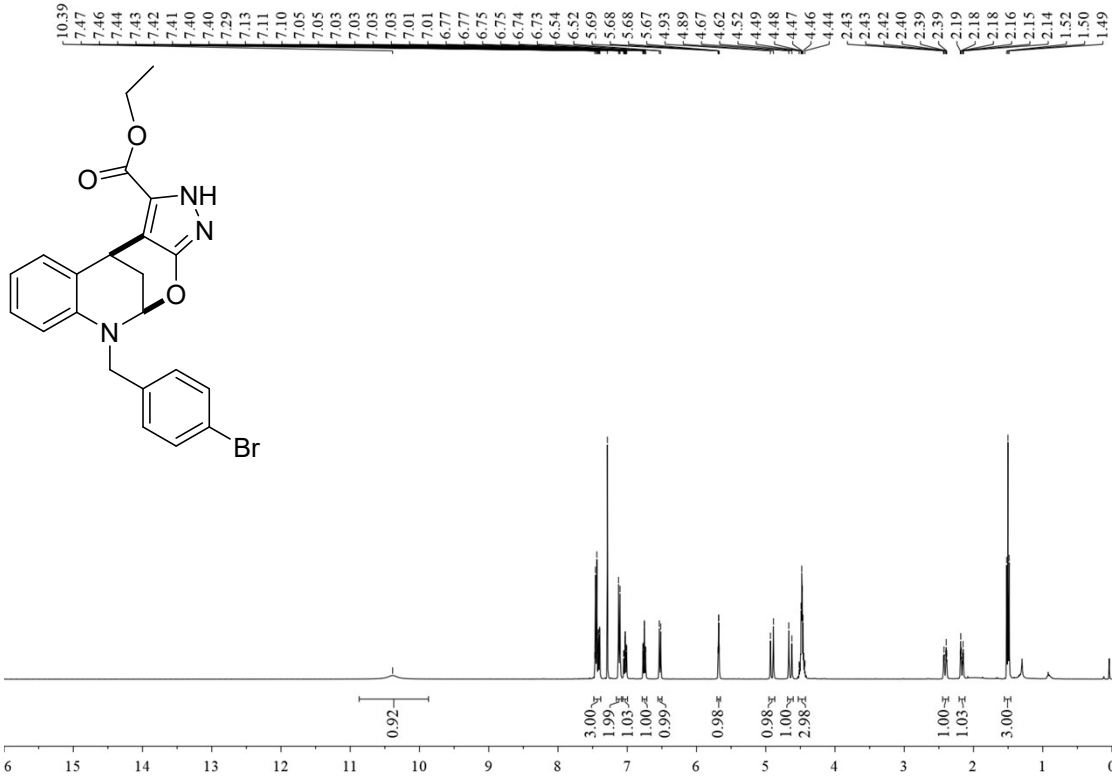
^{1}H-NMR spectrum of C_{28}



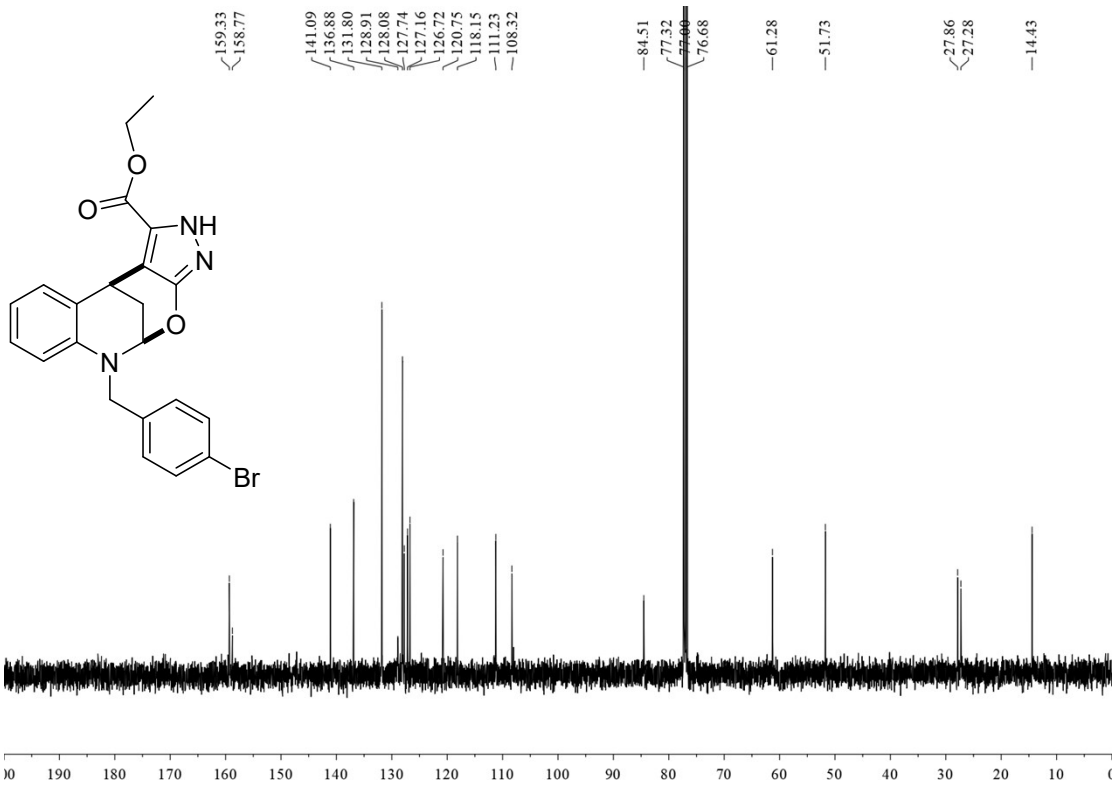
^{13}C-NMR spectrum of C_{28}



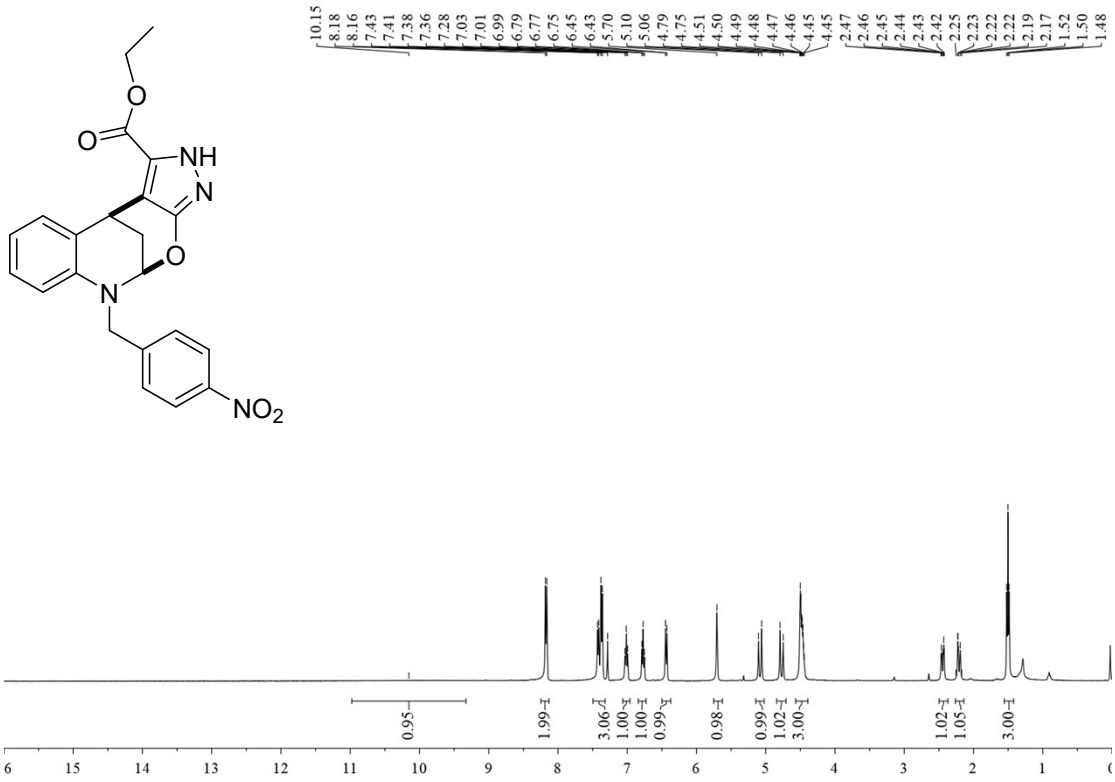
^{1}H-NMR spectrum of C_{29}



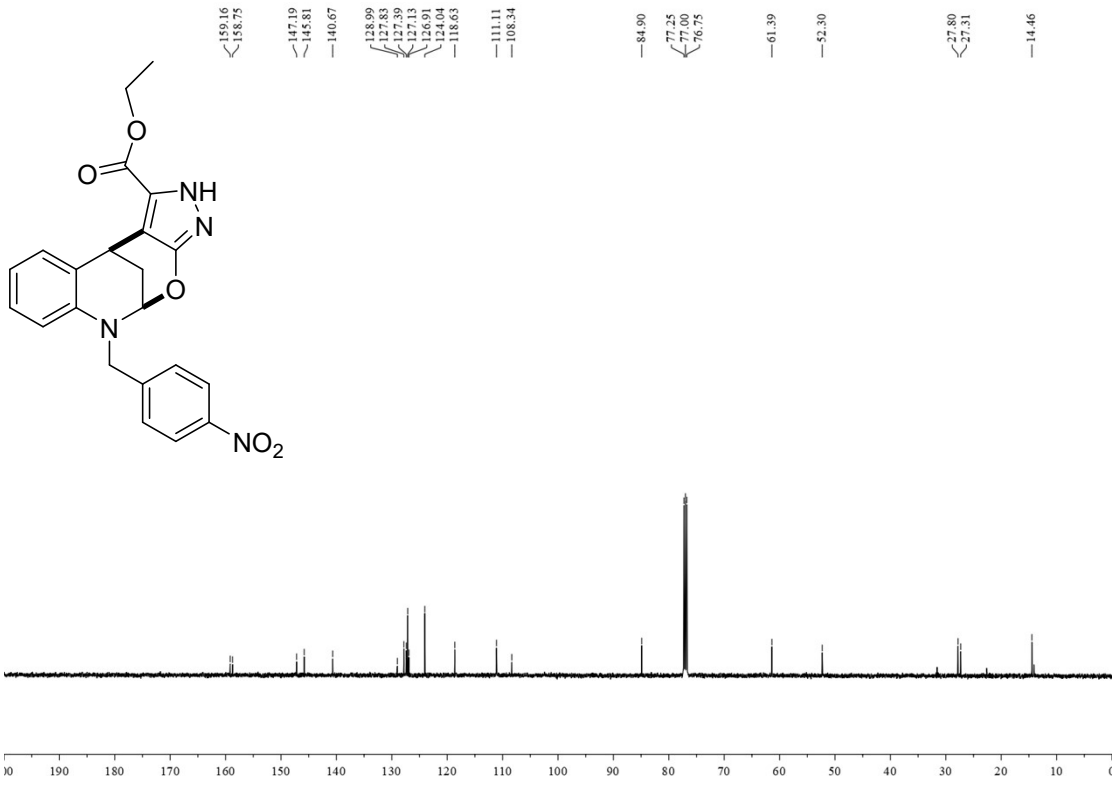
^{13}C-NMR spectrum of C_{29}



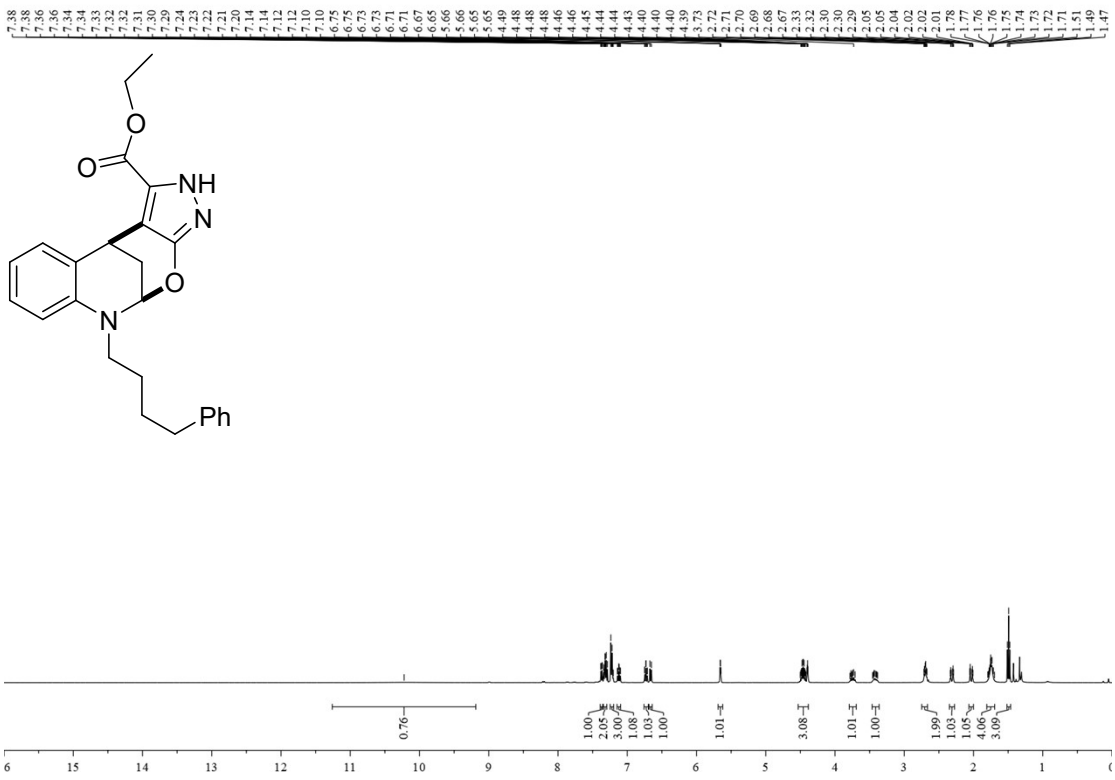
