Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Practical Three-Component Synthesis of Crowded Arenes with Donor-Acceptor Substitution

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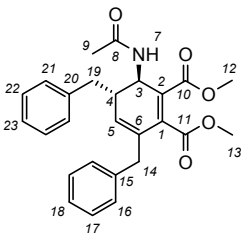
Electronic Supporting Information

General procedure for preparative one-pot syntheses of cyclohexadienes starting from saturated aldehydes:

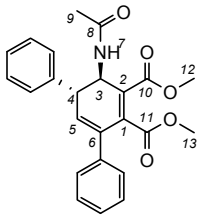
Carboxamide (1 equiv.), aldehyde (2 equiv.), dimethyl acetylenedicarboxylate (1 equiv.), acetic anhydride (1 equiv.), *p*-toluenesulfonic acid monohydrate (3 mol%) and toluene (0.8-1.8 mL/mmol amide) were combined in a reaction tube. The tube was sealed with a septum and the reaction stirred at elevated temperature (110 °C). After 24 h, the solvent and other volatile compounds were removed by oil pump vacuum. For work-up, see the paragraph pertinent to the respective product. (The atom numbering in the chemical structures refer to NMR assignments only.)

Dimethyl 6-acetylamino-3,5-dibenzylcyclohexa-1,3-dien-1,2-dicarboxylate (3)



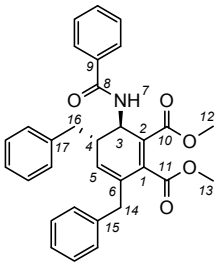
Batch size: 0.78 g (13.2 mmol) acetamide, 3.54 g **(**26.4 mmol) 3-phenylpropionaldehyde, 1.88 g (13.2 mmol) dimethyl acetylene-dicarboxylate and 1.34 g (13.2 mmol) acetic anhydride in 18 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 2:1, R_f = 0.37), white solid; **Yield**: 66%, **mp** 149-151 °C, **IR** (ATR) 1/λ [cm^{-1}] = 3385 (w), 2948 (w), 2354 (w), 1721 (s), 1680 (s), 1490 (m), 1432 (m), 1367 (w), 1259 (s), 1065 (w), 1031 (w); **LR MS** (positive ESI, Methanol/ CH_2Cl_2), m/z = 456 $[M+Na]^+$, 343, 307, 253, 245, 132; **HR MS** (ESI, [u]) found: 456.179 $[M+Na]^+$, calcd: 456.1787; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ =7.37 - 7.22 (m, 7 H, H-Arom., H-7), 7.15-7.07 (m, 4 H, H-Arom.), 5.40 (d, 1 H, ^3J = 4.6 Hz, H-5), 5.15 (dd, 1 H, ^3J = 3.6/9.9 Hz, H-3), 3.87 and 3.69 (2s, 6 H, H-12, H-13), 3.52 (m, 1 H, H-5), 3.22-3.15 (m, 2 H, H-14), 2.89 (d, 1 H, ^3J = 9.79 Hz, H-19), 2.78 (dd, 1 H, ^2J = 13.2 Hz, ^3J = 4.3 Hz, H-19'), 1.57 (s, 3 H, H-9); **^{13}C-NMR** (150 MHz, APT, $CDCl_3$), δ = 169.1 (C-8), 168.3 and 166.8 (C-10, C-11), 138.5 (C-2), 137.4 and 136.9 (C-15, C-20) 134.6 (C-1), 131.7, 129.5, 128.5, 127.7 127.0, 126.5, 125,8 (all C-H_{Arom}, C-5), 52.7 and 52.6 (C-12, C-13), 45.8 (C-4), 39.7 (C-3), 39.5 (C-14), 38.2 (C-19), 22.5 (C-9)

Dimethyl 6-acetylamino-3,5-diphenylcyclohexa-1,3-dien-1,2-dicarboxylate (5)



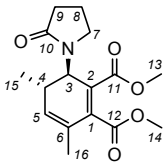
Batch size: 0.19 g (3.3 mmol) acetamide, 0.79 g (6.6 mmol) phenylacetaldehyde, 0.79 g (3.3 mmol) dimethyl acetylenedicarboxylate and 0.34 g (3.3 mmol) acetic anhydride in 6 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.20), white solid; **Yield**: 49% ; **mp** 88 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3358 (m), 3262 (m), 3023 (m), 2948 (m), 2245 (w), 1724 (s), 1649 (s), 1520 (s), 1433 (s), 1256 (s), 1194 (m), 1164 (m), 1068 (m), 1035 (m), 910 (m), 729 (s), 697 (s); **LR MS** (positive ESI, Methanol, CH_2Cl_2), m/z = 428 $[M+Na]^+$, 315, 303, 271, 244, 229; **HR MS** (ESI, [u]) found: 428.147 $[M+Na]^+$, calcd: 428.1474; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.27-7.22 (m, 10 H, H-Arom.), 6.26 (d, 1 H, ^3J = 4.6 Hz, H-5), 6.19 (dd, 1 H, ^3J = 9.7/3.9 Hz, H-3), 5.38 (d, 1 H, ^3J = 9.7 Hz, H-7), 4.61 (m, 1 H, H-4), 3.82 and 3.60 (2s, 6 H, H-12, H-13), 1.67 (s, 3 H, H-9); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 169.6 (C-8), 167.8 and 166.1 (C-10, C-11), 140.0 (C-1), 137.0, 136.9, 133.3, 133.0 (C-2, C-6, 2 C_q), 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.2, 127.6, 127.5, 126.1 (10 C-$H_{Arom.}$, C-5), 53.1 and 52.4 (C-12, C-13), 45.1 (C-3), 43.9 (C-4), 23.2 (C-9)

Dimethyl 6-benzoylamino-3,5-dibenzylcyclohexa-1,3-dien-1,2-dicarboxylate (6)



Batch size: 0.40 g (3.3 mmol) benzamide, 0.88 g **(**6.6 mmol) 3-phenylpropionaldehyde, 0.79 g (3.3 mmol) dimethyl acetylenedicarboxylate and 0.34 g (3.3 mmol) acetic anhydride in 6 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.43), white solid; **Yield**: 63% ; **mp** 121 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3386 (w), 3020 (w), 2946 (w), 2360 (w), 2253 (w), 1719 (s), 1660 (s), 1477 (s), 1432 (s), 1316 (m), 1256 (s), 1133 (m), 1067 (m), 1027 (m), 906 (m), 698 (s); **LR MS** (positive ESI, Methanol, Ethyl acetate), m/z = 518 $[M+Na]^+$, 307, 91; **HR MS** (ESI, [u]) found: 518.194 $[M+Na]^+$, calcd: 518.1943; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.50 - 7.18 (m, 12 H, H-Arom.), 7.08 (m, 3 H, H-Arom.), 5.45 (dd, 1 H, ^3J = 9.7/4.2 Hz, H-3), 5.44 (d, 1 H, ^3J = 4.3 Hz, H-5), 4.00 (d, 1 H, ^3J = 9.7 Hz, H-7), 3.89 and 3.68 (2s, 6 H, H-12, H-13), 3.59 (m, 1 H, H-4), 3.26 (s, 2 H, H-14), 3.18 and 2.12 (2dd, 2 H, ^1J = 13.6 Hz, ^3J = 4.4 Hz, H-16); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 167.8 and 167.6 (C-10 and C-11), 166.8 (C-8), 138.5, 138.4, 136.9, 136.7, 134.5, 134.3 (C-1, C-2, C-6, C-9, C-15, C-17), 131.5, 131.2, 129.6, 128.7, 128.5, 128.2, 127.8, 127.5, 127.2, 126.5, 126.1 (all C-$H_{Arom.}$, C-5), 52.7 and 52.6 (C-12, C-13), 46.5 (C-3), 39.6 (C-4), 39.5 (C-16), 38.3 (C-14)

Dimethyl 3,5-dimethyl-6-(2-oxo-pyrrolidin-1-yl)-cyclohexa-1,3-dien-1,2-dicarboxylate (8)



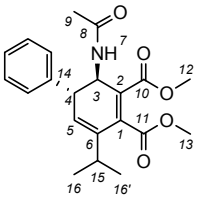
Batch size: 0.28 g (3.3 mmol) 2-pyrrolidinone, 0.38 g **(**6.6 mmol) propionaldehyde, 0.79 g (3.3 mmol) dimethyl acetylenedicarboxylate and 0.34 g (3.3 mmol) acetic anhydride in 6 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 2:1, R_f = 0.31), colorless oil; **Yield**: 59% ; **IR** (ATR) 1/λ [cm^{-1}] = 3613 (w), 3453 (w), 2950 (m), 1720, (s), 1683 (s), 1430 (s), 1412 (s), 1253 (s), 1193 (s), 1156 (s), 1052 (m), 1023 (m), 985 (m), 939 (w), 757 (w); **LR MS** (DIP EI, ethyl acetate), m/z = 307 $[M]^+$, 292 $[M-CH_3]^+$, 277 $[M-2CH_3]^+$, 260, 228, 216, 191, 177, 133, 105; **HR MS** (EI, [u]) found: 307.141 $[M]^+$, calcd: 307.1419; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 5.63 (m, 1 H, H-5), 5.36 (d, 1 H, ^3J = 5.30 Hz, H-3), 3.74 and 3.72 (2s, 6 H, H-13, H-14), 3.19 (m, 2 H, H-7), 3.03 (td, 1 H, ^3J = 9.2/5.4 Hz, H-4), 2.38 (t, 2 H, ^3J = 8.1 Hz, H-9), 1.99 (m, 2 H, H-8), 1.59 (s, 3 H, H-16), 1.15 (d, 3 H, ^3J = 7.1 Hz, H-15); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 175.3 (C-10), 167.3 and 167.0 (C-11, C-12), 140.1 (C-6), 131.8 (C-1), 129.3 (C-5), 127.5 (C-2), 52.5 and 52.4 (C-13, C-14), 50.0 (C-3), 42.6 (C-7), 32.5 (C-4), 31.2 (C-9), 20.3 (C-15), 19.5 (C-16), 17.9 (C-8)

General procedure for preparative one-pot syntheses of cyclohexadienes starting from *α,β*-unsaturated aldehydes:

Carboxamide (4 mmol, 1 equiv.), aldehyde (4 mmol, 1 equiv.), dimethyl acetylenedicarboxylate (8 mmol, 2 equiv.), *p*-toluenesulfonic acid monohydrate (3 mol%) and toluene (10 mL) were combined in a reaction tube. The tube was sealed with a septum and the reaction stirred at elevated temperature (110 °C). After 24 h, the solvent and other volatile compounds were removed by oil

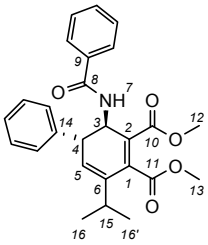
pump vacuum. For work-up, see the paragraph pertinent to the respective product.**Error! Bookmark not defined.**

Dimethyl 6-acetylamino-3-isopropyl-5-phenylcyclohexa-1,3-dien-1,2-dicarboxylate (9)



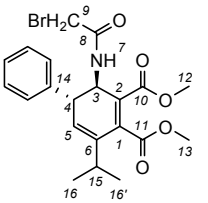
Work-up: crude product was purified by column chromatography (ethyl acetate, R_f = 0.38), white solid; **Yield**: 88% ; **mp** 94°C ; **IR** (ATR) 1/λ [cm^{-1}] = 3366 (w), 3286 (w), 2953 (m), 1721 (s), 1658 (s), 1596 (s), 1433 (s), 1366 (m), 1259 (s), 1230 (s), 1193 (m), 1166 (m), 1066 (s), 1026 (m), 966 (m), 913 (m), 753 (m), 726 (s), 695 (s); **LR MS** (positive ESI, Methanol, $CHCl_3$), m/z = 394 $[M+Na]^+$, 281, 239; **HR MS** (ESI, [u]) found: 394.163 $[M+Na]^+$, calcd: 394.1631; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.38 (m, 2 H, H-Arom.), 7.27 (m, 3 H, H-Arom.), 6.16 (d, 1 H, ^3J = 4.55 Hz, H-5), 6.06 (dd, 1 H, ^3J = 9.9/4.82 Hz, H-3), 5.06 (d, 1 H, ^3J = 9.9 Hz, H-7), 3.73 and 3.72 (2s, 6 H, H-12, H-13), 3.37 (m, 1 H, H-4), 2.12 (m, 1 H, H-15), 1.76 (s, 3 H, H-9), 1.11 and 0.79 (2 d, ^3J = 6.76 Hz, H-16, H-16'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 169.0 (C-8), 167.5 and 167.4 (C-10, C-11), 137.6, 137.6, 136.7, 134.8 (C-1, C-2, C-6, C-14), 128.7, 128.6, 128.3, 128.2, 126,1, 124.9 (C-5, 5 C-$H_{Arom.}$), 52.7 and 52.6 (C-12, C-13), 44.9 (C-3), 43.8 (C-4), 30.2 (C-15), 23.3 (C-9), 21.2 and 17.7 (C-16, C-16')

Dimethyl 6-(benzoylamino)-3-isopropyl-5-phenylcyclohexa-1,3-dien-1,2-dicarboxylate (11)



Work-up: crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:2, R_f = 0.30), yellow solid; **Yield**: 87% ; **mp** 71°C ; **IR** (ATR) 1/λ [cm^{-1}] = 3346 (w), 2952 (w), 1721 (s), 1662 (s), 1610 (w), 1503 (s), 1478 (s), 1430 (m), 1380 (w), 1313 (m), 1261 (s), 1166 (m), 1071 (m), 1020 (w), 911 (w), 693 (s); **LR MS** (positive ESI, MeOH/$CHCl_3$), m/z = 456 $[M+Na]^+$, 440, 271, 239; **HR MS** (ESI, [u]) found: 456.179 $[M+Na]^+$, calcd: 456,1787; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.55 (m, 4 H, H-Arom.), 7.53-7.25 (m, 5 H, H-Arom.), 6.35 (dd, 1 H, ^3J = 9.8/4.7 Hz, H-3), 6.29 (d, 1 H, ^3J = 4.8 Hz, H-5), 5.80 (d, 1 H, ^3J = 9.84 Hz, H-7), 3.82 and 3.77 (2s, 6 H, H-12, H-13), 3.50 (q*, 1 H, ^3J = 4.7 Hz, H-4), 2.24 (m, 1 H, H-15), 1.20 and 0.93 (2 d, ^3J = 6.8 Hz, H-16, H-16'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 167.6 and 167.5 (C-10, C-11), 166.7 (C-8), 138.1, 137.6, 136.9, 134.6 (C_q), 131.6, 128.7, 128.6, 128,2, 126.8, 126.1, 125.0 (all C-$H_{Arom.}$, C_5), 52.7 and 52.6 (C-12, C-13), 45.3 (C-3), 44.1 (C-4), 30.1 (C-15), 21.2 and 17.7 (C-16, C-16')

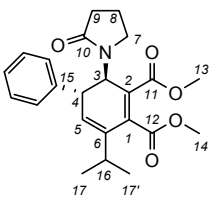
Dimethyl 6-(2-bromoacetylamino)-3-isopropyl-5-phenylcyclohexa-1,3-dien-1,2-dicarboxylate (12)



Work-up: crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:5, R_f = 0.16), yellow oil; **Yield**: 66% ; **IR** (ATR) 1/λ [cm^{-1}] = 3360 (w), 3026 (w), 2946 (m), 1720 (s), 1672 (s), 1503 (s), 1433 (s), 1262 (s), 1196 (m), 1166 (m), 1067 (m), 960 (w), 911 (m), 728 (s); **LR MS** (EI, ethyl acetate), m/z = 313 [M-$CBrH_2CONH$], 297 [M-$CBrH_2CONH$-CH_3], 281 [M-$CBrH_2CONH$-2CH_3], 265, 249, 222, 207, 193, 178, 165, 152; **HR MS** (ESI, [u]) found: 472.074 $[M+Na]^+$, calcd: 472.736; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.46 (m, 2 H, H-Arom.), 7.30 (m, 3 H, H-Arom.), 6.29 (m, 2 H, H-5, H-7), 6.06 (dd, 1 H, ^3J = 10.0/4.4 Hz, H-3), 3.83 and 3.79 (2 s, 6 H, H-12, H-13), 3.73 (m, 2 H, H-9),

3.44 (q*, 1 H, ^{3}J = 4.3 Hz, H-4), 2.22 (m, 1 H, H-15), 1.19 and 0.91 (2 d, 6 H, ^{3}J = 6.8 Hz, H-15, H-15'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 167.9 and 166.6 (C-10, C-11), 164.3 (C-8), 140.8, 137.5, 136.9, 132.3 (C-1, C-2, C-6, C-14), 128.7, 128.4, 128.3, 126.3, 125.3 (C-5, C-$H_{Arom.}$), 52.8 and 52.7 (C-12, C-13), 45.5 (C-3), 44.6 (C-4), 30.0 (C-15), 29.2 (C-9), 21.2 and 17.6 (C-16, C-16')

Dimethyl 3-isopropyl-6-(2-oxopyrrolidin-1-yl)-5-phenylcyclohexa-1,3-dien-1,2-dicarboxylate (13)

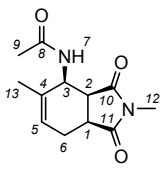


Work-up: crude product was purified by column chromatography (ethyl acetate/cyclohexane 2:1, R_f = 0.29), yellow solid; **Yield:** 89% ; **mp** 136°C ; **IR** (ATR) 1/λ [cm^{-1}] = 2953 (w), 2866 (w), 1724 (s), 1684 (s), 1430 (m), 1413 (m), 1256 (s), 1226 (s), 1195 (m), 1164 (m), 1069 (m), 984 (w), 916 (w), 797 (w), 738 (m), 696 (m); **LR MS** (positiv ESI, MeOH/$CHCl_3$), m/z = 420 $[M+Na]^+$, 398, 281, 271; **HR MS** (ESI, [u]) found: 420.178 $[M+Na]^+$, calcd: 420.1787; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.38 (m, 2 H, H-Arom.), 7.28 (m, 3 H, H-Arom.), 6.20 (m, 2 H, H-3, H-5), 3.80 and 3.76 (2s, 6 H, H-13, H-14), 3.43 (q*, 1 H, ^{3}J = 3.7 Hz, H-4), 3.28 and 2.91 (2 m, 2 H, H-7), 2.25-2.03 (m, 3 H, H-9, H-16), 1.83 and 1.59 (2 m, 2 H, H-8), 1.19 and 0.88 (2 d, ^{3}J = 6.9 Hz, H-17, H-17'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 175.1 (C-10), 167.4, 167.3 (C-11, C-12), 138.1, 138.0, 135.4, 133.7 (all C_q), 128.6, 128.2, 126.1 (C_5, C-$H_{Arom.}$), 52.7 and 52.5 (C-13, C-14), 47.7 (C-3), 43.5 (C-7), 43.2 (C-4), 31.1 (C-16), 30.7 (C-9), 21.3 and 18.2 (C-17, C-17'), 17.9 (C-8)

General procedure for preparative one-pot syntheses of cyclohexenes starting from *α,β*-unsaturated or saturated aldehydes:

Carboxamide (1 equiv.), saturated aldehyde (2 equiv.) or *α,β*-unsaturated aldehyde (1 equiv.), dienophile (1-3 equiv.), acetic anhydride (1 equiv., only for saturated aldehydes), *p*-toluenesulfonic acid monohydrate (3 mol%) and toluene (1.0-2.5 mL/mmol amide) were combined in a reaction tube. The tube was sealed with a septum and the reaction stirred at elevated temperature (110 °C). After 24-40 h, the solvent and other volatile compounds were removed by oil pump vacuum. For work-up, see the paragraph pertinent to the respective product.**Error! Bookmark not defined.**

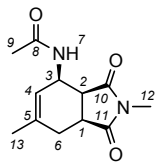
***N*-(2,5-dimethyl-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl)-acetamide (19)**



Batch size: 0.89 g (15 mmol) acetamide, 1.26 g (15 mmol) *trans*-2-methyl-2-butenal and 1.6 g (15 mmol) *N*-Methylmaleimide in 35 mL toluene were employed; **Work-up:** crude product was suspended in diethyl ether, filtration gave the desired product as a white solid; **Yield:** 76% ; **R_f:** 0.19 (ethyl acetate) ; **mp** 115 °C ; **IR** (ATR) 1/λ [cm-1] = 3386 (w), 2940 (w), 1770 (w), 1685 (s), 1513, 1433 (m), 1380 (m), 1323 (m), 1283 (m), 1123 (m), 1023 (m), 916 (w), 786 (w), 726 (w); **LR MS** (EI, ethyl acetate), m/z = 236 $[M]^+$, 218, 193 $[M-CH_3CO]^+$, 179 $[M-CH_3CONH]^+$, 165, 131, 120, 108; **HR MS** (EI, [u]) found: 236.116 $[M]^+$, calcd: 236.1161; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.35 (d, 1 H, ^{3}J = 8.0 Hz, H-7), 5.56 (m, 1 H, H-5), 4.72 (m, 1 H, H-3), 3.11 (m, 2 H, H-1, H-2), 2.94 (s, 3 H, H-12), 2.58 (dd, 1 H, ^{2}J = 15.3 Hz, ^{3}J = 7.3 Hz, H-6), 2.21 (m, 1 H, H-6'), 2.11 (s, 3 H, H-9), 1.64 (m, 1 H, H-13); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 179.8 and

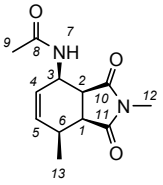
179.6 (C-10, C-11), 170.2 (C-8), 138.8 (C-4), 120.5 (C-5), 47.8 (C-3), 43.3 (C-2), 39.5 (C-1), 25.1 (C-12), 24.4 (C-6), 23.5 (C-9), 18.8 (C-13)

***N*-(2,6-dimethyl-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl)-acetamide (20)**



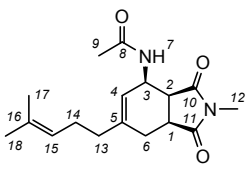
Batch size: 0.89 g (15 mmol) acetamide, 1.26 g (15 mmol) 3-methyl-2-butenal and 1.6 g (15 mmol) *N*-Methylmaleimide in 35 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate, Rf = 0.19), white solid; **Yield:** 76% ; **mp** 124 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3423 (w), 3340 (w), 2946 (w), 1721 (s), 1666 (s), 1503 (s), 1433 (m), 1263 (s), 1163 (m), 1066 (m), 900 (w), 729 (m); **LR MS** (positiv ESI, MeOH/CH_2Cl_2), m/z = 259 $[M+Na]^+$, 199, 126, 60; **HR MS** (ESI, [u]) found: 259.106 $[M+Na]^+$, calcd: 259.1059; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.21 (d, 1 H, ^3J = 7.4 Hz, H-7), 5.34 (m, 1 H, H-4), 4.62 (m, 1 H, H-3), 3.15 (m, 2 H, H-1, H-2), 2.92 (s, 3 H, H-12), 2.51 (d, 1 H, ^2J = 15.3 Hz, H-6), 2.22 (m, 1 H, H-6'), 2.06 (s, 3 H, H-9), 1.67 (s, 3 H, H-13); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 179.3 (C10, C-11), 170.0 (C-8), 136.8 (C-5), 124.8 (C-4), 45.8 (C-3), 42.2 (C-2), 39.0 (C-1), 29.2 (C-6), 25.6 (C-12), 23.5 (C-13), 23.1 (C-9)

***N*-(2,7-Dimethyl-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl)-acetamide (21)**



Batch size: 0.89 g (15 mmol) acetamide, 1.26 g (15 mmol) *trans*-2-pentenal and 1.6 g (15 mmol) *N*-Methylmaleimide in 35 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate, R_f = 0.16), white solid ; **Yield**: 54% ; **mp** 169 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3381 (br, w), 2934 (w), 1767 (m), 1684 (s), 1516 (s), 1432 (s), 1380 (s), 1332 (m), 1285 (s), 2110 (w), 1159 (w), 1103 (m), 1026 (w), 980 (w); **LR MS** (positiv ESI, MeOH), m/z = 259 $[M+Na]^+$, 237, 178; **HR MS** (ESI, [u]) found: 259.106 $[M+Na]^+$, calcd: 259.1059; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.33 (d, 1 H, ^3J = 8.2 Hz, H-7), 5.62 (m 2 H, H-4, H-5), 4.67 (m, 1 H, H-3), 3.18 (dd, 1 H, ^3J = 8.6/6.2 Hz, H-2), 3.05 (d*, ^3J = 7.5 Hz, H-1), 2.91 (s, 3 H, H-12), 2.51 (m, 1 H, H-6), 2.11 (s, 3 H, H-9), 1.40 (d, 3 H, ^3J = 7.4 Hz, H-13); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 179.2 ud 176.8 (C-10, C-11), 170.1 (C-8), 134.2 (C-5), 132.0 (C-4), 45.7 (C-3), 43.7 (C-1, C-2), 30.7 (C-6), 24.8 (C-12), 23.6 (C-9), 16.7 (C-13)

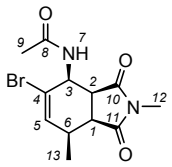
***N*-[2-Methyl-6-(4-methylpent-3-enyl)-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl]-acetamide (23b)**



Batch size: 0.29 g (5 mmol) acetamide, 0.76 g (5 mmol) citral (*cis/trans*-mixture) and 0.56 g (5 mmol) *N*-Methylmaleimide in 10 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:2, R_f = 0.13), colourless oil; **Yield**: 26%; **IR** (ATR) 1/λ [cm^{-1}] = 3383 (br, w), 3293 (br, w), 2921 (w), 1768 (w), 1692 (br, s), 1518 (br, s), 1433 (s), 1381 (s), 1325 (m), 1138 (m), 1105 (m), 1058 (m), 1005 (m); **LR MS** (EI,ethyl acetate), m/z = 304 $[M]^+$, 261 $[M-CH_3CO]^+$, 235, 193, 177, 109, 92, 69; **HR MS** (EI, [u]) found: 304.179 $[M]^+$, calcd: 304.1787; **^{1}H-NMR**

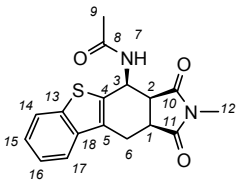
(300 MHz, $CDCl_3$), δ = 7.23 (d, 1 H, ^3J = 8.7 Hz, H-7), 5.33 (m, 1 H, H-4), 4.89 (m, 1 H, H-15), 4.64 (m, 1 H, H-3), 3.15 (m, 2 H, H_1, H-2), 2.98 (s, 3 H, H-12), 2.55 (d, 1 H, ^2J = 15.3 Hz, H-6), 2.23 (m, 1 H, H-6'), 2.05 (s, 3 H, H-9), 1.96-1.84 (m, 4 H, H-13, H-14), 1.62 (s, 3 H, H-18), 1.53 (s, 3 H, H-17); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 179.4 and 179.3 (C-10, C-11), 170.4 (C-8), 140.5 (C-5), 132.3 (C-16), 124.8 (C-4), 123.1 (C-15), 45.8 (C-3), 42.6 and 39.0 (C-1, C-2), 36.6 (C-14), 28.1 (C-6), 25.8 (C-18), 25.7 (C-13), 25.0 (C-12), 23.6 (C-9), 17.8 (C-17)

N-(5-Bromo-2,7-dimethyl-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl)-acetamide (24)



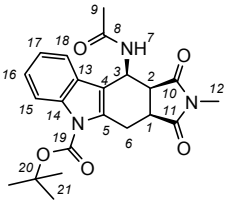
Batch size: 0.07 g (1.2 mmol) acetamide, 0.19 g (1.2 mmol) 2-Bromo-2-pentenal and 0.13 g (1.2 mmol) *N*-Methylmaleimide in 5 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.27), white solid; **Yield**: 70% ; **mp** 181 °C; **IR** (ATR) 1/λ [cm^{-1}] = 3392 (w), 2933 (w), 1769 (w), 1681 (s), 1503 (m), 1433 (m), 1381 (m), 1329 (m), 1287 (m), 1211 (w), 1122 (w), 1030 (w), 925 (w); **LR MS** (EI, ethyl acetate), m/z = 315 $[M]^+$, 271 $[M\text{-}CH_3CO]^+$, 256 $[M\text{-}CH_3CONH]^+$, 235 $[M\text{-}Br]^+$, 186, 161, 124, 107; **elemental analysis** for $C_{12}H_{15}BrN_2O_3$ (%), found: N, 8.79; C, 45.63; H, 4.91; calcd: N, 8.89; C, 45.73; H, 4.80 ; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.36 (d, 1 H, ^3J = 6.4 Hz, H-7), 6.05 (d, 1 H, ^3J = 2.7 Hz, H-5), 4.91 (m, 1 H, H-3), 3.30 (m, 1 H, H-2), 3.06 (t*, 1 H, ^3J = 7.9 Hz, H-1), 2.95 (s, 3 H, H-12), 2.62 (td, 1 H, ^3J = 7.2/3.5 Hz, H-6), 2.15 (s, 3 H, H-9), 1.41 (d, 3 H, ^3J = 7.2 Hz, H-13); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 178.0 and 176.2 (C-10, C-11), 170.7 (C-8), 134.2 (C-5), 123.5 (C-4), 48.2 (C-3), 44.6 (C-2), 44.0 (C-1), 33.6 (C-6), 25.2 (C-12), 23.5 (C-9), 16.8 (C-13)

