Supplementary Information

Synthesis of 1,2-Bisalkylidenecyclopentanes from 1,6-Allenynes *via* Stereoselective Addition of Nucleophiles to Ruthenacyclopentenes

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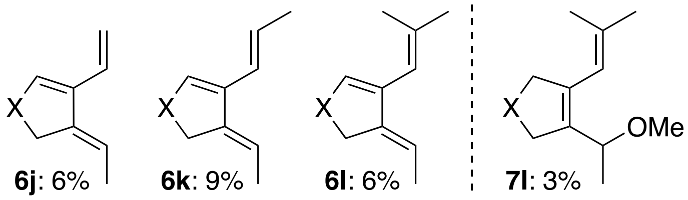
Additional Information

When 1,6-allenynes **3j–l** were employed (Table 1, runs 10–12), cycloisomerization products **6j–l** and MeOH adduct **7l** were obtained in low yields. Formation of these by-products is rationalized by b-hydride elimination from **C** or **E** followed by reductive elimination, as explained in CpRu-catalyzed enyne cycloisomerization. See: B. M. Trost and F. D. Toste, *J. Am. Chem. Soc.*, 2000, **122**, 714. These results also suggested that the reaction proceeded via ruthenacyclopentenes **C** and **E**.



6j: 6% **6k**: 9% **6l**: 6% **7l**: 3%

Experimental Procedure and Spectral Data

General Experimental Details

All manipulations were performed under an argon atmosphere unless stated otherwise. THF, Et_2O, toluene and DMF were purified under argon using The Ultimate Solvent System (Glass Counter Inc.). MeOH, EtOH, ^{i}PrOH, and ^{t}BuOH were distilled from sodium under argon atmosphere. AcOH was dried by azeotropic removal of water with benzene and then distilled under reduced pressure. All other solvents and reagents were purified when necessary by standard procedures. Chromatography was performed on silica gel 60 (Merck, 230–400 mesh) with the indicated solvent as eluent. IR spectra were obtained on a Perkin-Elmer FTIR 1605 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopy were carried out on a Jeol ECX400 or a Jeol ECS400 NMR spectrometer, and ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectroscopy were carried out on a Jeol ECA500 NMR spectrometer. Mass spectra were obtained on a Jeol JMS-100GCv mass spectrometer for EI-LRMS and EI-HRMS, and on a Jeol JMS-T100LP or a Thermo Scientific Exactive mass spectrometer for ESI-LRMS and ESI-HRMS.

General Procedure for Ruthenium-Catalyzed Reactions

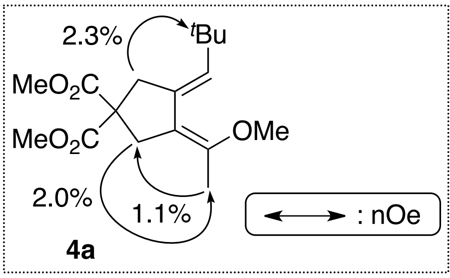
Method A (Without Acid Treatment)
A mixture of an allenyne and Cp*RuCl(cod) (5 mol% to the allenyne) in degassed MeOH (0.1 M) was stirred at room temperature under argon atmosphere (1 atm). After removal of volatiles, the residue was purified by column chromatography on silica gel to give a product.

Method B (With Acid Treatment)
A mixture of an allenyne and Cp*RuCl(cod) (5 mol% to the allenyne) in degassed MeOH (0.1 M) was stirred at room temperature under argon atmosphere (1 atm). To the mixture was added 10% HCl aqueous solution at 0 °C and the mixture was stirred at room temperature for ca. 10 min. To the mixture was added saturated $NaHCO_3$ aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to give a product.

Method C (Without Acid Treatment, Table 2)
A mixture of an allenyne, $[Cp^*Ru(MeCN)_3]PF_6$ (5 mol% to the allenyne) and a nucleophile (10 equiv. to the allenyne) in degassed THF (0.1 M) was stirred at room temperature under argon

atmosphere (1 atm). After removal of volatiles, the residue was purified by column chromatography on silica gel to give a product.

Dimethyl (3*E*,4*Z*)-3-(2,2-dimethylpropylidene)-4-(1-methoxyethylidene)cyclopentane-1,1-dicarboxylate (4a). According to the General Procedure (*Method A*), a crude product, which was obtained from **3a** (19.5 mg, 70.0 μmol) and Cp*RuCl(cod) (1.3 mg, 3.4 μmol) in MeOH (0.70 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1) to give **4a** (20.4 mg, 94%) as a colorless oil. IR (neat) 1738, 1656, 1435, 1269, 1205 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.41 (t, J = 2.3 Hz, 1H), 3.72 (s, 6H), 3.60 (s, 3H), 3.09 (d, J = 2.3 Hz, 2H), 2.88 (br s, 2H), 1.90 (s, 3H), 1.13 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.0 (2C), 147.1, 136.1, 133.2, 115.1, 58.2, 54.7, 52.7 (2C), 39.1, 37.8, 32.8, 30.7 (3C), 15.7; ESI-HRMS calcd for $C_{17}H_{26}O_5Na$ 333.16725 [(M+Na)$^+$], found 333.16748.



Dimethyl 3-acetyl-4-neopentylcyclopent-3-ene-1,1-dicarboxylate (5a). According to the General Procedure (*Method B*), a crude product, which was obtained from **3a** (21.2 mg, 76.1 μmol), Cp*RuCl(cod) (1.5 mg, 3.9 μmol) in MeOH (0.76 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1) to give **5a** (24.5 mg, quant) as a colorless oil. IR (neat) 1734, 1681, 1606, 1268, 1216 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.33 (s, 2H), 3.18 (s, 2H), 2.49 (s, 2H), 2.22 (s, 3H), 0.94 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 197.2, 171.8 (2C), 152.2, 134.0, 57.2, 53.0 (2C), 47.3, 42.2, 41.9, 33.1, 30.6, 30.3 (3C); ESI-HRMS calcd for $C_{16}H_{24}O_5Na$ 319.15160 [(M+Na)$^+$], found 319.15162.

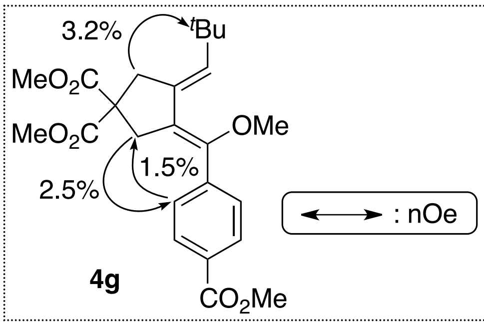
1-Acetyl-4,4-bis[(benzyloxy)methyl]-2-neopentylcyclopentene (5b). According to the General Procedure (*Method B*), a crude product, which was obtained from **3b** (42.6 mg, 105 μmol) and Cp*RuCl(cod) (2.0 mg, 5.3 μmol) in MeOH (1.06 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **5b** (36.6 mg, 82%) as a colorless oil. IR (neat) 1678, 1604, 1227, 1100 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.36-7.26 (m, 10H), 4.53 (s, 4H), 3.44 (s, 4H), 2.60 (s, 2H), 2.49 (d, J = 6.9 Hz, 4H), 2.17 (s, 3H), 0.93 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 198.6, 153.9, 138.5 (2C), 135.2, 128.3 (2C), 127.49 (4C), 127.47 (4C), 73.5 (2C), 73.2 (2C), 46.6, 45.1, 42.5, 40.9, 32.9, 30.6, 30.5 (3C); EI-LRMS *m/z* 420 (M$^+$), 329, 299, 91, 57, 43; EI-HRMS calcd for $C_{28}H_{36}O_3$ 420.26644, found 420.26483.

1-Acetyl-4,4-bis(hydroxymethyl)-2-neopentylcyclopentene (5c). According to the General Procedure (*Method B*), a crude product, which was obtained from **3c** (15.0 mg, 67.5 μmol) and Cp*RuCl(cod) (1.2 mg, 3.2 μmol) in MeOH (0.67 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 1/1) to give **5c** (14.1 mg, 87%) as a colorless oil. IR (film, $CHCl_3$) 3399, 1671, 1600, 1039 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.68 (dd, J = 12.7, 10.4 Hz, 4H), 2.87 (br s, 2H), 2.56 (s, 2H), 2.48 (s, 2H), 2.43 (t, J = 2.0 Hz, 2H), 2.20 (s, 3H), 0.93 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 198.9, 153.8, 135.2, 69.3 (2C), 46.1, 45.7, 42.7, 40.2, 32.9, 30.6, 30.5 (3C); EI-LRMS *m/z* 240 (M$^+$), 184, 153, 57, 43; EI-HRMS calcd for $C_{14}H_{24}O_3$ 240.17254, found 240.17175.

Dimethyl 3-neopentyl-4-propionylcyclopent-3-ene-1,1-dicarboxylate (5d). According to the General Procedure (*Method B*), a crude product, which was obtained from **3d** (57.1 mg, 195 μmol) and Cp*RuCl(cod) (3.7 mg, 9.7 μmol) in MeOH (1.95 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1) to give **5d** (60.7 mg, quant) as a colorless oil.

IR (neat) 1738, 1685, 1609, 1263, 1202 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 6H), 3.31 (br s, 2H), 3.15 (br s, 2H), 2.48 (q, J = 7.2 Hz, 2H), 2.48 (s, 2H), 1.03 (t, J =7.2 Hz, 3H), 0.93 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 199.8, 171.8 (2C), 151.8, 133.6, 57.4, 53.0 (2C), 47.1, 42.1, 41.4, 35.7, 33.0, 30.3 (3C), 7.4; EI-LRMS *m/z* 310 (M^+), 281, 251, 197, 195, 59, 57; EI-HRMS calcd for $C_{17}H_{26}O_5$ 310.17802, found 310.17759.

Dimethyl 3-[(2-hydroxy)ethanoyl]-4-neopentylcyclopent-3-ene-1,1-dicarboxylate (5e). According to the General Procedure (*Method B*), a crude product, which was obtained from **3e** (30.6 mg, 104 μmol) and Cp*RuCl(cod) (2.1 mg, 9.7 μmol) in MeOH (1.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 5/2) to give **5e** (27.4 mg, 84%) as a colorless oil. IR (neat) 3466, 1737, 1683, 1266, 1207 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.29 (d, J = 3.4 Hz, 2H), 3.75 (s, 6H), 4.29 (t, J = 3.4 Hz, 1H), 3.25 (s, 2H), 3.21 (s, 2H), 2.58 (s, 2H), 0.96 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.4, 171.5 (2C), 157.3, 129.9, 67.8, 57.6, 53.1 (2C), 47.3, 42.8, 39.3, 33.4, 30.3 (3C); EI-LRMS *m/z* 312 (M^+), 281, 253, 221, 59, 57; EI-HRMS calcd for $C_{16}H_{24}O_6$ 312.15729, found 312.15730.

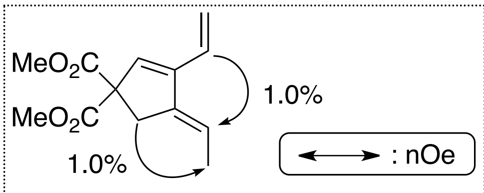


Dimethyl (3*E*,4*Z*)-3-(2,2-dimethylpropylidene)-4-[methoxy(phenyl)methylene]cyclopentane-1,1-dicarboxylate (4f). According to the General Procedure (*Method A*), a crude product, which was obtained from **3f** (26.5 mg, 77.8 μmol) and Cp*RuCl(cod) (1.6 mg, 4.2 μmol) in MeOH (0.78 mL) for 16 h, was purified by column chromatography on silica gel (toluene) to give **4f** (28.9 mg, quant) as a colorless oil. IR (neat) 1738, 1647, 1435, 1261 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 6.65 (t, J = 2.3 Hz, 1H), 3.67 (s, 6H), 3.39 (s, 3H), 3.16 (d, J = 2.3 Hz, 2H), 2.85 (s, 2H), 1.19 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.7 (2C), 149.9, 137.8, 135.9, 133.3, 128.9 (2C), 128.2 (2C), 128.0, 119.4, 58.6, 56.6, 52.7 (2C), 38.9, 38.7, 33.0, 30.6 (3C); EI-LRMS *m/z* 372 (M^+), 357, 313, 281, 77, 57; EI-HRMS calcd for $C_{22}H_{28}O_5$ 372.19367, found 372.19303.

Dimethyl (3*E*,4*Z*)-3-(2,2-dimethylpropylidene)-4-{methoxy[4-(methoxycarbonyl)phenyl] methylene}cyclopentane-1,1-dicarboxylate (4g). According to the General Procedure (*Method A*), a crude product, which was obtained from **3g** (30.2 mg, 75.8 μmol) and Cp*RuCl(cod) (1.3 mg, 3.4 μmol) in MeOH (0.76 mL) for 75 h, was purified by column chromatography on silica gel (hexane/AcOEt = 9/1) to give **4g** (27.3 mg, 84%) as a colorless oil. IR (neat) 1736, 1607, 1435, 1279, 1207 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 6.67 (t, J = 2.3 Hz, 1H), 3.92 (s, 3H), 3.67 (s, 6H), 3.40 (s, 3H), 3.16 (d, J = 2.3 Hz, 2H), 2.87 (s, 2H), 1.18 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.5 (2C), 166.7, 148.8, 140.7, 139.0, 133.1, 129.53 (2C), 129.48 (2C), 128.8, 121.8, 58.6, 56.9, 52.7 (2C), 52.1, 38.7 (2C), 33.1, 30.5 (3C); EI-LRMS *m/z* 430 (M^+), 415, 373, 339, 313; EI-HRMS calcd for $C_{24}H_{30}O_7$ 430.19915, found 430.19910.

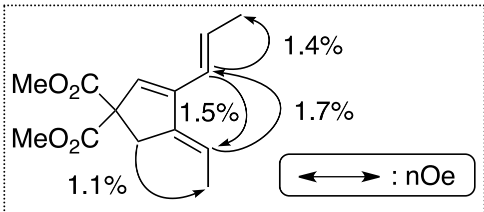
Dimethyl (3*E*,4*Z*)-3-(2,2-dimethylpropylidene)-4-{methoxy[4-(methoxy)phenyl]methylene}cyclopentane-1,1-dicarboxylate (4h). According to the General Procedure (*Method A*), a crude product, which was obtained from **3h** (20.7 mg, 55.9 μmol) and Cp*RuCl(cod) (1.0 mg, 2.6 μmol) in MeOH (0.56 mL) for 5 h, was purified by column chromatography on silica gel (toluene/CH_2Cl_2 = 5/1) to give **4h** (18.9 mg, 84%) as a colorless oil. IR (neat) 1737, 1645, 1436, 1251, 1173 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 6.92-6.88 (m, 2H), 6.61 (t, J = 2.3 Hz, 1H), 3.83 (s, 3H), 3.67 (s, 6H), 3.39 (s. 3H), 3.15 (d, J = 2.3 Hz, 2H), 2.84 (br s, 2H), 1.18 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.8 (2C), 159.2, 149.7, 137.3, 133.3, 130.2 (2C), 128.2, 118.7, 113.6 (2C), 58.6, 56.5, 55.2, 52.7 (2C), 38.9, 38.8, 33.0, 30.6 (3C); EI-LRMS m/z 402 (M^+), 387, 371, 345, 311, 295, 59; EI-HRMS calcd for $C_{23}H_{30}O_6$ 402.20424, found 402.20315.

Dimethyl (3*Z*,4*E*)-3-(2,2-dimethylpropylidene)-4-[methoxy(methoxycarbonyl)methylene]cyclopentane-1,1-dicarboxylate (4i). According to the General Procedure (*Method A*), a crude product, which was obtained from **3i** (28.3 mg, 87.8 μmol) and Cp*RuCl(cod) (1.8 mg, 4.8 μmol) in MeOH (0.88 mL) for 72 h, was purified by column chromatography on silica gel (hexane/AcOEt = 8/1) to give **4i** (19.5 mg, 63%) as a colorless oil. IR (neat) 1738, 1634, 1436, 1268, 1202 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.87 (t, J = 2.3 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 6H), 3.56 (s, 3H), 3.36 (s, 2H), 3.10 (d, J = 2.3 Hz, 2H), 1.15 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.6 (2C), 165.3, 145.3, 140.1, 138.7, 133.2, 58.2, 58.1, 52.8 (2C), 51.7, 38.8, 38.0, 33.4, 30.2 (3C); EI-LRMS m/z 354 (M^+), 297, 59, 57; EI-HRMS calcd for $C_{18}H_{26}O_7$ 354.16785, found 354.16753.



6j

Dimethyl 3-acetyl-4-ethylcyclopent-3-ene-1,1-dicarboxylate (5j) and (*E*)-Dimethyl 4-ethylidene-3-vinylcyclopent-2-ene-1,1-dicarboxylate (6j). According to the General Procedure (*Method B*), a crude product, which was obtained from **3j** (51.0 mg, 216 μmol) and Cp*RuCl(cod) (4.2 mg, 11.1 μmol) in MeOH (2.15 mL) for 24 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **5j** (44.6 mg, 81%) as a colorless oil, and **6j** (3.1 mg, 6%) as a colorless oil, respectively. **5j**: IR (neat) 1737, 1683, 1435, 1263, 1201 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.71 (s, 6H), 3.30-3.28 (m, 2H), 3.15 (br s, 2H), 2.51 (q, J = 7.5 Hz, 2H), 2.20 (s, 3H), 1.03 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.5, 171.8 (2C), 155.6, 131.6, 56.5, 52.9 (2C), 44.8, 41.8, 30.2, 23.0, 12.0; EI-LRMS m/z 254 (M^+), 195, 163, 152, 135, 59, 43; EI-HRMS calcd for $C_{13}H_{18}O_5$ 268.11542, found 268.11512. **6j**: IR (film, $CHCl_3$) 1737, 1435, 1252, 1056 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.35 (dd, J = 17.6, 11.3 Hz, 1H), 6.07 (s, 1H), 5.63 (dd, J = 17.6, 1.7 Hz, 1H), 5.62-5.57 (m, 1H), 5.29 (dd, J = 11.3, 1.7 Hz, 1H), 3.75 (s, 6H), 3.17 (br s, 2H), 1.73 (d, J = 6.9 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.2 (2C), 145.1, 141.4, 128.5, 127.3, 118.6, 116.0, 63.3, 52.9 (2C), 35.9, 14.8; EI-LRMS m/z 236 (M^+), 177, 145, 117; EI-HRMS calcd for $C_{13}H_{16}O_4$ 236.10486, found 236.10446.

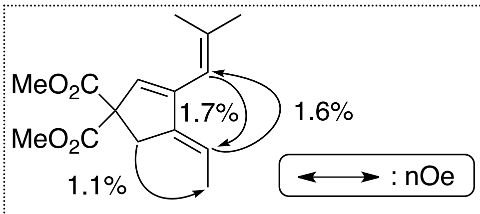


6k

Dimethyl 3-acetyl-4-propylcyclopent-3-ene-1,1-dicarboxylate (5k) and (*E*)-Dimethyl 4-ethylidene-3-[(*E*)-prop-1-enyl]cyclopent-2-ene-1,1-dicarboxylate (6k). According to the General Procedure (*Method B*), a crude product, which was obtained from **3k** (56.5 mg, 226 μmol) and Cp*RuCl(cod) (4.3 mg, 11.3 μmol) in MeOH (2.25 mL) for 24 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **5k** (46.8 mg, 77%) as a colorless oil, and **6k** (5.1 mg, 9%) as a colorless oil, respectively. **5k**: IR (neat) 1737, 1683, 1435, 1253, 1201 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.34-3.32 (m, 2H), 3.18-3.16 (m, 2H), 2.50 (tt, J = 1.2, 7.6 Hz, 2H), 2.24 (s, 3H), 1.50 (ttq, J = 1.9, 7.6, 7.6 Hz, 2H), 0.93 (t, J = 7.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.6, 171.8 (2C), 154.2, 132.3, 56.5, 52.9 (2C), 45.2, 41.8, 31.6, 30.3, 21.0, 13.9; EI-LRMS m/z 268 (M^+), 237, 209, 177, 166, 149, 59, 43; EI-HRMS calcd for $C_{14}H_{20}O_5$ 268.13107, found 238.13065. **6k**: IR (neat) 1737, 1435, 1263, 1172 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.15 (dq, J = 15.5, 6.6 Hz, 1H), 6.02 (dq, J = 15.5, 1.7 Hz, 1H), 5.97 (s, 1H), 5.57 (tq, J =

2.5, 6.9 Hz, 1H), 3.74 (s, 6H), 3.16-3.14 (m, 2H), 1.81 (dd, J = 6.6, 1.7 Hz, 3H), 1.72 (d, J = 6.9 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.4 (2C), 144.8, 141.8, 130.4, 125.7, 122.3, 115.6, 63.3, 52.9 (2C), 35.8, 18.7, 14.8; EI-LRMS m/z 250 (M^+), 191, 159, 131, 59; EI-HRMS calcd for $C_{14}H_{18}O_4$ 250.12051, found 250.12019.

Dimethyl 3-acetyl-4-isobutylcyclopent-3-ene-1,1-dicarboxylate (5l), (*E*)-Dimethyl 4-ethylidene-3-(2-methylprop-1-enyl)cyclopent-2-ene-1,1-dicarboxylate (6l), and Dimethyl 3-(1-methoxyethyl)-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (7l). According to the General Procedure (*Method B*), a crude product, which was obtained from **3l** (57.8 mg, 219 μmol) and Cp*RuCl(cod) (4.2 mg, 11.1 μmol) in MeOH (2.2 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **5l** (52.0 mg, 84%) as a colorless oil, **6l** (3.5 mg, 6%) as a colorless oil, and **7l** (2.1 mg, 3%) as a colorless oil, respectively. **5l**: IR (neat) 1737, 1684, 1435, 1254, 1201 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 6H), 3.33-3.32 (m, 2H), 3.14-3.13 (m, 2H), 2.42-2.39 (m, 2H), 2.23 (s, 3H), 1.85 (septet, J = 6.8 Hz, 1H), 0.88 (d, J = 6.8 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.8, 171.9 (2C), 153.5, 133.1, 56.7, 53.0 (2C), 45.6, 41.9, 38.5, 30.5, 27.6, 22.5 (2C); EI-LRMS m/z 282 (M^+), 267, 251, 223, 191, 163, 59, 43; EI-HRMS calcd for $C_{15}H_{22}O_5$ 282.14672, found 282.14611. **6l**: IR (neat) 1736, 1436, 1250, 1172 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.83 (br s, 1H), 5.71-5.69 (m, 1H), 5.44 (tq, J = 2.4, 7.0 Hz, 1H), 3.75 (s, 6H), 3.13-3.11 (m, 2H), 1.82 (br s, 3H), 1.80-1.78 (m, 3H), 1.71 (d, J = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.6 (2C), 144.2, 143.2, 139.8, 128.5, 116.4, 115.6, 63.8, 52.9 (2C), 35.0, 26.5, 20.1, 14.7; EI-LRMS m/z 264 (M^+), 205, 173, 145, 59; EI-HRMS calcd for $C_{15}H_{20}O_4$ 264.13616, found 264.13546. **7l**: IR (neat) 1737, 1435, 1259, 1199, 1087 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.77 (br s, 1H), 4.13 (q, J = 6.6 Hz, 1H), 3.74 (s, 3H), 3.74 (s, 3H), 3.31-3.17 (m, 2H), 3.15 (s, 3H), 3.01 (br s, 2H), 1.80 (br s, 3H), 1.74 (br s, 3H), 1.22 (d, J = 6.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.7, 172.6, 136.3, 136.2, 134.5, 118.5, 72.4, 57.7, 55.8, 52.80, 52.75, 44.4, 38.1, 27.0, 20.0, 19.2; EI-LRMS m/z 296 (M^+), 281, 265, 264, 205, 59; EI-HRMS calcd for $C_{16}H_{24}O_5$ 296.16237, found 296.16201.



6l

Dimethyl 3-acetyl-4-[(methoxycarbonyl)methyl]cyclopent-3-ene-1,1-dicarboxylate (5m). According to the General Procedure (*Method B*), a crude product, which was obtained from **3m** (69.8 mg, 249 μmol) and Cp*RuCl(cod) (4.8 mg, 12.6 μmol) in MeOH (2.5 mL) for 85 h, was purified by column chromatography on silica gel (hexane/AcOEt = 8/1) to give **5m** (19.8 mg, 27%) as a colorless oil. IR (neat) 1737, 1685, 1436, 1257, 1203 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 6H), 3.68 (s, 3H), 3.65-3.63 (m, 2H), 3.39-3.38 (m, 2H), 3.27-3.25 (m, 2H), 2.23 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.6, 171.5 (2C), 170.1, 144.8, 134.4, 57.0, 53.1 (2C), 52.0, 45.3, 41.6, 34.9, 30.2; EI-LRMS m/z 298 (M^+), 267, 239, 207, 179, 59; EI-HRMS calcd for $C_{14}H_{18}O_7$ 298.10525, found 298.10558.

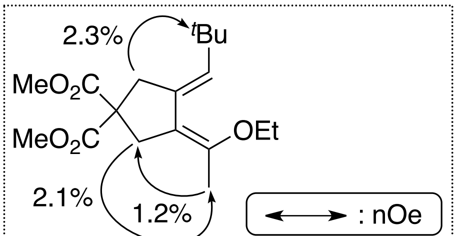
Compound 4f-D. According to the General Procedure (*Method A*), a crude product, which was obtained from **3f** (26.3 mg, 77.3 μmol) and Cp*RuCl(cod) (1.5 mg, 3.9 μmol) in MeOH (0.77 mL) for 44 h, was purified by column chromatography on silica gel (toluene/CH_2Cl_2 = 5/1) to give **4f-D** (24.0 mg, 83%) as a colorless oil. IR (neat) 1737, 1645, 1435, 1261 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 5H), 6.65 (d, J = 2.8 Hz, 1H), 3.68 (s, 6H), 3.14 (d, J = 2.8 Hz, 1H), 2.85 (s, 2H), 1.19 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.72, 171.70, 149.9, 137.8, 135.9, 133.2, 128.9 (2C), 128.2 (2C), 128.0, 119.4, 58.5, 55.7 (septet, J = 21.8 Hz), 52.6 (2C), 38.7, 38.6 (t, J = 20.5 Hz), 33.0, 30.6 (3C); EI-LRMS m/z 376 (M^+), 361, 317, 77; EI-HRMS calcd for $C_{22}H_{24}D_4O_5$

376.21878, found 376.21776.

Dimethyl 3-ethyl-4-propionylcyclopent-3-ene-1,1-dicarboxylate (5n). According to the General Procedure (*Method B*), a crude product, which was obtained from **3n** (50.0 mg, 200 μmol) and Cp*RuCl(cod) (3.8 mg, 10 μmol) in MeOH (2.0 mL) for 24 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **5n** (45.9 mg, 86%) as a colorless oil. IR (neat) 1737, 1683, 1435, 1263, 1201 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.72 (s, 6H), 3.30 (br s, 2H), 3.13 (br s, 2H), 2.52 (q, J = 7.4 Hz, 2H), 2.48 (q, J = 7.6 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 199.4, 171.9 (2C), 155.3, 131.0, 56.8, 53.0 (2C), 44.6, 41.5, 35.4, 23.0, 12.0, 7.4; EI-LRMS m/z 269 [$(M+H)^+$], 268 (M^+), 209, 177, 152, 149, 59, 57; EI-HRMS calcd for $C_{14}H_{20}O_5$ 268.13107, found 268.13076.

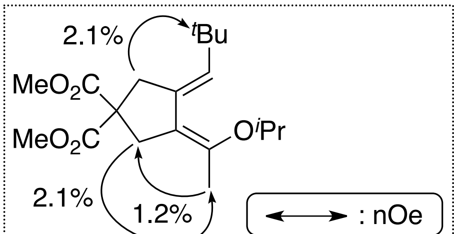
Compound 4a and 5a (Table 2, run 1). According to the General Procedure (*Method C*), a crude product, which was obtained from **3a** (28.1 mg, 101 μmol), $[Cp^*Ru(MeCN)_3]PF_6$ (2.6 mg, 5.2 μmol), and MeOH (41 μL, 1.01 mmol) in THF (1.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et_3N) to give **4a** (27.0 mg, 86%) as a colorless oil and **5a** (2.2 mg, 7%) as a colorless oil, respectively.

Dimethyl (3*E*,4*Z*)-3-(2,2-dimethylpropylidene)-4-(1-ethoxyethylidene)cyclopentane-1,1-dicarboxylate (4o). According to the General Procedure (*Method C*), a crude product, which was obtained from **3a** (25.8 mg, 92.7 μmol), $[Cp^*Ru(MeCN)_3]PF_6$ (2.3 mg, 4.6 μmol), and EtOH (54 μL, 0.92 mmol) in THF (0.92 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et_3N) to give **4o** (22.2 mg, 74%) as a colorless oil and **5a** (4.4 mg, 16%) as a colorless oil, respectively. IR (neat) 1738, 1655, 1435, 1259, 1201 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.53 (t, J = 2.2 Hz, 1H), 3.84 (q, J = 7.0 Hz, 2H), 3.72 (s, 6H), 3.09 (d, J = 2.2 Hz, 2H), 2.88 (br s, 2H), 1.90 (br s, 3H), 1.28 (t, J = 7.0 Hz, 3H), 1.13 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.0 (2C), 146.4, 136.2, 133.2, 115.5, 62.9, 58.2, 52.7 (2C), 39.1, 37.7, 32.8, 30.7 (3C), 16.2, 15.2; ESI-HRMS calcd for $C_{18}H_{29}O_5$ [$(M+H)^+$] 325.20150, found 325.20155.



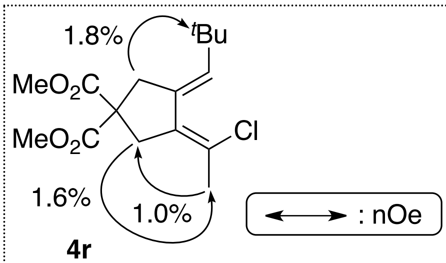
4o

Dimethyl (3*E*,4*Z*)-3-(2,2-dimethylpropylidene)-4-(1-isopropoxyethylidene)cyclopentane-1,1-dicarboxylate (4p). According to the General Procedure (*Method C*), a crude product, which was obtained from **3a** (27.1 mg, 97.4 μmol), $[Cp^*Ru(MeCN)_3]PF_6$ (2.5 mg, 5.0 μmol), and ^{i}PrOH (75 μL, 0.97 mmol) in THF (0.97 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et_3N) to give **4p** (28.9 mg, 88%) as a colorless oil and **5a** (1.4 mg, 5%) as a colorless oil, respectively. **4p**: IR (neat) 1739, 1655, 1435, 1269, 1213 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.61 (t, J = 2.0 Hz, 1H), 4.24 (septet, J = 6.1 Hz, 1H), 3.71 (s, 3H), 3.71 (s, 3H), 3.07 (d, J = 2.0 Hz, 2H), 2.87 (br s, 2H), 1.85 (s, 3H), 1.20 (d, J = 6.1 Hz, 6H), 1.11 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.0 (2C), 144.7, 136.3, 132.8, 118.3, 69.2, 58.3, 52.7 (2C), 39.0, 37.9, 32.8, 30.7 (3C), 22.6 (2C), 16.7; ESI-HRMS calcd for $C_{19}H_{31}O_5$ [$(M+H)^+$] 339.21715, found 339.21695.



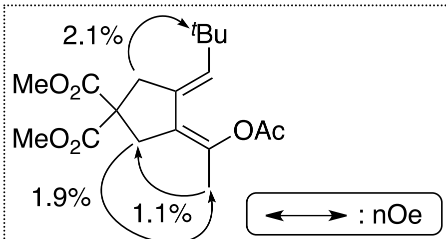
4p

Dimethyl (3*Z*,4*E*)-3-(1-acetoxyethylidene)-4-(2,2-dimethylpropylidene)cyclopentane-1,1-dicarboxylate (4q). According to the General Procedure (*Method C*), a crude product, which was obtained from **3a** (28.0 mg, 101 μmol), [Cp*Ru(MeCN)$_3$]PF$_6$ (2.7 mg, 5.4 μmol), and AcOH (57 μL, 1.00 mmol) in THF (1.0 mL) for 19 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et$_3$N) to give **4q** (25.4 mg, 75%) as a white solid. mp: 110-112 °C; IR (film, CHCl$_3$) 1745, 1736, 1436, 1370 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$) δ 5.99 (t, *J* = 2.2 Hz, 1H), 3.72 (s, 6H), 3.06 (d, *J* = 2.2 Hz, 2H), 2.93 (br s, 2H), 2.12 (s, 3H), 1.93 (s, 3H), 1.10 (s, 9H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 171.5 (2C), 168.5, 139.4, 138.2, 132.2, 124.5, 57.9, 52.8 (2C), 38.6, 37.2, 32.9, 30.5 (3C), 21.0, 18.9; EI-LRMS *m/z* 338 (M$^+$), 296, 281, 240, 181; EI-HRMS calcd for $C_{18}H_{26}O_6$ 338.17294, found 338.17268.



4r

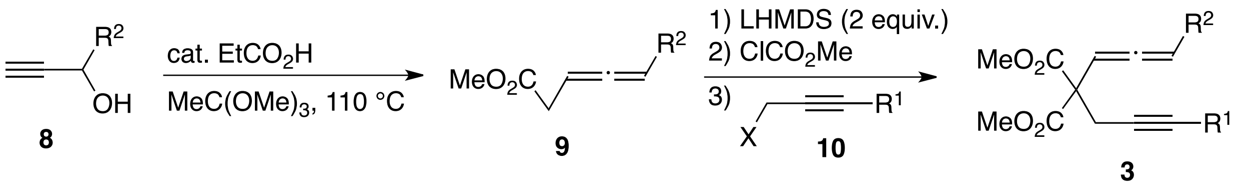
Dimethyl (3*Z*,4*E*)-3-(1-chloroethylidene)-4-(2,2-dimethylpropylidene)cyclopentane-1,1-dicarboxylate (4r). According to the General Procedure (*Method C*), a crude product, which was obtained from **3a** (27.7 mg, 99.5 μmol), [Cp*Ru(MeCN)$_3$]PF$_6$ (2.5 mg, 5.0 μmol), and a solution of HCl in Et$_2$O (1.0 mL, 1.0 M, 1.0 mmol) in THF (1.0 mL) for 6 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1 with 1% Et$_3$N) to give **4r** (20.6 mg, 61%) as a colorless oil. IR (film, CHCl$_3$) 1739, 1640, 1435, 1263, 1206 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$) δ 6.66 (t, *J* = 2.3 Hz, 1H), 3.74 (s, 6H), 3.13 (d, *J* = 2.3 Hz, 2H), 2.98 (d, *J* = 1.1 Hz, 2H), 2.15 (br s, 3H), 1.14 (s, 9H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 171.5 (2C), 140.3, 132.5, 132.1, 121.1, 57.5, 52.9 (2C), 39.7, 38.7, 33.1, 30.5 (3C), 25.9; EI-LRMS *m/z* 314 (M$^+$), 279, 278, 219, 195, 59; EI-HRMS calcd for $C_{16}H_{23}ClO_4$ 314.12849, found 314.12726.



4q

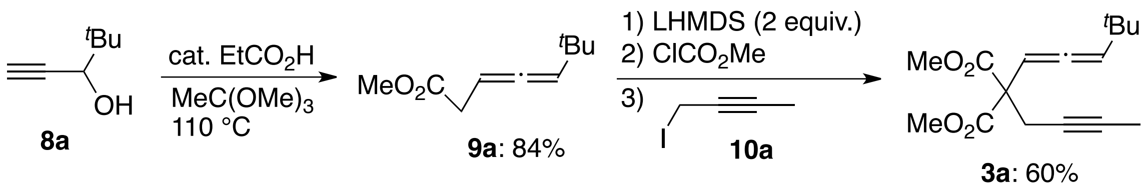
Preparation of 1,6-Allenynes

A new synthetic route to 1,6-allenynes bearing dialkyl malonate moieties has been established (Scheme S1).[1] Thus, methyl α-allenylcarboxylate **9** was easily prepared from the corresponding alcohol **8** and trimethyl orthoacetate via the Johnson-Claisen rearrangement.[2] Next, **9** was treated with 2 equivalents of LHMDS at -78 °C, then the anion of **9** was successively reacted with methyl chloroformate and propargyl halide **10** in a one pot to give 1,6-allenyne **3**.



Scheme S1.** General procedure for the synthesis of 1,6-allenynes **3

~ *Preparation of **3a*** ~



Scheme S2.** Preparation of **3a

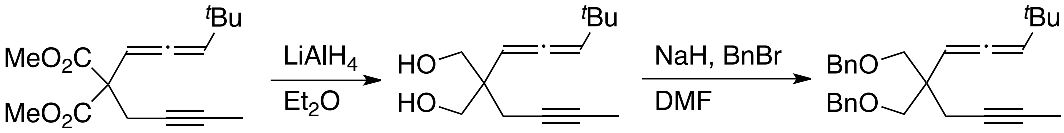
Methyl 6,6-dimethylhepta-3,4-dienoate (9a). Into a flask equipped with a Dean-Stark trap were placed **8a**[3] (2.243 g, 20.00 mmol), trimethyl orthoacetate (15.0 mL, 120 mmol), and propanoic acid (0.30 mL, 4.02 mmol). The mixture was stirred and heated at 110 °C for 48 h and remaining trimethyl orthoacetate was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give **9a** (2.840 g, 84%) as a colorless oil. IR (neat) 1968, 1737, 1435, 1229, 1061 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.27 (dt, J = 6.5, 7.2 Hz, 1H), 5.18 (dt, J = 6.5, 2.9 Hz, 1H), 3.69 (s, 3H), 3.02 (dd, J = 7.2, 2.9 Hz, 2H), 1.02 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 202.3, 172.0, 104.2, 85.7, 51.8, 35.1, 31.8, 30.0 (3C); EI-LRMS m/z 168 (M^+), 153, 140, 125, 111, 109, 57; EI-HRMS calcd for $C_{10}H_{16}O_2$ 168.11503, found 168.11467.

5,5-Bis(methoxycarbonyl)-9,9-dimethyldeca-6,7-dien-2-yne (3a). To a solution of **9a** (917.7 mg, 5.455 mmol) in THF (6.4 mL) was slowly added a solution of LHMDS in THF (1.60 M, 7.1 mL, 11.4 mmol) at -78 °C, and the mixture was stirred at the same temperature for 25 min. To the mixture was slowly added methyl chloroformate (0.42 mL, 5.44 mmol) at -78 °C, and the mixture was stirred at the same temperature for 5 min. To the mixture was slowly added **10a**[4] (1.950 g, 10.84 mmol) in THF (3.0 mL) at -78 °C, and the mixture was allowed to warm to room temperature over 1 h and stirred at the same temperature overnight. To the mixture was added saturated NH_4Cl aqueous solution, and the aqueous layer was extracted with AcOEt. The organic layer was washed

[1] For the synthesis of 1,6-allenyne via direct coupling of malonate derivative and bromoallenes, see: V. Pardo-Rodríguez, J. Marco-Martínez, E. Buñuel and D. J. Cárdenas, *Org. Lett.*, 2009, **11**, 4548.
[2] G. Lai and W. K. Anderson, *Synth. Commun.*, 1995, **25**, 4087.
[3] M. A. Henderson and C. H. Heathcock, *J. Org. Chem.*, 1988, **53**, 4736.
[4] A. Fürstner, K. Grela, C. Mathes and C. W. Lehmann, *J. Am. Chem. Soc.*, 2000, **122**, 11799.

with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give **3a** (915.3 mg, 60%) as a colorless oil. IR (neat) 1968, 1741, 1435, 1230, 1203 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.79 (d, J = 6.3 Hz, 1H), 5.38 (d, J = 6.3 Hz, 1H), 3.74 (s, 6H), 2.89-2.79 (m, 2H), 1.73 (t, J = 2.6 Hz, 3H), 1.03 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.4, 169.8, 169.7, 107.5, 91.8, 78.5, 73.7, 58.1, 52.82, 52.80, 32.2, 29.8 (3C), 25.3, 3.5; ESI-HRMS calcd for $C_{16}H_{22}O_4Na$ 301.1410, found 301.1407.

~ *Preparation of **3b** and **3c*** ~



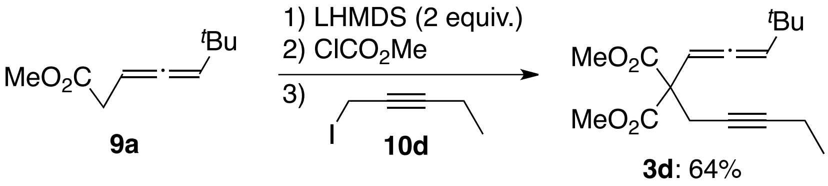
3a **3c**: 61% **3b**: 98%

Scheme S3. *Preparation of **3b** and **3c***

5,5-Bis(hydroxymethyl)-9,9-dimethyldeca-6,7-dien-2-yne (3c). To a solution of $LiAlH_4$ (50.1 mg, 1.32 mmol) in Et_2O (2.7 mL) was added to a solution of **3a** (118.4 mg, 425.4 μmol) in Et_2O (1.5 mL) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. To the mixture was added $Na_2SO_4 \cdot 10H_2O$/Celite® (1 to 1 mixture) at 0 °C, and the resulting mixture was stirred at room temperature overnight. The mixture was filtered, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 2/1) to give **3c** (58.1 mg, 61%) as a white solid. mp; 84-86 °C; IR (film, $CHCl_3$) 3310, 1959, 1037 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.29 (d, J = 6.5 Hz, 1H), 5.19 (d, J = 6.5 Hz, 1H), 3.71 (s, 4H), 2.39-2.30 (m, 2H), 2.08-2.04 (br, 2H), 1.79 (t, J = 2.6 Hz, 3H), 1.05 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.5, 105.7, 94.6, 78.4, 75.4, 67.6, 67.5, 44.4, 31.7, 30.1 (3C), 23.4, 3.6; EI-LRMS m/z 207 [$(M-Me)^+$], 191, 57; EI-HRMS calcd for $C_{13}H_{19}O_2$ 207.13850, found 207.13806.

5,5-Bis[(benzyloxy)methyl]-9,9-dimethyldeca-6,7-dien-2-yne (3b). To a suspension of NaH (60% dispersion in mineral oil, 15.8 mg, 395 μmol) in DMF (0.60 mL) was added a solution of **3c** (25.9 mg, 117 μmol) in DMF (0.60 mL) at 0 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture were slowly added BnBr (41.5 μL, 349 μmol) at 0 °C, and the resulting mixture was stirred at room temperature for 11 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **3b** (46.0 mg, 98%) as a colorless oil. IR (neat) 1959, 1101, 735, 697 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.32-7.30 (m, 8H), 7.28-7.24 (m, 2H), 5.33 (d, J = 6.3 Hz, 1H), 5.21 (d, J = 6.3 Hz, 1H), 4.52 (d, J = 2.1 Hz, 4H), 3.49 (d, J = 4.1 Hz, 4H), 2.42-2.33 (m, 2H), 1.74 (t, J = 2.6 Hz, 3H), 1.02 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.2, 138.8 (2C), 128.2 (4C), 127.38 (2C), 127.34 (2C), 127.27 (2C), 105.1, 95.5, 77.4, 76.0, 73.3 (2C), 73.2, 72.9, 43.5, 31.7, 30.1 (3C), 24.0, 3.6; EI-LRMS m/z 387 [$(M-Me)^+$], 349, 311, 281, 255, 91, 57; EI-HRMS calcd for $C_{27}H_{31}O_2$ 387.23240, found 387.23210.

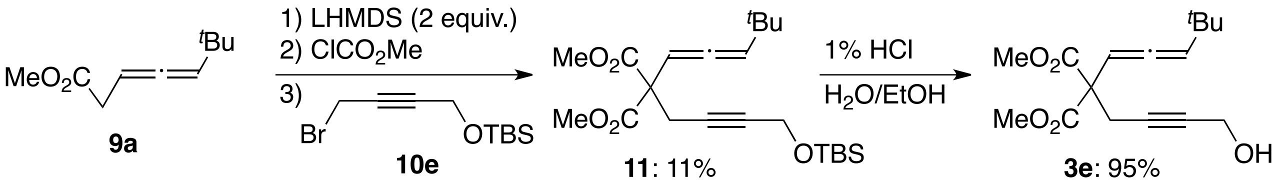
~ *Preparation of* ***3d*** ~



Scheme S4. *Preparation of* ***3d***

6,6-Bis(methoxycarbonyl)-2,2-dimethylundeca-3,4-dien-8-yne (3d). Similar to the synthesis of **3a** from **9a**, a crude product, which was obtained from **9a** (339.2 mg, 2.645 mmol), LHMDS in THF (1.00 M, 4.40 mL, 4.40 mmol), methyl chloroformate (159 μL, 2.06 mmol), and **10d**[5] (724 mg, 3.73 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give **3d** (379.6 mg, 64%) as a colorless oil. IR (neat) 1968, 1737, 1435, 1229, 1061 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.78 (d, J = 6.3 Hz, 1H), 5.36 (d, J = 6.3 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 2.88-2.78 (m, 2H), 2.09 (tq, J = 2.5, 7.6 Hz, 2H), 1.05 (t, J = 7.6 Hz, 3H), 1.02 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.3, 169.8, 169.7, 107.5, 91.8, 84.6, 74.0, 58.1, 52.7 (2C), 32.1, 29.8 (3C), 25.3, 14.5, 12.3; EI-LRMS *m/z* 293 [$(M+H)^+$], 233, 225, 201, 173, 59, 57; EI-HRMS calcd for $C_{17}H_{25}O_4$ 293.17528, found 293.17454.

