# Supporting Information

## Imidazolium and Pyridinium Ionic Liquids from Mandelic Acid Derivatives: Synthesis and Bacteria and Algae Toxicity Evaluation

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## Material and Methods

### Material

All chemicals were purchased at Sigma-Aldrich. Pyridine (99.8 %), bromoacetyl bromide (≥ 98 %), thionyl chloride (≥ 99 %), thionyl bromide (97 %) were used without further purification. 1-methylimidazole (99 %) was distilled before use and all organic solvents also dried before use. All NMR spectra were recorded in deuterated chloroform (99.8 % D), acetonitrile (99.8 % D) or dimethylsulfoxide (99.8 % D) on a Bruker 400 MHz or 600 MHz spectrometer (NMR spectra described in Supporting Information). MS data for reactive intermediates **11**, **13**, **14**, **16**, **17** and **18** could not be obtained. The ILs used in this study are: methyl 2-(3,4-methylenedioxyphenyl)-2-pyridinium acetate, bromide salt **(**IL **1)**, methyl 2-(3,4-methylenedioxyphenyl)-2-(3-methylimidazolium)acetate, chloride salt **(**IL **2)**, butyl 2-(3,4-methylenedioxyphenyl)-2-pyridinium acetate, bromide salt **(**IL **3)**, butyl 2-(3,4-methylenedioxyphenyl)-2-imidazolium acetate, bromide salt **(**IL **4)**, methyl 2-(3,4-dimethoxyphenyl)-2-pyridinium acetate, chloride salt **(**IL **5)**, methyl 2-(3,4-methylenedioxyphenyl)-2-(2-pyridiniumacetoxy)acetate, bromide salt **(**IL **6)**, butyl-2-(3,4-methylenedioxyphenyl)-2-(2-pyridiniumacetoxy)acetate, bromide salt **(**IL **7)**, butyl-2-(3,4-methylenedioxyphenyl)-2-[2-(3-methylimidazolium)acetoxy]acetate, bromide salt **(**IL **8).** All the ILs synthesized in this work and also all the intermediates formed were presented in Tables 1 and 2.

### Methods

#### *Synthesis and purification of ILs*

**Preparation of methyl 2-(3,4-methylenedioxyphenyl)-2-pyridinium acetate, bromide salt (IL 1):**

To a stirred solution of methyl 2-bromo-2-(3,4-methylenedioxyphenyl) acetate **11** (1.946 g, 7.13 mmol) in diethyl ether (20 mL) at -15 $^{o}$C under a $N_2$ atmosphere was added pyridine (0.69 mL, 8.55 mmol) dropwise and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred overnight, then refluxed for 8 h and stirred at room temperature for another 12 h. The precipitate, was collected by filtration, washed with diethyl ether (2 x 5 mL) and dried under reduced pressure to give the title compound **1** as a white powder in 79 % yield (1.969 g, 5.59 mmol).

m.p.: 146-147 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, δ): 9.50-9.49 (m, 2H, ArC*H*), 8.65-8.61 (m, 1H, ArC*H*), 8.27 (s, 1H, NC*H*), 8.13-8.09 (m, 2H, ArC*H*), 7.19-7.17 (m, 2H, ArC*H*), 6.81 (d, *J* = 8.4 Hz, 1H, ArC*H*), 5.97 (d, part A of an AB system, *J* = 1.0 Hz, 1H, OC$H_2$O), 5.95 (d, part B of an AB system, *J* = 1.0 Hz, 1H, OC$H_2$O), 3.81 (s, 3H, OC$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 167.73 (*C*OO), 149.96 (Ar*C*), 148.96 (Ar*C*), 147.12 (Ar*C*), 144.84 (2Ar*C*), 127.95 (2Ar*C*), 124.39 (Ar*C*), 124.25 (Ar*C*H), 109.87 (Ar*C*H), 109.46 (Ar*C*H), 102.18 (O*C*$H_2$O), 73.05 (N*C*H), 54.34 (O*C*$H_3$)**.**IR (neat) $\nu_{max}$: 3038, 3016, 2854, 2830, 1741, 1627, 1486, 1441, 1396, 1239, 1215, 1025, 1003, 915, 760 cm$^{-1}$ .ESI-HRMS calc. for $C_{15}H_{14}NO_4$ [M-Br]$^{+}$: 272.0923, found: 272.0919

**Preparation of methyl 2-(3,4-methylenedioxyphenyl)-2-(3-methylimidazolium)acetate, chloride salt (IL 2):**

To a stirred solution of methyl 2-chloro-2-(3,4-methylenedioxyphenyl) acetate **14** (2.134 g, 9.34 mmol) in diethyl ether (20 mL) at −15 $^{o}$C under a $N_2$ atmosphere was added 1-methylimidazole (0.70 mL, 8.78 mmol) dropwise and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred for 48 h, then refluxed for 4 h and stirred at room temperature for another 24 h. The precipitate was collected by filtration, washed with diethyl ether (5 × 10 mL) and dried under reduced pressure to give the title compound **2** as a white powder in 97 % yield (2.816 g, 9.07 mmol).

m.p.: 124-125 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, δ): 10.54 (s, 1H, ArC*H*), 7.65 (s, 1H, ArC*H*), 7.52 (s, 1H, ArC*H*), 7.34 (s, 1H, NC*H*), 7.03-7.00 (m, 2H, ArC*H*), 6.72 (d, *J* = 8.0 Hz, 1H, ArC*H*), 5.89 (d, *J* = 1.2 Hz, 2H, OC$H_2$O), 3.98 (s, 3H, NC$H_3$), 3.70 (s, 3H, OC$H_3$).$^{13}$C NMR (100 MHz, $CDCl_3$, δ): 168.45 (*C*OO), 149.40 (Ar*C*), 148.78 (Ar*C*), 137.99 (Ar*C*), 125.97 (Ar*C*), 123.35 (Ar*C*), 123.22 (Ar*C*), 121.85 (Ar*C*H), 109.35 (Ar*C*H), 108.97 (Ar*C*H), 102.05 (O*C*$H_2$O), 63.73 (N*C*H), 53.89 (O*C*$H_3$), 36.96 (N*C*$H_3$).IR (neat) $\nu_{max}$: 3408, 3013, 2951, 1755, 1742, 1492, 1449, 1257, 1238, 1167, 1035 cm$^{-1}$. ESI-HRMS calc. for $C_{14}H_{15}N_2O_4$ [M-Cl]$^{+}$: 275.1032, found: 275.1019.

**Preparation of butyl 2-(3,4-methylenedioxyphenyl)-2-pyridinium acetate, bromide salt (IL 3)**

To a stirred solution of butyl-2-bromo-2-(3,4-methylenedioxyphenyl) acetate **17** (2.06 g, 6.54 mmol) in diethyl ether (20 mL) at RT was added pyridine (0.53 mL, 6.54 mmol) dropwise and the reaction mixture was stirred at room temperature for 12 h. The

precipitate was collected by filtration, washed with diethyl ether (2 × 20 mL) and dried under high vacuum to give the title compound **3** as a white powder in 90 % yield (1.33 g, 3.37 mmol).

m.p.: 123-125 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, δ): 9.44 (m, 2H, ArC*H*), 8.61 (m, 1H, ArC*H*), 8.11 (s, 1H, NC*H*), 8.10 (m, 2H, ArC*H*), 7.18 (d, *J* = 1.6 Hz, 1H, ArC*H*), 7.15 (dd, *J* = 8.0, 1.6 Hz, 1H, ArC*H*), 6.80 (d, 1H, *J* = 8.0 Hz, ArC*H*), 5.96 (d, part A of an AB system, *J* = 4.0 Hz, 1H, OC$H_2$O), 5.95 (d, part B of an AB system, *J* = 4.0 Hz, 1H, OC$H_2$O), 4.26 (dt, *J* = 10.8, 6.8 Hz, 1H, C$H_2$), 4.16 (dt, *J* = 10.8, 6.8 Hz, 1H, C$H_2$), 1.57 (tt, *J* = 7.2, 6.8, 2H, C$H_2$), 1.23 (tq, *J* = 7.6, 7.2 Hz, 2H, C$H_2$), 0.81 (t, *J* = 7.6 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 167.32 (*C*OO), 149.86 (Ar*C*), 148.90 (Ar*C*), 146.74 (Ar*C*H), 144.82 (2Ar*C*H), 127.94 (2Ar*C*H), 124.26 (Ar*C*), 124.24 (Ar*C*H), 109.86 (Ar*C*H), 109.31 (Ar*C*H), 102.06 (O*C*$H_2$O), 73.17 (N*C*H), 67.62 (O*C*$H_2$), 30.13 (*C*$H_2$), 18.83 (*C*$H_2$), 13.53 (*C*$H_3$).IR (neat) $\nu_{max}$: 3023, 2960, 1736, 1630, 1498, 1479, 1447, 1369, 1304, 1261, 1239, 1210, 1151, 1108, 1028, 922, 809, 757 cm$^{-1}$. ESI-HRMS calc. for $C_{18}H_{20}NO_4$ [M-Br]$^{+}$: 314.1387, found: 314.1392.

**Preparation of butyl 2-(3,4-methylenedioxyphenyl)-2-imidazolium acetate, bromide salt (IL 4)**

To a stirred solution of butyl-2-bromo-2-(3,4-methylenedioxyphenyl) acetate **17** (2.24 g, 7.11 mmol) in diethyl ether (25 mL) at RT was added 1-methylimidazole (0.57 mL, 7.11 mmol) dropwise and the reaction mixture was stirred for 12 h. The viscous ionic liquid was washed with diethyl ether (5 × 20 mL) and dried under high vacuum to give the title compound **4** as a brown oil in 58 % yield (1.65 g, 4.15 mmol).

$T_g$ = −3.3 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, δ): 10.18 (s, 1H, ArC*H*), 7.66 (t, *J* = 1.6 Hz, 1H, ArC*H*), 7.46 (t, *J* = 1.6 Hz, 1H, ArC*H*), 7.05 (s, 1H, NC*H*), 6.97 (dd, *J* = 8.0, 1.6 Hz, 1H, ArC*H*), 6.96 (d, *J* = 1.8 Hz, 1H, ArC*H*), 6.69 (d, *J* = 8.0 Hz, 1H, ArC*H*), 5.87 (d, part A of an AB system, *J* = 3.6 Hz, 1H, OC$H_2$O), 5.86 (d, part B of an AB system, *J* = 3.6 Hz, 1H, OC$H_2$O), 4.12 (dt, *J* = 10.8, 6.8 Hz, 1H, C$H_2$), 4.05 (dt, *J* = 10.8, 6.8 Hz, 1H, C$H_2$), 3.97 (s, 3H, C$H_3$), 1.46 (tt, *J* = 7.2, 6.8, 2H, C$H_2$), 1.13 (tq, *J* = 7.6, 7.2 Hz, 2H, C$H_2$), 0.73 (t, *J* = 7.6 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 167.73 (*C*OO), 149.31 (Ar*C*), 148.67 (Ar*C*), 137.52 (Ar*C*), 125.63 (Ar*C*), 123.05 (Ar*C*), 123.01 (Ar*C*H), 121.76 (Ar*C*), 109.20 (Ar*C*H), 108.78 (Ar*C*H), 101.92 (O*C*$H_2$O), 67.10 (O*C*$H_2$), 63.76 (N*C*H), 36.93 (N*C*$H_3$), 30.22 (*C*$H_2$), 18.89 (*C*$H_2$), 13.60 (*C*$H_3$).IR (neat) $\nu_{max}$: 3074, 2960, 1741, 1628, 1577, 1552, 1504, 1491, 1447, 1367, 1250, 1234, 1210,

1161, 1105, 1033, 925, 795, 759, 717 $cm^{-1}$.ESI-HRMS calc. for $C_{16}H_{18}NO_4$ $[M\text{-}Cl]^+$: 288.1236, found: 288.1223.