N-(2-Methyl-1,3-dioxo-2,3,3a,4,10,10a-hexahydro-1*H*-9-thia-2-azacyclopenta[*b*]fluoren-10-yl)-acetamide (26)



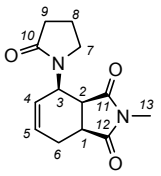
Batch size: 0.07 g (1.2 mmol) acetamide, 0.21 g (1.2 mmol) 3-methyl-1-benzothiophene-2-carbaldehyde and 0.13 g (1.2 mmol) *N*-Methylmaleimide in 5 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate, R_f = 0.30), white solid; **Yield**: 46% ; **mp** 200 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3380 (w), 3053 (w), 2915 (w), 1773 (m), 1689 (s), 1506 (m), 1433 (s), 1381 (s), 1322 (m), 1281 (m), 1123 (m), 1089 (w), 1020 (m), 980 (w), 907 (m), 726 (s); **LR MS** (EI,ethyl acetate), m/z = 328 $[M]^+$, 285 $[M\text{-}CH_3CO]^+$, 269 $[M\text{-}CH_3CONH]^+$, 253, 200, 184, 175, 160, 147, 115; **HR MS** (EI, [u]) found: 328.088 $[M]^+$, calcd: 328.0881; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.68 and 7.67 (2m, 1 H, H-14, H-17), 7.72 (d, 1 H, ^3J = 9.1 Hz, H-7), 7.36 (m, 2 H, H-15, H-16), 5.69 (m, 1 H, H-3), 3.64 (d, 1 H, ^2J = 15.9 Hz, H-6), 3.52 (m, 2 H, H-1, H-2), 2.87 (m, 1 H, H-6'), 2.79 (s, 3 H, H-12), 2.24 (s, 3 H, H-9); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 178.7 and 178.4 (C-10, C-11), 170.4 (C-8), 138.7 and 138.6 (C-13, C-18), 137.9 (C-4), 127.9 (C-5), 124.5, 124.4, 122.7, 121.0 (C-14, C-15, C-16, C-17), 45.9 (C-3), 43.6 (C-2), 39.8 (C-1), 25.3 (C-12), 23.4 (C-9), 23.2 (C-6)

tert-Butyl 10-acetylamino-2-methyl-1,3-dioxo-2,3,3a,4,10,10a-hexahydro-1*H*-pyrrolo[3,4-*b*]carbazol-5-carboxylate (27)



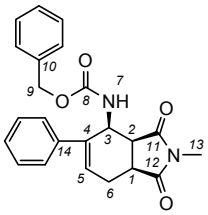
Batch size: 0.07 g (1.2 mmol) acetamide, 0.31 g (1.2 mmol) 3-Formyl-2-methyl-indole-1-carboxylic acid tert-butyl ester and 0.13 g (1.2 mmol) *N*-Methylmaleimide in 5 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.15), white solid; **Yield**: 27% ; **mp** 179 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3242 (br, w), 2978 (w), 1692 (s), 1518 (m), 1453 (s), 1433 (s), 1359 (s), 1318 (s), 1276 (s), 1216 (m), 1143 (s), 1115 (s), 1011 (m), 838 (w), 746 (s); **LR MS** (positiv ESI, MeOH), m/z = 434 $[M+Na]^+$, 378, 299, 253, 168; **HR MS** (ESI, [u]) found: 434.169 $[M+Na]^+$, calcd: 434.1692; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 8.17 and 7.57 (2 m, 2 H, H-15, H-18), 7.45 (d, 1 H, ^3J = 9.4 Hz, H-7), 7.25 (, 2 H, H-16, H-17), 5.69 (m, 1 H, H-3), 4.22 (d, 1 H, ^2J = 16.7 Hz, H-6), 3.45 (m, 2 H, H-1, H-2), 3.04 (m, 1 H, H-6'), 2.88 (s, 3 H, H-12), 2.25 (s, 3 H, H-9), 1.71 (s, 9 H, H-21); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 178.4.8 and 177.9 (C-10, C-11), 170.5 (C-8), 150.0 (C-19), 135.9 (C-14), 132.8 (C-5), 126.7 (C-13), 124.2 and 123.1 (C-16, C-17), 118.5 and 115.2 (C-15, C-18), 108.9 (C-4), 84.7 (C-20), 44.2 (C-3), 43.6 (C-1), 39.3 (C-2), 28.2 (C-21), 25.2 (C-12), 23.7 (C-6), 23.6 (C-9)

2-Methyl-4-(2-oxopyrrolidin-1-yl)-3a,4,7,7a-tetrahydroisoindol-1,3-dione (28)



Batch size: 0.43 g (5 mmol) 2-pyrrolidinone, 0.35 g (5 mmol) *trans*-2-butenal and 0.56 g (5 mmol) *N*-Methylmaleimide in 10 mL toluene were employed; **Work-up:** crude product was suspended in cold ethyl acetate, filtration gave the desired product as a white solid; **Yield**: 77% ; **R_f** = 0.16 (ethyl acetate) ; **mp** 124 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3449 (br, w), 2940 (w), 1771 (w), 1671 (s), 1421 (s), 1380 (m), 2181 (s), 1121 (m), 1016 (m), 915 (w); **LR MS** (EI,ethyl acetate), m/z = 248 $[M]^+$, 220 $[M-CO]^+$, 205 $[M-COCH_2]^+$, 192 $[M-COCH_2CH_2]$, 163, 137, 122, 109, 94, 82; **HR MS** (EI, [u]) found: 248.116 $[M]^+$, calcd: 248.1161; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 5.99 (m, 2 H, H-4 and H-5), 4.71 (d*, 1 H, ^3J = 7.1 Hz, H-3), 3.58 (dt, 1 H, ^3J = 7.7 Hz, H-2), 3.52 (dd, 2 H, ^3J = 7.9/5.8 Hz, H-7), 3.15 (m, 1 H, H-1), 2.90 (s, 3 H, H-13), 2.76 (m, 1 H, H-6), 2.49 (t, 1 H, ^3J = 4.9 Hz, H-9), 2.41 (m, 1 H, H-9'), 2.18 (m, 2 H, H-6, H-8), 2.04 (m, 1 H, H-8'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 179.5 and 177.3 (C-11, C-12), 175.9 (C-10), 128.8 (C-4), 126.5 (C-5), 48.5 (C-3), 46.3 (C-7), 41.9 (C-2), 38.8 (C-1), 31.37 (C-9), 25.1 (C-13), 23.8 (C-6), 18.9 (C-8)

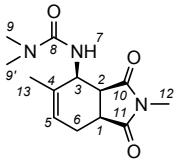
***N*-(2-Methyl-5-phenyl-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl)-benzyloxycarbonylamine (30)**



Batch size: 2.27 g (15 mmol) benzyl carbamate, 2.19 g (15 mmol) *trans*-2-phenyl-2-butenal and 1.6 g (15 mmol) *N*-Methylmaleimide in 35 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.35), white solid; **Yield**: 98% ; **mp** 75 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3401 (w), 3029 (w), 1691 (s), 1510 (m), 1435 (m), 1383 (m), 1323 (m), 1230 (m), 1050 (m), 757 (m); **LR MS** (positiv ESI, MeOH), m/z = 413 $[M+Na]^+$, 381, 131; **HR MS** (ESI, [u]) found: 413.148 $[M+Na]^+$, calcd: 413.1477; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.26 - 7.24 (m, 8 H, H-Arom.), 7.02 (m, 2 H, H-Arom.), 6.25 (d, 1 H, ^3J = 9.77 Hz, H-7), 5.84 (quint, 1 H, ^3J = 3.38 Hz, H5), 5.11 (d, 1 H, ^2J = 12.35 Hz, H-9), 5.00 (d, 1 H, ^3J = 12.4 Hz, H-9'), 4.89 (m,

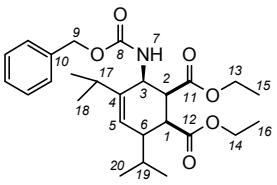
1 H, H-3), 3.35 (dd, 1 H, ^{3}J = 8.8/5.3 Hz, H-2), 3.27 (m, 1 H, H-1), 2.99 (s, 3 H, H-13), 2.84 (ddd, 1 H, ^{2}J = 15.8 Hz, ^{3}J = 7.2/1.5 Hz, H-6'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 179.3 and 178.8 (C-11, C-12), 156.0 (C-8), 144.1 (C-14), 137.8 (C-4), 136.5 (C-10), 128.5 - 127.5 (10 C-$H_{Arom.}$)124.6 (C-5), 66.7 (C-9), 49.4 (C-3), 44.2 (C-2), 39.28 (C-1), 25.0 (C-13), 24.6 (C-6)

3-(2,5-Dimethyl-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl)-1,1-dimethyl urea (32)



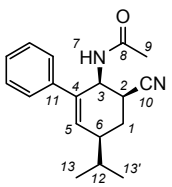
Batch size: 0.44 g (5 mmol) *N,N*-Dimethylurea, 0.42 g (5 mmol) *trans*-2-methyl-2-butenal and 0.56 g (5 mmol) *N*-Methylmaleimide in 10 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate, R_f = 0.13), white solid; **Yield**: 75% ; **mp** 111 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3586 (w), 3416 (w), 2933 (w), 1769 (w), 1681 (s), 1642 (s), 1513 (s), 1433 (s), 1379 (s), 1282 (s), 1210 (m), 1126 (m), 1029 (s), 918 (w), 786 (w), 727 (s); **LR MS** (EI, ethyl acetate), m/z = 265 [M], 220 [M-$N(CH_3)_2$]$^+$, 193 [M-$(CH_3)_2NCO$]$^+$, 179 [M-$(CH_3)_2NCONH$]$^+$, 108, 93, 72; **HR MS** (EI, [u]) found: 265.143 [M]$^+$, calcd: 265.1426; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 6.35 (d, 1 H, ^{3}J = 8.99 Hz, H-7), 5.49 (m, 1 H, H-5), 4.61 (m, 1 H, H-3), 3.11 (m, 2 H, H-1, H-2), 2.95 (s, 6 H, H-9, H-9'), 2.88 (s, 1 H, H-12) 2.54 (dd, 1 H, ^{2}J = 15.17 Hz, ^{3}J = 7.39 Hz, H-6), 2.19 (m, 1 H, H-6'), 1.61 (m, 1 H, H-13); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 180.4 and 179.9 (C-10, C-11), 158.1 (C-8), 140.0 (C-4), 119.8 (C-5), 49.2 (C-3), 43.9 and 39.8 (C-1, C-2), 36.3 (C-9,C-9'), 25.0 (C-12), 24.4 (C-6), 19.1 (C-13)

Diethyl 3-benzyloxycarbonylamino-4,6-diisopropylcyclohex-4-ene-1,2-dicarboxylate (33)



Batch size: 2.27 g (15 mmol) benzyl carbamate, 2.58 g (30 mmol) 3-methylbutanal, 2.6 g (15 mmol) Diethyl fumarate and 1.53 (15 mmol) acetic anhydride in 35 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.47), white solid (diastereomeric mixture); **Yield**: 79% ; **mp** 123 °C (higher melting diastereomer); **IR** (ATR) 1/λ [cm^{-1}] = 3353 (m), 2959 (m), 2871 (w), 1731 (s), 1520 (s), 1370 (m), 1303 (m), 1229 (s), 1042 (m), 859 (w); **LR MS** (positiv ESI, Methanol, CH_2Cl_2), m/z = 482 [M+Na]$^+$, 378, 310, 263; **HR MS** (ESI, [u]) found: 482.253 [M+Na]$^+$, calcd: 482.2519; **^{1}H-NMR** (300 MHz, $CDCl_3$), main diastereomer, δ = 7.33 (m, 6 H, H-Arom., H-7), 5.65 (d, 1 H, ^{3}J = 3.5 Hz, H-5), 5.08 (m, 2 H, H-9), 4.69 (m, 1 H, H-3), 4.09 (m, 4 H, H-13, H-14), 3.22 (dd, 1 H, ^{3}J = 7.9/6.1 Hz, H-2), 3.03 (m, 1 H, H-1), 2.26 (m, 2 H, H-6, H-17/H-19), 1.71 (sept, 1 H, ^{3}J = 6.8 , Hz, H-17/H-19), 1.51 (m, 6 H, H-15, H-16), 1.07 and 0.91 (m, 12 H, H-18, H-18', H-20, H-20'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), main diastereomer, δ= 173.6, 172.7 and 172.1 (C-8, C-11, C-12), 156.0 (C-10), 142.6 (C-4), 128.6 - 128.2 (5 C-$H_{Arom.}$), 122.1 (C-5), 66.8 (C-9), 61.4 and 60.7 (C-13, C-14), 49.4, 47.3, 43.4 and 41.2 (C-1, C-2, C-3, C-6), 29.9, 29.4 (C-17, C-19), 23.0, 22.9, 22.1 and 21.5 (C-18, C-18', C-20, C-20'), 14.2 (C-15, C-16)

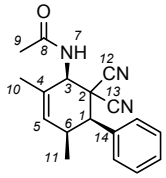
***N*-(6-Cyano-4-isopropyl-2-phenylcyclohex-2-enyl)-acetamide (34)**



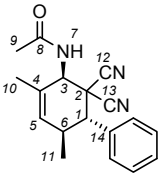
Batch size: 0.24 g (4 mmol) acetamide, 0.75 g (4 mmol) *trans*-5-methyl-2-phenyl-2-hexenal and 0.63 g (12 mmol) acrylonitrile in 12 mL toluene were employed; **Work-**

up: crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:3, R_f = 0.22), white solid; **Yield**: 25% ; **mp** 77 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3280 (br,w), 3040 (w), 1956 (m), 2240 (w), 1652 (s), 1529 (s), 1369 (m), 1283 (m), 11, 26 (w), 1030 (w), 910 (w), 759 (s), 730 (s); **LR MS** (EI, ethyl acetate), m/z = 282 $[M]^+$, 255 $[M\text{-}CN]^+$, 223 $[M\text{-}CH_3CONH]^+$, 197, 180, 166, 152, 129, 115, 91; **HR MS** (EI, [u]) found: 282.173 $[M]^+$, calcd: 282.1732; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.40 - 7.29 (m, 5 H, H-Arom.), 6.22 (m, 1 H, H-5), 5.56 - 5.52 (m, 2 H, H_3, H-7), 2.96 (td, 1 H, ^3J = 13.2/2.9 Hz, H-2), 2.25 (m, 1 H, H-6), 2.15 (m, 1 H, H-1), 1.94 (s, 3 H, H-9), 1.85 (m, 1 H, ^3J = 6.9 Hz, H-12), 1.61 (q, 1 H, ^3J = 13.2 Hz, H-1'), 1.03 and 0.99 (2 d, 6 H, ^3J = 7.2 Hz, H-13, H-13'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 170.0 (C-8), 137.8 (C-4), 135.6 (C-11), 131.9 (C-5), 128.9, 128.2, 125.6 (5 C-$H_{Arom.}$), 120.2 (C-10), 43.7 (C-3), 41.9 (C-6), 32.6 (C-2), 32.0 (C-12), 24.5 (C-1), 23.2 (C-9), 19.8 and 19.3 (C-13, C-13')

N-(6,6-Dicyano-2,4-dimethyl-5-phenylcyclohex-2-enyl)-acetamide (35)



Batch size: 0.33 g (3.3 mmol) acetamide, 0.32 g (3.3 mmol) *trans*-2-methyl-2-pentenal and 0.51 g (3.3 mmol) 2-benzylidene malonodinitrile in 10 mL toluene were employed; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.42), white solid (*syn* diastereomer); **Yield**: 35% ; **mp** 88-90 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3283 (w), 2973 (w), 1666 (s), 1530 (s), 1453 (m), 1371 (m), 1261 (m), 1129 (m), 1051 (w), 910 (m), 729 (s); **LR MS** (EI, ethyl acetate), m/z = 293 $[M]^+$, 268 $[M\text{-}CN]^+$, 251 $[M\text{-}CH_3CO]^+$, 224 $[M\text{-}CH_3CO\text{-}CN]^+$, 209 $[M\text{-}CH_3CONH\text{-}CN]^+$, 192, 178, 154, 139, 115, 91; **HR MS** (EI, [u]) found: 293.153 $[M]^+$, calcd: 293.1528; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.46 - 7.38 (m, 5 H, 5 H-Arom.), 5.83 (m, 1 H, H-7), 5.75 (s, 1 H, ^3J = 11.3 Hz, H-5), 5.38 (d, 1 H, ^3J = 10.4 Hz, H-3), 3.56 (d, 1 H, ^3J = 6.4 Hz, H-1), 2.89 (m, 1 H, H-6), 1.99 (s, 3 H, H-9), 1.78 (s, 3 H, H-10), 1.06 (d, 3 H, ^3J = 7.4 Hz, H-11); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 170.1 (C-8), 135.4 (C-14), 131.6 (C-5), 129.2, 129.1, 128.8 (5 C-$H_{Arom.}$, C-4), 115.1 and 114.5 (C-12, C-13), 53.4 (C-3), 48.9 (C-1), 41.4 (C-2), 33.8 (C-6), 23.1 (C-9), 20.0 (C-10), 16.2 (C-11)

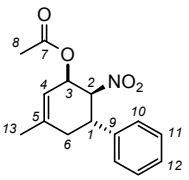


Yield: 11% (*anti* diastereomer); **mp** 301 °C ; **R_f** = 0.19 (ethyl acetate/cyclohexane 1:1) ; **mp** >300 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3266 (w), 2960 (w), 1650 (s), 1530 (s), 1450 (m), 1370 (m), 1266 (m), 1096 (m), 910 (m), 726 (s); **LR MS** (EI, ethyl acetate), m/z = 293 $[M]^+$, 268 $[M\text{-}CN]^+$, 251 $[M\text{-}CH_3CO]^+$, 224 $[M\text{-}CH_3CO\text{-}CN]^+$, 209 $[M\text{-}CH_3CONH\text{-}CN]^+$, 192, 178, 154, 139, 115, 91; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.46 - 7.42 (m, 5 H, 5 H-Arom.), 5.72 (m, 2 H, H-5, H-7), 5.15 (d, 1 H, ^3J = 9.7 Hz, H-3), 2.90 (m, 1 H, H-6), 2.57 (d, 1 H, ^3J = 11.0 Hz, H-1), 2.15 (s, 3 H, H-9), 1.82 (s, 3 H, H-10), 0.94 (d, 3 H, ^3J = 6.9 Hz, H-11); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 170.1 (C-8), 135.7 (C-14), 132.6 (C-5), 129.4, 129.1, 128.7 (5 C-$H_{Arom.}$, C-4), 113.5 (C-12, C-13), 52.6 (C-3), 49.2 (C-1), 44.3 (C-2), 33.4 (C-6), 23.7 (C-9), 20.9 (C-10), 19.2 (C-11)

3-Methyl-6-nitro-5-phenylcyclohex-2-enyl acetate (37)

Acetic anhydride (12 mmol, 2 equiv.), 3-methyl-2-butenal (6 mmol, 1 equiv.), *trans*-β-nitrostyrene (2 equiv.), *p*-toluenesulfonic acid monohydrate (3 mol%) and toluene (8 mL) were combined in a reaction tube. The tube was sealed with a septum and the reaction was stirred at elevated

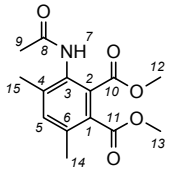
temperature (110 °C). After 28 h, the solvent and other volatile compounds were removed by oil pump vacuum. The crude product was purified by column chromatography (MTBE/cyclohexane 1:3, R_f = 0.26) to get the desired product as a yellow solid in a diastereomeric mixture (*syn*/*anti* 7:1).



Yield: 69%; **mp** ~106 °C (; **IR** (ATR) 1/λ [cm^{-1}] = 2913 (w), 1741 (m), 1555 (s), 1436 (w), 1370 (m), 1225 (s), 1016 (m), 904 (s), 723 (s); **LR MS** (positiv ESI, $MeOH/CH_2Cl_2$), m/z = 298 $[M+Na]^+$, 282, 263, 169; **HR MS** (ESI, [u]) found: 298.105 $[M+Na]^+$, calcd: 298.1005; **^{1}H-NMR** (300 MHz, $CDCl_3$), main diastereomer, δ = 7.37-7.24 (m, 5 H, 5 H-Arom.), 5.83 (t*, 1 H, ^3J = 4.3 Hz, H-3), 5.69 (d, 1 H, ^3J = 4.3 Hz, H_4), 5.10 (dd, 1 H, ^3J = 12.2/3.9 Hz, H_2), 3.80 (td, 1 H, ^3J = 11.9/6.1, Hz, H-1), 2.6 (dd, 1 H, ^2J = 18.7 Hz, ^3J = 6.1 Hz, H-6), 2.26 (dd, 1 H, ^2J = 18.4 Hz, ^3J = 11.2 Hz, H-6'), 2.07 (s, 3 H, H-8), 1.79 (s, 3 H, H-13); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), main diastereomer, δ = 170.0 (C-7), 141.9 (C-5), 140.7 (C-9), 129.1, 12.9, 127.6, 127.5, 127.1 (C-$H_{Arom.}$), 117.2 (C-4), 87.3 (C-2), 67.0 (C-3), 39.6 (C-6), 38.6 (C-1), 22.9 (C-13), 21.0 (C-8)

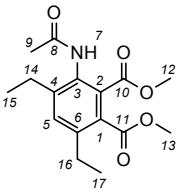
General procedure for the aromatization of (amino)cyclohexadienes and aminocyclohexenes:
The cyclohexadiene or cyclohexene derivative (1 equiv.), MnO_2 (85%, 3-10 equiv.) and toluene (2.0-20 mL/mmol cyclohexadiene or cyclohexene) were combined in a reaction tube. The tube was sealed with a septum and the reaction stirred at elevated temperature (110 °C). After 24-48 h, the solvent and other volatile compounds were removed by oil pump vacuum. For work-up, see the paragraph pertinent to the respective product.**Error! Bookmark not defined.**

Dimethyl 3-acetylamino-4,6-dimethylphthalate (38)



Conditions: 2.5 mmol cyclohexadiene derivative and 7.5 mmol MnO_2 (85%) in 12 mL toluene were stirred at 110 °C for 5 h**; Work-up:** crude product was purified by column chromatography (ethyl acetate, R_f = 0.27), yellow solid; **Yield**: 96% ; **mp** 137 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3249 (m), 3003 (m), 2950 (m), 2361 (w), 1726, 1659 (s), 1599 (m), 1571 (m), 1518 (s), 1433 (s), 1367 (m), 1313 (s), 1280 (s), 1207 (s), 1147 (s), 1056 (s), 1014 (m), 977 (m), 882 (m); **LR MS** (DIP EI 70 V, CH_2Cl_2) m/z = 279 $[M]^+$, 263 $[M-CH_3]^+$, 248 $[M-2CH_3]^+$, 232, 205, 190, 161, 147, 119, 91; **HR MS** (ESI, [u]) found: 302.101 $[M+Na]^+$, calcd: 302.1005; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 8.05 (s, 1 H, H-7), 7.19 (s, 1 H, H-5), 3.84 and 3.82 (2s, 6 H, H-12, H-13), 2.34 and 2.22 (2s, 6 H, H-14, H-15), 2.14 (s, 3 H, H-9); **^{13}C-NMR** (150 MHz, APT, $CDCl_3$), δ = 168.7 (C-8), 168.4 and 167.9 (C-10, C-11), 138.7 (C_q), 135.8 (C-5), 135.0, 132.4, 130.5, 127.5 (5 C_q), 52.9 and 52.4 (C-12, C-13), 23.6 (C-9), 19.8 and 18.9 (C-14, C-15)

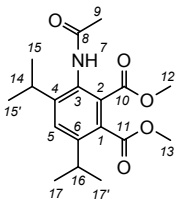
Dimethyl 3-acetylamino-4,6-diethylphthalate (39)



Conditions: 2.5 mmol cyclohexadiene derivative and 7.5 mmol MnO_2 (85%) in 12 mL toluene were stirred at 110 °C for 5 h**; Work-up:** crude product was purified by column chromatography (ethyl acetate, R_f = 0.36), yellow solid; **Yield**: 84% ; **mp** 123 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3255 (m), 2966 (m), 2873 (w), 2354 (m), 1726 (s), 1660 (s), 1568 (m), 1510 (s), 1434 (s), 1367 (m), 1284 (s), 1203 (s), 1147 (s), 1074 (s),

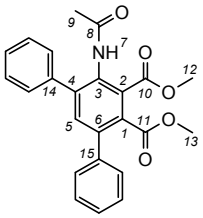
1000 (m), 960 (m), 926 (m), 892 (m), 793 (w), 729 (m); **LR MS** (EI, ethyl acetate) m/z = 307 $[M]^+$, 292 $[M\text{-}CH_3]^+$, 277 $[M\text{-}2CH_3]^+$ 260, 243, 218, 189, 172, 147, 130; **HR MS** (ESI, [u]) found: 330.132 $[M+Na]^+$, calcd: 330.1317; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.84 (s, 1 H, H-7), 7.28 (s, 1 H, H-5), 3.85 and 3.82 (2s, 6 H, H-12, H-13), 2.72-2.58 (m, 4 H, H-14, H-16), 2.15 (s, 3 H, H-9), 1.22 and 1.20 (2t, 6 H, ^3J = 7.6 Hz, H-15, H-17); **^{13}C-NMR** (150 MHz, APT, $CDCl_3$), δ = 169.1 (C-8), 168.6 and 168.0 (C-10, C-11), 144.3, 141.5, 132.5 (3 C_q), 131.6 (C-5), 52.8 and 52.2 (C-12, C-13), 26.9 and 24.8 (C-14, C-16), 23.7 (C-9), 15.9 and 13.9 (C-15, C-17)

Dimethyl 3-acetylamino-4,6-diisopropylphthalate (40)



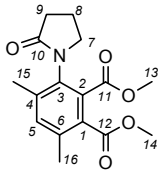
Conditions: 2.5 mmol cyclohexadiene derivative and 25 mmol MnO_2 (85%) in 12 mL toluene were stirred at 110 °C for 24 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.25), yellow solid; **Yield**: 79% ; **mp** 149 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3282 (w), 2965 (w), 1732 (s), 1666 (m), 1515 (m), 1437 (m), 1308 (m), 1278 (m), 1208 (m), 913 (s), 743 (s); **LR MS** (EI, ethyl acetate) m/z = 336 $[M]^+$, 318 $[M\text{-}CH_3]^+$, 304, 289, 260; **HR MS** (ESI, [u]) found: 358.162 $[M+Na]^+$, calcd: 358.1631; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.66 (s, 1 H, H-7), 7.42 (s, 1 H, H-5), 3.85 and 3.82 (2s, 6 H, H-12, H-13), 3.00 (m, 2 H, H-14, H-16), 2.16 (s, 3 H, H-9), 1.22 (m, 12 H, H-15, H-15', H-17, H-17'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 169.9, 168.7, 167.8 (C-8, C-10, C-11), 148.9, 145.8, 130.5, 127.7 (4 $C_{quart.}$), 127.2 (C-5), 53.3 and 53.2 (C-12, C-13), 30.6 and 28.9 (C-14, C-16), 24.3, 23.9, 23.8, 23.5, 23.3 (C-9, C-15, C-15', C-17, C-17'), 1 $C_{quart.}$ obscured

Dimethyl 3-acetylamino-4,6-diphenylphthalate (41)



Conditions: 0.15 mmol cyclohexadiene derivative and 0.45 mmol MnO_2 (85%) in 3 mL toluene were stirred at 110 °C for 15 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.14), yellow solid; **Yield**: 84% ; **mp** 188 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3257 (w), 3024 (w) 2948 (w), 2246 (w), 1726 (s), 1665 (m), 1495 (m), 1431 (m), 1287 (m), 1227 (s), 1126 (m), 1068 (m), 906 (m), 728 (s); **LR MS** (EI, ethyl acetate) m/z = 403 $[M]^+$, 361 $[M\text{-}CH_3CO]^+$, 344 $[M\text{-}CH_3CONH]^+$, 328, 312, 169 $[M\text{-}CH_3CONH\text{-}Ph]^+$, 243, 228, 213, 189, 165, 139; **HR MS** (EI, [u]) found: 403.142 $[M]^+$, calcd: 403.1420; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.52 (s, 1 H, H-7), 7.44 - 7.32 (m, 11 H-Arom.), 3.85 and 3.58 (2s, 6 H, H-12, H-13), 1.94 (s, 3 H, H-9); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 168.8 (C-8), 168.6 and 167.3 (C-10, C-11), 149.3, 140.7, 139.4, 139.1, 138.2, 132.6, 131.6 (7 C_q), 134.8, 128.8 - 127.2 (11 C-$H_{Arom.}$), 53.5 and 52.4 (C-12, C-13), 23.6 (C-9)

