Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

New Approaches to Ondansetron and Alosetron Inspire a Versatile, Flow Photochemical Method for Indole Synthesis.

Wei Sun,[a]* William A. T. Raimbach,[a] Luke D. Elliott,[b] Kevin I. Booker-Milburn,[b] and David C. Harrowven.[a]*

[a] Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, UK

[b] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

Experimental Procedures

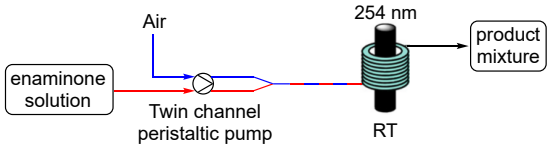
1. General Remarks

All air sensitive reactions were carried out under argon using flame dried apparatus. Reactions were monitored by TLC on Merck Silica Gel 60 Å F TLC plates and visualised with 254 nm UV followed by aqueous 1% $KMnO_4$ or PMA. Column chromatography was performed using Sigma Aldrich 40–63 μm 60 Å 230–400 Å silica and the stated solvent system under slight positive pressure. Reaction and chromatography solvents were removed using a rotary evaporator equipped with a diaphragm pump. ^1H and ^{13}C NMR spectroscopy was performed on a Bruker AV400 (400/100 MHz) spectrometer at 298 K in $CDCl_3$. Chemical shifts are quoted as δ values in ppm using residual solvent peaks as the reference. Coupling constants *J* are given in Hz and multiplicity is described as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad. HRMS data were obtained using a Bruker APEX III FT-ICR-MS with samples run in HPLC grade methanol. Electrospray mass spectrometry was performed on a directly injected Waters quadrupole MSD using ESI^+ or ESI^- ionisation with MeOH as solvent. Infrared spectroscopy was performed on a Nicolet iS5 Laboratory FT-IR spectrometer and spectra of solids were acquired from films deposited by evaporation of $CDCl_3$ or DCM solutions. Absorption maxima (ν_{max}) are quoted in wavenumbers (cm^{-1}) with the following abbreviations used to describe their intensity: s, strong; m, medium; w, weak; br, broad. All other starting materials and reagents were used as supplied from commercial sources.

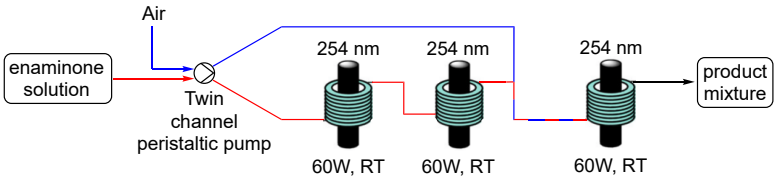
2. Photochemical Set-Ups

Set-up A: as detailed in *Angew. Chem., Int. Ed.,* 2015, **54**, 4531, scaled to accommodate a 36 or 60W Philips UVC PL36/10/4P lamp and with a reactor capacity of 120 mL.[1]

Set-up B: as above but with a twin channel peristaltic pump drawing in separate streams of air and a solution of the starting material. Those streams are combined using a Y-connector giving to a segmented stream of air bubbles and the reaction solution which is passed into the photoreactor.

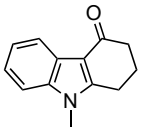


Set-up C (for scale-up): as above but with three reactors connected in series, each equipped with a 60W Philips UVC PL36/10/4P lamp and with a Y-connector introducing air into the final photoreactor.



3. Cyclisation Procedures

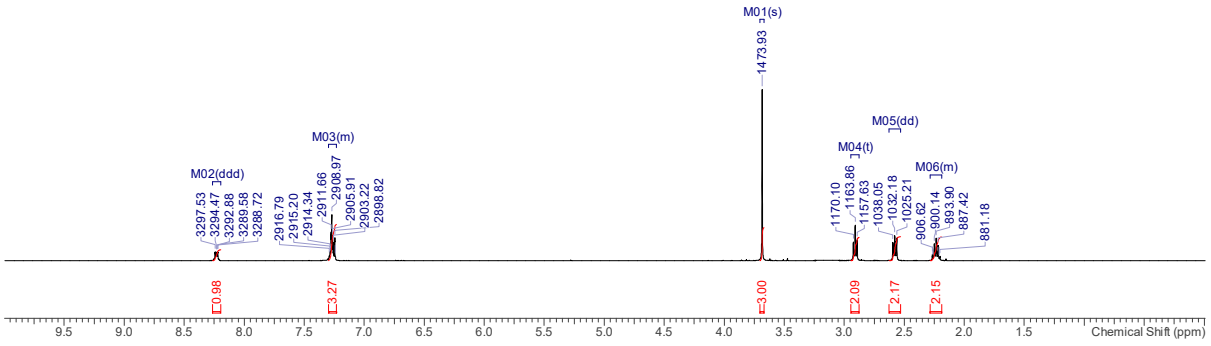
9-Methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 4

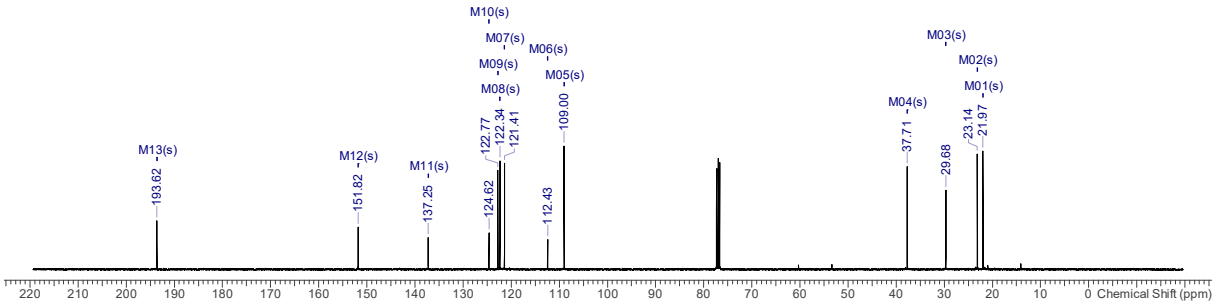


Using flow photochemical set-up A: A solution of enaminone **5a** (412 mg, 2.06 mmol) and iodine (25.4 mg, 0.100 mmol, 5 mol%) in MeCN (105 mL) was irradiated with a 36W UVA lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* to a brown oil that was triturated with cold EtOAc to afford the *title compound* **4** (352 mg, 1.78 mmol, 86%) as an off-white solid.

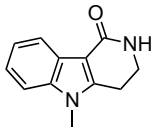
Using flow photochemical set-up B: A solution of enaminone **5a** (150 mg, 0.746 mmol) in MeCN (75 mL) was segmented with bubbles of air then irradiated with a 36W UVA lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* then triturated with cold EtOAc to afford the *title compound* **4** (116 mg, 0.583 mmol, 78%) as a yellow solid.

Using flow photochemical set-up C: A solution of enaminone **5a** (8.72 g, 43.3 mmol) in MeCN (1.45 L) was irradiated firstly with 2×60W UVA lamps for a residence time of 1 h then by a 60W UVA lamp under segmented flow with bubbles of air for a residence time of 15 min. The resulting solution was concentrated *in vacuo* then washed with cold EtOAc to afford the *title compound* **4** (6.64 g, 33.3 mmol, 77%) as a yellow solid. **MP** 193 – 194 °C (MeOH), Lit.[2b] 195 – 196 °C (EtOAc/hexane). **IR** ν_{max} (film, cm^{-1}): 2953 (br), 1630 (s), 1475 (s), 1093 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (1 H, m, Ar**H**), 7.29 – 7.24 (3 H, m, 3 × Ar**H**), 3.68 (3 H, s, C**H**$_3$), 2.91 (2 H, app. t, *J* = 6.2 Hz, C**H**$_2$), 2.58 (2 H, dd, *J* = 7.2, 5.7 Hz, C**H**$_2$), 2.24 (2 H, app. quin, *J* = 6.4 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.6 (**C**), 151.8 (**C**), 137.3 (**C**), 124.6 (**C**), 122.8 (**C**H), 122.3 (**C**H), 121.4 (**C**H), 112.4 (**C**), 109.0 (**C**H), 37.7 (**C**H$_2$), 29.7 (**C**H$_3$), 23.1 (**C**H$_2$), 22.0 (**C**H$_2$) ppm. **LRMS** (ESI^+): 200 $[M+H]^+$. Data consistent with literature values.[2]

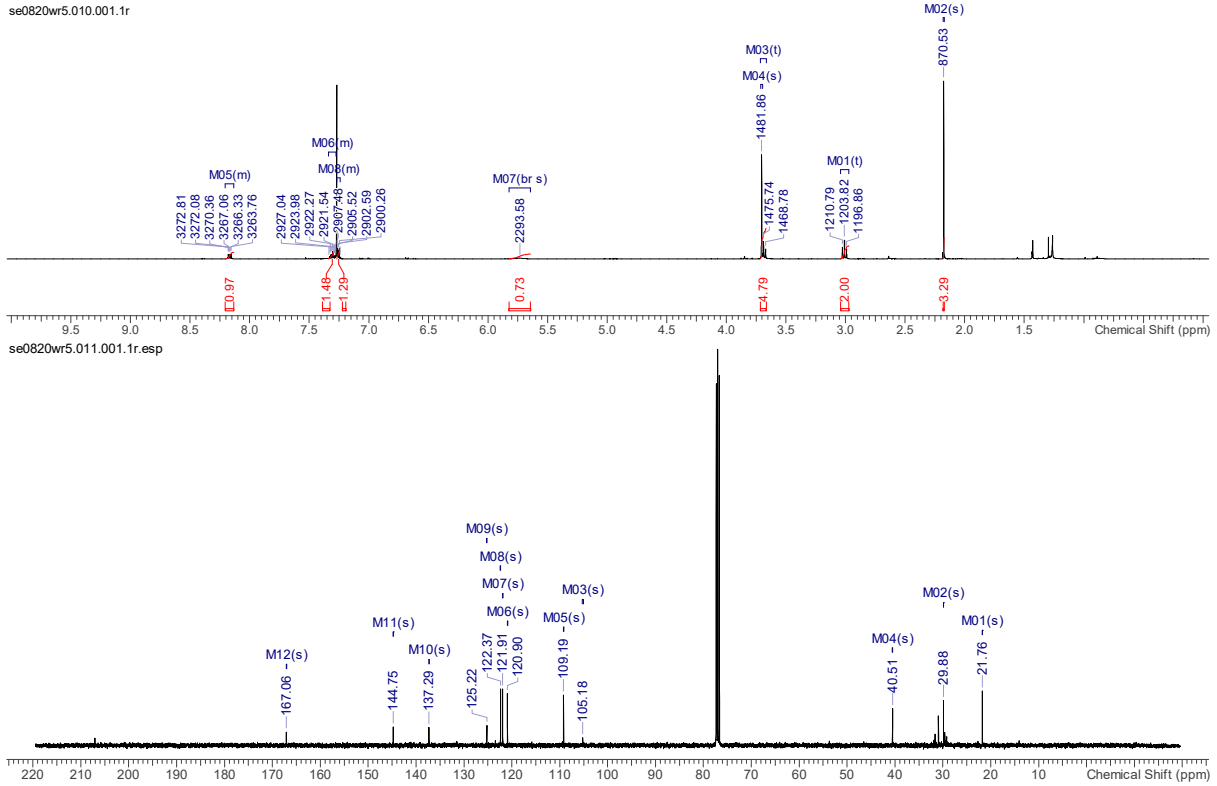




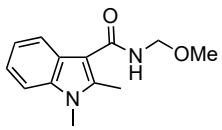
5-Methyl-2,3,4,5-tetrahydro-1*H*-pyrido[4,3-*b*]indol-1-one, 14



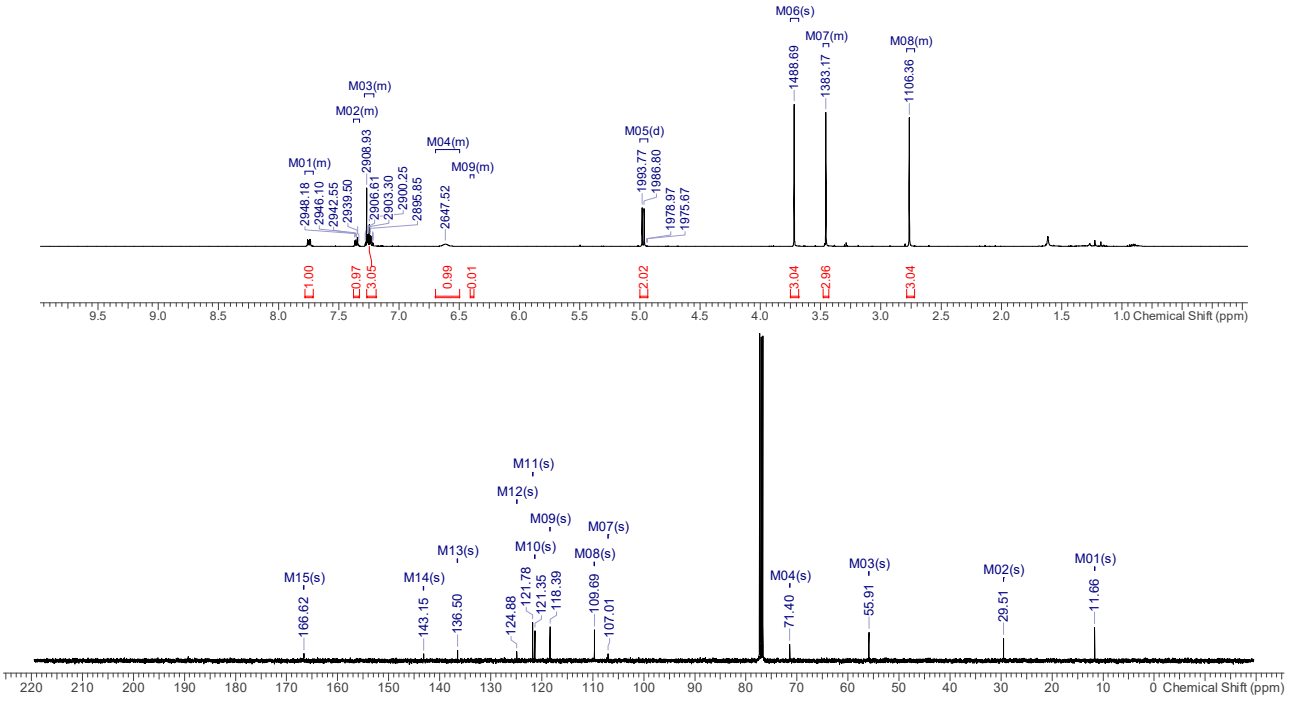
Using flow photochemical set-up B: A solution of dihydropyridone **17** (420 mg, 1.39 mmol) in MeCN (139 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for 30 min. To the resultant solution was added TFA (0.40 mL, 5.22 mmol) and after 15 h at RT, sat. $NaHCO_3$ (10 mL) was added. The aqueous phase was separated and washed with DCM (3 x 30 mL), then the combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (20 – 40% acetone in DCM) to afford the *title compound* (175 mg, 0.875 mmol, 63%) as a yellow solid. **MP** 242 – 245 °C (acetone/CH_2Cl_2), Lit.[3b] 242 – 244 °C (petrol/CH_2Cl_2/MeOH). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17 (m, 1H, Ar**H**), 7.34 – 7.24 (m, 3H, 3 x Ar**H**), 5.73 (br s, 1H, N**H**), 3.70 (s, 3H, C$\mathbf{H}_3$), 3.69 (t, *J* = 7.0 Hz, 2H, C$\mathbf{H}_2$), 3.01 (t, *J* = 7.0 Hz, 2H, C$\mathbf{H}_2$), 2.18 (s, 3H, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.1 (**C**), 144.8 (**C**), 137.3 (**C**), 125.2 (**C**), 122.4 (**C**H), 121.9 (**C**H), 120.9 (**C**H), 109.2 (**C**H), 105.2 (**C**), 40.5 (C$\mathbf{H}_2$), 29.9 (C$\mathbf{H}_3$), 21.8 (C$\mathbf{H}_2$) ppm. **LRMS** (ESI$^+$): 201 ((M+H)$^+$, 100%). Data consistent with literature values.[3]



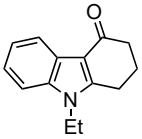
***N*-(Methoxymethyl)-1,2-dimethyl-1*H*-indole-3-carboxamide, 15**



Using flow photochemical set-up B: A solution of dihydropyridone **16** (173 mg, 0.865 mmol) in MeOH (86 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (50 – 80% EtOAc in petrol) to afford the *title compound* **16** (162 mg, 0.698 mmol, 81%) as a yellow solid. **MP**: 131 – 132 °C. **IR** ν_{max} (film, cm^{-1}): 3319 (br), 2931 (br), 1636 (s), 1545 (m), 1507 (m), 1473 (s), 1404 (m), 1225 (m), 1171 (m), 1116 (m), 1069 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (1 H, m, Ar**H**), 7.35 (1 H, m, Ar**H**), 7.78 – 7.22 (2 H, m, 2 × Ar**H**), 6.62 (1 H, br. s, N**H**), 4.97 (2 H, d, *J* = 7.0 Hz, C$\mathbf{H}_2$), 3.72 (3 H, s, C$\mathbf{H}_3$), 3.46 (3 H, s, C$\mathbf{H}_3$), 2.77 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6 (**C**), 143.2 (**C**), 136.5 (**C**), 124.9 (**C**), 121.8 (**C**H), 121.4 (**C**H), 118.4 (**C**H), 109.7 (**C**H), 107.0 (**C**), 71.4 (C$\mathbf{H}_2$), 55.9 (C$\mathbf{H}_3$), 29.5 (C$\mathbf{H}_3$), 11.7 (C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 255 (40%, [M + Na]$^+$), 233 (10%, [M + H]$^+$), 172 (100%, [M – $NHCH_2OCH_3$]$^+$). **HRMS** (ESI$^+$): Found 255.1106, $C_{13}H_{16}N_2NaO_2$ [M+Na]$^+$ requires 255.1104.

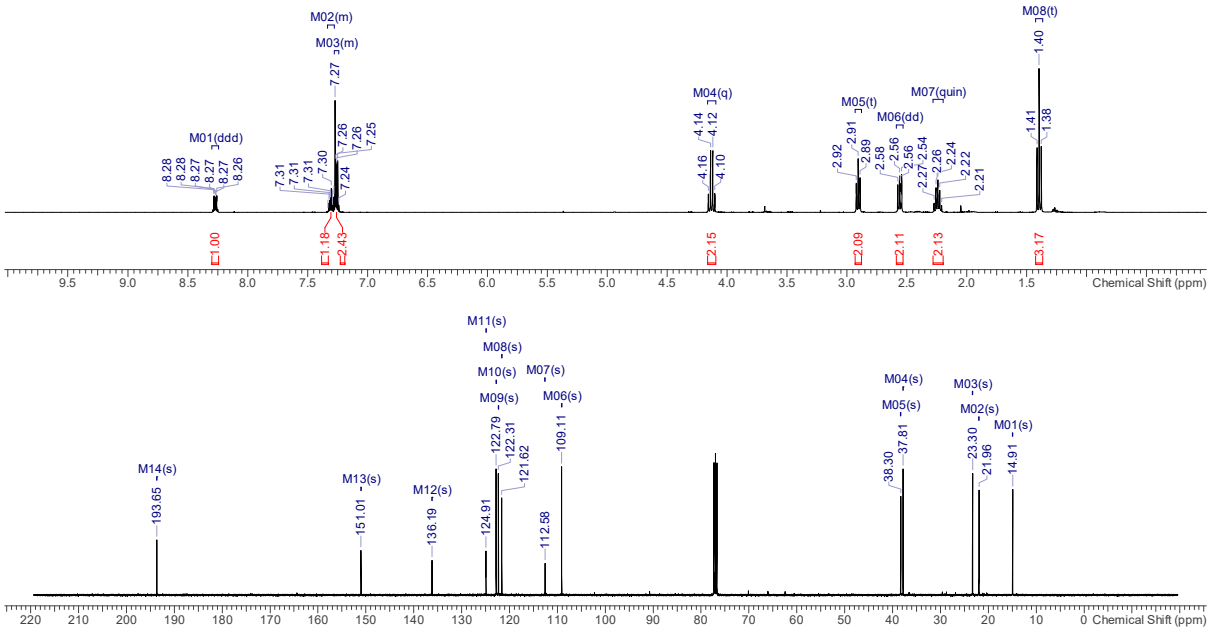


9-Ethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 18b

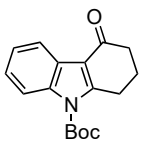


Using flow photochemical set-up A: A solution of enaminone **5b** (284 mg, 1.32 mmol) and iodine (16.8 mg, 0.066 mmol, 5 mol%) in MeCN (66 mL, 0.02 M) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18b** (205 mg, 0.962 mmol, 73%) as an off-white solid.

Using flow photochemical set-up B: A solution of enaminone **5b** (231 mg, 1.07 mmol) in MeCN (107 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18b** (162 mg, 0.760 mmol, 71%) as an off-white solid. **MP**: 104 – 105 °C. **IR** ν_{max} (film, cm^{-1}): 2937 (br), 1637 (s), 1442 (s), 1092 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (1 H, m, Ar**H**), 7.30 (1 H, m, Ar**H**), 7.26 (2 H, m, 2 × Ar**H**), 4.13 (2 H, q, *J* = 7.6, Hz, CH_2), 2.91 (2 H, app. t, *J* = 6.2 Hz, CH_2), 2.56 (2 H, dd, *J* = 7.3, 5.6 Hz, CH_2), 2.24 (2 H, app. quin, *J* = 6.2 Hz, CH_2), 1.40 (3 H, t, *J* = 7.3 Hz, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.7 (**C**), 151.0 (**C**), 136.2 (**C**), 124.9 (**C**), 122.8 (**C**H), 122.3 (**C**H), 121.6 (**C**H), 112.6 (**C**), 109.1 (**C**H), 38.3 (**C**H_2), 37.8 (**C**H_2), 23.3 (**C**H_2), 22.0 (**C**H_2), 14.9 (**C**H_3) ppm. **LRMS** (ESI^+): 214 $[M+H]^+$. **HRMS** (ESI^+): Found 214.1228, $C_{14}H_{16}NO_2$ $[M+H]^+$ requires 214.1226.

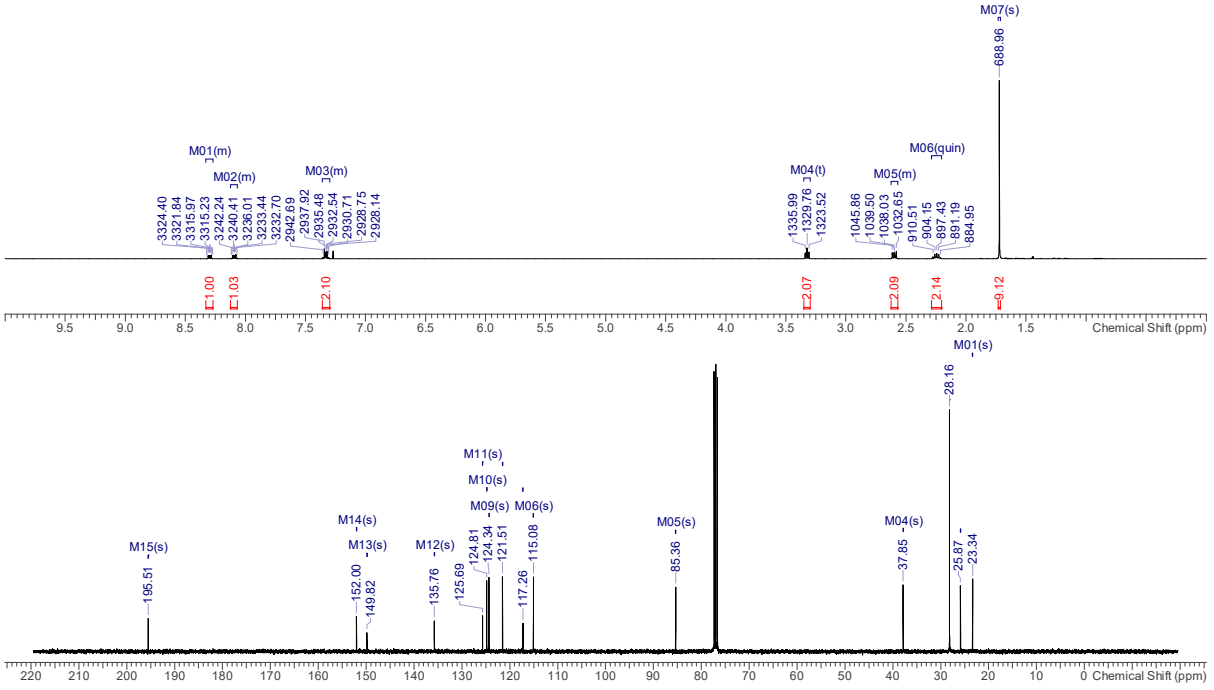


9-(*tert*-Butyloxycarbonyl)-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 18c

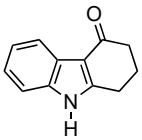


Using flow photochemical set-up A: A solution of enaminone **5c** (286 mg, 1.00 mmol) and iodine (12 mg, 0.05 mmol, 5 mol%) in MeCN (50 mL, 0.02 M) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18c** (231 mg, 0.810 mmol, 81%) as a yellow solid.

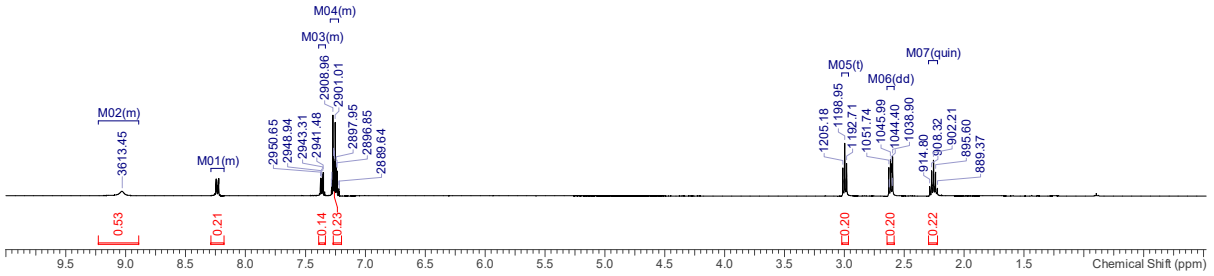
Using flow photochemical set-up B: A solution of enaminone **5c** (265 mg, 0.923 mmol) in MeCN (92 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18c** (60 mg, 0.210 mmol, 23%) as a yellow solid. **MP** 143 – 144 °C (Et_2O/petrol), Lit.[2c] 144 – 148 °C. **IR** ν_{max} (film, cm^{-1}): 2977 (br), 1738 (s), 1663 (s), 1366 (s), 1350 (s), 1295 (s), 1151 (s), 1139 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.30 (1 H, m, Ar**H**), 8.09 (1 H, m, Ar**H**), 7.35 – 7.31 (2 H, m, 2 × Ar**H**), 3.32 (2 H, app. t, *J* = 6.2 Hz, CH_2), 2.26 – 2.58 (2 H, m, CH_2), 2.24 (2 H, app. quin, *J* = 6.4 Hz, CH_2), 1.72 (9 H, s, 3 × CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.5 (**C**), 152.0 (**C**), 149.8 (**C**), 135.8 (**C**), 125.7 (**C**), 124.8 (**C**H), 124.3 (**C**H), 121.5 (**C**H), 117.3 (**C**), 115.1 (**C**H), 83.4 (**C**), 37.9 (CH_2), 28.2 (3 × CH_3), 25.9 (CH_2), 23.3 (CH_2) ppm. **LRMS** (ESI$^+$): 286 $[M+H]^+$. Data consistent with literature values.[2]

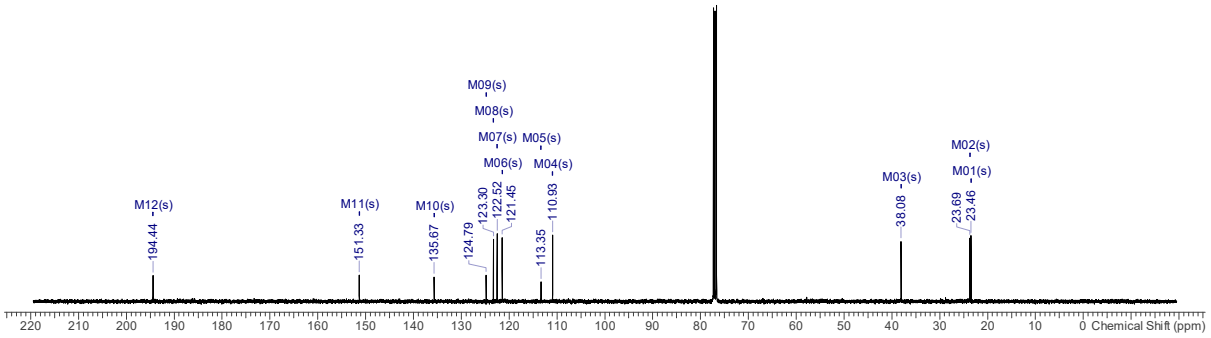


9-Methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 3



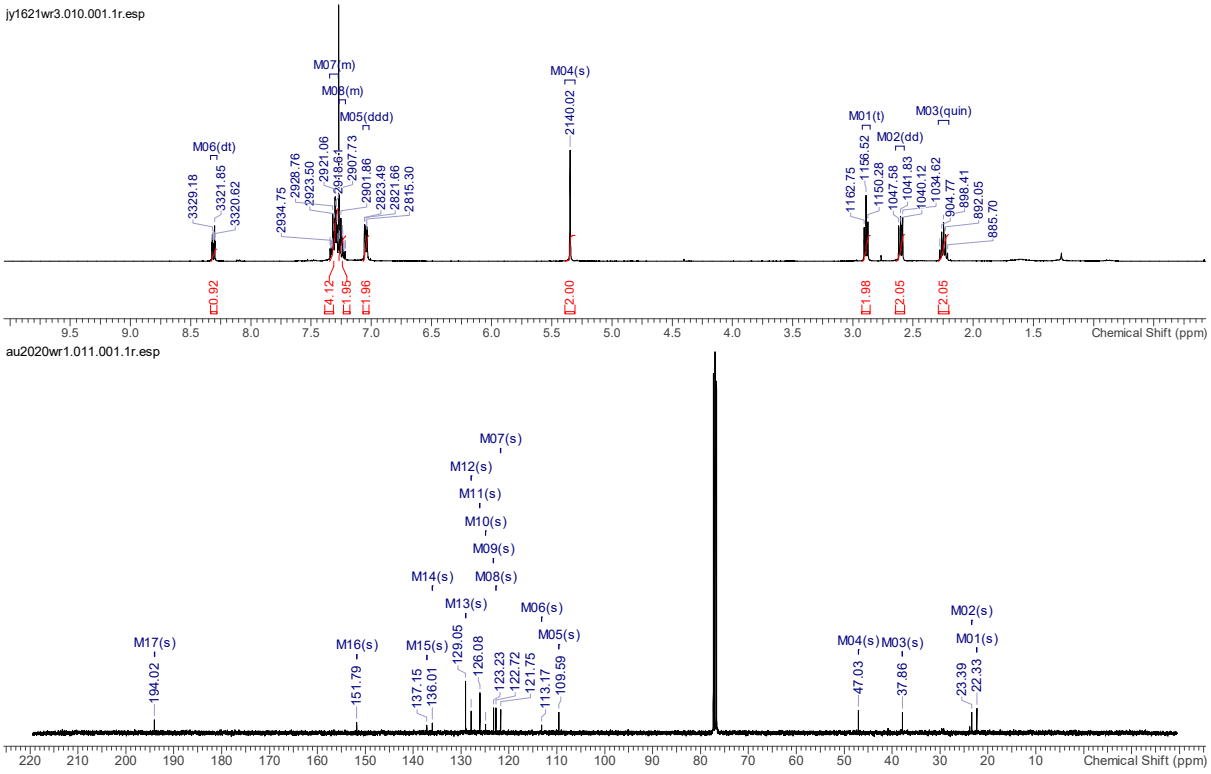
To a solution of **18c** (310 mg, 1.09 mmol) in DCM (10 mL) at RT was added TFA (5 mL) dropwise. After 48 hours, sat. Na_2CO_3 (50 mL) was added, then the aqueous phase was separated and extracted with DCM (3 × 50 mL). The organic phases were combined, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography (50 – 60% EtOAc/hexane) to afford the *title compound* **3** (167 mg, 0.903 mmol, 83%) as a white solid. **MP** 215 – 216 °C (EtOAc/hexane), Lit.[4b] 216 – 217 °C. **IR** ν_{max} (film, cm^{-1}): 3143 (br), 1623 (s), 1467 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.03 (1 H, br s, N**H**), 8.23 (1 H, m, Ar**H**), 7.36 (1 H, m, Ar**H**), 7.28 – 7.22 (2 H, m, 2 × Ar**H**), 3.00 (2 H, app. t, *J* = 6.2 Hz, CH_2), 2.61 (2 H, app. dd, *J* = 7.2, 5.6 Hz, CH_2), 2.25 (2 H, app. quin, *J* = 6.5 Hz, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.4 (**C**), 151.3 (**C**), 135.7 (**C**), 124.8 (**C**), 123.3 (**C**H), 122.5 (**C**H), 121.5 (**C**H), 113.4 (**C**), 110.9 (**C**H), 38.1 (CH_2), 23.7 (CH_2), 23.5 (CH_2) ppm. **LRMS** (ESI$^+$): 186 $[M+H]^+$. Data consistent with literature values.[4]



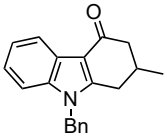


9-Benzyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 18d

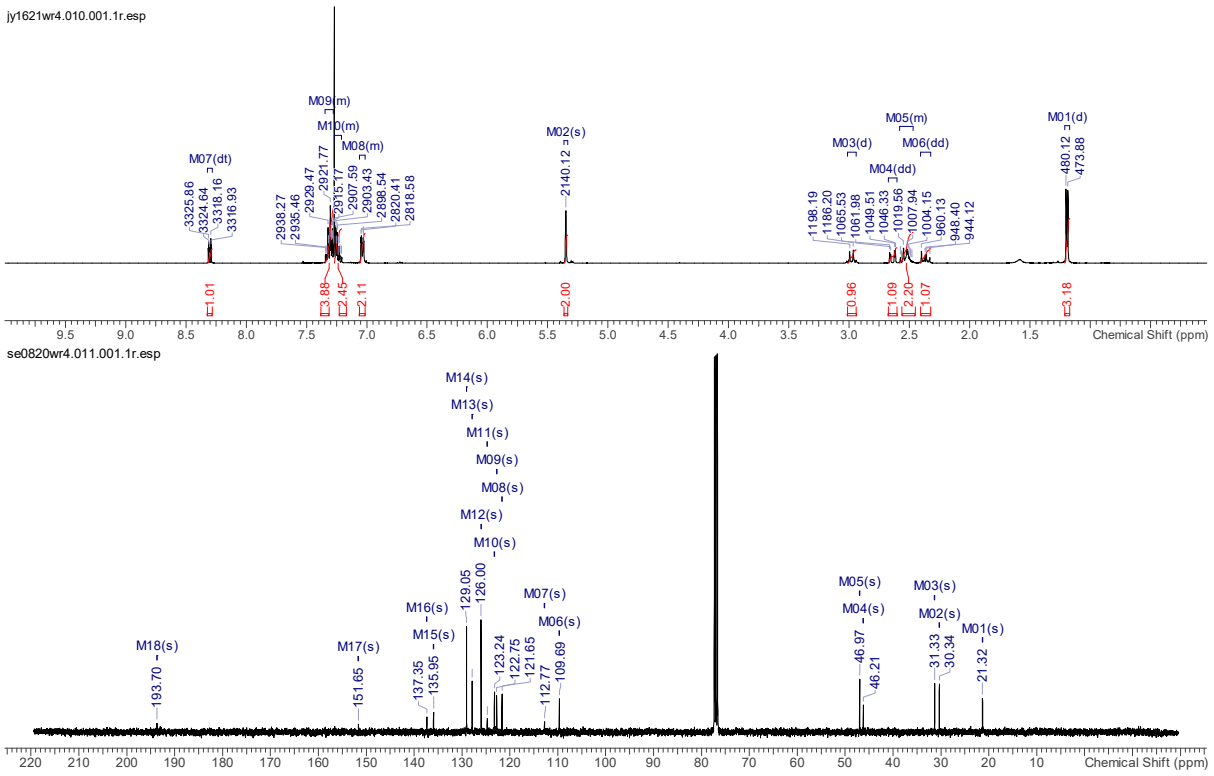
Using flow photochemical set-up B: A solution of enaminone **5d** (200 mg, 0.722 mmol) in MeCN (72 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (50 – 70% EtOAc in petrol) to afford the *title compound* **18d** (139 mg, 0.505 mmol, 70%) as a yellow solid. **MP** 148 – 151 °C (acetone/CH_2Cl_2), Lit.[5b] 148 – 150 °C (aq. EtOH). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (1H, m, Ar**H**), 7.35 – 7.21 (6H, m, 6 x Ar**H**), 7.04 (2H, m, 2 x Ar**H**), 5.35 (2H, s, C$\mathbf{H}_2$), 2.89 (2H, app. t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.60 (2H, dd, *J* = 7.3, 5.8 Hz, C$\mathbf{H}_2$), 2.25 (2H, app. quin., *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 194.0 (**C**), 151.8 (**C**), 137.2 (**C**), 136.0 (**C**), 129.1 (2 x **C**H), 127.9 (**C**H), 126.1 (2 x **C**H), 124.9 (**C**), 123.2 (**C**H), 122.7 (**C**H), 121.8 (**C**H), 113.2 (**C**), 109.6 (**C**H), 47.0 (**C**H_2), 37.9 (**C**H_2), 23.4 (**C**H_2), 22.3 (**C**H_2) ppm. **LRMS** (ESI^+): 276 (100%, $(M+H)^+$). Data consistent with literature values.[5]



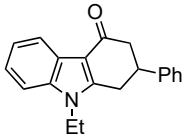
9-Benzyl-2-methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 18f



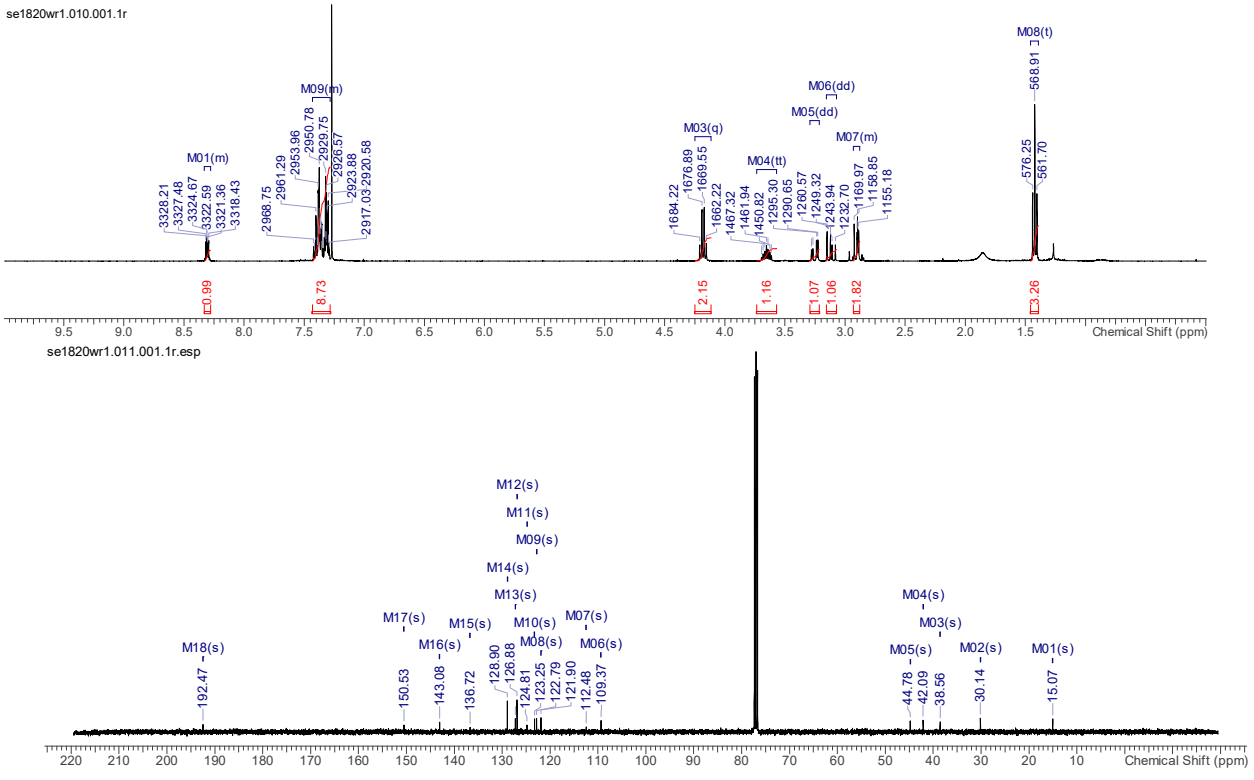
Using flow photochemical set-up B: A solution of enaminone **5f** (200 mg, 0.687 mmol) in MeCN (69 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **18f** (137 mg, 0.474 mmol, 69%) as an off-white solid. **MP** 148 – 149 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.30 (1H, dt, *J* = 7.7, 1.1 Hz, Ar**H**), 7.35 – 7.21 (6H, m, 6 x Ar**H**), 7.06 – 7.01 (2H, m, 2 x Ar**H**), 5.35 (2H, s, C$\mathbf{H}_2$), 2.98 (1H, m, C**H**H), 2.64 (1H, dd, *J* = 15.8, 3.4 Hz, C**H**H), 2.58 – 2.47 (2H, m, C**H**H + C**H**), 2.36 (1H, dd, *J* = 16.0, 11.7 Hz, C**H**H), 1.19 (3H, d, *J* = 6.2 Hz, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.7 (**C**), 151.7 (**C**), 137.4 (**C**), 136.0 (**C**), 129.1 (2 x **C**H), 127.9 (**C**H), 126.0 (2 x **C**H), 124.8 (**C**), 123.2 (**C**H), 122.8 (**C**H), 121.7 (**C**H), 112.8 (**C**), 109.7 (**C**H), 47.0 (**C**H_2), 46.2 (**C**H_2), 31.3 (**C**H_2), 30.3 (**C**H), 21.3 (**C**H_3) ppm. **LRMS** (ESI^+): 290 $[M+H]^+$. **HRMS** (ESI^+): Found 290.1543, $C_{20}H_{20}NO$ $[M+H]^+$ requires 290.1539.



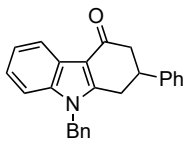
9-Ethyl-2-phenyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, **18g**



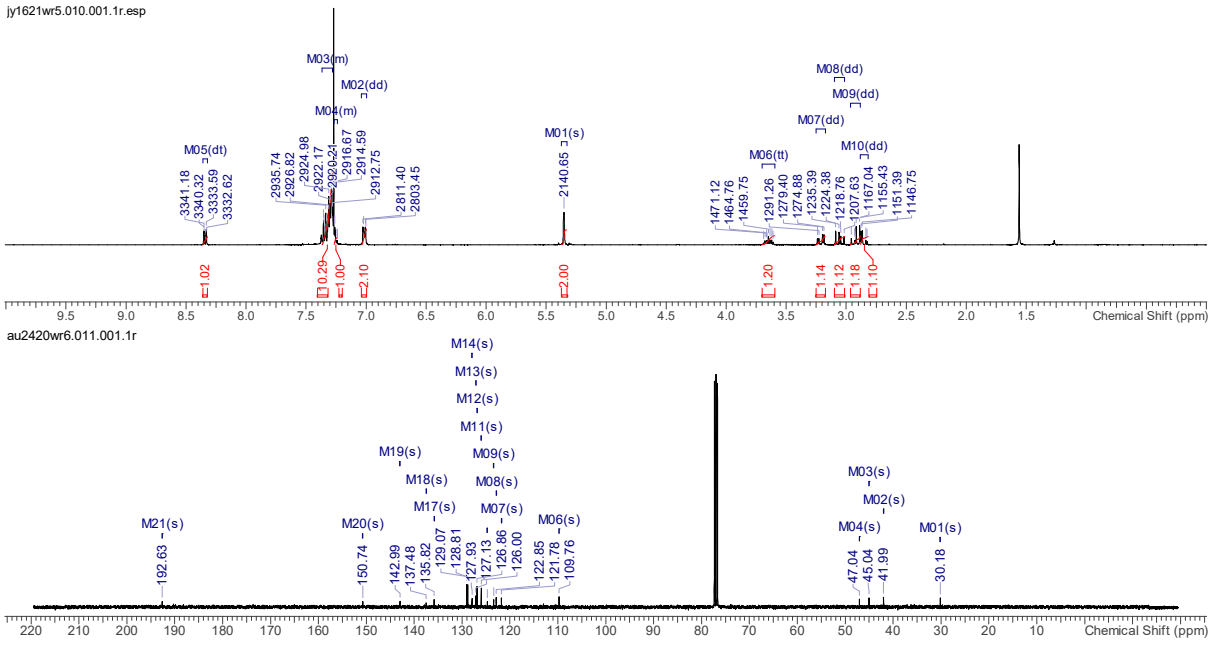
Using flow photochemical set-up B: A solution of enaminone **5g** (200 mg, 0.687 mmol) in MeCN (69 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (20 – 60% EtOAc in petrol) to afford the *title compound* **18g** (116 mg, 0.401 mmol, 58%) as a yellow solid. **MP** 177 – 179 °C. **IR** ν_{max} (film, cm^{-1}): 2980 (br), 1639 (s), 1475 (m), 1454 (s), 1131 (w), 1098 (w). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (1H, m, Ar**H**), 7.41 – 7.28 (8H, m, 8 x Ar**H**), 4.18 (2H, q, *J* = 7.3 Hz, C**H**$_2$), 3.65 (1H, app. tt, *J* = 11.6, 4.8 Hz, C**H**), 3.25 (1H, dd, *J* = 16.8, 5.0 Hz, C**H**H), 3.12 (1H, dd, *J* = 16.8, 11.3 Hz, CH**H**), 2.93 – 2.86 (2H, m, C**H**$_2$), 1.42 (3H, t, *J* = 7.3 Hz, C**H**$_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.5 (**C**), 150.5 (**C**), 143.1 (**C**), 136.7 (**C**), 128.9 (2 x **C**H), 127.2 (**C**H), 126.9 (2 x **C**H), 124.8 (**C**), 123.2 (**C**H), 122.8 (**C**H), 121.9 (**C**H), 112.5 (**C**), 109.4 (**C**H), 44.8 (**C**H$_2$), 42.1 (**C**H), 38.5 (**C**H$_2$), 30.1 (**C**H$_2$), 15.1 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 290 [M+H]$^+$. **HRMS** (ESI$^+$): Found 290.1540, $C_{20}H_{20}NO$ [M+H]$^+$ requires 290.1539.



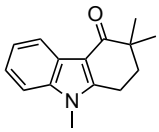
9-Benzyl-2-phenyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, **18h**



Using flow photochemical set-up B: A solution of enaminone **5h** (200 mg, 0.567 mmol) in MeCN (57 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (5 – 30% EtOAc in petrol) to afford the *title compound* **18h** (85 mg, 0.242 mmol, 42%) as a yellow solid. **MP** 173-174 °C. **IR** ν_{max} (film, cm^{-1}): 2981 (br), 2360 (m), 1647 (s), 1457 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (1H, dt, *J* = 7.6, 1.0 Hz, Ar**H**), 7.38 – 7.23 (11H, m, 11 x Ar**H**), 7.01 (2H, dd, *J* = 7.5, 1.8 Hz, 2 x Ar**H**), 5.35 (2H, s, C**H**$_2$), 3.65 (1H, app. tt, *J* = 11.1, 4.8 Hz, C**H**), 3.21 (1H, dd, *J* = 16.9, 5.1 Hz, C**H**H), 3.05 (1H, dd, *J* = 16.6, 11.0 Hz, C**H**H), 2.92 (1H, dd, *J* = 16.4, 11.6 Hz, CH**H**), 2.85 (1H, dd, *J* = 16.6, 4.7 Hz, CH**H**) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.6 (**C**), 150.7 (**C**), 143.0 (**C**), 137.5 (**C**), 135.8 (**C**), 129.1 (2 x **C**H), 128.8 (2 x **C**H), 127.9 (**C**H), 127.1 (**C**H), 126.9 (2 x **C**H), 126.0 (2 x **C**H), 124.7 (**C**), 123.4 (**C**H), 122.9 (**C**H), 121.8 (**C**H), 111.9 (**C**), 109.8 (**C**H), 47.0 (**C**H$_2$), 45.0 (**C**H$_2$), 42.0 (**C**H), 30.2 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 352 [M+H]$^+$. **HRMS** (ESI$^+$): Found 352.1697, $C_{25}H_{22}NO$ [M+H]$^+$ requires 352.1696.

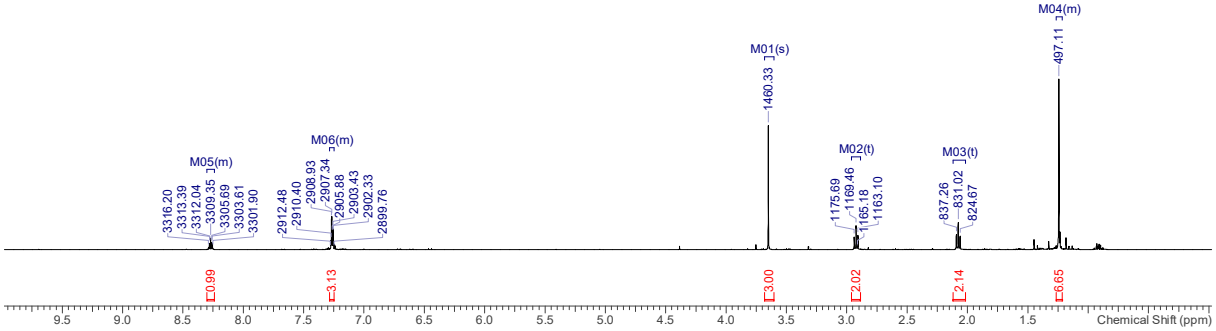


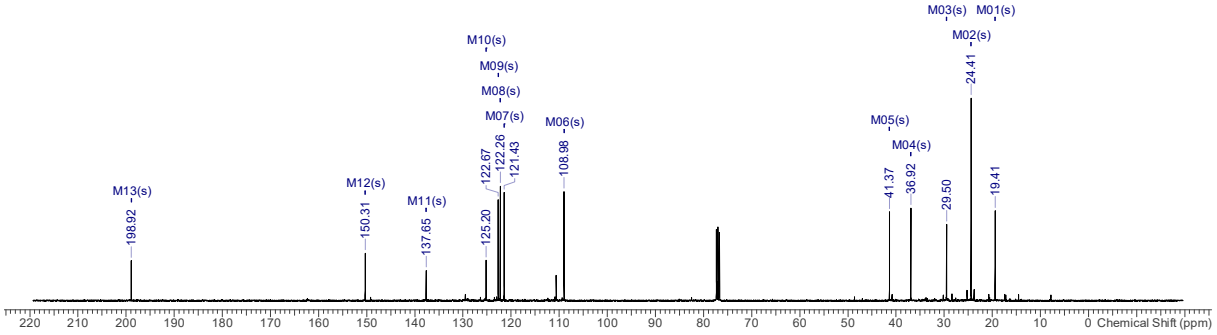
3,3,9-Trimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 18i



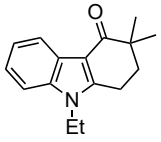
Using flow photochemical set-up A: A solution of enaminone **5i** (285 mg, 1.24 mmol) and iodine (15.8 mg, 0.062 mmol, 5 mol%) in MeCN (62 mL, 0.02 M) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18i** (182 mg, 0.802 mmol, 65%) as an off-white oil.

