Manganese Catalyzed $\alpha$-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<sub>254</sub> 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.

<sup>1</sup>H, and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 298 K, on Bruker, AVANCE 400 spectrometer at 400.1 and 100.6 MHz, respectively. <sup>1</sup>H and <sup>13</sup>C NMR spectra were calibrated against the residual solvent signal at the corresponding central peak (<sup>1</sup>H: CDCl<sub>3</sub> 7.26 ppm; <sup>13</sup>C: CDCl<sub>3</sub> 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<sup>TM</sup>-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 a<sub>16-a21</sub> were synthesized according to literature procedure.<sup>1</sup>

Manganese complex 5 was synthesized according to literature procedure. <sup>2</sup>

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 <sup>1</sup>H NMR of the crude mixture and confirmed with GC/GC-Mass analysis. The crude residue was purified by column chromatography (SiO<sub>2</sub>, 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

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

According to general procedure, 1-tetralone a3 (67 µl, 0.5 mmol) gave the title compound b3 as a colorless oil (30 mg, 38%).
\[ ^1H\text{ NMR (300.1 MHz, Chloroform-d)} \delta 8.00 (d, J = 7.8 \text{ Hz, } 1H), 7.42 (t, J = 7.2 \text{ Hz, } 1H), 7.33 - 7.10 (m, 2H), 3.01-2.94 (m, 2H), 2.62-2.49 (m, 1H), 2.16 (dq, J = 13.2, 4.4 \text{ Hz, } 1H), 2.00 - 1.67 (m, 1H), 1.24 (d, J = 6.7 \text{ Hz, } 3H). \]

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

3-methyl-2,3-dihydropenanthen-4(1H)-one \(b_4\)

According to general procedure, 2,3-dihydropenanthen-4(1H)-one \(a_4\) (98 mg, 0.5 mmol) gave the title compound \(b_4\) as an ivory solid (83 mg, 79%).

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

\[ ^{13}C\{^1H\} \text{ NMR (75.5 MHz, Chloroform-d)} \delta 203.4, 145.9, 133.8, 132.8, 131.4, 128.6, 128.3, 127.0, 126.6, 125.8, 125.0, 124.1, 43.9, 31.3, 30.4, 16.0. \]

2-Methyl-1-indanone \(b_5\)

According to general procedure, 1-indanone \(a_5\) (66 mg, 0.5 mmol) gave the title compound \(b_5\) as a colorless oil (34 mg, 46%).

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

\[ ^{13}C\{^1H\} \text{ NMR (75.5 MHz, Chloroform-d)} \delta 209.5, 153.6, 136.5, 134.8, 127.4, 126.6, 124.1, 42.1, 35.1, 16.4. \]

2-Benzylidene-6-methylcyclohexanone \(b_6\)

According to general procedure, 2-benzylidenecyclohexanone \(a_6\) (93 mg, 0.5 mmol) gave the title compound \(b_6\) as a white solid (51 mg, 51%).

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

\[ ^{13}C\{^1H\} \text{ NMR (101.6 MHz, Chloroform-d)} \delta 204.9, 137.5, 136.0, 134.8, 130.2, 128.41, 128.41, 44.5, 32.1, 29.4, 23.1, 16.5. \]
2-Methyl-1-{2',4',6'-trimethylphenyl}-1-propanone b7

![Structure of 2-Methyl-1-(2',4',6'-trimethylphenyl)-1-propanone b7](image)

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-$d$) $\delta$ 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-$d$) $\delta$ 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

![Structure of 2-Methyl-1-(2'-Methylphenyl)-1-propanone b8](image)

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-$d$) $\delta$ 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-$d$) $\delta$ 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

![Structure of 1-{4'-Chlorophenyl}-2-methyl-1-propanone b9](image)

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-$d$) $\delta$ 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-$d$) $\delta$ 203.3, 139.3, 134.6, 129.9, 129.1, 35.6, 19.2.
1-(2'-Aminophenyl)-2-methyl-propan-1-one b10

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) $\delta$ 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) $\delta$ 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) $\delta$ 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

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) $\delta$ 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) $\delta$ 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
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) $\delta$ 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) $\delta$ 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

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) $\delta$ 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) $\delta$ 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) $\delta$ 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) $\delta$ 196.7, 142.4, 139.4, 131.1, 127.6, 36.6, 19.5.

