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Manganese Catalyzed α-methylation of ketones with methanol as C1 source

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General information.

All reactions were carried out with oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon or in an argon-filled glove-box. Toluene, THF, diethyl ether, and dichloromethane were dried over a MBraun MB-SPS-800 solvent purification system and degassed by thaw-freeze cycles. MeOH (Honeywell, Chromasolv for HPLC, gradient grade ≥ 99.9%) was degassed and stored on molecular sieves 4 Å. Technical grade petroleum ether and ethyl acetate were used for chromatography column. Analytical TLC was performed on Merck $60F_{254}$ silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 µm, 60 Å). All reagents were obtained from commercial sources and liquid reagents were dried on 4 Å molecular sieves and degassed prior to use. Manganese pentacarbonyl bromide, min. 98%, was purchased from Strem Chemicals.

^{1}H, and ^{13}C NMR spectra were recorded in $CDCl_3$ at 298 K, on Bruker, AVANCE 400 spectrometer at 400.1 and 100.6 MHz, respectively. ^{1}H and ^{13}C NMR spectra were calibrated against the residual solvent signal at the corresponding central peak (^{1}H: $CDCl_3$ 7.26 ppm; ^{13}C: $CDCl_3$ 77.16 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet, and br. for broad).

Ace® pressure tube with front seal (15 mL) were used for the methylation reaction.

GC analyses were performed with GC-2014 (Shimadzu) 2010 equipped with a 30 m capillary column (Supelco, SPB™-20, fused silica capillary column, 30 m × 0.25 mm × 0.25 mm film thickness).

GC-MS were obtained on a QP2010 Ultra GC/MS apparatus from Shimadzu equipped with a 30 m capillary column (Phenomenex, Zebron, ZB-5ms, fused silica capillary column, 30 M × 0.25 mm × 0.25 mm film thickness).

HR-MS spectra were performed by the mass spectrometry service of the "Institut de Chimie de Toulouse".

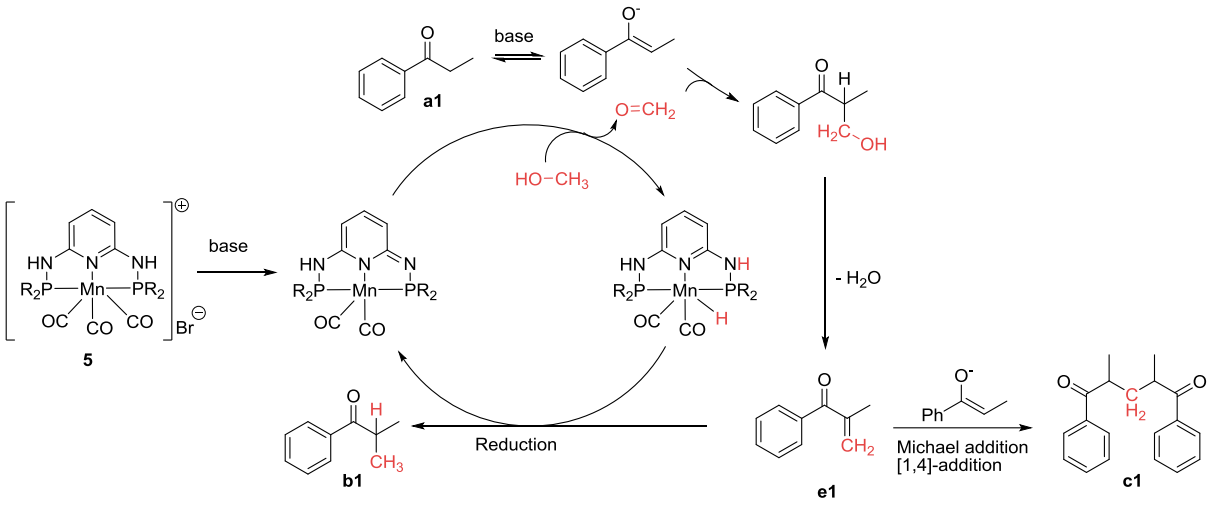
Dihydrochalcones derivatives **a16-a21** were synthesized according to literature procedure.[1]

Manganese complex **5** was synthesized according to literature procedure. [2]

General procedure for α-methylation of ketones.

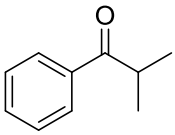
In an argon filled glove box, a 15 mL Ace® pressure tube was charged with ketone (0.5 mmol), MeOH (2 mL), Toluene (4 mL), **5** (3 mol%, 8.4 mg) and NaOtBu (50 mol%, 24.0mg), in that order. The closed pressure tube was then heated at 120 °C for 20 h. After cooling to room temperature, the solution was diluted with ethyl acetate (2.0 mL) and filtered through a small pad of celite (2 cm in a Pasteur pipette). The celite was washed with ethyl acetate (2×2.0 mL). Yield were determined by analysis of ^{1}H NMR of the crude mixture and confirmed with GC/GC-Mass analysis. The crude residue was purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate as eluent, 90/10 for ketones, and 99/1 for esters).

Proposed mechanism



Characterization of the products of the catalysis

Isobutyrophenone b1 [3]



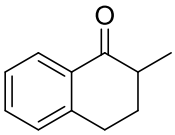
According to general procedure, propiophenone **a1** (66 µl, 0.5 mmol) gave the title compound **b1** as a colorless oil (47 mg, 64%).

Alternatively, according to general procedure, acetophenone **a2** (58 µl, 0.5 mmol) gave the title compound **b1** as a colorless oil (32 mg, 43%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.99 – 7.91 (m, 2H), 7.61 – 7.51 (m, 1H), 7-48 - 7.46 (m, 2H), 3.56 (hept, *J* = 6.8 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 6H).

^{13}C {^{1}H} NMR (75.5 MHz, Chloroform-*d*) δ 204.6, 136.3, 132.9, 128.7, 128.4, 35.4, 19.3.

2-Methyl-1-tetralone b3 [3]

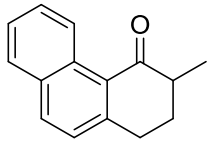


According to general procedure, 1-tetralone **a3** (67 µl, 0.5 mmol) gave the title compound **b3** as a colorless oil (30 mg, 38%).

^{1}H NMR (300.1 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.33 – 7.10 (m, 2H), 3.01-2.94 (m, 2H), 2.62-2.49 (m, 1H), 2.16 (dq, *J* = 13.2, 4.4 Hz, 1H), 2.00 – 1.67 (m, 1H), 1.24 (d, *J* = 6.7 Hz, 3H).

^{13}C {^{1}H} NMR (75.5 MHz, Chloroform-*d*) δ 200.9, 144.3, 133.2, 132.5, 128.8, 127.5, 126.7, 42.8, 31.5, 29.0, 15.6.

3-methyl-2,3-dihydrophenanthren-4(1*H*)-one b4 [4]

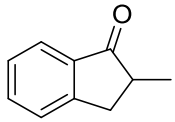


According to general procedure, 2,3-dihydrophenanthren-4(1*H*)-one **a4** (98 mg, 0.5 mmol) gave the title compound **b4** as an ivory solid (83 mg, 79%).

^{1}H NMR (300.1 MHz, Chloroform-*d*) δ 9.38 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.61 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.48 (ddd, *J* = 7.9, 6.8, 1.0 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 3.24-3.03 (m, 2H), 2.84 – 2.64 (m, 1H), 2.28-2.20 (m, 1H), 2.06 – 1.85 (m, 1H), 1.32 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75.5 MHz, Chloroform-*d*) δ 203.4, 145.9, 133.8, 132.8, 131.4, 128.6, 128.3, 127.3, 127.0, 126.6, 125.8, 43.9, 31.3, 30.4, 16.0.

2-Methyl-1-indanone b5 [5]

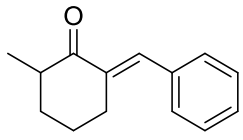


According to general procedure, 1-indanone **a5** (66 mg, 0.5 mmol) gave the title compound **b5** as a colorless oil (34 mg, 46%).

^{1}H NMR (300.1 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.4 Hz, 1H), 7.64 – 7.49 (m, 1H), 7.45 – 7.42 (m, 1H), 7.38 – 7.32 (m, 1H), 3.43 – 3.34 (m, 1H), 2.84 – 2.52 (m, 2H), 1.30 (d, *J* = 7.2 Hz, 3H).

^{13}C {^{1}H} NMR (75.5 MHz, Chloroform-*d*) δ 209.5, 153.6, 136.5, 134.8, 127.4, 126.6, 124.1, 42.1, 35.1, 16.4.

2-Benzylidene-6-methylcyclohexanone b6 [6]

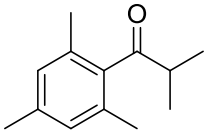


According to general procedure, 2-benzylidenecyclohexanone **a6** (93 mg, 0.5 mmol) gave the title compound **b6** as a white solid (51 mg, 51%).

^{1}H NMR (300.1 MHz, Chloroform-*d*) δ 7.42 – 7.35 (m, 5H), 7.34 – 7.27 (m, 1H), 3.12 – 2.92 (m, 1H), 2.73-2.61 (m, 1H), 2.54 – 2.39 (m, 1H), 2.12-2.04 (m, 1H), 1.95-1.84 (m, 1H), 1.78 – 1.54 (m, 2H), 1.20 (d, *J* = 6.8 Hz, 3H).

^{13}C {^{1}H NMR (101.6 MHz, Chloroform-*d*) δ 204.9, 137.5, 136.0, 134.8, 130.2, 128.41, 128.41, 44.5, 32.1, 29.4, 23.1, 16.5.

2-Methyl-1-(2',4',6'-trimethylphenyl)- 1-propanone b7

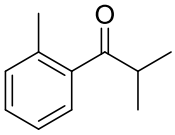


According to general procedure, 2'-4'-6' trimethylacetophenone **a7** (83 µl, 0.5 mmol) gave the title compound **b7** as a colorless oil (63 mg, 66%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 6.84 (s, 2H), 2.98 (hept, *J* = 6.9 Hz, 1H), 2.28 (s, 3H), 2.19 (s, 6H), 1.17 (d, *J* = 6.9 Hz, 6H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 214.4, 139.2, 138.4, 133.4, 128.7, 42.4, 21.2, 19.8, 18.1.

2-Methyl-1-(2'-Methylphenyl)-1-propanone b8 [7]

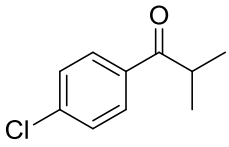


According to general procedure, 2'-methylacetophenone **a8** (65 µl, 0.5 mmol) gave the title compound **b8** as a colorless oil (57 mg, 71%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 – 7.10 (m, 2H), 3.34 (hept, *J* = 6.9 Hz, 1H), 2.42 (s, 3H), 1.17 (d, *J* = 6.9 Hz, 6H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 209.4, 138.8, 137.5, 131.7, 130.7, 127.5, 125.6, 38.9, 20.9, 18.7.

1-(4'-Chlorophenyl)-2-methyl-1-propanone b9 [5]

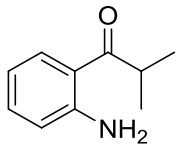


According to general procedure, 4'-chloroacetophenone **a9** (65 µl, 0.5 mmol) gave the title compound **b9** as a yellow oil (51 mg, 56%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 3.49 (hept, *J* = 6.8 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 6H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 203.3, 139.3, 134.6, 129.9, 129.1, 35.6, 19.2.

1-(2'-Aminophenyl)-2-methyl-propan-1-one b10 [8]

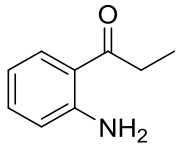


According to general procedure, 2'-aminoacetophenone **a10** (68 mg, 0.5 mmol) gave the title compound **b10** as a yellow oil (33 mg, 40%). The GC-MS of the crude mixture shows the presence of only **a10**, **b10** and the mono-methylated product 1-(2'-aminophenyl)-propan-1-oneb **b10'**, isolated in c.a. 15% yield, see ^{1}H NMR, figure S19)

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.78-7.76 (m, 1H), 7.34 – 7.14 (m, 1H), 6.68-6.64 (m, 2H), 6.28 (br. s, 2H), 3.59 (hept, *J* = 6.8 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 6H).

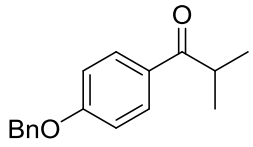
^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 207.2, 151.0, 134.2, 131.1, 117.7, 117.0, 115.9, 35.4, 19.8.

1-(2'-Aminophenyl)-propan-1-one b10'



^{1}H NMR (300.1 MHz, Chloroform-*d*) δ 7.86 – 7.70 (m, 1H), 7.36 – 7.12 (m, 1H), 6.70 – 6.59 (m, 2H), 6.26 (s, 2H), 2.97 (q, *J* = 7.3 Hz, 2H), 1.20 (t, *J* = 7.1 Hz 3H).

1-(4-(benzyloxy)phenyl)-2-methylpropan-1-one b11 [9]

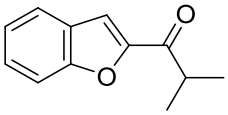


According to general procedure, 1-(4-(benzyloxy)phenyl)ethanone **a11** (113 mg, 0.5 mmol) gave the title compound **b11** as a white solid (99 mg, 78%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.53 – 7.31 (m, 5H), 7.02 (d, *J* = 8.9 Hz, 2H), 5.13 (s, 2H), 3.52 (hept, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 203.2, 162.5, 136.4, 130.7, 129.5, 128.8, 128.4, 127.6, 114.7, 70.3, 35.1, 19.4.

1-(Benzofuran-2-yl)-2-methylpropan-1-one b12 [10]

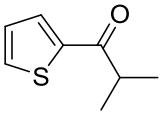


According to general procedure, 1-(benzofuran-2-yl)ethanone **a12** (80 mg, 0.5 mmol) gave the title compound **b12** as a yellow oil (43 mg, 46 %).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.9 Hz 1H), 7.59 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.52 (d, *J* = 1.0 Hz, 1H), 7.47 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.31 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 3.49 (hept, *J* = 6.9 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 195.7, 155.8, 152.3, 128.2, 127.2, 124.0, 123.3, 113.0, 112.6, 36.9, 18.9.

2-methyl-1-(thiophen-2-yl)propan-1-one b13 [9]

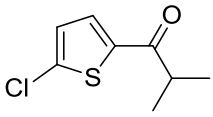


According to general procedure, 1-(thiophen-2-yl)ethanone **a13** (54 µL, 0.5 mmol) gave the title compound **b13** as a colorless liquid (32 mg, 41 %).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.60 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 3.37 (hept, *J* = 6.9 Hz, 1H), 1.22 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 197.5, 143.7, 133.5, 131.6, 128.1, 37.3, 19.5.

1-(5-Chloro-thiophen-2-yl)-2-methyl-propan-1-one b14

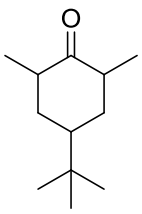


According to general procedure, 1-(5-chlorothiophen-2-yl)ethanone **a14** (80 mg, 0.5 mmol) gave the title compound **b14** as a colorless oil (32 mg, 34 %).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 4.1 Hz, 1H), 6.95 (d, *J* = 4.1 Hz, 1H), 3.30 (hept, *J* = 6.8 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 6H).

^{13}C{^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 196.7, 142.4, 139.4, 131.1, 127.6, 36.6, 19.5.

4-tertbutyl-2,6-dimethylcyclohexanone b15 [11]

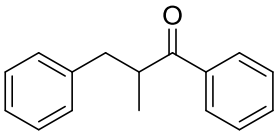


According to general procedure, 4-(tert-butyl)cyclohexanone **a15** (77 mg, 0.5 mmol) gave the title compound **b15** as a colorless liquid (21 mg, 23 %).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 2.46-2.36 (m, 2H), 2.11-2.06 (m, 2H), 1.69 (tt, *J* = 12.2, 3.2 Hz, 1H), 1.16 (q, *J* = 12.8 Hz, 2H), 1.01 (d, *J* = 6.5 Hz, 6H), 0.90 (s, 9H).

^{13}C{^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 215.1, 47.1, 44.5, 38.3, 32.5, 27.8, 14.9

2-Methyl-1,3-diphenylpropan-1-one b16 [5]

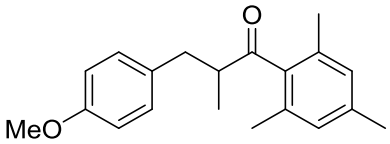


According to general procedure, 3-phenylpropiophenone **a16** (105 mg, 0.5 mmol) gave the title compound **b16** as a colorless oil (90 mg, 80%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.94-7.91 (m, 2H), 7.60 – 7.49 (m, 1H), 7.48 – 7.40 (m, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 3.84 – 3.71 (m, 1H), 3.17 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.69 (dd, *J* = 13.7, 7.9 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 203.9, 140.1, 136.6, 133.1, 129.2, 128.8, 128.5, 128.4, 126.3, 42.9, 39.5, 17.5.

1-Mesityl-3-(4-methoxyphenyl)-2-methylpropan-1-one b17



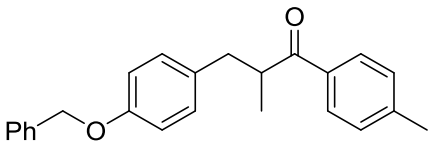
According to general procedure, 1-mesityl-3-(4-methoxyphenyl)propan-1-one **a17** (141 mg, 0.5 mmol) gave the title compound **b17** as a colorless oil (142 mg, 93%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.92 – 6.65 (m, 4H), 3.79 (s, 3H), 3.24 – 3.01 (m, 2H), 2.52 (dd, *J* = 13.3, 9.1 Hz, 1H), 2.28 (s, 3H), 2.17 (s, 6H), 1.08 (d, *J* = 6.9 Hz, 3H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 213.3, 158.2, 138.8, 138.6, 133.6, 132.1, 130.3, 128.9, 113.9, 55.4, 50.1, 37.2, 21.2, 19.8, 15.6.

HRMS (DCI-CH_4) m/z th for $C_{20}H_{24}O_2$ [$M^{+\cdot}$]= 296.1776 measured m/z = 296.1767 (3 ppm); m/z th for $C_{20}H_{25}O_2$ [MH^+]= 297.1855 measured m/z = 297.1851 (1 ppm)

3-(4-(Benzyloxy)phenyl)-2-methyl-1-(4-methylphenyl)propan-1-one b18



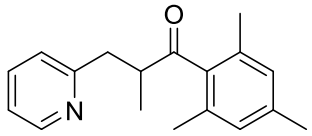
According to general procedure, 3-(4-(benzyloxy)phenyl)-1-(p-tolyl)propan-1-one **a18** (165 mg, 0.5 mmol) gave the title compound **b18** as a white solid (148 mg, 86%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.33 (m, 5H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.05 (s, 2H), 3.95 – 3.47 (m, 1H), 3.15 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.67 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.43 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 203.5, 157.3, 143.7, 137.2, 134.0, 132.5, 130.1, 129.4, 128.6, 128.5, 127.9, 127.5, 114.8, 70.1, 42.8, 38.7, 21.7, 17.5.

HRMS (DCI-CH_4) m/z th for $C_{24}H_{24}O_2$ [$M^{+\cdot}$]= 344.1776 measured m/z = 344.1767 (3 ppm); m/z th for $C_{24}H_{25}O_2$ [MH^+]= 345.1855 measured m/z = 345.1848 (2 ppm)

1-Mesityl-2-methyl-3-(pyridin-2-yl)propan-1-one b19



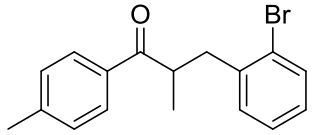
According to general procedure, 1-mesityl-3-(pyridin-2-yl)propan-1-one **a19** (125 mg, 0.5 mmol) gave the title compound **b19** as a colorless oil (68 mg, 51%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 4.1 Hz, 1H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.09 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 6.79 (s, 2H), 3.61 – 3.46 (m, 1H), 3.35 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.76 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.25 (s, 3H), 2.13 (s, 6H), 1.12 (d, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 212.9, 160.0, 149.4, 138.50, 138.47, 136.3, 133.6, 128.8, 124.4, 121.3, 48.1, 40.2, 21.1, 19.7, 16.1.

HRMS (DCI-CH_4) m/z th for $C_{18}H_{22}NO$ [MH^+]= 268.1701 measured m/z = 268.1692 (3 ppm)

3-(2-Bromophenyl)-2-methyl-1-(4-methyl)propan-1-one b20



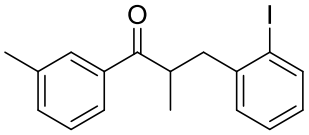
According to general procedure, 3-(2-bromophenyl)-1-(p-tolyl)propan-1-one **a20** (152 mg, 0.5 mmol) gave the title compound **b20** as a colorless oil (130 mg, 82%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.89 – 7.81 (m, 2H), 7.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.16 (td, *J* = 7.4, 1.3 Hz, 1H), 7.03 (ddd, *J* = 7.9, 7.2, 2.0 Hz, 1H), 3.93 (sex, *J* = 7.0 Hz, 1H), 3.24 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.85 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.39 (s, 3H), 1.20 (d, *J* = 7.0 Hz, 3H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 203.5, 143.9, 139.4, 134.1, 133.0, 132.1, 129.4, 128.6, 128.1, 127.4, 124.7, 40.3, 39.7, 21.7, 17.8.

HRMS (DCI-CH_4) m/z th for $C_{17}H_{18}OBr$ [MH^+]= 317.0541 measured m/z = 317.0538 (1 ppm)

3-(2-Iodophenyl)-2-methyl-1-(3-methylphenyl)propan-1-one b21



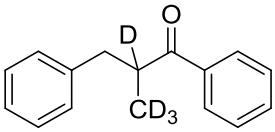
According to general procedure, 3-(2-iodophenyl)-1-(m-tolyl)propan-1-one **a21** (87 mg, 0.25 mmol) gave the title compound **b21** as a colorless oil (38 mg, 42%). The product is contaminated with 10% of the dehalogenated product according to ^{1}H NMR.

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.42 – 7.27 (m, 2H), 7.23 – 7.14 (m, 2H), 6.89-6.82 (m, 1H), 3.92 (h, *J* = 7.0 Hz, 1H), 3.25 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.84 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.38 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 3H).

^{13}C {^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 204.0, 142.7, 139.7, 138.5, 136.6, 133.9, 131.2, 129.1, 128.6, 128.3, 128.2, 125.7, 100.9, 43.8, 40.8, 21.5, 17.9.

HRMS (DCI-CH_4) m/z th for $C_{17}H_{18}OI$ [MH^+]= 365.0402 measured m/z = 365.0410 (2 ppm)

2-(Methyl-*d*$_3$)-2-*d*-1,3-diphenylpropan-1-one b22



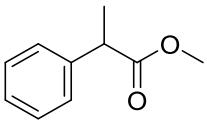
According to general procedure using CD_3OD instead of MeOH, 3-phenylpropiophenone **a16** (105 mg, 0.5 mmol) gave the title compound **b22** as a colorless oil (93 mg, 82%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.45 – 7.41 (m, 2H), 7.30 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 3.18 (d, *J* = 13.7 Hz, 1H), 2.71 (d, *J* = 13.7 Hz, 1H).

^{13}C {^{1}H} NMR (101 MHz, Chloroform-*d*) δ 203.8, 140.0, 136.5, 133.0, 129.1, 128.7, 128.4, 128.3, 126.3, 42.2 (t, *J* = 19.2 Hz), 39.3, 16.6 (hept, *J* = 19.2 Hz). (One additional signal is present at 42.6 ppm belonging to the same compound with a proton at the carbon C*H*(CD_3)).

HRMS (DCI-CH_4) m/z th for $C_{16}H_{12}D_4O$ [$M^{+\cdot}$]= 228.1452 measured m/z = 228.1454 (1 ppm); m/z th for $C_{16}H_{13}D_4O$ [MH^+]= 229.1530 measured m/z = 229.1525 (2 ppm)

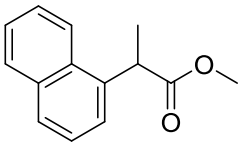
Methyl 2-phenylpropanoate b23



According to general procedure, methyl 2-phenylacetate **a23** (88 µl, 0.5 mmol) gave the title compound **b23** (95% conversion).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.21 (m, 5H), 3.73 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H).

Methyl 2-(naphthalen-1-yl)propanoate b24 [12]

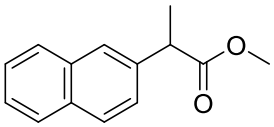


According to general procedure, methyl 2-(naphthalen-1-yl)acetate **a24** (88 µl, 0.5 mmol) gave the title compound **b24** as a colorless oil (33 mg, 31%).

^{1}H NMR (300.1 MHz, Chloroform-*d*) δ 8.09 (d, = 8.3 Hz, 1H), 7.89-7.86 (m, 1H), 7.83 – 7.75 (m, 1H), 7.61 – 7.45 (m, 4H), 4.52 (q, *J* = 7.1 Hz, 1H), 3.66 (s, 3H), 1.67 (d, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (75.5 MHz, Chloroform-*d*) δ 175.6, 136.9, 134.1, 131.4, 129.1, 127.9, 126.5, 125.8, 125.7, 124.6, 123.2, 52.3, 41.5, 18.4.

Methyl 2-(naphthalen-2-yl)propanoate b25 [13]

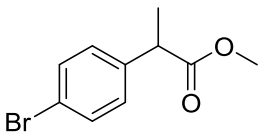


According to general procedure (using 50mol% NaOtBu), methyl 2-(naphthalen-2-yl)acetate **a25** (88 µl, 0.5 mmol) gave the title compound **b25** as a colorless oil (40 mg, 37%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.78 (m, 3H), 7.77 – 7.72 (m, 1H), 7.49-7.43 (m, 3H), 3.91 (q, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 1.61 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.1, 138.1, 133.6, 132.7, 128.5, 127.9, 127.7, 126.29, 126.25, 125.9, 125.8, 52.2, 45.7, 18.7.

Methyl 2-(4-bromophenyl)propanoate b26 [13]

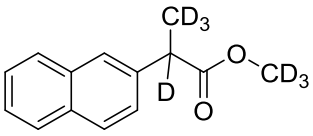


According to general procedure, methyl 2-(4-bromophenyl)acetate **a26** (114 mg, 0.5 mmol) gave the title compound **b26** as a colorless oil (43 mg, 35%).

^{1}H NMR (300.1 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 3.69 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H).

^{13}C {^{1}H} NMR (75.5 MHz, Chloroform-*d*) δ 174.6, 139.6, 131.9, 129.4, 121.2, 52.3, 45.0, 18.6.

Methyl-*d*$_3$ 2-(naphthalen-2-yl)-2,3,3,3-*d*$_4$-propanoate b27



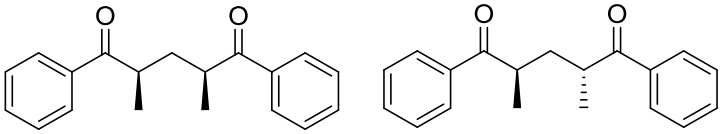
According to general procedure using CD_3OD, methyl 2-(naphthalen-2-yl)acetate **a25** (88 µl, 0.5 mmol) gave the title compound **b27** as a colorless oil (22 mg, 20%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.77 (m, 3H), 7.79-7.74 (m, 1H), 7.48 – 7.33 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.1, 138.0, 133.6, 132.7, 128.5, 127.9, 127.8, 126.3, 126.3, 126.0, 125.8. (Note : *C*D$_3$ and *C*D signals were not detected)

HRMS (DCI-CH_4) m/z th for $C_{14}H_7D_7O_2$ [$M^{+\cdot}$]= 221.1433 measured m/z = 221.1419 (2 ppm); m/z th for $C_{14}H_8D_7O_2$ [MH^+]= 222.1506 measured m/z = 222.1499 (3 ppm)

2,4-Dimethyl-1,5-diphenylpropan-1,5-dione c1 [3]



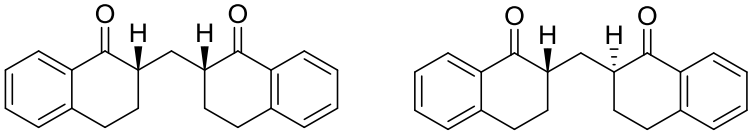
According to an alternative procedure, an Ace® pressure tube was charged with propiophenone **a1** (66 µl, 0.5 mmol), MeOH (0.5 mL), toluene (0.5 mL), Mn-complex **5** (3 mol%, 8 mg) and, NaOtBu (1 equiv., 48 mg), in that order. The same work up gave the title compound **c1**, obtained as a mixture of two diastereoisomers, as a colorless oil (44 mg, 63%).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.11 – 7.97 (m, 4H), 7.81 – 7.75 (m, 4H), 7.62 – 7.42 (m, 8H), 7.38 – 7.28 (m, 4H), 3.63 (h, *J* = 7.0 Hz, 2H), 3.50 (h, 7.0 Hz, 2H), 2.44 (dt, *J* = 13.7, 7.2 Hz, 1H), 2.01 (t, *J* = 7.1 Hz, 2H), 1.49 (dt, *J* = 13.9, 7.1 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 6H), 1.17 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 204.5, 203.9, 136.6, 136.4, 133.2, 133.1, 128.9, 128.7, 128.6, 128.3, 38.7, 38.2, 37.4, 37.1, 18.8, 17.7.

