Iodine-Mediated Intramolecular Amination of Ketones: the Synthesis of 2-Acylindoles and 2-Acylindolines by Tuning *N*-Protecting Groups

(Supplementary Information)

*Wen-Chao Gao, Shan Jiang, Ruo-Lin Wang, and Chi Zhang**

State Key Laboratory of Elemento-Organic Chemistry, The Research Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. of China

Fax: 86-(22)-23503627

E-mail: zhangchi@nankai.edu.cn

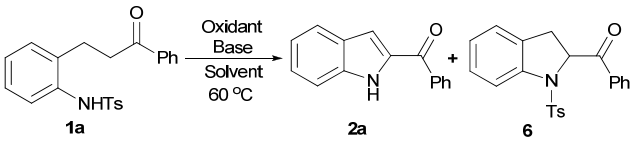
Table of contents

General Information

The ^{1}H NMR spectra were recorded at 400 MHz or 300 MHz and ^{13}C NMR spectra were measured at 100 MHz or 75 MHz using Bruker AV400 instrument with $CDCl_3$ or DMSO-d_6 as the solvent. The chemical shifts (δ) were measured in ppm and with the solvents as references (For $CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.00 ppm; for DMSO-d_6, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.43 ppm). The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. The known compounds were identified by the comparison of their NMR spectra with reported data in the literatures. The new compounds were characterized by NMR, IR, HRMS and melting point for solid samples. IR spectra were recorded on a FT-IR Bruker EQUINOX55 spectrometer and only major peaks are reported in cm^{-1}. High resolution mass spectral analyses (HR-MS) were performed on a high resolution ESI-FTICR mass spectrometer (Varian 7.0 T). Melting points were recorded on a RY-1 type apparatus. All solvents were obtained from commercial sources and were purified according to standard procedures. Petroleum ether (PE), where used, has the boiling point range 60-90 ^{o}C.

Optimization of the Reaction Conditions

Table S1. Condition optimization for 2-benzoylindole.[a]

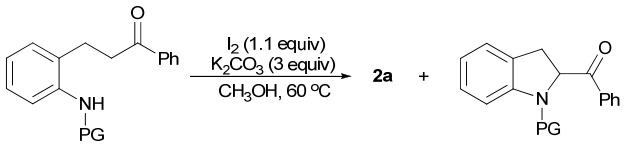


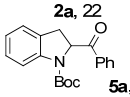
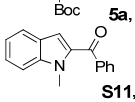
1a **2a** **6**

Entry	Oxidant (1.1 equiv)	Base (equiv)	Solvent	*t* (h)	Yield (%)[b]	
					2a	**6**
1	I_2	K_2CO_3 (2)	CH_3OH	12	20	52
2	I_2	none	CH_3OH	12	0	5
3	I_2	K_2CO_3 (2.5)	CH_3OH	12	67	13
4	I_2	K_2CO_3 (3)	CH_3OH	2	91	0
5[c]	I_2	K_2CO_3 (3)	CH_3OH	8	82	16
6	I_2	$KHCO_3$ (3)	CH_3OH	12	20	75
7	I_2	Na_2CO_3 (3)	CH_3OH	12	54	21
8	I_2	DBU (3)	CH_3OH	12	60	13
9	I_2	K_2CO_3 (3)	EtOH	12	61	10
10	I_2	K_2CO_3 (3)	EtOAc	12	23	26
11	I_2	K_2CO_3 (3)	Toluene	11	0	79
12	PIDA	K_2CO_3 (3)	CH_3OH	2	29	0
13	NBS	K_2CO_3 (3)	CH_3OH	2	39	0

[a] All the reactions were run with 0.2 mmol of **1a** in 3 mL of solvent. [b] Isolated yield. [c] The reaction was run at room temperature.

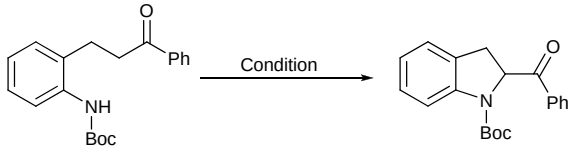
Table S2. Screening of *N*-protecting groups[a]



Entry	Protecting Group	*t* (h)	Yield (%)[b]
1	4-Toluenesulfonyl (Ts)	2	**2a**, 91
2	Benzenesulfonyl (Bs)	2.5	**2a**, 87
3	4-Nitrobenzenesulfonyl (Ns)	5	**2a**, 85
4	Methanesulfonyl (Ms)	3	**2a**, 93
5[c]	Acetyl (Ac)	24	**2a**, 22
6	*t*-Butoxycarbonyl (Boc)	24	 **5a**, 90
7[d]	Dimethyl	2	 **S11**, 70

[a] All the reactions were run with 0.2 mmol of substrate in 3 mL of solvent. [b] Isolated yield. [c] The use of tosyl group is preferable on the basis of cost consideration. [d] *N*-Acetyl-2-benzoylindoline was isolated in 75% yield. [e] With 2 equiv of I_2.

Table S3. Condition optimization for *N*-Boc-2-benzoylindoline.[a]



3a **4a**

Entry	Condition	Yield(%)[b]
1	I_2 (1.1 equiv), K_2CO_3 (3 equiv), 60 oC, 24 h, CH_3OH	90
2	I_2 (1.5 equiv), K_2CO_3 (3 equiv), 60 oC, 1 h, CH_3OH	91
3	I_2 (1.5 equv), K_2CO_3 (2.5 equiv), 60 oC, 1 h, CH_3OH	91
4	I_2 (1.5 equiv), K_2CO_3 (2.5 equiv), rt, 1.5 h, CH_3OH	91
5	I_2 (1.5 equiv), K_2CO_3 (2.2 equiv), rt, 1.5 h, CH_3OH	91
6[c]	I_2 (1.1 equiv), K_2CO_3 (2.2 equiv), rt, 4 h, CH_3OH	72
7[d]	I_2 (1.5 equiv), K_2CO_3 (2.2 equiv), rt, 12 h, THF	18
8[e]	I_2 (1.5 equiv), K_2CO_3 (2.2 equiv), rt, 12 h, CH_3CN	25

[a] The reactions were run with 0.3 mmol of substrate. [b] Isolated yield. [c] Conversion: 80%. [d] Conversion: 25%. [e] Conversion: 32%.

Gram-scale Reaction and A Control Experiment

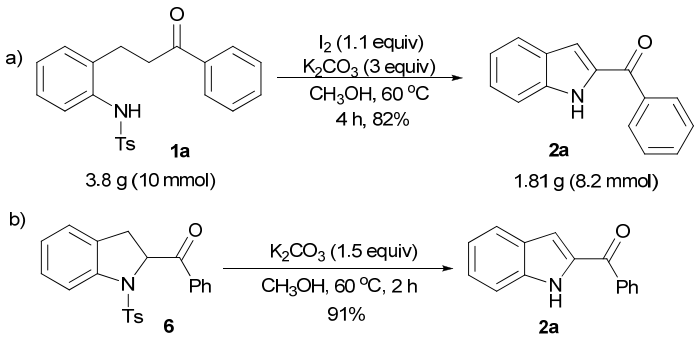


Figure 1 a) Gram-scale reaction for indole synthesis; b) the convertion from **6** to **2a**.

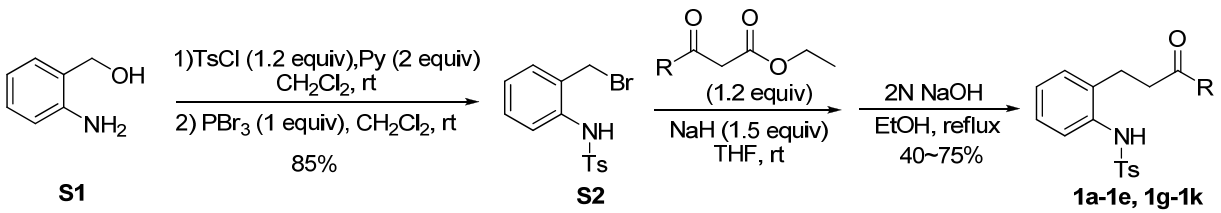
Representative Procedure for 2a and 4a

2-Benzoylindole (2a):[S1] Iodine (56 mg, 0.22 mmol) was added to a mixture of **1a** (76 mg, 0.2 mmol) and K_2CO_3 (83 mg, 0.6 mmol) in methanol (3 mL) at room temperature, and then the resulting mixture was stirred at 60 °C. After the reaction was complete by TLC analysis, methanol was evaporated in *vacuo* followed by adding saturated aq. solution of $Na_2S_2O_3$. The mixture was extracted by EtOAc and dried over Na_2SO_4. After removal of solvent, the residue was purified by flash column chromatography with petroleum ether/EtOAc (10:1) to give the 2-benzoylindole (**2a**). Yield: 91%; white solid; m.p. 139-141 ^oC; TLC, R_f = 0.44 (PE:EtOAc = 9:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 9.59 (br s, 1H), 8.01 (d, 2H, J = 8.0 Hz), 7.73 (d, 1H, J = 8.4 Hz), 7.64 (t, 1H, J = 7.2 Hz), 7.56 (t, 2H, J = 7.6 Hz), 7.51 (d, 1H, J = 8.4 Hz), 7.39 (t, 1H, J = 7.2 Hz), 7.20-7.16 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.24, 137.98, 137.56, 134.30, 132.34, 129.21, 128.45, 127.69, 126.50, 123.20, 121.01, 112.86, 112.21; IR (neat) v: 3415, 3313, 1624, 1516, 1342, 1257, 745 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{15}H_{12}NO$ $[M+H]^+$: 222.0913, found: 222.0917.

***N*-Boc-2-benzoylindoline (4a):** Iodine (114 mg, 0.45 mmol) was added to a mixture of **3a** (97 mg, 0.3 mmol) and K_2CO_3 (91 mg, 0.66 mmol) in methanol (3 mL), and the reaction was stirred at room temperature for 1 h. Methanol was evaporated in *vacuo* followed by adding saturated aq. solution of $Na_2S_2O_3$ and extracting with EtOAc. After removal of solvent, the residue was purified by flash column chromatography with petroleum ether/EtOAc (10:1) to give the *N*-Boc-2-benzoylindoline (**4a**). Yield: 91%; white solid; m.p. 76-79 ^oC; TLC, R_f = 0.35 (PE:EtOAc = 9:1); ^1H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 8.01-7.95 (m, 2.64H), 7.61-7.58 (m, 1.35H), 7.49 (t, 2H, J = 7.2 Hz), 7.24-7.21 (m, 1H), 7.08 (d, 1H, J = 7.2 Hz), 6.95 (t, 1H, J = 7.2 Hz), 5.87-5.67 (m, 1H), 3.65-3.57 (m, 1H), 3.10-3.00 (m, 1H), 1.60 (s, 3H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.11, 151.53, 143.01, 134.14, 133.41, 128.79, 128.29, 127.98, 124.43, 122.41, 114.62, 81.13, 63.04, 32.54, 28.32, 27.95; IR (neat) v: 3383, 2974, 2930, 1701, 1488, 1399, 1152, 758 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{20}H_{22}NO_3$ $[M+H]^+$: 324.1594, found: 324.1596.

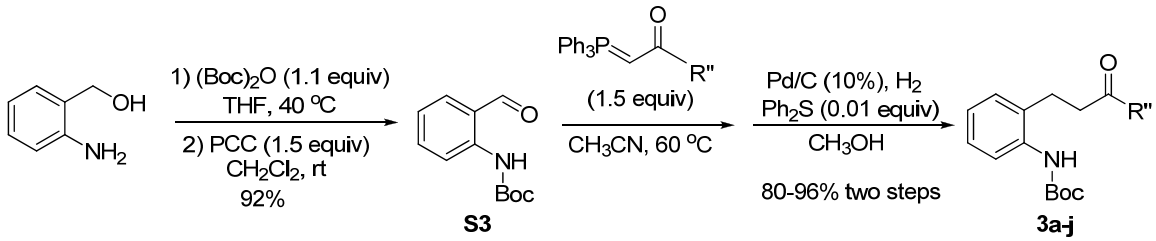
Synthesis of Starting Materials

Substrates **(1a-1e**, **1g-1k)** were synthesized from the commercial available 2-aminobenzyl alcohol by the general procedure 1. Substrates **(3a-3j**, **1f)** were prepared from 2-aminobenzylalcohol by the general procedure 2. Non-commercial aminobenzyl alcohols for **1l**, **1m**, **3k** and **3l** were prepared from the commercially available aminobenzoic acids by the reported method,[S2] and transformed to the corresponding substrates according to general procedure 2.



General Procedure 1: To a solution of 2-aminobenzylalcohol (**S1**) (1.2 g, 10 mmol) and pyridine (1.6 mL, 20 mmol) in anhydrous CH_2Cl_2 (40 mL) was added TsCl (2.7g, 12 mmol) at 0 ^oC, and then the mixture was stirred for 4 h at room temperature. The reaction was diluted with CH_2Cl_2 and washed with 1N HCl and brine. The organic layer was dried over anhydrous Na_2SO_4. After evaporation in *vacuo*, the residual solid product was dissolved in CH_2Cl_2 (50 mL) and to the solution was added PBr_3 (1.3 mL, 10 mmol) dropwise at 0 ^oC. The mixture was stirred for 1 h then quenched with water (20 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation in *vacuo* gave a white solid residue. Recrystallization from CH_2Cl_2/*n*-hexane afforded **S2**.[S3] Yield: 85%; white solid; m.p. 134-137 ^oC; TLC, R_f = 0.77 (PE:EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, 2H, J = 8.7 Hz), 7.33-7.23 (m, 5H), 7.16-7.12 (m, 1H), 6.87 (br s, 1H), 4.23 (s, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.01, 136.28, 134.93, 131.07, 131.51, 129.88, 129.68, 170.02, 126.33, 125.17, 30.10, 21.54.

S2 (1.0 g, 3.0 mmol) was dissolved in dry THF (5 mL) and added to a solution of NaH (60% in mineral oil, 180 mg, 4.5 mmol) and ethyl benzoylacetate (0.7 g, 3.6 mmol) in dry THF (20 mL), and the resulted mixture was stirred for 1 h at room temperature. After the reaction was quenched with saturated NH_4Cl solution and extracted with EtOAc, the organic layer was dried over Na_2SO_4, filtered and concentrated to give a viscous material. To this material was added 2N NaOH (4 mL) and ethanol (4 mL), and then the reaction mixture was heated at reflux overnight. The solution was cooled to room temperature, poured into 10% aq. HCl (10 mL), and extracted with EtOAc. The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed with petroleum ether/EtOAc (3:1) to give **1a**. Yield: 73%; white solid; m.p. 120-122 ^oC; TLC, R_f = 0.22 (PE:EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.66 (s, 1H), 7.89 (d, 2H, J = 7.6 Hz), 7.65 (d, 2H, J = 8.0 Hz), 7.54 (t, 1H, J = 7.2 Hz), 7.41 (t, 3H, J = 6.0 Hz), 7.19-7.10 (m, 5H), 3.24 (t, 2H, J = 6.0 Hz), 2.60 (t, 2H, J = 6.0 Hz), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.26, 143.22, 137.24, 135.95, 135.09, 134.68, 133.59, 130.11, 129.44, 128.56, 128.12, 127.22, 127.01, 126.19, 125.55, 40.15, 23.45, 21.43. IR (neat) v: 3442, 3144, 1665, 1493, 1335, 1163, 1091, 748 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{22}NO_3S$ $[M+H]^+$: 380.1315, found: 380.1319.



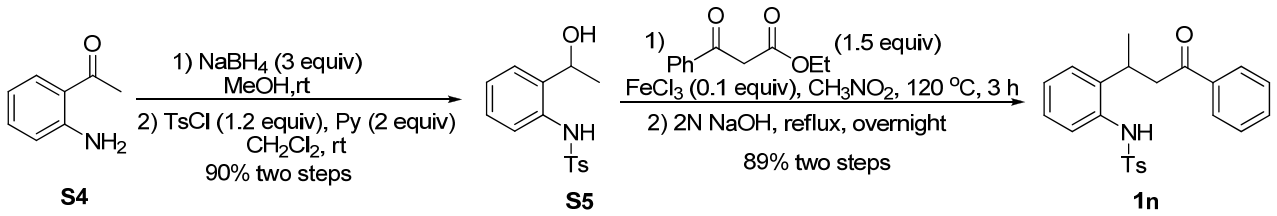
General Procedure 2:[S4] A THF solution (12 mL) of 2-aminobenzyl alcohol (500 mg, 4.0 mmol) and di-*tert*-butyl carbonate (960 mg, 4.4 mmol) was stirred at 40 °C for 24 h. The solvent was evaporated in *vacuo* to produce residual viscous crude. The crude was dissolved in CH_2Cl_2 (20 mL), mixed with PCC (1.3 g, 6.0 mmol) and silica gel (1.5 g), and then stirred for 6 h at room temperature. After the reaction was complete by TLC analysis, the solvent was evaporated in *vacuo*, and residual powder was purified by chromatography with petroleum ether/EtOAc (10:1) to give **S3**.[S5] Yield: 95%; white solid; m.p. 57-58 °C; TLC, R_f = 0.31 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.39 (s, 1H), 9.89 (s, 1H), 8.45 (d, 1H, J = 8.5 Hz), 7.63 (dd, 1H, J = 8.0, 1.6 Hz), 7.56 (td, 1H, J = 8.0, 1.6 Hz), 7.13 (td, 1H, J = 7.6, 0.9 Hz), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.01, 152.85, 141.77, 136.05, 135.92, 121.46, 121.17, 118.19, 80.92, 28.24.

A CH_3CN solution of **S3** (812 mg, 2.5 mmol) and (benzoylmethylene)triphenylphosphorane (1.4 g, 3.7 mmol) was stirred at 60 °C until the reaction was complete by TLC analysis. After evaporation of CH_3CN in *vacuo*, the crude was purified by chromatography with petroleum ether/EtOAc (3:1) to give (E)-2'-*tert*-butyloxycarbonylamino-chalcone. Yield: 90%; pale yellow solid; m.p. 98-101 °C; TLC, R_f = 0.29 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (d, 2H, J = 7.6 Hz), 7.99 (d, 1H, J = 6.8 Hz), 7.81 (d, 1H, J = 8.0 Hz), 7.63 (d, 1H, J = 8.0 Hz), 7.56 (t, 1H, J = 7.2 Hz), 7.51-7.45 (m, 3H), 7.37 (t, 1H, J = 7.2 Hz), 7.13 (t, 1H, J = 7.8 Hz), 6.81 (br s, 1H), 1.51 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.72, 152.91, 139.19, 137.79, 137.15, 132.88, 130.93, 128.53, 128.39, 127.08, 124.21, 123.64, 80.82, 77.31, 76.99, 76.68, 28.14.

After two vacuum/H_2 cycles to replace air in the reaction flask, the mixture of (E)-2'-*tert*-butyloxycarbonylamino-chalcone (323 mg, 1.0 mmol), Pd/C (10% wt of the substrate), and diphenylsulfide (1.7 μL, 10.0 μmol) in MeOH (4 mL) was vigorously stirred at room temperature and detected by TLC analysis. The reaction mixture was filtered with Celite, and the filtrate was concentrated and purified by chromatography with petroleum ether/EtOAc (10:1) to provide **3a**. Yield: 91%; white solid; m.p. 82-85 °C; TLC, R_f = 0.25 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, 2H, J = 7.6 Hz), 7.72 (d, 1H, J = 7.2 Hz), 7.60 (s, 1H), 7.56 (t, 1H, J = 7.6 Hz), 7.45 (t, 2H, J = 7.6 Hz), 7.21-7.17 (m, 2H), 7.04 (t, 1H, J = 7.6 Hz), 3.38 (t, 2H, J = 6.4 Hz), 3.02 (t, 2H, J = 6.4 Hz), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.85, 153.82, 136.45, 136.06, 133.35, 131.97, 129.44, 128.59, 128.07, 126.93,

124.21, 123.26, 80.07, 39.56, 28.37, 24.42; IR (neat) *v*: 3314, 2971, 1689, 1528, 1246, 1160 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NO_3$ $[M+H]^+$: 326.1751, found: 326.1752.

Synthesis of 1n:[S6]

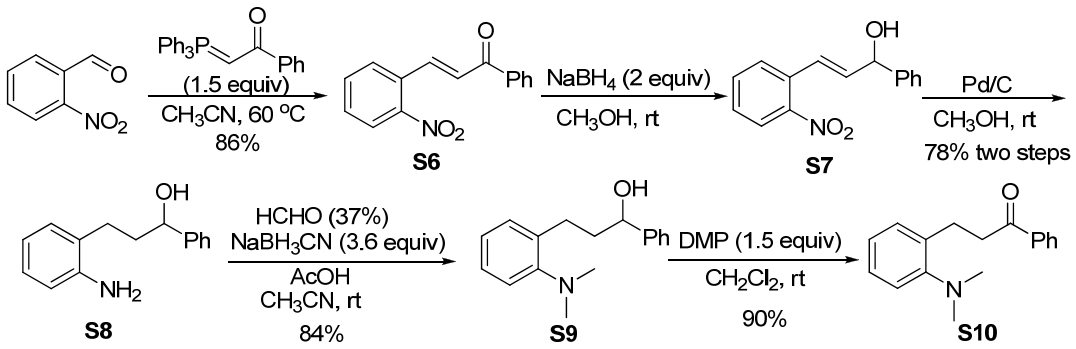


$NaBH_4$ (454 mg, 12.0 mmol) was added dropwise to a solution of **S4** (540 mg, 4.0 mmol) in MeOH (20 mL) at 0 °C. The resulting mixture was stirred at room temperature for 3h. After evaporation of MeOH, the solution was extracted with EtOAc, dried over anhydrous Na_2SO_4 and concentrated in *vacuo* to give yellow oil. Then the crude oil was dissolved in CH_2Cl_2 (15 mL), and mixed with TsCl (980 mg, 4.8 mmol) and pyridine (0.6 mL, 8 mmol) at 0 °C, and then stirred for 3 h at room temperature. The reaction was diluted with CH_2Cl_2 and washed with 1N HCl and brine. The organic layer was dried over Na_2SO_4, concentrated in *vacuo* and purified by chromatography with petroleum ether/EtOAc (2:1) to give **S5**. Yield: 90%; yellow syrup; TLC, R_f = 0.18 (PE:EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.51 (s, 1H), 7.67 (d, 2H, J = 7.6 Hz), 7.41 (d, 1H, J = 8.0 Hz), 7.21 (d, 2H, J = 8.0 Hz), 7.16 (t, 1H, J = 8.0 Hz), 7.09-7.01 (m, 2H), 4.84 (q, 1H, J = 6.4 Hz), 2.36 (s, 3H), 1.34 (d, 3H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.70, 136.79, 135.59, 134.09, 129.57, 128.40, 127.10, 126.98, 124.61, 121.75, 69.64, 22.80, 21.48. IR (neat) *v*: 3480, 3243, 2976, 2926, 1494, 1328, 1157, 1091, 932, 757 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}NO_3S$ $[M-H]^-$: 290.0856, found: 290.0851.

Anhydrous $FeCl_3$ (16 mg, 0.10 mmol) was added to a solution of **S5** (290 mg, 1.0 mmol) and ethyl benzoylacetate (288 mg, 1.5 mmol) in CH_3NO_2 (4 mL), the mixture was heated at 120 °C for 3 h. The reaction mixture was quenched with water followed by extraction with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated to afford a crude material. To this residual material was added 2N aq. NaOH (5 mL), and the reaction was heated at reflux overnight. The solution was cooled to room temperature, poured into 10% aq. HCl and extracted with EtOAc. After concentration in *vacuo*, the residue was chromatographed by petroleum ether/EtOAc (10:1) to give **1n**. Yield: 89%; white solid; TLC, R_f = 0.22 (PE:EtOAc = 9:1); m.p. 165-167 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.66 (s, 1H), 7.85 (d, 2H, J = 7.2 Hz), 7.64 (d, 2H, J = 8.0 Hz), 7.53-7.46 (m, 2H), 7.38 (t, 2H, J = 7.6 Hz), 7.19 (d, 2H, J = 8.4 Hz), 7.14-7.13 (m, 3H), 3.30-3.18 (m, 2H), 3.09-3.05 (m, 1H), 2.33 (s, 3H), 0.79 (d, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.93, 143.13, 140.70, 137.26, 135.90, 133.66, 133.51, 129.38, 128.49, 128.03, 127.07, 126.86, 126.78, 126.22, 48.22, 27.19, 21.44, 21.31; IR (neat) *v*: 3307, 2977, 2889, 1681, 1489,

1317, 1152, 1091, 922, 750 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}NO_3S$ $[M+H]^+$: 394.1471, found: 394.1481.

Synthesis of 3-(2-(dimethylamino)phenyl)-1-phenylpropan-1-one (S10):



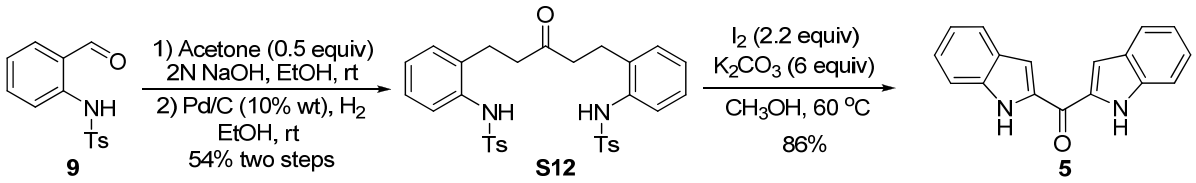
A CH_3CN solution of 2-nitrobenzaldehyde (552 mg, 2.5 mmol) and (benzoylmethylene)triphenylphosphorane (1.4 g, 3.7 mmol) was stirred at 60 °C until the reaction was complete as indicated by TLC. After evaporation of CH_3CN in *vacuo*, the crude was purified by chromatography with petroleum ether/EtOAc (3:1) to give **S6**.[S7] Yield: 86%; white solid; m.p. 124-126 °C; TLC, R_f = 0.32 (PE:EtOAc = 9:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.13 (d, 1H, J = 16.0 Hz), 8.07 (d, 1H, J = 8.0 Hz), 8.02 (d, 1H, J = 6.4 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.69 (d, 1H, J = 7.6 Hz), 7.65-7.48 (m, 4H), 7.32 (d, 1H, J = 16.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.48, 148.55, 140.16, 137.41, 133.53, 133.12, 131.34, 130.32, 129.23, 128.78, 128.71, 127.38, 124.98.

$NaBH_4$ (152 mg, 4.0 mmol) was added in portions to a solution of **S6** (510 mg, 2.0 mmol) in MeOH (10 mL) at 0 °C. The resulting mixture was stirred at room temperature overnight. After evaporation of MeOH, water was added and the solution was extracted with EtOAc. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the allylic alcohol **S7** which was used directly without purification. After two vacuum/H_2 cycles to replace air inside the reaction flask, the solution of **S7** (253 mg, 1.0 mmol) in CH_3OH (10 mL) was treated with Pd/C (10% wt of the substrate) and vigorously stirred at room temperature under 1 atm of hydrogen for 12 h. The resulting mixture was filtered through Celite, and the filtrate was concentrated to provide a viscous material which could be purified by chromatography to give **S8**. Yield: 78%; white solid; m.p. 77-81 °C; TLC, R_f = 0.11 (PE:EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32 (d, 4H, J = 4.4 Hz), 7.29-7.23 (m, 1H), 7.03 (t, 2H, J = 7.2 Hz), 6.74 (t, 1H, J = 7.2 Hz), 6.66 (d, 1H, J = 8.0 Hz), 4.64 (dd, 1H, J = 8.8, 4.4 Hz), 3.34 (br s, 2H), 2.62 (t, 2H, J = 8.0 Hz), 2.09-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.54, 144.10, 129.59, 128.43, 127.50, 127.03, 126.36, 125.75, 119.03, 115.91, 73.28, 38.54, 27.01. IR (neat) v: 3373, 3215, 3024, 2921, 1498, 1453, 1061, 759 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}NO$ $[M-H]^-$: 226.1237, found: 226.1238.

S9 was prepared by the reported procedure.[S8] To a stirred solution of **S8** (341 mg, 1.5 mmol) and 37% aqueous formaldehyde (1.5 mL) in acetonitrile (6 mL) was added $NaBH_3CN$ (340 mg, 5.4 mmol). Glacial acetic acid (0.3 mL) was added over 10 min, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was poured into CH_2Cl_2, basified with 1N aq. NaOH, and washed with brine. The organic layers were dried and concentrated. The residue was purified by chromatography to afford **S9**. Yield: 84%; colorless oil; TLC, R_f = 0.38 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (d, 4H, J = 4.0 Hz), 7.25-7.19 (m, 4H), 7.13 (t, 1H, J = 7.2 Hz), 5.99 (s, 1H), 4.25 (dd, 1H, J = 11.2, 6.4 Hz), 3.19 (td, 1H, J = 12.8, 4.8 Hz), 2.75 (s, 6H), 2.72-2.66 (m, 1H), 2.04-1.96 (m, 1H), 1.90-1.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.01, 144.70, 136.42, 130.82, 128.12, 127.23, 126.77, 125.51, 125.17, 119.35, 70.57, 45.73, 41.91, 26.72. IR (neat) v: 3273, 2934, 2866, 1492, 1452, 1087, 1060, 1037, 763 cm^{-1}; HRMS (MALDI) m/z calcd. for $C_{17}H_{22}NO$ $[M+H]^+$: 256.1696, found: 256.1695.

To a solution of **S9** (127 mg, 0.5 mmol) in CH_2Cl_2 (4 mL) was added Dess-Martin reagent (318 mg, 0.75 mmol) in portions at room temperature. After being stirred for 30 min, a saturated solution of $Na_2S_2O_3$ was added. The mixture was extracted with EtOAc, dried over Na_2SO_4, and concentrated in *vacuo*. The crude residue was purified by chromatography to give **S10**. Yield: 90%; yellow oil; TLC, R_f = 0.23 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (d, 2H, J = 7.2 Hz), 7.56 (t, 1H, J = 7.2 Hz), 7.46 (t, 2H, J = 7.2 Hz), 7.22 (t, 2H, J = 7.6 Hz), 7.15 (d, 1H, J = 7.6 Hz), 7.04 (t, 1H, J = 7.2 Hz), 3.33 (t, 2H, J = 7.2 Hz), 3.14 (t, 2H, J = 7.2 Hz), 2.68 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.93, 152.96, 136.98, 136.26, 132.86, 129.92, 128.51, 128.10, 127.08, 123.67, 119.89, 45.13, 39.67, 26.56; IR (neat) v: 3059, 2937, 2825, 1683, 1597, 1493, 1449, 746 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{19}NONa$ $[M+Na]^+$: 276.1359, found: 276.1357.

Synthesis of Bis(1*H*-2-indolyl)methanone (5):



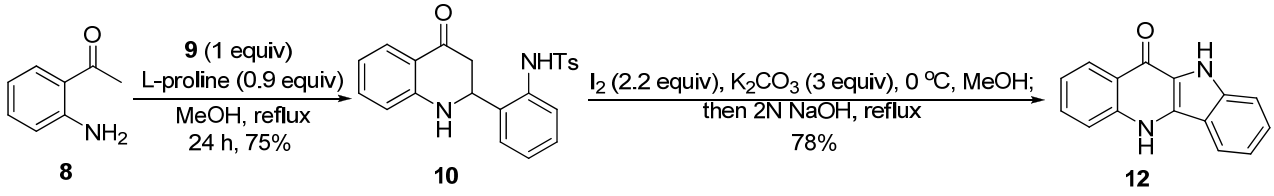
9 **S12** **5**

2N aq. NaOH (2.5 mL, 5 mmol) was added dropwise to the solution of aldehyde **9** (550 mg, 2.0 mmol) and acetone (58 mg, 1 mmol) in EtOH (10 mL). The reaction mixture was stirred at room temperature for 12 h. After the removal of solvent, the residue was treated with 1N HCl until pH < 7 and extracted with EtOAc. The organic layer was separated, dried over Na_2SO_4, and concentrated to give a crude product, after purification by column chromatograph with petroleum ether/EtOAc (3:1), the

corresponding dienone could be isolated as pale yellow solid. Then Pd/C (10% wt of the substrate) was added to the solution of dienone (570 mg, 1.0 mmol) in EtOH (10 mL). After two vacuum/H_2 cycles to replace air inside the reaction flask, the reaction was stirred at room temperature overnight, followed by filtration with Celite. The filtrate was concentrated and purified by colum chromatography with dichloromethane/acetone (95:5) to give **S12**. Yield: 54%; white solid; m.p. 59-62 ^{o}C; TLC, R_f = 0.64 (CH_2Cl_2:CH_3OH = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (s, 2H), 7.64 (d, 4H, J = 7.6 Hz), 7.23-7.19 (m, 6H), 7.13-7.05 (m, 4H), 6.99 (d, 2H, J = 7.6 Hz), 2.56 (dd, 8H, J = 14.8, 5.6 Hz), 2.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.58, 143.53, 137.07, 135.30, 134.32, 129.99, 129.59, 127.27, 127.15, 126.56, 125.62, 43.57, 23.98, 21.52; IR (neat) v: 3446, 3265, 1700, 1493, 1331, 1160, 1091, 922 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{31}H_{32}N_2O_5S_2Na$ $[M+Na]^+$: 599.1645, found: 599.1645.

Iodine (112 mg, 0.44 mmol) was added to a mixture of **S12** (115 mg, 0.2 mmol) and K_2CO_3 (166 mg, 1.2 mmol) in methanol (6.0 mL) at room temperature, and then the resulting mixture was stirred at 60 °C. After the reaction was complete by TLC analysis, methanol was evaporated in *vacuo* followed by adding saturated aq. solution of $Na_2S_2O_3$. The mixture was extracted by EtOAc and dried over Na_2SO_4. After removal of solvent, the residue was purified by flash column chromatography with petroleum ether/EtOAc (3:1) to give **5**.[S9] Yield: 86%; yellow solid; m.p. 270-272 ^{o}C; TLC, R_f = 0.52 (PE:EtOAc = 2:1); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.99 (s, 2H), 7.76 (d, 2H, J = 7.6 Hz), 7.62 (s, 2H), 7.51 (d, 2H, J = 8.0 Hz), 7.31 (t, 2H, J = 7.6 Hz), 7.12 (t, 2H, J = 7.2 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 176.68, 137.65, 134.47, 127.21, 125.27, 122.67, 120.29, 112.59, 109.52.

Synthesis of Quindolinone (12):

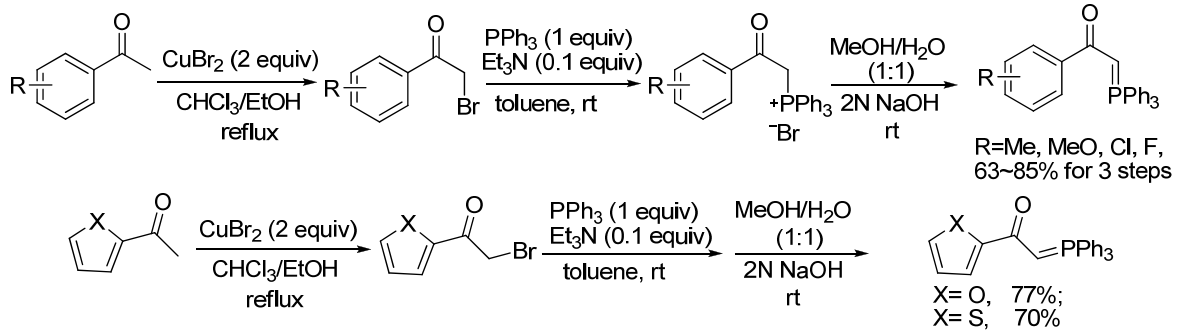


L-proline (0.6 mmol) was stirred in 8 mL of methanol for 10 min, 2-aminoacetophenone (300 mg, 2 mmol) and **9** (550 mg, 2 mmol) were then added. The resulting mixture was stirred at reflux for 2 h, then two further portions of L-proline (0.6 mmol each time) was added, once every 2 h. The reaction detected by TLC analysis until the substrates were disappeared. The reaction solution was evaporated in *vacuo*, quenched with saturated ammonium chloride solution and extracted with EtOAc. The combined organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography with petroleum ether/EtOAc (7:1) to give **10**. Yield: 75%; pale yellow solid; m.p.:185-188 ^{o}C; TLC, R_f = 0.11 (PE:EtOAc = 7:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (s, 1H), 7.84 (d, 1H, J = 7.6 Hz), 7.59 (d, 2H, J = 8.0 Hz),

7.40-7.32 (m, 2H), 7.24-7.19 (m, 5H), 6.84 (t, 1H, J = 7.6 Hz), 6.71 (d, 1H, J = 8.0 Hz), 4.87 (dd, 1H, J = 12.0, 2.8 Hz), 4.56 (s, 1H), 2.72-2.63 (m, 1H), 2.45-2.43 (m, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.20, 151.24, 144.17, 136.30, 135.42, 134.55, 133.71, 129.75, 129.11, 128.61, 127.56, 127.18, 126.64, 125.12, 119.47, 116.78, 55.43, 43.90, 21.56; IR (neat) v: 3274, 3150, 1655, 1606, 1498, 1481, 1332, 1308, 1160, 1088, 932, 789 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{20}N_2O_3SNa$ $[M+Na]^+$: 415.1087, found: 415.1083.

