Supplementary Information

Consecutive four-component coupling-addition-aza-anellation-*Pictet-Spengler* synthesis of tetrahydro-β-carbolines – Optimized Michael addition and computational study on the aza-anellation step

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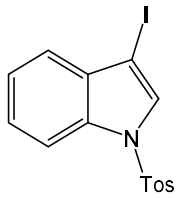
1. Synthesis of starting materials

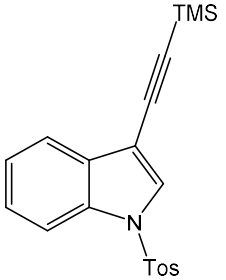
1.1. 3-Iodo-1-tosyl-1*H*-indole [1]



$C_{15}H_{12}INO_2S$
[397.23]

To a solution of indole (4.69 g, 40.00 mmol) and KOH (5.61 g, 100.00 mmol) in DMF (70 mL), iodine (10.15 g, 40.00 mmol) dissolved in DMF (70 mL) was added at rt over a period of 30 min under oxygen atmosphere. After 1 h of stirring at rt, KOH (5.61 g, 100.00 mmol) was added to the reaction mixture at 0 °C, followed by a dropwise addition of a solution of tosyl chloride (16.01 g, 84.00 mmol) dissolved in DMF (40 mL). The cooling bath was withdrawn and after a reaction time of 3 h at RT, the reaction mixture was diluted with cold water (150 mL), the resulting precipitate was separated from the solution by filtration and washed repeatedly with *n*-hexane to give after drying in vacuo 3-iodo-1-tosyl-1*H*-indole (14.45 g, 91%) as a colorless solid, Mp 131-133 °C (Lit.: 129-131 °C) [1], R_f = 0.58 (*n*-hexane/ethyl acetate 10:1). ^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.24 – 2.41 (m, 3H), 7.25 – 7.54 (m, 5H), 7.85 – 8.00 (m, 3H), 8.06 (s, 1H). ^{13}C NMR (DMSO-d_6, 150 MHz): δ 21.04 (CH_3), 68.52 (C_{quat}), 113.15 (CH), 121.68 (CH), 124.21 (CH), 125.84 (CH), 126.87 (2 CH), 130.14 (CH), 130.36 (2 CH), 132.14 (C_{quat}), 133.68 (C_{quat}), 133.78 (C_{quat}), 145.84 ($C_{quat.}$). EI-MS (70 eV, *m*/*z* (%)): 397 ([M]$^+$, 73), 242 ([C_8H_5IN]$^+$, 100), 155 ([$C_7H_7O_2S$]$^+$, 49), 115 ([M-C_8H_5N]$^{2+}$, 69), 91 ([C_7H_7]$^+$, 90). IR: $\tilde{\nu}$ [cm^{-1}] 3150 (w), 3121 (w), 3046 (w), 1593 (w), 1574 (w), 1500 (w), 1472 (w), 1437 (w), 1400 (w), 1368 (m), 1294 (w), 1267 (m), 1171 (s), 1153 (w), 1126 (s), 1109 (m), 1086 (m), 1022 (m), 1013 (m), 970 (m), 939 (m), 922 (w), 814 (w), 770 (m), 745 (m), 702 (m), 687 (s), 656 (s).

1.2. 1-Tosyl-3-((trimethylsilyl)ethynyl)-1*H*-indole [2]

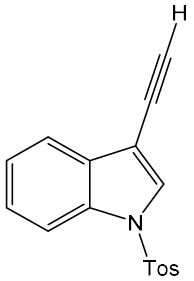


$C_{20}H_{21}NO_2SSi$
[367.54]

$PdCl_2$ (44 mg, 0.24 mmol), PPh_3 (124 mg, 0.48 mmol), CuI (92 mg, 0.48 mmol), and 3-iodo-1-tosyl-1*H*-indole (3.18 g, 8.00 mmol) were suspended in degassed CH_3CN (40 mL) for 5 min.

Subsequently, (TMS)acetylene (1.33 mL, 9.60 mmol) and NEt_3 (1.11 mL, 8.00 mmol) were added successively, and the mixture was stirred at rt for 1 h. The reaction product was adsorbed on celite© under reduced pressure and purified by column chromatography (silica gel) with an eluent mixture of *n*-hexane and ethyl acetate in a ratio of 20:1. After evaporation of the solvent, the crude product was repeatedly suspended in *n*-hexane and separated from the solution by centrifugation. After drying in vacuo 1-tosyl-3-((trimethylsilyl)ethynyl)-1*H*-indole (2.79 g, 95%) was obtained as a colorless solid, Mp 160-162 °C, R_f = 0.42 (*n*-hexane/ethyl acetate 20:1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.28 (s, 9H), 2.34 (s, 3H), 7.22 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.27 – 7.31 (m, 1H), 7.33 – 7.37 (m, 1H), 7.62 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.74 – 7.79 (m, 3H), 7.96 (d, $^3J_{HH}$ = 8.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 0.16 (3 CH_3), 21.73 (CH_3), 95.90 (C_{quat}), 99.39 (C_{quat}), 105.34 (C_{quat}), 113.67 (CH), 120.73 (CH), 123.86 (CH), 125.60 (CH), 127.08 (2 CH), 129.58 (CH), 130.13 (2 CH), 130.98 (C_{quat}), 134.23 (C_{quat}), 135.05 (C_{quat}), 145.47 (C_{quat}). EI-MS (m/z (%)): 367 ([M]$^+$, 100), 352 ([$CH_{16}H_{18}NO_2SSi$]$^+$, 13), 212 ([$C_6H_4O_2S$]$^+$, 55),197 ([$C_{12}H_{11}NSi$]$^+$, 23), 196 (33) , 168 (21), 155 ([$C_7H_7O_2S$]$^+$, 21), 91 ([C_7H_7]$^+$, 44). IR: $\tilde{\nu}$ [cm^{-1}] 3676 (w), 3510 (w), 3140 (w), 3127 (w), 2959 (w), 2920 (w), 2156 (w), 1593 (w), 1445 (w), 1371, 1296 (w), 1275 (w), 1250 (w), 1219 (w), 1182 (m), 1134 (m), 1125 (m), 1094 (m), 1086 (w), 1016 (w), 974 (w), 856 (m), 841 (s), 810 (m), 754 (s), 702 (m), 669 (s), 648 (m), 613 (m).

3-Ethynyl-1-tosyl-1*H*-indole (**2e**)

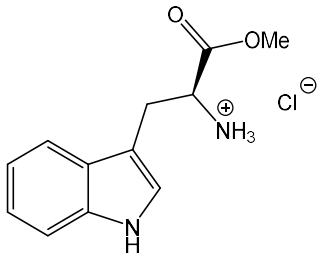


2e
$C_{17}H_{13}NO_2S$
[295.36]

At 0 °C TBAF (8 mL, 8.00 mmol, 1 M in THF) was added dropwise to a solution of 1-tosyl-3-((trimethylsilyl)ethynyl)-1*H*-indole (1.47 g, 8.00 mmol) in THF (3 mL) under oxygen atmosphere. After the cooling bath was removed, the solution was stirred at rt for 5 min. To the reaction mixture was added a saturated NH_4Cl solution (60 mL) and it was then extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried with Na_2SO_4, adsorbed onto Celite© under reduced pressure and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 20:1) to give compound **2e** (1.75 g, 74%) as a colorless solid, Mp 167-169 °C (Lit.: 162-164 °C) [3], R_f = 0.31 (*n*-hexane/ethyl acetate 10:1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.35 (s, 3H), 3.26 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 7.24 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.30 (td, $^3J_{HH}$

= 8.4 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.36 (ddd,$^3J_{HH}$ = 8.3, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.64 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.76-7.81 (m, 3H), 7.97 (d, $^3J_{HH}$ = 8.3 Hz, 1H). ^{13}C NMR: δ 21.74 (CH_3), 75.08 (C_{quat}), 81.66 (CH), 104.18 (C_{quat}), 113.70 (CH), 120.62 (CH), 123.95 (CH), 125.68 (CH), 127.10 (2CH), 130.06 (CH), 130.18 (2CH), 130.88 (C_{quat}), 134.20 (C_{quat}), 134.98 (C_{quat}), 145.56 (C_{quat}). EI-MS (m/z (%)): 296 ([M]$^+$, 13), 295 ([M]$^+$, 74), 155 ([$C_7H_7O_2S$]$^+$, 45), 141 (12), 140 ([$C_{10}H_6N$]$^+$, 100), 113 ([C_9H_5]$^{3+}$, 40), 91 ([C_7H_7]$^+$, 68), 87 (11), 65 (24), 63 (17). IR: $\tilde{\nu}$[cm^{-1}] 3260 (w), 3129 (w), 3059 (w), 1593 (w), 1541 (w), 1449 (w), 1398 (w), 1373 (m), 1331 (w), 1281 (w), 1223 (m), 1188 (m), 1173 (m), 1136 (m), 1121 (m), 1094 (m), 1080 (w), 1040 (w),1016 (w), 964 (m), 943 (w), 829 (w), 812 (m), 750 (s), 739 (m), 712 (m), 700 (m), 664 (s), 650 (m).

1.3. (*S*)-3-(1*H*-indol-3-yl)-1-methoxy-1-oxopropan-2-aminium chloride (3b) [4]



3b
$C_{12}H_{15}ClN_2O_2$
[254.71]

After suspending *S*-tryptophan (4.00 g, 19.60 mmol)) in MeOH (200 mL), $SOCl_2$ (3.6 mL, 49.00 mmol) was added slowly at a temperature of 0 °C under oxygen atmosphere. After removal of the cooling bath, the solution was heated to reflux for 4 h and subsequently the solvent was evaporated under reduced pressure to give compound **3b** (4.91 g, 98%) as a colorless solid, Mp 212-213 °C (Lit.: 214 °C) [4]. ^{1}H NMR (600 MHz, DMSO-d_6): δ 3.26 – 3.38 (m, 2H), 3.64 (s, 3H), 4.20 (dd, $^3J_{HH}$ = 6.8, 5.6 Hz, 1H), 7.01 (ddd, $^3J_{HH}$ = 7.9, 6.9 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.09 (ddd, $^3J_{HH}$ = 8.1, 6.9 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.25 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 7.37 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.51 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 8.67 (s, 3H), 11.09 – 11.18 (m, 1H). ^{13}C NMR (151 Hz, DMSO-d_6): δ 26.08, 52.60, 52.64, 106.32, 111.59, 118.04, 118.60, 121.14, 125.00, 126.89, 136.20, 169.74. EI-MS (m/z (%)): 218 ([M-HCl]$^+$, 131 (11), 130 ([C_9H_8N]$^+$, 100). IR: $\tilde{\nu}$ [cm^{-1}] 3264 (w), 3237 (w), 2997 (w), 2931 (w), 2928 (w), 2874 (w), 2857 (w), 2832 (w), 2818, (w) 2797 (w), 2770 (w), 2731 (w), 2710 (w), 2698 (w), 2683 (w), 2598 (w), 1748 (m), 1580 (w), 1504 (w), 1485 (w), 1460 (w), 1437 (w), 1387 (w), 1362 (w), 1352 (w), 1335 (w), 1285 (w), 1261 (w), 1229 (w), 1211 (w), 1180 (w), 1140 (w), 1126 (w), 1109 (w), 1074 (w), 1059 (w), 1007 (w), 982 (w), 939 (w), 889 (w), 864 (w), 820 (w), 754 (w), 731 (s), 704 (w), 662 (w), 638 (w), 608 (m).

1.4. Optimization of the aza-*Michael* addition

Ynone **6** (1.00 equiv) and the additive were dissolved in solvent (5 mL) followed by dropwise addition of a solution of tryptamine (**3a**) (1.00 equiv) in the same solvent (5 mL). The solution was stirred for the reaction temperature and time indicated (see Table S1). The conversion of the reaction was monitored by TLC (with reference to the corresponding enaminone **7**).

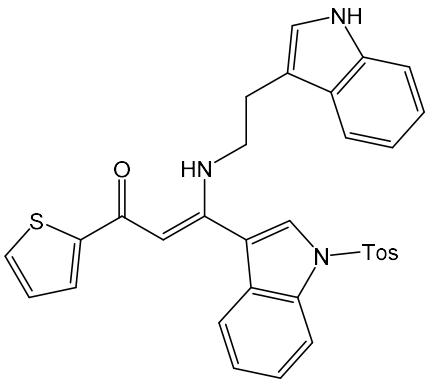
Table S1. Experimental data on the optimization screening of aza-*Michael* addition of selected ynones **6** with tryptamine (**3a**) to give enaminones **7**.

6 **7**

Entry	R^1	R^2	R^3	additive	solvent	temperature *T*	time *t*	conversion
1	nitrophenyl	TMS	H		DCM	50 °C	48 h	-
2	nitrophenyl	TMS	H	MeOH 1 equiv	DCM	50 °C	24 h	-
3	nitrophenyl	TMS	H	$ZnCl_2$ 10 mol%	DCM	50 °C	24 h	-
4	nitrophenyl	TMS	H	$AlCl_3$ 10 mol%	DCM	50 °C	24 h	-
5	nitrophenyl	phenyl	phenyl	$Yb(OTf)_3$ 10 mol%	DCM	rt	3 h	+
6	nitrophenyl	phenyl	phenyl	$Yb(OTf)_3$ 10 mol%	THF	rt	24 h	-
7	nitrophenyl	TMS	H	$Yb(OTf)_3$ 10 mol%	THF	rt	16 h	-
8	thiophenyl	butyl	butyl	$Yb(OTf)_3$ 1 mol%	THF	40-70 °C	16 h	-
9	nitrophenyl	TMS	H	$Yb(OTf)_3$ 5 mol%	CH_3CN	80 °C	2 h	+
10	nitrophenyl	TMS	H	$Yb(OTf)_3$ 4 mol%	CH_3CN	80 °C	2 h	+
11	nitrophenyl	TMS	H	$Yb(OTf)_3$ 3 mol%	CH_3CN	80 °C	2 h	+
12	nitrophenyl	TMS	H	$Yb(OTf)_3$ 2 mol%	CH_3CN	80 °C	2 h	+
13	nitrophenyl	TMS	H	$Yb(OTf)_3$ 1 mol%	CH_3CN	80 °C	2 h	+

– incomplete conversion. + full conversion. All results monitored by TLC.

1.5. (Z)-3-((2-(1*H*-Indol-3-yl)ethyl)amino)-1-(thiophen-2-yl)-3-(1-tosyl-1*H*-indol-3-yl)prop-2-en-1-one (7a)



5a
$C_{32}H_{27}N_3O_3S_2$
[565.71]

Ynone **6a** (406 mg, 1.00 mmol) and $Yb(OTf)_3$ (7 mg, 0.01 mmol) were dissolved in CH_3CN (5 mL) followed by dropwise addition of a solution of tryptamine (**3a**) (163 mg, 1.02 mmol) in CH_3CN (5 mL). The resulting solution was stirred for 4 h at a reaction temperature of 80 °C, then absorbed onto Celite© under reduced pressure and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 7:3) to give compound **5a** (521 mg, 92%) as a yellow solid, Mp 121-123 °C, R_f = 0.31 (hexane/ethyl acetate 7:3). ^{1}H NMR (600 MHz, DMSO-d_6): δ2.23 (s, 3H), 2.86 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 3.41 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.85 (s, 1H), 6.81 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.02 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.07 (d, $^3J_{HH}$ = 2.4 Hz, 1H), 7.11 (dd, $^3J_{HH}$ = 4.9, 3.7 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.26 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.29 – 7.33 (m, 2H), 7.41 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.51 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.72 (dd, $^3J_{HH}$ = 3.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.75 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 7.90 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.97 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 8.13 (s, 1H), 10.85 (s, 1H), 11.00 (t, $^3J_{HH}$ = 6.1 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 20.97 (CH_3), 26.38 (CH_2), 45.32 (CH_2), 92.90 (CH), 110.63 (C_{quat}), 111.34 (CH), 113.45 (CH), 116.92 (C_{quat}), 118.04 (CH), 118.24 (CH), 120.51 (CH), 120.95 (CH), 123.05 (CH), 124.32 (CH), 125.52 (CH), 126.73 (CH), 126.79 (C_{quat}), 126.94 (2 CH), 128.18 (C_{quat}), 128.24 (CH), 128.37 (CH), 130.30 (2 CH), 131.19 (CH), 133.69 (C_{quat}), 133.83 (C_{quat}), 136.19 (C_{quat}), 145.83 (C_{quat}), 147.07 (C_{quat}), 157.24 (C_{quat}), 180.44 (C_{quat}). EI-MS (70 eV): m/z (%) 565 ([M]$^+$, 2), 436 ([$C_{23}H_{19}N_2O_3S_2$]$^+$, 11), 435 ([$C_{23}H_{19}N_2O_3S_2$]$^+$, 40), 425 (13), 424 (26), 423 (100), 410 ([$C_{25}H_{20}N_3OS$]$^+$, 23), 281 (15), 280 (13), 267 (21), 144 ([$C_{10}H_{10}N$]$^+$, 13), 143 ([$C_{10}H_{10}N$]$^+$, 39), 130 ([C_9H_8N]$^+$, 42), 111 ([C_5H_3OS]$^+$, 79), 97 (55), 91 ([C_7H_7]$^+$, 24), 44 (26). IR: $\tilde{\nu}$ [cm^{-1}] 3319 (s), 3306 (s), 3294 (s), 3281 (s), 3051 (s), 2920 (s), 1587 (w), 1568 (m), 1547 (m), 1520 (m), 1489 (m), 1445 (m), 1418 (m), 1375 (m), 1360 (m), 1339 (m), 1319 (m), 1306 (m), 1287 m), 1269(m), 1231 (m), 1206 (m), 1171 (w), 1134 (m), 1121 (m), 1088 (w), 1063 (m), 1001 (m), 951 (m), 920(s), 899 (s), 876 (s), 853 (s), 810 (m), 733 (w), 712 (m), 702 (w), 685 (m), 662 (w), 635 (s).

2. NMR spectra

THBC **5** (especially compounds **5g** and **5l**) tend to form solvates of solvents used in the chromatographic purification. This is seen in the recorded NMR spectra by corresponding signals of diethyl ether or ethyl acetate. Even prolonged heating at 100 °C (oil bath) under vacuum ($1 \cdot 10^{-3}$ mbar) for several days did not remove these solvates.

2.1. 3-Iodo-1-tosyl-1*H*-indole

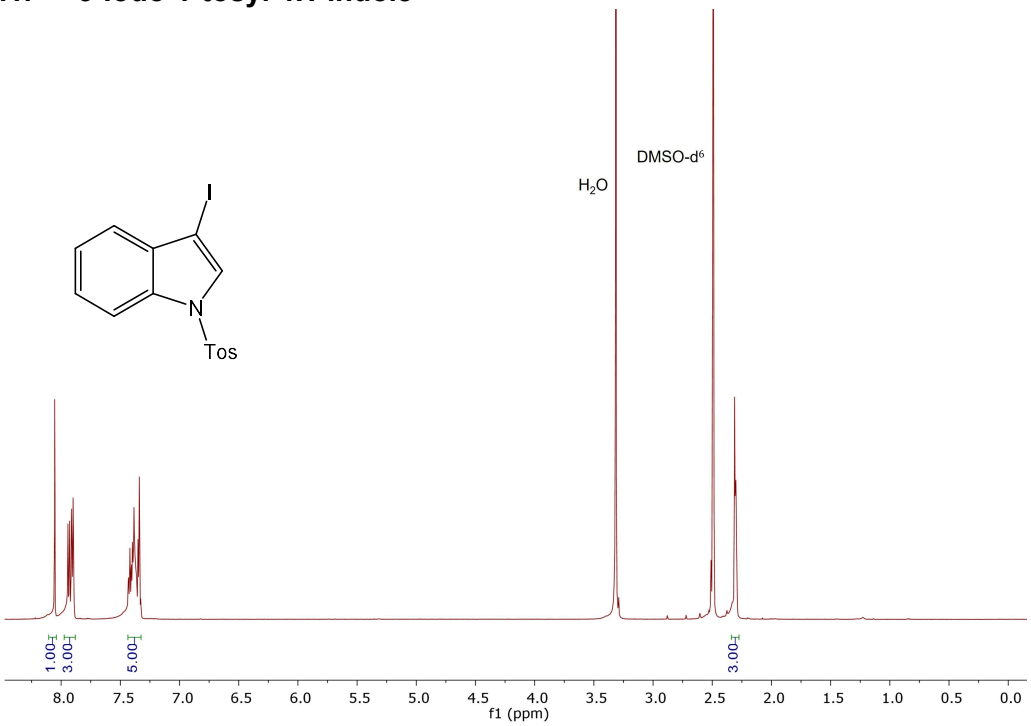


Figure S1. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of 3-iodo-1-tosyl-1*H*-indole.

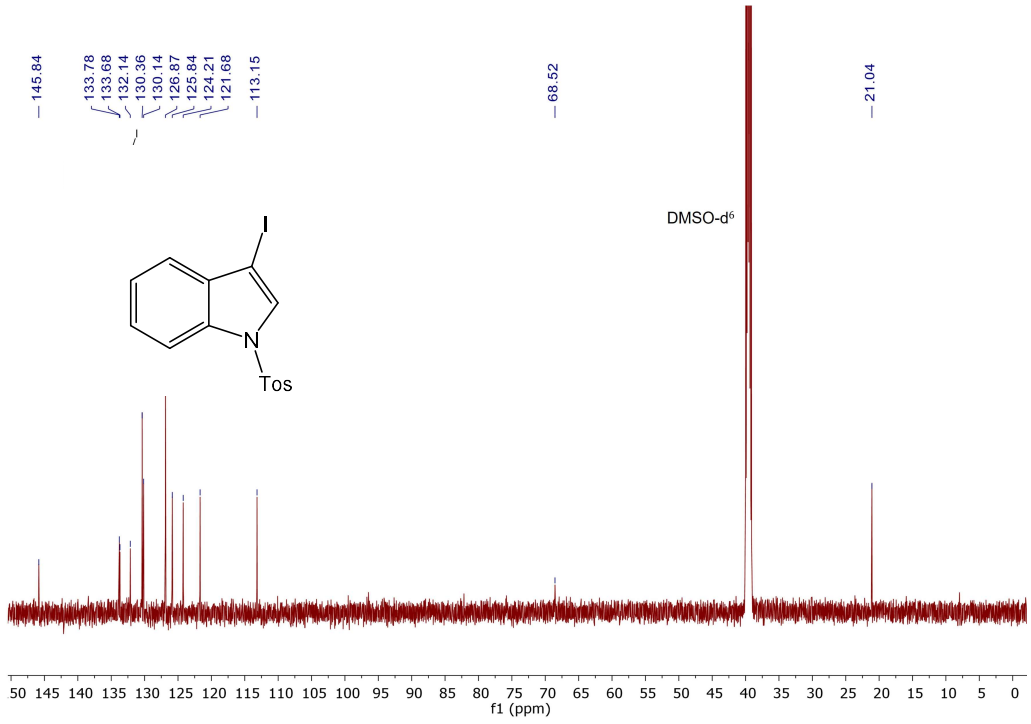


Figure S2. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of 3-iodo-1-tosyl-1*H*-indole.

2.2. 1-Tosyl-3-((trimethylsilyl)ethynyl)-1*H*-indole

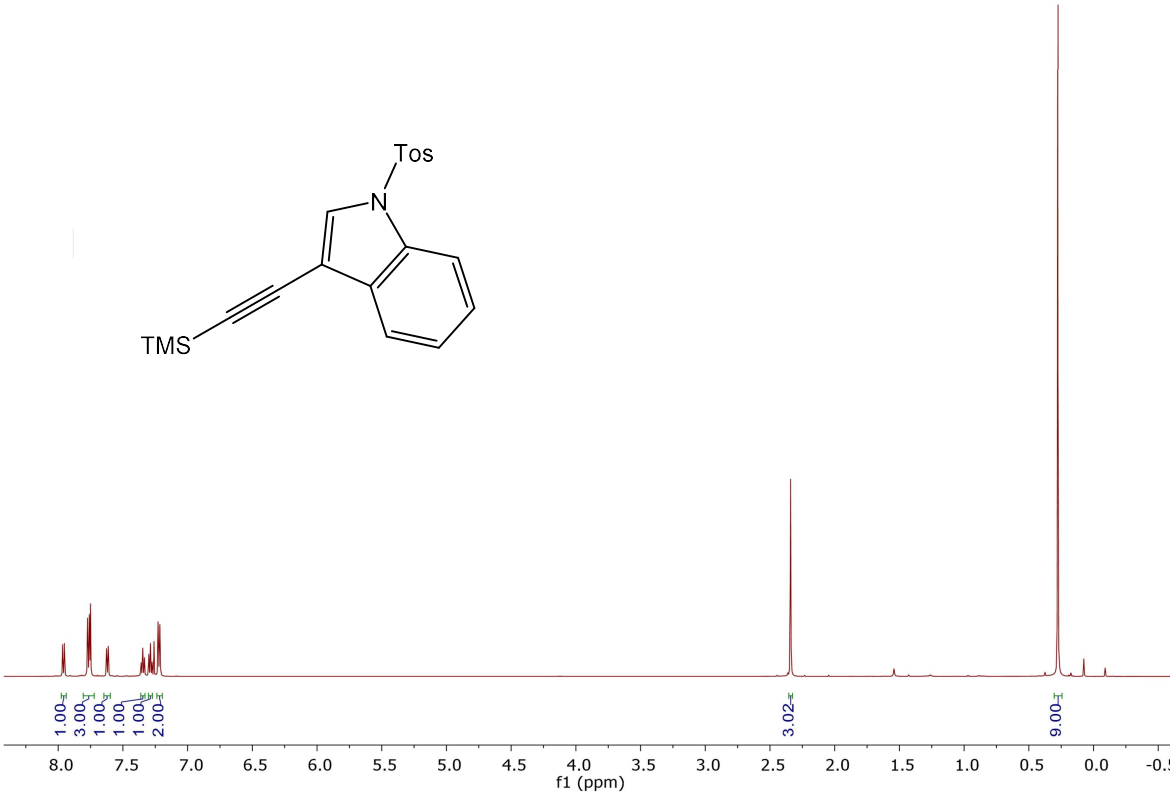


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 1-tosyl-3-((trimethylsilyl)ethynyl)-1*H*-indole.

