

Supporting Information

Oxime Derivatives as α -Electrophiles – from α -Tetralone Oximes to Tetracyclic Frameworks

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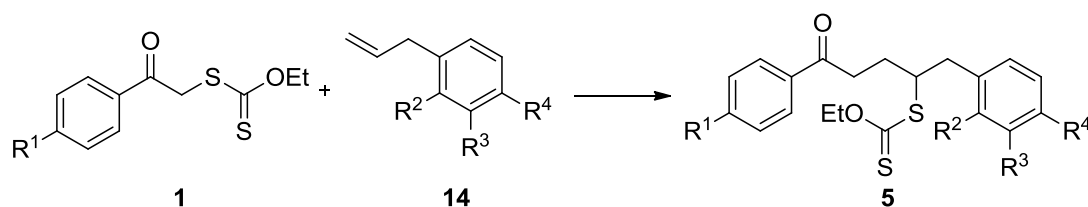
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General Methods.

Solvents and reagents were used as supplied by commercial sources unless stated otherwise. Petroleum ether refers to the fraction of light petroleum ether, bp = 40–60 °C. All reactions were carried out under dry, oxygen free N₂. Column chromatography was performed on silica gel (SDS, 60 Å, C.C. 40–63 µm). Thin layer chromatography was performed on aluminium plates pre-coated with silica gel (Merck, 60 F₂₅₄), which were visualized by the extinction of UV fluorescence ($\lambda_{\text{max}} = 254 \text{ nm}$), and/or by staining with vanillin in acidic ethanol, followed by heating. IR spectra were recorded from solutions in CCl₄. Absorption maxima (ν_{max}) are reported in wavenumbers (cm⁻¹). Magnetic resonance spectra were recorded at ambient temperature on a Bruker Advance DPX 400 instrument. ¹H-NMR spectra were recorded at 400.0 MHz, ¹³C-NMR spectra were recorded at 100.6 MHz. Chemical shift (δ_{H} , δ_{C}) are quoted in ppm and referenced to the residual solvent peak. Low resolution mass spectra (m/z) were recorded by chemical ionisation (CI) on a Hewlett-Packard HP 5989 instrument. High resolution mass spectra were recorded by electron impact ionisation at 70 eV on a JMS-GCmate II instrument. The quoted masses are accurate to $\pm 5 \text{ ppm}$.

General Procedure A: Radical Addition of Xanthates **1** to Olefins **14** to form Xanthates **5**.



The xanthate (**1**, 1 equiv.) was dissolved in ethyl acetate (1 ml/mmol) and the olefin (**14**, 2 equiv.) was added. The mixture was heated to reflux and DLP was added portionwise every 20 min in portions of 2.5 mol% until the starting material was consumed. The solvents were removed *in vacuo* and the crude mixture subjected to column chromatography (PE/EE).

O-ethyl-5-oxo-1,5-diphenylpentan-2-yl carbonodithioate (**5a**). ¹H-NMR (CDCl₃): 1.40 (t, $J = 7.1 \text{ Hz}$, 3 H, OCH₂CH₃), 1.94 (ddt, $J = 5.3, 9.3, 14.4 \text{ Hz}$, 1 H, 3-H_a), 2.23 (ddt, $J = 4.5, 9.1, 14.4 \text{ Hz}$, 1 H, 3-H_b), 2.92 (dd, $J = 8.6, 13.9 \text{ Hz}$, 1 H, 1'-H_a), 3.00–3.17 (m, 2 H, 1'-H_b, 4'-H_a), 3.22 (dd, $J = 5.3, 13.6 \text{ Hz}$, 1 H, 4'-H_b), 4.07 (m, 1 H, 2'-H), 4.61 (q, $J = 7.1 \text{ Hz}$, 2 H, OCH₂CH₃), 7.19–7.34 (m, 6 H, 4''-H, 1'''-H, 2'''-H, 3'''-H, 4'''-H, 5'''-H, 6'''-H), 7.39–7.42 (m, 2 H, 3''-H, 5''-H), 7.83–7.85 (m, 2 H, 2''-H, 6''-H) ppm. ¹³C-NMR (CDCl₃): 13.69 (OCH₂CH₃), 26.85 (C-3'), 35.94 (C-4'), 41.52 (C-1'), 51.80

(C-2'), 69.90 (OCH₂CH₃), 126.6 (C-4'''), 128.4, 128.8 (C-2''', C-3''', C-5''', C-6'''), 129.0 (C-4''), 129.2, 129.3 (C-2'', C-3'', C-5'', C-6'') 134.9 (C-1''), 138.2 (C-1'''), 197.7 (C-5'), 213.7 (C-1) ppm. **MS** (IC), *m/z* = 237 [M-SCSOEt]⁺, 359 [M+H]⁺, 376 [M+NH₄]⁺. **HRMS** (IE): 237.1288 [M-SCSOEt]⁺, measured; 237.1274[M-SCSOEt]⁺, calculated. **IR**: 3088, 30666, 3030, 2988, 2938, 2925, 1961, 1945, 1896, 1814, 1691, 1599, 1582, 1496, 1449, 1412, 1366, 1320, 1292, 1277, 1219, 1180, 1146, 1112, 1054.

O-ethyl-5-(4-Methoxyphenyl)-5-oxo-1-phenylpentan-2-yl carbonodithioate (**5b**). **¹H-NMR** (CDCl₃): 1.39 (t, *J* = 7.1 Hz, 3 H, OCH₂CH₃), 1.92 (ddt, *J* = 5.3, 9.6, 14.9 Hz, 1 H, 3'-H_a), 2.21 (ddt, *J* = 4.8, 8.6, 14.9 Hz, 1 H, 3'-H_b), 2.91 (dd, *J* = 8.3, 13.9 Hz, 1 H, 1'-H_a), 3.01 (ddd, *J* = 6.1, 9.3, 17.2 Hz, 1 H, 4'-H_a), 3.11 (ddd, *J* = 5.1, 9.6, 17.2 Hz, 1 H, 4'-H_b), 3.20 (dd, *J* = 6.1, 13.9 Hz, 1 H, 1'-H_b), 3.85 (s, 3 H, OCH₃), 4.05 (dddd, *J* = 4.0, 6.1, 8.3, 10.1 Hz, 1 H, 2'-H), 4.59 (dq, *J* = 7.1, 14.4 Hz, 1 H, OCH_aH_bCH₃), 4.64 (dq, *J* = 7.1, 14.4 Hz, 1 H, OCH_aH_bCH₃), 6.88–6.92 (m, 2 H, 3''-H, 5''-H), 7.20–7.25 (m, 1 H, Ph-H), 7.28–7.33 (m, 4 H, Ph-H), 7.87–7.90 (m, 2 H, 2''-H, 6''-H) ppm. **¹³C-NMR** (CDCl₃): 13.71 (OCH₂CH₃), 27.21 (C-3'), 35.64 (C-4'), 41.53 (C-1'), 51.95 (C-2'), 55.41 (OCH₃), 69.86 (OCH₂CH₃), 113.64 (C-3'', C-5''), 126.63 (C-Ph), 128.39 (2 x C-Ph), 129.30 (2 x C-Ph), 130.23 (C-2'', C-6''), 138.29 (C-Ph_q), 163.40 (C-1'''), 197.59 (C-5'), 213.87 (C-1) ppm. **HRMS** (IE): 267.1386 [M-SCSOEt]⁺, measured; 267.1385 [M-SCSOEt]⁺, calculated. **IR**: 3517, 3332, 3086, 3065, 2932, 2856, 2578, 2246, 2239, 2060, 1948, 1908, 1808, 1683, 1603, 1509, 1496, 1456, 1420, 1365, 1105.

1-(2-methoxyphenyl)-5-phenyl-5-oxopentan-2-yl O-ethyl carbonodithioate (**5c**). **¹H-NMR** (CDCl₃): 1.38 (t, *J* = 7.1 Hz, 3 H, OCH₂CH₃), 2.02 (ddt, *J* = 5.3, 9.6, 14.9 Hz, 3-H_a), 2.20 (ddt, *J* = 5.3, 10.4, 14.9 Hz, 1 H, 3-H_b), 3.00–3.13 (m, 3 H,), 3.20 (ddd, *J* = 5.3, 9.6, 17.4 Hz, 1 H,), 3.82 (s, 3 H, OCH₃), 5.3, 7.6, 14.9 Hz, 1 H, 2-H'), 4.57 (q, *J* = 7.1 Hz, OCH₂CH₃), 6.85 (d, *J* = 8.1 Hz, 1 H, 3'''-H), 6.90 (t, *J* = 7.6 Hz, 1 H, 5'''-H), 7.19–7.24 (m, 2 H, 4'''-H, 6'''-H), 7.42–7.46 (t, *J* = 7.6 Hz, 2 H, 3''-H, 5''-H), 7.51–7.55 (m, 1 H, 4''-H), 7.93 (d, *J* = 7.6 Hz, 2 H, 2''-H, 6''-H) ppm. **¹³C-NMR** (CDCl₃): 13.81 (OCH₂CH₃), 27.93 (C-3'), 35.08 (C-1'), 36.07 (C-2'), 51.02 (C-4'), 55.33 (OCH₃), 69.80 (OCH₂CH₃), 110.4 (C-3'''), 120.5 (C-5'''), 126.8 (C-1'''), 128.1 (C-2'', C-6'', C-4'''), 128.6 (C-3'', C-5''), 131.1 (C-6'''), 133.1 (C-4''), 136.9 (C-1''), 157.7 (C-2'''), 199.4 (C-5'), 214.2 (C-1) ppm. **MS** (IC), *m/z* = 267 [M-SCSOEt]⁺, 389 [M+H]⁺, 406 [M+NH₄]⁺. **HRMS** (IE): 388.1166 [M]⁺, measured; 388.1167 [M]⁺, calculated. **IR**: 3363, 3067, 3029, 2989, 2939, 2837, 2416, 2062, 1977, 1961, 1897, 1815, 1691, 1599, 1588, 1549, 1494, 1465, 1449, 1440, 1412, 1387, 1367, 1338, 1320, 1290, 1245, 1218, 1180, 1146, 1112, 5054.

1-(2,3-dimethoxyphenyl)-5-phenyl-5-oxopentan-2-yl O-ethyl carbonodithioate (**5d**). **¹H-NMR** (CDCl₃): 1.38 (t, *J* = 7.1 Hz, 3 H, OCH₂CH₃), 1.97 (ddt, *J* = 5.3, 9.1, 14.7 Hz, 1 H, 3'-H_a), 2.19 (dddd, *J* = 4.5, 6.1, 9.3, 14.1 Hz, 1 H, 3'-H_b), 3.00–3.08 (m, 3 H, 1'-H₂, 4'-H_a), 3.15 (ddd, *J* = 5.3, 9.3, 17.4 Hz, 1 H,

4'-H_b), 3.85 (s, 3 H, 2 OCH₃), 4.11 (m, 1 H, 2'-H), 4.78 (q, $J = 7.1$ Hz, 2 H, OCH₂CH₃), 6.71–6.80 (m, 1 H, 4''-H), 6.81 (dd, $J = 1.3, 8.1$ Hz, 1 H, 4'''-H), 6.88 (dd, $J = 1.3, 8.1$ Hz, 1 H, 6'''-H), 6.99 (t, $J = 8.1$ Hz, 1 H, 5-H'''), 7.57 (dt, $J = 2.1, 8.3$ Hz, 2' H, 3''-H, 5''-H), 7.77 (dt, $J = 2.1, 8.3$ Hz, 2' H, 2''-H, 6''-H) ppm. **¹³C-NMR** (CDCl₃): 13.71 (OCH₂CH₃), 27.62 (C-3'), 34.82 (C-1'), 35.91 (C-4'), 51.10 (C-2'), 55.63 (OCH₃), 60.65 (OCH₃), 69.83 (OCH₂CH₃), 111.0 (C-4'''), 122.5 (C-6'''), 123.8 (C-5'''), 128.1 (C-4''), 129.5 (C-2'', C-6''), 131.8 (C-3'', C-5''), 132.0 (C-1'''), 135.4 (C-1''), 147.4 (C-2'''), 152.6 (C-3'''), 198.2 (C-5'), 213.8 (C-1) ppm. **MS** (IC), $m/z = 297$ [M-SCSOEt]⁺, 419 [M+H]⁺, 436 [M+NH₄]⁺. **HRMS** (IE): 418.1270 [M]⁺, measured; 418.1273 [M]⁺, calculated. **IR**: 3364, 3066, 2990, 2958, 2936, 2836, 1901, 1815, 1691, 1599, 1585, 1482, 1449, 1366, 1269, 1216, 1179, 1146, 1112, 1085, 1053, 1011.

1-(2,3-dimethoxyphenyl)-5-(4-bromophenyl)-5-oxopentan-2-yl O-ethyl carbonodithioate (**5e**). **¹H-NMR**: 1.38 (t, $J = 7.1$ Hz, 3 H, OCH₂CH₃), 1.98 (ddt, $J = 5.3, 9.1, 14.4$ Hz, 1 H, 3'-H_a), 2.19 (m, 1 H, 3'-H_b), 3.00–3.08 (m, 3 H, 1'-H₂, 4'-H_b), 3.14 (ddd, $J = 5.3, 9.3, 17.2$ Hz, 1 H, 4'-H_b), 3.85 (s, 6 H, 2 OCH₃), 4.11 (m, 1 H, 2'-H), 4.58 (q, $J = 7.1$ Hz, 2 H, OCH₂CH₃), 6.81 (d, $J = 7.8$ Hz, 1 H, 4'''-H), 6.88 (d, $J = 7.8$ Hz, 1 H, 6'''-H), 6.99 (t, $J = 7.8$ Hz, 1 H, 5'''-H), 7.57 (d, $J = 8.6$ Hz, 2 H, 3''-H, 5''-H), 7.77 (d, $J = 8.6$ Hz, 2 H, 2''-H, 6''-H) ppm. **¹³C-NMR** (CDCl₃): 13.72 (OCH₂CH₃), 27.57 (C-3'), 34.81 (C-1'), 35.91 (C-4'), 51.08 (C-2'), 55.61 (OCH₃), 60.67 (OCH₃), 69.85 (OCH₂CH₃), 110.9 (C-4'''), 122.5 (C-6'''), 123.8 (C-5'''), 128.1 (C-4''), 129.5 (C-2'', C-6''), 131.8 (C-3'', C-5''), 131.9 (C-1'''), 135.4 (C-1''), 147.4 (C-2'''), 152.6 (C-3'''), 198.2 (C-5'), 213.8 (C-1) ppm. **MS** (IC), $m/z = 497, 499$ [M+H]⁺; 514, 516 [M+NH₄]⁺. **HRMS** (IE): 496.0380 [M]⁺, measured; 496.0377 [M]⁺, calculated. **IR**: 3042, 2961, 2938, 2872, 2838, 2260, 2247, 2250, 1732, 1686, 1586, 1569, 1480, 1442, 1432, 1397, 1367, 1269, 1219, 1177, 1148, 1112, 1050, 1008.

O-ethyl-5-(phenyl)-5-oxo-1-(4-fluorophenylpentan)-2-yl carbonodithioate (**5g**). **¹H-NMR** (CDCl₃): 1.38 (t, $J = 7.1$ Hz, 3 H, OCH₂CH₃), 1.91 (m, 1 H, 3'-H_a), 2.17–2.26 (m, 1 H, 3'-H_b), 2.89 (dd, $J = 8.3, 13.9$ Hz, 1 H, 1'-H_a), 3.07 (ddd, $J = 6.3, 8.8, 17.7$ Hz, 1 H, 4'-H_a), 3.12–3.20 (m, 2 H, 1'-H_b, 4'-H_b), 4.00 (m, 1 H, 2'-H), 4.62 (q, $J = 7.1$ Hz, 2 H, OCH₂CH₃), 6.99 (t, $J = 8.8$ Hz, 2 H, 3'''-H, 5'''-H), 7.31 (m, 2 H, 2'''-H, 6'''-H), 7.44 (m, 2 H, 3''-H, 5''-H), 7.55 (m, 1 H, 4''-H), 7.90–7.92 (m, 2 H, 2''-H, 6''-H) ppm. **¹³C-NMR** (CDCl₃): 13.71 (OCH₂CH₃), 26.95 (C-3), 35.93 (C-2), 40.76 (C-1'), 52.00 (C-4), 69.96 (OCH₂CH₃), 115.2 (d, $J_{C-F} = 21.2$ Hz, C-3''', C-5'''), 127.9 (C-2'', C-6''), 128.5 (C-3'', C5''), 130.8 (d, $J_{C-F} = 8.1$ Hz, C-2''', C-6'''), 133.1 (C-1'''), 133.1 (C-4''), 133.9 (d, $J_{C-F} = 3.3$ Hz, C-1'''), 136.6 (C-1''), 161.7 (d, $J_{C-F} = 244.8$ Hz, C-4'''), 199.0 (C-5), 213.8 (C-1) ppm. **MS** (IC), $m/z = 377$ [M+H]⁺, 394 [M+NH₄]⁺. **HRMS** (IE): 255.1145 [M-SCSOEt]⁺, measured; 255.1180 [M-SCSOEt]⁺, calculated. **IR**: 2988, 2926, 1691, 1599, 1582, 1510, 1449, 1366, 1320, 1289, 1274, 1224, 1181, 1158, 1147, 1113, 1053.

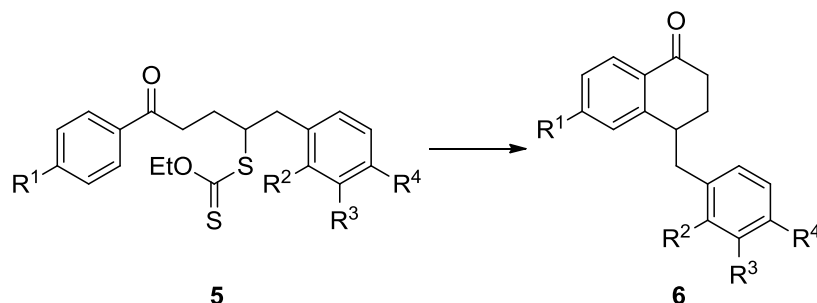
O-ethyl-5-(4-fluorophenyl)-5-oxo-1-phenylpentan-2-yl carbonodithioate (**5k**). **¹H-NMR** (CDCl₃): 1.40 (t, *J* = 7.3 Hz, 3 H, OCH₂CH₃), 1.94 (ddt, *J* = 5.3, 9.8, 14.9 Hz, 1 H, 3'-H_a), 2.23 (dddd, *J* = 4.3, 6.3, 9.3, 14.9 Hz, 1 H, 3'-H_b), 2.91 (dd, *J* = 8.6, 13.9 Hz, 1 H, 1'-H_a), 3.03 (ddd, *J* = 6.3, 9.1, 17.4 Hz, 1 H, 4'-H_a), 3.13 (ddd, *J* = 5.3, 9.3, 17.4 Hz, 1 H, 4'-H_b), 3.21 (dd, *J* = 5.9, 13.9 Hz, 1 H, 1'-H_b), 4.06 (dddd, *J* = 4.3, 5.9, 8.6, 9.8 Hz, 1 H, 2'-H), 4.60 (q, *J* = 7.3 Hz, 2 H, OCH₂CH₃), 7.10 (t, *J* = 8.6 Hz, 2 H, 3''-H, 5''-H), 7.22–7.27 (m, 1 H, Ph-H), 7.28–7.33 (m, 4 H, Ph-H), 7.93 (dd, *J* = 5.3, 8.6 Hz, 2 H, 2''-H, 6''-H) ppm. **¹³C-NMR** (CDCl₃): 13.72 (OCH₂CH₃), 27.03 (C-3'), 35.94 (C-4'), 41.57 (C-1'), 51.88 (C-2'), 69.91 (OCH₂CH₃), 115.6 (d, *J*_{C-F} = 21.6 Hz, C-3'', C-5''), 126.7 (C-Ph), 128.4 (2 C-Ph), 129.3 (2 C-Ph), 130.6 (d, *J*_{C-F} = 9.5 Hz, C-2'', C-6''), 133.1 (d, *J*_{C-F} = 2.9 Hz, 1''-H), 138.2 (C_q-Ph), 165.7 (d, *J*_{C-F} = 154.7 Hz C-4''), 197.4 (C-5'), 213.8 (C-1) ppm. **MS** (IC), *m/z* = 391 [M+H]⁺, 408 [M+NH₄]⁺. **HRMS** (IE): 270.1420 [M-SCSOEt]⁺, measured; 270.1420 [M-SCSOEt]⁺, calculated. **IR**: 3086, 3066, 3029, 2986, 2939, 2860, 2255, 1685, 1599, 1507, 1497, 1455, 1410, 1368, 1291, 1220, 1156, 1112, 1051.

O-ethyl-5-(4-chlorophenyl)-5-oxo-1-phenylpentan-2-yl carbonodithioate (**5l**). **¹H-NMR** (CDCl₃): 1.40 (t, *J* = 7.2 Hz, 3 H, OCH₂CH₃), 1.95 (ddt, *J* = 5.1, 9.6, 14.7 Hz, 1 H, 3'-H_a), 2.24 (ddt, *J* = 4.3, 6.1, 14.7 Hz, 1 H, 3'-H_b), 2.92 (dd, *J* = 8.6, 13.6 Hz, 1 H, 1'-H_a), 3.07 (ddd, *J* = 6.3, 9.1, 17.2 Hz, 1 H, 4'-H_a), 3.17 (ddd, *J* = 5.3, 9.3, 17.7 Hz, 1 H, 4'-H_b), 3.22 (dd, *J* = 6.1, 13.6 Hz, 1 H, 1'-H_b), 4.07 (dddd, *J* = 4.0, 6.0, 8.3, 10.1 Hz, 1 H, 2'-H), 4.60 (q, *J* = 7.2 Hz, 2 H, OCH₂CH₃), 7.22–7.27 (m, 1 H, Ph-H), 7.29–7.34 (m, 4 H, Ph-H), 7.42–7.46 (m, 2 H, 3''-H, 5''-H), 7.90–7.92 (m, 2 H, 2''-H, 6''-H) ppm. **¹³C-NMR**: 13.71 (OCH₂CH₃), 26.97 (C-3'), 35.98 (C-4'), 41.53 (C-1'), 51.87 (C-2'), 69.88 (OCH₂CH₃), 126.6 (C-4'''), 127.9 (C-4''), 128.4, 128.5 (C-2''', C-3''', C-5''', C-6'''), 129.3 (C-2'', C-6''), 133.0 (C-3'', C-5''), 136.6 (C-1'), 138.2 (C-1'''), 199.0 (C-5'), 213.8 (C-1) ppm. **MS** (IC), *m/z* = 393 [M+H]⁺. **HRMS** (IE): 272.0943 [M-SCSOEt]⁺, measured; 272.0968 [M-SCSOEt]⁺, calculated. **IR**: 3087, 3065, 3030, 2985, 2927, 2855, 2264, 1686, 1590, 1571, 1489, 1455, 1444, 1401, 1367, 1265, 1220, 1177, 1147, 1112, 1094, 1051, 1013.

O-ethyl-5-(4-bromophenyl)-5-oxo-1-phenylpentan-2-yl carbonodithioate (**5m**). **¹H-NMR** (CDCl₃): 1.45 (t, *J* = 6.8 Hz, 3 H, OCH₂CH₃), 1.98 (ddt, *J* = 5.3, 9.3, 14.7 Hz, 1 H, 3'-H_a), 2.23–2.31 (m, 1 H, 3'-H_b), 2.95 (dd, *J* = 8.6, 13.9 Hz, 1 H, 1'-H_a), 3.07 (ddd, *J* = 6.6, 9.3, 17.4 Hz, 1 H, 4'-H_a), 3.6 (ddd, *J* = 4.3, 9.1, 17.4 Hz, 1 H, 4'-H_b), 3.26 (dd, *J* = 6.1, 13.9 Hz, 1 H, 1'-H_b), 4.06–4.13 (m, 1 H, 2'-H), 4.65 (dq, *J* = 6.8, 14.4 Hz, 1 H, OCH₂CH₃), 4.66 (dq, *J* = 6.8, 14.4 Hz, 1 H, OCH₂CH₃), 7.22–7.34 (m, 5 H, Ph-H), 7.57 (d, *J* = 8.6 Hz, 2 H, 3''-H, 5''-H), 7.76 (d, *J* = 8.6 Hz, 2 H, 2''-H, 6''-H) ppm. **¹³C-NMR** (CDCl₃): 13.72 (OCH₂CH₃), 26.87 (C-3'), 35.96 (C-4'), 41.55 (C-1'), 51.82 (C-2'), 69.93 (OCH₂CH₃), 126.7 (C-4'''), 128.2 (C-4''), 128.4, 129.3 (C-2''', C-3''', C-5''', C-6'''), 129.5 (C-2'', C-6''), 131.8 (C-3'', C-5''), 135.3 (C-1'), 138.2 (C-1'''), 197.9 (C-5'), 213.8 (C-1) ppm. **HRMS** (IE): 436.0163

$[M]^+$, measured; 436.0166 $[M]^+$, calculated. **IR**: 3087, 3065, 3030, 2986, 2927, 2856, 2260, 2250, 1686, 1586, 1569, 1495, 1485, 1454, 1444, 1397, 1365, 1312, 1291, 1274.

General Procedure B: Intramolecular Radical Cyclisation of Xanthates 5 to Tetralones 6.



The xanthate **5** was dissolved in ethyl acetate (12 mL/mmol), heated to reflux and DLP was added portionwise every 60 min in portions of 20 % until the starting material was consumed. The solvents were removed *i. vak.* and the crude mixture subjected to column chromatography (PE/EE).

4-benzyl-3,4-dihydronaphthalen-1(2H)-one (**6a**). **¹H-NMR** ($CDCl_3$): 1.95 (ddd, $J = 4.8, 9.6, 13.6$ Hz, 1 H, 3- H_a), 2.15 (tt, $J = 4.5, 12.1$ Hz, 1 H, 3- H_b), 2.58 (dt, $J = 17.7, 4.8$ Hz, 1 H, 2- H_a), 2.79–2.89 (m, 2 H, 2- H_b , 1'- H_a), 3.12 (dd, $J = 6.1, 13.4$ Hz, 1 H, 1'- H_b), 3.23 (m, 1 H, 4-H), 7.19 (m, 3 H, 5-H, 3''-H, 5''-H), 7.25–7.27 (m, 1 H, 4''-H), 7.31–7.36 (m, 3 H, 7-H, 2''-H, 6''-H), 7.47 (dt, $J = 1.0, 7.6$ Hz, 1 H, 6-H), 8.06 (d, $J = 7.6$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** ($CDCl_3$): 25.97 (C-3), 34.66 (C-2), 39.92 (C-4), 41.19 (C-1'), 126.4 (C-4''), 126.9 (C-7), 127.3 (C-8), 128.4 (C-5), 128.5 (C-2'', C-6''), 129.0 (C-3'', C-5''), 131.9 (C-8a), 133.5 (C-6), 139.7 (C-1''), 147.3 (C-4a), 198.2 (C-1) ppm. **HRMS** (IE): 236.1200 $[M]^+$, measured; 236. 1201 $[M]^+$, calculated. **IR**: 3362, 3066, 3029, 2930, 2870, 1944, 1863, 1689, 1599, 1495, 1454, 1416, 1327, 1285, 1235, 1193, 1158, 1113, 1030.

4-benzyl-6-methoxy-3,4-dihydronaphthalen-1(2H)-one (**6b**). **¹H-NMR** ($CDCl_3$): 1.95 (ddd, $J = 4.8, 9.3, 13.6$ Hz, 1 H, 3- H_a), 2.16 (m, 1 H, 3- H_b), 2.53 (dt, $J = 4.8, 17.9$ Hz, 1 H, 2- H_a), 2.78 (m, 1 H, 2- H_b), 2.88 (dd, $J = 9.1, 13.5$ Hz, 1 H, 1'- H_a), 3.07 (dd, $J = 6.3, 13.5$ Hz, 1 H, 1'- H_b), 3.14–3.20 (m, 1 H, 4-H), 3.75 (s, 3 H, OMe), 6.52 (d, $J = 2.5$ Hz, 1 H, 5-H), 6.83 (dd, $J = 2.5, 8.7$ Hz, 1 H, 7-H), 7.15–7.17 (m, 2 H, 2''-H, 6''-H), 7.22–7.26 (m, 1 H, 4''-H), 7.29–7.33 (m, 2 H, 3''-H, 5''-H), 8.03 (d, $J = 8.7$ Hz, 1 H, 8-H). **¹³C-NMR** ($CDCl_3$): 26.44 (C-3), 34.39 (C-2), 40.45 (C-4), 41.15 (C-1'), 55.32 (OMe), 112.4 (C-5), 113.3 (C-7), 125.5 (8a-C), 126.4 (C-4''), 128.5, 129.1 (C-2'', C-3'', C-5'', C-6''), 129.8 (C-8), 139.7 (Ph-1''), 149.8 (4a-C), 163.4 (C-6), 196.9 (C-1) ppm. **HRMS** (IE): 266.1311 $[M]^+$, measured; 266.1307 $[M]^+$, calculated. **IR**: 3087, 3066, 3029, 2942, 2869, 2842, 2269, 2250, 1670, 1595, 1572, 1493, 1464, 1455, 1415, 1358, 1329, 1264, 1192, 1122, 1111, 1042, 1023.

4-(2-methoxybenzyl)-3,4-dihydronaphthalen-1(2H)-one (**6c**). **¹H-NMR** (CDCl₃): 1.93 (ddd, $J = 4.5, 9.4, 13.6$ Hz, 1 H, 3-H_a), 2.12 (tt, $J = 4.5, 13.4$ Hz, 1 H, 3-H_b), 2.57 (dt, $J = 4.5, 17.7$ Hz, 1 H,), 2.87–2.98 (m, 2 H,), 3.10 (dd, $J = 5.6, 13.1$ Hz, 1 H,), 3.29 (dq, $J = 4.5, 9.4$ Hz, 1 H,), 3.82 (s, 3 H, OCH₃), 6.89 (d, $J = 8.3$ Hz, 1 H, 3''-H), 6.91 (dt, $J = 1.0, 8.3$ Hz, 1 H, 5''-H), 6.08 (dd, $J = 1.5, 7.3$ Hz, 1 H, 6''-H), 7.22–7.26 (m, 2 H, 5-H, 4''-H), 7.32 (dt, $J = 1.0, 7.5$ Hz, 1 H, 7-H), 7.47 (dt, $J = 1.5, 7.3$ Hz, 1 H, 6-H), 8.05 (dd, $J = 1.3, 7.8$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 25.96 (C-3), 34.68 (C-2), 35.64 (C-1'), 38.35 (C-4), 55.20 (OCH₃), 110.4 (C-3''), 120.4 (C-5''), 126.6 (C-7), 127.1 (C-8), 127.7 (C-4''), 128.2 (C-1''), 128.6 (C-5), 130.8 (C-6''), 131.9 (C-8a), 133.3 (C-6), 148.1 (C-4a), 157.7 (C-2''), 198.6 (C-1) ppm. **MS** (IC), $m/z = 267$ [M+H]⁺, 284 [M+NH₄]⁺. **HRMS** (IE): 266.1309 [M]⁺, measured; 266.1307 [M]⁺, calculated. **IR**: 3070, 3025, 3003, 2928, 2856, 2837, 1688, 1600, 1588, 1555, 1548, 1494, 1466, 1455, 1439, 1416, 1326, 1287, 1244, 1194, 1177, 1159, 1150, 1119, 1106, 1050, 1031.

4-(2,3-dimethoxybenzyl)-3,4-dihydronaphthalen-1(2H)-one (**6d**). **¹H-NMR** (CDCl₃): 1.93 (ddd, $J = 4.3, 9.1, 13.1$ Hz, 1 H, 3-H_a), 2.11 (tt, $J = 4.8, 12.9$ Hz, 1 H, 3-H_b), 2.57 (dt, $J = 4.7, 17.9$ Hz, 1 H, 2-H_a), 2.89–3.01 (m, 2 H, 2-H_b, 1-H_a), 3.06 (dd, $J = 5.6, 13.4$ Hz, 1 H, 1-H_b), 3.28 (m, 1 H, 4-H), 3.81 (s, 3 H, OCH₃), 3.88 (s, 3 H, OCH₃), 6.75 (d, $J = 7.7$ Hz, 1 H, 4''-H), 6.83 (d, $J = 7.7$ Hz, 1 H, 6''-H), 7.81 (t, $J = 7.7$ Hz, 1 H, 5''-H), 7.48 (d, $J = 7.5$ Hz, 1 H, 5-H), 7.32 (t, $J = 7.5$ Hz, 1 H, 7-H), 7.28 (t, $J = 7.5$ Hz, 1 H, 6-H), 8.05 (d, $J = 7.5$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 25.74 (C-3), 34.67 (C-1'), 35.37 (C-2), 39.11 (C-4), 55.65 (OCH₃), 60.51 (OCH₃), 110.7 (C-4''), 122.4 (C-6''), 123.8 (C-5''), 126.7 (C-7), 127.2 (C-8), 128.5 (C-5), 131.8 (C-8a), 133.5 (C-6), 133.6 (C-1''), 147.5 (C-4a), 147.9 (C-2''), 152.8 (C-3''), 198.6 (C-1) ppm. **MS** (IC), $m/z = 297$ [M+H]⁺, 314 [M+NH₄]⁺. **HRMS** (IE): 296.1409 [M]⁺, measured; 296.1412 [M]⁺, calculated. **IR**: 3534, 3359, 3068, 2932, 2856, 2013, 1970, 1902, 1709, 1688, 1599, 1585, 1481, 1454, 1289, 1275, 1225, 1172, 1085, 1011.

4-(2,3-dimethoxybenzyl)-6-bromo-3,4-dihydronaphthalen-1(2H)-one (**6e**). **¹H-NMR** (CDCl₃): 1.91 (ddd, $J = 4.8, 9.6, 13.9$ Hz, 1 H, 3-H_a), 2.08 (m, 1 H, 3-H_b), 2.55 (dt, $J = 4.5, 17.9$ Hz, 1 H, 2-H_a), 2.86–2.94 (m, 2 H, 2-H_b, 1'-H_a), 3.03 (dd, $J = 5.3, 8.1$ Hz, 1 H, 1'-H_b), 3.20–3.26 (m, 1 H, 4-H), 3.82 (s, 3 H, OCH₃), 3.89 (s, 3 H, OCH₃), 6.73 (d_{br}, $J = 8.1$ Hz, 1 H, 4''-H), 6.85 (d_{br}, $J = 8.1$ Hz, 1 H, 6''-H), 7.02 (t_{br}, $J = 8.1$ Hz, 1 H, 5''-H), 7.42 (s_{br}, 1 H, 5-H), 7.46 (dd, $J = 1.5, 8.3$ Hz, 1 H, 7-H), 7.90 (d, $J = 8.3$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 25.58 (C-3), 34.51 (C-1'), 35.24 (C-2), 39.02 (C-4), 55.69 (OCH₃), 60.57 (OCH₃), 110.9 (C-4''), 122.4 (C-6''), 123.9 (C-5''), 128.6 (C-8a), 129.0 (C-7), 130.2 (C-8), 130.6 (C-6), 131.5 (C-5), 133.0 (C-1''), 147.5 (C-2''), 149.6 (C-4a), 152.8 (C-3''), 197.6 (C-1) ppm. **HRMS** (IE): 374.0525 [M]⁺, measured; 374.0518 [M]⁺, calculated. **IR**: 3533, 2929, 2856, 1710, 1691, 1586, 1482, 1431, 1355, 1275, 1225, 1084, 1011.

4-(4''-brombenzyl)-6-bromo-3,4-dihydronaphthalen-1(2H)-one (**6f**). **¹H-NMR** (CDCl₃): 1.92 (ddd, $J = 4.8, 9.2, 13.6$ Hz, 1 H, 3-Ha), 2.14 (m, 1H, 3-Hb), 2.56 (dt, $J = 4.9, 17.7$ Hz, 1 H, 2-Ha), 2.74–2.84 (m, 2 H, 2-Hb, 1'-Ha), 3.04 (dd, $J = 6.3, 13.6$ Hz, 1 H, 1'-Hb), 3.18 (mc, 1 H, 4-H), 7.02 (d, $J = 8.1$ Hz, 2 H, 2''-H, 6''-H), 7.13 (d, $J = 7.8$ Hz, 1 H, 5-H), 7.32 (m, 1 H, 7-H), 7.42 (d, $J = 8.1$ Hz, 2 H, 3''-H, 5''-H), 7.45 (m, 1 H, 6-H), 8.05 (d, $J = 7.8$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 26.04 (C-3), 35.51 (C-2), 39.71 (C-4), 40.51 (C-1), 120.1 (C-4''), 126.9 (C-7), 127.3 (C-8), 128.2 (C-5), 130.6 (C-3''), 131.5 (C-2'', C-6''), 131.8 (C-8a), 133.4 (C-6), 138.6 (C-1''), 146.7 (C-4a), 197.7 (C-1) ppm. **HRMS** (IE): 314.0302 [M]⁺, measured; 314.0306 [M]⁺, calculated. **IR**: 3071, 3026, 2931, 2870, 1972, 1947, 1895, 1862, 1836, 1779, 1689, 1599, 1488, 1454, 1416, 1404, 1324, 1287, 1235, 1193, 1145, 1073, 1012, 954.

4-(4-fluorobenzyl)-3,4-dihydronaphthalen-1(2H)-one (**6g**). **¹H-NMR** (CDCl₃): 1.94 (ddd, $J = 5.1, 9.6, 13.6$ Hz, 1 H, 3-Ha), 2.17 (ddt, $J = 4.8, 12.4, 13.6$ Hz, 1 H, 3-Hb), 2.58 (dt, $J = 4.8, 17.9$ Hz, 1 H, 2-Ha), 2.81 (ddd, $J = 5.1, 12.4, 17.9$ Hz, 1 H, 2-Hb), 2.85 (dd, $J = 9.3, 13.6$ Hz, 1 H, 1'-Ha), 3.07 (dd, $J = 6.3, 13.8$ Hz, 1 H, 1'-Hb), 3.15–3.22 (m, 1 H, 4-H), 7.00 (tt, $J = 2.2, 8.8$ Hz, 2 H, C-3'', C-5''), 7.08–7.14 (m, 3 H, 5-H, C-2'', C-6''), 7.33 (dt, $J = 1.0, 7.4$ Hz, 1 H, 7-H), 7.46 (dt, 1.5, 7.4 Hz, 1 H, 6-H), 8.06 (dt, $J = 1.5, 7.6$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 26.09 (C-3), 34.58 (C-1'), 40.04 (C-4), 40.39 (C-2), 115.3 (d, $J_{C-F} = 21.2$ Hz, C-3'', C-5''), 127.0 (C-7), 127.4 (C-8), 128.4 (C-5), 130.4 (d, $J_{C-F} = 8.1$ Hz, C-1'', C-6''), 131.9 (C-8a), 133.4 (C-6), 135.3 (d, $J_{C-F} = 3.3$ Hz, C-1'), 146.9 (C-4a), 161.5 (d, $J_{C-F} = 245.2$ Hz, C-4''), 198.0 (C-1) ppm. **HRMS** (IE): 254.1101 [M]⁺, measured; 254.1107 [M]⁺, calculated. **IR**: 3070, 3039, 2930, 2857, 1883, 1689, 1600, 1511, 1454, 1414, 1285, 1227, 1158, 1113, 1093, 1029.

4-(2-hydroxybenzyl)-3,4-dihydronaphthalen-1(2H)-one (**6h**). **¹H-NMR** (CDCl₃): 1.99 (ddd, $J = 4.5, 8.8, 13.4$ Hz, 1 H, 3-Ha), 1.14 (dt, $J = 4.8, 13.4$ Hz, 1 H, 3-Hb), 2.63 (dt, $J = 4.5, 13.6$ Hz, 1 H, 2-Ha), 3.00 (dd, $J = 10.1, 13.4$ Hz, 1 H, 1'-Ha), 3.05–3.14 (m, 2 H, 2-Hb, 1'-Hb), 3.39 (m, 1 H, 4-H), 6.89 (dt, $J = 1.0, 7.6$ Hz, 1 H, 3''-H), 6.94 (d_{br}, $J = 7.8$ Hz, 1 H, 5''-H), 7.07–7.17 (m, 3 H, 6''-H, 4''-H, OH), 7.33–7.36 (m, 2 H, 5-H, 7-H), 7.51 (dt, $J = 1.3, 7.4$ Hz, 1 H, 6-H), 8.11 (dd, $J = 1.5, 8.3$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 25.56 (C-3), 34.61 (C-2), 35.32 (C-1'), 38.41 (C-4), 115.4 (C-3''), 120.2 (C-5''), 126.2 (C-1''), 126.7 (C-7), 127.2, 127.6 (C-8, C-4''), 128.7 (C-5), 131.0 (C-6''), 131.5 (C-8a), 133.9 (C-6), 148.6 (C-4a), 154.5 (C-2''), 200.5 (C-1) ppm. **HRMS** (IE): 252.1150 [M]⁺, measured; 252.1150 [M]⁺, calculated. **IR**: 3608, 3258, 3071, 3032, 2928, 2871, 1761, 1738, 1688, 1664, 1596, 1504, 1489, 1455, 1413, 1325, 1296, 1253, 1235, 1178, 1149, 1115, 1096, 954.

4-benzyl-6-methyl-3,4-dihydronaphthalen-1(2H)-one (**6i**). **¹H-NMR** (CDCl₃): 1.92 (ddd, $J = 4.8, 8.8, 13.6$ Hz, 1 H, 3-Ha), 2.12 (m_c, 1 H, 3-Hb), 2.36 (s, 3 H, CH₃), 2.54 (dt, $J = 4.8, 17.9$ Hz, 1 H, 2-Ha), 2.80 (ddd, $J = 5.1, 12.1, 17.9$ Hz, 1 H, 2-Hb), 2.85 (dd, $J = 9.9, 13.4$ Hz, 1 H, 1'-Ha), 3.11 (dd, $J = 5.8,$

13.4 Hz, 1 H, 1'-H_b), 3.17 (m_c, 1 H, 4-H), 7.00 (s, 1 H, 5-H), 7.15 (d, $J = 8.1$ Hz, 1 H, 7-H), 7.19 (d, $J = 7.4$ Hz, 2 H, 2''-H, 6''-H), 7.25 (t, $J = 7.4$ Hz, 1 H, 4''-H), 7.34 (t, $J = 7.4$ Hz, 2 H, 3''-H, 5''-H), 7.96 (d, $J = 8.1$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 21.73 (CH₃), 25.85 (C-3), 34.54 (C-2), 39.90 (C-4), 41.11 (C-1'), 126.3 (Ph-C), 127.4, 127.8 (C-7, C-8), 128.4 (2 x Ph-C), 128.8 (C-5), 128.9 (2 x Ph-C), 129.6 (C-8a), 139.8 (C-1''), 144.2 (C-6), 147.4 (C-4a), 197.8 (C-1) ppm. **HRMS** (IE): 250.1360 [M]⁺, measured; 250.1358 [M]⁺, calculated. **IR**: 3066, 3029, 2928, 2867, 1943, 1685, 1609, 1496, 1454, 1415, 1355, 1328, 1285, 1236, 1191, 1144, 1125, 1077, 1032, 1013, 959.

4-Benzyl-6-phenyl-3,4-dihydronaphthalen-1(2H)-one (**6j**). **¹H-NMR** (CDCl₃): 2.02 (m_c, 1 H, 3-H_a), 2.23 (m_c, 1 H, 3-H_b), 2.63 (dt, $J = 4.8, 17.9$ Hz, 1 H, 2-H_a), 2.88 (m, 1 H, 2-H_b), 2.95 (dd, $J = 9.3, 13.5$ Hz, 1 H, 1''-H_a), 3.15 (dd, $J = 6.8, 13.5$ Hz, 1 H, 1''-H_b), 3.29 (m_c, 1 H, 4-H), 7.18–7.20 (m, 2 H, 2'''-H, 6'''-H), 7.27–7.29 (m, 2 H, 5-H, 4'''-H), 7.35 (m_c, 2 H, 3'''-H, 5'''-H), 7.38–7.41 (m, 1 H, 4'-H), 7.44 (m_c, 2 H, 3'-H, 5'-H), 7.49–7.51 (m, 2 H, 2'-H, 6'-H), 7.56 (dd, $J = 1.8, 8.3$ Hz, 1 H, 7-H), 8.14 (d, $J = 8.2$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 26.32 (C-3), 34.58 (C-2), 40.29 (C-4), 41.32 (C-1''), 125.7 (C-4'), 126.4 (C-4'''), 127.2 (C-7), 127.3 (2 x Ph-C, C-2', C-6'), 128.0, 128.2 (C-5, C-8), 128.6 (2 x Ph-C, C-2''', C-6'''), 128.8 (2 x Ph-C, C-3', C-5'), 129.1 (2 x Ph-C, C-3''', C-5'''), 130.7 (C-8a), 139.7 (C-1'''), 140.0 (C-1'), 145.9 (C-6), 147.5 (C-4a), 197.8 (C-1) ppm. **HRMS** (IE): 312.1515 [M]⁺, measured; 312.1514 [M]⁺, calculated. **IR**: 3066, 3030, 2938, 2899, 2871, 2247, 1967, 1949, 1885, 1811, 1678, 1603, 1561, 1503, 1496, 1454, 1406, 1357, 1329, 1280, 1242, 1193, 1126, 1077, 1047, 1031.

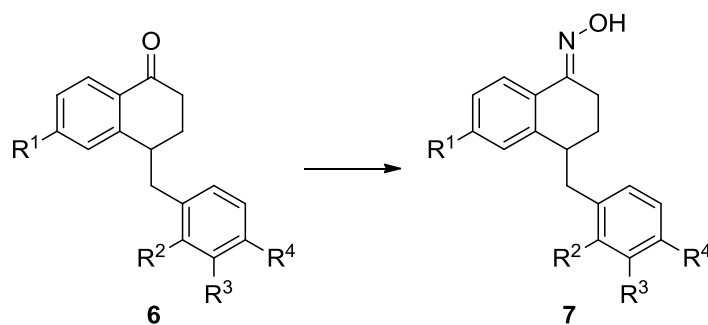
4-benzyl-6-fluoro-3,4-dihydronaphthalen-1(2H)-one (**6k**). **¹H-NMR** (CDCl₃): 1.94 (ddd, $J = 5.1, 10.1, 13.9$ Hz, 1 H, 3-H_a), 2.11–2.19 (m, 1 H, 3-H_b), 2.55 (dt, $J = 5.1, 17.8$ Hz, 1 H, 2-H_a), 2.80 (ddd, $J = 5.1, 10.1, 17.8$ Hz, 1 H, 2-H_b), 2.86 (dd, $J = 9.3, 13.6$ Hz, 1 H, 1'-H_a), 3.11 (dd, $J = 6.1, 13.6$ Hz, 1 H, 1'-H_b), 3.18–3.22 (m, 1 H, 4-H), 6.85 (dd, $J = 2.4, 9.6$ Hz, 1 H, 5-H), 7.01 (dt, $J = 2.4, 8.6$ Hz, 1 H, 7-H), 7.15–7.18 (m, 2 H, Ph-H), 7.24–7.28 (m, 1 H, Ph-H), 7.31–7.35 (m, 1 H, Ph-H), 8.09 (dd, $J = 6.1, 8.6$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 26.24 (C-3), 34.68 (C-2), 40.22 (C-4), 41.05 (C-1'), 114.6 (d, $J_{C-F} = 22.0$ Hz), 114.8 (d, $J_{C-F} = 21.6$ Hz, C-5, C-7), 126.7 (C-Ph), 128.7 (2 C-Ph, C-8a), 129.0 (2 C-Ph), 130.6 (d, $J_{C-F} = 9.9$ Hz, C-8), 139.3 (C_q-Ph), 150.5 (d, $J_{C-F} = 8.8$ Hz, C-4a), 165.8 (d, $J_{C-F} = 255.0$ Hz, C-6), 196.6 (C-1) ppm. **HRMS** (IE): 254.1100 [M]⁺, measured; 254.1107 [M]⁺, calculated. **IR**: 3070, 3039, 2930, 2857, 1883, 1689, 1600, 1511, 1454, 1414, 1285, 1227, 1158, 1113, 1093, 1029.

4-benzyl-6-chloro-3,4-dihydronaphthalen-1(2H)-one (**6l**). **¹H-NMR** (CDCl₃): 1.94 (ddd, $J = 5.1, 9.6, 13.6$ Hz, 1 H, 3-H_a), 1.09–1.28 (m, 1 H, 3-H_b), 2.56 (dt, $J = 5.1, 17.7$ Hz, 1 H, 2-H_a), 2.76–2.83 (m, 1 H, 2-H_b), 2.85 (dd, $J = 9.6, 12.8$ Hz, 1 H, 1'-H_a), 3.11 (dd, $J = 5.3, 12.8$ Hz, 1 H, 1'-H_b), 3.19 (tt_{br}, $J = 4.5, 9.7$ Hz, 1 H, 4-H), 7.16–7.18 (m, 3 H, 2 Ph-H, 5-H), 2.24–2.35 (m, 4 H, 3 Ph-H, 7-H), 8.00 (d, $J = 8.1$ Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 25.86 (C-3), 34.52 (C-2), 39.90 (C-4), 40.97 (C-1'), 126.6 (Ph-C), 127.4, 128.3 (C-5, C-7), 128.6 (2 C-Ph), 128.9 (2 C-Ph), 129.1 (C-8), 130.3 (C-8a), 139.2,

139.7 (C-6, C_q-Ph), 148.9 (C-4a), 197.0 (C-1) ppm. **HRMS** (IE): 270.0817 [M]⁺, measured; 270.0811 [M]⁺, calculated. **IR**: 3689, 3066, 3029, 2929, 2856, 2251, 1683, 1591, 1496, 1455, 1411, 1356, 1329, 1299, 1279, 1233, 1194, 1129, 1094, 1032.

4-benzyl-6-bromo-3,4-dihydronaphthalen-1(2H)-one (**6m**). **¹H-NMR** (CDCl₃): 1.93 (ddd, *J* = 4.8, 9.6, 13.9 Hz, 1 H, 3-H_a), 2.09–2.05 (m, 1 H, 3-H_b), 2.56 (dt, *J* = 5.3, 17.9 Hz, 1 H, 2-H_a), 2.75–2.83 (m, 1 H, 2-H_b), 2.85 (dd, *J* = 9.6, 13.4 Hz, 1 H, 1'-H_a), 3.10 (dd, *J* = 5.8, 13.4 Hz, 1 H, 1'-H_b), 3.15–3.21 (m, 1 H, 4-H), 7.15–7.17 (m, 2 H, Ph-H), 7.24–7.28 (m, 1 H, Ph-H), 7.32–7.35 (m, 3 H, 5-H, 2 Ph-H), 7.47 (dd, *J* = 1.5, 8.6 Hz, 1 H, 7-H), 7.91 (d, *J* = 8.6 Hz, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 25.81 (C-3), 34.49 (C-2), 39.85 (C-4), 40.99 (C-1'), 126.6 (Ph-C), 128.6 (2 Ph-C, C-8a), 128.9 (2 Ph-C), 129.1 (C-7), 130.3 (C-8), 130.7 (C-6), 131.4 (C-5), 139.1 (C_q-Ph), 149.0 (C-4a), 197.2 (C-1) ppm. **HRMS** (IE): 314.0317 [M]⁺, measured; 314.0306 [M]⁺, calculated. **IR**: 3350, 3087, 3066, 3029, 2935, 2871, 2250, 1685, 1586, 1561, 1496, 1472, 1454, 1406, 1356, 1329, 1295, 1279, 1234, 1208, 1192, 1123, 1089, 1076, 1033.

General Procedure C: Preparation of Oxims 7 from α-Tetralones 6.



The tetralone **6** was dissolved in EtOH (2 mL/mmol) and hydroxylamine hydrochloride (1.3 equiv.) and sodium acetate (1.3 equiv.) were added. The mixture was heated to reflux until the substrate was consumed. After cooling to r.t., the mixture was poured on to water, extracted with ethyl acetate, dried over MgSO₄ and the solvents removed i. Vak. The crude product was recrystallized from EE/PE.

4-benzyl-3,4-dihydronaphthalen-1(2H)-one oxime (**7a**). **¹H-NMR** (CDCl₃): 1.81–1.86 (m, 2 H, 3-H₂), 2.75 (dd, *J* = 9.6, 13.6 Hz, 1 H,), 2.78–2.88 (m, 1 H,), 2.94–3.02 (m, 2 H), 3.10 (m, 1 H, 4-H), 7.05–7.07 (m, 1 H, 5-H), 7.16–7.18 (m, 2 H, 2''-H, 6''-H), 7.23–7.27 (m, 3 H, 6-H, 7-H, 4''-H), 7.29–7.33 (m, 2 H, 3''-H, 5''-H), 7.92–7.94 (m, 1 H, 8-H) 8.94 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.86 (C-2), 23.79 (C-3), 40.59 (C-4), 40.88 (C-1'), 124.2 (C-8), 126.1 (C-4''), 126.7 (C-7), 128.4 (C-3''), 128.4 (C-5), 129.0 (C-2'', C-6''), 129.2 (C-6), 129.8 (C-8a), 140.1 (C-1''), 142.8 (C-4a), 155.1 (C-1) ppm. **MS** (IC), *m/z* = 252 [M+H]⁺. **HRMS** (IE): 251.1309 [M]⁺, measured; 251.1310 [M]⁺,

calculated. **IR**: 3582, 3288, 3065, 3029, 2868, 2250, 1949, 1810, 1625, 1601, 1494, 1486, 1455, 1355, 1334, 1293, 1273, 1244, 1121, 1077, 1057, 1030, 1017.

4-benzyl-6-bromo-3,4-dihydronaphthalen-1(2H)-one oxime (**7b**). **¹H-NMR** (CDCl₃): 1.81–1.85 (m, 2 H, 3-H₂), 2.74–2.83, 2.91–3.03 (2 x m, 4 H, 1'-H₂, 2-H₂), 3.05 (m_c, 1 H, 4-H), 3.72 (s, 3 H, O-CH₃), 6.48 (d, *J* = 2.2 Hz, 1 H, 5-H), 6.80 (dd, *J* = 2.2, 8.8 Hz, 1 H, 7-H), 7.15 (d, *J* = 7.8 Hz, 2 H, Ph-H), 7.21–7.26 (m, 1 H, Ph-H), 7.29–7.32 (m, 2 H, Ph-H), 7.85 (d, *J* = 8.8 Hz, 1 H, 8-H) 8.81 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.80 (C-2), 24.09 (C-3), 40.83 (C-4), 40.95 (C-1'), 55.16 (OMe), 112.7 (C-5), 113.4 (C-7), 122.5 (C-8a), 125.8 (C-8), 126.1 (Ph-C), 128.4 (2 x Ph-C), 129.1 (2 x Ph-C), 140.1 (Ph-C_q), 144.4 (C-4a), 154.7 (C-1), 160.2 (C-6) ppm. **MS** (IC), *m/z* = 282 [M+H]⁺. **HRMS** (IE): 281.1415 [M]⁺, measured; 281.1416 [M]⁺, calculated. **IR**: 3585, 3289, 3029, 2939, 2840, 2254, 1622, 1602, 1571, 1497, 1466, 1455, 1325, 1275, 1264, 1237, 1157, 1132, 1119, 1078, 1052, 1030.