^{1}H-NMR spectrum of C_{30}



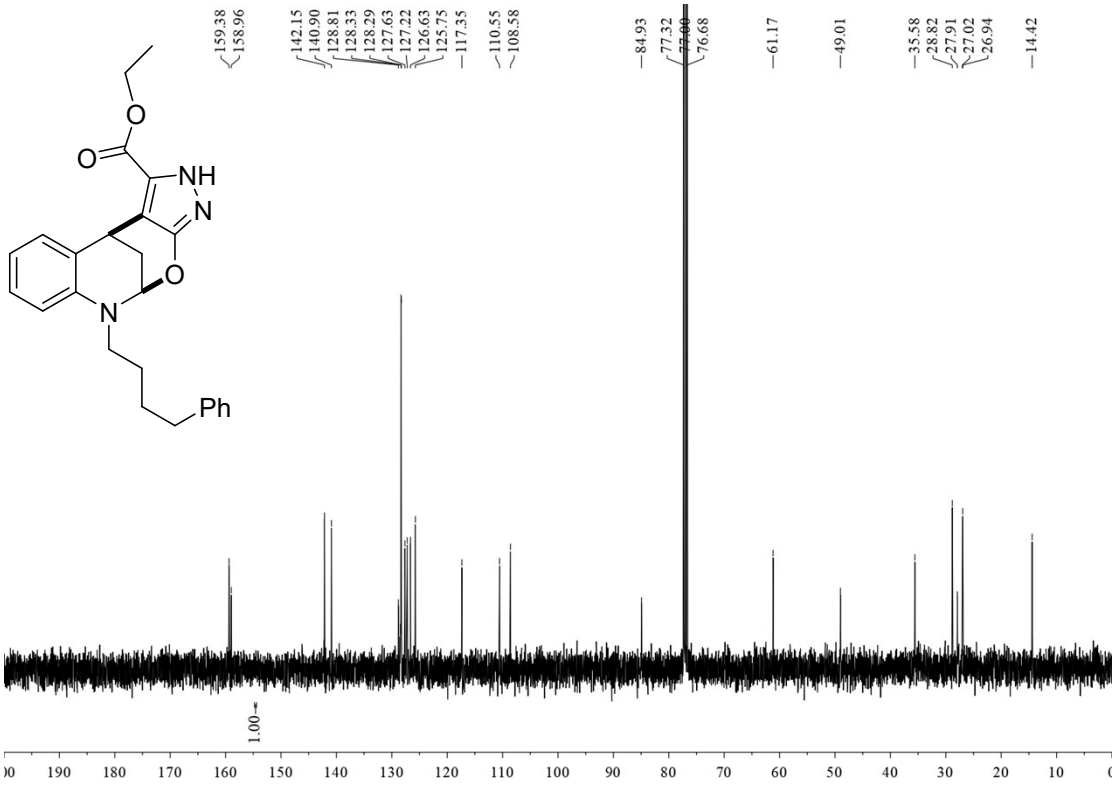
^{13}C-NMR spectrum of C_{30}



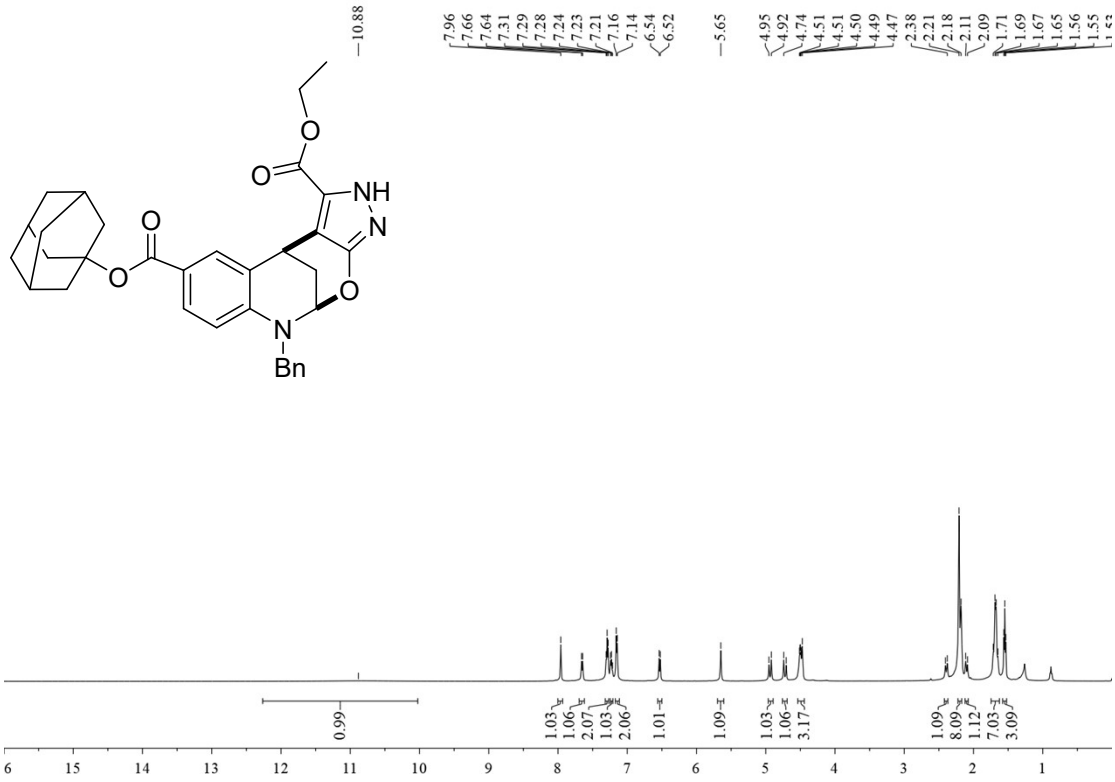
^{1}H-NMR spectrum of C_{31}



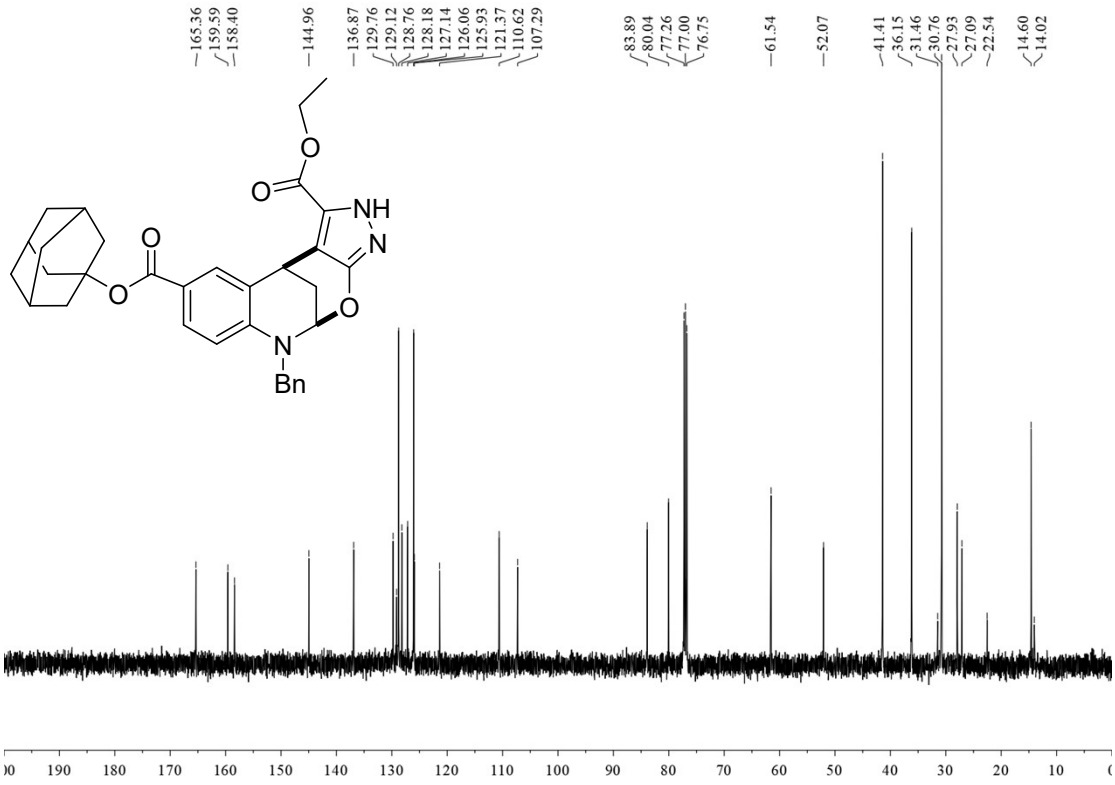
^{13}C-NMR spectrum of C_{31}



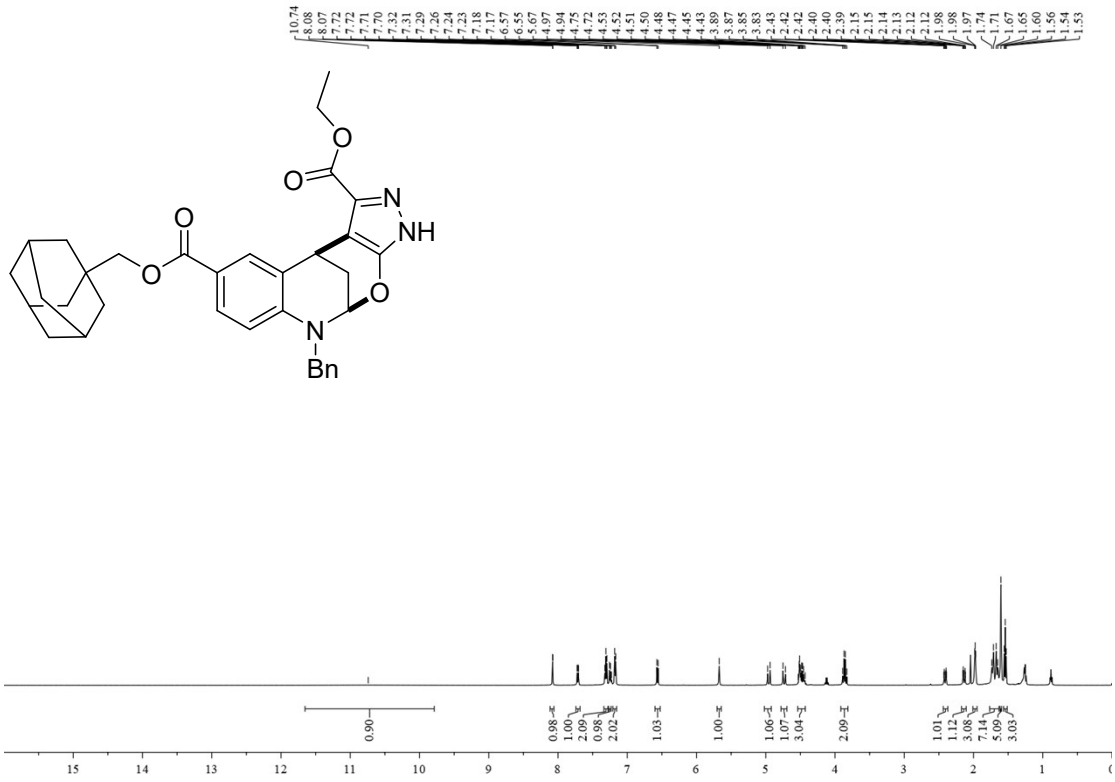
^{1}H-NMR spectrum of C_{32}



