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Supporting Information

Geminal Difunctionalization of Vinylarenes : Concise Synthesis of 1,3-Dioxolan-4-ones

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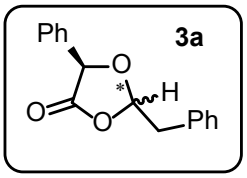
1. General Experimental Methods

All reactions were carried out in oven-dried apparatus using dry solvents under anhydrous conditions, unless otherwise noted. Reaction mixtures were stirred magnetically unless otherwise stated. Analytical grade solvents were distilled and dried according to literature procedures.[1] Analytical TLC was performed on commercial plates coated with silica gel GF_{254} (0.25 mm). Visualization of TLC was accomplished using UV light or PMA stain. Silica gel (230 - 400 mesh) was used for column chromatography. NMR spectra were recorded on 400 MHz spectrometer. The chemical shifts (δ, ppm) are reported with reference to either internal standard $SiMe_4$ (for ^1H) or the central line (77.0 ppm) of $CDCl_3$. The following abbreviations explain the multiplicity s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of a doublet, quint = quintet, m = multiplet, and br = broad. IR spectra were recorded as thin films on NaCl plates on a FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF mass spectrometer. Isolated yields refer to chromatographically and spectroscopically (^1H-NMR) homogeneous materials, unless otherwise stated.

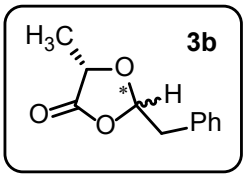
All the α-hydroxy carboxylic acids **1c, 1d**, and **1f** were synthesized starting from aminoacids L-valine, L-leucine, and L-isoleucine respectively according to the literature procedure.[2] All commercially available reagent grade styrenes **2a-2s**, the *R*-(-)-mandelic acid **1a**, L-lactic acid **1b**, D-3-phenyl lactic acid **1e**, α-hydroxy isobutyric acid **1g**, glycolic acid **1h** , benzoic acid **4**, *p*-tolylacetic acid **6**, 3-phenyl-1-propanol **8**, benzamide **10**, acetamide **12**, NBS, and **AgOTf** were used as received, without further purification.

2. General procedure for the synthesis of 1,3-dioxolan-4-ones **3a-3s**

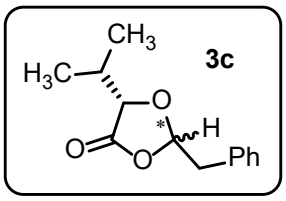
To a well-stirred colorless solution of the appropriate α-hydroxy carboxylic acid (0.50 mmol) and the appropriate styrene (0.75 mmol) in CH_2Cl_2 (5 mL) in a well dried Schlenk flask under argon atmosphere was added NBS (0.60 mmol) and AgOTf (0.70 mmol) at room temperature [25 °C]. The reaction mixture turned from colorless to a white cloudy solution, then to a colorless solution with a pale yellow suspension, and finally to a colorless solution with the formation of pale grey precipitate in 1 h. The progress of the reaction was monitored by TLC. After stirring the reaction mixture for 1 h at room temperature, H_2O (3 mL), sat. soln. of aq. $NaHCO_3$ (4mL) and sat. soln. of aq. $Na_2S_2O_3$ (4 mL) were added in succession and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried (anhyd. Na_2SO_4), filtered and concentrated *in vacuo.* The crude product obtained was purified by flash chromatography (pentane: Et_2O, 25:1) to furnish 1,3-dioxolan-4-ones in pure form.



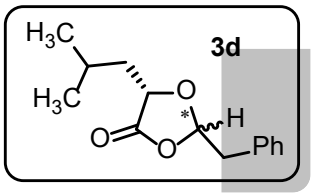
(*5R*)-2-Benzyl-5-phenyl-1,3-dioxolan-4-one (**3a**) (97 mg, 76%): *Diastereomer **A***: white solid; mp 82-84 °C; $[\alpha]_D^{24}$ -89.7 (*c* 1.0, $CHCl_3$); IR (thin film): 3032, 2924, 1796, 1496, 1454, 1401, 1274, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 10H), 5.86 (t, *J* =4.5 Hz, 1H), 5.19 (s, 1H), 3.30-3.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 133.5, 133.0, 130.2, 129.2, 128.6, 128.5, 127.3, 127.0, 103.9, 76.8, 40.5; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{16}H_{14}O_3Na$, 277.0841; found, 277.0843. *Diastereomer **B***: white solid; mp 53 -54°C; $[\alpha]_D^{24}$ -38.2 (*c* 1.0, $CHCl_3$); IR (thin film): 3031, 2924, 1797, 1495, 1454, 1215, 1177, 1109, 992, 934 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 10H), 6.02 (t, *J* = 3.9 Hz, 1H), 5.11 (s, 1H), 3.21 (d, *J* = 4.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 126.6, 126.0, 123.2, 122.0, 121.9, 121.6, 120.4, 118.9, 97.9, 68.3, 34.3; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{16}H_{14}O_3Na$, 277.0841; found, 277.0850.



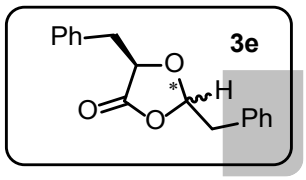
(*5S*)-2-Benzyl-5-methyl-1,3-dioxolan-4-one (**3b**) (92 mg, 63%): *Diastereomer **A***: colourless oil; $[\alpha]_D^{24}$ +28.9 (*c* 1.0, $CHCl_3$); IR (thin film): 3032, 2930, 1798, 1497, 1450, 1405, 1206, 1131, 978 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 5H), 5.68 (m, 1H), 4.34-4.28 (m, 1H), 3.12 (d, *J* = 4.6 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 133.3, 130.0, 128.5, 127.3, 103.8, 71.4, 40.8, 16.3; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{11}H_{12}O_3Na$, 215.0684; found, 215.0686. *Diastereomer **B***: colorless oil; $[\alpha]_D^{24}$ -8.9 (*c* 1.0, $CHCl_3$); IR (thin film): 3030, 2930, 1800, 1218, 981 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.22 (m, 5H), 5.87 (t, *J* = 4.3 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 1H), 3.09 (d, *J* = 4.3 Hz, 2H), 1.39 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 133.2, 130.1, 128.6, 127.3, 104.1, 70.2, 41.2, 16.2; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{11}H_{12}O_3Na$, 215.0684; found, 215.0685.



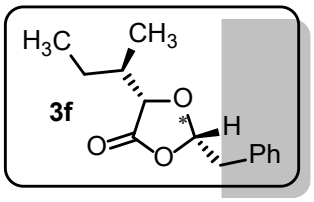
(*5S*)-2-Benzyl-5-isopropyl-1,3-dioxolan-4-one (**3c**) (80 mg, 72%): *Diastereomer **A***: colorless oil; $[\alpha]_D^{24}$ -3.6 (*c* 2.0, $CHCl_3$); IR (thin film): 2967, 2929, 1796, 1496, 1462, 1285, 1213, 1113, 997, 950, 909 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 5H), 5.65 (t, *J* = 4.6 Hz, 1H), 4.09 (d, *J* = 3.9 Hz, 1H), 3.12 (d, *J* = 4.6 Hz, 2H), 2.13-2.05 (m, 1H), 1.03(d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 133.4, 130.0, 128.4, 127.2, 103.6, 79.2, 40.6, 29.6, 18.3, 16.5; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{13}H_{16}O_3Na$, 243.0997; found, 243.0996. *Diastereomer **B***: colorless oil; $[\alpha]_D^{21}$ -24.6 (*c* 2.0, $CHCl_3$); IR (thin film): 3030, 2967, 2879, 1797, 1748, 1497, 1480, 1387, 1367, 1214, 1106, 991 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 5H), 5.85 (t, *J* = 3.6 Hz, 1H), 3.88 (d, *J* = 3.5 Hz, 1H), 3.07 (t, *J* = 3.3 Hz, 2H), 2.10-2.03 (m, 1H), 1.03(d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 133.2, 130.2, 128.5, 127.3, 105.0, 78.5, 41.8, 30.6, 18.2, 16.9; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{13}H_{16}O_3Na$, 243.0997; found, 243.0993.



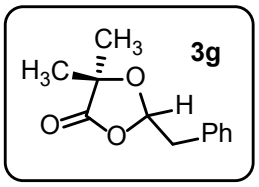
(*5S*)-2-Benzyl-5-isobutyl-1,3-dioxolan-4-one (**3d**) (72 mg, 61%): *Diastereomer **A***: colorless oil; $[\alpha]_D^{21}$ -4.9 (*c* 2.5, $CHCl_3$); IR (thin film): 2958, 2930, 2873, 1798, 1461, 1307, 1118 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.21 (m, 5H), 5.68 (t, *J* = 4.4 Hz, 1H), 4.24 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.12 (d, *J* = 4.4 Hz, 2H), 1.87-1.78 (m, 1H), 1.67-1.60 (m, 1H), 1.43-1.36 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 133.3, 130.1, 128.4, 127.2, 103.9, 73.6, 40.8, 39.7, 24.9, 22.8, 21.7; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^+$ calcd for $C_{14}H_{18}O_3Na$, 257.1154; found, 257.1155. *Diastereomer **B***: colorless oil; $[\alpha]_D^{24}$ -17.7 (*c* 1.0, $CHCl_3$); IR (thin film): 2958, 2873, 1798, 1750, 1458, 1210, 990 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 5H), 5.85 (t, *J* = 4.2 Hz, 1H), 4.06 (dd, *J* = 18.8, 4.9 Hz, 1H), 309 (d, *J* = 4.1 Hz, 2H), 1.86-1.76 (m, 2H), 1.61-1.54 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 133.3, 130.1, 128.6, 127.3, 104.2, 72.6, 41.3, 39.2, 24.9, 22.8, 21.6; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^+$ calcd for $C_{14}H_{18}O_3Na$, 257.1154; found, 257.1152.



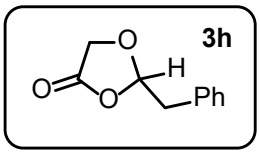
(*5R*)-2,5-Dibenzyl-1,3-dioxolan-4-one (**3e**) (73 mg, 54%): *Diastereomer **A***: colorless oil; $[\alpha]_D^{21}$ +41.2 (*c* 1.0, $CHCl_3$); IR (thin film): 3063, 3031, 2923, 2854, 1797, 1497, 1218, 1178, 1118, 969 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.20 (m, 10H), 5.67-5.64 (m, 1H), 4.50-4.47 (m, 1H), 3.14 (dd, *J* = 14.6, 3.8 Hz, 1H), 2.93 (d, *J* = 4.6 Hz, 2H), 2.84 (dd, *J* = 14.6, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 135.8, 133.3, 130.0, 129.6, 128.5, 127.3, 127.1, 104.3, 75.6, 40.8, 37.0; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^+$ calcd for $C_{17}H_{16}O_3Na$, 291.0997; found, 291.0995. *Diastereomer **B***: colorless oil; $[\alpha]_D^{24}$ +26.0 (*c* 1.0, $CHCl_3$); IR (thin film): 3063, 3031, 2924, 2852, 1797, 1751, 1496, 1453, 1221, 1175, 1113, 1078, 990 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 5.50-5.48 (m, 1H), 4.35-4.38 (m, 1H), 3.11-2.96 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 135.3, 133.0, 130.1, 129.5, 128.6, 128.5, 127.3, 127.2, 104.8, 74.9, 41.3, 37.0; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^+$ calcd for $C_{17}H_{16}O_3Na$, 291.0997; found, 291.0995.



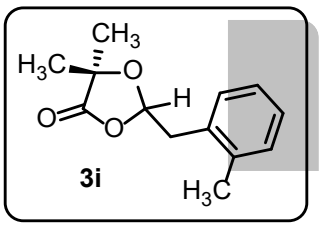
(*2S*,*5S*)-2-Benzyl-5-((*R*)-sec-butyl)-1,3-dioxolan-4-one (**3f**): colorless oil (68 mg, 58%); $[\alpha]_D^{21}$ -0.9 (*c* 2.0, $CHCl_3$); IR (thin film): 2966, 2930, 2880, 1797, 1458, 1401, 1114, 999 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 5H), 5.65-5.63 (m, 1H), 4.12 (d, *J* = 4.1 Hz, 1H), 3.12 (d, *J* = 4.6 Hz, 2H), 1.86-1.79 (m, 1H), 1.45-1.20 (m, 2H), 1.0 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 133.4, 130.0, 128.4, 127.2, 103.6, 78.8, 40.6, 36.1, 24.0, 14.9, 11.5; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^+$ calcd for $C_{14}H_{18}O_3Na$, 257.1154; found, 257.1162.



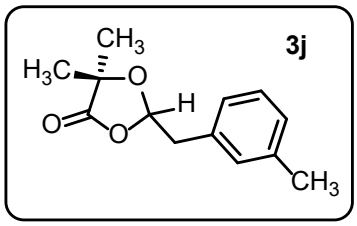
2-Benzyl-5,5-dimethyl-1,3-dioxolan-4-one (**3g**): colorless oil (67 mg, 65%); IR (thin film): 3032, 2985, 2929, 1797, 1497, 1456, 1387, 1360, 1278, 1210, 1148, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 5.74 (t, J = 4.4 Hz, 1H), 3.10 (d, J = 3.9 Hz, 2H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 133.4, 130.1, 128.4, 127.2, 101.9, 77.2, 41.0, 24.4, 21.8; HRMS (ESI-QTOF) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{14}O_3Na$, 229.0841; found, 229.0839.



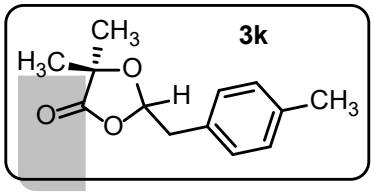
2-Benzyl-1,3-dioxolan-4-one (**3h**):[3] colorless oil (43 mg, 48%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 5.81 (t, J = 4.5 Hz, 1H), 4.14 (d, J = 2.9 Hz, 2H), 3.13 (d, J = 3.0 Hz, 1H), 3.12 (d, J = 2.9 Hz, 1H).



5,5-Dimethyl-2-(2-methylbenzyl)-1,3-dioxolan-4-one (**3i**): colorless oil (64 mg, 58%); IR (thin film): 2982, 2930, 1800, 1460, 1390, 1280, 1151, 982 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.12 (m, 4H), 5.74 (t, J = 4.5 Hz, 1H), 3.12 (d, J = 4.5 Hz, 2H), 2.35 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 137.2, 131.9, 130.8, 130.3, 127.3, 125.9, 102.0, 77.2, 38.0, 24.5, 21.8, 19.9; HRMS (ESI-QTOF) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{16}O_3Na$, 243.0997; found, 243.0998.

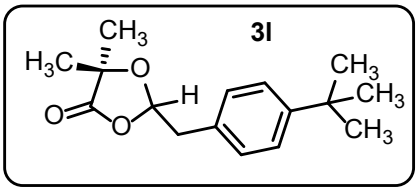


5,5-Dimethyl-2-(3-methylbenzyl)-1,3-dioxolan-4-one (**3j**): colorless oil (68 mg, 61%); IR (thin film): 3024, 2983, 2926, 1799, 1391, 1360, 1280, 1206, 1151, 1103, 1033, 984 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.05 (m, 4H), 5.72 (t, J = 4.5 Hz, 1H), 3.05 (d, J = 4.6 Hz, 2H), 2.34 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 138.0, 133.3, 130.8, 128.3, 127.9, 127.0, 102.1, 77.2, 41.1, 24.5, 21.8, 21.3; HRMS (ESI-QTOF) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{16}O_3Na$, 243.0997; found, 243.0996.