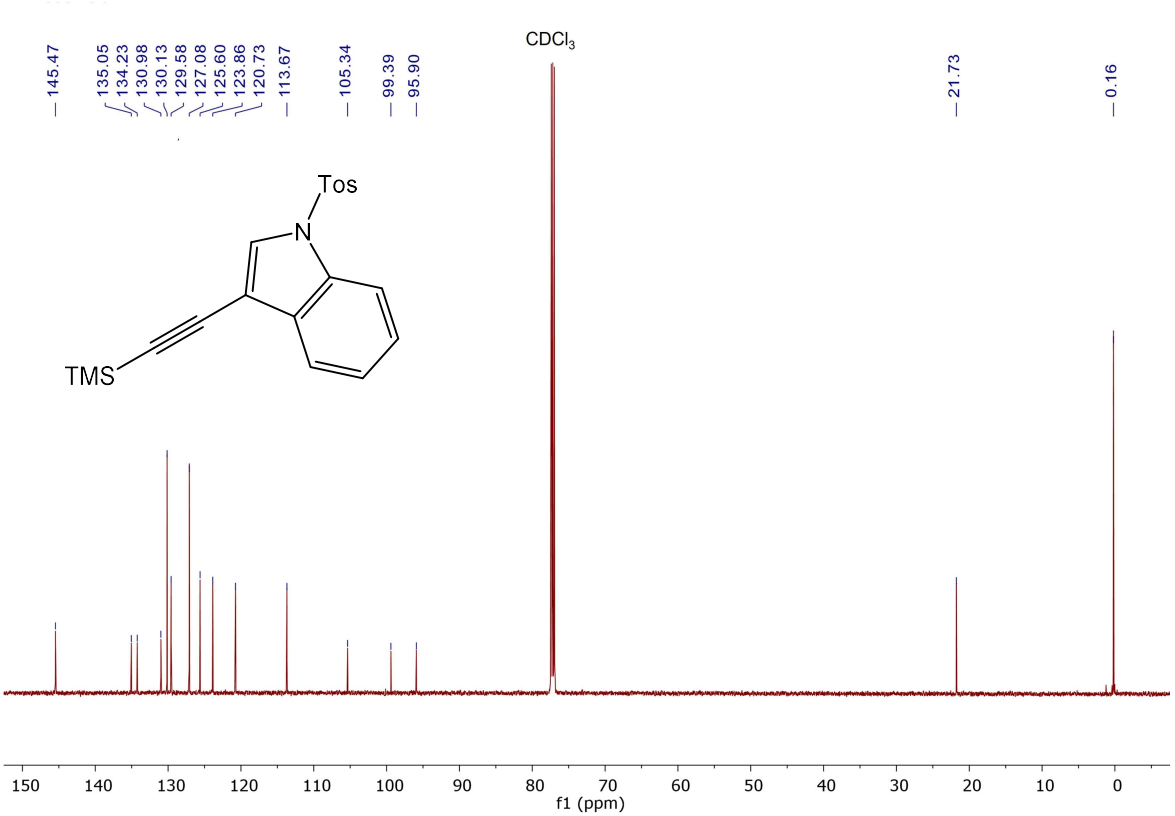


Figure S4. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of 1-tosyl-3-((trimethylsilyl)ethynyl)-1*H*-indole.

2.3. 3-Ethynyl-1-tosyl-1*H*-indole (2e)

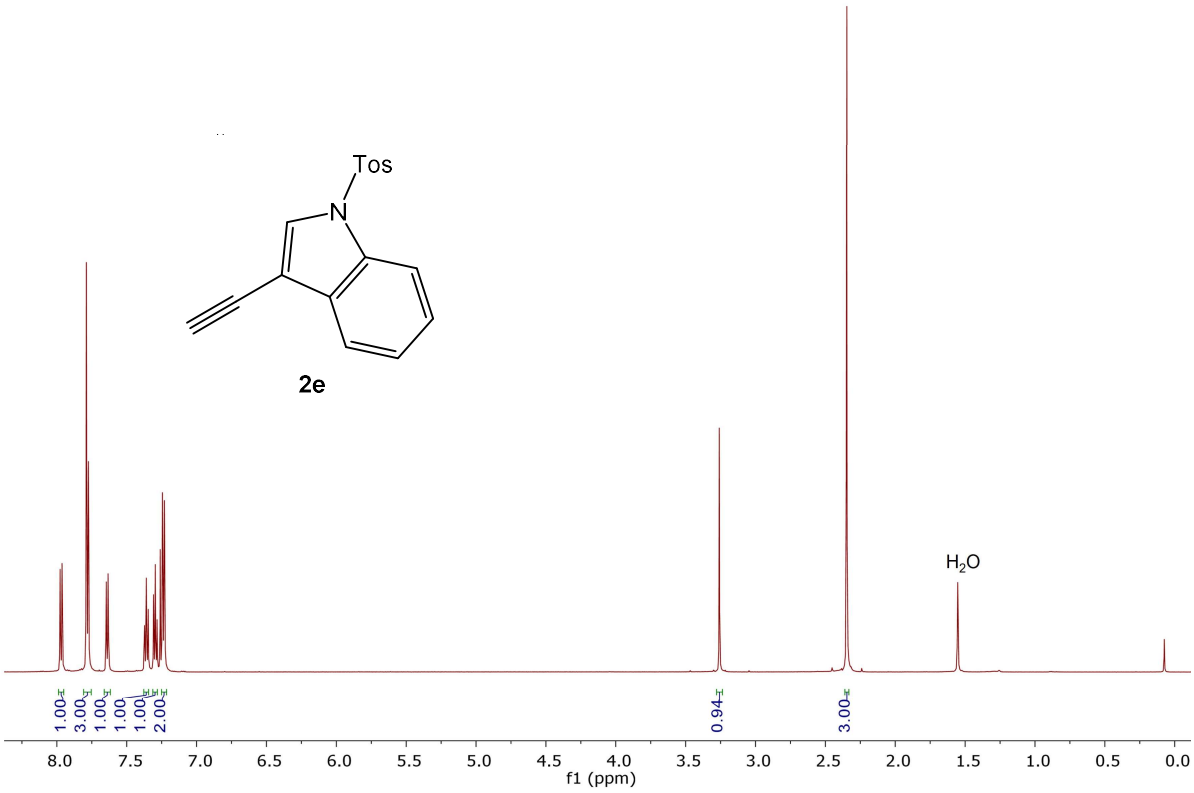


Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **2e**.

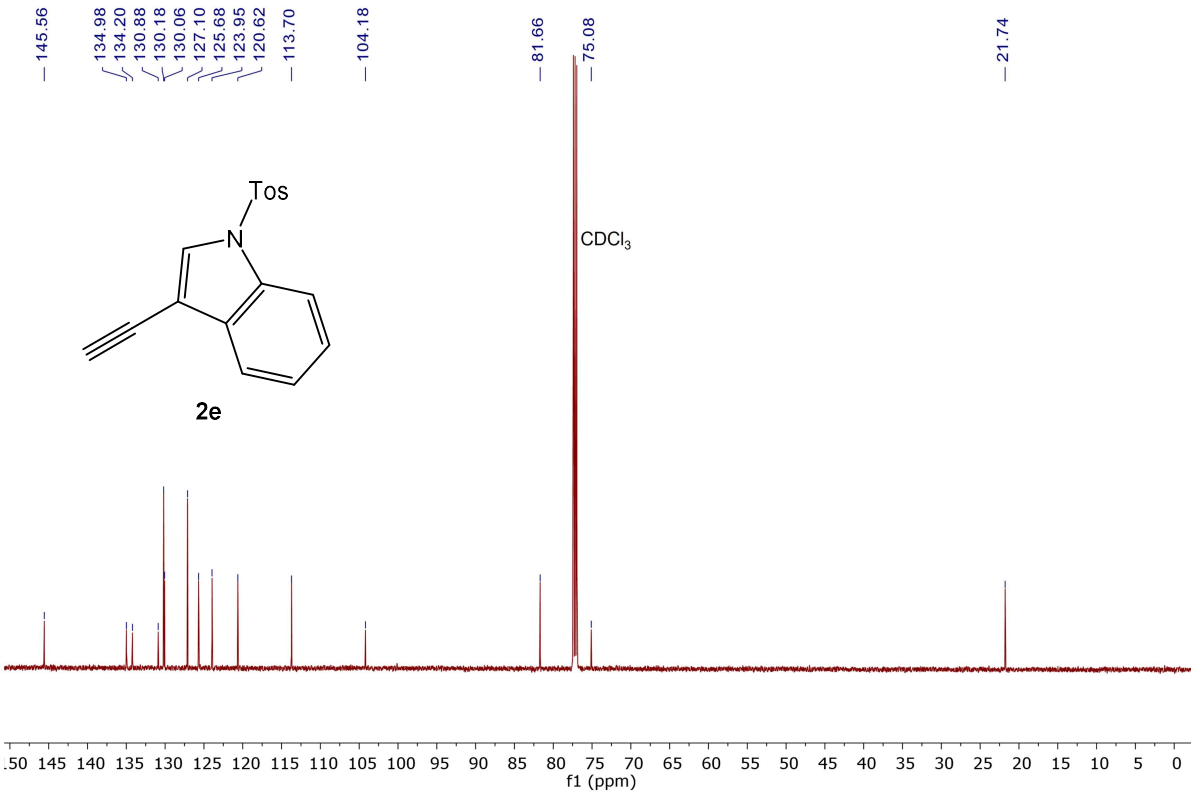


Figure S6. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **2e**.

2.4. (*S*)-3-(1*H*-indol-3-yl)-1-methoxy-1-oxopropan-2-aminium chloride (3c)

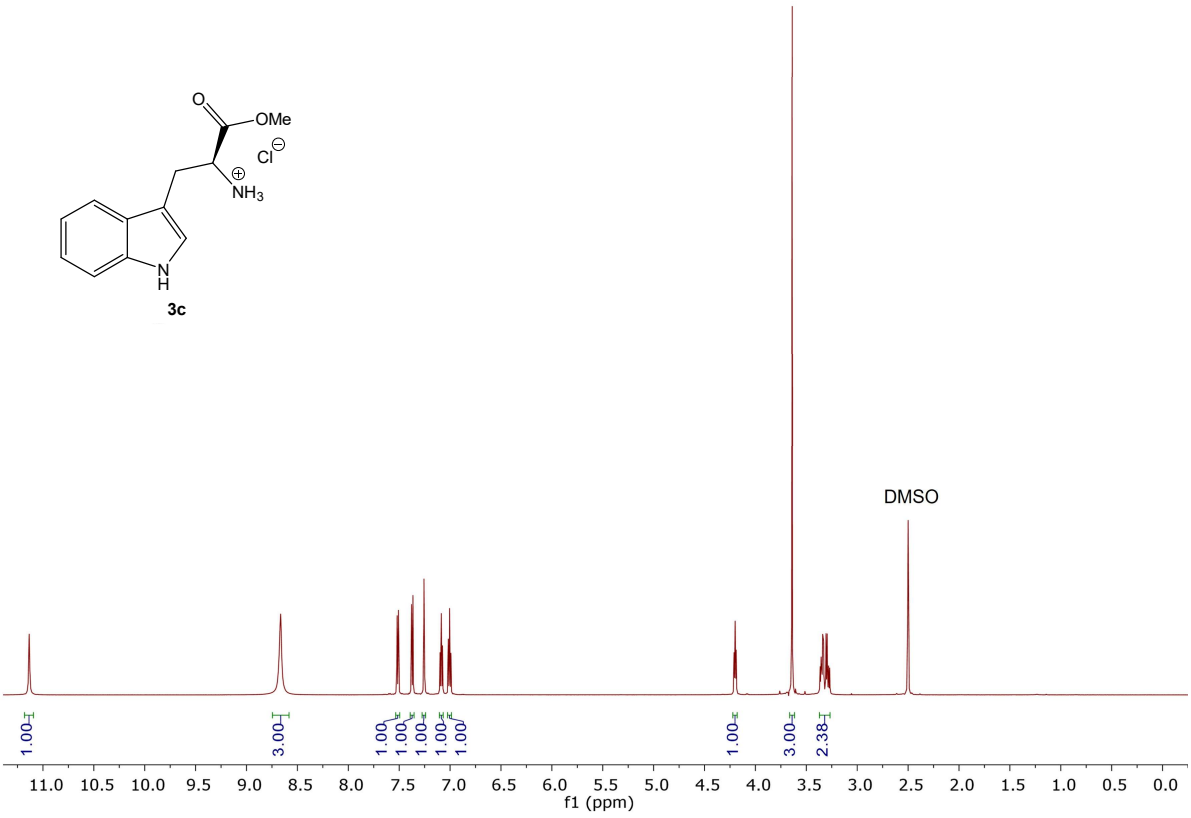


Figure S7. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **3c**.

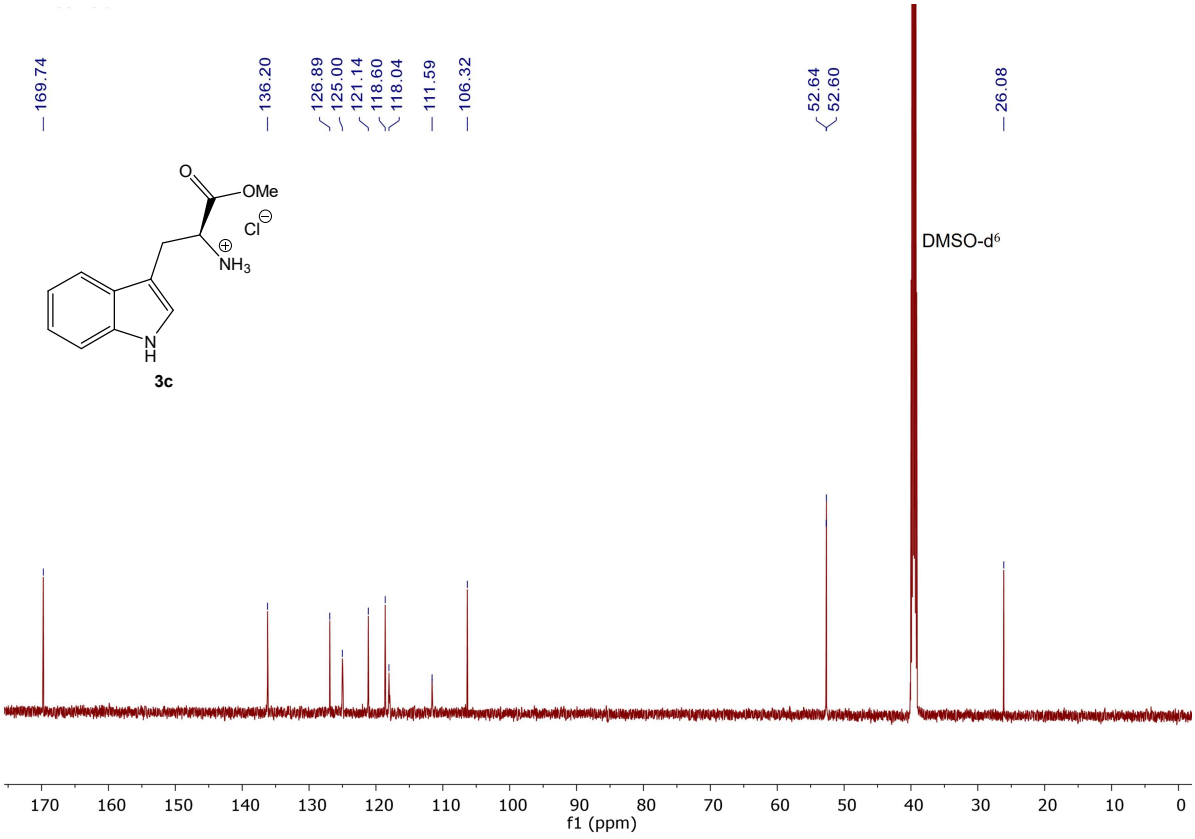


Figure S8. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of compound **3c**.

2.5. (*Z*)-3-((2-(1*H*-Indol-3-yl)ethyl)amino)-1-(thiophen-2-yl)-3-(1-tosyl-1*H*-indol-3-yl)prop-2-en-1-one (7a)

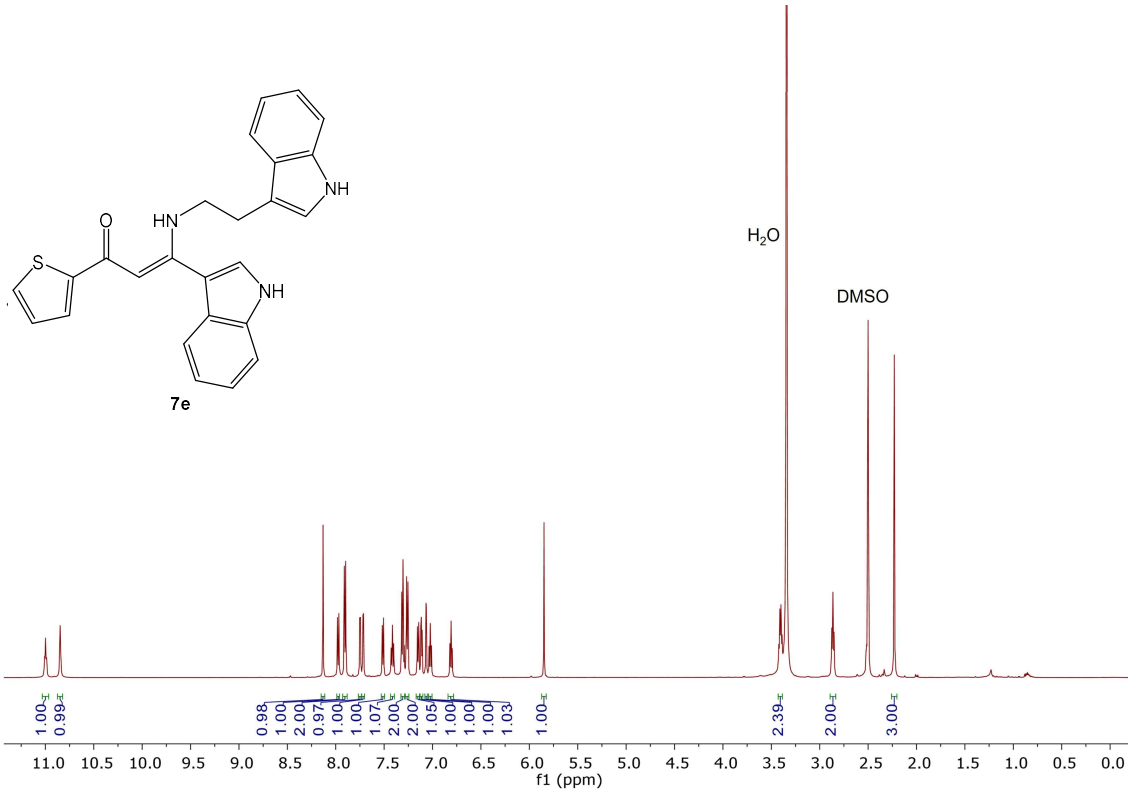


Figure S9. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **7a**.

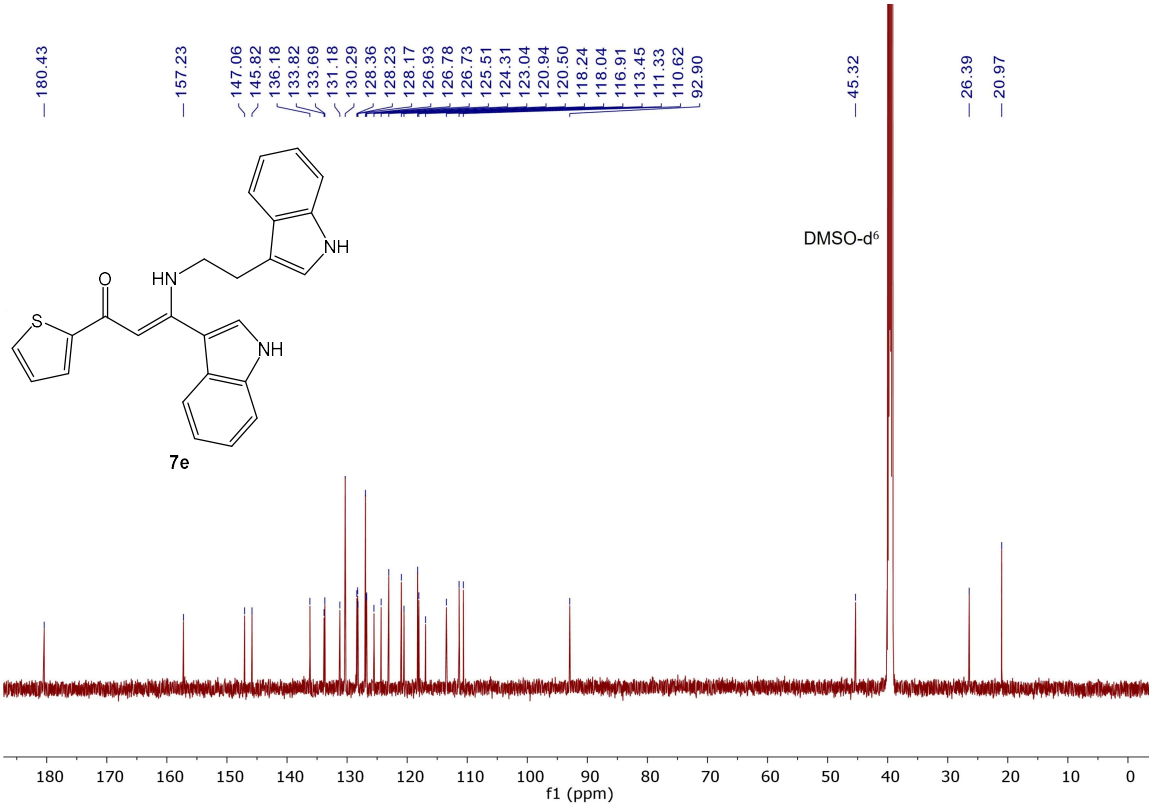


Figure S10. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of compound **7a**.

2.6. *rac*-12b-Butyl-1-(thiophene-2-carbonyl)-2,3,6,7,12,12b-hexahydroindolo-[2,3-*a*]quinolizin-4-one (5a)

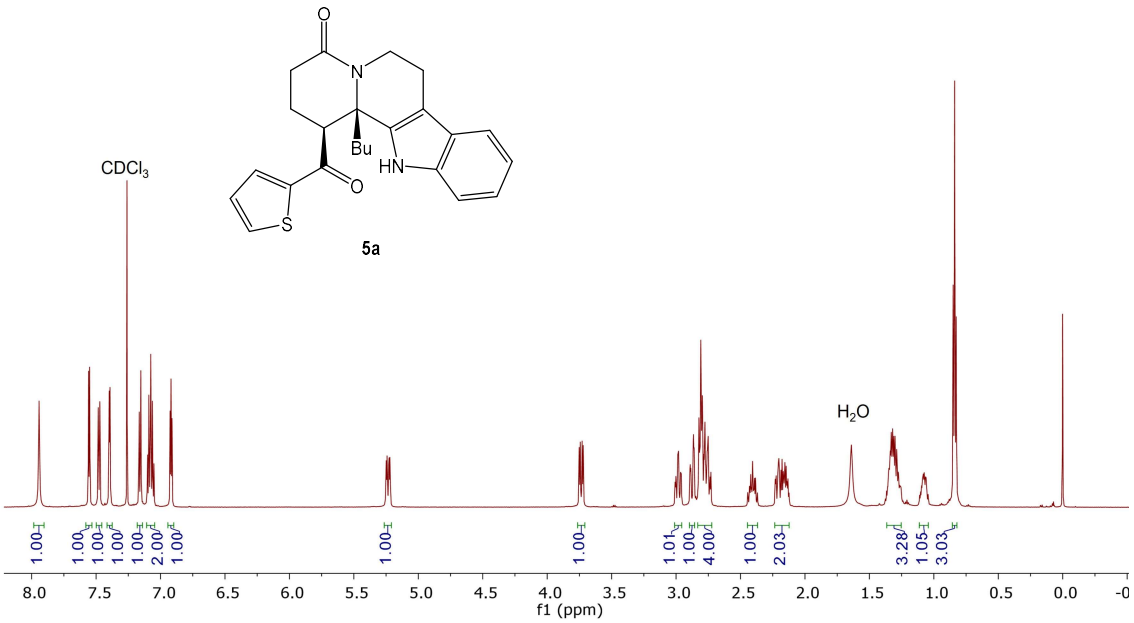


Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5a**.

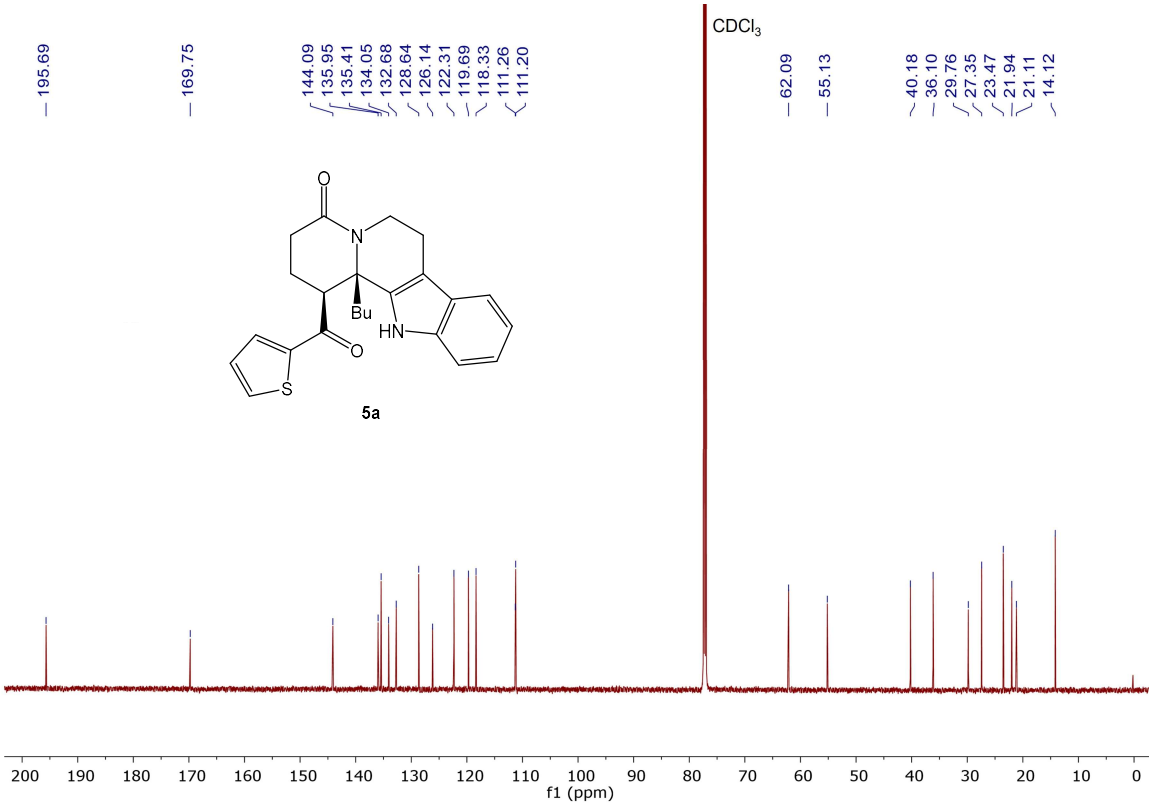


Figure S12. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5a**.

