Supporting Information

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Synthesis of bicyclo[4.2.0]octane ring of kingianin via [2+2] ketene cycloaddition

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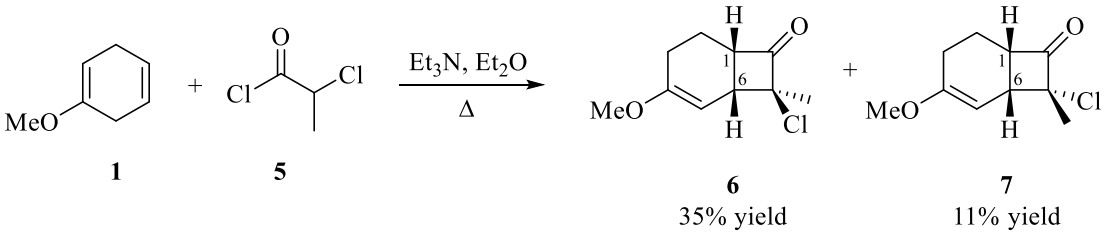
S1:Synthesis protocol and spectroscopic data analysis

S.1.1: Generals

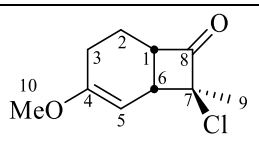
All reactions were carried out in heat-dried glassware under an atmosphere of nitrogen unless otherwise stated. All liquid transfers were conducted using standard syringe or cannula techniques. THF, Et_2O, DCM, toluene and MeOH were purified by a MBraun® Solvent Purification system. DMF and cyclohexane were dried under 4 Å molecular sieves. All other reagents were obtained from Merck, Across, Alfa-Aesar or Aldrich and used as received. Column chromatography was performed on silica gel (Merck, 60 Å C. C. 40-63 μm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F_{254}), which were visualised by the quenching of UV fluorescence when applicable (λ_{max} = 254 nm and/or 366 nm) and/or by spraying with vanillin or anisaldehyde in acidic ethanol, followed by heating with a heat gun. HRMS was run on a JEOL JMS-GCmate II mass spectrometer. NMR spectra were recorded on a Bruker Avance (400 MHz for ^{1}H NMR, 100.6 MHz for ^{13}C NMR) spectrometer system. Data were analysed via TopSpin software package. Spectra were referenced to TMS or residual solvent ($CDCl_3$ = 7.26 ppm in ^{1}H NMR spectroscopy and 77.0 ppm in ^{13}C NMR spectroscopy).

S1.2: Synthetic sequence starting from 4-methoxy-1,4-cyclohexadiene.



1 **5** **6** 35% yield **7** 11% yield

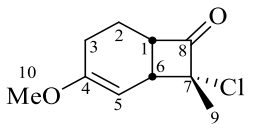
7-Chloro-4-methoxy-7-methyl-bicyclo[4.2.0]oct-4-en-8-ones (6 and **7).** Triethylamine (1.18 mL, 30.0 mmol) was added to a refluxing mixture of 4-methoxy-1,4-cyclohexadiene **1** (5.59 g, 50.8 mmol) and 2-chloropropanoyl chloride **5** (3.81 g, 30.0 mmol) in diethyl ether (25 mL). The reaction mixture was stirred at room temperature for 1.5 hrs and then filtered. The solid residue was rinsed with diethyl ether. The filtrate was washed with 1 M HCl, 1 M NaOH and then brine. After drying (Na_2SO_4), the organic layer was concentrated, and the crude product was distilled with a Kugelrohr apparatus at 150 °C (0.62 mbar) to give a mixture of diastereoisomers **6** (2.11 g, 35 %) and **7** (0.66 g, 11 %).

(1*R**,6*S**,7*R**)-7-Chloro-4-methoxy-7-methyl-bicyclo[4.2.0]oct-4- en-8-one **6**	

Pale yellow oil. $R_f \approx 0.30$ [UV-active, EtOAc/Pet. ether 5 %, anisaldehyde (yellow spot)]. IR (neat): ν_{max} 2939 (m), 2855 (w), 2836 (w), 1786 (s, C=O), 1656 (m), 1443 (m), 1380 (m), 1285 (w), 1219 (m), 1197 (m), 1174 (m), 1139 (m), 1066 (m), 1031 (m), 952 (m), 826 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) 1.48 (3H, s, H9), 1.67 (1H, m, H2a), 1.95–2.15 (3H, m, H2b, H3), 3.26 (1H, ddt, *J* = 10.0, 5.0, 1.0 Hz, H6), 3.55 (3H, s, H10), 4.12 (1H, dddd, *J* = 10.0, 6.0, 3.5, 1.5 Hz, H1), 4.73 (1H, dd, *J* = 5.0, 1.5 Hz, H5). ^{13}C NMR ($CDCl_3$) 19.2 (C9), 19.4 (C3), 24.7 (C2), 40.7 (C6), 53.9 (C1), 54.1 (C10), 77.3 (C7),

90.3 (C5), 158.7 (C4), 206.1 (C8). MS *m/z* (positive CI, NH_3) 110, 129, 137, 165, 167, 183, 201 (MH^+ with ^{35}Cl), 202, 203 (MH^+ with ^{37}Cl), 204, 222, 257. MS *m/z* (EI) **105, 109, 110, 111, 112, 113, 125, 132, 135, 137, 147, 150, 151, 162, 170, 182, 200 ($M^{+\bullet}$ with ^{35}Cl), 202 ($M^{+\bullet}$ with ^{37}Cl). HRMS** *m/z* (EI)**:** 200.0599 ($M^{+\bullet}$ $C_{10}H_{13}{}^{35}ClO_2{}^{+\bullet}$ requires 200.0599)**.**

NOESY ($CDCl_3$) Observed correlations: H5 – H9, H5 – H10.
Correlations not observed: H1 – H9, H6 – H9.

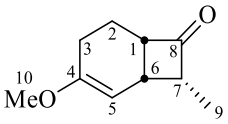
(1*R**,6*S**,7*S**)-7-Chloro-4-methoxy-7-methyl-bicyclo[4.2.0]oct-4- en-8-one **7**	

Pale yellow oil. $R_f \approx 0.20$ [UV-active, EtOAc/Pet. ether 5 %, anisaldehyde (dark orange spot)]. **IR (neat)**: ν_{max} 3049 (m), 2984 (m), 2306 (m), 2685 (w), 1796 (m, C=O), 1723 (m) 1688 (w), 1443 (m), 1422 (m), 1263 (s), 1155 (w) 1070 (w) 1024 (w), 895 (m) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.68 (1H, m, H2a), 1.77 (3H, s, H9), 1.94 (1H, m, H3a), 2.05–2.17 (2H, m, H2b, H3b), 3.05 (1H, ddt, *J* = 10.0, 5.0, 1.0 Hz, H6), 3.54 (3H, s, H10), 3.67 (1H, distorted dddd, *J* = 10.0, 6.0, 3.0, 1.0 Hz, H1), 4.69 (1H, dd, *J* = 5.0, 1.5 Hz, H5). **^{13}C NMR ($CDCl_3$)** 19.8 (C3), 24.3 (C2), 26.2 (C9), 38.5 (C6), 51.6 (C1), 54.2 (C10), 77.4 (C7), 91.4 (C5), 157.6 (C4), 206.7 (C8). **MS *m/z* (positive CI, NH_3)** 110, 137, 158, 165, 167, 183, 201 (MH^+ with ^{35}Cl), 202, 203 (MH^+ with ^{37}Cl), 204, 206, 218 (MH^+..NH_3 with ^{35}Cl). **MS *m/z* (EI)** 109, 110, 111, 112, 113, 125, 132, 135, 137, 150, 151, 158, 162, 182, 200 ($M^{+\bullet}$ with ^{35}Cl), 202 ($M^{+\bullet}$ with ^{37}Cl). **HRMS *m/z* (EI)**: 200.0606 ($M^{+\bullet}$ $C_{10}H_{13}{}^{35}ClO_2{}^{+\bullet}$ requires 200.0599)**.**

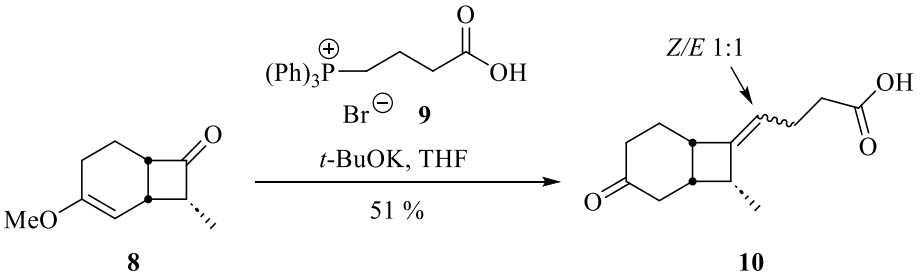
NOESY ($CDCl_3$) Observed correlations: H5 – H10 (very intense), H6 – H9 (moderate).
Correlation not observed: H5 – H9.

6 **8**
45% yield

4-Methoxy-7-methyl-bicyclo[4.2.0]oct-4-en-8-one (8). To mixture of 2.00 g (30.7 mmol) of Zn dust and 4.5 mL of TMEDA (29.0 mmol) in 10 mL of absolute EtOH at 0 °C was added 2.00 mL (33.0 mmol) of AcOH. The reaction mixture was maintained at 0 °C while a solution of enol ether **6** (1.10 g, 5.0 mmol) in 2.0 mL of EtOH was added over 10 min period. After an additional 15 min at 0 °C the reaction mixture was allowed to warm to room temperature and stirred for 15 min. The resulting grey mixture was filtered, and the solid residue was rinsed with diethyl ether. The filtrated was washed with ice cold 1 M HCl (10 mL), H_2O (10 mL), sat. $NaHCO_3$ (10 mL) and sat. NaCl (10 mL). The resulting material was dried over $MgSO_4$ and concentrated under reduced pressure to afford 0.37 g (45 %) of desired enol ether **8** which was of sufficient purity for subsequent transformation.

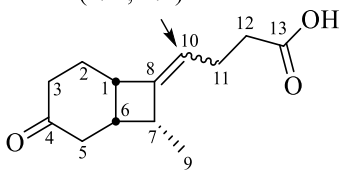
(1*R**,6*S**,7*R**)-4-Methoxy-7-methyl-bicyclo[4.2.0]oct-4- en-8-one **8**	

Colourless oil. $R_f \approx 0.30$ [UV-active, EtOAc/Pet. ether 5 %, anisaldehyde (yellow spot)]. **IR (neat)**: ν_{max} 3020 (s), 2985 (m), 2401 (w), 1771 (s, C=O), 1713 (s), 1553 (m), 1422 (m), 1264 (s), 1216 (s), 1017 (m), 890 (s) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 0.91 (3H, d, *J* = 8.4 Hz, H9), 1.65 (1H, m, H2a), 1.87 (1H, m, H3a), 1.98–2.12 (2H, m, H2b, H3b), 3.07 (1H, qd, *J* = 8.4, 4.6 Hz, H7), 3.31 (1H, td, *J* = 9.1, 4.6 Hz, H6), 3.47 (3H, s, H10), 3.52 (1H, m, H1), 4.55 (1H, dd, *J* = 4.6, 2.0 Hz, H5). **^{13}C NMR ($CDCl_3$)** 8.8 (C9), 19.2 (C2), 24.6 (C3), 27.6 (C7), 53.9 (C10), 54.5 (C1), 56.0 (C6), 91.0 (C5), 157.4 (C4), 213.9 (C8). **MS *m/z* (positive CI, NH_3)** 165, 167 (MH^+), 171, 172, 183, 200. **MS *m/z* (EI)** 109, 114, 121, 124, 135, 137, 151, 152, 161, 166 ($M^{+\bullet}$). **HRMS *m/z* (EI)**: 166.0993 ($M^{+\bullet}$ $C_{10}H_{14}O_2^{+\bullet}$ requires 166.0989)**.**

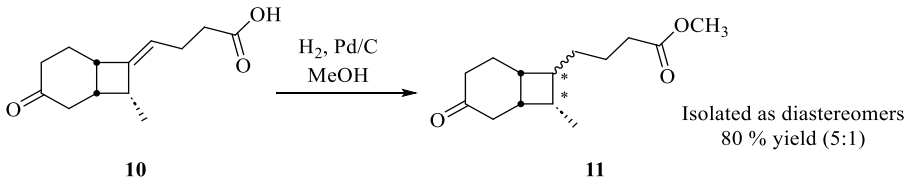


8 **10**

7-Methyl-4-oxobicyclo[4.2.0]octan-8-ylidene)butanoic acid (10). To a stirred slurry of (3-carboxypropyl)-triphenylphosphonium bromide (**9**) (2.11 g, 4.9 mmol) in dry THF (10 mL) under nitrogen at −75 °C was added potassium *tert*-butoxide (1.38 g, 12.3 mmol). After 15 min at −75 °C, a solution of enol ether **8** (0.68 g, 4.1 mmol) in dry THF (5.0 mL) was added to a mixture and stirred at −75 °C for 10 min. The mixture was continuously stirred at room temperature overnight. The mixture was pouring into 5 % Na_2CO_3 solution (30 mL), washed with ethyl acetate (30 mL mL), and then acidified with conc. HCl. The aqueous layer was extracted with ether (3 × 50 mL) and the combined extracts were concentrated to 20 mL and kept at −20 °C for 2 hrs. The resulting precipitate was filtered off and discarded. Evaporation of the filtrate gave a yellowish oil (0.79 g) which was purified by column chromatography on silica gel, eluted with petroleum ether/ethyl acetate (7:3) to give the desired product **10** as a mixture of the two geometrical isomers (1:1) (0.46 g, 51 %).

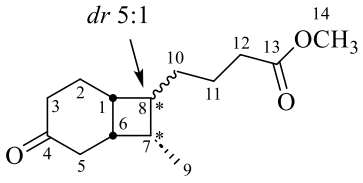
(1*R**,6*S**,7*R**)-7-Methyl-4-oxobicyclo[4.2.0]octan-8-ylidene)butanoic acid **10**	(*Z*/*E*; 1:1) 

Yellowish oil. $R_f \approx 0.20$ [UV-active, EtOAc/Pet. ether 50 %, anisaldehyde (violet spot)]. **IR (neat)**: ν_{max} 2950 (m), 2362 (w), 1736 (s, C=O), 1708 (m, C=O), 1438 (w), 1170 (m), 923 (w), 634 (w) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.13 (3H, d, *J* = 7.7 Hz, H9), 1.90 (1H, m, H2a), 2.02 (1H, m, H2b), 2.24 (1H, m, H3b), 2.31 – 2.47 (5H, m, H5, H11, H12a), 2.51 (1H, m, H3b), 2.55 (1H, m, H12b), 2.61 (1H, m, H6), 3.22 (1H, m, H1), 3.34 (1H, m, H7), 5.22 (1H, t, *J* = 7.7 Hz, H10). **^{13}C NMR ($CDCl_3$)** 13.5 (C9), 23.2 (C2), 23.5 (C11), 31.7 (C6), 34.5 (C12), 36.8 (C3), 37.8 (C1), 38.2 (C5), 38.5 (C7), 121.5 (C10), 148.4 (C8), 178.5 (C13), 214.5 (C4). **MS *m/z* (EI)** 167,177, 195, 205, 221, 223 (MH^+), 240, 241, 256. **HRMS *m/z* (EI)**: 222.1252 ($M^{+\bullet}$ $C_{13}H_{18}O_3^{+\bullet}$ requires 222.1251)**.**

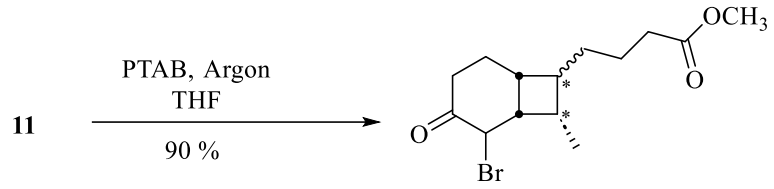


10 **11**

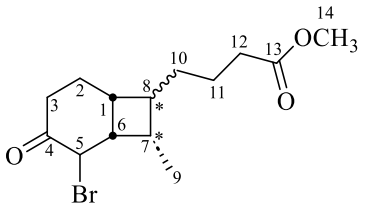
Methyl-({7-methyl-4-oxobicyclo[4.2.0]octan-8-yl})butanoate (11). To a solution of the bicycloalkene **10** (0.24 g, 1.1 mmol) in MeOH (5.0 mL) was added 10 % Pd/C (10 % w/w, 0.02 g), and the resulting mixture was hydrogenated at 1 atm for 12 hrs. Filtration through Celite and evaporation of the filtrate in vacuo afforded **11** as a yellowish oil (0.21 g, 80 %).

Methyl-({(1*R**,6*S**,7*R**)-7-methyl-4-oxobicyclo[4.2.0] octan-8-yl})butanoate **11**	*dr* 5:1 

Yellowish oil. $R_f \approx 0.40$ [non UV-active, EtOAc/Pet. ether 50 %, anisaldehyde (red-violet spot)]. **IR (neat)**: ν_{max} 2933 (m), 1738 (s, C=O), 1714 (s, C=O), 1455 (w), 1436 (w), 1377 (w), 1197 (m), 1170 (m), 1112 (w), 1015 (w), 883 (w) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.05 (3H, d, *J* = 7.4 Hz, H9), 1.46 (2H, m, H10), 1.56 (2H, m, H11), 1.87 (1H, m, H2a), 1.97 – 2.06 (2H, m, H2b, H3a), 2.19 (1H, m, H5a), 2.34 (2H, t, *J* = 7.2 Hz, H12), 2.40 – 2.62 (4H, m, H1, H3b, H5b, H8), 2.72 (1H, qd, *J* = 8.1, 2.0 Hz, H7), 2.79 (1H, q, *J* = 8.1 Hz, H6), 3.69 (3H, s, H14). **^{13}C NMR ($CDCl_3$)** 12.3 (C9), 22.1 (C2), 23.9 (C11), 26.0 (C10), 31.3 (C6), 34.2 (C12), 32.7 (C7), 34.4 (C1), 37.2 (C8), 37.4 (C5), 38.4 (C3), 51.5 (C14), 173.8 (C13), 214.4 (C4). **MS *m/z* (EI)** 110, 123, 135, 151, 162, 182, 195, 206, 224, 236, 238 ($M^{+\bullet}$). **HRMS *m/z* (EI)**: 238.1562 ($M^{+\bullet}$ $C_{14}H_{22}O_3^{+\bullet}$ requires 238.1563).

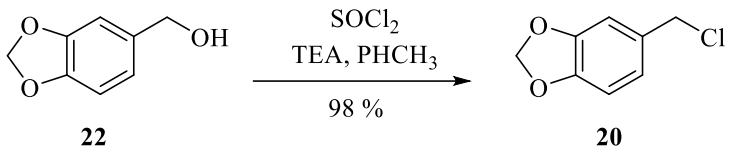


Methyl-{5-bromo-7-methyl-4-oxobicyclo[4.2.0]octan-8-yl})butanoate (13). To a stirred solution of the bicyclic ketone **11** (0.19 g, 0.8 mmol) in dry THF (10 mL) at −75 °C under argon was added phenyltrimethylammonium tribromide (298 mg, 0.79 mmol). The mixture was stirred at −75 °C for 20 min and then allowed to slowly warm to room temperature over 30 min. Brine (10 mL) was added, and then the resulting mixture was extracted with ether (2 × 20 mL). The combined extracts were dried ($MgSO_4$) and concentrated to give an orange oil (0.23 g). Analysis by ^{1}H and ^{13}C NMR spectroscopy revealed that this crude product contained mostly the bromoketone **13**.

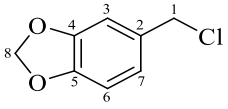
Methyl-{(1*R**,6*S**,7*R**)-5-bromo-7-methyl-4-oxobicyclo [4.2.0]octan-8-yl})butanoate **13**	

Orange oil. $R_f \approx 0.15$ [non UV-active, EtOAc/Pet. ether 30 %, anisaldehyde (red-violet spot)]. **IR (neat)**: ν_{max} 2937 (m), 1738 (s, C=O), 1731 (s, C=O), 1455 (w), 1436 (w), 1379 (w), 1246 (w), 1170 (w), 1066 (w), 1030 (w), 884 (w), 755 (w) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.24 (3H, d, *J* = 8.2 Hz, H9), 1.49 (2H, m, H10), 1.58 (2H, m, H11), 1.97 (1H, m, H2a), 2.15 (1H, dd, *J* = 8.2, 5.4 Hz, H2b), 2.37 (2H, m, H12), 2.49 (1H, dd, *J* = 8.2, 5.4 Hz, H3a), 2.62 – 2.68 (4H, m, H1, H3b, H8), 2.89 (1H, qd, *J* = 8.2, 2.9 Hz, H7), 3.04 (1H, q, *J* = 8.2 Hz, H6), 3.71 (3H, s, H14), 4.86 (1H, d, *J* = 8.2 Hz, H5). **^{13}C NMR ($CDCl_3$)** 11.5 (C9), 22.4 (C2), 23.7 (C11), 25.3 (C10), 33.1 (C7), 34.1 (C12), 36.2 (C8), 37.0 (C1), 37.6 (C3), 41.9 (C6), 51.6 (C14), 53.5 (C5), 174.0 (C13), 203.6 (C4). **MS *m/z* (positive CI, NH_3)** 223, 237, 239, 255, 271, 287, 317 (MH^+), 333, 334 ($MH^+..NH_3$), 335, 336. **MS *m/z* (EI)** 110, 123, 142, 151, 177, 187, 205, 237, 259, 287, 299, 316 ($M^{+\bullet}$ with ^{79}Br), 318 ($M^{+\bullet}$ with ^{81}Br). **HRMS *m/z* (EI)**: 316.0670 ($M^{+\bullet}$ $C_{14}H_{21}{}^{79}BrO_3{}^{+\bullet}$ requires 316.0669)**.**

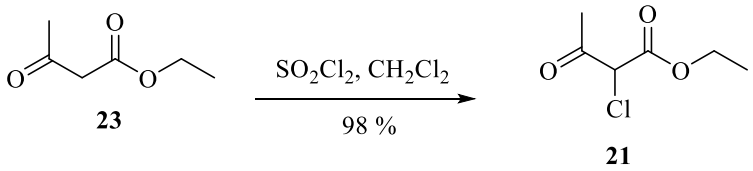
3.0 Synthetic sequence involving cycloaddition with 1,3-cyclohexadiene.



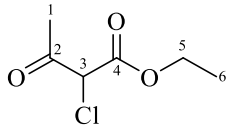
Piperonyl chloride (20). Piperonyl alcohol (**22**) (10.0 g, 65.7 mmol) was dissolved in dry toluene (100 mL). Triethylamine (7.98 g, 78.9 mmol) and thionyl chloride (15.6 g, 131 mmol) were added. The reaction mixture was stirred for 24 hrs at 0 °C and then washed with saturated $NaHCO_3$ (2 × 100 mL) and extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to give the desired product **20** as a brown oil (10.9 g, 98 %) which was of sufficient purity for subsequent transformation.