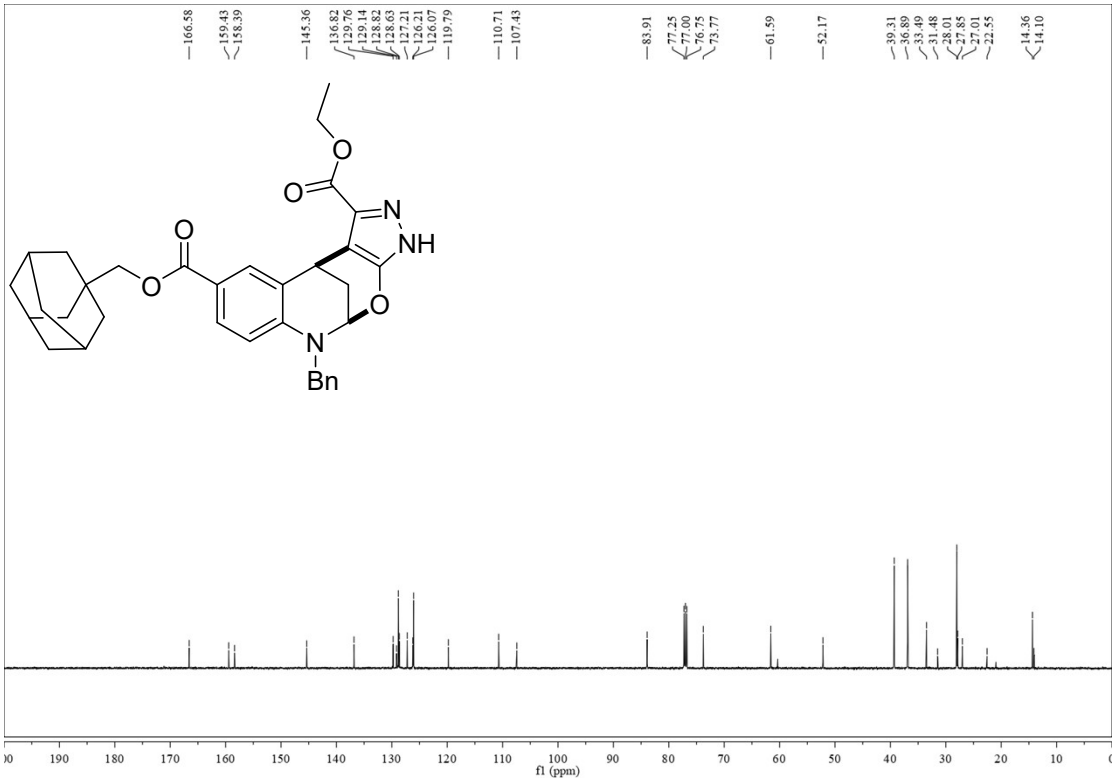
^{13}C-NMR spectrum of C_{32}



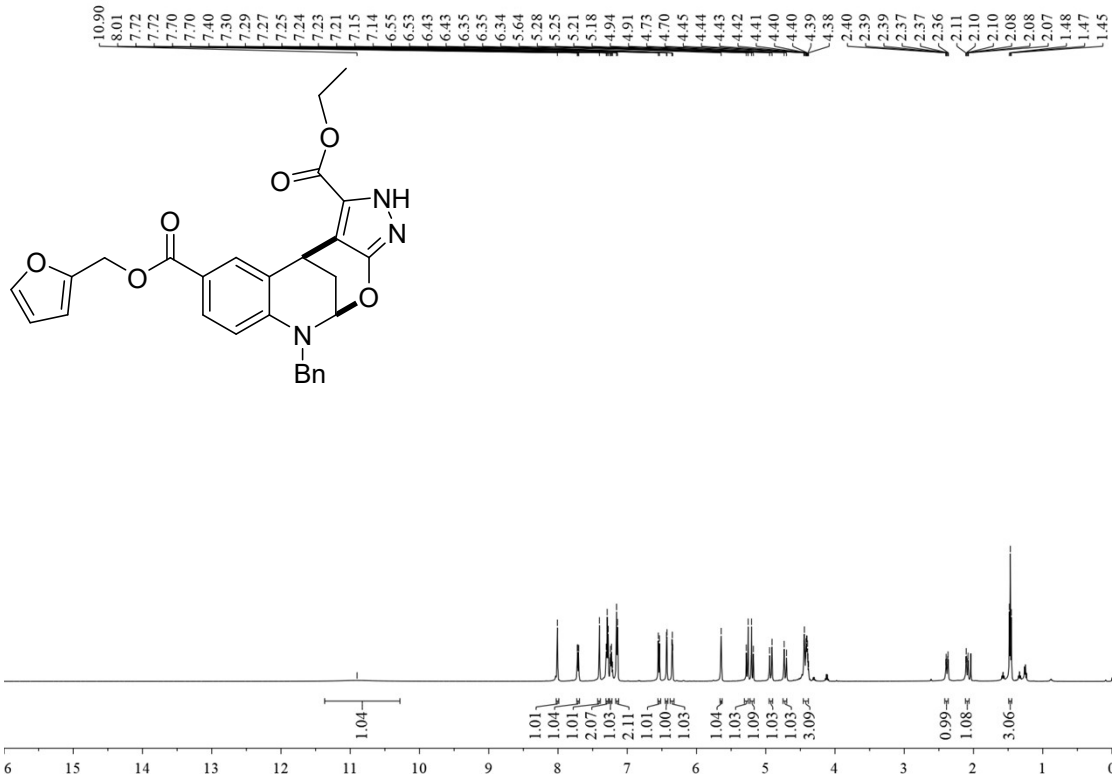
^{1}H-NMR spectrum of C_{33}



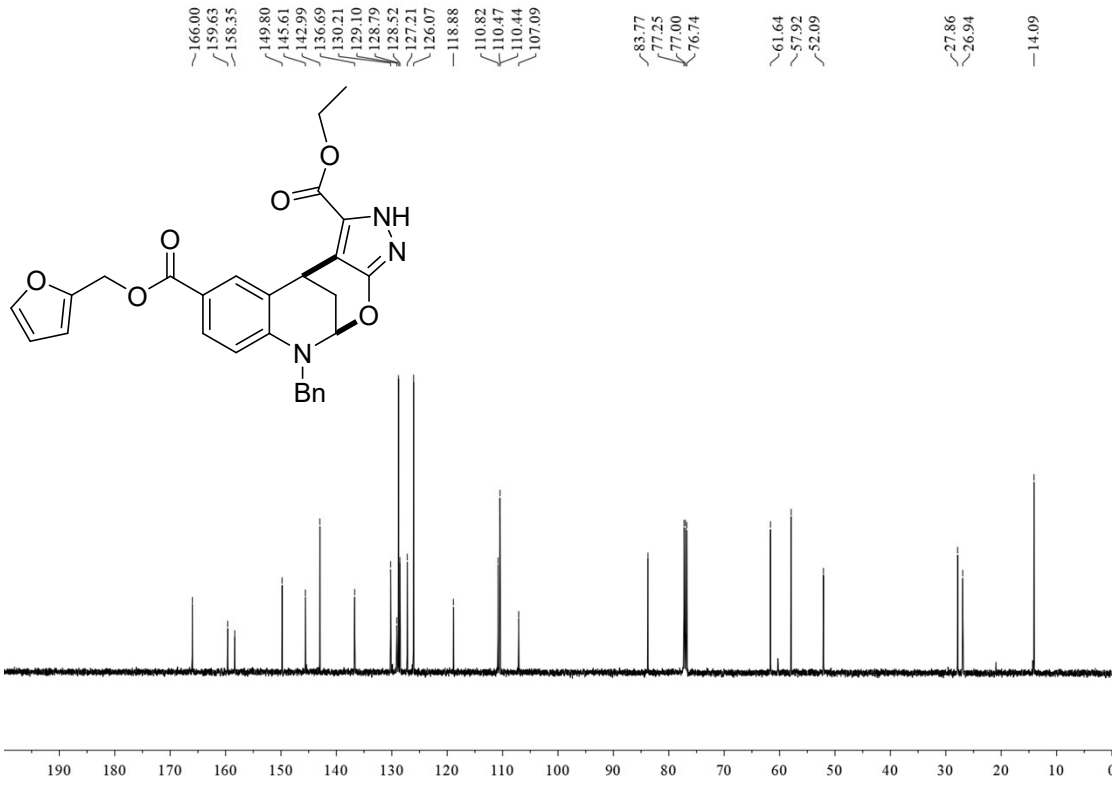
^{13}C-NMR spectrum of C_{33}



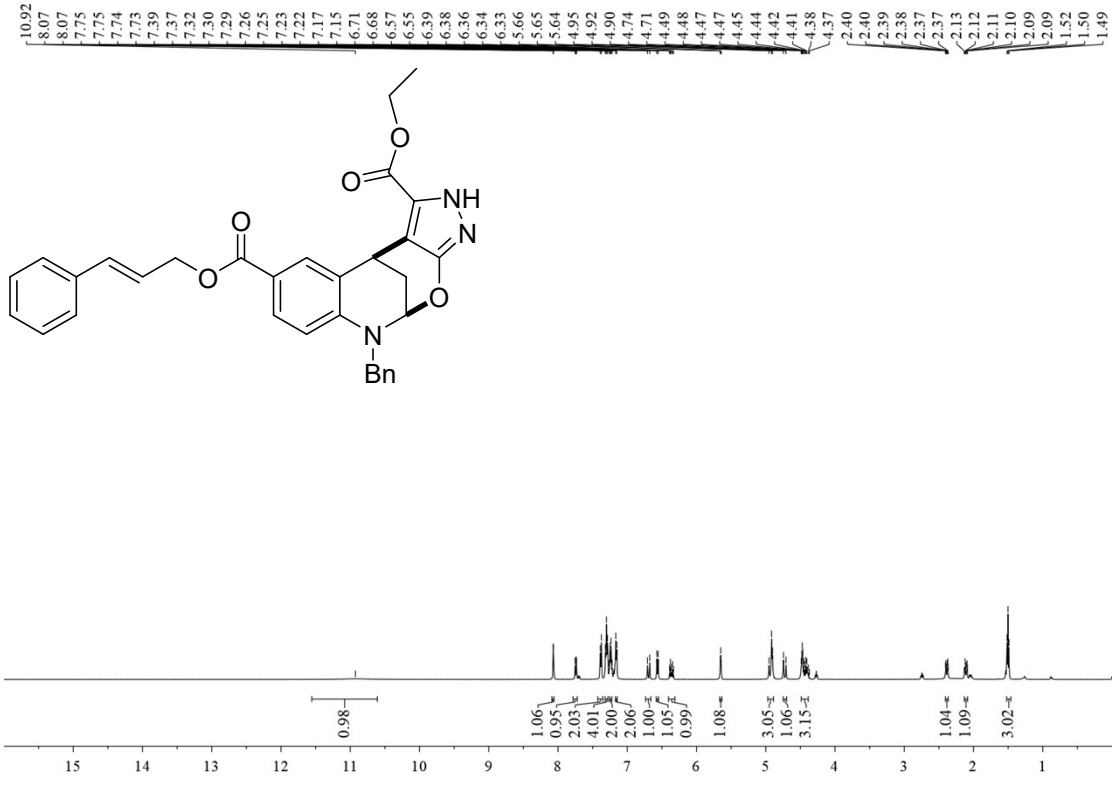
^{1}H-NMR spectrum of C_{34}



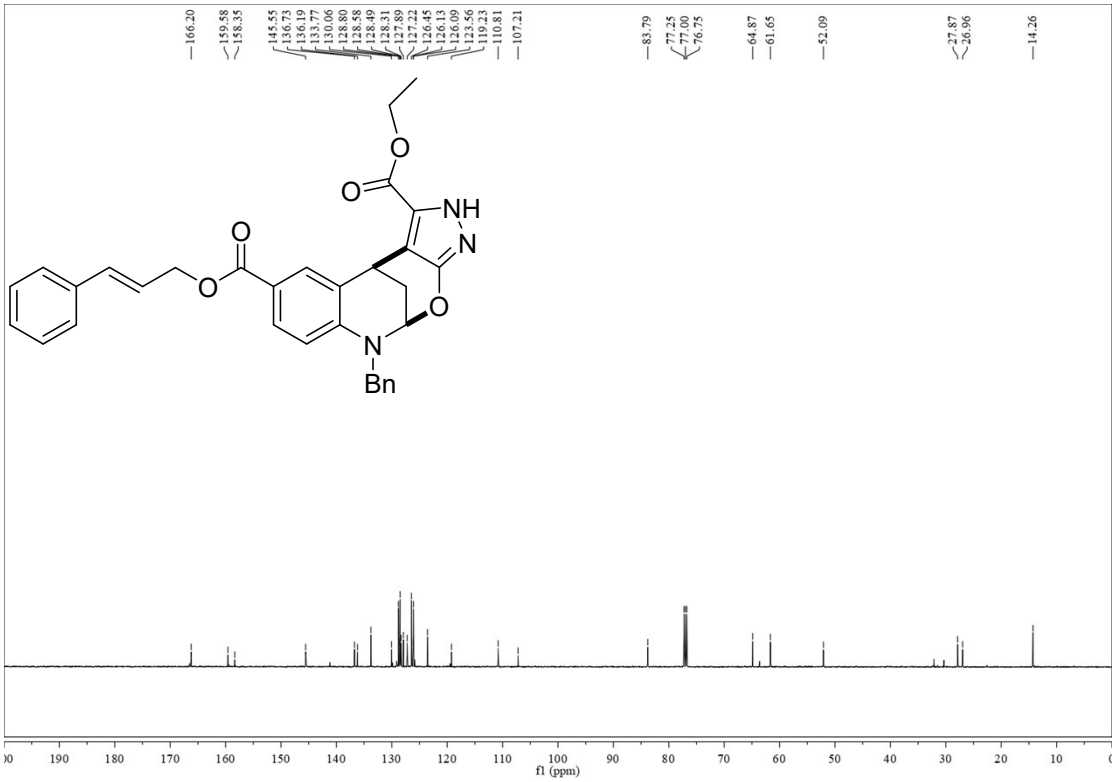