4-tertbutyl-2,6-dimethylcyclohexanone b15

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) $\delta$ 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) $\delta$ 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

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) $\delta$ 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) $\delta$ 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) $\delta$ 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) $\delta$ 196.7, 142.4, 139.4, 131.1, 127.6, 36.6, 19.5.

4-tertbutyl-2,6-dimethylcyclohexanone b15
According to general procedure, 4-(tert-butyl)cyclohexanone \textbf{a15} (77 mg, 0.5 mmol) gave the title compound \textbf{b15} as a colorless liquid (21 mg, 23%).

\(^1\)H NMR (400.1 MHz, Chloroform-d) \(\delta\) 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) \(\delta\) 215.1, 47.1, 44.5, 38.3, 32.5, 27.8, 14.9

2-Methyl-1,3-diphenylpropan-1-one \textbf{b16} \(^5\)

\[\text{\includegraphics{2-Methyl-1,3-diphenylpropan-1-one.png}}\]

According to general procedure, 3-phenylpropioophenone \textbf{a16} (105 mg, 0.5 mmol) gave the title compound \textbf{b16} as a colorless oil (90 mg, 80%).

\(^1\)H NMR (400.1 MHz, Chloroform-d) \(\delta\) 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) \(\delta\) 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 \textbf{b17}

\[\text{\includegraphics{1-Mesityl-3-(4-methoxyphenyl)-2-methylpropan-1-one.png}}\]

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

\(^1\)H NMR (400.1 MHz, Chloroform-d) \(\delta\) 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) \(\delta\) 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\(^+\)] = 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 \textbf{b18}

\[\text{\includegraphics{3-(4-(Benzyloxy)phenyl)-2-methyl-1-(4-methylphenyl)propan-1-one.png}}\]

According to general procedure, 3-(4-(benzyloxy)phenyl)-1-(p-tolyl)propan-1-one \textbf{a18} (165 mg, 0.5 mmol) gave the title compound \textbf{b18} as a white solid (148 mg, 86%).
**1-H NMR (400.1 MHz, Chloroform-\textit{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).

**13C (\textit{1}H) NMR (101.6 MHz, Chloroform-\textit{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\textsubscript{4})** m/z th for C\textsubscript{24}H\textsubscript{24}O\textsubscript{2} [M\textsuperscript{+}]= 344.1776 measured m/z = 344.1767 (3 ppm); m/z th for C\textsubscript{24}H\textsubscript{25}O\textsubscript{2} [MH\textsuperscript{+}]= 345.1855 measured m/z = 345.1848 (2 ppm)

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

![Mesityl-2-methyl-3-(pyridin-2-yl)propan-1-one](image)

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-\textit{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).

**13C (\textit{1}H) NMR (101.6 MHz, Chloroform-\textit{d})** δ 212.9, 160.0, 149.4, 138.5, 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\textsubscript{4})** m/z th for C\textsubscript{18}H\textsubscript{22}NO [MH\textsuperscript{+}]= 268.1701 measured m/z = 268.1692 (3 ppm)

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

![3-(2-Bromophenyl)-2-methyl-1-(4-methyl)propan-1-one](image)

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-\textit{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 (ddd, \( J = 13.6, 7.5 \) Hz, 1H), 2.39 (s, 3H), 1.20 (d, \( J = 7.0 \) Hz, 3H).