HRMS (DCI-CH_4) m/z th for $C_{19}H_{21}O_2$ [MH^+]= 281.1542 measured m/z = 281.1533 (3 ppm)

2,2'-Methyleneditetralone c3



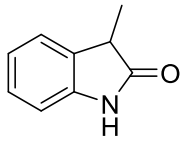
According to an alternative procedure, an Ace® pressure tube was charged with 1-tetralone **a3** (268 µl, 2 mmol), MeOH (1mL), toluene (1mL), Mn-complex **5** (1.5 mol%, 16 mg) and, NaOH (1 equiv., 80mg), in that order. The same work up gave the title compound **c3,** obtained as a mixture of the two diastereoisomers (ratio 1:1), as a colorless oil (116 mg, 38%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 8.01 (dt, *J* = 7.9, 1.7 Hz, 4H), 7.46 (tt, *J* = 7.5, 1.5 Hz, 4H), 7.33 – 7.27 (m, 4H), 7.24 (m, 4H), 3.05 (m, 8H), 2.88 – 2.75 (m, 4H), 2.74-2.96 (m, 1H), 2.33 (m, 4H), 2.04 (t, *J* = 6.6 Hz, 2H), 1.94 (m, 4H), 1.63-1.56 (m, 1H).

^{13}C{^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 201.0, 200. 5, 144.1, 144.0, 133.35, 133.34, 132.7, 132.6, 128.9 (2C), 127.6, 127.5, 126.7 (2C), 46.0 45.0, 31.0, 30.1, 29.5, 29.3, 28.7, 28.6.

HRMS (DCI-CH_4) m/z th for $C_{21}H_{21}O_2$ [MH^+]= 305.1542 measured m/z = 305.1543 (0 ppm)

3-methylindolin-2-one b28[9]



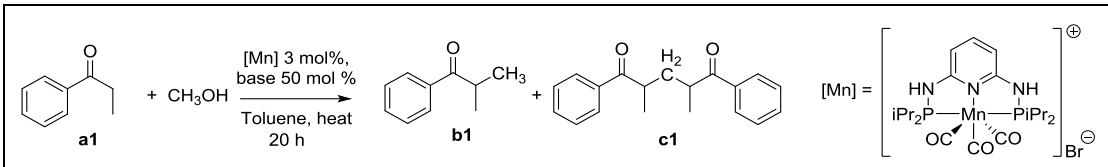
According to general procedure, 2-oxindole **a28** (67 mg, 0.5 mmol) gave the title compound **b28** as a white solid (52 mg, 71%).

^{1}H NMR (400.1 MHz, Chloroform-*d*) δ 9.45 (s, 1H), 7.25 – 7.16 (m, 2H), 7.07 – 6.98 (m, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 3.48 (q, *J* = 7.7 Hz, 1H), 1.51 (d, *J* = 7.7 Hz, 3H).

^{13}C{^{1}H} NMR (101.6 MHz, Chloroform-*d*) δ 182.0, 141.5, 131.4, 128.0, 123.8, 122.4, 110.0, 41.3, 15.3.

Supplementary tables

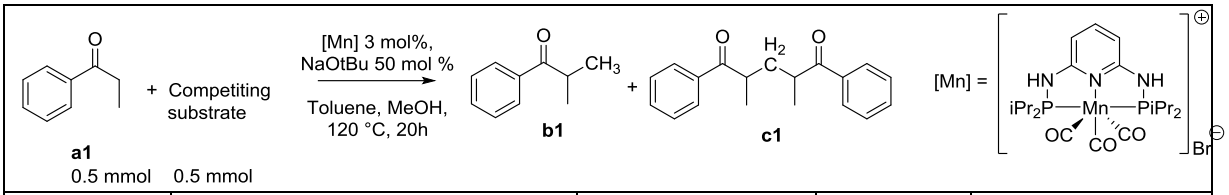
Table S1: Influence of the nature of the base for the α-methylation of propiophenone **a1**.[a]

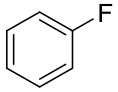
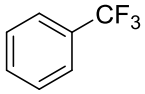
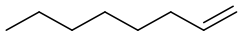
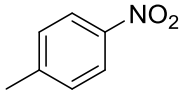
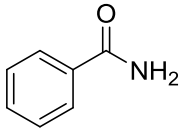
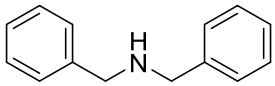
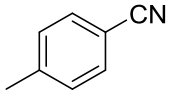


Entry	Base (mol%)	CH_3OH (mL)	Toluene (mL)	Temp. (°C)	Conv. (%)	Nmr yield [b]	
						b. (isol yield)	c. (isol yield)
1	*t*BuONa (50)	2	4	120	99	87(64)	13
2	*t*BuOK (50)	2	4	120	99	86	14
3	KHMDS (50)	2	4	120	99	77	23
4	K_3PO_4 (50)	2	4	120	99	82	18

[a] Reaction conditions: in a glovebox, an Ace® pressure tube was charged with propiophenone **a1** (0.5 mmol, 66 µL), MeOH, toluene, **5** (3 mol%, 8.4 mg), and base, in that order. The closed pressure tube was then heated at 120 °C for 20 h. [b] NMR yield was determined by ^{1}H NMR spectroscopy, and compared with GC/MS, on the crude mixture.

Table S2: Competitive experiments for the α-methylation of propiophenone **a1.**



Entry	Competiting Substrate	Conversion **a1**[a]	Yield **b1**/**c1** [a]	Recovery of competiting substrate [a]
1	None	99 %	87/13	
2[a]		> 98%	86/14	n.d.[b]
3		> 98%	86/14	n.d. [b]
4		> 98%	84/16	n.d. [b]
5		95%	84/16	c.a. 95%[c]
6		95%	66/34	c.a. 90%
7		> 95%	70/30	65%[d]
8		95%	85/15	0%[e]

Reaction conditions: in a glovebox, an Ace® pressure tube was charged with propiophenone **a1** (0.5 mmol, 66 µL), competiting substrate (0.5 mmol), MeOH, toluene, **5** (3 mol%, 8.4 mg), and NaOtBu (0.25 mmol, 24 mg), in that order. [a] Determined by ^{1}H NMR spectroscopy on the crude mixture. [b] Competiting substrate was evaporated during the workup. [c] Under the same conditions, the methylation of 4-nitroacetophenone led to a complicated mixture of products. [d] *N*-formyl-*N*,*N*-dibenzylamine was detected as the main competiting product (c.a. 35%). [e] 4-methylbenzonitrile was hydrolysed to 4-methylbenzamide.

NMR Spectra of the products of the catalysis

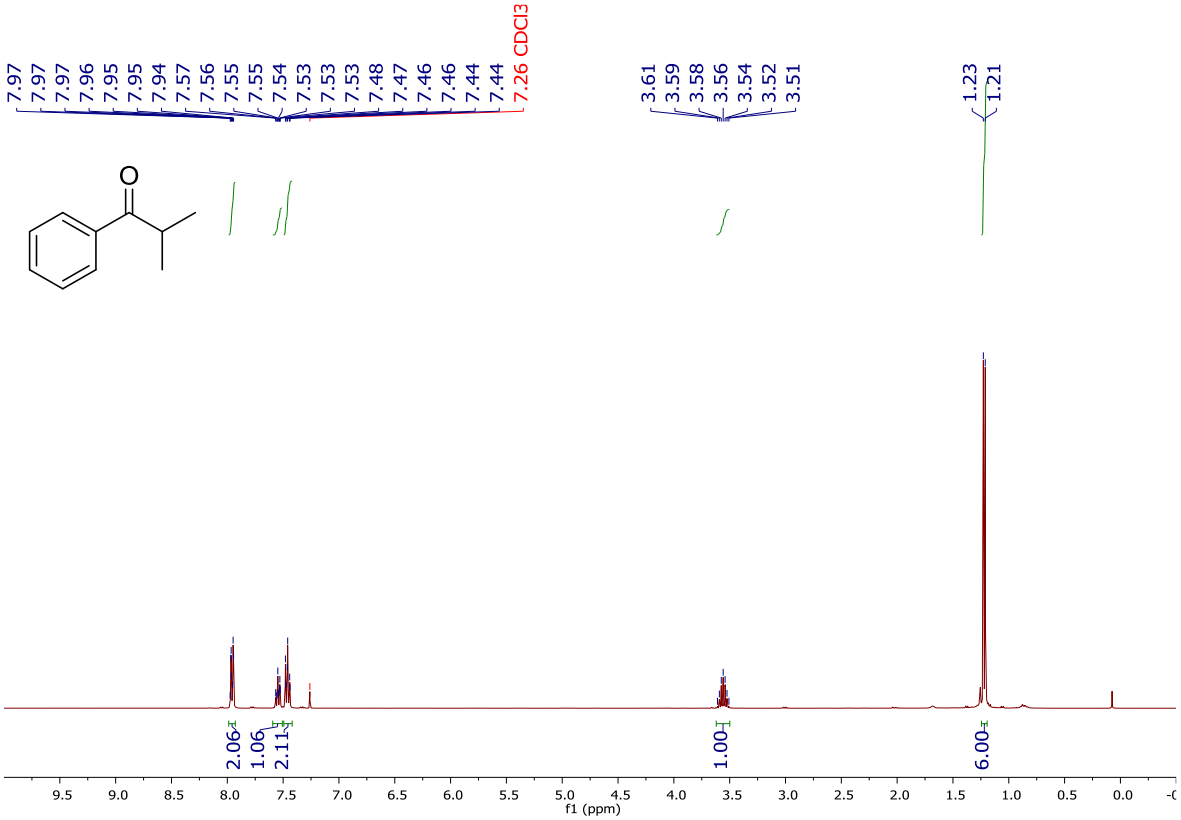


Figure S1: ^{1}H NMR spectrum of the compound **b1** in $CDCl_3$ recorded at 400.1 MHz.

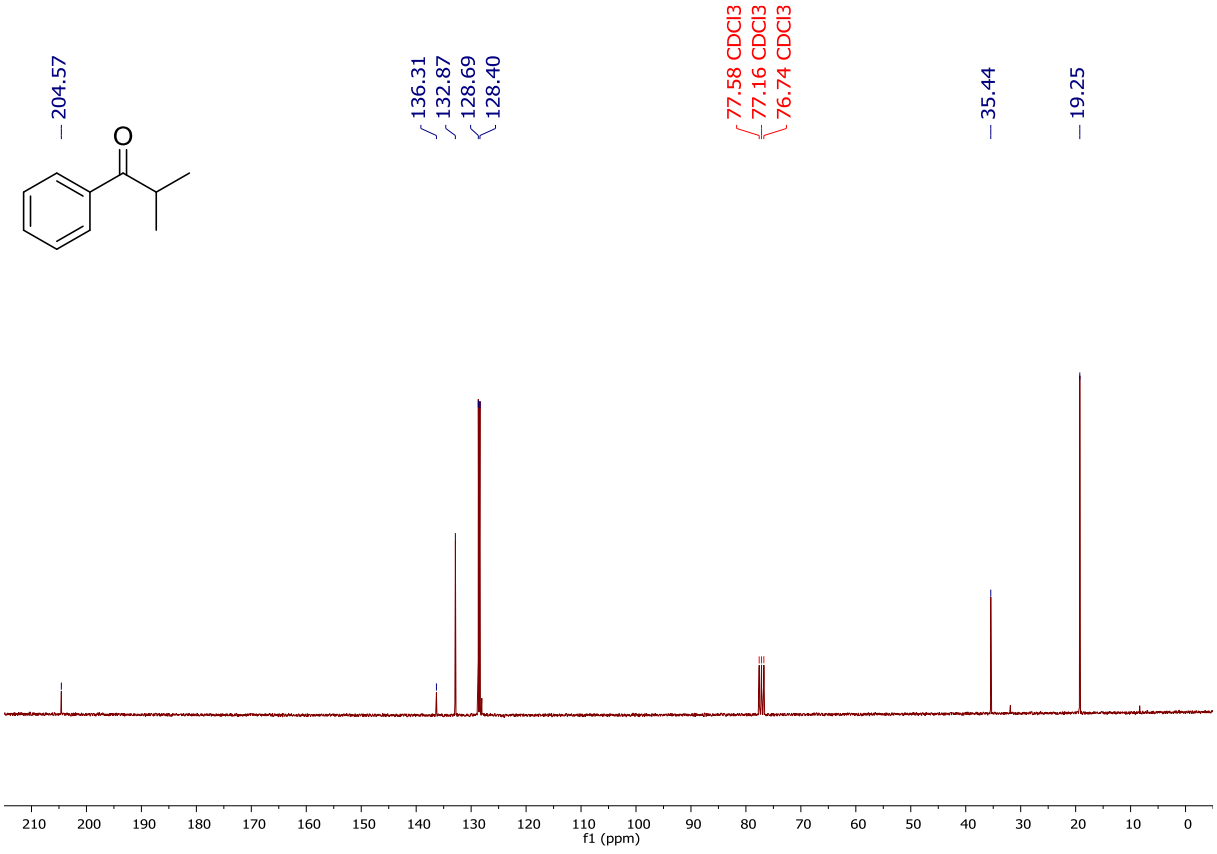


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b1** in $CDCl_3$ recorded at 75.5 MHz.

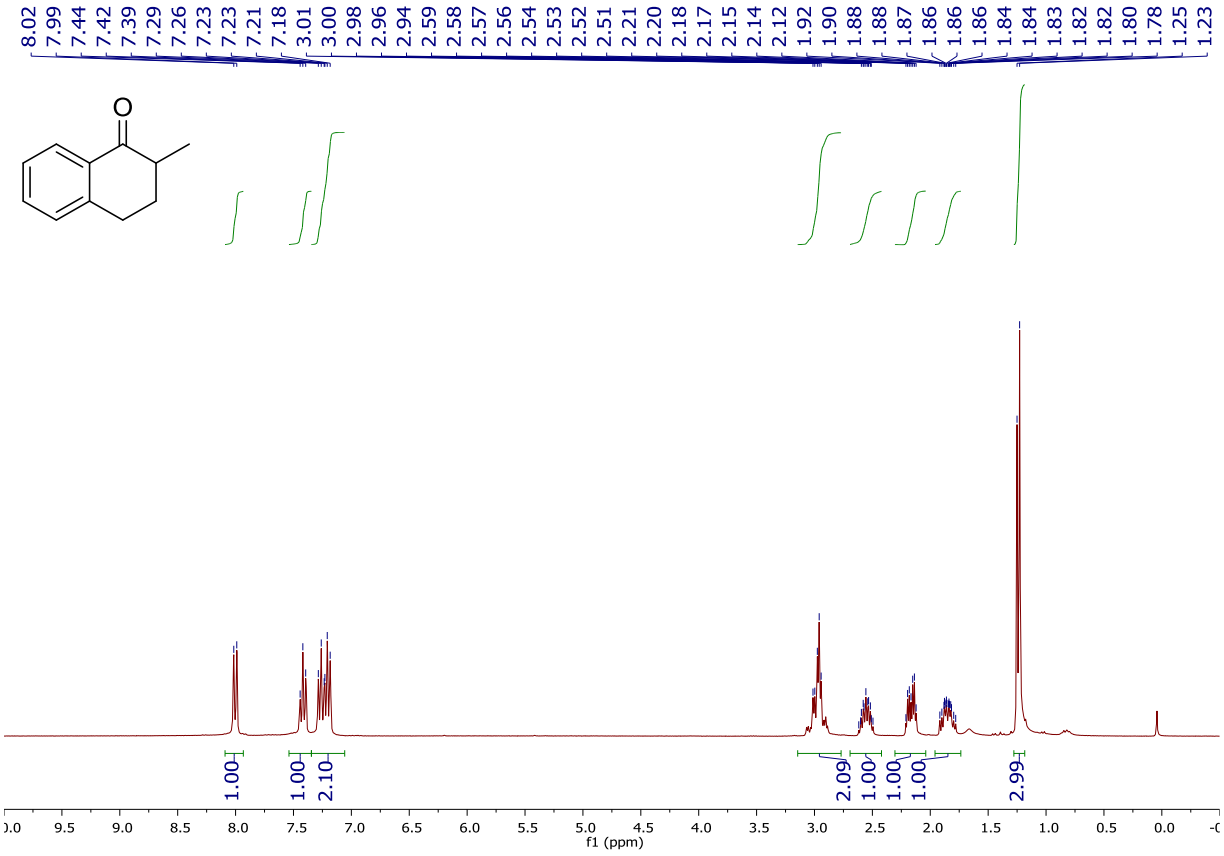


Figure S3: ^{1}H NMR spectrum of the compound **b3** in $CDCl_3$ recorded at 300.1 MHz.

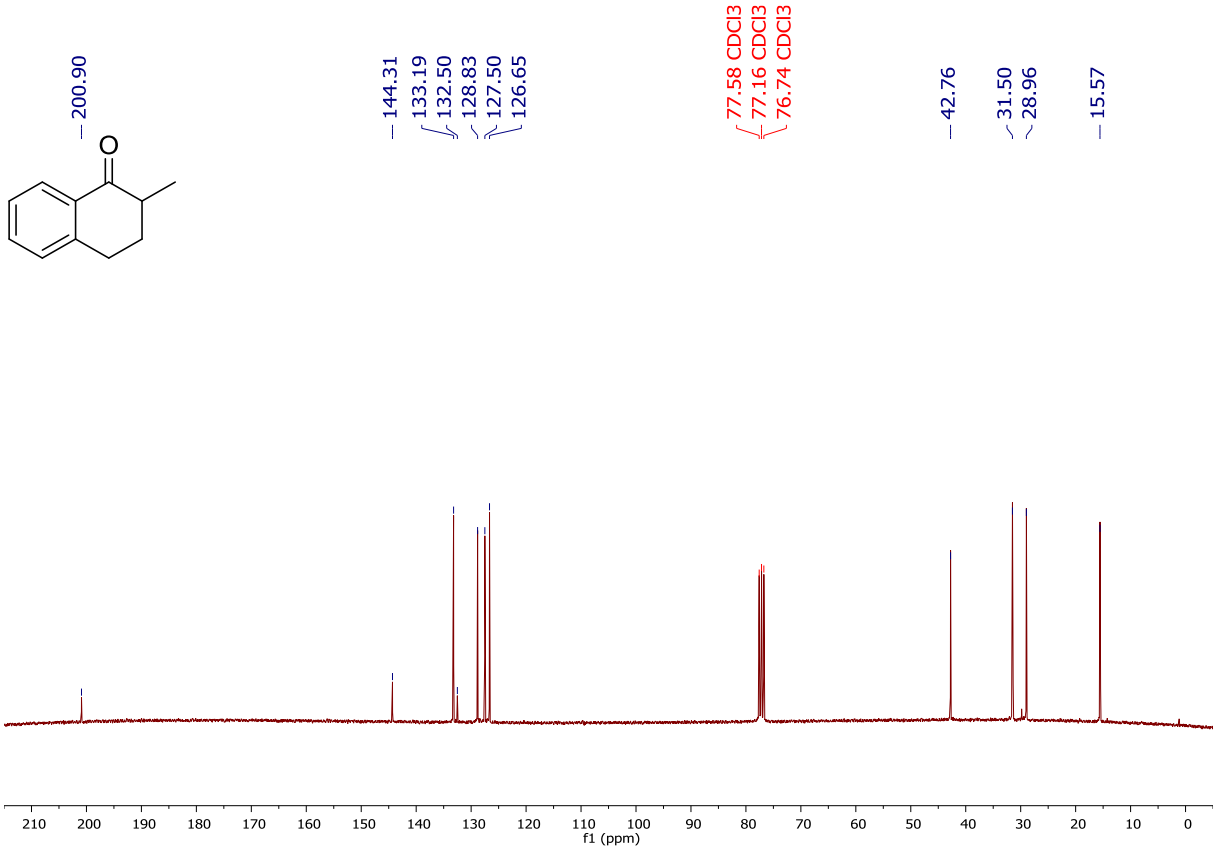


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b3** in $CDCl_3$ recorded at 75.5 MHz.

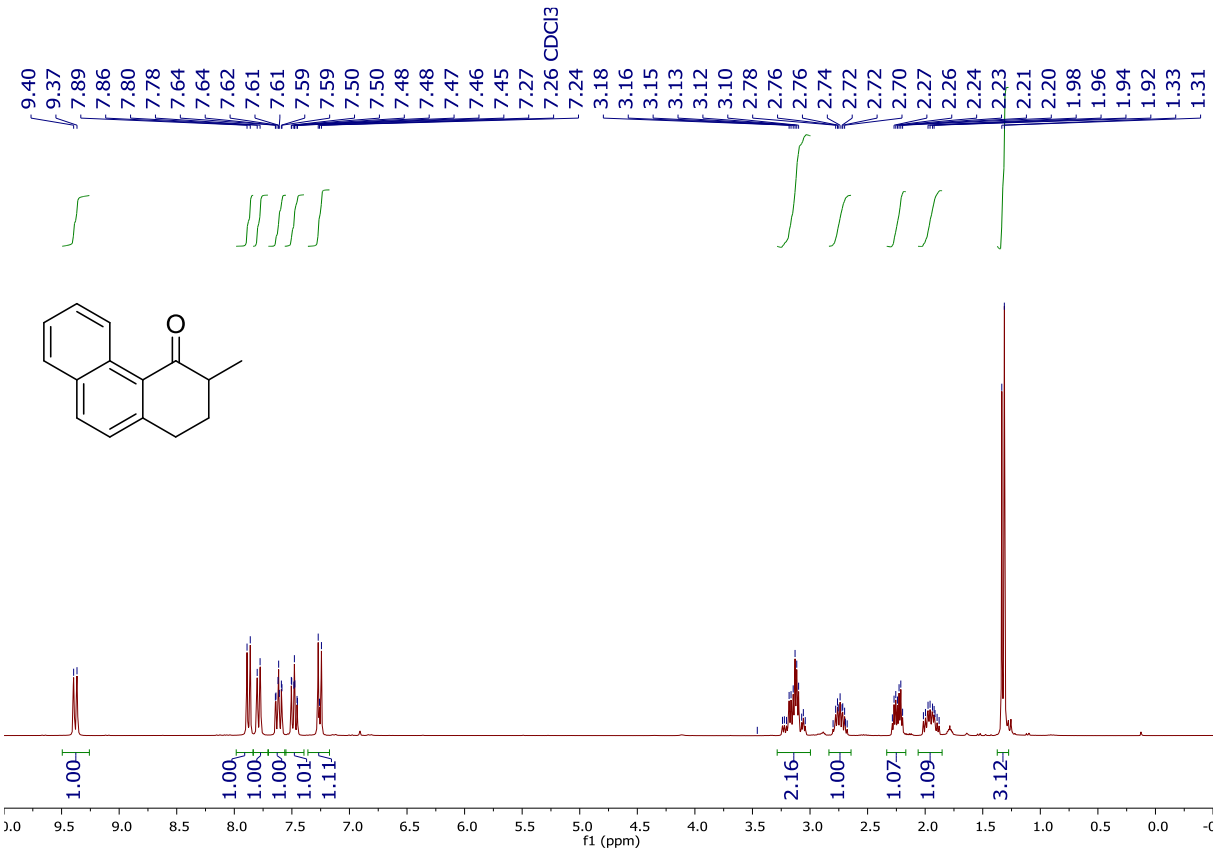


Figure S5: ^{1}H NMR spectrum of the compound **b4** in $CDCl_3$ recorded at 300.1 MHz.

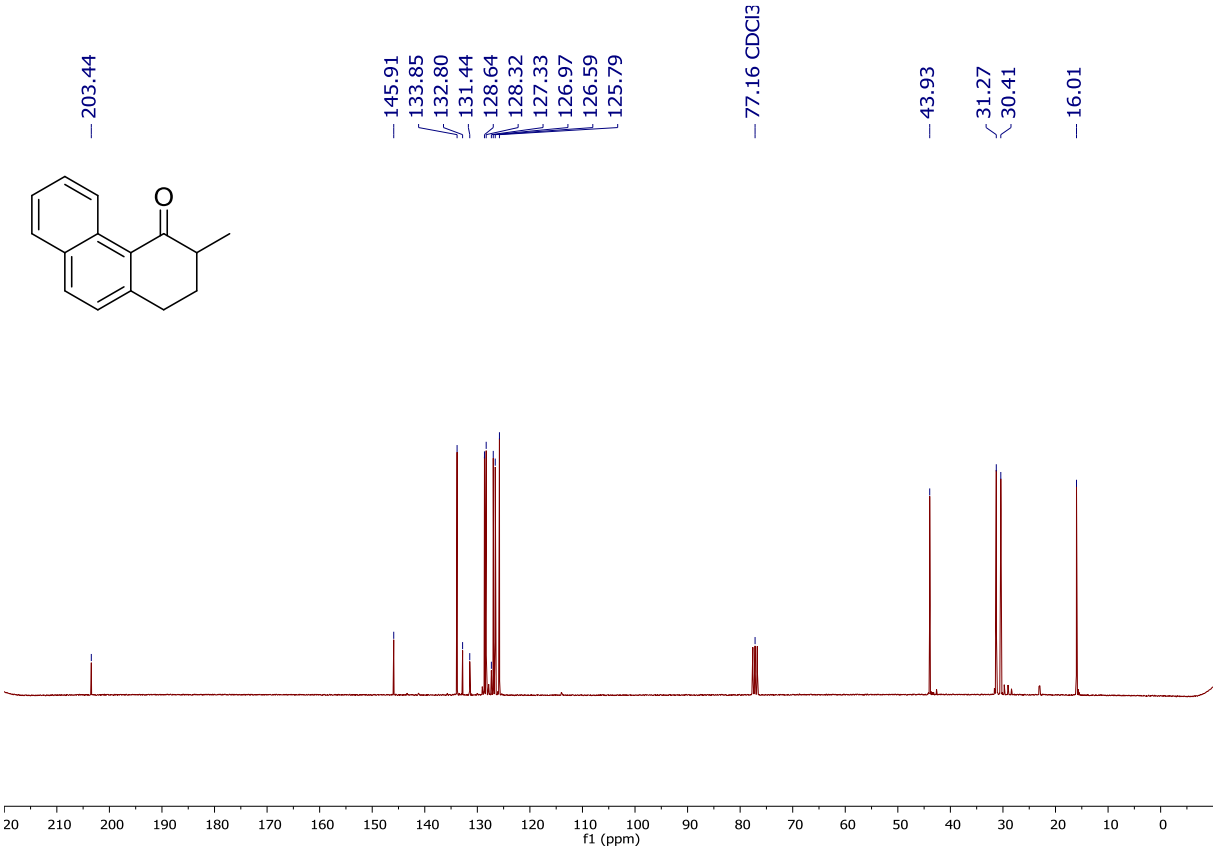


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b4** in $CDCl_3$ recorded at 75.5 MHz.

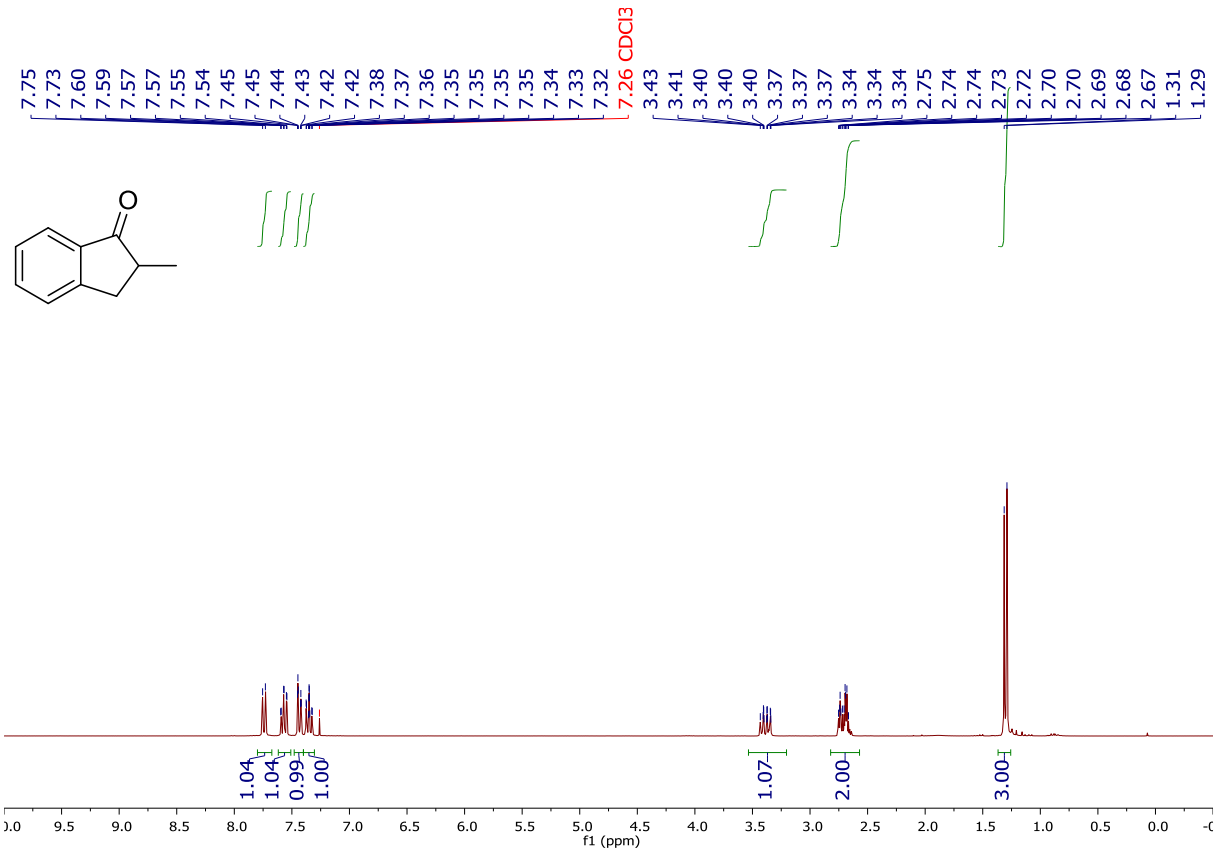


Figure S7: ^{1}H NMR spectrum of the compound **b5** in $CDCl_3$ recorded at 300.1 MHz.

