Electronic Supplementary Material (ESI) for Green Chemistry.

Tin-free visible light photoredox catalysed cyclization of enamides as a mild procedure for the synthesis of γ-lactams

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General Information

All reactions were performed with oven-dried glassware and under an inert atmosphere (argon) unless otherwise stated.

Acetonitrile was distilled from calcium hydride and stored over 4Å molecular sieves under nitrogen/argon atmosphere. Tetrahydrofuran was distilled from Solvona®/benzophenone. Pentane was distilled in standard distillation apparatus. Other solvents were used as purchased unless otherwise stated.

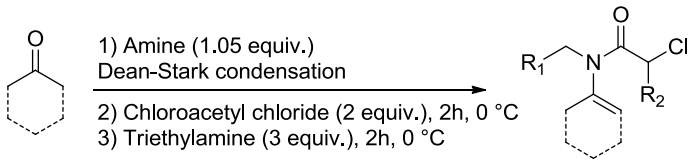
Commercial reagents were used as purchased without further purification.

Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was carried out using Merck Kieselgel 60 silica gel (230-400 mesh). Thin-layer chromatography was carried out using Merck Kieselgel 60 F_{254} (230-400 mesh) fluorescent treated silica and were visualized under UV light (254 nm) or by staining with aqueous potassium permanganate solutions or vanillin alcoholic solution.

^{1}H NMR spectra were recorded in deuterated solvents on Inova 400 or Varian 600 spectrometers at 400 or 600 MHz (respectively), with residual protic solvent as the internal standard. ^{13}C NMR spectra were recorded in deuterated solvents on Inova 400 or Varian 600 spectrometers at 101 or 151 MHz, with the central peak of the deuterated solvent as the internal standard. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (*J*) are given in Hertz (Hz) rounded to the nearest 0.1 Hz. The ^{1}H NMR spectra are reported as δ/ppm downfield from tetramethylsilane (multiplicity, coupling constant *J*/Hz, number of protons). The ^{13}C NMR spectra are reported as δ/ppm. Assignments are aided by the use of DEPT-135, COSY and HMQC spectra where necessary. IR spectra were recorded on a Perkin Elmer 1760 FTIR spectrometer. Low resolution mass spectra (EI/CI) were recorded on a Thermo Finnigan SSQ 7000 mass spectrometer (EI) or a Thermo Finnigan MAT 95 mass spectrometer (CI).

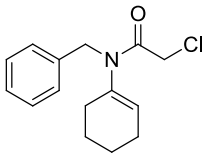
Melting points were recorded on a Büchi Melting Point M-565 apparatus, at ambient pressure and are uncorrected.

Preparation and Characterization of Substrates



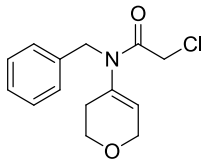
Following the general procedure,[1] the corresponding ketone (1 equiv.) and amine (1.05 equiv.) were condensed in refluxing toluene for 3 hours using a Dean-Stark trap. After cooling, three quarter of toluene was evaporated under reduced pressure and the resulting mixture was added dropwise to a solution of chloroacetyl chloride (2 equiv.) in toluene at 0 °C. After stirring the reaction for 2 hours at 0 °C, triethylamine was added dropwise at the same temperature and stirred for further 2 hours. The mixture was then quenched with a saturated solution of $NaHCO_3$ and diluted with EtOAc. The organic phase was extracted two times with water to remove the excess of base, dried over $MgSO_4$, filtered and concentrated under reduce pressure. Purification was performed by column chromatography using a gradient mixture of Pentane/EtO_2 as eluent.

N-benzyl-2-chloro-*N*-(cyclohex-1-en-1-yl)acetamide (1a)



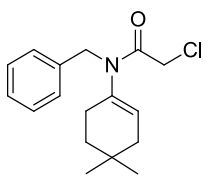
Substrate **1a** was prepared following the general procedure. The product was obtained in 67% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.14 (m, 5H), 5.45 (bs, 1H), 4.61 (s, 2H), 4.11 (s, 2H), 2.01 (dt, *J* = 6.0, 3.1 Hz, 4H), 1.77–1.60 (m, 2H), 1.59–1.45 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 137.4, 137.1, 129.3, 128.8, 128.3, 127.4, 49.9, 41.8, 27.9, 24.7, 22.6, 21.3. Physical data were previously reported.[1]

N-benzyl-2-chloro-*N*-(3,6-dihydro-*H*-pyran-4-yl)acetamide (1b)



Substrate **1b** was prepared following the general procedure. The product was obtained in 63% yield as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.18 (m, 5H), 5.50 (bs, 1H), 4.64 (s, 2H), 4.19–4.05 (m, 4H), 3.78 (t, *J* = 5.4 Hz, 2H), 2.26–2.07 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 136.7, 135.1, 128.7, 128.5, 127.7, 127.4, 64.7, 64.2, 49.7, 41.5, 28.2; **MS** = m/z (EI) 265 ($[M]^+$, 31%), 230 ($[M\text{-}Cl]^+$, 100%), 188 ($[M\text{-}COCH_2Cl]^+$, 15%), 174 ($[M\text{-}PhCH_2]^+$, 35%), 91 ($[PhCH_2]^+$, 91%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2941, 1661, 1388, 1214, 1132, 705.

N-benzyl-2-chloro-*N*-(4,4-dimethylcyclohex-1-en-1-yl)acetamide (1c)

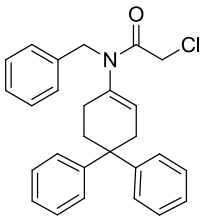


Substrate **1c** was prepared following the general procedure. The product was obtained in 63% yield as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H), 5.41 (t, *J* = 3.8 Hz, 1H), 4.66 (s, 2H), 4.15 (s, 2H), 2.07 (d, *J* = 1.4 Hz, 2H), 1.84 (d, *J* = 3.0 Hz, 2H), 1.46 (t, *J* = 6.4 Hz, 2H), 0.92 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.9, 137.1, 136.3, 128.9, 128.5, 128.4, 127.5, 50.0, 41.8, 38.7, 35.4, 28.2, 28.0, 25.6; **MS** =

[1] O. Tamura, H. Matsukida, A. Toyao, Y. Takeda and H. Ishibashi, *J. Org. Chem.*, 2002, **67**, 5537–5545.

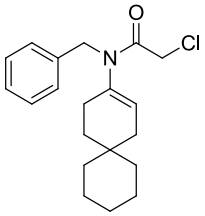
m/z (EI) 291 ([M]$^+$, 19%), 256 ([M-Cl]$^+$, 100%), 214 ([M-COCH$_2$Cl]$^+$, 14%), 200 ([M-PhCH$_2$]$^+$, 8%), 91 ([PhCH$_2$]$^+$, 91%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2937, 1659, 1401, 1235, 1198, 702.

N-benzyl-2-chloro-*N*-(3',6'-dihydro-2'*H*-[1,1':1',1"-terphenyl]-4'-yl)acetamide (1d)



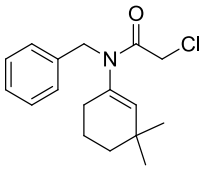
Substrate **1d** was prepared following the general procedure. The product was obtained in 44% yield as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41–7.12 (m, 15H), 5.69 (t, *J* = 3.7 Hz, 1H), 4.58 (bs, 2H), 3.85 (s, 2H), 2.70 (s, 2H), 2.51 (t, *J* = 6.0 Hz, 2H), 1.94–1.82 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.0, 147.2, 137.5, 137.2, 128.9, 128.4, 128.3, 128.2, 127.6, 126.8, 126.3, 50.0, 44.6, 41.6, 37.3, 33.1, 26.0; **MS** = m/z (EI) 415 ([M]$^+$, 60%), 380 ([M-Cl]$^+$, 100%), 338 ([M-COCH$_2$Cl]$^+$, 6%), 324 ([M-PhCH$_2$]$^+$, 3%), 91 ([PhCH$_2$]$^+$, 87%); **FT-IR** ν_{max}(ATR) cm^{-1}: 3037, 2931, 1659, 1493, 1406, 1238, 1003, 912, 703.

N-benzyl-2-chloro-*N*-(spiro[5.5]undec-2-en-3-yl)acetamide (1e)



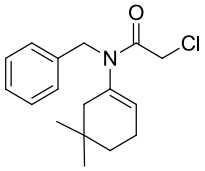
Substrate **1e** was prepared following the general procedure. The product was obtained in 58% yield as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.20 (m, 5H), 5.38–5.29 (m, 1H), 4.61 (bs, 2H), 4.09 (s, 2H), 2.03–1.92 (m, 2H), 1.87–1.78 (m, 2H), 1.48 (t, *J* = 6.3 Hz, 2H), 1.44–1.27 (m, 6H), 1.29–1.08 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 137.1, 136.3, 128.9, 128.3, 128.2, 127.4, 50.0, 41.8, 36.3, 36.2, 32.7, 30.6, 26.5, 24.7, 21.7; **MS** = m/z (EI) 331 ([M]$^+$, 15%), 296 ([M-Cl]$^+$, 100%), 254 ([M-COCH$_2$Cl]$^+$, 10%), 240 ([M-PhCH$_2$]$^+$, 2%), 91 ([PhCH$_2$]$^+$, 43%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2916, 1758, 1658, 1413, 1219, 709.

N-benzyl-2-chloro-*N*-(3,3-dimethylcyclohex-1-en-1-yl)acetamide (1f)



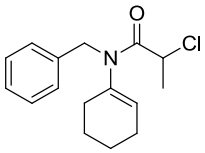
Substrate **1f** was prepared following the general procedure. The product was obtained in 21% yield as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.14 (m, 5H), 5.08 (s, 1H), 4.60 (bs, 2H), 4.07 (s, 2H), 1.97 (td, *J* = 6.2, 1.4 Hz, 2H), 1.66 (dtd, *J* = 9.1, 6.2, 3.1 Hz, 2H), 1.51–1.26 (m, 2H), 0.86 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 139.5, 136.8, 134.9, 129.1, 128.2, 127.5, 49.5, 41.7, 36.1, 32.3, 28.8, 27.7, 19.6; **MS** = m/z (EI) 291 ([M]$^+$, 13%), 256 ([M-Cl]$^+$, 100%), 214 ([M-COCH$_2$Cl]$^+$, 6%), 200 ([M-PhCH$_2$]$^+$, 4%), 91 ([PhCH$_2$]$^+$, 81%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2937, 1658, 1403, 1229, 1155, 921, 698.

N-benzyl-2-chloro-*N*-(5,5-dimethylcyclohex-1-en-1-yl)acetamide (1g)



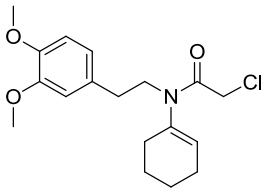
Substrate **1g** was prepared following the general procedure. The product was obtained in 41% yield as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.18 (m, 5H), 5.39 (d, *J* = 1.6 Hz, 1H), 4.59 (s, 2H), 4.11 (s, 2H), 2.03 (dd, *J* = 6.2, 2.6 Hz, 2H), 1.85–1.78 (m, 2H), 1.28 (t, *J* = 6.3 Hz, 2H), 0.91 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 137.1, 136.2, 128.9, 128.3, 128.2, 127.4, 49.7, 41.7, 41.3, 34.0, 29.8, 27.9, 22.5; **MS** = m/z (EI) 291 ([M]$^+$, 13%), 256 ([M-Cl]$^+$, 100%), 214 ([M-COCH$_2$Cl]$^+$, 9%), 200 ([M-PhCH$_2$]$^+$, 3%), 91 ([PhCH$_2$]$^+$, 69%); **FT-IR** ν_{max}(ATR) cm^{-1}: 3035, 2937, 1665, 1405, 1238, 1165, 1019, 788, 719.

_N_-benzyl-2-chloro-_N_-(cyclohex-1-en-1-yl)propanamide (1h)



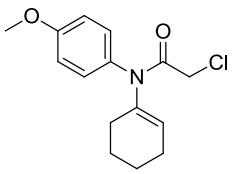
Substrate **1h** was prepared following the general procedure. The product was obtained in 45% yield as a solid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.18 (m, 5H), 5.56–5.34 (m, 1H), 4.82–4.68 (m, 1H), 4.63 (bs, 1H), 2.20–2.07 (m, 1H), 2.07–1.98 (m, 2H), 1.98–1.85 (m, 1H), 1.71–1.59 (m, 5H), 1.59–1.43 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 137.6, 137.4, 129.0, 128.6, 128.3, 127.3, 50.3, 50.0, 28.2, 24.7, 22.7, 21.6, 21.3; **MS** = m/z (EI) 277 ($[M]^+$, 13%), 242 ($[M\text{-}Cl]^+$, 100%), 186 ($[M\text{-}COCH_2Cl]^+$, 17%), 91 ($[PhCH_2]^+$, 83%); **FT-IR** ν_{max}(ATR) cm^{-1}: 3029, 2933, 1655, 1412, 1219, 1070, 996, 758, 699.

2-chloro-_N_-(cyclohex-1-en-1-yl)-_N_-(3,4-dimethoxyphenethyl)acetamide (1i)



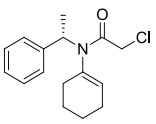
Substrate **1i** was prepared following the general procedure. The product was obtained in 31% yield as a brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82–6.66 (m, 3H), 5.62–5.51 (m, 1H), 4.12–3.99 (m, 2H), 3.89–3.76 (m, 6H), 3.58 (bs, 2H), 2.78 (dd, J = 14.5, 6.9 Hz, 2H), 2.16–1.98 (m, 4H), 1.82–1.66 (m, 2H), 1.64–1.50 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 148.9, 147.5, 138.0, 131.3, 128.4, 120.6, 112.0, 111.2, 55.9, 55.9, 47.8, 41.7, 33.5, 27.6, 24.7, 22.6, 21.4; **MS** = m/z (EI) 337 ($[M]^+$, 10%), 302 ($[M\text{-}Cl]^+$, 1%), 164 ($[M\text{-}CH_2CH_2Ph(MeO)_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2935, 1658, 1513, 1441, 1237, 1148, 1026, 927, 778.

2-chloro-_N_-(cyclohex-1-en-1-yl)-_N_-(4-methoxyphenyl)acetamide (1j)



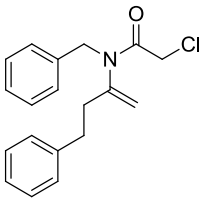
Substrate **1j** was prepared following the general procedure. The product was obtained in 60% yield as a brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) **rotamers in ratio 1:1.4** δ 7.24–7.11 (m, 4.8H), 6.97–6.81 (m, 4.8H), 5.96 (bs, 1.4H), 5.66 (bs, 1H), 4.29 (s, 2.8H), 3.91–3.72 (m, 9.2H), 2.29–2.18 (m, 4.4H), 2.16–1.97 (m, 5.2H), 1.74–1.52 (m, 9.6H); **^{13}C NMR** (151 MHz, CDCl3) δ 166.0, 165.7, 140.1, 139.0, 134.1, 132.2, 130.8, 128.9, 128.1, 127.2, 124.8, 122.0, 114.9, 114.2, 55.5, 55.4, 42.4 (2C), 27.5, 27.0 (2C), 24.6 (2C), 22.6, 21.5, 21.4; **MS** = m/z (EI) 279 ($[M]^+$, 22%), 244 ($[M\text{-}Cl]^+$, 100%), 202 ($[M\text{-}COCH_2Cl]^+$, 12%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2929, 2851, 1667, 1505, 1359, 1241, 1030, 826.