~ *Preparation of* ***3e*** ~



Scheme S5. *Preparation of* ***3e***

5,5-bis(methoxycarbonyl)-1-(*tert*-butyldimethylsilyloxy)-9,9-dimethyldeca-6,7-dien-2-yne (11). Similar to the synthesis of **3a** from **9a**, a crude product, which was obtained from **9a** (445.6 mg, 2.649 mmol), LHMDS in THF (1.00 M, 5.40 mL, 5.40 mmol), methyl chloroformate (205 μL, 2.65 mmol), and the crude **10e**[6] (819.9 mg, 3.12 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give **11** (119.1 mg, 11%) as a colorless oil. IR (neat) 1968, 1742, 1318, 1230, 1081 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.79 (d, J = 6.3 Hz, 1H), 5.37 (d, J = 6.3 Hz, 1H), 4.23 (t, J = 2.0 Hz, 2H), 3.732 (s, 3H), 3.728 (s, 3H), 2.97-2.87 (m, 2H), 1.02 (s, 9H), 0.88 (s, 9H), 0.08 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.4, 169.6, 169.4, 107.7, 91.7, 81.4, 79.7, 57.7, 52.9 (2C), 51.8, 32.2, 29.9 (3C), 25.8 (3C), 25.3, 18.2, -5.2 (2C); EI-LRMS *m/z* 351 [$(M-^{t}Bu)^+$], 277, 225, 57; EI-HRMS calcd for $C_{18}H_{27}O_5Si$ 351.16277, found 351.16276.

5,5-Bis(methoxylcarbonyl)-9,9-dimethyldeca-6,7-dien-2-yn-1-ol (3e). To a solution of **11** (47.2 mg, 115 μmol) in EtOH (3.1 mL) was added 10% HCl aqueous solution (0.35 mL) at 0 °C, and the mixture was stirred at room temperature for 2.5 h. To the mixture was added saturated $NaHCO_3$ aqueous solution, and the mixture was diluted with MeOH, dried over Na_2SO_4, and concentrated.

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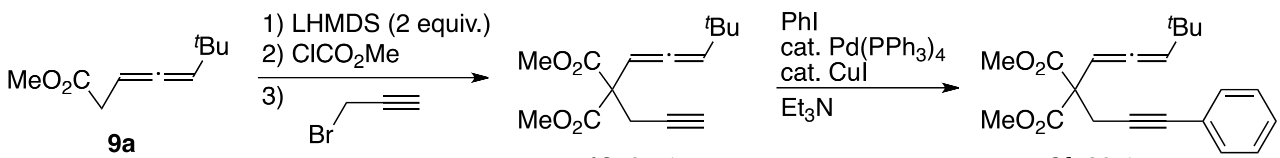
[5] B. Flachsbarth, M. Fritzsche, P. J. Weldon and S. Schulz, *Chem. Biodiv.*, 2009, **6**, 1.
[6] N. E. Schore and S. D. Najdi, *J. Org. Chem.*, 1987, **52**, 5296.

The residue was purified by column chromatography on silica gel (hexane/Et_2O = 5/3) to give **3e** (32.4 mg, 95%) as a colorless oil. IR (film, $CHCl_3$) 3470, 1739, 1232, 1018 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.77 (d, *J* = 6.3 Hz, 1H), 5.39 (d, *J* = 6.3 Hz, 1H), 4.18 (d, *J* = 2.0 Hz, 2H), 3.74 (s, 3H), 3.74 (s, 3H), 2.91 (dt, *J* = 1.8 Hz, 2.0 Hz, 2H), 1.99 (br s, 1H), 1.02 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.4, 169.6, 169.5, 107.8, 91.6, 81.2, 80.8, 57.7, 52.94, 52.93, 51.0, 32.2, 29.8 (3C), 25.2; EI-LRMS *m/z* 225 [$(M-C_4H_5O)^+$], 203, 59, 57; EI-HRMS calcd for $C_{12}H_{17}O_4$ 225.11268, found 225.11269.

*~ Preparation of **3f** ~*

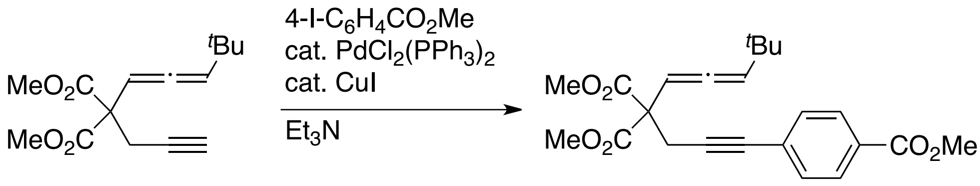


Scheme S6**. Preparation of **3f

4,4-Bis(methoxylcarbonyl)-8,8-dimehylnona-5,6-diene-1-yne (12). Similar to the synthesis of **3a** from **9a**, a crude product, which was obtained from **9a** (169.2 mg, 1.006 mmol), LHMDS in THF (1.00 M, 2.00 mL, 2.00 mmol), methyl chloroformate (77 μL, 1.00 mmol), and 3-bromopropyne (95 μL, 1.07 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give **12** (92.3 mg, 35%) as a colorless oil. IR (neat) 3291, 1967, 1740, 1436, 1231, 1204 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.80 (d, *J* = 6.3 Hz, 1H), 5.40 (d, *J* = 6.3 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.88 (d, *J* = 2.6, 1.4 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.03 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.5, 169.4, 169.3, 107.9, 91.5, 79.2, 71.0, 57.6, 52.90, 52.88, 32.2, 29.9 (3C), 24.8; EI-LRMS *m/z* 264 (M^+), 205, 173, 145, 57; EI-HRMS calcd for $C_{15}H_{20}O_4$ 264.13616, found 264.13557.

4,4-Bis(methoxylcarbonyl)-8,8-dimethylnona-1-phenyl-5,6-diene-1-yne (3f). To a solution of **12** (66.0 mg, 250 μmol) and iodobenzene (31 μL, 277 μmol) in Et_3N (2.5 mL) were added CuI (8.2 mg, 43 μmol) and $Pd(PPh_3)_4$ (3.1 mg, 2.7 μmol), and the mixture was degassed by Freeze Pump Thaw cycle. The resulting reaction mixture was stirred at 40 °C for 12 h under argon (1 atm) and concentrated. To the mixture was added saturated NH_4Cl aqueous solution, and the aqueous layer was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 9/1) to give **3f** (75.3 mg, 89%) as a colorless oil. IR (neat) 1967, 1740, 1201 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.36-7.23 (m, 5H), 5.86 (d, *J* = 6.3 Hz, 1H), 5.41 (d, *J* = 6.3 Hz, 1H), 3.77 (s, 6H), 3.12 (dd, *J* = 17.0, 21.0 Hz, 2H), 1.05 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.5, 169.6, 169.5, 131.6 (2C), 128.1 (2C), 127.9, 123.3, 107.8, 91.8, 84.5, 83.1, 58.0, 52.90, 52.89, 32.2, 29.9 (3C), 25.9; EI-LRMS *m/z* 340 (M^+), 325, 281, 249, 225, 221, 59, 57; EI-HRMS calcd for $C_{21}H_{24}O_4$ 340.16746, found 340.16773.

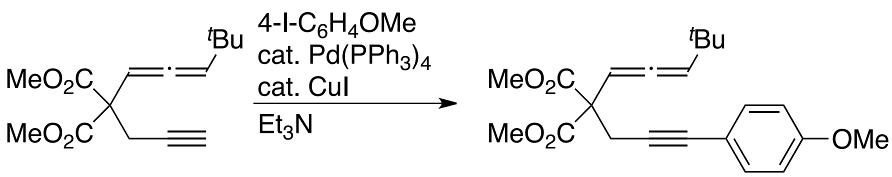
~ *Preparation of* ***3g*** ~



Scheme S7. *Preparation of* ***3g***

4,4-Bis(methoxylcarbonyl)-1-(4-methoxycarbonylphenyl)-8,8-dimethylnona-5,6-diene-1-yne (3g). To a solution of **12** (71.7 mg, 271μmol) and methyl *p*-iodobenzoate (78.1 mg, 298 μmol) in Et_3N (2.7 mL) were added CuI (8.0 mg, 42 μmol) and $PdCl_2(PPh_3)_2$ (1.9 mg, 2.7 μmol), and the mixture was degassed by Freeze Pump Thaw cycle. The resulting reaction mixture was stirred at 40 °C for 12 h under argon (1 atm) and concentrated. To the mixture was added saturated NH_4Cl aqueous solution, and the aqueous layer was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 9/1) to give **3g** (94.3 mg, 87%) as a colorless oil. IR (neat) 1967, 1740, 1727, 1276, 1201 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 5.85 (d, *J* = 6.3 Hz, 1H), 5.42 (d, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 6H), 3.13 (dd, *J* = 17.0, 19.5 Hz, 2H), 1.03 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.5, 169.5, 169.4, 166.5, 131.5 (2C), 129.3, 129.2, 128.0 (2C), 107.9, 91.7, 88.2, 82.5, 57.8, 52.94, 52.93, 52.1, 32.2, 29.8 (3C), 25.8; EI-LRMS *m/z* 398 (M^+), 367, 339, 307, 279, 263, 225; EI-HRMS calcd for $C_{23}H_{26}O_6$ 398.17294, found 398.17278.

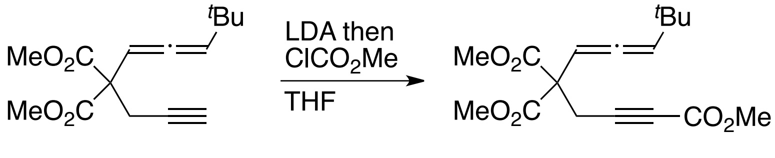
~ *Preparation of* ***3h*** ~



Scheme S8. *Preparation of* ***3h***

4,4-Bis(methoxylcarbonyl)-1-(4-methoxyphenyl)-8,8-dimethylnona-5,6-diene-1-yne (3h). Similar to the synthesis of **3f** from **12**, a crude product, which was obtained from **12** (55.5 mg, 210 μmol), *p*-iodoanisole (60.9 mg, 260 μmol), CuI (6.6 mg, 35 μmol), and $Pd(PPh_3)_4$ (2.2 mg, 1.9 μmol) in Et_3N (2.1 mL) at 40 °C for 12 h, was purified by column chromatography on silica gel (toluene) to give **3h** (89.2 mg, quant) as a colorless oil. IR (neat) 1968, 1739, 1248, 1202 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 6.80-6.76 (m, 2H), 5.86 (d, *J* = 6.3 Hz, 1H), 5.41 (d, *J* = 6.3 Hz, 1H), 3.78 (s, 3H), 3.764 (s, 3H), 3.761 (s, 3H), 3.14-3.06 (m, 2H), 1.05 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.4 169.65, 169.56, 159.2, 133.0 (2C), 115.4, 113.7 (2C), 107.7, 91.8, 83.1, 82.9, 58.1, 55.2, 52.8 (2C), 32.2, 29.9 (3C), 25.9; EI-LRMS *m/z* 370 (M^+), 355, 311, 279, 263, 251, 225; EI-HRMS calcd for $C_{22}H_{26}O_5$ 370.17802, found 370.17762.

~ *Preparation of **3i*** ~

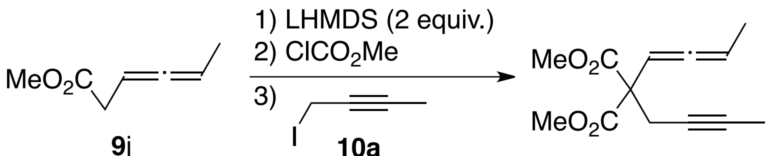


12 **3i**: 83%

Scheme S9. *Preparation of **3i***

Methyl 5,5-bis(methoxycarbonyl)-9,9-dimethyldeca-6,7-dien-2-ynecarboxylate (3i). To a solution of *i*-Pr_2NH (237 μL, 1.68 mmol) in THF (2.0 mL) was slowly added a solution of *n*-BuLi in hexane (1.65 M, 1.02 mL, 1.68 mmol) at -78 °C, and the mixture was stirred at 0 °C for 30 min. To a solution of **12** (93.1 mg, 352 μmol) in THF (3.0 mL) was slowly added quarter amount of the mixture at -78 °C, and the resulting mixture was stirred at the same temperature for 1 h. To the mixture was slowly added methyl chloroformate (54.5 μL, 705 μmol) at -78 °C, and the mixture was stirred at the same temperature for 30 min and allowed to warm to room temperature over 1 h and stirred at the same temperature for 8 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 10/1) to give **3i** (94.3 mg, 83%) as a colorless oil. IR (neat) 1967, 1741, 1719, 1262, 1204 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.77 (d, J = 6.3 Hz, 1H), 5.43 (d, J = 6.3 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.01 (s, 2H), 1.02 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 200.6, 169.0, 168.8, 153.6, 108.4, 91.2, 84.0, 74.8, 57.0, 53.14, 53.11, 52.5, 32.2, 29.8 (3C), 24.8; EI-LRMS *m/z* 322 (M^+), 263, 231, 225, 203; EI-HRMS calcd for $C_{17}H_{22}O_6$ 322.14164, found 322.14123.

~ *Preparation of **3j*** ~



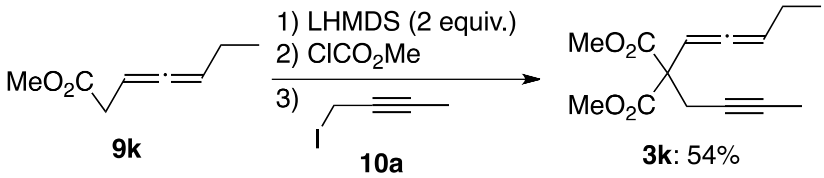
9j **3j**: 42%

Scheme S10. *Preparation of **3j***

5,5-Bis(methoxycarbonyl)nona-6,7-diene-2-yne (3j). Similar to the synthesis of **3a** from **9a**, a crude product, which was obtained from **9j**[7] (389.1 mg, 3.084 mmol) in THF (3.3 mL), LHMDS in THF (1.00 M, 6.5 mL, 6.5 mmol), methyl chloroformate (250 μL, 3.24 mmol), and **10a** (556.0 mg, 3.089 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **3j** (307.7 mg, 42%) as a colorless oil. IR (neat) 1970, 1740, 1436, 1230 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.66 (dq, J = 6.6, 3.2 Hz, 1H), 5.34 (dq, J = 6.6, 6.8 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.84 (q, J = 2.6 Hz, 2H), 1.74 (t, J = 2.6 Hz, 3H), 1.68 (dd, J = 3.2, 6.8 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 204.1, 169.7, 169.6, 90.4, 89.4, 78.2, 73.6, 57.7, 52.8 (2C), 24.7, 13.6, 3.4; EI-LRMS *m/z* 236 (M^+), 183, 177, 145, 117; EI-HRMS calcd for $C_{13}H_{16}O_4$ 236.10486, found 236.10473.

[7] S. Tsuboi, T. Masuda and A. Takeda, *J. Org. Chem.*, 1982, **47**, 4478.

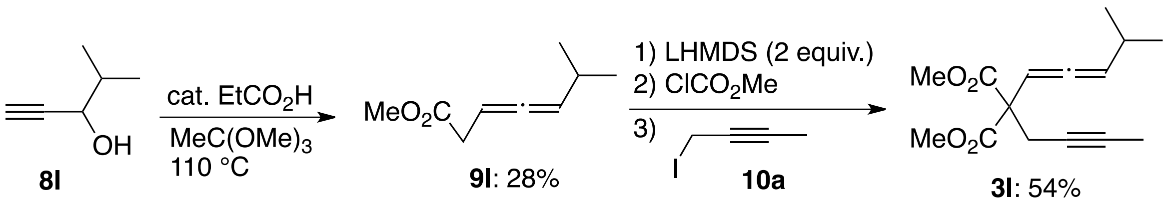
~ *Preparation of* ***3k*** ~



Scheme S11. *Preparation of* ***3k***

5,5-Bis(methoxycarbonyl)deca-6,7-dien-2-yne (3k). Similar to the synthesis of **3a** from **9a**, a crude product, which was obtained from **9k**[8] (702.0 mg, 5.008 mmol) in THF (5.0 mL), LHMDS in THF (1.00 M, 10.0 mL, 10.0 mmol), methyl chloroformate (400 μL, 5.18 mmol), and **10a** (903.0 mg, 5.017 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **3k** (680.5 mg, 54%) as a colorless oil. IR (neat) 1967, 1740, 1436, 1228 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.69 (dt, *J* = 6.5, 3.1 Hz, 1H), 5.40 (dt, *J* = 6.5, 6.4 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.79 (q, *J* = 2.5 Hz, 2H), 2.00 (ddt, *J* = 3.1, 6.4, 7.1 Hz, 2H), 1.69 (t, *J* = 2.5 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 202.8, 169.7, 169.6, 97.4, 90.6, 78.2, 73.6, 57.8, 52.74, 52.71, 24.9, 21.4, 12.9, 3.3; EI-LRMS *m/z* 250 (M^+), 191, 159, 131, 59; EI-HRMS calcd for $C_{14}H_{18}O_4$ 250.12051, found 250.12033.

~ *Preparation of* ***3l*** ~



Scheme S12. *Preparation of* ***3l***

Methyl 6-methylhepta-3,4-dienoate (9l). Similar to the synthesis of **9a** from **8a**, a crude product, which was obtained from **8l** (3.886 g, 39.60 mmol), trimethyl orthoacetate (15.0 mL, 120 mmol), and propanoic acid (0.30 mL, 4.0 mmol) at 110 °C for 6 h, was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give **9l** (1.735 mg, 28%) as a colorless oil. IR (neat) 1965, 1743, 1437, 1246, 1032 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.27-5.22 (m, 1H), 5.21-5.16 (m, 1H), 3.68 (s, 3H), 3.01 (dd, *J* = 7.4, 2.9 Hz, 2H), 2.33-2.22 (m, 1H), 0.98 (dd, *J* = 6.9, 1.1 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 203.5, 172.0, 99.6, 85.1, 51.8, 35.0, 27.7, 22.32, 22.28; EI-LRMS *m/z* 154 (M^+), 139, 123, 111, 95, 59, 43; EI-HRMS calcd for $C_9H_{14}O_2$ 154.09938, found 154.09972.

5,5-Bis(methoxycarbonyl)-9-methyldeca-6,7-dien-2-yne (3l). Similar to the synthesis of **3a** from **9a**, a crude product, which was obtained from **9l** (773.4 mg, 5.015 mmol) in THF (5.0 mL), LHMDS in THF (1.00 M, 10.0 mL, 10.0 mmol), methyl chloroformate (400 μL, 5.18 mmol), and **10a** (903.5 mg, 5.020 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **3l** (719.4 mg, 54%) as a colorless oil. IR (neat) 1967, 1740, 1436, 1227 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.76 (dd, *J* = 6.3, 2.9 Hz, 1H), 5.38 (dd, *J* = 6.3, 6.0 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.84-2.82 (m, 2H), 2.35-2.28 (m, 1H), 1.72 (dd, *J* = 2.6, 2.6 Hz, 3H), 0.99 (dd, *J* = 6.9, 1.1 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 201.6, 169.7, 169.6, 103.0, 91.2, 78.3, 73.6, 57.9,

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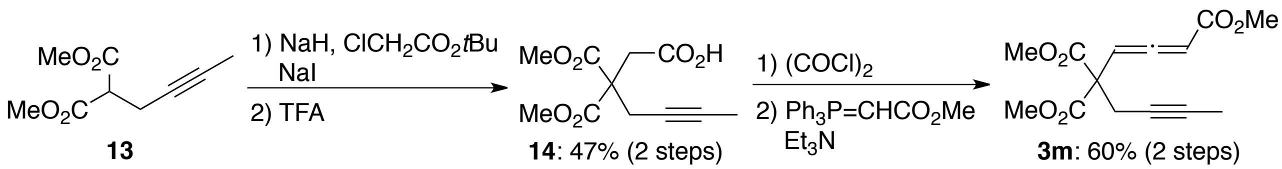
8 S. Tsuboi, T. Masuda, S. Mimura and A. Takeda, *Org. Syn.*, 1988, **66**, 22.

52.74, 52.72, 27.9, 25.1, 22.2, 22.0, 3.4; EI-LRMS *m/z* 264 (M^+), 205, 173, 145, 59; EI-HRMS calcd for $C_{15}H_{20}O_4$ 264.13616, found 264.13591.

~ *Preparation of* ***3m*** ~



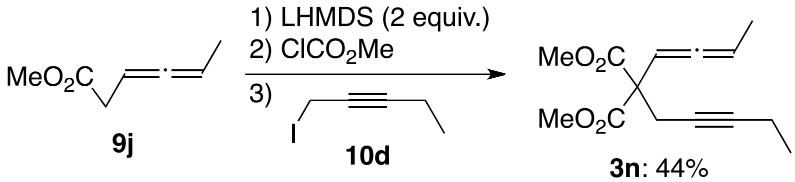
Scheme S13. *Preparation of* ***3m***

3,3-Bis(methoxycarbonyl)hept-5-ynoic acid (14). To a suspension of NaH (60% dispersion in mineral oil, 823.3 mg, 20.58 mmol) and NaI (276.1 mg, 1.842 mmol) in THF (56 mL) was slowly added a solution of **13**[9] (3.017 g, 16.38 mmol) in THF (8 mL) at 0 °C, and the mixture was stirred at room temperature for 5 min. To the mixture was added *tert*-butyl chloroacetate (2.93 mL, 20.5 mmol) at 0 °C, and the resulting mixture was stirred at room temperature overnight. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was roughly purified by short column chromatography on silica gel (hexane/AcOEt = 12/1) to give a crude *tert*-butyl ester (4.260 g) as a yellow oil. To a solution of the crude *tert*-butyl ester (4.260 g) in CH_2Cl_2 (50 mL) was added TFA (11.0 mL, 143 mmol) at room temperature, and the mixture was stirred at the same temperature for 18 h. After removal of the solvent and TFA, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 10/1) to give **14** (1.847 g, in 2 steps 47%) as a white solid. mp; 119-121 °C; IR (film, $CHCl_3$) 1740, 1714, 1438 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 10.95 (br s, 1H), 3.74 (s, 6H), 3.22 (s, 2H), 2.94 (q, *J* = 2.6 Hz, 2H), 1.75 (t, *J* = 2.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 176.6, 169.4 (2C), 79.8, 72.9, 54.8, 53.1 (2C), 36.6, 23.9, 3.5; EI-LRMS *m/z* 242 (M^+), 224, 196, 183, 151, 123, 59, 53; EI-HRMS calcd for $C_{11}H_{14}O_6$ 242.07904, found 242.07878.

Methyl 5,5-bis(methoxycarbonyl)nona-2,3-dien-8-ynecarboxylate (3m). To a solution of **14** (459.9 mg, 1.727 mmol) in CH_2Cl_2 (3.4 mL) was slowly added oxalyl chloride (165 μL, 1.92 mmol) at room temperature, and the mixture was stirred at 35 °C for 2.5 h. After removal of the volatiles, the resulting crude acyl chloride was diluted with CH_2Cl_2 (3.4 mL) and added slowly to a stirred solution of $Ph_3P{=}CHCO_2Me$ (698.2 mg, 2.088 mmol) and Et_3N (290 μL, 2.081 mmol) in CH_2Cl_2 (2.8 mL) at 0 °C. The mixture was stirred for 3 h at room temperature and concentrated. The crude product was purified by column chromatography on silica gel (hexane/AcOEt = 5/1) to give **3m** (290.8 mg, in 2 steps 60%) as a colorless oil. IR (neat) 1971, 1741, 1725 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.24 (d, *J* = 6.3 Hz, 1H), 5.80 (d, *J* = 6.3 Hz, 1H), 3.76 (s, 6H), 3.71 (s, 3H), 2.92-2.83 (m, 2H), 1.73 (t, *J* = 2.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 211.2, 168.5 (2C), 165.3, 94.5, 91.6, 79.3, 72.7, 57.6, 53.2 (2C), 52.2, 25.3, 3.5; EI-LRMS *m/z* 280(M^+), 227, 221, 189, 161; EI-HRMS calcd for $C_{14}H_{16}O_6$ 280.09469, found 280.09512.

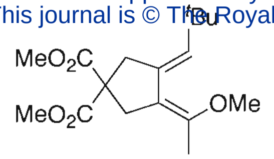
[9] B. M. Trost and M. T. Rudd, *J. Am. Chem. Soc.*, 2005, **127**, 4763.

~ Preparation of ***3n*** *~*



Scheme S14**. Preparation of **3n

6,6-Bis(methoxycarbonyl)deca-7,8-3-yne (3n). Similar to the synthesis of **3a** from **9a**, a crude product, which was obtained from **9j** (379.3 mg, 3.01 mmol) in THF (3.3 mL), LHMDS in THF (1.00 M, 6.6 mL, 6.6 mmol), methyl chloroformate (239 μL, 3.09 mmol), and **10d** (1.086 g, 5.60 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give **3n** (327.6 mg, 44%) as a colorless oil. IR (neat) 1970, 1741, 1436, 1231, 1061 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.65 (dq, *J* = 6.5, 3.3 Hz, 1H), 5.32 (dq, *J* = 6.5, 7.0 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.83 (t, *J* = 2.5 Hz, 2H), 2.09 (tq, *J* = 2.5, 7.5 Hz, 2H), 1.66 (dd, *J* = 7.0, 3.3 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 204.1, 169.74, 169.68, 90.4, 89.4, 84.4, 73.9, 57.8, 52.80, 52.78, 24.8, 14.1, 13.7, 12.3; EI-LRMS *m/z* 251 [$(M+H)^+$], 191, 183, 159, 131, 59; EI-HRMS calcd for $C_{14}H_{19}O_4$ 251.12833, found 251.12735.



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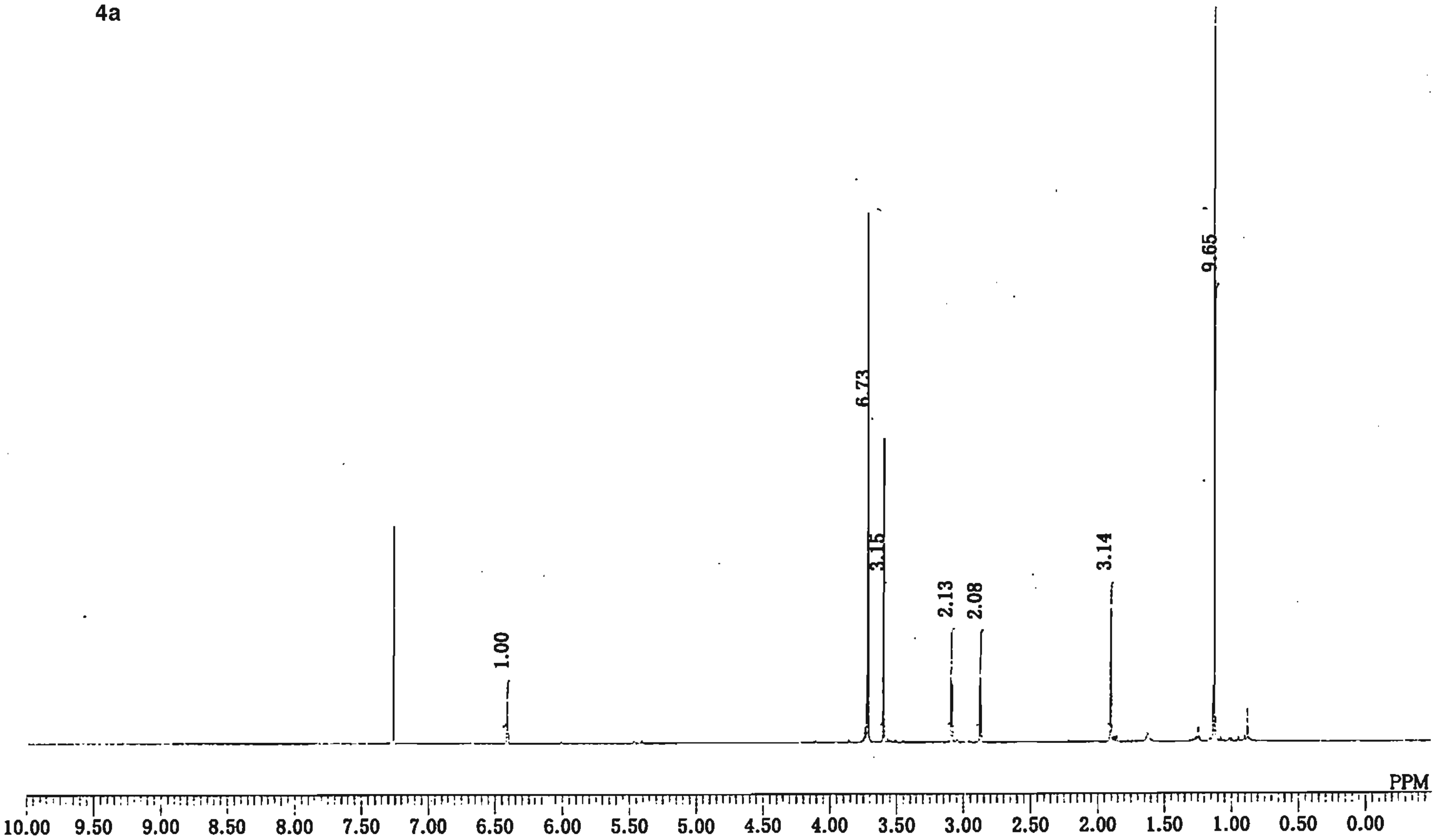
OMe

4a



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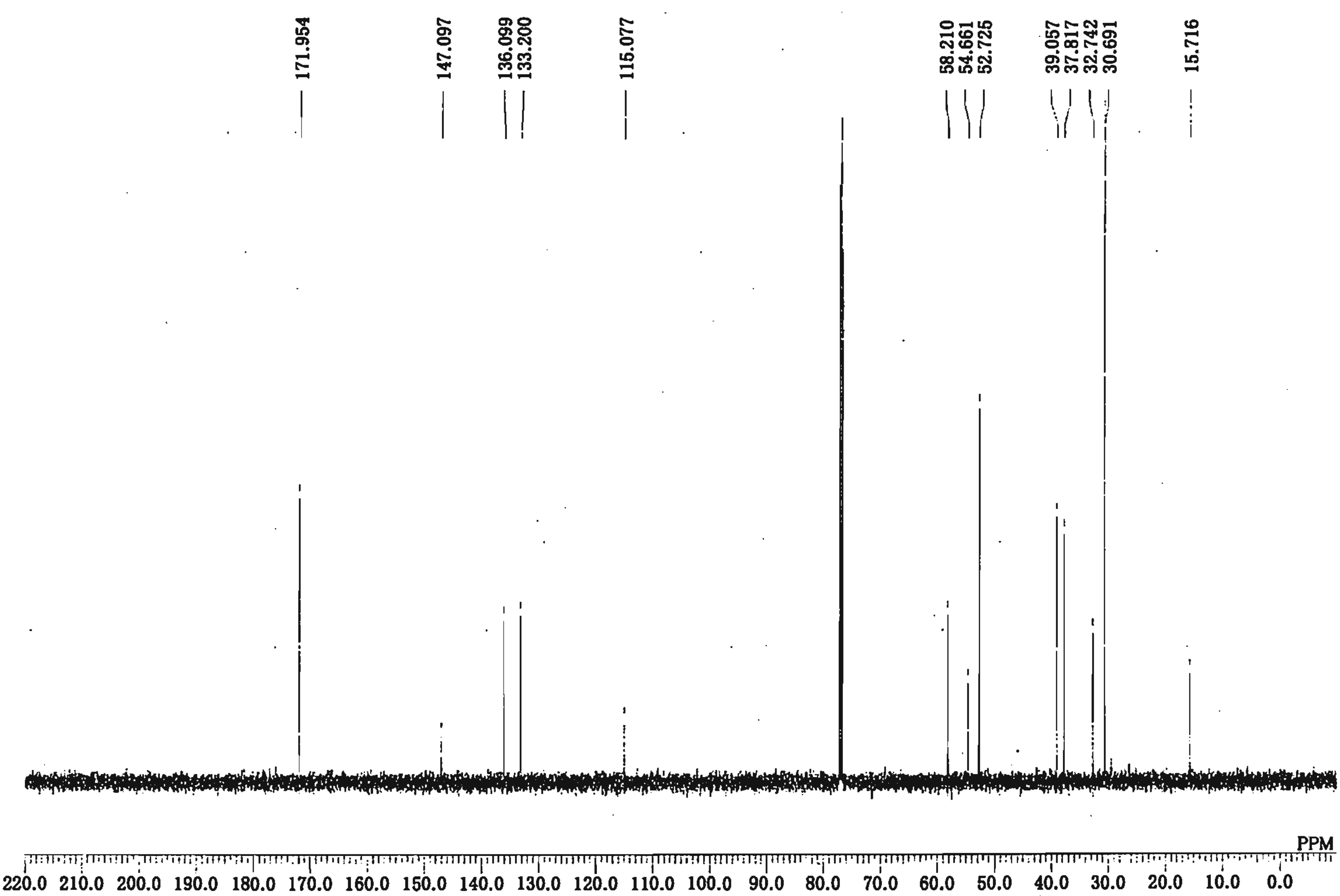

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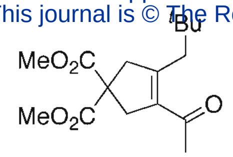
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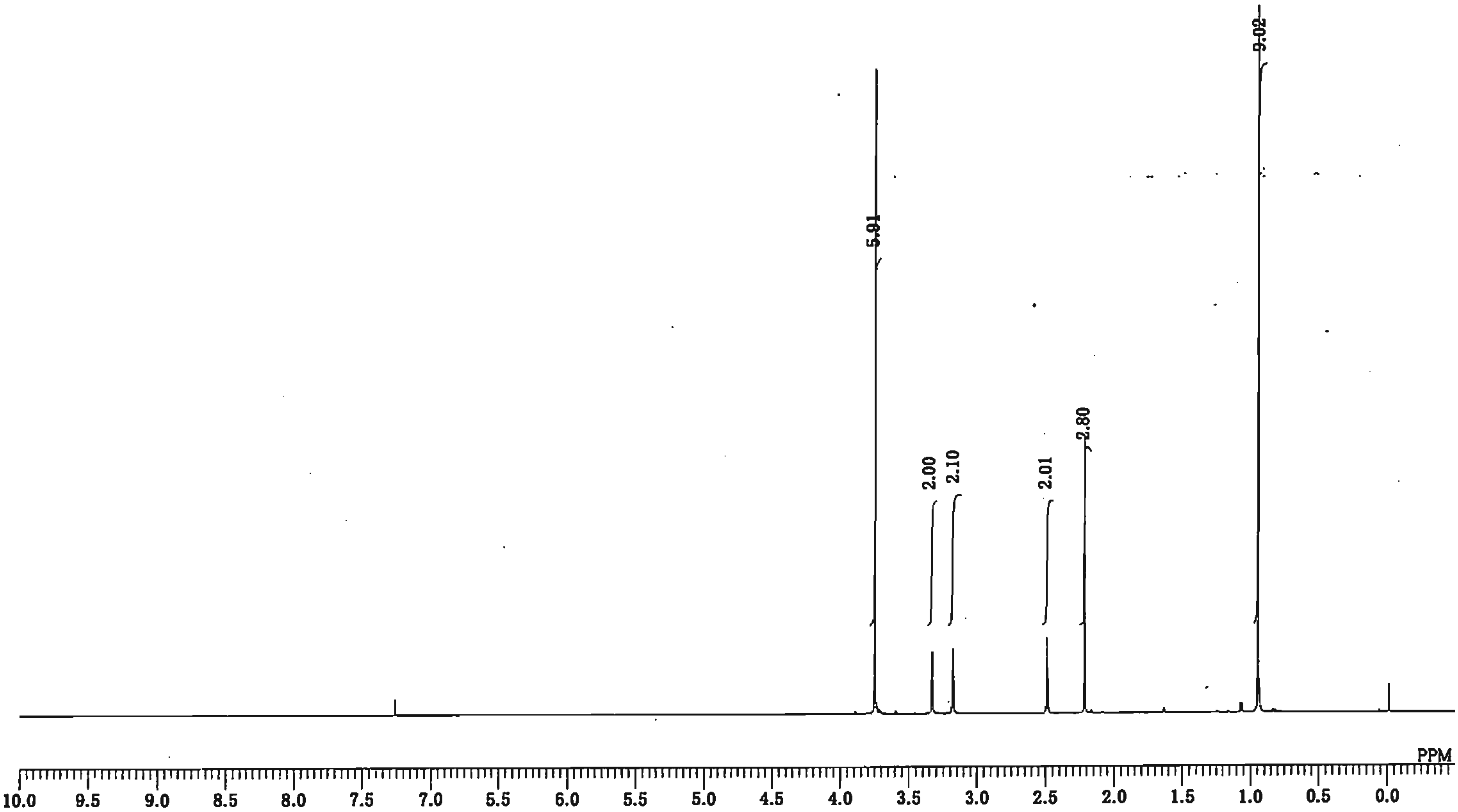
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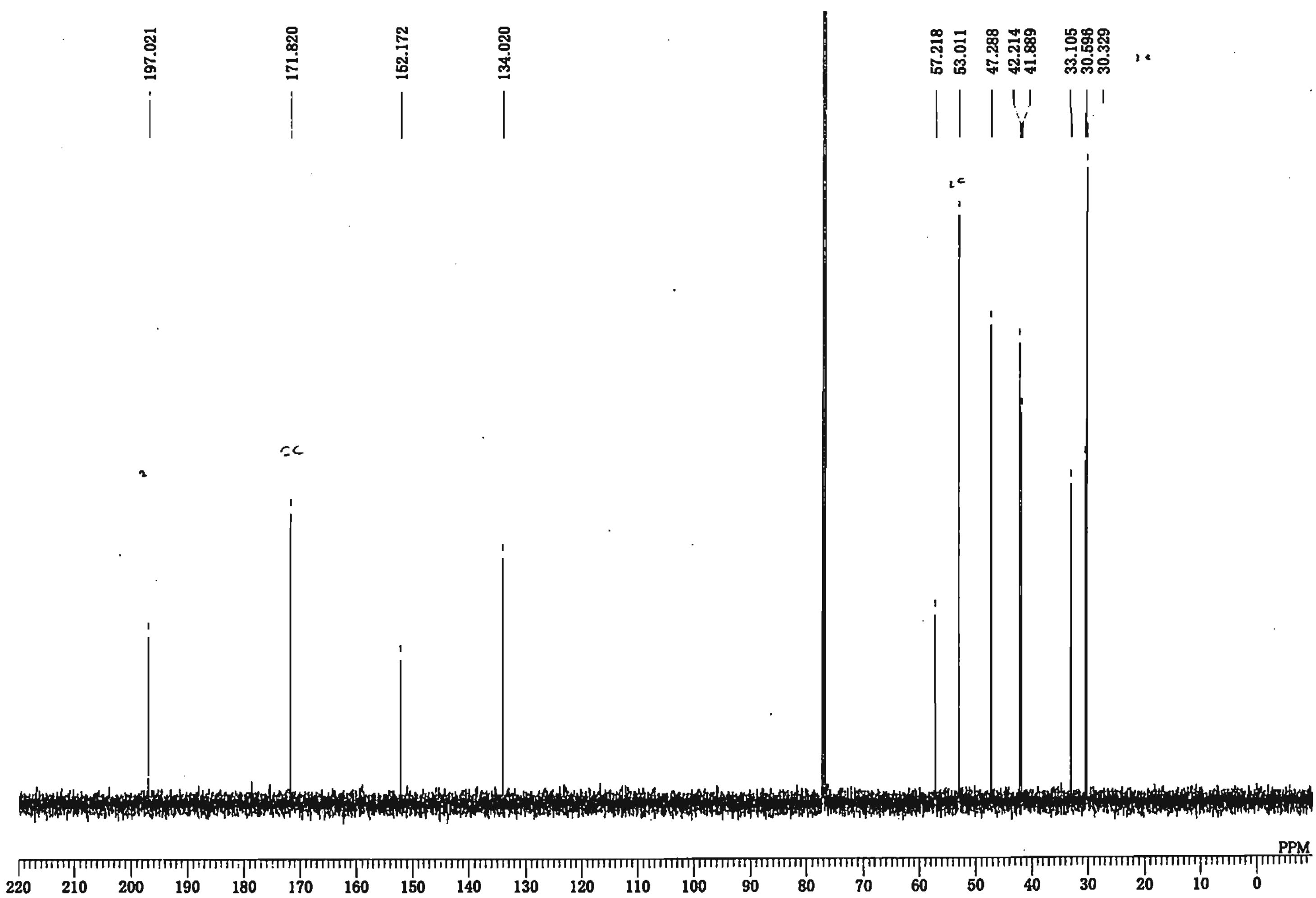
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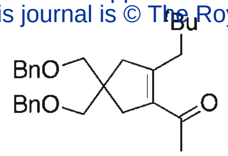
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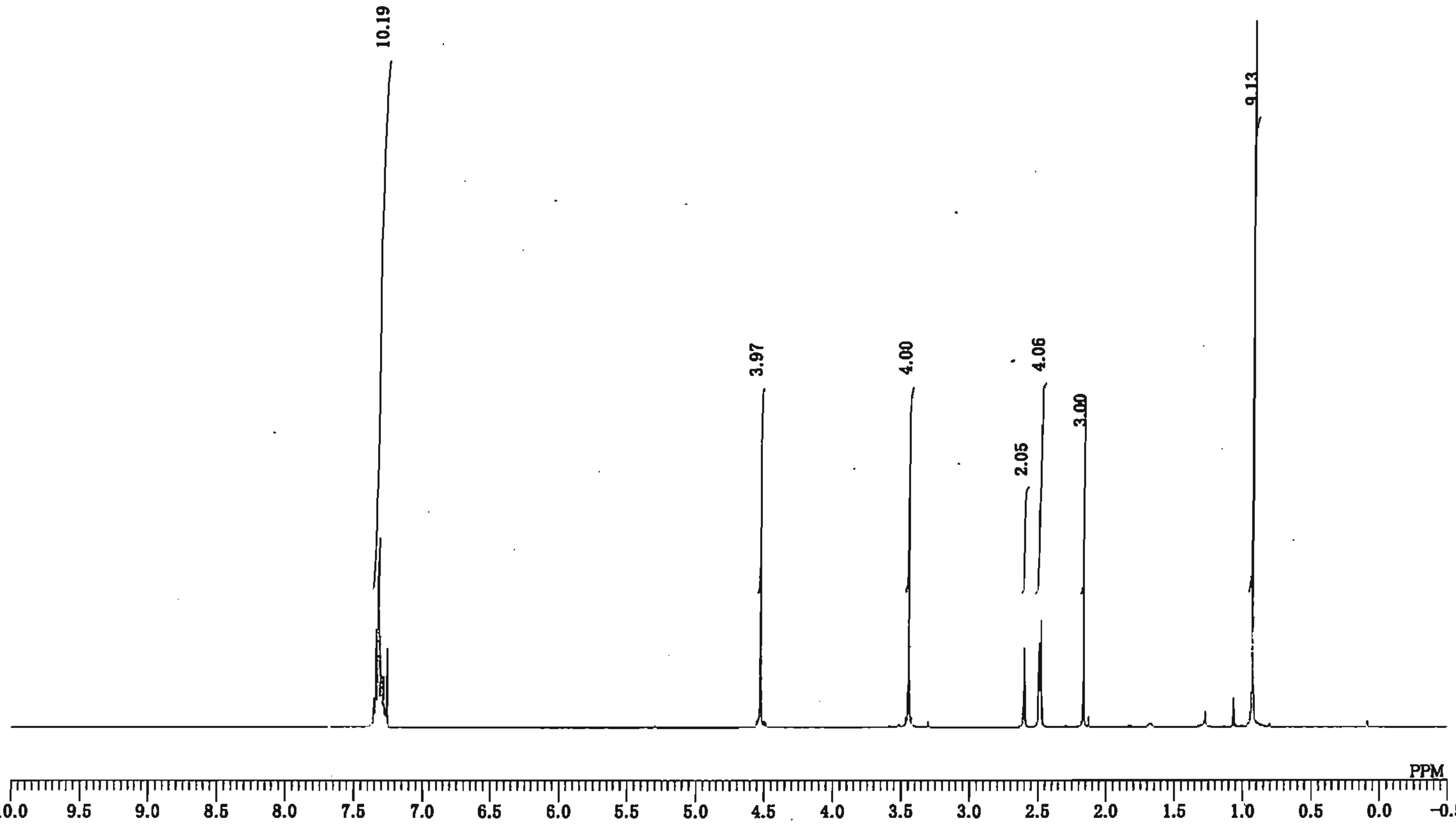
O