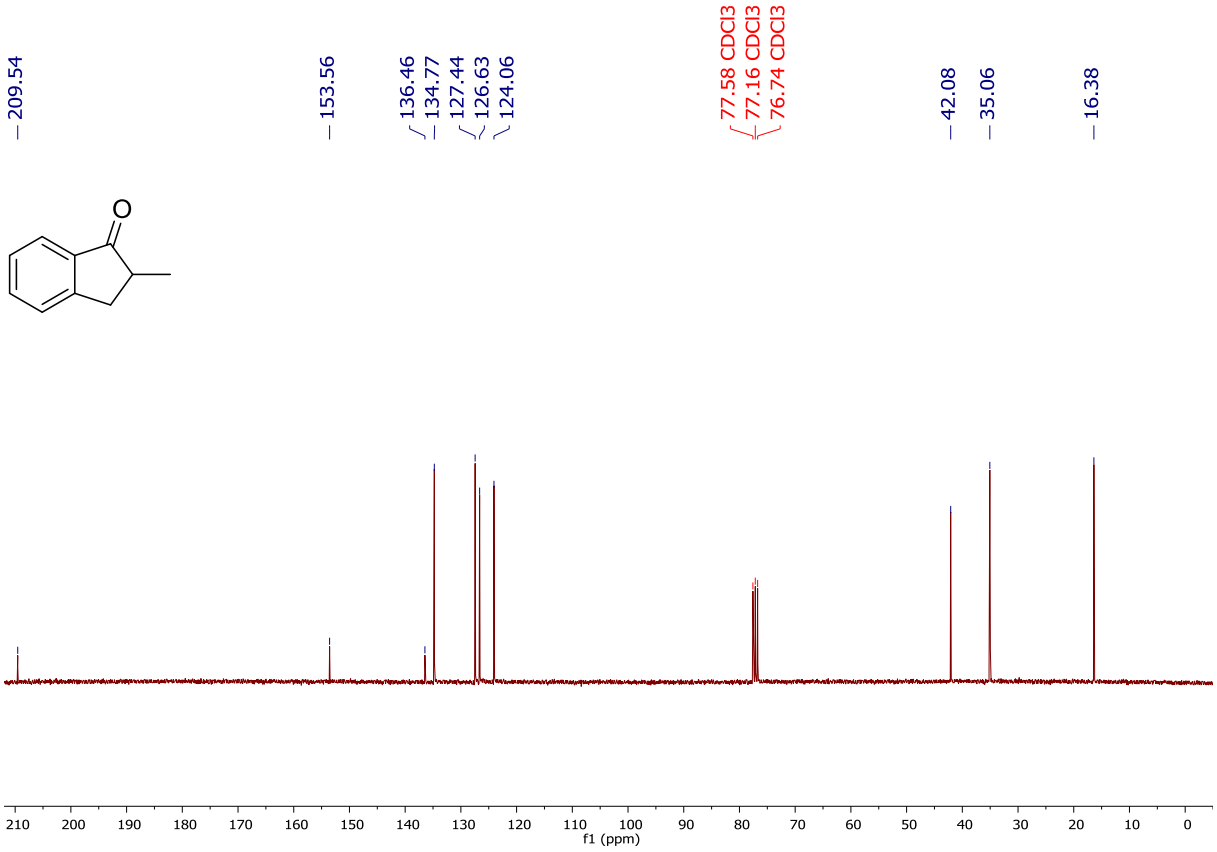


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b5** in $CDCl_3$ recorded at 75.5 MHz.

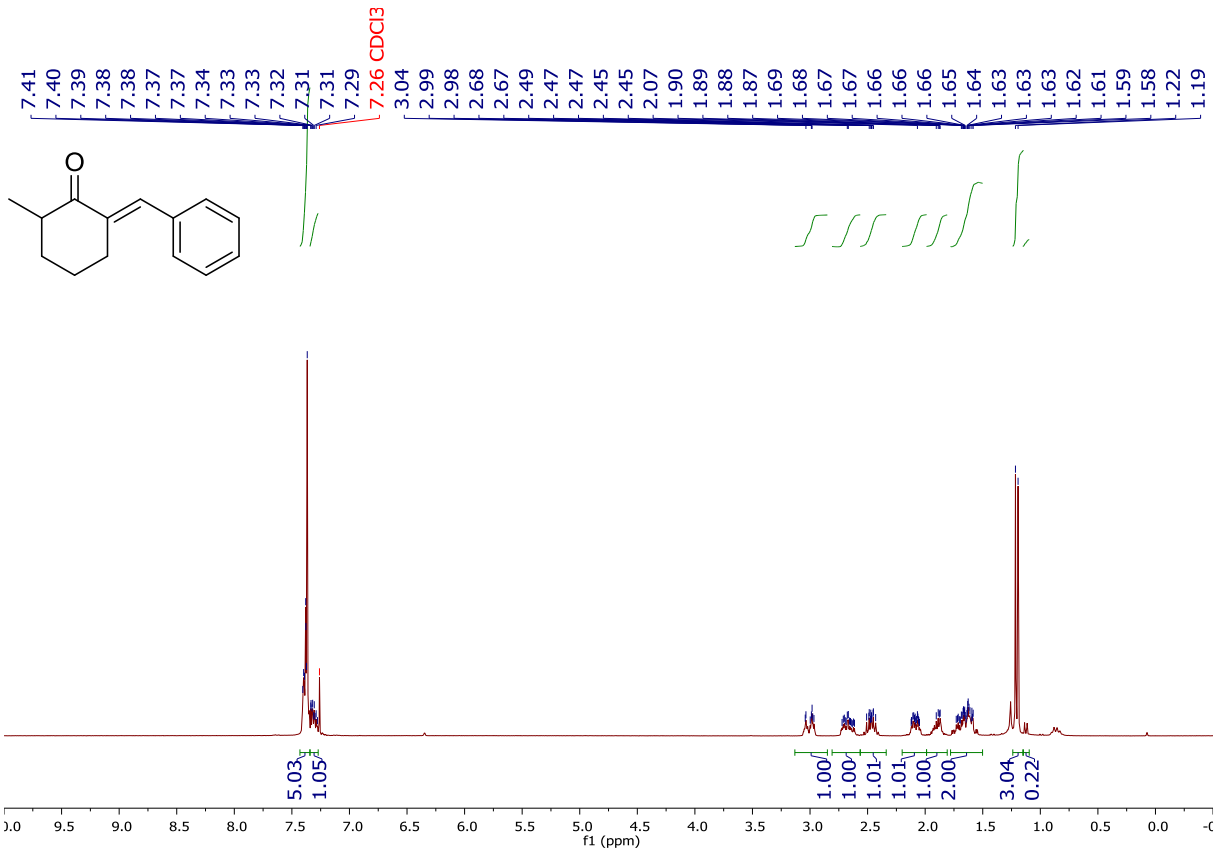


Figure S9: ^{1}H NMR spectrum of the compound **b6** in $CDCl_3$ recorded at 300.1 MHz.

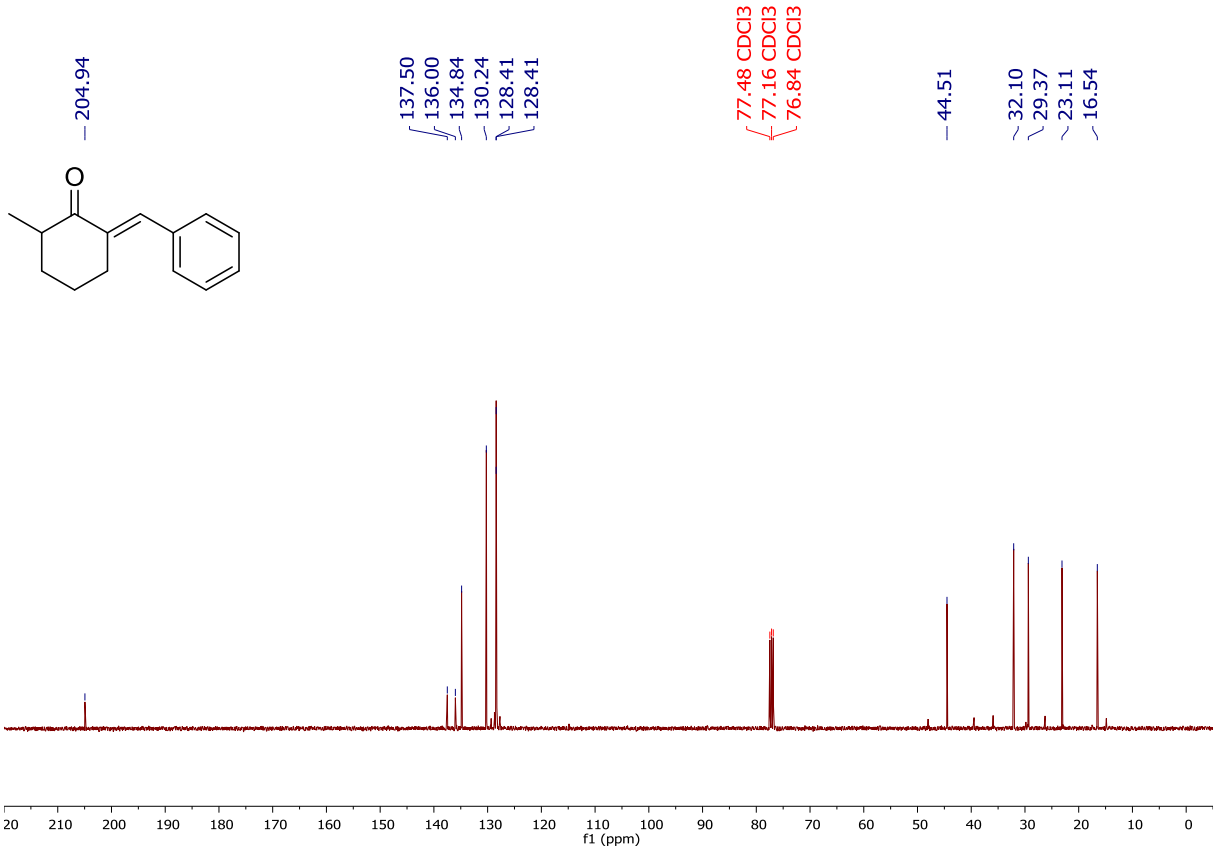


Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b6** in $CDCl_3$ recorded at 101.6 MHz.

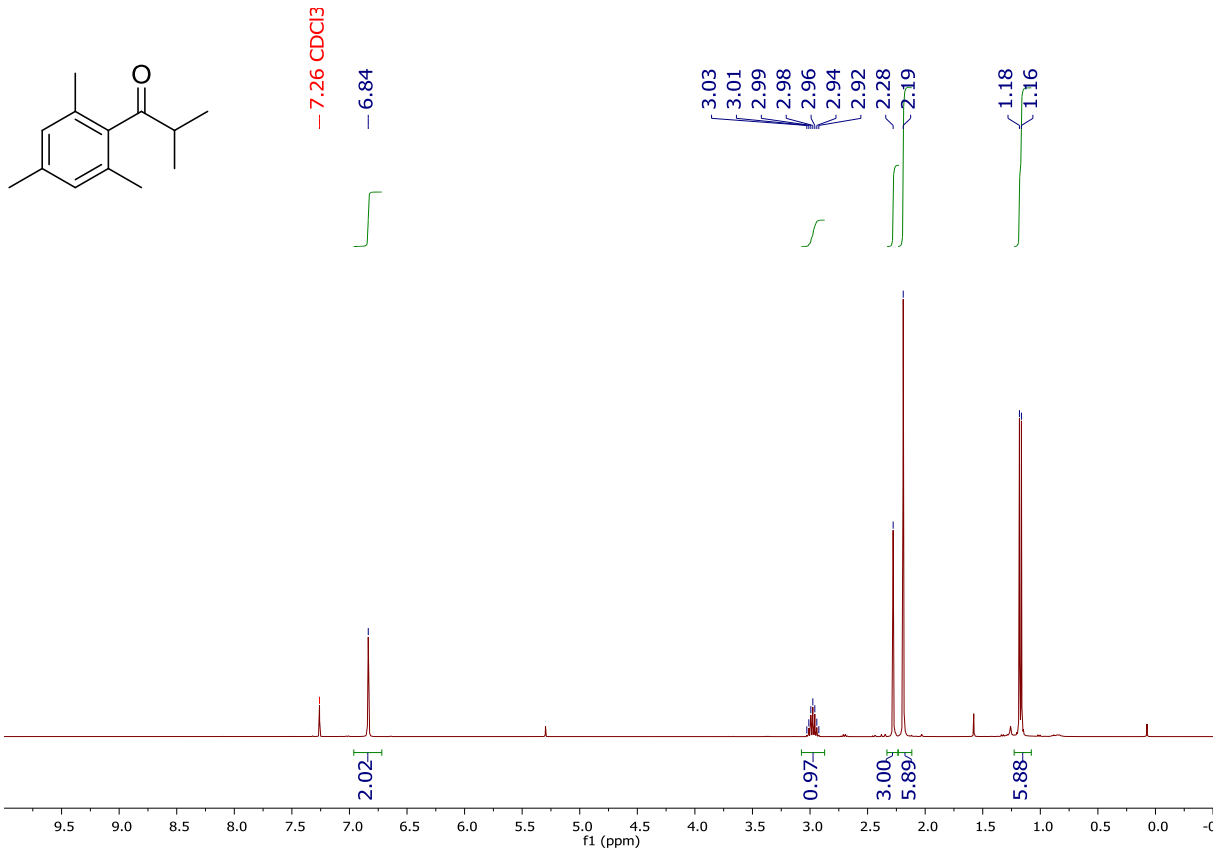


Figure S11: ^{1}H NMR spectrum of the compound **b7** in $CDCl_3$ recorded at 400.1 MHz.

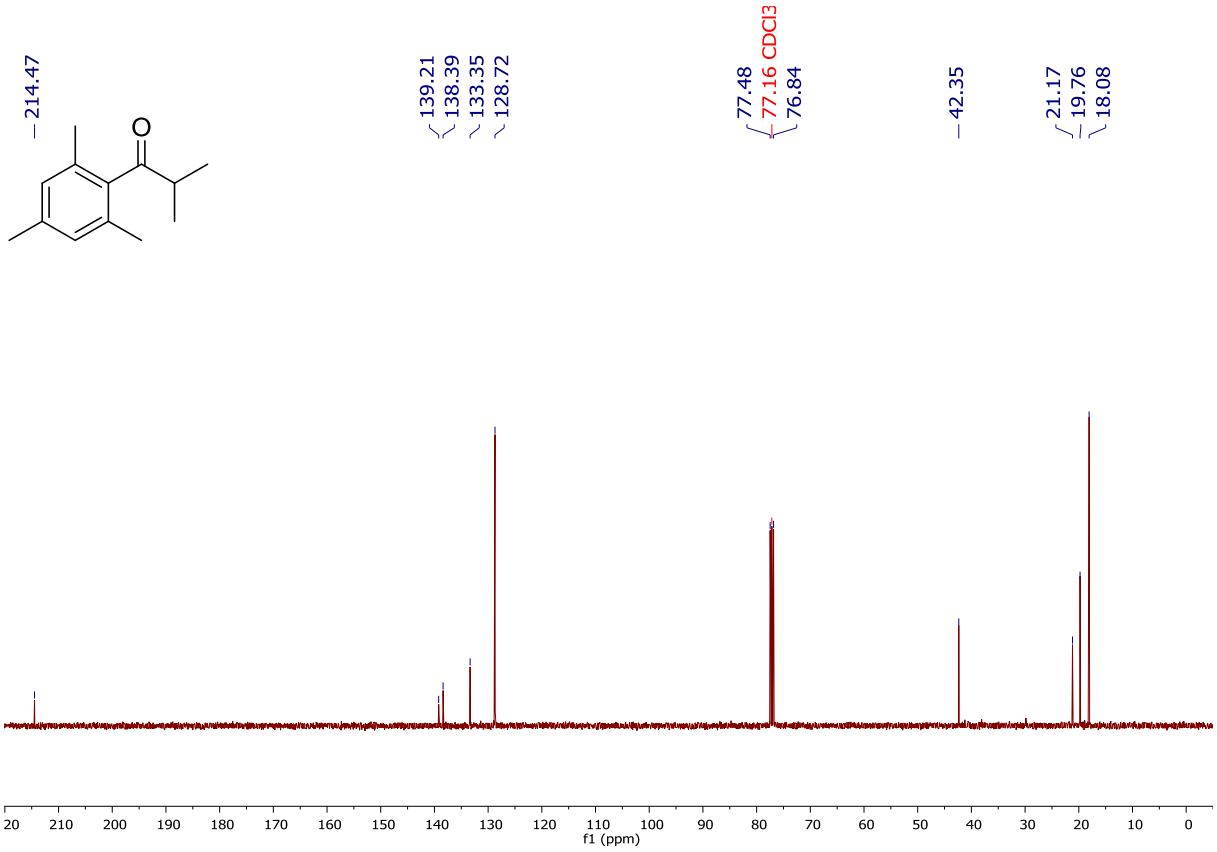


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b7** in $CDCl_3$ recorded at 101.6 MHz.

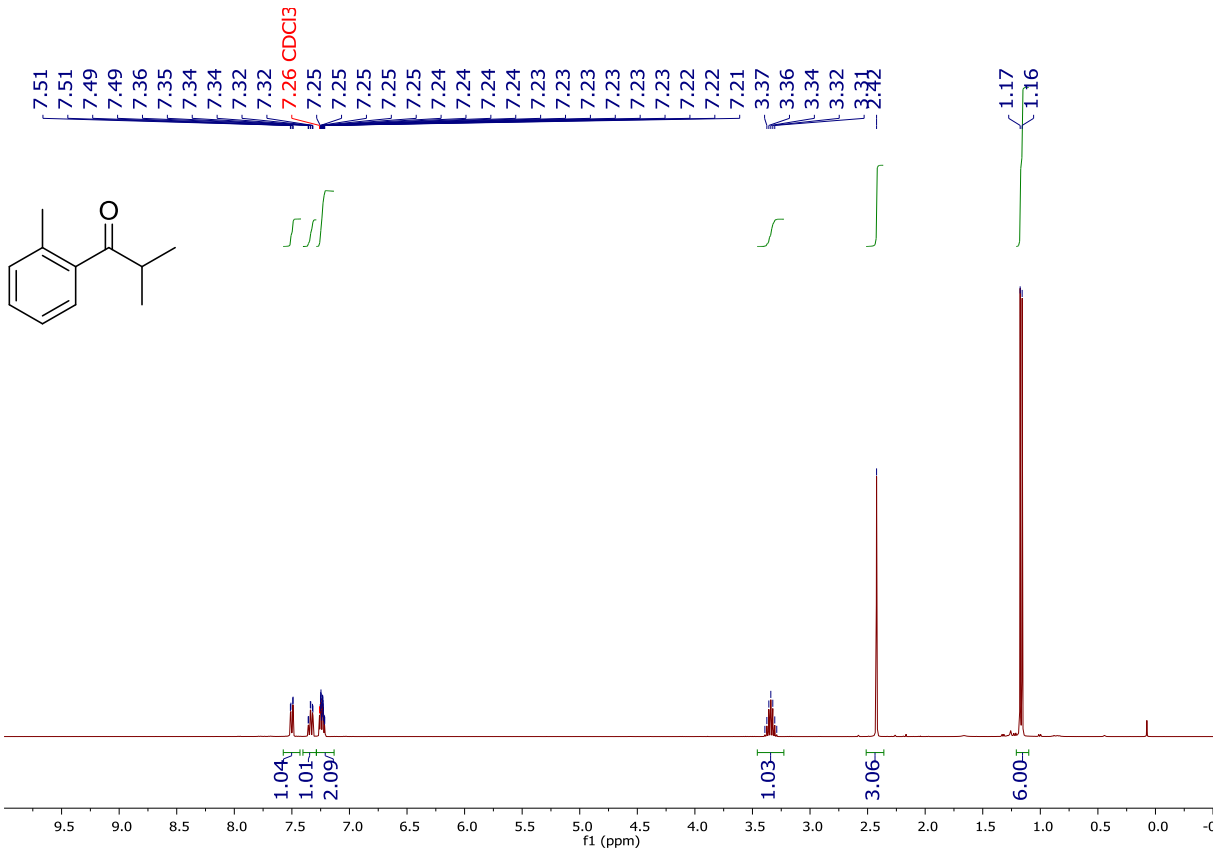


Figure S13: ^{1}H NMR spectrum of the compound **b8** in $CDCl_3$ recorded at 400.1 MHz.

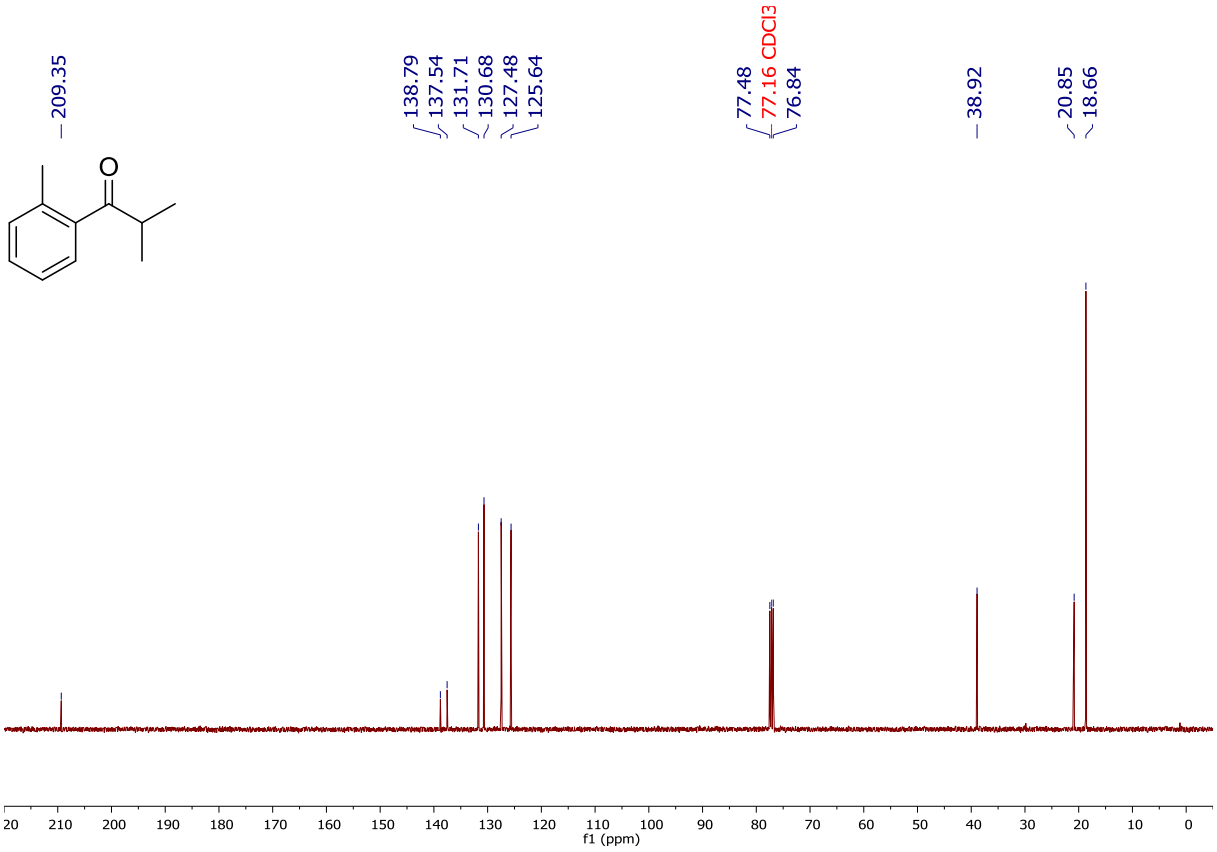


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b8** in $CDCl_3$ recorded at 101.6 MHz.

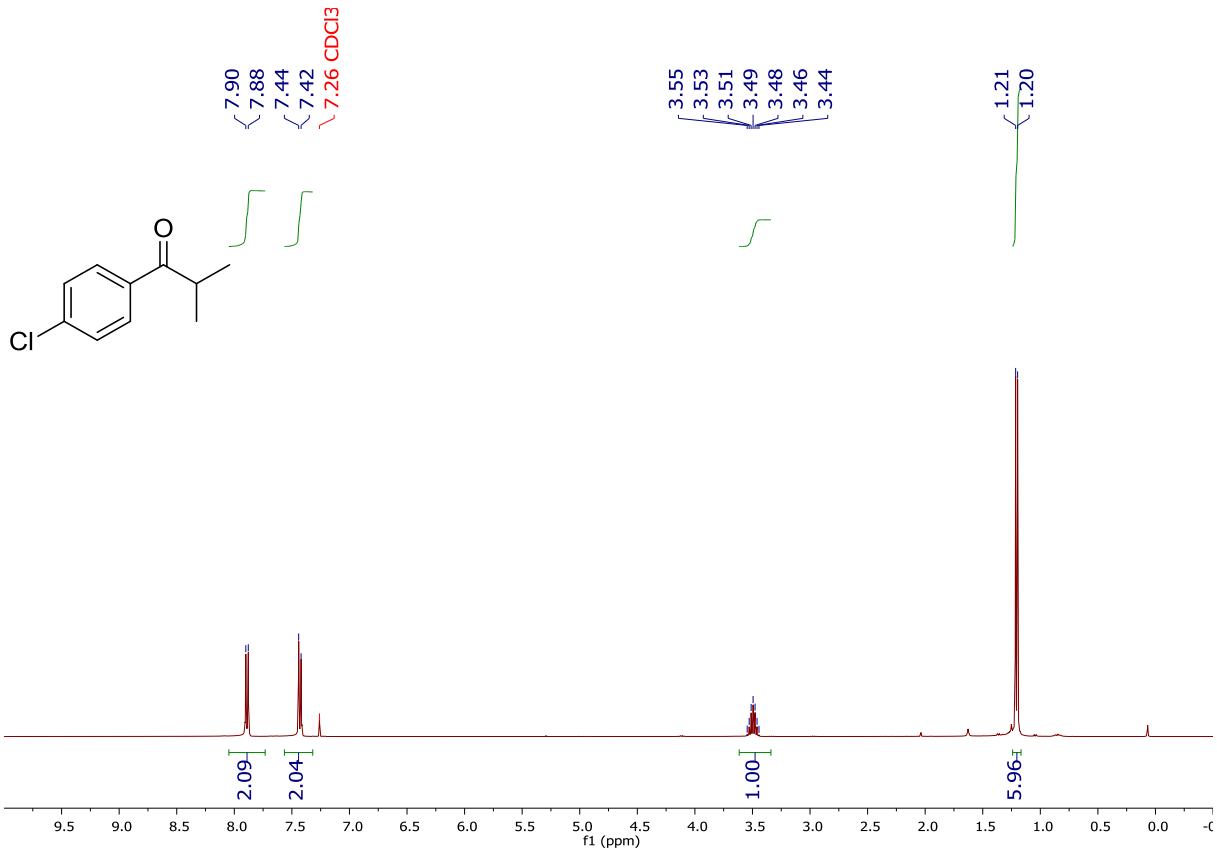


Figure S15: ^{1}H NMR spectrum of the compound **b9** in $CDCl_3$ recorded at 400.1 MHz.