4-(2-methoxybenzyl)-3,4-dihydronaphthalen-1(2H)-one oxime (**7c**). **¹H-NMR** (CDCl₃): 1.80 (m, 2 H, 3-H₂), 2.79 (dd, *J* = 9.3, 13.1 Hz, 1 H, 1'-H_a), 2.84–3.05 (m, 3 H, 2-H₂, 1'-H_b), 3.17 (m, 1 H, 4-H), 3.82 (s, 3 H, OCH₃), 6.87–6.91 (m, 2 H, 3''-H, 5''-H), 7.04–7.10 (m, 2 H, 5-H, 4''-H), 7.21–7.28 (m, 3 H, 6-H, 7-H, 6''-H), 7.93 (dd, *J* = 1.8, 7.3 Hz, 1 H, 8-H), 9.18 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.78 (C-2), 23.86 (C-3), 35.39 (C-1'), 38.71 (C-4), 55.20 (OCH₃), 110.3 (C-3''), 120.2 (C-5''), 124.0 (C-8), 126.5 (C-6''), 127.4 (C-7), 128.6 (C-4'), 128.6 (C-1''), 129.1 (C-6), 129.7 (C-8), 130.4 (C-5), 143.5 (C-4a), 155.3 (C-1), 157.7 (C-2'') ppm. **MS** (IC), *m/z* = 282 [M+H]⁺. **HRMS** (IE): 281.1418 [M]⁺, measured; 281.1416 [M]⁺, calculated. **IR**: 3597, 3294, 3071, 2938, 2836, 2335, 1955, 1926, 1892, 1740, 1691, 1601, 1587, 1549, 1494, 1465, 1455, 1439, 1287, 1271, 1244, 1177, 1110, 1051, 1032.

4-(2,3-dimethoxybenzyl)-3,4-dihydronaphthalen-1(2H)-one oxime (**7d**). **¹H-NMR** (CDCl₃): 1.83 (m, 2 H, 3-H₂), 2.78 (dd, *J* = 9.6, 13.1 Hz, 1 H, 1'-H_a), 2.85–3.05 (m, 3 H, 1'-H_b, 2-H₂), 3.18 (m, 1 H, 4-H), 3.80 (s, 3 H, OCH₃), 3.89 (s, 3 H, OCH₃), 6.73 (d, *J* = 7.6 Hz, 1 H, 6''-H), 6.83 (d, *J* = 7.6 Hz, 1 H, 4''-H), 7.00 (t, *J* = 7.6 Hz, 1 H, 5''-H), 7.13 (d, *J* = 7.5 Hz, 1 H, 5-H), 7.22–7.30 (m, 2 H, 6-H, 7-H), 7.93 (d, *J* = 7.5 Hz, 1 H, 8-H), 8.87 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.77 (C-2), 23.81 (C-3), 35.12 (C-1'), 39.50 (C-4), 55.65 (OCH₃), 60.49 (OCH₃), 110.5 (C-4''), 122.6 (C-6), 123.6 (C-5''), 124.1 (C-8), 126.6 (C-7), 128.5 (C-5), 129.2 (C-6), 129.8 (C-8a), 134.0 (C-1''), 143.2 (C-2''), 147.5 (C-4a), 152.8 (C-3''), 155.2 (C-1) ppm. **MS** (IC), *m/z* = 312 [M+H]⁺. **HRMS** (IE): 311.1516 [M]⁺, measured; 311.1521 [M]⁺, calculated. **IR**: 3597, 3253, 3068, 3001, 2933, 2856, 2836, 1901, 1819, 1691, 1599, 1585, 1481, 1430, 1340, 1307, 1272, 1225, 1174, 1084, 1055, 1012.

4-(2,3-dimethoxybenzyl)-6-bromo-3,4-dihydronaphthalen-1(2H)-one oxime (**7e**). **¹H-NMR** (CDCl₃): 1.73–1.82 (m, 2 H, 3-H₂), 2.73–2.30 (m, 4 H, 2-H₂, 1'-H₂), 3.08–3.14 (m, 1 H, 4a-H), 3.80 (s, 3 H, OCH₃), 3.88 (s, 3 H, OCH₃), 6.69 (d_{br}, *J* = 8.1 Hz, 6''-H), 6.83 (d_{br}, *J* = 8.1 Hz, 1 H, 4''-H), 6.99 (t_{br}, *J* = 8.1 Hz, 1 H, 5''-H), 7.26 (d, *J* = 1.0 Hz, 1 H, 5-H), 7.34 (dd, *J* = 1.0, 8.6 Hz, 1 H, 7-H), 7.74 (d,

$J = 8.6$ Hz, 1 H, 8-H) 8.18 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.66 (C-2), 23.53 (C-3), 35.00 (C-1'), 39.36 (C-4), 55.70 (OCH₃), 60.55 (OCH₃) 110.8 (C-4''), 122.5 (C-6''), 123.5 (C-6), 123.7 (C5''), 125.8 (C-8), 128.8 (C-8a), 129.8 (C-7), 131.4 (C-5), 133.4 (C-1''), 145.2 (C-4a), 147.5 (C-2''), 152.8 (C-3''), 154.7 (C-1) ppm. **MS** (IC), $m/z = 390, 392$ [M+H]⁺. **HRMS** (IE): 389.0636 [M]⁺, measured; 389.0627 [M]⁺, calculated. **IR**: 3595, 3243, 2930, 2856, 1707, 1585, 1481, 1430, 1305, 1274, 1225, 1084, 1011.

4 (4-bromobenzyl) 6-bromo-3,4-dihydronaphthalen-1(2H)-one oxime (**7f**). **¹H-NMR** (CDCl₃): 1.86–1.91 (m, 2 H, 3-H₂), 2.77 (dd, $J = 9.1, 13.5$ Hz, 1 H, 1''-H_a), 2.86 (dd, $J = 8.6, 18.9$ Hz, 1 H, 2-H_a), 2.93 (dd, $J = 6.6, 13.5$ Hz, 1 H, 1''-H_b), 3.03 (dt, $J = 4.8, 18.9$ Hz, 1 H, 2-H_b), 3.07–3.13 (m, 1 H, 4-H), 7.02–7.04 (m, 1 H,), 7.06 (d_{br}, $J = 8.3$ Hz, 2 H, 2''-H, 6''-H), 7.28–7.32 (m, 2 H, 6-H, 7-H), 7.46 (d, $J = 8.3$ Hz, 2 H, 3''-H, 5''-H), 7.95–7.98 (m, 1 H, 8-H) 9.04 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.82 (C-2), 23.99 (C-3), 40.30, 40.54 (C-4, C-1'), 120.0 (C-4''), 124.3 (C-8), 126.9 (C-7), 128.4 (C-5), 129.2 (C-6), 129.8 (C-8a), 130.8 (C-3'', C-5''), 131.4 (C-2'', C-6''), 139.1 (C-1''), 142.2 (C-4a), 154.8 (C-1) ppm. **HRMS** (IE): 329.0410 [M]⁺, measured; 329.0415 [M]⁺, calculated. **IR**: 3596, 3295, 3072, 3020, 2937, 2865, 1958, 1925, 1896, 1625, 1488, 1454, 1404, 1287, 1245, 1100, 1073, 1012, 974, 947.

4-(4-fluorobenzyl)-3,4-dihydronaphthalen-1(2H)-one oxime (**7g**). **¹H-NMR** (CDCl₃): 1.84 (dt, $J = 4.6, 9.0$ Hz, 2 H, 3-H₂), 2.74 (dd, $J = 9.0, 13.6$ Hz, 1 H, 1'-H_a), 2.82 (dd, $J = 9.0, 18.4$ Hz, 1 H, 2-H_a), 2.90 (dd, $J = 6.8, 13.6$ Hz, 1 H, 1'-H_b), 2.99 (dt, $J = 4.6, 18.9$ Hz, 1 H, 2-H_b), 3.05 (m, 1 H, 4-H), 6.98 (m, 3 H, C-3'', C-5''), 7.07 (m, 2 H, C-2'', C-6''), 7.25 (m, 2 H, 6-H, 7-H), 7.91 (m, 1 H, 8-H) ppm. **¹³C-NMR** (CDCl₃): 19.82 (C-2), 23.89 (C-3), 40.05 (C-1''), 40.75 (C-4), 115.1 (d, $J_{C-F} = 20.9$ Hz, C-3'', C-5''), 124.3 (C-8), 126.8 (C-7), 128.5 (C-5), 129.2(C-6), 129.8 (C-8a), 130.4 (d, $J_{C-F} = 8.1$ Hz, C-2'', C-6''), 135.7 (d, $J_{C-F} = 3.3$ Hz, C-1''), 142.4 (C-4a), 154.9 (C-1), 161.4 (d, $J_{C-F} = 244.1$ Hz, C-4'') ppm. **HRMS** (IE): 269.1222 [M]⁺, measured; 269.1216 [M]⁺, calculated. **IR**: 3071, 3040, 2931, 2870, 1971, 1943, 1883, 1689, 1600, 1567, 1511, 1480, 1454, 1415, 1320, 1295, 1227, 1195, 1158, 1113, 1094, 1029, 1016.

4-(2-hydroxybenzyl)-3,4-dihydronaphthalen-1(2H)-one oxime (**7h**). **¹H-NMR** (CD₃OD): 1.64–1.73 (m, 1 H, 3-H_a), 1.76–1.83 (m, 1 H, 3-H_b), 2.72–2.93 (m, 4 H, 1'-H₂, 2-H₂), 3.16–3.22 (m, 1 H, 4-H), 4.61 (s_{br}, 1 H, OH), 6.71 (t, $J = 7.6$ Hz, 1 H, 5''-H), 6.78 (d, $J = 7.6$ Hz, 1 H, 3''-H), 6.93 (dd, $J = 1.0, 7.6$ Hz, 1 H, 6''-H), 7.02 (dt, $J = 1.5, 7.6$ Hz, 1 H, 4''-H), 7.08 (d, $J = 7.4$ Hz, 1 H, 5-H), 7.14 (dt, $J = 1.5, 7.4$ Hz, 1 H, 7-H), 7.19 (dt, $J = 1.5, 7.4$ Hz, 1 H, 6-H), 7.89 (dd, $J = 1.0, 7.4$ Hz, 1 H, 8-H), not visible: N-OH. **¹³C-NMR** (CD₃OD): 20.63 (C-2), 25.03 (C-3), 36.62 (C-1'), 40.00 (C-4), 116.0 (C-3''), 120.4 (C-5''), 125.1 (C-8), 127.2 (C-7), 128.0 (C-1''), 128.3, 129.7 (C-5, C-4''), 129.8 (C-6''), 131.6 (C-8a), 132.1 (C-6), 144.7 (C-4a), 155.6 (C-1), 156.8 (C-2'') ppm. **HRMS** (IE): 267.1261 [M]⁺, measured;

267.1259 $[M]^+$, calculated. **IR**: 3608, 3248, 3069, 3033, 2928, 2856, 1709, 1593, 1502, 1489, 1456, 1364, 1325, 1309, 1285, 1253, 1216, 1167, 1151, 1096, 1052, 1037, 985, 940.

4-benzyl-6-methyl-3,4-dihydronaphthalen-1(2H)-one oxime (**7i**). **$^1\text{H-NMR}$** (CDCl_3): 1.77–1.82 (m, 2 H, 3- H_2), 2.32 (s, 3 H, CH_3), 2.73 (dd, $J = 10.1, 13.4$ Hz, 1 H, 1'- H_a), 2.80 (ddd, $J = 7.8, 10.4, 18.2$ Hz, 1 H, 2- H_a), 2.93–3.01 (m, 2 H, 2- H_b , 1'- H_b), 3.02–3.08 (m, 1 H, 4-H), 9.90 (s, 1 H, 5-H), 7.07 (d, $J = 8.0$ Hz, 1 H, 7-H), 7.17–7.19 (m, 2 H, 2''-H, 6''-H), 7.22–7.26 (m, 1 H, 4''-H), 7.30–7.34 (m, 2 H, 3''-H, 5''-H), 7.82 (d, $J = 8.0$ Hz, 1 H, 8-H) 8.50 (s_{br} , 1 H, OH) ppm. **$^{13}\text{C-NMR}$** (CDCl_3): 19.74 (C-2), 21.35 (CH_3), 23.62 (C-3), 40.53, 40.87 (C-4, C-1'), 124.2 (C-7), 126.1 (C-4''), 127.0 (C-8a), 127.7 (C-8), 128.4 (2 C, C-2'', C-6''), 128.9 (C-5), 129.0 (2 C, C-3'', C-5''), 139.3 (C-1''), 140.1 (C-6), 142.8 (C-4a), 155.1 (C-1) ppm. **HRMS** (IE): 265.1454 $[M]^+$, measured; 265.1467 $[M]^+$, calculated. **IR**: 3597, 3238, 3062, 3028, 2927, 2855, 1957, 1940, 1741, 1696, 1626, 1603, 1559, 1551, 1496, 1455, 1377, 1283, 1271, 1240, 1073, 1045.

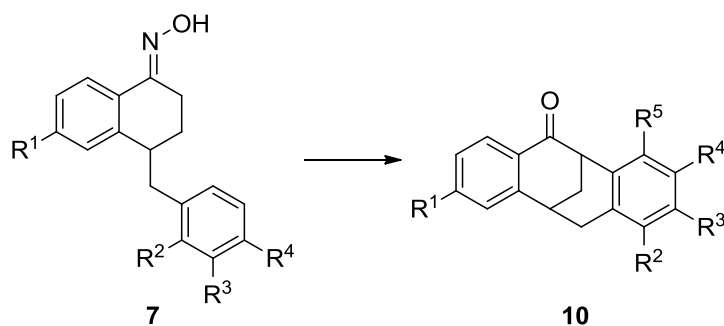
4-benzyl-6-phenyl-3,4-dihydronaphthalen-1(2H)-one oxime (**7j**). **$^1\text{H-NMR}$** (CDCl_3): 1.89 (m, 2 H, 3- H_2), 2.84 (dd, $J = 9.1, 13.5$ Hz, 1 H, 1''- H_a), 2.88 (ddd, $J = 7.6, 10.6, 18.4$ Hz, 1 H, 2- H_a), 3.01 (dd, $J = 6.8, 13.5$ Hz, 1 H, 1''- H_b), 3.08 (dt, $J = 4.8, 18.4$ Hz, 1 H, 2- H_b), 3.16–3.21 (m, 1 H, 4-H), 7.19–7.22 (m, 3 H, 2'''-H, 6'''-H, 5-H), 7.28 (mc, 1 H, 4'''-H), 7.34 (m, 2 H, 3'''-H, 5'''-H), 7.38 (mc, 1 H, 4'-H), 7.45 (m, 2 H, 3'-H, 5'-H), 7.48–7.52 (m, 3 H, 7-H, 2'-H, 6'-H), 8.03 (d, $J = 8.1$ Hz, 1 H, 8-H), 9.44 (s_{br} , 1 H, OH) ppm. **$^{13}\text{C-NMR}$** (CDCl_3): 19.86 (C-2), 24.00 (C-3), 40.89, 40.98 (C-4, C-1''), 124.7 (C-8), 125.6, 126.2, 127.0 (2 x Ph-C), 127.2, 127.5 (2 x Ph-C, C-4', C-4'''), 128.4 (2 x Ph-C), 128.7 (2 x Ph-C), 129.1 (2 x Ph-C), 140.1, 140.5 (C-1', C-1'''), 141.7 (C-6), 143.0 (C-4a), 154.8 (C-1) ppm. **HRMS** (IE): 327.1634 $[M]^+$, measured; 327.1623 $[M]^+$, calculated. **IR**: 3596, 3284, 3065, 3030, 2935, 1960, 1943, 1801, 1686, 1623, 1601, 1558, 1551, 1483, 1454, 1405, 1348, 1305, 1283, 1246, 1077, 1023.

4-benzyl-6-fluoro-3,4-dihydronaphthalen-1(2H)-one oxime (**7k**). **$^1\text{H-NMR}$** (CDCl_3): 1.82 (dt, $J = 4.3, 8.6$ Hz, 2 H, 3-H), 2.71–2.85 (m, 2 H, 2- H_2 , 1' H_2), 2.91–2.99 (m, 2 H, 2- H_2 , 1' H_2), 3.06 (m, 1 H, 4-H), 6.74 (dd, $J = 2.8, 9.3$ Hz, 1 H, 5-H), 6.94 (dt, $J = 2.5, 8.7$ Hz, 1 H, 7-H), 7.14–7.16 (m, 2 H, Ph-H), 7.22–7.26 (m, 1 H, Ph-H), 7.30–7.33 (m, 2 H, Ph-H), 7.91 (dd, $J = 5.8, 8.7$ Hz, 1 H, 8-H) ppm. Not visible: OH. **$^{13}\text{C-NMR}$** (CDCl_3): 19.81 (C-2), 23.84 (C-3), 40.62 (2 C, C-4, C-1'), 114.2 (d, $J_{C-F} = 22.3$ Hz, C-7), 114.7 (d, $J_{C-F} = 20.9$ Hz, C-5), 126.0 (d, $J_{C-F} = 2.9$ Hz, C-8a), 126.3 (Ph-C), 126.5 (d, $J_{C-F} = 8.4$ Hz, C-8), 128.5 (2 Ph-C), 129.0 (2 Ph-C), 139.6 (Ph- C_q), 145.3 (d, $J_{C-F} = 7.3$ Hz, C-4a), 154.4 (C-1), 163.2 (d, $J_{C-F} = 249.6$ Hz, C-6) ppm. **HRMS** (IE): 269.1229 $[M]^+$, measured; 269.1216 $[M]^+$, calculated. **IR**: 3595, 3296, 3087, 3066, 3029, 2935, 2866, 2336, 1944, 1871, 1803, 1689, 1628, 1604, 1584, 1568, 1497, 1454, 1427, 1356, 1292, 1276, 1250, 1227, 1145, 1109, 1078, 1050, 1031.

4-benzyl-6-chloro-3,4-dihydronaphthalen-1(2H)-one oxime (**7l**). **¹H-NMR** (CDCl₃): 1.78–1.83 (m, 2 H, 3-H₂), 2.73 (dd, *J* = 9.6, 13.5 Hz, 1 H, 1'-H_a), 2.79 (ddd, *J* = 7.3, 10.6, 18.7 Hz, 1 H, 2-H_a), 2.96 (dd, *J* = 5.3, 13.5 Hz, 1 H, 1'-H_b), 2.92–3.00 (m, 1 H, 2-H_b), 3.02–3.08 (m, 1 H, 4-H), 7.05 (d, *J* = 2.0 Hz, 1 H, 5-H), 7.15 (d_{br}, *J* = 7.1 Hz, 2 H, Ph-H), 7.21 (dd, *J* = 2.0, 8.7 Hz, 1 H, 7-H), 7.23–7.27 (m, 1 H, Ph-H), 7.32 (t, *J* = 7.1 Hz, 2 H, Ph-H), 7.85 (d, *J* = 8.7 Hz, 1 H, 8-H) 8.84 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.70 (C-2), 23.55 (C-3), 40.47, 40.64 (C-4, C-1'), 125.7 (C-8), 126.4 (C-Ph), 127.0 (C-7), 128.3 (C-5), 128.4 (C-8a), 128.5 (2 C-Ph), 129.0 (2 C-Ph), 135.0 (C-6), 139.6 (C_q-Ph), 144.4 (C-4a), 154.4 (C-1) ppm. **HRMS** (IE): 285.0914 [M]⁺, measured; 285.0920 [M]⁺, calculated. **IR**: 3581, 3291, 3029, 2929, 2856, 2250, 1683, 1623, 1590, 1495, 1488, 1481, 1453, 1351, 1282, 1093, 1048.

4-benzyl-6-bromo-3,4-dihydronaphthalen-1(2H)-one oxime (**7m**). **¹H-NMR** (CDCl₃): 1.76–1.81 (m, 2 H, 3-H₂), 2.69–2.81, 2.91–2.98 (2 x m, 4 H, 1'-H₂, 2-H₂), 3.04 (m_C, 1 H, 4-H), 7.14 (d_{br}, *J* = 7.3 Hz, 2 H, Ph-H), 7.20 (d, *J* = 1.8 Hz, 1 H, 5-H), 7.24 (m, 1 H, Ph-H), 7.32 (t_{br}, *J* = 7.3 Hz, 2 H, Ph-H), 7.35 (dd, *J* = 1.8, 8.6 Hz, 1 H, 7-H), 7.79 (d, *J* = 8.6 Hz, 1 H, 8-H) 8.23 (s_{br}, 1 H, OH) ppm. **¹³C-NMR** (CDCl₃): 19.50 (C-2), 23.51 (C-3), 40.41 (C-4), 40.69 (C-1'), 123.4 (C-6), 126.0 (C-8), 126.4 (Ph-C), 128.5 (2 C-Ph, C-8a), 129.0 (2 C-Ph), 129.9 (C-7), 131.2 (C-5), 139.6 (C_q-Ph), 144.6 (C-4a), 154.5 (C-1) ppm. **HRMS** (IE): 329.0414 [M]⁺, measured; 329.0415 [M]⁺, calculated. **IR**: 3238, 3065, 2955, 2923, 2854, 1600, 1582, 1554, 1494, 1478, 1453, 1400, 1377, 1307, 1290, 1172, 1100, 1076, 1060, 1036.

General Procedure D: Electrophilic Aromatic Substitution Reaction of Tetralone Oxims **7** to form the Tetracyclic Products **10**.



The tetralone oxime **7** was dissolved in Ac₂O (10 equiv.) and heated to 80 °C for 40 min. After cooling to 0 °C, acetic acid (35 equiv.) and methanesulfonic acid (5 equiv.) were added and the mixture was heated to 130 °C for 30 min. The mixture was cooled to 0 °C, MeOH was added the reaction, the mixture was poured on sat. NaHCO₃-solution and stirred for 1 h. After dilution with ethyl acetate an extraction was performed with ethyl acetate and after drying over MgSO₄, the solvents were removed i. Vak. [In the case of **7h** the crude was taken up in Ac₂O (10 equiv.) and Et₃N (4 equiv.), stirred for 20 min then

washed with water and sat. NaHCO₃-solution.] The crude product was subjected to column chromatography on silica gel (PE/EE).

11,12-Dihydro-6,12-methano-dibenzo[a,e]cycloocten-5-one (**10a**). ¹H-NMR (CDCl₃): 2.32 (ddd, *J* = 2.5, 3.3, 12.9 Hz, 1 H, 13-H_a), 2.65 (ddt, *J* = 2.3, 6.1, 12.9 Hz, 1 H, 13-H_b), 2.90 (d_{br}, *J* = 16.7 Hz, 1 H, 11-H_a), 3.47 (dd_{br}, *J* = 6.1, 16.7 Hz, 1 H, 11-H_b), 3.52 (m, 1 H, 12-H), 3.87 (t_{br}, *J* = 2.4 Hz, 1 H, 6-H), 6.99 (m, 1 H, 10-H), 7.10–7.17 (m, 2 H, 8-H, 9-H), 7.26 (dt, *J* = 1.3, 6.8 Hz, 1 H, 3-H), 7.32 (dd, *J* = 2.5, 6.1 Hz, 1 H, 7-H), 7.34 (d_{br}, *J* = 7.1 Hz, 1 H, 1-H), 7.49 (dt, *J* = 1.0, 7.3 Hz, 1 H, 2-H), 7.92 (dd, *J* = 1.0, 7.8 Hz, 4-H) ppm. ¹³C-NMR (CDCl₃): 29.68 (C-13), 33.21 (C-12), 36.28 (C-11), 48.39 (C-6), 126.5 (C-8*, C-9*), 127.1 (C-3), 127.4 (C-4), 127.8 (C-8*, C-9*), 128.5 (C-1), 129.4 (C-7), 129.8 (C-10), 130.3 (C-4a), 133.1 (C-10a), 133.8 (C-2), 134.0 (C-6a), 147.1 (C-12a), 197.7 (C-5) ppm. HRMS (IE): 234.1045 [M]⁺, measured; 234.1045 [M]⁺, calculated. IR: 3067, 3025, 2930, 2266, 2249, 1684, 1602, 1492, 1472, 1456, 1383, 1295, 1262, 1229, 1148, 1096, 1007.

11,12-Dihydro-6,12-methano-9,10-dimethoxy-6-dibenzo[a,e]cycloocten-5-one (**10b**). ¹H-NMR (CDCl₃): 2.30 (ddd, *J* = 2.3, 3.3, 12.9 Hz, 1 H, 13-H_a), 2.62 (ddd, *J* = 2.5, 4.8, 12.9 Hz, 1 H, 13-H_b), 2.88–2.94 (m, 1 H, 12-H_a), 3.42–3.47 (m, 2 H, 12-H_b, 12-H), 3.80 (t_{br}, *J* = 2.5 Hz, 1 H, 6-H), 3.84 (s, 3 H, OCH₃), 6.78 (dd, *J* = 2.7, 8.6 Hz, 1 H, 3-H), 6.80 (d, *J* = 2.7 Hz, 1 H, 1-H), 6.98–7.00 (m, 1 H, 7-H), 7.13 (m_c, 2 H, 8-H, 9-H), 7.33 (m, 1 H, 10-H), 7.88 (d, *J* = 8.6 Hz, 1 H, 4-H) ppm. ¹³C-NMR (CDCl₃): 29.77 (C-13), 33.63 (C-12), 36.19 (C-11), 48.21 (C-6), 55.38 (O-CH₃), 112.7 (C-1), 113.3 (C-3), 123.7 (C-4a), 126.4, 127.6 (C-8, C-9), 129.2 (C-10), 129.7 (C-7), 129.8 (C-4), 133.5 (C-10a), 133.9 (C-6a), 149.5 (C-12a), 164.0 (C-2), 196.7 (C-5) ppm. HRMS (IE): 264.1149 [M]⁺, measured; 264.1150 [M]⁺, calculated. IR: 3367, 3073, 3000, 2931, 2856, 2837, 1968, 1943, 1772, 1692, 1602, 1549, 1490, 1455, 1423, 1355, 1332, 1279, 1226, 1149, 1120, 1095, 1080, 1063, 1032, 1012.

9-acetyl -11,12-dihydro-6,12-methano-10-methoxy-6-dibenzo[a,e]cycloocten-5-one (**10ca**). ¹H-NMR (CDCl₃): 2.28 (dt, *J* = 2.8, 13.1 Hz, 1 H, 13-H_a), 2.54–2.59 (m, 1 H, 13-H_b), 2.59 (s, 3 H, COCH₃), 2.93 (d, *J* = 18.0 Hz, 1 H, 11-H_a), 3.12 (dd, *J* = 6.3, 18.0 Hz, 1 H, 11-H_b), 3.50 (s_{br}, 1 H, 12-H), 3.77 (s, 3 H, OCH₃), 5.08 (t_{br}, *J* = 2.8 Hz, 1 H, 6-H), 6.64 (d, *J* = 8.6 Hz, 1 H, 7-H), 7.25 (dt, *J* = 0.8, 7.5 Hz, 1 H, 3-H), 7.34 (d, *J* = 7.5 Hz, 1 H, 1-H), 7.35 (d, *J* = 8.6 Hz, 1 H, 8-H), 7.48 (dt, *J* = 1.5, 7.5 Hz, 1 H, 2-H), 7.89 (d, *J* = 7.5 Hz, 1 H, 4-H) ppm. ¹³C-NMR (CDCl₃): 27.46 (C-13), 29.63, 29.70, 30.87 (C-11), 40.11 (C-6), 54.31 (OCH₃), 106.07 (C-7), 123.3 (C-9), 126.0, 126.4, 126.5 (C-3, C-4, C-8), 127.5 (C-10a), 128.9 (C-1), 132.0, 132.0 (C-4a, C-6a), 132.9 (C-2), 146.9 (C-12a), 158.2 (C-10), 196.3 (C-5), 202.5 (COCH₃) ppm.

7-acetyl -11,12-dihydro-6,12-methano-10-methoxy-6-dibenzo[a,e]cycloocten-5-one (**10cb**).

¹H-NMR (CDCl₃): 2.19 (ddd, *J* = 2.5, 3.3, 13.0 Hz, 1 H, 13-H_a), 2.47 (s, 3 H, COCH₃), 2.62 (ddt, *J* = 2.3, 3.5, 13.0 Hz, 1 H, 13-H_b), 3.31 (dt, *J* = 1.5, 18.8 Hz, 1 H, 11-H_a), 3.50 (m, 1 H, 12-H), 3.68 (dd,

$J = 6.1, 18.8$ Hz, 1 H, 11- H_b), 3.93 (s, 3 H, OCH_3), 4.34 (m, 1 H, 6-H), 6.73 (d, $J = 8.7$ Hz, 1 H, 7-H), 7.23 (dt, $J = 1.3, 7.6$ Hz, 1 H, 3-H), 7.32 (d, $J = 7.6$ Hz, 1 H, 1-H), 7.45 (dt, $J = 1.3, 7.6$ Hz, 1 H, 2-H), 7.70 (d, $J = 8.7$ Hz, 1 H, 8-H), 7.87 (dd, $J = 1.3, 7.8$ Hz, 1 H, 4-H) ppm. ^{13}C -NMR ($CDCl_3$): 29.03 (C-13), 29.34 ($COCH_3$), 32.47 (C-12), 36.20 (C-11), 41.44 (C-6), 55.89 (OCH_3), 107.0 (C-9), 123.1 (C-10), 126.9 (C-3), 127.1 (C-4), 128.6 (C-1), 129.8 (C-7), 130.6 (C-4a), 132.0 (C-8), 133.7 (C-2), 137.9 (C-6a), 147.3 (C-12a), 160.6 (C-10), 196.8 (C-5), 199.7 ($COCH_3$) ppm. **MS** (IC), $m/z = 307$ $[M+H]^+$. **HRMS** (IE): 306.1257 $[M]^+$, measured; 306.1256 $[M]^+$, calculated. **IR**: 3073, 3005, 2935, 2841, 2335, 1694, 1602, 1590, 1574, 1545, 1476, 1455, 1433, 1354, 1292, 1279, 1257, 1238, 1152, 1125, 1094, 1072.

11,12-dihydro-6,12-methano-9,10-dimethoxy-6-dibenzo[a,e]cycloocten-5-one (**6d**). 1H -NMR ($CDCl_3$): 2.25 (d_{br} , $J = 12.9$ Hz, 1 H, 13- H_a), 2.60 (d_{br} , $J = 12.9$ Hz, 1 H, 13- H_b), 3.04 (d_{br} , $J = 17.7$ Hz, 1 H, 11- H_a), 3.22 (dd, $J = 6.1, 17.9$ Hz, 1 H, 11- H_b), 3.53 (s_{br} , 1 H, 12-H), 3.71 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.90 (m, 1 H, 6-H), 6.75 (d, $J = 6.8$ Hz, 1 H, H-8), 7.06 (d, $J = 8.5$ Hz, 1 H, H-9), 7.24 (d, $J = 7.3$ Hz, 1 H, 3-H), 7.34 (d, $J = 7.8$ Hz, 1 H, 1-H), 7.47 (t, $J = 7.3$ Hz, 1 H, 2-H), 7.91 (d, $J = 7.8$ Hz, 1 H, 4-H) ppm. ^{13}C -NMR ($CDCl_3$): 29.42 (C-13), 31.17 (C-11), 32.50 (C-12), 47.57 (C-6), 55.63 (OCH_3), 59.80 (OCH_3), 110.8 (C-8), 124.7 (C-7), 126.0 (C-6a), 127.0 (C-3), 127.3 (C-4), 128.3 (C-10a), 128.5 (C-1), 130.2 (C-4a), 133.8 (C-2), 146.9 (C-12a), 147.2 (C-10), 151.9 (C-9), 197.7 (C-5) ppm. **MS** (IC), $m/z = 295$ $[M+H]^+$, 312 $[M+NH_4]^+$. **HRMS** (IE): 294.1257 $[M]^+$, measured; 294.1256 $[M]^+$, calculated. **IR**: 3367, 3073, 3000, 2931, 2856, 2837, 1968, 1943, 1772, 1692, 1602, 1549, 1490, 1455, 1423, 1355, 1332, 1279, 1226, 1149, 1120, 1095, 1080, 1063, 1032, 1012.

2-Bromo-11,12-dihydro-6,12-methano-9,10-dimethoxy-6-dibenzo[a,e]cycloocten-5-one (**10e**). 1H -NMR ($CDCl_3$): 3.24 (ddd, $J = 2.5, 3.3, 12.9$ Hz, 1 H,), 3.58 (ddt, $J = 2.1, 3.8, 13.1$ Hz,), 3.04 (dt_{br} , $J = 2.1, 17.7$ Hz, 1 H,), 3.21 (dd, $J = 6.1, 17.9$ Hz, 1 H,), 3.49 (m, 1 H,), 3.74 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.80 (m, 1 H,), 6.75 (d, $J = 8.6$ Hz, 1 H,), 7.04 (d, $J = 8.3$ Hz, 1 H,), 7.39 (dd, $J = 2.0, 8.3$ Hz, 1 H,), 7.51 (d, $J = 2.0$ Hz, 1 H,), 7.76 (d, $J = 8.3$ Hz, 1 H,) ppm. ^{13}C -NMR ($CDCl_3$): 29.17 (C-13), 31.00 (C-11), 32.44 (C-12), 47.78 (C-6), 55.67 (OCH_3), 59.89 (OCH_3), 111.0 (C-8), 124.7 (C-7), 125.5 (C-6a), 127.9 (C-10a), 128.8 (C-4a), 129.1 (C-4), 129.1 (C-2), 130.6 (C-3), 131.4 (C-1), 146.9 (C-10), 148.9 (C-12a), 152.0 (C-9), 196.7 (C-5) ppm. **MS** (IC), $m/z = 373, 374$ $[M+H]^+$, 390, 392 $[M+NH_4]^+$. **HRMS** (IE): 372.0352 $[M]^+$, measured; 372.0361 $[M]^+$, calculated. **IR**: 3369, 3000, 2933, 2857, 2837, 2227, 192, 1846, 1769, 1694, 1588, 1565, 1490, 1465, 1456, 1423, 1407, 1351, 1329, 1276, 1225, 1171, 1152, 1129, 1095, 1085, 1074, 1060, 1034, 1013.

8-Bromo-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-one (**10f**). 1H -NMR ($CDCl_3$): 2.27 (dt, $J = 2.6, 13.1$ Hz, 1 H, 13- H_a), 2.62 (dt, $J = 1.8, 13.1$ Hz, 1 H, 13- H_b), 2.84 (d_{br} , $J = 17.2$ Hz, 1 H, 11- H_a), 3.37 (dd_{br} , $J = 5.8, 17.2$ Hz, 1 H, 11- H_b), 3.50 (s_{br} , 1 H, 12-H), 3.80 (s_{br} , 1 H, 6-H), 6.85 (d, $J = 8.3$ Hz, 1 H,

10-H), 7.23 (dd, $J = 1.8, 8.3$ Hz, 1 H, 9-H), 7.26 (t_{br}, $J = 7.8$ Hz, 1 H, 3-H), 7.33 (d, $J = 7.8$ Hz, 1 H, 1-H), 7.48 (d, $J = 1.8$ Hz, 1 H, 7-H), 7.49 (t_{br}, $J = 7.8$ Hz, 1 H, 2-H), 7.91 (d, $J = 7.8$ Hz, 1 H, 4-H) ppm. **¹³C-NMR** (CDCl₃): 29.31 (C-13), 32.87 (C-12), 35.82 (C-11), 48.11 (C-6), 119.9 (C-8), 127.3, 127.4 (C-3, C-4), 128.5 (C-1), 130.1 (C-4a), 130.8, 131.4, 131.9 (C-7, C-9, C-10), 132.9 (C-10a), 134.1 (C-2), 135.1 (C-6a), 146.8 (C-12a), 196.9 (C-5) ppm. **HRMS** (IE): 312.0148 [M]⁺, measured; 312.0150 [M]⁺, calculated. **IR**: 3073, 3023, 2931, 2867, 1971, 1944, 1895, 1836, 1737, 1694, 1604, 1591, 1570, 1481, 1455, 1430, 1400, 1355, 1295, 1240, 1227, 1180, 1149, 1120, 1071, 1043, 979, 908.

8-Fluoro-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-one (**10g**). **¹H-NMR** (CDCl₃): 2.29 (ddd, $J = 2.5, 3.0, 12.9$ Hz, 1 H, 13-H_a), 3.62 (m, 1 H, 13-H_b), 2.88 (d, $J = 16.9$ Hz, 1 H, 11-H_a), 3.40 (dd, $J = 5.8, 16.9$ Hz, 1 H, 11-H_b), 3.51 (s_{br}, 1 H, 12-H), 3.82 (s_{br}, 1 H, 6-H), 6.83 (dt, $J = 2.8, 8.5$ Hz, 1 H, 9-H), 6.94 (dd, $J = 5.8, 8.5$ Hz, 1 H, 10-H), 7.04 (dd, $J = 2.8, 6.6$ Hz, 1 H, 7-H), 7.26 (dt, $J = 7.6, 1.0$ Hz, 1 H, 3-H), 7.34 (d_{br}, $J = 7.6$ Hz, 1 H, 1-H), 7.49 (dt, $J = 1.0, 7.6$ Hz, 1 H, 2-H), 7.92 (dd, $J = 1.0, 7.6$ Hz, 1 H, 4-H) ppm. **¹³C-NMR** (CDCl₃): 29.36 (C-13), 33.10 (C-12), 35.61 (C-11), 48.47 (C-6), 115.0 (d, $J_{C-F} = 21.6$ Hz, C-9), 115.5 (d, $J_{C-F} = 20.9$ Hz, C-7), 127.2, 127.4, 128.5 (C-1, C-3, C-4), 129.4 (d, $J_{C-F} = 3.3$ Hz, C-10a), 130.1 (C-4a), 131.1 (d, $J_{C-F} = 7.7$ Hz, C-10), 134.0 (C-2), 134.8 (d, $J_{C-F} = 7.3$ Hz, C-6a), 146.9 (C-12a), 161.2 (d, $J_{C-F} = 245.5$ Hz, C-8), 197.0 (C-5) ppm. **HRMS** (IE): 252.0952 [M]⁺, measured; 252.0952 [M]⁺, calculated. **IR**: 3071, 3025, 2935, 1968, 1943, 1742, 1694, 1614, 1602, 1553, 1500, 1455, 1433, 1356, 1294, 1275, 1246, 1237, 1138, 1120, 1104, 1044, 980, 939, 921.

10-acetoxy-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-one (**10h**). **¹H-NMR** (CDCl₃): 2.29 (s, 3 H, CH₃), 2.29–2.33 (m, 1 H, 13-H_a), 2.61–2.66 (m, 1 H, 13-H_b), 2.82 (dd, $J = 17.3, 1.3$ Hz, 1 H, 11-H_a), 3.13 (dd, $J = 6.1, 17.3$ Hz, 1 H, 11-H_b), 3.54 (m, 1 H, 12-H), 3.90 (s_{br}, 1 H, 6-H), 6.91 (d_{br}, $J = 8.1$ Hz, 1 H, 9-H), 7.17 (t_{br}, $J = 7.8$ Hz, 1 H, 3-H), 7.25–7.29 (m, 2 H, 7-H, 8-H), 7.33 (d_{br}, $J = 7.3$ Hz, 1 H, 1-H), 7.50 (m, 1 H, 2-H), 7.92 (d_{br}, $J = 7.8$ Hz, 1 H, 4-H) ppm. **¹³C-NMR** (CDCl₃): 20.80 (CH₃), 29.15 (C-13), 30.83, 32.38 (C-11, C-12), 48.12 (C-6), 121.2 (C-9), 126.6 (C-10a), 127.1, 127.2, 127.3, 127.5, 128.5 (C-1, C-3, C-4, C-7, C-8), 130.1 (C-4a), 134.1 (C-2), 134.9 (C-6a), 146.9 (C-12a), 149.4 (C-10), 168.9 (O(C=O)CH₃), 197.2 (C-5) ppm. **HRMS** (IE): 292.1199 [M]⁺, measured; 292.1099 [M]⁺, calculated. **IR**: 3073, 3025, 2938, 2868, 2264, 2246, 1761, 1686, 1602, 1581, 1457, 1371, 1296, 1209, 1186, 1176, 1121, 1024.

2-Fluoro-11,12-dihydro-6,12-methano-dibenzo[a,e]cycloocten-5-one (**10k**). **¹H-NMR** (CDCl₃): 2.33 (m_c, 1 H, 13-H_a), 2.63 (m_c, 1 H, 13-H_b), 2.90 (m_c, 1 H, 11-H_a), 3.44–3.51 (m, 2 H, 11-H_b, 12-H), 3.85 (m, 1 H, 6-H), 6.94 (dt, $J = 2.0, 8.7$ Hz, 1 H, 3-H), 7.00–7.03 (m, 2 H, 1-H, 10-H), 7.14 (m_c, 2 H, 8-H, 9-H), 7.31 (dd, $J = 2.0, 6.8$ Hz, 1 H, 7-H), 7.94 (dd, $J = 6.1, 8.7$ Hz, 1 H, 4-H) ppm. **¹³C-NMR** (CDCl₃): 29.57 (C-13), 33.51 (C-12), 36.06 (C-11), 48.10 (C-6), 114.8 (d, $J_{C-F} = 21.2$ Hz, C-1), 114.8 (d, $J_{C-F} = 21.2$ Hz, 1-C, 3-C), 126.6 (8-C*, 9-C*), 126.9 (C-4a), 127.9, 129.4, 129.8 (7-C, 8-C*, 9-C*,

C-10), 130.5 (d, J_{C-F} = 9.5 Hz, C-4), 132.9, 133.7 (C-6a, C-10a), 150.1 (d, J_{C-F} = 9.1 Hz, C-12a), 166.1 (d, J_{C-F} = 255.0 Hz, C-2), 196.2 (C-5) ppm. **MS** (IC), m/z = 253 $[M+H]^+$, 270 $[M+NH_4]^+$. **HRMS** (IE): 252.0960 $[M]^+$, measured; 252.0950 $[M]^+$, calculated. **IR**: 3062, 3022, 2931, 1336, 1694, 1609, 1588, 1554, 1489, 1453, 1354, 1271, 1254, 1170, 1153, 1109.

2-Methyl-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-one (**10i**). **1H -NMR** ($CDCl_3$): 2.30 (dt, J = 2.612.9 Hz, 1 H, 13- H_a), 2.37 (s, 3 H, CH_3), 2.58–2.63 (m, 1 H, 13- H_b), 2.87–2.93 (m, 1 H, 11- H_a), 3.42–3.48 (m, 2 H, 12-H, 11- H_b), 3.84 (s_{br} , 1 H, 6-H), 6.98–7.00 (m, 1 H, 10-H), 7.06 (d, J = 8.1 Hz, 1 H, 3-H), 7.11–7.14 (m, 2 H, 8-H, 9-H), 7.15 (s, 1 H, 1-H), 7.33–7.35 (m, 1 H, 7-H), 7.82 (d, J = 8.1 Hz, 1 H, 4-H) ppm. **^{13}C -NMR** ($CDCl_3$): 21.64 (CH_3), 29.68 (C-13), 33.11 (C-12), 36.17 (C-11), 48.34 (C-6), 126.3 (C-8*, C-9*), 127.4, 127.6 (C-3, C-4), 127.9 (C-4a), 128.1 (C-8*, C-9*), 128.9 (C-1), 129.2 (C-7), 129.7 (C-10), 133.2 (C-10a), 134.0 (C-6a), 144.6 (C-2), 147.1 (C-12a), 197.4 (C-5) ppm. **HRMS** (IE): 248.1202 $[M]^+$, measured; 248.1201 $[M]^+$, calculated. **IR**: 3345, 3066, 3022, 2931, 2865, 2835, 2262, 2246, 1952, 1924, 1893, 1838, 1805, 1731, 1679, 1610, 1489, 1452, 1429, 1375, 1354, 1314, 1292, 1247, 1171, 1134, 1075, 1043, 1007, 981.

2-Phenyl-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-one (**10i**). **1H -NMR** ($CDCl_3$): 2.37 (d_{br} , J = 13.1 Hz, 1 H, 13- H_a), 2.69 (d_{br} , J = 13.1 Hz, 1 H, 13- H_b), 2.97 (d, J = 17.0 Hz, 1 H, 11- H_a), 3.51 (dd, J = 6.1, 17.0 Hz, 1 H, 11- H_b), 3.59 (s_{br} , 1 H, 12-H), 3.89 (s_{br} , 1 H, 6-H), 7.00–7.02 (m, 1 H, 10-H), 7.12–7.17 (m, 2 H, 8-H, 9-H), 7.34–7.36 (m, 1 H, 7-H), 7.38–7.42 (m, 1 H, 4'-H), 7.45 (d, J = 8.0 Hz, 1 H, 3-H), 7.46–7.50 (m, 2 H, 3'-H, 5'-H), 7.56 (s, 1 H, 1-H), 7.61 (d, J = 7.1 Hz, 2 H, 2'-H, 6'-H), 7.99 (d, J = 8.1 Hz, 1 H, 4-H) ppm. **^{13}C -NMR** ($CDCl_3$): 29.71 (C-13), 33.46 (C-12), 36.45 (C-11), 48.40 (C-6), 126.0 (C-8*, C-9*), 126.5 (C-4'), 127.1 (C-7), 127.2 (2 C, C-2', C-6'), 127.8 (C-8*, C-9*), 128.1, 128.2 (C-1, C-4), 128.9 (2 C, 3'-C, 5'-C), 129.2 (C-4a), 129.4 (C-7), 129.9 (C-10), 133.2, 134.0 (C-6a, C-10a), 140.0 (C-1'), 146.6 (C-2), 147.6 (C-12a), 197.4 (C-5) ppm. **HRMS** (IE): 310.1357 $[M]^+$, measured; 310.1358 $[M]^+$, calculated. **IR**: 3066, 3033, 2932, 2866, 2248, 1952, 1925, 1889, 1809, 1728, 1682, 1606, 1562, 1504, 1490, 1452, 1355, 1292, 1282, 1246, 1135, 1023, 980.

2-Phenyl-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-acetylimin (**10ji**). **1H -NMR** ($CDCl_3$): 2.30 (ddd, J = 2.0, 3.5, 12.9 Hz, 1 H, 13- H_a), 2.40 (s, 3 H, CH_3), 2.59 (m, 1 H, 13- H_b), 2.96 (d_{br} , J = 16.8 Hz, 1 H, 11- H_a), 3.43 (dd_{br} , J = 5.6, 16.8 Hz, 1 H, 11- H_b), 3.55 (m_{br} , 1 H, 12-H), 4.05 (m_{br} , 1 H, 6-H), 6.99–7.01 (m, 1 H, 10-H), 7.14 (mc , 2 H, 8-H, 9-H), 7.36–7.40 (m, 2 H, 7-H, 4'-H), 7.44 (dd, J = 1.6, 8.3 Hz, 1 H, 3-H), 7.43–7.47 (m, 2 H, 3'-H, 5'-H), 7.51 (d, J = 1.6 Hz, 1 H, 1-H), 7.58–7.61 (m, 2 H, 2'-H, 6'-H), 7.93 (d, J = 8.3 Hz, 1 H, 4-H) ppm. **^{13}C -NMR** ($CDCl_3$): 26.42 (CH_3), 30.28 (13-C), 33.18 (12-C), 37.29 (11-C), 41.56 (6-C), 125.9, 126.5 (C-8, C-9), 127.1 (3 C, 10-C, 2'-C, 6'-C), 127.7, 127.8, 128.0 (C-1', C-4, C-7), 128.9 (2 C, 3'-C, 5'-C), 129.4 (C-4a), 129.8, 129.9 (C-1, C-3), 133.7, 134.1 (C-6a, C-10a), 140.1 (C-1'), 145.0, 145.7 (C-2, C-12a), 164.0 (5-C), 185.6 (1''-C) ppm. **HRMS** (IE): 351.1618 $[M]^+$, measured;

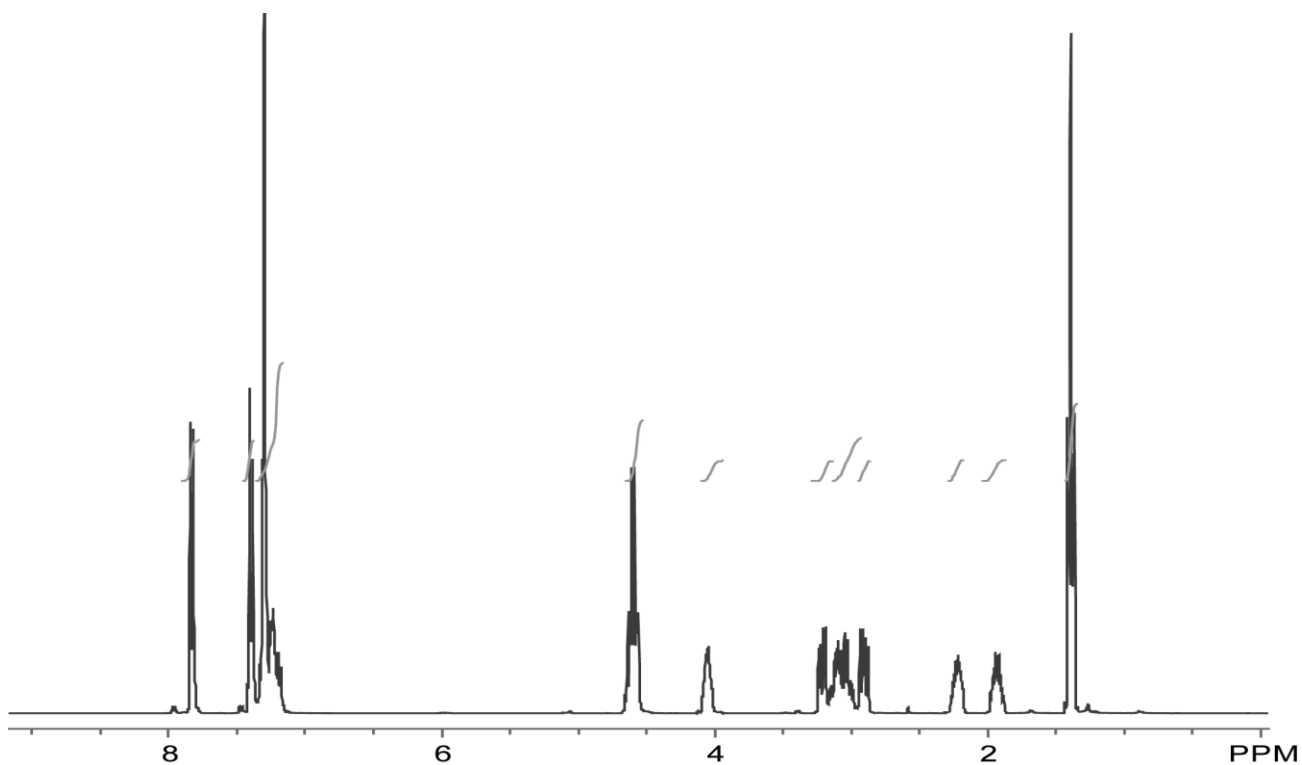
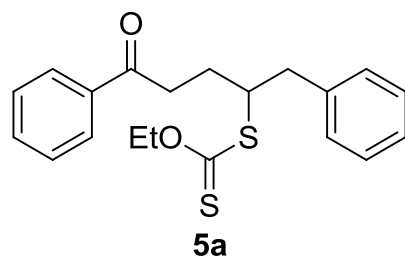
351.1623 [M]⁺, calculated. **IR**: 3540, 3421, 3065, 3033, 2932, 2865, 1946, 1690, 1606, 1562, 1492, 1452, 1429, 1408, 1354, 1344, 1291, 1282, 1244, 1227, 1134, 1077, 1037, 1006, 979.

2-Chloro-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-one (**10l**). **¹H-NMR** (CDCl₃): 2.33 (ddd, *J* = 2.3, 3.3, 12.9 Hz, 1 H, 13-H_a), 2.62–2.68 (m, 1 H, 13 H_b), 2.90 (d_{br}, *J* = 16.7 Hz, 1 H, 11-H_a), 3.47 (dd, *J* = 6.0, 16.7 Hz, 1 H, 11-H_b), 3.51 (m_{br}, 1 H, 12-H), 3.87 (t_{br}, *J* = 2.5 Hz, 1 H, 6-H), 6.98–7.00 (m, 1 H, 10-H), 7.10–7.17 (m, 2 H, 8-H, 9-H), 7.24–7.28 (m, 1 H, 1-H), 7.33 (dd, *J* = 2.5, 7.0 Hz, 1 H, 7-H), 7.34 (d, *J* = 7.8 Hz, 1 H, 3-H), 7.92 (dd, *J* = 1.0, 7.8 Hz, 1 H, 4-H) ppm. **¹³C-NMR** (CDCl₃): 29.44 (C-13), 33.20 (C-12), 36.08 (C-11), 48.10 (C-6), 126.7 (C-8*, C-9*), 127.7 (C-1), 128.0 (C-3), 128.4 (C-8*, C-9*), 128.8 (C-4a), 129.1 (C-7), 129.4 (C-4), 129.8 (C-10), 132.7, 133.7 (C-10a, C-6a), 140.0 (C-2), 148.7 (C-12a), 196.5 (C-5) ppm. **HRMS** (IE): 268.0644 [M]⁺, measured; 268.0655 [M]⁺, calculated. **IR**: 3066, 3024, 2928, 2856, 2246, 2258, 1685, 1592, 1566, 1489, 1453, 1430, 1413, 1354, 1344, 1286, 1277, 1286, 1227, 1167, 1150, 1128, 1096, 1073, 1042, 1006.

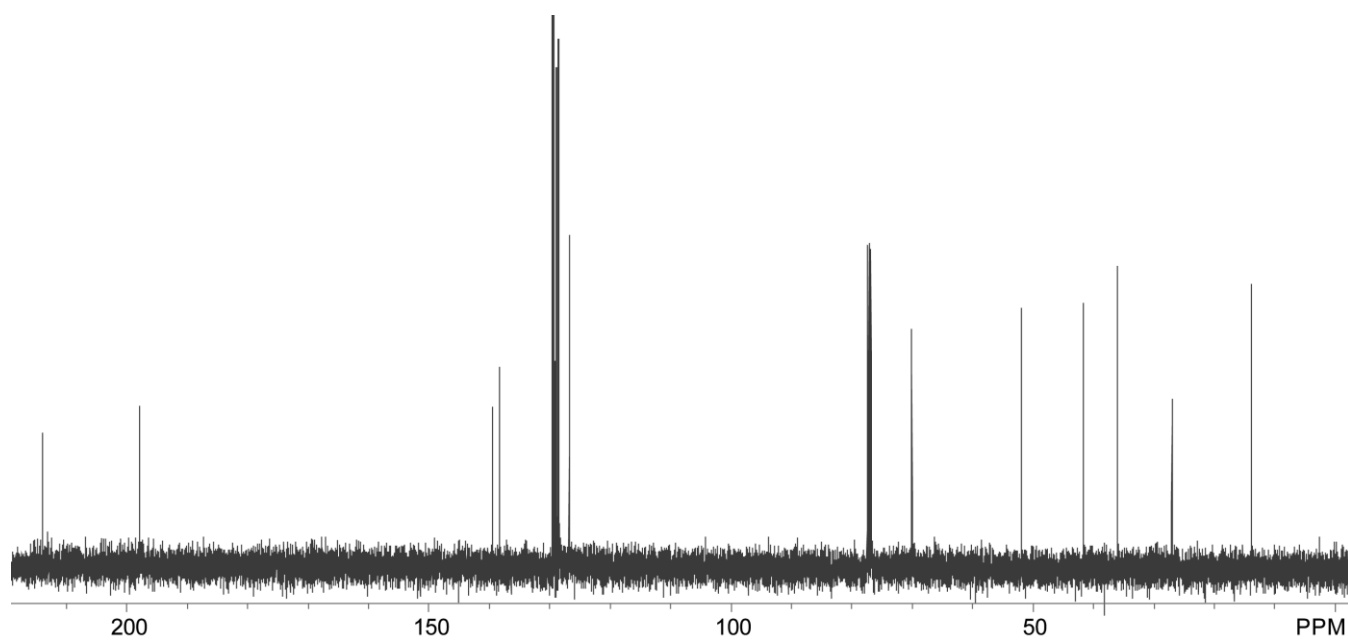
2-Bromo-11,12-dihydro-6-dibenzo[a,e]cycloocten-5-one (**10m**). **¹H-NMR** (CDCl₃): 2.32 (ddd_{br}, *J* = 2.0, 3.1, 12.9 Hz, 1 H, 13-H_a), 2.59–2.64 (m_{br}, 1 H, 13-H_b), 2.87–2.93 (m_{br}, 1 H, 11-H_a), 3.43–3.49 (m_{br}, 2 H, 11-H_b, 12-H), 3.86 (m_{br}, 1 H, 6-H), 6.99–7.02 (m, 1 H, 10-H), 7.11–7.18 (m, 2 H, 8-H, 9-H), 7.30–7.32 (m, 1 H, 7-H), 7.39 (dd, *J* = 1.8, 8.3 Hz, 1 H, 3-H), 7.52 (d, *J* = 1.8 Hz, 1 H, 1-H), 7.77 (d, *J* = 8.3 Hz, 1 H, 4-H) ppm. **¹³C-NMR** (CDCl₃): 29.39 (C-13), 33.10 (C-12), 36.07 (C-11), 48.07 (C-6), 126.7, 128.0 (C-8, C-9), 128.9 (C-4a), 129.1 (C-4), 129.2 (C-2), 129.4 (C-7), 129.8 (C-10), 130.6 (C-3), 131.4 (C-1), 132.6 (C-10a), 133.6 (C-6a), 148.7 (C-12a), 196.6 (C-5) ppm. **HRMS** (IE): 312.0159 [M]⁺, measured; 312.0150 [M]⁺, calculated. **IR**: 3066, 3024, 2935, 2868, 2254, 1690, 1588, 1561, 1489, 1471, 1453, 1429, 1408, 1354, 1344, 1314, 1287, 1240, 1227, 1166, 1151, 1130, 1085, 1069, 1042, 1007.