Using flow photochemical set-up B: A solution of enaminone **5i** (231 mg, 1.01 mmol) in MeCN (101 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18i** (152 mg, 0.670 mmol, 67%) as an off-white oil. **IR** ν_{max} (film, cm^{-1}): 2924 (br), 1637 (s), 1474 (s), 1456 (s), 1416 (m), 1067 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (1 H, m, Ar**H**), 7.28 – 7.26 (3 H, m, 3 × Ar**H**), 3.65 (3 H, s, C**H**$_3$), 2.92 (2 H, t, *J* = 6.3 Hz, C**H**$_2$), 2.08 (2 H, t, *J* = 6.3 Hz, C**H**$_2$), 1.24 (6 H, s, 2 × C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.9 (**C**), 150.3 (**C**), 137.7 (**C**), 131.0 (**C**), 125.2 (**C**), 122.7 (**C**H), 122.3 (**C**H), 121.4 (**C**H), 109.0 (**C**H), 41.4 (**C**), 36.9 (**C**H$_2$), 29.5 (**C**H$_3$), 24.4 (2 × **C**H$_3$), 19.4 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 228 [M+H]$^+$. Data consistent with literature values, though the product proved sensitive to column chromatography leading to some decomposition.[2]

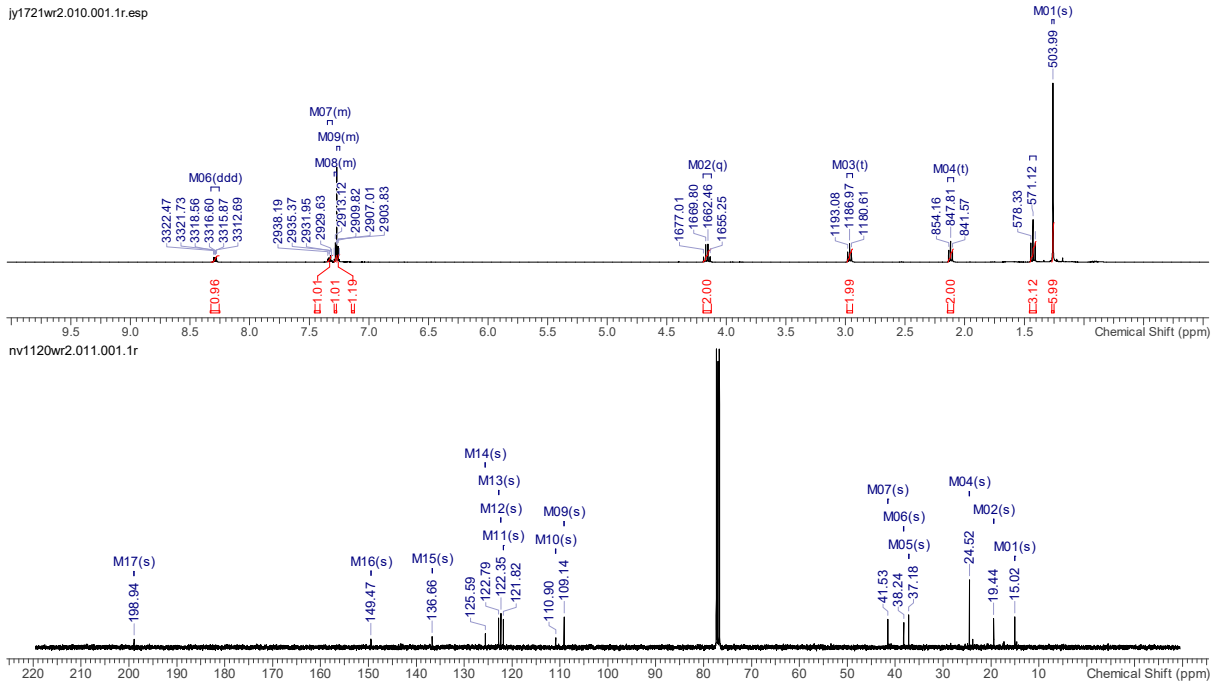




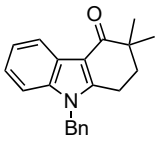
9-Ethyl-3,3-dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, **18j**



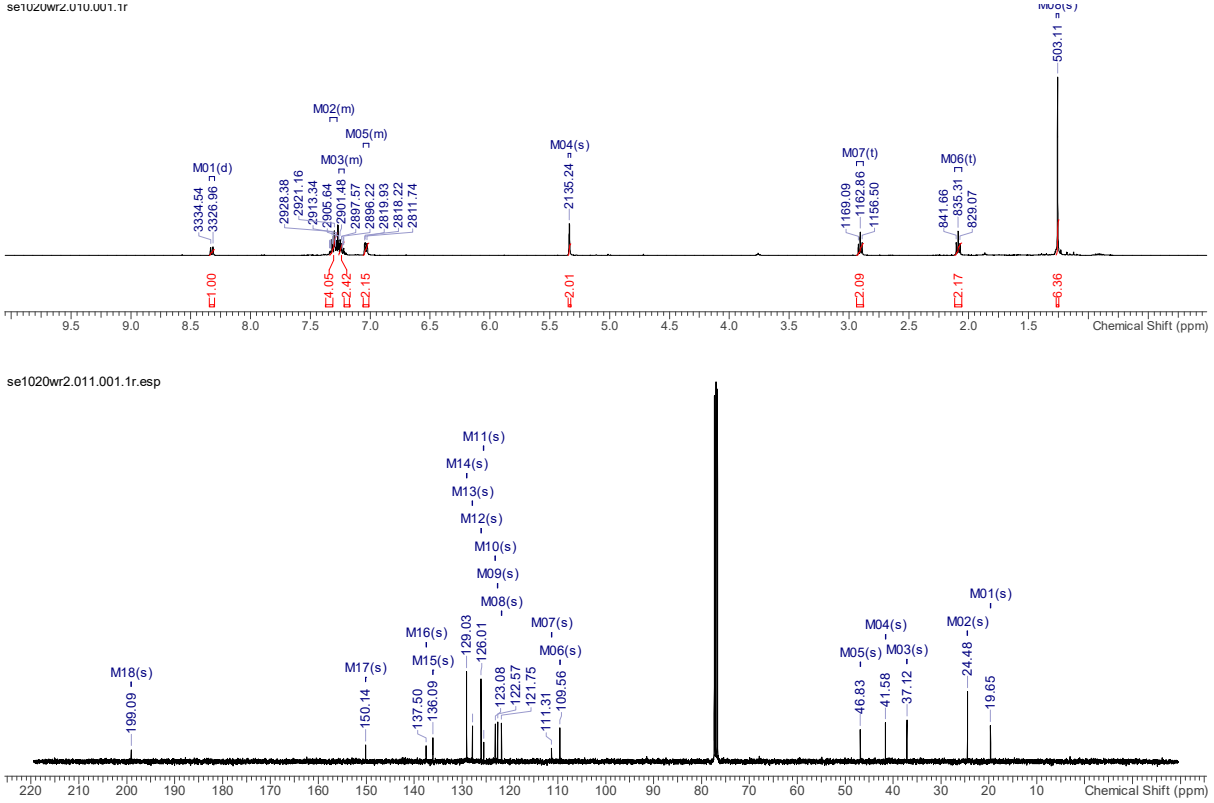
Using flow photochemical set-up B: A solution of enaminone **5j** (200 mg, 0.823 mmol) in MeCN (82 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the *title compound* **18j** as an off-white solid (146 mg, 0.606 mmol, 74%). **MP** 121 – 124 °C. **IR** ν_{max} (film, cm^{-1}): 2961 (br), 2927 (w), 1640 (s), 1455 (s), 1067 (m), 753 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29 (1H, m, Ar**H**), 7.33 (1H, m, Ar**H**), 7.24 – 7.29 (2H, m, 2 x Ar**H**), 4.16 (2H, q, *J* = 7.2 Hz, C$\mathbf{H}_2$), 2.97 (2H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.12 (2H, t, *J* = 6.3 Hz, C$\mathbf{H}_2$), 1.43 (3H, t, *J* = 7.3 Hz, C$\mathbf{H}_3$), 1.26 (6H, s, 2 x C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 198.9 (**C**), 149.5 (**C**), 136.7 (**C**), 125.6 (**C**), 122.8 (**C**H), 122.4 (**C**H), 121.8 (**C**H), 110.9 (**C**), 109.1 (**C**H), 41.5 (**C**), 38.2 (**C**H$_2$), 37.2 (**C**H$_2$), 24.5 (2 x **C**H$_3$), 19.4 (**C**H$_2$), 15.0 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 242 [M+H]$^+$. **HRMS** (ESI$^+$): Found 242.1542, $C_{16}H_{20}NO$ [M+H]$^+$ requires 242.1539.



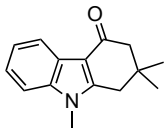
9-Benzyl-3,3-dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, **18k**



Using flow photochemical set-up B: A solution of enaminone **5k** (200 mg, 0.656 mmol) in MeCN (65 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the *title compound* **18k** as a yellow solid (147 mg, 0.485 mmol, 75%). **MP** 171 – 173 °C (EtOAc/petrol), Lit.[6] 171 – 172 °C (EtOAc). **IR** ν_{max} (film, cm^{-1}): 2960 (w), 2925 (w), 1645 (s), 1456 (s), 1067 (m), 753 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (1H, d, *J* = 7.6 Hz, Ar**H**), 7.35 – 7.21 (6H, m, 6 x Ar**H**), 7.06 – 7.01 (2H, m, 2 x Ar**H**), 5.34 (2H, s, C$\mathbf{H}_2$), 2.91 (2H, t, *J* = 6.3 Hz, C$\mathbf{H}_2$), 2.09 (2H, t, *J* = 6.3 Hz, C$\mathbf{H}_2$), 1.26 (6H, s, 2 x C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 199.1 (**C**), 150.1 (**C**), 137.5 (**C**), 136.1 (**C**), 129.0 (2 x **C**H), 127.8 (**C**H), 126.0 (2 x **C**H), 125.5 (**C**), 123.1 (**C**H), 122.6 (**C**H), 121.8 (**C**H), 111.3 (**C**), 109.6 (**C**H), 46.8 (**C**H$_2$), 41.6 (**C**), 37.1 (**C**H$_2$), 24.5 (2 x **C**H$_3$), 19.7 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 304 [M+H]$^+$. Data consistent with literature values.[6]

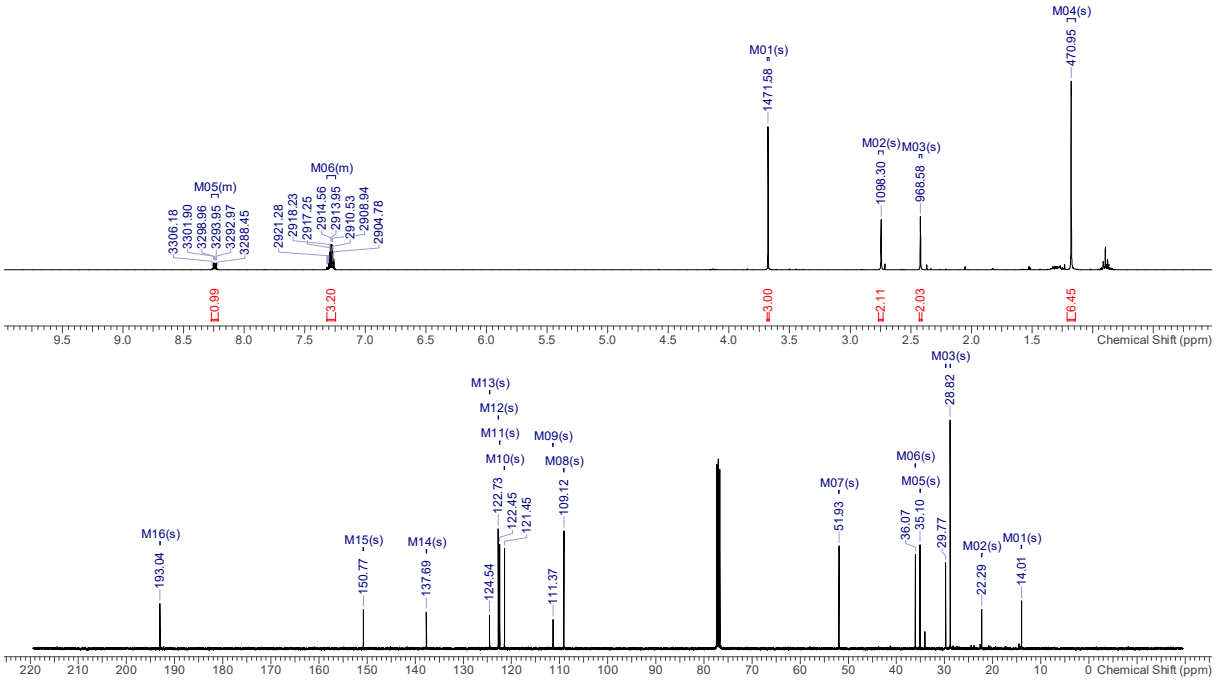


2,2,9-Trimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 18l

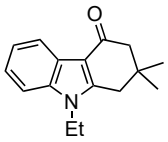


Using flow photochemical set-up A: A solution of enaminone **5l** (101 mg, 0.441 mmol) and iodine (5.6 mg, 0.022 mmol, 5 mol%) in MeCN (22 mL, 0.02 M) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18l** (75 mg, 0.330 mmol, 76%) as a yellow solid.

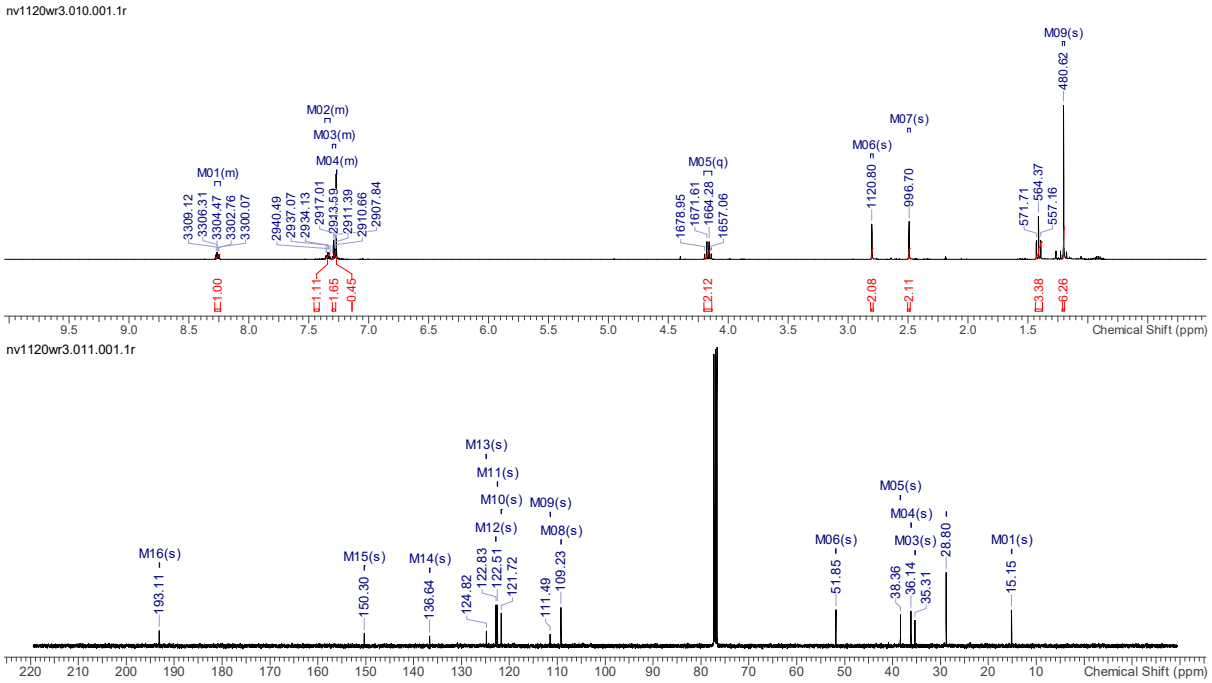
Using flow photochemical set-up B: A solution of enaminone **5l** (130 mg, 0.568 mmol) in MeCN (57 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **18l** (96 mg, 0.423 mmol, 71%) as a yellow solid. **MP** 118 – 119 °C (Et_2O/petrol), Lit.[7b] 115 °C. **IR** ν_{max} (film, cm^{-1}): 2954 (br), 1617 (m), 1549 (s), 1492 (m), 1382 (m), 1281 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (1 H, m, Ar**H**), 7.31 – 7.26 (3 H, m, 3 × Ar**H**), 3.68 (3 H, s, C$\mathbf{H}_3$), 2.74 (2 H, s, C$\mathbf{H}_2$), 2.42 (2 H, s, C$\mathbf{H}_2$), 1.18 (6 H, s, 2 × C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.0 (**C**), 150.8 (**C**), 137.7 (**C**), 124.5 (**C**), 122.7 (**C**H), 122.5 (**C**H), 121.5 (**C**H), 113.4 (**C**), 109.1 (**C**H), 51.9 (**C**H_3), 36.1 (**C**H_2), 35.1 (**C**H_2), 29.8 (**C**), 24.4 (2 × **C**H_3) ppm. **LRMS** (ESI$^+$): 228 $[M+H]^+$. Data consistent with literature values.[7]



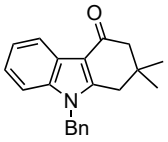
9-Ethyl-2,2-dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, **18m**



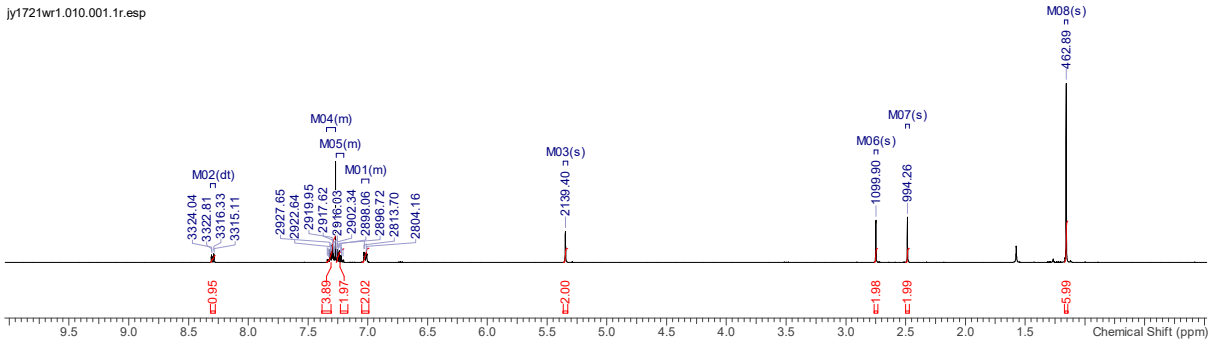
Using flow photochemical set-up B: A solution of enaminone **5m** (200 mg, 0.823 mmol) in MeCN (82 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the *title compound* **18m** (131 mg, 0.544 mmol, 66%) as an off-white solid. **MP** 91 – 94 °C (EtOAc/petrol), Lit.[8] 93 – 95 °C (Et_2O/hexane). **IR** ν_{max} (film, cm^{-1}): 2959 (br), 1644 (s), 1455 (s), 1092 (m), 748 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (1H, m, Ar**H**), 7.34 (1H, m, Ar**H**), 7.30 – 7.27 (2H, m, 2 x Ar**H**), 4.17 (2H, q, *J* = 7.3 Hz, C$\mathbf{H}_2$), 2.80 (2H, s, C$\mathbf{H}_2$), 2.49 (2H, s, C$\mathbf{H}_2$), 1.41 (3H, t, *J* = 7.3 Hz, C$\mathbf{H}_3$), 1.20 (6H, s, 2 x C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.1 (**C**), 150.3 (**C**), 136.6 (**C**), 124.8 (**C**), 122.8 (**C**H), 122.5 (**C**H), 121.7 (**C**H), 111.5 (**C**), 109.2 (**C**H), 51.9 (C$\mathbf{H}_2$), 38.4 (C$\mathbf{H}_2$), 36.1 (C$\mathbf{H}_2$), 35.3 (**C**), 28.8 (2 x C$\mathbf{H}_3$), 15.2 (C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 242 $[M+H]^+$. Data consistent with literature values.[8]

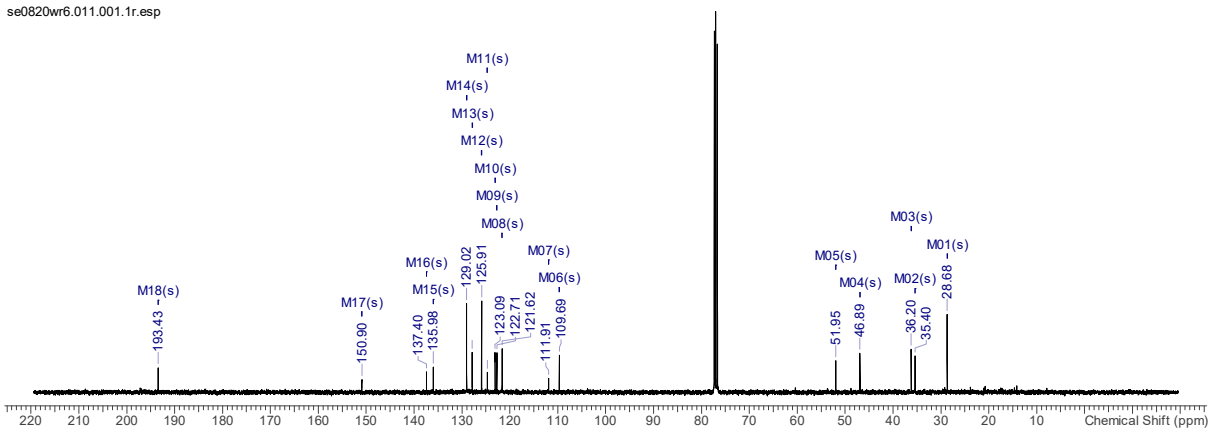


9-Benzyl-2,2-dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, **18n**

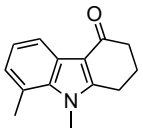


Using flow photochemical set-up B: A solution of enaminone **5n** (200 mg, 0.656 mmol) in MeCN (65 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (10 – 40% EtOAc in petrol) to afford the *title compound* **18n** (135 mg, 0.446 mmol, 69%) as a yellow solid. **MP** 143 – 147 °C (EtOAc/petrol), Lit.[9] 140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.30 (1H, dt, *J* = 7.7, 1.1 Hz, Ar**H**), 7.34 – 7.20 (6H, m, 6 x Ar**H**), 7.05 – 6.99 (2H, m, 2 x Ar**H**), 5.35 (2H, s, C$\mathbf{H}_2$), 2.75 (2H, s, C$\mathbf{H}_2$), 2.48 (2H, s, C$\mathbf{H}_2$), 1.16 (6H, s, 2 x C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.4 (**C**), 150.9 (**C**), 137.4 (**C**), 136.0 (**C**), 129.0 (2 x **C**H), 127.9 (**C**H), 125.9 (2 x **C**H), 124.7 (**C**), 123.1 (**C**H), 122.7 (**C**H), 121.6 (**C**H), 111.9 (**C**), 109.7 (**C**H), 52.0 (C$\mathbf{H}_2$), 46.9 (C$\mathbf{H}_2$), 36.2 (C$\mathbf{H}_2$), 35.4 (**C**), 28.7 (2 x C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 304 $[M+H]^+$. Data consistent with literature values.[9]



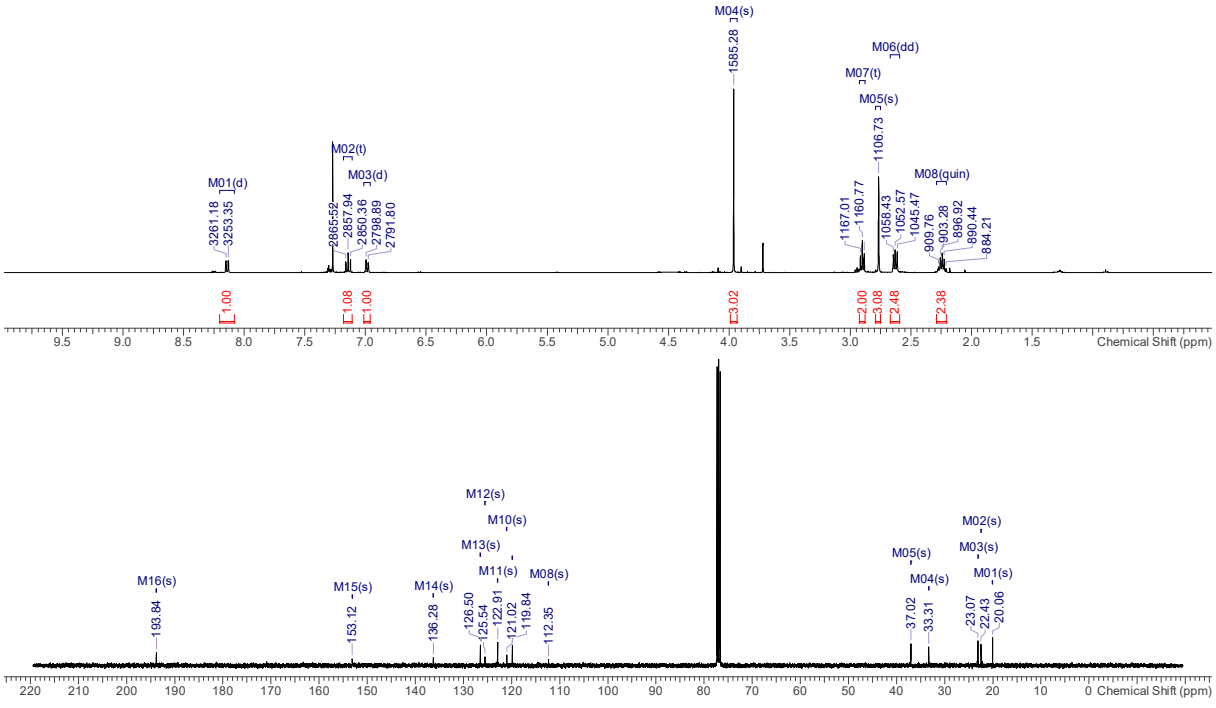


8,9-Dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20a

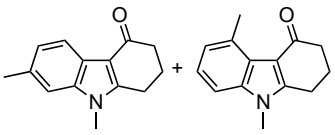


Using flow photochemical set-up A: A solution of enaminone **19a** (205 mg, 0.953 mmol) and iodine (12 mg, 0.05 mmol, 5 mol%) in dry MeCN (48 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **20a** (73 mg, 0.343 mmol, 36%) as an off-white solid.

Using flow photochemical set-up B: A solution of enaminone **19a** (350 mg, 1.63 mmol) in MeCN (163 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **20a** (132 mg, 0.620 mmol, 38%) as an off-white solid. **MP** 165 – 166 °C (Et_2O/petrol), Lit.[10] 186 – 187 °C. **IR** ν_{max} (film, cm^{-1}): 2940 (br), 1637 (s), 1465 (s), 1409 (m), 1105 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (1 H, d, *J* = 7.8 Hz, Ar**H**), 7.14 (1 H, app. t, *J* = 7.6 Hz, Ar**H**), 6.99 (1 H, d, *J* = 7.1 Hz, Ar**H**), 3.96 (3 H, s, CH_3), 2.90 (2 H, app. t, *J* = 6.2 Hz, CH_2), 2.77 (3 H, s, CH_3), 2.63 (2 H, dd, *J* = 7.2, 5.8 Hz, CH_2), 2.24 (2 H, app. quin, *J* = 6.4 Hz, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8 (**C**), 153.1 (**C**), 136.3 (**C**), 126.5 (**C**H), 125.5 (**C**), 122.9 (**C**H), 121.0 (**C**), 119.8 (**C**H), 112.4 (**C**), 37.0 (CH_2), 33.3 (CH_3), 23.1 (CH_2), 22.4 (CH_2), 20.1 (CH_3) ppm. **LRMS** (ESI^+): 236 $[M + Na]^+$, 214 $[M + H]^+$. Data consistent with literature values.[10]



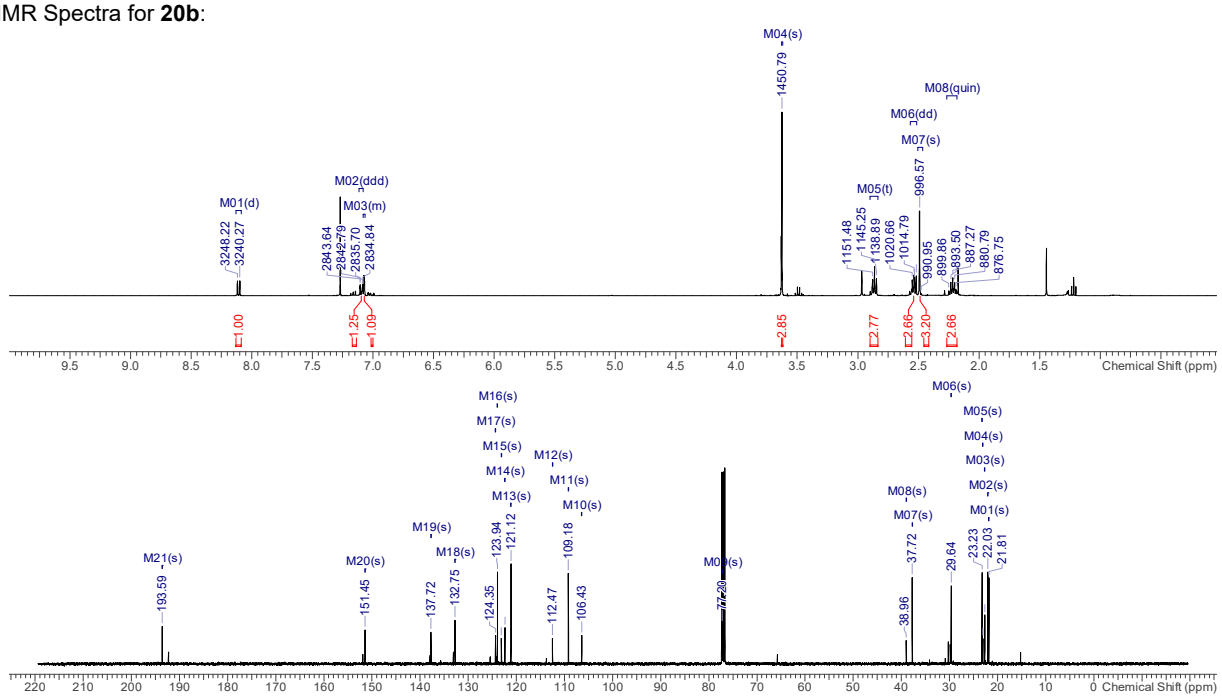
5,9-Dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20b and 7,9-dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20b'



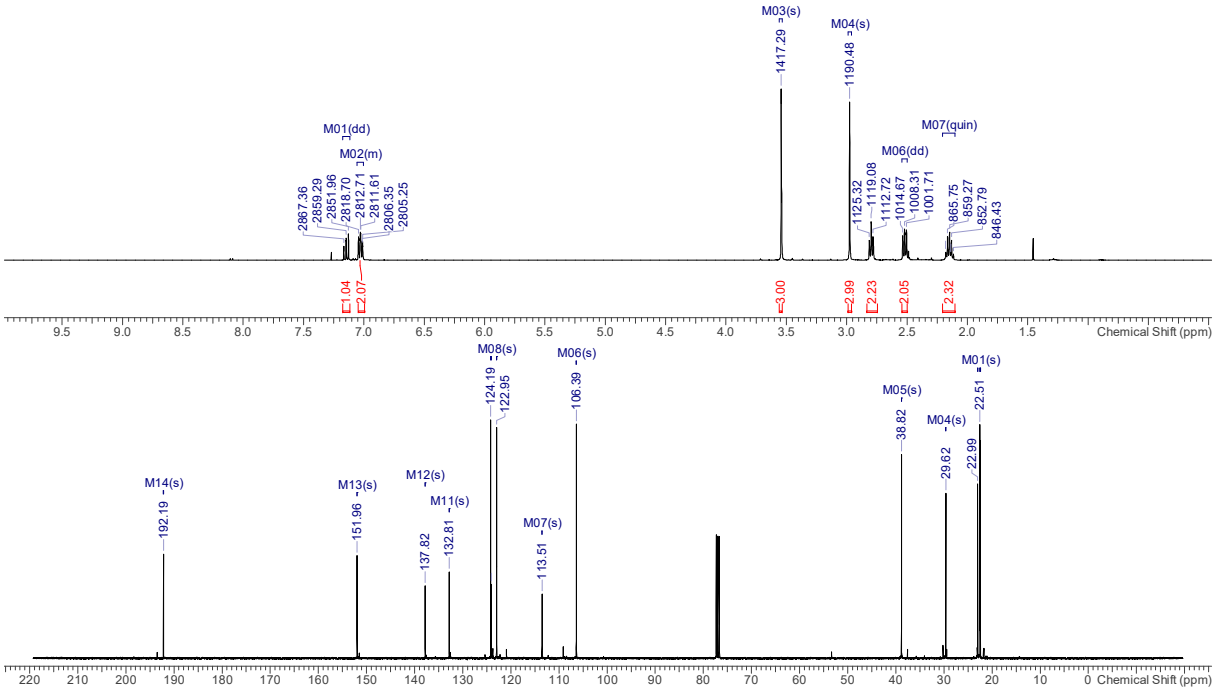
Using flow photochemical set-up B: A solution of enaminone **19b** (290 mg, 1.26 mmol) in MeCN (126 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 40% Et_2O in petrol) to afford firstly *title compound* **20b** (210 mg, 0.986 mmol, 51%) as an off-white solid. **MP**: 169 – 170 °C. **IR** ν_{max} (film, cm^{-1}): 2933 (br), 1629 (s), 1476 (m), 1432 (m), 1087 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (1 H, d, *J* = 8.0 Hz, Ar**H**), 7.10 (1 H, ddd, *J* = 8.0, 1.3, 0.6 Hz, Ar**H**), 7.07 (1 H, m, Ar**H**), 3.63 (3 H, s, CH_3), 2.86 (2 H, app. t, *J* = 6.3 Hz, CH_2), 2.53 (2 H, dd, *J* = 7.1, 5.9 Hz, CH_2), 2.49 (3 H, s, CH_3), 2.22 (2 H, app. quin, *J* = 6.5 Hz, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.6 (**C**), 151.5 (**C**), 137.7 (**C**), 132.8 (**C**), 123.9 (**C**H), 122.4 (**C**), 121.1 (**C**H), 112.5 (**C**), 109.2

(**C**H), 37.7 (**C**H$_2$), 29.6 (**C**H$_3$), 23.2 (**C**H$_2$), 22.0 (**C**H$_2$), 21.8 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 236 [M + Na]$^+$, 214 [M + H]$^+$. **HRMS** (ESI$^+$): Found 214.1232, $C_{14}H_{16}NO$ [M+H]$^+$ requires 214.1226. Followed by *title compound* **20b'** (123 mg, 0.577 mmol, 30%) as an off-white solid. **MP**: 185 – 186 °C. **IR** ν_{max} (film, cm^{-1}): 2932 (br), 1634 (s), 1480 (m), 1408 (m), 1021 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.15 (1 H, dd, *J* = 8.1, 7.3 Hz, Ar**H**), 7.04 – 7.01 (2 H, m, 2 × Ar**H**), 3.43 (3 H, s, C**H**$_3$), 2.98 (3 H, s, C**H**$_3$), 2.80 (2 H, app. t, *J* = 6.3 Hz, C**H**$_2$), 2.52 (2 H, dd, *J* = 7.0, 5.9 Hz, C**H**$_2$), 2.15 (2 H, app. quin, *J* = 6.4 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.2 (**C**), 152.0 (**C**), 137.8 (**C**), 132.8 (**C**), 124.2 (**C**H), 124.1 (**C**), 123.0 (**C**H), 113.5 (**C**), 106.4 (**C**H), 38.8 (**C**H$_2$), 29.6 (**C**H$_3$), 23.0 (**C**H$_2$), 22.51 (**C**H$_2$), 22.45 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 236 [M + Na]$^+$, 214 [M + H]$^+$. **HRMS** (ESI$^+$): Found 214.1230, $C_{14}H_{16}NO$ [M+H]$^+$ requires 214.1226.

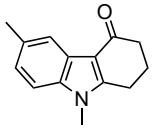
• NMR Spectra for **20b**:



NMR Spectra for **20b'**:

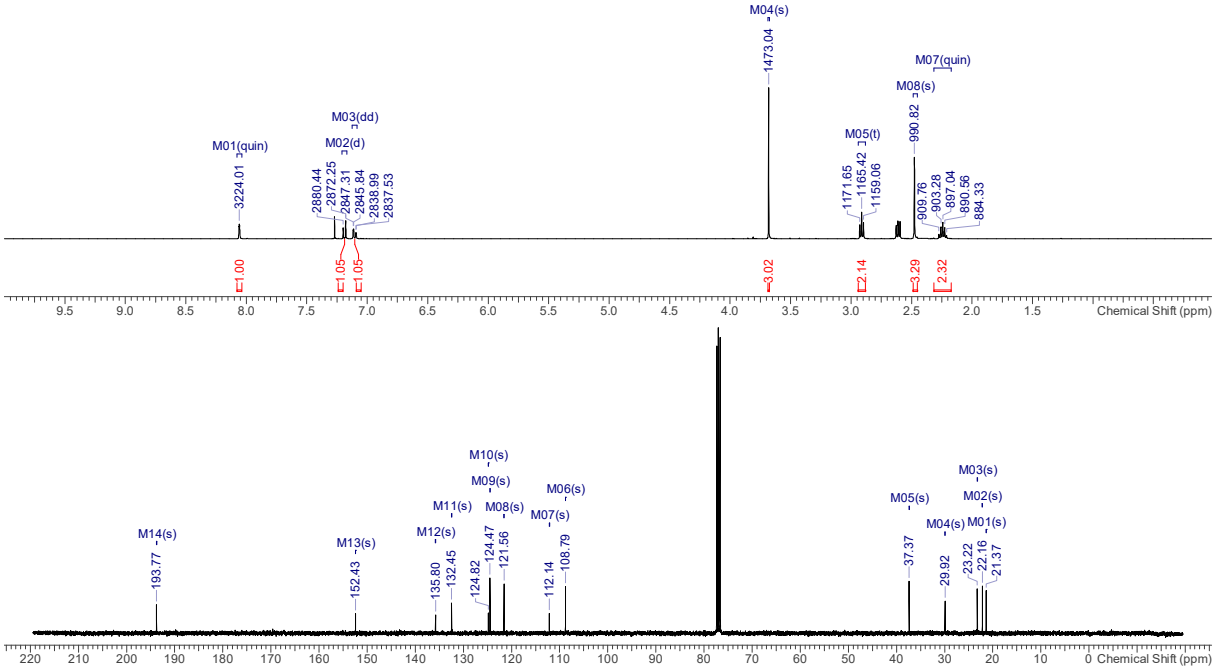


6,9-Dimethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20c

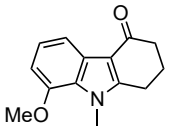


Using flow photochemical set-up B: A solution of enaminone **19c** (388 mg, 1.81 mmol) in MeCN (180 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% Et_2O in petrol) to afford the *title compound* **20c** (272 mg, 1.28 mmol, 71%) as an off-white solid. **MP** 160 – 161 °C (Et_2O/petrol), Lit.[10] 166 – 169 °C. **IR** ν_{max} (film, cm^{-1}): 2926 (br), 1627 (s), 1459 (s), 1323 (m), 1092 (s). **^{1}H NMR**

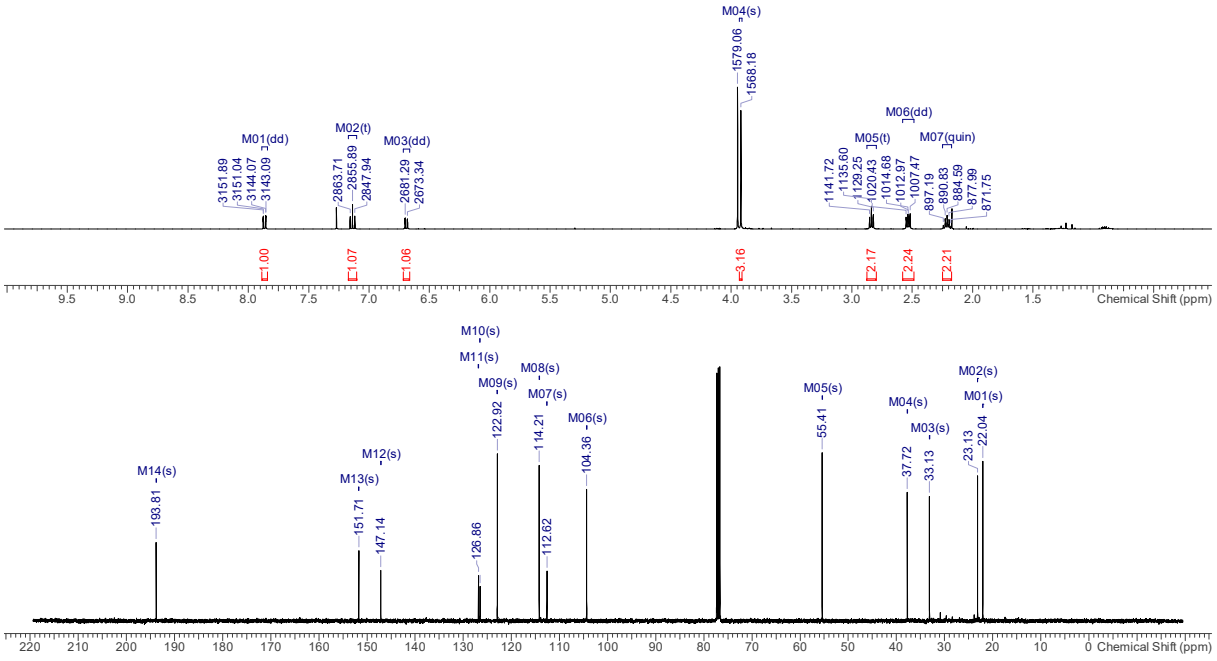
(400 MHz, $CDCl_3$): δ 8.06 (1 H, app. quin, *J* = 0.9 Hz, Ar**H**), 7.19 (1 H, d, *J* = 8.2 Hz, Ar**H**), 7.10 (1 H, dd, *J* = 8.3, 1.5 Hz, Ar**H**), 3.68 (3 H, s, CH_3), 2.91 (2 H, app. t, *J* = 6.3 Hz, CH_2), 2.61 (2 H, dd, *J* = 7.2, 5.8 Hz, CH_2), 2.48 (3 H, s, CH_3), 2.24 (2 H, app. quin, *J* = 6.4 Hz, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8 (**C**), 152.4 (**C**), 135.8 (**C**), 132.5 (**C**), 124.8 (**C**), 124.5 (**C**H), 121.6 (**C**H), 112.1 (**C**), 108.8 (**C**H), 37.4 (CH_2), 29.9 (CH_3), 23.2 (CH_2), 22.2 (CH_2), 21.4 (CH_3) ppm. **LRMS** (ESI$^+$): 236 [M + Na]$^+$, 214 [M + H]$^+$. Data consistent with literature values.[10]



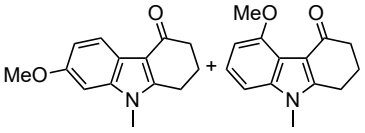
8-Methoxy-9-methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20d



Using flow photochemical set-up B: A solution of enaminone **19d** (332 mg, 1.44 mmol) in MeCN (144 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 1 hour. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **20d** (227 mg, 0.991 mmol, 69%) as an off-white solid. **MP**: 139 – 140 °C. **IR** ν_{max} (film, cm^{-1}): 2938 (br), 1638 (s), 1613 (s), 1452 (s), 1264 (m), 1109 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (1 H, dd, *J* = 7.9, 0.9 Hz, Ar**H**), 7.15 (1 H, t, *J* = 7.9 Hz, Ar**H**), 6.69 (1 H, dd, *J* = 8.0, 0.7 Hz, Ar**H**), 3.95 (1 H, s, CH_3), 3.92 (1 H, s, CH_3), 2.84 (2 H, app. t, *J* = 6.2 Hz, CH_2), 2.92 (2 H, app. dd, *J* = 7.2, 5.8 Hz, CH_2), 2.22 (2 H, app. quin, *J* = 6.4 Hz, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8 (**C**), 151.7 (**C**), 147.1 (**C**), 126.9 (**C**), 126.5 (**C**), 122.9 (**C**H), 114.2 (**C**H), 112.6 (**C**), 104.4 (**C**H), 55.4 (CH_3), 37.7 (CH_2), 33.1 (CH_3), 23.1 (CH_2), 22.0 (CH_2) ppm. **LRMS** (ESI$^+$): 252 [M + Na]$^+$, 230 [M + H]$^+$. **HRMS** (ESI$^+$): Found 230.1179, $C_{14}H_{16}NO_2$ [M+H]$^+$ requires 230.1176.

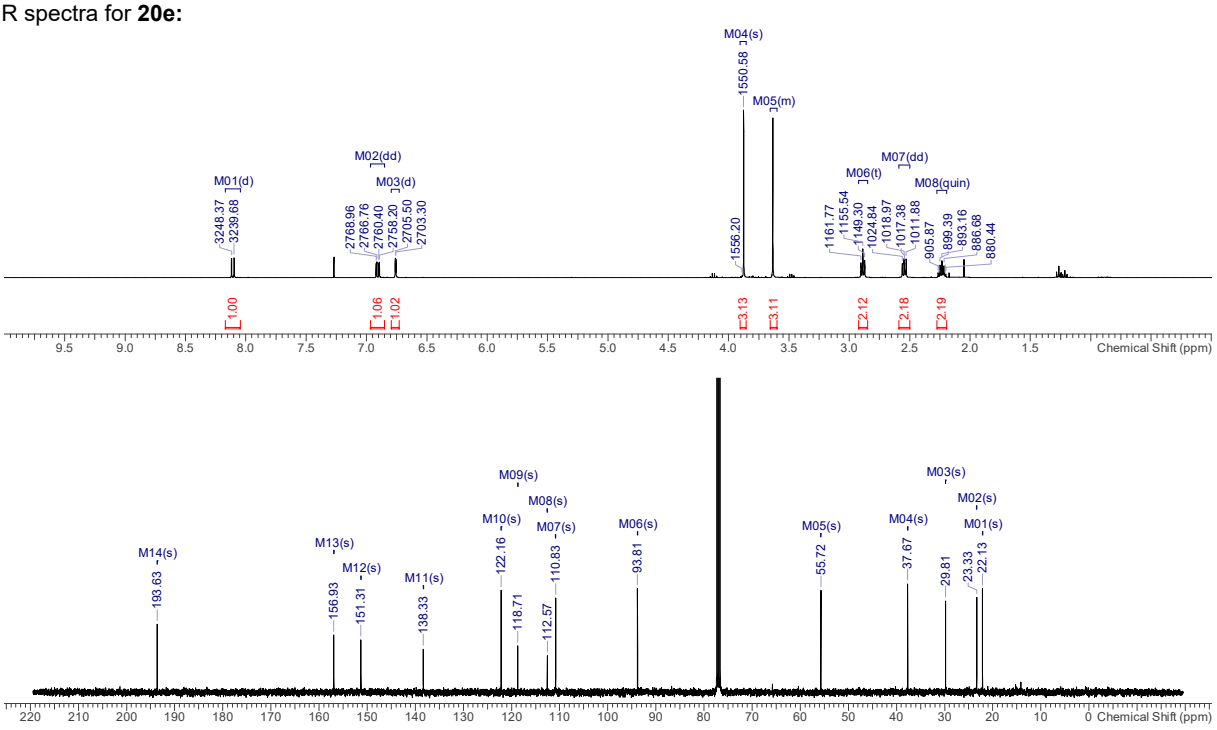


5-Methoxy-9-methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20e and 7-methoxy-9-methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20e'

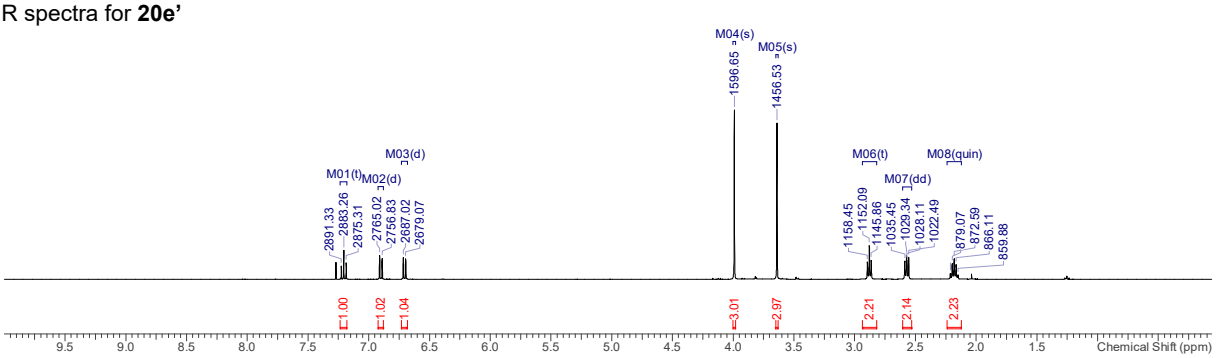


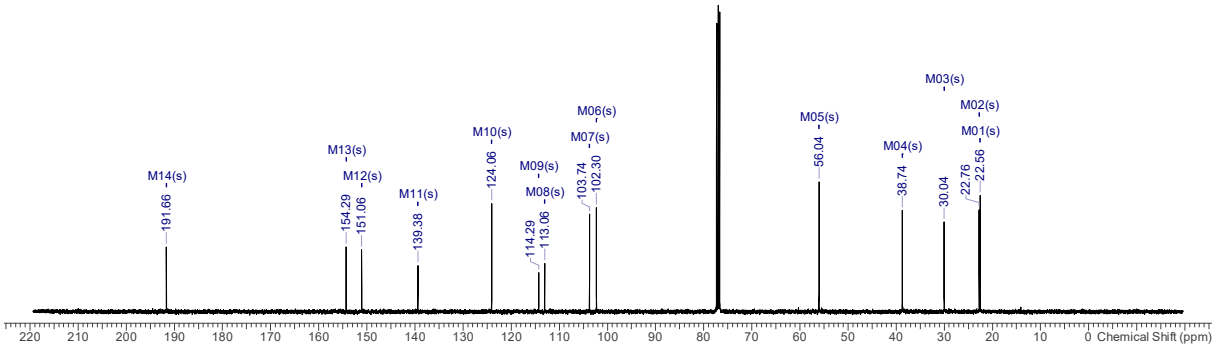
Using flow photochemical set-up B: A solution of enaminone **19e** (290 mg, 1.26 mmol) in MeCN (126 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 40% Et_2O in petrol) to afford firstly *title compound* **20e** (127 mg, 0.555 mmol, 44%) as an off-white solid. **MP**: 197 – 199 °C. **IR** ν_{max} (film, cm^{-1}): 2950 (br), 1629 (s), 1476 (m), 1245 (m), 1080 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (1 H, d, *J* = 8.7 Hz, Ar**H**), 6.91 (1 H, dd, *J* = 8.6, 2.2 Hz, Ar**H**), 6.76 (1 H, d, *J* = 2.2 Hz, Ar**H**), 3.88 (3 H, s, C$\mathbf{H}_3$), 3.63 (3 H, s, C$\mathbf{H}_3$), 2.89 (2 H, app. t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.55 – 2.53 (2 H, m, C$\mathbf{H}_2$), 2.23 (2 H, app. quin, *J* = 6.5 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.6 (**C**), 156.9 (**C**), 151.3 (**C**), 138.3 (**C**), 122.2 (**C**H), 118.7 (**C**), 112.6 (**C**), 110.8 (**C**H), 93.8 (**C**H), 55.7 (**C**H_3), 37.7 (**C**H_2), 29.8 (**C**H_3), 23.3 (**C**H_2), 22.1 (**C**H_2) ppm. **LRMS** (ESI^+): 230 $[M + H]^+$. **HRMS** (ESI^+): Found 230.1182, $C_{14}H_{16}NO_2$ $[M+H]^+$ requires 230.1176. Followed by *title compound* **20e'** (71 mg, 0.310 mmol, 25%) as a yellow solid. **MP**: 195 – 196 °C. **IR** ν_{max} (film, cm^{-1}): 2933 (br), 1644 (s), 1479 (m), 1262 (s), 1144 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21 (1 H, t, *J* = 8.0 Hz, Ar**H**), 6.90 (1 H, br. d, *J* = 8.2 Hz, Ar**H**), 6.71 (1 H, d, *J* = 8.0 Hz, Ar**H**), 3.99 (3 H, s, C$\mathbf{H}_3$), 3.64 (3 H, s, C$\mathbf{H}_3$), 2.88 (2 H, app. t, *J* = 6.3 Hz, C$\mathbf{H}_2$), 2.57 (2 H, dd, *J* = 7.1, 5.9 Hz, C$\mathbf{H}_2$), 2.18 (2 H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.7 (**C**), 154.3 (**C**), 151.1 (**C**), 139.4 (**C**), 124.1 (**C**H), 114.3 (**C**), 113.1 (**C**), 103.7 (**C**H), 102.3 (**C**H), 56.0 (**C**H_3), 38.7 (**C**H_2), 30.0 (**C**H_3), 22.8 (**C**H_2), 22.6 (**C**H_2) ppm. **LRMS** (ESI^+): 230 $[M + H]^+$. **HRMS** (ESI^+): Found 230.1177, $C_{14}H_{16}NO_2$ $[M+H]^+$ requires 230.1176.

NMR spectra for **20e:**

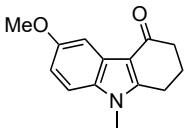


NMR spectra for **20e'**



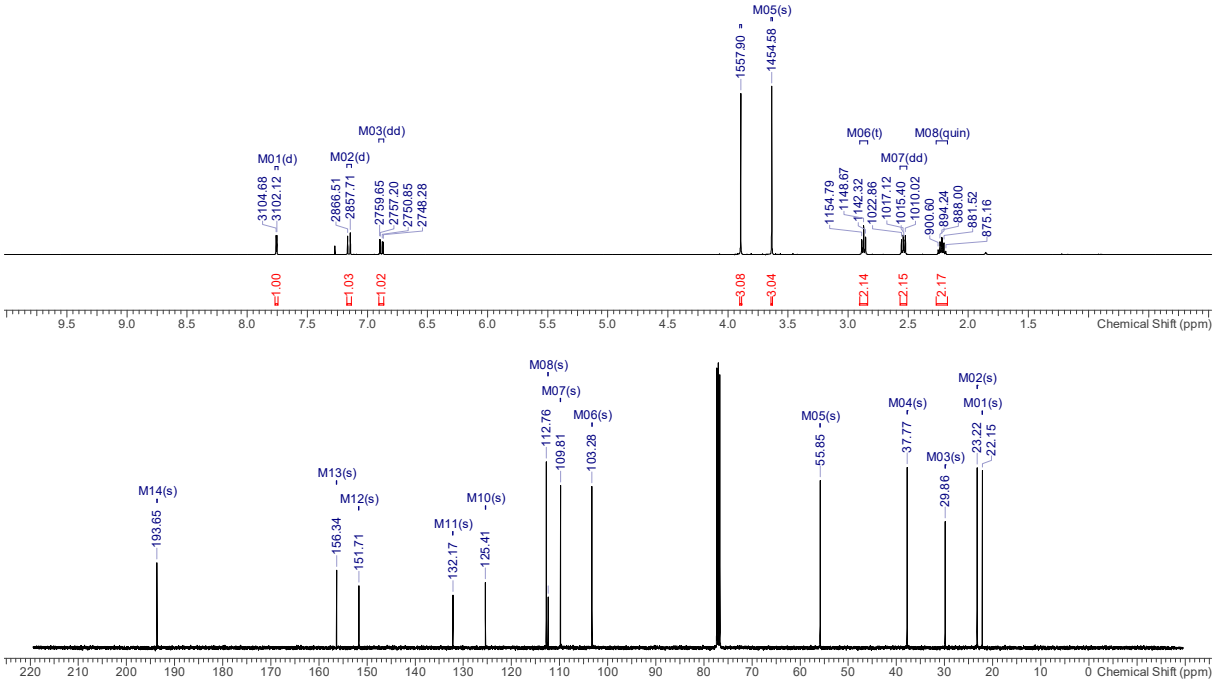


6-Methoxy-9-methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20f

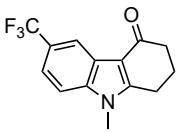


Using flow photochemical set-up A: A solution of enaminone **19f** (239 mg, 1.03 mmol) and iodine (13 mg, 0.05 mmol, 5 mol%) in dry MeCN (52 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **20f** (193 mg, 0.842 mmol, 81%) as an off-white solid.

