Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

for

One-pot coupling-addition-cyclocondensation sequence (CACS) to 2-substituted 3-acylpyrroles initiated by a copper-free alkynylation

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Content

1 General consideration

All cross-coupling reactions were carried out in oven-dried Schlenk tubes using syringes under a nitrogen or argon atmosphere. Dry dichloromethane was supplied by MBraun system MB-SPS-800. Triethylamine was used as received. Di-(1-Adamantyl)-benzyl-phosphonium bromide (cataCXium® ABn·HBr) was prepared recording to literature procedure.[1] Chemicals were either commercially obtained from *ABCR GmbH & Co KG*, *Acros Organics*, *Alfa Aesar GmbH & Co KG*, *Fluka*, *Merck KGaA*, *Riedel-de Haën*, *Sigma-Aldrich Co* and used as supplied or were already available in the research group. All products were purified by column chromatography on silica gel 60 M (0.04–0.063 mm) from *Machery Nagel GmbH & Co KG* using flash technique under a pressure of 2 bar. The crude mixtures were absorbed on Celite® 545 (0.02–0.10 mm) from Merck KGaA Darmstadt before chromatographic purification. The reaction progress was observed qualitatively by using TLC Silica gel 60 F254 aluminium sheets. The spots were detected with UV light at 254 nm. The ^{1}H-, ^{13}C- and 135-DEPT-spectra were recorded on a Bruker AVIII-300 or Bruker Avance III- 600 spectrometer. DMSO-d_6 or $CDCl_3$ was used as a solvent. The resonance of DMSO-d_6 and $CDCl_3$ were locked as internal standard ($CDCl_3$: ^{1}H δ 7.26, ^{13}C δ 77.0 and DMSO-d_6: ^{1}H δ 2.50, ^{13}C δ 39.53). The multiplicities of signals were abbreviated as follows: s: singlet; d: doublet; dd: doublet of doublets; dt: doublet of triplets, dq: doublet of quartets; ddd: doublet of doublets of doublets; t: triplet; sext: sextet; sept: septet; and m: multiplet. The type of carbon atom was determined on the basis of 135-DEPT NMR spectra. The EI mass spectra were measured on a Finnigen MAT 8200 spectrometer and the GC mass spectra were measured on a GCMS-QP2010 S spectrometer from *Shimadzu*. IR spectra were obtained on Shimadzu IRAffinity-1. The intensity of the signals is abbreviated as following: s (strong), m (medium), w (weak). The melting points (uncorrected) were measured on a Büchi Melting Point B-540. Combustion analyses were carried out on Perkin Elmer Series II Analyser 2400 in the microanalytical laboratory of the Institut für Pharmazeutische und Medizinische Chemie at the Heinrich-Heine-Universität Düsseldorf.

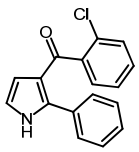
[1] a) A. Köllhofer, H. Plenio, *Chem. Eur. J.* **2003**, *9*, 1416-1425 b) J. R. Goerlich, R. Schmutzler, *Phosphorus. Sulfur. and Silicon* **1995**, *102*, 211-215; c) J. R. Goerlich, R. Schmutzler, *Phosphorus. Sulfur. and Silicon* **1993**, *102*, 141-148

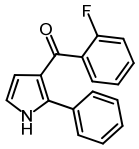
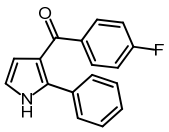
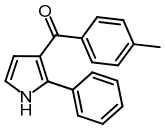
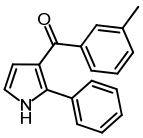
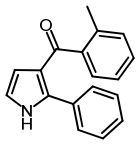
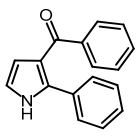
2 Preparation of 2-substituted 3-acylpyrroles by Coupling-Addition-Cyclocondensation-Sequence (CACS)

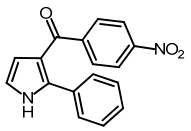
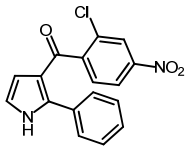
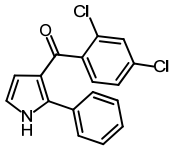
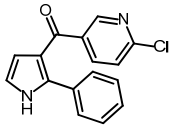
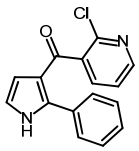
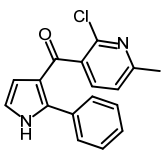
2.1 General procedure for the synthesis

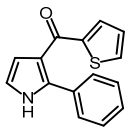
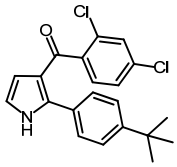
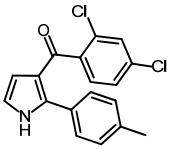
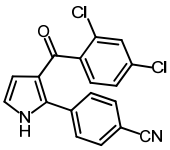
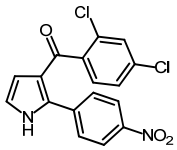
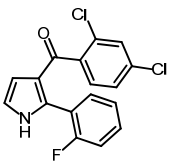
Palladium(II) chloride (3.5 mg, 0.02 mmol, 1mol-%) and di(1-adamantyl)benzylphosphonium hydrobromide (18.9 mg, 0.04 mmol, 2 mol-%) were placed in a dry Schlenk tube under an argon atmosphere and 2 mL of dry dichloromethane were added. Acid chloride **5** (2.00 mmol), terminal alkyne **6** (2.00 mmol), and reagent grade triethylamine (300 µL, 2.15 mmol) were added to the mixture, and stirring at room temperature was continued until complete conversion (monitored by TLC). Then aminoacetaldehyde diethylacetal (**4**) (281 mg, 2.07 mmol) was added and the reaction mixture was stirred for 16 h at 40 °C (oil bath). Then the reaction mixture was allowed to cool to room temperature and methanesulfonic acid (401 mg, 4.13 mmol) was successively added. After stirring for 24 h at 40 °C (oil bath) the reaction mixture was allowed to cool to room temperature. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate) to give the 2-substituted 3-acylpyrroles.

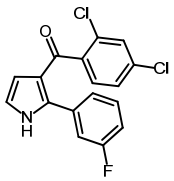
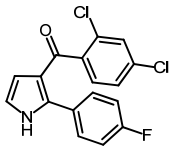
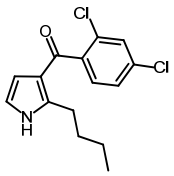
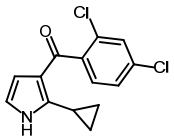
Tabelle 1: Experimental details for the three-component synthesis of 3-acylpyrroles **1a-w**.

Entry	Acid chloride **5**	Alkyne **6**	3-acylpyrrole **1** (isolated yield)	Chromatographic Purification (eluent), R_f
1	2-Chlorobenzoyl chloride (**5a**) 360 mg (2.00 mmol)	Phenylacetylene (**6a**) 209 mg (2.00 mmol)	351 mg (1.25 mmol, 62 %)  **1a**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.16

2	2-Fluorobenzoyl chloride (**5b**) 320 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	265 mg (1.00 mmol, 50 %)  **1b**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.10
3	4-Fluorobenzoyl chloride (**5c**) 324 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	106 mg (0.40 mmol, 20 %)  **1c**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.17
4	4-Toluoyl chloride (**5d**) 312 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	55 mg (0.20 mmol, 11 %)  **1d**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.09
5	3-Toluoyl chloride (**5e**) 313 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	102 mg (0.39 mmol, 20 %)  **1e**	(*n*-hexane/EtOAc) = 9:2 R_f (*n*-hexane/acetone 4:1) = 0.2
6	2-Toluoyl chloride (**5f**) 315 mg (2.02 mmol)	**6a** 209 mg (2.00 mmol)	133 mg (0.51 mmol, 26 %)  **1f**	(*n*-hexane/EtOAc) = 4:1 R_f (*n*-hexane/acetone 4:1) = 0.12
7	Benzoyl chloride (**5g**) 284 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	146 mg (0.59 mmol, 30 %)  **1g**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.19

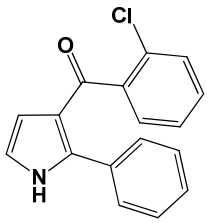
8	4-Nitrobenzoyl chloride (**5h**) 379 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	252 mg (0.86 mmol, 43 %)  **1h**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.20
9	2-Chloro-4-nitrobenzoyl chloride (**5i**) 449 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	326 mg (1.00 mmol, 50 %)  **1i**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.19
10	2,4-Dichloro-benzoyl chloride (**5j**) 428 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	375 mg (1.19 mmol, 59 %)  **1j**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.19
11	6-Chloronicotinoyl chloride (**5k**) 360 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	241 mg (0.85 mmol, 43 %)  **1k**	(*n*-hexane/EtOAc) = 2:1 R_f (*n*-hexane/acetone 4:1) = 0.10
12	2-Chloronicotinoyl chloride (**5l**) 363 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	320 mg (1.13 mmol, 57 %)  **1l**	(*n*-hexane/EtOAc) = 2:1 R_f (*n*-hexane/acetone 4:1) = 0.05
13	2-Chloro-6-methylnicotinoyl chloride (**5m**) 392 mg (2.00 mmol)	**6a** 209 mg (2.00 mmol)	436 mg (1.47 mmol, 73 %)  **1m**	(*n*-hexane/EtOAc) = 2:1 R_f (*n*-hexane/acetone 4:1) = 0.09

14	2-Thiophene-carbonyl chloride chloride (**5n**) 303 mg (2.02 mmol)	**6a** 209 mg (2.00 mmol)	183 mg (0.72 mmol, 36 %)  **1n**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.12
15	**5j** 428 mg (2.00 mmol)	4-tert. Butyl-phenylacetylene (**6b**) 330 mg (2.00 mmol)	439 mg (1.18 mmol, 59 %)  **1o**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.24
16	**5j** 428 mg (2.00 mmol)	4-Tolyacetylene (**6c**) 237 mg (2.00 mmol)	362 mg (1.10 mmol, 55 %)  **1p**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.23
17	**5j** 428 mg (2.00 mmol)	4-Ethynyl-benzonitrile (**6d**) 262 mg (2.00 mmol)	442 mg (1.30 mmol, 65 %)  **1q**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.09
18	**5j** 428 mg (2.00 mmol)	4-Nitro-phenylacetylene (**6e**) 300 mg (2.00 mmol)	149 mg (0.41 mmol, 21 %)  **1r**	(*n*-hexane/EtOAc) = 5:2 R_f (*n*-hexane/acetone 4:1) = 0.12
19	**5j** 428 mg (2.00 mmol)	2-Fluoro-phenylacetylene (**6f**) 248 mg (2.00 mmol)	459 mg (1.37 mmol, 69 %)  **1s**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.16

20	**5j** 428 mg (2.00 mmol)	3-Fluoro-phenylacetylene (**6g**) 246 mg (2.00 mmol)	219 mg (0.66 mmol, 33 %)  **1t**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.20
21	**5j** 428 mg (2.00 mmol)	4-Fluoro-phenylacetylene (**6h**) 248 mg (2.02 mmol)	258 mg (0.77 mmol, 39 %)  **1u**	(*n*-hexane/EtOAc) = 3:1 R_f (*n*-hexane/acetone 4:1) = 0.19
22	**5j** 428 mg (2.00 mmol)	1-Hexyne (**6i**) 168 mg (2.02 mmol)	175 mg (0.59 mmol, 30 %)  **1v**	(*n*-hexane/EtOAc) = 4:1 R_f (*n*-hexane/acetone 4:1) = 0.25
23	**5j** 428 mg (2.00 mmol)	Cycopropyl-acetylene (**6j**) 140 mg (2.05 mmol)	256 mg (0.91 mmol, 46 %)  **1w**	(*n*-hexane/EtOAc) = 4:1 R_f (*n*-hexane/acetone 4:1) = 0.20

2.2 Spectroscopic Data for the 2-substituted 3-acylpyrroles 1

2.2.1 (2-chlorophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1a)

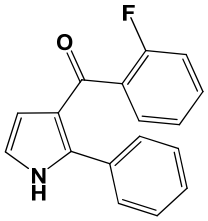


$C_{17}H_{12}ClNO$
281.74 g/mol

Reaction time of the copper-free alkynylation: 2 h

351 mg, (1.25 mmol, 62 %) as a orange/yellow solid. M.p. 131 °C. ^{1}H NMR (300MHz, $CDCl_3$, rt): δ = 6.50 (t, J = 2.9 Hz, 1H), 6.70-6.74 (m, 1H), 7.10 (td, J = 7.3, 1.4 Hz, 1H), 7.15-7.25 (m, 6H), 7.37-7.44 (m, 2H), 8.89 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$, rt): δ = 113.4 (CH), 118.4 (CH), 121.0 (C_{quat}), 126.2 (CH), 128.2 (2 CH), 128.4 (CH), 128.9 (2 CH), 129.2 (CH), 129.8 (CH), 130.4 (CH), 131.2 (C_{quat}), 131.7 (C_{quat}), 138.6 (C_{quat}), 140.6 (C_{quat}), 190.6 (C_{quat}). EI+MS (*m/z* (%)): 283.1 ([$M^+(Cl^{37})$], 14), 281.1 ($M^+(Cl^{35})$ 41), 246.1 ([M^+ - Cl], 6), 170.1 ([M^+ - C_6H_4Cl], 100), 141.1 ([M^+ - C_7H_4ClO], 7), 141.1 ([$M^+(Cl^{37})$ - $C_{10}H_8N$], 7), 139.1 ([$M^+(Cl^{35})$ - $C_{10}H_8N$], 5), 115.1 ([M^+ - C_8H_6ClNO], 50), 113.1 ([$M^+(Cl^{37})$ - $C_{11}H_8NO$], 9) 111.0 ([$M^+(Cl^{35})$ - $C_{11}H_8NO$], 15); IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3156 (m), 3100 (m), 3067 (m), 3053 (m), 3005 (w), 2951 (m), 2907 (w), 2853 (w), 2808 (w), 2749 (w), 1587 (ν (C=O), s), 1570 (ν (C=C und C=N), m), 1528 (w), 1503 (w), 1476 (m), 1450 (m), 1433 (s), 1410 (w), 1346 (m), 1300 (m), 1275 (w), 1258 (w), 1184 (m), 1161 (w), 1099 (w), 1072 (w), 1051 (w), 1034 (w), 908 (w), 883 (s), 862 (w), 831 (w), 785 (m), 756 (s), 737 (s), 694 (s), 679 (w), 650 (m), 615 (m). Anal. calcd for $C_{17}H_{12}ClNO$ [281.7]: C 72.47, H 4.29, N 4.97; Found: C 72.23, H 4.54, N 4.79.

2.2.2 (2-fluorophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1b)

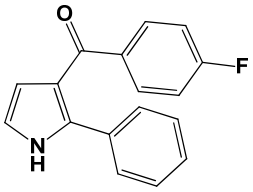


$C_{17}H_{12}FNO$
265.28 g/mol

Reaction time of the copper-free alkynylation: 3.5 h

265 mg (1.00 mmol, 50 %) as a brown/reddish solid. M.p. 118 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 6.33 (t, J = 2.6 Hz, 1H), 6.90 (t, J = 2.7 Hz, 1H), 7.08-7.12 (m, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.25-7.31 (m, 3H), 7.37-7.43 (m, 2H), 7.44-7.47 (m, 2H), 11.87 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 112.4 (CH), 115.6 (d, $^{2}J_{C-F}$ = 21.6 Hz, CH), 119.0 (CH), 120.6 (C_{quat}), 124.0 (d, $^{3}J_{C-F}$ = 3.1 Hz, CH), 127.7 (2 CH), 127.8 (CH), 128.9 (2 CH), 129.6 (d, $^{2}J_{C-F}$ = 15.5 Hz, C_{quat}), 129.8 (d, $^{3}J_{C-F}$ = 3.2 Hz, CH), 131.7 (C_{quat}), 131.9 (d, $^{4}J_{C-F}$ = 8.3 Hz, CH), 137.4 (C_{quat}), 158.8 (d, $^{1}J_{C-F}$ = 247.8 Hz, C_{quat}), 187.3 (C_{quat}). EI+MS (*m/z* (%)): 265.1 ([M^+], 67), 170.1 ([M^+ - C_6H_4F], 100), 142.1 ([M^+ - C_7H_4FO], 8), 123.0 ([M^+ - $C_{10}H_8N$], 9), 115.1 ([M^+ - C_8H_6FNO], 59), 95.0 ([M^+ - $C_{11}H_8NO$], 23); IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3233 (ν (N-H), m), 3109 (w), 2988 (m), 2972 (m), 2901 (m), 2795 (w), 1620 (s), 1609 (ν (C=O), s), 1578 (w), 1558 (w), 1474 (s), 1452 (s), 1431 (s), 1396 (s), 1362 (w), 1306 (m), 1290 (w), 1267 (w), 1225 (m), 1211 (w), 1177 (w), 1152 (w), 1101 (m), 1076 (m), 1057 (m), 999 (w), 901 (m), 885 (s), 812 (m), 787 (w), 756 (s), 739 (w), 721 (m), 689 (s), 677 (m), 654 (m), 613 (w). Anal. calcd for $C_{17}H_{12}FNO$ [265.3]: C 76.97, H 4.56, N 5.28; Found: C 76.77, H 4.75, N 5.03.

2.2.3 (4-fluorophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1c)

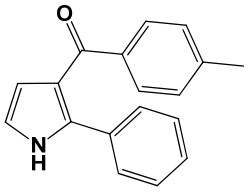


$C_{17}H_{12}FNO$
265.28 g/mol

Reaction time of the copper-free alkynylation: 18 h

106 mg (0.40 mmol, 20 %) as a brown solid. M.p. 129 °C. ^{1}H NMR (300MHz, DMSO-d_6, rt): δ = 5.77 (t, J = 2.6 Hz, 1H), 6.29 (t, J = 2.8 Hz, 1H), 6.45-6.56 (m, 2H), 6.57-6.68 (m, 3H), 6.72 (dq, J = 4.2, 2.4 Hz, 2H), 7.00-7.10 (m, 2H), 11.15 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6): δ = 113.3 (CH), 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, 2 CH), 119.6 (CH), 120.1 (C_{quat}), 128.3 (CH), 128.8 (2 CH), 129.1 (2 CH), 132.5 (C_{quat}), 132.5 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz, 2 CH), 136.6 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, C_{quat}), 137.3 (C_{quat}), 164.7 (d, $^{1}J_{C\text{-}F}$ = 249.9 Hz, C_{quat}), 191.3 (C_{quat}). EI+MS (*m/z* (%)): 265.1 ([M^+], 73), 248.1 ([M^+ - F], 11), 236.2 ([M^+ - CH_2N], 5), 170.1 ([M^+ - C_6H_4F], 100), 142.1 ([M^+ - C_7H_4FO], 10), 123.1 ([M^+ - $C_{10}H_8N$], 16), 115.1 ([M^+ - C_8H_6FNO], 80), 95.1 ([M^+ - $C_{11}H_8NO$], 66), 75.0 ([M^+ - $C_{11}H_8FNO$], 51); IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3260 (ν (N-H), m), 3109 (w), 3059 (w), 2988 (w), 2974 (w), 2901 (w), 1618 (s), 1595 (ν (C=O), s), 1580 (w), 1558 (w), 1501 (m), 1474 (s), 1450 (m), 1429 (s), 1395 (s), 1333 (w), 1319 (m), 1308 (m), 1292 (m), 1223 (s), 1175 (w), 1155 (s), 1107 (w), 1074 (m), 1057 (w), 1013 (w), 899 (w), 883 (s), 851 (s), 783 (s), 760 (s), 743 (s), 718 (s), 689 (s), 671 (s), 635 (m), 613 (m). ESI HR-MS for $C_{17}H_{12}FNO+H^+$: calcd.: 266.09757; Found: 266.09740.

2.2.4 (2-phenyl-1*H*-pyrrol-3-yl)(*p*-tolyl)methanone (1d)

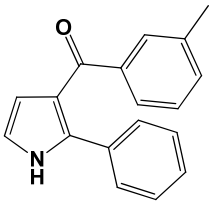


$C_{18}H_{15}NO$
261.32 g/mol

Reaction time of the copper-free alkynylation: 19 h

55 mg (0.20 mmol, 11 %) as a brown solid. M.p. 146 °C. ^{1}H NMR (300MHz, DMSO-d_6, rt): δ = 2.33 (s, 3H), 6.35 (t, J = 2.6 Hz, 1H), 6.92 (t, J = 2.7 Hz, 1H), 7.17-7.36 (m, 5H), 7.42-7.49 (m, 2H), 7.58-7.64 (m, 2H), 11.78 (s, 1H). ^{13}C-NMR (75MHz, DMSO-d_6 rt): δ = 21.1 (CH_3), 112.7 (CH), 118.5 (CH), 119.8 (C_{quat}), 127.3 (CH), 128.0 (2 CH), 128.4 (2 CH), 128.6 (2 CH), 129.3 (2 CH), 132.2 (C_{quat}), 135.8 (C_{quat}), 136.9 (C_{quat}), 141.7 (C_{quat}), 191.1 (C_{quat}). EI+MS (*m/z* (%)): 261.1 ([M^+], 70), 246.1 ([M^+ - CH_3], 9), 170.1 ([M^+ - $C_{11}H_8NO$], 100), 142.1 ([M^+ - C_8H_7O], 8), 119.1 [(M^+ - $C_{10}H_8N$], 6), 115.1 ([M^+ - C_9H_9NO], 66), 91.1 ([M^+ - $C_{11}H_8NO$], 32); IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3246 (ν (N-H), w), 3111 (w), 3032 (w), 2961 (w), 2924 (w), 2853 (w), 1714 (w), 1614 (m), 1599 (ν (C=O), s), 1568 (w), 1557 (w), 1472 (m), 1452 (w), 1433 (m), 1398 (w), 1325 (w), 1312 (w), 1292 (m), 1260 (m), 1209 (w), 1182 (w), 1165 (m), 1103 (w), 1082 (w), 1028 (m), 1020 (m), 883 (s), 866 (w), 835 (w), 791 (m), 779 (s), 760 (s), 737 (s), 714 (m), 696 (s), 669 (w), 642 (w), 627 (w). ESI HR-MS for $C_{18}H_{15}NO+H^+$: calcd.: 262.12264; Found: 266.12276.

2.2.5 (2-phenyl-1*H*-pyrrol-3-yl)(*m*-tolyl)methanone (1e)

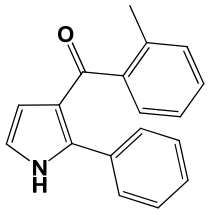


$C_{18}H_{15}NO$
261.32 g/mol

Reaction time of the copper-free alkynylation: 20 h

102 mg (0.39 mmol, 20 %) as a brown oil. ^{1}H NMR (300MHz, DMSO-d_6, rt): δ = 2.27 (s, 3H), 6.38 (t, *J* = 2.8 Hz,1H), 6.92 (t, J = 2.8 Hz, 1H), 7.23-7.27 (m, 1H), 7.28-7.31 (m, 4H), 7.42-7.44 (m, 2H), 7.45-7.48 (m, 2H), 11.79 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6 rt): δ = 20.8 (CH_3), 112.7 (CH), 118.5 (CH), 119.8 (C_{quat}), 126.3 (CH), 127.3 (CH), 127.9 (CH), 127.9 (2 CH), 128.5 (2 CH), 129.7 (CH), 132.1 (CH), 132.2 (C_{quat}), 136.1 (C_{quat}), 137.2 (C_{quat}), 139.5 (C_{quat}), 191.4 (C_{quat}). EI+MS (*m/z* (%)): 261.1 ([M^+], 55), 246.1 ([M^+ - CH_3], 2), 170.1 ([M^+ - $C_{11}H_8NO$], 100), 142.2 ([M^+ - C_8H_7O], 5), 119.1 [(M^+ - $C_{10}H_8N$], 2), 115.1 ([M^+ - C_9H_9NO], 38), 91.1 ([M^+ - $C_{11}H_8NO$], 13). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3258 (ν (N-H), w), 3107 (w), 3057 (w), 2953 (w), 2920 (w), 2851 (w), 1709 (w), 1620 (m), 1599 (ν (C=O), s), 1580 (m), 1557 (w), 1531 (w), 1472 (s), 1451 (s), 1431 (s), 1393 (m), 1294 (s), 1200 (w), 1184 (w), 1150 (m), 1103 (w), 1074 (w), 1040 (w), 1024 (w), 999 (w), 972 (w), 934 (w), 920 (w), 893 (w), 862 (w), 826 (m), 816 (m), 793 (m), 772 (m), 752 (s), 733 (s), 694 (s), 669 (s), 625 (m). ESI HR-MS for $C_{18}H_{15}NO+H^+$: calcd.: 262.12264; Found: 262.12283.

2.2.6 (2-phenyl-1*H*-pyrrol-3-yl)(*o*-tolyl)methanone (1f)

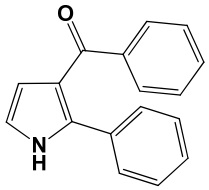


$C_{18}H_{15}NO$
261.32 g/mol

Reaction time of the copper-free alkynylation: 2 h

133 mg (0.51 mmol, 26 %) as a yellow solid. M.p. 140 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 2.25 (s, 3H), 6.18 (t, J = 2.6 Hz, 1H), 6.87 (t, J = 2.8 Hz, 1H), 7.10 (td, J = 7.5, 1.1 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.21 (dd, J = 7.7, 1.4 Hz, 1H), 7.25 (td, J = 7.5, 1.5 Hz, 1H), 7.27-7.32 (m, 3H), 7.47-7.51 (m, 2H), 11.81 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 19.3 (CH_3), 112.8 (CH), 118.7 (CH), 120.8 (C_{quat}), 124.9 (CH), 127.6 (CH), 127.6 (CH), 127.7 (2 CH), 128.8 (2 CH), 129.1 (CH), 130.3 (CH), 131.9 (C_{quat}), 134.9 (C_{quat}), 136.8 (C_{quat}), 141.2 (C_{quat}), 193.0 (C_{quat}). EI+MS (*m/z* (%)): 262.2 ([M^+], 17), 261.2 ([M^+], 100), 246.2 ([M^+ - CH_3], 2), 244.1 ([M^+ - HN], 32), 232.1 ([M^+ – CH_2N], 11), 184.1 ([M^+ - C_6H_5], 76) 170.1 ([M^+ - $C_{11}H_8NO$], 73), 142.1 ([M^+ - C_8H_7O], 8), 118.1 [(M^+ - $C_{10}H_8N$], 46), 115.1 ([M^+ - C_9H_9NO], 69), 91.1 ([M^+ - $C_{11}H_8NO$], 30). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3227 (ν (N-H), w), 3175 (w), 3107 (w), 2926 (w), 2911 (w), 1614 (ν (C=O), s), 1599 (m), 1578 (w), 1557 (w), 1472 (m), 1451 (m), 1431 (s), 1396 (m), 1375 (w), 1317 (w), 1304 (m), 1283 (w), 1240 (w), 1177 (w), 1107 (w), 1076 (w), 1036 (w), 881 (s), 854 (w), 804 (w), 766 (s), 741 (s), 718 (m), 689 (s), 677 (s), 660 (s), 615 (w). ESI HR-MS for $C_{18}H_{15}NO+H^+$: calcd.: 262.12264; Found: 262.12286.

2.2.7 phenyl(2-phenyl-1*H*-pyrrol-3-yl)methanone (1g)

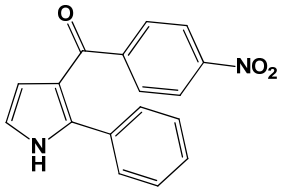


$C_{17}H_{13}NO$
247.29 g/mol

Reaction time of the copper-free alkynylation: 19 h

146 mg (0.59 mmol, 30 %) as a light red solid. M.p. 132 °C. ^{1}H NMR (300MHz, CDCl3, rt): δ = 6.59 (t, J = 2.8 Hz, 1H), 6.79 (t, J = 2.8 Hz, 1H), 7.22-7.35 (m, 5H), 7.38-7.46 (m, 3H), 7.74-7.80 (m, 2H), 8.79 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$, rt): δ = 113.8 (CH), 117.9 (CH), 120.5 (C_{quat}), 128.0 (2 CH), 128.1 (CH), 128.5 (2 CH), 128.6 (2 CH), 129.8 (2 CH), 131.7 (CH), 132.2 (C_{quat}), 137.3 (C_{quat}), 139.7 (C_{quat}), 192.7 (C_{quat}). EI+MS (*m/z* (%)): 247.1 ([M^+], 62), 218.1 ([M^+ - CH_2N], 4), 170.1 ([M^+ - C_6H_5], 100), 142.1 ([M^+ - C_7H_5O], 7), 115.1 ([M^+ - C_8H_7NO], 52). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3298 (ν (N-H), m), 3065 (w), 2988 (w), 2972 (w), 2901 (w), 1622 (ν (C=O), m), 1597 (m), 1576 (w), 1557 (w), 1476 (m), 1451 (m), 1429 (m), 1395 (m), 1325 (w), 1298 (m), 1260 (w), 1233 (w), 1217 (w), 1177 (w), 1167 (w), 1155 (w), 1105 (w), 1076 (m), 1057 (m), 1026 (w), 1013 (w), 1001 (w), 974 (w), 901 (w), 880 (s), 853 (w), 804 (w), 772 (m), 719 (s), 698 (s), 679 (s), 665 (s), 613 (m). ESI HR-MS for $C_{17}H_{13}NO+H^+$: calcd.: 248.10699; Found: 248.10650.

2.2.8 (4-nitrophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1h)

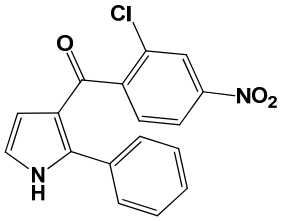


$C_{17}H_{12}N_2O_3$
292.29 g/mol

Reaction time of the copper-free alkynylation: 18 h

252 mg (0.86 mmol, 43 %) as a brown solid. M.p. 175 °C. ^{1}H NMR (300MHz, $CDCl_3$, rt): δ = 6.61 (t, J = 2.9 Hz, 1H), 6.85 (dd, J = 3.1, 2.4 Hz, 1H), 7.27 (dt, J = 4.9, 1.7 Hz, 3H), 7.33-7.41 (m, 2H), 7.77.-7.85 (m, 2H), 8.06-8.16 (m, 2H), 8.81 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$, rt): δ = 113.5 (CH), 118.6 (CH), 120.0 (C_{quat}), 123.2 (2 CH), 128.6 (2 CH), 128.7 (CH), 128.8 (2 CH), 130.3 (2 CH), 131.6 (C_{quat}), 138.3 (C_{quat}), 145.2 (C_{quat}), 149.3 (C_{quat}), 190.4 (C_{quat}). EI+MS (*m/z* (%)): 292.1 ([M^+], 55), 224.0 ([M^+ - NO_2], 9), 170.1 ([M^+ - $C_6H_4NO_2$], 100), 142.1 ([M^+ - $C_7H_4NO_3$], 8), 122.9 ([M^+ - $C_{11}H_8NO$], 2), 115.1 ([M^+ - $C_8H_6N_2O_3$], 52). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3262 (ν (N-H), s), 3102 (w), 3059 (w), 2928 (w), 2851 (w), 2361 (w), 2342 (w), 1614 (m), 1595 (ν (C=O), m), 1574 (w), 1553 (w), 1516 (ν (Ar-NO_2), m), 1470 (m), 1447 (w), 1425 (m), 1377 (m), 1344 (s), 1325 (m), 1312 (m), 1298 (m), 1269 (w), 1225 (w), 1177 (w), 1159 (w), 1101 (m), 1078 (w), 1013 (w), 970 (w), 885 (m), 843 (s), 835 (m), 799 (w), 772 (m), 743 (s), 712 (m), 696 (s), 679 (m), 611 (w). Anal. calcd for $C_{17}H_{12}N_2O_3$ [292.3]: C 69.86, H 4.14, N 9.58; Found: C 69.65, H 4.04, N 9.81.

2.2.9 (2-chloro-4-nitrophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1i)

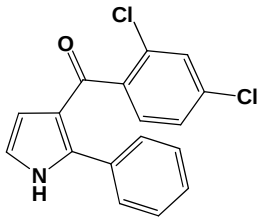


$C_{17}H_{11}ClN_2O_3$
326.73 g/mol

Reaction time of the copper-free alkynylation: 5 h

326 mg (1.00 mmol, 50 %) as a yellow solid. M.p. 234 °C. ^{1}H NMR (300MHz, DMSO-d_6, rt): δ = 6.27 (dd, J = 3.0, 2.4 Hz, 1H), 6.88-6.92 (m, 1H), 7.23-7.31 (m, 3H), 7.38-7.47 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 8.06 (dd, J = 8.4, 2.2 Hz, 1H), 8.16 (d, J = 2.1 Hz, 1H), 11.99 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6, rt): δ = 112.3 (CH), 119.4 (C_{quat}), 119.7 (CH), 122.1 (CH), 124.4 (CH), 127.8 (2 CH), 128.2 (CH), 129.1 (2 CH), 129.7 (CH), 130.6 (C_{quat}), 131.3 (C_{quat}), 138.5 (C_{quat}), 146.4 (C_{quat}), 147.8 (C_{quat}), 187.2 (C_{quat}). EI+MS (*m/z* (%)): 328.1 ([$M^+(Cl^{37})$], 10), 326.1 ([$M^+(Cl^{35})$], 31), 281.0 ([$M^+(Cl^{37})$ - NO_2], 2), 279.1 ([$M^+(Cl^{35})$ - NO_2], 4), 244.2 ([M^+ - $ClNO_2$], 2), 170.1 ([M^+ - $C_6H_3ClNO_2$], 100), 142.1 ([M^+ - $C_7H_3ClNO_3$], 11), 115.1 ([M^+ - $C_8H_5ClN_2O_3$], 67). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3242 (ν (N-H), m), 1599 (ν (C=O), s), 1574 (w), 1558 (w), 1516 (ν (NO_2), s), 1477 (w), 1466 (w), 1437 (s), 1385 (m), 1341 (s), 1290 (m), 1179 (w), 1138 (w), 1121 (w), 1070 (w), 905 (w), 889 (m), 868 (s), 839 (m), 831 (w), 745 (s), 718 (w), 698 (s), 683 (w), 665 (w). Anal. calcd for $C_{17}H_{11}ClN_2O_3$ [326.7]: C 62.49, H 3.39, N 8.57; Found: C 62.27, H 3.29, N 8.41.

2.2.10 (2,4-dichlorophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1j)

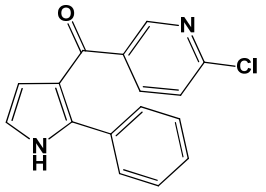


$C_{17}H_{11}Cl_2NO$
316.18 g/mol

Reaction time of the copper-free alkynylation: 2.5 h

375 mg (1.19 mmol, 59 %) as a light orange solid. M.p. 167 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 6.28 (t, J = 2.8 Hz, 1H), 6.90 (t, J =2.7 Hz, 1H), 7.30 (dt, J = 4.5, 2.8 Hz, 3H), 7.31-7.33 (m, 2H), 7.41-7.45 (m, 2H), 7.51 (d, J = 1.7 Hz, 1H), 11.91 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 112.3 (CH), 119.3 (CH), 119.9 (C_{quat}), 126.9 (CH), 127.7 (2 CH), 127.9 (CH), 128.9 (CH), 129.0 (2 CH), 130.1 (CH), 130.8 (C_{quat}), 131.5 (C_{quat}), 134.2 (C_{quat}), 138.0 (C_{quat}), 139.5 (C_{quat}), 188.0 (C_{quat}). EI+MS (*m/z* (%)):317.1 ([M^+($Cl^{37}Cl^{35}$)], 18), 315.1 ([M^+(Cl_2^{35})], 26), 280.1 ([M^+ - Cl], 6), 170.1 ([M^+ - $C_6H_3Cl_2$], 100), 147.0 ([M^+($Cl^{37}Cl^{35}$) - $C_{11}H_8NO$], 8), 145.0 ([M^+(Cl_2^{35}) - $C_{11}H_8NO$], 12), 141.1 ([M^+ - $C_7H_3Cl_2O$], 8), 115.1 ([M^+ - $C_8H_5Cl_2NO$], 65), 111.0 ([M^+(Cl^{37}) - $C_{11}H_8ClNO$], 7), 109.0 ([M^+(Cl^{35}) - $C_{11}H_8ClNO$], 19). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3237 (ν (N-H), m), 1599 (ν (C=O), s), 1587 (s), 1576 (m), 1556 (m), 1526 (w), 1464 (w), 1445 (s), 1435 (s), 1377 (m), 1341 (m), 1294 (m), 1182 (w), 1101 (m), 1074 (m), 912 (m), 881 (s), 827 (m), 791 (m), 779 (m), 762 (s), 743 (m), 718 (m), 696 (s), 683 (w), 669 (w). Anal. calcd for $C_{17}H_{11}Cl_2NO$ [316.2]: C 64.58, H 3.51, N 4.43; Found: C 64.40, H 3.63, N 4.28.