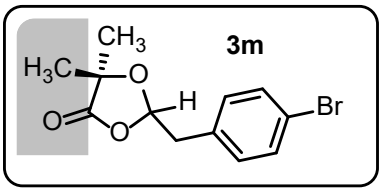


5,5-Dimethyl-2-(4-methylbenzyl)-1,3-dioxolan-4-one (**3k**): colorless oil (63 mg, 57%); IR (thin film): 2985, 2925, 1800, 1515, 1458, 1392, 1201, 1151, 982 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17-7.11 (m, 4H), 5.71

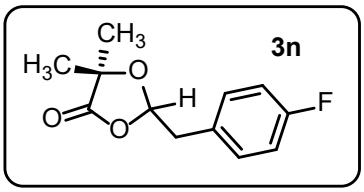
(t, J = 4.5 Hz, 1H), 3.06 (d, J = 4.4 Hz, 2H), 2.33 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 136.8, 130.3, 129.9, 129.1, 102.1, 77.2, 40.7, 24.5, 21.8, 21.0; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{13}H_{16}O_3Na$, 243.0997; found, 243.0994.



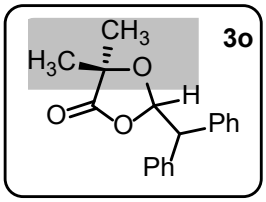
5,5-Dimethyl-2-(4-*tert*-butyl benzyl)-1,3-dioxolan-4-one (**3l**): colorless oil (88 mg, 67%); IR (thin film): 2961, 1799, 1275, 1209, 1186, 1143, 984 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 6.5, 1.8 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 5.71 (t, J = 4.6 Hz, 1H), 3.06 (d, J = 4.5 Hz, 2H), 1.39 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 150.1, 130.4, 129.7, 125.4, 102.2, 77.2, 40.6, 34.4, 31.3, 24.5, 21.8; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{16}H_{22}O_3Na$, 285.1467; found, 285.1466.



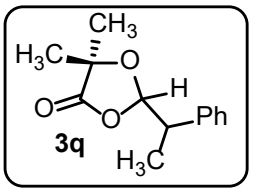
5,5-Dimethyl-2-(4-bromobenzyl)-1,3-dioxolan-4-one (**3m**): colorless oil (89 mg, 62%); IR (thin film): 2984, 2924, 2850, 1797, 1489, 1182, 1147, 985 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 5.70 (t, J = 8.5 Hz, 1H), 3.05 (d, J = 1.9 Hz, 1H), 3.04 (d, J = 2.2 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 132.2, 131.9, 131.5, 121.3, 101.3, 77.2, 40.3, 24.4, 21.8; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{12}H_{13}BrO_3Na$, 308.9946; found, 308.9945.



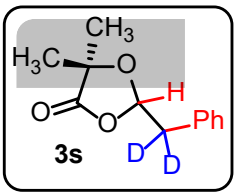
5,5-Dimethyl-2-(4-fluorobenzyl)-1,3-dioxolan-4-o ne (**3n**): colorless oil (68 mg, 60%); IR (thin film): 2986, 2929, 1790, 1512, 1221, 1149, 985 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 8.4, 5.5 Hz, 2H), 7.0 (dd, J = 8.6 Hz, 2H), 5.70 (t, J = 4.3 Hz, 1H), 3.06 (dd, J = 3.9 Hz, 2H), 1.39 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.32, 162.1 (d, $^1J_{C\text{-}F}$ = 243.9 Hz), 131.7 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 129.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 115.3 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 101.6, 77.3, 40.0, 24.4, 21.8; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{12}H_{13}FO_3Na$, 247.0746; found, 247.0749.



2-Benzhydryl-5,5-dimethyl-1,3-dioxolan-4-one (**3o**): colorless oil (122 mg, 86%); IR (thin film): 3030, 2984, 2909, 1800, 1496, 1454, 1386, 1284, 1184, 1151, 972 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 10H), 6.16 (d, J = 3.3 Hz, 1H), 4.36 (d, J = 3.3 Hz, 1H), 1.42 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 137.83, 137.76, 129.6, 129.5, 128.4, 127.25, 127.22, 102.7, 77.1, 55.2, 24.0, 22.5; HRMS (ESI-QTOF) *m/z*: $[M+ Na]^+$ calcd for $C_{18}H_{18}O_3Na$, 305.1154; found, 305.1150.



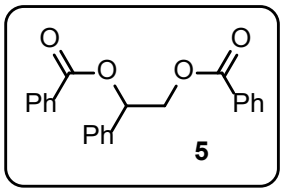
5,5-Dimethyl-2-(1-phenylethyl)-1,3-dioxolan-4-one (**3q**): [mixture of diastereomers; inseparable in ^{1}H NMR]; colorless oil (100 mg, 90%); IR (thin film): 2982, 2908, 1799, 1457, 1279, 1210, 964 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5H), 5.65 (d, J = 3.8 Hz, 0.5H, *1A*), 5.63 (d, J = 3.7 Hz, 0.5H, *1B*), 3.16-3.09 (m, 1H), 1.40-1.37 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 175.5, 139.4, 139.2, 128.7, 128.5, 128.4, 128.31, 128.26, 127.23, 104.3, 77.2, 77.1, 43.6, 24.3, 24.2, 22.1, 21.8, 14.2, 14.1; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^{+}$ calcd for $C_{13}H_{16}O_3Na$, 243.0997; found, 243.0995.



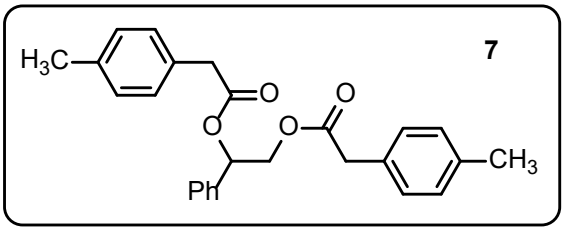
5,5-Dimethyl-2-(phenylmethyl-d_2)-1,3-dioxolan-4-one (**3s**): colorless oil (66 mg, 63%); IR (thin film): 2984, 2926, 1798, 1387, 1281, 1183, 1008, 986 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 5H), 5.72 (s, 1H, $\underline{H}CCD_2Ph$), 1.38 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 133.3, 130.1, 128.4, 127.2, 101.9, 77.2, 40.4 (quint, $^{3}J_{C\text{-}D}$ = 19.6 Hz), 24.4, 21.8; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^{+}$ calcd for $C_{12}H_{12}D_2O_3Na$, 231.0966; found, 231.0969.

3. General procedure for the addition of mono-functionalized nucleophiles **4-12** to styrene **2a**

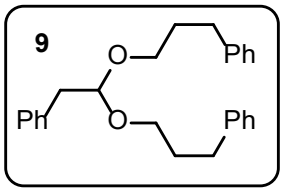
To a well-stirred colorless solution of the appropriate nucleophile (1.2 mmol) and styrene **2a** (0.50 mmol) in 5 mL of CH_2Cl_2 in a well dried Schlenk flask under argon atmosphere was added NBS (0.60 mmol) and AgOTf (0.70 mmol) at room temperature [25 °C]. The reaction mixture turned from colorless to a white cloudy solution, then to a colorless solution with a pale yellow suspension, and finally to a colorless solution with the formation of pale grey precipitate in 1 h. The progress of the reaction was monitored by TLC. After stirring the reaction mixture for 1 h at room temperature 3 mL of H_2O (3 mL), sat. soln. of aq. $NaHCO_3$ (4 mL) and sat. soln. of aq. $Na_2S_2O_3$ (4 mL) were added in succession and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried (anhyd. Na_2SO_4), filtered and concentrated *in vacuo.* The crude product obtained was purified by flash chromatography (petroleum ether: EtOAc) to furnish the respective products in pure form.



1-Phenylethane-1,2-diyl dibenzoate (**5**):[4] white solid (118 mg, 68%); mp 99 °C (lit.[4] mp 94-95 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.98 (m, 4H), 7.57-7.32 (m, 11H), 6.42 (dd, J = 8.0, 3.7 Hz, 1H), 4.78-4.65 (m, 2H).

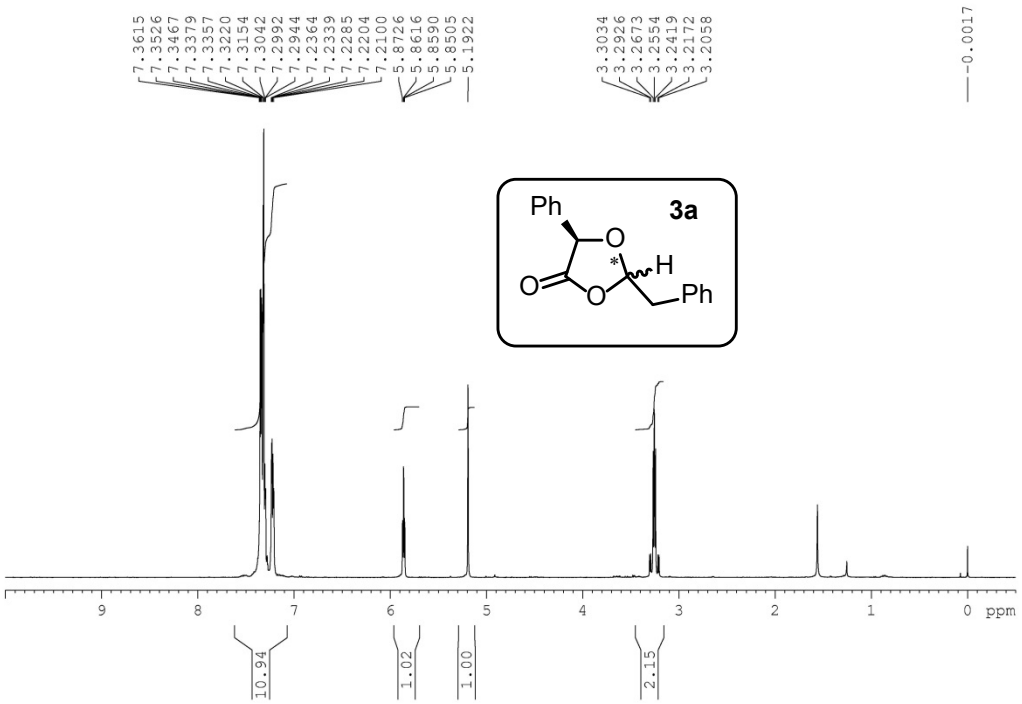


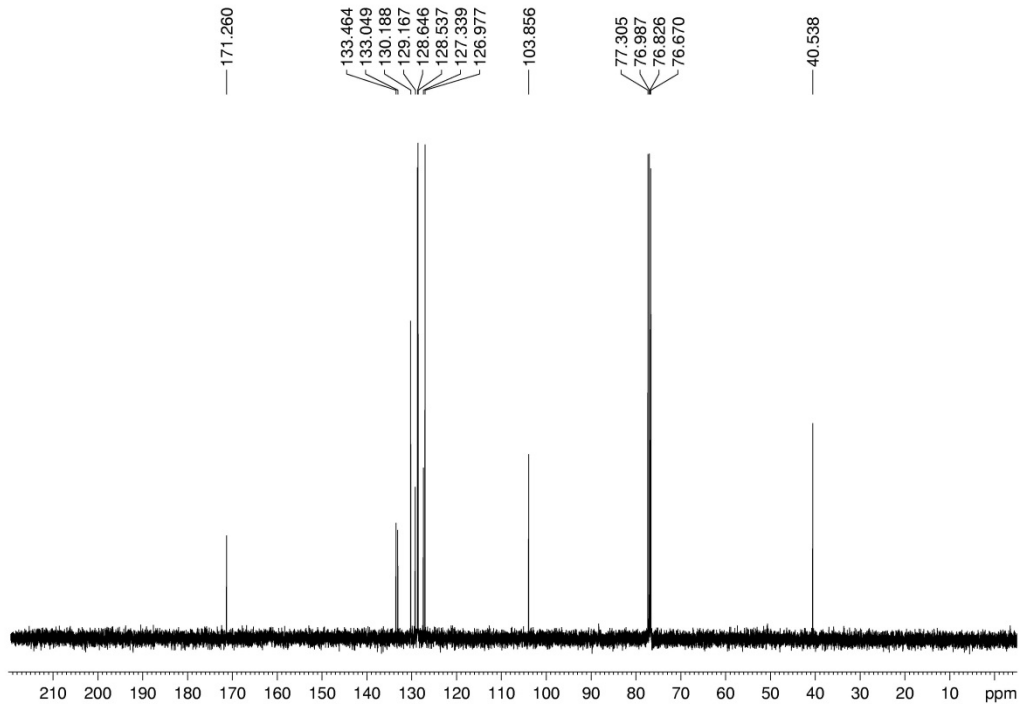
1-Phenylethane-1,2-diyl bis(2-(*p*-tolyl)acetate) (**7**): colorless oil (110 mg, 54%); IR (thin film): 3028, 2950, 2971, 2858, 1727, 1493, 1451, 1300, 1021 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.07 (m, 13H), 6.0 (dd, J = 7.3 4.6 Hz, 1H), 4.29 (t, J = 4.2 Hz, 2H), 3.57 (s, 2H), 3.48 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.6, 136.7, 136.2, 130.64, 130.59, 129.21, 129.19, 129.12, 129.10, 128.53, 128.49, 126.6, 73.4, 66.2, 40.9, 40.6, 21.0; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^+$ calcd for $C_{26}H_{26}O_4Na$, 425.1729; found, 425.1733.



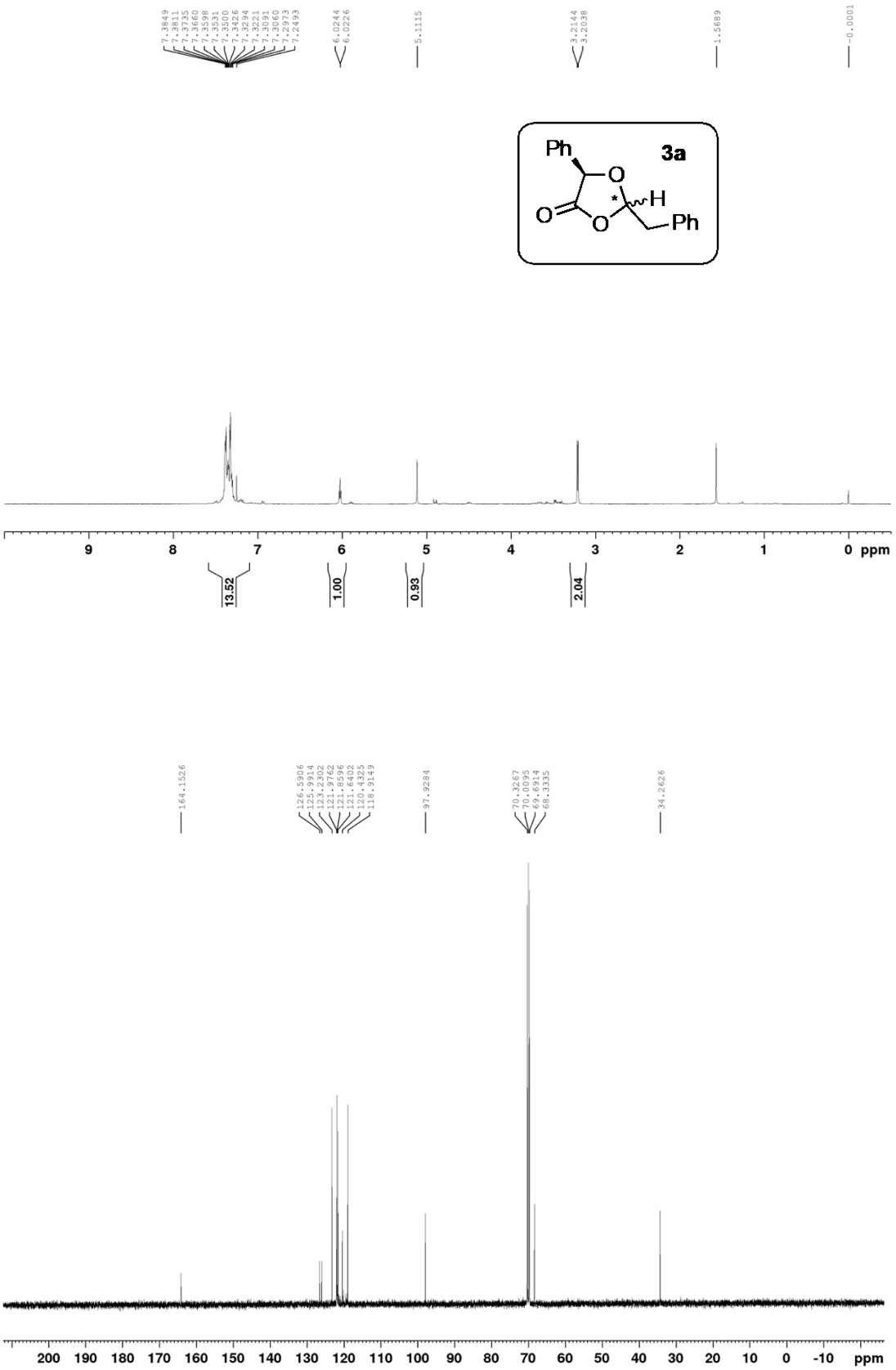
(((2-phenylethane-1,1-diyl)bis(oxy))bis(propane-3,1-diyl))Dibenzene (**9**): colorless oil (97 mg, 52%); IR (thin film): 3027, 2932, 2866, 1602, 1495, 1452, 1351, 1121, 1057 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.09 (m, 15H), 4.61 (t, J = 5.7 Hz, 1H), 3.66-3.61 (m, 2H), 3.41-3.36 (m, 2H), 2.94 (d, J = 5.6 Hz, 2H), 2.61 (t, J = 7.4 Hz, 4H), 1.90-1.789 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 137.3, 129.6, 128.4, 128.3, 128.2, 126.3, 125.7, 104.2, 65.5, 40.8, 32.3, 31.4; HRMS (ESI-QTOF) *m/z*: [M+ Na]$^+$ calcd for $C_{26}H_{30}O_2Na$, 397.2143; found, 397.2150.