^{13}C-NMR spectrum of C_{34}



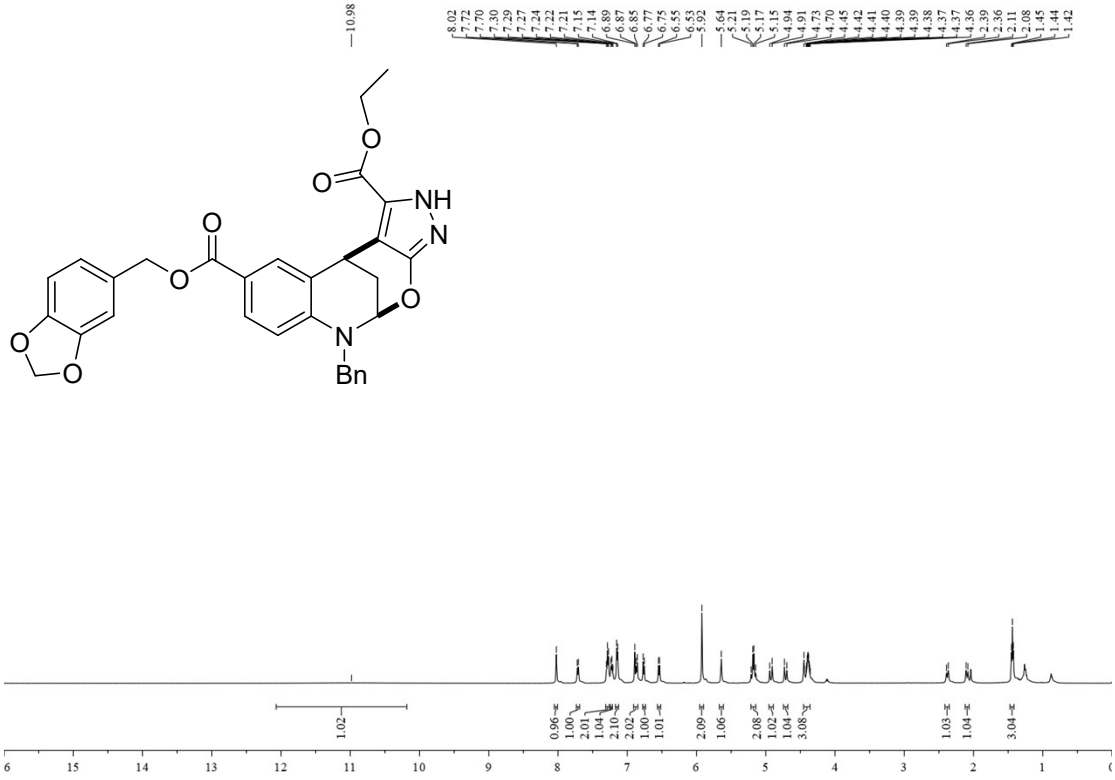
^{1}H-NMR spectrum of C_{35}



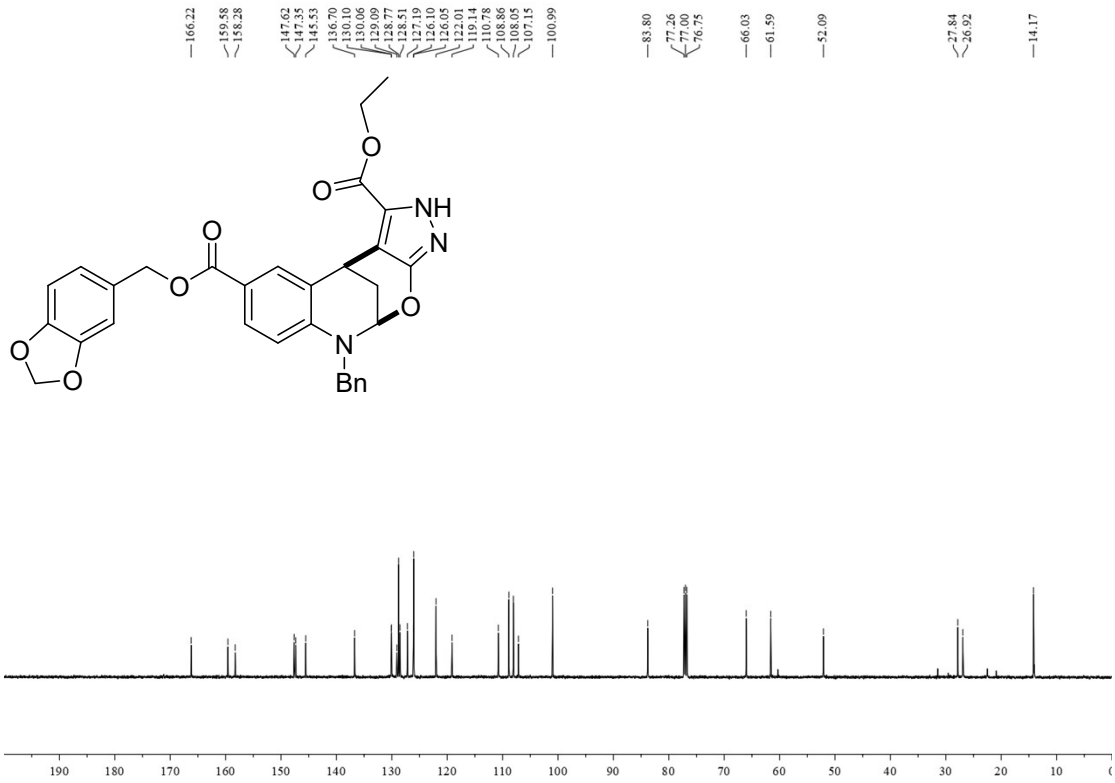
^{13}C-NMR spectrum of C_{35}



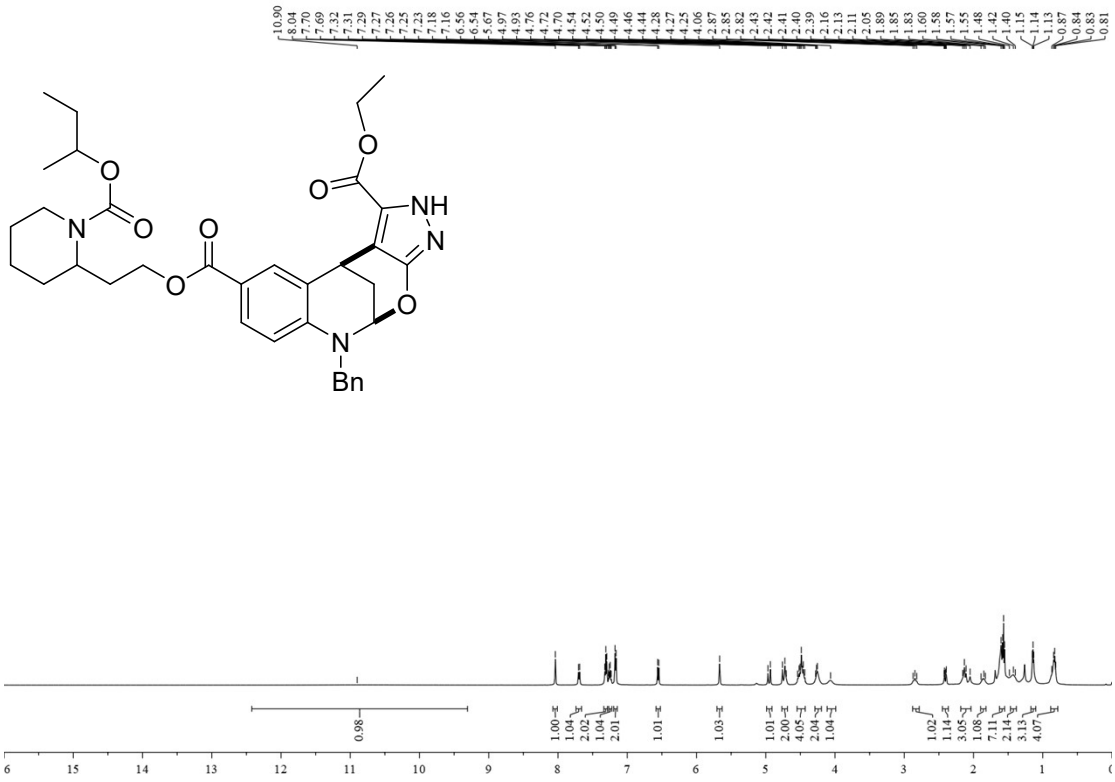
^{1}H-NMR spectrum of C_{36}



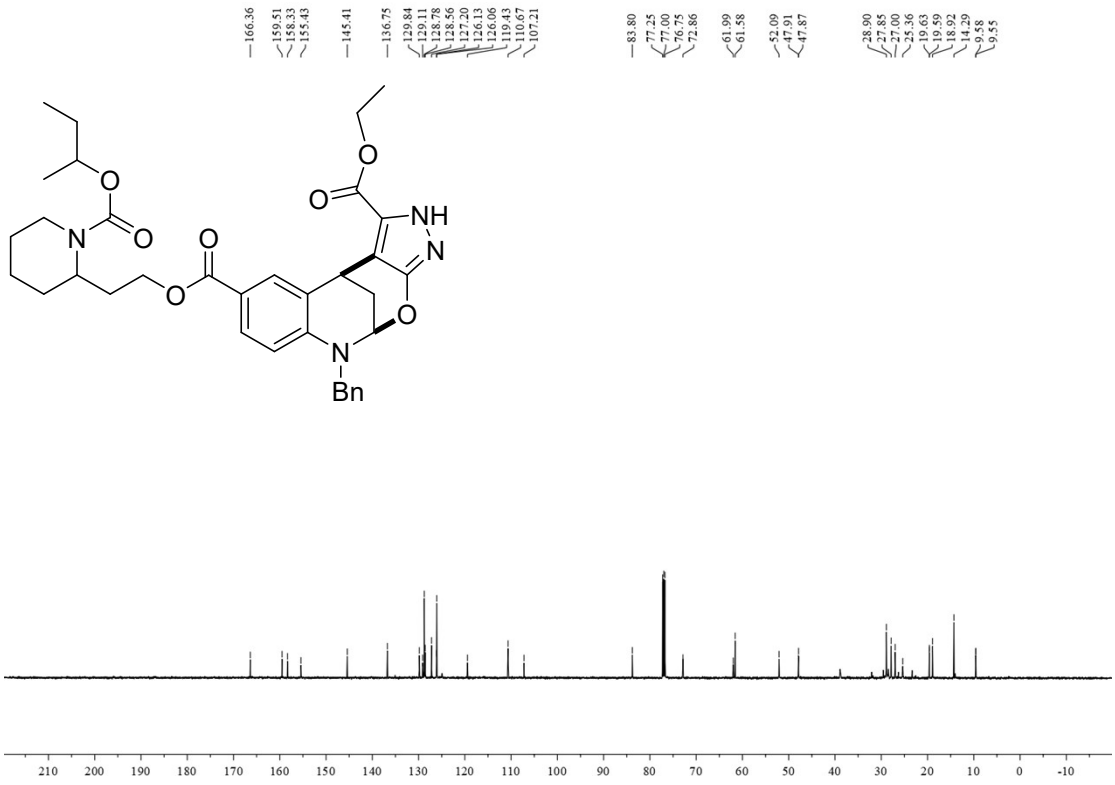
^{13}C-NMR spectrum of C_{36}