2.7. *rac*-1-Benzoyl-12b-butyl-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5b)

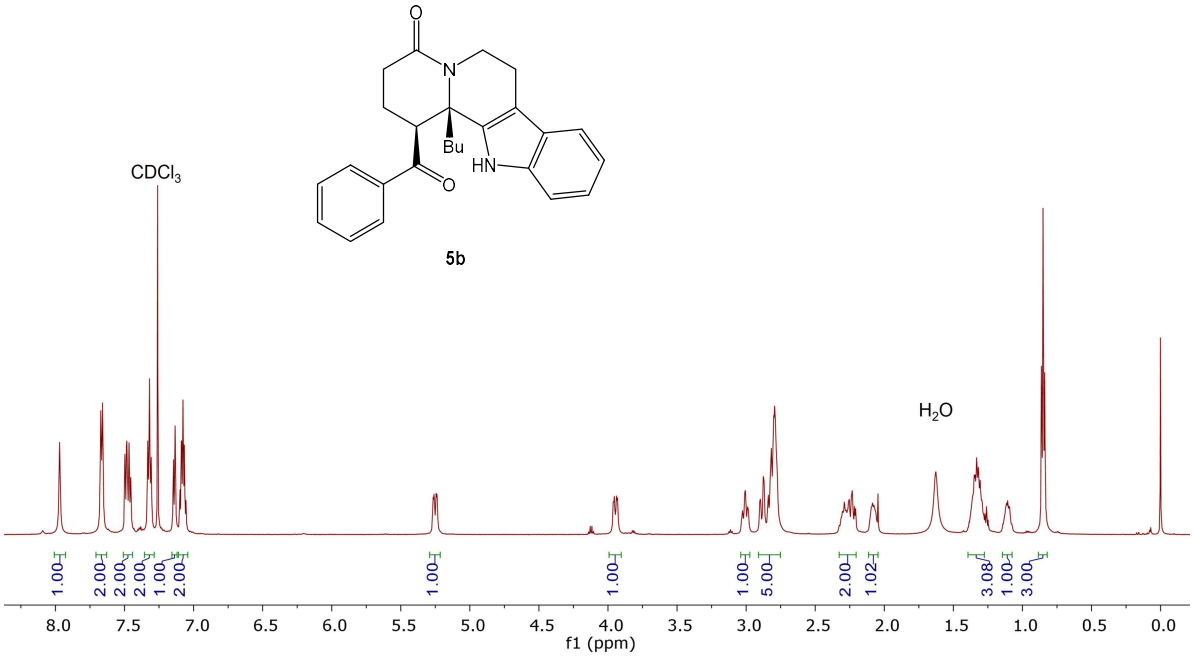


Figure S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5b**.

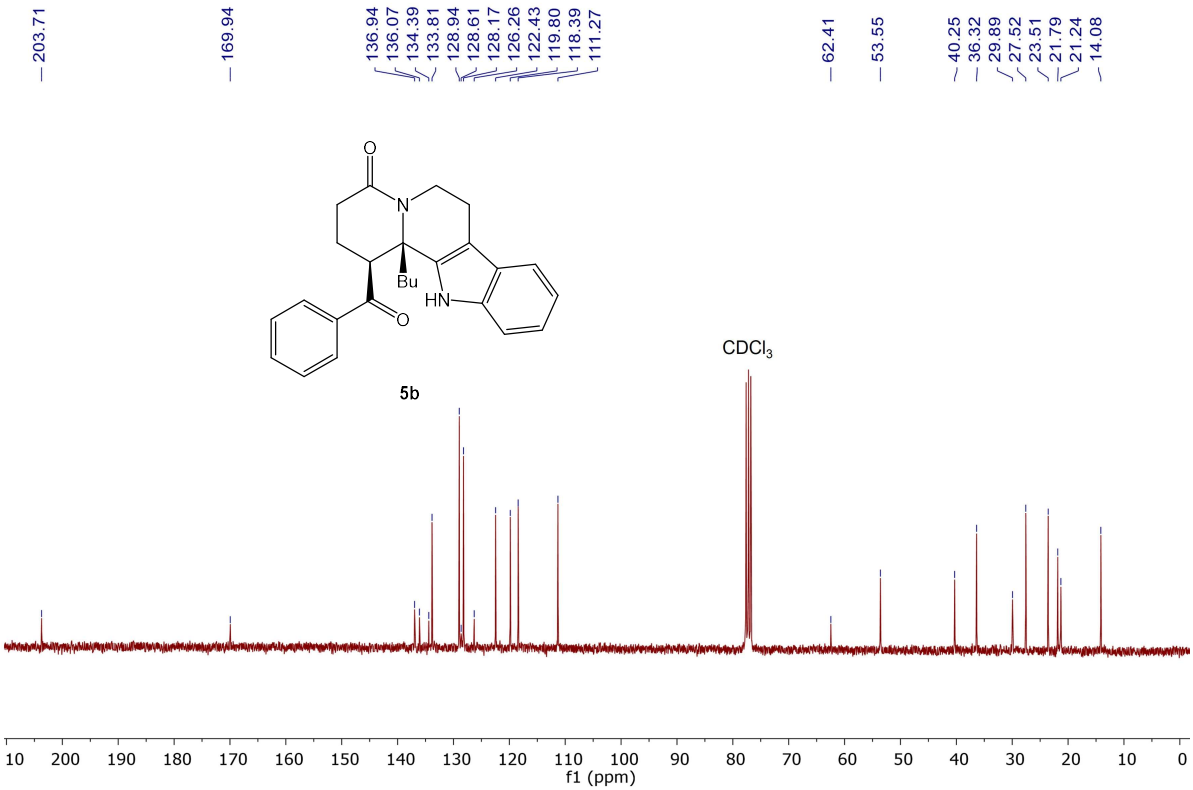


Figure S14. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5b**.

2.8. *rac*-12b-Butyl-1-(4-methylbenzoyl)-2,3,6,7,12,12b-hexahydroindolo-[2,3-*a*]quinolizin-4(1*H*)-one (5c)

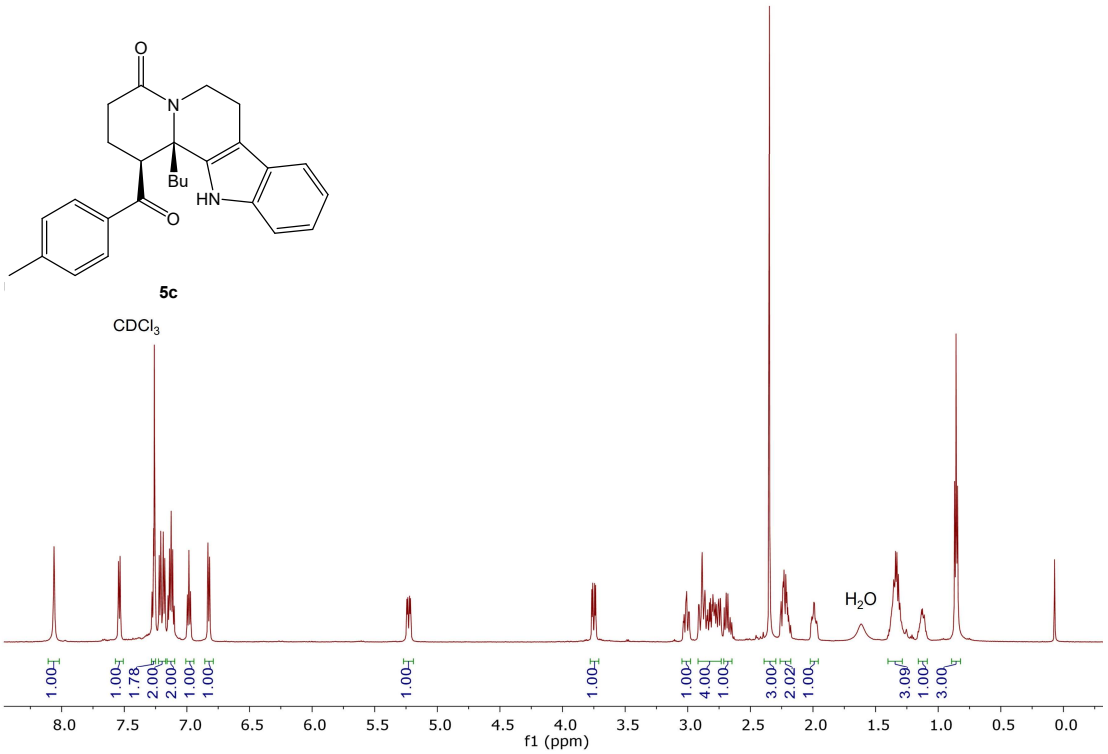


Figure S15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5c**.

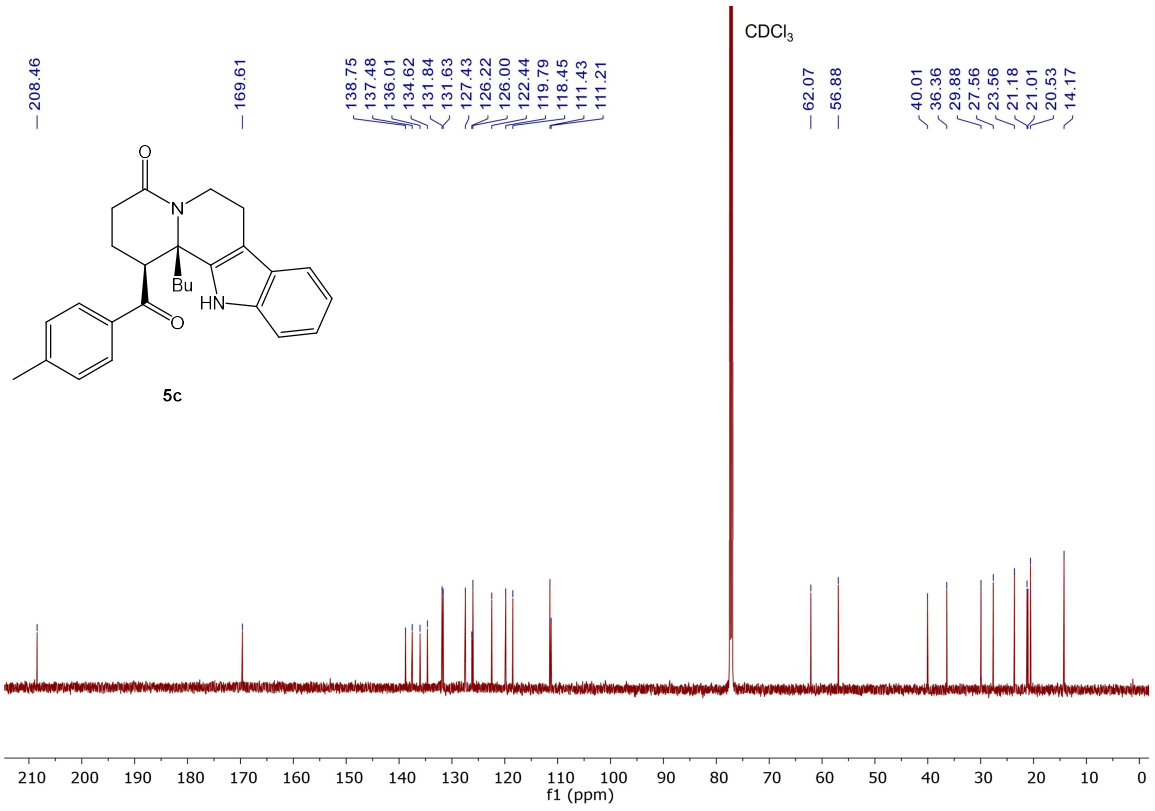


Figure S16. ^{13}H NMR spectrum (151 MHz, $CDCl_3$) of compound **5c**.

2.9. *rac*-12b-Butyl-1-(4-methoxybenzoyl)-2,3,6,7,12,12b-hexahydroindolo-[2,3*a*]quinolizin-4(1*H*)-one (5d)

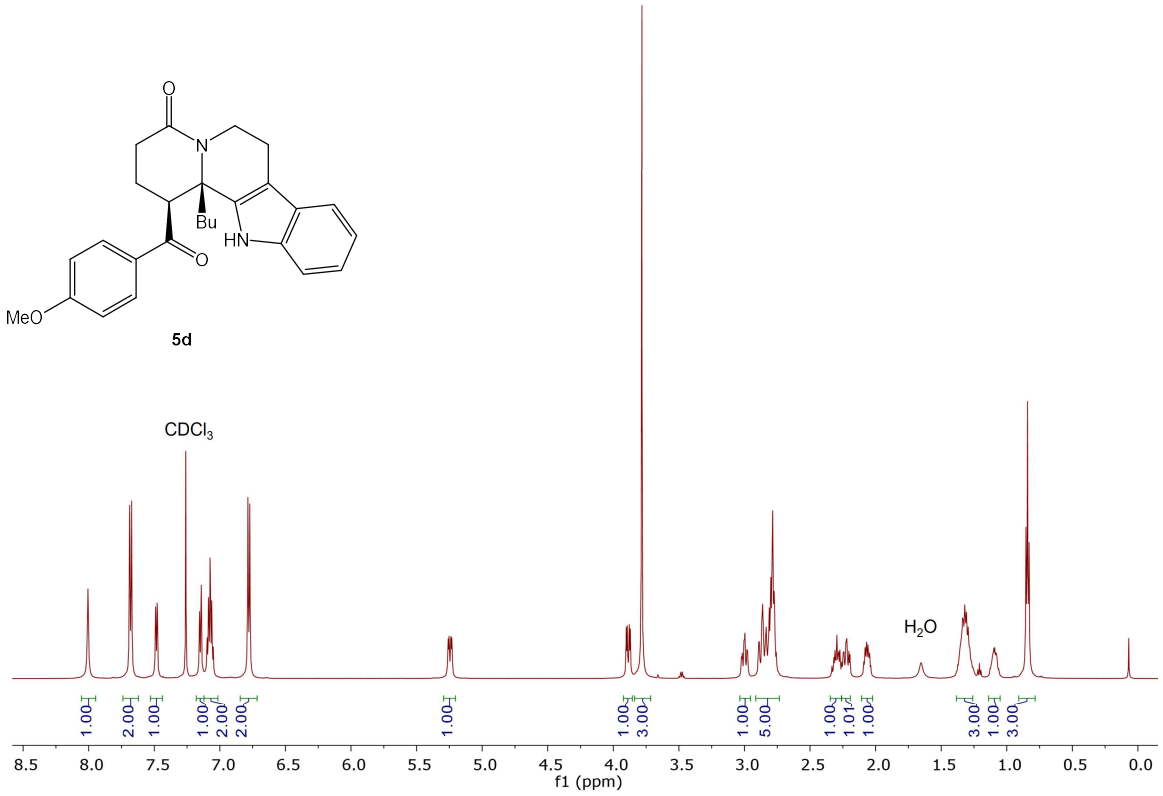


Figure S17. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5d**.

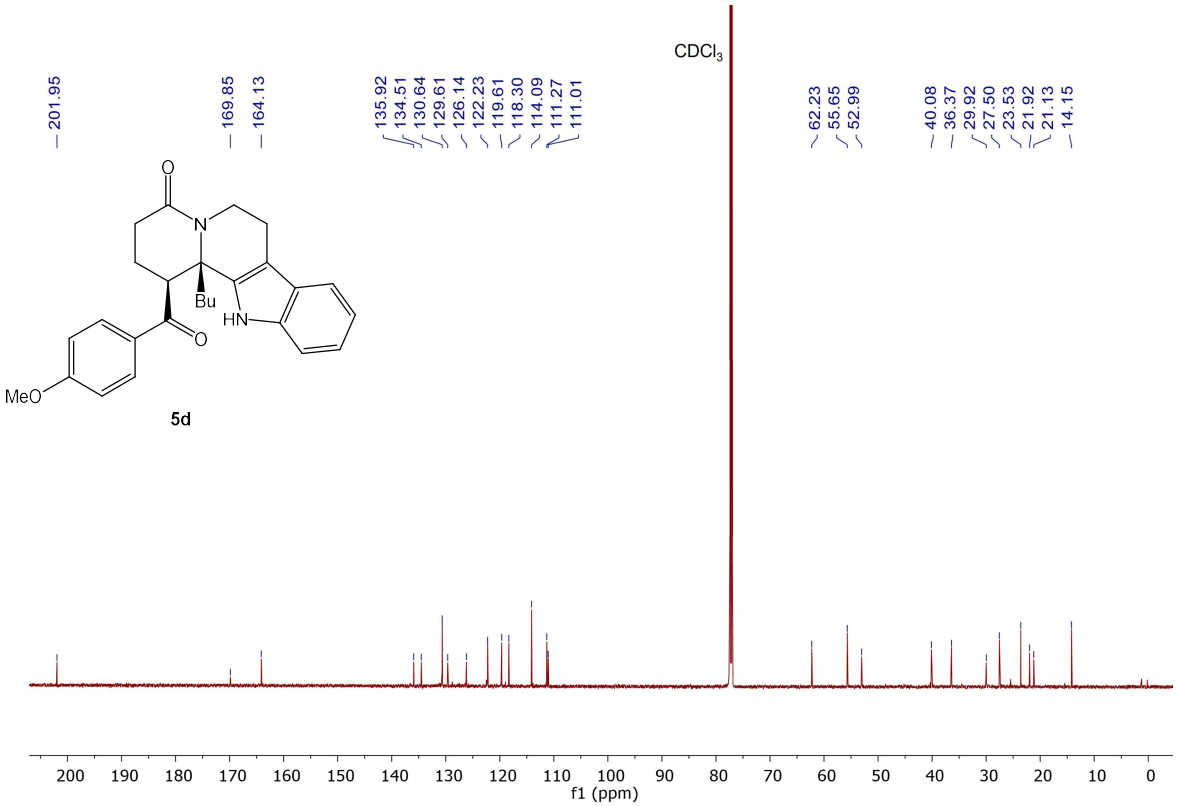


Figure S18. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5d**.

2.10. *rac*-12b-Butyl-1-(6-chloronicotinoyl)-2,3,6,7,12,12b-hexahydroindolo-[2,3*a*]quinolizin-4(1*H*)-one (5e)

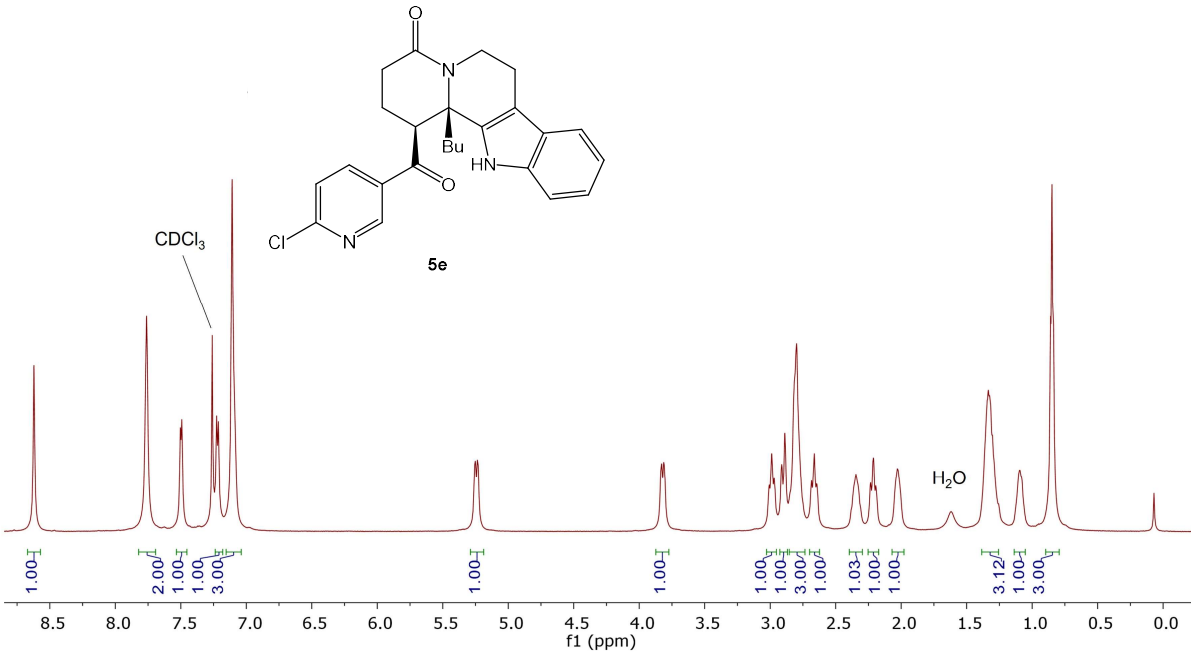


Figure S19. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5e**.

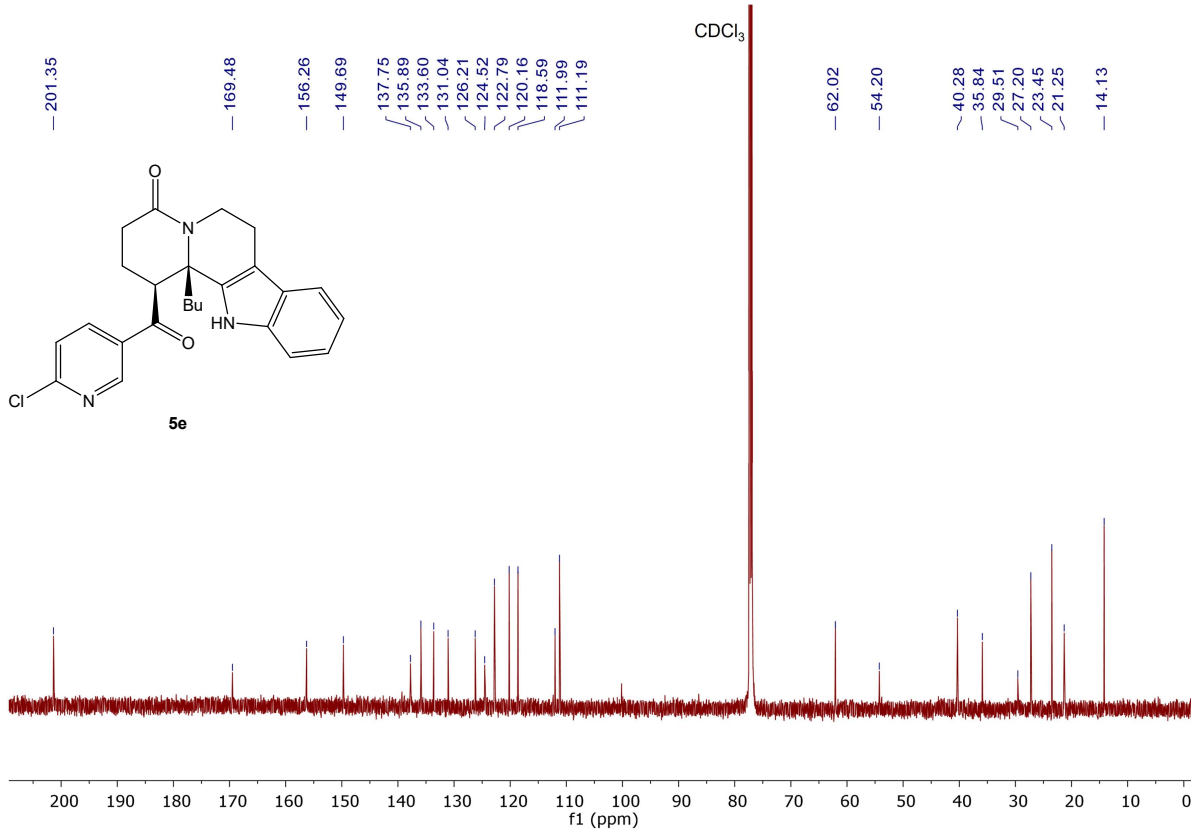


Figure S20. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5e**.

2.11. *rac*-1-(4-Bromobenzoyl)-12b-butyl-2,3,6,7,12,12b-hexahydroindolo-[2,3-*a*]quinolizin-4(1*H*)one (5f)

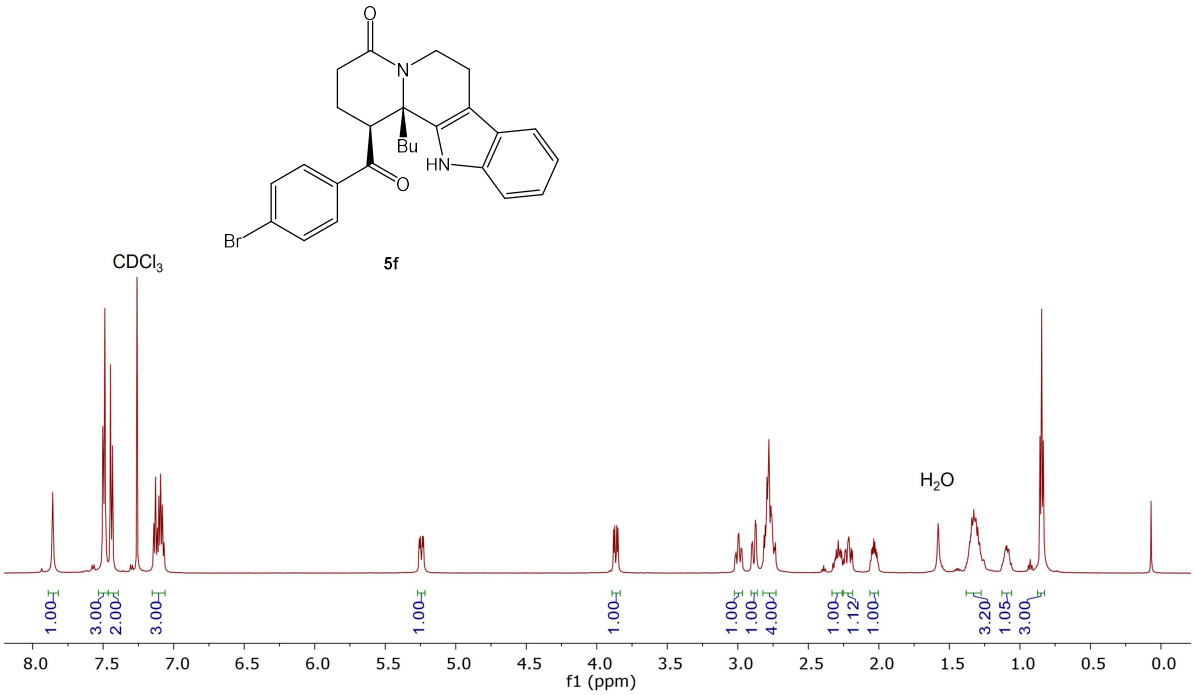


Figure S21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5f**.