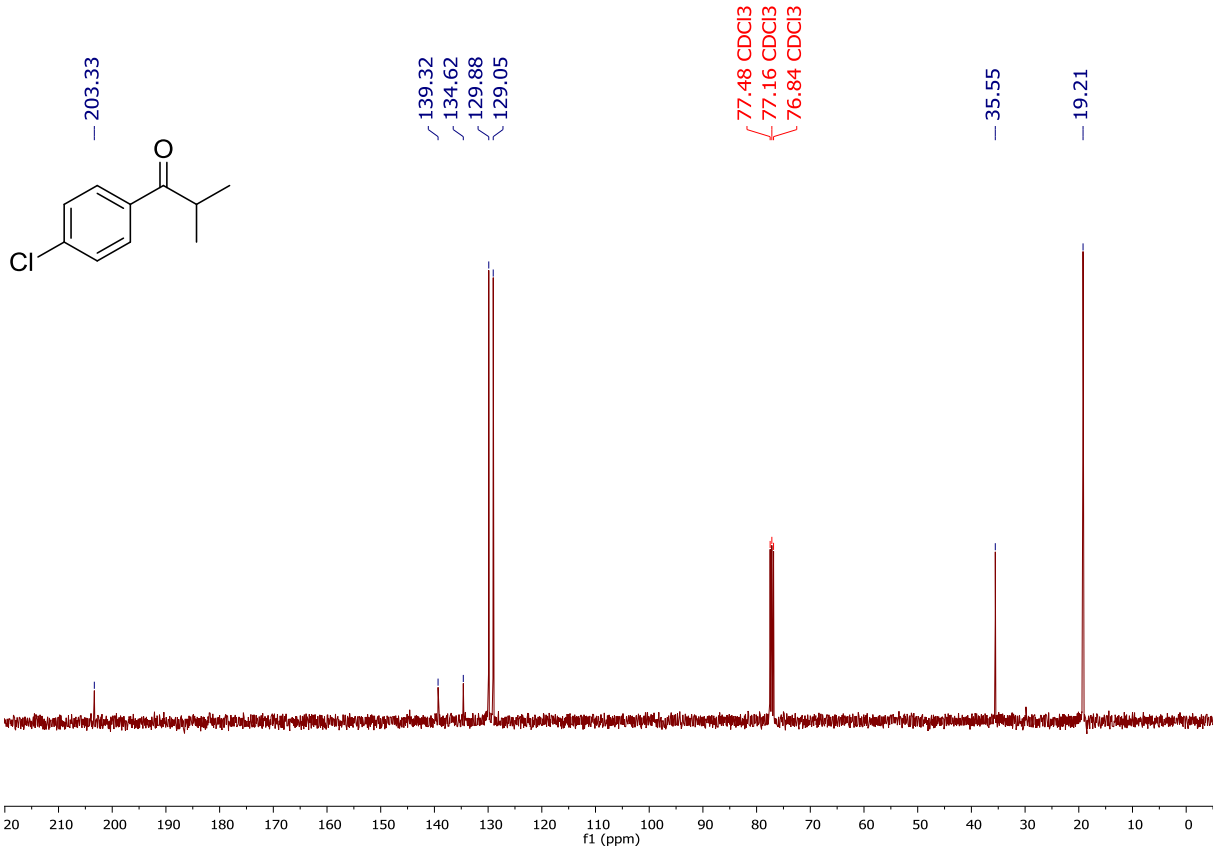


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b9** in $CDCl_3$ recorded at 101.6 MHz.

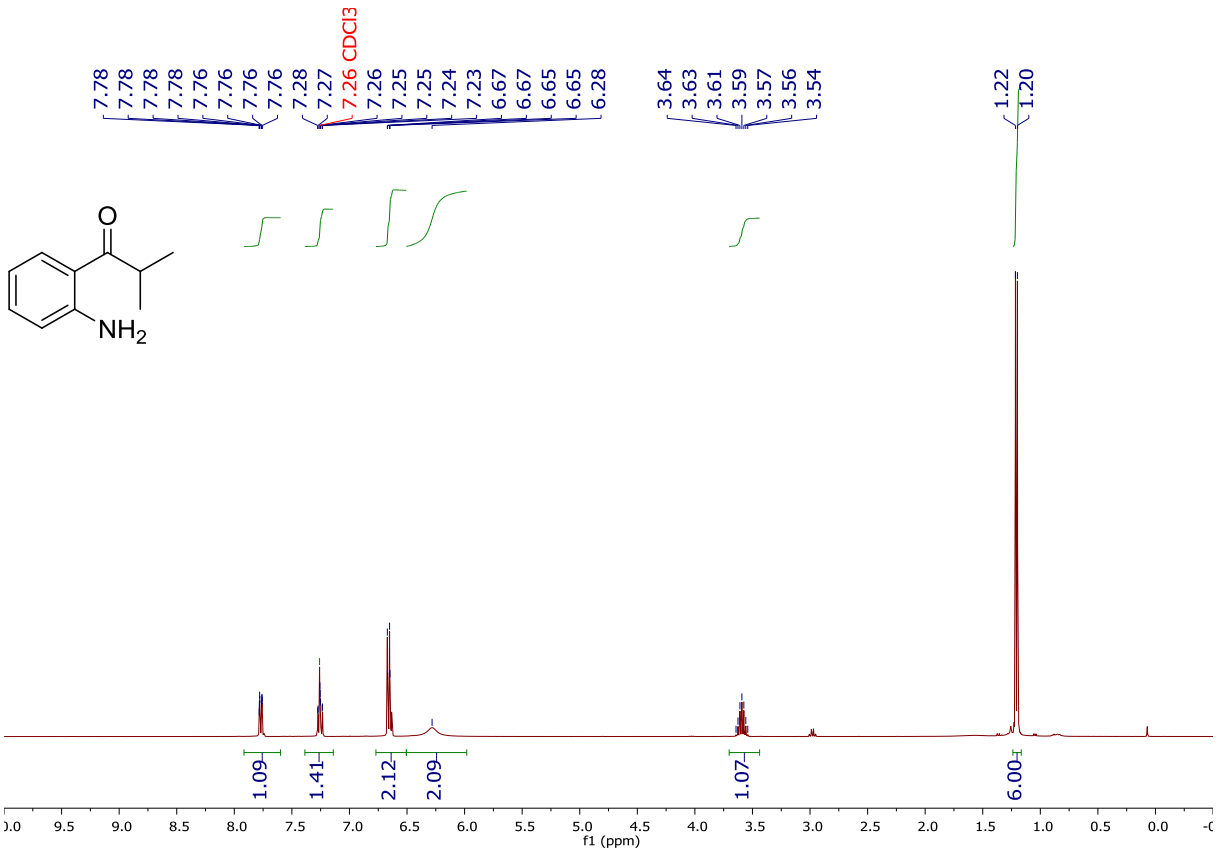


Figure S17: ^{1}H NMR spectrum of the compound **b10** in $CDCl_3$ recorded at 400.1 MHz.

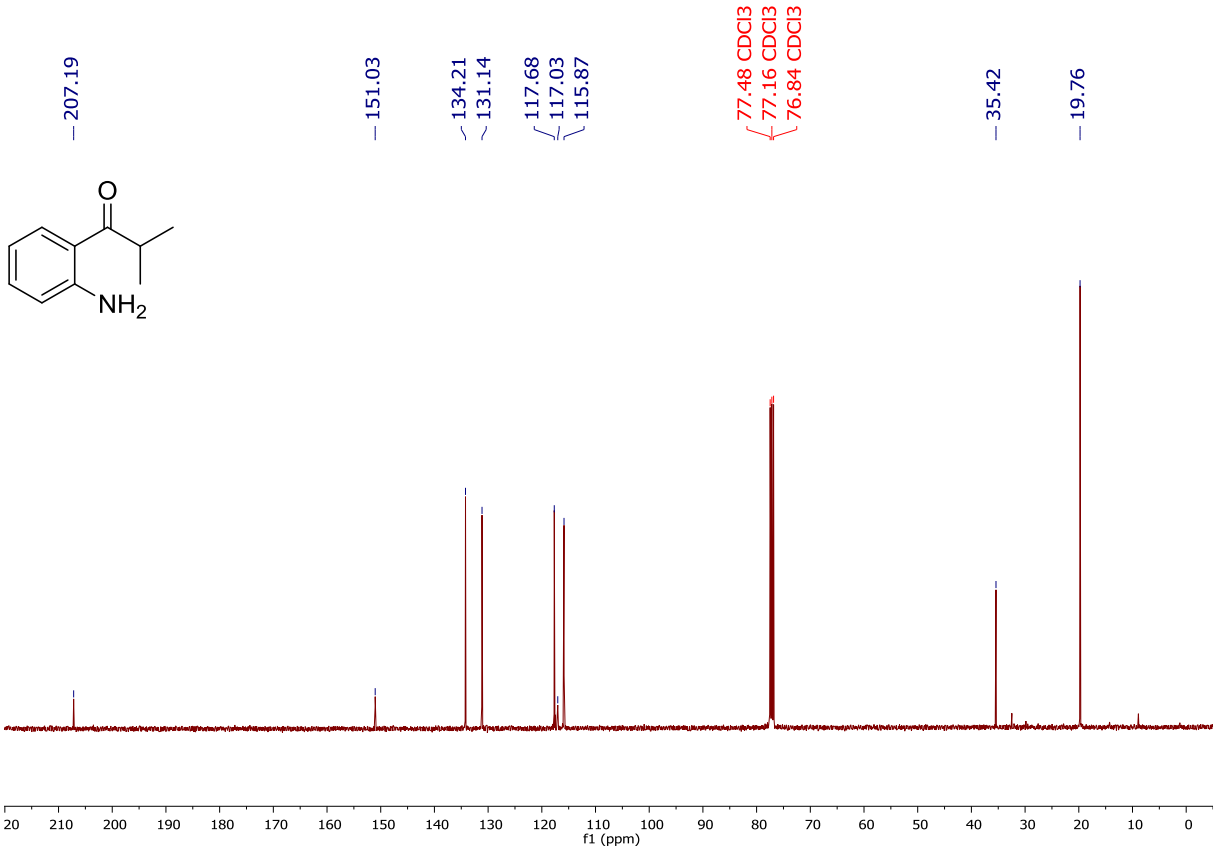


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b10** in $CDCl_3$ recorded at 101.6 MHz.

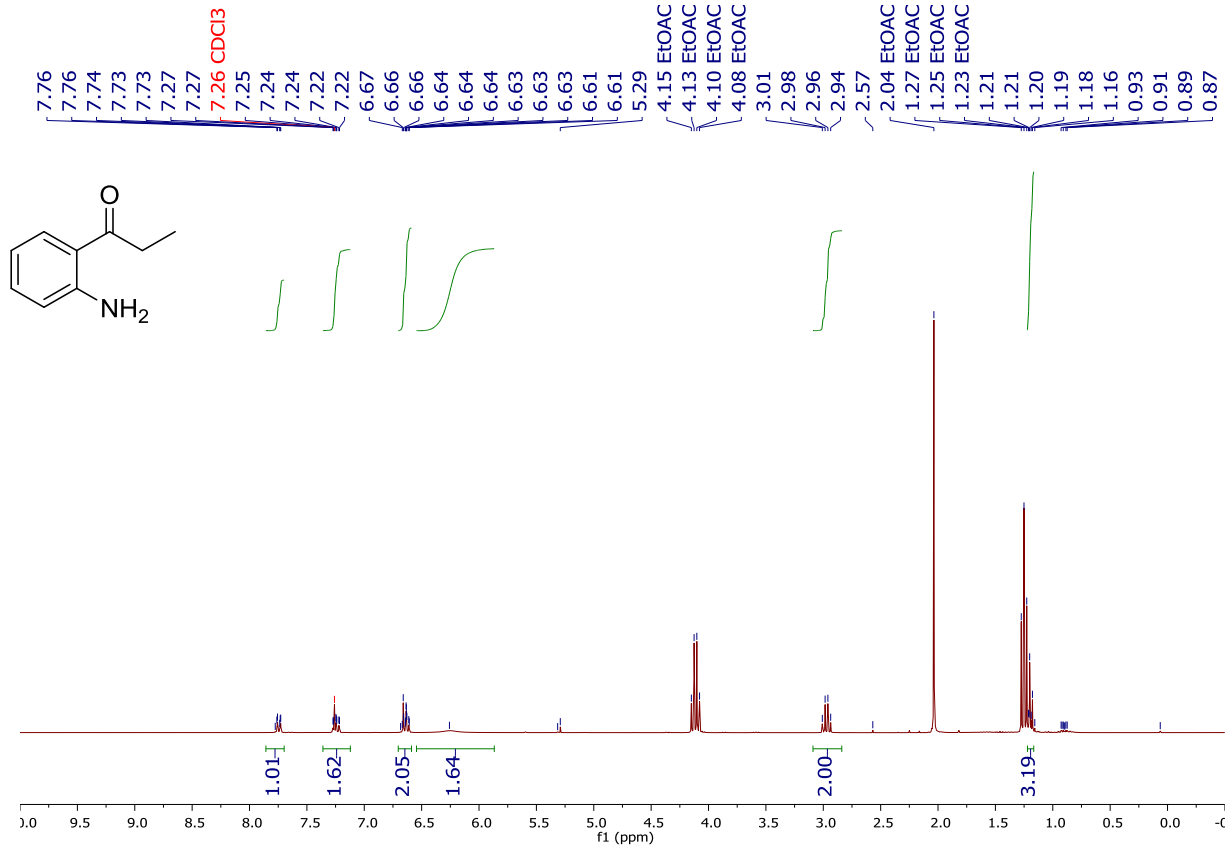


Figure S19: ^{1}H NMR spectrum of the compound **b10'** in $CDCl_3$ recorded at 300.1 MHz.

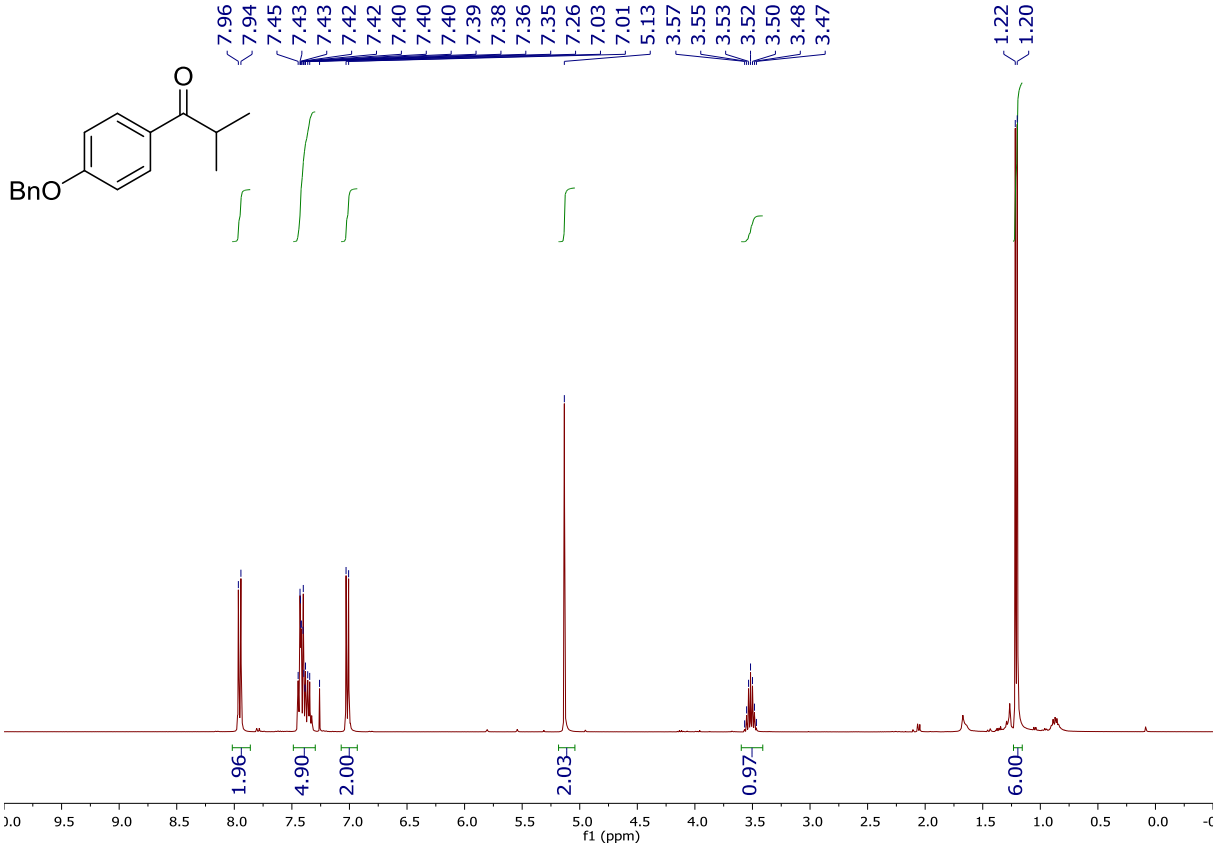


Figure S20: ^{1}H NMR spectrum of the compound **b11** in $CDCl_3$ recorded at 300.1 MHz.

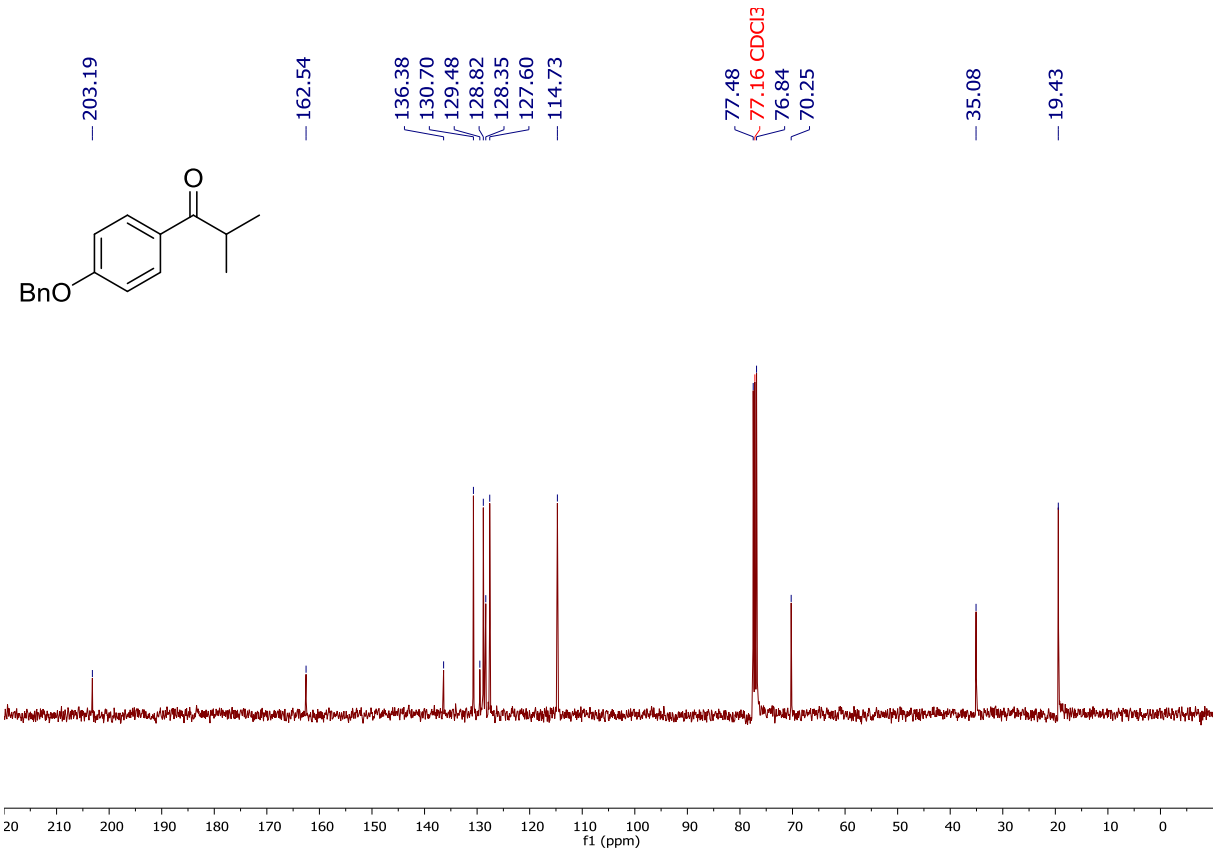


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b11** in $CDCl_3$ recorded at 101.6 MHz.

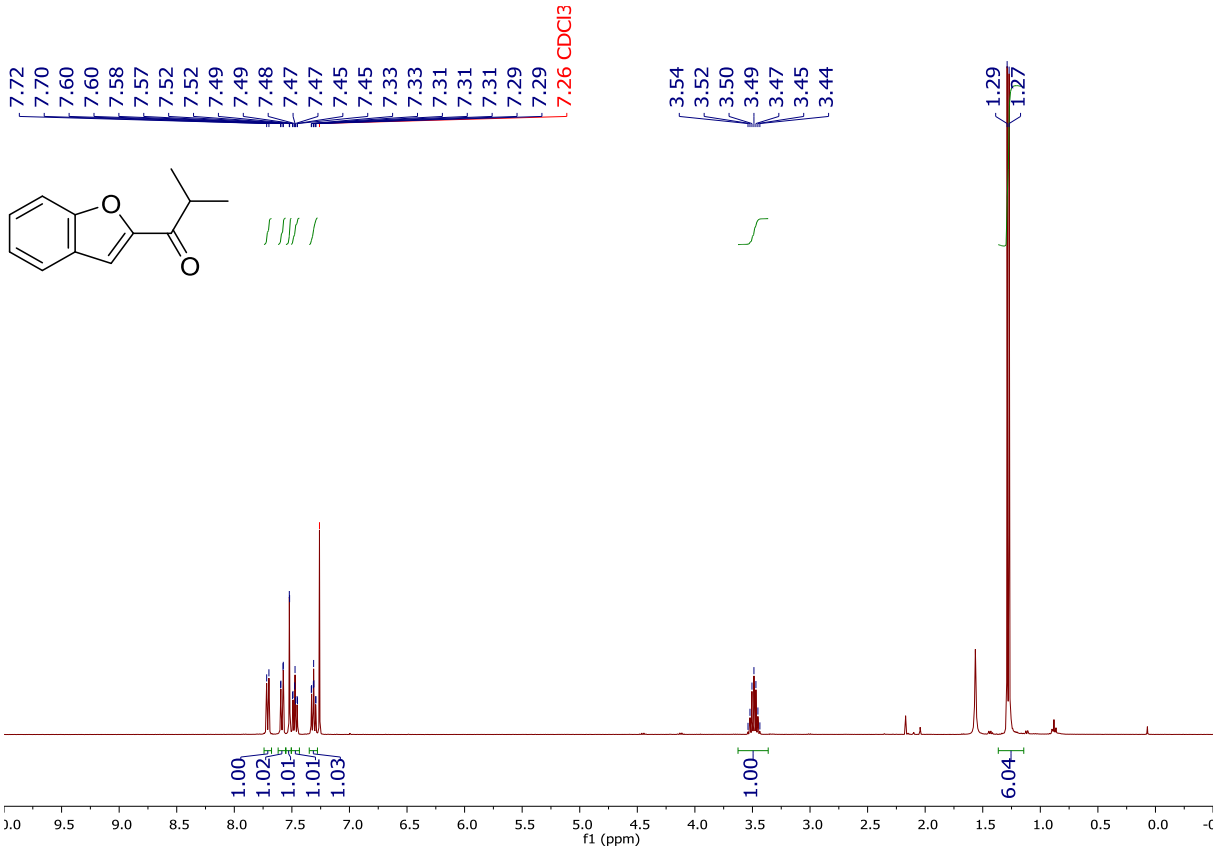


Figure S22: ^{1}H NMR spectrum of the compound **b12** in $CDCl_3$ recorded at 400.1 MHz.

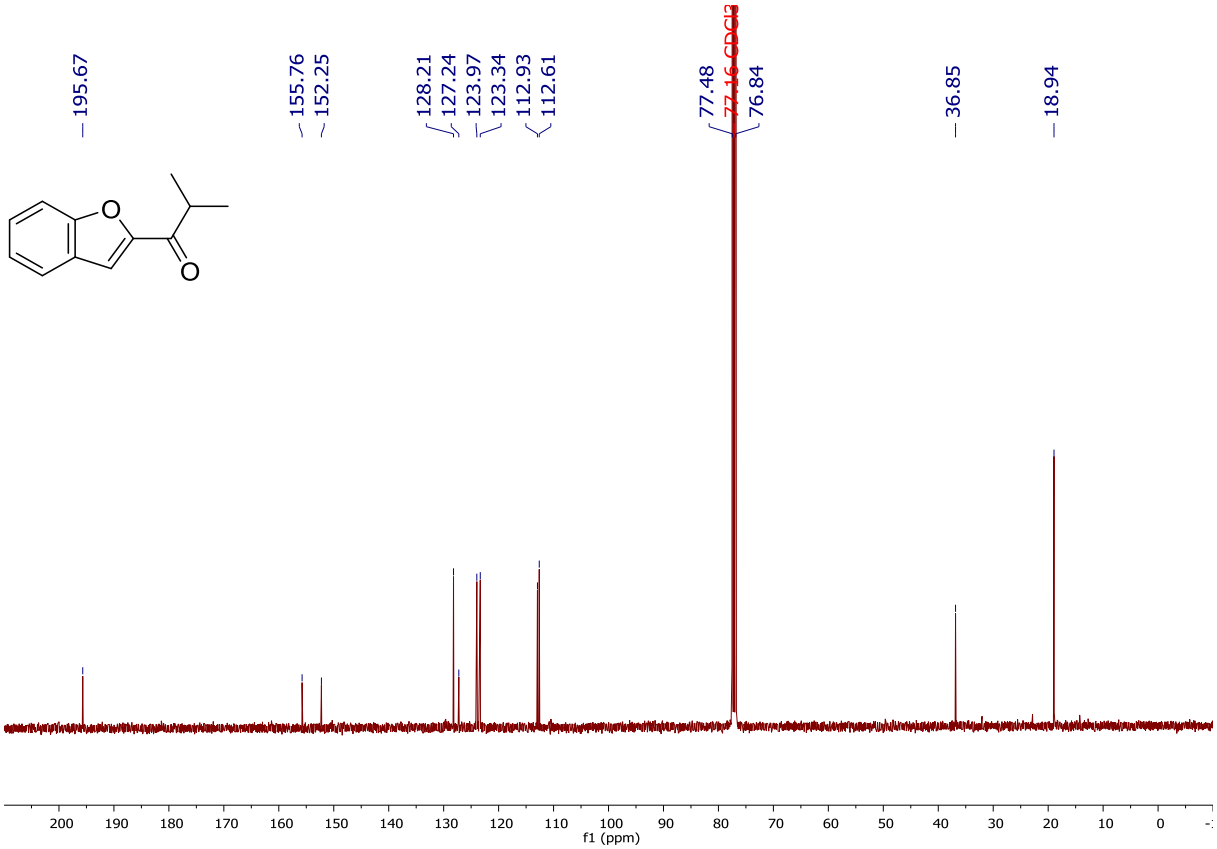


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b12** in $CDCl_3$ recorded at 101.6 MHz.

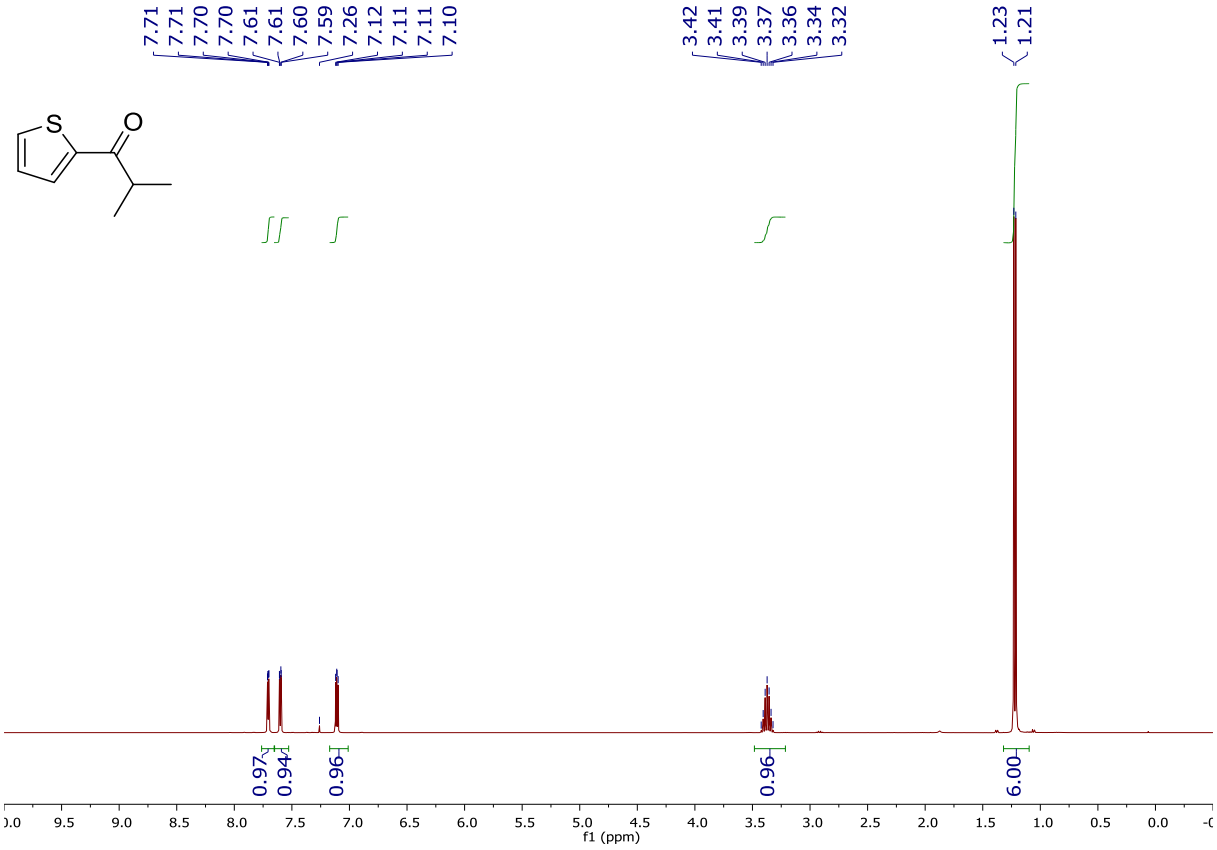


Figure S24: ^{1}H NMR spectrum of the compound **b13** in $CDCl_3$ recorded at 400.1 MHz.