2.2.11 (6-chloropyridin-3-yl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1k)

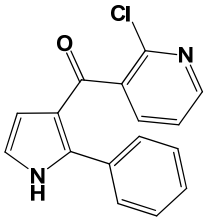


$C_{16}H_{11}ClN_2O$
282.72 g/mol

Reaction time of the copper-free alkynylation: 19 h

241 mg (0.85 mmol, 43 %) as a brown/reddish solid. M.p. 146 °C. ^{1}H NMR (300MHz, $CDCl_3$, rt): δ = 6.59 (t, J = 2.8 Hz, 1H), 6.83 (t, J = 2.8 Hz, 1H), 7.20-7.33 (m, 4H), 7.33-7.39 (m, 2H), 7.94 (dd, J = 8.2, 2.4 Hz, 1H), 8.63 (dd, J = 2.4, 0.7 Hz, 1H), 9.04 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$, rt): δ = 113.3 (CH), 118.7 (CH), 120.0 (C_{quat}), 123.8 (CH), 128.7 (3 CH), 128.9 (2 CH), 131.6 (C_{quat}), 134.1 (C_{quat}), 138.2 (C_{quat}), 139.5 (CH), 150.9 (CH), 153.9 (C_{quat}), 189.0 (C_{quat}). EI+MS (*m/z* (%)): 284.1 ([$M^+(Cl^{37})$], 20), 282.1 ([$M^+(Cl^{35})$], 59), 255.1 ([$M^+(Cl^{37})$ - HCN], 2), 253.1 ([$M^+(Cl^{35})$ - HCN], 6), 247.1 ([M^+ - Cl]$^+$, 5), 170.1 ([M^+ - C_5H_3ClN], 100), 142.1 ([M^+ - C_7H_3ClNO], 11), 141.1 ([M^+ - C_6H_4ClNO], 11), 115.1 ([M^+ - $C_7H_5ClN_2O$], 71), 114.1 ([$M^+(Cl^{37})$ - $C_{11}H_8NO$], 14), 112.0 ([$M^+(Cl^{35})$ - $C_{11}H_8NO$], 13). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3190 (ν (N-H), m), 3177 (m), 3103 (m), 3053 (w), 1634 (ν (C=O), s), 1580 (s), 1560 (m), 1466 (m), 1449 (s), 1433 (s), 1396 (w), 1356 (w), 1325 (m), 1283 (m), 1103 (s), 881 (s), 841 (m), 764 (s), 752 (s), 723 (s), 698 (s), 677 (m). ESI HR-MS for $C_{16}H_{11}ClN_2O+H^+$: calcd.: 283.06327; Found: 283.06380.

2.2.12 (2-chloropyridin-3-yl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1l)

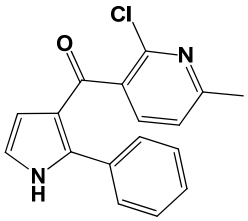


$C_{16}H_{11}ClN_2O$
282.72 g/mol

Reaction time of the copper-free alkynylation: 4 h

320 mg (1.13 mmol, 57 %) as a light yellow solid. M.p. 195 °C. ^{1}H NMR (300MHz, DMSO-d_6, rt): δ = 6.32 (dd, J = 3.0, 2.4 Hz, 1H), 6.91 (t, J = 2.8 Hz, 1H), 7.24-7.33 (m, 4H), 7.38-7.45 (m, 2H), 7.75 (dd, J = 7.5, 1.9 Hz, 1H), 8.32 (dd, J = 4.9, 1.9 Hz, 1H), 11.95 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6, rt): δ = 112.1 (CH), 119.5 (CH), 119.9 (C_{quat}), 122.6 (CH), 127.8 (2 CH), 128.1 (CH), 129.0 (2 CH), 131.4 (C_{quat}), 136.7 (C_{quat}), 137.8 (CH), 138.3 (C_{quat}), 145.9 (C_{quat}), 149.8 (CH), 187.3 (C_{quat}). EI+MS (*m/z* (%)): 284.1 ([$M^+(Cl^{37})$], 13), 282.1 ([$M^+(Cl^{35})$], 34), 247.1 ([M^+ - Cl], 2), 170.1 ([M^+ - C_5H_3ClN], 100), 142.1 ([M^+ - C_7H_3ClNO], 9), 141.1 ([M^+ - $C_6H_4ClNO]^+$, 9), 115.1 ([M^+ - $C_7H_5ClN_2O$], 68), 114.1 ([$M^+(Cl^{37})$ - $C_{11}H_8NO$], 14) 112.0 ([$M^+(Cl^{35})$ - $C_{11}H_8NO$], 13). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3202 (ν (N-H), m), 3144 (w), 3088 (w), 1649 (ν (C=O), s), 1601 (w), 1576 (m), 1557 (m), 1470 (m), 1450 (m), 1433 (m), 1393 (s), 1321 (w), 1298 (s), 1277 (w), 1258 (w), 1244 (w), 1207 (w), 1128 (w), 1098 (m), 1070 (m), 1057 (m), 1032 (m), 901 (m), 880 (s), 862 (w), 820 (s), 779 (s), 754 (s), 727 (s), 692 (s), 679 (s), 652 (m), 613 (w). Anal. calcd for $C_{16}H_{11}ClN_2O$ [282.7]: C 67.97, H 3.92, N 9.91; Found: C 68.03, H 4.14, N 9.63.

2.2.13 (2-chloro-6-methylpyridin-3-yl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1m)

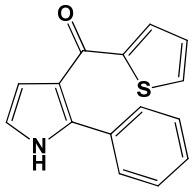


$C_{17}H_{13}ClN_2O$
296.75 g/mol

Reaction time of the copper-free alkynylation: 2.3 h

436 mg (1.47 mmol, 73 %) as a yellow solid. M.p. 127 °C. ^{1}H NMR (300MHz, $CDCl_3$, rt): δ = 2.44 (s, 3H), 6.56 (t, J = 2.9 Hz, 1H), 6.79 (dd, J = 3.1, 2.4 Hz, 1H), 6.89 (dd, J = 7.7, 0.6 Hz, 1H), 7.23 (dd, J = 5.1, 1.9 Hz, 3H), 7.33-7.39 (m, 2H), 7.42 (d, J = 7.6 Hz, 1H), 8.91 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$, rt): δ = 24.0 (CH_3), 112.9 (CH), 118.7 (CH), 121.1 (C_{quat}), 121.3 (CH), 128.3 (2 CH), 128.5 (CH), 129.0 (2 CH), 131.5 (C_{quat}), 133.8 (C_{quat}), 138.3 (CH), 138.9 (C_{quat}), 146.9 (C_{quat}), 159.9 (C_{quat}), 188.8 (C_{quat}). EI+MS (*m/z* (%)): 298.1 ([$M^+(Cl^{37})$], 12), 296.1 ([$M^+(Cl^{35})$], 37), 261.1 ([M^+ - Cl], 5), 233.1 ([M^+ - CHClN], 9), 170.1 ([M^+ - C_6H_5ClN], 100), 154.1 ([$M^+(Cl^{35})$ - $C_{10}H_8N$], 1.4), 142.1 ([M^+ - C_7H_5ClNO], 8), 128.1 ([$M^+(Cl^{37})$ - $C_{11}H_8NO$], 2) 126.1 ([$M^+(Cl^{35})$ - $C_{11}H_8NO$], 3), 115.1 ([M^+ - $C_8H_7ClN_2O$], 59). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3207 (ν (N-H), m), 3107 (w), 3053 (w), 1638 (m), 1589 (ν (C=O), s), 1553 (m), 1472 (m), 1431 (s), 1385 (m), 1339 (s), 1294 (m), 1277 (w), 1140 (m), 1092 (s), 1061 (m), 1032 (w), 999 (w), 914 (s), 880 (m), 854 (m), 822 (s), 804 (w), 783 (m), 768 (s), 752 (m), 739 (w), 698 (s), 681 (s), 611 (m). Anal. calcd for $C_{17}H_{13}ClN_2O$ [296.8]: C 68.81, H 4.42, N 9.44; Found: C 68.64, H 4.23, N 9.23.

2.2.14 (2-phenyl-1*H*-pyrrol-3-yl)(thiophen-2-yl)methanone (1n)

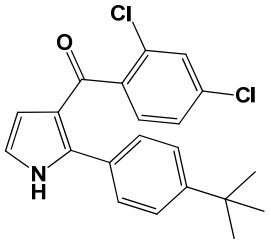


$C_{15}H_{11}NOS$
253.32 g/mol

Reaction time of the copper-free alkynylation: 3.5 h

183 mg, (0.72 mmol, 36 %) as a red solid. M.p. 134 °C. 1H NMR (300MHz, CDCl3, rt): δ = 6.71 (t, J = 2.8 Hz, 1H), 6.78 (t, *J* = 2.7 Hz, 1H), 7.02 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.22-7.34 (m, 3H), 7.44-7.51 (m, 2H), 7.56 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.61 (dd, *J* =3.8, 1.2 Hz, 1H), 8.90 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$, rt): δ = 113.0 (CH), 118.0 (CH), 120.3 (C_{quat}), 127.6 (CH), 128.1 (CH), 128.4 (2 CH), 128.6 (2 CH), 132.1 (C_{quat}), 132.8 (CH), 133.7 (CH), 136.5 (C_{quat}), 145.8 (C_{quat}), 184.1 (C_{quat}). EI+MS (*m/z* (%)): 253.0 ([M^+], 100), 224.0 ([M^{2+} - CH_2N], 17), 220.1 ([M^{2+} - S], 45), 170.1 ([M^+ - C_4H_3S], 70), 142.1 ([M^+ - C_5H_5SN], 10), 141.1 ([M^+ - C_5H_3OS], 9), 115.1 ([M^+ - $C_6H_5SN_2$], 84), 111.0 ([M^+ - $C_{10}H_8N$], 26), 83.0 ([M^+ - $C_{11}H_8NO$], 12). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3219 (ν (N-H), m), 3107 (w), 3055 (w), 2947 (w), 1591 (ν (C=O), s), 1557 (m), 1512 (m), 1497 (w), 1470 (m), 1452 (m), 1433 (s), 1412 (s), 1352 (m), 1325 (m), 1310 (m), 1298 (s), 1273 (m), 1233 (m), 1209 (w), 1169 (m), 1111 (w), 1086 (w), 1074 (w), 1059 (m), 1032 (w), 1024 (w), 1003 (w), 991 (w), 976 (w), 924 (w), 897 (w), 864 (w), 854 (w), 812 (s), 762 (s), 718 (s), 702 (s), 679 (s), 669 (s), 613 (m). ESI HR-MS for $C_{15}H_{11}NOS+H^+$: calcd: 254.06341; Found: 254.06383.

2.2.15 (2-(4-(*tert*-butyl)phenyl)-1*H*-pyrrol-3-yl)(2,4-dichlorophenyl)methanone (1o)

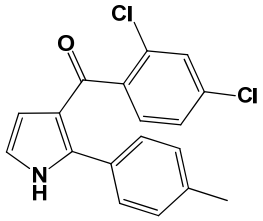


$C_{21}H_{19}Cl_2NO$
372.29 g/mol

Reaction time of the copper-free alkynylation: 2.75 h

439 mg (1.18 mmol, 59 %) as a yellow solid. M.p. 74 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 1.26 (s, 9H), 6.36 (t, J = 2.7 Hz, 1H), 6.89 (t, J = 2.7 Hz, 1H), 7.20-7.24 (m, 2H), 7.25 (s, 4H), 7.42 (d, J = 1.7 Hz, 1H), 11.82 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 31.0 (3 CH_3), 34.3 (C_{quat}), 111.6 (CH), 119.1 (CH), 120.2 (C_{quat}), 124.3 (2 CH), 126.7 (CH), 128.6 (C_{quat}), 128.7 (CH), 128.8 (2 CH), 130.2 (CH), 130.8 (C_{quat}), 133.9 (C_{quat}), 138.6 (C_{quat}), 139.5 (C_{quat}), 150.5 (C_{quat}), 187.9 (C_{quat}). EI+MS (*m/z* (%)): 373.1 ([M^+($Cl^{37}Cl^{35}$)], 31), 371.1 ([M^+(Cl_2^{35})], 47), 358.0 ([M^+($Cl^{37}Cl^{35}$) - CH_3], 38), 356.1 ([M^+(Cl_2^{35}) - CH_3], 60), 316.1 ([M^+($Cl^{37}Cl^{35}$) - C_4H_9], 5), 314.0 ([M^+(Cl_2^{35}) - C_4H_9], 9), 226.1 ([M^+ - $C_6H_3Cl_2$], 7), 174.9 ([M^+($Cl^{37}Cl^{35}$) - $C_{14}H_{16}N$], 67), 172.9 ([M^+(Cl_2^{35}) - $C_{14}H_{16}N$], 100), 170.2 ([M^+ - $C_8H_5Cl_2NO$], 15), 147.0 ([M^+($Cl^{37}Cl^{35}$) - $C_{15}H_{16}NO$], 29), 145.0 ([M^+(Cl_2^{35}) - $C_{15}H_{16}NO$], 34), 91.6 ([M^+ - $C_{14}H_{11}Cl_2NO$], 54), 57.1 ([M^+ - $C_{17}H_{10}Cl_2NO$], 68). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3265 (ν (N-H), m), 3121 (w), 3084 (w), 2961 (ν (C-H), m), 2903 (w), 2866 (w), 1730 (w), 1709 (w), 1607 (m), 1584 (ν (C=O), m), 1555 (w), 1510 (w), 1476 (w), 1441 (s), 1391 (m), 1373 (m), 1364 (m), 1325 (w), 1296 (m), 1269 (m), 1252 (w), 1180 (w), 1140 (w), 1103 (m), 1072 (m), 1057 (m), 1024 (w), 1003 (w), 951 (w), 912 (m), 901 (m), 883 (s), 866 (w), 835 (m), 826 (m), 791 (m), 781 (m), 733 (m), 714 (m), 685 (m), 669 (m), 633 (w), 619 (w). Anal. calcd for $C_{21}H_{19}Cl_2NO$ [372.3]: C 67.75, H 5.14, N 3.76; Found: C 67.47, H 5.31, N 3.61.

2.2.16 (2,4-dichlorophenyl)(2-(*p*-tolyl)-1*H*-pyrrol-3-yl)methanone (1p)

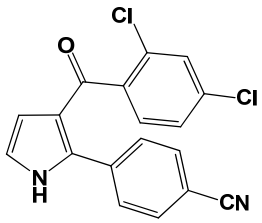


$C_{18}H_{13}Cl_2NO$
330.21 g/mol

Reaction time of the copper-free alkynylation: 4 h

362 mg (1.10 mmol, 55 %) as a light red solid. M.p. 171 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 2.30 (s, 3H), 6.23 (t, J = 2.7 Hz, 1H), 6.86 (t, J = 2.7 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 7.30-7.35 (m, 4H), 7.52 (d, J = 1.7 Hz, 1H), 11.85 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 20.8 (CH_3), 112.3 (CH), 119.0 (CH), 119.7 (C_{quat}), 126.9 (CH), 128.2 (2 CH), 128.6 (C_{quat}), 128.8 (2 CH), 128.9 (CH), 130.1 (CH), 130.7 (C_{quat}), 134.1 (C_{quat}), 137.4 (C_{quat}), 138.1 (C_{quat}), 139.6 (C_{quat}), 187.9 (C_{quat}). EI+MS (*m/z* (%)): 331.1 ([$M^+(Cl^{37}Cl^{35})$], 25), 329.1 ([$M^+(Cl_2^{35})$], 38), 316.1 ([$M^+(Cl^{37}Cl^{35})$ - CH_3], 1), 314.1 ([$M^+(Cl_2^{35})$ - CH_3], 2), 294.1 ([M^+ - Cl], 7), 184.1 ([M^+ - $C_6H_3Cl_2$], 100), 175.0 ([$M^+(Cl^{37}Cl^{35})$ - $C_{11}H_{10}N$], 6), 173.0 ([$M^+(Cl_2^{35})$ - $C_{11}H_{10}N$], 8), 156.1 ([M^+ - $C_7H_3Cl_2O$], 9), 147.0 ([$M^+(Cl^{37}Cl^{35})$ - $C_{12}H_{10}NO$], 15), 145.0 ([$M^+(Cl_2^{35})$ - $C_{12}H_{10}NO$], 19), 128.2 ([M^+ - $C_8H_5Cl_2NO$], 45), 111.1 [$M^+(Cl^{37})$ - $C_{12}H_{10}ClNO$], 11), 109.0 [$M^+(Cl^{35})$ - $C_{12}H_{10}ClNO$], 25). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3192 (ν (N-H), m), 3130 (m), 3115 (m), 3075 (w), 2997 (w), 2951 (m), 2918 (m), 2864 (w), 2793 (w), 1599 (ν (C=O), s), 1585 (s), 1557 (m), 1514 (m), 1472 (m), 1439 (s), 1396 (m), 1373 (m), 1341 (m), 1296 (m), 1269 (w), 1248 (w), 1179 (m), 1098 (w), 1074 (m), 1057 (m), 1005 (m), 916 (m), 881 (s), 872 (m), 812 (s), 785 (s), 750 (m), 725 (m), 702 (w), 671 (w). Anal. calcd for $C_{18}H_{13}Cl_2NO$ [330.2]: C 65.47, H 3.97, N 4.24; Found: C 65.28, H 3.93, N 4.05.

2.2.17 4-(3-(2,4-dichlorobenzoyl)-1*H*-pyrrol-2-yl)benzonitrile (1q)

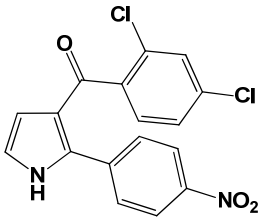


$C_{18}H_{10}Cl_2N_2O$
341.19 g/mol

Reaction time of the copper-free alkynylation: 5.3 h

442 mg (1.30 mmol, 65 %) as a light brown solid. M.p. 219 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 6.27 (t, J = 2.6 Hz, 1H), 7.00 (t, J = 2.8 Hz, 1H), 7.41 (d, J = 1.4 Hz, 2H), 7.57-7.60 (m, 1H), 7.67-7.72 (m, 2H), 7.79-7.84 (m, 2H), 12.20 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 110.1 (C_{quat}), 113.3 (CH), 118.7 (C_{quat}), 120.5 (CH), 120.1 (C_{quat}), 127.1 (CH), 129.0 (CH), 129.6 (2 CH), 130.2 (CH), 130.8 (C_{quat}), 131.7 (2 CH), 134.6 (C_{quat}), 135.2 (C_{quat}), 136.0 (C_{quat}), 139.2 (C_{quat}), 188.2 (C_{quat}). EI+MS (*m/z* (%)): 342.0 ([$M^+(Cl^{37}Cl^{35})$], 23), 340.0 ([$M^+(Cl_2{}^{35})$], 35), 317.0 ([$M^+(Cl^{37}Cl^{35})$ - CN], 11), 315.0 ([$M^+(Cl_2{}^{35})$ - CN], 13), 282.0 ([$M^+(Cl^{35})$ - CClN], 27), 195.0 ([M^+ - $C_6H_3Cl_2$], 100), 172.9 ([$M^+(Cl^{37}Cl^{35})$ - $C_{11}H_7N_2$], 8), 170.9 ([$M^+(Cl_2{}^{35})$ - $C_{11}H_7N_2$], 13), 144.9 ([$M^+(Cl_2{}^{35})$ - $C_{12}H_7N_2O$], 6). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3184 (m), 3156 (m), 3129 (m), 3109 (m), 2997 (w), 2947 (w), 2905 (w), 2845 (w), 2795 (w), 2228 (ν (Ar-CN), m), 1601 (ν (C=O), s), 1585 (s), 1555 (w), 1506 (w), 1472 (m), 1439 (s), 1395 (m), 1375 (w), 1342 (m), 1296 (m), 1269 (w), 1252 (w), 1186 (m), 1103 (m), 1072 (m), 1055 (w), 1007 (m), 916 (w), 881 (s), 841 (s), 824 (s), 789 (s), 752 (s), 735 (m), 718 (m), 704 (m), 671 (w). Anal. calcd for $C_{18}H_{10}Cl_2N_2O$ [341.2]: C 63.36, H 2.95, N 8.21; Found: C 63.08, H 3.19, N 7.97.

2.2.18 (2,4-dichlorophenyl)(2-(4-nitrophenyl)-1*H*-pyrrol-3-yl)methanone (1r)

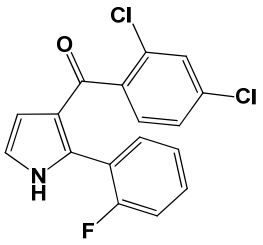


$C_{17}H_{10}Cl_2N_2O_3$
361.18 g/mol

Reaction time of the copper-free alkynylation: 6 h

149 mg (0.41 mmol, 21 %) as a red solid. M.p. 228 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 6.26 (t, J = 2.7 Hz, 1H), 7.03 (t, J = 2.8 Hz, 1H), 7.42-7.45 (m, 2H), 7.61 (d, J = 1.7 Hz, 1H), 7.77-7.82 (m, 2H), 8.18-8.23 (m, 2H), 12.30 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 113.7 (CH), 120.8 (CH), 121.2 (C_{quat}), 123.0 (2 CH), 127.2 (CH), 129.1 (CH), 129.9 (2 CH), 130.2 (CH), 130.8 (C_{quat}), 134.5 (C_{quat}), 134.6 (C_{quat}), 137.9 (C_{quat}), 139.2 (C_{quat}), 146.5 (C_{quat}), 188.3 (C_{quat}). EI+MS (*m/z* (%)): 362.0 ([M^+($Cl^{37}Cl^{35}$)], 6), 360.0 ([M^+(Cl_2^{35})], 10), 304.0 ([M^+($Cl^{37}Cl^{35}$) - $CHNO_2$], 33), 302.0 ([M^+(Cl_2^{35}) - $CHNO_2$], 95), 215.0 ([M^+ - $C_6H_3Cl_2$], 23), 186.9 ([M^+ - $C_7H_3Cl_2O$], 7), 174.8 ([M^+($Cl^{37}Cl^{35}$) - $C_{10}H_7N_2O_2$], 66), 172.8 ([M^+(Cl_2^{35}) - $C_{10}H_7N_2O_2$], 100), 146.9 ([M^+($Cl^{37}Cl^{35}$) - $C_{11}H_7N_2O_3$], 14), 144.9 ([M^+(Cl_2^{35}) - $C_{11}H_7N_2O_3$], 20). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3192 (ν (N-H), m), 3163 (w), 3107 (w), 3082 (w), 1599 (ν (C=O), s), 1516 (ν (Ar-NO_2), s), 1472 (w), 1439 (s), 1396 (w), 1375 (w), 1342 (s), 1296 (m), 1285 (m), 1265 (w), 1180 (w), 1144 (w), 1103 (m), 1092 (w), 1074 (m), 1051 (w), 1007 (w), 910 (w), 883 (s), 854 (s), 827 (m), 789 (s), 745 (s), 714 (s), 694 (m), 669 (w), 610 (w). Anal. calcd for $C_{17}H_{10}Cl_2N_2O_3$ [361.2]: C 56.53, H 2.79, N 7.76; Found: C 56.81, H 3.00, N 7.51.

2.2.19 (2,4-dichlorophenyl)(2-(2-fluorophenyl)-1*H*-pyrrol-3-yl)methanone (1s)

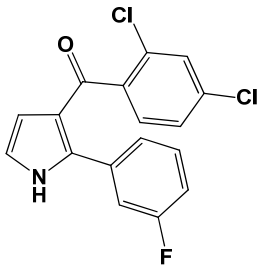


$C_{17}H_{10}Cl_2FNO$
334.17 g/mol

Reaction time of the copper-free alkynylation: 4 h

459 mg (1.37 mmol, 69 %) as a yellow solid. M.p. 180 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 6.40 (t, J = 2.8 Hz, 1H), 6.98 (t, J = 2.8 Hz, 1H), 7.08-7.14 (m, 2H), 7.27-7.33 (m, 3H), 7.35 (tdd, J = 7.4, 5.2, 1.8 Hz, 1H), 7.46 (d, J = 1.2 Hz, 1H), 11.97 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 111.2 (CH), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, CH), 119.9 (d, $^{2}J_{C\text{-}F}$ = 15.1 Hz, C_{quat}), 119.9 (CH), 121.7 (C_{quat}), 123.7 (CH), 126.8 (CH), 128.8 (CH), 130.1 (CH), 130.3 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz, CH), 130.8 (C_{quat}), 130.9 (C_{quat}), 131.8 (d, $^{4}J_{C\text{-}F}$ = 1.6 Hz, CH), 134.3 (C_{quart}), 138.7 (C_{quat}), 159.2 (d, $^{1}J_{C\text{-}F}$ = 247.4 Hz, C_{quat}), 187.7 (C_{quat}). EI+MS (m/z (%)): 334.9 ([M^+($Cl^{37}Cl^{35}$)], 14), 332.9 ([M^+(Cl_2^{35})], 23), 315.9 ([M^+($Cl^{37}Cl^{35}$) - F], 6), 313.9 ([M^+(Cl_2^{35}) - F], 10), 297.9 ([M^+ - Cl], 4), 270.0 ([M^+(Cl^{35}) - CH_2ClN], 2), 235.0 ([M^+ - CH_2Cl_2N], 3), 188.0 ([M^+ - $C_6H_3Cl_2$], 100), 174.9 ([M^+($Cl^{37}Cl^{35}$) - $C_{10}H_7FN$], 2), 173.0 ([M^+(Cl_2^{35}) - $C_{10}H_7FN$], 3), 160.0 ([M^+ - $C_7H_3Cl_2O$], 7), 147.0 ([M^+($Cl^{37}Cl^{35}$) - $C_{11}H_7FNO$], 5), 145.0 ([M^+(Cl_2^{35}) - $C_{11}H_7FNO$], 7), 133.0 ([M^+ - $C_8H_5Cl_2NO$], 35). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3198 (ν (N-H), m), 3177 (m), 3134 (w), 3115 (w), 3061 (w), 2994 (w), 2955 (w), 1603 (ν (C=O), s), 1584 (s), 1555 (m), 1531 (w), 1499 (w), 1474 (m), 1452 (s), 1435 (s), 1396 (w), 1377 (w), 1346 (m), 1300 (m), 1261 (w), 1221 (m), 1180 (w), 1142 (w), 1103 (m), 1074 (m), 1053 (w), 912 (m), 883 (s), 822 (m), 812 (s), 787 (s), 750 (s), 737 (m), 718 (m), 698 (m), 673 (w), 660 (w), 625 (w). Anal. calcd for $C_{17}H_{10}Cl_2FNO$ [334.2]: C 61.10, H 3.02, N 4.19; Found: C 60.82, H 3.22, N 3.95.

2.2.20 (2,4-dichlorophenyl)(2-(3-fluorophenyl)-1*H*-pyrrol-3-yl)methanone (1t)

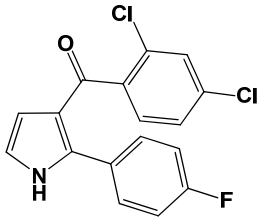


$C_{17}H_{10}Cl_2FNO$
334.17 g/mol

Reaction time of the copper-free alkynylation: 3 h

219 mg (0.66 mmol, 33 %) as a light yellow solid. M.p. 169 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 6.25 (t, J = 2.7 Hz, 1H), 6.92 (t, J = 2.8 Hz, 1H), 7.13 (dddd, J = 9.1, 8.2, 2.5, 1.2 Hz, 1H), 7.27-7.29 (m, 1H), 7.29-7.31 (m, 1H), 7.32-7.37 (m, 3H), 7.54 (d, J = 1.6 Hz, 1H), 12.02 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 112.7 (CH), 114.7 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz, CH), 115.7 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz, CH), 119.7 (CH), 120.3 (C_{quat}), 125.0 (CH), 127.0 (CH), 128.9 (CH), 129.7 (d, J = 8.5 Hz, CH), 130.2 (CH), 130.8 (C_{quat}), 133.6 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz, C_{quat}), 134.3 (C_{quat}), 136.1 (C_{quat}), 139.4 (C_{quat}), 161.4 (d, $^{1}J_{C\text{-}F}$ = 242.9 Hz, C_{quat}), 188.1 (C_{quat}). EI+MS (*m/z* (%)): 335.0 ([M^+($Cl^{37}Cl^{35}$)], 17), 333.0 ([M^+(Cl_2^{35}], 26), 298.1 ([M^+ - Cl], 6), 272.0 ([M^+(Cl^{37}) - CH_2ClN], 2), 270.0 ([M^+(Cl^{35}) - CH_2ClN], 6), 235.1 ([M^+ - CH_2Cl_2N], 6), 188.0 ([M^+ - $C_6H_3Cl_2$], 100), 174.9 ([M^+($Cl^{37}Cl^{35}$) - $C_{10}H_7FN$], 2), 173.0 ([M^+(Cl_2^{35}) - $C_{10}H_7FN$], 3), 160.1 ([M^+ - $C_7H_3Cl_2O$], 6), 147.1 ([M^+($Cl^{37}Cl^{35}$) - $C_{11}H_7FNO$], 5), 145.0 ([M^+(Cl_2^{35}) - $C_{11}H_7FNO$], 6), 133.1 ([M^+ - $C_8H_5Cl_2NO$], 31). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3196 (ν (N-H), m), 3175 (m), 3132 (m), 3115 (w), 3080 (w), 2984 (w), 2953 (w), 2365 (w), 1609 (ν (C=O), s), 1584 (s), 1558 (m), 1522 (w), 1506 (w), 1474 (m), 1452 (s), 1443 (s), 1427 (s), 1396 (w), 1375 (w), 1341 (m), 1296 (m), 1261 (w), 1219 (m), 1190 (w), 1153 (w), 1142 (w), 1103 (m), 1078 (m), 1057 (w), 934 (s), 889 (s), 874 (m), 853 (m), 829 (m), 783 (s), 752 (m), 725 (m), 694 (s), 665 (m). Anal. calcd for $C_{17}H_{10}Cl_2FNO$ [334.2]: C 61.10, H 3.02, N 4.19; Found: C 60.82, H 3.27, N 3.99.

2.2.21 (2,4-dichlorophenyl)(2-(4-fluorophenyl)-1*H*-pyrrol-3-yl)methanone (1u)

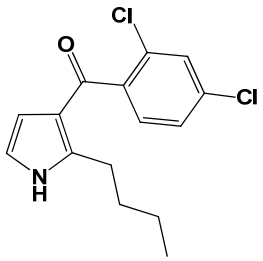


$C_{17}H_{10}Cl_2FNO$
334.17 g/mol

Reaction time of the copper-free alkynylation: 3.5 h

258 mg (0.77 mmol, 39 %) as a yellow solid. M.p. 207 °C. ^{1}H NMR (600MHz, DMSO-d_6, rt): δ = 6.26 (t, J = 2.7 Hz, 1H), 6.90 (t, J = 2.7 Hz, 1H), 7.13-7.18 (m, 2H), 7.36 (d, J = 2.0 Hz, 2H), 7.50 (ddd, J = 8.6, 5.3, 2.6 Hz, 2H), 7.54 (d, J = 1.5 Hz, 1H), 11.95 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 112.3 (CH), 114.6 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, 2 CH), 119.3 (CH), 120.0 (C_{quat}), 127.0 (CH), 127.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz, C_{quat}), 128.9 (CH), 130.1 (CH), 130.7 (C_{quat}), 131.2 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz, 2 CH), 134.2 (C_{quat}), 136.8 (C_{quat}), 139.5 (C_{quat}), 161.8 (d, $^{1}J_{C\text{-}F}$ = 245.5 Hz, C_{quat}), 188.0 (C_{quat}). EI+MS (*m/z* (%)): 335.0 ([M^+($Cl^{37}Cl^{35}$], 14), 333.0 ([M^+(Cl_2^{35})], 20), 297.9 ([M^+ - Cl], 4), 272.0 ([M^+(Cl^{37}) - CH_2ClN], 1), 270.0 ([M^+(Cl^{35}) - CH_2ClN], 3), 235.0 ([M^+ - CH_2Cl_2N], 4), 188.0 ([M^+ - $C_6H_3Cl_2$], 100), 174.9 ([M^+($Cl^{37}Cl^{35}$) - $C_{10}H_7FN$], 2), 173.0 ([M^+(Cl_2^{35}) - $C_{10}H_7FN$], 3), 160.0 ([M^+ - $C_7H_3Cl_2O$], 8), 147.0 ([M^+($Cl^{37}Cl^{35}$) - $C_{11}H_7FNO$], 5), 145.0 ([M^+(Cl_2^{35}) - $C_{11}H_7FNO$], 7), 133.1 ([M^+ - $C_8H_5Cl_2NO$], 36). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3177 (ν (N-H), m), 3130 (m), 3113 (m), 3065 (w), 2990 (m), 2951 (m), 2900 (w), 1601 (ν (C=O), s), 1591 (s), 1556 (m), 1539 (w), 1510 (m), 1470 (m), 1439 (s), 1398 (m), 1373 (m), 1341 (m), 1296 (m), 1275 (w), 1236 (w), 1219 (s), 1184 (m), 1157 (m), 1140 (w), 1101 (m), 1074 (m), 1055 (m), 1007 (m), 916 (m), 881 (s), 870 (m), 841 (s), 812 (s), 789 (s), 752 (m), 727 (m), 704 (m), 671 (w), 602 (m). Anal. calcd for $C_{17}H_{10}Cl_2FNO$ [334.2]: C 61.10, H 3.02, N 4.19; Found: C 60.87, H 3.22, N 4.00.

2.2.22 (2-butyl-1*H*-pyrrol-3-yl)(2,4-dichlorophenyl)methanone (1v)

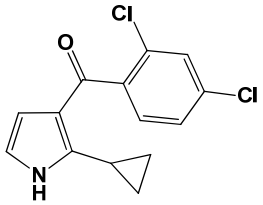


$C_{15}H_{15}Cl_2NO$
296.19 g/mol

Reaction time of the copper-free alkynylation: 15.5 h

175 mg (0.59 mmol, 30 %) as a light orange/brown resin. ^{1}H NMR (300MHz, DMSO-d_6, rt): δ = 0.85 (t, J = 7.3 Hz, 3H), 1.26 (dt, J = 14.7, 7.4 Hz, 2H), 1.53 (tt, J = 7.8, 6.5 Hz, 2H), 2.70-2.82 (m, 2H), 5.94 (t, J = 2.7 Hz, 1H), 6.63 (dd, J = 3.1, 2.3 Hz, 1H), 7.37-7.43 (m, 1H), 7.49 (dd, J = 8.2, 2.0 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 11.52 (s, 1H). ^{13}C NMR (75MHz, DMSO-d_6, rt): δ = 13.6 (CH_3), 21.9 (CH_2), 26.5 (CH_2), 31.1 (CH_2), 111.1 (CH), 117.1 (CH), 118.8 (C_{quat}), 127.2 (CH), 129.1 (CH), 129.5 (CH), 130.4 (C_{quat}), 134.0 (C_{quat}), 140.0 (C_{quat}), 141.2 (C_{quat}), 188.0 (C_{quat}). EI+MS (*m/z* (%)): 297.1 ([M^+($Cl^{37}Cl^{35}$)], 21), 295.1 ([M^+(Cl_2^{35})], 30), 268.1 ([M^+($Cl^{37}Cl^{35}$) - C_2H_5], 17), 266.0 ([M^+(Cl_2^{35}) - C_2H_5], 28), 260.1 ([M^+ - Cl], 44), 254.0 ([M^+($Cl^{37}Cl^{35}$) - C_3H_7], 9), 252.0 ([M^+(Cl_2^{35}) - C_3H_7], 14), 217.0 ([M^+(Cl^{35}) - C_3H_7Cl], 44), 175.0 ([M^+($Cl^{37}Cl^{35}$) - $C_8H_{12}N$], 71), 173.0 ([M^+(Cl_2^{35}) - $C_8H_{12}N$], 100), 150.2 ([M^+ - $C_6H_3Cl_2$], 15), 147.0 ([M^+($Cl^{37}Cl^{35}$) - $C_9H_{12}NO$], 20), 145.0 ([M^+(Cl_2^{35}) - $C_9H_{12}NO$], 31), 120.2 ([M^+ - $C_7H_3Cl_2O$], 15), 108.1 ([M^+ - $C_7H_4Cl_2NO$], 35), 79.1 ([M^+ - $C_9H_6Cl_2NO$], 85). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3211 (ν (N-H), m), 3102 (w), 3078 (w), 2932 (w), 2857 (w), 1714 (w), 1609 (s), 1584 (ν (C=O), s), 1560 (m), 1487 (m), 1462 (s), 1379 (s), 1329 (m), 1290 (m), 1271 (m), 1236 (w), 1215 (w), 1182 (w), 1144 (w), 1126 (w), 1101 (m), 1086 (m), 1045 (w), 997 (w), 962 (w), 912 (m), 878 (s), 864 (m), 837 (s), 810 (m), 787 (s), 745 (m), 725 (s), 714 (m), 675 (m), 635 (w). ESI HR-MS for $C_{15}H_{15}Cl_2NO+H^+$: calcd: 296.06035; Found: 266.06040.