5b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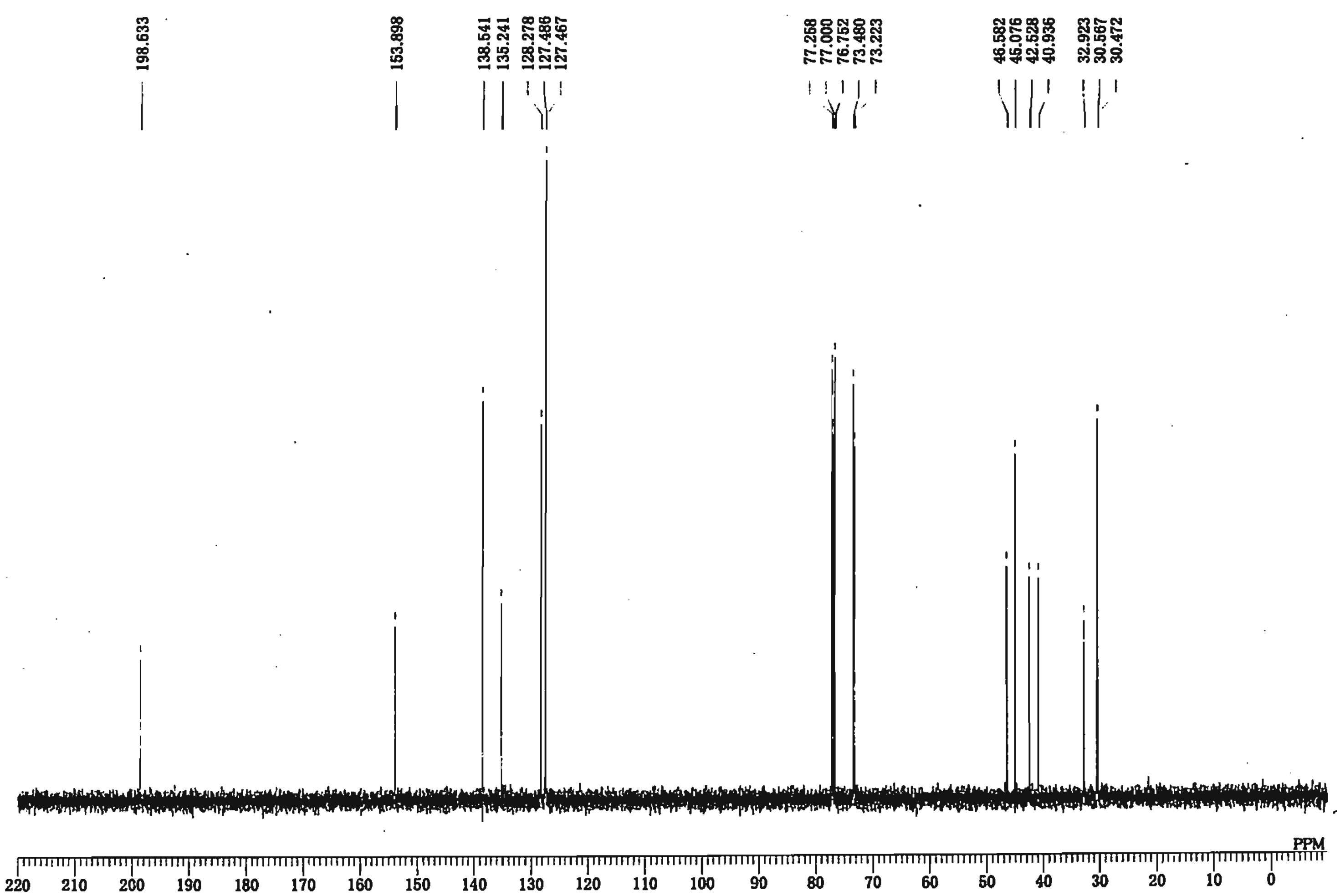
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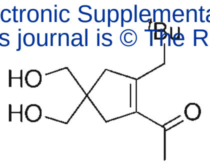
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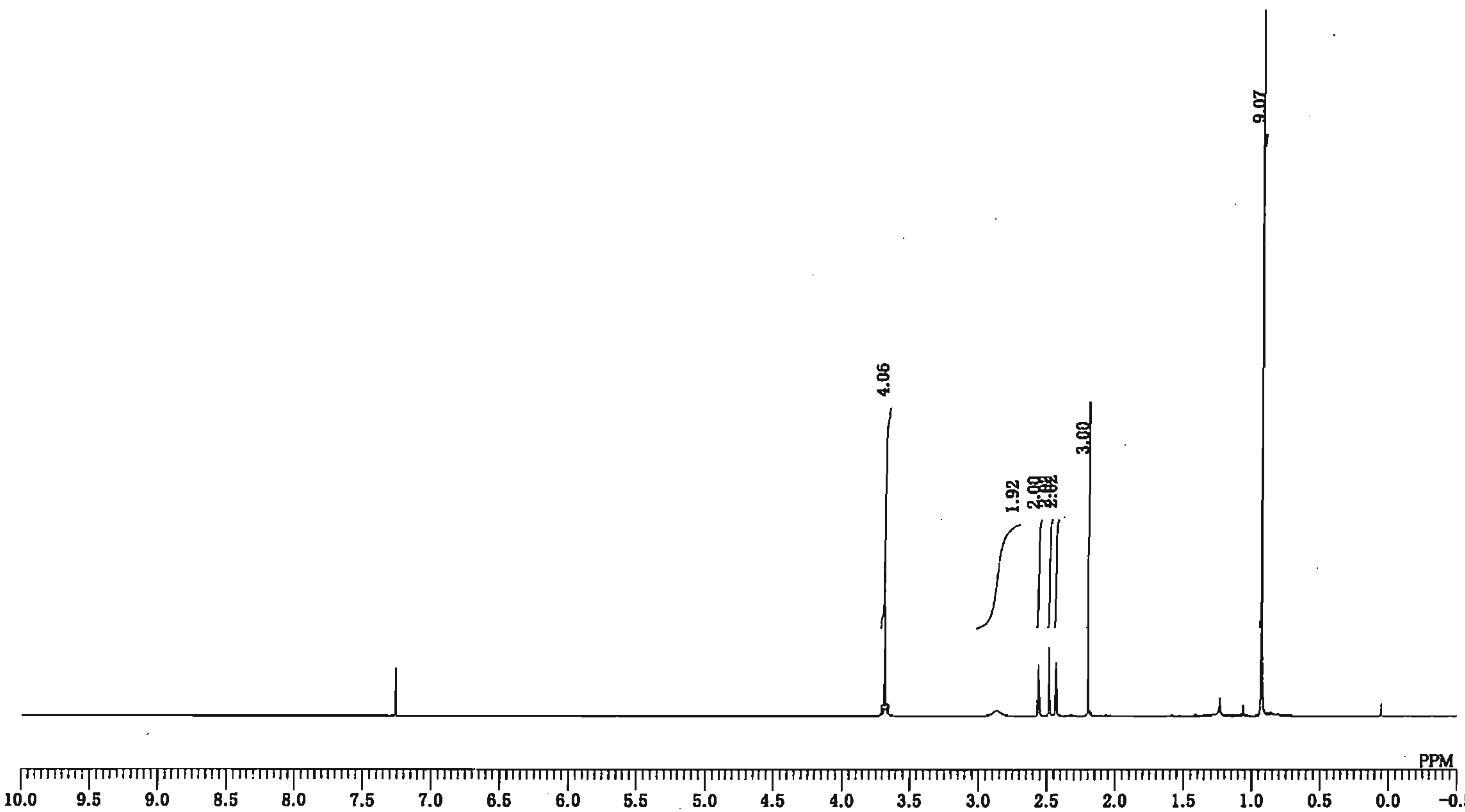
5c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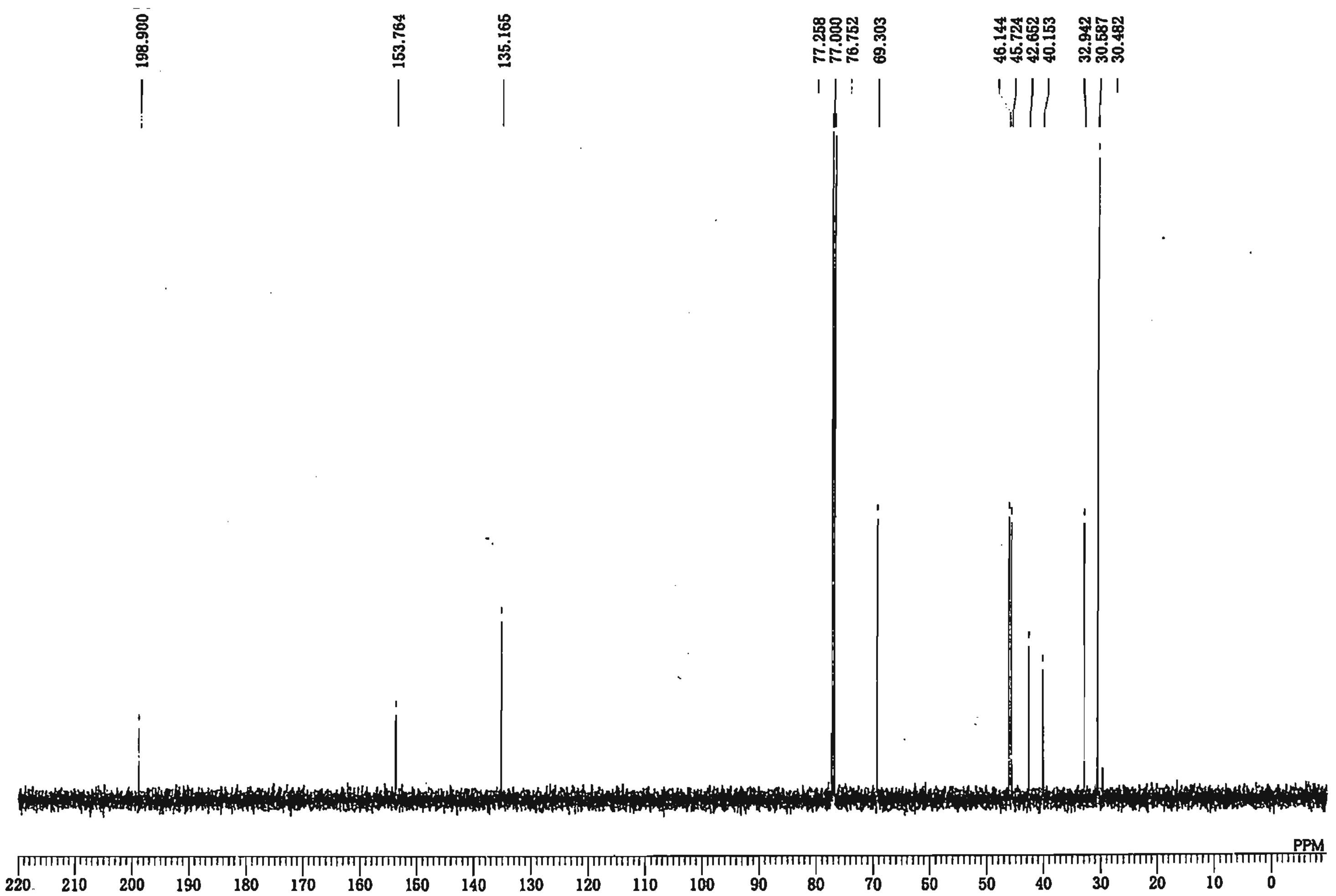
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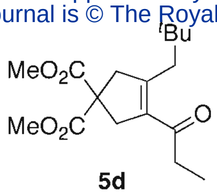
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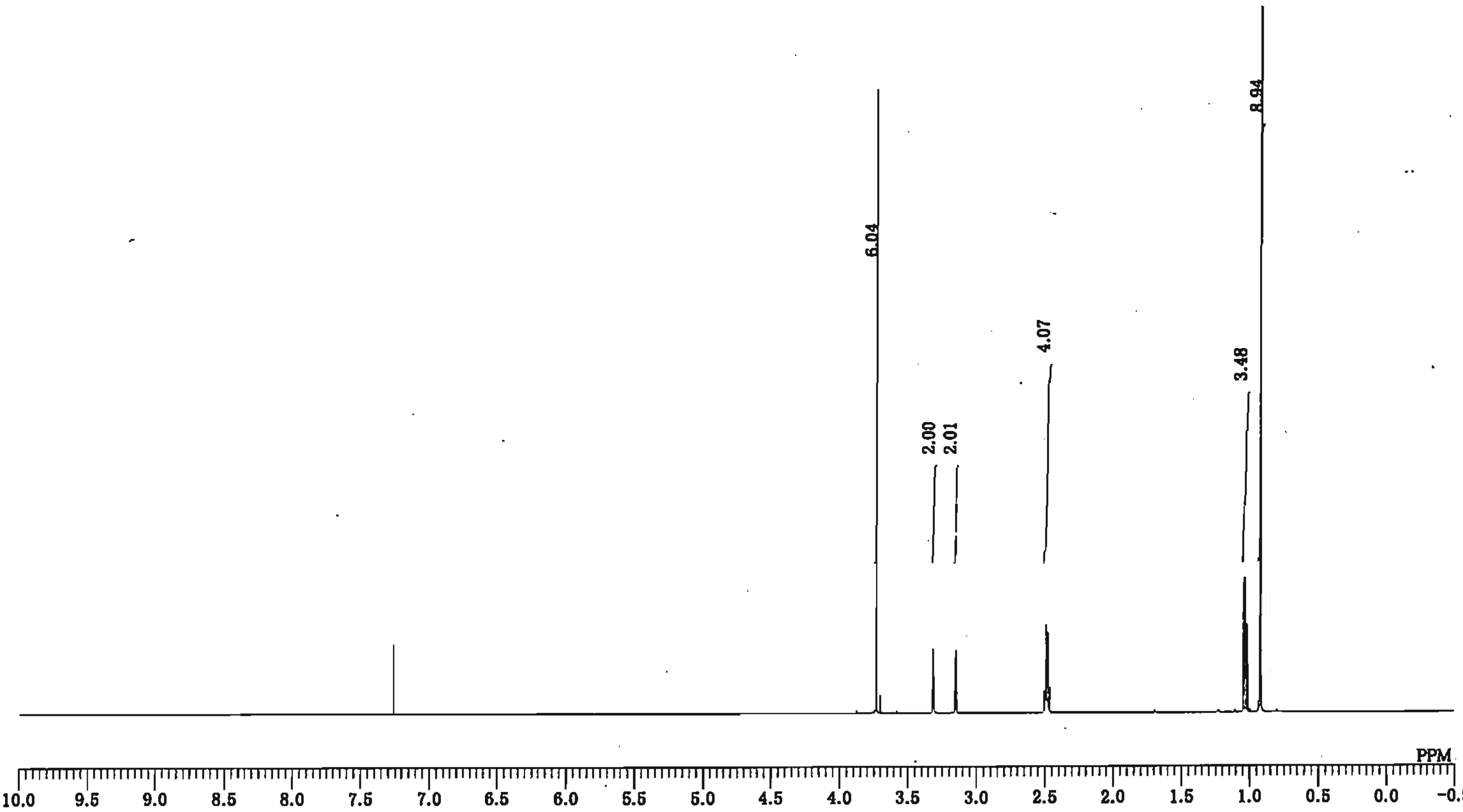
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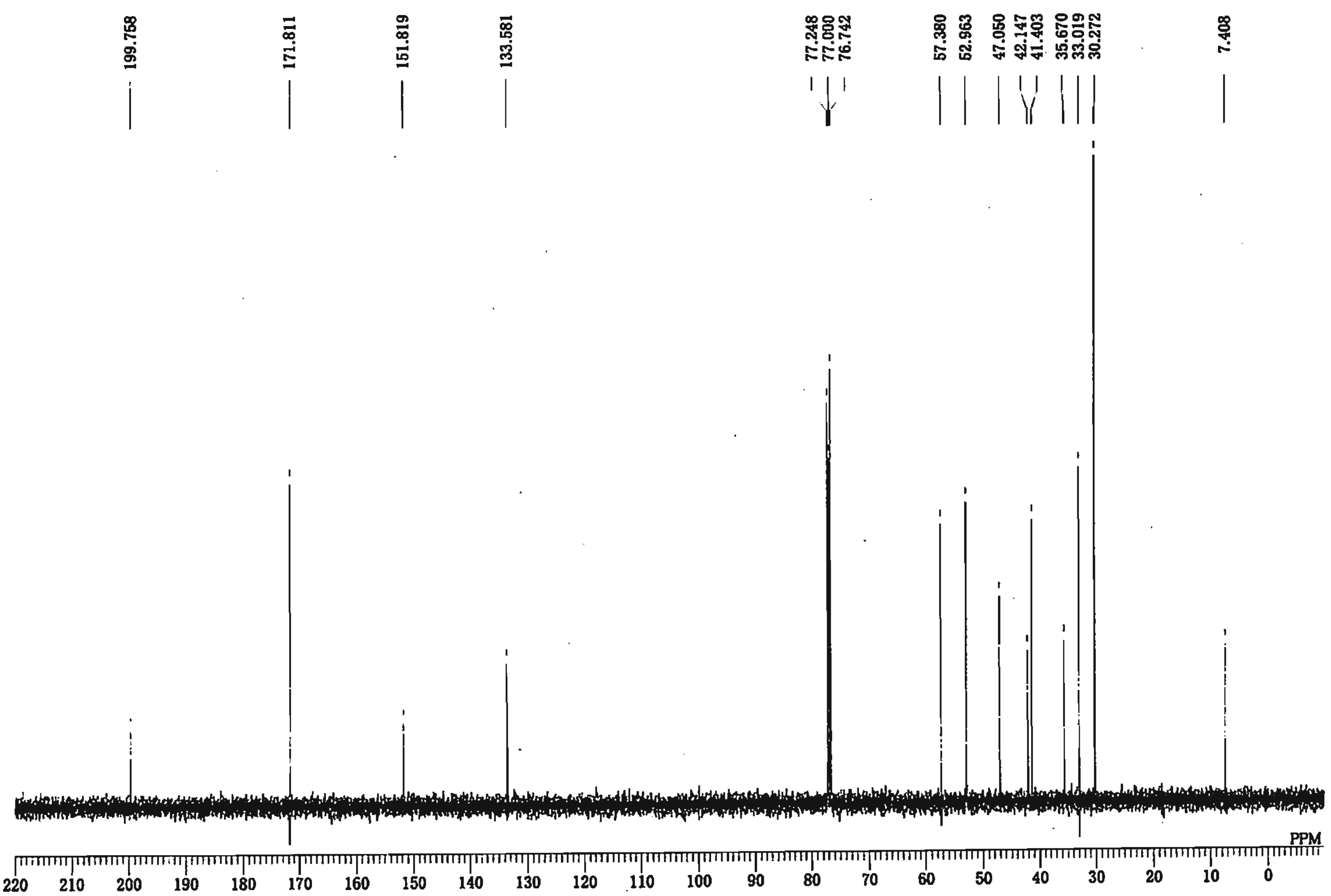
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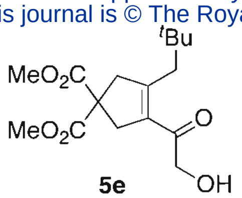

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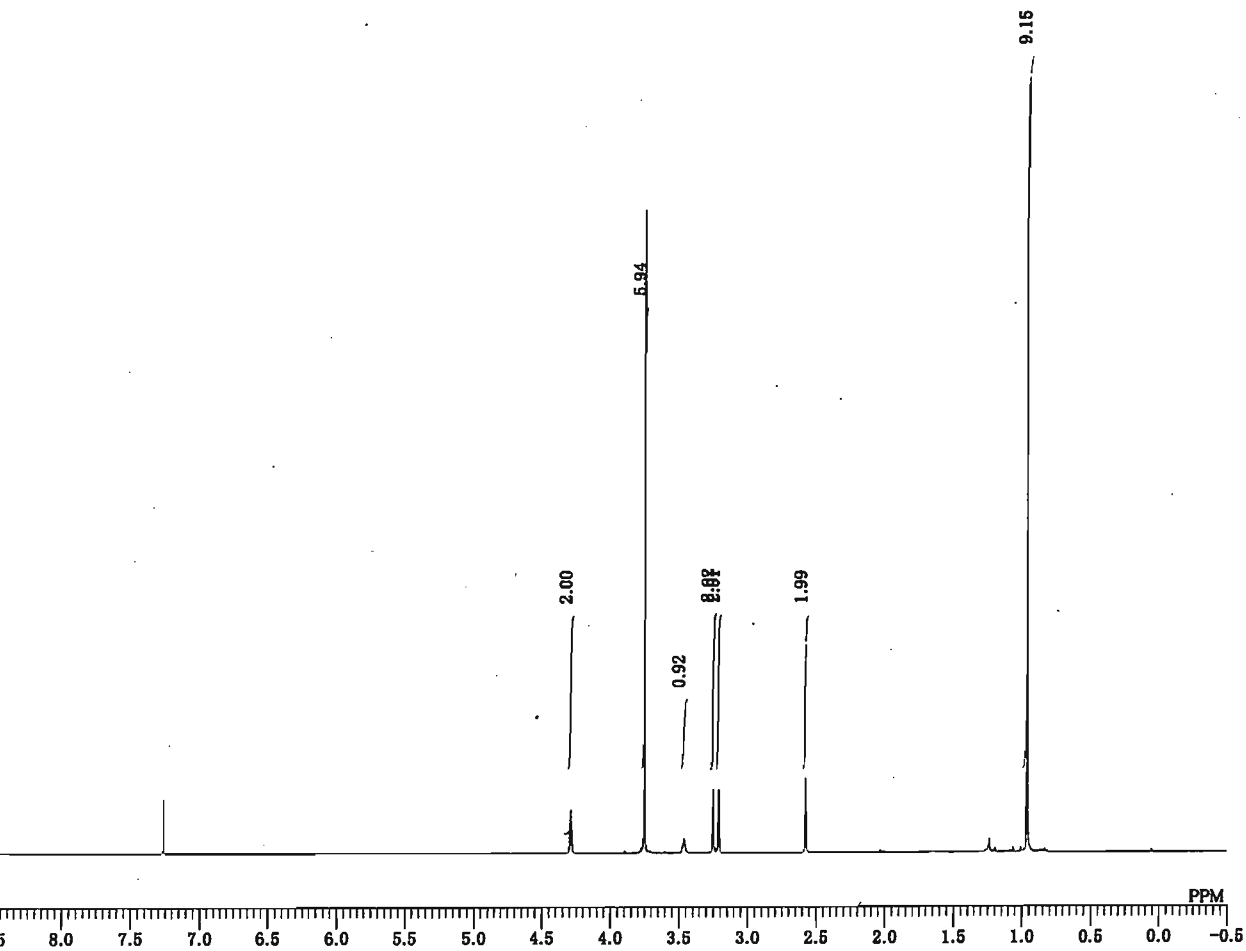
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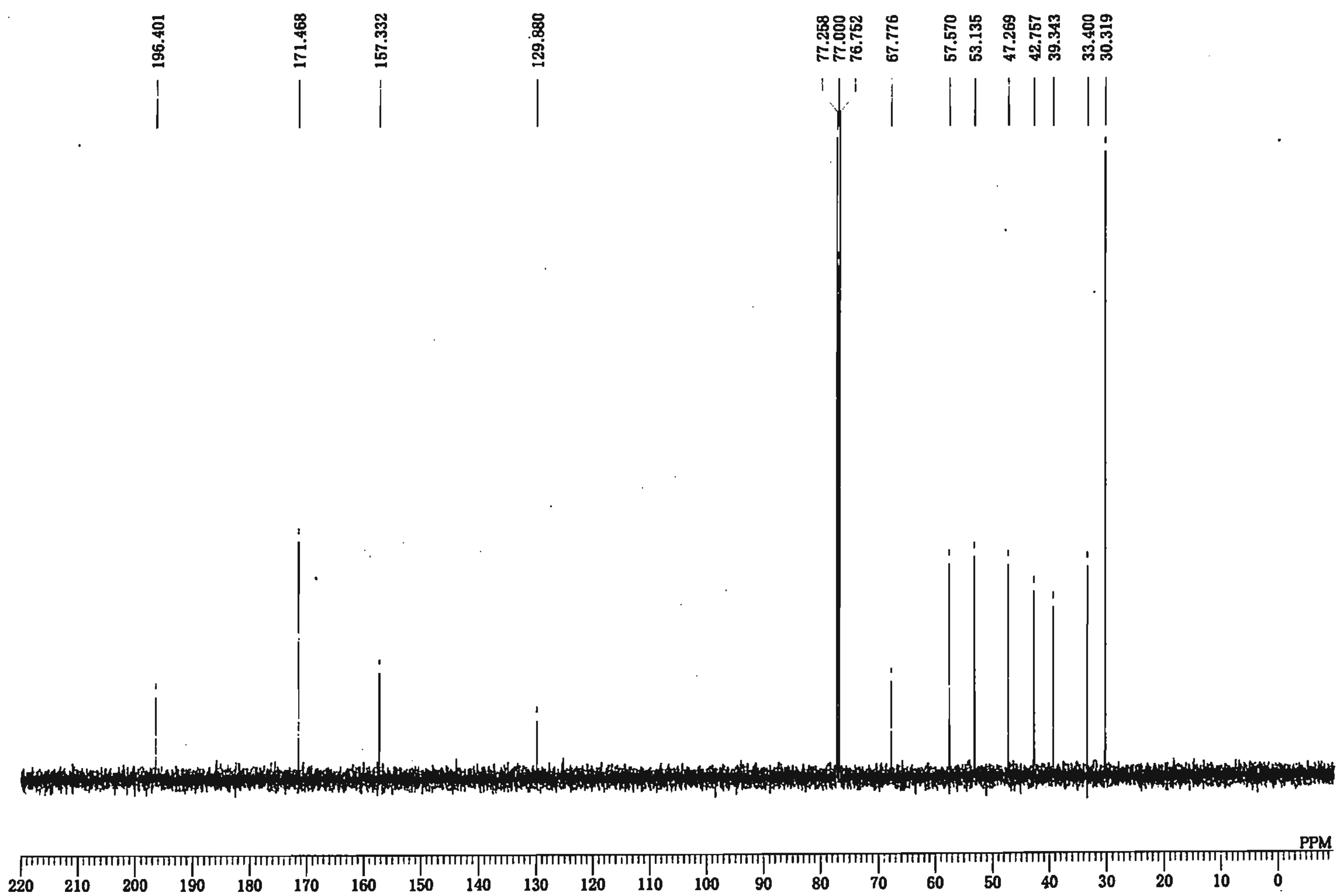
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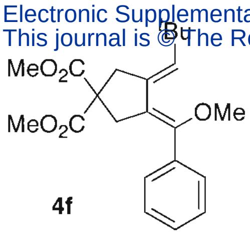
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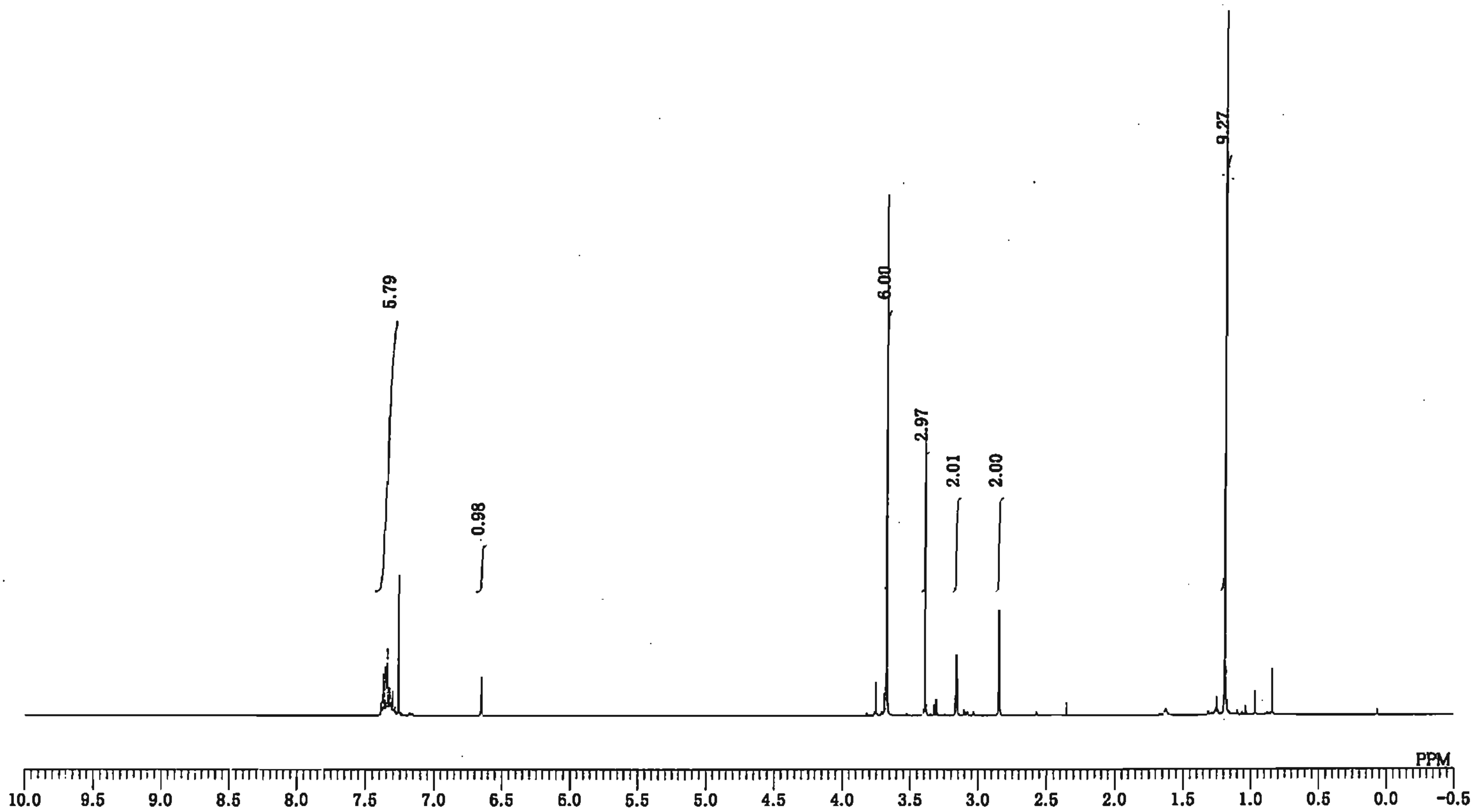
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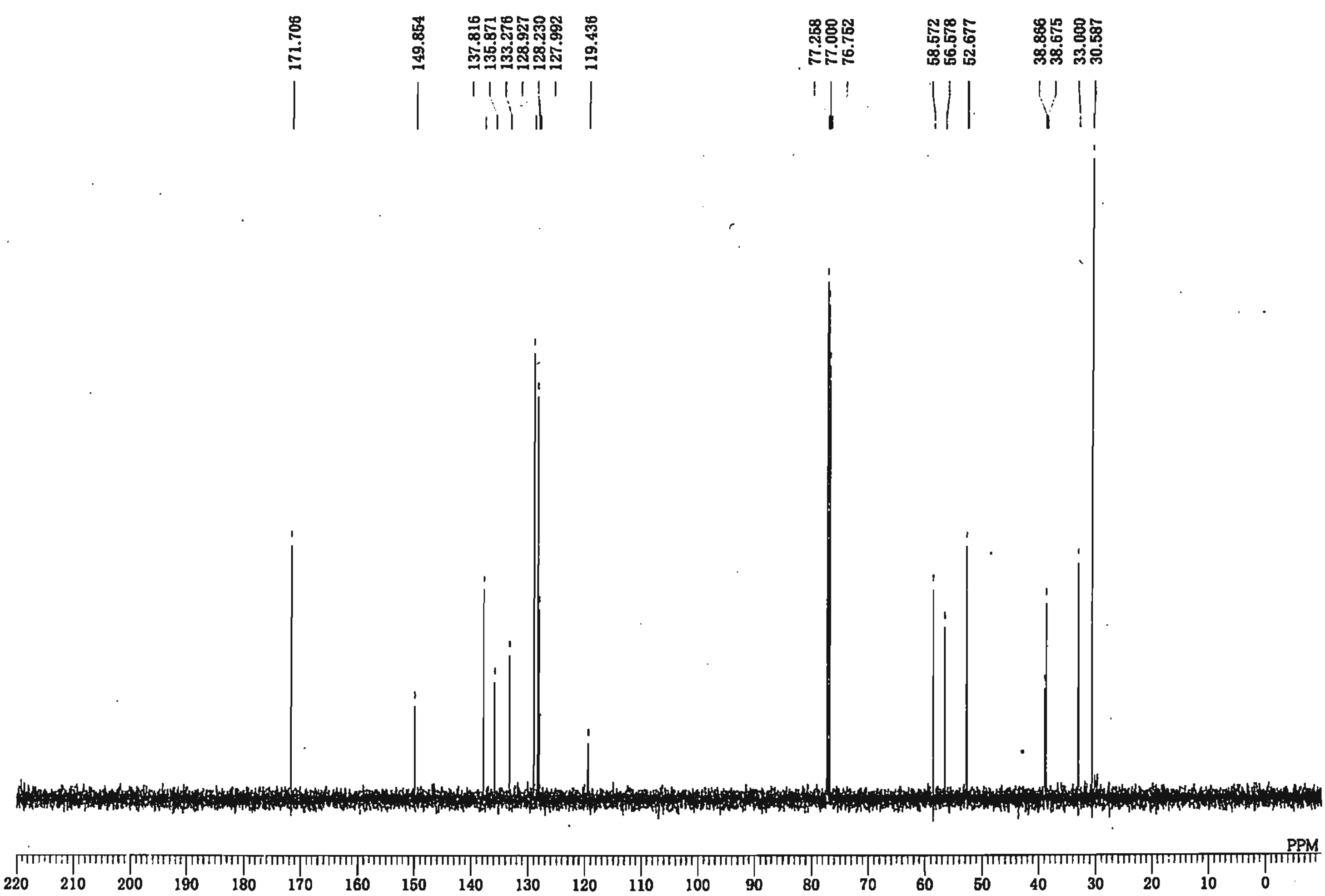
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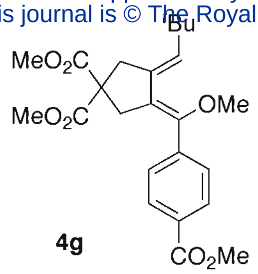

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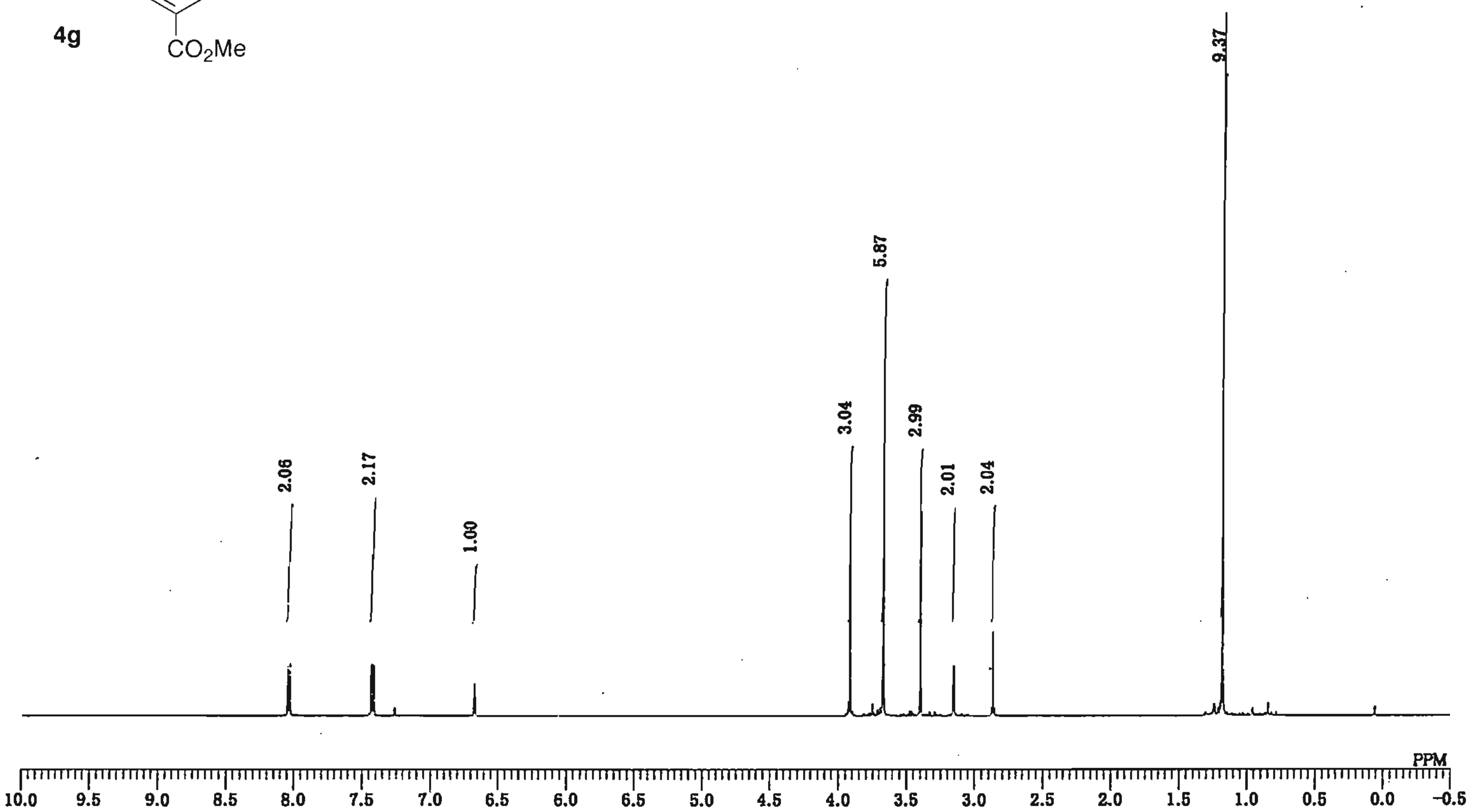
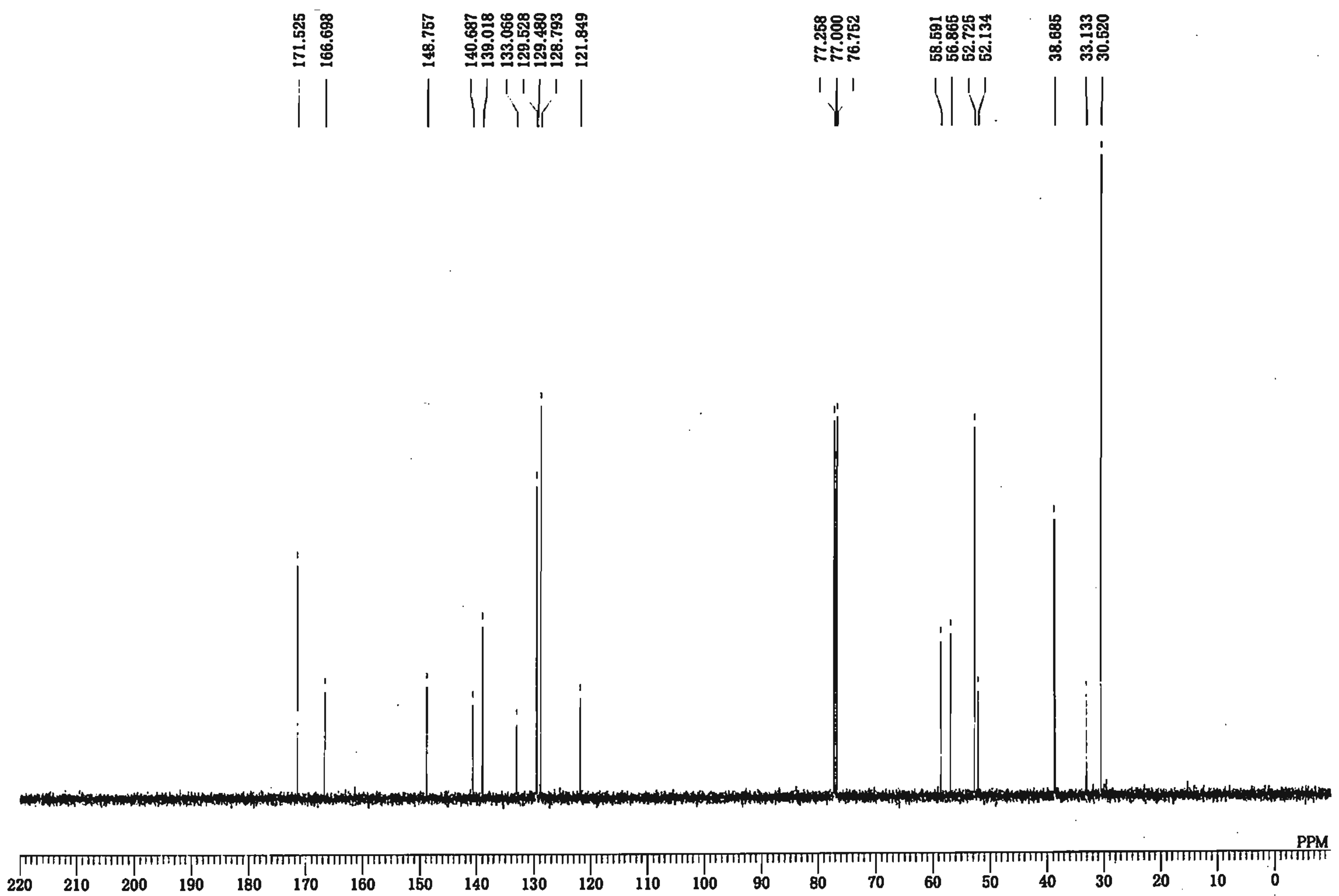
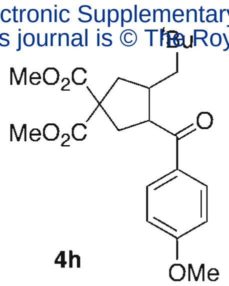




Electronic Supplementary Material (ESI) for Chemical Communications



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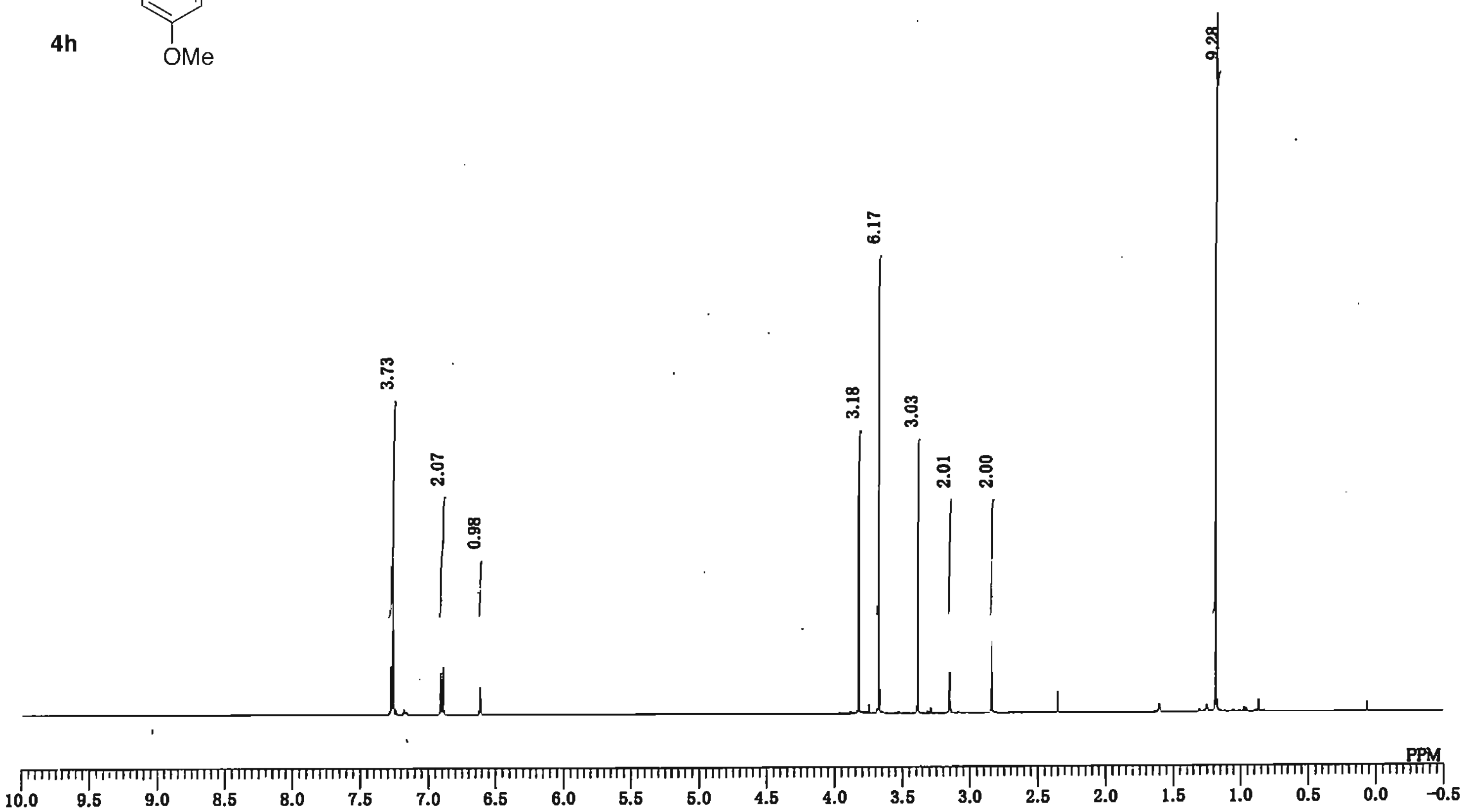

