UNIVERSITÄT STUTTGART – INSTITUT FÜR ORGANISCHE CHEMIE

SUPPORTING INFORMATION

Catalytic Direct Dehydrogenative Cross-Couplings of C-H (Pro)Nucleophiles and Allylic Alcohols without an Additional Oxidant

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1. Experimental

All reactions were performed in oven-dried (150 °C) glassware under a positive pressure of nitrogen (about 0.2 bar). For all reactions liquids and solutions were added *via* syringes and septa. For catalysis all glassware used (also for catalyst activation and preparation of stock solutions) was washed intensively with demineralized water to remove traces of chloride. *N*,*N*-Dimethylformamide was stored in crown-capped bottles under argon over 4Å molecular sieves. Acetonitrile and dichloromethane (DCM) were purified by distillation and subsequently by a solvent purification system. 2,2,2-Trifluoroethanol was dried and degassed prior to use. *n*-Hexane (HPLC grade) and *iso*-propanol (HPLC grade) were used as purchased. For work-up procedures and column chromatography technical grade solvents (petrol ether and ethyl acetate) were purified by distillation prior to use. Solvents were mostly removed at a heating bath temperature of 40 °C and 600 – 10 mbar pressure by rotary evaporation. Non-volatile compounds were dried *in vacuo* at 0.1 mbar. [**FBIP-Cl]$_2$**,[1] **[RuBIP-Cl]$_2$**[2] and **[FBIPP-Cl]$_2$**[3] were prepared according to literature procedures. 1-Ethyl-1H-indole (**4b**),[4] 1-benzyl-1H-indole (**4c**),[5] 1-(4-bromobenzyl)-1H-indole (**4e**),[5] 5-(benzyloxy)-1-methyl-1H-indole (**4g**),[4] 5-phenylpent-1-en-3-ol (**5B**),[6] 1-cyclohexylprop-2-en-1-ol (**5E**)[6] *tert*-butyl 2-cyano-2-phenylacetate,[7] and 2,4-dimethylpentan-3-yl 2-cyano-2-phenylacetate[7] were prepared according to literature procedures. All other laboratory chemicals were purchased from commercial suppliers and were used without purification unless otherwise indicated.

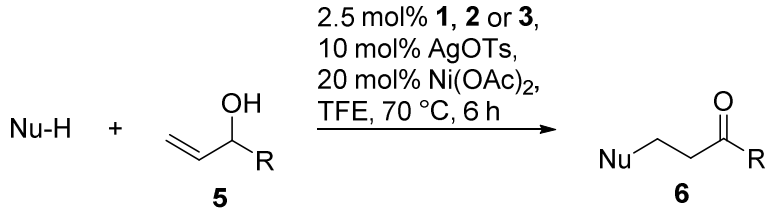
Yields refer to chromatographically purified compounds and are calculated in mol% of the used starting material. Catalytic reactions were carried out in a parallel synthesizer at 400 rpm. For thin layer chromatography (TLC), silica gel plates from *Merck* (silica gel 60 F_{254}) were used. Visualization occurred by fluorescence quenching under UV light and/or by staining with $KMnO_4$ / NaOH followed by heating (230 °C). Purification by flash-chromatography was performed on silica gel 0.040 – 0.063 mm provided by *Merck*, using a forced flow of eluent at 0.2-0.4 bar pressure.

NMR-spectra were recorded at 21 °C on spectrometers operating at 500, 300 MHz or 250 MHz (^{1}H), 125, 75 MHz or 63 MHz (^{13}C) and 235 MHz (^{19}F). Deuterated solvents were used as purchased and are stated for the corresponding compound characterizations after the corresponding frequency. Chemical shifts are referred in terms of ppm and *J*-coupling constants are given in Hz. Abbreviations for multiplicities are as follows: *s* (singulet), *d* (doublet), *t* (triplet), *m* (multiplet), *b* (broad signal). IR-spectra were recorded by the IR service of the Universität Stuttgart on a spectrometer with an ATR unit. The aggregation state of the sample is stated in parentheses, signals are given by wavenumbers (cm^{-1}). Optical rotation was measured on a polarimeter operating at the sodium D line with a 100 mm path cell length. Melting points were measured in open glass

capillaries and are uncorrected. Mass spectra were obtained from the MS service of the Universität Stuttgart. The ionization method is stated in parentheses. Single crystal X-ray analyses were performed by Dr. Wolfgang Frey (Universität Stuttgart). Enantiomeric excesses (*ee*'s) were determined by high performance liquid chromatography (HPLC). The applied method is given in the description of the respective product.

1.1 General Procedures (GPs)

1.1.1 General Procedure for the Catalytic Direct Dehydrogenative Cross-Coupling (GP1)

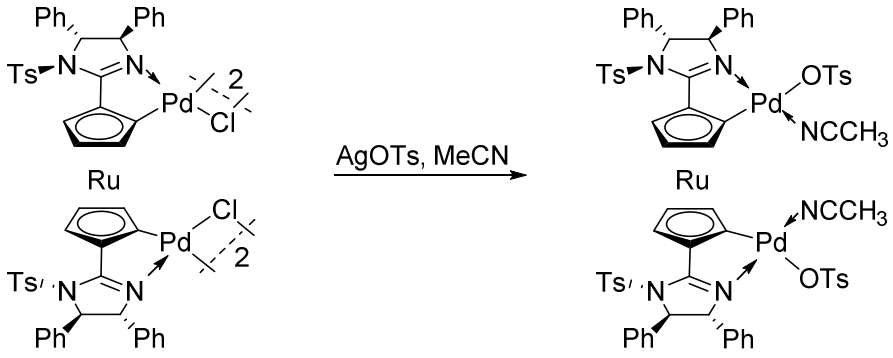


The respective catalyst dimer (1.00 equiv.) and silver tosylate (4.00 equiv.) were dissolved in MeCN (0.2 mL/mg) under nitrogen atmosphere. The mixture was stirred overnight at room temperature and subsequently filtered through Celite. The filtercake was extracted with MeCN until the organic solution was colorless. The solvent was removed by a steady stream of nitrogen and finally by high vacuum. A stock solution of the activated catalyst was prepared by dissolving the solid in dry, degassed TFE (40 mmol/L).

This stock solution was then used to add 5 mol% of the activated catalyst to the nucleophile (0.16 mmol, 1.00 equiv.), the allylic alcohol **5** (0.48 mmol, 3.00 equiv.) and $Ni(OAc)_2$ (0.03 mmol 20 mol%) under a nitrogen atmosphere. The reaction tube was sealed and the reaction mixture was shaken at 400 rpm for 6 h at 70 °C. The reaction mixture was afterwards suspended in petrol ether/ethyl acetate (10:1) and subsequently purified by filtration over silica gel.

1.2 Activation of the Catalyst

1.2.1 {Acetonitrile-[(η^5-(*4''R*,*5''R*)-(1-*S*$_P$)-2-(2''-4'',5''-dihydro-4'',5''-diphenyl-1''-tosyl-1''H-imidazolyl)cyclopentadienyl, κ*C*1, κ*N*3]-*para*-toluenesulfonato-palladium(II)]}-{acetonitrile-[(η^5-(*4'''R*,*5'''R*)-(1'-*S*$_P$)-2'-(2'''-4''',5'''-dihydro-4''',5'''-diphenyl-1'''-tosyl-1'''H-imidazolyl)cyclopentadienyl, κ*C*1', κ*N*3']- *para*-toluenesulfonato-platinum(II)]}-iron(II) (RuBIP-OTs)



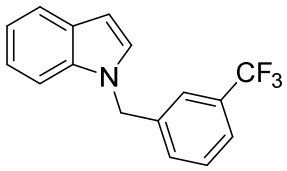
[RuBIP-Cl]$_2$ **RuBIP-OTs**

A solution of silver *para*-toluenesulfonate (8.1 mg, 0.03 mmol, 4.00 equiv.) in MeCN (0.4 ml) was added to [**RuBIP-Cl]$_2$** (18.4 mg, 7.29 µmol, 1.00 equiv.) under N_2-atmosphere. The mixture was stirred overnight at room temperature. The reaction mixture was then filtered through celite and subsequently the solvent was removed by a stream of N_2 and finally by vacuum. **RuBIP-OTs** was isolated as a yellow solid (23.5 mg, 14.5 µmol, 99%).

$C_{72}H_{64}N_6O_{10}Pd_2RuS_4$, **MW**: 1615.49 g/mol. **[α]$_D^{23}$**: +126.3 (c = 0.076 g/dL, $CHCl_3$). **Mp.**: >200 °C (decomposition). **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ = 7.51-7.44 (*m*, 6H, arom. *H*), 7.38-7.33 (*m*, 4H, arom. *H*), 7.31-7.27 (*m*, 4H, arom. *H*), 7.23-7.16 (*m*, 6H, arom. *H*), 7.14-7.07 (*m*, 8H, arom. *H*), 6.89 (*d*, *J* = 7.8, 4H, arom. *H*), 6.70 (*d*, *J* = 7.8, 4H, arom. *H*), 5.71 (*d*, *J* = 2.4, 2H, Cp-*H*), 5.39 (*d*, *J* = 2.4, 2H, Cp-*H*), 5.10 (*d*, *J* = 3.3, 2H, C*H*Ph), 4.89 (*d*, *J* = 3.3, 2H, C*H*Ph), 4.59 (*t*, *J* = 2.4, 2H, Cp-*H*), 2.60 (*s*, 6H, Ts-CH_3), 2.40 (*s*, 6H, Ts-CH_3), 2.26 (*s*, 6H, NCCH_3), 2.00 (*s*, 6H, solvent NCCH_3). **^{13}C-NMR (125 MHz, $CDCl_3$)**: δ = 169.1, 145.5, 141.6, 140.0, 139.9, 139.4, 135.1, 130.1, 129.6, 129.5, 128.8, 128.6, 127.9, 127.6, 127.4, 125.9, 125.8, 122.3, 92.5, 78.8, 78.0, 74.9, 74.6, 73.1, 71.8, 21.8, 21.4, 3.7, 2.1. **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3032, 2925, 2329, 2243, 1596, 1555, 1494, 1456, 1361, 1339, 1306, 1246, 1158, 1111, 1029, 1003, 974, 910, 865, 813, 759, 730, 711, 699, 680, 670, 646, 605, 565, 554, 542, 529. **MS (ESI) *m/z***: 1361.0 (16%, $[M - 2xCH_3CN - OTs]^+$), 595.0 (100%, $[M - 2xCH_3CN - 2xOTs]^{2+}$). **HRMS (ESI) *m/z***: calculated for ($[M - 2xCH_3CN - OTs]^+$): 1361.0063; measured: 1361.0047.

1.3 Synthesis of Substrates for the Catalysis

1.3.1 1-(3-(Trifluoromethyl)benzyl)-1H-indole (4d)



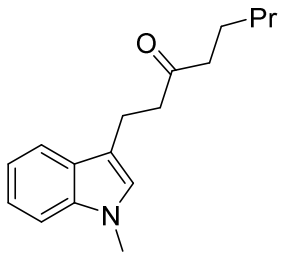
4d

NaH (55% in mineral oil, 185 mg, 4.23 mmol, 1.6 equiv) was placed in a flask under nitrogen atmosphere and cooled to 0 °C. A solution of indolee (500 mg, 2.64 mmol, 1.0 equiv) in DMF (2.5 mL/mmol) was added. The reaction mixture was warmed to room temperature and stirred for 30 min. After cooling back to 0 °C, 3-(trifluoromethyl)benzyl bromide (484 µL, 758 mg, 3.17 mmol, 1.2 equiv) was added. The reaction mixture was again warmed to room temperature and stirred for 5 h. Afterwards water was added and the reaction mixture was diluted with CH_2Cl_2. The phases were separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (silica gel, petrol ether/ethyl acetate 20:1) gave the product as a yellow liquid (727 mg, 2.64 mmol, >99%).

$C_{23}H_{27}NO$, **MW**: 275.27 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.68 (*d*, *J* = 7.9, 1H, indole C(4)*H*), 7.52 (*d*, *J* = 7.9, 1H, arom. *H*), 7.46 (*s*, 1H, arom. *H*), 7.37 (*t*, *J* = 7.9, 1H, arom. *H*), 7.25-7.11 (*m*, 5H, arom. *H*), 6.60 (*d*, *J* = 3.1, indole C(3)*H*), 5.35 (*s*, 2H, N-CH_2Ar). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 138.8 (N-CH_2-^{q}*C*), 136.3 (HC=*C*(NMe)(^{q}C)), 131.2 (*q*, *J* = 32.3, phenyl-*C*3-CF_3),130.1 (phenyl-*C*6), 129.5 (phenyl-*C*5), 128.9 (HC=*C*(^{q}C)(CH)), 128.2 (indole-*C*2), 124.7 (*q*, *J* = 3.8, phenyl-*C*2/4), 124.1 (*q*, *J* = 272.4, *C*F_3), 123.6 (*q*, *J* = 3.8, phenyl-*C*2/4), 122.1 (indole-*C*6), 121.3 (indole-*C*5), 119.9 (indole-*C*4), 109.6 (indole-*C*7), 102.4 (indole-*C*3), 49.7 (N-*C*H_2-Ph). **^{19}F-NMR (235 MHz, $CDCl_3$)**: δ = –62.6 (*s*, 3F, C*F*$_3$). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3057, 1613, 1513, 1484, 1462, 1437, 1397, 1353, 1328, 1312, 1255, 1196, 1161, 1115, 1096, 1072, 1045, 1012, 962, 921, 885, 844, 795, 765, 737, 718, 669, 660, 576. **MS (EI) *m/z***: 275.1 (100%, $[M]^+$), 159.0 (70%, [M - indole]$^+$). **HRMS (ESI) *m/z***: calculated for ($[M + H]^+$): 276.0995; measured: 276.0984.

1.4 Catalytic Synthesis of Products 6

1.4.1 1-(1-Methyl-1H-indole-3-yl)octan-3-one (6aA)

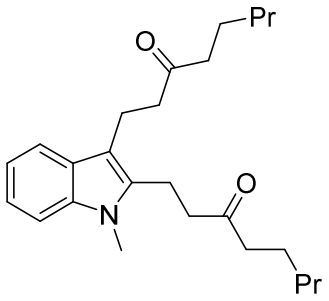


6aA

4a was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6aA** as a colorless oil (34.2 mg, 83%).

$C_{17}H_{23}NO$, **MW**: 257.38 g/mol. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ = 7.57 (*d*, *J* = 8.0, 1H, indole C(4)*H*), 7.30-7.25 (*m*, 1H, indole C(6)*H*), 7.24-7.20 (*m*, 1H, indole C(7)*H*), 7.13-7.08 (*m*, 1H, indole C(5)*H*), 6.84 (*s*, 1H, indole C(2)*H*), 3.73 (*s*, 3H, N-CH_3), 3.03 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.80 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.38 (*t*, *J* = 7.4, 2H, C(O)-CH_2), 1.60-1.52 (*m*, 2H, C(O)-CH_2-CH_2), 1.33-1.18 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.87 (*t*, *J* = 7.3, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.3 (O=*C*), 137.1 (HC=*C*(NMe)(^{q}C)), 127.7 (HC=*C*(^{q}C)(CH)), 126.5 (indole-*C*2), 121.7 (indole-*C*6), 118.9 (indole-*C*5), 118.8 (indole-*C*4), 114.0 (indole-*C*3), 109.3 (indole-*C*7), 43.5 (Ar-CH_2-*C*H_2-C(O)), 43.1 (C(O)-*C*H_2), 32.7 (N-*C*H_3), 31.5 (Ar-*C*H_2-CH_2-C(O)), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 19.4 (CH_2-*C*H_2-CH_3), 14.1 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3054, 2956, 2928, 2855, 2359, 1711, 1615, 1554, 1485, 1470, 1425, 1409, 1376, 1325, 1249, 1207, 1154, 1128, 1082, 1059, 1012, 739, 559. **MS (EI) *m/z***: 257.2 (34%, $[M]^+$), 158.1 (20%, $[M - C(O)C_5H_{11}]^+$), 144.1 (100%, [1,2-Dimethyl-1H-indole]$^+$). **HRMS (EI) *m/z***: calculated for ($[M]^+$): 257.1780; measured: 257.1779.

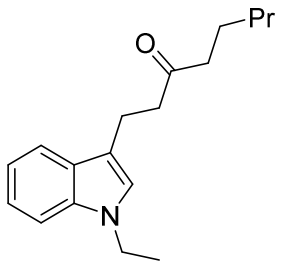
Sideproduct caused by double alkylation:



4a was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded the double addition product as a yellow oil (1.8 mg, 3%).

$C_{25}H_{37}NO_2$, **MW**: 383.58 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.52-7.45 (*m*, 1H, indole C(4)*H*), 7.28-7.22 (*m*, 1H, indole C(6)*H*), 7.21-7.14 (*m*, 1H, indole C(7)*H*), 7.11-7.05 (*m*, 1H, indole C(5)*H*), 3.65 (*s*, 3H, N-CH_3), 3.10-2.94 (*m*, 4H, 2x indole-CH_2-CH_2-C(O)), 2.77-2.61 (*m*, 4H, 2x indole-CH_2-CH_2-C(O)), 2.40 (*t*, *J* = 7.5, 2H, C(O)-CH_2), 2.35 (*t*, *J* = 7.5, 2H, C(O)-CH_2), 1.65-1.48 (*m*, 4H, 2x C(O)-CH_2-CH_2), 1.36-1.15 (*m*, 8H, 2x C(O)-CH_2-CH_2-CH_2-CH_2), 0.88 (*t*, *J* = 6.9, 3H, CH_2-CH_3), 0.87 (*t*, *J* = 6.9, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.3 (O=*C*), 209.8 (O=*C*), 137.0 (HC=*C*(NMe)(^{q}C)), 135.9 (indole-*C*2), 127.3 (HC=*C*(^{q}C)(CH)), 121.1 (indole-*C*6), 119.1 (indole-*C*5), 118.2 (indole-*C*4), 110.5 (indole-*C*3), 109.0 (indole-*C*7), 43.7 (Ar-CH_2-*C*H_2-C(O)), 43.3 (C(O)-*C*H_2), 43.1 (C(O)-*C*H_2), 42.7 (Ar-CH_2-*C*H_2-C(O)), 31.5 (2x *C*H_2-CH_2-CH_3), 29.7 (N-*C*H_3), 23.6 (2x C(O)-CH_2-*C*H_2), 22.6 (CH_2-*C*H_2-CH_3), 18.8 (Ar-*C*H_2-CH_2-C(O)), 18.5 (Ar-*C*H_2-CH_2-C(O)), 14.0 (2x CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3054, 2956, 2928, 2871, 2856, 1711, 1658, 1613, 1565, 1470, 1434, 1407, 1370, 1332, 1292, 1270, 1243, 1203, 1185, 1148, 1127, 1077, 1013, 919, 895, 841, 739, 556. **MS (ESI) *m/z***: 406.27 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 406.2717; measured: 406.2727.