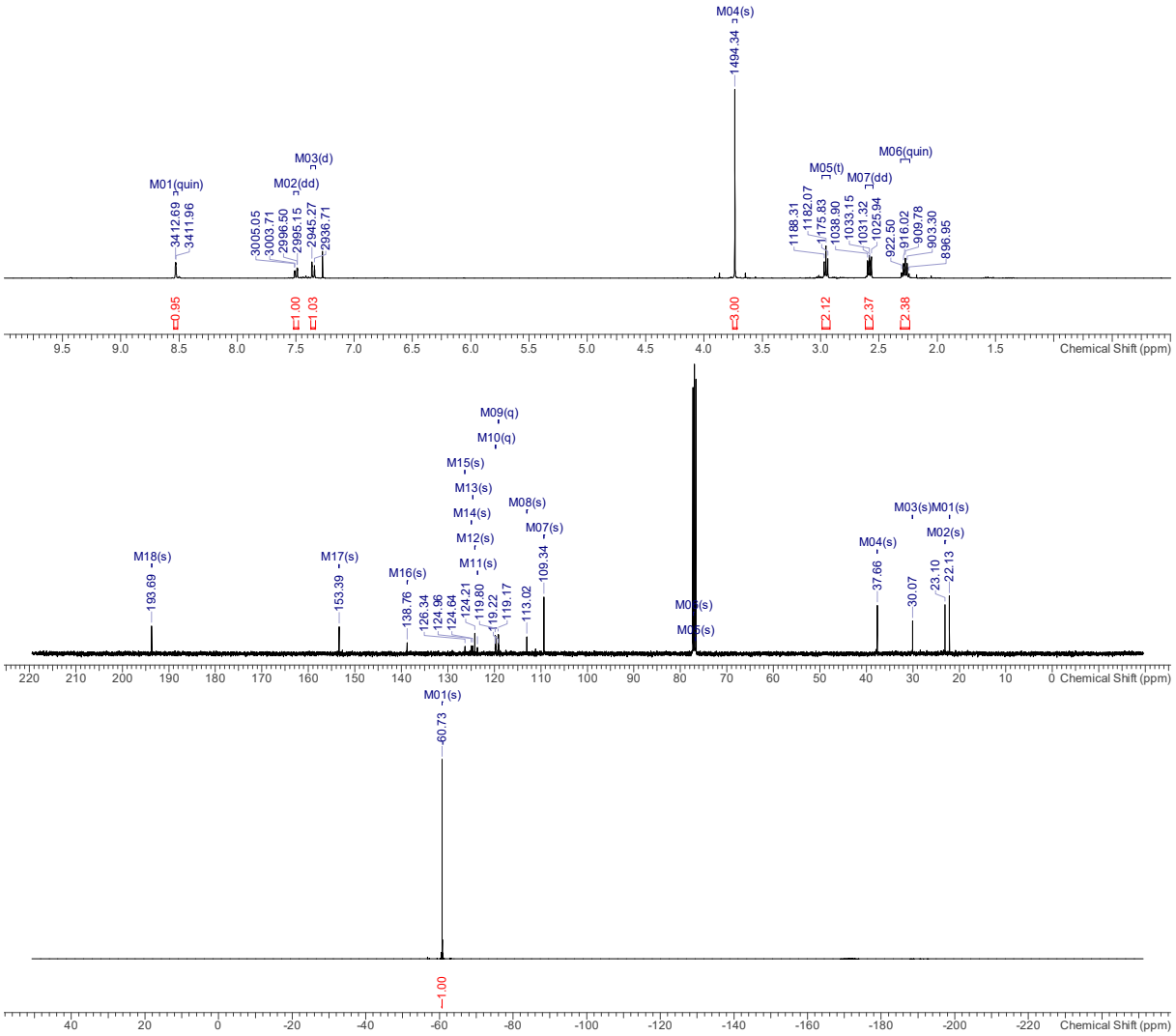
Using flow photochemical set-up B: A solution of enaminone **19f** (134 mg, 0.585 mmol) in MeCN (58 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **20f** (33 mg, 0.144 mmol, 25%) as an off-white solid. **MP** 151 – 152 °C (Et_2O/petrol), Lit.[10] 148 – 150 °C. **IR** ν_{max} (film, cm^{-1}): 3335 (br), 2944 (br), 1723 (m), 1636 (s), 1477 (s), 1120 (s), 1090 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (1 H, d, *J* = 2.6 Hz, Ar**H**), 7.15 (1 H, d, *J* = 8.8 Hz, Ar**H**), 6.88 (1 H, dd, *J* = 8.9, 2.5 Hz, Ar**H**), 3.89 (1 H, s, C$\mathbf{H}_3$), 3.64 (3 H, s, C$\mathbf{H}_3$), 2.87 (2 H, app. t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.54 (2 H, dd, *J* = 7.3, 5.6 Hz, C$\mathbf{H}_2$), 2.22 (2 H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.7 (**C**), 156.3 (**C**), 151.2 (**C**), 132.2 (**C**), 125.4 (**C**), 112.8 (**C**H), 112.4 (**C**), 109.8 (**C**H), 103.3 (**C**H), 55.9 (**C**H_3), 37.8 (**C**H_2), 29.9 (**C**H_3), 23.2 (**C**H_2), 22.2 (**C**H_2) ppm. **LRMS** (ESI$^+$): 252 [M + Na]$^+$, 230 [M + H]$^+$. Data consistent with literature values.[10]



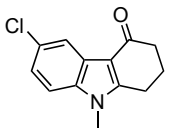
9-Methyl-6-trifluoromethyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, 20g



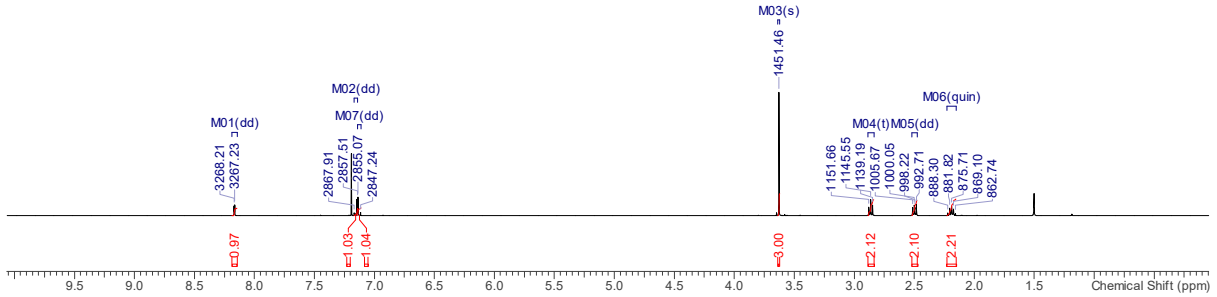
Using flow photochemical set-up B: A solution of enaminone **19g** (213 mg, 0.792 mmol) in MeCN (79 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 50% Et_2O in petrol) to afford the *title compound* **20g** (77 mg, 0.288 mmol, 37%, purity ~95%) as a yellow solid. **MP**: 198 – 200 °C. **IR** ν_{max} (film, cm^{-1}): 2944 (br), 1641 (s), 1458 (s), 1327 (s), 1109 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.52 (1 H, br s, Ar**H**), 7.50 (1 H, dd with fine splitting, *J* = 8.6, 1.3 Hz, Ar**H**), 7.35 (1 H, d with fine splitting, *J* = 8.6 Hz, Ar**H**), 3.73 (3 H, s, C$\mathbf{H}_3$), 2.95 (2 H, app. t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.58 (2 H, dd, *J* = 7.4, 5.6 Hz, C$\mathbf{H}_2$), 2.27 (2 H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.7 (**C**), 153.4 (**C**), 138.8 (**C**), 125.0 (q, $J_{C\text{-}F}$ = 271 Hz, **C**F_3), 124.8 (q, $J_{C\text{-}F}$ = 32 Hz, **C**), 124.2 (**C**), 119.8 (q, $J_{C\text{-}F}$ = 3.7 Hz, **C**H), 119.1 (q, $J_{C\text{-}F}$ = 3.9 Hz, **C**H), 113.0 (**C**), 100.3 (**C**H), 37.7 (**C**H_2), 30.1 (**C**H_3), 23.1 (**C**H_2), 22.1 (**C**H_2) ppm. **^{19}F{H} NMR** (376 MHz, $CDCl_3$): –60.74 (3 F, s, C$\mathbf{F}_3$) ppm. **LRMS** (ESI$^+$): 268 [M + H]$^+$. **HRMS** (ESI$^+$): Found 268.0951, $C_{14}H_{13}F_3NO_2$ [M+H]$^+$ requires 268.0944.

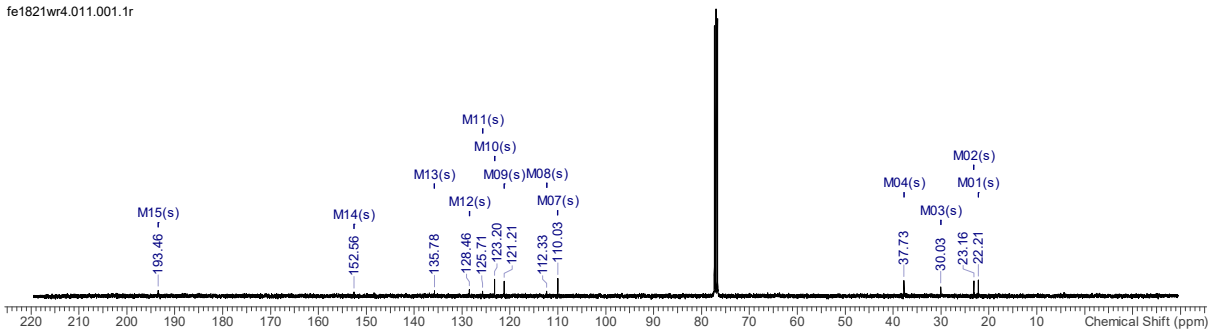


6-Chloro-9-methyl-1,2,3,9-tetrahydro-4*H*-carbazole-4-one, **20h**

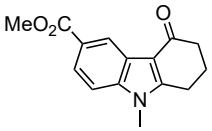


Using flow photochemical set-up B: A solution of enaminone **19h** (200 mg, 0.851 mmol) in MeCN (61 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (50 – 60% EtOAc in petrol) to afford the *title compound* **20h** (96 mg, 0.412 mmol, 49%) as an off-white solid. **MP** 209 – 212 °C (EtOAc/petrol), Lit.[10] 215 – 216 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 1.8, 0.9 Hz, 1H, Ar**H**), 7.15 (dd, *J* = 8.6, 1.8 Hz, 1H, Ar**H**), 7.13 (dd, *J* = 8.6, 0.8 Hz, 1H, Ar**H**), 3.63 (s, 3H, C$\mathbf{H}_3$), 2.86 (2H, app. t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.50 (2H, dd, *J* = 7.4, 5.6 Hz, C$\mathbf{H}_2$), 2.23 – 2.15 (2H, m, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.5 (**C**), 152.6 (**C**), 135.8 (**C**), 128.5 (**C**), 125.7 (**C**), 123.2 (**C**H), 121.2 (**C**H), 112.3 (**C**), 110.0 (**C**H), 37.7 (**C**H_3), 30.0 (**C**H_2), 23.2 (**C**H_2), 22.2 (**C**H_2) ppm. **LRMS** (ESI^+): 234 [M+H^+]. Data consistent with literature values.[10]

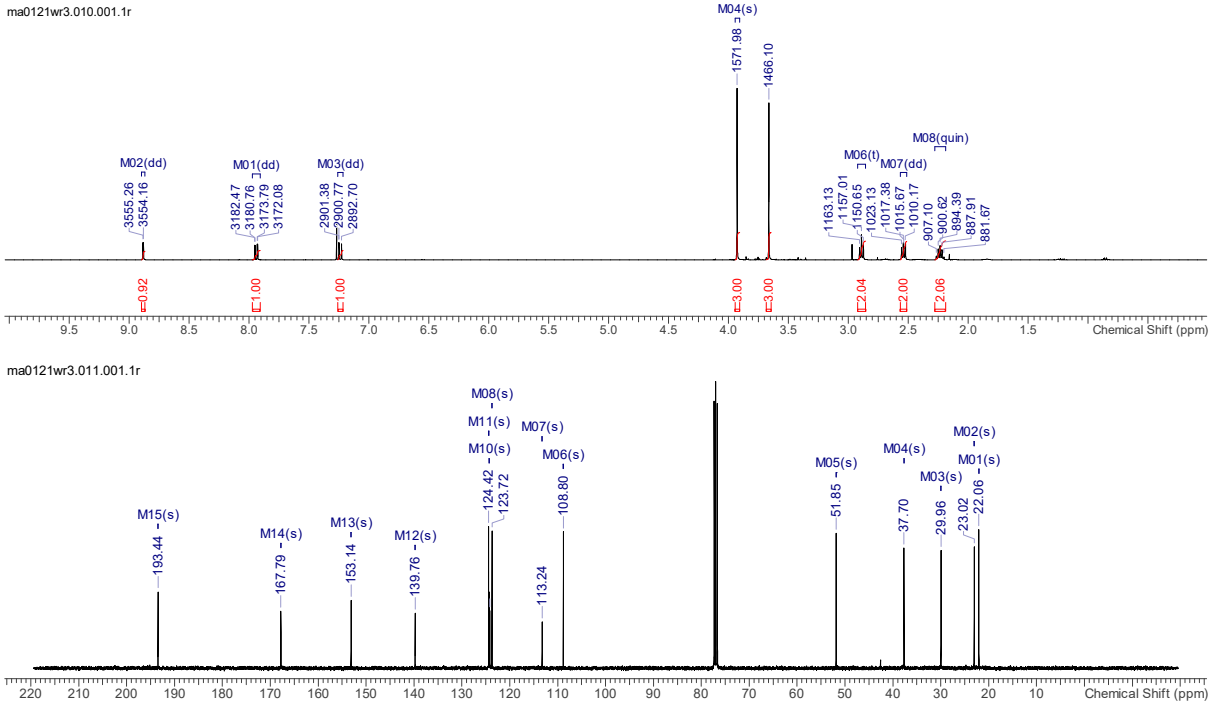




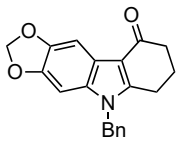
Methyl 9-methyl-4-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-6-carboxylate, **20k**



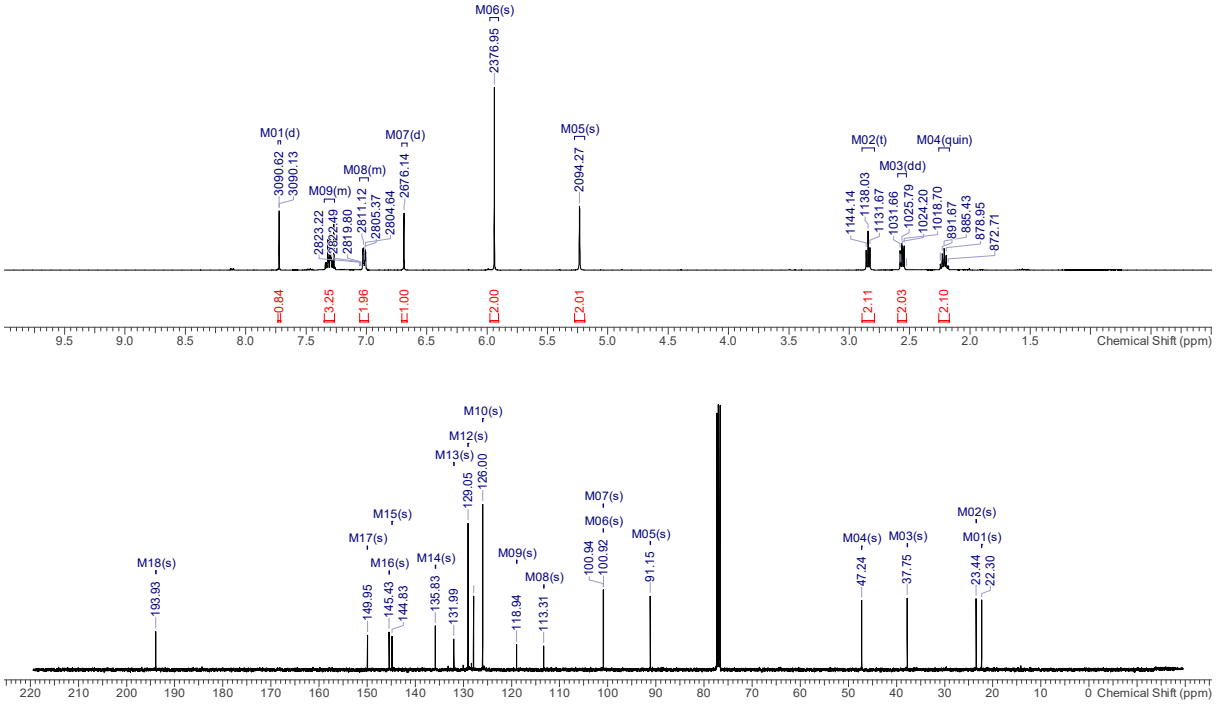
Using flow photochemical set-up B: A solution of enaminone **19k** (200 mg, 0.778 mmol) in MeCN (39 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the *title compound* **20k** (144 mg, 0.560 mmol, 73%) as a white solid. **MP** 212 – 214 °C (EtOAc/petrol), Lit.[11] 214 – 217 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.88 (1H, dd, *J* = 1.7, 0.6 Hz, Ar**H**), 7.94 (1H, dd, *J* = 8.7, 1.7 Hz, Ar**H**), 7.24 (1H, dd, *J* = 8.6, 0.6 Hz, Ar**H**), 3.93 (3H, s, C**H**$_3$), 3.66 (3H, s, C**H**$_3$), 2.89 (2H, t, *J* = app. 6.2 Hz, C**H**$_2$), 2.54 (1H, dd, *J* = 7.3, 5.6 Hz, C**H**$_2$), 2.28 – 2.19 (2H, m, C**H**$_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.4 (**C**), 167.8 (**C**), 153.1 (**C**), 139.8 (**C**), 124.4 (**C**H), 124.3 (**C**), 124.2 (**C**), 123.7 (**C**H), 113.2 (**C**), 108.8 (**C**H), 51.9 (**C**H$_3$), 37.7 (**C**H$_2$), 30.0 (**C**H$_3$), 23.0 (**C**H$_2$), 22.1 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 258 [M+H$^+$]. Data consistent with literature values.[11]



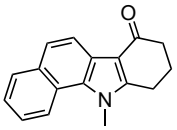
5-Benzyl-5,6,7,8-tetrahydro-9*H*-[1,3]dioxolo[4,5-*b*]carbazol-9-one, 20l



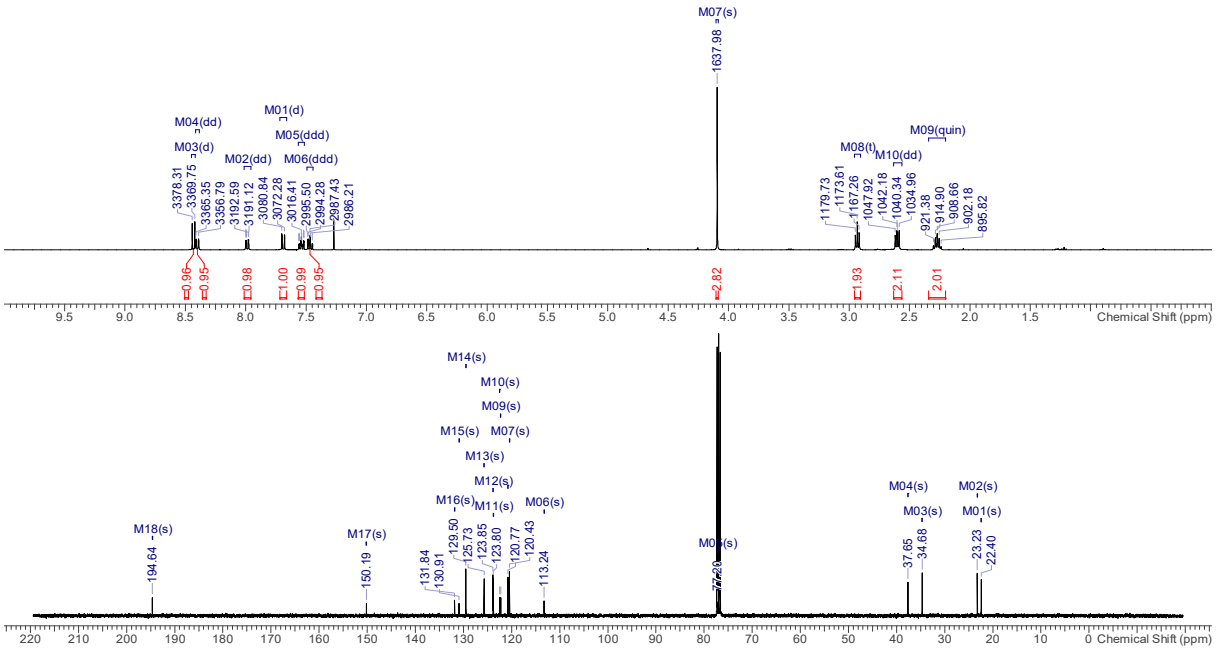
Using flow photochemical set-up B: A solution of enaminone **19l** (340 mg, 1.08 mmol) in MeCN (108 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **20l** (234 mg, 0.734 mmol, 68%) as an off-white solid. **MP**: 175 – 176 °C. **IR** ν_{max} (film, cm^{-1}): 2945 (br), 1617 (m), 1546 (s), 1491 (s), 1396 (m), 1323 (m), 1268 (m), 1189 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (1 H, d, *J* = 0.5 Hz, Ar**H**), 7.35 – 7.26 (3 H, m, 3 × Ar**H**), 7.05 – 7.00 (2 H, m, 2 × Ar**H**), 6.69 (1 H, d, *J* = 0.5 Hz, Ar**H**), 5.94 (2 H, s, C**H**$_2$), 5.23 (2 H, s, C**H**$_2$), 2.84 (2 H, app. t, *J* = 6.2 Hz, C**H**$_2$), 2.56 (2 H, dd, *J* = 7.3, 5.7 Hz, C**H**$_2$), 2.21 (2 H, app. quin, *J* = 6.5 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.9 (**C**), 150.0 (**C**), 145.4 (**C**), 144.8 (**C**), 135.8 (**C**), 132.0 (**C**), 129.1 (2 × **C**H), 127.9 (**C**H), 126.0 (2 × **C**H), 118.9 (**C**), 113.3 (**C**), 100.94 (**C**H$_2$), 100.92 (**C**H), 91.2 (**C**H), 47.2 (**C**H$_2$), 37.8 (**C**H$_2$), 23.4 (**C**H$_2$), 22.3 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 342 [M + Na]$^+$, 320 [M + H]$^+$. **HRMS** (ESI$^+$): Found 320.1284, $C_{20}H_{17}NO_3$ [M+H]$^+$ requires 320.1281.



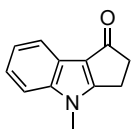
1-(1,2-Dimethyl-1*H*-benzo[*g*]indol-3-yl)ethan-1-one, 20m



Using flow photochemical set-up A: A solution of enaminone **19m** (330 mg, 1.33 mmol) in MeCN (133 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **20m** (181 mg, 0.727 mmol, 56%) as an off-white solid. **MP**: 201 – 202 °C. **IR** ν_{max} (film, cm^{-1}): 2935 (br), 1636 (s), 1528 (m), 1458 (m), 1417 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.43 (1 H, d, *J* = 8.6 Hz, Ar**H**), 8.40 (1 H, dd, *J* = 8.6, 0.7 Hz, Ar**H**), 7.99 (1 H, app. dd, *J* = 8.1, 1.5 Hz, Ar**H**), 7.69 (1 H, d, *J* = 8.6 Hz, Ar**H**), 7.54 (1 H, ddd, *J* = 8.4, 7.0, 1.5 Hz, Ar**H**), 7.47 (1 H, ddd, *J* = 8.1, 6.9, 1.2 Hz, Ar**H**), 4.09 (3 H, s, C**H**$_3$), 2.93 (2 H, t, *J* = app. 6.2 Hz, C**H**$_2$), 2.60 (2 H, dd, *J* = 7.4, 5.6 Hz, C**H**$_2$), 2.27 (2 H, app. quin, *J* = 6.4 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.6 (**C**), 150.2 (**C**), 131.8 (**C**), 130.9 (**C**), 129.5 (**C**H), 125.7 (**C**H), 123.9 (**C**H), 123.8 (**C**H), 122.5 (**C**), 122.3 (**C**), 120.8 (**C**H), 120.4 (**C**H), 113.2 (**C**), 37.7 (**C**H$_2$), 34.7 (**C**H$_3$), 23.2 (**C**H$_2$), 22.4 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 250 [M + H]$^+$. **HRMS** (ESI$^+$): Found 250.1233, $C_{17}H_{16}NO$ [M+H]$^+$ requires 250.1226.

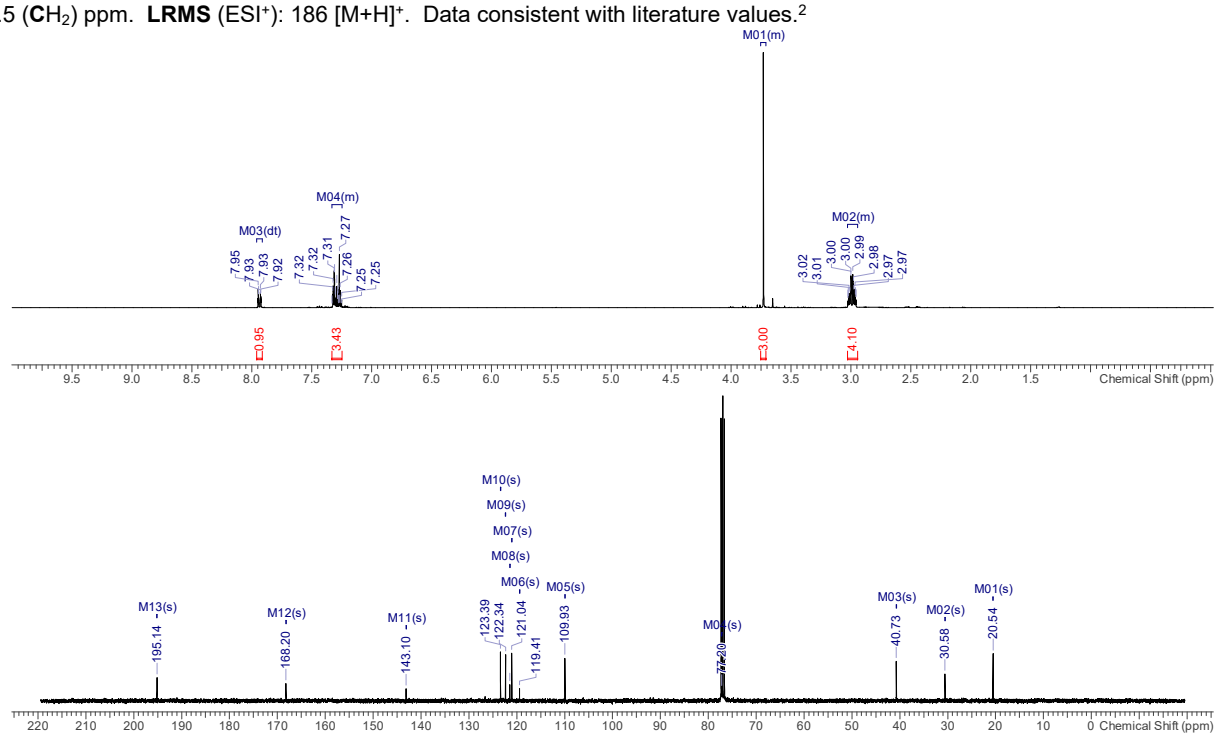


4-Methyl-3,4-dihydrocyclopenta[*b*]indol-1(2*H*)-one, 22a

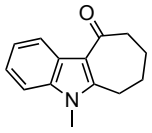


Using flow photochemical set-up B: A solution of enaminone **21a** (214 mg, 1.14 mmol) in MeCN (114 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 60W UVC lamp for a residence time of 2 hour. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **22a** (75 mg, 0.405 mmol, 35%) as a yellow solid. **MP** 211 – 212 °C (Et_2O/petrol), Lit.[2d] 214 – 216 °C. **IR** ν_{max} (film, cm^{-1}): 2922 (br), 1669 (s), 1476 (m), 1132 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (1 H, dt, *J* = 7.5,

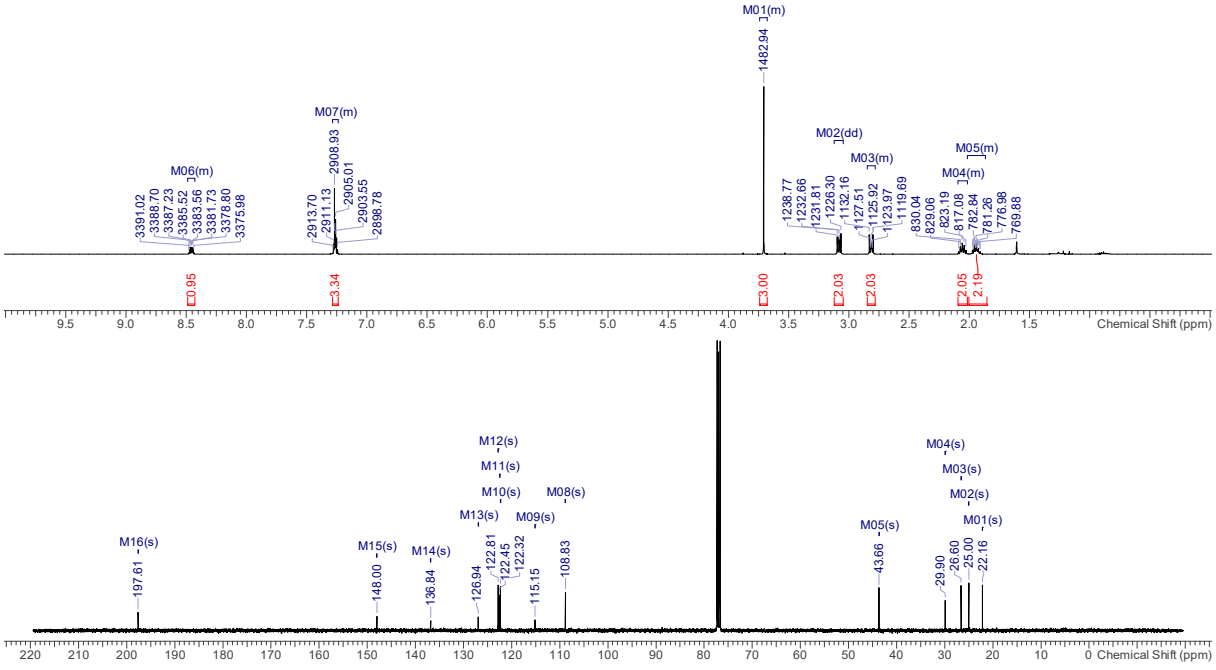
1.2 Hz, Ar**H**), 7.33 – 7.25 (3 H, m, 3 × Ar**H**), 3.74 (3 H, s, CH_3), 3.03 – 2.96 (4 H, m, 2 × CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.1 (**C**), 168.2 (**C**), 143.1 (**C**), 123.4 (**C**H), 122.3 (**C**H), 121.5 (**C**), 121.0 (**C**H), 119.4 (**C**), 109.9 (**C**H), 40.7 (CH_2), 30.6 (CH_3), 20.5 (CH_2) ppm. **LRMS** (ESI$^+$): 186 [M+H]$^+$. Data consistent with literature values.[2]



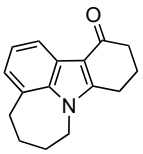
5-Methyl-6,7,8,9-tetrahydrocyclohepta[*b*]indol-10(5*H*)-one, 22b



Using flow photochemical set-up A: A solution of enaminone **21b** (310 mg, 1.44 mmol) and iodine (18 mg, 0.07 mmol, 5 mol%) in dry MeCN (72 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **22b** (170 mg, 0.798 mmol, 56%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2932 (br), 1697 (m), 1606 (s), 1470 (s), 1409 (s), 1127 (m), 1094 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (1 H, m, Ar**H**), 7.28 – 7.24 (3 H, m, 3 × Ar**H**), 3.71 (3 H, s, CH_3), 3.08 (2 H, app. dd, J = 7.0, 5.5 Hz, CH_2), 2.83 – 2.80 (2 H, m, CH_2), 2.09 – 2.03 (2 H, m, CH_2), 1.97 – 1.91 (2 H, m, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.6 (**C**), 148.0 (**C**), 136.8 (**C**), 126.9 (**C**), 122.8 (**C**H), 122.4 (**C**H), 122.3 (**C**H), 115.2 (**C**), 108.8 (**C**H), 43.7 (CH_3), 29.9 (CH_2), 26.6 (CH_2), 25.0 (CH_2), 22.2 (CH_2) ppm. **LRMS** (ESI$^+$): 214 [M+H]$^+$. **HRMS** (ESI$^+$): Found 214.1231, $C_{14}H_{16}NO$ [M+H]$^+$ requires 214.1226.

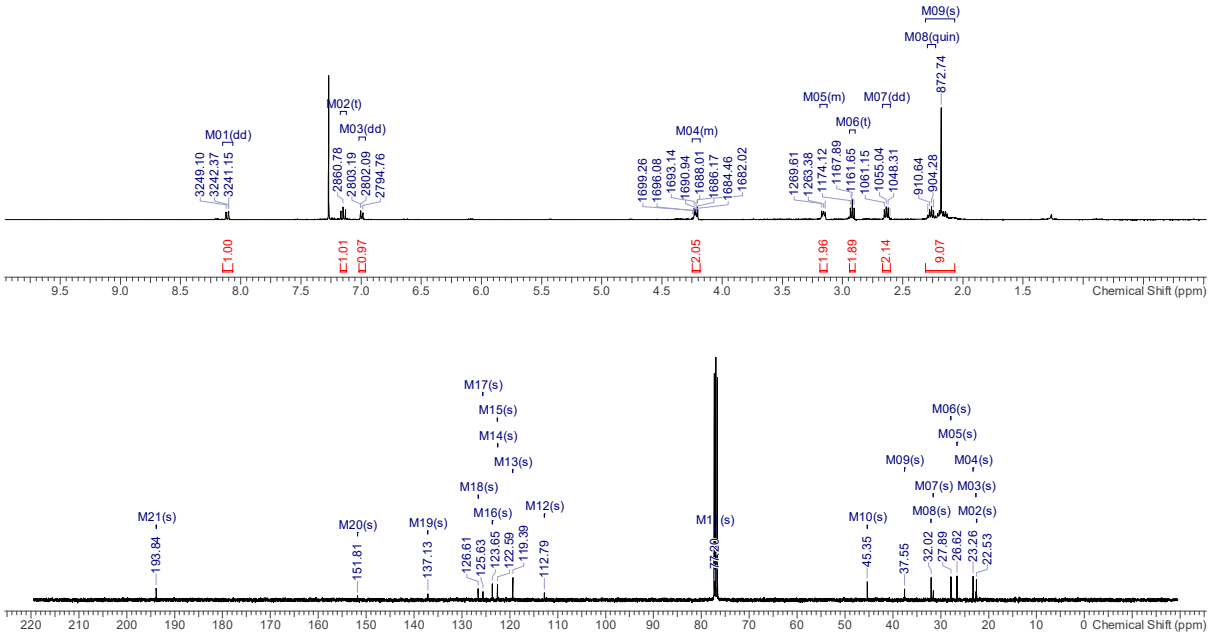


4,5,6,7,10,11-Hexahydroazepino[3,2,1-*jk*]carbazol-12(9*H*)-one, 22f

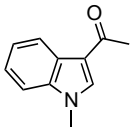


Using flow photochemical set-up B: A solution of enaminone **21f** (240 mg, 1.00 mmol) in MeCN (100 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 60W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol)

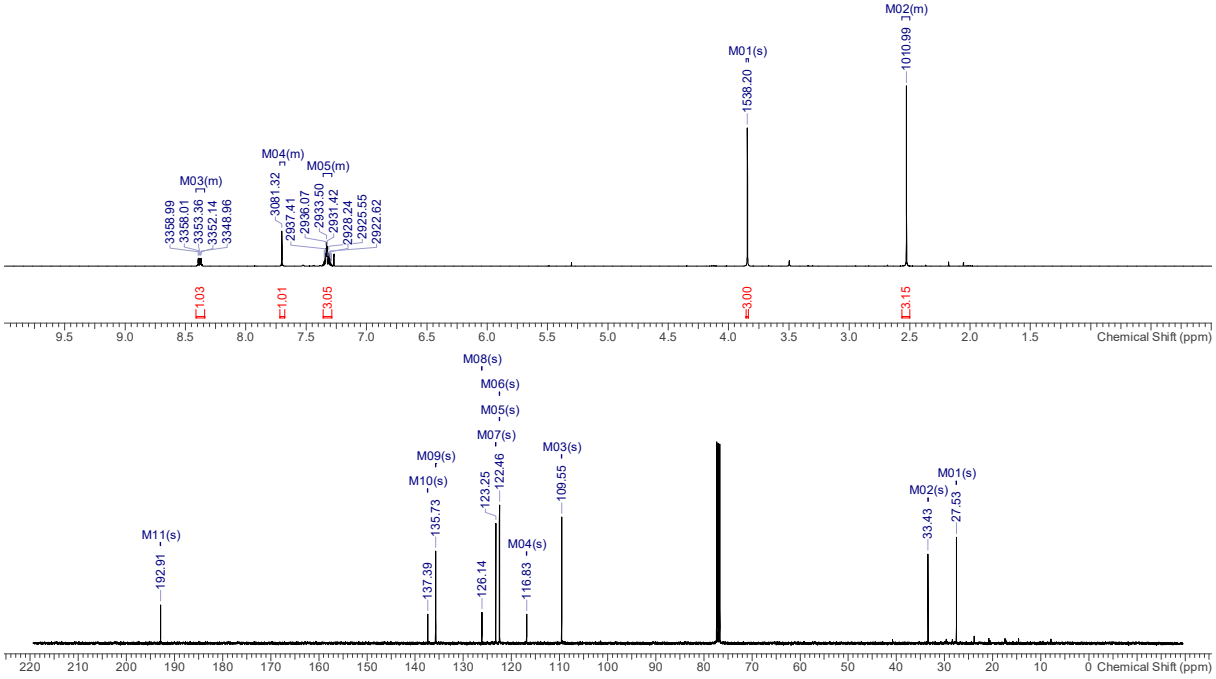
to afford the *title compound* **22f** (127 mg, 0.531 mmol, 53%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2932 (br), 1640 (s), 1455 (s), 1444 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (1 H, app. dd, *J* = 7.9, 1.2 Hz, Ar**H**), 7.15 (1 H, app. t, *J* = 7.4 Hz, Ar**H**), 6.99 (1 H, dd, *J* = 7.3, 1.1 Hz, Ar**H**), 4.23 – 4.20 (2 H, m, C**H**$_2$), 3.17 – 3.14 (2 H, m, C**H**$_2$), 2.92 (2 H, app. t, *J* = 6.2 Hz, C**H**$_2$), 2.64 (2 H, dd, *J* = 7.0, 5.9 Hz, C**H**$_2$), 2.26 (2 H, app. quin, *J* = 6.5 Hz, C**H**$_2$), 2.23 – 2.13 (4 H, m, 2 × C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8 (**C**), 151.8 (**C**), 137.1 (**C**), 126.6 (**C**), 125.6 (**C**), 123.7 (**C**H), 122.6 (**C**H), 119.4 (**C**H), 112.8 (**C**), 45.4 (**C**H$_2$), 37.6 (**C**H$_2$), 32.0 (**C**H$_2$), 27.9 (**C**H$_2$), 26.6 (**C**H$_2$), 23.3 (**C**H$_2$), 22.5 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 262 [M+Na]$^+$, 240 [M+H]$^+$. **HRMS** (ESI$^+$): Found 240.1381, $C_{16}H_{18}NO$ [M+H]$^+$ requires 240.1383.



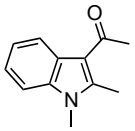
3-Acetyl-1-methylindole, 24a



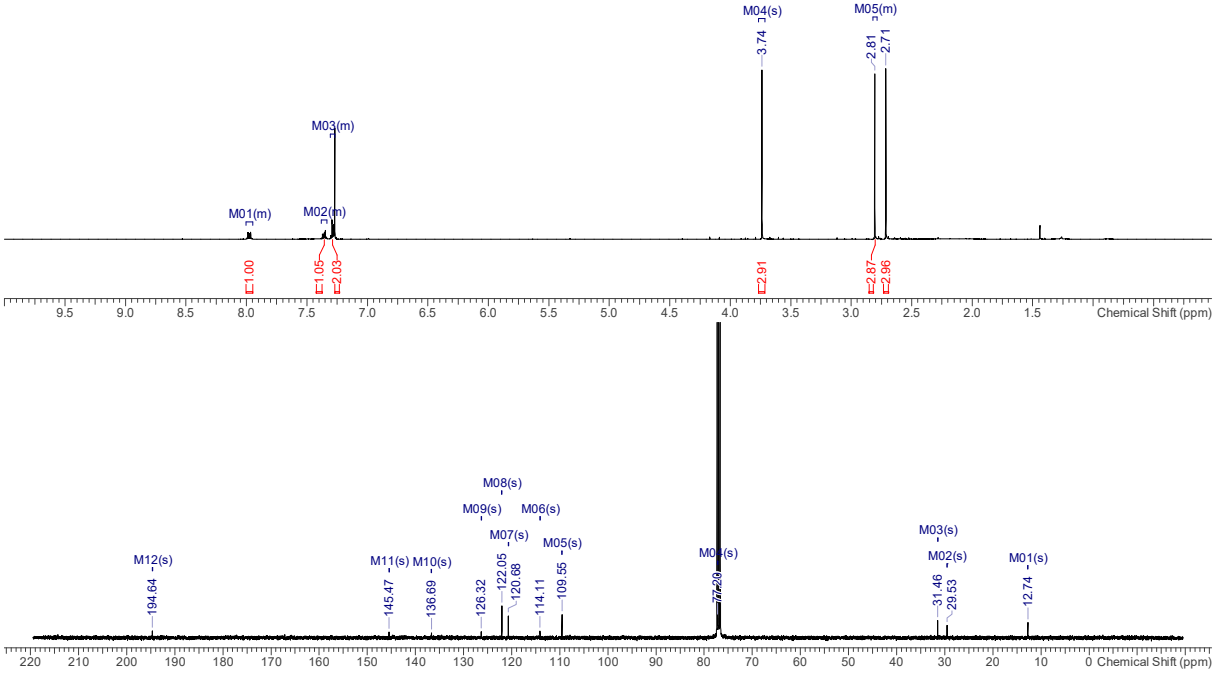
Using flow photochemical set-up A: A solution of enaminone **23a** (160 mg, 0.914 mmol) in MeCN (455 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **24a** (104 mg, 0.601 mmol, 66%) as a yellow solid. **MP** 104 – 104 °C (Et_2O/petrol), Lit.[12b] 108 – 109 °C (EtOH). **IR** ν_{max} (film, cm^{-1}): 2920 (br), 1636 (s), 1526 (s), 1463 (m), 1473 (s), 1372 (m), 1225 (m), 1100 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.41 – 8.36 (1 H, m, Ar**H**), 7.70 (1 H, s, C**H**), 7.35 – 7.29 (3 H, m, 3 × Ar**H**), 3.84 (3 H, s, C**H**$_3$), 2.53 (3 H, s, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.9 (**C**), 137.4 (**C**), 135.7 (**C**H), 126.1 (**C**), 123.3 (**C**H), 122.48 (**C**H), 121.46 (**C**H), 116.8 (**C**), 109.6 (**C**H), 33.4 (**C**H$_3$), 27.5 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 174 [M + H]$^+$. Data consistent with literature values.[12]



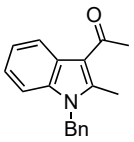
3-Acetyl-1,2-dimethylindole, 24b



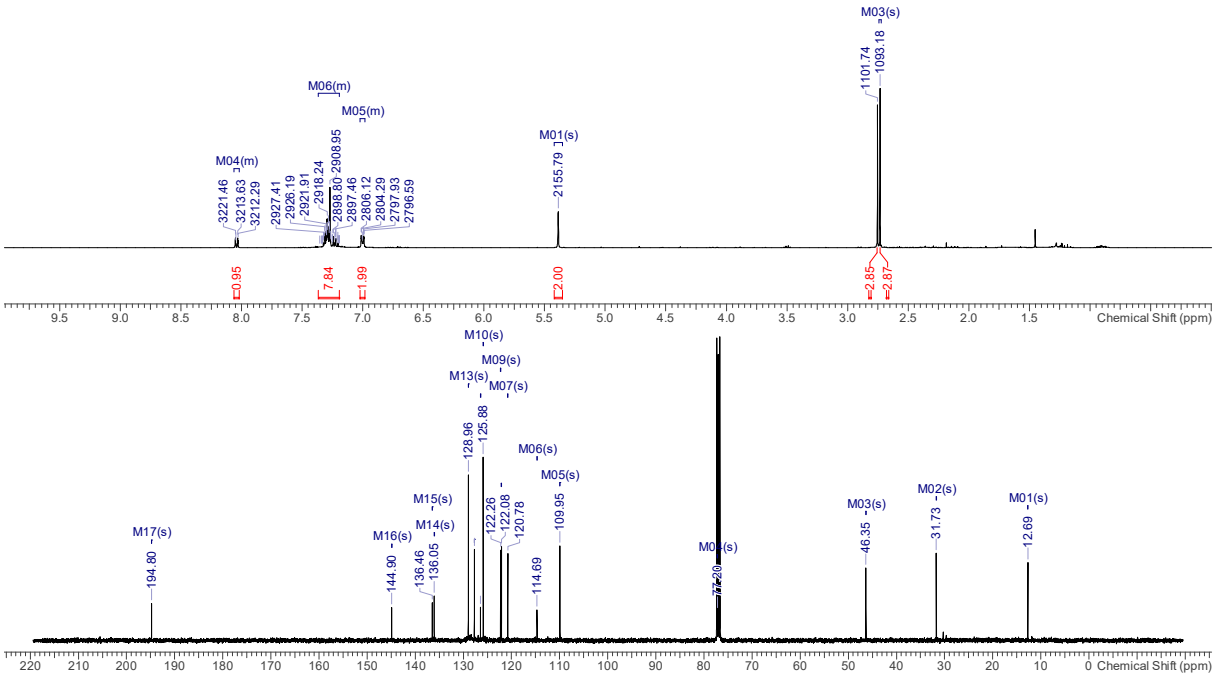
Using flow photochemical set-up A: A solution of enaminone **23b** (160 mg, 0.847 mmol) in MeCN (420 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the *title compound* **24b** (97 mg, 0.519 mmol, 61%) as a yellow solid. **MP** 108 – 109 °C (Et_2O/petrol), Lit.[12b] 113 – 114 °C (EtOH). **IR** ν_{max} (film, cm^{-1}): 2924 (br), 1634 (s), 1511 (m), 1400 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (1 H, m, Ar**H**), 7.36 (1 H, m, Ar**H**), 7.30 – 7.27 (2 H, m, 2 × Ar**H**), 3.74 (3 H, s, CH_3), 2.81 (3 H, s, CH_3), 2.71 (3 H, s, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.8 (**C**), 145.5 (**C**), 136.7 (**C**), 126.3 (**C**), 122.1 (2 × **C**H), 120.7 (**C**H), 114.1 (**C**), 109.6 (**C**H), 31.5 (**C**H_3), 29.5 (**C**H_3), 12.7 (**C**H_3) ppm. **LRMS** (ESI$^+$): 188 [M + H]$^+$. Data consistent with literature values.[12]



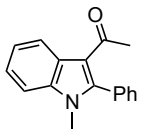
3-Acetyl-1-benzyl-2-methylindole, 24c



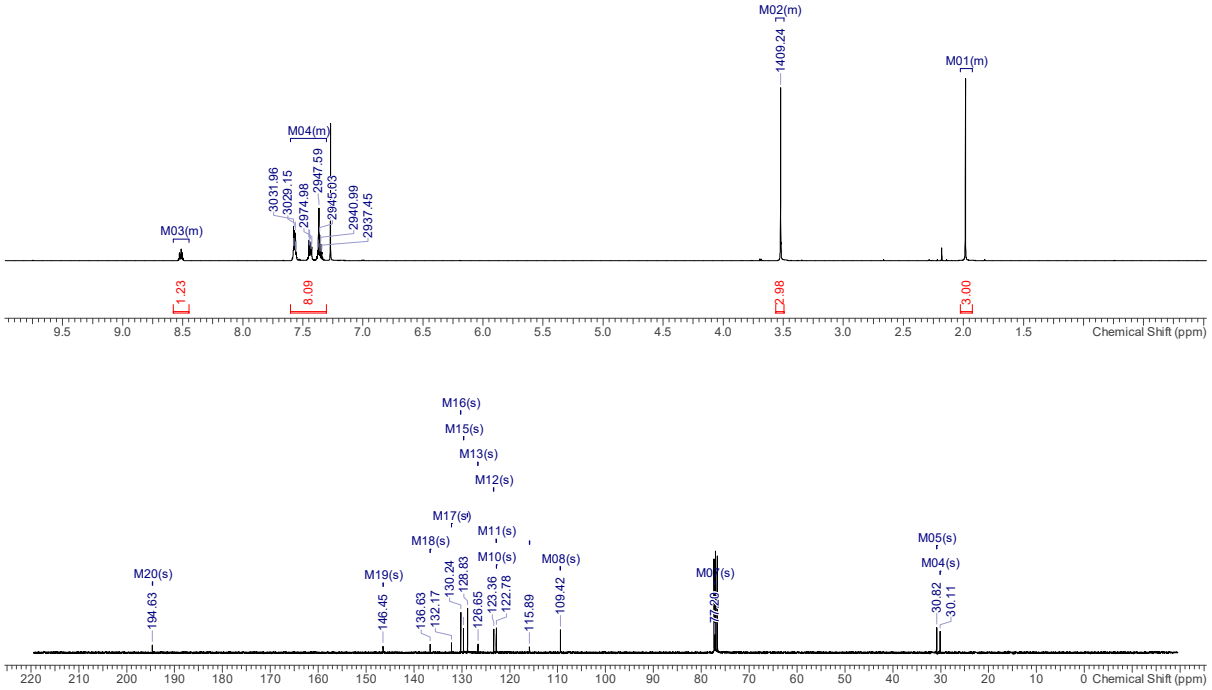
Using flow photochemical set-up A: A solution of enaminone **23c** (130 mg, 0.491 mmol) in MeCN (250 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **24c** (76 mg, 0.289 mmol, 58%) as a yellow solid. **MP** 100 – 101 °C (Et_2O/petrol), Lit.[13b] 107 – 109 °C (MeOH). **IR** ν_{max} (film, cm^{-1}): 2922 (br), 1636 (s), 1515 (m), 1454 (m), 1406 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (1 H, m, Ar**H**), 7.35 – 7.20 (6 H, m, 6 × Ar**H**), 7.02 – 6.98 (2 H, m, 2 × Ar**H**), 5.39 (2 H, s, CH_2), 2.75 (3 H, s, CH_3), 2.73 (3 H, s, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.8 (**C**), 144.9 (**C**), 136.5 (**C**), 136.1 (**C**), 129.0 (2 × **C**H), 127.7 (**C**H), 126.4 (**C**), 125.9 (2 × **C**H), 122.3 (**C**H), 122.1 (**C**H), 120.8 (**C**H), 114.7 (**C**), 110.0 (**C**H), 46.4 (**C**H_2), 31.7 (**C**H_3), 12.7 (**C**H_3) ppm. **LRMS** (ESI$^+$): 264 [M + H]$^+$. Data consistent with literature values.[13]



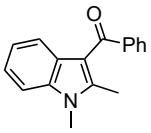
3-Acetyl-1-methyl-2-phenylindole, 24d



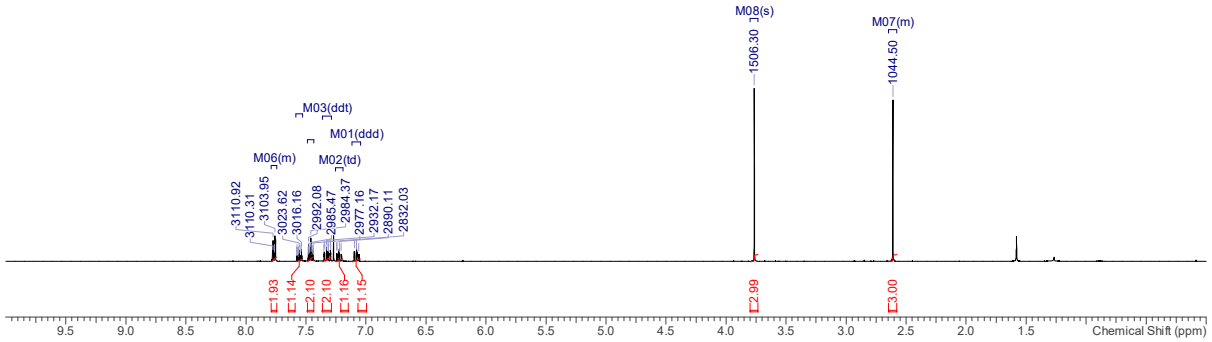
Using flow photochemical set-up A: A solution of enaminone **23d** (150 mg, 0.598 mmol) in MeCN (300 mL, 0.002 M) was irradiated with a 36W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (30 – 70% EtOAc in petrol) to afford the *title compound* **24d** (100 mg, 0.402 mmol, 67%) as an off-white oil. **IR** ν_{max} (film, cm^{-1}): 3054 (br), 2970 (w), 1635 (s), 1465 (s), 1394 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.51 (1 H, m, Ar**H**), 7.58 – 7.55 (3 H, m, 3 × Ar**H**), 7.45 – 7.43 (2 H, m, 2 × Ar**H**), 7.38 – 7.34 (3 H, m, 3 × Ar**H**), 3.52 (3 H, s, C**H**$_3$), 1.98 (3 H, s, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.6 (**C**), 146.5 (**C**), 136.6 (**C**), 132.2 (**C**), 130.2 (2 × **C**H), 129.7 (**C**H), 128.8 (2 × **C**H), 126.7 (**C**), 123.4 (**C**H), 122.81 (**C**H), 122.78 (**C**H), 115.9 (**C**), 109.4 (**C**H), 30.8 (**C**H$_3$), 30.1 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 272 [M + Na]$^+$, 250 [M + H]$^+$. Data consistent with literature values.[12]