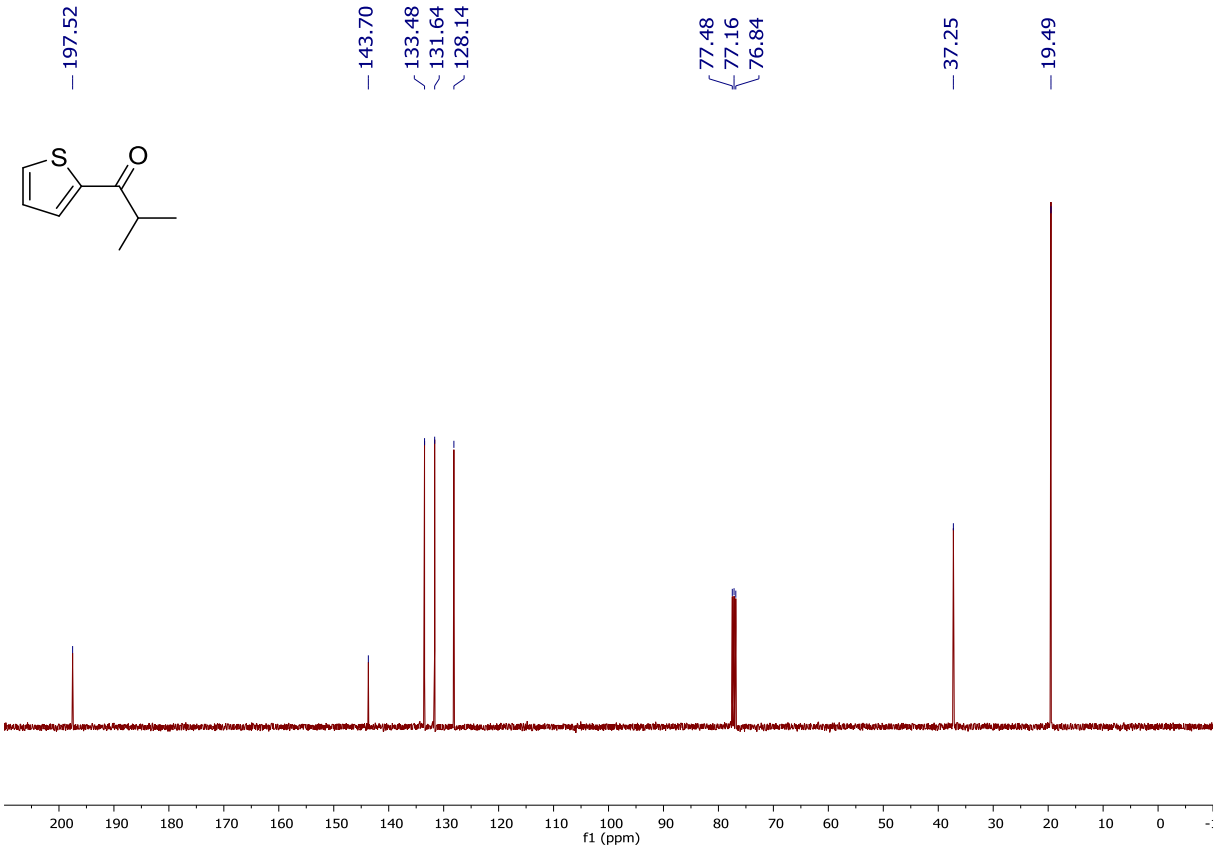


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b13** in $CDCl_3$ recorded at 101.6 MHz.

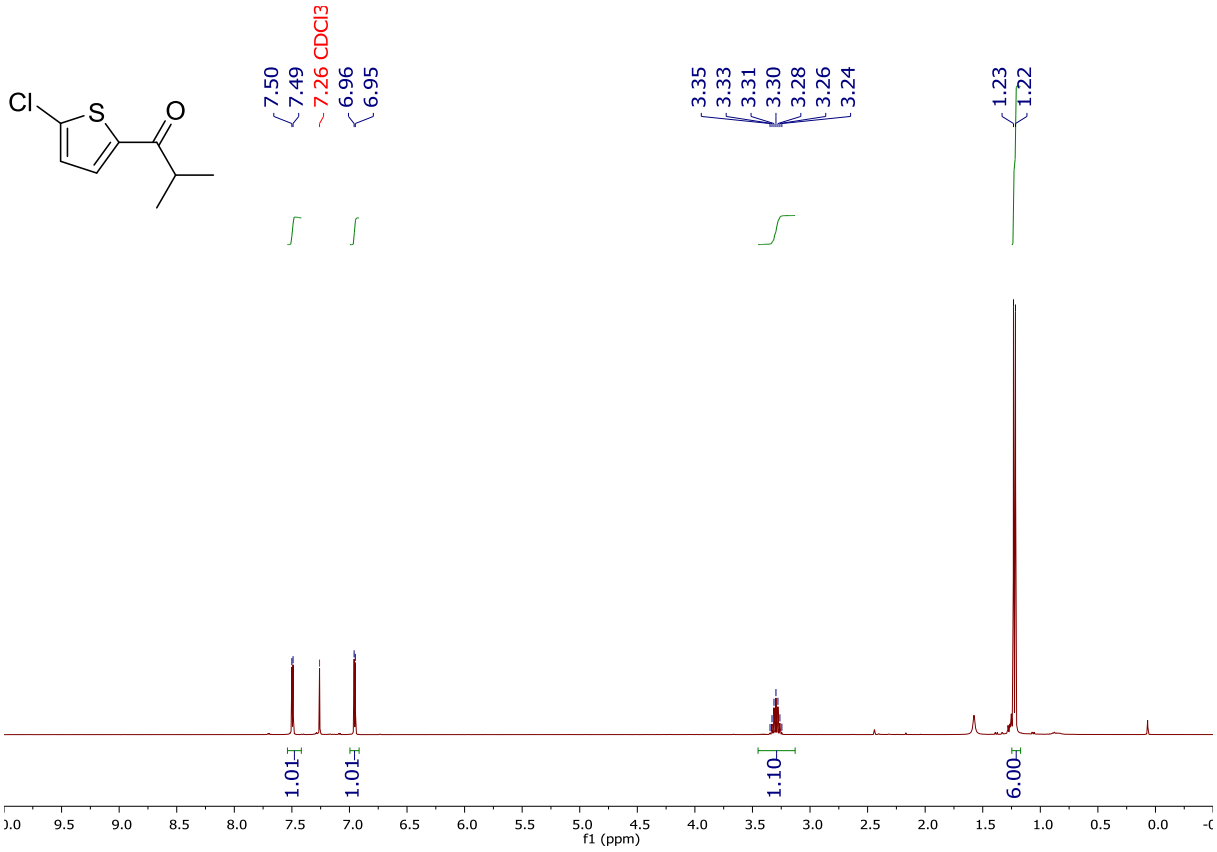


Figure S26: ^{1}H NMR spectrum of the compound **b14** in $CDCl_3$ recorded at 400.1 MHz.

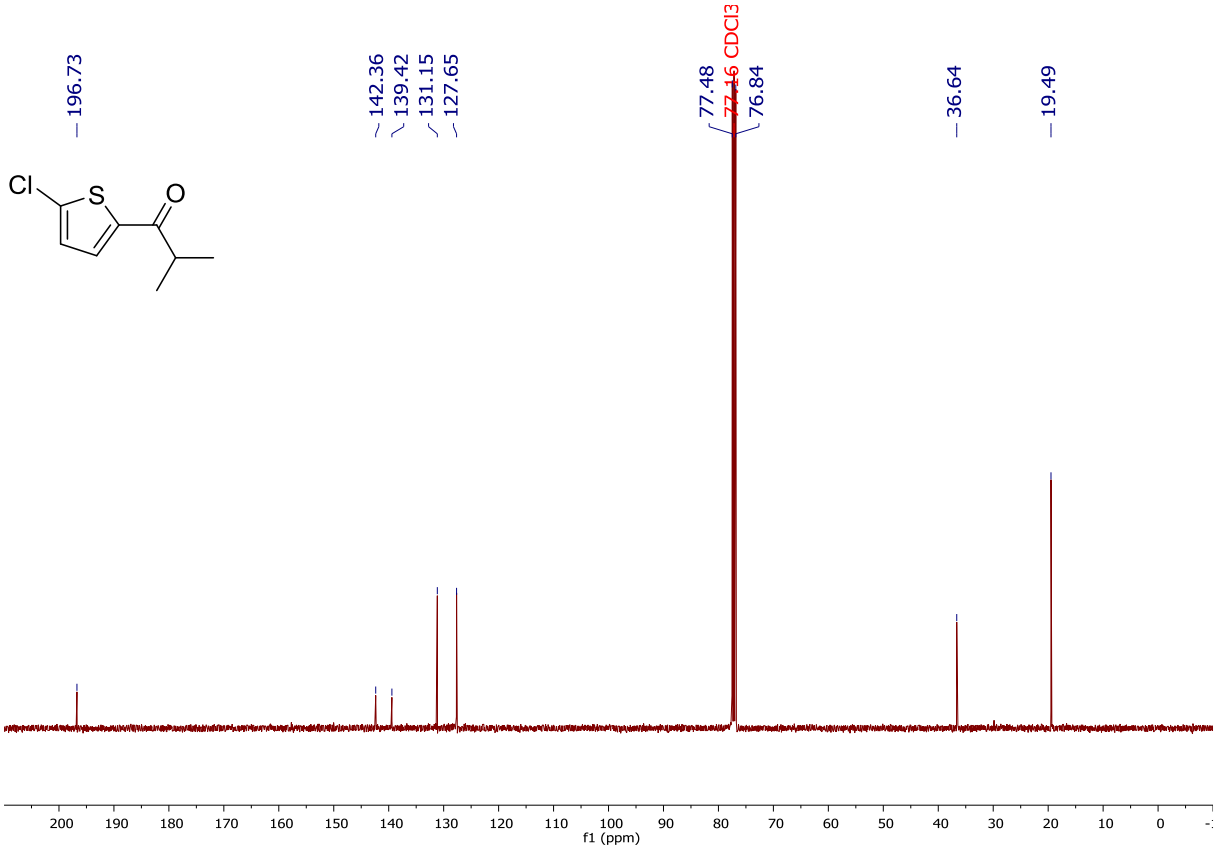


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b14** in $CDCl_3$ recorded at 101.6 MHz.

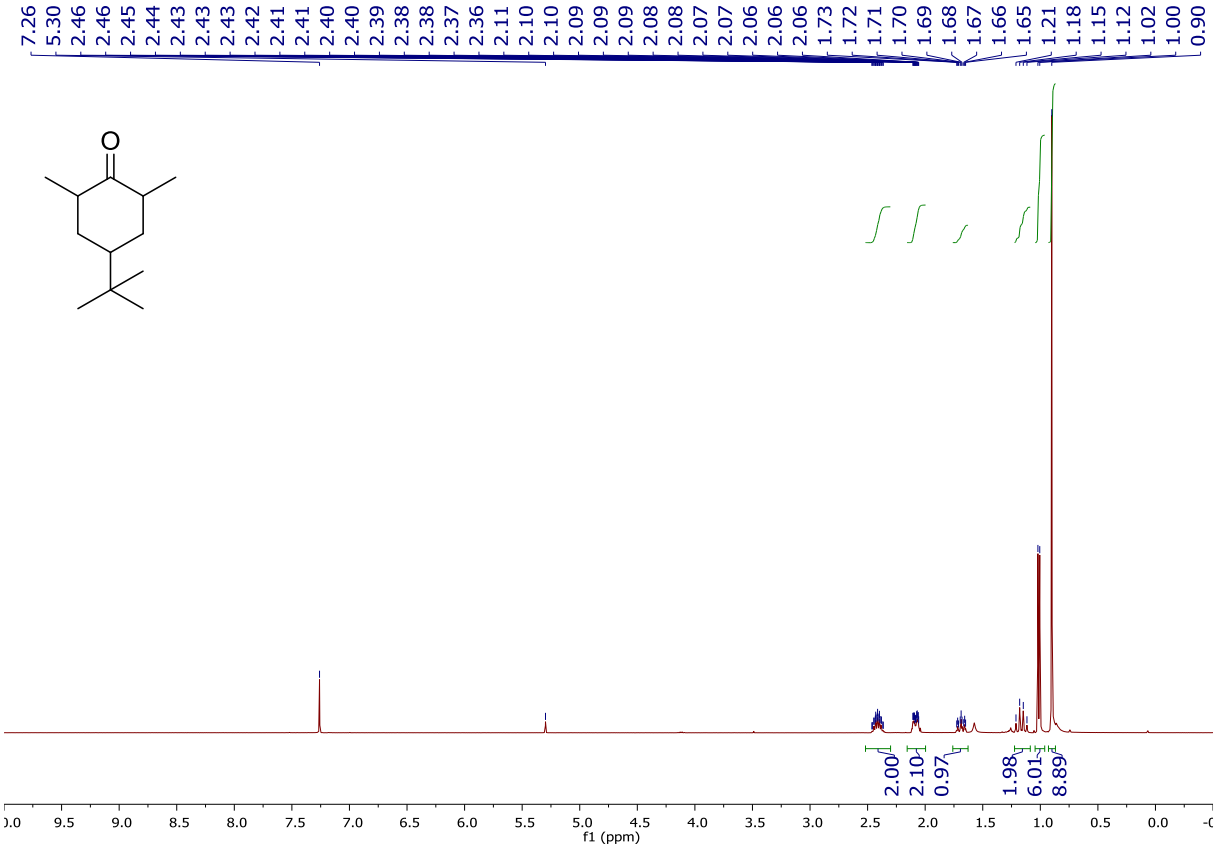


Figure S28: ^{1}H NMR spectrum of the compound **b15** in $CDCl_3$ recorded at 400.1 MHz.

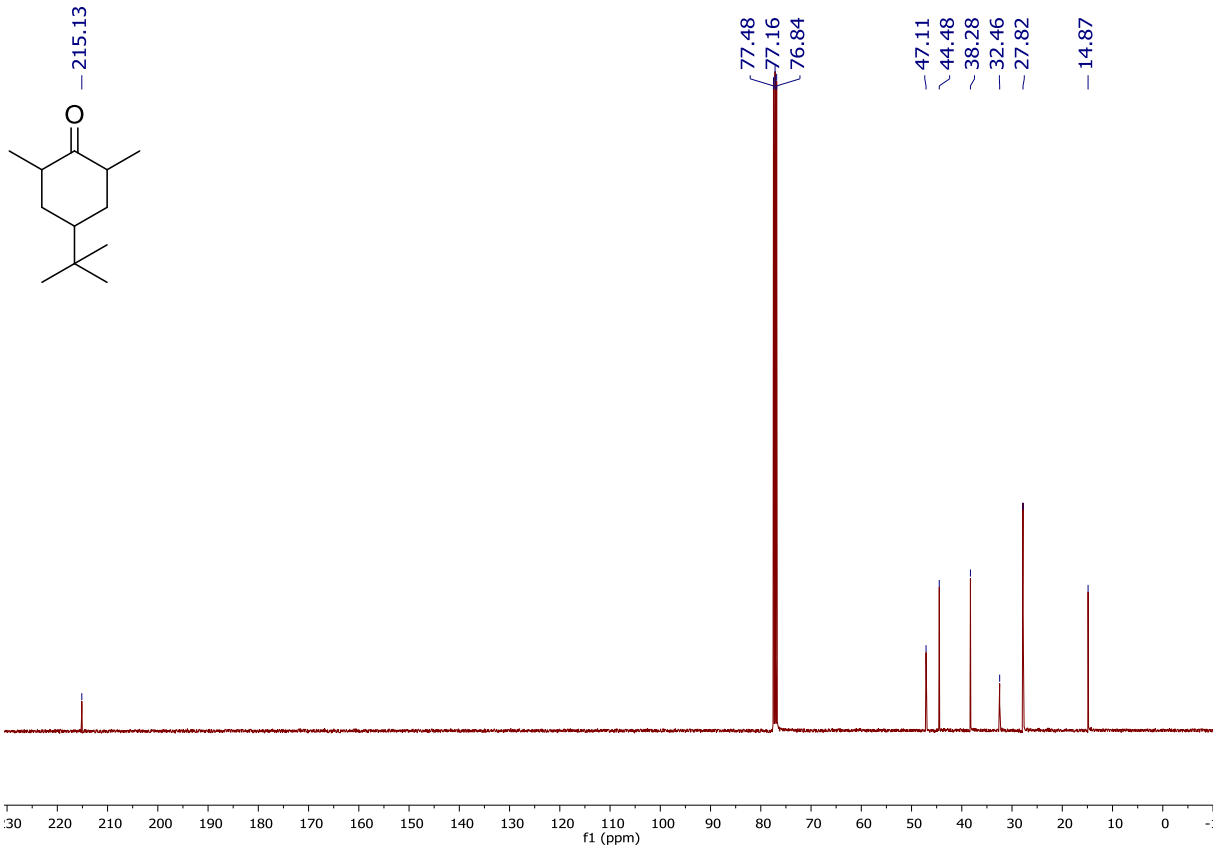


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b15** in $CDCl_3$ recorded at 101.6 MHz.

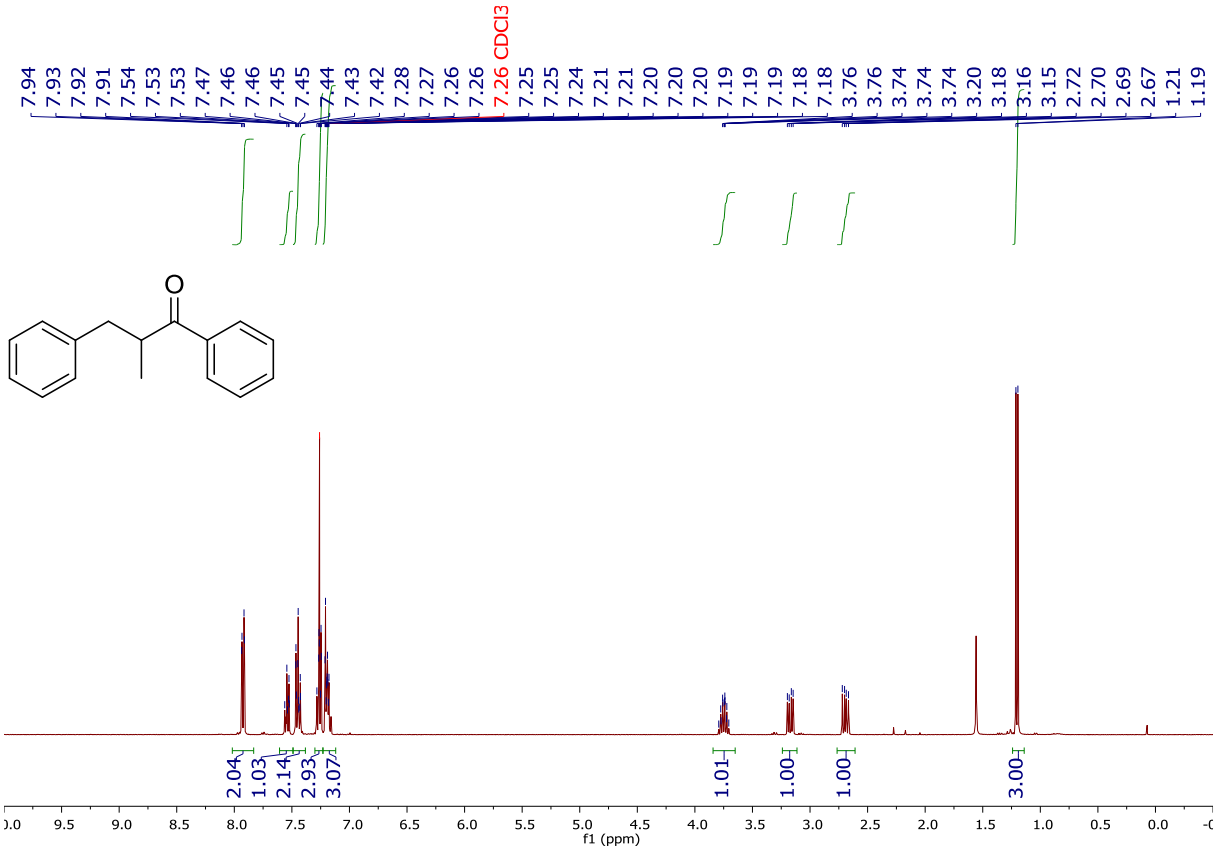


Figure S30: ^{1}H NMR spectrum of the compound **b16** in $CDCl_3$ recorded at 400.1 MHz.

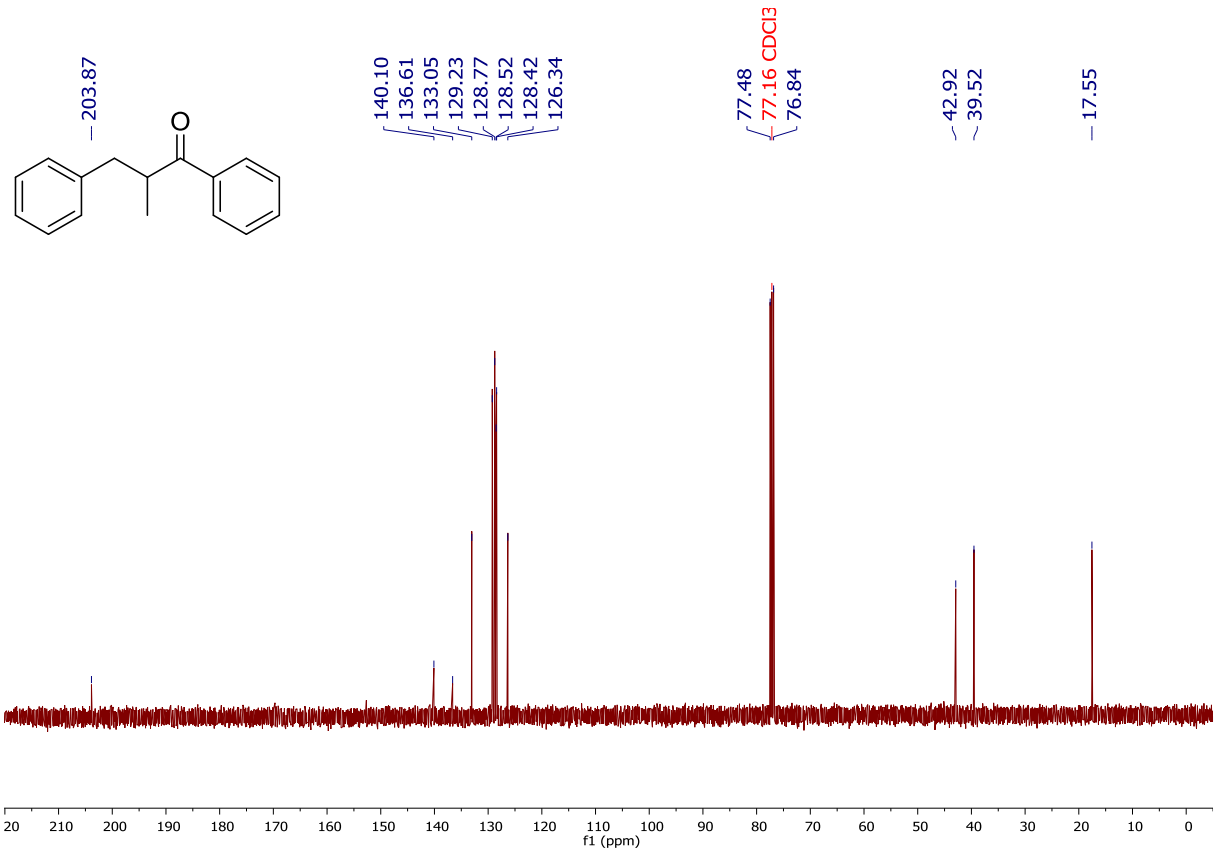


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b16** in $CDCl_3$ recorded at 101.6 MHz.

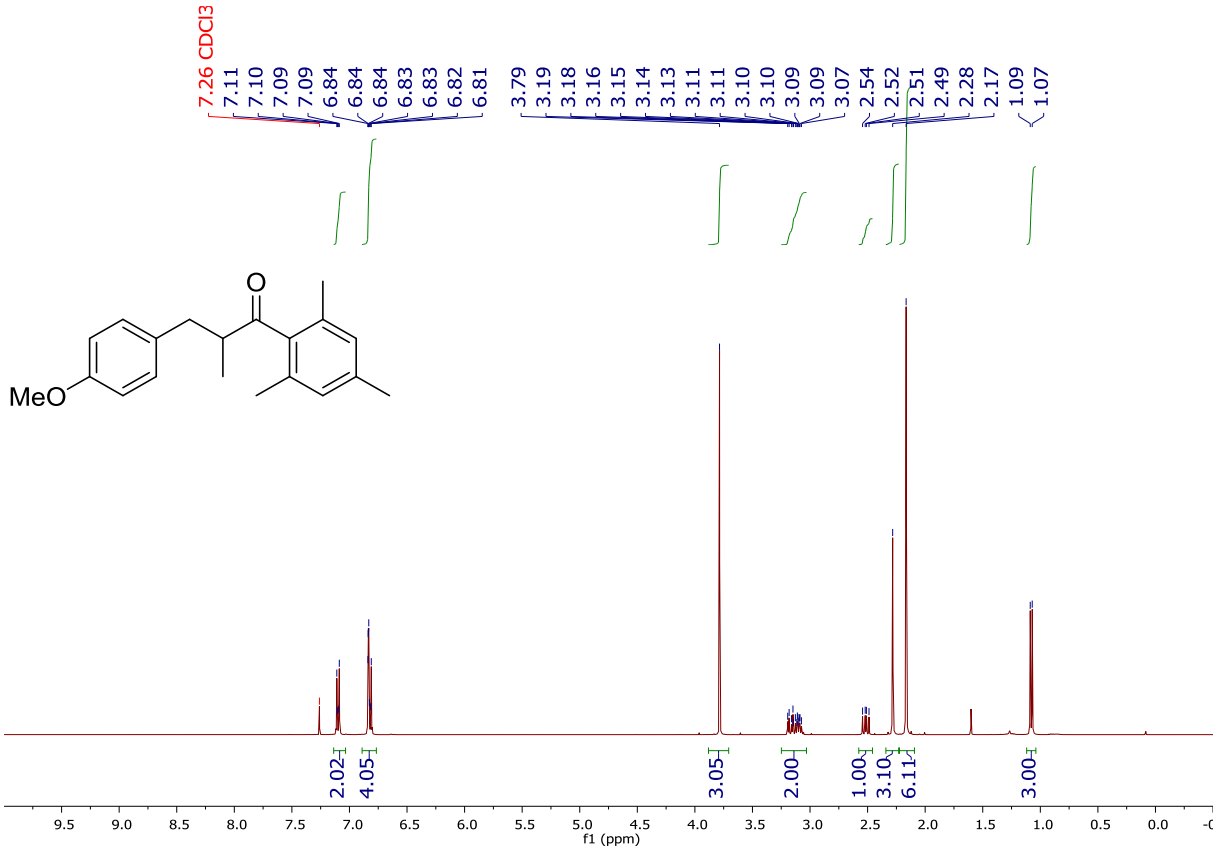


Figure S32: ^{1}H NMR spectrum of the compound **b17** in $CDCl_3$ recorded at 400.1 MHz.