NMR-Spectra:

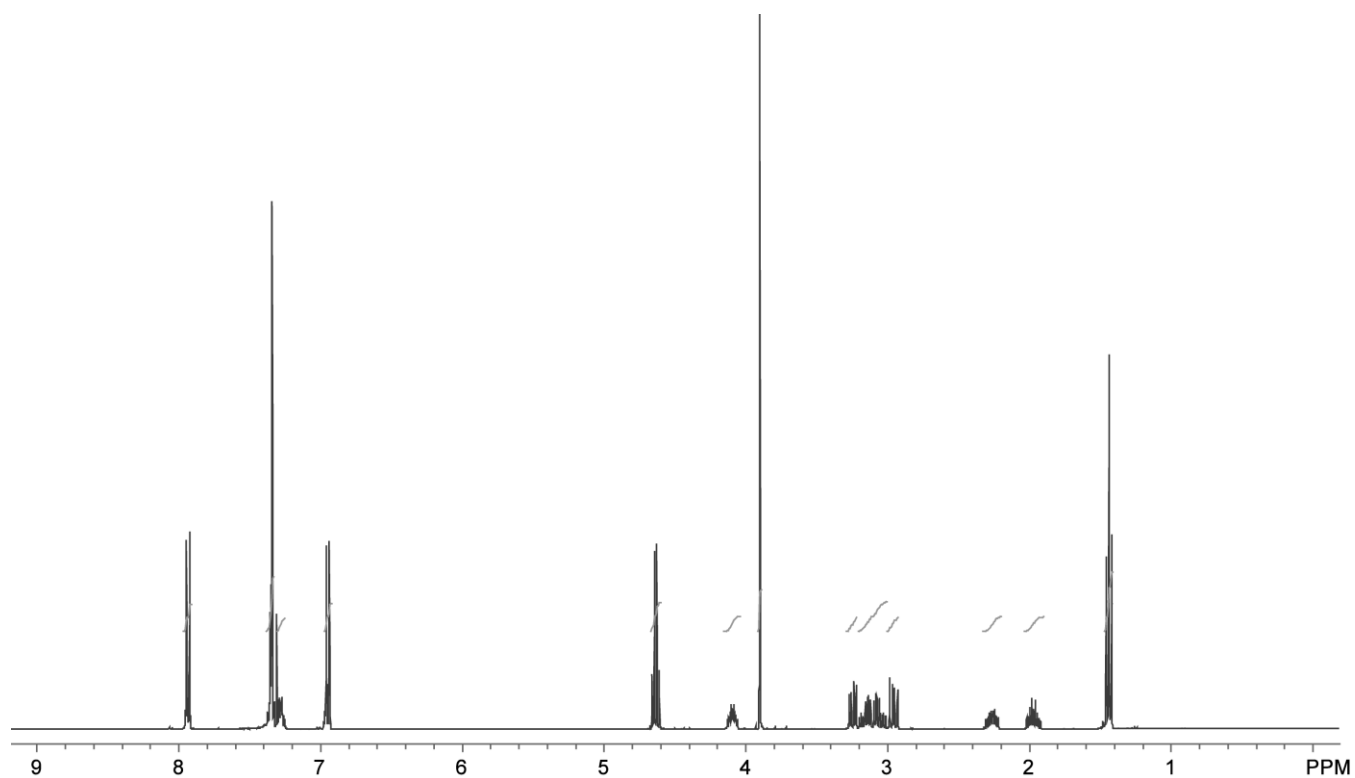
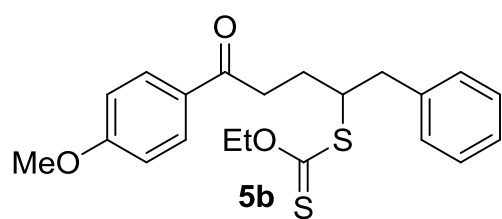
Xanthates 5:



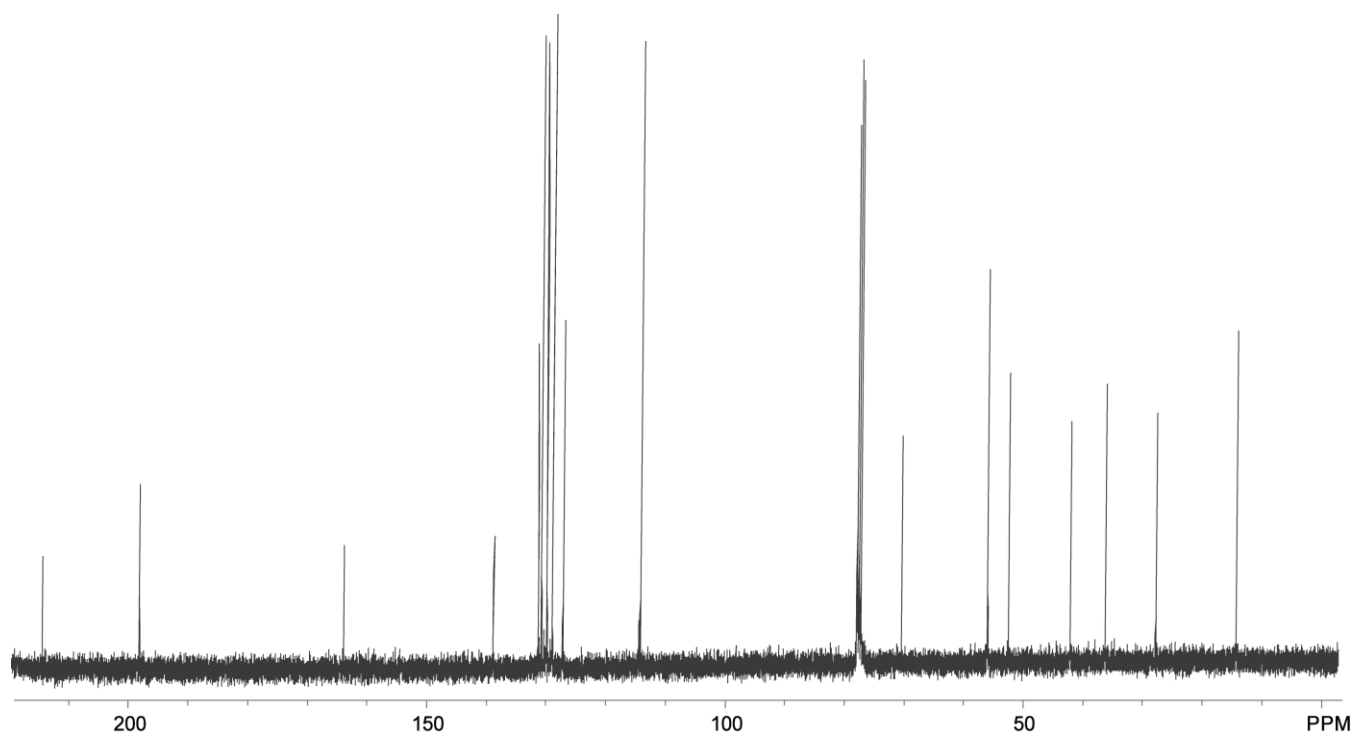
^1H -NMR-spectrum of Xanthate **5a** (CDCl₃).



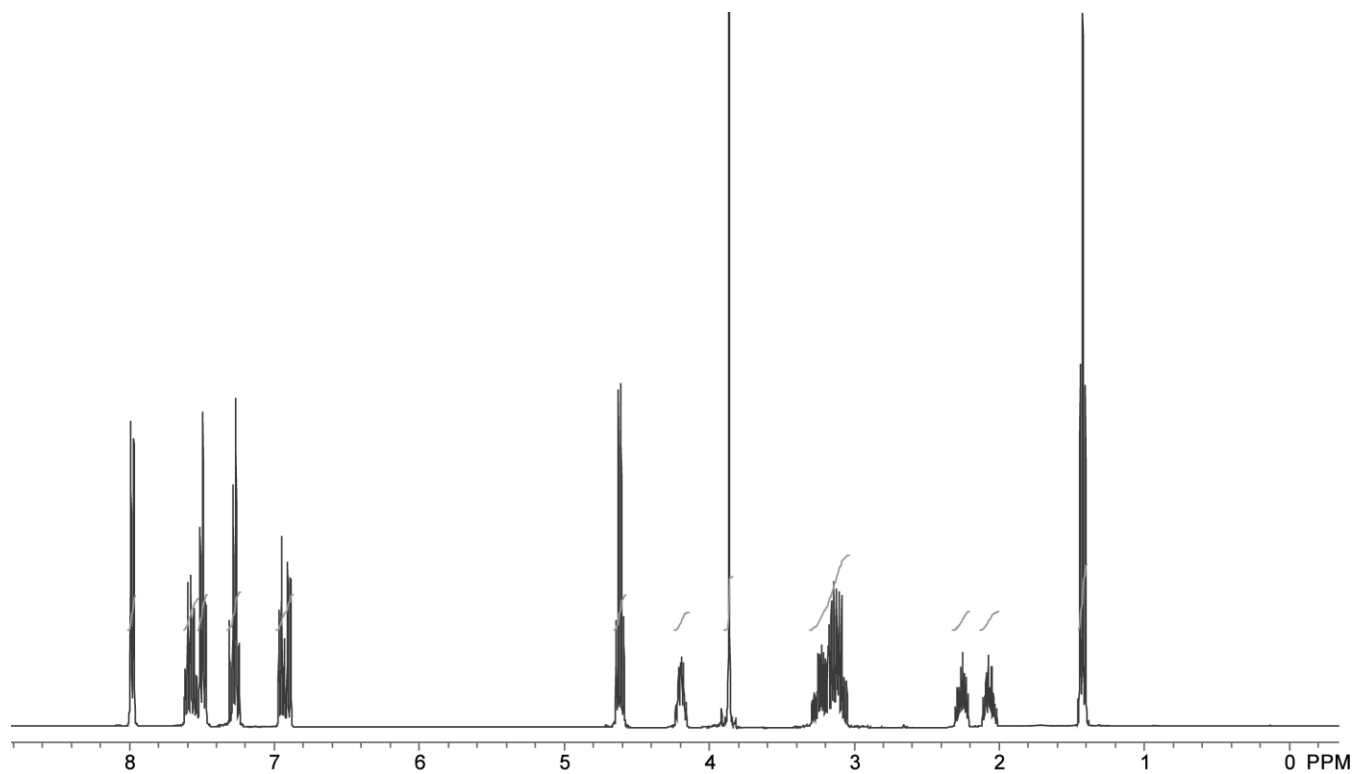
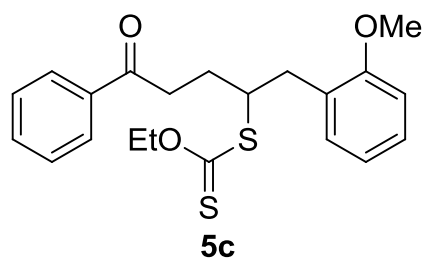
^{13}C -NMR-spectrum of Xanthate **5a** (CDCl_3).



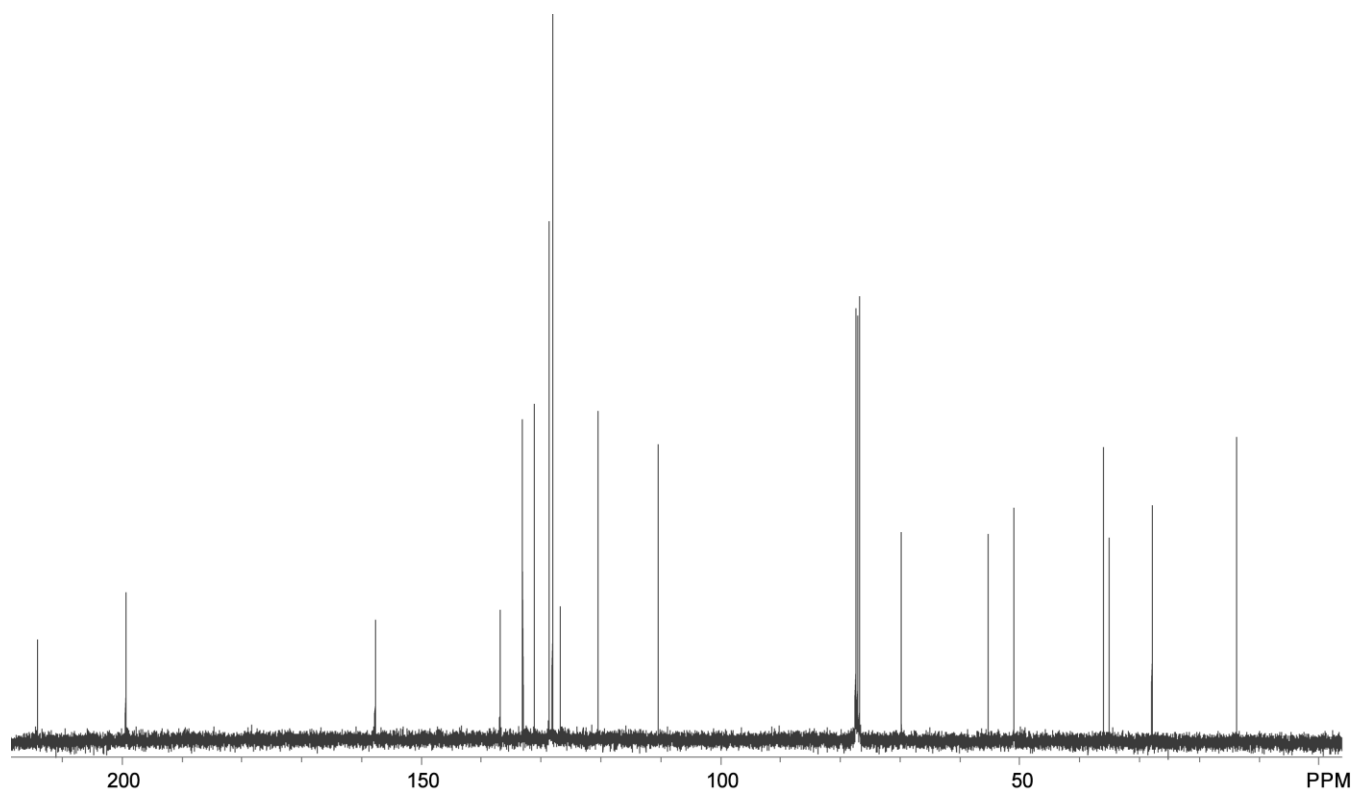
^1H -NMR-spectrum of Xanthate **5b** (CDCl_3).



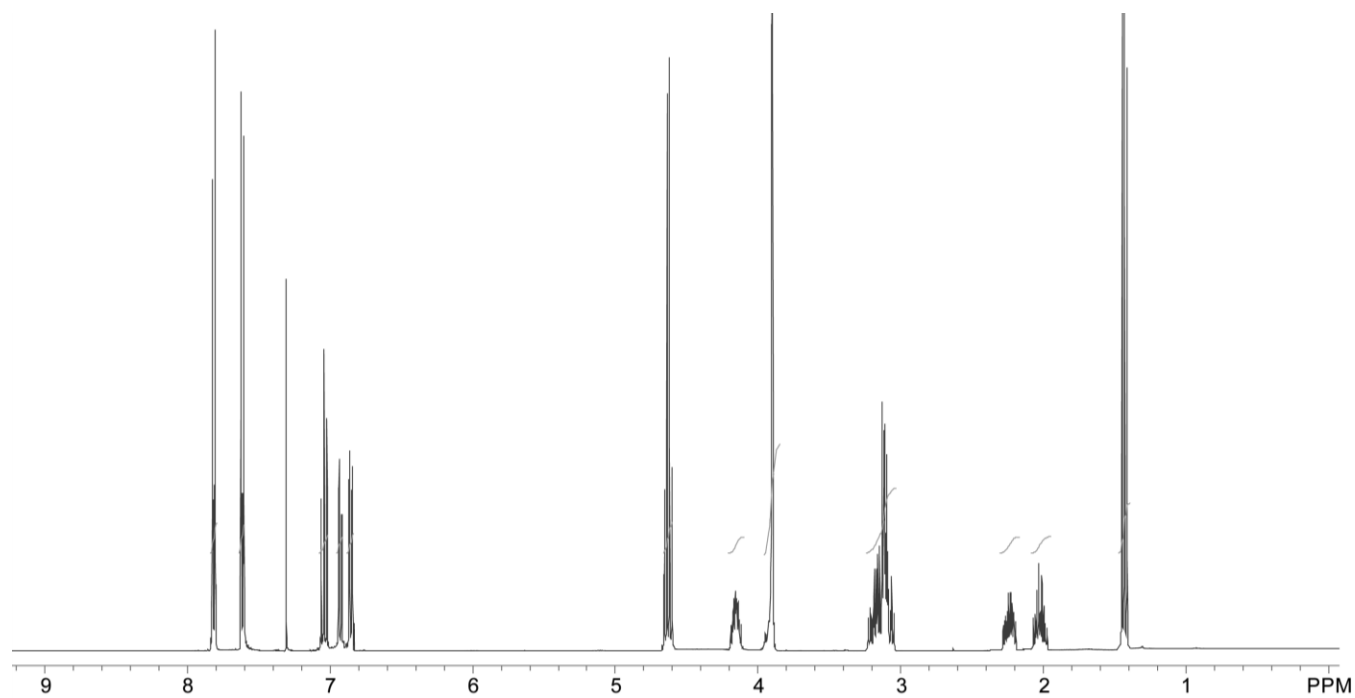
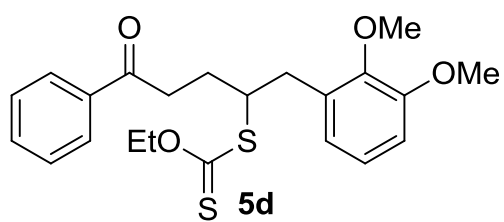
^{13}C -NMR-spectrum of Xanthate **5b** (CDCl_3).



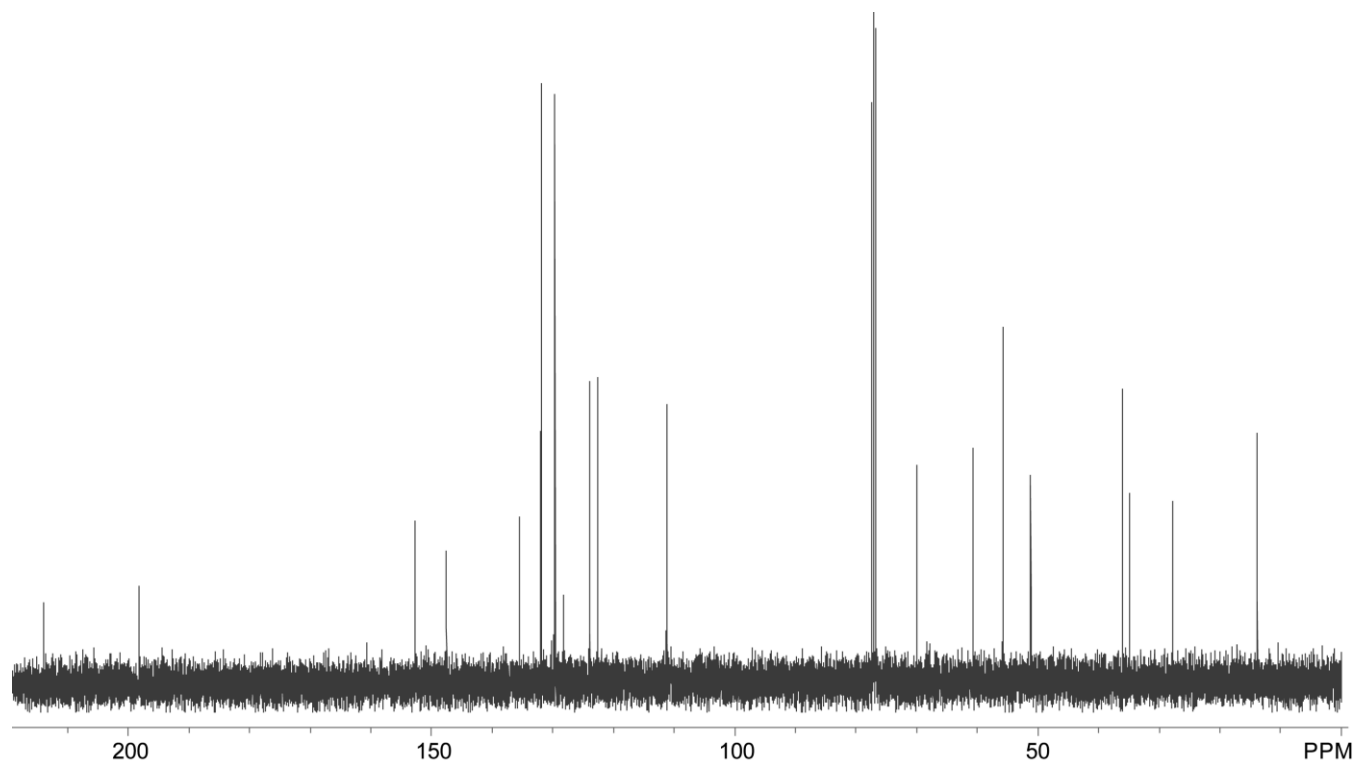
¹H-NMR-spectrum of Xanthate 5c (CDCl₃).



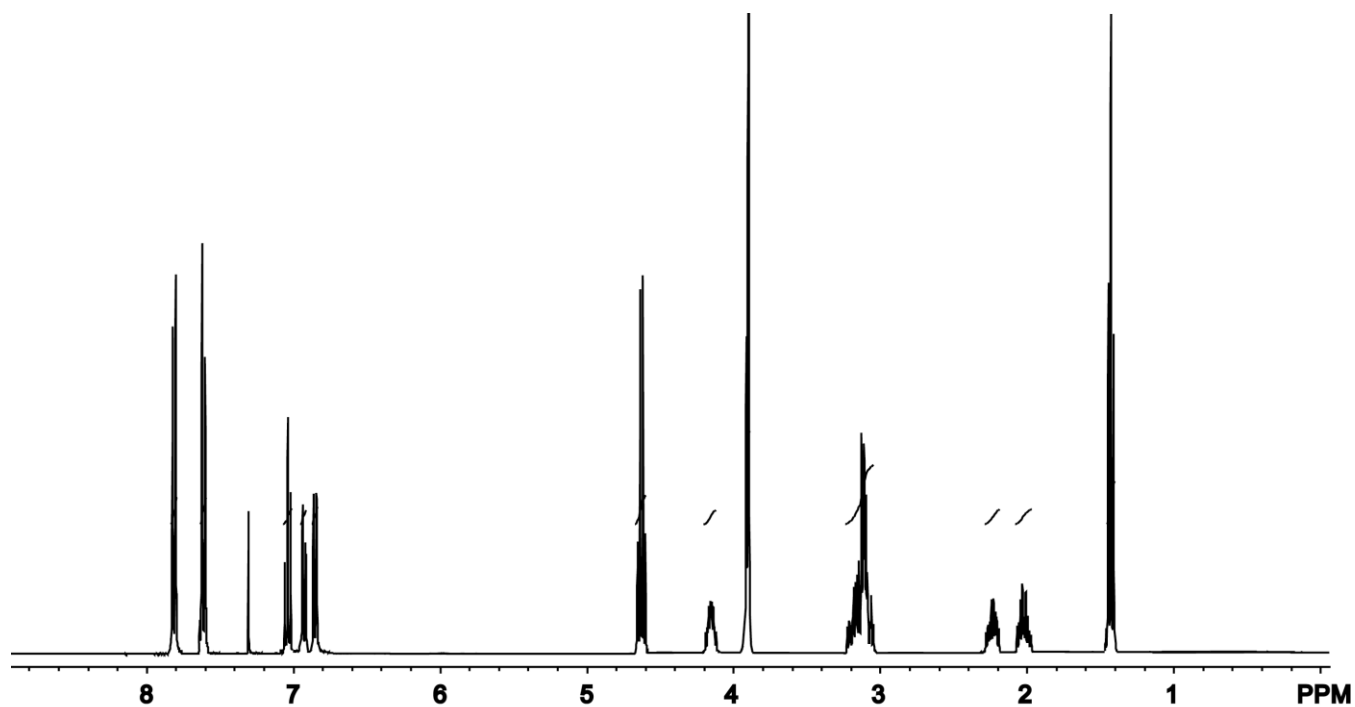
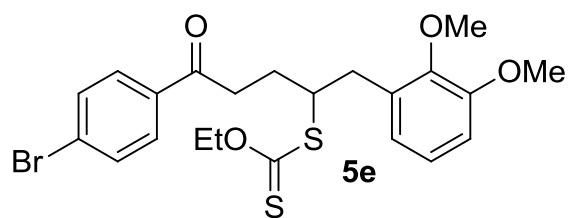
^{13}C -NMR-spectrum of Xanthate **5c** (CDCl_3).



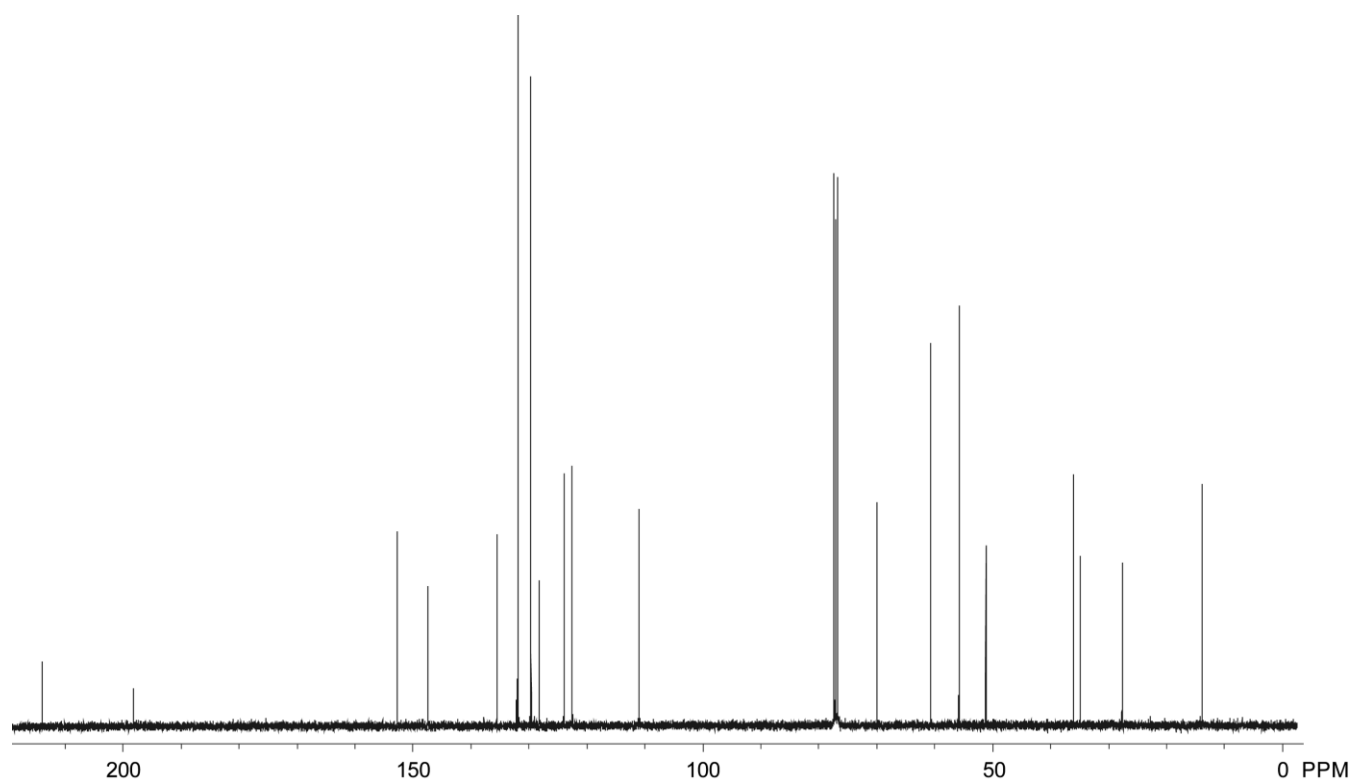
^1H -NMR-spectrum of Xanthate **5d** (CDCl_3).



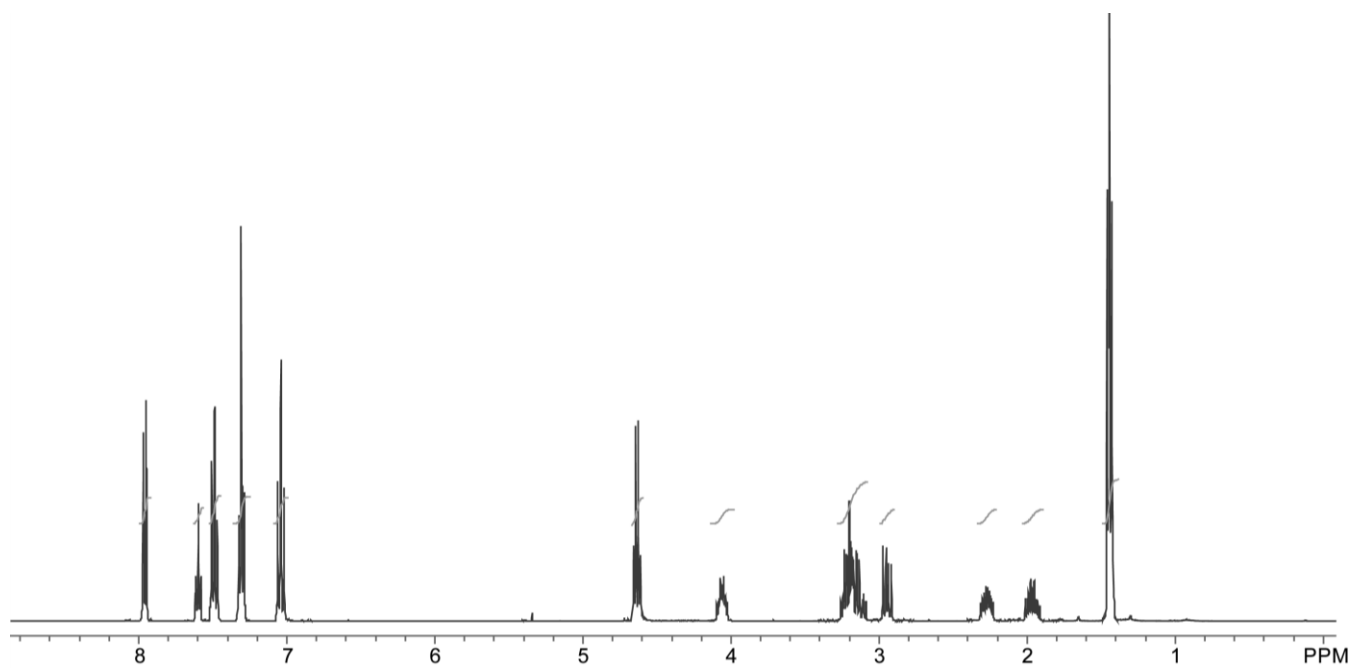
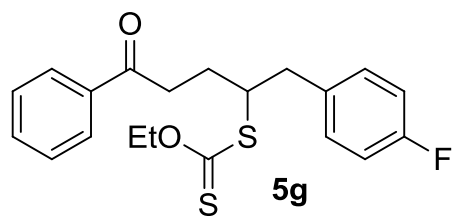
^{13}C -NMR-spectrum of Xanthate **5d** (CDCl_3).



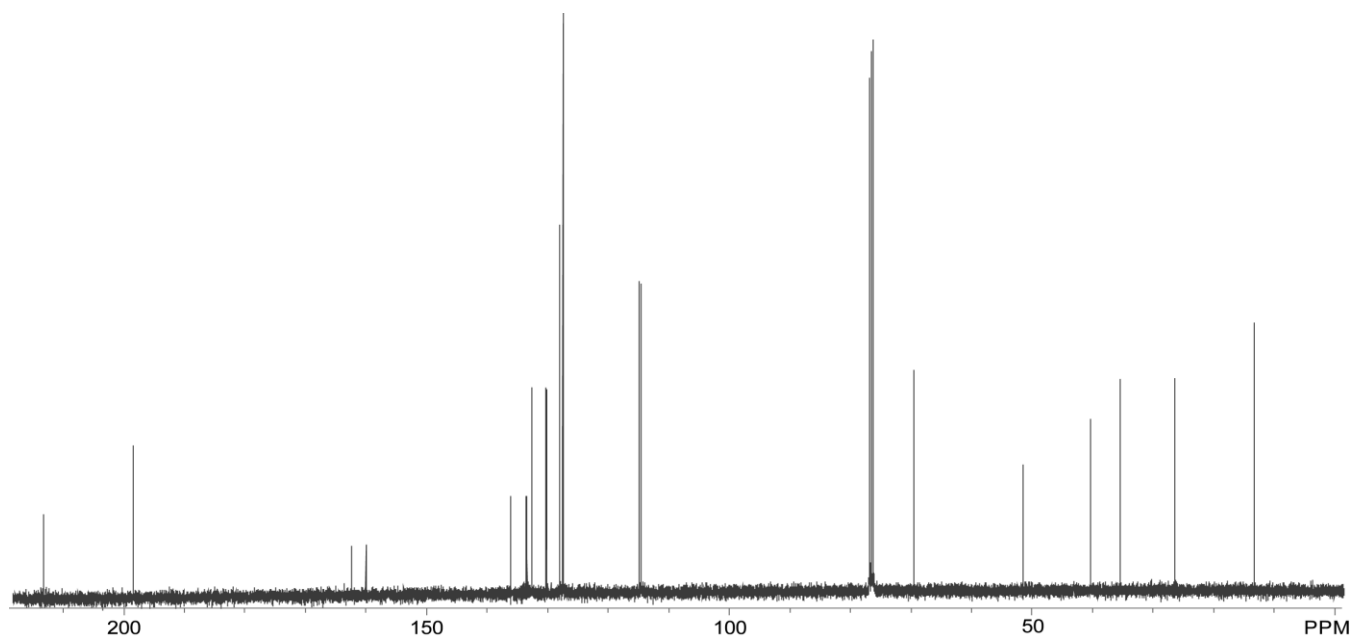
^1H -NMR-spectrum of Xanthate **5e** (CDCl_3).



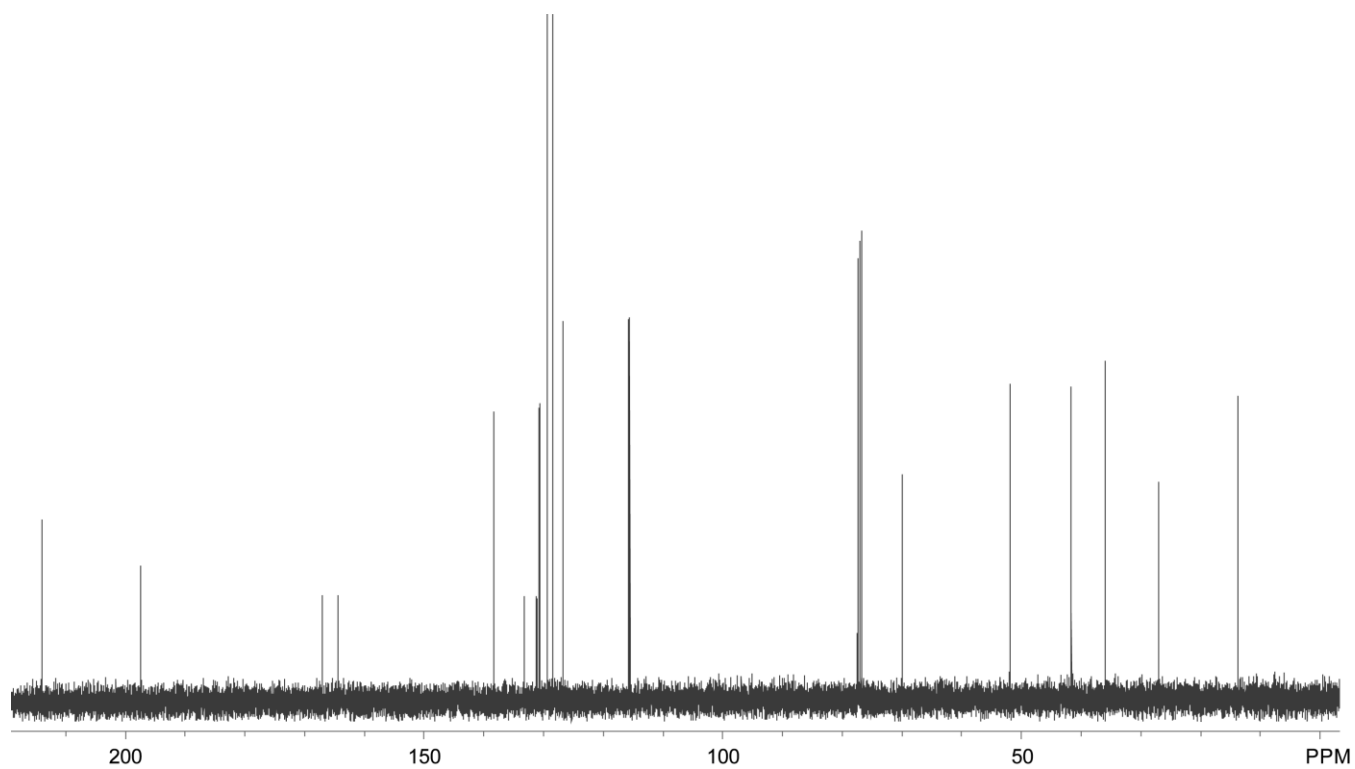
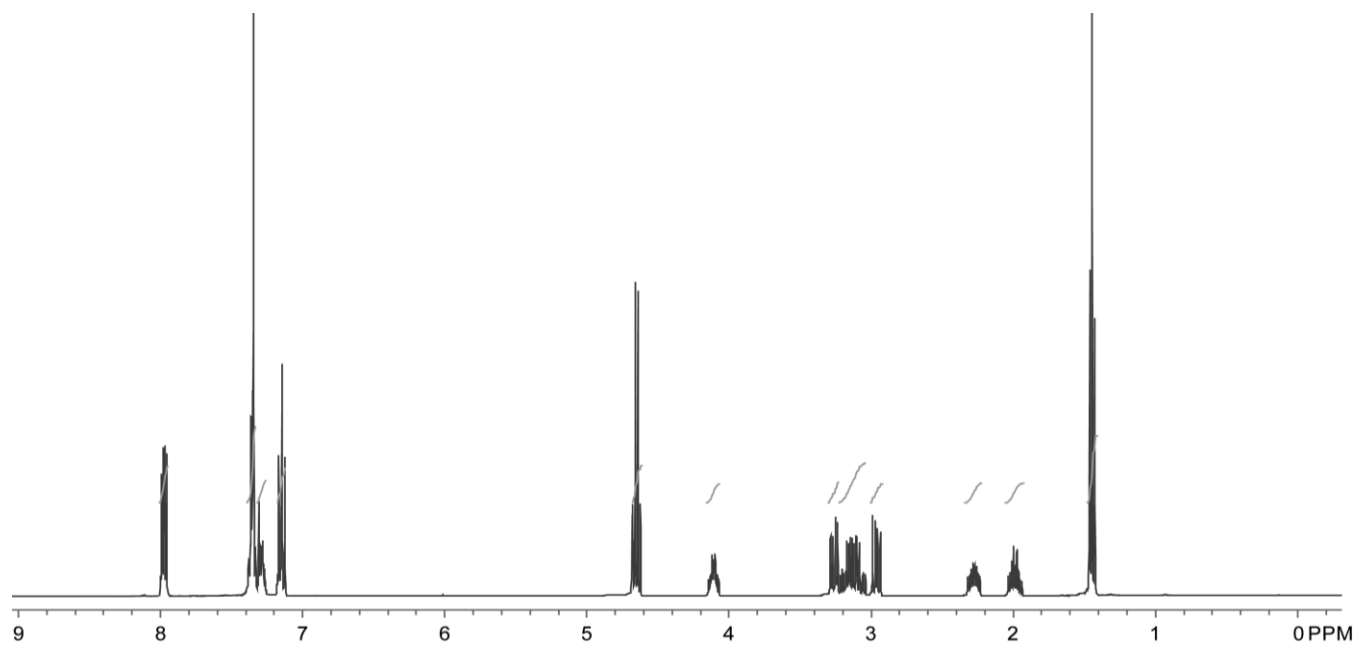
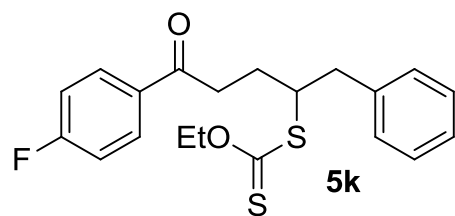
^{13}C -NMR-spectrum of Xanthate **5e** (CDCl_3).

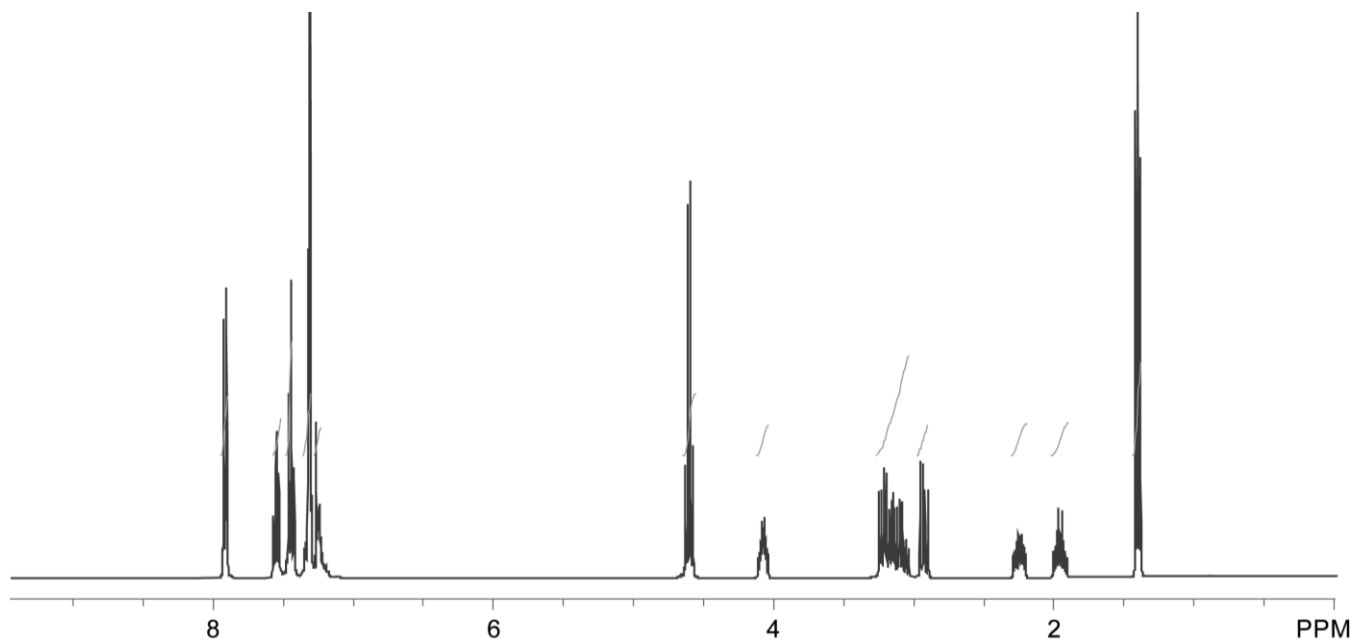
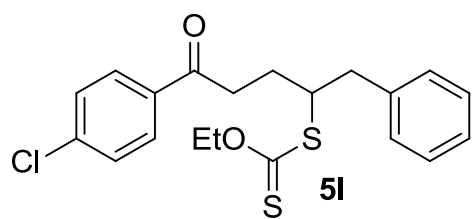


^1H -NMR-spectrum of Xanthate **5g** (CDCl_3).

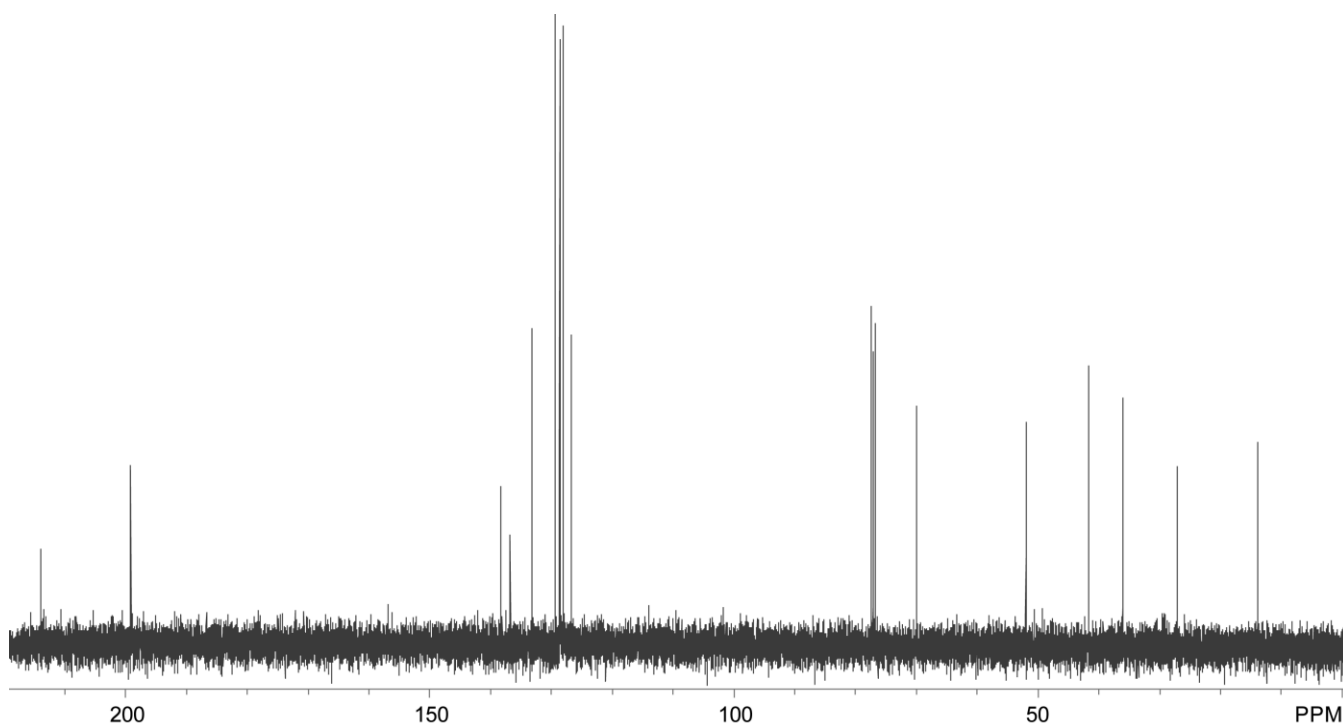


^{13}C -NMR-spectrum of Xanthate **5g** (CDCl_3).

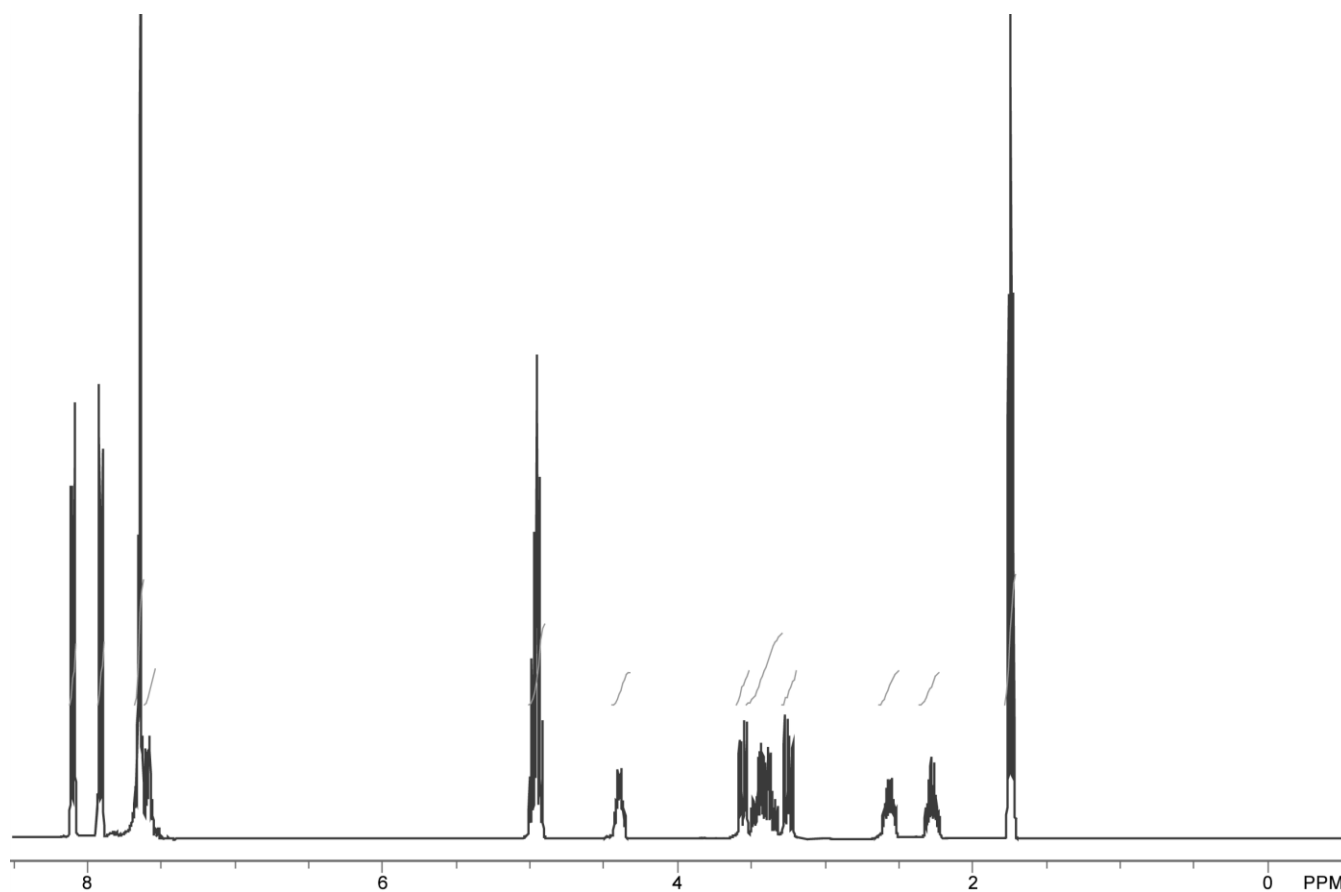
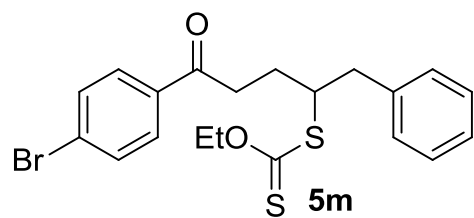




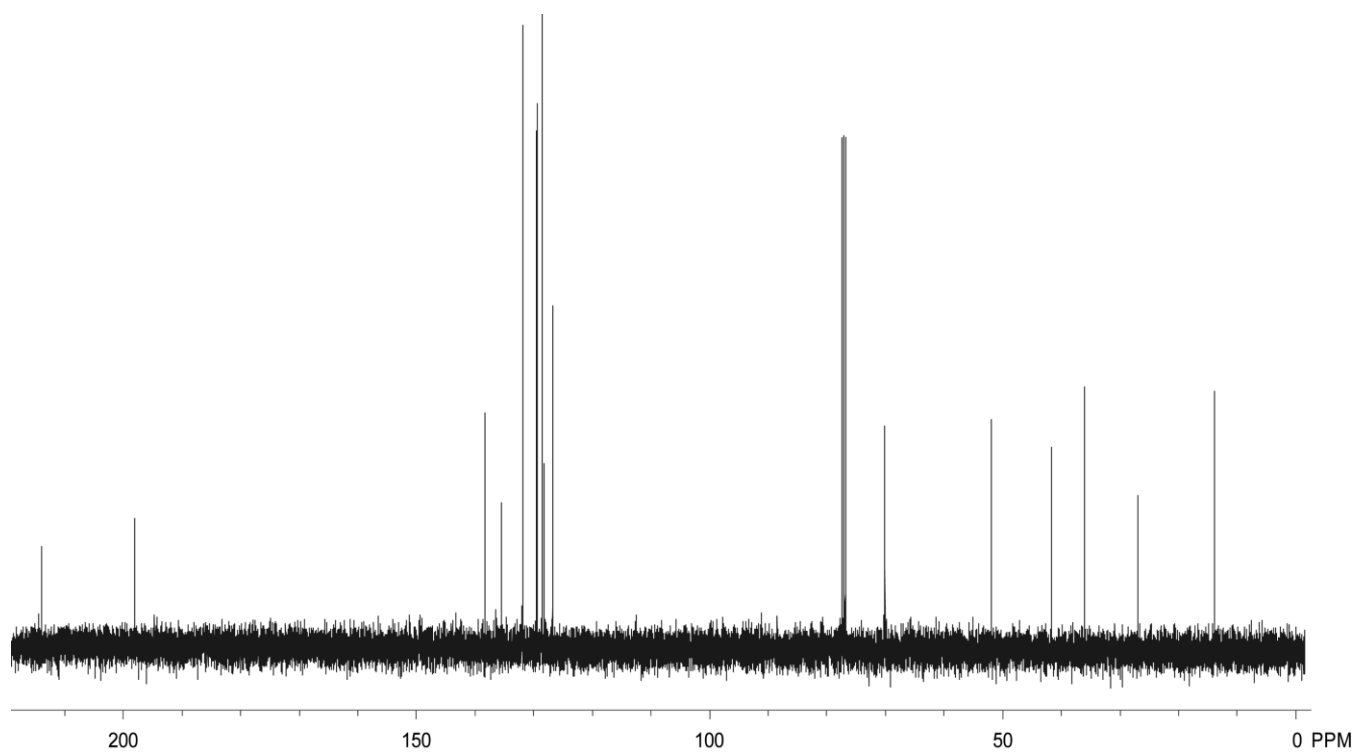
^1H -NMR-spectrum of Xanthate **5I** (CDCl_3).



^{13}C -NMR-spectrum of Xanthate **5I** (CDCl_3).