2.2.23 (2-cyclopropyl-1*H*-pyrrol-3-yl)(2,4-dichlorophenyl)methanone (1w)



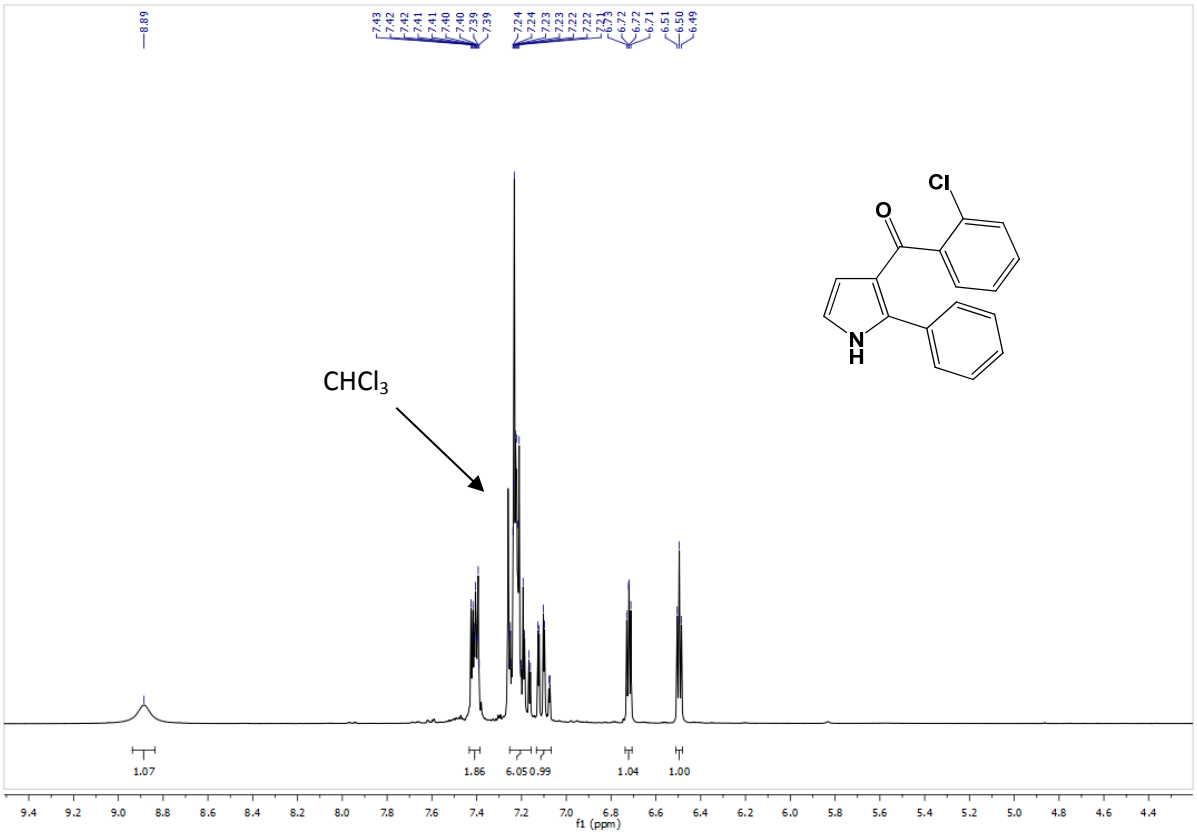
$C_{14}H_{11}Cl_2NO$
280.15 g/mol

Reaction time of the copper-free alkynylation: 14.0 h

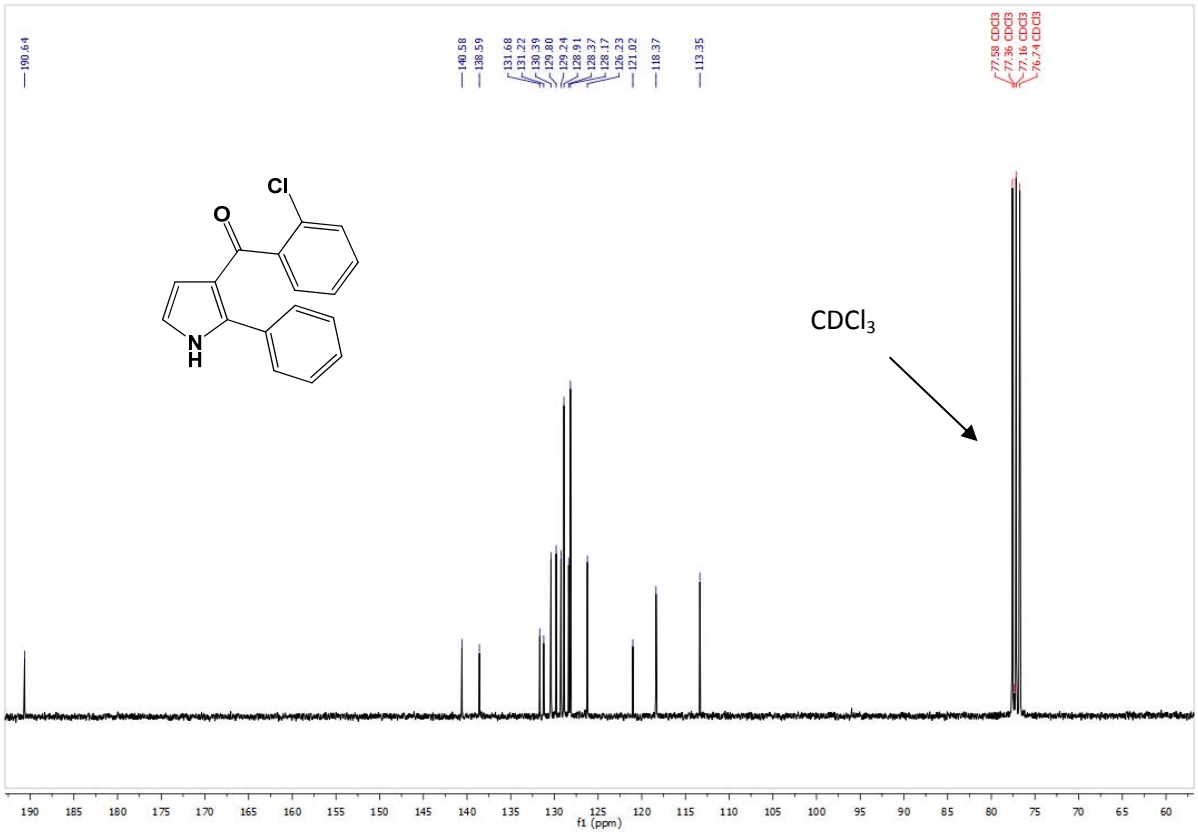
256 mg (0.91 mmol, 46 %) as a light yellow solid. M.p. 129 °C. ^{1}H NMR (600MHz, DMSO-d6, rt): δ = 0.78-0.85 (m, 2H), 0.85-0.93 (m, 2H), 2.41-2.48 (m, 1H), 5.94 (dd, J = 3.1, 2.3 Hz, 1H), 6.57 (dd, J = 3.1, 2.4 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.49 (dd, J = 8.2, 2.0 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 11.11 (s, 1H). ^{13}C NMR (150MHz, DMSO-d_6, rt): δ = 8.7 (2 CH_2), 8.7 (CH), 111.1 (CH), 117.0 (CH), 120.2 (C_{quat}), 127.3 (CH), 129.1 (CH), 129.6 (CH), 130.4 (C_{quat}), 133.9 (C_{quat}), 140.2 (C_{quat}), 142.5 (C_{quat}), 188.0 (C_{quat}). EI+MS (*m/z* (%)): 281.1 ([$M^+(Cl^{37}Cl^{35})$], 26), 279.1 ([$M^+(Cl_2{}^{35})$], 45), 266.1 ([$M^+(Cl^{37}Cl^{35})$ - HN], 69), 264.1 ([$M^+(Cl_2{}^{35})$ - HN], 100), 244.1 ([M^+ - Cl], 13), 209.1 ([M^+ - Cl_2], 16), 175.0 ([$M^+(Cl^{37}Cl^{35})$ - C_7H_8N], 7), 173.1 ([$M^+(Cl_2{}^{35})$ - C_7H_8N], 12), 150.2 ([M^+ - $C_6H_3Cl_2$], 14.7), 147.0 ([$M^+(Cl^{37}Cl^{35})$ - C_8H_8NO], 18), 145.1 ([$M^+(Cl_2{}^{35})$ - C_8H_8NO], 31), 134.1 ([M^+ - $C_6H_3Cl_2$], 26), 106.1 ([M^+ - $C_7H_3Cl_2O$], 75), 79 ([M^+ - $C_8H_5Cl_2NO$], 75). IR (diamond): $\tilde{\upsilon}$ [cm^{-1}] = 3275 (ν (N-H), m), 3188 (w), 3113 (w), 3086 (w), 1611 (ν (C=O), s), 1580 (m), 1557 (m), 1454 (s), 1393 (w), 1356 (s), 1315 (w), 1279 (w), 1190 (w), 1103 (w), 1078 (w), 1059 (w), 1045 (w), 1020 (w), 972 (w), 922 (s), 883 (s), 864 (s), 833 (m), 789 (m), 777 (m), 733 (s), 716 (s), 683 (m), 671 (w), 642 (w), 613 (w). Anal. calcd for $C_{14}H_{11}Cl_2NO$ [280.2]: C 60.02, H 3.96, N 5.00; Found: C 59.95, H 4.06, N 4.71.

3 ^{1}H and ^{13}C NMR spectra of 2-substituted 3-acylpyrroles 1

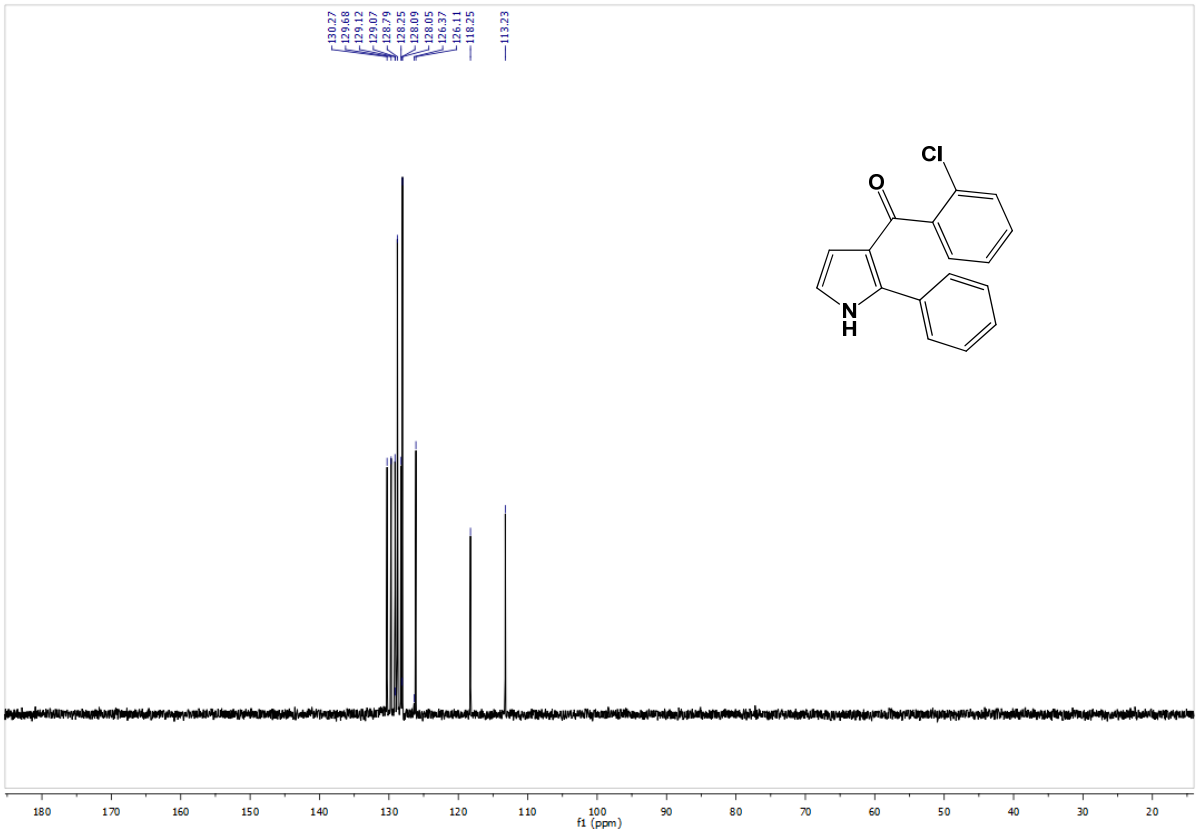
3.1 (2-Chlorophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (1a)



^{1}H NMR of **1a** in $CDCl_3$ at 298 K.

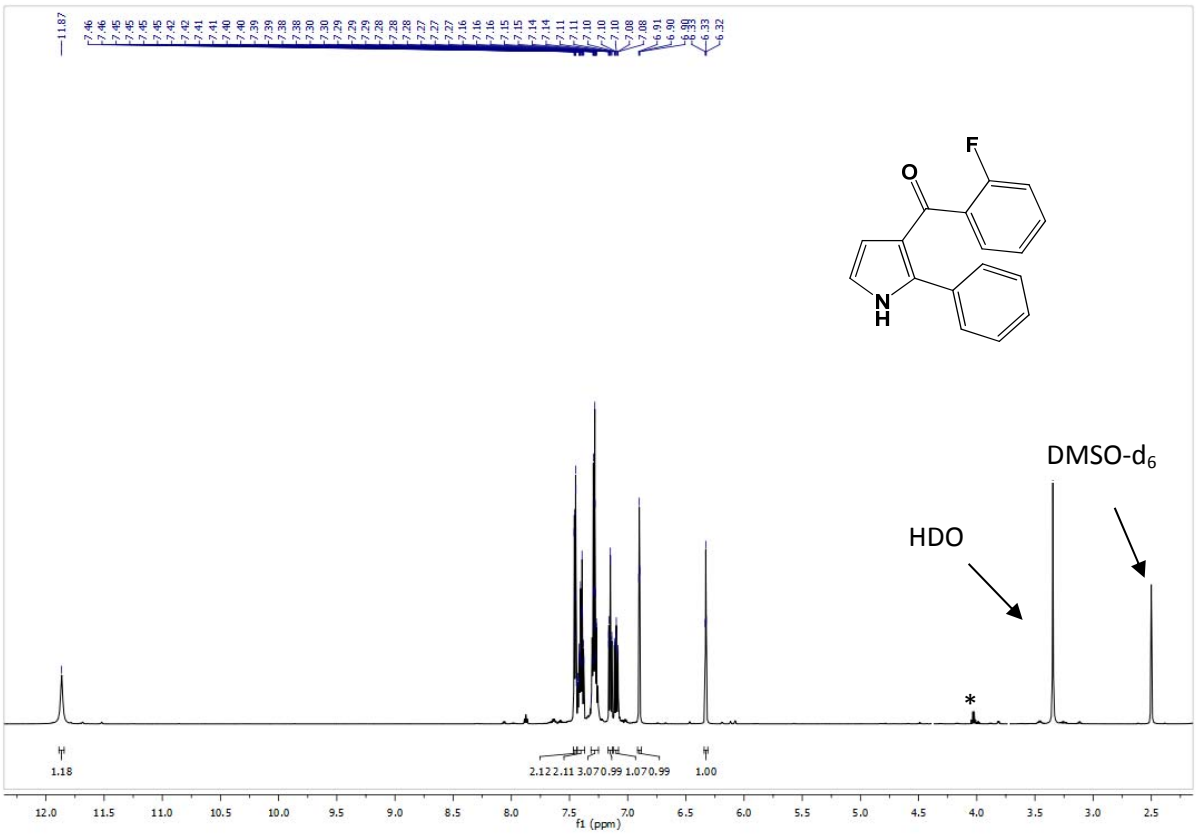


^{13}C NMR of **1a** in $CDCl_3$ at 298 K (δ in ppm).

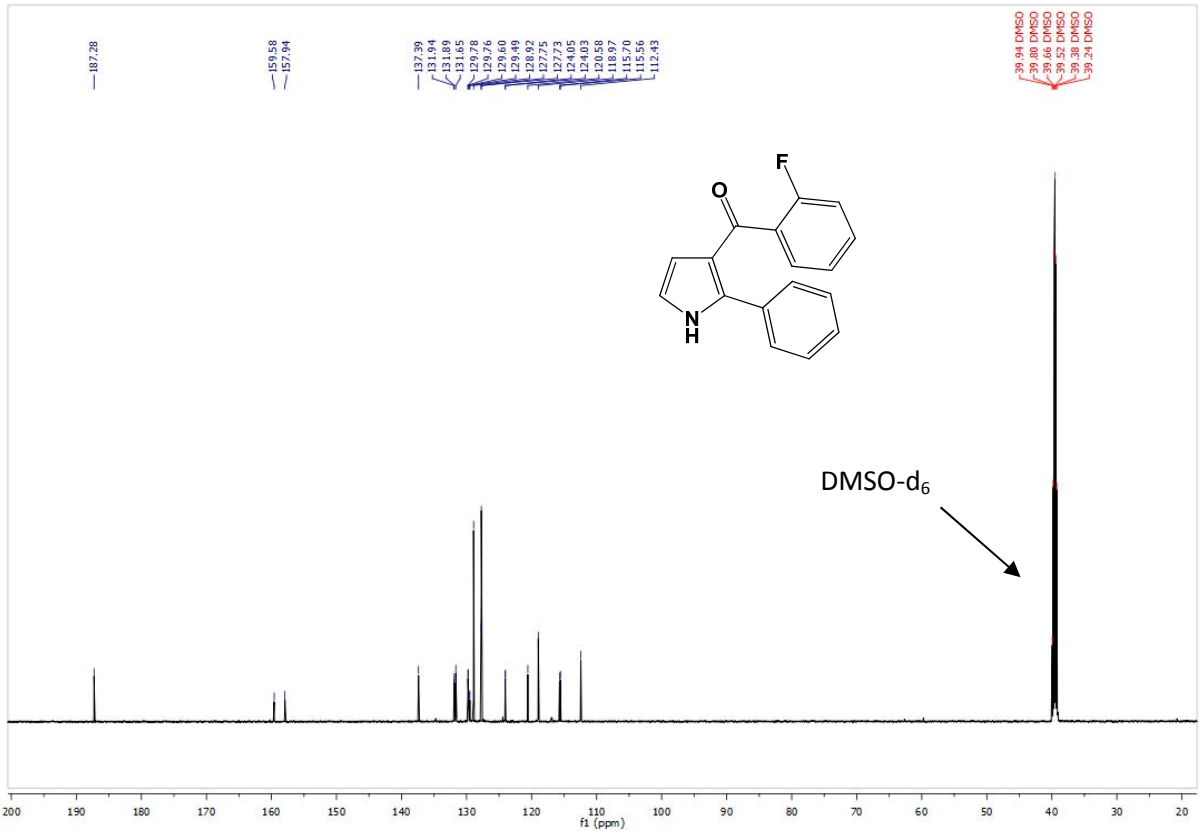


^{13}C DEPT 135-NMR of **1a** in $CDCl_3$ at 298 K (δ in ppm).

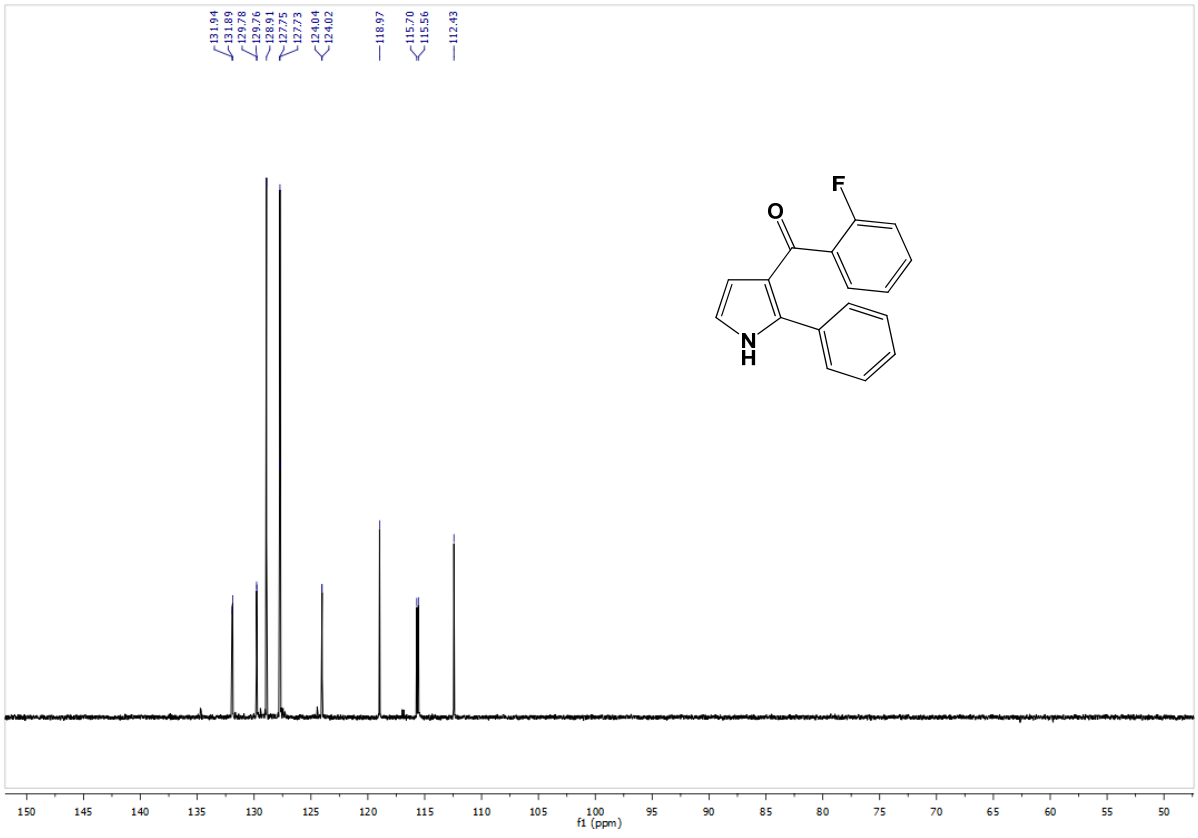
3.2 (2-Fluorophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (1b)



^{1}H NMR of **1b** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

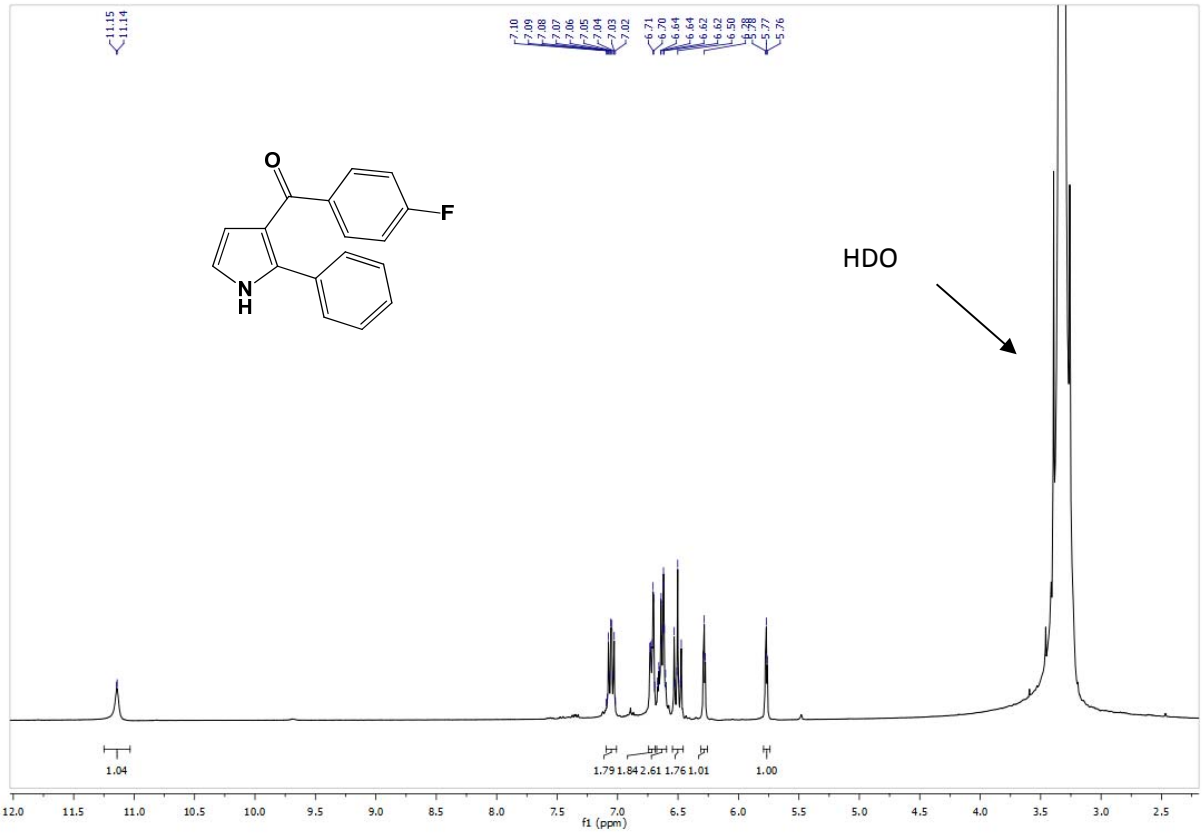


^{13}C NMR of **1b** in DMSO-d_6 at 298 K (δ in ppm).

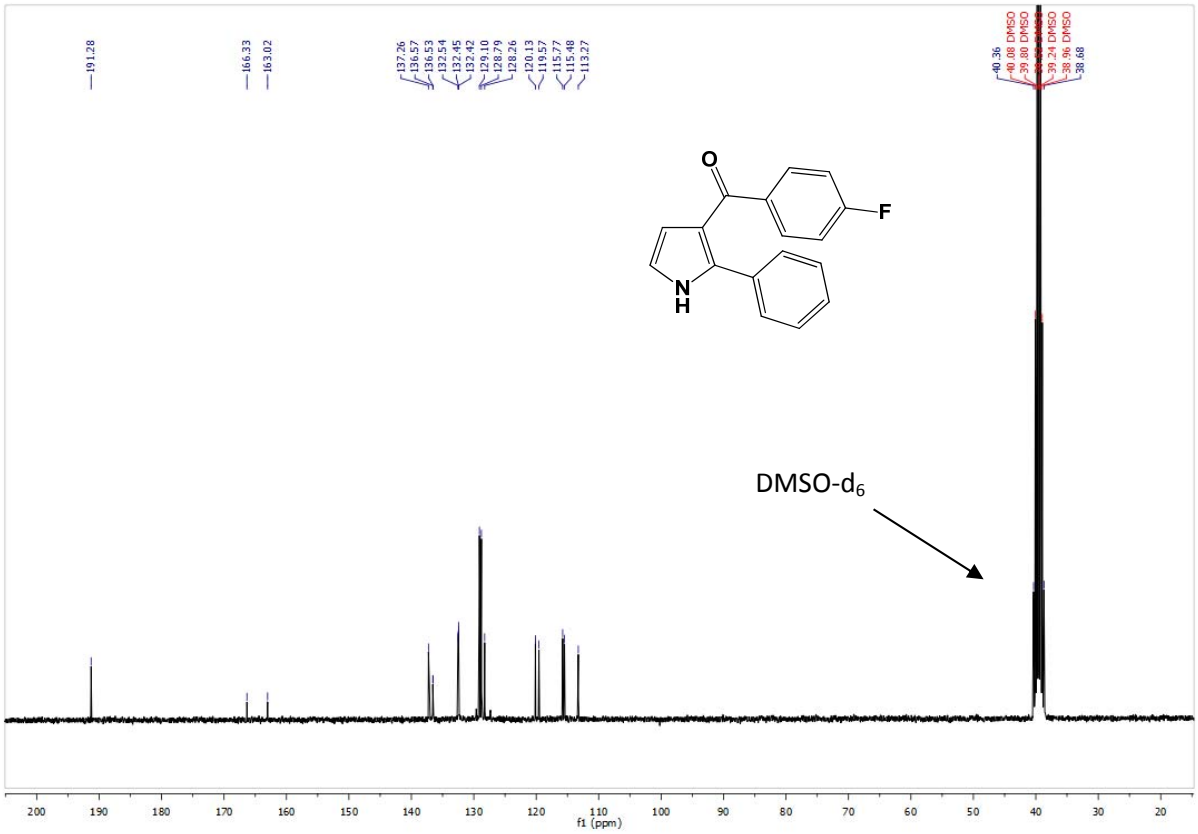


^{13}C DEPT 135-NMR of **1b** in DMSO-d_6 at 298 K (δ in ppm).

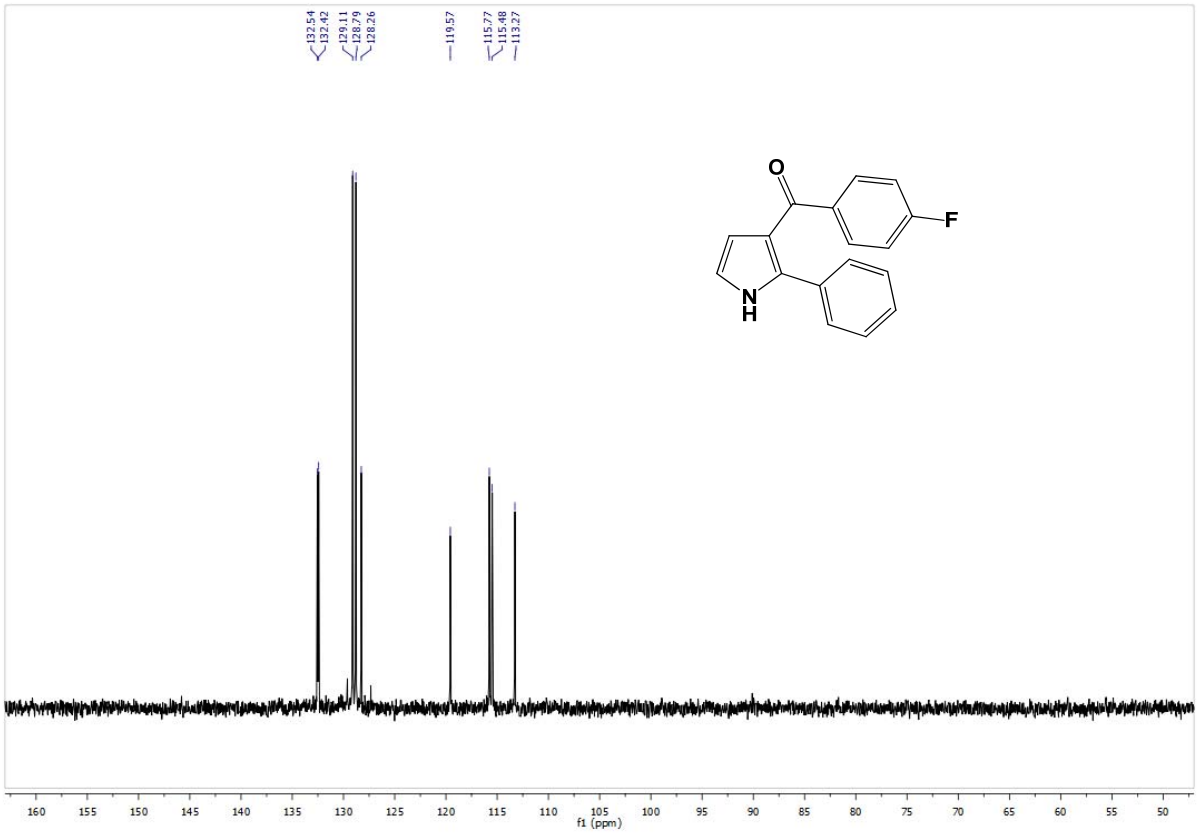
3.3 (4-Fluorophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (1c)



^{1}H NMR of **1c** in DMSO-d_6 at 298 K.

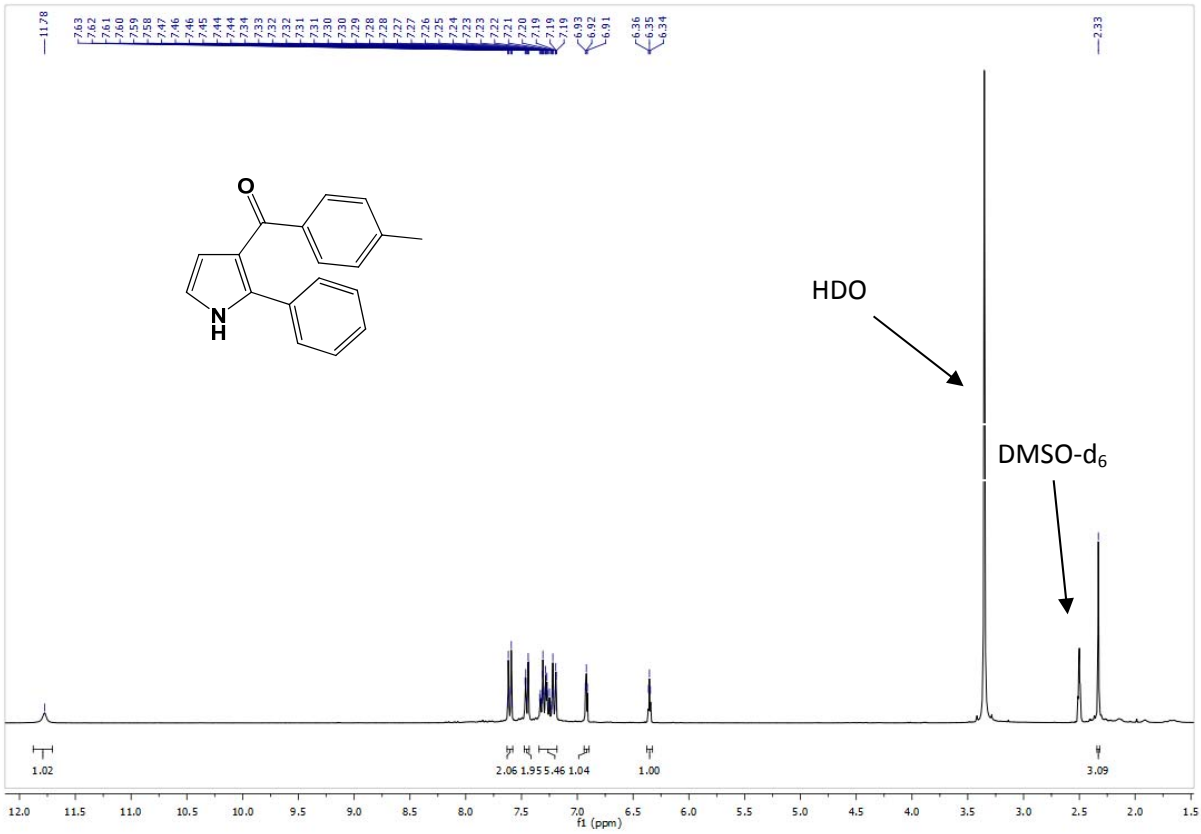


^{13}C NMR of **1c** in DMSO-d_6 at 298 K (δ in ppm).

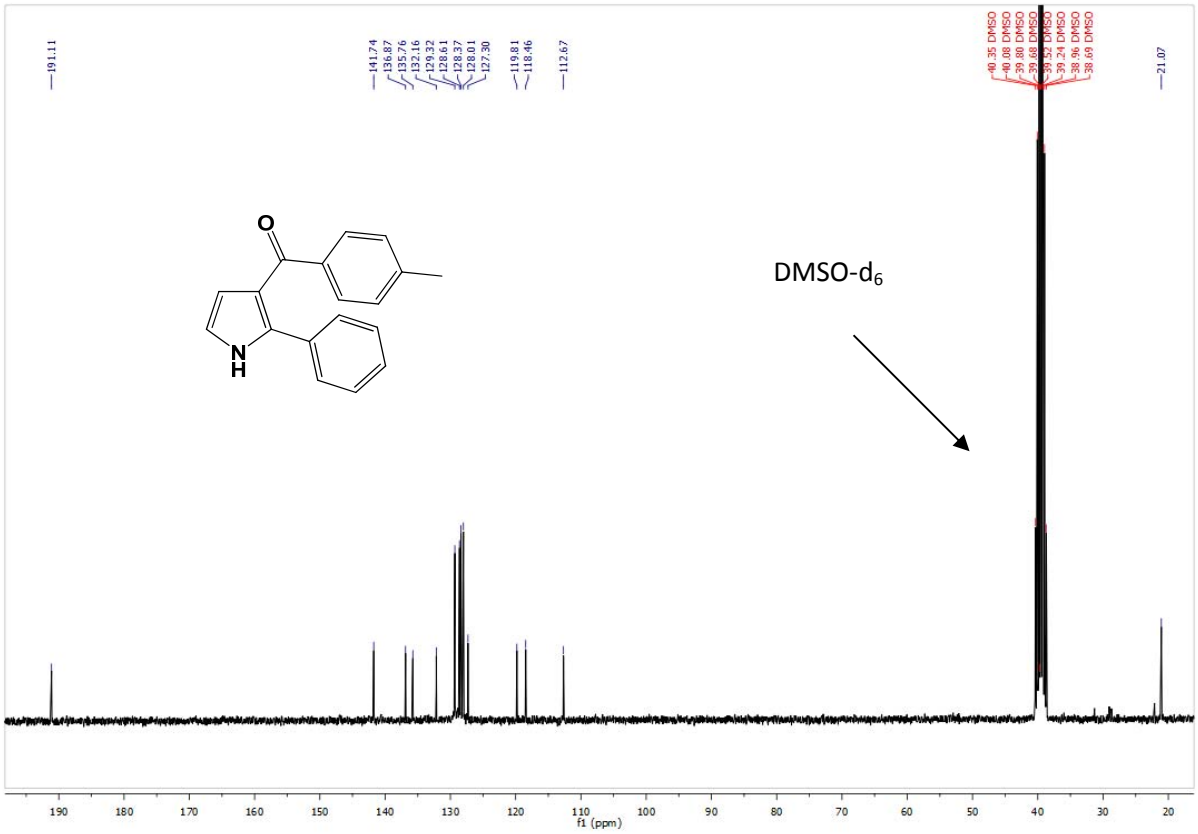


^{13}C DEPT 135-NMR of **1c** in DMSO-d_6 at 298 K (δ in ppm).