1.4.2 1-(1-Ethyl-1H-indole-3-yl)octan-3-one (6bA)

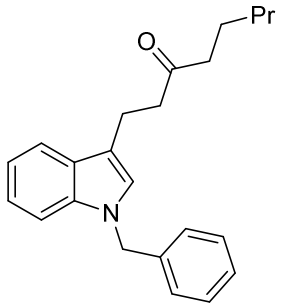


6bA

4b was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6bA** as a colorless oil (28.4 mg, 69%).

$C_{18}H_{25}NO$, **MW**: 271.40 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.59 (*d*, *J* = 7.9, 1H, indole C(4)*H*), 7.32 (*d*, *J* = 7.9, 1H, indole C(7)*H*), 7.25-7.18 (*m*, 1H, indole C(6)*H*), 7.15-7.07 (*m*, 1H, indole C(5)*H*), 6.91 (*s*, 1H, indole C(2)*H*), 4.12 (*q*, *J* = 7.3, 2H, N-CH_2CH$_3$), 3.05 (*t*, *J* = 7.5, 2H, indole-CH$_2$-CH_2-C(O)), 2.81 (*t*, *J* = 7.5, 2H, indole-CH_2-CH$_2$-C(O)), 2.39 (*t*, *J* = 7.5, 2H, C(O)-CH_2), 1.63-1.51 (*m*, 2H, C(O)-CH$_2$-CH_2), 1.44 (*t*, *J* = 7.3, 2H, N-CH$_2$CH_3), 1.35-1.17 (*m*, 4H, C(O)-CH$_2$-CH$_2$-CH_2-CH_2), 0.88 (*t*, *J* = 7.1, 3H, CH$_2$-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.4 (O=*C*), 136.1 (HC=*C*(N)(^{q}C)), 127.8 (HC=*C*(^{q}C)(CH)), 124.7 (indole-*C*2), 121.5 (indole-*C*6), 119.0 (indole-*C*5), 118.8 (indole-*C*4), 114.0 (indole-*C*3), 109.4 (indole-*C*7), 43.5 (Ar-CH$_2$-*C*H$_2$-C(O)), 43.1 (C(O)-*C*H$_2$), 40.8 (N-*C*H$_2$-CH$_3$), 31.5 (Ar-*C*H$_2$-CH$_2$-C(O)), 23.6 (C(O)-CH$_2$-*C*H$_2$), 22.6 (*C*H$_2$-CH$_2$-CH$_3$), 19.5 (CH$_2$-*C*H$_2$-CH$_3$), 15.6 (N-CH$_2$-*C*H$_3$), 14.0 (CH$_2$-*C*H$_3$). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 2955, 2929, 2854, 2358, 1711, 1613, 1553, 1483, 1467, 1446, 1399, 1373, 1354, 1331, 1230, 1203, 1154, 1124, 1070, 1014, 802, 736, 603, 556. **MS (EI) *m/z***: 271.2 (40%, [M]$^+$), 172.1 (17%, [M – C(O)C$_5$H$_{11}$]$^+$), 158.1 (20%, [M – CH$_3$ – C(O)C$_5$H$_{11}$]$^+$), 130.1 (8%, [1-Methyl-1H-indole – H]$^+$). **HRMS (ESI) *m/z***: calculated for ([M + Na]$^+$): 294.1828; measured: 294.1815.

1.4.3 1-(1-Benzyl-1H-indole-3-yl)octan-3-one (6cA)

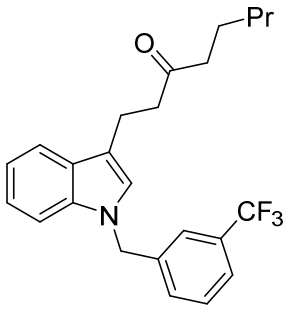


6cA

4c was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6cA** as a white solid (36.2 mg, 75%).

$C_{23}H_{27}NO$, **MW**: 333.48 g/mol. **MP**: 34.5 – 35.0 °C. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.60 (*d*, *J* = 7.9, 1H, indole C(4)*H*), 7.32-7.20 (*m*, 3H, arom. *H*), 7.20-7.06 (*m*, 4H, arom. *H*), 6.91 (*s*, 1H, indole C(2)*H*), 5.25 (*s*, 2H, N-CH_2Ph), 3.05 (*t*, *J* = 7.5, 2H, indole-CH_2-CH_2-C(O)), 2.80 (*t*, *J* = 7.5, 2H, indole-CH_2-CH_2-C(O)), 2.37 (*t*, *J* = 7.5, 2H, C(O)-CH_2), 1.62-1.49 (*m*, 2H, C(O)-CH_2-CH_2), 1.34-1.15 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.87 (*t*, *J* = 7.1, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.2 (O=*C*), 137.8 (N-CH_2-^{q}*C*), 136.8 (HC=*C*(N)(^{q}C)), 128.8 (phenyl-*C*3/5), 128.0 (HC=*C*(^{q}C)(CH)), 127.7 (indole-*C*2), 126.9 (phenyl-*C*2/6), 125.8 (phenyl-*C*4), 121.9 (indole-*C*6), 119.1 (indole-*C*5), 119.0 (indole-*C*4), 114.7 (indole-*C*3), 109.8 (indole-*C*7), 50.0 (N-*C*H_2-Ph), 43.4 (Ar-CH_2-*C*H_2-C(O)), 43.2 (C(O)-*C*H_2), 31.5 (Ar-*C*H_2-CH_2-C(O)), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 19.5 (CH_2-*C*H_2-CH_3), 14.1 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3060, 3028, 2955, 2927, 2854, 1711, 1613, 1554, 1495, 1467, 1452, 1410, 1375, 1356, 1330, 1260, 1200, 1178, 1126, 1077, 1029, 1014, 966, 800, 735, 698, 594, 558. **MS (EI) *m/z***: 333.2 (84%, $[M]^+$), 234.1 (18%, $[M - C_6H_{11}O]^+$), 220.1 (100%, $[M - C_7H_{13}O]^+$), 91.1 (90%, $[PhCH_2]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 356.1985; measured: 356.1993.

1.4.4 1-(1-(3-(Trifluoromethyl)benzyl)-1H-indole-3-yl)octan-3-one (6dA)

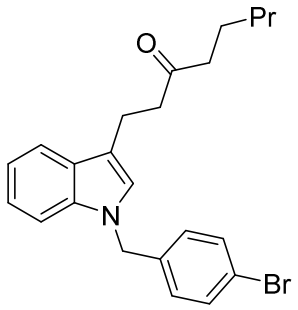


6dA

4d was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6dA** as a white solid (33.8. mg, 58%).

$C_{23}H_{27}NO$, **MW**: 401.47 g/mol. **MP**: 33.4 – 34.9 °C. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.62 (*d*, *J* = 7.9, 1H, indole C(4)*H*), 7.52 (*d*, *J* = 7.7, 1H, arom. *H*), 7.46-7.35 (m, 2H, arom. *H*), 7.23-7.10 (*m*, 4H, arom. *H*), 6.92 (*s*, 1H, indole C(2)*H*), 5.31 (*s*, 2H, N-CH_2Ar), 3.06 (*t*, *J* = 7.5, 2H, indole-CH_2-CH_2-C(O)), 2.82 (*t*, *J* = 7.5, 2H, indole-CH_2-CH_2-C(O)), 2.38 (*t*, *J* = 7.5, 2H, C(O)-CH_2), 1.62-1.49 (*m*, 2H, C(O)-CH_2-CH_2), 1.36-1.16 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.87 (*t*, *J* = 7.1, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.1 (O=*C*), 138.9 (N-CH_2-^{q}*C*), 136.7 (HC=*C*(NMe)(^{q}C)), 131.2 (*q*, *J* = 32.3, phenyl-*C*3-CF_3),130.1 (phenyl-*C*6), 129.5 (phenyl-*C*5), 128.1 (HC=*C*(^{q}C)(CH)), 125.6 (indole-*C*2), 124.6 (*q*, *J* = 3.8, phenyl-*C*2/4), 124.1 (*q*, *J* = 272.4, *C*F_3), 123.6 (*q*, *J* = 3.8, phenyl-*C*2/4), 122.2 (indole-*C*6), 119.4 (indole-*C*5), 119.2 (indole-*C*4), 115.3 (indole-*C*3), 109.6 (indole-*C*7), 49.6 (N-*C*H_2-Ph), 43.3 (Ar-CH_2-*C*H_2-C(O)), 43.2 (C(O)-*C*H_2), 31.5 (Ar-*C*H_2-CH_2-C(O)), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 19.4 (CH_2-*C*H_2-CH_3), 14.0 (CH_2-*C*H_3). **^{19}F-NMR (235 MHz, $CDCl_3$)**: δ = -62.6 (*s*, 3F, C*F*$_3$). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3056, 2958, 2929, 2873, 2856, 1711, 1614, 1598, 1556, 1466, 1449, 1438, 1411, 1376, 1355, 1327, 1270, 1196, 1163, 1122, 1095, 1074, 1015, 968, 921, 882, 868, 795, 740, 702, 657, 561, 541. **MS (ESI) *m/z***: 424.19 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 424.1859; measured: 424.1862.

1.4.5 1-(1-(4-Bromobenzyl)-1H-indole-3-yl)octan-3-one (6eA)

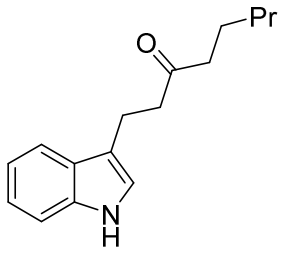


6eA

4e was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6eA** as a white solid (18.4 mg, 32%).

$C_{23}H_{27}NO$, **MW**: 412.37 g/mol. **MP**: 42.8 - 43.2 °C. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.60 (*d*, *J* = 7.9, 1H, indole C(4)*H*), 7.40 (*d*, *J* = 8.4, 2H, arom. *H*), 7.22-7.08 (*m*, 3H, arom. *H*), 6.95 (*d*, *J* = 8.4, 2H, arom. *H*), 6.89 (*s*, 1H, indole C(2)*H*), 5.20 (*s*, 2H, N-CH_2Ar), 3.05 (*t*, *J* = 7.5, 2H, indole-CH_2-CH_2-C(O)), 2.81 (*t*, *J* = 7.5, 2H, indole-CH_2-CH_2-C(O)), 2.37 (*t*, *J* = 7.5, 2H, C(O)-CH_2), 1.62-1.49 (*m*, 2H, C(O)-CH_2-CH_2), 1.34-1.15 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.87 (*t*, *J* = 7.1, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.2 (O=*C*), 136.9 (N-CH_2-^{q}*C*), 136.7 (HC=*C*(N)(^{q}C)), 132.0 (phenyl-*C*3/5), 128.5 (phenyl-*C*2/6), 128.1 (HC=*C*(^{q}C)(CH)), 125.7 (indole-*C*2), 122.1 (indole-*C*6), 121.6 (*C*^{q}-Br), 119.3 (indole-*C*5), 119.2 (indole-*C*4), 115.0 (indole-*C*3), 109.7 (indole-*C*7), 49.4 (N-*C*H_2-Ph), 43.3 (Ar-CH_2-*C*H_2-C(O)), 43.2 (C(O)-*C*H_2), 31.5 (Ar-*C*H_2-CH_2-C(O)), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 19.4 (CH_2-*C*H_2-CH_3), 14.1 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3056, 3046, 3026, 2956, 2928, 2870, 2855, 1711, 1613, 1592, 1574, 1555, 1487, 1466, 1438, 1407, 1374, 1351, 1331, 1297, 1258, 1199, 1177, 1126, 1108, 1071, 1011, 969, 932, 844, 801, 740, 667, 611, 586, 571, 540, 527. **MS (ESI) *m/z***: 450.1 (40%, $[M + K]^+$), 434.1 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 434.1090; measured: 434.1079.

1.4.6 1-(1H-indole-3-yl)octan-3-one (6fA)

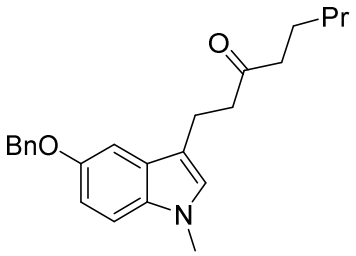


6fA

4f was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6fA** as a white solid (23.7 mg, 57%).

$C_{16}H_{21}NO$, **MW**: 243.35 g/mol. **MP**: 81.0 – 82.5 °C. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.97 (*bs*, 1H, N*H*), 7.60 (*d*, *J* = 8.0, 1H, indole C(4)*H*), 7.35 (*d*, 1H, indole C(6)*H*), 7.24-7.16 (*m*, 1H, indole C(7)*H*), 7.16-7.09 (*m*, 1H, indole C(5)*H*), 6.98 (*d*, *J* = 2.3, 1H, indole C(2)*H*), 3.05 (*t*, *J* = 7.4, 2H, indole-CH_2-C*H*$_2$-C(O)), 2.82 (*t*, *J* = 7.4, 2H, indole-C*H*$_2$-CH_2-C(O)), 2.38 (*t*, *J* = 7.4, 2H, C(O)-C*H*$_2$), 1.60-1.50 (*m*, 2H, C(O)-CH_2-C*H*$_2$), 1.37-1.17 (*m*, 4H, C(O)-CH_2-CH_2-C*H*$_2$-C*H*$_2$), 0.87 (*t*, *J* = 7.3, 3H, CH_2-C*H*$_3$). **^{13}C-NMR (63 MHz, $CDCl_3$)**: δ = 211.3 (O=*C*), 136.4 (HC=*C*(NMe)(^{q}C)), 127.3 (HC=*C*(^{q}C)(CH)), 122.1 (indole-*C*2), 121.6 (indole-*C*6), 119.4 (indole-*C*5), 118.8 (indole-*C*4), 115.5 (indole-*C*3), 111.3 (indole-*C*7), 43.3 (Ar-CH_2-*C*H_2-C(O)), 43.1 (C(O)-*C*H_2), 31.5 (Ar-*C*H_2-CH_2-C(O)), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 19.5 (CH_2-*C*H_2-CH_3), 14.0 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3270, 3059, 2956, 2928, 2852, 1698, 1620, 1577, 1494, 1458, 1441, 1413, 1381, 1353, 1336, 1271, 1249, 1221, 1124, 1104, 1062, 1007, 908, 881, 827, 801, 771, 737, 666, 587, 564, 471, 457, 426. **MS (ESI) *m/z***: 282.14 (100%, $[M + K]^+$), 266.15 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 266.1515; measured: 266.1508.

1.4.7 1-(5-(Benzyloxy)-1-methyl-1H-indole-3-yl)octan-3-one (6gA)

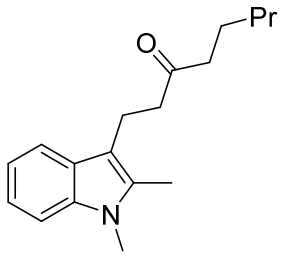


6gA

4g was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6gA** as a yellowish oil (30.7 mg, 50%).

$C_{24}H_{29}NO_2$, **MW**: 363.50 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.53-7.47 (*m*, 2H, phenyl C(2/6)*H*), 7.44-7.29 (*m*, 3H, phenyl C(3/5)*H*, indole C(7)*H*), 7.21-7.16 (*m*, 1H, phenyl C(4)*H*), 7.12-7.09 (*m*, 1H, indole C(4)*H*), 7.00-6.94 (*m*, 1H, indole C(6)*H*), 6.82 (*s*, 1H, indole C(2)*H*), 5.13 (*s*, 2H, O-CH_2-Ph), 3.70 (*s*, 3H, N-CH_3), 2.99 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.77 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.38 (*t*, *J* = 7.4, 2H, C(O)-CH_2), 1.64-1.50 (*m*, 2H, C(O)-CH_2-CH_2), 1.37-1.17 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.88 (*t*, *J* = 7.3, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.3 (O=*C*), 152.9 (indole-*C*5-OBn), 137.9 (HC=*C*(NMe)(^{q}C)), 132.7 (^{q}*C*-CH_2-O), 128.6 (phenyl-*C*3/5), 127.92 (HC=*C*(^{q}C)(CH)), 127.89 (phenyl-*C*4), 127.7 (phenyl-*C*2/6), 127.2 (indole-*C*2), 113.4 (indole-*C*3), 112.5 (indole-*C*6), 110.1 (indole-*C*7), 102.7 (indole-*C*4), 71.2 (O-*C*H_2-Ph), 43.3 (Ar-CH_2-*C*H_2-C(O)), 43.2 (C(O)-*C*H_2), 32.9 (N-*C*H_3), 31.5 (Ar-*C*H_2-CH_2-C(O)), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 19.4 (CH_2-*C*H_2-CH_3), 14.1 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3032, 2927, 2858, 1708, 1621, 1576, 1488, 1454, 1424, 1372, 1298, 1254, 1215, 1136, 1121, 1080, 1055, 1025, 924, 829, 789, 735, 696, 633, 608, 506, 473, 429. **MS (ESI) *m/z***: 402.19 (3%, $[M + K]^+$), 386.21 (100%, $[M + Na]^+$), 364.23 (3%, $[M + H]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 386.2091; measured: 386.2095.

1.4.8 1-(1,2-Dimethyl-1H-indole-3-yl)octan-3-one (6hA)

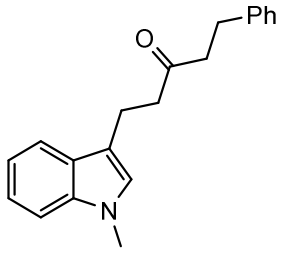


6hA

4h was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6hA** as a colorless oil (38.7 mg, 90%).