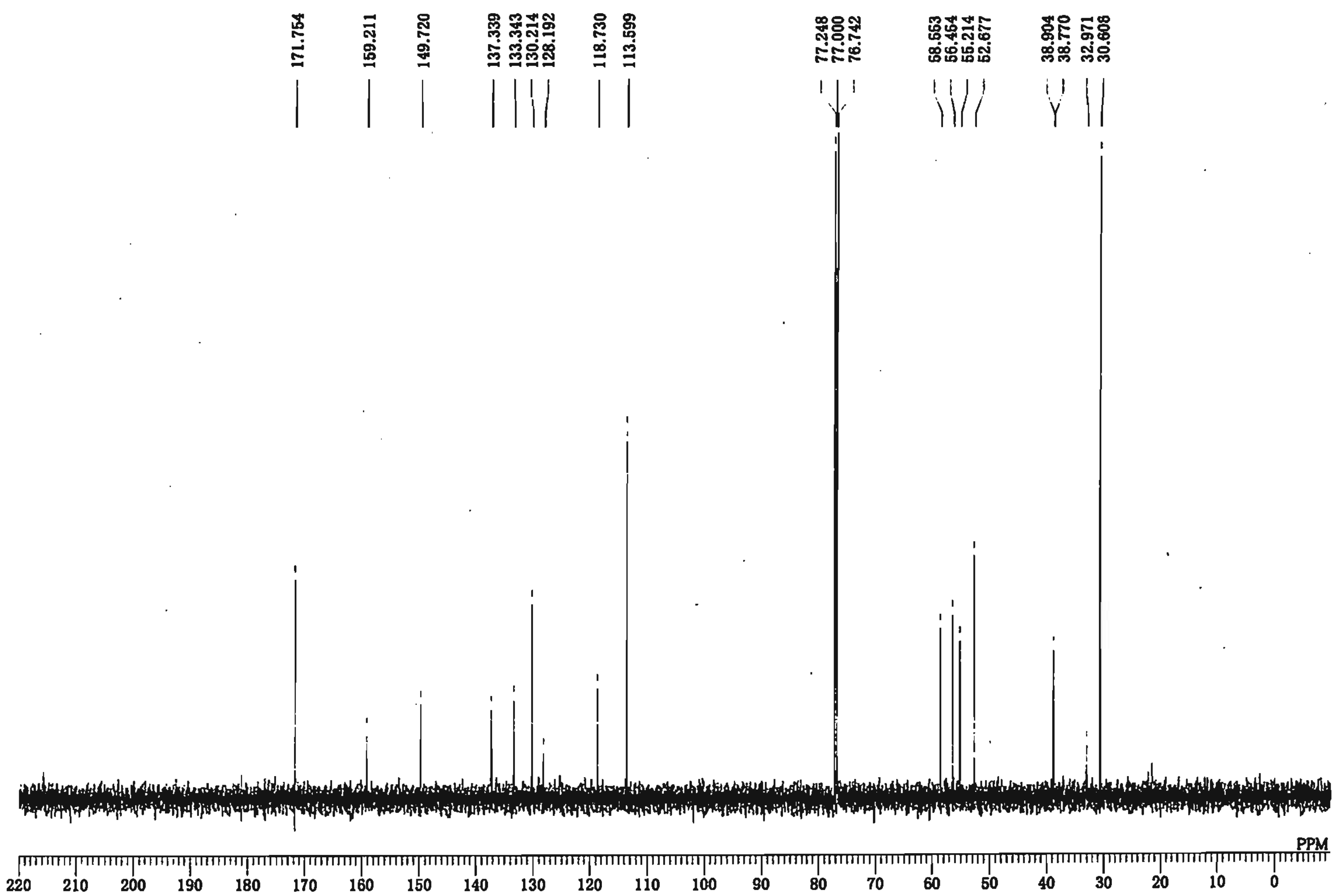

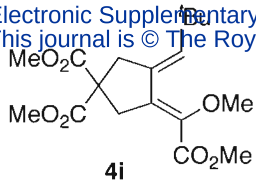

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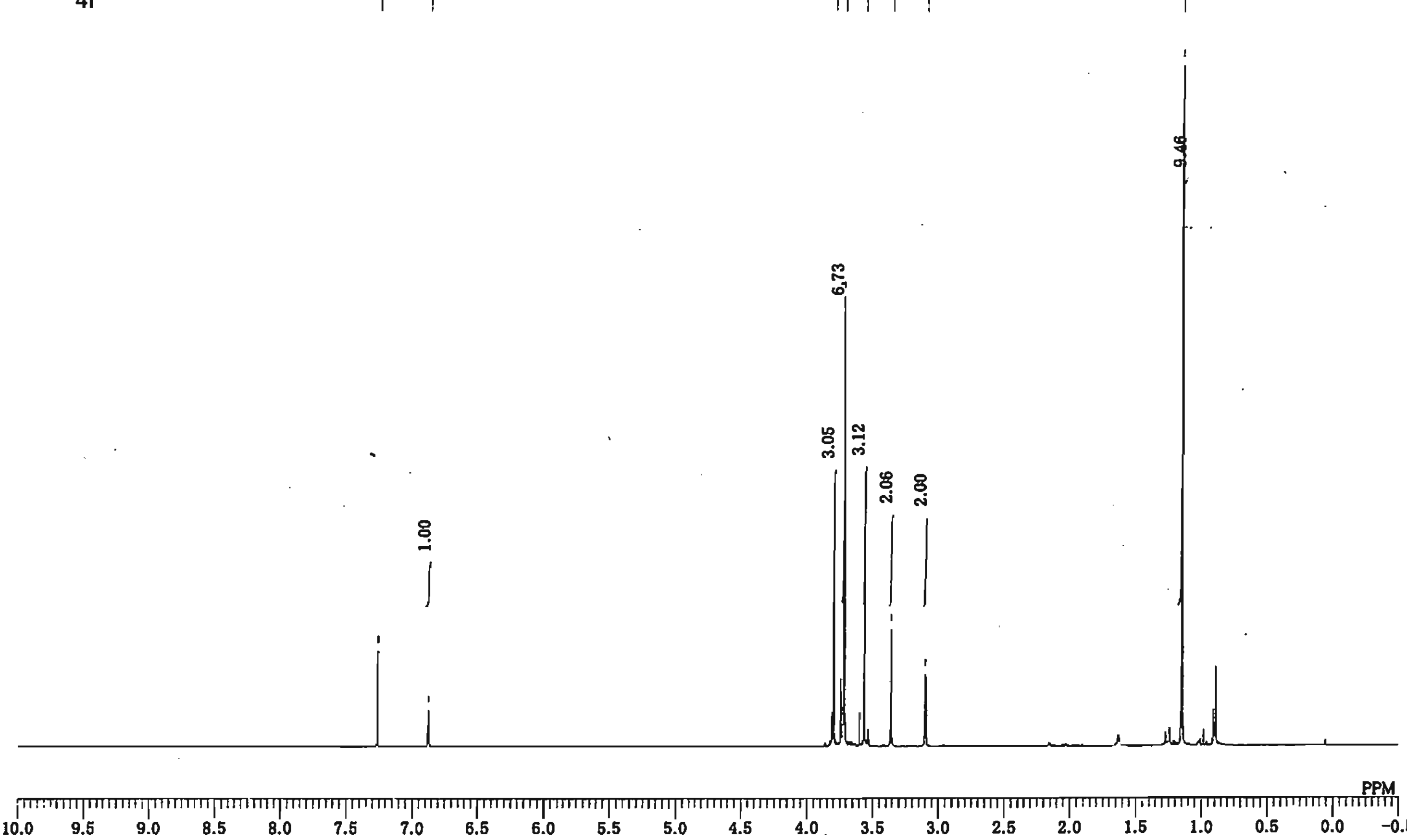

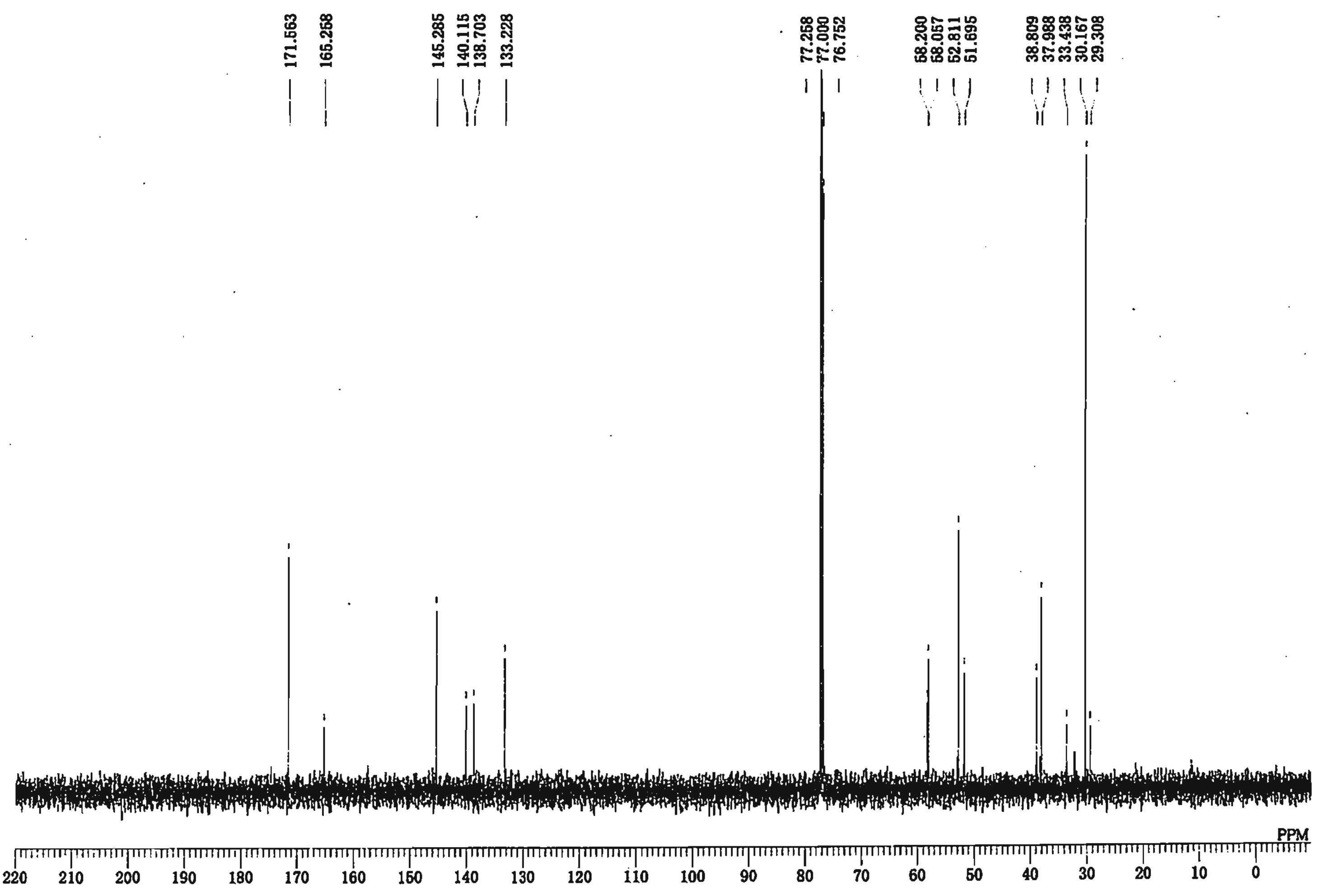

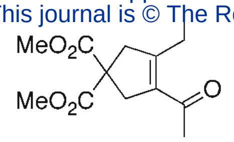

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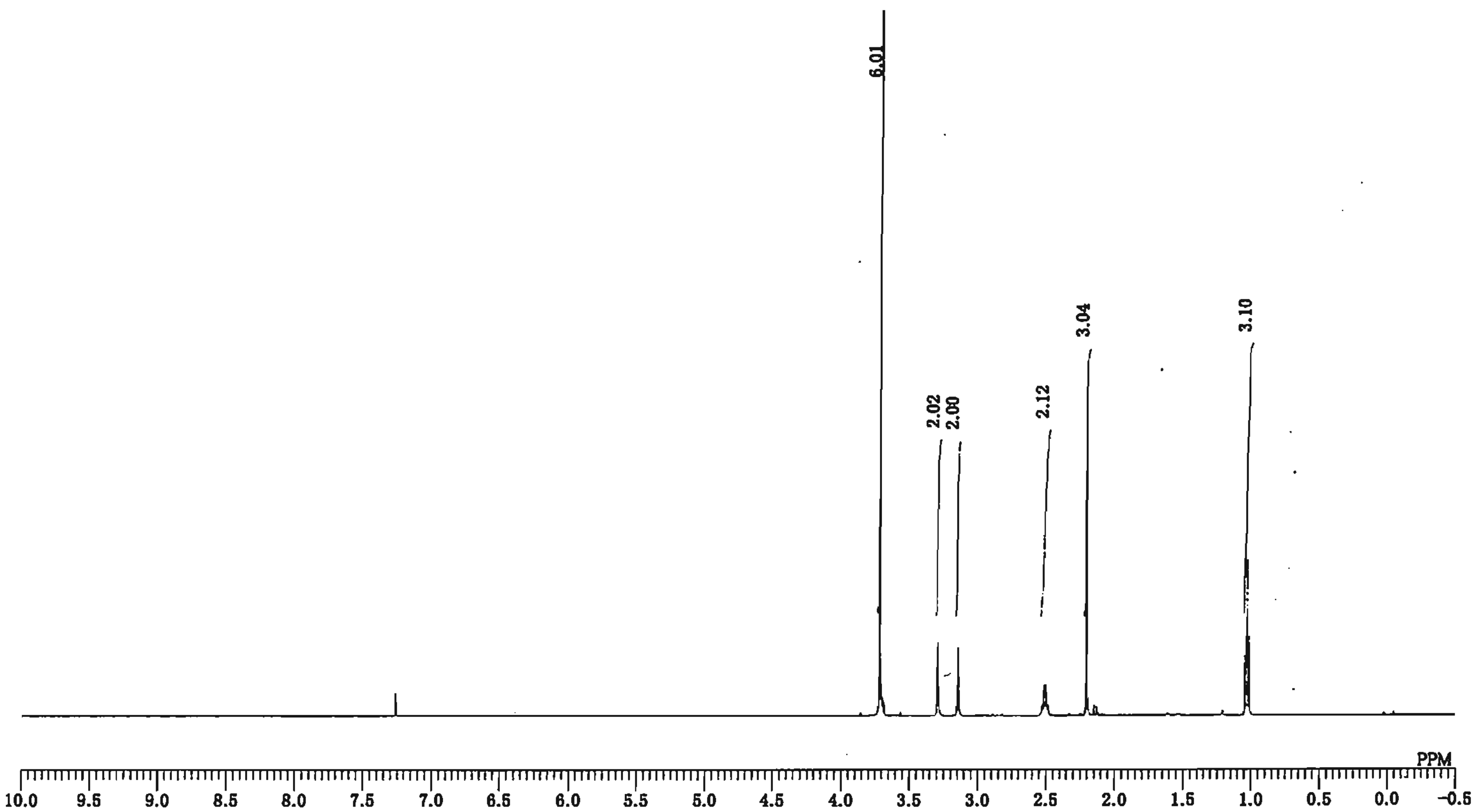
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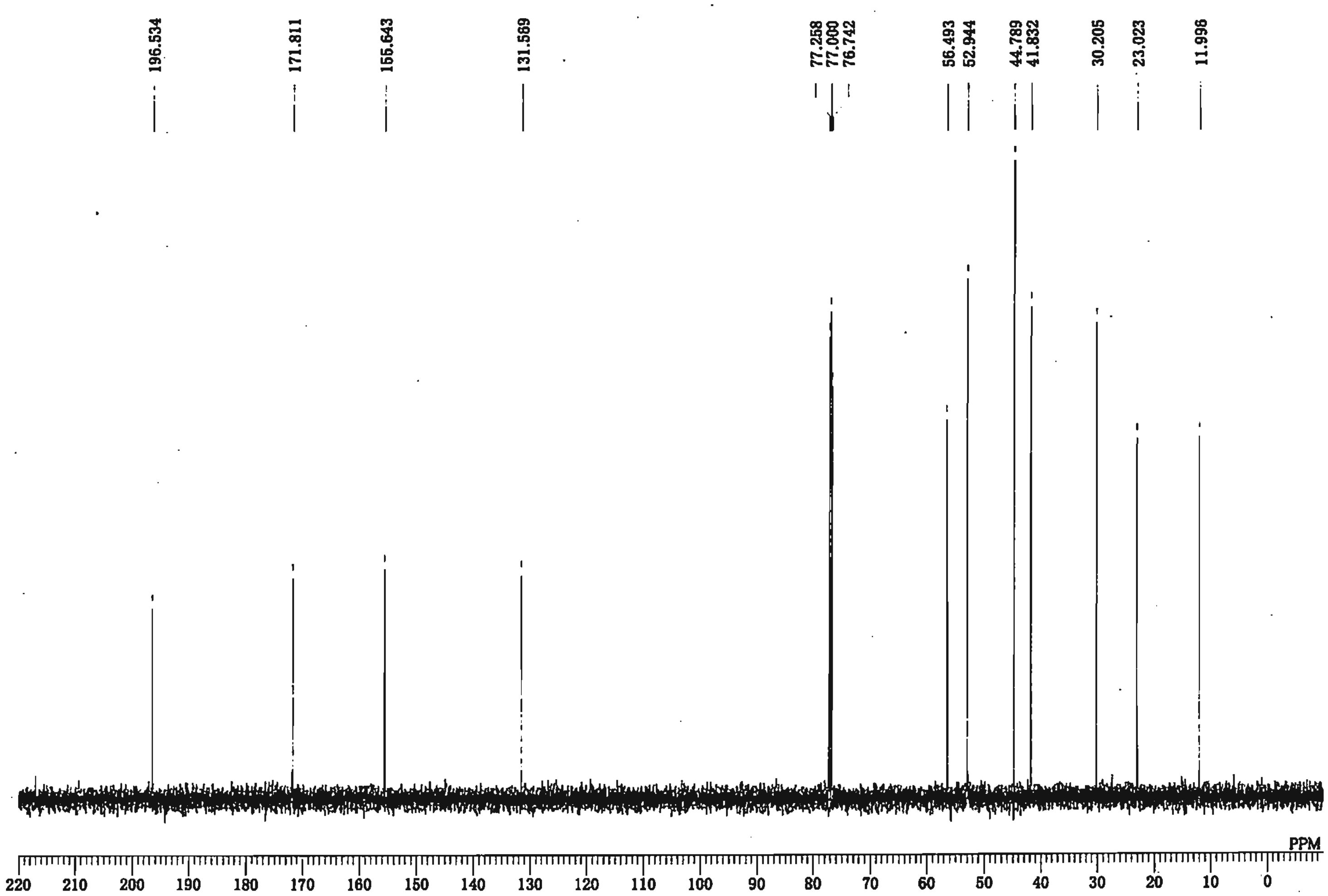
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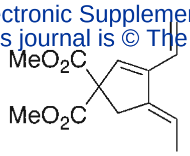
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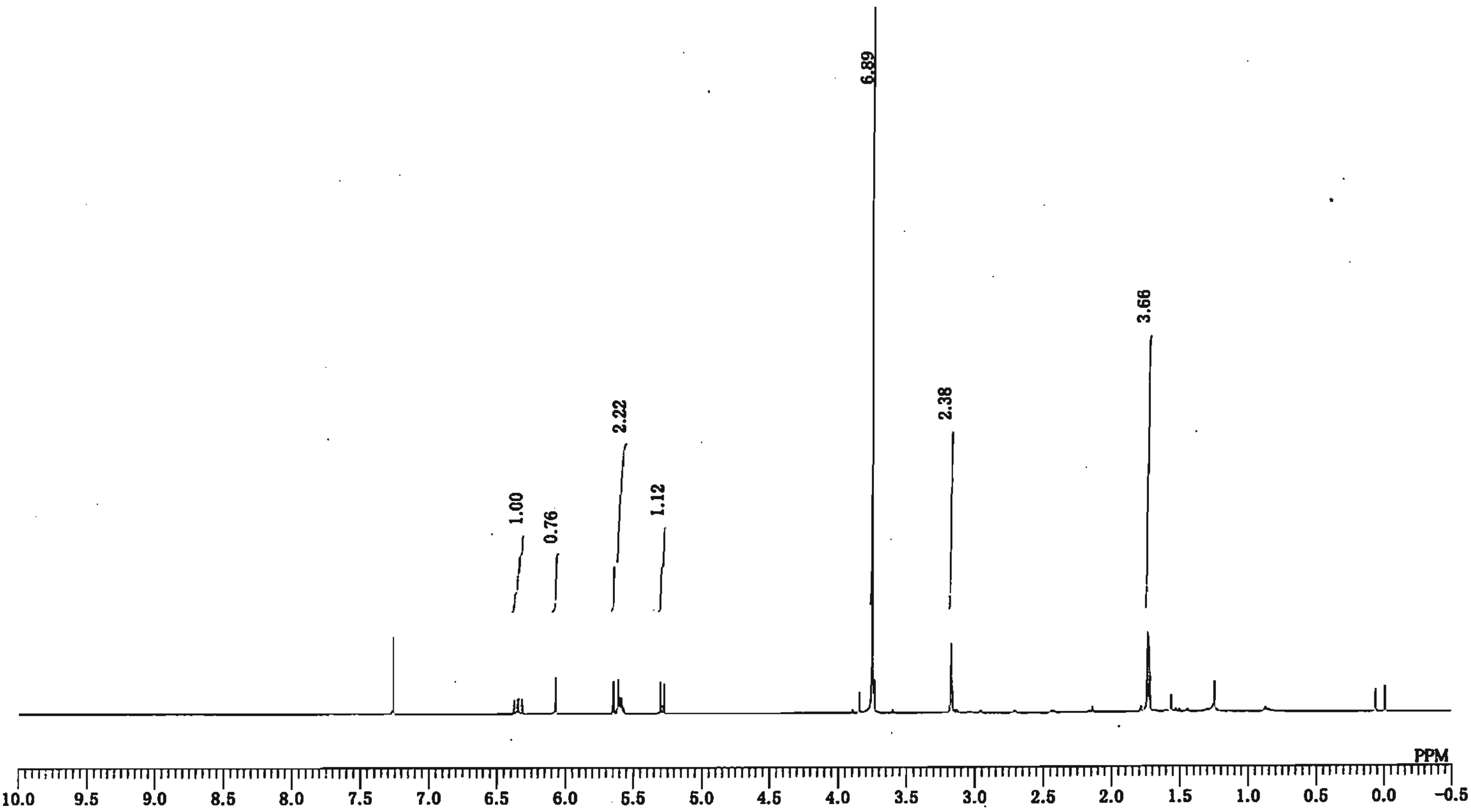
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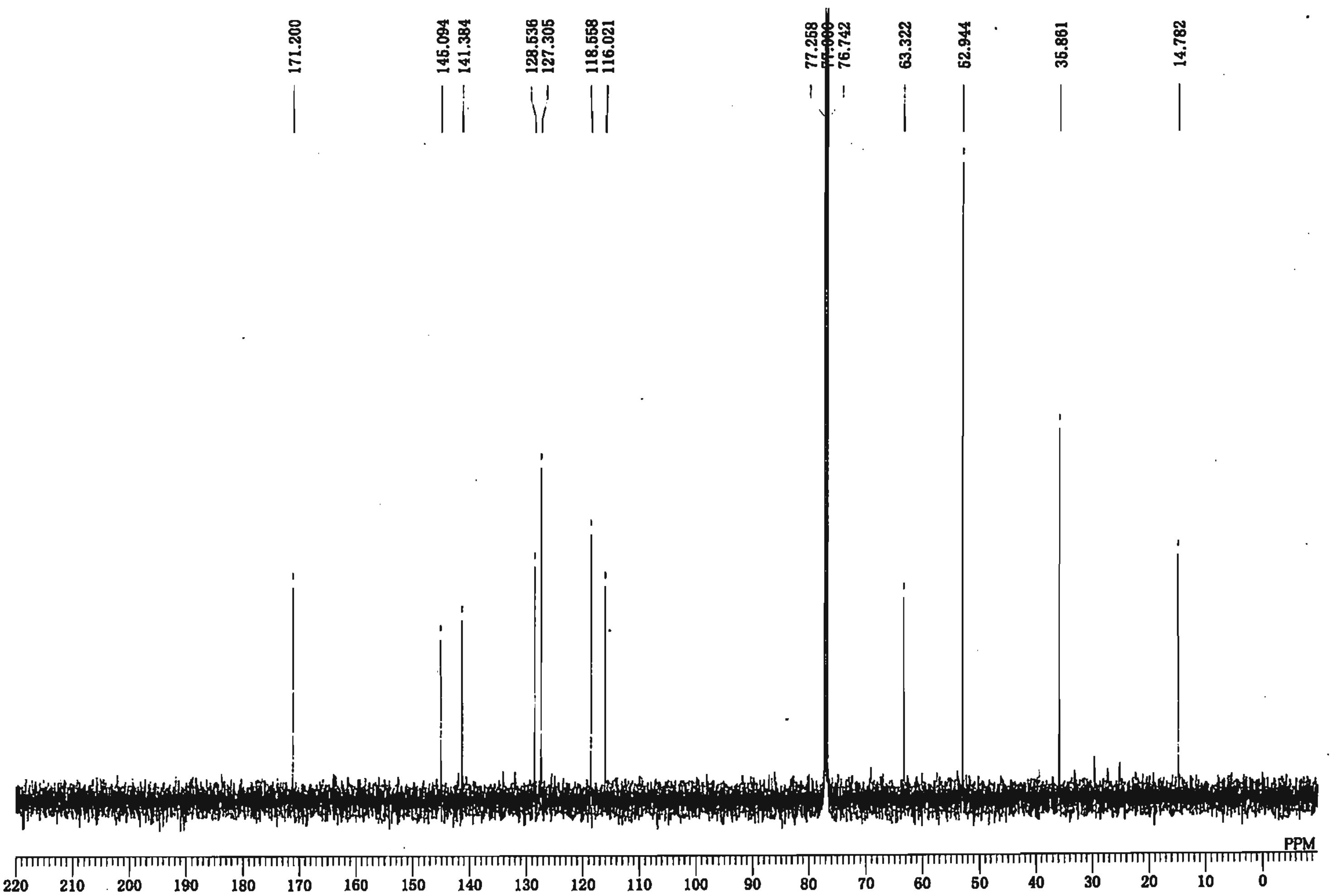
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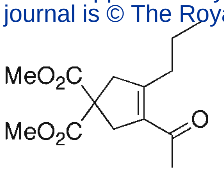
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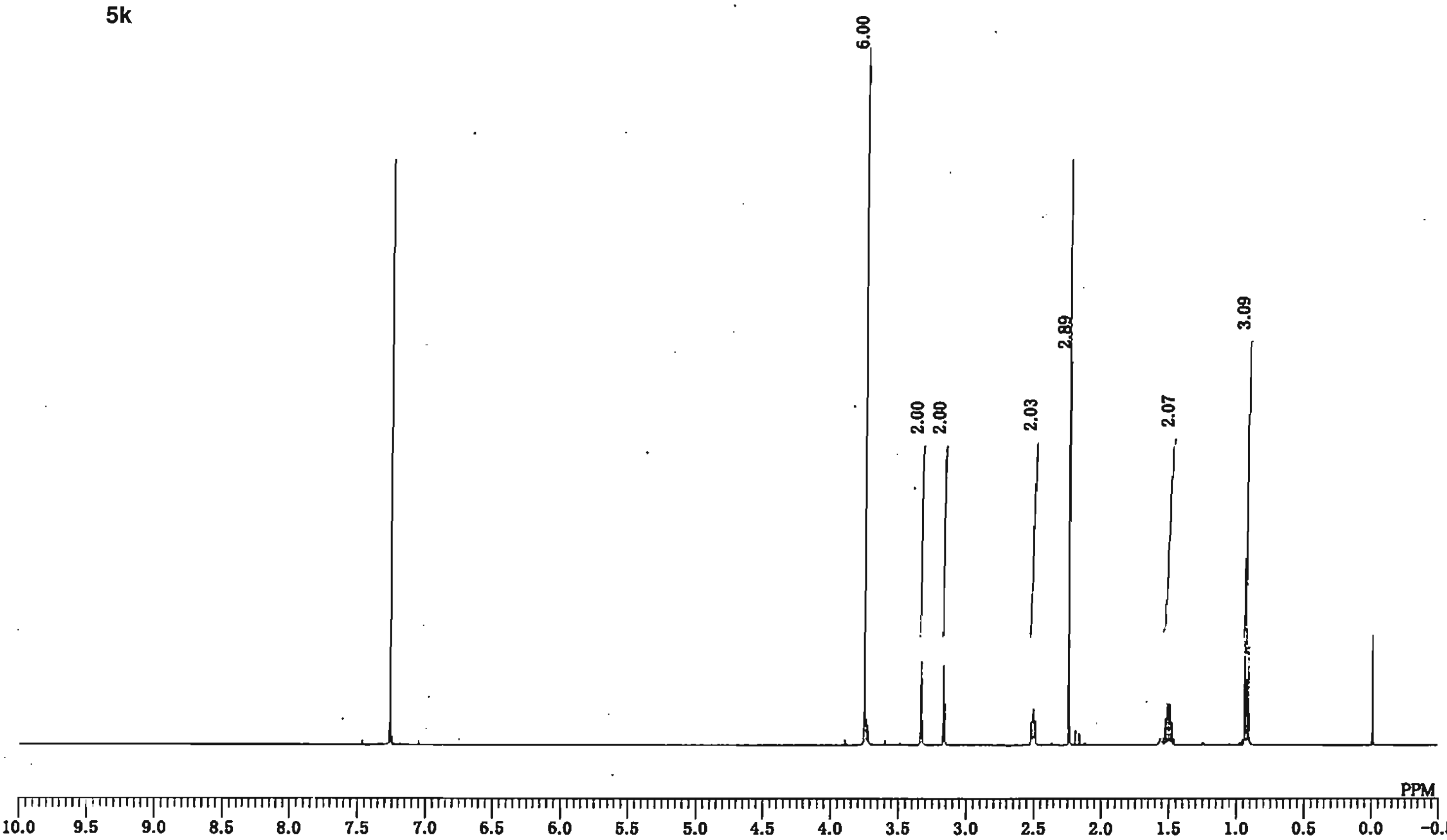
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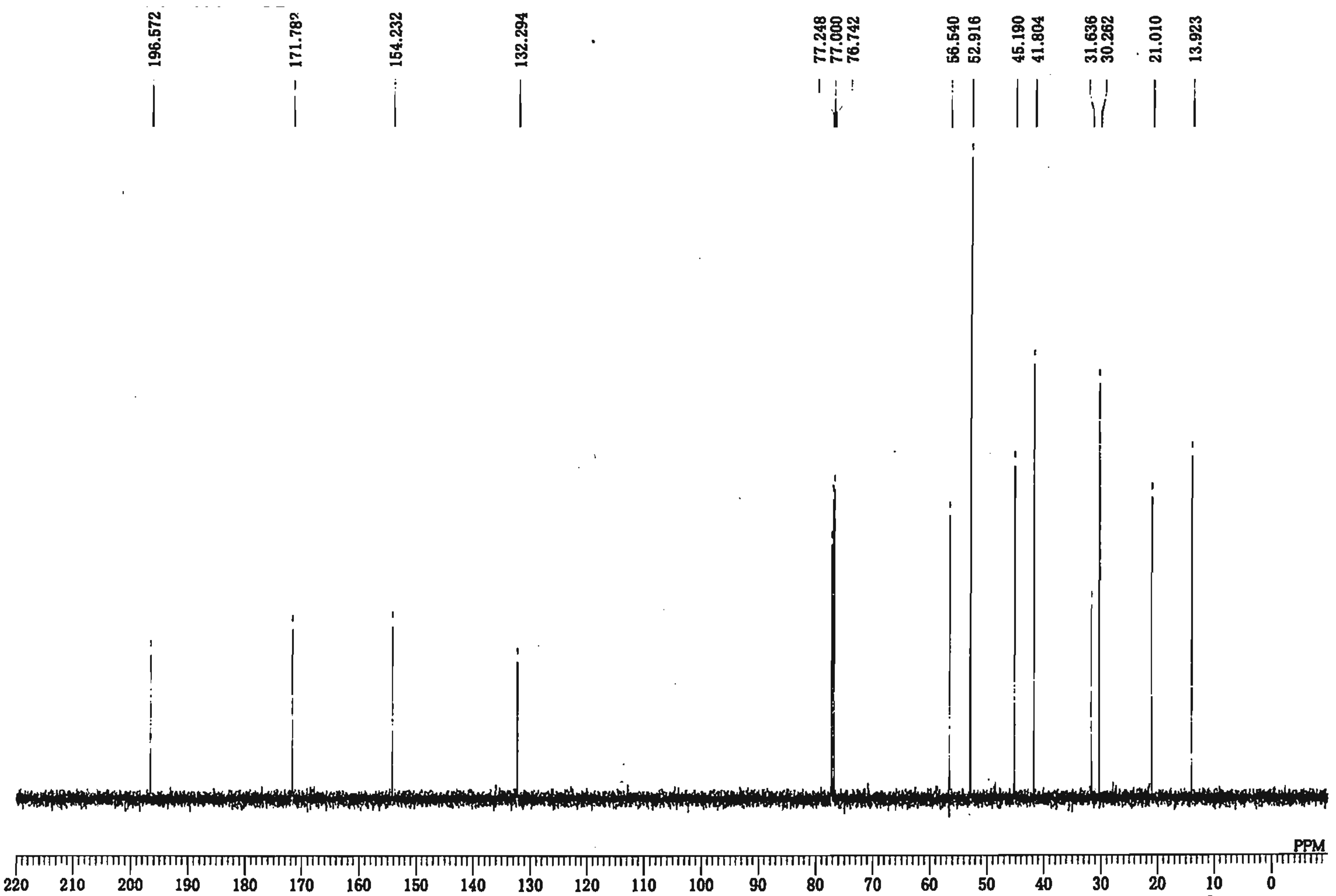
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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56.540
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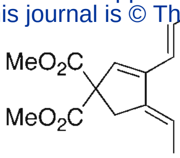
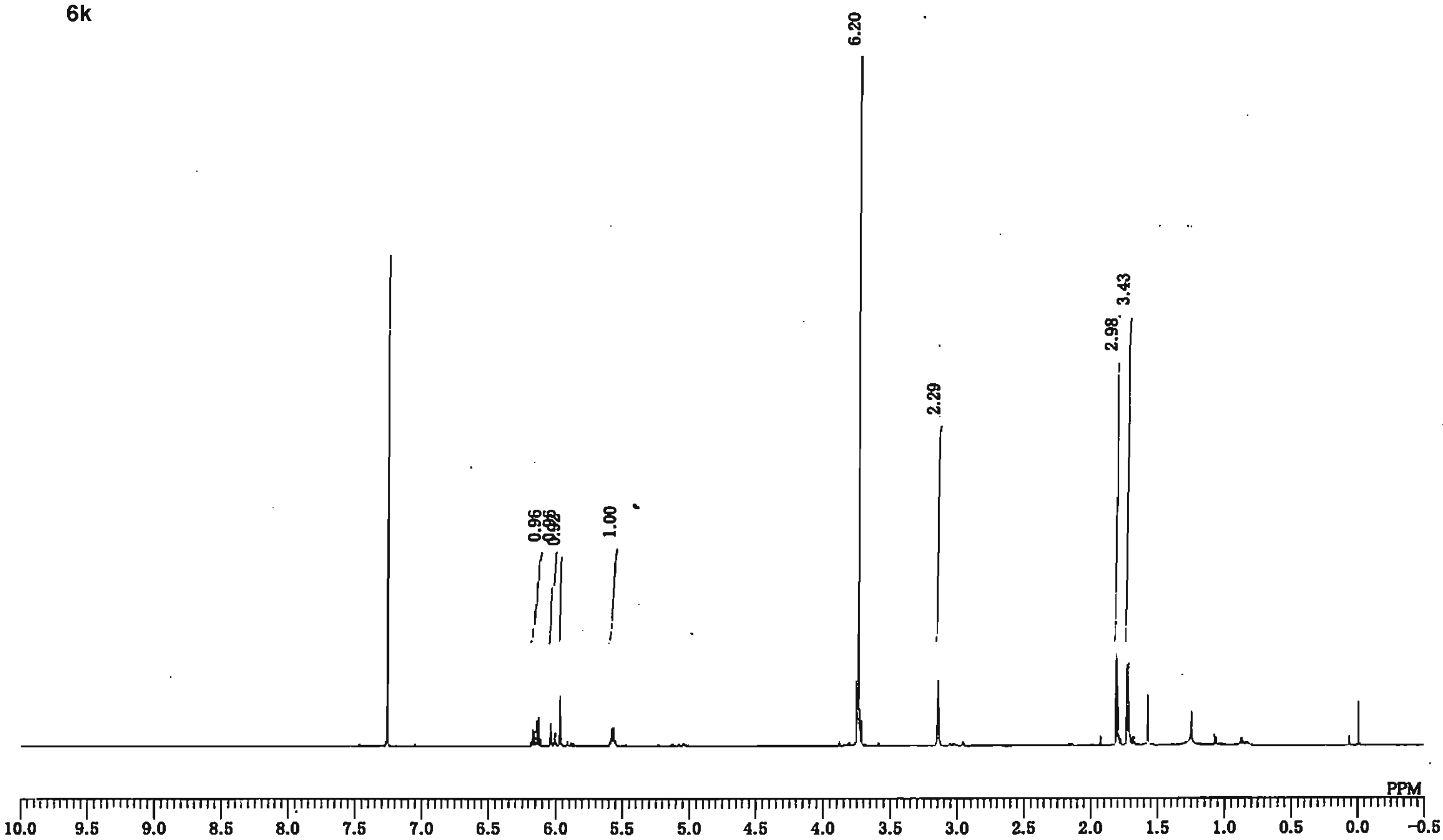
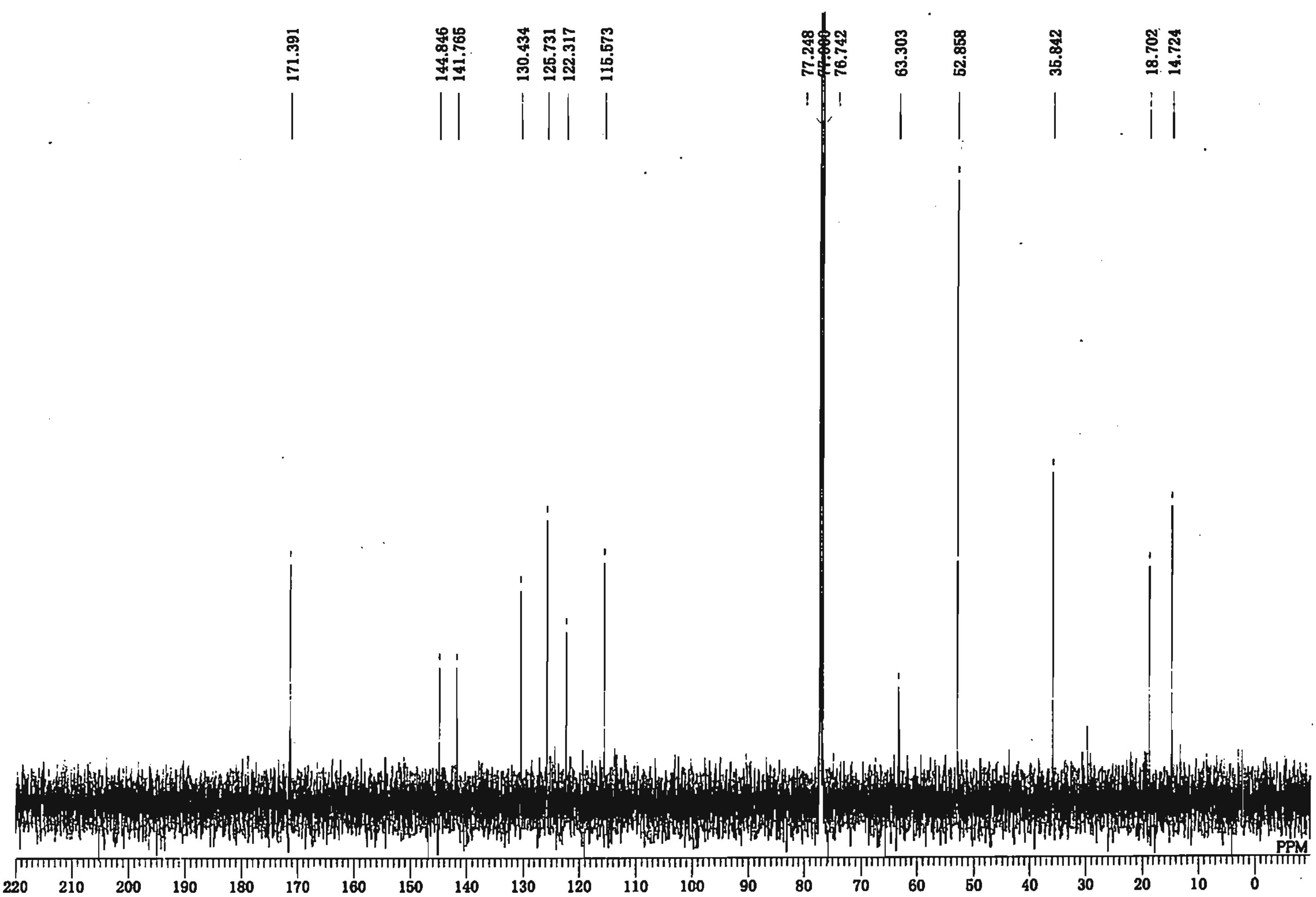
31.636
30.262
21.010
13.923
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



6k


6.20
2.29
2.98
3.43
0.96
1.00
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5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141.765
130.434
125.731
122.317
115.573
77.248
76.742
63.303
52.858
35.842
18.702
14.724
PPM
220
210
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150
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70
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40
30
20
10
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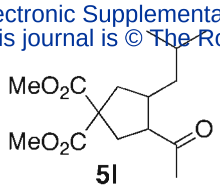
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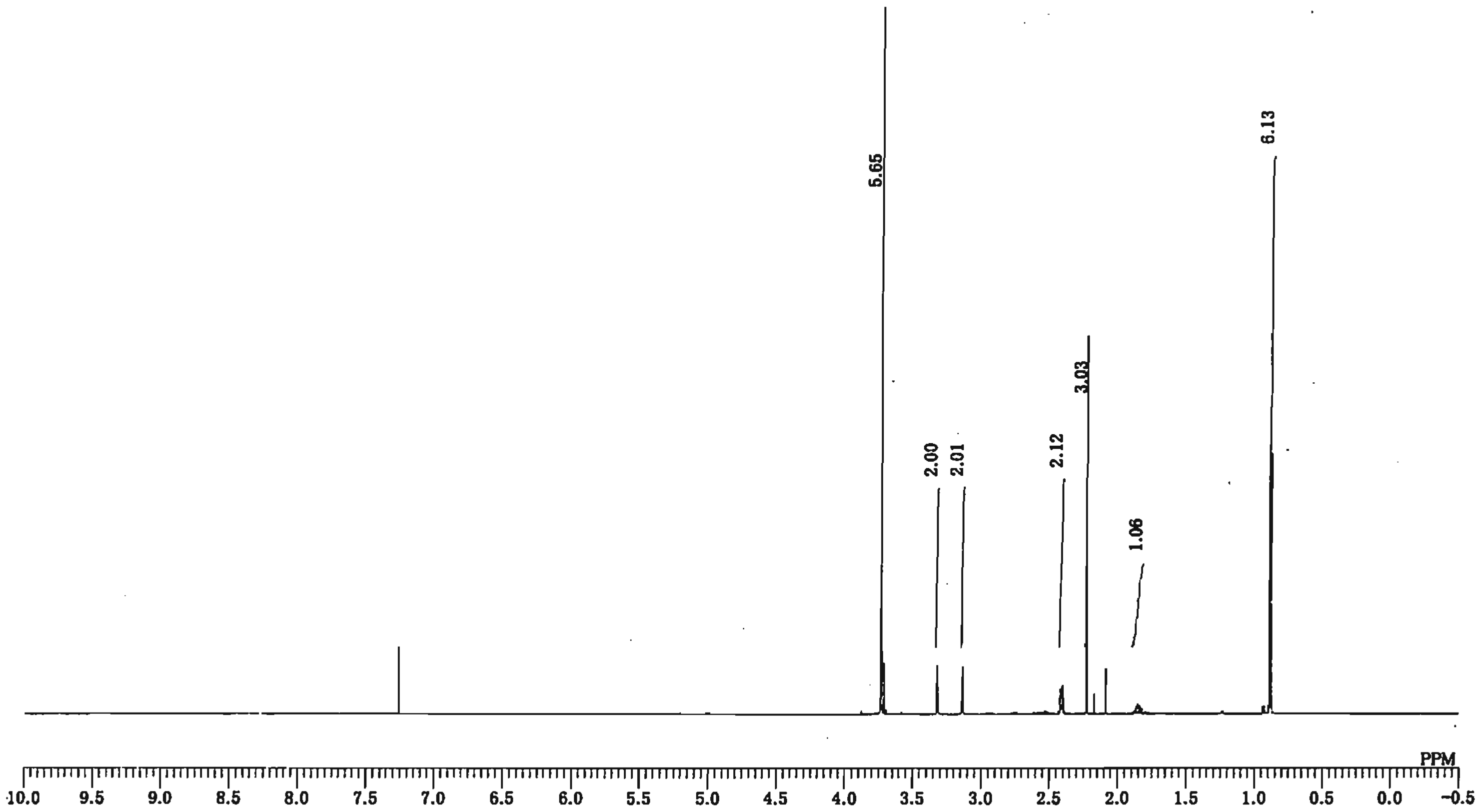
MeO2C
O