Piperonyl chloride **20**	

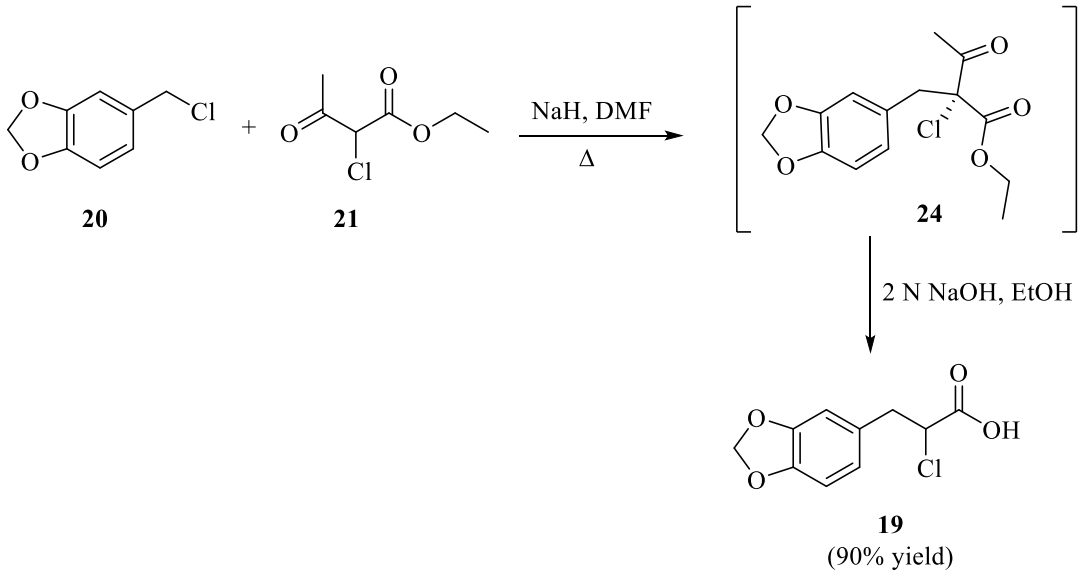
Pale yellow oil. R_f ≈ 0.30 [UV-active, EtOAc/Pet. ether 5 %, anisaldehyde (dark blue spot)]. **IR (neat)**: ν_{max} 2962 (w), 2886 (m, C-H aromatic), 2777 (w), 1504 (s), 1491 (s), 1447 (s), 1363 (s), 1251 (s), 1194 (m), 1100 (m), 1043 (s, O-CH_2-O), 947 (m), 932 (s, O-CH_2-O) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 4.41 (2H, s, H1), 5.84 (2H, s, H8), 6.64-6.77 (3H, m, H3, H6, H7). **^{13}C NMR ($CDCl_3$)** 46.5 (C1), 101.2 (C8), 108.1 (C6), 109.0 (C3), 122.2 (C7), 131.2 (C2), 147.7 (C4), 147.8 (C5). **MS *m/z* (positive CI, NH_3)** 118, 136, 148, 152, 161, 171 (MH^+), 172, 180, 208, 225. **MS *m/z* (EI)** 105, 117, 121, 135, 136, 170 ($M^{+\bullet}$ with ^{35}Cl), 171, 172 ($M^{+\bullet}$ with ^{37}Cl). **HRMS *m/z* (EI)**: 170.0137 ($M^{+\bullet}$ $C_8H_7{}^{35}ClO_2{}^{+\bullet}$ requires 170.0129)**.**



Ethyl-2-chloro-3-oxobutanoate (21). Sulfuryl chloride (11.4 g, 84.5 mmol) was added dropwise by dropping funnel to ethyl acetoacetate **23** (10.0 g, 76.8 mmol) in CH_2Cl_2 (65 mL) and maintained at 0 °C. The mixture was stirred overnight at room temperature. The mixture was washed with H_2O (2 × 100 mL), dried over $MgSO_4$ and concentrated under vacuum to give the desired product **21** as a yellowish oil (12.3 g, 98 %) which was of sufficient purity for subsequent transformation.

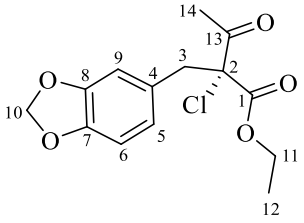
Ethyl-2-chloro-3-oxobutanoate **21**	

Pale yellow oil. **IR (neat):** ν_{max} 2985 (m), 2941 (w), 1735 (s, C=O), 1645 (w), 1616 (w), 1445 (w), 1369 (m), 1255 (s), 1163 (s), 1096 (w), 1070 (w), 1034 (m) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.23-1.31 (3H, m, H6), 2.32 (3H, s, H1), 4.20-4.34 (2H, m, H5), 4.71 (1H, s, H3). **^{13}C NMR ($CDCl_3$)** 13.5 (C6), 25.9 (C1), 61.0 (C3), 62.7 (C5), 164.6 (C4), 196.1 (C2). **MS *m/z* (positive CI, NH_3)** 103, 135, 137, 148, 152, 162, 165 (MH^+), 170, 182, 184. **MS *m/z* (EI)** 118, 120, 121, 122, 124, 136, 164 ($M^{+\bullet}$ with ^{35}Cl), 166 ($M^{+\bullet}$ with ^{37}Cl). **HRMS *m/z* (EI)**: 164.0245 ($M^{+\bullet}$ $C_6H_9{}^{35}ClO_3{}^{+\bullet}$ requires 164.0235)**.**

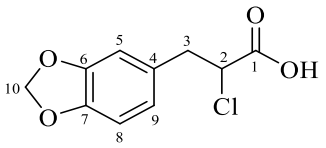


2-Chloro-3-(3,4-methylenedioxyphenyl)propanoic acid (19). A solution of ethyl 2-chloro-acetoacetate (**21**) (2.47 g, 15.0 mmol) in DMF (25 mL) was treated with 60 % NaH in oil (0.60 g, 15.0 mmol) at room temperature for 20 min. A solution of 3,4-methylenedioxybenzyl chloride (**20**) (2.56 g, 15.0 mmol) in DMF (5.0 mL) was added thereto, and the mixture was stirred at 80 °C for 2 hrs, poured into ice-H_2O and extracted with EtOAc (100 mL). The extract was washed with H_2O (2 × 50 mL), dried over $MgSO_4$ and concentrated under vacuum to give the desired product **24** as a brown oil, which was of sufficient purity for subsequent transformation.

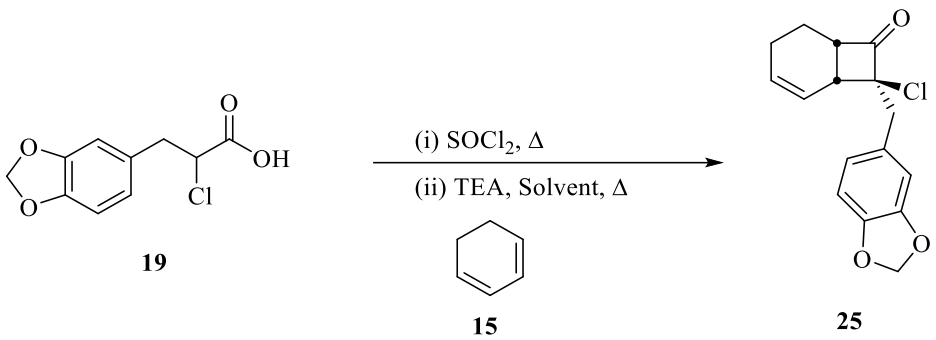
A stirred solution of crude product **24** in EtOH (50.00 mL) was treated with 2 N NaOH (20 mL) at room temperature for 1 h. The solvent was removed at reduced pressure, and the residue was taken up with EtOAc (25 mL) and H_2O (50 mL). The aqueous phase was acidified with conc. HCl (5.0 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated at reduced pressure to give solid **19** (3.10 g, 90 %).

Ethyl 2-acetyl-2-chloro-3-(3,4-methylenedioxyphenyl) propionate **24**	

Brown liquid. **^{1}H NMR ($CDCl_3$)** 1.20 (3H, t, J = 7.0 Hz, H12), 2.22 (3H, s, H14), 3.33 (2H, AB system, δ_A 3.26, δ_B 3.38, J_{AB} = 16.1 Hz, H3), 4.17 (2H, q, J = 7.0 Hz, H11), 5.89 (2H, s, H10), 6.57 – 6.66 (3H, m, H5, H6, H9). **^{13}C NMR ($CDCl_3$)** 13.8 (C12), 26.3 (C14), 41.8 (C3), 63.0 (C11), 75.4 (C2), 101.0 (C10), 107.9 (C6), 110.1 (C9), 123.8 (C5), 127.4 (C4), 147.0 (C7), 147.4 (C8), 166.8 (C1), 198.4 (C13).

2-chloro-3-(3,4-methylenedioxyphenyl)propanoic acid **19**	

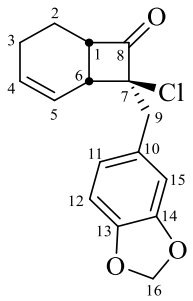
Amorphous white solid. $R_f \approx 0.15$ [non UV-active, EtOAc/Pet. ether 50 %, anisaldehyde (red-violet spot)]. **IR (neat):** ν_{max} 3155 (w), 2895 (w), 2902 (w), 2253 (s, C=O), 1795 (w), 1728 (w), 1490 (w), 1469 (m), 1447 (w), 1384 (m), 1166 (w), 1097 (m), 1044 (w, O-CH_2-O) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 3.21 (2H, AB part of an ABX system, δ_A 3.12, δ_B 3.31, J_{AB} = 14.1, J_{AX} = 7.7, J_{BX} = 7.7 Hz, H3), 4.44 (1H, t, J = 7.7 Hz, H2), 5.95 (2H, s, H10), 6.70 (1H, dd, J = 7.3, 1.6 Hz, H9), 6.73 (1H. d, J = 1.6 Hz, H-5), 6.76 (1H, d, J = 7.3 Hz, H-8). **^{13}C NMR ($CDCl_3$)** 40.6 (C3), 57.2 (C2), 101.1 (C10), 108.5 (C8), 109.7 (C5), 122.7 (C9), 129.1 (C4), 147.0 (C7), 147.9 (C6), 173.3 (C1). **MS *m/z* (positive CI, NH_3)** 135, 137, 152, 175, 192, 195, 210, 229 (MH^+ with ^{35}Cl), 230, 246, 248. **MS *m/z* (EI)** 117, 120, 122, 135, 136, 152, 170, 175, 192, 220, 118, 228 ($M^{+\bullet}$ with ^{35}Cl), 230 ($M^{+\bullet}$ with ^{37}Cl). **HRMS *m/z* (EI)**: 228.0186 ($M^{+\bullet}$ $C_{10}H_9{}^{35}ClO_4{}^{+\bullet}$ requires 228.0184)**.**



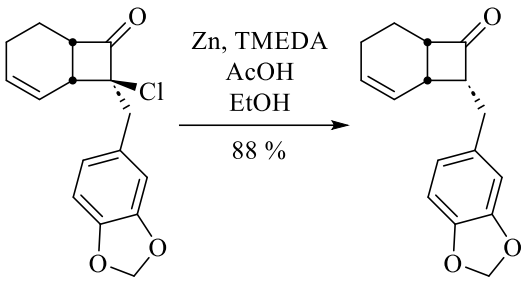
19 **15** **25**

7-Chloro-7-(3,4-methylenedioxyphenyl)bicyclo[4.2.0]oct-4-en-8-one (25). The 2-chlorocarboxylic acid **19** (0.46 g, 2.0 mmol) was added to 2.0 mL (28.0 mmol) of $SOCl_2$, and the reaction solution heated under reflux condition for 3 hrs. The reaction solution was cooled, and the solvent was removed *in v*acuo. The residue was then dissolved in cyclohexane (5.0 mL).

The residue and cyclohexadiene **15** (504 mg, 6.3 mmol) was treated with triethylamine (0.44 g, 4.3 mmol) within 10 min. The reaction mixture was stirred at reflux for 3 hrs and then filtered. The solid residue was rinsed with cyclohexane (5.0 mL). The filtrate was washed with 1 M HCl (10 mL), 1 M $NaHCO_3$ (10 mL) and brine (20 mL). After drying over $MgSO_4$, the organic layer was concentrated and the crude product was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (95:5) to afford **25** (0.15 g, 25 %).

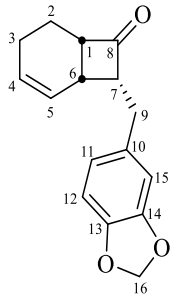
(1*R**,6*S**,7*S**)-7-Chloro-7-(3,4-methylenedioxyphenyl)bicyclo [4.2.0]oct-4-en-8-one **25**	

Yellowish oil. $R_f \approx 0.40$ [UV-active, EtOAc/Pet. ether 15 %, anisaldehyde (violet spot)]. **IR (neat):** ν_{max} 3030 (w), 2932 (m), 2775 (w), 1788 (s, C=O), 1742 (s), 1505 (s), 1490 (s), 1445 (s), 1249 (s), 1239 (s), 1191 (w), 1120 (w), 1045 (s) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.47 (1H, m, H2a), 1.91–2.01 (3H, m, H2b, H3), 2.96 (2H, dd, *J* = 6.0, 4.4 Hz, H9), 3.11 (1H, m, H6), 4.01 (1H, m, H1), 5.81 (2H, s, H16), 5.84 (1H, m, H5), 5.96 (1H, m, H4), 6.64 (2H, d, *J* = 8.0, H11, H12), 6.74 (1H, s, H15). **^{13}C NMR ($CDCl_3$)** 18.5 (C2), 21.1(C3), 37.0 (C9), 40.6 (C6), 54.4 (C1), 80.2 (C7), 100.7 (C16), 107.7 (C12), 110.4 (C15), 123.1 (C5), 124.1 (C4), 128.7 (C10), 132.1 (C11), 146.2 (C13), 147.2 (C14), 204.6 (C8). **MS *m/z* (positive CI, NH_3)** 108, 136, 170, 255, 274, 291 (MH^+ with ^{35}Cl), 293 (MH^+ with ^{37}Cl), 308 ($MH^+..NH_3$ with ^{35}Cl), 310 ($MH^+..NH_3$ with ^{37}Cl), 342. **MS *m/z* (EI)** 105, 135, 136, 149, 170, 179, 210, 235, 255. 267, 290 ($M^{+\bullet}$ with ^{35}Cl). **HRMS *m/z* (EI)**: 290.0711 ($M^{+\bullet}$ $C_{16}H_{15}{}^{35}ClO_3{}^{+\bullet}$ requires 290.0704)**.**

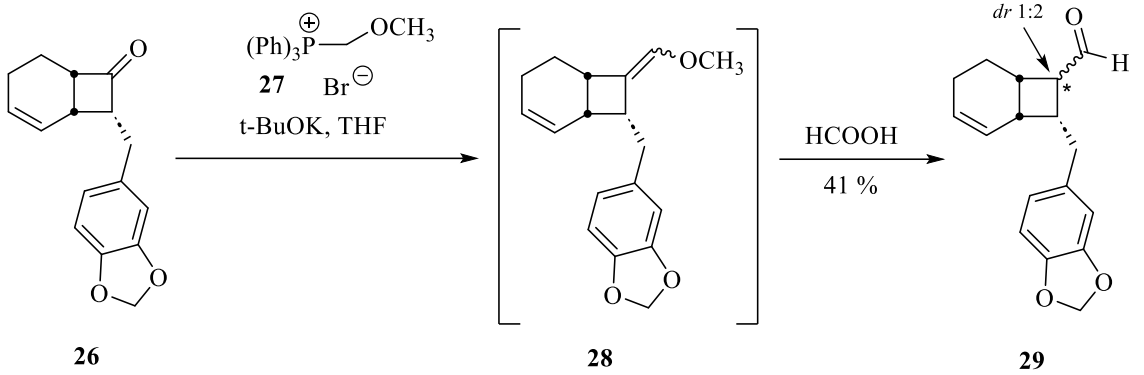


25 **26**

7-(3,4-Methylenedioxyphenyl)bicyclo[4.2.0]oct-4-en-8-one (26). To a mixture of Zn dust (43.3 mmol, 1.30 g) and TMEDA (20.1 mmol, 3.00 mL) in absolute EtOH (7.0 mL) at 0 °C was added AcOH (30.9 mmol, 1.50 mL). The reaction mixture was maintained at 0 °C while a solution of cyclobutanone **25** (1.00 g, 3.44 mmol) in EtOH (3.0 mL) was added over a 10 min period. After an additional 15 min at 0 °C, the reaction mixture was allowed to warm to room temperature and further stirred for 2 hrs. The resulting grey mixture was filtered, and the solid residue was rinsed with diethyl ether. The filtrate was washed with 1 M HCl (10 mL), H_2O (10 mL), sat. $NaHCO_3$ (10 mL) and sat NaCl (10 mL). The resulting material was dried over $MgSO_4$ and concentrated under reduced pressure to afford 0.78 g (88 %) of desired cyclobutanone **26** which was of sufficient purity for subsequent transformation.

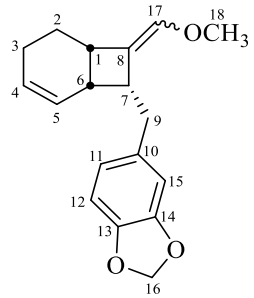
(1*R**,6*S**,7*S**)-7-(3,4-Methylenedioxyphenyl) bicyclo[4.2.0]oct-4-en-8-one **26**	

Yellowish oil. $R_f \approx 0.35$ [UV-active, EtOAc/Pet. ether 15 %, anisaldehyde (violet spot)]. **IR (neat):** ν_{max} 3025 (m), 2931 (s), 2653 (m), 2774 (m), 1773 (s, C=O), 1645 (w), 1610 (w), 1505 (s), 1489 (s), 1445 (s), 1413 (w), 1366 (w), 1293 (w), 1247 (s), 1189 (m), 1099 (m), 1043 (s), 942 (m) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.43 (1H, m, H2a), 1.87-2.02 (3H, m, H2b, H3), 2.60 (2H, AB part of an ABX system, δ_A 2.73, δ_B 2.49, J_{AB} = 15.0, J_{AX} = 5.7, J_{BX} = 9.7 Hz, H9), 3.00 (1H, m, H6), 3.50-3.55 (2H, m, H1, H7), 5.70 (1H, m, H5), 5.84 (2H, s, H16), 5.91 (1H, m, H4), 6.55-6.66 (3H, m, H11, H12, H15). **^{13}C NMR ($CDCl_3$)** 18.5 (C2), 21.3 (C3), 27.7 (C6), 30.3 (C9), 55.0 (C7), 61.9 (C1), 100.8 (C16), 108.1 (C12), 108.7 (C15), 121.0 (C11), 125.8 (C4), 130.4 (C5), 133.5 (C10), 145.7 (C13), 147.5 (C14), 212.3 (C8). **MS *m/z* (positive CI, NH_3)** 136, 149, 157, 177, 183, 202, 211, 228, 240, 257 (MH^+), 274 ($MH^+..NH_3$), 275. **MS *m/z* (EI)** 105, 122, 135, 148, 175, 176, 186, 210, 220, 236, 256 ($M^{+\bullet}$), 258. **HRMS *m/z* (EI)**: 256.1097 ($M^{+\bullet}$ $C_{16}H_{16}O_3^{+\bullet}$ requires 256.1094**).**

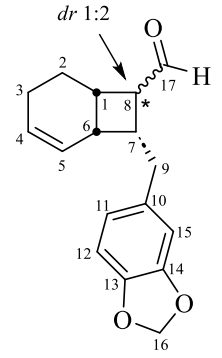


7-(3,4-Methylenedioxyphenyl)bicyclo[4.2.0]oct-4-ene-8-carbaldehyde (29). To a stirred slurry of (methoxymethyl)-triphenylphosphonium chloride **27** (0.58 g, 1.7 mmol) in dry THF (7.0 mL) at −75 °C was added potassium *tert*-butoxide (0.14 g, 1.3 mmol). After 15 min at −75 °C, a solution of bicyclo[4.2.0] oct-4-en-8-one **26** (0.22 g, 0.86 mmol) in dry THF (3.0 mL) was added to the mixture, which was further stirred at −75 °C for 10 min, and then at room temperature overnight. The mixture was diluted with water (20 mL) and extracted with ether (30.00 mL). The organic extract was washed with brine (2 × 20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give **28** as a yellowish oil, which was used as such in the next transformation.

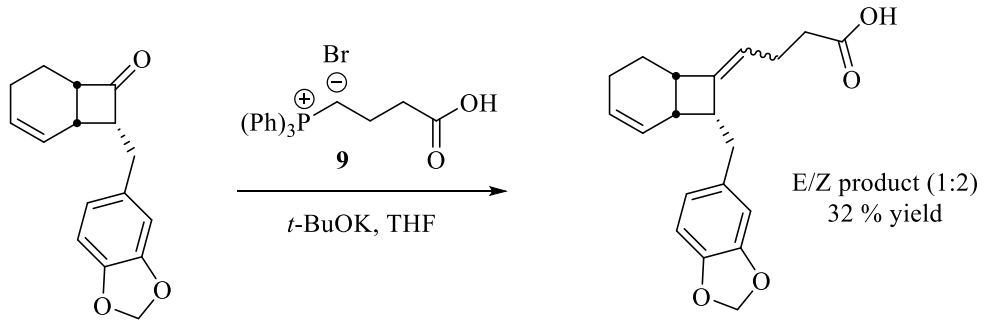
The crude bicyclo[4.2.0]oct-4-ene **28** was stirred with 90 % formic acid (10 mL) at room temperature for 1 h. The mixture was poured into a saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a yellowish oil. Purification by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (95:5), gave the desired product **29** as a yellowish oil (94 mg, 41 %, *dr* 1:2).

(1*R**,6*S**,7*S**)-8-(Methoxymethylene)-7-(3,4-methylenedioxy phenyl)bicyclo[4.2.0]oct-4-ene **28**	

Yellowish oil. $R_f \approx 0.50$ [UV-active, EtOAc/Pet. ether 10 %, anisaldehyde (violet spot)]. **^{1}H NMR ($CDCl_3$)** 1.90 – 1.45 (3H, m, H2, H3), 2.39 – 2.78 (3H, m, H6, H9), 3.32 – 3.60 (2H, m, H1, H7), 4.07 (3H, s, H18), 5.10 (1H, s, H17), 5.52 – 5.82 (2H, m, H4, H5), 5.85 (2H, s, H16) 6.49 – 6.68 (3H, m, H11, H12, H15). **^{13}C NMR ($CDCl_3$)** 20.7 (C3), 21.9 (C2), 34.2 (C6), 35.2 (C9), 37.4 (C7), 44.8 (C1), 59.7 (C18), 100.6 (C16), 108.0 (C12), 108.9 (C15), 121.2 (C11), 126.8 (C4), 128.8 (C8), 131.4 (C5), 133.7 (C10), 139.6 (C17), 145.4 (C13), 147.6 (C14).

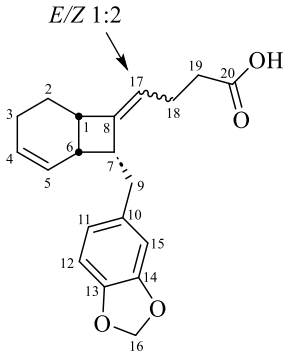
(1*R**,6*S**,7*S**)-7-(3,4-Methylenedioxyphenyl)bicyclo[4.2.0]oct-4-ene-8-carbaldehyde **29**	

Yellowish oil. **IR (neat):** ν_{max} 2928 (m), 1717 (s, C=O), 1504 (m), 1484 (s), 1444 (w), 1372 (w), 1226 (m), 1179 (m), 1039 (m, O-CH_2-O), 1096 (w), 939 (m, m, O-CH_2-O), 8669 (w) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 0.75 – 2.45 (10H, m, H1, H2, H3, H6, H7, H8, H9), 5.68 (1H, m, H5), 5.82 (2H, s, H16), 5.95 (1H, m, H5), 6.47 – 6.74 (3H, m, H11, H12, H15), 9.33 (1H, s, H17). **^{13}C NMR ($CDCl_3$)** 21.2 (C3), 29.8 (C2), 31.2 (C9), 34.4 (C6), 36.7 (C1), 41.1 (C7), 51.8 (C8), 100.7 (C16), 108.3 (C12), 109.7 (C15), 121.2 (C11), 126.4 (C5), 129.5 (C4), 130.6 (C10), 145.8 (C13), 146.7 (C14), 202.6 (C17). **MS *m/z* (EI)** 115, 135, 173, 190, 224, 252, 270 **(**$M^{+\bullet}$), 298, 304. **HRMS *m/z* (EI)**: 270.1262 ($M^{+\bullet}$ $C_{17}H_{18}O_3^{+\bullet}$ requires 270.1250)**.**

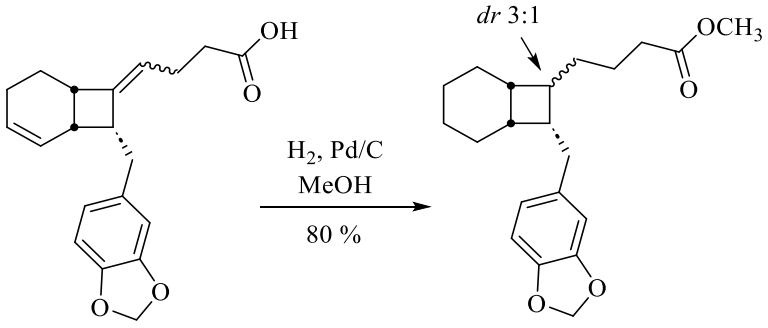


26 **30**

4-[7-(3,4-Methylenedioxyphenyl)bicyclo[4.2.0]oct-4-en-8-ylidene]butanoic acid (30). To a stirred slurry of (3-carboxypropyl)-triphenylphosphonium bromide **9** (0.77 g, 1.8 mmol) in dry THF (7.0 mL) at −75 °C was added potassium *tert*-butoxide (0.35 g, 3.1 mmol). After 15 min at −75 °C, a solution of cyclobutanone **26** (0.21 g, 0.8 mmol) in dry THF (3.0 mL) was added to the mixture, which was further stirred at −75 °C for 10 min, and then at room temperature overnight. The mixture was poured into 5 % Na_2CO_3 solution (20 mL), washed with ethyl acetate (20 mL), and then acidified with conc. HCl. The aqueous layer was extracted with ether (3 × 20 mL) and the combined extract was concentrated to 20 mL, then kept at −20 °C for 2 hrs. The resulting precipitate was filtered off and discarded. Evaporation the filtrate gave a yellowish oil (0.66 g) which was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (7:3), to give the desired product **30** in *Z/E* isomer ratio of 2:1, as a yellowish oil (0.26 g, 32 %).