Iodine (112 mg, 0.44 mmol) was added to a mixture of **10** (79 mg, 0.2 mmol) and K_2CO_3 (83 mg, 0.6 mmol) in methanol (4.0 mL) at 0 ^{o}C. After the reaction mixture was stirred at 0 ^{o}C for 4 h, 2N aq NaOH (2.5 mL, 5 mmol) was added to the mixture and refluxed for overnight. The reaction mixture was cooled to room temperature and methanol was evaporated in *vacuo*. Aq. $Na_2S_2O_3$ was added to the residue and extracted with EtOAc. The combined organic layer was dried (Na_2SO_4), concentrated, and purified by column chromatography with CH_2Cl_2/MeOH (95:1) to give **12**.[S10] Yield: 78%; yellow solid; m.p. > 300 ^{o}C; TLC, R_f = 0.23 (CH_2Cl_2:MeOH = 9:1); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.46 (s, 1H), 11.71 (s, 1H), 8.36 (d, 1H, J = 8.0 Hz), 8.19 (d, 1H, J = 8.0 Hz), 7.73 (d, 1H, J = 8.0 Hz), 7.70-7.65 (m, 1H), 7.52 (d, 1H, J = 8.4 Hz), 7.47 (t, 1H, J = 7.6 Hz), 7.29 (t, 1H, J = 8.0 Hz), 7.20 (t, 1H, J = 8.0 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.34, 138.98, 138.55, 130.62, 128.85, 127.36, 125.13, 123.01, 122.79, 120.76, 120.43, 118.84, 117.70, 115.80, 112.56.

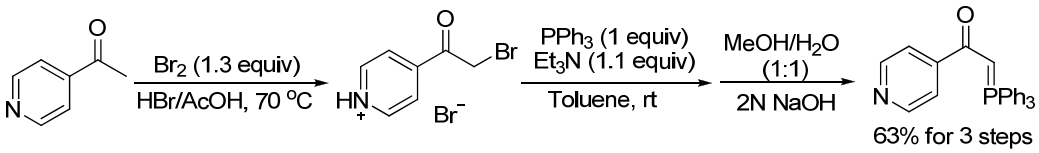
General Procedure for the phosphorane ylides:[S11]



To a solution of the ketone in a mixture of $CHCl_3$ and EtOH (v:v =1:1, 0.5 M), $CuBr_2$ (2 equiv) was added under N_2 at room temperature, then the mixture was heated to reflux. After the reaction was complete by GC analysis, and then the dark-green suspension was filtered while it was hot, the residue was washed with EtOAc. The filtrate was then concentrated under reduced pressure to give the crude α-bromide ketone.

Then Et_3N (0.1 equiv) was added to a stirred solution of the resulting α-bromo carbonyl compound (1.0 equiv) in toluene (0.30 M), followed by addition of a solution of PPh_3 (1.0 equiv) in toluene. The mixture was stirred at room temperature until the α-bromo carbonyl compound was consumed as indicated by TLC. The reaction mixture was then filtrated and the precipitate was washed with Et_2O and collected for the next step.

The resulting crude phosphorane salt was added to a mixture of H_2O and MeOH (v:v = 1:1, 0.25 M), then the reaction solution was stirred at RT for 1 h, followed by adding 2N NaOH aq. to the mixture until the pH = 7-8 and vigorously stirring for another 2-3 h. The resulting suspension was extracted with EtOAc (30 mL×3). The combined organic layers were dried over Na_2SO_4 and concentrated to give the phosphorane ylides without purification.

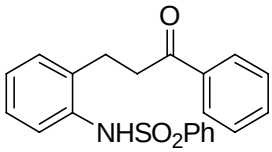


Br_2 (2.7 mL, 52 mmol) was added dropwise to a stirred solution of 2-acetylpyridine (4.84g, 40 mmol) in 48% aq. HBr (7.0 mL) and AcOH (36 mL) at 0 °C, and then the mixture was stirred at 70 °C for 2 h. The resulting precipitated white solid was collected by filtration, washed with Et_2O for 3 times, and dried by suction at room temperature.

The bromide salt (2.8 g, 10mmol) was dissolved into toluene, and Et_3N (1.6 mL, 11.0 mmol) was added dropwise. After the color of solution was changed, PPh_3 (2.6 g, 10 mmol) was added in one portion, and the resulting mixture was stirred overnight at room temperature. The pale yellow precipitation was filtered and washed with petroleum ether for 3 times.

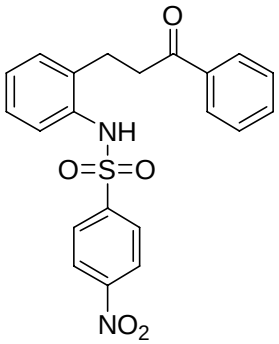
Characterization Data for Substrates and products

N-(2-(3-oxo-3-phenylpropyl)phenyl)benzenesulfonamide



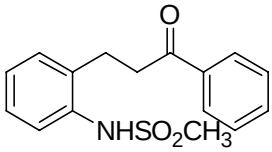
Yield: 75%; white solid; m.p. 123-126 °C; TLC, R_f = 0.22 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (s, 1H), 7.90 (d, 2H, J = 7.6 Hz), 7.77 (d, 2H, J = 7.2 Hz), 7.55 (t, 1H, J = 7.2 Hz), 7.49 (d, 1H, J = 7.2 Hz), 7.44-7.38 (m, 5H), 7.16-7.09 (m, 3H), 3.25 (t, 2H, J = 6.0 Hz), 2.55 (t, 2H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.36, 140.17, 135.93, 135.20, 134.61, 133.67, 132.49, 130.13, 128.87, 128.59, 128.16, 127.30, 126.97, 126.34, 125.78, 40.22, 23.35; IR (neat) v: 3435, 3149, 1667, 1448, 1167, 1156, 1091, 752 cm^{-1}; HRMS (MALDI) m/z calcd. for $C_{21}H_{19}NO_3SNa$ $[M+Na]^+$: 388.0978, found: 388.0984.

_N_-(2-(3-oxo-3-phenylpropyl)phenyl)-4-nitrobenzenesulfonamide



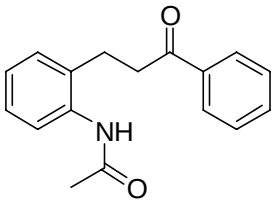
Yield: 63%; white solid; m.p. 162-164 °C; TLC, R_f = 0.45 (PE:EtOAc = 2:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.32 (s, 1H), 8.26 (d, 2H, J = 8.8 Hz), 7.97 (d, 2H, J = 7.2 Hz), 7.92 (d, 2H, J = 7.6 Hz), 7.57 (t, 1H, J = 7.2 Hz), 7.46-7.42 (m, 3H), 7.22-7.10 (m, 3H), 3.32 (t, 2H, J = 6.0 Hz), 2.53 (t, 2H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.84, 149.87, 146.10, 135.70, 135.05, 134.02, 133.77, 130.43, 128.72, 128.27, 128.23, 127.68, 126.92, 125.74, 124.14, 40.43, 23.40; IR (neat) v: 3446, 3167, 3100, 1670, 1529, 1348, 1169, 738 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{17}N_2O_5S$ $[M-H]^-$: 409.0864, found: 409.0862.

_N_-(2-(3-oxo-3-phenylpropyl)phenyl)methanesulfonamide



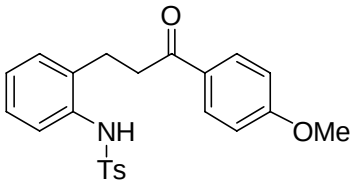
Yield: 40%; white solid; m.p. 118-121 °C; TLC, R_f = 0.15 (PE:EtOAc = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, 1H), 7.94 (d, 2H, J = 7.2 Hz), 7.56 (t, 1H, J = 7.2 Hz), 7.49 (d, 1H, J = 8.0 Hz), 7.43 (t, 2H, J = 7.6 Hz), 7.26-7.13 (m, 3H), 3.45 (t, 2H, J = 6.0 Hz), 3.08 (t, 2H, J = 6.4 Hz), 3.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.32, 136.00, 135.06, 134.27, 133.68, 130.44, 128.63, 128.17, 127.56, 126.09, 124.06, 40.26, 40.00, 24.12; IR (neat) v: 3325, 3264, 1674, 1326, 1150, 977, 750 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{16}H_{17}NO_3SNa$ $[M+Na]^+$: 326.0821, found: 326.0823.

_N_-(2-(3-oxo-3-phenylpropyl)phenyl)acetamide



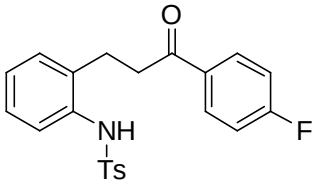
Yield: 84%; white solid; m.p. 63-66 ^{o}C; TLC, R_f = 0.35 (PE:EtOAc = 2:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.23 (s, 1H), 7.95 (d, 2H, J = 7.6 Hz), 7.82 (d, 1H, J = 8.0 Hz), 7.57 (t, 1H, J = 7.2 Hz), 7.45 (t, 2H, J = 7.6 Hz), 7.20 (t, 2H, J = 7.2 Hz), 7.07 (t, 1H, J = 7.2 Hz), 3.45 (t, 2H, J = 6.0 Hz), 3.03 (t, 2H, J = 6.0 Hz), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.98, 168.96, 136.19, 135.70, 133.67, 132.67, 129.85, 128.65, 128.12, 126.97, 125.03, 124.31, 40.35, 24.34, 23.96; IR (neat) v: 3431, 3259, 1676, 1632, 1534, 1287, 758 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found: 268.1330.

_N_-(2-(3-(4-methoxyphenyl)-3-oxopropyl)phenyl)-4-methylbenzenesulfonamide (1b)



Yield: 71%; white solid; m.p. 121-123 ^{o}C; TLC, R_f = 0.22 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.90 (s, 1H), 7.88 (d, 2H, J = 8.8 Hz), 7.65 (d, 2H, J = 8.0 Hz), 7.42 (d, 1H, J = 8.0 Hz), 7.19-7.08 (m, 5H), 6.88 (d, 2H, J = 8.4 Hz), 3.84 (s, 3H), 3.19 (t, 2H, J = 5.6 Hz), 2.56 (t, 2H, J = 5.6 Hz), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.74, 163.86, 143.14, 137.38, 135.15, 134.83, 130.50, 130.15, 129.43, 129.06, 127.20, 127.02, 126.04, 125.42, 113.71, 55.47, 39.83, 23.53, 21.46; IR (neat) v: 3433, 3150, 1650, 1600, 1572, 1336, 1247, 1168, 1093, 1029, 773 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{24}NO_4S$ $[M+H]^+$: 410.1421, found: 410.1426.

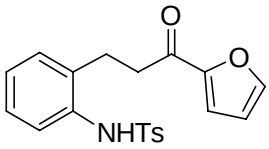
_N_-(2-(3-(4-fluorophenyl)-3-oxopropyl)phenyl)-4-methylbenzenesulfonamide (1c)



Yield: 62%; pale yellow solid; m.p. 97-100 ^{o}C; TLC, R_f = 0.20 (PE:EtOAc = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (s, 1H), 7.94 (dd, 2H, J = 8.4, 5.6 Hz), 7.65 (d, 2H, J = 8.0 Hz), 7.40 (d, 1H, J = 7.6 Hz), 7.19 (d, 2H, J = 8.0 Hz), 7.16-7.09 (m, 5H), 3.22 (t, 2H, J = 5.6 Hz), 2.60 (t, 2H, J = 5.6 Hz), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.64, 165.97 (d, J = 254.2 Hz), 143.27, 137.26, 135.08, 134.69, 132.46, 130.87 (d, J = 9.3 Hz), 130.12, 129.47, 127.31, 127.05, 126.28, 125.65, 115.73 (d, J = 21.7 Hz), 40.09, 23.54, 21.46; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -103.97; IR (neat) v: 3450, 3153, 3081, 1558, 1596,

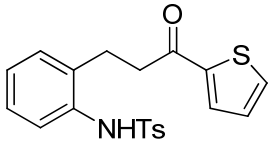
1493, 1330, 1234, 1160, 1091, 756 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{21}FNO_3S$ $[M+H]^+$: 398.1221, found: 398.1227.

_N_-(2-(3-(furan-2-yl)-3-oxopropyl)phenyl)-4-methylbenzenesulfonamide (1d)



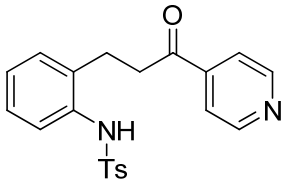
Yield: 72%; white solid; m.p. 99-102 °C; TLC, R_f = 0.26 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (s, 1H), 7.62 (d, 2H, J = 8.0 Hz), 7.54 (s, 1H), 7.36 (d, 1H, J = 7.6 Hz), 7.19-7.17 (m, 3H), 7.14-7.08 (m, 3H), 6.49 (dd, 1H, J = 7.2, 6.5 Hz), 3.08 (t, 2H, J = 6.0 Hz), 2.58 (t, 2H, J = 6.0 Hz), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.24, 152.09, 146.71, 143.26, 137.17, 134.94, 134.53, 130.07, 129.42, 127.24, 126.97, 126.23, 125.57, 117.81, 112.43, 39.67, 23.29, 21.40; IR (neat) *v*: 3434, 3210, 3126, 1666, 1473, 1401, 1325, 1153, 1091, 980, 767 cm^{-1}; HRMS (MALDI) *m*/*z* calcd. for $C_{20}H_{19}NO_4SNa$ $[M+Na]^+$: 392.0927, found: 392.0923.

_N_-(2-(3-oxo-3-(thiophen-2-yl)propyl)phenyl)-4-methylbenzenesulfonamide (1e)



Yield: 70%; white solid; m.p. 104-106 °C; TLC, R_f = 0.18 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.49 (s, 1H), 7.67-7.62 (m, 4H), 7.38 (d, 1H, J = 8.0 Hz), 7.19 (d, 2H, J = 8.0 Hz), 7.15-7.07 (m, 4H), 3.19 (t, 2H, J = 6.0 Hz), 2.60 (t, 2H, J = 6.0 Hz), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.03, 143.24, 143.03, 137.29, 134.87, 134.69, 134.34, 132.58, 130.11, 129.46, 128.18, 127.33, 127.05, 126.20, 125.55, 40.64, 23.56, 21.46; IR (neat) *v*: 3447, 3241, 1658, 1494, 1658, 1415, 1336, 1162, 1092, 740 cm^{-1}; HRMS (MALDI) *m*/*z* calcd. for $C_{20}H_{19}NO_3S_2NO_2$ $[M+Na]^+$: 408.0699, found: 408.0691.

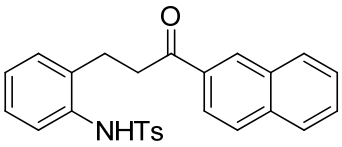
_N_-(2-(3-oxo-3-(pyridin-4-yl)propyl)phenyl)-4-methylbenzenesulfonamide (1f)



Yield: 54%; white solid; m.p. 42-45 °C; TLC, R_f = 0.31 (CH_2Cl_2:CH_3OH = 99:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.77 (d, 2H, J = 4.8 Hz), 8.05 (d, 1H, J = 4.8 Hz), 7.66 (d, 3H, J = 6.4 Hz), 7.63 (s, 1H), 7.32 (d, 1H, J = 7.6 Hz), 7.20 (d, 2H, J = 8.0 Hz), 7.16-7.11 (m, 3H), 3.23 (t, 2H, J = 6.4 Hz), 2.69 (t, 2H, J = 6.4 Hz), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.69, 151.00, 143.45, 141.87, 137.19, 135.08, 134.53, 130.07, 129.55, 127.48, 127.13, 126.64, 126.02, 120.95, 40.39, 23.53, 21.47; IR (neat) *v*: 3250,

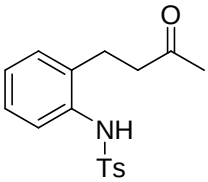
3061, 2921, 2819, 1696, 1493, 1408, 1332, 1159, 1092, 815, 770 cm^{-1}; HRMS (MALDI) *m/z* calcd. for $C_{21}H_{21}N_2O_3S$ $[M+H]^+$: 381.1267, found: 381.1272.

_N_-(2-(3-(naphthalen-2-yl)-3-oxopropyl)phenyl)-4-methylbenzenesulfonamide (1g)



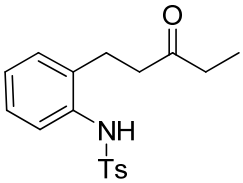
Yield: 75%; white solid; m.p. 138-140 °C; TLC, R_f = 0.33 (PE:EtOAc = 3:1); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.68 (s, 1H), 8.42 (s, 1H), 7.96 (d, 1H, J = 8.4 Hz), 7.91 (d, 1H, J = 8.4 Hz), 7.84 (d, 2H, J = 8.4 Hz), 7.68 (d, 2H, J = 9.0 Hz), 7.62-7.51 (m, 2H), 7.45-7.42 (m, 1H), 7.20-7.10 (m, 5H), 3.38 (t, 2H, J = 6.0 Hz), 2.67 (t, 2H, J = 6.0 Hz), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.17, 143.23, 137.41, 135.73, 135.15, 134.81, 133.40, 132.34, 130.17, 130.06, 129.56, 129.46, 128.70, 128.45, 127.73, 127.28, 127.09, 126.86, 126.20, 125.54, 123.63, 40.24, 23.75, 21.42; IR (neat) *v*: 3461, 3284, 3059, 1677, 1490, 1360, 1317, 1150, 1123, 1091, 768 cm^{-1}; HRMS (MALDI) *m/z* calcd. for $C_{26}H_{23}NO_3SNa$ $[M+Na]^+$: 452.1291, found: 452.1288.

_N_-(2-(3-oxobutyl)phenyl)-4-methylbenzenesulfonamide (1h)



Yield: 57%; white solid; m.p. 125-126 °C; TLC, R_f = 0.23 (PE:EtOAc = 3:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.38 (s, 1H), 7.62 (d, 2H, J = 8.4 Hz), 7.36 (d, 1H, J = 8.0 Hz), 7.20 (d, 2H, J = 8.0 Hz), 7.14 (td, 1H, J = 7.2, 1.6 Hz), 7.08 (td, 1H, J = 7.6, 1.2 Hz), 7.01 (dd, 1H, J = 8.0, 1.2 Hz), 2.72 (t, 2H, J = 6.0 Hz), 2.40 (t, 2H, J = 6.0 Hz), 2.38 (s, 3H), 2.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 209.71, 143.22, 137.34, 134.89, 134.66, 130.02, 129.45, 127.25, 127.01, 126.15, 125.41, 45.02, 29.66, 23.39, 21.47; IR (neat) *v*: 3382, 3096, 2983, 2811, 1703, 1328, 1156, 1091, 931, 825, 762 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}NO_3S$ $[M+H]^+$: 318.1158, found: 318.1162.

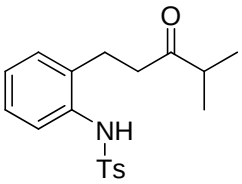
_N_-(2-(3-oxopentyl)phenyl)-4-methylbenzenesulfonamide (1i)



Yield: 60%; white solid; m.p. 108-110 °C; TLC, R_f = 0.31 (PE:EtOAc = 9:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.47 (s, 1H), 7.63 (d, 2H, J = 8.4 Hz), 7.38 (d, 1H, J = 8.0 Hz), 7.20 (d, 2H, J = 8.0 Hz), 7.14 (t,

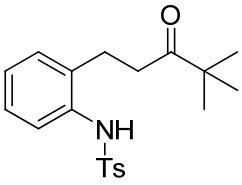
1H, *J* = 7.2 Hz), 7.08 (t, 1H, *J* = 7.2 Hz), 7.01 (d, 1H, *J* = 7.2 Hz), 2.69 (t, 2H, *J* = 6.0 Hz), 2.40 (t, 2H, *J* = 6.0 Hz), 2.38 (s, 3H), 2.33 (q, 2H, *J* = 7.2 Hz), 0.99 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.41, 143.19, 137.37, 134.95, 134.70, 130.02, 129.44, 127.26, 127.05, 126.11, 125.42, 43.73, 35.71, 23.35, 21.49, 7.60; IR (neat) *v*: 3396, 3191, 3095, 2977, 1709, 1446, 1325, 1155, 1091, 928, 826 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NO_3S$ $[M+H]^+$: 332.1315, found: 332.1321.

_N_-(2-(4-methyl-3-oxopentyl)phenyl)-4-methylbenzenesulfonamide (1j)



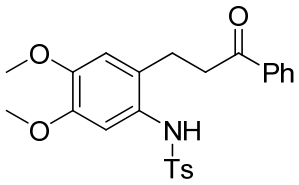
Yield: 66%; white solid; m.p. 44-47 ^{o}C; TLC, R_f = 0.24 (PE:EtOAc = 6:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 1H), 7.63 (d, 2H, *J* = 8.4 Hz), 7.38 (d, 1H, *J* = 7.6 Hz), 7.20 (d, 2H, *J* = 8.0 Hz), 7.14 (t, 1H, *J* = 8.0 Hz), 7.08 (t, 1H, *J* = 7.6 Hz), 7.01 (d, 1H, *J* = 7.6 Hz), 2.73 (t, 2H, *J* = 6.0 Hz), 2.52-2.45 (m, 1H), 2.40 (t, 2H, *J* = 6.0 Hz), 2.37 (s, 3H), 0.98 (d, 6H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.84, 143.18, 137.35, 134.92, 134.65, 129.95, 129.43, 127.23, 127.06, 126.06, 125.31, 41.86, 40.68, 23.43, 21.49, 18.05; IR (neat) *v*: 3173, 2972, 2933, 2875, 1689, 1492, 1323, 1150, 1091, 935, 774 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{24}NO_3S$ $[M+H]^+$: 346.1471, found: 346.1478.

_N_-(2-(4,4-dimethyl-3-oxopentyl)phenyl)-4-methylbenzenesulfonamide (1k)



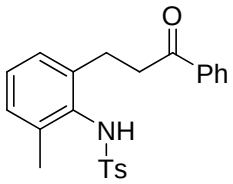
Yield: 53%; white solid; m.p. 109-111 ^{o}C; TLC, R_f = 0.61 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (s, 1H), 7.64 (d, 2H, *J* = 8.4 Hz), 7.38 (d, 1H, *J* = 8.0 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), 7.14 (t, 1H, *J* = 7.6 Hz), 7.07 (t, 1H, *J* = 7.6 Hz), 7.01 (d, 1H, *J* = 7.6 Hz), 2.75 (t, 2H, *J* = 6.0 Hz), 2.40 (t, 2H, *J* = 6.0 Hz), 2.38 (s, 3H), 1.01 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 217.29, 143.18, 137.28, 134.93, 134.61, 129.89, 129.41, 127.15, 127.04, 126.03, 125.24, 43.91, 38.39, 26.21, 23.61, 21.47; IR (neat) *v*: 3433, 3362, 3129, 2971, 2869, 1692, 1493, 1328, 1159, 1092, 943, 756 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}NO_3S$ $[M+H]^+$: 360.1628, found: 360.1637.

_N_-(4,5-dimethoxy-2-(3-oxo-3-phenylpropyl)phenyl)-4-methylbenzenesulfonamide (1l)



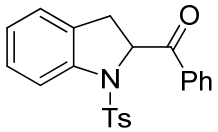
Yield: 40%; white solid; m.p. 175-176 °C; TLC, R_f = 0.28 (PE:EtOAc = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.34 (s, 1H), 7.88 (d, 2H, J = 7.6 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.54 (t, 1H, J = 7.2 Hz), 7.41 (t, 2H, J = 8.0 Hz), 7.18 (d, 2H, J = 8.0 Hz), 6.91 (s, 1H), 6.53 (s, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.16 (t, 2H, J = 6.0 Hz), 2.43 (t, 2H, J = 6.0 Hz), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.18, 147.63, 147.56, 143.19, 136.98, 136.06, 133.54, 129.38, 128.56, 128.24, 128.11, 127.14, 127.04, 111.91, 110.54, 55.89, 55.84, 40.13, 23.27, 21.44; IR (neat) v: 3401, 3211, 2933, 1676, 1517, 1450, 1338, 1205, 1163, 1106, 1092, 995, 746 cm^{-1}; HRMS (MALDI) m/z calcd. for $C_{24}H_{25}NO_5SNa$ $[M+Na]^+$: 462.1346, found: 462.1345.

_N_-(2-methyl-6-(3-oxo-3-phenylpropyl)phenyl)-4-methylbenzenesulfonamide (1m)



Yield: 66%; white solid; m.p. 127-129 °C; TLC, R_f = 0.37 (PE:EtOAc = 6:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (s, 1H), 7.87 (d, 2H, J = 7.2 Hz), 7.64 (d, 2H, J = 8.0 Hz), 7.53 (t, 1H, J = 7.6 Hz), 7.41 (t, 2H, J = 8.0 Hz), 7.22 (d, 2H, J = 8.0 Hz), 7.10-7.06 (m, 2H), 6.96 (dd, 1H, J = 6.8, 2.4 Hz), 3.18 (t, 2H, J = 6.0 Hz), 2.49 (t, 2H, J = 6.0 Hz), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.12, 143.24, 139.83, 138.94, 137.84, 136.21, 133.44, 133.07, 129.49, 128.55, 128.10, 127.60, 127.39, 127.25, 40.64, 24.06, 21.49, 19.58; IR (neat) v: 3447, 3229, 1681, 1597, 1446, 1333, 1208, 1160, 1092, 912, 746 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{23}NO_3SNa$ $[M+Na]^+$: 364.1319, found: 364.1318.

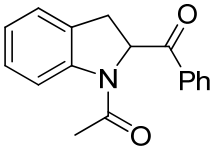
phenyl(1-tosylindolin-2-yl)methanone (6)



White solid; m.p. 172-174 °C; TLC, R_f = 0.25 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, 2H, J = 7.2 Hz), 7.74 (d, 2H, J = 8.0 Hz), 7.61 (t, 1H, J = 7.2 Hz), 7.55 (d, 1H, J = 8.0 Hz), 7.49 (t, 2H, J = 7.6 Hz), 7.25 (d, 2H, J = 7.6 Hz), 7.21 (d, 1H, J = 7.6 Hz), 7.05-6.96 (m, 2H), 5.62 (dd, 1H, J = 11.2, 5.2 Hz), 3.35 (dd, 1H, J = 16.0, 11.2 Hz), 3.08 (dd, 1H, J = 16.0, 5.2 Hz) 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.10, 144.32, 141.75, 134.87, 134.08, 133.57, 129.72, 129.45, 128.90, 128.78, 128.17,

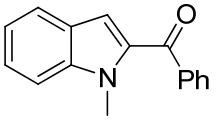
127.49, 125.01, 124.20, 115.43, 65.32, 33.08, 21.55; IR (neat) *v*: 3396, 3067, 1706, 1354, 1167, 764 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{20}NO_3S$ $[M+H]^+$: 378.1158, found: 378.1155.

1-(2-benzoylindolin-1-yl)ethanone



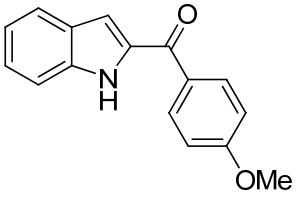
Yield: 75%; white solid; m.p.: 119-121 °C; TLC, R_f = 0.19 (PE:EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz, two isomers ration 1:1): δ 8.34 (d, 0.45H, *J* = 8.0 Hz), 8.00 (s, 2H), 7.66 (t, 0.46H, *J* = 7.2 Hz), 7.60 (t, 0.54H, *J* = 7.2 Hz), 7.56-7.48 (m, 2H), 7.26-7.22 (m, 1.65H), 7.17-7.00 (m, 2 H), 6.09 (dd, 0.49H, *J* = 11.2, 2.8 Hz), 5.79 (d, 0.45H, *J* = 11.2 Hz), 3.82 (t, 0.46H, *J* = 11.2), 3.60 (dd, 0.53H, *J* = 15.6, 9.0 Hz), 3.18 (d, 0.47H, *J* = 16.4 Hz), 3.02 (d, 0.54H, *J* = 16.4 Hz), 2.52 (s, 1.48H), 2.04 (s, 1.62H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.20, 194.98, 168.94, 168.14, 143.35, 141.84, 134.14, 133.48, 129.12, 128.75, 128.66, 128.15, 127.93, 125.80, 124.26, 123.78, 123.23, 117.29, 113.70, 64.36, 62.64, 33.77, 31.42, 24.53, 23.83. IR (neat) *v*: 3424, 1689, 1655, 1483, 1400, 1218, 749 cm^{-1}; HRMS (MALDI) *m*/*z* calcd. for $C_{17}H_{15}NNaO_2$ $[M+Na]^+$: 288.0995, found: 288.0993.

(1-methyl-1*H*-indol-2-yl)(phenyl)methanone (S11)[S13]



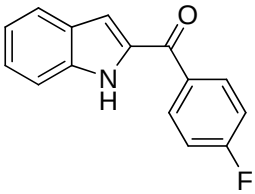
Yield: 70%; yellow oil; TLC, R_f = 0.33 (PE:EtOAc = 19:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, 2H, *J* = 7.2 Hz), 7.68 (d, 1H, *J* = 8.0 Hz), 7.61 (t, 1H, *J* = 7.2 Hz), 7.51 (t, 2H, *J* = 7.6 Hz), 7.47-7.40 (m, 2H), 7.18 (t, 1H, *J* = 7.2 Hz), 7.03 (s, 1H), 4.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.61, 140.28, 139.36, 134.93, 132.14, 129.68, 128.16, 125.91, 125.80, 122.97, 120.73, 114.83, 110.32, 31.94; IR (neat) *v*: 3058, 2944, 1636, 1512, 1464, 1391, 1259, 1233, 946, 738 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1070, found: 236.1067.

(1*H*-indol-2-yl)(4-methoxyphenyl)methanone (2b)[S1]



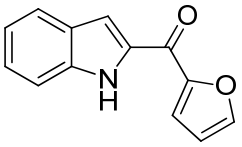
Yield: 93%; white solid; m.p. 183-185 °C; TLC, R_f = 0.61 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.64 (s, 1H), 8.06 (d, 2H, J = 8.8 Hz), 7.73 (d, 1H, J = 8.0 Hz), 7.50 (d, 1H, J = 8.4 Hz), 7.37 (t, 1H, J = 7.6 Hz), 7.17 (t, 2H, J = 7.2 Hz), 7.04 (d, 2H, J = 8.4 Hz), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.84, 163.17, 137.31, 134.48, 131.53, 130.62, 127.73, 126.13, 123.02, 120.87, 113.75, 112.15, 111.83, 55.48; IR (neat) ν: 3411, 3293, 1620, 1593, 1507, 1255, 1168, 771 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{16}H_{13}NO_2Na$ $[M+Na]^+$: 274.0838, found: 274.0835.

(4-fluorophenyl)(1*H*-indol-2-yl)methanone (2c)[S1]



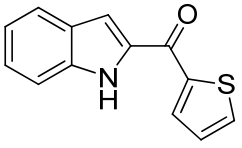
Yield: 92%; white solid; m.p. 178-181 °C; TLC, R_f = 0.24 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.63 (s, 1H), 8.08 (dd, 2H, J = 8.8, 5.6 Hz), 7.76 (d, 1H, J = 8.0 Hz), 7.53 (d, 1H, J = 8.0 Hz), 7.42 (t, 1H, J = 8.0 Hz), 7.29 (d, 1H, J = 4.8 Hz), 7.25-7.18 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.69, 165.37 (d, J = 252 Hz), 137.58, 134.05, 131.70 (d, J = 9.0 Hz), 127.65, 126.62, 123.19, 121.11, 115.63 (d, J = 21.7 Hz), 112.44 (d, J = 45.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ −106.18; IR (neat) ν: 3310, 1626, 1598, 1503, 1342, 1230, 1154, 770 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{15}H_{11}FNO$ $[M+H]^+$: 240.0819, found: 240.0822.

furan-2-yl(1*H*-indol-2-yl)methanone (2d)[S1]



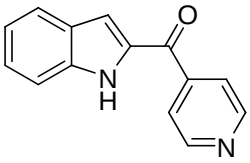
Yield: 79%; pale yellow solid; m.p. 169-171 °C; TLC, R_f = 0.47 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.48 (s, 1H), 7.76 (d, 1H, J = 8.0 Hz), 7.72 (d, 2H, J = 4.8 Hz), 7.49-7.46 (m, 2H), 7.37 (t, 1H, J = 8.0 Hz), 7.17 (t, 1H, J = 7.2 Hz), 6.64 (t, 1H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.57, 152.74, 146.46, 137.25, 133.45, 128.00, 126.46, 123.33, 120.98, 118.52, 112.44, 112.09, 111.44; IR (neat) ν: 3421, 3301, 1606, 1563, 1464, 1344, 1278, 1130, 743 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{13}H_9NO_2Na$ $[M+Na]^+$: 234.0525, found: 234.0525.

(1*H*-indol-2-yl)(thiophen-2-yl)methanone (2e)[S1]



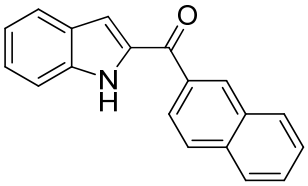
Yield: 88%; yellow solid; m.p. 152-155 °C; TLC, R_f = 0.45 (PE:EtOAc = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.59 (s, 1H), 8.06 (d, 1H, J = 3.6 Hz), 7.78-7.72 (m, 2H), 7.51 (d, 1H, J = 8.4 Hz), 7.46 (s, 1H), 7.38 (t, 1H, J = 7.6 Hz), 7.24 (t, 1H, J = 4.4 Hz), 7.18 (t, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.86, 142.47, 137.38, 134.07, 133.22, 132.97, 128.07, 127.76, 126.40, 123.13, 121.07, 112.20, 110.66; IR (neat) v: 3433, 3314, 1584, 1520, 1414, 1259, 744 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{13}H_9NOSNa$ $[M+Na]^+$: 250.0297, found: 250.0293.

(1*H*-indol-2-yl)(pyridin-4-yl)methanone (2f)[S12]



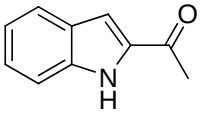
Yield: 82%; white solid; m.p. 162-164 °C; TLC, R_f = 0.22 (CH_2Cl_2:CH_3OH = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.68 (s, 1H), 8.87 (d, 2H, J = 4.4 Hz), 7.78 (d, 2H, J = 5.2 Hz), 7.73 (d, 1H, J = 8.0 Hz), 7.50 (d, 1H, J = 8.0 Hz), 7.42 (t, 1H, J = 8.0 Hz), 7.22-7.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.58, 150.41, 144.58, 138.09, 133.50, 127.57, 127.36, 123.47, 122.45, 121.43, 113.86, 112.30.