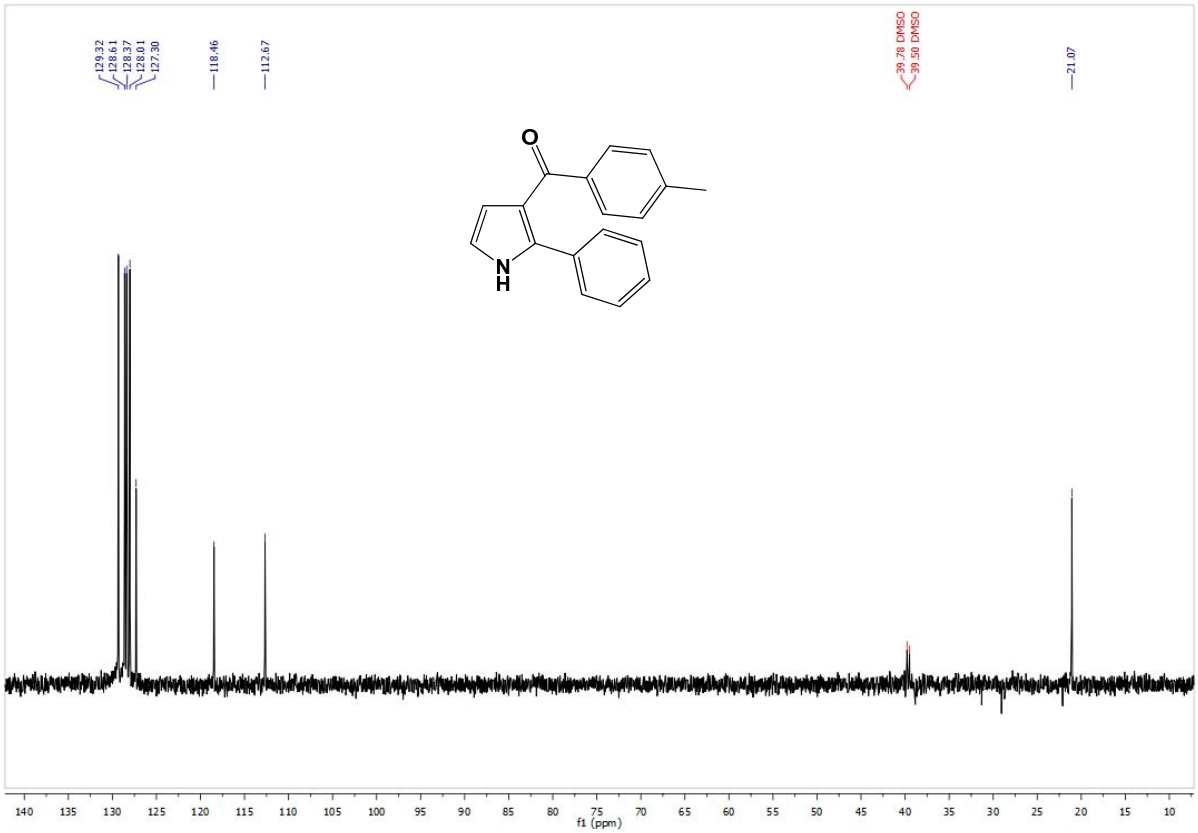
3.4 (2-phenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (1d)



^{1}H NMR of **1d** in DMSO-d$_6$ at 298 K.

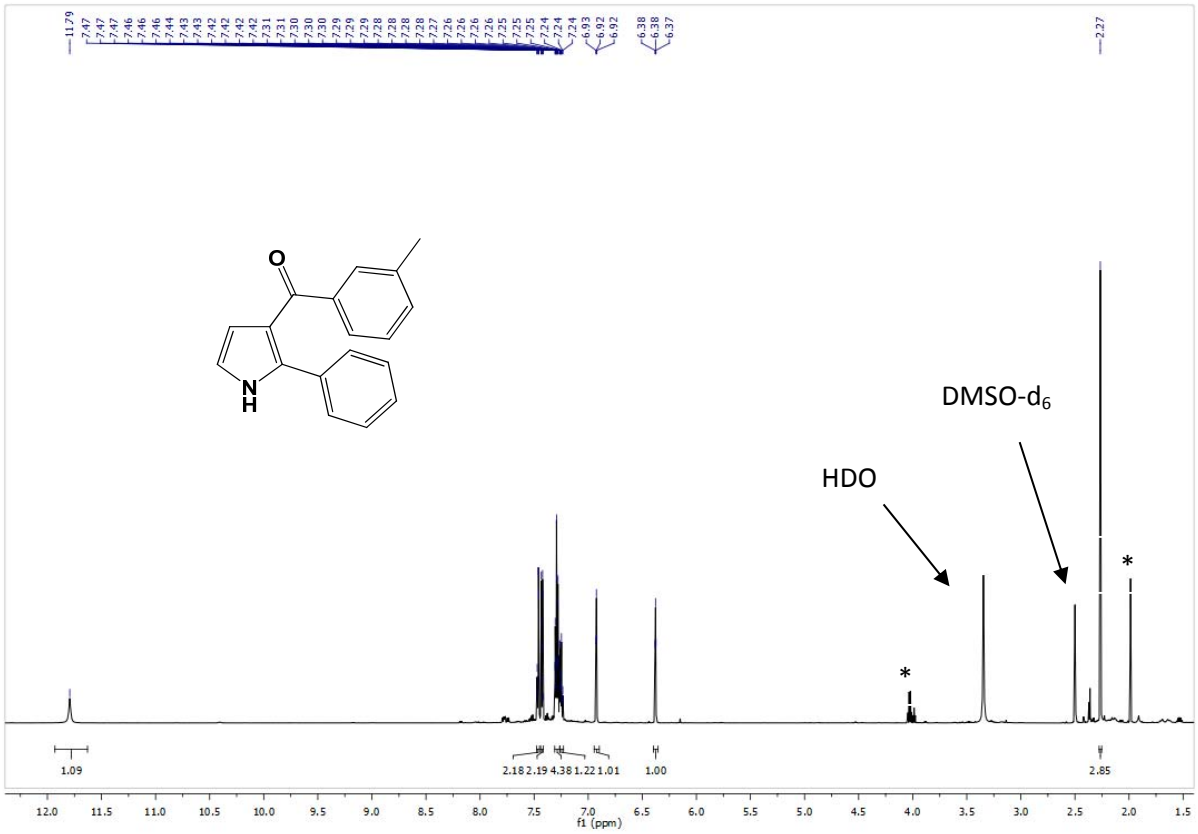


^{13}C NMR of **1d** in DMSO-d_6 at 298 K (δ in ppm).

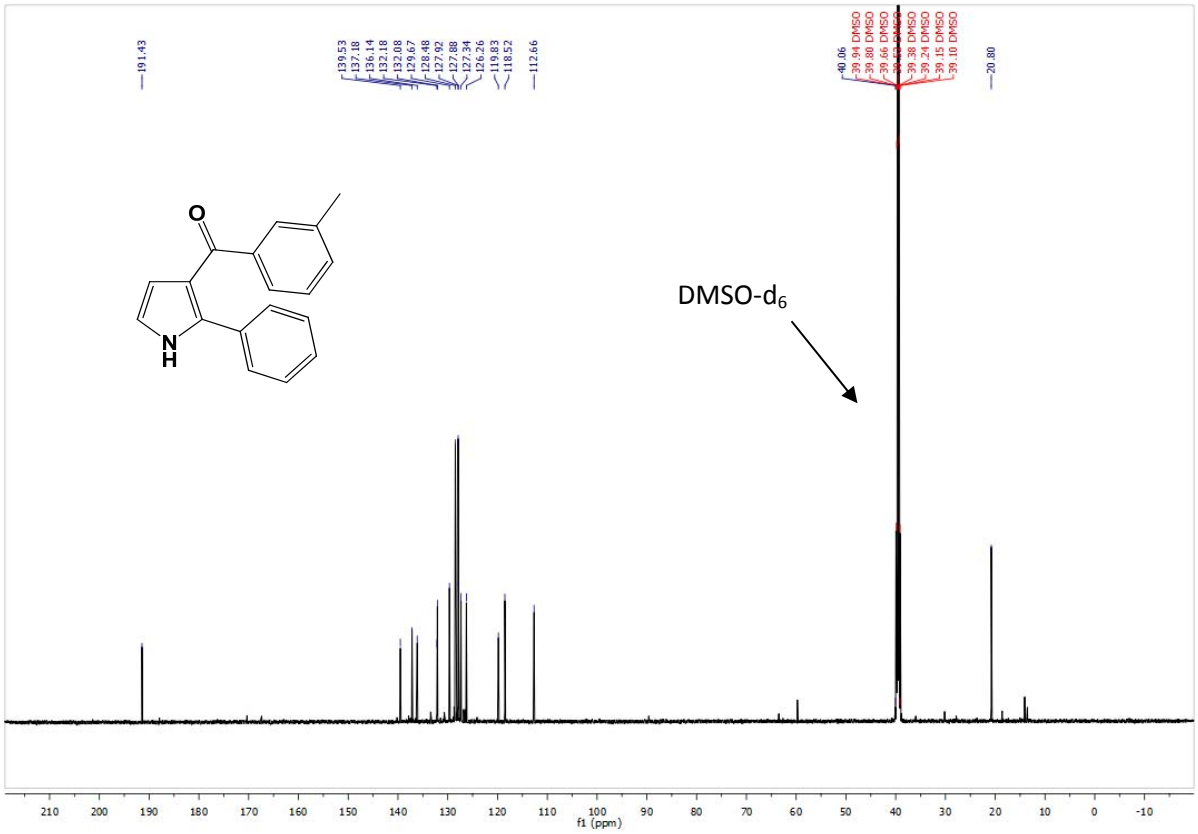


^{13}C DEPT 135-NMR of **1d** in DMSO-d_6 at 298 K (δ in ppm).

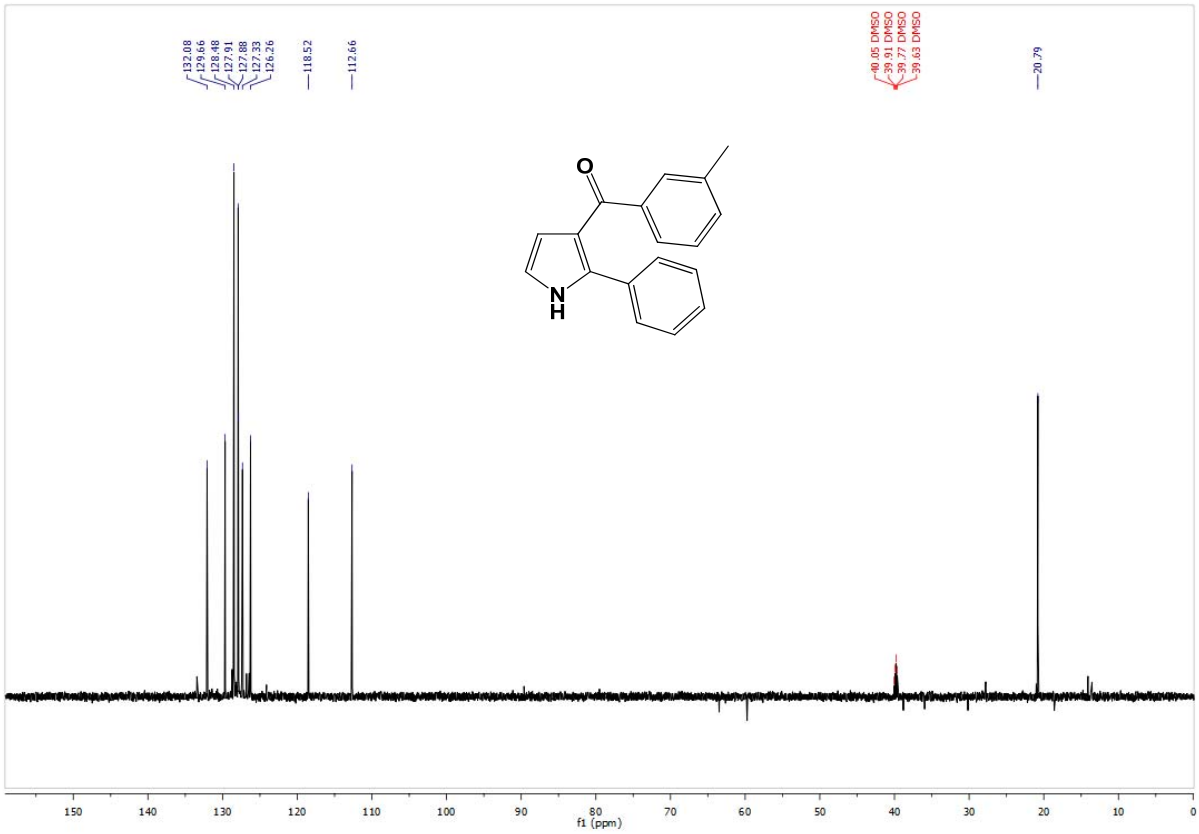
3.5 (2-phenyl-1H-pyrrol-3-yl)(m-tolyl)methanone (1e)



^{1}H NMR of **1e** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

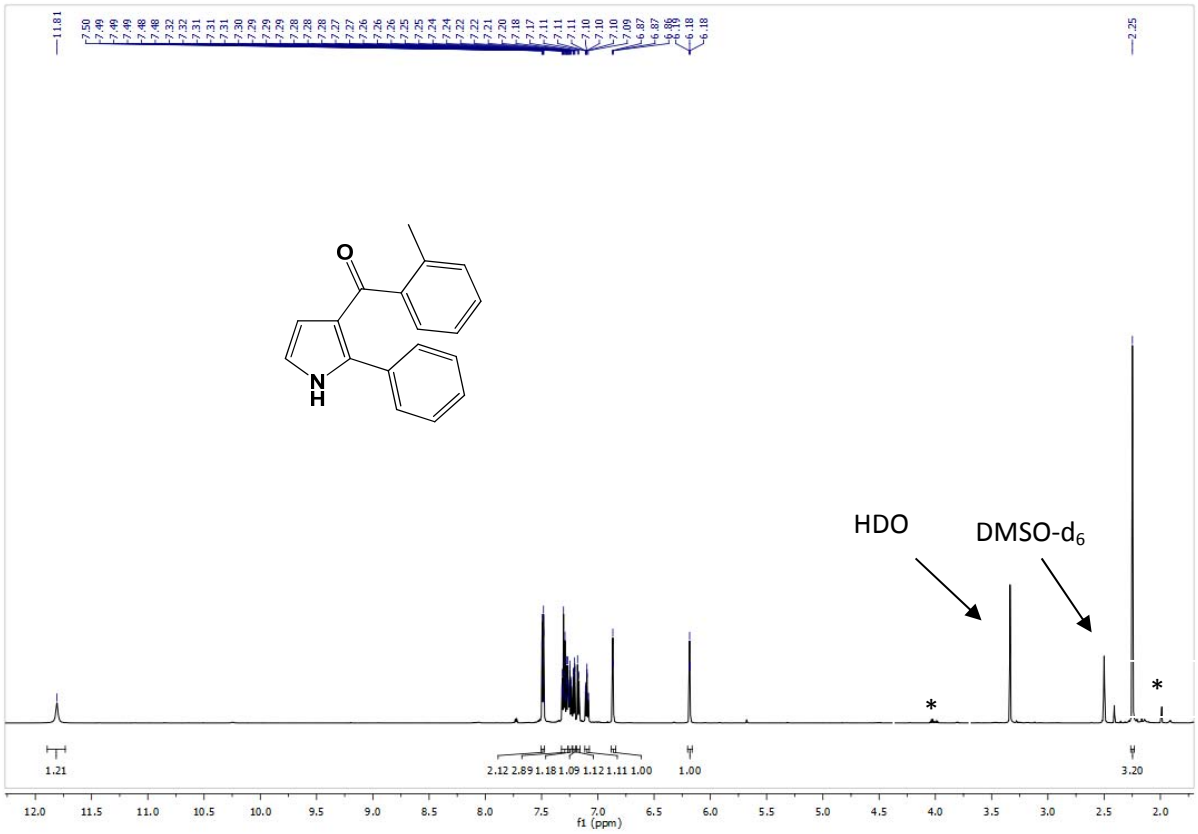


^{13}C NMR of **1e** in DMSO-d_6 at 298 K (δ in ppm).

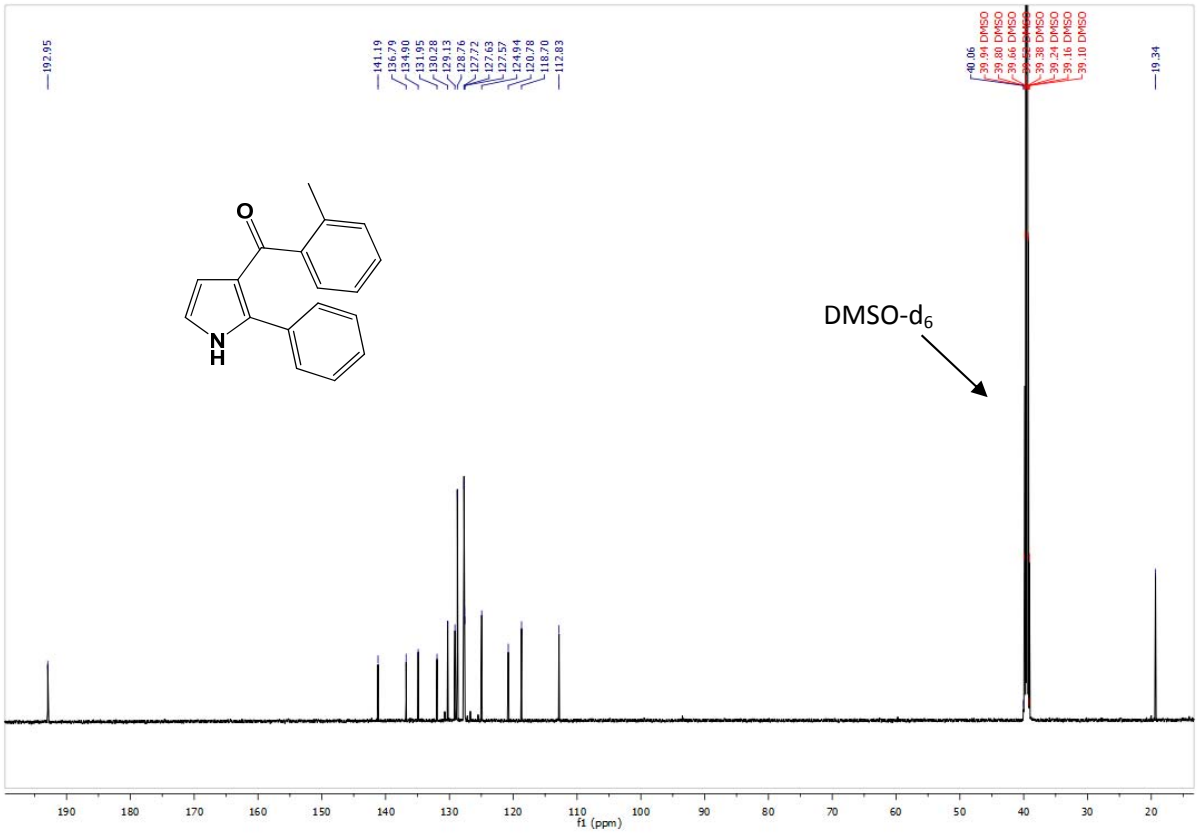


^{13}C DEPT 135-NMR of **1e** in DMSO-d_6 at 298 K (δ in ppm).

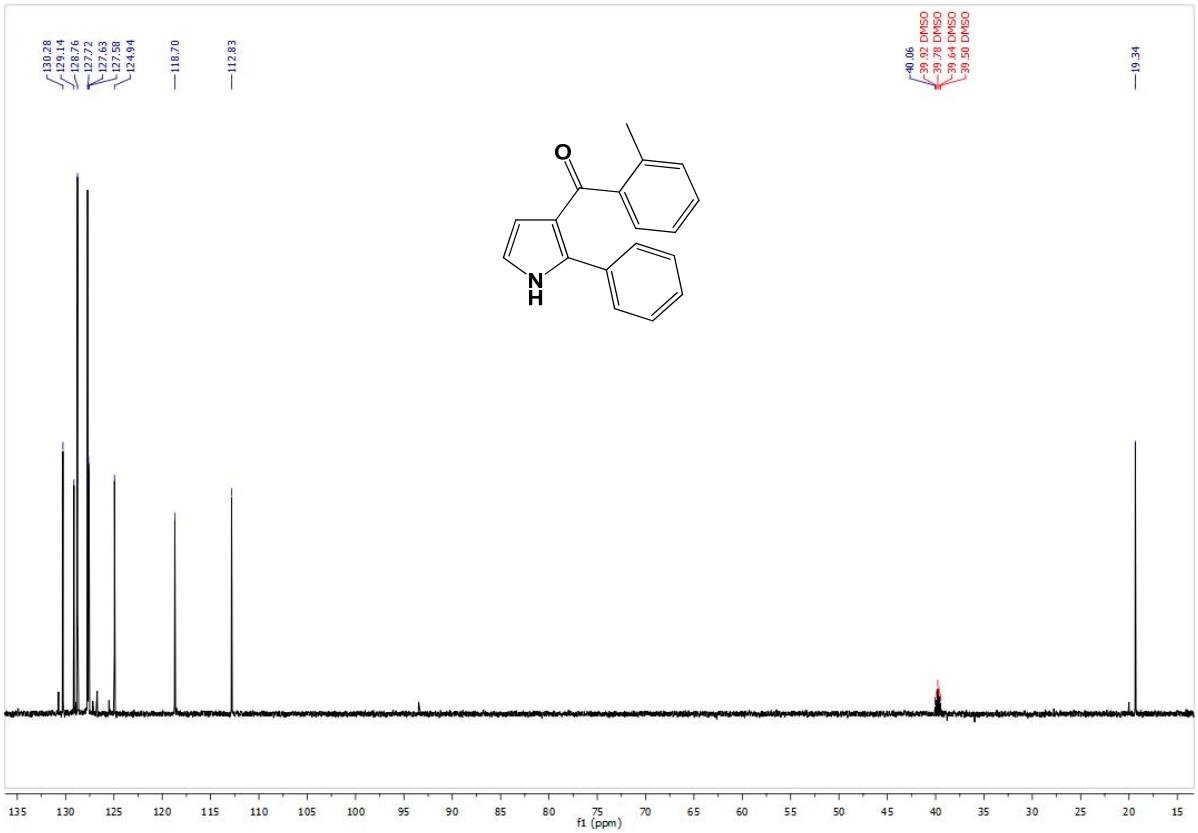
3.6 (2-phenyl-1H-pyrrol-3-yl)(o-tolyl)methanone (1f)



^{1}H NMR of **1f** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

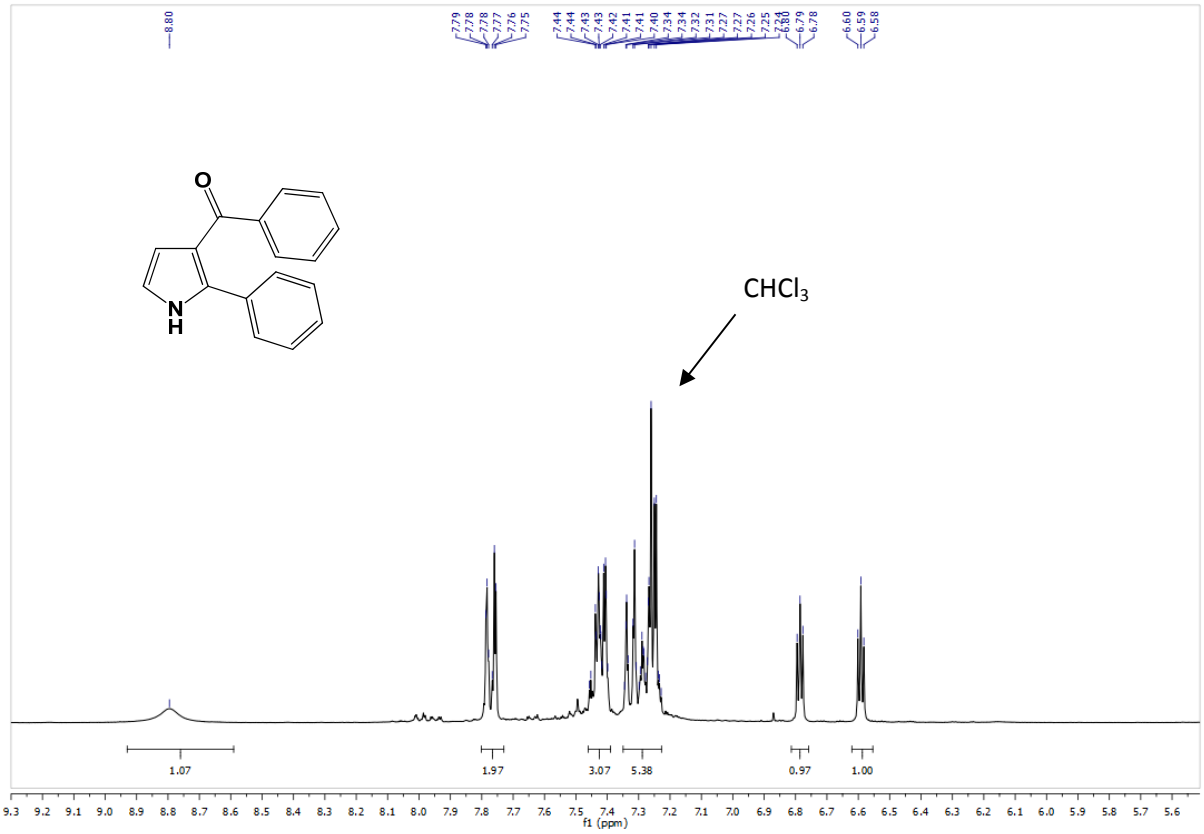


^{13}C NMR of **1f** in DMSO-d_6 at 298 K (δ in ppm).

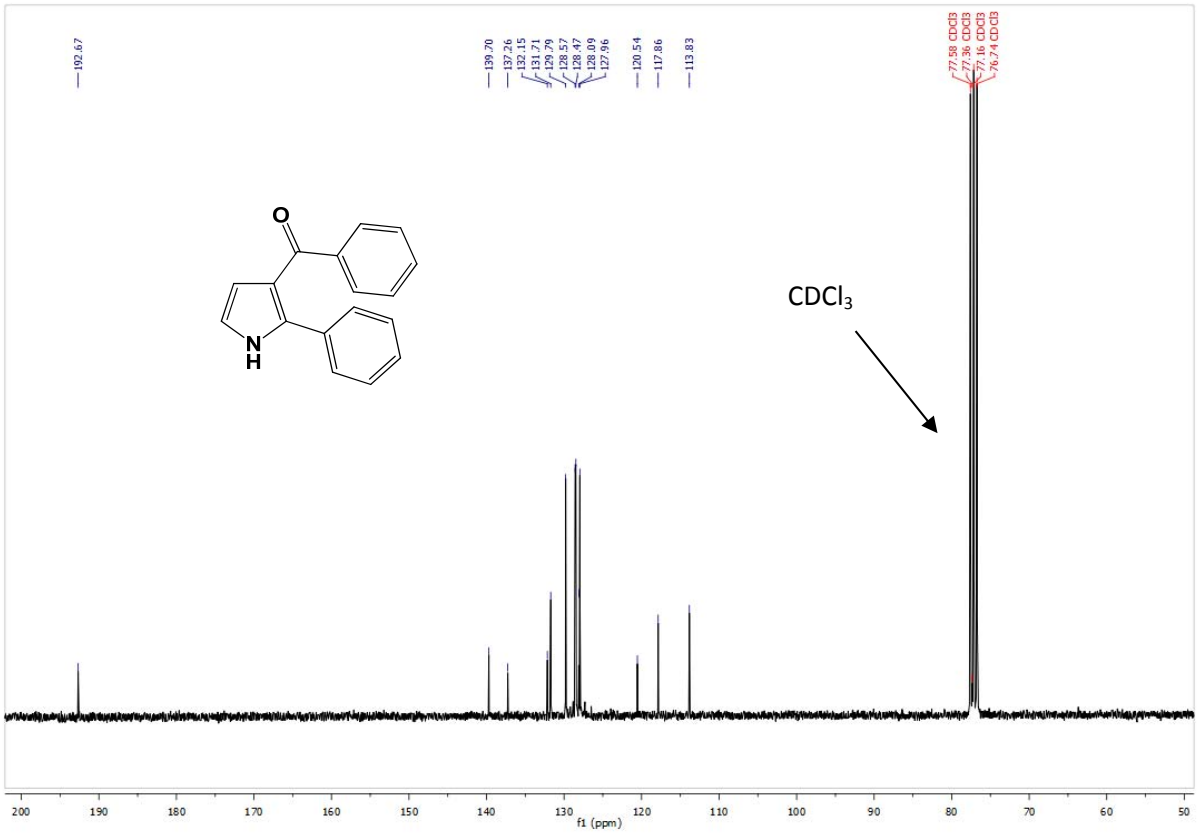


^{13}C DEPT 135-NMR of **1f** in DMSO-d_6 at 298 K (δ in ppm).

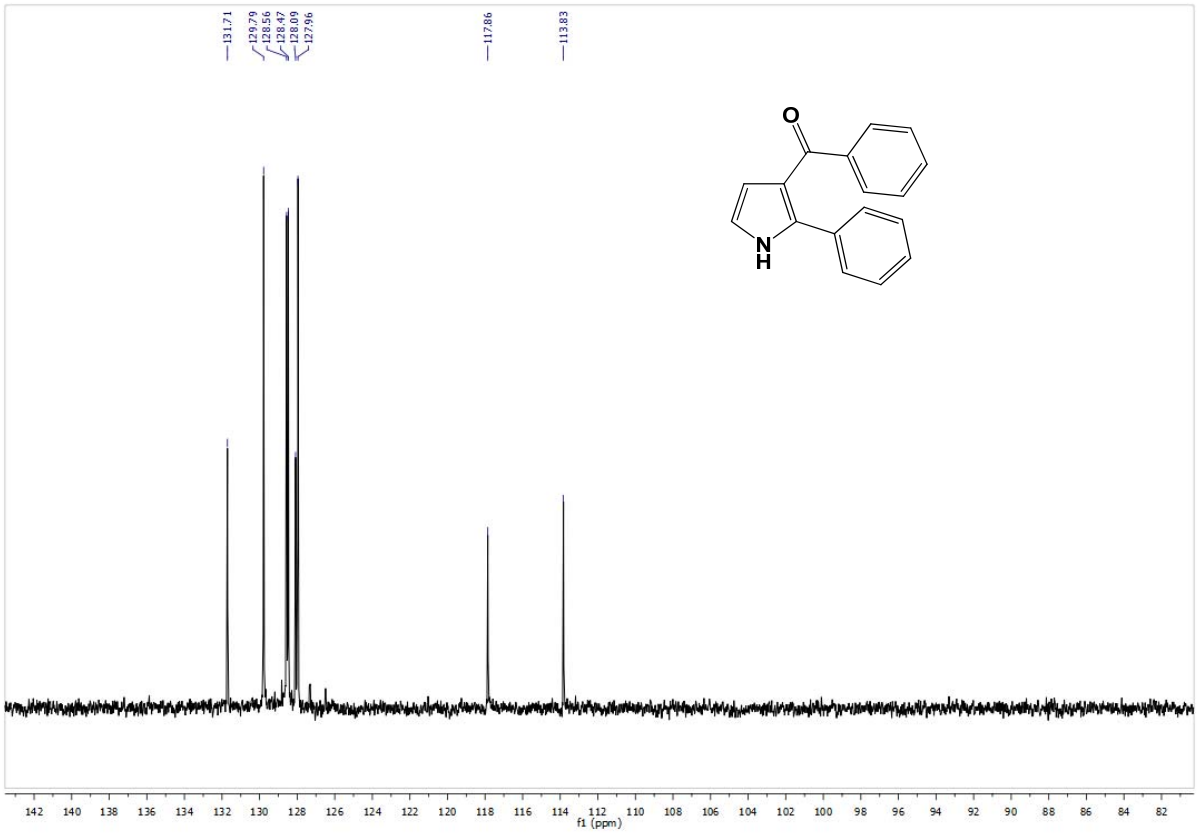
3.7 Phenyl(2-phenyl-1H-pyrrol-3-yl)methanone (1g)



^{1}H NMR of **1g** in $CDCl_3$ at 298 K.

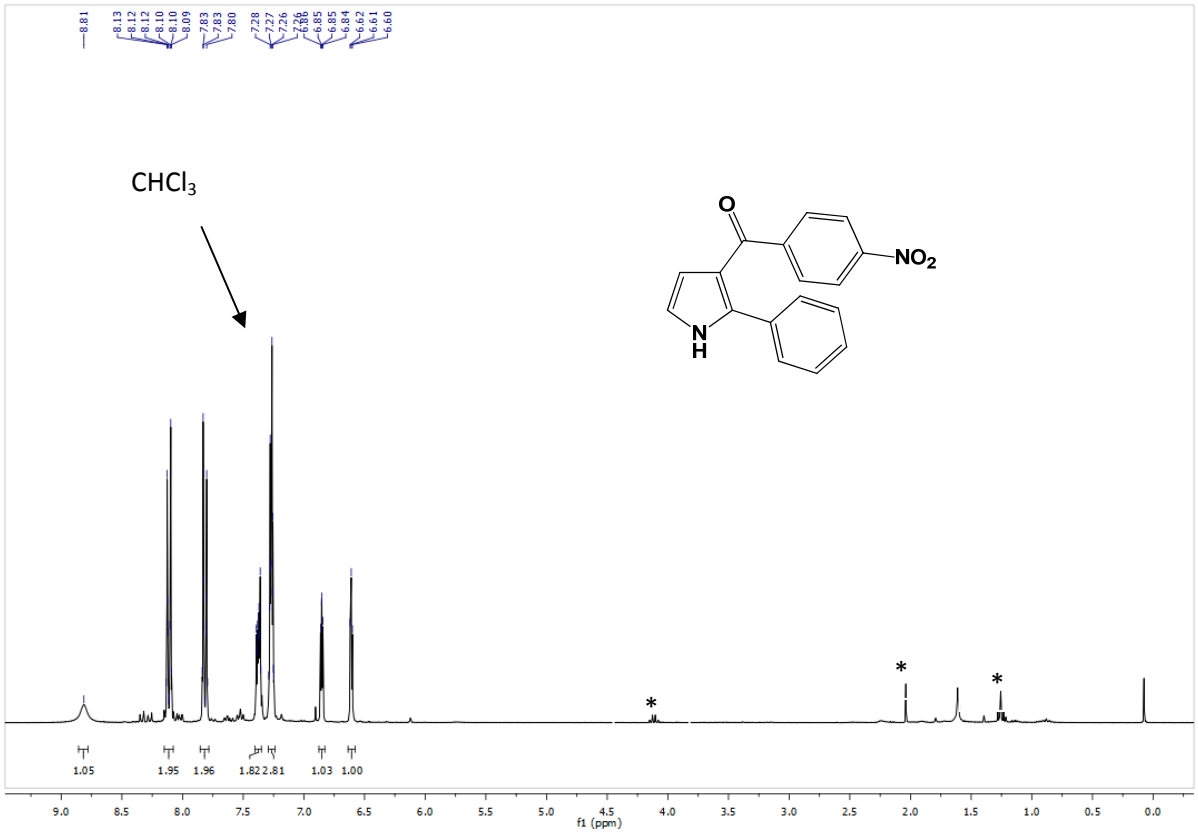


^{13}C NMR of **1g** in $CDCl_3$ at 298 K (δ in ppm).