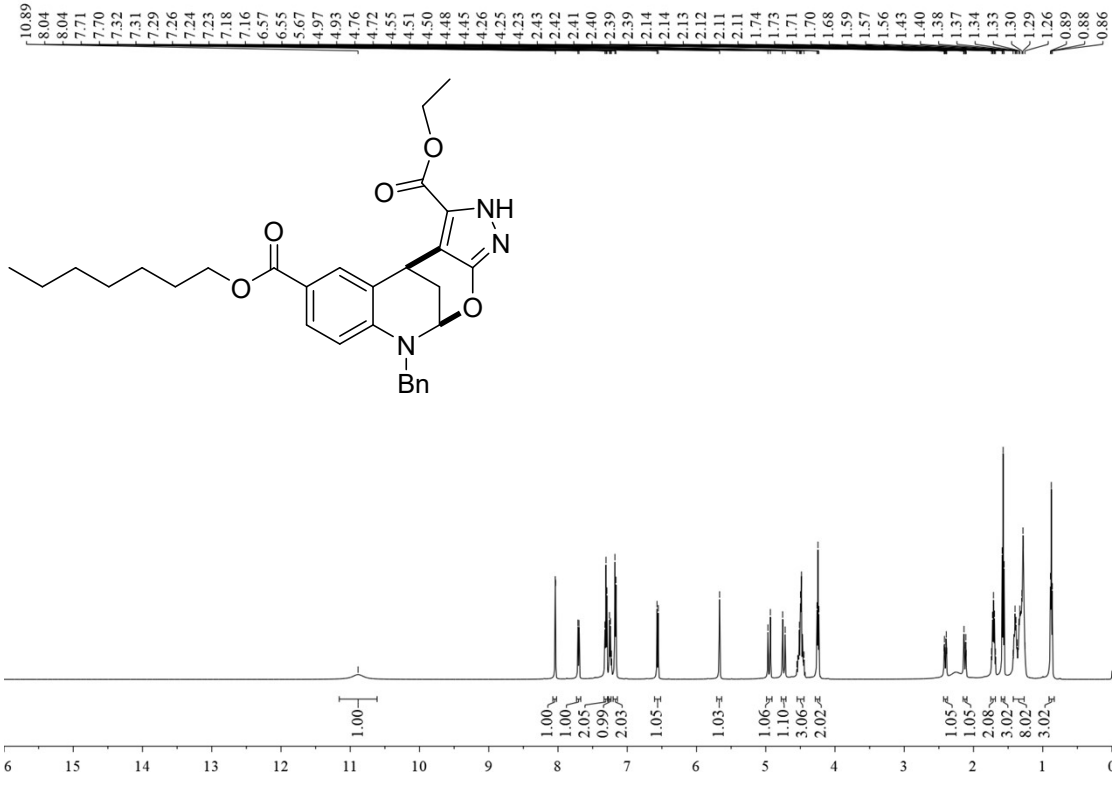
^{1}H-NMR spectrum of C_{37}



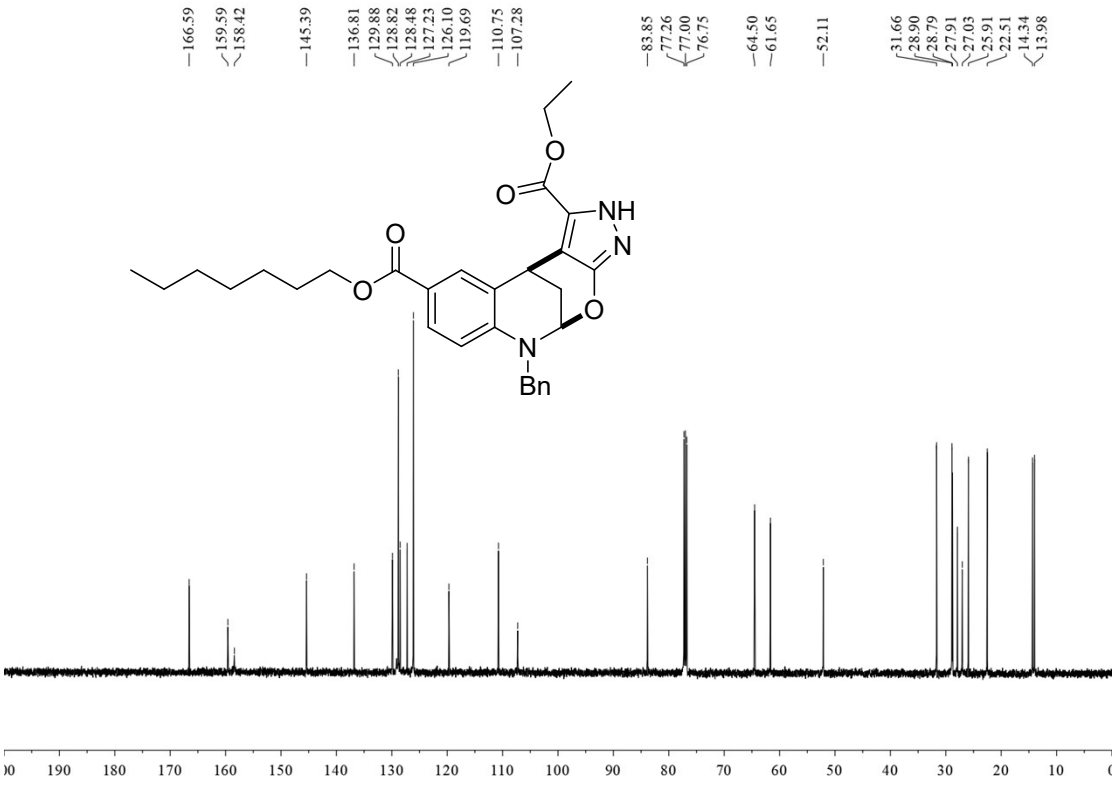
^{13}C-NMR spectrum of C_{37}



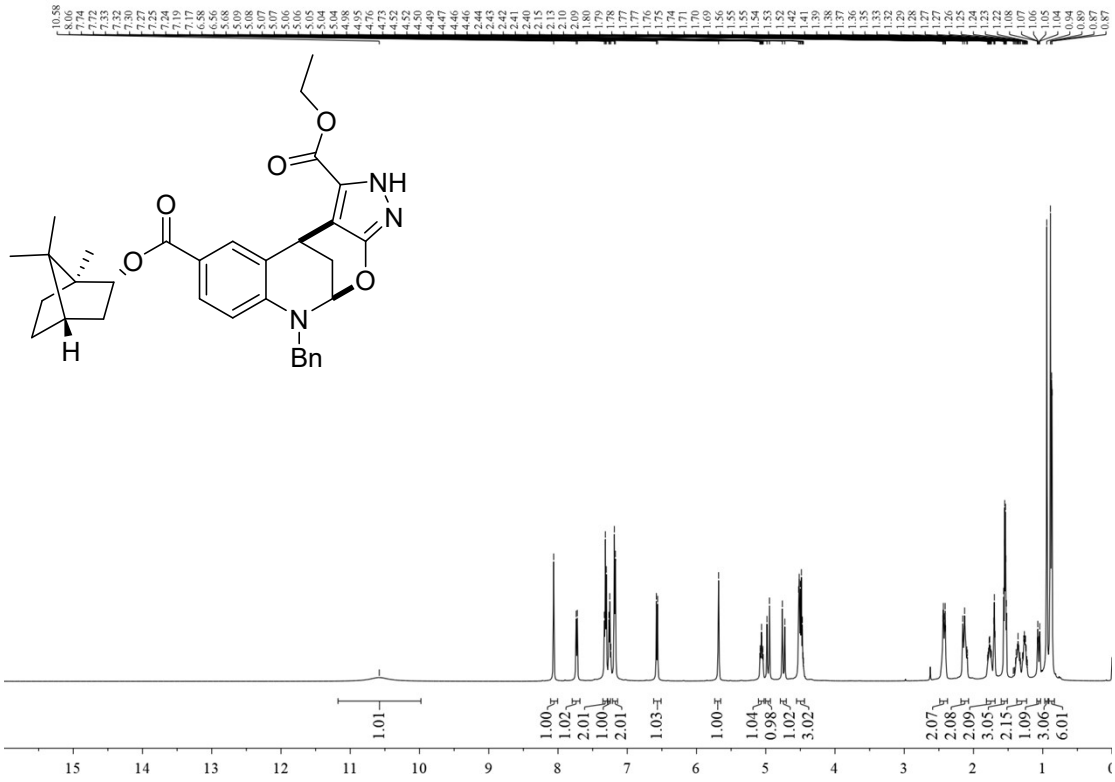
^{1}H-NMR spectrum of C_{38}



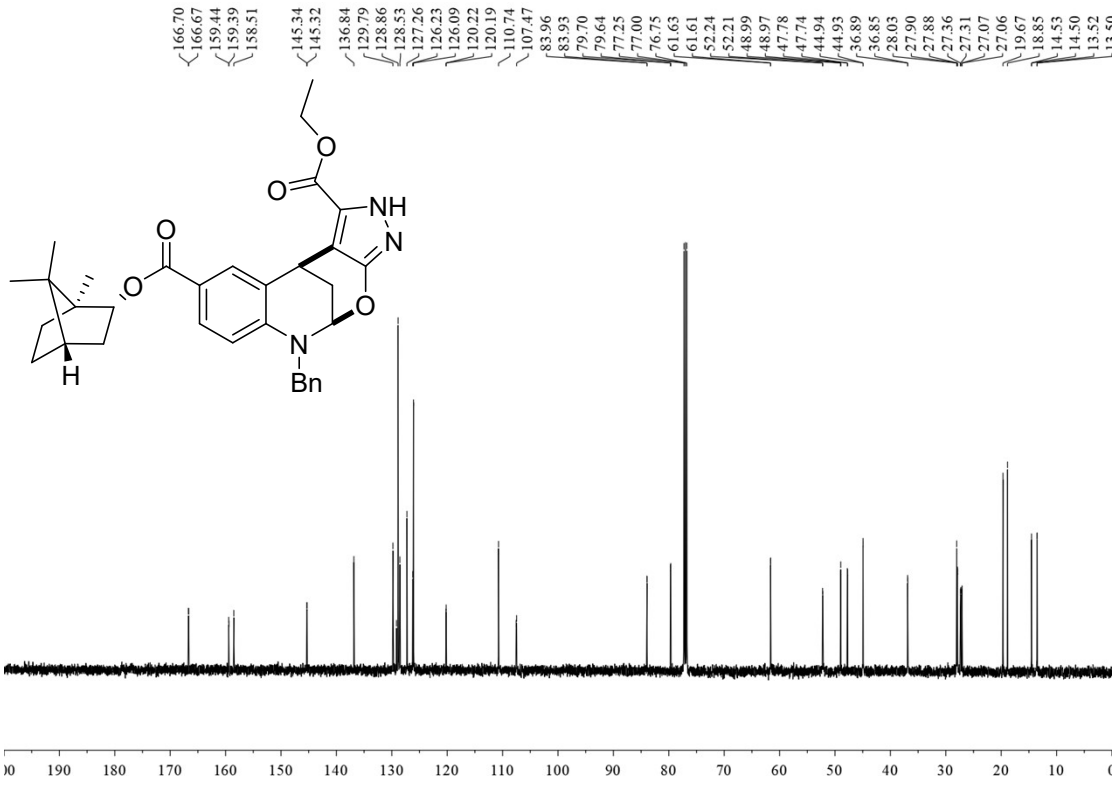
^{13}C-NMR spectrum of C_{38}



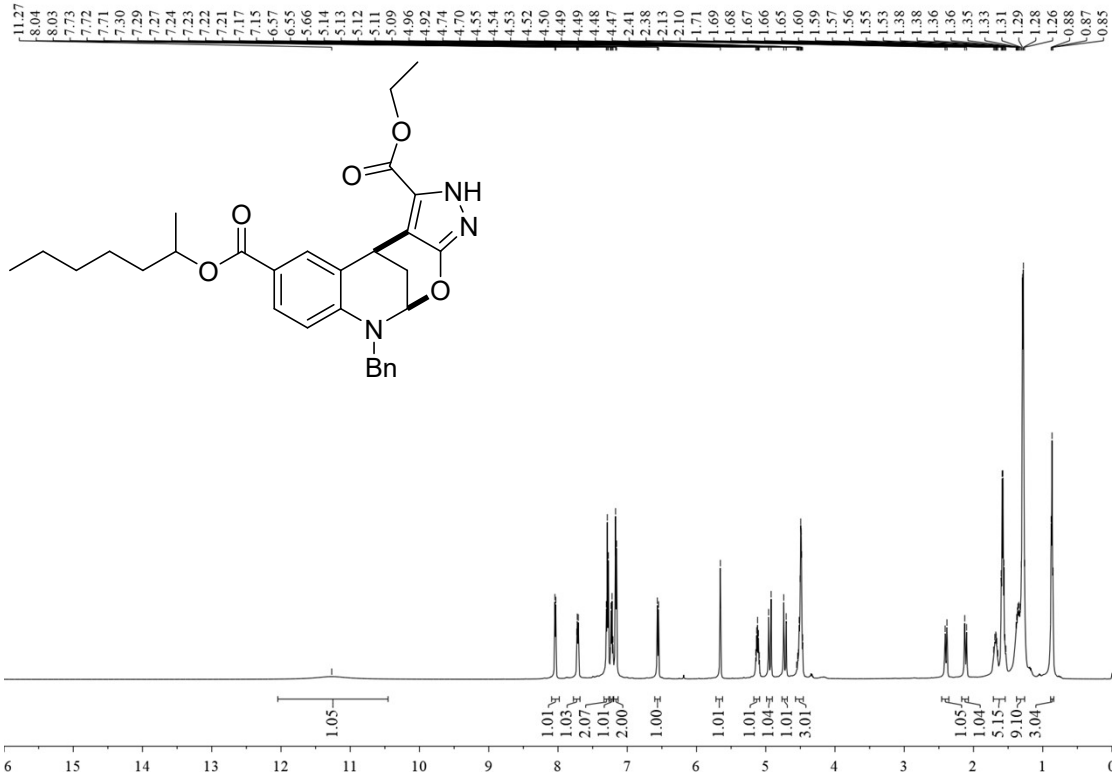