^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **A*** of compound **3a**

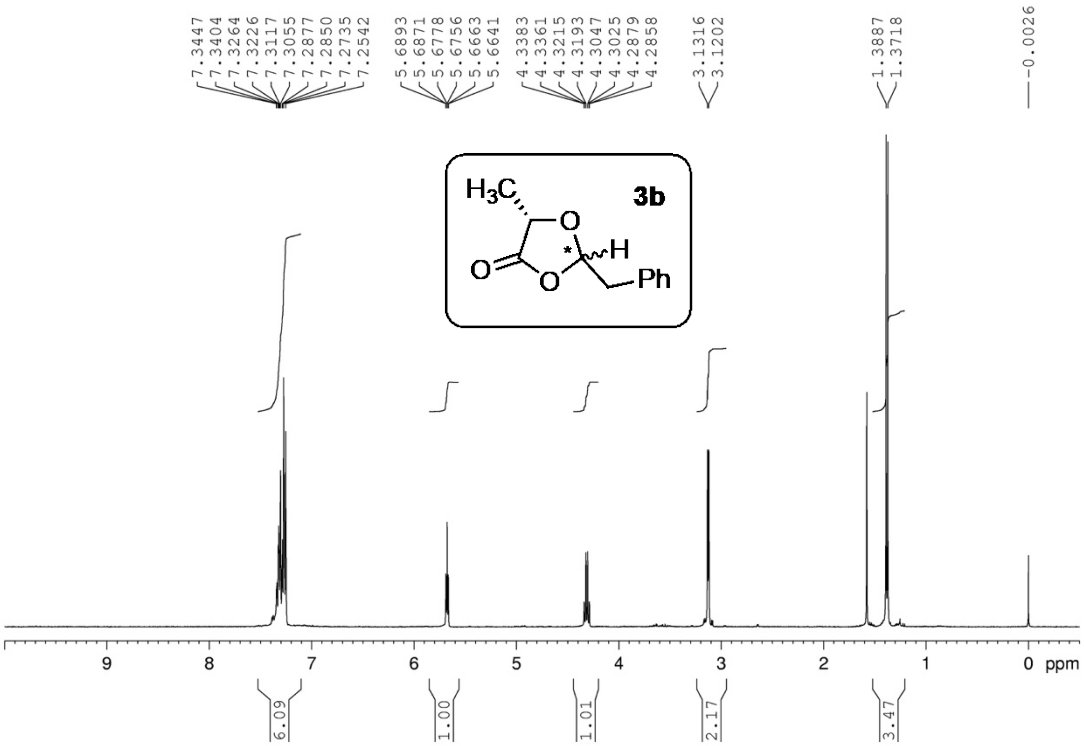


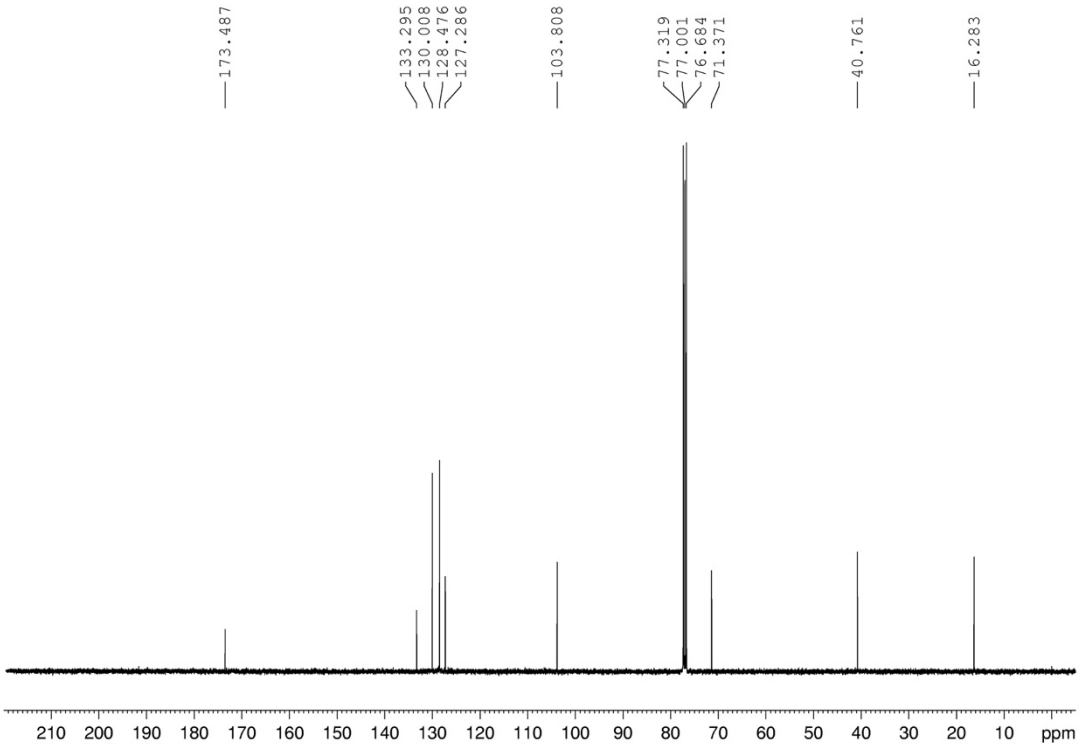


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **B*** of compound **3a**

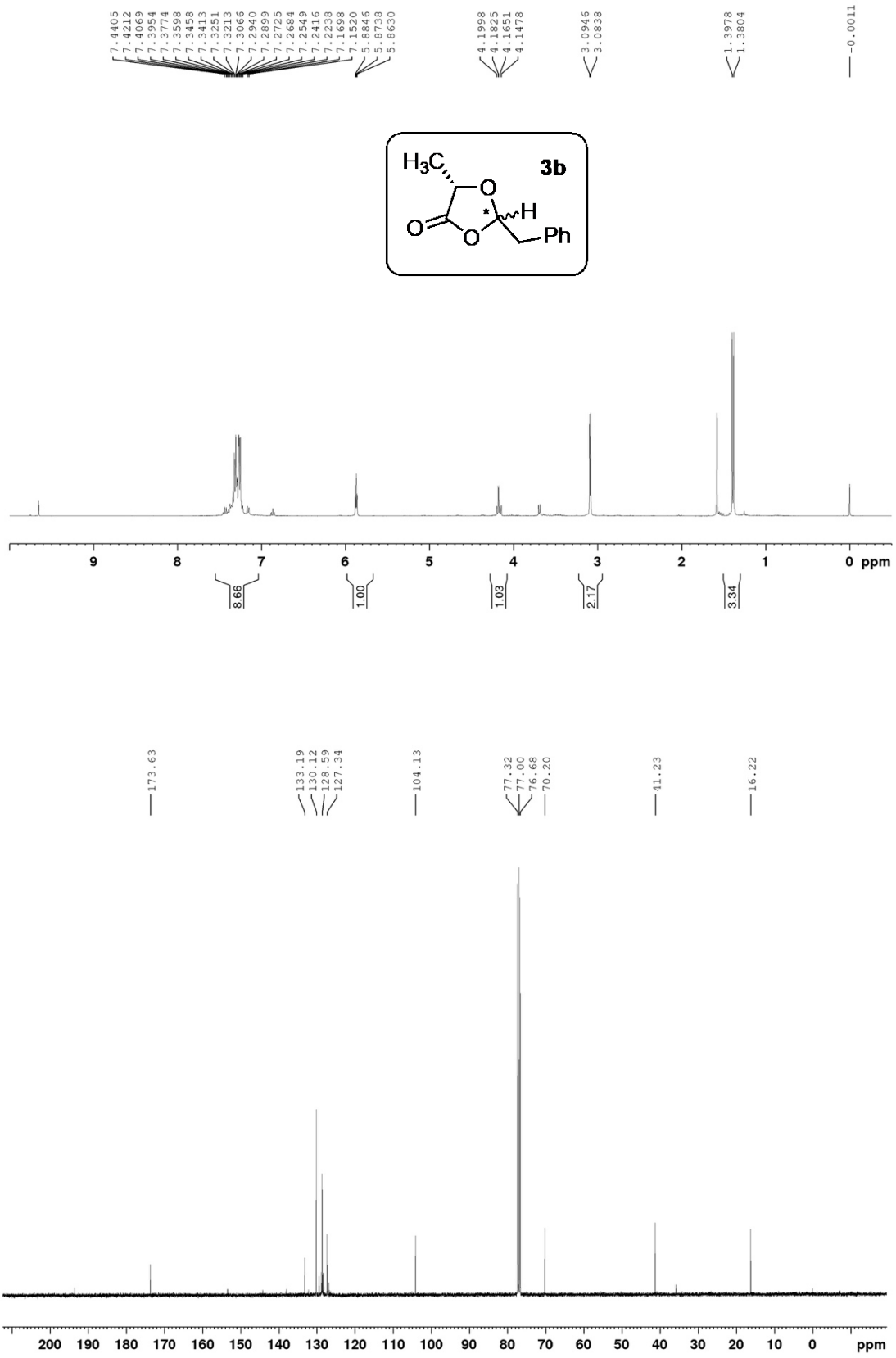


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of diastereomer **A** of compound **3b**

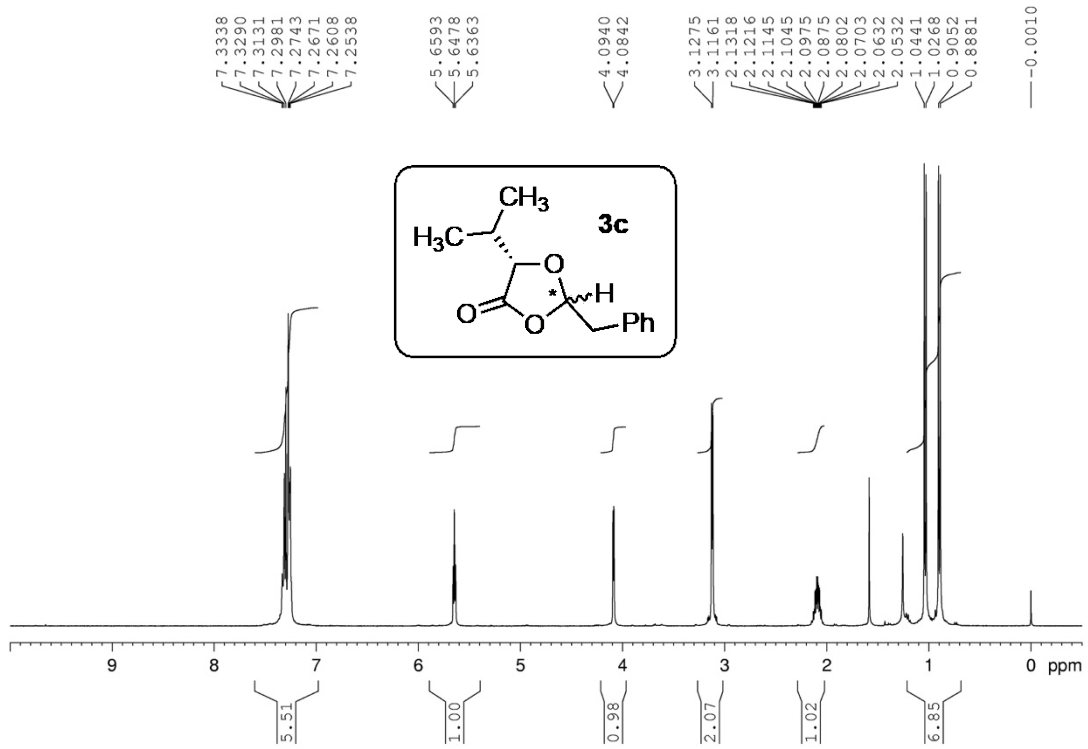


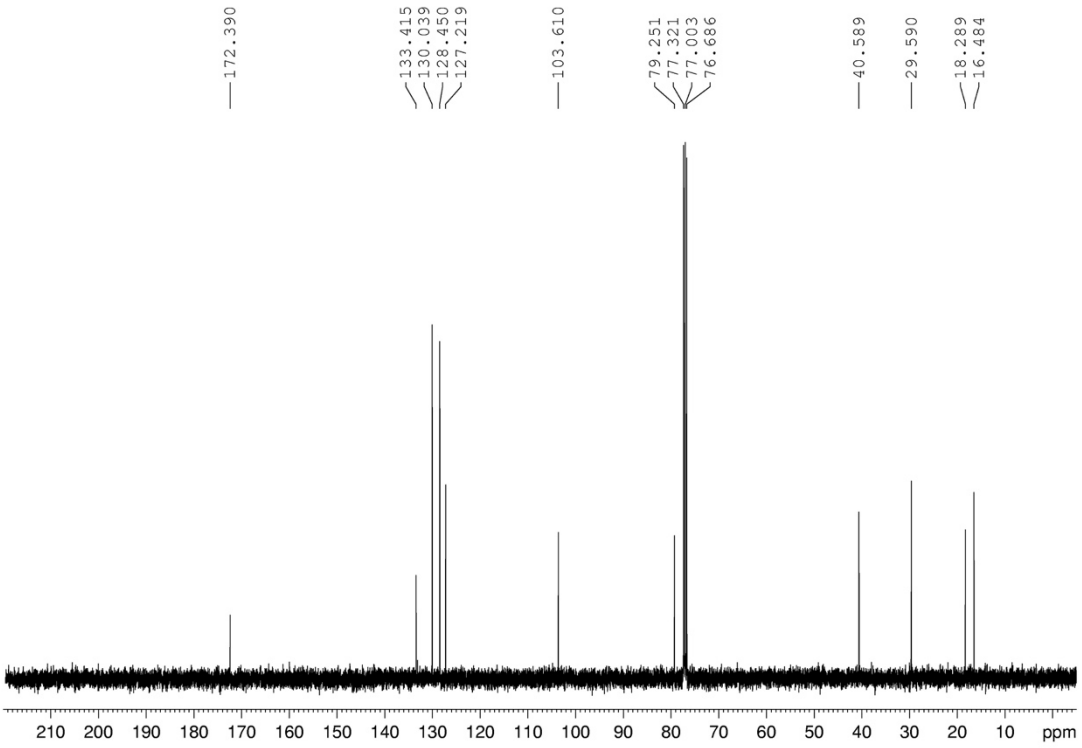


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of diastereomer **B** of compound **3b**