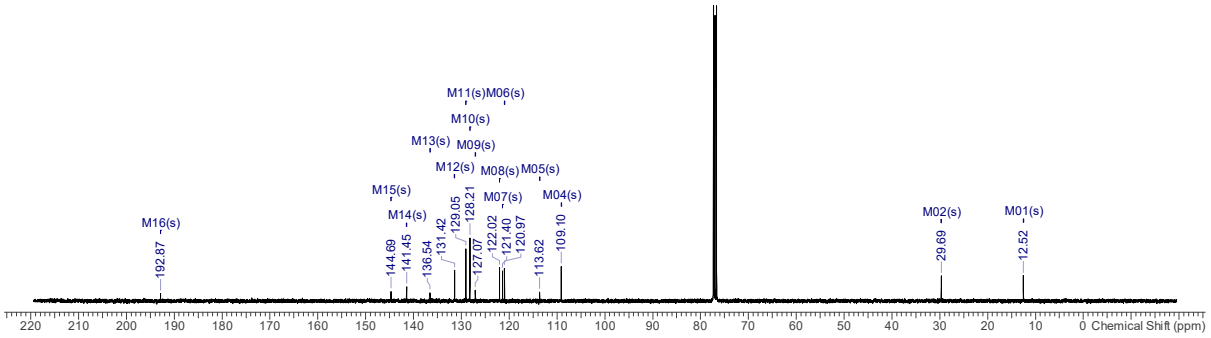


3-Benzoyl-1,2-dimethylindole, 24e

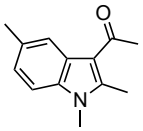


Using flow photochemical set-up A: A solution of **23e** (401 mg, 1.60 mmol) in MeCN (800 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 40 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (60 – 100% DCM/petrol) to afford the *title compound* **24e** (248 mg, 1.00 mmol, 63%) as an off-white solid. **IR** ν_{max} (film, cm^{-1}): 3056 (br), 1716 (s), 1597 (s), 1401 (s), 1228 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 – 7.75 (2 H, m, 2 × Ar**H**), 7.56 (1 H, m, Ar**H**), 7.48 – 7.44 (2 H, m, 2 × Ar**H**), 7.32 (2 H, m, 2 × Ar**H**), 7.22 (1 H, app. td, *J* = 7.6, 1.2 Hz, Ar**H**), 7.08 (1 H, ddd, *J* = 8.0, 7.1, 1.1 Hz, Ar**H**), 3.76 (3 H, s, C**H**$_3$), 2.61 (3 H, s, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.9 (**C**), 144.7 (**C**), 141.6 (**C**), 136.5 (**C**), 132.4 (**C**H), 129.1 (2 × **C**H), 128.2 (2 × **C**H), 127.1 (**C**), 122.0 (**C**H), 121.4 (**C**H), 121.0 (**C**H), 113.6 (**C**), 109.1 (**C**H), 29.7 (**C**H$_3$), 12.5 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 250 [M + H]$^+$. Data consistent with literature values.[14]

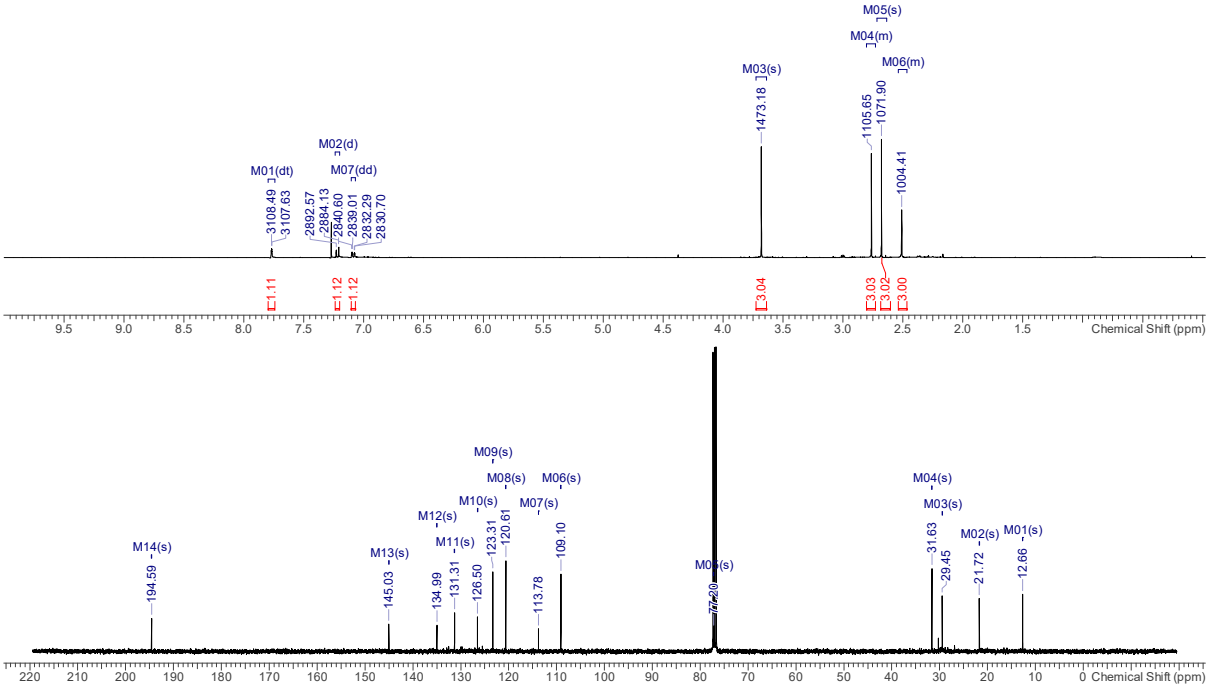




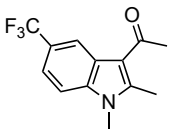
3-Acetyl-1,2,5-trimethylindole, 24f



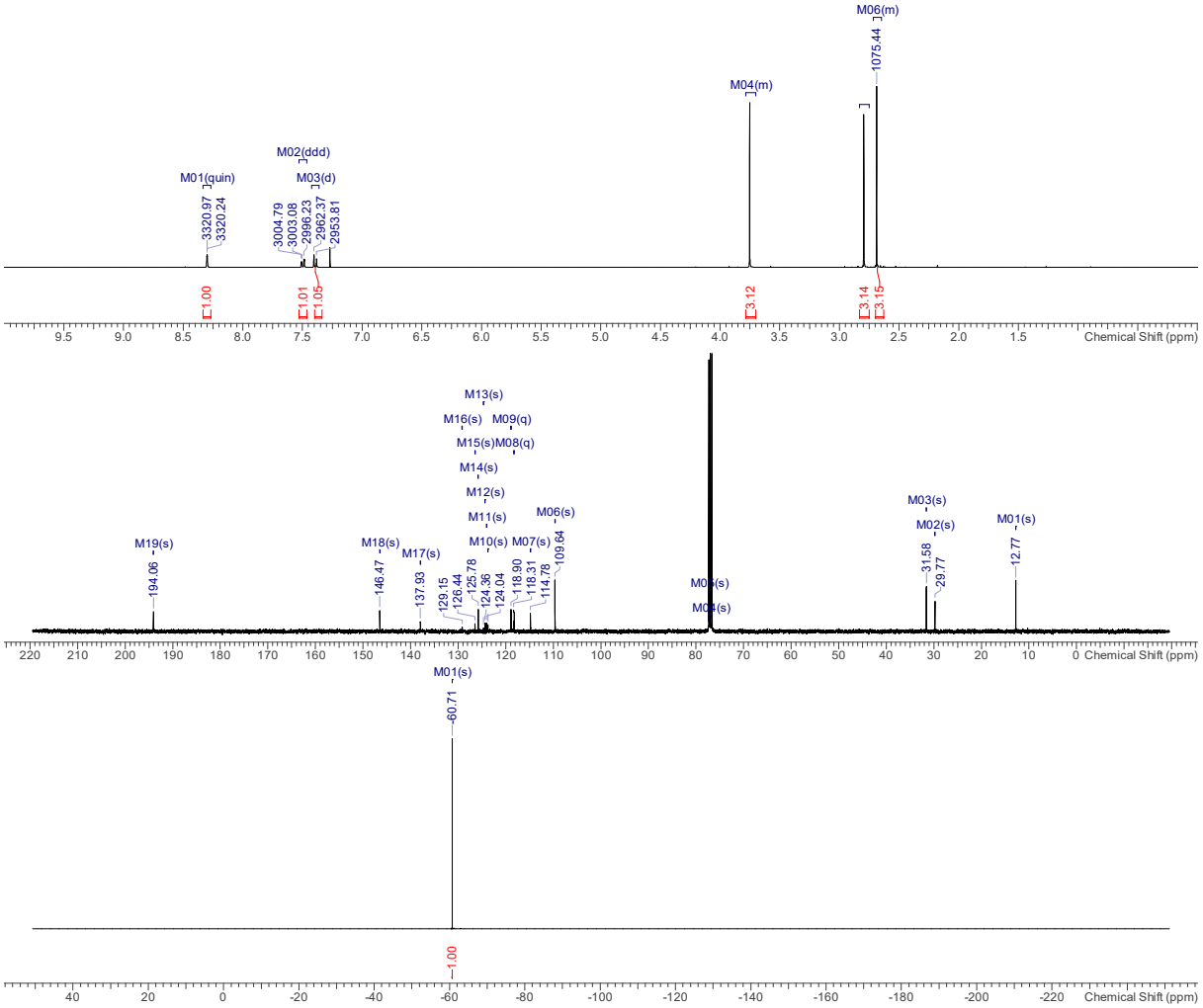
Using flow photochemical set-up A: A solution of the crude enaminone **23f** (195 mg, 0.961 mmol) in MeCN (480 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **24f** (122 mg, 0.607 mmol, 64%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2919 (br), 1635 (s), 1511 (m), 1487 (m), 1402 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (1 H, dt, *J* = 1.6, 0.8 Hz, Ar**H**), 7.22 (1 H, d, *J* = 8.4 Hz, Ar**H**), 7.09 (1 H, dd, *J* = 8.3, 1.6 Hz, Ar**H**), 3.68 (3 H, s, C$\mathbf{H}_3$), 2.76 (3 H, s, C$\mathbf{H}_3$), 2.68 (3 H, s, C$\mathbf{H}_3$), 2.51 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.6 (**C**), 145.0 (**C**), 135.0 (**C**), 131.3 (**C**), 126.5 (**C**), 123.3 (**C**H), 120.6 (**C**H), 113.8 (**C**), 109.1 (**C**H), 31.6 (**C**H_3), 29.5 (**C**H_3), 21.7 (**C**H_3), 12.7 (**C**H_3) ppm. **LRMS** (ESI^+): 202 $[M + H]^+$. Data consistent with literature values.[12]



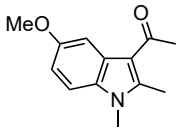
3-Acetyl-1,2-dimethyl-5-trifluoromethylindole, 24g



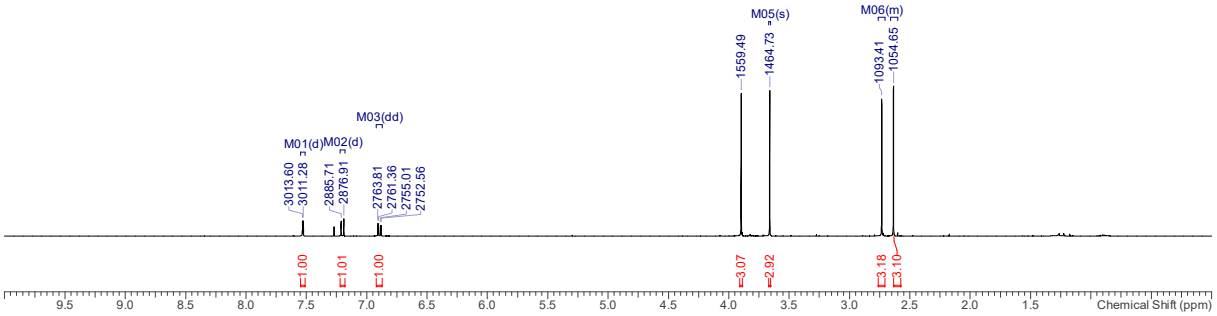
Using flow photochemical set-up A: A solution of the crude enaminone **23g** (171 mg, 0.665 mmol) in MeCN (335 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **24g** (80 mg, 0.314 mmol, 47%) as a yellow solid. **MP**: 141 – 142 °C. **IR** ν_{max} (film, cm^{-1}): 3081 (br), 1630 (s), 1326 (s), 1140 (s), 1103 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.30 (1 H, m, Ar**H**), 7.20 (1 H, ddd, *J* = 8.6, 1.7, 0.7 Hz, Ar**H**), 7.39 (1 H, br. d, *J* = 8.6 Hz, Ar**H**), 3.75 (3 H, s, C$\mathbf{H}_3$), 2.80 (3 H, s, C$\mathbf{H}_3$), 2.69 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.1 (**C**), 146.5 (**C**), 137.9 (**C**), 129.2 (**C**), 127.8 (**C**F_3, $J_{C\text{-}F}$ = 270 Hz), 125.8 (**C**), 124.2 (**C**, $J_{C\text{-}F}$ = 32.3 Hz), 118.9 (**C**H, $J_{C\text{-}F}$ = 3.2 Hz), 118.3 (**C**H, $J_{C\text{-}F}$ = 3.9 Hz), 109.6 (**C**H), 31.6 (**C**H_3), 29.8 (**C**H_3), 12.7 (**C**H_3) ppm. **^{19}F{H} NMR** (376 MHz, $CDCl_3$): –60.71 (3 F, s, C**F**$_3$) ppm. **LRMS** (ESI^+): 256 $[M + H]^+$. **HRMS** (ESI^+): Found 256.0948, $C_{13}H_{18}F_{13}NO$ $[M+H]^+$ requires 256.0944.

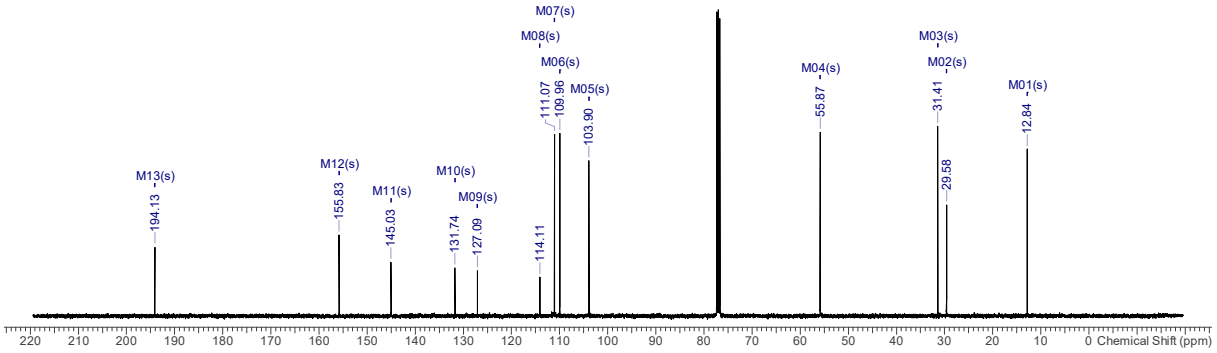


3-Acetyl-1,2-dimethyl-5-methoxyindole, 24h

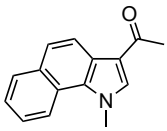


Using flow photochemical set-up A: A solution of the crude enaminone **23h** (187 mg, 0.854 mmol) in MeCN (427 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **24h** (113 mg, 0.521 mmol, 61%) as an off-white solid. **IR** ν_{max} (film, cm^{-1}): 2934 (br), 1629 (s), 1486 (s), 1404 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (1 H, d, *J* = 2.3 Hz, Ar**H**), 7.20 (1 H, d, *J* = 8.8 Hz, Ar**H**), 6.89 (1 H, dd, *J* = 8.8, 2.5 Hz, Ar**H**), 3.90 (3 H, s, CH_3), 3.66 (3 H, s, CH_3), 2.73 (3 H, s, CH_3), 2.64 (3 H, s, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.1 (**C**), 155.8 (**C**), 145.0 (**C**), 131.7 (**C**), 127.1 (**C**), 114.1 (**C**), 111.1 (**C**H), 110.0 (**C**H), 103.9 (**C**H), 55.9 (**C**H_3), 31.4 (**C**H_3), 29.6 (**C**H_3), 12.8 (**C**H_3) ppm. **LRMS** (ESI$^+$): 218 [M + H]$^+$. Data consistent with literature values.[15]

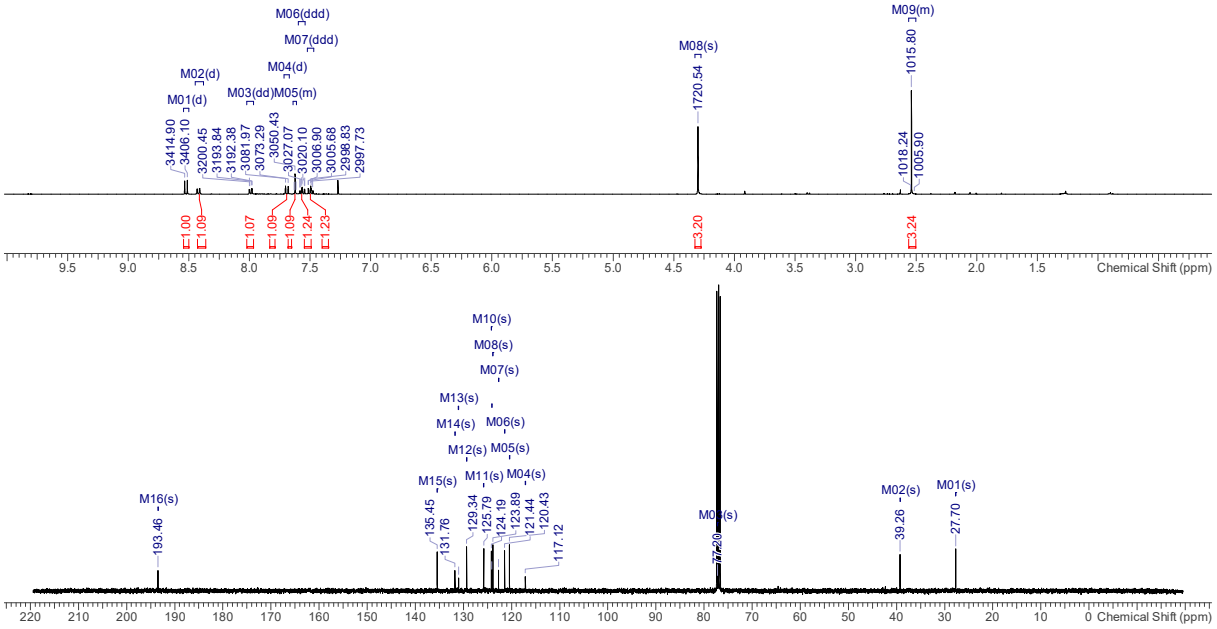




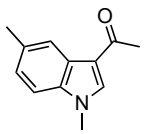
3-Acetyl-1-methyl-1*H*-benzo[*g*]indole, 24i



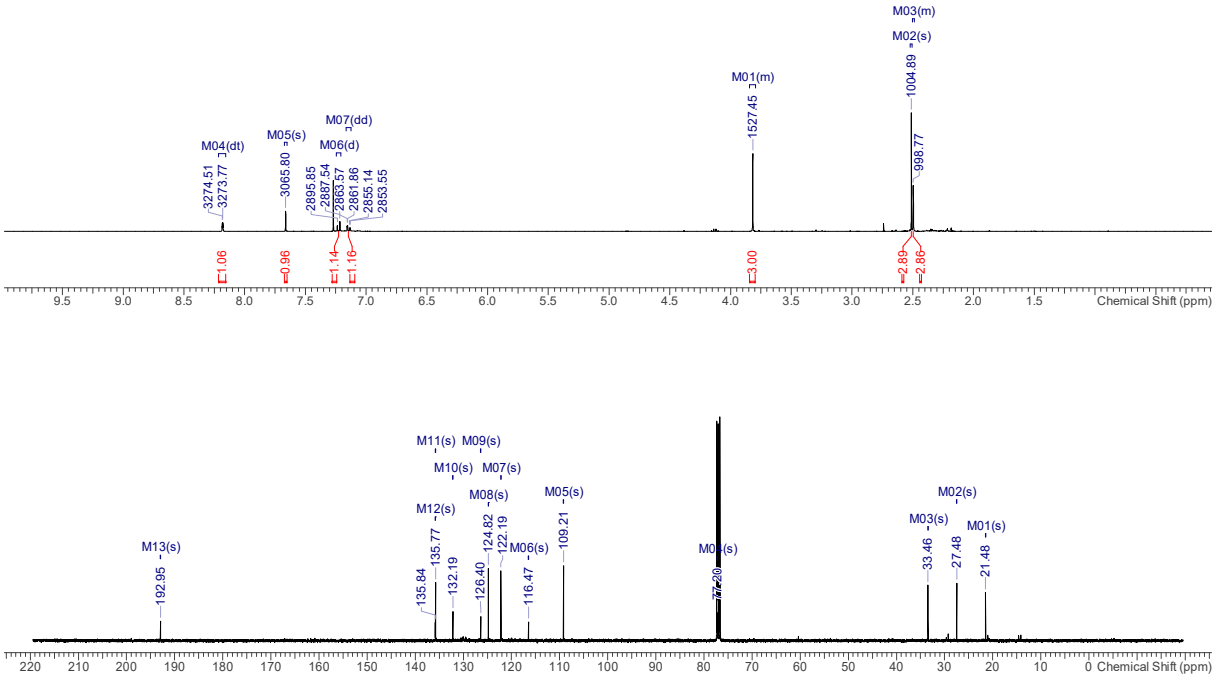
Using flow photochemical set-up A: A solution of the crude enaminone **23i** (298 mg, 1.32 mmol) in MeCN (662 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **24i** (203 mg, 0.910 mmol, 69%) as an off-white solid. **MP**: 161 °C (dec.). **IR** ν_{max} (film, cm^{-1}): 3109 (br), 1639 (s), 1533 (m), 1359 (m), 1126 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.52 (1 H, d, *J* = 8.8 Hz, Ar**H**), 8.42 (1 H, br d, *J* = 8.6 Hz, Ar**H**), 7.99 (1 H, app. dd, *J* = 8.0, 1.3 Hz, Ar**H**), 7.69 (1 H, d, *J* = 8.7 Hz, Ar**H**), 7.62 (1 H, s, C**H**), 7.57 (1 H, ddd, *J* = 8.4, 6.9, 1.5 Hz, Ar**H**), 7.49 (1 H, ddd, *J* = 8.1, 6.9, 1.2 Hz, Ar**H**), 4.30 (3 H, s, C$\mathbf{H}_3$), 2.54 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.5 (**C**), 134.5 (**C**H), 131.8 (**C**), 131.0 (**C**), 129.3 (**C**H), 125.8 (**C**H), 124.2 (**C**H), 124.1 (**C**), 123.9 (**C**H), 122.7 (**C**), 121.4 (**C**H), 120.4 (**C**H), 117.1 (**C**), 39.3 (**C**H_3), 27.7 (**C**H_3) ppm. **LRMS** (ESI$^+$): 224 [M + H]$^+$. **HRMS** (ESI$^+$): Found 224.1072, $C_{16}H_{16}NO$ [M+H]$^+$ requires 224.1070.



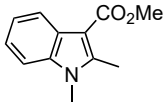
3-Acetyl-1,5-dimethylindole, 24j



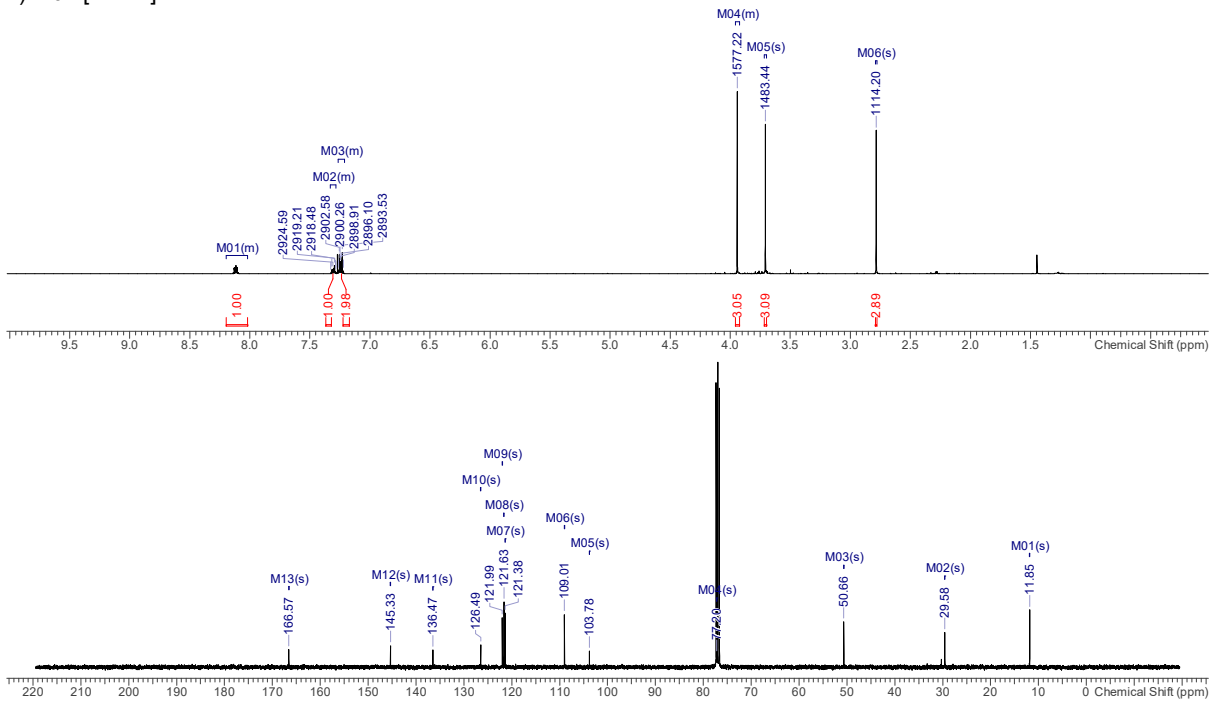
Using flow photochemical set-up A: A solution of the crude enaminone **23j** (170 mg, 0.899 mmol) in MeCN (900 mL, 0.001 M) was irradiated with a 60W UVC lamp for a residence time of 60 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% Et_2O in petrol) to afford the *title compound* **24j** (130 mg, 0.695 mmol, 78%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2944 (br), 1635 (s), 1466 (s), 1388 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (1 H, app. br d, *J* = 1.6, Ar**H**), 7.66 (1 H, s, C**H**), 7.23 (1 H, d, *J* = 8.3 Hz, Ar**H**), 7.14 (1 H, d, *J* = 8.3, 1.7 Hz, Ar**H**), 3.82 (3 H, s, C$\mathbf{H}_3$), 2.51 (3 H, s, C$\mathbf{H}_3$), 2.50 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.0 (**C**), 135.84 (**C**), 135.77 (**C**H), 132.2 (**C**), 126.4 (**C**), 124.8 (**C**H), 122.2 (**C**H), 116.5 (**C**), 109.2 (**C**H), 33.5 (**C**H_3), 27.5 (**C**H_3), 21.5 (**C**H_3) ppm. **LRMS** (ESI$^+$): 188 [M + H]$^+$. Data consistent with literature values.[12]



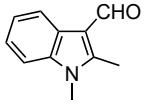
Methyl 1,2-dimethyl-1*H*-indole-3-carboxylate, 24k



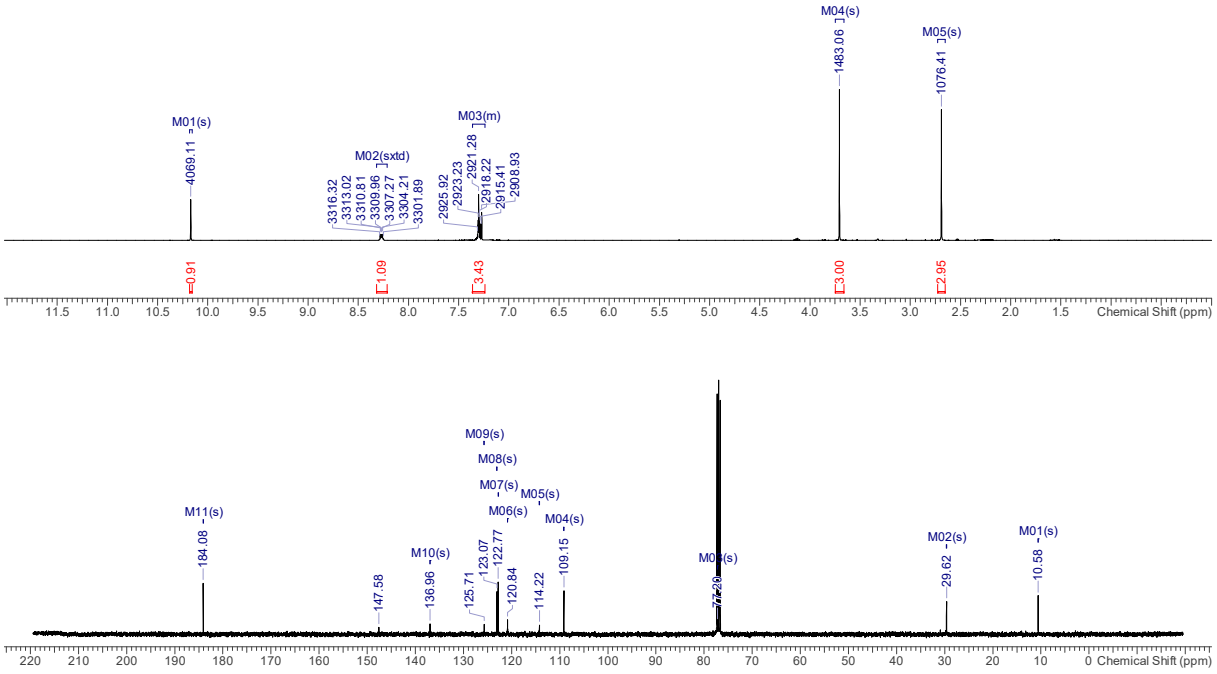
Using flow photochemical set-up A: A solution of the crude ester **27k** (217 mg, ~1.00 mmol) in MeCN (500 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the *title compound* **28k** (99 mg, 0.488 mmol, 46%, over 2 steps) as an off-white solid. **IR** ν_{max} (film, cm^{-1}): 2948 (br), 1689 (s), 1533 (m), 1437 (m), 1213 (s), 1159 (m), 1104 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (1 H, m, Ar**H**), 7.31 (1 H, m, C**H**), 7.26 – 7.22 (2 H, m, 2 × Ar**H**), 3.94 (3 H, s, C$\mathbf{H}_3$), 3.71 (3 H, s, C$\mathbf{H}_3$), 2.78 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6 (**C**), 145.3 (**C**), 136.5 (**C**), 126.5 (**C**), 122.0 (**C**H), 121.6 (**C**H), 121.4 (**C**H), 109.0 (**C**H), 103.8 (**C**), 50.7 (**C**H_3), 29.6 (**C**H_3), 11.9 (**C**H_3) ppm. **LRMS** (ESI$^+$): 204 [M + H]$^+$. Data consistent with literature values.[2]



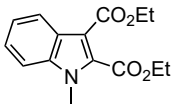
3-Formyl-1,2-dimethylindole, 24l



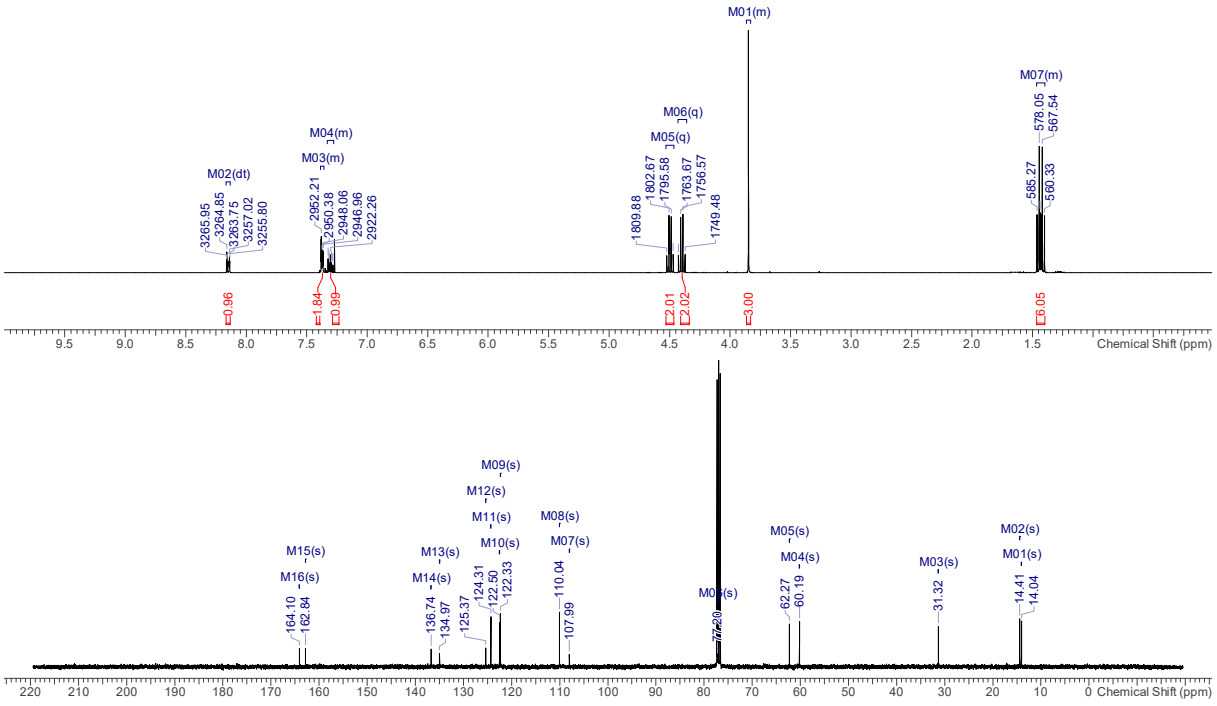
Using flow photochemical set-up A: A solution of enaminal **23l** (201 mg, 1.15 mmol) in MeCN (574 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (40 – 70% EtOAc in petrol) to afford the *title compound* **24l** (118 mg, 0.682 mmol, 59%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2965 (br), 1745 (m), 1648 (s), 1325 (s), 1035 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.17 (1 H, s, C**H**), 8.27 (1 H, m, Ar**H**), 7.31 – 7.28 (3 H, m, 3 × Ar**H**), 3.71 (3 H, s, C$\mathbf{H}_3$), 2.69 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 184.1 (**C**H), 147.6 (**C**), 137.0 (**C**H), 125.7 (**C**), 123.1 (**C**H), 122.8 (**C**H), 120.8 (**C**), 114.2 (**C**), 109.2 (**C**H), 29.6 (**C**H_3), 10.6 (**C**H_3) ppm. **LRMS** (ESI$^+$): 174 [M + H]$^+$. Data consistent with literature values.[16]



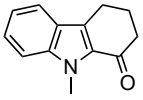
Dimethyl 1-methyl-1*H*-indole-2,3-dicarboxylate, 24m



Using flow photochemical set-up A: A solution of diester **23m** (97 mg, 0.411 mmol) and acetic acid (10 drops) in MeCN (250 mL, 0.002 M) was with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the *title compound* **24m** (71 mg, 0.258 mmol, 63%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2981 (br), 1699 (s), 1531 (m), 1243 (s), 1209 (s), 1103 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (1 H, dt, *J* = 7.9, 1.1 Hz, Ar**H**), 7.38 – 7.36 (2 H, m, 2 × Ar**H**), 7.30 (1 H, m, Ar**H**), 4.50 (2 H, q, *J* = 7.1 Hz, C**H**$_2$), 4.40 (2 H, q, *J* = 7.1 Hz, C**H**$_2$), 3.85 (3 H, s, C**H**$_3$), 1.44 (3 H, t, *J* = 7.2 Hz, C**H**$_3$), 1.42 (3 H, t, *J* = 7.2 Hz, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.1 (**C**), 162.8 (**C**), 136.7 (**C**), 135.0 (**C**), 125.4 (**C**), 124.3 (**C**H), 122.5 (**C**H), 122.3 (**C**H), 110.0 (**C**H), 108.0 (**C**), 62.3 (**C**H$_2$), 60.2 (**C**H$_2$), 31.3 (**C**H$_3$), 14.4 (**C**H$_3$), 14.0 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 298 [M + Na]$^+$, 276 [M + H]$^+$. Data consistent with literature values.[17]

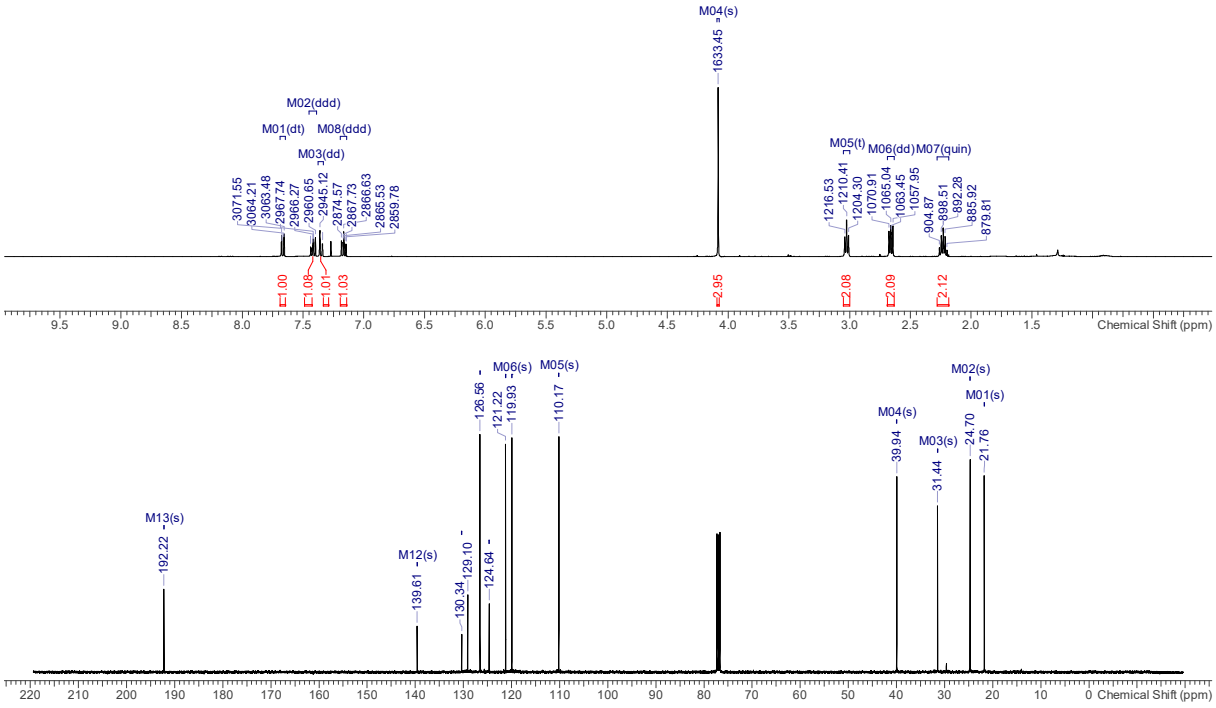


9-Methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one, 28a

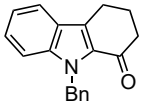


Using flow photochemical set-up A: A solution of enaminone **27a** (262 mg, 1.32 mmol) and iodine (16.3 mg, 0.066 mmol, 5 mol%) in dry MeCN (262 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **30a** (186 mg, 0.935 mmol, 71%) as an off-white solid. **MP** 95 – 96 °C (EtOAc/petrol), Lit.[18] 95 – 97 °C. **IR** ν_{max} (film, cm^{-1}): 2927 (br), 1648 (s), 1470 (m), 1430 (m), 1410 (m), 1231 (m),

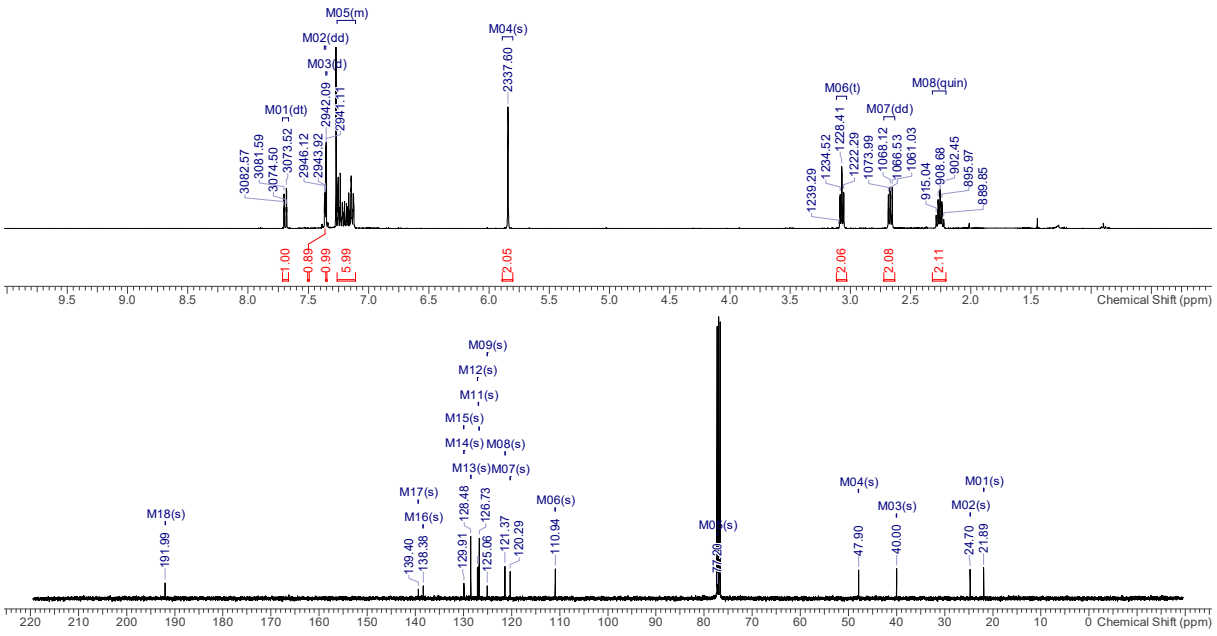
1186 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (1 H, dt, *J* = 8.1, 0.9 Hz, Ar**H**), 7.42 (1 H, ddd, *J* = 8.6, 6.7, 1.1 Hz, Ar**H**), 7.35 (1 H, dd, *J* = 8.4, 0.5 Hz, Ar**H**), 7.35 (1 H, ddd, *J* = 8.0, 6.9, 1.1 Hz, Ar**H**), 4.08 (3 H, s, C**H**$_3$), 3.03 (2 H, app. t, *J* = 6.1 Hz, C**H**$_2$), 2.66 (2 H, dd, *J* = 7.3, 5.7 Hz, C**H**$_2$), 2.23 (2 H, app. quin, *J* = 6.5 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.2 (**C**), 139.6 (**C**), 130.3 (**C**), 129.1 (**C**), 126.6 (**C**H), 124.6 (**C**), 121.2 (**C**H), 119.9 (**C**H), 110.2 (**C**H), 39.9 (**C**H$_2$), 31.4 (**C**H$_3$), 24.7 (**C**H$_2$), 21.8 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 200 [M + H]$^+$. Data consistent with literature values.[18]



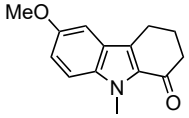
9-Benzyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one, 28b



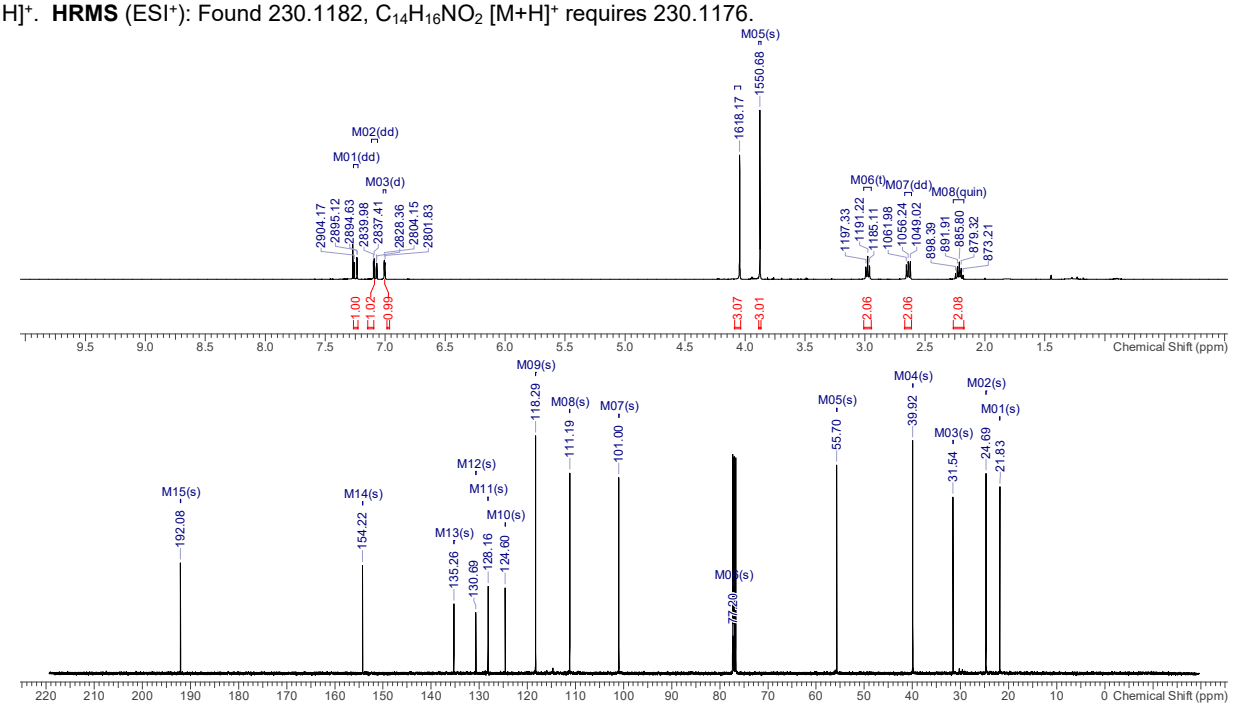
Using flow photochemical set-up A: A solution of enaminone **27b** (96 mg, 0.391 mmol) and iodine (5 mg, 0.02 mmol, 5 mol%) in dry MeCN (78 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **28b** (71 mg, 0.289 mmol, 73%) as a yellow solid. **MP** 107 – 108 °C (EtOAc/petrol), Lit.[19] 108 – 109 °C. **IR** ν_{max} (film, cm^{-1}): 2929 (br), 1652 (s), 1453 (m), 1262 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (1 H, dd, *J* = 8.1, 1.0 Hz, Ar**H**), 7.40 – 7.35 (2 H, m, 2 × Ar**H**), 7.27 – 7.12 (6 H, m, 6 × Ar**H**), 5.84 (2 H, s, C**H**$_2$), 3.07 (2 H, app. t, *J* = 6.1 Hz, C**H**$_2$), 2.67 (2 H, dd, *J* = 7.3, 5.7 Hz, C**H**$_2$), 2.26 (2 H, app. quin, *J* = 6.3 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.0 (**C**), 139.4 (**C**), 138.4 (**C**), 130.0 (**C**), 129.1 (**C**), 128.5 (2 × **C**H), 127.1 (**C**H), 126.9 (**C**H), 126.7 (2 × **C**H), 125.1 (**C**), 121.4 (**C**H), 120.3 (**C**H), 110.9 (**C**H), 47.9 (**C**H$_2$), 40.0 (**C**H$_2$), 24.7 (**C**H$_2$), 21.9 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 246 [M + H]$^+$. Data consistent with literature values.[19]



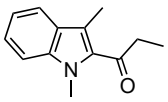
6-Methoxy-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one, 28c



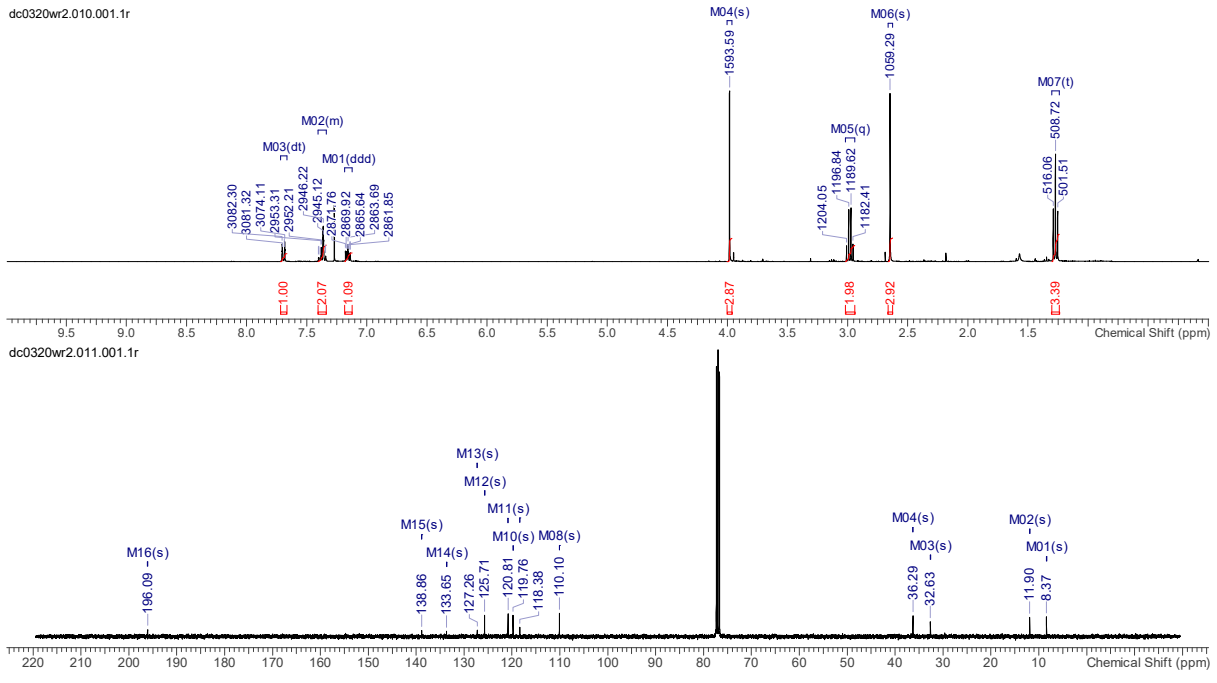
Using flow photochemical set-up A: A solution of enaminone **27c** (296 mg, 1.28 mmol) and iodine (16.3 mg, 0.06 mmol, 5 mol%) in dry MeCN (64 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the *title compound* **28c** (200 mg, 0.873 mmol, 66%) as a yellow solid. **MP**: 153 –154 °C. **IR** ν_{max} (film, cm^{-1}): 2938 (br), 1647 (s), 1493 (s), 1206 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25 (1 H, dd, *J* = 9.1, 0.5 Hz, Ar**H**), 7.08 (1 H, dd, *J* = 9.1, 2.5 Hz, Ar**H**), 7.01 (1 H, br. d, *J* = 2.3 Hz, Ar**H**), 4.04 (3 H, s, C**H**$_3$), 3.88 (3 H, s, C**H**$_3$), 2.98 (2 H, app. t, *J* = 6.1 Hz, C**H**$_2$), 2.64 (2 H, dd, *J* = 7.4, 5.6 Hz, C**H**$_2$), 2.21 (2 H, app. quin, *J* = 6.5 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.1 (**C**), 154.2 (**C**), 135.3 (**C**), 130.7 (**C**), 128.2 (**C**), 124.6 (**C**), 118.3 (**C**H), 111.2 (**C**H), 101.0 (**C**H), 55.7 (**C**H$_3$), 39.9 (**C**H$_2$), 31.5 (**C**H$_3$), 24.7 (**C**H$_2$), 21.8 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 230 [M + H]$^+$. **HRMS** (ESI$^+$): Found 230.1182, $C_{14}H_{16}NO_2$ [M+H]$^+$ requires 230.1176.