5l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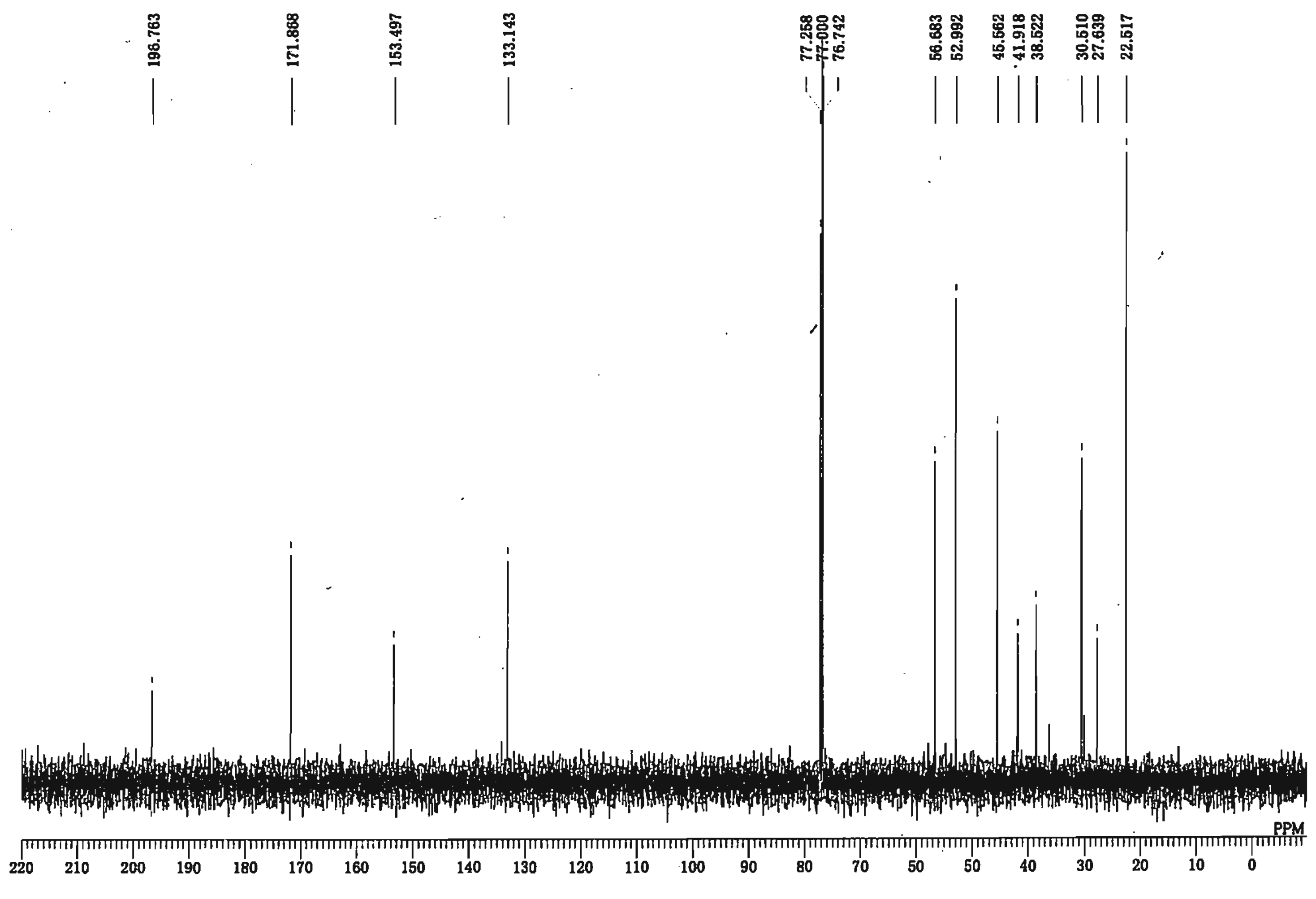
2.00
2.01
2.12
3.03
1.06
6.13
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5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153.497
133.143
77.258
77.000
76.742
56.683
52.992
45.562
41.918
38.522
30.510
27.639
22.517
PPM
220
210
200
190
180
170
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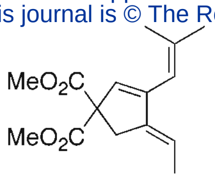
90
80
70
60
50
40
30
20
10
0

Electronic Supplementary Material (ESI) for Chemical Communications



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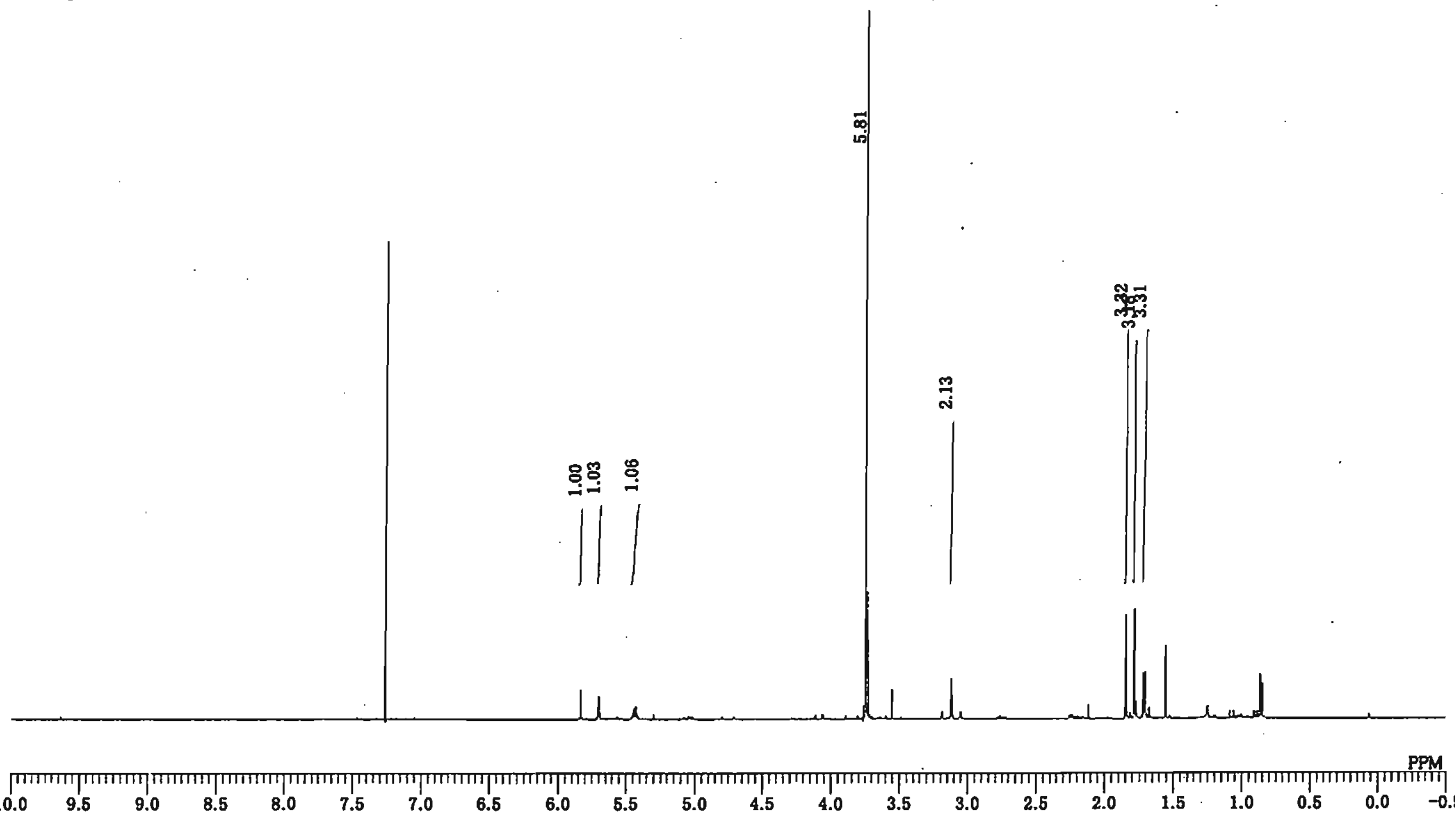

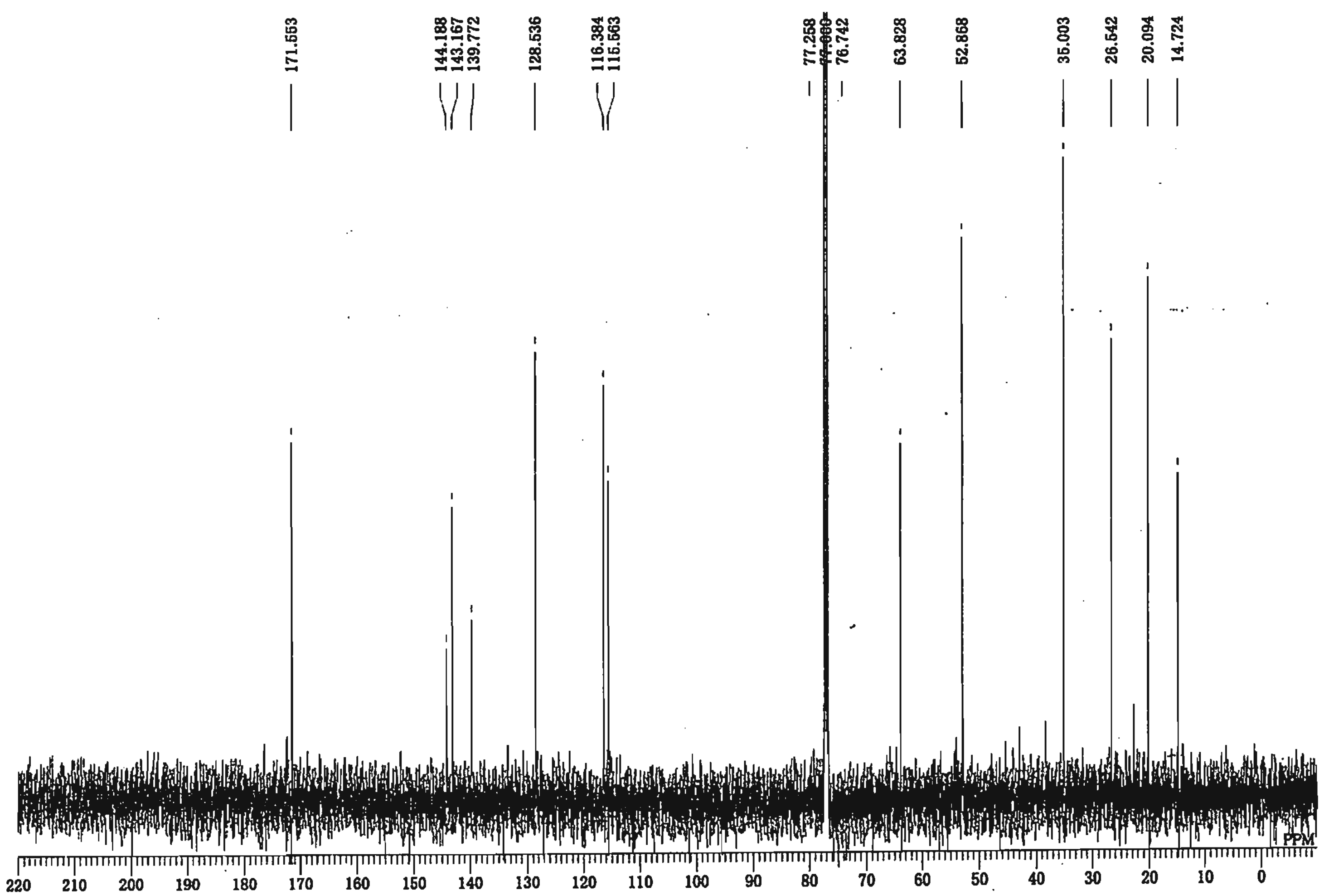

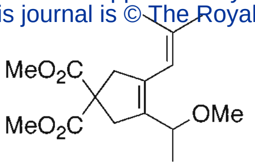
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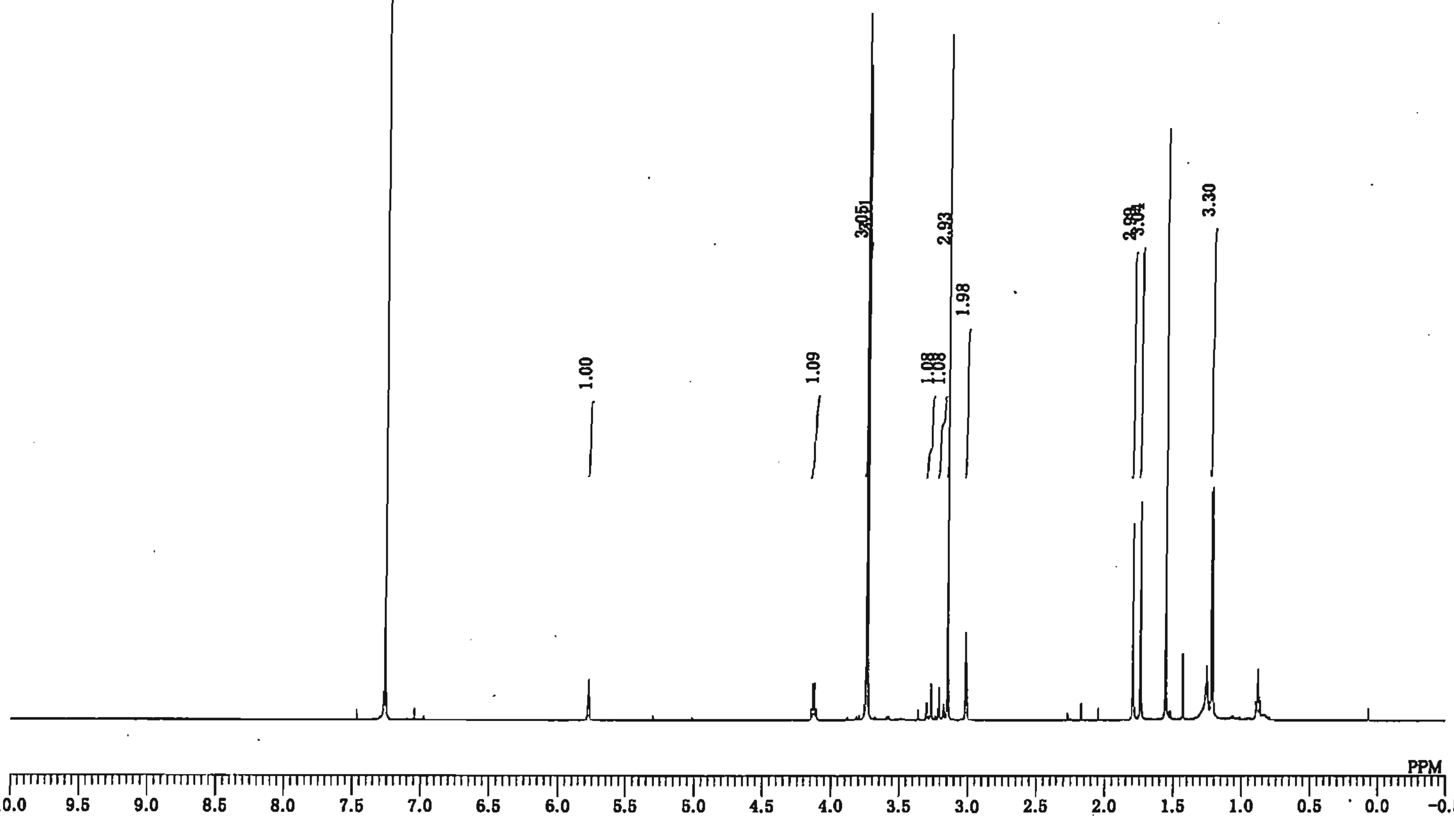
MeO2C
OMe

7l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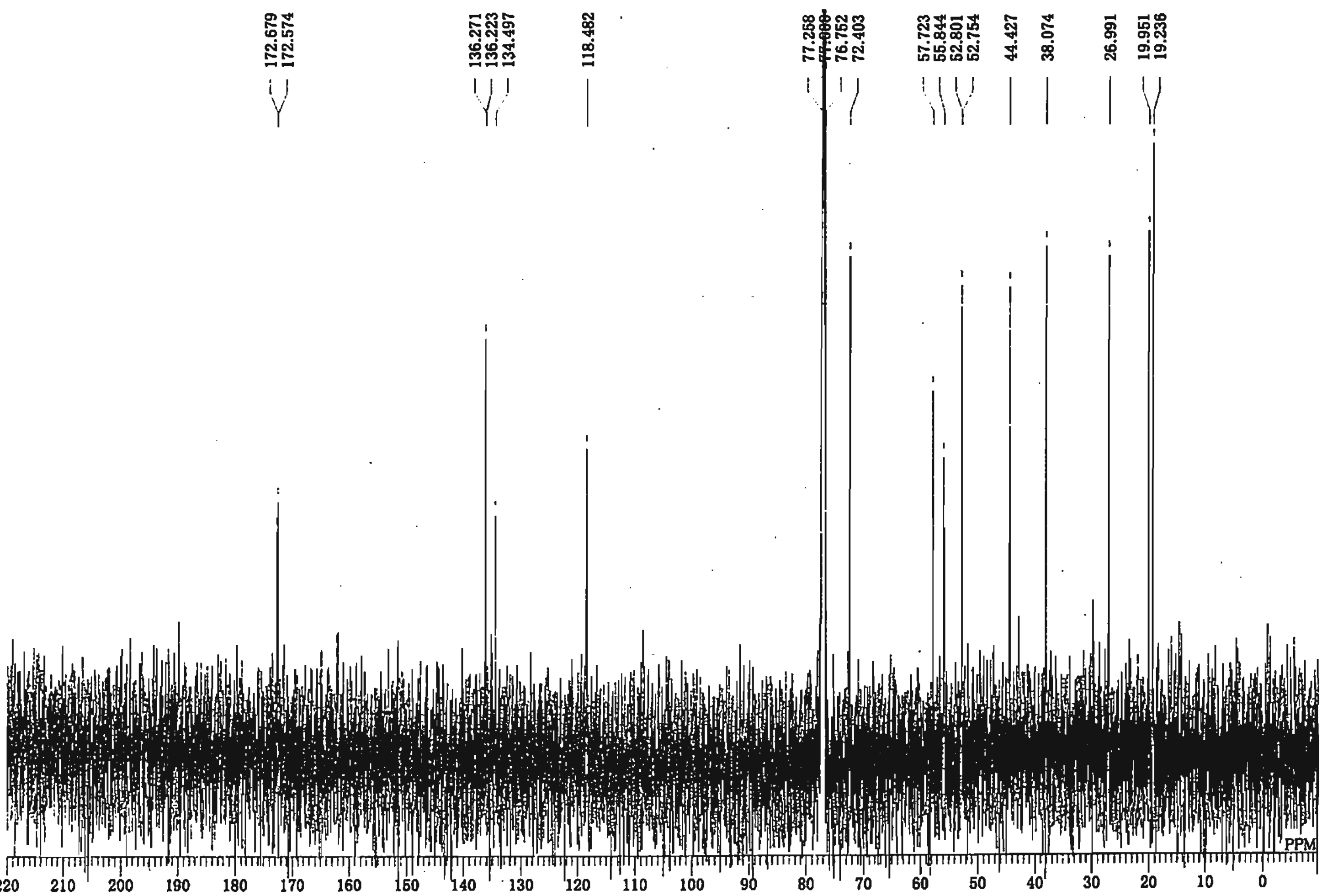
1.09
2.93
1.98
3.30
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5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76.752
72.403
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52.801
52.754
44.427
38.074
26.991
19.951
19.236
PPM
220
210
200
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150
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110
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30
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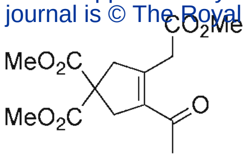
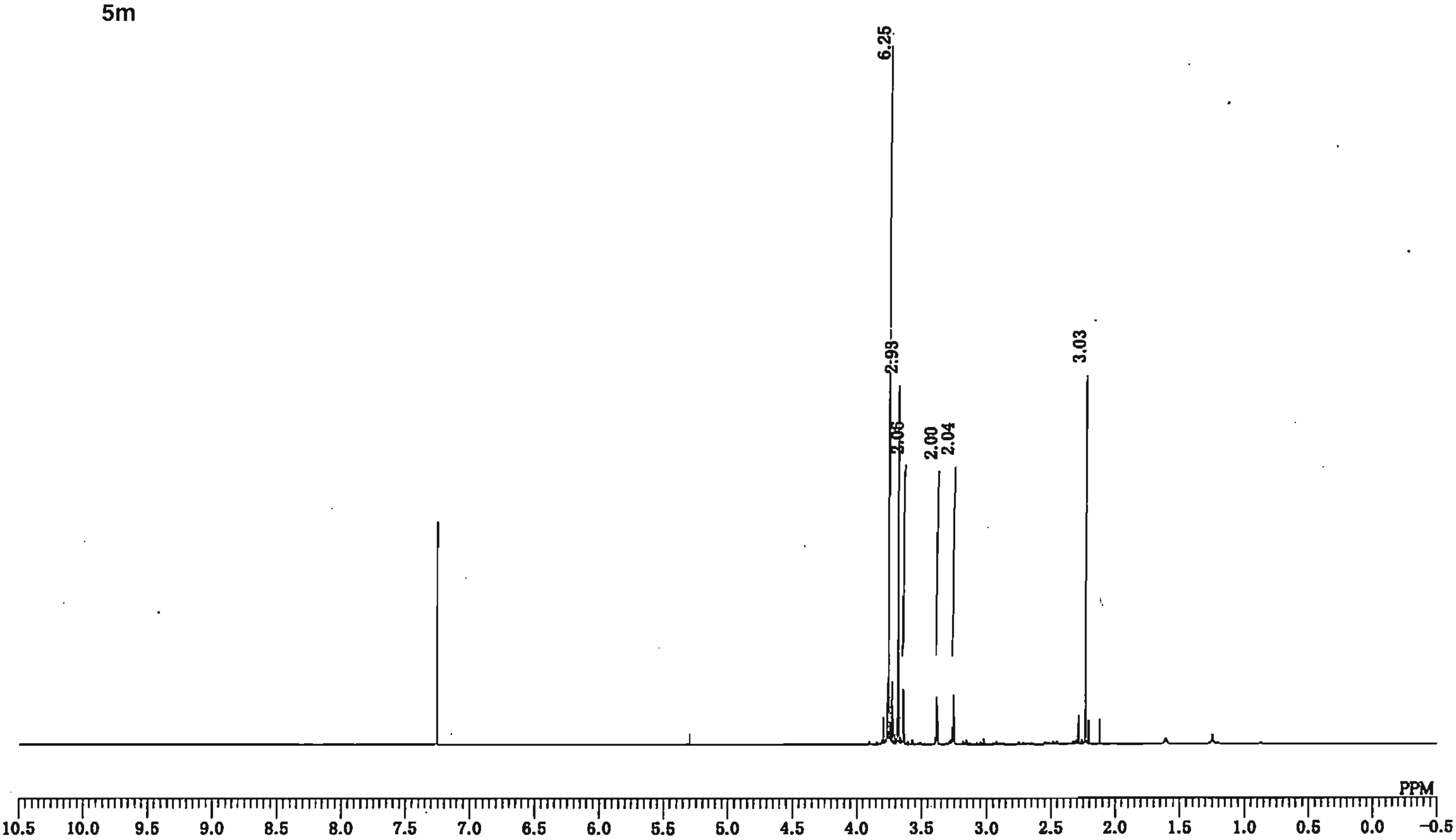
10
0


CO2Me
MeO2C
MeO2C
O

5m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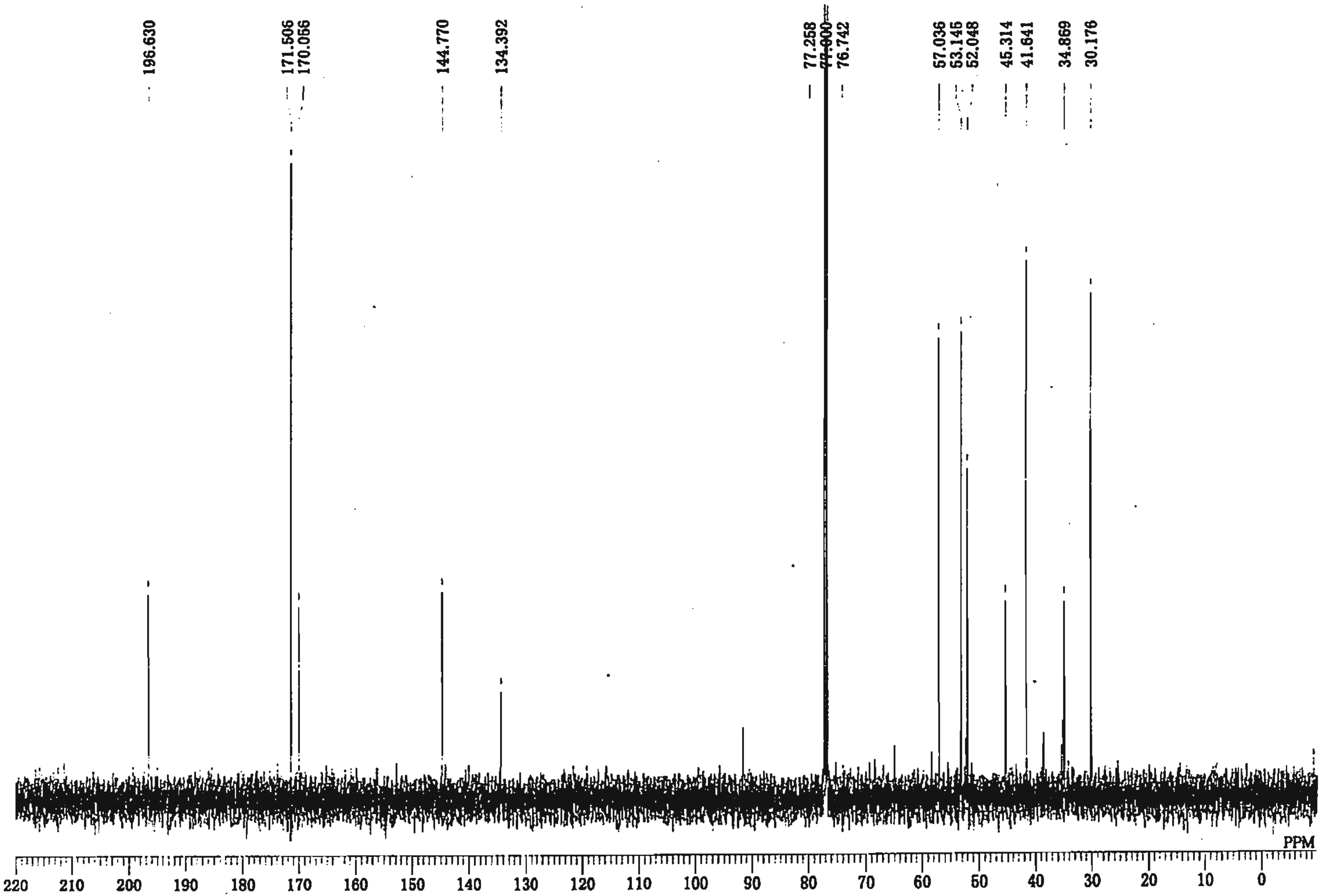
2.93
3.06
2.00
2.04
3.03
PPM
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5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77.000
76.742
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53.145
52.048
45.314
41.641
34.869
30.176
PPM
220
210
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180
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150
140
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120
110
100
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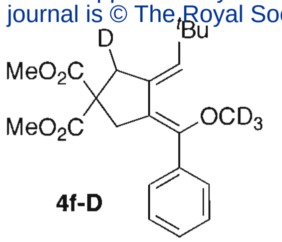
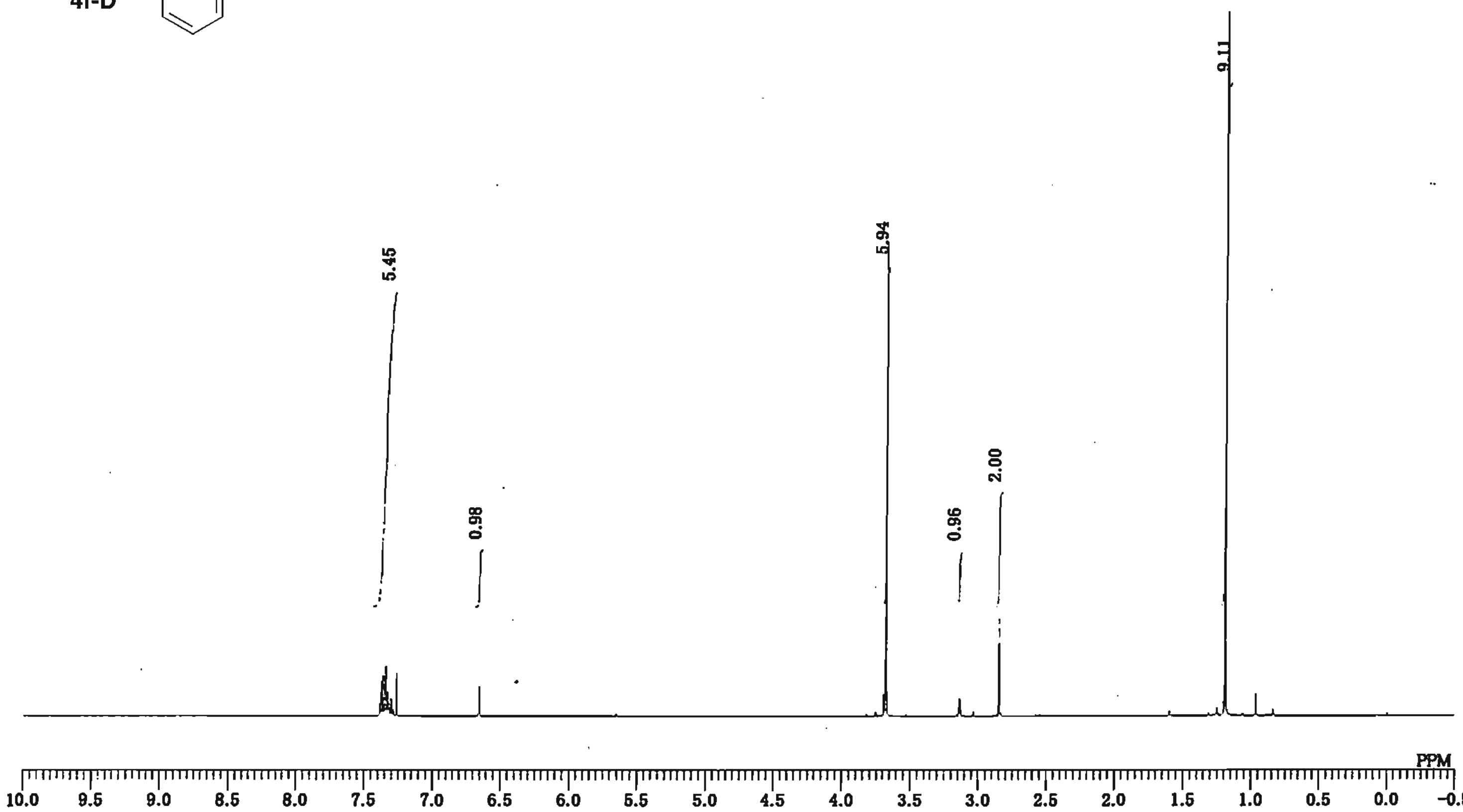
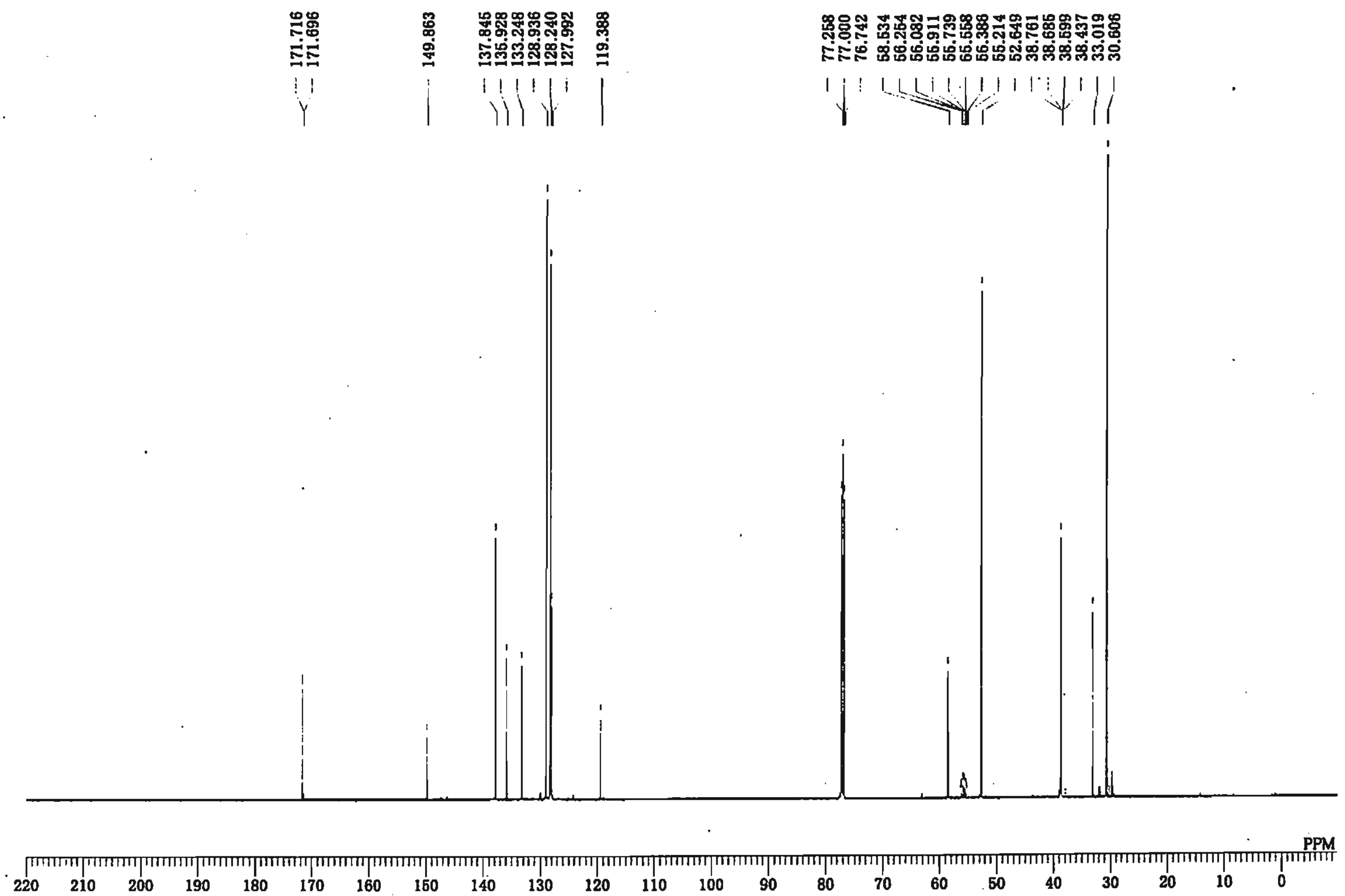
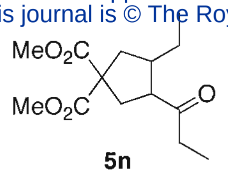
80
70
60
50
40
30
20
10
0



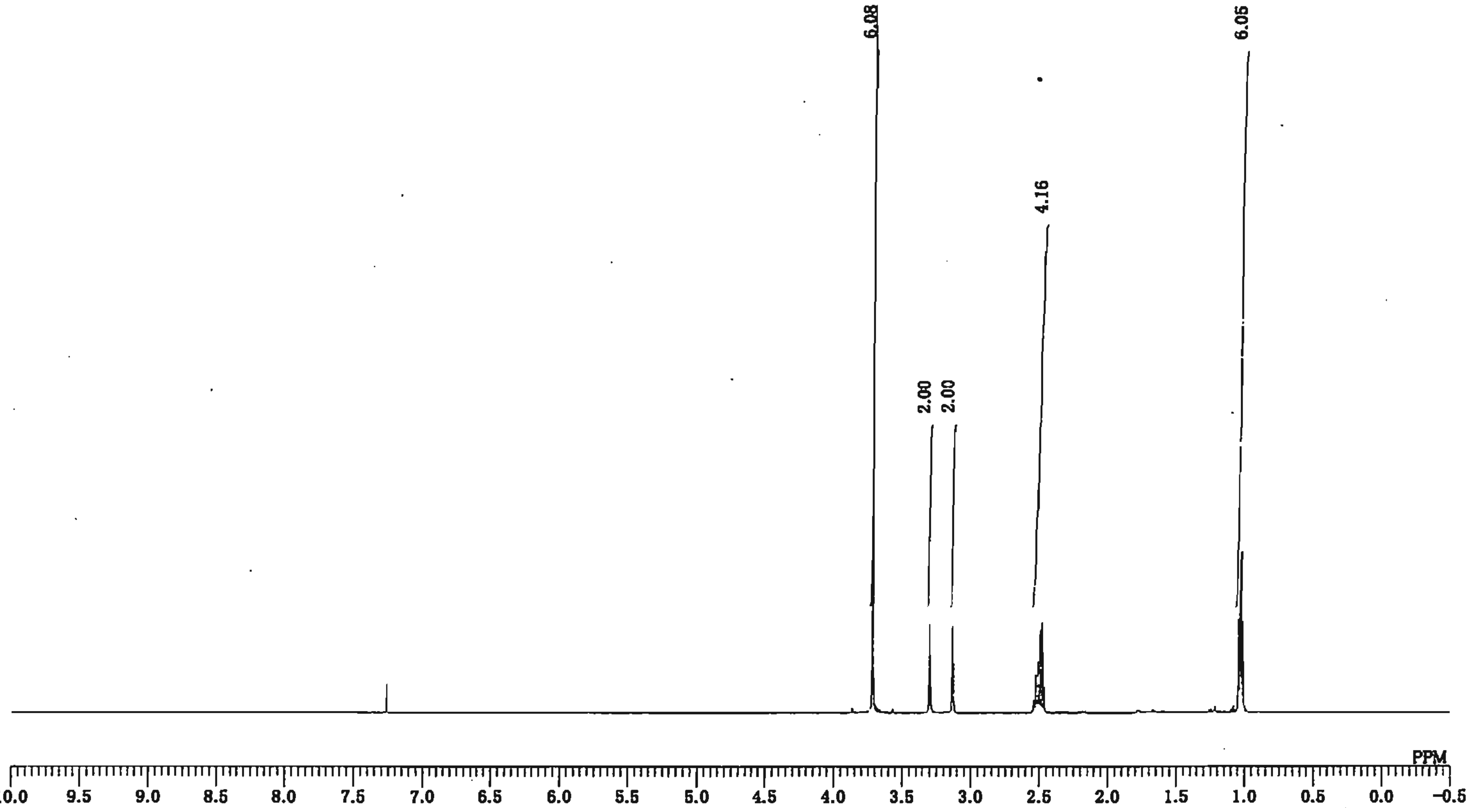
4f-D






MeO2C
MeO2C
O

5n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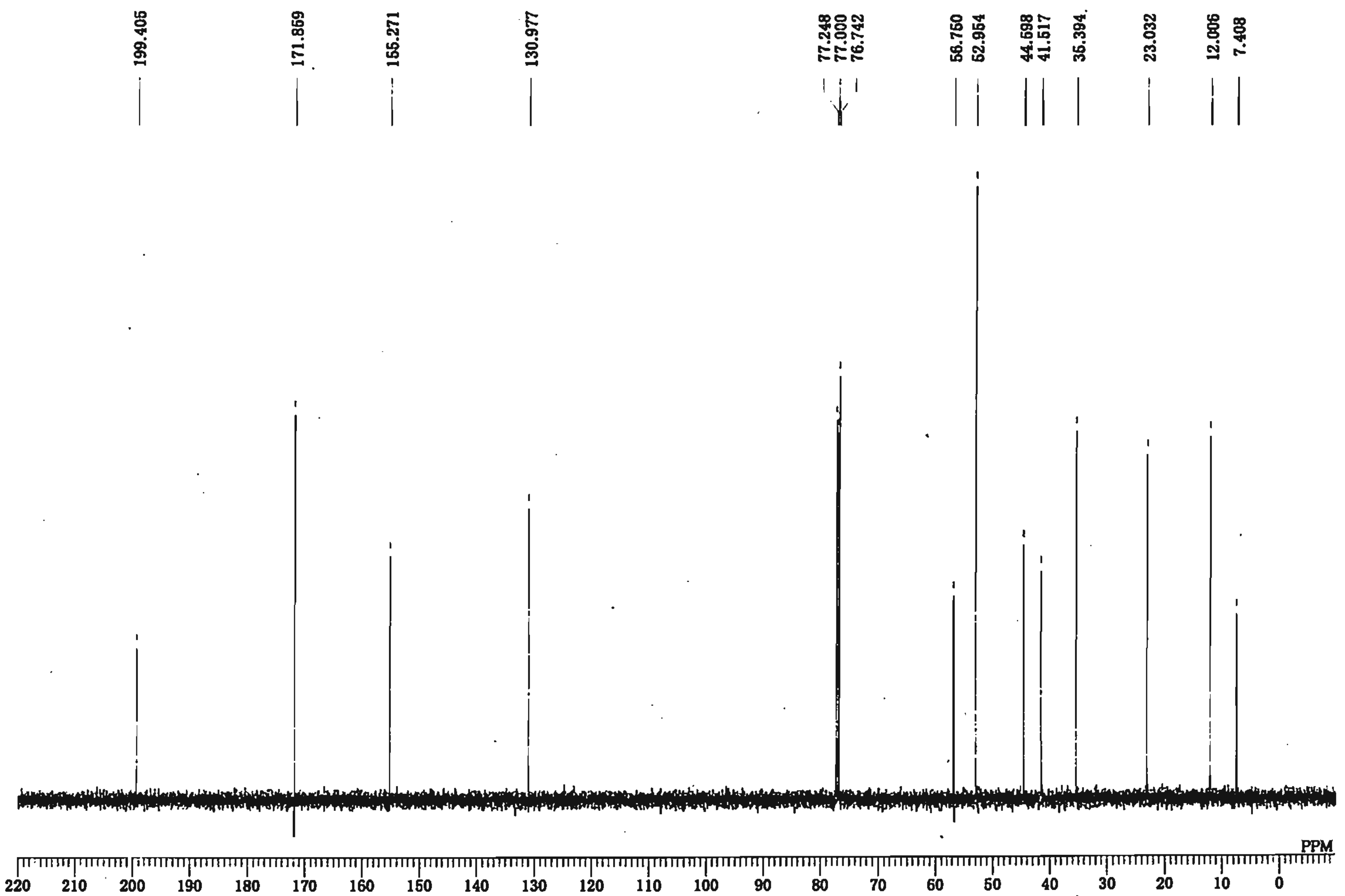
2.00
2.00
4.16
6.05
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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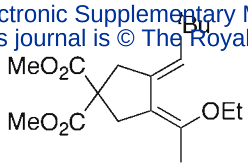
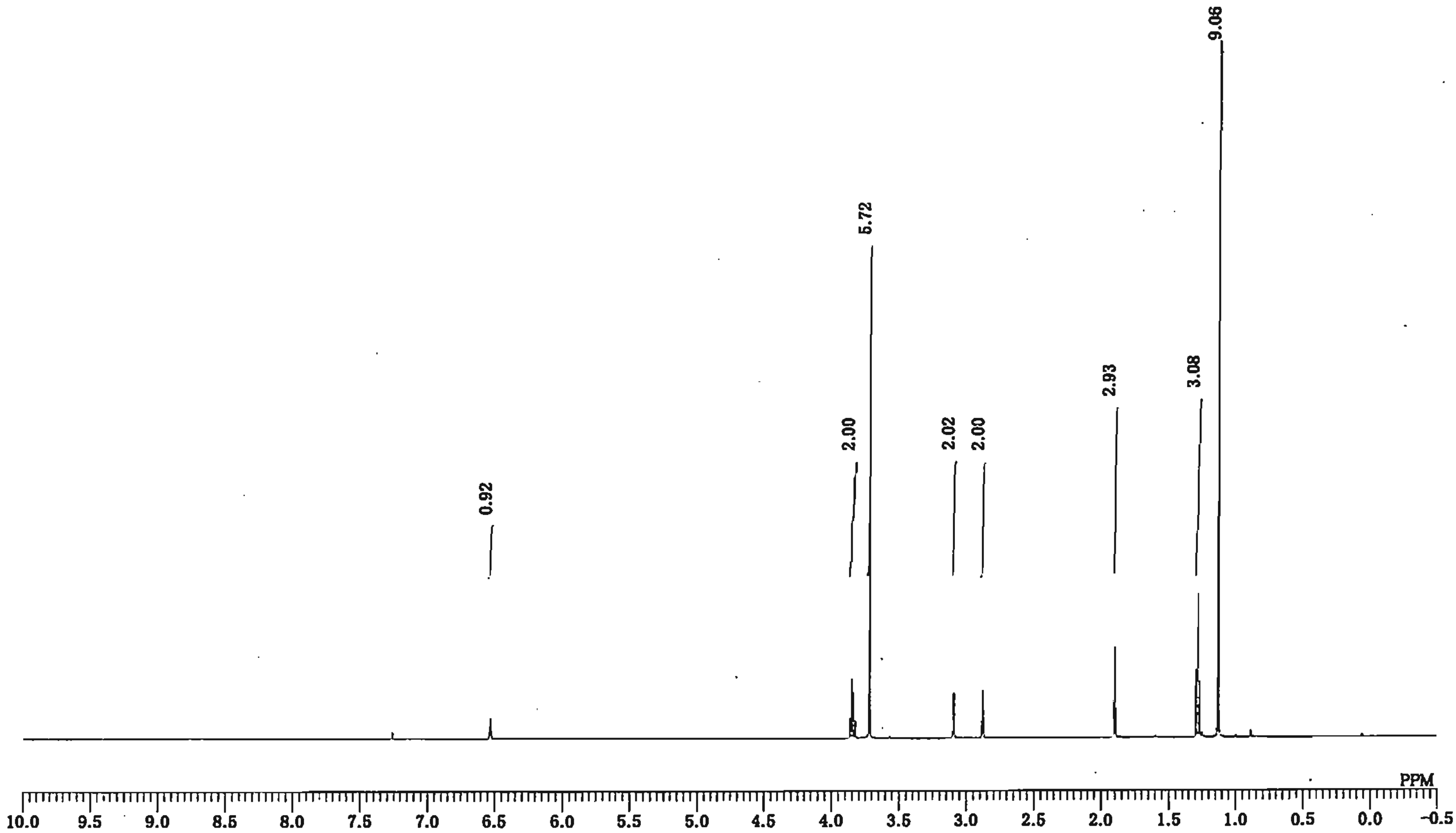
77.248
77.000
76.742
56.750
52.954
44.598
41.517
35.394
23.032
12.006
7.408
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