^{1}H-NMR spectrum of C_{39}



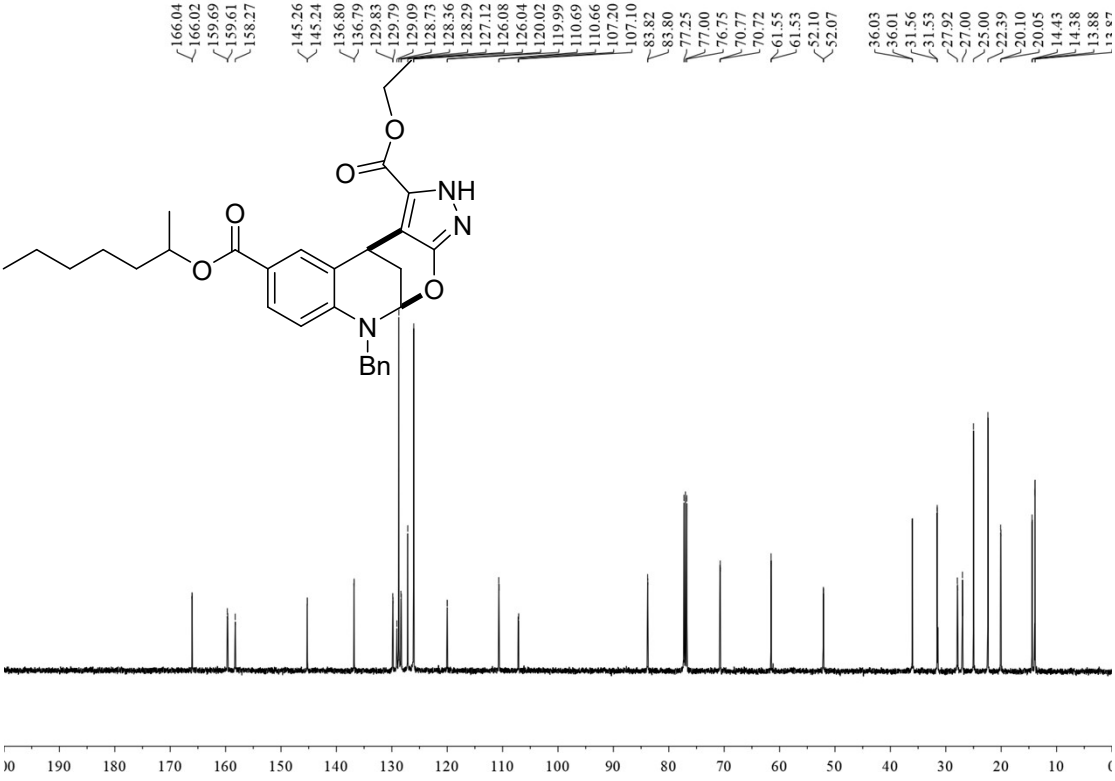
^{13}C-NMR spectrum of C_{39}



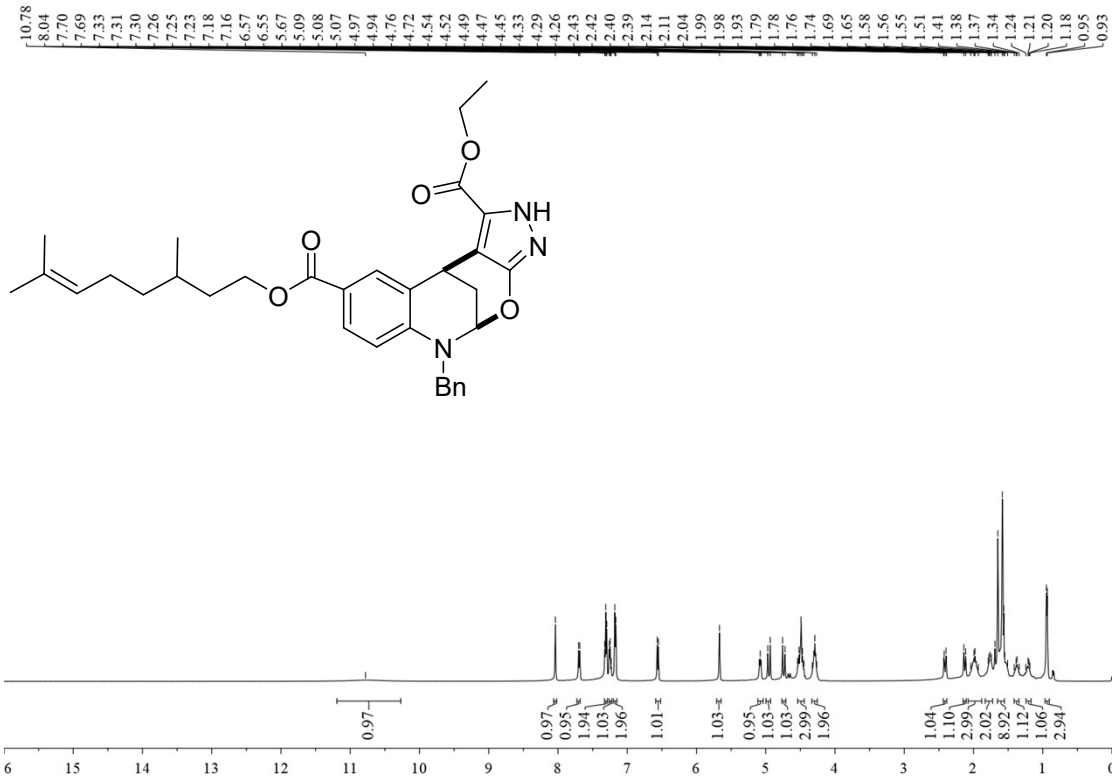
^{1}H-NMR spectrum of C_{40}



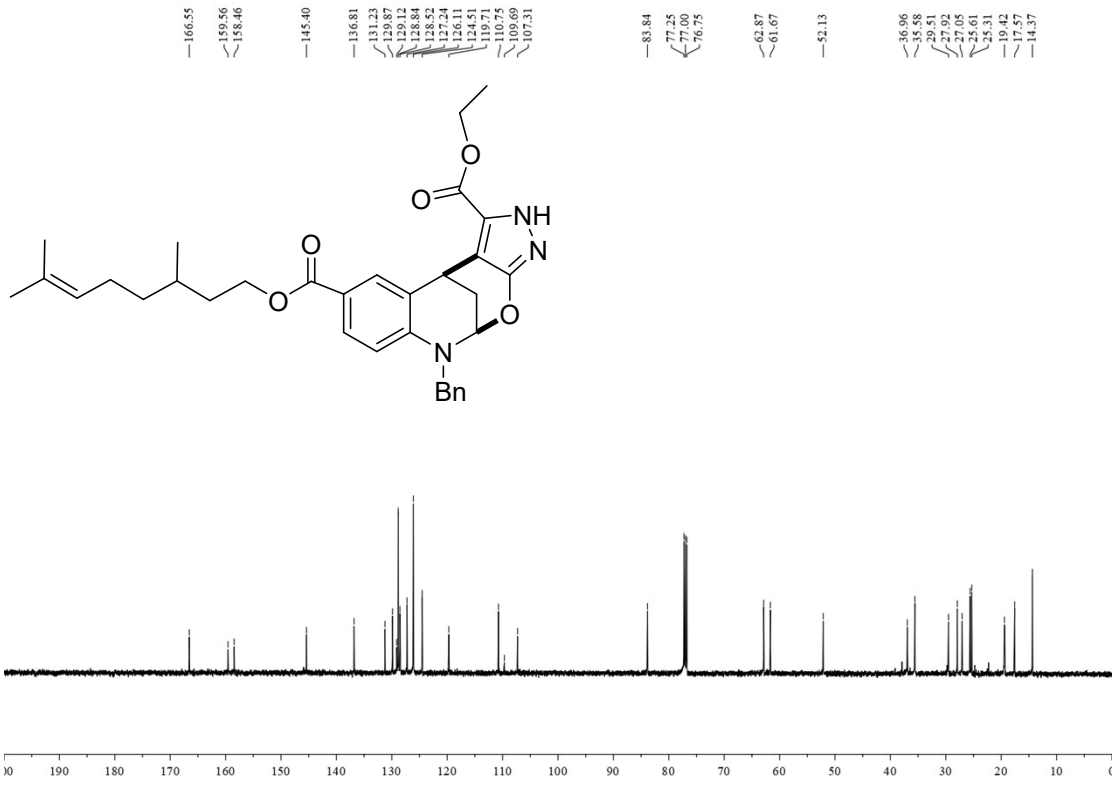
^{13}C-NMR spectrum of C_{40}



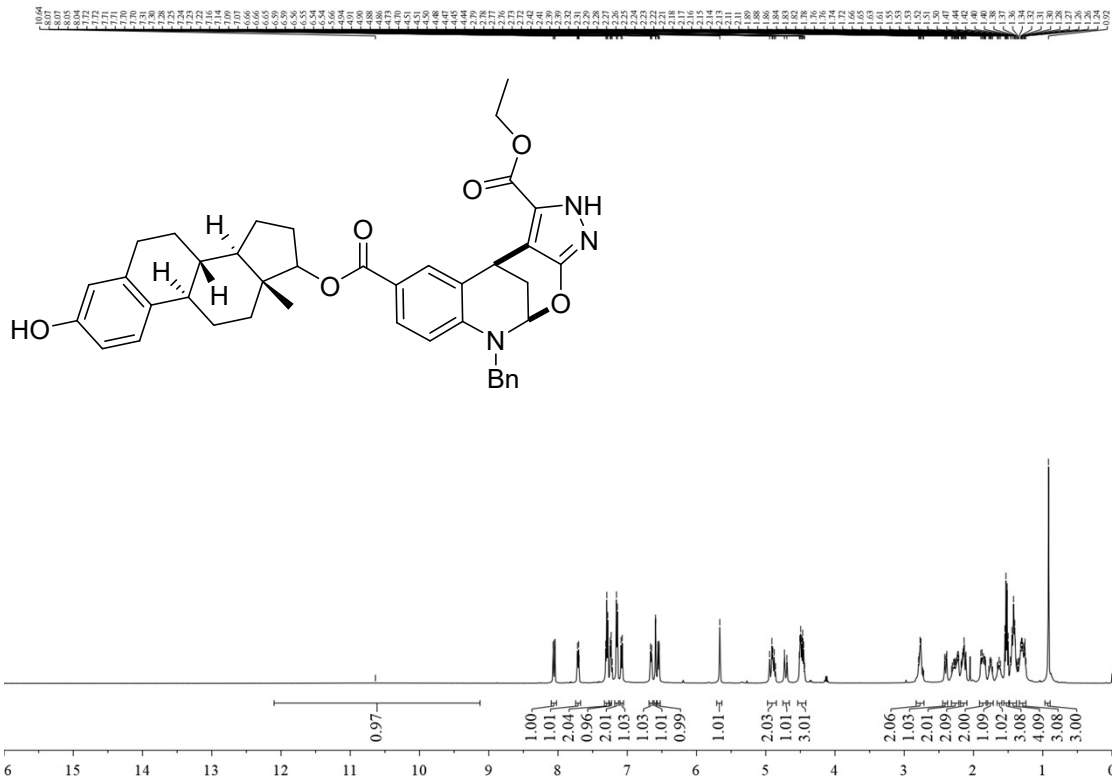
^{1}H-NMR spectrum of C_{41}