(1*H*-indol-2-yl)(naphthalen-2-yl)methanone (2g)



Yield: 90%; white solid; m.p. 166-169 °C; TLC, R_f = 0.48 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.44 (s, 1H), 8.55 (s, 1H), 8.06-7.97 (m, 3H), 7.93 (d, 1H, J = 7.2 Hz), 7.74 (d, 1H, J = 8.0 Hz), 7.63-7.58 (m, 2H), 7.51 (d, 1H, J = 8.0 Hz), 7.39 (t, 1H, J = 7.2 Hz), 7.25 (s, 1H), 7.18 (t, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.06, 137.54, 135.28, 134.55, 132.45, 130.56, 129.38, 128.44, 128.19, 127.86, 127.80, 126.85, 126.53, 125.26, 123.24, 121.09, 112.76, 112.17; IR (neat) v: 3396, 3309, 1616, 1521, 1344, 1276, 1181, 1131, 773 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{19}H_{13}NONa$ $[M+Na]^+$: 294.0889, found: 294.0887.

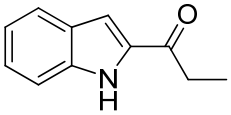
1-(1*H*-indol-2-yl)ethanone (2h)[S14]



Yield: 75%; pale yellow solid; m.p. 145-148 °C; TLC, R_f = 0.52 (PE:EtOAc = 14:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.09 (s, 1H), 7.72 (d, 1H, J = 10.8 Hz), 7.43 (d, 1H, J = 11.2 Hz), 7.35 (t, 1H, J = 10.0 Hz), 7.21 (s, 1H), 7.16 (t, 1H, J = 10.0 Hz), 2.60 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.65, 137.44,

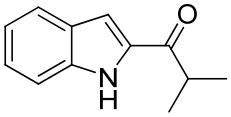
135.32, 127.49, 126.31, 122.98, 120.86, 112.25, 109.93, 25.82; IR (neat) *v*: 3248, 3302, 1645, 618, 1523, 1338, 1247, 1183, 799 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{10}H_{10}NO$ $[M+H]^+$: 160.0757, found: 160.0756.

1-(1*H*-indol-2-yl)propan-1-one (2i)[S15]



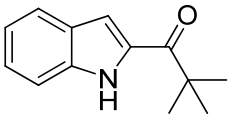
Yield: 71%; yellow solid; m.p. 140-142 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): TLC, R_f = 0.49 (PE:EtOAc = 9:1); δ 9.31 (s, 1H), 7.71 (d, 1H, J = 8.0 Hz), 7.45 (d, 1H, J = 8.4 Hz), 7.35 (t, 1H, J = 8.4 Hz), 7.22 (s, 1H), 7.16 (t, 1H, J = 8.0 Hz), 3.01 (q, 2H, J = 7.6 Hz), 1.29 (t, 3H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.01, 137.17, 134.90, 127.55, 126.14, 122.95, 120.85, 112.17, 108.85, 31.47, 8.75; IR (neat) *v*: 3321, 2969, 1652, 1522, 1409, 1169, 801, 738 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}NO$ $[M+H]^+$: 174.0913, found: 174.0911.

1-(1*H*-indol-2-yl)-2-methylpropan-1-one (2j)



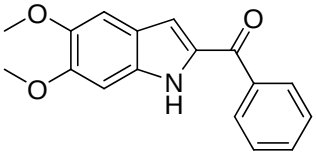
Yield: 84%; white solid; m.p. 92-94 ^oC; TLC, R_f = 0.53 (PE:EtOAc = 9:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 9.22 (s, 1H), 7.71 (d, 1H, J = 8.0 Hz), 7.44 (d, 1H, J = 8.0 Hz), 7.35 (t, 1H, J = 7.6 Hz), 7.23 (s, 1H), 7.16 (t, 1H, J = 7.6 Hz), 3.53-3.46 (m, 1H), 1.29 (d, 6H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.70, 137.35, 134.19, 127.54, 126.15, 122.96, 120.84, 112.20, 108.89, 36.15, 19.63; IR (neat) *v*: 3302, 2970, 1641, 1518, 1230, 1135, 749 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{12}H_{14}NO$ $[M+H]^+$: 188.1070, found: 188.1071.

1-(1*H*-indol-2-yl)-2,2-dimethylpropan-1-one (2k)[S1]



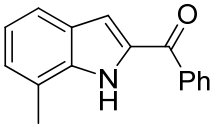
Yield: 63%; white solid; m.p. 119-121 ^oC; TLC, R_f = 0.55 (PE:EtOAc = 19:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 9.36 (s, 1H), 7.71 (d, 1H, J = 8.0 Hz), 7.44 (d, 1H, J = 8.4 Hz), 7.33 (t, 1H, J = 7.6 Hz), 7.26 (s, 1H), 7.14 (t, 1H, J = 7.6 Hz), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.07, 135.93, 132.18, 127.73, 125.89, 122.93, 120.75, 111.94, 109.02, 43.39, 28.50; IR (neat) *v*: 3330, 2968, 1640, 1513, 1403, 1340, 1158, 1137, 750 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{16}NO$ $[M+H]^+$: 202.1226, found: 202.1227.

(5,6-dimethoxy-1*H*-indol-2-yl)(phenyl)methanone (2l)[S1]



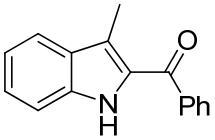
Yield: 89%; white solid; m.p. 178-180 °C; TLC, R_f = 0.35 (PE:EtOAc = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.51 (s, 1H), 7.97 (d, 2H, J = 7.2 Hz), 7.60 (t, 1H, J = 7.2 Hz), 7.52 (t, 2H, J = 7.2 Hz), 7.05 (d, 2H, J = 8.8 Hz), 6.91 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.11, 151.12, 146.41, 138.36, 133.40, 131.97, 129.08, 128.35, 120.81, 113.18, 102.61, 93.66, 56.10, 56.04; IR (neat) v: 3304, 1602, 1520, 1498, 1288, 1255, 1216, 1127 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{15}NO_3Na$ $[M+Na]^+$: 304.0944, found: 304.0941.

(7-methyl-1*H*-indol-2-yl)(phenyl)methanone (2m)[S1]



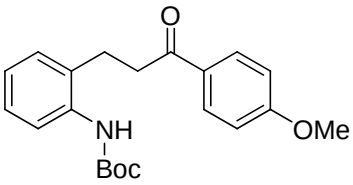
Yield: 83%; white solid; m.p. 165-168 °C; TLC, R_f = 0.42 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.25 (s, 1H), 8.99 (d, 2H, J = 8.0 Hz), 7.63 (t, 1H, J = 7.2 Hz), 7.58-7.52 (m, 3H), 7.18 (s, 2H), 7.09 (t, 1H, J = 8.0 Hz), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.26, 138.04, 137.38, 134.08, 132.30, 129.18, 128.44, 127.33, 126.68, 121.51, 121.32, 120.82, 113.39, 16.73; IR (neat) v: 3426, 3281, 1621, 1527, 1334, 1255, 731 cm^{-1}; HRMS (MALDI) m/z calcd. for $C_{16}H_{14}NO$ $[M+H]^+$: 381.1267, found: 381.1272.

(3-methyl-1*H*-indol-2-yl)(phenyl)methanone (2n)[S1]



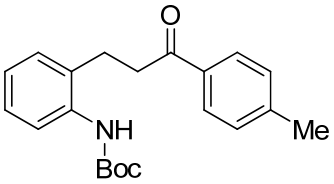
Yield: 78%; pale yellow solid; m.p. 139-142 °C; TLC, R_f = 0.52 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (s, 1H), 7.78 (d, 2H, J = 6.8 Hz), 7.68 (d, 1H, J = 8.0 Hz), 7.60 (t, 1H, J = 7.2 Hz), 7.52 (t, 2H, J = 7.6 Hz), 7.42-7.35 (m, 2H), 7.17 (t, 1H, J = 8.0 Hz), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.28, 139.40, 136.54, 131.97, 131.59, 129.02, 128.80, 128.47, 126.51, 121.26, 120.46, 120.21, 111.82, 11.20; IR (neat) v: 3411, 3313, 1607, 1523, 1338, 1270, 951, 739 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1070, found: 236.1074.

tert-butyl 2-(3-(4-methoxyphenyl)-3-oxopropyl)phenylcarbamate (3b)



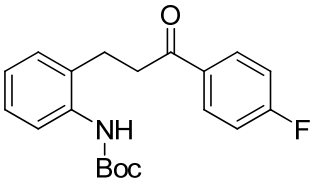
Yield: 82%; white solid; m.p. 90-92 °C; TLC, R_f = 0.21 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, 2H, J = 9.2 Hz), 7.72 (d, 2H, J = 8.4 Hz), 7.18 (t, 2H, J = 9.2 Hz), 7.03 (t, 1H, J = 7.6 Hz), 6.91 (d, 2H, J = 8.8 Hz), 3.86 (s, 3H), 3.33 (t, 2H, J = 6.4 Hz), 3.00 (t, 2H, J = 6.4 Hz), 1.54 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.39, 163.67, 153.87, 136.12, 132.08, 130.39, 129.56, 129.46, 126.87, 124.12, 123.17, 113.71, 80.03, 55.46, 39.23, 28.39, 24.52; IR (neat) v: 3381, 2980, 1701, 1671, 1523, 1454, 1239, 1161, 1025, 790 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{26}NO_4$ $[M+H]^+$: 356.1856, found: 356.1860.

tert-butyl 2-(3-oxo-3-_p_-tolylpropyl)phenylcarbamate (3c)



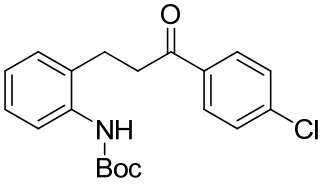
Yield: 96%; white solid; m.p. 88-89 °C; TLC, R_f = 0.25 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, 2H, J = 8.0 Hz), 7.73 (d, 1H, J = 7.6 Hz), 7.65 (s, 1H), 7.25 (d, 2H, J = 8.0 Hz), 7.18 (t, 2H, J = 8.4 Hz), 7.04 (t, 1H, J = 7.2 Hz), 3.36 (t, 2H, J = 6.4 Hz), 3.01 (t, 2H, J = 6.4 Hz), 2.41 (s, 3H), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.50, 153.84, 144.22, 136.10, 134.02, 132.03, 129.44, 129.27, 128.20, 126.90, 124.16, 123.20, 80.05, 39.45, 28.40, 24.48, 21.63; IR (neat) v: 3373, 2983, 1700, 1686, 1521, 1454, 1240, 1163, 781 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{26}NO_3$ $[M+H]^+$: 340.1907, found: 340.1911.

tert-butyl 2-(3-(4-fluorophenyl)-3-oxopropyl)phenylcarbamate (3d)



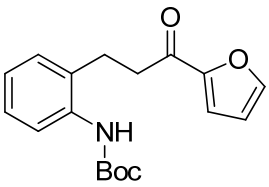
Yield: 89%; white solid; m.p. 89-92 °C; TLC, R_f = 0.28 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.96 (m, 2H), 7.70 (d, 1H, J = 7.6 Hz), 7.54 (s, 1H), 7.21-7.15 (m, 2H), 7.11 (t, 2H, J = 8.4 Hz), 7.04 (t, 1H, J = 7.2 Hz), 3.34 (t, 2H, J = 6.4 Hz), 3.01 (t, 2H, J = 6.4 Hz), 1.54 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.25, 165.88 (d, J = 253.5 Hz), 153.84, 136.05, 132.92, 131.98, 130.75 (d, J = 9.3 Hz), 129.44, 127.01, 124.31, 123.40, 115.72 (d, J = 21.8 Hz), 80.13, 39.49, 28.38, 24.46; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −104.58; IR (neat) v: 3373, 3314, 2979, 1690, 1597, 1525, 1244, 1157 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{20}H_{23}FNO_3$ $[M+H]^+$: 344.1656, found: 344.1659.

tert-butyl 2-(3-(4-chlorophenyl)-3-oxopropyl)phenylcarbamate (3e)



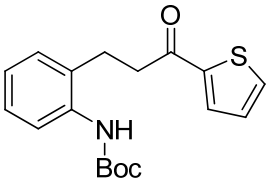
Yield: 95%; white solid; m.p. 85-87 °C; TLC, R_f = 0.25 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, 2H, J = 8.4 Hz), 7.70 (d, 1H, J = 7.6 Hz), 7.50 (s, 1H), 7.42 (d, 2H, J = 8.4 Hz), 7.22-7.15 (m, 2H), 7.04 (t, 1H, J = 7.6 Hz), 3.34 (t, 2H, J = 6.4 Hz), 3.01 (t, 2H, J = 6.4 Hz), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.66, 153.83, 139.85, 136.02, 134.77, 131.93, 129.50, 129.44, 128.93, 127.04, 124.35, 123.44, 80.16, 39.56, 28.38, 24.40; IR (neat) v: 3383, 2979, 1696, 1522, 1454, 1243, 1165 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{20}H_{23}ClNO_3$ $[M+H]^+$: 360.1361, found: 360.1362.

tert-butyl 2-(3-(furan-2-yl)-3-oxopropyl)phenylcarbamate (3f)



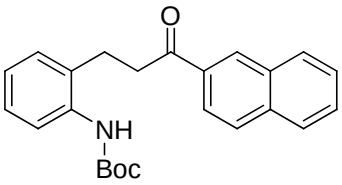
Yield: 87%; white solid; m.p. 78-82 °C; TLC, R_f = 0.26 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, 1H, J = 8.0 Hz), 7.57 (s, 1H), 7.50 (br s, 1H), 7.20-7.15 (m, 3H), 7.03 (t, 1H, J = 7.6 Hz), 6.52-6.51 (m, 1H), 3.23 (t, 2H, J = 6.8 Hz), 2.98 (t, 2H, J = 6.8 Hz), 1.54 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.92, 153.80, 152.36, 146.54, 136.00, 131.67, 129.43, 126.99, 124.22, 123.32, 117.47, 112.32, 80.08, 39.28, 28.38, 24.22; IR (neat) v: 3415, 3391, 1980, 1707, 1664, 1468, 1236, 1159, 1020, 774 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{22}NO_4$ $[M+H]^+$: 316.1543, found: 316.1545.

tert-butyl 2-(3-oxo-3-(thiophen-2-yl)propyl)phenylcarbamate (3g)



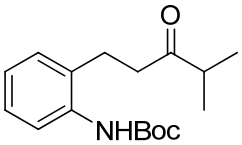
Yield: 90%; white solid; m.p. 92-94 °C; TLC, R_f = 0.25 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (t, 2H, J = 4.0 Hz), 7.62 (d, 1H, J = 4.8 Hz), 7.48 (br s, 1H), 7.21-7.16 (m, 2H), 7.10 (t, 1H, J = 4.0 Hz), 7.04 (t, 1H, J = 7.6 Hz), 3.31 (t, 2H, J = 6.8 Hz), 3.00 (t, 2H, J = 6.8 Hz), 1.54 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.64, 153.80, 143.55, 135.99, 133.89, 132.20, 129.40, 128.12, 126.98, 124.27, 123.42, 80.06, 40.08, 28.35, 24.56; IR (neat) v: 3335, 2977, 1704, 1647, 1521, 1455, 1414, 1242, 1158, 1052, 739 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{22}NO_3S$ $[M+H]^+$: 332.1315, found: 332.1313.

tert-butyl 2-(3-(naphthalen-2-yl)-3-oxopropyl)phenylcarbamate (3h)



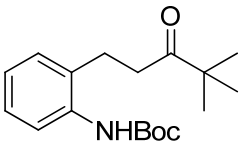
Yield: 91%; white solid; m.p. 105-108 °C; TLC, R_f = 0.16 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.47 (s, 1H), 8.03 (d, 1H, J = 8.8 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.89-7.85 (m, 2H), 7.74 (d, 1H, J = 7.6 Hz), 7.63-7.53 (m, 3H), 7.21 (t, 2H, J = 7.6 Hz), 7.06 (t, 1H, J = 7.6 Hz), 3.52 (t, 2H, J = 6.4 Hz), 3.08 (t, 2H, J = 6.4 Hz), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.79, 153.87, 136.09, 135.65, 133.77, 132.41, 132.06, 129.89, 129.55, 129.49, 128.60, 128.45, 127.75, 126.97, 126.83, 124.27, 123.70, 123.33, 80.12, 39.67, 28.39, 24.57; IR (neat) v: 3411, 2980, 2931, 1727, 1675, 1507, 1439, 1231, 1149 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{24}H_{26}NO_3$ $[M+H]^+$: 376.1907, found: 376.1905.

tert-butyl 2-(4-methyl-3-oxopentyl)phenylcarbamate (3i)



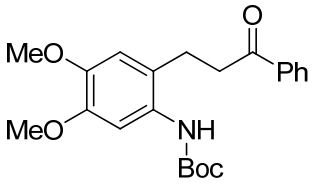
Yield: 89%; white solid; m.p. 89-90 °C; TLC, R_f = 0.20 (PE:EtOAc = 15:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7,68 (d, 1H, J = 7.6 Hz), 7.40 (br s, 1H), 7.18 (t, 1H, J = 7.2 Hz), 7.10 (d, 1H, J = 6.4 Hz), 7.02 (t, 1H, J = 7.2 Hz), 2.85-2.80 (m, 4H), 2.59-2.52 (m, 1H) 1.53 (s, 9H), 1.04 (d, 6H, J = 6.8Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.96, 153.80, 135.93, 131.99, 129.31, 126.87, 124.17, 123.27, 80.03, 41.05, 40.94, 28.39, 24.27, 18.10; IR (neat) v: 3344, 2973, 2931, 2895, 2878, 1716, 1697, 1587, 1515, 1242, 1161 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{26}NO_3$ $[M+H]^+$: 292.1907, found: 292.1912.

tert-butyl 2-(4,4-dimethyl-3-oxopentyl)phenylcarbamate (3j)



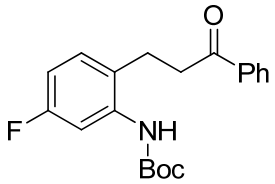
Yield: 70%; white solid; m.p. 63-66 °C; TLC, R_f = 0.16 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, 1H, J = 8.0 Hz), 7.33 (br s, 1H), 7.18 (t, 1H, J = 7.6 Hz), 7.10 (d, 1H, J = 7.6 Hz), 7.02 (t, 1H, J = 7.6 Hz), 2.87-2.80 (m, 4H), 1.53 (s, 9H), 1.07 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 216.25, 153.78, 135.91, 132.00, 129.30, 126.85, 124.13, 123.18, 80.04, 44.02, 37.52, 28.39, 26.26, 24.62; IR (neat) v: 3379, 3354, 2973, 2934, 2870, 1720, 1689, 1589, 1519, 1449, 1366, 1302, 1237, 1155, 1047, 763 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{28}NO_3$ $[M+H]^+$: 306.2064, found: 306.2066.

tert-butyl 4,5-dimethoxy-2-(3-oxo-3-phenylpropyl)phenylcarbamate (3k)



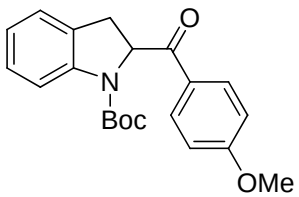
Yield: 85%; white solid; m.p. 109-111 °C; TLC, R_f = 0.29 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, 2H, J = 7.6 Hz), 7.55 (t, 1H, J = 7.2 Hz), 7.44 (t, 3H, J = 7.6 Hz), 7.26 (s, 1H), 6.65 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.34 (t, 2H, J = 6.4 Hz), 2.96 (t, 2H, J = 6.4 Hz), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.98, 154.13, 147.53, 145.95, 136.54, 133.33, 129.01, 128.58, 128.06, 124.59, 112.33, 107.92, 79.91, 56.14, 55.93, 39.78, 28.41, 24.40; IR (neat) v: 3355, 2995, 2934, 1723, 1671, 1525, 1448, 1167, 1120, 863, 759 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{28}NO_5$ $[M+H]^+$: 386.1962, found: 386.1959.

tert-butyl 5-fluoro-2-(3-oxo-3-phenylpropyl)phenylcarbamate (3l)[S16]



Yield: 83%; white solid; m.p. 82-83 °C; TLC, R_f = 0.28 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, 2H, J = 7.6 Hz), 7.85 (br s, 1H), 7.63 (d, 1H, J = 10.8 Hz), 7.57 (t, 1H, J = 7.6 Hz), 7.45 (t, 2H, J = 8.0 Hz), 7.09 (dd, 1H, J = 8.4, 6.4 Hz), 6.71 (td, 1H, J = 8.4, 6.8 Hz), 3.36 (t, 2H, J = 6.4 Hz), 2.97 (t, 2H, J = 6.4 Hz), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.89, 161.50 (d, J = 241.7 Hz), 153.33, 137.59 (d, J = 11.0 Hz), 136.30, 133.50, 130.37 (d, J = 9.2 Hz), 128.62, 128.07, 126.39, 110.43 (d, J = 21.3 Hz), 109.21 (d, J = 25.7 Hz), 80.48, 39.56, 28.32, 23.69; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −114.76; IR (neat) v: 3397, 2979, 1700, 1528, 1472, 1242, 1166, 978 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{20}H_{23}FNO_3$ $[M+H]^+$: 344.1656, found: 344.1656.

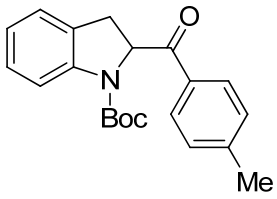
tert-butyl 2-(4-methoxybenzoyl)indoline-1-carboxylate (4b)



Yield: 81%; white solid; m.p. 110-112 °C; TLC, R_f = 0.29 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 7.99-7.56 (m, 3H), 7.24-7.17 (m, 1H), 7.07 (d, 1H, J = 7.2 Hz), 6.97-6.87 (m, 3H), 5.83-5.59 (m, 1H), 3.88 (s, 3H), 3.60 (dd, 1H, J = 16.4, 12.0 Hz), 3.09-2.98 (m, 1H), 1.60 (s, 3H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.78, 163.72, 153.95, 151.67, 143.13, 138.86,

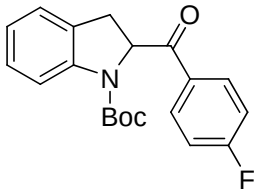
135.85, 131.21, 130.62, 127.99, 127.09, 124.43, 122.39, 114.70, 114.03, 81.10, 80.20, 62.94, 55.47, 32.79, 28.41, 28.04; IR (neat) *v*: 3350, 2976, 1681, 1599, 1484, 1377, 1235, 1166 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{27}N_2O_4$ $[M+NH_4]^+$: 371.1965, found: 371.1971.

tert-butyl 2-(4-methylbenzoyl)indoline-1-carboxylate (4c)



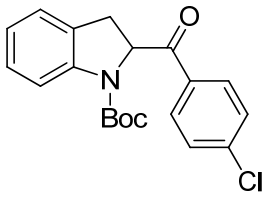
Yield: 84%; white solid; m.p. 141-143 °C; TLC, R_f = 0.48 (PE:EtOAc = 19:1); ^1H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 7.98 (d, 0.67H, J = 7.6 Hz), 7.86 (d, 2H, J = 7.2 Hz), 7.57 (d, 0.35H, J = 7.6 Hz), 7.30-7.20 (m, 3H), 7.06 (d, 1H, J = 6.8 Hz), 6.93 (t, 1H, J = 6.0 Hz), 5.84-5.64 (m, 1H), 3.63-3.56 (m, 1H), 3.07-2.97 (m, 1H), 2.42 (s, 3H), 1.60 (s, 3H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.77, 151.64, 144.33, 143.11, 131.67, 129.52, 128.47, 128.01, 124.43, 122.40, 114.69, 82.11, 81.12, 63.04, 62.38, 32.69, 29.66, 28.03, 21.66; IR (neat) *v*: 3373, 2974, 1701, 1488, 1399, 1161, 1051, 756 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{24}NO_3$ $[M+H]^+$: 338.1751, found: 338.1754.

tert-butyl 2-(4-fluorobenzoyl)indoline-1-carboxylate (4d)



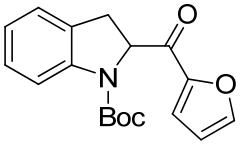
Yield: 85%; pale yellow solid; m.p. 68-70 °C; TLC, R_f = 0.42 (PE:EtOAc = 19:1); ^1H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 7.99 (t, 2.58H, J = 7.2 Hz), 7.56 (d, 0.36H, J = 7.2 Hz), 7.23 (d, 1H, J = 6.8 Hz), 7.17 (t, 2H, J = 8.0 Hz), 7.09 (d, 1H, J = 7.2 Hz), 6.96 (t, 1H, J = 6.8 Hz), 5.82-5.61 (m, 1H), 3.66-3.58 (m, 1H), 3.10-2.98 (m, 1H), 1.59 (s, 3.25H), 1.32 (s, 5.75H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.74, 165.90 (d, J = 254.2 Hz), 151.49, 142.97, 131.00 (d, J = 9.6 Hz), 128.16, 124.51, 122.58, 116.08 (d, J = 21.4 Hz), 114.75, 81.32, 63.15, 32.59, 28.36, 28.02; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −104.06, −104.35; IR (neat) *v*: 3363, 2979, 1713, 1689, 1600, 1487, 1397, 1226, 1157, 749 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{21}FNO_3$ $[M+H]^+$: 342.1500, found: 342.1505.

tert-butyl 2-(4-chlorobenzoyl)indoline-1-carboxylate (4e)



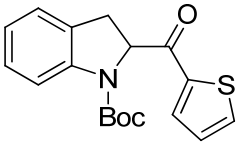
Yield: 85%; white solid; m.p. 114-117 ^{o}C; TLC, R_f = 0.41 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 7.98 (d, 0.58H, J = 7.6 Hz), 7.89 (d, 2H, J = 7.6 Hz), 7.56 (d, 0.40H, J = 7.2 Hz), 7.47 (d, 2H, J = 8.0 Hz), 7.25-7.21 (m, 1H), 7.08 (d, 1H, J = 7.2 Hz), 6.95 (t, 1H, J = 7.2 Hz), 5.79-5.60 (m, 1H), 3.64-3.57 (m, 1H), 3.08-2.97 (m, 1H), 1.59 (s, 3H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.08, 151.43, 142.94, 139.98, 132.53, 129.97, 129.72, 129.21, 128.15, 127.34, 124.50, 122.58, 114.71, 82.33, 81.34, 63.15, 62.44, 32.50, 28.33, 28.02; IR (neat) v: 3389, 2977, 1702, 1488, 1396, 1160, 1090, 757 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{20}H_{21}ClNO_3$ $[M+H]^+$: 358.1204, found: 358.1204.

tert-butyl 2-(furan-2-carbonyl)indoline-1-carboxylate (4f)



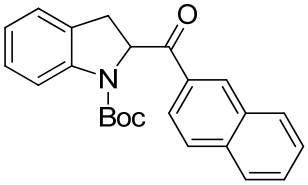
Yield: 86%; white solid; m.p. 113-116 ^{o}C; TLC, R_f = 0.28 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 7.95 (d, 0.65H, J = 6.4 Hz), 7.63 (s, 1H), 7.55 (s, 0.3H), 7.21 (s, 2H), 7.08 (d, 1H, J = 7.2 Hz), 6.94 (t, 1H, J = 7.2 Hz), 6.55-6.54 (m, 1H), 5.57-5.27 (m, 1H), 3.62-3.54 (m, 1H), 3.10-3.04 (m, 1H), 1.59 (s, 3H), 1.34 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.99, 151.45, 150.20, 146.88, 142.89, 127.93, 124.44, 122.53, 118.02, 114.58, 112.39, 81.33, 63.30, 32.56, 28.34, 27.91; IR (neat) v: 3345, 3130, 2981, 1704, 1678, 1484, 1391, 1279, 1166, 1054, 759 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{23}N_2O_4$ $[M+NH_4]^+$: 331.1652, found: 331.1651.

tert-butyl 2-(thiophene-2-carbonyl)indoline-1-carboxylate (4g)



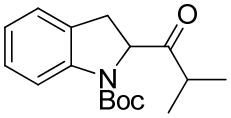
Yield: 82%; white solid; m.p. 100-103 ^{o}C; TLC, R_f = 0.51 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 7.97 (d, 0.61H, J = 6.0 Hz), 7.71-7.67 (m, 2.3H), 7.26-7.22 (m, 1H), 7.13-7.08 (m, 2H), 6.98-6.92 (m, 1H), 5.62-5.39 (m, 1H), 3.64-3.56 (m, 1H), 3.17-3.12 (m, 1H), 1.58 (s, 3H), 1.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.05, 151.49, 142.79, 140.30, 134.11, 131.96, 128.30, 128.01, 127.69, 124.53, 122.65, 114.64, 81.57, 64.61, 32.93, 28.29, 27.88; IR (neat) v: 3398, 2977, 1704, 1672, 1484, 1392, 1160, 762 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{23}N_2O_3S$ $[M+NH_4]^+$: 347.1424, found: 347.1425.

tert-butyl 2-(2-naphthoyl)indoline-1-carboxylate (4h)



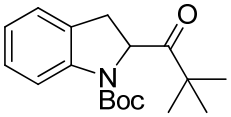
Yield: 82%; pale yellow solid; m.p. 141-143 ^{o}C; TLC, R_f = 0.38 (PE:EtOAc = 19:1); ^{1}H NMR (DMSO-d_6, 400 MHz, two isomers ratio 2.7:1): δ 8.82 (s, 1H), 8.16 (d, 1H, J = 8.0 Hz), 8.10-8.03 (m, 3H), 7.83 (d, 0.74H, J = 7.6 Hz), 7.72 (t, 1H, J = 7.6 Hz), 7.67 (t, 1H, J = 7.6 H), 7.51 (d, 0.3H, J = 7.6 Hz), 7.22 (t, 1H, J = 7.6 Hz), 7.16 (d, 1H, J = 6.8 Hz), 6.95 (t, 1H, J = 7.2 Hz), 6.18-6.13 (m, 1H), 3.82-3.74 (m, 1H), 3.08-2.98 (m, 1H), 1.54 (s, 2.7H), 1.24 (s, 6.3H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 196.32, 150.98, 142.89, 135.23, 132.13, 131.05, 130.41, 129.58, 128.98, 128.67, 128.48, 127.71, 127.44, 127.11, 124.82, 123.68, 122.21, 113.53, 80.20, 62.13, 32.14, 27.56; IR (neat) v: 3431, 2976, 2926, 1689, 1485, 1392, 1367, 1160, 761 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{24}H_{24}NO_3$ $[M+H]^+$: 374.1751, found: 374.1754.

tert-butyl 2-isobutyrylindoline-1-carboxylate (4i)



Yield: 75%; white solid; m.p. 74-77 ^{o}C; TLC, R_f = 0.30 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1) : δ 7.92 (d, 0.6H, J = 6.8 Hz), 7.48 (d, 0.4H, J = 2.8 Hz), 7.22-7.15 (m, 1H), 7.08 (d, 1H, J = 7.2 Hz), 6.93 (t, 1H, J = 7.2 Hz), 5.10-4.94 (m, 1H), 3.56-3.44 (m, 1H), 2.96-2.84 (m, 2H), 1.59 (s, 3H), 1.48 (s, 6H), 1.14 (d, 6H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 210.65, 151.78, 142.99, 127.94, 127.62, 124.77, 124.35, 122.52, 114.82, 81.38, 65.10, 64.38, 37.31, 36.52, 31.96, 31.10, 28.30, 19.12, 18.10; IR (neat) v: 3381, 2973, 2934, 2874, 1729, 1701, 1602, 1484, 1465, 1393, 1322, 1147, 1062, 1009, 775 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{24}NO_3$ $[M+H]^+$: 290.1751, found: 290.1749.

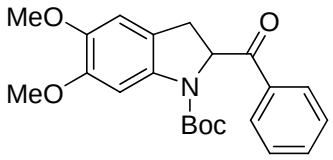
tert-butyl 2-pivaloylindoline-1-carboxylate (4j)



Yield: 88%; white solid; m.p. 100-103 ^{o}C;TLC, R_f = 0.35 (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers ratio 5:4) : δ 7.95 (s, 0.42H), 7.50 (s, 0.5H), 7.17 (s, 1H), 7.05 (d, 1H, J = 7.6 Hz), 6.90 (t, 1H, J = 7.2 Hz), 5.38-5.24 (m, 1H), 3.52-3.38 (m, 1H), 2.94-2.75 (m, 1H), 1.57 (s, 4.9H), 1.49 (s, 4.1H), 1.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.03, 209.72, 152.17, 151.65, 143.38, 142.41, 128.46, 127.74, 127.22, 124.63, 124.16, 122.23, 122.06, 114.88, 114.50, 81.74, 81.25, 62.00, 60.85, 43.05, 42.56, 32.28, 31.81, 28.38, 27.60, 26.92; IR (neat) v: 3333, 2980, 2969, 2932, 2871, 1694, 1600, 1485,

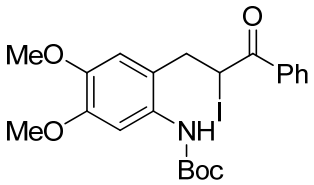
1395, 1367, 1322, 1266, 1145, 1070, 1022, 746 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{26}NO_3$ $[M+H]^+$: 304.1907, found: 304.1909.

tert-butyl 2-benzoyl-5,6-dimethoxyindoline-1-carboxylate (4k)



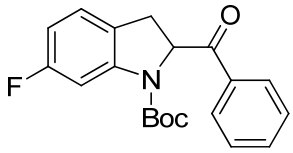
Yield: 79%; white solid; m.p. 121-124 °C; TLC, R_f = 0.31 (PE:EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2.5:1): δ 8.00-7.93 (m, 2H), 7.71 (s, 0.68H), 7.60 (q, 1H, J = 7.6 Hz), 7.50 (t, 2H, J = 7.6 Hz), 7.32 (s, 0.28H), 6.65-6.63 (m, 1H), 5.87-5.65 (m, 1H), 3.94 (s, 2.17H), 3.89 (s, 0.8H), 3.81 (s, 3H), 3.61-3.53 (m, 1H), 3.05-2.92 (m, 1H), 1.60 (s, 3H), 1.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.18, 151.57, 148.78, 144.66, 136.77, 134.12, 133.41, 128.78, 128.65, 128.58, 128.27, 117.95, 108.62, 108.32, 100.10, 99.65, 80.99, 63.65, 56.33, 55.98, 32.37, 28.30, 27.99; IR (neat) v: 3379, 2991, 2934, 1697, 1508, 1407, 1304, 1218, 1155, 1122, 857 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}NO_5$ $[M+H]^+$: 384.1805, found: 384.1811.

tert-butyl 2-(2-iodo-3-oxo-3-phenylpropyl)-4,5-dimethoxyphenylcarbamate (7)



Yield: 18%; pale yellow solid; m.p. 188-190 °C; TLC, R_f = 0.30 (PE:EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, 2H, J = 8.0 Hz), 7.55 (t, 1H, J = 7.2 Hz), 7.43 (t, 2H, J = 7.2 Hz), 7.36 (s, 1H), 7.11 (brs, 1H), 6.68 (s, 1H), 5.63 (dd, 1H, J = 10.0, 3.6 Hz) 3.82 (s, 6H), 3.72 (t, 1H, J = 12.4 Hz), 3.29 (dd, 1H, J = 14.4 Hz, 3.6 Hz), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.23, 154.23, 148.22, 146.26, 133.84, 133.75, 128.96, 128.73, 128.71, 123.78, 112.58, 108.68, 80.18, 56.21, 55.88, 36.27, 28.45, 23.60; IR (neat) v: 3346, 2975, 2934, 1716, 1678, 1597, 1521, 1448, 1366, 1159, 9993 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}NO_5$ $[M+Na]^+$: 534.0748, found: 534.0742.