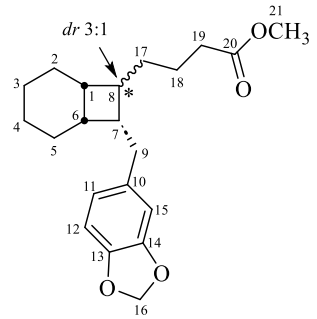
4-[(1*R**,6*S**,7*S**)-7-(3,4-Methylenedioxyphenyl) bicyclo[4.2.0]oct-4-en-8-ylidene]butanoic acid **30**	

Yellowish oil. $R_f \approx 0.30$ [UV-active, EtOAc/Pet. ether 60 %, anisaldehyde (blue spot)]. **IR (neat):** ν_{max} 2928 (s), 2863 (m), 1738 (s, C=O), 1504 (m), 1490 (m), 1441 (m), 1246 (s), 1188 (m), 1040 (m, O-CH_2-O), 927 (m, O-CH_2-O), 859 (w), 810 (w) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.44 (1H, m, H2a), 1.86 – 1.97 (3H, m, H2b, H3), 2.20 – 2.36 (4H, m, H18, H19), 2.53 (2H, dd, *J* = 6.0, 4.4 Hz, H9), 2.79 (1H, m, H6), 3.22 (2H, m, H1, H7), 4.97 (1H, t, *J* = 7.2 Hz, H17), 5.57 (1H, m, H5), 5.84 (2H, s, H16), 5.92 (1H, m, H4), 6.54 (1H, dd, *J* = 8.1, 2.0 Hz, H11), 6.60 (1H, d, *J* = 2.0 Hz, H15), 6.63 (1H, d, *J* = 8.1 Hz, H12). **^{13}C NMR ($CDCl_3$)** 21.9 (C3), 23.1 (C2), 23.7 (C18), 33.6 (C6), 34.2 (C19), 34.9 (C9), 39.2 (C7), 46.6 (C1), 100.7 (16), 108.0 (C12), 109 (C15), 118.0 (C17), 121.2 (C11), 126.8 (C5), 129.9 (C4), 135.0 (C10), 145.4 (C13), 146.6 (C8), 147.4 (C14), 179.0 (C20). **MS *m/z* (EI)** 106, 132, 135, 136, 137, 148, 149, 174, 185, 239, 272, 274, 298, 326 ($M^{+\bullet}$). **HRMS *m/z* (EI)**: 326.1515 ($M^{+\bullet}$ $C_{20}H_{22}O_4^{+\bullet}$ requires 326.1513).



30 **31**

Methyl 4-[7-(3,4-methylenedioxyphenyl)bicyclo[4.2.0]octan-8-yl]butanoate (31). To a solution of the bicycloalkene **30** (55 mg, 0.2 mmol) in MeOH (2.0 mL) was added 10 % Pd/C (10 % w/w, 5.5 mg), and the resulting mixture was hydrogenated at 1 atm for 12 hrs. Filtration through Celite and evaporation of the filtrate in vacuo afforded pure **31** (*dr* 3:1) as yellowish oil (47 mg, 80 %).

Methyl 4-[(1*R**,6*S**,7*S**)-7-(3,4-methylenedioxyphenyl)bicyclo [4.2.0]octan-8-yl]butanoate **31**	

Yellowish oil. $R_f \approx 0.35$ [UV-active, EtOAc/Pet. ether 60 %, anisaldehyde (blue spot)]. **IR (neat):** ν_{max} 2929 (s), 2863 (m), 1739 (s, C=O), 1504 (s), 1490 (s), 1442 (m), 1246 (s), 1188 (m), 1122 9w), 1096 (w), 1040 (m, O-CH2-O), 927 (m, O-CH2-O), 861 (w), 811 (w) cm^{-1}. **^{1}H NMR ($CDCl_3$)** 1.14 – 1.23 (4H, m, H3, H4), 1.39 – 1.59 (H8, m, H2, H5, H17, H18), 2.15 – 2.24 (3H, m, H8, H19), 2.30 – 2.40 (2H, H1, H6), 2.62 – 2.74 (3H, m, H7, H9), 3.58 (3H, s, H21), 5.82 (2H, s, H16), 6.55 (1H, dd, *J* = 8.1, 1.7 Hz, H11), 6.60 (1H, d, *J* = 1.7 Hz, H15), 6.62 (1H, d, *J* = 8.1 Hz, H12). **^{13}C NMR ($CDCl_3$)** 22.6 (C3), 22.7 (C4), 23.1 (C2), 23.2 (C5), 24.8 (C18), 27.6 (C17), 32.9 (C9), 33.8 (C6), 34.1 (C8), 34.4 (C19), 40.2 (C1), 40.3 (C7), 51.6 (C21), 100.6 (C16), 108.1 (C12), 108.9 (C15), 121.2 (C11), 136.2 (C10), 145.2 (C13), 147.4 (C14), 174.3 (C20). **MS *m/z* (EI)** 102, 145, 158, 167, 194, 214, 239, 279, 295, 313, 325, 331, 344 ($M^{+\bullet}$), 362, 380. **HRMS *m/z* (EI)**: 344.1992 ($M^{+\bullet}$ $C_{21}H_{28}O_4^{+\bullet}$ requires 344.1982)**.**

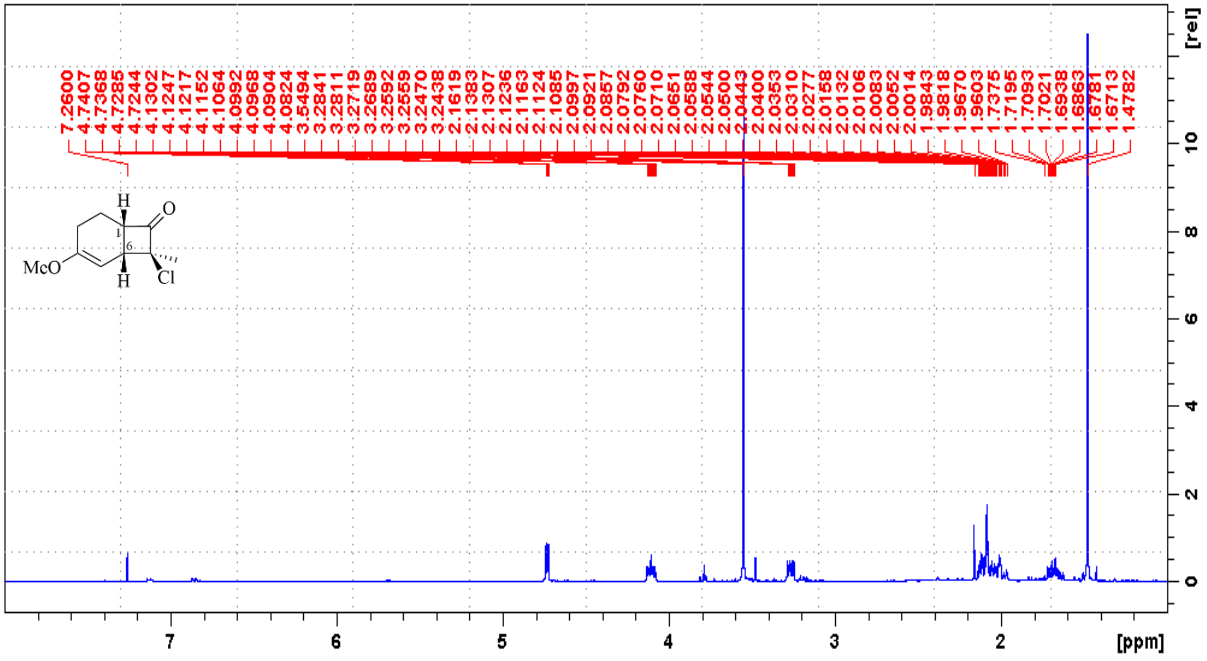


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **6**.

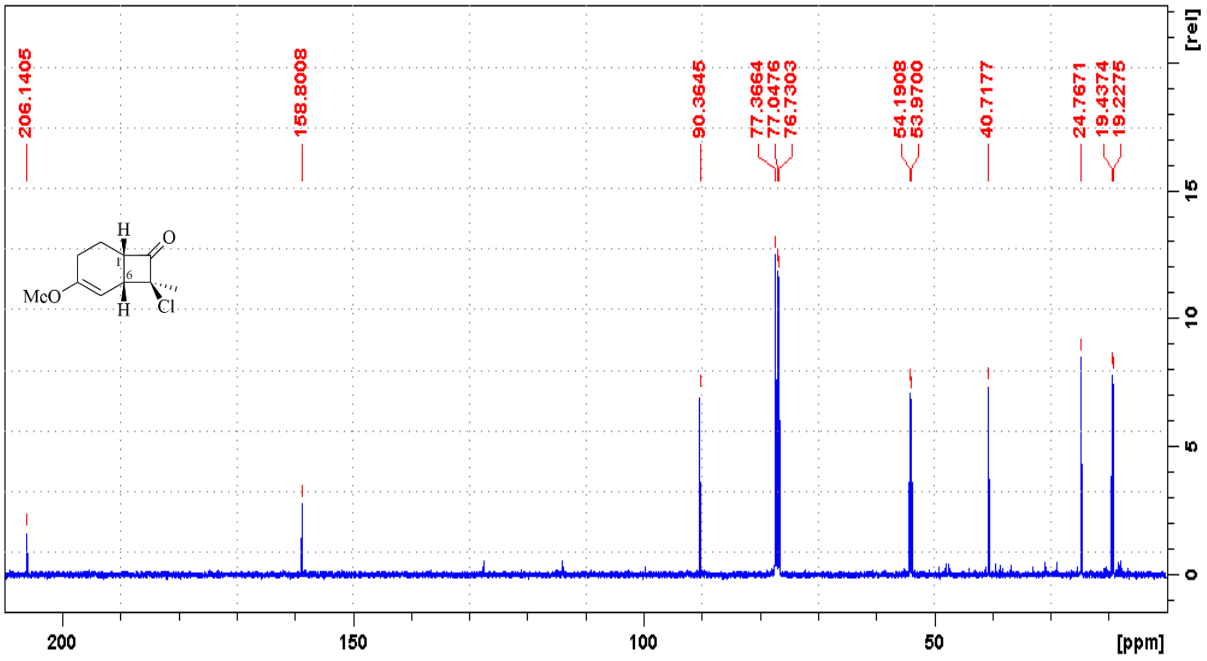


Figure S2: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **6**.

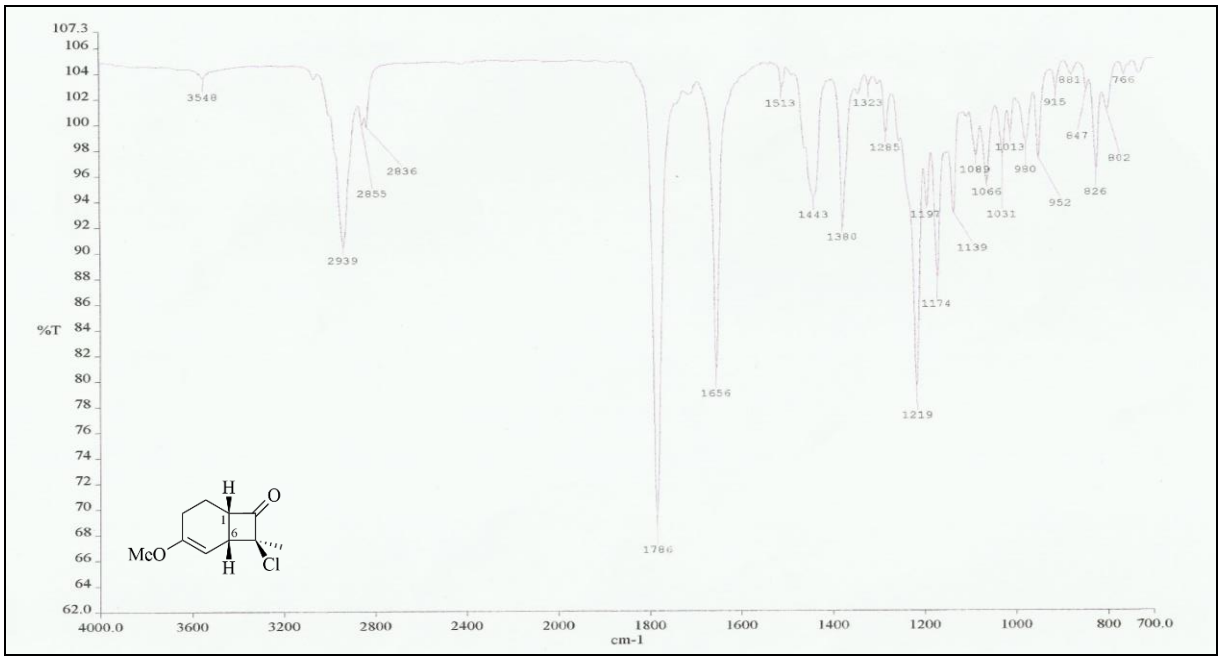


Figure S3: IR spectrum. of compound **6**.

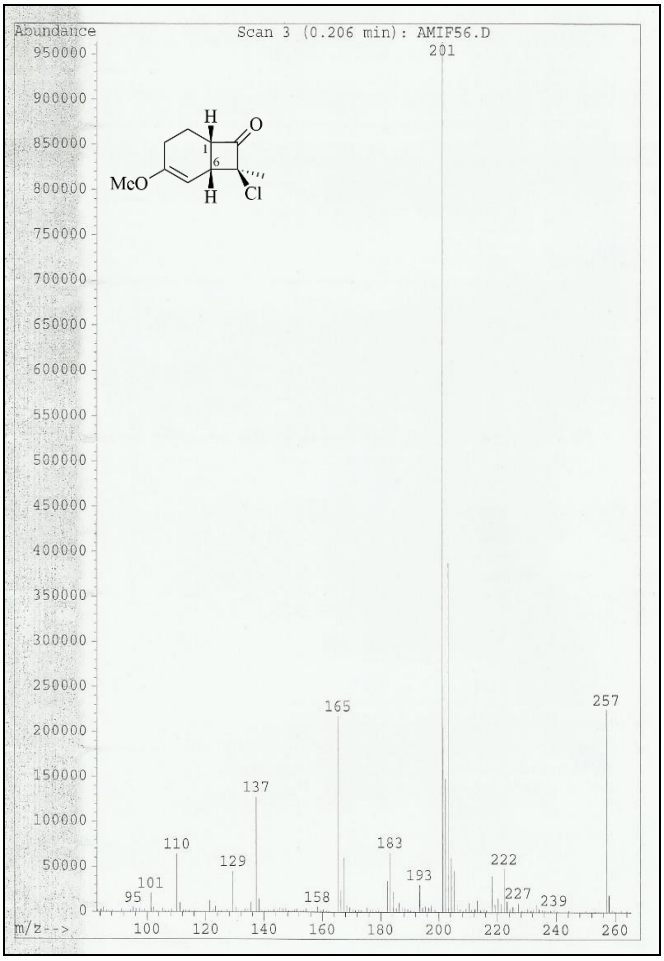


Figure S4: MS spectrum (positive CI**,** NH_3). of compound **6**.

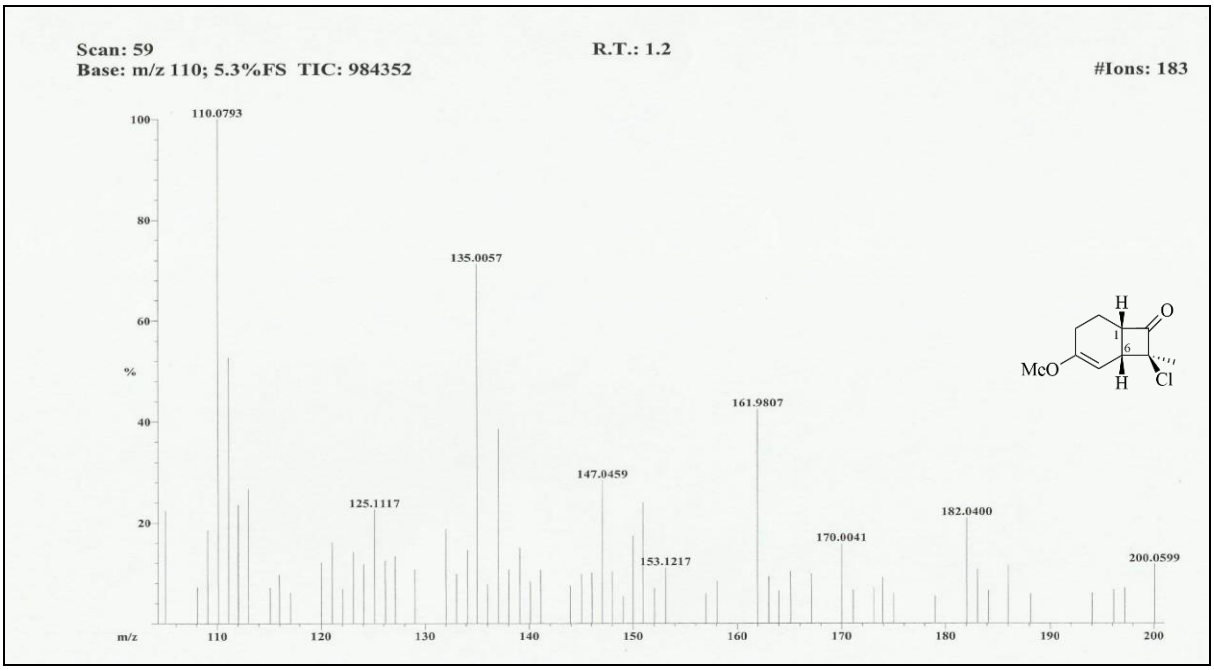


Figure S5: HRMS spectrum (EI) of compound **6**.

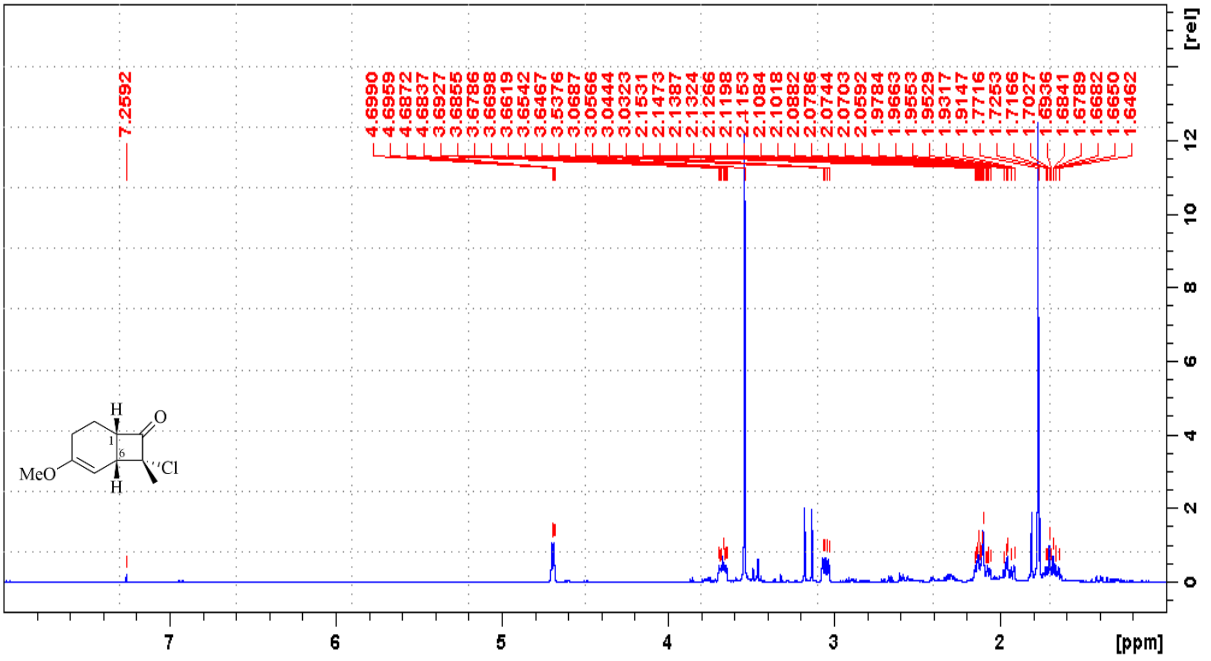


Figure S6: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **7**.

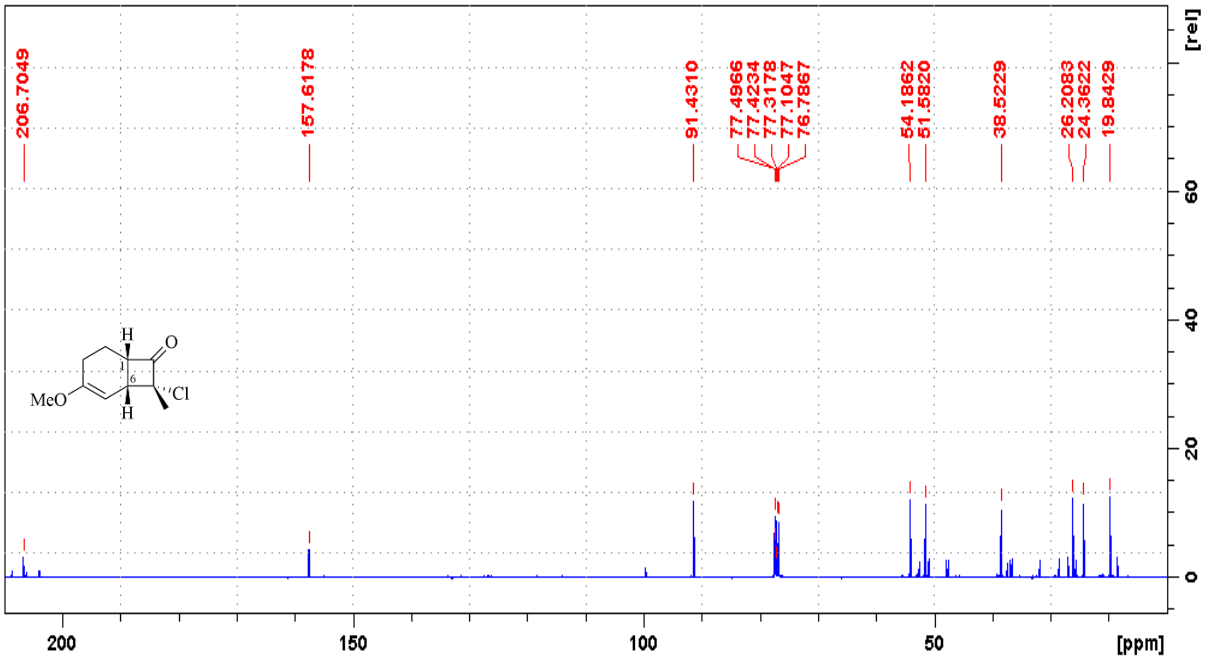


Figure S7: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **7**.

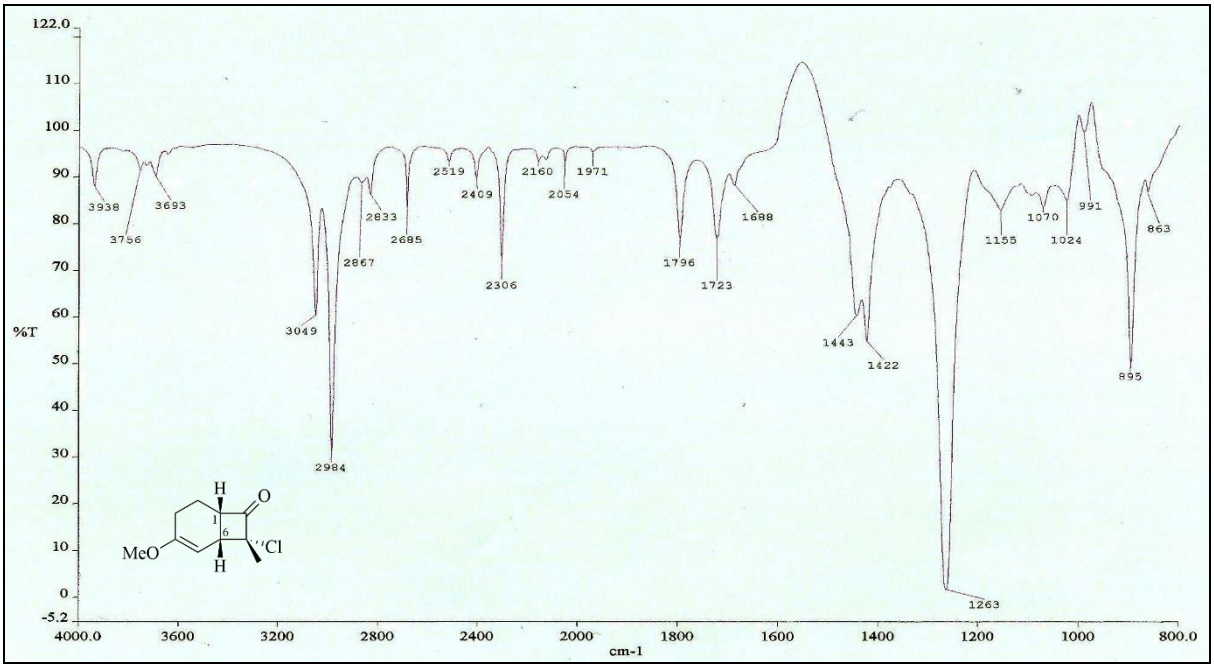


Figure S8: IR spectrum of compound **7**.