(_S_)-2-chloro-_N_-(cyclohex-1-en-1-yl)-_N_-(1-phenylethyl)acetamide (1k)



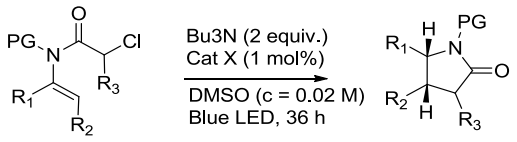
Substrate **1k** was prepared following the general procedure. The product was obtained in 45% yield as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.16 (m, 5H), 5.89–5.57 (overlapping of two signals, 2H), 4.13–3.88 (m, 2H), 2.28–1.81 (m, 3H), 1.60–1.25 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 140.3, 135.9, 131.3, 128.1, 127.6, 127.5, 52.6, 42.4, 30.1, 25.0, 22.7, 21.1, 17.1; **MS** = m/z (EI) 277 ($[M]^+$, 31%), 242 ($[M\text{-}Cl]^+$, 45%), 200 ($[M\text{-}COCH_2Cl]^+$, 11%), 172 ($[M\text{-}PhCH_2]^+$, 27%), 105 ($[Ph(CH_3)CH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 3036, 2940, 1756, 1657, 1384, 1243, 1207, 1071, 918, 767, 693.

***N*-benzyl-2-chloro-*N*-(4-phenylbut-1-en-2-yl)acetamide (1l)**



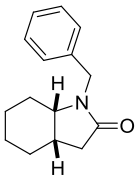
Substrate **1l** was prepared following the general procedure. The product was obtained in 56% yield as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.16 (m, 8H), 7.11 (d, *J* = 7.5 Hz, 2H), 5.11 (bs, 1H), 4.83 (bs, 1H), 4.68 (bs, 2H), 4.04 (s, 2H), 2.79–2.70 (m, 2H), 2.51 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 146.1, 140.1, 136.7, 128.7, 128.6, 128.5, 128.2, 127.6, 126.4, 115.7, 49.4, 41.4, 35.3, 32.9; **MS** = m/z (EI) 313 ($[M]^+$, 7%), 278 ($[M\text{-}Cl]^+$, 48%), 236 ($[M\text{-}COCH_2Cl]^+$, 8%), 222 ($[M\text{-}PhCH_2]^+$, 38%), 91 ($[PhCH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 3030, 2935, 2327, 2094, 1657, 1396, 1224, 910, 723.

Preparation and Characterization of Products



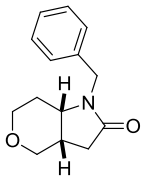
A 10 ml flask was charged with α-chloroenamide (1 equiv.), photocatalyst (1 mol%) and *n*-Bu_3N (2 equiv.). The flask was capped with a septum and twice evacuated and backfilled with argon. Degassed DMSO (6.5 ml, 0.02M) was added *via* syringe. The flask was placed in a 100 ml beaker containing a blue LEDs strip glued on the inner wall and stirred for 48 hours. After this period, the mixture was diluted with Et_2O and the organic phase was extracted three times with brine, dried over $MgSO_4$, filtered and evaporated under reduce pressure. The residue was purified by column chromatography using a mixture of Hexane/EtOAc as eluent.

***cis*-1-benzylhexahydro-1H-indol-2(3*H*)-one (2a)**



The title compound was synthesized according to the general procedure employing **1a** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 67%; **dr** > 50:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.08 (m, 5H), 4.93 (d, *J* = 15.0 Hz, 1H), 3.95 (d, *J* = 15.0 Hz, 1H), 3.37 (dd, *J* = 11.3, 5.7 Hz, 1H), 2.46–2.31 (m, 1H), 2.30–2.05 (m, 2H), 1.74–1.51 (m, 3H), 1.48–1.36 (m, 2H), 1.36–1.07 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6, 137.0, 128.5, 127.9, 127.3, 56.0, 43.8, 37.0, 32.4, 27.2, 26.6, 22.4, 21.1; **MS** = m/z (EI) 229 ($[M]^+$, 76%), 186 ($[M\text{-}COCH_3]^+$, 100%), 138 ($[M\text{-}CH_2Ph]^+$, 37%), 91 ($[PhCH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2928, 2856, 1683, 1413, 1265, 732, 701.

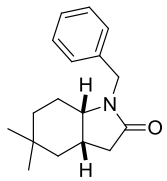
***cis*-1-benzylhexahydropyrano[4,3-*b*]pyrrol-2(3*H*)-one (2b)**



The title compound was synthesized according to the general procedure employing **1b** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 62%; **dr** > 50:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.08 (m, 5H), 4.88 (d, *J* = 15.0 Hz, 1H), 4.03 (d, *J* = 15.0 Hz, 1H), 3.66 (dd, *J* = 12.1, 4.5 Hz, 1H), 3.61–3.45 (m, 3H), 3.42–3.35 (m, 1H), 2.51–2.22 (m, 3H),

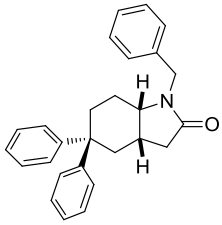
1.83 (dddd, *J* = 14.4, 7.2, 5.2, 3.9 Hz, 2H), 1.66 (dtd, *J* = 10.6, 6.9, 3.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 136.6, 128.7, 128.0, 127.6, 67.5, 63.6, 53.2, 44.1, 33.7, 31.7, 26.9; **MS** = m/z (EI) 231 ($[M]^+$, 85%), 140 ($[M\text{-}CH_2Ph]^+$, 26%), 91 ($[PhCH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2935, 2856, 1679, 1418, 1295, 1243, 1093, 876, 702.

cis-1-benzyl-5,5-dimethylhexahydro-1*H*-indol-2(3*H*)-one (2c)



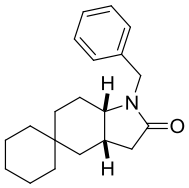
The title compound was synthesized according to the general procedure employing **1c** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 59%; **dr** > 50:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31–7.18 (m, 5H), 4.94 (d, *J* = 15.1 Hz, 1H), 3.96 (d, *J* = 15.1 Hz, 1H), 3.48 (dd, *J* = 8.1, 4.7 Hz, 1H), 2.52 (dd, *J* = 16.2, 7.1 Hz, 1H), 2.29 (ddd, *J* = 16.9, 11.4, 5.4 Hz, 1H), 2.03 (d, *J* = 16.2 Hz, 1H), 1.78 (ddd, *J* = 15.2, 7.3, 3.7 Hz, 1H), 1.60 (ddt, *J* = 15.3, 12.9, 4.5 Hz, 1H), 1.33–1.22 (m, 1H), 1.13–1.04 (m, 2H), 1.00 (td, *J* = 13.2, 3.9 Hz, 1H), 0.86 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.2, 136.9, 128.5, 127.9, 127.3, 55.1, 43.6, 40.9, 39.3, 32.8, 32.3, 29.4 (2C), 24.2, 21.7; **MS** = m/z (EI) 257 ($[M]^+$, 70%), 166 ($[M\text{-}CH_2Ph]^+$, 39%), 91 ($[PhCH_2]^+$, 87%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2935, 2325, 2098, 1807, 1683, 1412, 1256, 932, 703.

cis-1-benzyl-5,5-diphenylhexahydro-1*H*-indol-2(3*H*)-one (2d)



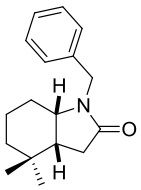
The title compound was synthesized according to the general procedure employing **1d** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 43%; **dr** > 50:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35–7.15 (m, 12H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.06–6.99 (m, 2H), 4.88 (d, *J* = 15.0 Hz, 1H), 4.17 (d, *J* = 15.0 Hz, 1H), 3.43 (d, *J* = 2.4 Hz, 1H), 2.60–2.46 (m, 3H), 2.28–2.20 (m, 1H), 2.14 (d, *J* = 15.9 Hz, 1H), 1.96 (dd, *J* = 15.3, 2.9 Hz, 1H), 1.88–1.74 (m, 2H), 1.62–1.52 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.1, 150.0, 143.9, 137.0, 128.6 (2C), 128.2, 128.0, 127.8, 127.4, 126.1, 126.0, 125.8, 55.3, 45.4, 43.9, 39.5, 39.0, 30.1, 29.9, 22.2; **MS** = m/z (EI) 381 ($[M]^+$, 4%), 290 ($[M\text{-}CH_2Ph]^+$, 2%), 91 ($[PhCH_2]^+$, 100%), 77 ($[Ph]^+$, 5%); **FT-IR** ν_{max}(ATR) cm^{-1}: 3037, 2934, 1680, 1421, 1308, 1029, 917, 749, 697.

cis-1-benzylhexahydrospiro[cyclohexane-1,5-indol]-2(3*H*)-one (2e)



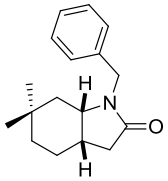
The title compound was synthesized according to the general procedure employing **1e** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 41%; **dr** > 50:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.11 (m, 5H), 4.93 (d, *J* = 15.0 Hz, 1H), 3.96 (d, *J* = 15.1 Hz, 1H), 3.47 (dd, *J* = 9.0, 4.7 Hz, 1H), 2.52 (dd, *J* = 16.3, 7.3 Hz, 1H), 2.27 (td, *J* = 11.9, 6.1 Hz, 1H), 2.02 (d, *J* = 16.3 Hz, 1H), 1.77–1.09 (m, 15H), 1.04–0.87 (m, 1H); **^{13}C NMR** (151 MHz, CDCl3) δ 176.1, 136.9, 128.5, 127.9, 127.3, 55.8, 43.6, 40.6, 39.3, 38.6 (bs), 32.7, 31.81, 30.3 (bs), 28.5, 26.6, 21.6, 21.4, 21.0; **MS** = m/z (EI) 298 ($[M+H]^+$, 71%), 297 ($[M]^+$, 80%), 206 ($[M\text{-}CH_2Ph]^+$, 74%), 91 ($[PhCH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2921, 2854, 2318, 2101, 1684, 1411, 1304, 1257, 917, 703.

cis-1-benzyl-4,4-dimethylhexahydro-1*H*-indol-2(3*H*)-one (2f)



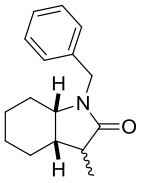
The title compound was synthesized according to the general procedure employing **1f** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 43%; **dr** > 50:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.14 (m, 5H), 4.91 (d, *J* = 15.1 Hz, 1H), 3.93 (d, *J* = 15.1 Hz, 1H), 3.46–3.29 (m, 1H), 2.41–2.18 (m, 2H), 2.04–1.87 (m, 2H), 1.50–1.45 (m, 1H), 1.35–1.17 (m, 3H), 1.09–0.95 (m, 1H), 0.88 (overlapping of two singlets, 3H+3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 137.1, 128.6, 127.9, 127.4, 55.2, 44.2, 34.0, 32.4, 31.4, 30.3, 29.3, 27.6, 27.4, 18.9; **MS** = m/z (EI) 258 ($[M+H]^+$, 83%), 257 ($[M]^+$, 90%), 166 ($[M-CH_2Ph]^+$, 63%), 91 ($[PhCH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2930, 1681, 1429, 1363, 1232, 741, 700.

cis-1-benzyl-6,6-dimethylhexahydro-1*H*-indol-2(3*H*)-one (2g)



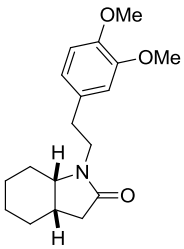
The title compound was synthesized according to the general procedure employing **1g** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 64%; **dr** > 50:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.17 (m, 5H), 5.01 (d, *J* = 15.1 Hz, 1H), 3.83 (d, *J* = 15.1 Hz, 1H), 3.44–3.35 (m, 1H), 2.40–2.22 (m, 2H), 1.82–1.63 (m, 1H), 1.62–1.43 (m, 2H), 1.37–1.03 (m, 4H), 0.91 (s, 3H), 0.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 136.9, 128.6, 127.9, 127.4, 54.5, 43.8, 39.3, 35.0, 34.2, 31.6, 31.2, 29.6, 25.5, 22.8; **MS** = m/z (EI) 258 ($[M+H]^+$, 74%), 257 ($[M]^+$, 81%), 166 ($[M-CH_2Ph]^+$, 62%), 91 ($[PhCH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2925, 1682, 1422, 1361, 1307, 1248, 938, 701.

1-benzyl-3-methylhexahydro-1H-indol-2(3H)-one (2h)



The title compound was synthesized according to the general procedure employing **1h** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 53%; **dr** = 3:1:0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.10 (m, 17.5H), 4.94 (overlapping of two d, *J* = 15.0, 3.3H), 4.72 (d, *J* = 15.0 Hz, 1H), 4.14 (d, *J* = 15.0 Hz, 1H), 3.95 (overlapping of two d, *J* = 15.0, 3.3H), 3.42–3.38 (m, 0.3H), 3.25 (dt, *J* = 9.3, 6.1 Hz, 3H), 2.84–2.68 (m, 1H), 2.49 (dt, *J* = 14.3, 7.2 Hz, 0.6H), 2.33 (dq, *J* = 9.8, 7.0 Hz, 3H), 2.18–2.08 (m, 0.6H), 2.08–1.91 (m, 2.6H), 1.91–1.60 (m, 15H), 1.60–1.38 (m, 10H), 1.38–1.02 (overlapping of signals, 23.8H); **^{13}C NMR** of the two major diastereoisomers (101 MHz, $CDCl_3$) δ 178.3, 177.1, 137.5, 137.2, 128.5, 128.5, 127.9, 127.8, 127.3, 127.2, 61.4, 54.5, 50.8, 44.2, 44.1, 42.5, 40.7, 38.9, 29.5, 27.8, 27.3, 25.9, 25.5, 24.5, 22.3, 21.5, 13.8, 13.0; **MS** = m/z (EI) 244 ($[M+H]^+$, 74%), 243 ($[M]^+$, 80%), 152 ($[M-CH_2Ph]^+$, 66%), 91 ($[PhCH_2]^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2927, 2864, 1682, 1429, 1271, 1078, 946, 703.