$C_{18}H_{25}NO$, **MW**: 271.40 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.50 (*d*, *J* = 7.8, 1H, indole C(4)*H*), 7.25 (*d*, *J* = 7.8, 1H, indole C(6)*H*), 7.20-7.13 (*m*, 1H, indole C(7)*H*), 7.12-7.05 (*m*, 1H, indole C(5)*H*), 3.65 (*s*, 3H, N-CH_3), 3.01 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.73 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.38 (*s*, 3H, indole C(2)-CH_3), 2.34 (*t*, *J* = 7.4, 2H, C(O)-CH_2), 1.62-1.47 (*m*, 2H, C(O)-CH_2-CH_2), 1.36-1.15 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.87 (*t*, *J* = 7.3, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.5 (O=*C*), 136.7 (HC=*C*(NMe)(^{q}C)), 133.1 (indole-*C*2), 127.4 (HC=*C*(^{q}C)(CH)), 120.7 (indole-*C*6), 118.8 (indole-*C*5), 117.8 (indole-*C*4), 110.0 (indole-*C*3), 108.7 (indole-*C*7), 43.6 (Ar-CH_2-*C*H_2-C(O)), 43.3 (C(O)-*C*H_2), 31.5 (Ar-*C*H_2-CH_2-C(O)), 29.6 (N-*C*H_3), 23.6 (C(O)-CH_2-*C*H_2), 22.5 (*C*H_2-CH_2-CH_3), 18.9 (CH_2-*C*H_2-CH_3), 14.0 (CH_2-*C*H_3) 10.3 (indole C(2)-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3050, 2952, 2928, 2858, 1709, 1614, 1567, 1471, 1408, 1369, 1330, 1269, 1248, 1186, 1148, 1127, 1079, 1057, 1012, 973, 918, 736, 576, 557, 490, 434. **MS (ESI) *m/z***: 294.18 (100%, $[M + Na]^+$), 272.20 (8%, $[M + H]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 294.1828; measured: 294.1828.

1.4.9 1-(1-Methyl-1H-indole-3-yl)-5-phenylpentan-3-one (6aB)

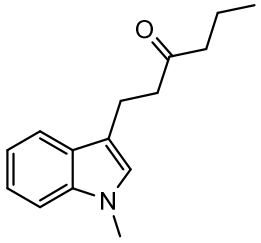


6aB

4a was treated with **5B** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6aB** as a white solid (28.0 mg, 60%).

$C_{20}H_{21}NO$, **MW**: 291.39 g/mol. **MP**: 42.1 – 42.7 °C. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.62-7.55 (*m*, 1H, indole C(4)*H*), 7.35-7.09 (*m*, 8H, indole-*H* + Ph-*H*), 6.83 (*s*, 1H, indole C(2)*H*), 3.75 (*s*, 3H, N-CH_3), 3.06 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.92 (*t*, *J* = 7.4, 2H, C(O)-CH_2-CH_2-Ph), 2.82 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.74 (*t*, *J* = 7.4, 2H, C(O)-CH_2-CH_2-Ph). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 210.0 (O=*C*), 141.2 (Ph-*C*1), 137.1 (HC=*C*(NMe)(^{q}C)), 128.6 (Ph-*C*3/5), 128.5 (Ph-*C*2/6), 127.6 (HC=*C*(^{q}C)(CH)), 126.5 (indole-*C*2), 126.2 (Ph-*C*4), 121.7 (indole-*C*6), 118.9 (indole-*C*5), 118.8 (indole-*C*4), 113.8 (indole-*C*3), 109.3 (indole-*C*7), 44.6 (Ar-CH_2-*C*H_2-C(O)), 43.8 (C(O)-*C*H_2-CH_2-Ph), 32.7 (N-*C*H_3), 29.9 (C(O)-CH_2-*C*H_2-Ph), 19.4 (Ar-*C*H_2-CH_2-C(O)). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3026, 2926, 1709, 1603, 1554, 1472, 1453, 1424, 1408, 1373, 1325, 1249, 1207, 1155, 1130, 1091, 1074, 1030, 1012, 976, 923, 801, 737, 699, 607, 550, 506. **MS (ESI) *m/z***: 346.14 (20%, $[M + O_2 + Na]^+$), 330.15 (20%, $[M + O + Na]^+$), 314.15 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 314.1515; measured: 314.1512.

1.4.10 1-(1-Methyl-1H-indole-3-yl)hexan-3-one (6aC)

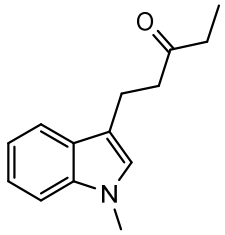


6aC

4a was treated with **5C** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6aC** as a colorless oil (23.9 mg, 65%).

$C_{15}H_{19}NO$, **MW**: 229.32 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.62-7.56 (*m*, 1H, indole C(4)*H*), 7.32-7.27 (*m*, 1H, indole C(6)*H*), 7.27-7.20 (*m*, 1H, indole C(7)*H*), 7.16-7.08 (*m*, 1H, indole C(5)*H*), 6.85 (*s*, 1H, indole C(2)*H*), 3.74 (*s*, 3H, N-CH_3), 3.05 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.80 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.38 (*t*, *J* = 7.4, 2H, C(O)-CH_2), 1.68-1.53 (*m*, 2H, C(O)-CH_2-CH_2), 0.91 (*t*, *J* = 7.4, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.1 (O=*C*), 137.1 (HC=*C*(NMe)(^{q}C)), 127.7 (HC=*C*(^{q}C)(CH)), 126.5 (indole-*C*2), 121.7 (indole-*C*6), 118.9 (indole-*C*5), 118.8 (indole-*C*4), 113.9 (indole-*C*3), 109.3 (indole-*C*7), 45.0 (Ar-CH_2-*C*H_2-C(O)), 43.5 (C(O)-*C*H_2), 32.7 (N-*C*H_3), 19.3 (Ar-*C*H_2-CH_2-C(O)), 17.4 (CH_2-*C*H_2-CH_3), 13.9 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3053, 2960, 2932, 2874, 1710, 1615, 1554, 1485, 1470, 1425, 1409, 1375, 1325, 1249, 1207, 1154, 1125, 1081, 1056, 1013, 923, 791, 738, 604, 555. **MS (ESI) *m/z***: 268.13 (5%, $[M + K]^+$), 252.14 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 252.1359; measured: 252.1368.

1.4.11 1-(1-Methyl-1H-indole-3-yl)pentan-3-one (6aD)

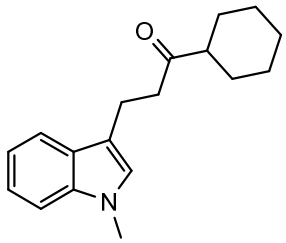


6aD

4a was treated with **5D** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6aD** as a colorless oil (25.2 mg, 73%).

$C_{14}H_{17}NO$, **MW**: 215.30 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: $\delta = \delta$ = 7.56 (*d*, *J* = 7.9, 1H, indole C(4)*H*), 7.32-7.16 (*m*, 2H, indole C(6)*H*, indole C(7)*H*), 7.15-7.05 (*m*, 1H, indole C(5)*H*), 6.83 (*s*, 1H, indole C(2)*H*), 3.71 (*s*, 3H, N-CH_3), 3.03 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.79 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.40 (*q*, *J* = 7.3, 2H, C(O)-CH_2), 1.03 (*t*, *J* = 7.3, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 211.5 (O=*C*), 137.1 (HC=*C*(NMe)(^{q}C)), 127.7 (HC=*C*(^{q}C)(CH)), 126.5 (indole-*C*2), 121.7 (indole-*C*6), 118.9 (indole-*C*5), 118.8 (indole-*C*4), 113.9 (indole-*C*3), 109.3 (indole-*C*7), 43.2 (Ar-CH_2-*C*H_2-C(O)), 36.2 (C(O)-*C*H_2-CH_3), 32.7 (N-*C*H_3), 19.4 (Ar-*C*H_2-CH_2-C(O)), 7.9 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3053, 2974, 2935, 2878, 1711, 1615, 1554, 1485, 1471, 1446, 1425, 1410, 1375, 1352, 1324, 1249, 1207, 1154, 1131, 1111, 1072, 1051, 1012, 974, 924, 894, 807, 738, 604, 555. **MS (ESI) *m/z***: 254.11 (25%, $[M + K]^+$), 238.12 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 238.1202; measured: 238.1191.

1.4.12 1-Cyclohexyl-3-(1-methyl-1H-indole-3-yl)propan-1-one (6aE)

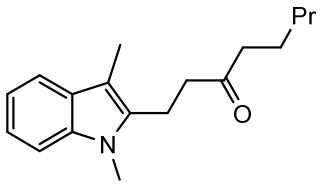


6aE

4a was treated with **5E** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **6aE** as a colorless oil (38.4 mg, 89%).

$C_{18}H_{23}NO$, **MW**: 269.39 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.59 (*d*, *J* = 7.9, 1H, indole C(4)*H*), 7.29 (*d*, *J* = 7.9, 1H, indole C(6)*H*), 7.26-7.20 (*m*, 1H, indole C(7)*H*), 7.15-7.08 (*m*, 1H, indole C(5)*H*), 6.84 (*s*, 1H, indole C(2)*H*), 3.74 (*s*, 3H, N-CH_3), 3.03 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.84 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.42-2.26 (*m*, 1H, C(O)-C*H*), 1.90-1.72 (*m*, 4H, Cyclohexyl-*H*), 1.71-1.59 (*m*, 1H, Cyclohexyl-*H*), 1.43-1.12 (*m*, 5H, Cyclohexyl-*H*). **^{13}C-NMR (63 MHz, $CDCl_3$)**: δ = 214.0 (O=*C*), 137.1 (HC=*C*(NMe)(^{q}C)), 127.7 (HC=*C*(^{q}C)(CH)), 126.4 (indole-*C*2), 121.6 (indole-*C*6), 118.9 (indole-*C*5), 118.8 (indole-*C*4), 114.2 (indole-*C*3), 109.3 (indole-*C*7), 51.0 (Ar-CH_2-*C*H_2-C(O)), 41.5 (C(O)-*C*H), 32.7 (N-*C*H_3), 28.6 (Cyclohexyl-*C*(2/6)), 26.0 (Cyclohexyl-*C*(4)), 25.8 (Cyclohexyl-*C*(3/5)), 19.3 (Ar-*C*H_2-CH_2-C(O)). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3053, 2925, 2852, 1702, 1615, 1555, 1472, 1447, 1424, 1408, 1374, 1344, 1325, 1291, 1248, 1206, 1142, 1087, 1062, 1012, 989, 919, 889, 799, 735, 606, 557, 513. **MS (ESI) *m/z***: 324.16 (7%, $[M + O_2 + Na]^+$), 308.16 (11%, $[M + O + Na]^+$), 292.17 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 292.1672; measured: 292.1671.

1.4.13 1-(1,3-Dimethyl-1H-indole-2-yl)octan-3-one (8)

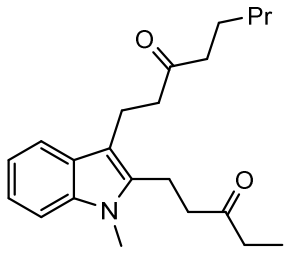


8

7 was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **8** as a colorless oil (13.2 mg, 59%).

$C_{18}H_{25}NO$, **MW**: 271.40 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.50 (*d*, *J* = 8.0, 1H, indole C(4)*H*), 7.28-7.22 (*m*, 1H, indole C(6)*H*), 7.21-7.14 (*m*, 1H, indole C(7)*H*), 7.12-7.05 (*m*, 1H, indole C(5)*H*), 3.67 (*s*, 3H, N-CH_3), 3.05 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.66 (*t*, *J* = 7.4, 2H, indole-CH_2-CH_2-C(O)), 2.38 (*t*, *J* = 7.4, 2H, C(O)-CH_2), 2.27 (*s*, 3H, indole C(3)-CH_3), 1.63-1.51 (*m*, 2H, C(O)-CH_2-CH_2), 1.37-1.17 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.88 (*t*, *J* = 7.3, 3H, CH_2-CH_3). **^{13}C-NMR (126 MHz, $CDCl_3$)**: δ = 210.0 (O=*C*), 136.7 (HC=*C*(NMe)(^{q}C)), 135.5 (indole-*C*3), 128.4 (HC=*C*(^{q}C)(CH)), 121.0 (indole-*C*6), 118.8 (indole-*C*5), 118.2 (indole-*C*4), 108.8 (indole-*C*2), 106.8 (indole-*C*7), 43.2 (Ar-CH_2-*C*H_2-C(O)), 42.4 (C(O)-*C*H_2), 31.5 (Ar-*C*H_2-CH_2-C(O)), 29.7 (N-*C*H_3), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 18.6 (CH_2-*C*H_2-CH_3), 14.0 (CH_2-*C*H_3), 8.9 (indole C(3)-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3053, 2954, 2927, 2859, 1711, 1615, 1567, 1470, 1408, 1382, 1366, 1329, 1244, 1189, 1150, 1128, 1078, 1012, 974, 917, 839, 737, 664, 569, 548, 510, 457, 438, 416. **MS (ESI) *m/z***: 294.18 (100%, $[M + Na]^+$), 272.20 (75%, $[M + H]^+$), 158.10 (71%, [1-Methyl-2,3-dimethylenindoleine + $H]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + H]^+$): 272.2009; measured: 272.1998, calculated for ($[M + Na]^+$): 294.1828; measured: 294.1818.

1.4.14 1-(1-Methyl-2-(3-oxopentyl)-1H-indole-3-yl)octan-3-one (9)

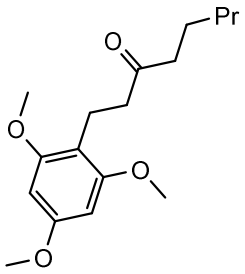


9

6aA was treated with **5D** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **9** as a yellow oil (21.3 mg, 64%).

$C_{22}H_{31}NO_2$, **MW**: 341.50 g/mol. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ = 7.48 (*d*, *J* = 7.5, 1H, indole C(4)*H*), 7.25 (*d*, *J* = 7.5, 1H, indole C(6)*H*), 7.19-7.14 (*m*, 1H, indole C(7)*H*), 7.10-7.05 (*m*, 1H, indole C(5)*H*), 3.65 (*s*, 3H, N-CH_3), 3.06 (*t*, *J* = 7.3, 2H, indole C(2)-CH_2-CH_2-C(O)), 2.98 (*t*, *J* = 7.1, 2H, indole C(3)-CH_2-CH_2-C(O)), 2.73 (*t*, *J* = 7.1, 2H, indole C(3)-CH_2-CH_2-C(O)), 2.66 (*t*, *J* = 7.3, 2H, indole C(2)-CH_2-CH_2-C(O)), 2.43 (*q*, *J* = 7.3, 2H, C(O)-CH_2-CH_3), 2.34 (*t*, *J* = 7.3, 2H, C(O)-CH_2-CH_2), 1.57-1.49 (*m*, 2H, C(O)-CH_2-CH_2), 1.30-1.17 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 1.07 (*t*, *J* = 7.4, 3H, C(O)-CH_2-CH_3), 0.86 (*t*, *J* = 7.0, 3H, CH_2-CH_3). **^{13}C-NMR (126 MHz, $CDCl_3$)**: δ = 211.3 (O=*C*), 210.1 (O=*C*), 137.0 (HC=*C*(NMe)(^{q}C)), 135.9 (indole-*C*2), 127.4 (HC=*C*(^{q}C)(CH)), 121.1 (indole-*C*6), 119.1 (indole-*C*5), 118.2 (indole-*C*4), 110.5 (indole-*C*3), 109.0 (indole-*C*7), 43.7 (Ar-CH_2-*C*H_2-C(O)), 43.3 (C(O)-*C*H_2), 42.4 (Ar-CH_2-*C*H_2-C(O)), 36.3 (C(O)-*C*H_2-CH_3), 31.5 (*C*H_2-CH_2-CH_3), 29.8 (N-*C*H_3), 23.6 (C(O)-CH_2-*C*H_2), 22.6 (CH_2-*C*H_2-CH_3), 18.8 (Ar-*C*H_2-CH_2-C(O)), 18.6 (Ar-*C*H_2-CH_2-C(O)), 14.0 (CH_2-*C*H_3), 7.9 (C(O)-CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 3053, 2931, 2872, 1709, 1613, 1565, 1470, 1435, 1408, 1368, 1333, 1241, 1187, 1147, 1112, 1079, 1014, 971, 739, 557. **MS (ESI) *m/z***: 364.23 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 364.2247; measured: 364.2251.

1.4.15 1-(2,4,6-Trimethoxyphenyl)octan-3-one (10)

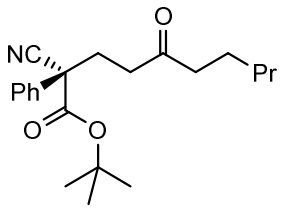


10

1,3,5-Trimethoxybenzene was treated with **5A** according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **10** as a white solid (32.0 mg, 73%).

$C_{17}H_{26}O_4$, **MW**: 294.39 g/mol. **MP**: 49.6 – 50.1 °C. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 6.11 (*s*, 2H, phenyl C(3/5)*H*), 3.80 (*s*, 3H, phenyl C(4)OCH_3), 3.78 (*s*, 6H, phenyl C(2/6)OCH_3), 2.83 (*t*, *J* = 7.4, 2H, phenyl-CH_2-CH_2-C(O)), 2.52 (*t*, *J* = 7.4, 2H, phenyl-CH_2-CH_2-C(O)), 2.39 (*t*, *J* = 7.4, 2H, C(O)-CH_2), 1.63-1.51 (*m*, 2H, C(O)-CH_2-CH_2), 1.38-1.19 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.89 (*t*, *J* = 7.3, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz (500er), $CDCl_3$)**: δ = 212.2 (O=*C*), 159.6 (phenyl-*C*4), 158.9 (phenyl-*C*2/6), 109.9 (phenyl-*C*1), 90.6 (phenyl-*C*3/5), 55.7 (2x *o*-OCH_3), 55.5 (*p*-OCH_3), 42.7 (Ar-CH_2-*C*H_2-C(O)), 42.6 (C(O)-*C*H_2), 31.6 (Ar-*C*H_2-CH_2-C(O)), 23.8 (C(O)-CH_2-*C*H_2), 22.6 (*C*H_2-CH_2-CH_3), 17.7 (CH_2-*C*H_2-CH_3), 14.1 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 2936, 2838, 1710, 1609, 1595, 1499, 1456, 1417, 1367, 1320, 1230, 1205, 1150, 1125, 1078, 1060, 1042, 950, 812, 632, 510. **MS (ESI) *m/z***: 317.17 (100%, $[M + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 317.1723; measured: 317.1709.