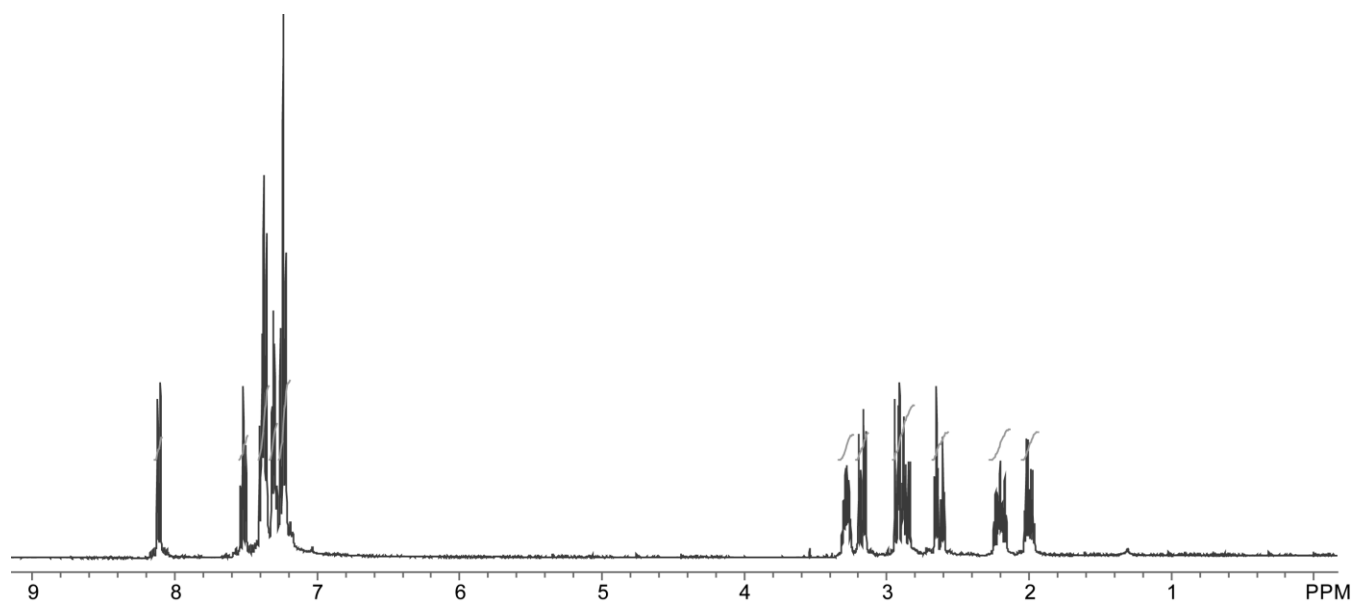
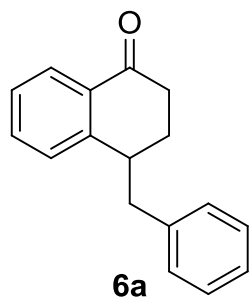


^1H -NMR-spectrum of Xanthate **5m** (CDCl_3).

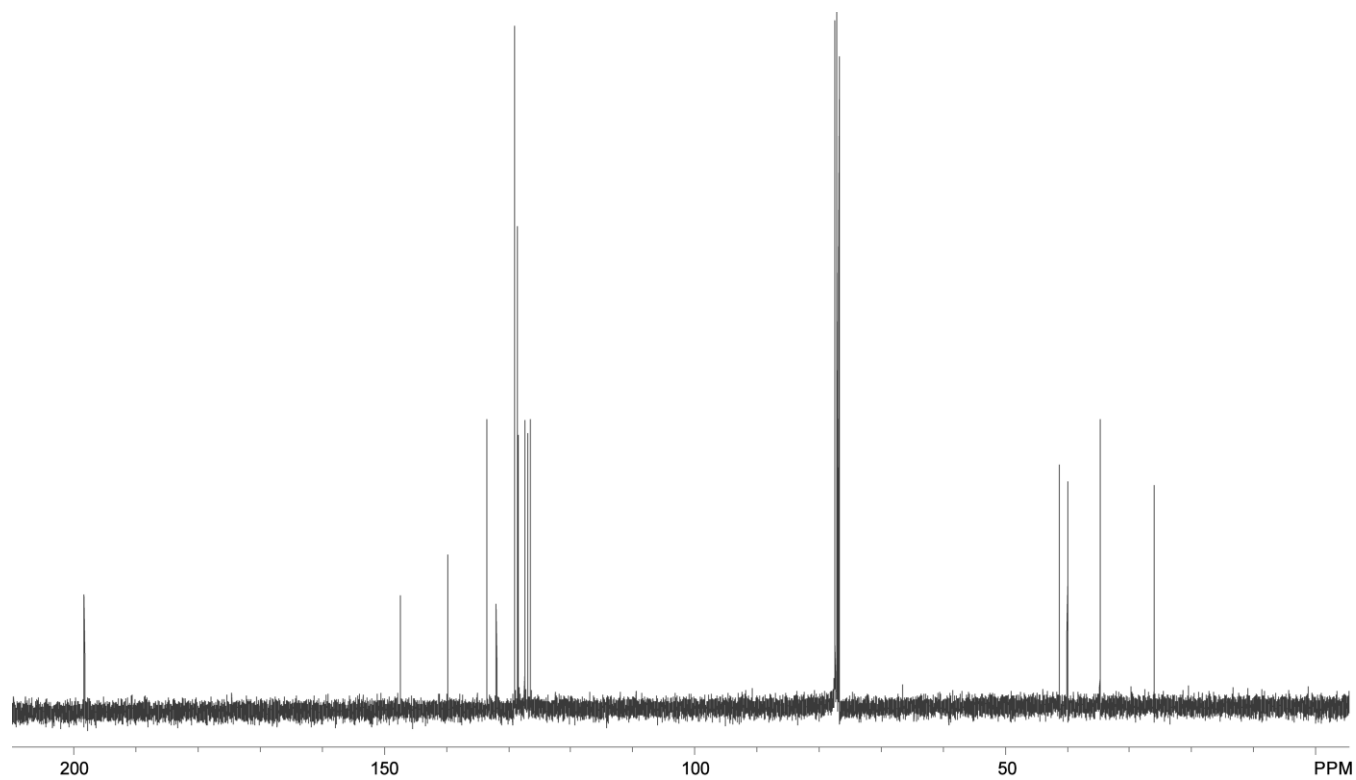


^{13}C -NMR-spectrum of Xanthate **5m** (CDCl_3).

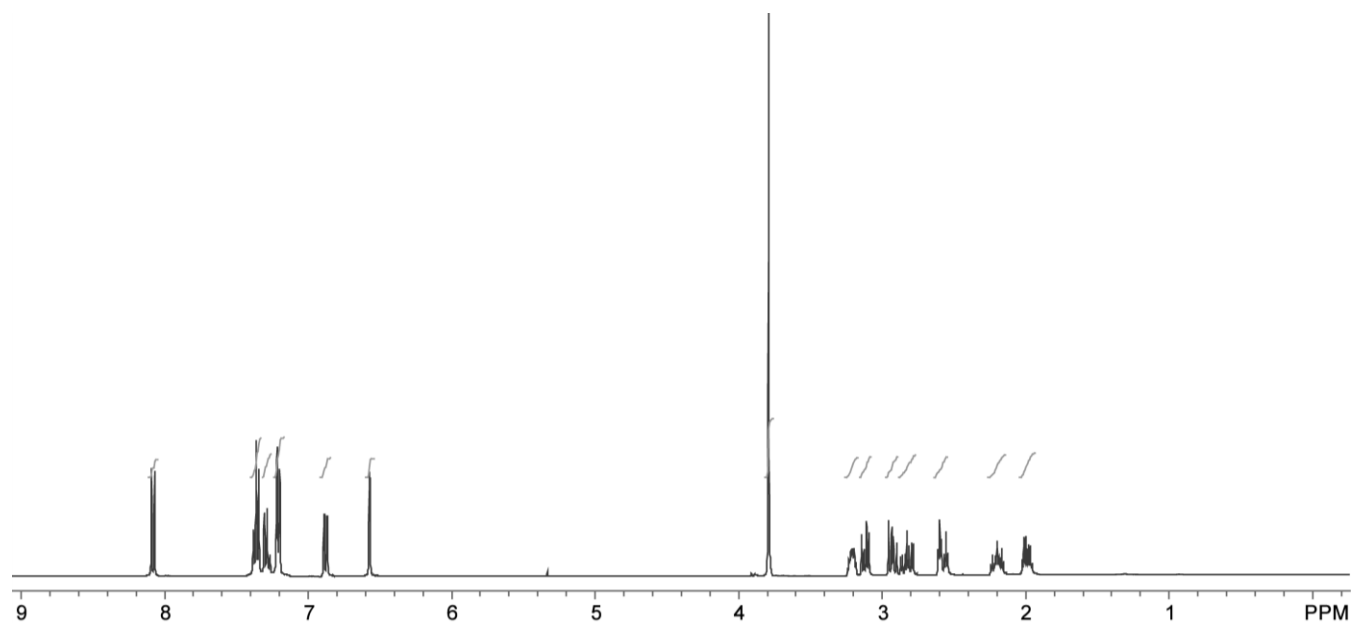
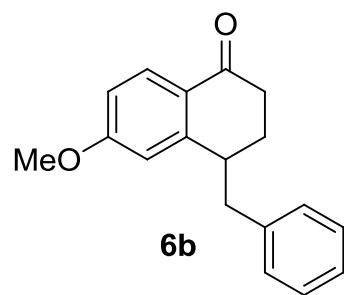
Tetralones 6:



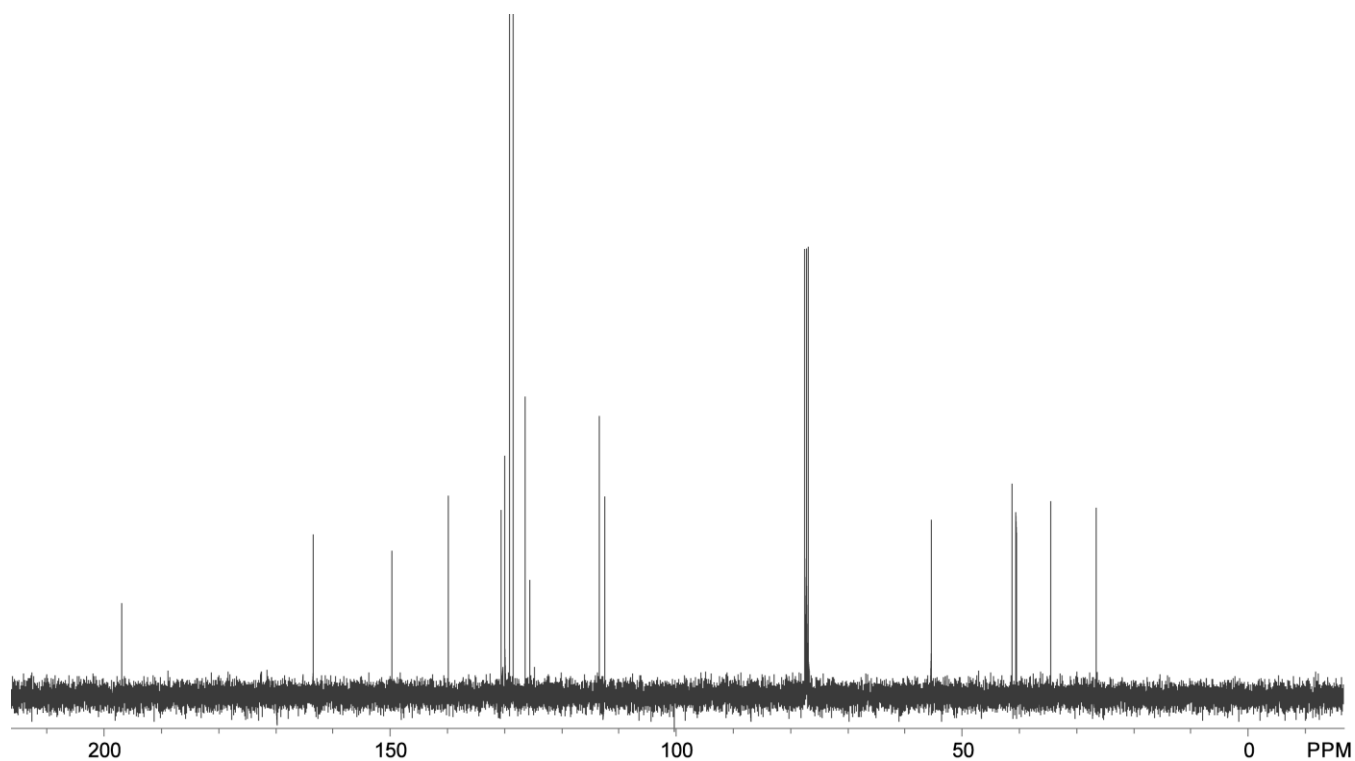
^1H -NMR-spectrum of Tetralone **6a** (CDCl_3).



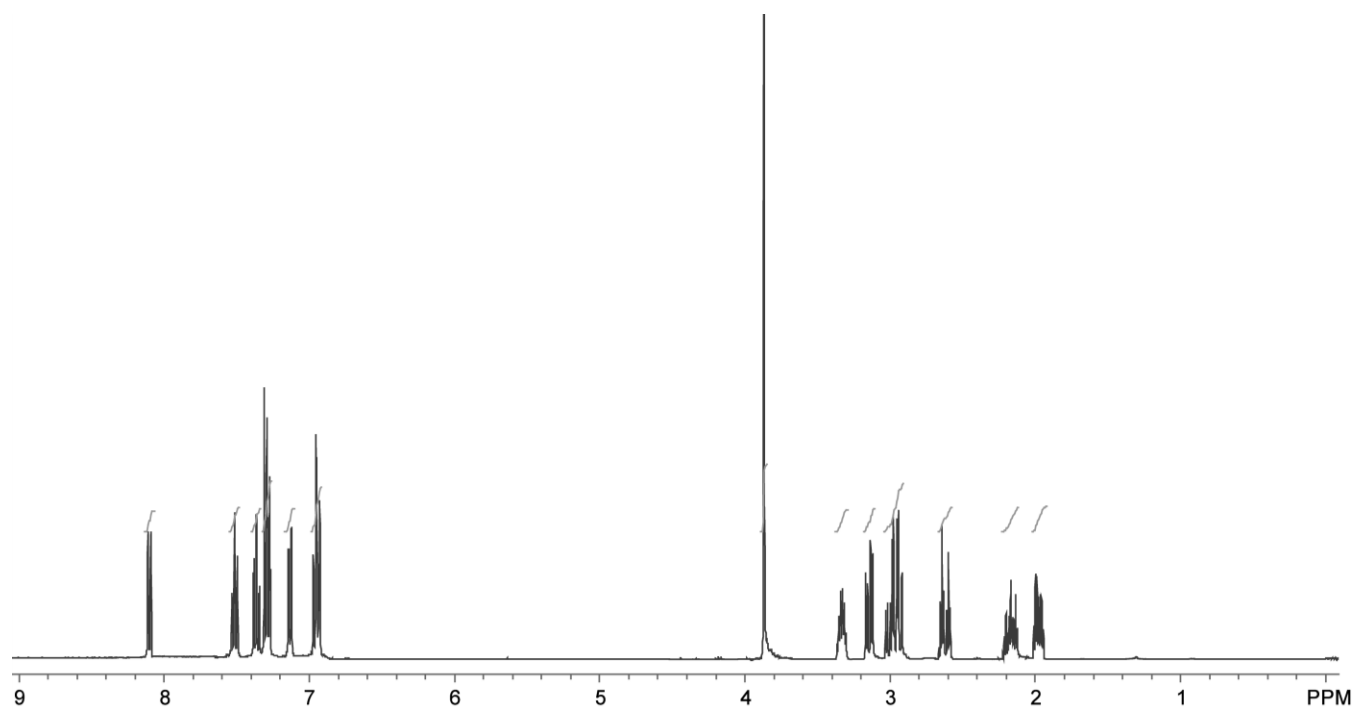
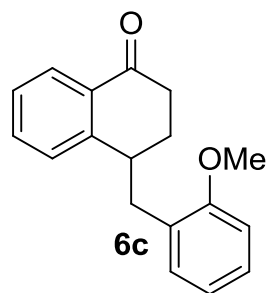
^{13}C -NMR-spectrum of Tetralone **6a** (CDCl_3).



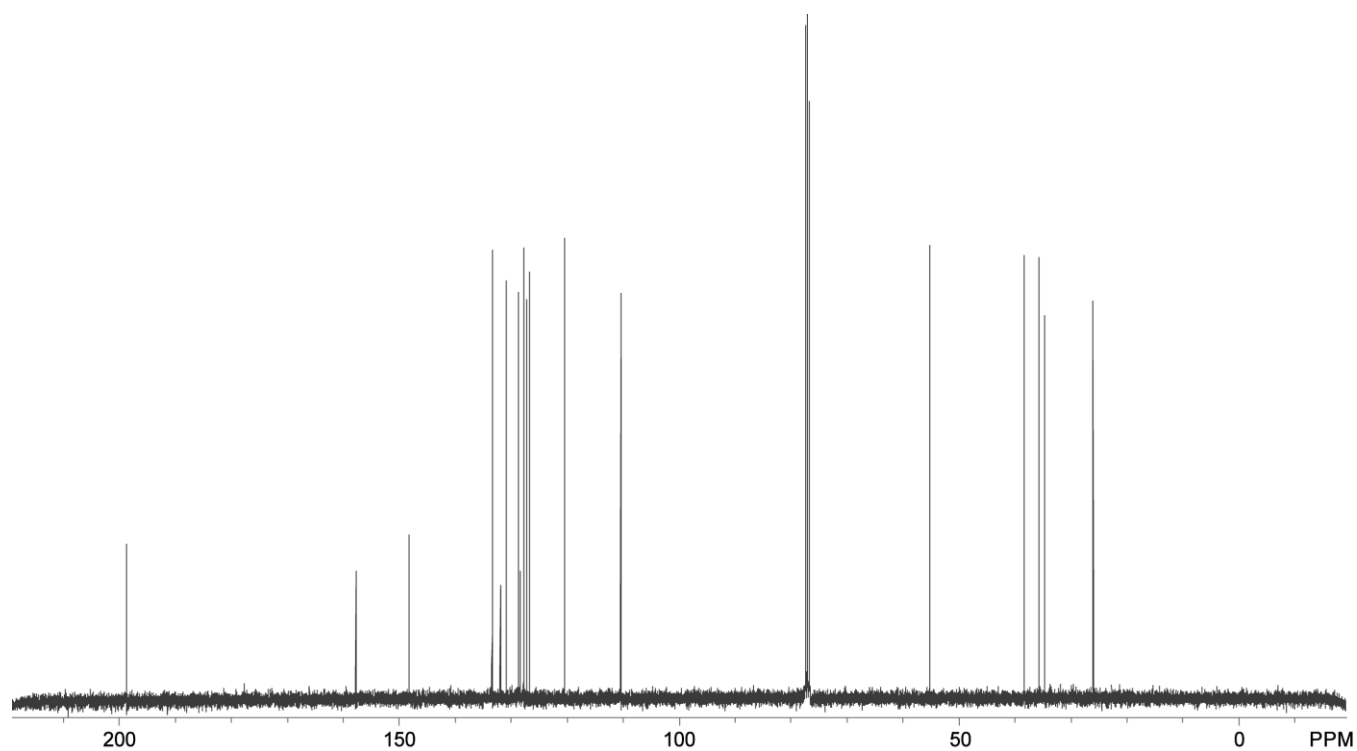
^1H -NMR-spectrum of Tetralone **6b** (CDCl_3).



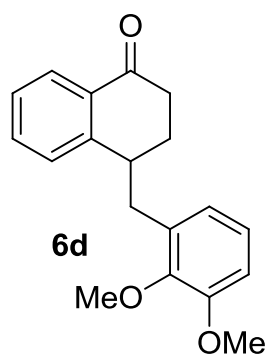
^{13}C -NMR-spectrum of Tetralone **6b** (CDCl_3).

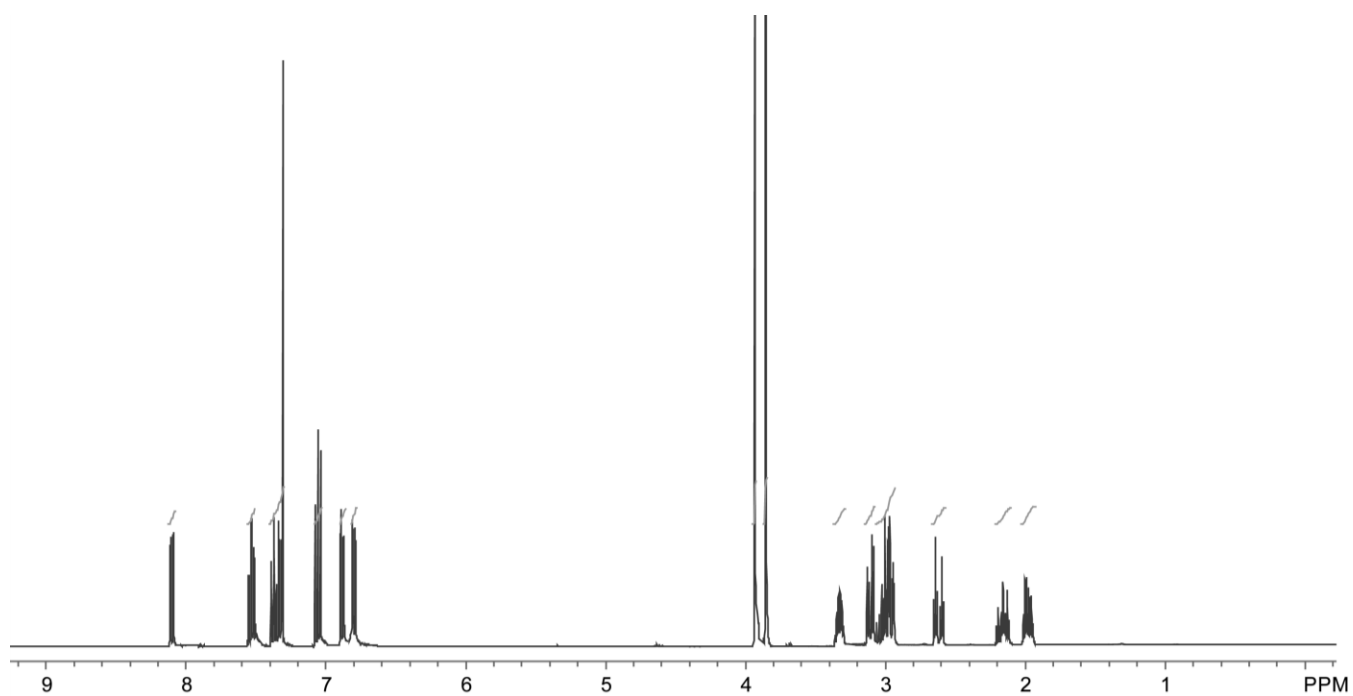


^1H -NMR-spectrum of Tetralone **6c** (CDCl_3).

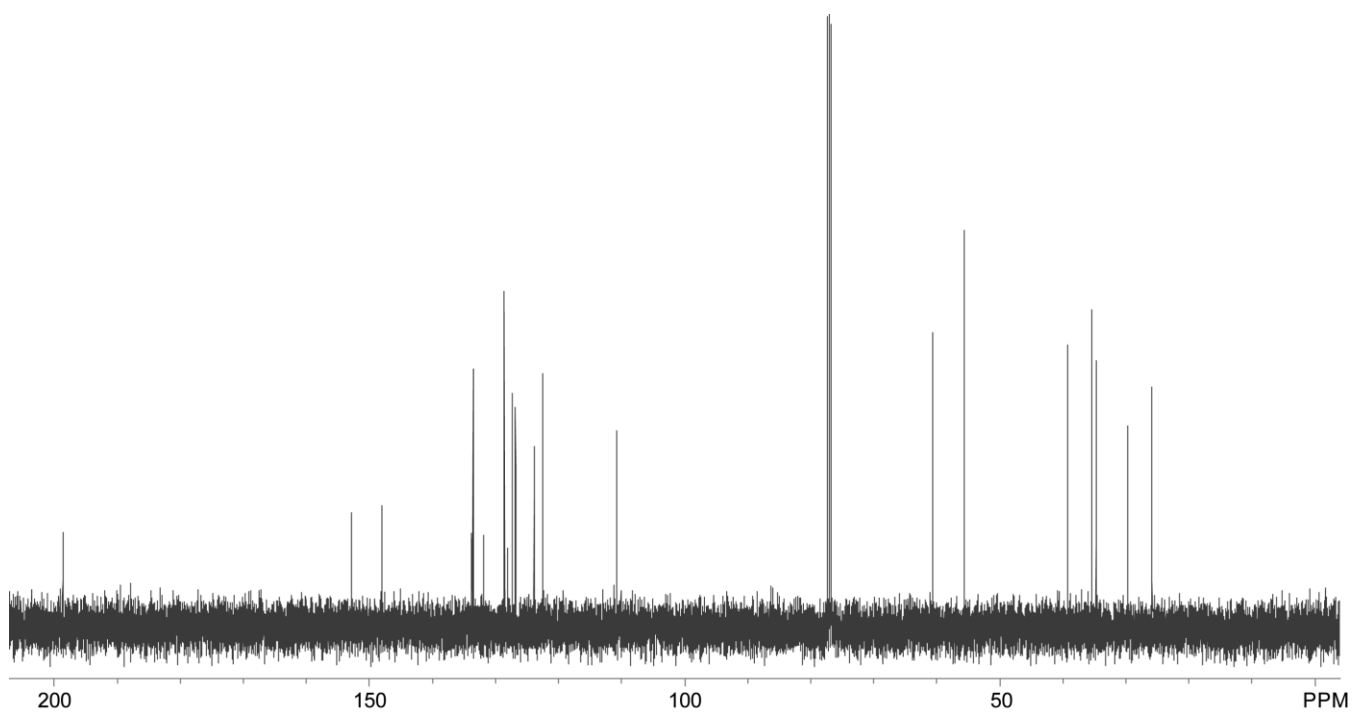


^{13}C -NMR-spectrum of Tetralone **6c** (CDCl_3).

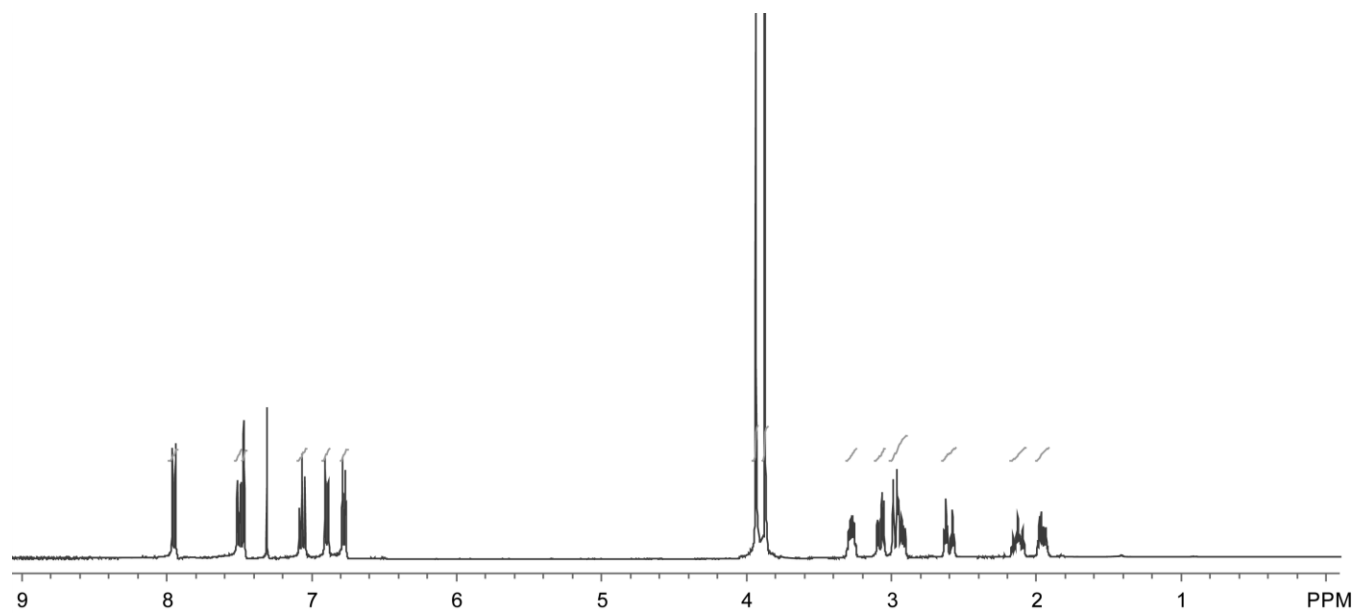
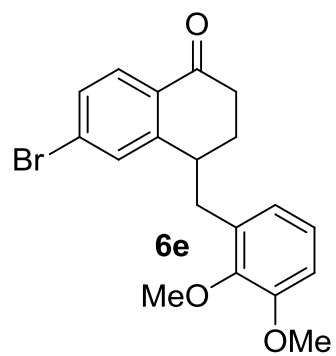




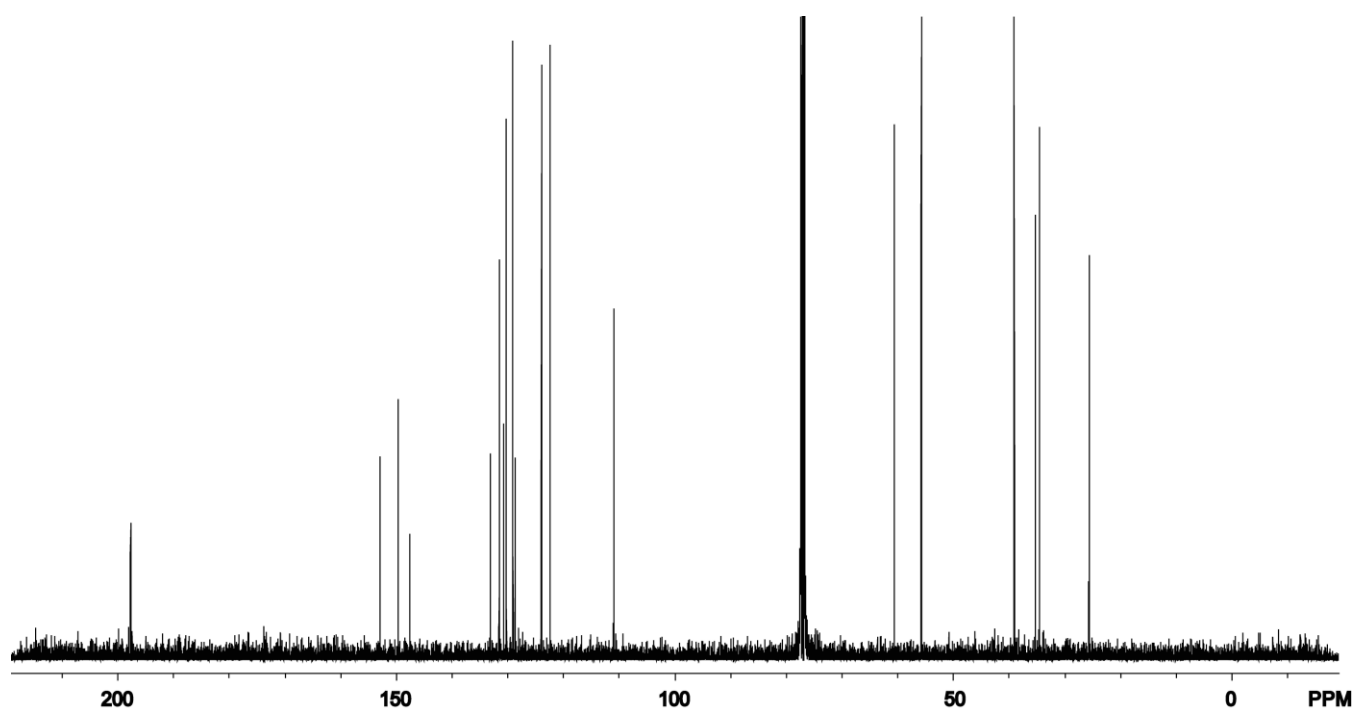
^1H -NMR-spectrum of Tetralone **6d** (CDCl_3).



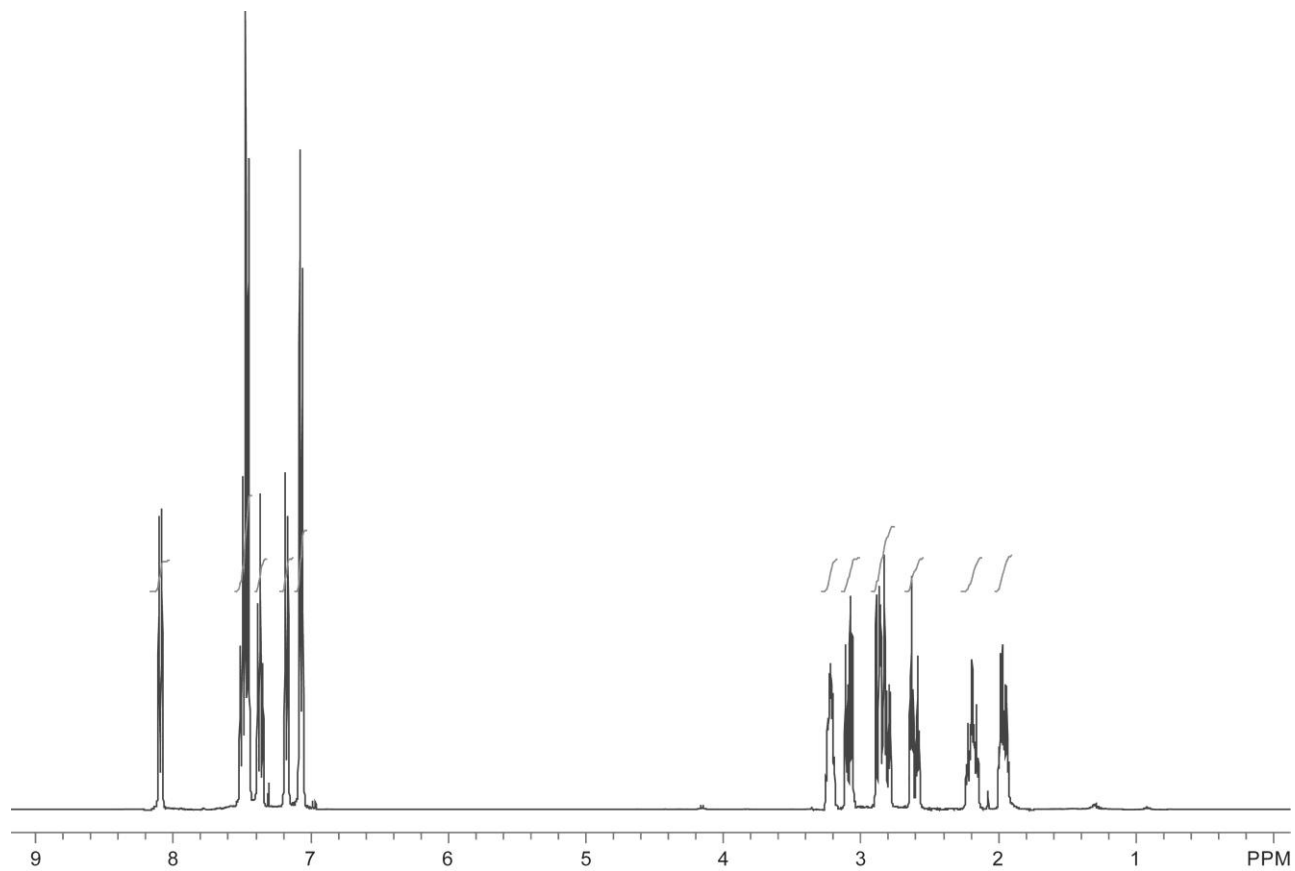
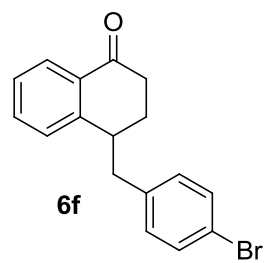
^{13}C -NMR-spectrum of Tetralone **6d** (CDCl_3).



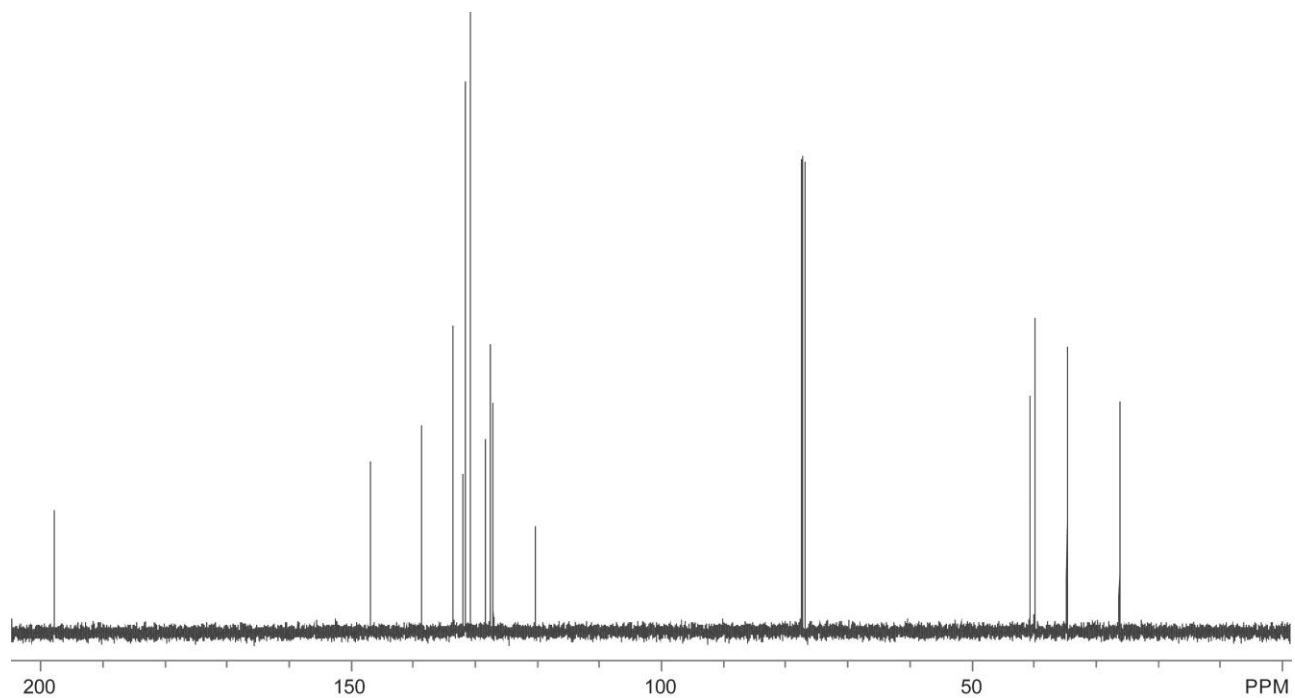
^1H -NMR-spectrum of Tetralone **6e** (CDCl_3).



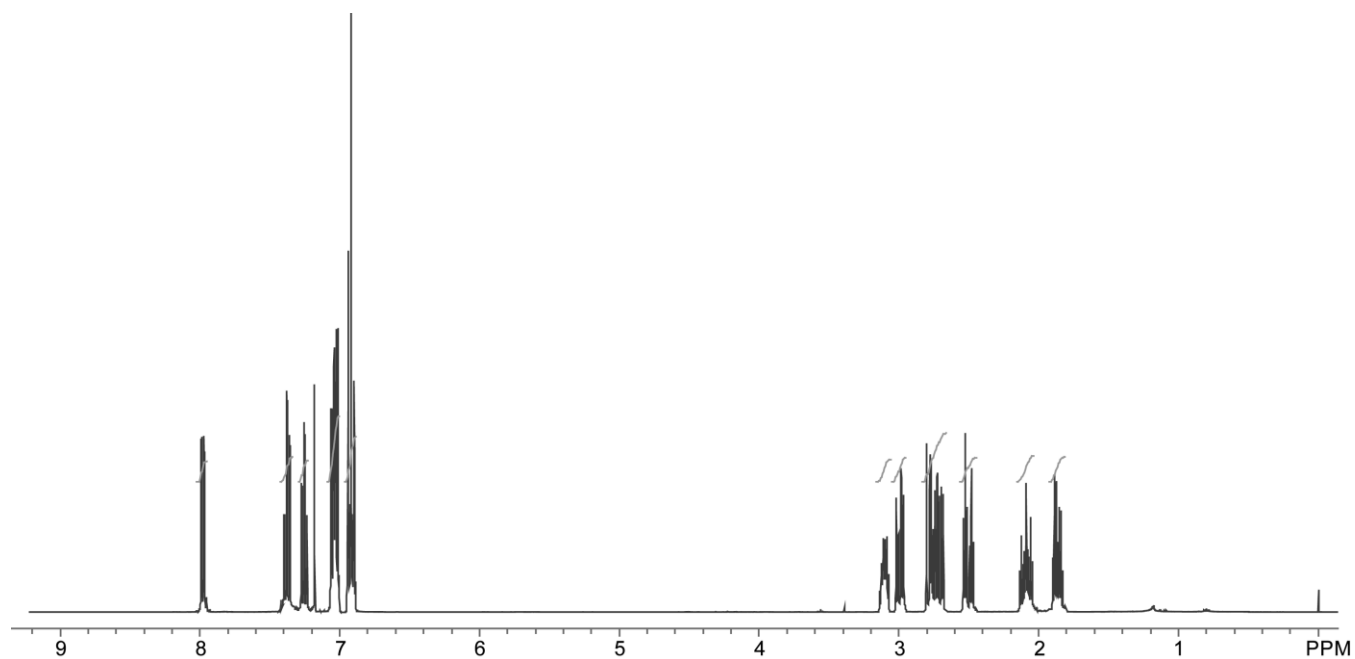
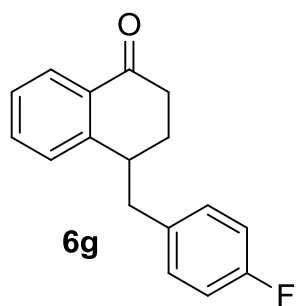
^{13}C -NMR-spectrum of Tetralone **6e** (CDCl_3).



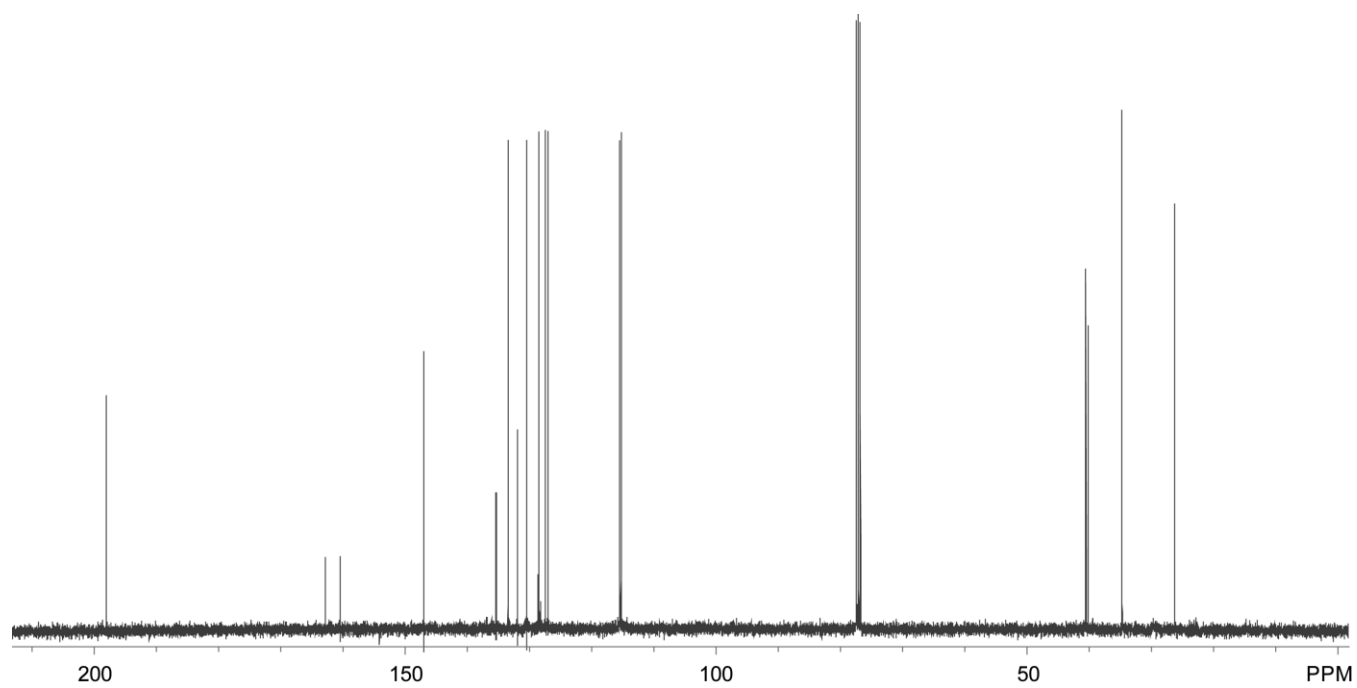
^1H -NMR-spectrum of Tetralone **6f** (CDCl_3).



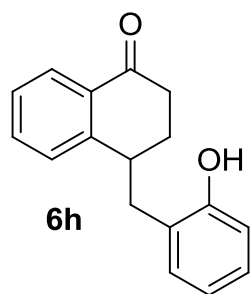
^{13}C -NMR-spectrum of Tetralone **6f** (CDCl_3).

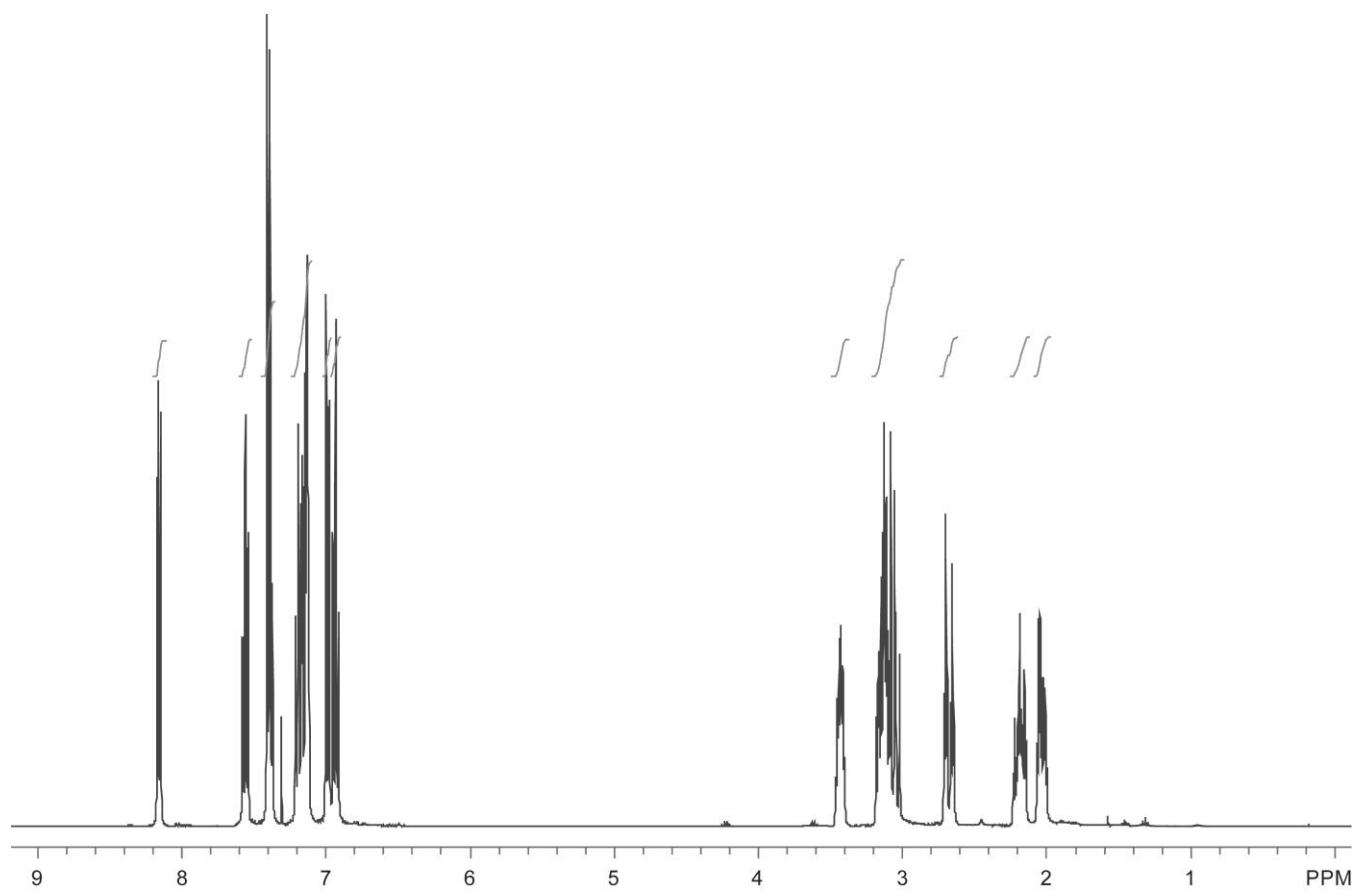


^1H -NMR-spectrum of Tetralone **6g** (CDCl_3).

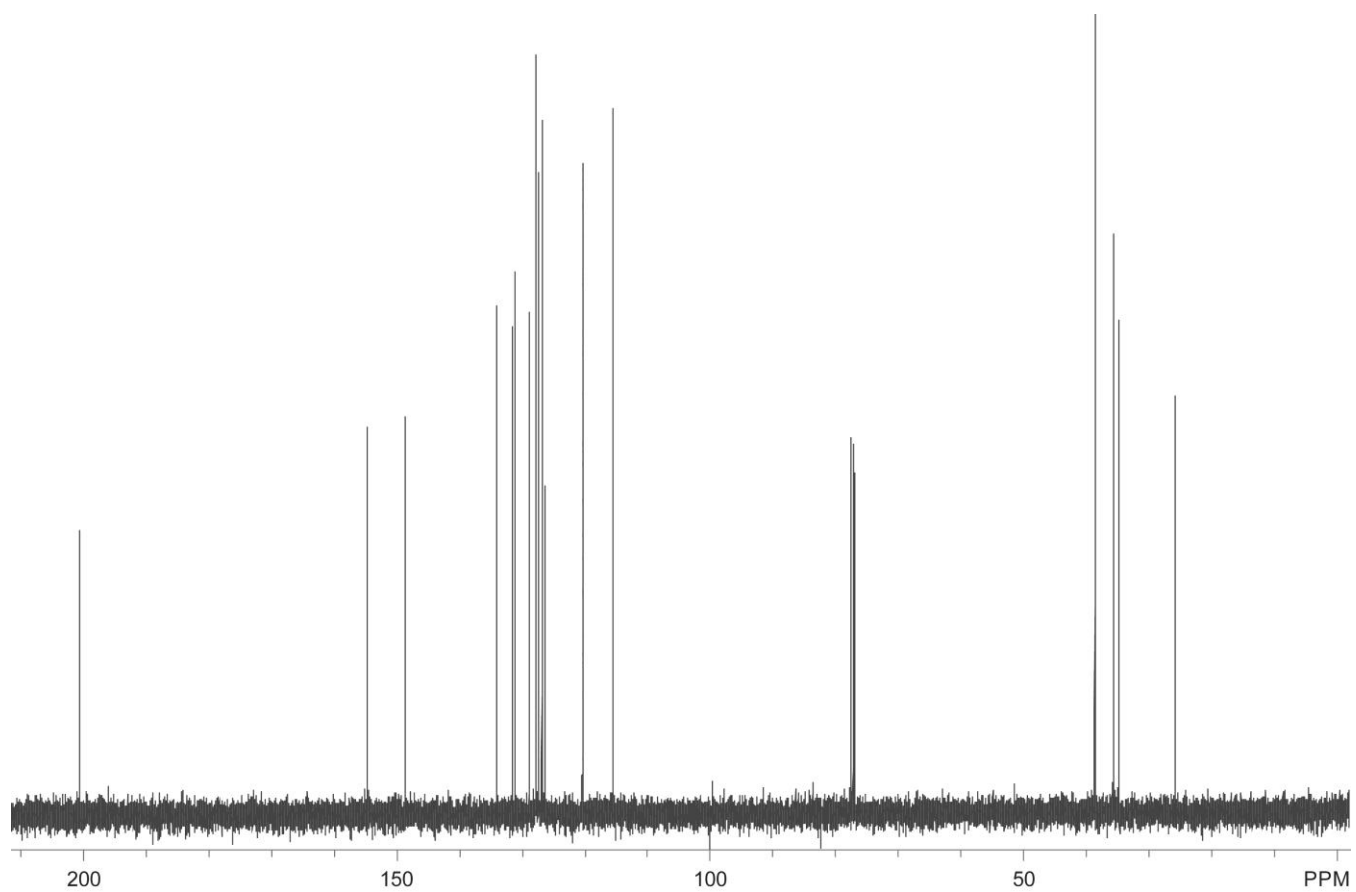


^{13}C -NMR-spectrum of Tetralone **6g** (CDCl_3).