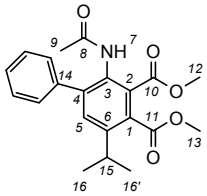
Dimethyl 4,6-dimethyl-3-(2-oxopyrrolidin-1-yl)-phthalate (43)



Conditions: 0.15 mmol cyclohexadiene derivative and 0.45 mmol MnO_2 (85%) in 3 mL toluene were stirred at 110 °C for 15 h;**Work-up:** crude product was purified by

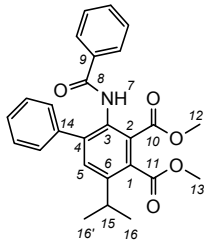
column chromatography (ethyl acetate/cyclohexane 2:1, R_f = 0.14), yellow solid; **Yield**: 65% ; **mp** 66 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 2950 (w), 1726 (s), 1692 (s), 1600 (w), 1433 (m), 1409 (m), 1315 (m), 1300 (s), 1266 (s), 1209 (s), 1114 (s), 1051 (m),1016 (m), 978 (w), 888 (w); **LR MS** (EI, ethyl acetate), m/z = 305 $[M]^+$, 290 $[-CH_3]^+$, 273, 258, 241, 218, 202, 187, 161, 144, 130; **HR MS** (EI, [u]) found: 305.126 $[M]^+$, calcd : 305.1263; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.24 (s, 1 H, H-5), 3.85 and 3.82 (2s, 6 H, H-13, H-14), 3.76 and 3.61 (2m, 2 H, H-7), 2.51 (m, 2 H, H-9), 2.38 (s, 3 H, H-16), 2.22 (s, 3 H, H-15), 2.16 (m, 2 H, H-8); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 175.6 (C-10), 167.8 and 167.3 (C-11, C-12), 139.6 (C-1), 137.4 (C-3), 135.5 (C-5), 133.6 (C-4),132.1 (C-2), 130.6 (C-6), 52.8 and 82.4 (C-13, C-14), 50.4 (C-7), 31.1 (C-9), 20.2 (C-16), 19.5 (C-8), 17.7 (C-15)

Dimethyl 3-acetylamino-4-phenyl-6-isopropylphthalate (44)



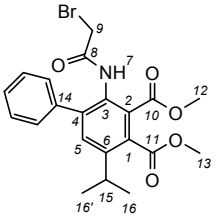
Conditions: 2.5 mmol cyclohexadiene derivative and 7.5 mmol MnO_2 (85%) in 12 mL toluene were stirred at 110 °C for 5 h**; Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 2:1, R_f = 0.47), yellow solid; **Yield**: 88% ; **mp** 129 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3253 (w), 2961 (w), 1730 (s), 1666 (s), 1513 (m), 1433 (s), 1366 (w), 1322 (s), 1272 (s), 1207 (s), 1152 (m), 1109 (m), 1031 (m), 998 (w), 909 (w), 729 (s); **LR MS** (EI, ethyl acetate) m/z = 369 $[M]^+$, 352 $[M-CH_3]^+$, 338 $[M-2CH_3]^+$, 320, 294, 280; **HR MS** (EI, [u]) found: 369.157 $[M+Na]^+$, calcd: 369.1576; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.52 (s, 1 H, H-7), 7.45 - 7.33 (m, 5 H, H-5, H-Arom.), 3.88 and 3.83 (2s, 6 H, H-12, H-13), 3.15 (sept, 1 H, ^3J = 6.8 Hz, H-15), 1.89 (s, 3 H, H-9), 1.24 (d*, 6 H, ^3J = 6.8 Hz, H-16, H-16'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 168.7 (C_8), 168.6 and 167.3 (C-10, C-11), 145.0, 141.0, 138.8, 132.1 (C_q), 130.1, 129.1, 128.6, 128.4 ($C\text{-}H_{Arom.}$), 53.1 and 52.6 (C-12, C-13), 30.6 (C-15), 23.9 (C-16, C-16'), 23.5 (C-9)

Dimethyl 3-benzamido-4-phenyl-6-isopropylphthalate (46)



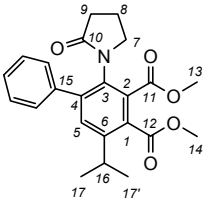
Conditions: 2.5 mmol cyclohexadiene derivative and 7.5 mmol MnO_2 (85%) in 12 mL toluene were stirred at 110 °C for 5 h**; Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:2, R_f = 0.27), yellow solid; **Yield**: 94% ; **mp** 218 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3286 (br, w), 2953 (w), 2360 (w), 2240 (w), 1726 (s), 1650 (s), 1573 (w), 1503 (s), 1476 (s), 1430 (s), 1406 (m), 1316 (s), 1260 (s), 1200 (s), 1150 (s), 1100 (s), 1006 (m), 903 (s), 793 (m), 729 (s); **LR MS** (positiv ESI, MeOH), m/z = 454 [M+Na], 400, 380, 266, 249, 234, 60; **HR MS** (ESI, [u]) found: 454.163 $[M+Na]^+$, calcd: 454.1631; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 8.41 (s, 1 H, H-7), 7.55 (m, 2 H, H-Arom.), 7.53 - 7.26 (m, 9 H, H-Arom.), 3.83 and 3.74 (2s, 6 H, H-12, H-13), 3.07 (sept, 1 H, ^3J = 6.9 Hz, H-15), 1.20 (d, 6 H, ^3J = 6.9 Hz, H-16, H-16'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 168.8 and 167.3 (C-10, C-11), 165.5 (C-8), 144.7, 140.9, 140.0, 134.1, 132.2 (C_q), 131.8 ($C\text{-}H_{Arom.}$), 131.2 (C_q), 131.0, 128.6, 128.4, 127.9, 127.1 ($C\text{-}H_{Arom.}$), 126.7 (C_q), 52.9 and 52.5 (C-12, C-13), 30.6 (C-15), 23.9 (C-16, C-16')

Dimethyl 3-(bromomethylcarbonylamino)-4-phenyl-6-isopropylphthalate (47)



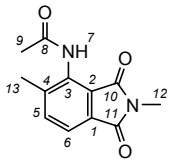
Conditions: 1.3 mmol cyclohexadiene derivative and 7.8 mmol MnO_2 (85%) in 9 mL toluene were stirred at 110 °C for 48 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.42), yellow solid; **Yield**: 44% ; **mp** 131 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3274 (br, w), 2954 (w), 1725 (s), 1670 (m), 1503 (m), 1433 (m), 1322 (m), 1260 (s), 1206 (s), 1106 (m), 980 (w), 907 (m), 726 (s); **LR MS** (positiv ESI, MeOH), m/z = 470 $[M+Na]^+$, 416, 336, 72, 60; **HR MS** (ESI, [u]) found: 470.059 $[M+Na]^+$, calcd: 470.0579; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 8.52 (s, 1 H, H-7), 7.34 (m, 6 H, H-Arom., H-5), 3.89 and 3.86 (2s, 6 H, H-12, H-13), 3.69 (s, 2 H, H-9), 3.14 (sep, 1 H, ^3J = 6.9 Hz, H-15), 1.26 and 1.24 (2s, 6 H, H-16, H-16'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 168.4 and 166.9 (C-10, C-11), 163.8 (C-8), 145.6 (C-6), 141.1 (C_q), 138.4 (C-4), 132.3 (C_q), 130.9, 128.8, 128.7, 128.6, 128.3 and 128.2 (5 C-$H_{Arom.}$, C-5), 129.9 (C_q), 127.4 (C_q), 52.8 and 52.7 (C-12, C-13), 30.7 (C-15), 28.8 (C-9), 23.9 (C-16, C-16')

Dimethyl 3-(2-oxopyrrolidin-1-yl)-4-phenyl-6-isopropylphthalate (48)



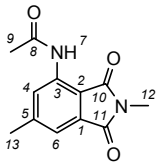
Conditions: 2.5 mmol cyclohexadiene derivative and 7.5 mmol MnO_2 (85%) in 12 mL toluene were stirred at 110 °C for 5 h**; Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 2:1, R_f = 0.14), yellow solid; **Yield**: 63% ; **mp** 66 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 2946 (w), 2880 (w), 1731 (s), 1690 (s), 1593 (w), 1433 (m), 1300 (s), 1203 (s), 1103 (m), 1013 (w), 910 (w), 726 (m); **LR MS** (positiv ESI, MeOH), m/z = 418 $[M+Na]^+$, 364, 332, 249; **HR MS** (ESI, [u]) found: 418.163 $[M+Na]^+$, calcd: 418.1631; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.36 - 7.33 (m, 6 H, H-5, H-Arom.), 3.87 and 3.82 (2s, 6 H, H-13, H-14), 3.47 (m, 1 H, H-7), 3.17 (sept*, 1 H, ^3J = 6.81 Hz, H-9), 2.88 (td, 1 H, ^3J = 8.8/4.2 Hz, H-7'), 2.33 (m, 2 H, H-9', H-16), 2.03 and 1.41 (2m, 2 H, H-8), 1.25 (m, 6 H, H-17, H-17'); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 176.6 (C-10), 168.3 and 166.9 (C-11, C-12), 147.0, 143.0, 138.0, 132.8, 132.9, 131.2 (C_q), 130.6, 130.0, 128.5, 128.4, 128.3 (C-$H_{Arom.}$), 53.0 and 52.8 (C-13, C-14), 50.3 (C-7), 31.2 (C-9), 30.7 (C-16), 24.0 and 23.9 (C-17, C-17'), 19.5 (C-8)

***N*-(2,5-Dimethyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-4-yl)-acetamide (50)**



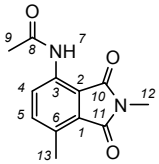
Conditions: 0.8 mmol cyclohexene derivative and 8.0 mmol MnO_2 (85%) in 5 mL toluene were stirred at 110 °C for 48 h; **Conditions:** 0.8 mmol cyclohexene derivative and 8.0 mmol MnO_2 (85%) in 5 mL toluene were stirred at 110 °C for 48 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate, R_f = 0.33), white solid; **Yield**: 65% ; **mp** 222 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3225 (m), 3007 (w), 1753 (m), 1710 (s), 1656 (s), 1611 (w), 1531, 1479 (m), 1439 (s), 1381 (s), 1332 (w), 1252 (m), 1209 (w), 1057 (m), 999 (m), 918 (w), 852 (w), 738 (m); **LR MS** (EI, ethyl acetate), m/z = 232 $[M]^+$, 217 $[M-CH_3]^+$, 190 $[M-CH_3CO]^+$, 175 $[M-CH_3CONH]^+$, 161, 146, 131, 117, 105, 91; **HR MS** (EI, [u]) found: 232.084 $[M]^+$, calcd: 232.0848; **^{1}H-NMR** (400 MHz, $CDCl_3$), δ = 8.21 (s, 1 H, H-7), 7.58 and 7.55 (2d, 2 H, ^3J = 7.6 Hz, H-5, H-6), 3.13 (s, 3 H, H-12), 2.36 (s, 3 H, H-13), 2.28 (s, 3 H, H-9); **^{13}C-NMR** (100 MHz, APT, $CDCl_3$), δ = 169.2 and 168.6 (C-10, C-11), 167.9 (C-8), 142.2 (C-3), 137.1 (C-5), 134.3 (C-4), 130.1 (C-1), 120.8 (C-6), 23.9 (C-9, C-12), 19.7 (C-13), C-2 obscured

***N*-(2,6-Dimethyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-4-yl)-acetamide (51)**



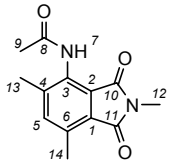
Conditions: 0.8 mmol cyclohexene derivative and 8.0 mmol MnO_2 (85%) in 5 mL toluene were stirred at 110 °C for 24 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:2, R_f = 0.25), white solid; **Yield**: 58% ; **mp** 175 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3344 (w), 2914 (w), 1759 (m), 1690 (s), 1612 (m), 1525 (m), 1438 (m), 1415 (m), 1377 (m), 1255 (m), 1002 (w), 872 (w), 747 (m); **LR MS** (EI, ethyl acetate) m/z = 232 $[M]^+$, 190 $[M\text{-}CH_3CO]^+$, 175, 161, 146, 133, 119, 105, 89, 77; **HR MS** (EI, [u]) found: 232.085 $[M]^+$, calcd: 232.0848; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 9.40 (s, 1 H, H-7), 8.56 (s, 1 H, H-4), 7.31 (s, 1 H, H-6), 3.14 (s, 3 H, H-12), 2.47 (s, 3 H, H-13), 2.26 (s, 3 H, H-9); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 170.3 and 168.3 (C-10, C-11), 169.4 (C-8), 147.8 (C-5), 137.2 (C-3), 132.0 (C-1), 124.8 (C-4), 119.0 (C-6), 113.2 (C-2), 25.1 (C-9), 23.9 (C-12), 22.7 (C-13)

***N*-(2,7-Dimethyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-4-yl)-acetamide (52)**



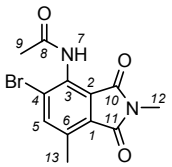
Conditions: 0.8 mmol cyclohexene derivative and 4.0 mmol MnO_2 (85%) in 5 mL toluene were stirred at 110 °C for 24 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:2, R_f = 0.27), white solid; **Yield**: 74% ; **mp** 105 °C ; **IR** (ATR), 1/λ [cm^{-1}] = 3348 (w), 2923 (w), 1752 (m), 1688 (s), 1627 (m), 1514 (s), 1491 (s), 1437 (s), 1375 (s), 1347 (s), 1288 (s), 1245 (s), 1163 (m), 1003 (s), 958 (w), 891 (w), 834 (w), 756 (m); **LR MS** (EI, ethyl acetate) m/z = 232 $[M]^+$, 190 $[M\text{-}CH_3CO]^+$, 175, 157, 146, 133, 118, 105, 89, 77; **HR MS** (300 MHz, $CDCl_3$), δ = 9.55 (s, 1 H, H-7), 8.63 (d, 1 H, ^3J = 8.7 Hz, H-5), 7.40 (d, 1 H, ^3J = 8.7 Hz, H-4), 3.15 (s, 3 H, H-12), 2.62 (s, 3 H, H-13), 2.27 (s, 3 H, H-9); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 170.3 and 168.7 (C-10, C-11), 169.3 (C-8), 138.3 (C-5), 135.6 (C-1), 132.6 (C-3), 127.9 (C-6), 124.7 (C-4), 115.9 (C-2), 25.1 (C-9), 23.7 (C-12), 17.1 (C-13)

***N*-(2,5,7-Trimethyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-4-yl)-acetamide (53)**



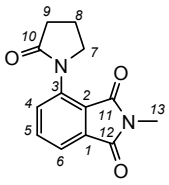
Conditions: 0.4 mmol cyclohexene derivative and 4.0 mmol MnO_2 (85%) in 5 mL toluene were stirred at 110 °C for 24 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.34), yellow solid; **Yield**: 66% ; **mp** 192 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3233 (w), 3026 (w), 1760 (m), 1702 (s), 1663 (m), 1520 (m), 1486 (m), 1433 (m), 1375 (m), 1256 (m), 1053 (w), 996 (w); **LR MS** (EI, ethyl acetate) m/z = 246 $[M]^+$, 204 $[M\text{-}CH_3CO]^+$, 189 $[M\text{-}CH_3CONH]^+$, 171, 147, 119, 104, 91, 77; **HR MS** (EI, [u]) found: 246.1004 $[M]^+$, calcd: 246.100; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 8.15 (s, 1 H, H-7), 7.30 (s, 1 H, H-5), 3.11 (s, 3 H, H-12), 2.60 (s, 3 H, H-14), 2.32 (s, 3 H, H-13), 2.26 (s, 3 H, H-9); **^{13}C-NMR** (100 MHz, APT, $CDCl_3$), δ = 169.3, 169.2, 168.5 (C-10, C-11, C-8), 141.8 (C-4), 139.3 (C-5), 135.3 (C-1), 132.3 (C-3), 126.5 (C-6), 123.4 (C-2), 29.9 (C-12), 23.7 (C-9), 19.4 (C-13), 17.2 (C-14)

***N*-(5-Bromo-2,7-dimethyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-4-yl)-acetamide (55)**



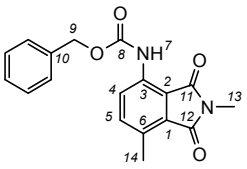
Conditions: 0.16 mmol cyclohexene derivative and 1.6 mmol MnO_2 (85%) in 3 mL toluene were stirred at 110 °C for 48 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 2:1, R_f = 0.35), white solid; **Yield**: 68% ; **mp** 234 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3226 (w), 3181 (w), 2923 (w), 1766 (m), 1703 (s), 1677 (s), 1518 (m), 1433 (m), 1378 (m), 1259 (m), 1099 (w), 1014 (m), 903 (w); **LR MS** (EI, ethyl acetate) m/z = 311 [M], 295 $[M\text{-}CH_3]^+$, 269 $[M\text{-}CH_3CO]^+$, 253 $[M\text{-}CH_3CONH]^+$, 231 $[M\text{-}Br]^+$, 211, 189, 145; **HR MS** (ESI, [u]) found: 332.984 $[M+Na]^+$, calcd: 332.9845; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.72 (s, 1 H, H-5), 7.56 (s, 1 H, H-7), 3.12 (s, 3 H, H-12), 2.64 (s, 3 H, H-13), 2.28 (s, 3 H, H-9); **^{13}C-NMR** (125 MHz, APT, $CDCl_3$), δ = 168.8 (C-8), 167.9 and 166.8 (C-10, C-11), 140.8 (C-5), 137.0 (C-1), 131.1 (C-2), 128.6 (C-6), 127.0 (C-4), 126.6 (C-3), 24.0 (C-12), 23.7 (C-9), 17.2 (C-13)

2-Methyl-4-(2-oxo-pyrrolidin-1-yl)-isoindole-1,3-dione (59)



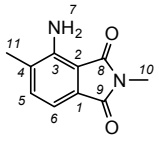
Conditions: 2.5 mmol cyclohexene derivative and 12.5 mmol MnO_2 (85%) in 15 mL toluene were stirred at 110 °C for 19 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:3, R_f = 0.34), white solid; **Yield**: 72% ; **mp** 164 °C **IR** (ATR) 1/λ [cm^{-1}] = 2912 (w), 1760 (w), 1697 (s), 1604 (w), 1476 (m), 1439 (m), 1378 (m), 1313 (m), 1226 (m), 1167 (w), 1105 (w), 1004 (m), 744 (s), 573 (m); **LR MS** (EI, ethyl acetate) m/z = 244 $[M]^+$, 216, 202 $[M\text{-}CH_3CO]^+$, 189, 161, 144, 131, 117, 104, 89, 75; **HR MS** (EI, [u]) found: 244.085 $[M]^+$, calcd: 244.0848; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.73 (m, 2 H, H-5, H-6), 7.63 (m, 1 H, H-4), 3.98 (t, 2 H, ^3J = 7.0 Hz, H-7), 3.15 (s, 3 H, H-13), 2.63 (t, 2 H, ^3J = 7.9 Hz, H-9), 2.27 (quint., 2 H, ^3J = 7.0 Hz, H-8); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 175.6 (C-10), 167.8 and 167.7 (C-11, C-12), 135.0 and 132.7 (C-5, C-6), 122.0 (C-4), 50.6 (C-7), 31.5 (C-9), 24.1 (C-13), 19.3 (C-8), C-1, C-2 and C-3 obscured

***N*-(2,7-Dimethyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-4-yl)-benzyloxycarbonylamine (60)**



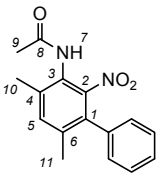
Conditions: 2.5 mmol cyclohexene derivative and 12.5 mmol MnO_2 (85%) in 15 mL toluene were stirred at 110 °C for 24 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:2, R_f = 0.48), white solid; **Yield**: 55% ; **mp** 130 °C ; **IR** (ATR) 1/λ [cm^{-1}] = 3344 (w), 2948 (w), 1736 (s), 1691 (s), 1630 (m), 1612 (m), 1518 (s), 1437 (m), 1379 (m), 1349 (m), 1224 (s), 1199 (s), 1096 (m), 1054 (m), 1003 (m), 905 (w); **LR MS** (EI, ethyl acetate) m/z = 324 $[M]^+$, 280, 217 $[M\text{-}PhCH_2O]^+$, 203, 190 $[M\text{-}PhCH_2OCO]^+$, 159, 131, 106, 91 $[Bn]^+$; **HR MS** (EI, [u]) found: 324.111 $[M]^+$, calcd: 324.1110; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 9.02 (s, 1 H, H-7), 8.38 (d, 1 H, ^3J = 8.6 Hz, C-4), 7.37 (m, 6 H, H-Arom., H-5), 5.23 (s, 2 H, H-9), 3.11 (s, 3 H, H-13), 2.59 (s, 3 H, H-14); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 169.9 and 169.8 (C-11, C-12), 168.7 (C-8), 153.2 (C-10), 138.3 (C-5), 135.8 (C-1), 135.5 (C-6), 131.8 (C-3), 130.3, 128.8, 128.6, 128.5 (all C-$H_{Arom.}$), 123.3 (C-4), 115.6 (C-2), 67.5 (C-9), 23.7 (C-13), 17.0 (C-14)

4-Amino-2,5-dimethyl-isoindoline-1,3-dione (62)



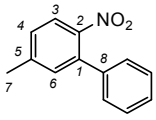
Conditions: 0.16 mmol cyclohexene derivative **32** and 1.6 mmol MnO_2 (85%) in 3 mL toluene were stirred at 110 °C for 24 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.66), yellow solid; **Yield**: 78% ; **mp** 130 °C ; **IR** (ATR), 1/λ [cm^{-1}] = 3466 (w), 3367 (w), 2921 (w), 1745 (m), 1686 (s), 1633 (s), 1593 (m), 1486 (m), 1445 (m), 1365 (m), 1274 (w), 1204 (m), 1047 (m), 992 (m), 745 (m); **LR MS** (EI, ethyl acetate) m/z = 190 $[M]^+$, 175 $[M\text{-}CH_3]^+$, 161 $[M\text{-}2CH_3]^+$, 146 $[M\text{-}2CH_3\text{-}NH_2]^+$, 131, 105, 77; **HR MS** (EI, [u]) found: 190.074 $[M]^+$, calcd: 190.0742; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.25 (d, 1 H, ^3J = 7.3 Hz, H-5), 7.03 (d, 1 H, ^3J = 7.3 Hz, H-6), 5.21 (s, br, 2 H, H-7), 3.08 (s, 3 H, H-10), 2.21 (s, 3 H, H-11); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 170.7 and 168.9 (C-8, C-9), 143.9 (C-4), 135.3 (C-5), 130.9 (C-3), 129.5 (C-2), 112.7 (C-6), 111.3 (C-1), 29.8 (C-10), 23.6 (C-11)

N-(4,6-Dimethyl-2-nitrobiphenyl-3-yl)acetamide (64)



Conditions: 0.35 mmol cyclohexene derivative **36** and 1.75 mmol MnO_2 (85%) in 4 mL toluene were stirred at 110 °C for 24 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:1, R_f = 0.56), yellow solid; **Yield**: 75% ; IR : (ATR), 1/λ [cm^{-1}] = 2920 (m), 2860 (w), 1720 (w), 1607 (m), 1486 (m), 1441 (m), 1383 (m), 1250 (m), 1223 (s), 1061 (s), 926 (m), 759 (s), 700 (s); **LR MS** (ESI, MeOH), m/z = 238 $[M\text{-}NO_2]^+$, 223 $[M\text{-}NO_2\text{-}CH_3]^+$, 213, 186, 137, 129, 105; **^{1}H-NMR** (500 MHz, MeOD d_4), δ = 7.46 - 7.35 (m, 5 H, H-Arom.), 7.08 (s, 1 H, H-5), 2.54 (s, 3 H, H 9), 2.52 and 2.27 (2s, 6 H, H-10, H-11), H-7 obscured; **^{13}C-NMR** (125 MHz, APT, MeOD d_4), δ = 165.1 (C-8), 150.5 (C-2), 138.9, 136.4 and 133.5 (3 C_q), 131.0 and 129.4 ($C\text{-}H_{Arom}$), 128.7 (C_q), 128.6 and 128.5 ($C\text{-}H_{Arom}$), 123.7 (C_q), 19.8 (C-9), 16.3 and 14.1 (C-10, C-11)

5-Methyl-2-nitrobiphenyl (65)



Conditions: 1.0 mmol cyclohexene derivative **37** and 5.0 mmol MnO_2 (85%) in 7 mL toluene were stirred at 110 °C for 12 h; **Work-up:** crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:3, R_f = 0.49), yellow oil; **Yield**: 77% ; **mp** 130 °C ; **IR** (ATR), 1/λ [cm^{-1}] = 3027 (w), 1517 (s), 1443 (w), 1348 (s), 1280 (w), 1227 (w), 1074 (w), 828 (s), 767 (s), 752 (s); **LR MS** (EI, ethyl acetate) m/z = 213 $[M]^+$, 198 $[M\text{-}CH_3]^+$, 185, 168, 151, 128, 113; **HR MS** (EI, [u]) found: 213.079 $[M]^+$, calcd: 213.0790; **^{1}H-NMR** (300 MHz, $CDCl_3$), δ = 7.80 (d, 1 H, ^3J = 8.2 Hz, H-3), 7.42 - 7.39 (m, 3 H, H-Arom.), 7.32 - 7.23 (m, 4 H, H-Arom.), 2.46 (s, 3 H, H-7); **^{13}C-NMR** (75 MHz, APT, $CDCl_3$), δ = 147.2 (C-1), 143.5 (C-5), 137.9 (C-2), 136.7 (C-8), 132.7 (C-4), 128.8 bis 127.9 (6 $C\text{-}H_{Arom}$), 124.5 (C-3), 21.5 (C-7)

Crystal Structure Data

The following crystal structures have been deposited at the Cambridge Crystallographic Data Centre. The allocated deposition number is indicated in the paragraph (CCDC).

Data for **19**

CCDC	832710
Empirical formula	$C_{12}H_{16}N_2O_3$
Formula weight	236.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 10.9806(6) Å, α = 90 deg. b = 8.1088(4) Å, β= 90 deg. c = 26.2218(15) Å, γ = 90 deg.
Volume	2334.8(2) Å^3
Z, Calculated density	8, 1.344 Mg/m^3
Absorption coefficient	0.098 mm^-1
F(000)	1008
Crystal size	0.25 x 0.2 x 0.04 mm
Theta range for data collection	1.55 deg. to 27.00 deg.
Limiting indices	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -33 ≤ l ≤ 23
Reflections collected / unique	12480 / 2549 [R(int) = 0.0724]
Reflection observed [I>2σ (I)]	1563
Completeness to theta = 27.00	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2549 / 0 / 172
Goodness-of-fit on F^2	1.009
Final R indices [I>2σ (I)]	R1 = 0.0412, wR2 = 0.0945
R indices (all data)	R1 = 0.0900, wR2 = 0.1257
Largest diff. peak and hole	0.190 and -0.248 e. Å^-3

Table 1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **19**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

.	x	y	z	U(eq)
O(1)	2632(1)	1166(2)	1357(1)	29(1)
O(2)	164(1)	-2334(2)	2238(1)	36(1)
O(3)	-127(1)	2760(2)	-141(1)	28(1)
N(1)	1563(1)	-554(2)	1890(1)	25(1)
N(2)	1153(2)	2021(2)	496(1)	24(1)
C(1)	1806(2)	177(2)	1429(1)	23(1)
C(2)	542(2)	-1574(2)	1873(1)	26(1)
C(3)	11(2)	-1515(2)	1342(1)	23(1)
C(4)	896(2)	-434(2)	1038(1)	21(1)
C(5)	261(2)	1038(2)	772(1)	22(1)
C(6)	889(2)	2823(2)	58(1)	23(1)
C(7)	1916(2)	3817(2)	-169(1)	27(1)
C(8)	-474(2)	1967(2)	1173(1)	22(1)
C(9)	-1223(2)	1050(2)	1452(1)	26(1)
C(10)	-1286(2)	-781(2)	1363(1)	27(1)
C(11)	-276(2)	3782(2)	1247(1)	30(1)
C(12)	2272(2)	-283(4)	2351(1)	37(1)

Table 2 Anisotropic displacement parameters (A^2 x 10^3) for **19**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
O(1)	22(1)	29(1)	37(1)	5(1)	-5(1)	-5(1)
O(2)	37(1)	36(1)	33(1)	9(1)	4(1)	-3(1)
O(3)	24(1)	31(1)	30(1)	2(1)	-6(1)	-2(1)
N(1)	26(1)	23(1)	25(1)	2(1)	-3(1)	-1(1)
N(2)	17(1)	26(1)	28(1)	3(1)	-2(1)	-3(1)
C(1)	19(1)	21(1)	31(1)	1(1)	0(1)	4(1)
C(2)	27(1)	20(1)	31(1)	1(1)	4(1)	3(1)
C(3)	22(1)	19(1)	28(1)	1(1)	1(1)	-1(1)
C(4)	18(1)	21(1)	26(1)	-2(1)	1(1)	1(1)
C(5)	17(1)	22(1)	27(1)	1(1)	-2(1)	-1(1)
C(6)	22(1)	21(1)	25(1)	-3(1)	0(1)	2(1)
C(7)	24(1)	30(1)	27(1)	3(1)	0(1)	-1(1)
C(8)	16(1)	24(1)	27(1)	1(1)	-3(1)	2(1)
C(9)	19(1)	27(1)	31(1)	-3(1)	1(1)	5(1)
C(10)	17(1)	29(1)	34(1)	2(1)	2(1)	-3(1)
C(11)	27(1)	24(1)	38(1)	0(1)	1(1)	3(1)
C(12)	41(2)	39(2)	32(2)	4(1)	-11(1)	-4(1)

Table 3 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **19**.

	x	y	z	U(eq)
H(1)	1920(20)	2090(20)	653(8)	30(6)
H(3)	-15	-2650	1194	28
H(4)	1325	-1123	778	26
H(5)	-325	579	517	26
H(7A)	1903	3708	-541	41
H(7B)	2695	3408	-38	41
H(7C)	1818	4980	-76	41
H(9)	-1717	1548	1707	31
H(10A)	-1713	-1005	1038	32
H(10B)	-1753	-1310	1642	32
H(11A)	-862	4203	1498	45
H(11B)	-393	4355	922	45
H(11C)	554	3975	1371	45
H(12A)	2960(20)	420(30)	2281(10)	57(8)
H(12B)	2600(30)	-1290(40)	2454(12)	79(10)
H(12C)	1770(30)	240(40)	2639(12)	75(9)

Data for *syn*-**23a**

CCDC	832711
Empirical formula	$C_{17}H_{24}N_2O_3$
Formula weight	304.38
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.9089(7) Å, α = 90.566(5) deg.
	b = 9.6396(9) Å, β = 97.780(5) deg.
	c = 10.547(8) Å, γ = 97.777(4) deg.