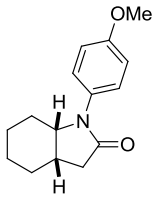
cis-1-(3,4-dimethoxyphenethyl)hexahydro-1H-inden-2(3H)-one (2i)



The title compound was synthesized according to the general procedure employing **1i** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu_3N. **Yield** = 63%; **dr** > 50:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.80–6.68 (m, 3H), 3.87–3.84 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.38 (dd, *J* = 11.2, 5.9 Hz, 1H), 3.08–2.98 (m, 1H), 2.82–2.65 (m, 2H), 2.31–2.05 (m, 3H), 1.77–1.66 (m, 1H), 1.55 (dd, *J* = 8.1, 5.4 Hz, 1H), 1.49–1.18 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 148.9, 147.5, 131.5, 120.6, 111.9, 111.2, 56.8, 55.9 (2C),

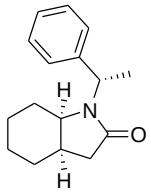
41.5, 37.0, 33.6, 32.5, 27.1, 26.9, 22.3, 21.2; **MS** = m/z (EI) 303 ([M+H]$^+$, 12%), 164 ([(OMe)$_2$C$_6$H$_5$CH$_2$CH$_3$]$^+$, 100%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2928, 2855, 2089, 1678, 1513, 1448, 1416, 1261, 1235, 1147, 1026, 807, 763.

cis-1-(4-methoxyphenyl)hexahydro-1H-inden-2(3H)-one (2j)



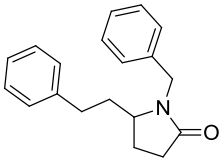
The title compound was synthesized according to the general procedure employing **1j** (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu$_3$N. **Yield** = 63%; **dr** > 50:1; **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.22 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.07–3.98 (m, 1H), 3.79 (s, 3H), 2.56–2.45 (m, 2H), 2.32 (dd, *J* = 15.6, 5.1 Hz, 1H), 1.73–1.60 (m, 2H), 1.59–1.50 (m, 2H), 1.40–1.31 (m, 2H), 1.29–1.23 (m, 2H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 175.1, 157.6, 130.3, 126.0, 114.3, 59.3, 55.4, 38.1, 32.5, 27.4, 26.8, 22.5, 21.0; **MS** = m/z (EI) 245 ([M+H]$^+$, 100%), 244 ([M]$^+$, 21%); **FT-IR** ν_{max}(ATR) cm^{-1}: 2927, 2852, 1680, 1508, 1442, 1379, 1239, 1120, 1033, 826, 691.

(3a*R*,7a*R*)-1-((*S*)-1-phenylethyl)hexahydro-1H-inden-2(3H)-one (2k)



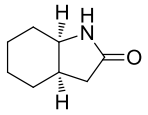
The title compound was synthesized according to the general procedure employing 1k (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu$_3$N. Yield = 47%; dr > 50:1; **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.43 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.39–7.33 (m, 1H), 5.56 (q, *J* = 7.2 Hz, 1H), 3.69 (dt, *J* = 8.2, 5.5 Hz, 1H), 2.51–2.36 (m, 3H), 1.73 (d, *J* = 7.2 Hz, 3H), 1.71–1.62 (m, 2H), 1.51–1.43 (m, 1H), 1.43–1.34 (m, 1H), 1.30–1.15 (m, 3H), 1.09–0.99 (m, 1H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 175.1, 142.1, 128.3, 127.5, 127.4, 55.9, 49.0, 35.9, 33.7, 29.1, 27.0, 22.1, 21.4, 16.4; **MS** = m/z (EI) 243 ([M+H]$^+$, 35%), 242 ([M]$^+$, 5%), 105 ([M-CH$_3$CHPh]$^+$, 100%), 77 ([Ph]$^+$, 19%); FT-IR ν_{max}(ATR) cm^{-1}: 2930, 2857, 1677, 1448, 1411, 1357, 1275, 1180, 758, 699.

1-benzyl-5-phenethylpyrrolidin-2-one (2l)



The title compound was synthesized according to the general procedure employing 1l (0.13 mmol), 1 mol% of **PC** and 2 equiv. of Bu$_3$N. Yield = 50%; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.31–7.21 (m, 5H), 7.20–7.14 (m, 3H), 7.10–7.00 (m, 2H), 4.95 and 3.95 (d, roof effect, *J* = 15.0 Hz, 2H), 3.44 (tdd, *J* = 8.4, 5.4, 3.0 Hz, 1H), 2.64–2.55 (m, 1H), 2.55–2.34 (m, 3H), 2.13 (dddd, *J* = 12.9, 9.8, 7.9, 6.4 Hz, 1H), 2.06–1.97 (m, 1H), 1.81–1.70 (m, 1H), 1.69–1.63 (m, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 175.1, 140.9, 136.6, 128.6, 128.5, 128.1, 128.0, 127.4, 126.1, 77.3, 77.0, 76.7, 56.5, 44.2, 34.4, 30.7, 30.2, 23.9; **MS** = m/z (EI) 280 ([M+H]$^+$, 56%), 279 ([M]$^+$, 80%), 174 ([M-CH$_2$CH$_2$Ph]$^+$, 87%), 91 ([CH$_2$Ph]$^+$, 100%); FT-IR ν_{max}(ATR) cm^{-1}: 3027, 2928, 2322, 2097, 1881, 1678, 1424, 1308, 1258, 1082, 701.

(3a*R*,7a*R*)-hexahydro-1*H*-indol-2(3*H*)-one (6)

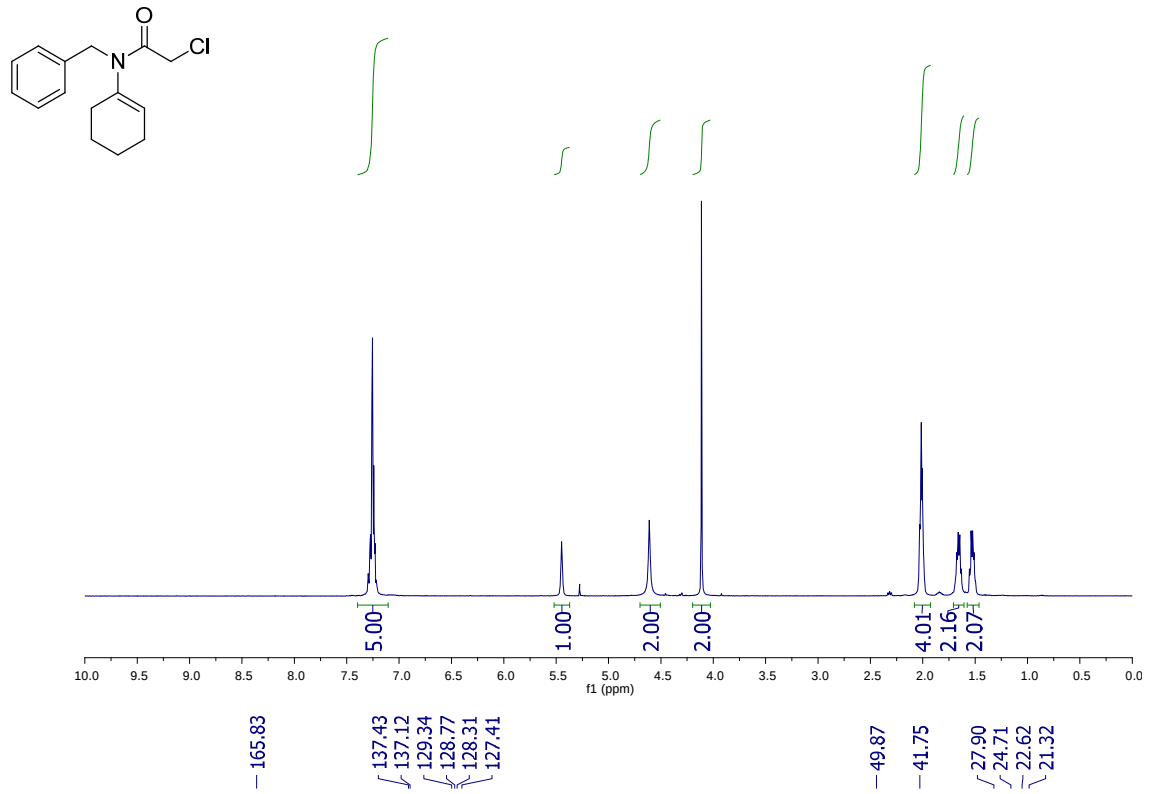


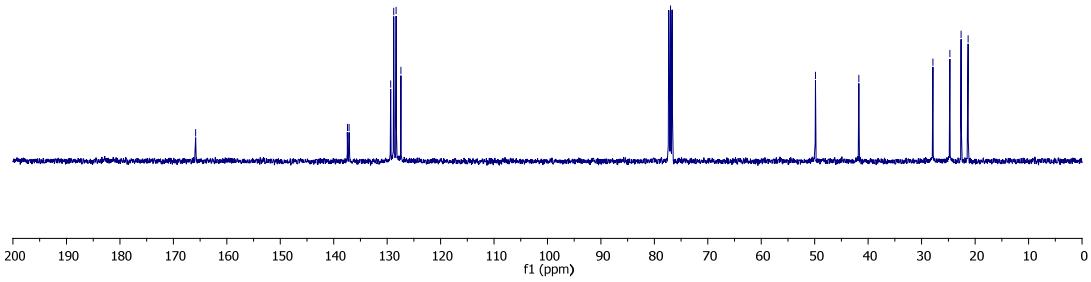
The title compound was synthesized following the reported procedure[2]: a solution of **2k** dissolved in 2 ml of dry THF was added dropwise to sodium (6 equiv.) in liquid ammonia (circa 3 ml) at -78 °C. The mixture was stirred at this temperature for 30 minutes and subsequently quenched with a saturated solution of ammonium chloride and extraction with diethylether. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica gel (gradient DCM/*i*PrOH, 99:1). Yield = 40%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.63 (br s, 1H), 3.71 (q, *J* = 5.0 Hz, 1H), 2.48–2.34 (m, 2H), 2.16–2.02 (m, 1H), 1.76–1.28 (m, 8H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.1, 53.6, 37.7, 34.4, 28.8, 27.2, 22.6, 20.6; $[\alpha]_D^{RT}$ = -24 (*c* = 0.388, EtOH).

[2] H. Ishibashi, Y. Fuke, T. Yamashita and M. Ikeda, *Tetrahedron: Asymmetry,* 1996, **7**, 2531–2538.

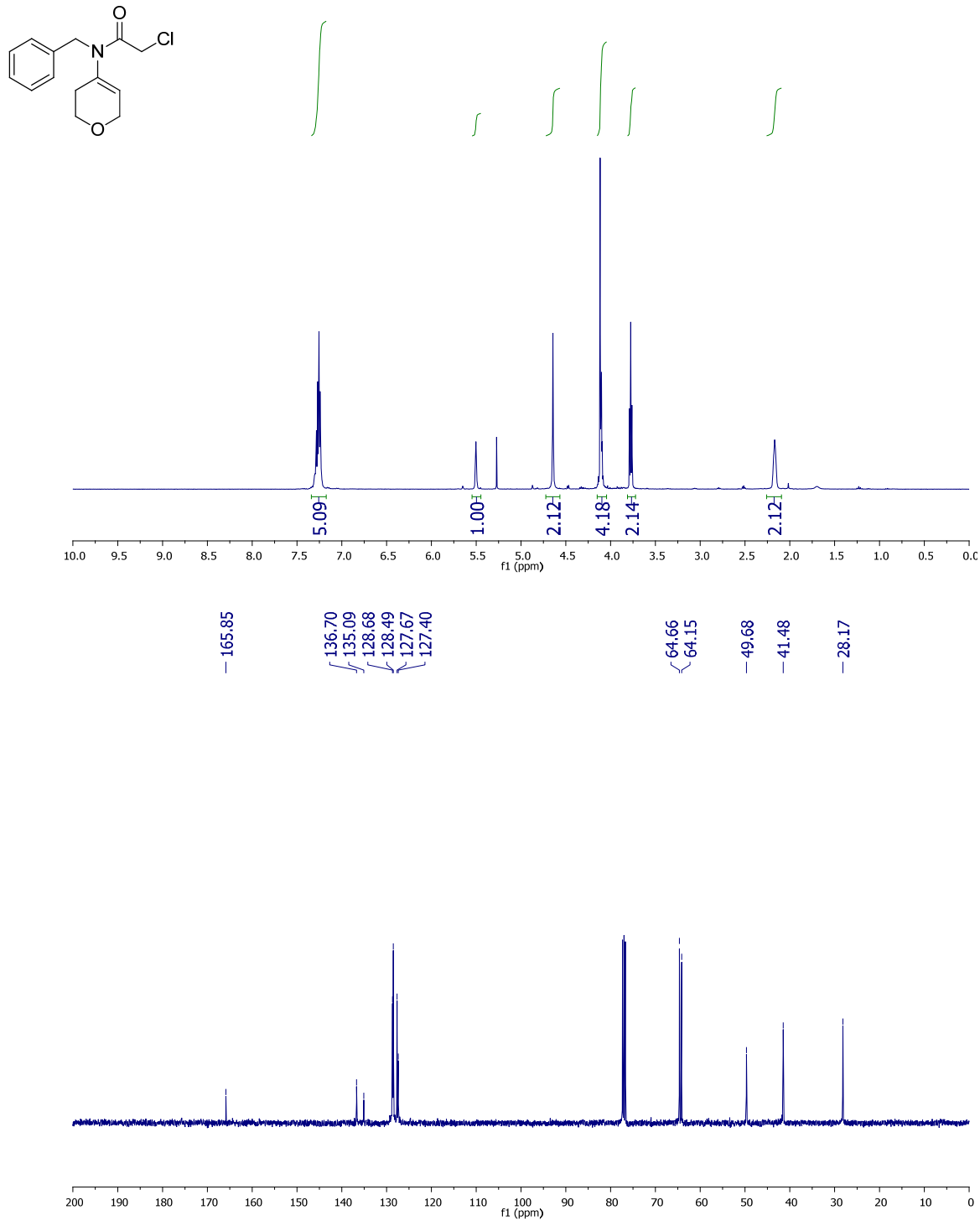
NMR Spectra

N-benzyl-2-chloro-*N*-(cyclohex-1-en-1-yl)acetamide (1a)