**Preparation of methyl 2-(3,4-dimethoxyphenyl)-2-pyridinium acetate, chloride salt (IL 5):**

Pyridine (0.63 mL, 7.81 mmol) was added to methyl 2-chloro-2-(3,4-dimethoxyphenyl) acetate **16** (0.955 g, 3.90 mmol) and the reaction mixture was stirred in the dark with a drying tube at 55 $^oC$ for 2 hours. The yellow precipitate was washed with diethyl ether (3 × 10 mL) and coevaporated with toluene ten times. Then product was washed with hot acetone (6 × 10 mL) and the white powder collected by filtration to give the title compound **5** in 61 % yield (0.770 g, 2.38 mmol).

m.p.: 118-119 $^oC$.$^1H$ NMR (400 MHz, $CDCl_3$, δ): 9.56-9.55 (m, 2H, ArC*H*), 8.53-8.49 (m, 1H, ArC*H*), 8.29 (s, 1H, NC*H*), 8.04-8.01 (m, 2H, ArC*H*), 7.49 (d, *J* = 2.0 Hz, 1H, ArC*H*), 7.04 (dd, *J* = 8.2, 2.0 Hz, 1H, ArC*H*), 6.81 (d, *J* = 8.2 Hz, 1H, ArC*H*), 3.77 (s, 3H, OC$H_3$), 3.76 (s, 3H, OC$H_3$), 3.72 (s, 3H, OC$H_3$).$^{13}C$ NMR (150 MHz, $CDCl_3$, δ): 167.87 (*C*OO), 150.94 (Ar*C*), 149.94 (Ar*C*), 146.55 (Ar*C*), 144.99 (2Ar*C*), 128.09 (Ar*C*), 127.98 (Ar*C*), 123.40 (Ar*C*), 121.78 (Ar*C*H), 113.38 (Ar*C*H), 111.58 (Ar*C*H), 73.32 (N*C*H), 56.42 (O*C*$H_3$), 56.96 (O*C*$H_3$), 53.95 (O*C*$H_3$).IR (neat) $\nu_{max}$: 3358, 3007, 2941, 2841, 1736, 1518, 1461, 1446, 1264, 1232, 1144, 1023, 1005, 812, 744 $cm^{-1}$. ESI-HRMS calc. for $C_{16}H_{18}NO_4$ $[M\text{-}Cl]^+$: 288.1236, found: 288.1223.

**Preparation of methyl 2-(3,4-methylenedioxyphenyl)-2-(2-pyridiniumacetoxy)acetate, bromide salt (IL 6):**

To a stirred solution of methyl 2-(2-bromoacetoxy)-2-(3,4-methylenedioxyphenyl)acetate **18** (1.502 g, 4.54 mmol) in diethyl ether (10 mL) at −15 $^oC$ under a $N_2$ atmosphere was added pyridine (0.37 mL, 4.54 mmol) dropwise and the reaction mixture was allowed to warm to room temperature. After stirring for 48 h the reaction mixture was refluxed for 4 h and then stirred at room temperature for further 16 h. The precipitate was washed with diethyl ether (2 × 5 mL) and dried under reduced pressure to give the title compound **6** as a white powder in 90 % yield (1.682 g, 4.10 mmol).

m.p.: 148-149 $^oC$. $^1H$ NMR (400 MHz, $CD_3CN$, δ): 8.92-8.90 (m, 2H, ArC*H*), 8.64-8.60 (m, 1H, ArC*H*), 8.13-8.09 (m, 2H, ArC*H*), 6.952 (dd, *J* = 8.3, 1.9 Hz, 1H, ArC*H*),

6.947 (d, *J* = 1.9 Hz, 1H, ArC*H*), 6.88 (d, *J* = 8.3 Hz, 1H, ArC*H*), 6.011 (d, part A of an AB system, *J* = 1.2 Hz, 1H, OC*H*$_2$O), 6.006 (d, part B of an AB system, *J* = 1.2 Hz, 1H, OC*H*$_2$O), 6.00 (s, 1H, C*H*), 5.77 (d part A of an AB system, *J* = 17.8 Hz, 1H, C*H*$_2$), 5.73 (d part B of an AB system, *J* = 17.8 Hz, 1H, C*H*$_2$), 3.70 (s, 3H, C*H*$_3$).$^{13}$C (150 MHz, $CD_3CN$, δ): 169.15 (*C*OO), 166.32 (*C*OO), 149.80 (Ar*C*), 149.08 (Ar*C*), 148.22 (Ar*C*H), 147.07 (2Ar*C*H), 129.11 (2Ar*C*H), 127.36 (Ar*C*), 123.12 (Ar*C*H), 109.25 (Ar*C*H), 108.72 (Ar*C*H) 102.91 (O*C*H$_2$O), 76.79 (*C*H), 61.37 (*C*H$_2$N), 53.53 (O*C*H$_3$). IR (neat) $\nu_{max}$: 3386, 3021, 2967, 1743, 1637, 1496, 1451, 1195, 1242, 1171, 1107, 1026 cm$^{-1}$. ESI-HRMS calc. for $C_{17}H_{16}NO_6$ [M-Br]$^+$: 330.0978 , found: 330.0977.

**Preparation of butyl-2-(3,4-methylenedioxyphenyl)-2-(2-pyridiniumacetoxy)acetate, bromide salt (IL 7):**

To a stirred solution of butyl-2-(2-bromoacetoxy)-2-(3,4-methylenedioxyphenyl)acetate **13** (11.56 g, 30.98 mmol) in diethyl ether (150 mL), pyridine (2.51 mL, 30.98 mmol) was added dropwise at RT under a $N_2$ atmosphere. After stirring overnight a white precipitate, was separated from the solvent by decantation. The solid was washed with diethyl ether (5 × 100 mL) and dried under high vacuum to give the title compound **7** as a white solid in 50 % yield (7.00 g, 15.48 mmol).

m.p.: 150-152 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ): 9.39 (m, 2H, ArC*H*), 8.53 (m, 1H, ArC*H*), 8.07 (m, 2H, ArC*H*), 6.89 (dd, *J* = 8.0, 2.0 Hz, 1H, ArC*H*), 6.86 (d, *J* = 2.0 Hz, 1H, ArC*H*), 6.76 (d, *J* = 8.0 Hz, 1H, ArC*H*), 6.50 (d part A of an AB system, *J* = 17.2 Hz, 1H, C*H*$_2$), 6.21 (d part B of an AB system, *J* = 17.2 Hz, 1H, C*H*$_2$), 5.971 (d, part A of an AB system, *J* = 4.8 Hz, 1H, OC*H*$_2$O), 5.968 (d, part B of an AB system, *J* = 4.8 Hz, 1H, OC*H*$_2$O), 5.88 (s, 1H, C*H*), 4.08 (dt, *J* = 10.8, 6.8 Hz, 2H, C*H*$_2$), 1.52 (tt, *J* = 7.2, 6.8 Hz, 2H, C*H*$_2$), 1.22 (tq, *J* = 7.6, 7.2 Hz, 2H, C*H*$_2$), 0.83 (t, *J* = 7.2 Hz, 3H, C*H*$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 168.02 (*C*OO), 165.46 (*C*OO), 148.87 (Ar*C*), 148.12 (Ar*C*), 146.70 (2Ar*C*H), 146.54 (Ar*C*H), 127.92 (2Ar*C*H), 126.05 (Ar*C*), 122.36 (Ar*C*H), 108.68 (Ar*C*H), 108.12 (Ar*C*H), 101.64 (O*C*H$_2$O), 76.52 (O*C*H), 66.09 (O*C*H$_2$), 61.04 (O*C*H$_2$), 30.36 (*C*H$_2$), 18.90 (*C*H$_2$), 13.65 (*C*H$_3$). IR (neat) $\nu_{max}$: 3135, 3037, 2960, 1746, 1720, 1634, 1576, 1491, 1448, 1367, 1251, 1197, 1177, 1112, 1029, 922, 824, 760 cm$^{-1}$. ESI-HRMS calc. for $C_{20}H_{22}NO_6$ [M-Br]$^+$: 372.1442, found: 372.1447.

**Preparation of butyl-2-(3,4-methylenedioxyphenyl)-2-[2-(3-methylimidazolium)acetoxy]acetate, bromide salt (IL 8):**

To a stirred solution of butyl-2-(2-bromoacetoxy)-2-(3,4-methylenedioxyphenyl)acetate **13** (2.86 g, 7.66 mmol) in diethyl ether (50 mL), 1-methylimidazole (0.61 mL, 7.66 mmol) was added dropwise at RT under a $N_2$ atmosphere. After stirring overnight a white precipitate was separated from the solvent by decantation. The solid was washed with diethyl ether (5 × 50 mL) and dried under high vacuum to give the title compound **8** as a white solid in 60 % yield (2.11 g, 4.63 mmol).

m.p.: 94-96 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ): 10.17 (s, 1H, ArC*H*), 7.59 (t, *J* = 1.8 Hz, 1H, ArC*H*), 7.53 (t, *J* = 1.8 Hz, 1H, ArC*H*), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H, ArC*H*), 6.84 (d, *J* = 2.0 Hz, 1H, ArC*H*), 6.77 (d, *J* = 8.0 Hz, 1H, ArC*H*), 5.973 (d, part A of an AB system, *J* = 3.2 Hz, 1H, OC$H_2$O), 5.970 (d, part B of an AB system, *J* = 3.2 Hz, 1H, OC$H_2$O), 5.85 (s, 1H, C*H*), 5.73 (d part A of an AB system, *J* = 17.6 Hz, 1H, C$H_2$), 5.45 (d part B of an AB system, *J* = 17.6 Hz, 1H, C$H_2$), 4.15-4.03 (m, 5H, C$H_2$, C$H_3$), 1.56-1.49 (m, 2H, C$H_2$), 1.22 (tq, *J* = 7.6, 7.2 Hz, 2H, C$H_2$), 0.83 (t, *J* = 7.2 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 168.14 (*C*OO), 165.72 (*C*OO), 148.86 (Ar*C*), 148.12 (Ar*C*), 138.48 (Ar*C*H), 126.05 (Ar*C*), 123.75 (Ar*C*H), 123.26 (Ar*C*H), 122.31 (Ar*C*H), 108.64 (Ar*C*H), 108.04 (Ar*C*H), 101.64 (O*C*H$_2$O), 76.19 (O*C*H), 66.07 (O*C*H$_2$), 50.24 (O*C*H$_2$), 37.01 (N*C*H$_3$), 30.36 (*C*H$_2$), 18.90 (*C*H$_2$), 13.64 (*C*H$_3$). IR (neat) $\nu_{max}$: 2961.34, 1749.89, 1608.08, 1579.73, 1502.12, 1491.05, 1449.55, 1347.55, 1239.72, 1190.52, 1023.88, 918.09, 757.01 cm$^{-1}$. ESI-HRMS calc. for $C_{19}H_{23}N_2O_6$ [M-Br]$^+$: 375.1556, found: 375.1559.

**Preparation of methyl 2-bromo-2-(3,4-methylenedioxyphenyl) acetate (11) [3]**

To a stirred solution of methyl (3,4-methylenedioxy)mandelate **10** [3] (6.596 g, 31.41 mmol) in $CH_2Cl_2$ (60 mL) at 0 °C was added thionyl bromide (2.44 mL, 31.41 mmol) dropwise, followed by triethylamine (4.36 mL, 31.41 mmol) also added dropwise and the reaction mixture was allowed to warm to room temperature. After stirring for 35 min the reaction mixture was washed with distilled water (3 × 15 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oil was purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$, 50:50) to give the title compound **11** as a colorless oil in 68 % yield (5.843 g, 21.40 mmol).

$^1$H NMR (400 MHz, $CDCl_3$, δ): 7.12 (d, *J* = 2.0 Hz, 1H, ArC*H*), 6.94 (dd, *J* = 8.0, 2.0 Hz, 1H, ArC*H*), 6.74 (d, *J* = 8.0 Hz, 1H, ArC*H*), 5.97 (d, part A of an AB system, *J* = 1.4 Hz, 1H, OC$H_2$O), 5.97 (d, part B of an AB system, *J* = 1.4 Hz, 1H, OC$H_2$O), 5.31 (s, 1H, C*H*), 3.78 (s, 3H, OC$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 168.99 (*C*OO), 148.86 (Ar*C*), 148.42 (Ar*C*), 129.51 (Ar*C*), 122.89 (Ar*C*H), 109.39 (Ar*C*H), 108.39 (Ar*C*H), 101.84 (O*C*$H_2$O), 53.66 (O*C*$H_3$), 46.96 (*C*H). IR (neat) $\nu_{max}$: 2956, 2901, 1749, 1503, 1489, 1444, 1246, 1160, 1036 cm$^{-1}$. Data are in agreement with literature values. [3]

**Preparation of butyl-3,4-methylenedioxymandelate (12)**

To a stirred solution of 3,4-methylenedioxymandelic acid **9** [1, 2] (11.06 g, 56.38 mmol) in butanol (70 mL) was added thionyl chloride (2.06 mL, 28.19 mmol) dropwise at room temperature. After stirring for 3 h the reaction was quenched with water and the product was extracted with ethyl acetate (5 × 50 mL). The combined extracts were washed with saturated aqueous sodium bicarbonate (50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under high vacuum to give the title compound **12** as off white solid in 95 % yield (13.45 g, 53.31 mmol).

m.p.: 47-49 °C. $^1$H NMR (400 MHz, $CDCl_3$, δ): 6.89 (dd, *J* = 8.0, 2.0 Hz, 1H, ArC*H*), 6.88 (d, *J* = 2.0 Hz, 1H, ArC*H*), 6.78 (d, *J* = 8.0 Hz, 1H, ArC*H*), 5.96 (s, 2H, OC$H_2$O), 5.05 (s, 1H, C*H*), 4.16 (dt, *J* = 10.8, 6.8 Hz, 2H, C$H_2$), 3.37 (bs, 1H, O*H*), 1.57 (tt, *J* = 7.6, 6.8 Hz, 2H, C$H_2$), 1.27 (tq, *J* = 7.6, 7.2 Hz, 2H, C$H_2$), 0.87 (t, *J* = 7.2 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, DMSO, δ): 172.68 (*C*OO), 147.16 (Ar*C*), 146.86 (Ar*C*), 133.70 (Ar*C*), 120.22 (Ar*C*H), 107.99 (Ar*C*H), 106.96 (Ar*C*H), 101.03 (O*C*$H_2$O), 72.14 (*C*HOH), 64.00 (O*C*$H_2$), 30.11(*C*$H_2$), 18.44 (*C*$H_2$), 13.49 (*C*$H_3$). IR (neat) $\nu_{max}$: 3456, 2961, 2946, 2890, 1730, 1498, 1487, 1443, 1397, 1295, 1260, 1233, 1194, 1173, 1100, 1082, 1033, 929, 818, 763 cm$^{-1}$.