**13C (\textit{1}H) NMR (101.6 MHz, Chloroform-\textit{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\textsubscript{4})** m/z th for C\textsubscript{17}H\textsubscript{18}OBr [MH\textsuperscript{+}]= 317.0541 measured m/z = 317.0538 (1 ppm)

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

![3-(2-Iodophenyl)-2-methyl-1-(3-methylphenyl)propan-1-one](image)
According to general procedure, 3-(2-iodophenyl)-1-(m-tolyl)propan-1-one \textbf{a21} (87 mg, 0.25 mmol) gave the title compound \textbf{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-$d$) $\delta$ 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 MHz, Chloroform-$d$) $\delta$ 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 [M$^+$]$^+$ = 365.0402 measured m/z = 365.0410 (2 ppm)

\section*{2-(Methyl-$d_3$)-2-$d$-1,3-diphenylpropan-1-one \textbf{b22}}

According to general procedure using CD$_3$OD instead of MeOH, 3-phenylpropiophenone \textbf{a16} (105 mg, 0.5 mmol) gave the title compound \textbf{b22} as a colorless oil (93 mg, 82%).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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-$d$) $\delta$ 203.8, 142.0, 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 CH(CD$_3$)).

HRMS (DCI-CH$_4$) m/z th for C$_{16}$H$_{12}$D$_4$O [M$^+$]$^+$ = 228.1452 measured m/z = 228.1454 (1 ppm); m/z th for C$_{16}$H$_{12}$D$_4$O [M$^+$]$^+$ = 229.1530 measured m/z = 229.1525 (2 ppm)

\section*{Methyl 2-phenylpropanoate \textbf{b23}}
According to general procedure, methyl 2-phenylacetate \textbf{a23} (88 µl, 0.5 mmol) gave the title compound \textbf{b23} (95% conversion).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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 \textbf{b24}**

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

$^1$H NMR (300.1 MHz, Chloroform-$d$) $\delta$ 8.09 (d, $J = 8.3$ 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-$d$) $\delta$ 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 \textbf{b25}**

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

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 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-$d$) $\delta$ 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 \textbf{b26}**

According to general procedure, methyl 2-phenylacetate \textbf{a23} (88 µl, 0.5 mmol) gave the title compound \textbf{b23} (95% conversion).
According to general procedure, methyl 2-(4-bromophenyl)acetate \(a_26\) (114 mg, 0.5 mmol) gave the title compound \(b_{26}\) as a colorless oil (43 mg, 35%).

\(^1\)H NMR (300.1 MHz, Chloroform-\(d\)) \(\delta\) 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-\(d\)) \(\delta\) 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 \(b_{27}\)

According to general procedure using CD\(_3\)OD, methyl 2-(naphthalen-2-yl)acetate \(a\) \(25\) (88 µl, 0.5 mmol) gave the title compound \(b_{27}\) as a colorless oil (22 mg, 20%).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.87 – 7.77 (m, 3H), 7.79 – 7.74 (m, 1H), 7.48 – 7.33 (m, 3H).

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

HRMS (DCI-CH\(_4\)) m/z th for C\(_{14}\)H\(_7\)D\(_7\)O\(_2\) [\(\text{M}^+\)] = 221.1433 measured m/z = 221.1419 (2 ppm); m/z th for C\(_{14}\)H\(_8\)D\(_7\)O\(_2\) [\(\text{MH}^+\)] = 222.1506 measured m/z = 222.1499 (3 ppm)

2,4-Dimethyl-1,5-diphenylpropan-1,5-dione \(c_1\)

According to an alternative procedure, an Ace\(^\circ\) pressure tube was charged with propiophenone \(a\) \(1\) (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 \(c_1\), obtained as a mixture of two diastereoisomers, as a colorless oil (44 mg, 63%).