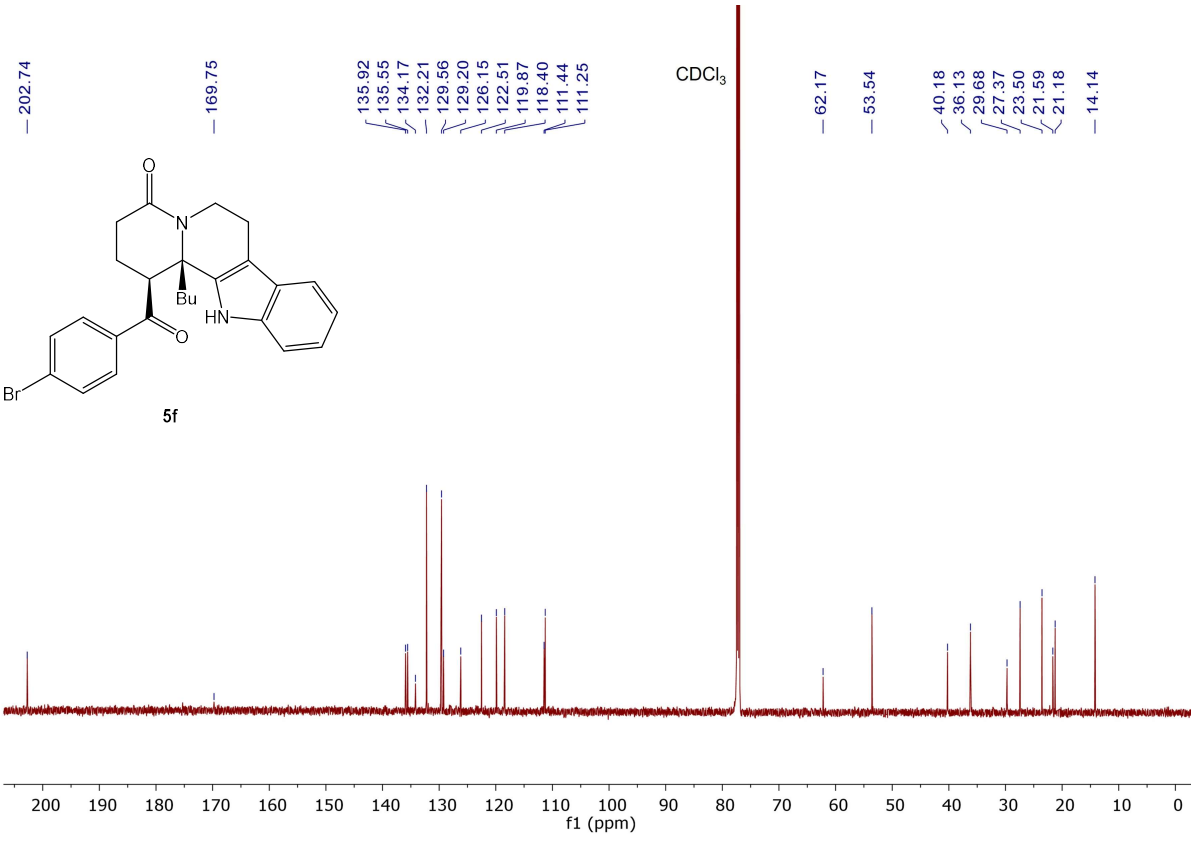


Figure S22. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5f**.

2.12. *rac*-12b-Butyl-1-(2-fluorobenzoyl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]-quinolizin-4(1*H*)one (5g)

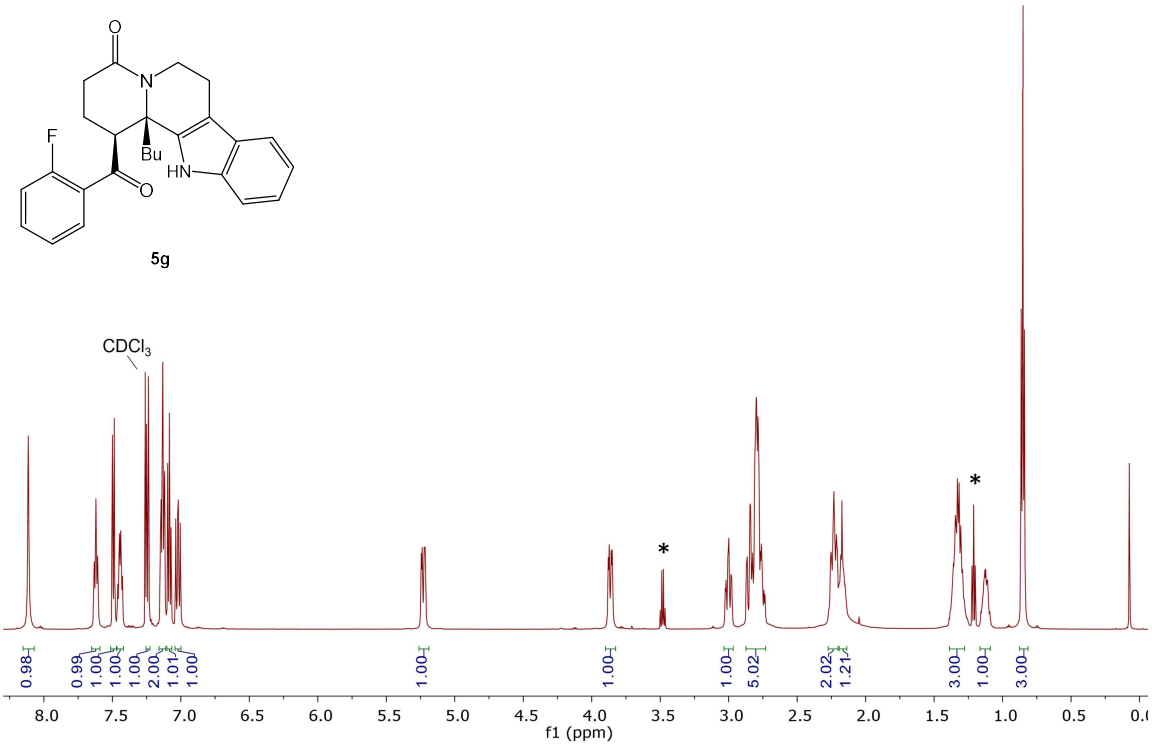


Figure S23. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5g**. * Impurities from residual solvent.

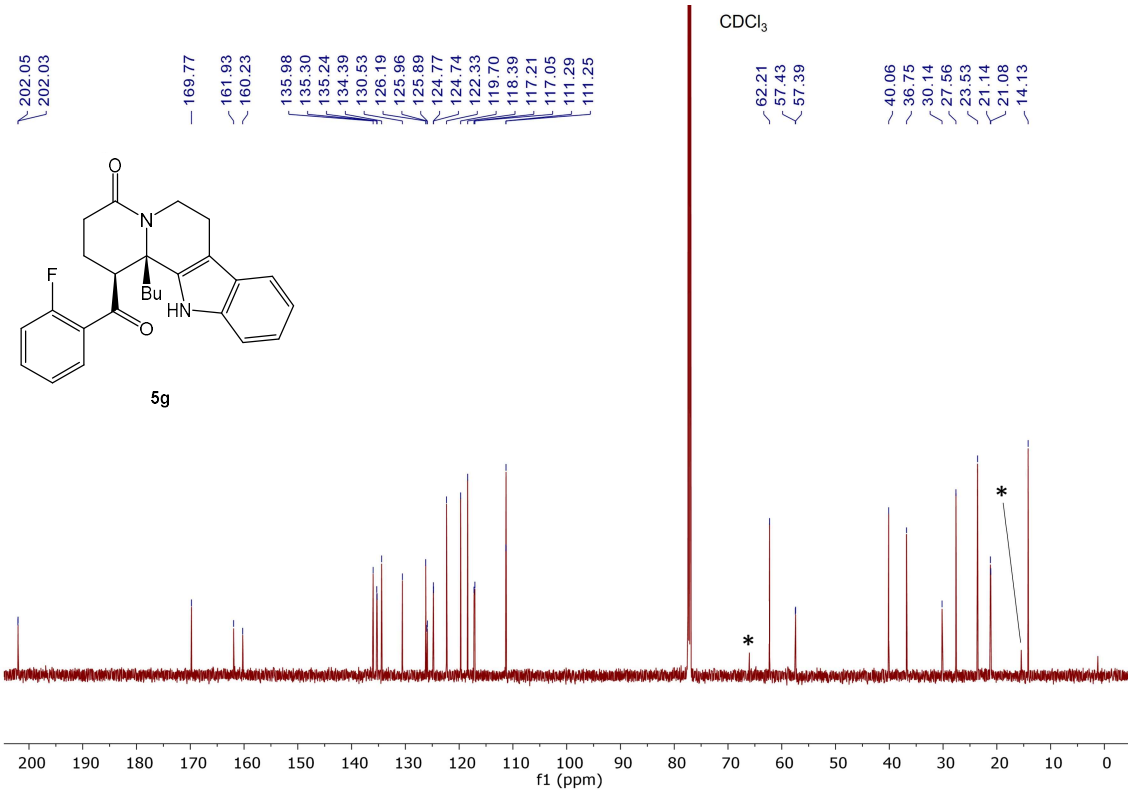


Figure S24. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5g**. * Impurities from residual solvent.

2.13. *rac*-12b-Butyl-1-(4-nitrobenzoyl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]-quinolizin-4(1*H*)-one (5h)

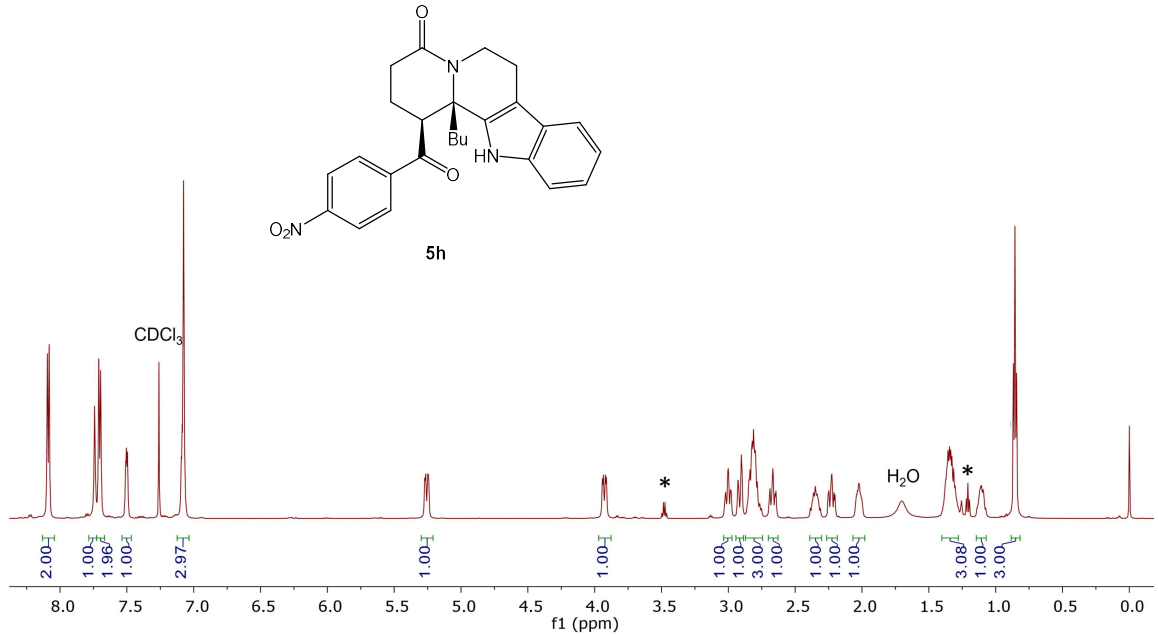


Figure S25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5h**. * Impurities from residual solvent.

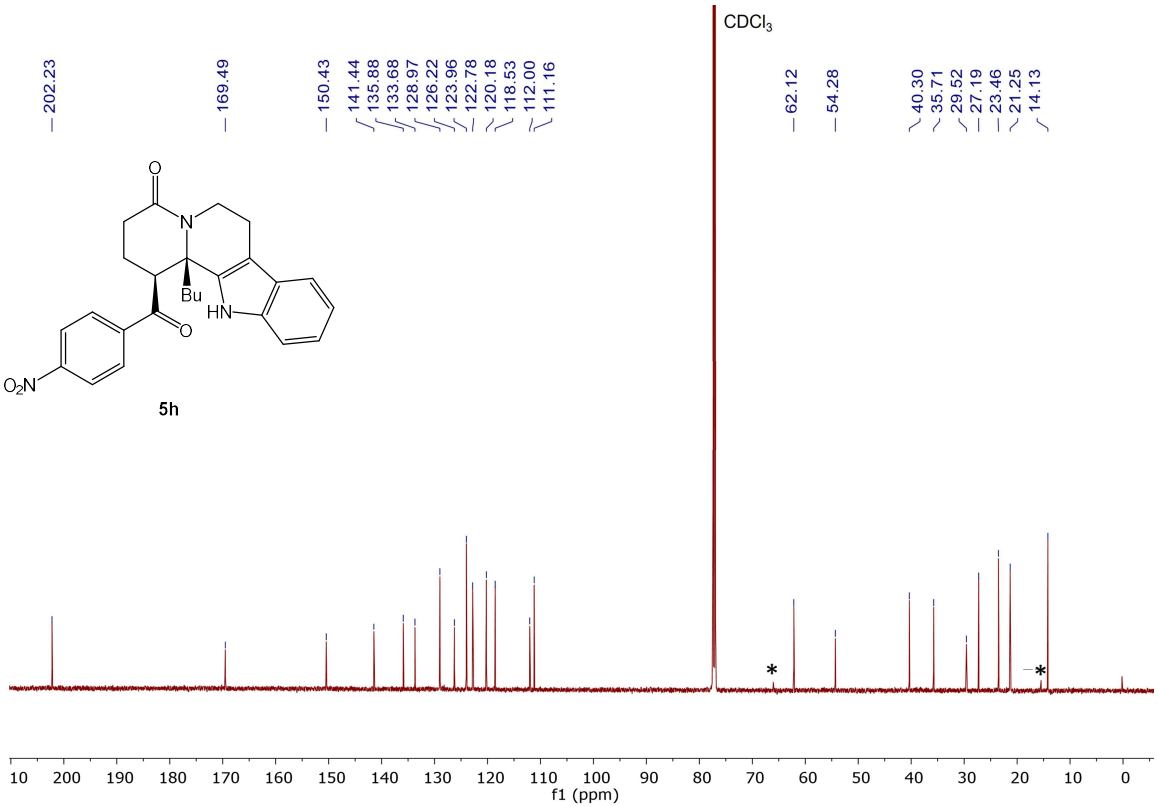


Figure S26. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5h**. * Impurities from residual solvent.

2.14. *rac*-12b-Phenyl-1-(thiophene-2-carbonyl)-2,3,6,7,12,12b-hexahydroindolo-[2,3-*a*]quinolizin-4(1*H*)-one (5i)

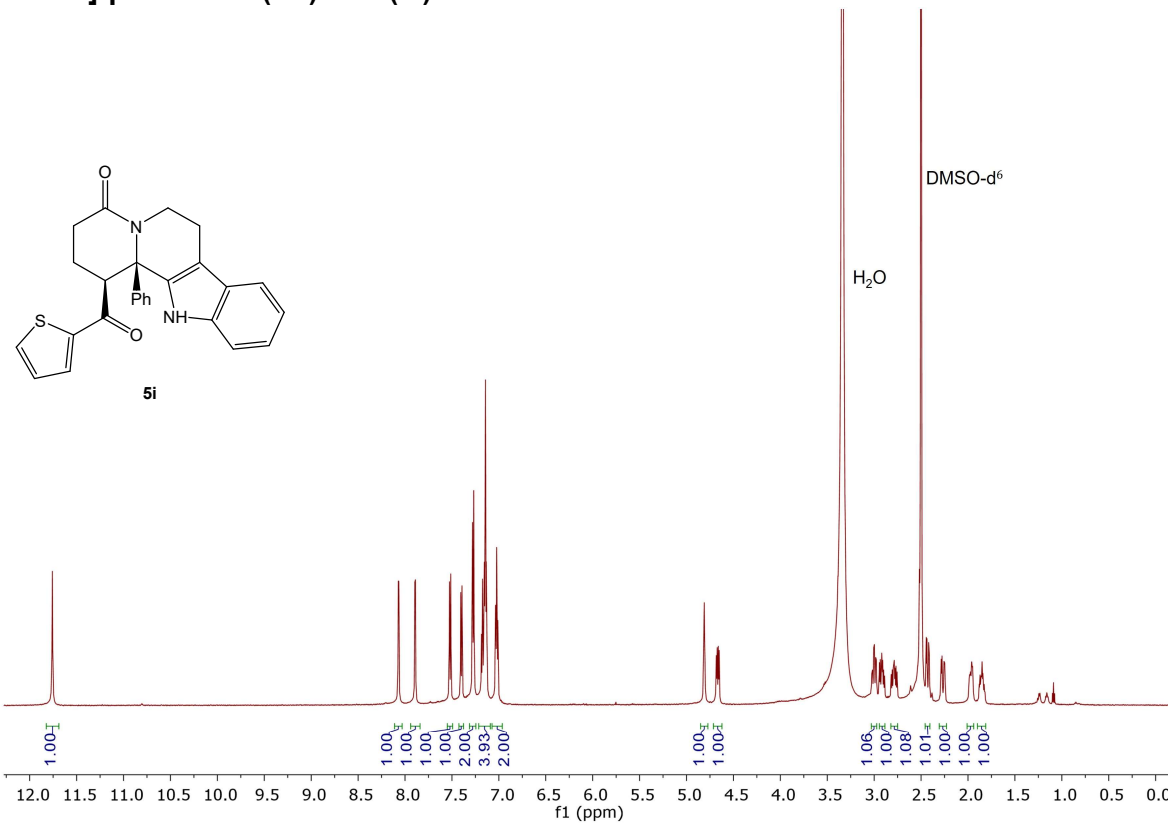


Figure S27. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5i**.

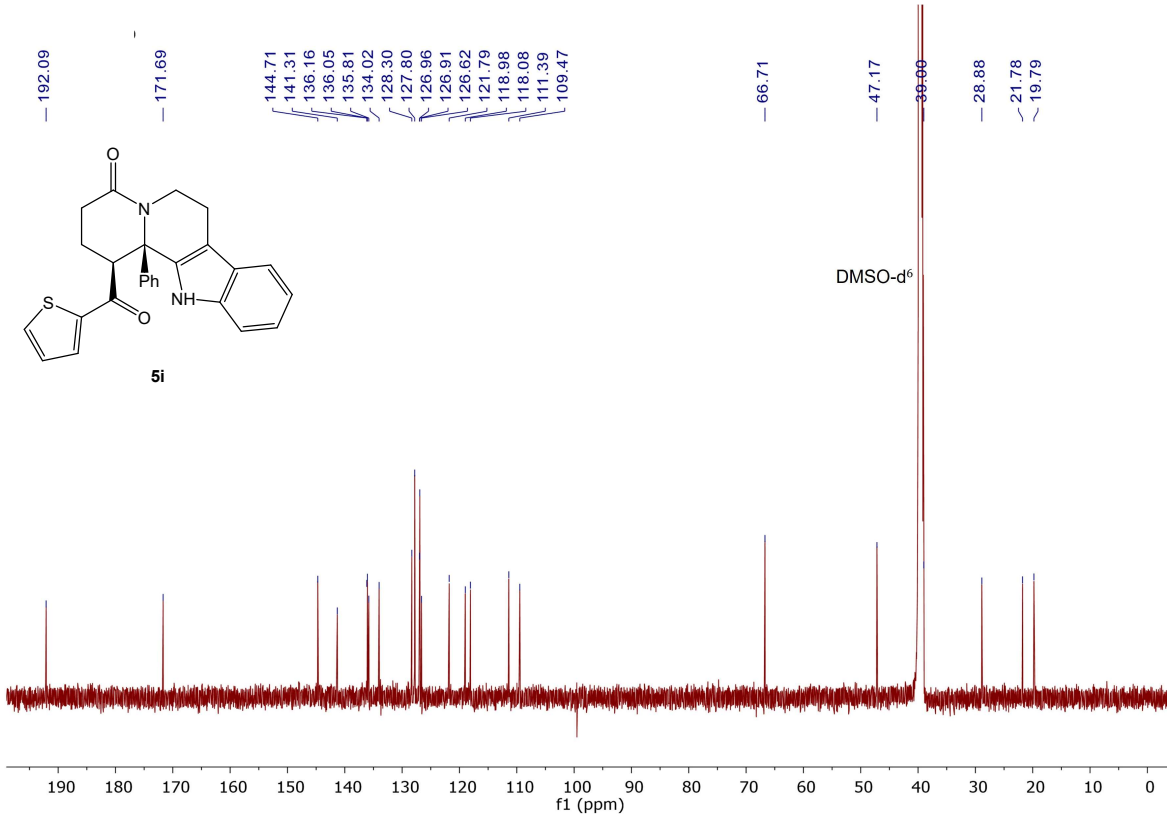


Figure S28. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5i**.

2.15. *rac*-1-(4-Methoxybenzoyl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5j)

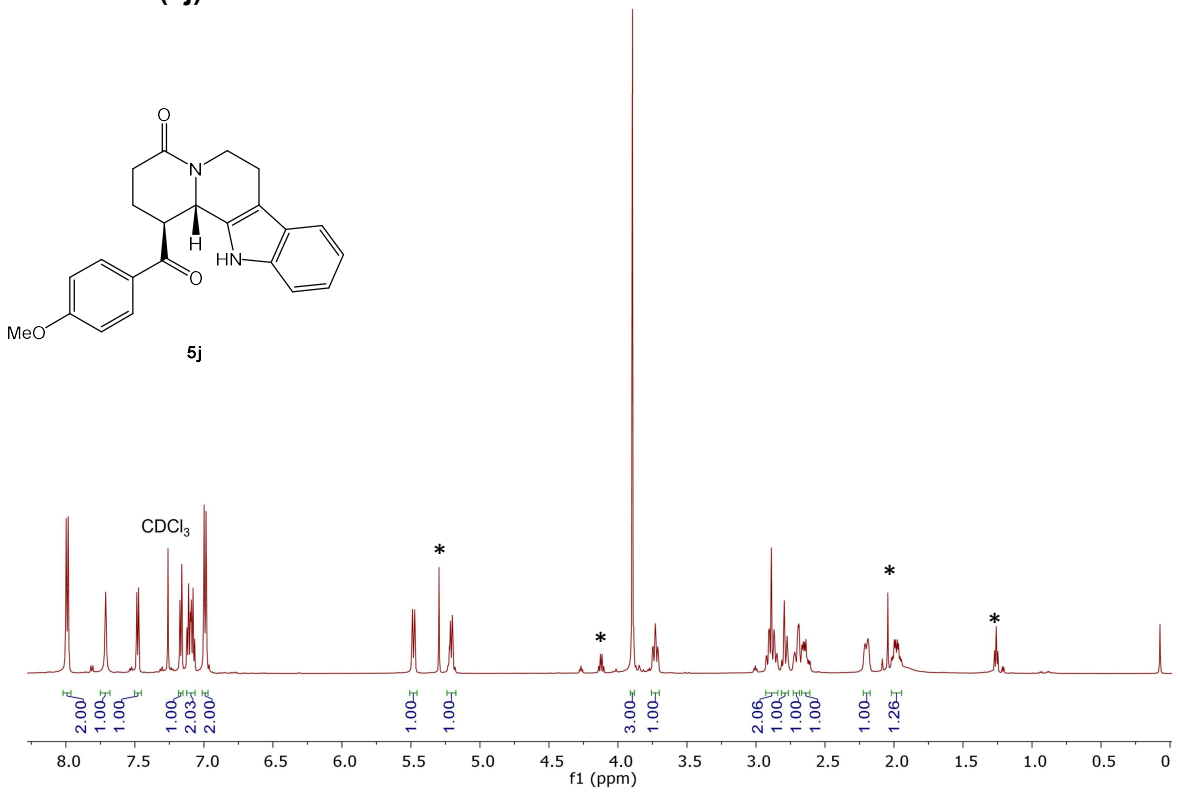


Figure S29. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5j**. * Impurities from residual solvent.

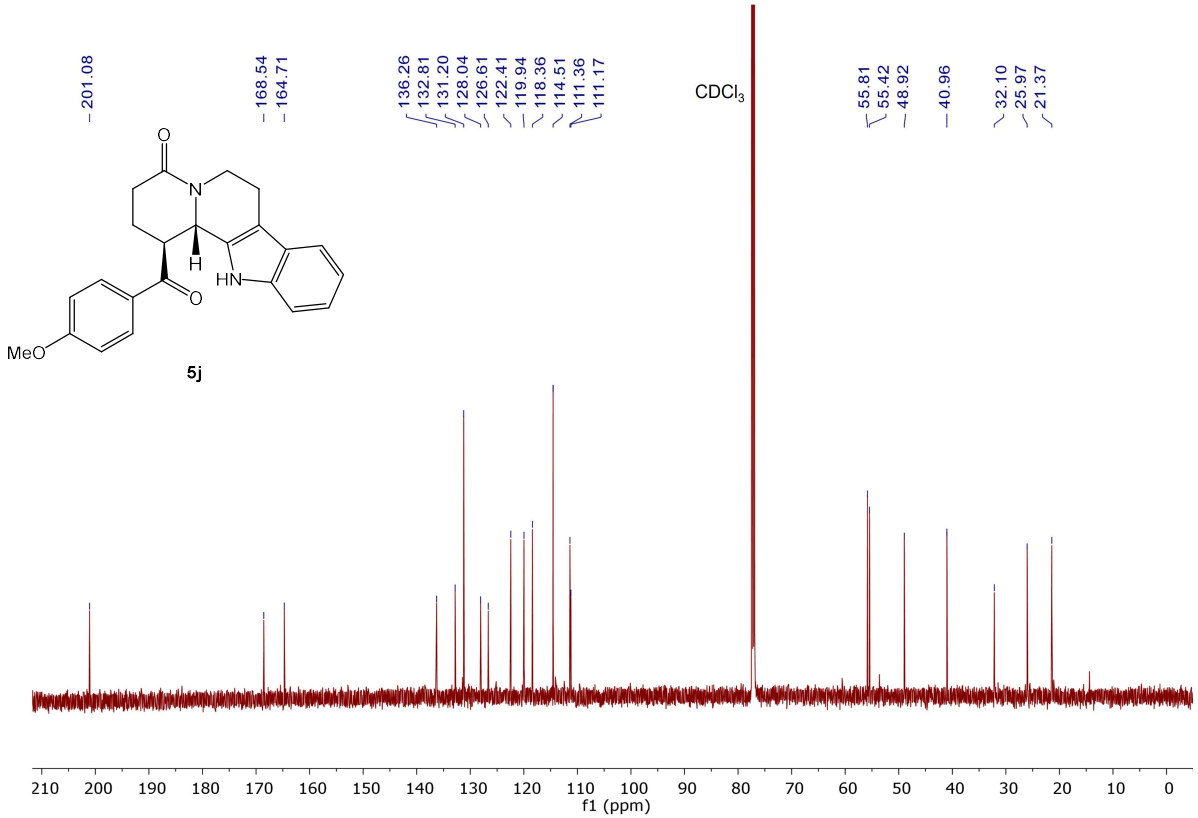


Figure S30. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5j**.