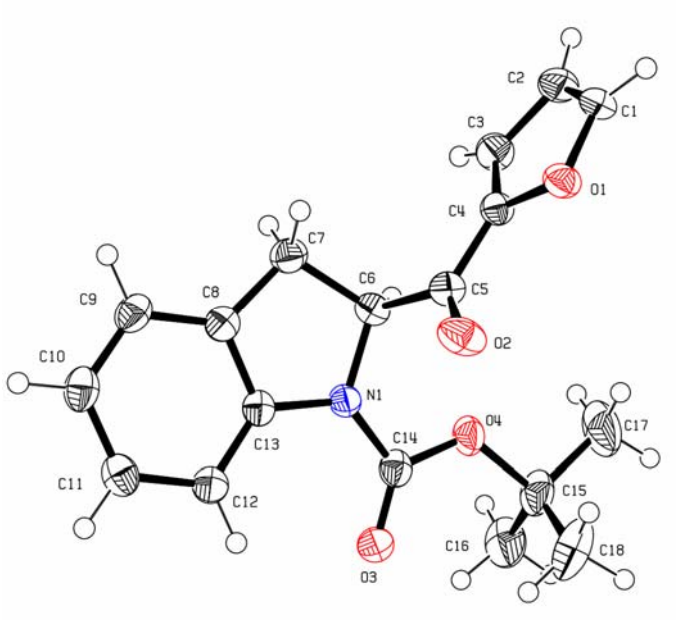
tert-butyl 2-benzoyl-6-fluoroindoline-1-carboxylate (4l)



Yield: 92%; pale yellow solid; m.p. 94-96 °C; TLC, R_f = 0.35 (PE:EtOAc = 9:1); ^1H NMR ($CDCl_3$, 400 MHz, two isomers ratio 2:1): δ 7.95 (d, 2H, J = 7.6 Hz), 7.74 (d, 0.69H, J = 6.4 Hz), 7.61 (t, 1H, J = 6.8

Hz), 7.51 (t, 2H, J = 7.2 Hz), 7.29 (d, 0.33H, J = 6.4 Hz), 6.69 (t, 1H, J = 6.8 Hz), 6.61 (t, 1H, J = 8.0 Hz) 5.90-5.72 (m, 1H), 3.60-3.52 (m, 1H), 3.02-2.94 (m, 1H), 1.60 (s, 3H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.74, 162.97 (d, J = 240.9 Hz), 151.37, 144.54 (d, J = 12.1 Hz), 134.01, 133.60, 128.89, 128.31, 125.28, 125.20, 124.83 (d, J = 10.0 Hz), 122.86, 108.75 (d, J = 22.8 Hz), 103.01 (d, J = 29.3 Hz), 81.60, 63.74, 31.90, 27.93; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −113.83, −113.93; IR (neat) v: 3408, 3004, 2978, 1703, 1492, 1396, 1155, 859 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{20}H_{21}FNO_3$ $[M+H]^+$: 364.1319, found: 364.1318.

Figure 1. Crystallographic Data of the Product 4f



The X-ray diffraction data were collected on Bruker SMART-1000 CCD diffractometer. Crystal data for **4f** C_{18} $H_{19}NO_4$: Mr = 313.34, colorless, T = 113(2) K**,** size = 0.14 x 0.12 x 0.06 mm^3, Monoclinic, space group $P2(1)/c$, λ = 0.71073 Å, a = 14.325(5) Å, b = 7.607(2) Å, c = 16.273(6) Å, α = 90°, β = 106.477(7)°, γ = 90°, V = 1700.4(10) Å^3, Z = 4, ρ_{calcd} = 1.224 Mg/m^3, μ = 0.087 mm^{-1}, reflections collected/unique = 17109/4041, R(int) = 0.0436, R_1 = 0.0497, wR_2 = 0.1036 ($I > 2\sigma I$), GOF = 1.039. CCDC 901326 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References:

S1 Q.-Q. Yang, C. Xiao, L.-Q. Lu, J. An, F. Tan, B.-J. Li and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 9137.

S2 J. Fan, C. Wan, G. Sun and Z. Wang, *J. Org. Chem.*, 2008, **73**, 8608.

S3 V. Sriramurthy and O. Kwon, *Org. Lett.*, 2010, **12**, 1084.

S4 (*a*) G. Cremonesi, P. D. Croce, F. Fontana and C. L. Rosaa, *Heterocycles*, 2007, **74**, 1015; (*b*) A. Mori, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa and H. Sajiki, *Org. Lett.*, 2006, **8**, 3279.

S5 B. M. Nugent, A. L. Williams, E. N. Prabhakaran and J. N. Johnston, *Tetrahedron*, 2003, **59**, 8877.

S6 J. Kischel, K. Mertins, D. Michalik, A. Zapf and M. Beller, *Adv. Synth. Catal*., 2007, **349**, 865.

S7 Z. Hu, J. Liu, Z. Dong, L. Guo, D.Wang and P. Zeng, *J. Chem. Res*., 2004, **2**, 158.

S8 D. Solé, X. Urbaneja, A. C. Vargas and J. Bonjoch, *Tetrahedron*, 2007, **63**, 10177.

S9 S. Mahboobi, T. Burgemeister, S. Dove, S. Kuhr and A. Popp, *J. Org. Chem.*, 1999, **64**, 8130.

S10 (*a*) R. C. Crouch, A. O. Davis, T. D. Spitzer and G. E. Martin, *J. Heterocycl. Chem*., 1995, **32**, 1077. (*b*) J. Lavrado, G. G. Cabal, M. Prudêncio, M. M. Mota, J. Gut, P. J. Rosenthal, C. Díaz, R. C. Guedes, D. J. V. A. dos Santos, E. Bichenkova, K. T. Douglas, R. Moreira and A. Paulo, *J. Med. Chem.*, 2011, **54**, 734.

S11 X.-L. An, J.-R. Chen, C.-F. Li, F.-G. Zhang, Y.-Q. Zou, Y.-C. Guo and W.-J. Xiao, *Chem. Asian J.*, 2010, **5**, 2258.

S12 A. Jackson, N. D. V. Wilson, A. J. Grskell and J. A. Joule, *J. Chem. Soc. C*, 1969, 2738.

S13 M. A. Sukari and J. M. Vernon, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2219.

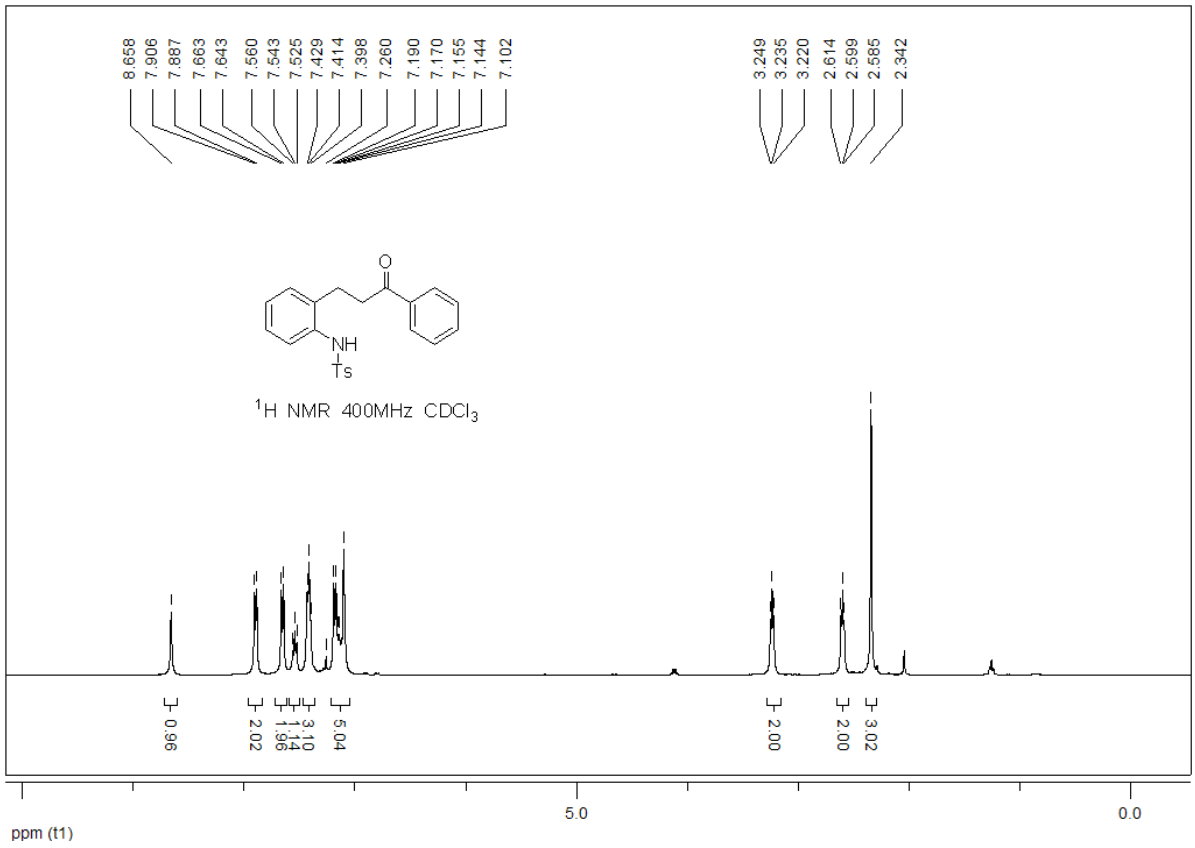
S14 J. Castells, Y. Troin, A. Diez and M. Rubiralta, *Tetrahedron*, 1991, **47**, 7911.

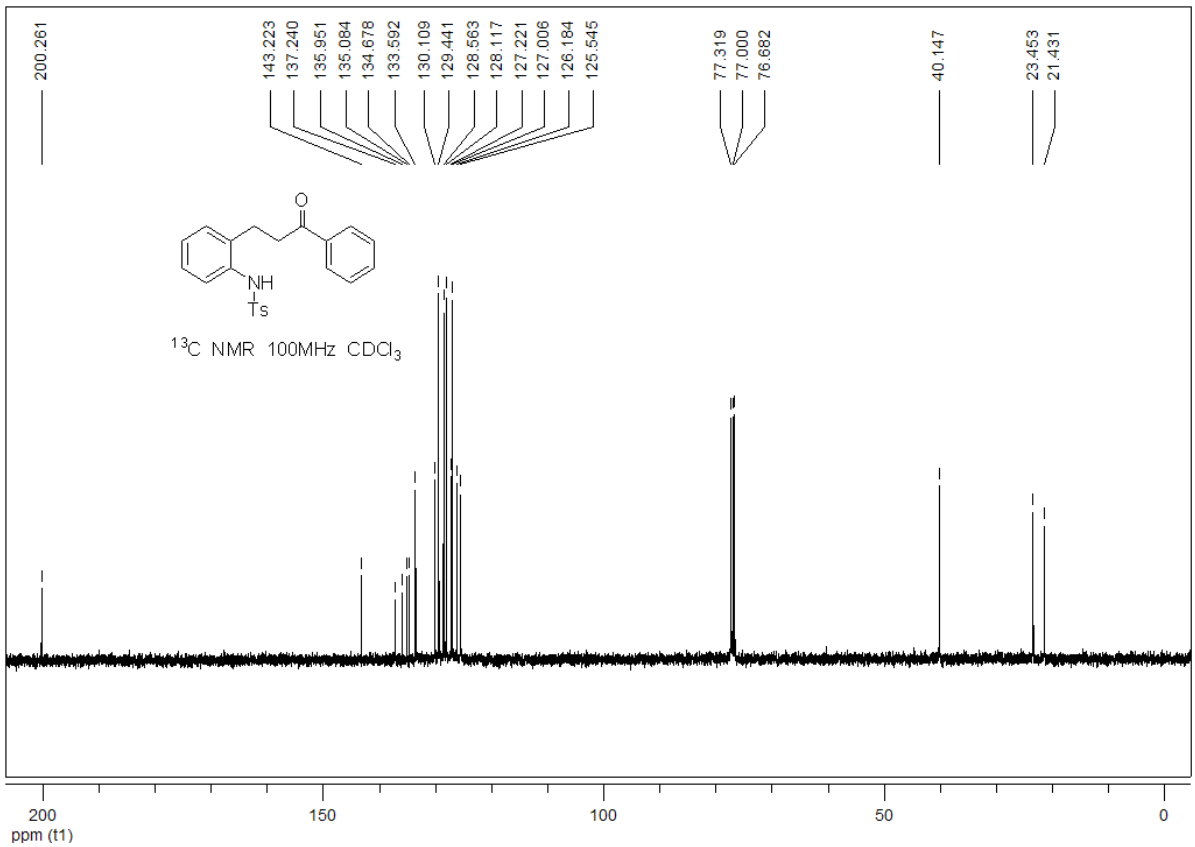
S15 N. E. Golantsov, A. V. Karchava and M. A. Yurovskaya, *Chem. Heterocycl. Compd.*, 2006, **42**, 1021.

S16 For this substrate, an alternative method was used to introduce the *N*-Boc group: S. V. Chankeshwara and A. K. Chakraborti, *Org. Lett.*, 2006, **8**, 3259.

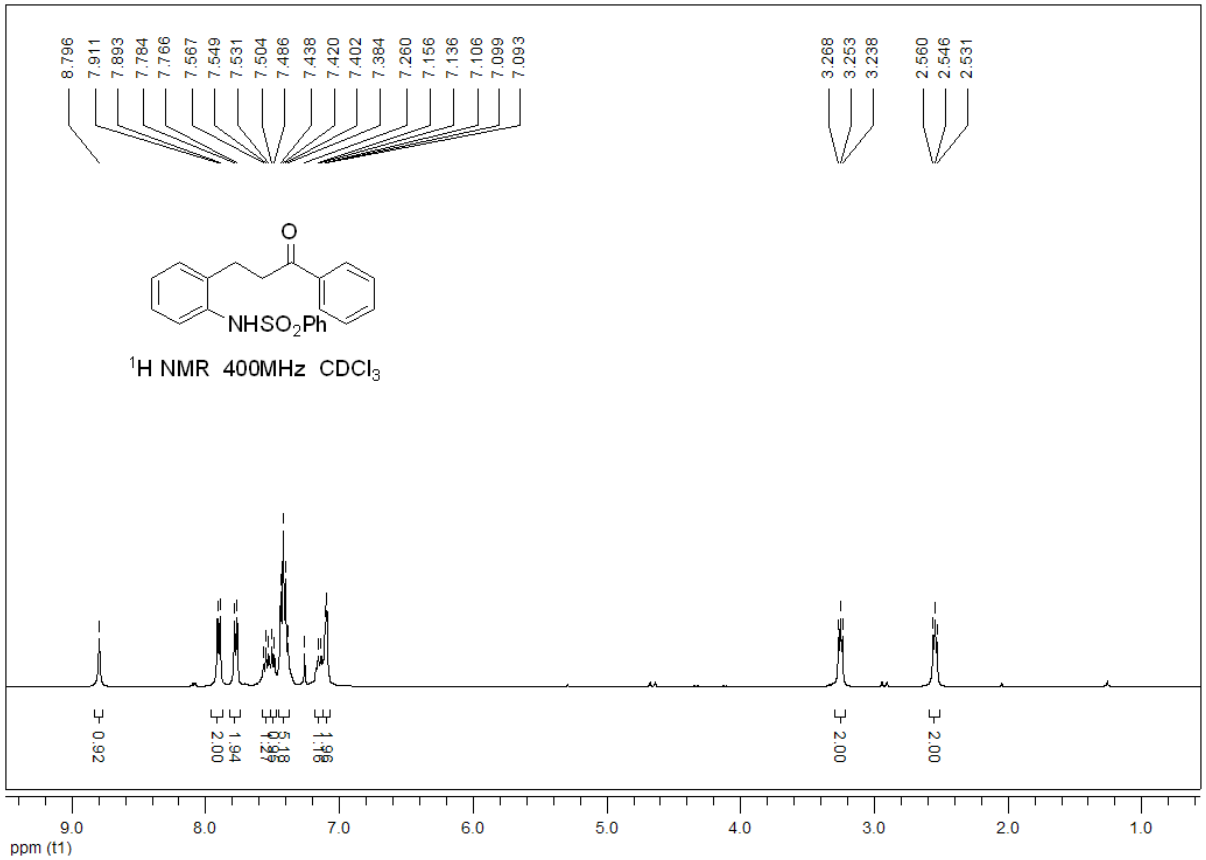
NMR Spectra of the Substrates and Products

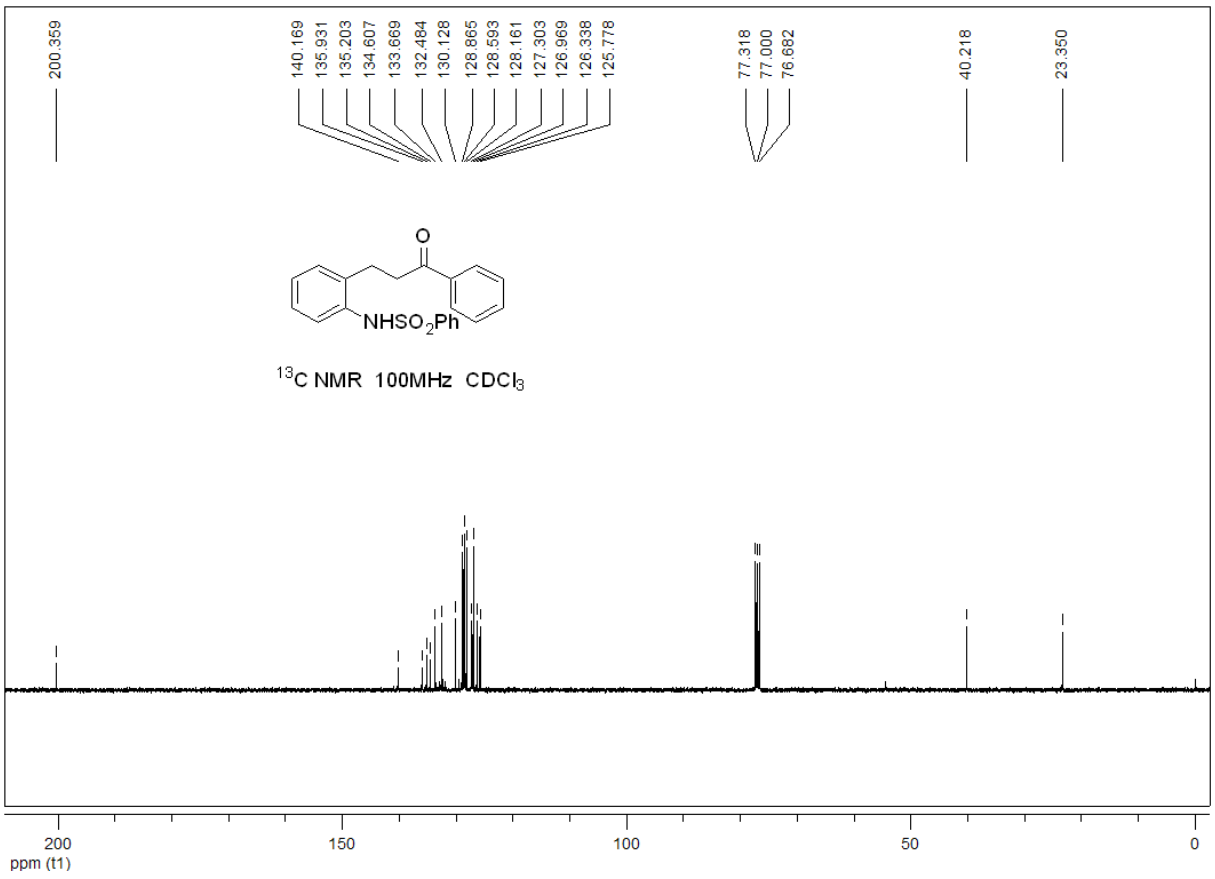
Compound **1a**:



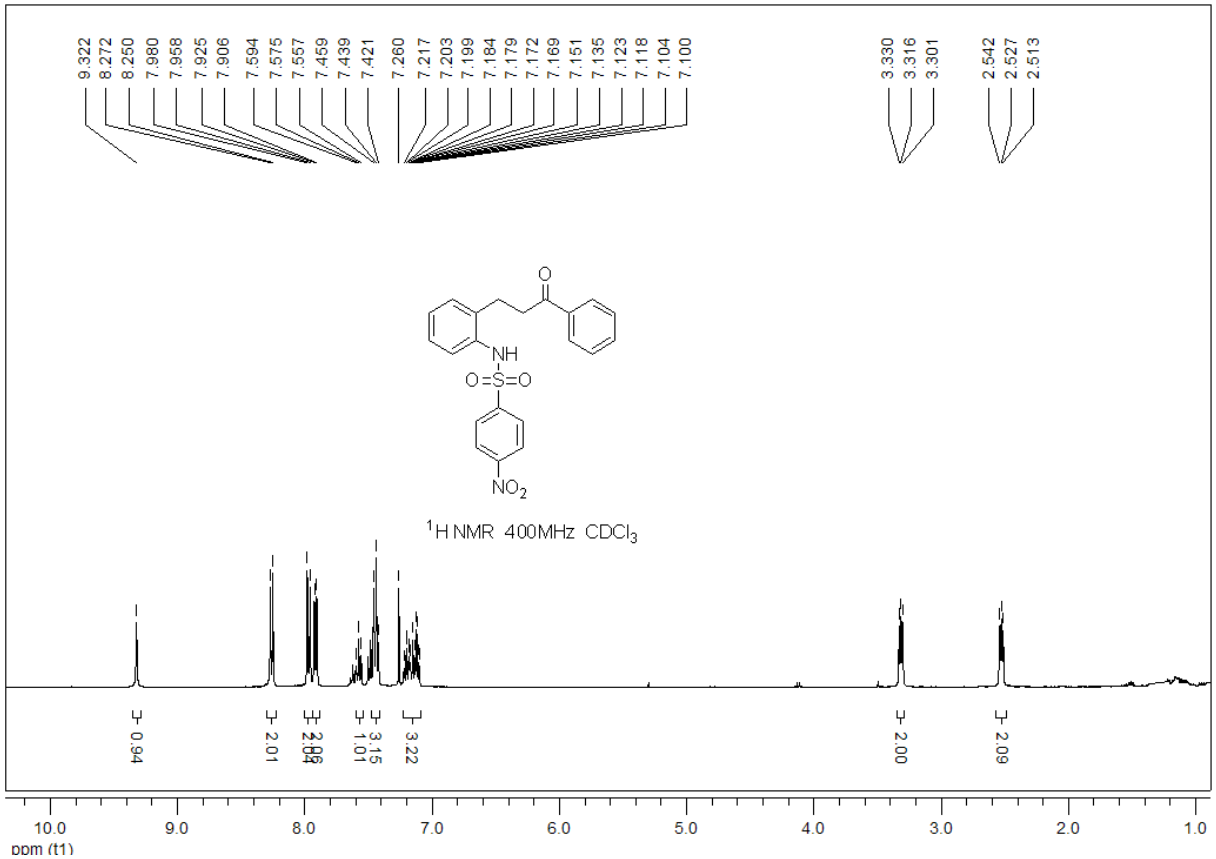


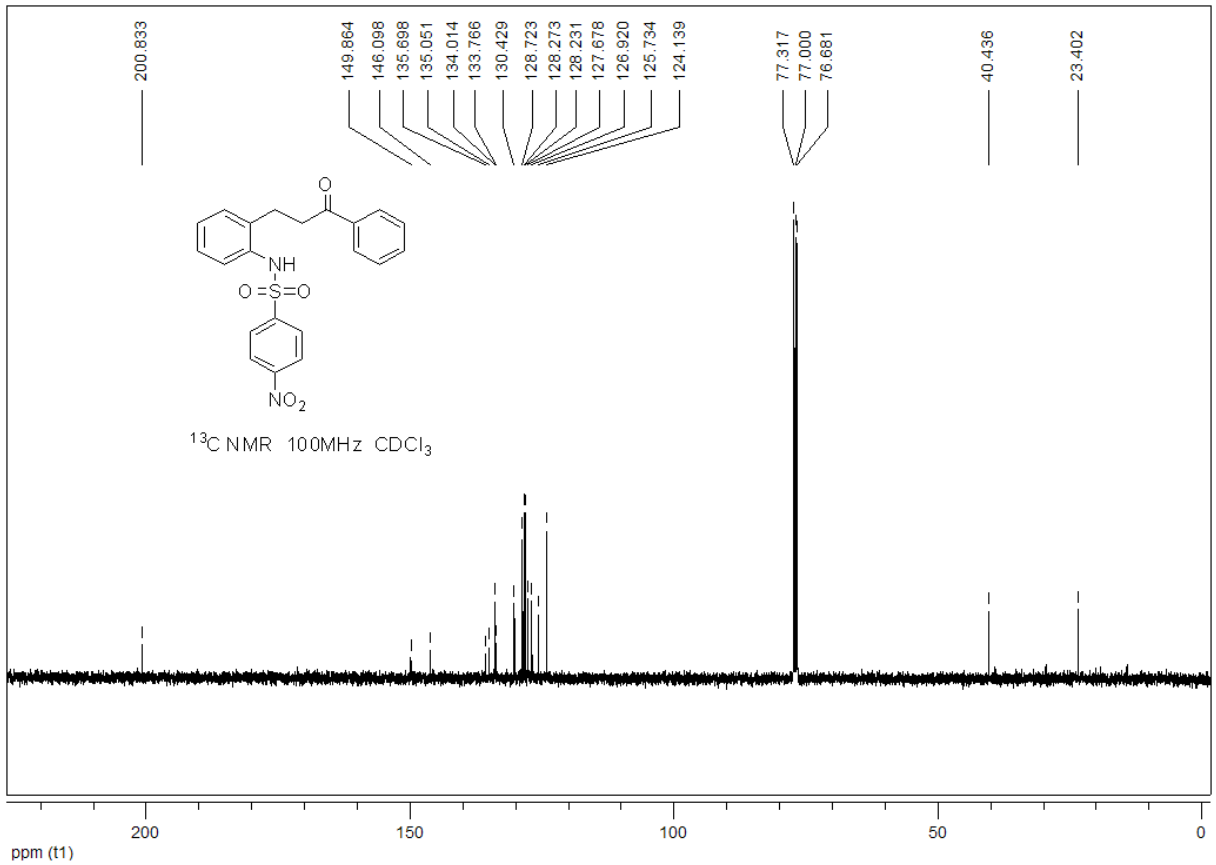
***N*-(2-(3-oxo-3-phenylpropyl)phenyl)benzenesulfonamide**:



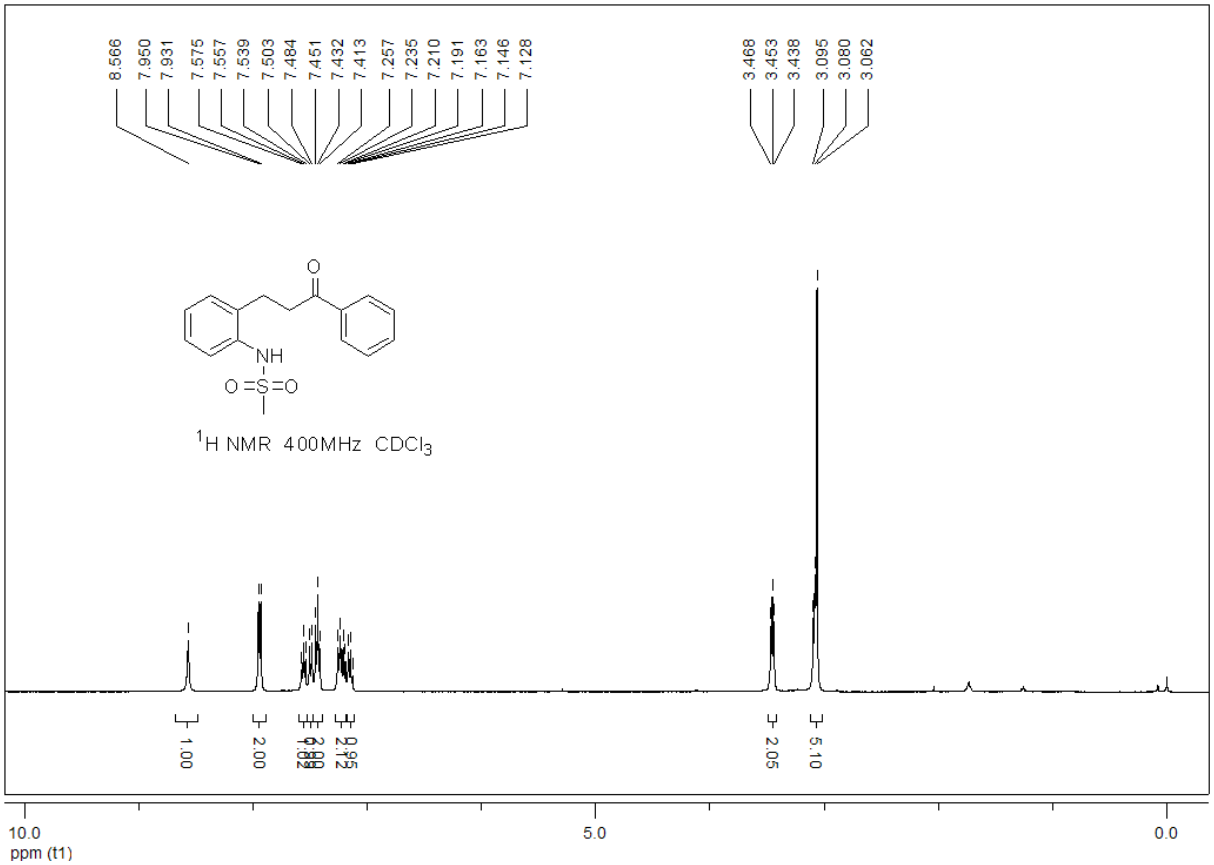


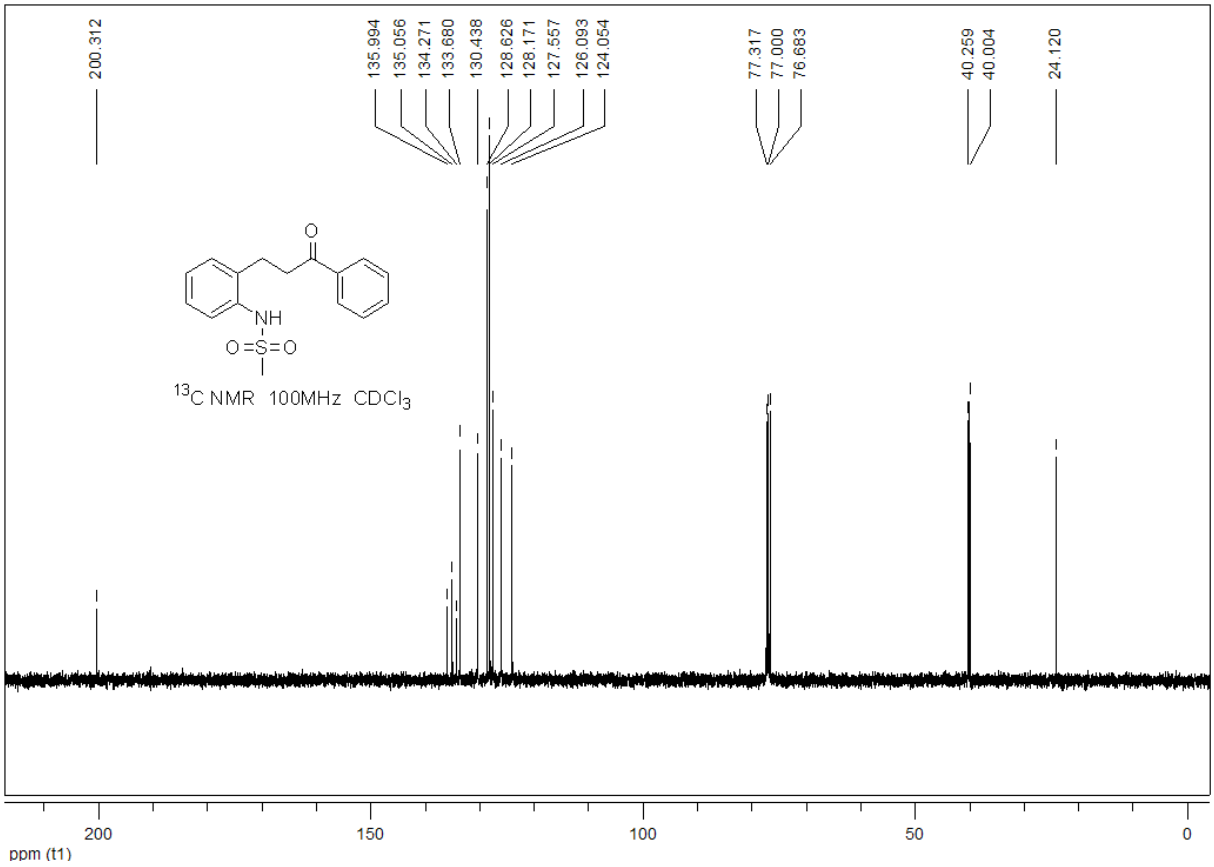
_N_-(2-(3-oxo-3-phenylpropyl)phenyl)-4-nitrobenzenesulfonamide :



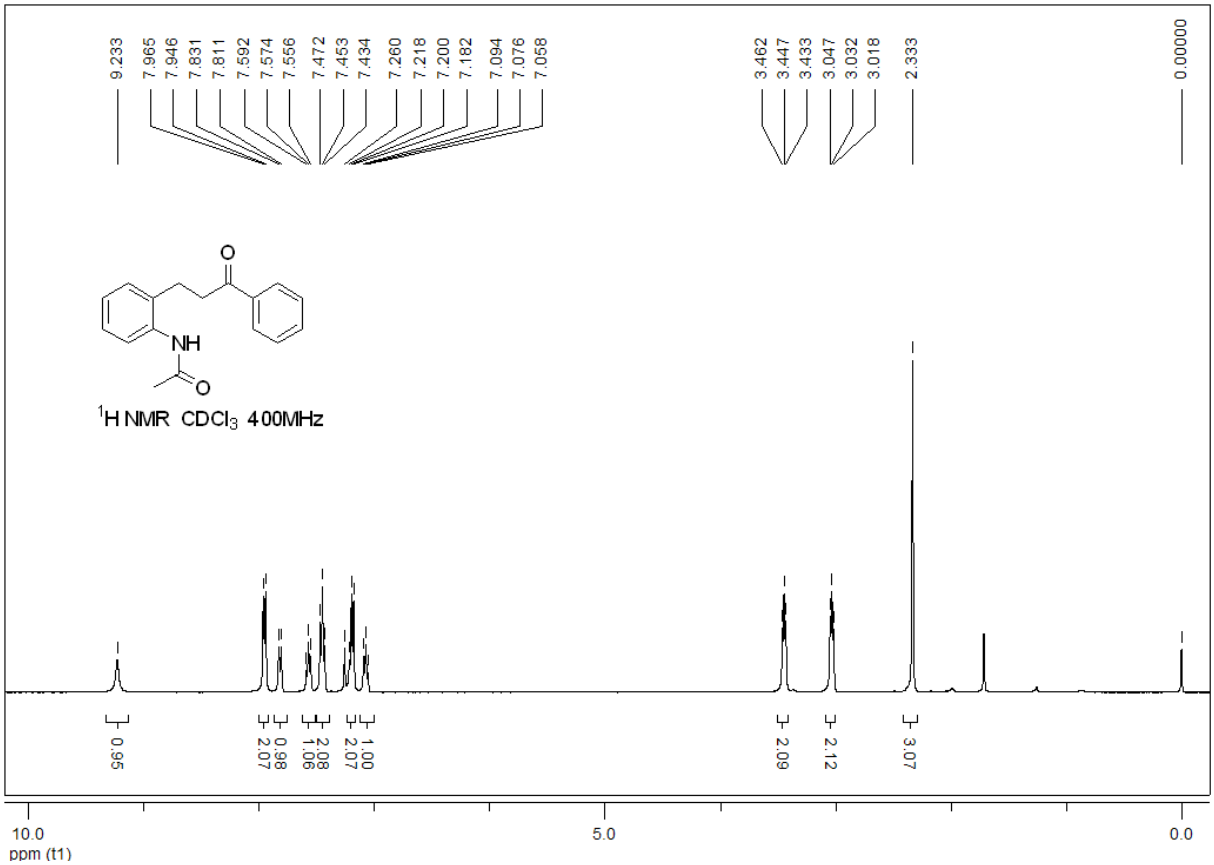


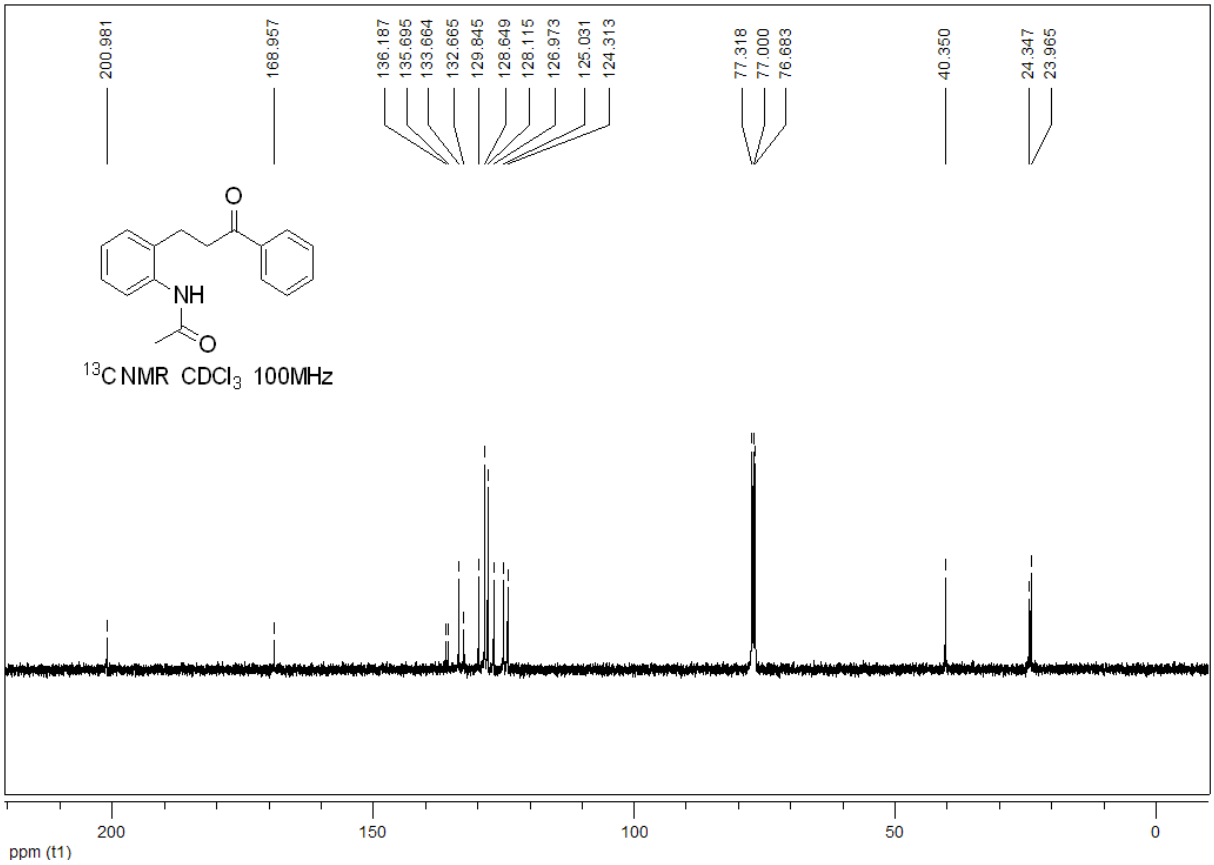
***N*-(2-(3-oxo-3-phenylpropyl)phenyl)methanesulfonamide**:



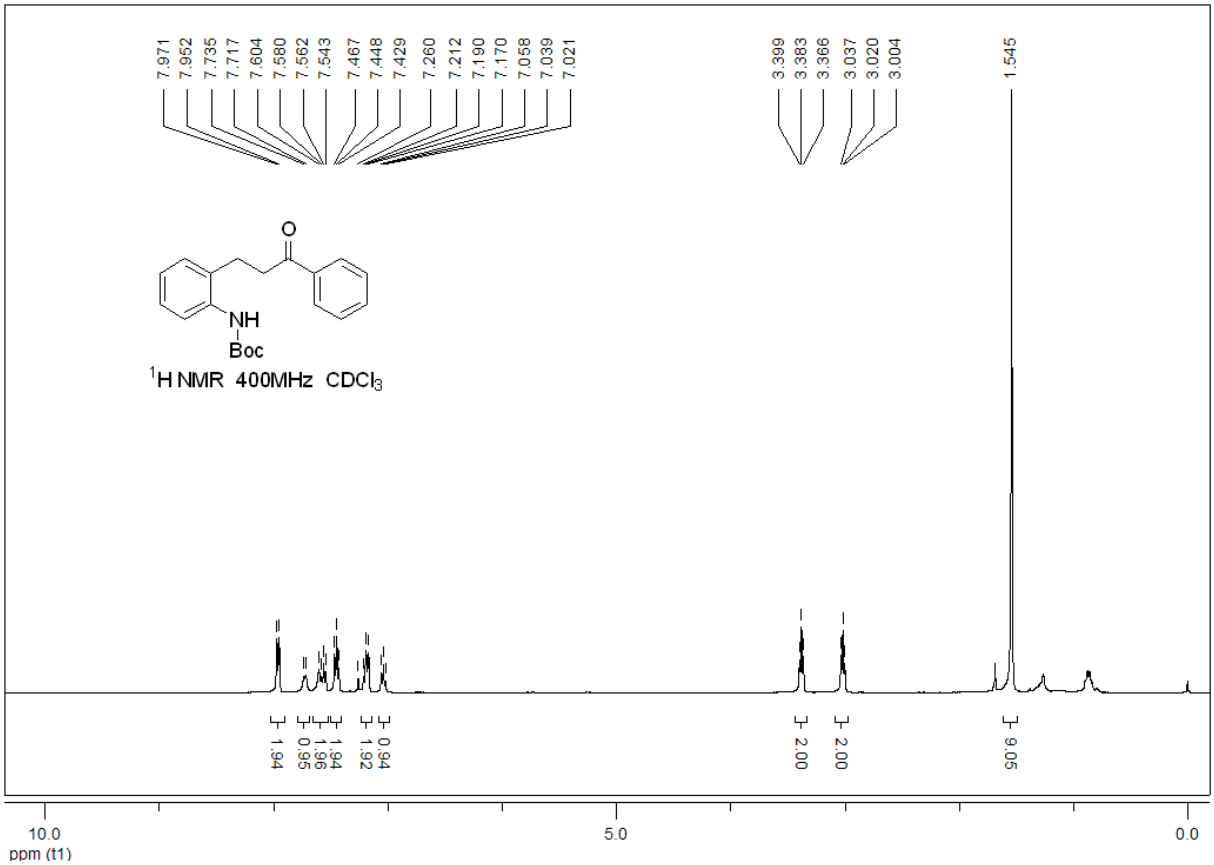


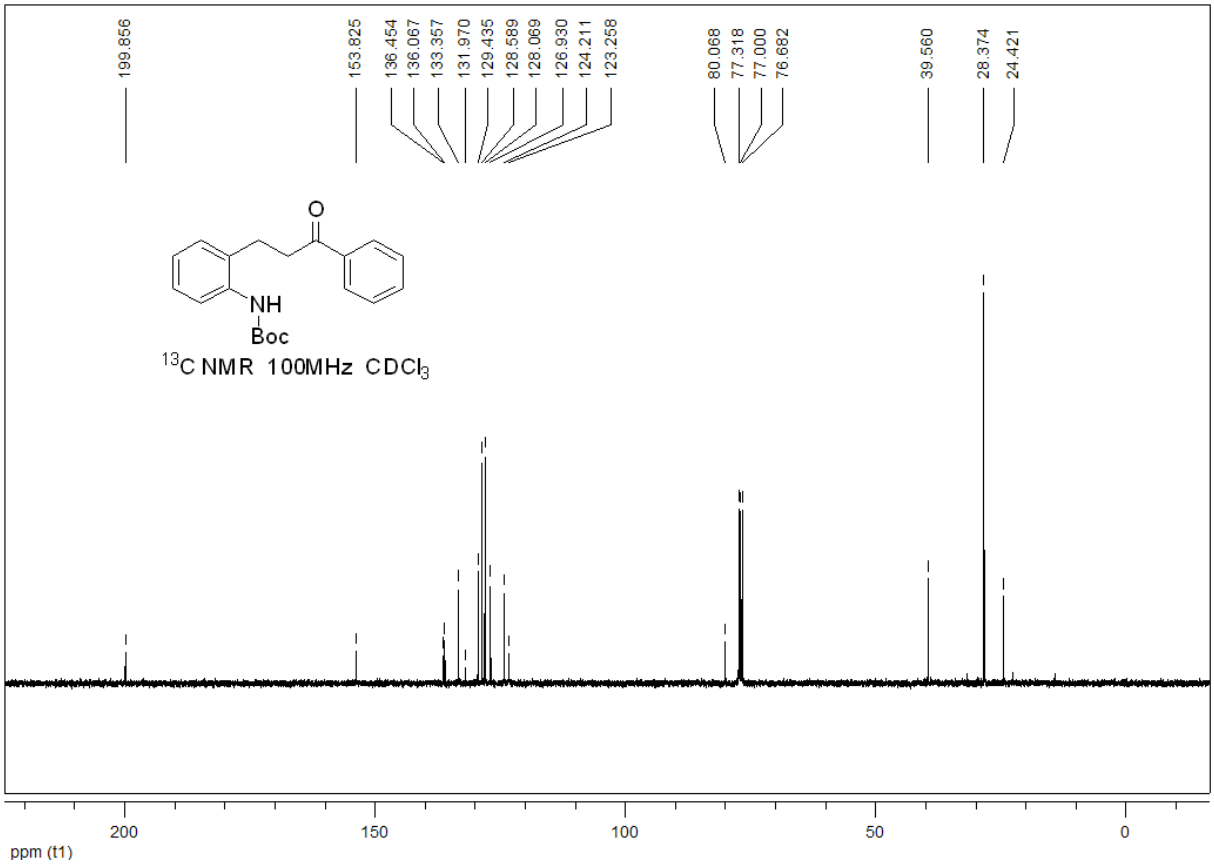
_N_-(2-(3-oxo-3-phenylpropyl)phenyl)acetamide:


9.233
7.965
7.946
7.831
7.811
7.592
7.574
7.556
7.472
7.453
7.434
7.260
7.218
7.200
7.182
7.094
7.076
7.058
3.462
3.447
3.433
3.047
3.032
3.018
2.333
0.00000
O
NH
O
1H NMR CDCl3 400MHz
0.95
2.07
0.98
1.06
2.08
2.07
1.00
2.09
2.12
3.07
10.0
5.0
0.0
ppm (t1)

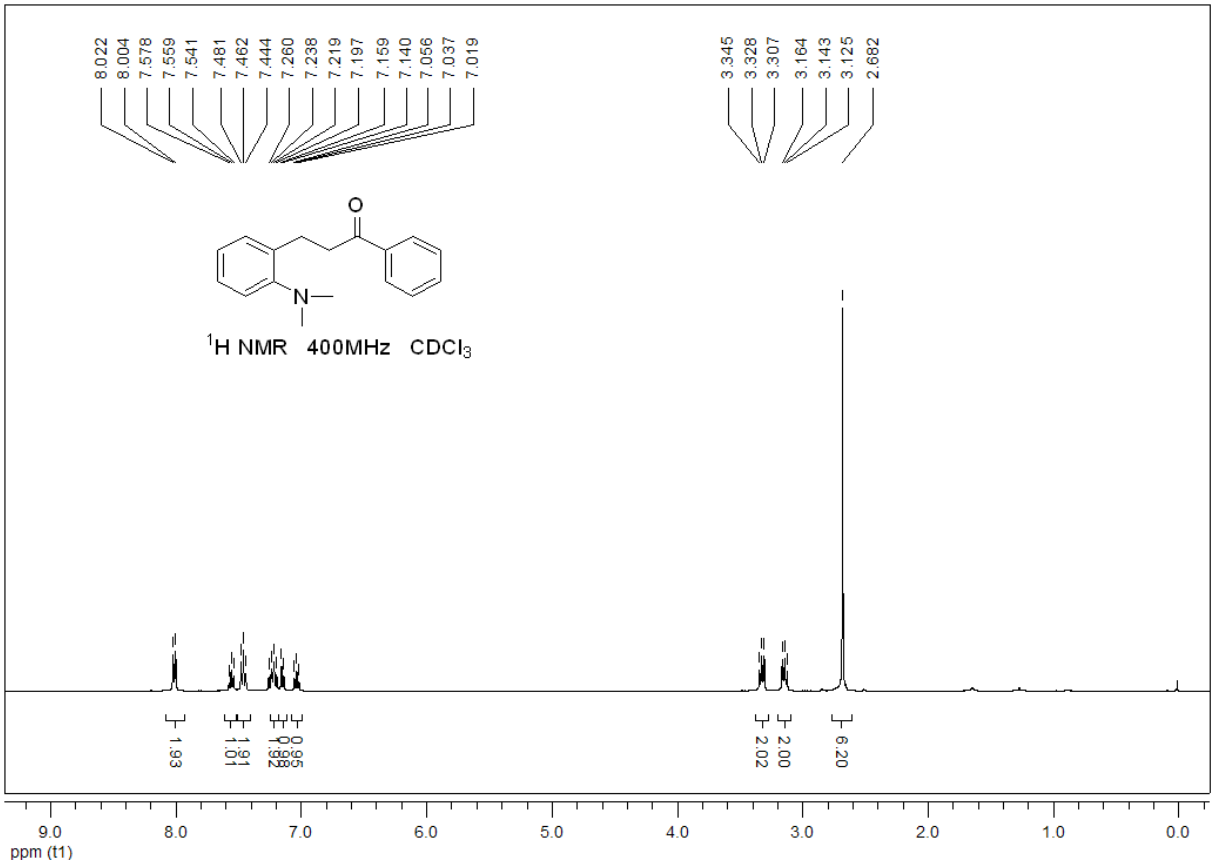

200.981
168.957
136.187
135.695
133.664
132.665
129.845
128.649
128.115
126.973
125.031
124.313
77.318
77.000
76.683
40.350
24.347
23.965
O
NH
O
13C NMR CDCl3 100MHz
200
150
100
50
0
ppm (t1)

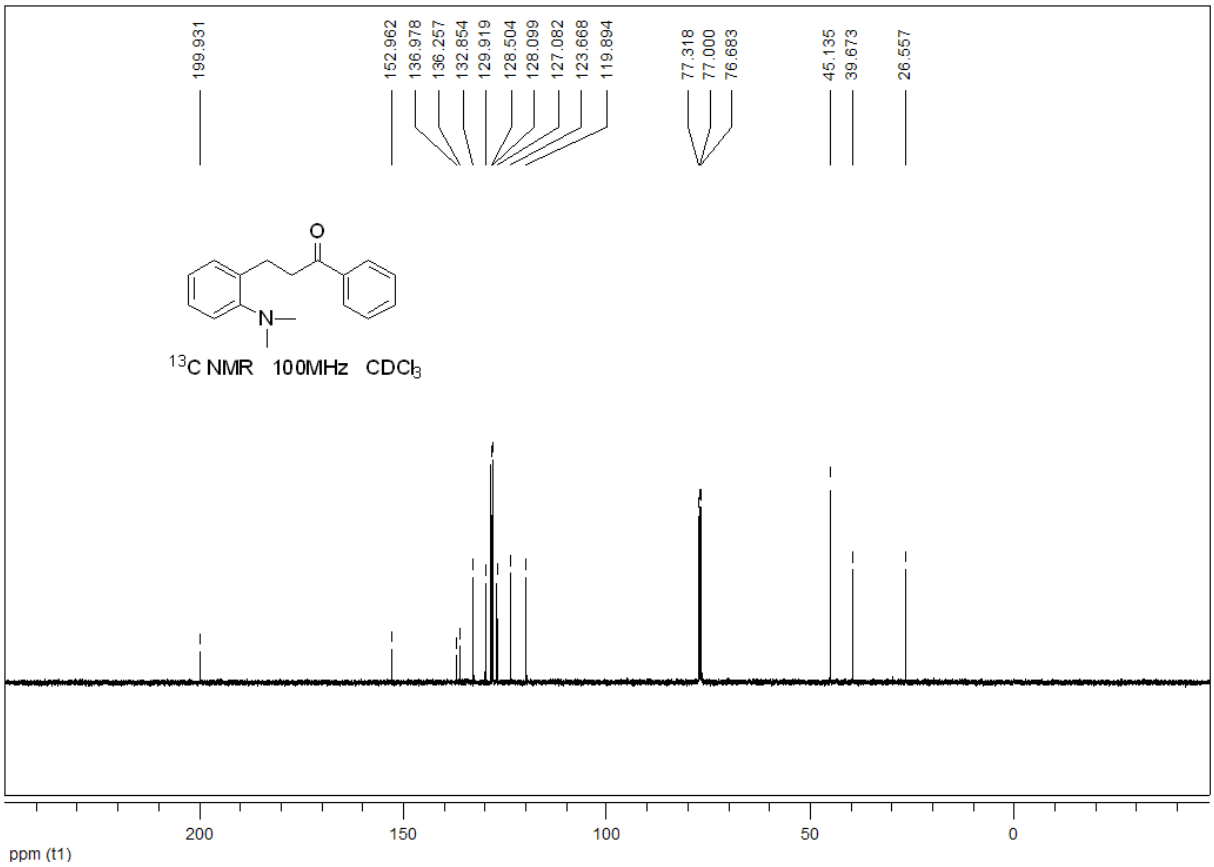
Compound **3a**:



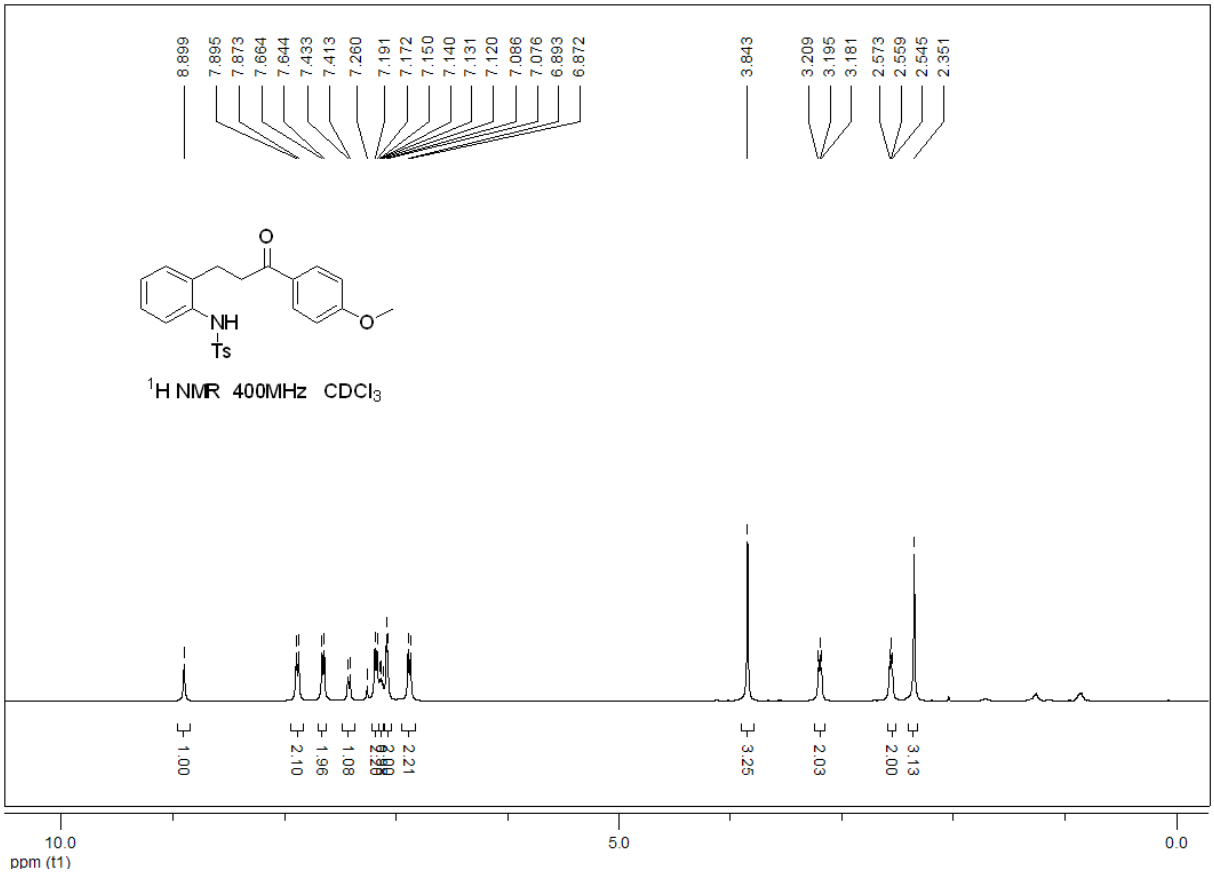


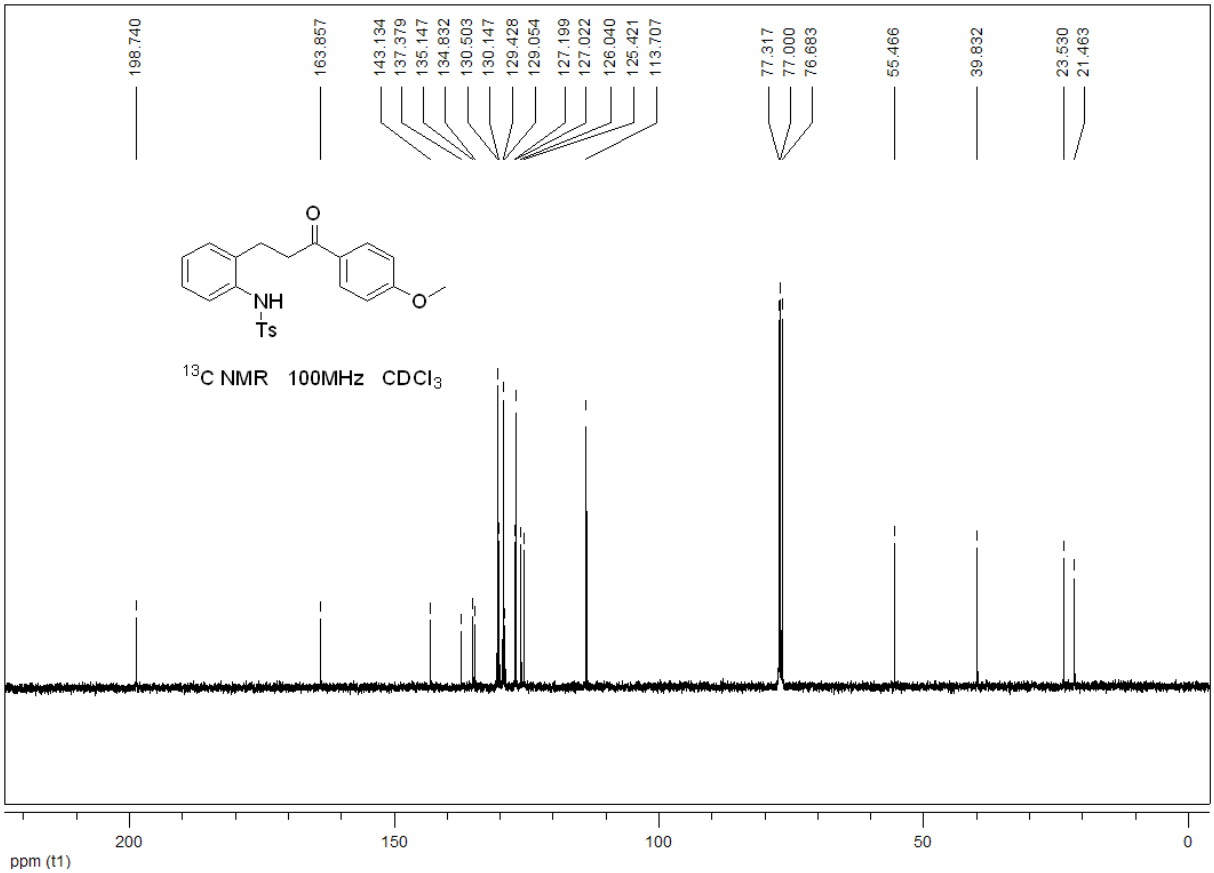
Compound **S10**:


8.022
8.004
7.578
7.559
7.541
7.481
7.462
7.444
7.260
7.238
7.219
7.197
7.159
7.140
7.056
7.037
7.019
3.345
3.328
3.307
3.164
3.143
3.125
2.682
O
N
1H NMR 400MHz CDCl3
1.93
1.91
1.01
0.98
0.95
2.02
2.00
6.20
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

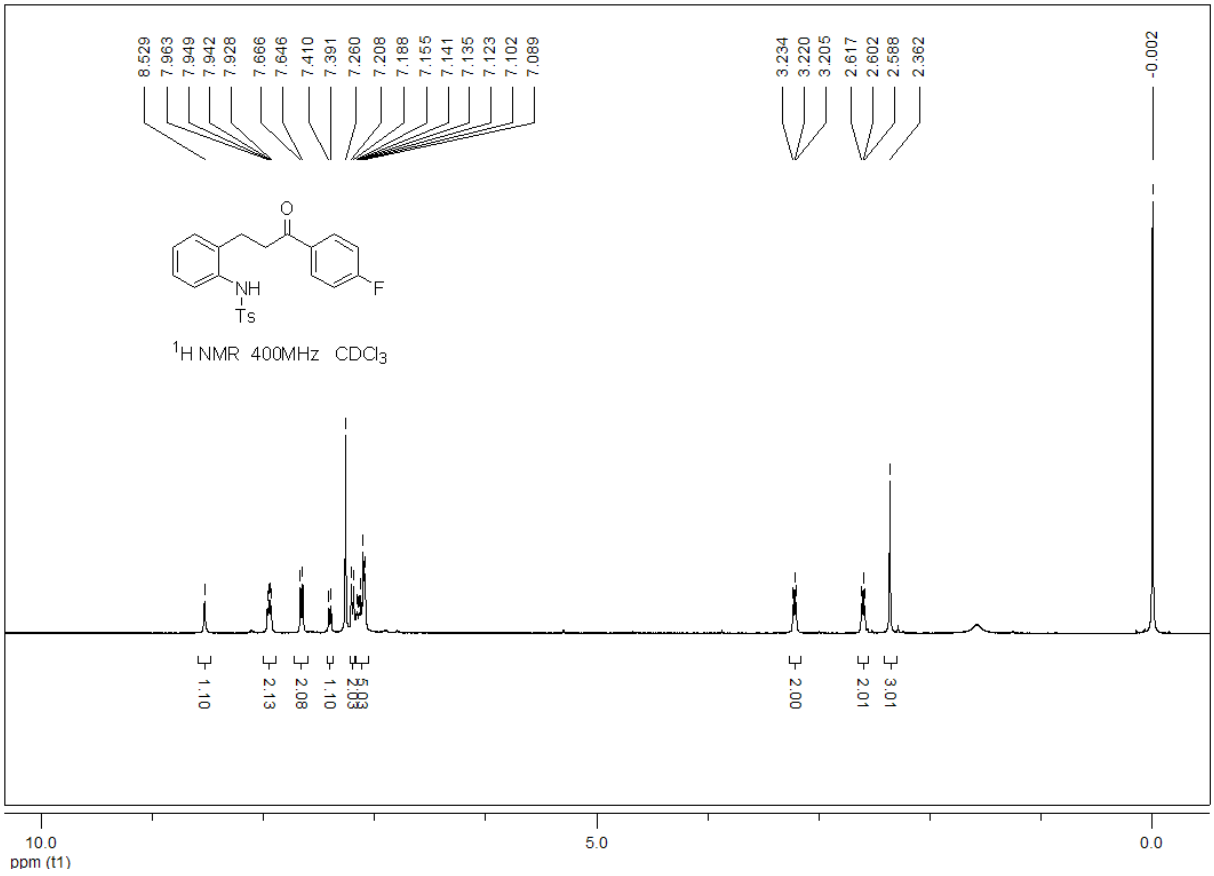

199.931
152.962
136.978
136.257
132.854
129.919
128.504
128.099
127.082
123.668
119.894
77.318
77.000
76.683
45.135
39.673
26.557
O
N
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

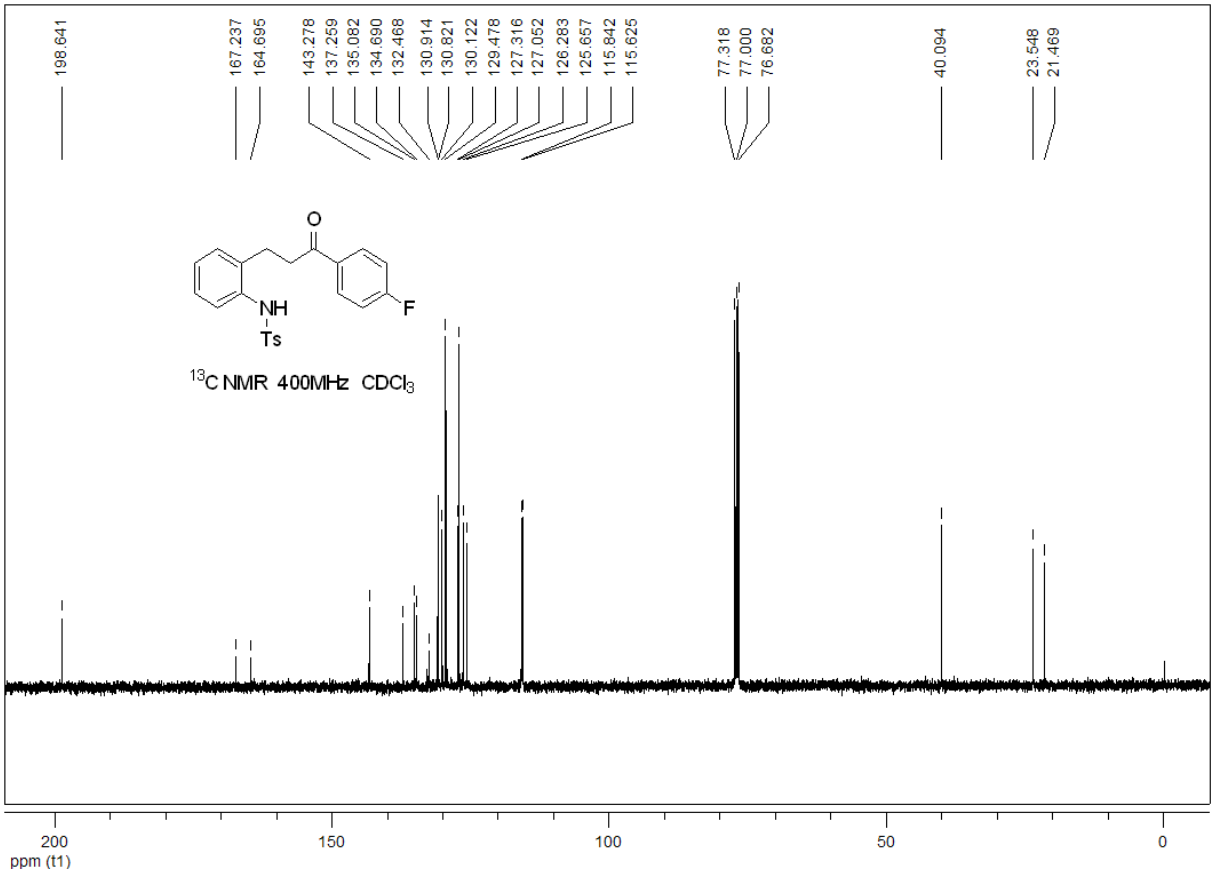
Compound **1b**:

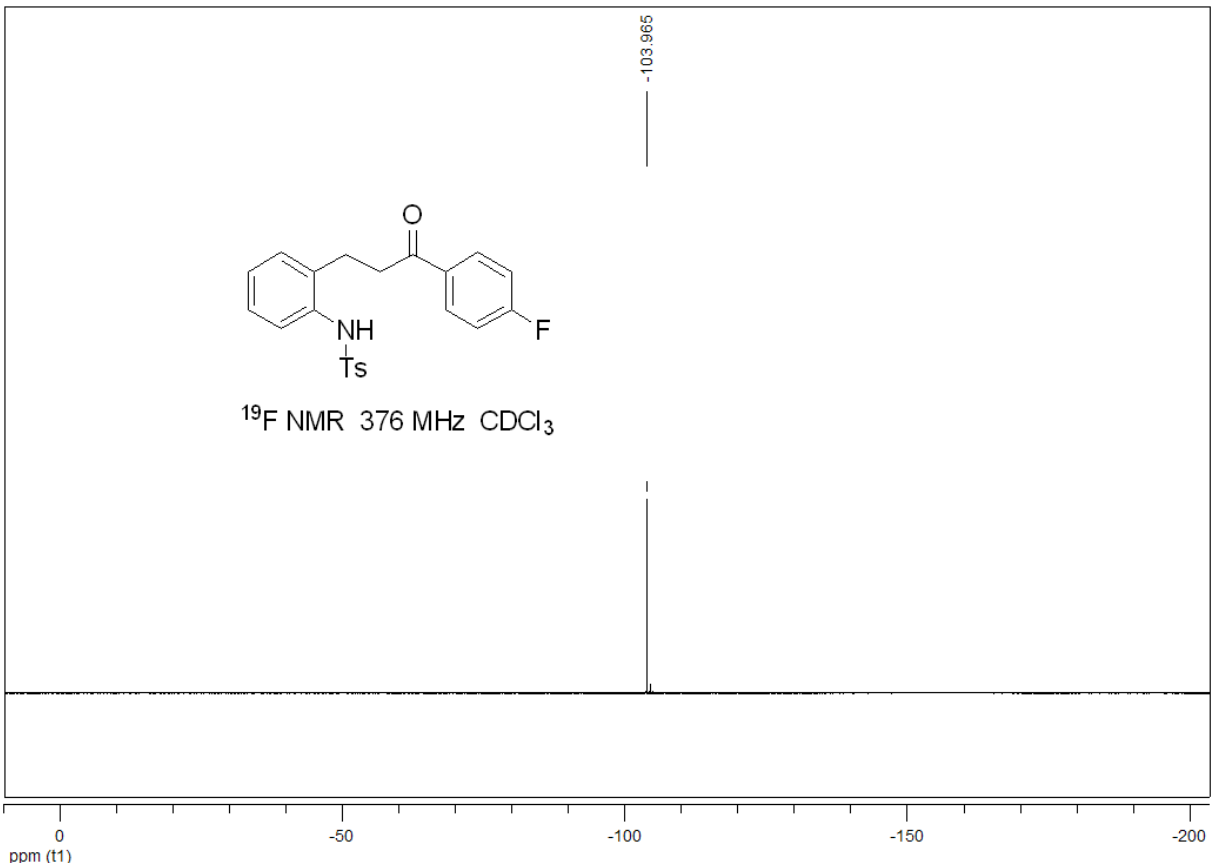

8.899
7.895
7.873
7.664
7.644
7.433
7.413
7.260
7.191
7.172
7.150
7.140
7.131
7.120
7.086
7.076
6.893
6.872
3.843
3.209
3.195
3.181
2.573
2.559
2.545
2.351
O
NH
Ts
O
1H NMR 400MHz CDCl3
1.00
2.10
1.96
1.08
2.03
3.25
2.03
2.00
3.13
10.0
5.0
0.0
ppm (t1)


198.740
163.857
143.134
137.379
135.147
134.832
130.503
130.147
129.428
129.054
127.199
127.022
126.040
125.421
113.707
77.317
77.000
76.683
55.466
39.832
23.530
21.463
O
NH
Ts
O
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