1,3-Dimethyl-2-(1-oxo-propyl)indole, 28d

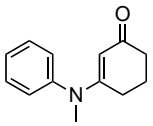


Using flow photochemical set-up A: A solution of enaminone **27d** (200 mg, 1.00 mmol) in MeCN (500 mL) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated *in vacuo* and purified by column chromatography (5 – 40% EtOAc in hexanes) to afford the *title compound* **28d** as a yellow solid (79 mg, 0.393 mmol, 39%). **MP** 110 – 111 °C (EtOAc/hexane), Lit.[20] 113 – 114 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (1H, dt, *J* = 8.2, 0.9 Hz, Ar**H**), 7.41 – 7.34 (2H, m, 2 x Ar**H**), 7.16 (1H, ddd, *J* = 8.0, 6.1, 1.8 Hz, Ar**H**), 3.98 (3H, s, C**H**$_3$), 2.98 (2H, q, *J* = 7.2 Hz, C**H**$_2$), 2.65 (3H, s, C**H**$_3$), 1.27 (3H, t, *J* = 7.3 Hz, C**H**$_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.1 (**C**), 138.9 (**C**), 133.7 (**C**), 127.3 (**C**), 125.7 (**C**H), 120.8 (**C**H), 119.8 (**C**H), 118.4 (**C**), 110.1 (**C**H), 36.3 (**C**H$_2$), 32.6 (**C**H$_3$), 11.9 (**C**H$_3$), 8.4 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 202 [M+H]$^+$. Data consistent with literature values.[20]

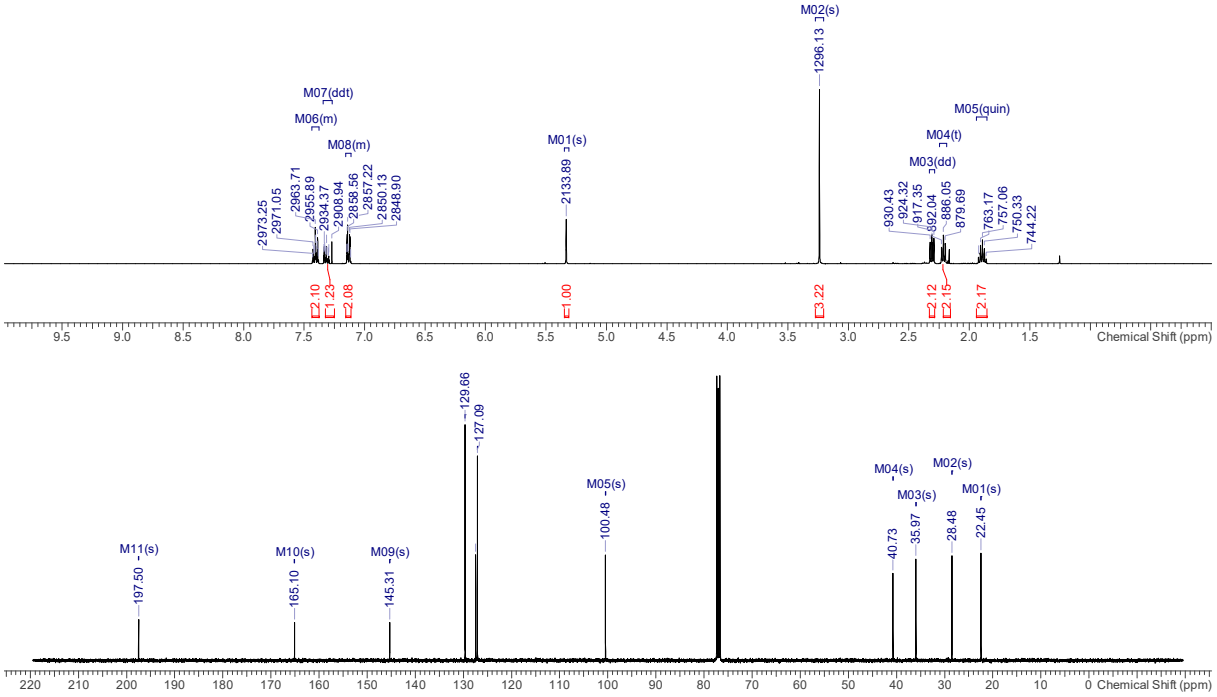


4. Preparation of Starting Materials

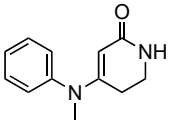
3-(Methyl(phenyl)amino)cyclohex-2-en-1-one, 5a



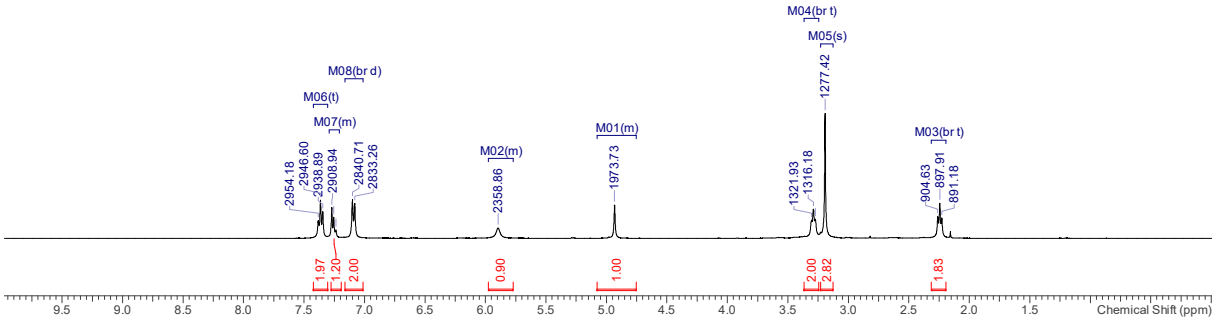
N-methylaniline (3.42 g, 32.0 mmol), 1,3-cyclohexanedione **12** (3.58 g, 32.0 mmol) and *p*TSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 20% acetone/DCM) to afford the *title compound* **5a** (5.15 g, 25.6 mmol, 80%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2939 (br), 1609 (s), 1549 (s), 1489 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 – 7.38 (2 H, m, 2 × Ar**H**), 7.32 (1 H, ddt, *J* = 8.2, 6.6, 1.2 Hz, Ar**H**), 7.15 – 7.11 (2 H, m, 2 × Ar**H**), 5.33 (1 H, s, C**H**), 3.24 (3 H, s, C$\mathbf{H}_3$), 2.31 (2 H, d, *J* = 7.1, 6.0 Hz, C$\mathbf{H}_2$), 2.21 (2 H, app. t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 1.89 (2 H, app. quin, *J* = 6.5 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.5 (**C**), 165.1 (**C**), 145.3 (**C**), 129.7 (2 × **C**H), 122.4 (**C**H), 127.1 (2 × **C**H), 100.5 (**C**H), 40.7 (**C**H_2), 36.0 (**C**H_3), 28.5 (**C**H_2), 22.5 (**C**H_2) ppm. **LRMS** (ESI$^+$): 202 [M+H]$^+$. Data consistent with literature values.[21]

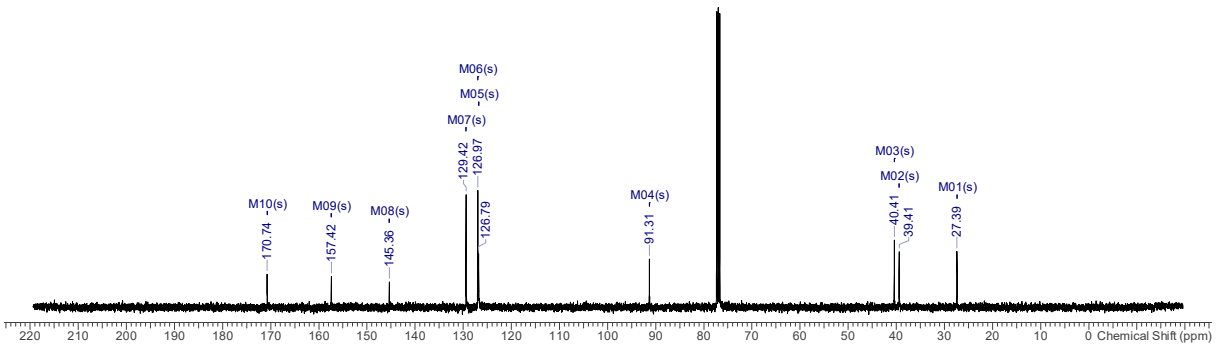


4-(Methyl(phenyl)amino)-5,6-dihydropyridin-2(1*H*)-one, 16

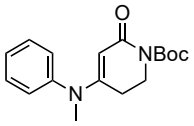


N-methylaniline (1.00 mL, 9.23 mmol), piperidine-2,4-dione (1.02 g, 9.01 mmol) and *p*TSA (30 mg, 0.174 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (5 – 15% acetone/DCM) to afford the *title compound* **16** (1.47 g, 7.27 mmol, 81%) as a yellow solid. **MP**: 156 – 157 °C. **IR** ν_{max} (film, cm^{-1}): 3174 (br), 2950 (br), 1628 (s), 1568 (s), 1475 (m), 1387 (m), 1136 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (2 H, t, *J* = 7.6 Hz, 2 × Ar**H**), 7.26 (1 H, m, Ar**H**), 7.09 (2 H, br d, *J* = 7.5 Hz, 2 × Ar**H**), 5.90 (1 H, br. s, N**H**), 4.93 (1 H, br s, C**H**), 3.29 (2 H, br. t, *J* = 5.9 Hz, C$\mathbf{H}_2$), 3.19 (3 H, s, C$\mathbf{H}_3$), 2.24 (2 H, br. t, *J* = 6.7 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.7 (**C**), 157.4 (**C**), 145.4 (**C**), 129.4 (2 × **C**H), 127.0 (2 × **C**H), 126.8 (**C**H), 91.3 (**C**H), 40.4 (**C**H_3), 39.4 (**C**H_2), 27.4 (**C**H_2) ppm. **LRMS** (ESI$^+$): 405 [2M+H]$^+$, 203 [M+H]$^+$. **HRMS** (ESI$^+$): Found 203.1180, $C_{12}H_{15}N_2O$ [M+H]$^+$ requires 203.1179.

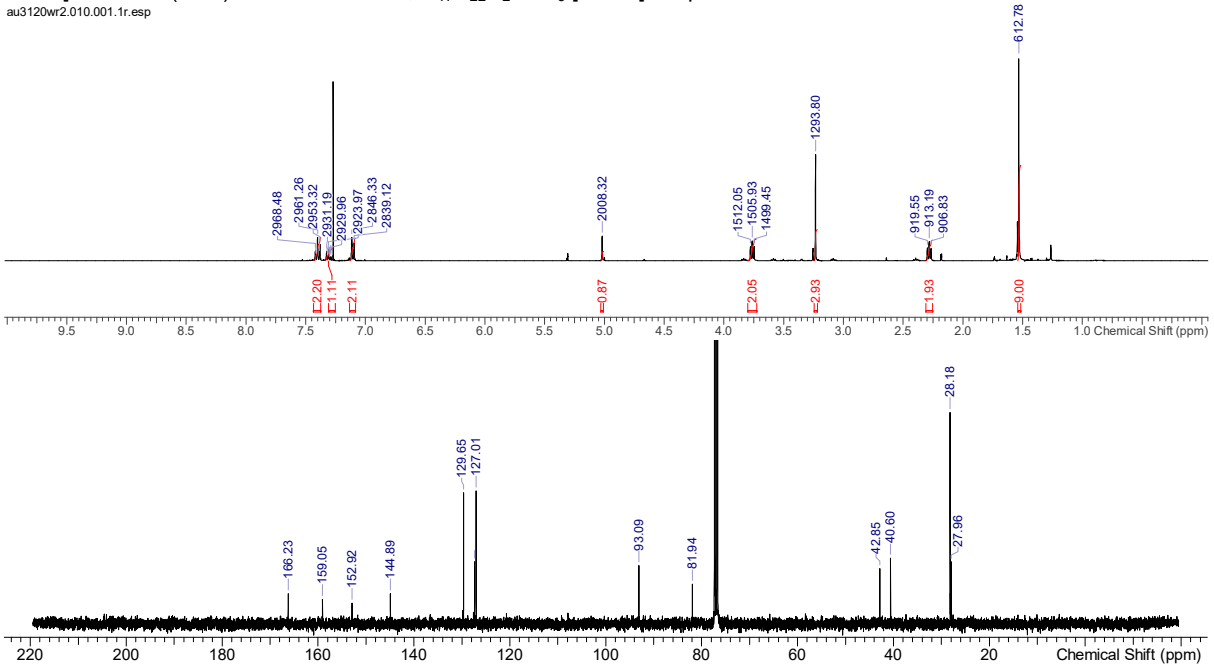




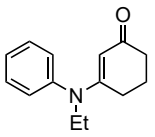
***tert*-Butyl 4-(methyl(phenyl)amino)-6-oxo-3,6-dihydropyridine-1(2*H*)-carboxylate, 17**



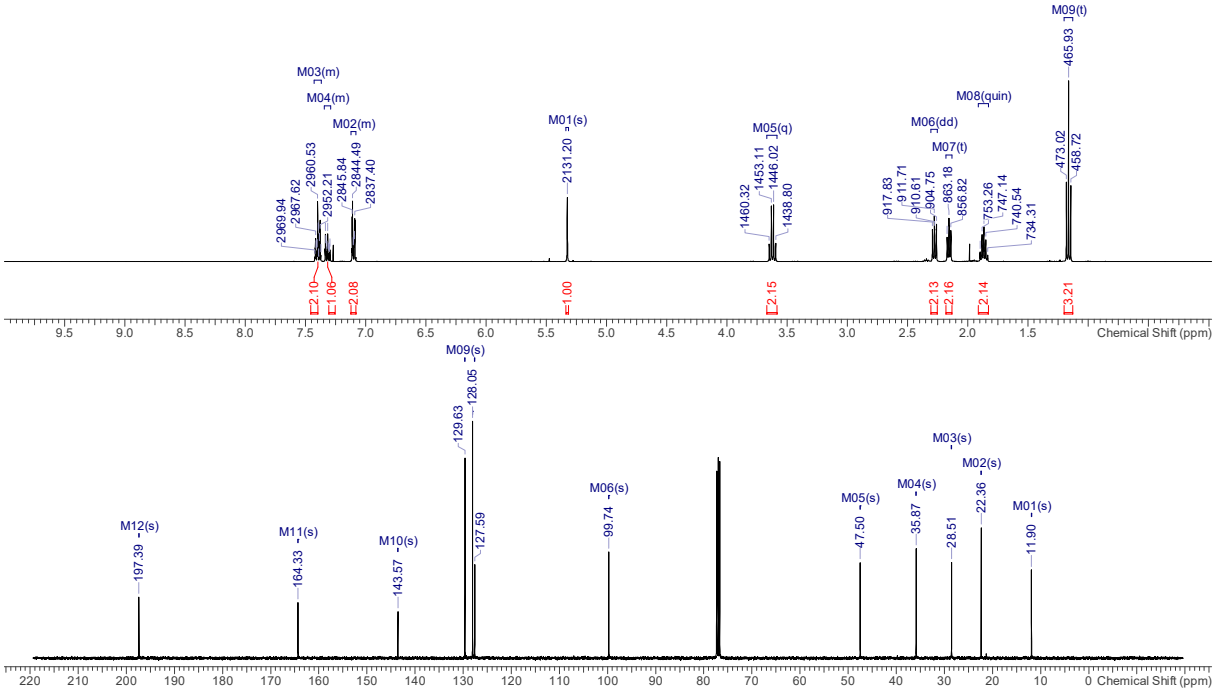
To a solution of **16** (514 mg, 2.54 mmol) in dry THF at –78 °C was added NaH (203 mg, 5.08 mmol). After warming to RT over 1 hour, Di-*tert*-butyl dicarbonate (742 mg, 3.30 mmol) was added. The resulting solution was heated to 40 ºC for 22 h then cooled to RT and sat. NH_4Cl (14 mL) and Et_2O (30 mL) were added. The aqueous phase was separated and extracted with Et_2O (2 × 30 mL) then the organic phases were combined, dried over $MgSO_4$, concentrated in *vacuo* and purified by column chromatography (0 – 30% acetone in DCM) to afford the *title compound* **17** (420 mg, 1.39 mmol, 55%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 – 7.37 (2H, m, 2 × Ar**H**), 7.31 (1H, m, Ar**H**), 7.12 – 7.09 (2H, m, 2 × Ar**H**), 5.02 (1H, s, C**H**), 3.76 (2H, t, *J* = 6.3 Hz, C$\mathbf{H}_2$), 3.23 (3H, s, C$\mathbf{H}_3$), 2.28 (2H, t, *J* = 6.4 Hz, C$\mathbf{H}_2$), 1.53 (9H, s, 3 × C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.2 (**C**), 159.1 (**C**), 152.9 (**C**) 144.9 (**C**), 129.7 (2 × **C**H), 127.1 (**C**H), 127.0 (2 × **C**H), 93.1 (**C**H), 82.0 (**C**), 42.7 (C$\mathbf{H}_2$), 40.6 (C$\mathbf{H}_3$), 28.2 (3 × C$\mathbf{H}_3$), 28.0 (C$\mathbf{H}_2$) ppm. **LRMS** (ESI$^+$): 303 $[M+H]^+$, 247 $[M+H-{}^t\mathrm{Bu}]^+$. **HRMS** (ESI$^+$): Found 325.1529, $C_{17}H_{22}N_2NaO_3$ $[M+Na]^+$ requires 325.1523.



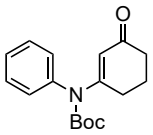
3-(Ethyl(phenyl)amino)cyclohex-2-en-1-one, 5b



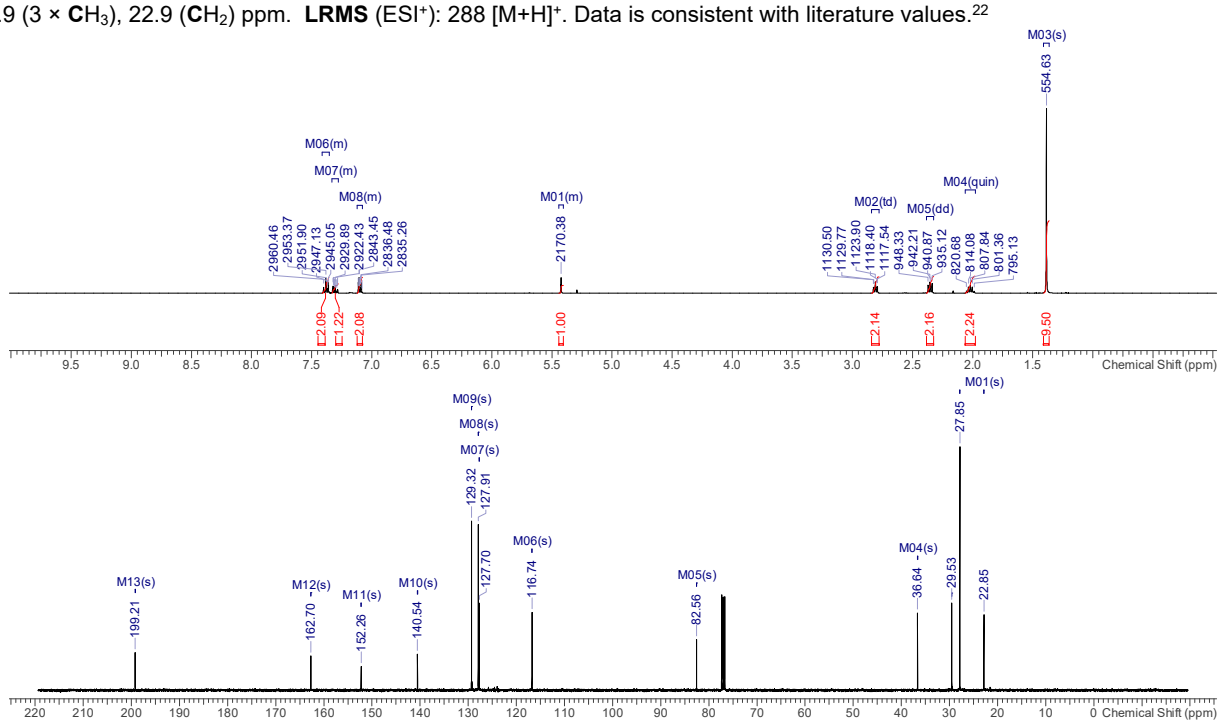
N-Ethylaniline (1.26 mL, 10.0 mmol), 1,3-cyclohexanedione (1.12 g, 10.0 mmol) and *p*TSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **5b** (1.74 g, 8.08 mmol, 81%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2949 (br), 1603 (s), 1548 (s), 1256 (s), 1190 (s), 1132 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.37 (2 H, m, 2 × Ar**H**), 7.31 (1 H, m, Ar**H**), 7.12 – 7.09 (2 H, m, 2 × Ar**H**), 5.33 (1 H, s, C**H**), 3.62 (2 H, q, *J* = 7.2, Hz, C$\mathbf{H}_2$), 2.28 (2 H, dd, *J* = 7.1, 6.0 Hz, C$\mathbf{H}_2$), 2.16 (2 H, app. t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 1.87 (2 H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$), 1.16 (3 H, t, *J* = 7.2 Hz, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4 (**C**), 164.3 (**C**), 143.6 (**C**), 129.6 (2 × **C**H), 128.1 (2 × **C**H), 127.6 (**C**H), 99.7 (**C**H), 47.5 (C$\mathbf{H}_2$), 35.9 (C$\mathbf{H}_2$), 28.5 (C$\mathbf{H}_2$), 22.4 (C$\mathbf{H}_2$), 11.9 (C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 431 $[2M+H]^+$, 216 $[M+H]^+$. Data is consistent with literature values.[8]



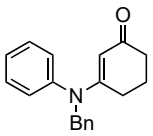
***tert*-Butyl (3-oxocyclohex-1-en-1-yl)(phenyl)carbamate, 5c**



To a solution of 3-(phenylamino)cyclohex-2-en-1-one (730 mg, 3.90 mmol), Di-*tert*-butyl dicarbonate (1275 mg, 5.85 mmol) in dry MeCN (20 mL) under argon was added DMAP (48 mg, 0.4 mmol). The reaction mixture was stirred at RT for 16 h. The resulting solution was concentrated *in vacuo* then purified by column chromatography (70 – 90% EtOAc/Petro) to afford the *title compound* **5c** (871 mg, 3.03 mmol, 81%) as a off-white solid. **IR** ν_{max} (film, cm^{-1}): 2970 (br), 1718 (s), 1644 (s), 1582 (s), 1243 (s), 1152 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (2 H, m, 2 × Ar**H**), 7.31 (1 H, m, Ar**H**), 7.12 – 7.08 (2 H, m, 2 × Ar**H**), 5.42 (1 H, app. s, C**H**), 2.81 (2 H, td, *J* = 6.1, 0.7 Hz, C$\mathbf{H}_2$), 2.35 (2 H, dd, *J* = 7.1, 6.1 Hz, C$\mathbf{H}_2$), 2.02 (2 H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$), 1.39 (9 H, s, 3 × C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.2 (**C**), 162.7 (**C**), 152.3 (**C**), 140.5 (**C**), 129.3 (2 × **C**H), 127.9 (2 × **C**H), 127.7 (**C**H), 116.7 (**C**H), 82.6 (**C**), 36.6 (C$\mathbf{H}_2$), 29.5 (C$\mathbf{H}_2$), 27.9 (3 × C$\mathbf{H}_3$), 22.9 (C$\mathbf{H}_2$) ppm. **LRMS** (ESI$^+$): 288 [M+H]$^+$. Data is consistent with literature values.[22]

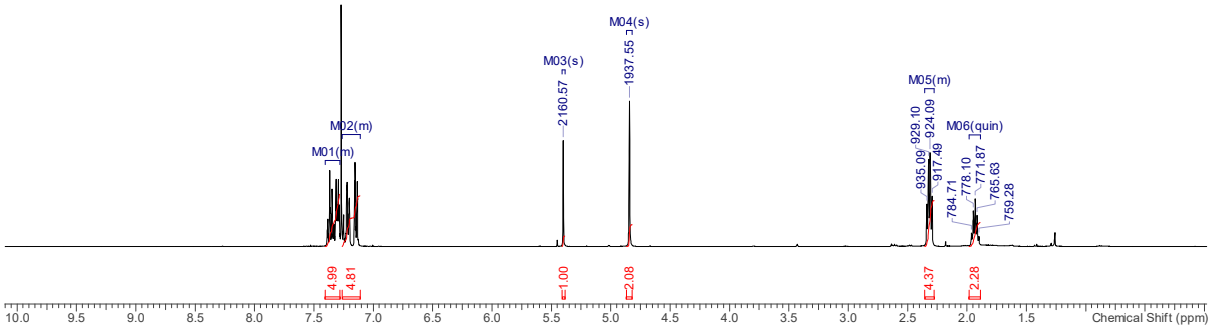


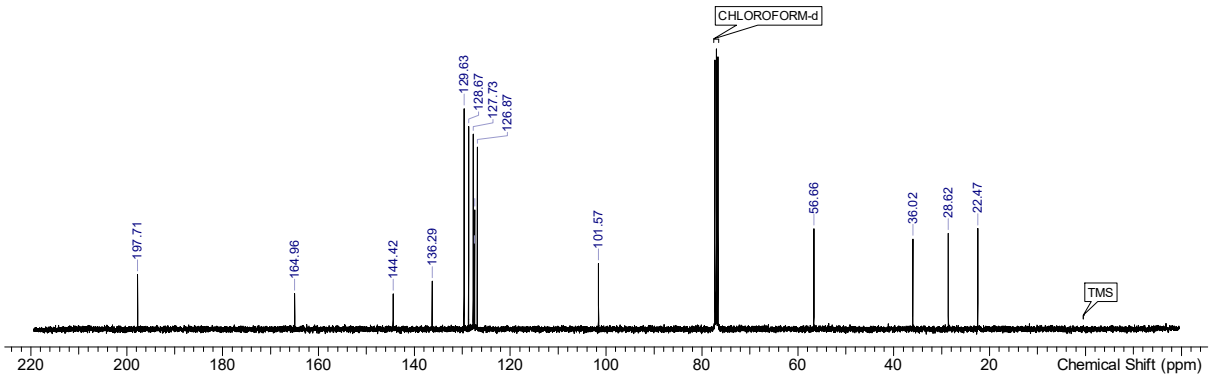
3-(Benzyl(phenyl)amino)cyclohex-2-en-1-one, 5d



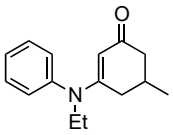
A solution of *N*-benzylaniline (916 mg, 5.00 mmol), 1,3-cyclohexadione (561 mg, 5.00 mmol) and *p*TSA (5 mg) in toluene (50 mL) was heated at reflux for 17 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (5 – 30% acetone in DCM) to afford the *title compound* **5d** (1.15 g, 4.14 mmol, 83%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2981 (br), 2360 (w), 1617 (m), 1558 (s), 1187 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 - 7.28 (5H, m, 5 × Ar**H**) 7.27 – 7.12 (5H, m, 5 × Ar**H**), 5.40 (1H, s, C**H**), 4.84 (2H, s, C$\mathbf{H}_2$) 2.33 (2H, dd, *J* = 5.5, 1.3 Hz, C$\mathbf{H}_2$), 2.30 (2H, dd, *J* = 6.0, 1.1 Hz, C$\mathbf{H}_2$), 1.93 (2H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.7

(**C**), 165.0 (**C**), 144.4 (**C**), 136.3 (**C**), 129.6 (2 × **C**H), 128.7 (2 × **C**H), 127.7 (2 × **C**H), 127.5 (**C**H), 127.4 (**C**H), 126.9 (2 × **C**H), 101.6 (**C**H), 56.7 (**C**H_2), 36.0 (**C**H_2), 28.6 (**C**H_2), 22.5 (**C**H_2) ppm. **LRMS** (ESI$^+$): 278 [M+H]$^+$. Data is consistent with literature values.[23]

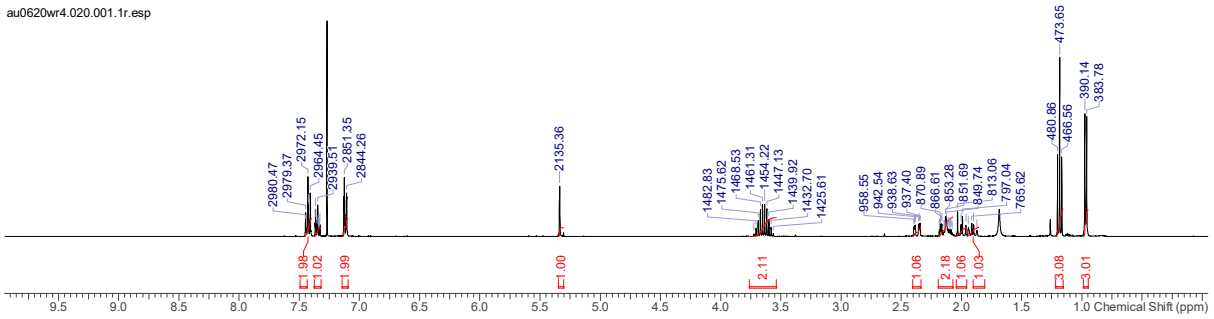


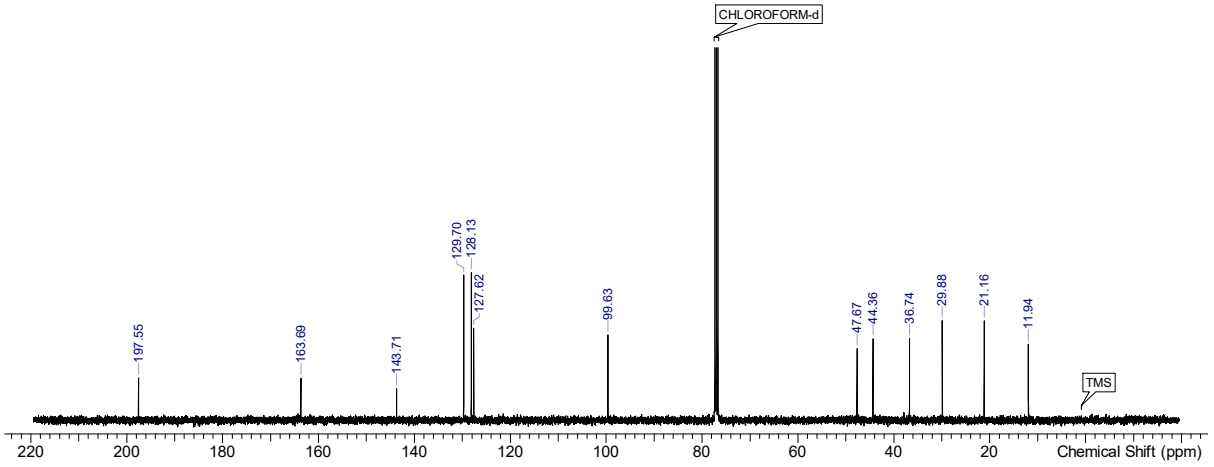


3-(Ethyl(phenyl)amino)-5-methylcyclohex-2-en-1-one, 5e

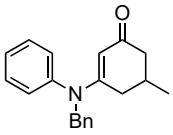


A solution of *N*-ethylaniline (0.63 mL, 5.00 mmol), 5-methyl-1,3-cyclohexadione (0.63 g, 5.00 mmol) and *p*TSA (5 mg) in toluene was heated at reflux for 17 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% acetone in DCM) to afford the *title compound* **5e** (796 mg, 3.47 mmol, 69%) as a yellow solid. **MP** 104-105 °C. **IR** ν_{max} (film, cm^{-1}): 2954 (br), 1615 (m), 1548 (s), 1454 (s), 1251 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 – 7.40 (2H, m, 2 × Ar**H**), 7.35 (1H, tt, *J* = 7.5, 1.3 Hz, Ar**H**), 7.12 (2H, d with fine splitting, *J* = 7.1 Hz, 2 × Ar**H**), 5.34 (1H, s, C**H**), 3.72 – 3.56 (2H, m, CH_2), 2.37 (1H, ddd, *J* = 16.0, 3.8, 1.7 Hz, C**H**H), 2.19 – 2.09 (2H, m, CH**H** + C**H**), 2.00 (1H, dd, *J* = 15.8, 11.4 Hz, C**H**H), 1.91 (1H, dd, *J* = 17.6, 11.4 Hz, CH**H**), 1.18 (3H, t, *J* = 7.2 Hz, CH_3), 0.97 (3H, d, *J* = 6.4 Hz, CH_3) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.6 (**C**), 163.7 (**C**), 143.7 (**C**), 129.7 (2 × **C**H), 128.1 (2 × **C**H), 127.6 (**C**H), 99.6 (**C**H), 47.7 (**C**H_2), 44.4 (**C**H_2), 36.7 (**C**H_2), 29.9 (**C**H), 21.2 (**C**H_3), 11.9 (**C**H_3) ppm. **LRMS** (ESI$^+$): 230 [M+H]$^+$. **HRMS** (ESI$^+$): Found 230.1543, $C_{15}H_{20}NO$ [M+H]$^+$ requires 230.1539.

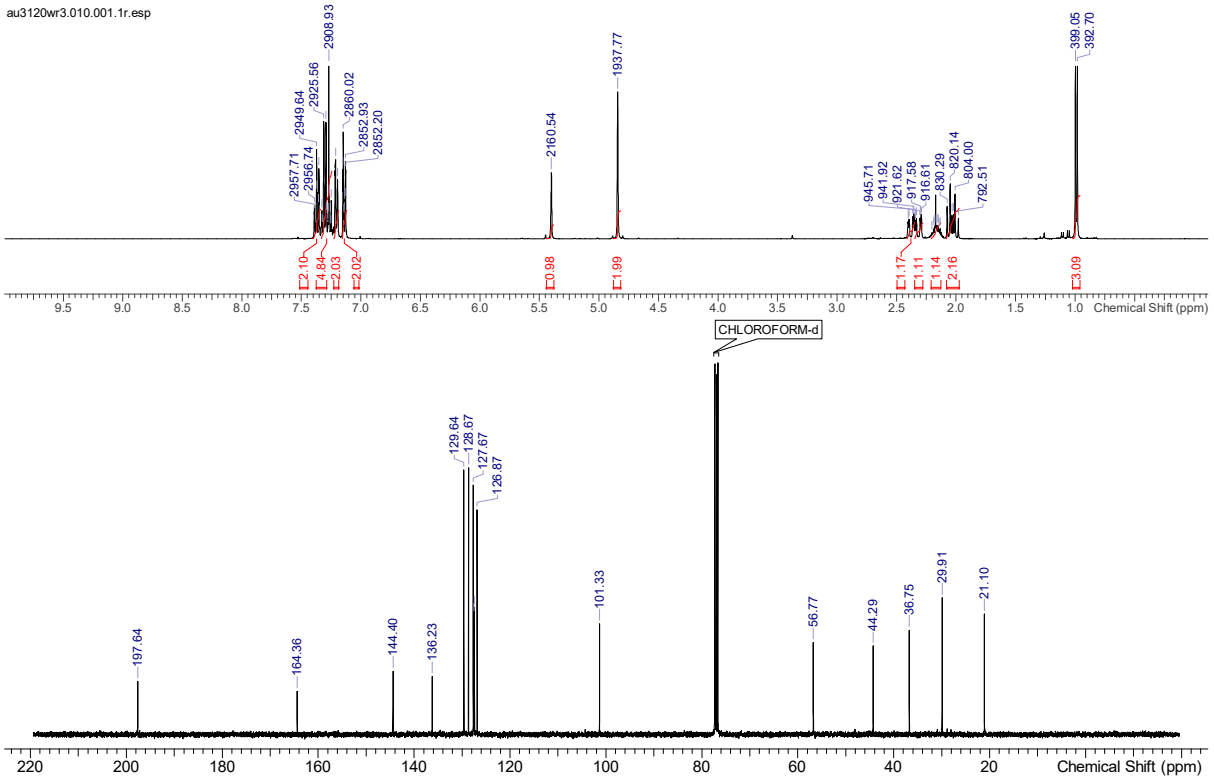




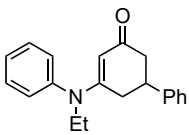
3-(Benzyl(phenyl)amino)-5-methylcyclohex-2-en-1-one, 5f



A solution of *N*-benzylaniline (1.10 g, 6.00 mmol), 5-methyl-1,3-cyclohexadione (631 mg, 5.00 mmol) and *p*TSA (5 mg) in toluene (50 mL) was heated at reflux for 18 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 50% acetone in DCM) to afford the *title compound* **5f** (1.38 g, 4.74 mmol, 95%) as an orange oil. **IR** ν_{max} (film, cm^{-1}): 2954 (br), 1622 (m), 1557 (s), 1233 (m), 701 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 – 7.34 (2H, m, 2 × Ar**H**), 7.34 – 7.24 (4H, m, 4 × Ar**H**), 7.22 – 7.18 (2H, m, 2 × Ar**H**), 7.16 – 7.11 (2H, m, 2 × Ar**H**), 5.40 (1H, s, C**H**), 4.84 (2H, s, C$\mathbf{H}_2$) 2.38 (1H, ddd, *J* = 16.0, 3.9, 1.2 Hz, C**H**H), 2.32 (1H, ddd, *J* = 16.3, 4.0, 1.2 Hz, CH**H**), 2.17 (1 H, m, C**H**), 2.05 (1H, dd, *J* = 11.5, 10.6 Hz, C**H**H), 2.01 (1H, dd, *J* = 11.2, 10.0 Hz, CH**H**), 0.99 (3H, dd, *J* = 6.4 Hz, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.6 (**C**), 164.3 (**C**), 144.4 (**C**), 136.2 (**C**), 129.6 (2 × **C**H), 128.7 (2 × **C**H), 127.7 (2 × **C**H), 127.5 (**C**H), 127.4 (**C**H), 126.9 (2 × **C**H), 101.3 (**C**H), 56.8 (C$\mathbf{H}_2$), 44.3 (C$\mathbf{H}_2$), 36.8 (C$\mathbf{H}_2$), 29.9 (**C**H), 21.1 (C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 292 [M+H]$^+$. **HRMS** (ESI$^+$): Found 292.1701, $C_{20}H_{22}NO$ [M+H]$^+$ requires 292.1696.

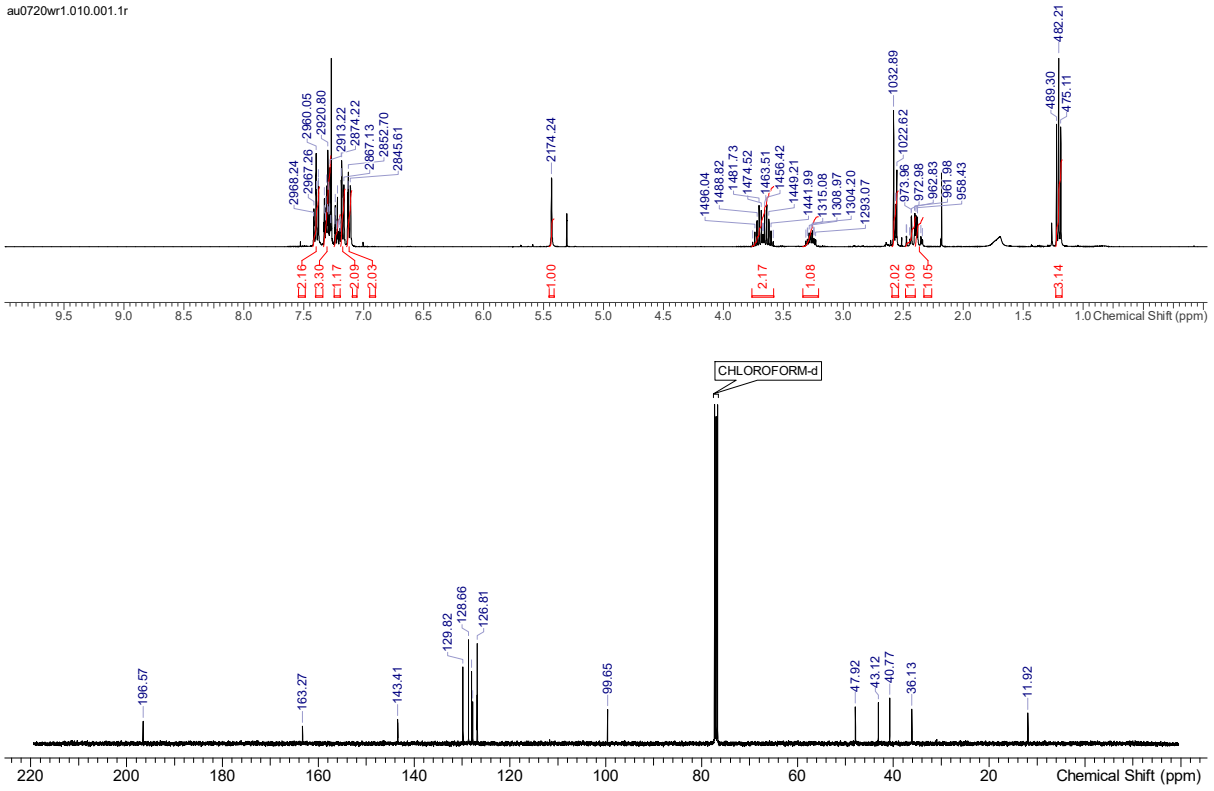


5-(Ethyl(phenyl)amino)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one, **5g**

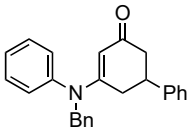


A solution of *N*-ethylaniline (0.63 mL, 5.00 mmol), 5-phenyl-1,3-cyclohexadione (0.94 g, 5.00 mmol) and *p*TSA (5 mg) in toluene (70 mL) was heated at reflux for 17 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% acetone in DCM) to afford the *title compound* **5g** (1.31 g, 4.50 mmol, 89%) as an off-white solid. **IR** ν_{max} (film, cm^{-1}): 2977 (br), 1615 (m), 1550 (s), 1492 (m), 1453 (m), 1254 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 (2H, ddd, *J* = 8.4, 7.2, 1.0 Hz, 2 × Ar**H**), 7.33 – 7.28 (3H, m, 3 × Ar**H**), 7.22 (1H, tt, *J* = 7.2, 1.3 Hz, Ar**H**), 7.18 (2H, dd, *J* = 7.8, 1.6 Hz, 2 × Ar**H**), 7.12 (2H, dd, *J* = 7.8, 1.6 Hz, 2 × Ar**H**), 5.43 (1H, s, C**H**), 3.76 – 3.58 (2H, m, C$\mathbf{H}_2$), 3.27 (1H, m, C**H**), 2.60 – 2.54 (2H, m, C$\mathbf{H}_2$), 2.42 (1H, ddd, *J* = 16.9, 11.1, 0.9 Hz, C**H**H), 2.37 (1H, dd, *J* = 16.9, 4.8 Hz, CH**H**), 1.21 (3H, t, *J* = 7.1 Hz, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.6 (**C**), 163.3 (**C**), 143.5 (**C**), 143.4 (**C**), 129.8 (2 × **C**H), 128.7 (2 × **C**H), 128.0 (**C**H), 127.8 (2 × **C**H), 126.9 (**C**H), 126.8 (2 × **C**H), 99.7 (**C**H), 47.9 (C$\mathbf{H}_2$), 43.1 (C$\mathbf{H}_2$),

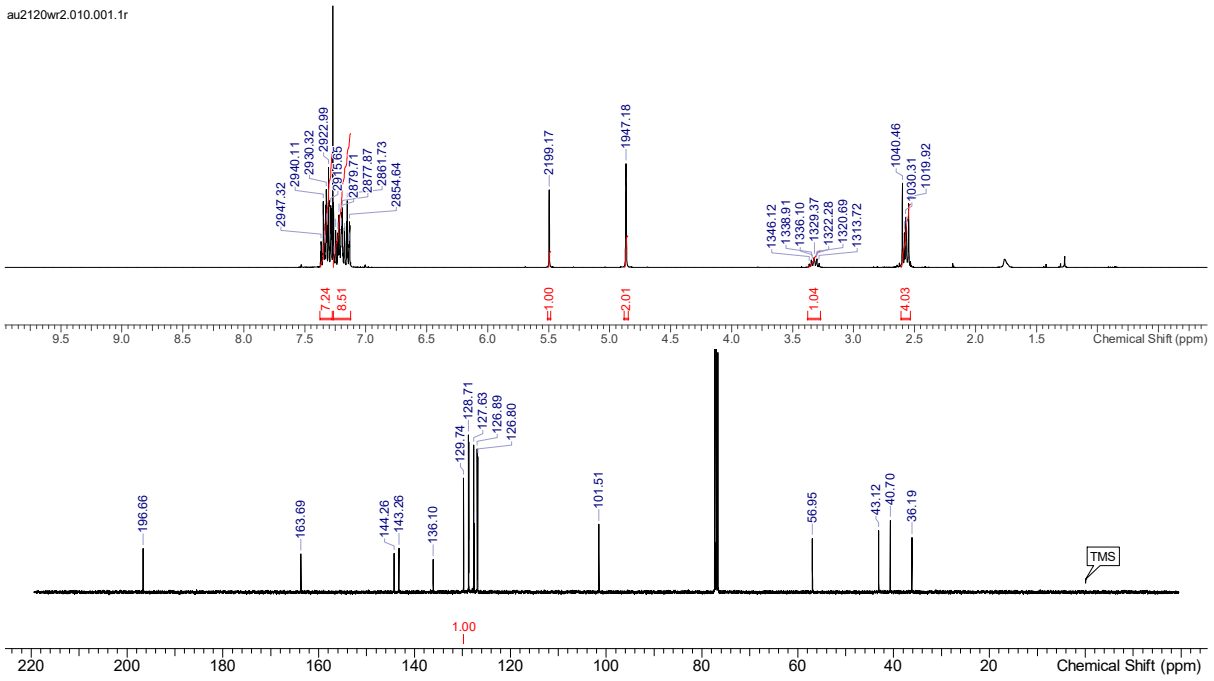
40.8 (**C**H), 36.1 (**C**H_2), 11.9 (**C**H_3) ppm. **LRMS** (ESI$^+$): 292 [M+H]$^+$. **HRMS** (ESI$^+$): Found 292.1700, $C_{20}H_{22}NO$ [M+H]$^+$ requires 292.1696.



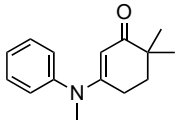
5-(Benzyl(phenyl)amino)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one, **5h**



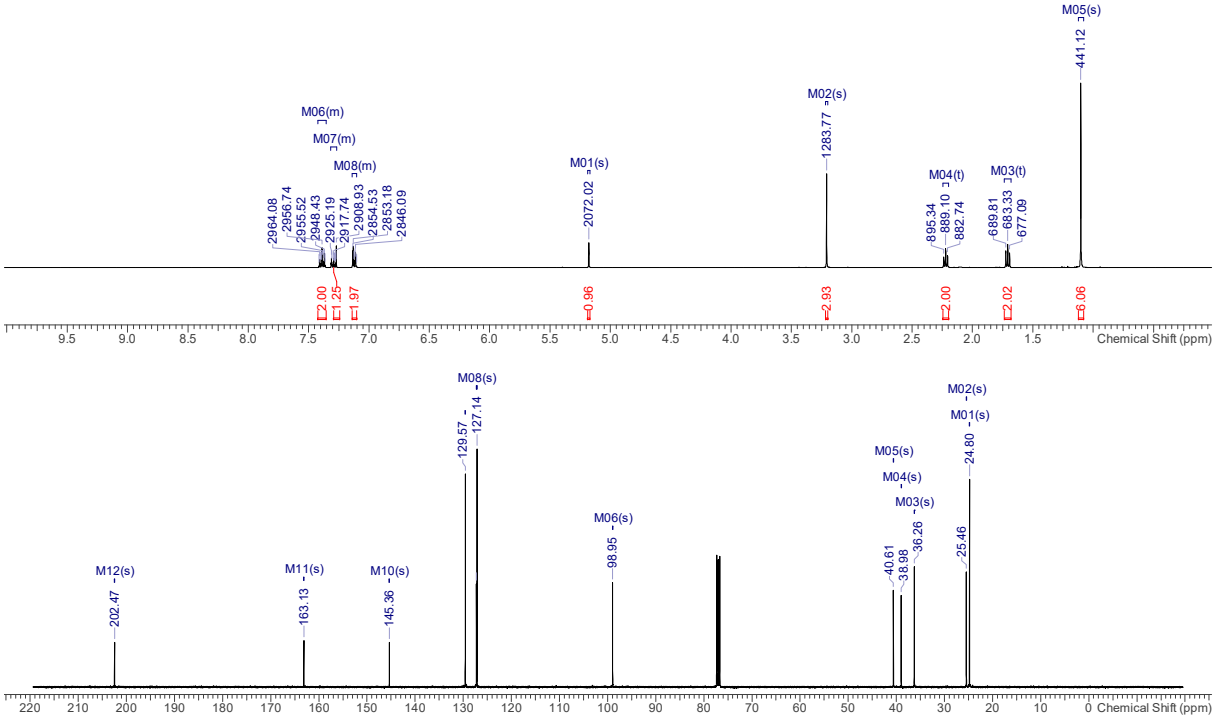
A solution of *N*-benzylaniline (916 mg, 5.00 mmol), 5-phenyl-1,3-cyclohexadione (941 mg, 5.00 mmol) and *p*TSA (5 mg) in toluene (50 mL) was heated at reflux for 16 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (0 – 30% acetone in DCM) to afford the *title compound* **5h** (1.70 g, 4.81 mmol, 96%) as an orange oil. **IR** ν_{max} (film, cm^{-1}): 2981 (br), 2359 (br), 1617 (m), 1550 (s), 1493 (m), 1236 (m), 757 (m), 698 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 – 7.27 (7H, m, 7 × Ar**H**), 7.27 – 7.12 (8H, m, 8 × Ar**H**), 5.50 (1H, s, C**H**), 4.87 (2H, s, CH_2), 3.33 (1H, m, C**H**), 2.61 – 2.53 (4H, m, 2 × CH_2) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.7 (**C**), 163.7 (**C**), 144.3 (**C**), 136.1 (**C**), 129.8 (**C**), 129.7 (2 × **C**H), 128.7 (2 × **C**H), 128.7 (2 × **C**H), 127.6 (2 × **C**H), 127.5 (**C**H), 126.9 (2 × **C**H), 126.9 (**C**H), 126.8 (2 × **C**H), 101.5 (**C**H), 57.0 (**C**H_2), 43.1 (**C**H_2), 40.7 (**C**H), 36.2 (**C**H_2) ppm. **LRMS** (ESI$^+$): 354 ((M+H)$^+$, 100%). **HRMS** (ESI$^+$): Found 354.1860, $C_{25}H_{24}NO$ [M+H]$^+$ requires 354.1852.



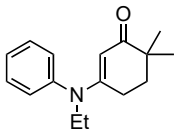
6,6-Dimethyl-3-(methyl(phenyl)amino)cyclohex-2-en-1-one, 5i



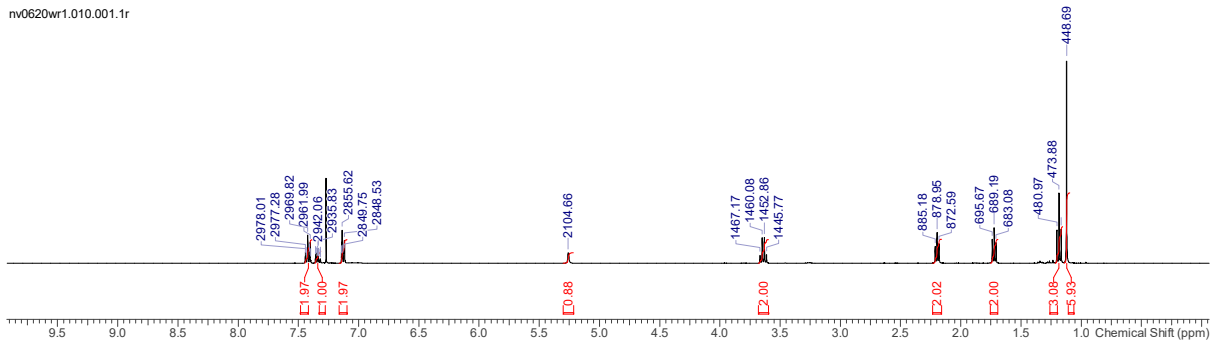
N-methylaniline (0.96 mL, 8.87 mmol), 6,6-dimethyl-3-(methyl(phenyl)amino)cyclohex-2-en-1-one (1.035 g, 7.43 mmol) and *p*TSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **5i** (1.35 g, 5.90 mmol, 80%) as a white solid. **MP**: 90 – 91 °C. **IR** ν_{max} (film, cm^{-1}): 2924 (br), 1648 (m), 1546 (s), 1392 (m), 1191 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 – 7.36 (2 H, m, 2 × Ar**H**), 7.29 (1 H, m, Ar**H**), 7.14 – 7.10 (2 H, m, 2 × Ar**H**), 5.18 (1 H, s, C**H**), 3.21 (3 H, s, C**H**$_3$), 2.22 (2 H, t, *J* = 6.3 Hz, C**H**$_2$), 1.71 (2 H, t, *J* = 6.4 Hz, C**H**$_2$), 1.10 (6 H, s, 2 × C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.5 (**C**), 163.1 (**C**), 145.4 (**C**), 129.6 (2 × **C**H), 127.3 (**C**H), 127.1 (2 × **C**H), 99.0 (**C**H), 40.6 (**C**H$_3$), 39.0 (**C**), 36.3 (**C**H$_2$), 25.5 (**C**H$_2$), 24.8 (2 × **C**H$_3$) ppm. **LRMS** (ESI$^+$): 230 [M+H]$^+$, 252 [M+Na]$^+$. **HRMS** (ESI$^+$): Found 354.1860, $C_{15}H_2NO$ [M+H]$^+$ requires 230.1539.

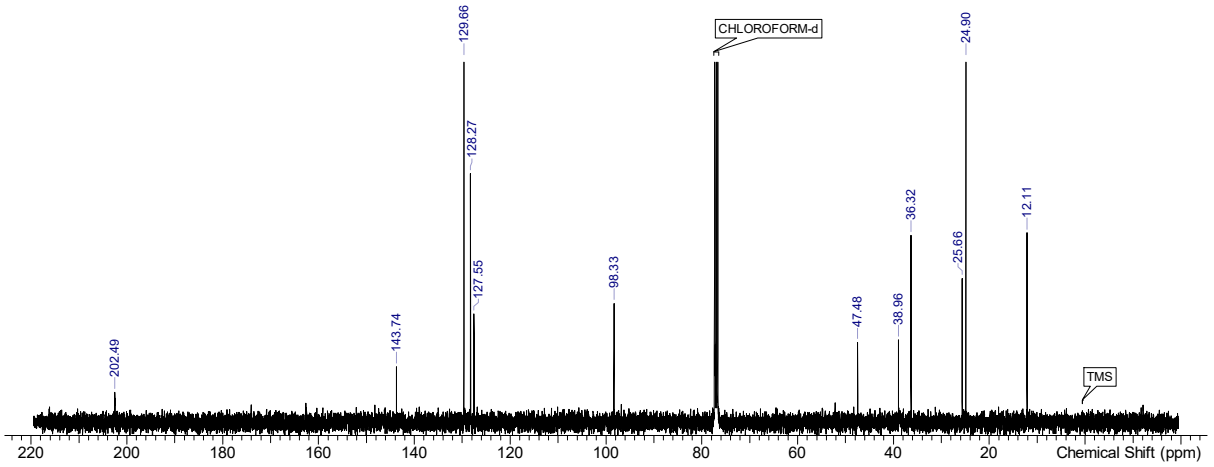


3-(Ethyl(phenyl)amino)-6,6-dimethylcyclohex-2-en-1-one, **5j**

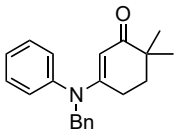


A solution of *N*-ethylaniline (1.26 mL, 10.0 mmol), 4,4-dimethyl-1,3-cyclohexadione (701 mg, 5.00 mmol) and *p*TSA (5 mg) in toluene (40 mL) was heated at reflux for 17 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% acetone in DCM) to afford the *title compound* **5j** (1.10 g, 4.52 mmol, 90%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2971 (br), 2359 (br), 1616 (w), 1558 (s), 1211 (m), 702 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 – 7.38 (2H, m, 2 × Ar**H**), 7.34 (1H, m, Ar**H**), 7.16 – 7.08 (2H, m, 2 × Ar**H**), 5.26 (1H, s, C**H**), 3.64 (2H, q, *J* = 7.1 Hz, C**H**$_2$) 2.20 (2H, t, *J* = 6.3 Hz, C**H**$_2$), 1.72 (2H, t, *J* = 6.3 Hz, C**H**$_2$), 1.18 (2H, t, *J* = 7.2 Hz, C**H**$_3$), 1.12 (6H, s, 2 × C**H**$_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 202.5 (**C**), 162.6 (**C**), 143.7 (**C**), 129.7 (2 × **C**H), 128.3 (2 × **C**H), 127.6 (**C**H), 98.3 (**C**H), 47.5 (**C**H$_2$), 39.0 (**C**), 36.3 (**C**H$_2$), 25.7 (**C**H$_2$), 24.9 (2 × **C**H$_3$), 12.1 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 244 [M+H]$^+$. **HRMS** (ESI$^+$): Found 244.1702, $C_{16}H_{22}NO$ [M+H]$^+$ requires 244.1696.