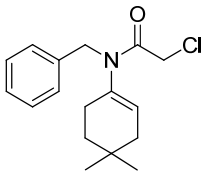


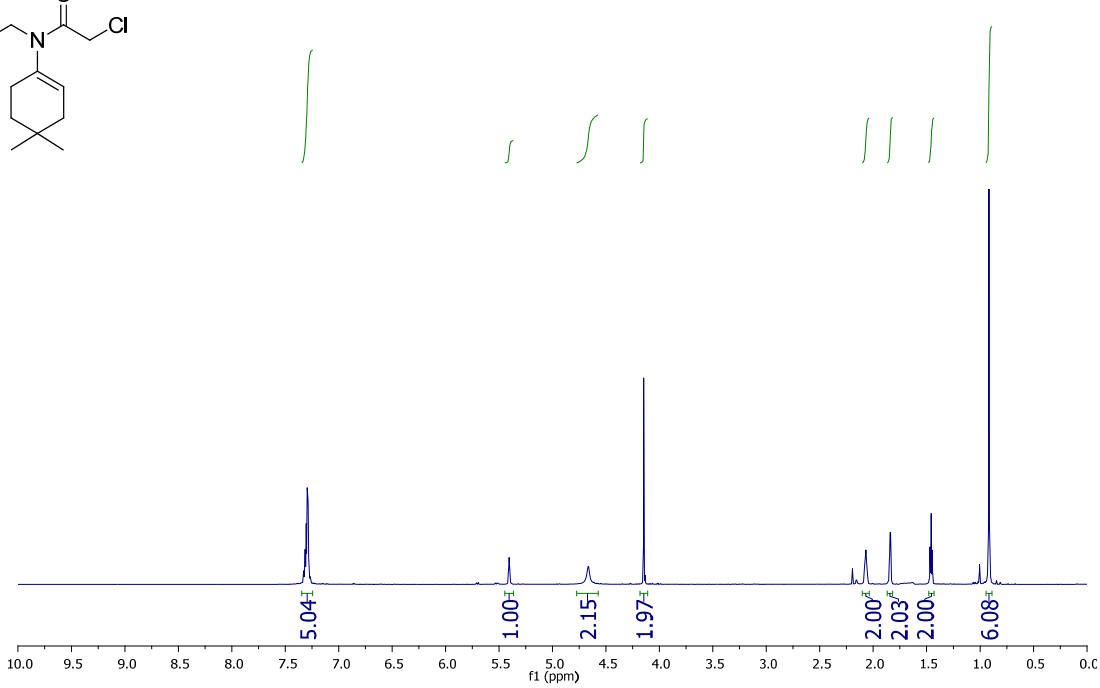


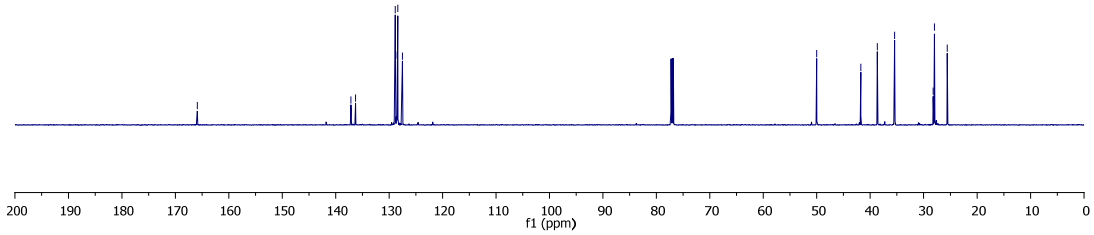
N-benzyl-2-chloro-*N*-(3,6-dihydro- *H*-pyran-4-yl)acetamide (1b)



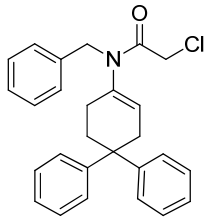
N-benzyl-2-chloro-*N*-(4,4-dimethylcyclohex-1-en-1-yl)acetamide (1c)

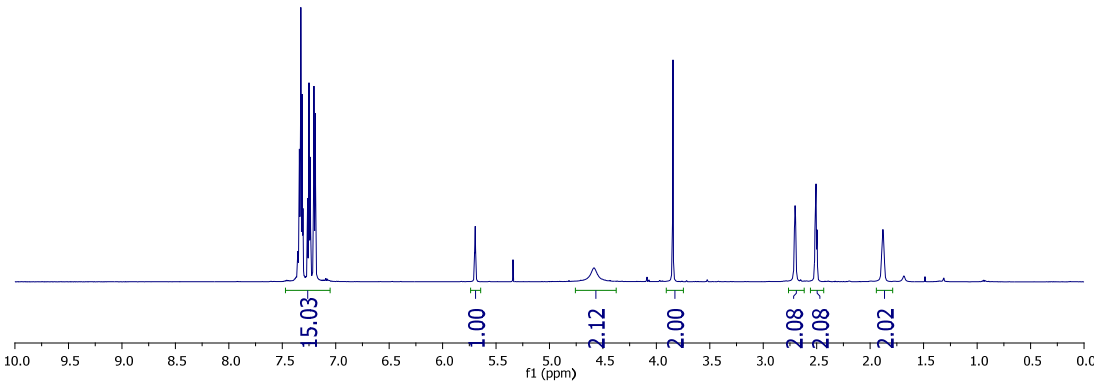


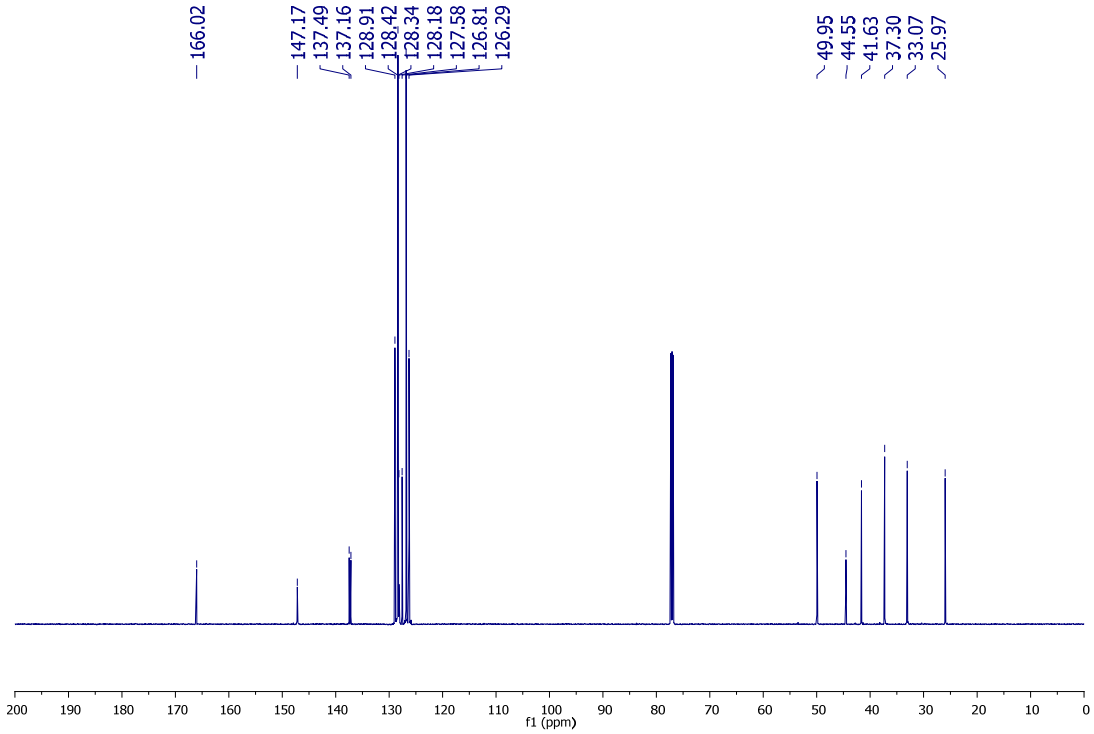




N-benzyl-2-chloro-*N*-(3',6'-dihydro-2'*H*-[1,1':1',1"-terphenyl]-4'-yl)acetamide (1d)







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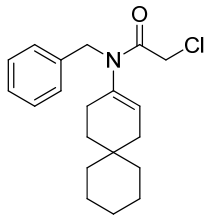

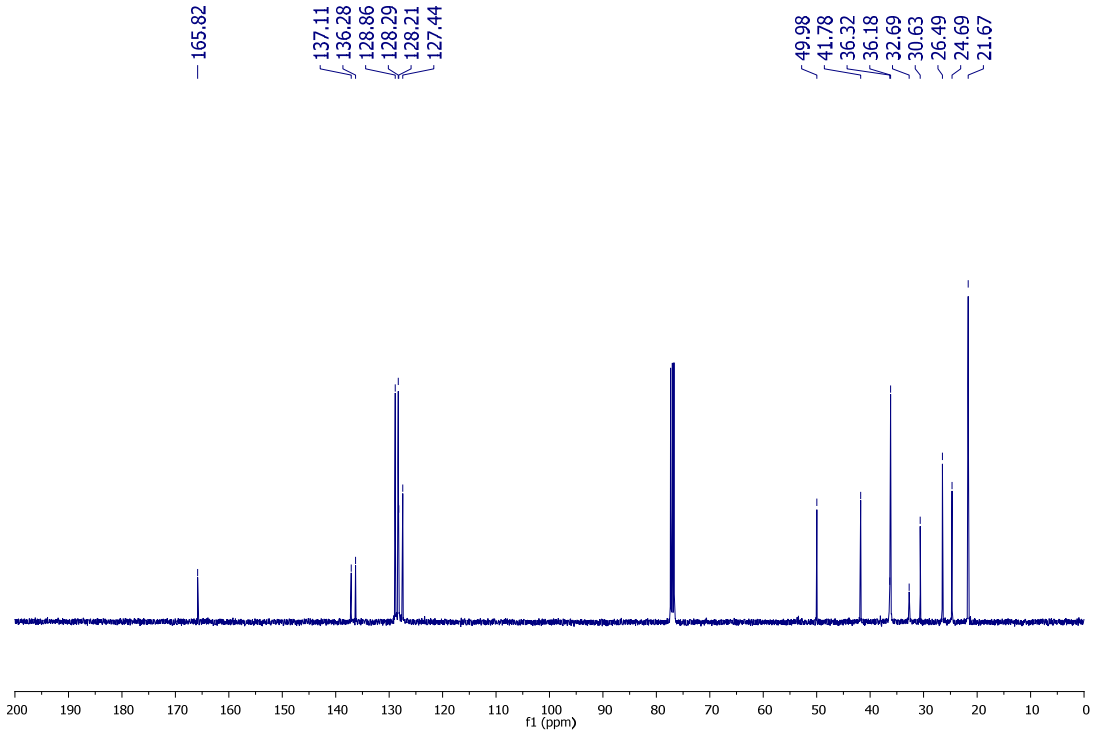

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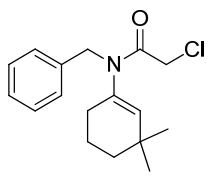

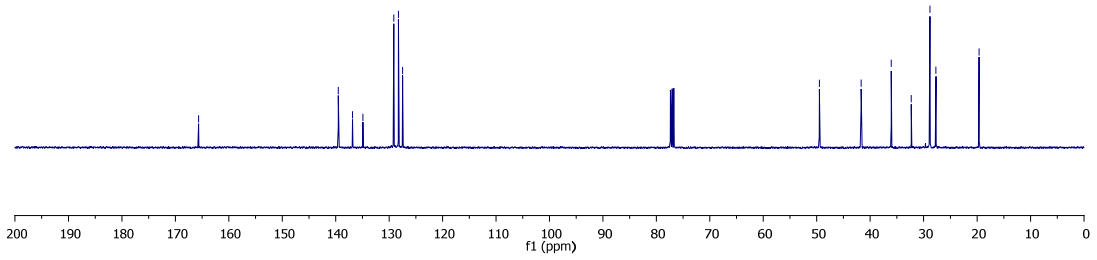

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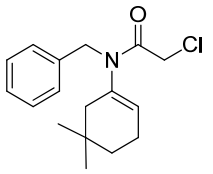
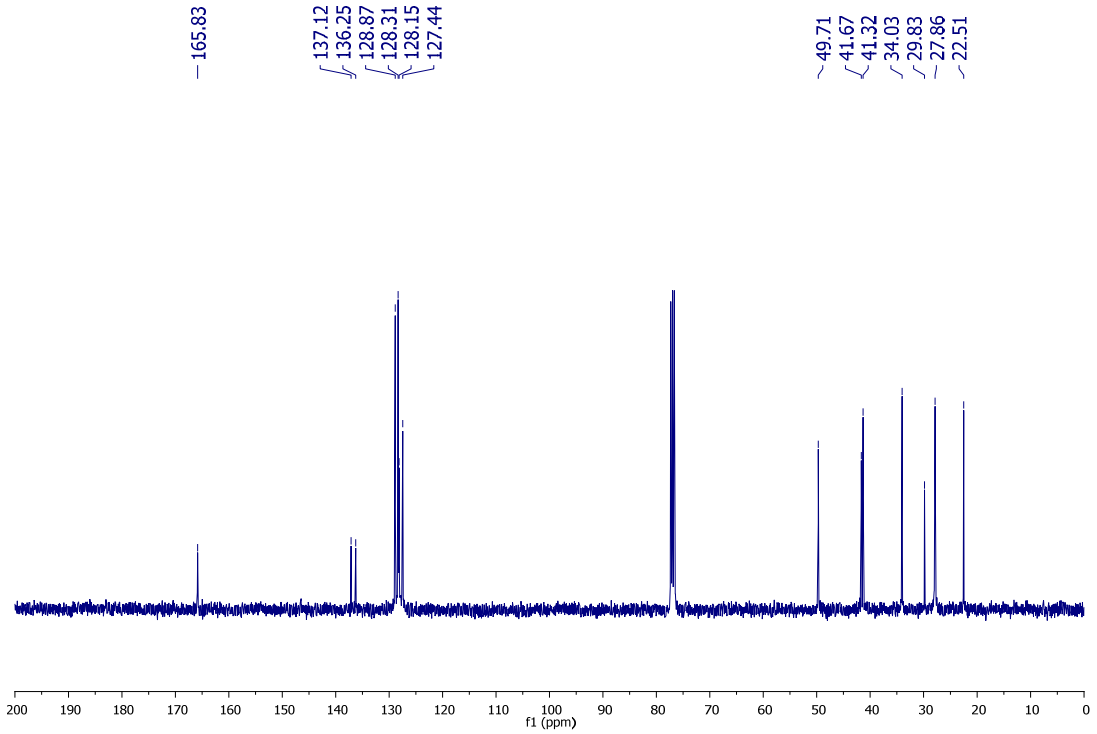
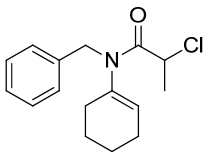
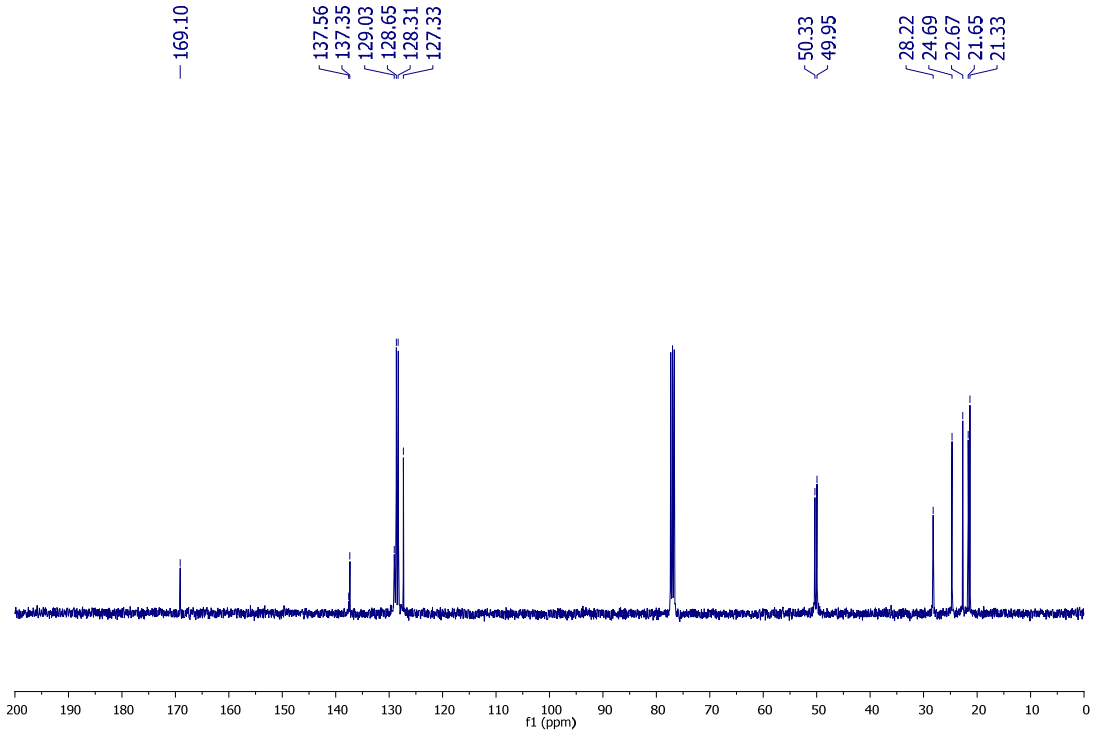