2.16. *rac*-1-(6-Chloronicotinoyl)-12b-phenyl-2,3,6,7,12,12b-hexahydroindolo-[2,3-*a*]quinolizin-4(1*H*)-one (5k)

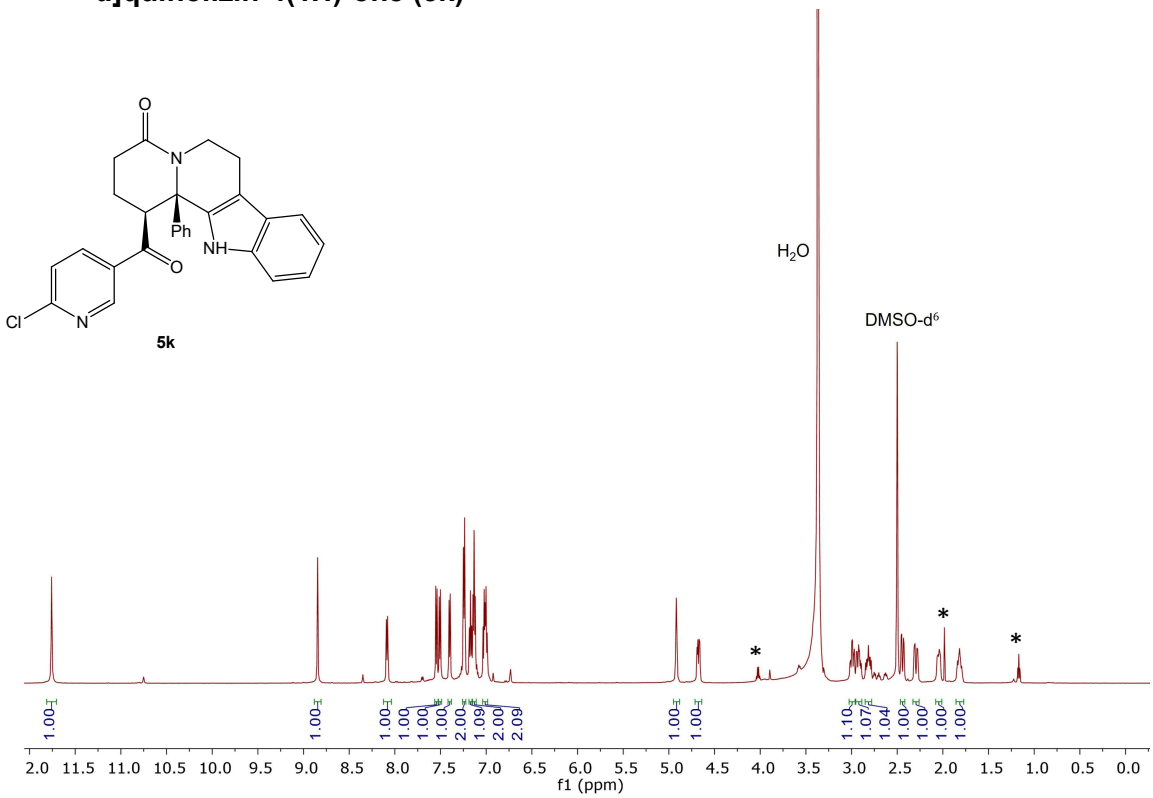


Figure S31. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **5k**. * Impurities from residual solvent.

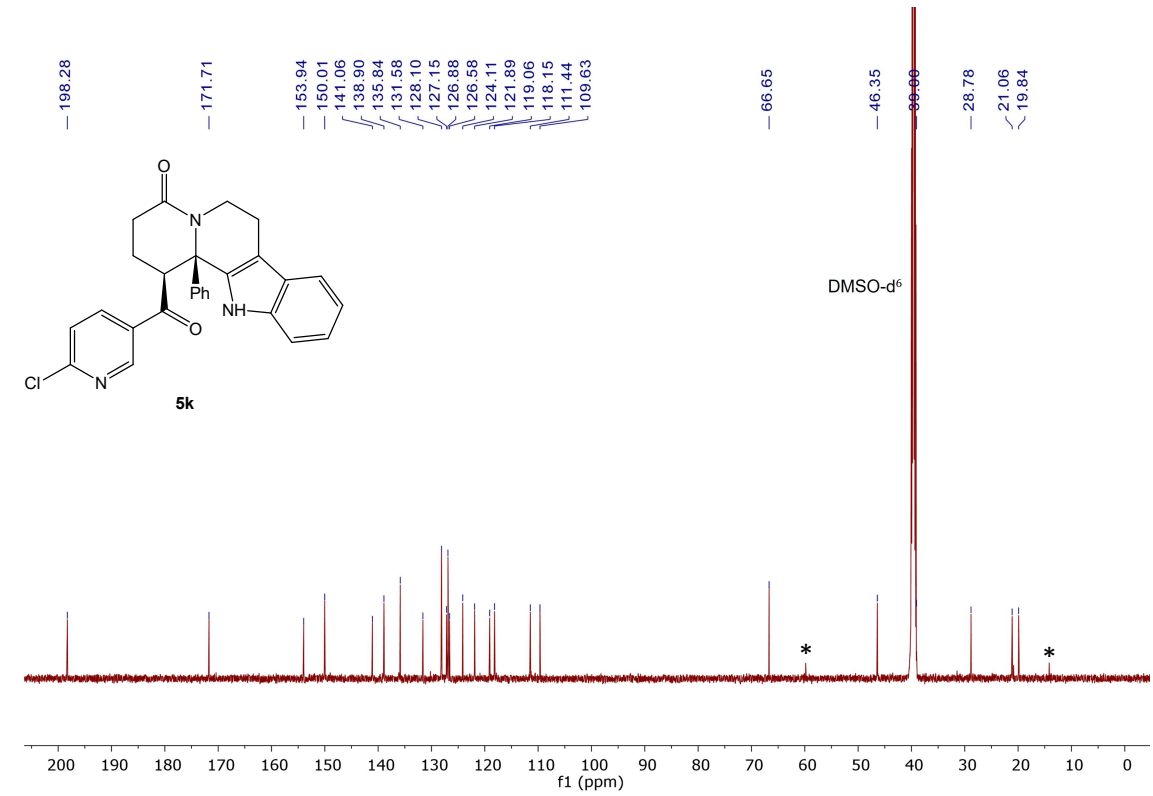


Figure S32. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of compound **5k**. * Impurities from residual solvent.

2.17. *rac*-1-(6-Chloronicotinoyl)-12b-cyclopropyl-2,3,6,7,12,12bhexahydro-indolo[2,3-*a*]quinolizin-4(1*H*)-one (5l)

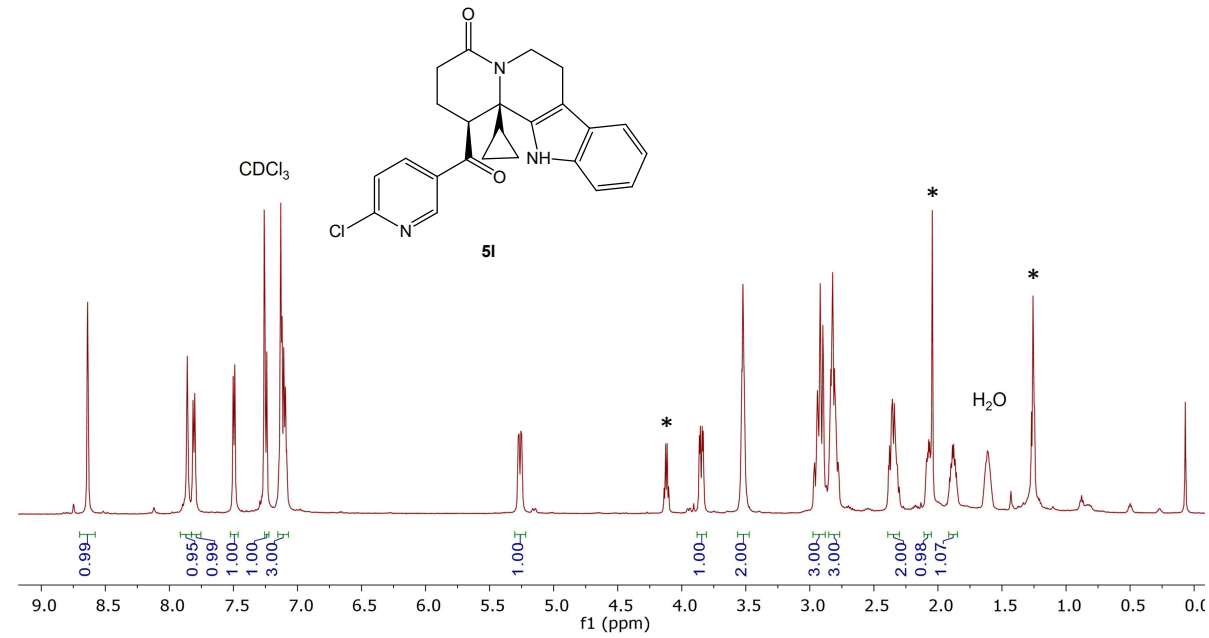


Figure S33. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5l**. * Impurities from residual solvent.

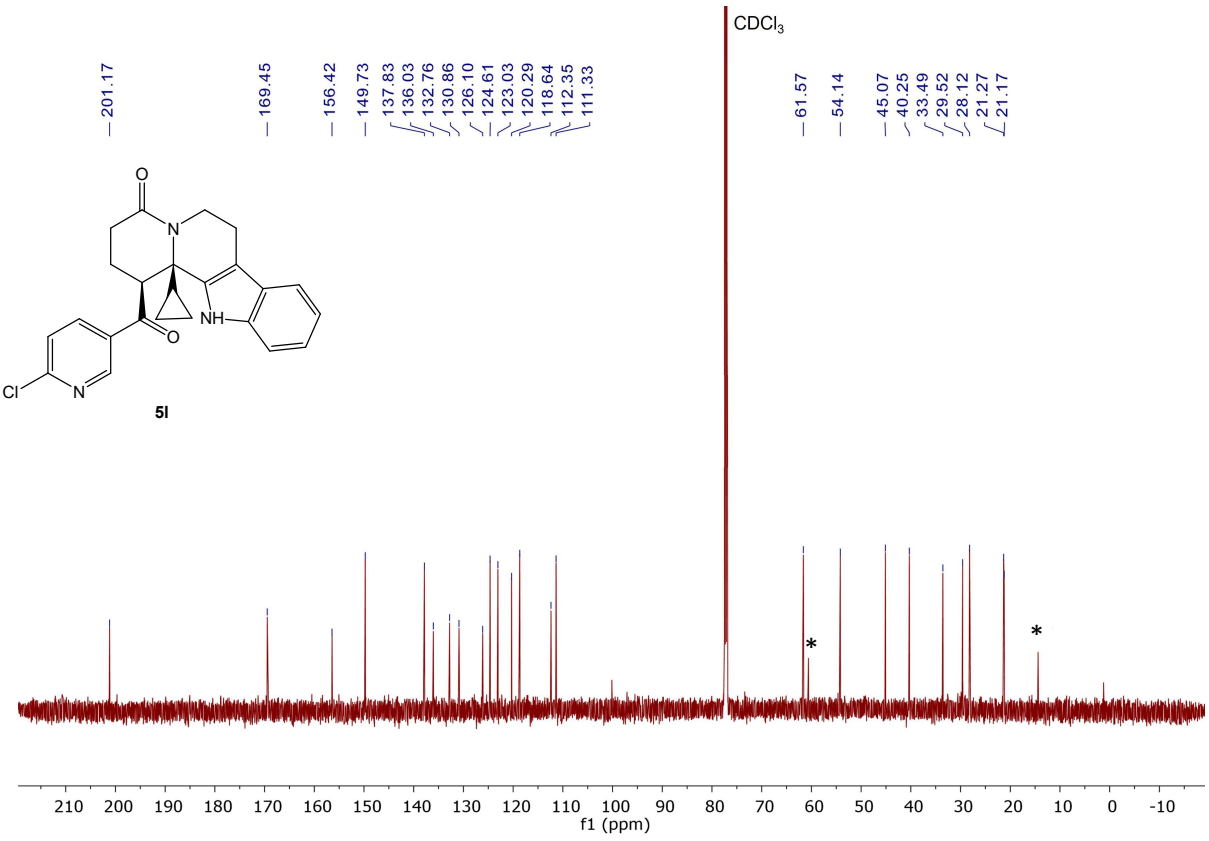


Figure S34. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5l**. * Impurities from residual solvent.

2.18. *rac*-1-(Thiophene-2-carbonyl)-12b-(1-tosyl-1*H*-indol-3-yl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5m)

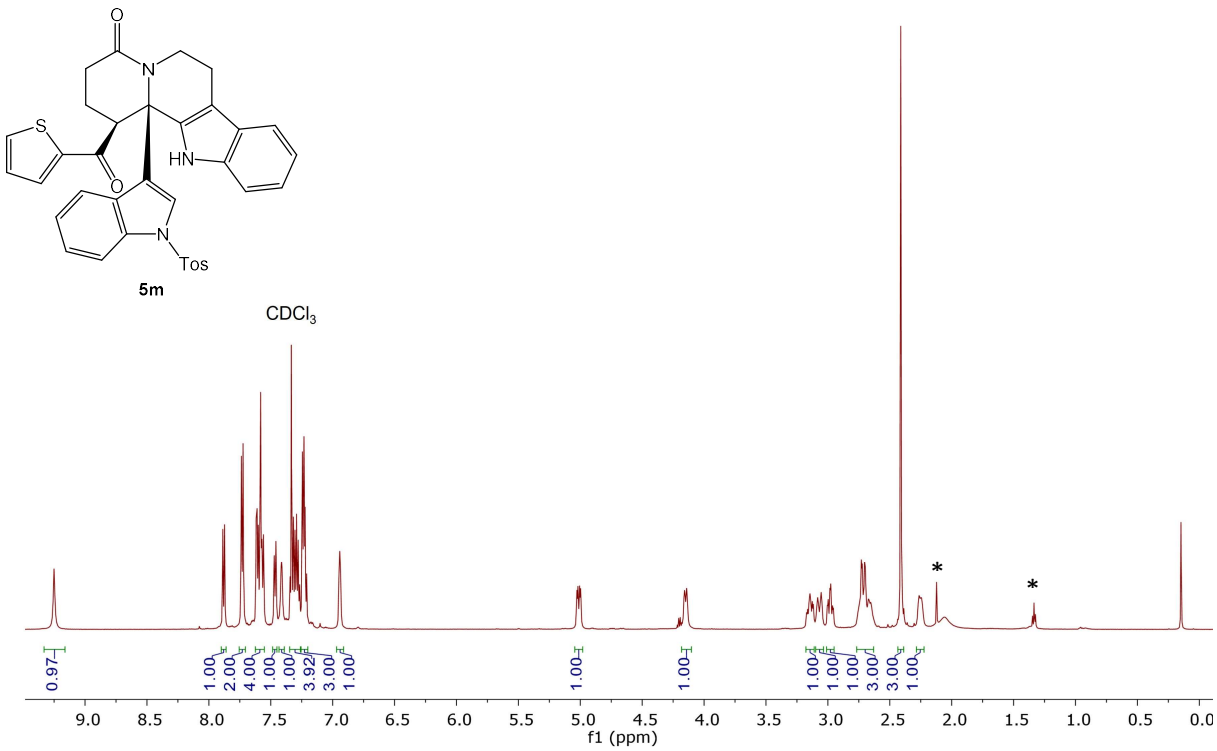


Figure S35. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5m**.

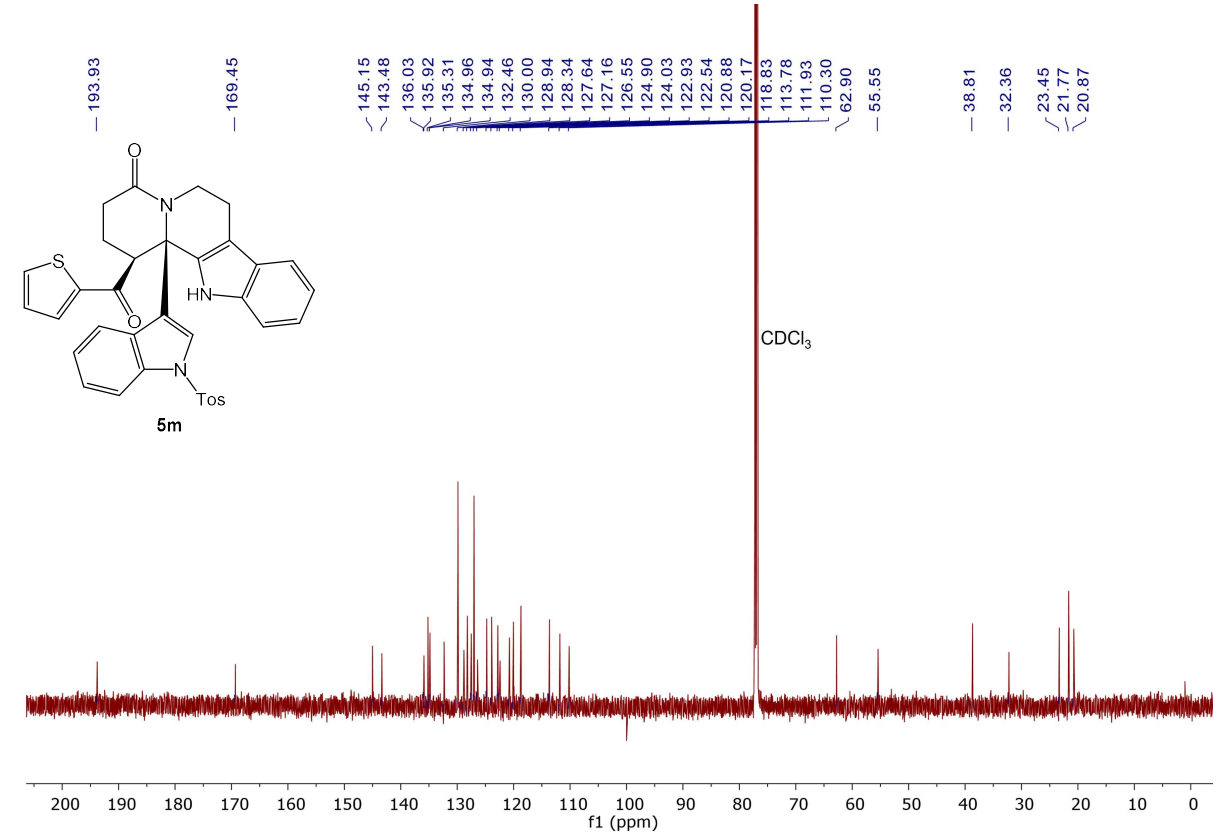


Figure S36. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5m**.

2.19. *rac*-1-(6-Chloronicotinoyl)-12b-(1-tosyl-1*H*-indol-3-yl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5n)

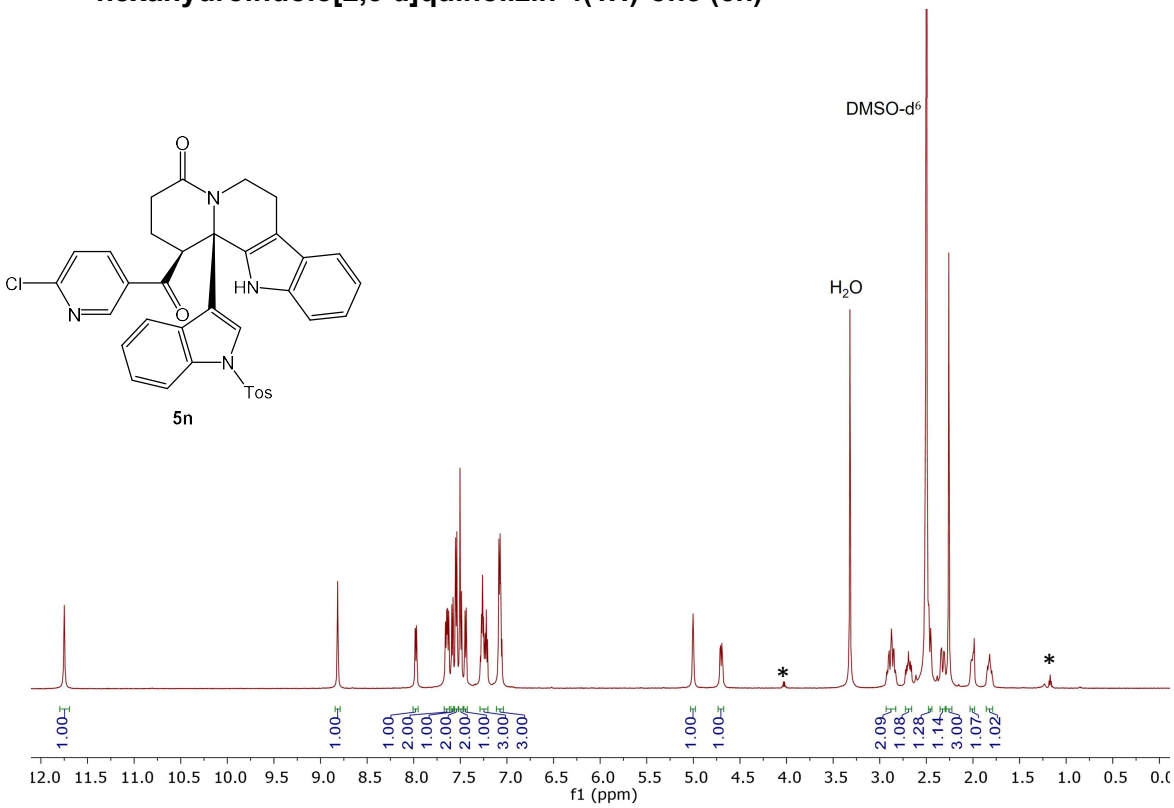


Figure S37. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **5n**. * Impurities from residual solvent.

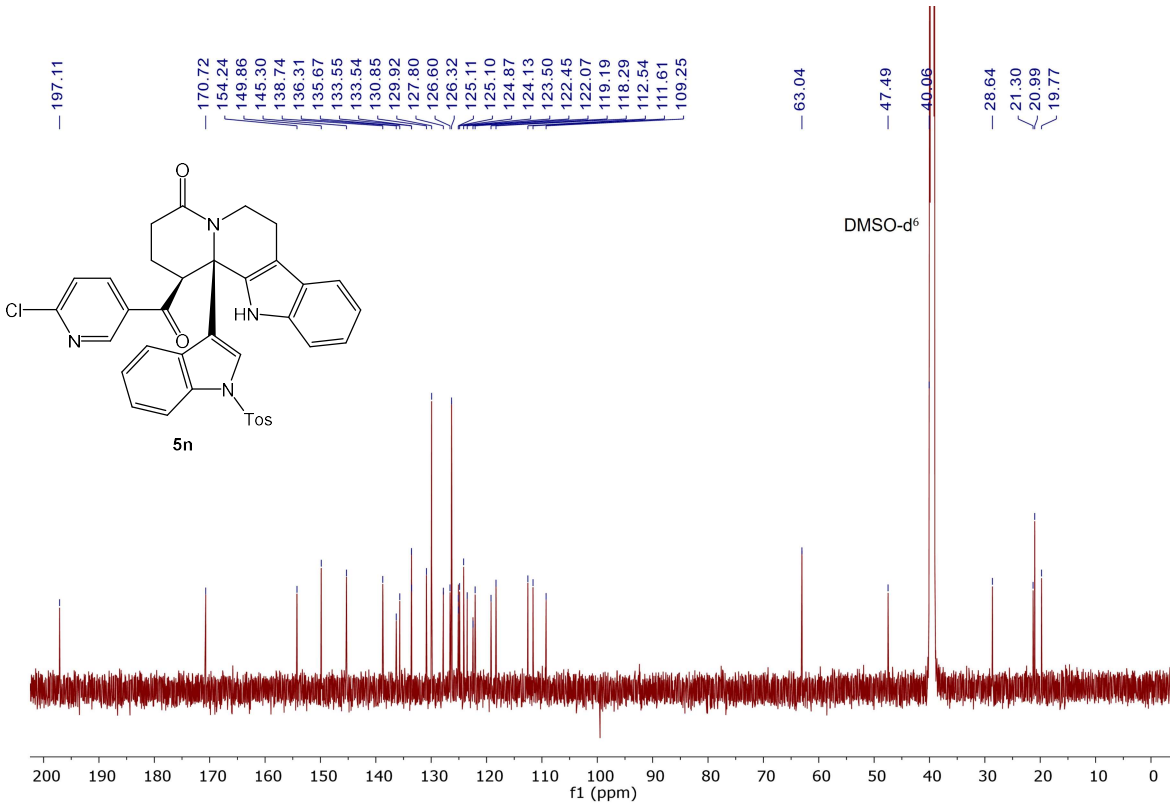


Figure S38. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of compound **5n**.

2.20. *rac*-1-(2-Fluorobenzoyl)-12b-(1-tosyl-1*H*-indol-3-yl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5o)

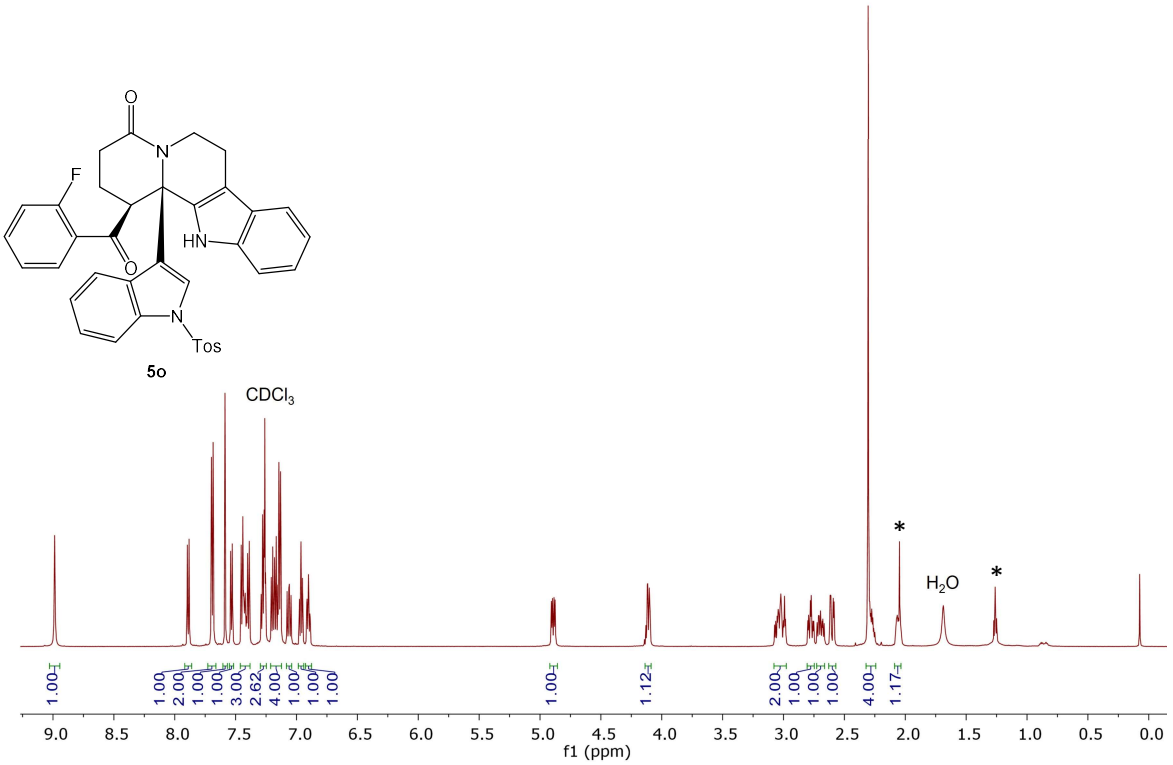


Figure S39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5o**. * Impurities from residual solvent.