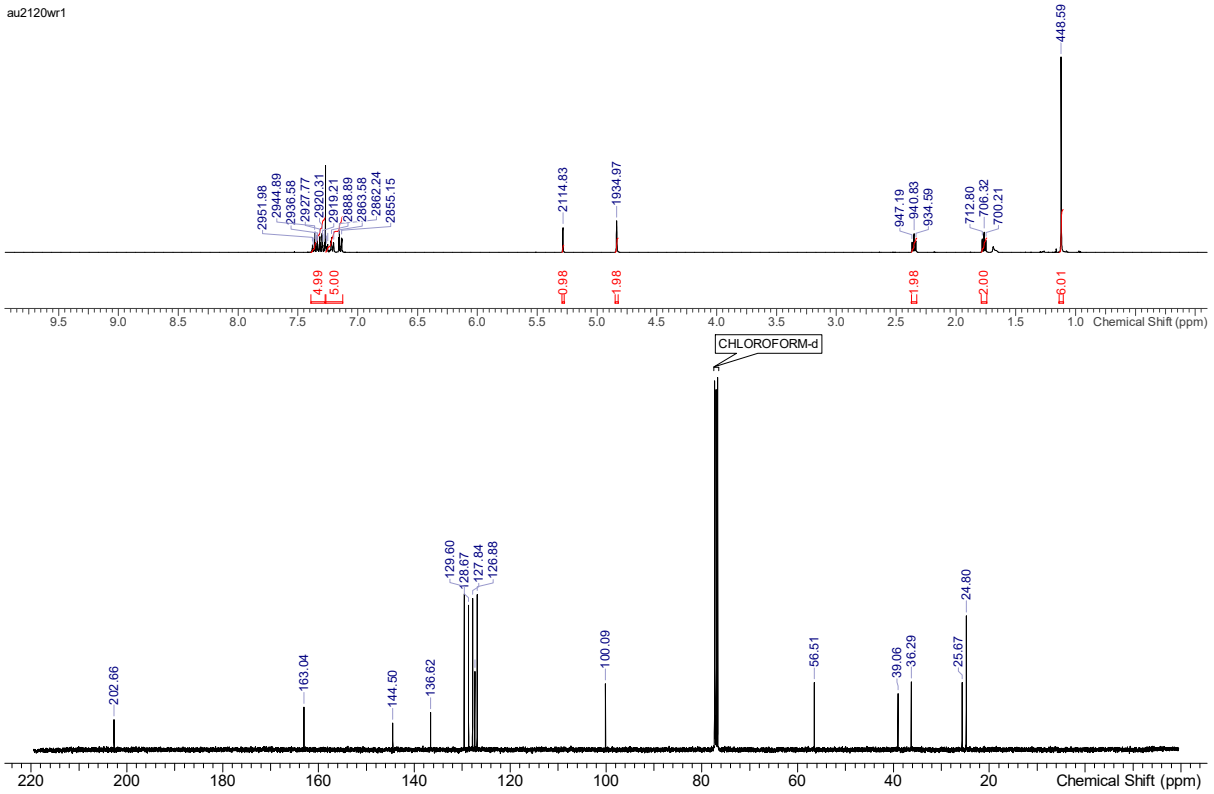




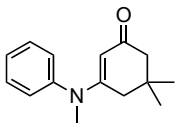
3-(Benzyl(phenyl)amino)-6,6-dimethylcyclohex-2-en-1-one, **5k**



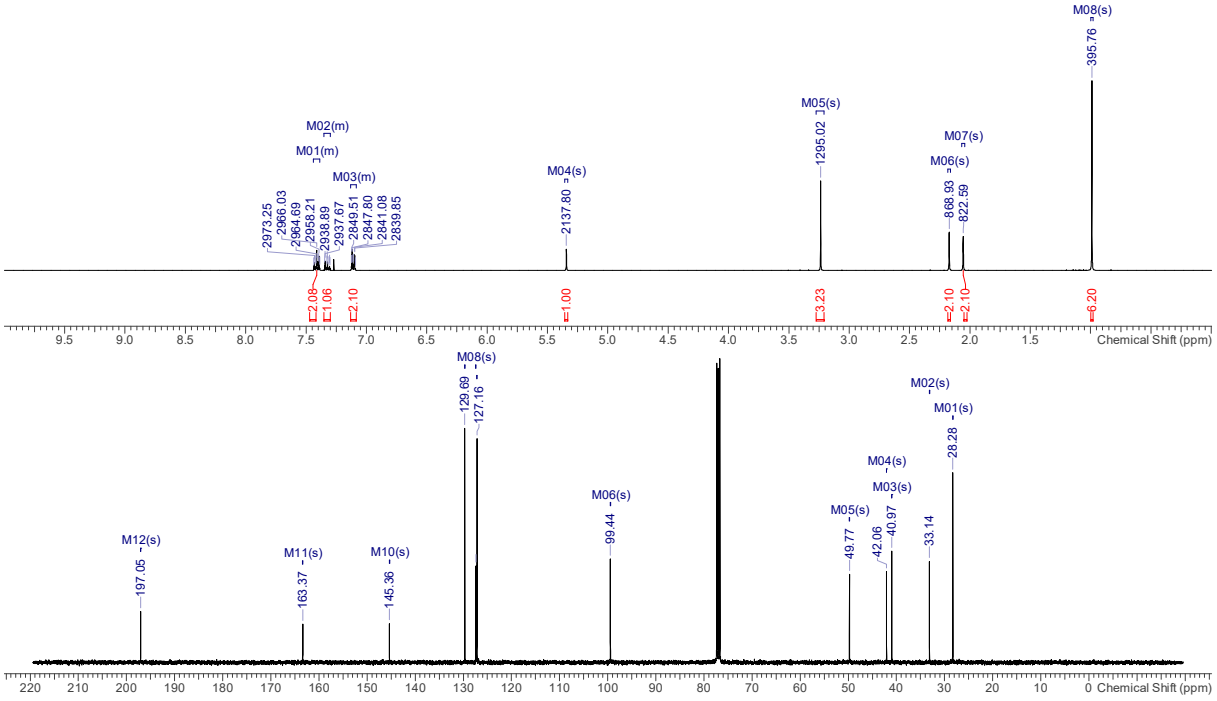
A solution of *N*-benzylaniline (916 mg, 5.00 mmol), 4,4-dimethyl-1,3-cyclohexadione (701 mg, 5.00 mmol) and *p*TSA (5 mg) in toluene (50 mL) was heated at reflux for 16 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (0 – 30% acetone in DCM) to afford the *title compound* **5k** (1.23 g, 4.03 mmol, 80%) as a yellow solid. **MP** 95–98 °C. **IR** ν_{max} (film, cm^{-1}): 2980 (br), 1622 (m), 1559 (s), 1205 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.27 (5H, m, 5 × Ar**H**), 7.25 (1H, m, Ar**H**), 7.23 – 7.19 (2H, m, 2 × Ar**H**), 7.16 – 7.12 (2H, m, 2 × Ar**H**), 5.29 (1H, s, C**H**), 4.84 (2H, s, C$\mathbf{H}_2$) 2.35 (2H, t, *J* = 6.3 Hz, C$\mathbf{H}_2$), 1.77 (2H, t, *J* = 6.3 Hz, C$\mathbf{H}_2$), 1.12 (6H, s, 2 × C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 202.7 (**C**), 163.0 (**C**), 144.5 (**C**), 136.6 (**C**), 129.6 (2 × **C**H), 128.7 (2 × **C**H), 127.8 (2 × **C**H), 127.4 (**C**H), 127.4 (**C**H), 126.9 (2 × **C**H), 100.1 (**C**H), 56.5 (**C**$\mathbf{H}_2$), 39.1 (**C**), 36.1 (**C**$\mathbf{H}_2$), 25.5 (**C**H), 24.6 (2 × **C**$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 306 [M+H]$^+$. Data is consistent with literature values.[24]



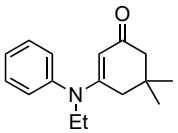
5,5-Dimethyl-3-(methyl(phenyl)amino)cyclohex-2-en-1-one, 5l



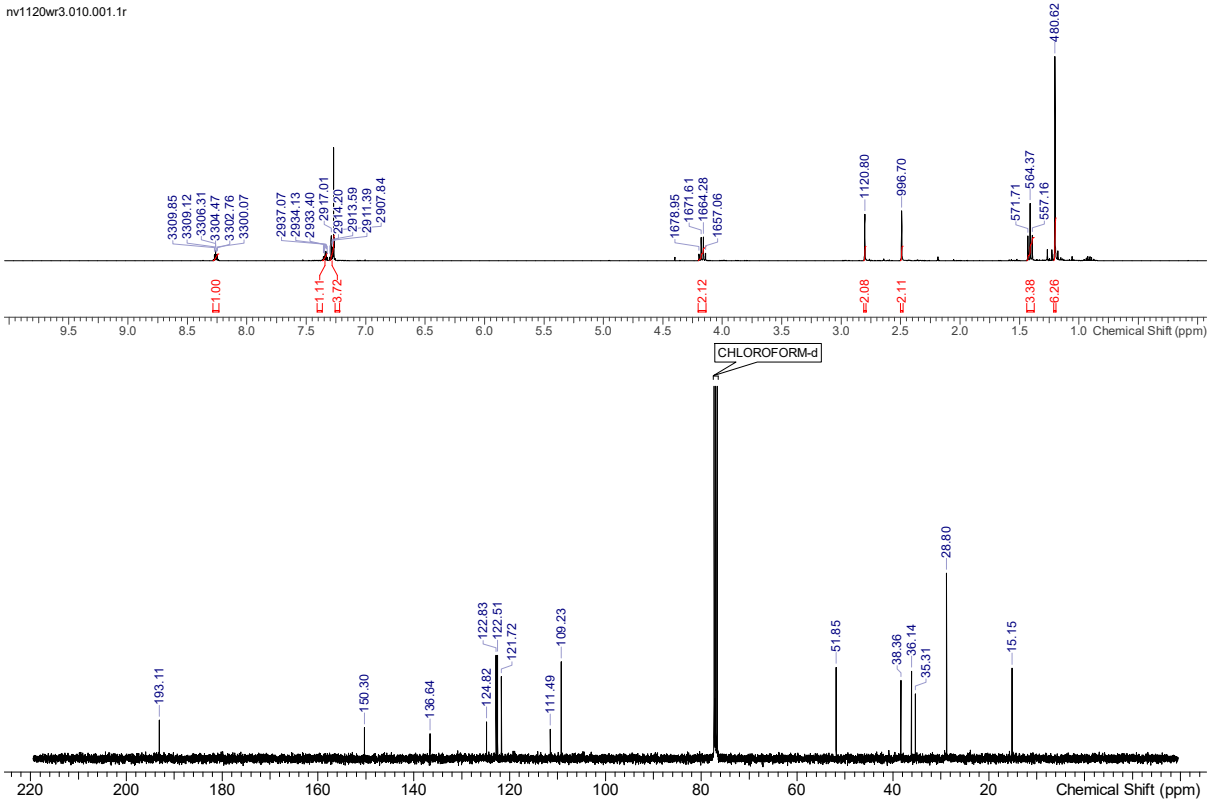
N-methylaniline (0.93 mL, 8.60 mmol), 5,5-dimethylcyclohexane-1,3-dione (1.00 g, 7.14 mmol) and *p*TSA (50 mg, 0.291 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **5l** (1.37 g, 6.03 mmol, 83%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2950 (br), 1615 (m), 1552 (s), 1394 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 – 7.39 (2 H, m, 2 × Ar**H**), 7.32 (1 H, m, Ar**H**), 7.12 – 7.09 (2 H, m, 2 × Ar**H**), 5.34 (1 H, s, C**H**), 3.24 (3 H, s, C$\mathbf{H}_3$), 2.17 (2 H, s, C$\mathbf{H}_2$), 2.06 (2 H, s, C$\mathbf{H}_2$), 0.99 (6 H, s, 3 × C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1 (**C**), 163.4 (**C**), 145.4 (**C**), 129.7 (2 × **C**H), 127.4 (**C**H), 127.2 (2 × **C**H), 99.4 (**C**H), 49.8 (**C**$\mathbf{H}_3$), 42.1 (**C**$\mathbf{H}_2$), 41.0 (**C**$\mathbf{H}_2$), 33.1 (**C**), 28.3 (2 × **C**$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 230 [M+H]$^+$. Data is consistent with literature values.[25]



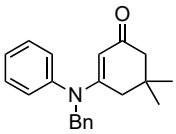
3-(Ethyl(phenyl)amino)-5,5-dimethylcyclohex-2-en-1-one, **5m**



A solution of *N*-ethylaniline (1.89 mL, 15.00 mmol), 5,5-dimethyl-1,3-cyclohexadione (701 mg, 5.00 mmol) and *p*TSA (5 mg) in toluene was heated at reflux for 17 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% acetone in DCM) to afford the *title compound* **5m** (590 mg, 2.42 mmol, 49%) as an off-white solid. **MP** 116–119 °C. **IR** ν_{max} (film, cm^{-1}): 2957 (br), 1541 (s), 1491 (m), 1252 (s), 1129 (m), 702 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (2H, m, 2 × Ar**H**), 7.36 (1H, m, Ar**H**), 7.13 – 7.08 (2H, m, 2 × Ar**H**), 5.37 (1H, s, C**H**), 3.66 (2H, q, *J* = 7.1 Hz, C**H**$_2$), 2.18 (2H, s, C**H**$_2$), 2.03 (2H, s, C**H**$_2$), 1.19 (3H, t, *J* = 7.1 Hz, C**H**$_3$), 1.00 (6H, s, 2 × C**H**$_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.0 (**C**), 162.9 (**C**), 143.7 (**C**), 129.8 (2 × **C**H), 128.1 (2 × **C**H), 127.7 (**C**H), 98.8 (**C**H), 49.6 (**C**H$_2$), 47.8 (**C**H$_2$), 42.2 (**C**H$_2$), 33.2 (**C**), 28.3 (2 × **C**H$_3$), 12.0 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 244 [M+H]$^+$. Data is consistent with literature values.[26]

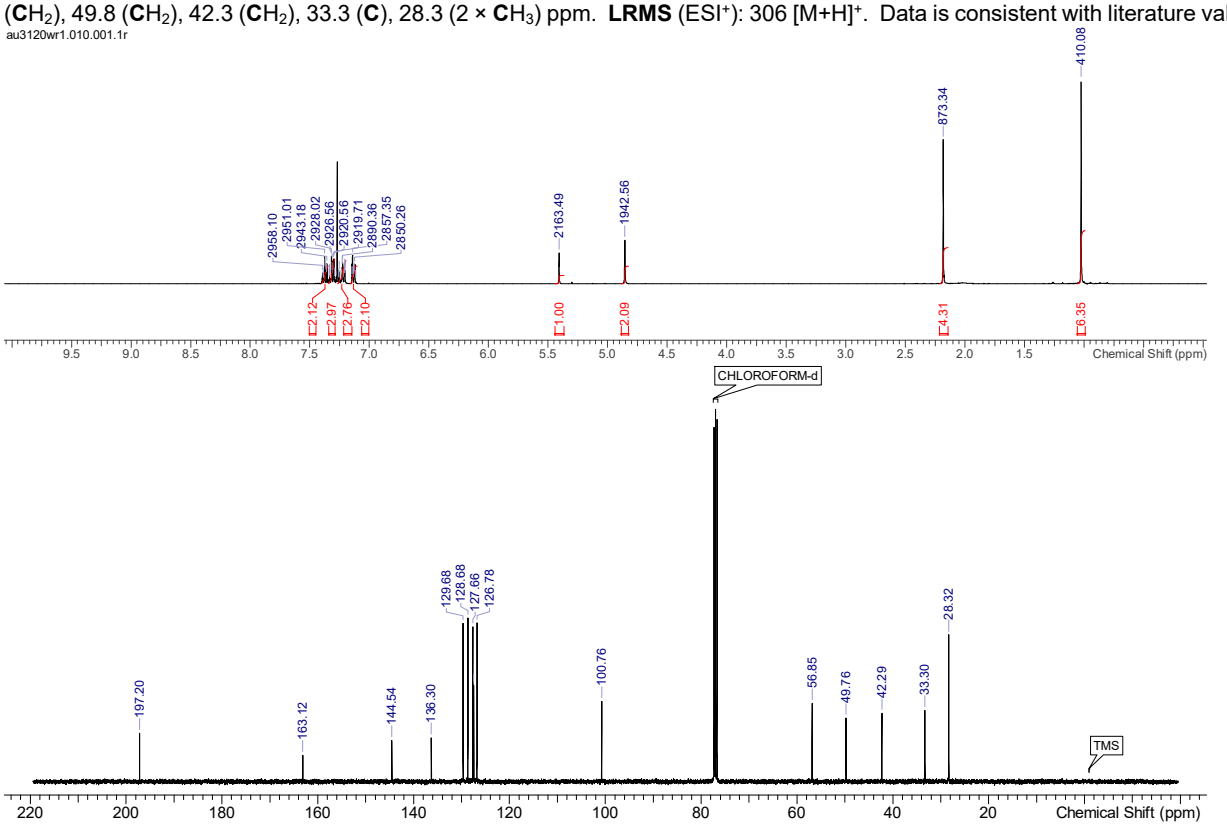


3-(Benzyl(phenyl)amino)-5,5-dimethylcyclohex-2-en-1-one, **5n**

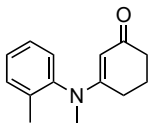


A solution of *N*-benzylaniline (1.50 g, 8.19 mmol), dimedone (701 mg, 5.00 mmol) and *p*TSA (5 mg) in toluene (50 mL) was heated at reflux for 57 h. The resulting solution was concentrated *in vacuo* and purified by

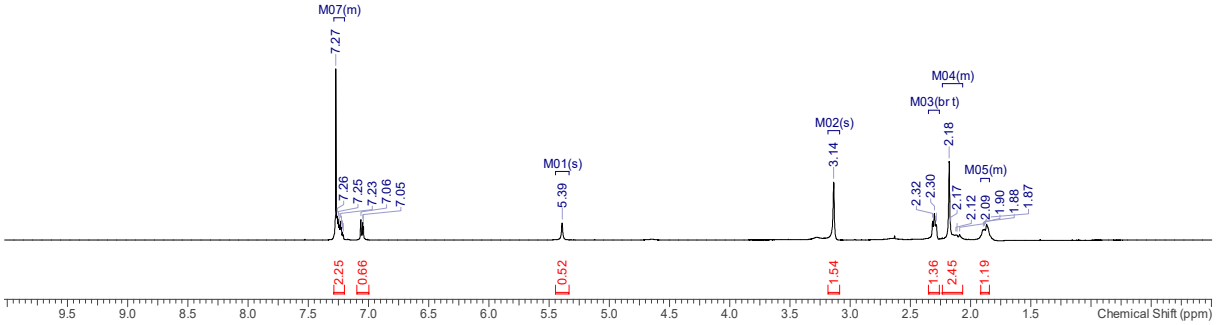
column chromatography (10 – 50% acetone in DCM) to afford the *title compound* **5n** (953 mg, 3.12 mmol, 62%) as a yellow solid. **MP** 112-113 °C. **IR** ν_{max} (film, cm^{-1}): 2957 (br), 2359 (br), 1622 (m), 1558 (s), 1492 (m), 1236 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 - 7.35 (m, 2H, 2 × Ar**H**), 7.34 – 7.25 (m, 3H, 3 × Ar**H**), 7.26 - 7.20 (m, 3H, 3 × Ar**H**), 7.15 – 7.11 (m, 2H, 2 × Ar**H**), 5.41 (s, 1H, C**H**), 4.85 (s, 2H, C$\mathbf{H}_2$) 2.18 (s, 4H, 2 × C$\mathbf{H}_2$), 1.02 (s, 6H, 2 × C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.2 (**C**), 163.1 (**C**), 144.5 (**C**), 136.3 (**C**), 129.7 (2 × **C**H), 128.7 (2 × **C**H), 127.7 (2 × **C**H), 127.5 (**C**H), 127.4 (**C**H), 126.8 (2 × **C**H), 100.8 (**C**H), 56.9 (C$\mathbf{H}_2$), 49.8 (C$\mathbf{H}_2$), 42.3 (C$\mathbf{H}_2$), 33.3 (**C**), 28.3 (2 × C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 306 [M+H]$^+$. Data is consistent with literature values.[27]

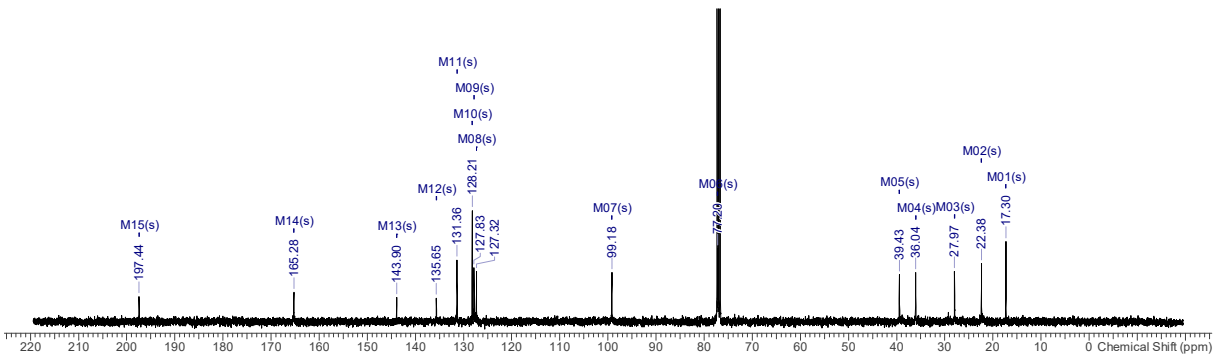


3-(Methyl(*o*-tolyl)amino)cyclohex-2-en-1-one, 19a

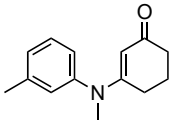


2-Methy-*N*-methylaniline (0.56 mL, 4.51 mmol), 1,3-cyclohexanedione (510 mg, 4.55 mmol) and *p*TSA (60 mg, 0.348 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19a** (731 mg, 3.40 mmol, 76%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2947 (br), 1615 (m), 1548 (s), 1490 (m), 1396 (m), 1322 (m), 1266 (m), 1188 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 – 7.21 (3 H, m, 3 × Ar**H**), 7.05 (1 H, m, Ar**H**), 5.39 (1 H, s, C**H**), 3.14 (3 H, s, C$\mathbf{H}_3$), 2.30 (2 H, br *t*, *J* = 5.9 Hz, C$\mathbf{H}_2$), 2.18 (3 H, s, C$\mathbf{H}_3$), 2.18 – 2.02 (2 H, m, C$\mathbf{H}_2$), 1.90 – 1.87 (2 H, m, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4 (**C**), 165.3 (**C**), 143.9 (**C**), 135.7 (**C**), 131.4 (**C**H), 128.2 (2 × **C**H), 127.8 (**C**H), 127.3 (**C**H), 99.2 (**C**H), 39.4 (C$\mathbf{H}_3$), 36.0 (C$\mathbf{H}_2$), 28.0 (C$\mathbf{H}_2$), 22.4 (C$\mathbf{H}_2$), 17.3 (C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 238 [M+Na]$^+$, 216 [M+H]$^+$. Data is consistent with literature values.[10]

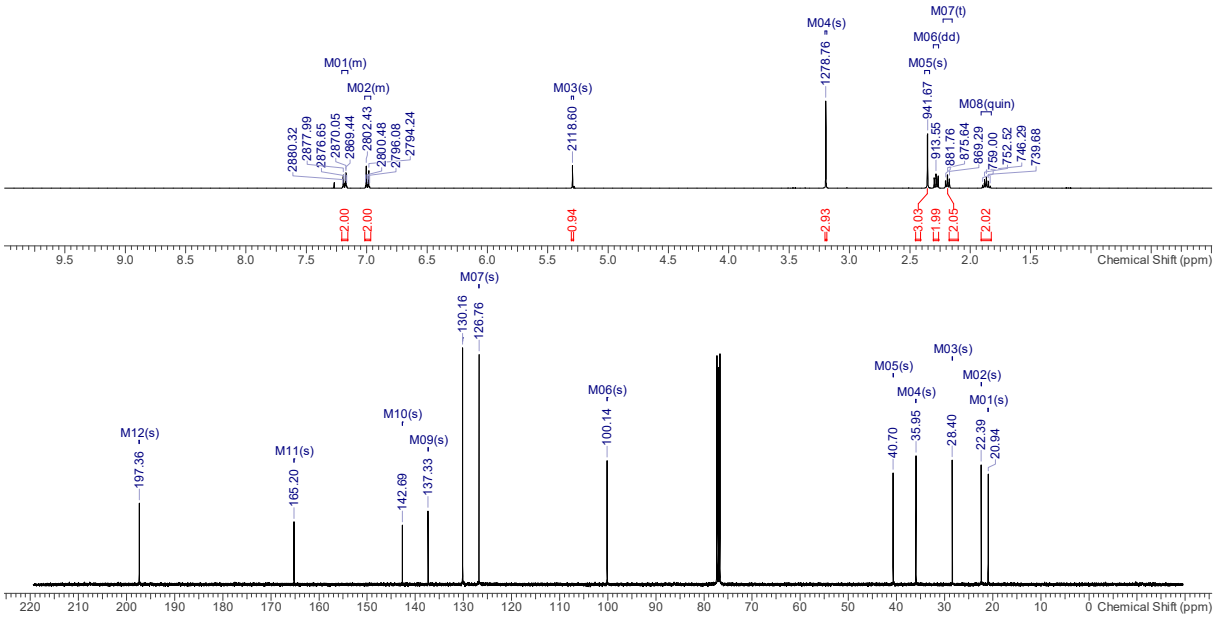




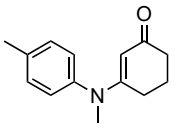
3-(Methyl(*m*-tolyl)amino)cyclohex-2-en-1-one, 19b



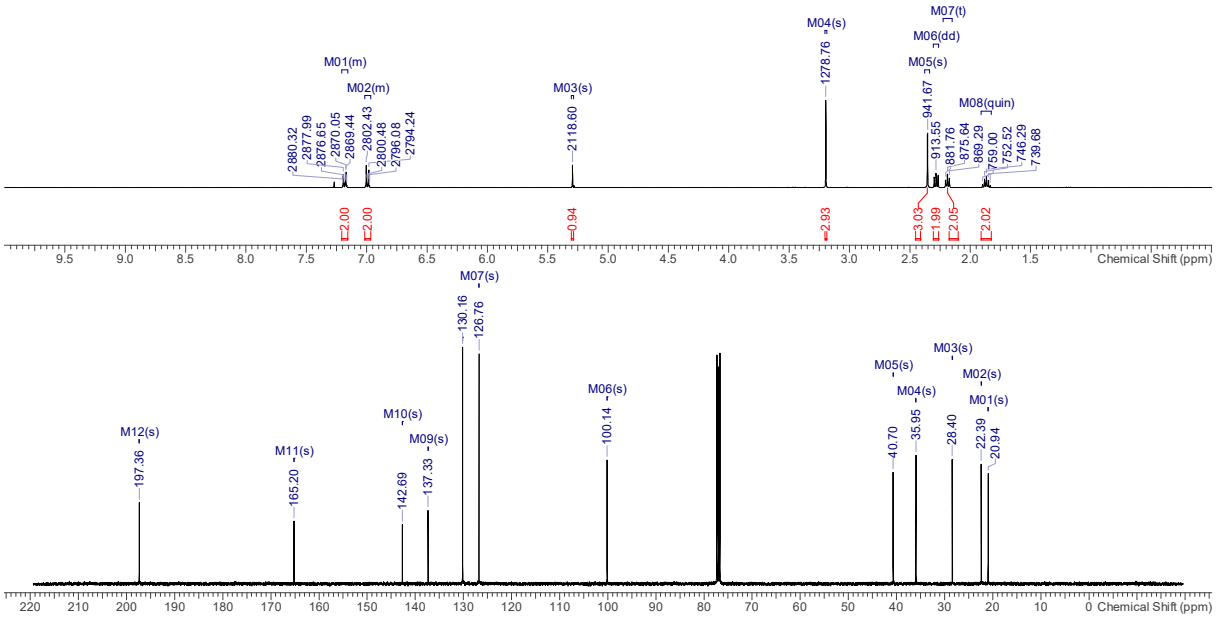
3-Methy-*N*-methylaniline (1.12 mL, 8.86 mmol), 1,3-cyclohexanedione (898 mg, 8.02 mmol) and *p*TSA (60 mg, 0.349 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19b** (1.187 g, 5.52 mmol, 69%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2952 (br), 1605 (s), 1549 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (1 H, t, *J* = 7.6 Hz, Ar**H**), 7.10 (1 H, app. br d, *J* = 7.6 Hz, Ar**H**), 6.93 – 6.90 (2 H, m, 2 × Ar**H**), 5.28 (1 H, s, C**H**), 3.20 (3 H, s, C$\mathbf{H}_3$), 2.35 (3 H, s, C$\mathbf{H}_3$), 2.28 (2 H, app. t, *J* = 6.1 Hz, C$\mathbf{H}_2$), 2.20 (2 H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.49 (3 H, s, C$\mathbf{H}_3$), 1.87 (2 H, quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4 (**C**), 165.0 (**C**), 145.2 (**C**), 139.7 (**C**), 129.3 (**C**H), 128.1 (**C**H), 127.6 (**C**H), 123.9 (**C**H), 100.2 (**C**H), 40.6 (**C**H_3), 36.0 (**C**H_2), 28.4 (**C**H_2), 22.4 (**C**H_2), 21.2 (**C**H_3) ppm. **LRMS** (ESI^+): 238 $[M+Na]^+$, 216 $[M+H]^+$. **HRMS** (ESI^+): Found 216.1388, $C_{14}H_{18}NO$ $[M+H]^+$ requires 216.1383.



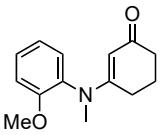
3-(Methyl(*p*-tolyl)amino)cyclohex-2-en-1-one, 19c



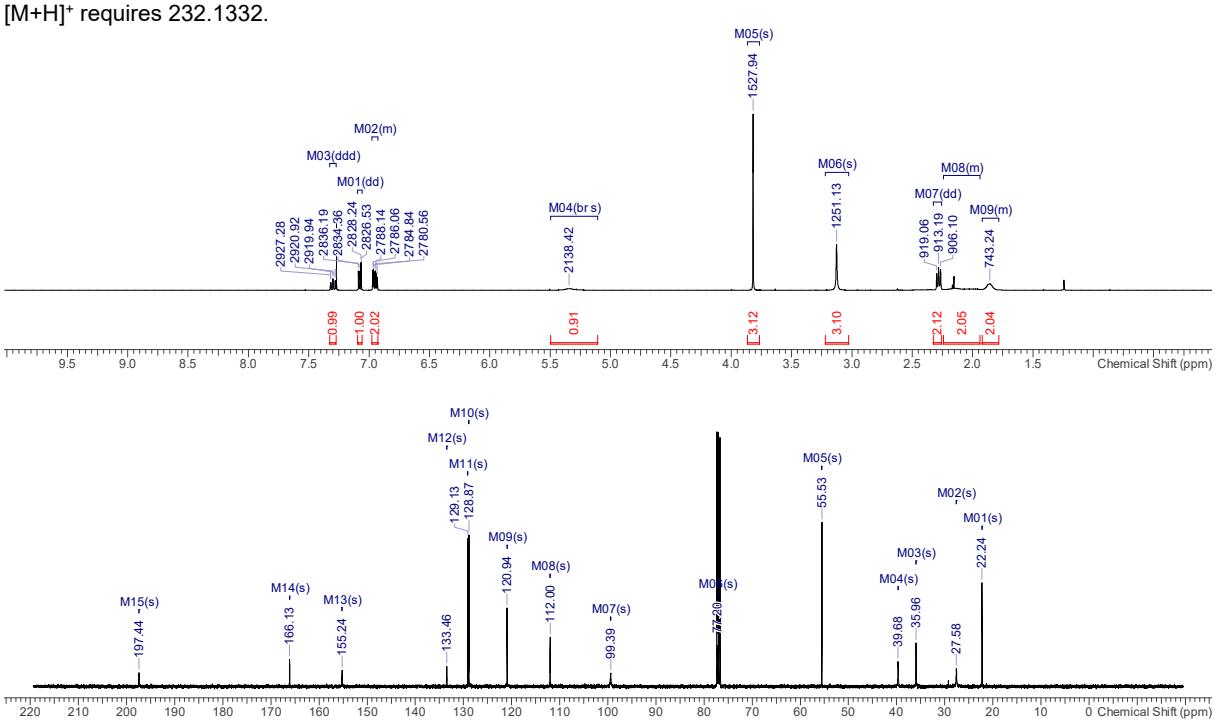
4-Methy-*N*-methylaniline (1.0 mL, 7.92 mmol), 1,3-cyclohexanedione (733 mg, 6.54 mmol) and *p*TSA (60 mg, 0.349 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19c** (1.075 g, 5.00 mmol, 77%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2940 (br), 1606 (s), 1559 (s), 1508 (s), 1370 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 – 7.17 (2 H, m, 2 × Ar**H**), 7.01 – 6.98 (2 H, m, 2 × Ar**H**), 5.29 (1 H, s, C**H**), 3.20 (3 H, s, C$\mathbf{H}_3$), 2.35 (3 H, s, C$\mathbf{H}_3$), 2.28 (2 H, dd, *J* = 6.2, 6.4 Hz, C$\mathbf{H}_2$), 2.19 (2 H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.24 (2 H, quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4 (**C**), 165.2 (**C**), 142.7 (**C**), 137.3 (**C**), 130.2 (2 × **C**H), 126.8 (2 × **C**H), 100.1 (**C**H), 40.7 (**C**H_2), 36.0 (**C**H_3), 28.4 (**C**H_4), 22.4 (**C**H_2), 20.9 (**C**H_3) ppm. **LRMS** (ESI^+): 453 $[2M+Na]^+$, 216 $[M+H]^+$. Data is consistent with literature values.[21]



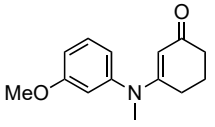
3-((2-Methoxyphenyl)(methyl)amino)cyclohex-2-en-1-one, 19d



2-Methoxy-*N*-methylaniline (956 mg, 6.98 mmol), 1,3-cyclohexanedione (782 mg, 6.98 mmol) and *p*TSA (60 mg, 0.349 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19d** (1.27 g, 5.50 mmol, 79%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2943 (br), 1615 (m), 1546 (s), 1496 (m), 1246 (m), 1186 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (1 H, ddd, *J* = 8.3, 7.3, 1.8 Hz, Ar**H**), 7.08 (1 H, dd, *J* = 7.9, 1.8 Hz, Ar**H**), 6.97 – 6.93 (2 H, m, 2 × Ar**H**), 5.34 (1 H, br s, C**H**), 3.82 (1 H, s, C$\mathbf{H}_3$), 3.13 (1 H, s, C$\mathbf{H}_3$), 2.28 (2 H, dd, *J* = 7.1, 5.9 Hz, C$\mathbf{H}_2$), 2.20 – 2.00 (2 H, br, C$\mathbf{H}_2$), 1.86 (2 H, br s, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4 (**C**), 166.1 (**C**), 155.2 (**C**), 133.5 (**C**), 129.1 (**C**H), 128.9 (**C**H), 120.9 (**C**H), 112.0 (**C**H), 99.4 (**C**H), 55.5 (**C**H_3), 39.7 (**C**H_3), 36.0 (**C**H_2), 27.6 (**C**H_2), 22.2 (**C**H_2) ppm. **LRMS** (ESI$^+$): 463 [2M+H]$^+$, 232 [M+H]$^+$. **HRMS** (ESI$^+$): Found 232.1336, $C_{14}H_{18}NO_2$ [M+H]$^+$ requires 232.1332.

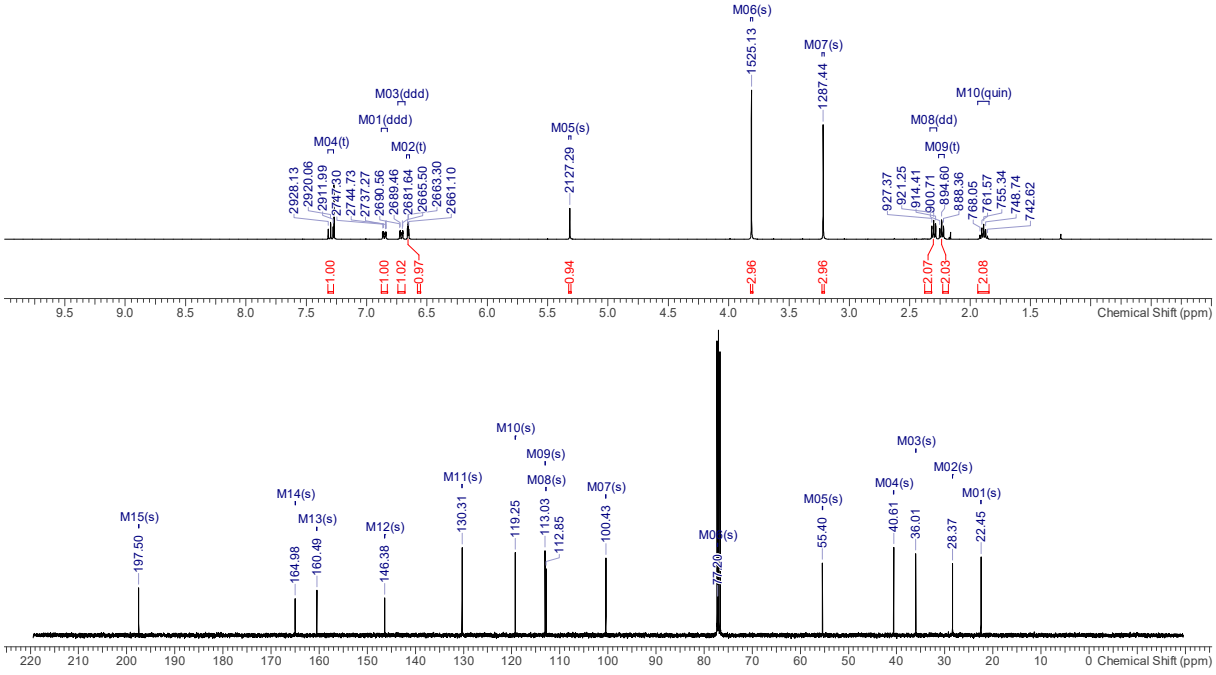


3-((3-Methoxyphenyl)(methyl)amino)cyclohex-2-en-1-one, 19e

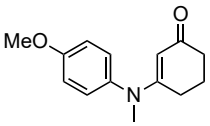


3-Methoxy-*N*-methylaniline (600 mg, 4.38 mmol), 1,3-cyclohexanedione (448 mg, 4.00 mmol) and *p*TSA (30 mg, 0.174 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19e** (758 mg, 3.28 mmol, 82%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2948 (br), 1613 (s), 1596 (s), 1550 (s), 1489 (s), 1247 (s), 1216 (s), 1186 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30

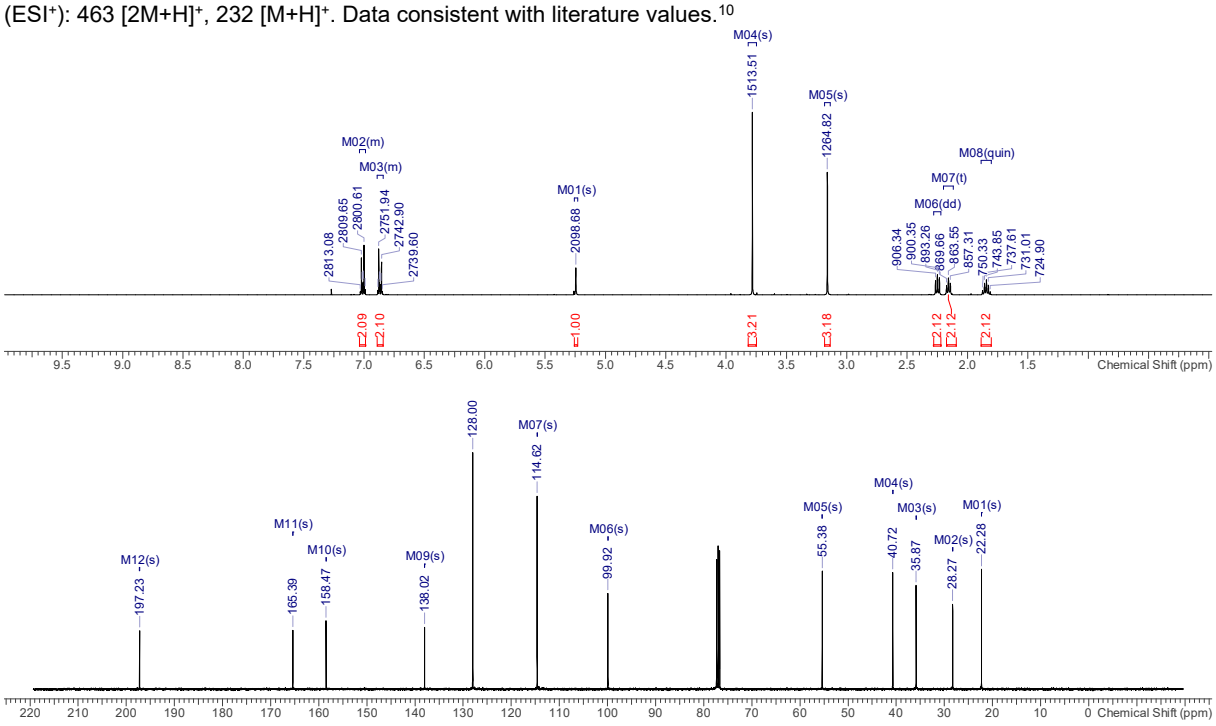
(1 H, t, *J* = 8.1 Hz, Ar**H**), 6.85 (1 H, ddd, *J* = 8.4, 2.5, 0.9 Hz, Ar**H**), 6.71 (1 H, ddd, *J* = 7.8, 2.0, 0.9 Hz, Ar**H**), 6.66 (1 H, t, *J* = 2.2 Hz, Ar**H**), 5.32 (1 H, s, C**H**), 3.81 (3 H, s, C$\mathbf{H}_3$), 3.22 (3 H, s, C$\mathbf{H}_3$), 2.30 (2 H, app. dd, *J* = 7.0, 6.0 Hz, C$\mathbf{H}_2$), 2.24 (2 H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 1.89 (2 H, quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.5 (**C**), 165.0 (**C**), 160.5 (**C**), 146.4 (**C**), 130.3 (**C**H), 119.3 (**C**H), 113.0 (**C**H), 112.9 (**C**H), 100.4 (**C**H), 55.4 (**C**H_3), 40.6 (**C**H_3), 36.0 (**C**H_2), 28.4 (**C**H_2), 22.5 (**C**H_2) ppm. **LRMS** (ESI^+): 463 $[2M+H]^+$, 254 $[M+Na]^+$, 232 $[M+H]^+$. **HRMS** (ESI^+): Found 232.1339, $C_{14}H_{18}NO_2$ $[M+H]^+$ requires 232.1332.



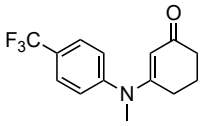
3-((4-Methoxyphenyl)(methyl)amino)cyclohex-2-en-1-one, 19f



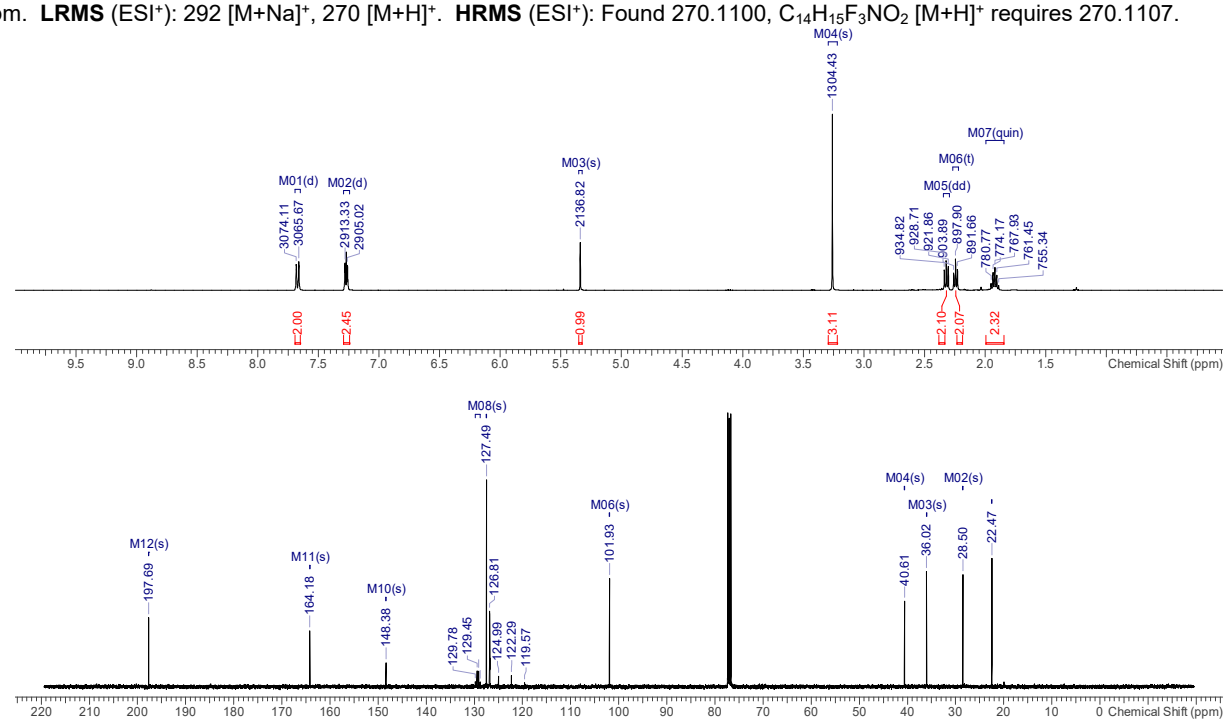
4-Methoxy-*N*-methylaniline (1.48 g, 10.8 mmol), 1 3-cyclohexanedione (1.00 g, 8.93 mmol) and *p*TSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19f** (1.83 g, 7.92 mmol, 88%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2939 (br), 1611 (s), 1551 (s), 1507 (s), 1238 (s), 1158 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.03 – 6.99 (2 H, m, 2 × Ar**H**), 7.89 – 6.85 (2 H, m, 2 × Ar**H**), 5.24 (1 H, s, C**H**), 3.78 (3 H, s, C$\mathbf{H}_3$), 3.16 (3 H, s, C$\mathbf{H}_3$), 2.25 (2 H, dd, *J* = 7.2, 5.9 Hz, C$\mathbf{H}_2$), 2.16 (2 H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 1.84 (2 H, quin, *J* = 6.5 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.2 (**C**), 165.4 (**C**), 158.2 (**C**), 138.0 (**C**), 128.0 (2 × **C**H), 114.6 (2 × **C**H), 99.9 (**C**H), 55.4 (**C**H_3), 40.7 (**C**H_2), 35.9 (**C**H_3), 28.3 (**C**H_2), 22.3 (**C**H_2) ppm. **LRMS** (ESI^+): 463 $[2M+H]^+$, 232 $[M+H]^+$. Data consistent with literature values.[10]



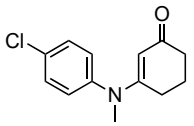
3-(Methyl(4-trifluoromethylphenyl)amino)cyclohex-2-en-1-one, 19g



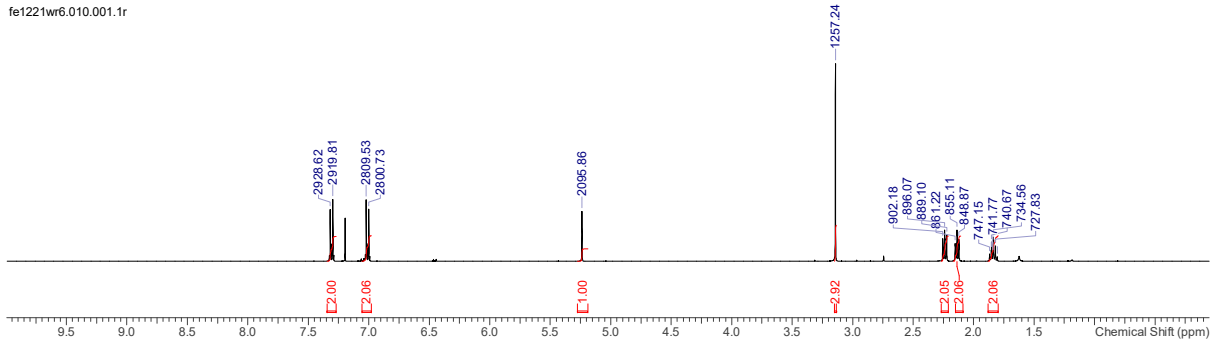
N-Methyl-4-(trifluoromethyl)aniline (1.00 g, 5.71 mmol), 1 3-cyclohexanedione (608 mg, 5.43 mmol) and *p*TSA (150 mg, 0.87 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19g** (968 mg, 3.6 mmol, 67%) as an orange solid. **MP**: 60 – 61 °C. **IR** ν_{max} (film, cm^{-1}): 2952 (br), 1607 (m), 1553 (s), 1320 (s), 1104 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (2 H, dd, *J* = 8.4 Hz, 2 × Ar**H**), 7.27 (2 H, d, *J* = 8.3 Hz, 2 × Ar**H**), 5.34 (1 H, s, C**H**), 3.26 (3 H, s, C**H**$_3$), 2.32 (2 H, dd, *J* = 6.9, 6.1 Hz, C**H**$_2$), 2.24 (2 H, t, *J* = 6.1 Hz, C**H**$_2$), 1.92 (2 H, quin, *J* = 6.6 Hz, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.7 (**C**), 164.2 (**C**), 148.4 (**C**), 129.3 (q, $J_{C\text{-}F}$ = 33 Hz, **C**), 127.5 (2 × **C**H), 126.8 (q, $J_{C\text{-}F}$ = 3.7 Hz, 2 × **C**H), 123.6 (q, $J_{C\text{-}F}$ = 272.2 Hz, **C**H), 101.9 (**C**H), 40.6 (**C**H$_2$), 36.0 (**C**H$_3$), 28.5 (**C**H$_2$), 22.5 (**C**H$_2$) ppm. **^{19}F{H} NMR** (376 MHz, $CDCl_3$): –62.81 (3 F, s, C**F**$_3$) ppm. **LRMS** (ESI$^+$): 292 [M+Na]$^+$, 270 [M+H]$^+$. **HRMS** (ESI$^+$): Found 270.1100, $C_{14}H_{15}F_3NO_2$ [M+H]$^+$ requires 270.1107.