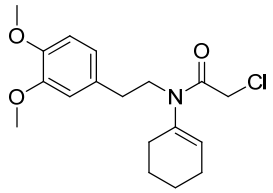


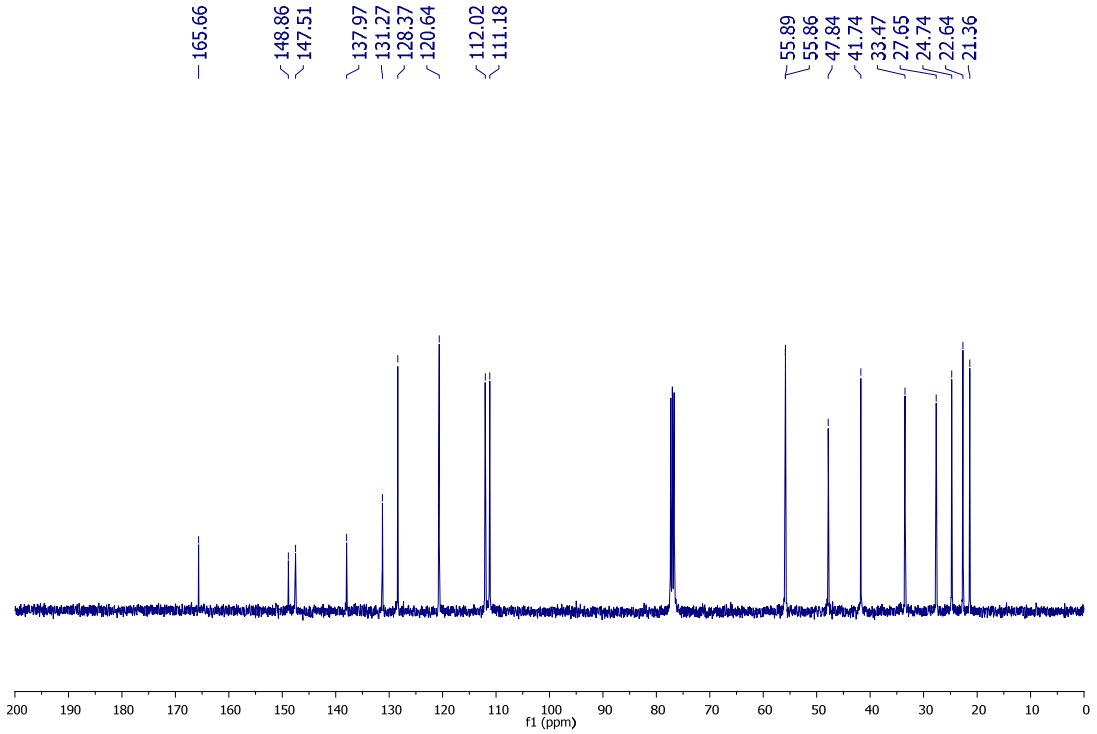
N-benzyl-2-chloro-*N*-(cyclohex-1-en-1-yl)propanamide (1h)





2-chloro-*N*-(cyclohex-1-en-1-yl)-*N*-(3,4-dimethoxyphenethyl)acetamide (1i)





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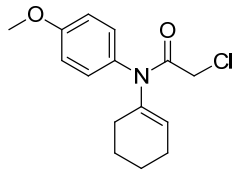

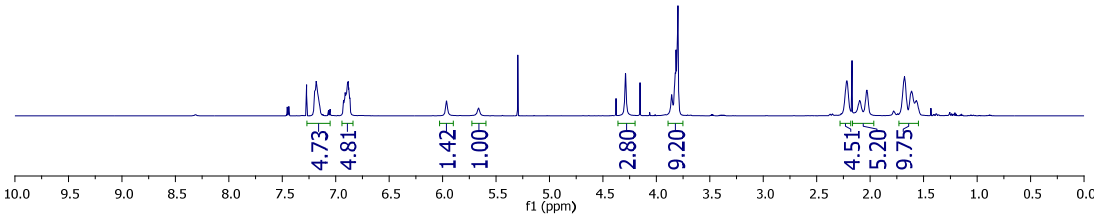

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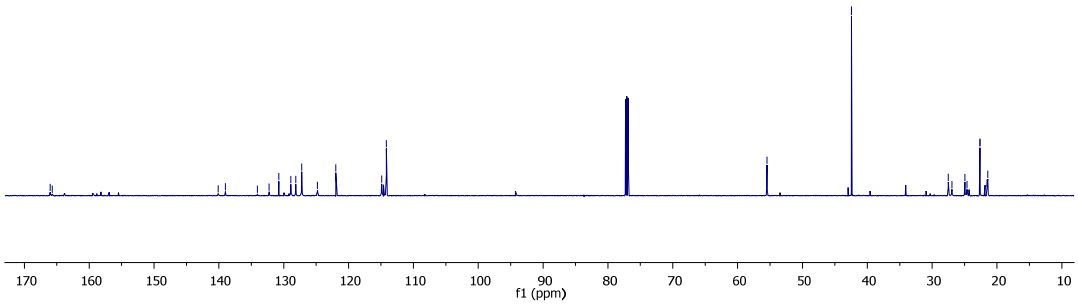
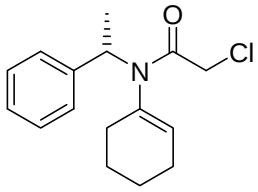
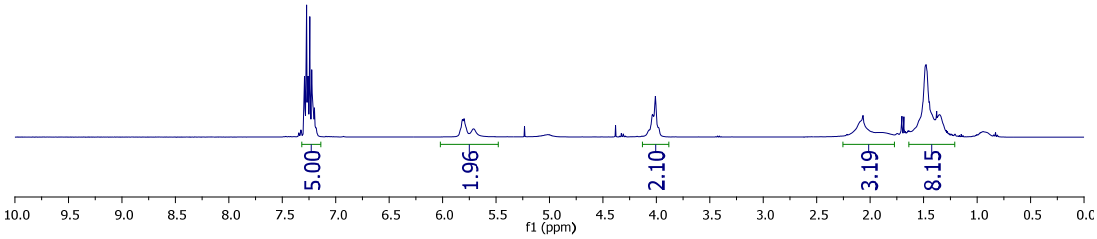
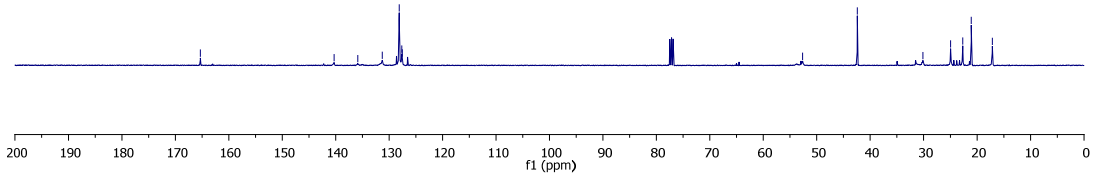


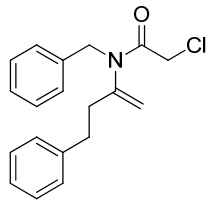
(*S*)-2-chloro-*N*-(cyclohex-1-en-1-yl)-*N*-(1-phenylethyl)acetamide (1k)

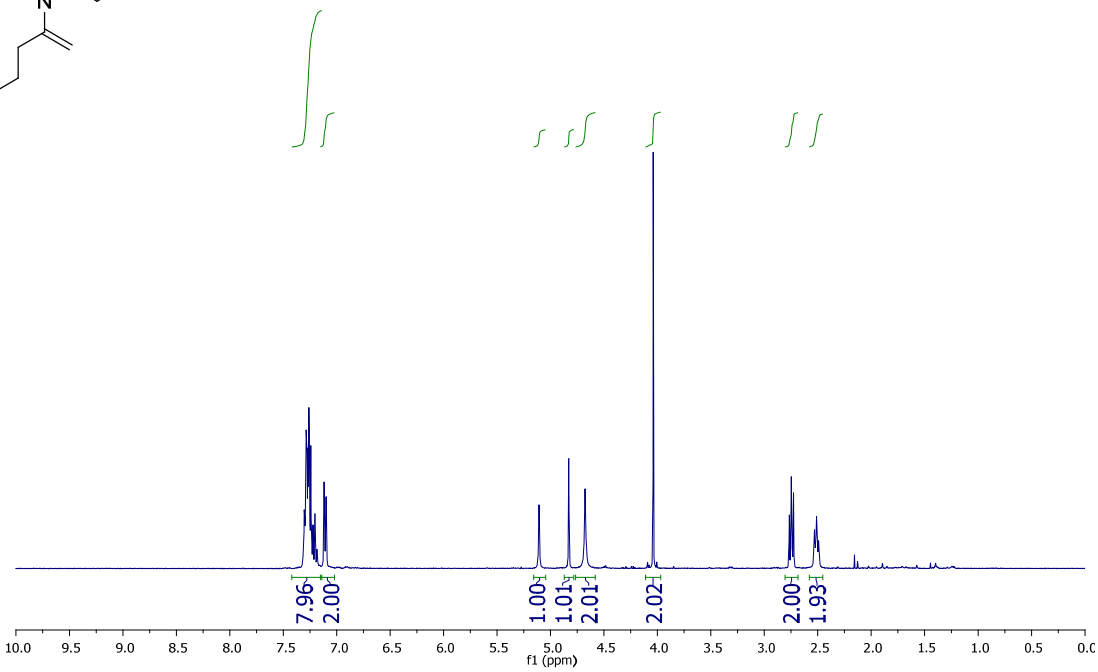


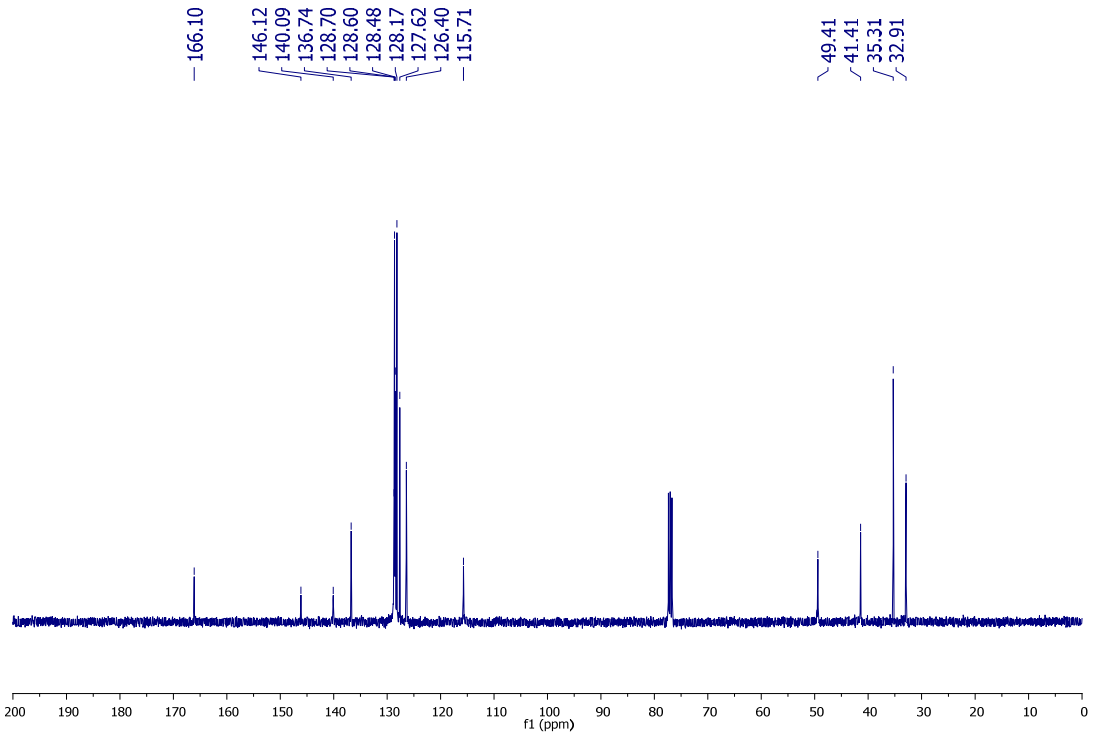




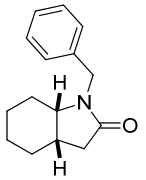
N-benzyl-2-chloro-*N*-(4-phenylbut-1-en-2-yl)acetamide (1l)