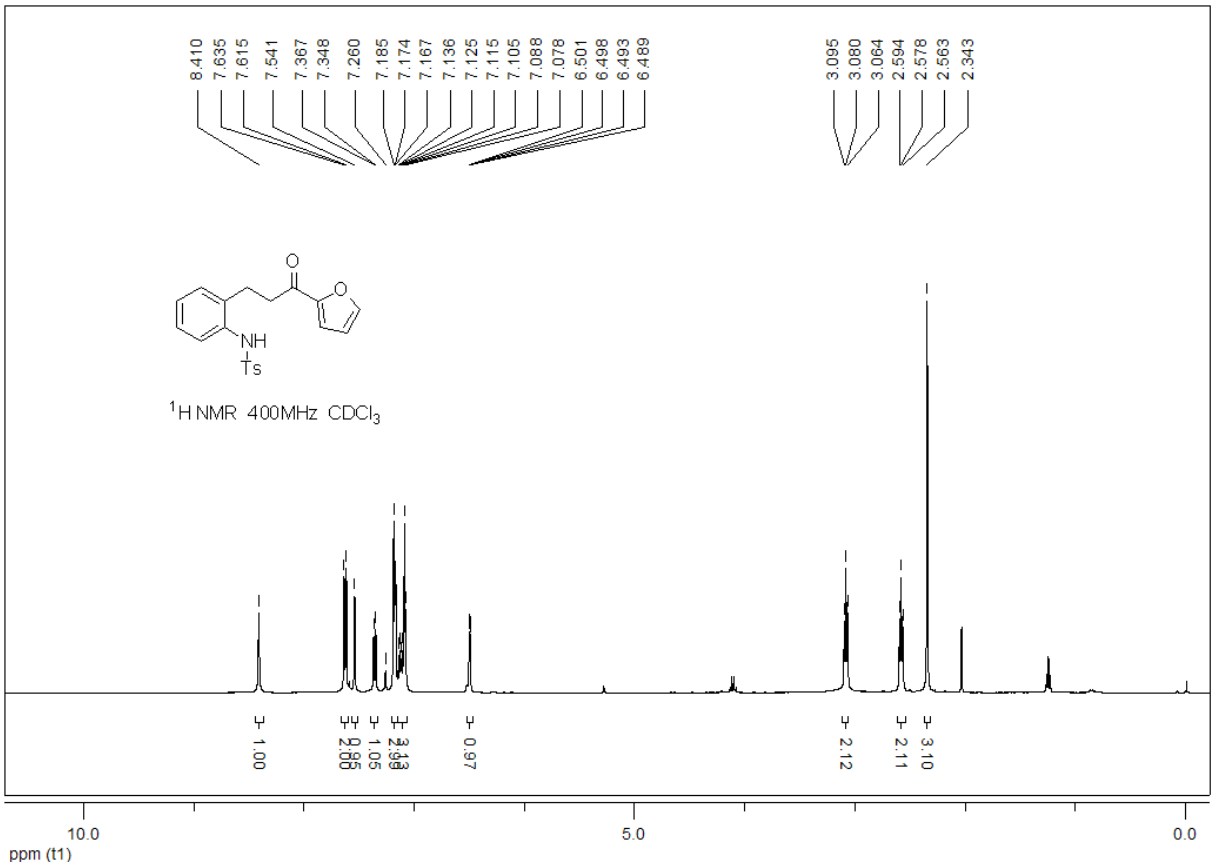
Compound **1c**:

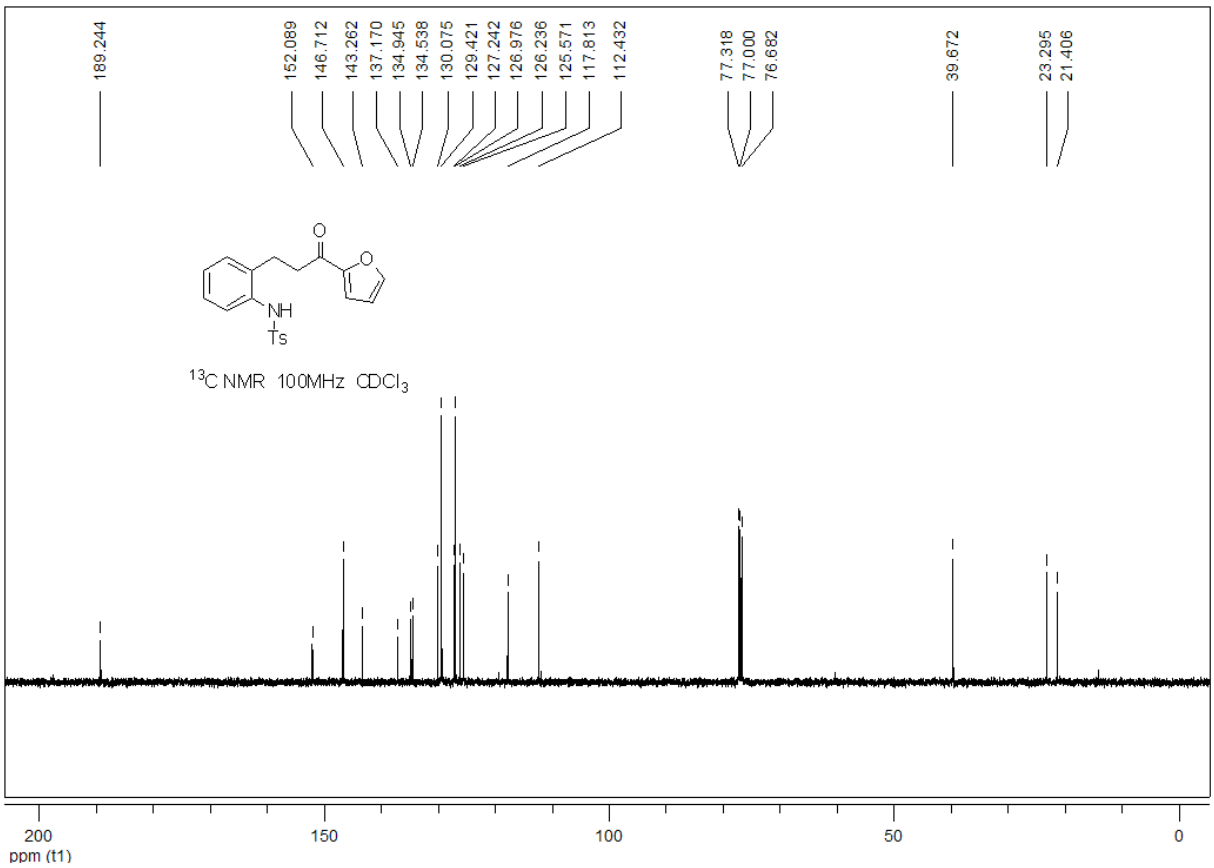

8.529
7.963
7.949
7.942
7.928
7.666
7.646
7.410
7.391
7.260
7.208
7.188
7.155
7.141
7.135
7.123
7.102
7.089
3.234
3.220
3.205
2.617
2.602
2.588
2.362
-0.002
O
NH
Ts
F
1H NMR 400MHz CDCl3
1.10
2.13
2.08
1.10
5.83
2.00
2.01
3.01
10.0
ppm (t1)
5.0
0.0


198.641
167.237
164.695
143.278
137.259
135.082
134.690
132.468
130.914
130.821
130.122
129.478
127.316
127.052
126.283
125.657
115.842
115.625
77.318
77.000
76.682
40.094
23.548
21.469
O
NH
Ts
F
13C NMR 400MHz CDCl3
200
ppm (t1)
150
100
50
0

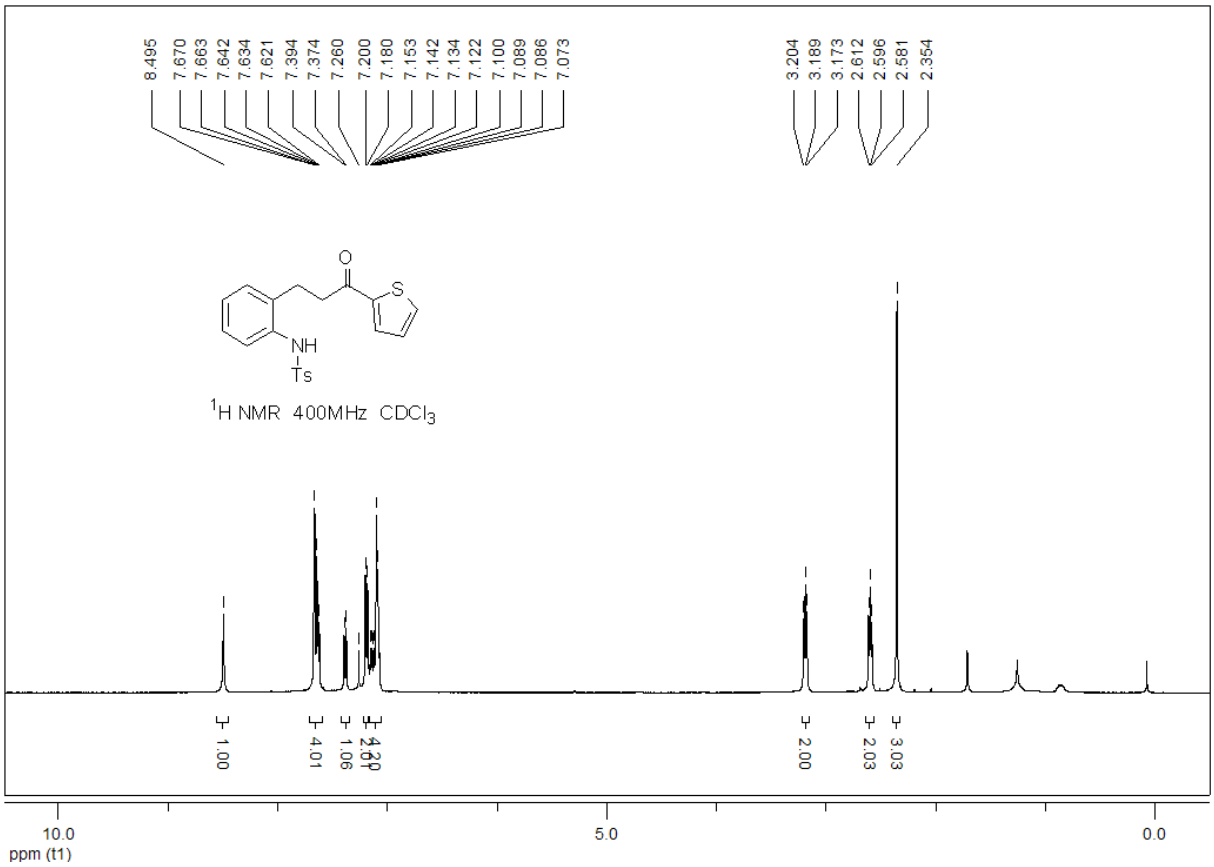

-103.965
O
NH
Ts
F
19F NMR 376 MHz CDCl3
0
-50
-100
-150
-200
ppm (t1)

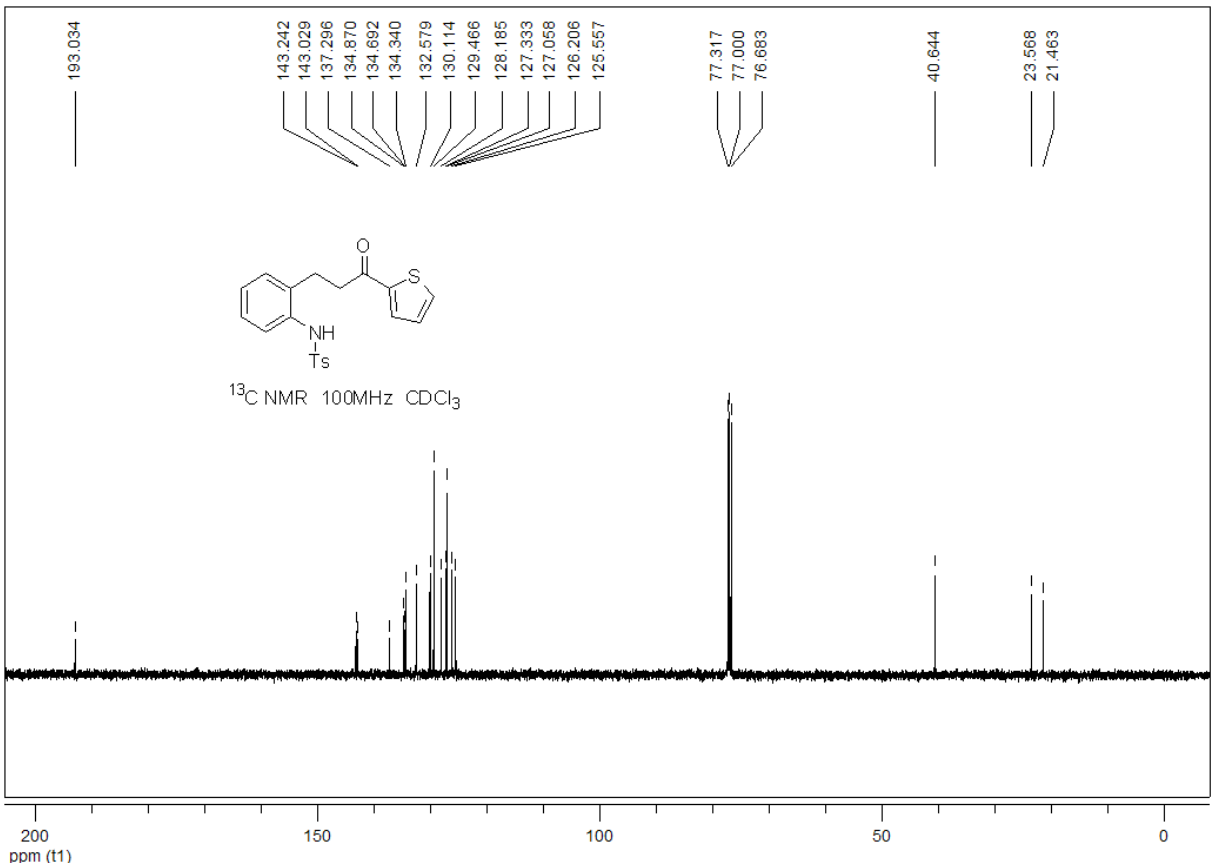
Compound **1d**:


8.410
7.635
7.615
7.541
7.367
7.348
7.260
7.185
7.174
7.167
7.136
7.125
7.115
7.105
7.088
7.078
6.501
6.498
6.493
6.489
3.095
3.080
3.064
2.594
2.578
2.563
2.343
O
O
NH
Ts
1H NMR 400MHz CDCl3
1.00
2.06
1.05
2.13
0.97
2.12
2.11
3.10
10.0
5.0
0.0
ppm (t1)

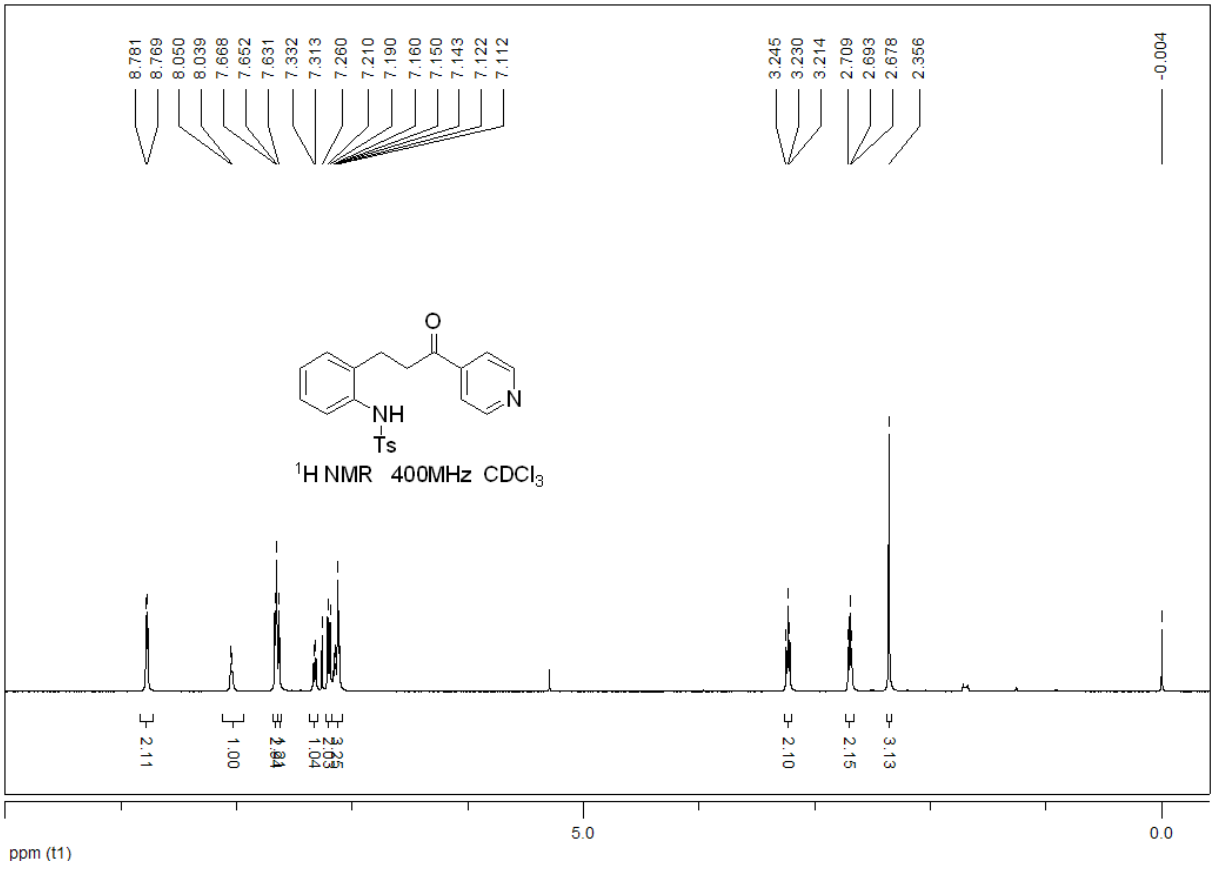

189.244
152.089
146.712
143.262
137.170
134.945
134.538
130.075
129.421
127.242
126.976
126.236
125.571
117.813
112.432
77.318
77.000
76.682
39.672
23.295
21.406
O
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

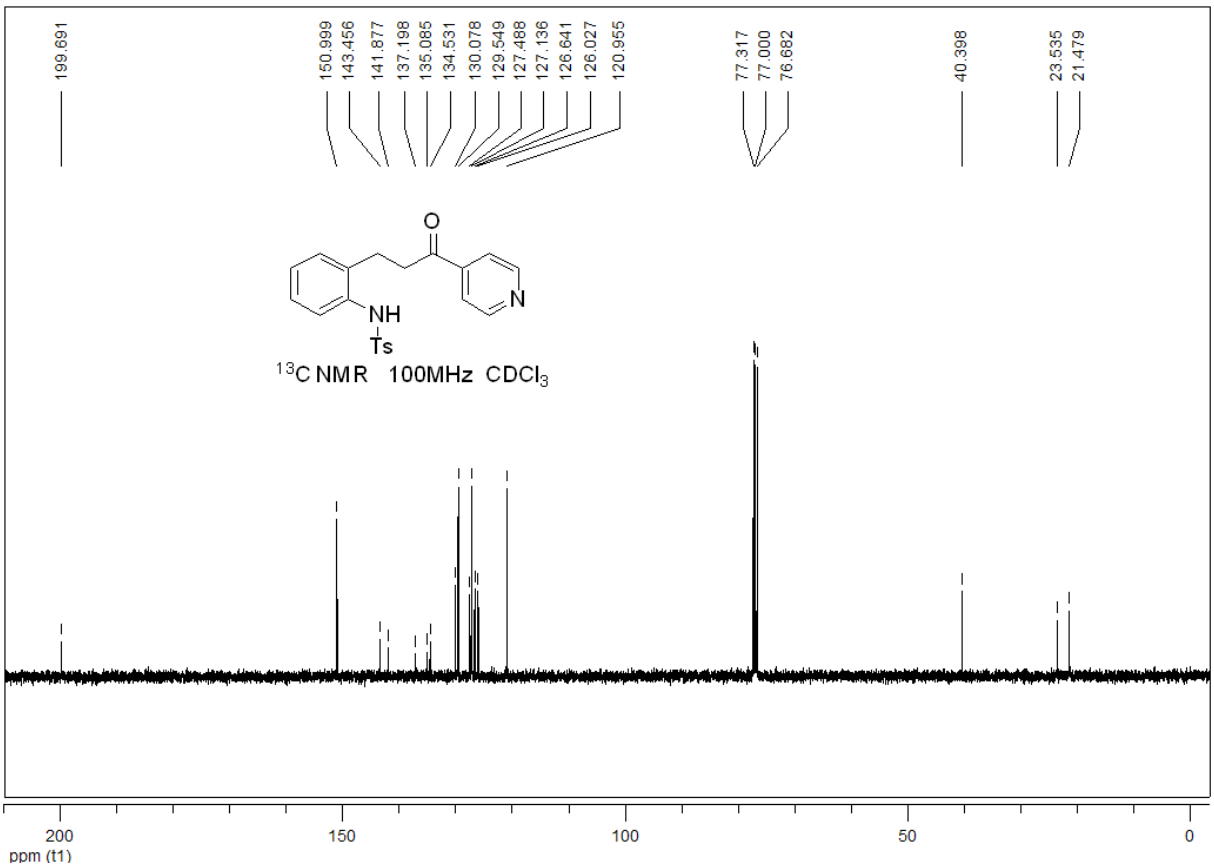
Compound **1e**:


8.495
7.670
7.663
7.642
7.634
7.621
7.394
7.374
7.260
7.200
7.180
7.153
7.142
7.134
7.122
7.100
7.089
7.086
7.073
3.204
3.189
3.173
2.612
2.596
2.581
2.354
O
S
NH
Ts
1H NMR 400MHz CDCl3
1.00
4.01
1.06
2.07
2.00
2.03
3.03
10.0
5.0
0.0
ppm (t1)

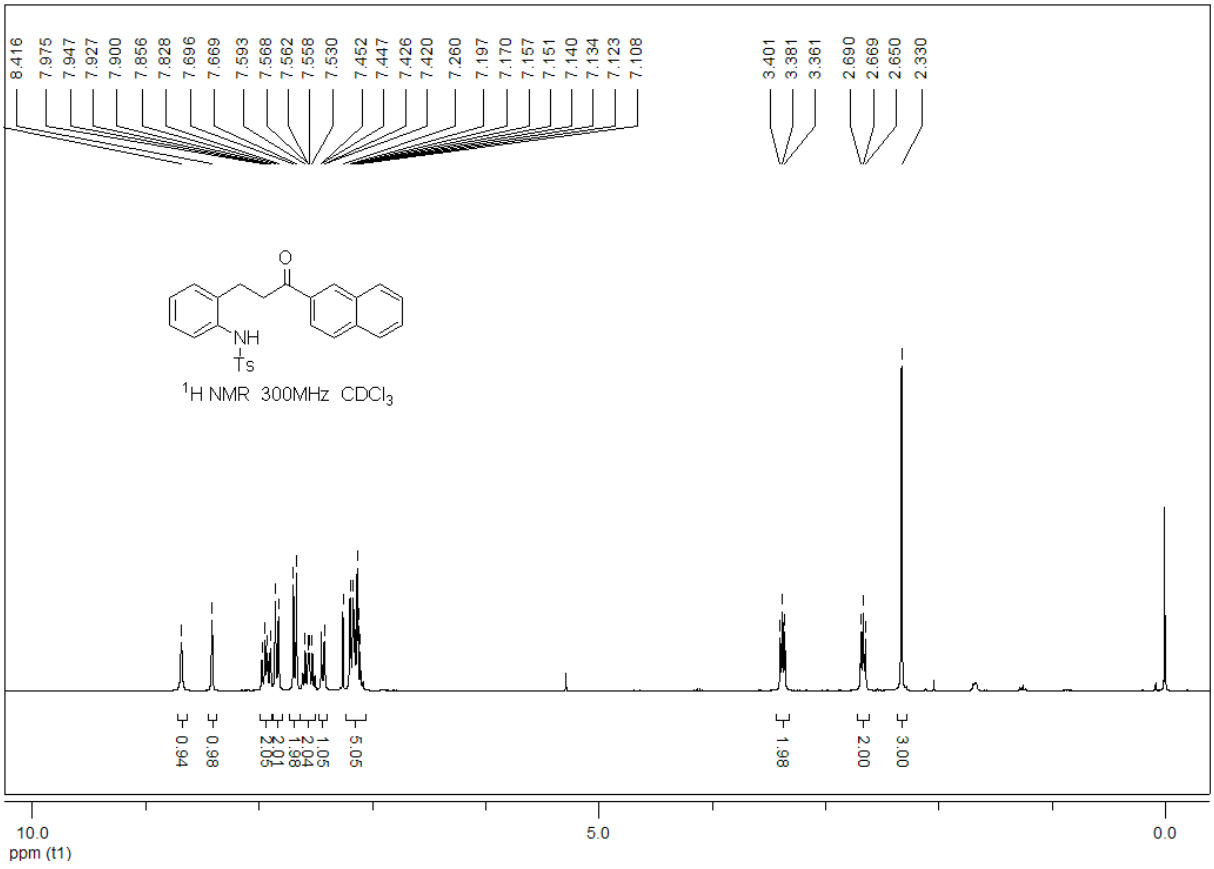

193.034
143.242
143.029
137.296
134.870
134.692
134.340
132.579
130.114
129.466
128.185
127.333
127.058
126.206
125.557
77.317
77.000
76.683
40.644
23.568
21.463
O
S
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

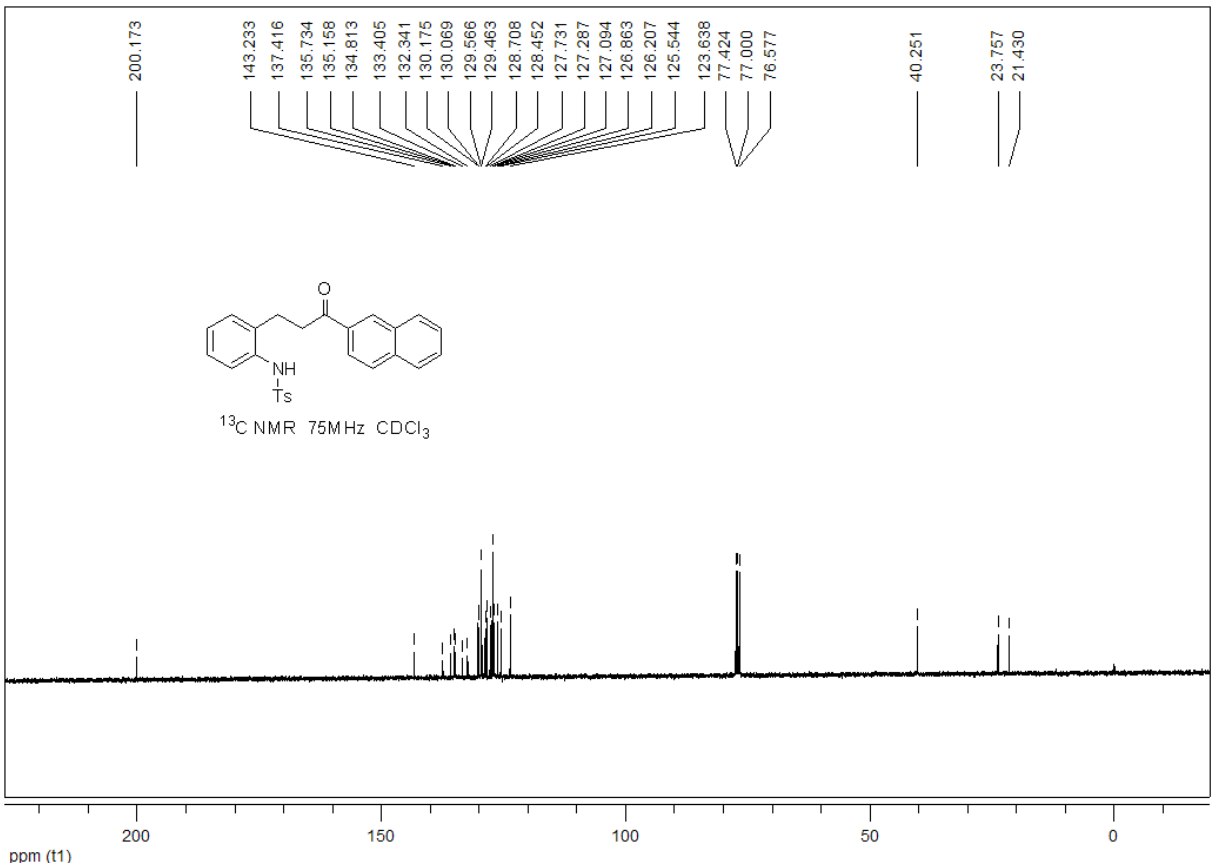
Compound **1f**:


8.781
8.769
8.050
8.039
7.668
7.652
7.631
7.332
7.313
7.260
7.210
7.190
7.160
7.150
7.143
7.122
7.112
3.245
3.230
3.214
2.709
2.693
2.678
2.356
-0.004
O
N
NH
Ts
1H NMR 400MHz CDCl3
2.11
1.00
2.10
2.15
3.13
5.0
0.0
ppm (t1)

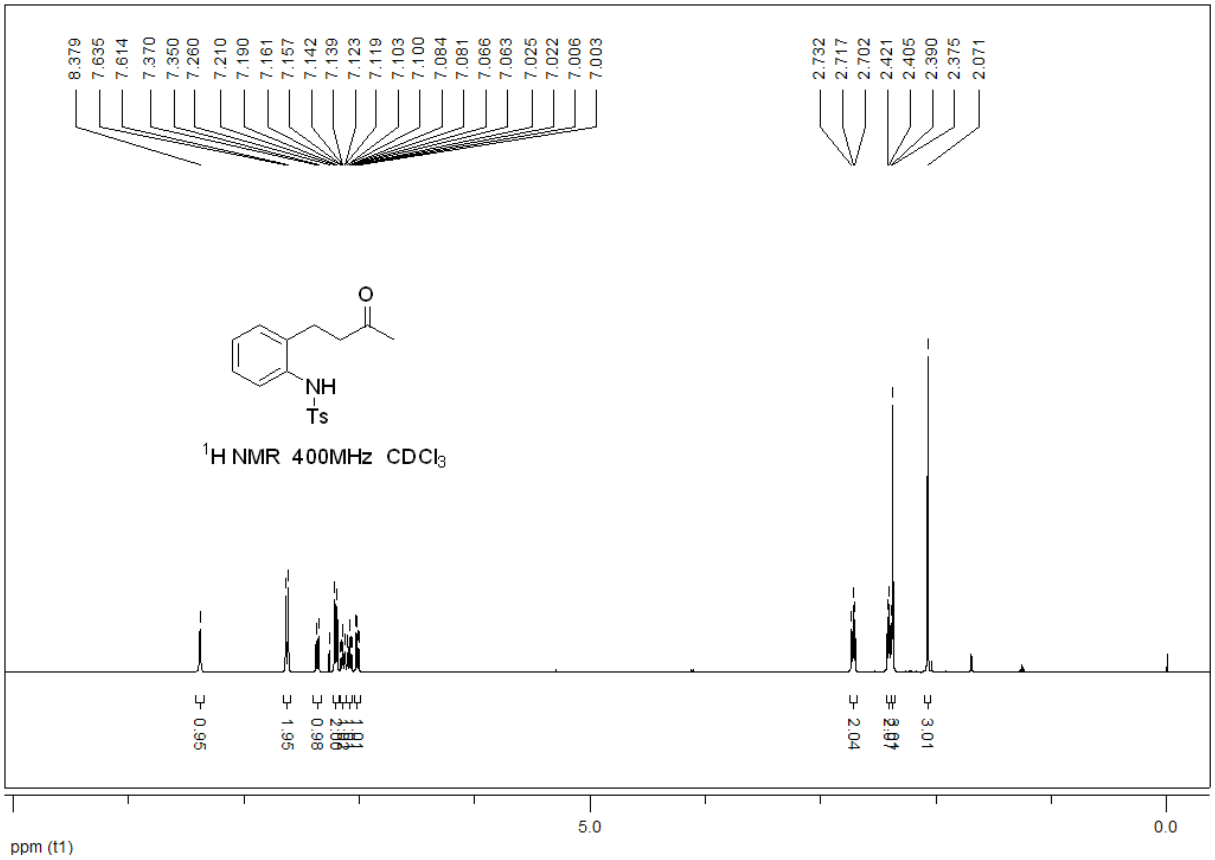

199.691
150.999
143.456
141.877
137.198
135.085
134.531
130.078
129.549
127.488
127.136
126.641
126.027
120.955
77.317
77.000
76.682
40.398
23.535
21.479
O
N
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

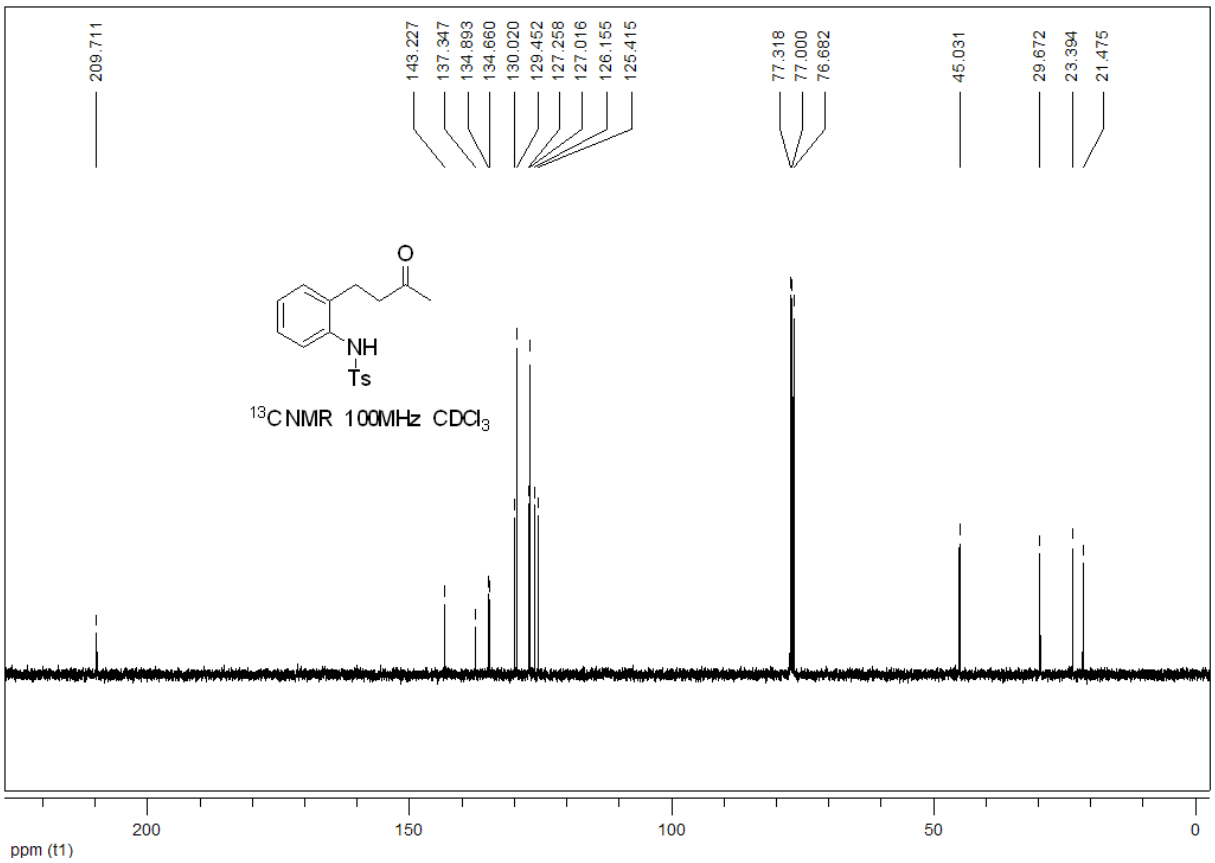
Compound **1g**:


8.416
7.975
7.947
7.927
7.900
7.856
7.828
7.696
7.669
7.593
7.568
7.562
7.558
7.530
7.452
7.447
7.426
7.420
7.260
7.197
7.170
7.157
7.151
7.140
7.134
7.123
7.108
3.401
3.381
3.361
2.690
2.669
2.650
2.330
O
NH
Ts
1H NMR 300MHz CDCl3
0.94
0.98
2.03
2.01
1.98
2.04
1.05
5.05
1.98
2.00
3.00
10.0
5.0
0.0
ppm (t1)