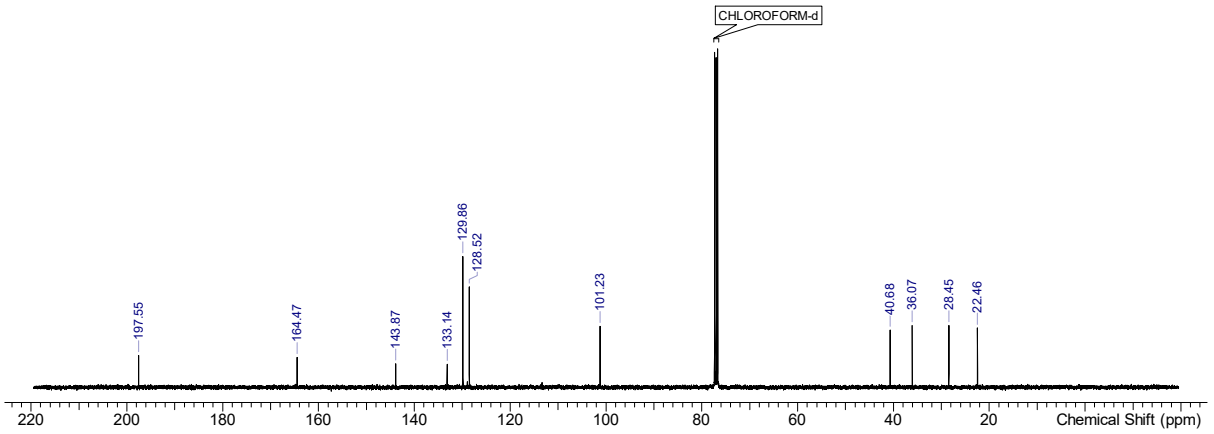


3-((4-Chlorophenyl)(methyl)amino)cyclohex-2-en-1-one, 19h

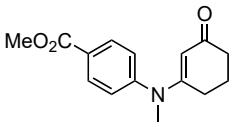


A solution of 4-chloro-*N*-methylaniline (1.196 g, 8.45 mmol), 1,3-cyclohexadione (901 mg, 8.04 mmol) and *p*TSA (20 mg) in toluene (100 mL) was heated at reflux for 17 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% acetone in DCM) to afford the *title compound* **19h** (1.44 g, 6.11 mmol, 76%) as a white solid. **MP** 162–164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (2H, d, *J* = 8.8 Hz, 2 × Ar**H**), 7.01 (2H, d, *J* = 8.8 Hz, 2 × Ar**H**), 5.24 (1H, s, C**H**), 3.14 (3H, s, C**H**$_3$), 2.24 (2H, dd, *J* = 7.1, 6.0 Hz, C**H**$_2$), 2.14 (2H, app. t, *J* = 6.2 Hz, C**H**$_2$), 1.88 – 1.80 (2H, m, C**H**$_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.8 (**C**), 164.5 (**C**), 143.9 (**C**), 133.1 (**C**), 129.9 (2 × **C**H), 128.5 (2 × **C**H), 101.2 (**C**H), 40.7 (**C**H$_3$), 36.1 (**C**H$_2$), 28.5 (**C**H$_2$), 22.5 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 236 [M(^{35}Cl)+H]$^+$. Data is consistent with literature values.[10]

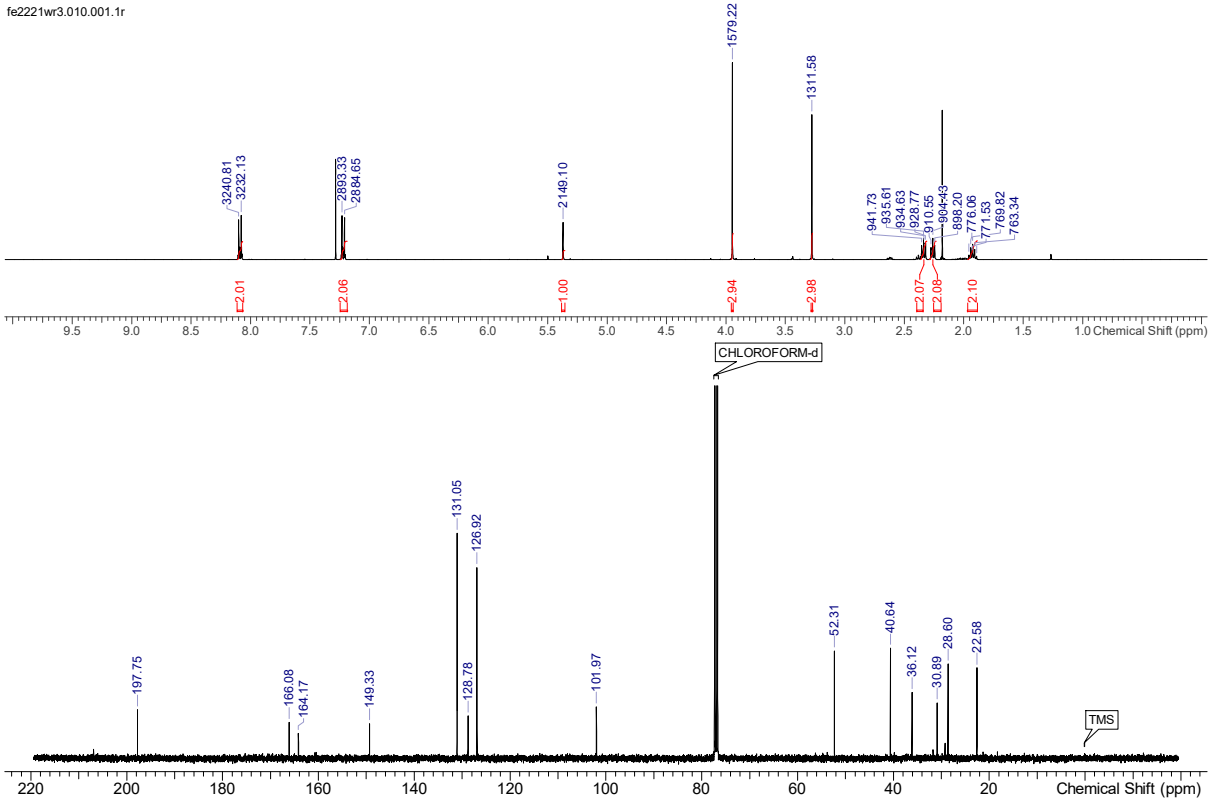




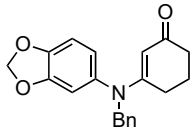
Methyl 4-(methyl(3-oxocyclohex-1-en-1-yl)amino)benzoate, **19k**



A solution of methyl-4-(methylamino)benzoate (991 mg, 6.00 mmol), 1,3-cyclohexa-dione (611 mg, 5.00 mmol) and *p*TSA (10 mg) in toluene (50 mL) was heated at reflux for 17 h. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 50% acetone in DCM) to afford the *title compound* **19k** (1.06 g, 4.09 mmol, 82%) as a yellow solid. **MP** 111–113 °C. **IR** ν_{max} (film, cm^{-1}): 2950 (w), 1719 (m), 1557 (s), 1273 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (2H, d, *J* = 8.7 Hz, 2 × Ar**H**), 7.22 (2H, d, *J* = 8.7 Hz, 2 × Ar**H**), 5.37 (1H, s, C**H**), 3.95 (3H, s, C$\mathbf{H}_3$), 3.28 (3H, s, C$\mathbf{H}_3$), 2.34 (2H, dd, *J* = 7.0, 6.0 Hz, C$\mathbf{H}_2$), 2.26 (2H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 1.92 (2H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.8 (**C**), 166.1 (**C**), 164.3 (**C**), 149.3 (**C**), 131.1 (2 × **C**H), 128.8 (**C**), 126.9 (2 × **C**H), 101.9 (**C**H), 52.4 (C$\mathbf{H}_3$), 40.7 (C$\mathbf{H}_3$), 36.1 (C$\mathbf{H}_2$), 28.6 (C$\mathbf{H}_2$), 22.6 (C$\mathbf{H}_2$) ppm. **LRMS** (ESI$^+$): 260 [M+H]$^+$. **HRMS** (ESI$^+$): Found 260.1285, $C_{15}H_{18}NO_3$ [M+H]$^+$ requires 260.1281.

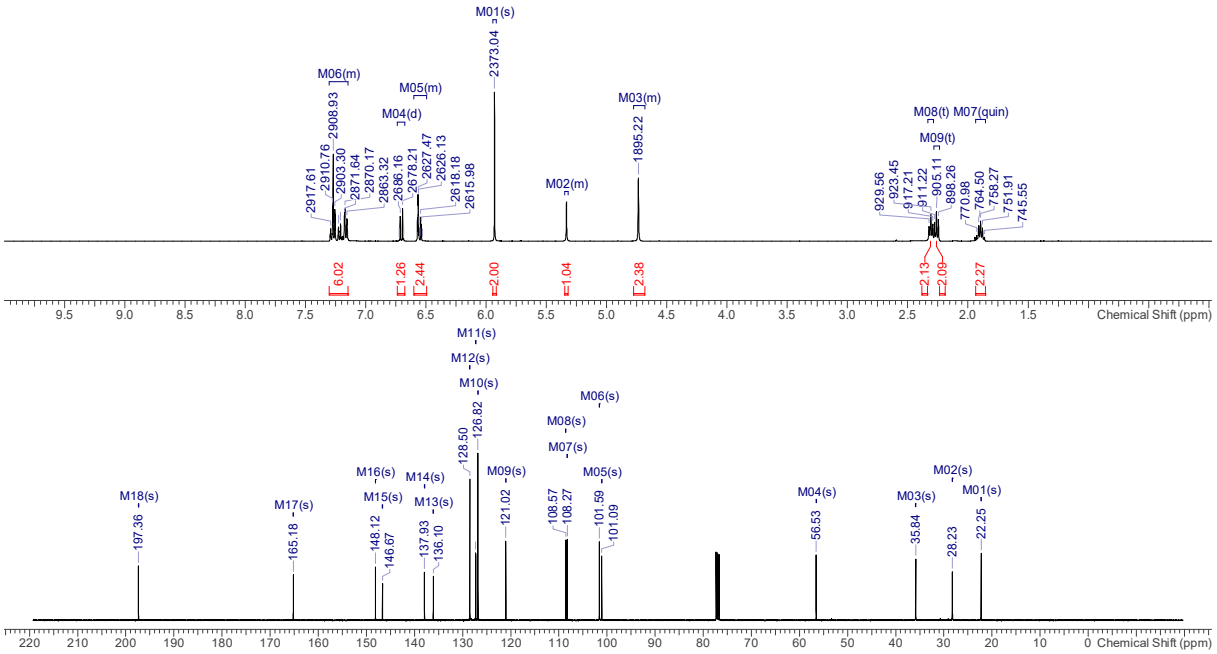


3-(Benzo[*d*][1,3]dioxol-5-yl(benzyl)amino)cyclohex-2-en-1-one, 19l

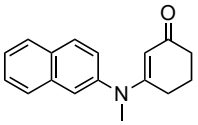


N-Benzylbenzo[d][1,3]dioxol-5-amine (787 mg, 3.47 mmol), 1,3-cyclohexanedione (350 mg, 3.13 mmol) and *p*TSA (50 mg, 0.290 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19l** (802 mg, 2.50 mmol, 81%) as an off-white oil. **IR** ν_{max} (film, cm^{-1}): 3391 (br), 2962 (br), 1607 (m), 1546 (s), 1481 (s), 1235 (m), 1183 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 – 7.16 (5 H, m, 5 × Ar**H**), 6.70 (1 H, d, *J* = 8.0 Hz, Ar**H**), 6.57 – 6.54 (2 H, m, 2 × Ar**H**), 5.93 (2 H, s, C$\mathbf{H}_2$), 5.33 (1 H, s, C**H**), 4.74 (2 H, s, C$\mathbf{H}_2$), 2.31 (2 H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.26 (2 H, t, *J* = 6.5 Hz, C$\mathbf{H}_2$), 1.89 (2 H, app. quin, *J* = 6.1 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4 (**C**), 165.2 (**C**), 148.1 (**C**), 146.7 (**C**), 137.9 (**C**), 136.1 (**C**), 128.5 (2 × **C**H), 127.3 (**C**H), 126.8 (2 × **C**H),

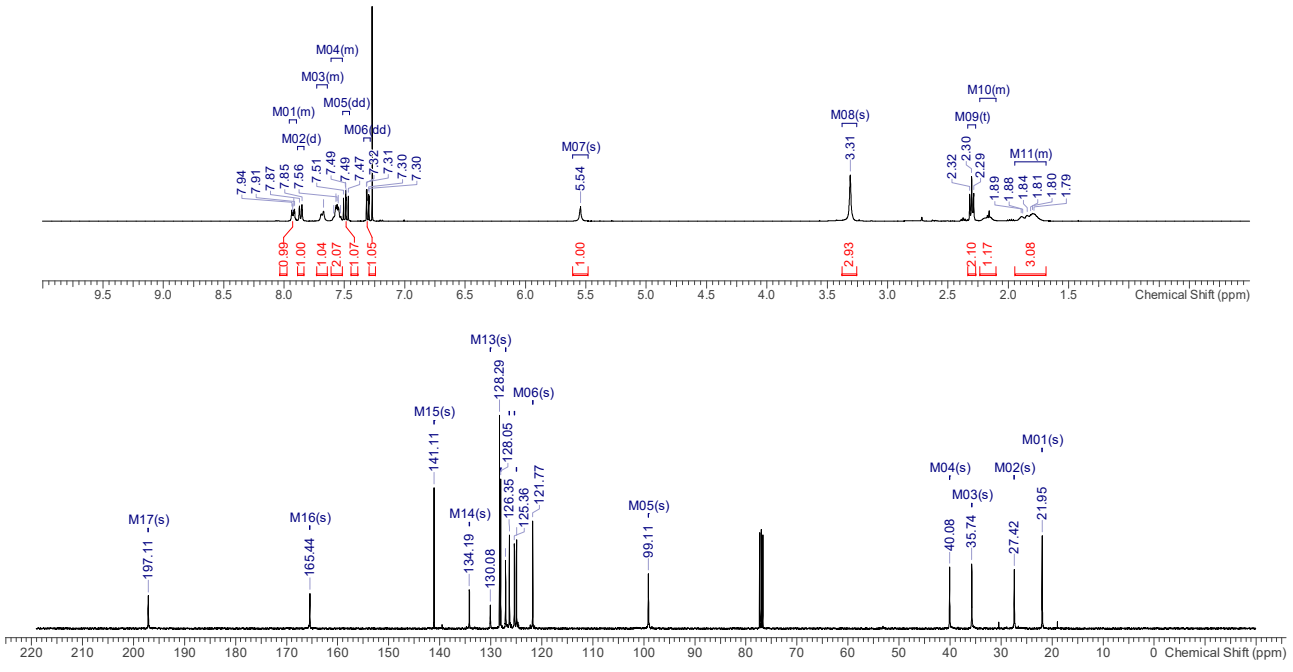
121.0 (**C**H), 108.6 (**C**H), 108.3 (**C**H), 101.6 (**C**H_2), 101.1 (**C**H), 56.2 (**C**H_2), 35.8 (**C**H_2), 28.2 (**C**H_2), 22.3 (**C**H_2) ppm. **LRMS** (ESI$^+$): 665 [2M+Na]$^+$, 344 [M+Na]$^+$, 322 [M+H]$^+$. **HRMS** (ESI$^+$): Found 322.1438, $C_{20}H_{20}NO_3$ [M+H]$^+$ requires 322.1444.



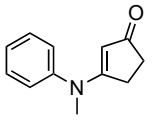
3-(Methyl(naphthalen-2-yl)amino)cyclohex-2-en-1-one, 19m



N-Methylnaphthalen-1-amine (1.07 g, 6.81 mmol), 1,3-cyclohexanedione (692 mg, 6.18 mmol) and *p*TSA (50 mg, 0.290 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **19m** (1.16 g, 4.62 mmol, 75%) as an off-white oil. **IR** ν_{max} (film, cm^{-1}): 2946 (br), 1615 (m), 1549 (s), 1396 (m), 1322 (m), 1190 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (1 H, m, Ar**H**), 7.86 (1 H, d, *J* = 8.2 Hz, Ar**H**), 7.69 (1 H, m, Ar**H**), 7.59 – 7.53 (2 H, m, 2 × Ar**H**), 7.49 (1 H, dd, *J* = 8.3, 7.3 Hz, Ar**H**), 7.31 (1 H, dd, *J* = 7.2, 1.1 Hz, Ar**H**), 5.54 (1 H, s, C**H**), 3.31 (3 H, s, CH_3), 2.30 (2 H, t, *J* = 6.5 Hz, CH_2), 2.17 (1 H, br, C**H**H), 1.89 – 1.79 (3 H, m, CH_2 + CH**H**) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1 (**C**), 165.4 (**C**), 141.1 (**C**), 134.2 (**C**), 130.1 (**C**), 128.3 (**C**H), 128.1 (**C**H), 127.1 (**C**H), 126.4 (**C**H), 125.4 (**C**H), 125.0 (**C**H), 121.8 (**C**H), 99.1 (**C**H), 40.1 (**C**H_2), 35.7 (**C**H_3), 27.4 (**C**H_2), 22.0 (**C**H_2) ppm. **LRMS** (ESI$^+$): 525 [2M+Na]$^+$, 503 [2M+H]$^+$, 274 [M+Na]$^+$, 252 [M+H]$^+$. **HRMS** (ESI$^+$): Found 252.1383, $C_{17}H_{18}NO$ [M+H]$^+$ requires 252.1389.

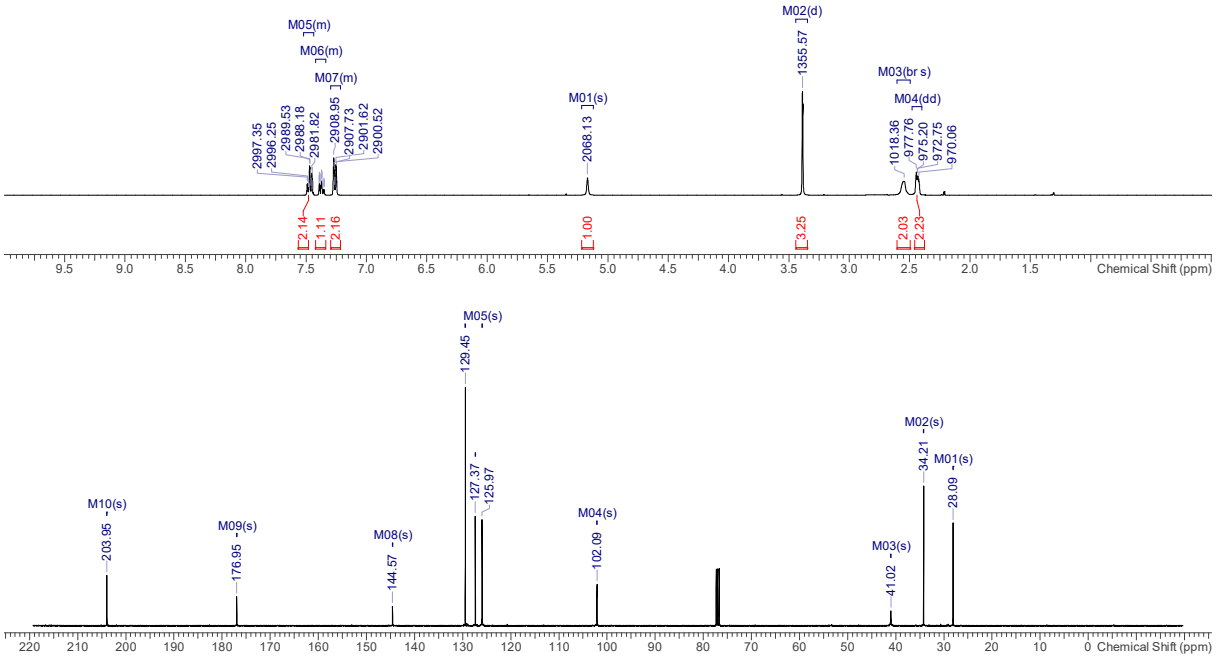


3-(Methyl(phenyl)amino)cyclopent-2-en-1-one, 21a

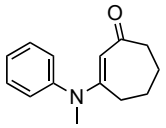


N-Methylaniline (1.16 mL, 10.7 mmol), 1,3-cyclopentanedione (960 mg, 9.80 mmol) and *p*TSA (30 mg, 0.174 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The

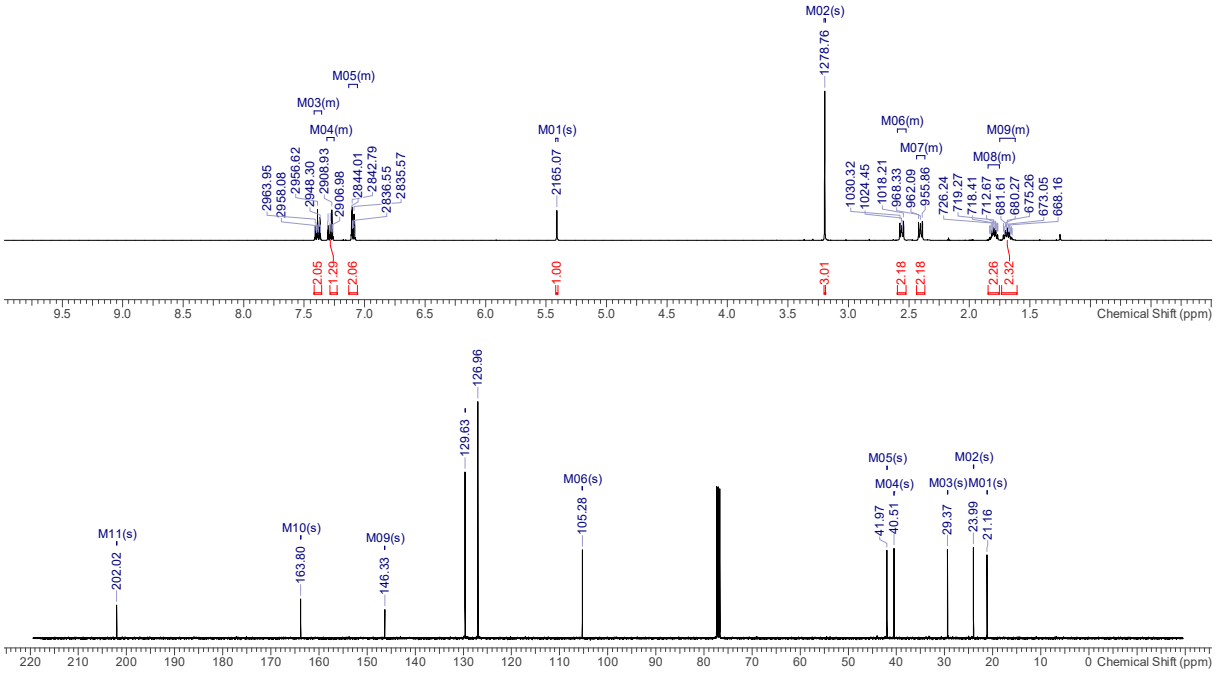
resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 20% acetone/DCM) to afford the *title compound* **21a** (1.42 g, 7.59 mmol, 78%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 3050 (br), 2924 (br), 1648 (s), 1541 (s), 1191 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 – 7.44 (2 H, m, 2 × Ar**H**), 7.37 (1 H, m, Ar**H**), 7.27 – 7.24 (2 H, m, 2 × Ar**H**), 5.17 (1 H, s, C**H**), 3.39 (3 H, br s, C$\mathbf{H}_3$), 2.55 (2 H, br s, C$\mathbf{H}_2$), 2.44 – 2.42 (2 H, m, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.0 (**C**), 177.0 (**C**), 144.6 (**C**), 129.5 (2 × **C**H), 127.4 (**C**H), 126.0 (2 × **C**H), 102.1 (**C**H), 41.0 (**C**H_3), 34.2 (**C**H_2), 28.1 (**C**H_2) ppm. **LRMS** (ESI^+): 188 $[M+H]^+$. Data is consistent with literature values.[28]



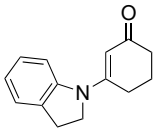
3-(Methyl(phenyl)amino)cyclohept-2-en-1-one, 21b



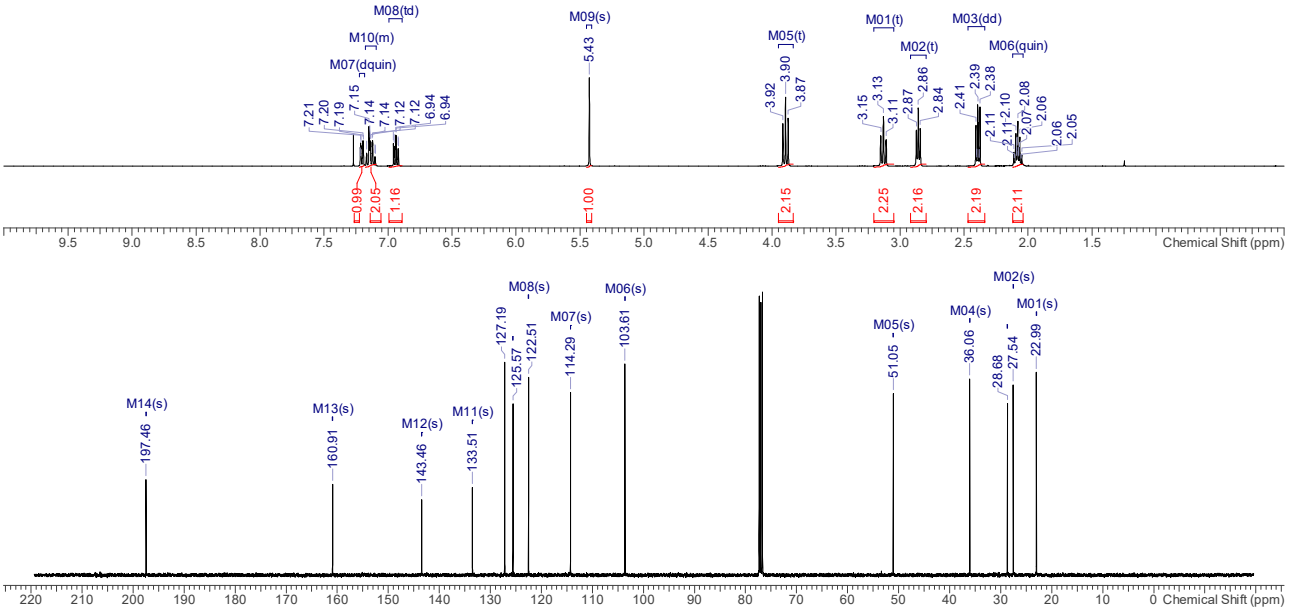
N-Methylaniline (1.00 mL, 9.22 mmol), 1,3-cycloheptanedione (0.88 mL, 7.68 mmol) and *p*TSA (150 mg, 0.87 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **21b** (1.10 g, 5.12 mmol, 66%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2949 (br), 1602 (m), 1546 (s), 1257 (m), 1199 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 – 7.36 (2 H, m, 2 × Ar**H**), 7.28 (1 H, m, Ar**H**), 7.11 – 7.08 (2 H, m, 2 × Ar**H**), 5.41 (1 H, s, C$\mathbf{H}_3$), 3.20 (3 H, s, C$\mathbf{H}_3$), 2.57 – 2.54 (2 H, m, C$\mathbf{H}_2$), 2.42 – 2.39 (2 H, m, C$\mathbf{H}_2$), 1.83 – 1.77 (2 H, m, C$\mathbf{H}_2$), 1.72 – 1.65 (2 H, m, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.0 (**C**), 163.8 (**C**), 146.3 (**C**), 129.6 (2 × **C**H), 127.0 (3 × **C**H), 105.3 (**C**H), 42.0 (**C**H_3), 40.5 (**C**H_2), 29.4 (**C**H_2), 24.0 (**C**H_2), 21.1 (**C**H_2) ppm. **LRMS** (ESI^+): 238 $[M+Na]^+$, 216 $[M+H]^+$. **HRMS** (ESI^+): Found 216.1383, $C_{14}H_{18}NO$ $[M+H]^+$ requires 216.1388.



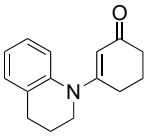
3-(Indolin-1-yl)cyclohex-2-en-1-one, 21d



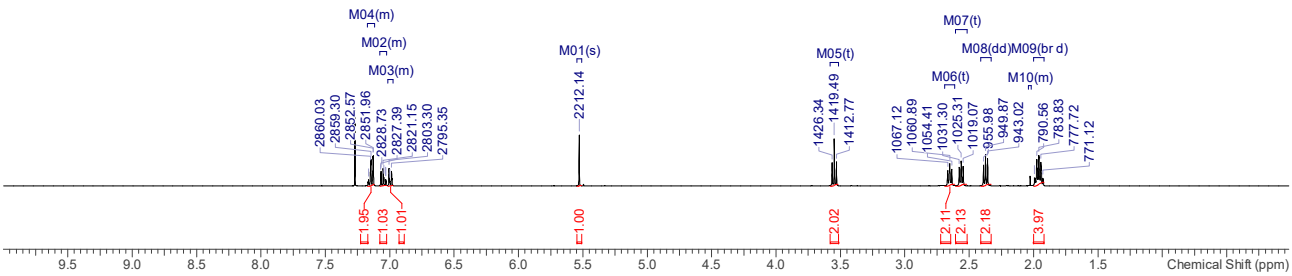
Indoline (1.2 mL, 10.7 mmol), 1,3-cyclohexanedione (1.14 g, 10.2 mmol) and *p*TSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **21f** (1.85 g, 8.70 mmol, 81%) as a brown solid. **MP**: 81 – 82 °C. **IR** ν_{max} (film, cm^{-1}): 2942 (br), 1617 (s), 1541 (s), 1460 (s), 1254 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 (1 H, dtd, *J* = 7.3, 1.1, 0.98 Hz, Ar**H**), 7.17 – 7.10 (2 H, m, 2 × Ar**H**), 6.94 (1 H, td, *J* = 7.2, 1.5 Hz, Ar**H**), 5.43 (1 H, s, C**H**), 3.89 (2 H, t, *J* = 8.3 Hz, C$\mathbf{H}_2$), 3.14 (2 H, t, *J* = 8.1 Hz, C$\mathbf{H}_2$), 2.86 (2 H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.39 (2 H, dd, *J* = 7.2, 5.9 Hz, C$\mathbf{H}_2$), 2.08 (2 H, quin, *J* = 6.7 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.5 (**C**), 160.9 (**C**), 143.5 (**C**), 133.5 (**C**), 127.2 (**C**H), 125.6 (**C**H), 122.5 (**C**H), 114.3 (**C**H), 103.6 (**C**H), 51.1 (**C**H_2), 36.1 (**C**H_2), 28.7 (**C**H_2), 27.5 (**C**H_2), 23.0 (**C**H_2) ppm. **LRMS** (ESI$^+$): 236 [M+Na]$^+$, 214 [M+H]$^+$. **HRMS** (ESI$^+$): Found 214.1226, $C_{14}H_{16}NO$ [M+H]$^+$ requires 214.1231.

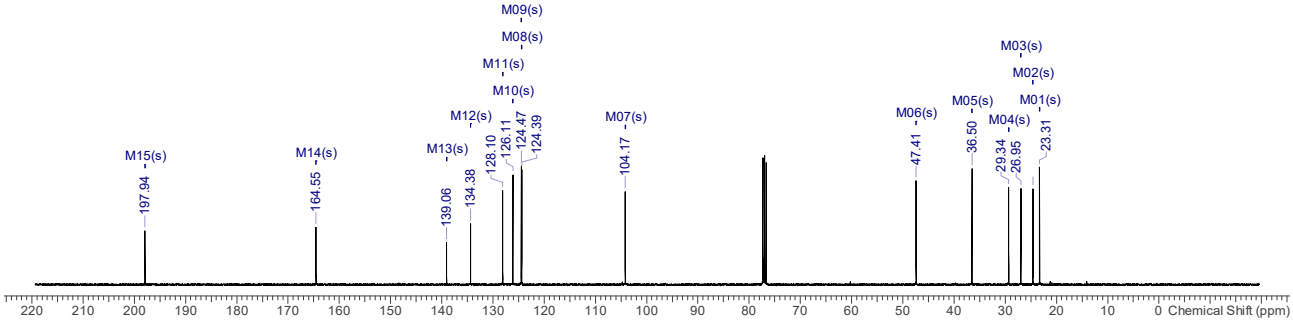


3-(3,4-dihydroquinolin-1(2H)-yl)cyclohex-2-en-1-one, 21e

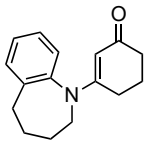


1,2,3,4-tetrahydroquinoline (1.2 mL, 9.56 mmol), 1,3-cyclohexanedione (1020 mg, 9.11 mmol) and *p*TSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **21e** (1.99 g, 8.78 mmol, 92%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2946 (br), 1610 (m), 1542 (s), 1487 (s), 1181 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 – 7.13 (2 H, m, 2 × Ar**H**), 7.05 (1 H, m, Ar**H**), 6.99 (1 H, m, Ar**H**), 5.53 (1 H, s, C**H**), 3.55 (2 H, t, *J* = 6.8 Hz, C$\mathbf{H}_2$), 2.65 (2 H, t, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.56 (2 H, t, *J* = 6.0 Hz, C$\mathbf{H}_2$), 2.37 (2 H, dd, *J* = 6.9, 6.1 Hz, C$\mathbf{H}_2$), 1.99 – 1.93 (4 H, m, 2 × C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.9 (**C**), 184.6 (**C**), 139.1 (**C**), 134.4 (**C**), 128.1 (**C**H), 126.1 (**C**H), 124.5 (**C**H), 124.4 (**C**H), 104.2 (**C**H), 47.4 (**C**H_2), 36.5 (**C**H_2), 29.3 (**C**H_2), 27.0 (**C**H_2), 24.6 (**C**H_2), 23.3 (**C**H_2) ppm. **LRMS** (ESI$^+$): 250 [M+Na]$^+$, 228 [M+H]$^+$. **HRMS** (ESI$^+$): Found 228.1389, $C_{15}H_{18}NO$ [M+H]$^+$ requires 228.1383.

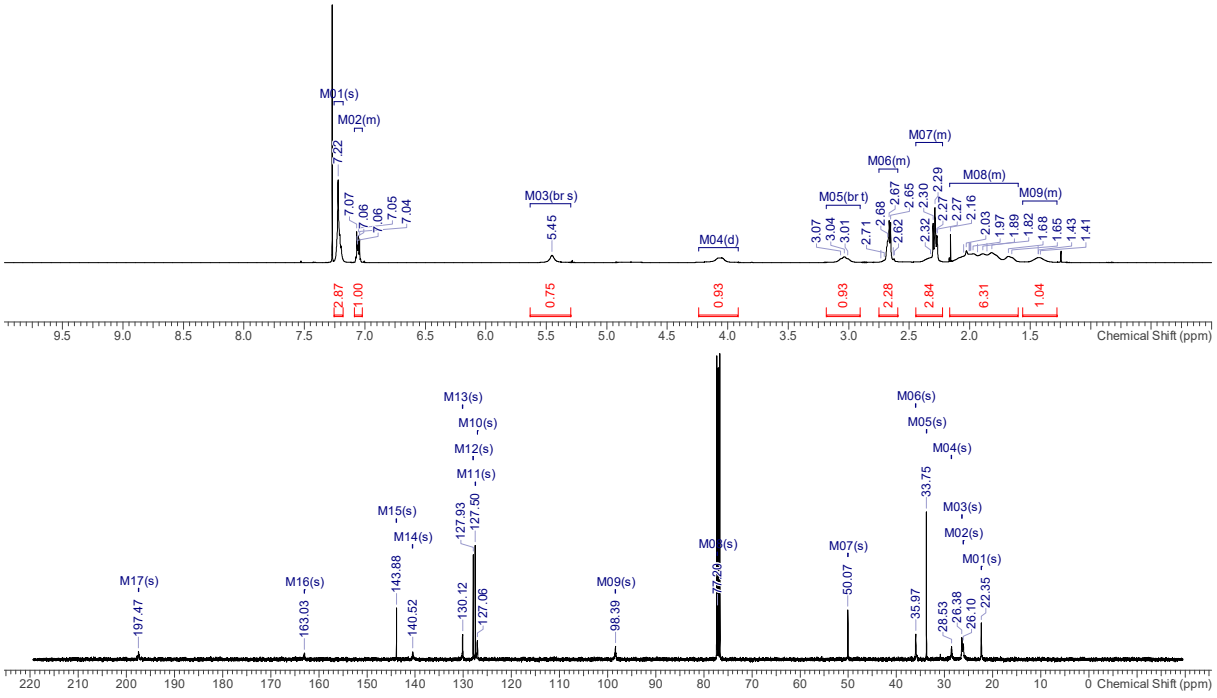




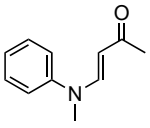
3-(2,3,4,5-Tetrahydro-1*H*-benzo[*b*]azepin-1-yl)cyclohex-2-en-1-one, 21f



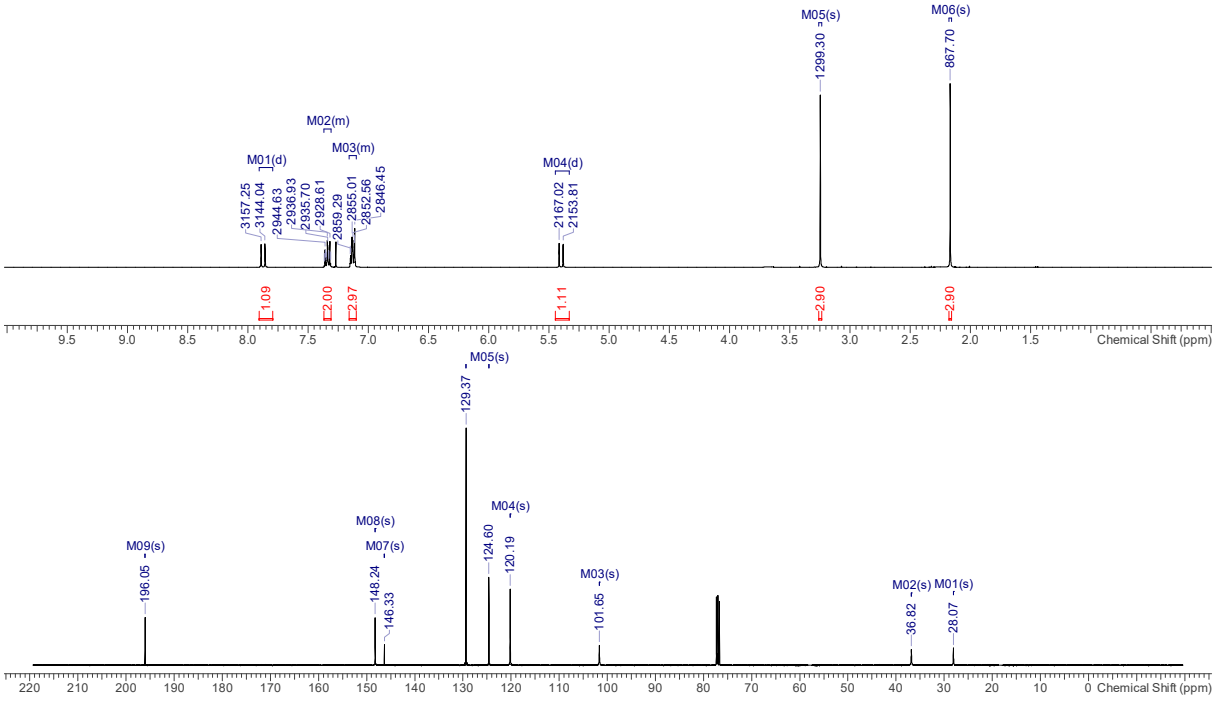
2,3,4,5-Tetrahydro-1*H*-benzo[b]azepine (939 mg, 6.39 mmol), 1,3-cyclohexanedione (680 mg, 6.07 mmol) and *p*TSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 30% acetone/DCM) to afford the *title compound* **21f** (1.23 g, 5.10 mmol, 84%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2940 (br), 1615 (m), 1541 (s), 1488 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (3 H, br s, 3 × Ar**H**), 7.06 (1 H, m, Ar**H**), 5.45 (1 H, br s, C**H**), 4.06 (1 H, br, C**H**H), 3.04 (1 H, br, CH**H**), 2.21 – 2.62 (2 H, m, CH_2), 2.40 – 2.27 (3 H, m, CH_2 + C**H**H), 2.03 – 1.65 (6 H, m, 3 × CH_2), 1.43 (1 H, br s, CH**H**) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.5 (**C**), 163.0 (**C**), 143.9 (**C**), 140.5 (**C**), 130.1 (**C**H), 127.9 (**C**H), 127.5 (**C**H), 127.1 (**C**H), 98.4 (**C**H), 50.1 (**C**H_2), 36.0 (**C**H_2), 33.8 (**C**H_2), 28.5 (**C**H_2), 26.4 (**C**H_2), 26.1 (**C**H_2), 22.4 (**C**H_2) ppm. **LRMS** (ESI^+): 264 $[M+Na]^+$, 242 $[M+H]^+$. **HRMS** (ESI^+): Found 242.1539, $C_{16}H_{20}NO$ $[M+H]^+$ requires 242.1546.



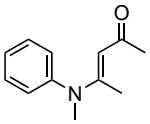
(*E*)-4-(Methyl(phenyl)amino)but-3-en-2-one, 23a



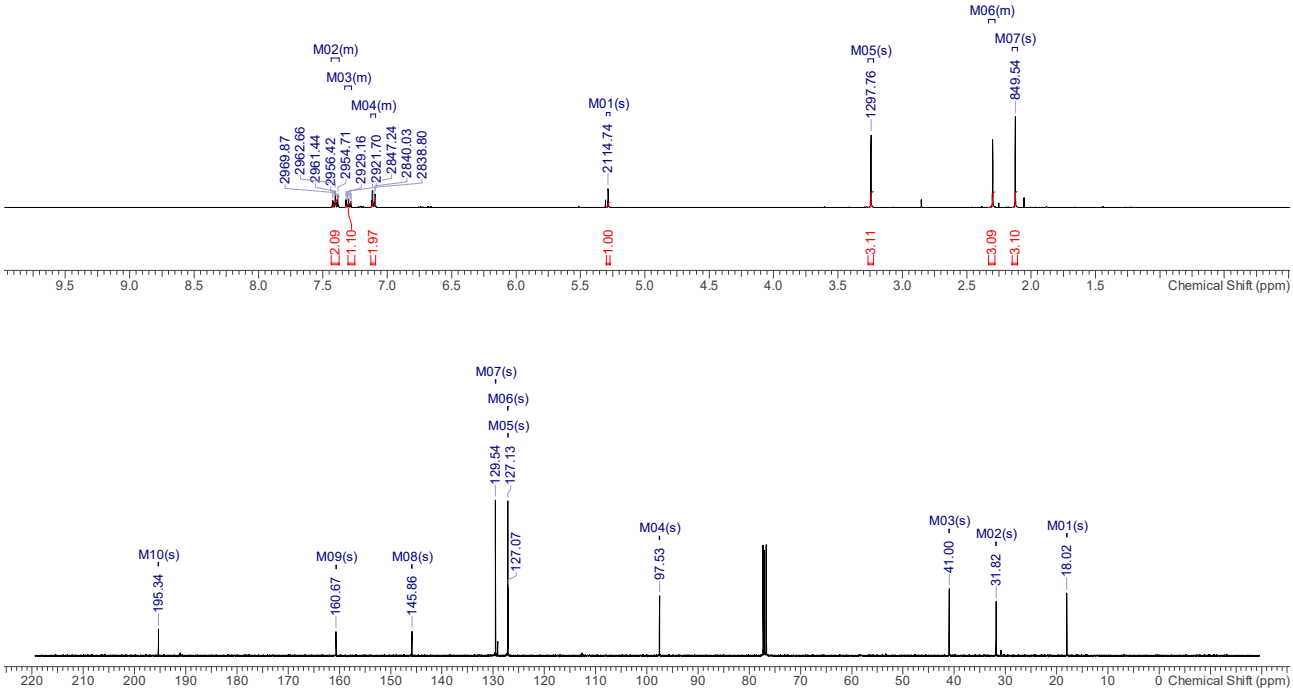
A solution of 3-butyn-2-one (0.94 mL, 12.02 mmol) in EtOH (10 mL) was added *N*-methylaniline (1.08 mL, 9.98 mmol). After 16 h at RT the resulting solution was concentrated *in vacuo* then purified by column chromatography (30 – 60% EtOAc/petrol) to afford the *title compound* **23a** (1.63 g, 0.95 mmol, 95%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 3465 (br), 3040 (br), 1544 (s), 1494 (s), 1346 (m), 1251 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (1 H, d, *J* = 13.2 Hz, =C**H**), 7.37 – 7.31 (2 H, m, 2 × Ar**H**), 7.15 – 7.11 (3 H, m, 3 × Ar**H**), 5.40 (1 H, d, *J* = 13.2 Hz, =C**H**), 3.25 (3 H, s, CH_3), 2.17 (3 H, s, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.1 (**C**), 148.2 (**C**H), 146.3 (**C**), 129.4 (2 × **C**H), 124.6 (2 × **C**H), 120.2 (**C**H), 101.7 (**C**H), 36.8 (**C**H_3), 28.1 (**C**H_3) ppm. **LRMS** (EI): 175 (75%, M^+), 160 (100%, $[M-Me]^+$), 132 (90%), 117 (73%). Data is consistent with literature values.[29]



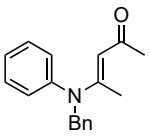
(*E*)-4-(Methyl(phenyl)amino)pent-3-en-2-one, 23b



N-Methylaniline (1.19 mL, 11.0 mmol), 2,4-pentanedione (1.02 mL, 9.95 mmol) and *p*TSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxhlet filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 40% Et_2O/petrol) to afford the *title compound* **23b** (1.27 g, 6.72 mmol, 67%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 3409 (br), 2934 (br), 1604 (s), 1508 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.38 (2 H, m, 2 × Ar**H**), 7.30 (1 H, m, Ar**H**), 7.11 (1 H, m, Ar**H**), 5.29 (1 H, s, C**H**), 3.24 (3 H, s, C$\mathbf{H}_3$), 2.30 (3 H, s, C$\mathbf{H}_3$), 2.12 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.3 (**C**), 160.7 (**C**), 145.9 (**C**), 129.5 (2 × **C**H), 127.13 (2 × **C**H), 127.07 (**C**H), 97.5 (**C**H), 41.0 (**C**H_3), 31.8 (**C**H_3), 18.0 (**C**H_3) ppm. **LRMS** (ESI^+): 212 $[M+Na]^+$, 190 $[M+H]^+$.[30]

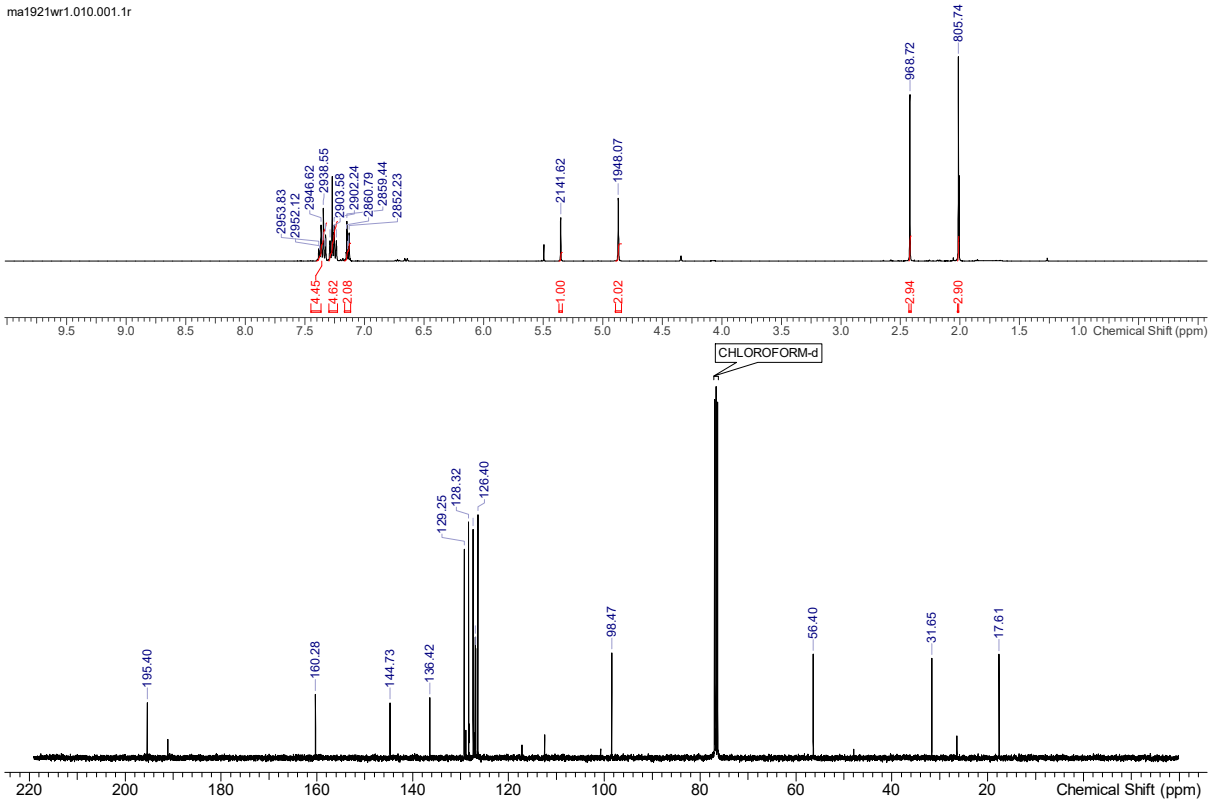


(*E*)-4-(Benzyl(phenyl)amino)pent-3-en-2-one, 23c

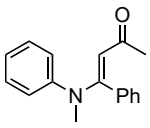


A solution of *N*-benzylaniline (1.83 g, 10.00 mmol), 2,4-pentanedione (1.23 mL, 12.00 mmol) and pTSA (10 mg) in toluene (100 mL) were heated at reflux under a soxhlet filled with 4Å molecular sieves for 40 h then cooled to RT. The resulting solution was concentrated in *vacuo* and purified by column chromatography (0 to 20%

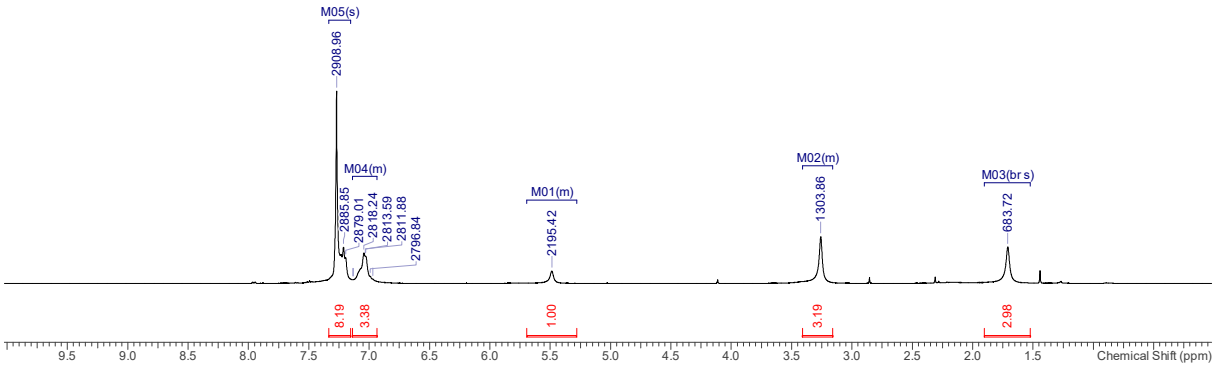
EtOAc in hexanes) to give the *title compound* **23c** (1.12 g, 4.22 mmol, 42%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 3030 (br), 1526 (s), 1490 (m), 1417 (m), 1176 (m), 698 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 – 7.31 (4H, m, 4 × Ar**H**), 7.30 – 7.22 (4H, m, 4 × Ar**H**), 7.17 – 7.12 (2H, m, 2 × Ar**H**), 5.35 (1H, s, C**H**), 4.87 (2H, s, C$\mathbf{H}_2$), 2.42 (3H, s, C$\mathbf{H}_3$), 2.01 (3H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 195.4 (**C**), 160.3 (**C**), 144.7 (**C**), 136.4 (**C**), 129.3 (2 × **C**H), 128.3 (2 × **C**H), 127.4 (2 × **C**H), 127.0 (**C**H), 126.9 (**C**H), 126.4 (2 × **C**H), 98.5 (**C**H), 56.4 (C$\mathbf{H}_2$), 31.7 (C$\mathbf{H}_3$), 17.6 (C$\mathbf{H}_3$) ppm. **LRMS** (EI): 265 (33%, M$^+$), 248 (77%), 222 (70%), 118 (80%), 91 (100%). **HRMS** (EI): Found 265.1464, $C_{18}H_{19}NO$ [M$^+$] requires 265.1461.

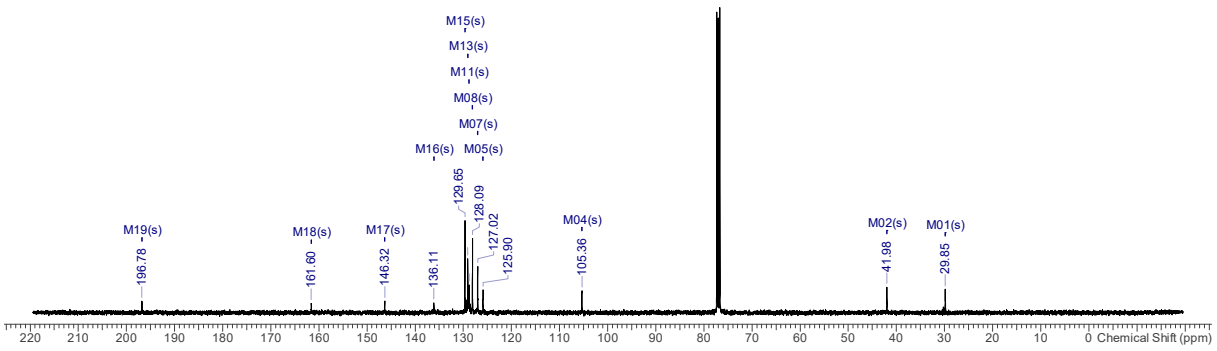


(*E*)-4-(Methyl(phenyl)amino)-4-phenylbut-3-en-2-one, 23d

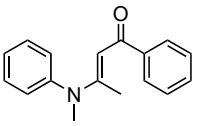


To a solution of 4-phenylbut-3-yn-2-one (0.50 mL, 3.44 mmol) in EtOH (10 mL) was added *N*-methylaniline (0.44 mL, 3.5 mmol). After 16 h at RT, the resulting solution was concentrated *in vacuo* then purified by column chromatography (40 – 50% EtOAc/petrol) to afford the *title compound* **23d** (803 mg, 3.2 mmol, 91%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 3058 (br), 1527 (s), 1487 (s), 1386 (m), 1258 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 – 7.20 (7 H, m, 7 × Ar**H**), 7.13 – 6.97 (3 H, m, 3 × Ar**H**), 5.49 (1 H, br s, C**H**), 3.28 (3 H, br s, C$\mathbf{H}_3$), 1.71 (3 H, br s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.8 (**C**), 161.6 (**C**), 146.3 (**C**), 136.1 (**C**), 129.7 (2 × **C**H), 129.1 (**C**H), 128.8 (**C**H), 128.59 (**C**H), 128.56 (**C**H), 128.1 (2 × **C**H), 127.0 (**C**H), 125.9 (**C**H), 105.4 (**C**H), 50.0 (C$\mathbf{H}_3$), 29.9 (C$\mathbf{H}_3$) ppm. **LRMS** (ESI$^+$): 274 [M+Na]$^+$, 252 [M+H]$^+$. **HRMS** (ESI$^+$): Found 252.1389, $C_{17}H_{18}NO$ [M+H]$^+$ requires 252.1383.