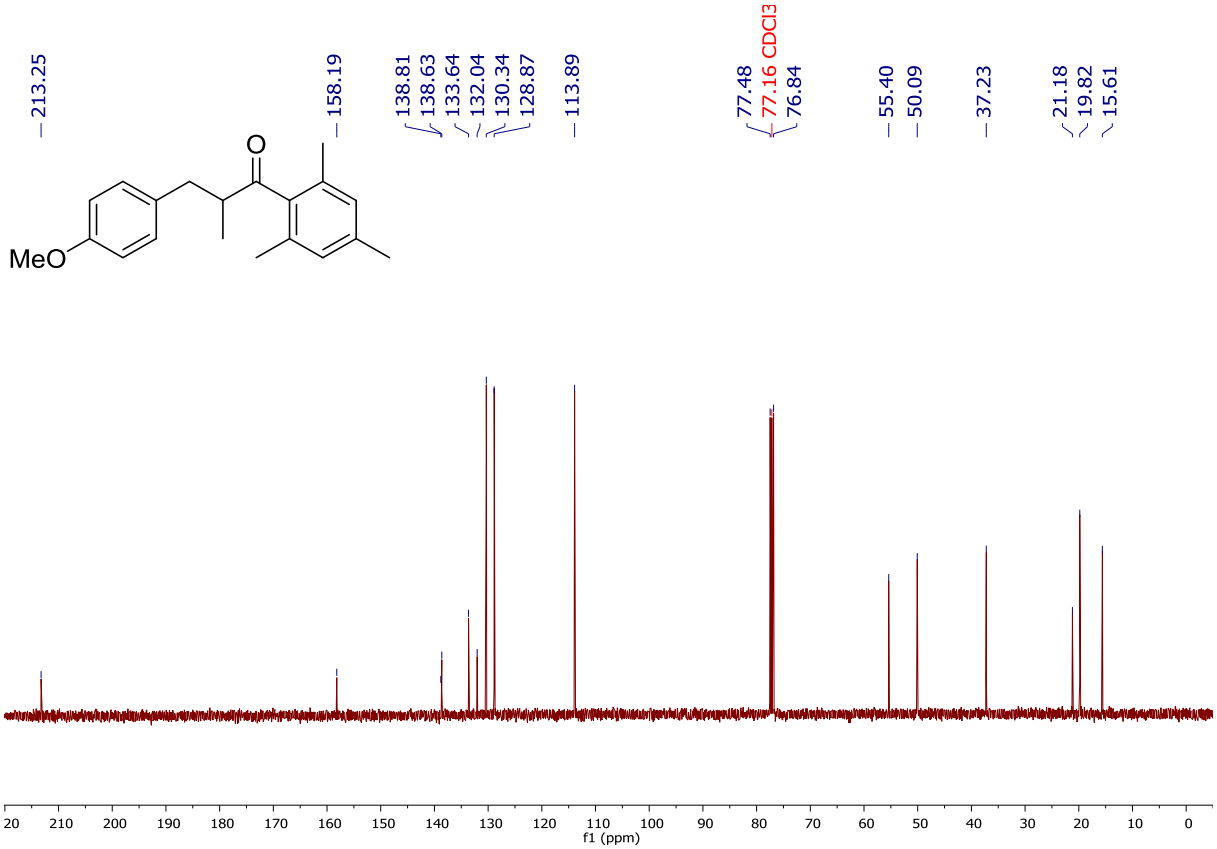


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b17** in $CDCl_3$ recorded at 101.6 MHz.

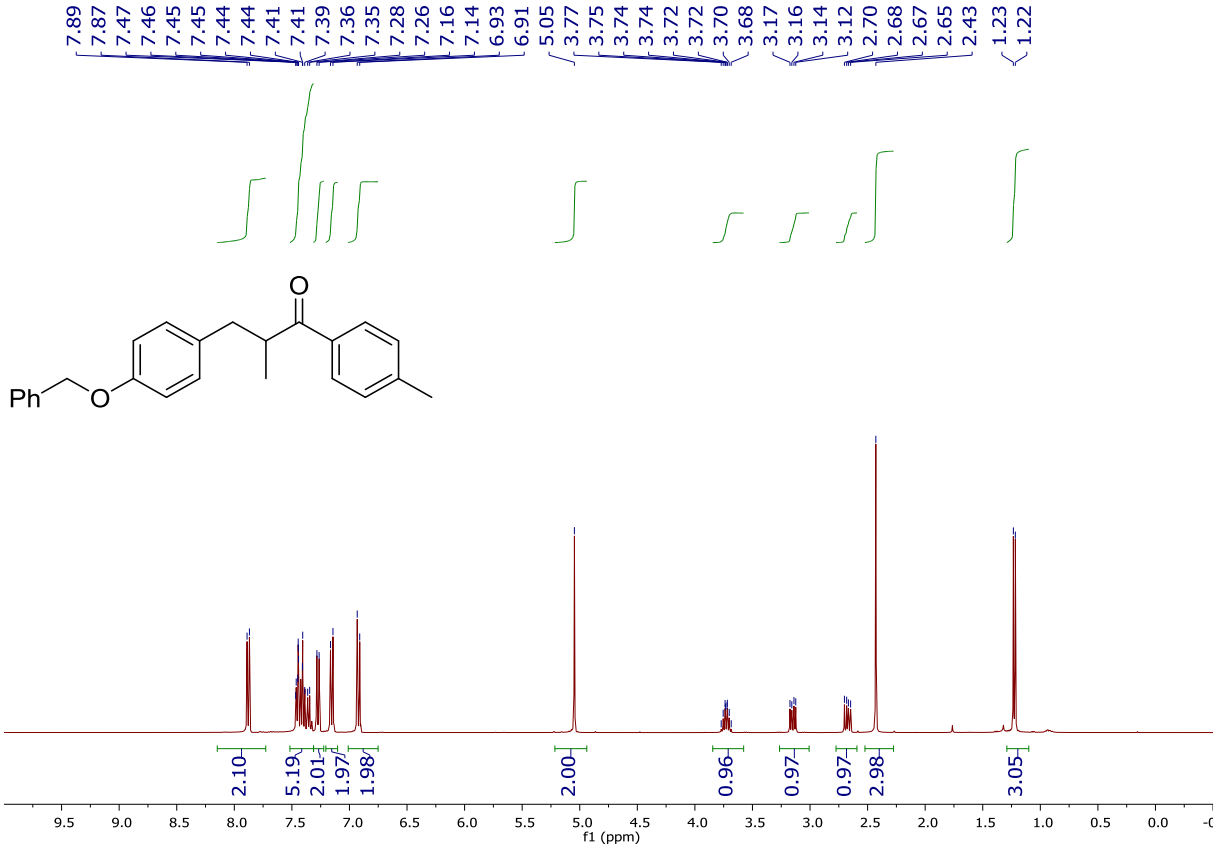


Figure S34: ^{1}H NMR spectrum of the compound **b18** in $CDCl_3$ recorded at 400.1 MHz.

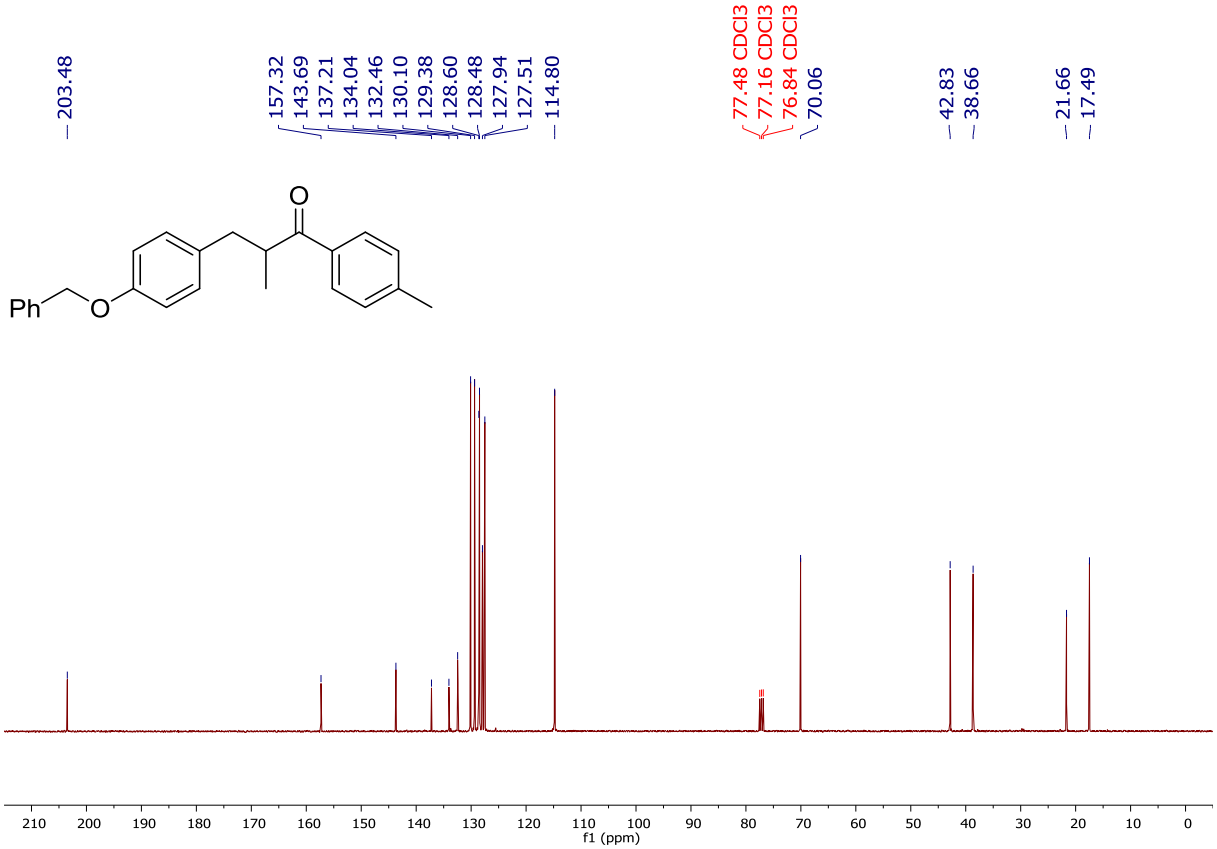


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b18** in $CDCl_3$ recorded at 101.6 MHz.

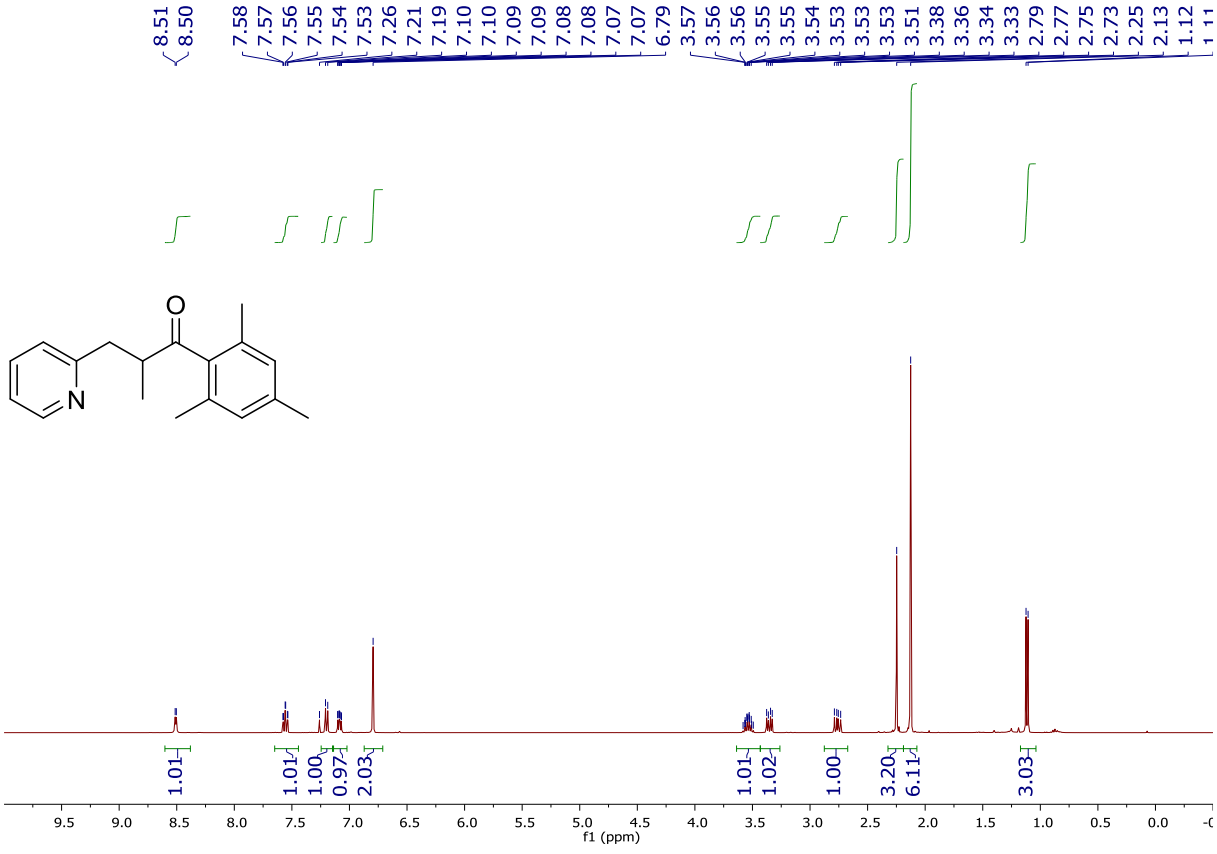


Figure S36: ^{1}H NMR spectrum of the compound **b19** in $CDCl_3$ recorded at 400.1 MHz.

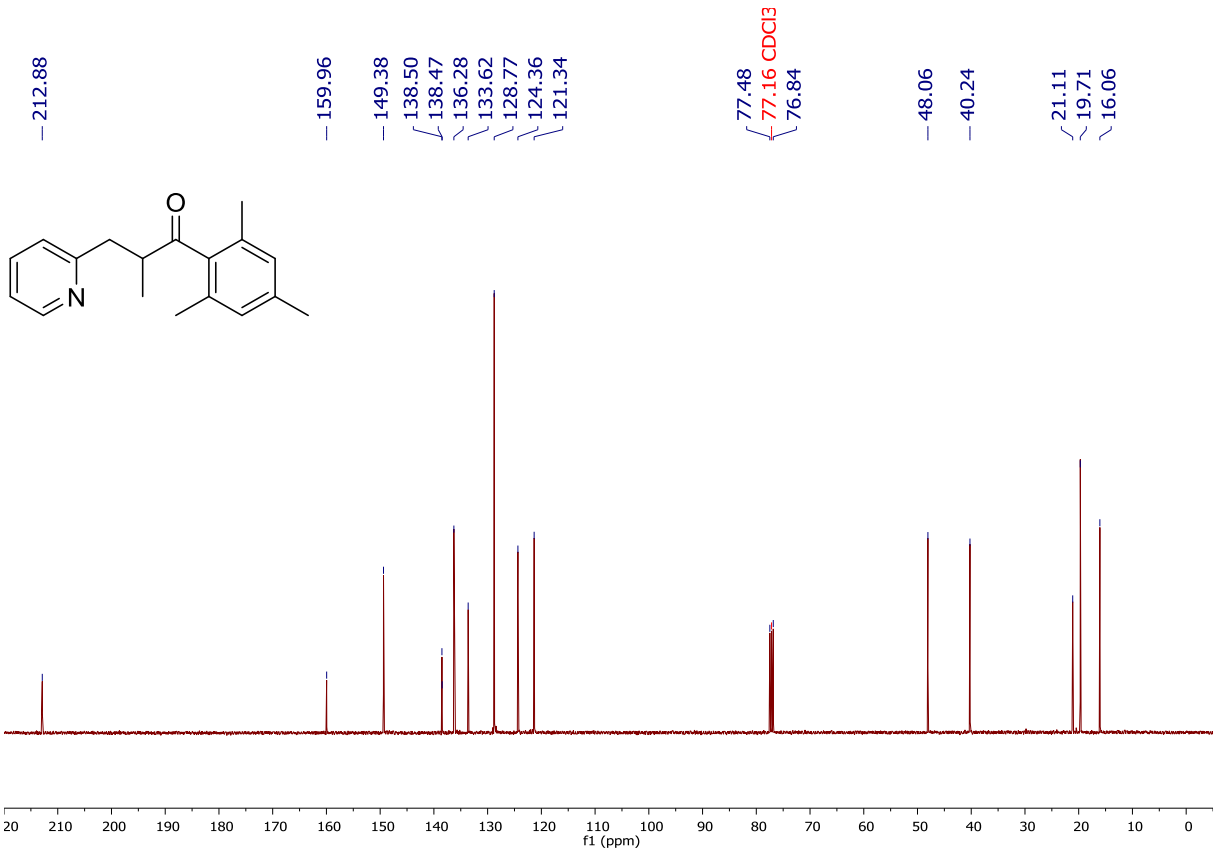


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b19** in $CDCl_3$ recorded at 101.6 MHz.

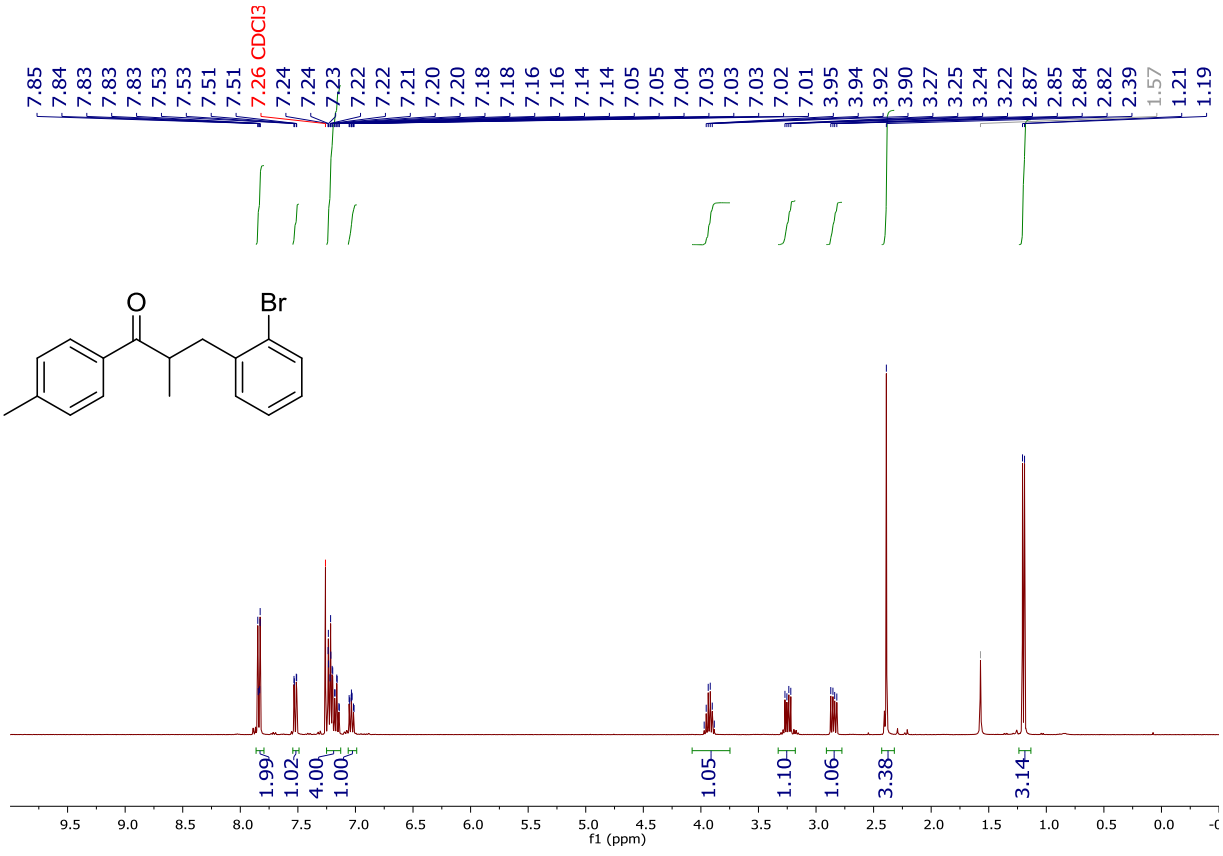


Figure S38: ^{1}H NMR spectrum of the compound **b20** in $CDCl_3$ recorded at 400.1 MHz.

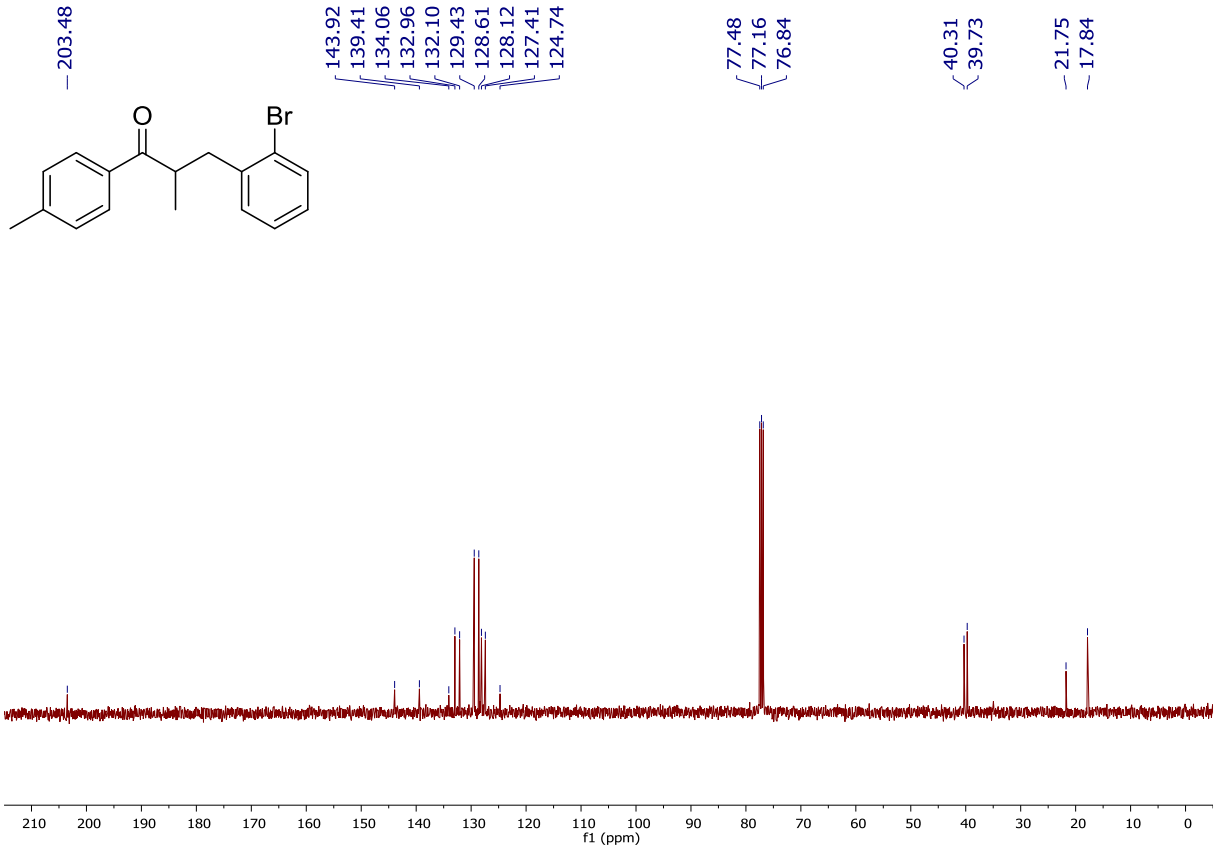


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b20** in $CDCl_3$ recorded at 101.6 MHz.

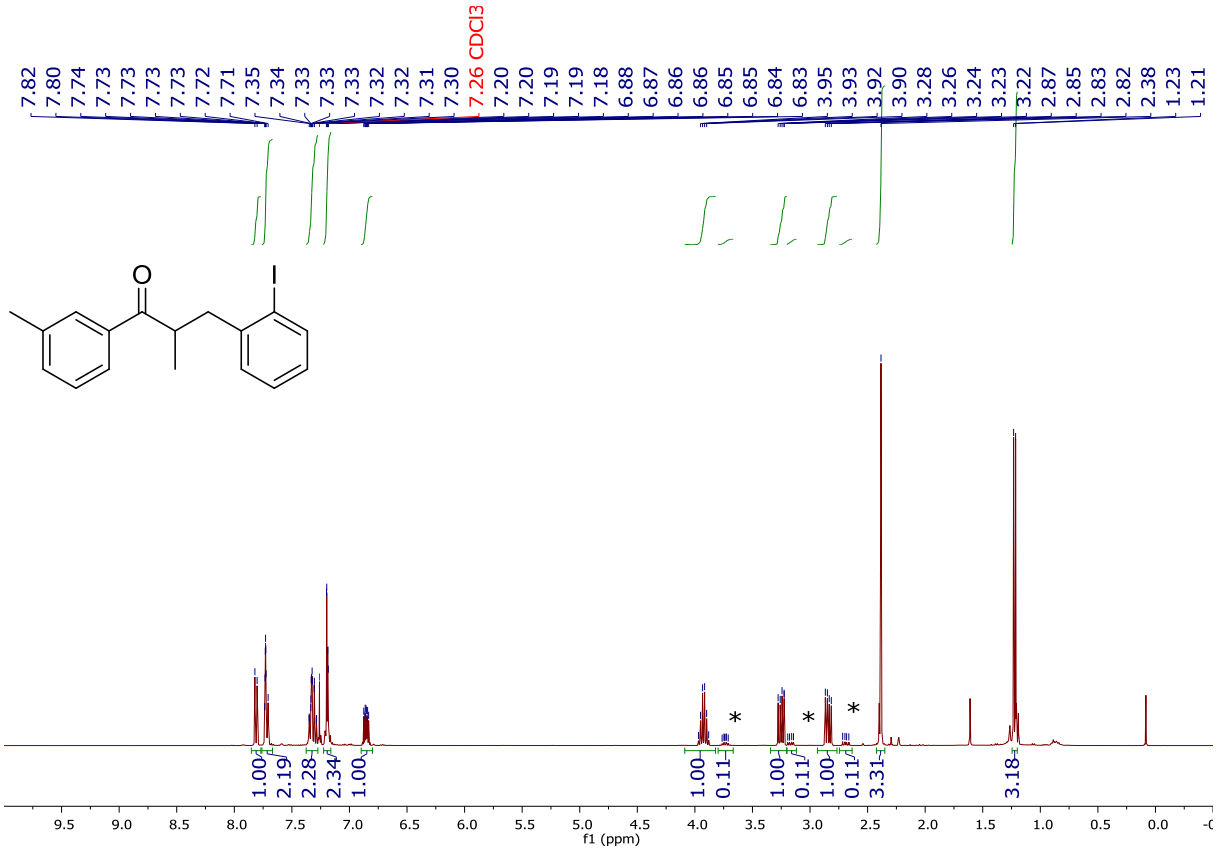


Figure S40: ^{1}H NMR spectrum of the compound **b21** in $CDCl_3$ recorded at 400.1 MHz (* = signals for deiodinated product).

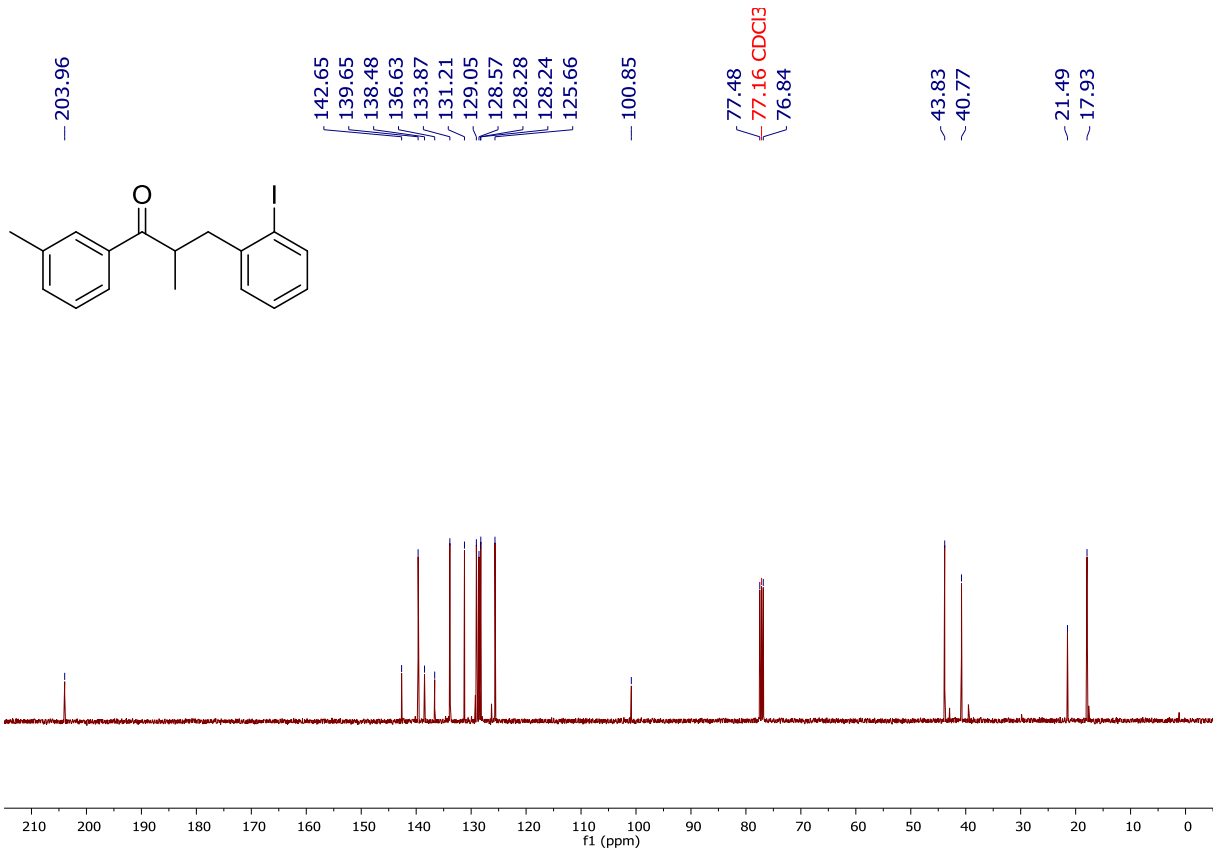


Figure S41: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b21** in $CDCl_3$ recorded at 101.6 MHz.