\(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 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-\(d\)) \(\delta\) 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\(_2\) [\(\text{MH}^+\)] = 281.1542 measured m/z = 281.1533 (3 ppm)

2,2'-Methyleneditetralone \(c_3\)
According to an alternative procedure, an Ace® pressure tube was charged with 1-tetralone \textbf{a3} (268 µl, 2 mmol), MeOH (1mL), toluene (1mL), Mn-complex \textbf{5} (1.5 mol%, 16 mg) and, NaOH (1 equiv., 80mg), in that order. The same work up gave the title compound \textbf{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) $\delta$ 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) $\delta$ 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 b$_{28}$

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

$^1$H NMR (400.1 MHz, Chloroform-d) $\delta$ 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) $\delta$ 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]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (mol%)</th>
<th>CH₃OH (mL)</th>
<th>Toluene (mL)</th>
<th>Temp. (°C)</th>
<th>Conv. (%)</th>
<th>Nmr yield [b] b. (isol yield)</th>
<th>Nmr yield [b] c. (isol yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>tBuONa (50)</td>
<td>2</td>
<td>4</td>
<td>120</td>
<td>99</td>
<td>87(64)</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>tBuOK (50)</td>
<td>2</td>
<td>4</td>
<td>120</td>
<td>99</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>KHMDS (50)</td>
<td>2</td>
<td>4</td>
<td>120</td>
<td>99</td>
<td>77</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>K₃PO₄ (50)</td>
<td>2</td>
<td>4</td>
<td>120</td>
<td>99</td>
<td>82</td>
<td>18</td>
</tr>
</tbody>
</table>

[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 ³¹H NMR spectroscopy, and compared with GC/MS, on the crude mixture.
Table S2: Competitive experiments for the α-methylation of propiophenone a1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Competing Substrate</th>
<th>Conversion a1</th>
<th>Yield b1/c1</th>
<th>Recovery of competing substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>99 %</td>
<td>87/13</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>F</td>
<td>&gt; 98%</td>
<td>86/14</td>
<td>n.d. [b]</td>
</tr>
<tr>
<td>3</td>
<td>CF₃</td>
<td>&gt; 98%</td>
<td>86/14</td>
<td>n.d. [b]</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>&gt; 98%</td>
<td>84/16</td>
<td>n.d. [b]</td>
</tr>
<tr>
<td>5</td>
<td>NO₂</td>
<td>95%</td>
<td>84/16</td>
<td>c.a. 95% [c]</td>
</tr>
<tr>
<td>6</td>
<td>NH₂</td>
<td>95%</td>
<td>66/34</td>
<td>c.a. 90%</td>
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<tr>
<td>7</td>
<td></td>
<td>&gt; 95%</td>
<td>70/30</td>
<td>65% [d]</td>
</tr>
<tr>
<td>8</td>
<td>CN</td>
<td>95%</td>
<td>85/15</td>
<td>0% [e]</td>
</tr>
</tbody>
</table>

Reaction conditions: in a glovebox, an Ace® pressure tube was charged with propiophenone a1 (0.5 mmol, 66 µL), competing 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 1H NMR spectroscopy on the crude mixture. [b] Competing 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 competing product (c.a. 35%). [e] 4-methylbenzonitrile was hydrolysed to 4-methylbenzamide.
Figure S1: $^{1}$H NMR spectrum of the compound $b{1}$ in CDCl$_3$ recorded at 400.1 MHz.

Figure S2: $^{13}$C{$^{1}$H} NMR spectrum of the compound $b{1}$ in CDCl$_3$ recorded at 75.5 MHz.

Figure S3: $^{1}$H NMR spectrum of the compound $b{1}$ in CDCl$_3$ recorded at 400.1 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.

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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 $b_{18}$ in CDCl$_3$ recorded at 101.6 MHz.

Figure S36: $^1$H NMR spectrum of the compound $b_{19}$ 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 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 CDCl₃ recorded at 400.1 MHz.

Figure S58: $^{13}$C($^1$H) NMR spectrum of the compound b28 in CDCl₃ recorded at 101.6 MHz.
References