1.4.16 *tert*-Butyl (*R*)-2-cyano-5-oxo-2-phenyldecanoate ((*R*)-11a)

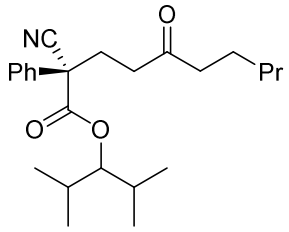


(*R*)-11a

The activation of the catalyst was done according to **GP1**. Then diglyme was used as the solvent for the stock solution as well as for the catalysis. Subsequently *tert*-butyl 2-cyano-2-phenylacetate was treated with **5A** and the catalyst stock solution according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **(*R*)-11a** as a colorless oil (37.6 mg, 68%, *ee* = 44%). The enantiomeric excess was determined by chiral column HPLC: Chiralcel OD-H, n-hexane/i-PrOH (99.8/0.2), 0.8 mL min^{-1}, 210 nm; 46.74 min (major enantiomer), 65.59 min (minor enantiomer). The absolute configuration of the major enantiomer was achieved by comparison with Michael addition products of Peters and Jautze.[7]

$C_{21}H_{29}NO_3$, **MW**: 343.47 g/mol. **$[\alpha]_D^{24}$**: –3.8 (c = 1 g/dL, $CHCl_3$, sample with ee = 44%). **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.54-7.47 (*m*, 2H, phenyl C(2/6)*H*), 7.44-7.32 (*m*, 3H, phenyl C(3/4/5)*H*), 2.68-2.32 (*m*, 6H, ^{q}C-CH_2-CH_2-C(O)-CH_2), 1.60-1.47 (*m*, 2H, C(O)-CH_2-CH_2), 1.41 (*s*, 9H, C(O)OC(CH_3)$_3$), 1.36-1.15 (*m*, 4H, C(O)-CH_2-CH_2-CH_2-CH_2), 0.86 (*t*, *J* = 7.0, 3H, CH_2-CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 208.7 (O=*C*(C)(C)), 166.1 (*C*(O)OC(CH_3)$_3$), 134.5 (phenyl-*C*1), 129.2 (phenyl *C*3/5), 128.9 (phenyl-*C*4), 126.1 (phenyl-*C*2/6), 118.6 (*C*N), 84.6 (C(O)O*C*(CH_3)$_3$), 54.1 (Ph-*C*(CN)(COOC(CH_3)$_3$)-CH_2), 43.0 (Ar-CH_2-*C*H_2-C(O)), 38.5 (C(O)-*C*H_2), 31.6 (Ar-*C*H_2-CH_2-C(O)), 31.4 (C(O)-CH_2-*C*H_2), 27.7 (C(O)O(*C*H_3)$_3$), 23.5 (*C*H_2-CH_2-CH_3), 22.5 (CH_2-*C*H_2-CH_3), 14.0 (CH_2-*C*H_3). **IR (in $CDCl_3$)**: $\tilde{\nu}$ = 2933, 2872, 1737, 1715, 1599, 1493, 1450, 1417, 1395, 1370, 1251, 1150, 1089, 1034, 916, 838, 730, 696, 646, 599, 507. **MS (ESI) *m/z***: 366.20 (100%, $[M + Na]^+$), 310.14 (60%, $[M - C_4H_8 + Na]^+$). **HRMS (ESI) *m/z***: calculated for ($[M + Na]^+$): 366.2040; measured: 366.2045.

1.4.17 2,4-Dimethylpentan-3-yl (*R*)-2-cyano-5-oxo-2-phenyldecanoate ((*R*)-11b)



(*R*)-11b

The activation of the catalyst was done according to **GP1**. Then diglyme was used as the solvent for the stock solution as well as for the catalysis. Subsequently 2,4-dimethylpentan-3-yl 2-cyano-2-phenylacetate was treated with **5A** and the catalyst stock solution according to **GP1**. Flash column chromatography (silica gel, petrol ether/ ethyl acetate = 20:1) yielded **(*R*)-11b** as a white solid (41.2 mg, 66%, *ee* = 68%). The enantiomeric excess was determined by chiral column HPLC: Chiralcel OD-H, n-hexane/i-PrOH (99.9/0.1), 0.8 mL min^{-1}, 210 nm; 56.30 min (minor enantiomer), 64.90 min (minor enantiomer).

$C_{24}H_{35}NO_3$, **MW**: 385.55 g/mol. **MP**: 50.6 – 51.4 °C. **$[\alpha]_D^{24}$**: –1.3 (c = 1 g/dL, $CHCl_3$, sample with ee = 68%). **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.59-7.52 (*m*, 2H, Phenyl C(2/6)*H*), 7.44-7.32 (*m*, 3H, Phenyl C(3/4/5)*H*), 4.57 (*t*, *J* = 6.1, 1H, OC*H*($CH(CH_3)_2)_2$), 2.72-2.55 (*m*, 2H, ^{q}C-C*H*$_2$-CH_2-C(O)-CH_2), 2.55-2.40 (*m*, 2H, ^{q}C-CH_2-C*H*$_2$-C(O)-CH_2), 2.40-2.31 (*m*, 2H, ^{q}C-CH_2-CH_2-C(O)-C*H*$_2$), 2.01-1.87 (*m*, 1H, OCH(C*H*($CH_3)_2)_2$), 1.87-1.73 (*m*, 1H, OCH(C*H*($CH_3)_2)_2$), 1.60-1.46 (*m*, 2H, C(O)-CH_2-C*H*$_2$), 1.36-1.15 (*m*, 4H, C(O)-CH_2-CH_2-C*H*$_2$-C*H*$_2$), 0.92-0.83 (*m*, 9H, OCH(CH(C*H*$_3)_2)_2$ + CH_2-C*H*$_3$), 0.63 (*d*, *J* = 6.7, 3H, OCH(CH(C*H*$_3)_2)_2$), 0.53 (*d*, *J* = 6.7, 3H, OCH(CH(C*H*$_3)_2)_2$). **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 208.6 (O=*C*(C)(C)), 167.3 (*C*(O)OCH($CH(CH_3)_2)_3$), 134.1 (Phenyl-*C*1), 129.3 (Phenyl *C*3/5), 129.1 (Phenyl-*C*4), 126.3 (Phenyl-*C*2/6), 118.3 (*C*N), 86.6 (C(O)O*C*H($CH(CH_3)_2)_3$), 53.6 (Ph-*C*(CN)(C(O)OCH($CH(CH_3)_2)_3$)-CH_2), 43.0 (^{q}C-CH_2-*C*H_2-C(O)), 38.5 (C(O)-*C*H_2), 31.4 (^{q}C-*C*H_2-CH_2-C(O)), 31.3 (C(O)-CH_2-*C*H_2), 29.5 (2xC(O)OCH(*C*H($CH_3)_2)_3$), 23.5 (*C*H_2-CH_2-CH_3), 22.5 (CH_2-*C*H_2-CH_3), 19.6 (C(O)OCH(CH(*C*$H_3)_2)_3$), 19.3 (C(O)OCH(CH(*C*$H_3)_2)_3$), 16.9 (C(O)OCH(CH(*C*$H_3)_2)_3$), 16.8 (C(O)OCH(CH(*C*$H_3)_2)_3$), 14.0 (CH_2-*C*H_3). **IR (in $CDCl_3$):** $\tilde{\nu}$ = 3065, 2963, 2935, 2875, 1742, 1716, 1599, 1495, 1450, 1417, 1390, 1371, 1320, 1235, 1185, 1132, 1097, 1075, 1050, 1034, 1000, 963, 935, 892, 767, 727, 697, 646, 594, 504. **MS (ESI) *m/z*:** 408.25 (100%, $[M + Na]^+$), 310.14 (9%, $[M - C_7H_{14} + Na]^+$). **HRMS (ESI) *m/z*:** calculated for ($[M + Na]^+$): 408.2509; measured: 408.2512.

2. References

[1] Jautze, S.; Diethelm, S.; Frey, W.; Peters, R. *Organometallics* **2009**, *28*, 2001-2004.

[2] Hellmuth, T.; Rieckhoff, S.; Weiss, M.; Dorst, K.; Frey, W.; Peters, R. *ACS Catal.* **2014**, 1850-1858.

[3] Weiss, M.; Frey, W.; Peters, R. *Organometallics* **2012**, *31*, 6365-6372.

[4] Faul, M. M.; Winneroski, L.L. *Tetrahedron Letters* **1997**, *27*, 4749-4752.

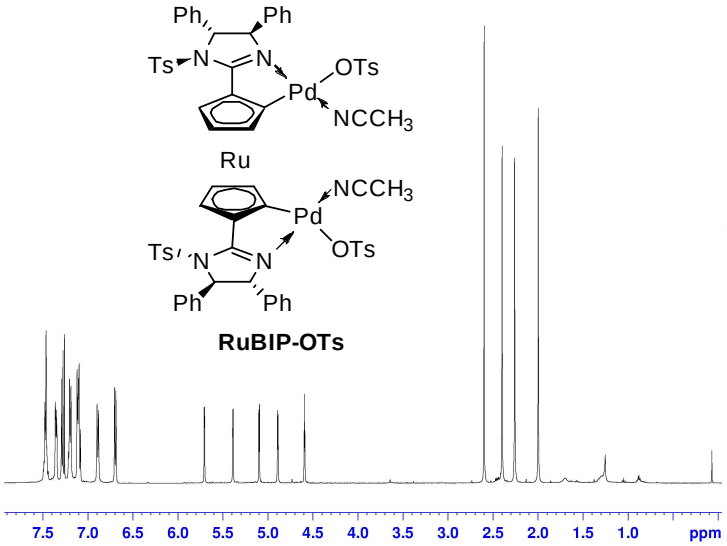
[5] Chen, M.; Huang, Z.-T.; Zheng, Q.-Y. *Chem. Commun.* **2012**, *48*, 11686-11688.

[6] Bouziane, A.; Carboni, B.; Bruneau, C.; Carreaux, F.; Renaud, J.-L. *Tetrahedron* **2008**, *64*, 11745-11750.

[7] Jautze, S.; Peters, R. *Angew. Chem. Int. Ed.* **2008**, *47*, 9284-9288.

3. NMR spectra

3.1 {Acetonitrile-[(η^5-(*4''R*,*5''R*)-(1-*S*$_P$)-2-(2''-4'',5''-dihydro-4'',5''-diphenyl-1''-tosyl-1''H-imidazolyl)cyclopentadienyl, κ*C*1, κ*N*3]-*para*-toluenesulfonato-palladium(II)]}-{acetonitrile-[(η^5-(*4'''R*,*5'''R*)-(1'-*S*$_P$)-2'-(2'''-4''',5'''-dihydro-4''',5'''-diphenyl-1'''-tosyl-1'''H-imidazolyl)cyclopentadienyl, κ*C*1', κ*N*3']- *para*-toluenesulfonato-platinum(II)]}-iron(II) (RuBIP-OTs)

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Current Data Parameters
NAME                  14-HA830
EXPNO                       40
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140909
Time                   12.09
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        32
DS                         0
SWH                10330.578 Hz
FIDRES             0.315264 Hz
AQ                 1.5860212 sec
RG                       322
DW                    48.400 usec
DE                    10.00 usec
TE                    296.8 K
D1                 2.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      11.23 usec
PL1                      1.00 dB
PL1W               19.75309753 W
SFO1               500.1560886 MHz

F2 - Processing parameters
SI                       16384
SF                 500.1530162 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
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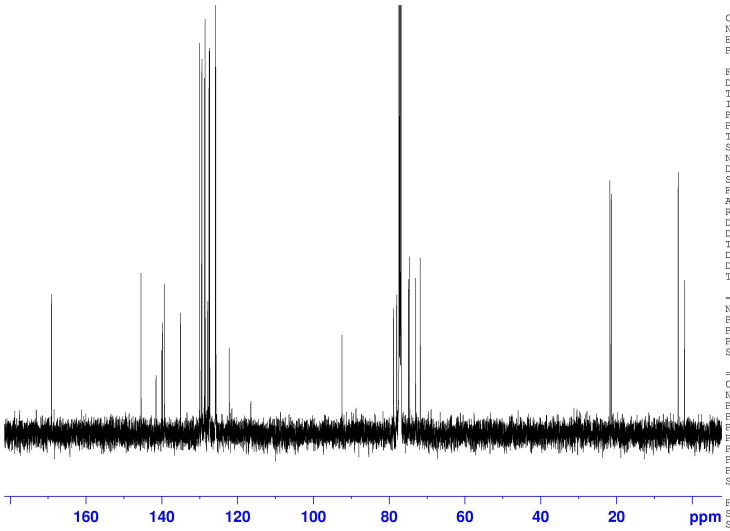
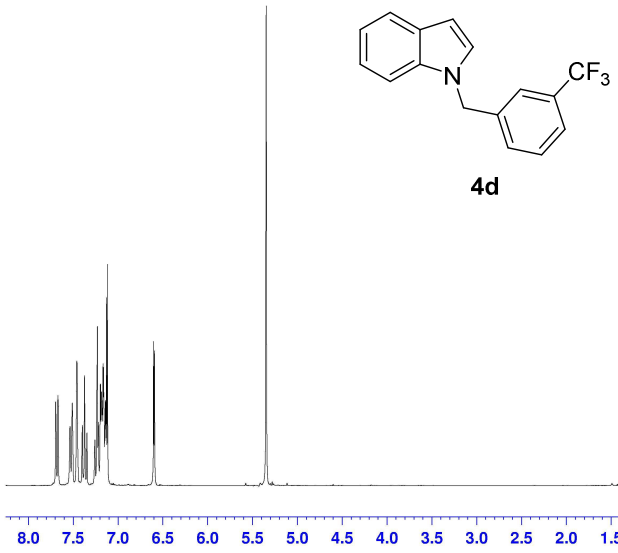
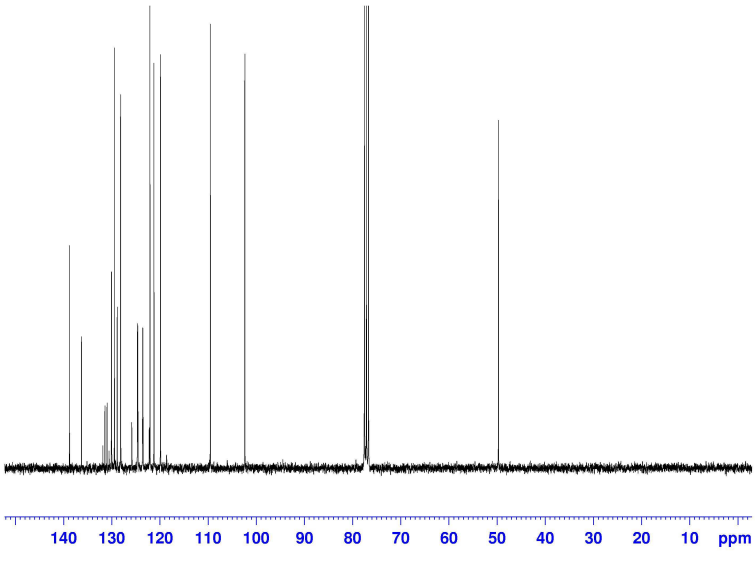



```
Current Data Parameters
NAME                  14-HA830
EXPNO                       42
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140909
Time                   13.03
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH                32894.738 Hz
FIDRES             0.501934 Hz
AQ                 0.9961972 sec
RG                      2890
DW                    15.200 usec
DE                    10.00 usec
TE                    296.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.20 usec
PL1                      1.50 dB
PL1W               51.74793243 W
SFO1               125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                      1.00 dB
PL12                    19.99 dB
PL13                    21.00 dB
PL2W               19.75309753 W
PL12W               0.24925002 W
PL13W               0.19753097 W
SFO2               500.1550006 MHz

F2 - Processing parameters
SI                       32768
SF                 125.7635574 MHz
WDW                         EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.40
```

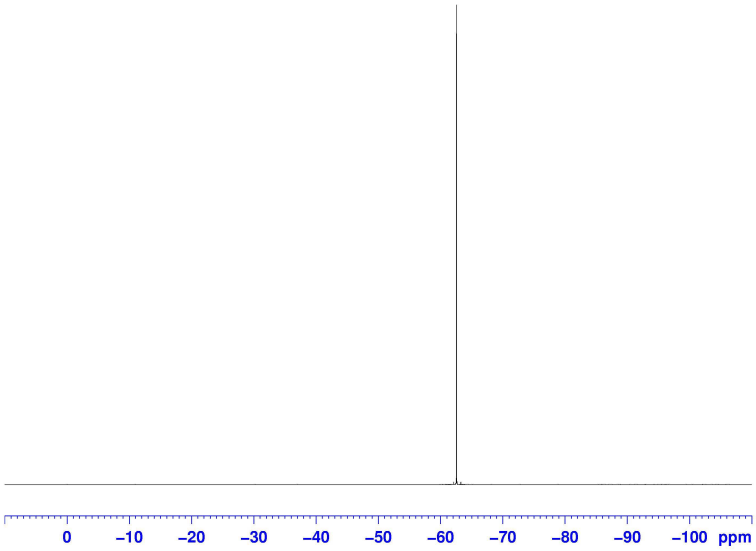
3.2 1-(3-(Trifluoromethyl)benzyl)-1H-indole (4d)




```
Current Data Parameters
NAME                  14-AK318
EXPNO                      500
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140505
Time                   17.32
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                6188.119 Hz
FIDRES             0.188846 Hz
AQ                2.64777044 sec
RG                       181
DW                    80.800 usec
DE                     8.00 usec
TE                    296.0 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      11.05 usec
PL1                     -2.00 dB
PL1W              37.02396774 W
SFO1             300.1318534 MHz

F2 - Processing parameters
SI                         16384
SF                300.1300154 MHz
WDW                           EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

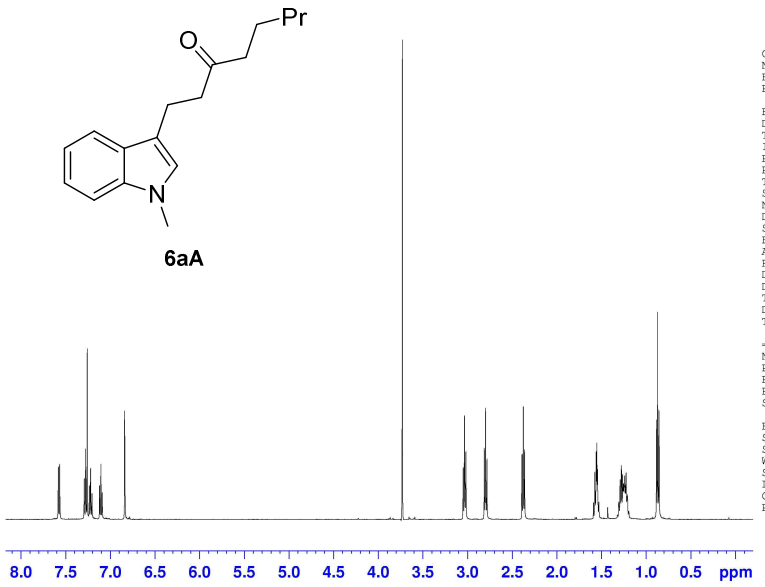