Volume	789.1(6) Å^3
Z, Calculated density	2, 1.281 Mg/m^3
Absorption coefficient	0.088 mm^-1
F(000)	328
Crystal size	0.15 x 0.15 x 0.07 mm
Theta range for data collection	1.95 deg. to 27.00 deg.
Limiting indices	-10 ≤ h ≤ 10, -9 ≤ k ≤ 12, -12 ≤ l ≤ 13
Reflections collected / unique	4616 / 3433 [R(int) = 0.0274]
Reflection observed [I>2σ(I)]	2229
Completeness to theta = 27.00	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3433 / 0 / 208
Goodness-of-fit on F^2	1.060
Final R indices [I>2σ(I)]	R1 = 0.0514, wR2 = 0.1151
R indices (all data)	R1 = 0.0923, wR2 = 0.1290
Largest diff. peak and hole	0.477 and -0.290 e. Å^-3

Table 4 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for *syn*-**23a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	-324(2)	1413(1)	1768(1)	30(1)
O(2)	2287(2)	5005(1)	-337(1)	30(1)
O(3)	561(2)	3380(1)	6384(1)	30(1)
N(1)	1082(2)	2994(2)	519(1)	23(1)
N(2)	180(2)	2435(2)	4390(2)	24(1)
C(1)	365(2)	2597(2)	1605(2)	23(1)
C(2)	1772(2)	4403(2)	575(2)	23(1)
C(3)	1738(2)	5001(2)	1896(2)	21(1)
C(4)	555(2)	3867(2)	2495(2)	22(1)
C(5)	1295(2)	3545(2)	3874(2)	22(1)
C(6)	-93(2)	2424(2)	5620(2)	22(1)
C(7)	-1256(3)	1186(2)	6015(2)	29(1)
C(8)	3099(2)	3218(2)	3852(2)	23(1)
C(9)	4204(2)	4048(2)	3256(2)	22(1)
C(10)	3555(3)	5369(2)	2689(2)	27(1)
C(11)	4847(3)	6295(2)	1998(2)	31(1)
C(12)	4203(3)	7622(2)	1524(2)	27(1)
C(13)	4723(3)	8930(2)	1967(2)	26(1)
C(14)	3934(3)	10141(2)	1356(2)	34(1)
C(15)	6097(3)	9338(2)	3077(2)	36(1)
C(16)	5996(3)	3763(2)	3167(2)	30(1)
C(17)	1032(3)	2082(2)	-599(2)	31(1)

Table 5 Anisotropic displacement parameters (A^2 x 10^3) for *syn*-**23a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
O(1)	36(1)	25(1)	26(1)	1(1)	6(1)	-4(1)

O(2)	36(1)	30(1)	24(1)	6(1)	10(1)	3(1)
O(3)	40(1)	27(1)	22(1)	-1(1)	8(1)	1(1)
N(1)	28(1)	22(1)	19(1)	1(1)	7(1)	3(1)
N(2)	29(1)	22(1)	20(1)	-3(1)	7(1)	-2(1)
C(1)	21(1)	25(1)	22(1)	3(1)	2(1)	4(1)
C(2)	20(1)	24(1)	25(1)	4(1)	4(1)	6(1)
C(3)	21(1)	20(1)	21(1)	3(1)	3(1)	3(1)
C(4)	22(1)	22(1)	22(1)	1(1)	6(1)	3(1)
C(5)	25(1)	22(1)	19(1)	1(1)	6(1)	1(1)
C(6)	23(1)	25(1)	21(1)	1(1)	6(1)	7(1)
C(7)	33(1)	29(1)	26(1)	2(1)	11(1)	2(1)
C(8)	25(1)	24(1)	21(1)	2(1)	3(1)	6(1)
C(9)	23(1)	23(1)	21(1)	-2(1)	2(1)	2(1)
C(10)	27(1)	26(1)	27(1)	4(1)	3(1)	2(1)
C(11)	26(1)	29(1)	38(1)	4(1)	6(1)	4(1)
C(12)	22(1)	27(1)	34(1)	6(1)	4(1)	3(1)
C(13)	23(1)	28(1)	27(1)	6(1)	10(1)	4(1)
C(14)	39(1)	26(1)	40(1)	6(1)	9(1)	6(1)
C(15)	37(1)	30(1)	40(1)	3(1)	4(1)	0(1)
C(16)	26(1)	28(1)	36(1)	3(1)	5(1)	4(1)
C(17)	40(1)	30(1)	23(1)	-2(1)	5(1)	7(1)

Table 6 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for *syn*-**23a**.

	x	y	z	U(eq)
H(3)	1174	5869	1813	25
H(4)	-598	4182	2501	26
H(5)	1362	4410	4420	26
H(7A)	-628	710	6707	43
H(7B)	-1637	535	5281	43
H(7C)	-2262	1506	6314	43
H(8)	3451	2413	4267	28
H(10)	3381	5948	3441	32
H(11A)	5933	6540	2589	37
H(11B)	5108	5757	1261	37
H(12)	3310	7513	817	33
H(14A)	3104	9798	607	51
H(14B)	4842	10825	1089	51
H(14C)	3343	10587	1975	51
H(15A)	6590	8505	3389	54
H(15B)	5598	9757	3765	54
H(15C)	7004	10019	2804	54
H(16A)	6187	2886	3592	45
H(16B)	6824	4534	3587	45
H(16C)	6153	3680	2265	45
H(17A)	789	2607	-1378	46
H(17B)	125	1284	-585	46
H(17C)	2147	1742	-585	46
H(1X)	-310(20)	1775(19)	3848(17)	24(5)

Data for **24**

CCDC	832712
Empirical formula	$C_{12}H_{15}BrN_2O_3$
Formula weight	315.17
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 10.8021(12) Å, α = 90 deg. b = 10.5357(7) Å, β = 124.200(6) deg. c = 13.5435(12) Å, γ = 90 deg.
Volume	1274.8(2) Å^3
Z, Calculated density	4, 1.642 Mg/m^3
Absorption coefficient	3.227 mm^-1
F(000)	640
Crystal size	0.2 x 0.2 x 0.03 mm
Theta range for data collection	2.28 deg. to 26.99 deg.
Limiting indices	-13 ≤ h ≤13, -11 ≤ k ≤ 13, -13 ≤ l ≤ 17
Reflections collected / unique	6562 / 2769 [R(int) = 0.0445]
Reflection observed [I>2σ(I)]	2063
Completeness to theta = 26.99	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2769 / 0 / 170
Goodness-of-fit on F^2	1.012
Final R indices [I>2σ(I)]	R1 = 0.0372, wR2 = 0.0777
R indices (all data)	R1 = 0.0608, wR2 = 0.0840
Largest diff. peak and hole	0.542 and -0.633 e. Å^-3

Table 7 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **24**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br(1)	2410(1)	-793(1)	-4647(1)	23(1)
O(1)	2388(3)	1504(2)	-2605(2)	24(1)
O(2)	4398(3)	-2966(2)	-1200(2)	23(1)
O(3)	189(3)	-5376(2)	-3214(2)	25(1)
N(1)	3299(3)	-487(2)	-2062(2)	19(1)
N(2)	2474(3)	-4385(2)	-2178(2)	17(1)
C(1)	1342(4)	-1474(3)	-4035(3)	17(1)
C(2)	1851(4)	-1088(2)	-2777(3)	16(1)
C(3)	3468(4)	783(3)	-2054(3)	18(1)
C(4)	5040(4)	1270(3)	-1335(3)	25(1)
C(5)	1800(3)	-2275(2)	-2127(3)	16(1)
C(6)	3075(4)	-3192(3)	-1765(3)	19(1)
C(7)	925(4)	-4413(3)	-2809(3)	20(1)
C(8)	357(3)	-3077(3)	-2873(3)	17(1)
C(9)	-716(3)	-2571(3)	-4166(3)	20(1)
C(10)	156(4)	-2186(3)	-4680(3)	21(1)

C(11)	-2026(4)	-3445(3)	-4980(3)	30(1)
C(12)	3404(4)	-5517(3)	-1869(3)	24(1)

Table 8 Anisotropic displacement parameters (A^2 x 10^3) for **24**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
Br(1)	28(1)	22(1)	26(1)	0(1)	19(1)	-2(1)
O(1)	25(2)	14(1)	31(1)	2(1)	15(1)	2(1)
O(2)	18(1)	17(1)	30(1)	0(1)	11(1)	0(1)
O(3)	26(1)	17(1)	33(1)	-2(1)	16(1)	-6(1)
N(1)	17(2)	14(1)	22(2)	1(1)	9(1)	2(1)
N(2)	19(2)	13(1)	21(1)	1(1)	12(1)	1(1)
C(1)	19(2)	14(2)	23(2)	4(1)	14(2)	3(1)
C(2)	16(2)	15(2)	19(2)	3(1)	11(2)	1(1)
C(3)	23(2)	15(2)	18(2)	-4(1)	13(2)	-2(2)
C(4)	24(2)	19(2)	28(2)	-3(1)	12(2)	-5(1)
C(5)	24(2)	14(1)	18(2)	-2(1)	15(2)	0(1)
C(6)	27(2)	16(2)	18(2)	1(1)	15(2)	0(1)
C(7)	26(2)	20(2)	22(2)	0(1)	18(2)	-3(1)
C(8)	17(2)	15(2)	23(2)	0(1)	14(2)	0(1)
C(9)	17(2)	19(2)	23(2)	0(1)	11(2)	-1(1)
C(10)	25(2)	18(2)	21(2)	4(1)	14(2)	2(1)
C(11)	24(2)	38(2)	24(2)	0(2)	12(2)	-7(2)
C(12)	26(2)	15(2)	31(2)	1(1)	16(2)	2(1)

Table 9 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **24**.

	x	y	z	U(eq)
H(1)	4020(40)	-840(30)	-1760(30)	14(10)
H(2)	1098	-472	-2853	20
H(4A)	5249	1718	-1860	38
H(4B)	5735	556	-953	38
H(4C)	5167	1854	-722	38
H(5)	1886	-1987	-1387	20
H(8)	-182	-3067	-2468	20
H(9)	-1162	-1773	-4096	24
H(10)	-151	-2454	-5455	25
H(11A)	-2729	-3010	-5736	44
H(11B)	-2536	-3672	-4593	44
H(11C)	-1656	-4217	-5137	44
H(12A)	4130	-5383	-2076	36
H(12B)	2768	-6246	-2314	36
H(12C)	3936	-5680	-1011	36

Data for **33a**

CCDC	832706
Empirical formula	$C_{26}H_{37}NO_6$
Formula weight	459.57
Temperature	100(2) K

Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P21/c
Unit cell dimensions	a = 13.7746(9) Å, α = 90 deg.
	b = 11.7176(8) Å, β= 127.838(4) deg.
	c = 19.9018(12) Å, γ= 90 deg.
Volume	2536.9(3) Å^3
Z, Calculated density	4, 1.203 Mg/m^3
Absorption coefficient	0.085 mm^-1
F(000)	992
Crystal size	0.4 x 0.4 x 0.3 mm
Theta range for data collection	2.07 deg. to 27.00 deg.
Limiting indices	-17 ≤ h ≤ 14, -13 ≤ k ≤ 14, -20 ≤ l ≤ 15
Reflections collected / unique	11443 / 5508 [R(int) = 0.0478]
Reflection observed [I>2sigma(I)]	2887
Completeness to theta = 27.00	99.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5508 / 0 / 308
Goodness-of-fit on F^2	0.838
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.0746
R indices (all data)	R1 = 0.1128, wR2 = 0.0866
Largest diff. peak and hole	0.194 and -0.214 e.A^-3

Table 10 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **33a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	5928(1)	-997(1)	-261(1)	25(1)
O(2)	4470(1)	-2154(1)	-412(1)	28(1)
O(3)	5605(1)	-4155(1)	-964(1)	21(1)
O(4)	3784(1)	-4977(1)	-1494(1)	26(1)
O(5)	2158(1)	-5867(1)	-3847(1)	23(1)
O(6)	4200(1)	-5584(1)	-2912(1)	22(1)
N(1)	4476(1)	-1728(1)	-1526(1)	19(1)
C(1)	4910(1)	-1687(1)	-709(1)	21(1)
C(2)	3426(1)	-2432(1)	-2158(1)	18(1)
C(3)	3870(1)	-3540(1)	-2318(1)	17(1)
C(4)	4397(1)	-4320(1)	-1560(1)	20(1)
C(5)	6165(1)	-4757(2)	-155(1)	24(1)
C(6)	7535(1)	-4648(2)	347(1)	30(1)
C(7)	2803(1)	-4115(1)	-3129(1)	17(1)
C(8)	3157(1)	-5255(1)	-3265(1)	18(1)
C(9)	2375(1)	-6980(1)	-4060(1)	24(1)
C(10)	1138(1)	-7550(1)	-4628(1)	30(1)
C(11)	2222(1)	-3351(1)	-3929(1)	18(1)
C(12)	2023(1)	-2176(1)	-3731(1)	19(1)
C(13)	2521(1)	-1750(1)	-2965(1)	17(1)
C(14)	2193(1)	-569(1)	-2836(1)	20(1)
C(15)	2943(1)	368(1)	-2858(1)	28(1)
C(16)	821(1)	-292(1)	-3475(1)	26(1)
C(17)	2877(1)	-3352(1)	-4342(1)	22(1)
C(18)	4091(1)	-2698(2)	-3850(1)	30(1)

C(19)	2003(1)	-2889(2)	-5253(1)	31(1)
C(20)	6438(1)	-751(2)	614(1)	29(1)
C(21)	7579(1)	-1438(2)	1235(1)	23(1)
C(22)	7537(1)	-2406(2)	1609(1)	34(1)
C(23)	8586(2)	-3011(2)	2197(1)	45(1)
C(24)	9696(2)	-2668(2)	2415(1)	48(1)
C(25)	9762(2)	-1707(2)	2040(1)	49(1)
C(26)	6895(1)	-1084(2)	1449(1)	38(1)

Table 11 Anisotropic displacement parameters (A^2 x 10^3) for **33a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
O(1)	21(1)	32(1)	16(1)	-8(1)	8(1)	-6(1)
O(2)	31(1)	38(1)	21(1)	0(1)	19(1)	-4(1)
O(3)	19(1)	25(1)	16(1)	4(1)	9(1)	0(1)
O(4)	25(1)	29(1)	23(1)	2(1)	14(1)	-6(1)
O(5)	19(1)	16(1)	27(1)	-5(1)	11(1)	-2(1)
O(6)	18(1)	24(1)	22(1)	-1(1)	11(1)	1(1)
N(1)	18(1)	23(1)	15(1)	-1(1)	10(1)	-4(1)
C(1)	19(1)	21(1)	19(1)	-1(1)	10(1)	4(1)
C(2)	16(1)	20(1)	16(1)	-4(1)	10(1)	-6(1)
C(3)	17(1)	19(1)	17(1)	1(1)	11(1)	0(1)
C(4)	21(1)	20(1)	21(1)	-4(1)	14(1)	0(1)
C(5)	25(1)	26(1)	17(1)	6(1)	11(1)	1(1)
C(6)	27(1)	33(1)	22(1)	6(1)	12(1)	4(1)
C(7)	16(1)	17(1)	18(1)	-1(1)	11(1)	-2(1)
C(8)	21(1)	20(1)	13(1)	2(1)	11(1)	-2(1)
C(9)	26(1)	17(1)	29(1)	-5(1)	16(1)	0(1)
C(10)	25(1)	26(1)	36(1)	-10(1)	16(1)	-5(1)
C(11)	16(1)	18(1)	15(1)	-2(1)	7(1)	1(1)
C(12)	16(1)	19(1)	19(1)	4(1)	10(1)	3(1)
C(13)	14(1)	18(1)	19(1)	0(1)	11(1)	-2(1)
C(14)	20(1)	20(1)	17(1)	-2(1)	11(1)	-1(1)
C(15)	29(1)	19(1)	36(1)	-1(1)	20(1)	1(1)
C(16)	25(1)	23(1)	30(1)	-1(1)	16(1)	4(1)
C(17)	28(1)	22(1)	18(1)	3(1)	15(1)	7(1)
C(18)	28(1)	44(1)	24(1)	4(1)	18(1)	3(1)
C(19)	35(1)	36(1)	21(1)	1(1)	16(1)	3(1)
C(20)	28(1)	35(1)	19(1)	-11(1)	12(1)	-1(1)
C(21)	23(1)	25(1)	15(1)	-5(1)	9(1)	2(1)
C(22)	40(1)	33(1)	30(1)	-3(1)	21(1)	-1(1)
C(23)	56(2)	44(1)	36(1)	5(1)	28(1)	13(1)
C(24)	49(2)	62(2)	23(1)	9(1)	17(1)	30(1)
C(25)	25(1)	82(2)	36(1)	0(1)	16(1)	7(1)
C(26)	33(1)	48(1)	31(1)	3(1)	20(1)	-1(1)

Table 12 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **33a**.

	x	y	z	U(eq)
H(1A)	6554(11)	1394(13)	1664(10)	21(5)
H(2)	4913	2658	1916	21
H(3)	6898	3348	2373	21
H(5A)	6182	5571	261	29
H(5B)	5737	4411	-160	29
H(6A)	7760	4989	-26	45
H(6B)	7053	5043	-893	45
H(6C)	7314	3839	-449	45
H(7)	5213	4257	3061	20
H(9A)	6481	7437	3538	29
H(9B)	7096	6893	4359	29
H(10A)	5110	7611	4328	46
H(10B)	6014	8314	4780	46
H(10C)	5738	7095	5146	46
H(11)	5750	3670	4367	21
H(12)	5691	1688	4203	22
H(14)	4665	558	2256	24
H(15A)	6181	-373	3417	43
H(15B)	6237	-223	2416	43
H(15C)	5481	-1109	2756	43
H(16A)	4643	205	4044	40
H(16B)	3956	-419	3309	40
H(16C)	3822	915	3481	40
H(17)	7441	4164	4381	27
H(18A)	8570	2643	4196	45
H(18B)	8027	3101	3319	45
H(18C)	7688	1929	3719	45
H(19A)	7040	2092	5238	46
H(19B)	6825	3345	5578	46
H(19C)	7926	2936	5524	46
H(20A)	5117	923	-698	35
H(20B)	5910	-72	-728	35
H(22)	5312	2658	-1458	41
H(23)	6087	3671	-2454	54
H(24)	7596	3088	-2823	58
H(25)	8344	1471	-2185	59
H(26)	7543	420	-1194	45

Data for **33b**

CCDC	832707
Empirical formula	$C_{26}H_{37}NO_6$
Formula weight	459.57
Temperature	100(2) K

Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P212121
Unit cell dimensions	a = 10.4445(10) A, α = 90 deg.
	b = 14.899(2) A, β = 90 deg.
	c = 16.596(2) A, γ = 90 deg.
Volume	2582.5(5) A^3
Z, Calculated density	4, 1.182 Mg/m^3
Absorption coefficient	0.083 mm^-1
F(000)	992
Crystal size	0.3 x 0.03 x 0.03 mm
Theta range for data collection	1.84 deg. to 25.00 deg.
Limiting indices	-12<=h<=10, -13<=k<=17, -19<=l<=18
Reflections collected / unique	11965 / 2590 [R(int) = 0.1433]
Reflection observed [I>2sigma(I)]	1275
Completeness to theta = 25.00	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2590 / 0 / 308
Goodness-of-fit on F^2	0.909
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1058
R indices (all data)	R1 = 0.1486, wR2 = 0.1299
Absolute structure parameter	-2(2)
Largest diff. peak and hole	0.357 and -0.217 e.A^-3

Table 13 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **33b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	-7585(3)	-45(2)	1332(2)	39(1)
O(2)	-5598(3)	-573(2)	1632(2)	39(1)
O(3)	-4171(3)	-12(3)	3(2)	46(1)
O(4)	-5062(4)	1052(3)	-739(3)	64(1)
O(5)	-4876(4)	3028(3)	-979(2)	45(1)
O(6)	-2825(4)	2643(2)	-766(2)	43(1)
N(1)	-5941(4)	879(3)	1236(3)	33(1)
C(1)	-6289(5)	37(4)	1419(3)	33(1)
C(2)	-4600(4)	1180(4)	1305(4)	36(2)
C(3)	-4042(5)	1467(4)	493(3)	39(2)
C(4)	-4465(5)	824(4)	-160(4)	36(2)
C(5)	-4697(7)	-686(4)	-546(4)	73(2)
C(6)	-4431(7)	-1595(5)	-223(4)	85(2)
C(7)	-4390(5)	2428(4)	308(3)	39(2)
C(8)	-3927(6)	2698(4)	-535(4)	39(2)
C(9)	-4567(5)	3241(4)	-1810(3)	43(2)
C(10)	-5822(5)	3364(4)	-2228(4)	58(2)
C(11)	-3782(5)	3063(4)	924(3)	35(1)
C(12)	-4104(4)	2737(4)	1752(3)	36(2)

C(13)	-4498(4)	1901(4)	1942(3)	31(1)
C(14)	-4900(5)	1642(4)	2787(3)	35(2)
C(15)	-3835(5)	1747(4)	3398(3)	58(2)
C(16)	-6075(6)	2167(4)	3060(4)	56(2)
C(17)	-4171(5)	4052(4)	792(4)	41(2)
C(18)	-3306(5)	4683(3)	1243(4)	52(2)
C(19)	-5576(5)	4231(4)	1019(4)	58(2)
C(20)	-8063(4)	-950(4)	1494(4)	45(2)
C(21)	-9499(5)	-877(4)	1556(4)	35(2)
C(22)	-10102(5)	-951(4)	2282(4)	46(2)
C(23)	-11438(6)	-908(4)	2334(5)	61(2)
C(24)	-12145(6)	-777(4)	1635(6)	69(2)
C(25)	-11528(6)	-689(4)	911(5)	69(2)
C(26)	-10210(5)	-748(4)	861(4)	54(2)

Table 14 Anisotropic displacement parameters (A^2 x 10^3) for **33b**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
O(1)	27(2)	36(2)	53(3)	3(2)	-2(2)	-3(2)
O(2)	36(2)	33(3)	49(3)	8(2)	-1(2)	4(2)
O(3)	55(2)	36(3)	47(3)	-4(2)	-5(2)	6(2)
O(4)	93(3)	54(3)	46(3)	-1(3)	-22(3)	3(3)
O(5)	46(2)	62(3)	27(3)	10(2)	1(2)	-10(2)
O(6)	45(2)	43(3)	41(3)	2(2)	1(2)	2(2)
N(1)	30(3)	24(3)	44(3)	4(3)	-5(2)	8(2)
C(1)	41(4)	33(4)	25(4)	-5(4)	-3(3)	2(3)
C(2)	31(3)	33(4)	44(4)	11(3)	0(3)	-1(2)
C(3)	40(3)	40(4)	37(4)	-1(3)	1(3)	1(3)
C(4)	41(3)	37(4)	31(4)	11(4)	-8(3)	-4(3)
C(5)	134(6)	34(4)	51(5)	-18(4)	-14(5)	-5(4)
C(6)	114(6)	70(6)	72(6)	-11(5)	-4(5)	-4(5)
C(7)	53(4)	37(4)	27(4)	2(3)	6(3)	-4(3)
C(8)	45(4)	34(4)	38(4)	3(3)	-8(4)	-8(3)
C(9)	47(4)	44(4)	38(4)	6(3)	3(3)	-10(3)
C(10)	54(4)	67(5)	54(5)	-8(4)	-14(4)	2(4)
C(11)	45(3)	34(4)	26(4)	3(3)	-4(3)	-14(3)
C(12)	34(3)	42(4)	34(4)	-1(3)	-8(3)	-2(3)
C(13)	26(3)	39(4)	27(4)	-2(3)	-1(3)	1(3)
C(14)	32(3)	35(4)	37(4)	-1(3)	0(3)	2(3)
C(15)	54(4)	80(5)	39(4)	20(4)	-7(3)	-17(4)
C(16)	66(4)	57(5)	47(4)	12(4)	23(4)	16(4)
C(17)	45(3)	39(4)	40(4)	19(4)	-1(3)	-4(3)
C(18)	60(4)	30(4)	65(5)	0(4)	15(4)	-2(3)
C(19)	54(4)	44(4)	75(5)	19(4)	11(4)	9(3)
C(20)	36(3)	40(4)	59(5)	1(4)	0(3)	1(3)
C(21)	31(3)	32(4)	42(4)	9(3)	-3(3)	-7(3)
C(22)	38(3)	47(4)	54(5)	8(4)	0(3)	-2(3)
C(23)	53(4)	38(5)	93(7)	11(4)	24(4)	-2(3)
C(24)	29(3)	47(5)	133(8)	28(5)	-7(5)	0(3)

C(25)	53(5)	57(5)	96(7)	31(5)	-26(4)	-16(3)
C(26)	43(4)	55(4)	66(5)	7(4)	-15(4)	-7(3)

Table 15 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **33b**.

	x	y	z	U(eq)
H(1A)	-6570(40)	1270(30)	1200(30)	38(17)
H(2)	-4088	655	1497	43
H(3)	-3089	1430	533	47
H(5A)	-4302	-620	-1085	88
H(5B)	-5633	-599	-602	88
H(6A)	-3504	-1681	-178	128
H(6B)	-4788	-2047	-588	128
H(6C)	-4825	-1656	310	128
H(7)	-5342	2494	332	47
H(9A)	-4075	2746	-2061	51
H(9B)	-4051	3798	-1840	51
H(10A)	-6344	2823	-2160	87
H(10B)	-5673	3470	-2804	87
H(10C)	-6271	3880	-1996	87
H(11)	-2832	3023	859	42
H(12)	-4025	3156	2181	44
H(14)	-5142	993	2775	42
H(15A)	-3107	1371	3241	86
H(15B)	-4143	1562	3930	86
H(15C)	-3565	2377	3418	86
H(16A)	-5860	2806	3098	85
H(16B)	-6352	1948	3589	85
H(16C)	-6768	2085	2669	85
H(17)	-4074	4186	205	50
H(18A)	-3453	4618	1823	77
H(18B)	-3491	5302	1080	77
H(18C)	-2412	4541	1119	77
H(19A)	-5695	4127	1598	87
H(19B)	-6134	3826	714	87
H(19C)	-5795	4855	891	87
H(20A)	-7699	-1183	2004	54
H(20B)	-7821	-1362	1051	54
H(22)	-9610	-1032	2757	55
H(23)	-11856	-968	2839	73
H(24)	-13053	-749	1658	83
H(25)	-12014	-585	437	83
H(26)	-9794	-700	353	65