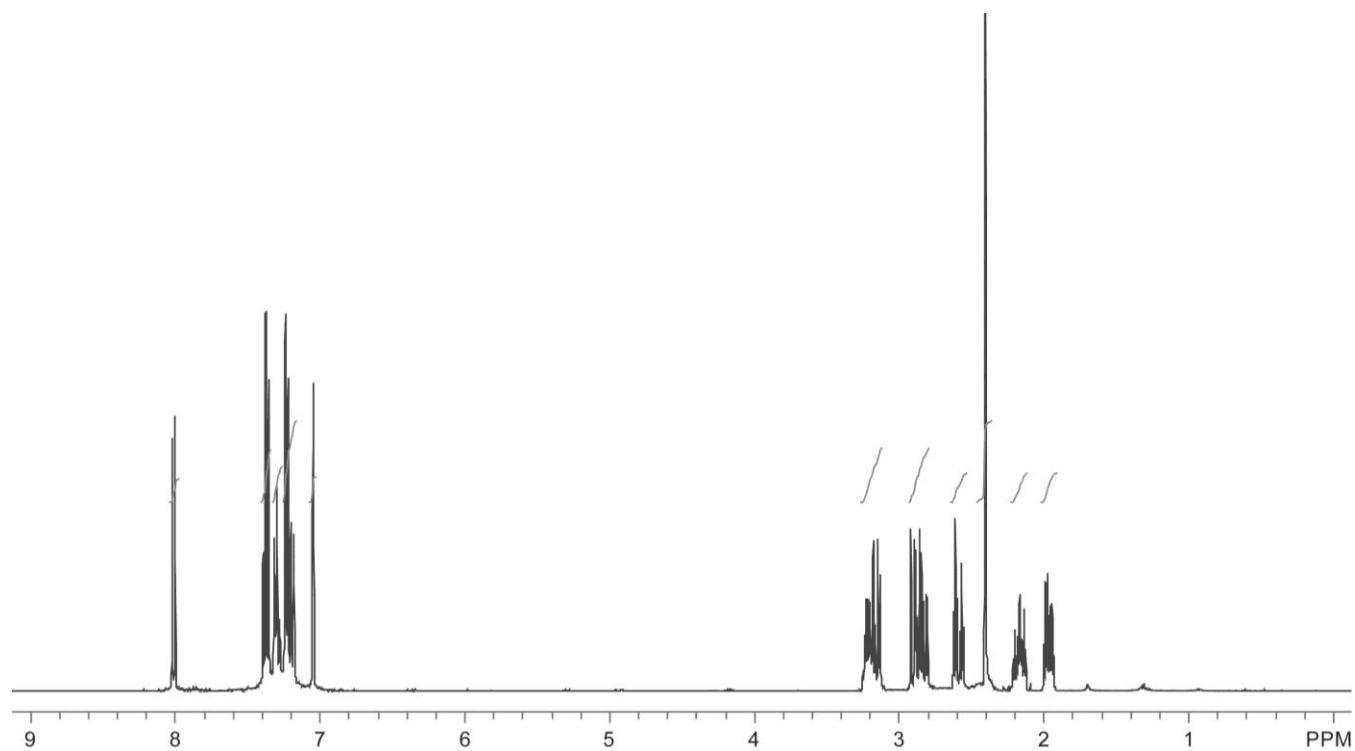
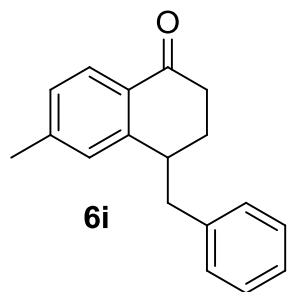




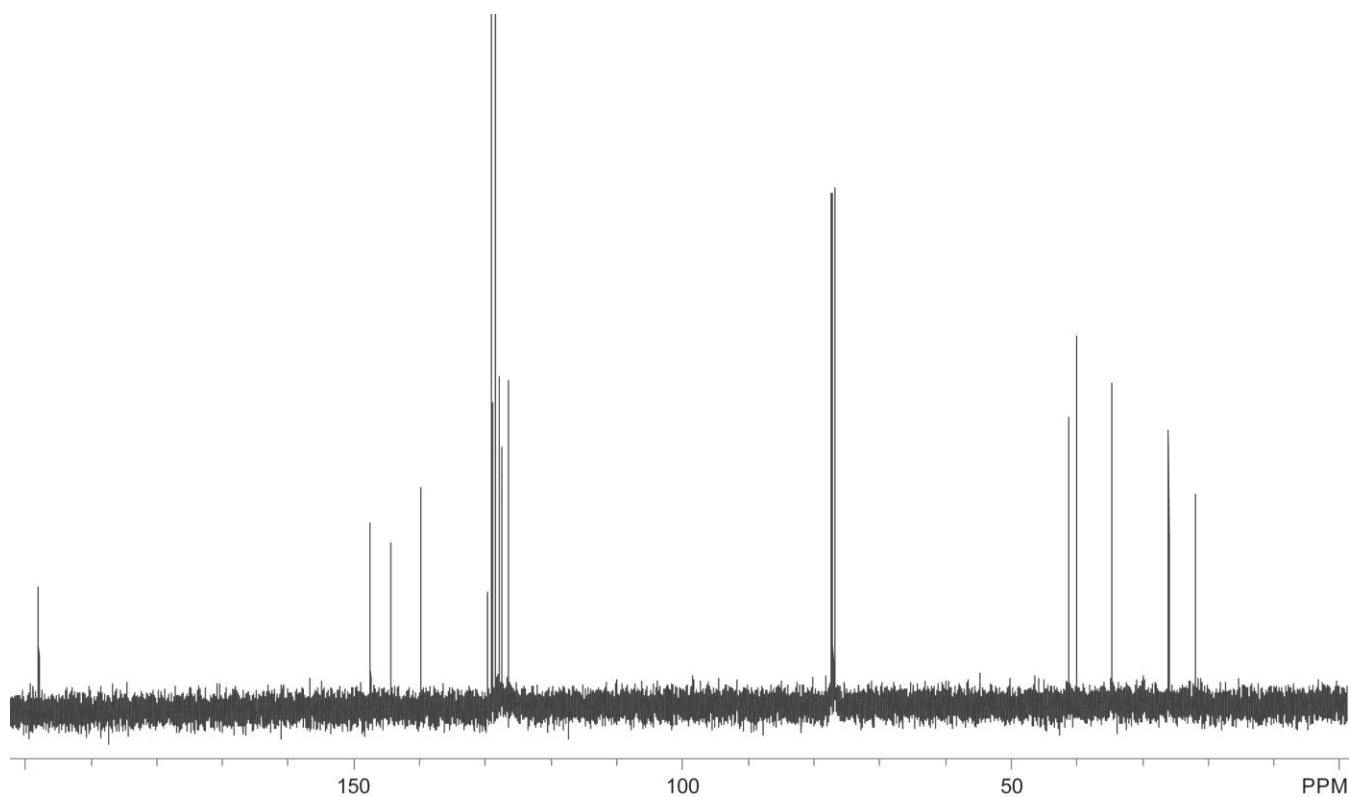
^1H -NMR-spectrum of Tetralone **6h** (CDCl_3).



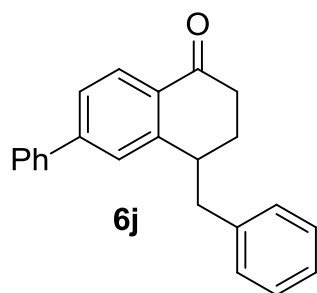
^{13}C -NMR-spectrum of Tetralone **6h** (CDCl_3).

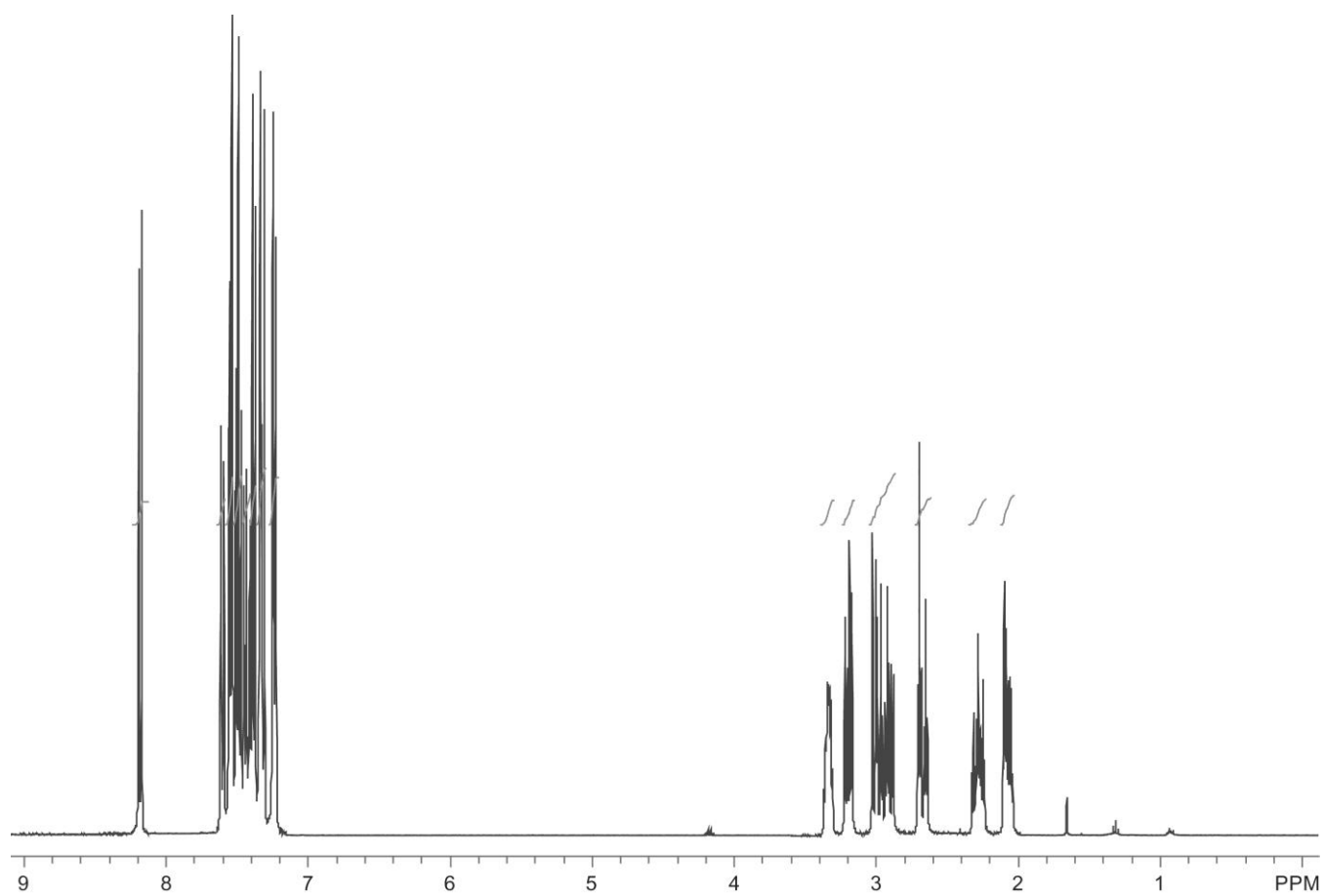


^1H -NMR-spectrum of Tetralone **6i** (CDCl_3).

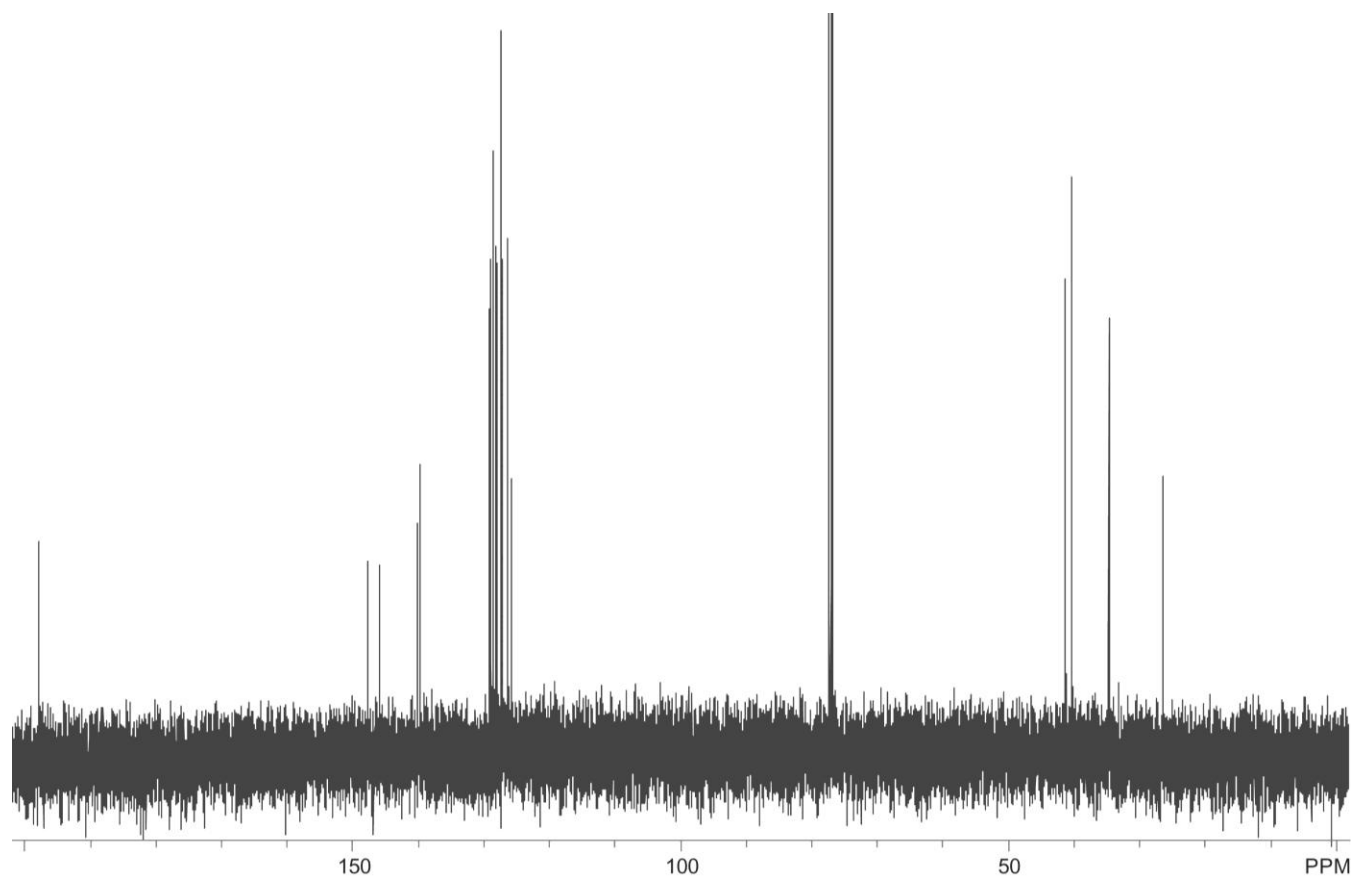


^{13}C -NMR-spectrum of Tetralone **6i** (CDCl_3).

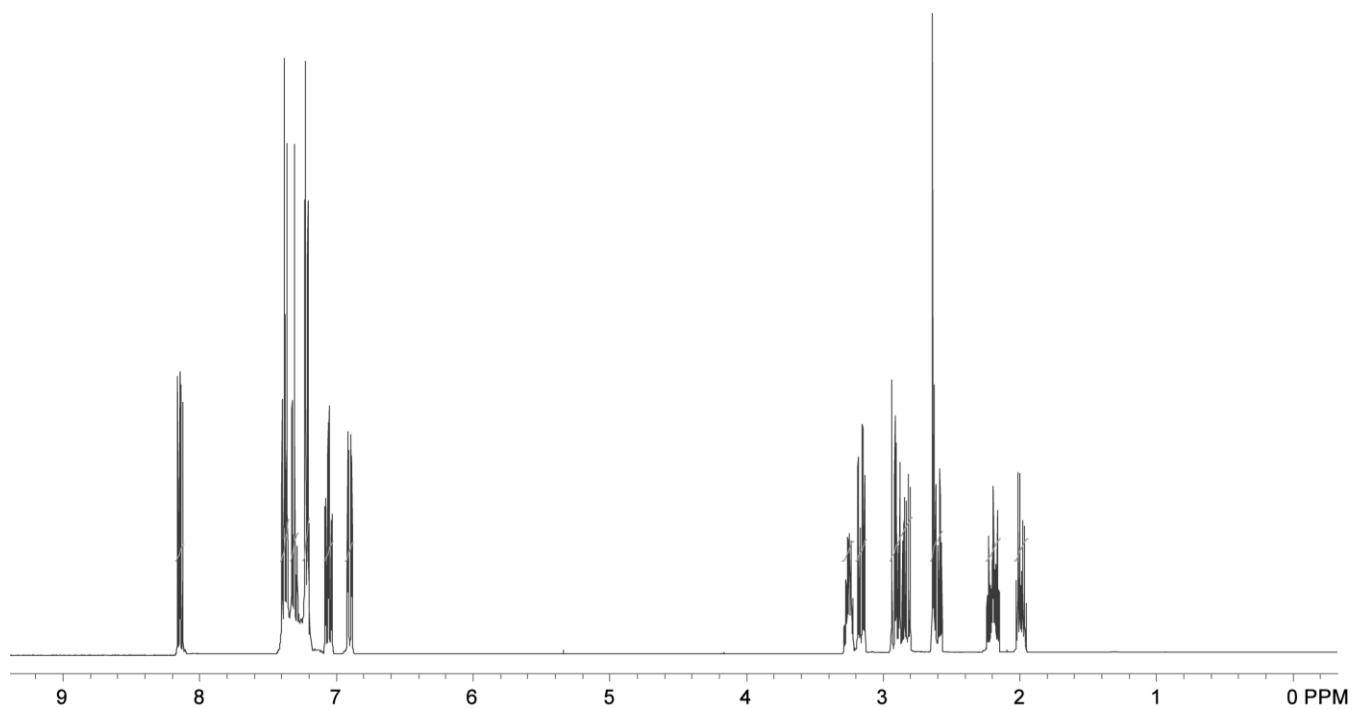
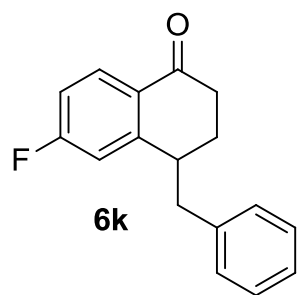




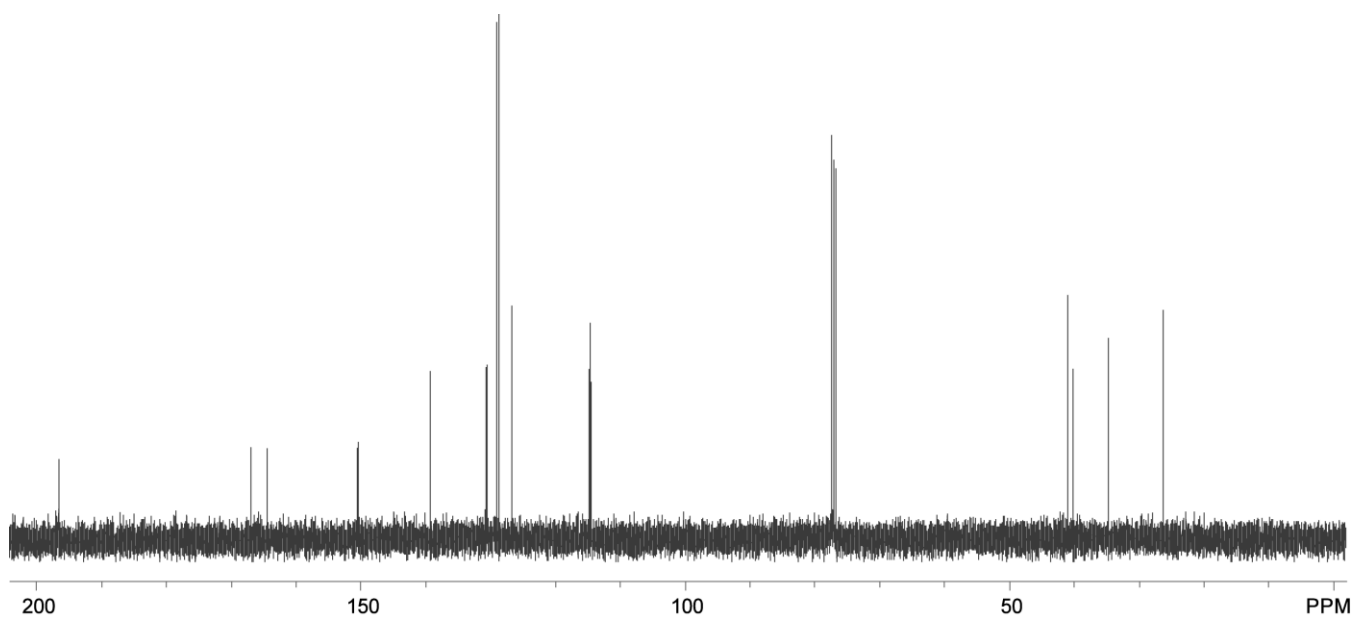
^1H -NMR-spectrum of Tetralone **6j** (CDCl_3).



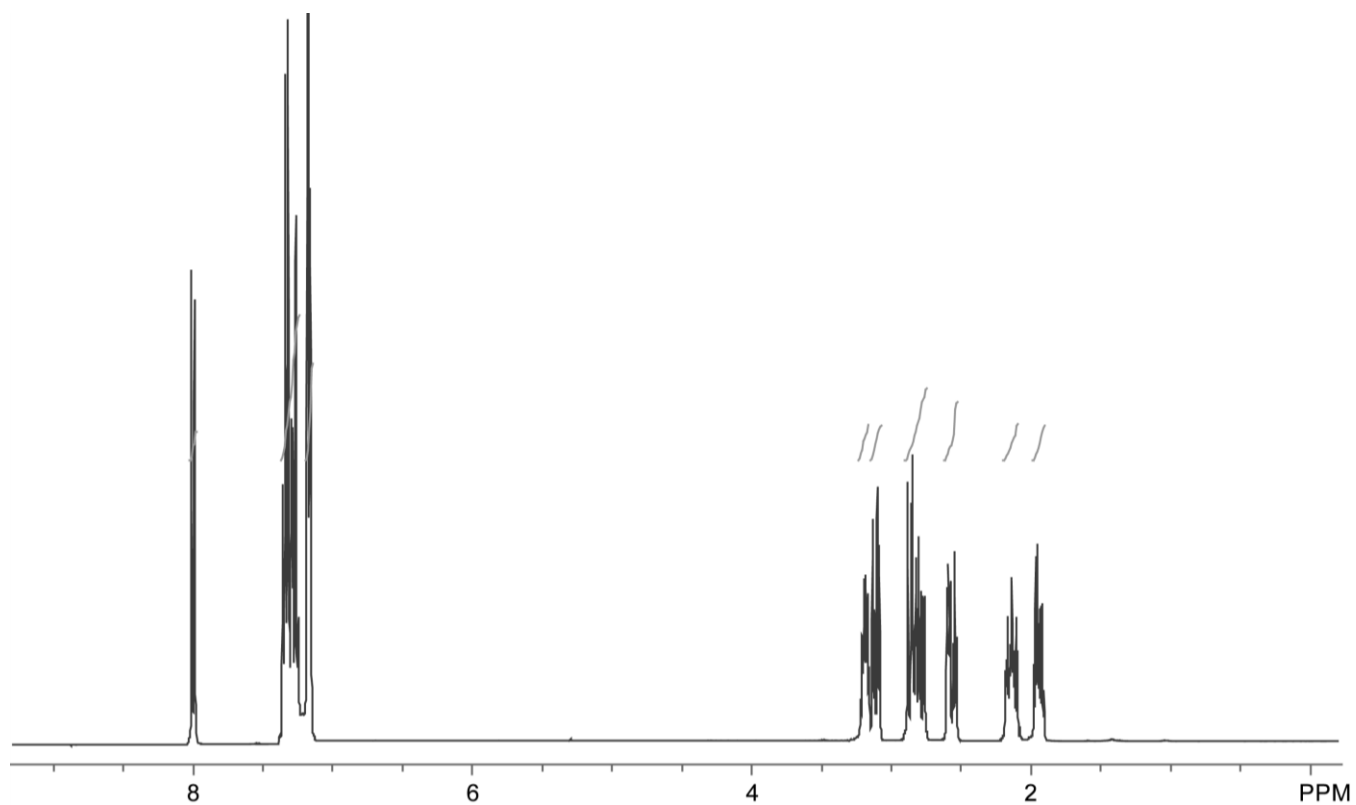
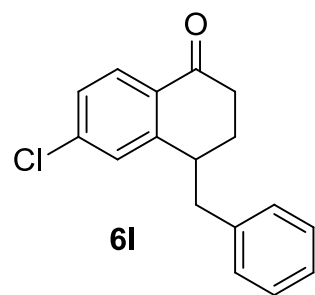
^{13}C -NMR-spectrum of Tetralone **6j** (CDCl_3).



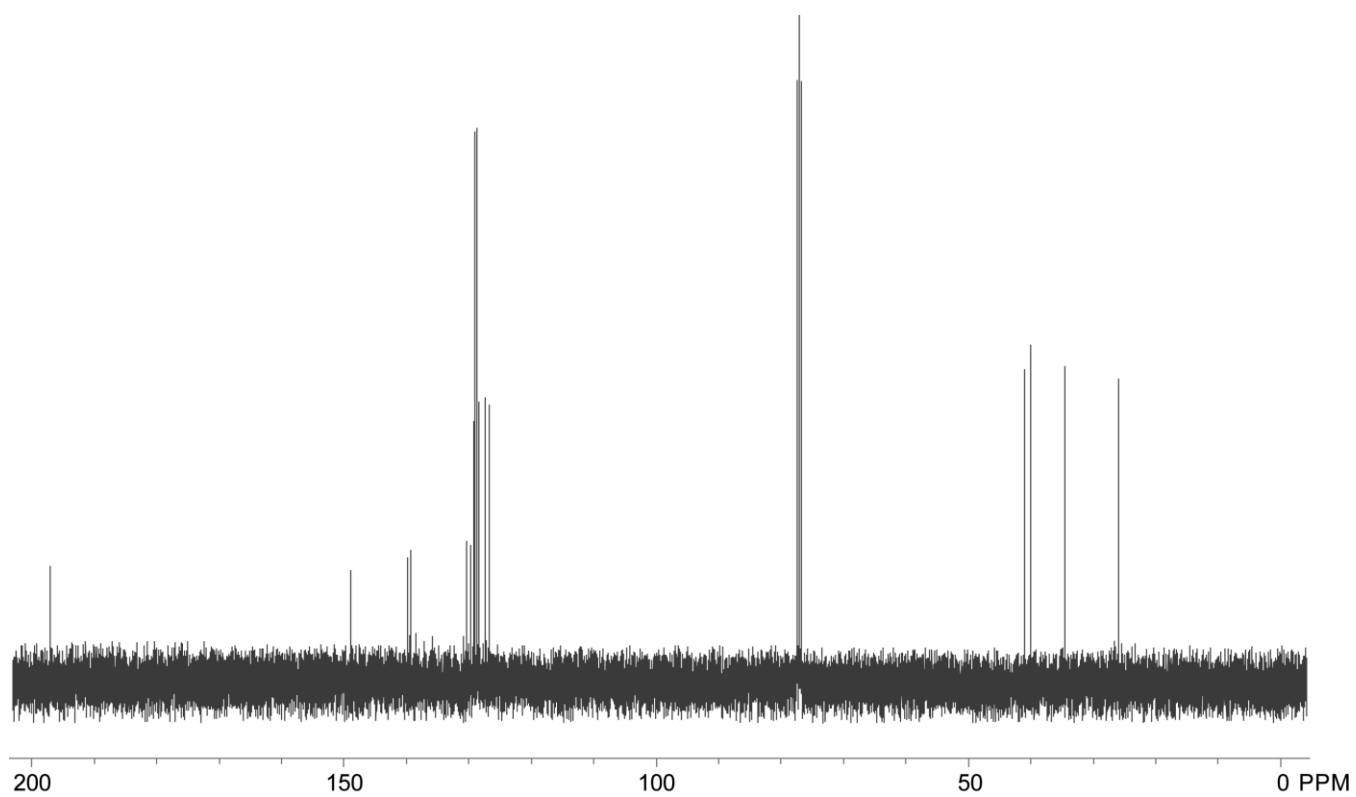
^1H -NMR-spectrum of Tetralone **6k** (CDCl_3).



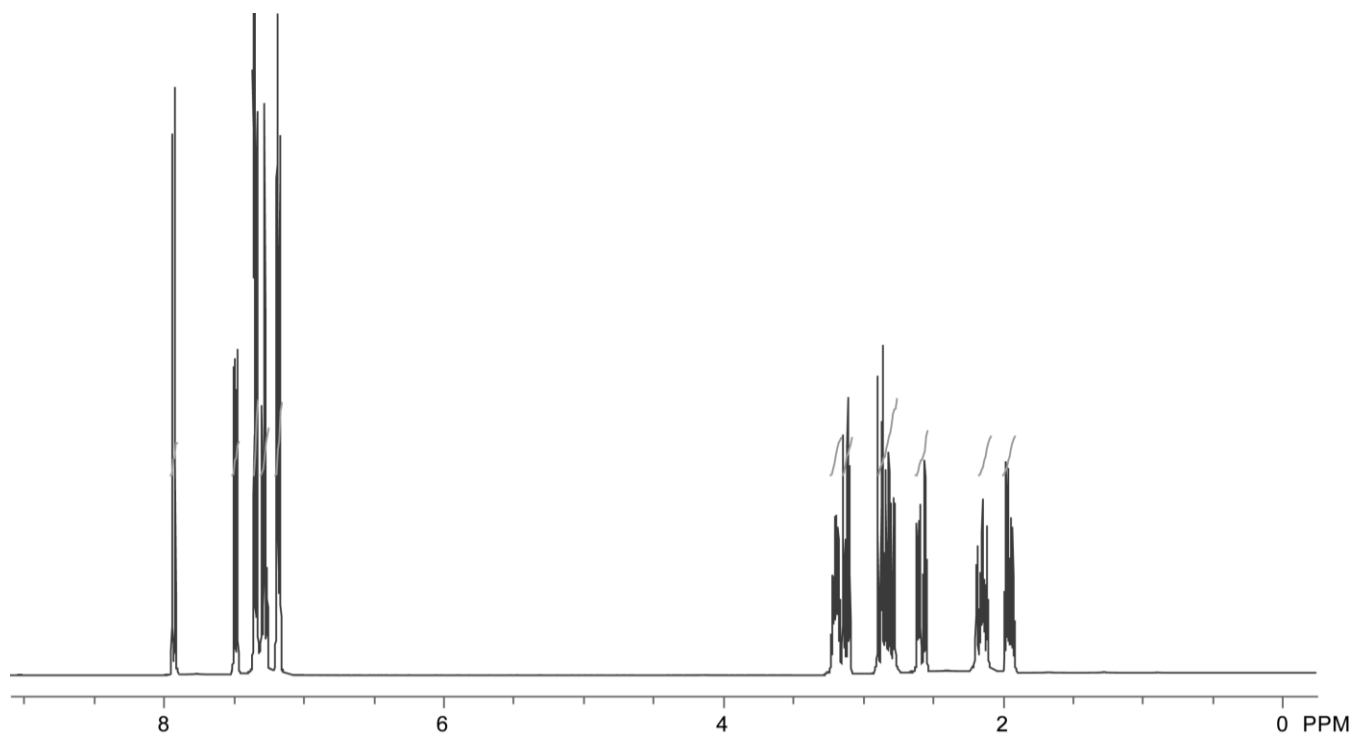
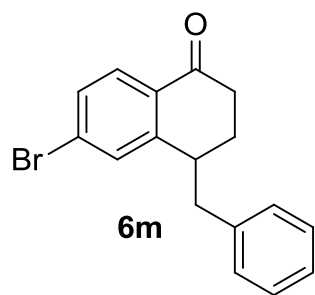
^{13}C -NMR-spectrum of Tetralone **6k** (CDCl_3).



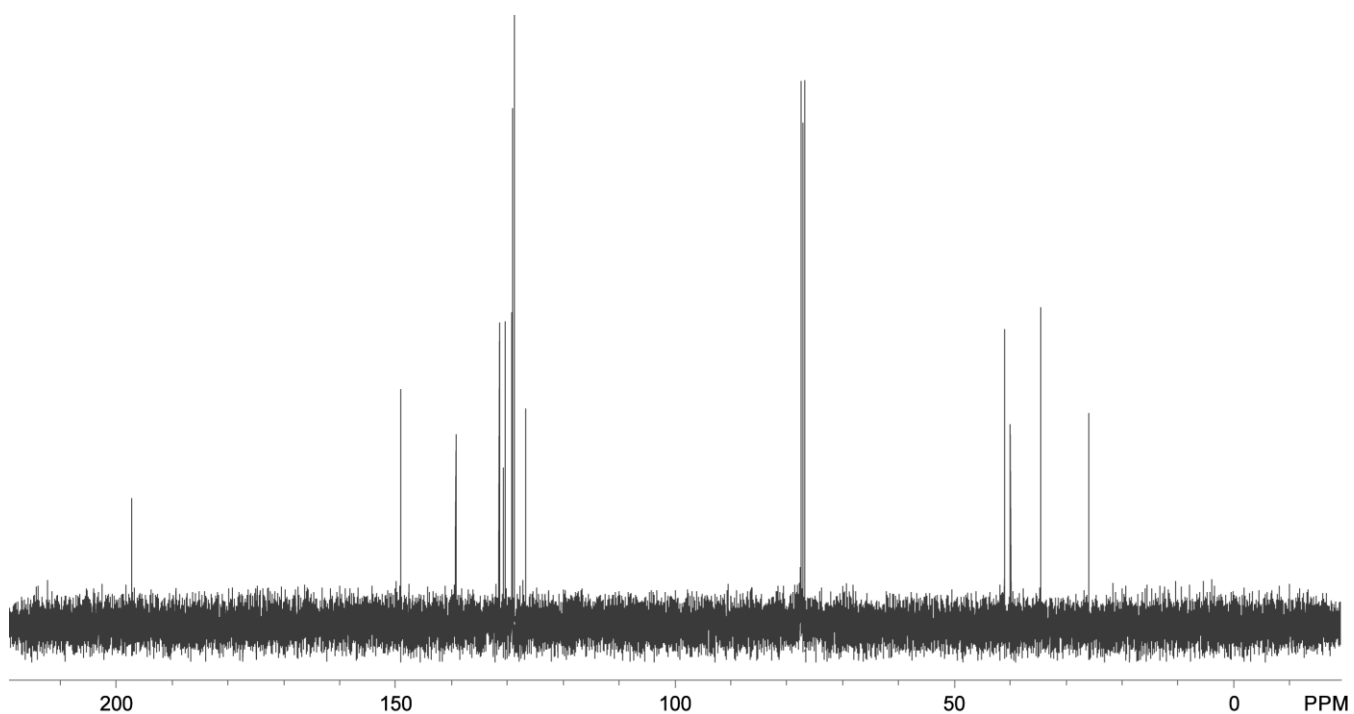
^1H -NMR-spectrum of Tetralone **6l** (CDCl_3).



^{13}C -NMR-spectrum of Tetralone **6l** (CDCl_3).

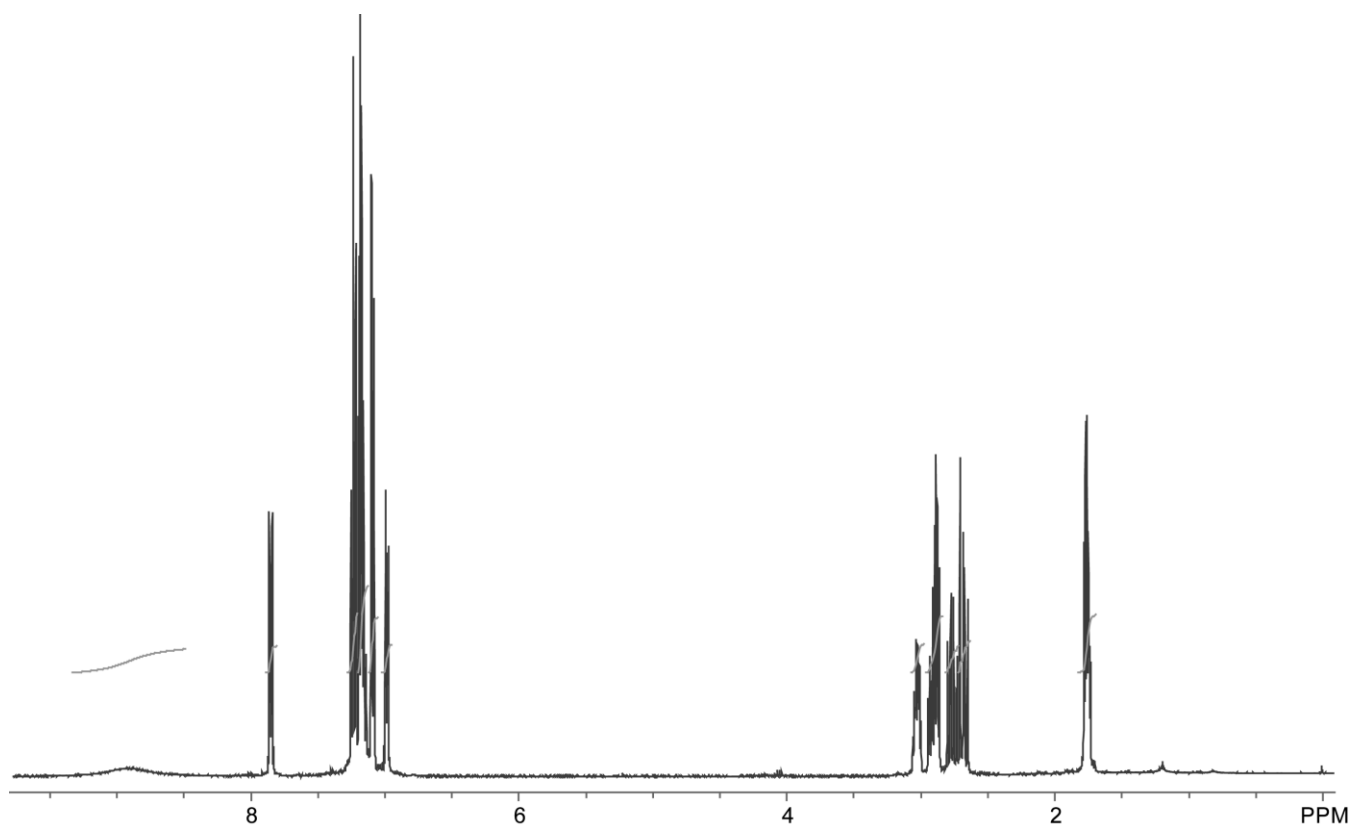
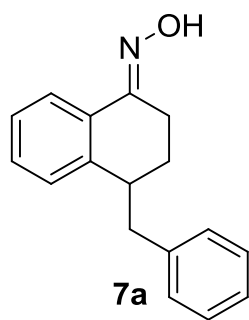


^1H -NMR-spectrum of Tetralone **6m** (CDCl_3).

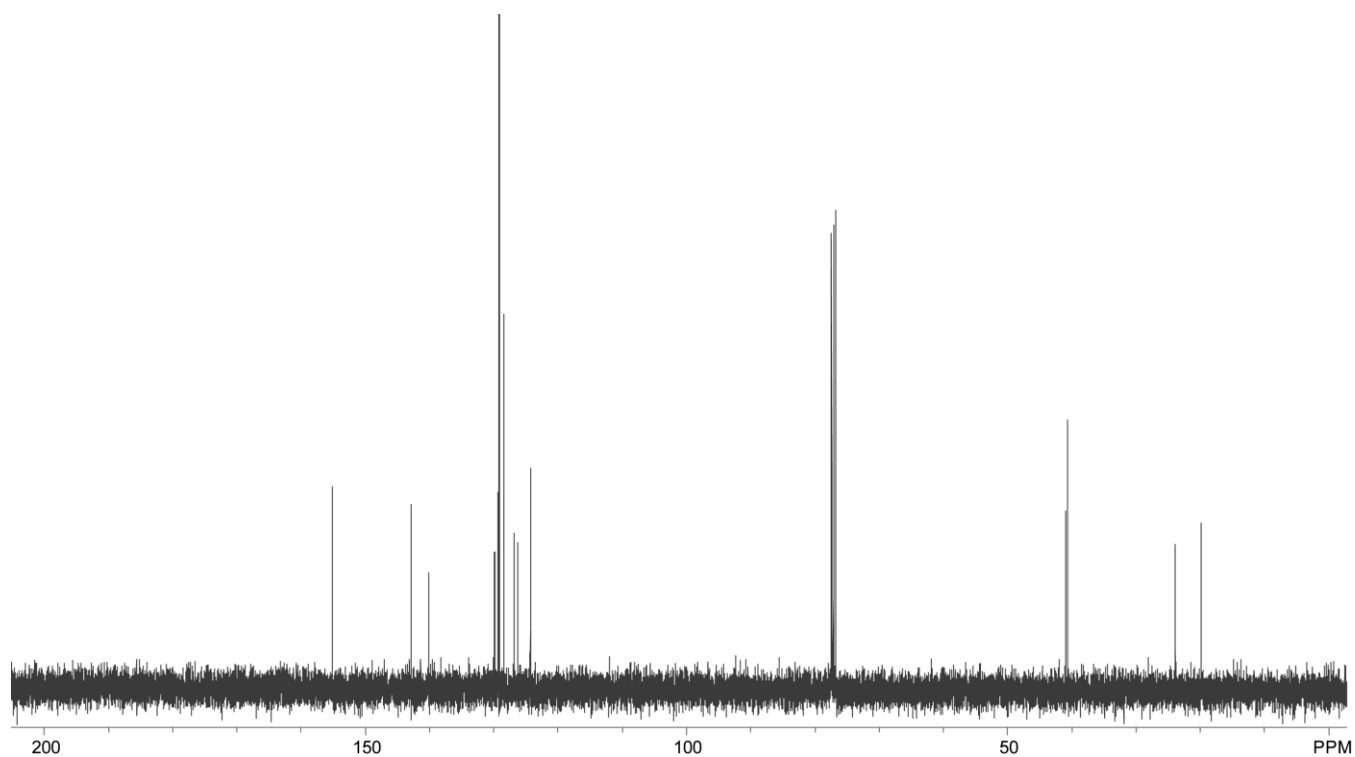


^{13}C -NMR-spectrum of Tetralone **6m** (CDCl_3).

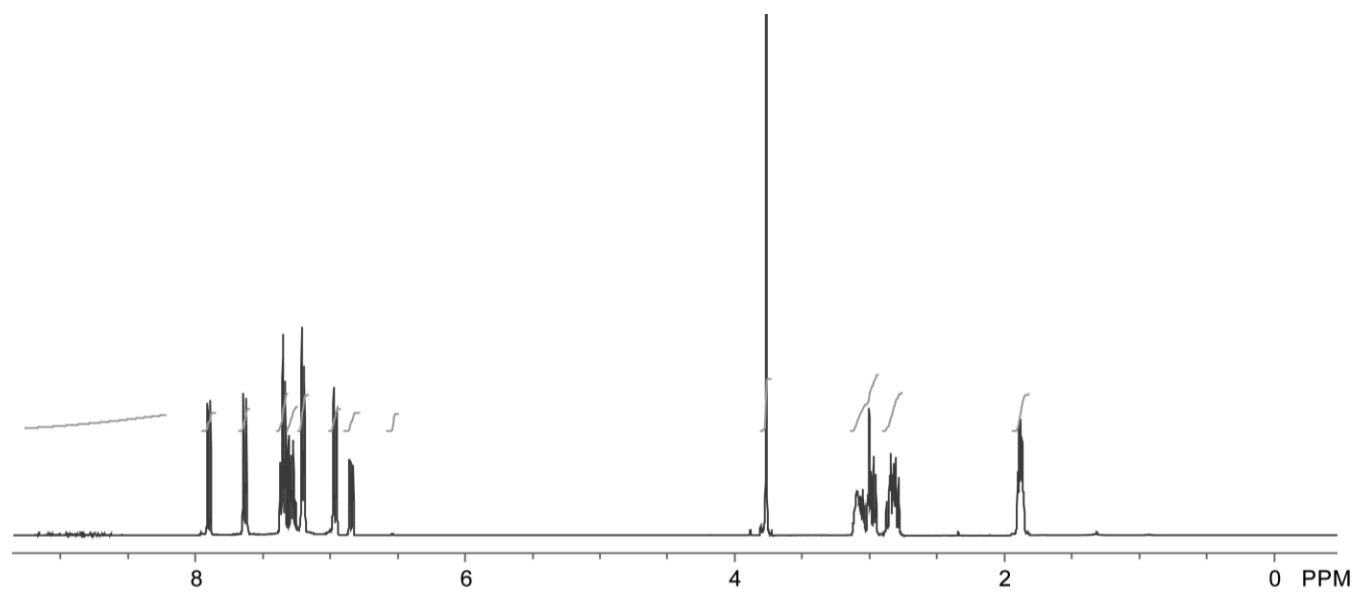
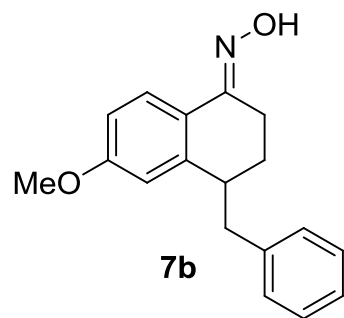
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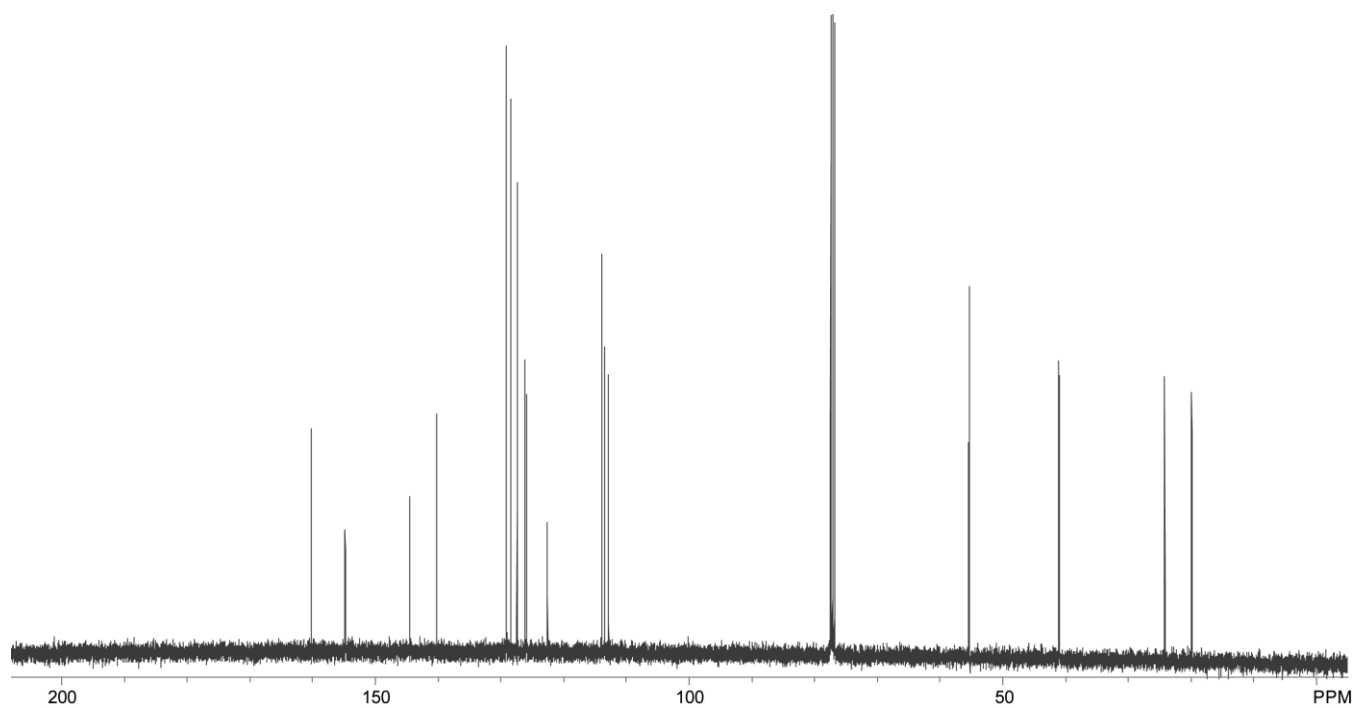
¹H-NMR-spectrum of Oxime **7a** (CDCl₃).



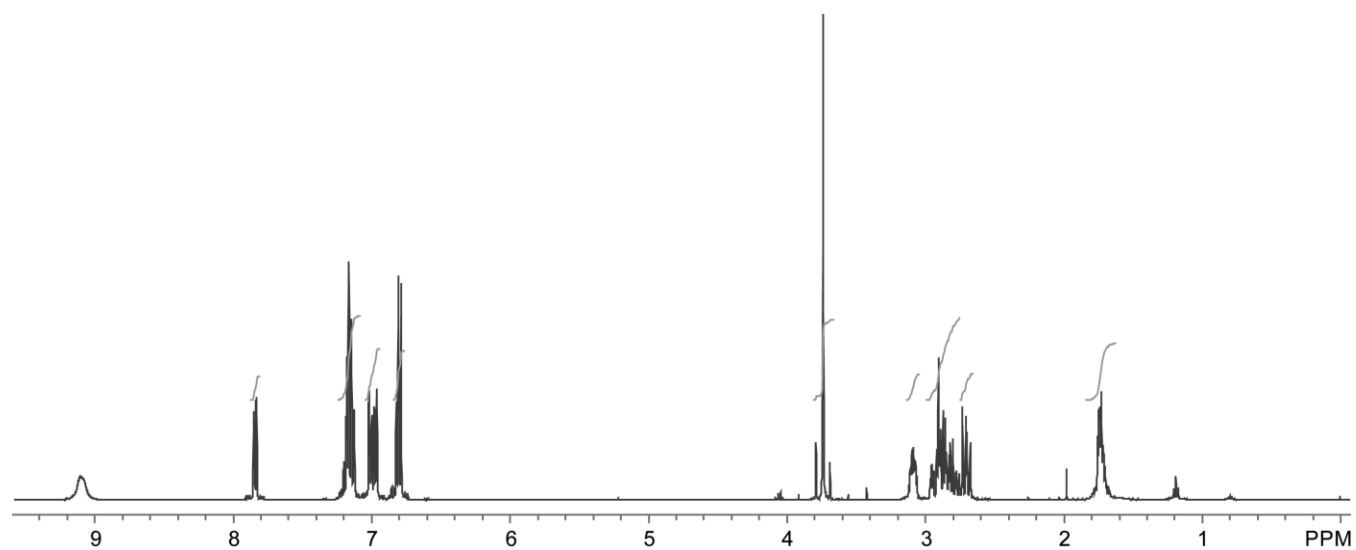
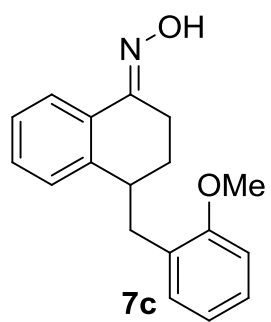
^{13}C -NMR-spectrum of Oxime **7a** (CDCl_3).



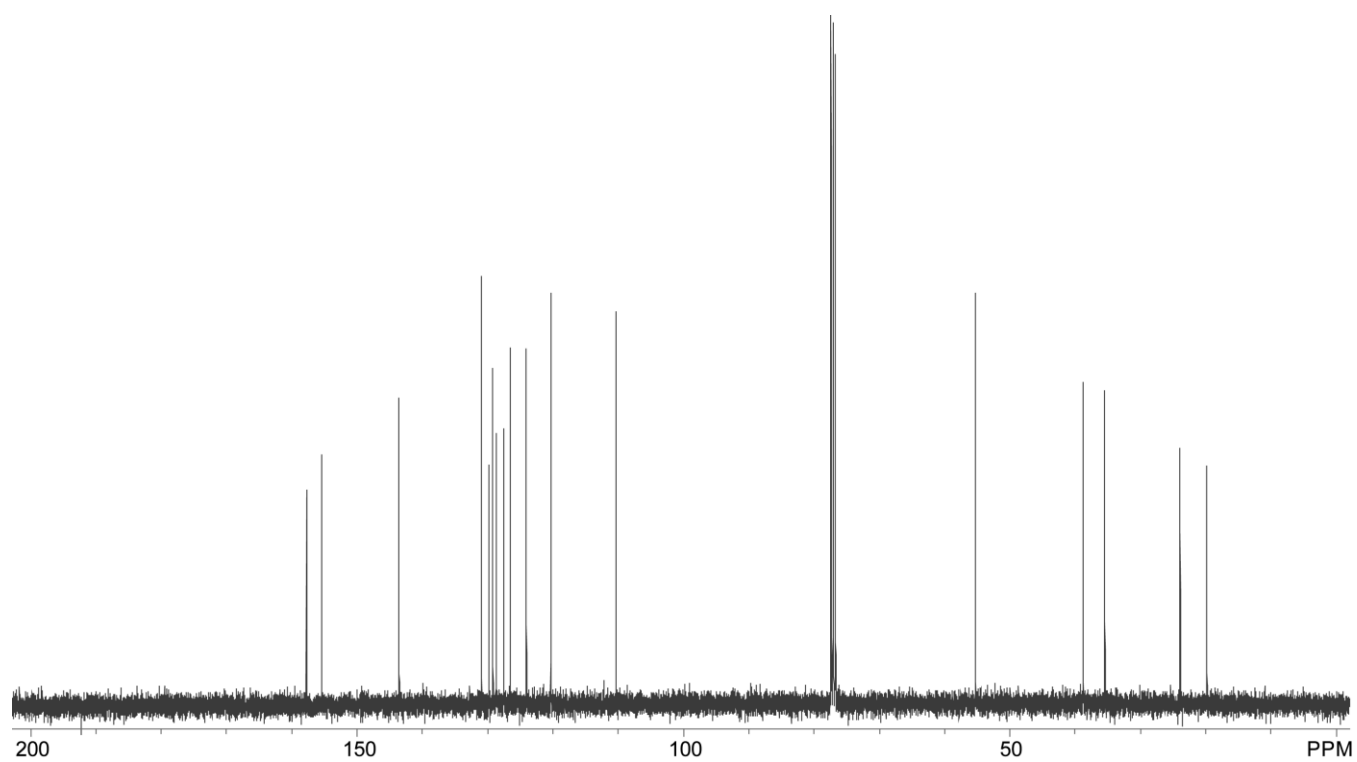
^1H -NMR-spectrum of Oxime **7b** (CDCl_3).



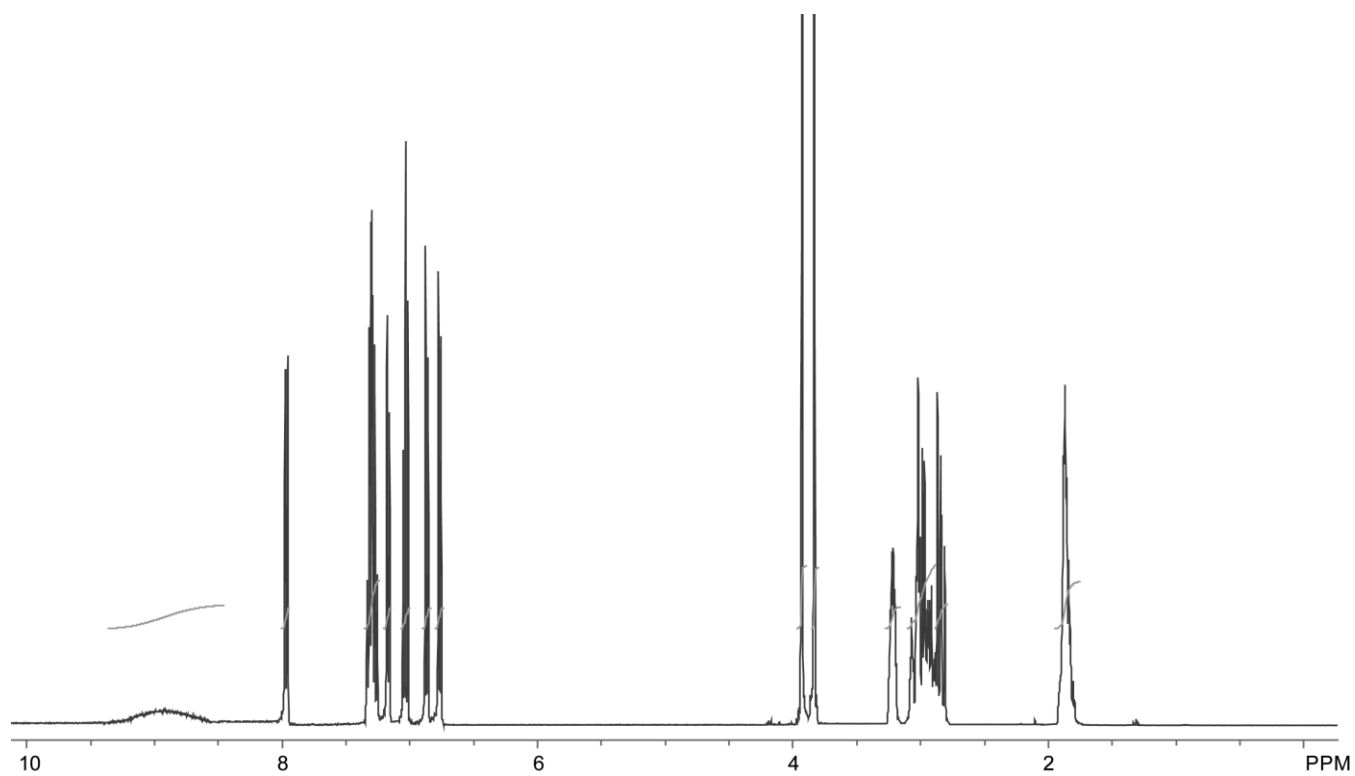
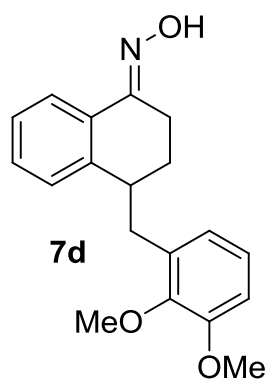
^{13}C -NMR-spectrum of Oxime **7b** (CDCl_3).