**Preparation of butyl 2-(2-bromoacetoxy)-2-(3,4-methylenedioxyphenyl)acetate (13)**

To a stirred solution of butyl-3,4-methylenedioxymandelate **12** (6.53 g, 25.88 mmol) in $CH_2Cl_2$ (65 mL) at 0 °C was added triethylamine (5.41 mL, 38.83 mmol) followed by bromoacetyl bromide (2.71 mL, 31.06 mmol). The reaction mixture was allowed to attain room temperature and stirred overnight. Water (50 mL) was added to the reaction mixture; organic layer was separated and washed with saturated $NH_4Cl$ solution (25 mL), 10 % $NaHCO_3$ solution (25 mL) and saturated brine solution (25 mL), dried over

anhydrous $MgSO_4$ and concentrated under high vacuum. The crude product was purified by column chromatography ($SiO_2$, hexane:EtOAc 90:10) to give the title compound **13** as a colourless liquid in 80 % yield (7.72 g, 20.68 mmol).

$^1$H NMR (400 MHz, $CDCl_3$, δ): 6.932 (dd, *J* = 8.4, 1.6 Hz, 1H, ArC*H*), 6.931 (d, *J* = 8.4 Hz, 1H, ArC*H*), 6.81 (d, *J* = 8.4 Hz, 1H, ArC*H*), 5.98 (bs, 2H, OC$H_2$O), 5.85 (s, 1H, C*H*), 4.14 (dt, *J* = 10.8, 6.8 Hz, 2H, C$H_2$), 3.97 (d, part A of an AB system, *J* = 14.4 Hz, 1H, C$H_2$), 3.94 (d, part B of an AB system, *J* = 14.4 Hz, 1H, C$H_2$), 1.58 (tt, *J* = 7.2, 6.8 Hz, 2H, C$H_2$), 1.29 (tq, *J* = 7.4, 7.2 Hz, 2H, C$H_2$), 0.88 (t, *J* = 7.4 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 168.32 (*C*OO), 166.69 (*C*OO), 148.73 (Ar*C*), 148.15 (Ar*C*), 126.83 (Ar*C*), 122.06 (Ar*C*H), 108.59 (Ar*C*H), 108.00 (Ar*C*H), 101.59 (O*C*$H_2$O), 75.77 (*C*H), 65.82 (*C*$H_2$), 30.48 (*C*$H_2$), 25.44 (*C*$H_2$), 19.00 (*C*$H_2$), 13.71 (*C*$H_3$). IR (neat) $\nu_{max}$: 2961, 2875, 1740, 1504, 1490, 1446, 1337, 1240, 1178, 1101, 1034, 976, 925, 865, 806, 762 cm$^{-1}$.

**Preparation of methyl 2-chloro-2-(3,4-methylenedioxyphenyl) acetate (14)** [4, 5]

To a stirred solution of methyl 3,4-methylenedioxymandelate **10** [3] (3.155 g, 15.03 mmol) in $CH_2Cl_2$ (50 mL) at 0 $^o$C was added thionyl chloride (1.10 mL, 15.03 mmol) dropwise, followed by TEA (2.10 mL, 15.03 mmol) also added dropwise and the reaction mixture was allowed to warm to room temperature. After stirring for 1 h the reaction mixture was washed with distilled water (4 ×15 mL). The organic phase was dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The resulting oil was purified by column chromatography ($SiO_2$, $CH_2Cl_2$) to give the title compound **14** as a colorless oil in 65 % yield (2.229 g, 9.76 mmol).

$^1$H NMR (400 MHz, $CDCl_3$, δ): 7.02 (d, *J* = 2.0 Hz, 1H, ArC*H*), 6.92 (dd, *J* = 8.0, 2.0 Hz, 1H, ArC*H*), 6.77 (d, *J* = 8.0 Hz, 1H, ArC*H*), 5.99 (d, part A of an AB system, *J* = 1.4 Hz, 1H, OC$H_2$O), 5.98 (d, part B of an AB system, *J* = 1.4 Hz, 1H, OC$H_2$O), 5.28 (s, 1H, C*H*), 3.78 (s, 3H, OC$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 169.06 (*C*OO), 148.79 (Ar*C*), 148.38 (Ar*C*), 129.52 (Ar*C*), 122.32 (Ar*C*H), 108.45 (2Ar*C*H), 101.78 (O*C*$H_2$O), 59.16 (O*C*$H_3$), 53.58 (*C*H). IR (neat) $\nu_{max}$: 2956, 2901, 1749, 1503, 1489, 1444, 1246, 1160, 1036 cm$^{-1}$. Data are in agreement with literature values. [4]

**Preparation of methyl 2-chloro-2-(3,4-dimethoxyphenyl) acetate (16)**

To a stirred solution of methyl 3,4-dimethoxymandelate **15** [6] (4.137 g, 18.31 mmol) in $CH_2Cl_2$ (40 mL) at 0 $^o$C was added thionyl chloride (1.34 mL, 18.31 mmol) dropwise,

followed by triethylamine (2.32 mL, 18.31 mmol) also added dropwise and the reaction mixture was allowed to warm to room temperature. After stirring for 1 h the reaction mixture was washed with distilled water (3 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oil was purified by column chromatography ($SiO_2$, hexane:EtOAc, 80:20) to give the title compound **16** as a colorless oil in 63 % yield (2.818 g, 11.52 mmol).

$^1$H NMR (400 MHz, $CDCl_3$, δ): 7.02 (d, *J* = 2.0 Hz, 1H, ArC*H*), 6.99 (dd, *J* = 8.2, 2.0 Hz, 1H, ArC*H*), 6.81 (d, *J* = 8.2 Hz, 1H, ArC*H*), 5.31 (s, 1H, C*H*), 3.88 (s, 3H, OC$H_3$), 3.86 (s, 3H, OC$H_3$), 3.75 (s, 3H, OC$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 169.23 (*C*OO), 150.20 (Ar*C*), 149.52 (Ar*C*), 128.23 (Ar*C*), 121.02 (Ar*C*H), 111.14 (Ar*C*H), 110.96 (Ar*C*H), 59.25 (*C*H), 56.22 (O*C*H$_3$), 56.18 (O*C*H$_3$), 53.53 (O*C*H$_3$). IR (neat) $\nu_{max}$: 2956, 2839, 1751, 1514, 1261, 1139, 1023, 760, 722 cm$^{-1}$.

**Preparation of butyl-2-bromo-2-(3,4-methylenedioxyphenyl) acetate (17)**

To a stirred solution of butyl (3,4-methylenedioxy)mandelate **12** (9.04 g, 35.84 mmol) and triethylamine (5.99 mL, 43.01 mmol) in $CH_2Cl_2$ (100 mL) at 0 $^o$C was added thionyl bromide (3.05 mL, 39.42 mmol) dropwise, and the reaction mixture was allowed to warm to room temperature. After stirring for 3 h the reaction mixture was washed with distilled water (3 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under high vacuum. The resulting oil was purified by column chromatography ($SiO_2$, EA:hexane, 20:80) to give the title compound **17** as a yellow oil in 76 % yield (8.62 g, 27.35 mmol).

$^1$H NMR (400 MHz, $CDCl_3$, δ): 7.13 (d, *J* = 2.0 Hz, 1H, ArC*H*), 6.95 (dd, *J* = 8.0, 2.0 Hz, 1H, ArC*H*), 6.73 (d, *J* = 8.0 Hz, 1H, ArC*H*), 5.96 (d, part A of an AB system, *J* = 1.2 Hz, 1H, OC$H_2$O), 5.95 (d, part B of an AB system, *J* = 1.2 Hz, 1H, OC$H_2$O), 5.29 (s, 1H, C*H*), 4.17 (dt, *J* = 10.8, 6.8 Hz, 2H, C$H_2$), 1.63 (tt, *J* = 7.4, 6.8 Hz, 2H, C$H_2$), 1.35 (tq, *J* = 7.4, 7.2 Hz, 2H, C$H_2$), 0.91 (t, *J* = 7.2 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 168.34 (*C*OO), 148.56 (Ar*C*), 148.14 (Ar*C*), 129.46 (Ar*C*), 122.66 (Ar*C*H), 109.20 (Ar*C*H), 108.12 (Ar*C*H), 101.58 (O*C*H$_2$O), 66.35 (O*C*H$_2$), 47.11 (*C*H), 30.41 (*C*H$_2$), 19.03 (*C*H$_2$), 13.71 (*C*H$_3$). IR (neat) $\nu_{max}$: 2960, 2875, 1737, 1503, 1489, 1445, 1370, 1315, 1245, 1177, 1139, 1102, 1036, 928, 815, 736 cm$^{-1}$.

**Preparation of methyl 2-(2-bromoacetoxy)-2-(3,4-methylenedioxyphenyl)acetate (18)**

To a stirred solution of methyl 3,4-methylenedioxymandelate **10** (3.350 g, 15.94 mmol) in $CH_2Cl_2$ (40 mL) at 0 $^oC$ was added potassium carbonate (3.488 g, 25.24 mmol) followed by bromoacetyl bromide (2.08 mL, 23.93 mmol) added dropwise and the reaction mixture was allowed to warm to room temperature. After stirring overnight the reaction mixture was filtered and further potassium carbonate (3.481 g, 25.19 mmol) and bromoacetyl bromide (2.08 mL, 23.93 mmol) were added at 0 $^oC$. After stirring overnight at room temperature the reaction mixture was filtered, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting product was purified by column chromatography ($SiO_2$, hexane:EtOAc 90:10) to give the title **18** compound as a colourless liquid in 69% yield (3.648 g, 11.02 mmol).

$^1H$ NMR (400 MHz, $CDCl_3$, δ): 6.91 (dd, *J* = 8.6, 1.6 Hz, 1H, ArC*H*), 6.92 (d, *J* = 1.6 Hz, 1H, ArC*H*), 6.80 (d, *J* = 8.6 Hz, 1H, ArC*H*), 5.97 (s, 2H, OC$H_2$O), 5.86 (s, 1H, C*H*), 3.97 (d, part A of an AB system, *J* = 12.8 Hz, 1H, C$H_2$), 3.93 (d, part B of an AB system, *J* = 12.8 Hz, 1H, C$H_2$) 3.72 (s, 3H, OC$H_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, δ): 168.85 (*C*OO), 166.80 (*C*OO), 148.94 (Ar*C*), 148.33 (Ar*C*), 126.73 (Ar*C*), 122.26 (Ar*C*H), 108.75 (Ar*C*H), 108.15 (Ar*C*H), 101.76 (O*C*$H_2$O), 75.72 (*C*H), 53.10 (O*C*$H_3$), 25.58 (*C*$H_2$). IR (neat) $\nu_{max}$: 2957, 2904, 1742, 1504, 1490, 1446, 1241, 1210, 1101, 1032 $cm^{-1}$.