Data for **36**

CCDC	832713
Empirical formula	$C_{16}H_{20}N_2O_3$

Formula weight	288.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 11.9261(5) Å, α = 90 deg.
	b = 17.9405(14) Å, β = 96.061(4) deg.
	c = 15.2365(11) Å, γ = 90 deg.
Volume	3241.8(4) A^3
Z, Calculated density	8, 1.182 Mg/m^3
Absorption coefficient	0.082 mm^-1
F(000)	1232
Crystal size	0.3 x 0.15 x 0.1 mm
Theta range for data collection	2.06 deg. to 27.00 deg.
Limiting indices	-15 ≤ h ≤ 12, -21 ≤ k ≤ 22, -13 ≤ l ≤ 19
Reflections collected / unique	15743 / 7009 [R(int) = 0.0484]
Reflection observed [I>2σ(I)]	3810
Completeness to theta = 27.00	99.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7009 / 0 / 393
Goodness-of-fit on F^2	0.920
Final R indices [I>2σ(I)]	R1 = 0.0504, wR2 = 0.0984
R indices (all data)	R1 = 0.1160, wR2 = 0.1154
Largest diff. peak and hole	0.201 and -0.181 e. Å^-3

Table 16 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **36**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	5464(1)	3149(1)	619(1)	36(1)
O(2)	5436(1)	2141(1)	-166(1)	51(1)
O(3)	3850(1)	1854(1)	1518(1)	41(1)
N(1)	5810(1)	2525(1)	464(1)	32(1)
N(2)	5442(1)	2264(1)	2298(1)	26(1)
C(1)	6724(1)	2187(1)	1100(1)	28(1)
C(2)	6170(1)	1782(1)	1834(1)	28(1)
C(3)	4311(1)	2264(1)	2096(1)	31(1)
C(4)	3653(1)	2802(1)	2594(1)	38(1)
C(5)	7076(2)	1447(1)	2477(1)	29(1)
C(6)	8121(2)	1710(1)	2538(1)	34(1)
C(7)	8537(1)	2348(1)	2030(1)	34(1)
C(8)	7577(1)	2768(1)	1473(1)	27(1)
C(9)	8044(1)	3254(1)	779(1)	26(1)
C(10)	8628(1)	2940(1)	123(1)	32(1)
C(11)	9114(2)	3391(1)	-473(1)	34(1)
C(12)	9018(1)	4155(1)	-435(1)	34(1)
C(13)	8429(1)	4471(1)	206(1)	38(1)
C(14)	7953(1)	4020(1)	808(1)	33(1)
C(15)	9234(2)	2882(2)	2636(2)	61(1)
C(16)	6708(2)	833(1)	3051(1)	37(1)
O(4)	726(1)	1678(1)	1180(1)	33(1)

O(5)	-497(1)	1066(1)	307(1)	43(1)
O(6)	1276(1)	1884(1)	-1163(1)	42(1)
N(3)	433(1)	1129(1)	738(1)	30(1)
N(4)	2420(1)	1447(1)	0(1)	27(1)
C(17)	1260(1)	504(1)	689(1)	26(1)
C(18)	2003(1)	689(1)	-51(1)	29(1)
C(19)	1986(2)	2001(1)	-523(1)	32(1)
C(20)	2412(2)	2766(1)	-273(1)	39(1)
C(21)	2961(1)	137(1)	-34(1)	32(1)
C(22)	3235(1)	-300(1)	653(1)	36(1)
C(23)	2692(1)	-310(1)	1496(1)	35(1)
C(24)	1940(1)	375(1)	1583(1)	27(1)
C(25)	1184(1)	281(1)	2321(1)	29(1)
C(26)	1321(1)	718(1)	3070(1)	35(1)
C(27)	670(2)	605(1)	3761(1)	42(1)
C(28)	-137(2)	49(1)	3704(2)	45(1)
C(29)	-297(2)	-386(1)	2954(2)	43(1)
C(30)	358(1)	-270(1)	2262(1)	36(1)
C(31)	3581(2)	-368(2)	2295(1)	55(1)
C(32)	3551(2)	134(1)	-859(1)	55(1)

Table 17 Anisotropic displacement parameters (A^2 x 10^3) for **36**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
O(1)	34(1)	32(1)	42(1)	4(1)	2(1)	4(1)
O(2)	63(1)	56(1)	31(1)	-11(1)	-12(1)	-2(1)
O(3)	39(1)	46(1)	35(1)	-4(1)	-9(1)	-13(1)
N(1)	36(1)	35(1)	25(1)	1(1)	3(1)	-5(1)
N(2)	25(1)	30(1)	24(1)	-5(1)	-1(1)	-2(1)
C(1)	31(1)	27(1)	24(1)	-1(1)	0(1)	4(1)
C(2)	34(1)	26(1)	23(1)	-4(1)	4(1)	-1(1)
C(3)	32(1)	31(1)	28(1)	8(1)	-2(1)	-6(1)
C(4)	27(1)	38(2)	48(1)	5(1)	4(1)	4(1)
C(5)	37(1)	26(1)	24(1)	-3(1)	7(1)	7(1)
C(6)	38(1)	41(2)	26(1)	5(1)	5(1)	15(1)
C(7)	29(1)	48(2)	26(1)	7(1)	3(1)	4(1)
C(8)	28(1)	29(1)	24(1)	-2(1)	5(1)	2(1)
C(9)	24(1)	29(1)	27(1)	-3(1)	2(1)	2(1)
C(10)	40(1)	28(1)	30(1)	-2(1)	5(1)	4(1)
C(11)	37(1)	37(2)	30(1)	-4(1)	11(1)	3(1)
C(12)	32(1)	37(2)	34(1)	2(1)	8(1)	-5(1)
C(13)	38(1)	25(1)	50(1)	-4(1)	10(1)	-1(1)
C(14)	33(1)	34(2)	36(1)	-8(1)	14(1)	-2(1)
C(15)	52(1)	81(2)	45(2)	17(1)	-14(1)	-29(1)
C(16)	49(1)	33(1)	29(1)	0(1)	4(1)	4(1)
O(4)	32(1)	26(1)	41(1)	-10(1)	3(1)	2(1)
O(5)	27(1)	38(1)	60(1)	-10(1)	-16(1)	6(1)
O(6)	40(1)	50(1)	34(1)	12(1)	-11(1)	-2(1)

N(3)	28(1)	29(1)	32(1)	-3(1)	0(1)	2(1)
N(4)	28(1)	30(1)	22(1)	0(1)	-1(1)	2(1)
C(17)	23(1)	21(1)	35(1)	-6(1)	-1(1)	4(1)
C(18)	30(1)	30(1)	26(1)	-7(1)	-3(1)	0(1)
C(19)	29(1)	40(2)	28(1)	5(1)	6(1)	4(1)
C(20)	41(1)	36(2)	39(1)	6(1)	2(1)	-2(1)
C(21)	29(1)	33(1)	34(1)	-11(1)	0(1)	2(1)
C(22)	26(1)	30(1)	50(2)	-9(1)	1(1)	6(1)
C(23)	30(1)	31(1)	45(1)	6(1)	3(1)	5(1)
C(24)	26(1)	24(1)	31(1)	-1(1)	-1(1)	-1(1)
C(25)	23(1)	29(1)	33(1)	6(1)	-1(1)	2(1)
C(26)	31(1)	39(2)	32(1)	2(1)	-1(1)	-2(1)
C(27)	42(1)	51(2)	30(1)	2(1)	3(1)	5(1)
C(28)	39(1)	54(2)	43(2)	17(1)	11(1)	6(1)
C(29)	34(1)	43(2)	53(2)	10(1)	6(1)	-3(1)
C(30)	31(1)	34(1)	43(1)	2(1)	2(1)	2(1)
C(31)	41(1)	69(2)	52(2)	15(1)	-1(1)	23(1)
C(32)	58(1)	63(2)	44(2)	-13(1)	13(1)	18(1)

Table 18 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **36**.

	x	**y**	**z**	**U(eq)**
H(1)	7132	1807	773	33
H(2)	5700	1366	1557	33
H(4A)	3441	3235	2221	57
H(4B)	4117	2966	3128	57
H(4C)	2971	2557	2758	57
H(6)	8659	1469	2946	41
H(7)	9045	2137	1611	41
H(8)	7197	3100	1878	32
H(10)	8693	2413	84	39
H(11)	9517	3170	-912	41
H(12)	9353	4462	-844	41
H(13)	8349	4997	234	45
H(14)	7556	4244	1249	40
H(15A)	8756	3108	3049	92
H(15B)	9544	3274	2284	92
H(15C)	9853	2610	2968	92
H(16A)	7360	651	3438	55
H(16B)	6389	423	2679	55
H(16C)	6137	1023	3411	55
H(17)	827	38	520	32
H(18)	1528	631	-628	35
H(20A)	2711	3000	-781	58
H(20B)	3012	2729	217	58
H(20C)	1793	3068	-91	58
H(22)	3836	-641	609	43
H(23)	2203	-764	1490	43
H(24)	2436	818	1722	33
H(26)	1872	1103	3113	41
H(27)	778	909	4273	50

H(28)	-579	-33	4178	54
H(29)	-856	-765	2910	52
H(30)	240	-569	1746	43
H(31A)	4037	-817	2242	82
H(31B)	3206	-396	2836	82
H(31C)	4069	73	2318	82
H(32A)	4191	-211	-784	82
H(32B)	3822	637	-969	82
H(32C)	3023	-27	-1360	82
H(1X)	2902(16)	1580(12)	486(13)	49(6)
H(2X)	5739(15)	2524(12)	2774(13)	45(6)

Data for **40**

CCDC	832708
Empirical formula	$C_{18}H_{25}NO_5$
Formula weight	335.39
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P21/c
Unit cell dimensions	a = 8.3411(13) Å, α = 90 deg.
	b = 17.2794(17) Å, β = 98.713(5) deg.
	c = 12.2343(19) Å, γ = 90 deg.
Volume	1743.0(4) Å^3
Z, Calculated density	4, 1.278 Mg/m^3
Absorption coefficient	0.093 mm^-1
F(000)	720
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	2.06 deg. to 27.00 deg.
Limiting indices	-10 ≤ h ≤ 10, -17 ≤ k ≤ 20, -15 ≤ l ≤ 10
Reflections collected / unique	7318 / 3532 [R(int) = 0.0418]
Reflection observed [I>2σ(I)]	1932
Completeness to theta = 27.00	92.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3532 / 0 / 240
Goodness-of-fit on F^2	0.879
Final R indices [I>2σ(I)]	R1 = 0.0456, wR2 = 0.0945
R indices (all data)	R1 = 0.1036, wR2 = 0.1098
Largest diff. peak and hole	0.261 and -0.226 e. Å^-3

Table 19 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **40**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	**y**	**z**	**U(eq)**
O(1)	6248(2)	-465(1)	1785(1)	27(1)
O(2)	6864(2)	140(1)	3421(1)	25(1)
O(3)	3747(2)	731(1)	2196(1)	29(1)
O(4)	10177(2)	53(1)	2848(1)	26(1)

O(5)	10355(2)	1060(1)	4035(1)	31(1)
N(1)	4652(2)	870(1)	546(2)	23(1)
C(1)	6701(2)	108(1)	2319(2)	23(1)
C(2)	6354(3)	-552(1)	3947(2)	32(1)
C(3)	7207(2)	848(1)	1835(2)	21(1)
C(4)	6199(2)	1193(1)	954(2)	22(1)
C(5)	3529(3)	654(1)	1183(2)	25(1)
C(6)	2014(2)	299(1)	568(2)	31(1)
C(7)	6727(2)	1857(1)	440(2)	22(1)
C(8)	8267(3)	2142(1)	843(2)	24(1)
C(9)	9294(2)	1821(1)	1727(2)	23(1)
C(10)	8725(2)	1166(1)	2231(2)	23(1)
C(11)	9824(2)	772(1)	3155(2)	25(1)
C(12)	11336(3)	-366(1)	3630(2)	34(1)
C(13)	10982(3)	2153(1)	2111(2)	26(1)
C(14)	10921(3)	2805(1)	2946(2)	36(1)
C(15)	11804(3)	2431(1)	1142(2)	35(1)
C(16)	5705(3)	2244(1)	-539(2)	26(1)
C(17)	6289(3)	2025(1)	-1620(2)	36(1)
C(18)	5671(3)	3126(1)	-420(2)	44(1)

Table 20 Anisotropic displacement parameters (A^2 x 10^3) for **40**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
O(1)	29(1)	25(1)	28(1)	-3(1)	7(1)	-3(1)
O(2)	27(1)	26(1)	23(1)	2(1)	7(1)	-4(1)
O(3)	27(1)	35(1)	26(1)	-2(1)	9(1)	0(1)
O(4)	23(1)	27(1)	28(1)	1(1)	3(1)	3(1)
O(5)	35(1)	33(1)	25(1)	1(1)	2(1)	-3(1)
N(1)	20(1)	29(1)	21(1)	-2(1)	6(1)	-1(1)
C(1)	17(1)	30(1)	23(1)	-1(1)	4(1)	2(1)
C(2)	37(1)	31(1)	30(1)	8(1)	8(1)	-7(1)
C(3)	19(1)	23(1)	23(1)	-2(1)	7(1)	0(1)
C(4)	20(1)	24(1)	24(1)	-4(1)	8(1)	0(1)
C(5)	21(1)	25(1)	30(1)	-2(1)	7(1)	4(1)
C(6)	25(1)	36(1)	35(1)	-6(1)	10(1)	-4(1)
C(7)	20(1)	24(1)	23(1)	-2(1)	7(1)	4(1)
C(8)	22(1)	24(1)	28(1)	3(1)	9(1)	0(1)
C(9)	21(1)	26(1)	24(1)	-3(1)	8(1)	0(1)
C(10)	22(1)	26(1)	22(1)	-2(1)	6(1)	1(1)
C(11)	20(1)	25(1)	30(1)	1(1)	9(1)	-4(1)
C(12)	30(1)	36(1)	34(1)	4(1)	1(1)	6(1)
C(13)	21(1)	25(1)	32(1)	5(1)	6(1)	1(1)
C(14)	30(1)	36(1)	40(2)	-3(1)	2(1)	-4(1)
C(15)	24(1)	42(1)	39(2)	9(1)	8(1)	-6(1)
C(16)	20(1)	31(1)	29(1)	3(1)	6(1)	-1(1)
C(17)	35(1)	45(1)	27(1)	2(1)	4(1)	-1(1)
C(18)	55(2)	37(1)	37(2)	3(1)	2(1)	12(1)

Table 21 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **40**.

	x	y	z	U(eq)
H(2A)	5282	-712	3574	48
H(2B)	6298	-442	4727	48
H(2C)	7137	-968	3897	48
H(6A)	2074	-265	641	47
H(6B)	1908	441	-215	47
H(6C)	1071	490	876	47
H(12A)	12363	-81	3758	50
H(12B)	11520	-880	3332	50
H(12C)	10911	-423	4330	50
H(14A)	10225	3223	2602	54
H(14B)	12018	3005	3183	54
H(14C)	10480	2607	3590	54
H(15A)	11753	2020	585	52
H(15B)	12941	2557	1410	52
H(15C)	11244	2892	810	52
H(17A)	7405	2206	-1607	54
H(17B)	5585	2266	-2241	54
H(17C)	6253	1461	-1707	54
H(18A)	5363	3261	298	65
H(18B)	4880	3345	-1013	65
H(18C)	6749	3337	-468	65
H(1)	8680(20)	2593(10)	487(14)	16(5)
H(2)	4570(30)	2049(10)	-553(16)	34(6)
H(3)	11620(20)	1730(10)	2471(15)	19(5)
H(4)	4430(30)	777(11)	-162(19)	35(7)

Data for **46**

CCDC	832709
Empirical formula	$C_{26}H_{25}NO_5$
Formula weight	431.47
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Cc
Unit cell dimensions	a = 14.6003(6) Å, alpha = 90 deg.
	b = 17.4066(8) Å, beta = 115.519(2) deg.
	c = 9.8449(3) Å, gamma = 90 deg.
Volume	2257.91(16) Å^3
Z, Calculated density	4, 1.269 Mg/m^3
Absorption coefficient	0.088 mm^-1
F(000)	912
Crystal size	0.15 x 0.07 x 0.07 mm
Theta range for data collection	1.94 deg. to 27.00 deg.
Limiting indices	-18 ≤ h ≤ 18, -22 ≤ k ≤ 22, -12 ≤ l ≤ 12
Reflections collected / unique	4577 / 2478 [R(int) = 0.0237]
Reflection observed [I>2σ(I)]	2111
Completeness to theta = 27.00	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	2478 / 2 / 297
Goodness-of-fit on F^2	1.045
Final R indices [I>2σ(I)]	R1 = 0.0334, wR2 = 0.0713
R indices (all data)	R1 = 0.0450, wR2 = 0.0749
Absolute structure parameter	0.5(9)
Largest diff. peak and hole	0.176 and -0.162 e. Å^-3

Table 22 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **46**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	532(1)	2747(1)	3544(2)	33(1)
O(2)	824(1)	733(1)	3992(2)	31(1)
O(3)	1115(1)	1553(1)	5901(2)	32(1)
O(4)	2770(1)	298(1)	6856(2)	26(1)
O(5)	1523(1)	3357(1)	5691(2)	39(1)
N(1)	2922(1)	354(1)	4672(2)	21(1)
C(1)	2256(2)	2422(1)	4660(2)	25(1)
C(2)	2212(2)	1622(1)	4735(2)	21(1)
C(3)	1313(2)	1240(1)	4810(2)	24(1)
C(4)	286(2)	1211(2)	6118(3)	48(1)
C(5)	2986(2)	1171(1)	4662(2)	21(1)
C(6)	2717(2)	-26(1)	5704(2)	22(1)
C(7)	2392(2)	-847(1)	5404(2)	24(1)
C(8)	2676(2)	-1332(1)	4528(2)	26(1)
C(9)	2387(2)	-2098(1)	4358(2)	32(1)
C(10)	1807(2)	-2382(1)	5038(2)	34(1)
C(11)	1484(2)	-1899(2)	5866(2)	31(1)
C(12)	1775(2)	-1134(1)	6047(2)	26(1)
C(13)	3780(2)	1526(1)	4464(2)	21(1)
C(14)	3777(2)	2326(1)	4356(2)	24(1)
C(15)	3037(2)	2790(1)	4457(2)	24(1)
C(16)	3089(2)	3661(1)	4353(2)	30(1)
C(17)	3531(2)	3933(2)	3281(3)	40(1)
C(18)	3695(2)	4006(2)	5925(3)	41(1)
C(19)	4618(2)	1099(1)	4329(2)	22(1)
C(20)	4841(2)	1255(1)	3116(2)	24(1)
C(21)	5664(2)	913(1)	3006(2)	28(1)
C(22)	6279(2)	417(1)	4119(2)	29(1)
C(23)	6061(2)	250(1)	5321(2)	30(1)
C(24)	5235(2)	587(1)	5429(2)	26(1)
C(25)	1417(2)	2896(1)	4724(2)	27(1)
C(26)	-336(2)	3145(2)	3557(3)	42(1)

Table 23 Anisotropic displacement parameters (A^2 x 10^3) for **46**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
O(1)	28(1)	44(1)	28(1)	2(1)	12(1)	10(1)
O(2)	26(1)	35(1)	31(1)	-1(1)	11(1)	-2(1)
O(3)	31(1)	41(1)	30(1)	1(1)	21(1)	4(1)
O(4)	37(1)	24(1)	22(1)	0(1)	17(1)	1(1)

O(5)	43(1)	35(1)	44(1)	-10(1)	24(1)	5(1)
N(1)	26(1)	20(1)	19(1)	-2(1)	12(1)	1(1)
C(1)	26(1)	28(1)	19(1)	-2(1)	9(1)	4(1)
C(2)	24(1)	25(1)	15(1)	-1(1)	10(1)	1(1)
C(3)	24(1)	26(1)	22(1)	5(1)	10(1)	6(1)
C(4)	38(2)	69(2)	50(2)	1(1)	31(1)	-2(1)
C(5)	26(1)	22(1)	15(1)	0(1)	9(1)	1(1)
C(6)	20(1)	25(1)	21(1)	0(1)	8(1)	3(1)
C(7)	23(1)	27(1)	17(1)	2(1)	5(1)	0(1)
C(8)	30(1)	26(1)	22(1)	0(1)	12(1)	-1(1)
C(9)	39(1)	27(1)	28(1)	-4(1)	12(1)	1(1)
C(10)	36(1)	28(1)	29(1)	0(1)	6(1)	-10(1)
C(11)	29(1)	36(2)	27(1)	1(1)	10(1)	-10(1)
C(12)	28(1)	29(1)	21(1)	0(1)	10(1)	-1(1)
C(13)	24(1)	20(1)	18(1)	1(1)	9(1)	1(1)
C(14)	23(1)	26(1)	23(1)	1(1)	11(1)	0(1)
C(15)	24(1)	24(1)	20(1)	-3(1)	7(1)	1(1)
C(16)	30(1)	21(1)	36(1)	-1(1)	11(1)	4(1)
C(17)	45(2)	27(1)	48(1)	8(1)	21(1)	2(1)
C(18)	44(2)	27(1)	47(1)	-10(1)	14(1)	-3(1)
C(19)	21(1)	21(1)	23(1)	-3(1)	10(1)	-1(1)
C(20)	26(1)	20(1)	24(1)	-2(1)	10(1)	-4(1)
C(21)	35(1)	26(1)	30(1)	-4(1)	20(1)	-4(1)
C(22)	30(1)	23(1)	39(1)	-5(1)	20(1)	1(1)
C(23)	32(1)	24(1)	34(1)	4(1)	16(1)	5(1)
C(24)	31(1)	24(1)	28(1)	3(1)	16(1)	1(1)
C(25)	32(1)	27(1)	26(1)	4(1)	17(1)	4(1)
C(26)	31(1)	54(2)	43(1)	7(1)	20(1)	17(1)

Table 24 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **46**.

	x	y	z	U(eq)
H(1)	2888(18)	97(15)	3900(30)	30(6)
H(4A)	-333	1231	5172	72
H(4B)	179	1496	6897	72
H(4C)	450	675	6432	72
H(8)	3069	-1138	4046	31
H(9)	2589	-2428	3769	39
H(10)	1627	-2910	4940	40
H(11)	1066	-2092	6307	38
H(12)	1554	-802	6613	31
H(14)	4311	2565	4206	28
H(16)	2379	3863	3963	36
H(17A)	4257	3810	3711	59
H(17B)	3440	4490	3138	59
H(17C)	3181	3674	2309	59
H(18A)	3367	3871	6576	62
H(18B)	3717	4566	5847	62
H(18C)	4387	3801	6357	62
H(20)	4424	1601	2354	29
H(21)	5803	1020	2168	34
H(22)	6853	190	4058	35

H(23)	6480	-97	6078	36
H(24)	5089	469	6257	32
H(25A)	-401	3016	4481	62
H(25B)	-953	2987	2681	62
H(25C)	-242	3701	3518	62

Selected NMR Spectra

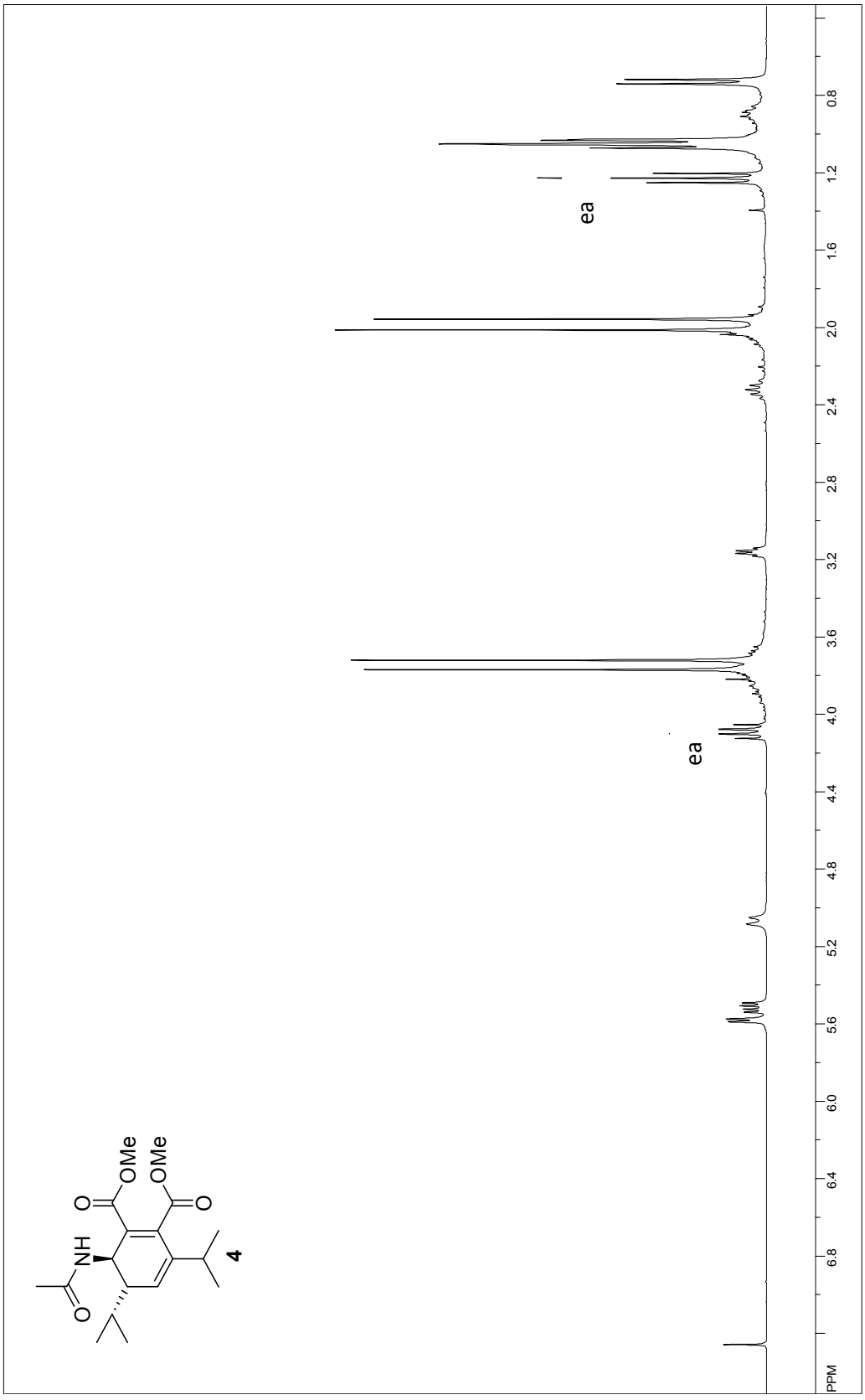


Figure S1 ^{1}H-NMR of compound **4** in $CDCl_3$ (300 MHz).

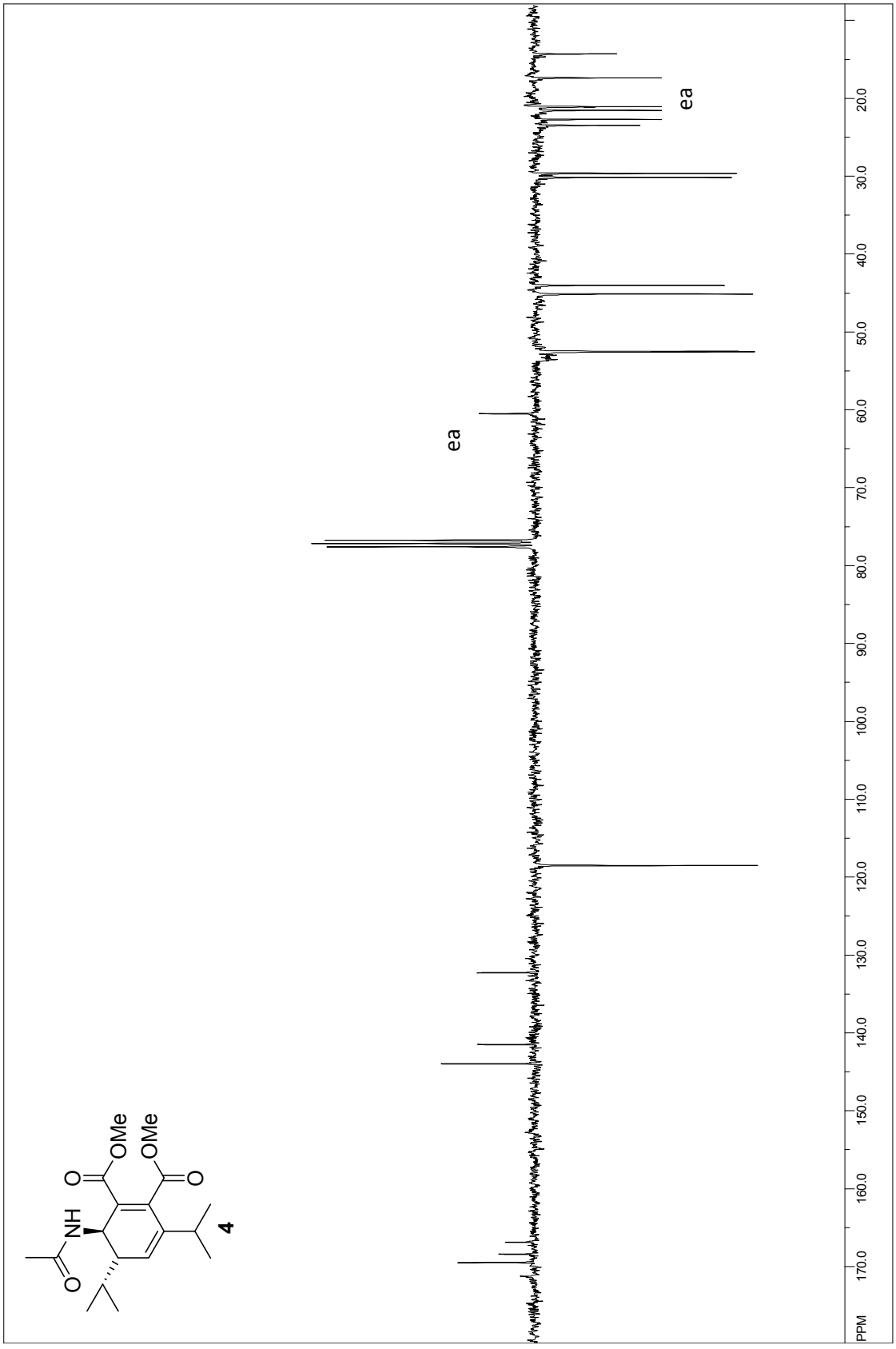


Figure S2 ^{13}C-APT-NMR of compound **4** in $CDCl_3$ (75 MHz).