```
Current Data Parameters
NAME                  14-AK318
EXPNO                      501
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140506
Time                    2.41
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH               18028.846 Hz
FIDRES             0.275098 Hz
AQ                1.8175818 sec
RG                      2890
DW                    27.733 usec
DE                     8.00 usec
TE                    296.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                      11.75 usec
PL1           0 dB
PL1W              31.14739227 W
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                     -2.00 dB
PL12                    17.05 dB
PL13                    19.00 dB
PL2W              37.02396774 W
PL12W              0.46076876 W
PL13W              0.29409182 W
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                75.4677414 MHz
WDW                           EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

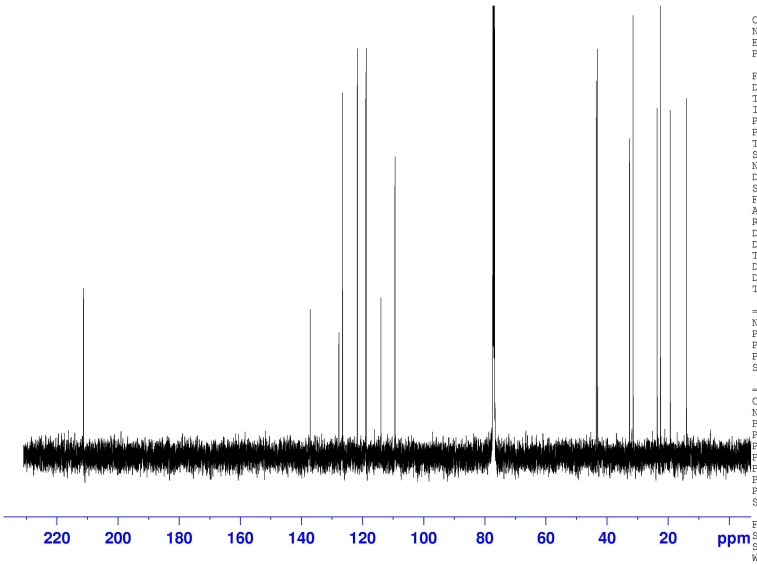



```
Current Data Parameters
NAME                  14-AK318
EXPNO                      100
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20140507
Time                      9.14
INSTRUM                  spect
PROBHD    5 mm QNP 1H/13
PULPROG                 zgflqn
TD                      131072
SOLVENT                   CDCl3
NS                           16
DS                            4
SWH                 56497.176 Hz
FIDRES               0.431039 Hz
AQ                  1.1600372 sec
RG                       724.1
DW                       8.850 usec
DE                       6.00 usec
TE                       300.0 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       19F
P1                       13.80 usec
PL1                      -6.00 dB
SFO1              235.3338140 MHz

F2 - Processing parameters
SI                       65536
SF                235.3573500 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

3.3 1-(1-Methyl-1H-indole-3-yl)octan-3-one (6aA)

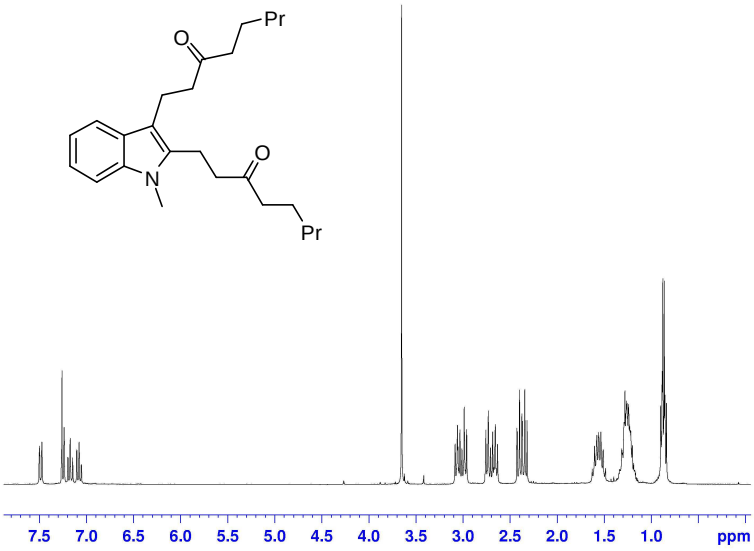



```
Current Data Parameters
NAME       14-AK269.1-f2
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140131
Time               12.02
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                    32
DS                     0
SWH            10330.578 Hz
FIDRES         0.315264 Hz
AQ             1.5860212 sec
RG                   456
DW                48.400 usec
DE                10.00 usec
TE                296.8 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.23 usec
PL1                1.00 dB
PL1W         19.75309753 W
SFO1         500.1560886 MHz

F2 - Processing parameters
SI                 16384
SF            500.1530159 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

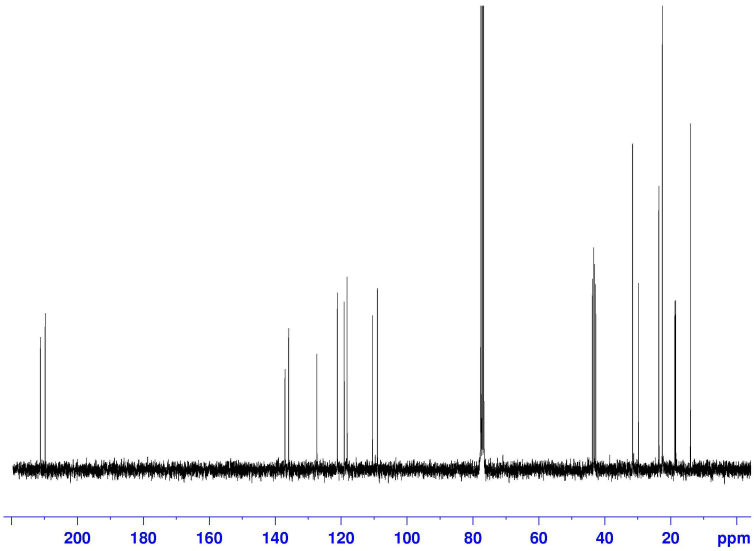



```
Current Data Parameters
NAME       14-AK269.1-f2
EXPNO                 41
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140131
Time               12.56
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                  1024
DS                     4
SWH            32894.738 Hz
FIDRES         0.501934 Hz
AQ             0.9961972 sec
RG                  3250
DW                15.200 usec
DE                10.00 usec
TE                296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.20 usec
PL1                1.50 dB
PL1W         51.74793243 W
SFO1         125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.00 dB
PL12               19.99 dB
PL13               21.00 dB
PL2W         19.75309753 W
PL12W         0.24925002 W
PL13W         0.19753097 W
SFO2         500.1550006 MHz

F2 - Processing parameters
SI                 32768
SF            125.7635564 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Data of the double alkylation product:

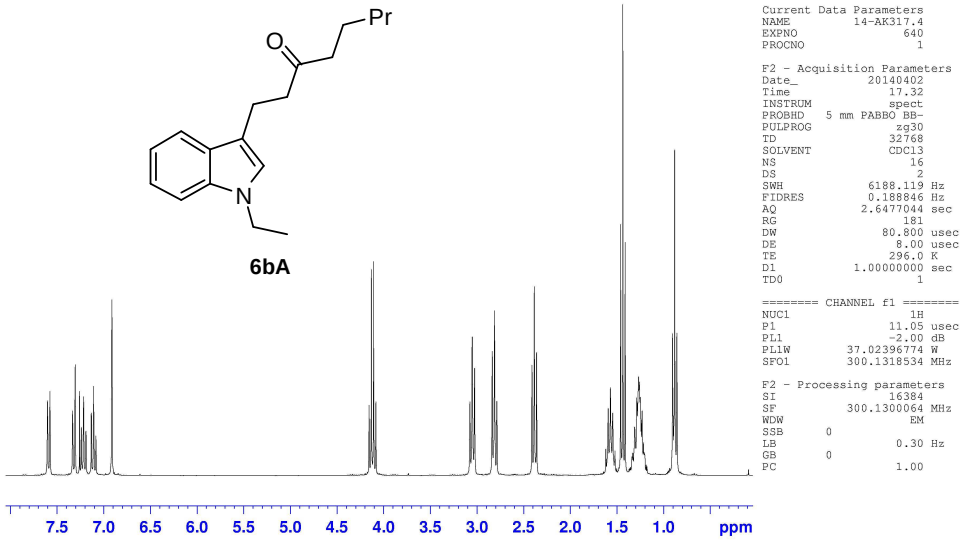



```
Current Data Parameters
NAME            14-AK331
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140501
Time              17.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6477044 sec
RG                   203
DW               80.800 usec
DE                8.00 usec
TE               296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1               -2.00 dB
PL1W        37.02396774 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300063 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

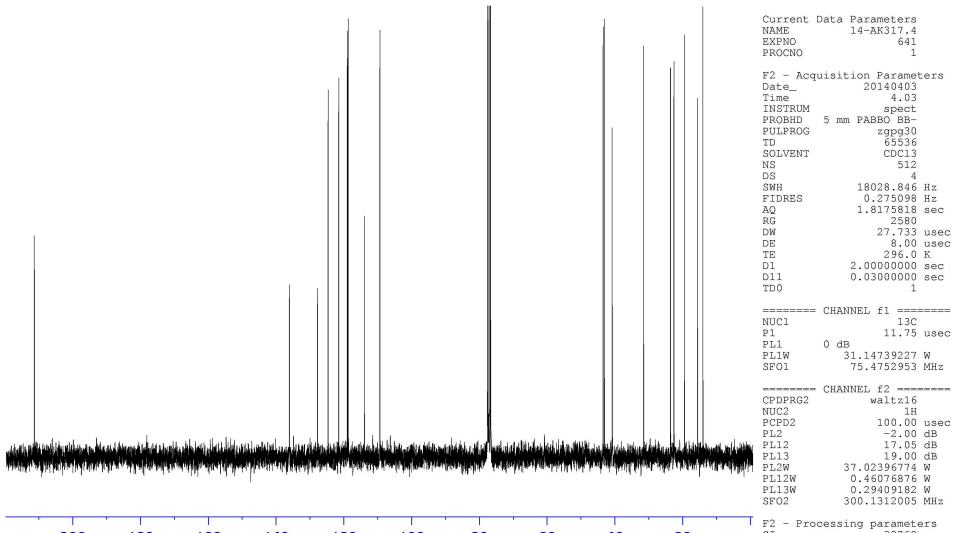



```
Current Data Parameters
NAME            14-AK331
EXPNO                 51
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140501
Time              23.18
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175818 sec
RG                  2300
DW               27.733 usec
DE                8.00 usec
TE               296.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.75 usec
PL1       0 dB
PL1W        31.14739227 W
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -2.00 dB
PL12              17.05 dB
PL13              19.00 dB
PL2W        37.02396774 W
PL12W        0.46076876 W
PL13W        0.29409182 W
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677398 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

3.4 1-(1-Ethyl-1H-indole-3-yl)octan-3-one (6bA)

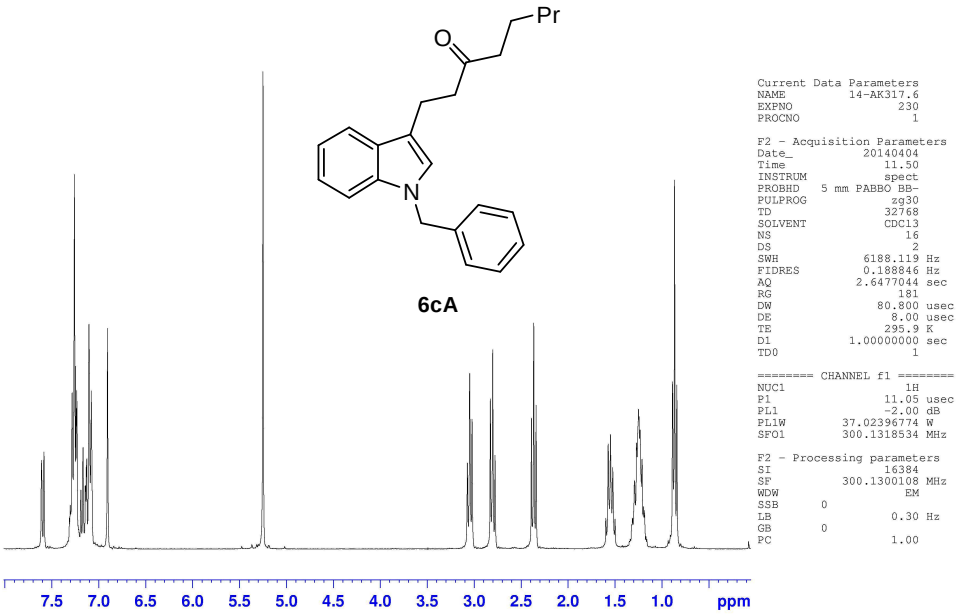



```
Current Data Parameters
NAME          14-AK317.4
EXPNO                640
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140402
Time               17.32
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ              2.6477044 sec
RG                   181
DW                80.800 usec
DE                 8.00 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300064 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

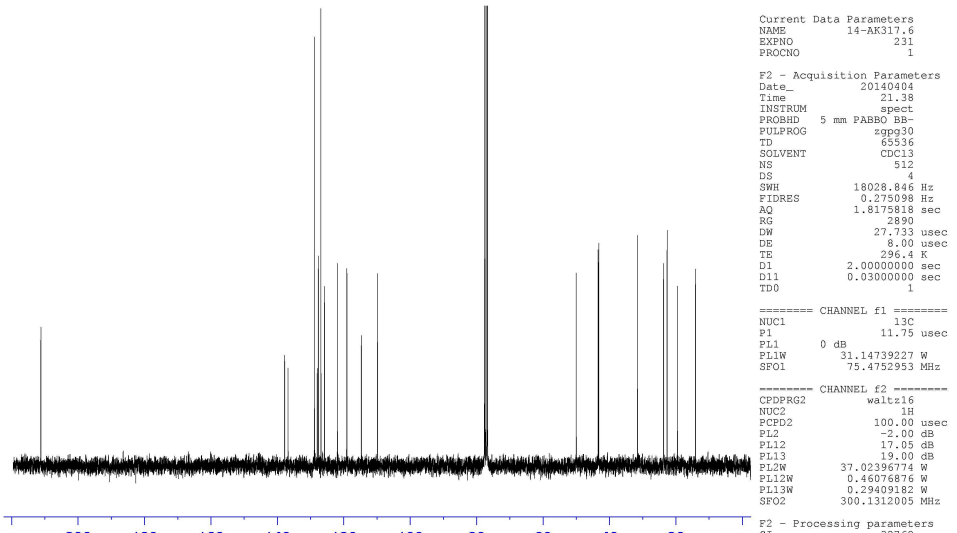



```
Current Data Parameters
NAME          14-AK317.4
EXPNO                641
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140403
Time               4.03
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175818 sec
RG                  2580
DW                27.733 usec
DE                 8.00 usec
TE                296.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.75 usec
PL1        0 dB
PL1W         31.14739227 W
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -2.00 dB
PL12               17.05 dB
PL13               19.00 dB
PL2W         37.02396774 W
PL12W         0.46076876 W
PL13W         0.29409182 W
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677405 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3.5 1-(1-Benzyl-1H-indole-3-yl)octan-3-one (6cA)

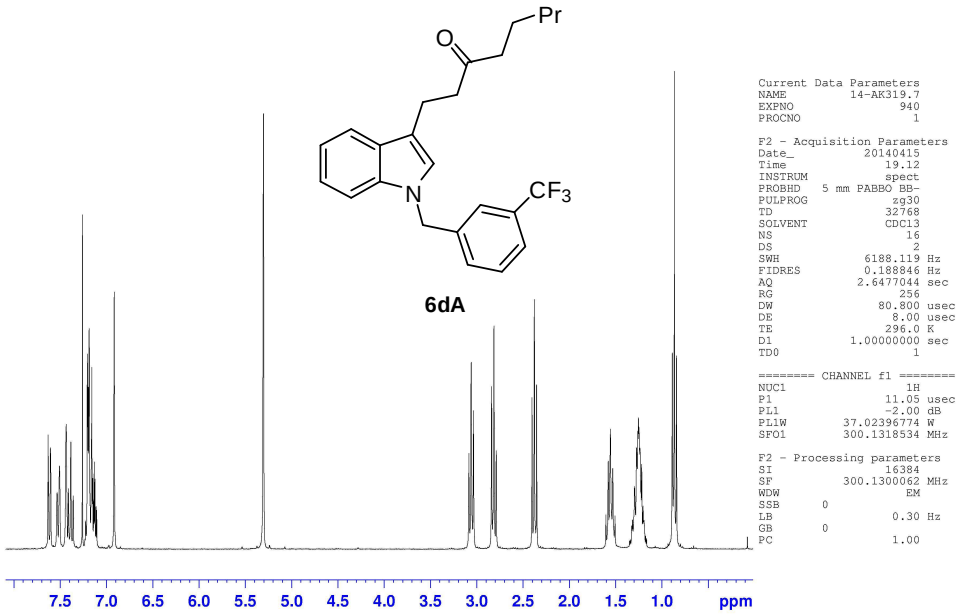



```
Current Data Parameters
NAME          14-AK317.6
EXPNO                230
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140404
Time               11.50
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT            CDC13
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                   181
DW                80.800 usec
DE                 8.00 usec
TE                295.9 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF           300.1300108 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