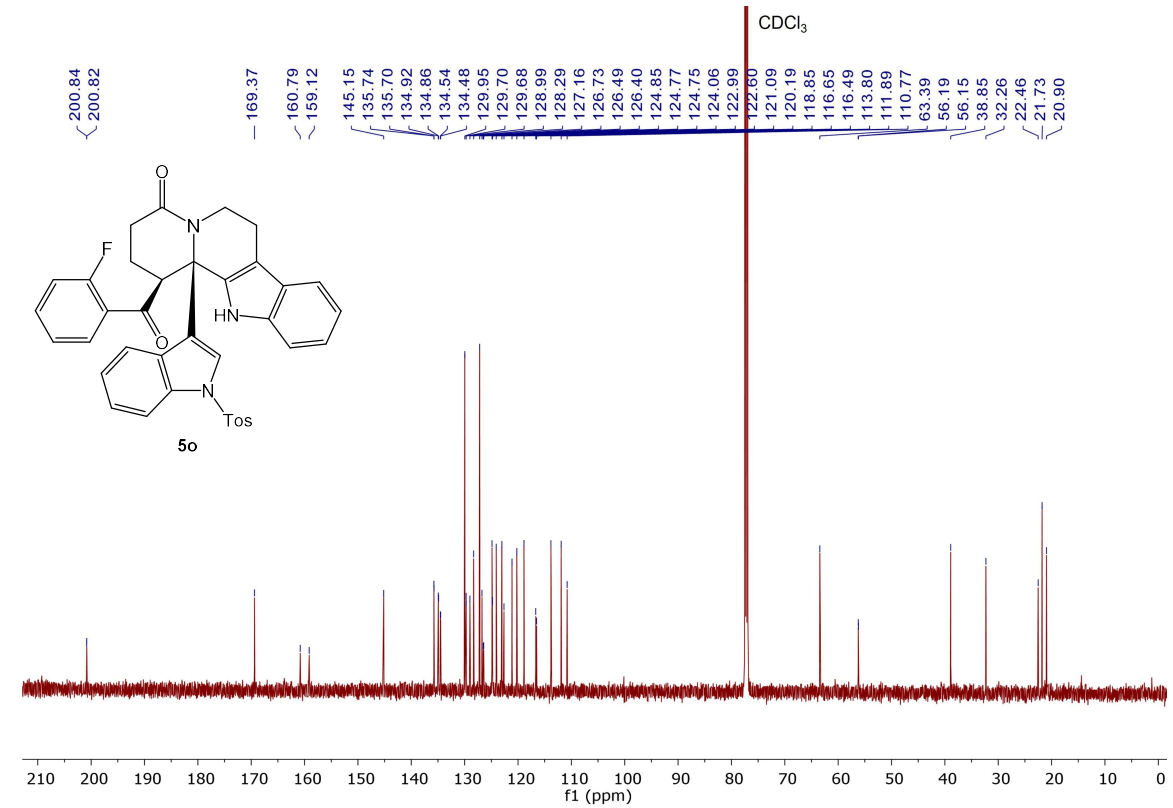


Figure S40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5o**.

2.21. *rac*-1-(4-Bromobenzoyl)-12b-(1-tosyl-1*H*-indol-3-yl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5p)

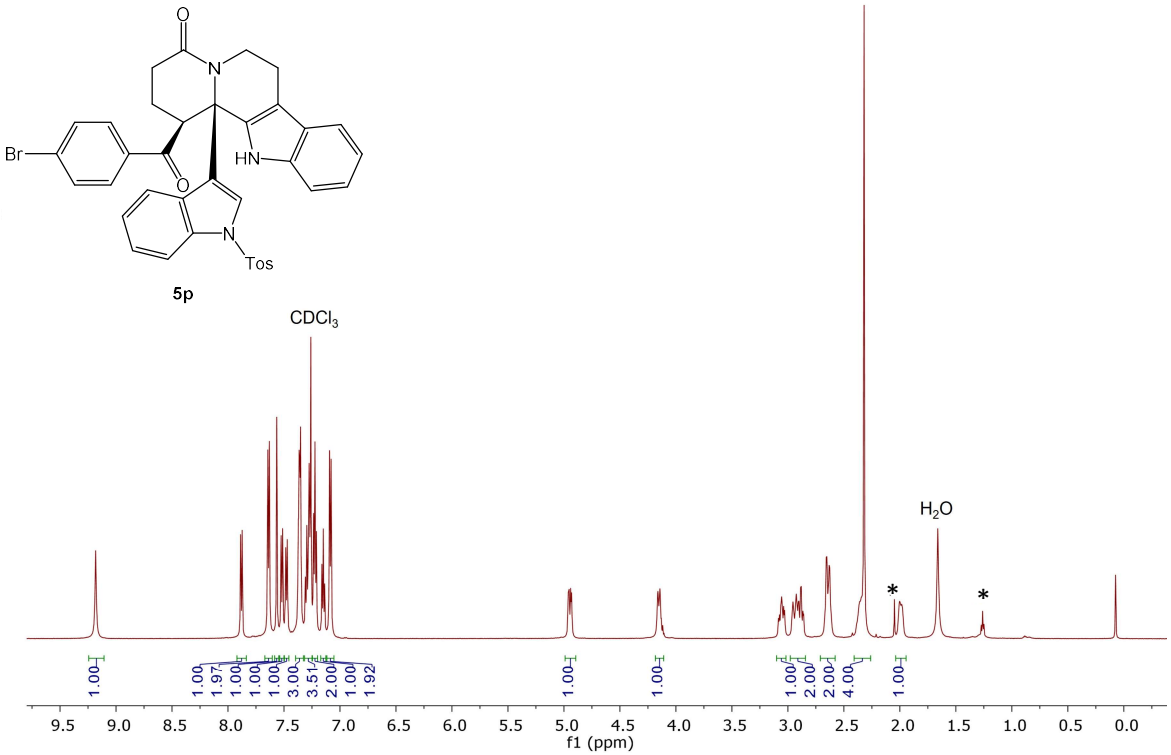


Figure S41. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5p**. * Impurities from residual solvent.

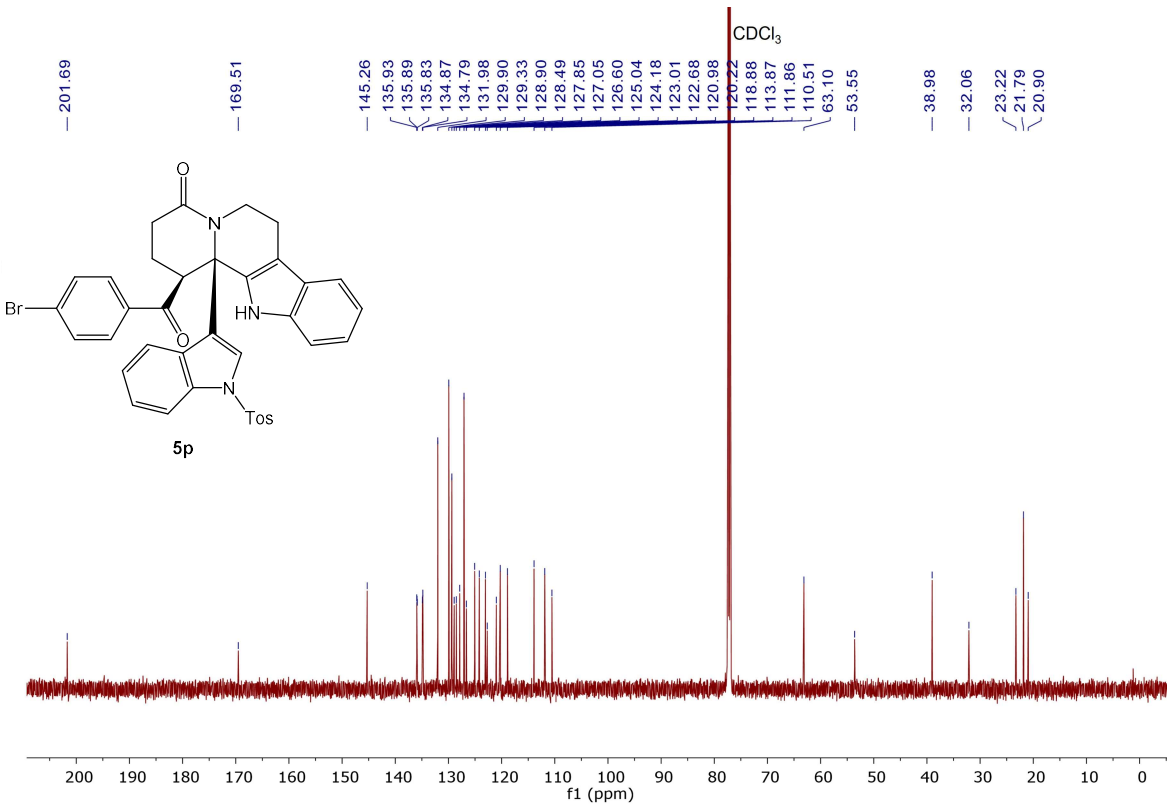


Figure S42. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5p**.

2.22. *rac*-1-Benzoyl-12b-(1-tosyl-1*H*-indol-3-yl)-2,3,6,7,12,12b-hexahydroindolo-[2,3-*a*]quinolizin-4(1*H*)-one (5q)

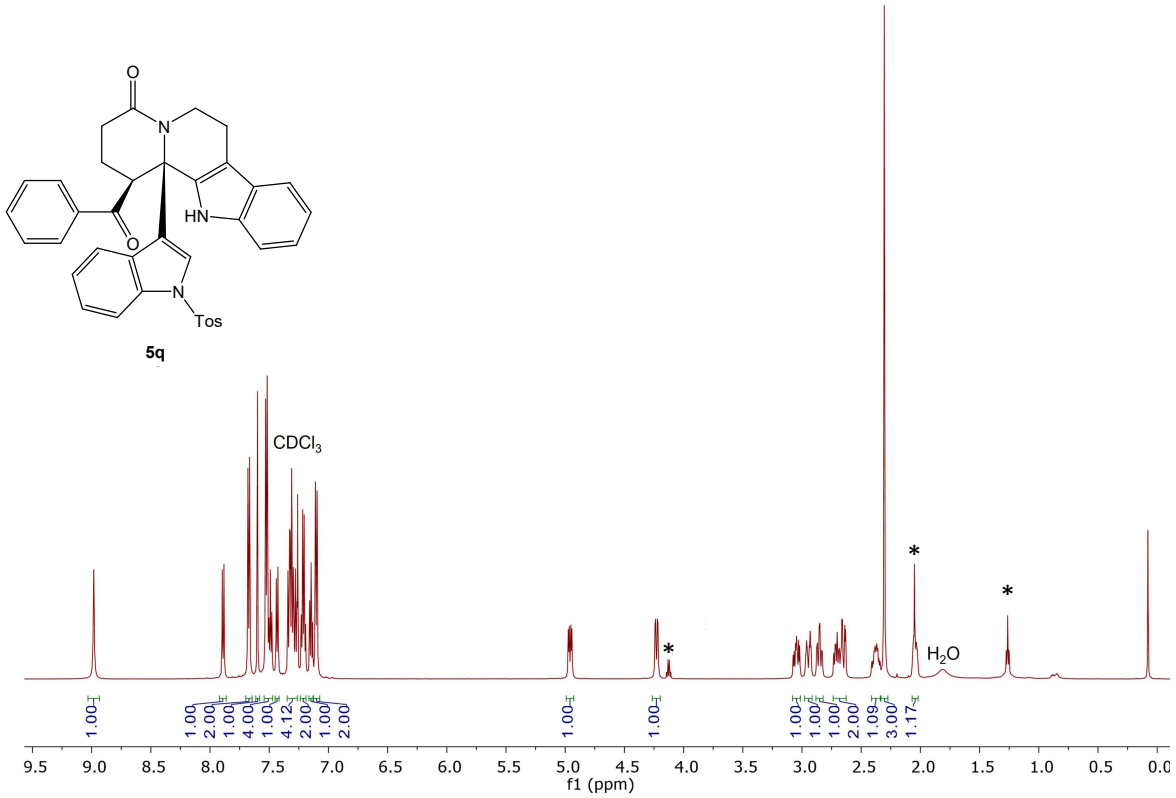


Figure S43. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5q**. * Impurities from residual solvent.

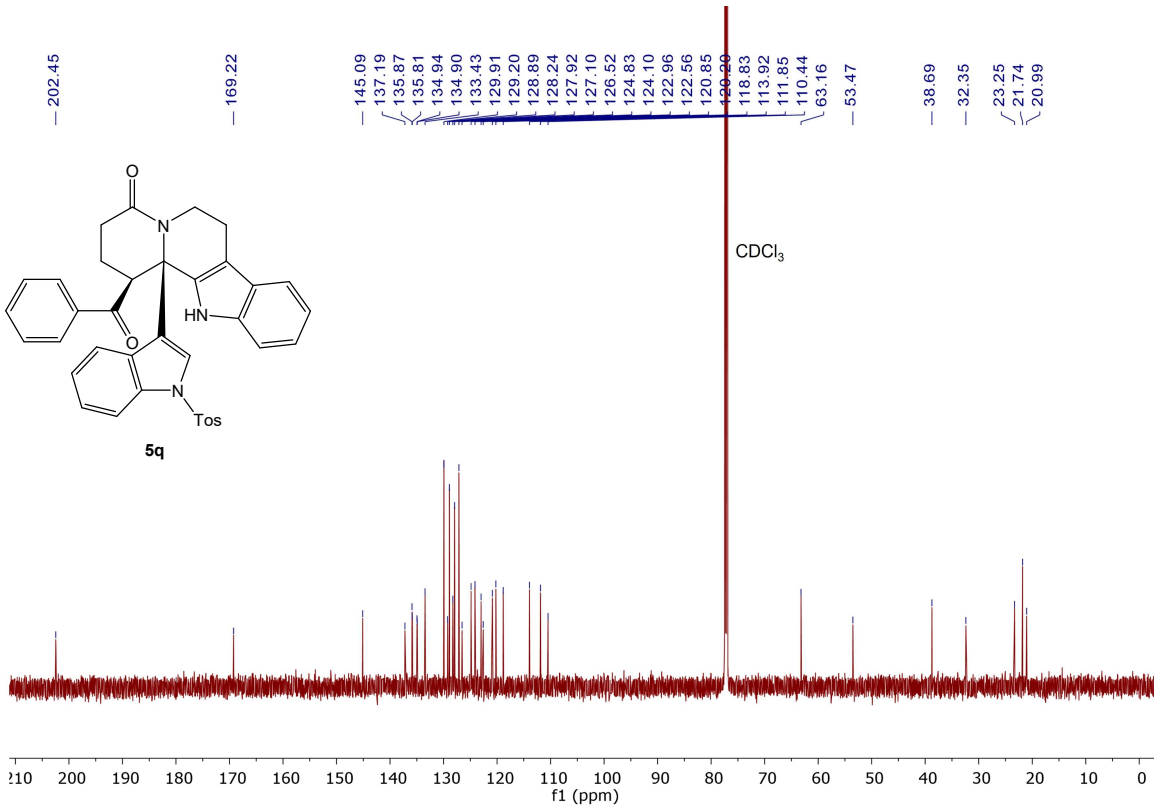


Figure S44. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5q**.

2.23. *rac*-1-(4-Methoxybenzoyl)-12b-(1-tosyl-1*H*-indol-3-yl)-2,3, 6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5r)

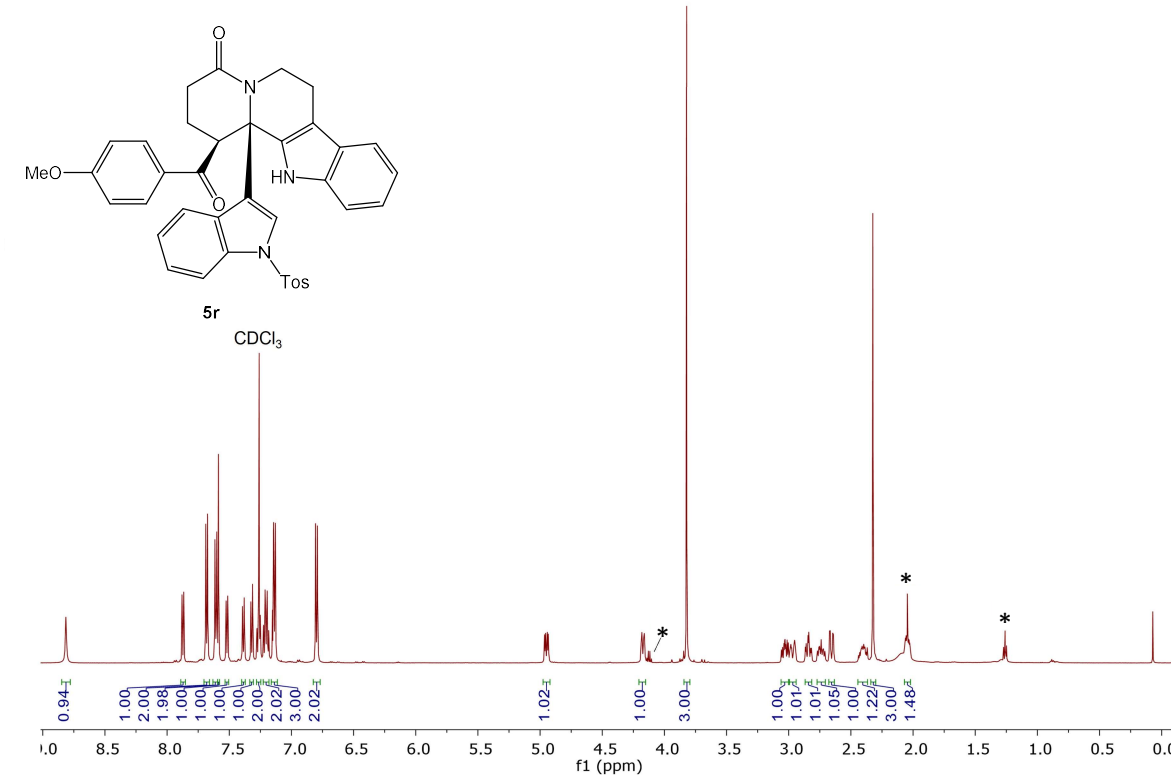


Figure S45. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5r**. * Impurities from residual solvent.

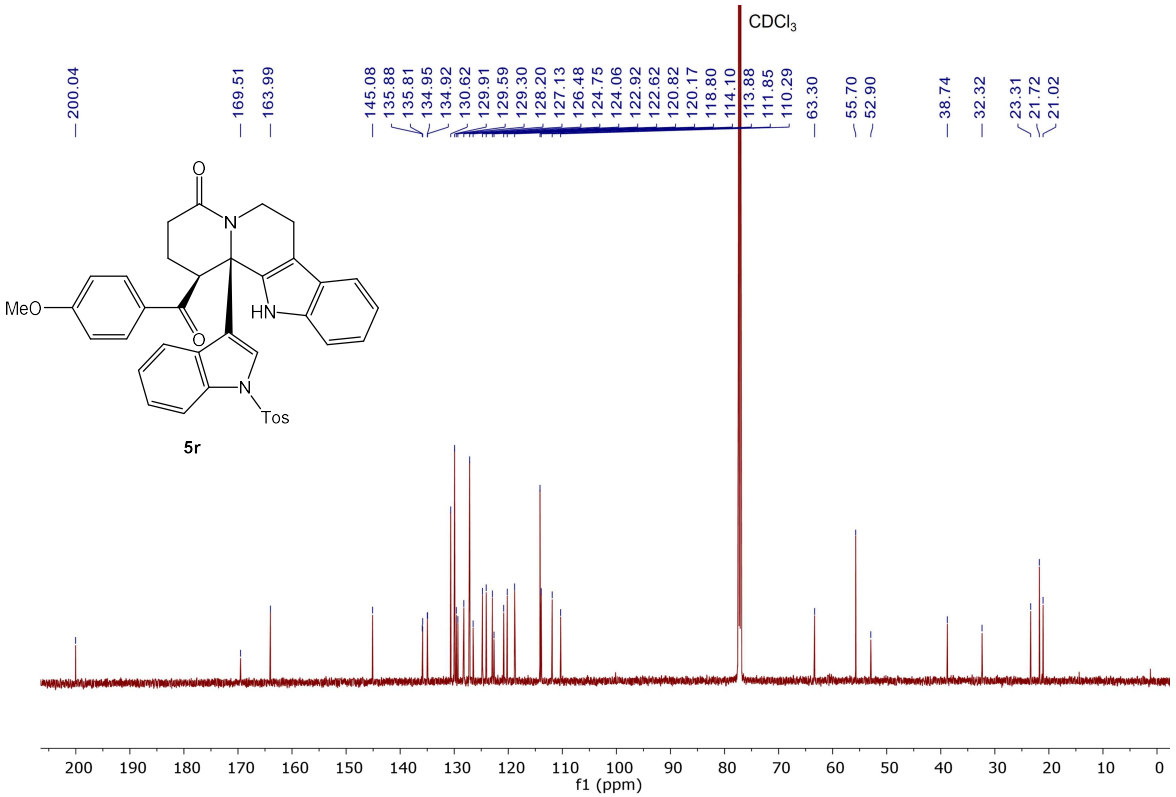


Figure S46. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5r**.

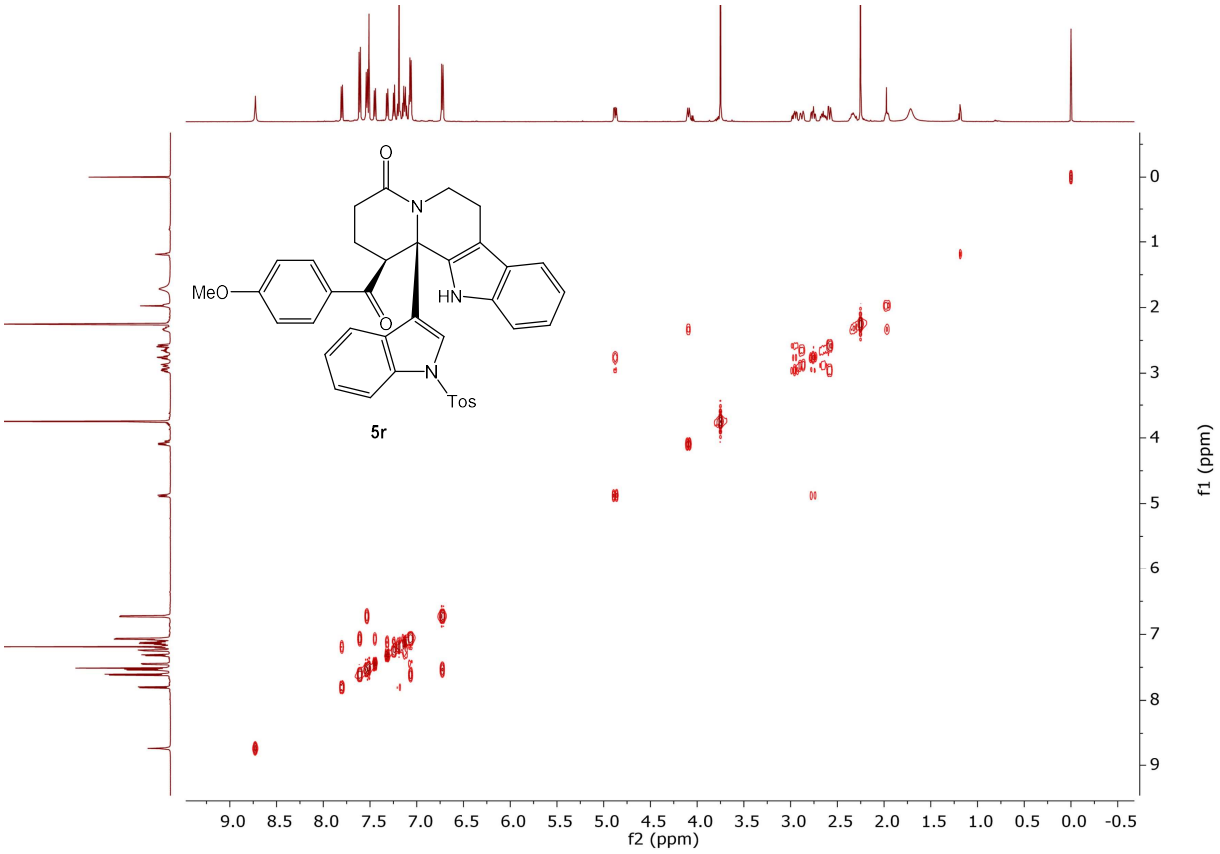


Figure S47. COSY spectrum (600 MHz, $CDCl_3$) of compound **5r**.