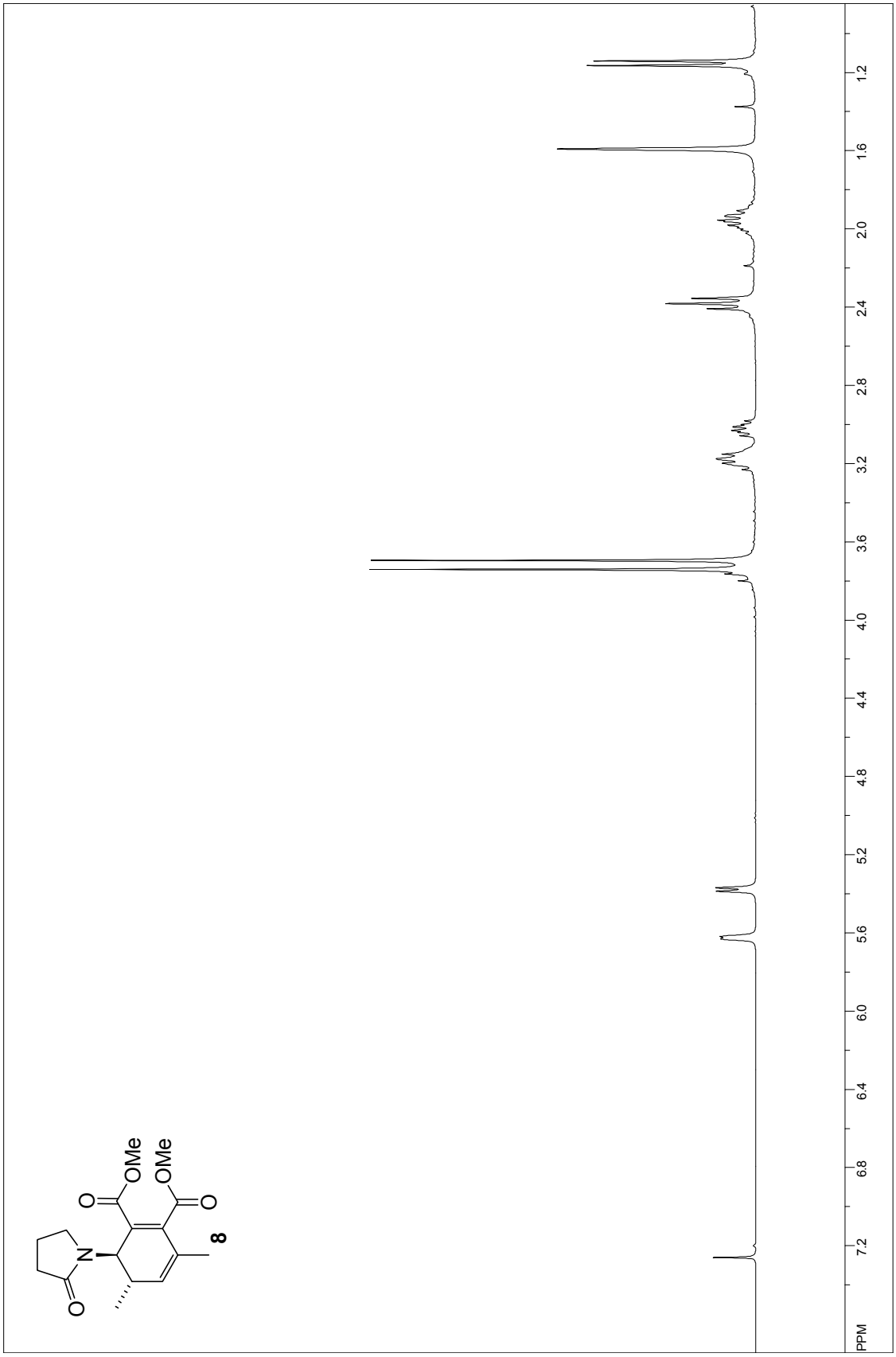


Figure S3 ^{1}H-NMR of compound **8** in $CDCl_3$ (300 MHz).

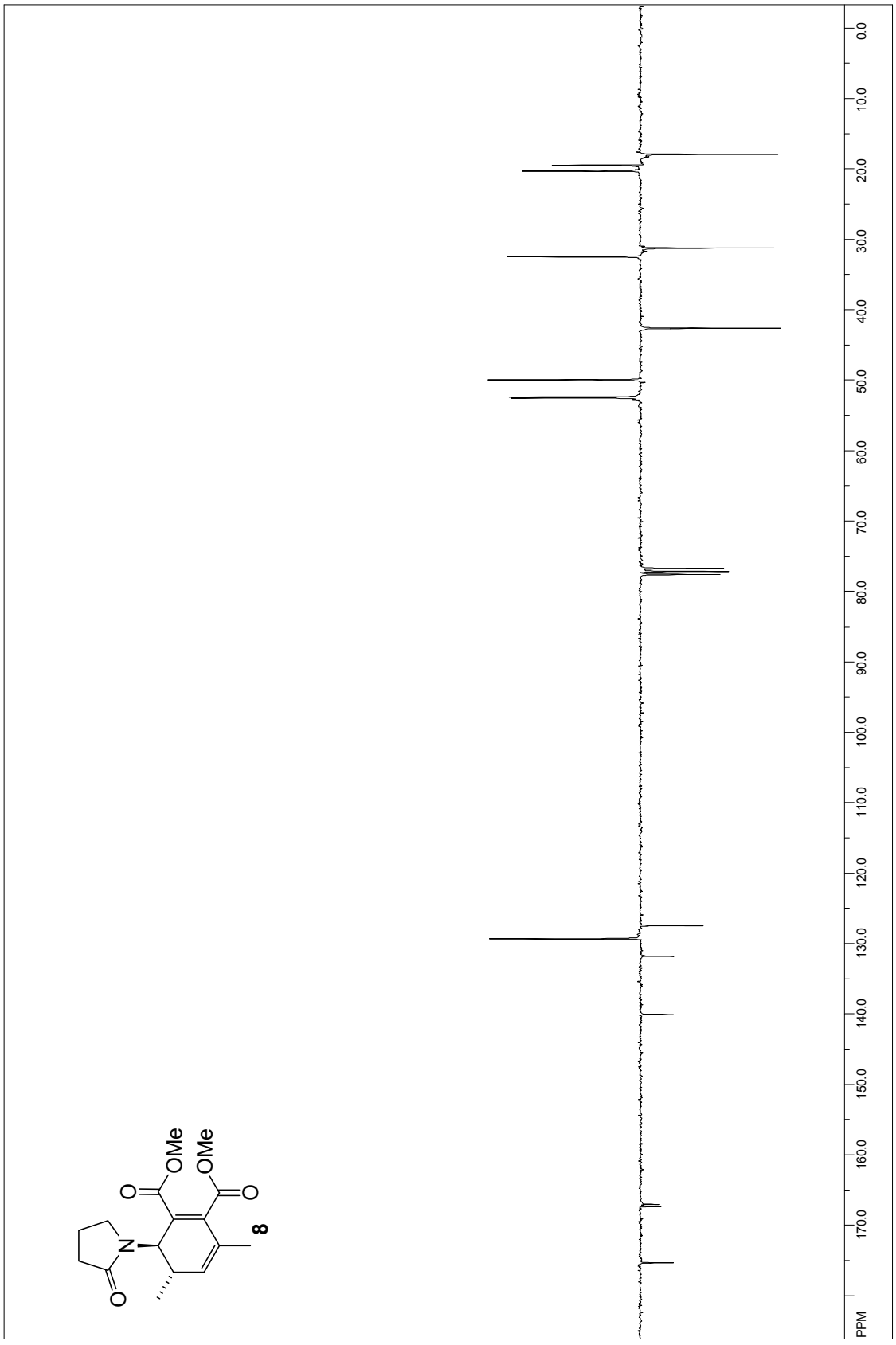


Figure S4 ^{13}C-APT-NMR of compound **8** in $CDCl_3$ (75 MHz).

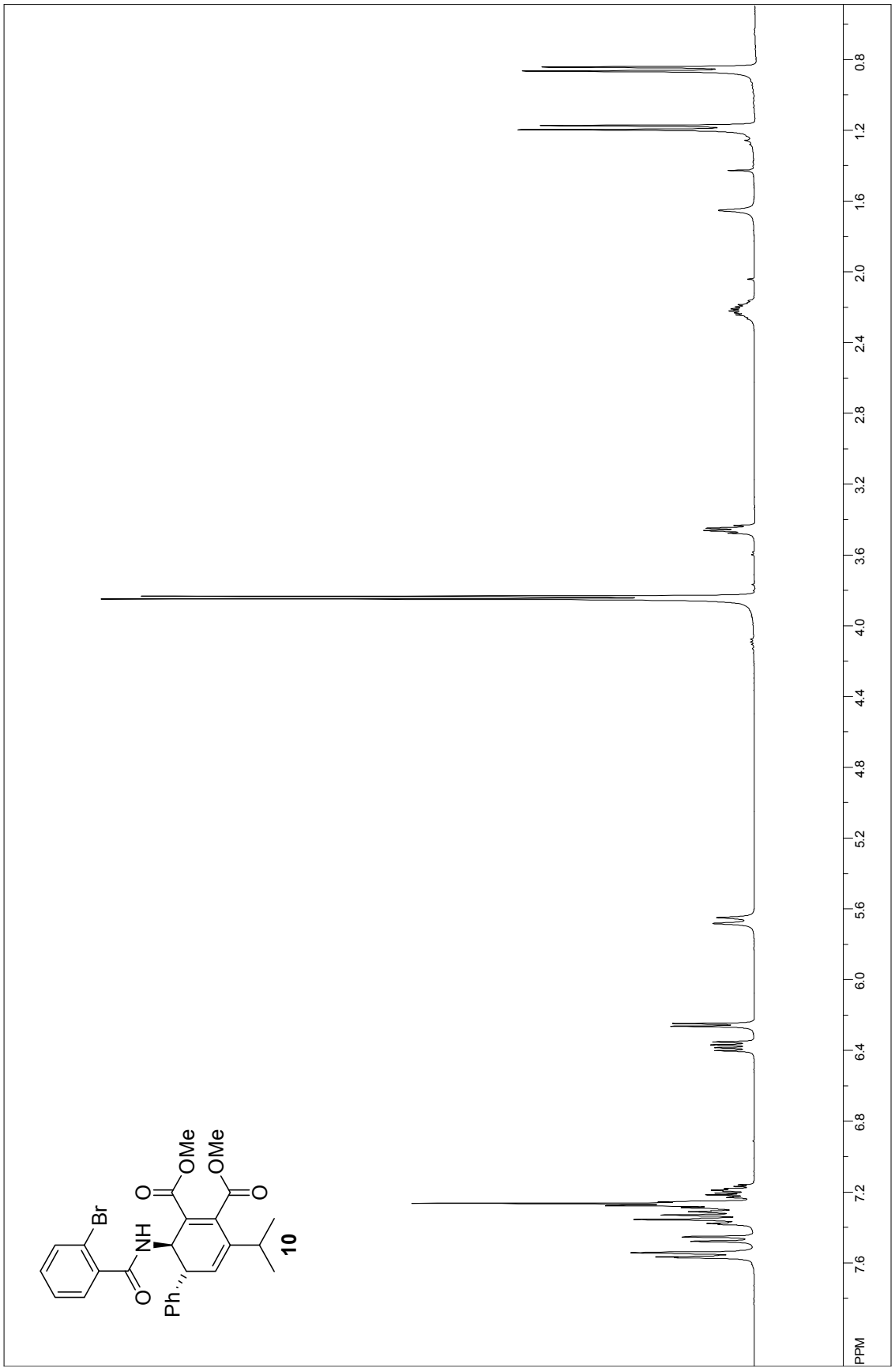


Figure S5 ^{1}H-NMR of compound **10** in $CDCl_3$ (600 MHz).

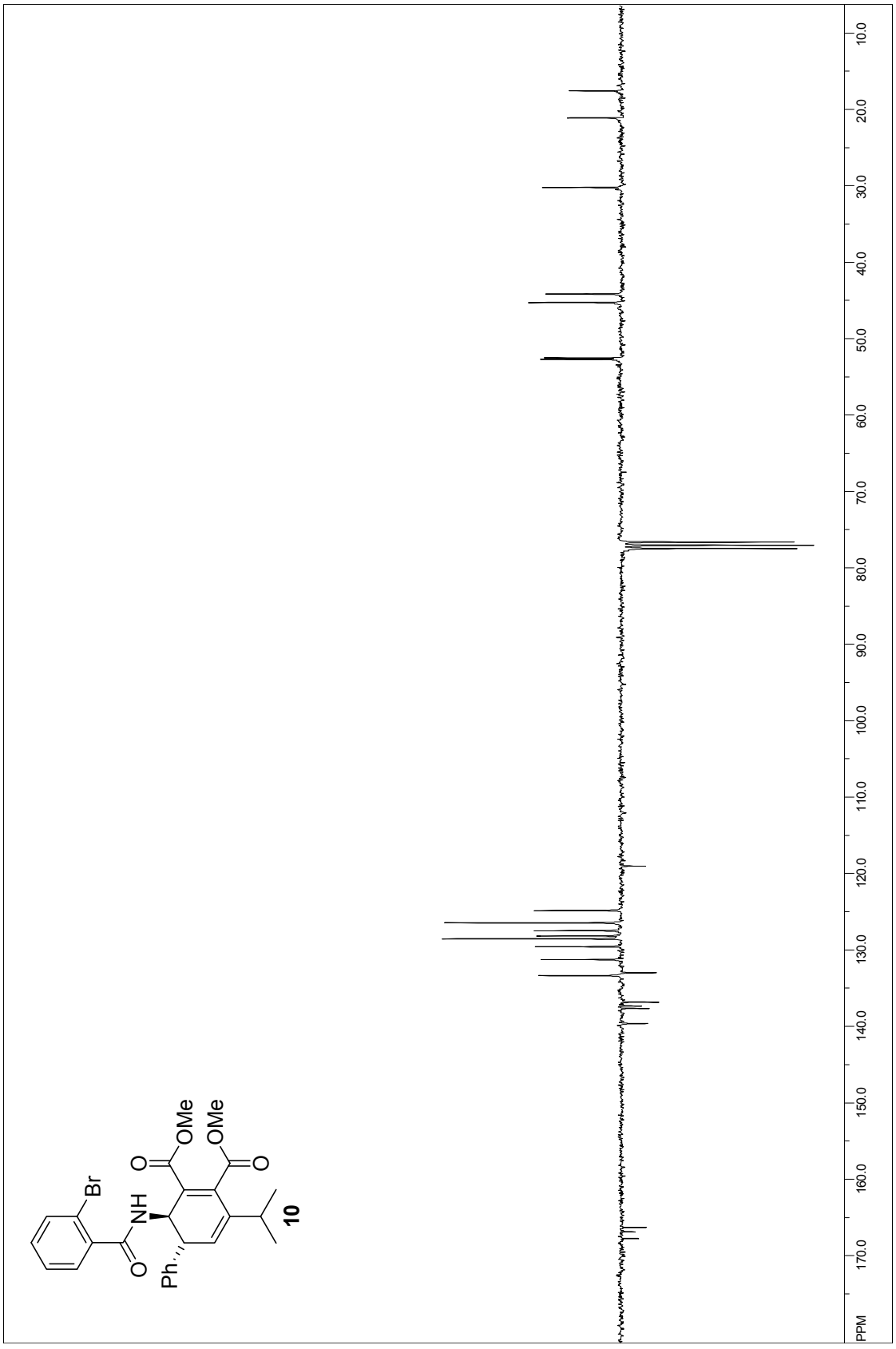


Figure S6 ^{13}C-APT-NMR of compound **10** in $CDCl_3$ (150 MHz).

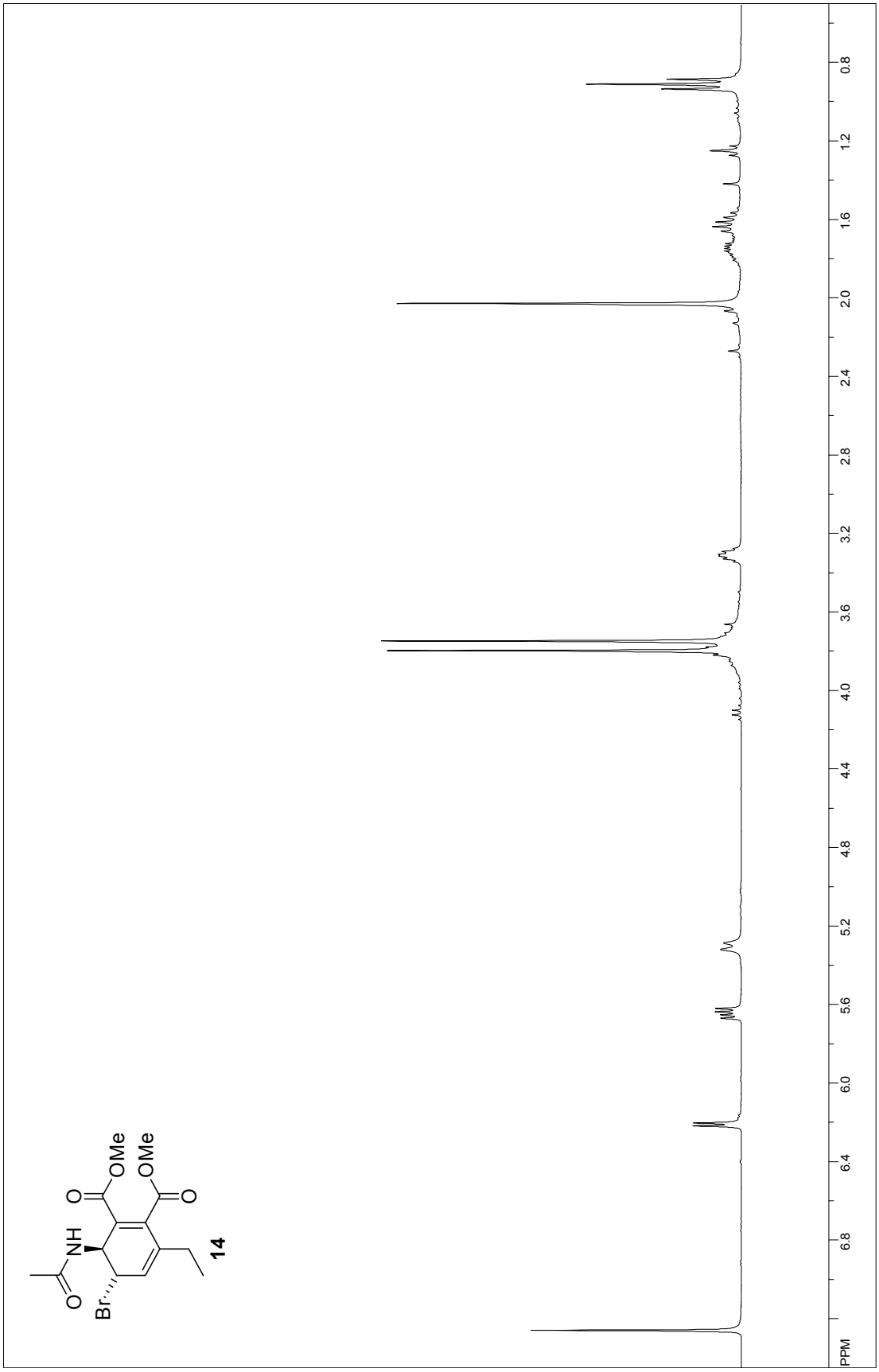


Figure S7 ^{1}H-NMR of compound **14** in $CDCl_3$ (300 MHz).

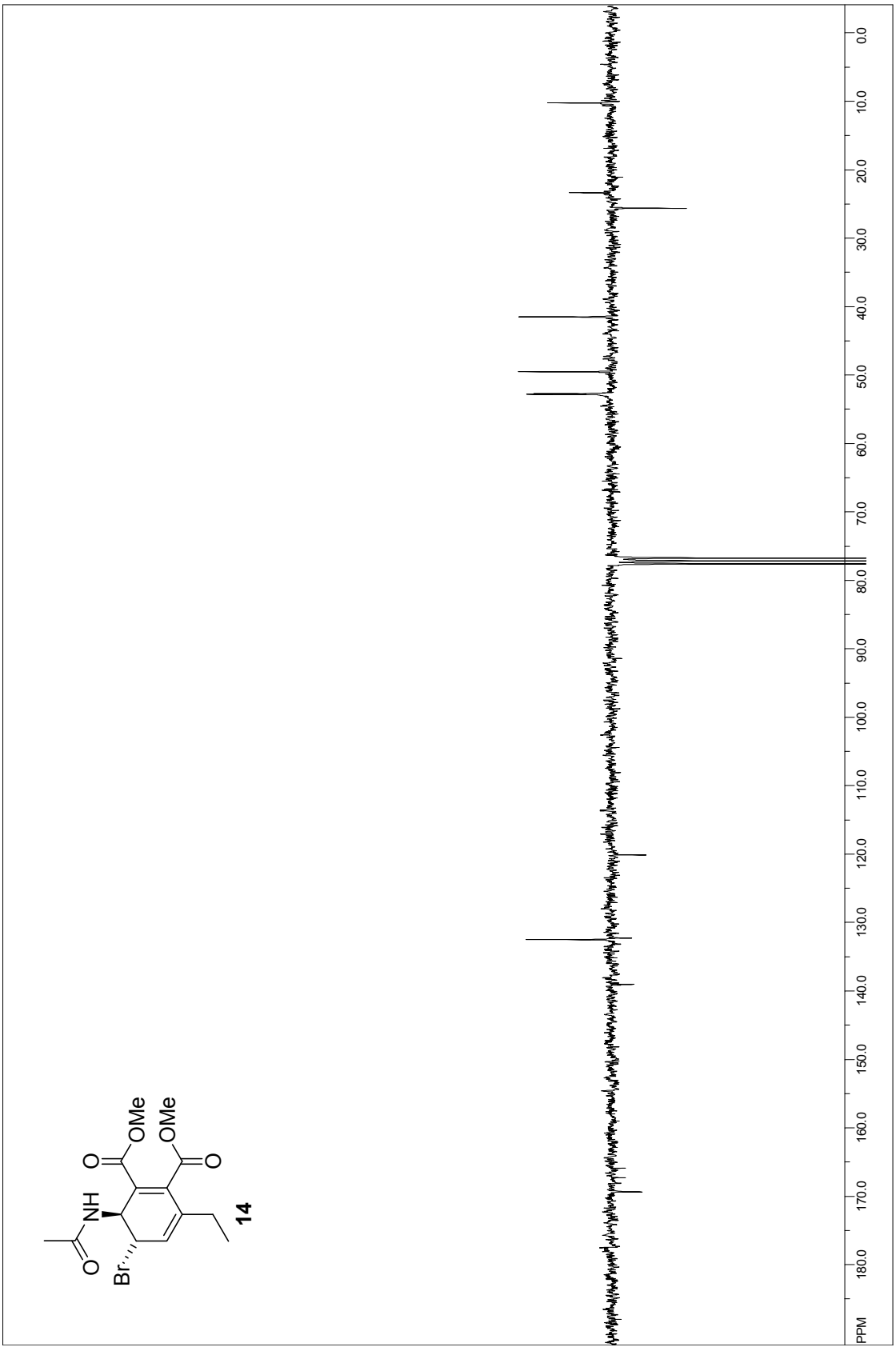


Figure S8 ^{13}C-APT-NMR of compound **14** in $CDCl_3$ (75 MHz).

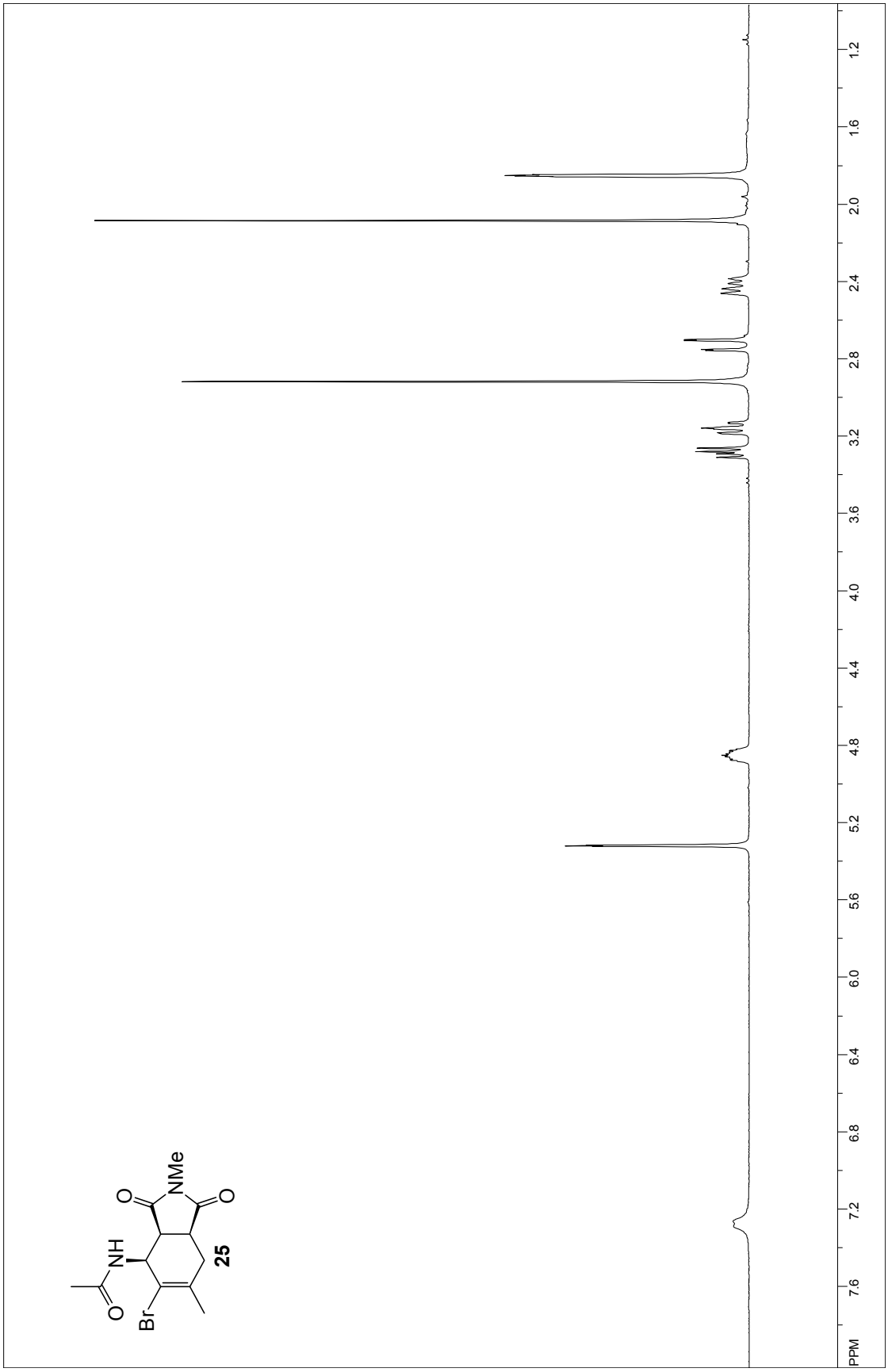


Figure S9 ^{1}H-NMR of compound **25** in CD_2Cl_2 (300 MHz).