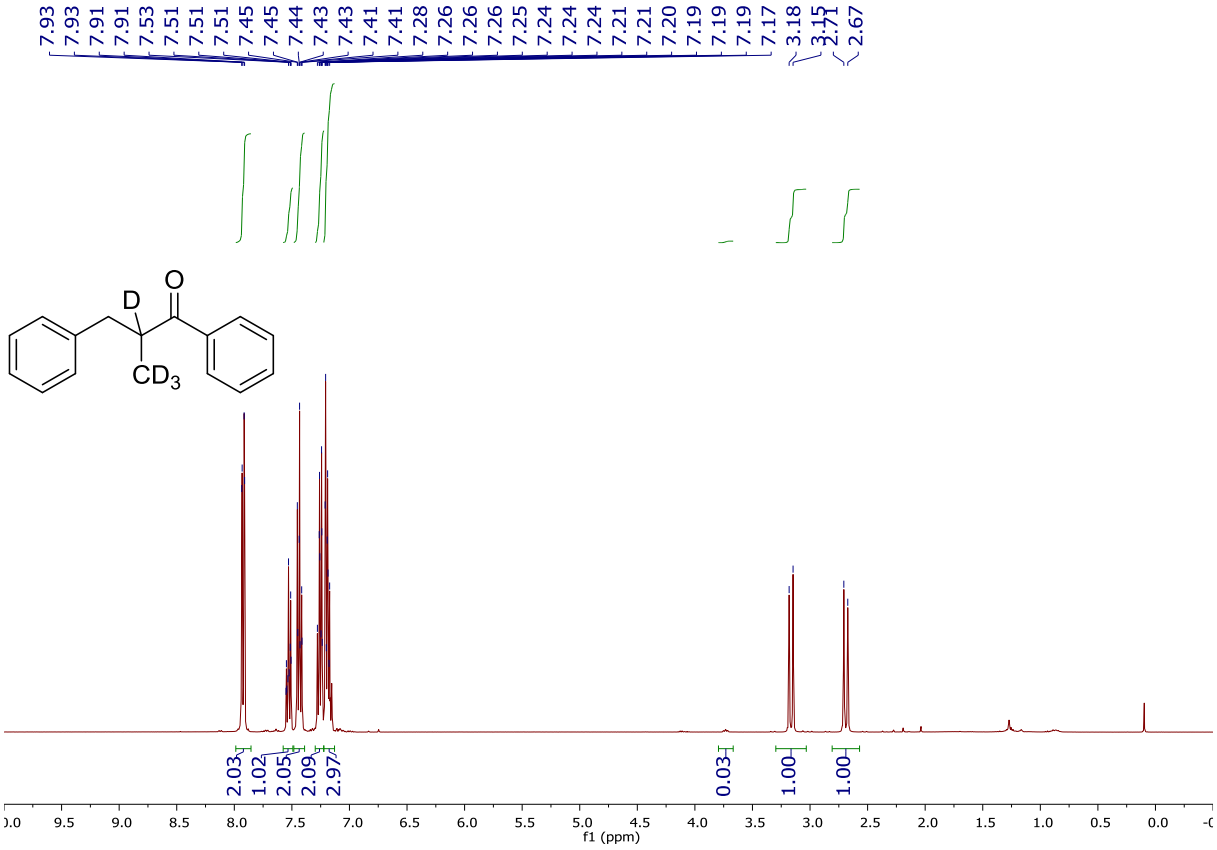


Figure S42: ^{1}H NMR spectrum of the compound **b22** in $CDCl_3$ recorded at 400.1 MHz.

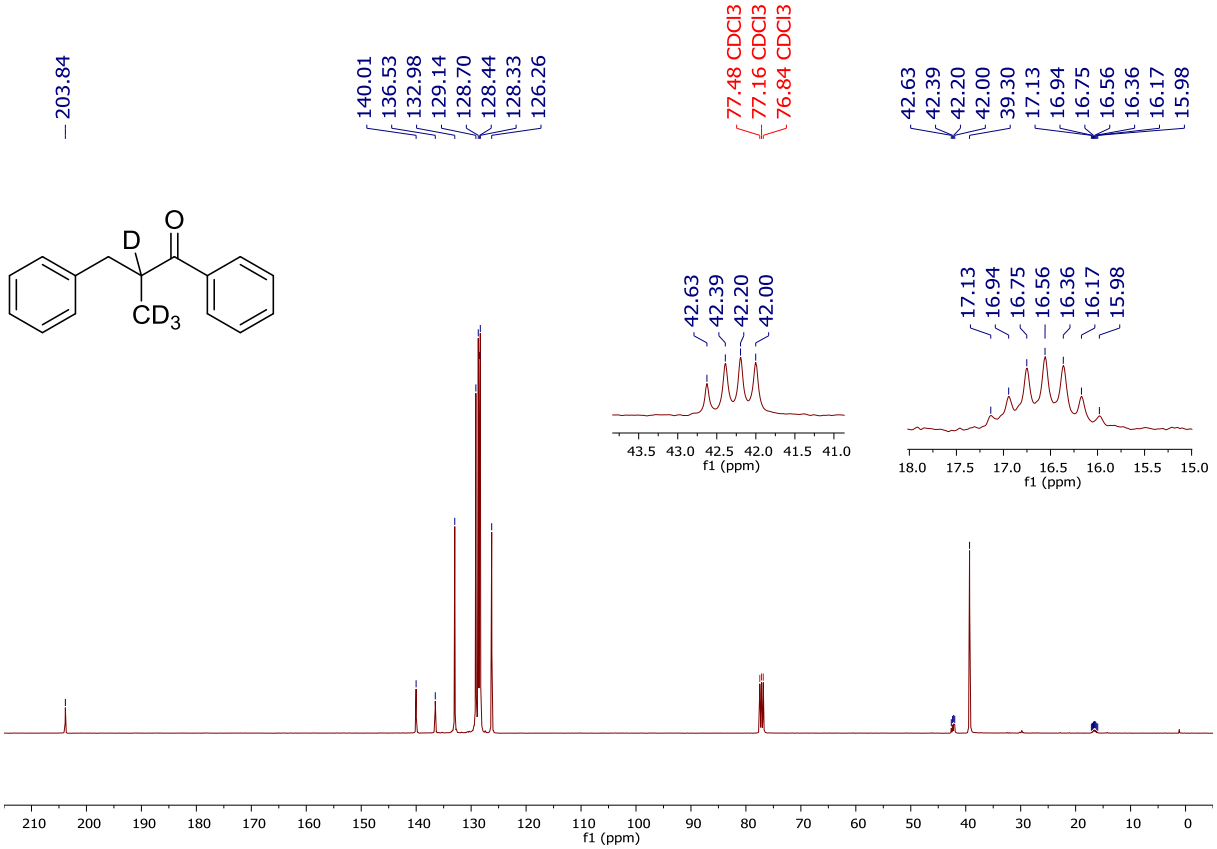


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b22** in $CDCl_3$ recorded at 101.6 MHz.

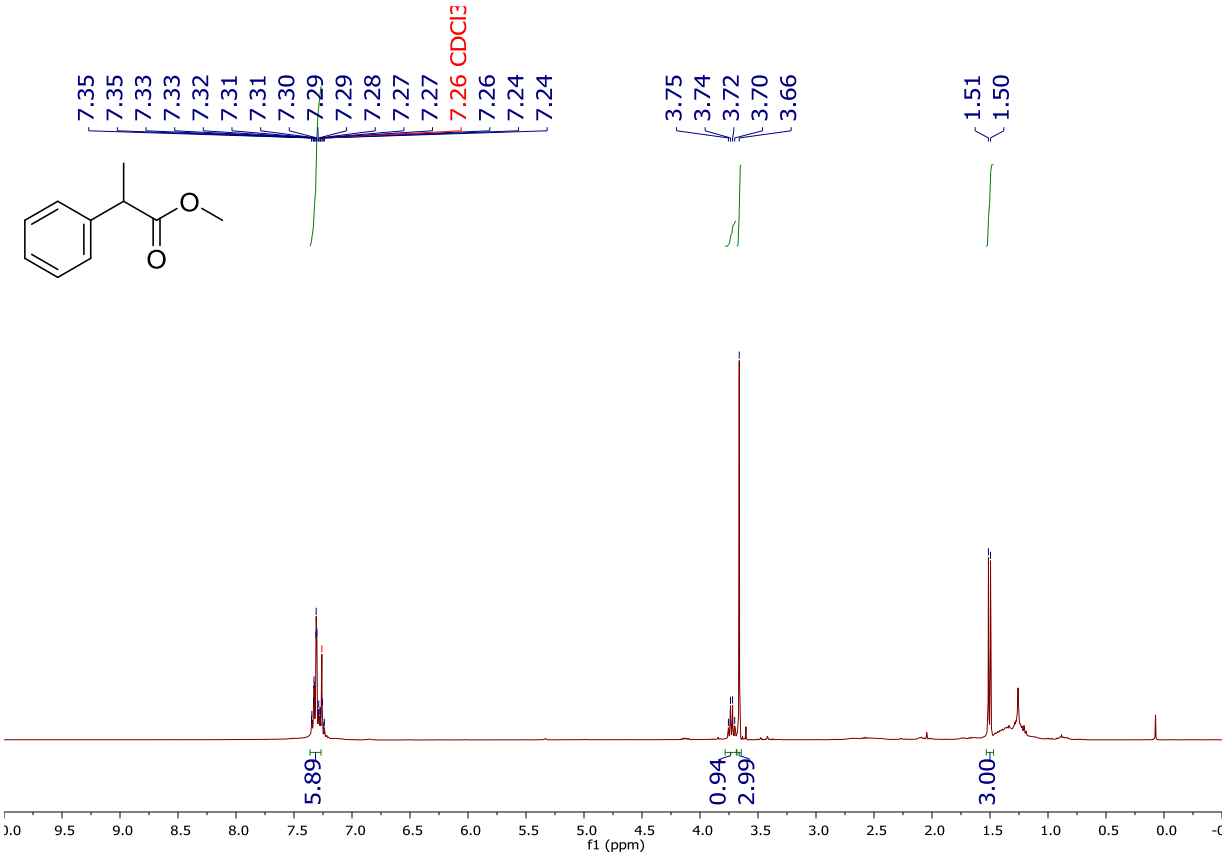


Figure S44: ^{1}H NMR spectrum of the crude mixture for compound **b23** in $CDCl_3$ recorded at 400.1 MHz.

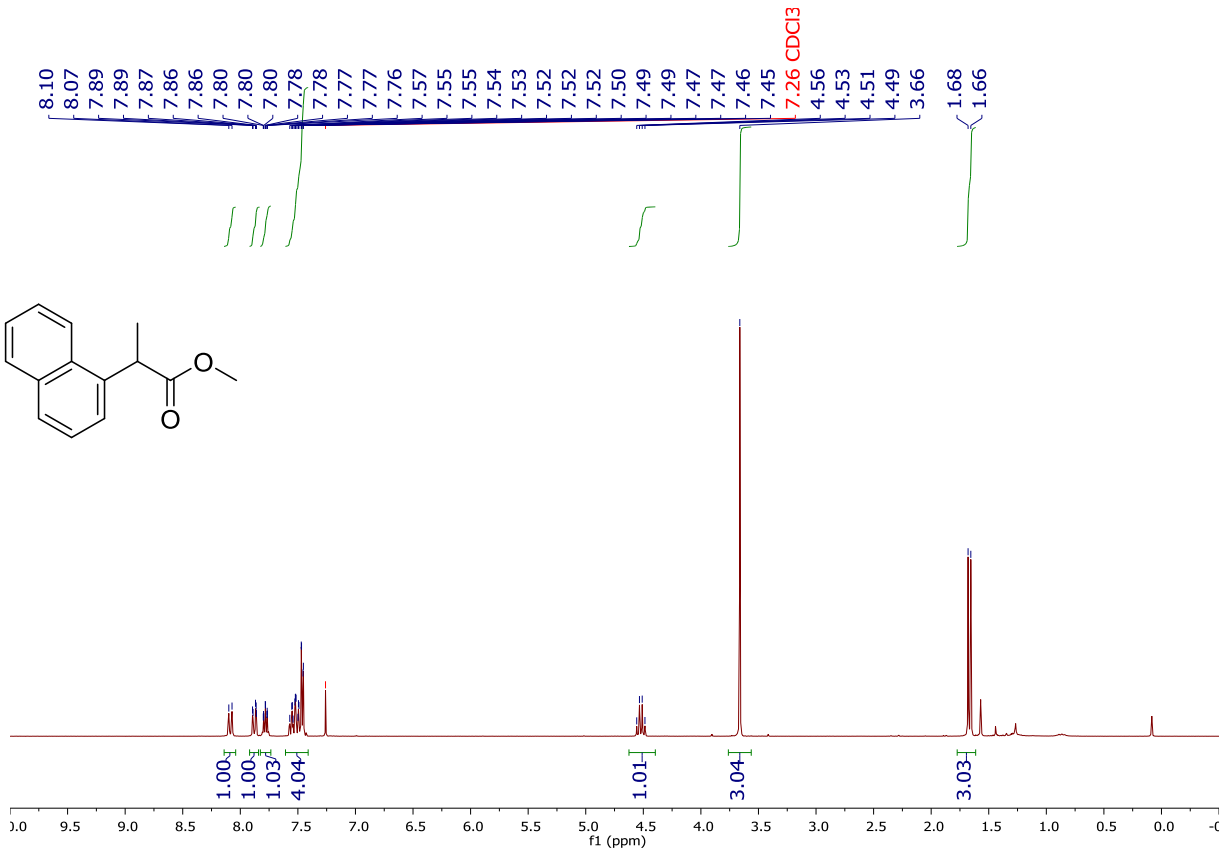


Figure S45: ^{1}H NMR spectrum of the compound **b24** in $CDCl_3$ recorded at 300.1 MHz.

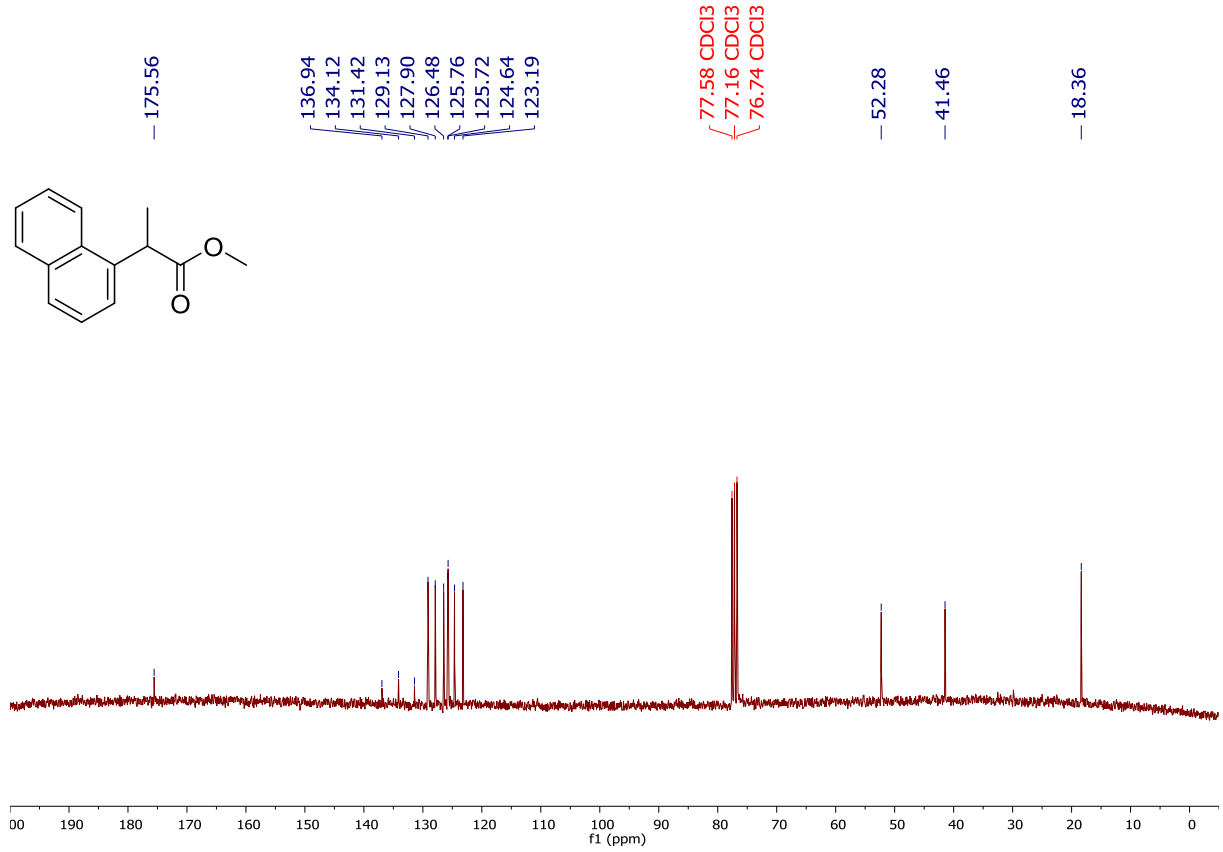


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b24** in $CDCl_3$ recorded at 75.5 MHz.

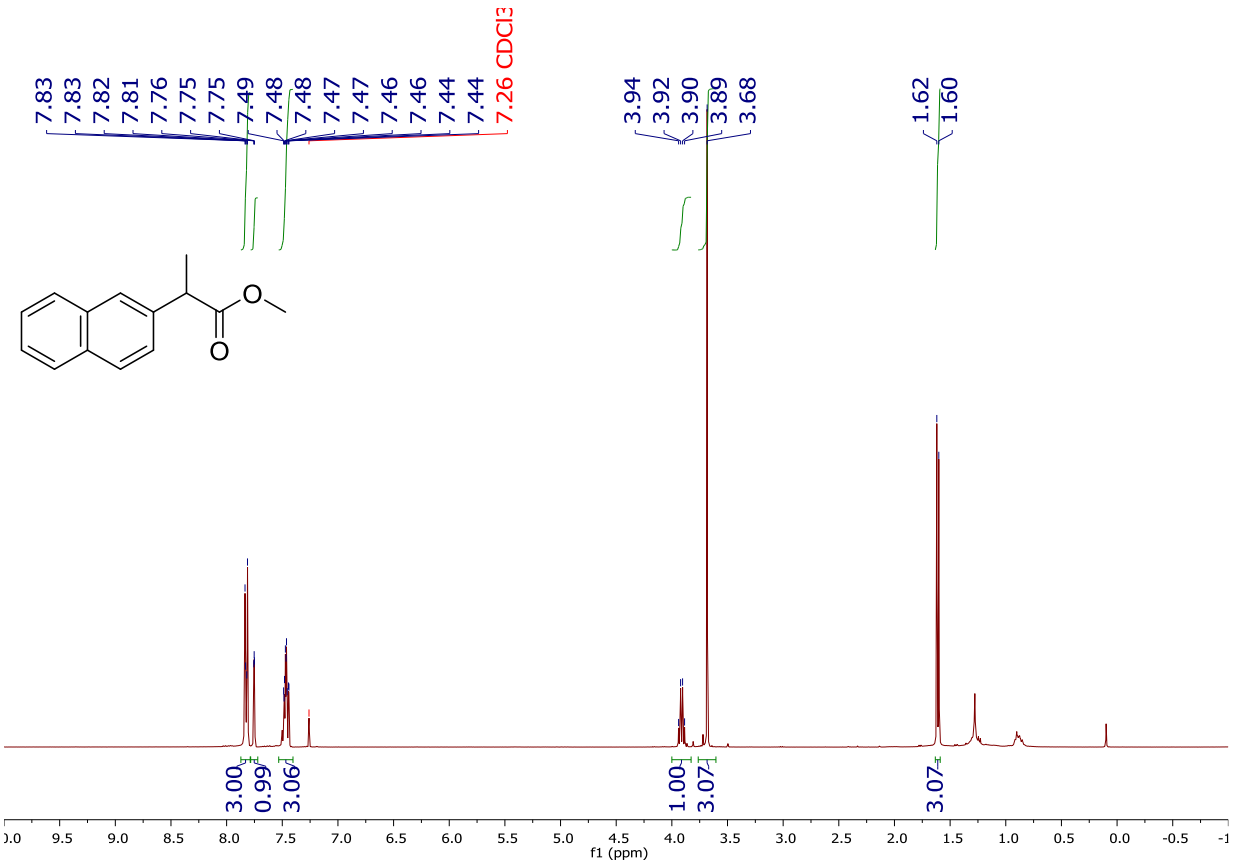


Figure S47: ^{1}H NMR spectrum of the compound **b25** in $CDCl_3$ recorded at 300.1 MHz.

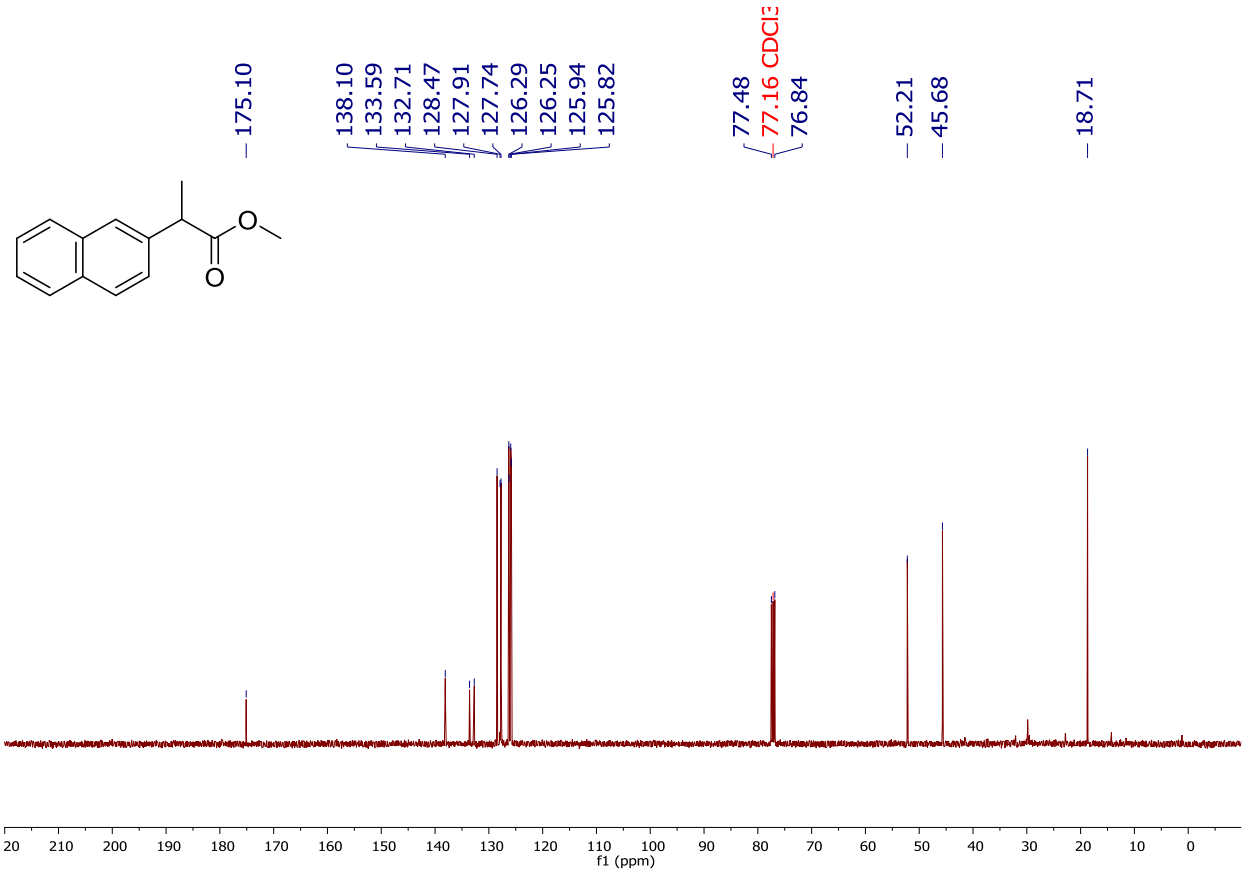


Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b25** in $CDCl_3$ recorded at 75.5 MHz.

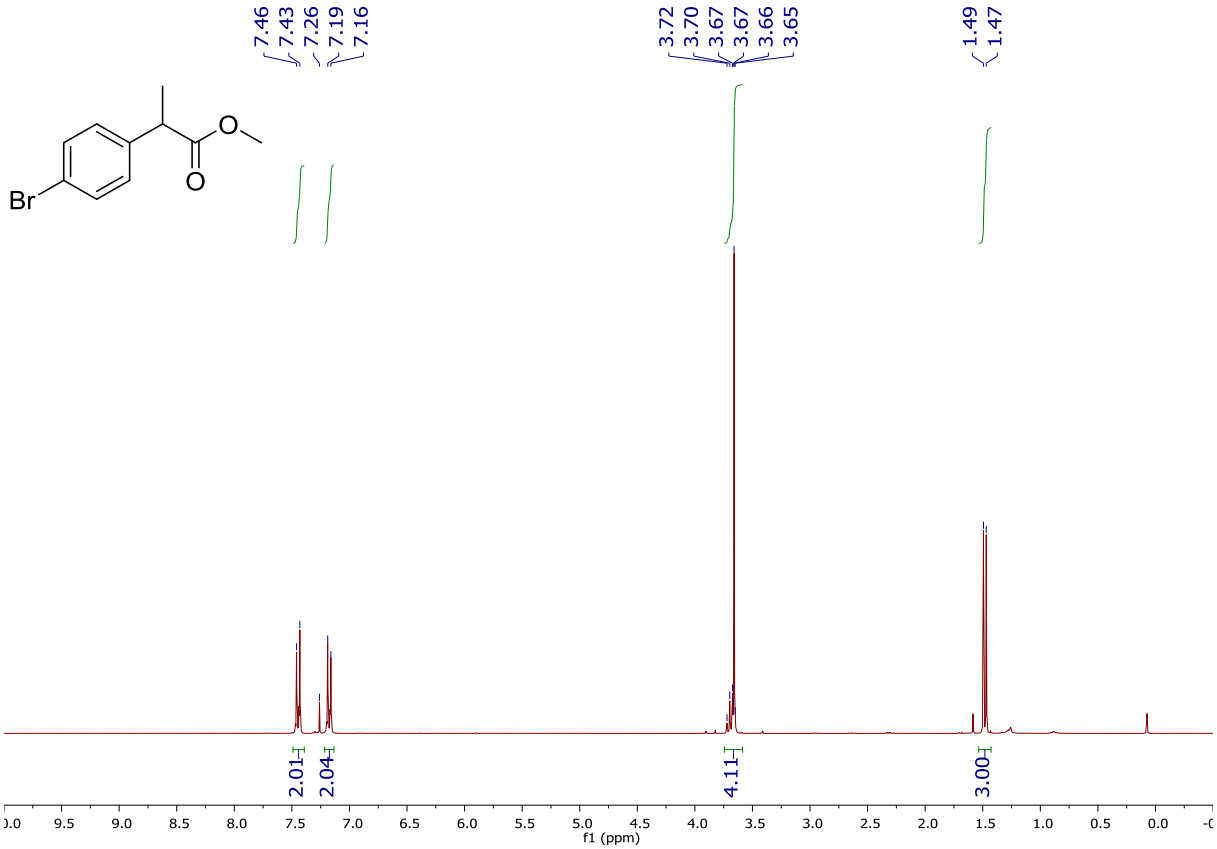


Figure S49: ^{1}H NMR spectrum of the compound **b26** in $CDCl_3$ recorded at 300.1 MHz.

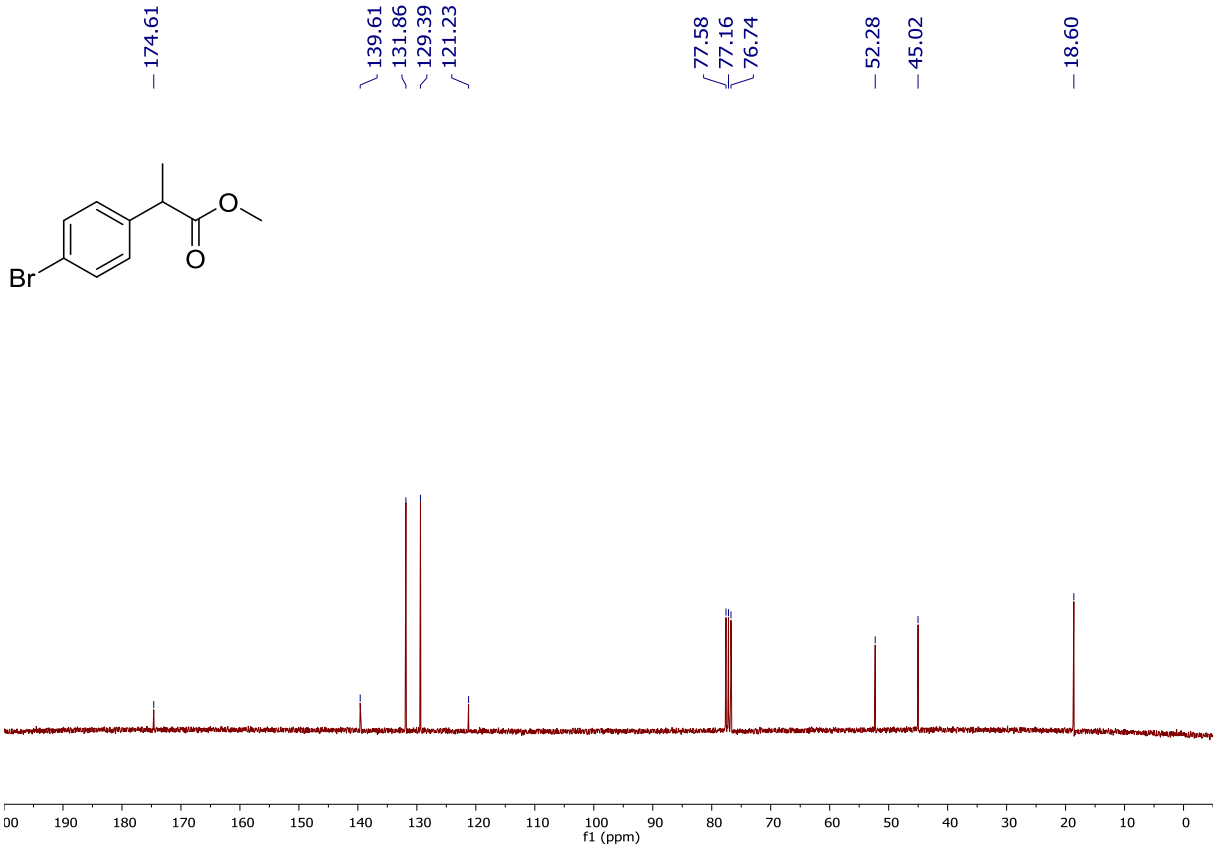


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b26** in $CDCl_3$ recorded at 75.5 MHz.