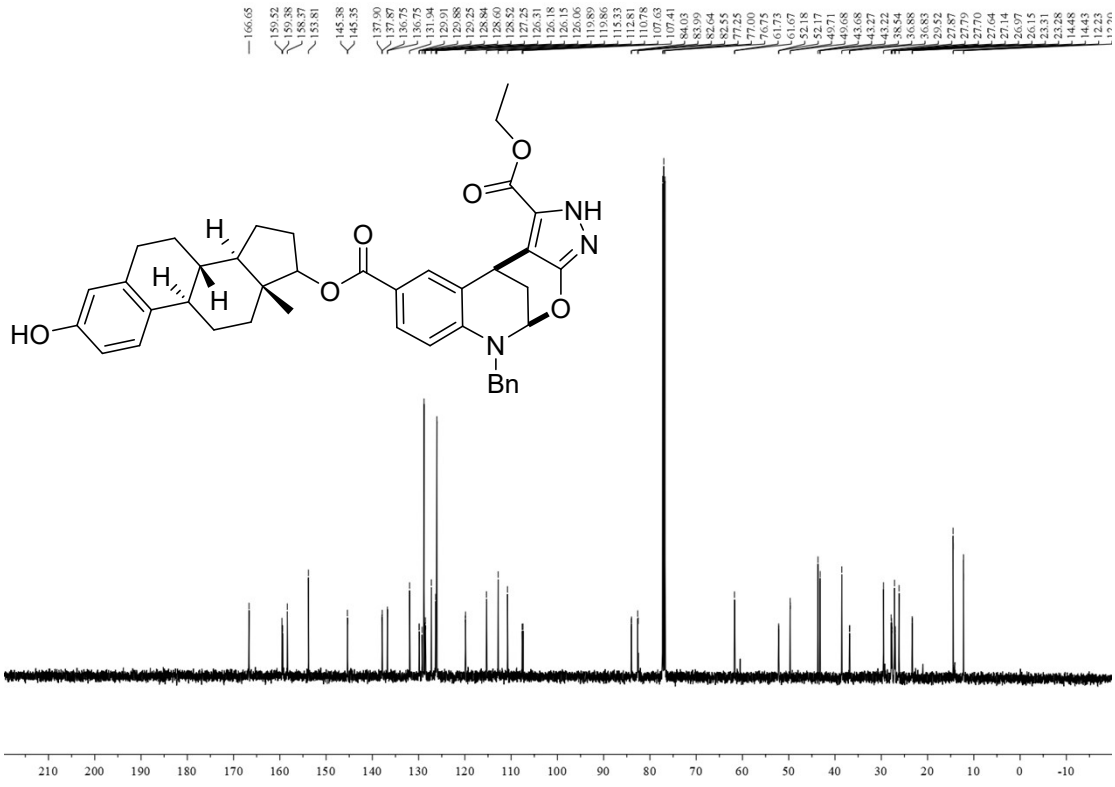
^{13}C-NMR spectrum of C_{41}



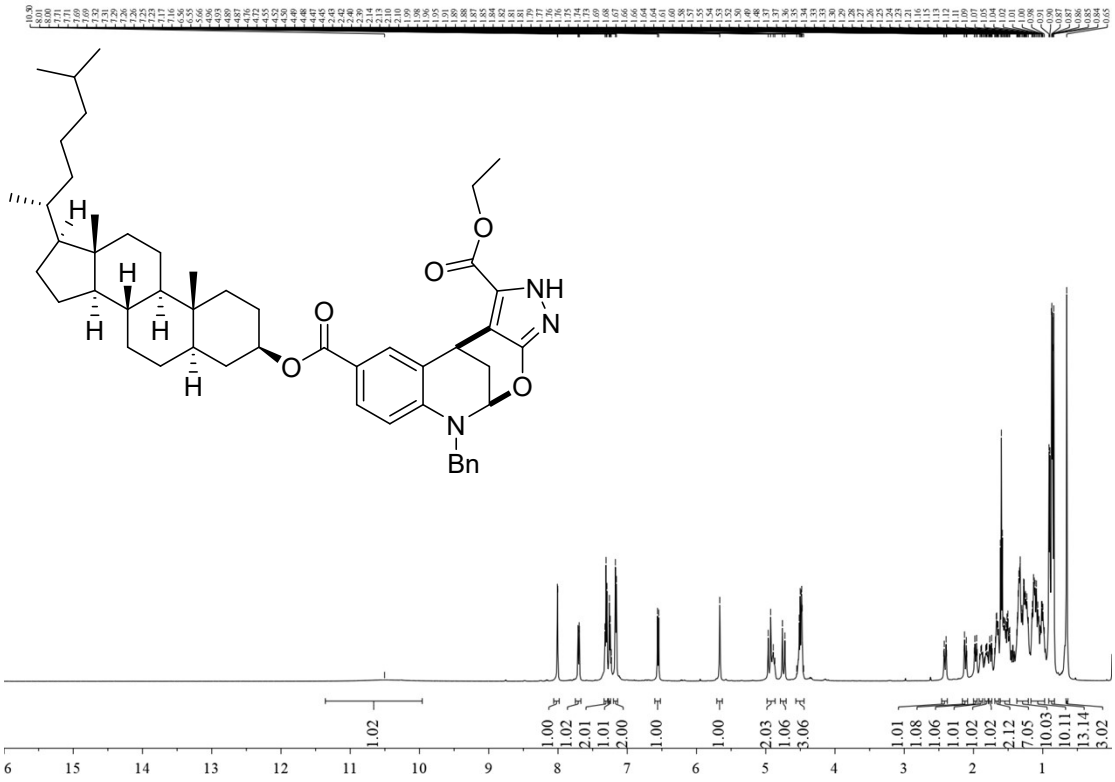
^{1}H-NMR spectrum of C_{42}



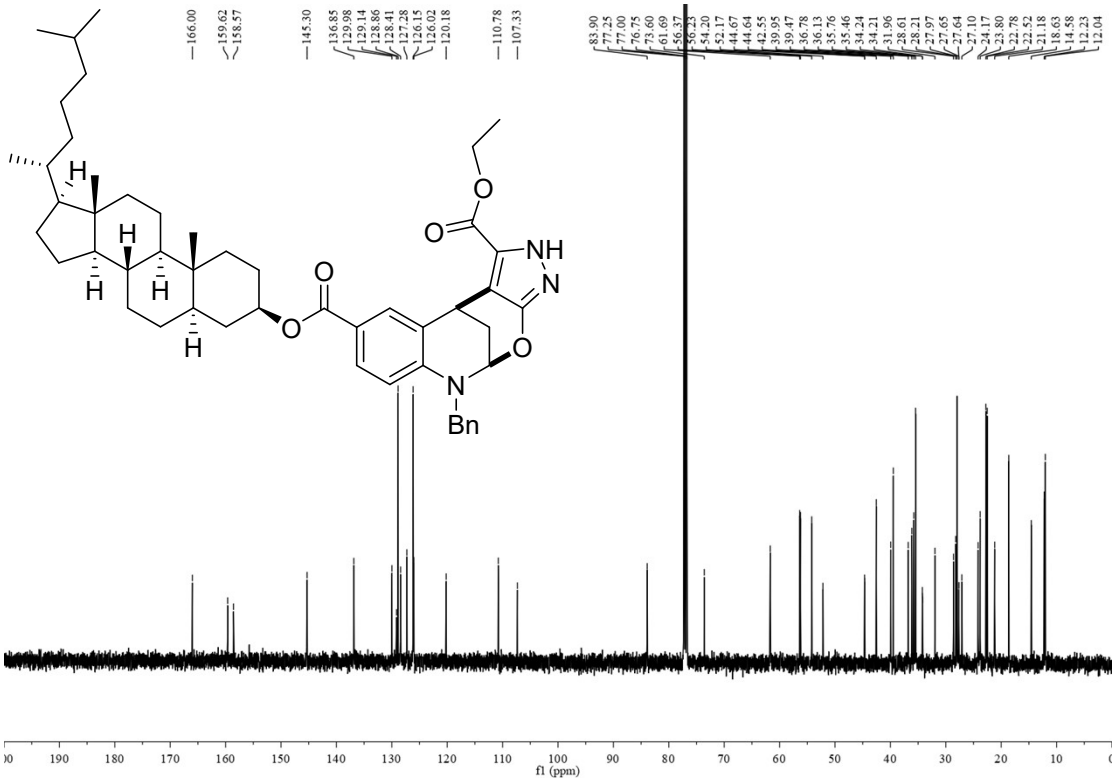
^{13}C-NMR spectrum of C_{42}



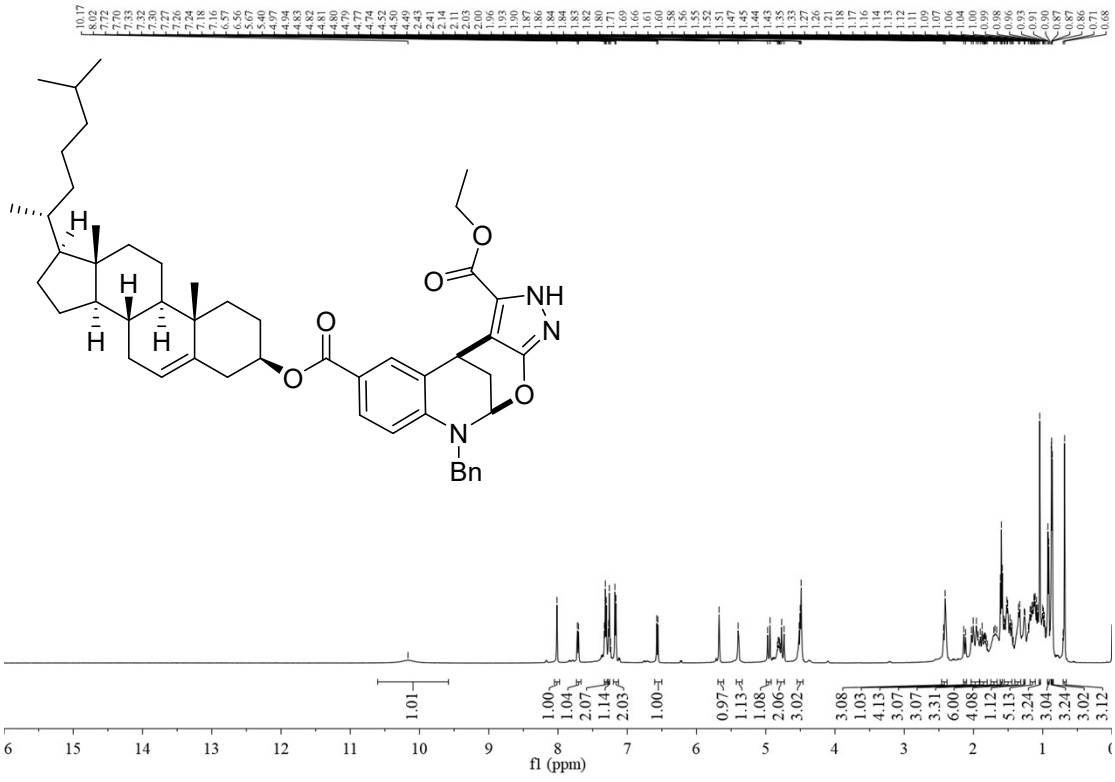
^{1}H-NMR spectrum of C_{43}



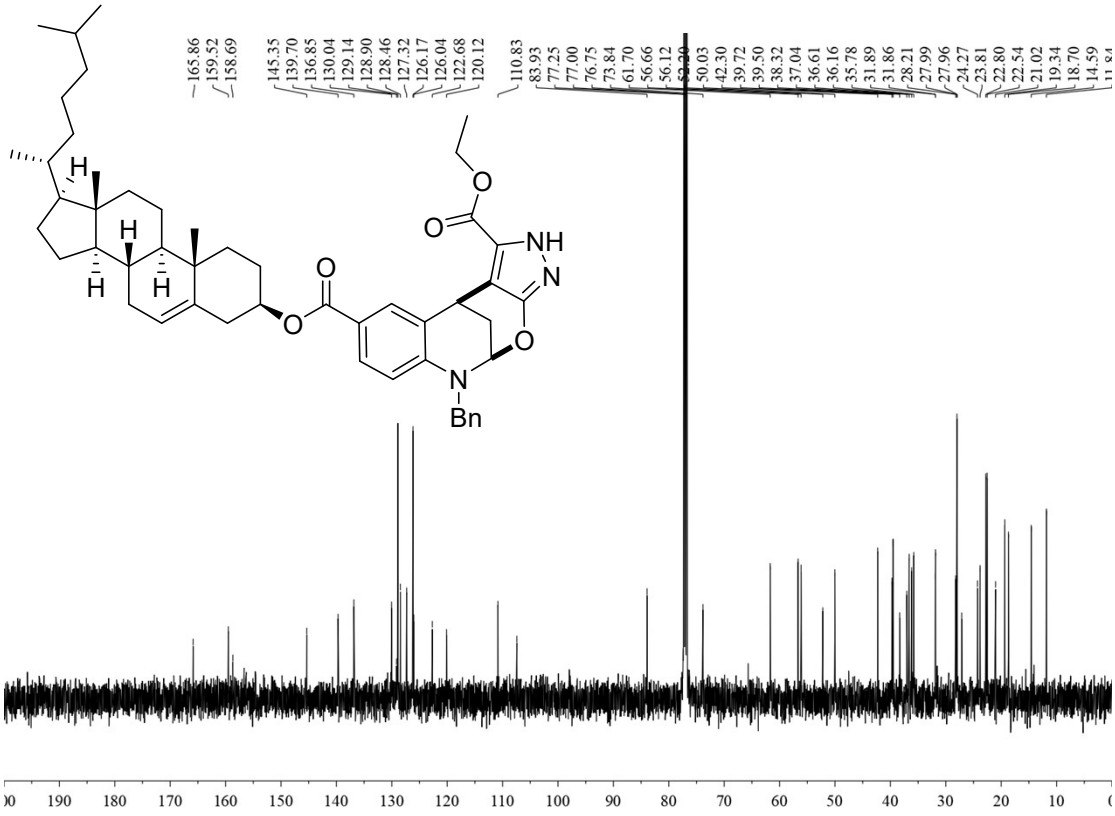