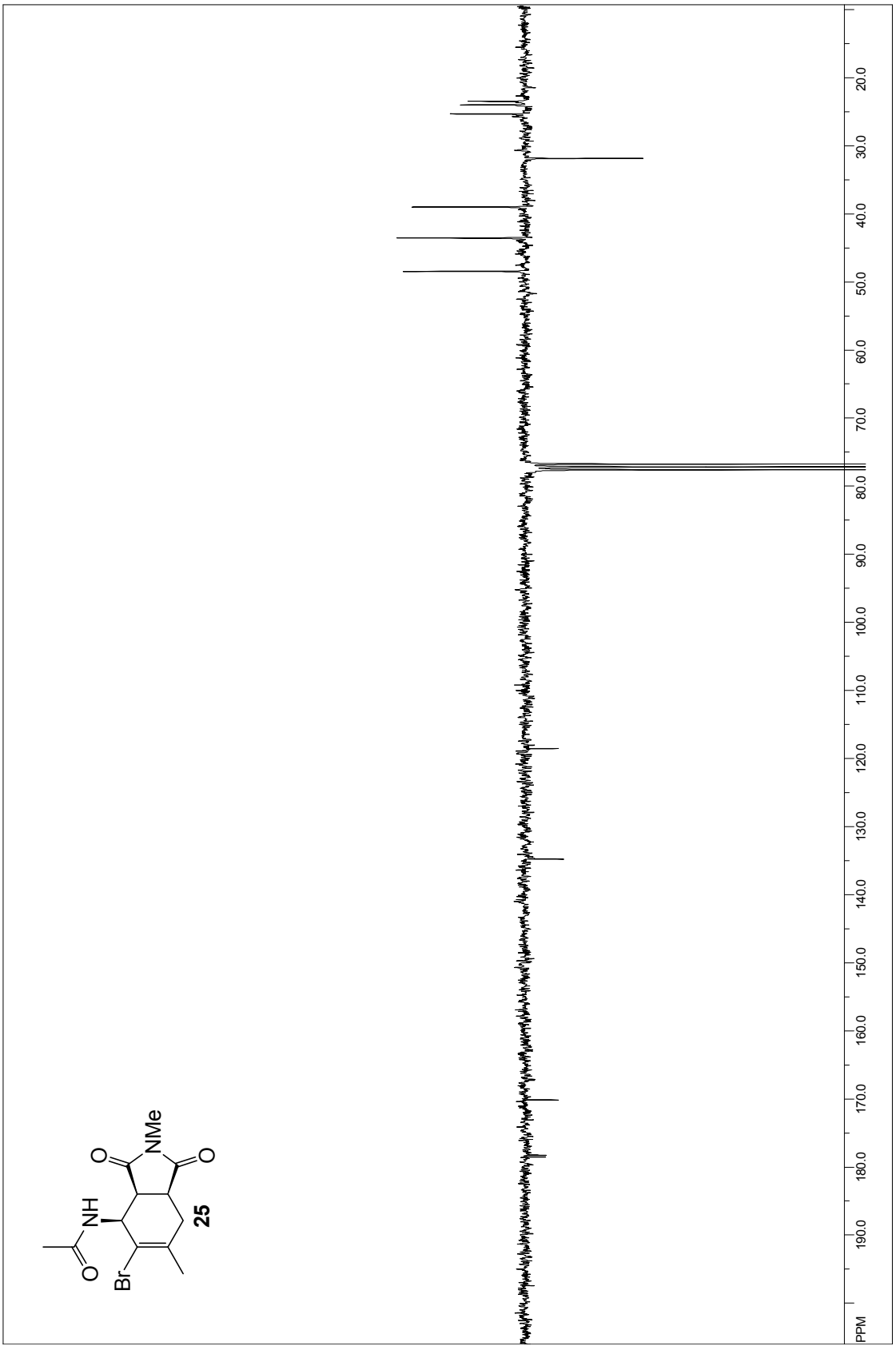


Figure S10 ^{13}C-APT-NMR of compound **25** in $CDCl_3$ (75 MHz).

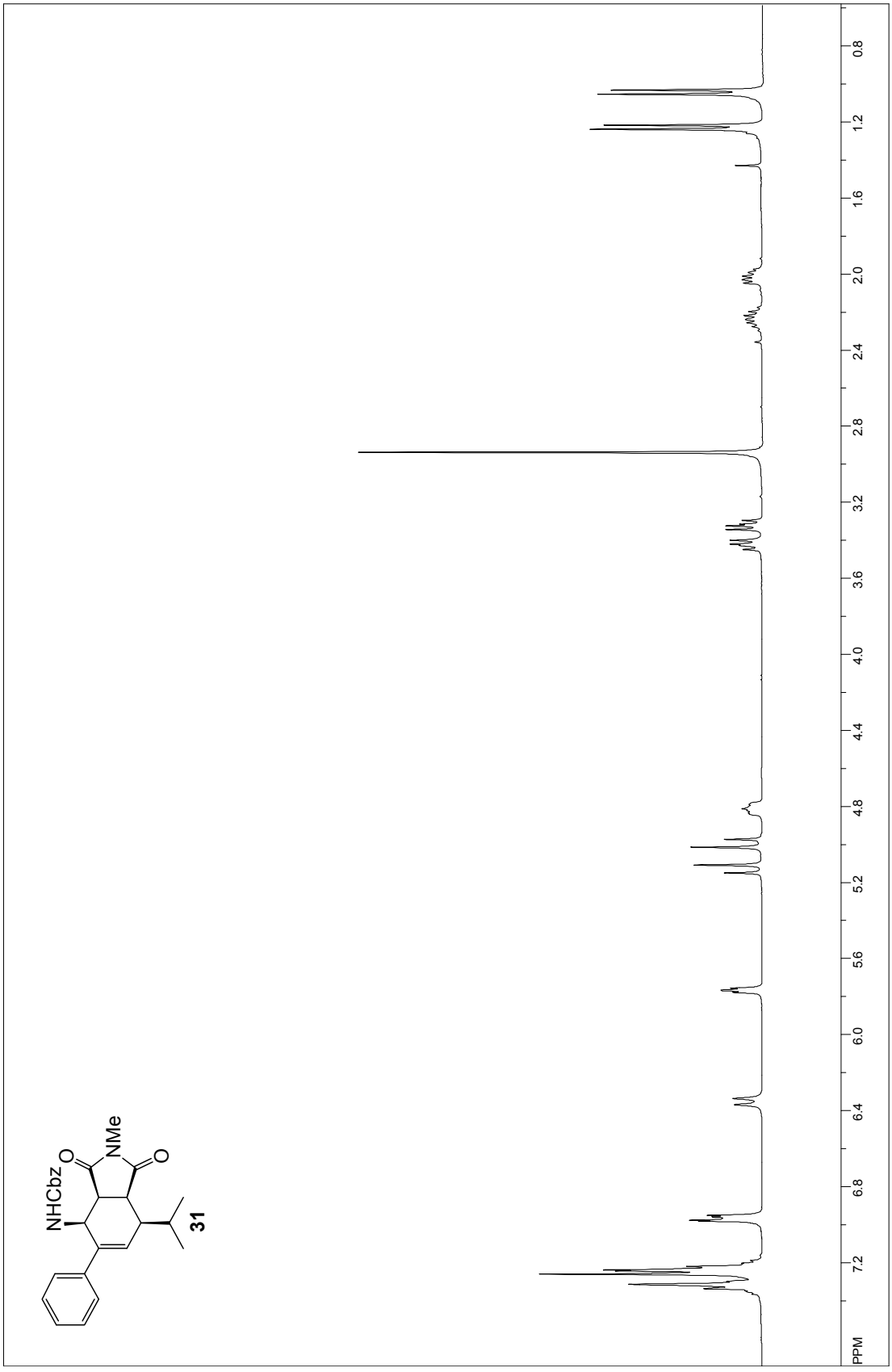


Figure S11 ^{1}H-NMR of compound **31** in $CDCl_3$ (300 MHz).

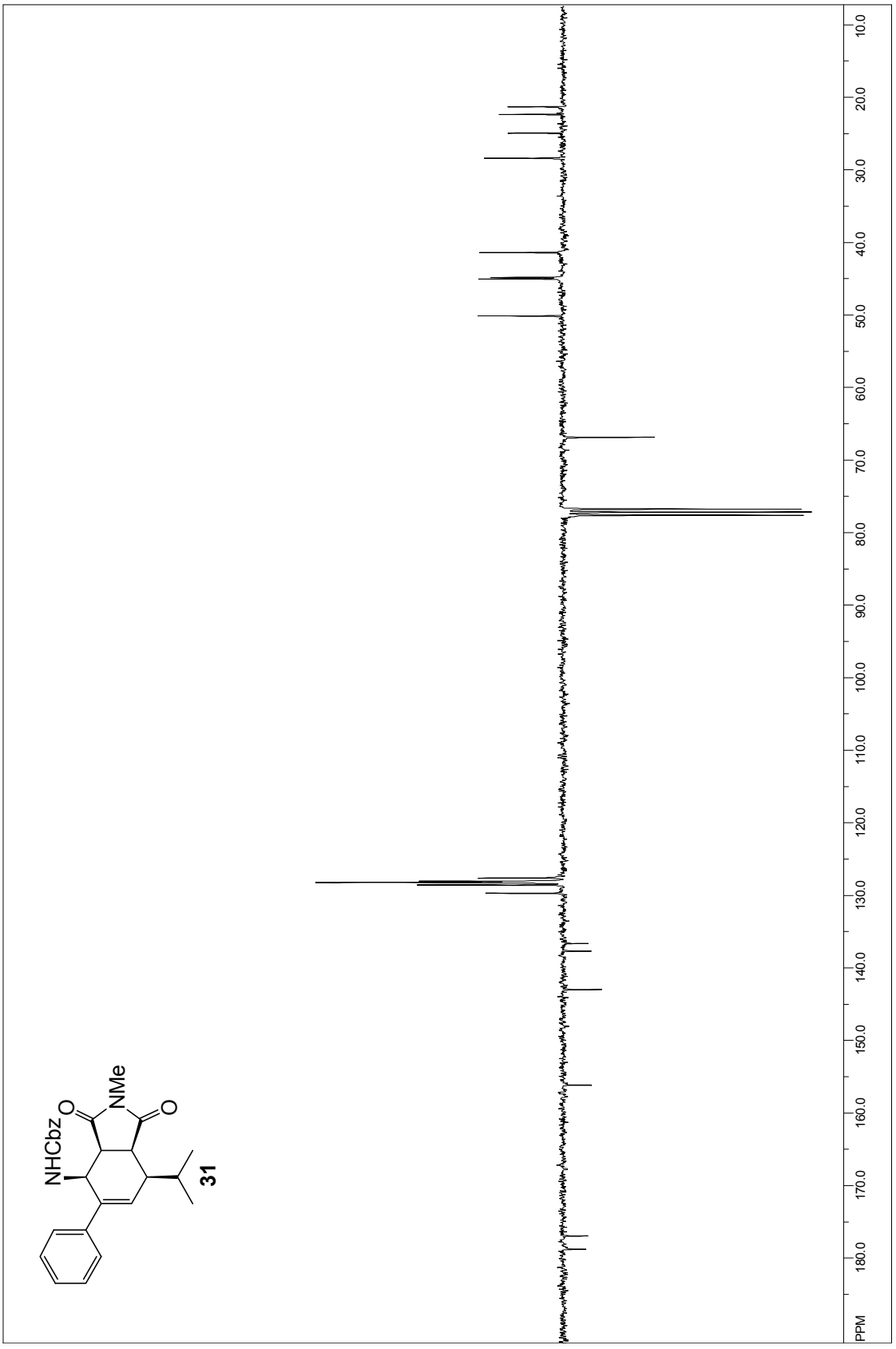


Figure S12 ^{13}C-APT-NMR of compound **31** in $CDCl_3$ (75 MHz).

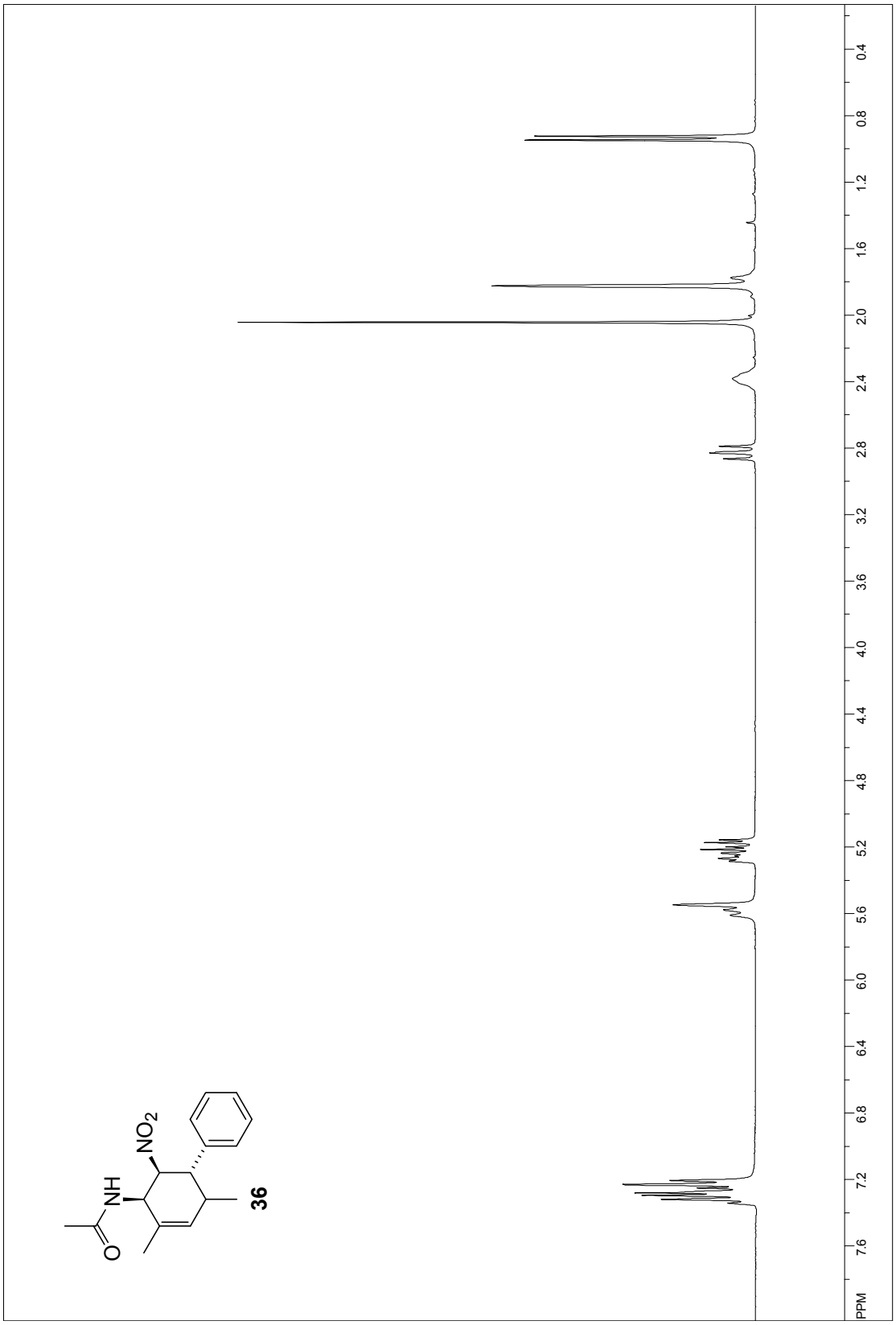


Figure S13 ^{1}H-NMR of compound **36** in $CDCl_3$ (300 MHz).

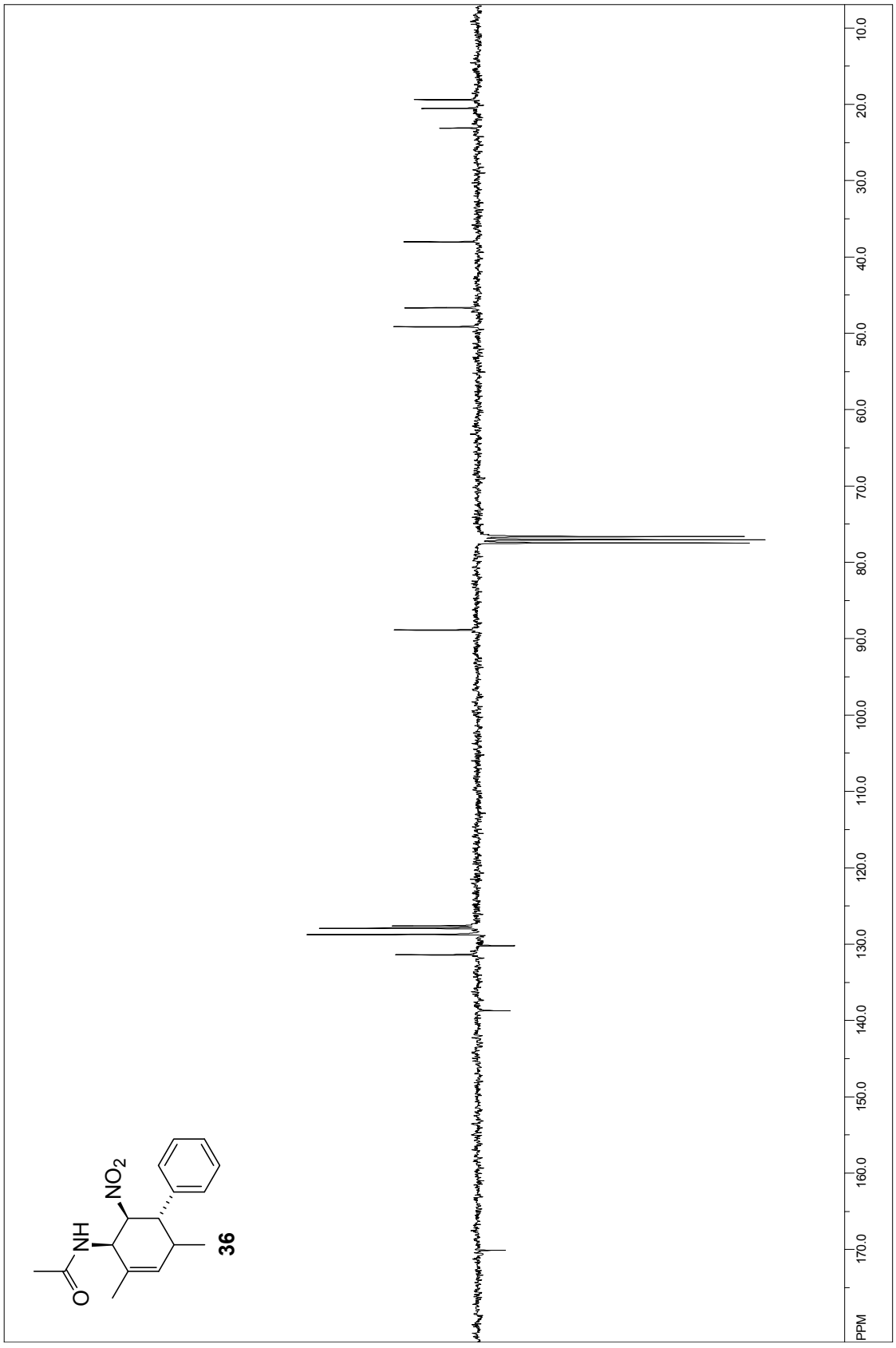


Figure S14 ^{13}C-APT-NMR of compound **36** in $CDCl_3$ (75 MHz).

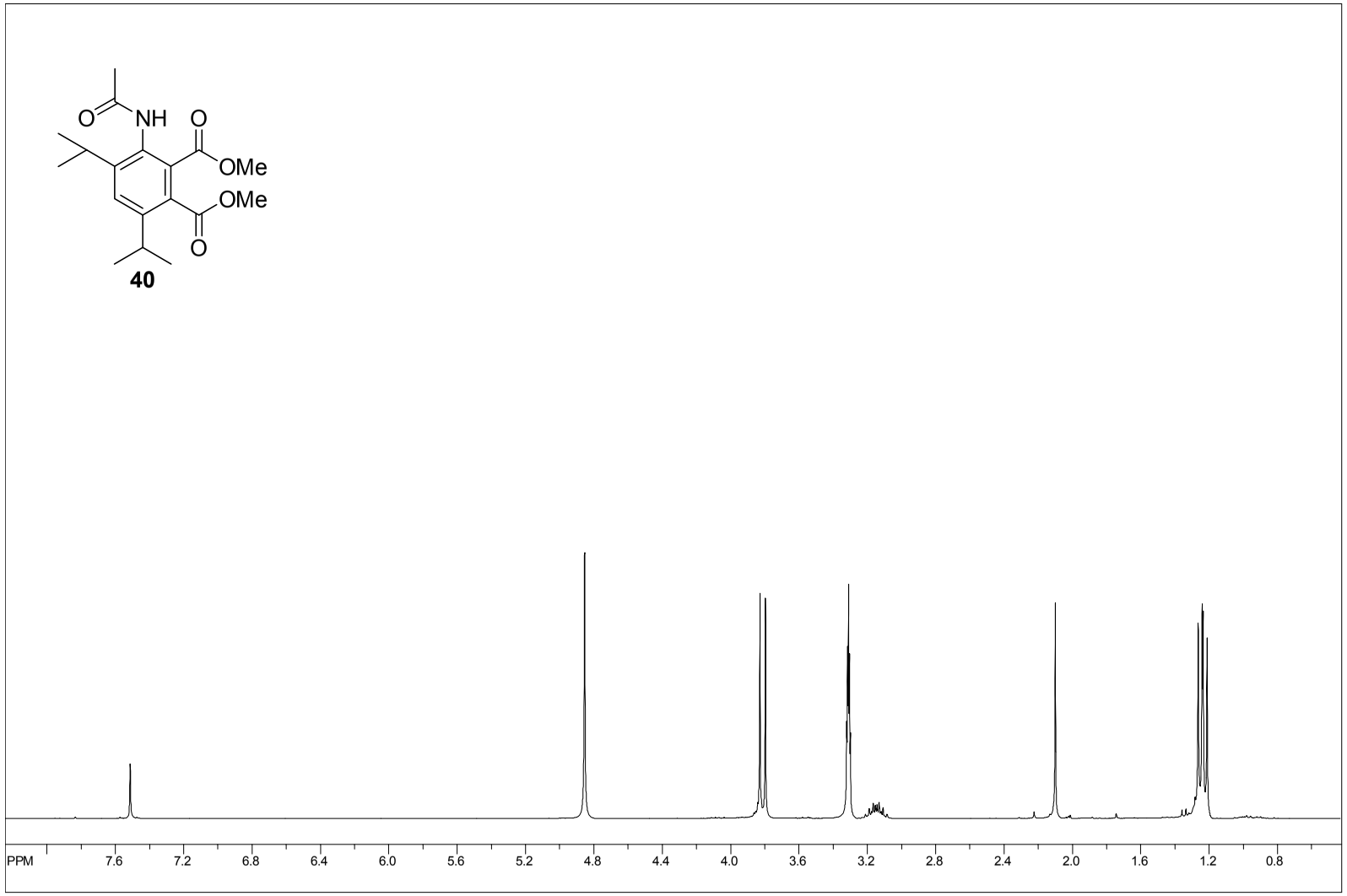


Figure S15 ^{1}H-NMR of compound **40** in MeOD-d4 (300 MHz).

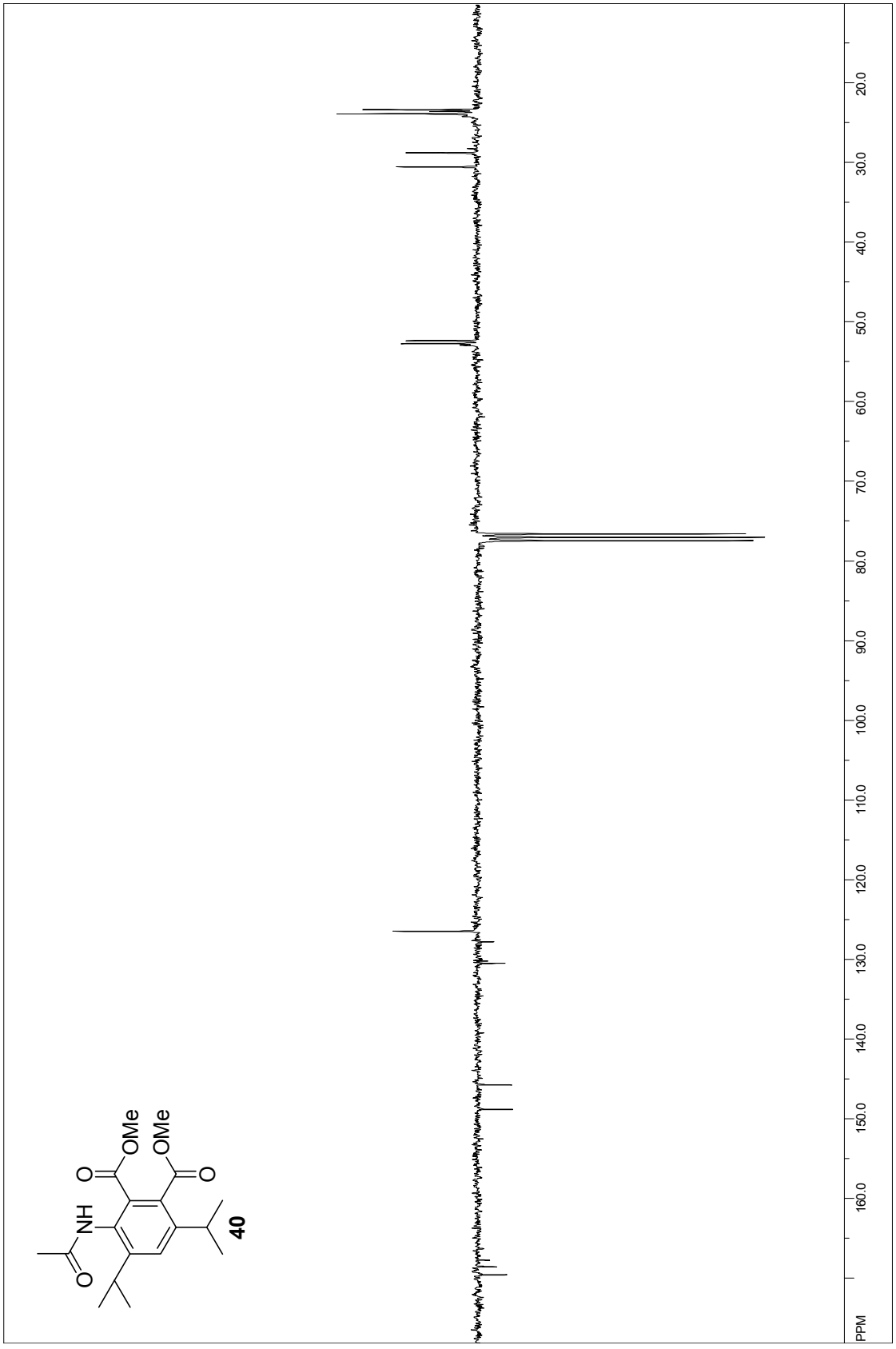


Figure S16 ^{13}C-APT-NMR of compound **40** in $CDCl_3$ (75 MHz).

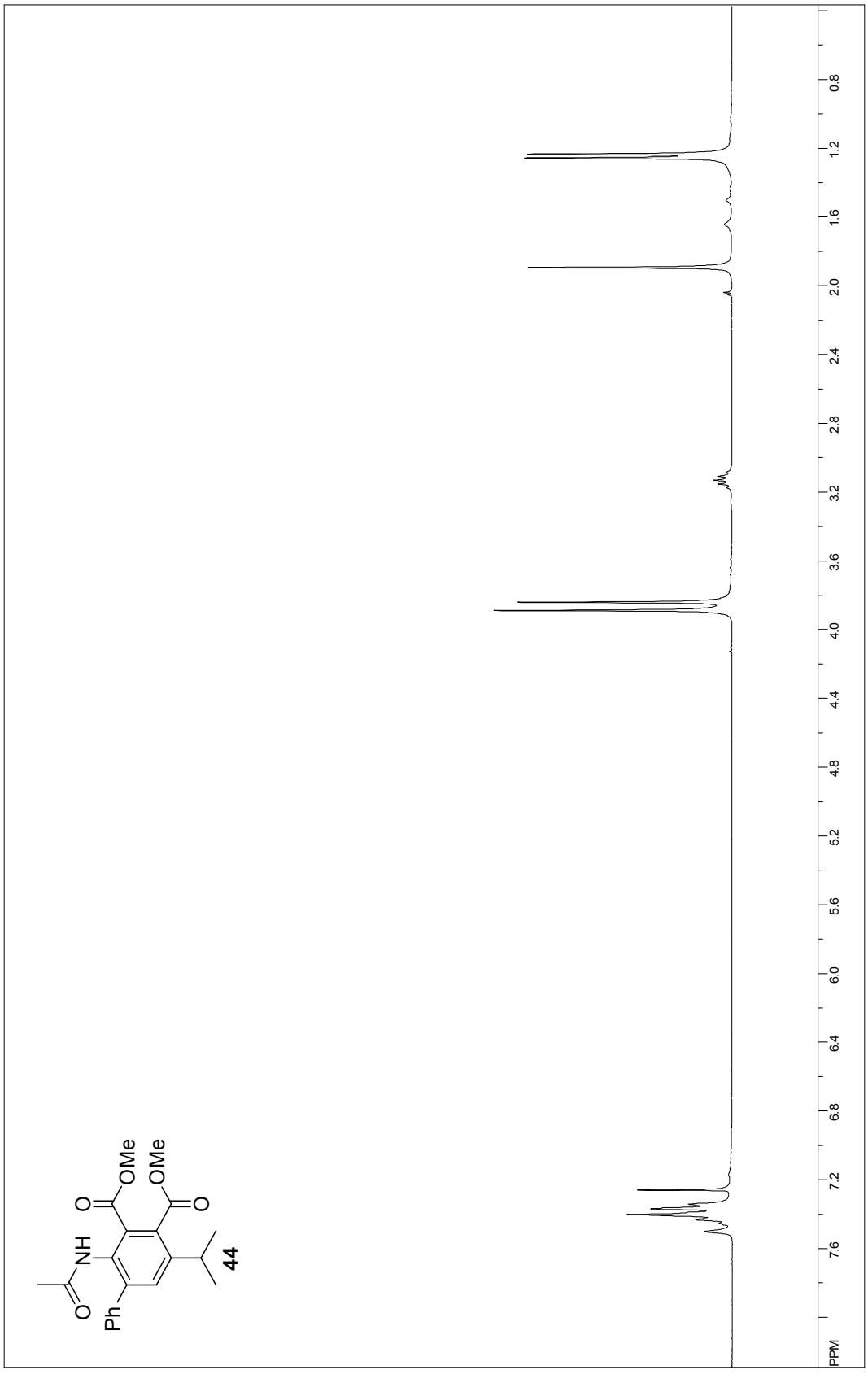


Figure S17 ^{1}H-NMR of compound **44** in $CDCl_3$ (300 MHz).