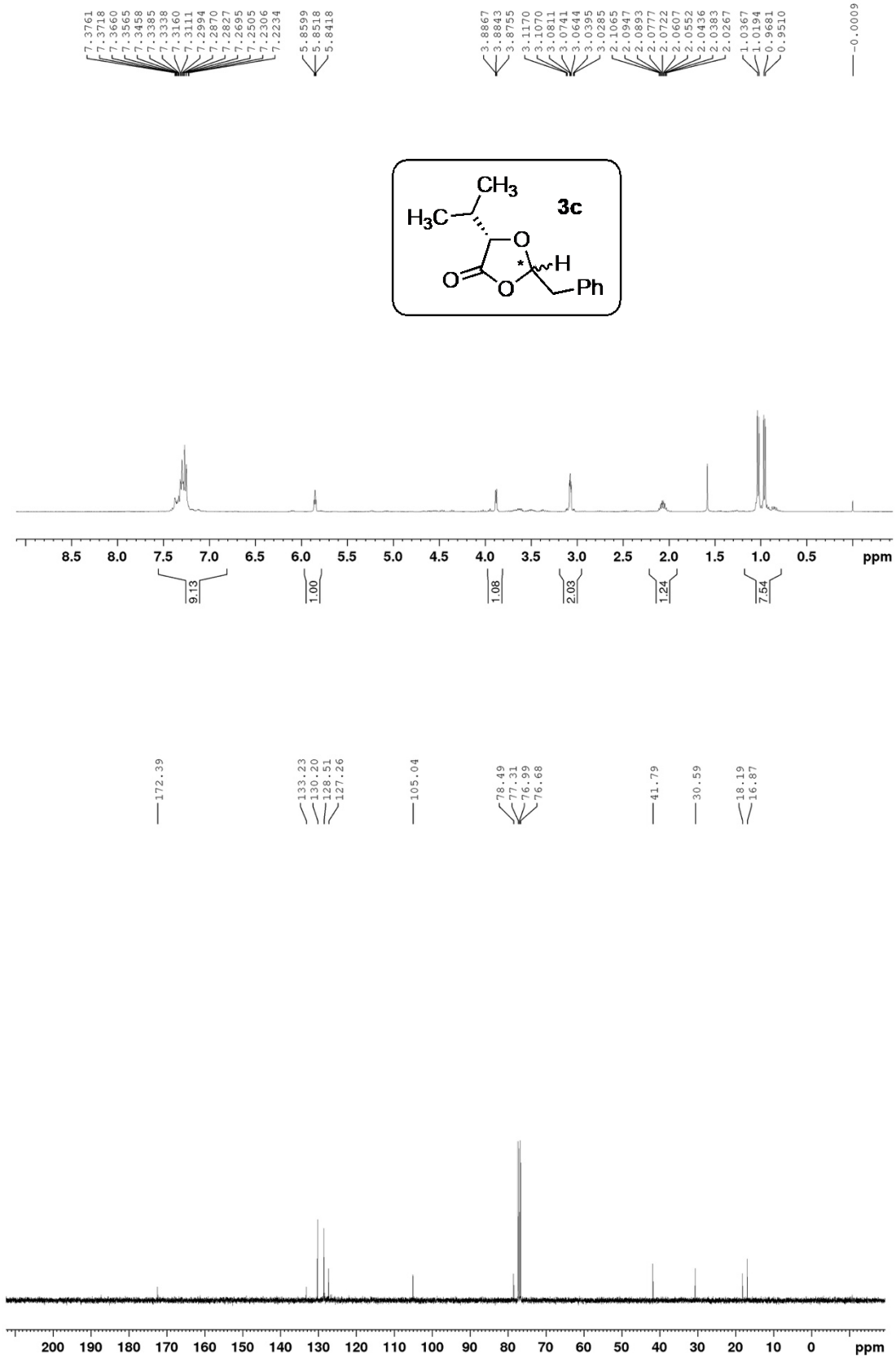


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **A*** of compound **3c**

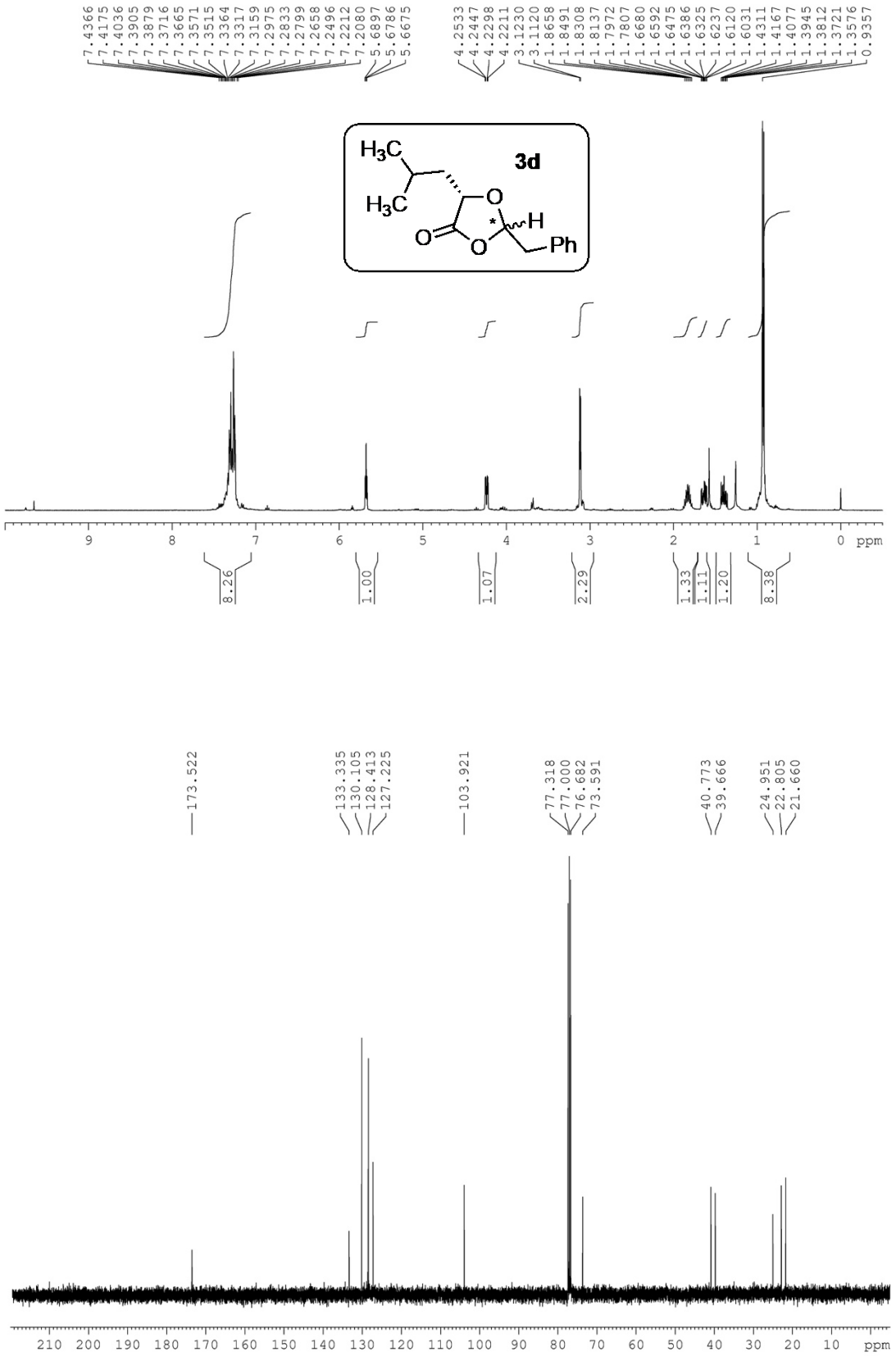




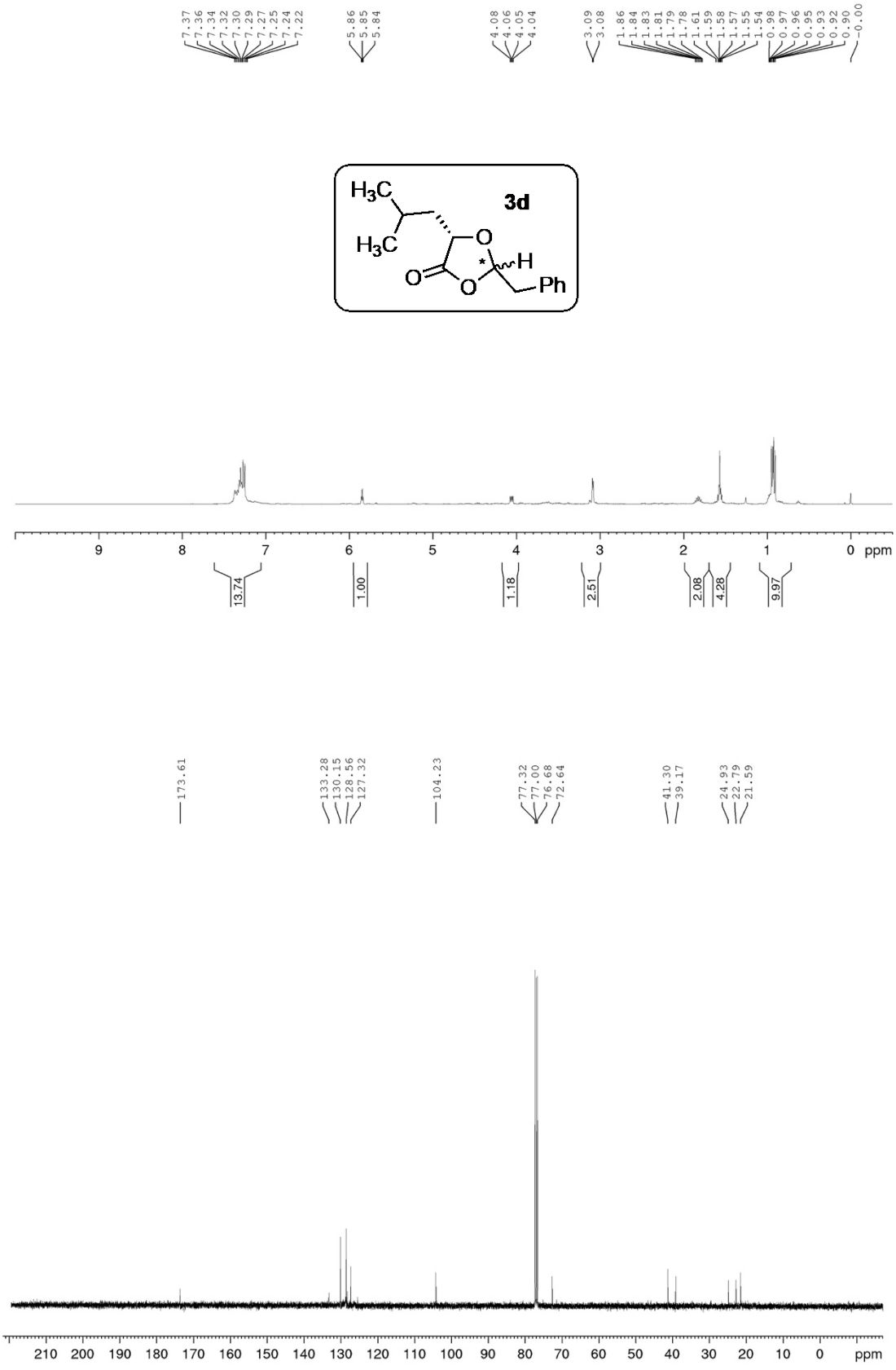
^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **B*** of compound **3c**



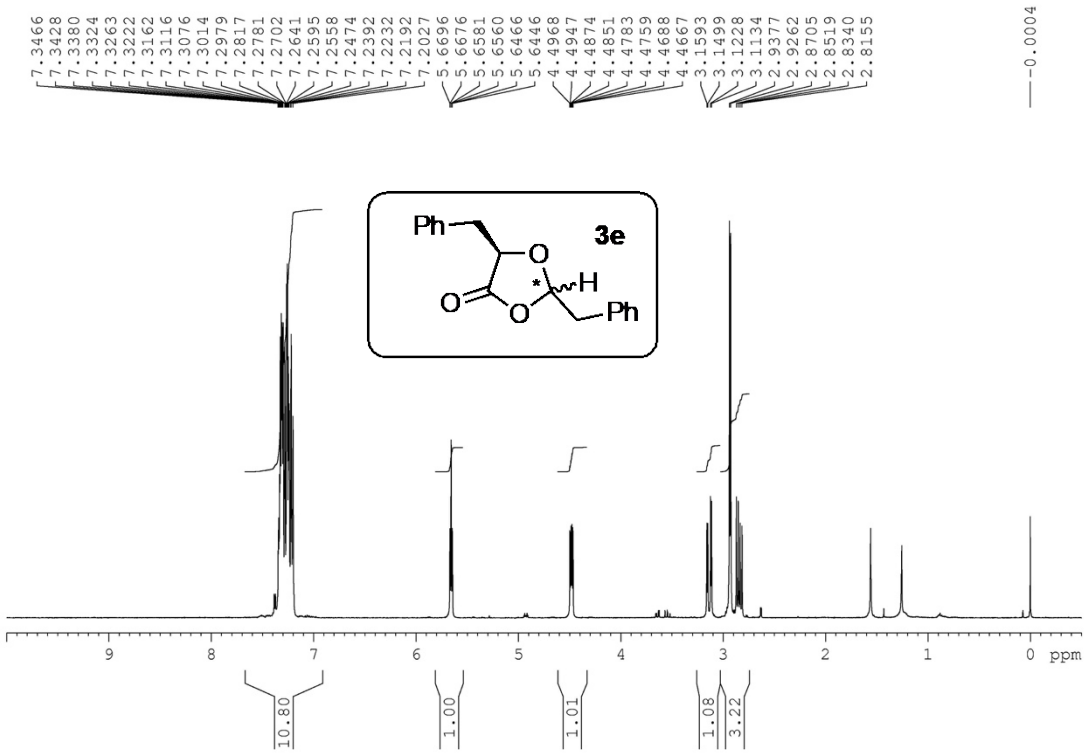
^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **A*** of compound **3d**