***Bacteria toxicity tests***

Mueller-Hinton broth was purchased from Oxoid. Five bacteria strains were used in this study: the Gram-positive bacterium *Bacillus subtilis* DSMZ 10 (*B. subtilis*) and the Gram-negative bacteria *Escherichia coli* DSMZ 498 *(E. coli)*, *Pseudomonas fluorescens* DSMZ 50090 (*P. fluorescence)*, *Pseudomonas putida* CP1 (*P. putida* CP1) and *Pseudomonas putida* KT2440 (*P. putida* KT2440). All strains were purchased at DSMZ (German Collection of Microorganisms and Cell Cultures).

$IC_{50}$ values for the compounds were determined using a modification of the broth microdilution method described by Amsterdam [7]. Strains were grown in nutrient broth overnight, washed with 0.01M sodium phosphate buffer (pH 7) and the cell number adjusted to give an optical density reading of 0.07 at 660nm. The antimicrobial activity of the ILs was tested in 96 well round bottom microplates. 180 µL of Mueller-Hinton broth was pipetted into **column** 1 of the wells and 100 µL into the other wells. 20 µL of

the chemical solution was transferred into **column** 1 giving a concentration of 200 mM. 100 µL of the solution from **column** 1 was then transferred to the next **column** and mixed. The procedure was repeated to give a series of two-fold dilutions. Each well was inoculated with 5 µL of bacterial culture. Wells containing medium only were used as blanks and wells containing medium and culture only were used as positive controls. All the toxicity tests were carried out in triplicate. The microplates were incubated overnight at 30°C. The presence or absence of growth was determined by measuring the optical density of the wells at a wavelength of 405nm using a plate reader. The $IC_{50}$ values were determined as the concentration or range of concentrations that caused a 50% reduction in growth.

***Ecotoxicity tests***

The present work reports a range of ecotoxicological tests using the marine bacteria *Vibrio fischeri* (Beijerinck) Lehmann and Neumann (Microtox® tests) and the freshwater green algae *Pseudokirchneriella subcapitata* (Korshikov) Hindak and *Chlorella vulgaris* Beijerinck.

*Microtox® tests*

The Microtox® toxicity test [8] was used to evaluate the inhibition of the luminescence in the marine bacteria *Vibrio fischeri*. This test was performed using a range of diluted aqueous solutions (from 0 to 100 percent) of each IL, where 100 percent of IL corresponds to the concentration of a stock solution previously prepared (with concentration in IL well known and dependent of the solubility of each IL - Table 1). After 5 and 15 minutes of exposure to the IL solution, the light output of the luminescent bacteria was measured and compared with the light output of a blank control sample. The toxicity was evaluated and a 50% reduction in luminescence was computed using Microtox® Omni™ Software version 4.3.0.1. [9].

*Freshwater Green Algae*

The growth inhibition of the ILs towards the green microalgae *P. subcapitata* and *C. vulgaris* was assessed using a static bioassay conducted according to adequate growth inhibition testing procedures [10] guidelines, with adaptation to 24-well microplate [11]. The algae were exposed during 72 h under continuous illumination to serial dilutions of the IL in MBL medium: 0 (control), 6.25, 12.5, 25, 50, 75 and 100%. Peripheral wells

of the microplates were excluded from the assay given that as an "edge-effect" the evaporation is greater in these wells, which would introduce unnecessary variability among replicates. Each microplate held two test treatments with three 3 replicates plus 2 replicates of a blank control. Each well was filled with 990 μL test solution plus 10 μL microalgae inoculum; this was prepared based on microscopic cell counting in a Neubauer haemocytometer by dilution of the exponential-growing batch culture to achieve a cell density of $10^6$ cells.mL$^{-1}$ so that the final nominal cell density at the beginning of the test could be set at $10^4$ cells.mL$^{-1}$. The test microplates were incubated as described above for algal cultures and the contents of each well were thoroughly mixed twice daily by repetitive pipetting to promote active gas exchange and prevent cell clumping. At the end of the bioassay, cell density was determined by microscopic cell counting in a Neubauer haemocytometer of a well-mixed aliquot collected from each replicate. Yield and the daily growth rate were calculated from the cell density measurements. $EC_{50}$ parameters and their 95% confidence limits were estimated on the basis of non-linear regression with former fitting of the data to the logistic equation through the least squares statistical method.

**Determination of glass transition temperature ($T_g$) for IL 4**

$T_g$ was determined using DSC Q200 instrument (manufacturer-TA). Temperature range = −90 to 130 degrees, DSC cycle mode, $N_2$ flow = 50 mL/min, heating rate = 10 degrees/min. IL **4** $T_g$ = −3.3 $^oC$.