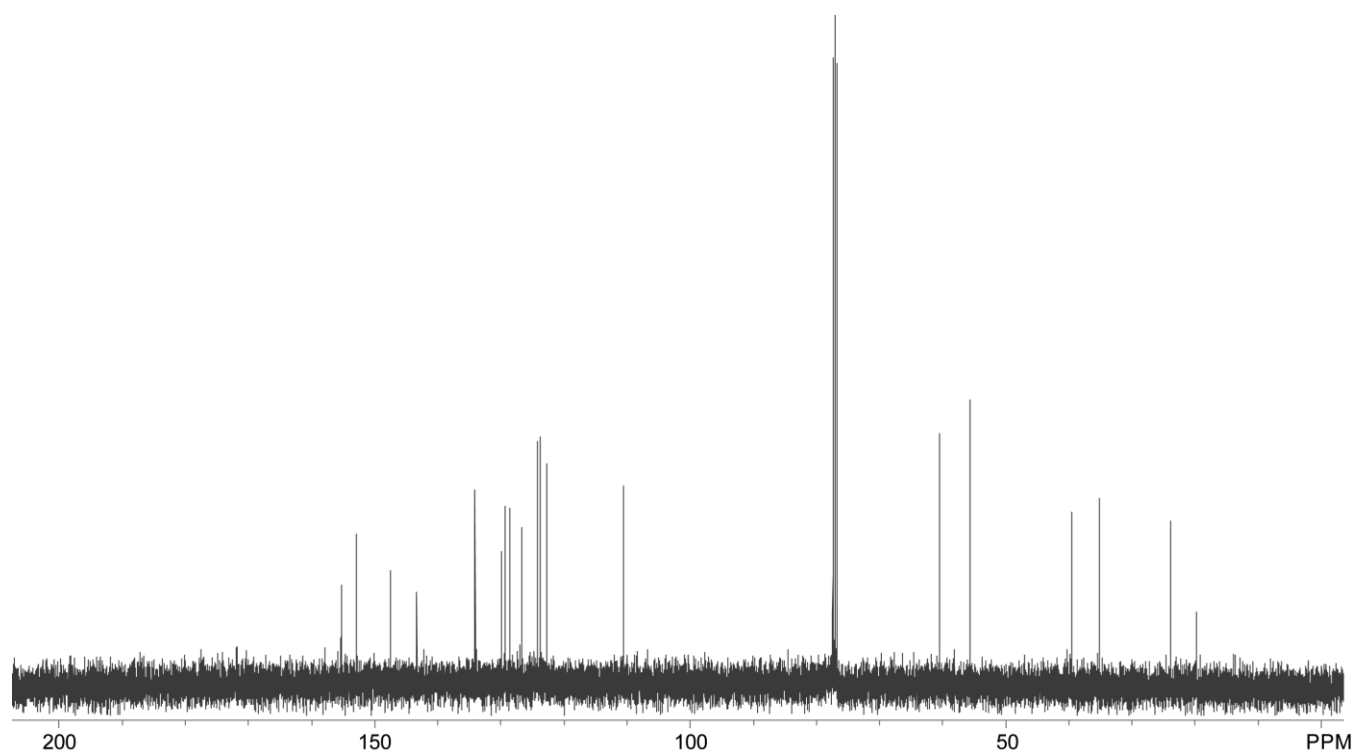
^1H -NMR-spectrum of Oxime **7c** (CDCl_3).



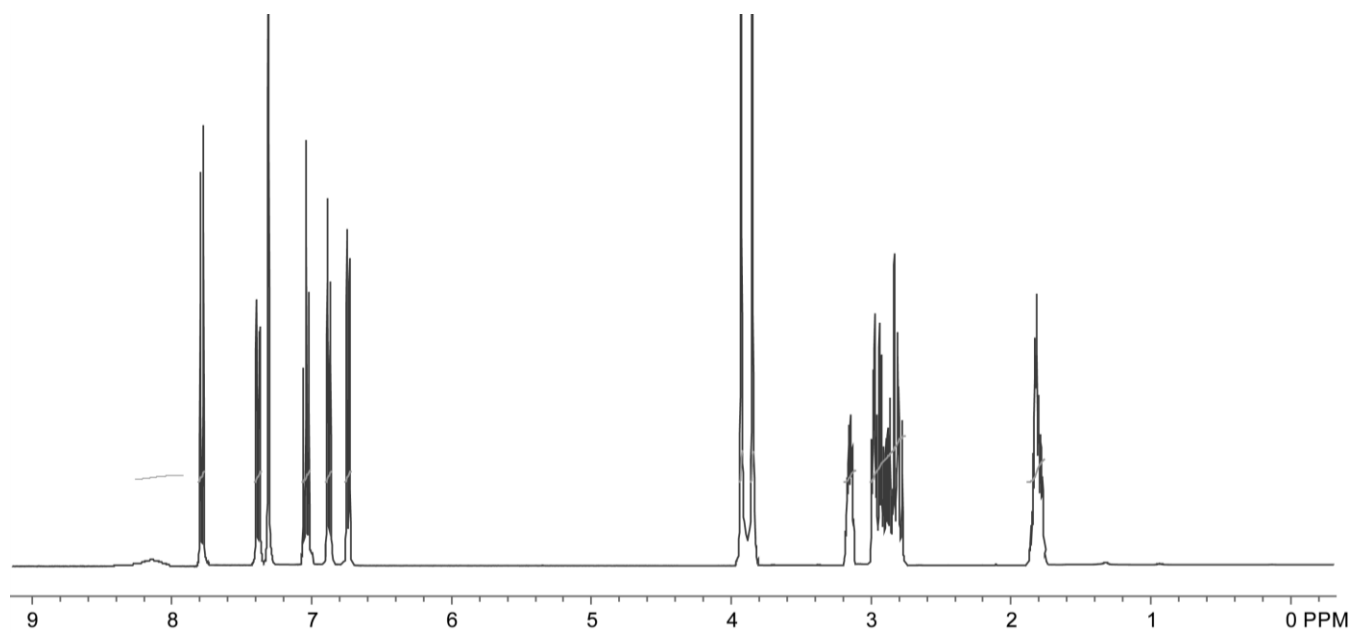
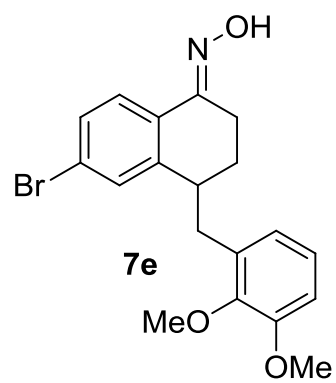
^{13}C -NMR-spectrum of Oxime **7c** (CDCl_3).



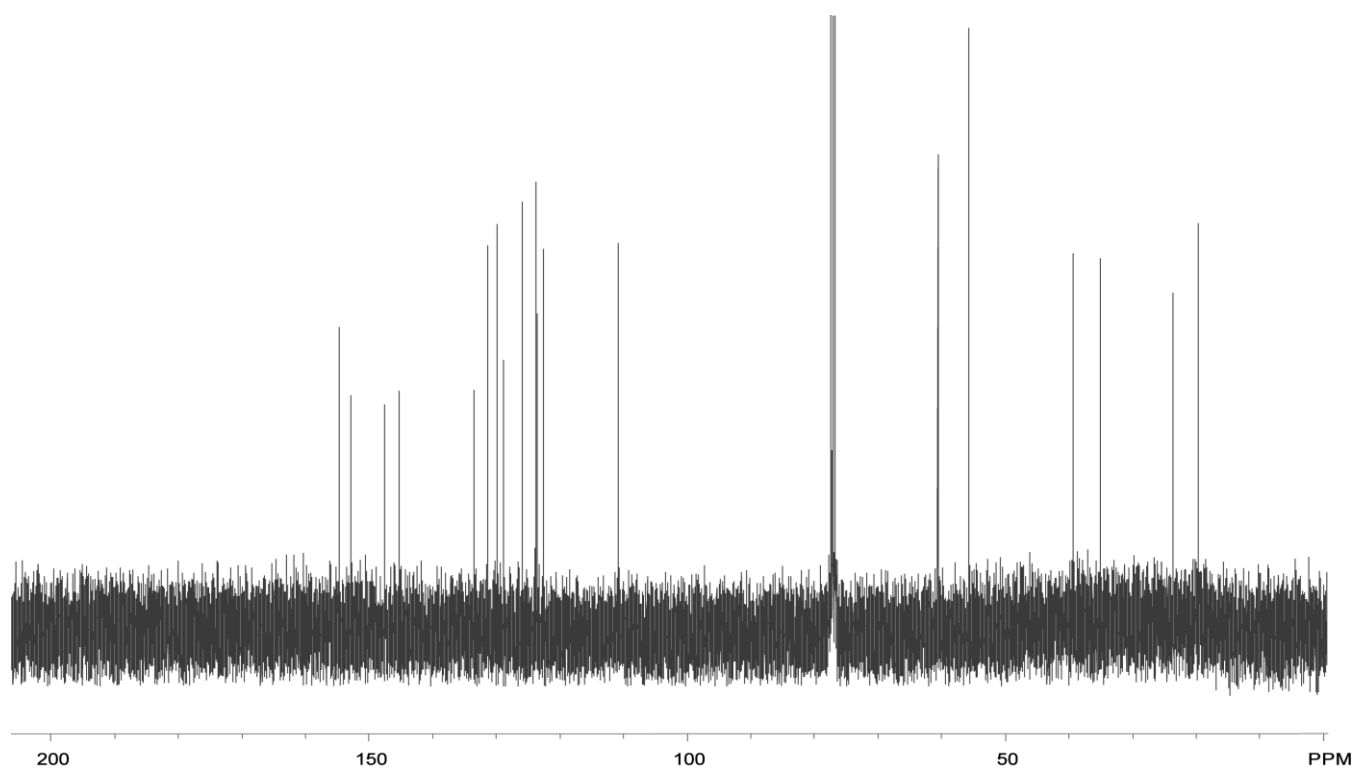
^1H -NMR-spectrum of Oxime **7d** (CDCl_3).



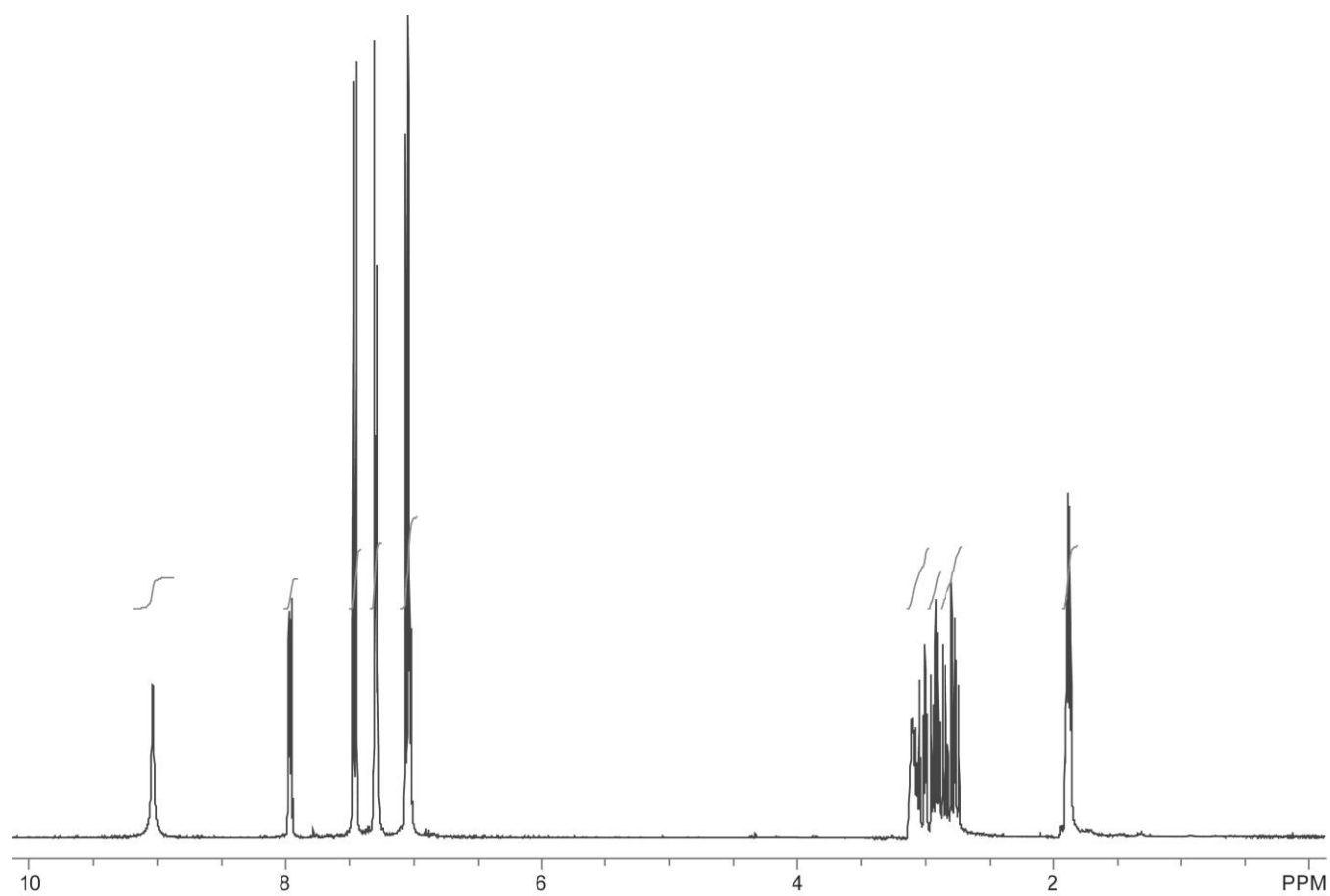
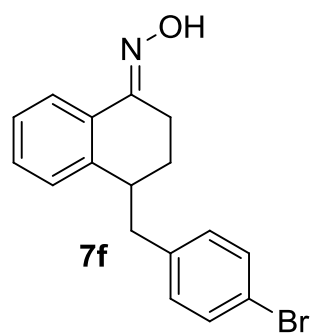
^{13}C -NMR-spectrum of Oxime **7d** (CDCl_3).



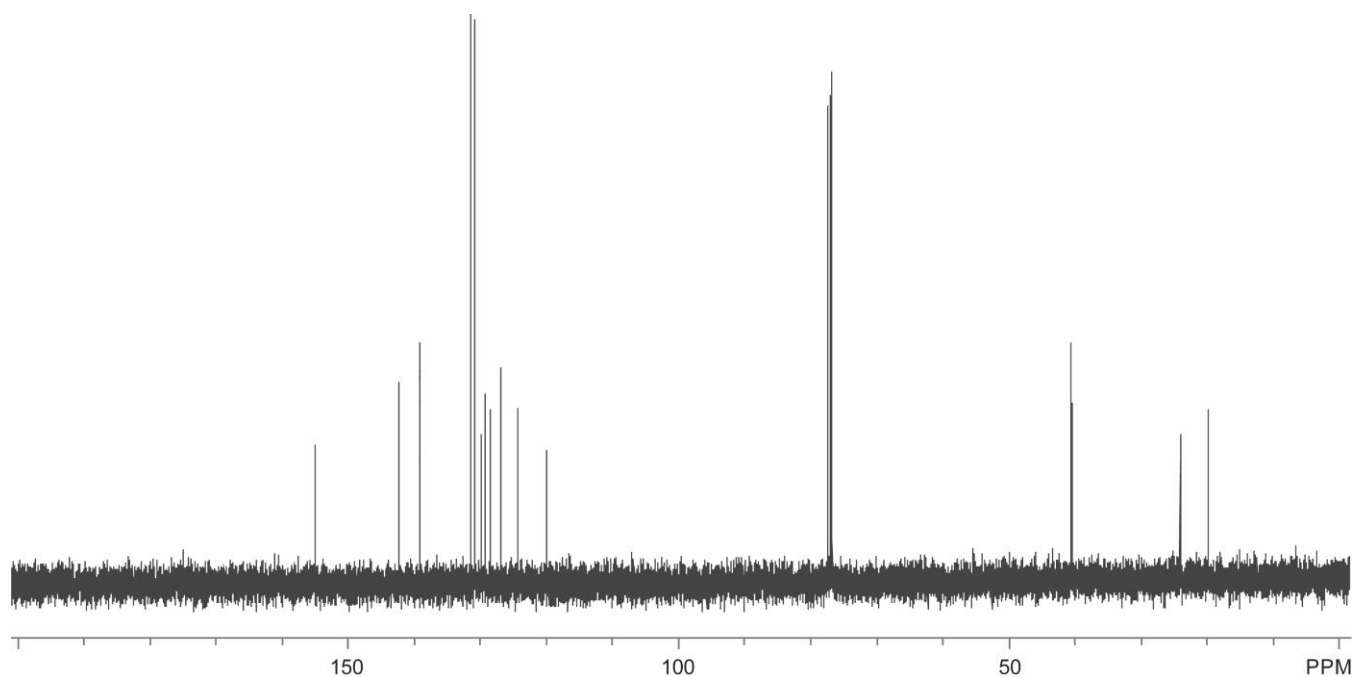
¹H-NMR-spectrum of Oxime **7e** (CDCl₃).



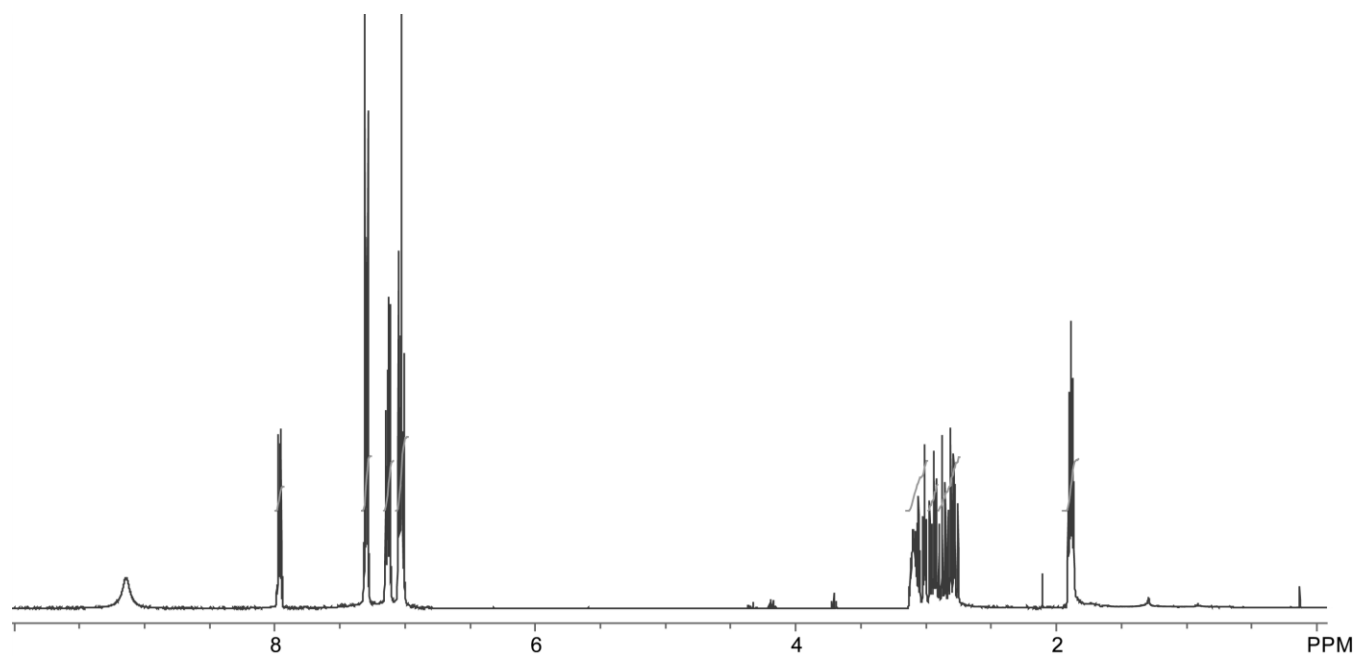
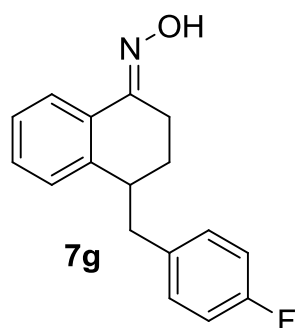
^{13}C -NMR-spectrum of Oxime **7e** (CDCl_3).



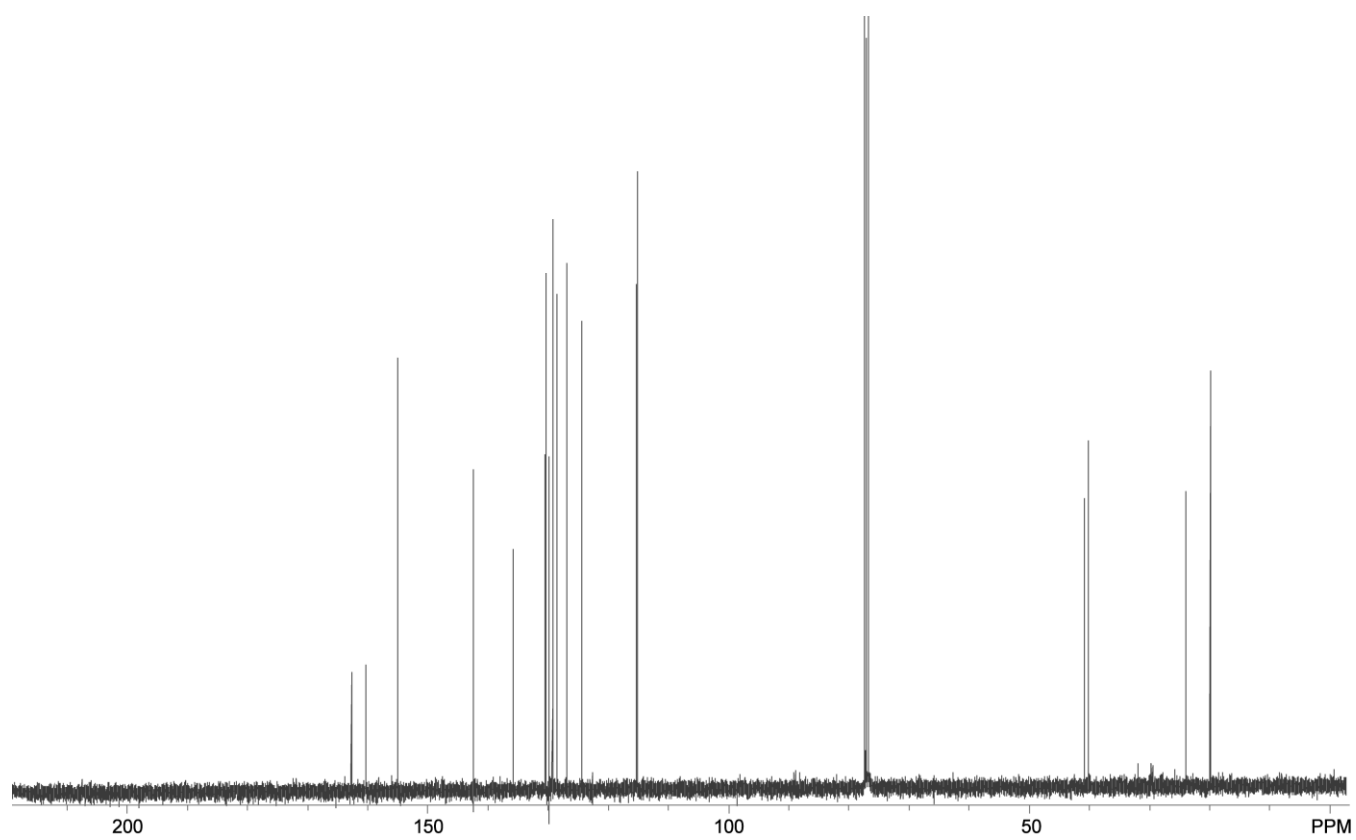
¹H-NMR-spectrum of Oxime **7f** (CDCl₃).



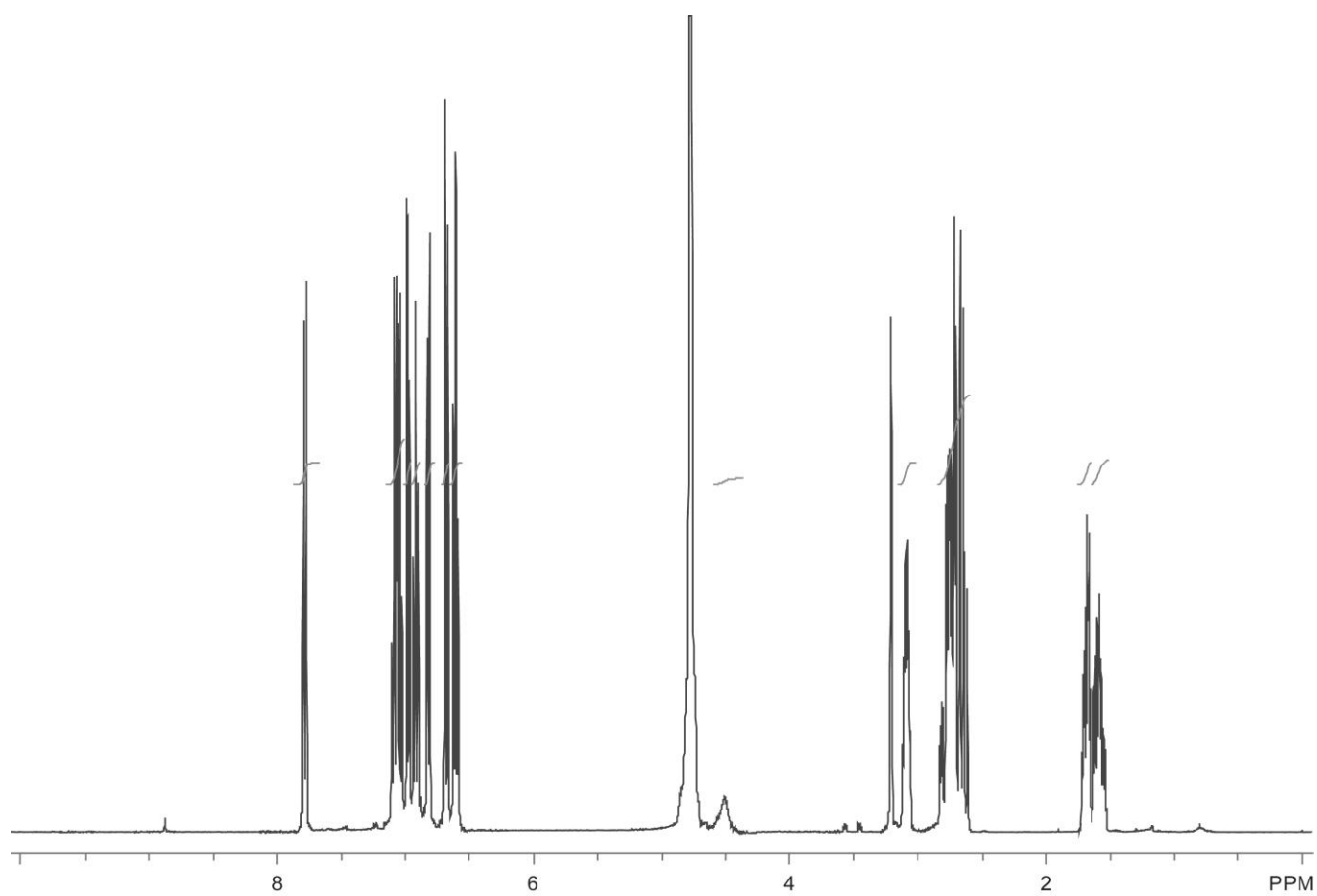
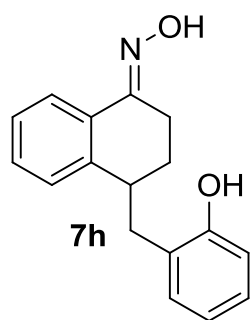
^{13}C -NMR-spectrum of Oxime **7f** (CDCl_3).



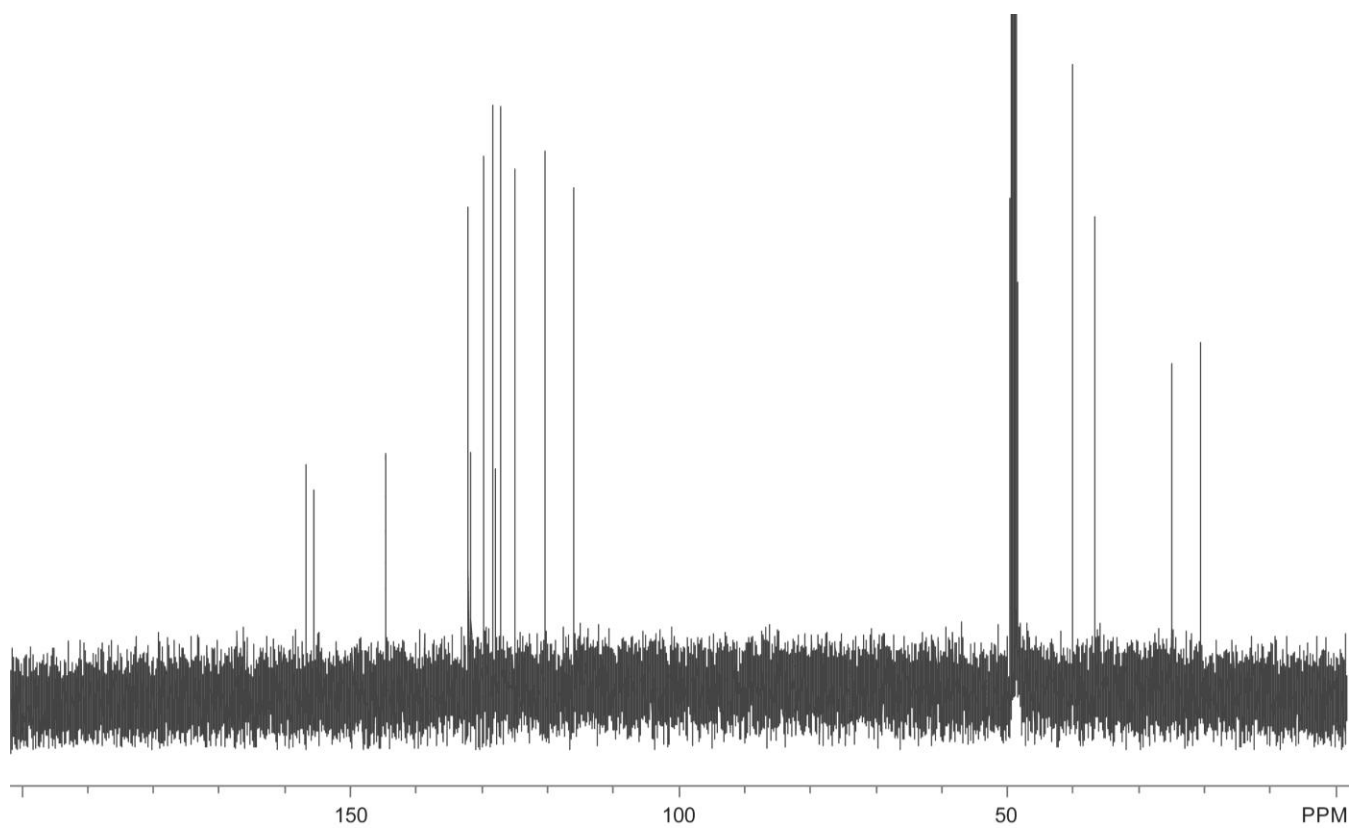
^1H -NMR-spectrum of Oxime **7g** (CDCl_3).



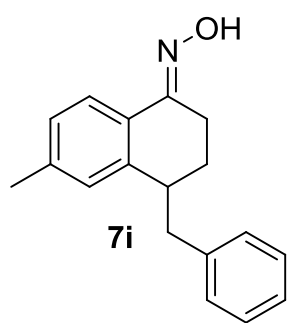
^{13}C -NMR-spectrum of Oxime **7g** (CDCl_3).

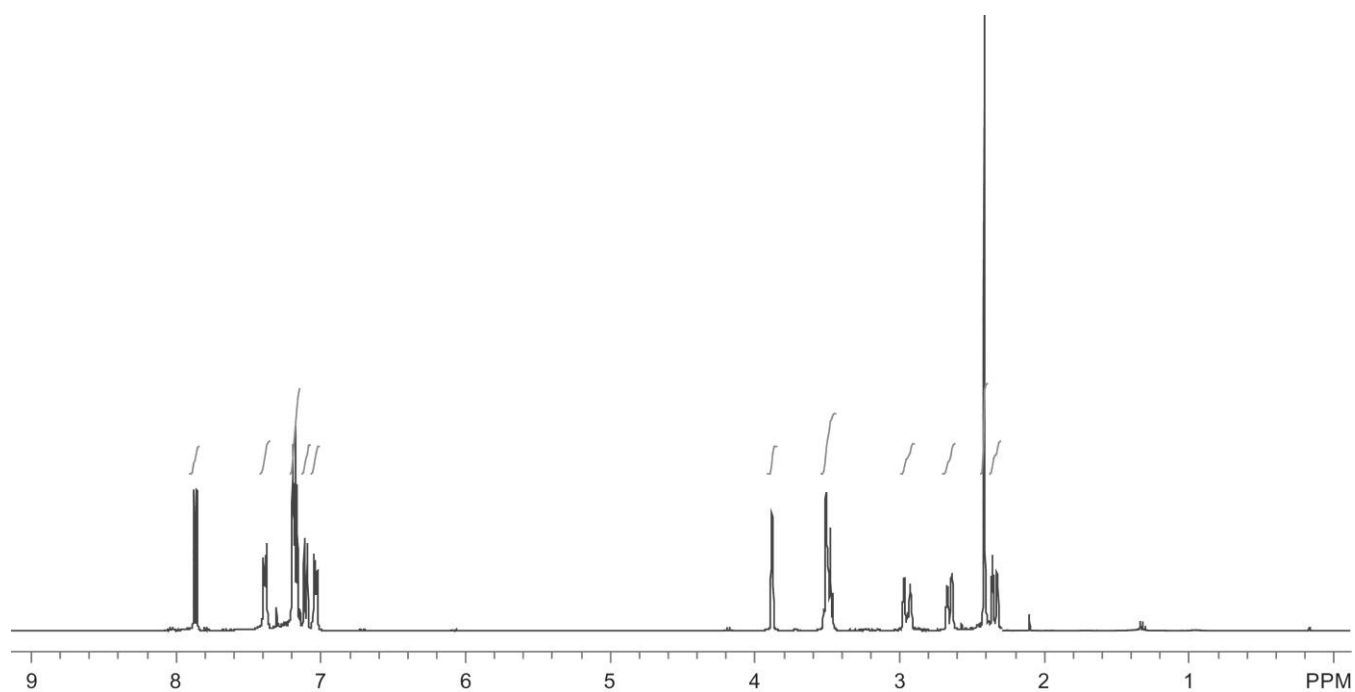


^1H -NMR-spectrum of Oxime **7h** (CD_3OD).

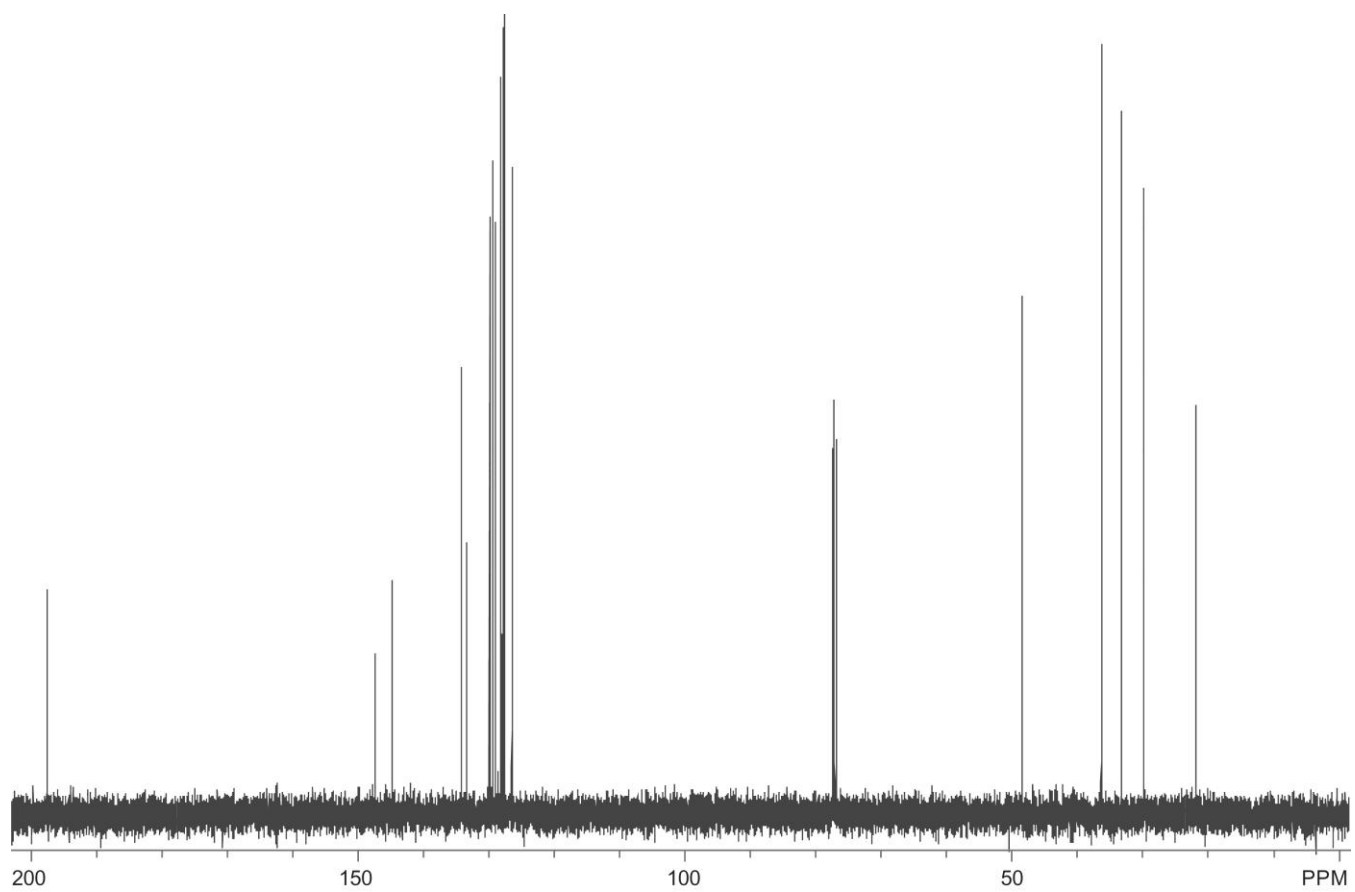


^{13}C -NMR-spectrum of Oxime **7h** (CD_3OD).

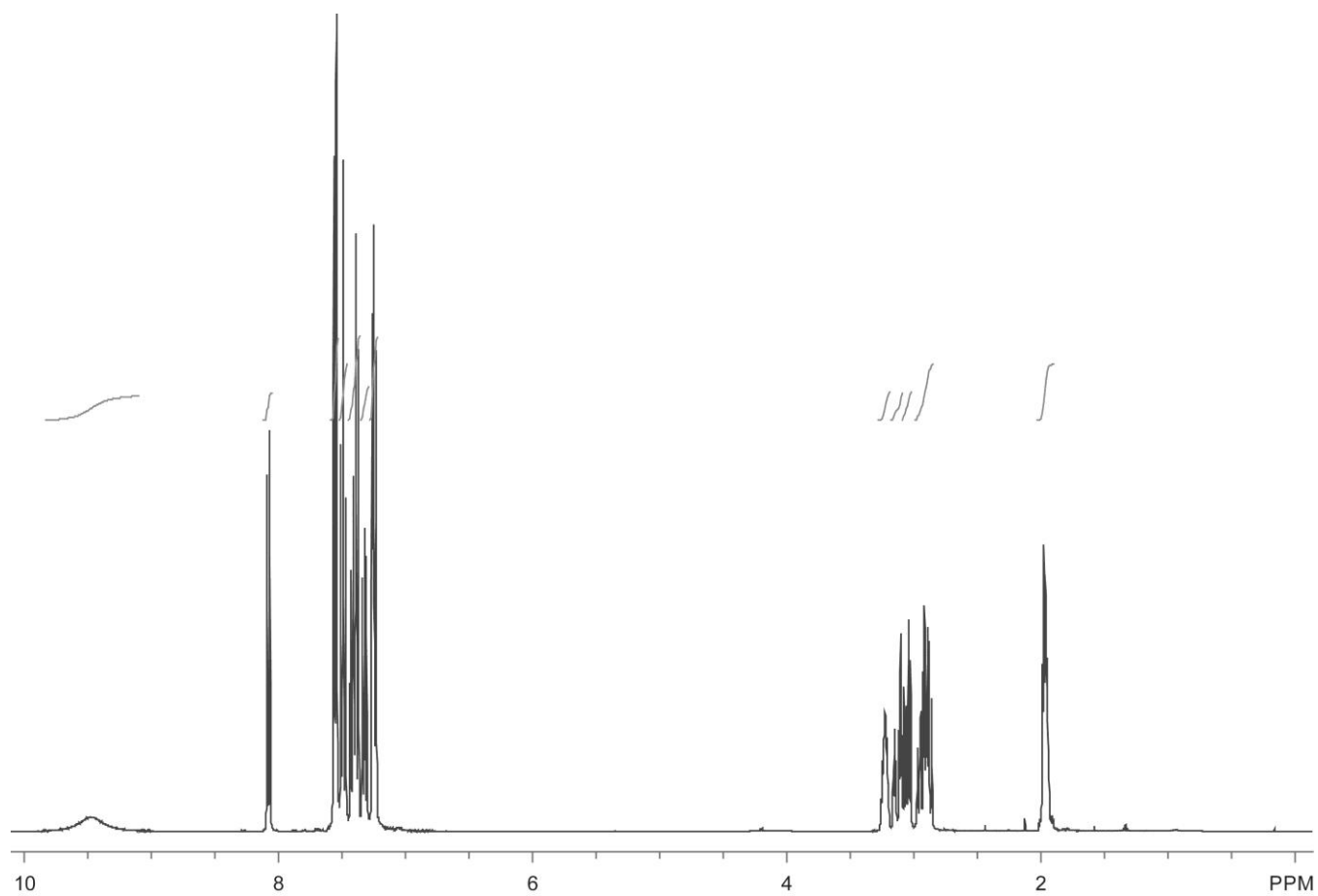
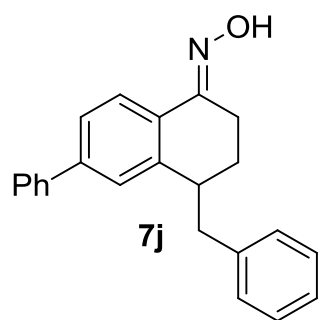




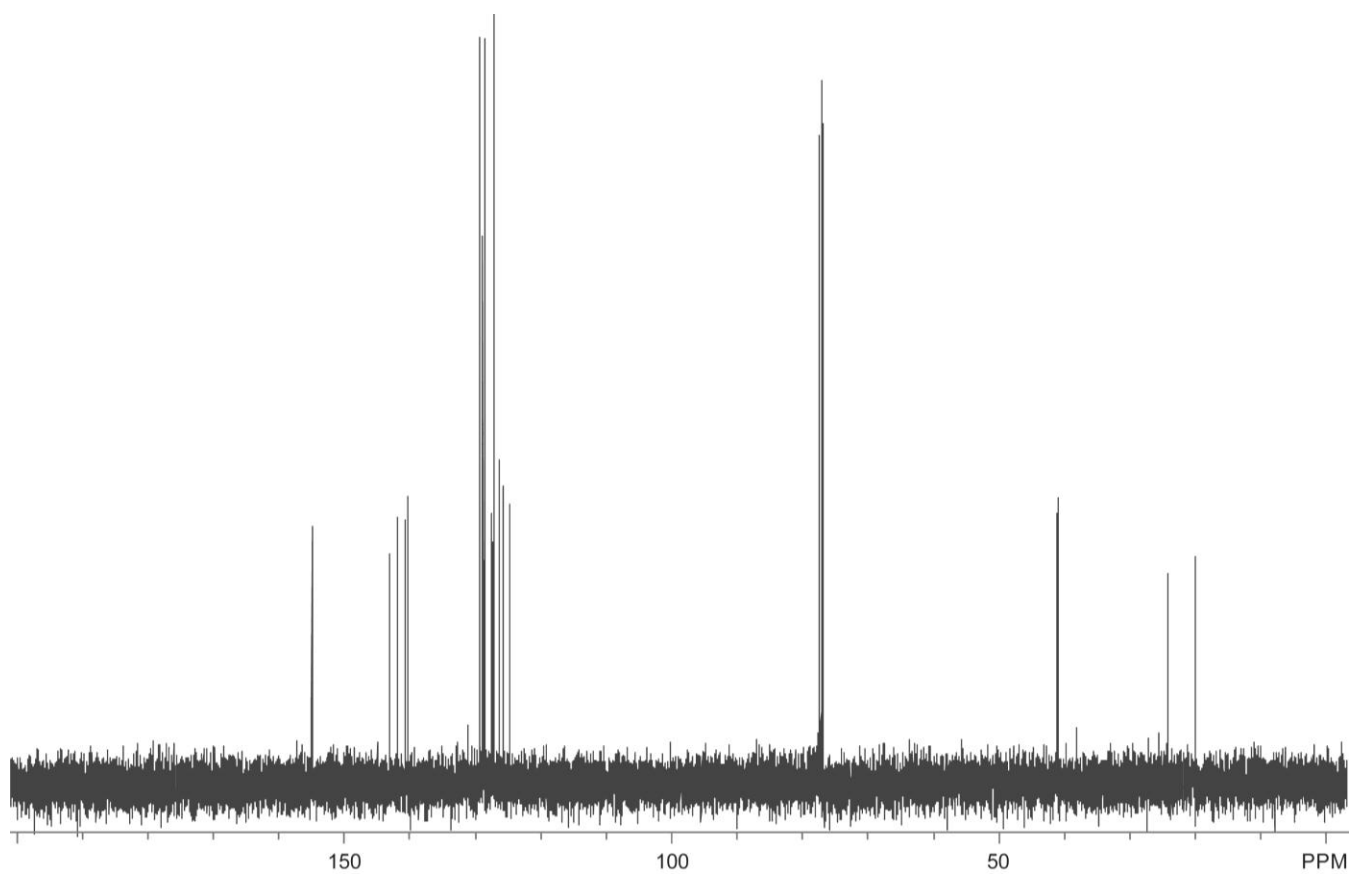
^1H -NMR-spectrum of Oxime **7i** (CDCl_3).



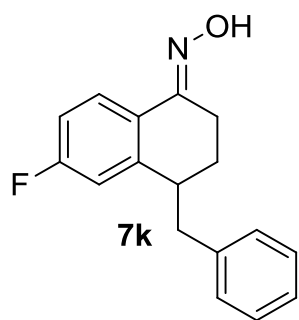
^{13}C -NMR-spectrum of Oxime **7i** (CDCl_3).

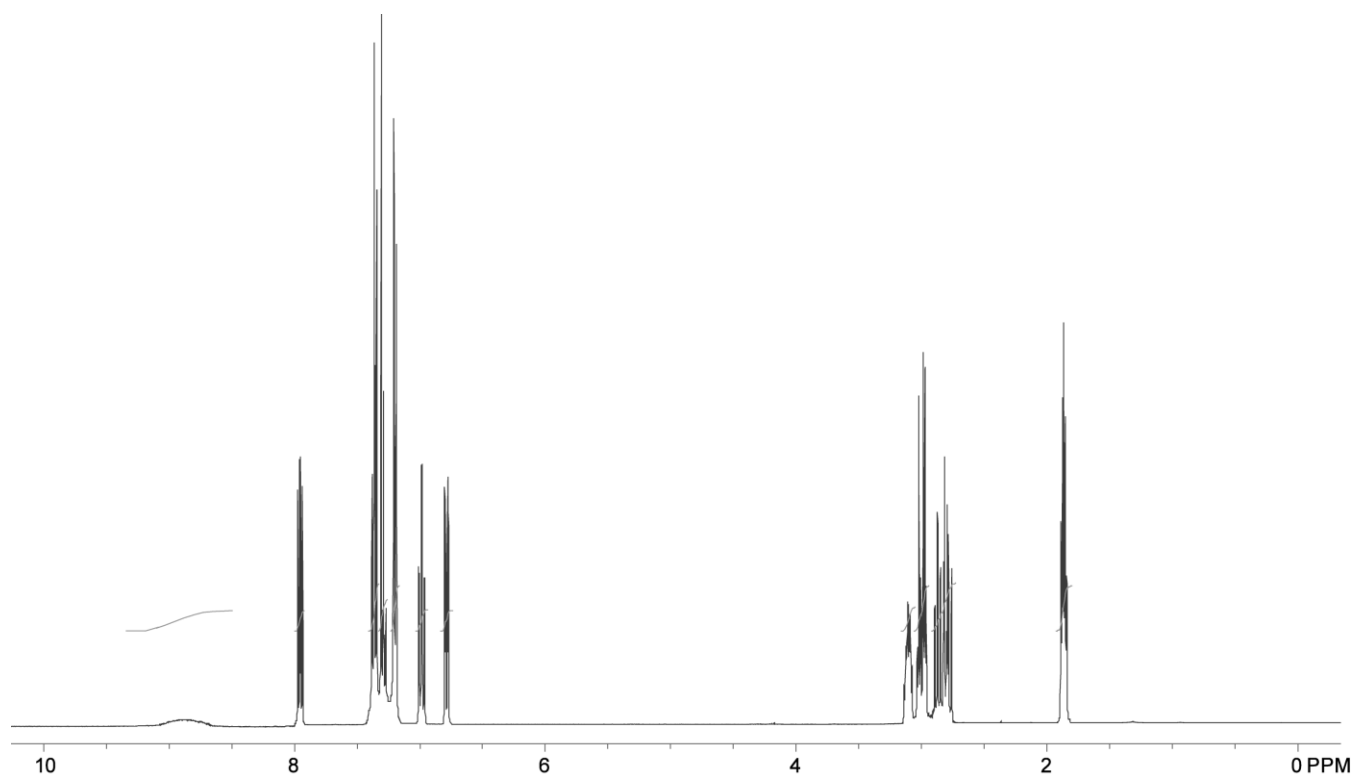


¹H-NMR-spectrum of Oxime **7j** (CDCl₃).

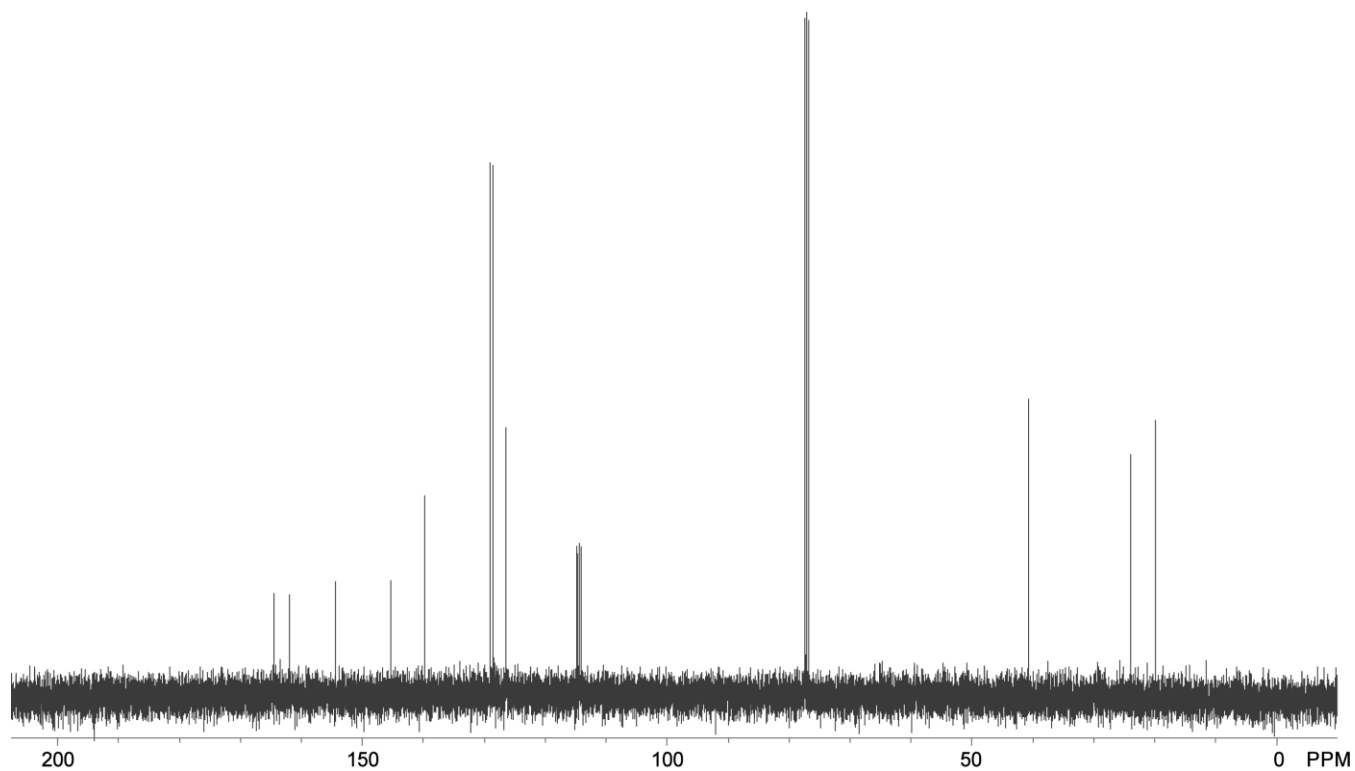


^{13}C -NMR-spectrum of Oxime **7j** (CDCl_3).