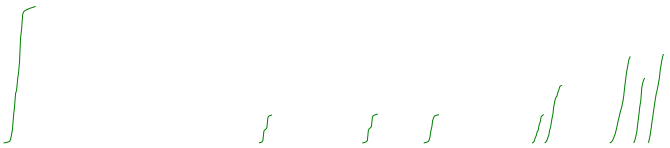


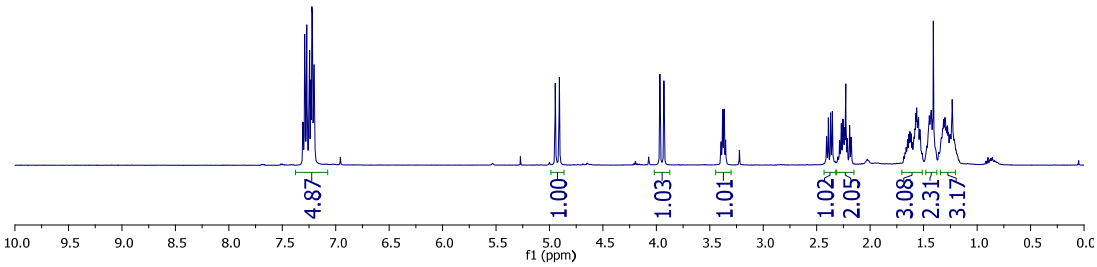


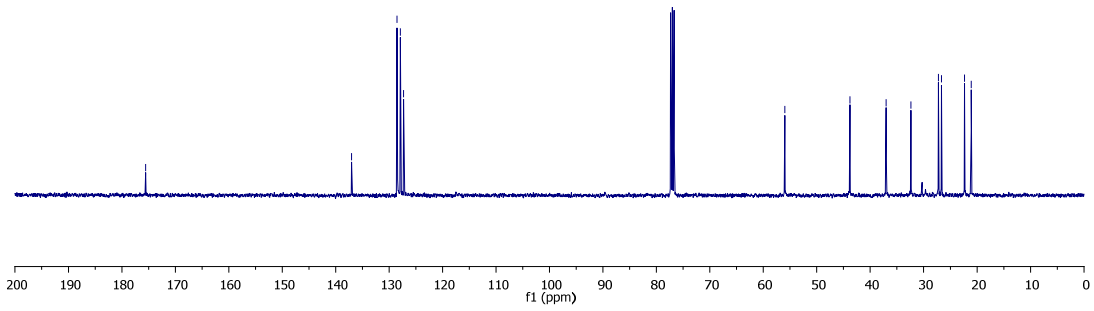


cis-1-benzylhexahydro-1*H*-inden-2(3*H*)-one (2a)

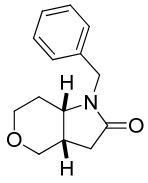


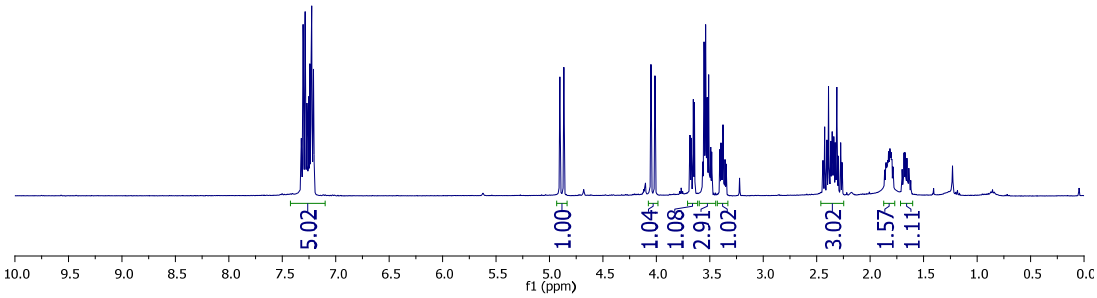


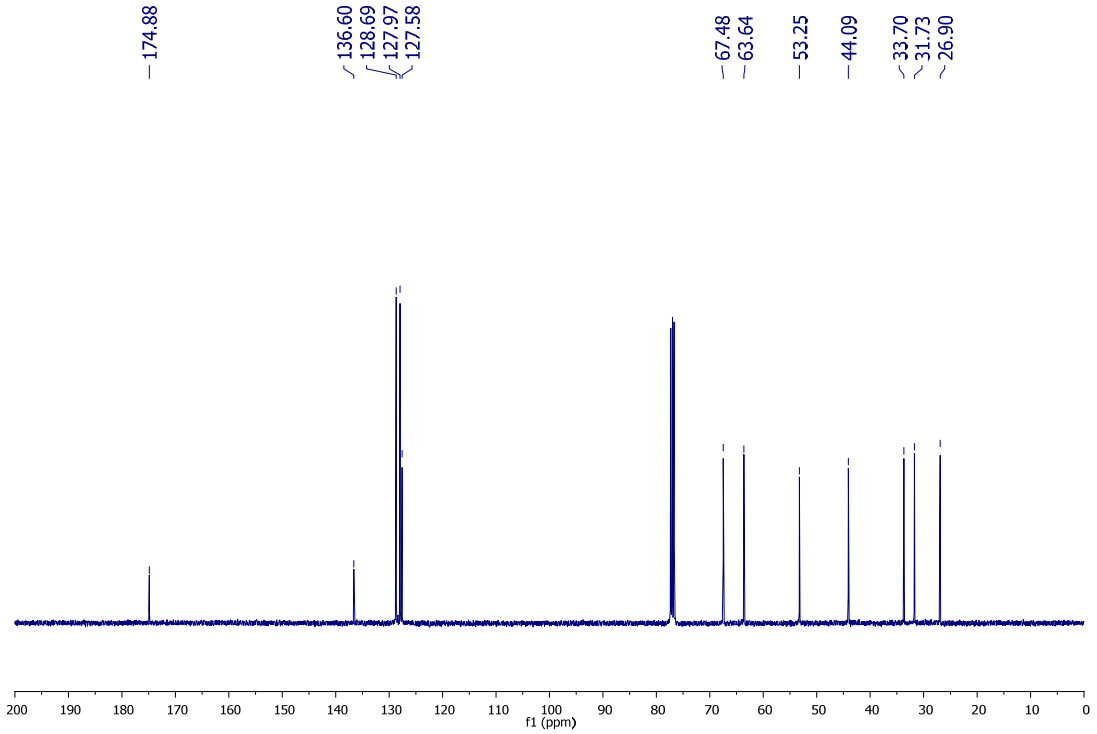




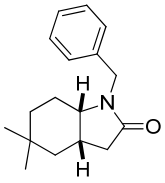
cis -1-benzylhexahydropyrano[4,3-*b*]pyrrol-2(3*H*)-one (2b)

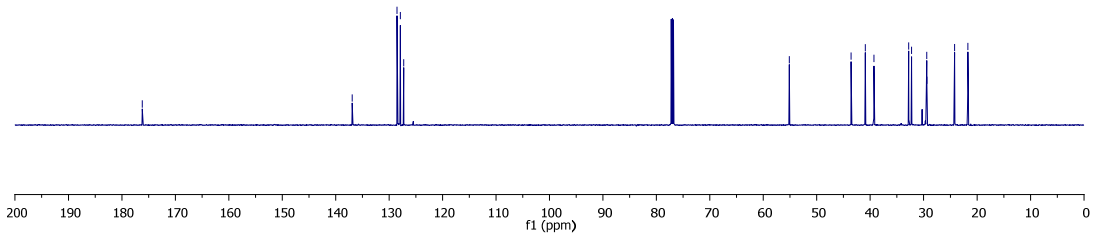




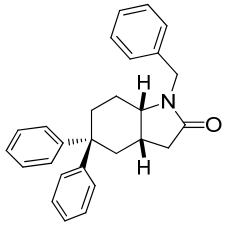


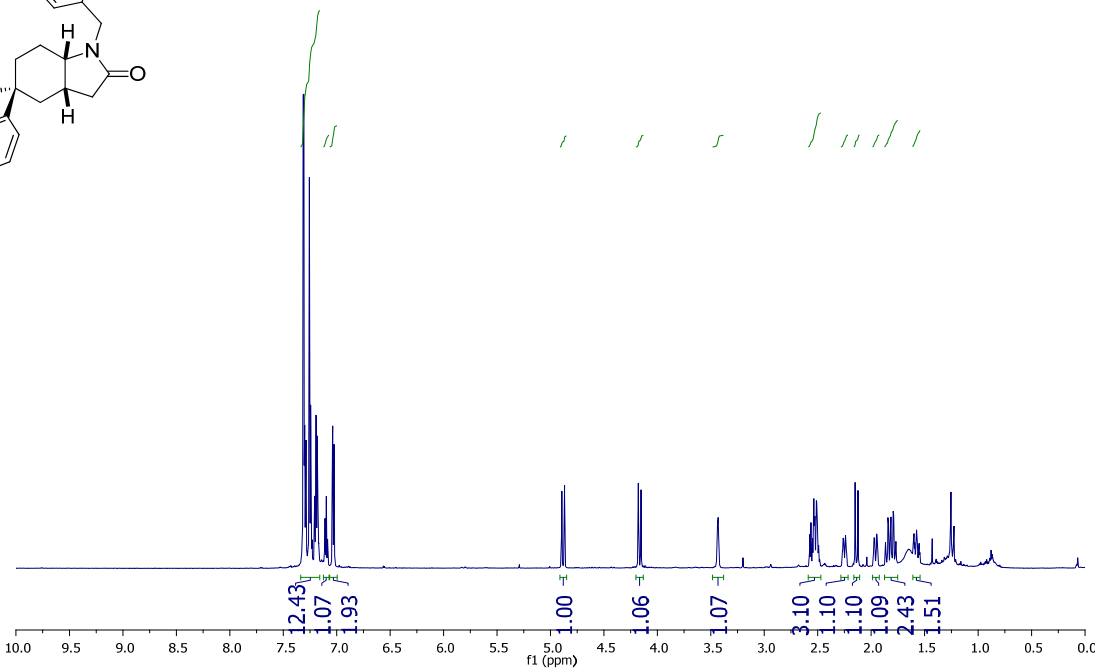
cis **-1-benzyl-5,5-dimethylhexahydro-1*H*-indol-2(3*H*)-one (2c)**

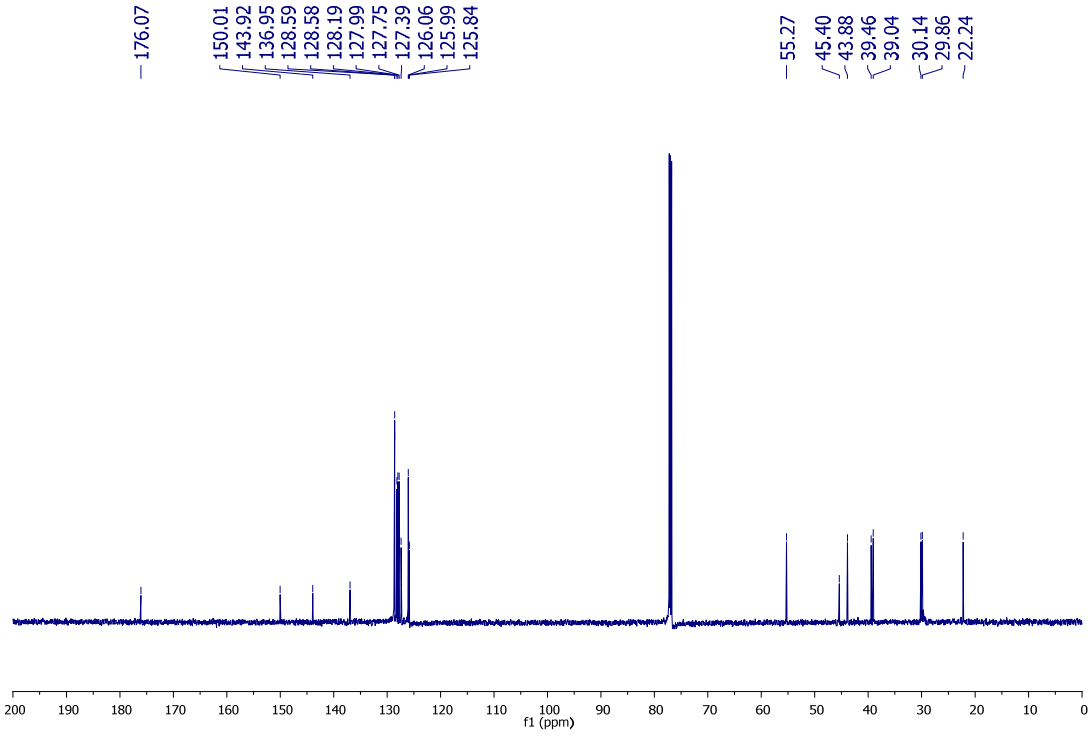




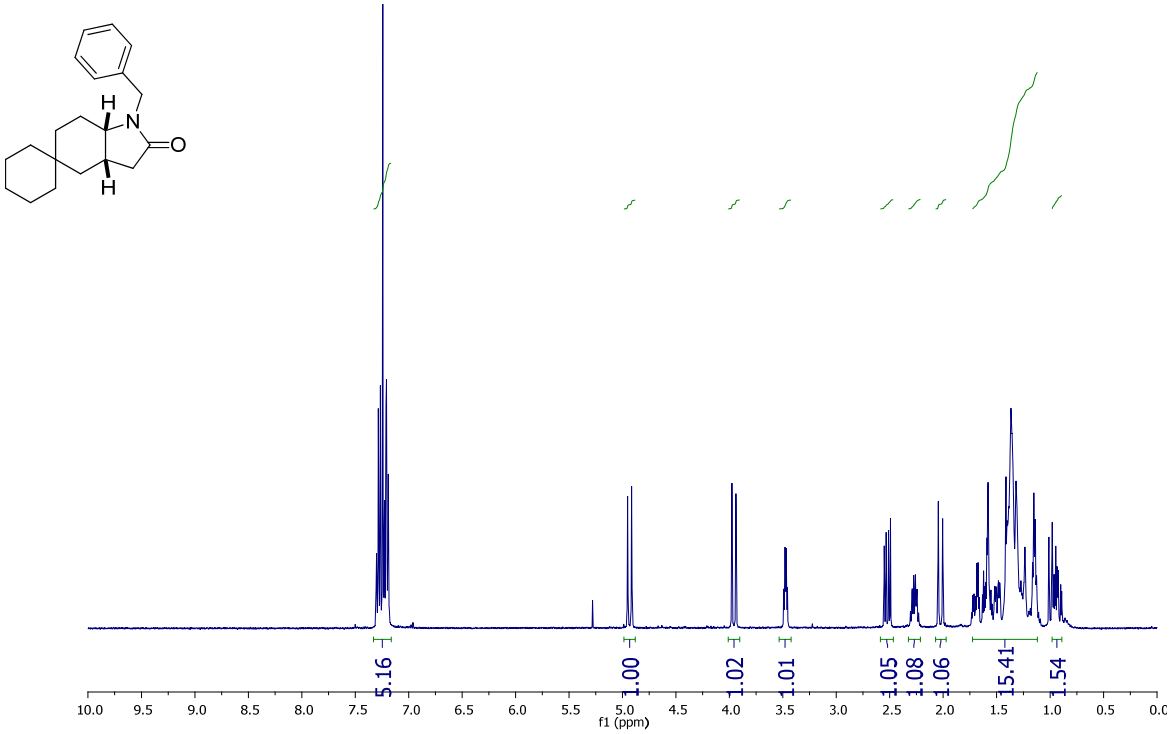
cis -1-benzyl-5,5-diphenylhexahydro-1*H*-indol-2(3*H*)-one (2d)