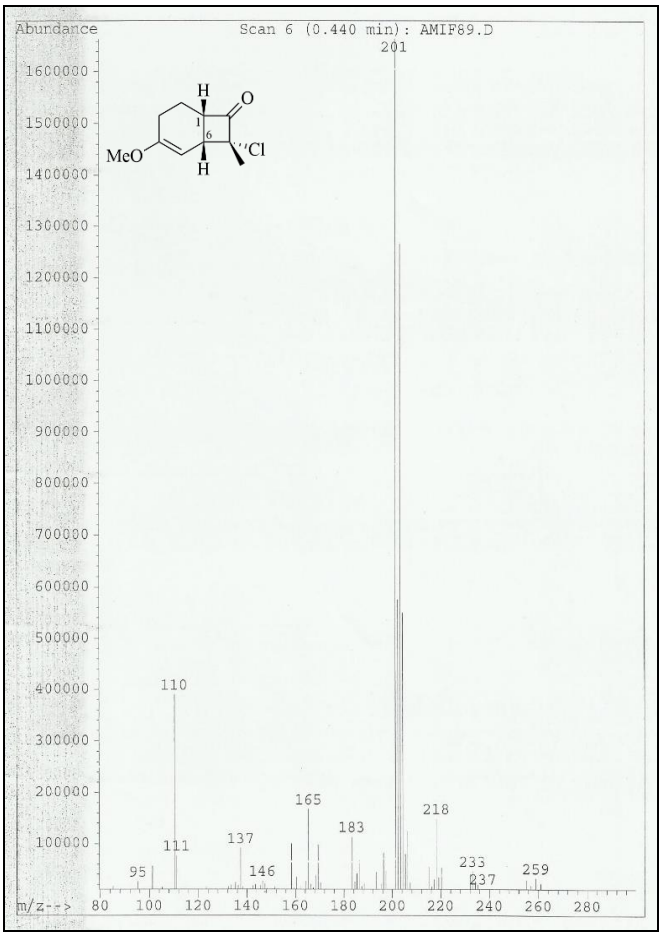


Figure S9: MS spectrum (positive CI, NH_3) of compound **7**.

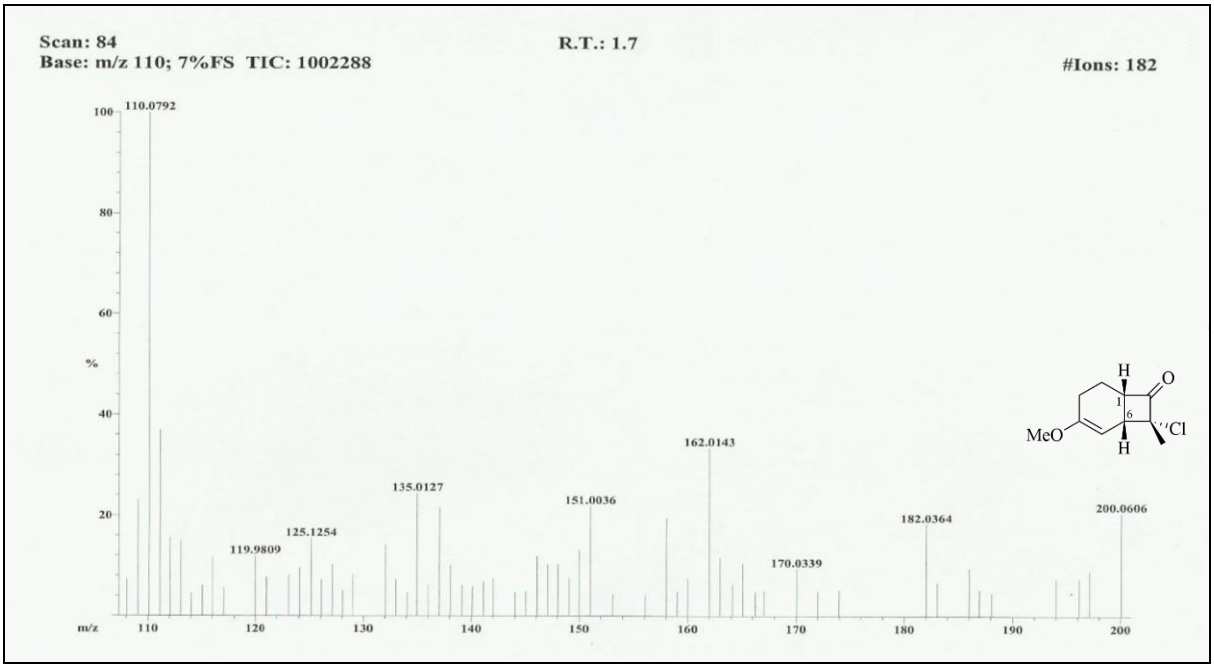


Figure S10: HRMS spectrum (EI) of compound **7**.

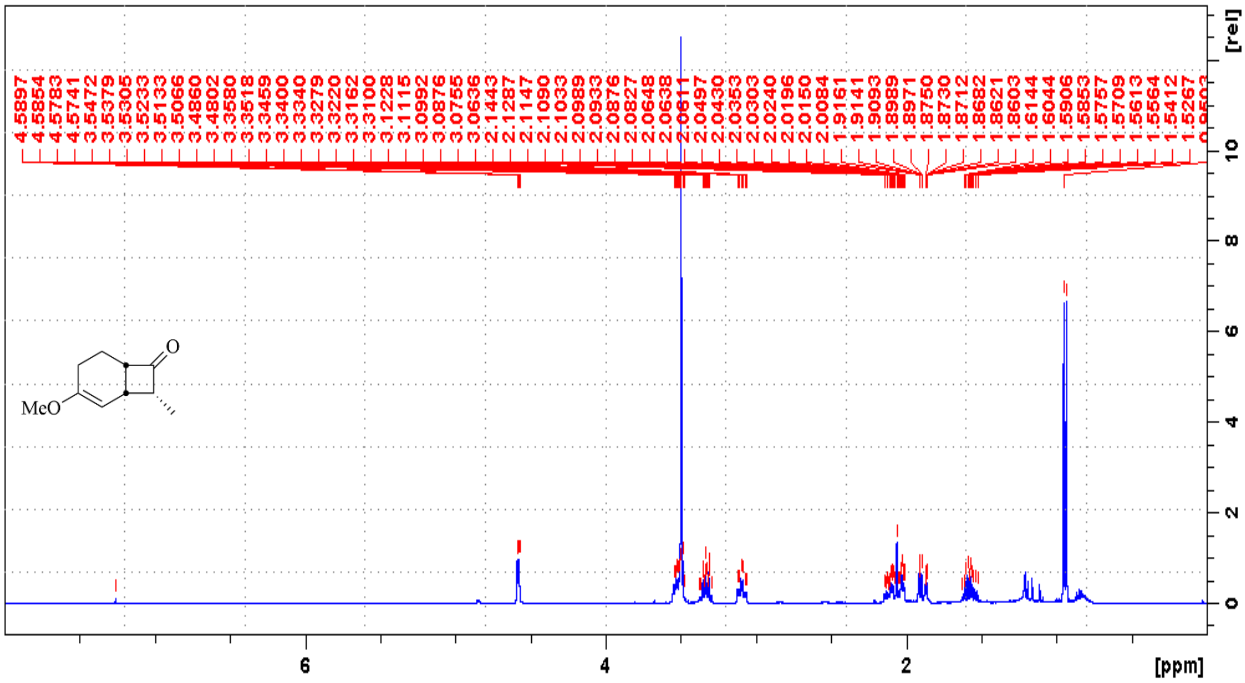


Figure S11: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8**.

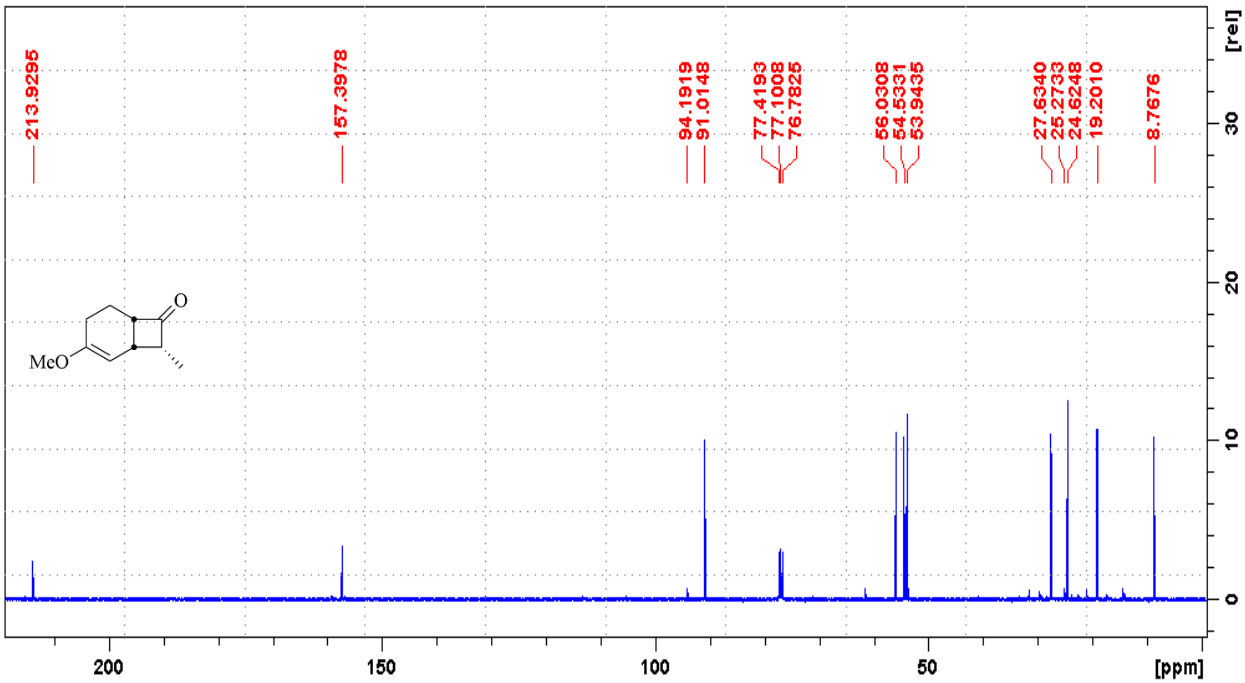


Figure S12: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **8**.

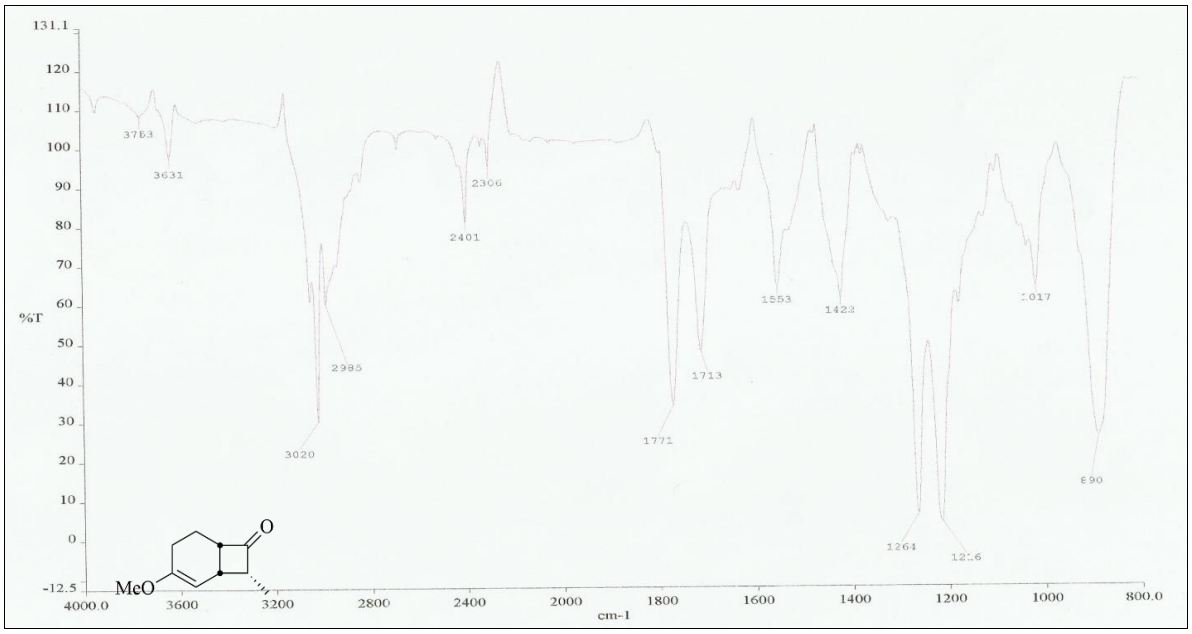


Figure S13: IR spectrum of compound **8**.

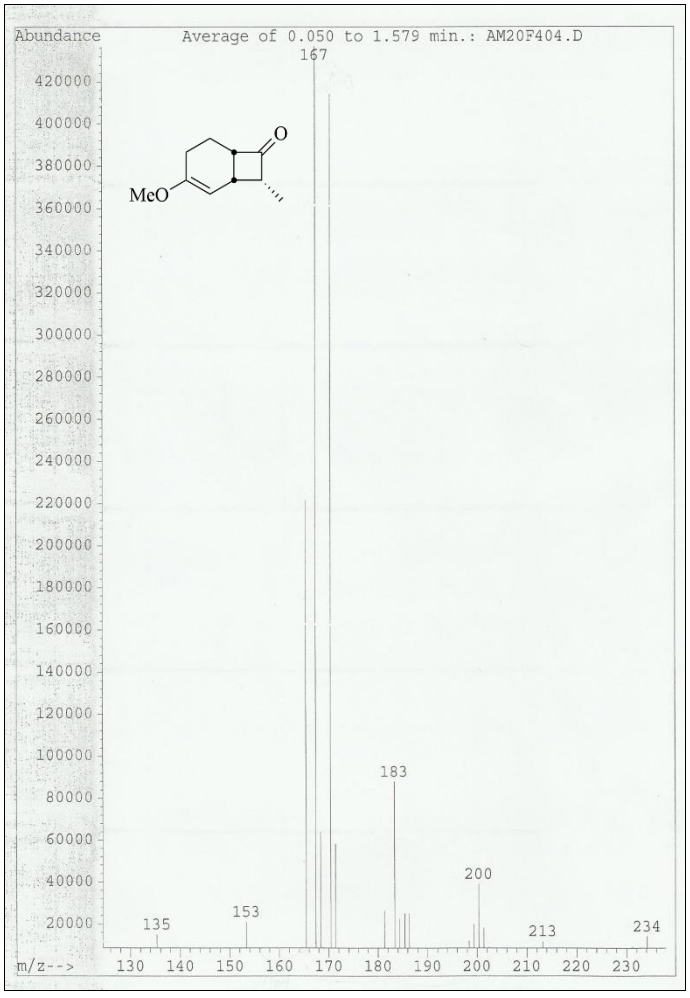


Figure S14: MS spectrum (positive CI, NH_3) of compound **8**.

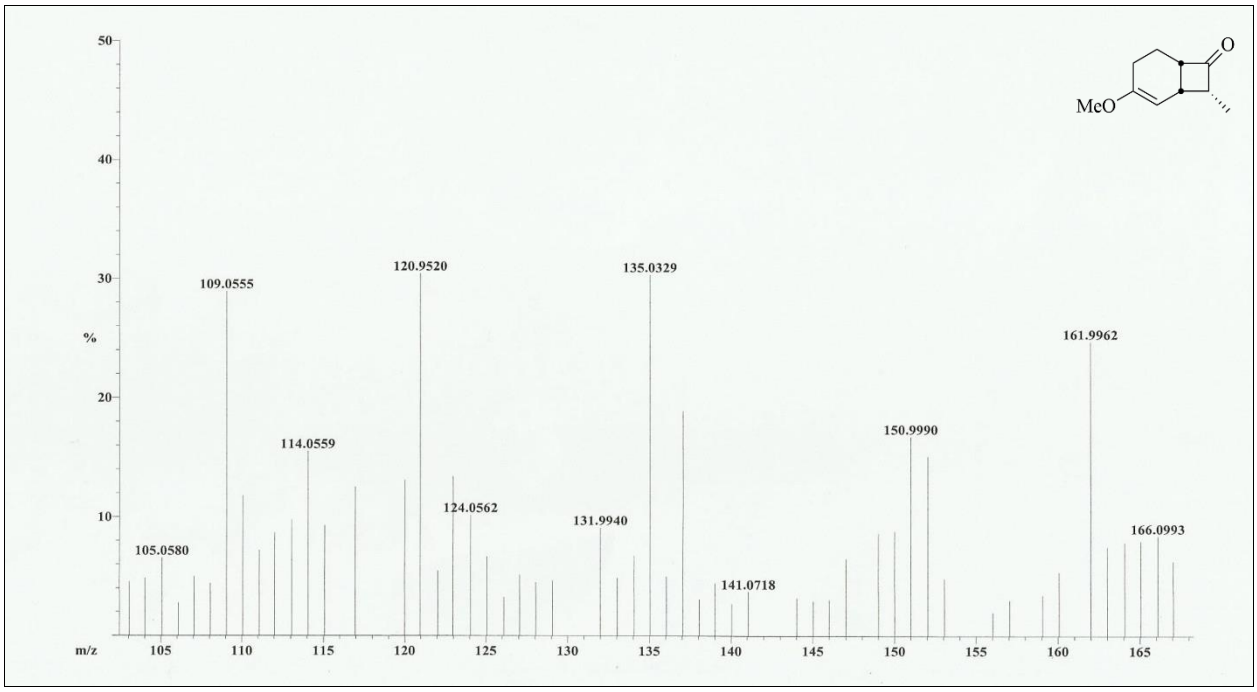


Figure S15: HRMS spectrum (EI) of compound **8**.

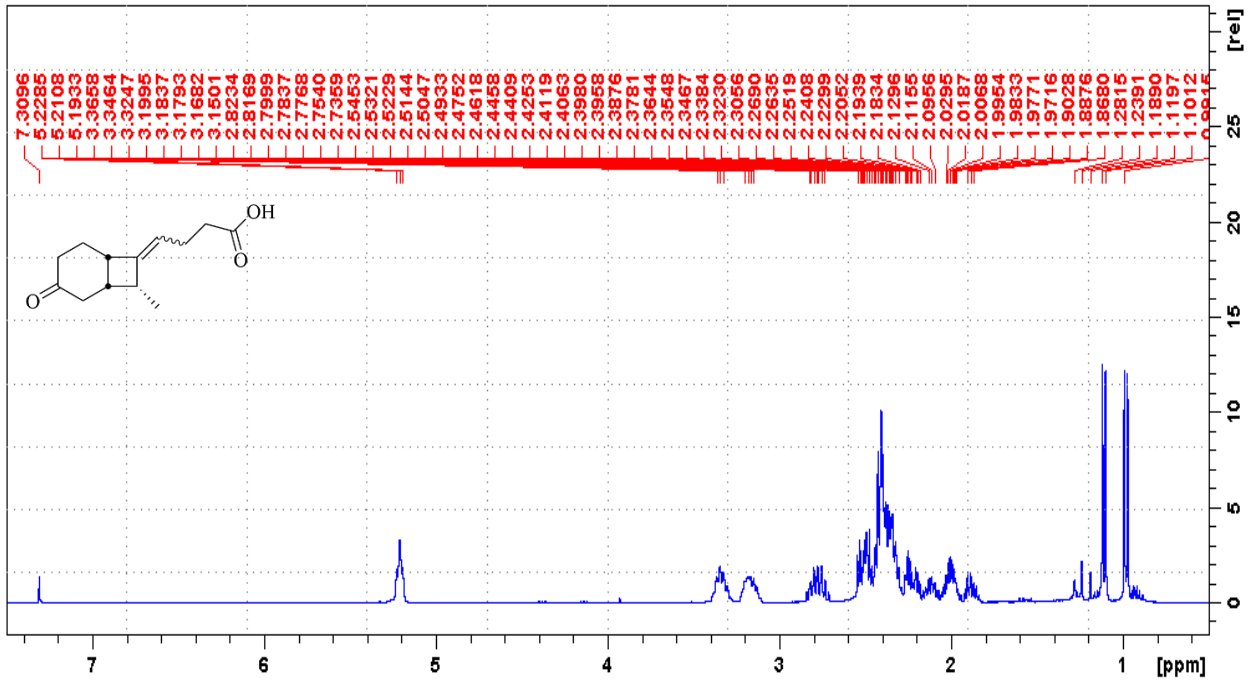


Figure S16: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **10**.

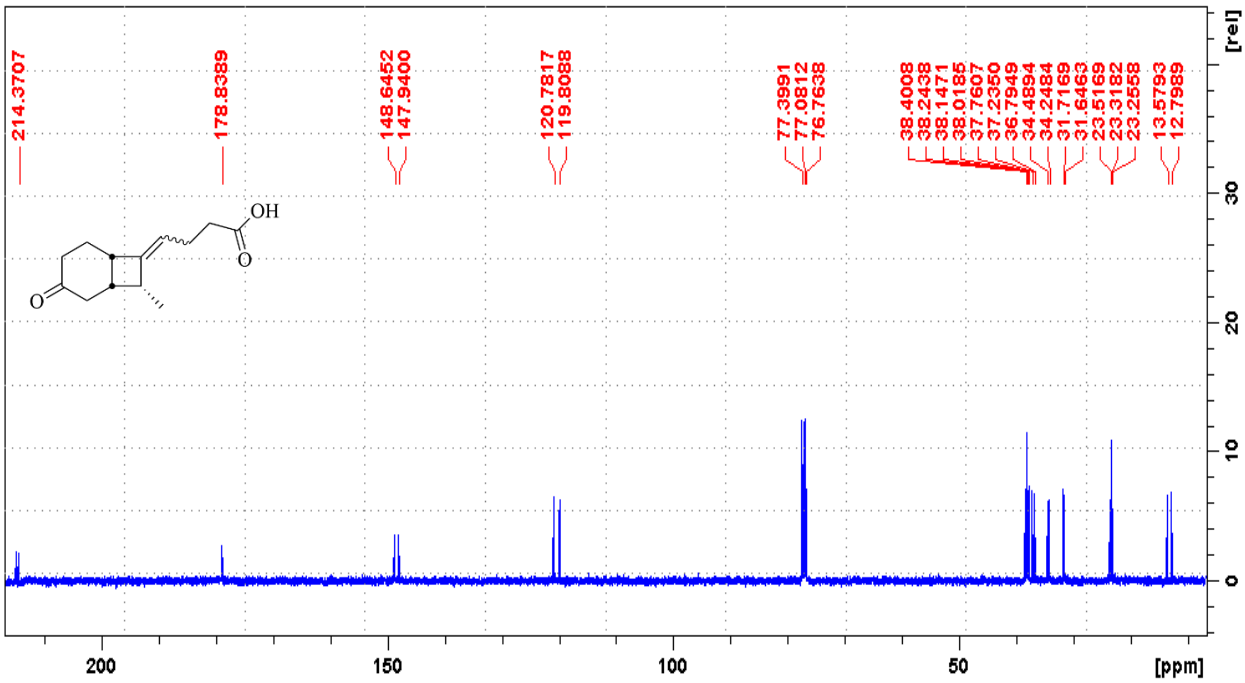


Figure S17: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **10**.