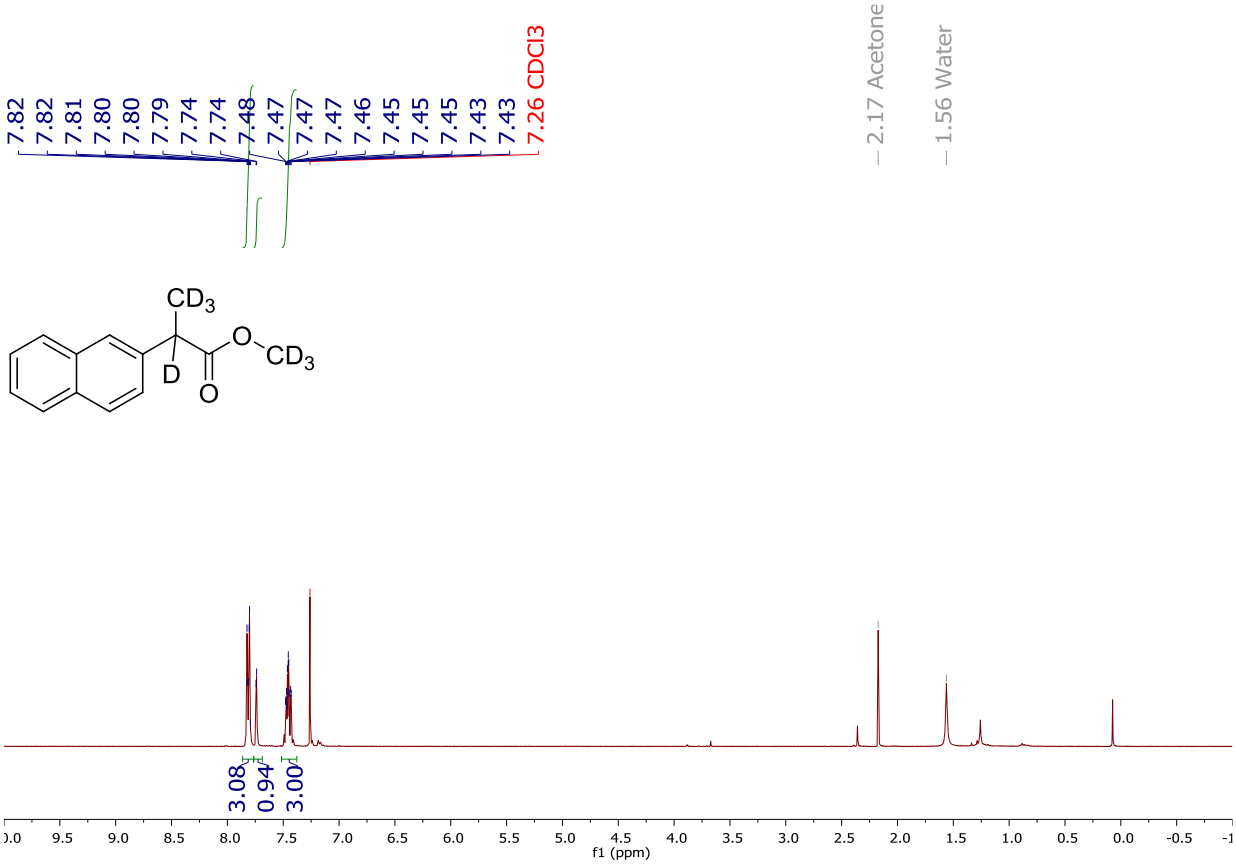


Figure S51: ^{1}H NMR spectrum of the compound **b27** in $CDCl_3$ recorded at 400.1 MHz.

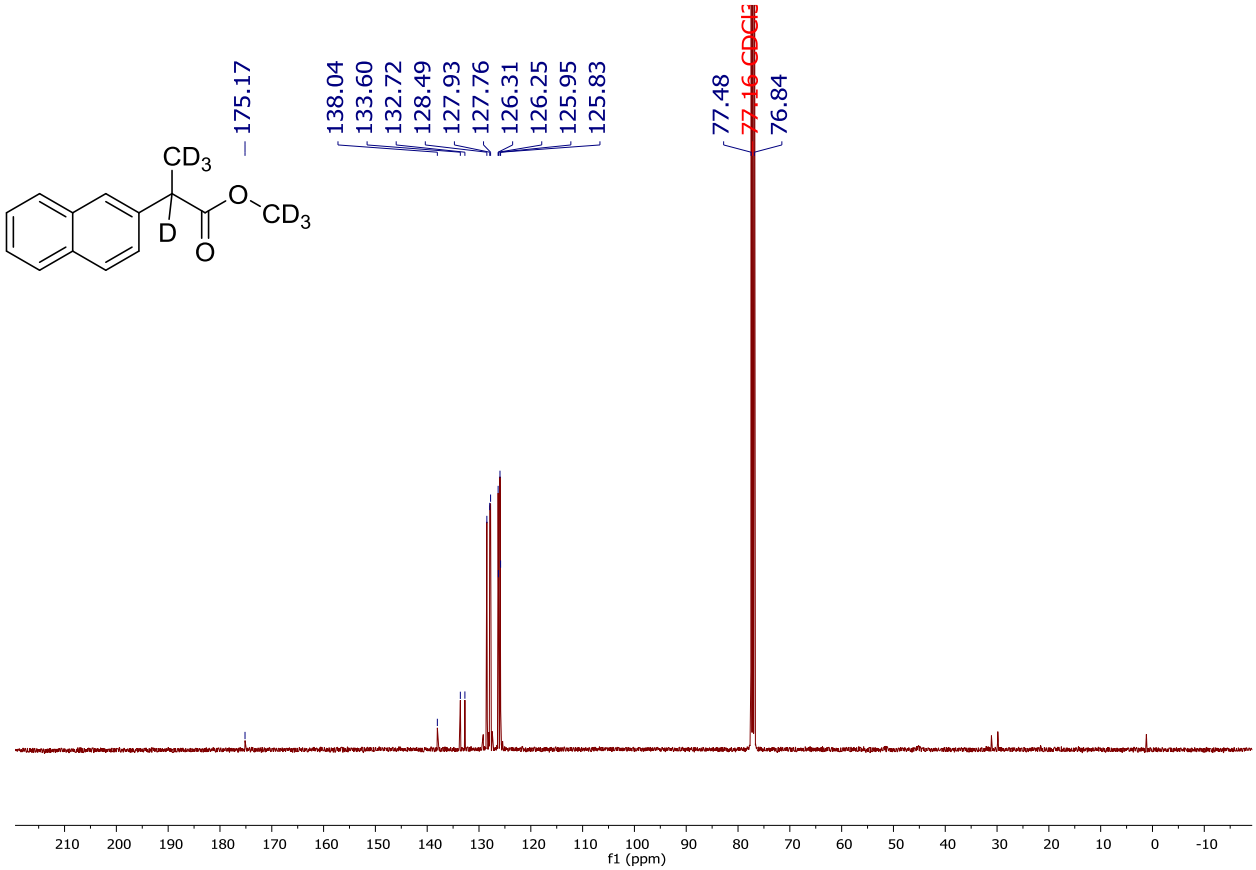


Figure S52: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b27** in $CDCl_3$ recorded at 100.6 MHz.

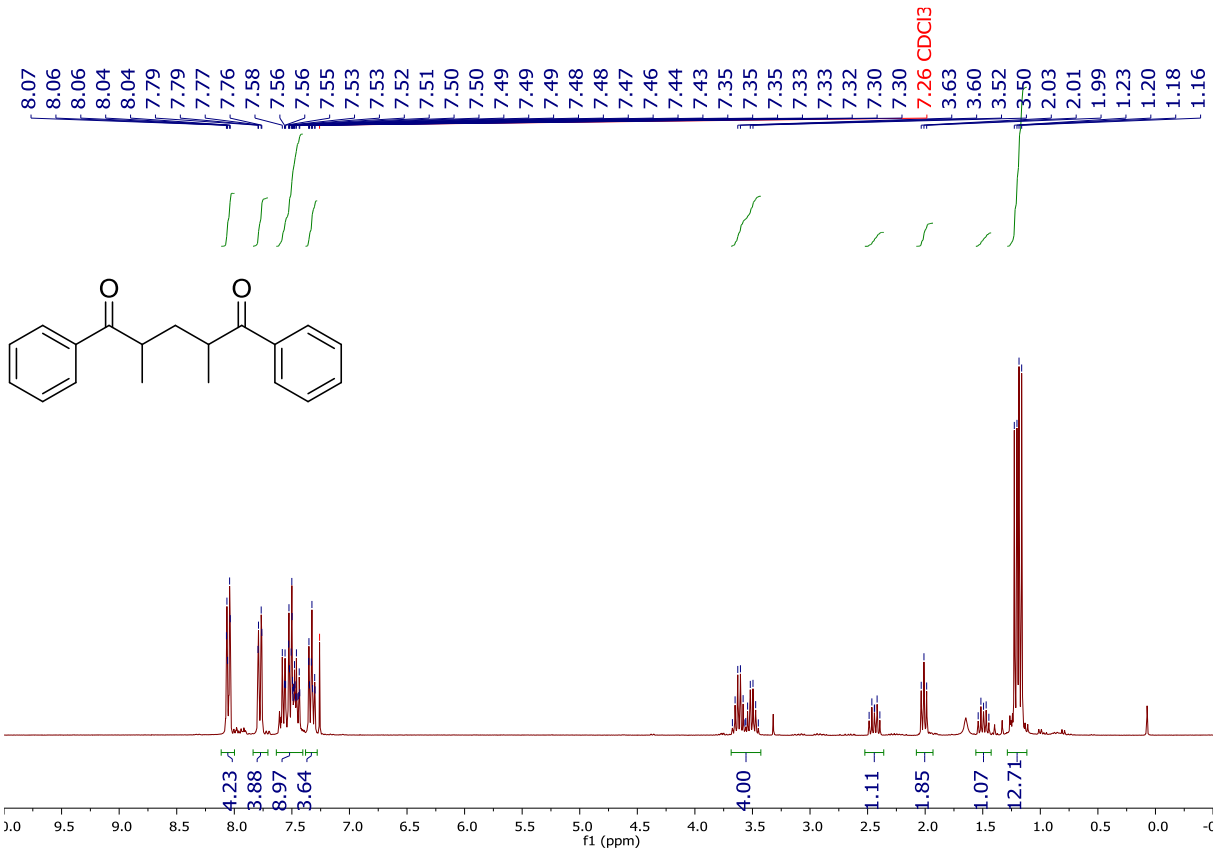


Figure S53: ^{1}H NMR spectrum of the compound **c1** in $CDCl_3$ recorded at 400.1 MHz.

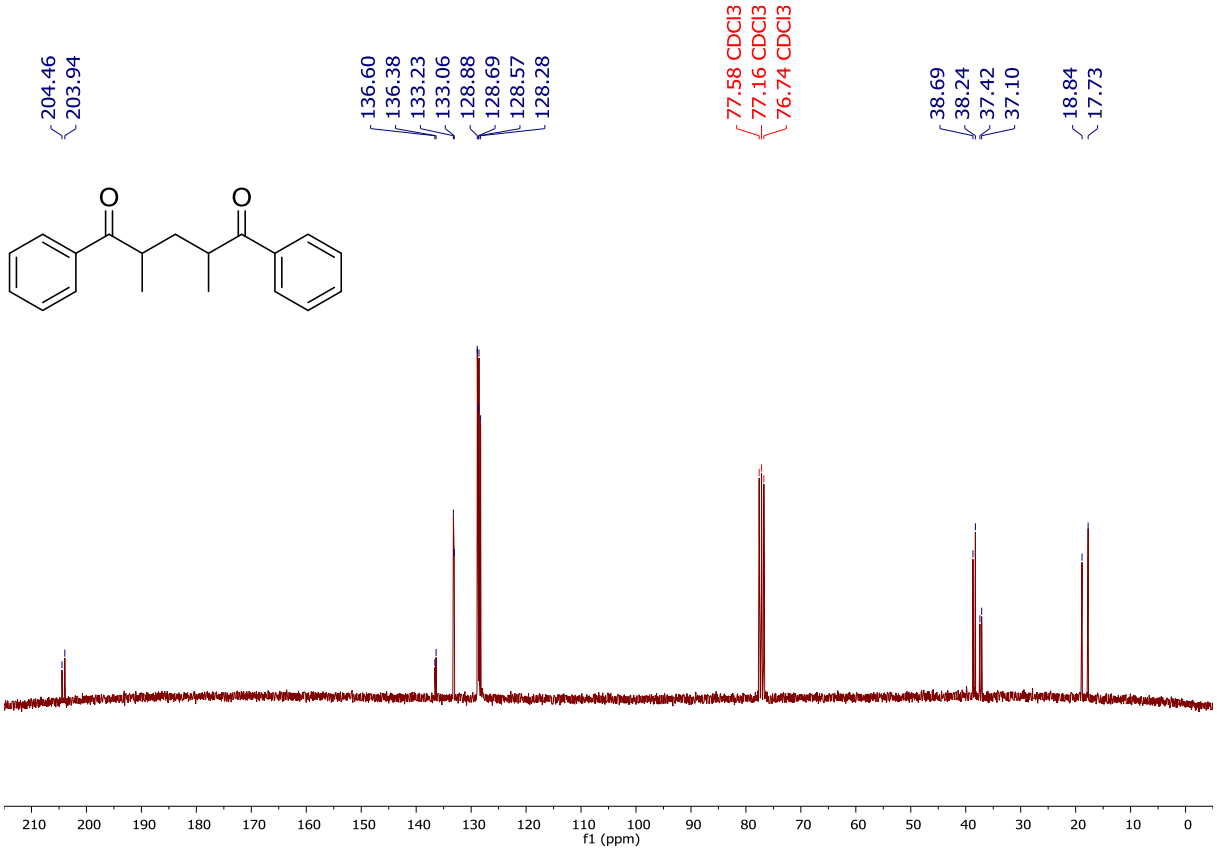


Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **c1** in $CDCl_3$ recorded at 101.6 MHz.

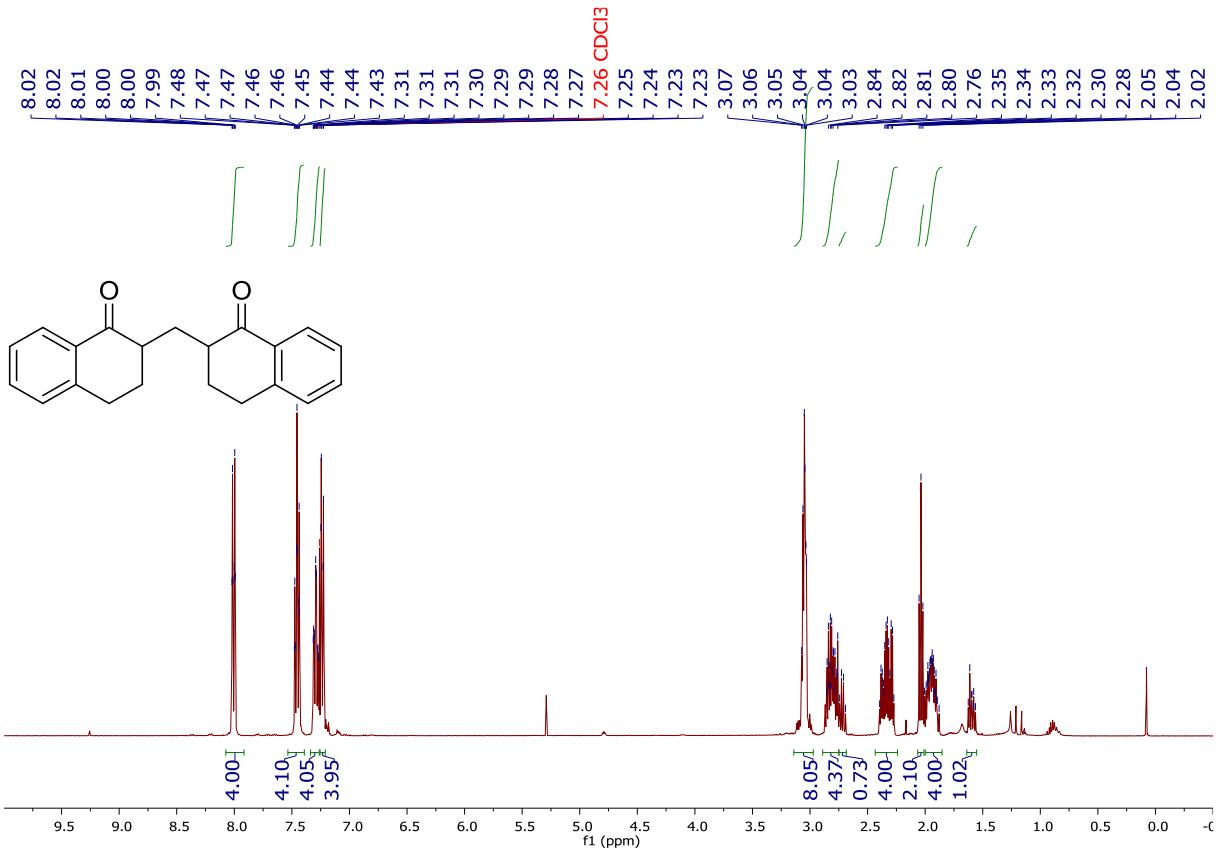


Figure S55: ^{1}H NMR spectrum of the compound **c3** in $CDCl_3$ recorded at 400.1 MHz.

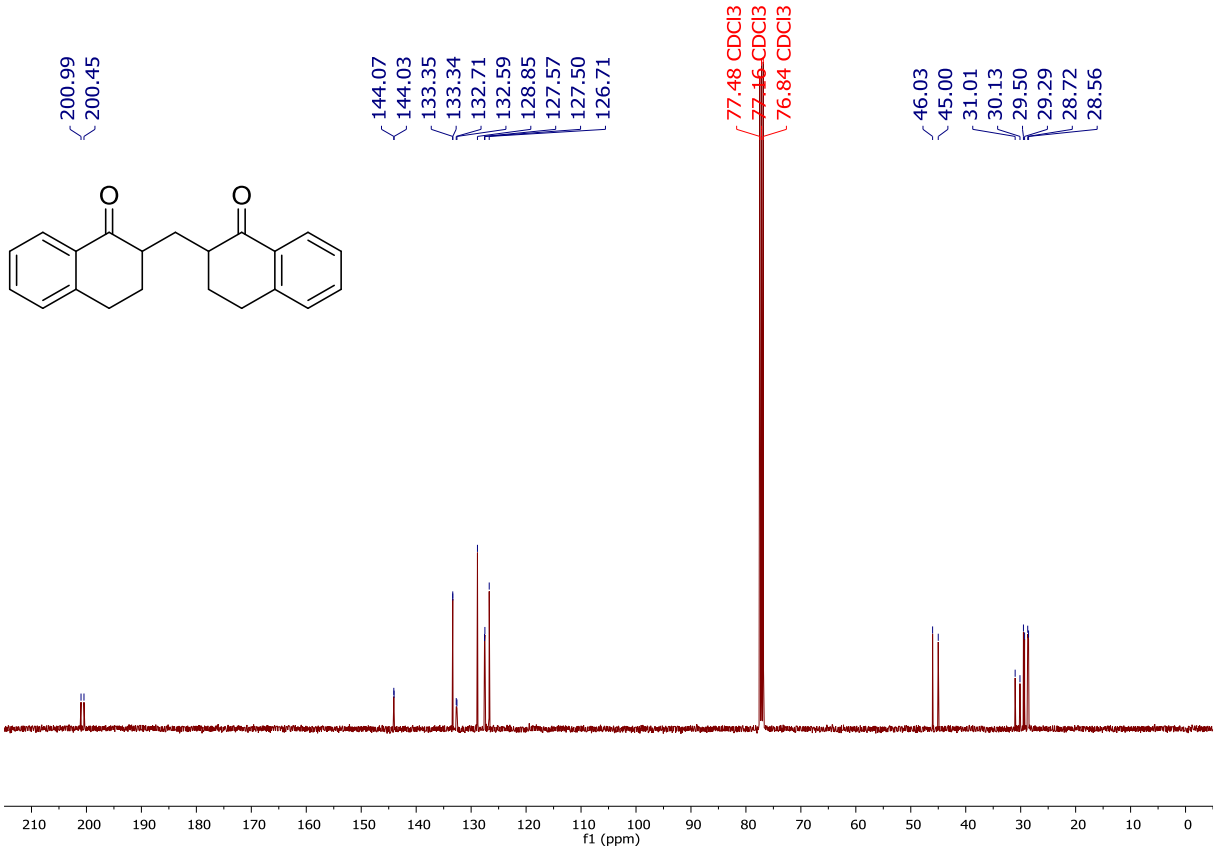


Figure S56: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **c3** in $CDCl_3$ recorded at 101.6 MHz.

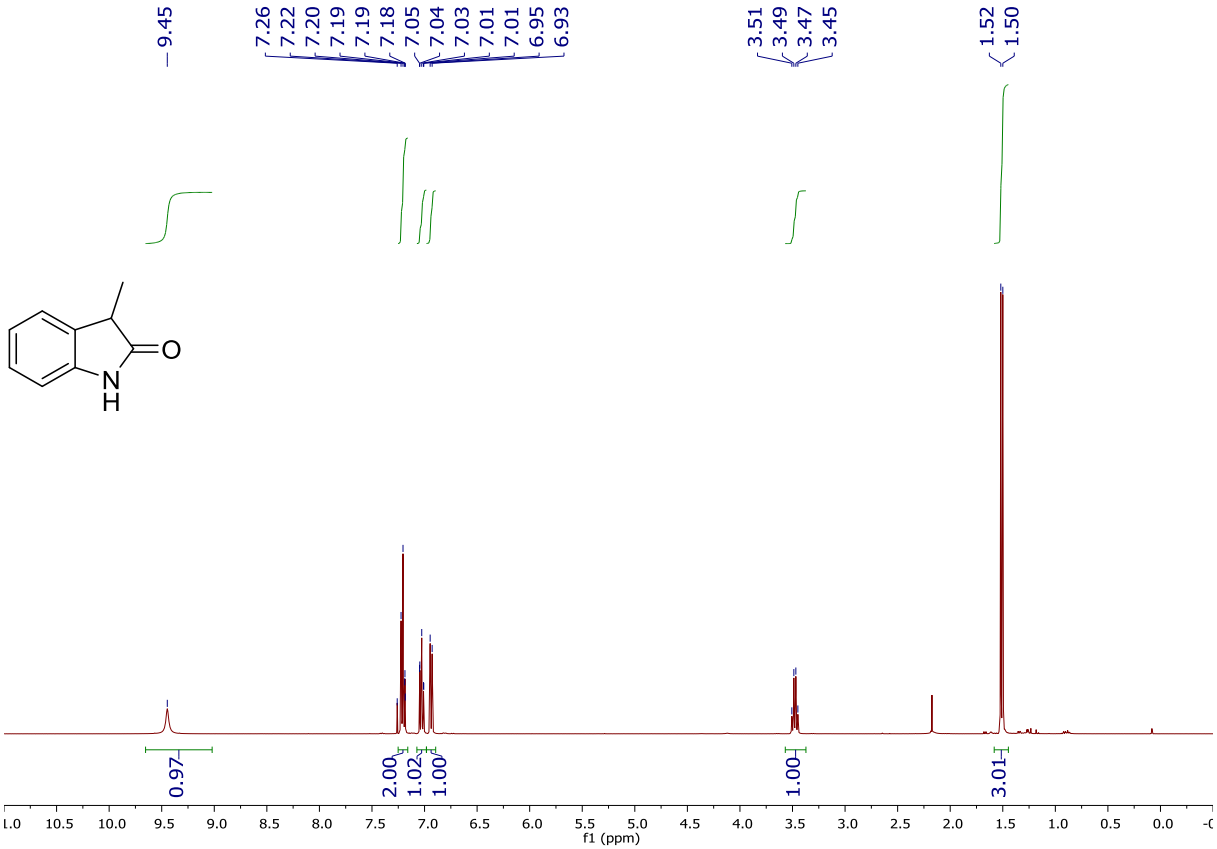


Figure S57: ^{1}H NMR spectrum of the compound **b28** in $CDCl_3$ recorded at 400.1 MHz.

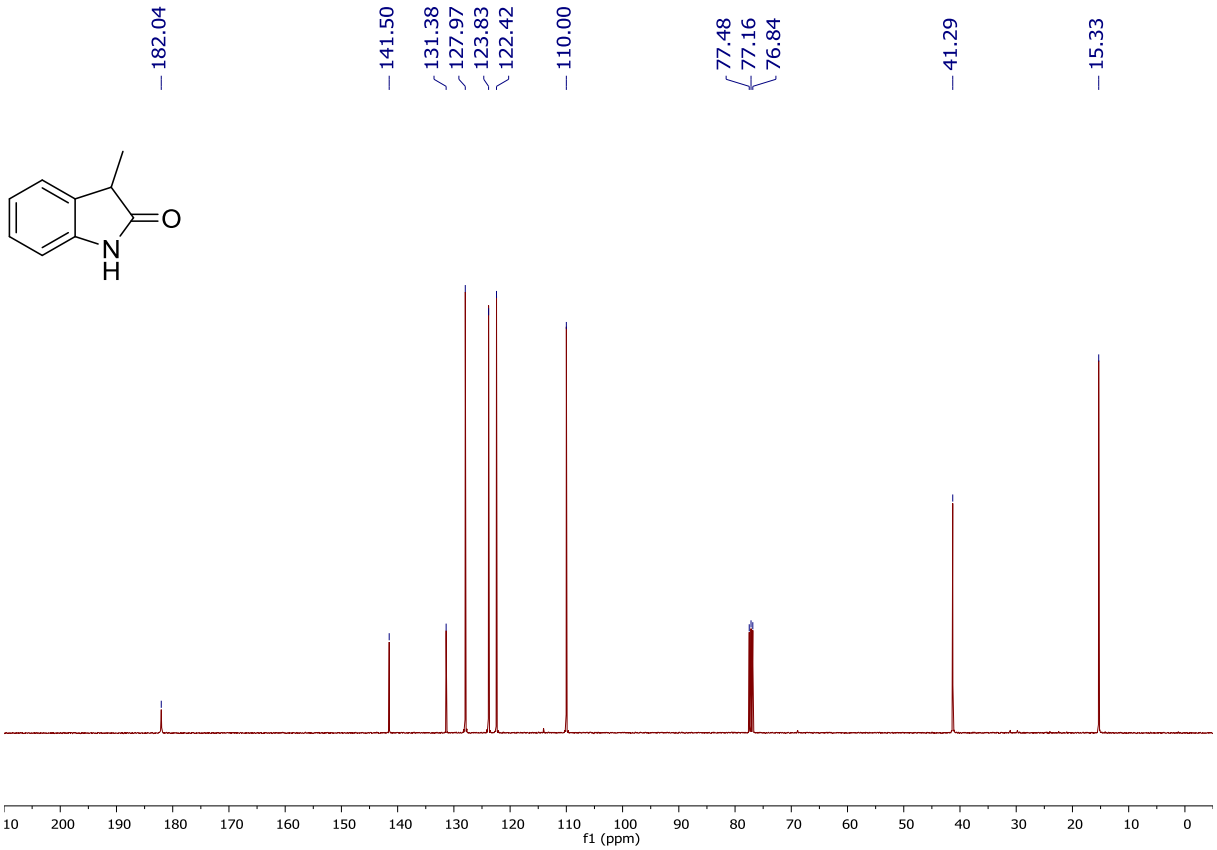


Figure S58: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **b28** in $CDCl_3$ recorded at 101.6 MHz.

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