# IL 1

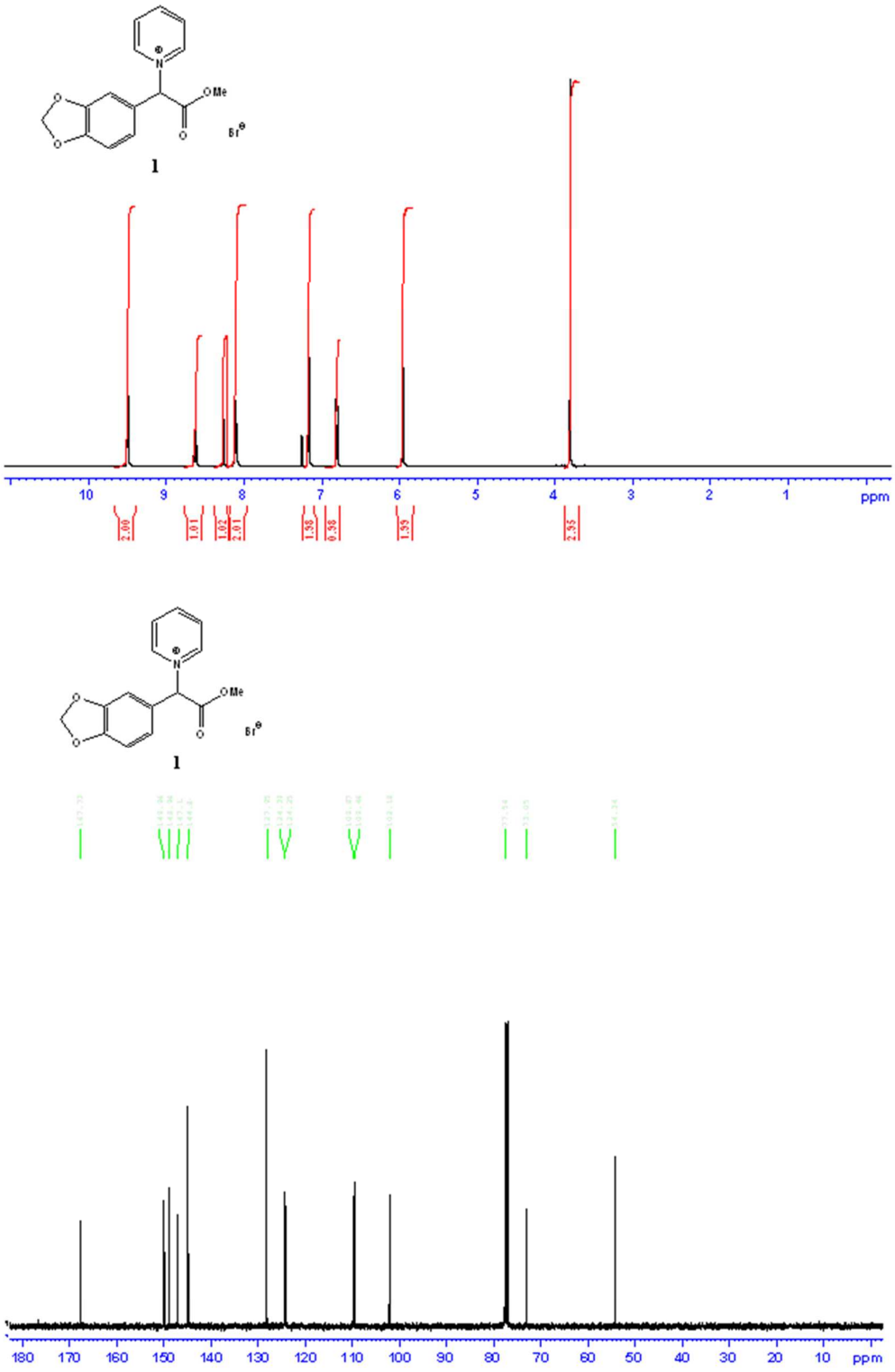


**Figure S.1.** NMR spectra for the IL **1**.

# IL 2

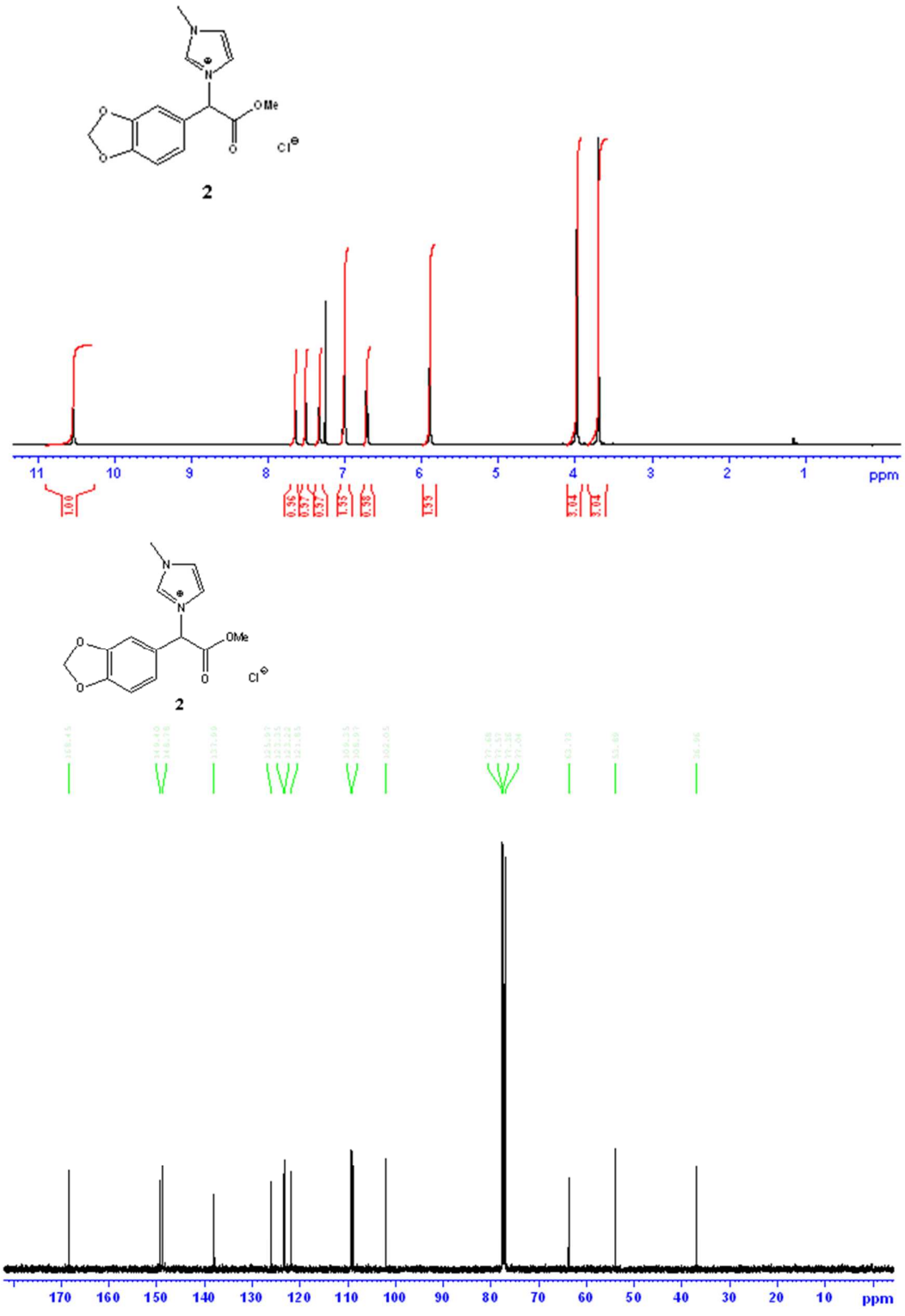


**Figure S.2.** NMR spectra for the IL **2**.

# IL 3

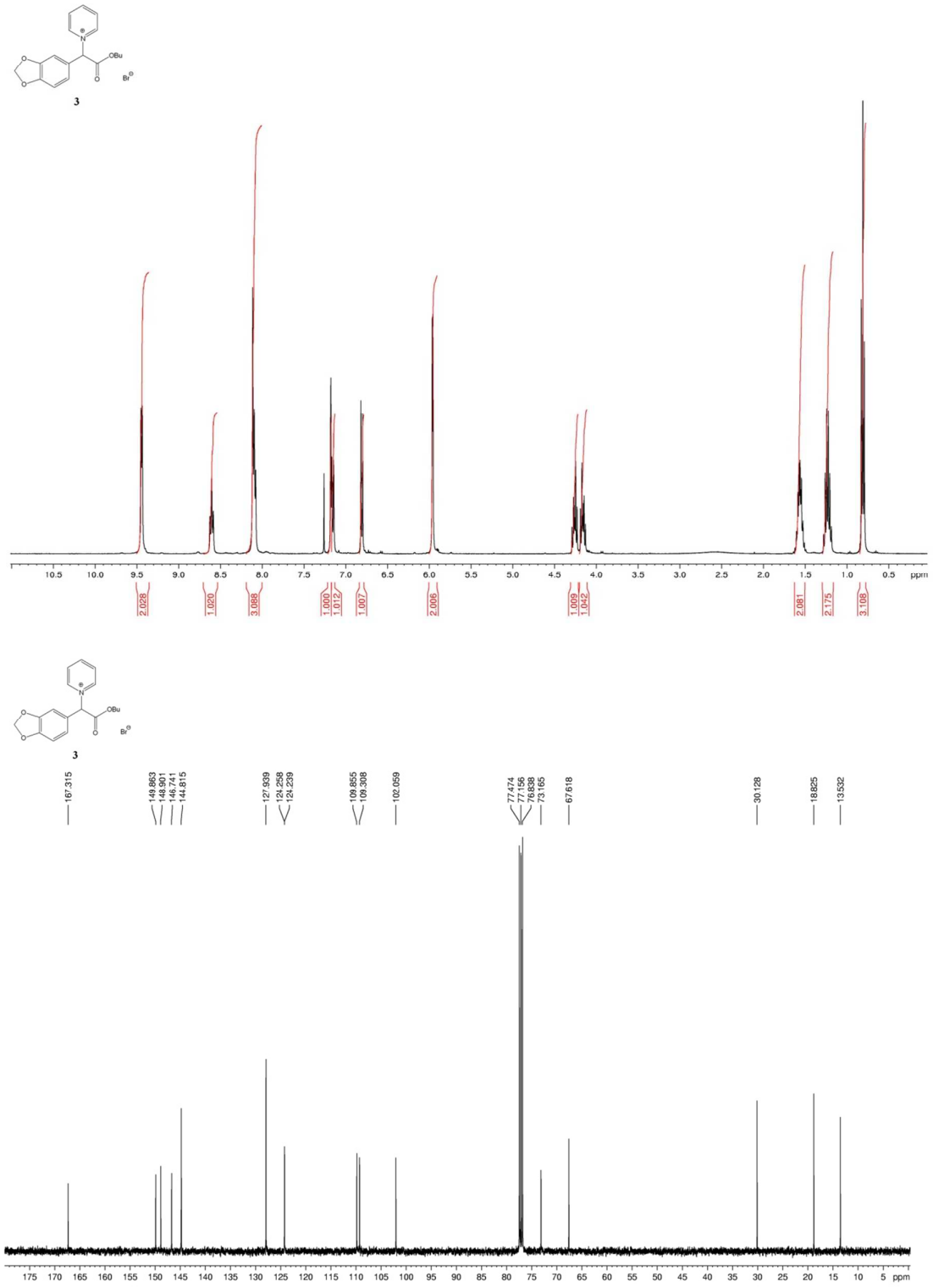


**Figure S.3.** NMR spectra for the IL **3**.

# IL 4

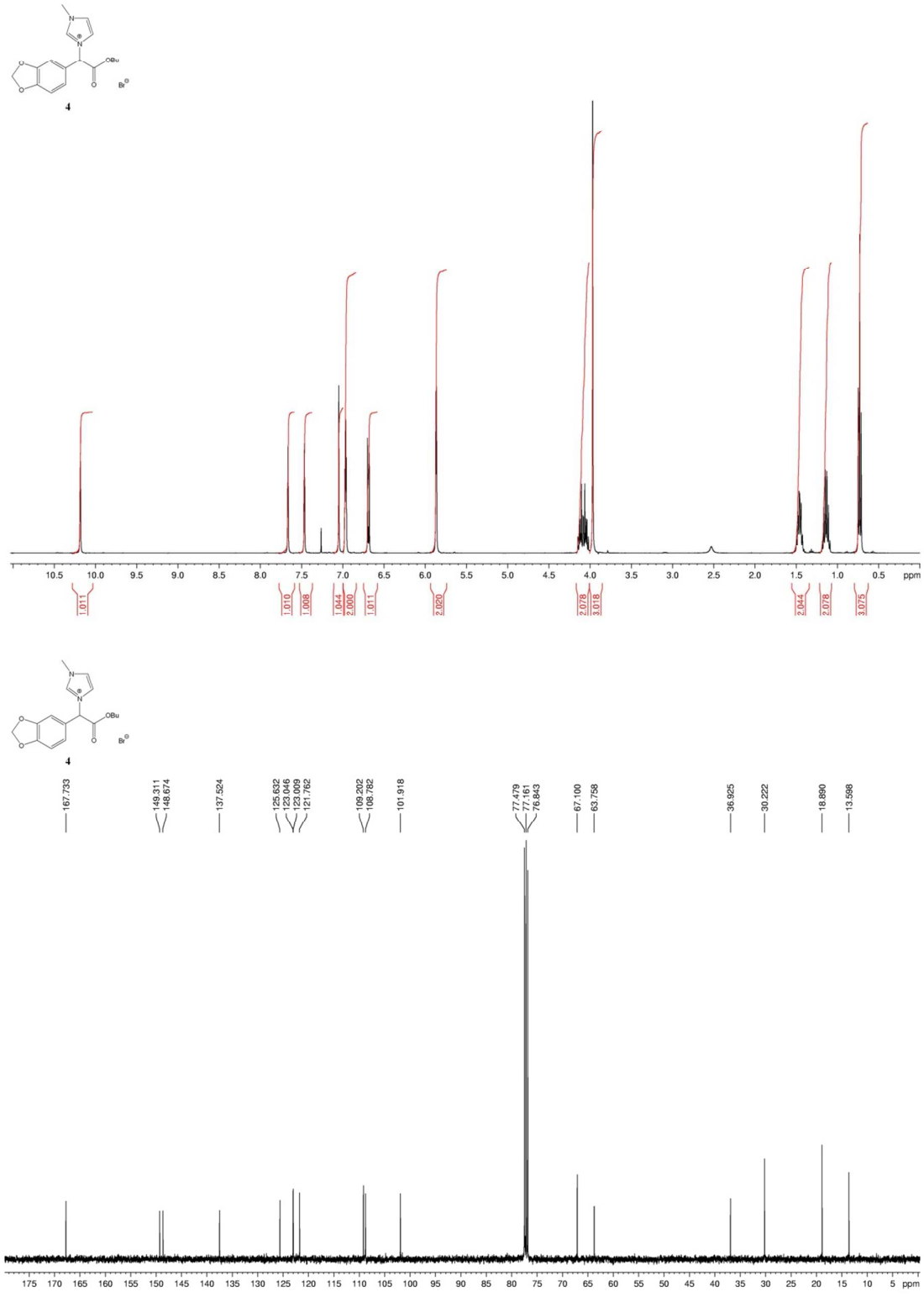


**Figure S.4.** NMR spectra for the IL **4**.

# IL 5

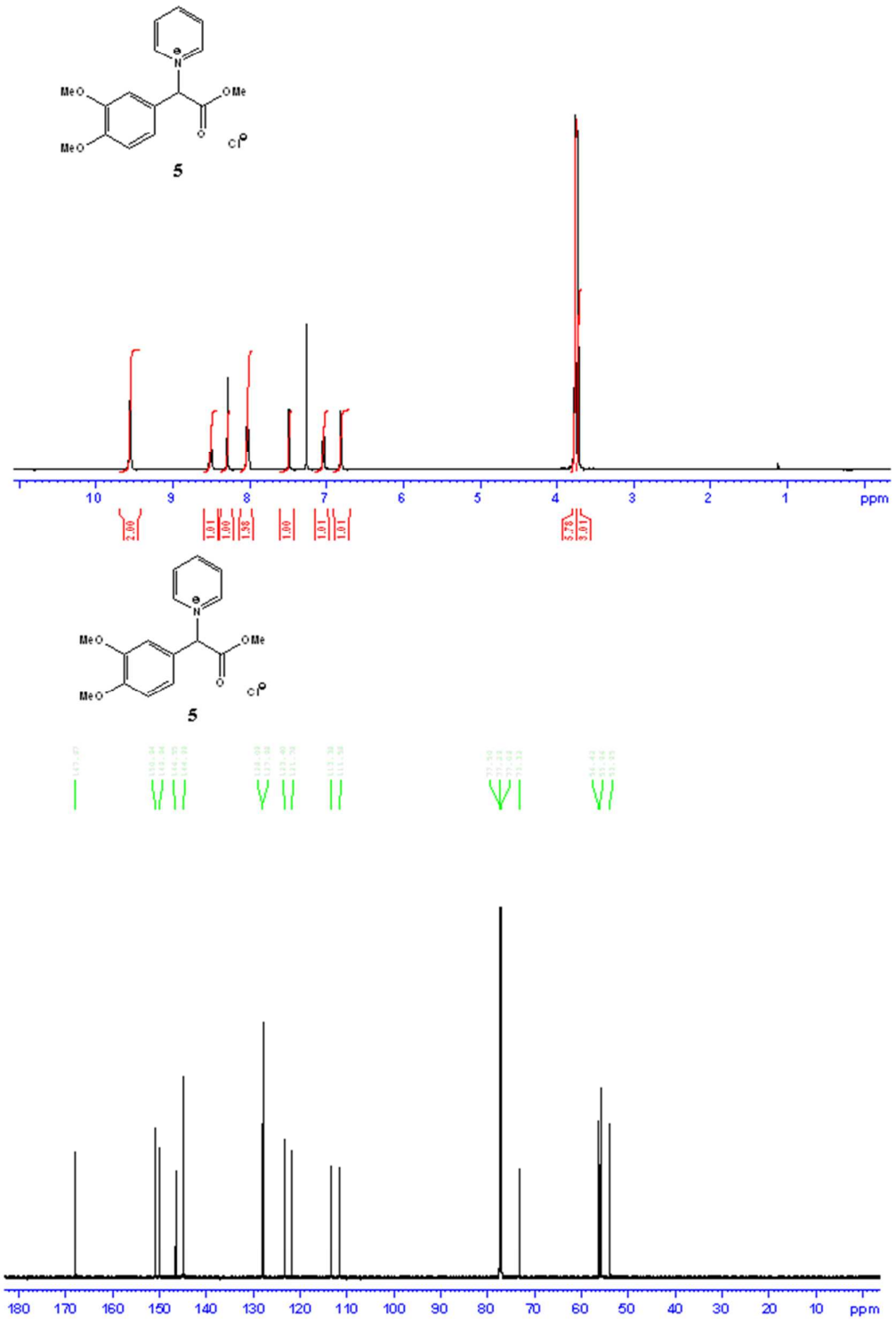