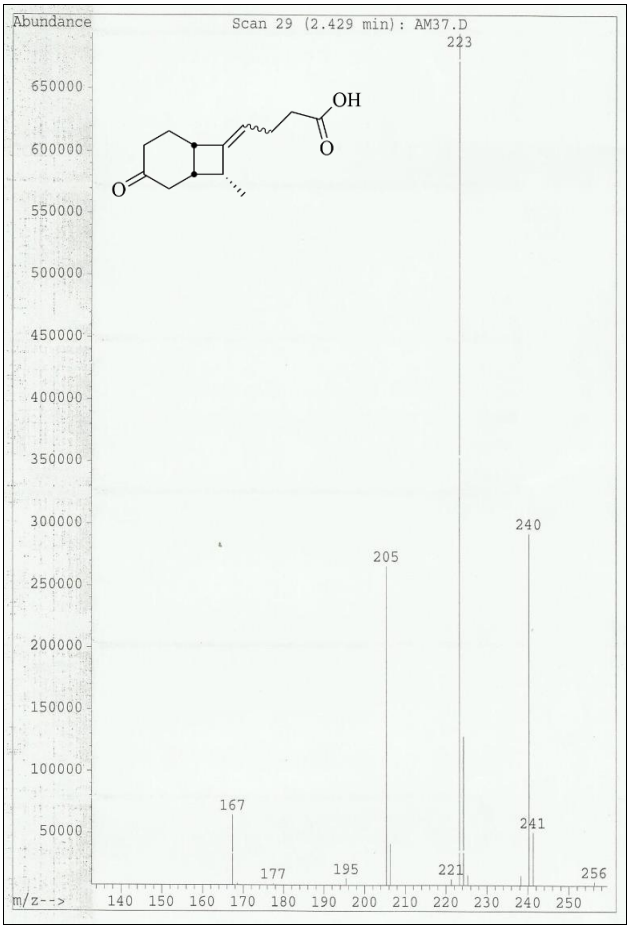


Figure S18:MS spectrum (EI) of compound **10**.

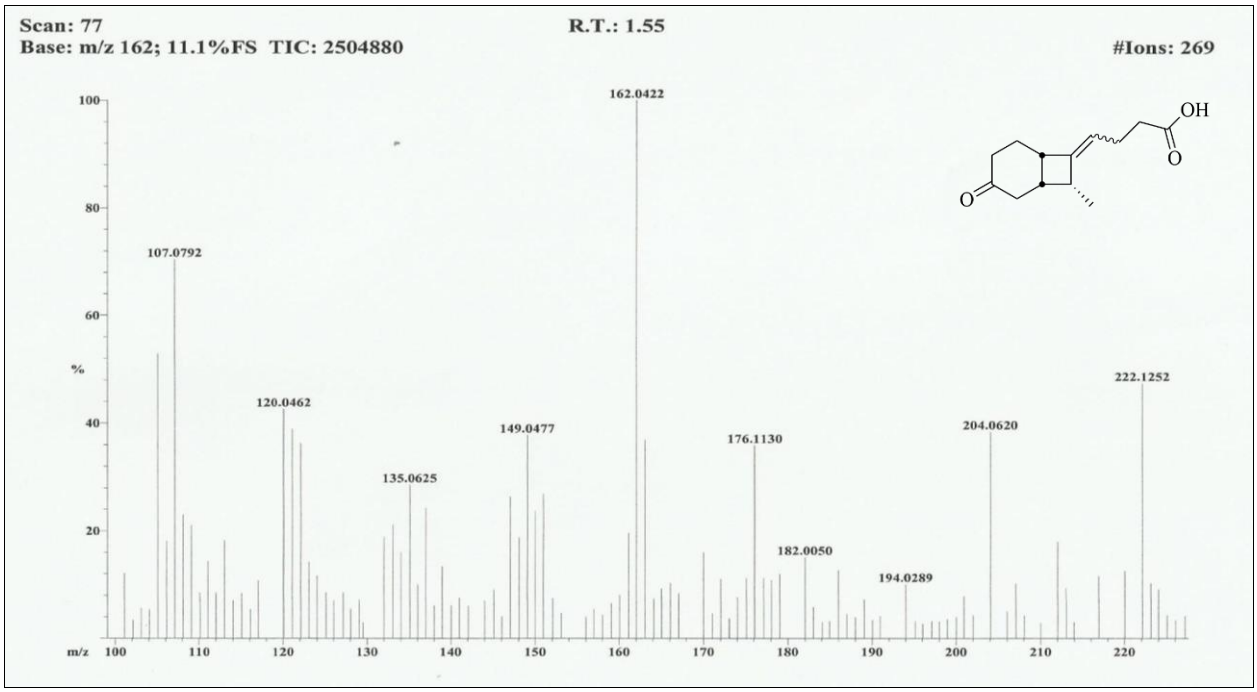


Figure S19: HRMS spectrum (EI) of compound **10**.

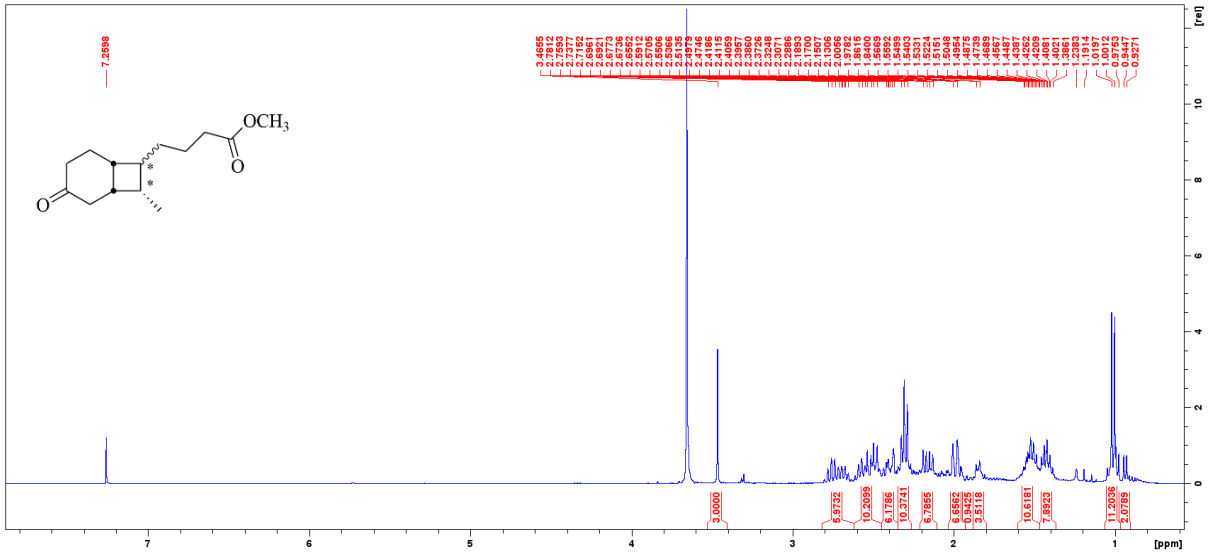


Figure S20: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **11**.

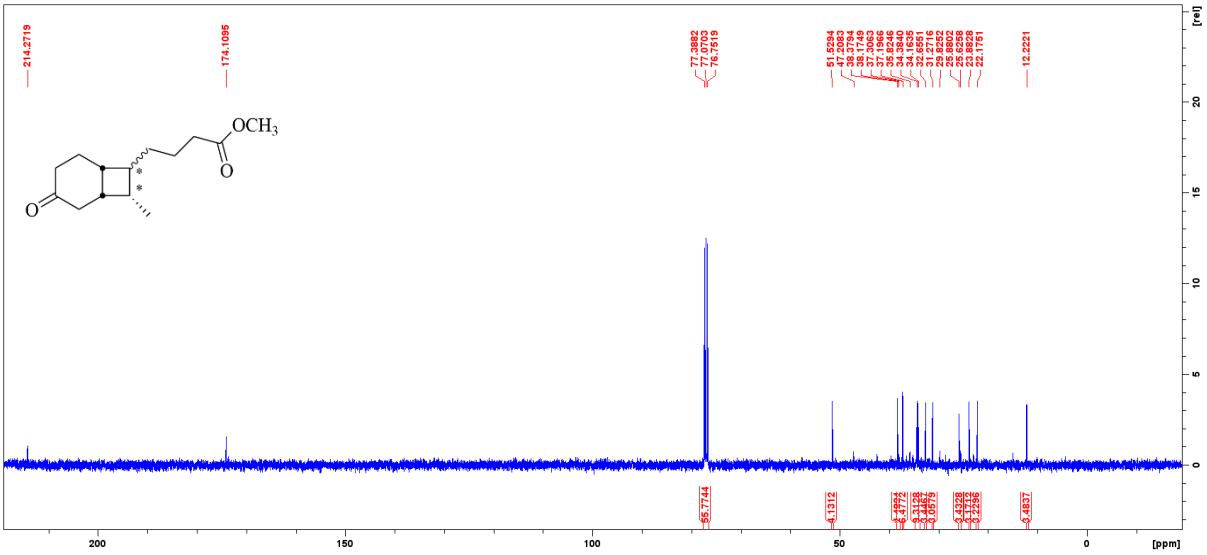


Figure S21: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **11**.

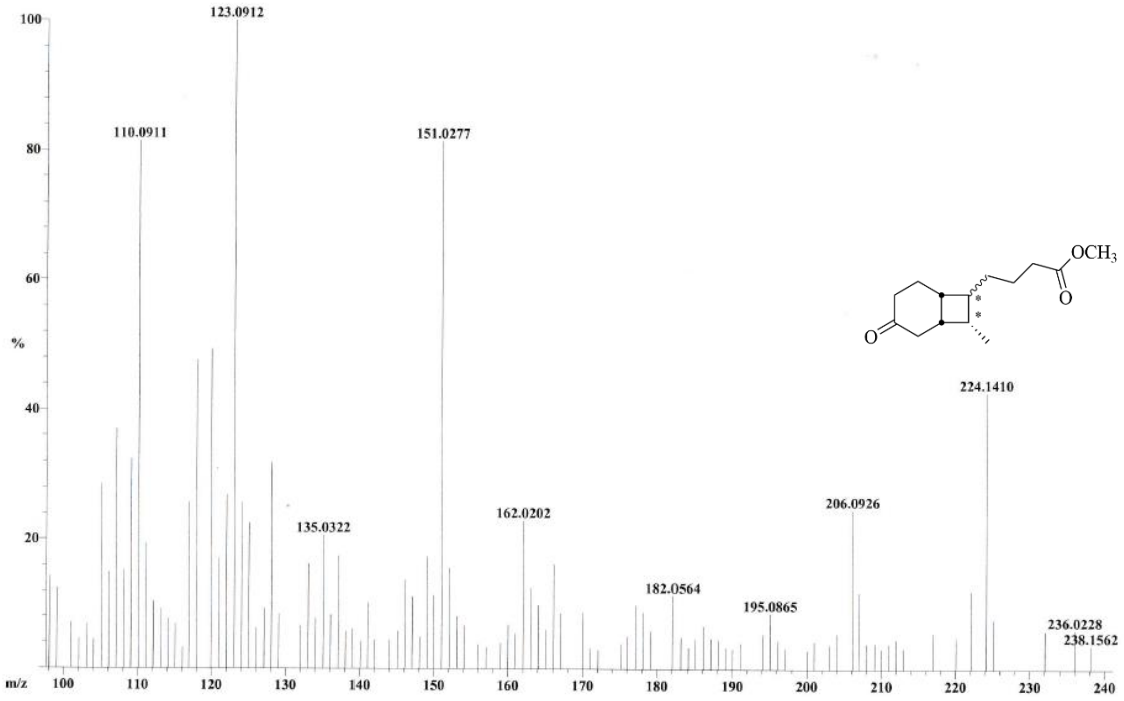


Figure S22: HRMS spectrum (EI) of compound **11**.

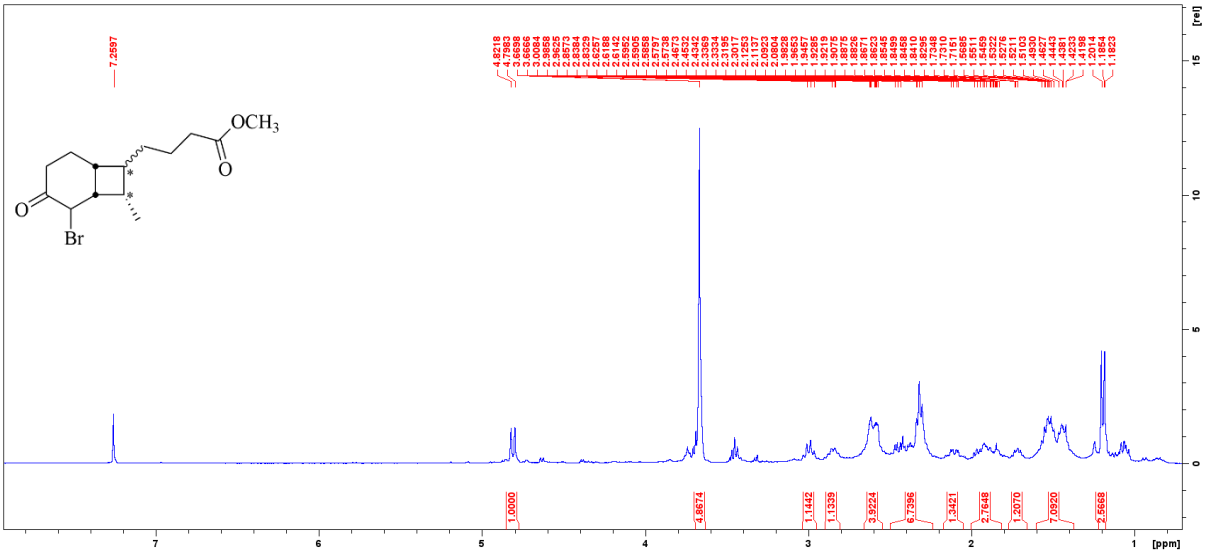


Figure S23: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **13**.

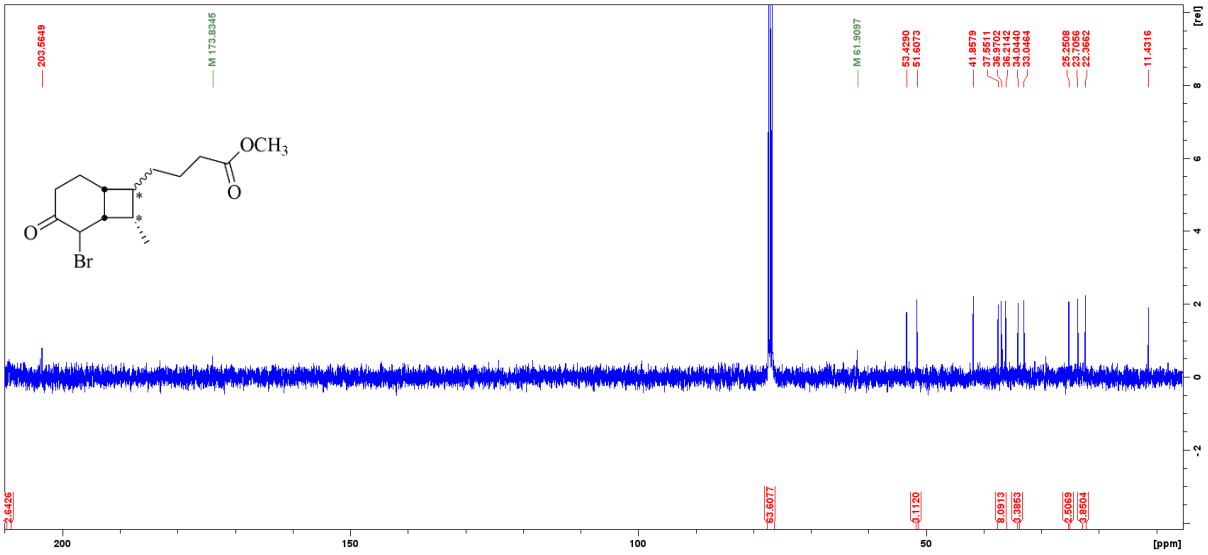


Figure S24: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **13**.

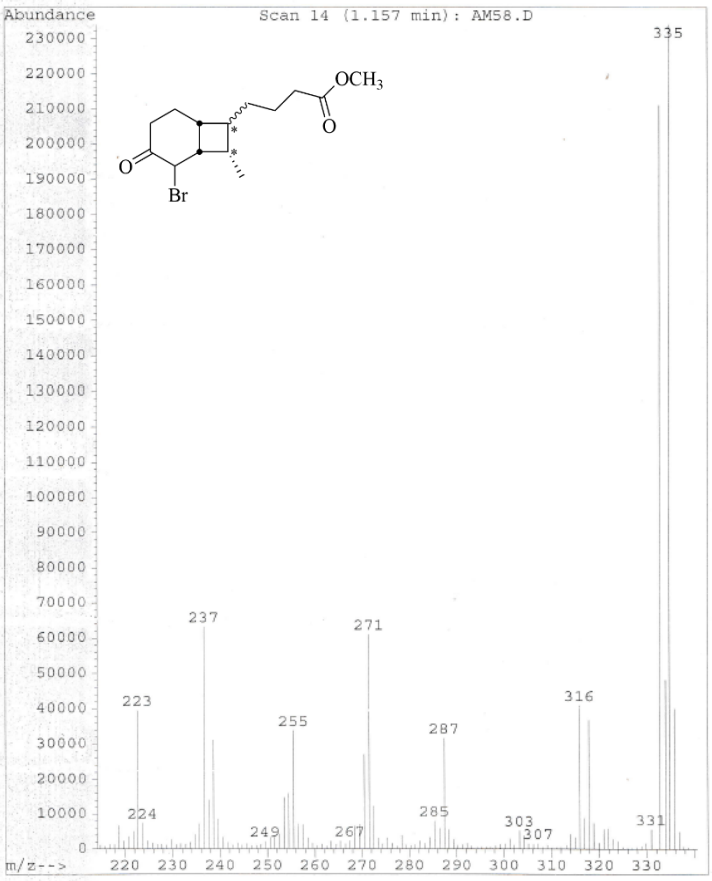


Figure S25: MS spectrum (positive CI, NH_3) of compound **13**.

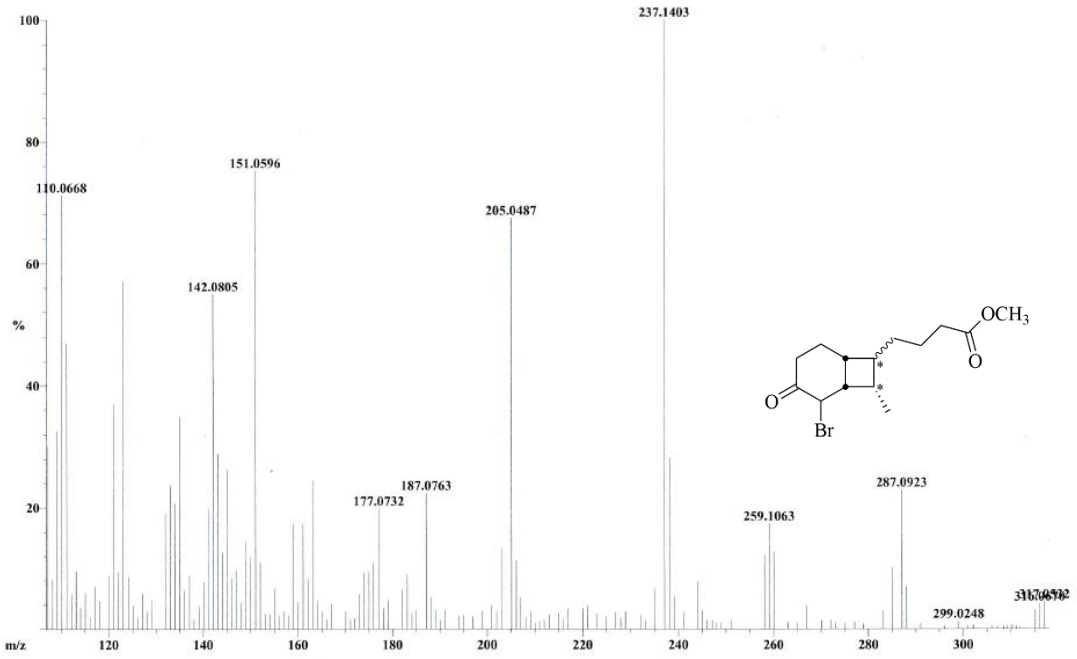


Figure S26:HRMS spectrum (EI) of compound **13**.

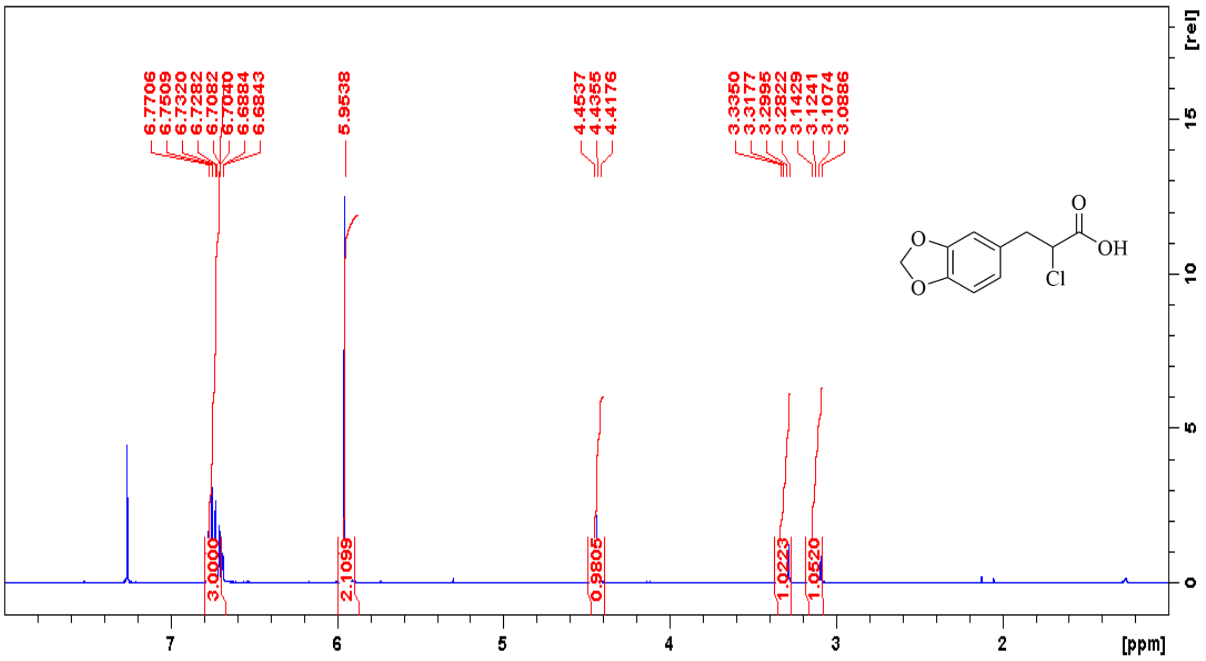


Figure S27: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **19**.

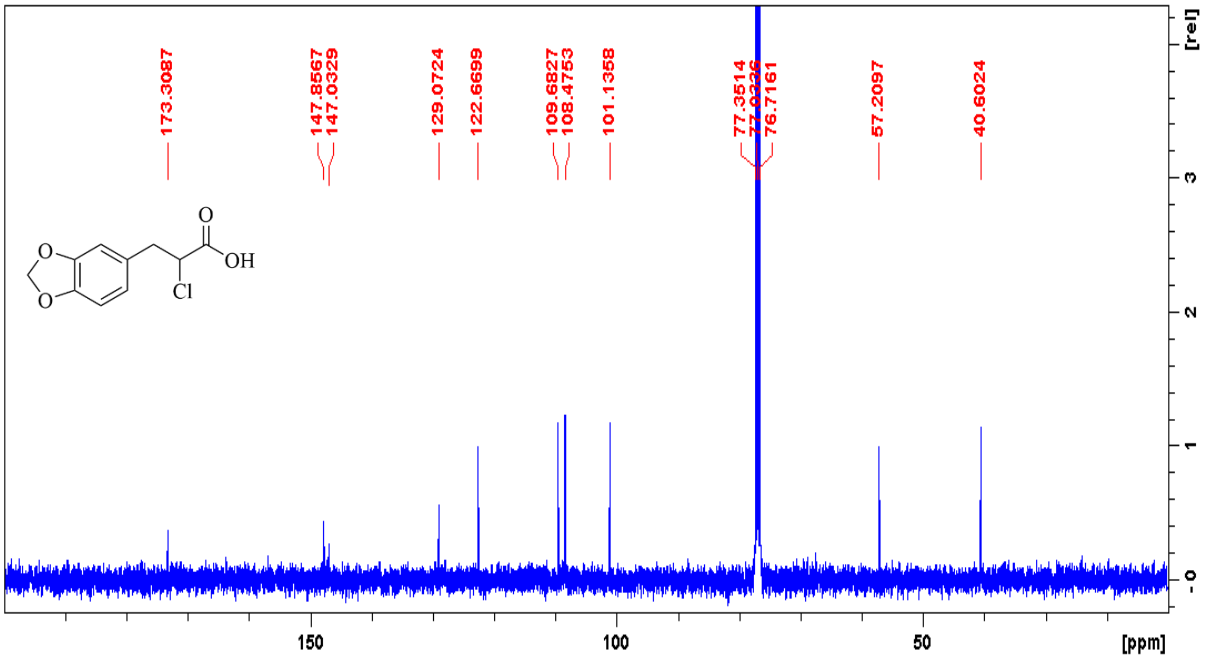


Figure S28: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **19**.