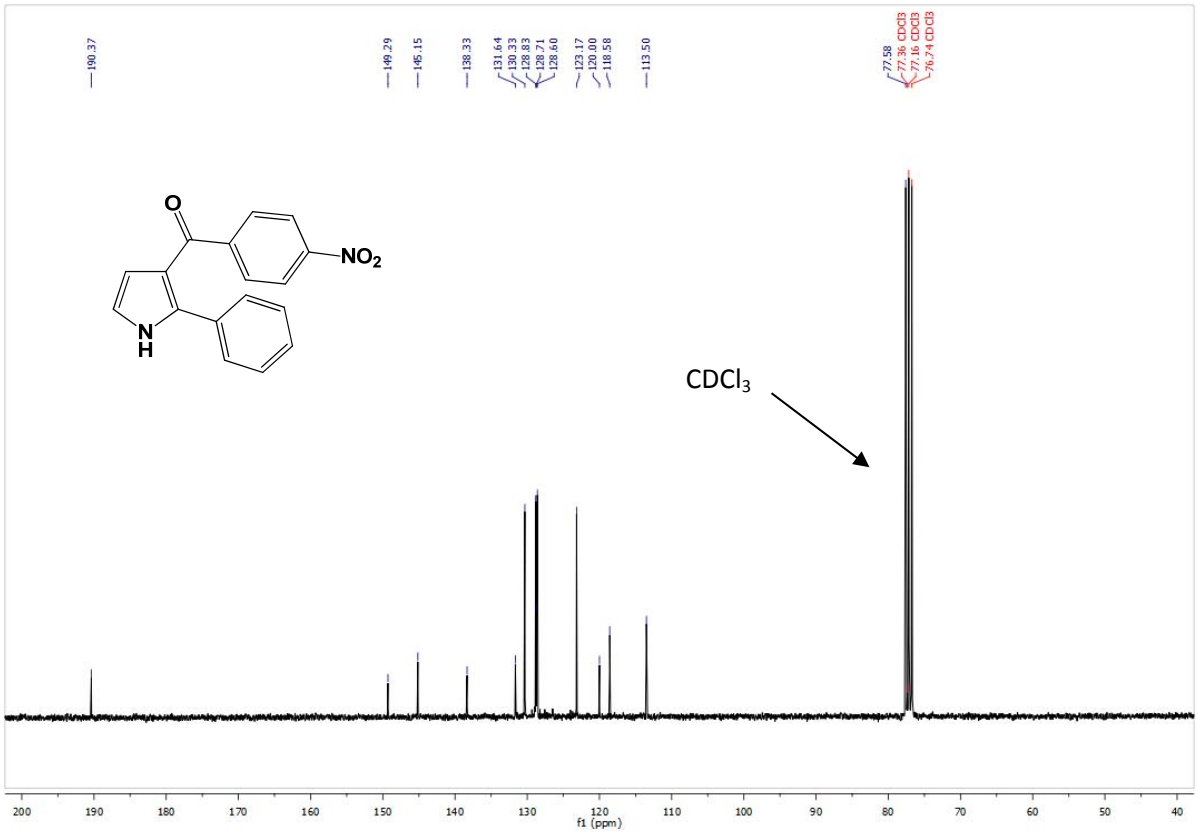


^{13}C DEPT 135-NMR of **1g** in $CDCl_3$ at 298 K (δ in ppm).

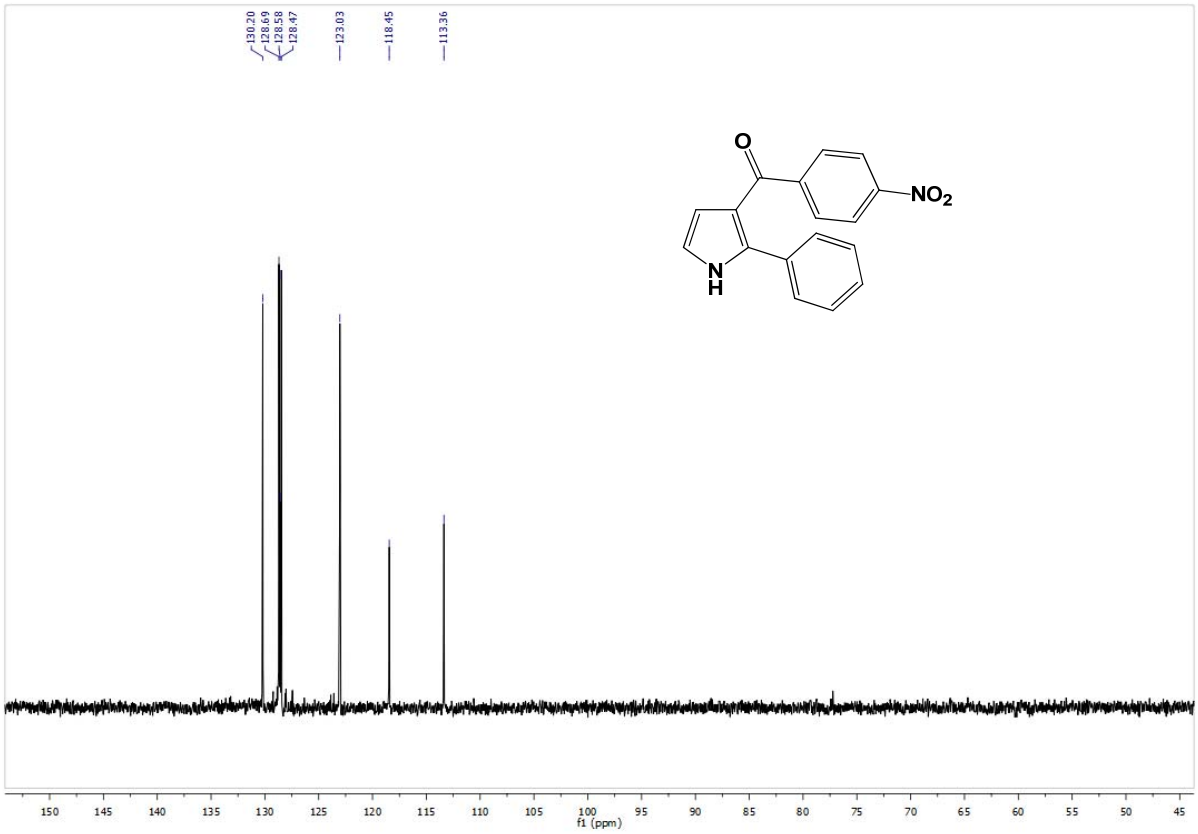
3.8 (4-nitrophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (1h)



^{1}H NMR of **1h** in $CDCl_3$ at 298 K. * Impurities from residual solvents.

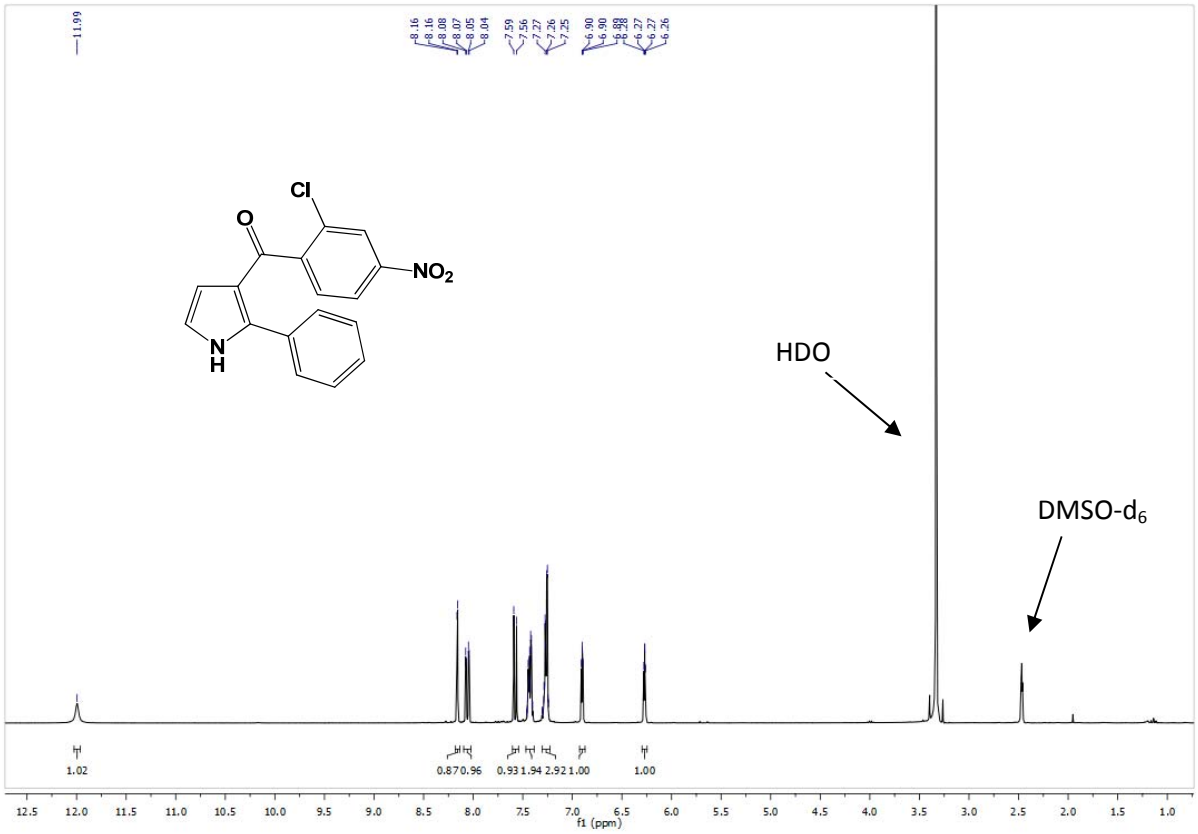


^{13}C NMR of **1h** in $CDCl_3$ at 298 K (δ in ppm).

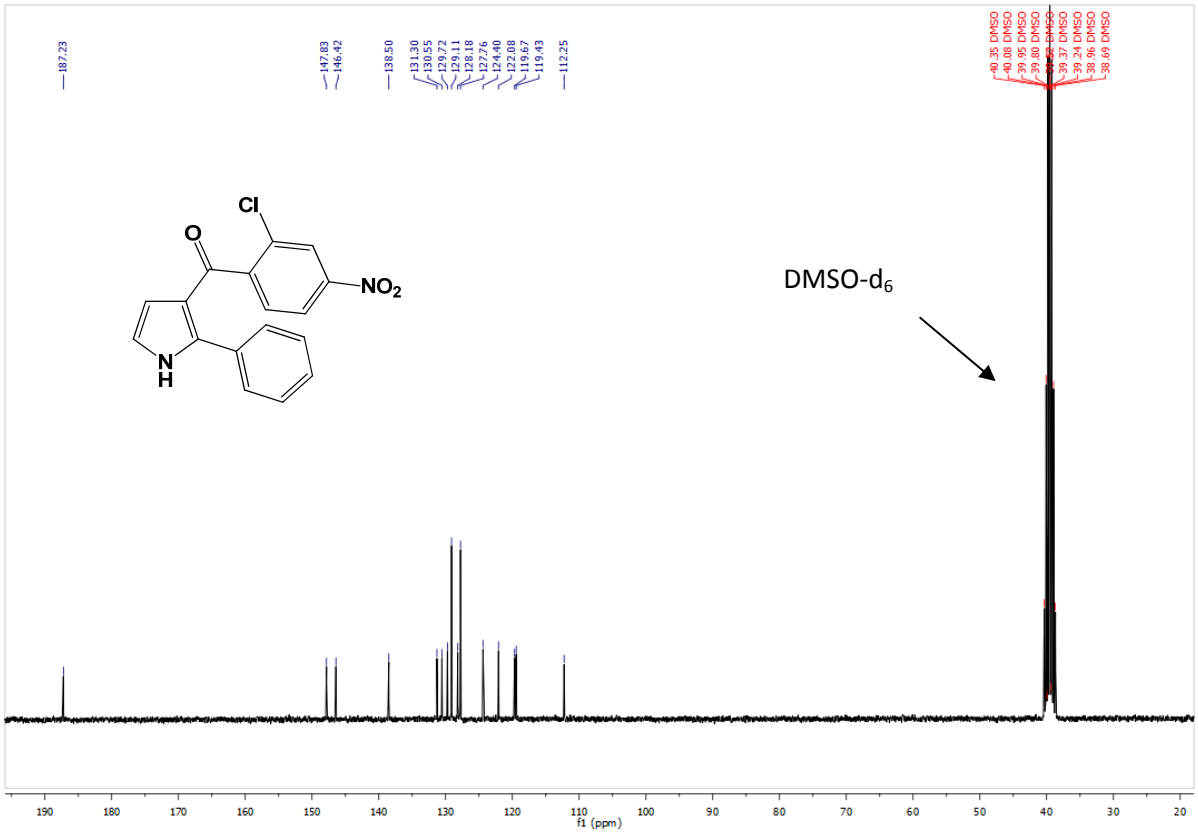


^{13}C DEPT 135-NMR of **1h** in $CDCl_3$ at 298 K (δ in ppm).

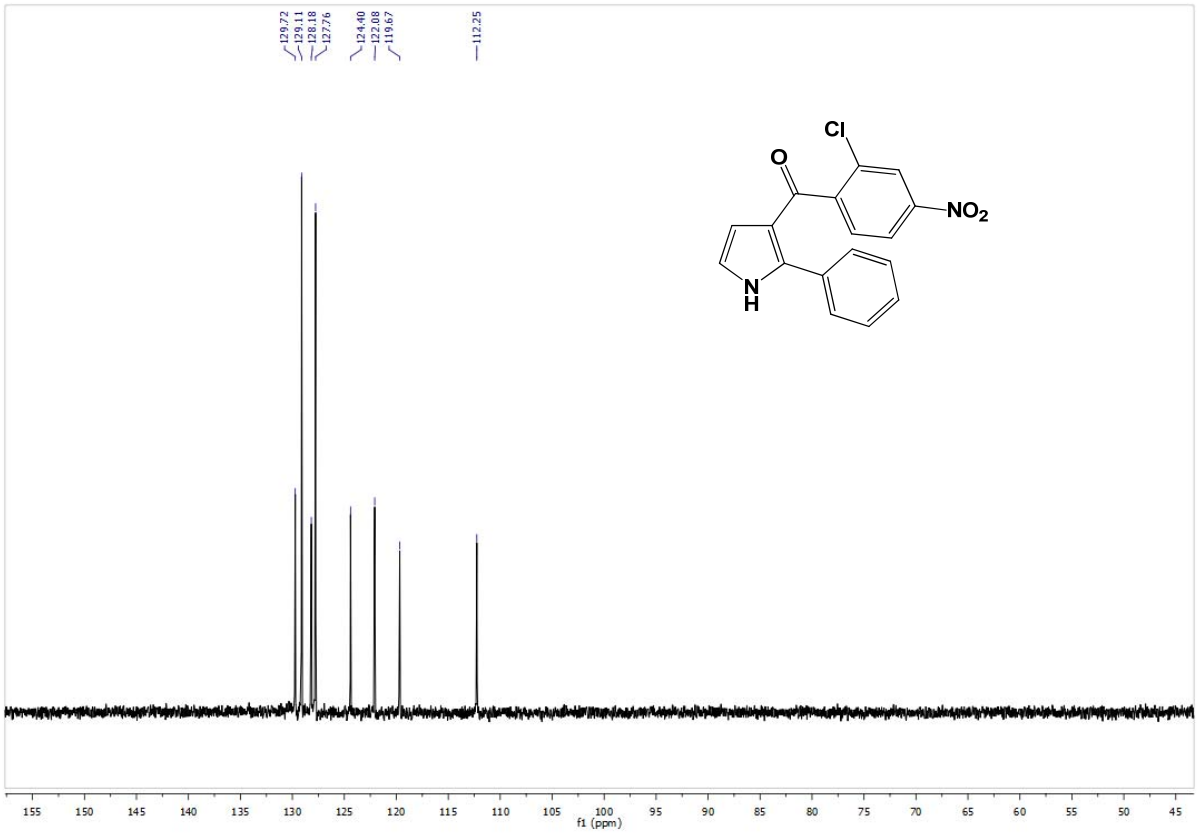
3.9 (2-chloro-4-nitrophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (1i)



^{1}H NMR of **1i** in DMSO-d_6 at 298 K.

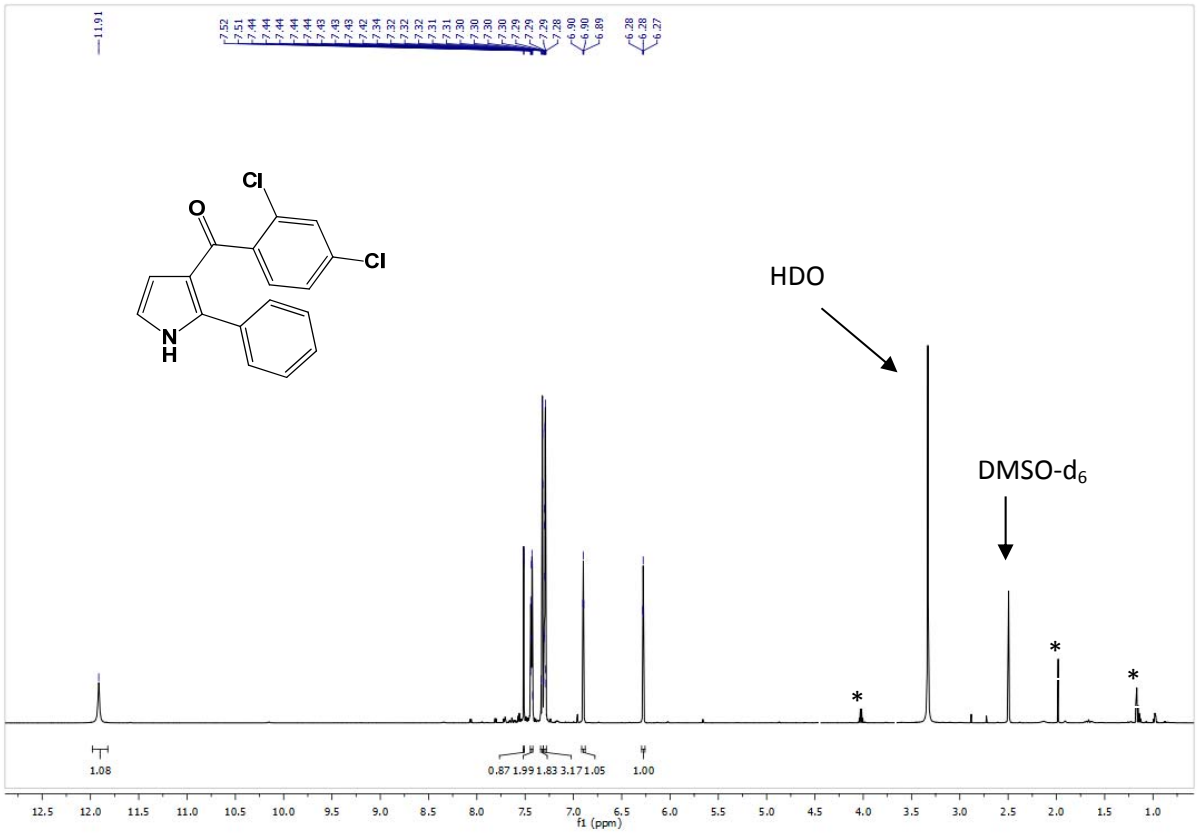


^{13}C NMR of **1i** in DMSO-d$_6$ at 298 K (δ in ppm).

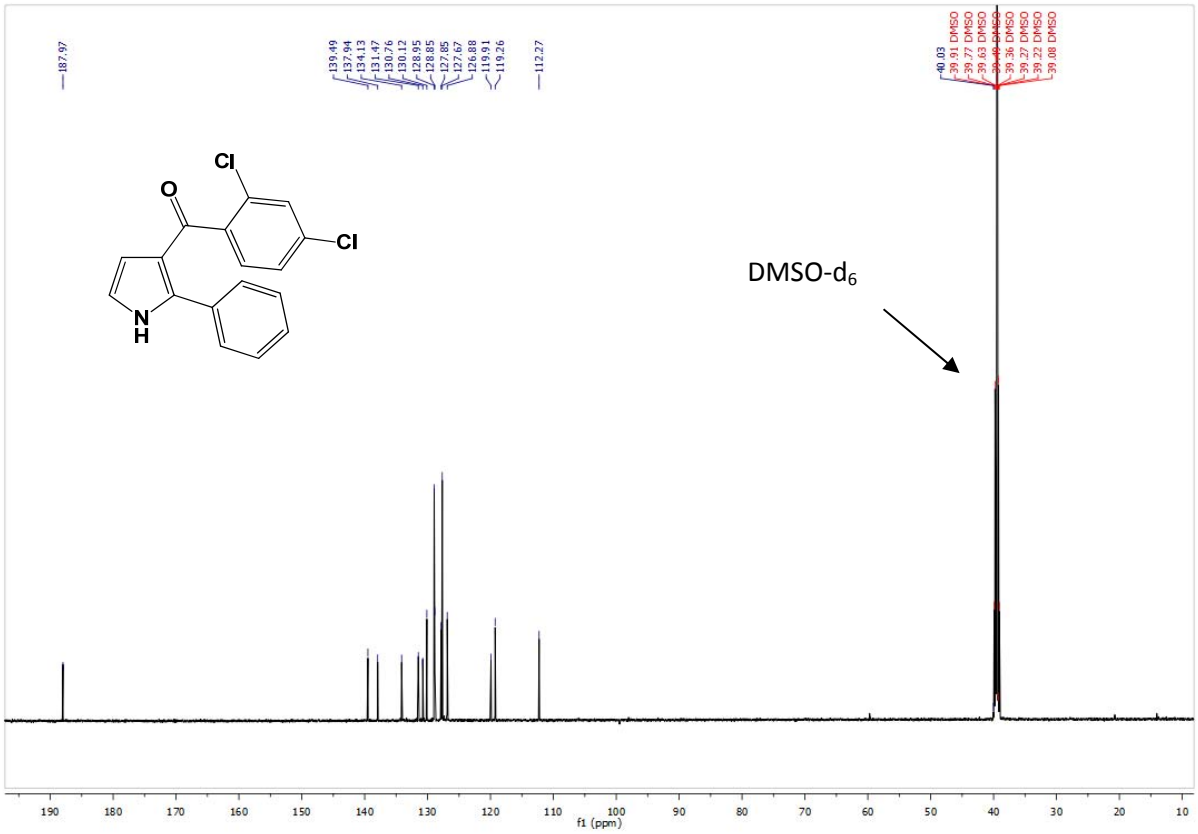


^{13}C DEPT 135-NMR of **1i** in DMSO-d$_6$ at 298 K (δ in ppm).

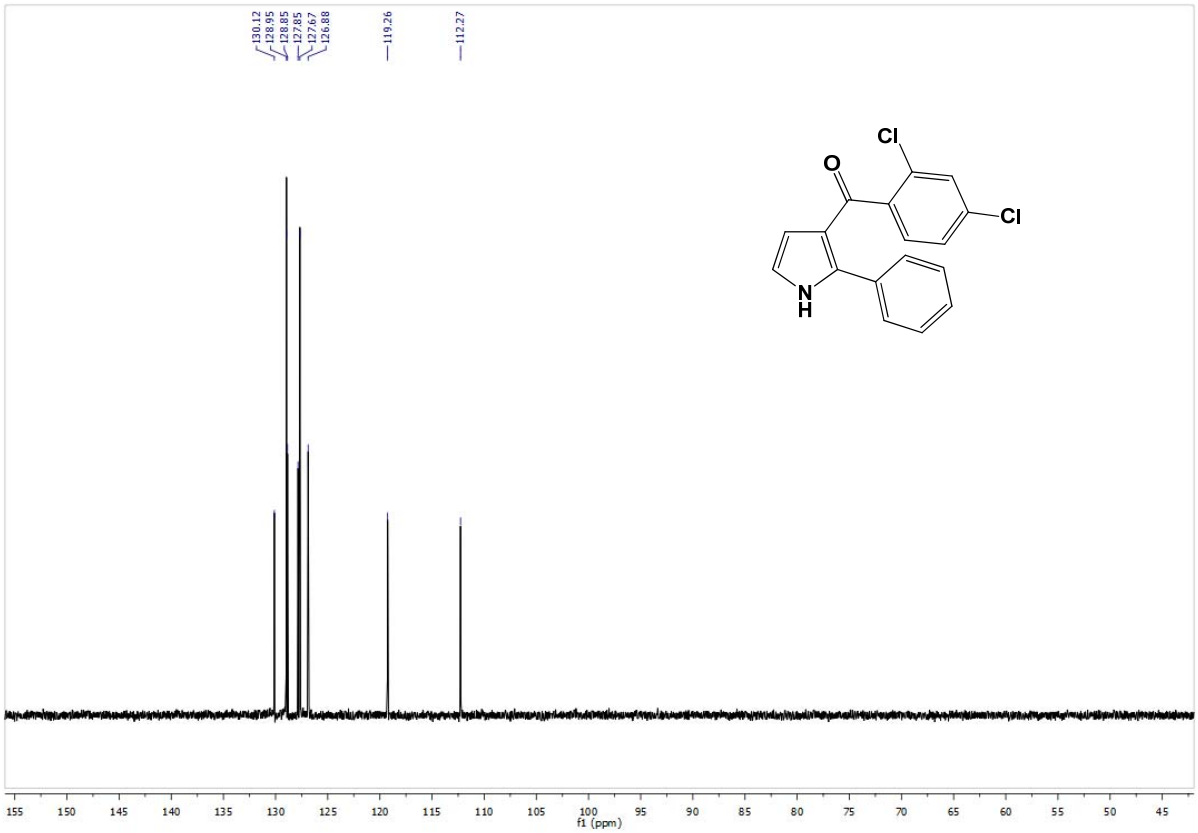
3.10 (2,4-dichlorophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (1j)



^{1}H NMR of **1j** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

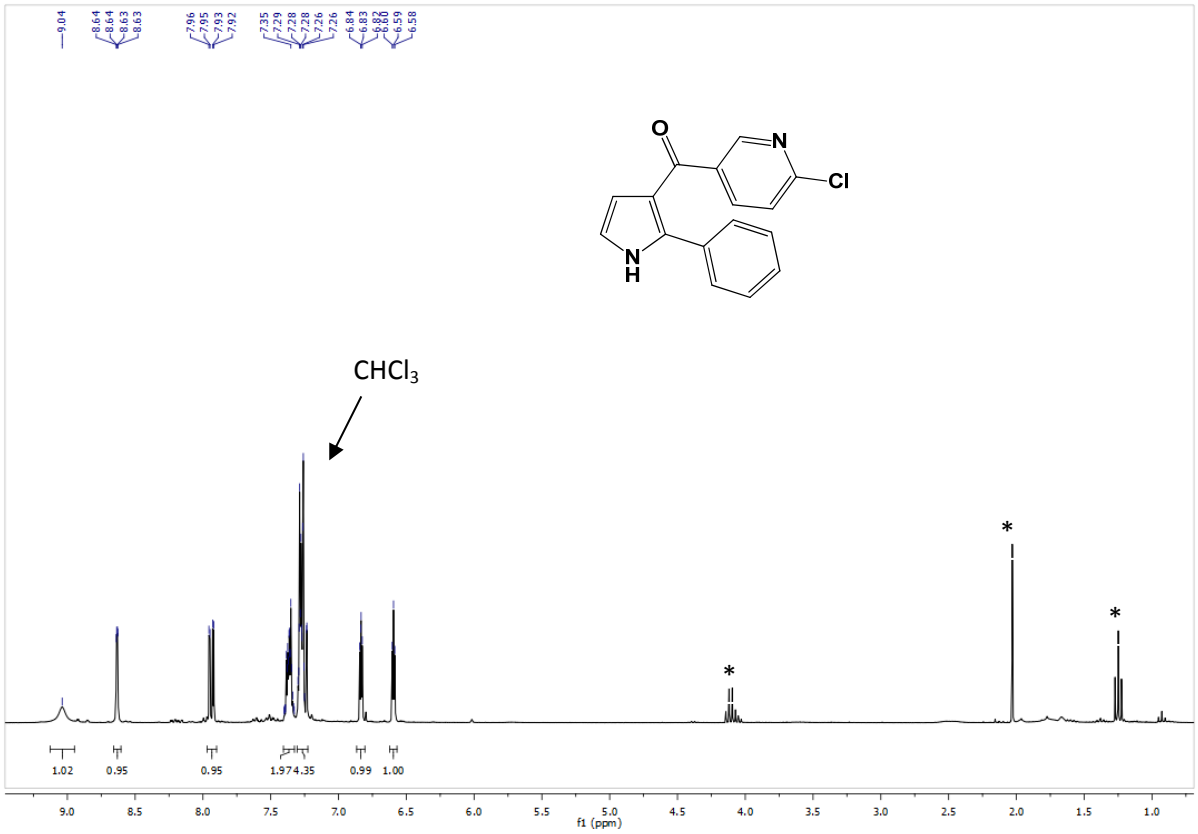


^{13}C NMR of **1j** in DMSO-d_6 at 298 K (δ in ppm).

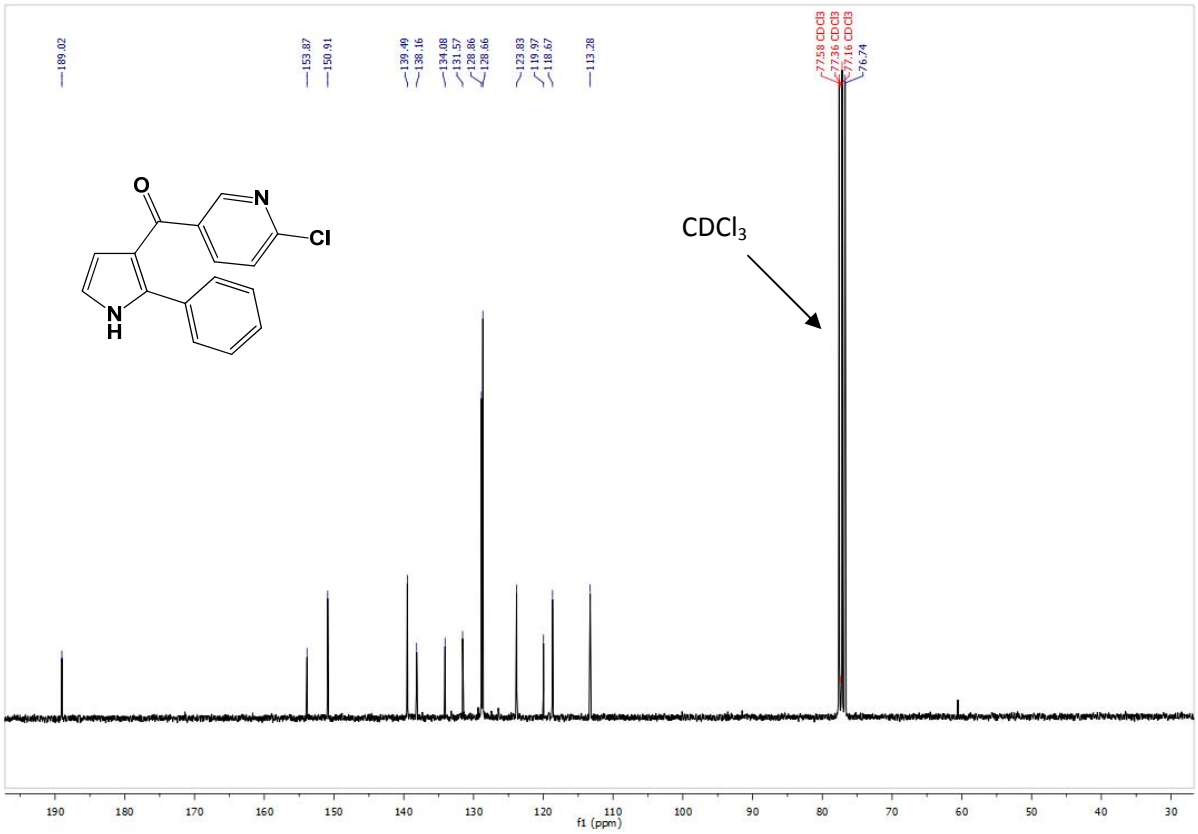


^{13}C DEPT 135-NMR of **1j** in DMSO-d_6 at 298 K (δ in ppm).

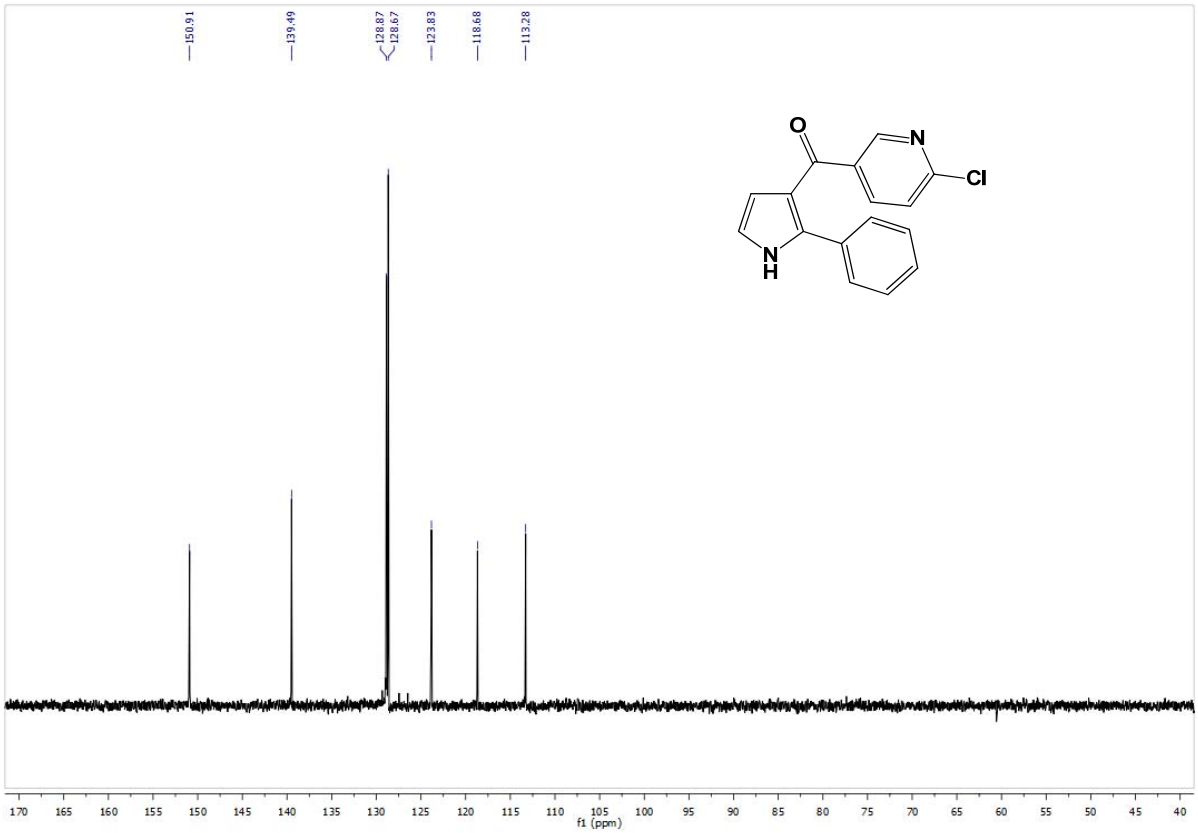
3.11 (6-chloropyridin-3-yl)(2-phenyl-1H-pyrrol-3-yl)methanone (1k)



^{1}H NMR of **1k** in $CDCl_3$ at 298 K. * Impurities from residual solvents.