**Figure S.5.** NMR spectra for the IL **5**.

# IL 6

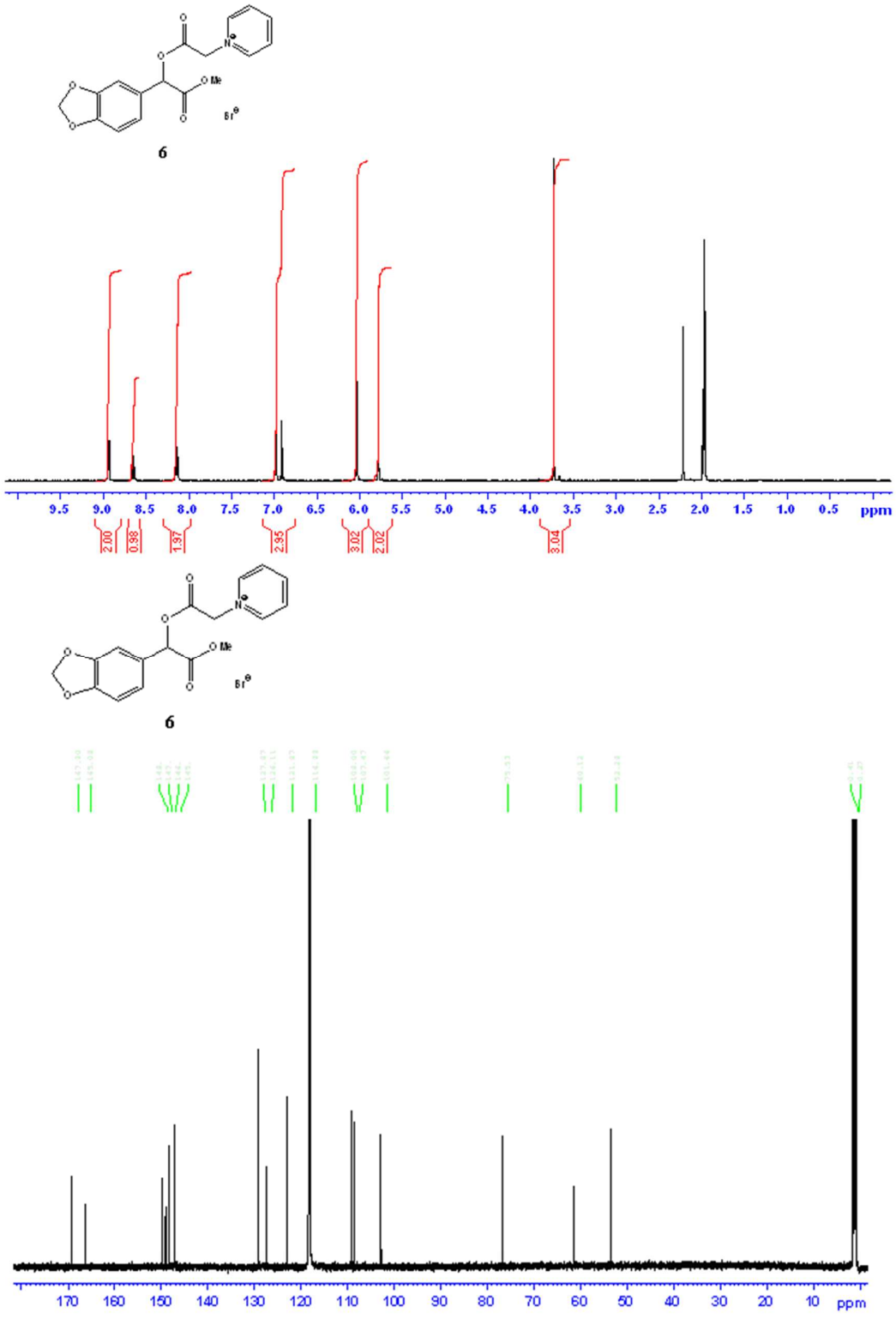


**Figure S.6.** NMR spectra for the IL **6**.

# IL 7

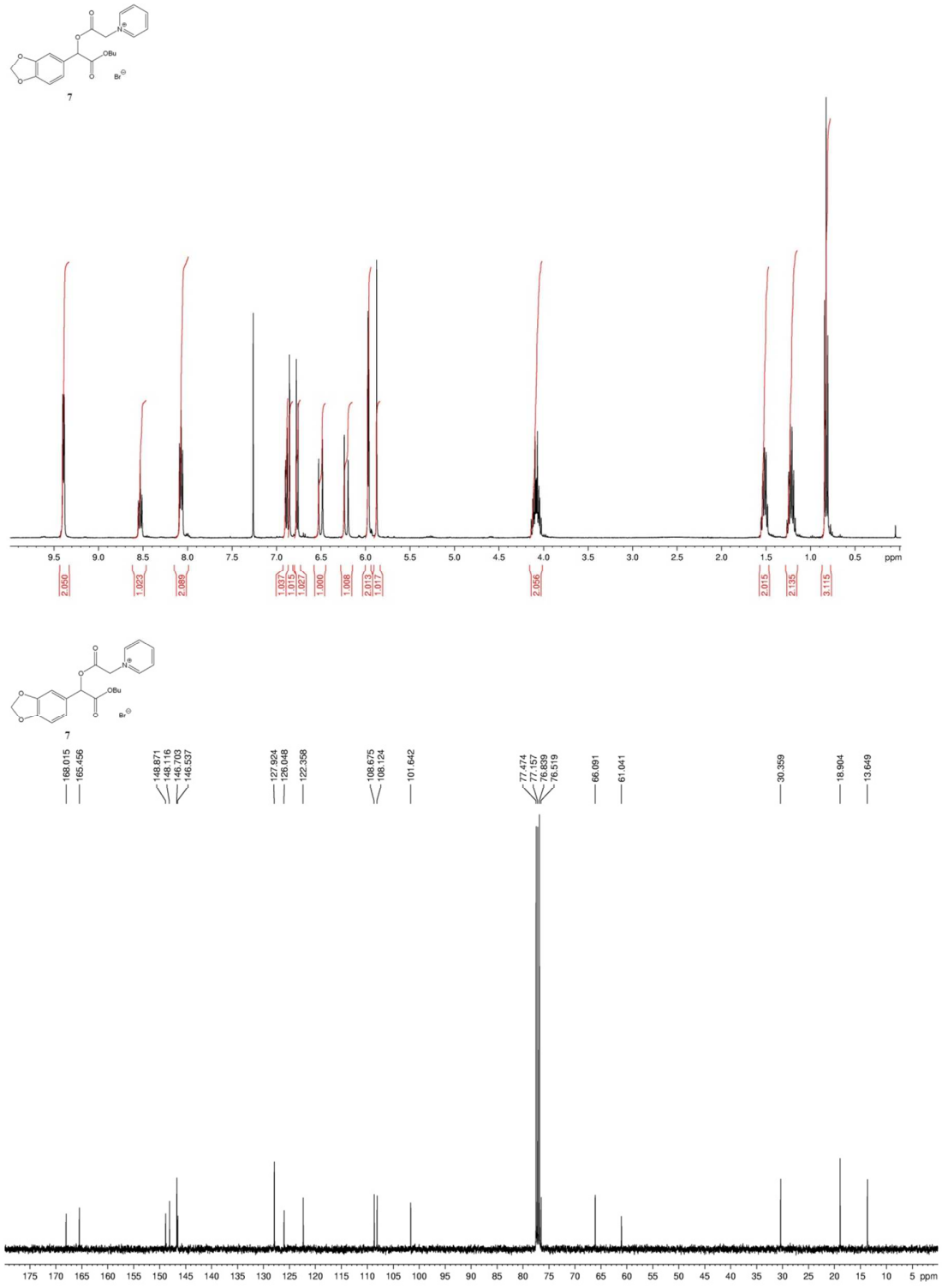


**Figure S.7.** NMR spectra for the IL **7**.

# IL 8

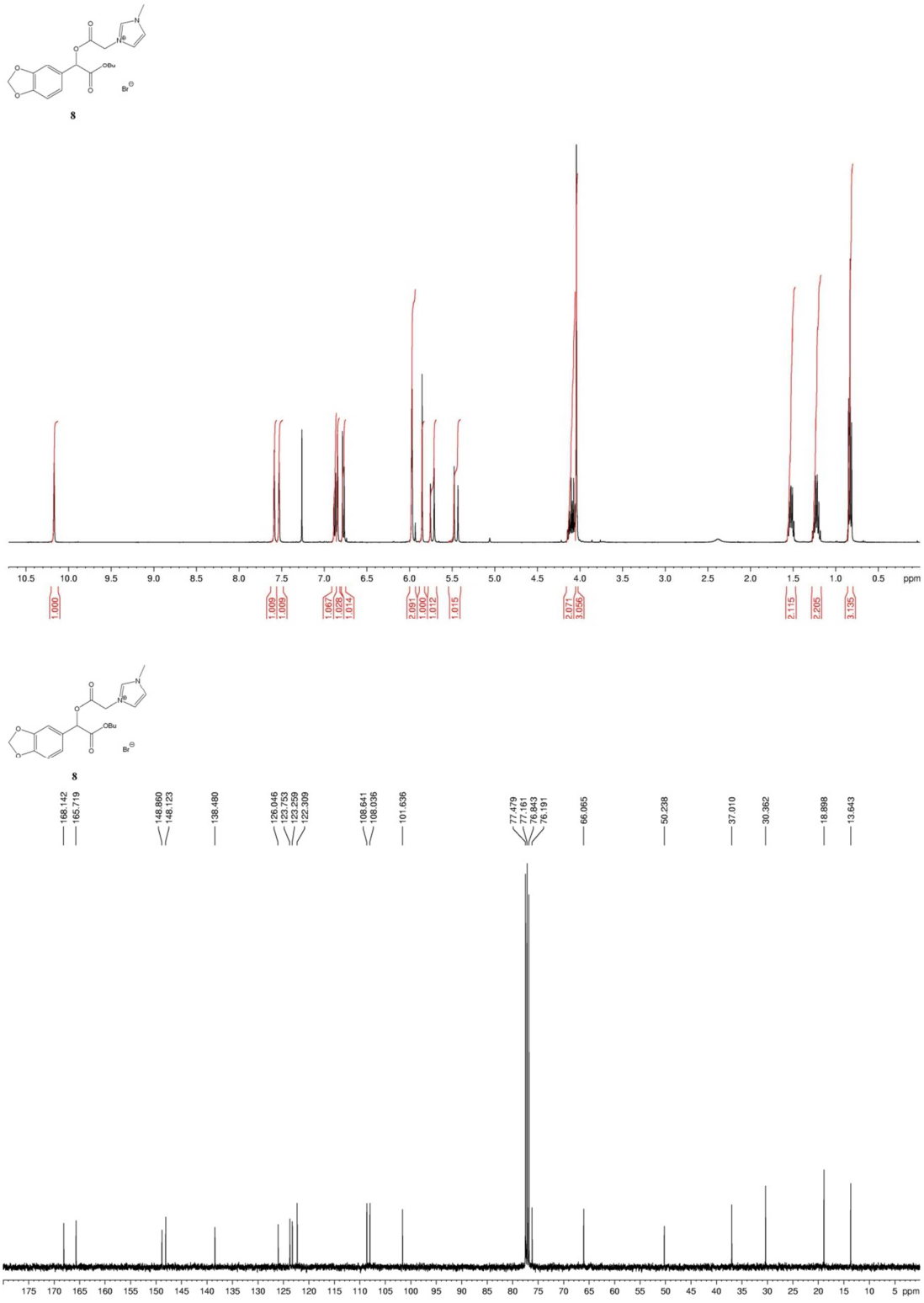


**Figure S.8.** NMR spectra for the IL **8**.

**11**

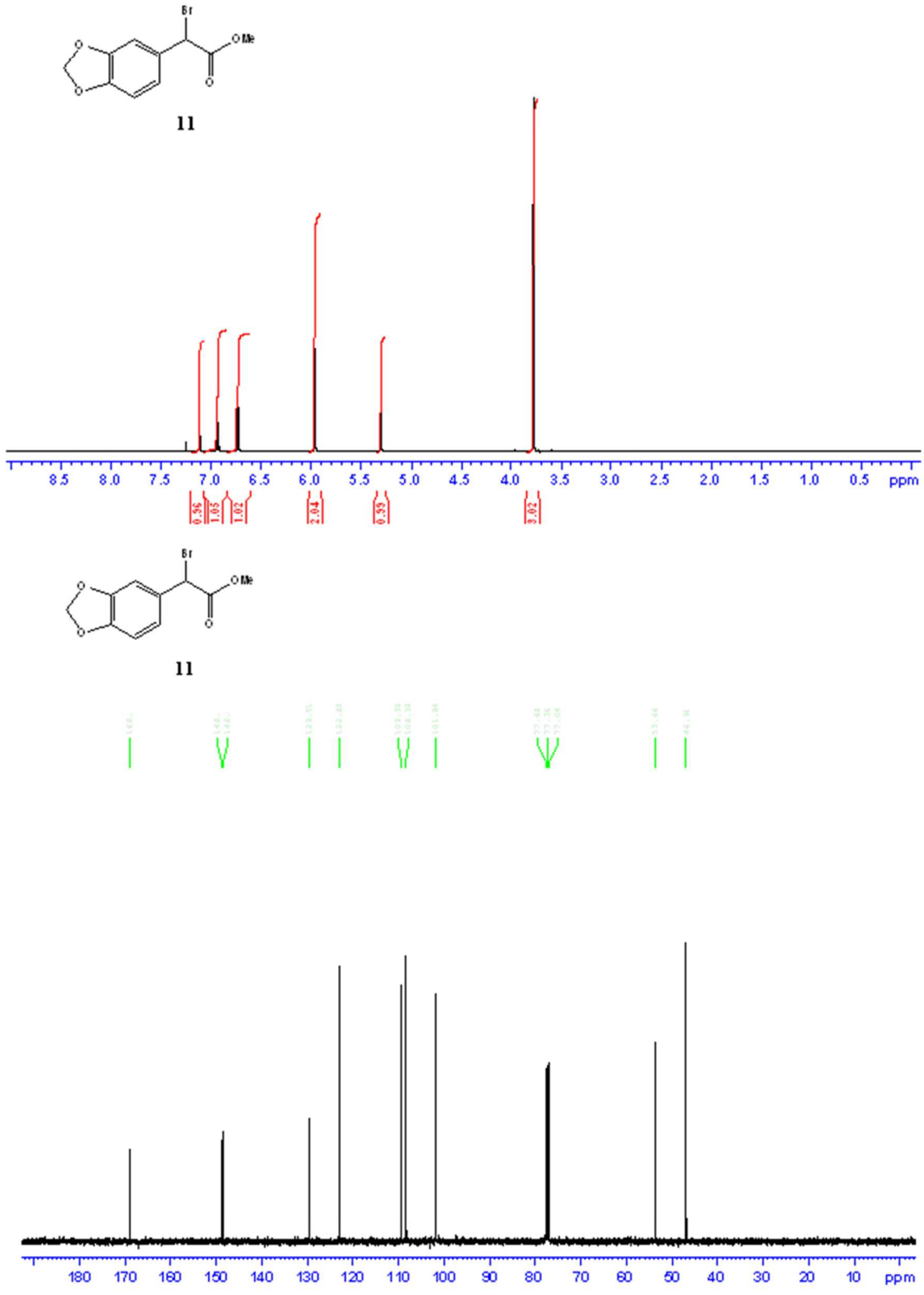