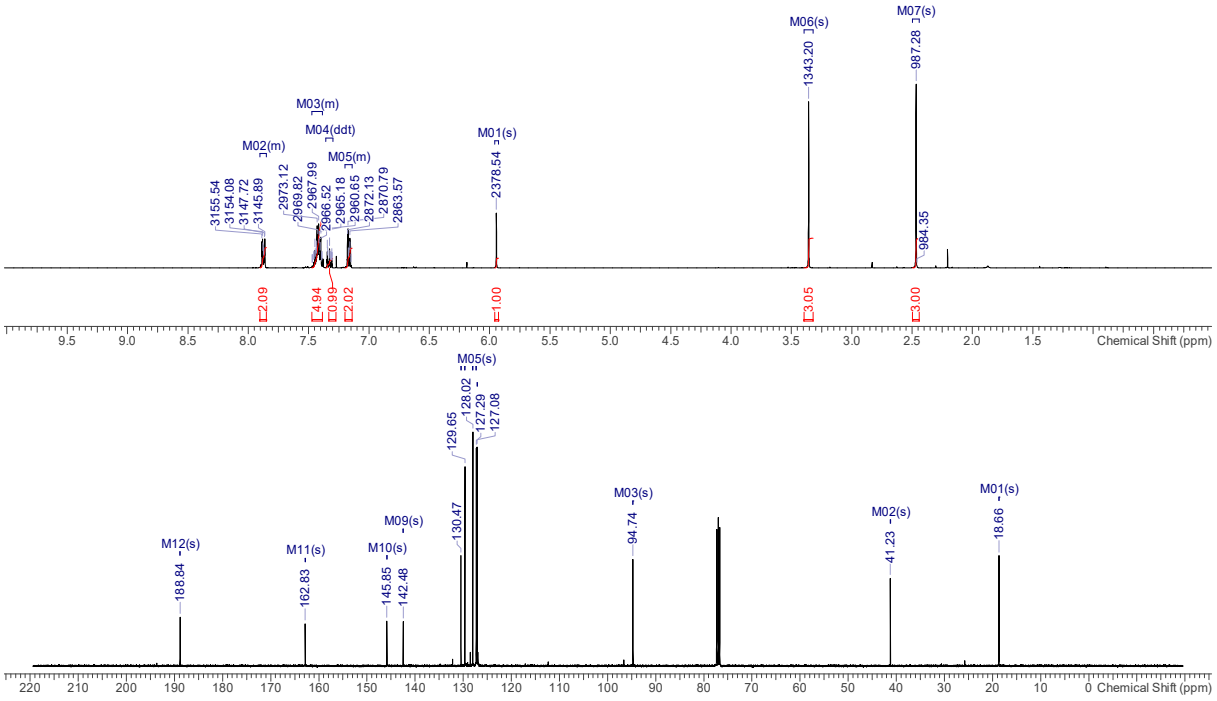




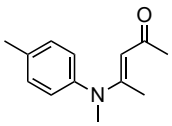
(*E*)-3-(Methyl(phenyl)amino)-1-phenylbut-2-en-1-one, 23e



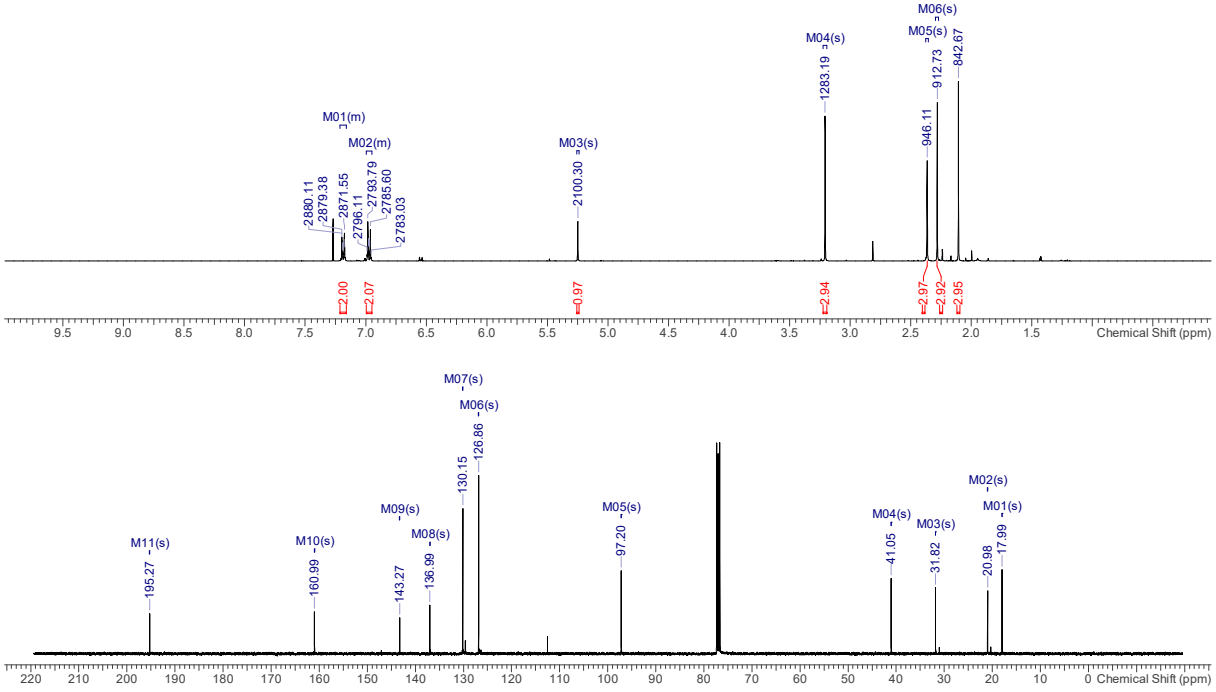
N-methylaniline (1.63 mL, 15.0 mmol), 1-phenyl-1,3-butanedione (2.44 g, 15.0 mmol) and *p*TSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxhlet extractor filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (20 – 50 % EtOAc/petrol) to afford the *title compound* **23e** (2.45 g, 9.76 mmol, 65%) as a yellow oil contaminated with some impurities due to hydrolysis on column chromatography. **IR** ν_{max} (film, cm^{-1}): 2923 (br), 1526 (s), 1215 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 – 7.56 (2 H, m, 2 × Ar**H**), 7.47 – 7.39 (5 H, m, 5 × Ar**H**), 7.33 (1 H, m, Ar**H**), 7.18 – 7.15 (2 H, m, 2 × Ar**H**), 5.94 (1 H, s, C**H**), 3.36 (3 H, s, C**H**$_3$), 2.27 (3 H, s, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.8 (**C**), 162.8 (**C**), 145.9 (**C**), 142.5 (**C**), 130.5 (2 × **C**H), 129.7 (2 × **C**H), 128.0 (2 × **C**H), 127.3 (2 × **C**H), 127.1 (2 × **C**H), 94.7 (**C**H), 41.2 (**C**H$_3$), 18.7 (**C**H$_3$) ppm. **LRMS** (EI): 251 (M$^+$, 20%), 234 (50%), 146 (100%), 106 (60%). **HRMS** (EI): Found 251.1299, $C_{17}H_{17}NO$ M$^+$ requires 251.1305.



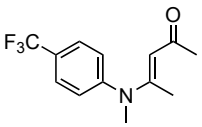
(*E*)-4-(Methyl(*p*-tolyl)amino)pent-3-en-2-one, 23f



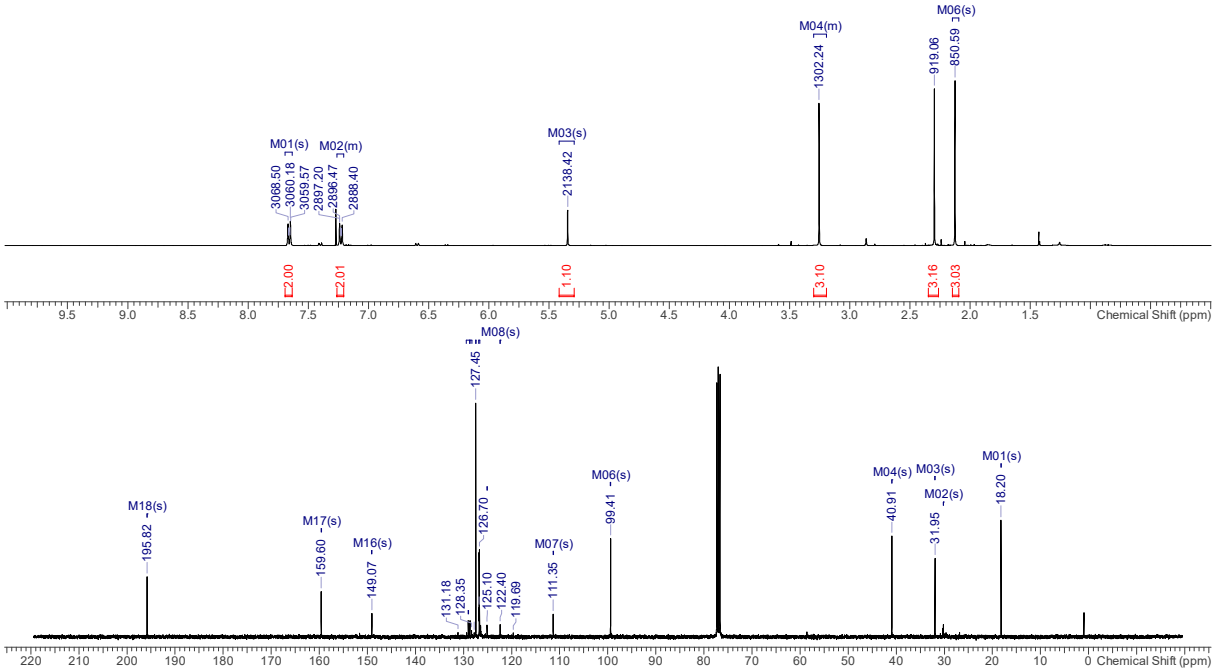
4-Methyl-*N*-methylaniline (1.26 mL, 9.98 mmol), 2,4-pentanedione (1.33 mL, 13.0 mmol) and *p*TSA (150 mg, 0.870 mmol) in toluene (150 mL) were heated at reflux under a soxhlet filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 40% Et_2O/petrol) to afford the *title compound* **23f** (1.44 g, 7.09 mmol, 71%) as a yellow oil contaminated with *ca.* 3 mol% 4-methyl-*N*-methylaniline due to hydrolysis during column chromatography. **IR** ν_{max} (film, cm^{-1}): 2920 (br), 1643 (m), 1530 (s), 1504 (s), 1413 (m), 1182 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 – 7.17 (2 H, m, 2 × Ar**H**), 6.99 – 6.96 (2 H, m, 2 × Ar**H**), 5.25 (1 H, s, C**H**), 3.21 (3 H, s, C**H**$_3$), 2.36 (3 H, s, C**H**$_3$), 2.28 (3 H, s, C**H**$_3$), 2.11 (3 H, s, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.3 (**C**), 161.0 (**C**), 143.3 (**C**), 137.0 (**C**), 130.2 (2 × **C**H), 126.9 (2 × **C**H), 97.2 (**C**H), 41.1 (**C**H$_3$), 31.8 (**C**H$_3$), 21.0 (**C**H$_3$), 18.0 (**C**H$_3$) ppm. **LRMS** (EI): 203 (100%, M$^+$), 188 (100%), 160 (100%), 144 (100%). **HRMS** (EI): Found 203.1305, $C_{13}H_{17}NO$ M$^+$ requires 203.1305.

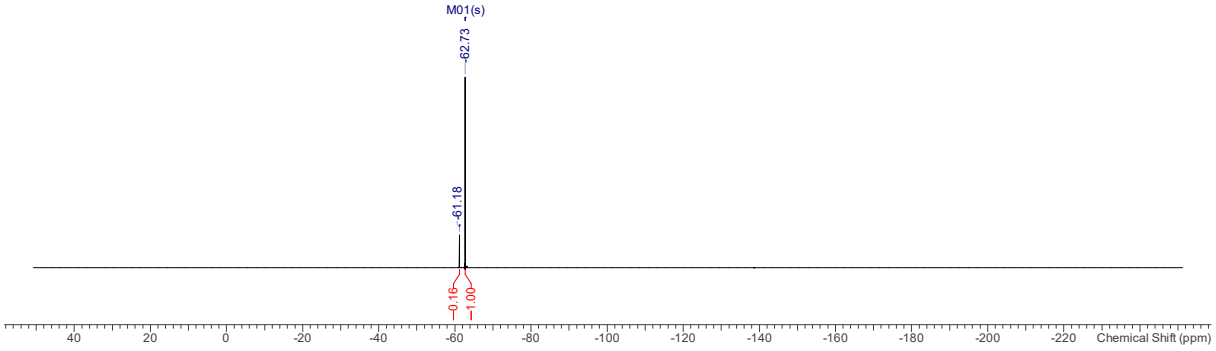


(*E*)-4-(Methyl(4-(trifluoromethyl)phenyl)amino)pent-3-en-2-one, 23g

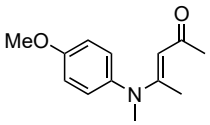


4-Trifluoromethyl-*N*-methylaniline (1.41 mL, 9.98 mmol), 2,4-pentanedione (1.12 mL, 11.0 mmol) and *p*TSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxhlet filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (10 – 40% Et_2O/petrol) to afford the *title compound* **23g** (1.57 g, 6.11 mmol, 61%) as a yellow oil contaminated with ~10 mol% 4-trifluoromethyl-*N*-methylaniline due to hydrolysis during column chromatography. **IR** ν_{max} (film, cm^{-1}): 2929 (br), 1541 (s), 1513 (s), 1324 (s), 1126 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 – 7.65 (2 H, m, 2 × Ar**H**), 7.24 – 7.22 (2 H, m, 2 × Ar**H**), 5.34 (1 H, s, C**H**), 3.25 (3 H, s, C**H**$_3$), 2.30 (3 H, s, C**H**$_3$), 2.13 (3 H, s, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.8 (**C**), 159.6 (**C**), 149.1 (**C**), 128.9 (**C**, $J_{C\text{-}F}$ = 33 Hz), 127.5 (2 × **C**H), 126.7 (2 × **C**H, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (**C**, $J_{C\text{-}F}$ = 272.2 Hz), 99.4 (CH), 40.9 (**C**H$_3$), 32.0 (**C**H$_3$), 18.2 (**C**H$_3$) ppm. **^{19}F{H} NMR** (376 MHz, $CDCl_3$): –62.73 (3 F, s, C**F**$_3$) ppm. **LRMS** (EI): 257 (35%, M^+), 242 (99%), 214 (100%). **HRMS** (EI): Found 256.0944, $C_{13}H_{13}F_3NO$ $[M–H]^+$ requires 256.0949.

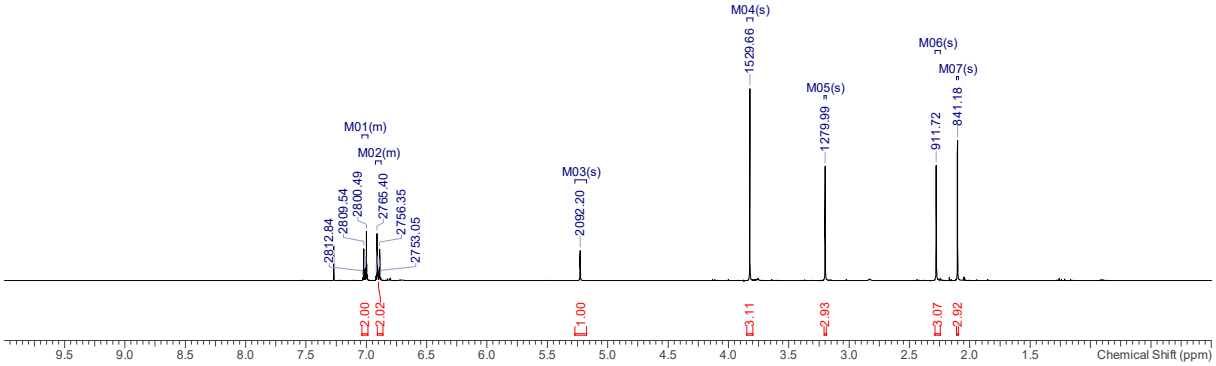


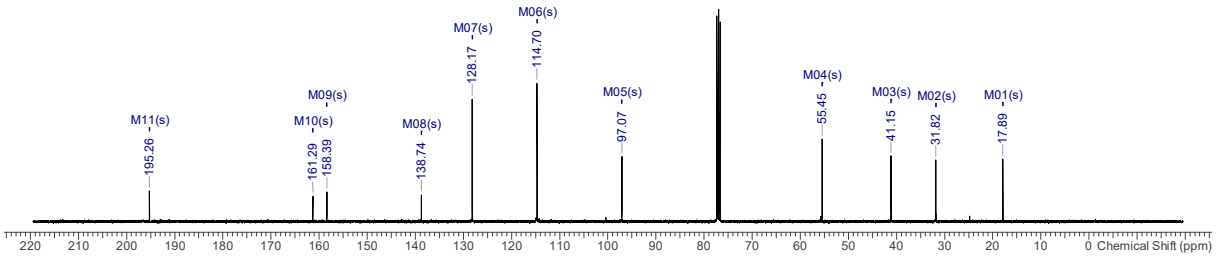


(*E*)-4-((4-Methoxyphenyl)(methyl)amino)pent-3-en-2-one, 23h

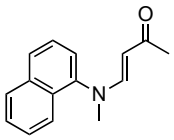


4-methoxy-*N*-methylaniline (1.40 g, 10.2 mmol), 2,4-pentanedione (1.04 mL, 10.2 mmol) and *p*TSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxhlet filled with 4Å MS for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (50 – 70 % EtOAc/petrol) to afford the *title compound* **23h** (1.58 g, 7.21 mmol, 71%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 2952 (br), 1534 (m), 1503 (s), 1419 (m), 1243 (m), 1182 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.03 – 6.99 (2 H, m, 2 × Ar**H**), 6.92 – 6.88 (2 H, m, 2 × Ar**H**), 5.23 (1 H, s, C**H**), 3.82 (3 H, s, C$\mathbf{H}_3$), 3.20 (3 H, s, C$\mathbf{H}_3$), 2.28 (3 H, s, C$\mathbf{H}_3$), 2.21 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.3 (**C**), 161.3 (**C**), 158.4 (**C**), 138.7 (**C**), 128.2 (2 × **C**H), 114.7 (2 × **C**H), 97.1 (**C**H), 55.5 (**C**H_3), 41.2 (**C**H_3), 31.8 (**C**H_3), 17.9 (**C**H_3) ppm. **LRMS** (EI): 219 (40%, M$^+$), 176 (50%), 161 (100%). **HRMS** (EI): Found 219.1254, $C_{13}H_{17}NO_2$ M$^{\bullet+}$ requires 219.1254.

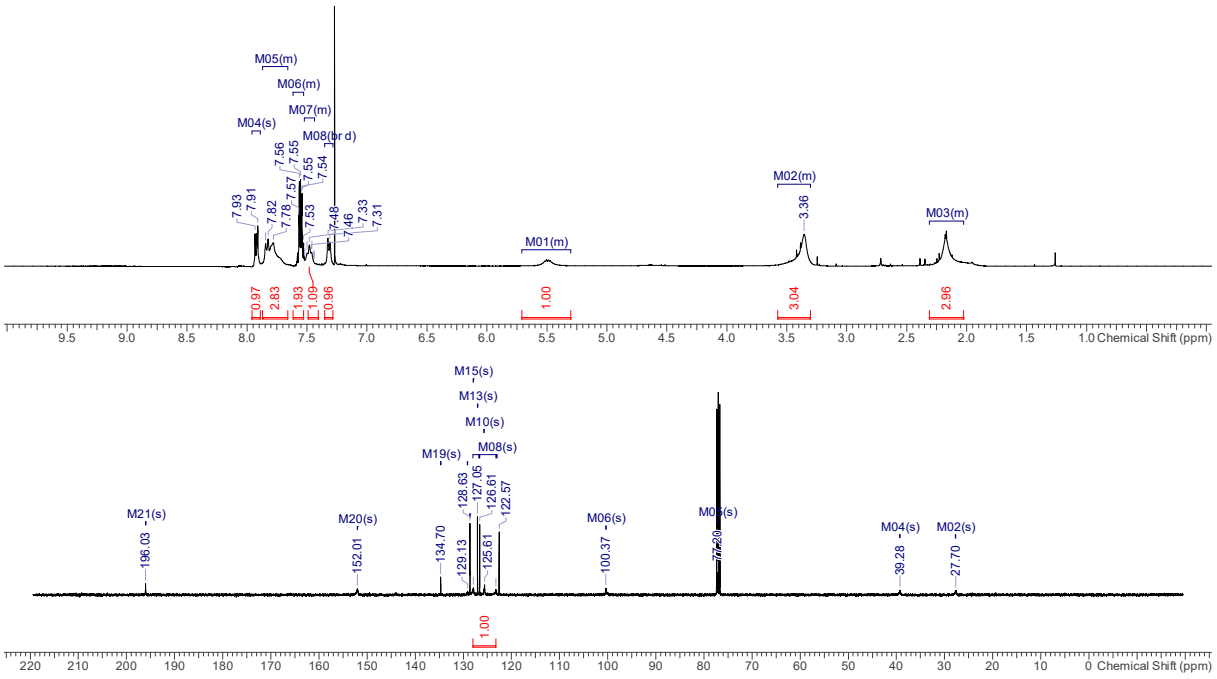




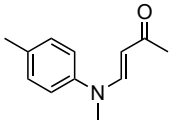
(*E*)-4-(Methyl(naphthalen-1-yl)amino)but-3-en-2-one, 23i



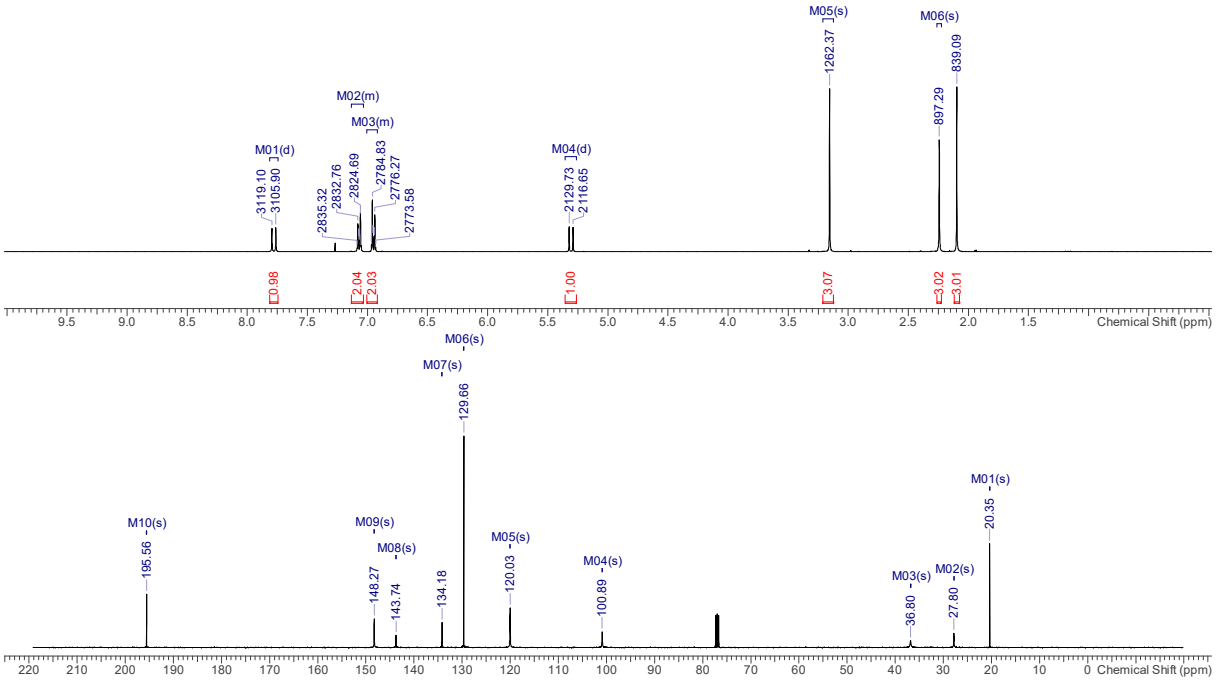
To a solution of but-3-yn-2-one (0.28 mL, 3.58 mmol) in EtOH (10 mL) was added *N*-methylnaphthalen-1-amine (559 mg, 3.58 mmol). After 16 h at RT, the resulting solution was concentrated *in vacuo* then purified by column chromatography (20 – 40% EtOAc/petrol) to afford the *title compound* **23i** (450 mg, 2.00 mmol, 56%) as a yellow oil. **IR** ν_{max} (film, cm^{-1}): 3491 (br), 3054 (br), 1605 (s), 1548 (s), 1267 (m), 1250 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (1 H, m, Ar**H**), 7.85 – 7.78 (3 H, m, 2 × Ar**H** + C**H**), 7.57 – 7.53 (2 H, m, 2 × Ar**H**), 7.48 (1 H, m, Ar**H**), 7.32 (1 H, d, *J* = 7.1 Hz, Ar**H**), 5.50 (1 H, br s, C**H**), 3.36 (3 H, br s, C$\mathbf{H}_3$), 2.18 (3 H, br s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.0 (**C**), 152.0 (**C**H), 144.0 (**C**), 134.7 (**C**), 129.1 (**C**), 128.6 (**C**H), 127.9 (**C**H), 127.1 (**C**H), 126.6 (**C**H), 125.6 (**C**H), 123.2 (**C**H), 122.6 (**C**H), 100.4 (**C**H), 39.3 (**C**H_3), 27.7 (**C**H_3) ppm. **LRMS** (EI): 225 (86%, M$^+$), 210 (95%), 182 (100%), 167 (76%). **HRMS** (EI): Found 225.1148, $C_{15}H_{15}NO$ M$^+$ requires 225.1148.



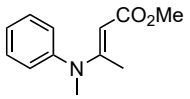
(*E*)-4-(Methyl(*p*-tolyl)amino)but-3-en-2-one, 23j



To a solution of but-3-yn-2-one (0.41 mL, 5.25 mmol) in EtOH (10 mL) was added 4-methyl-*N*-methylaniline (0.63 mL, 5.23 mmol). After 16 h at RT, the resulting solution was concentrated *in vacuo* then purified by column chromatography (20 – 50% EtOAc/petrol) to afford the *title compound* **23j** (775 mg, 4.10 mmol, 82%) as an off-white solid. **IR** ν_{max} (film, cm^{-1}): 2918 (br), 1550 (s), 1509 (s), 1252 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (1 H, d, *J* = 13.2 Hz, C**H**), 7.09 – 7.05 (2 H, m, 2 × Ar**H**), 6.97 – 6.93 (2 H, m, 2 × Ar**H**), 5.31 (1 H, d, *J* = 13.1 Hz, C**H**), 3.15 (3 H, s, C$\mathbf{H}_3$), 2.24 (3 H, s, C$\mathbf{H}_3$), 2.10 (3 H, s, C$\mathbf{H}_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.6 (**C**), 148.3 (**C**H), 143.7 (**C**), 134.2 (**C**), 129.7 (2 × **C**H), 120.0 (2 × **C**H), 100.9 (**C**H), 36.8 (**C**H_3), 27.8 (**C**H_3), 20.4 (**C**H_3) ppm. **LRMS** (ESI$^+$): 212 [M+Na]$^+$, 190 [M+H]$^+$. **HRMS** (ESI$^+$): Found 190.1230, $C_{12}H_{16}NO$ [M+H]$^+$ requires 190.1226.

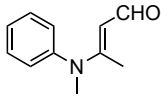


Methyl (*E*)-3-(methyl(phenyl)amino)but-2-enoate, 23k

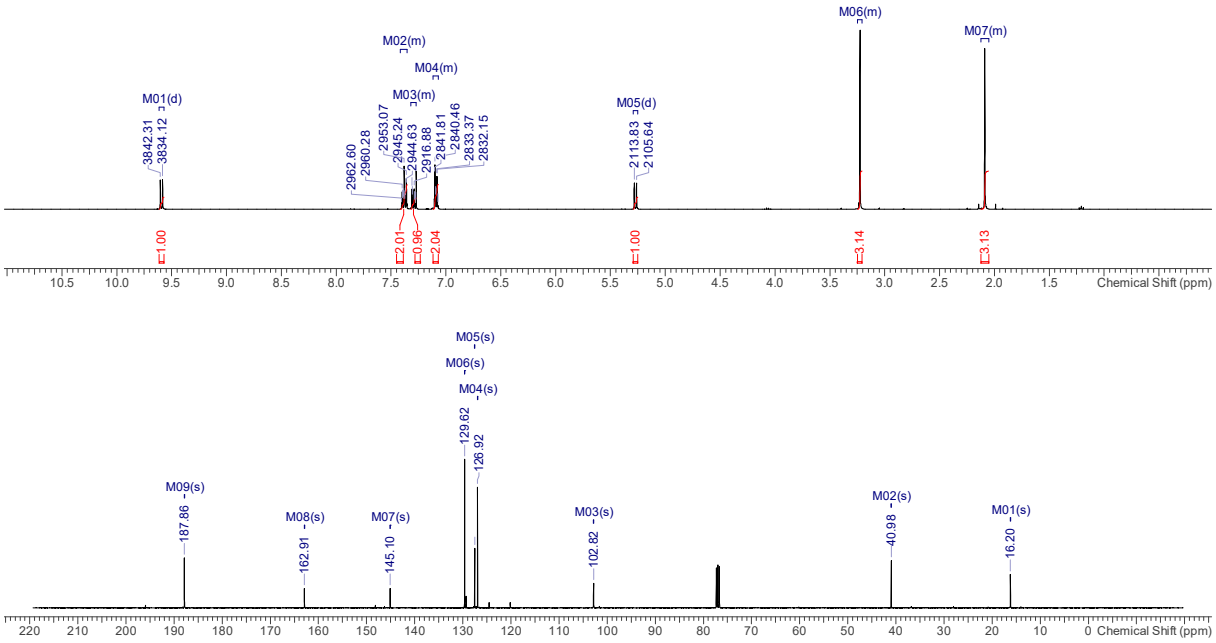


To a mixture of methyl acetoacetate (1.26 mL, 11.7 mmol) and *N*-methylaniline (1.26 mL, 11.6 mmol) was added $Yb(OTf)_3$ (20 mg). The reaction mixture was stirred at RT for 16 h then 50 mL DCM and 50 mL waster was added. The aqueous phase was separated and extracted with DCM (2 × 50 mL). The organic phases were combined, dried over $MgSO_4$ and concentrated *in vacuo* to afford the *title compound* **23k** (1.46 g, 8.24 mmol, 71%) as a yellow oil that was used without further purification due to its sensitivity towards hydrolysis under column chromatography.

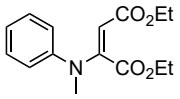
(*E*)-3-(Methyl(phenyl)amino)but-2-enal, 23l



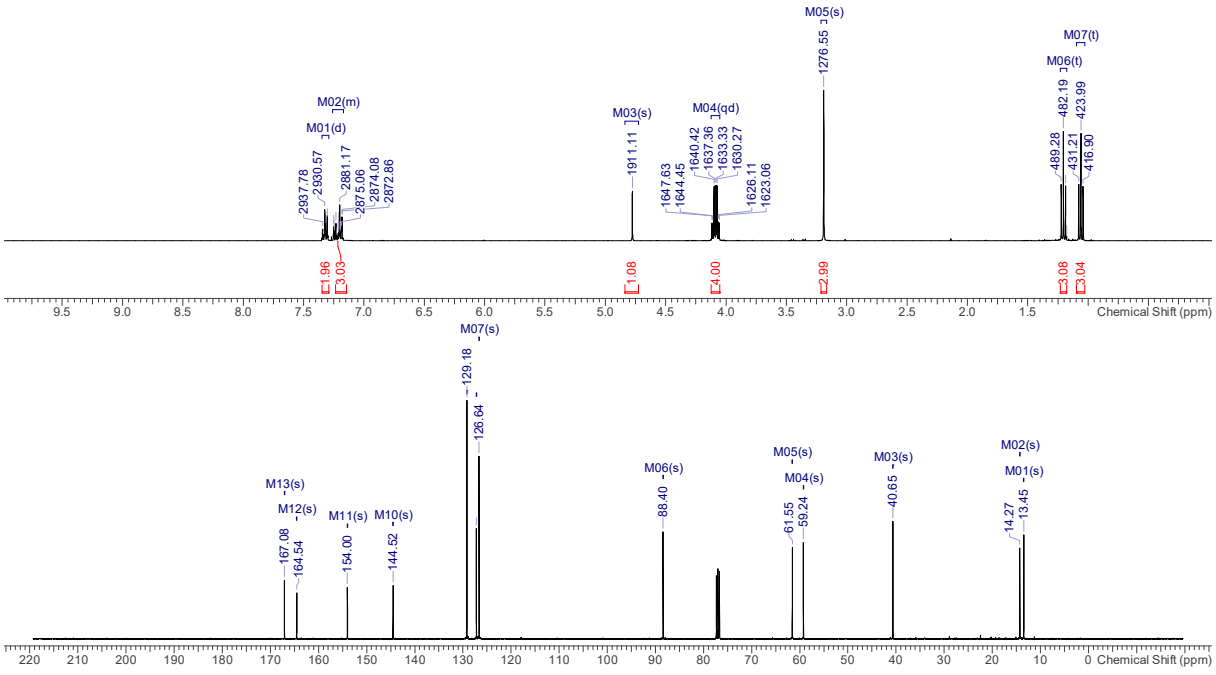
To a solution of but-2-ynal (680 mg, 10.0 mmol) in EtOH (10 mL) was added *N*-methylaniline (1.26 mL, 10.0 mmol). After stirred 16 h at 50 °C, the resulting solution was concentrated *in vacuo* then purified by column chromatography (20 – 50% EtOAc/petrol) to afford the *title compound* **23l** (1360 mg, 7.77 mmol, 78%) as a yellow solid. **IR** ν_{max} (film, cm^{-1}): 2931 (br), 1615 (s), 1553 (s), 1493 (s), 1190 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.59 (1 H, d, *J* = 8.2 Hz, C**H**), 7.40 – 7.35 (2 H, m, 2 × Ar**H**), 7.30 (1 H, m, C**H**), 7.11 – 7.07 (2 H, m, 2 × Ar**H**), 5.27 (1 H, d, *J* = 8.2 Hz, C**H**). 3.23 (3 H, s, C**H**$_3$), 2.09 (3 H, s, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.9 (**C**H), 162.9 (**C**), 145.1 (**C**), 129.6 (2 × **C**H), 127.5 (**C**H), 126.9 (2 × **C**H), 102.8 (**C**H), 41.0 (**C**H$_3$), 16.2 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 198 [M+Na]$^+$, 176 [M+H]$^+$. **HRMS** (ESI$^+$): Found 176.1070, $C_{11}H_{14}NO$ [M+H]$^+$ requires 176.1072.



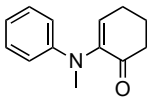
Diethyl 2-(methyl(phenyl)amino)maleate, 23m



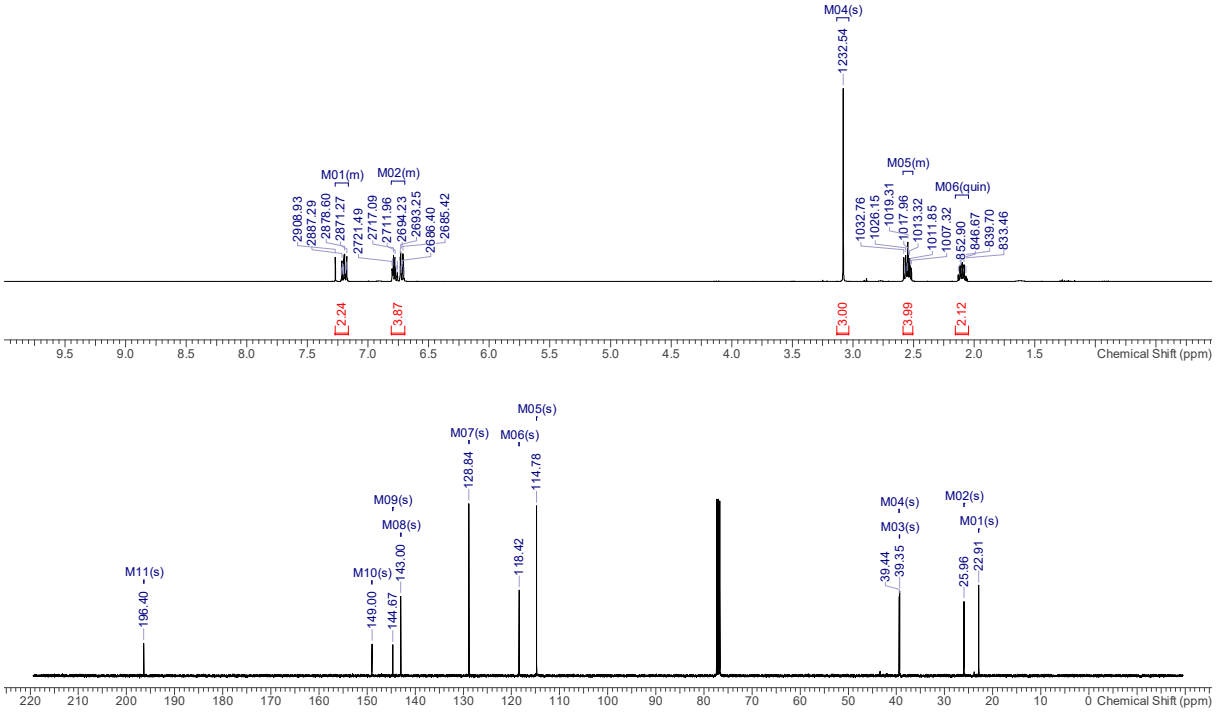
To a solution of diethyl acetylenedicarboxylate (0.96 mL, 6.00 mmol) in water (20 mL) was added *N*-methylaniline (0.65 mL, 6.01 mmol). After 16 h at RT, DCM (20 mL) was added then the aqueous phase was separated and extracted with further DCM (2 × 20 mL). The organic phases were combined, dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (20 – 60% EtOAc/petrol) to afford the *title compound* **23m** (1.63 g, 5.88 mmol, 95%) as an off-white oil. **IR** ν_{max} (film, cm^{-1}): 2978 (br), 1728 (s), 1687 (m), 1560 (s), 1127 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 – 7.30 (2 H, m, 2 × Ar**H**), 7.26 – 7.18 (3 H, m, 3 × Ar**H**), 4.78 (1 H, s, C**H**), 4.09 (2 H, q, *J* = 7.5 Hz, C**H**$_2$), 4.08 (2 H, q, *J* = 7.5 Hz, C**H**$_2$), 3.19 (3 H, s, C**H**$_3$), 1.21 (3 H, t, *J* = 7.2 Hz, C**H**$_3$), 1.06 (3 H, t, *J* = 7.2 Hz, C**H**$_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.1 (**C**), 164.5 (**C**), 154.0 (**C**), 144.5 (**C**), 129.2 (2 × **C**H), 127.2 (**C**H), 126.6 (2 × **C**H), 88.4 (**C**H), 61.6 (**C**H$_2$), 59.2 (**C**H$_2$), 40.7 (**C**H$_3$), 14.3 (**C**H$_3$), 13.5 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 300 [M+Na]$^+$, 278 [M+H]$^+$. Data is consistent with literature values.[31]



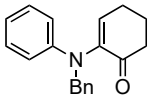
2-(Methyl(phenyl)amino)cyclohex-2-en-1-one, 27a



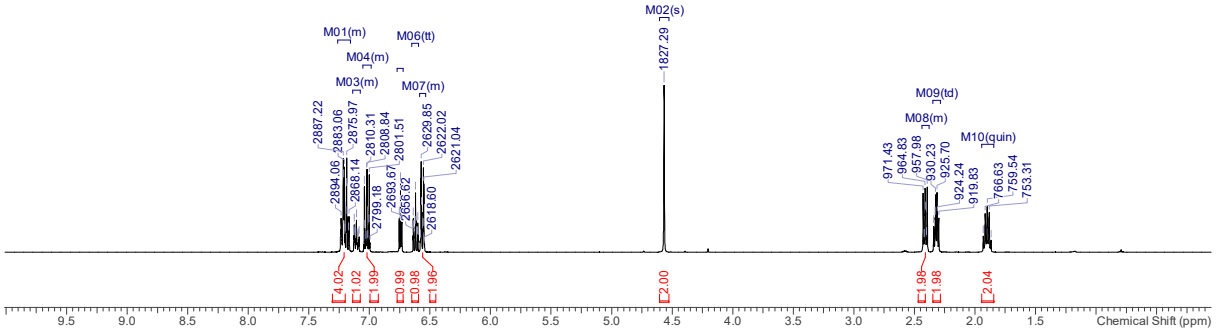
N-Methylaniline (0.7 mL, 6.50 mmol), 1,2-cyclohexanedione (730 mg, 6.51 mmol) and *p*TSA (50 mg) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (50 – 80% EtOAc/hexane) to afford the *title compound* **27a** (1.09 g, 5.42 mmol, 83%) as an off-white solid. **IR** ν_{max} (film, cm^{-1}): 2944 (br), 1680 (s), 1596 (S), 1497 (S). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 – 7.17 (2 H, m, 2 × Ar**H**), 6.80 – 6.70 (4 H, m, 3 × Ar**H** + C**H**), 3.08 (3 H, s, C$\mathbf{H}_3$), 2.58 – 2.52 (4 H, m, 2 × C$\mathbf{H}_2$), 2.10 (2 H, app. quin, *J* = 6.4 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.4 (**C**), 149.0 (**C**), 144.7 (**C**), 143.0 (**C**H), 128.8 (2 × **C**H), 118.4 (**C**H), 114.8 (2 × **C**H), 39.44 (**C**H_3), 39.35 (**C**H_2), 26.0 (**C**H_2), 22.9 (**C**H_2) ppm. **LRMS** (ESI+): 202 ([M+H]$^+$, 100%). Data is consistent with literature values.[32]

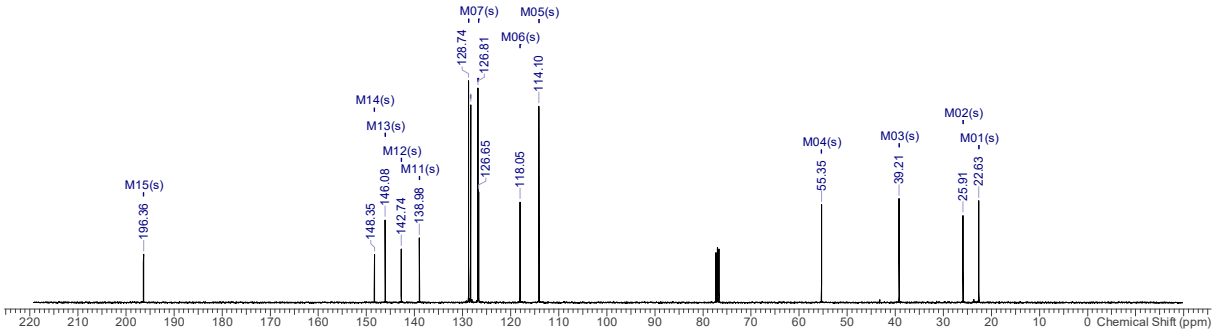


2-(Benzyl(phenyl)amino)cyclohex-2-en-1-one, 27b

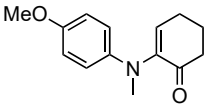


N-Benzylaniline (1.45 g, 7.90 mmol), 1,2-cyclohexanedione (886 mg, 7.91 mmol) and *p*TSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (50 – 90% EtOAc/petrol) to afford the *title compound* **27b** (1.44 g, 5.20 mmol, 66%) as a yellow solid. **MP**: 156 – 157 °C. **IR** ν_{max} (film, cm^{-1}): 2929 (br), 1672 (s), 1596 (m), 1496 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24 – 7.17 (4 H, m, 3 × Ar**H** + 1 **H**), 7.11 (1 H, m, Ar**H**), 7.05 – 7.00 (2 H, m, 2 × Ar**H**), 6.74 (1 H, m, Ar**H**), 6.62 (1 H, tt, *J* = 7.3, 1.1 Hz, Ar**H**), 6.58 – 6.54 (2 H, m, 2 × Ar**H**), 4.57 (2 H, s, C$\mathbf{H}_2$), 2.43 – 2.39 (2 H, m, C$\mathbf{H}_2$), 2.32 (2 H, td, *J* = 6.0, 4.5 Hz, C$\mathbf{H}_2$), 1.90 (2 H, app. quin, *J* = 6.1 Hz, C$\mathbf{H}_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.4 (**C**), 148.4 (**C**), 146.1 (**C**H), 142.7 (**C**), 139.0 (**C**), 128.7 (2 × **C**H), 128.3 (2 × **C**H), 126.8 (2 × **C**H), 126.7 (**C**H), 118.1 (**C**H), 114.1 (2 × **C**H), 55.4 (**C**H_2), 39.2 (**C**H_2), 25.9 (**C**H_2), 22.6 (**C**H_2) ppm. **LRMS** (ESI$^+$): 300 [M+Na]$^+$, 278 [M+H]$^+$.

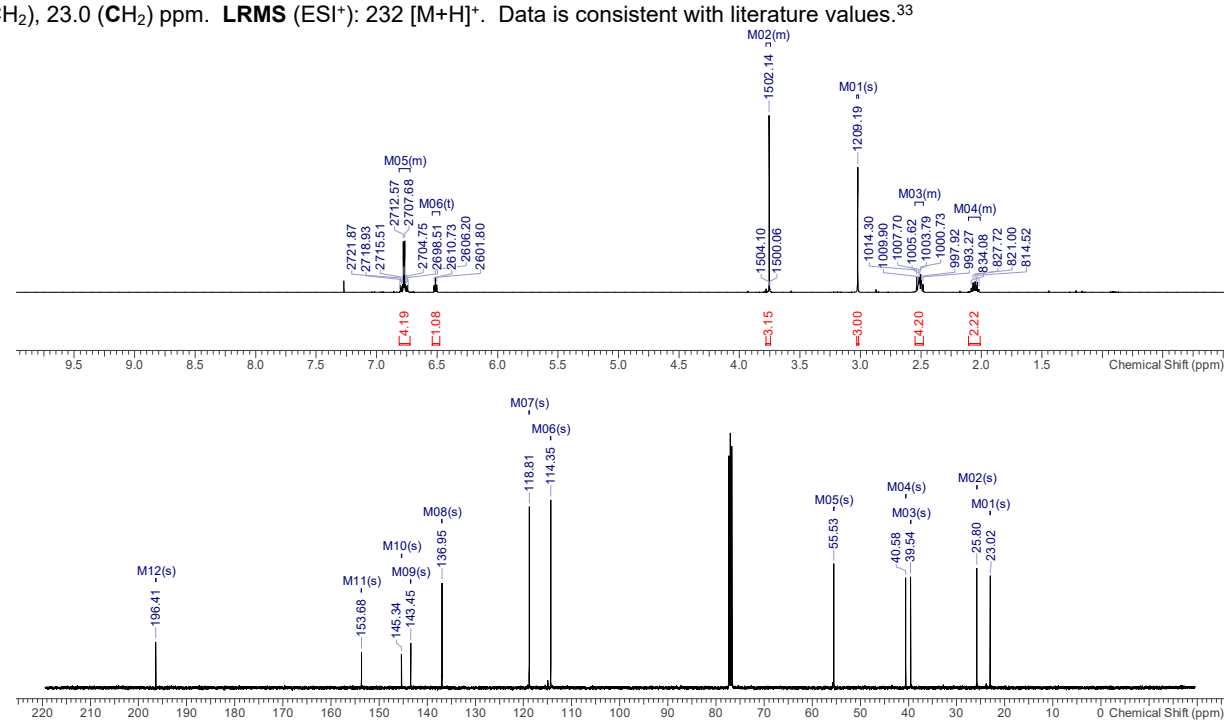




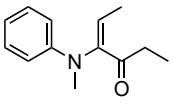
2-((4-Methoxyphenyl)(methyl)amino)cyclohex-2-en-1-one, 27c



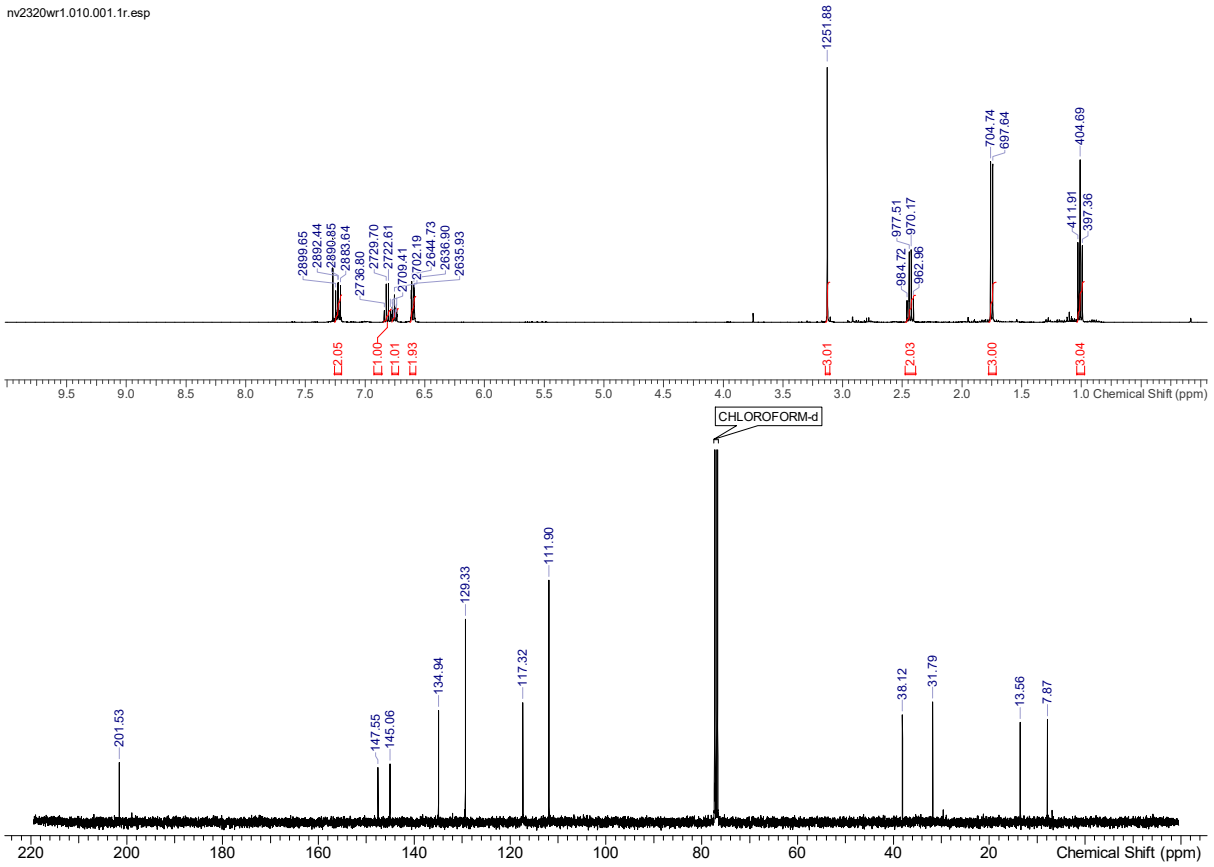
4-Methoxy-*N*-methylaniline (670 mg, 4.67 mmol), 1,2-cyclohexanedione (822 mg, 7.34 mmol) and *p*TSA (50 mg, 0.33 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated *in vacuo* then purified by column chromatography (50 – 80% EtOAc/hexane) to afford the *title compound* **27c** (878 mg, 3.80 mmol, 78%) as an off-white solid. **IR** ν_{max} (film, cm^{-1}): 2938 (br), 1680 (s), 1506 (s), 1237 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.81 – 6.74 (4 H, m, 4 × Ar**H**), 6.51 (1 H, t, *J* = 4.5 Hz, =C**H**), 3.75 (3 H, s, C**H**$_3$), 3.02 (3 H, s, C**H**$_3$), 2.53 – 2.48 (4 H, m, 2 × C**H**$_2$), 2.08 – 2.02 (2 H, m, C**H**$_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.4 (**C**), 153.7 (**C**), 145.3 (**C**), 143.5 (**C**), 137.0 (**C**H), 118.8 (2 × **C**H), 114.4 (2 × **C**H), 55.5 (**C**H$_3$), 40.6 (**C**H$_3$), 39.5 (**C**H$_2$), 25.8 (**C**H$_2$), 23.0 (**C**H$_2$) ppm. **LRMS** (ESI$^+$): 232 [M+H]$^+$. Data is consistent with literature values.[33]



(*E*)-4-(Methyl(phenyl)amino)hex-4-en-3-one, **27d**



The *title compound* was prepared following a modified literature procedure.[11] A solution of *N*-methylaniline (1.11 mL, 10.0 mmol), 3,4-hexanedione (5.86 mL, 50.0 mmol) and *p*TSA (95 mg) in toluene (50 mL) was heated at reflux under a soxhelet containing 4Å molecular sieves for 25 h. The resultant solution was diluted with ethyl acetate (30 mL), washed with water (2 x 50 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (5 – 30% EtOAc in petrol) to give the *title compound* **27d** as a yellow oil (1.52 g, 7.48 mmol, 75%). **IR** ν_{max} ($CDCl_3$, cm^{-1}): 2980 (br), 1683 (m), 1598 (s), 1500 (s), 1339 (w), 749 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): d 7.23 (2H, dd, *J* = 8.8, 7.2 Hz, 2 x Ar**H**), 6.81 (1H, q, *J* = 7.0 Hz, C**H**), 6.75 (1H, tt, *J* = 7.3, 1.0 Hz, Ar**H**), 6.60 (2H, dd, *J* = 8.9, 1.0 Hz, 2 x Ar**H**), 3.13 (3H, s, C**H**$_3$), 2.43 (2H, q, *J* = 7.2 Hz, C**H**$_2$), 1.75 (3H, d, *J* = 7.1 Hz, C**H**$_3$), 1.01 (3H, t, *J* = 7.2 Hz, C**H**$_3$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): d 201.5 (**C**O), 147.6 (**C**), 145.1 (**C**), 134.9 (**C**H), 129.3 (**C**H), 117.3 (**C**H), 111.9 (**C**H), 38.1 (**C**H$_3$), 31.8 (**C**H$_2$), 13.6 (**C**H$_3$), 7.9 (**C**H$_3$) ppm. **LRMS** (ESI$^+$): 204 ((M+H)$^+$, 100%). Data is consistent with literature values.[34]



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