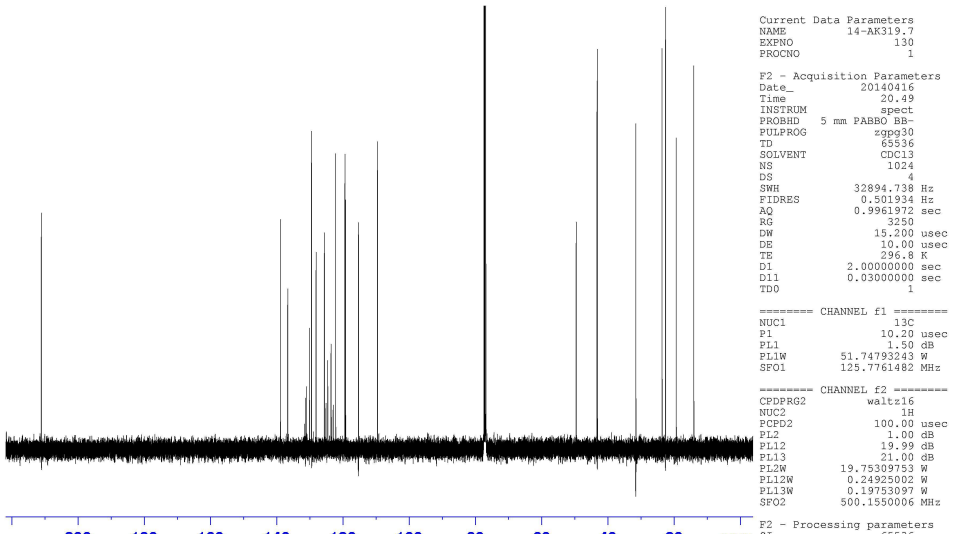



```
Current Data Parameters
NAME          14-AK317.6
EXPNO                231
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140404
Time               21.38
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            CDC13
NS                   512
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ             1.8175818 sec
RG                  2890
DW                27.733 usec
DE                 8.00 usec
TE                296.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.75 usec
PL1       0 dB
PL1W         31.14739227 W
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -2.00 dB
PL12               17.05 dB
PL13               19.00 dB
PL2W         37.02396774 W
PL12W         0.46076876 W
PL13W         0.29409182 W
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677399 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

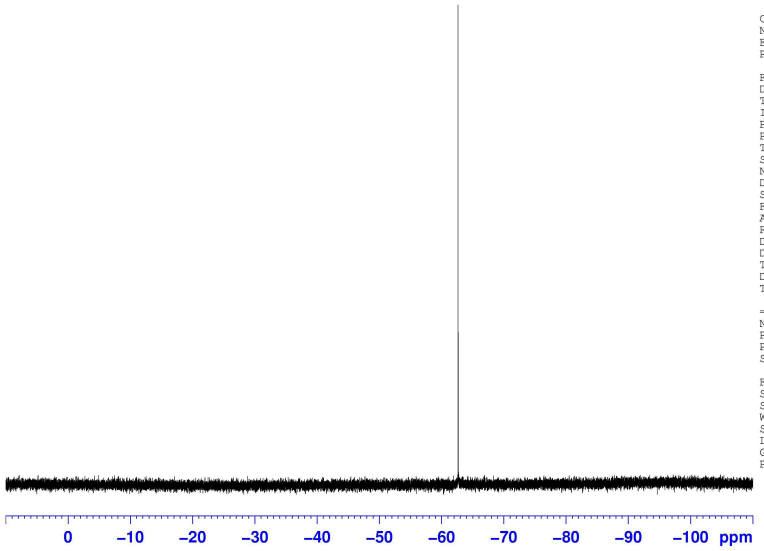
3.6 1-(1-(3-(Trifluoromethyl)benzyl)-1H-indole-3-yl)octan-3-one (6dA)




```
Current Data Parameters
NAME          14-AK319.7
EXPNO                940
PROCNO                 1

F2 - Acquisition Parameters
Date_          20140415
Time              19.12
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDC13
NS                  16
DS                   2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6477044 sec
RG                 256
DW              80.800 usec
DE               8.00 usec
TE              296.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               11.05 usec
PL1               -2.00 dB
PL1W        37.02396774 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                16384
SF         300.1300062 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

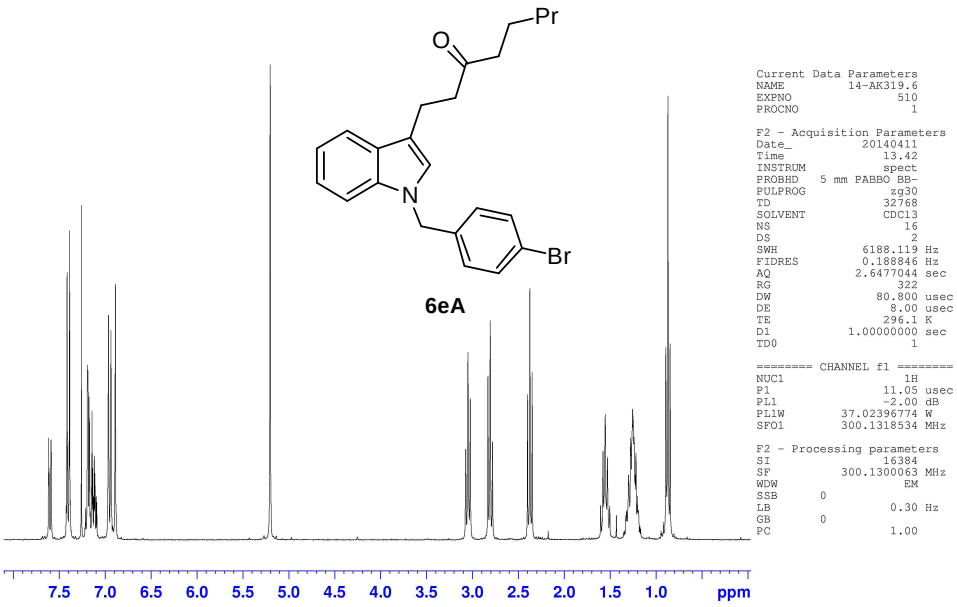



```
Current Data Parameters
NAME          14-AK319.7
EXPNO                130
PROCNO                 1

F2 - Acquisition Parameters
Date_          20140416
Time              20.49
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD               65536
SOLVENT          CDC13
NS                1024
DS                   4
SWH          32894.738 Hz
FIDRES        0.501934 Hz
AQ            0.9961972 sec
RG                3250
DW              15.200 usec
DE              10.00 usec
TE              296.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1               10.20 usec
PL1               1.50 dB
PL1W        51.74793243 W
SFO1       125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.00 dB
PL12             19.99 dB
PL13             21.00 dB
PL2W        19.75309753 W
PL12W        0.24925002 W
PL13W        0.19753097 W
SFO2       500.1550006 MHz

F2 - Processing parameters
SI                65536
SF         125.7635580 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                1.40
```

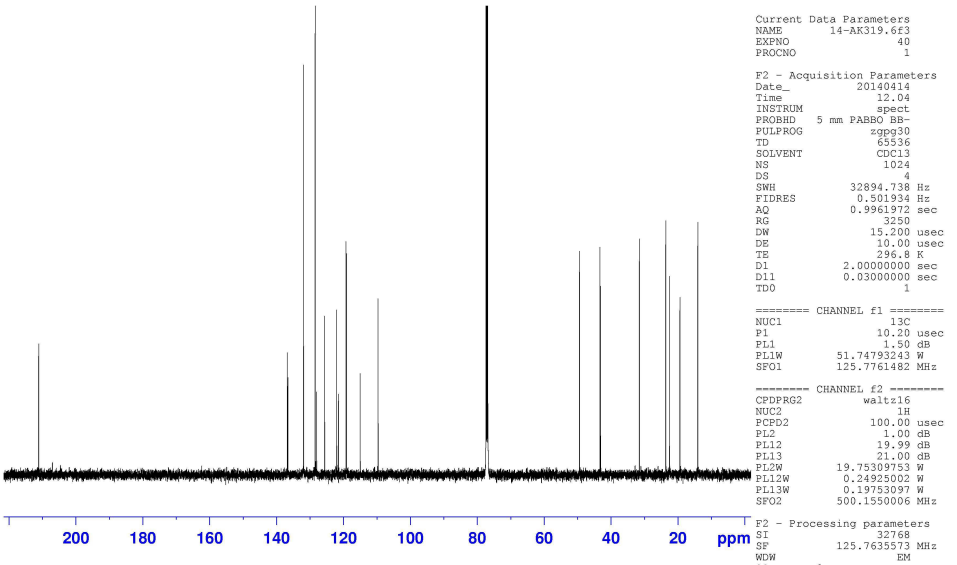



```
Current Data Parameters
NAME          14-AK319.7
EXPNO                110
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140507
Time                8.32
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgflqn
TD               131072
SOLVENT             CDC13
NS                     16
DS                      4
SWH           56497.176 Hz
FIDRES         0.431039 Hz
AQ             1.1600372 sec
RG                  1024
DW                 8.850 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  19F
P1                 13.80 usec
PL1                -6.00 dB
SFO1        235.3338140 MHz

F2 - Processing parameters
SI                 65536
SF          235.3573500 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

3.7 1-(1-(4-Bromobenzyl)-1H-indole-3-yl)octan-3-one (6eA)

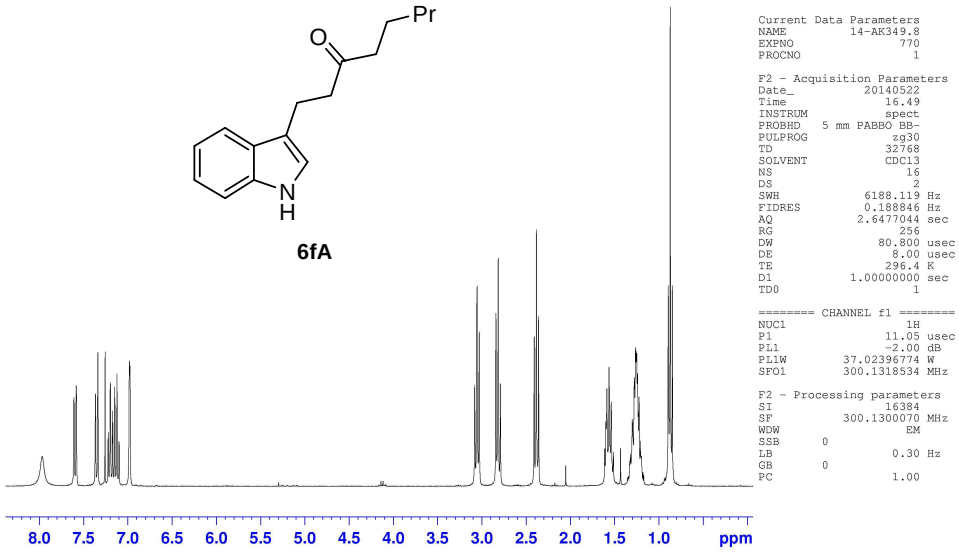



```
Current Data Parameters
NAME          14-AK319.6
EXPNO                510
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140411
Time               13.42
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDC13
NS                   16
DS                    2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ           2.6477044 sec
RG                  322
DW               80.800 usec
DE                8.00 usec
TE              296.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1               -2.00 dB
PL1W        37.02396774 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                16384
SF          300.1300063 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

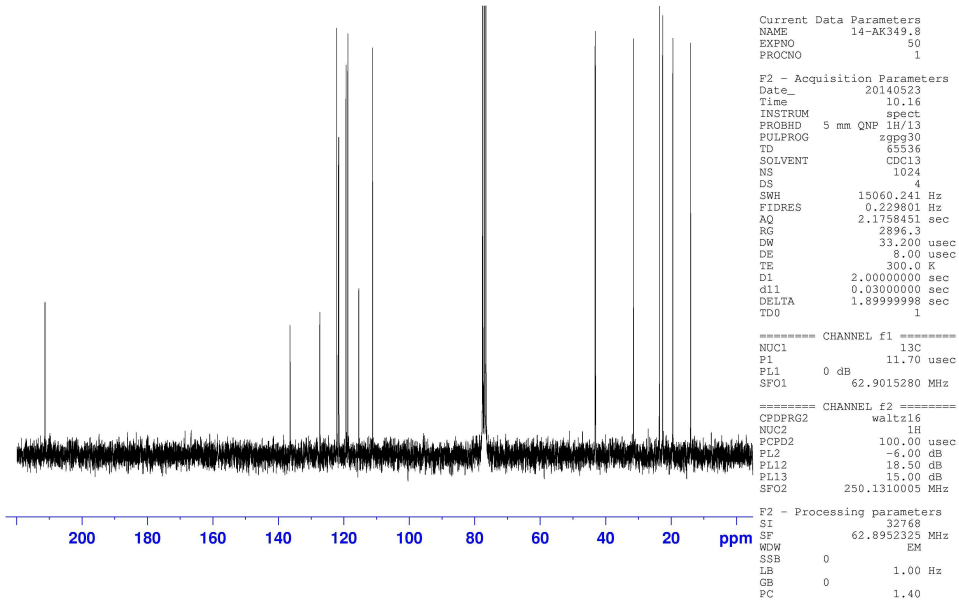



```
Current Data Parameters
NAME        14-AK319.6f3
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140414
Time               12.04
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                 1024
DS                    4
SWH           32894.738 Hz
FIDRES        0.501934 Hz
AQ           0.9961972 sec
RG                  320
DW               15.200 usec
DE               10.00 usec
TE              296.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.20 usec
PL1                1.50 dB
PL1W        51.74793243 W
SFO1       125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.00 dB
PL12              19.99 dB
PL13              21.00 dB
PL2W        19.75309753 W
PL12W        0.24925002 W
PL13W        0.19753097 W
SFO2       500.1550006 MHz

F2 - Processing parameters
SI                32768
SF          125.7635573 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

3.8 1-(1H-indole-3-yl)octan-3-one (6fA)

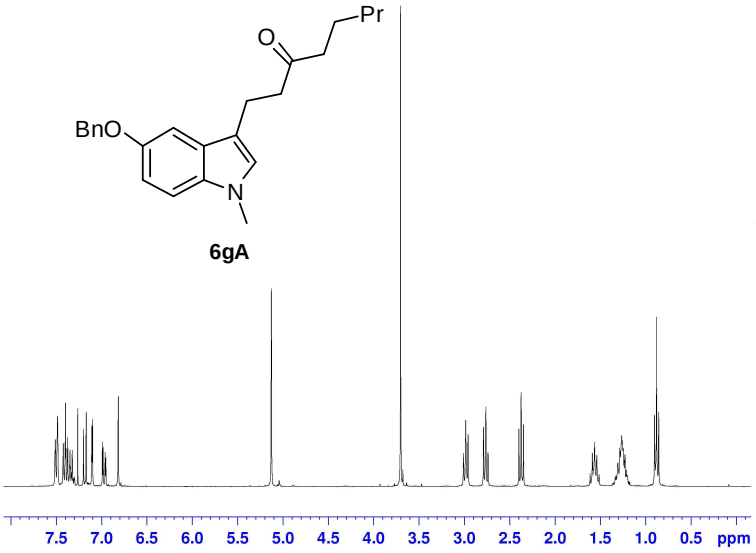



```
Current Data Parameters
NAME          14-AK349.8
EXPNO                770
PROCNO                 1

F2 - Acquisition Parameters
Date_          20140522
Time              16.49
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDC13
NS                  16
DS                   2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ           2.6477044 sec
RG                 256
DW              80.800 usec
DE               8.00 usec
TE              296.4 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               11.05 usec
PL1               -2.00 dB
PL1W        37.02396774 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                16384
SF          300.1300070 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

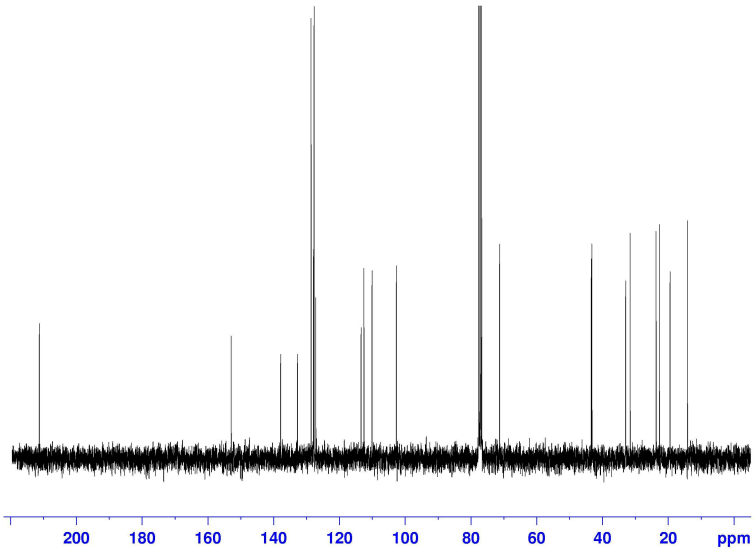



```
Current Data Parameters
NAME          14-AK349.8
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_          20140523
Time              10.16
INSTRUM           spect
PROBHD    5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT          CDC13
NS                 1024
DS                    4
SWH          15060.241 Hz
FIDRES        0.229801 Hz
AQ           2.1758451 sec
RG              2896.3
DW              33.200 usec
DE               8.00 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

========== CHANNEL f1 =========
NUC1                13C
P1               11.70 usec
PL1       0 dB
SFO1        62.9015280 MHz

========= CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              -6.00 dB
PL12             18.50 dB
PL13             15.00 dB
SFO2       250.1310005 MHz

F2 - Processing parameters
SI                32768
SF          62.8952325 MHz
WDW                  EM
SSB       0
LB              1.00 Hz
GB        0
PC              1.40
```

3.9 1-(5-(Benzyloxy)-1-methyl-1H-indole-3-yl)octan-3-one (6gA)

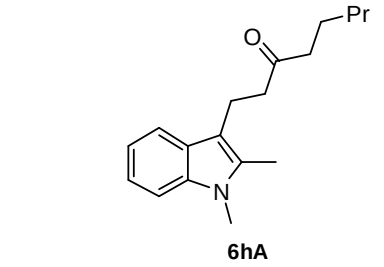



```
Current Data Parameters
NAME          14-AK349.3
EXPNO                370
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140520
Time               13.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                   256
DW                80.800 usec
DE                 8.00 usec
TE                296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300054 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



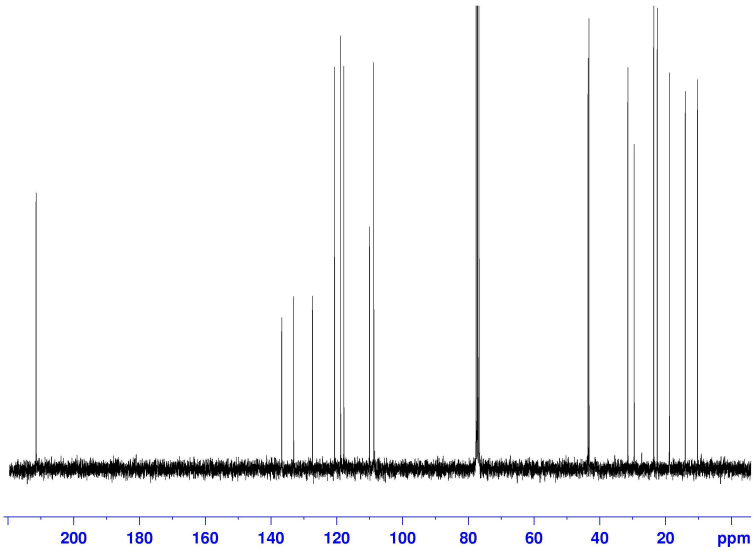