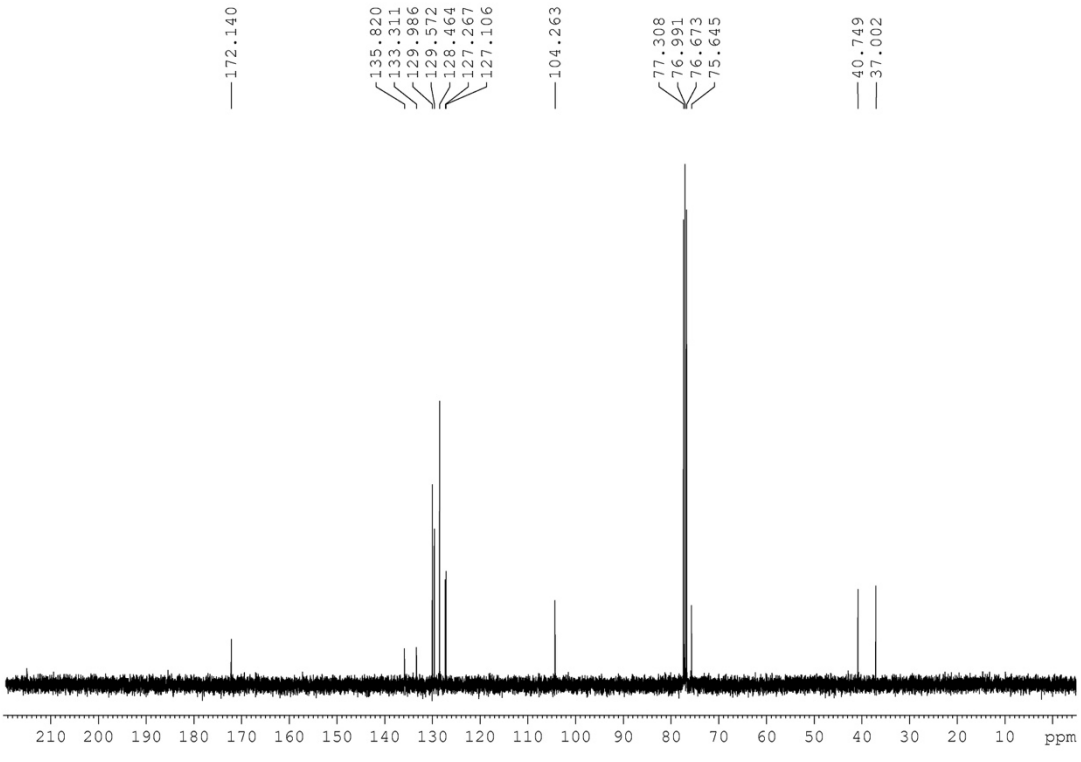


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **B*** of compound **3d**

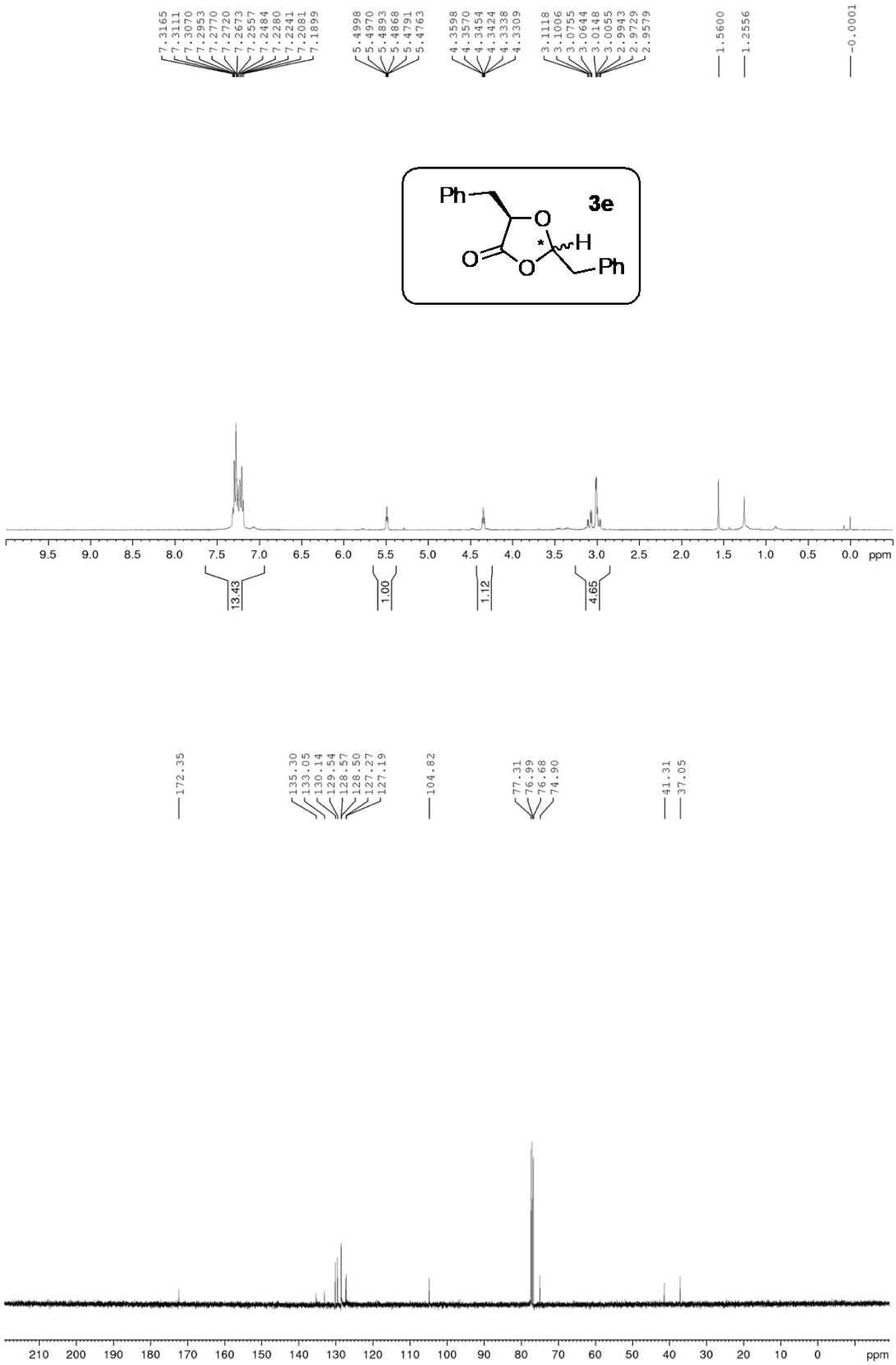


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **A*** of compound **3e**

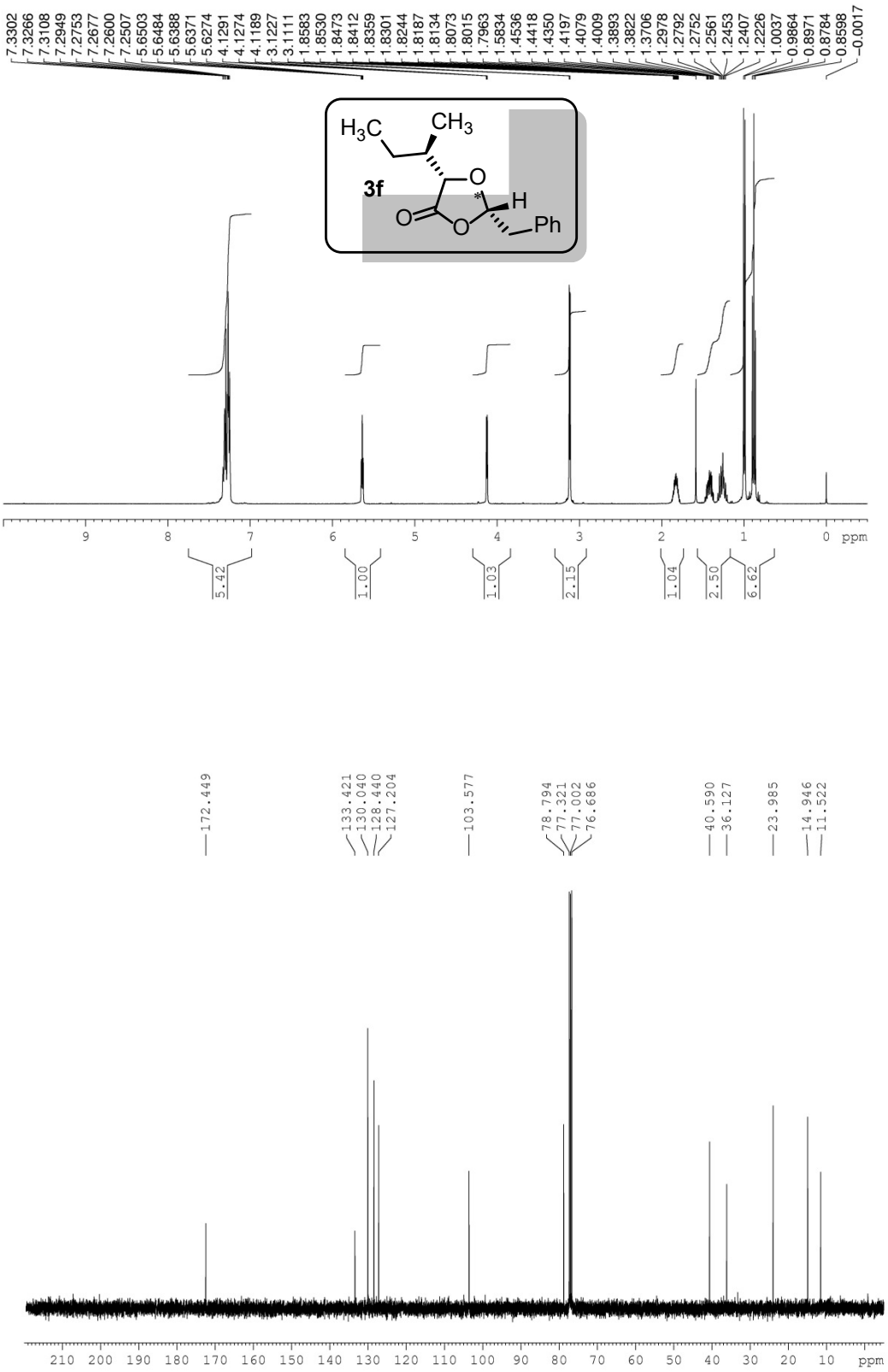




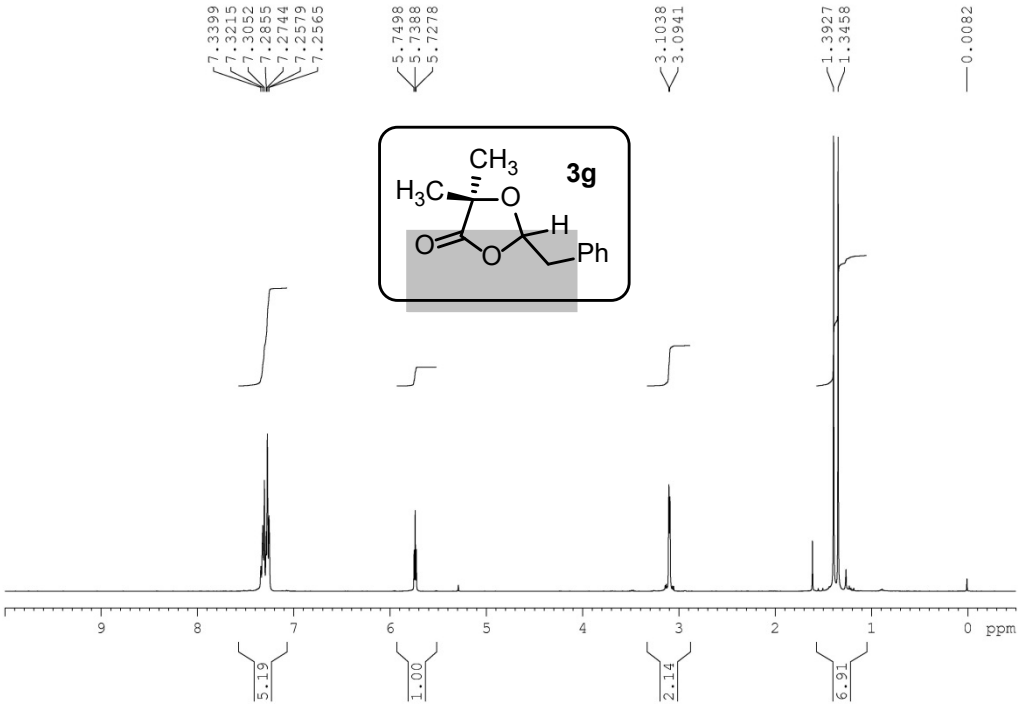
^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of *diastereomer **B*** of compound **3e**