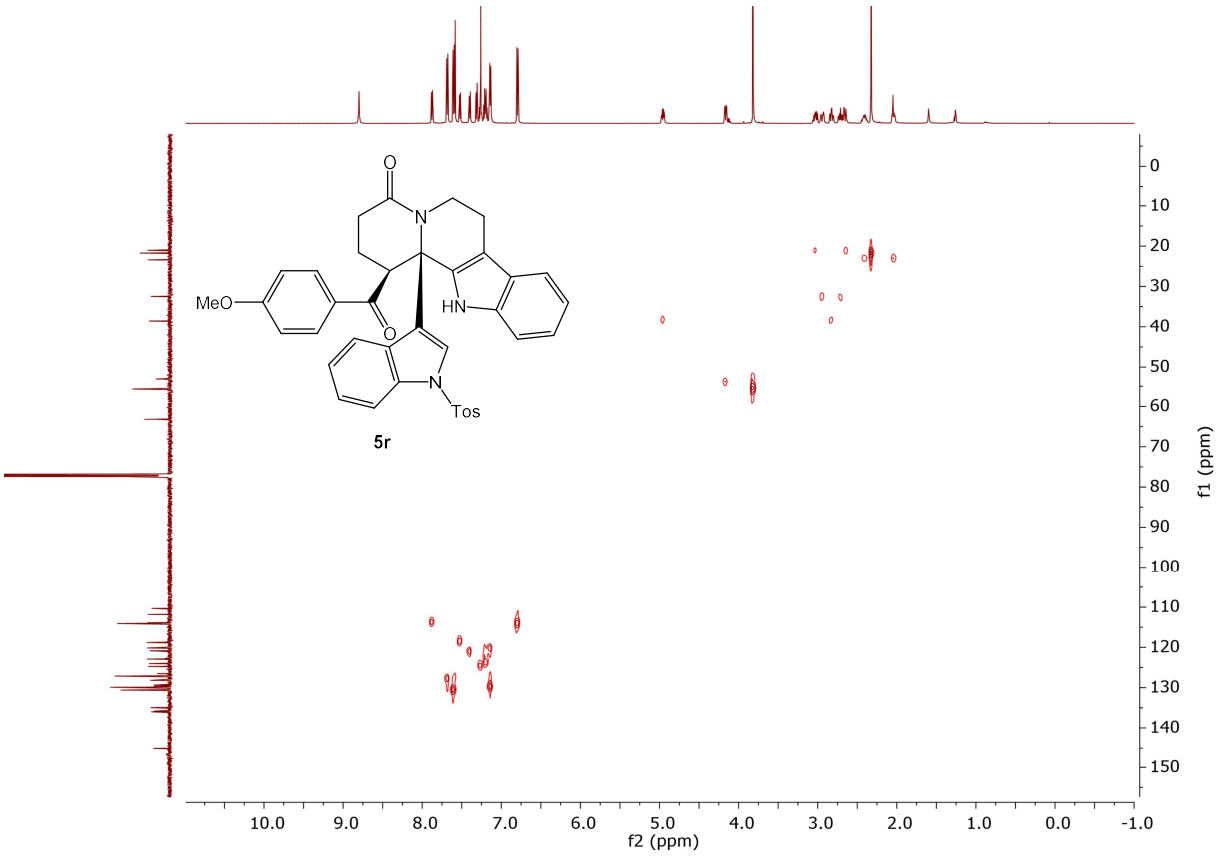


Figure S58. HSQC spectrum (600 MHz, 151 MHz, $CDCl_3$) of compound **5r**.

2.24. *rac*-1-(4-Methylbenzoyl)-12b-(1-tosyl-1*H*-indol-3-yl)-2,3,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4(1*H*)-one (5s)

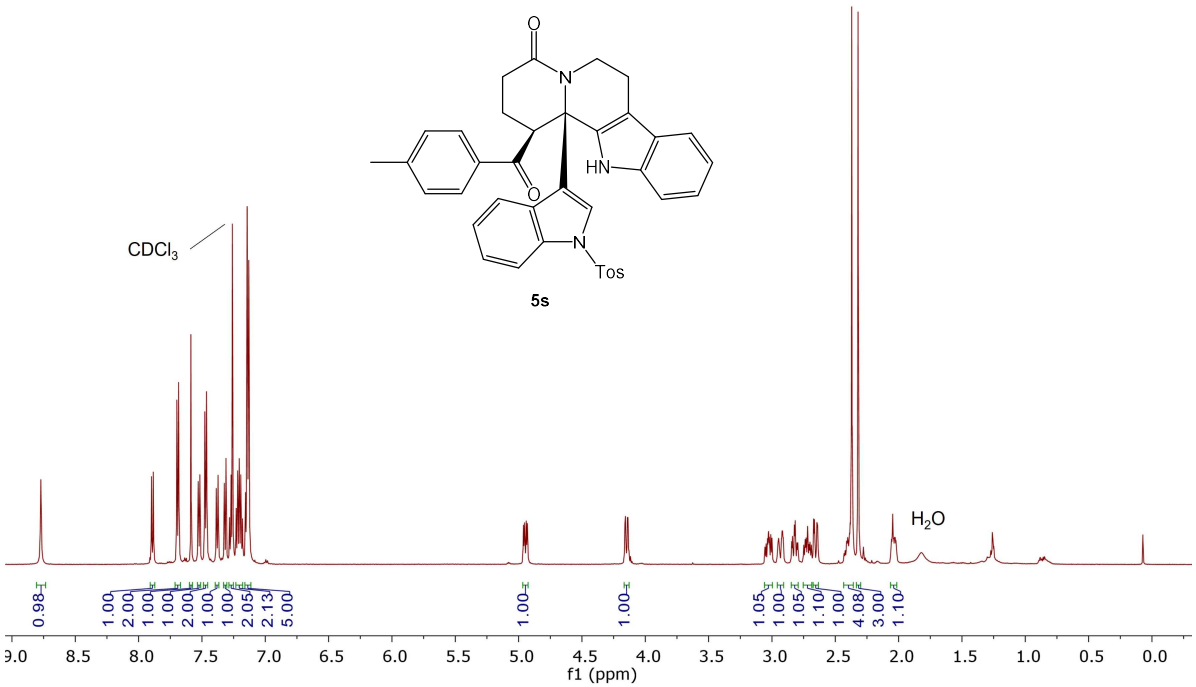


Figure S49. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5s**.

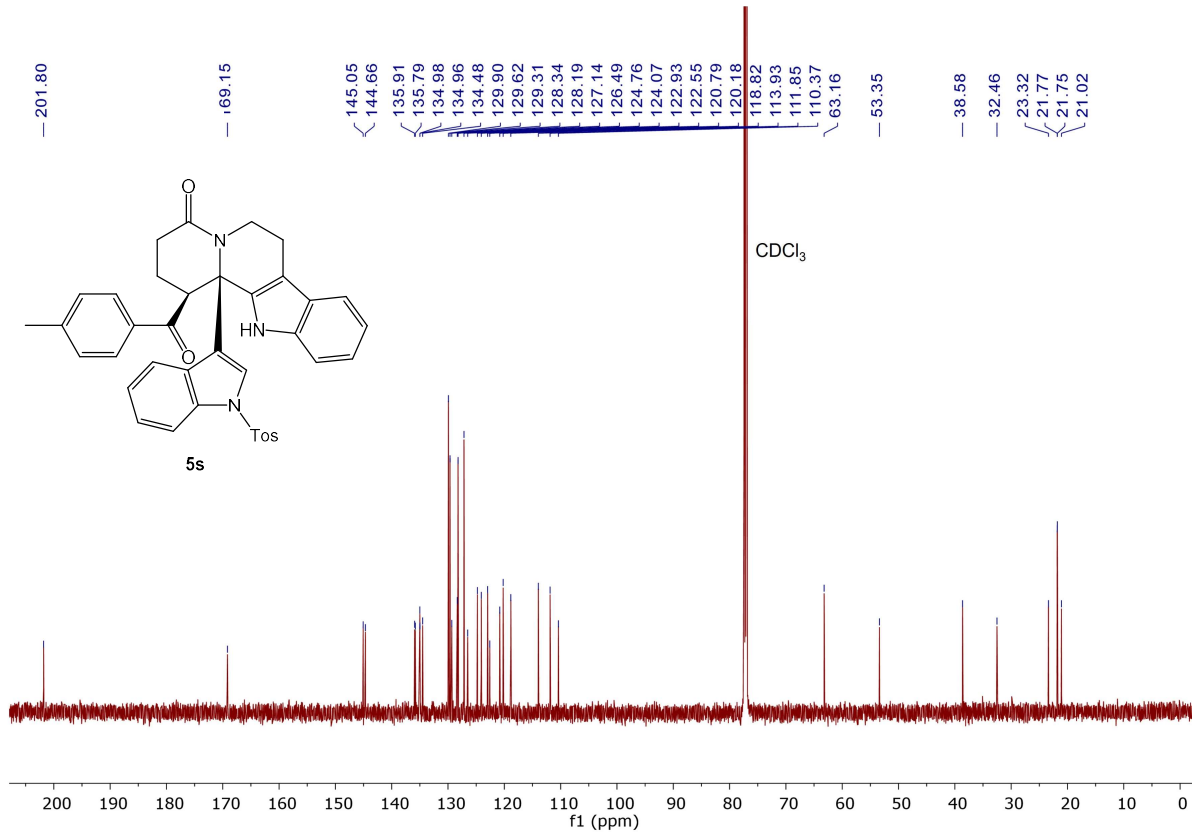


Figure S50. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5s**.

2.25. Methyl-(6*S*)-12b-butyl-1-(6-chloronicotinoyl)-4-oxo-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizin-6-carboxylate (5t)

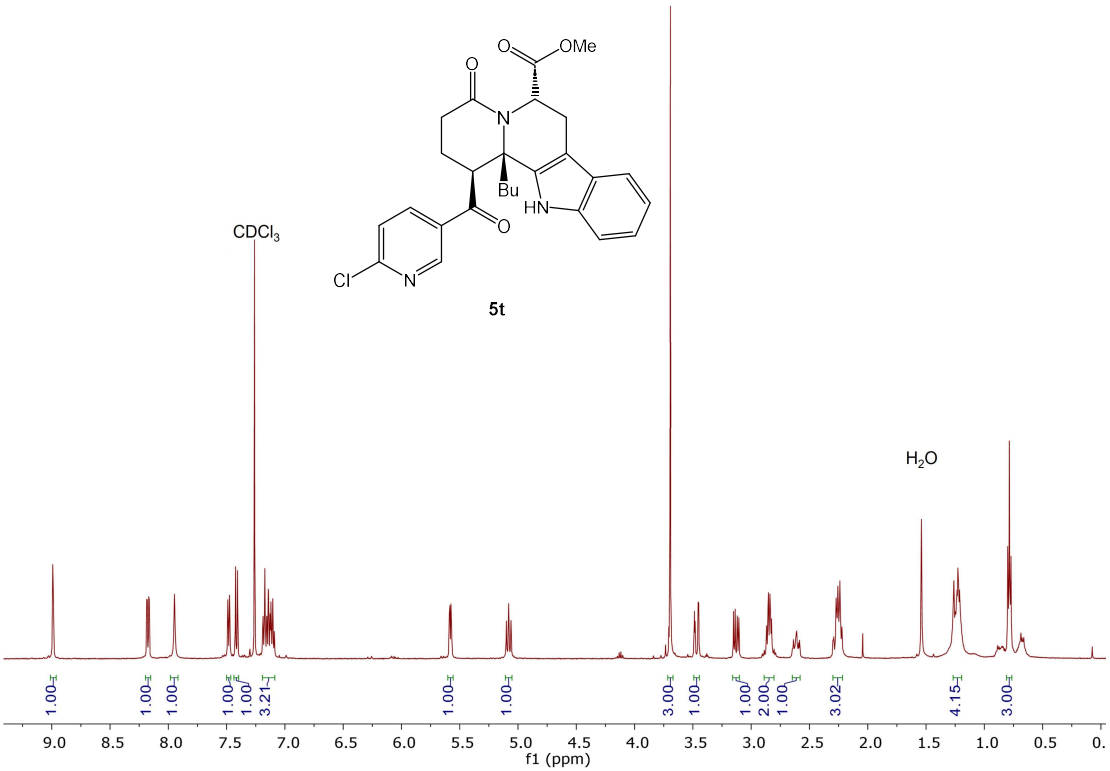


Figure S51. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5t**.

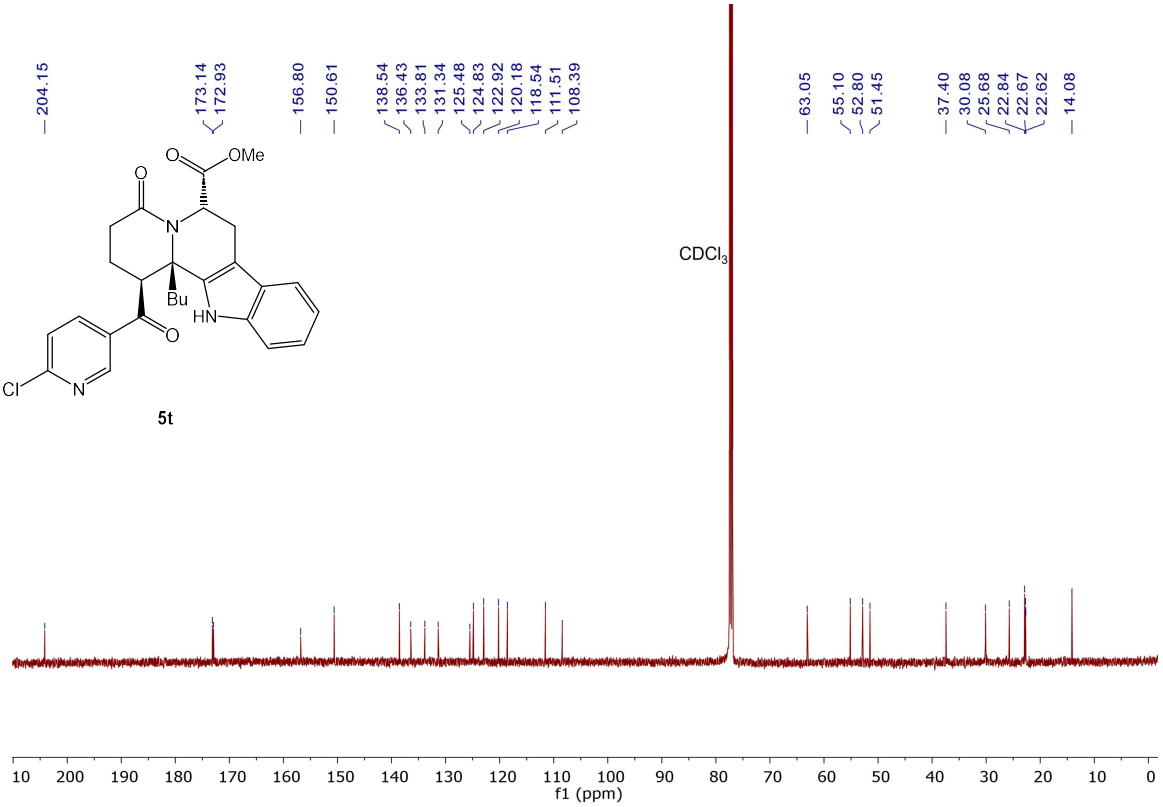


Figure S52. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5t**.

2.26. Methyl-(6*S*)-1-(4-bromobenzoyl)-12b-butyl-4-oxo-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizin-6-carboxylate (5u)

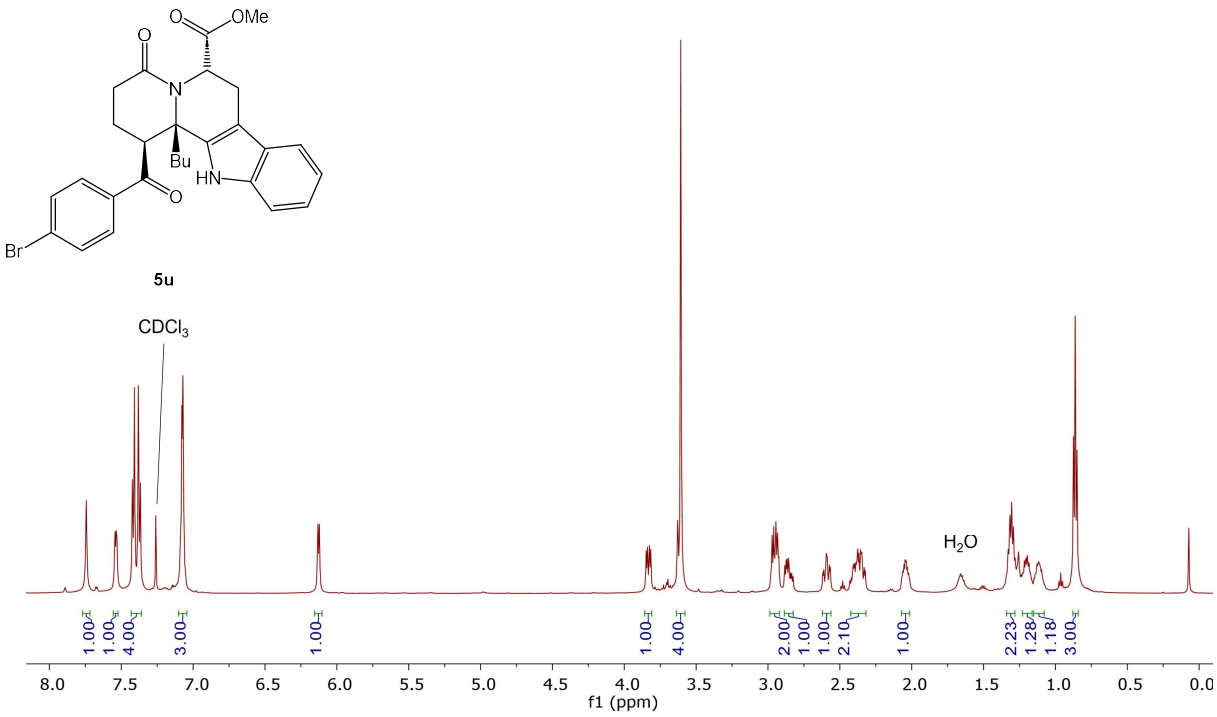


Figure S53. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **5u**.

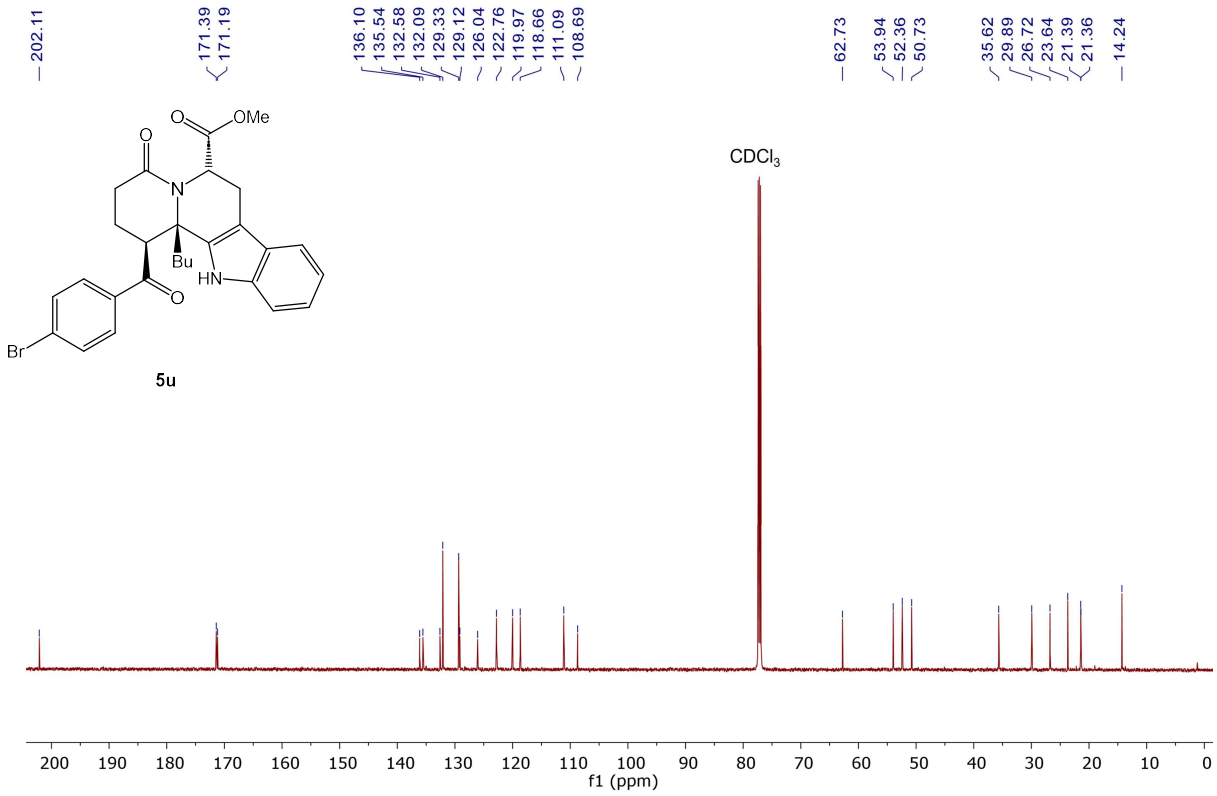


Figure S54. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of compound **5u**.

3. DFT calculations

3.1. General information and calculated energies

The DFT calculations on the structures and transition states were performed with the B3LYP hybrid functional and the G-31G* basis set using the conductor-like polarizable continuum model (C-PCM)[5] with a dipolar aprotic implicit dielectric medium with a dielectric constant of 37.22. The calculated energies are listed in Table S2. Minima were verified by the absence of imaginary frequencies and transition states were confirmed by the appearance of a single imaginary frequency.

Table S2. Energies (in Hartree, kJ/mol (absolute), and kJ/mol (relative) of the calculated minima and transition state structures and imaginary frequencies.

structure	energy [Hartree]	energy [kJ/mol]	energy [kJ/mol]	imaginary frequence
4 + 7b	−1802.203204	−4731684.872543	0.00	–
$TS_{(4+7b)\rightarrow 10}$	−1802.171823	−4731602.481721	82.39	i1343 cm-1
10	−1802.210376	−4731703.702630	−18.83	–
8	−1802.192741	−4731657.401934	27.47	–
$TS_{8\rightarrow 9}$	−1802.149754	−4731544.539557	140.33	i525 cm-1
9	−1802.207978	−4731697.406681	−12.53	–
11	−1802.228653	−4731751.688897	−66.92	–
$TS_{11\rightarrow 12}$	−1802.202609	−4731683.310370	1.56	i284 cm-1
12	−1802.233144	−4731763.480019	−78.61	–
$TS_{12\rightarrow 13}$	−1802.221127	−4731731.929383	−47.06	i285 cm-1
13	−1802.228003	−4731749.982322	−65.12	–
14 + HCl	−1802.233434	−4731764.241414	−79.37	–

3.2. xyz-Coordinates of the structures and transition states

3.2.1. xyz-Coordinates of the structures 4 + 7b

C	0.655342	1.534034	0.286969
C	0.147269	0.696942	1.329188
H	0.466042	0.862356	2.348865
C	-0.740103	-0.359290	1.117926
C	-1.192112	-1.156717	2.295570
C	-2.030034	-2.578341	4.565393
C	-0.251757	-1.774492	3.133456
C	-2.557596	-1.250679	2.611029
C	-2.972079	-1.954921	3.741630
C	-0.670535	-2.486882	4.258861
H	0.805570	-1.702428	2.894999

H	-3.290202	-0.755118	1.979490
H	-4.030278	-2.012530	3.981535
H	0.066222	-2.969900	4.894851
H	-2.354469	-3.129745	5.443666
C	1.662266	2.599370	0.628211
C	3.575053	4.599177	1.137024
C	1.845451	3.099877	1.928016
C	2.445910	3.125725	-0.412536
C	3.398868	4.110855	-0.161297
C	2.791661	4.094635	2.178575
H	1.235756	2.735178	2.748329
H	2.296817	2.744022	-1.417302
H	4.003846	4.499199	-0.976490
H	2.914648	4.477269	3.188285
H	4.315450	5.369743	1.334990
O	0.308486	1.414978	-0.921461
N	-1.230943	-0.642859	-0.103728
H	-0.854493	-0.024900	-0.827890
C	-1.873394	-1.877331	-0.545849
H	-2.592676	-1.602431	-1.323419
H	-2.430356	-2.315065	0.283413
C	-0.882807	-2.927127	-1.102912
H	-1.480404	-3.808276	-1.371404
H	-0.213965	-3.237849	-0.291011
C	-0.074116	-2.468946	-2.286598
C	-0.493990	-2.416140	-3.597240
N	0.512021	-1.921401	-4.401473
C	1.617440	-1.644994	-3.627852
C	1.284137	-1.978807	-2.282363
H	-1.445392	-2.697595	-4.029301
H	0.447630	-1.794634	-5.401725

C	2.872616	-1.136034	-3.985335
H	3.103069	-0.886209	-5.017692
C	2.257269	-1.795694	-1.280709
H	2.035708	-2.040552	-0.244861
C	3.809184	-0.963265	-2.971202
H	4.793083	-0.570808	-3.214727
C	3.504939	-1.292266	-1.631404
H	4.260774	-1.146811	-0.863869
H	-1.959602	2.700199	-0.691281
C	-2.807097	3.004225	-0.083548
H	-2.648093	3.801111	0.636851
C	-4.004213	2.410135	-0.188944
H	-4.849396	2.681431	0.432427
C	-4.197618	1.327694	-1.161721
O	-3.467939	0.936600	-2.022443
Cl	-5.836870	0.496276	-0.939958

3.2.2. xyz-Coordinates of the transition state $T_{(4+7b)\rightarrow 10}$

C	-2.148824	-2.886497	-0.107228
C	-0.817339	-2.297662	-0.609703
H	-0.247698	-3.199170	-0.871260
C	0.062290	-1.571907	0.413471
C	-0.280629	-1.555814	1.861155
C	-0.980968	-1.479243	4.572482
C	-0.428234	-0.324366	2.521809
C	-0.491397	-2.750146	2.568988
C	-0.828056	-2.706737	3.922779
C	-0.785208	-0.288657	3.868484
H	-0.295940	0.602678	1.973042
H	-0.374709	-3.708188	2.071568
H	-0.974777	-3.634225	4.468397

H	-0.911125	0.669685	4.364201
H	-1.254674	-1.449335	5.623323
C	-3.306513	-2.049291	0.324990
C	-5.569833	-0.621349	1.173884
C	-4.489399	-2.724182	0.681994
C	-3.276260	-0.646980	0.401328
C	-4.402524	0.060761	0.822930
C	-5.610959	-2.018373	1.102767
H	-4.506994	-3.807126	0.623258
H	-2.380855	-0.094456	0.141687
H	-4.366449	1.144789	0.878521
H	-6.515983	-2.553430	1.376734
H	-6.445039	-0.068029	1.503194
O	-2.250740	-4.110213	-0.130243
N	1.133334	-1.037907	-0.069555
H	1.066392	-0.986578	-1.330801
C	2.267028	-0.543477	0.721081
H	3.153298	-1.042580	0.313873
H	2.149083	-0.877396	1.754583
C	2.464269	0.981007	0.699994
H	3.112588	1.209996	1.558551
H	1.507525	1.469163	0.915751
C	3.054965	1.566421	-0.553970
C	3.988189	1.015348	-1.402511
N	4.345125	1.930496	-2.373485
C	3.638036	3.096528	-2.182882
C	2.816714	2.905638	-1.034920
H	4.444117	0.034478	-1.397036
H	4.965428	1.738920	-3.147517
C	3.646429	4.297486	-2.903797
H	4.278611	4.422332	-3.778835

C	1.993610	3.962738	-0.603155
H	1.361782	3.847923	0.274486
C	2.817636	5.321425	-2.455349
H	2.800330	6.266636	-2.991476
C	1.999706	5.156607	-1.315501
H	1.366675	5.978839	-0.991921
H	-1.491767	-0.540307	-1.744751
C	-0.986623	-1.490301	-1.937099
H	-1.638909	-2.076956	-2.596071
C	0.374123	-1.220372	-2.585143
H	0.878008	-2.089669	-2.999427
C	0.460891	-0.043289	-3.353279
O	-0.092533	1.017114	-3.384774
Cl	2.004775	-0.202800	-4.647616