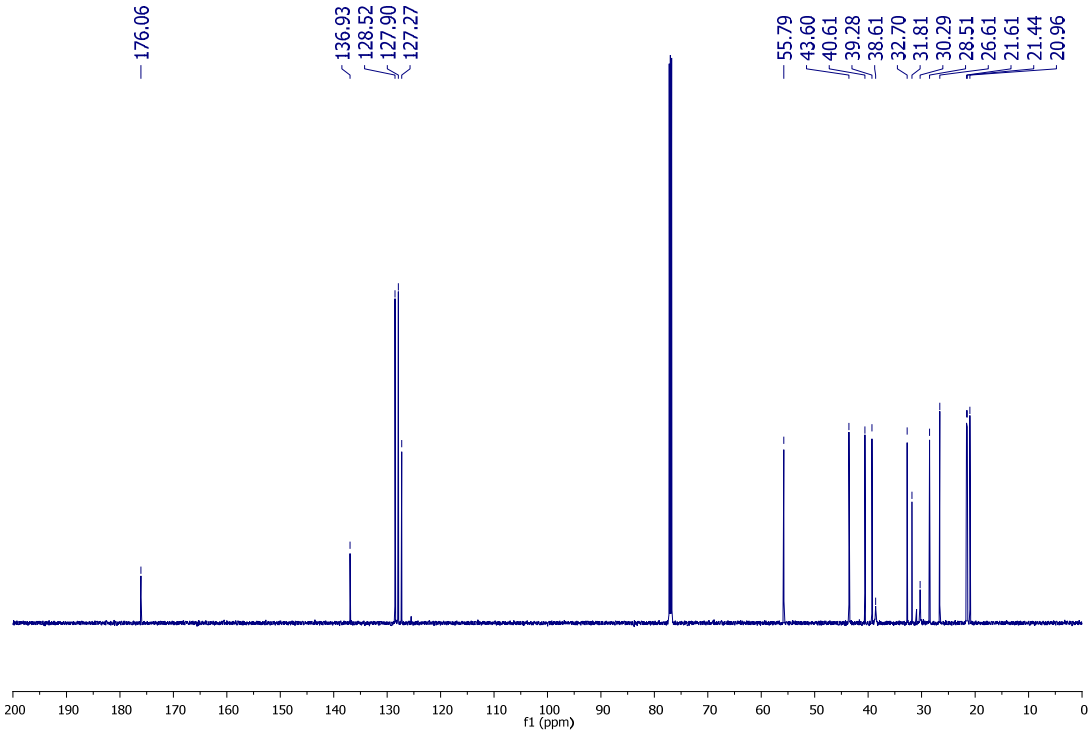




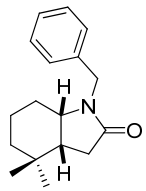


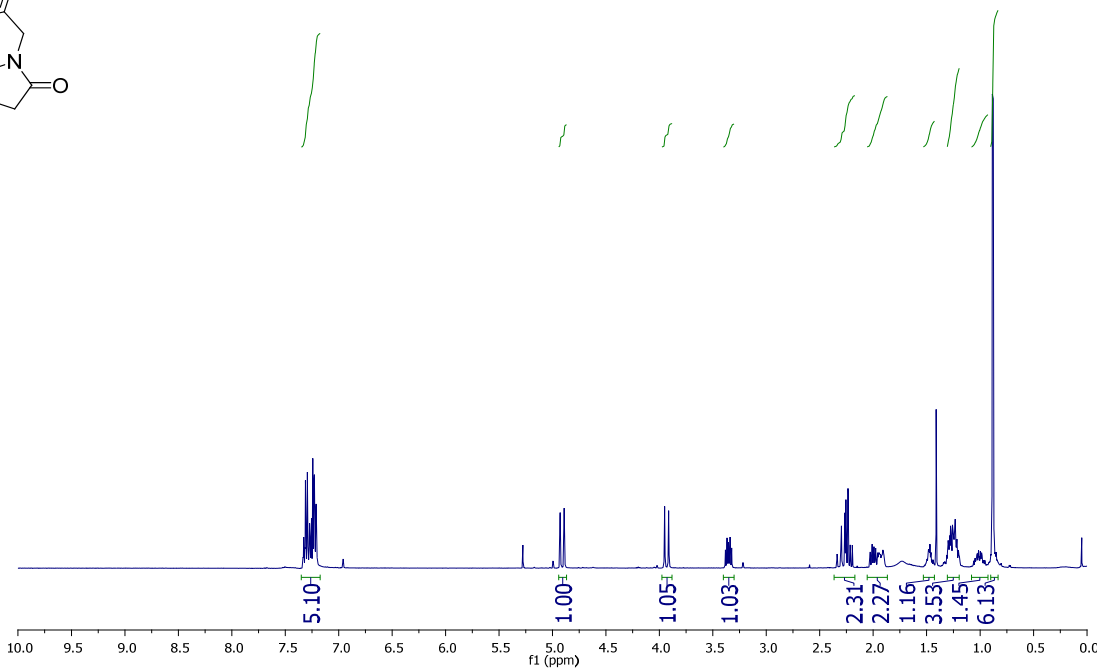
***cis*-1-benzylhexahydrospiro[cyclohexane-1,5-indol]-2(3*H*)-one (2e)**

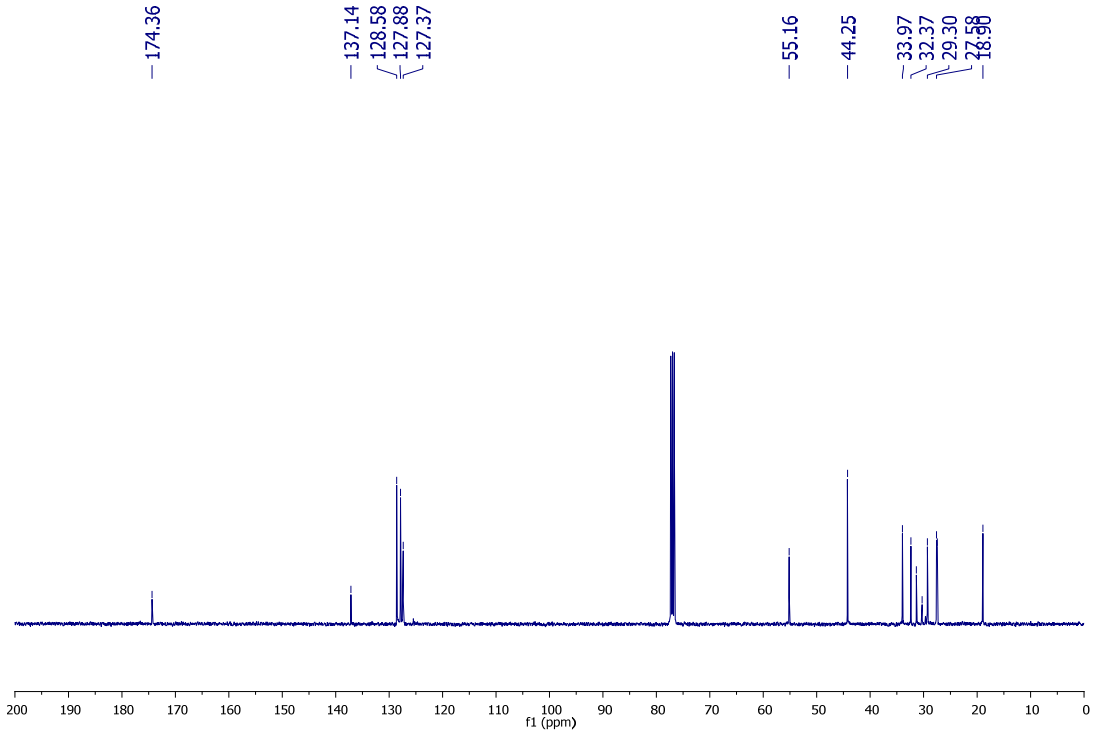




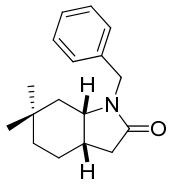
cis-1-benzyl-4,4-dimethylhexahydro-1*H*-indol-2(3*H*)-one (2f)

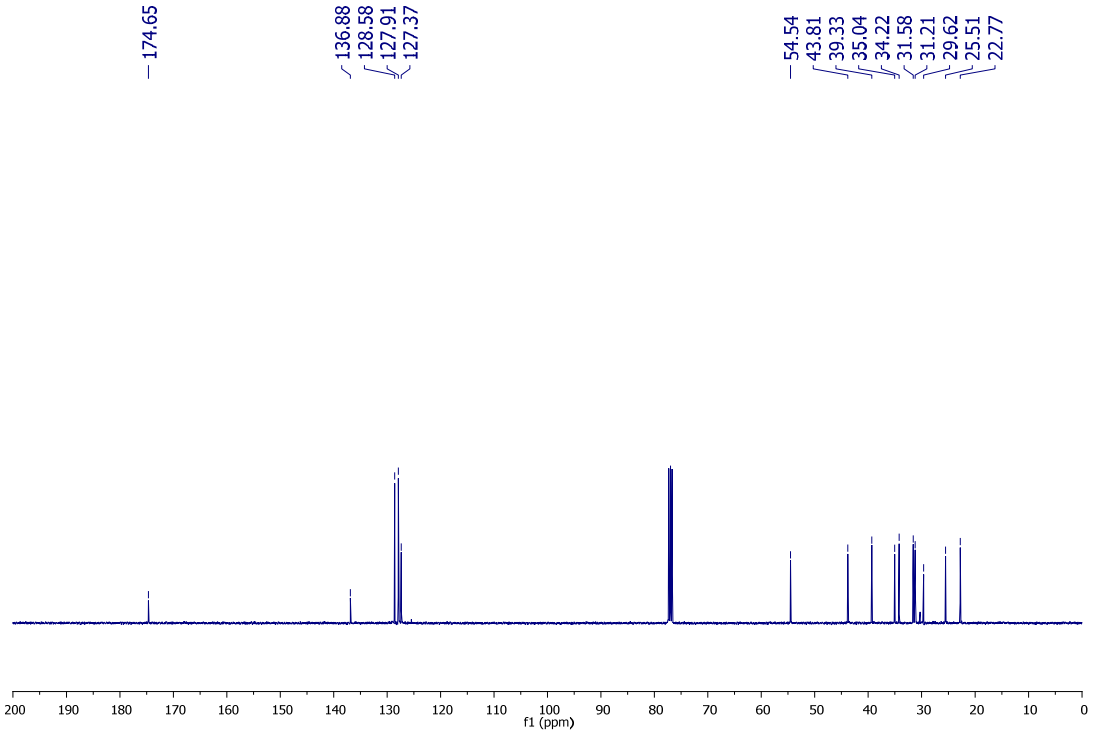




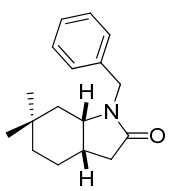


cis -1-benzyl-6,6-dimethylhexahydro-1*H*-indol-2(3*H*)-one (2g)





1-benzyl-3-methylhexahydro-1H-indol-2(3H)-one (2h)



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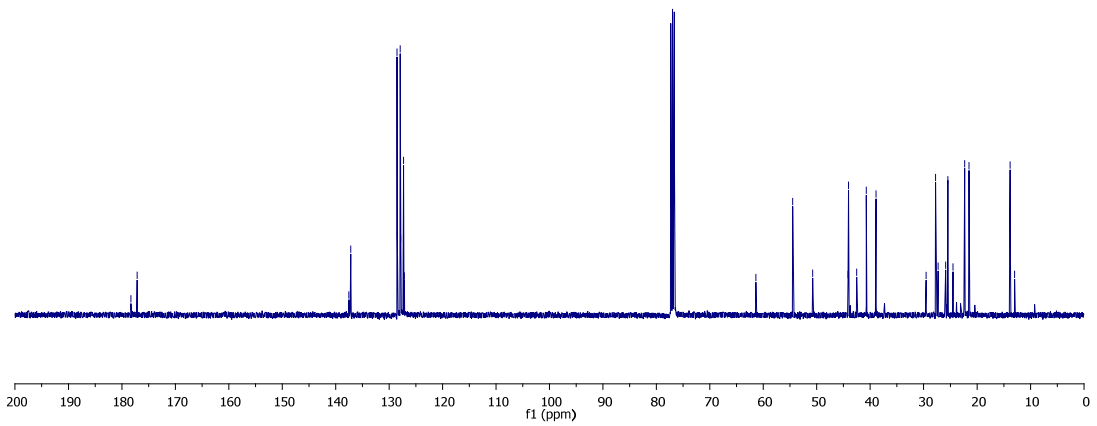
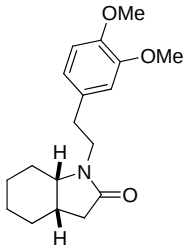
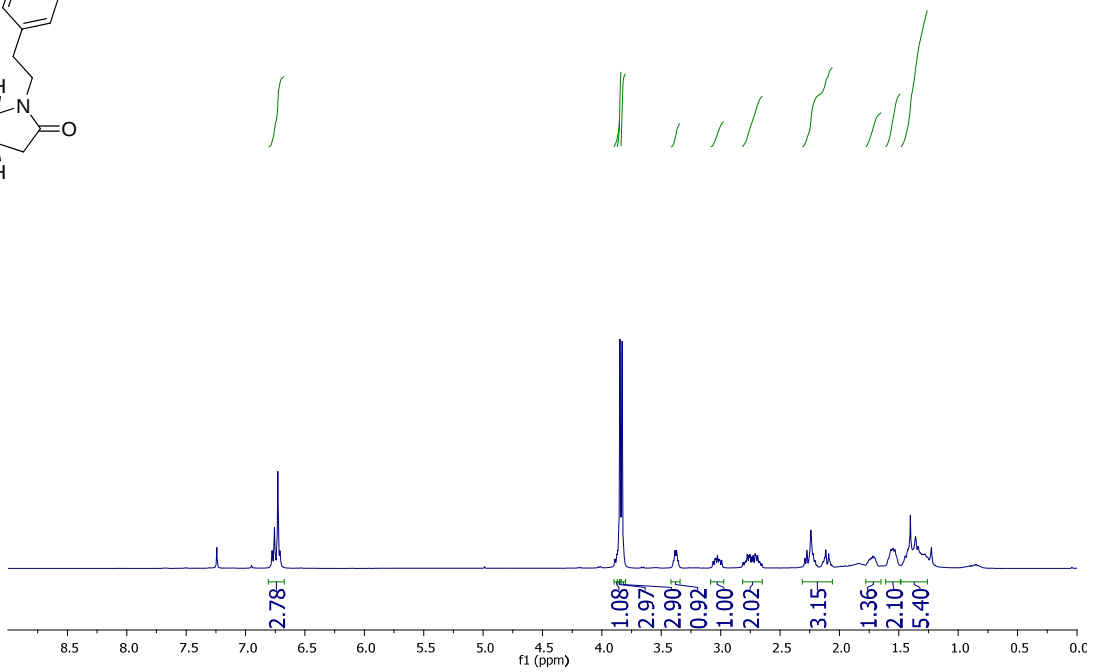
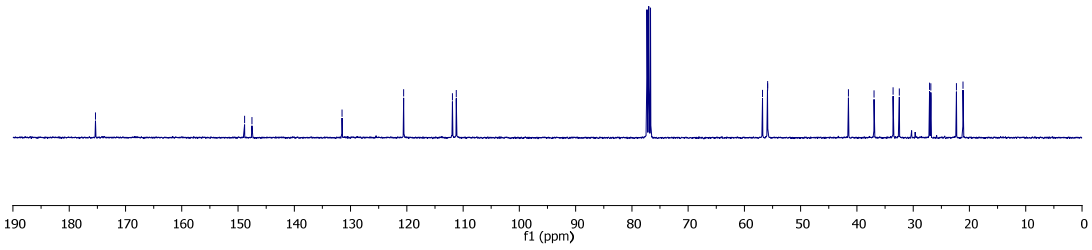