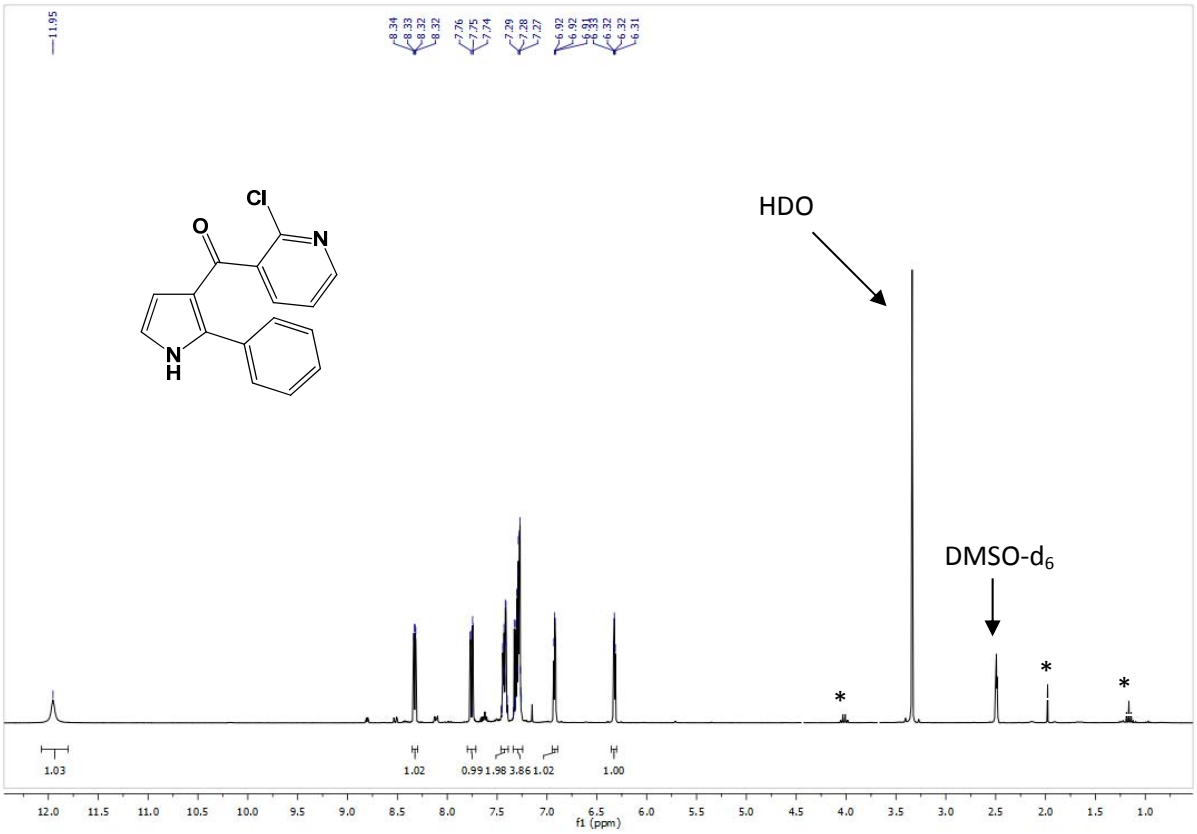


^{13}C NMR of **1k** in $CDCl_3$ at 298 K (δ in ppm).

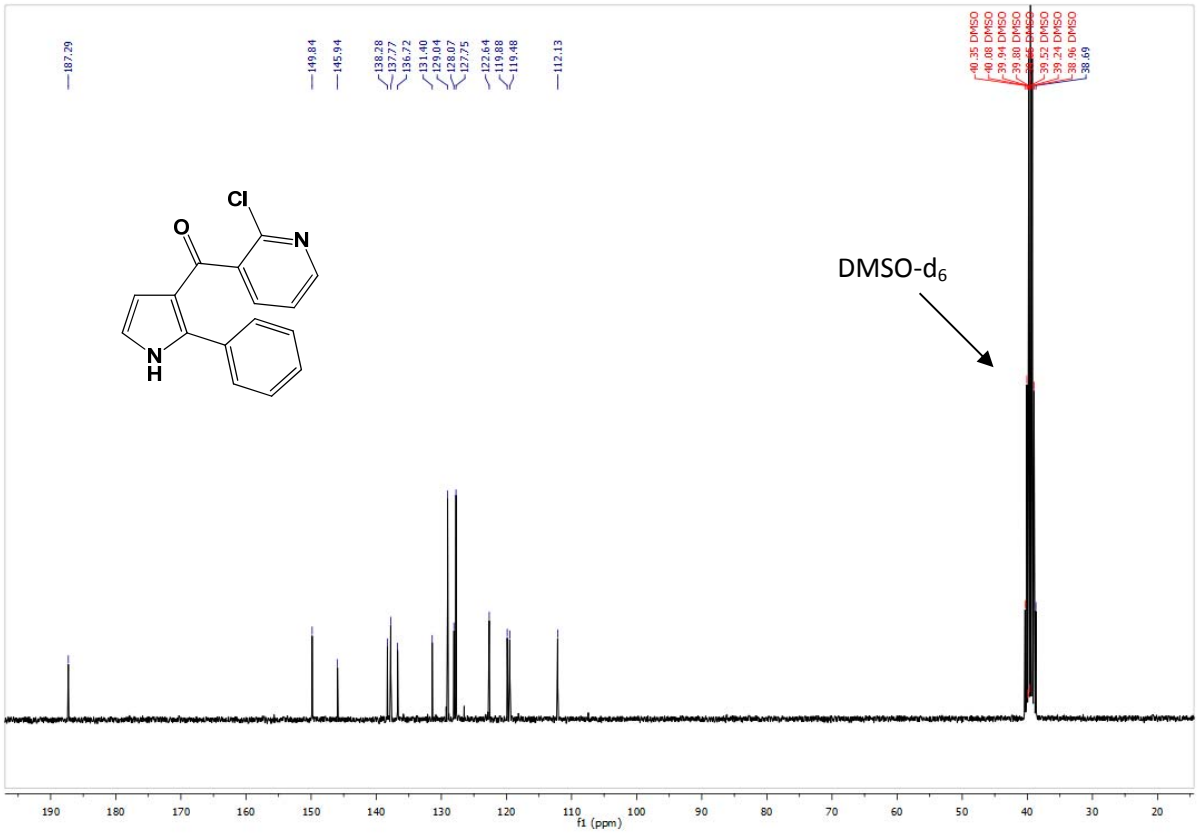


^{13}C DEPT 135-NMR of **1k** in $CDCl_3$ at 298 K (δ in ppm).

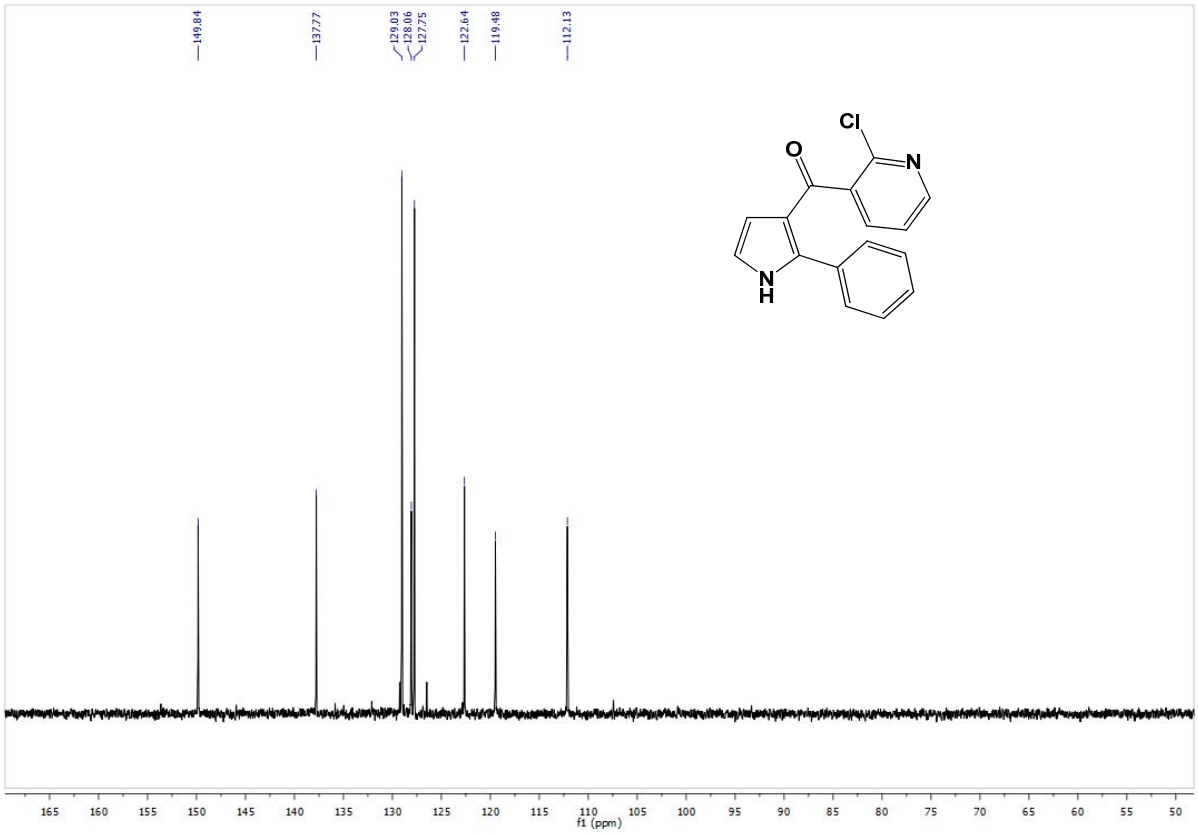
3.12 (2-chloropyridin-3-yl)(2-phenyl-1H-pyrrol-3-yl)methanone (1l)



^{1}H NMR of **1l** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

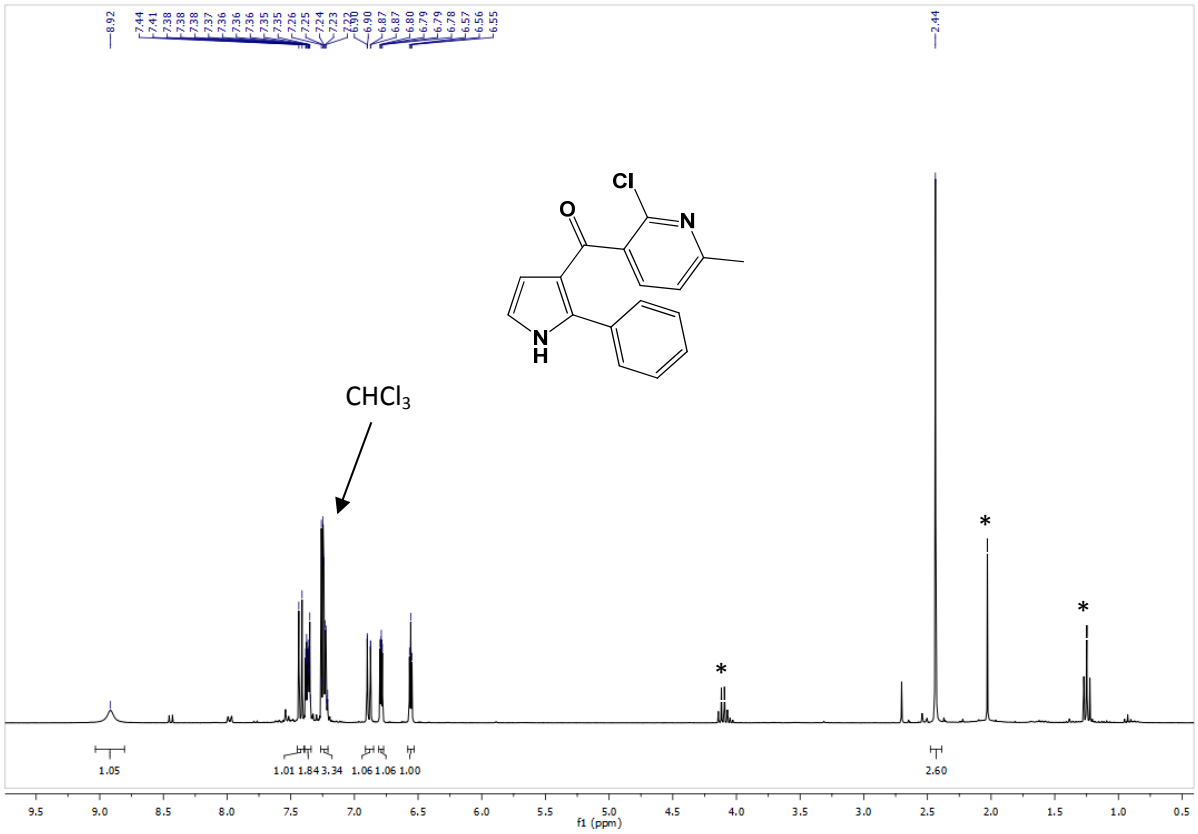


^{13}C NMR of **1l** in DMSO-d_6 at 298 K (δ in ppm).

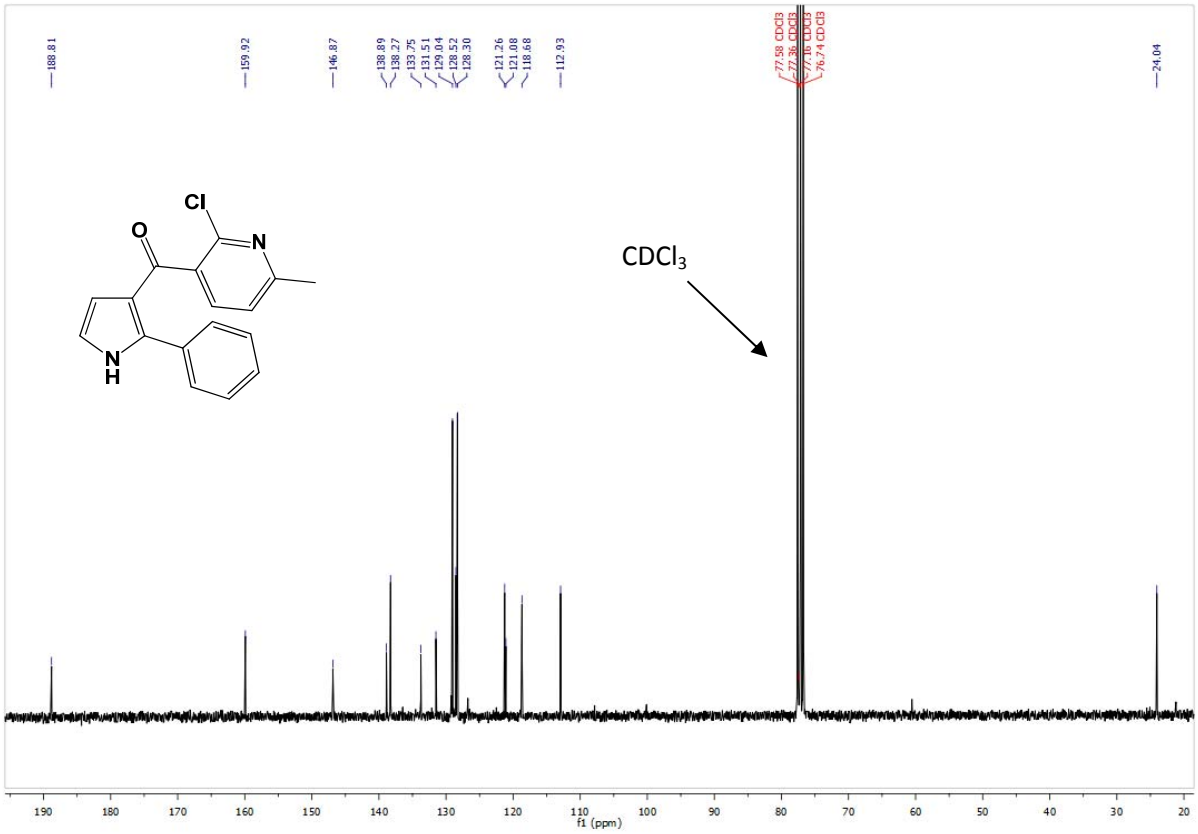


^{13}C DEPT 135-NMR of **1l** in DMSO-d_6 at 298 K (δ in ppm).

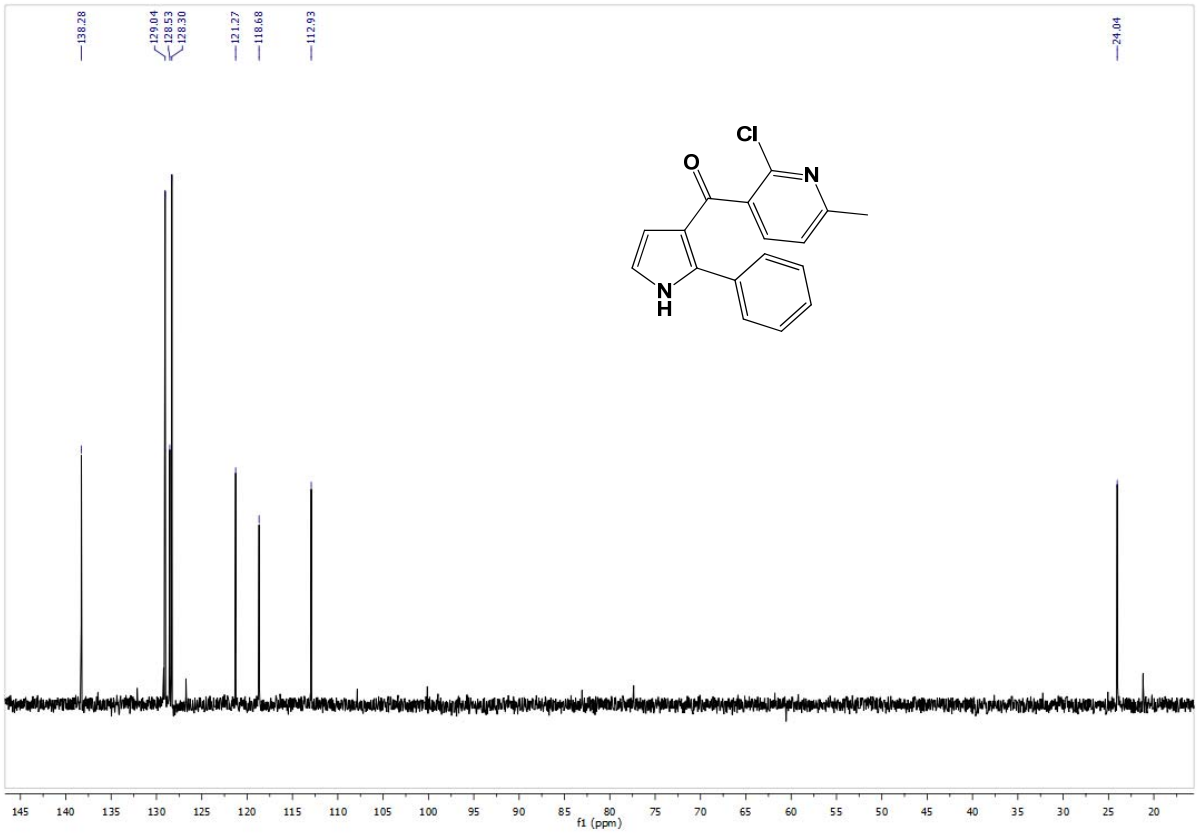
3.13 (2-chloro-6-methylpyridin-3-yl)(2-phenyl-1H-pyrrol-3-yl)methanone (1m)



^{1}H NMR of **1m** in $CDCl_3$ at 298 K. * Impurities from residual solvents.

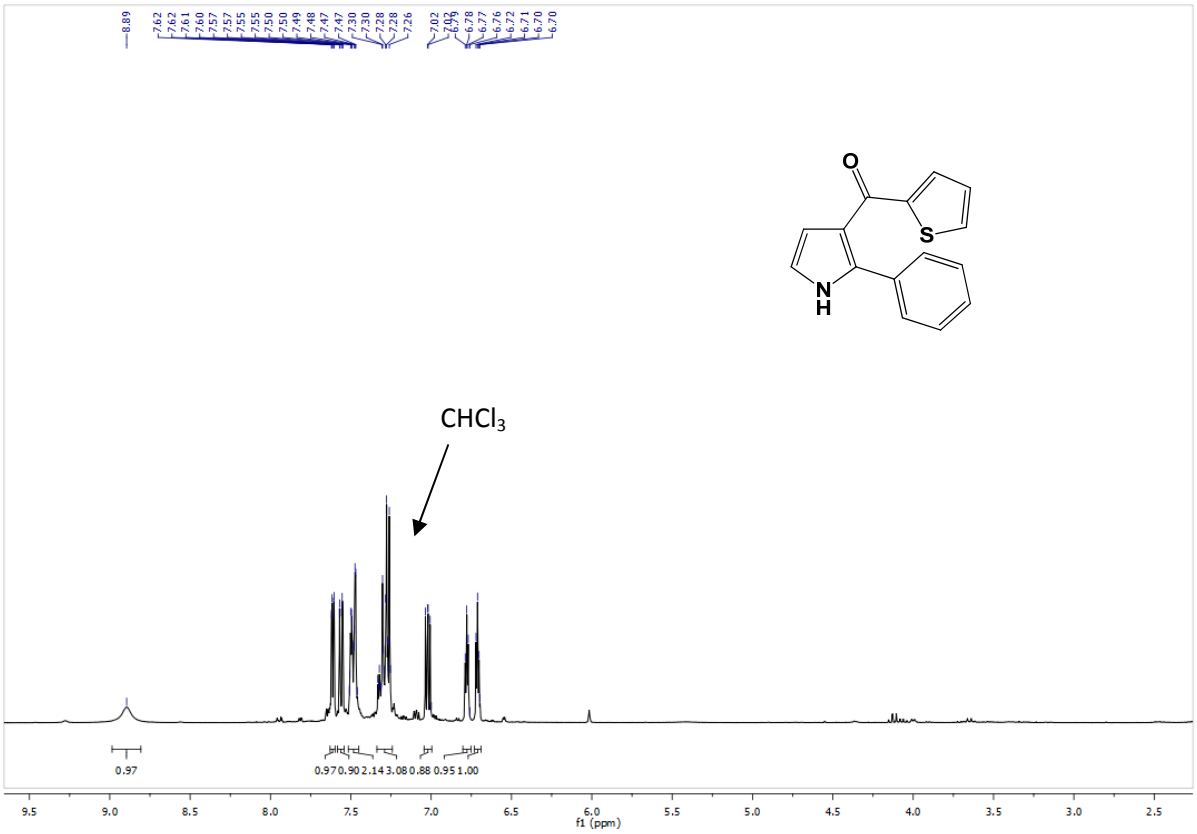


^{13}C NMR of **1m** in $CDCl_3$ at 298 K (δ in ppm).

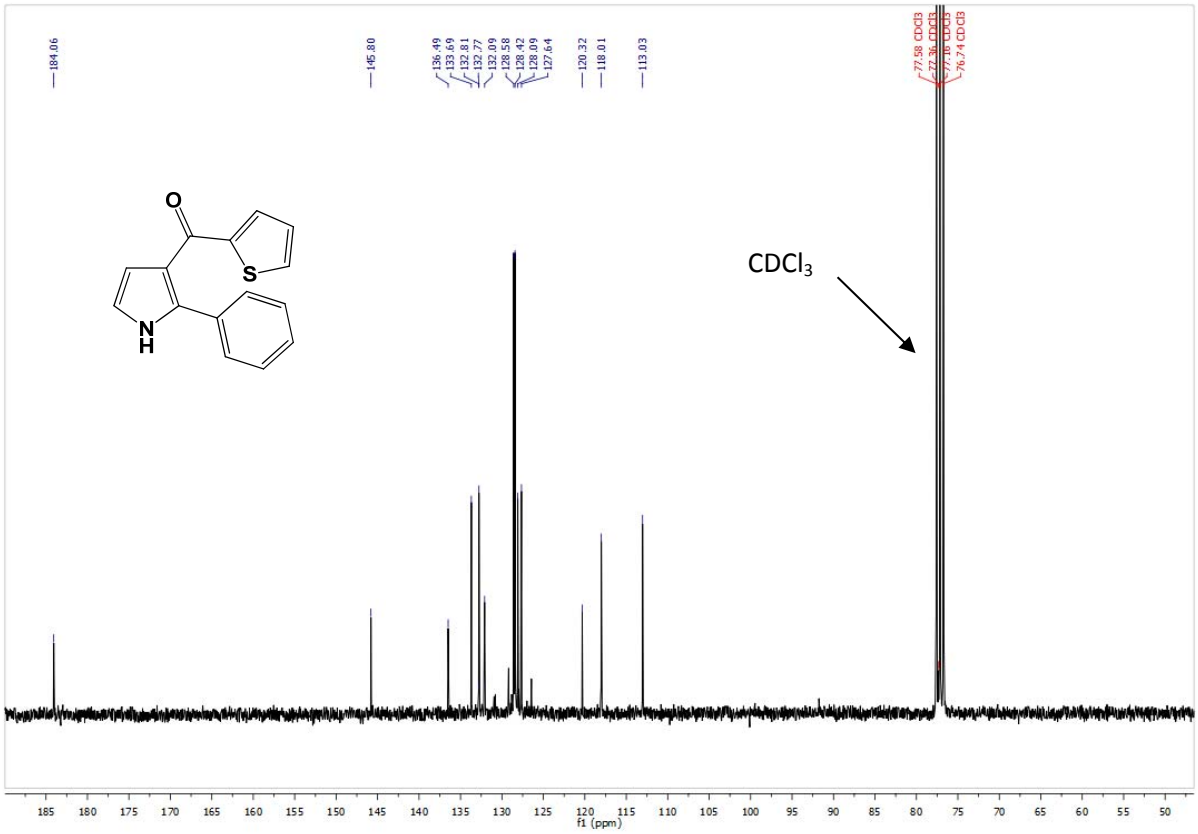


^{13}C DEPT 135-NMR of **1m** in $CDCl_3$ at 298 K (δ in ppm).

3.14 (2-phenyl-1H-pyrrol-3-yl)(thiophen-2-yl)methanone (1n)

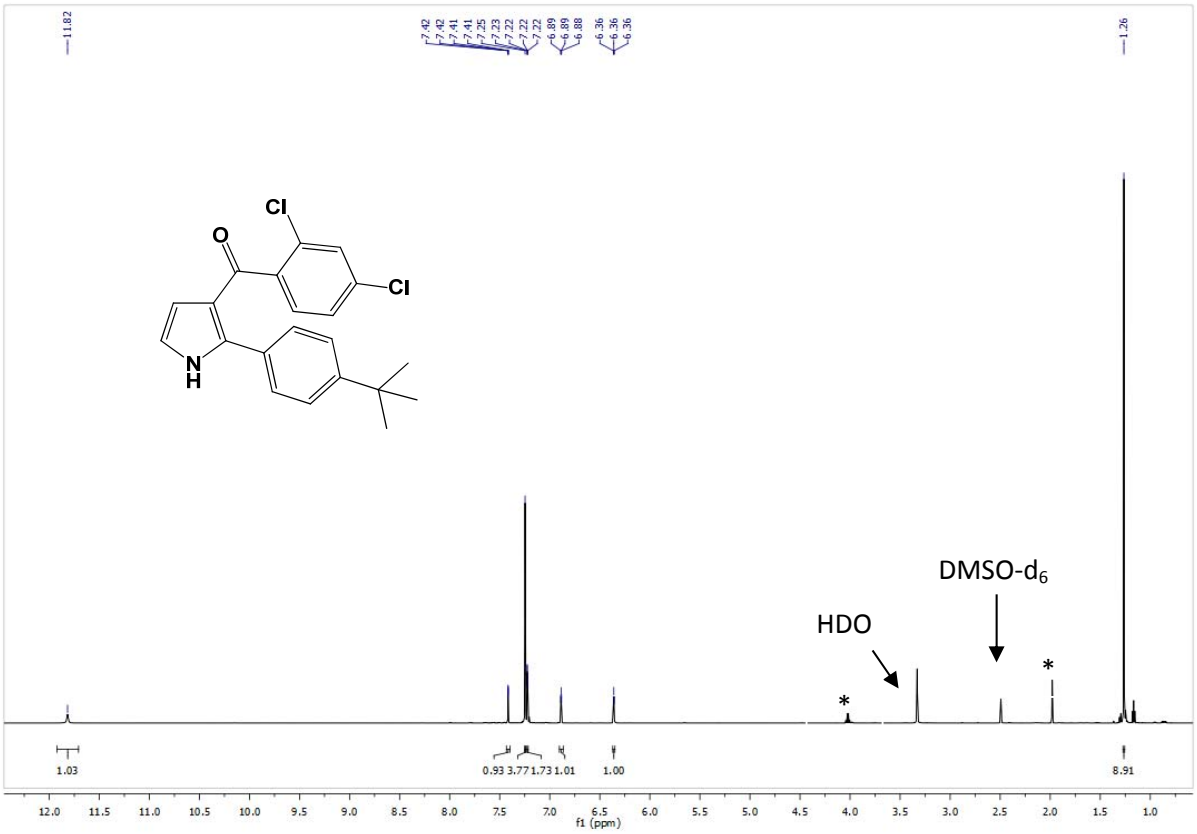


^{1}H NMR of **1n** in $CDCl_3$ at 298 K.

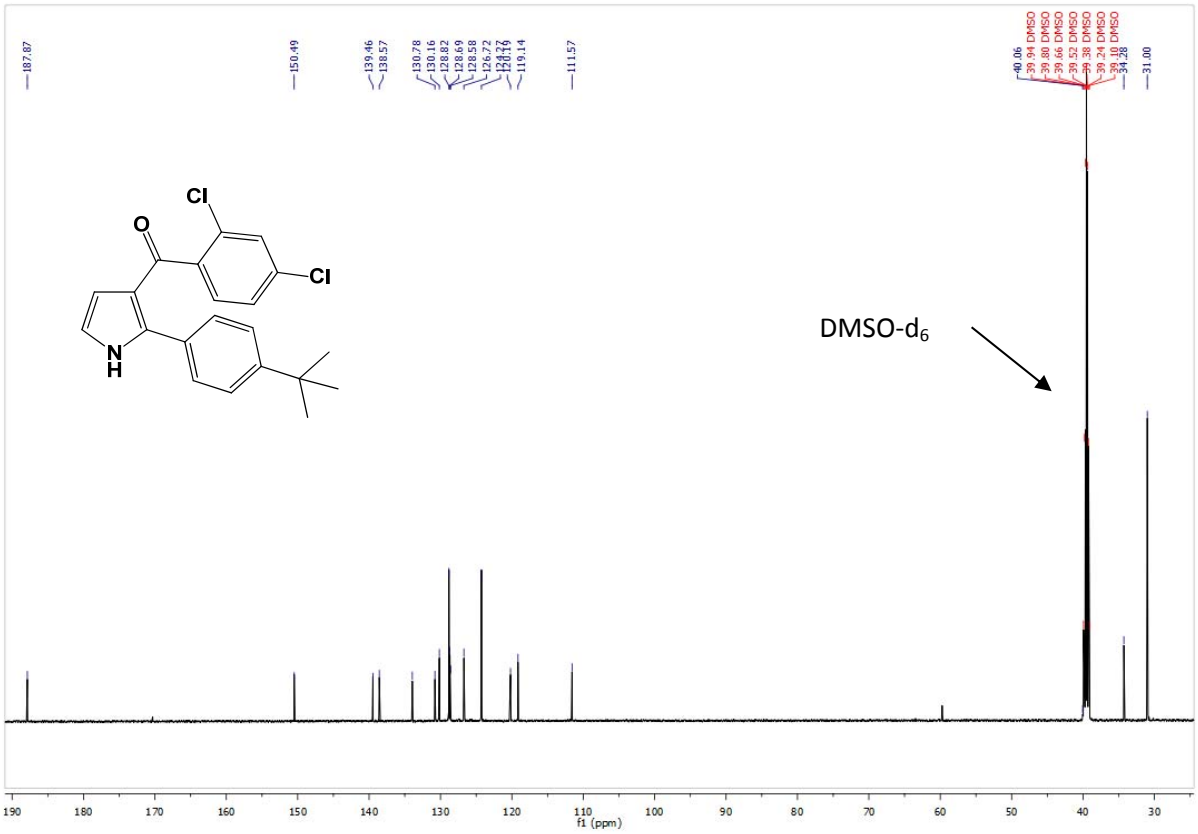


^{13}C NMR of **1n** in $CDCl_3$ at 298 K (δ in ppm).

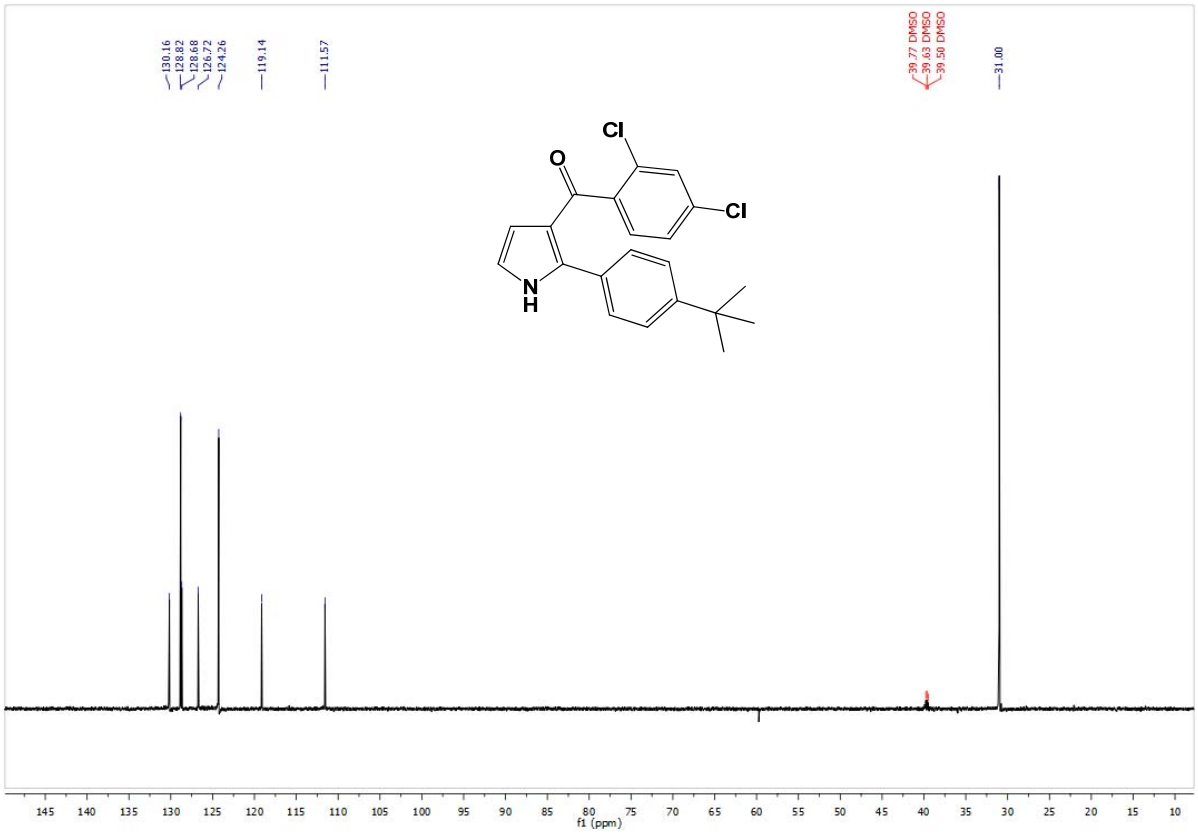
3.15 (2-(4-(tert-butyl)phenyl)-1H-pyrrol-3-yl)(2,4-dichlorophenyl)methanone (1o)



^{1}H NMR of **1o** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

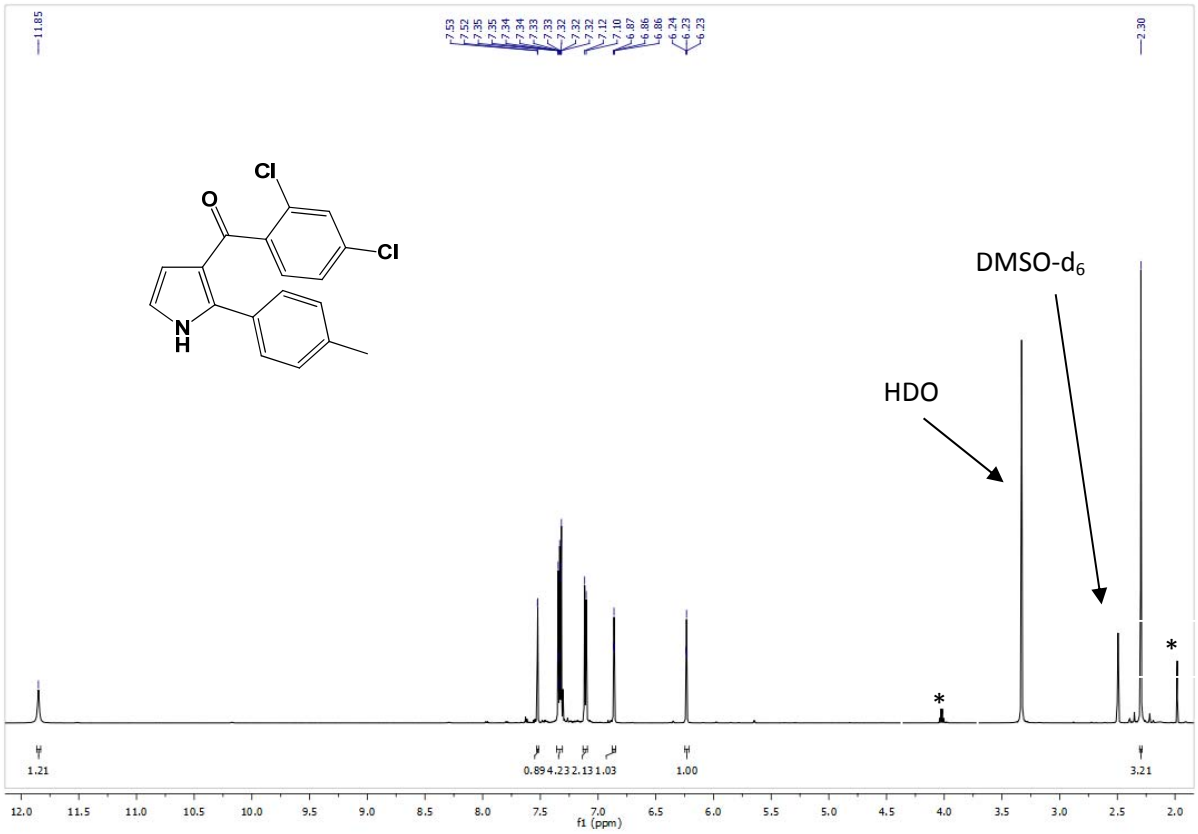


^{13}C NMR of **1o** in DMSO-d$_6$ at 298 K (δ in ppm).