```
Current Data Parameters
NAME          14-AK349.3
EXPNO                880
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140521
Time                4.36
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ             1.8175818 sec
RG                  2890
DW                27.733 usec
DE                 8.00 usec
TE                296.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.75 usec
PL1       0 dB
PL1W         31.14739227 W
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -2.00 dB
PL12               17.05 dB
PL13               19.00 dB
PL2W         37.02396774 W
PL12W         0.46076876 W
PL13W         0.29409182 W
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677393 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3.10 1-(1,2-Dimethyl-1H-indole-3-yl)octan-3-one (6hA)



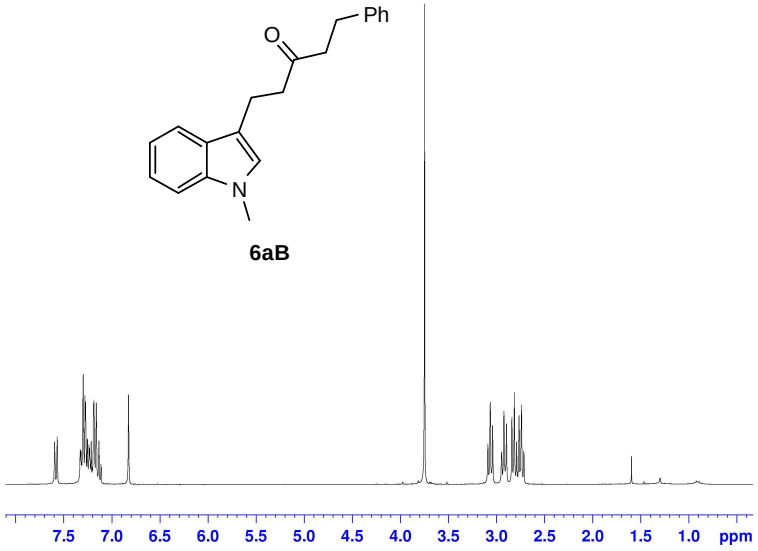
6hA


```
Current Data Parameters
NAME          14-AK356.2
EXPNO                430
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140604
Time               13.09
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ           2.6477044 sec
RG                   181
DW              80.800 usec
DE               8.00 usec
TE              296.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1               -2.00 dB
PL1W        37.02396774 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300064 MHz
WDW                   EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```

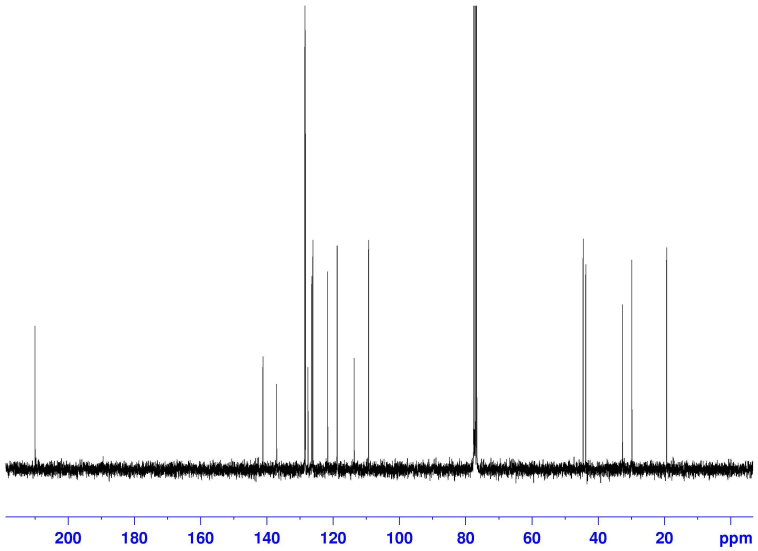



```
Current Data Parameters
NAME          14-AK356.2
EXPNO                431
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140605
Time               0.06
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1000
DS                     4
SWH          18028.846 Hz
FIDRES        0.275098 Hz
AQ           1.8175818 sec
RG                  2890
DW              27.733 usec
DE               8.00 usec
TE              296.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.75 usec
PL1       0 dB
PL1W        31.14739227 W
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2           100.00 usec
PL2               -2.00 dB
PL12              17.05 dB
PL13              19.00 dB
PL2W        37.02396774 W
PL12W        0.46076876 W
PL13W        0.29409182 W
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677415 MHz
WDW                   EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

3.11 1-(1-Methyl-1H-indole-3-yl)-5-phenylpentan-3-one (6aB)

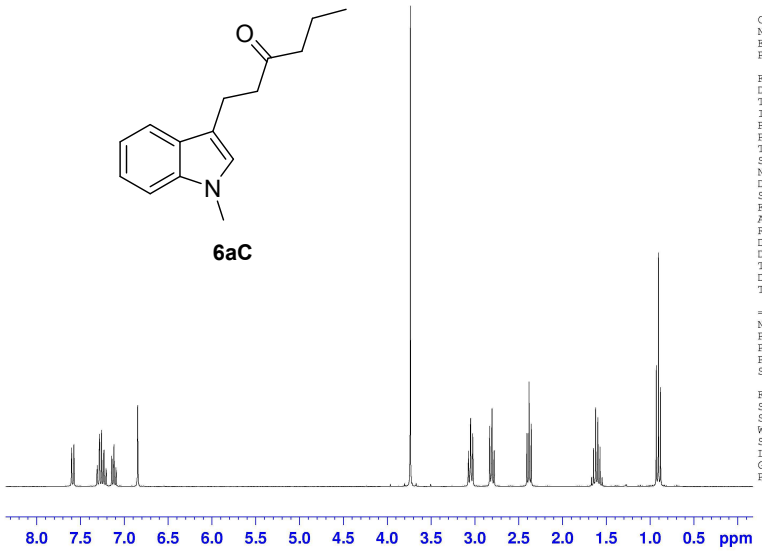



```
Current Data Parameters
NAME          14-AK381.3
EXPNO                 60
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140629
Time               16.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6477044 sec
RG                  256
DW               80.800 usec
DE                8.00 usec
TE              296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1               -2.00 dB
PL1W        37.02396774 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300000 MHz
WDW                   EM
SSB       0
LB               0.30 Hz
GB        0
PC                1.00
```

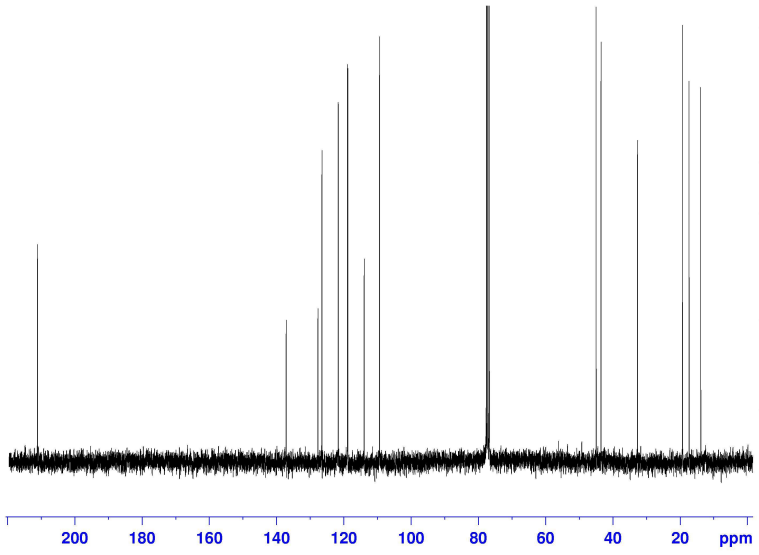



```
Current Data Parameters
NAME          14-AK381.3
EXPNO                 61
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140629
Time               18.16
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD               65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175818 sec
RG                 2890
DW               27.733 usec
DE                8.00 usec
TE              296.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.75 usec
PL1       0 dB
PL1W        31.14739227 W
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -2.00 dB
PL12              17.05 dB
PL13              19.00 dB
PL2W        37.02396774 W
PL12W        0.46076876 W
PL13W        0.29409182 W
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677408 MHz
WDW                   EM
SSB       0
LB               1.00 Hz
GB        0
PC                1.40
```

3.12 1-(1-Methyl-1H-indole-3-yl)hexan-3-one (6aC)

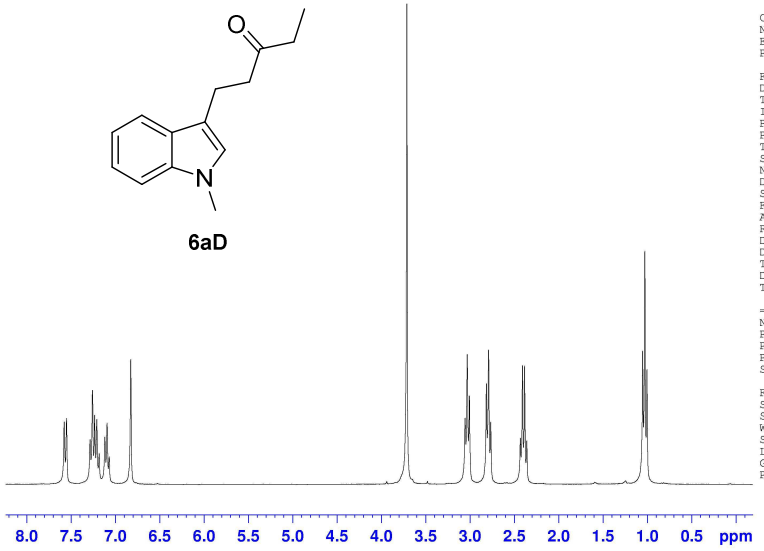



```
Current Data Parameters
NAME          14-AK342.2
EXPNO                380
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140512
Time               14.05
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6477044 sec
RG                  203
DW               80.800 usec
DE                8.00 usec
TE               295.6 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1               -2.00 dB
PL1W        37.02396774 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF            300.1300062 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



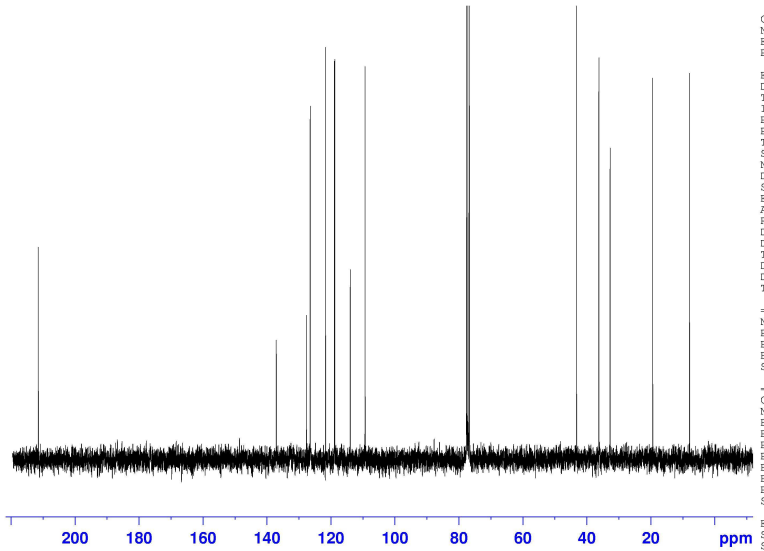

```
Current Data Parameters
NAME          14-AK342.2
EXPNO                381
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140513
Time               3.50
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175818 sec
RG                 3250
DW               27.733 usec
DE                8.00 usec
TE               296.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.75 usec
PL1       0 dB
PL1W        31.14739227 W
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -2.00 dB
PL12              17.05 dB
PL13              19.00 dB
PL2W        37.02396774 W
PL12W        0.46076876 W
PL13W        0.29409182 W
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677408 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

3.13 1-(1-Methyl-1H-indole-3-yl)pentan-3-one (6aD)



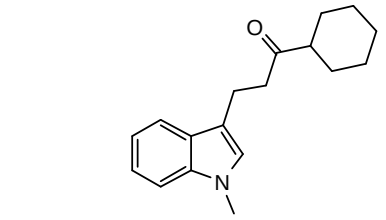
6aD

```
Current Data Parameters
NAME          14-AK342.3
EXPNO                910
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140512
Time               19.37
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                   203
DW                80.800 usec
DE                 8.00 usec
TE                295.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF           300.1300137 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



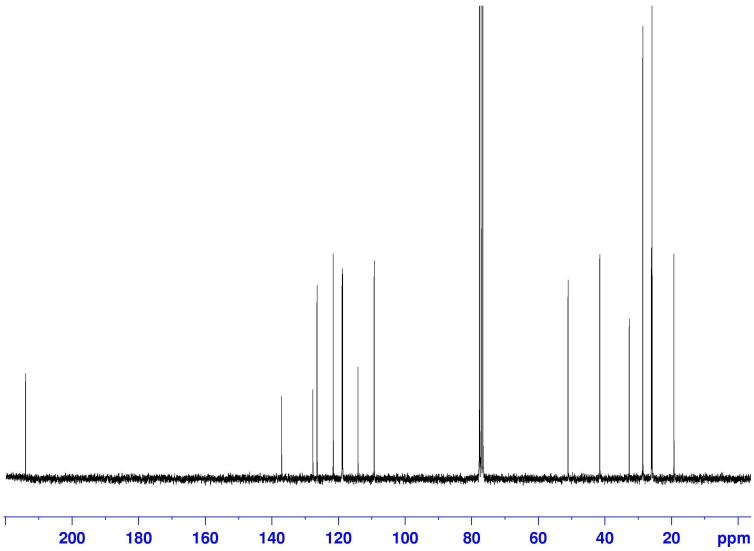

```
Current Data Parameters
NAME          14-AK342.3
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140513
Time               22.13
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ             1.8175818 sec
RG                  2300
DW                27.733 usec
DE                 8.00 usec
TE                296.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.75 usec
PL1       0 dB
PL1W         31.14739227 W
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -2.00 dB
PL12               17.05 dB
PL13               19.00 dB
PL2W         37.02396774 W
PL12W         0.46076876 W
PL13W         0.29409182 W
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677406 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3.14 1-Cyclohexyl-3-(1-methyl-1H-indole-3-yl)propan-1-one (6aE)



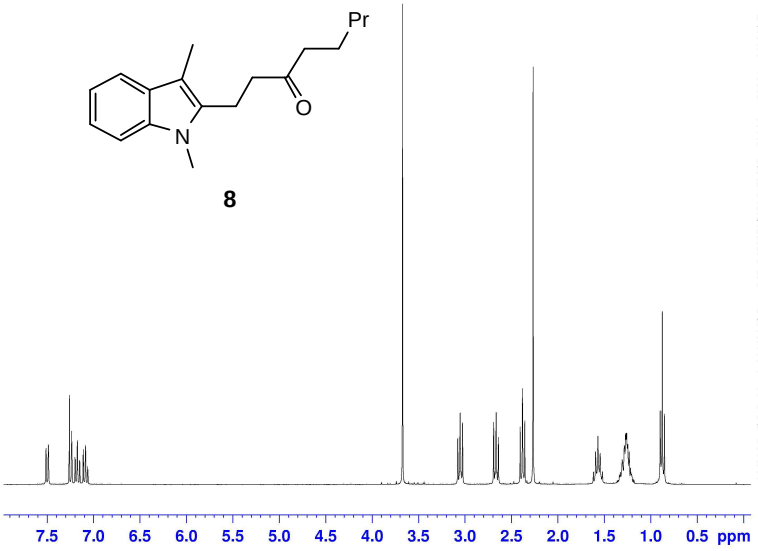
6aE


```
Current Data Parameters
NAME          14-AK381.4
EXPNO                520
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140630
Time               16.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ              2.6477044 sec
RG                   181
DW                80.800 usec
DE                 8.00 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300062 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

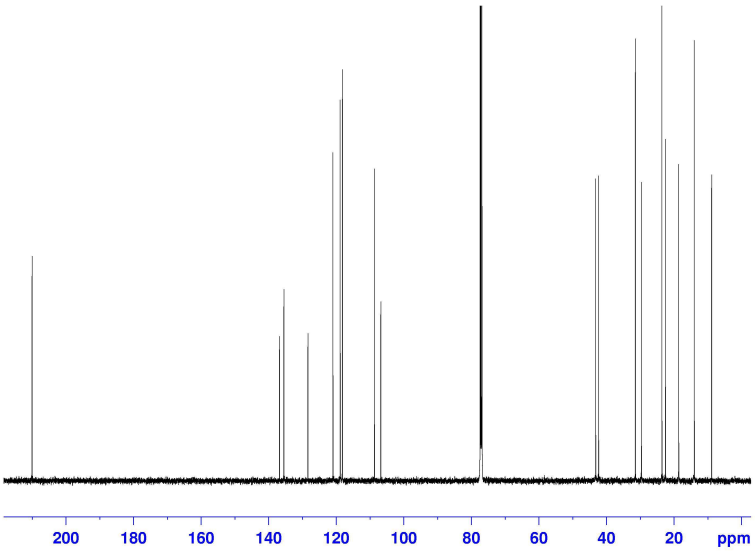



```
Current Data Parameters
NAME          14-AK381.4
EXPNO                210
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140701
Time               15.57
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   907
DS                     4
SWH            15060.241 Hz
FIDRES          0.229801 Hz
AQ              2.1758451 sec
RG                2896.3
DW                33.200 usec
DE                 8.00 usec
TE                300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.70 usec
PL1       0 dB
SFO1          62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -6.00 dB
PL12               18.50 dB
PL13               15.00 dB
SFO2         250.1310005 MHz

F2 - Processing parameters
SI                 32768
SF          62.8952339 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3.15 1-(1,3-Dimethyl-1H-indole-2-yl)octan-3-one (8)