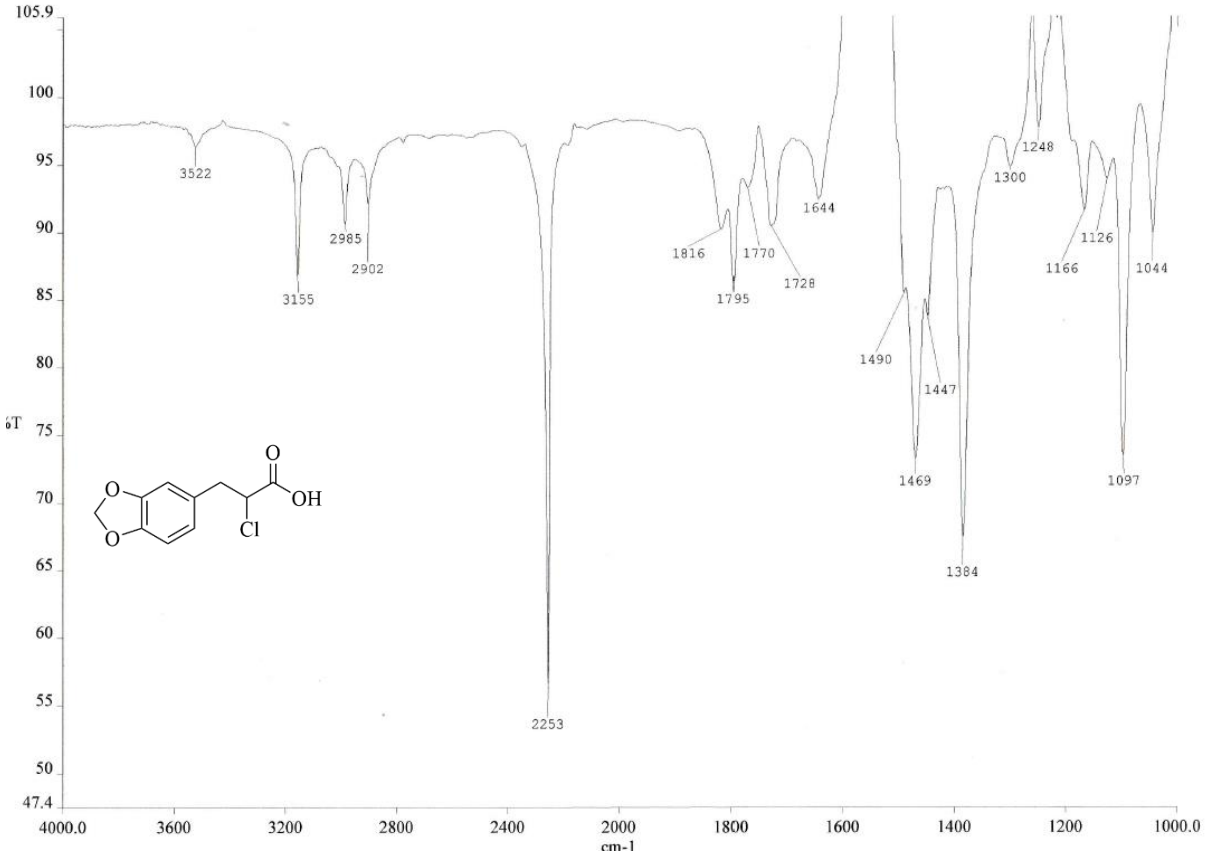


Figure S29: IR spectrum of compound **19**.

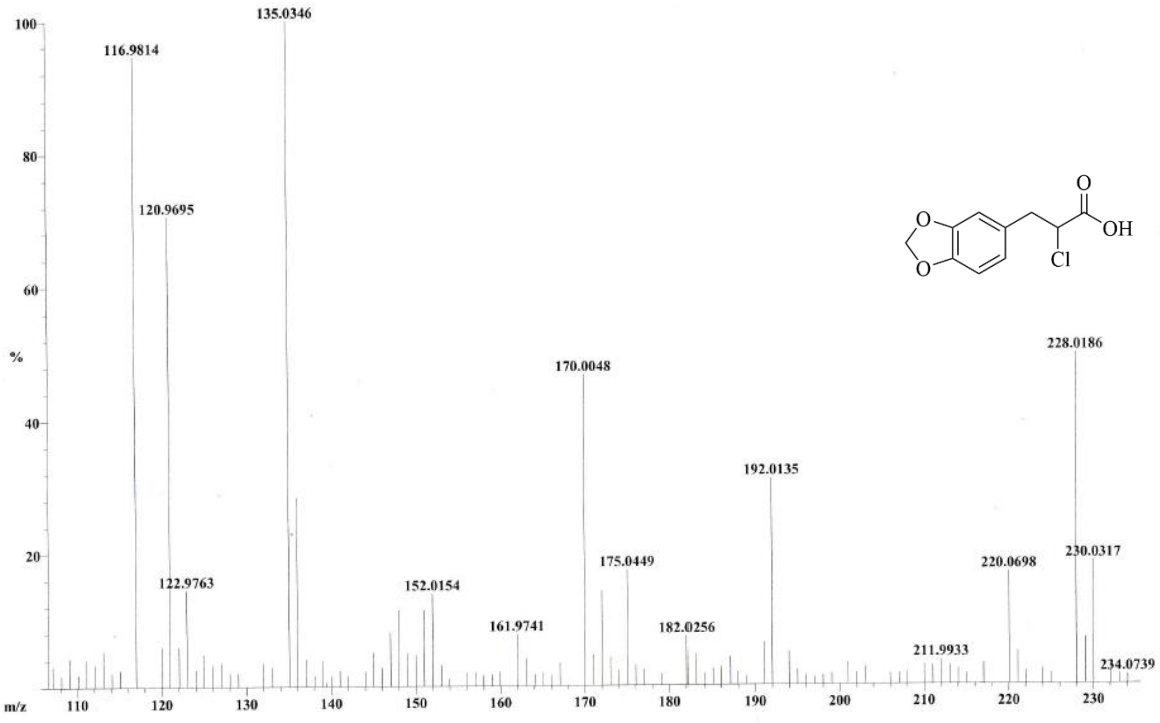


Figure S30: HRMS spectrum (EI) of compound **19**.

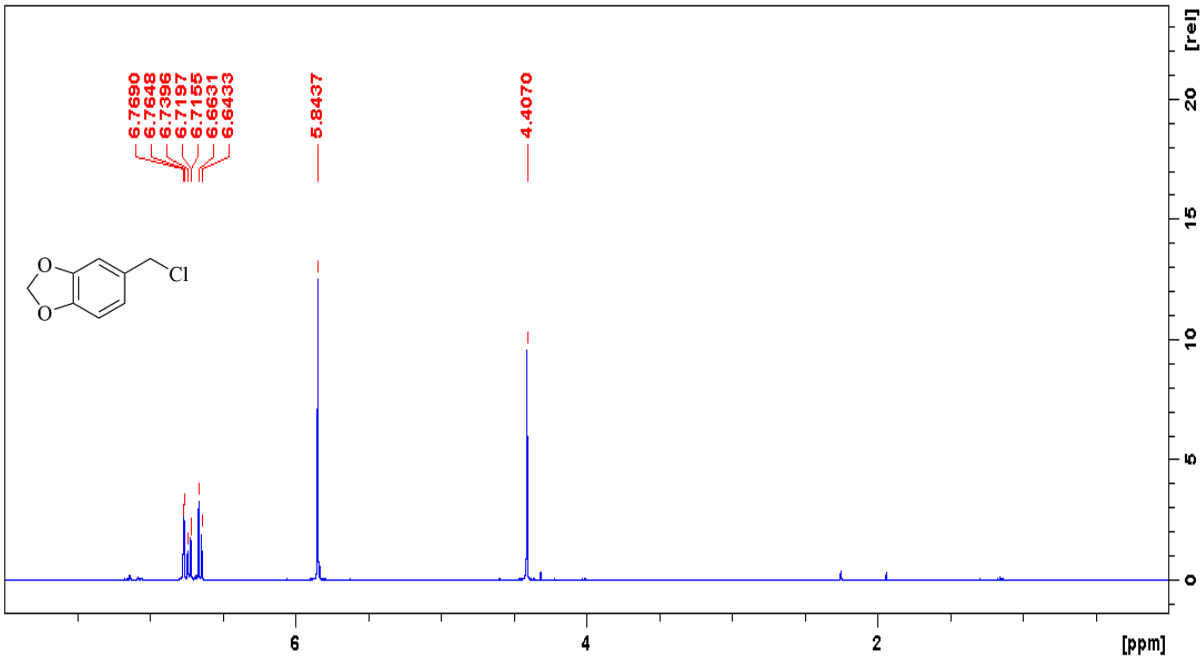


Figure S31: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **20**.

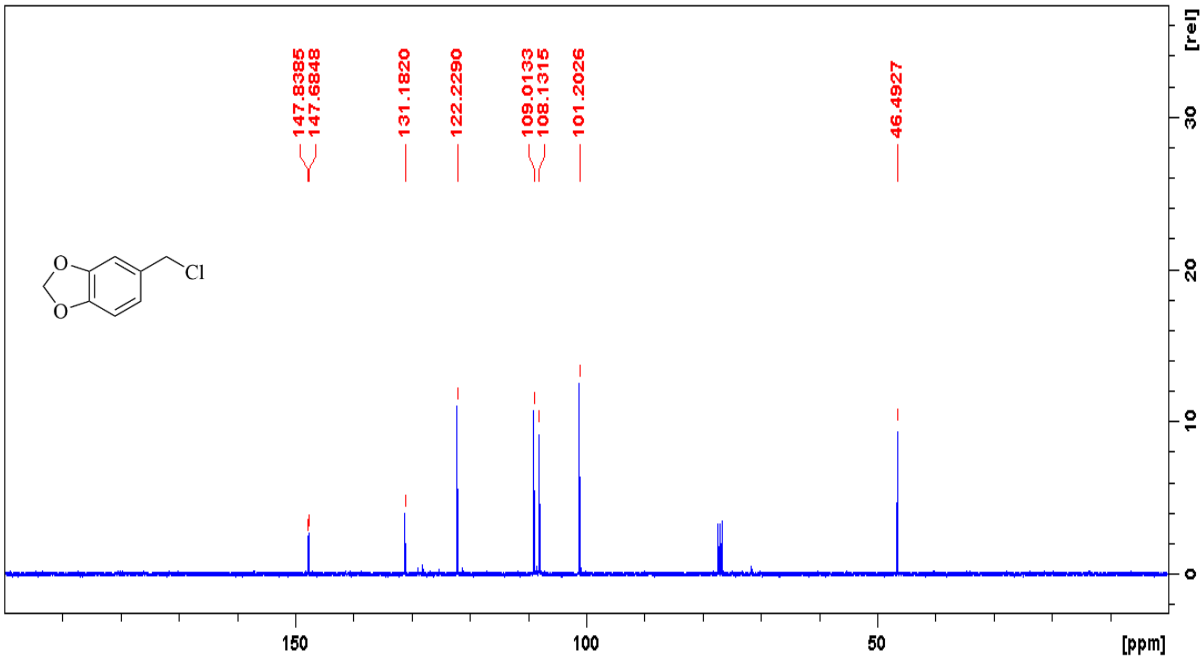


Figure S32: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **20**.

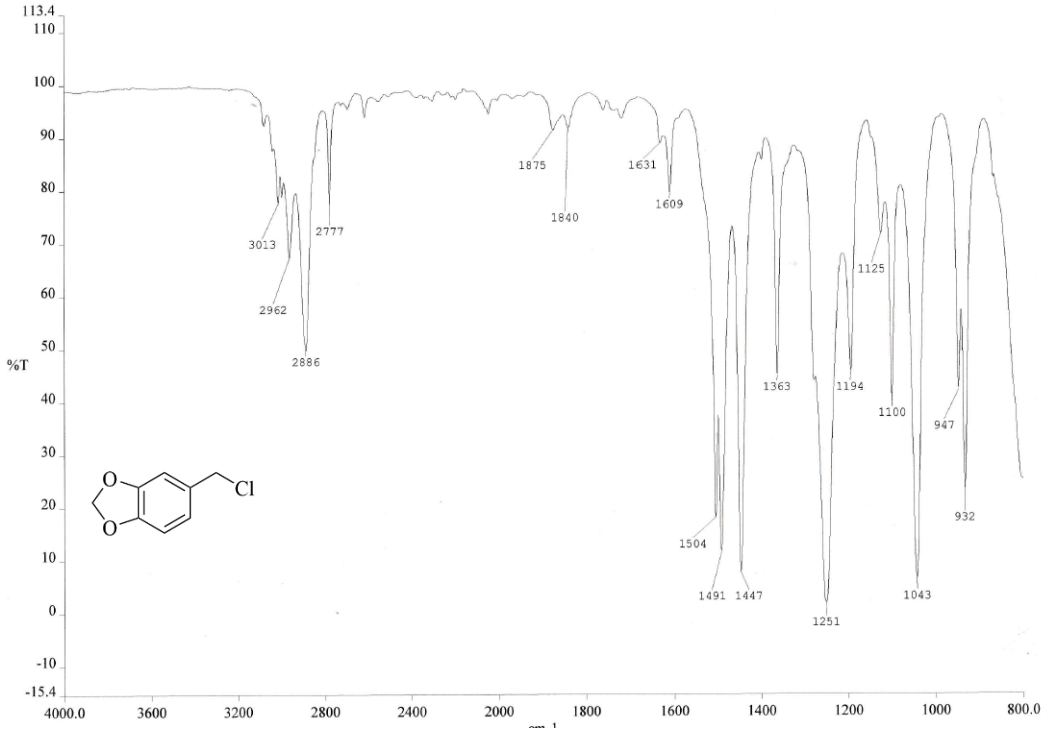


Figure S33: IR spectrum of compound **20**.

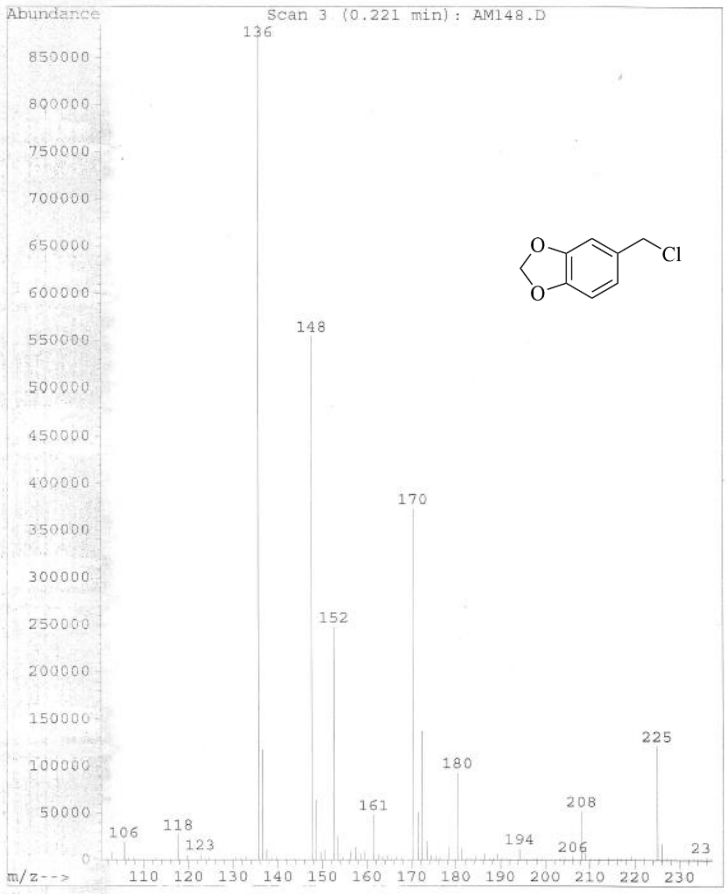


Figure S34: MS spectrum (positive CI, NH_3) of compound **20**.

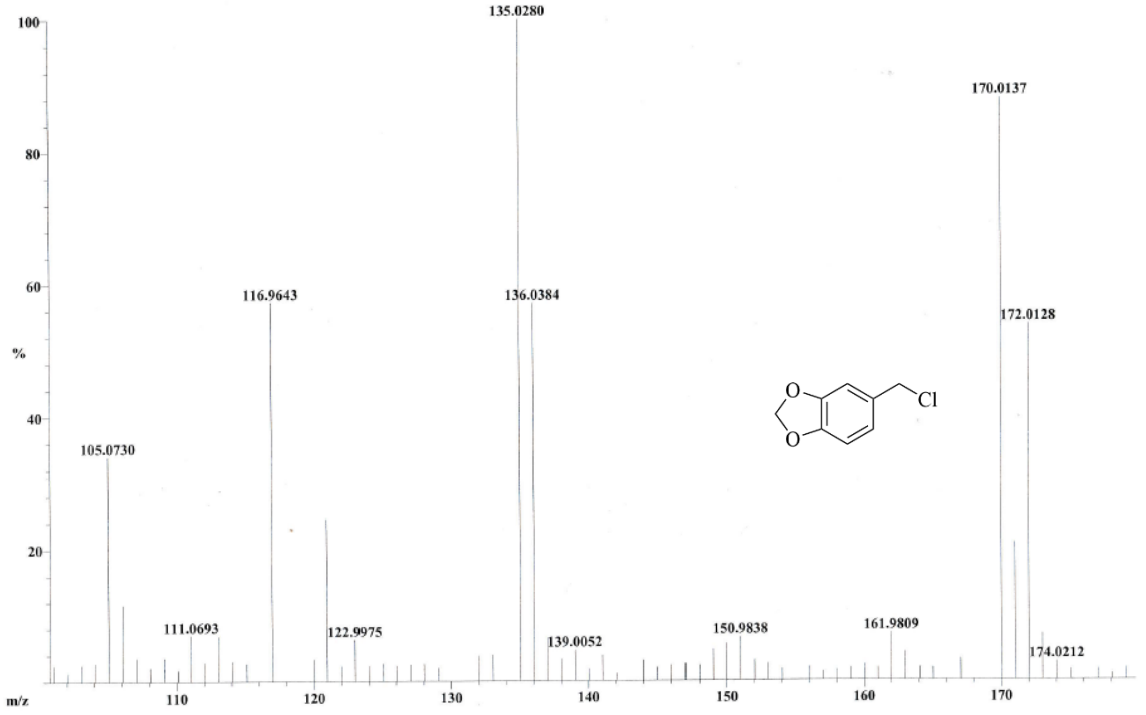


Figure S35: HRMS spectrum (EI) of compound **20**.

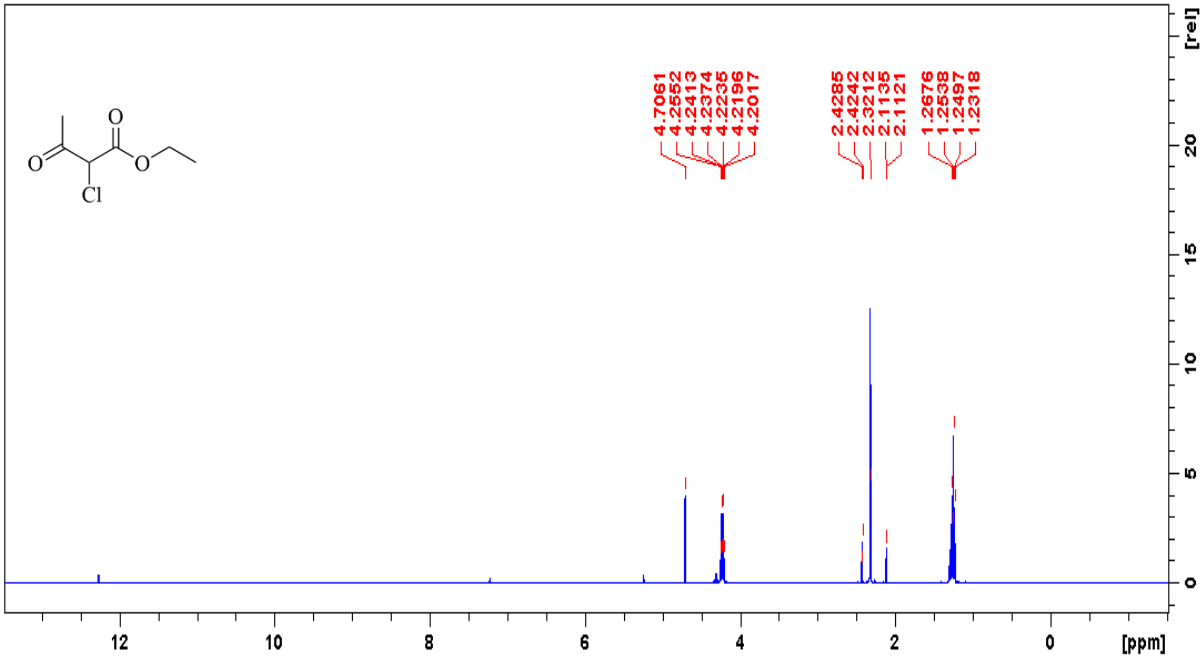


Figure S36: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **21**.

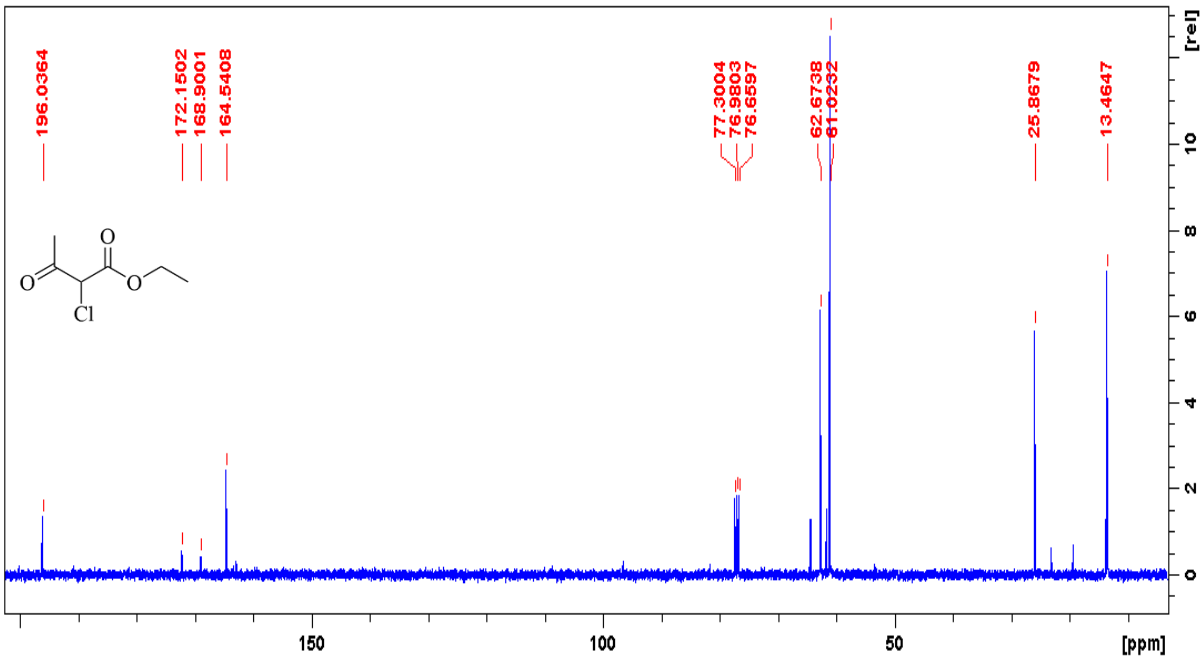


Figure S37: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **21**.