ᵗBu
MeO2C
MeO2C
OEt

4o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0.92
PPM
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9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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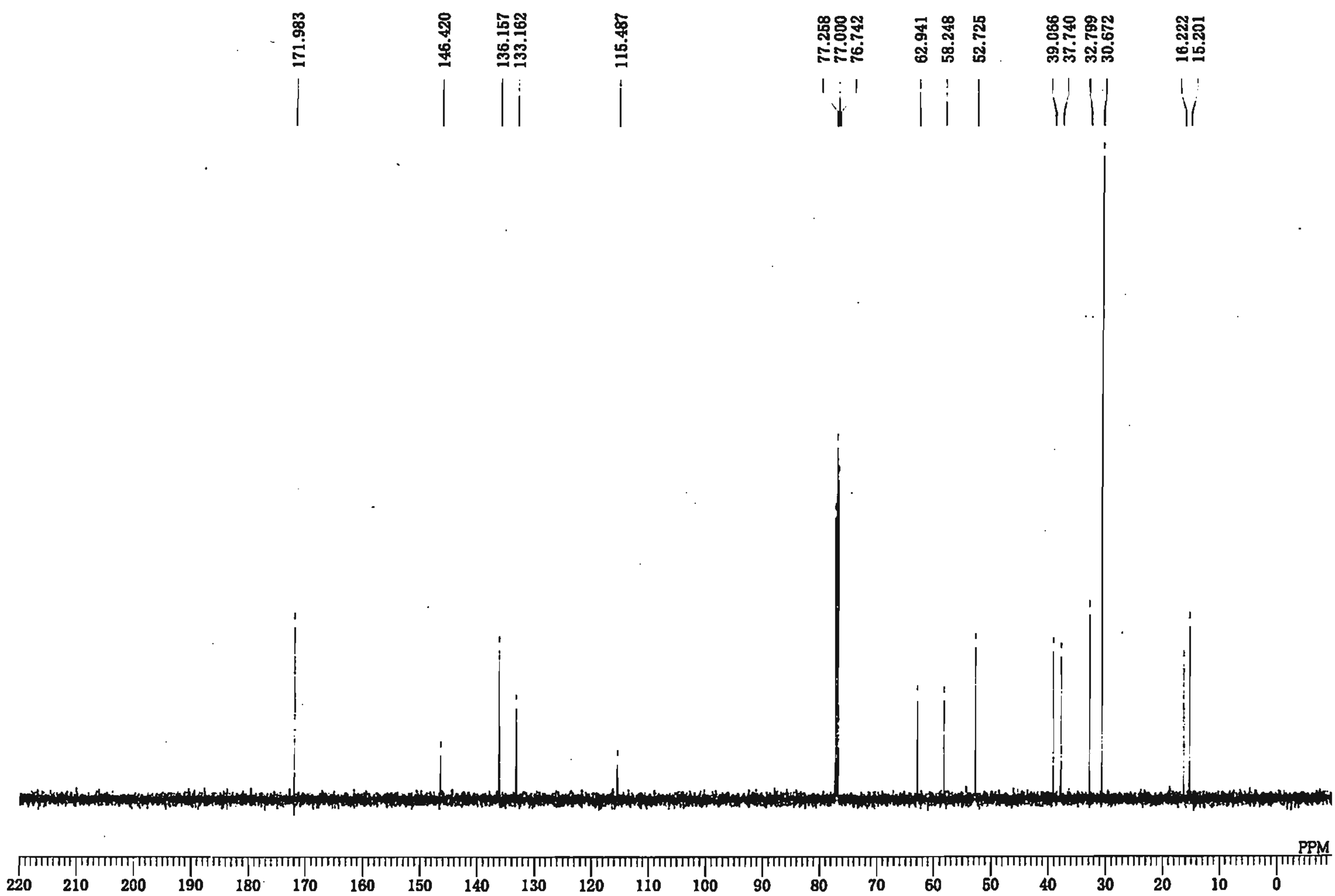
-0.5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77.000
76.742
62.941
58.248
52.725
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37.740
32.799
30.672
16.222
15.201
PPM
220
210
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30
20
10
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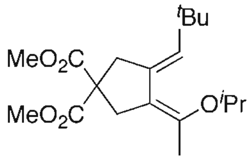
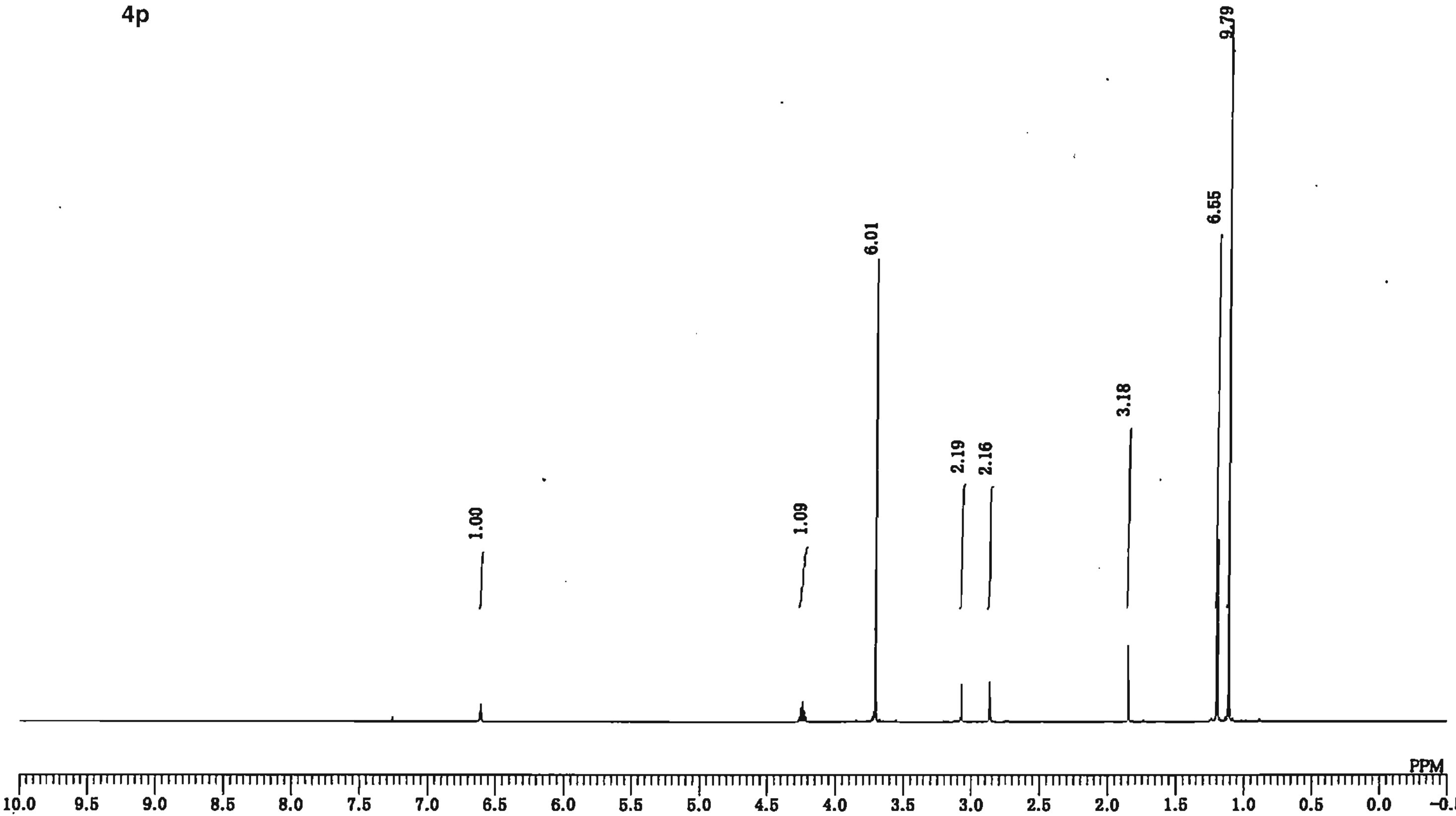


^tBu
MeO_2C
MeO_2C
O^iPr

4p



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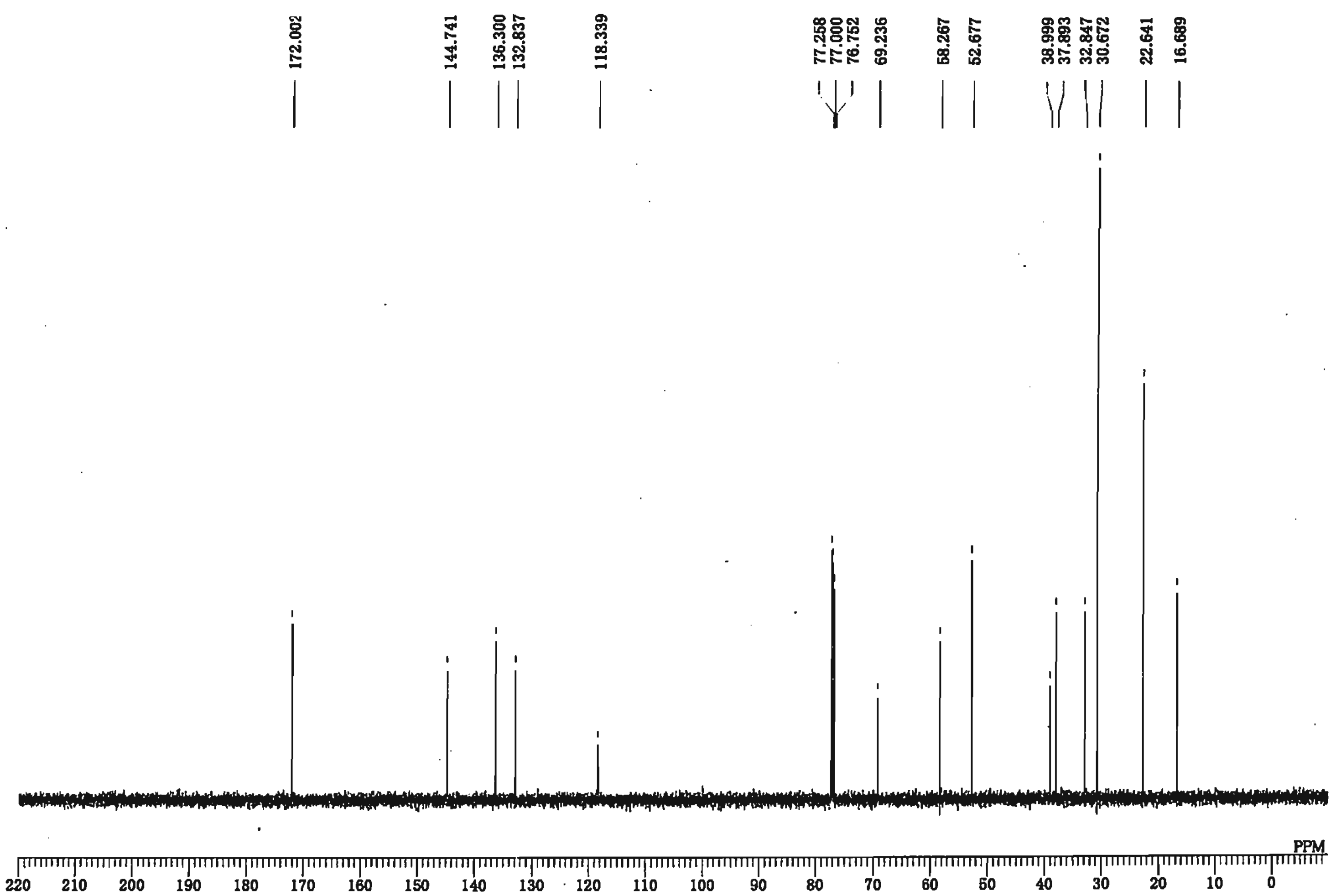
1.09
6.01
2.19
2.16
3.18
6.55
9.79
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5



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30.672
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16.689
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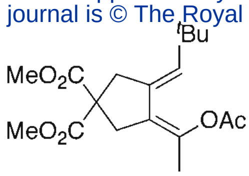
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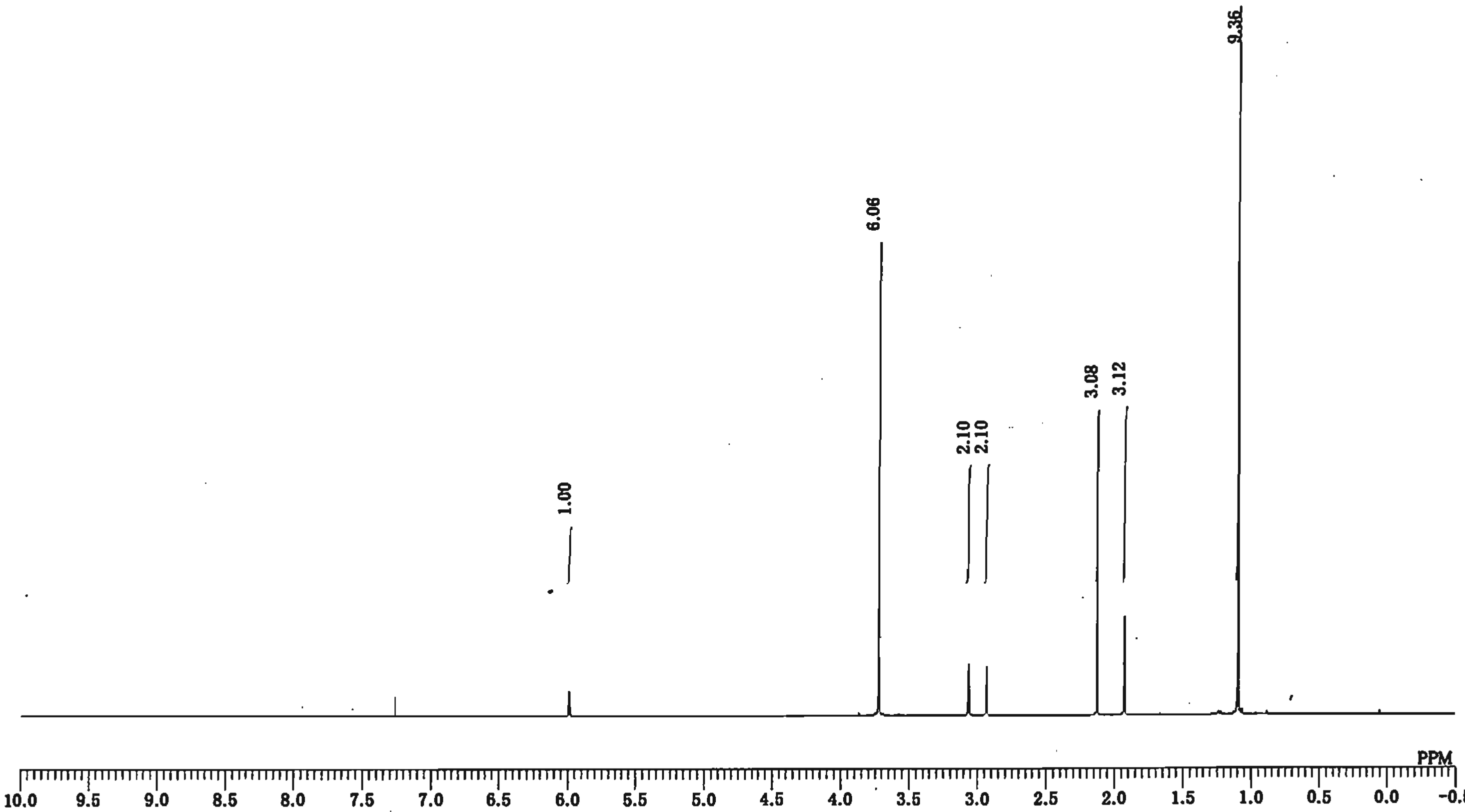
MeO2C
OAc

4q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3.12
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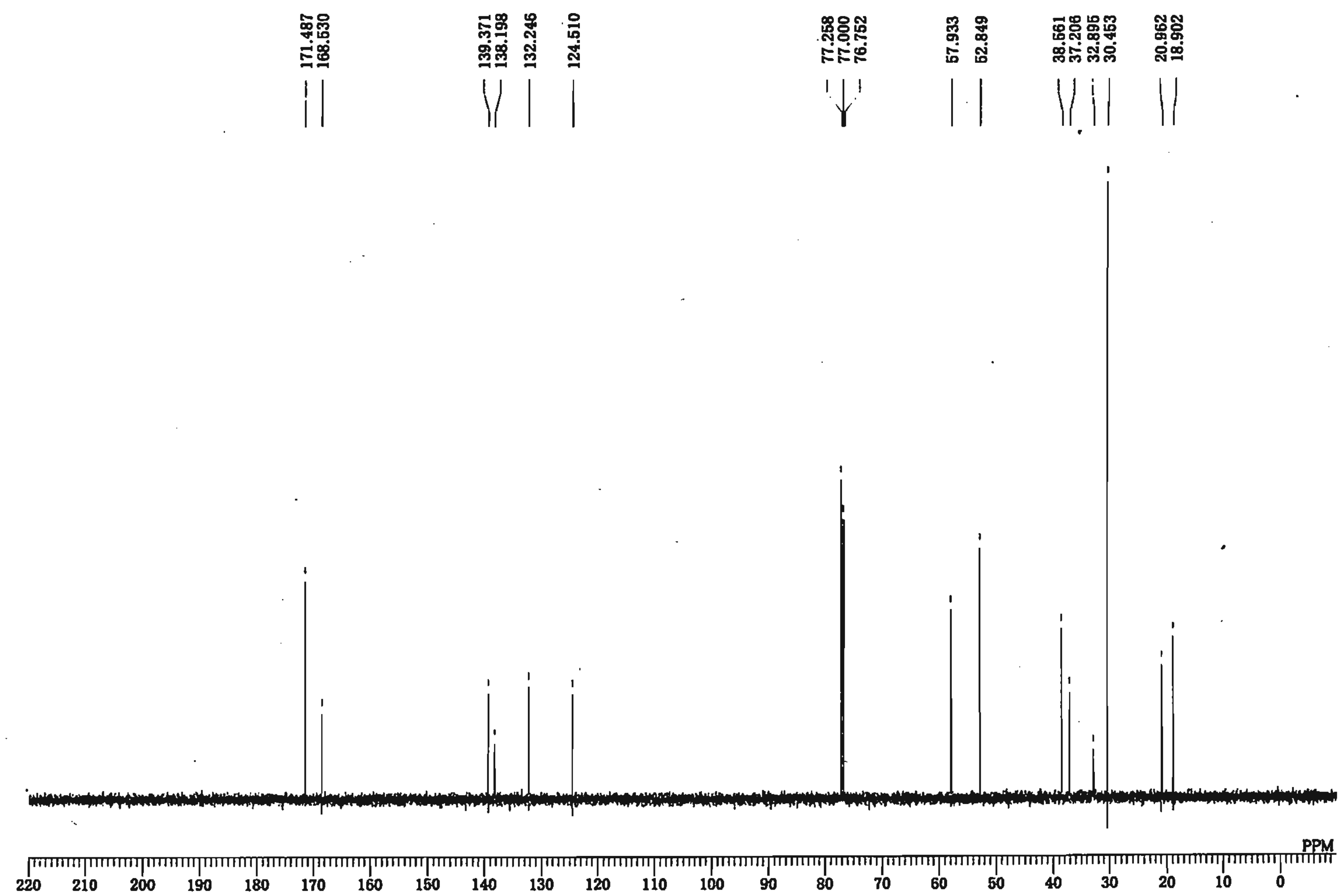
2.10
1.00
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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77.000
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37.206
32.895
30.453
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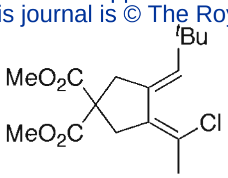
18.902
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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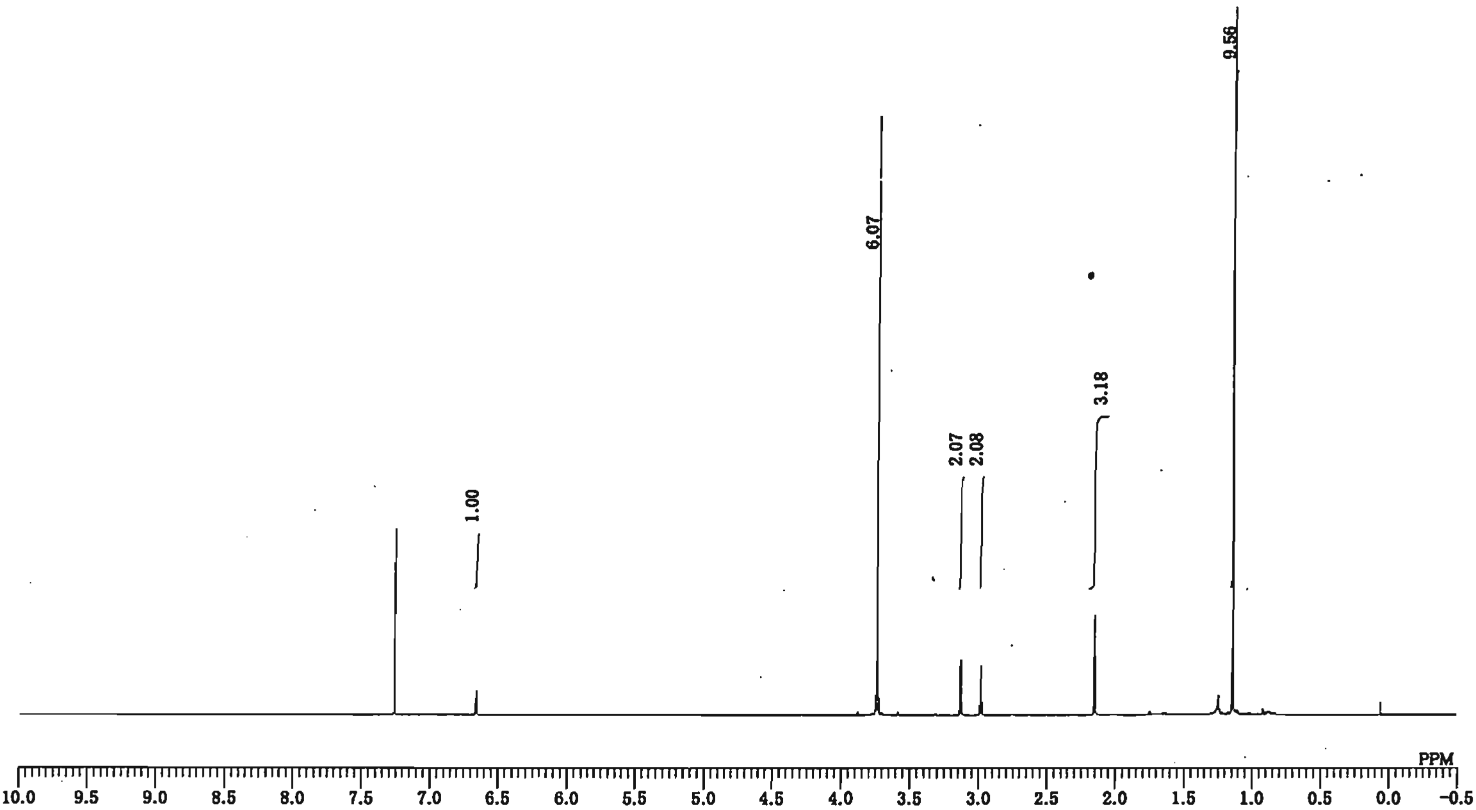
MeO2C
MeO2C
Cl

4r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7.5
7.0
6.5
6.0
5.5
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2.5
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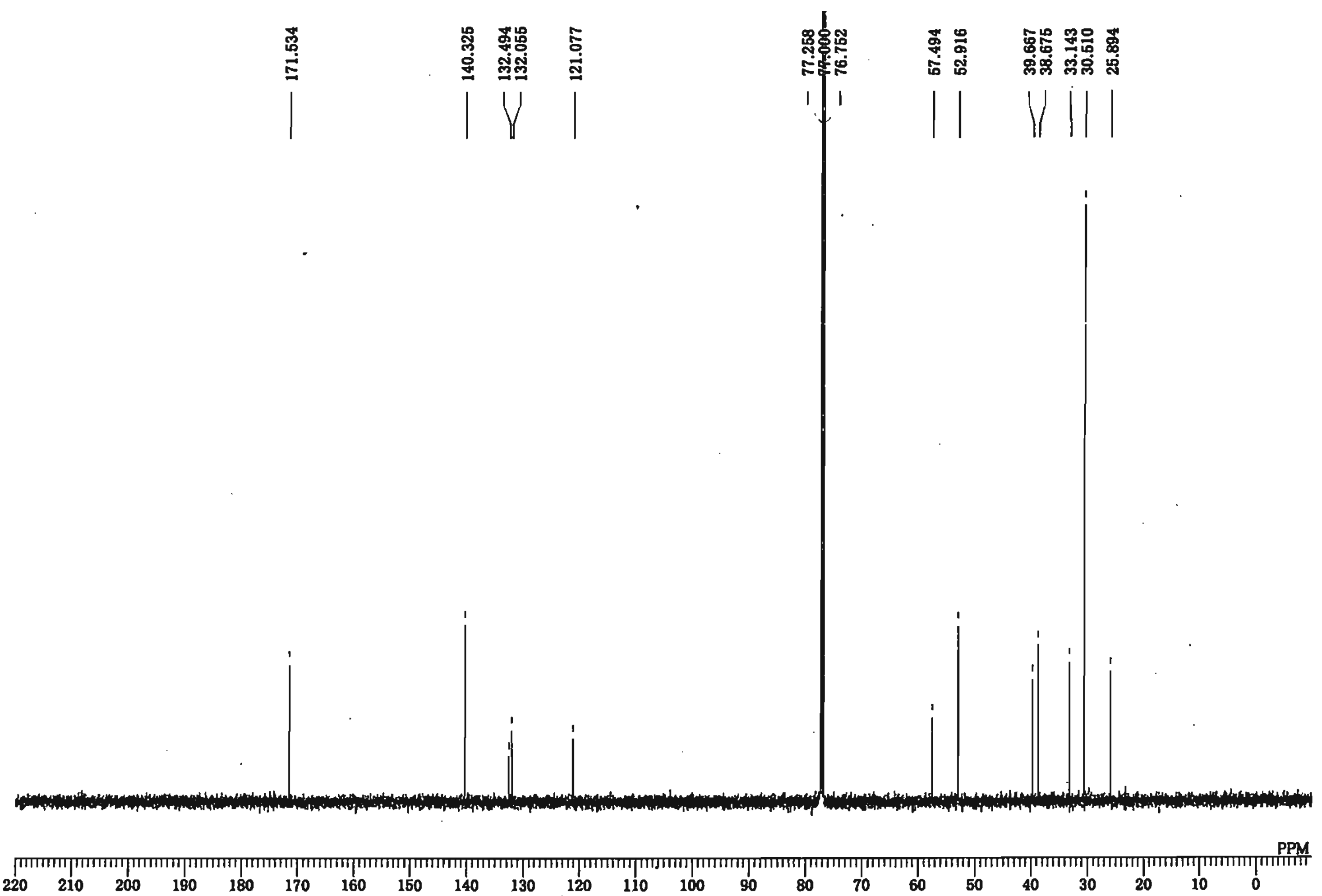
1.5
1.0
0.5
0.0
−0.5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77.000
76.752
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52.916
39.667
38.675
33.143
30.510
25.894
PPM
220
210
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10
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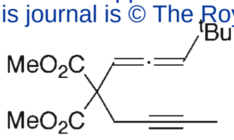
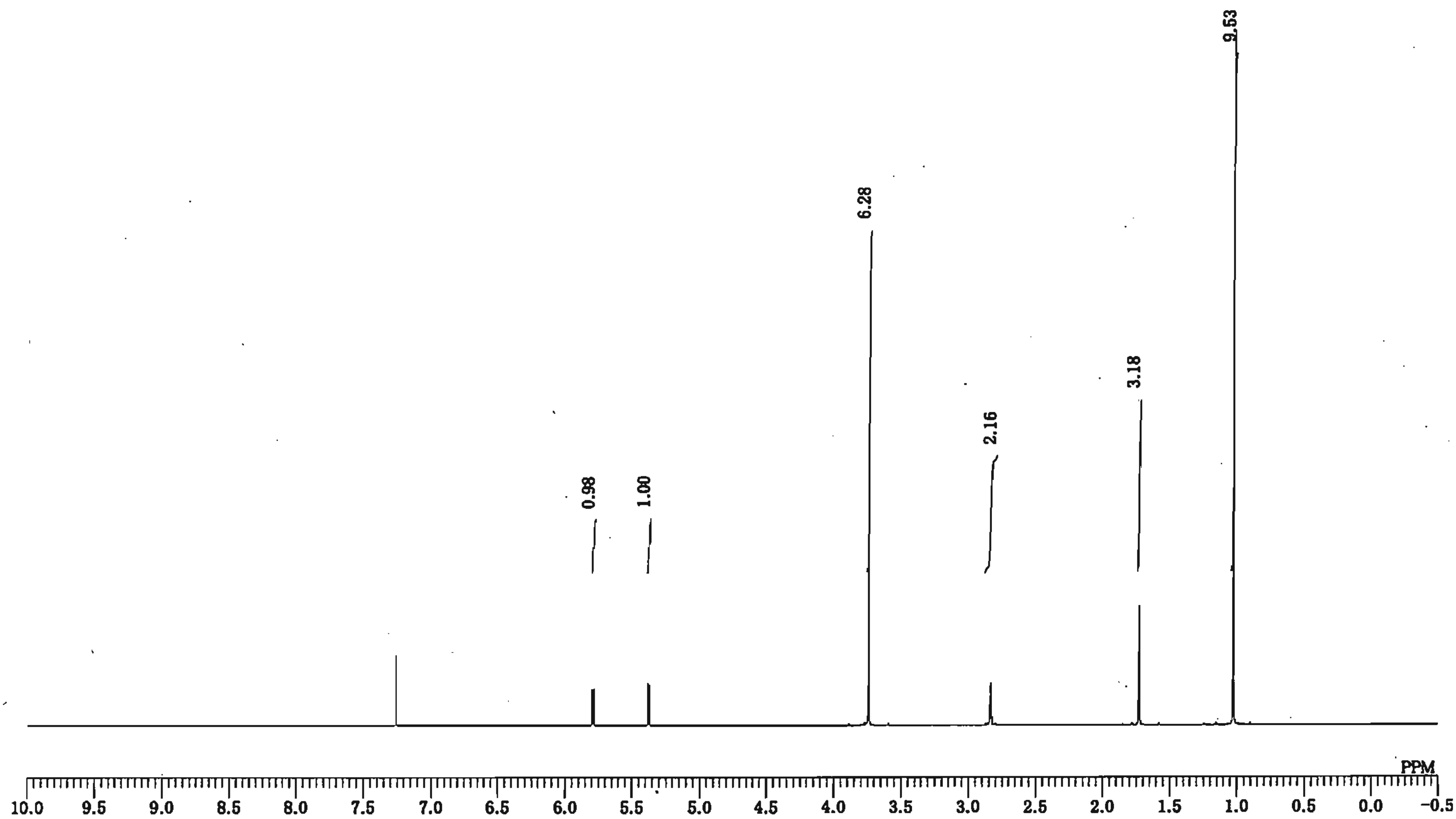


3a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3.18
9.53
PPM
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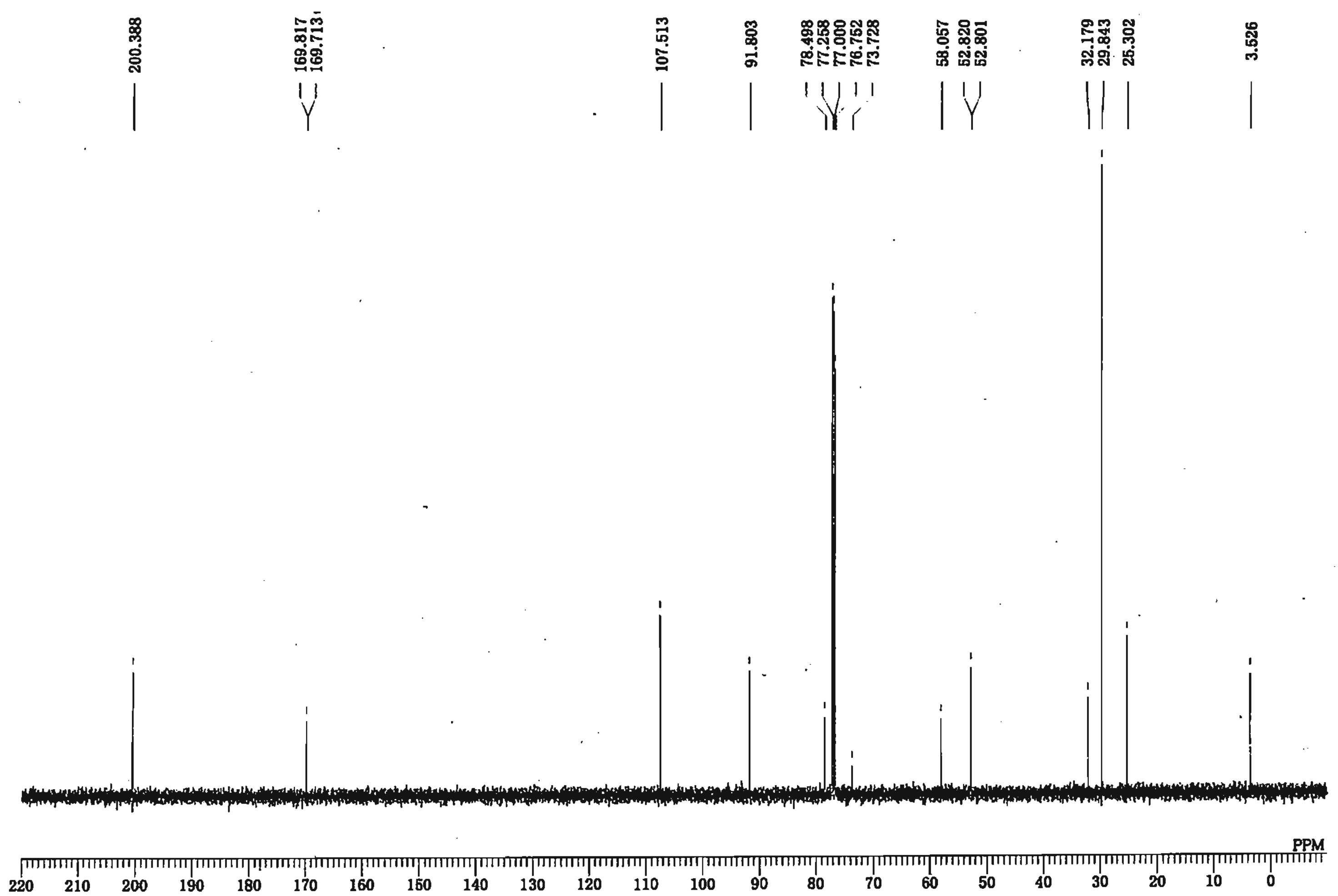
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5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77.000
76.752
73.728
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52.820
52.801
32.179
29.843
25.302
3.526
PPM
220
210
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70
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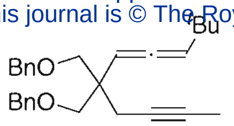
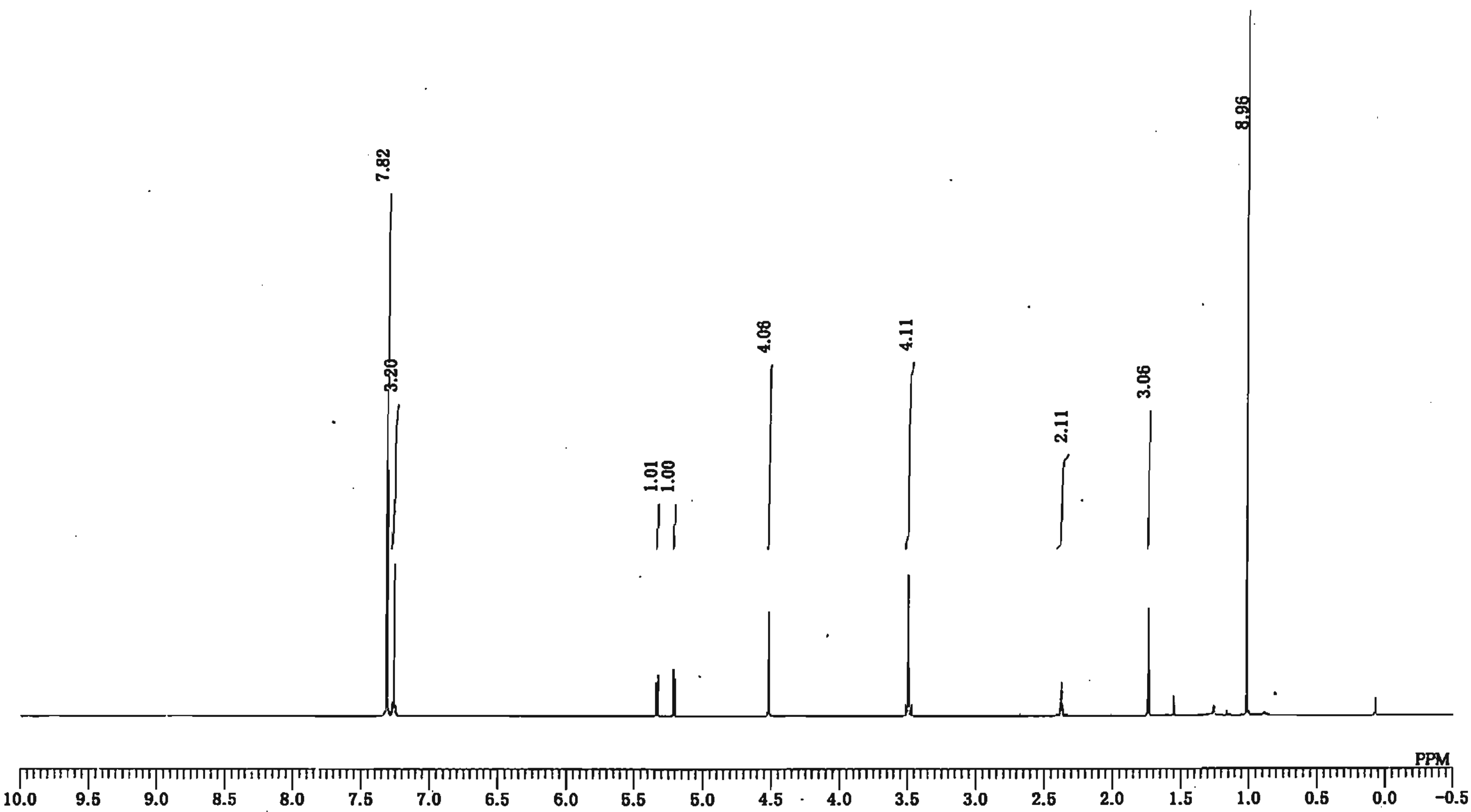
20
10
0


tBu
BnO
BnO

3b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3.06
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PPM
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
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2.5
2.0
1.5
1.0
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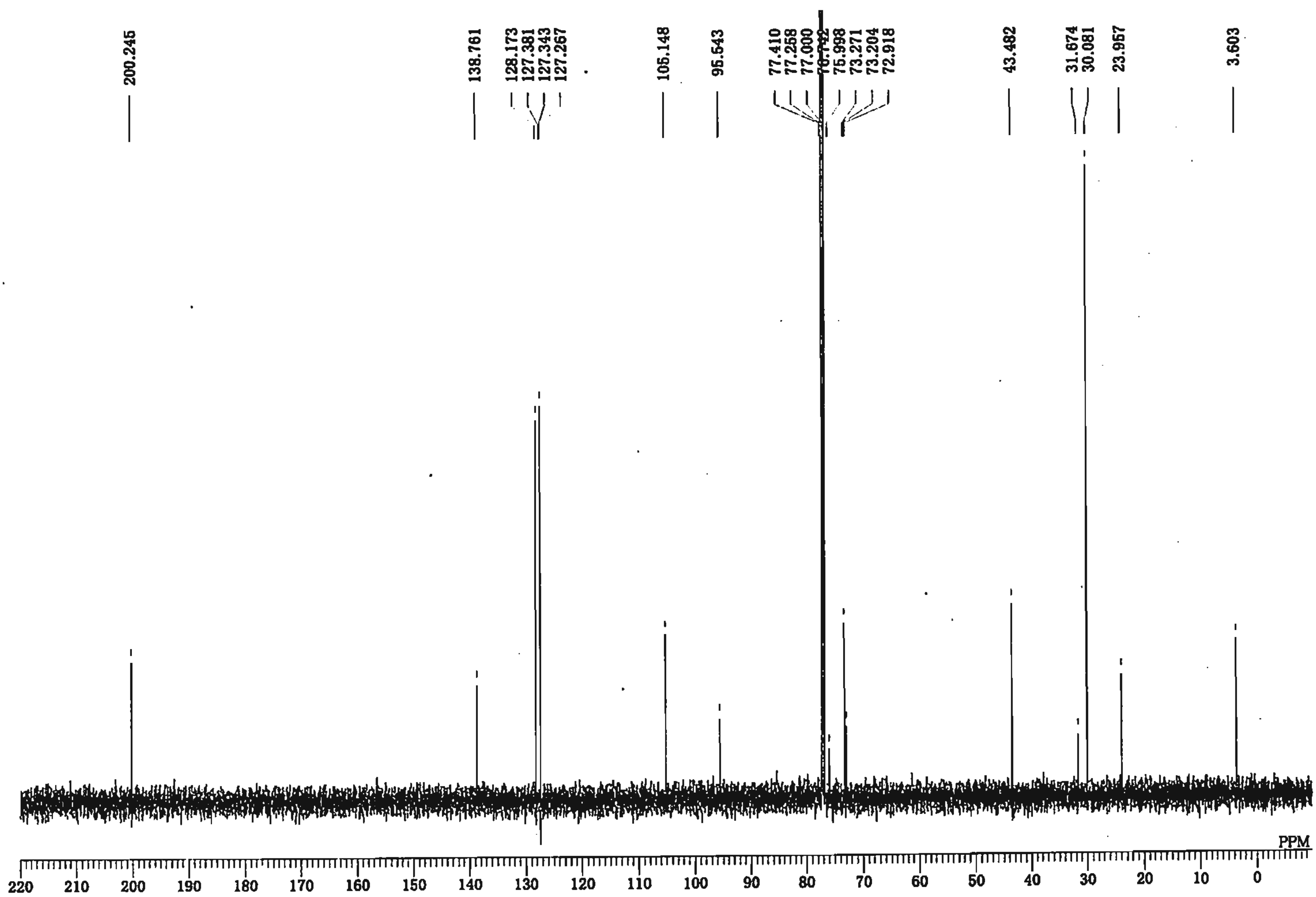
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95.543
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77.000
76.742
75.998
73.271
73.204
72.918
43.482
31.674
30.081
23.957
3.603
PPM
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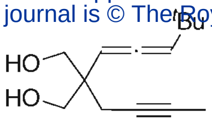
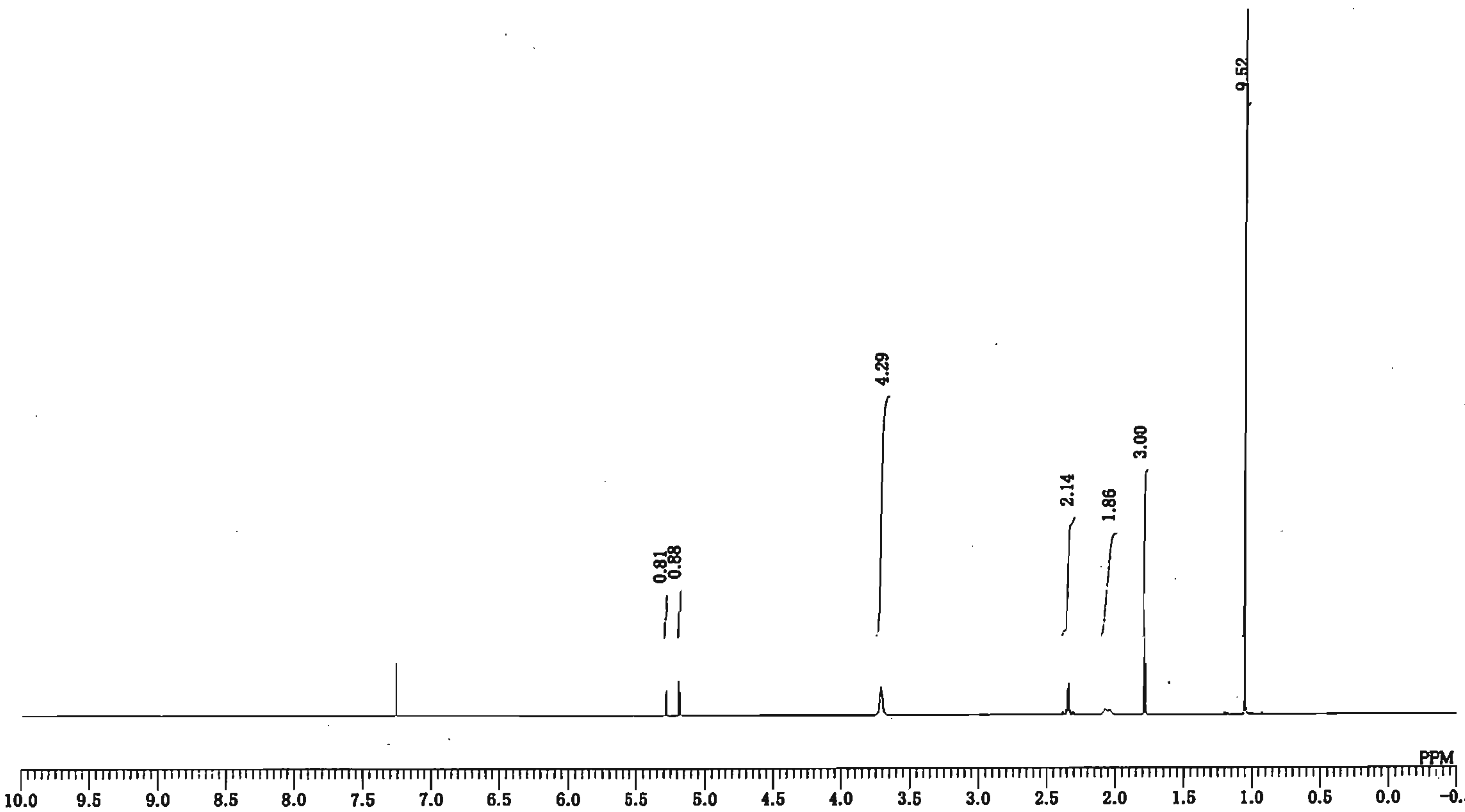