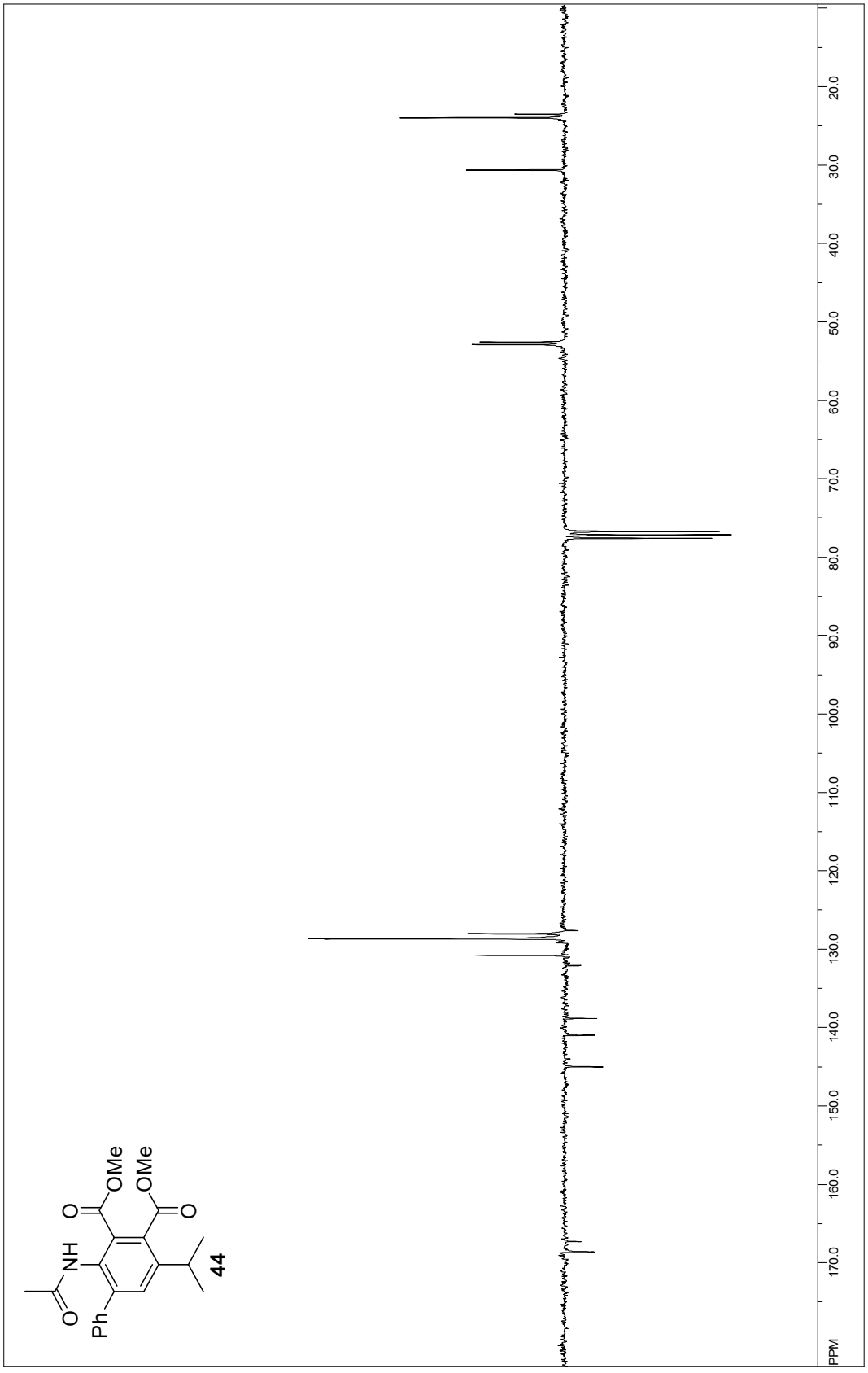


Figure S18 ^{13}C-APT-NMR of compound **44** in $CDCl_3$ (75 MHz).

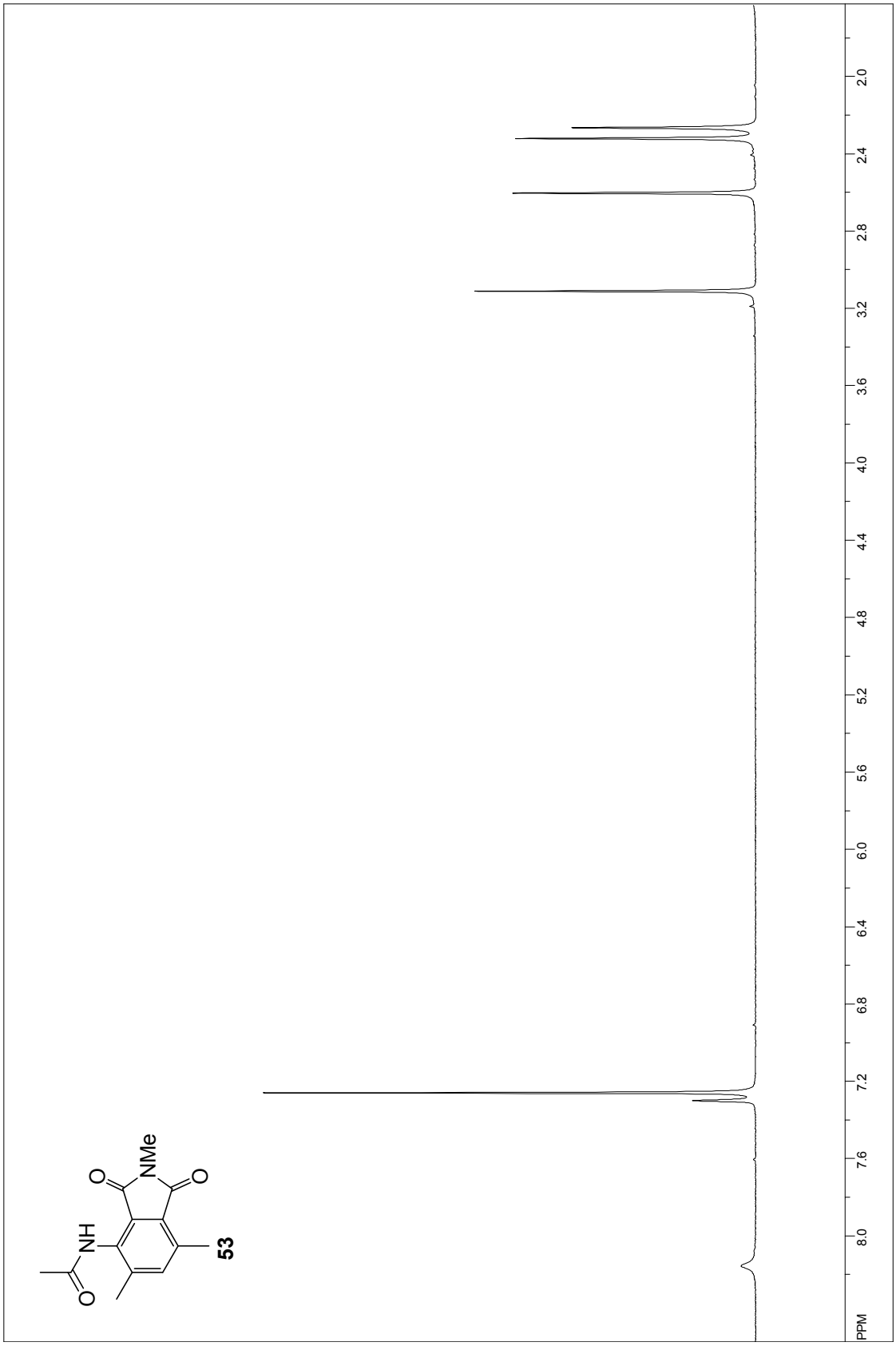


Figure S19 ^{1}H-NMR of compound **53** in $CDCl_3$ (300 MHz).

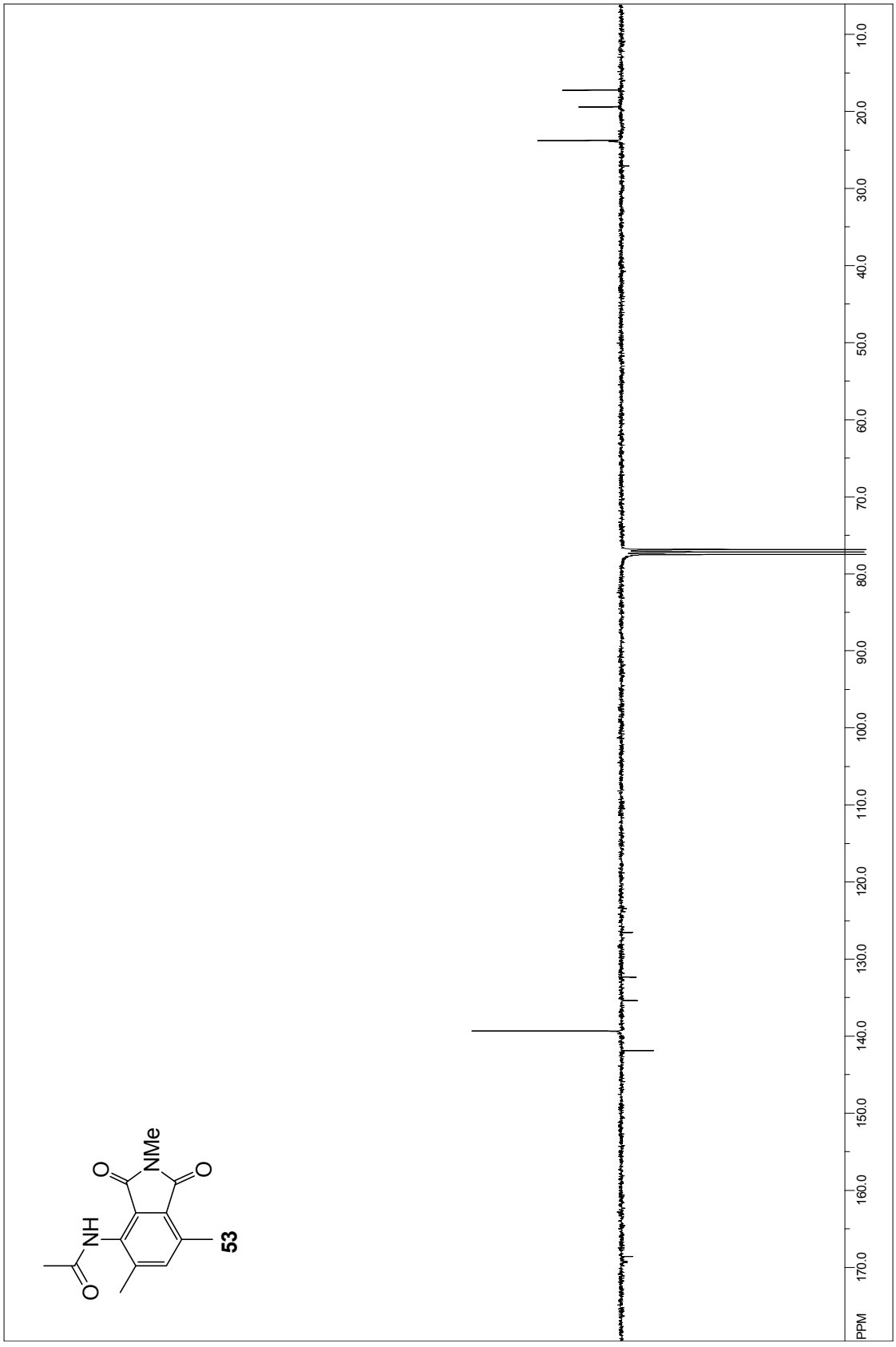


Figure S20 ^{13}C-APT-NMR of compound **53** in $CDCl_3$ (100 MHz).

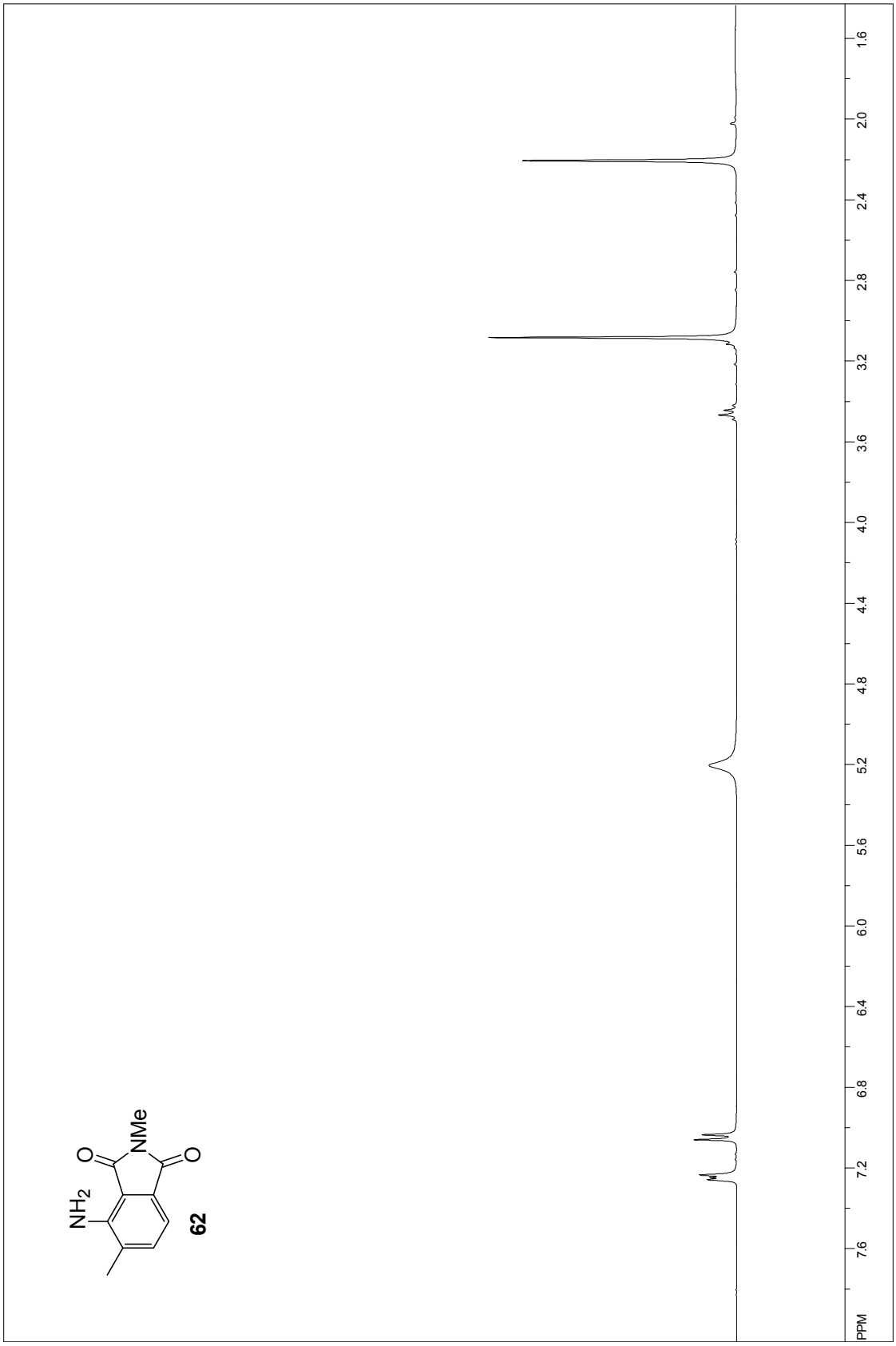


Figure S21 ^{1}H-NMR of compound **62** in $CDCl_3$ (300 MHz).

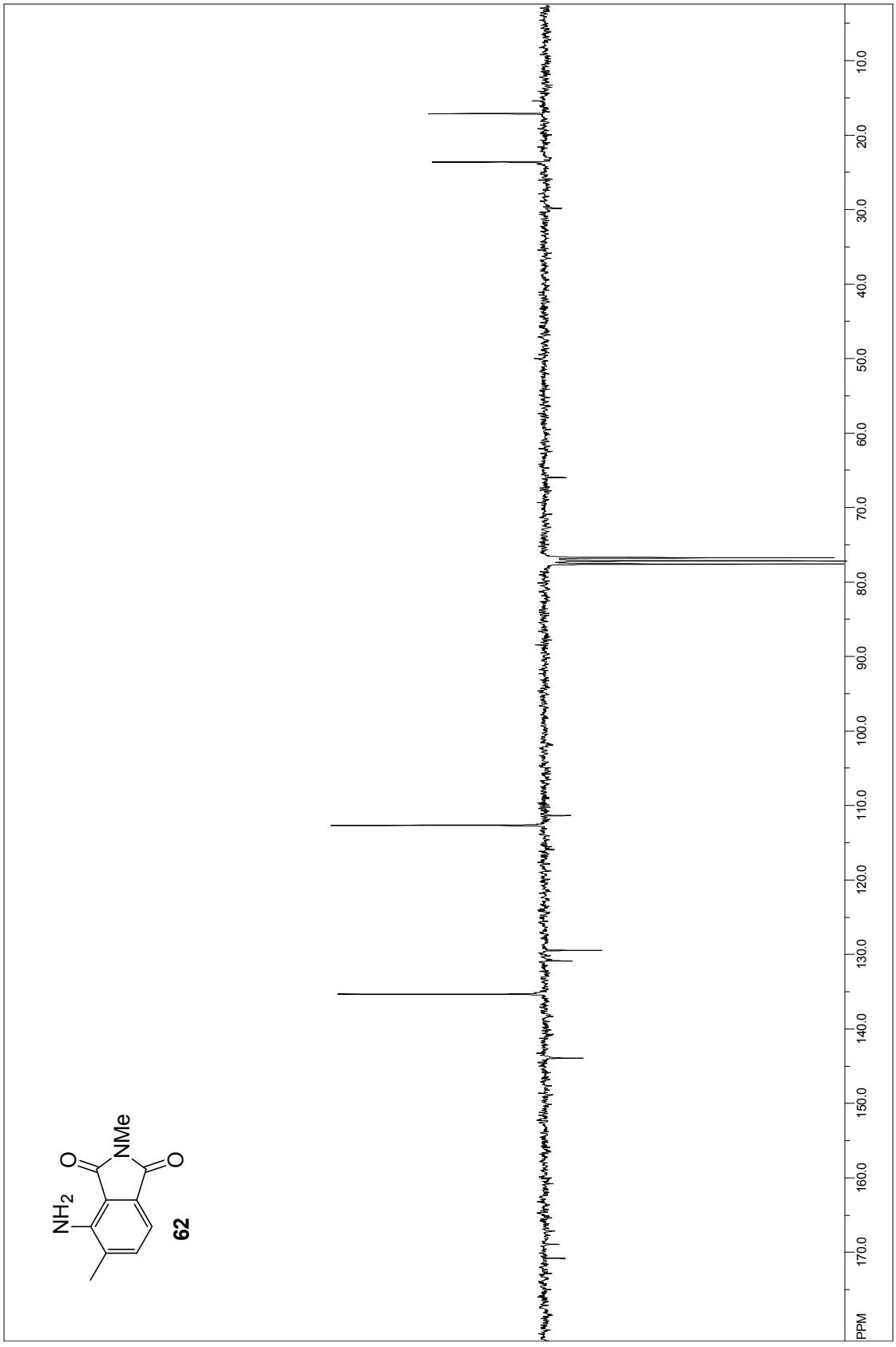


Figure S22 ^{13}C-APT-NMR of compound **62** in $CDCl_3$ (75 MHz).

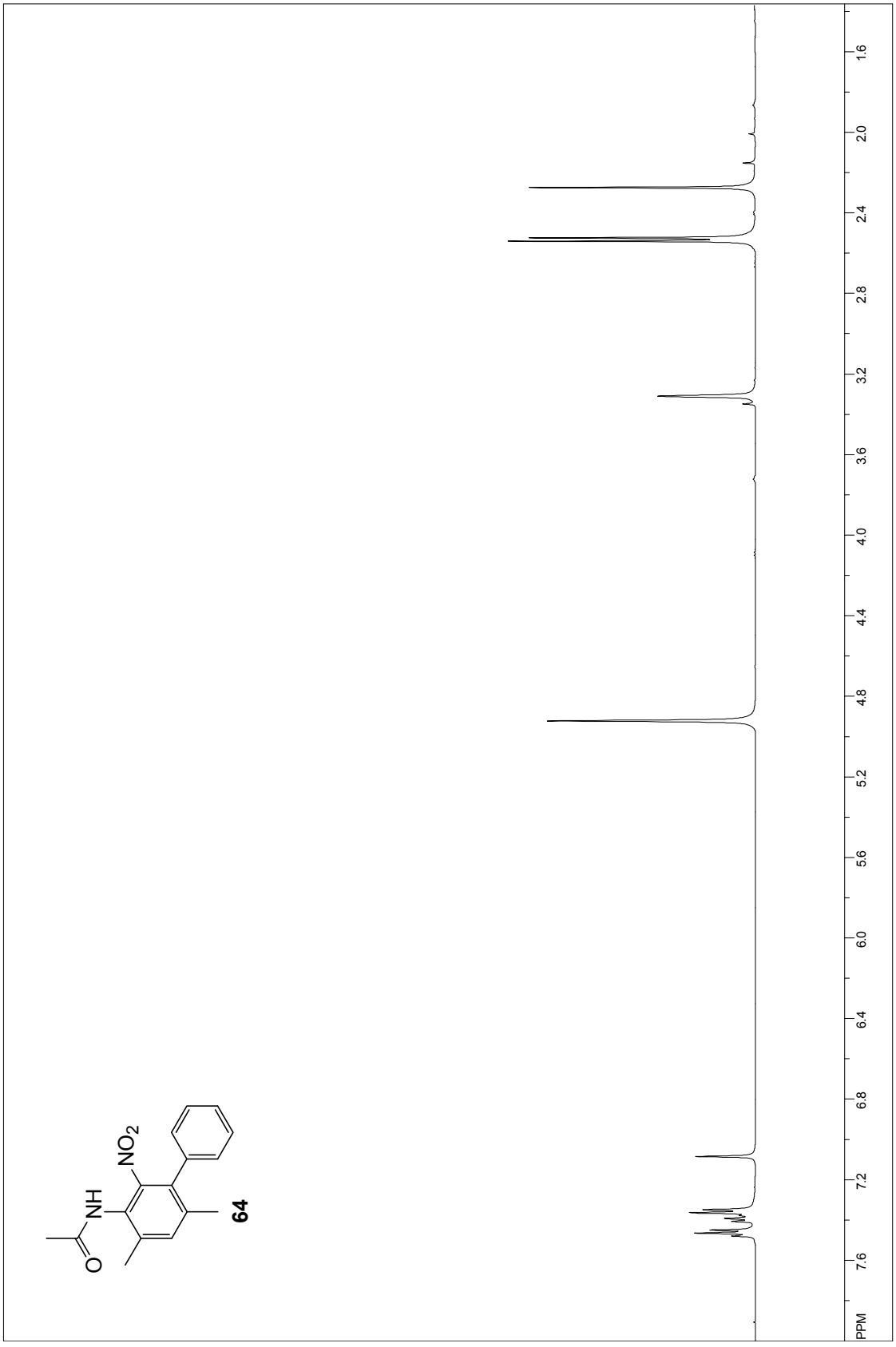


Figure S23 ^{1}H-NMR of compound **64** in MeOD-d4/H_2O (500 MHz).

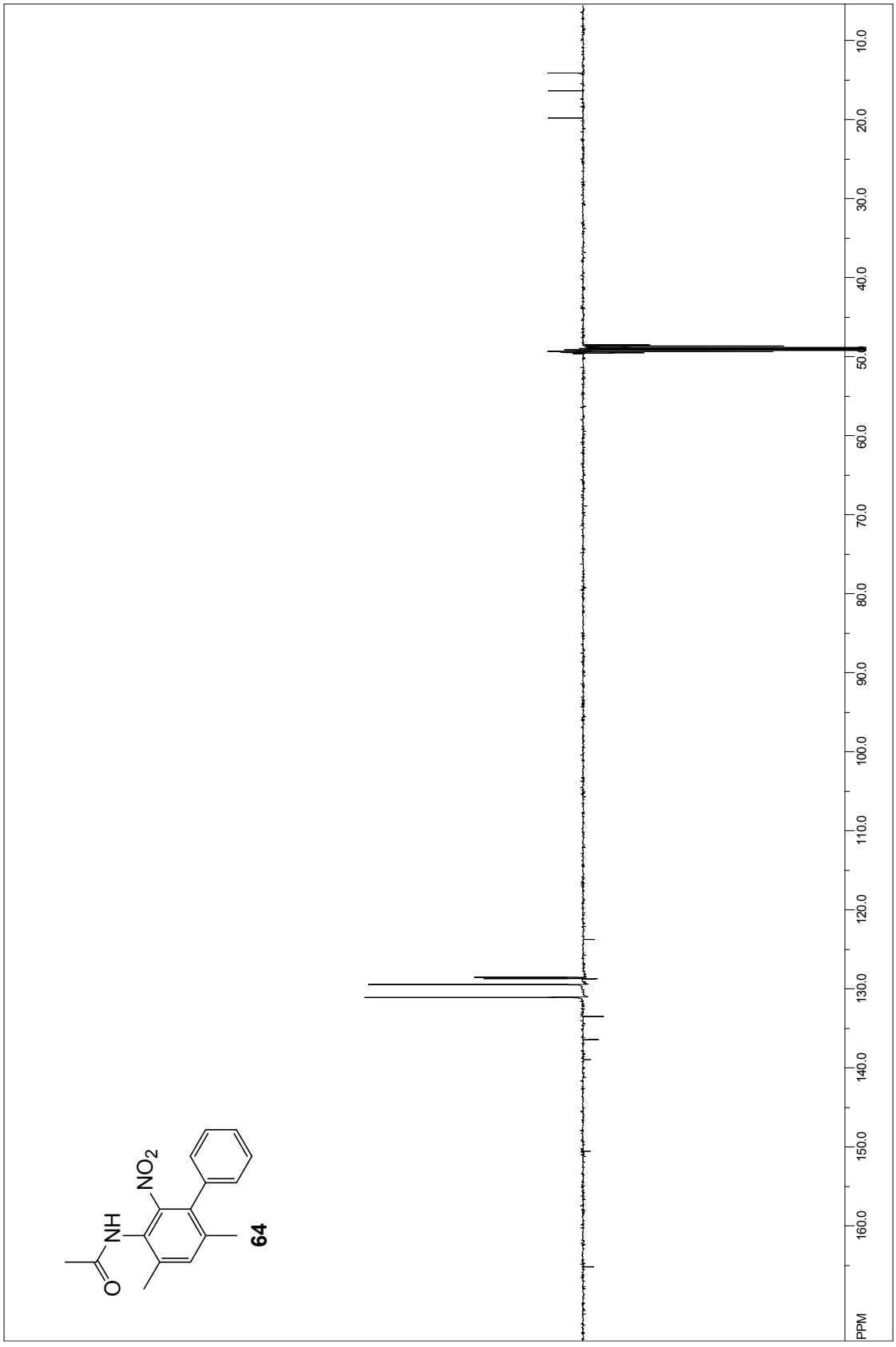


Figure S24 ^{13}C-APT-NMR of compound **64** in MeOD-d4/H_2O (125 MHz).