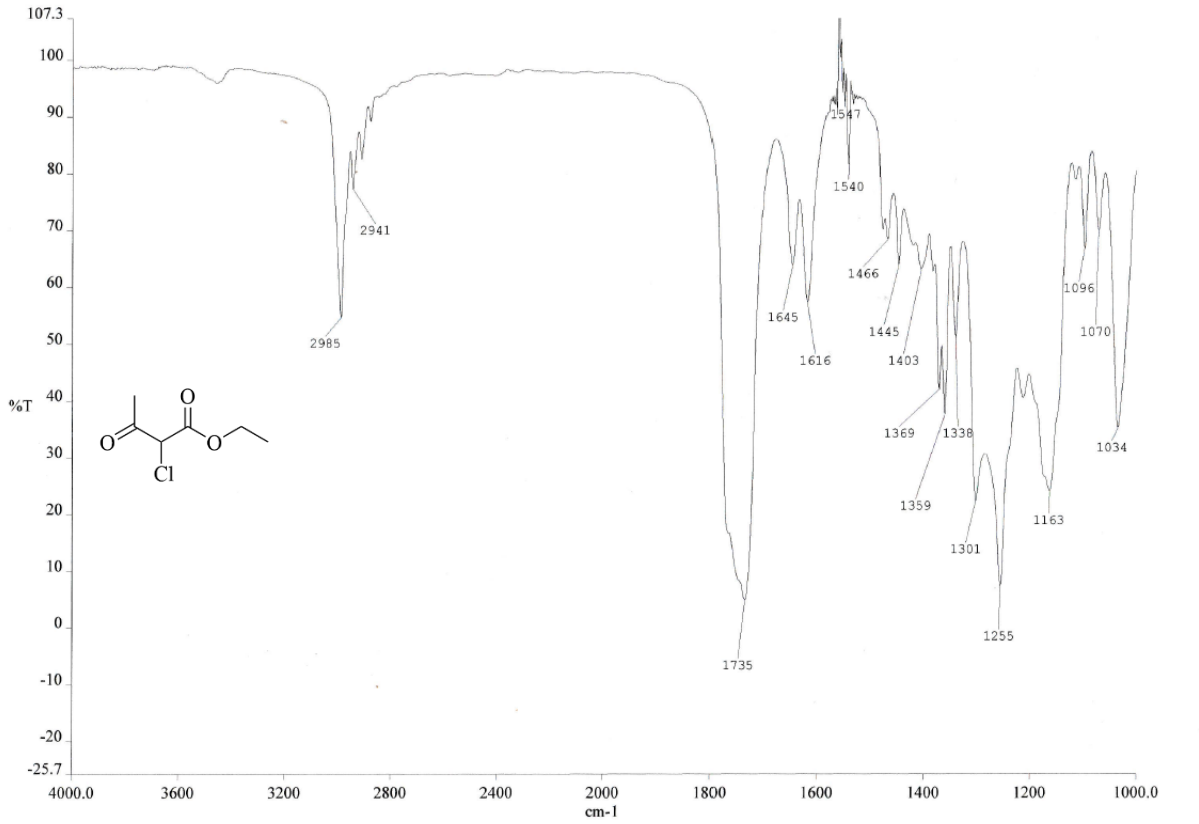


Figure S38: IR spectrum of compound **21**.

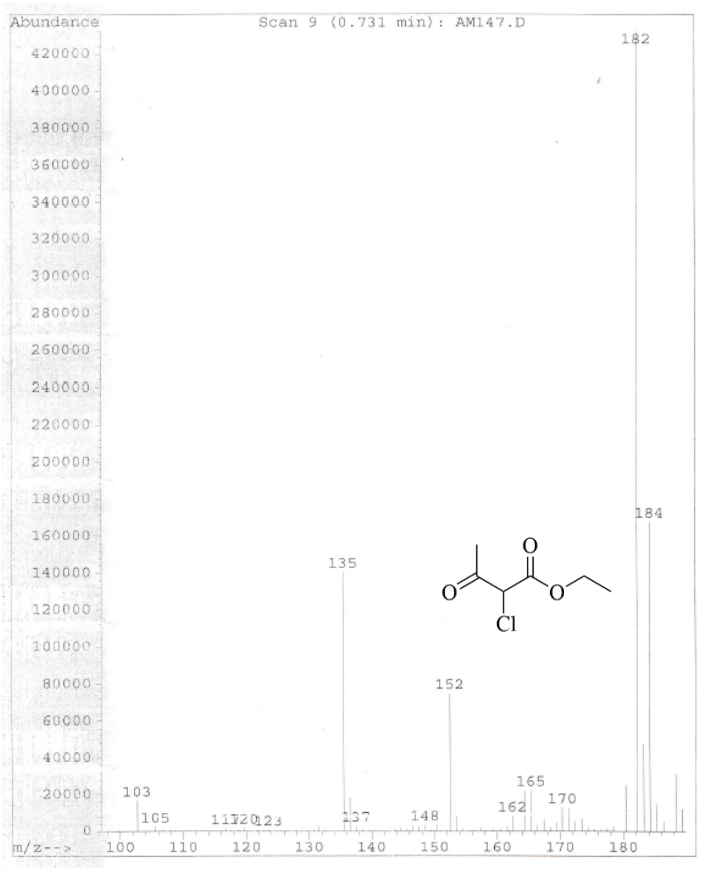


Figure S39:MS spectrum (positive CI, NH_3) of compound **21**.

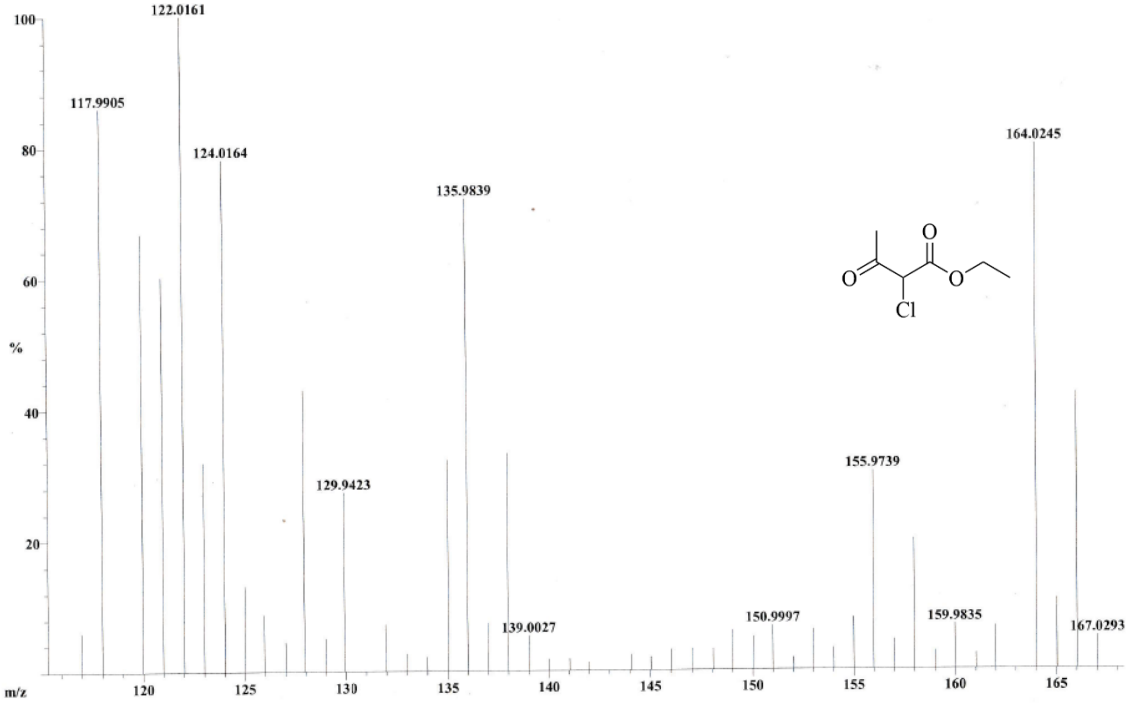


Figure S40: HRMS spectrum (EI) of compound **21**.

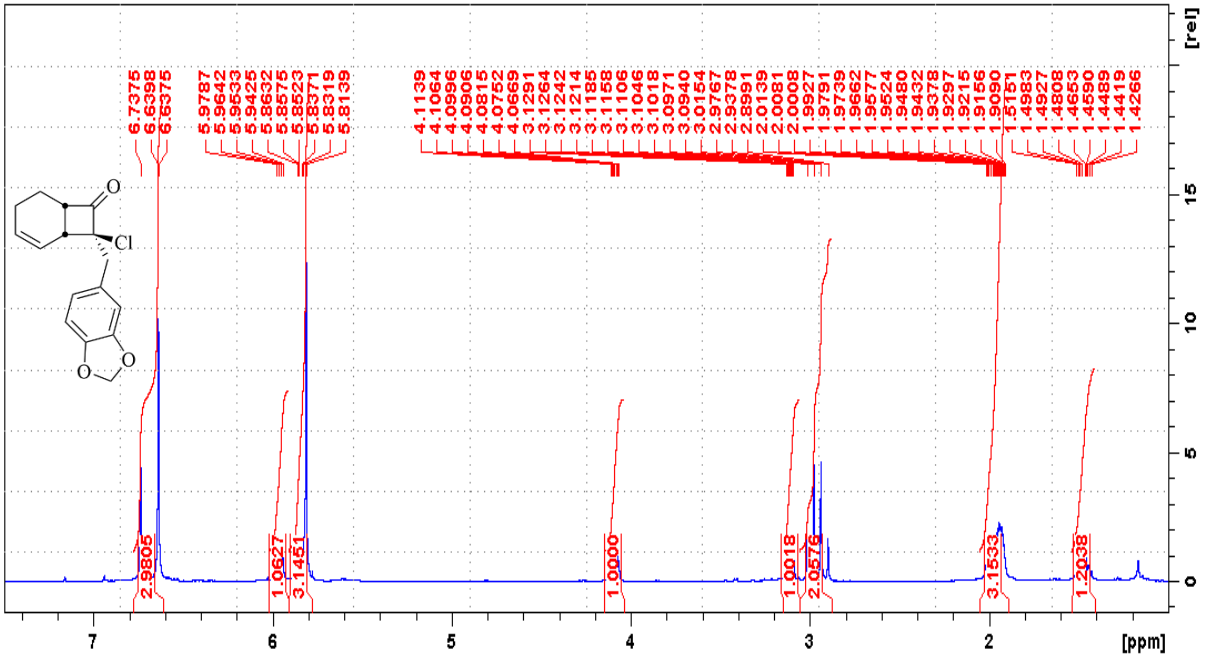


Figure S41: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **25**.

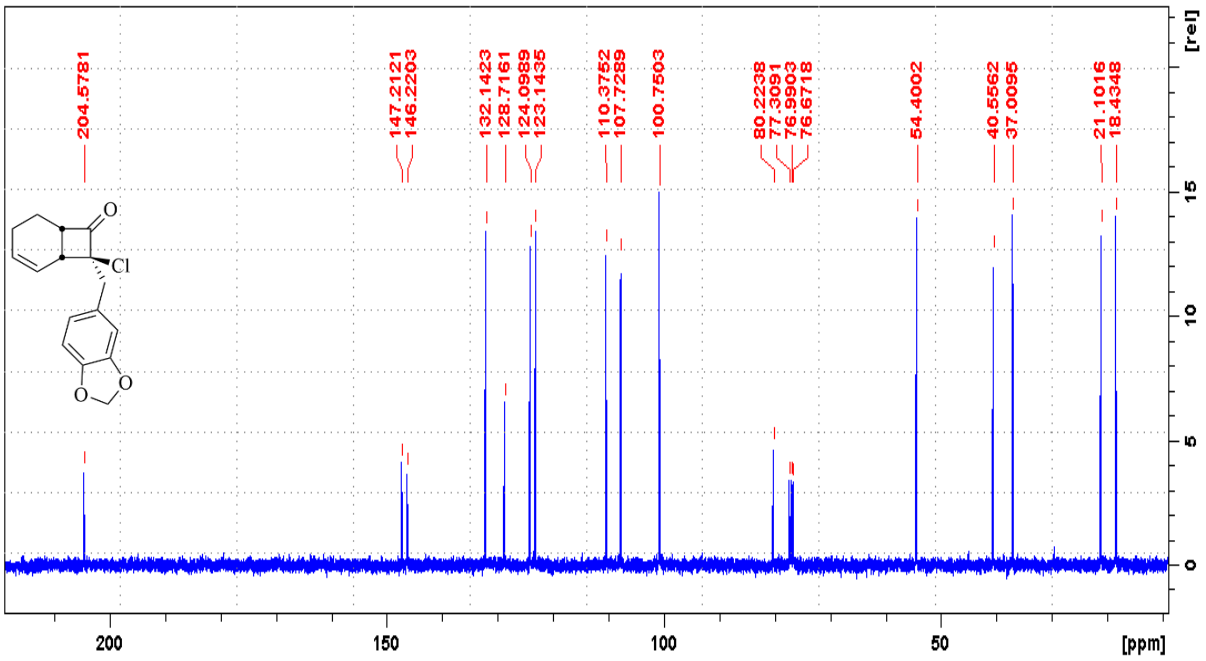


Figure S42: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **25**.

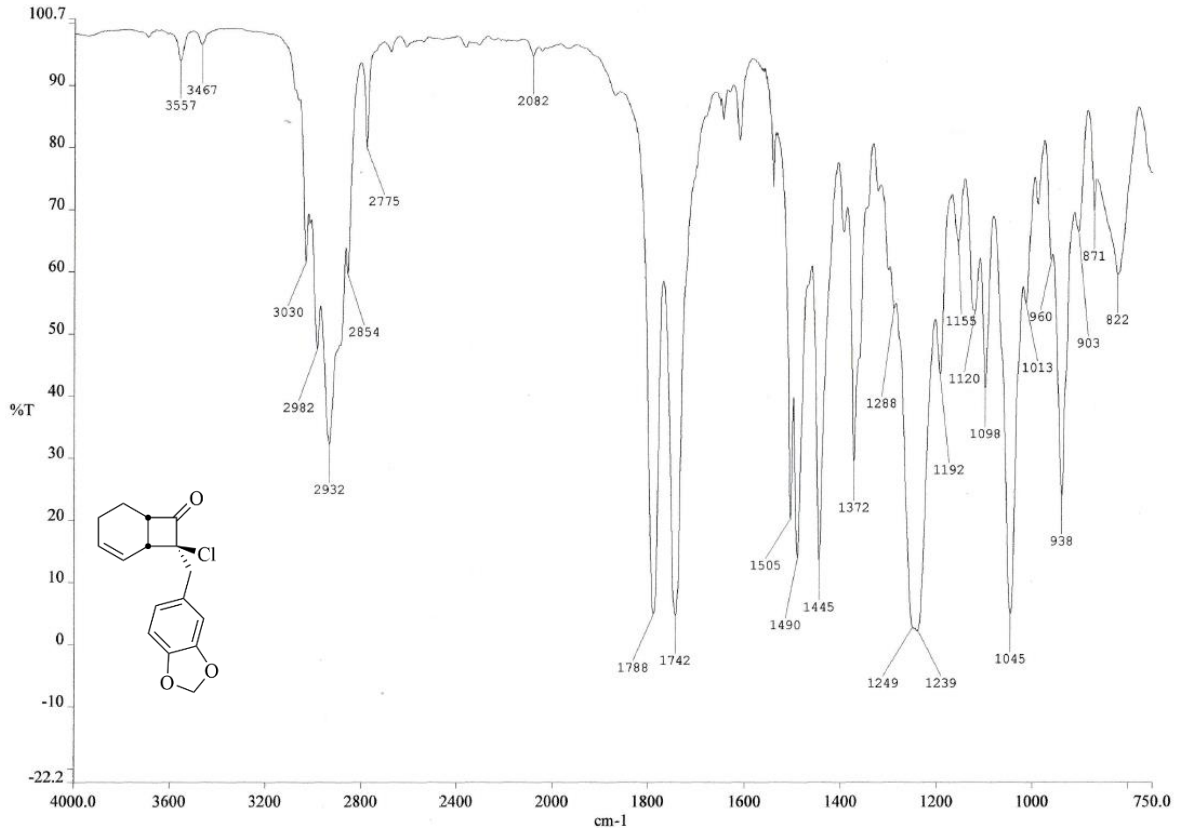


Figure S43: IR spectrum of compound **25**.

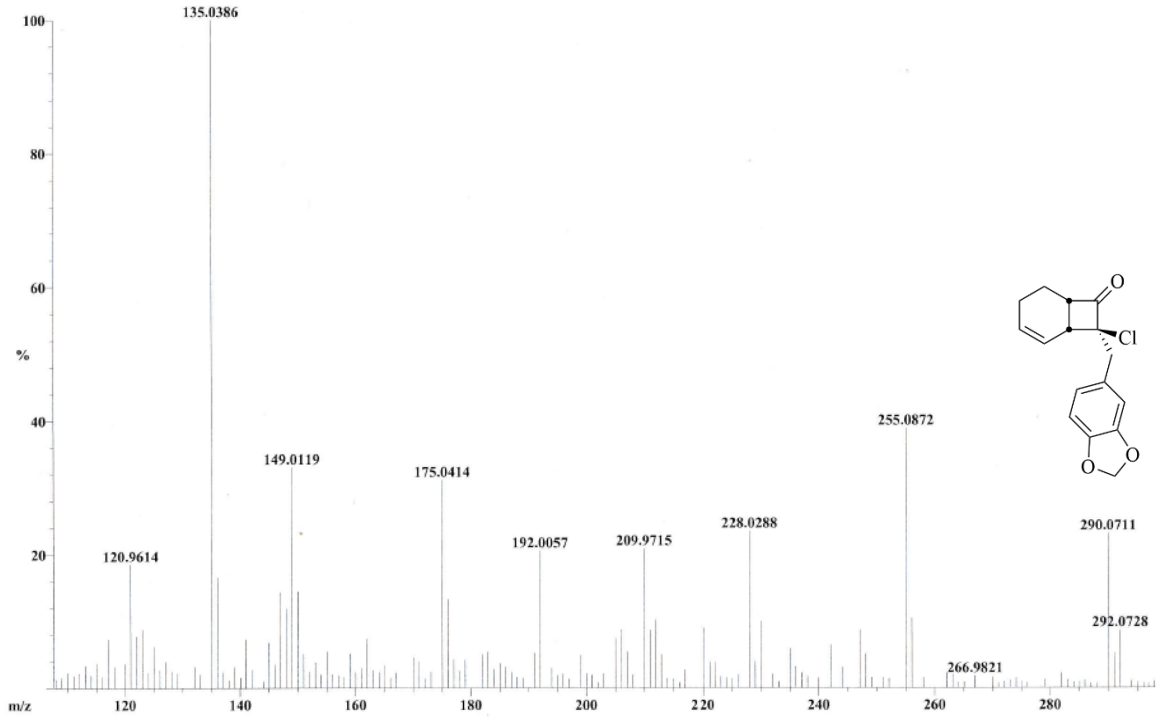


Figure S44: HRMS spectrum (EI) of compound **25**.

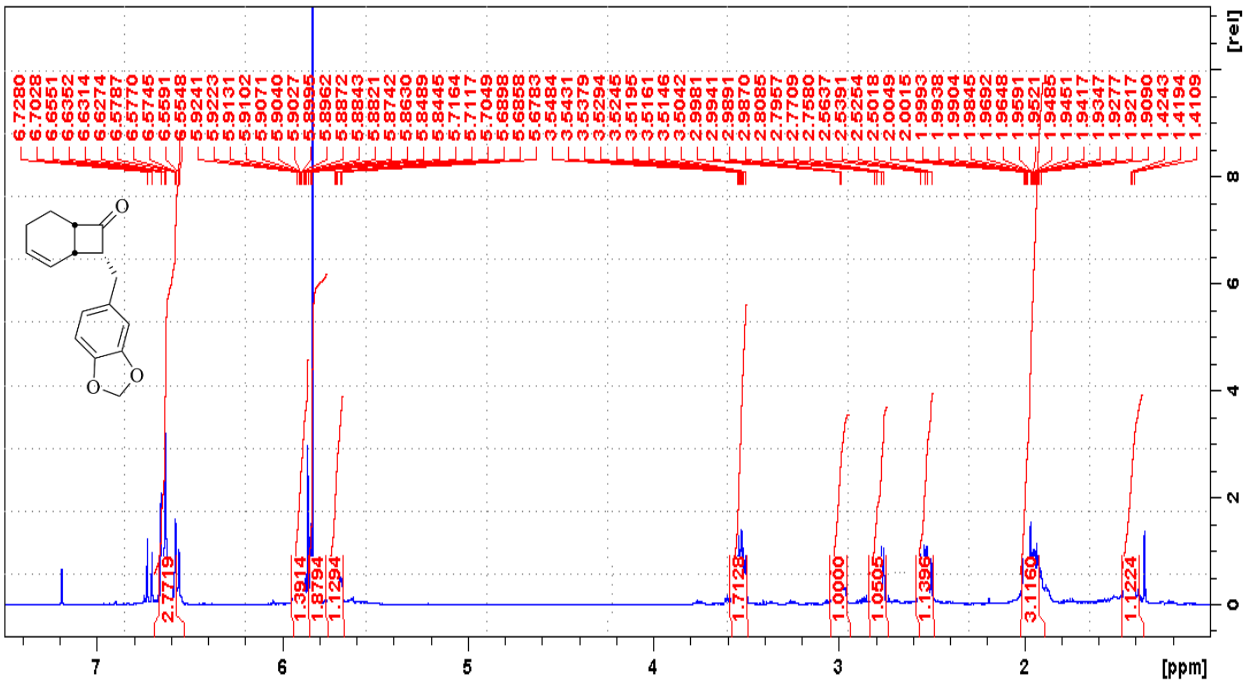


Figure S45: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **26**.

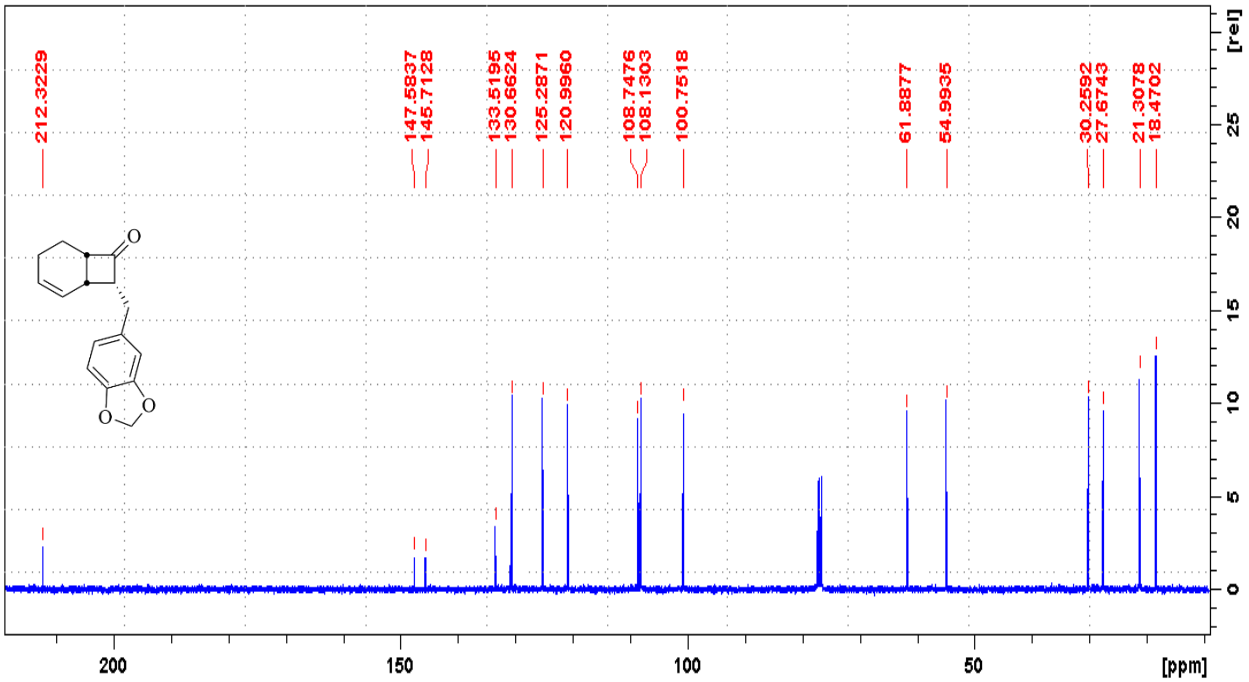


Figure S46: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **26**.