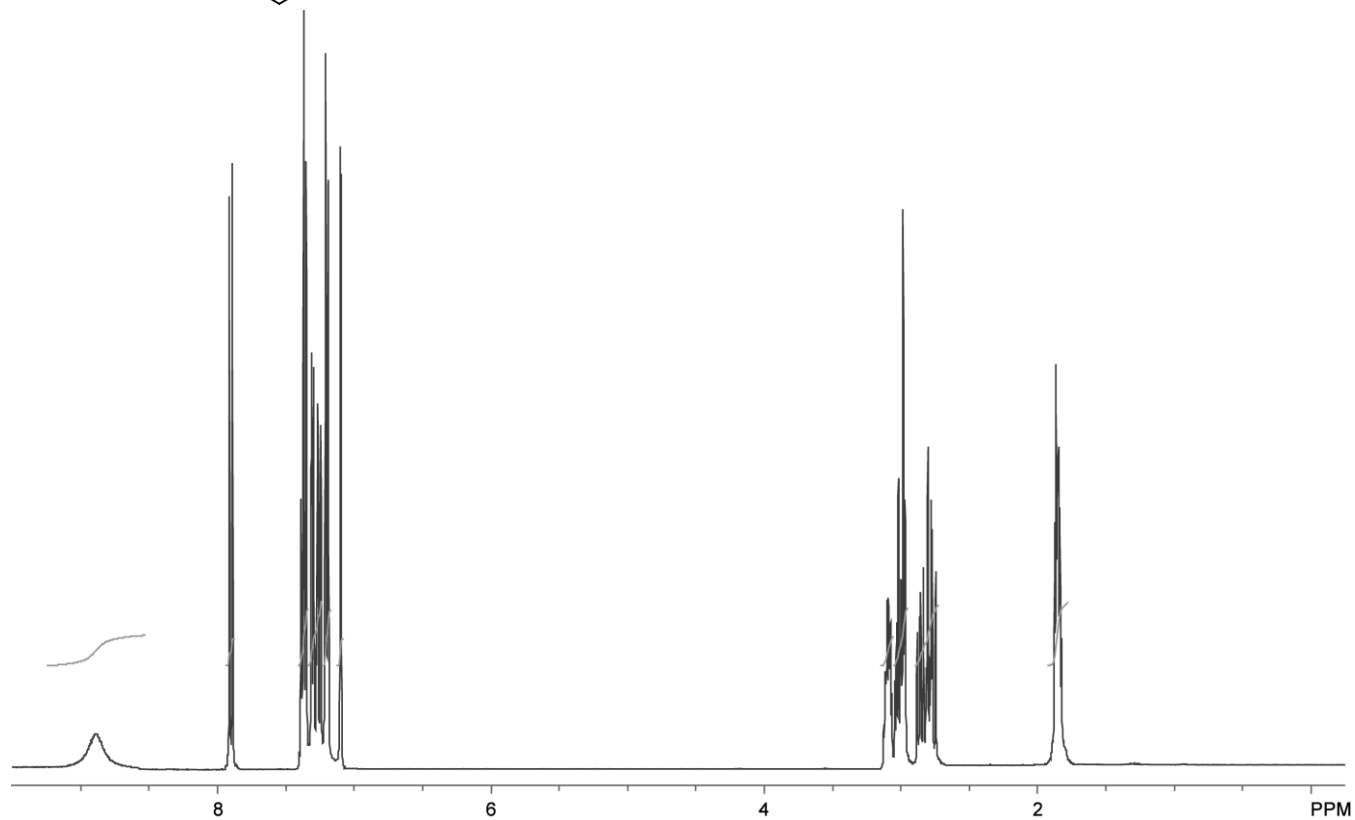
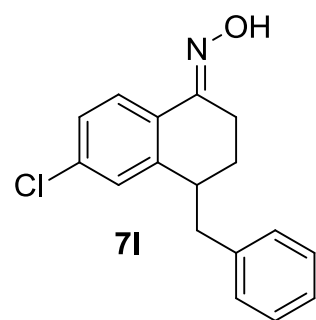




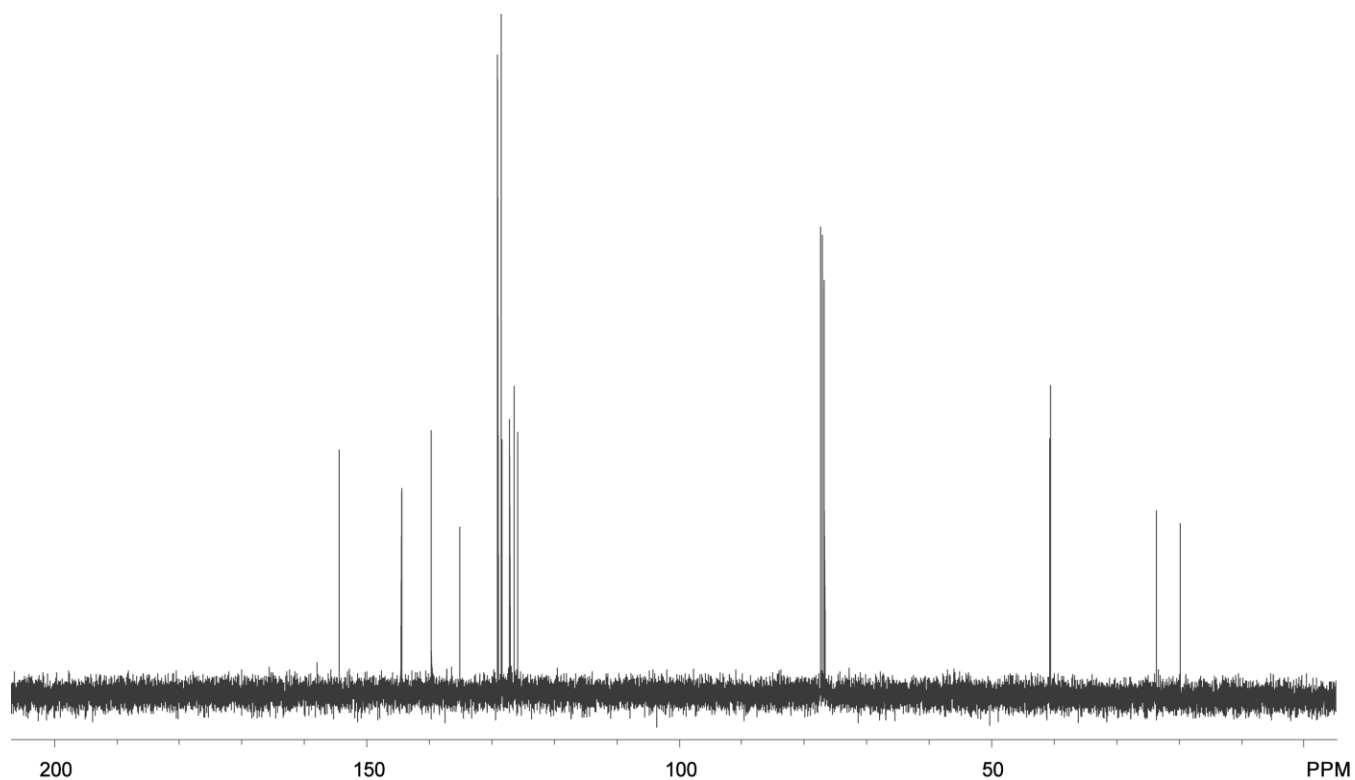
^1H -NMR-spectrum of Oxime **7k** (CDCl_3).



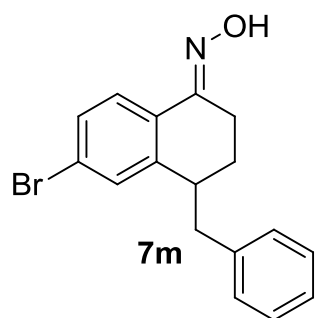
^{13}C -NMR-spectrum of Oxime **7k** (CDCl_3).

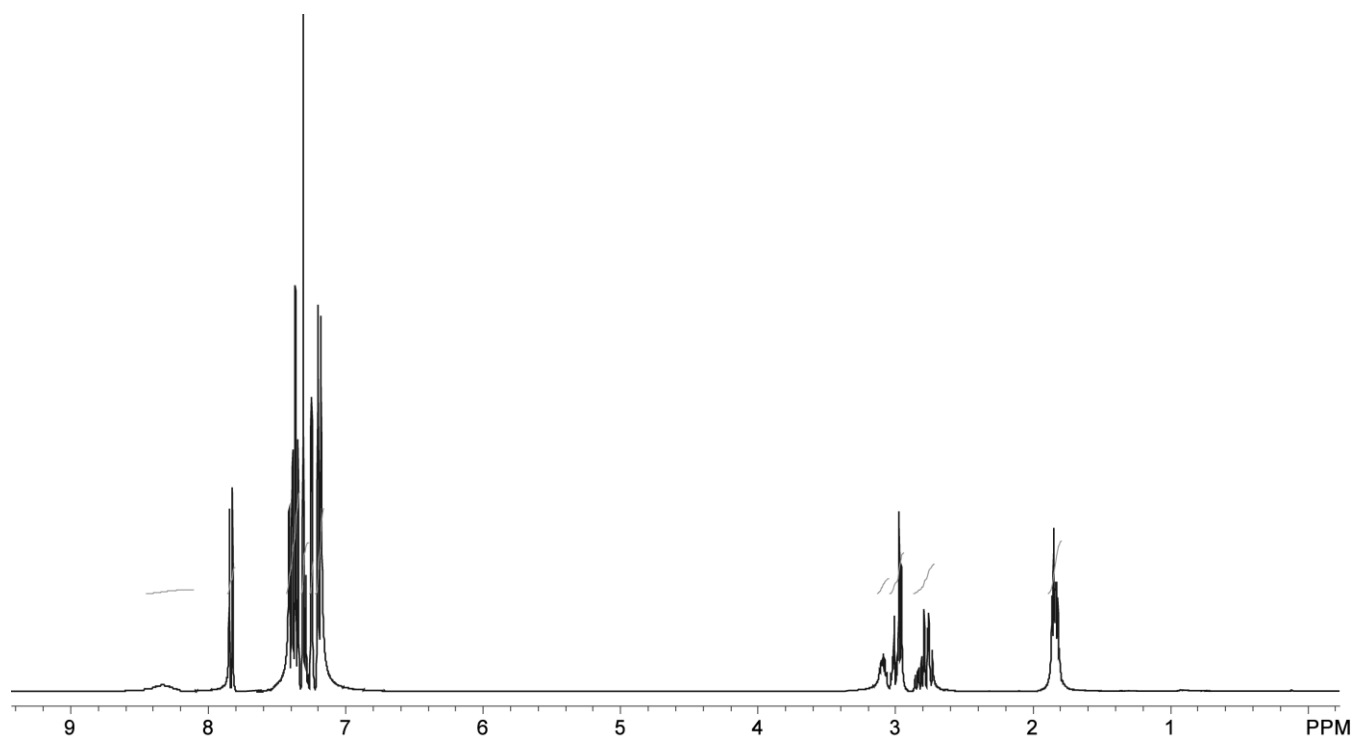


^1H -NMR-spectrum of Oxime **7I** (CDCl_3).

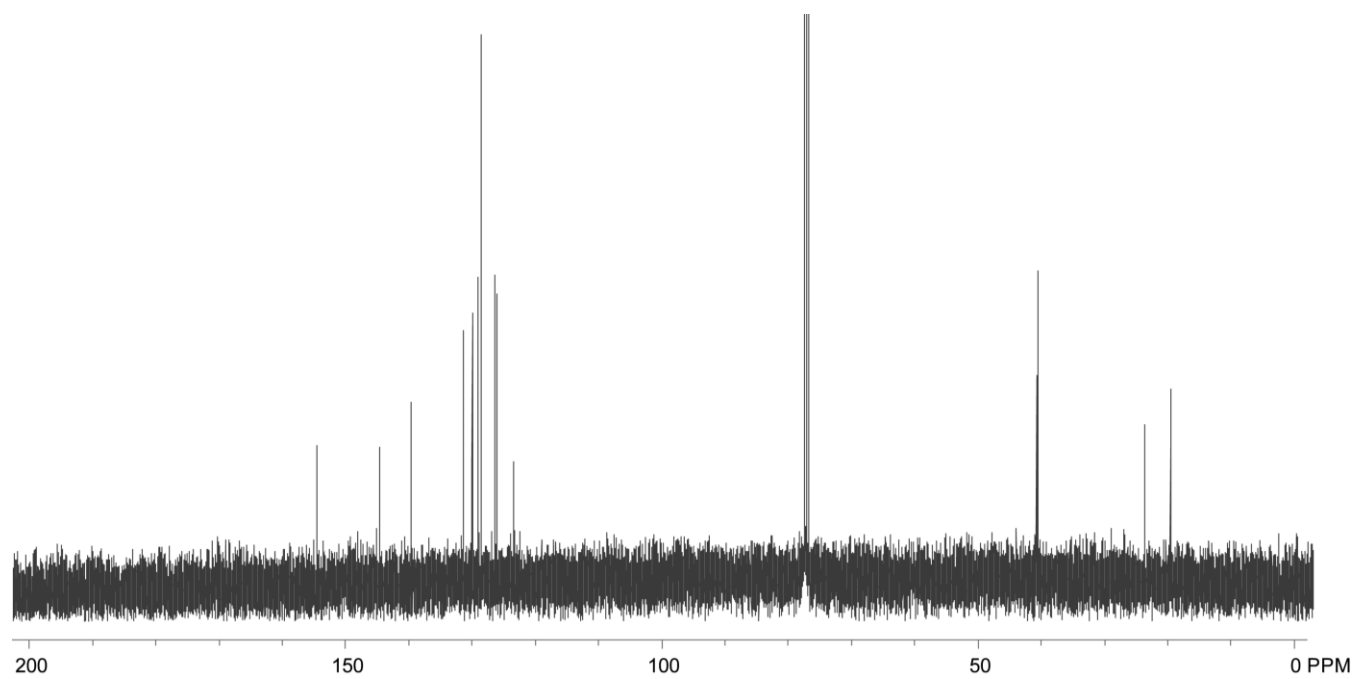


^{13}C -NMR-spectrum of Oxime **7l** (CDCl_3).



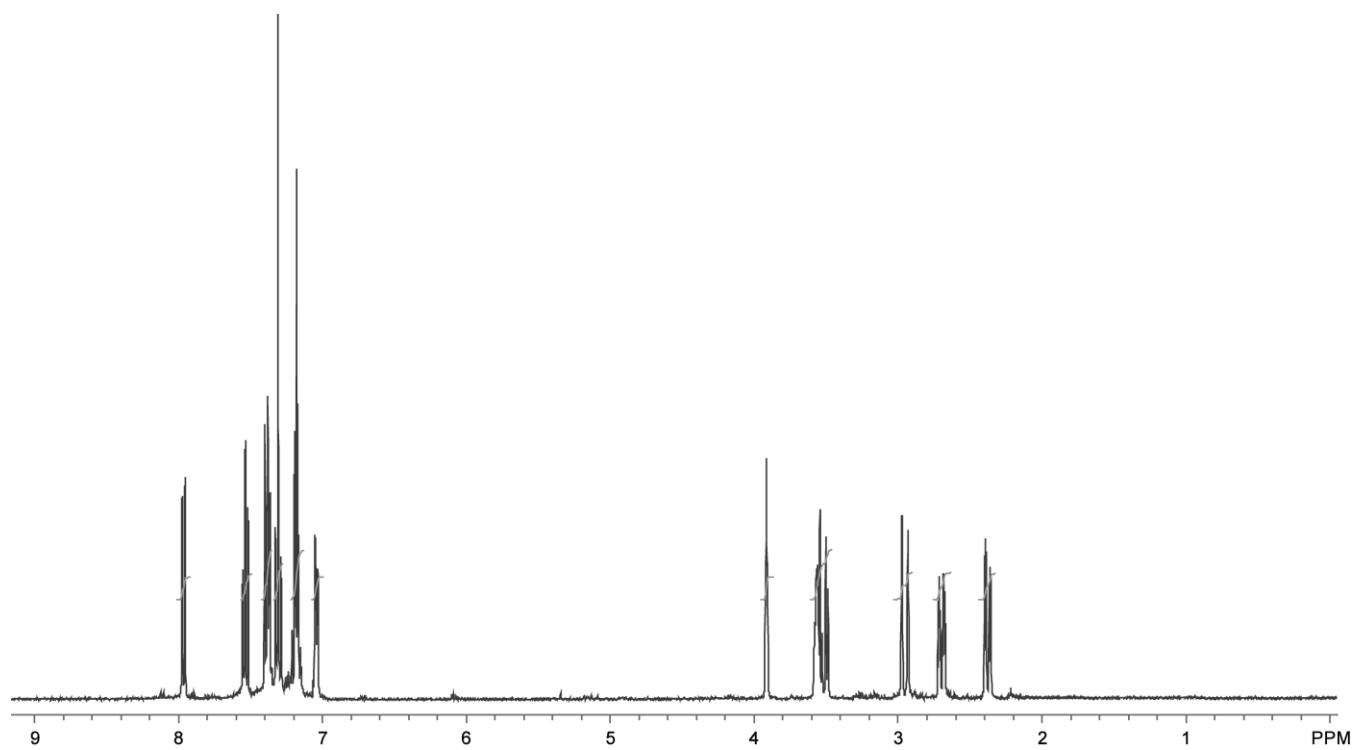
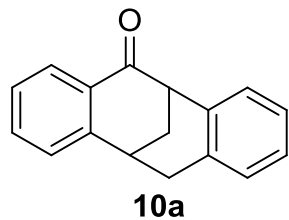


^1H -NMR-spectrum of Oxime **7m** (CDCl_3).

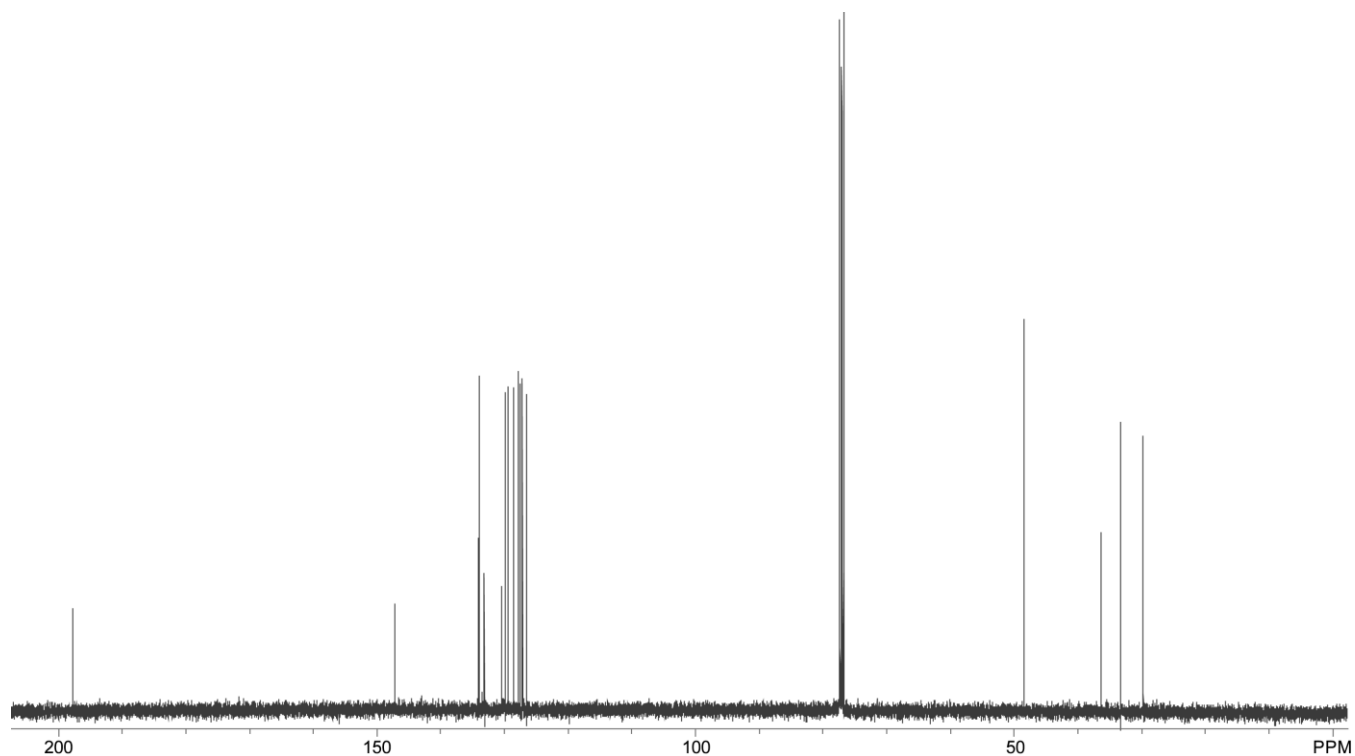


^{13}C -NMR-spectrum of Oxime **7m** (CDCl_3).

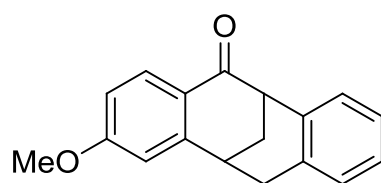
Tetracycles 10:



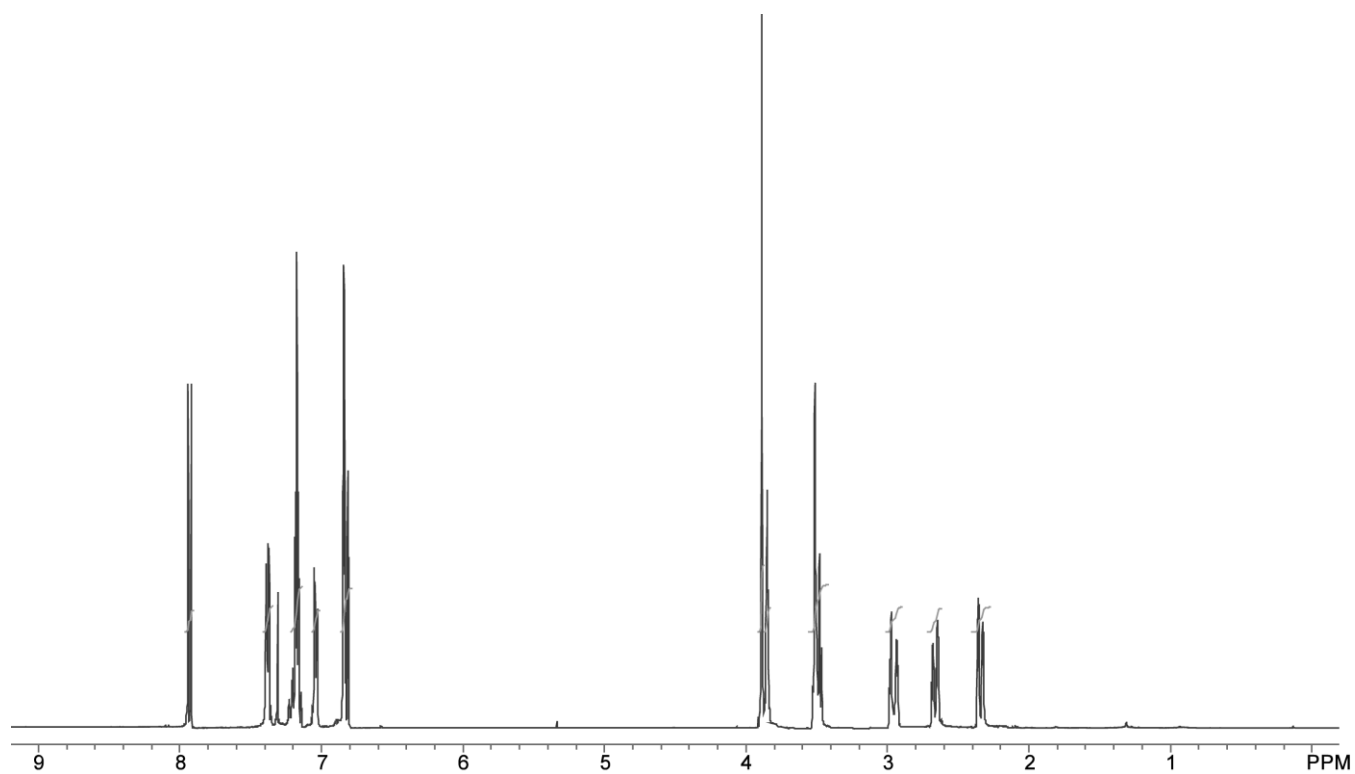
¹H-NMR-spectrum of Tetracycle **10a** (CDCl₃).



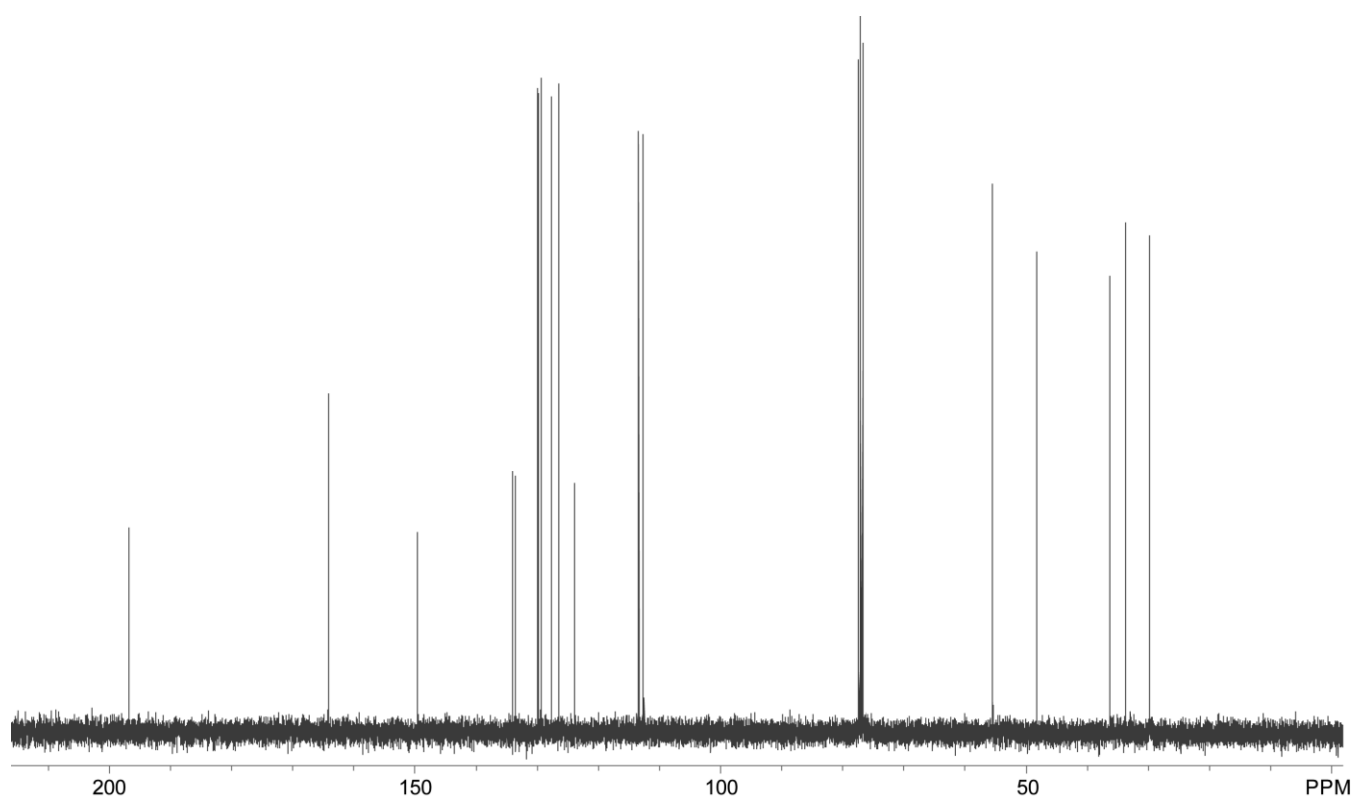
^{13}C -NMR-spectrum of Tetracycle **10a** (CDCl_3).



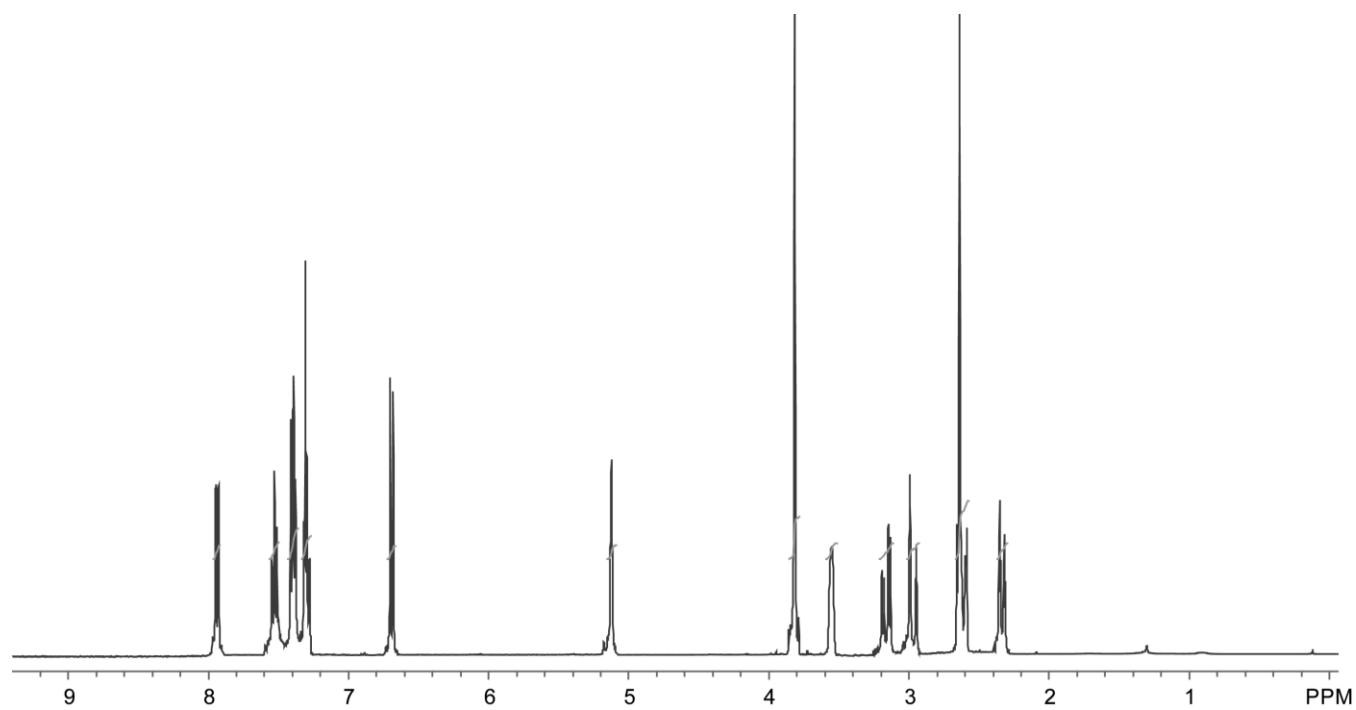
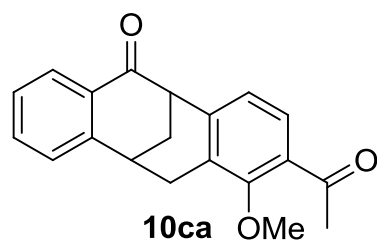
10b



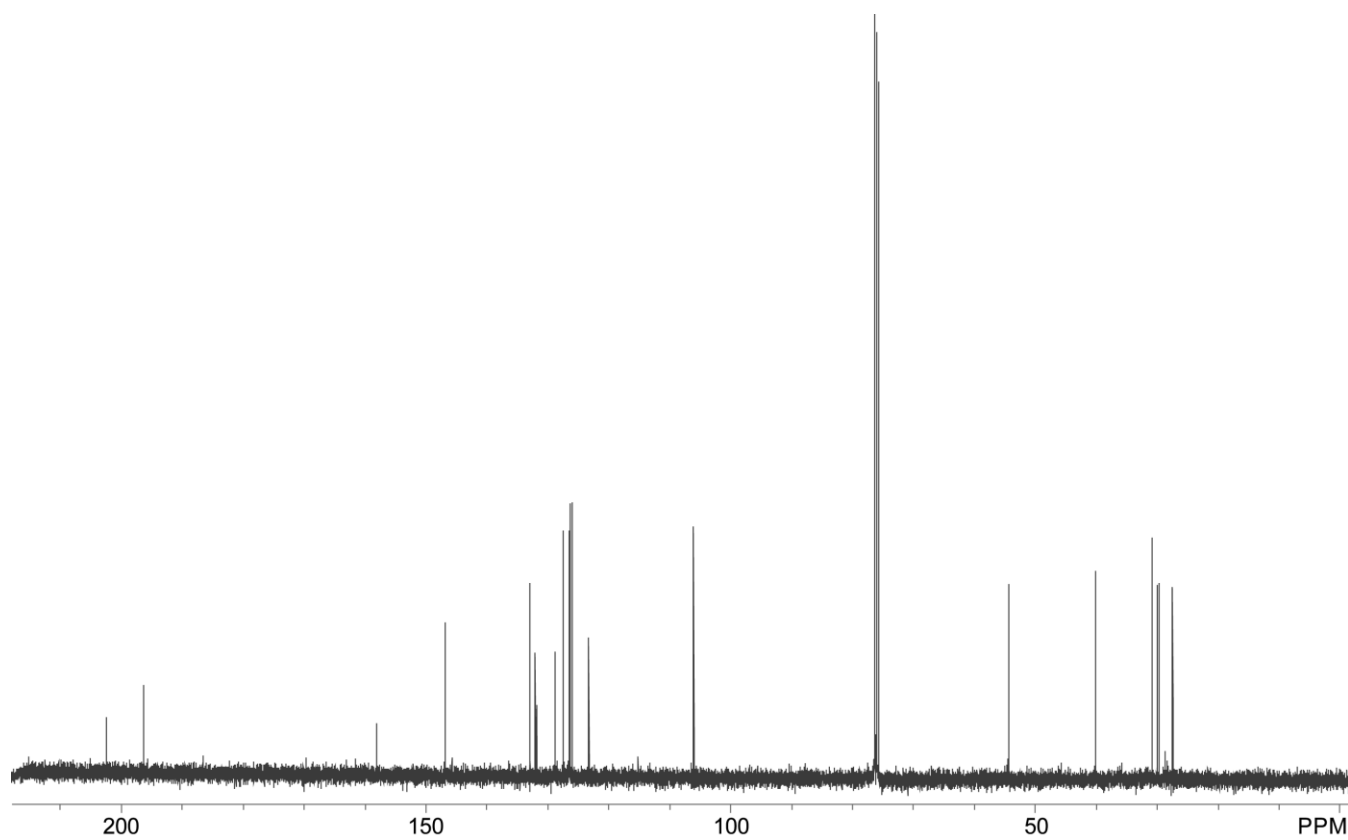
^1H -NMR-spectrum of Tetracycline **10b** (CDCl_3).



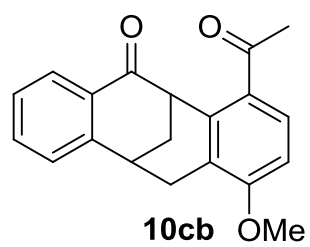
^{13}C -NMR-spectrum of Tetracycline **10b** (CDCl_3).

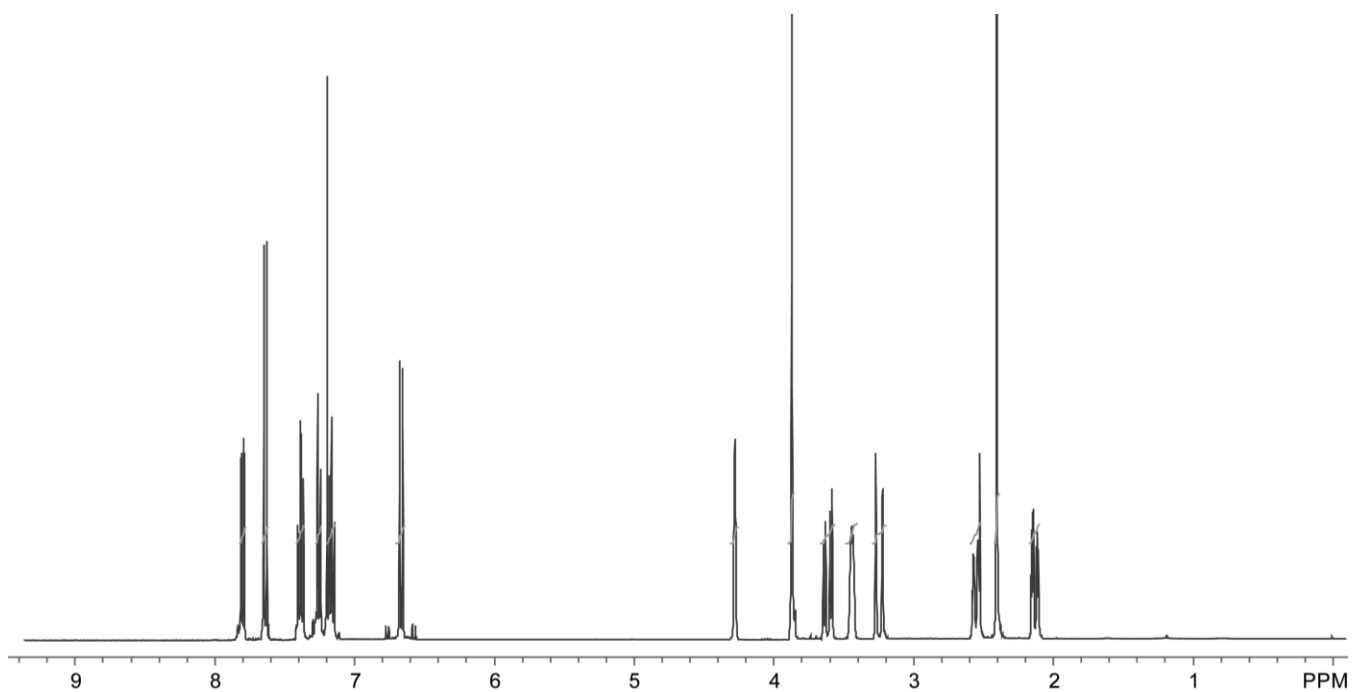


^1H -NMR-spectrum of Tetracycline **10ca** (CDCl_3).

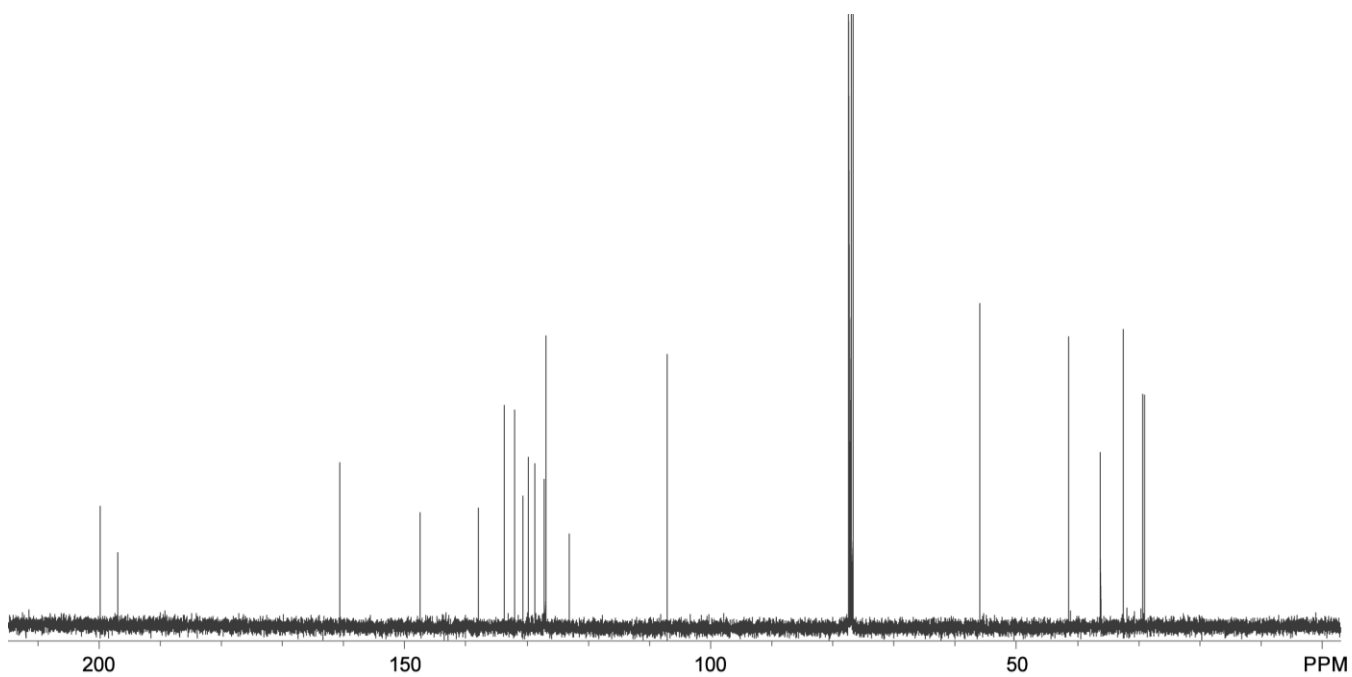


^{13}C -NMR-spectrum of Tetracycline **10ca** (CDCl_3).

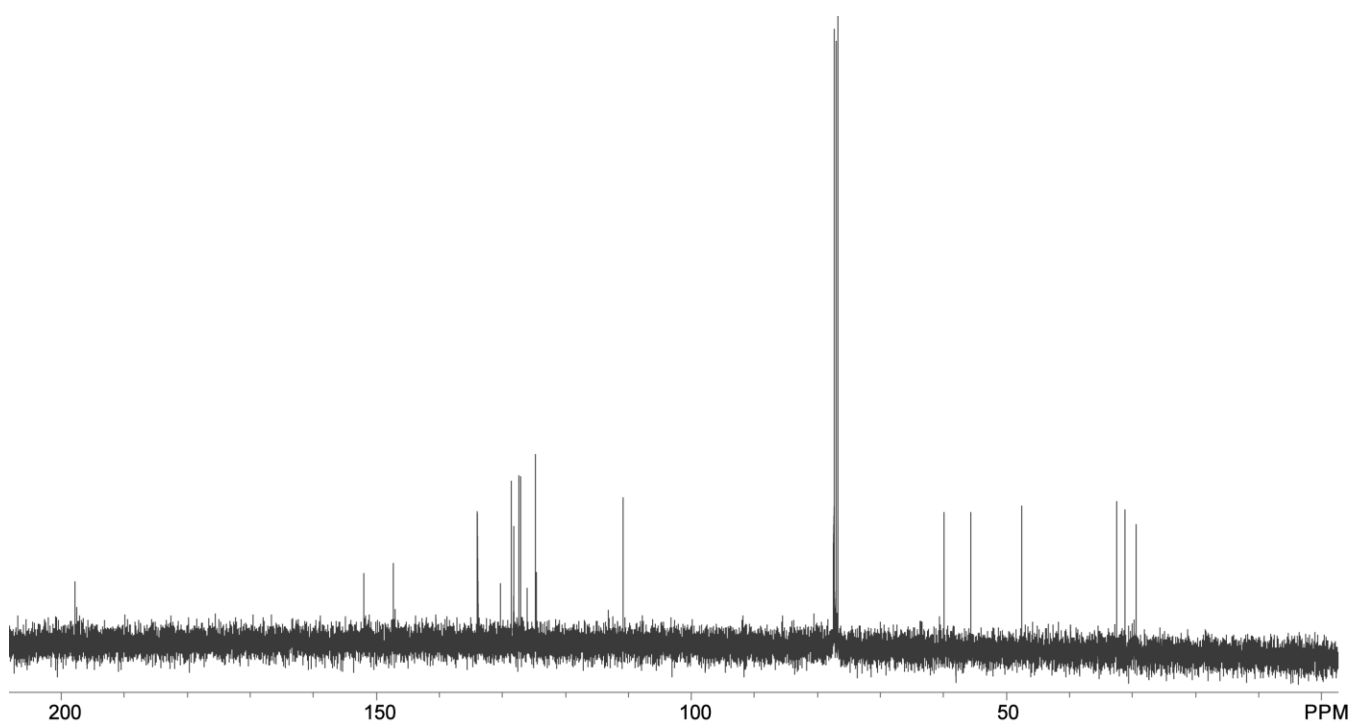
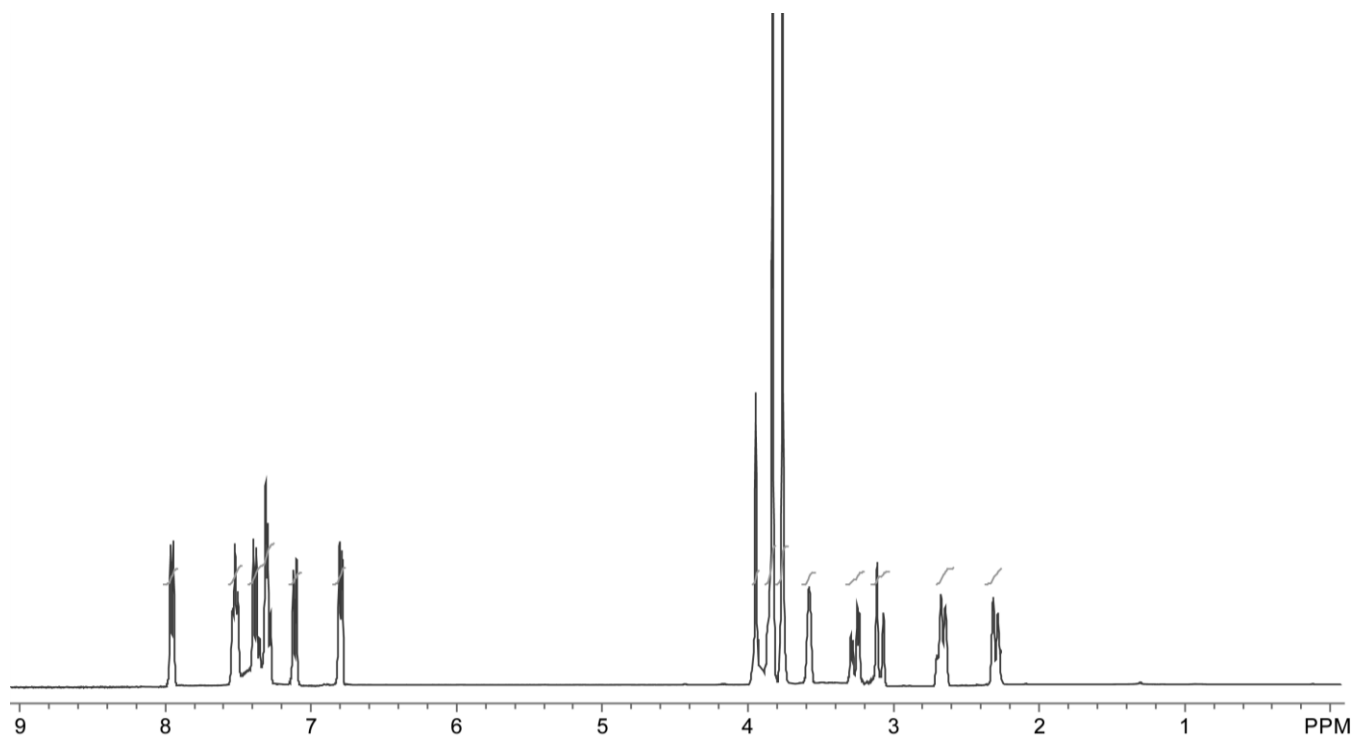
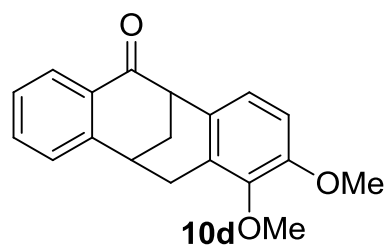




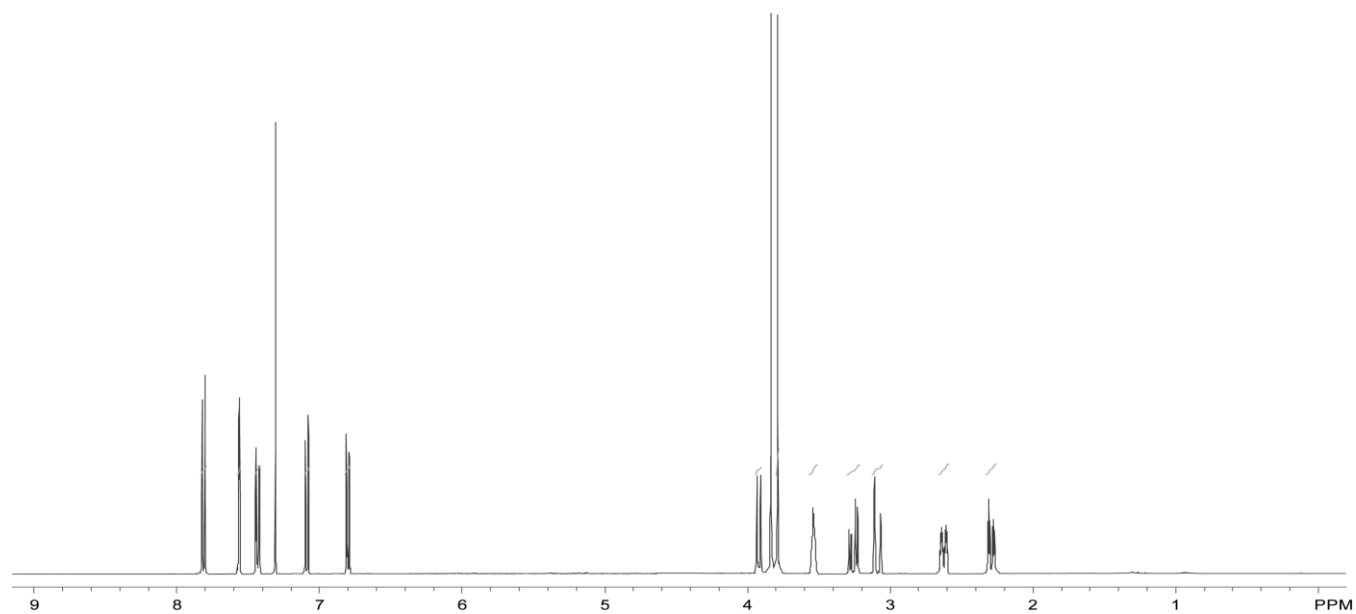
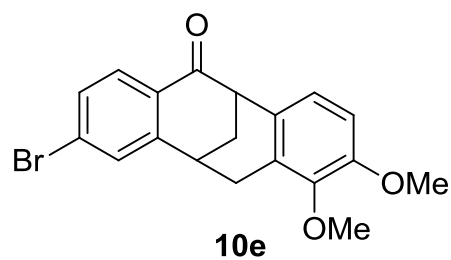
^1H -NMR-spectrum of Tetracycline **10cb** (CDCl_3).



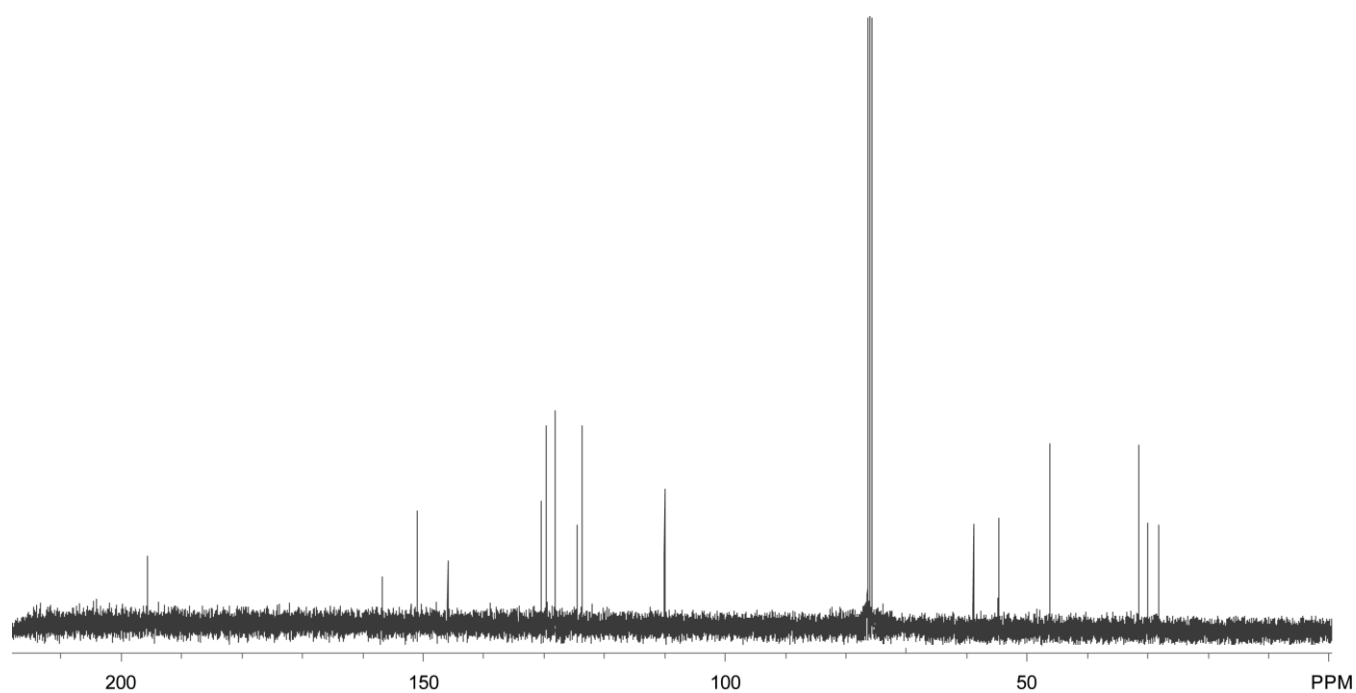
^{13}C -NMR-spectrum of Tetracycline **10cb** (CDCl_3).



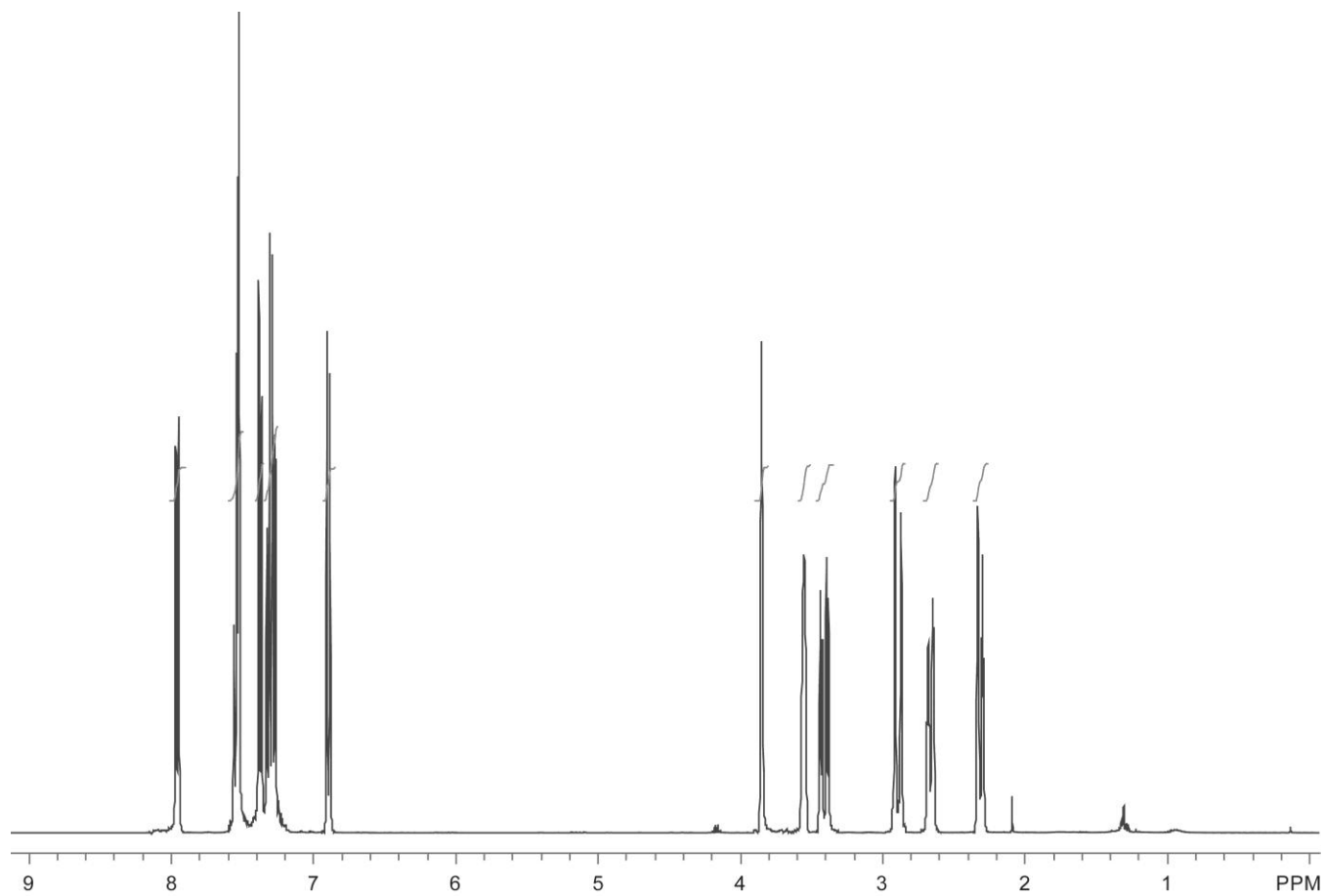
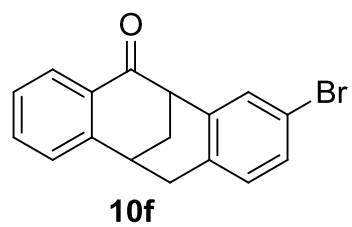
^{13}C -NMR-spectrum of Tetracycle **10d** (CDCl_3).