3.2.3. xyz-Coordinates of the structure 10

C	0.637738	-2.158536	-1.985982
C	1.557949	-2.413294	0.914895
C	1.640810	-4.895944	2.228231
C	0.427682	-2.899579	1.591450
C	2.727378	-3.189276	0.898845
C	2.770511	-4.418728	1.558395
C	0.469513	-4.134644	2.241293
H	-0.488013	-2.314560	1.598125
H	3.610421	-2.825376	0.380288
H	3.685793	-5.004252	1.545408
H	-0.414352	-4.501115	2.756478
H	1.672434	-5.856130	2.735926
C	-0.810978	-1.795641	-2.065557
C	-3.553105	-1.238409	-2.297136
C	-1.641177	-2.601161	-2.867504

C	-1.377348	-0.707293	-1.379597
C	-2.741594	-0.435326	-1.493321
C	-2.999054	-2.323727	-2.985906
H	-1.199941	-3.440010	-3.395441
H	-0.766578	-0.078365	-0.743645
H	-3.167018	0.404773	-0.951618
H	-3.627781	-2.949987	-3.612856
H	-4.614060	-1.021334	-2.387497
O	1.037216	-3.210213	-2.474969
C	1.245086	0.256007	2.142718
H	2.059941	0.934777	2.426941
H	1.372999	-0.667786	2.720608
C	-0.101093	0.902392	2.520140
H	-0.145738	0.940357	3.618572
H	-0.908948	0.226329	2.212235
C	-0.346516	2.268481	1.932009
C	0.568336	3.272690	1.711963
N	-0.057738	4.380244	1.172890
C	-1.400643	4.117505	1.028683
C	-1.621419	2.791122	1.502903
H	1.634973	3.292439	1.889464
H	0.406002	5.237925	0.908566
C	-2.436435	4.915219	0.525755
H	-2.244282	5.923132	0.167283
C	-2.930234	2.270900	1.472149
H	-3.134082	1.267426	1.838019
C	-3.716154	4.369527	0.503054
H	-4.541961	4.962226	0.118221
C	-3.961526	3.059716	0.972361
H	-4.974675	2.666720	0.945420
C	3.237952	2.092273	-2.651264

O	2.483331	2.571902	-3.433361
Cl	4.852269	2.956413	-2.326586
C	1.677496	-1.212042	-1.338654
H	2.616347	-1.757988	-1.497749
C	1.771701	0.128024	-2.097698
H	0.947242	0.790651	-1.826700
H	1.685594	-0.073763	-3.171320
C	1.505361	-1.099646	0.183469
N	1.348288	0.056319	0.701859
C	3.102901	0.841872	-1.833577
H	3.965442	0.204806	-2.067141
H	3.203735	1.121960	-0.779537

3.2.4. xyz-Coordinates of the structure 8

C	-0.205648	-0.040285	-1.688077
C	-0.503205	1.171446	-0.881241
H	-0.070221	2.101407	-1.230333
C	-1.260034	1.252624	0.236196
C	-1.459757	2.505123	0.996792
C	-1.887256	4.921882	2.364741
C	-2.659443	2.726124	1.698804
C	-0.470283	3.506675	1.006464
C	-0.686307	4.704917	1.682305
C	-2.869423	3.928721	2.371518
H	-3.441999	1.970587	1.717156
H	0.478944	3.338100	0.507165
H	0.089741	5.465027	1.687089
H	-3.804787	4.085118	2.901230
H	-2.051231	5.855639	2.895358
C	1.036593	-0.040547	-2.516966
C	3.342247	-0.174581	-4.107619

C	2.062814	0.908029	-2.362556
C	1.186232	-1.061410	-3.473094
C	2.327183	-1.125148	-4.266036
C	3.209713	0.837218	-3.153413
H	1.985199	1.690813	-1.615197
H	0.393885	-1.794169	-3.583429
H	2.428832	-1.912818	-5.007259
H	3.999936	1.570743	-3.022156
H	4.234677	-0.224388	-4.725464
O	-0.967512	-1.011183	-1.706076
C	-1.398989	-0.342172	2.160471
H	-1.932742	-1.248576	2.433400
H	-1.704439	0.449347	2.848962
C	0.115343	-0.537505	2.253186
H	0.323221	-0.628856	3.329651
H	0.623383	0.383910	1.944152
C	0.691606	-1.711676	1.510233
C	0.055782	-2.845670	1.060172
N	0.966673	-3.695737	0.465978
C	2.221371	-3.131310	0.521597
C	2.086765	-1.874543	1.178837
H	-0.987725	-3.125106	1.104508
H	0.738360	-4.585179	0.044857
C	3.456208	-3.604968	0.060843
H	3.536874	-4.565756	-0.440509
C	3.235052	-1.085405	1.379091
H	3.164472	-0.124856	1.884051
C	4.572048	-2.800351	0.270671
H	5.545737	-3.139046	-0.073666
C	4.463193	-1.552887	0.923956
H	5.356297	-0.951466	1.073178

H	-5.122631	-1.449656	-1.210227
C	-4.648710	-0.527406	-1.536661
H	-5.115304	-0.036963	-2.384843
C	-3.562784	0.013869	-0.971037
H	-3.156251	0.939576	-1.356562
Cl	-5.837771	0.797737	2.695672
N	-1.886561	0.077500	0.804693
C	-2.888907	-0.541984	0.200220
O	-3.293200	-1.652224	0.776066
H	-4.055261	-2.058301	0.323154

3.2.5. xyz-Coordinates of the transition state $T_{8\rightarrow9}$

C	-0.000617	-0.614470	2.818004
C	-1.691764	-0.690400	-0.489704
C	-4.039192	-0.498667	-2.000844
C	-2.538530	-1.803468	-0.617783
C	-2.037598	0.523873	-1.103013
C	-3.201927	0.610894	-1.866376
C	-3.708808	-1.701282	-1.370166
H	-2.287487	-2.738047	-0.123523
H	-1.392766	1.391204	-1.001645
H	-3.451578	1.548776	-2.354257
H	-4.362366	-2.563838	-1.461544
H	-4.947738	-0.426037	-2.591928
C	-0.377011	-0.027709	4.139937
C	-0.971255	0.983028	6.692739
C	0.000482	-0.733469	5.295892
C	-1.058776	1.192752	4.281678
C	-1.348522	1.694464	5.550480
C	-0.296166	-0.234455	6.561446
H	0.529260	-1.674261	5.184428

H	-1.356504	1.769497	3.412048
H	-1.867848	2.643755	5.645652
H	0.000612	-0.792811	7.445127
H	-1.200936	1.375568	7.679734
O	0.767817	-1.594214	2.768211
C	0.655105	-2.264596	-1.307247
H	-0.359345	-2.353692	-1.684081
H	0.993023	-3.265158	-1.028695
C	1.580324	-1.675094	-2.390598
H	1.763580	-2.506171	-3.083298
H	2.555326	-1.429974	-1.955244
C	1.031218	-0.492567	-3.143753
C	-0.002094	-0.521374	-4.054459
N	-0.230694	0.741055	-4.555845
C	0.660522	1.624108	-3.988089
C	1.478905	0.878173	-3.088919
H	-0.602152	-1.356576	-4.391404
H	-0.934679	0.974844	-5.242128
C	0.823978	3.000799	-4.187028
H	0.186286	3.546113	-4.877831
C	2.494889	1.554762	-2.385218
H	3.139691	1.017218	-1.694818
C	1.831076	3.639210	-3.470609
H	1.984150	4.707271	-3.600488
C	2.659248	2.921875	-2.579127
H	3.439140	3.450033	-2.036450
C	-0.499383	-0.023510	1.588241
H	-1.325241	0.671462	1.660328
C	2.292123	-0.094968	1.078886
H	3.074218	-0.096393	1.830702
C	1.425724	0.997058	0.954595

H	1.535901	1.839565	1.633714
H	0.937197	1.230762	0.017481
C	-0.470755	-0.757171	0.364482
N	0.596546	-1.474157	-0.039956
Cl	1.502637	-5.070361	0.987642
C	1.871379	-1.344501	0.647734
O	2.620720	-2.395839	0.745000
H	2.130655	-3.312890	0.781888

3.2.6. xyz-Coordinates of the structure 9

C	-1.266551	0.959924	2.128726
C	-0.933192	0.750844	-0.842684
C	-2.362133	2.557426	-2.435019
C	-2.110890	0.341642	-1.498847
C	-0.490717	2.078977	-0.978058
C	-1.196546	2.969425	-1.784611
C	-2.820956	1.245762	-2.284300
H	-2.480711	-0.670824	-1.368976
H	0.419662	2.406220	-0.486959
H	-0.835178	3.986600	-1.901973
H	-3.734486	0.925291	-2.775978
H	-2.914747	3.257655	-3.054727
C	-2.505252	0.160358	2.333947
C	-4.907946	-1.227784	2.726501
C	-3.648021	0.832777	2.806407
C	-2.581056	-1.216255	2.070217
C	-3.777294	-1.906244	2.265939
C	-4.840886	0.144022	2.997971
H	-3.581522	1.896577	3.008468
H	-1.710785	-1.769604	1.734346
H	-3.821503	-2.970778	2.055969
H	-5.719940	0.672128	3.356016

H	-5.840405	-1.765510	2.874632
O	-1.191654	2.124773	2.491959
C	0.288101	-1.768403	-1.740029
H	-0.307377	-1.082905	-2.333194
H	-0.124560	-2.770111	-1.842487
C	1.762244	-1.724285	-2.206434
H	1.749711	-2.140998	-3.221080
H	2.357338	-2.409355	-1.595187
C	2.369782	-0.349775	-2.218962
C	2.231952	0.588119	-3.218434
N	2.893770	1.746384	-2.879153
C	3.489205	1.587195	-1.647021
C	3.179824	0.270554	-1.195592
H	1.703977	0.517714	-4.160335
H	2.952591	2.572822	-3.457884
C	4.268386	2.475226	-0.894491
H	4.489764	3.474367	-1.260072
C	3.685748	-0.151256	0.049904
H	3.474358	-1.150315	0.422314
C	4.746164	2.029854	0.333580
H	5.353021	2.694211	0.943078
C	4.459135	0.728072	0.800276
H	4.853408	0.409184	1.761703
C	-0.000702	0.324542	1.478186
H	0.635884	1.201903	1.314092
C	0.880328	-2.024132	1.928717
H	1.196458	-2.809351	2.607404
C	0.750947	-0.629936	2.450262
H	0.242653	-0.656150	3.421066
H	1.748369	-0.218611	2.645386
C	-0.238591	-0.181869	0.073416
N	0.164183	-1.372093	-0.306061
Cl	-1.821954	-4.938658	-0.308668

C	0.641434	-2.367592	0.661757
O	0.832049	-3.597873	0.155941
H	-0.054891	-4.059884	-0.000963

3.2.7. xyz-Coordinates of the structure 11

C	-0.966228	-2.143283	0.682249
C	-0.916744	0.770079	0.224626
C	-2.473560	2.255560	2.010470
C	-2.000587	1.534156	-0.250130
C	-0.632449	0.740170	1.602458
C	-1.397939	1.500296	2.483979
C	-2.778351	2.262118	0.646144
H	-2.252436	1.523520	-1.306246
H	0.200051	0.154823	1.977505
H	-1.156088	1.495576	3.542417
H	-3.624535	2.833696	0.277215
H	-3.076955	2.834347	2.703674
C	-2.426047	-2.254051	0.412979
C	-5.192430	-2.536915	0.047782
C	-3.220930	-2.857583	1.406151
C	-3.037200	-1.791554	-0.764428
C	-4.413273	-1.936389	-0.943183
C	-4.592619	-2.997140	1.225936
H	-2.742608	-3.209575	2.313811
H	-2.467481	-1.319313	-1.559962
H	-4.872381	-1.578401	-1.860169
H	-5.196145	-3.463387	1.999517
H	-6.263918	-2.647137	-0.095468
O	-0.476662	-2.595022	1.711033
C	0.600064	1.866905	-2.047812
H	-0.133334	2.403465	-1.457650
H	0.372049	2.002036	-3.103795

C	2.018983	2.382570	-1.713283
H	2.028210	3.422528	-2.062479
H	2.756618	1.846606	-2.316654
C	2.381196	2.322573	-0.256541
C	2.010540	3.229338	0.712133
N	2.499929	2.841427	1.938526
C	3.211930	1.670004	1.795646
C	3.162744	1.311995	0.416582
H	1.424556	4.134327	0.620174
H	2.368425	3.347292	2.803411
C	3.895428	0.902570	2.747092
H	3.917327	1.195810	3.793218
C	3.844403	0.152441	-0.003554
H	3.852609	-0.136568	-1.051857
C	4.546078	-0.243183	2.301385
H	5.086016	-0.861738	3.013347
C	4.523682	-0.612802	0.938556
H	5.051933	-1.508455	0.622224
C	1.126231	-0.446534	-2.783269
O	1.605528	0.104631	-3.739426
C	0.023218	-1.550729	-0.351810
H	0.990616	-1.588653	0.175805
C	1.252339	-1.911516	-2.491221
H	2.230248	-2.033272	-2.002195
H	1.301215	-2.428514	-3.452741
C	0.145285	-2.450840	-1.598243
H	-0.796496	-2.477155	-2.149972
H	0.380673	-3.468977	-1.277563
C	-0.137427	-0.083547	-0.695046
N	0.453616	0.407564	-1.768197
Cl	-2.016918	-0.316192	-4.043153

3.2.8. xyz-Coordinates of the transition state $T_{11\rightarrow12}$

C	0.954693	0.746993	1.353170
C	0.423599	0.337376	-1.661689
C	2.098468	1.534936	-3.596135
C	-0.115372	0.929996	-2.818054
C	1.820818	0.385263	-1.486877
C	2.646630	0.974407	-2.438469
C	0.716022	1.517102	-3.775241
H	-1.188454	0.968038	-2.961537
H	2.284208	-0.050692	-0.610053
H	3.720377	0.989456	-2.275003
H	0.274283	1.962588	-4.661813
H	2.745267	1.982615	-4.345294
C	1.331339	2.194142	1.377594
C	2.121704	4.880225	1.581925
C	2.158663	2.619223	2.433419
C	0.921079	3.132696	0.414602
C	1.322099	4.464310	0.514712
C	2.540465	3.953509	2.542107
H	2.479830	1.892813	3.172970
H	0.315273	2.833945	-0.432833
H	1.005018	5.176493	-0.241688
H	3.162473	4.271925	3.373818
H	2.418473	5.922130	1.664672
O	1.683173	-0.083662	1.886430
C	-1.909880	-1.539536	-2.143300
H	-1.972691	-1.061001	-3.121926
H	-2.847473	-2.069462	-1.979977
C	-0.681215	-2.473083	-2.056364
H	0.045340	-2.228594	-2.835469
H	-1.001180	-3.506571	-2.225042
C	-0.020260	-2.341029	-0.701345

C	1.400288	-2.475058	-0.555897
N	1.710634	-2.944553	0.641696
C	0.546698	-3.224643	1.374932
C	-0.553714	-2.919636	0.545669
H	2.166709	-2.246056	-1.282985
H	2.657700	-3.039873	0.995760
C	0.424370	-3.720567	2.666076
H	1.296522	-3.930818	3.277008
C	-1.843439	-3.166292	1.026427
H	-2.722178	-2.986456	0.415305
C	-0.874046	-3.938023	3.133348
H	-1.019775	-4.325414	4.137007
C	-1.988218	-3.674502	2.322363
H	-2.984368	-3.873539	2.706136
C	-2.986652	-0.255745	-0.352284
O	-4.058899	-0.664440	-0.775202
C	-0.414198	0.257966	0.822747
H	-0.621229	-0.600564	1.470108
C	-2.887482	0.553267	0.918976
H	-3.045410	-0.153801	1.744707
H	-3.730314	1.250147	0.929646
C	-1.556993	1.270211	1.077669
H	-1.512428	2.117036	0.390488
H	-1.461121	1.663023	2.094582
C	-0.489401	-0.263383	-0.621192
N	-1.800358	-0.547108	-1.054081
Cl	-3.105469	3.522272	-1.996320

3.2.9. xyz-Coordinates of the structure 12

C	-0.905427	-1.662445	-0.883988
C	-1.833869	0.595472	1.087924
C	-3.414103	0.058282	3.374028

C	-1.551898	-0.496079	1.926385
C	-2.933944	1.402383	1.418706
C	-3.715025	1.139123	2.546628
C	-2.327989	-0.758733	3.056251
H	-0.725147	-1.159968	1.713372
H	-4.559002	1.785216	2.772363
H	-2.081023	-1.610419	3.684302
H	-4.018250	-0.148191	4.253215
C	0.400938	-2.328895	-1.173941
C	2.772003	-3.749105	-1.663214
C	1.255379	-1.947260	-2.222047
C	0.745484	-3.442961	-0.384712
C	1.926481	-4.139270	-0.618515
C	2.430571	-2.659512	-2.467033
H	1.005931	-1.116112	-2.873244
H	0.075831	-3.745828	0.413646
H	2.189003	-4.986649	0.008578
H	3.079903	-2.355753	-3.282697
H	3.692883	-4.294692	-1.850457
O	-1.801709	-2.299962	-0.342175
C	-0.785474	3.355196	-0.113756
H	-1.509100	3.939957	0.462850
H	-0.369118	4.006078	-0.887276
C	0.296051	2.738846	0.775183
H	-0.046003	2.617323	1.805953
H	1.218895	3.323063	0.786253
C	2.647616	0.272438	0.309075
C	1.476953	0.496244	1.049859
C	3.778512	-0.363983	0.801165
H	4.657922	-0.509639	0.182898
C	1.471915	0.126025	2.392559
H	0.622535	0.334421	3.031512
C	3.727232	-0.782195	2.133088

H	4.583012	-1.288429	2.568820
C	2.595024	-0.528152	2.916334
H	2.587338	-0.834369	3.958112
C	-2.280295	2.425764	-1.803011
O	-2.559758	3.580038	-2.139121
C	-1.165742	-0.204256	-1.298419
H	-0.467437	0.061008	-2.097476
C	-2.822089	1.228542	-2.555233
H	-2.329947	1.241759	-3.537265
H	-3.885691	1.409686	-2.741498
C	-2.596559	-0.112995	-1.865977
H	-3.314812	-0.264186	-1.055118
H	-2.752195	-0.926112	-2.581509
Cl	4.548957	0.848536	-3.250162
N	-1.423768	2.197309	-0.762153
C	-0.998947	0.897789	-0.177744
C	0.519989	1.307062	0.185420
C	1.328152	1.432611	-1.078185
H	1.041430	1.940472	-1.991566
N	2.482313	0.861688	-0.969072
H	3.213706	0.849085	-1.738415
H	-3.197640	2.244732	0.790500

3.2.10. xyz-Coordinates of the transition state $T_{12\rightarrow13}$

C	-2.148384	0.427489	1.056389
C	-0.317440	-0.649348	-1.013734
C	-1.166967	-0.449560	-3.706202
C	-0.387716	0.597579	-1.667417
C	-0.741086	-1.784292	-1.729425
C	-1.146559	-1.687111	-3.060100
C	-0.805381	0.694249	-2.994218
H	-0.134807	1.515320	-1.149895

H	-1.459044	-2.584473	-3.586595
H	-0.849611	1.672135	-3.465721
H	-1.479258	-0.374953	-4.744072
C	-2.881615	1.668694	1.455231
C	-4.371771	3.886167	2.310521
C	-2.256605	2.913575	1.647928
C	-4.265916	1.556067	1.680698
C	-5.004432	2.654241	2.110662
C	-3.001856	4.014812	2.070044
H	-1.196422	3.045635	1.456667
H	-4.741909	0.592873	1.529505
H	-6.069596	2.551388	2.297601
H	-2.509564	4.972322	2.214000
H	-4.945686	4.742774	2.653433
O	-2.752434	-0.566011	0.670963
C	1.099884	-2.987270	0.509609
H	0.975981	-3.121948	-0.560845
H	0.903461	-3.929791	1.013427
C	2.558427	-2.510046	0.785490
H	3.249414	-3.264119	0.398972
H	2.706481	-2.410857	1.865142
C	2.911269	0.390621	-1.516279
C	3.205789	-0.980227	-1.200310
C	3.271694	0.941251	-2.762984
H	3.037815	1.971084	-3.010909
C	3.882234	-1.801690	-2.142053
H	4.114836	-2.834830	-1.901219
C	3.918701	0.107589	-3.655552
H	4.201698	0.497627	-4.629399
C	4.229381	-1.252491	-3.353581
H	4.742947	-1.852695	-4.098204
C	-0.370011	-2.325000	2.316814
O	-0.333921	-3.483179	2.705434

C	-0.624056	0.374984	1.296721
H	-0.189089	1.337818	1.027657
C	-0.958046	-1.233830	3.176159
H	-0.724381	-1.500910	4.210273
H	-2.049230	-1.280376	3.080409
C	-0.423061	0.142813	2.807771
H	-0.934461	0.923280	3.376726
H	0.639582	0.214288	3.063625
Cl	1.260949	3.973859	-0.326073
N	0.164734	-1.990420	1.046232
C	0.078160	-0.705585	0.442729
C	2.693966	-1.223231	0.080001
C	1.994590	-0.029705	0.497638
H	1.975964	0.292164	1.532187
N	2.263823	0.951349	-0.464197
H	1.962790	1.939502	-0.403754
H	-0.804257	-2.749602	-1.243918

3.2.11. xyz-Coordinates of the structure 13

C	-0.829176	-1.736629	-1.422422
C	-1.760802	0.062362	0.778428
C	-3.421112	-1.037679	2.785675
C	-1.242155	-0.804550	1.749802
C	-3.133837	0.359855	0.830245
C	-3.954652	-0.184461	1.817762
C	-2.061060	-1.343006	2.745460
H	-0.197798	-1.086225	1.733193
H	-5.011819	0.066752	1.830583
H	-1.627018	-2.007466	3.487831
H	-4.057072	-1.457696	3.560096
C	0.424351	-2.487871	-1.756315
C	2.689324	-4.044140	-2.342997

C	1.510637	-1.931464	-2.458346
C	0.492961	-3.837807	-1.357650
C	1.615260	-4.606668	-1.642921
C	2.633326	-2.710080	-2.749215
H	1.500102	-0.896835	-2.787903
H	-0.347647	-4.264143	-0.820688
H	1.656637	-5.644071	-1.323089
H	3.462578	-2.269354	-3.295047
H	3.565881	-4.645210	-2.568815
O	-1.806913	-2.339544	-0.994664
C	-1.333573	2.998252	0.449429
H	-1.874370	2.598687	1.310495
H	-1.824457	3.910412	0.119640
C	0.125747	3.291550	0.846073
H	0.170754	3.885177	1.763634
H	0.600192	3.877621	0.045743
C	2.216649	0.260088	1.504757
C	1.837974	1.607043	1.871408
C	3.245779	-0.421122	2.192514
H	3.539080	-1.426235	1.909280
C	2.486210	2.256726	2.966860
H	2.198950	3.264116	3.250791
C	3.844664	0.247974	3.236395
H	4.635974	-0.247985	3.791556
C	3.470830	1.575660	3.630513
H	3.988762	2.035259	4.466002
C	-1.913750	2.496915	-1.861191
O	-2.187728	3.686915	-2.025121
C	-0.934084	-0.223119	-1.674326
H	-0.087225	0.108555	-2.278732
C	-2.159465	1.498012	-2.972680
H	-1.361375	1.634420	-3.714446
H	-3.094030	1.797269	-3.457105

C	-2.198968	0.051106	-2.501524
H	-3.095552	-0.157889	-1.910753
H	-2.220127	-0.623634	-3.363552
Cl	2.019283	2.029079	-2.900456
N	-1.413893	2.033920	-0.658030
C	-0.907964	0.663726	-0.364316
C	0.862434	2.014400	0.981973
H	-3.568088	1.039200	0.104414
C	0.623228	0.929904	-0.000249
H	1.077273	1.290977	-0.961909
N	1.460564	-0.155456	0.477060
H	1.670304	-0.981592	-0.073146

3.2.12. xyz-Coordinates of the structures 14 + HCl

C	0.857242	0.225715	-1.803209
C	-0.892500	2.194322	0.042804
C	-2.425514	4.422248	-0.792685
C	-2.176259	2.029654	-0.497960
C	-0.409714	3.504948	0.186346
C	-1.159511	4.605364	-0.235984
C	-2.932578	3.127235	-0.912505
H	-2.602633	1.039032	-0.602657
H	-0.752898	5.605840	-0.114002
H	-3.924499	2.964565	-1.326040
H	-3.014251	5.276532	-1.115667
C	1.852864	-0.587884	-2.573906
C	3.605250	-2.120029	-4.144627
C	2.931005	-1.269350	-1.981415
C	1.669035	-0.686425	-3.965401
C	2.538688	-1.442260	-4.745175
C	3.797042	-2.033398	-2.763558
H	3.100836	-1.223702	-0.910993

H	0.836150	-0.159579	-4.419068
H	2.387156	-1.505330	-5.819137
H	4.620625	-2.562157	-2.292165
H	4.283302	-2.714053	-4.751112
O	-0.174589	0.603567	-2.353539
C	-0.502252	1.322002	2.991166
H	-1.380368	1.893746	2.671542
H	-0.056275	1.814175	3.852711
C	-0.906687	-0.122526	3.299187
H	-1.771356	-0.124746	3.975470
H	-0.091533	-0.638338	3.826593
C	-2.021606	-2.159497	0.324954
C	-1.954891	-2.014980	1.741586
C	-2.677033	-3.236270	-0.284246
H	-2.721193	-3.327244	-1.366032
C	-2.564908	-2.989440	2.558217
H	-2.530664	-2.901105	3.641098
C	-3.266827	-4.182372	0.548192
H	-3.780736	-5.031936	0.106514
C	-3.211416	-4.061758	1.954350
H	-3.684498	-4.820673	2.571705
C	1.761870	1.757220	2.199696
O	2.093422	2.064299	3.351411
C	1.178464	0.589039	-0.353349
H	1.591144	-0.307988	0.123343
C	2.809292	1.793172	1.099433
H	3.498548	0.966811	1.319248
H	3.382431	2.715839	1.236210
C	2.285441	1.660532	-0.327039
H	1.895622	2.609271	-0.705573
H	3.101922	1.369217	-0.993634
N	0.487649	1.353405	1.901140
C	-0.046996	0.989647	0.549738

H	0.550397	3.688944	0.655115
C	-0.890878	-0.261300	0.779817
N	-1.356882	-1.089404	-0.232525
H	-1.316138	-0.880014	-1.220315
C	-1.236526	-0.793968	2.000747
H	0.081841	-3.174337	2.017462
Cl	1.251610	-3.745515	2.090945

4. Literature

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