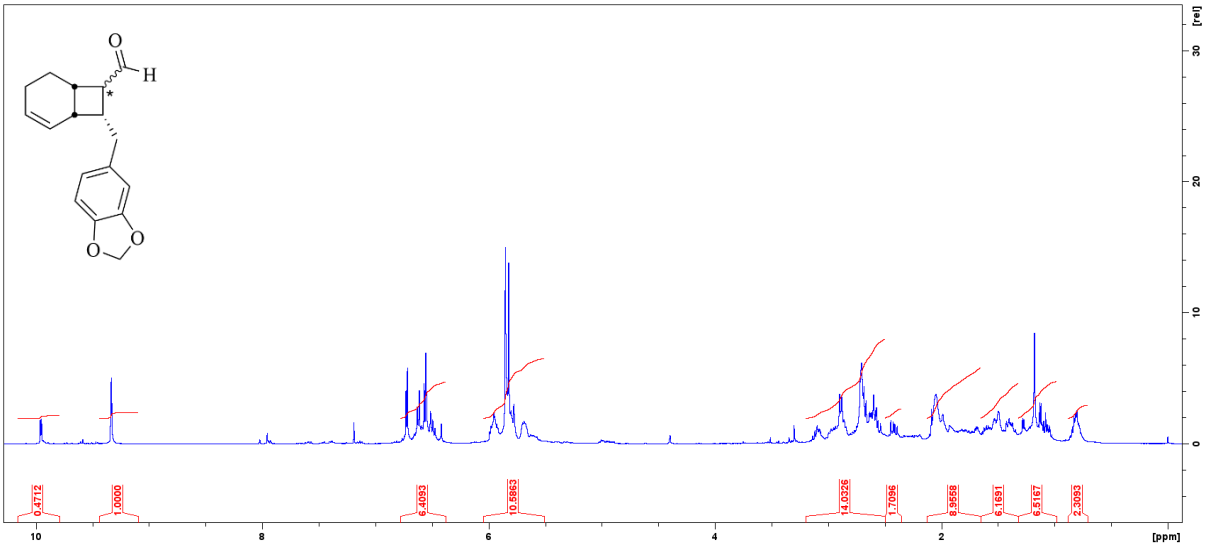


Figure S47: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **29**.

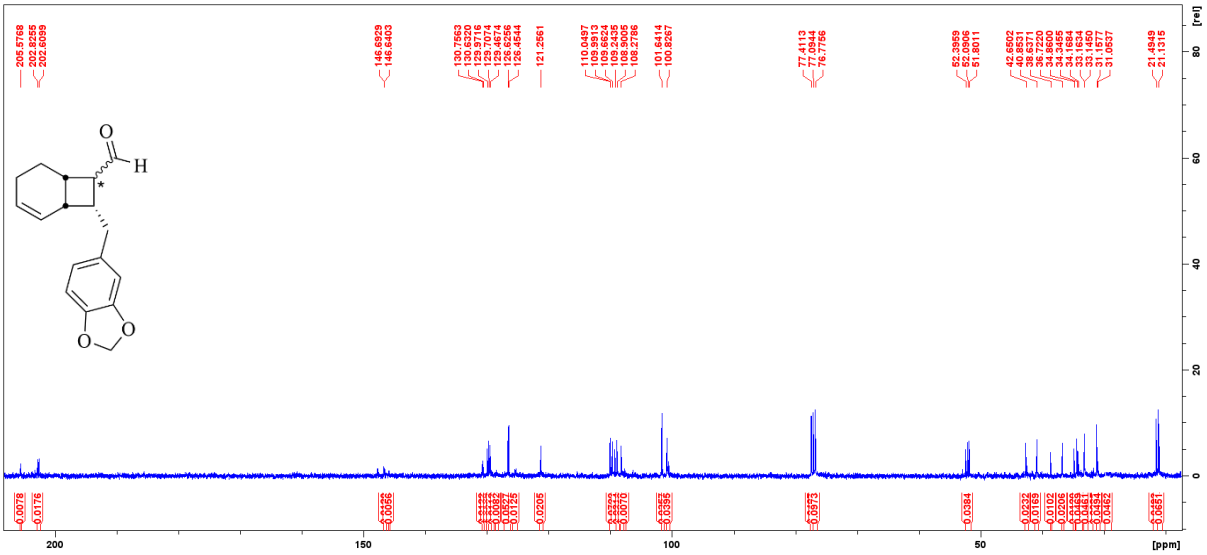


Figure S48: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **29**.

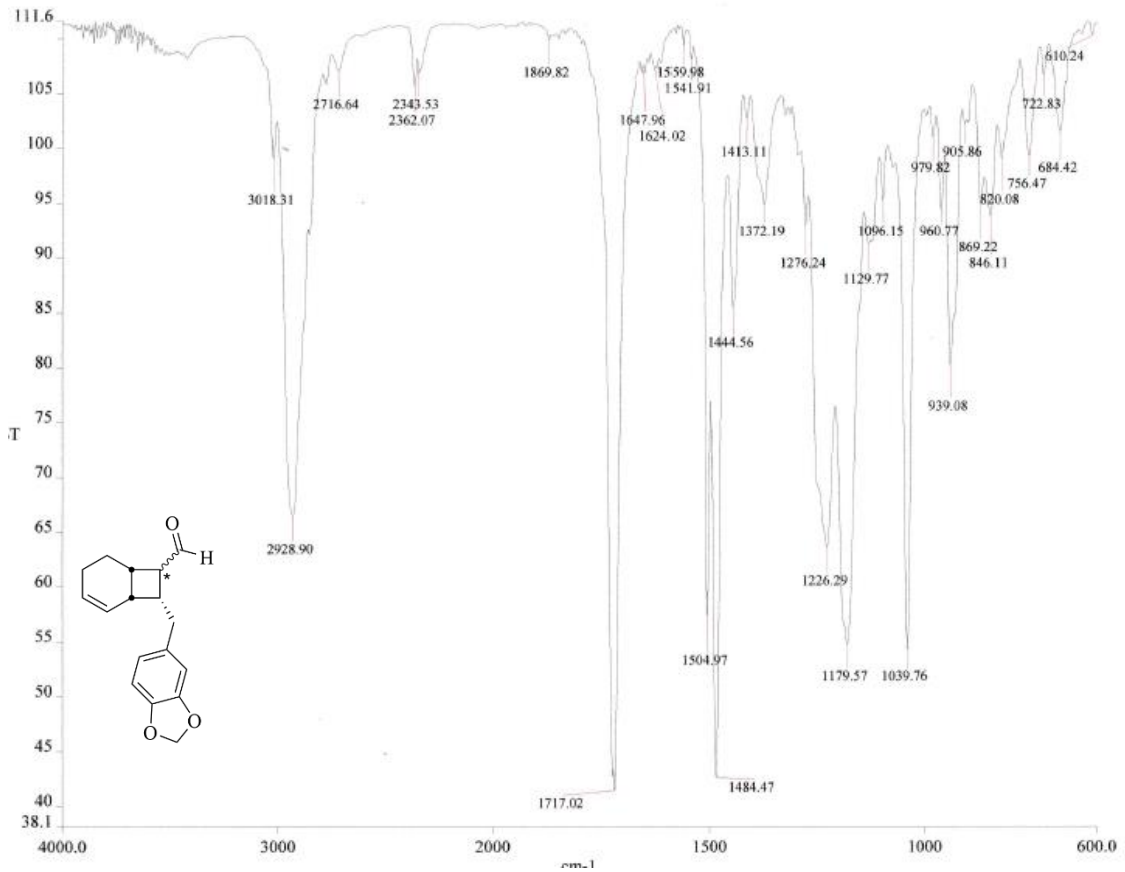


Figure S49: IR spectrum of compound **29**.

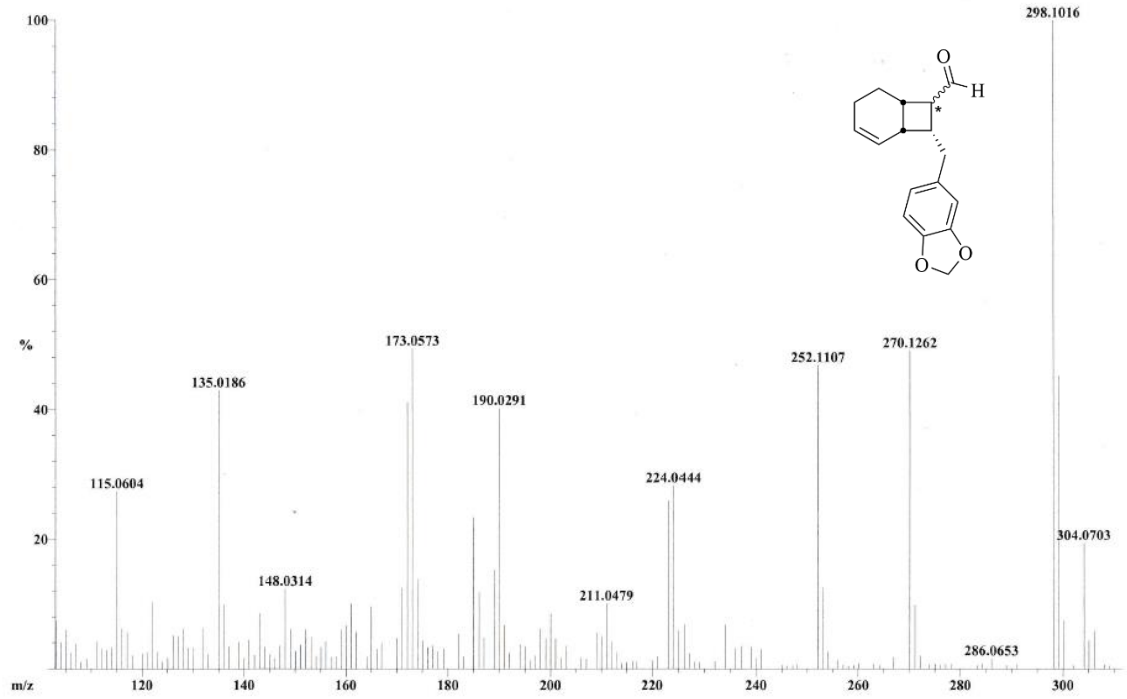


Figure S50: HRMS spectrum (EI) of compound **29**.

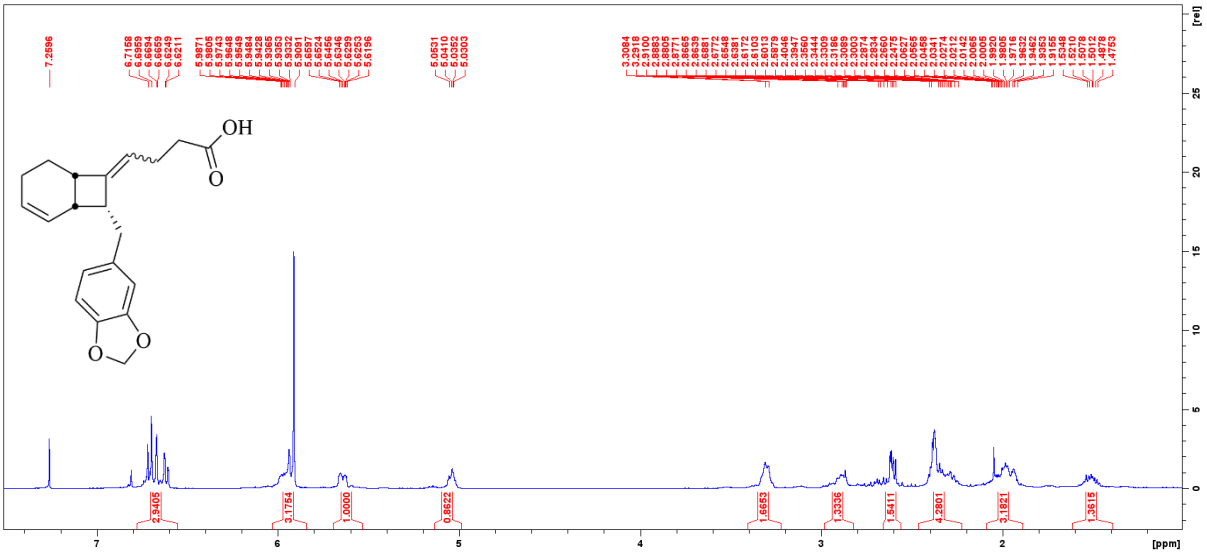


Figure S51: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **30**.

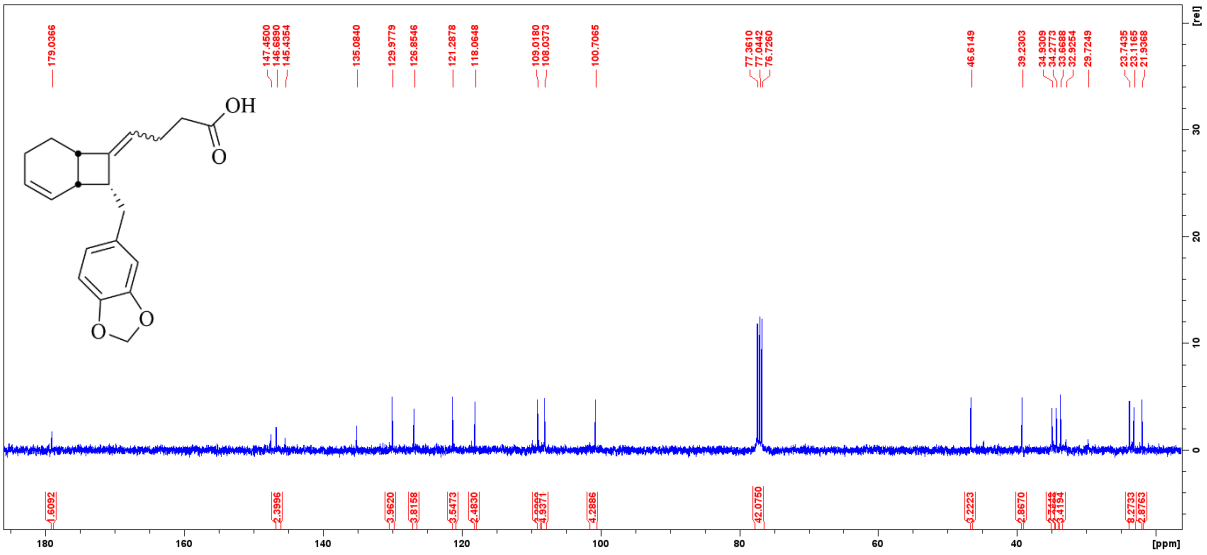


Figure S52: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **30**.

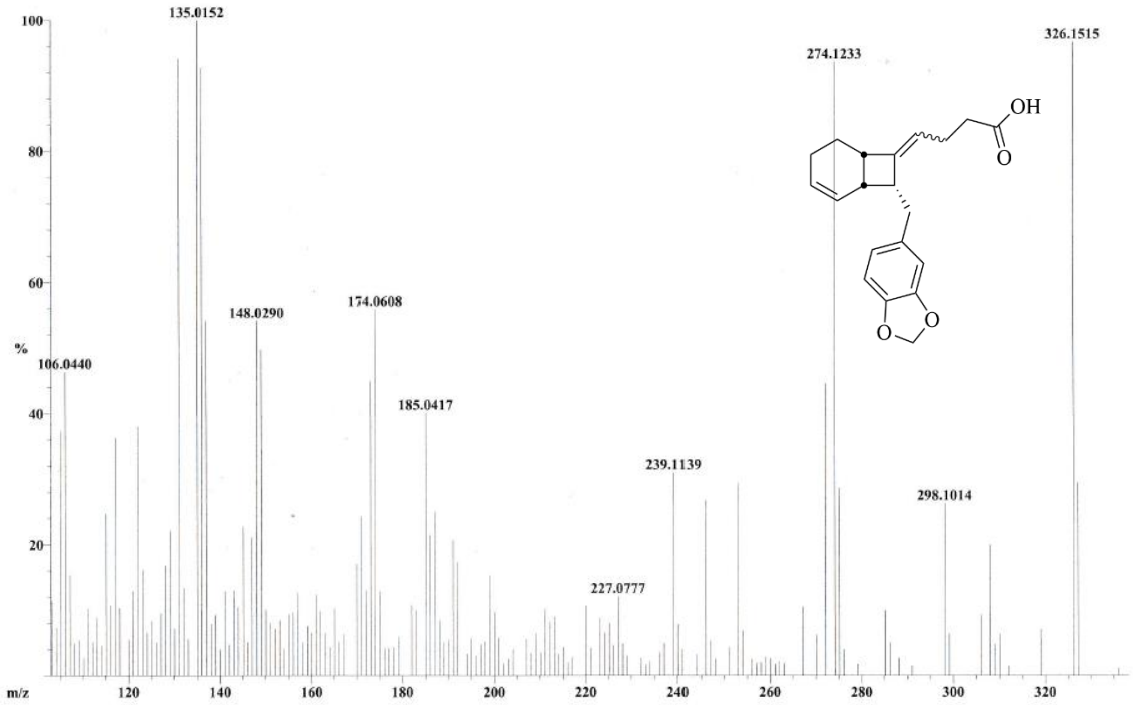


Figure S53: HRMS spectrum (EI) of compound **30**.

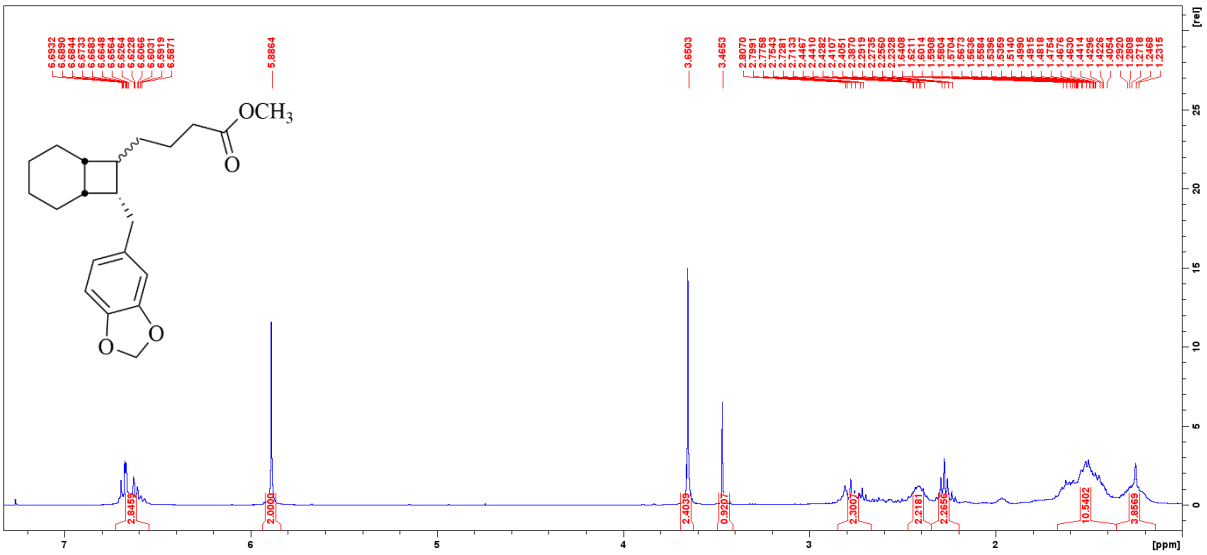


Figure S54: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **31**.

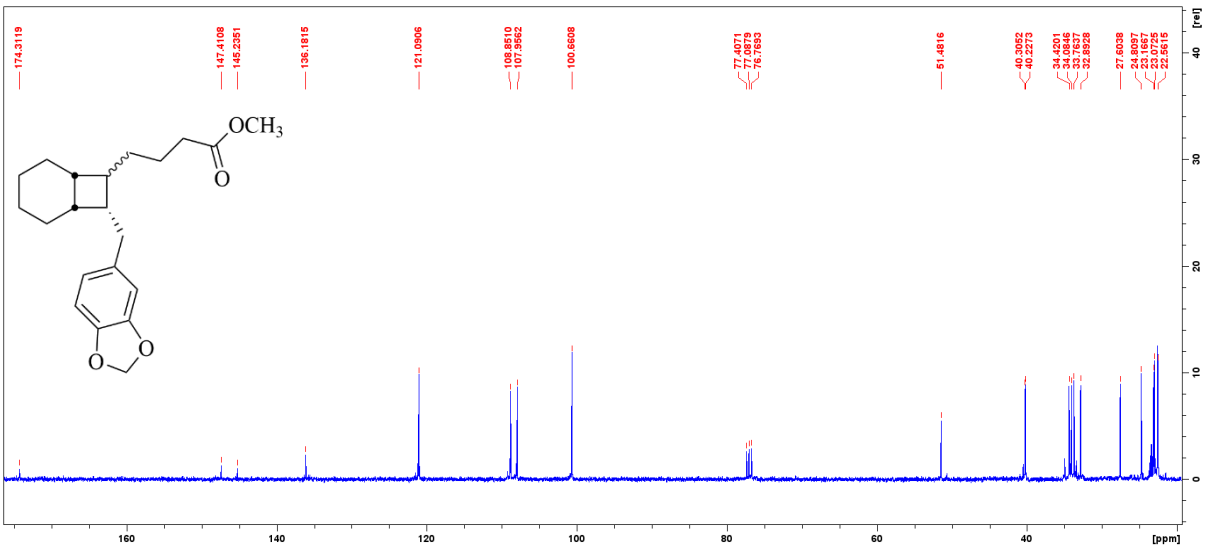


Figure S55: ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz) of compound **31**.

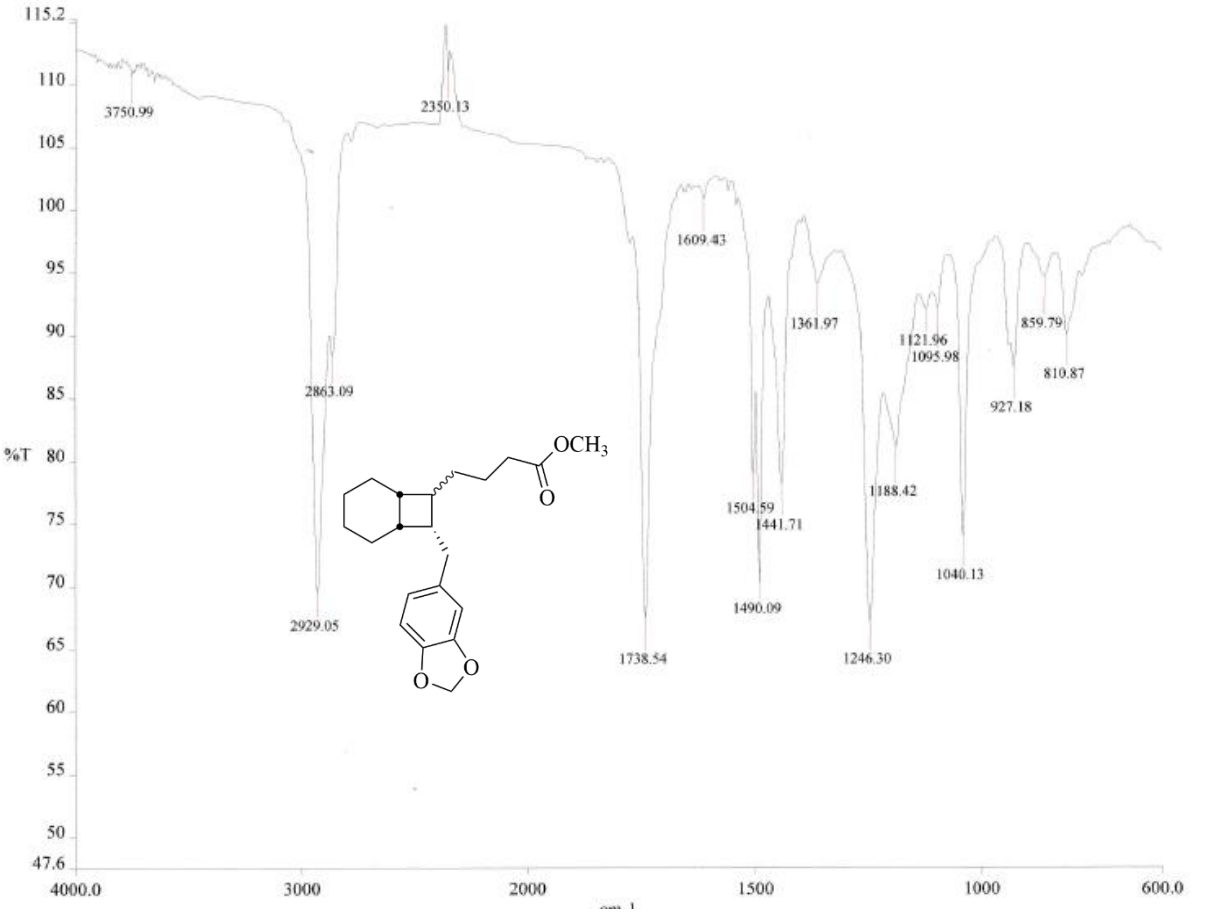


Figure S56: IR spectrum of compound **31**.