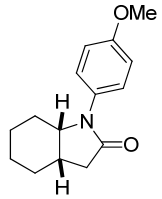
***cis*-1-(3,4-dimethoxyphenethyl)hexahydro-1H-inden-2(3H)-one (2i)**

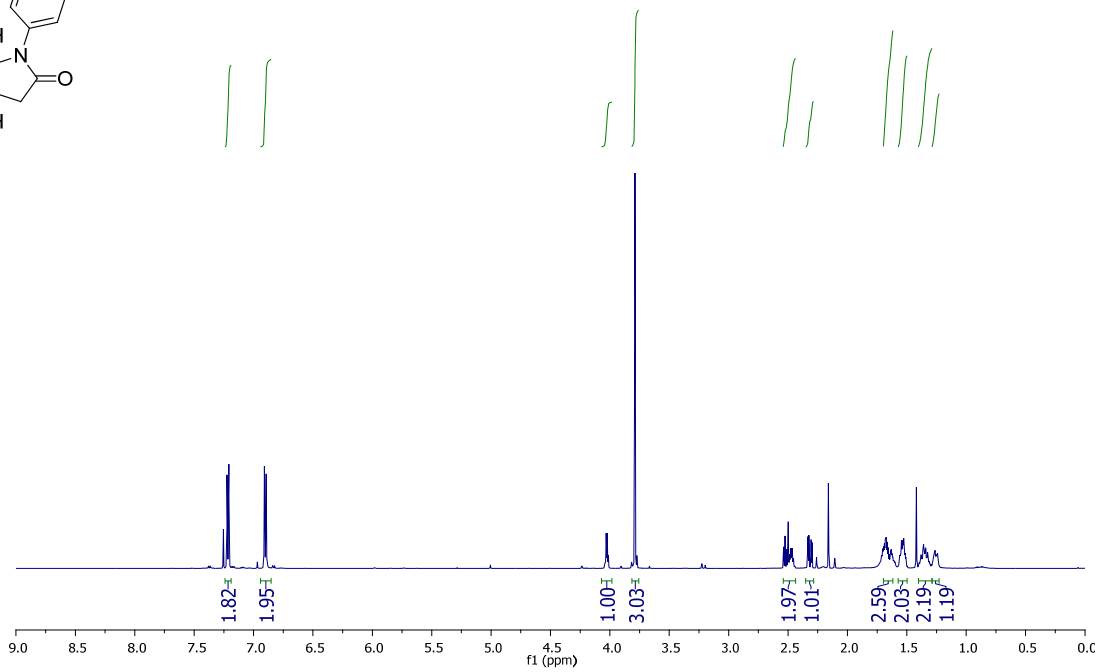


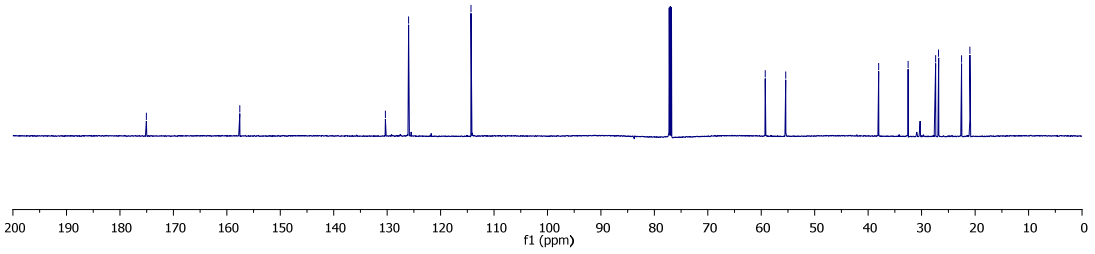




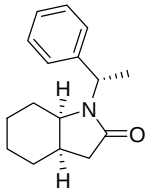
***cis*-1-(4-methoxyphenyl)hexahydro-1H-inden-2(3H)-one (2j)**

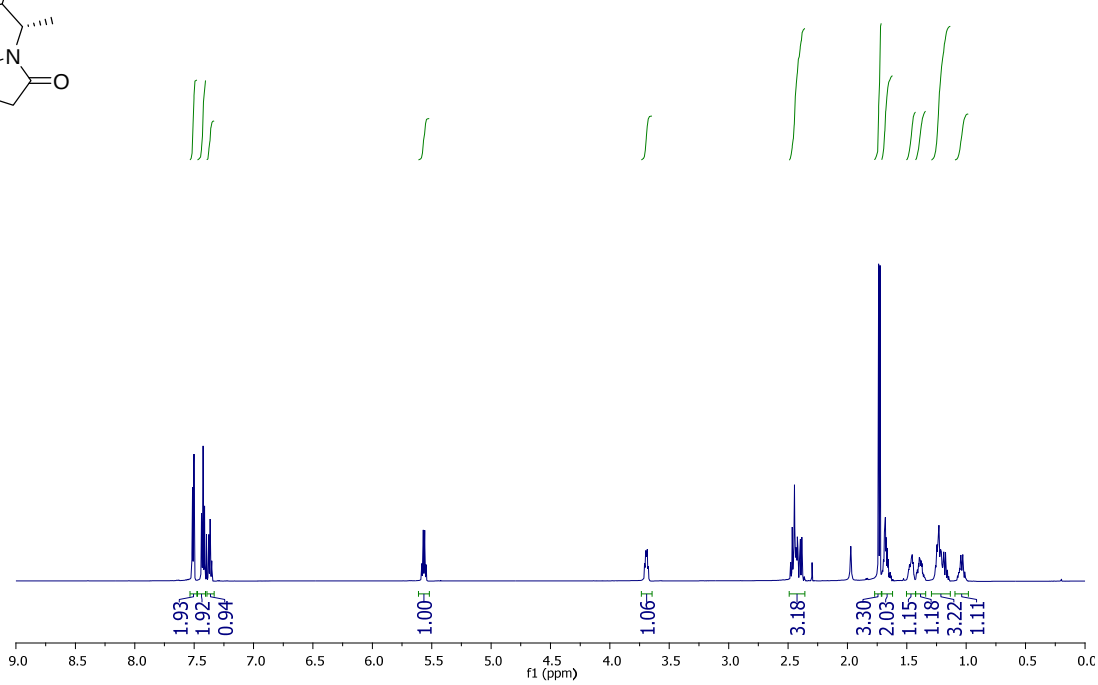


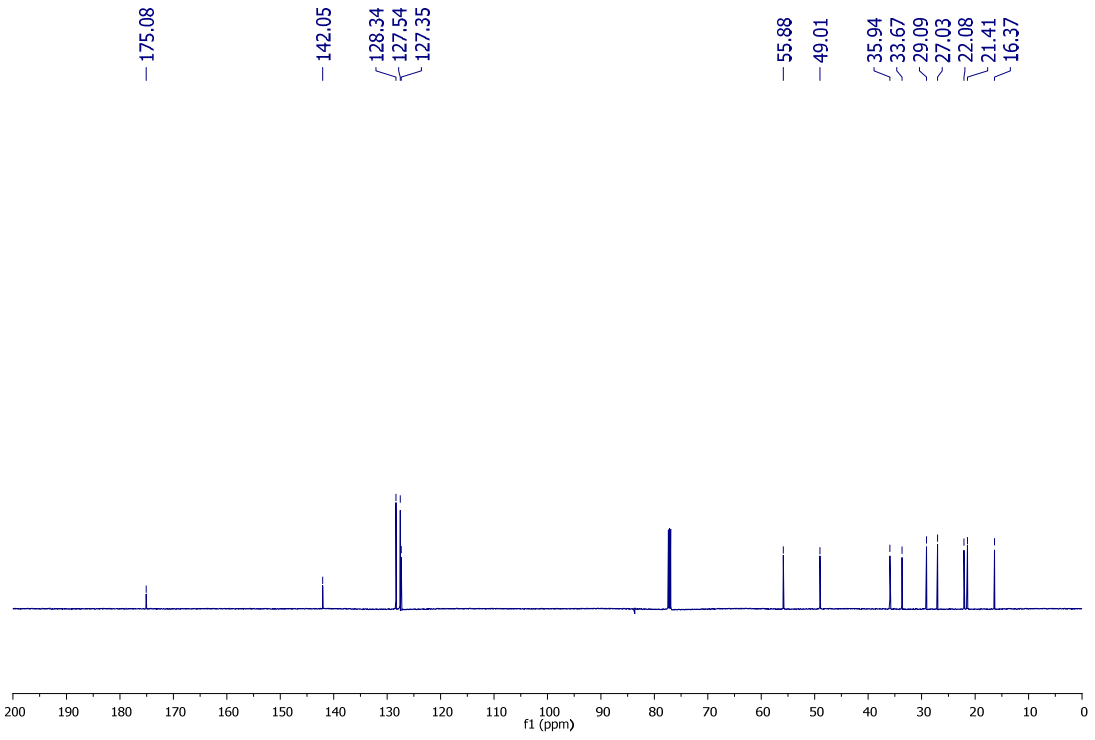




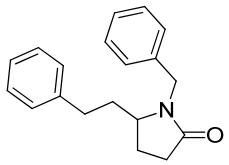
(3a*R*,7a*R*)-1-((*S*)-1-phenylethyl)hexahydro-1H-inden-2(3H)-one (2k)

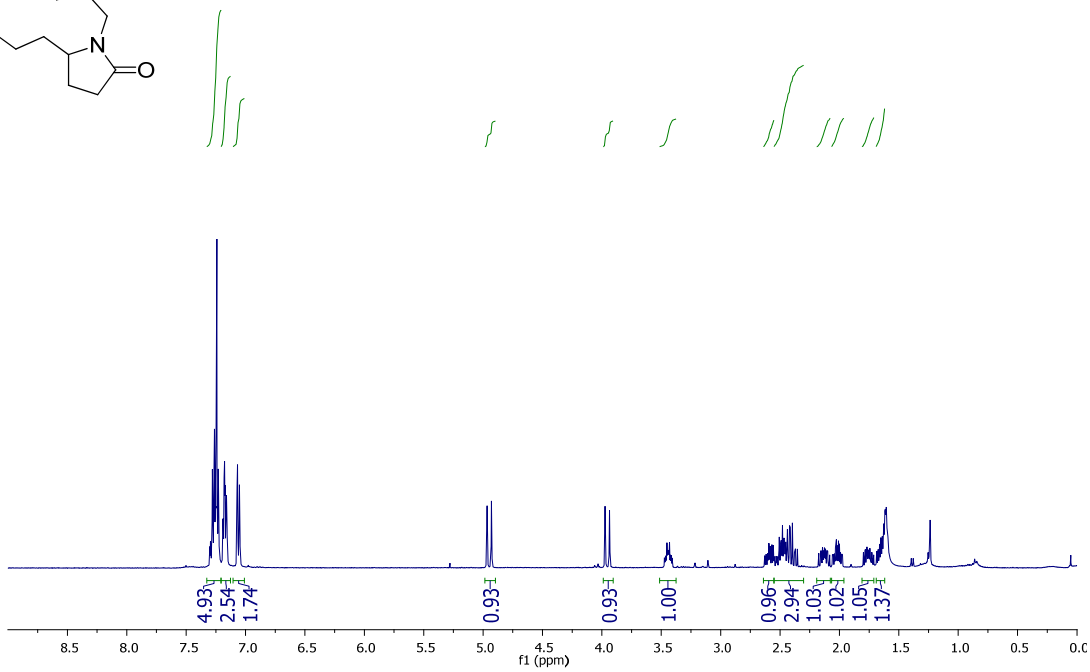


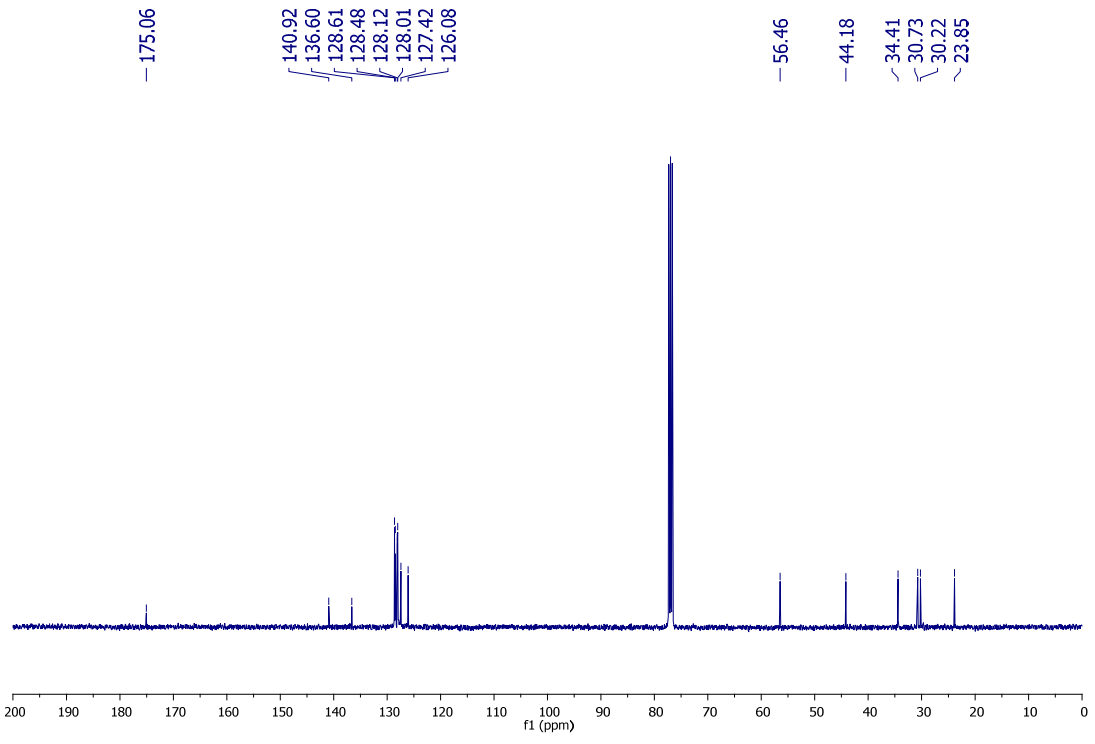




1-benzyl-5-phenethylpyrrolidin-2-one (2l)







(3a*R*,7a*R*)-hexahydro-1*H*-indol-2(3*H*)-one (6)