^{13}C-NMR spectrum of C_{43}



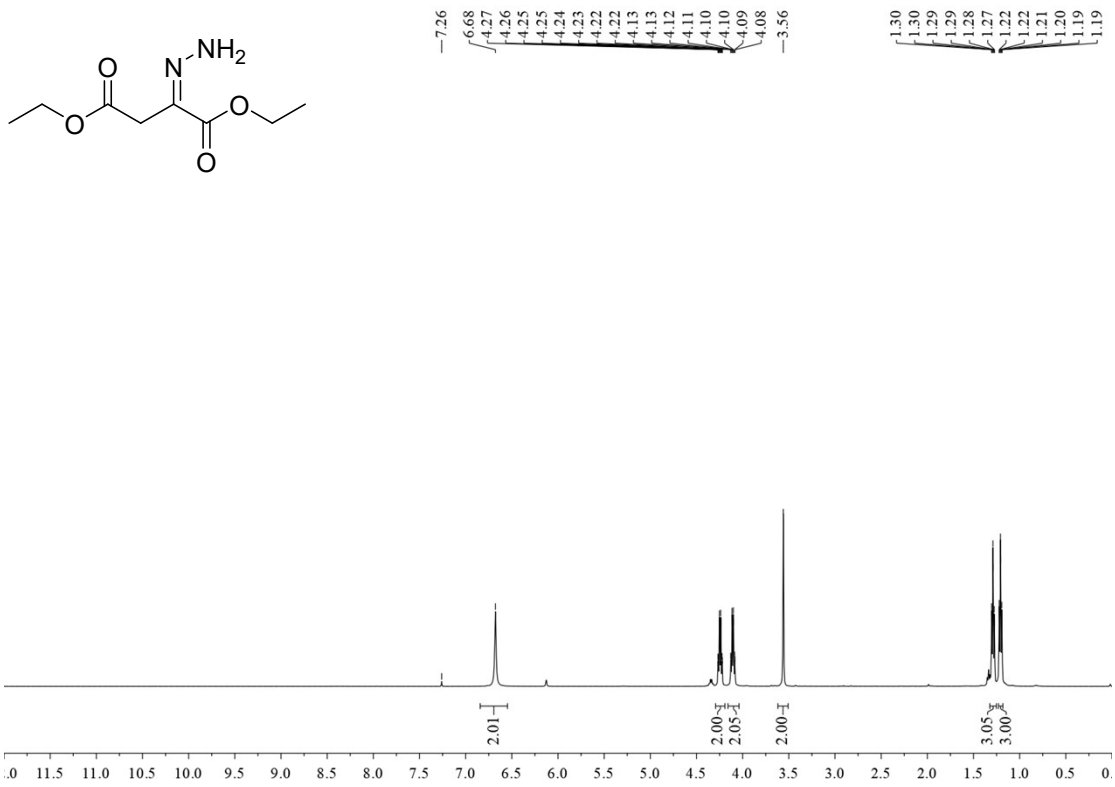
^{1}H-NMR spectrum of C_{44}



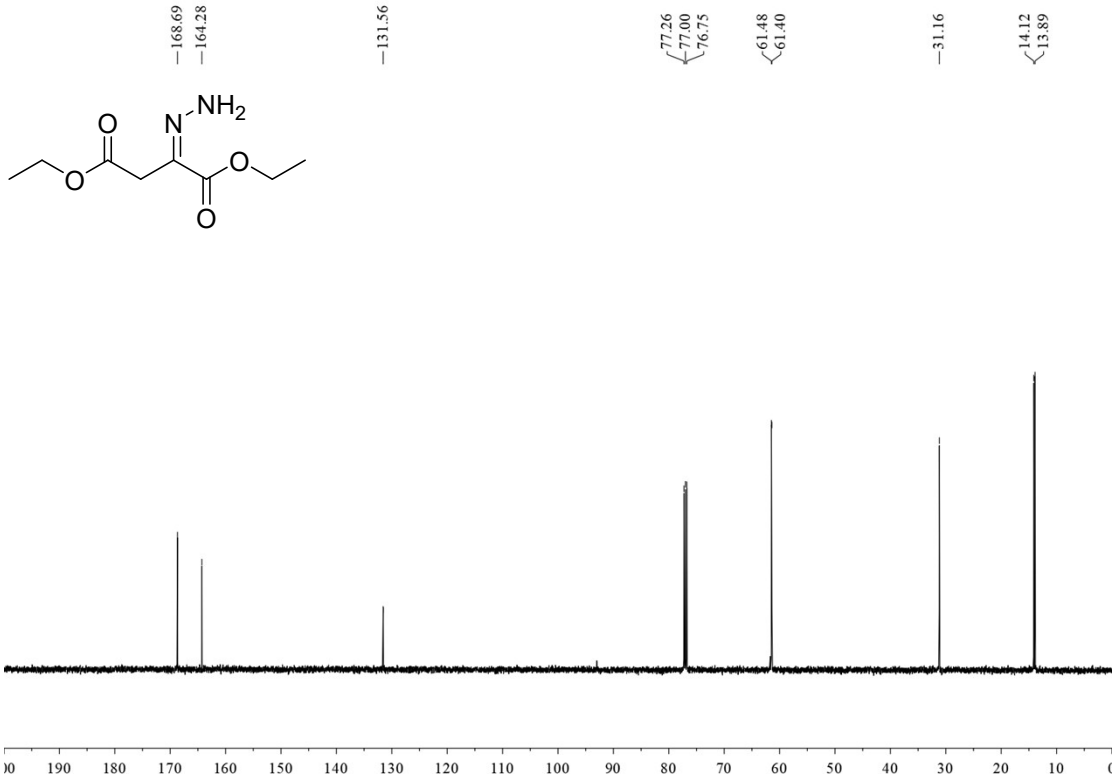
^{13}C-NMR spectrum of C_{44}



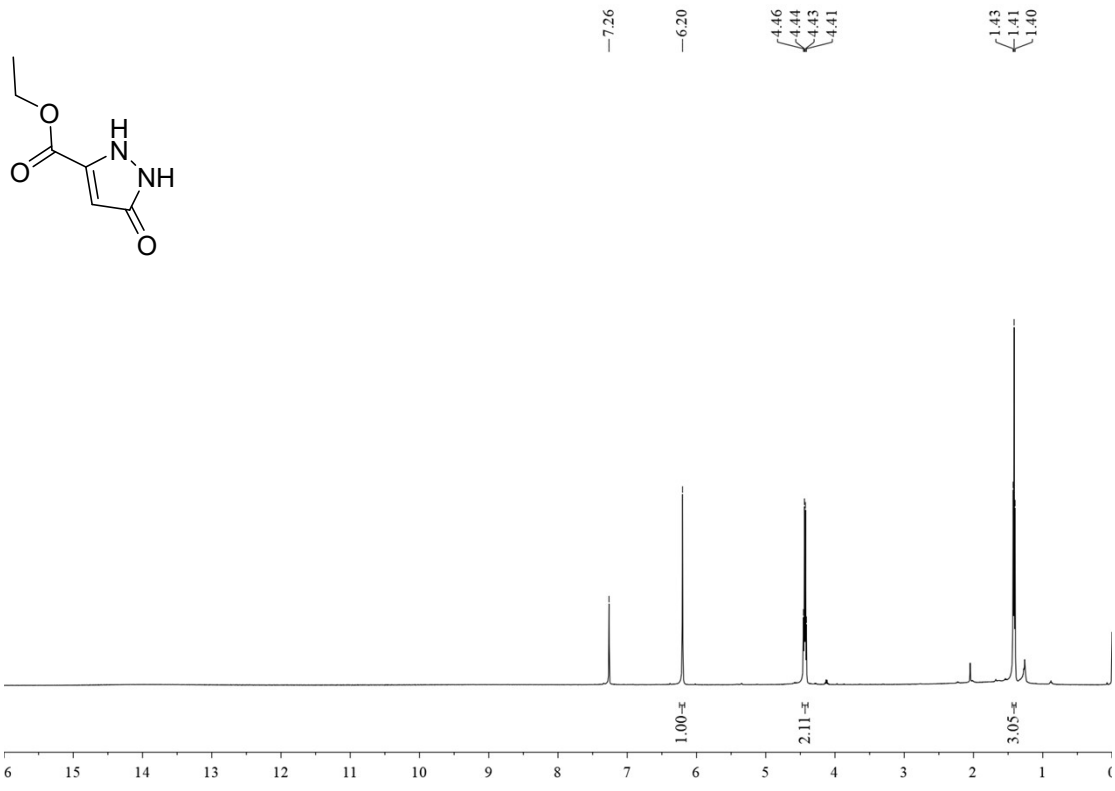
^{1}H-NMR spectrum of int-2



^{13}C-NMR spectrum of int-2



^{1}H-NMR spectrum of int-3



^{13}C-NMR spectrum of int-3