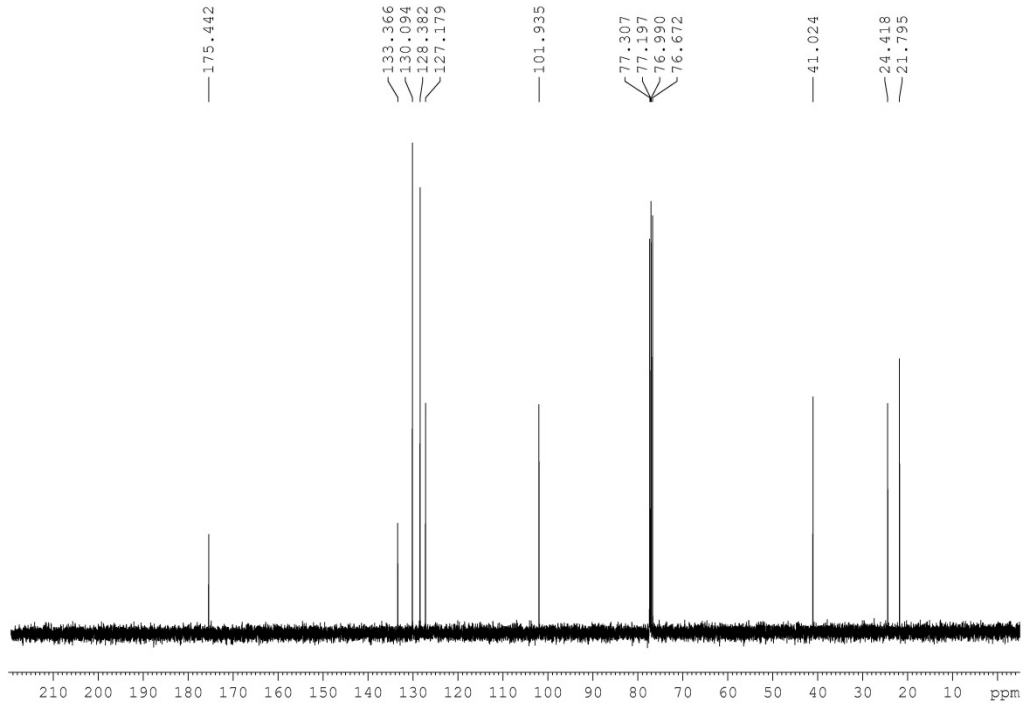


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3f**

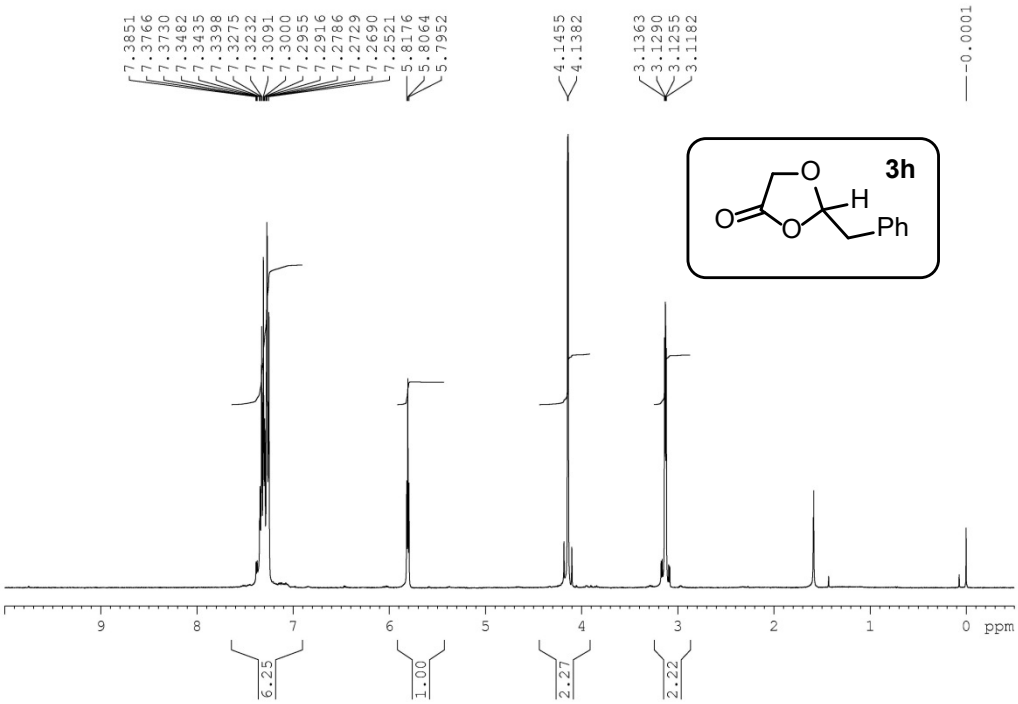


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3g**

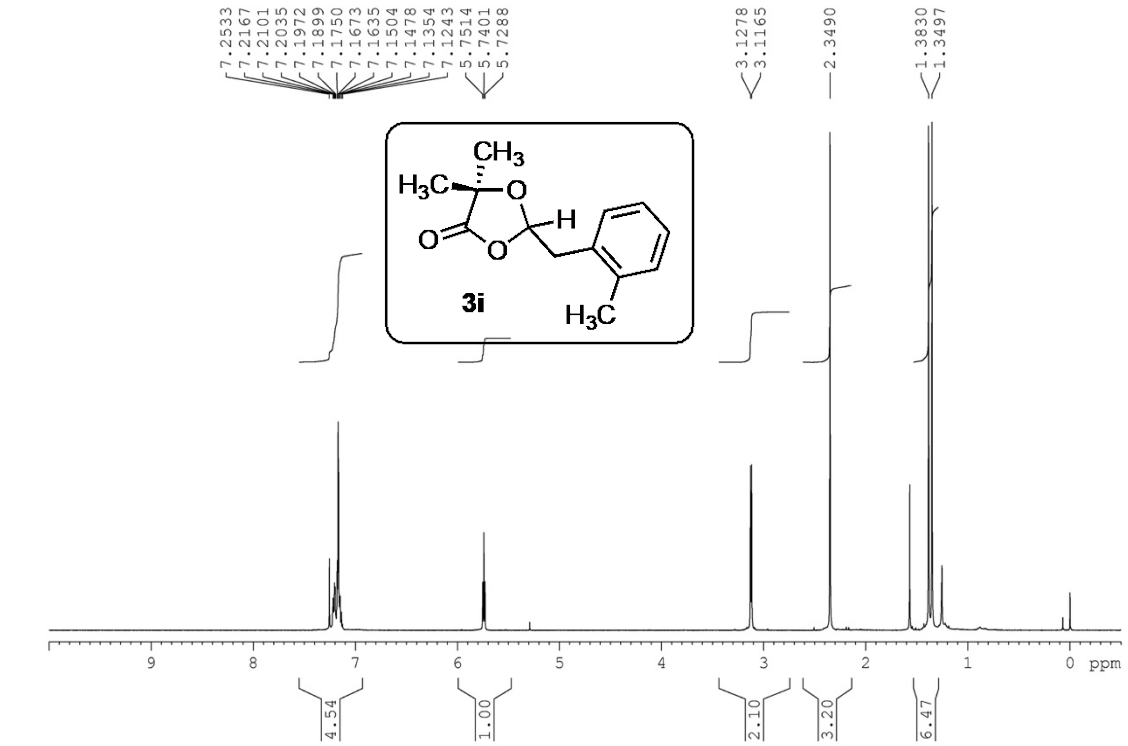


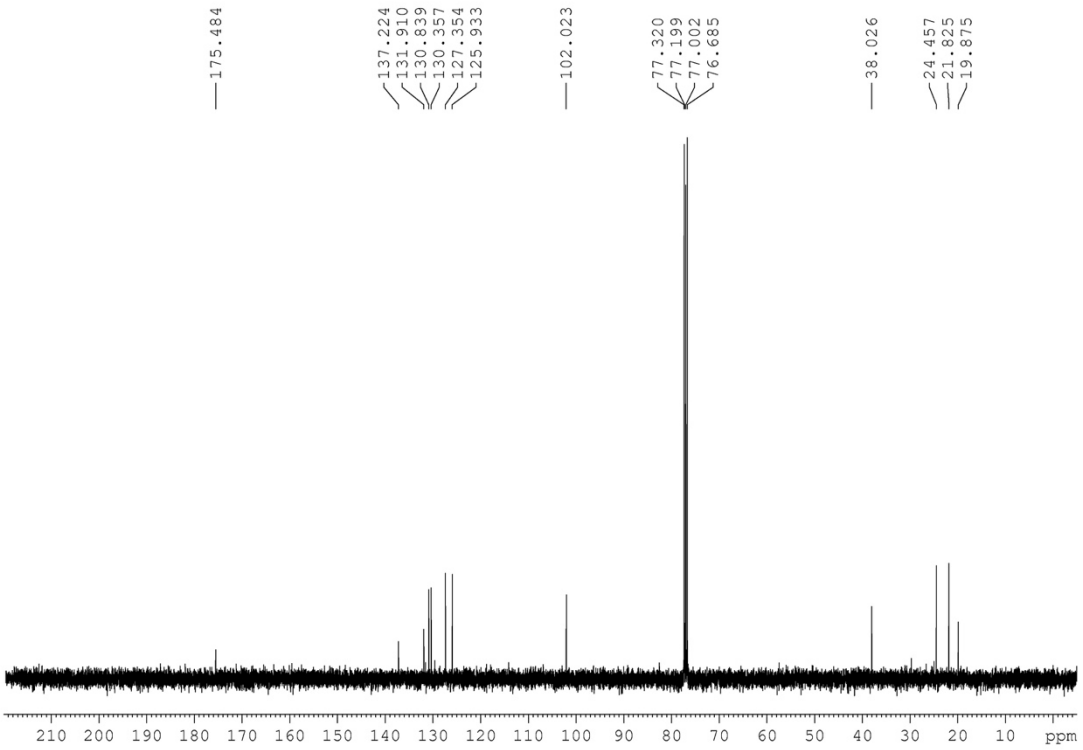


^{1}H NMR spectrum (400, $CDCl_3$) of compound **3h**

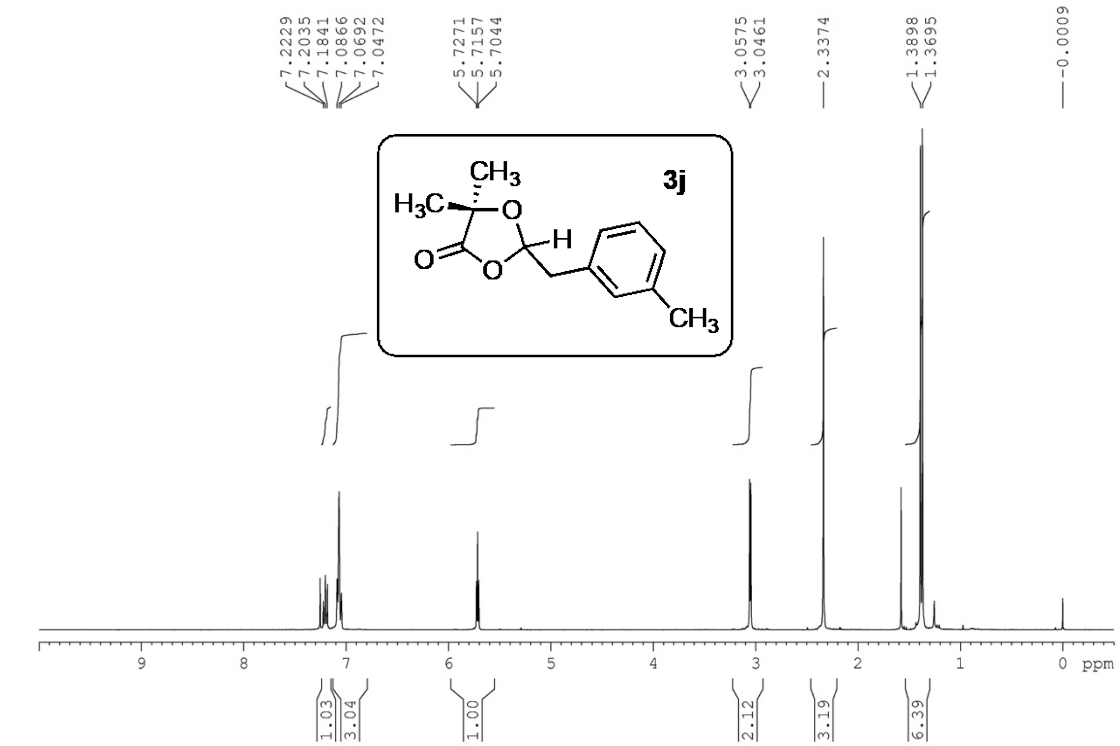


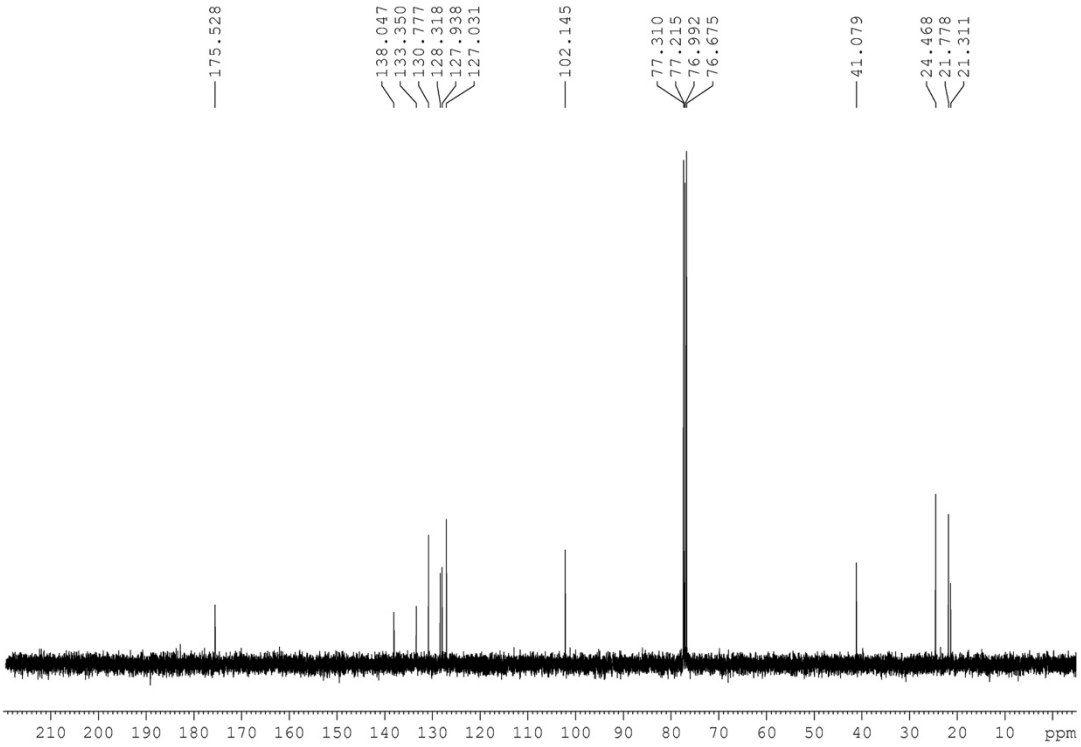
^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3i**