HO
HO
tBu

3c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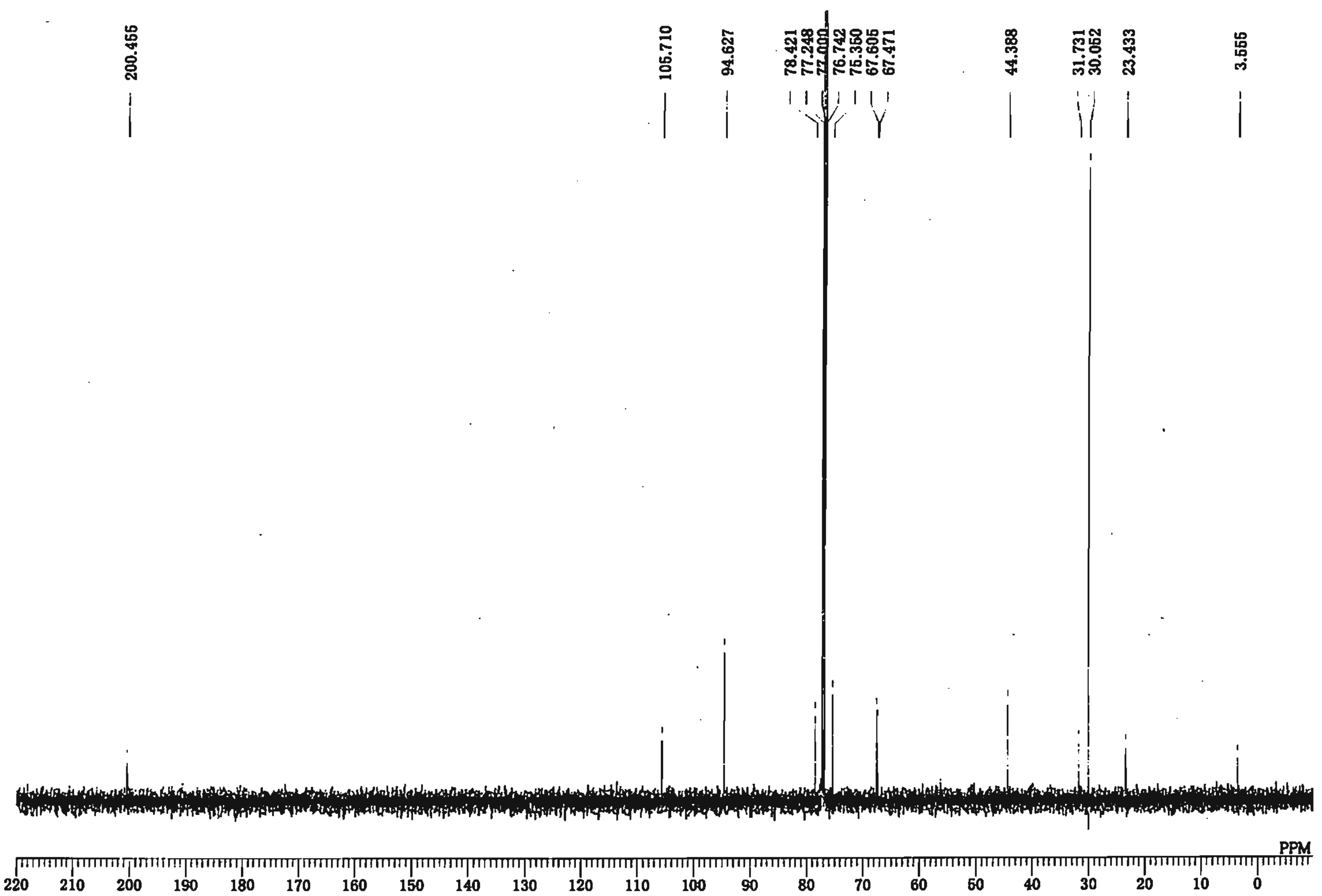
0.88
4.29
2.14
1.86
3.00
9.52
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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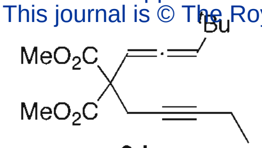
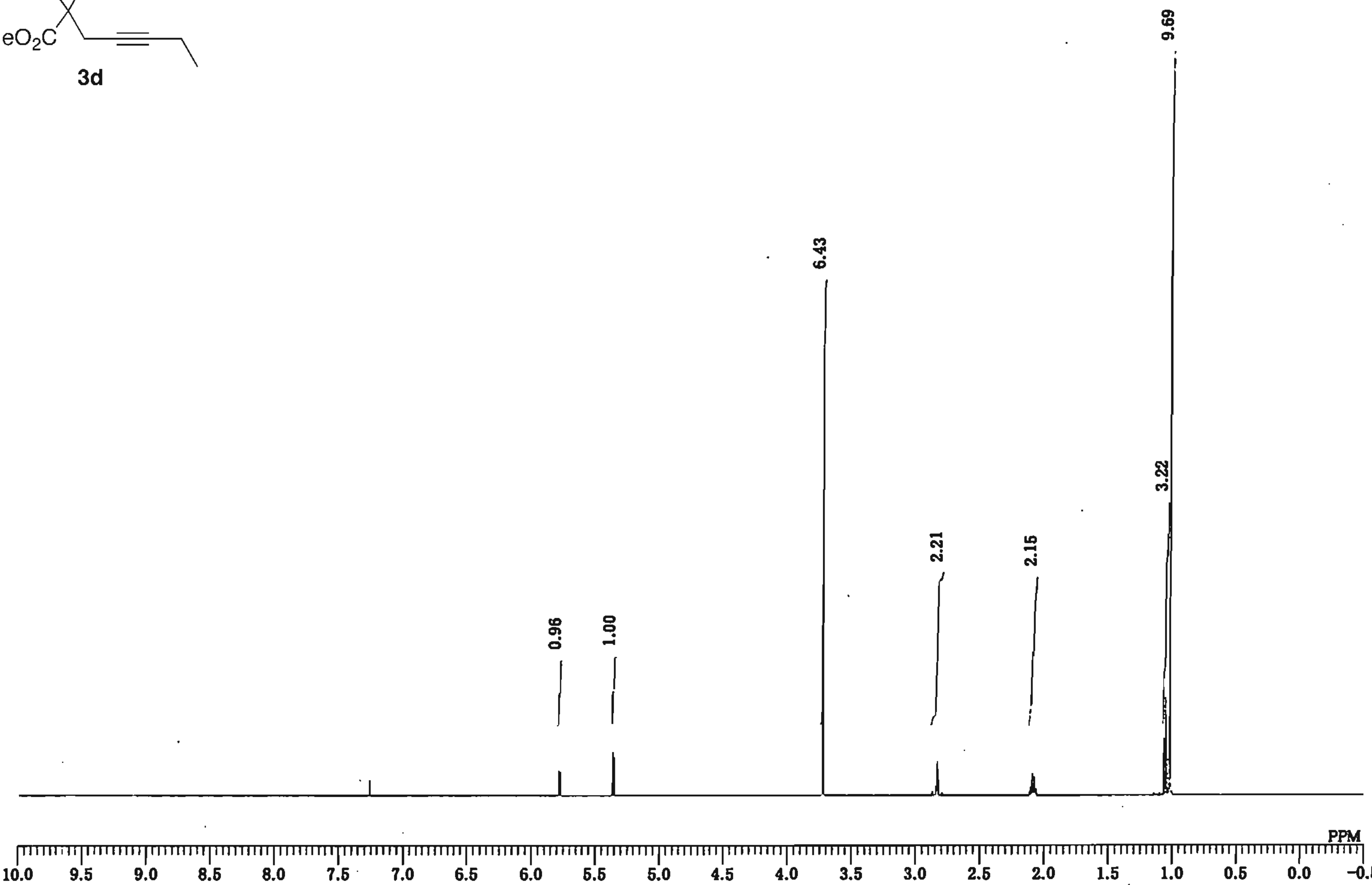
94.627
78.421
77.248
77.000
76.742
75.360
67.605
67.471
44.388
31.731
30.052
23.433
3.555
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


tBu
MeO2C
MeO2C

3d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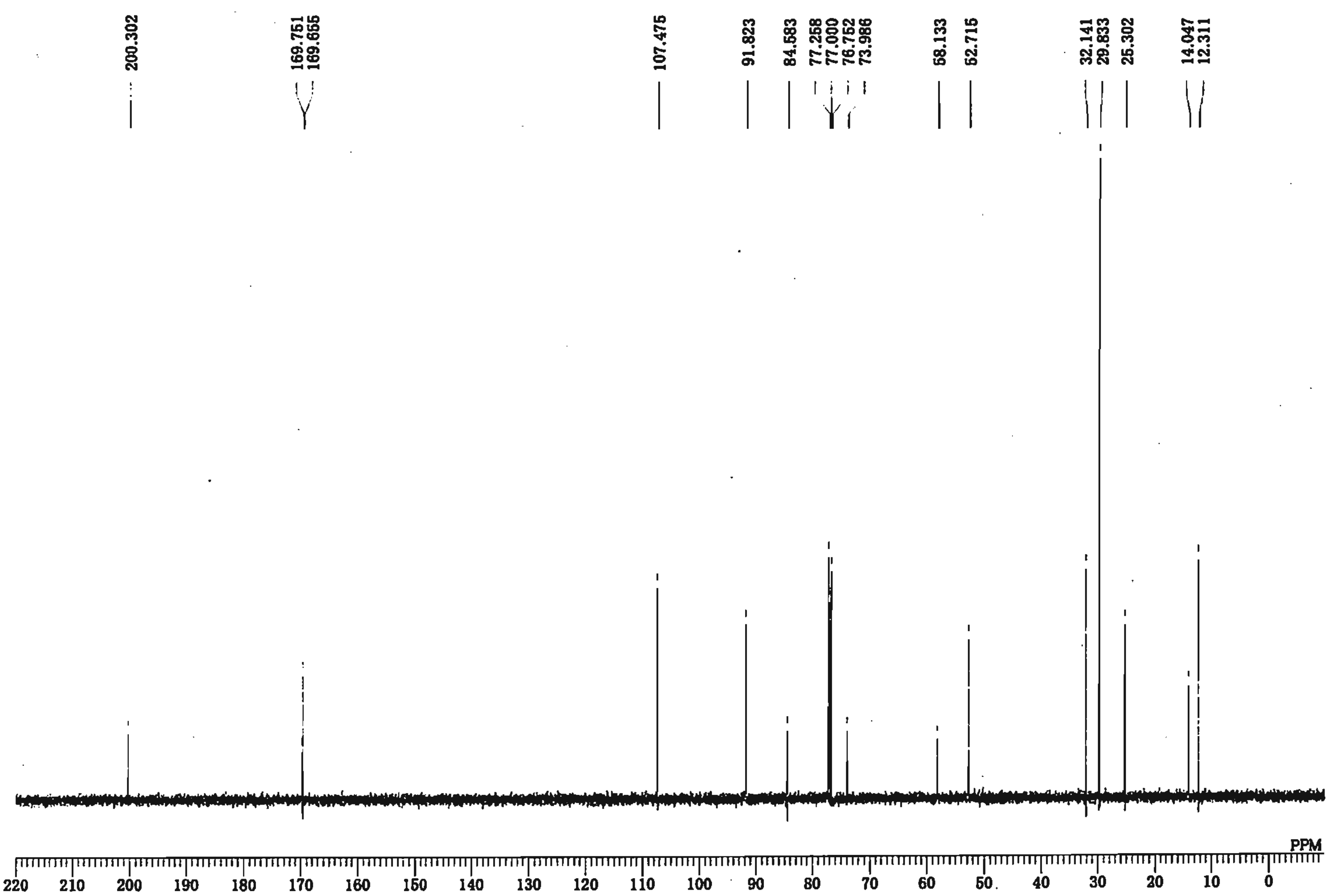
1.00
6.43
2.21
2.15
3.22
9.69
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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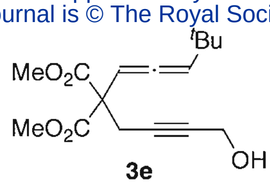
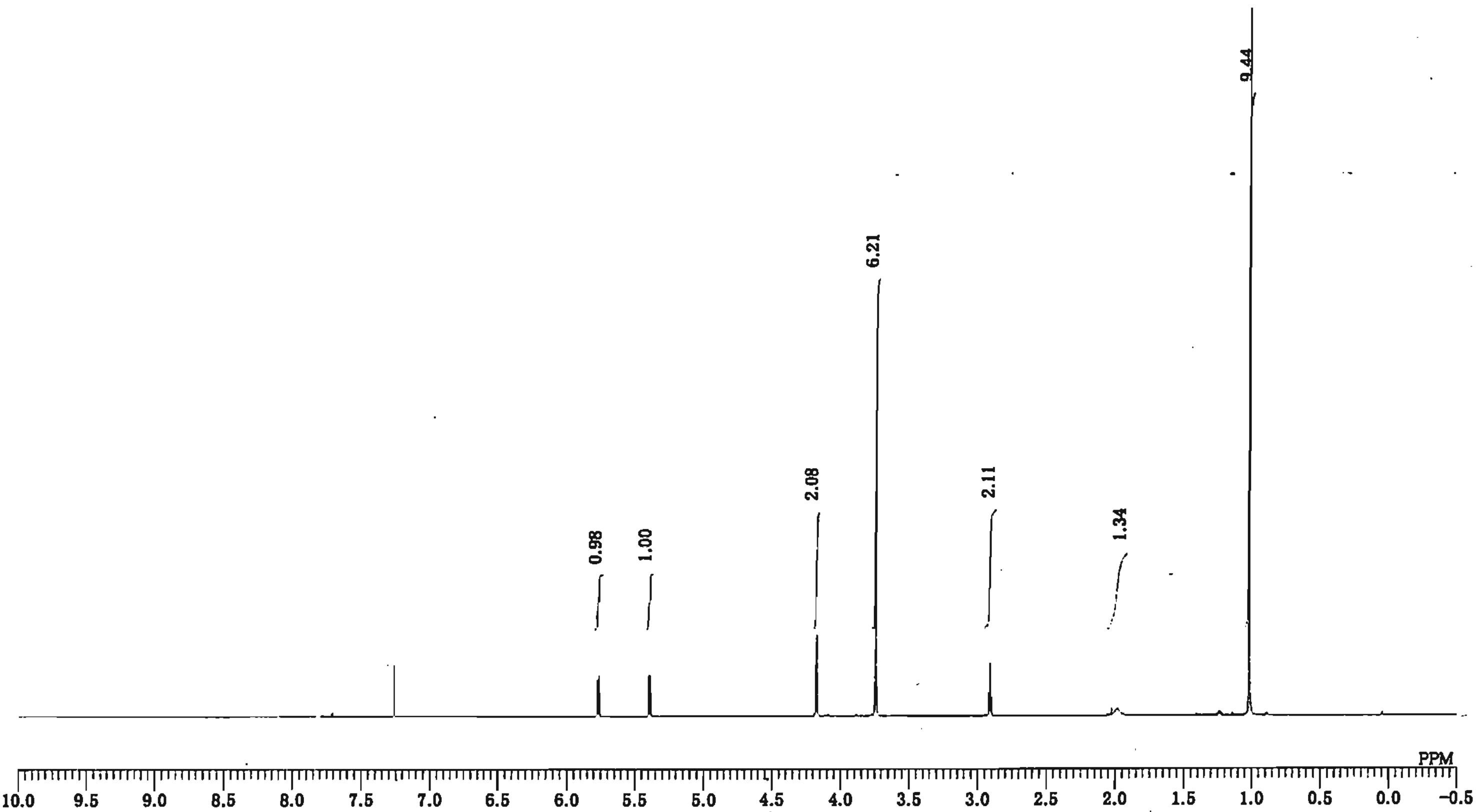
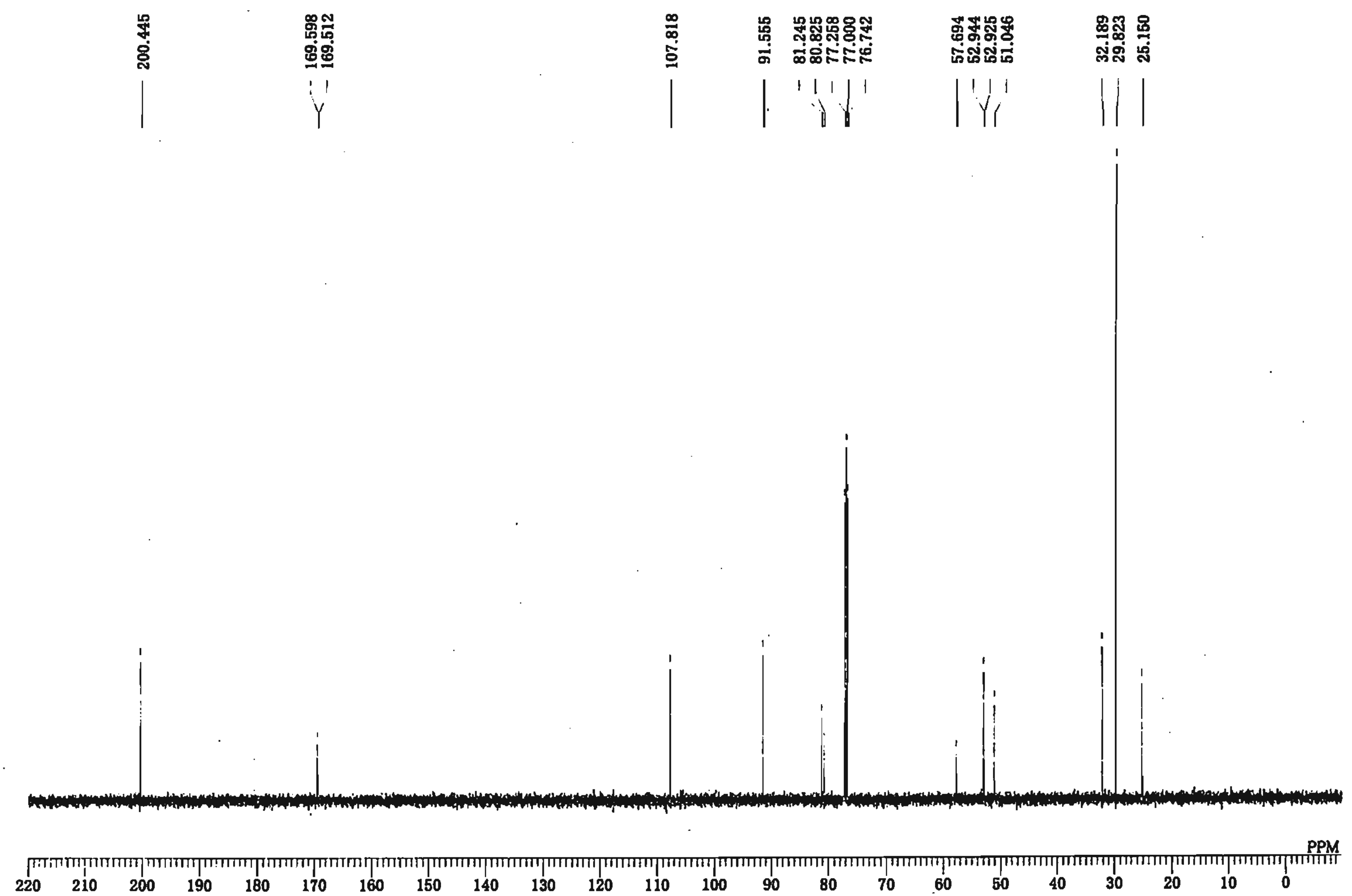
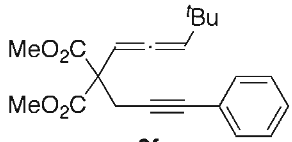
169.655
107.475
91.823
84.583
77.258
77.000
76.752
73.986
58.133
52.715
32.141
29.833
25.302
14.047
12.311
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



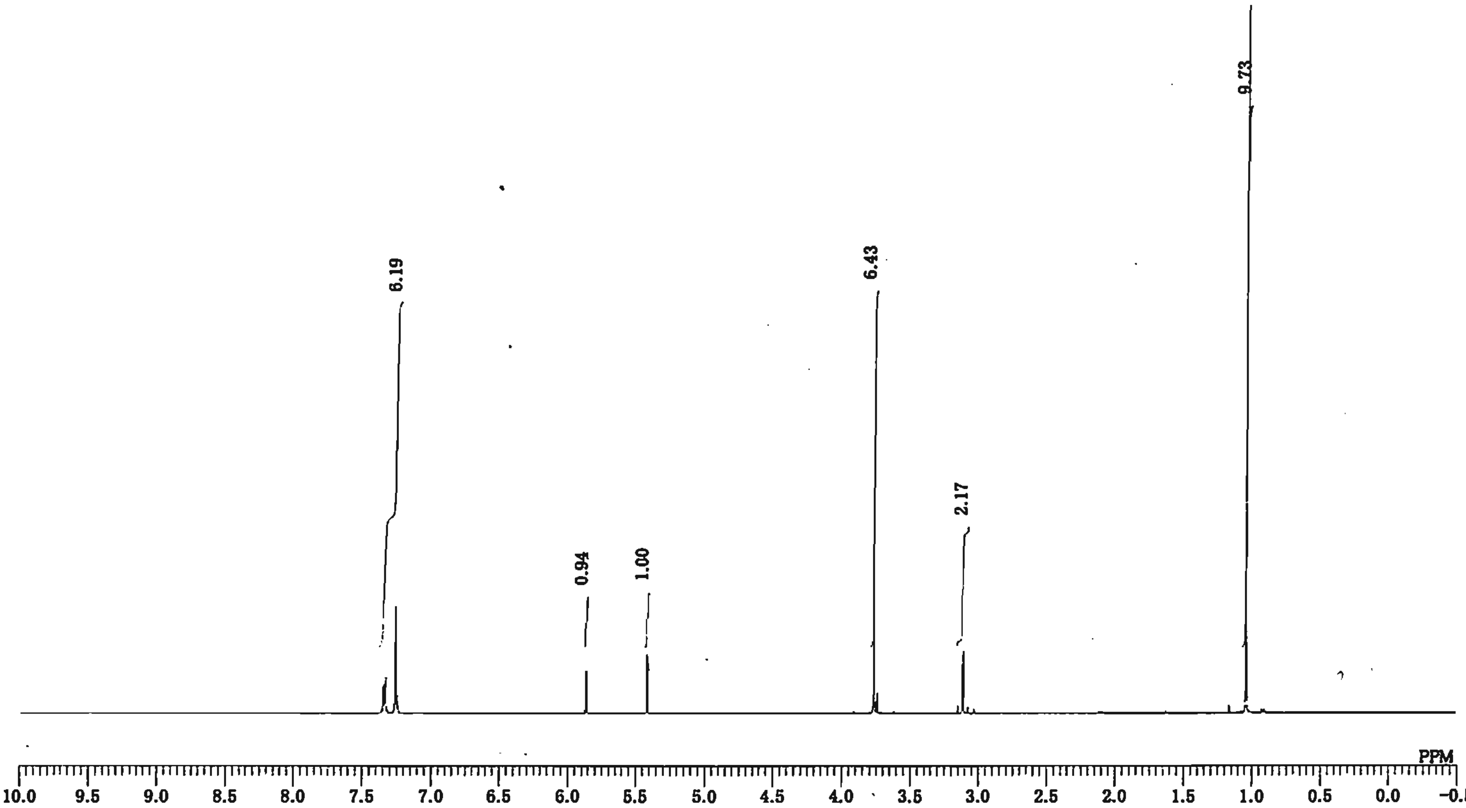
3e

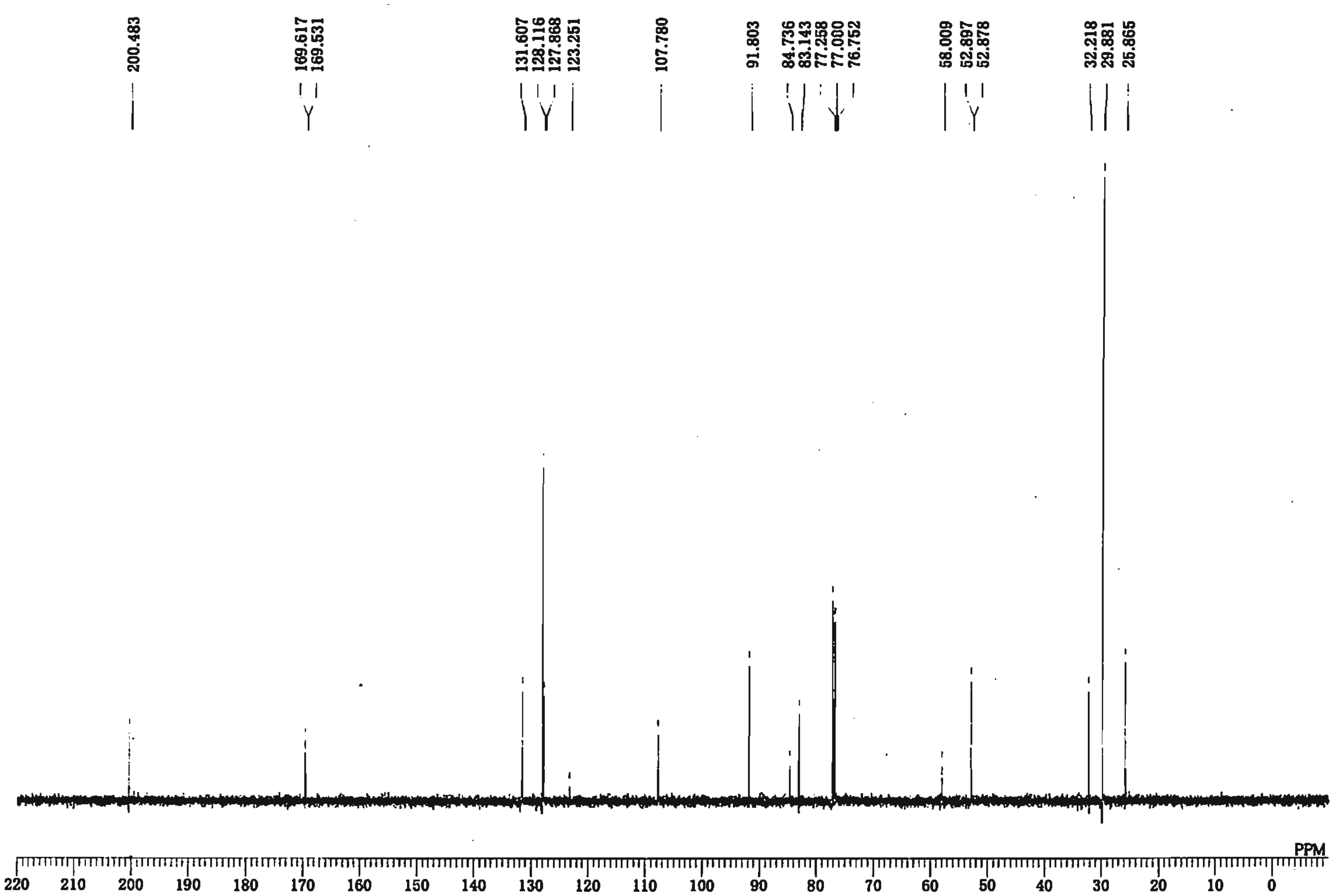





tBu
MeO2C
MeO2C

3f


6.19
0.94
1.00
6.43
2.17
9.73
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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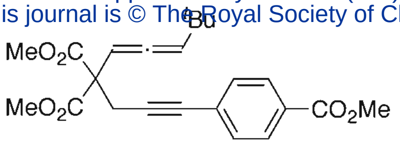
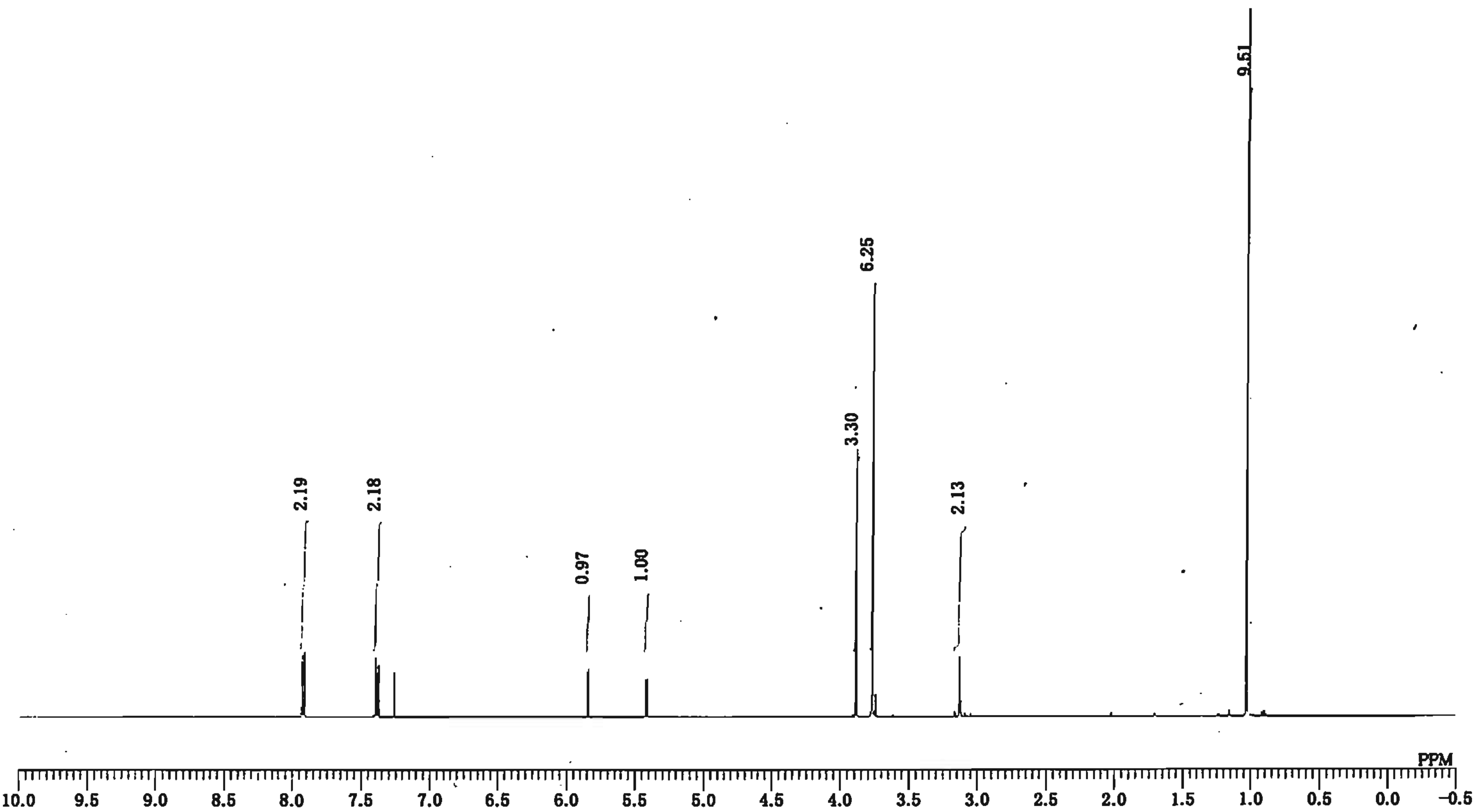
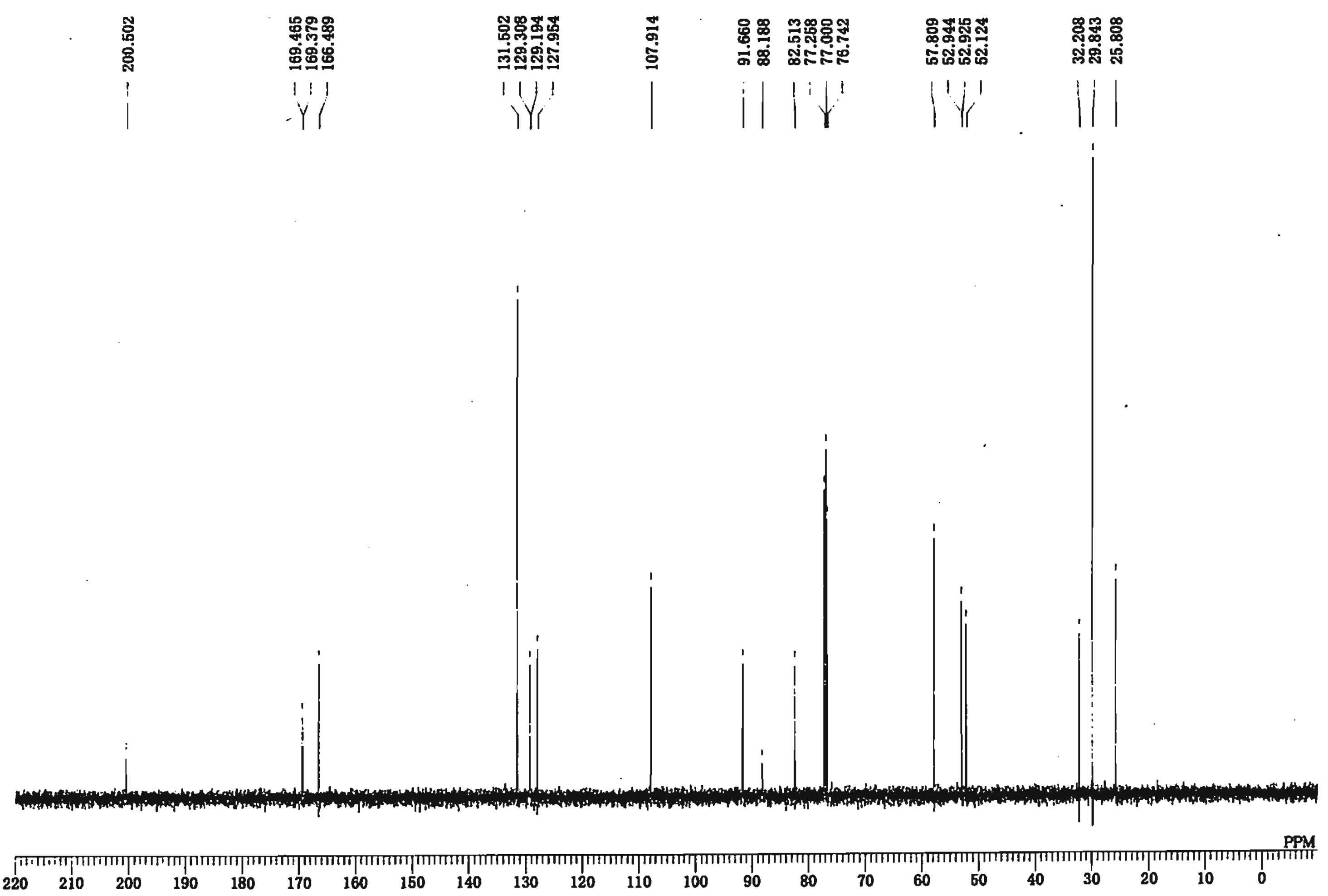
169.617
169.531
131.607
128.116
127.868
123.251
107.780
91.803
84.736
83.143
77.258
77.000
76.752
58.009
52.897
52.878
32.218
29.881
25.865
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

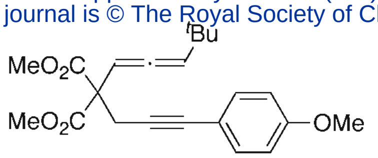
Electronic Supplementary Material (ESI) for Chemical Communications



3g

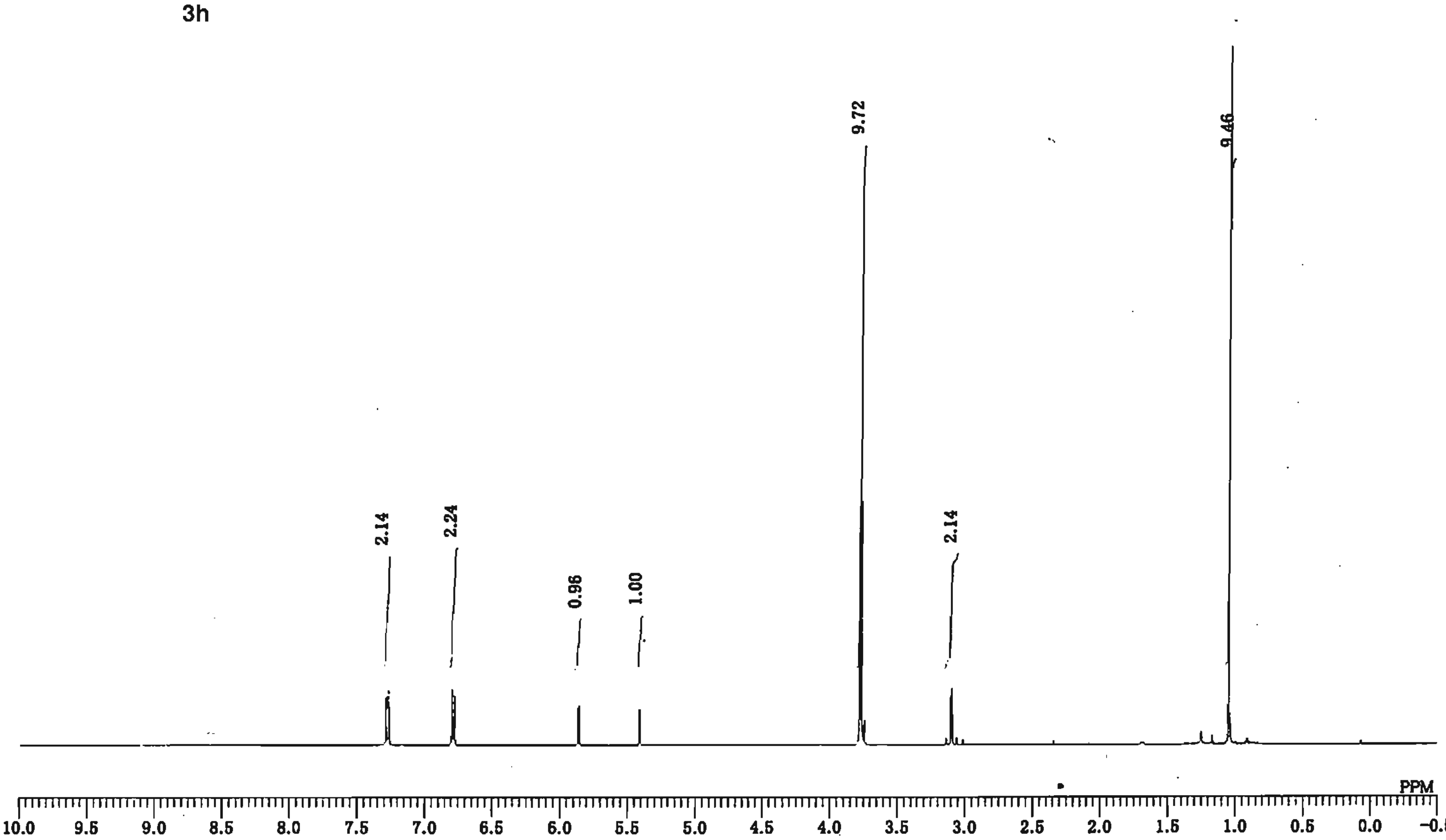




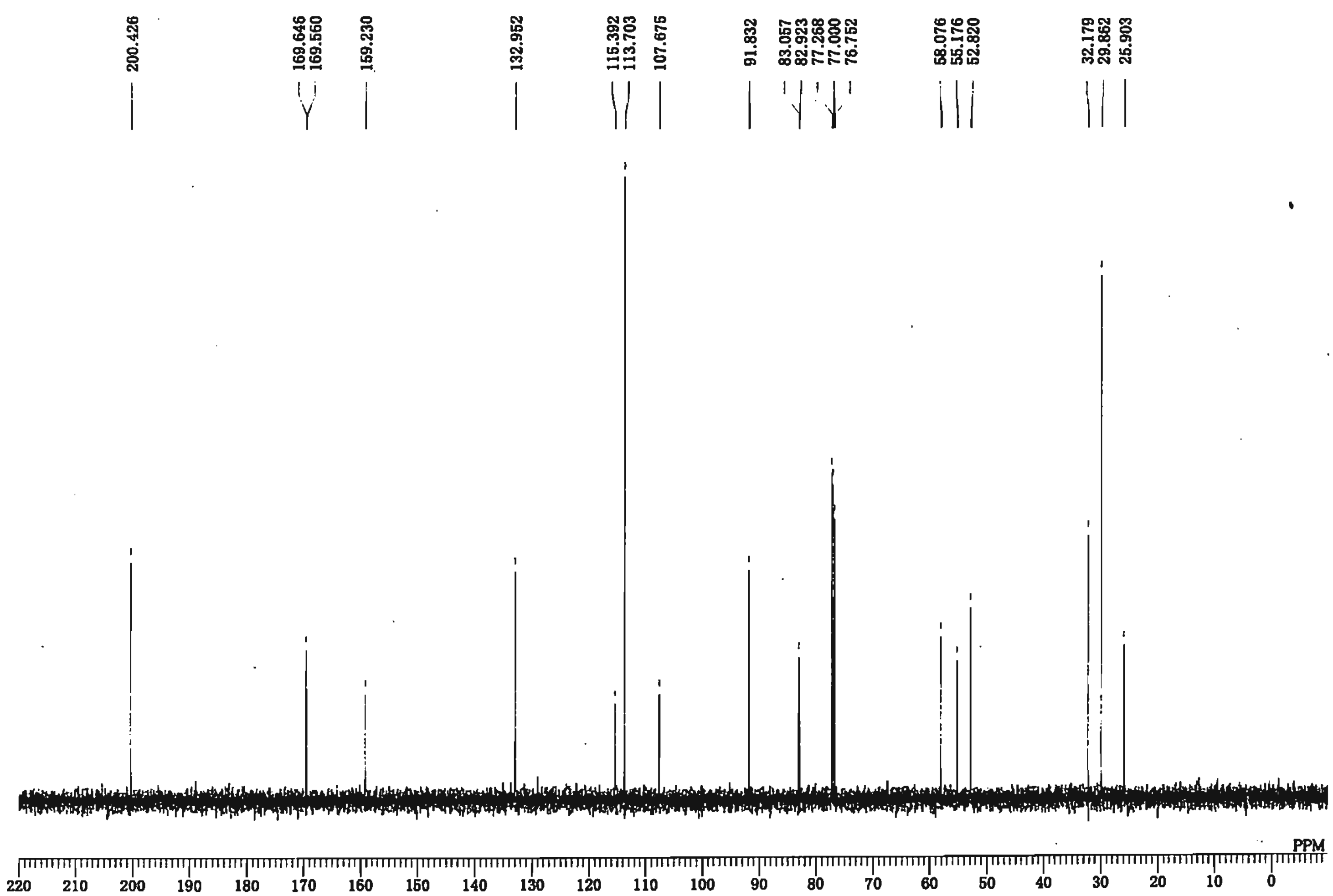


tBu
MeO2C
MeO2C
OMe

3h



9.72
9.46
2.14
2.24
0.96
1.00
2.14
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5