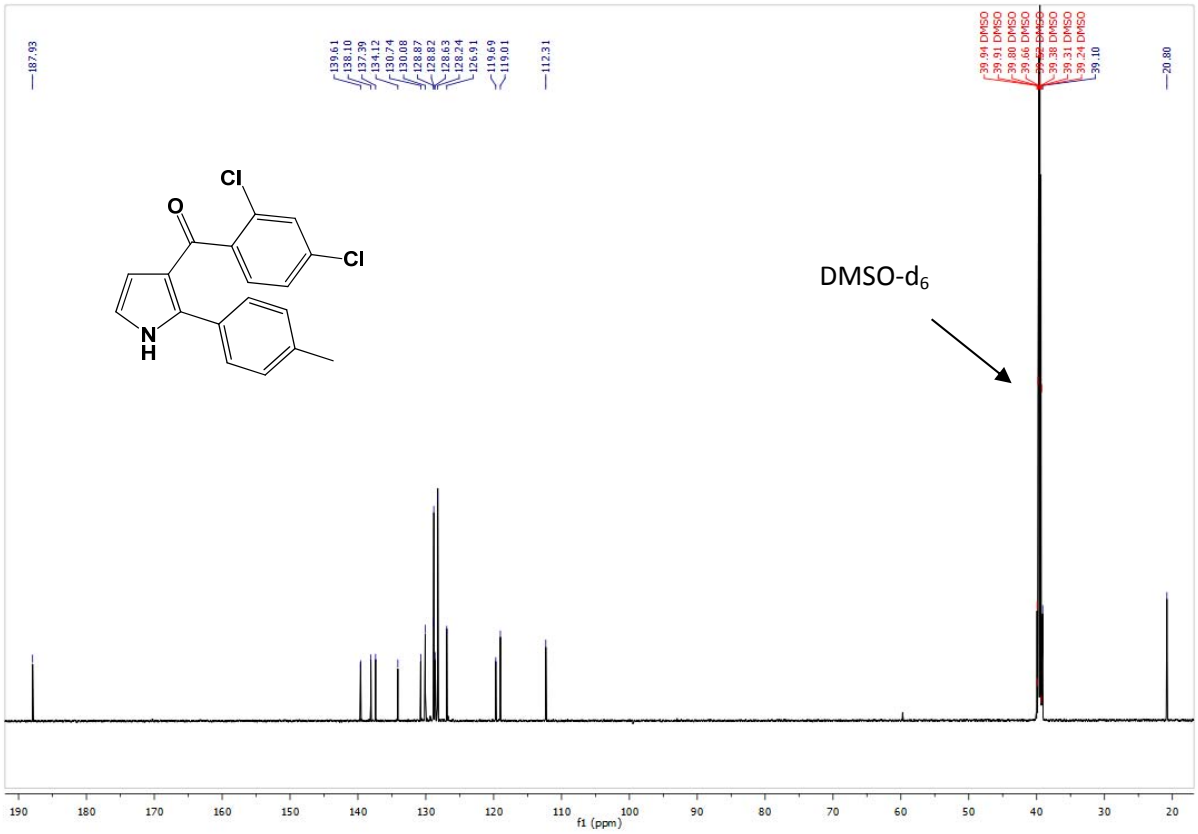


^{13}C DEPT 135-NMR of **1o** in DMSO-d$_6$ at 298 K (δ in ppm).

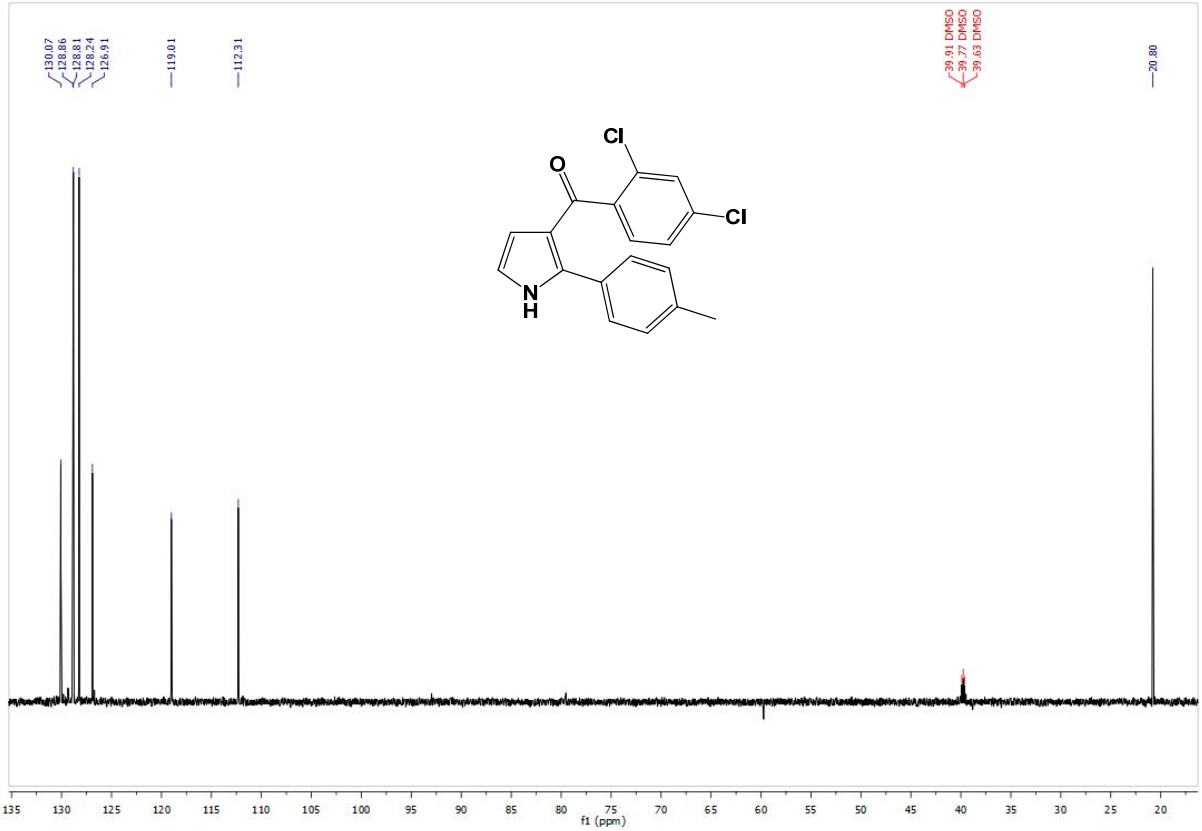
3.16 (2,4-dichlorophenyl)(2-(p-tolyl)-1H-pyrrol-3-yl)methanone (1p)



^{1}H NMR of **1p** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

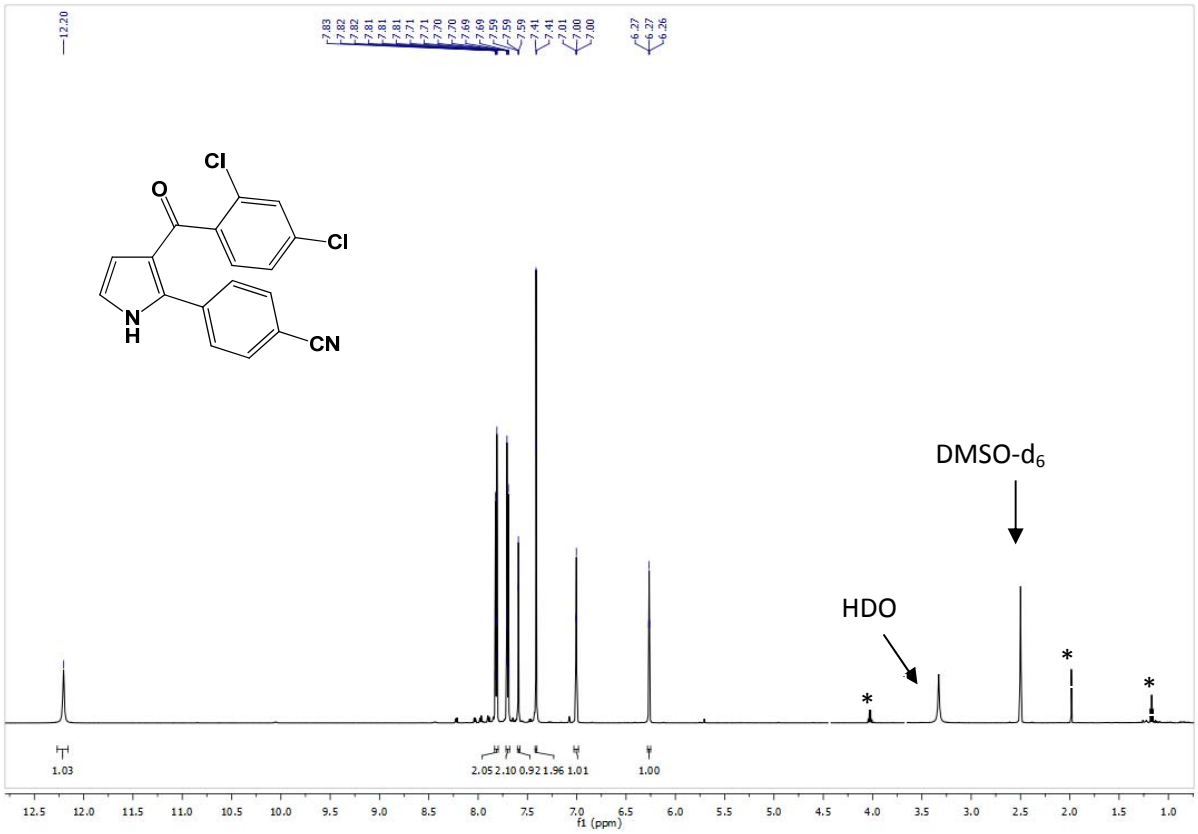


^{13}C NMR of **1p** in DMSO-d_6 at 298 K (δ in ppm).

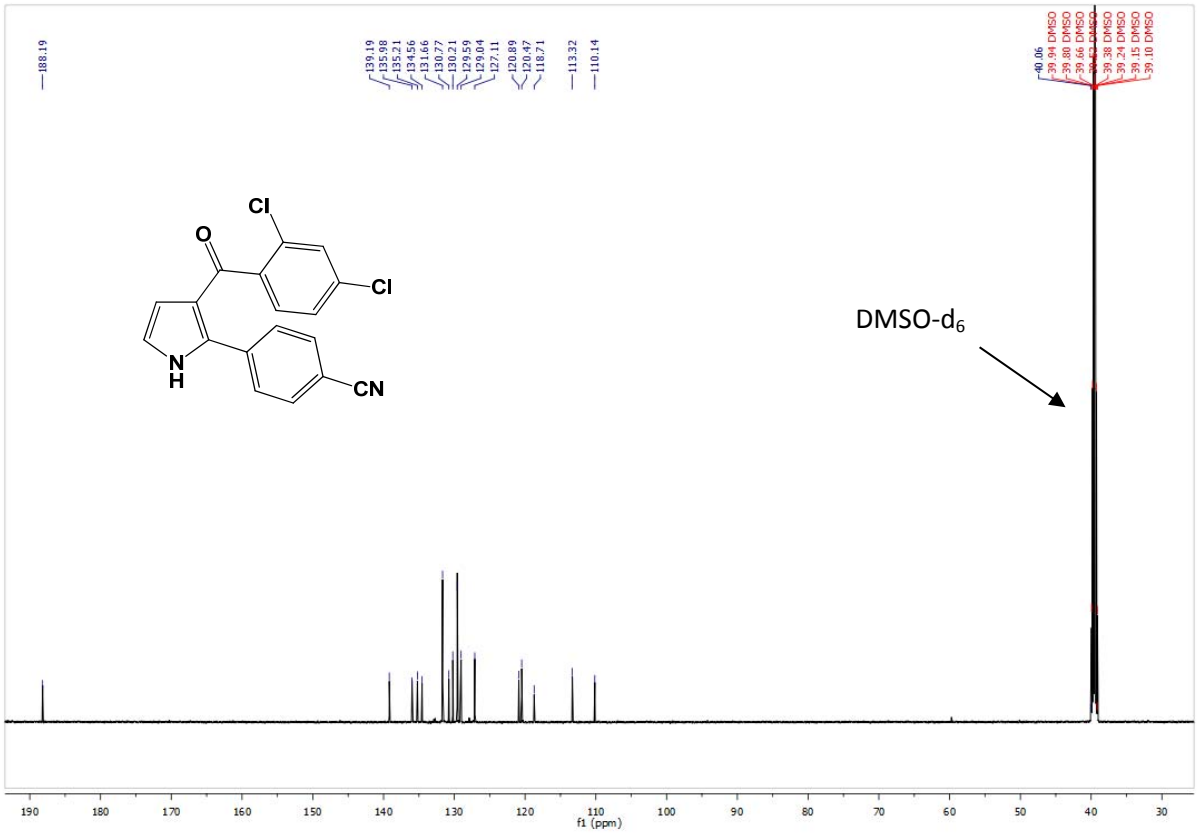


^{13}C DEPT 135-NMR of **1p** in DMSO-d_6 at 298 K (δ in ppm).

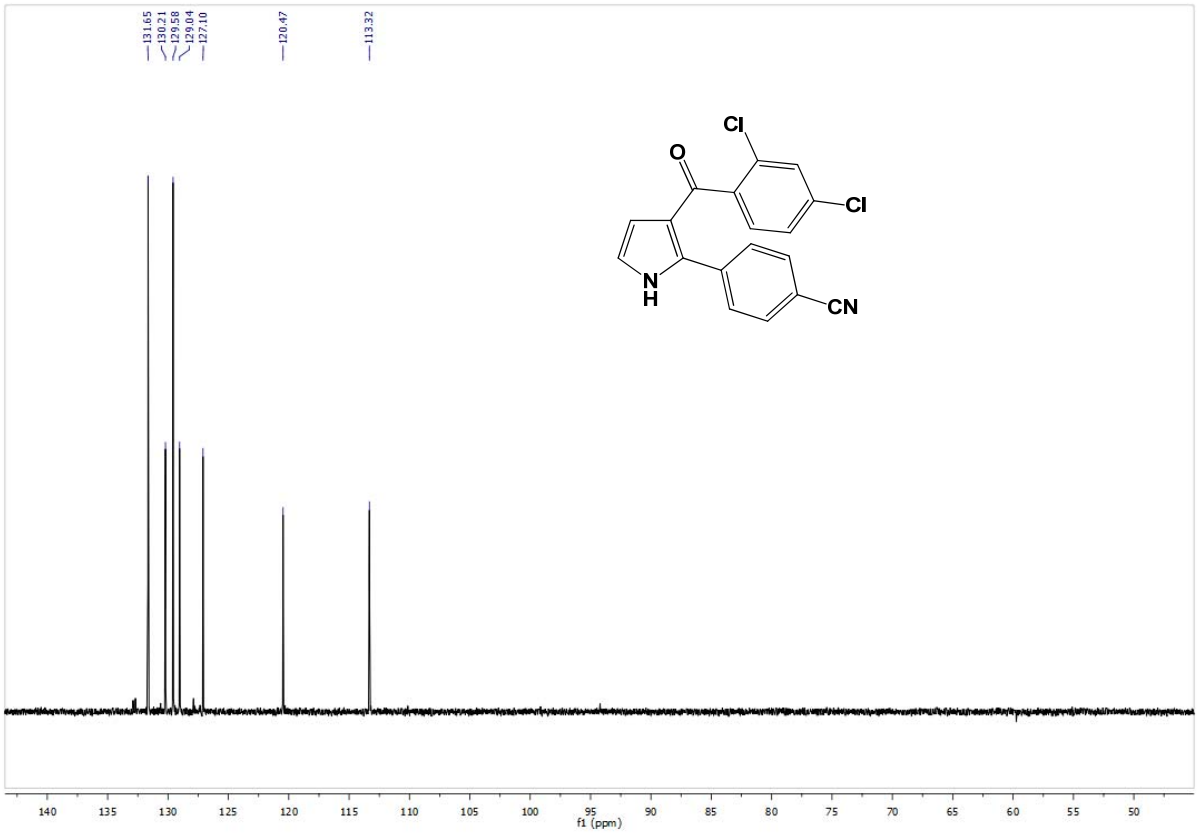
3.17 4-(3-(2,4-dichlorobenzoyl)-1H-pyrrol-2-yl)benzonitrile (1q)



^{1}H NMR of **1q** in DMSO-d$_6$ at 298 K. * Impurities from residual solvents.

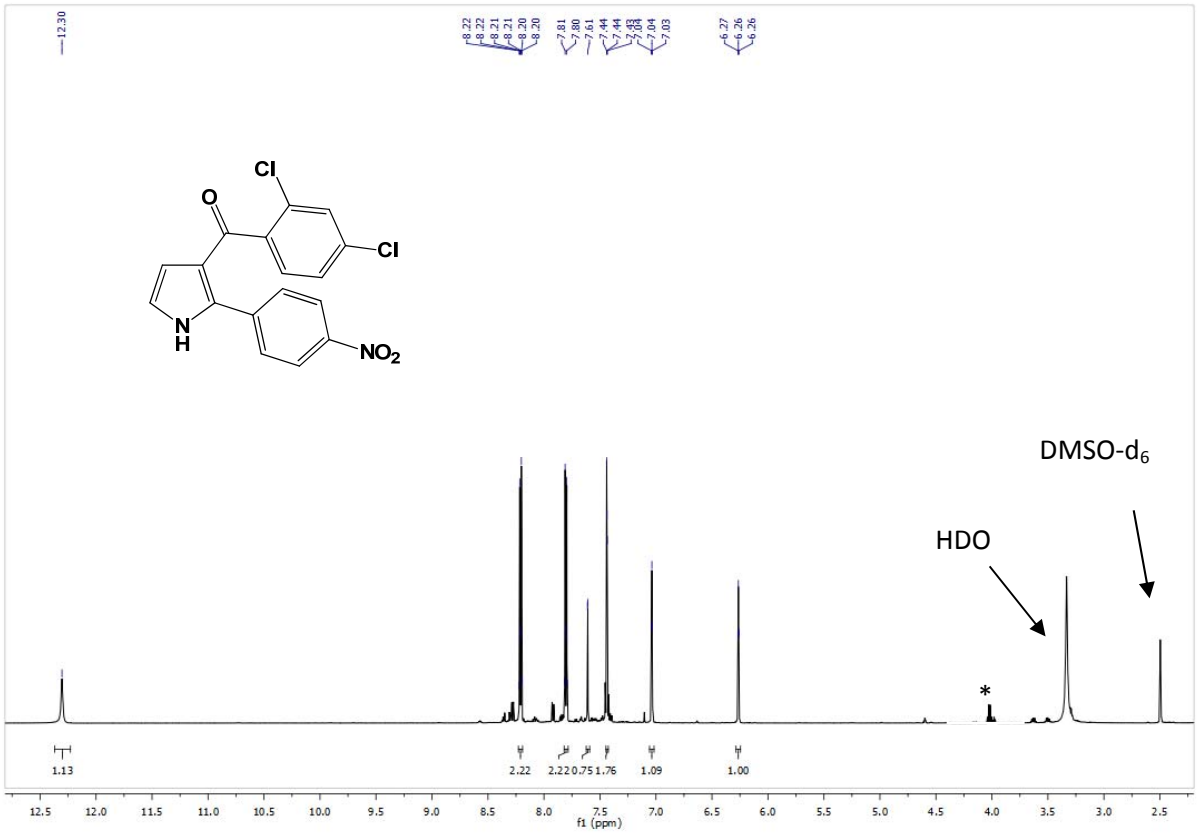


^{13}C NMR of **1q** in DMSO-d_6 at 298 K (δ in ppm).

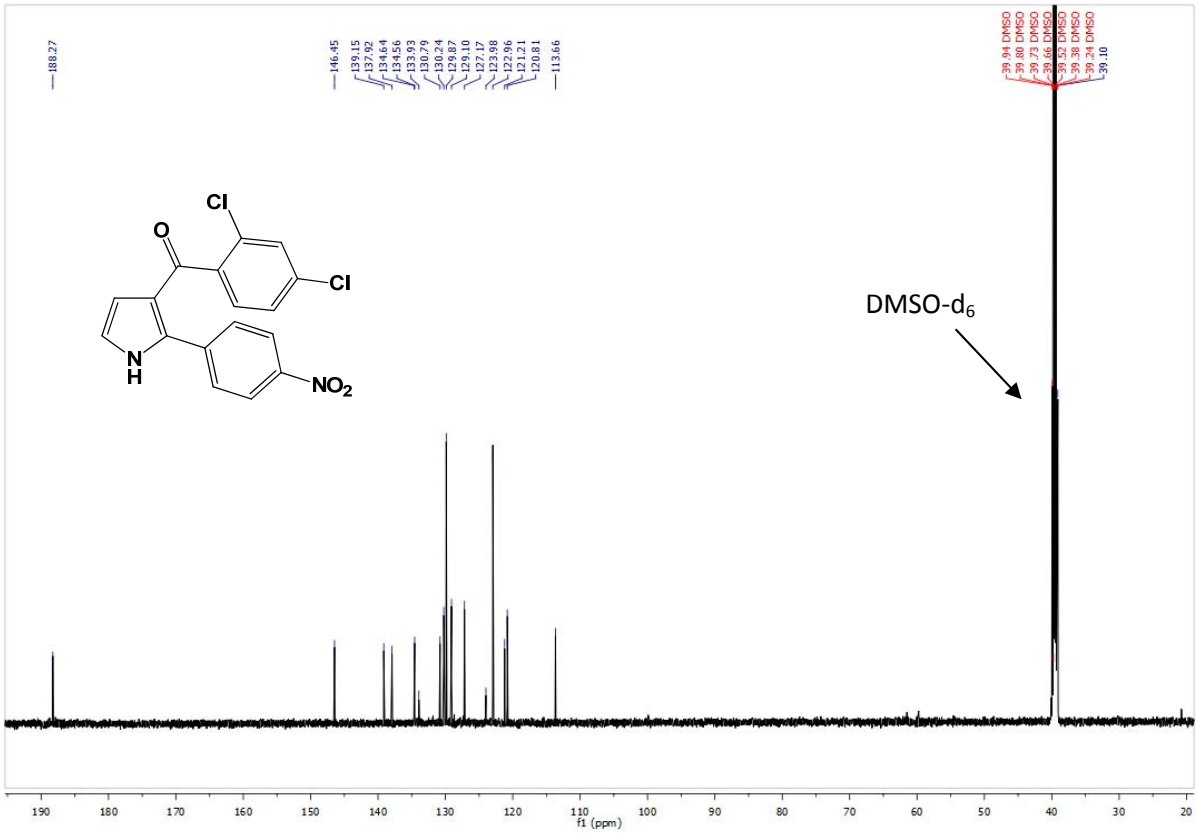


^{13}C DEPT 135-NMR of **1q** in DMSO-d_6 at 298 K (δ in ppm).

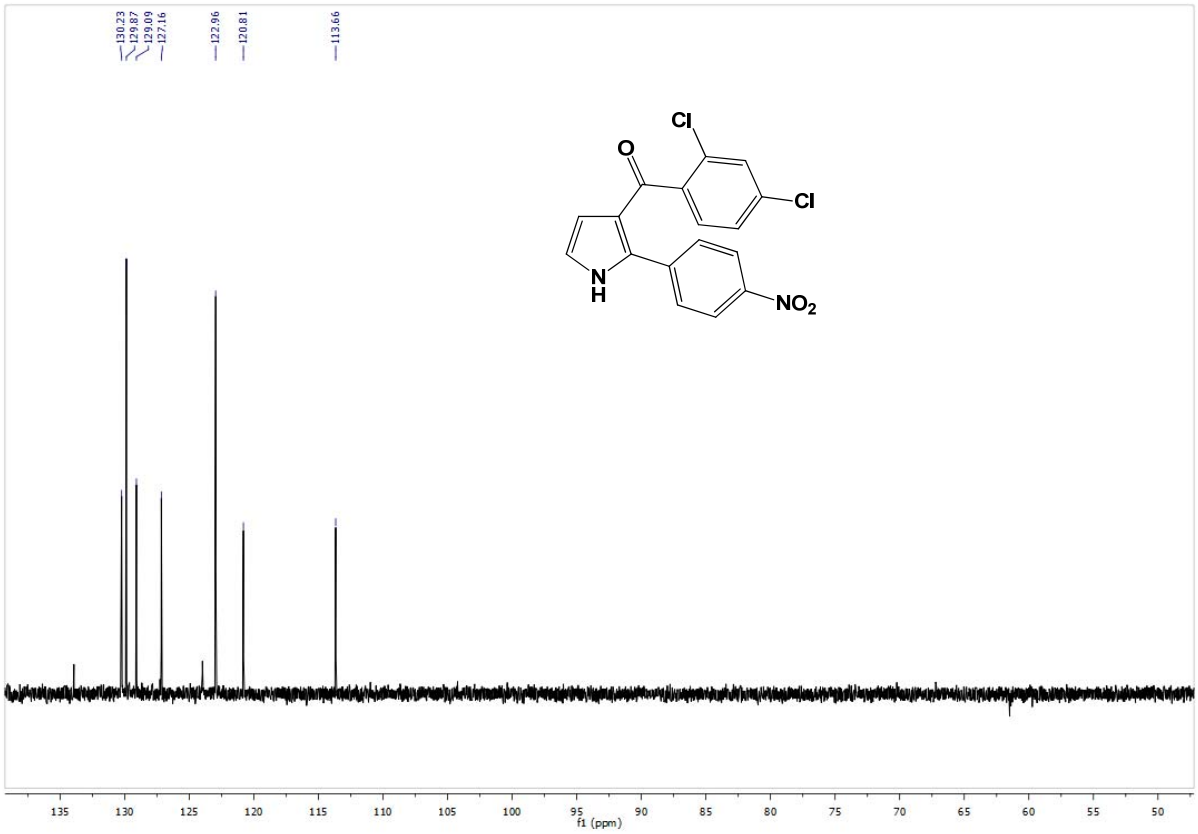
3.18 (2,4-dichlorophenyl)(2-(4-nitrophenyl)-1H-pyrrol-3-yl)methanone (1r)



^{1}H NMR of **1r** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

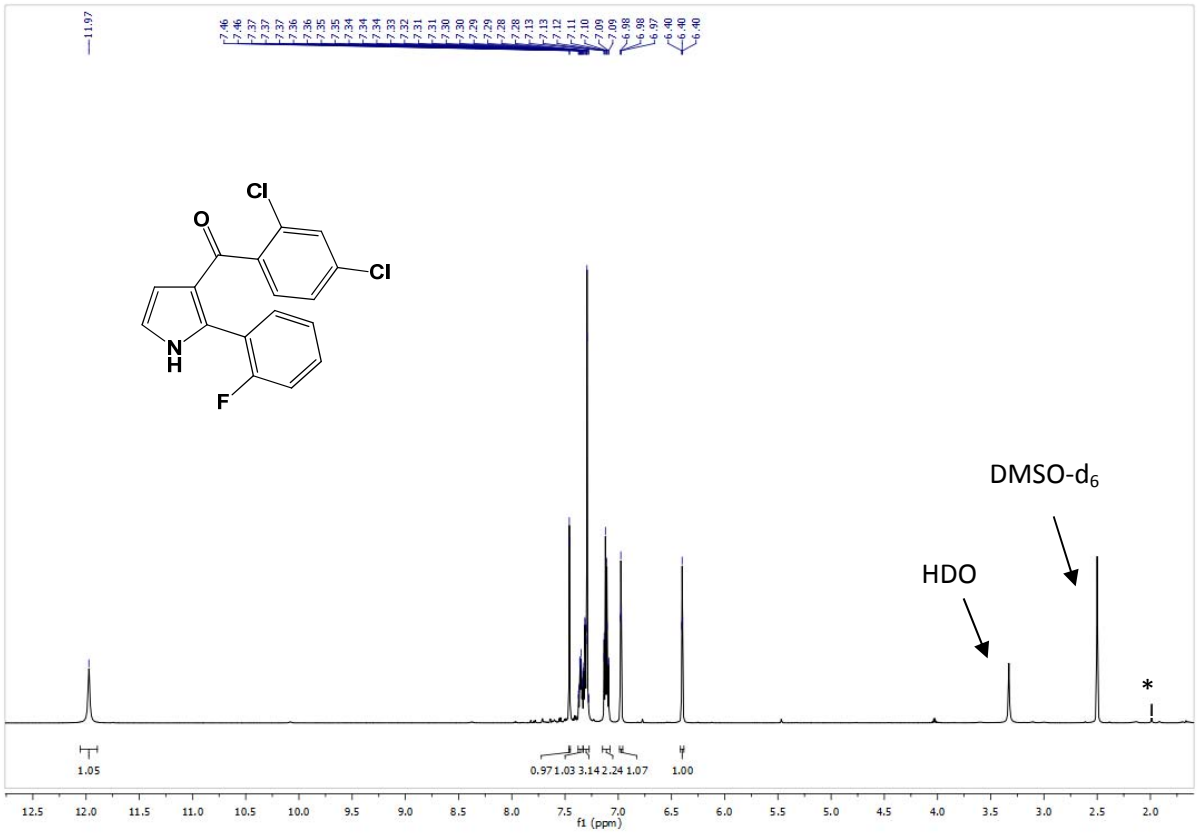


^{13}C NMR of **1r** in DMSO-d_6 at 298 K (δ in ppm).

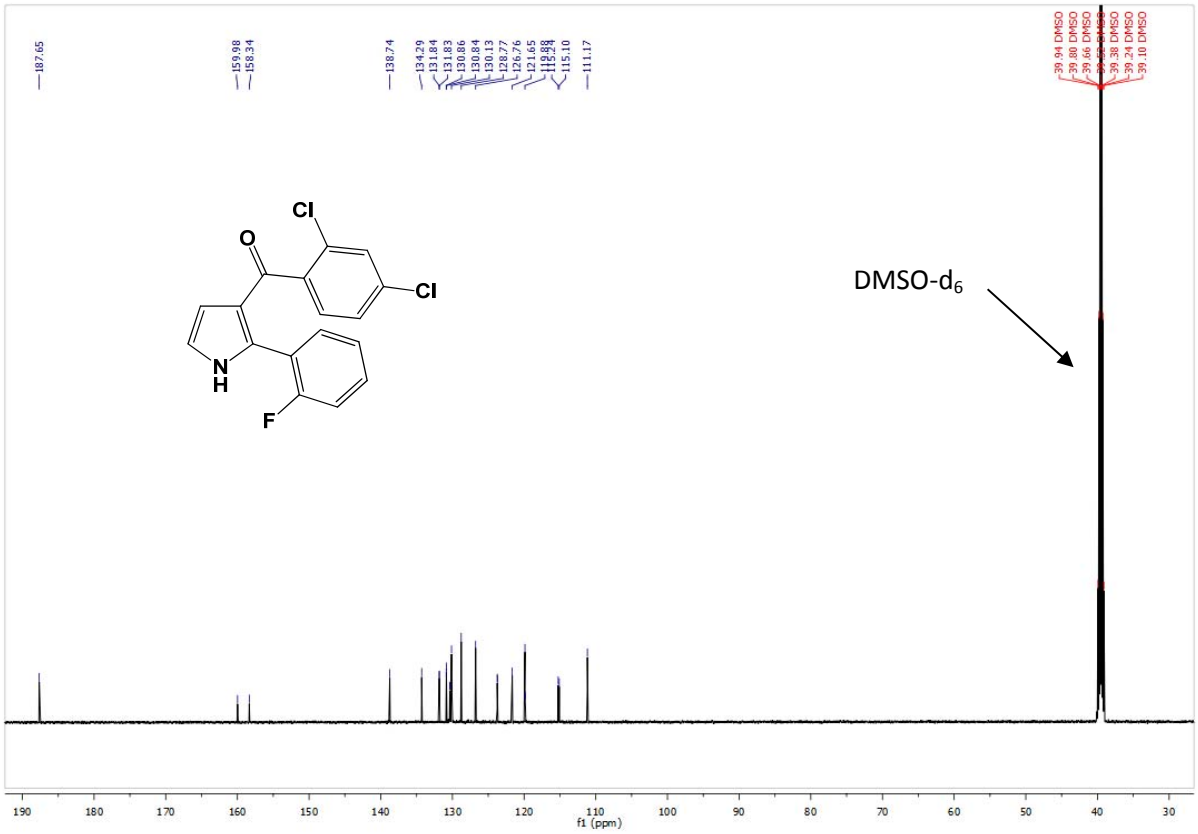


^{13}C DEPT 135-NMR of **1r** in DMSO-d_6 at 298 K (δ in ppm).

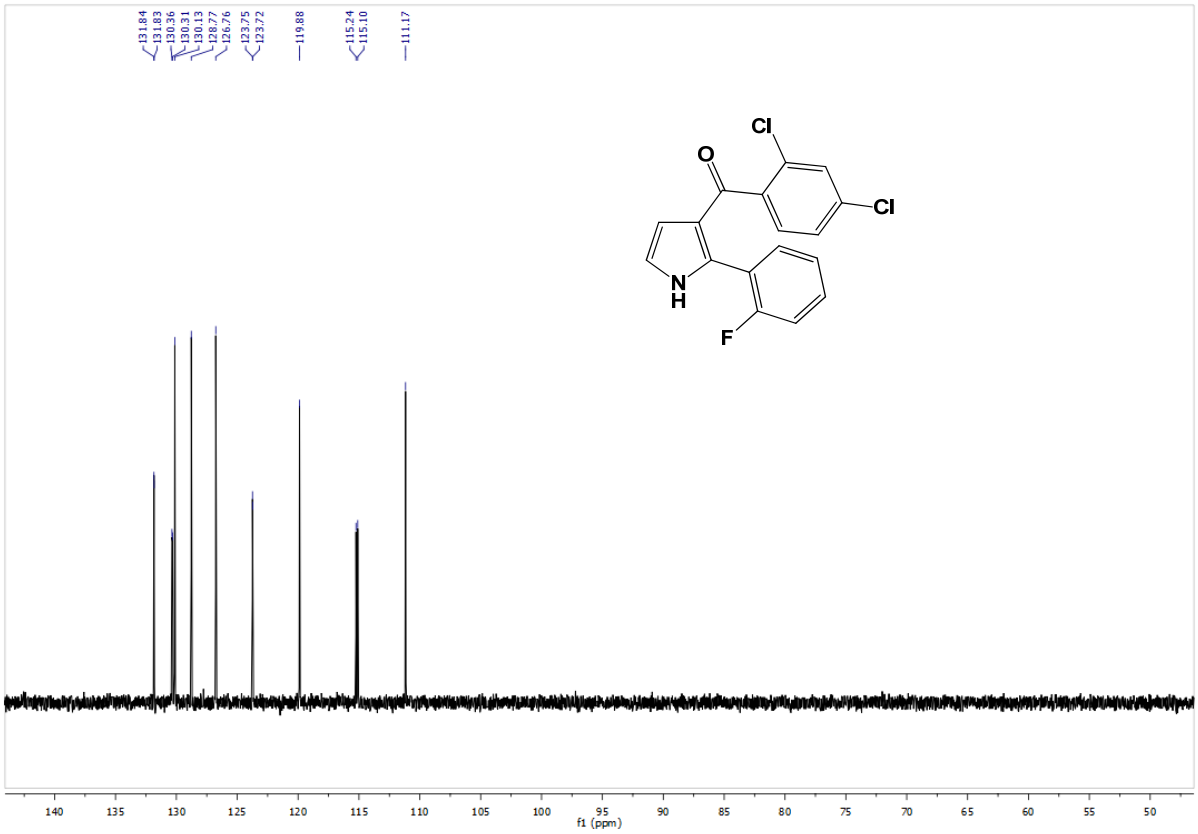
3.19 (2,4-dichlorophenyl)(2-(2-fluorophenyl)-1H-pyrrol-3-yl)methanone (1s)



^{1}H NMR of **1s** in DMSO-d_6 at 298 K. * Impurities from residual solvents.