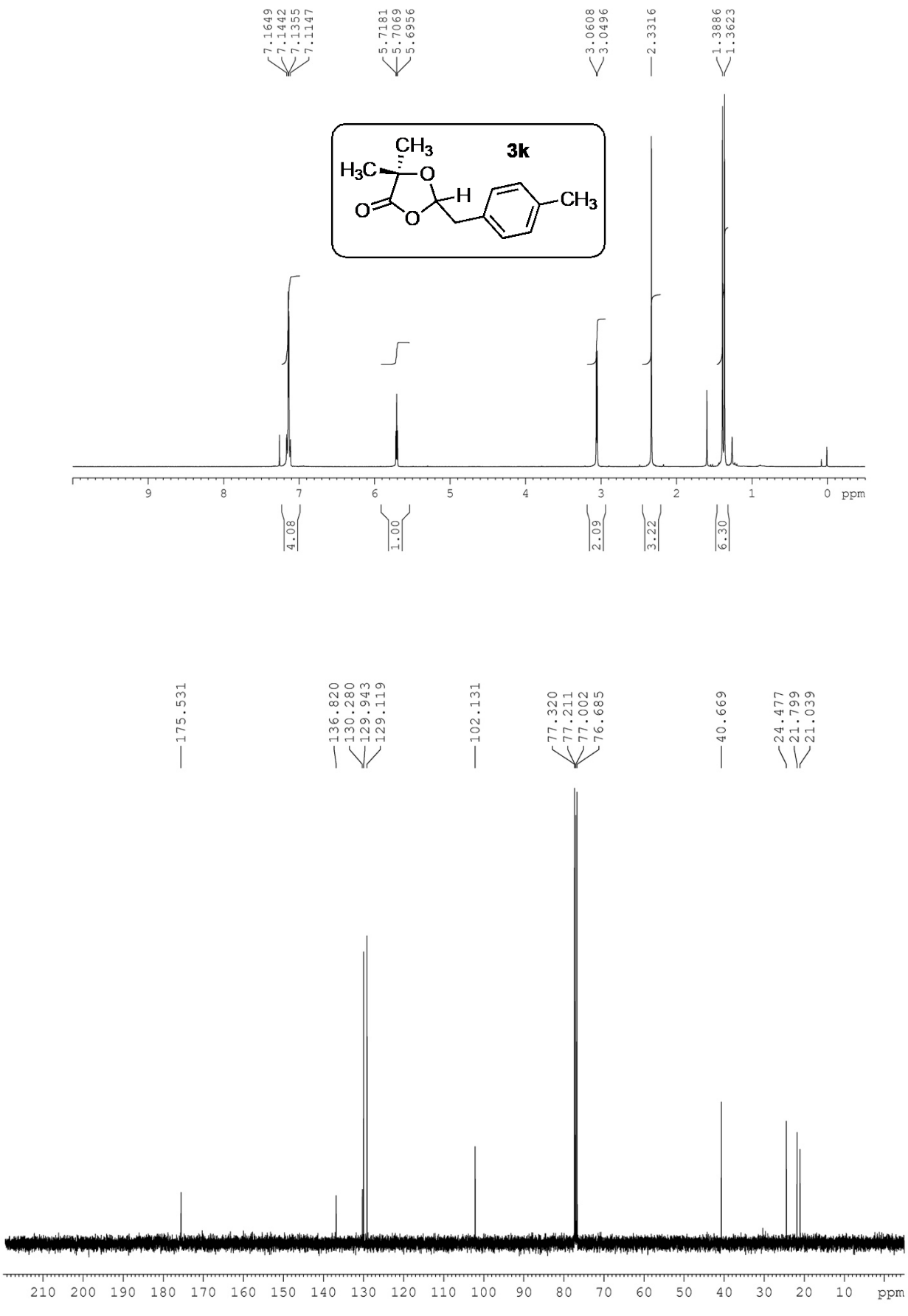


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3j**

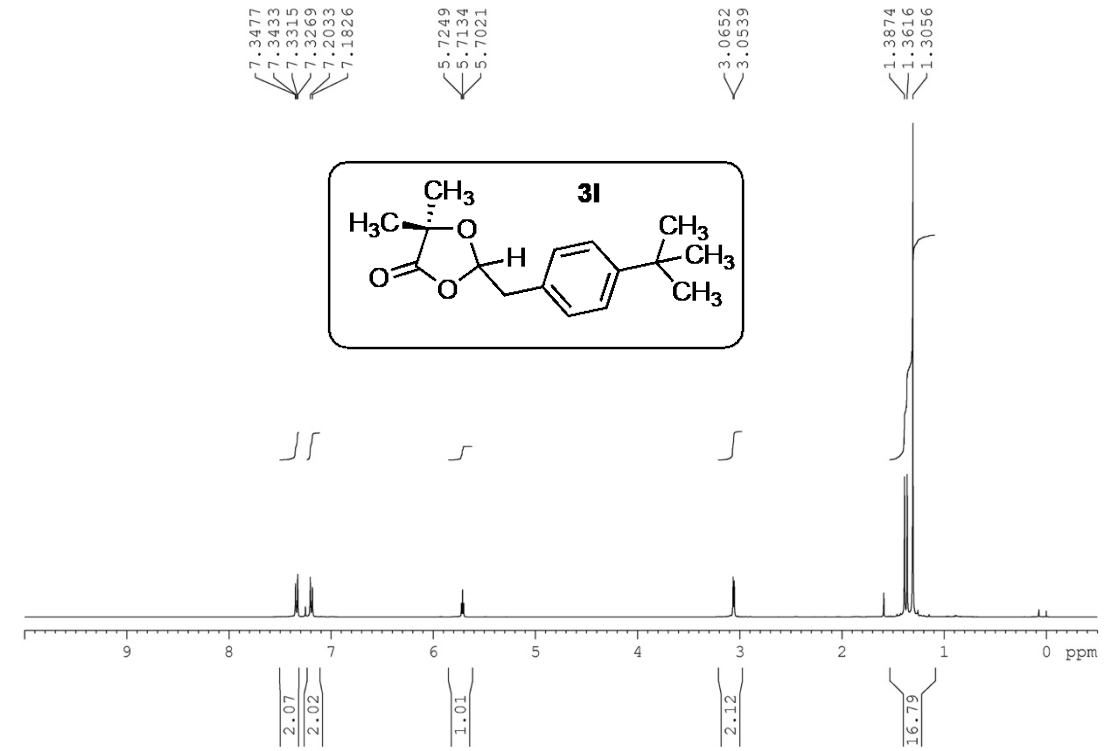


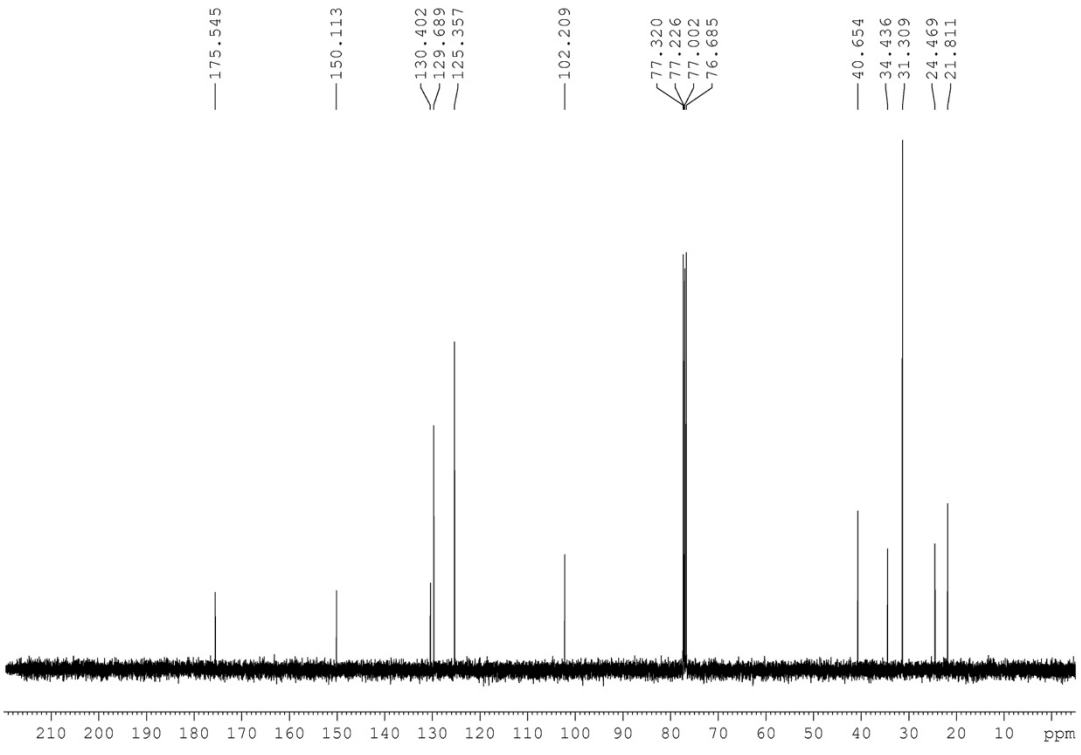


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3k**

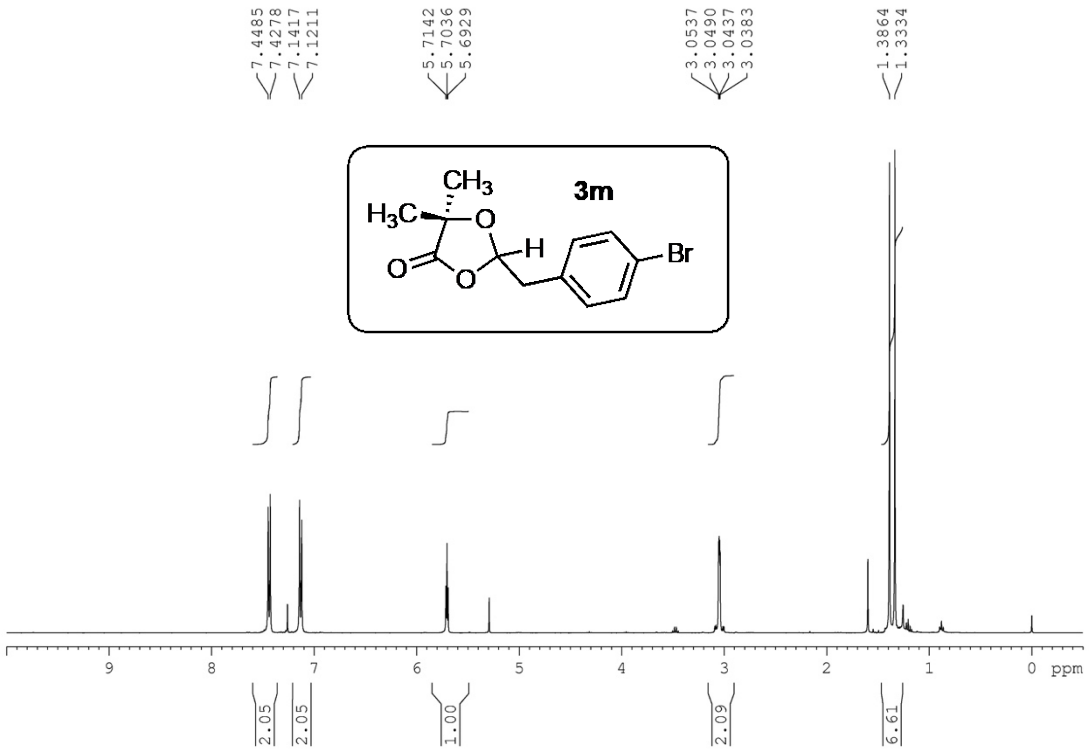


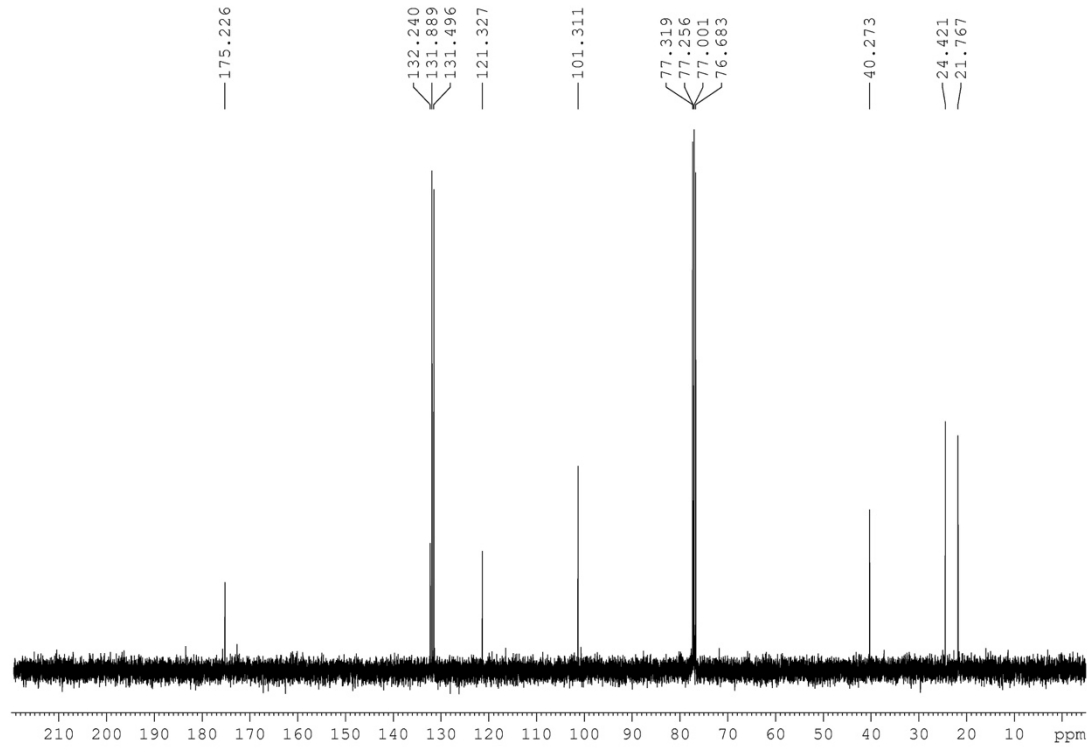
^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3l**