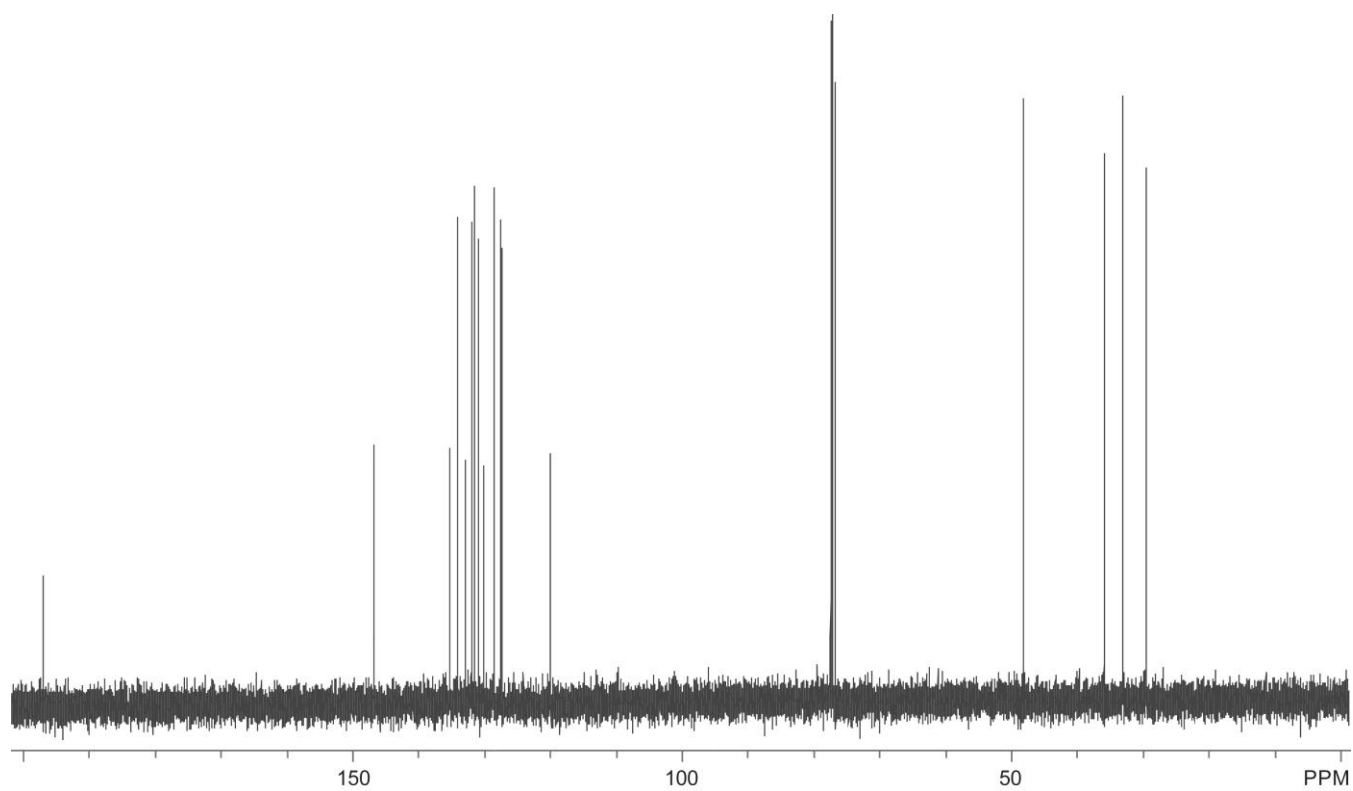
^1H -NMR-spectrum of Tetracycle **10e** (CDCl_3).



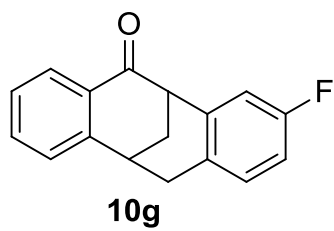
^{13}C -NMR-spectrum of Tetracycle **10e** (CDCl_3).

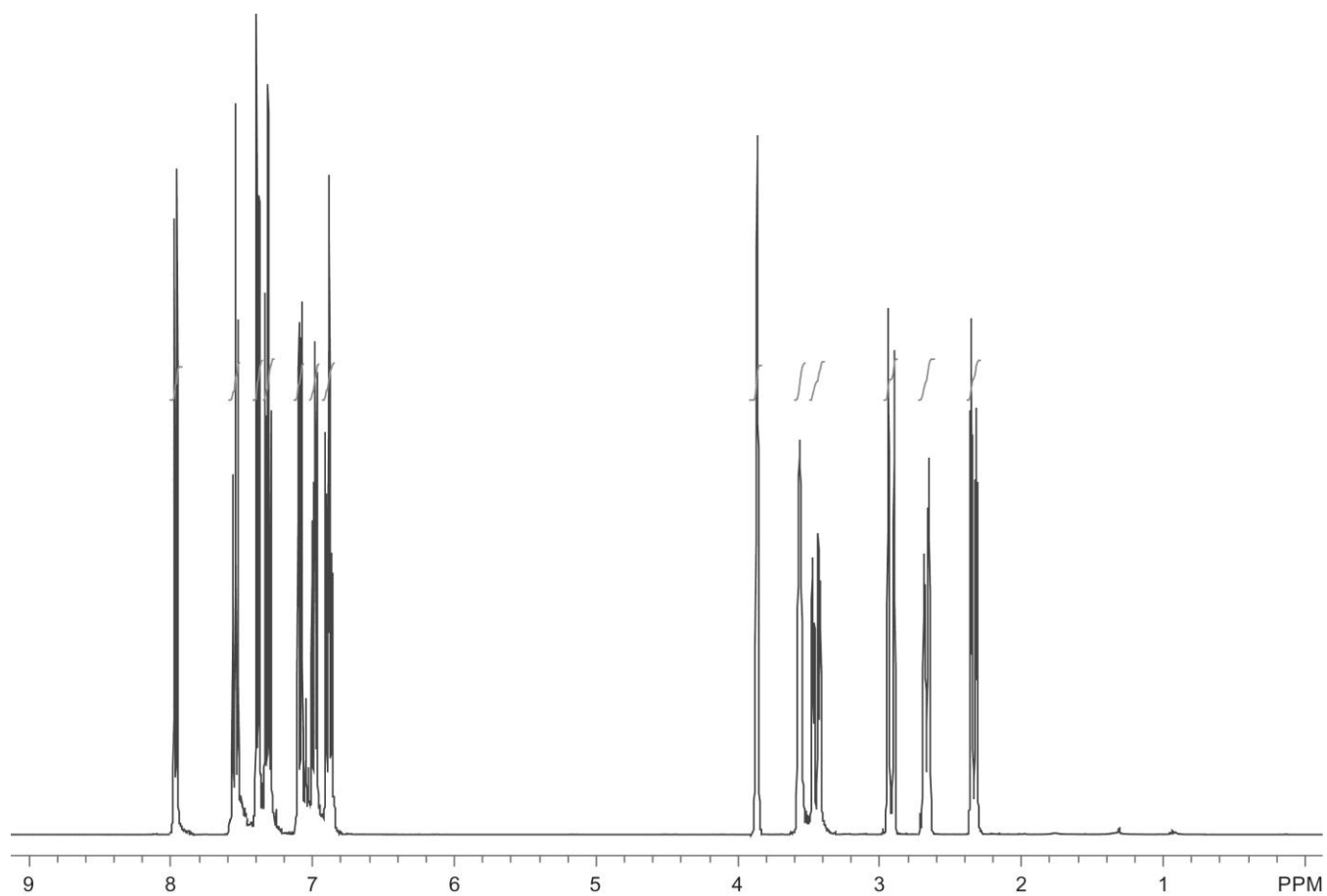


^1H -NMR-spectrum of Tetracycline **10f** (CDCl₃).

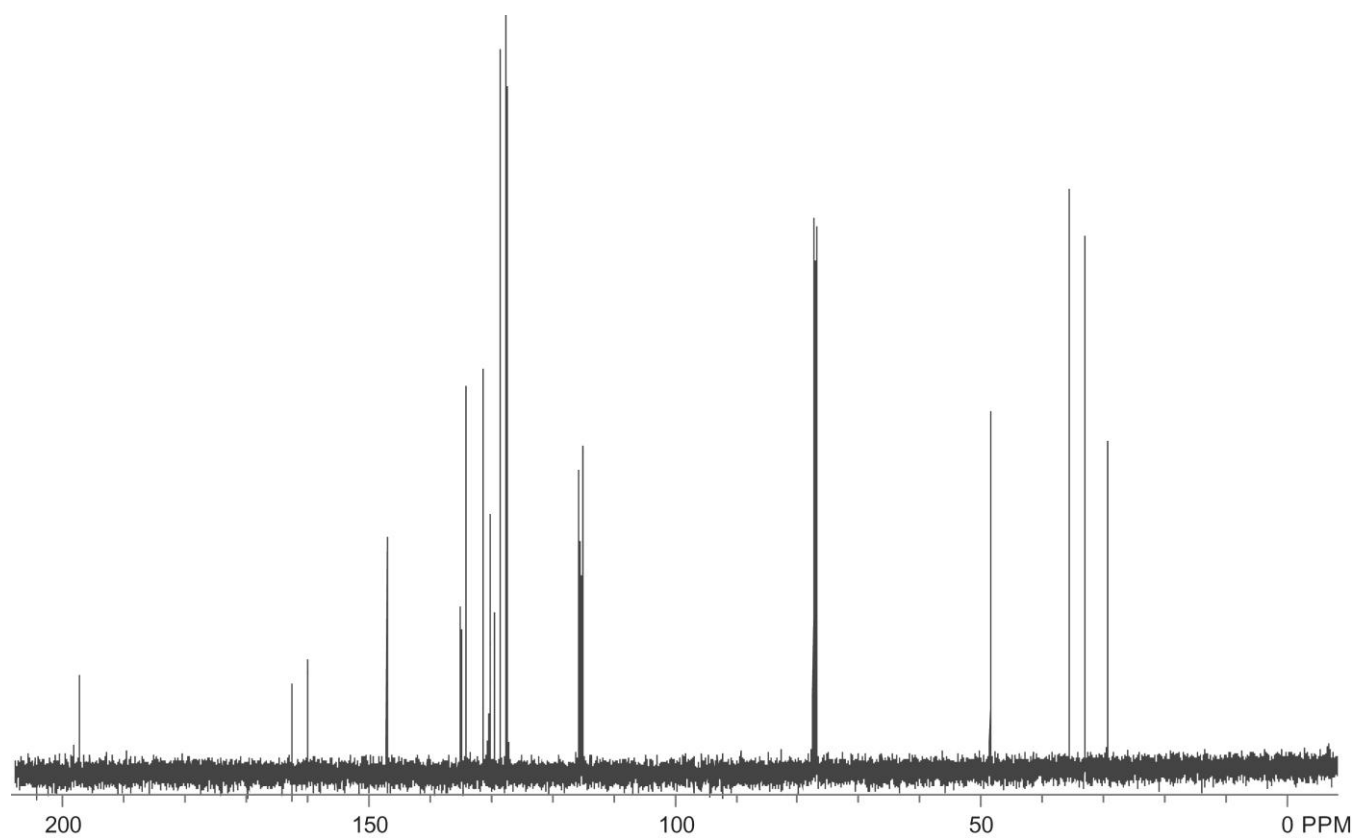


^{13}C -NMR-spectrum of Tetracycle **10f** (CDCl_3).

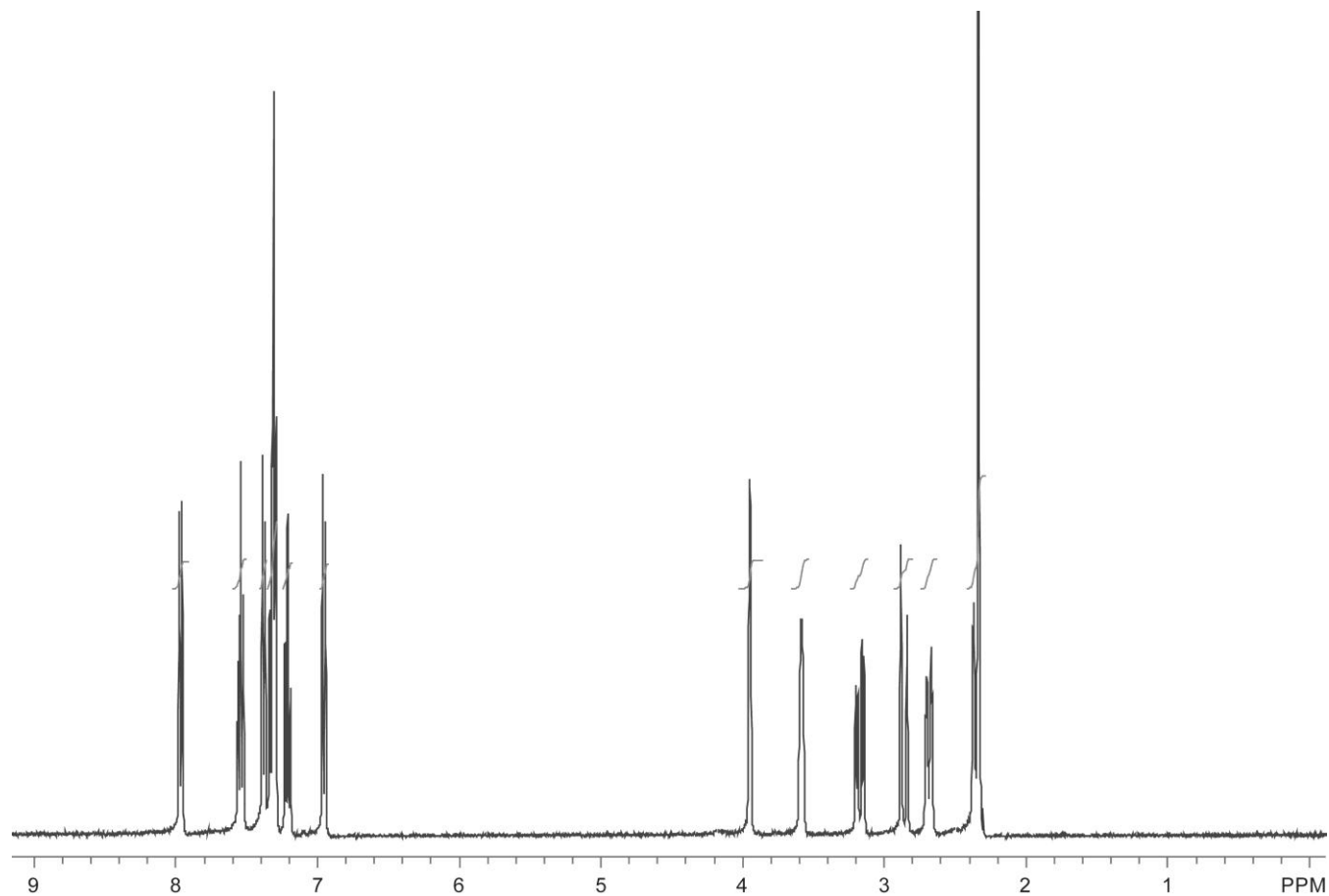
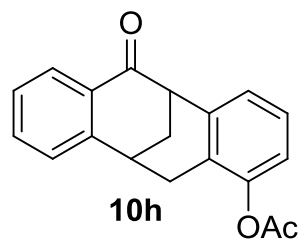




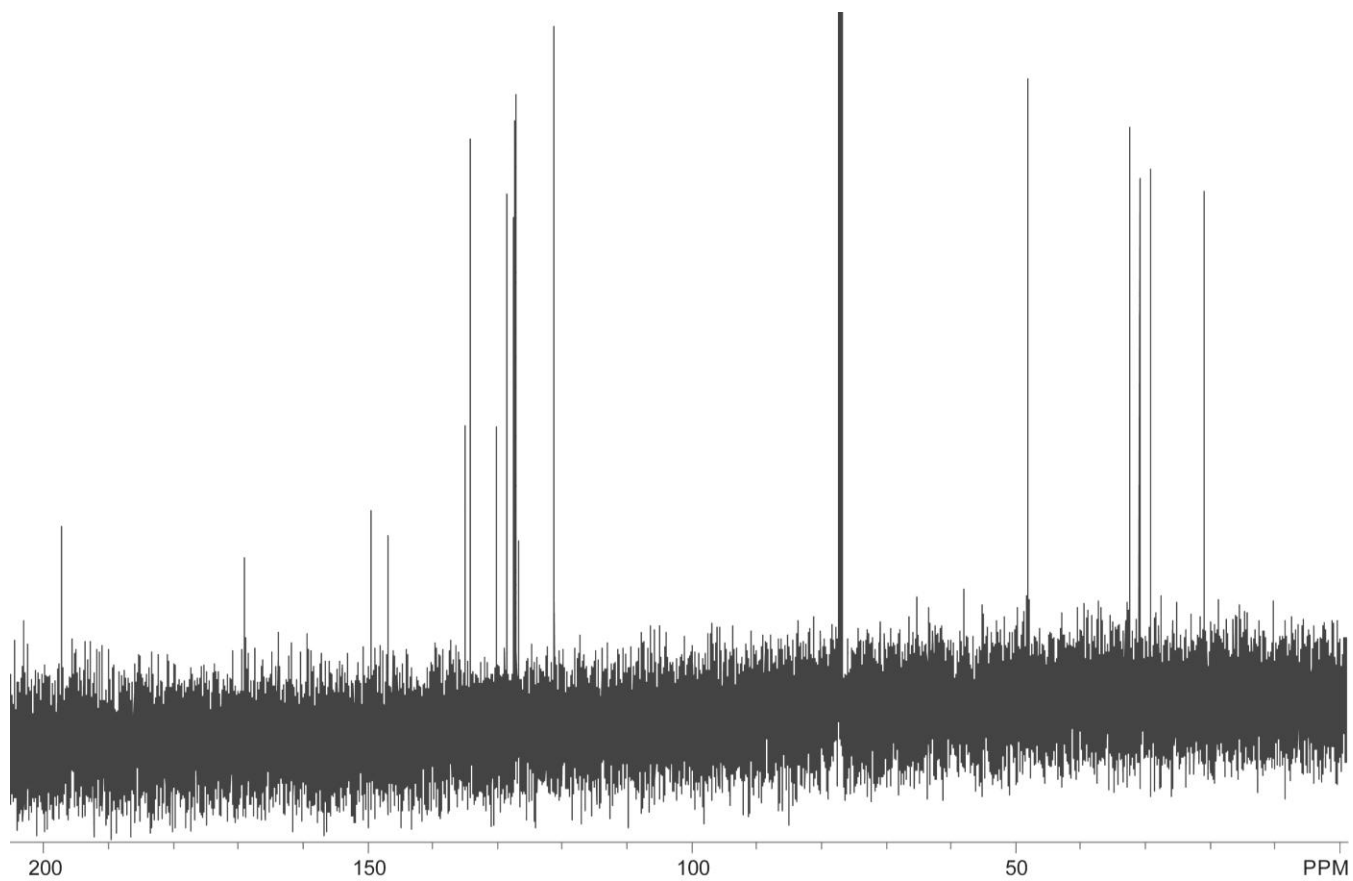
^1H -NMR-spectrum of Tetracycline **10g** (CDCl_3).



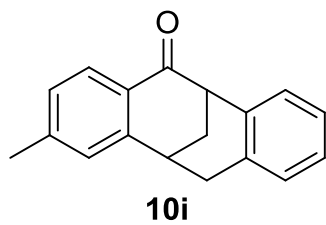
^{13}C -NMR-spectrum of Tetracycline **10g** (CDCl_3).

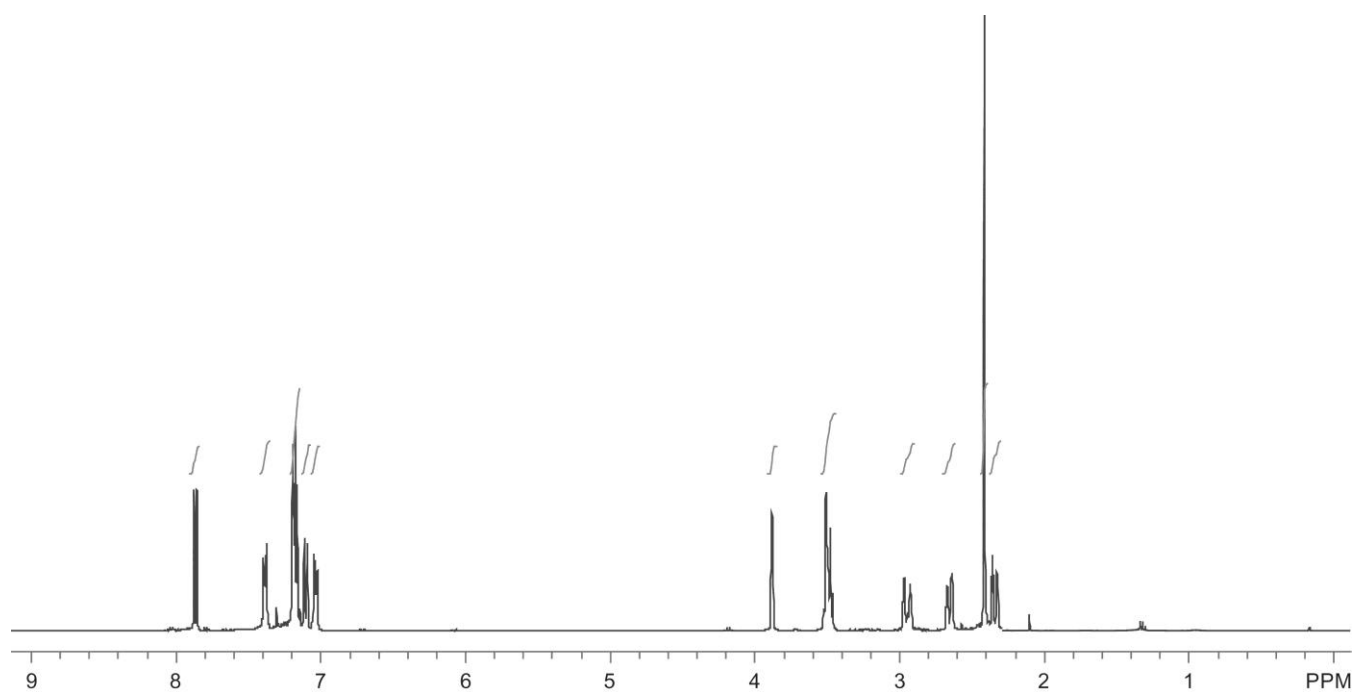


^1H -NMR-spectrum of Tetracycline **10h** (CDCl_3).

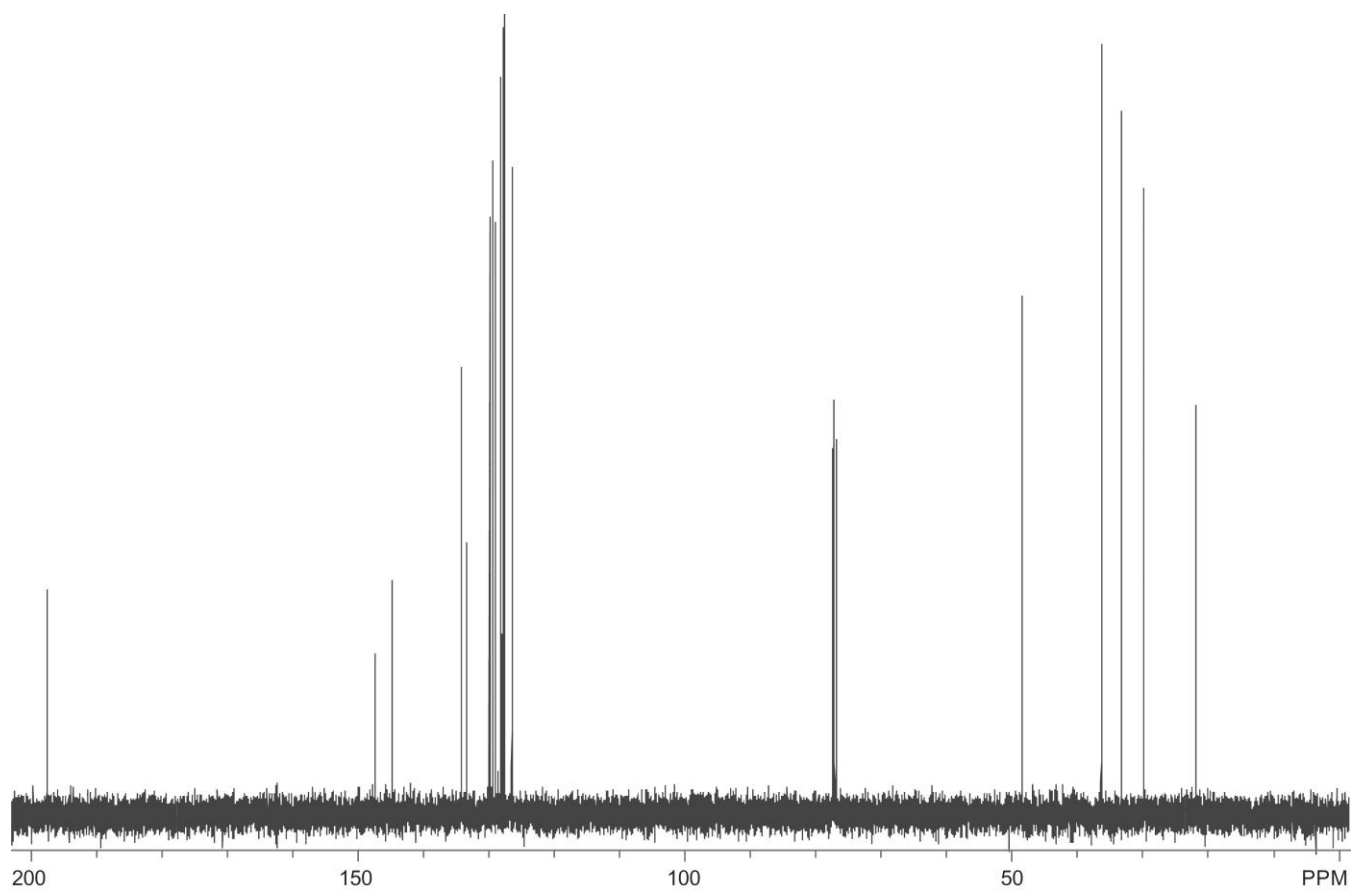


^{13}C -NMR-spectrum of Tetracycline **10h** (CDCl_3).

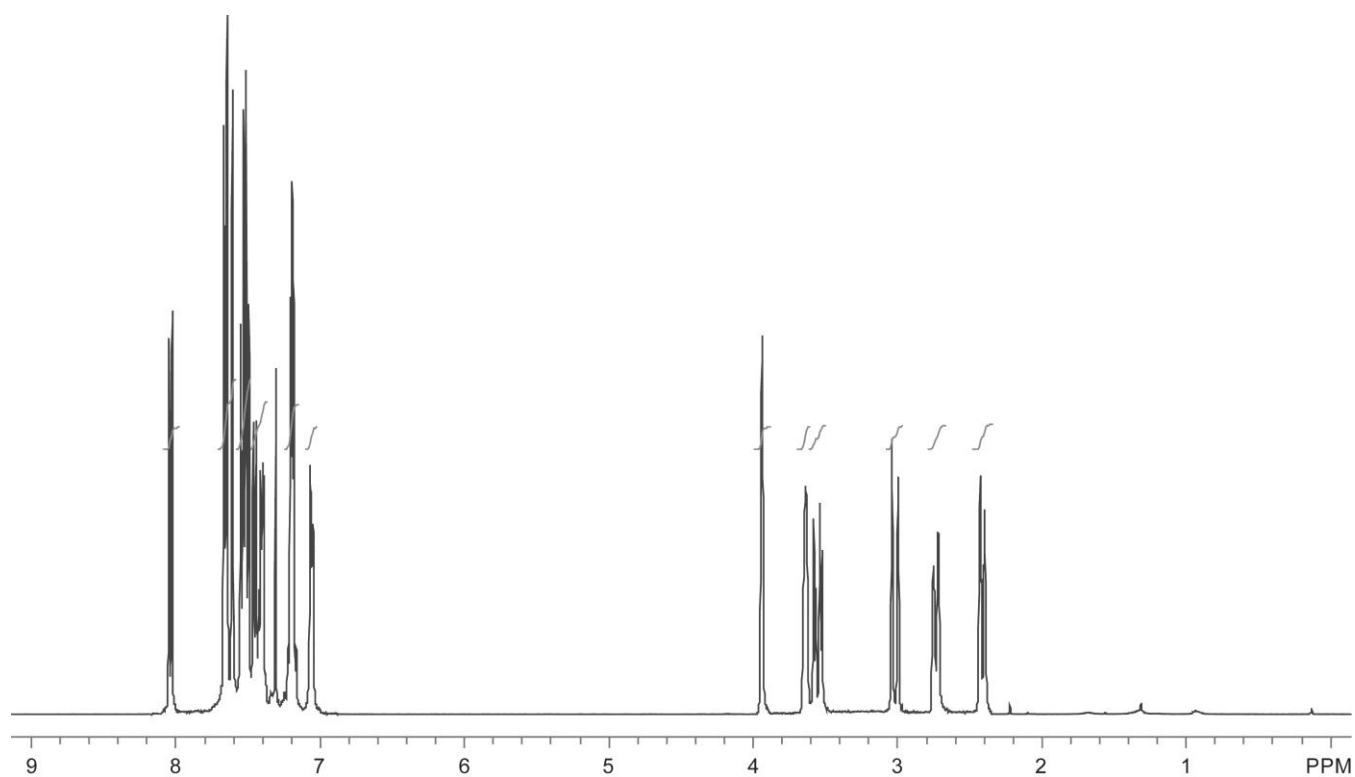
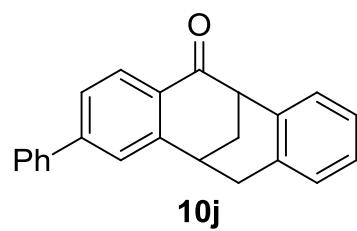




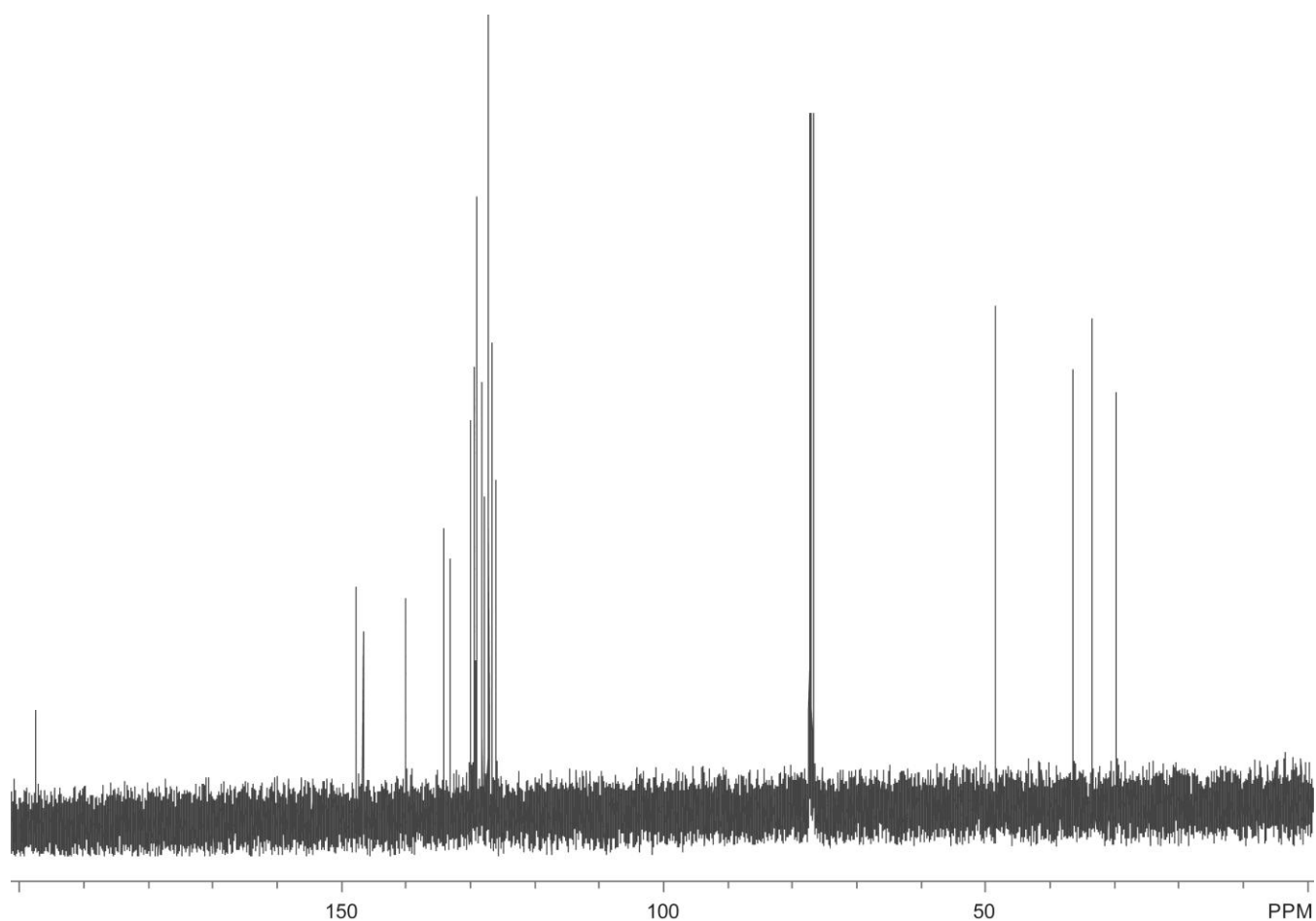
^1H -NMR-spectrum of Tetracycline **10i** (CDCl_3).



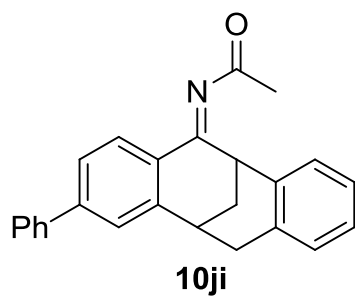
^{13}C -NMR-spectrum of Tetracycline **10i** (CDCl_3).

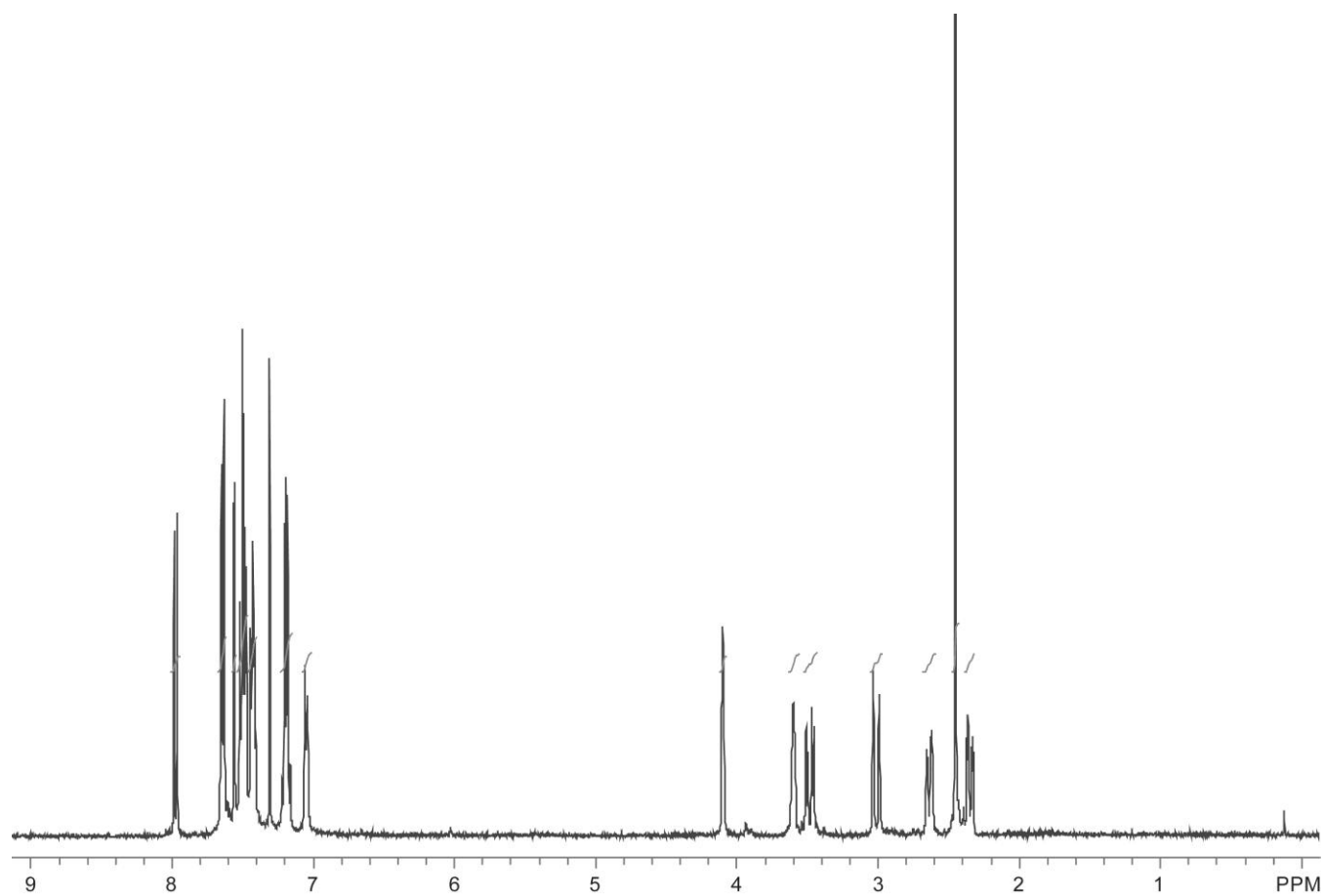


¹H-NMR-spectrum of Tetracycline **10j** (CDCl₃).

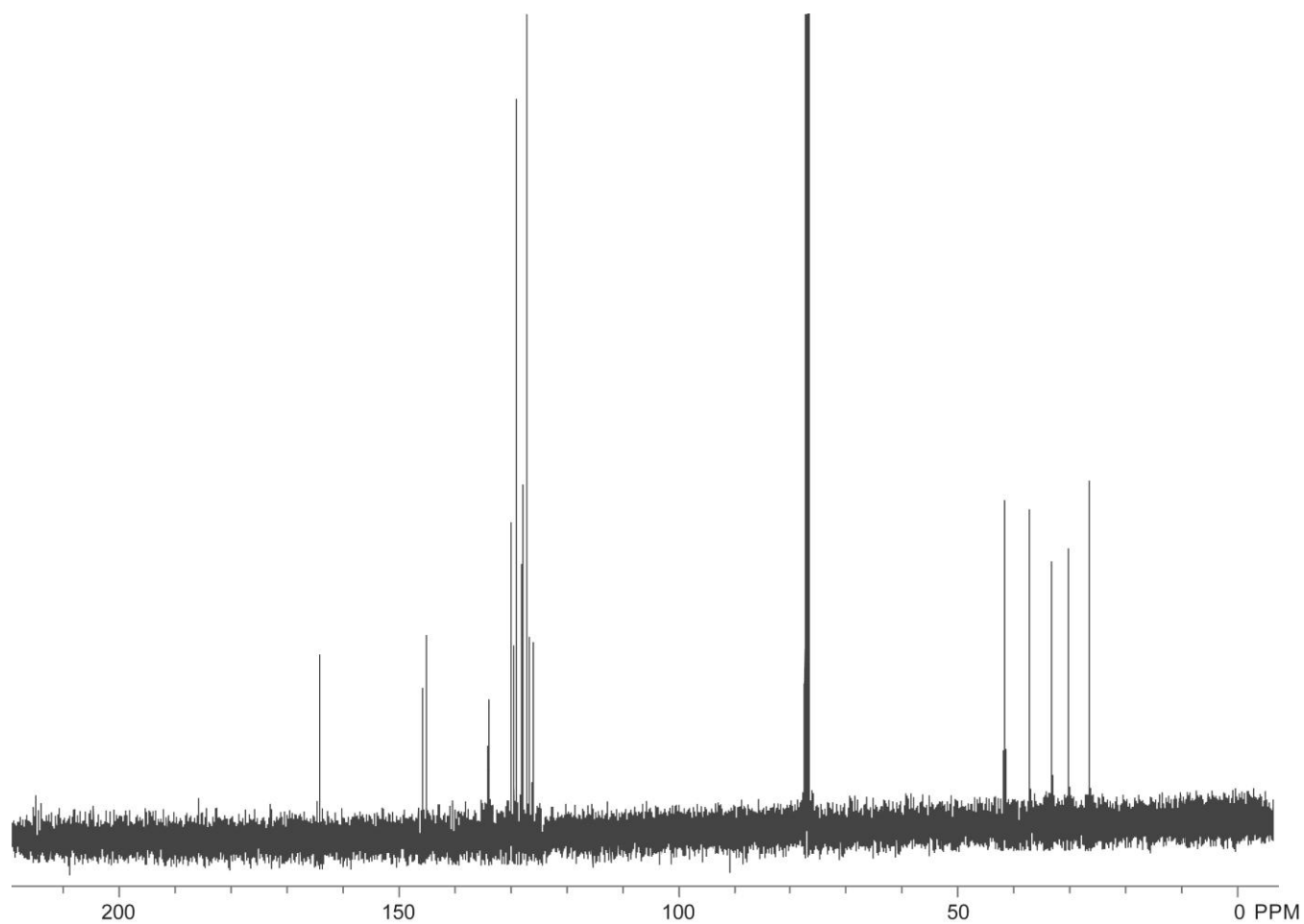


^{13}C -NMR-spectrum of Tetracycle **10j** (CDCl_3).

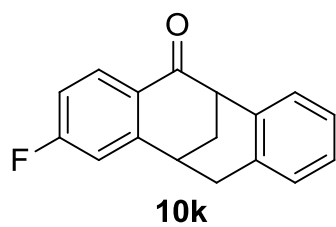


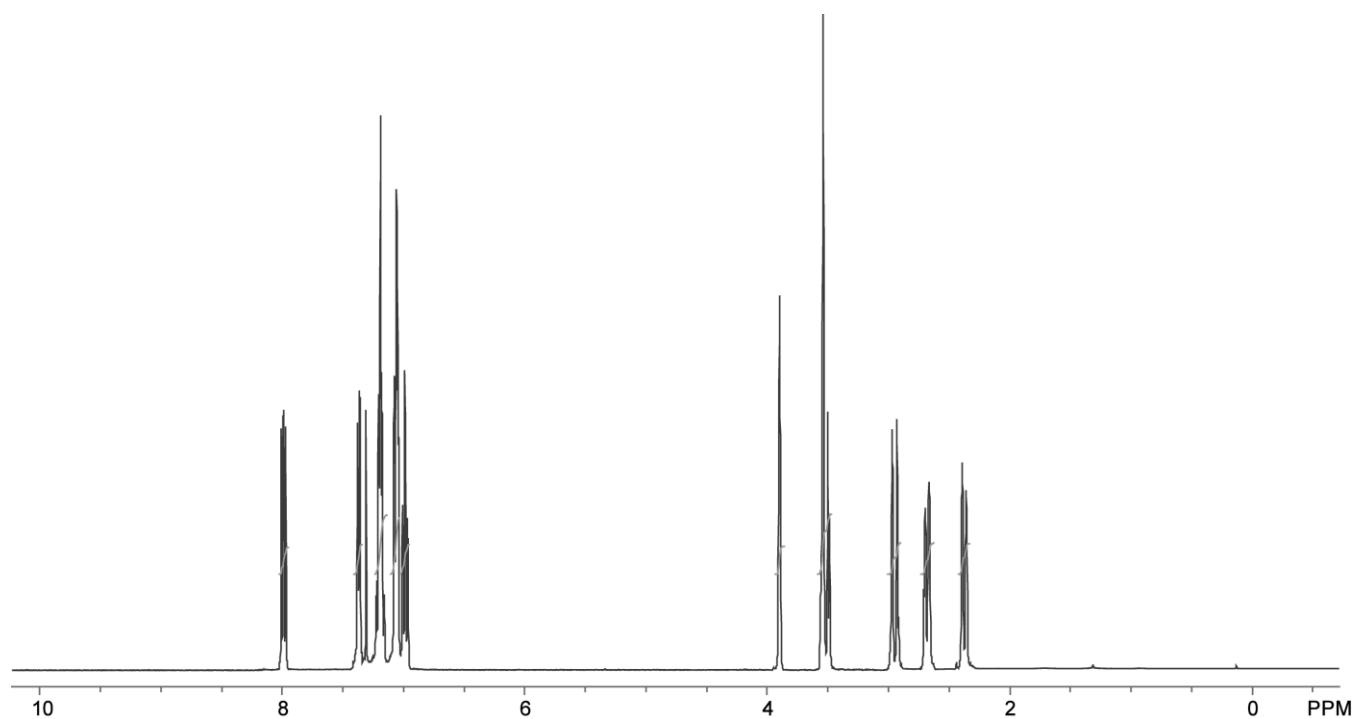


^1H -NMR-spectrum of Tetracyclic Acylimine **10ji** (CDCl_3).

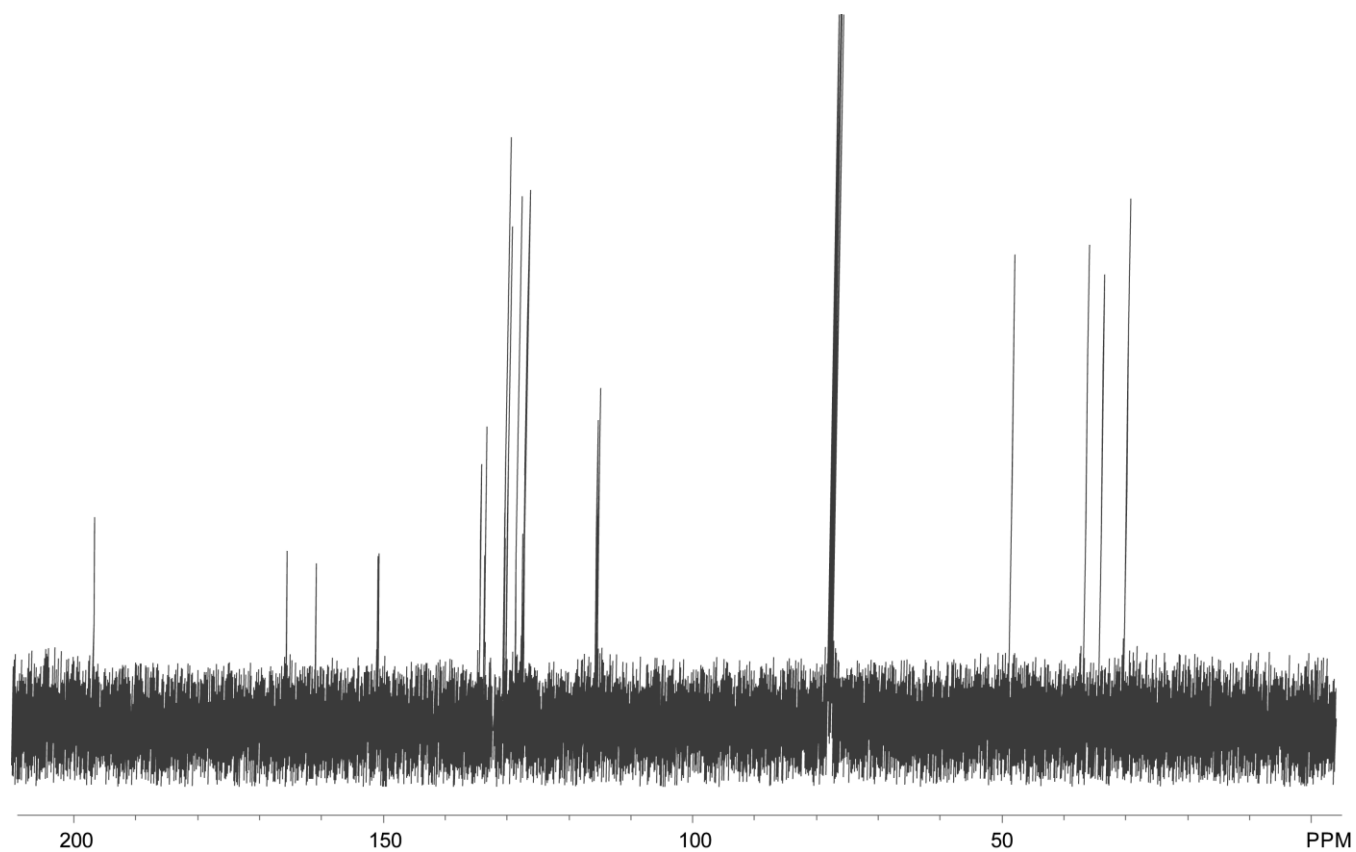


^{13}C -NMR-spectrum of Tetracyclic Acylimine **10ji** (CDCl_3).

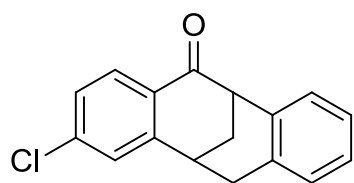




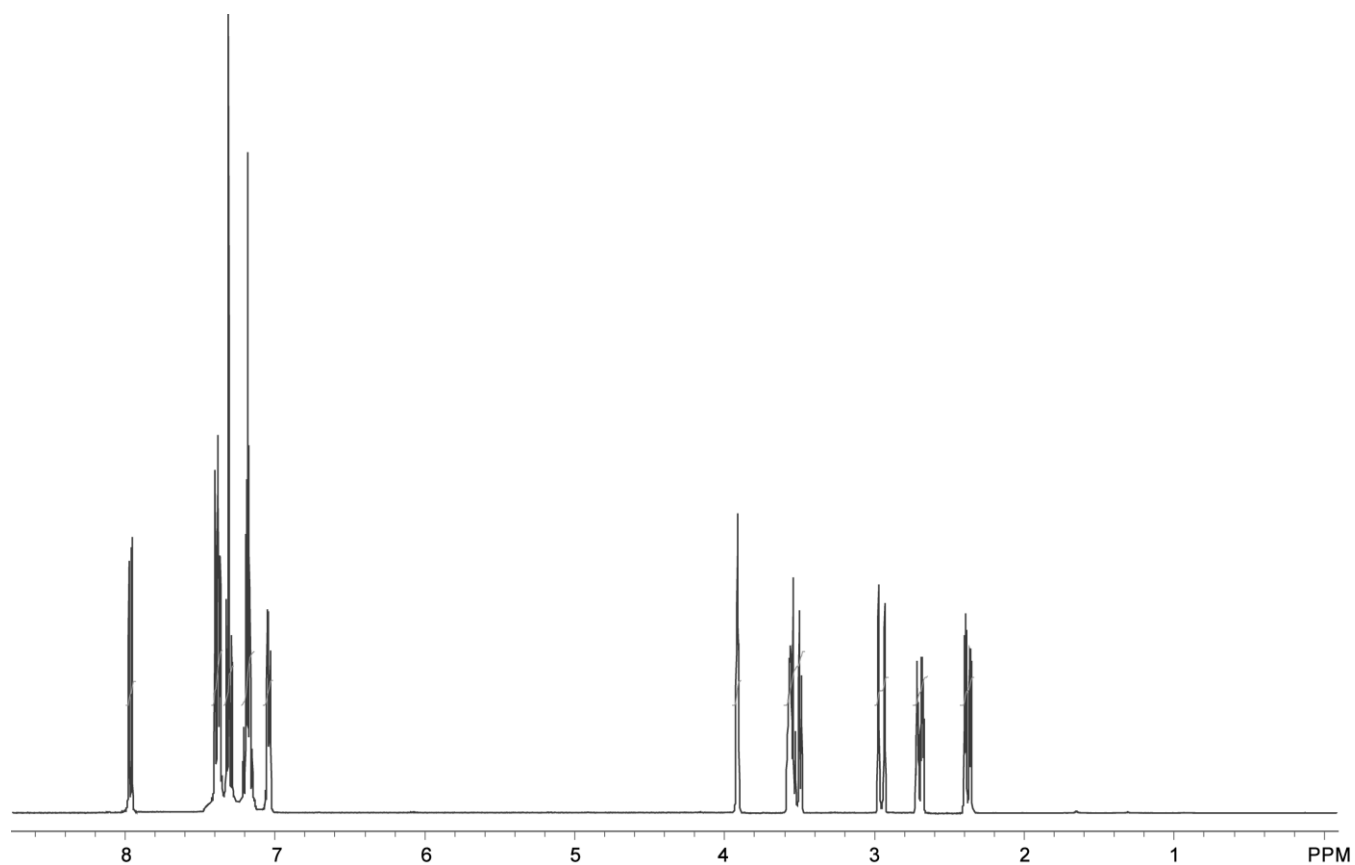
^1H -NMR-spectrum of Tetracycline **10k** (CDCl_3).



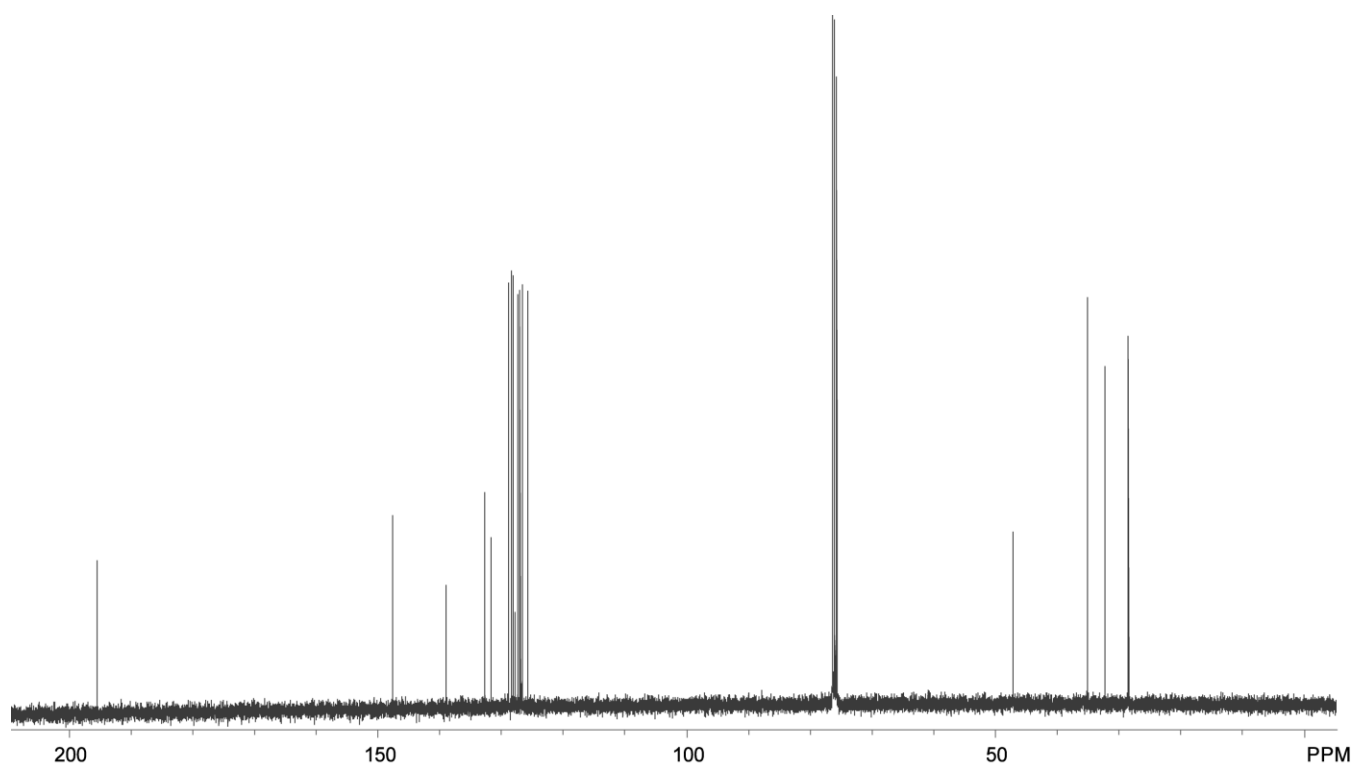
^{13}C -NMR-spectrum of Tetracycline **10k** (CDCl_3).



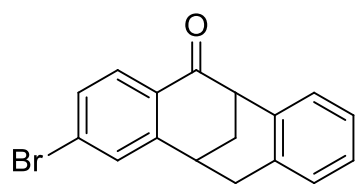
101



¹H-NMR-spectrum of Tetracycline **101** (CDCl₃).



^{13}C -NMR-spectrum of Tetracycle **10l** (CDCl_3).



10m