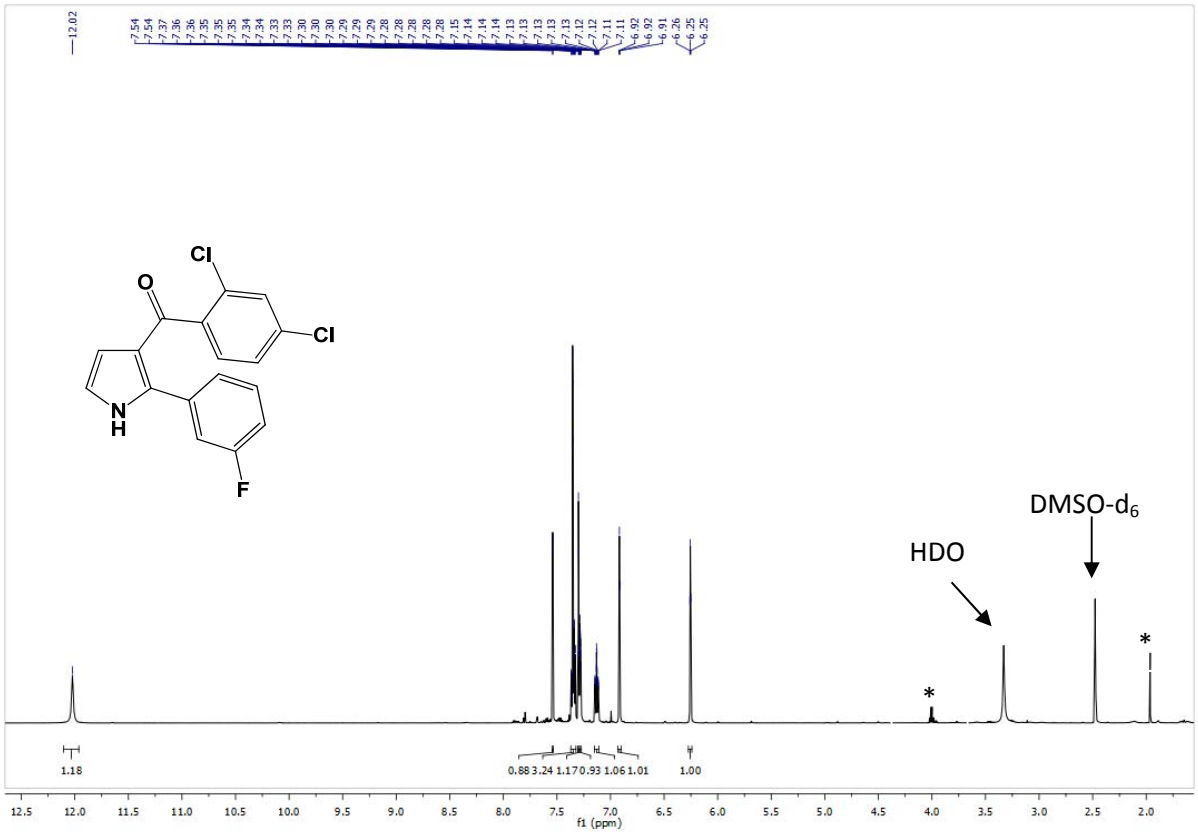


^{13}C NMR of **1s** in DMSO-d_6 at 298 K (δ in ppm).

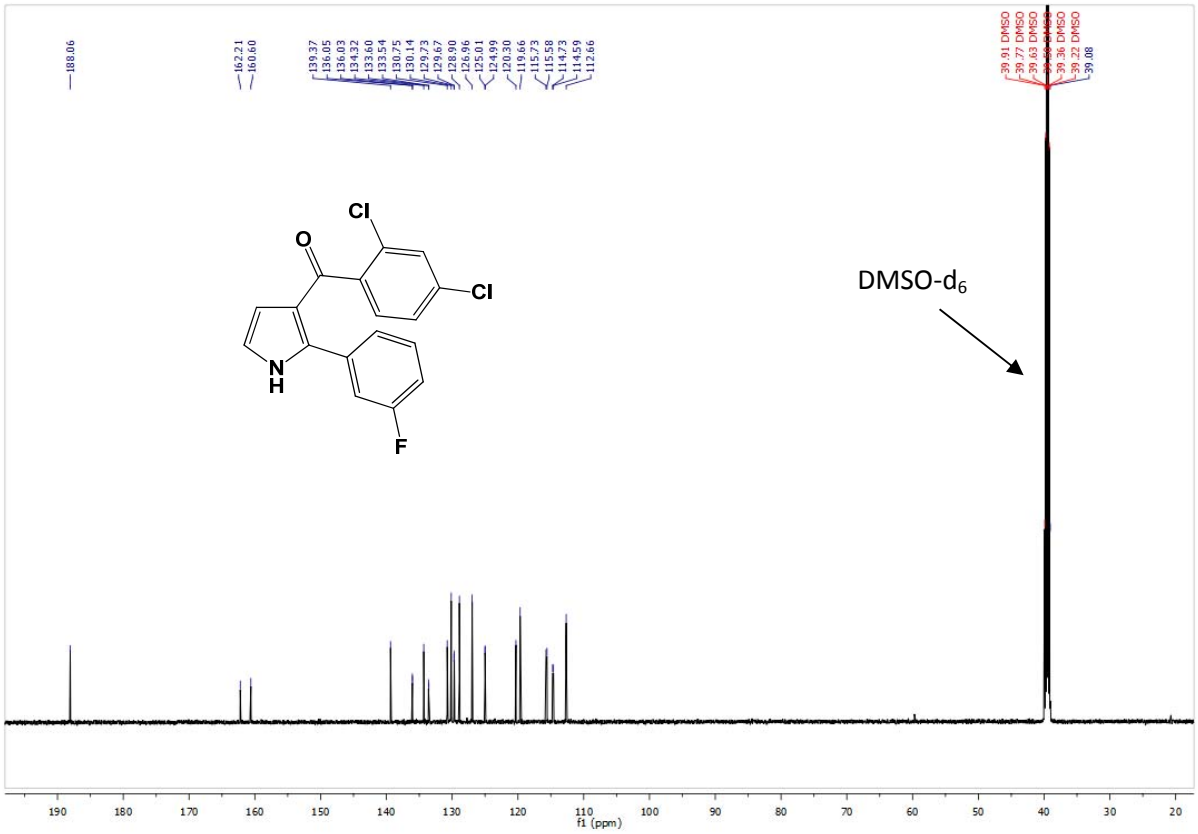


^{13}C DEPT 135-NMR of **1s** in DMSO-d_6 at 298 K (δ in ppm).

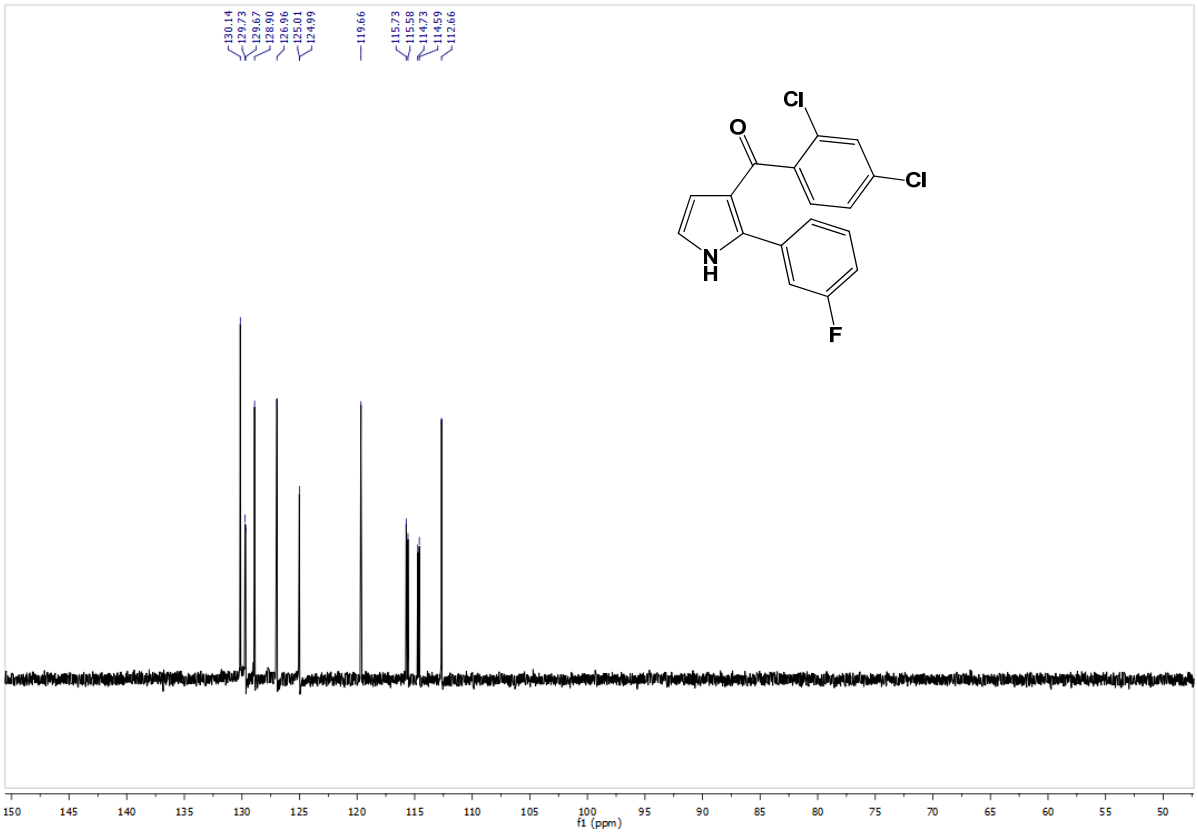
3.20 (2,4-dichlorophenyl)(2-(3-fluorophenyl)-1H-pyrrol-3-yl)methanone (1t)



^{1}H NMR of **1t** in DMSO-d$_6$ at 298 K. * Impurities from residual solvents.

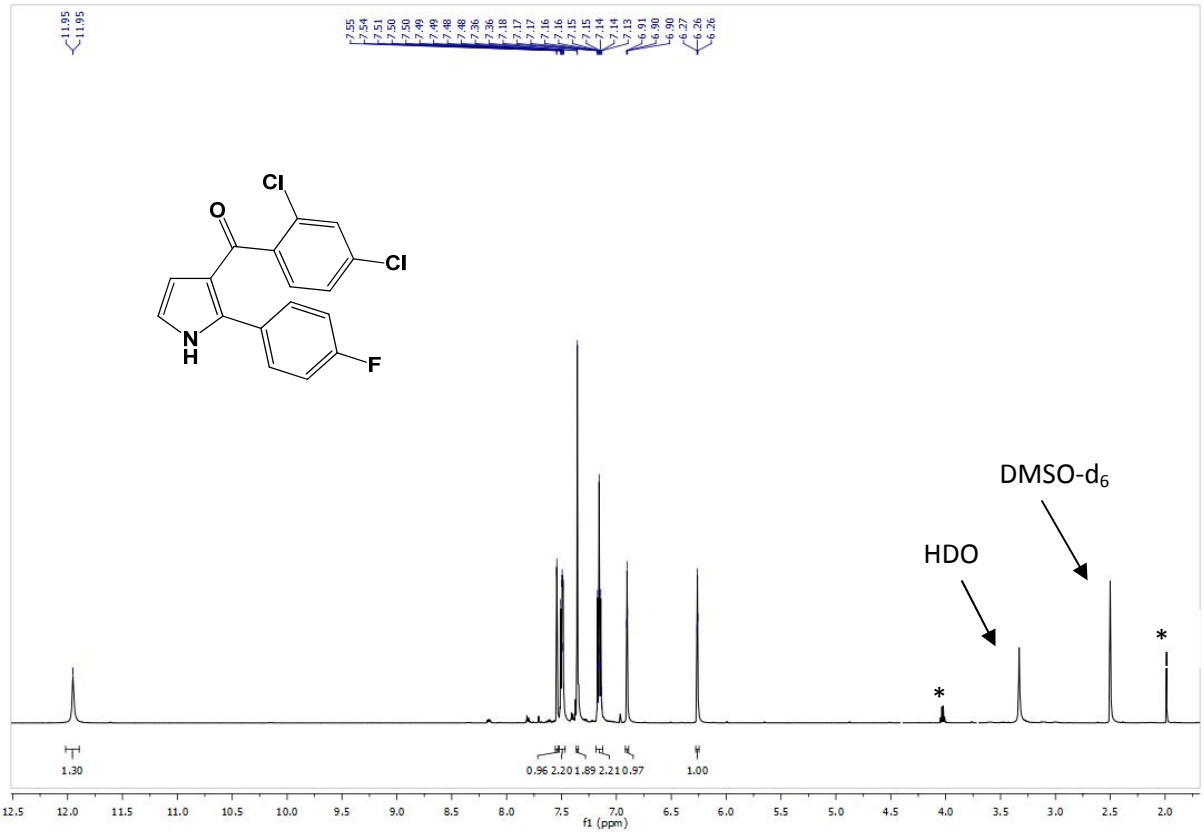


^{13}C NMR of **1t** in DMSO-d_6 at 298 K (δ in ppm).

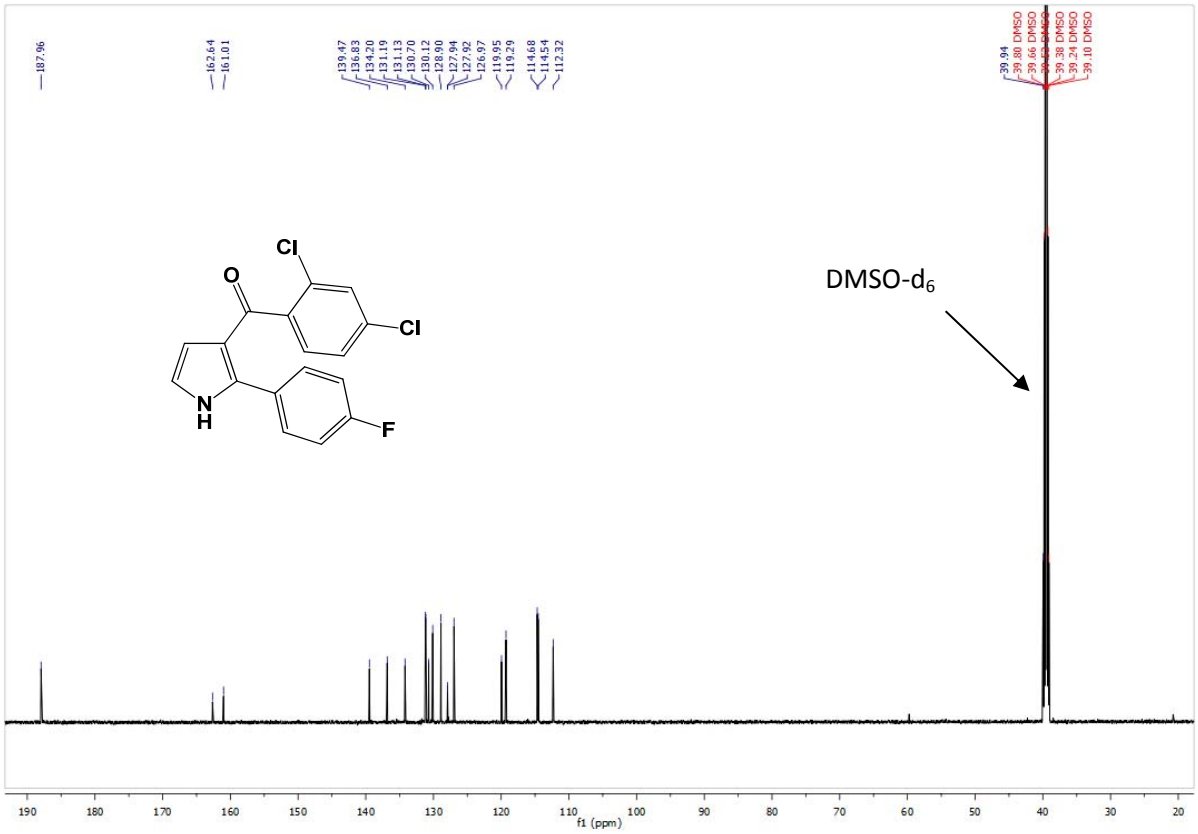


^{13}C DEPT 135-NMR of **1t** in DMSO-d_6 at 298 K (δ in ppm).

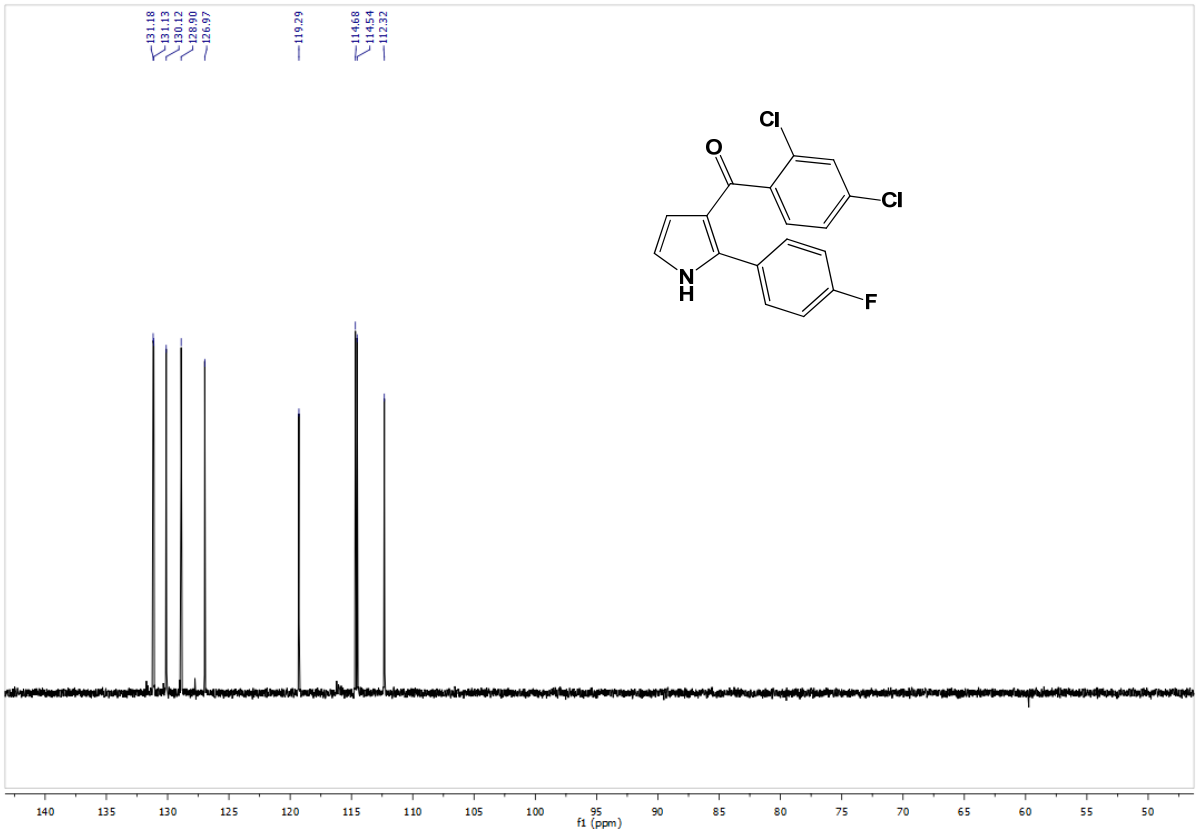
3.21 (2,4-dichlorophenyl)(2-(4-fluorophenyl)-1H-pyrrol-3-yl)methanone (1u)



^{1}H NMR of **1u** in DMSO-d$_6$ at 298 K. * Impurities from residual solvents.

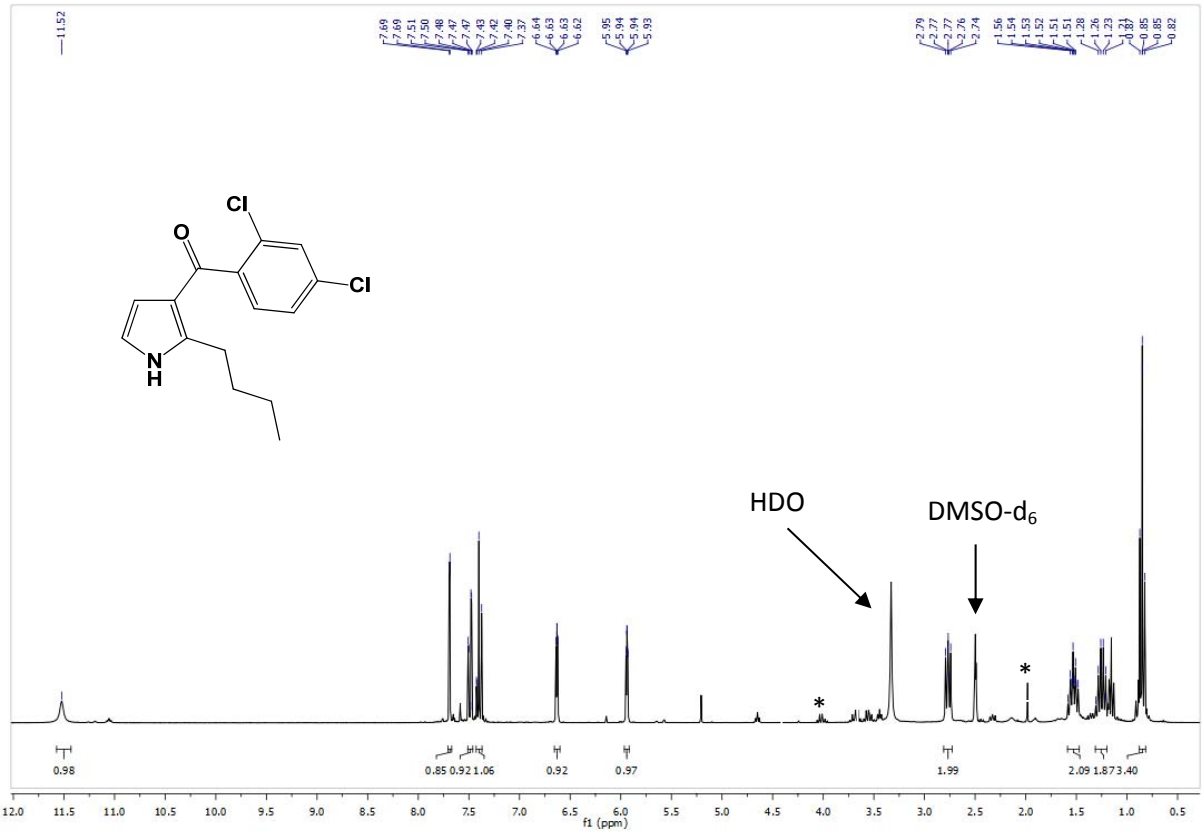


^{13}C NMR of **1u** in DMSO-d_6 at 298 K (δ in ppm).

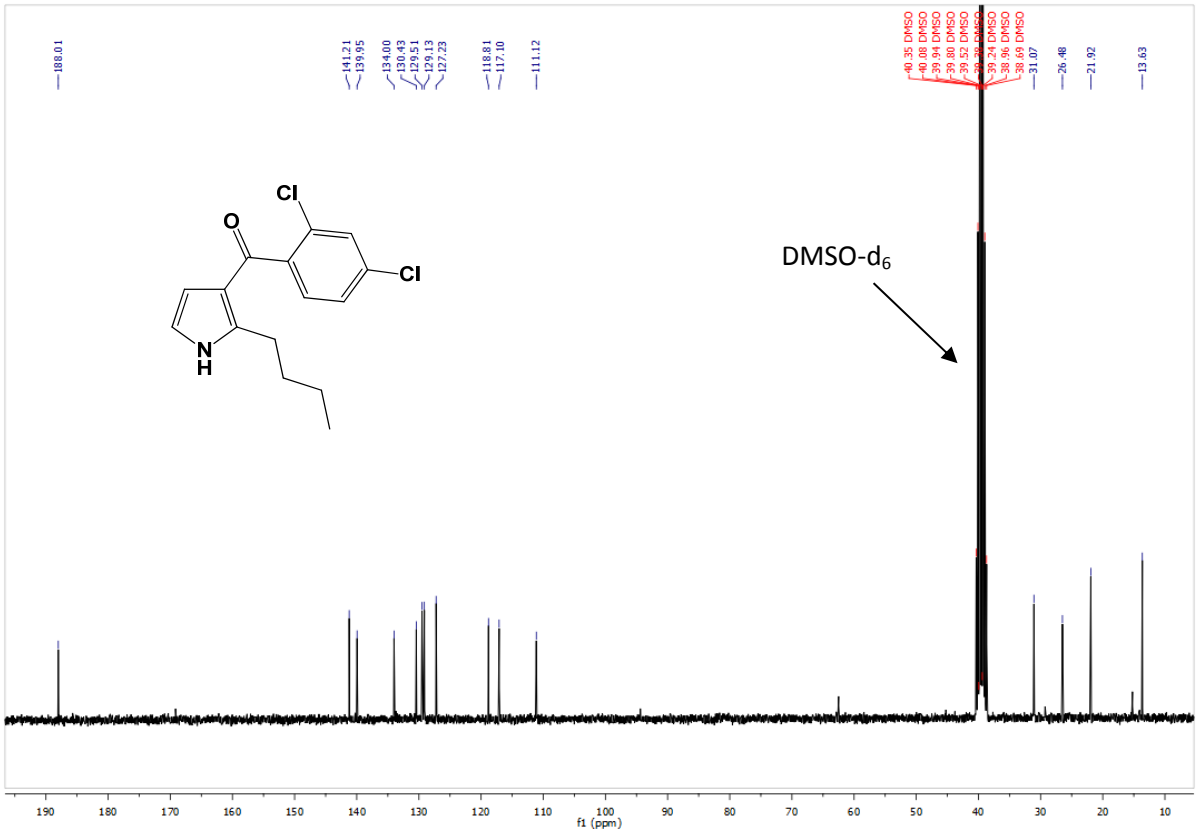


^{13}C DEPT 135-NMR of **1u** in DMSO-d_6 at 298 K (δ in ppm).

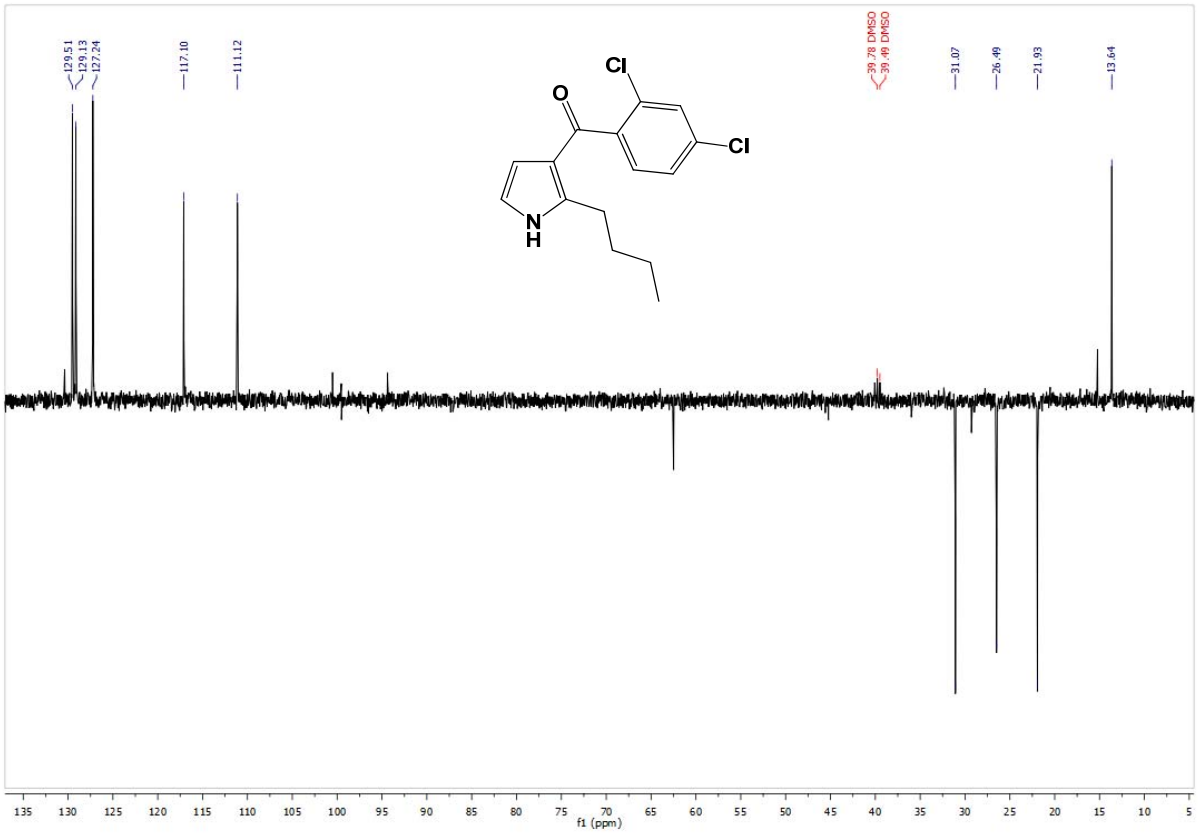
3.22 (2-butyl-1H-pyrrol-3-yl)(2,4-dichlorophenyl)methanone (1v)



^{1}H NMR of **1v** in DMSO-d$_6$ at 298 K. * Impurities from residual solvents.

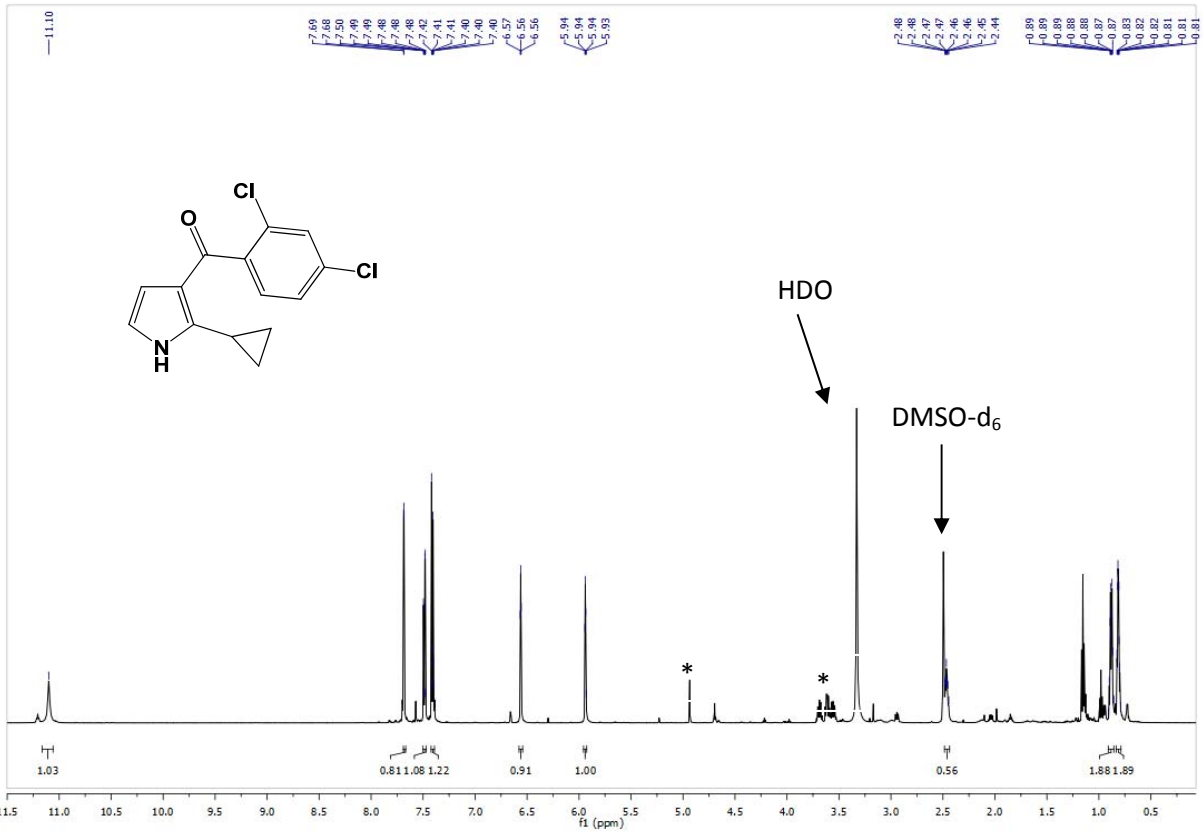


^{13}C NMR of **1v** in DMSO-d$_6$ at 298 K (δ in ppm).

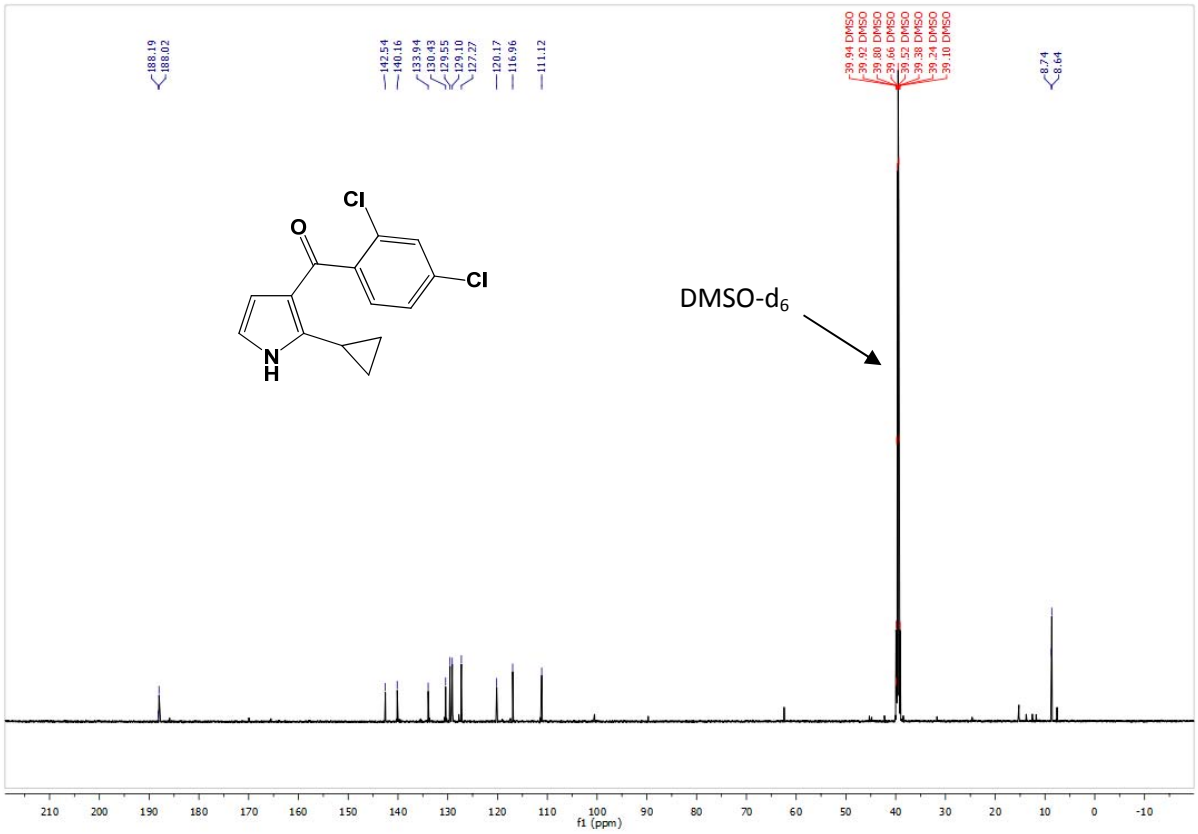


^{13}C DEPT 135-NMR of **1v** in DMSO-d$_6$ at 298 K (δ in ppm).

3.23 (2-cyclopropyl-1H-pyrrol-3-yl)(2,4-dichlorophenyl)methanone (1w)



^{1}H NMR of **1w** in DMSO-d$_6$ at 298 K. * Impurities from residual solvents.



^{13}C NMR of **1w** in DMSO-d_6 at 298 K (δ in ppm).

4 Preparation of (2,4-dichlorophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (1j) on a 20 mmol scale

Palladium(II) chloride (8.9 mg, 0.05 mmol, 0.25 mol-%) and di(1-adamantyl)benzylphosphonium hydrobromide (47.6 mg, 0.10 mmol, 0.50 mol-%) were placed in a dry Schlenk tube under an argon atmosphere and 20 mL of dry dichloromethane were added. 2,4-dichlorobenzoyl chloride **5j** (4.280 g, 20.00 mmol), phenylacetylene **6a** (2.090 g, 20.00 mmol), and reagent grade triethylamine (3.0 mL, 24.05 mmol) were added to the mixture, and stirring at room temperature was continued until complete conversion after 3 h (monitored by TLC). Then aminoacetaldehyde diethylacetal (**4**) (2.790 g, 20.60 mmol) was added and the reaction mixture was stirred for 16 h at 40 °C (oil bath). Then the reaction mixture was allowed to cool to room temperature and methanesulfonic acid (2.880 g, 30.00 mmol) was successively added. After stirring for 24 h at 40 °C (oil bath) the reaction mixture was allowed to cool to room temperature. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate 5:2) to give (2,4-dichlorophenyl)(2-phenyl-1*H*-pyrrol-3-yl)methanone (**1j**) as a light beige solid (3.600 g, 11.39 mmol, 57 % yield).