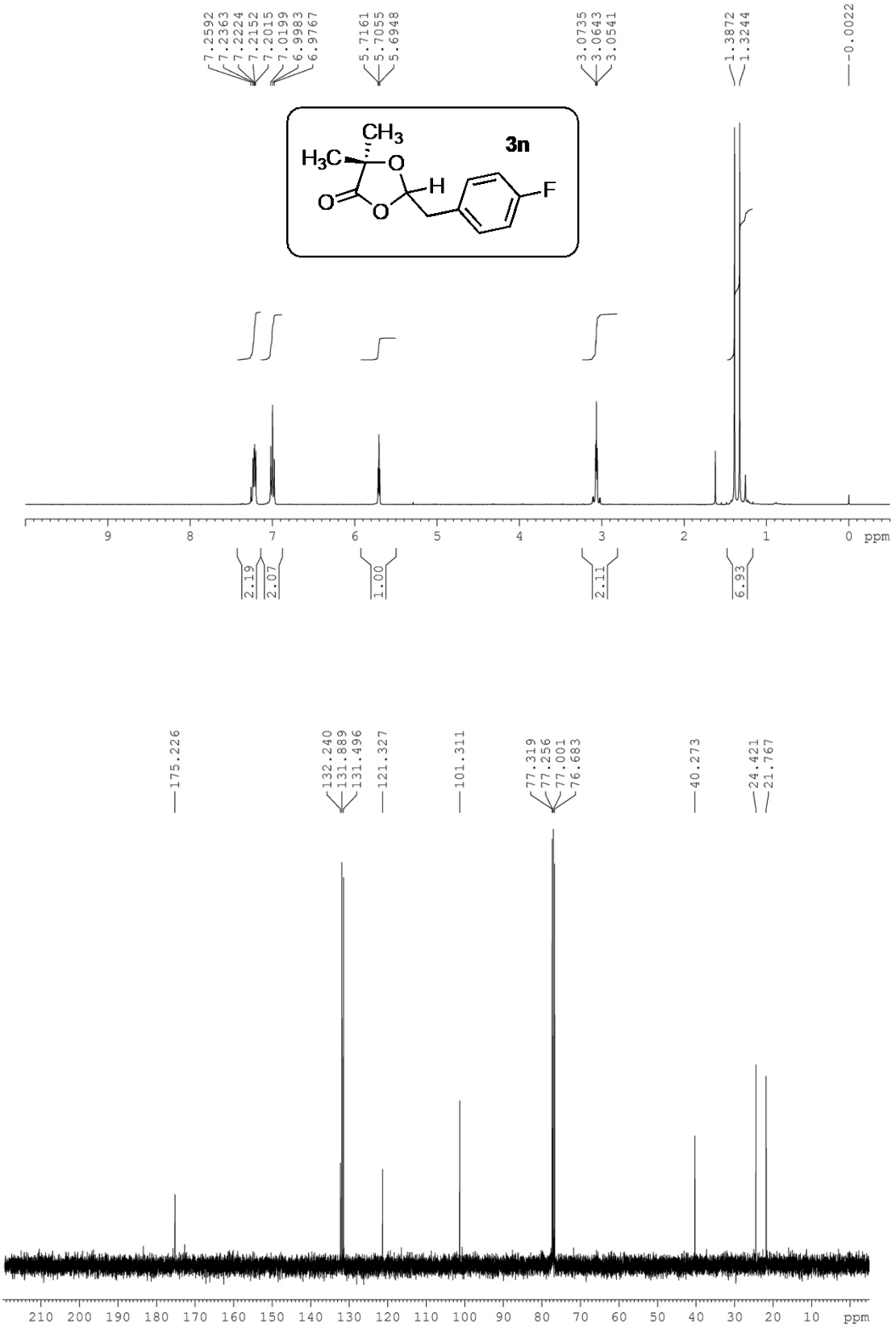


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3m**

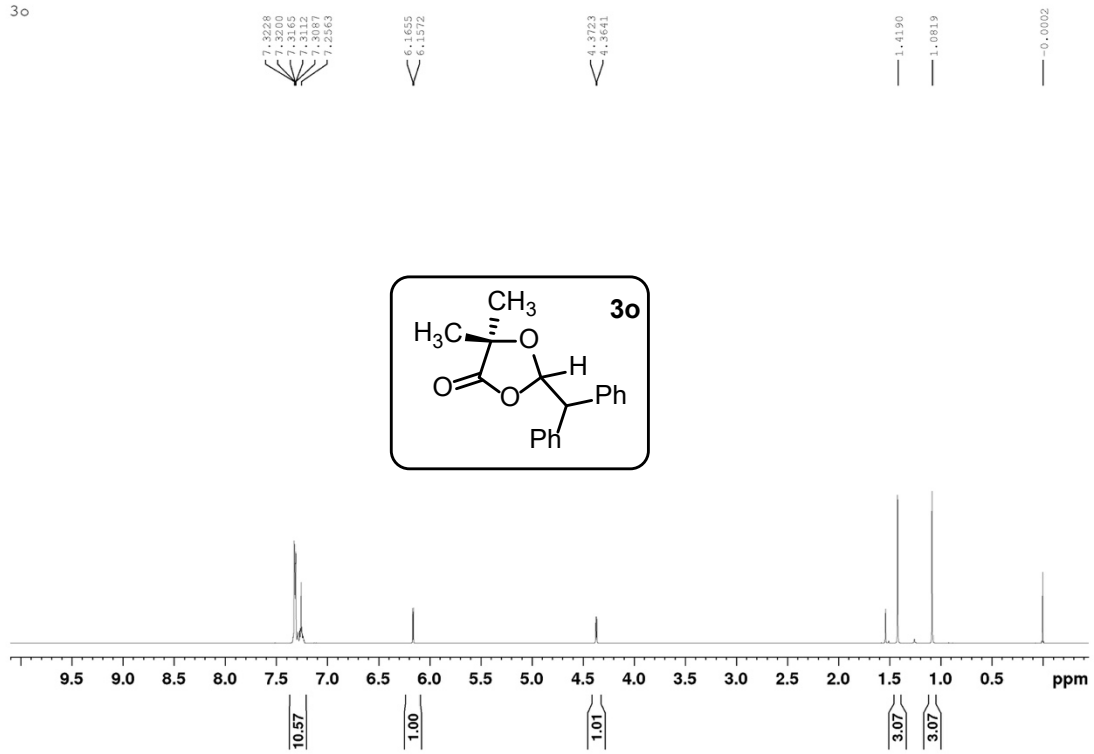


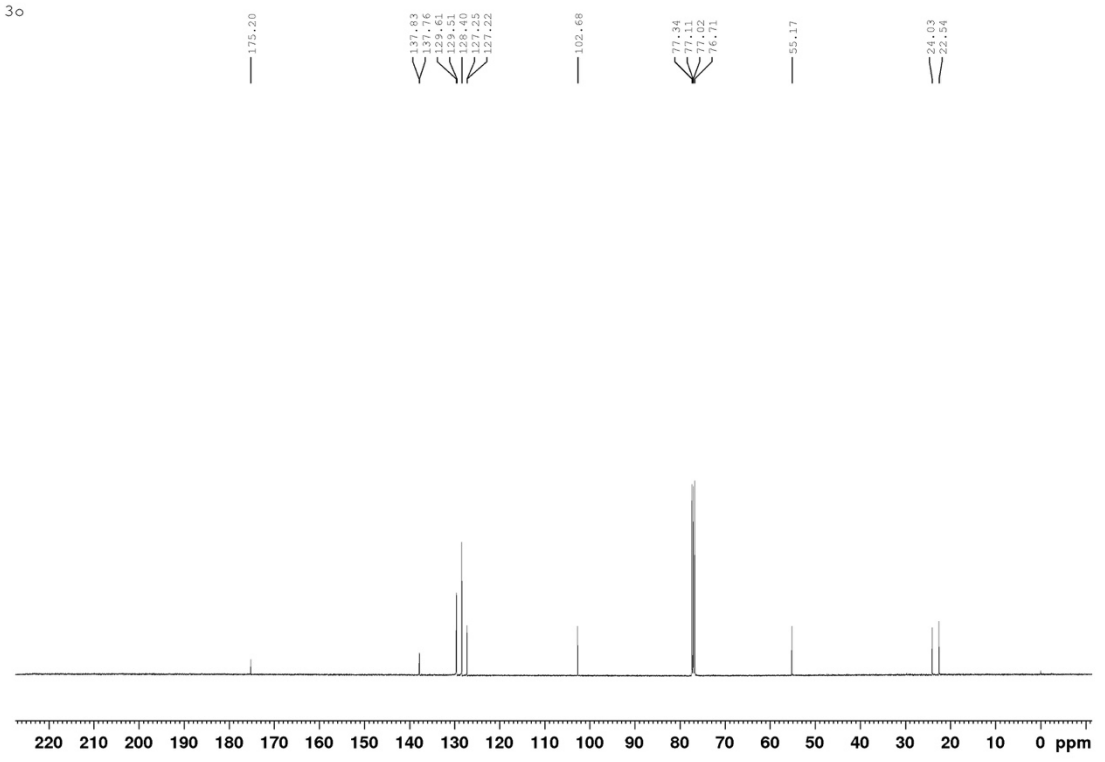


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3n**

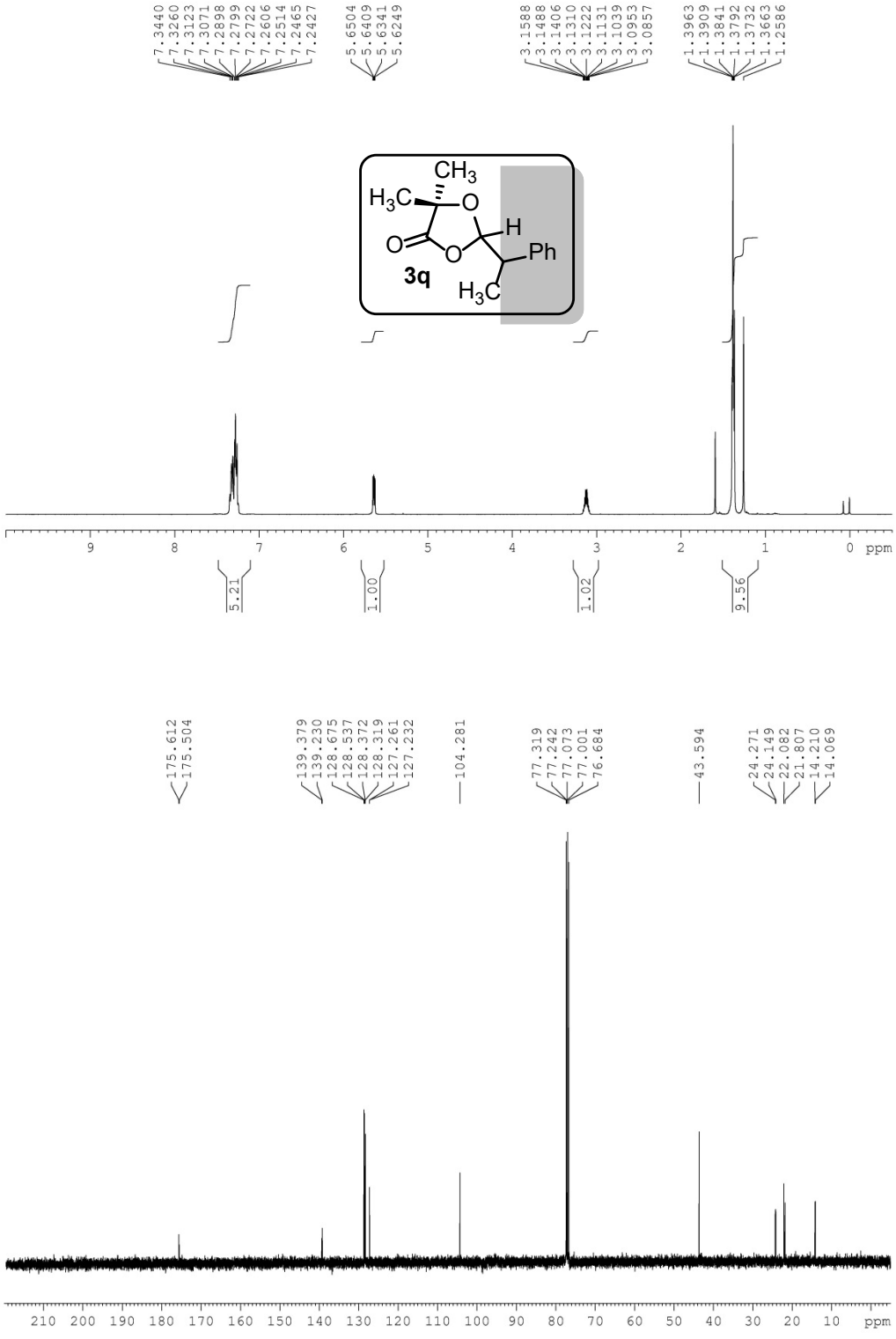


^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3o**

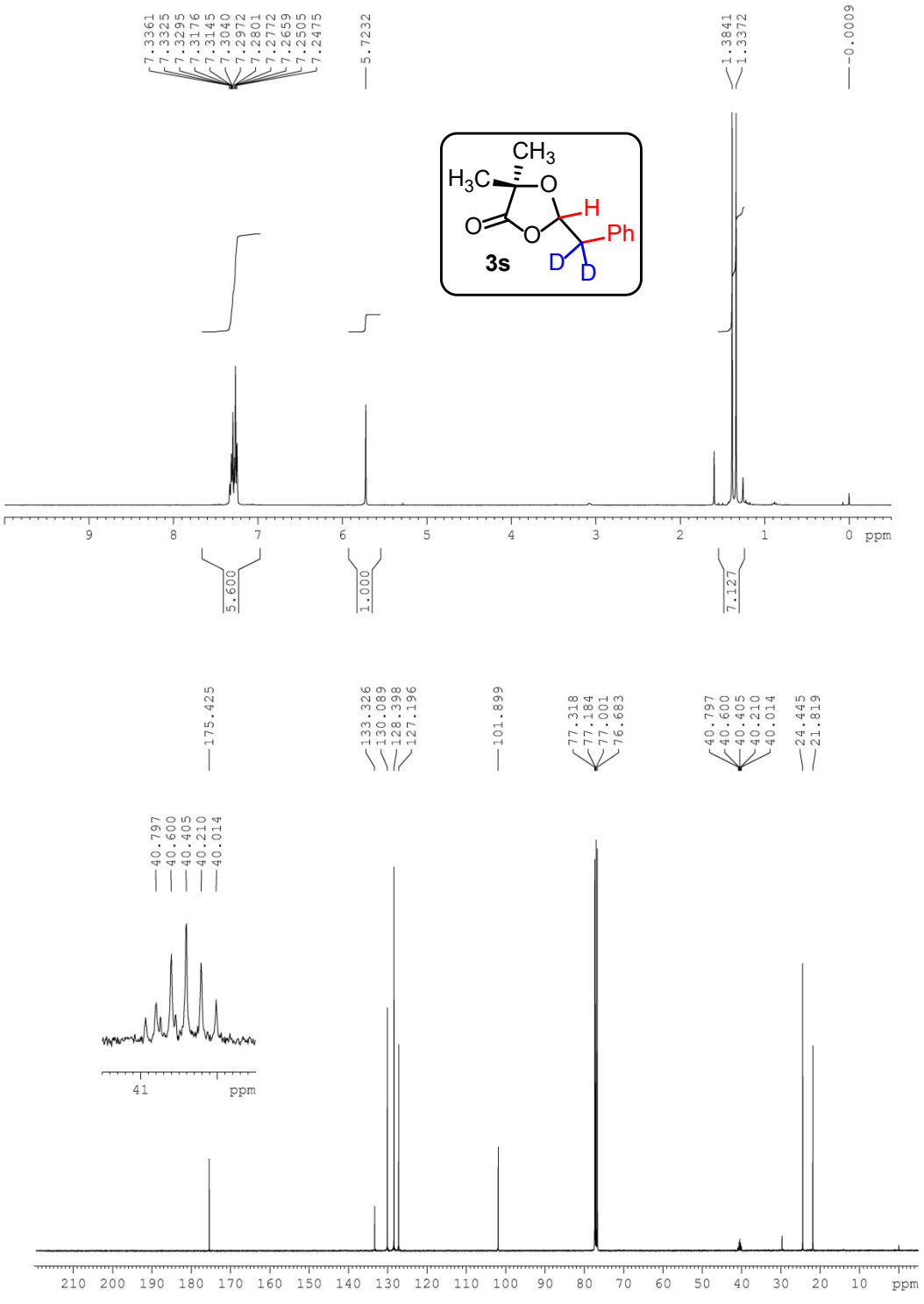




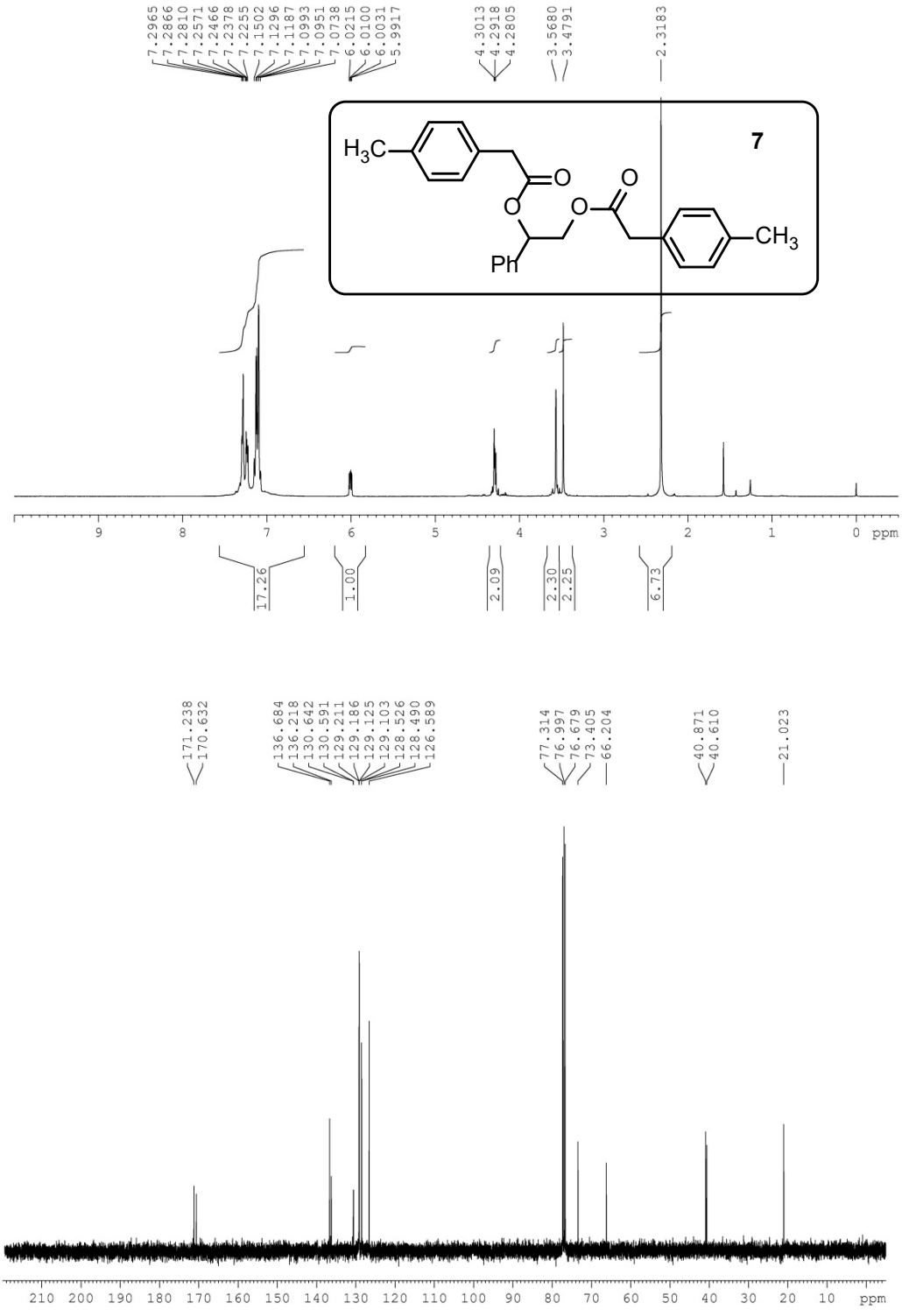
^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3q**



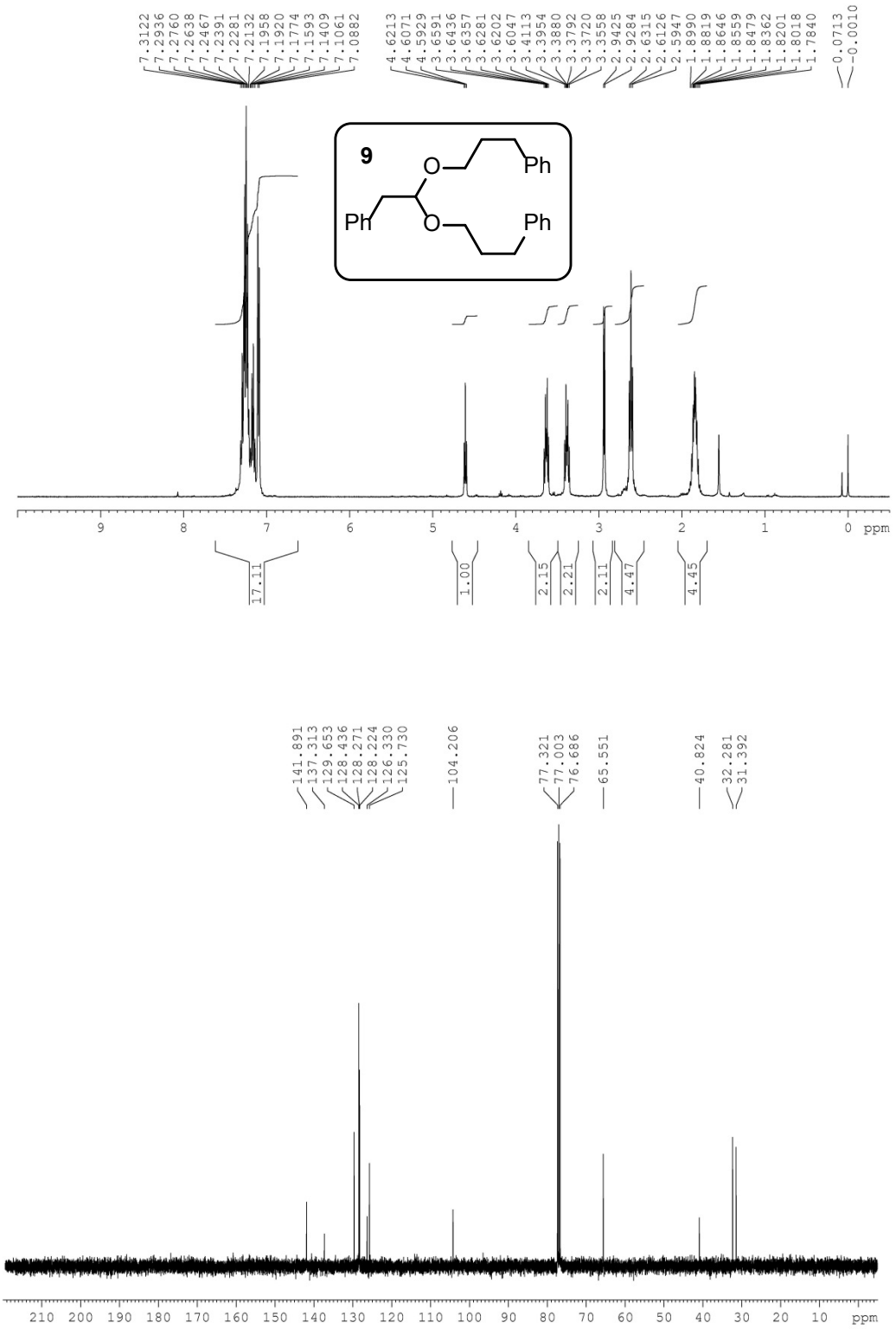
^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **3s**



^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **7**



^{1}H and ^{13}C NMR spectrum (400; 100 MHz, $CDCl_3$) of compound **9**



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