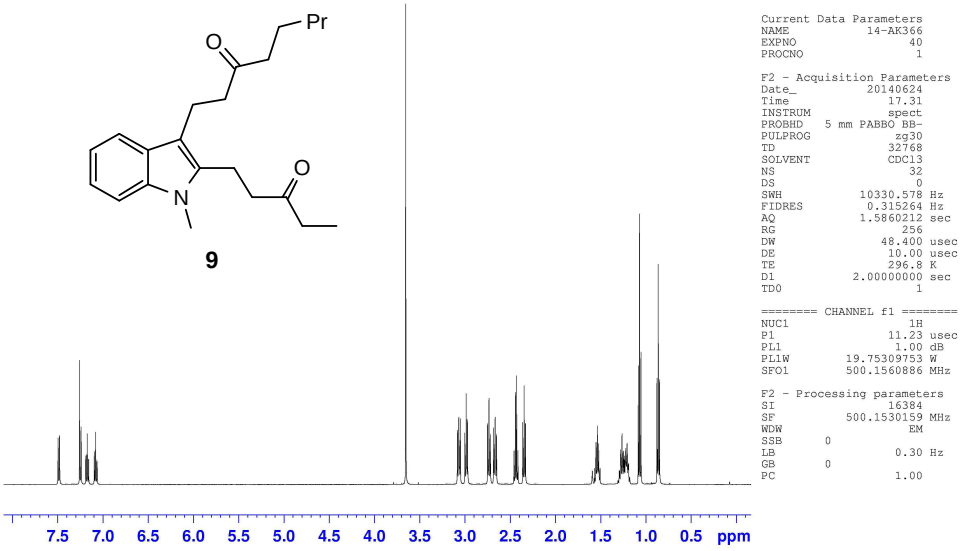



```
Current Data Parameters
NAME            14-AK357
EXPNO                280
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140605
Time               11.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             CDC13
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES             0.188846 Hz
AQ              2.6477044 sec
RG                   228
DW                80.800 usec
DE                 8.00 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF           300.1300064 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

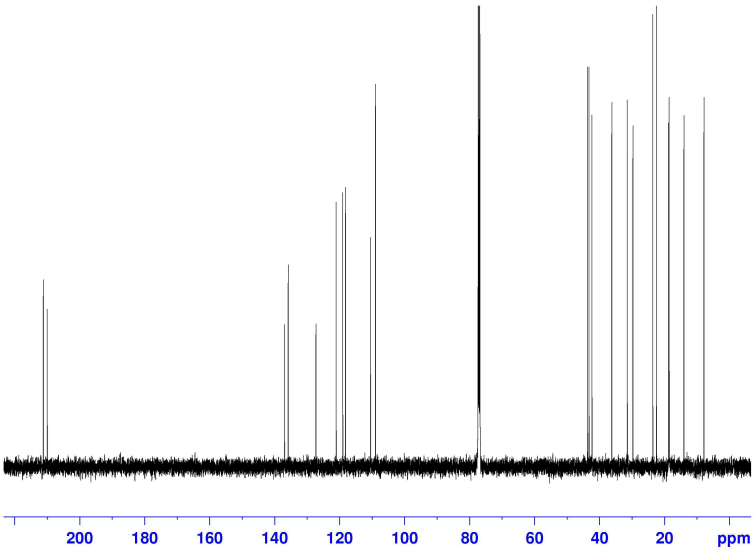



```
Current Data Parameters
NAME            14-AK357
EXPNO                180
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140609
Time               5.00
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             CDC13
NS                  4096
DS                     4
SWH            32894.738 Hz
FIDRES             0.501934 Hz
AQ              0.9961972 sec
RG                  3250
DW                15.200 usec
DE                10.00 usec
TE                296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                10.20 usec
PL1                1.50 dB
PL1W         51.74793243 W
SFO1         125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                1.00 dB
PL12              19.99 dB
PL13              21.00 dB
PL2W         19.75309753 W
PL12W         0.24925002 W
PL13W         0.19753097 W
SFO2         500.1550006 MHz

F2 - Processing parameters
SI                 32768
SF           125.7635588 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3.16 1-(1-Methyl-2-(3-oxopentyl)-1H-indole-3-yl)octan-3-one (9)

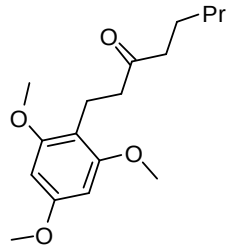



```
Current Data Parameters
NAME            14-AK366
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140624
Time               17.31
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDC13
NS                   32
DS                    0
SWH           10330.578 Hz
FIDRES        0.315264 Hz
AQ            1.5860212 sec
RG                  256
DW               48.400 usec
DE               10.00 usec
TE               296.8 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.23 usec
PL1                1.00 dB
PL1W        19.75309753 W
SFO1        500.1560886 MHz

F2 - Processing parameters
SI                 16384
SF          500.1530159 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

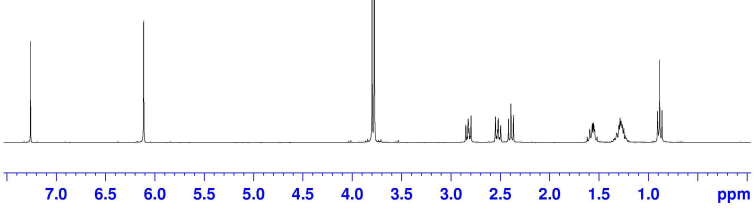



```
Current Data Parameters
NAME            14-AK366
EXPNO                 41
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140624
Time               18.25
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                 1024
DS                    4
SWH           32894.738 Hz
FIDRES        0.501934 Hz
AQ            0.9961972 sec
RG                 2890
DW               15.200 usec
DE               10.00 usec
TE               300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1               10.20 usec
PL1               1.50 dB
PL1W        51.74793243 W
SFO1        125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2           100.00 usec
PL2               1.00 dB
PL12             19.99 dB
PL13             21.00 dB
PL2W        19.75309753 W
PL12W        0.24925002 W
PL13W        0.19753097 W
SFO2        500.1550006 MHz

F2 - Processing parameters
SI                 32768
SF          125.7635570 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

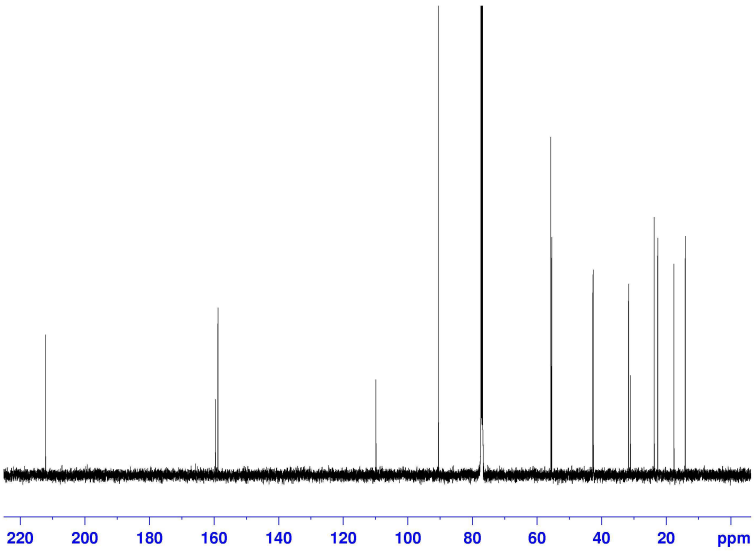
3.17 1-(2,4,6-Trimethoxyphenyl)octan-3-one (10)



10

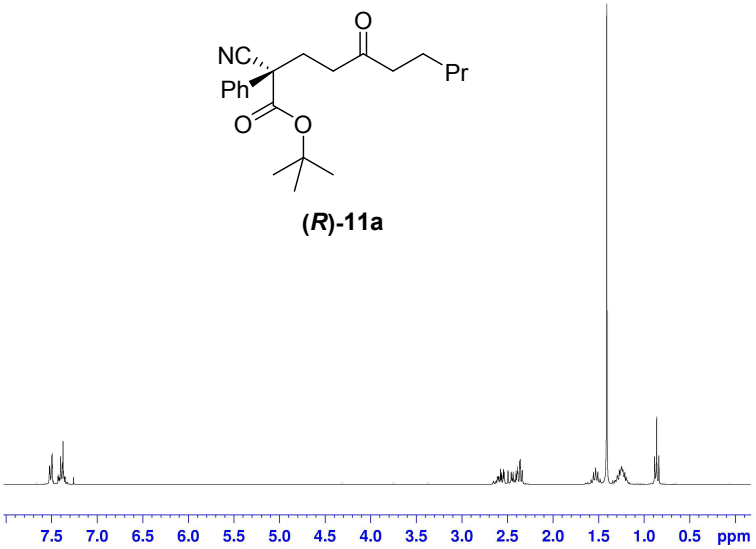



```
Current Data Parameters
NAME          14-AK351.9
EXPNO                710
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140528
Time               16.20
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                   406
DW                80.800 usec
DE                 8.00 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300063 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



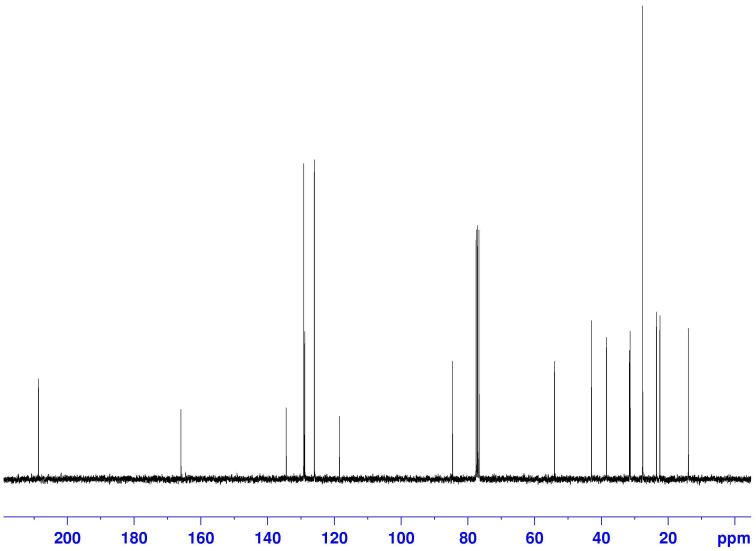

```
Current Data Parameters
NAME          14-AK351.9
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140530
Time               13.12
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            32894.738 Hz
FIDRES          0.501934 Hz
AQ             0.9961972 sec
RG                  3250
DW                15.200 usec
DE                10.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.20 usec
PL1                 1.50 dB
PL1W         51.74793243 W
SFO1        125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.00 dB
PL12               19.99 dB
PL13               21.00 dB
PL2W         19.75309753 W
PL12W         0.24925002 W
PL13W         0.19753097 W
SFO2        500.1550006 MHz

F2 - Processing parameters
SI                 32768
SF          125.7635556 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3.18 *tert*-Butyl (*R*)-2-cyano-5-oxo-2-phenyldecanoate ((*R*)-11a)



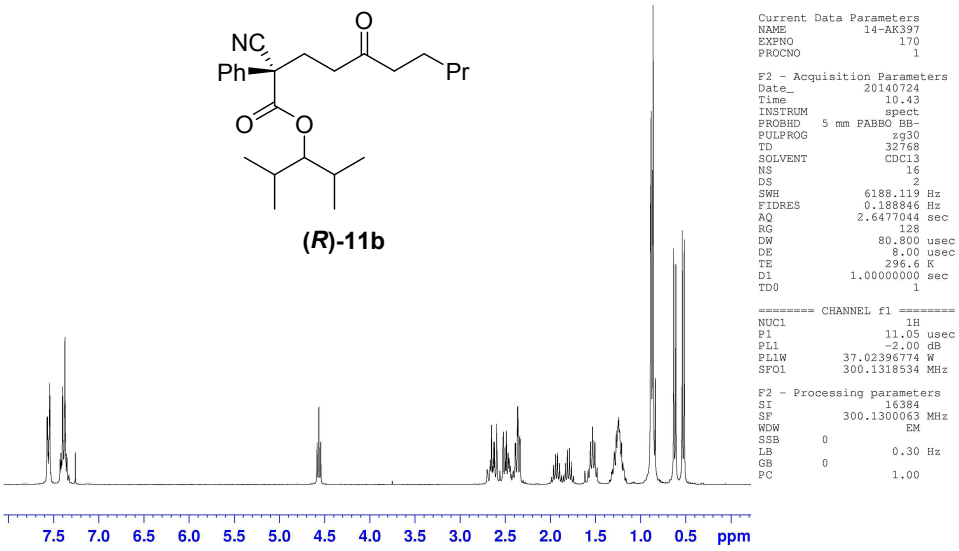
(*R*)-11a

```
Current Data Parameters
NAME          14-AK385.1
EXPNO                110
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140705
Time               18.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDC13
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ              2.6477044 sec
RG                   114
DW                80.800 usec
DE                 8.00 usec
TE                296.8 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300063 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

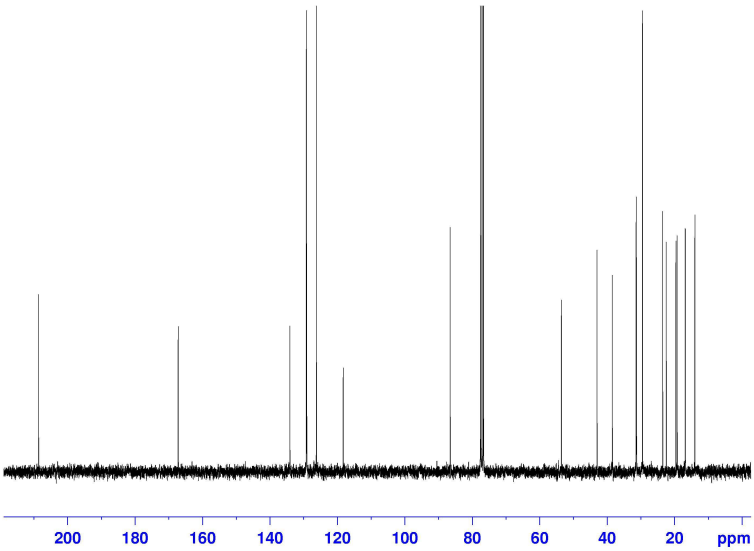



```
Current Data Parameters
NAME          14-AK385.1
EXPNO                111
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140705
Time               19.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                   512
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175818 sec
RG                  2580
DW                27.733 usec
DE                 8.00 usec
TE                297.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.75 usec
PL1       0 dB
PL1W         31.14739227 W
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                  1H
PCPD2              100.00 usec
PL2                -2.00 dB
PL12               17.05 dB
PL13               19.00 dB
PL2W         37.02396774 W
PL12W         0.46076876 W
PL13W         0.29409182 W
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677410 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3.19 2,4-Dimethylpentan-3-yl (*R*)-2-cyano-5-oxo-2-phenyldecanoate ((*R*)-11b)




```
Current Data Parameters
NAME            14-AK397
EXPNO                170
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140724
Time               10.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             CDC13
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.188846 Hz
AQ              2.6477044 sec
RG                   128
DW                80.800 usec
DE                 8.00 usec
TE                296.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                -2.00 dB
PL1W         37.02396774 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300063 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

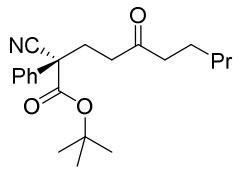



```
Current Data Parameters
NAME            14-AK397
EXPNO                171
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140724
Time               23.58
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             CDC13
NS                   512
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175818 sec
RG                  3640
DW                27.733 usec
DE                 8.00 usec
TE                297.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.75 usec
PL1       0 dB
PL1W         31.14739227 W
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              100.00 usec
PL2                -2.00 dB
PL12               17.05 dB
PL13               19.00 dB
PL2W         37.02396774 W
PL12W         0.46076876 W
PL13W         0.29409182 W
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677402 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

4 HPLC spectra

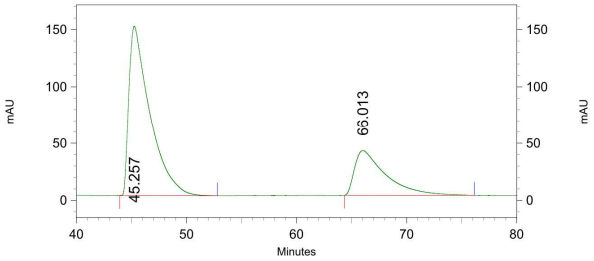
4.1 *tert*-Butyl (*R*)-2-cyano-5-oxo-2-phenyldecanoate ((*R*)-11a)

Compound:



(*R*)-11a

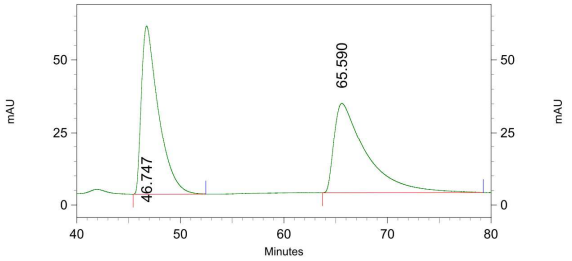
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99.8/0.2), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
45.257	595240	78941656	72.113
66.013	156127	30528423	27.887
Totals	751367	109470079	100.000

Nearly racemic reference:

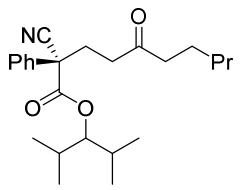


UV Results

Retention Time	Height	Area	Area %
46.747	231724	26663258	50.09
65.590	123666	26562310	49.91
Totals	355390	53225568	100.00

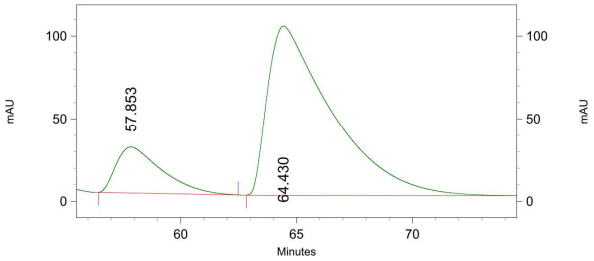
4.2 2,4-Dimethylpentan-3-yl (*R*)-2-cyano-5-oxo-2-phenyldecanoate ((*R*)-11b)

Compound:



(*R*)-11b

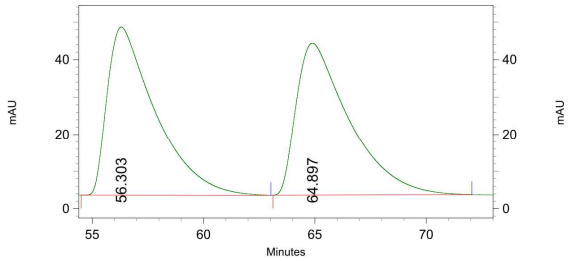
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99.9/0.1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
57.853	111247	15154202	16.058
64.430	408841	79220303	83.942
Totals	520088	94374505	100.000

Nearly racemic reference:



UV Results

Retention Time	Height	Area	Area %
56.303	180363	27242584	50.19
64.897	163030	27038378	49.81
Totals	343393	54280962	100.00