**Figure S.9.** NMR spectra for the chemical structure **11**.

# 12

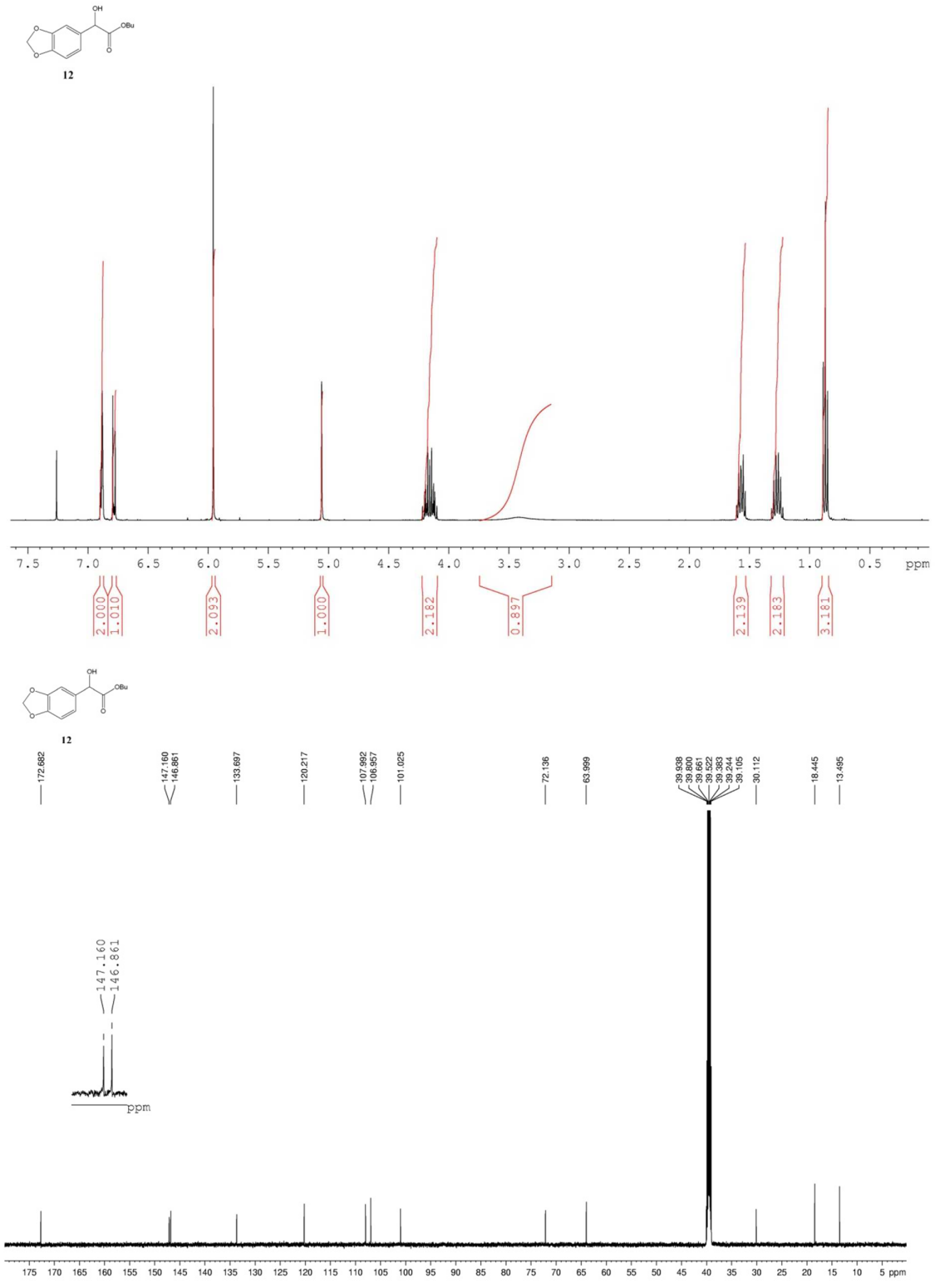


**Figure S.10.** NMR spectra for the chemical structure **12**.

# 13

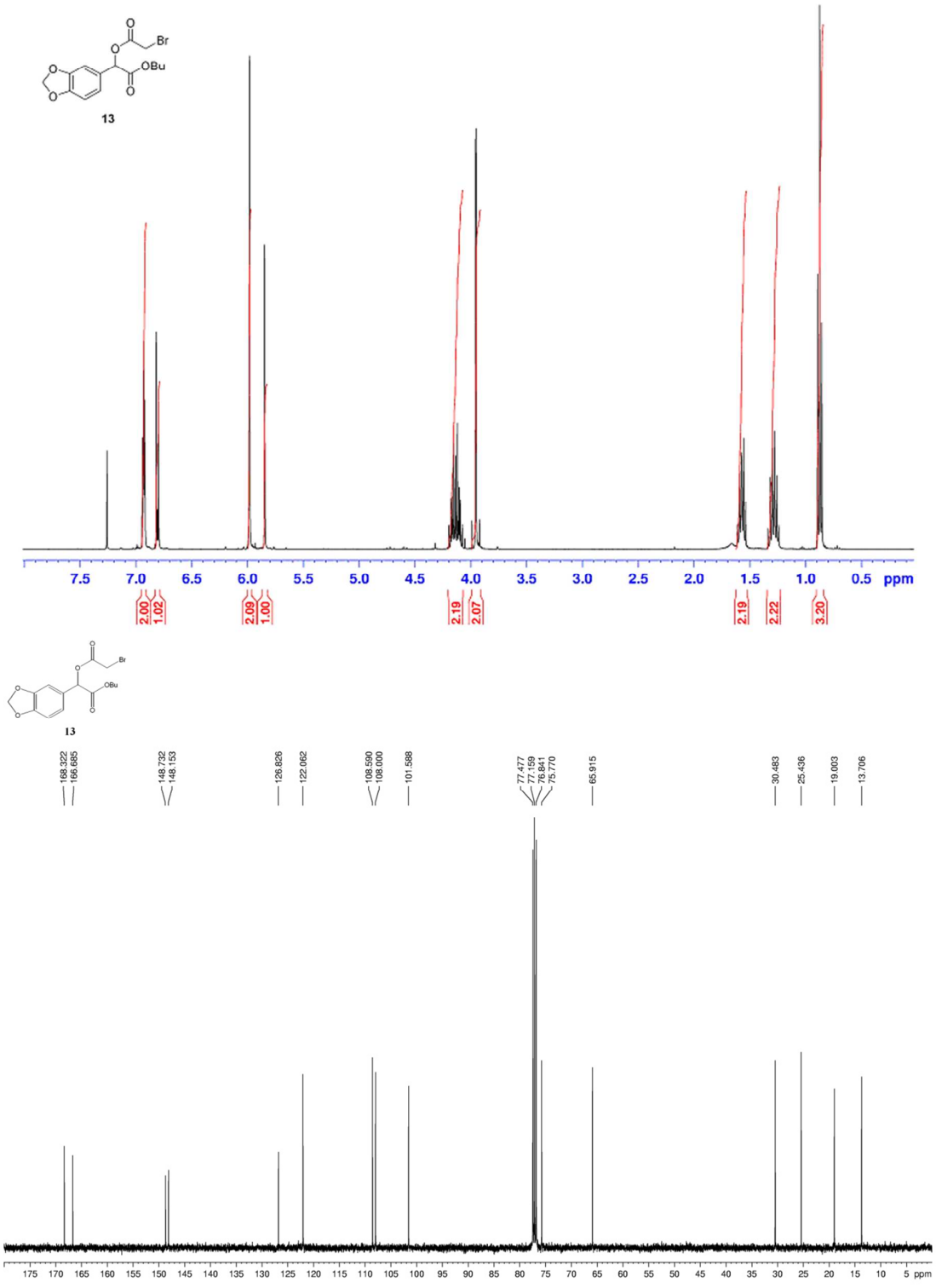


**Figure S.11.** NMR spectra for the chemical structure **13**.

# 14

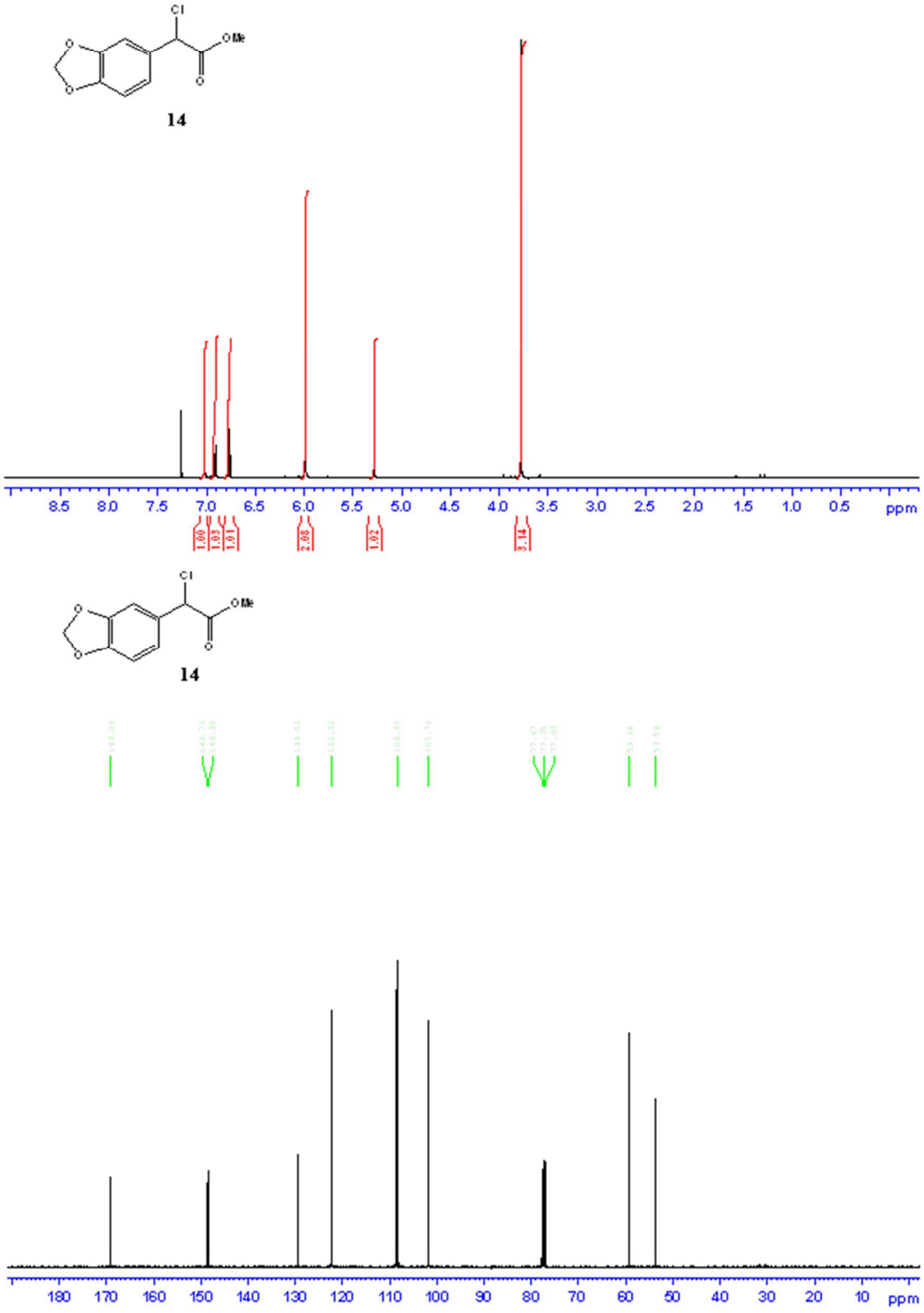