200.426
169.646
169.560
159.230
132.952
115.392
113.703
107.675
91.832
83.057
82.923
77.268
77.000
76.752
58.076
55.176
52.820
32.179
29.862
25.903
PPM
220
210
200
190
180
170
160
150
140
130
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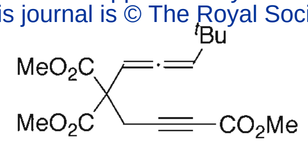
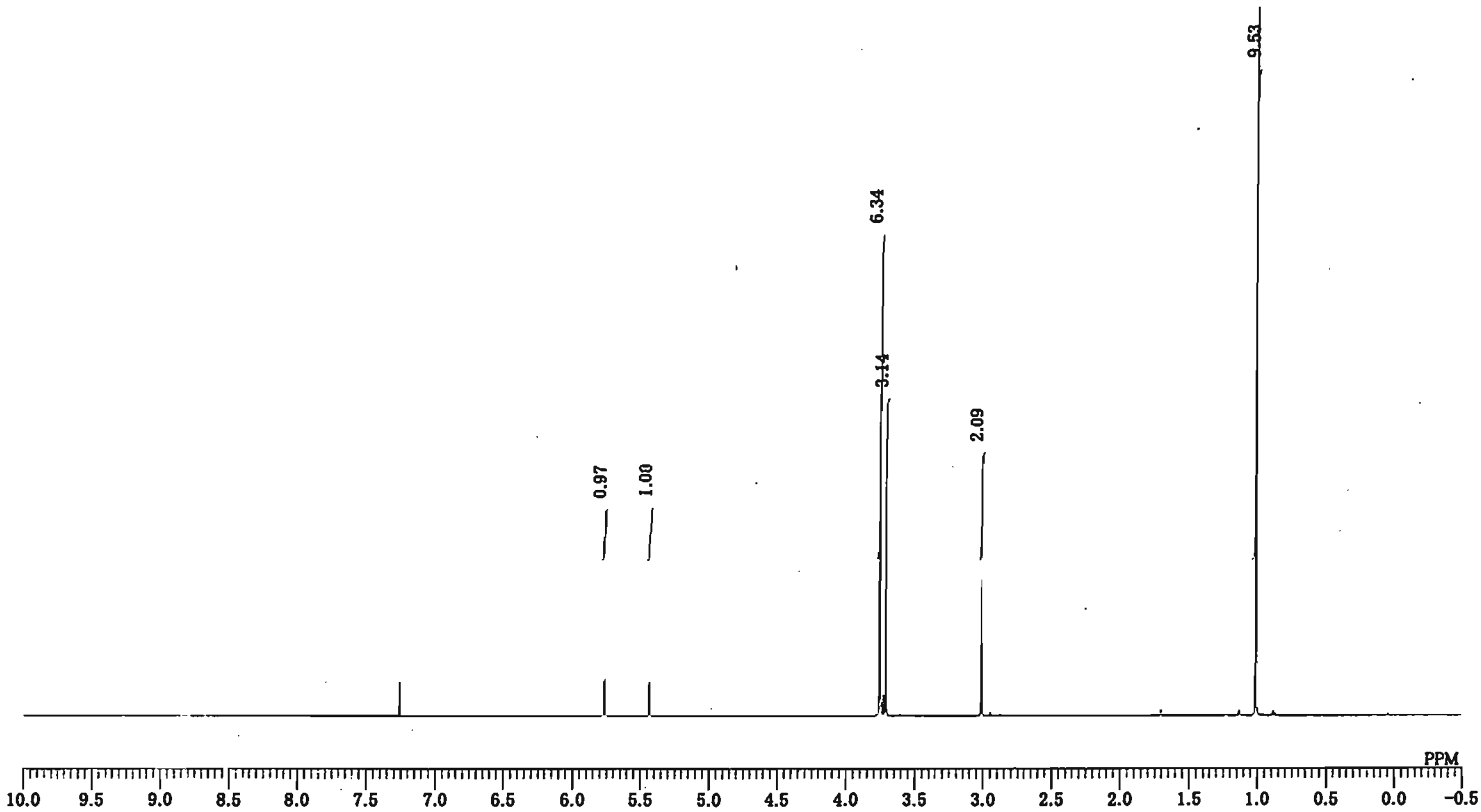
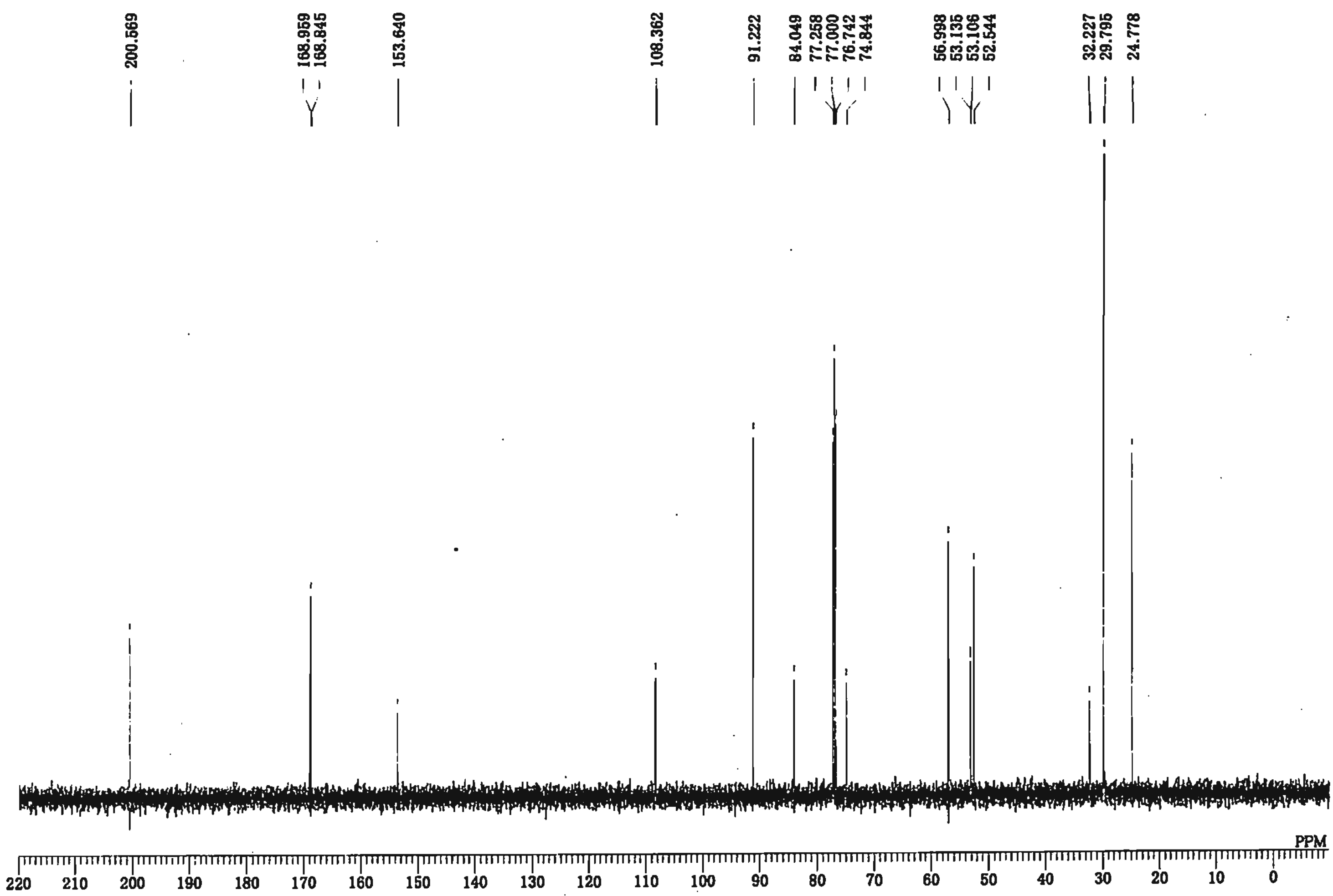
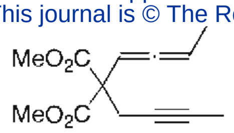
40
30
20
10
0



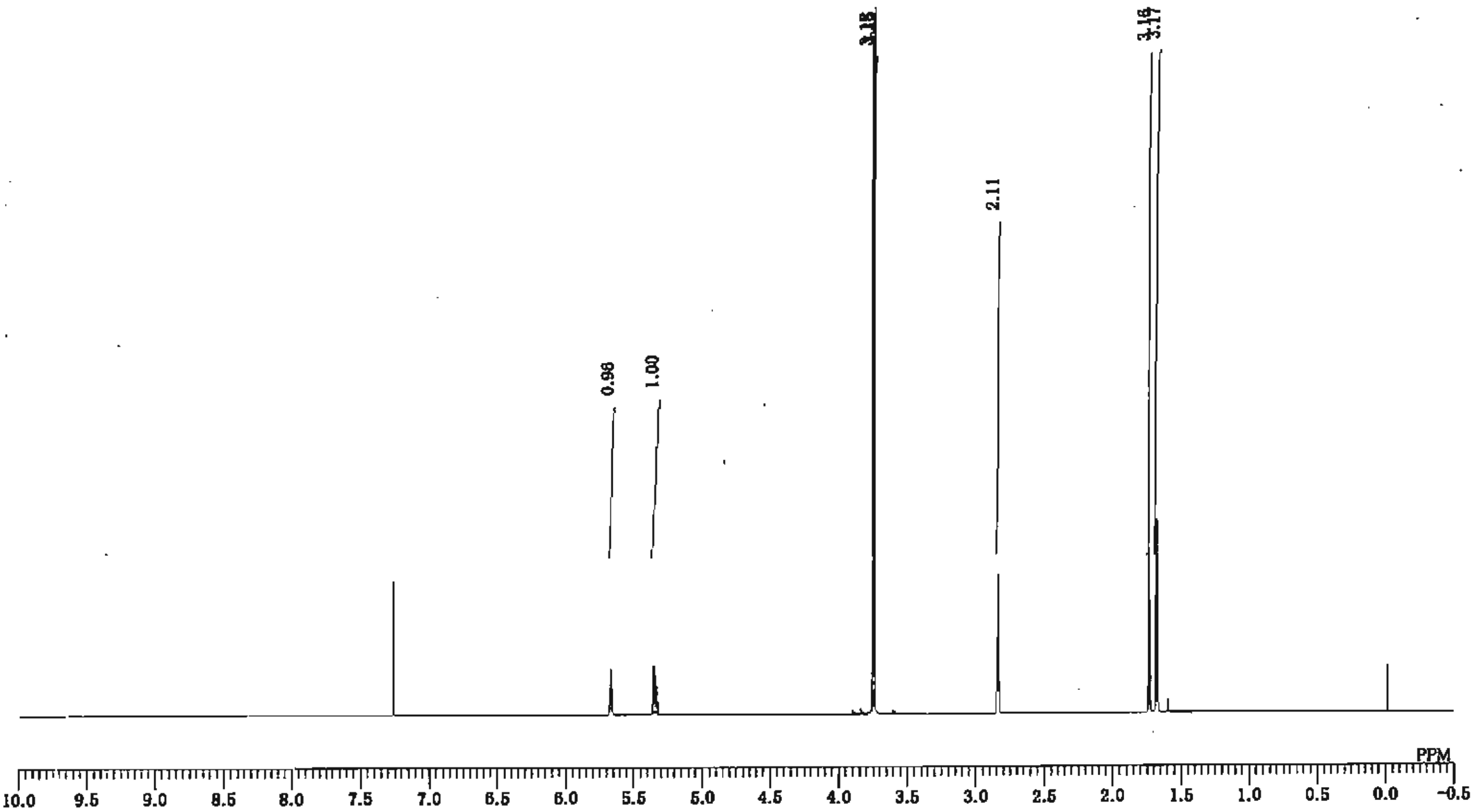
3i

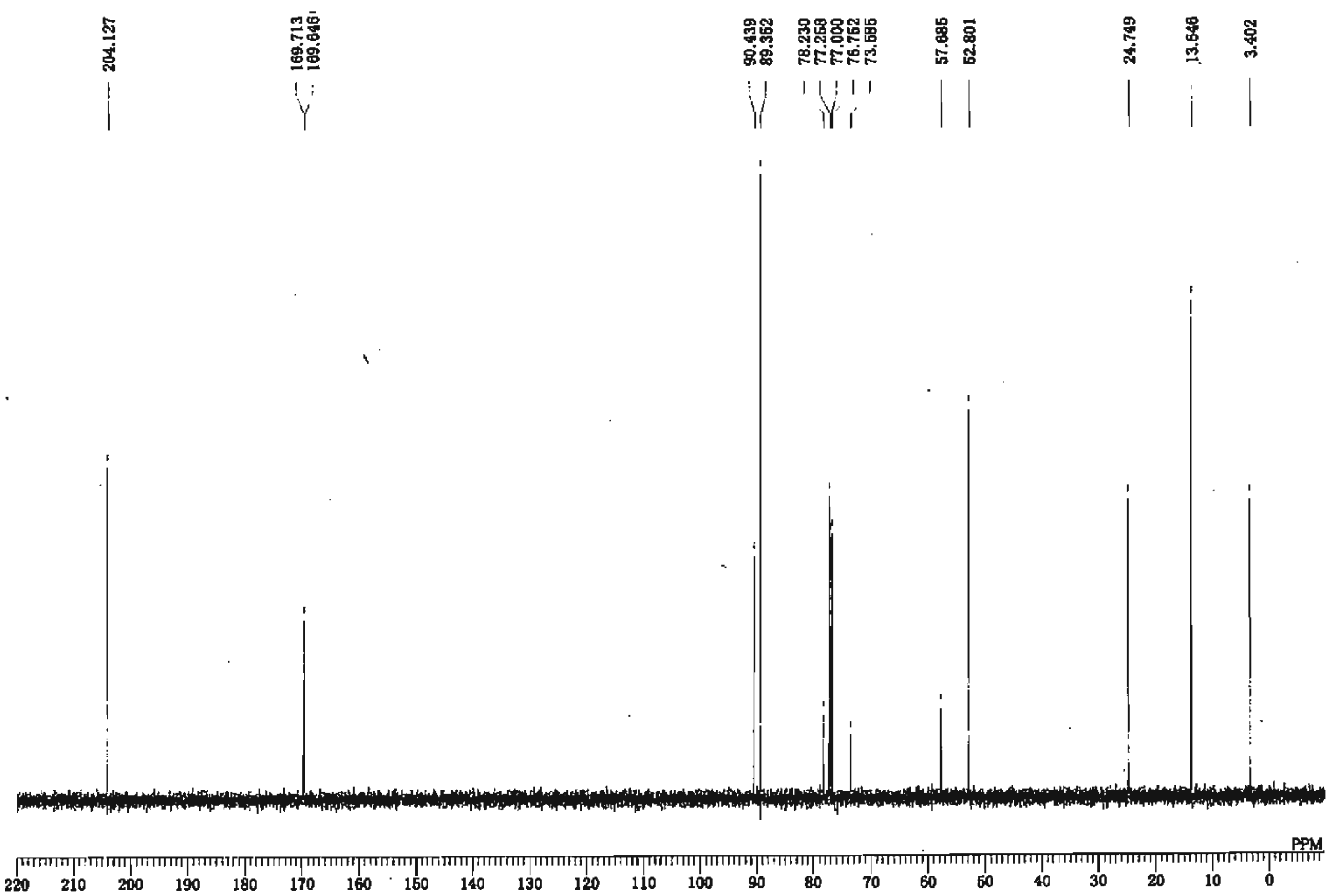


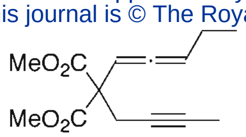



MeO2C
MeO2C

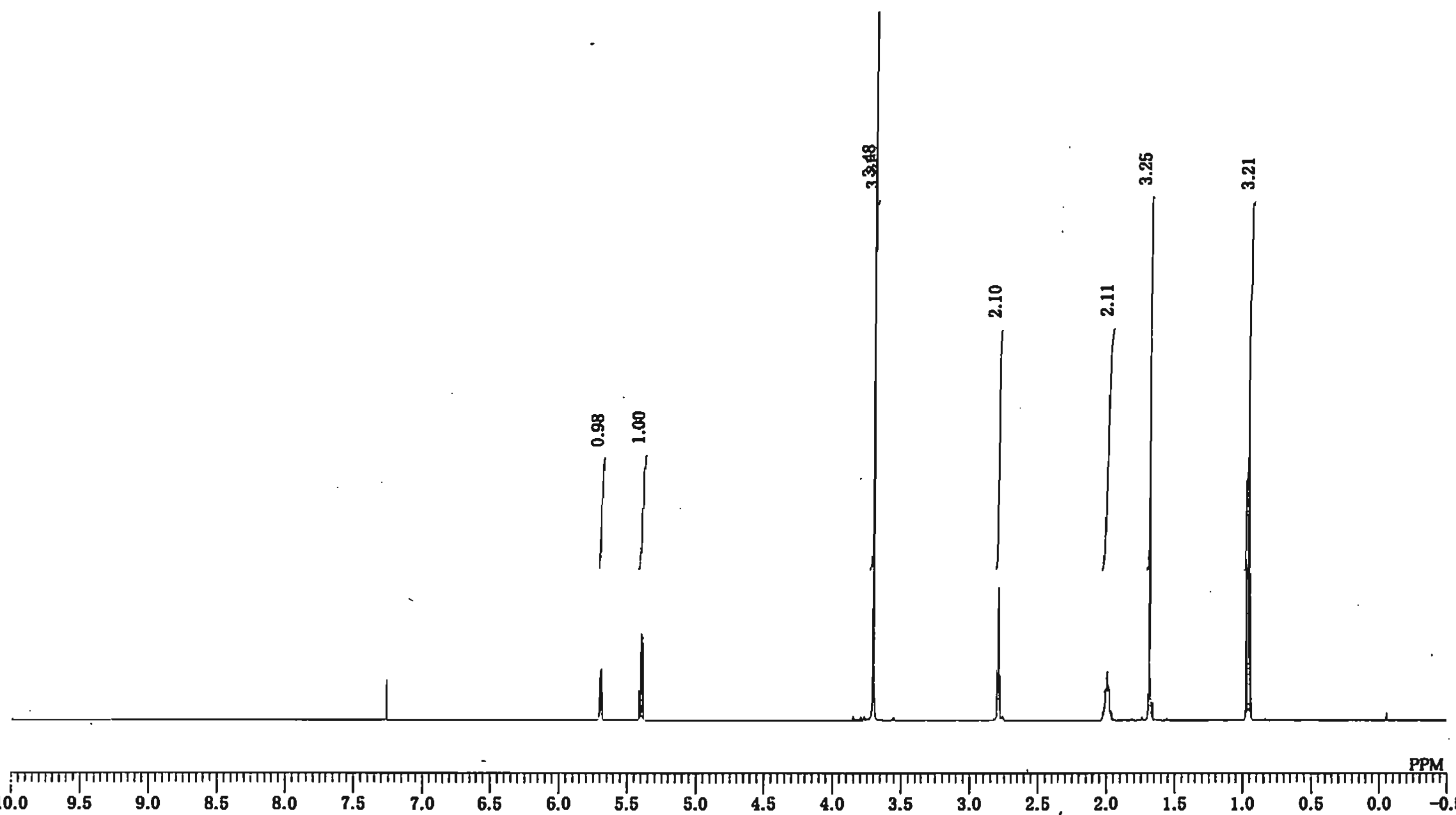
3j

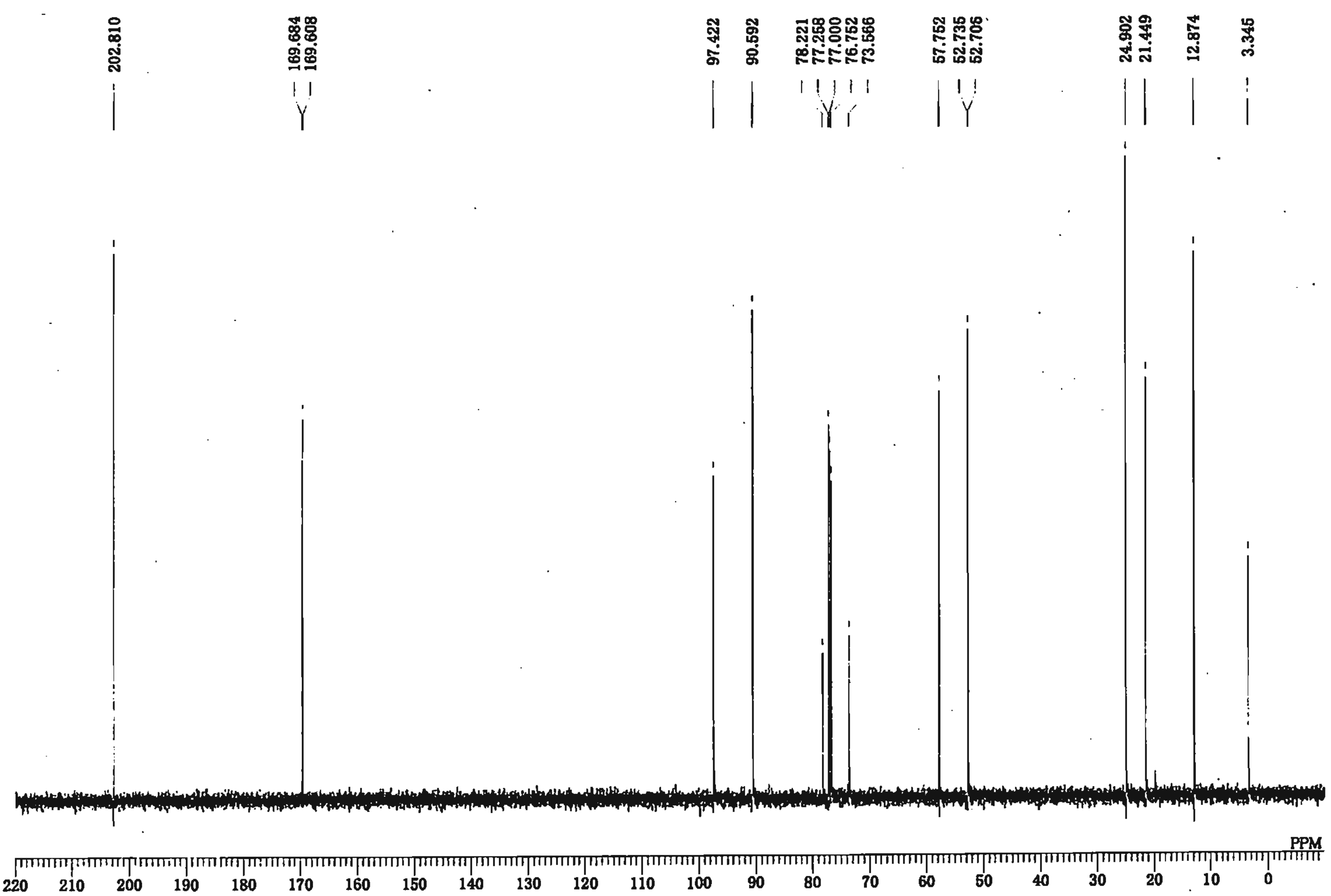

3.18
3.18
3.17
2.11
0.98
1.00
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5


204.127
169.713
169.646
90.439
89.352
78.230
77.258
77.000
76.752
73.686
57.685
52.801
24.749
13.646
3.402
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


MeO2C
MeO2C

3k


0.98
1.00
2.10
2.11
3.25
3.21
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


202.810
169.684
169.608
97.422
90.592
78.221
77.258
77.000
76.752
73.566
57.752
52.735
52.706
24.902
21.449
12.874
3.345
PPM
220
210
200
190
180
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160
150
140
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110
100
90
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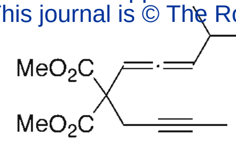
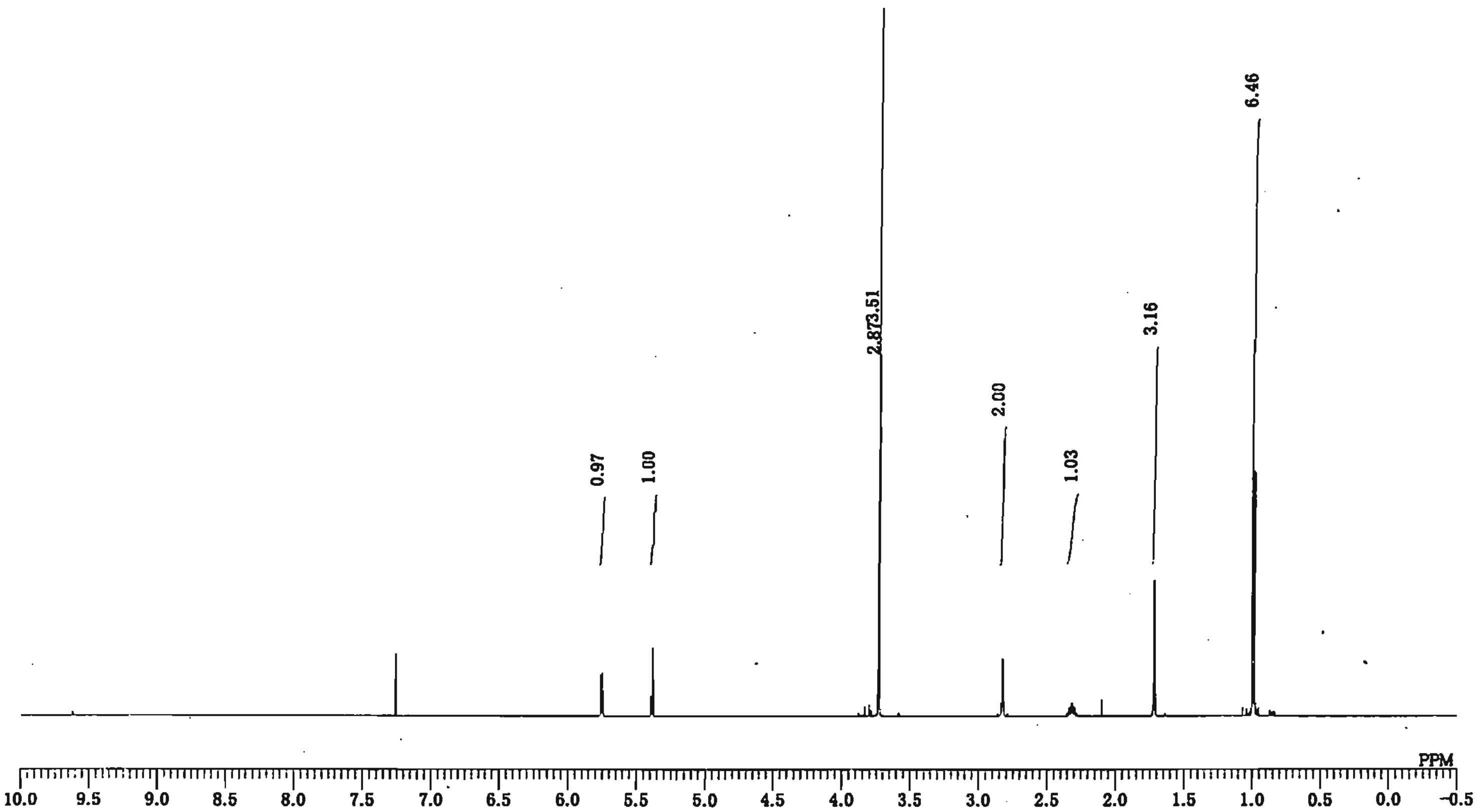
70
60
50
40
30
20
10
0


MeO2C
MeO2C

3l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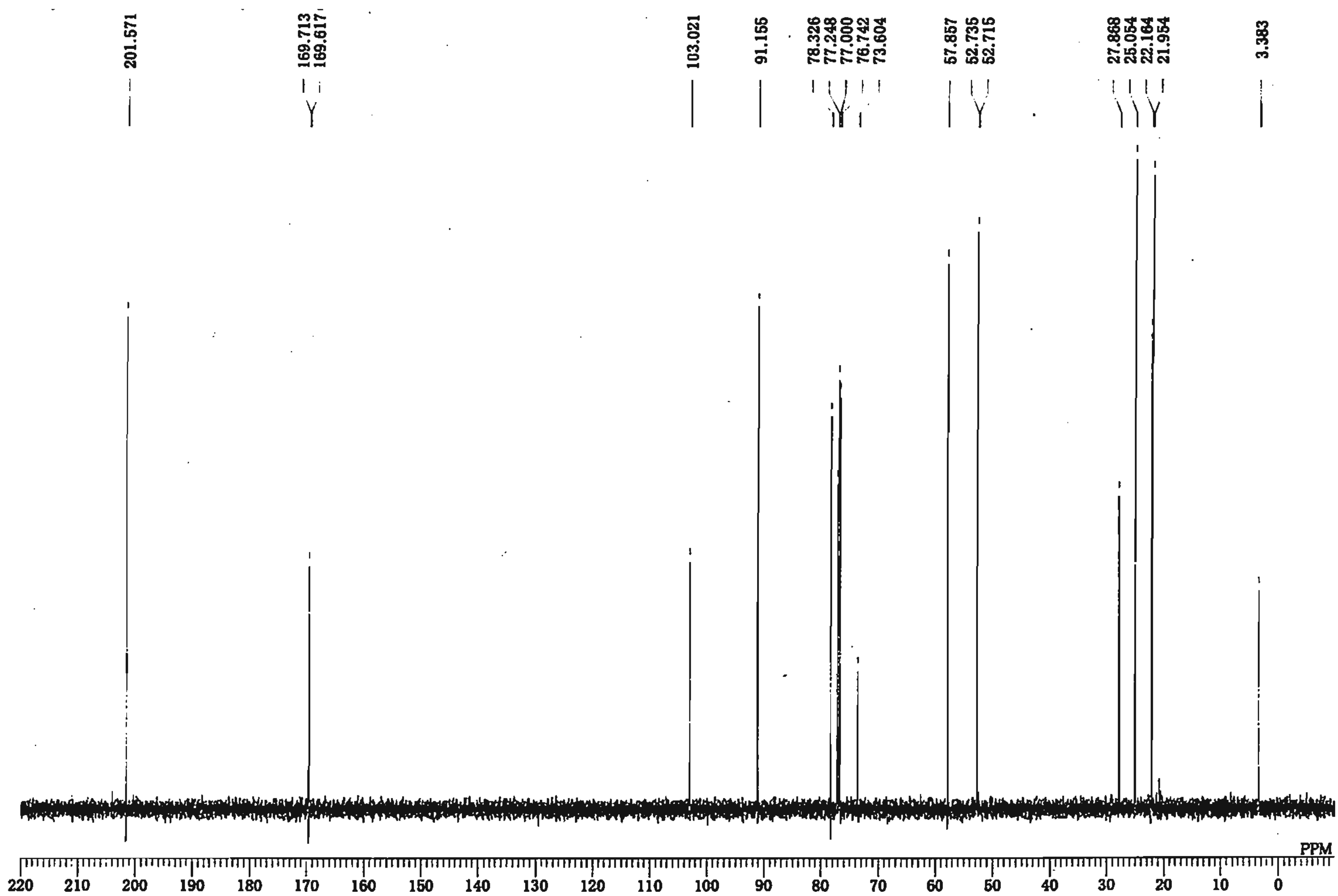
1.00
2.873.51
2.00
1.03
3.16
6.46
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


201.571
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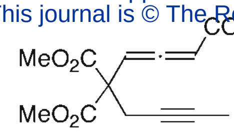
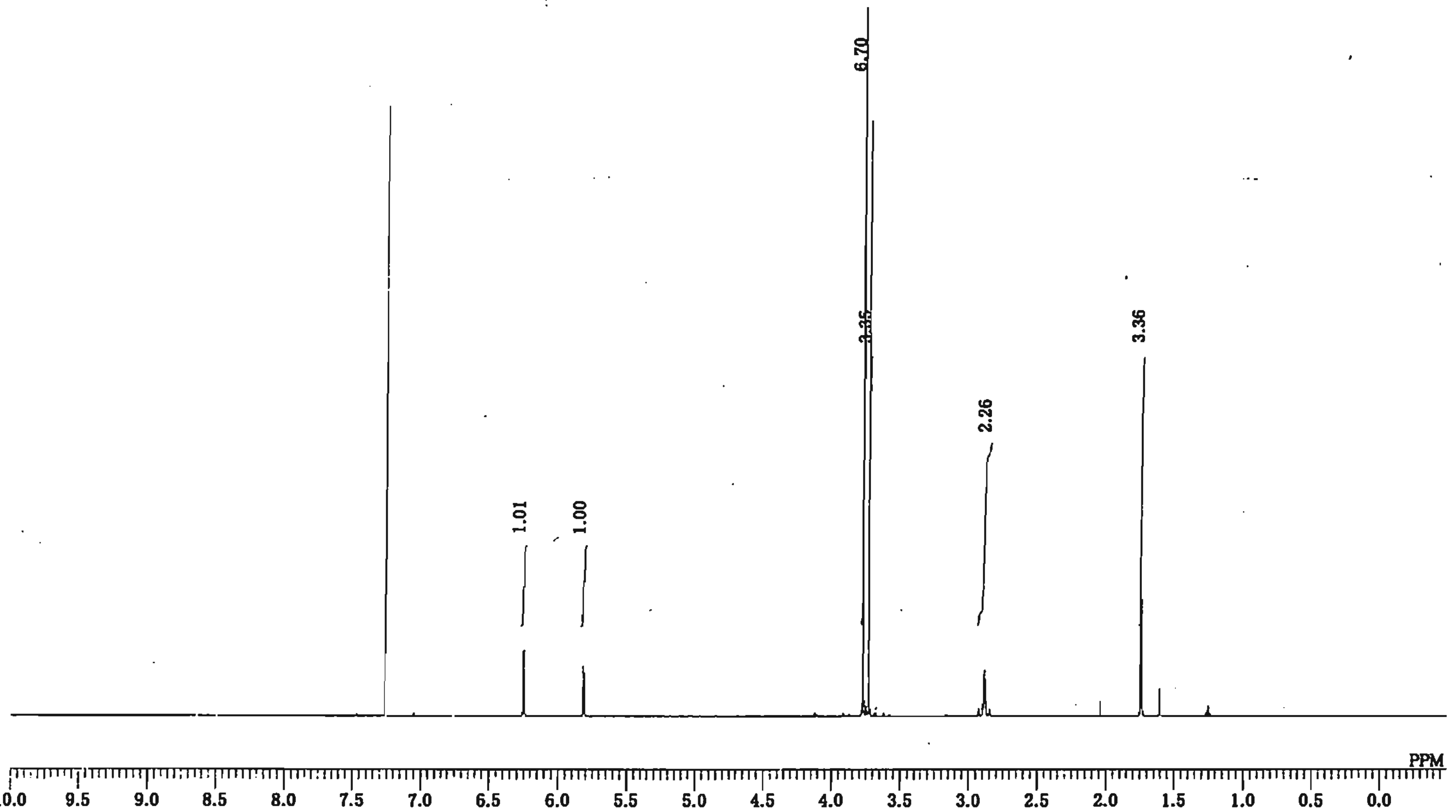
169.617
103.021
91.155
78.326
77.248
77.000
76.742
73.604
57.857
52.735
52.715
27.868
25.054
22.164
21.954
3.383
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



3m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3.35
3.36
2.26
1.01
1.00
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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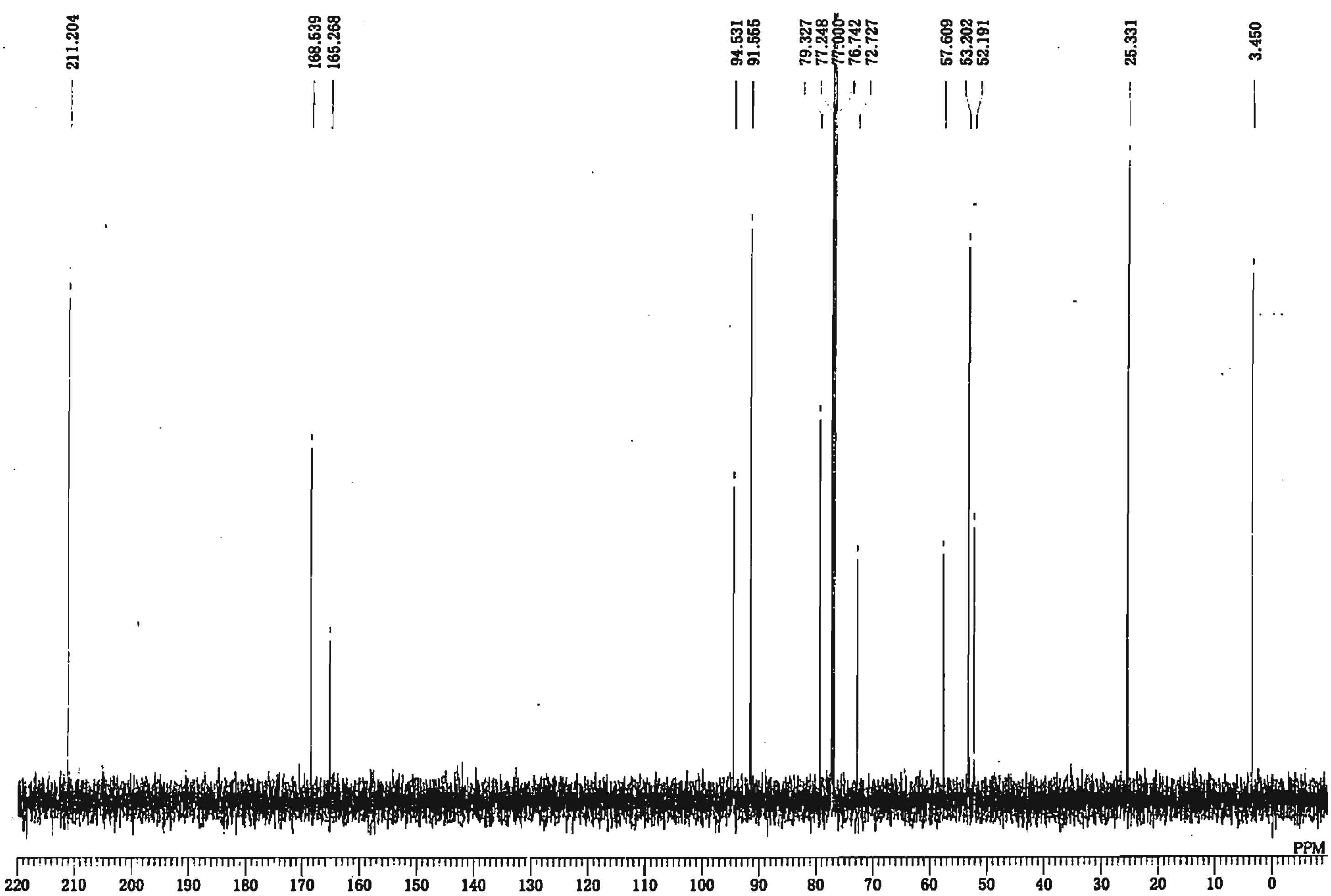
1.0
0.5
0.0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77.000
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72.727
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53.202
52.191
25.331
3.450
PPM
220
210
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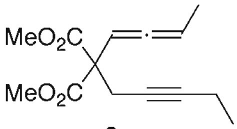
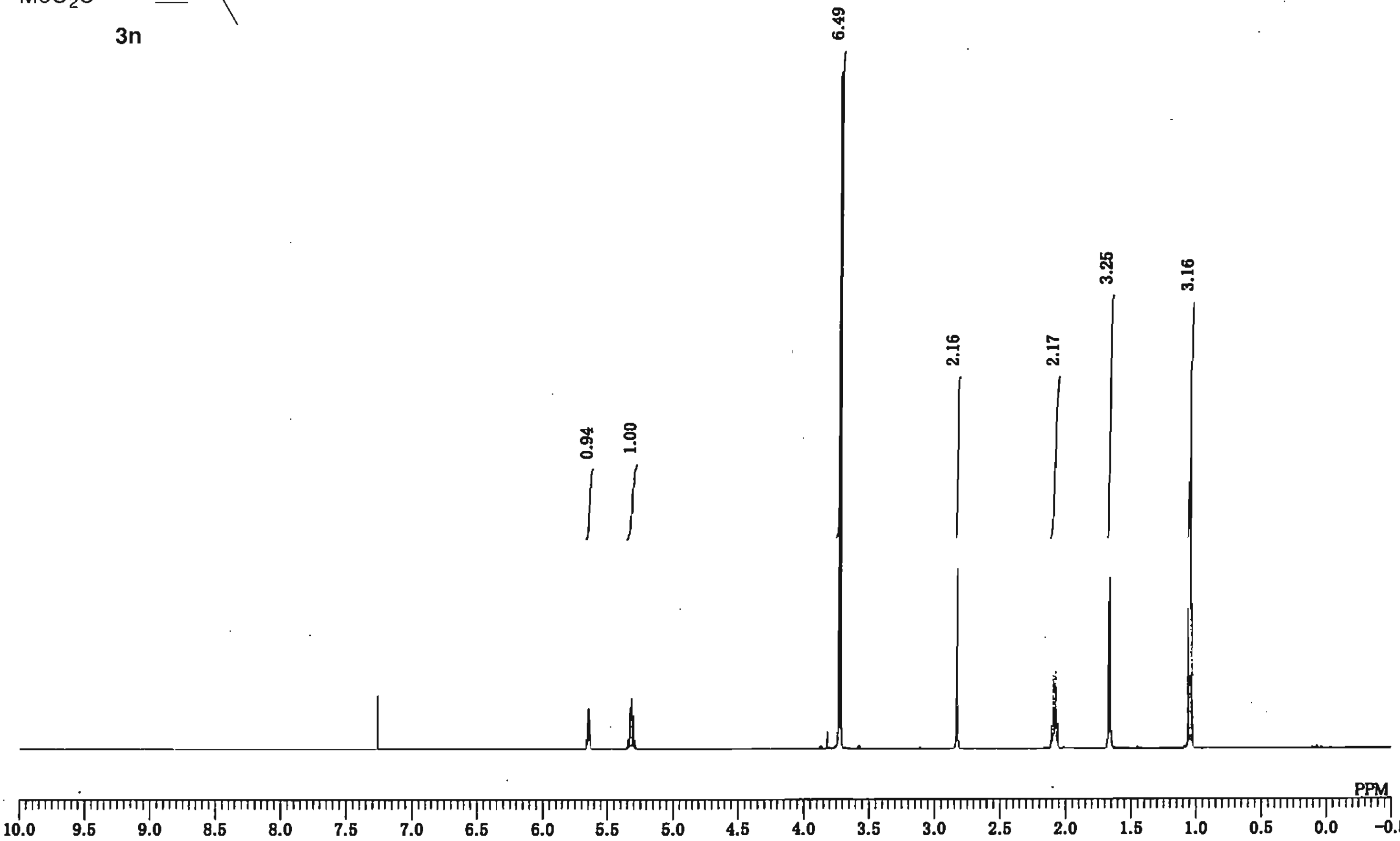


3n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2.17
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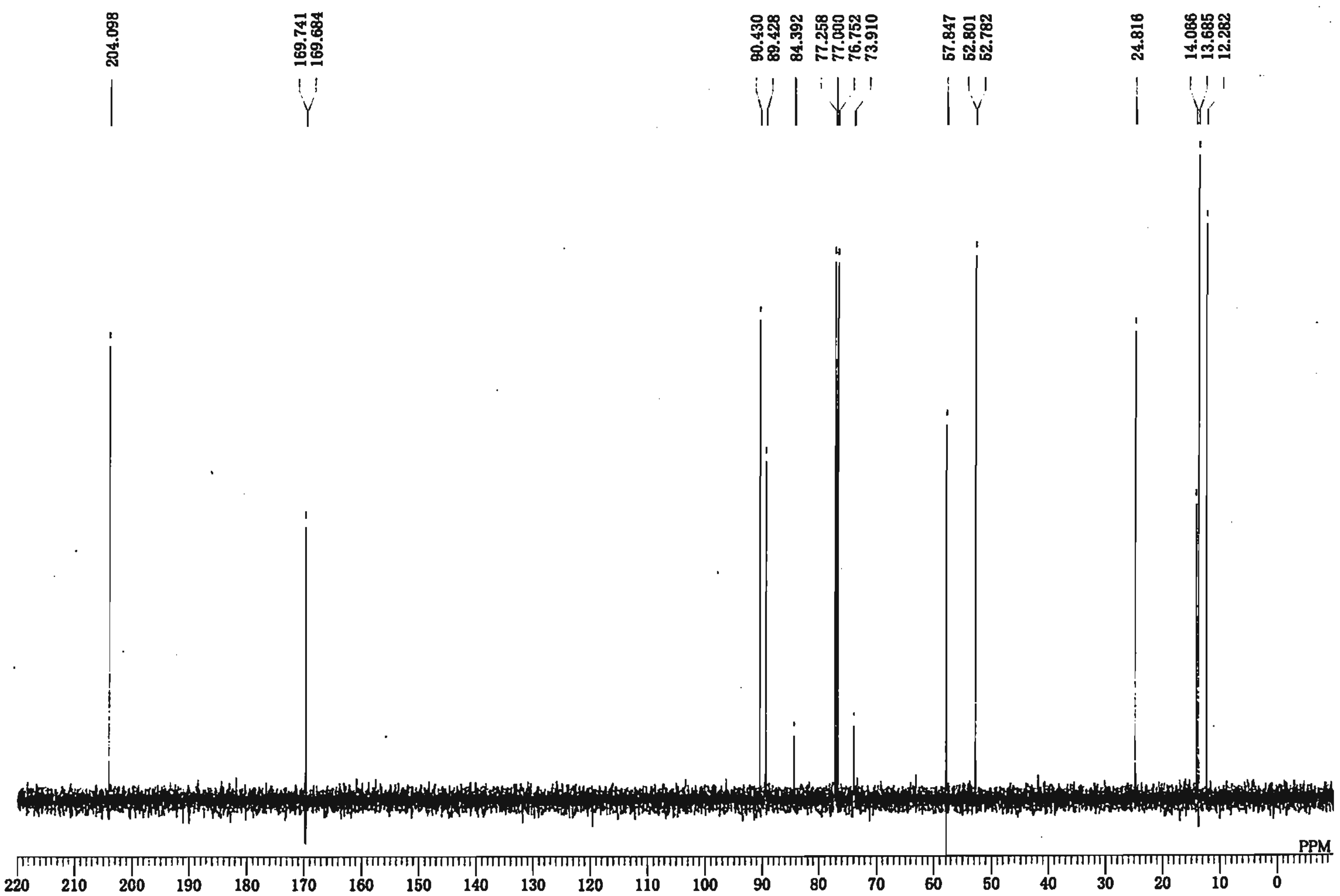
3.16
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5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77.000
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73.910
57.847
52.801
52.782
24.816
14.066
13.685
12.282
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0