**Figure S.12.** NMR spectra for the chemical structure **14**.

# 16

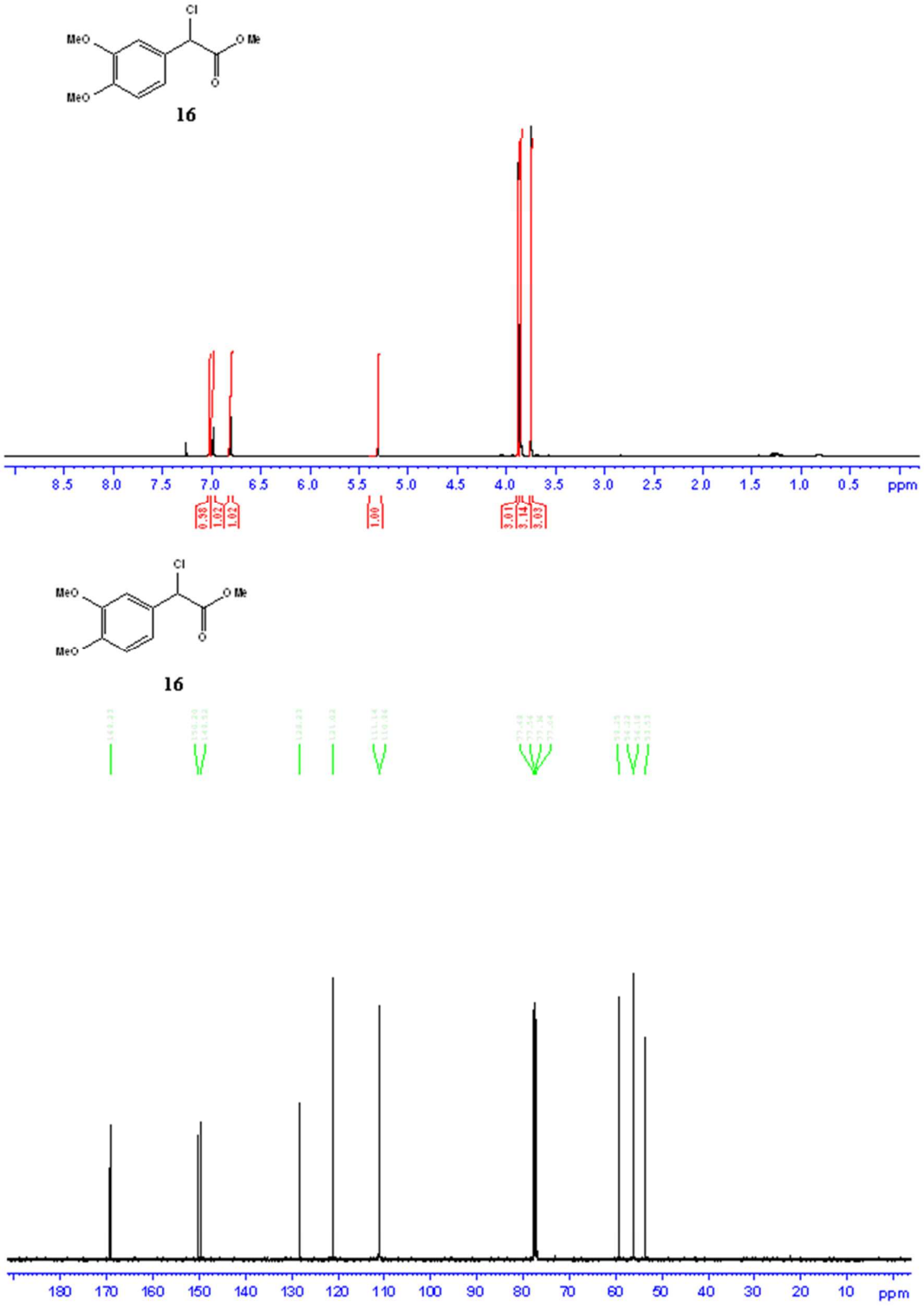


**Figure S.13.** NMR spectra for the chemical structure **16**.

# 17

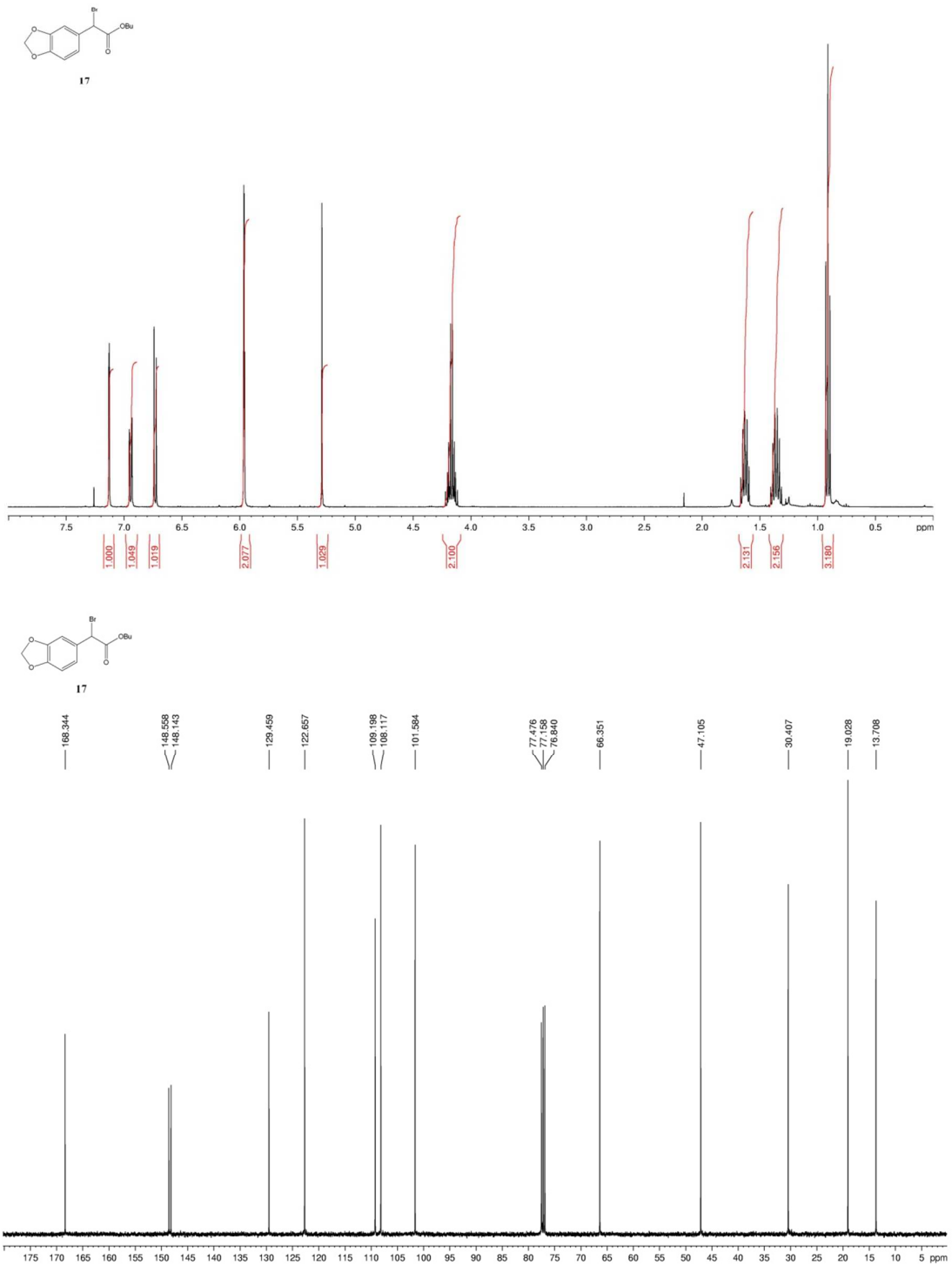


**Figure S.14.** NMR spectra for the chemical structure **17**.

# 18

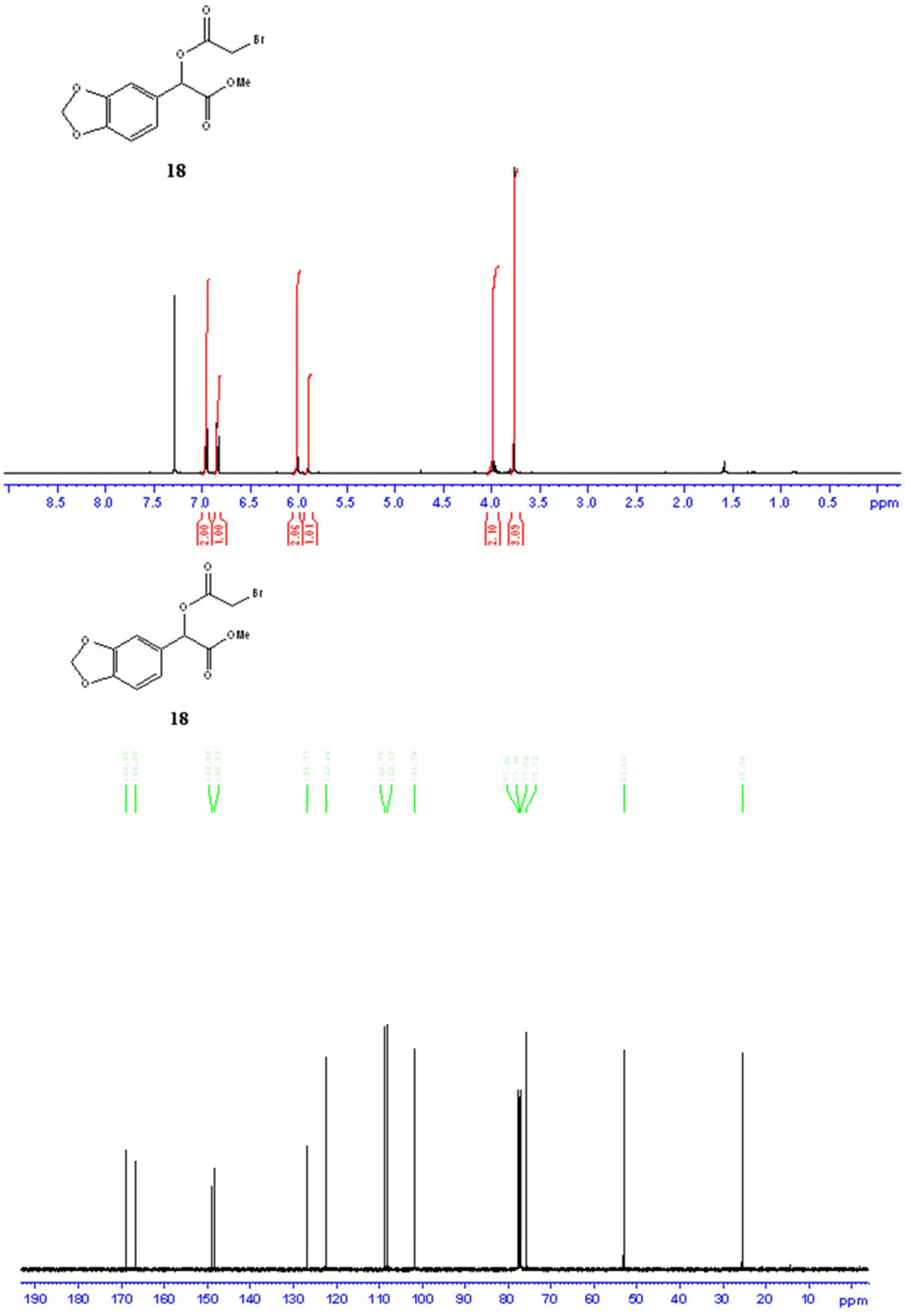


**Figure S.15.** NMR spectra for the chemical structure **18**.

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