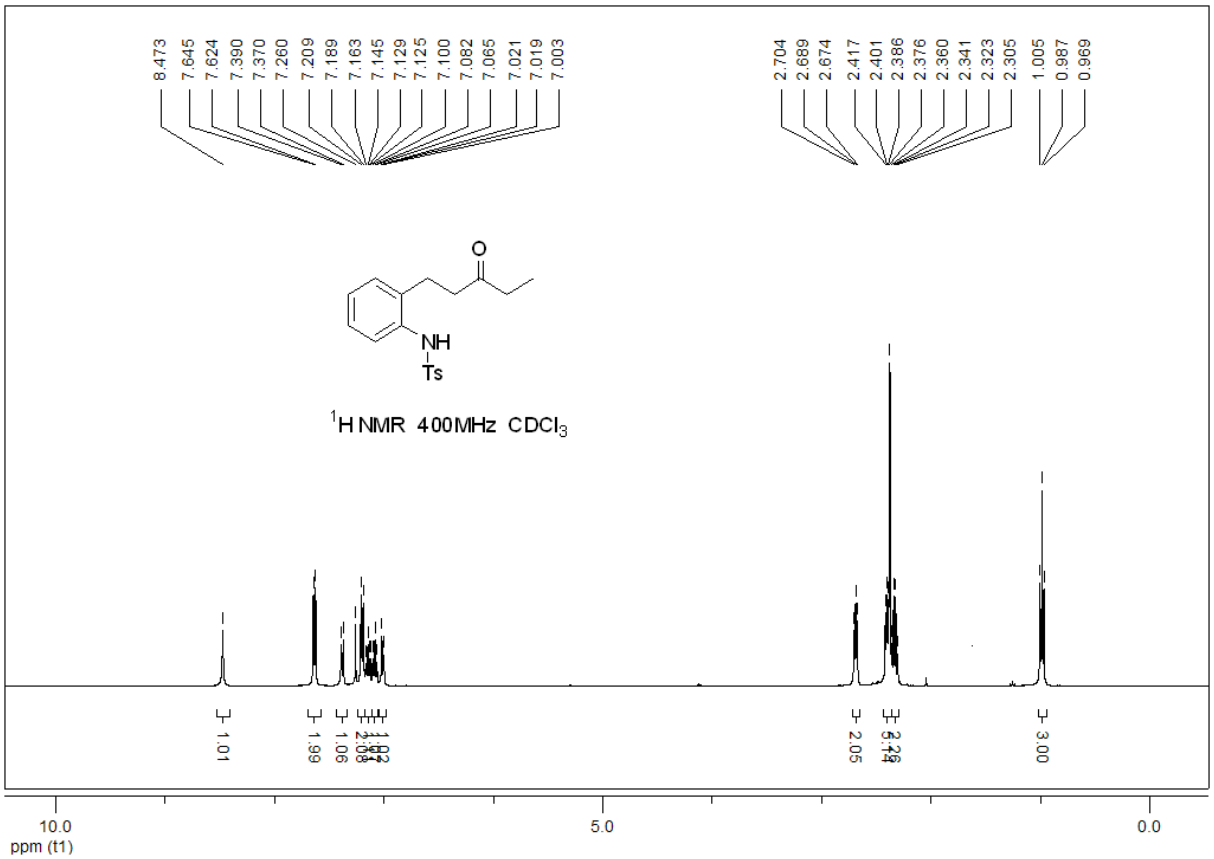

200.173
143.233
137.416
135.734
135.158
134.813
133.405
132.341
130.175
130.069
129.566
129.463
128.708
128.452
127.731
127.287
127.094
126.863
126.207
125.544
123.638
77.424
77.000
76.577
40.251
23.757
21.430
O
NH
Ts
13C NMR 75MHz CDCl3
200
150
100
50
0
ppm (t1)

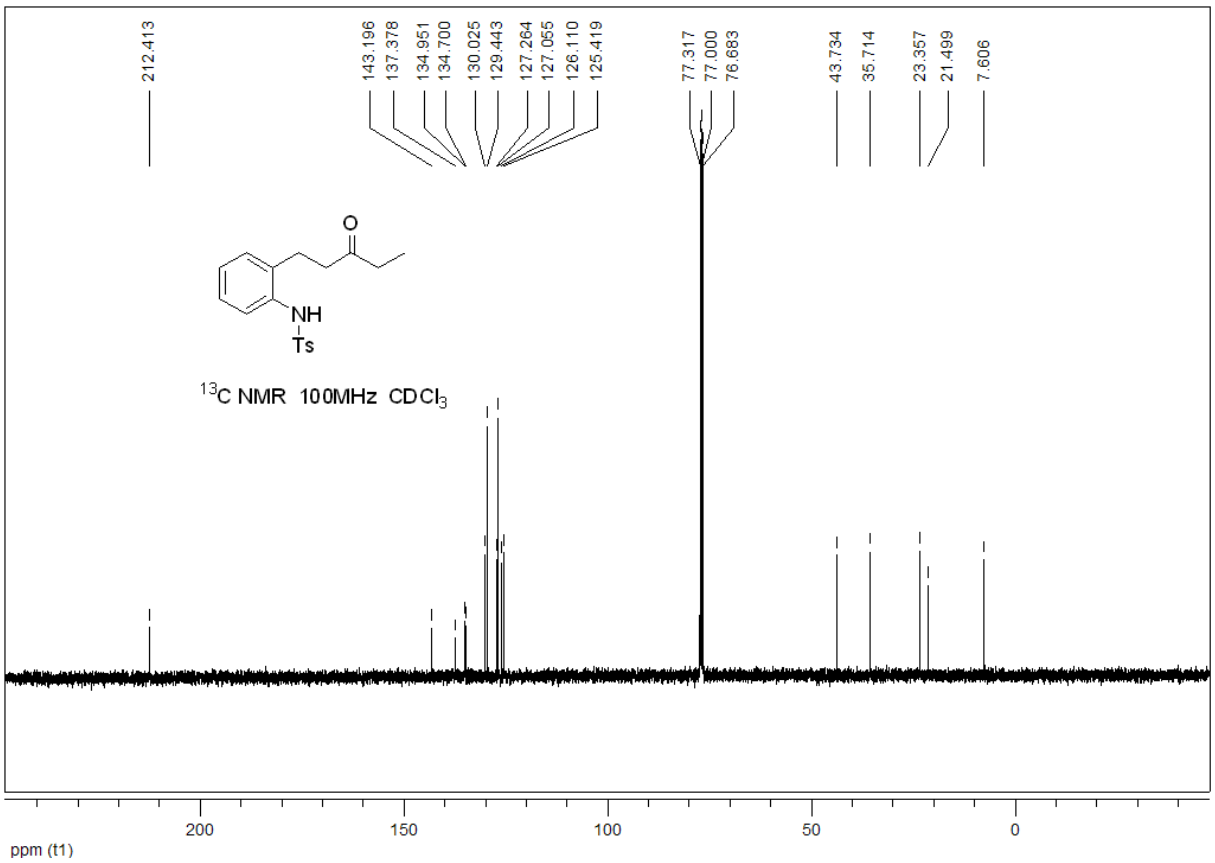
Compound **1h**:


8.379
7.635
7.614
7.370
7.350
7.260
7.210
7.190
7.161
7.157
7.142
7.139
7.123
7.119
7.103
7.100
7.084
7.081
7.066
7.063
7.025
7.022
7.006
7.003
2.732
2.717
2.702
2.421
2.405
2.390
2.375
2.071
O
NH
Ts
1H NMR 400MHz CDCl3
0.95
1.95
0.98
2.04
3.01
5.0
0.0
ppm (t1)

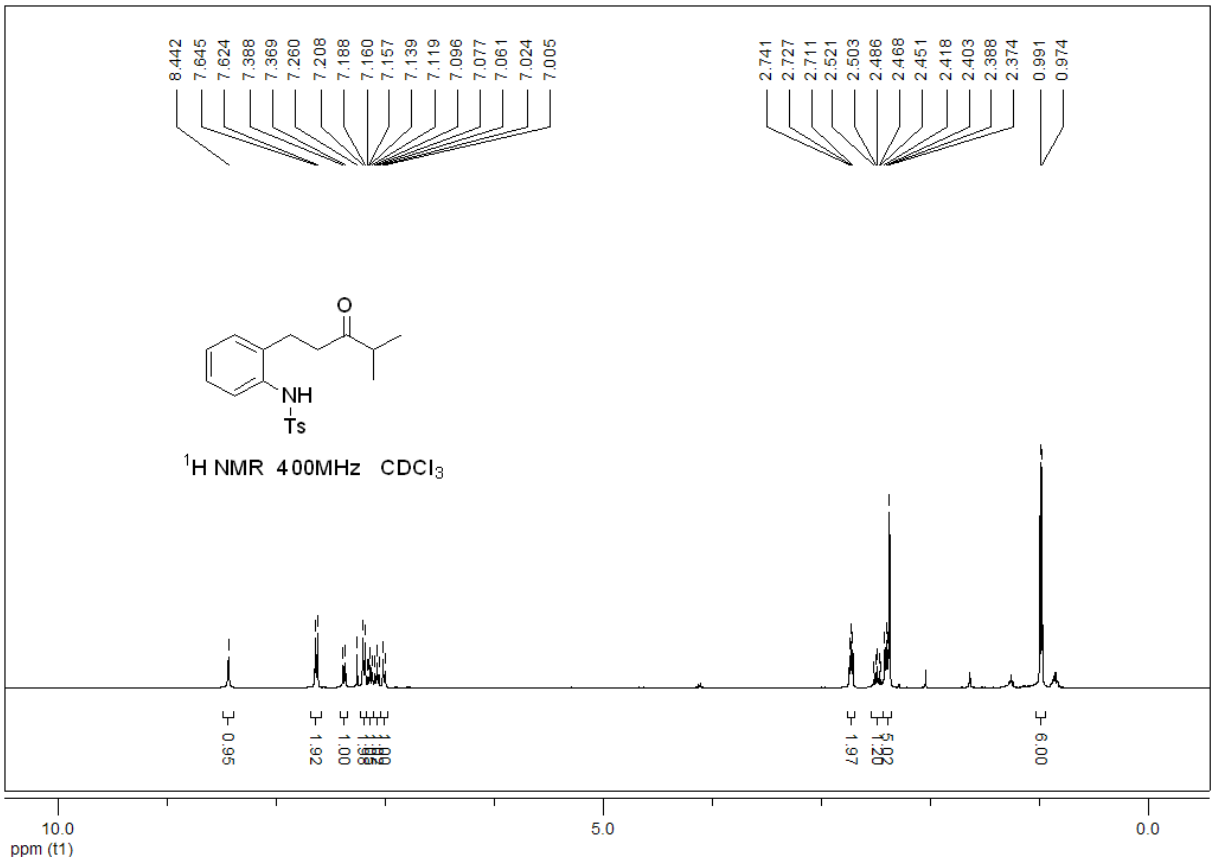

209.711
143.227
137.347
134.893
134.660
130.020
129.452
127.258
127.016
126.155
125.415
77.318
77.000
76.682
45.031
29.672
23.394
21.475
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

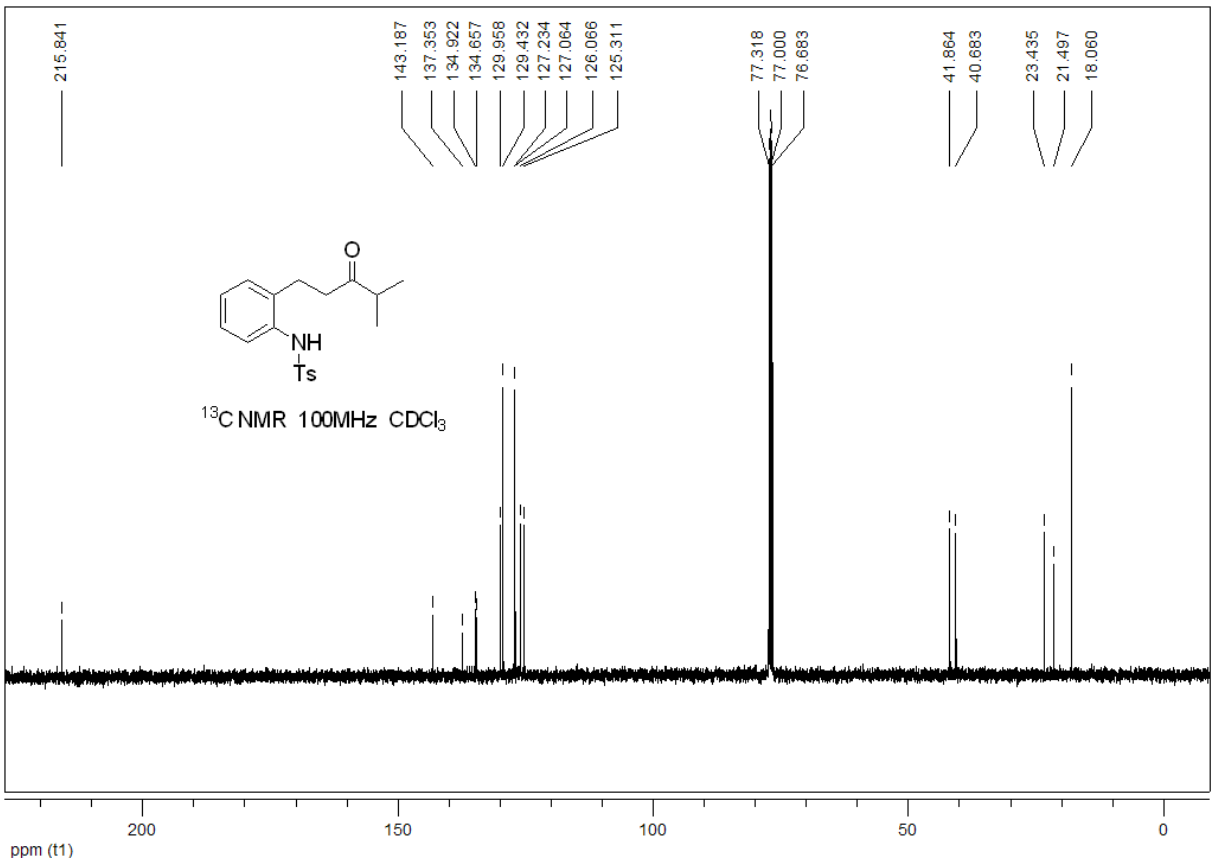
Compound **1i**:


8.473
7.645
7.624
7.390
7.370
7.260
7.209
7.189
7.163
7.145
7.129
7.125
7.100
7.082
7.065
7.021
7.019
7.003
2.704
2.689
2.674
2.417
2.401
2.386
2.376
2.360
2.341
2.323
2.305
1.005
0.987
0.969
O
NH
Ts
1H NMR 400MHz CDCl3
1.01
1.99
1.06
2.06
3.00
10.0
5.0
0.0
ppm (t1)

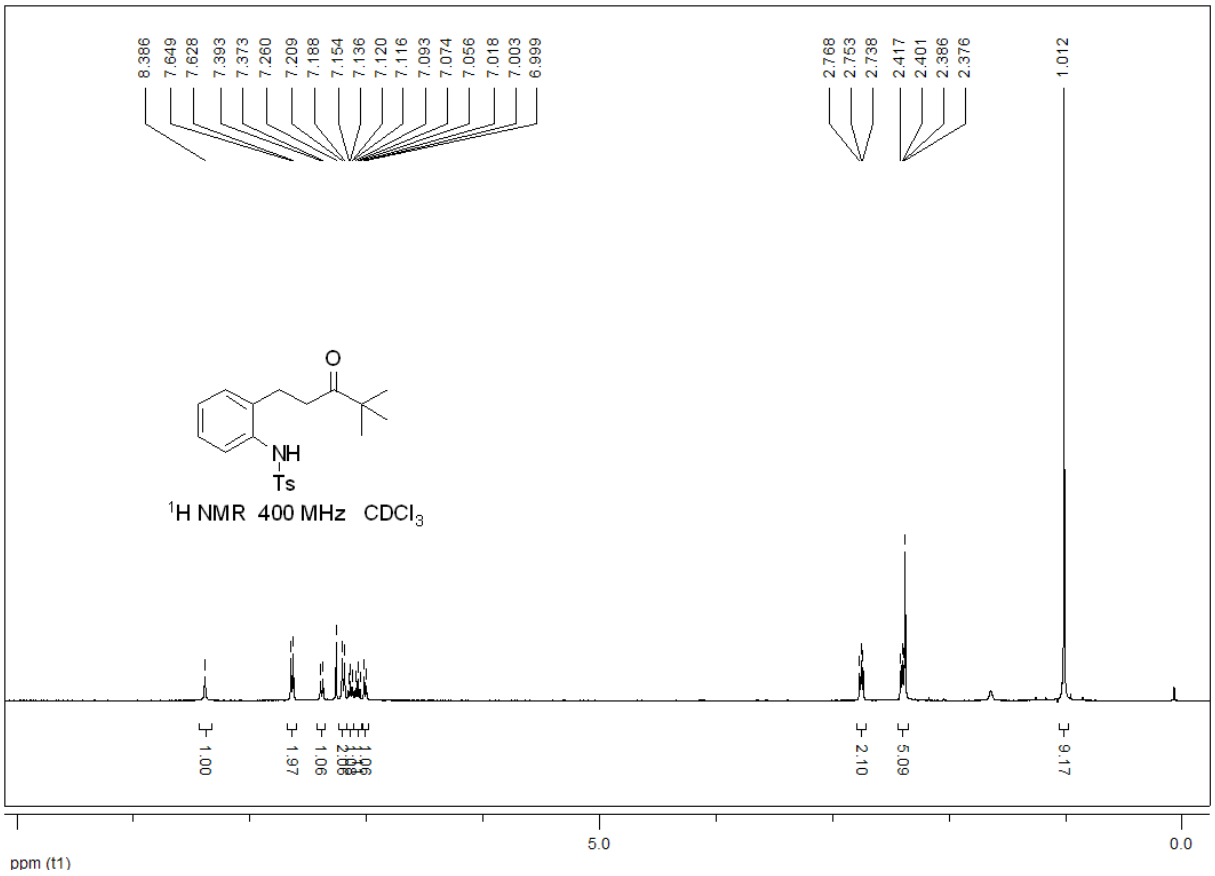

212.413
143.196
137.378
134.951
134.700
130.025
129.443
127.264
127.055
126.110
125.419
77.317
77.000
76.683
43.734
35.714
23.357
21.499
7.606
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

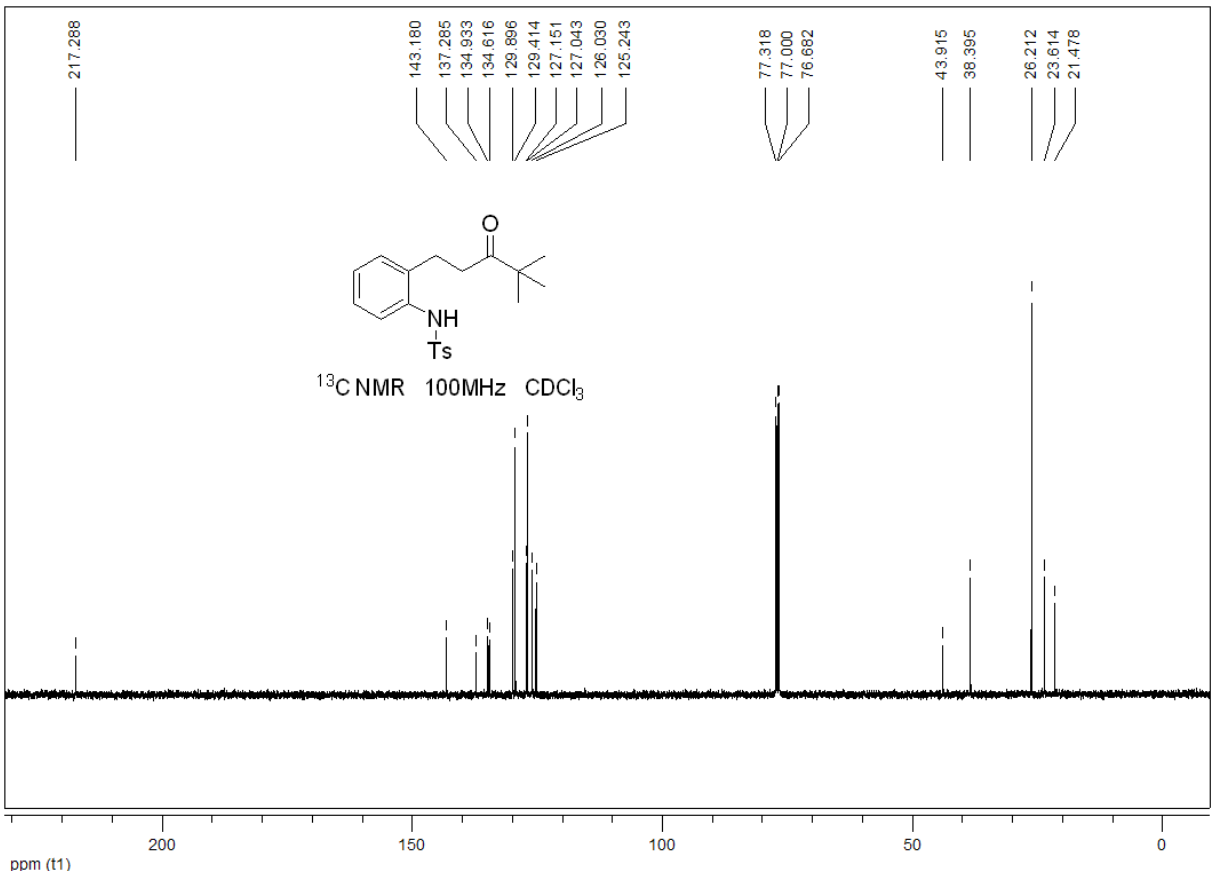
Compound **1j**:


8.442
7.645
7.624
7.388
7.369
7.260
7.208
7.188
7.160
7.157
7.139
7.119
7.096
7.077
7.061
7.024
7.005
2.741
2.727
2.711
2.521
2.503
2.486
2.468
2.451
2.418
2.403
2.388
2.374
0.991
0.974
O
NH
Ts
1H NMR 400MHz CDCl3
0.95
1.92
1.00
1.97
6.00
10.0
5.0
0.0
ppm (t1)

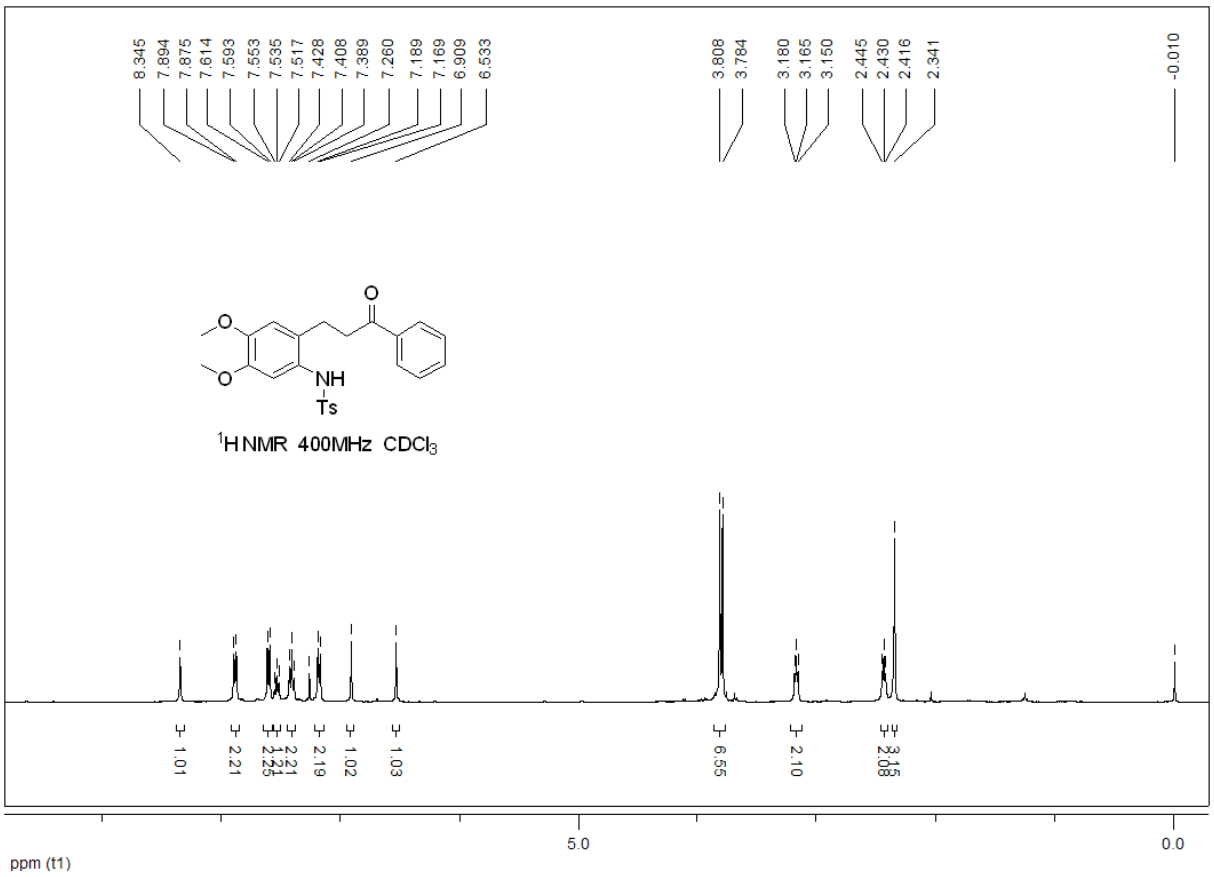

215.841
143.187
137.353
134.922
134.657
129.958
129.432
127.234
127.064
126.066
125.311
77.318
77.000
76.683
41.864
40.683
23.435
21.497
18.060
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

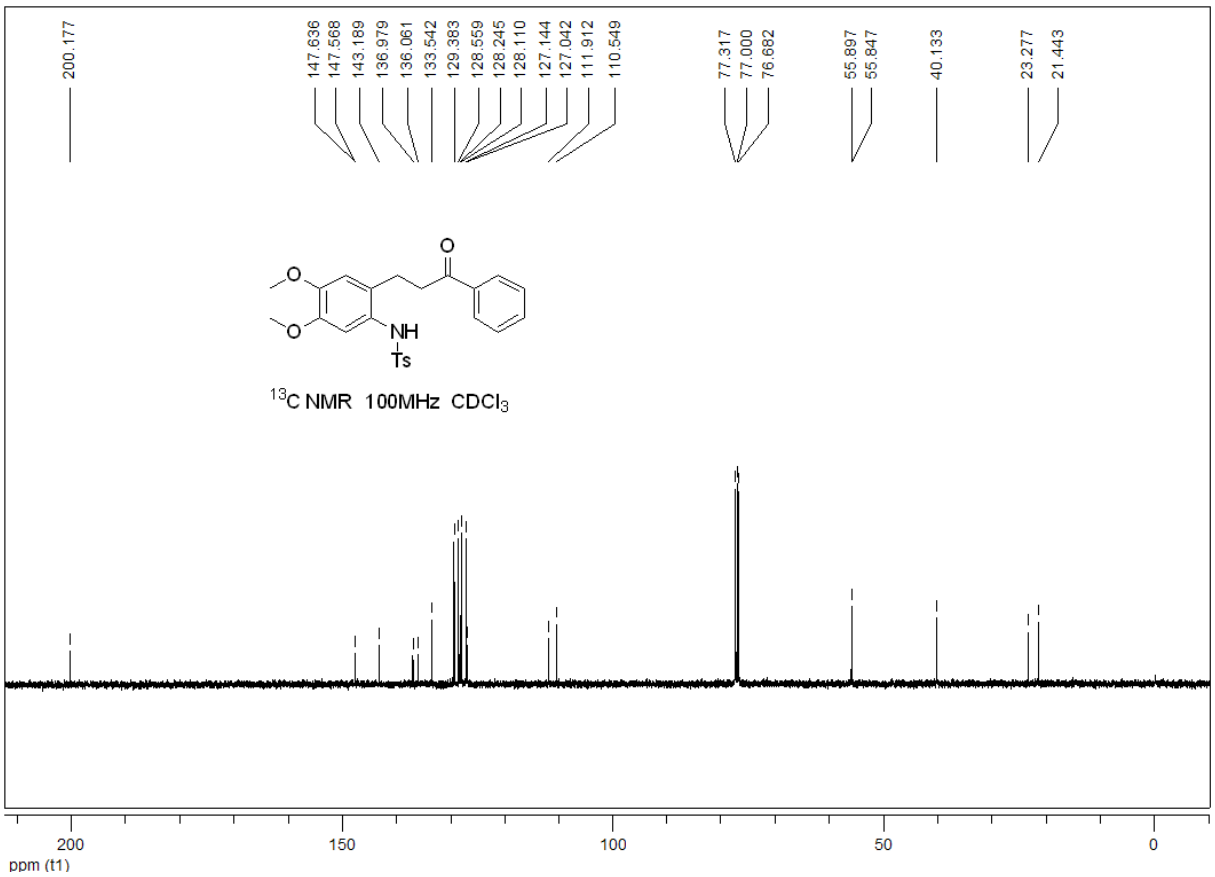
Compound **1k**:


8.386
7.649
7.628
7.393
7.373
7.260
7.209
7.188
7.154
7.136
7.120
7.116
7.093
7.074
7.056
7.018
7.003
6.999
2.768
2.753
2.738
2.417
2.401
2.386
2.376
1.012
O
NH
Ts
1H NMR 400 MHz CDCl3
1.00
1.97
1.06
2.10
5.09
9.17
5.0
0.0
ppm (t1)

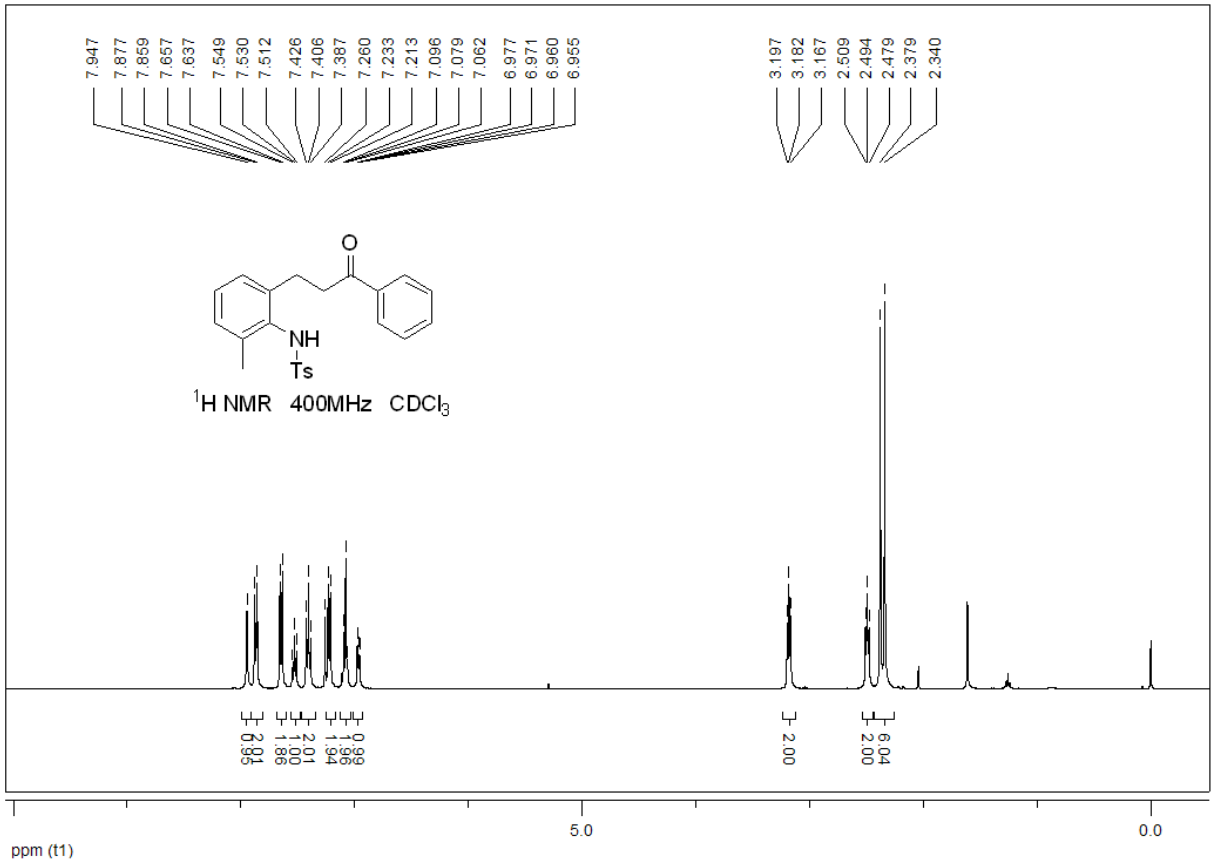

217.288
143.180
137.285
134.933
134.616
129.896
129.414
127.151
127.043
126.030
125.243
77.318
77.000
76.682
43.915
38.395
26.212
23.614
21.478
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

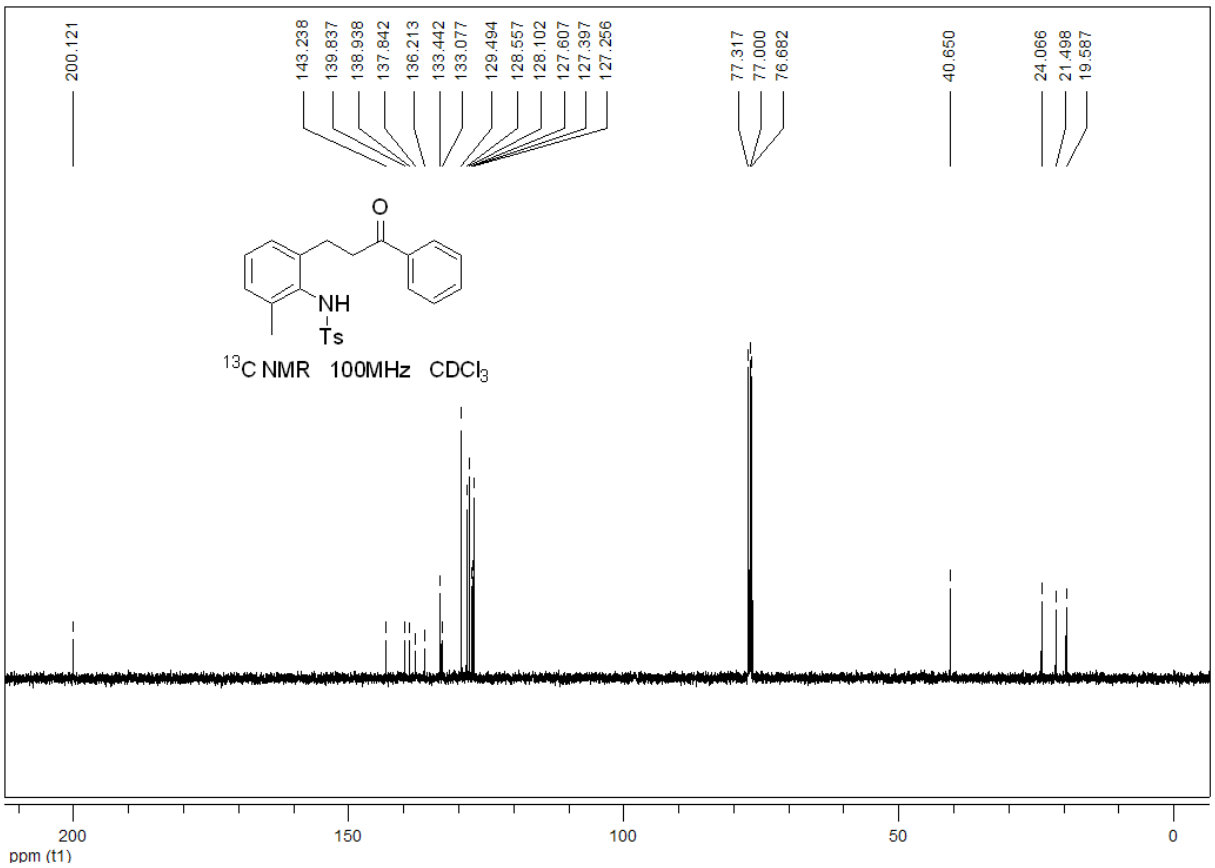
Compound **1l**:


8.345
7.894
7.875
7.614
7.593
7.553
7.535
7.517
7.428
7.408
7.389
7.260
7.189
7.169
6.909
6.533
3.808
3.784
3.180
3.165
3.150
2.445
2.430
2.416
2.341
-0.010
O
O
O
NH
Ts
1H NMR 400MHz CDCl3
1.01
2.21
1.25
2.21
2.19
1.02
1.03
6.55
2.10
3.15
3.08
5.0
0.0
ppm (t1)

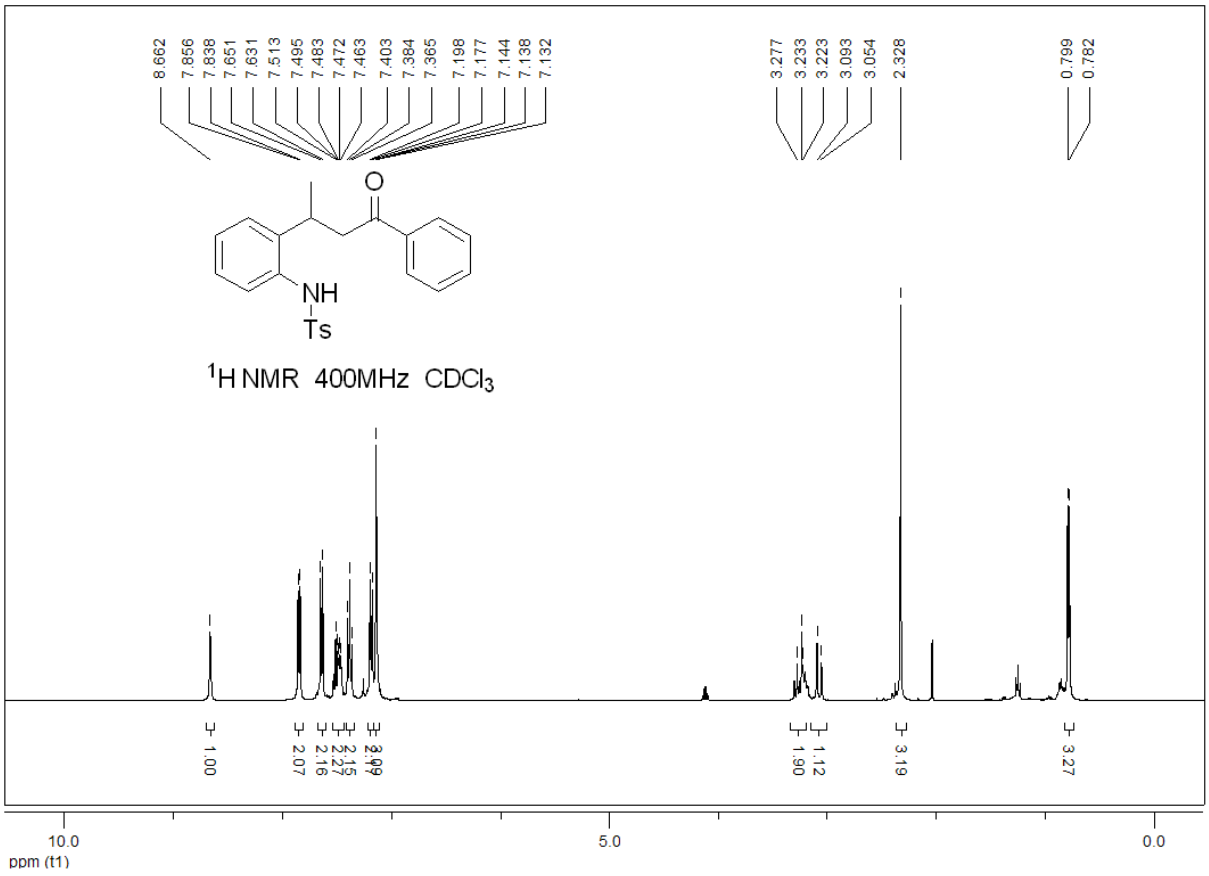

200.177
147.636
147.568
143.189
136.979
136.061
133.542
129.383
128.559
128.245
128.110
127.144
127.042
111.912
110.549
77.317
77.000
76.682
55.897
55.847
40.133
23.277
21.443
O
O
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

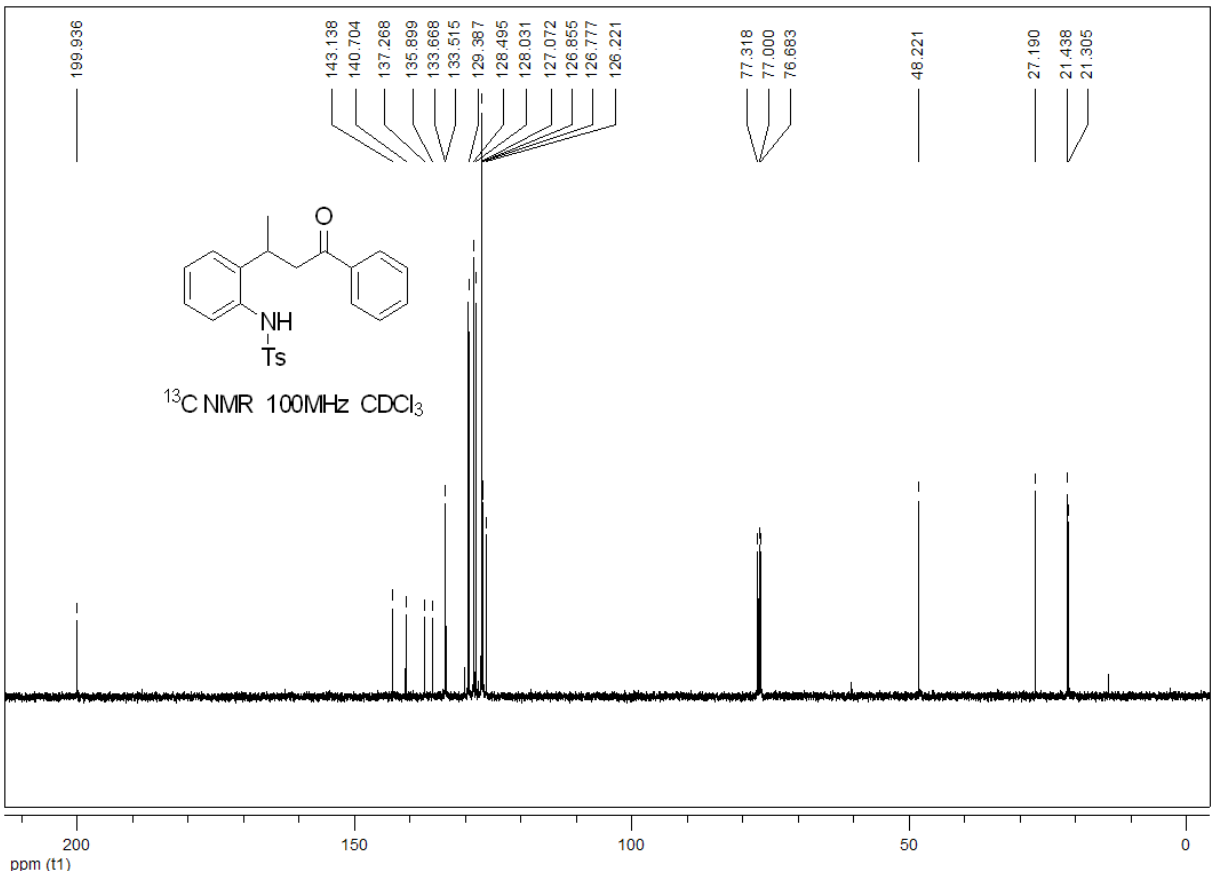
Compound **1m**:


7.947
7.877
7.859
7.657
7.637
7.549
7.530
7.512
7.426
7.406
7.387
7.260
7.233
7.213
7.096
7.079
7.062
6.977
6.971
6.960
6.955
3.197
3.182
3.167
2.509
2.494
2.479
2.379
2.340
O
NH
Ts
1H NMR 400MHz CDCl3
0.95
2.01
1.86
2.01
1.00
1.94
1.96
0.99
2.00
6.04
5.0
0.0
ppm (t1)

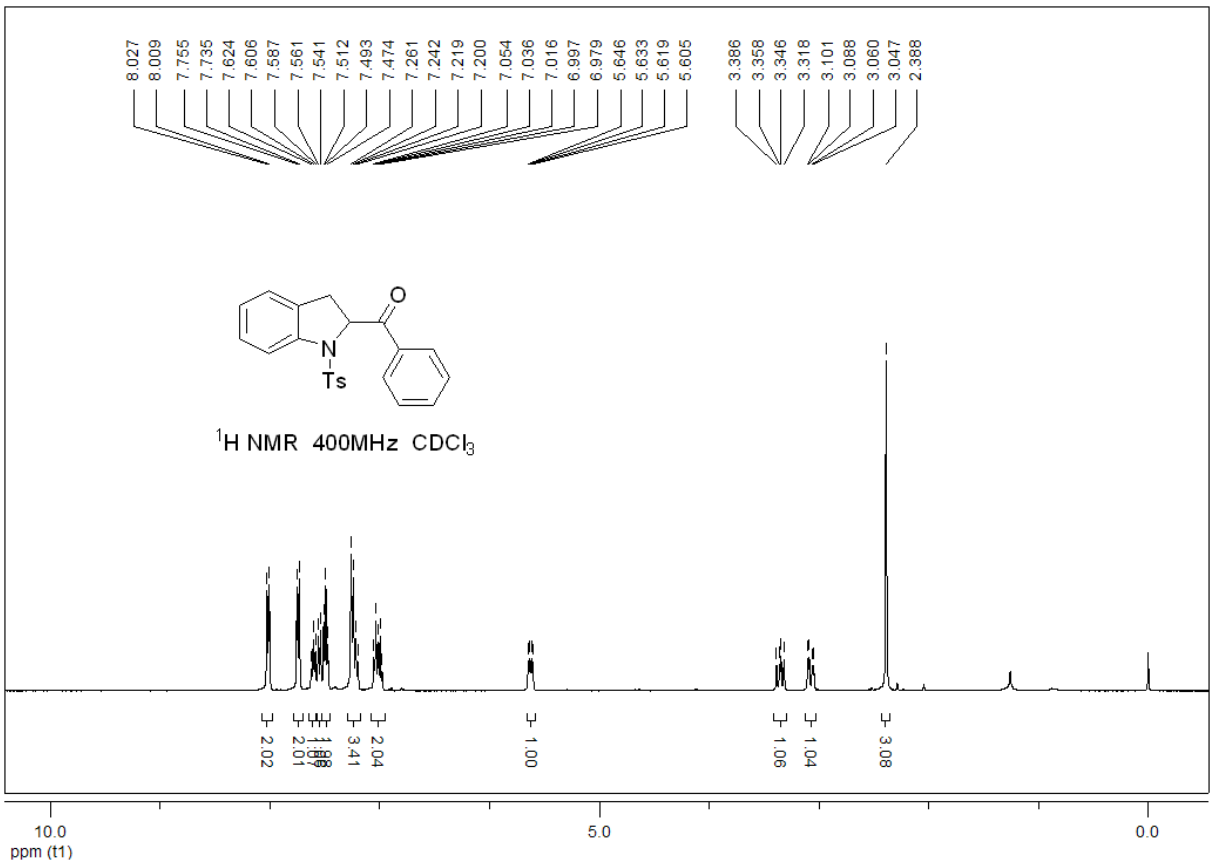

200.121
143.238
139.837
138.938
137.842
136.213
133.442
133.077
129.494
128.557
128.102
127.607
127.397
127.256
77.317
77.000
76.682
40.650
24.066
21.498
19.587
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

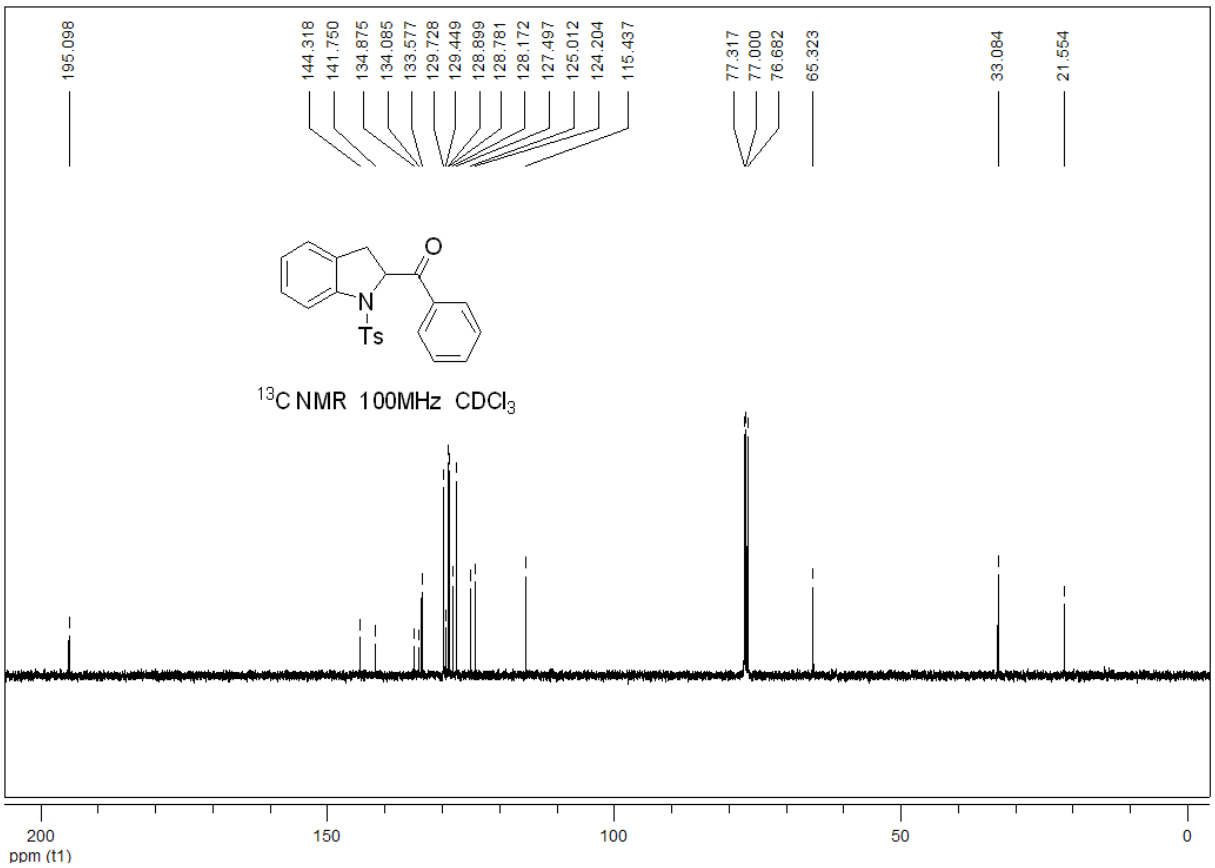
Compound **1n**:


8.662
7.856
7.838
7.651
7.631
7.513
7.495
7.483
7.472
7.463
7.403
7.384
7.365
7.198
7.177
7.144
7.138
7.132
3.277
3.233
3.223
3.093
3.054
2.328
0.799
0.782
O
NH
Ts
1H NMR 400MHz CDCl3
1.00
2.07
2.16
2.15
2.27
8.09
1.90
1.12
3.19
3.27
10.0
5.0
0.0
ppm (t1)

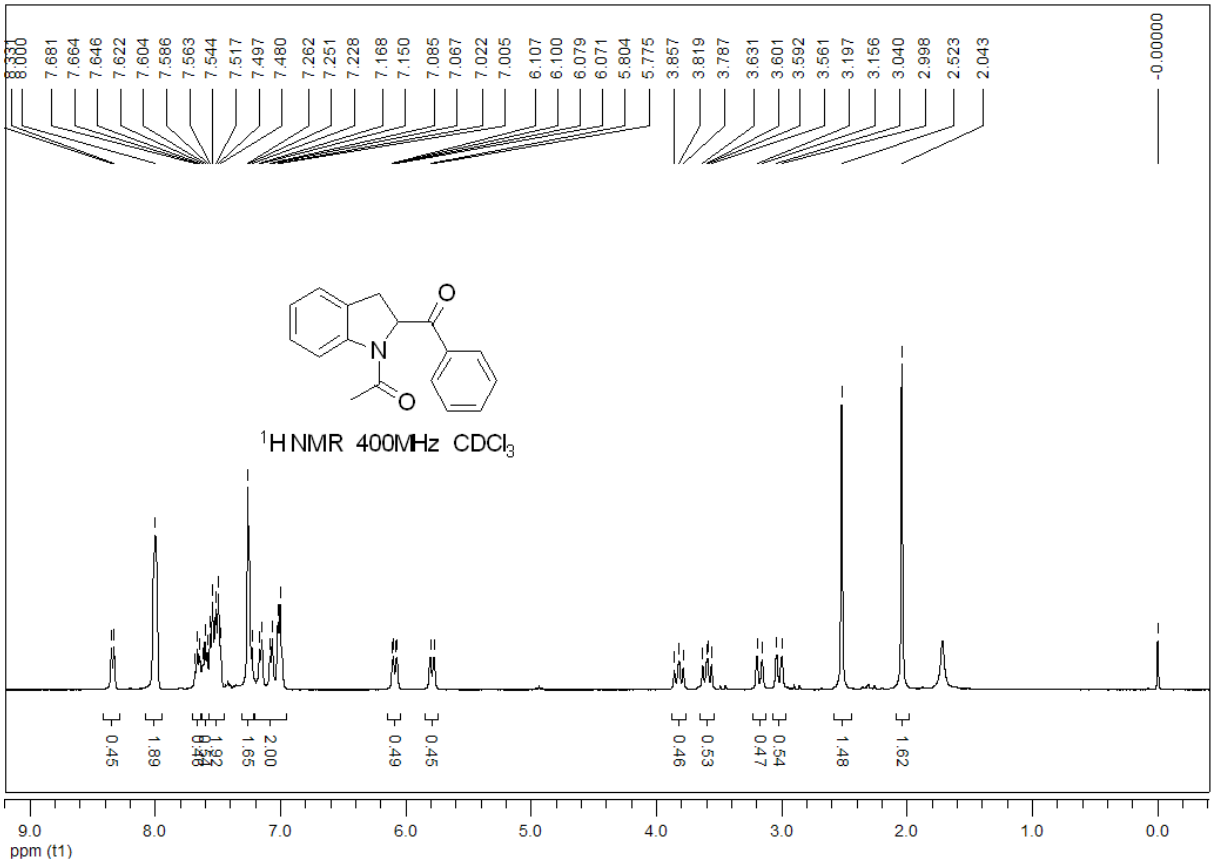

199.936
143.138
140.704
137.268
135.899
133.668
133.515
129.387
128.495
128.031
127.072
126.855
126.777
126.221
77.318
77.000
76.683
48.221
27.190
21.438
21.305
O
NH
Ts
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

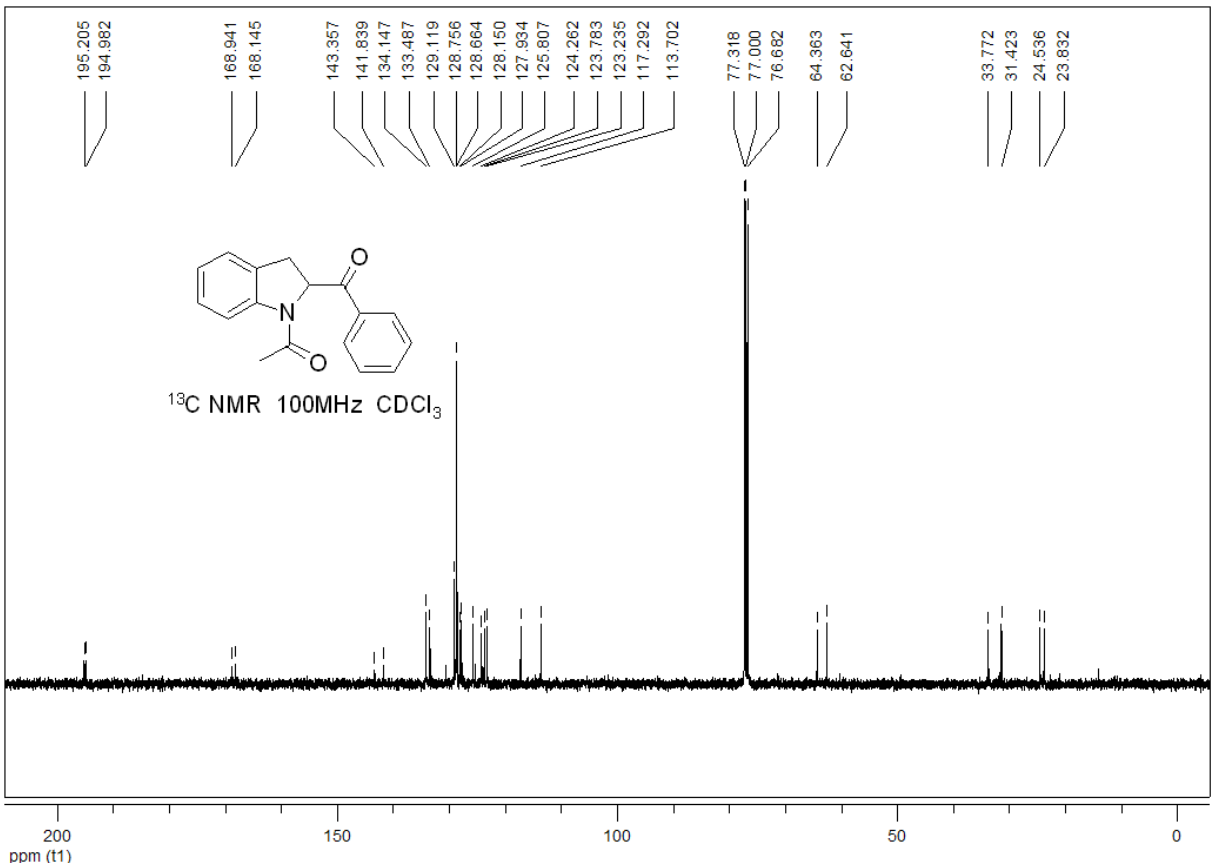
Compound **6**:


8.027
8.009
7.755
7.735
7.624
7.606
7.587
7.561
7.541
7.512
7.493
7.474
7.261
7.242
7.219
7.200
7.054
7.036
7.016
6.997
6.979
5.646
5.633
5.619
5.605
3.386
3.358
3.346
3.318
3.101
3.088
3.060
3.047
2.388
O
N
Ts
1H NMR 400MHz CDCl3
2.02
2.01
1.00
1.06
1.04
3.08
10.0
5.0
0.0
ppm (t1)

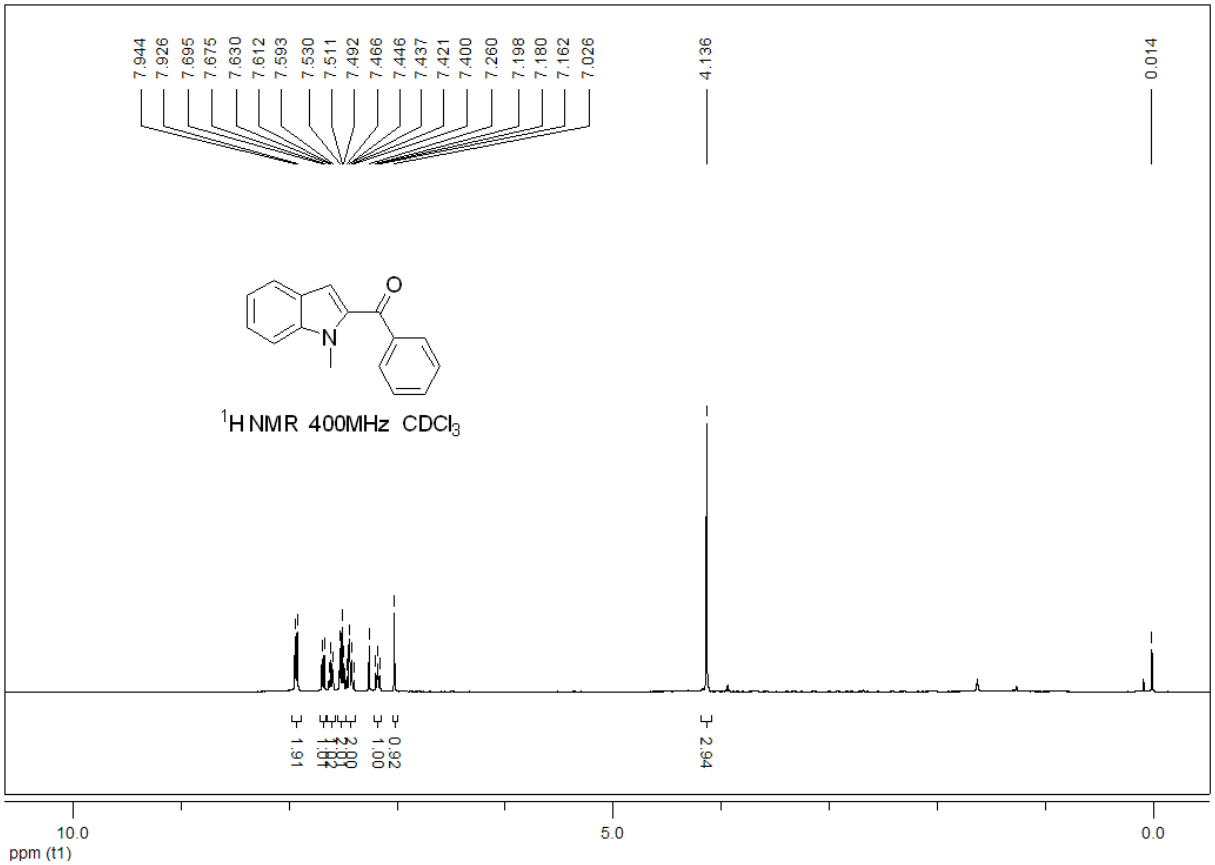


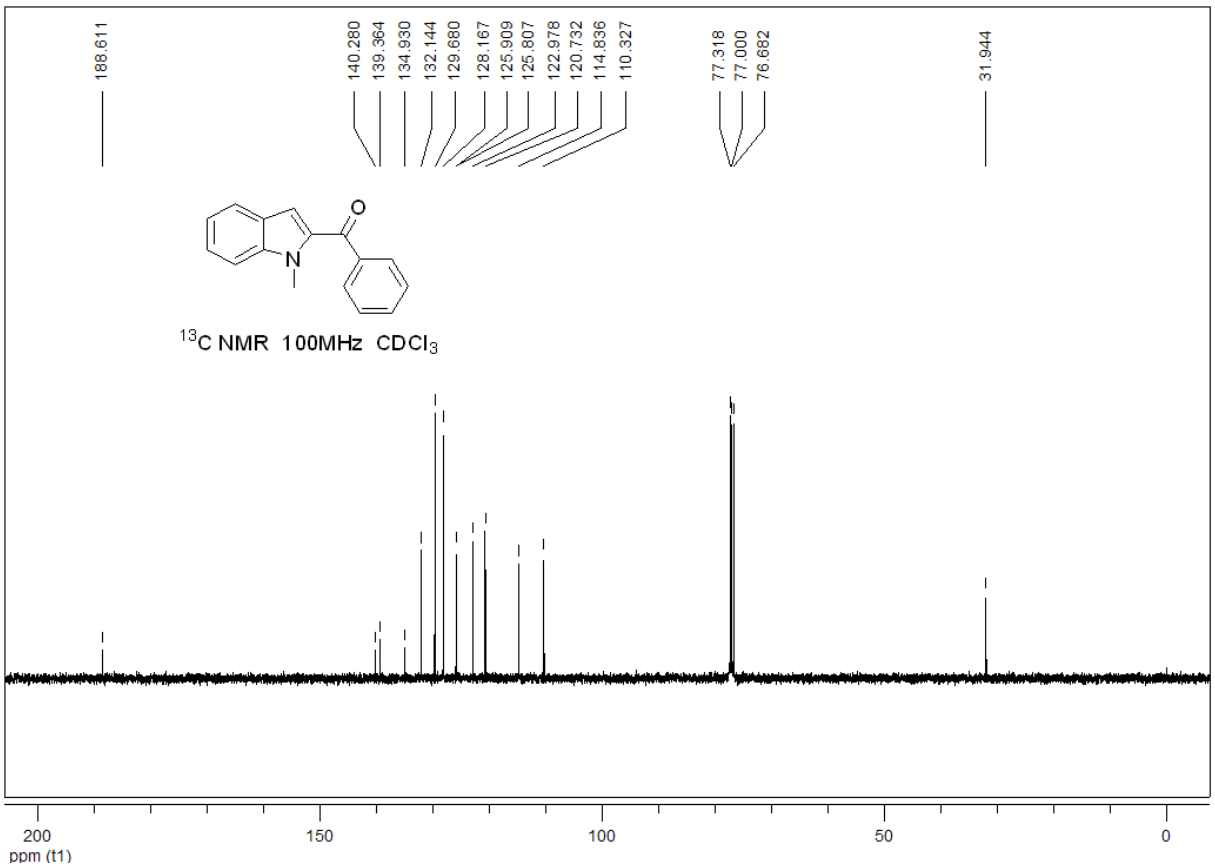
1-(2-benzoylindolin-1-yl)ethanone:



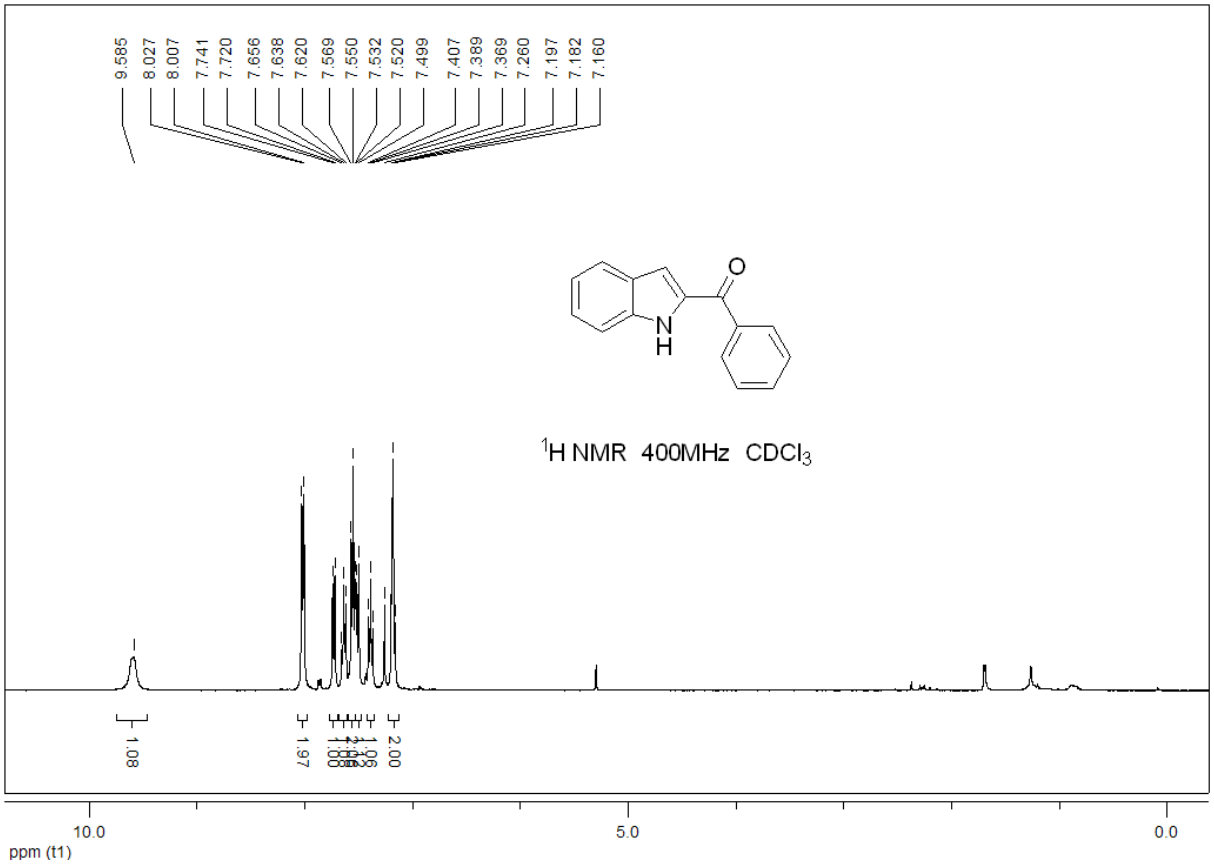


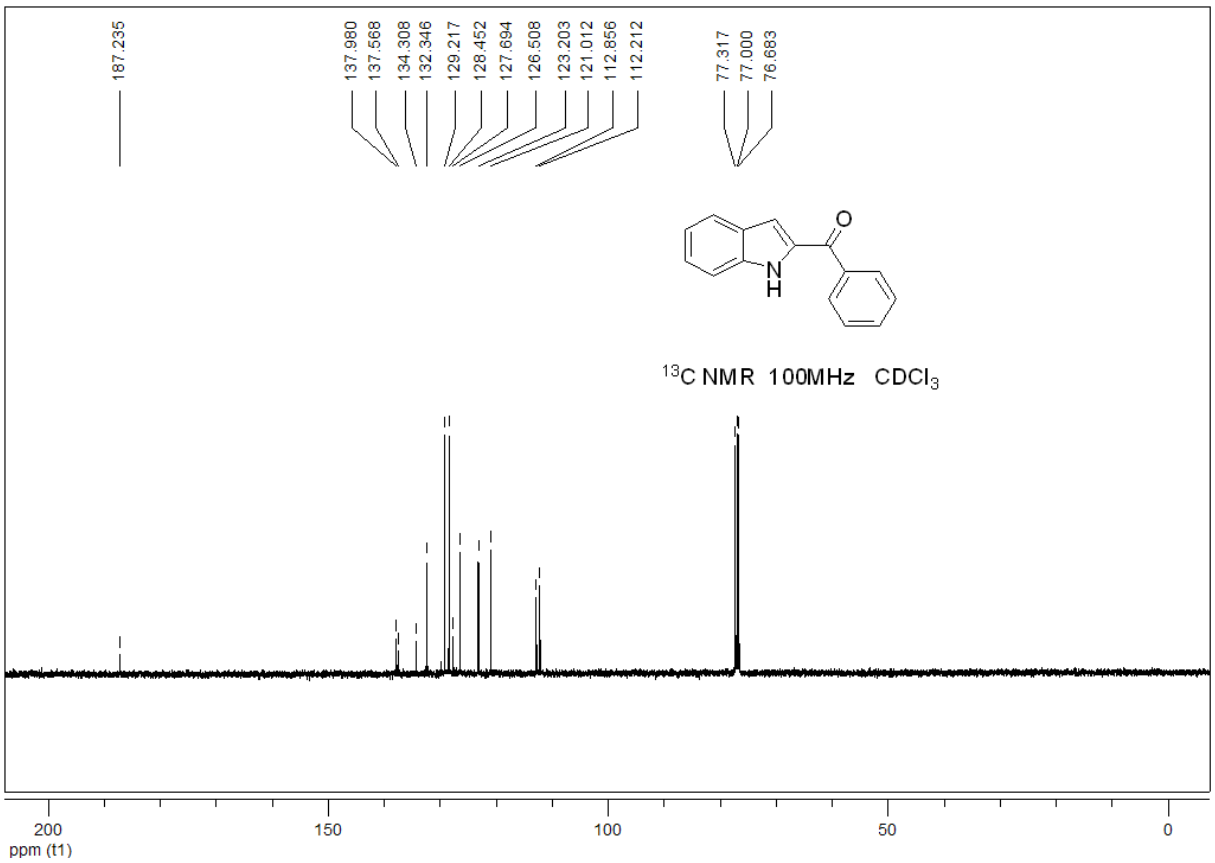
Compound **S11**:



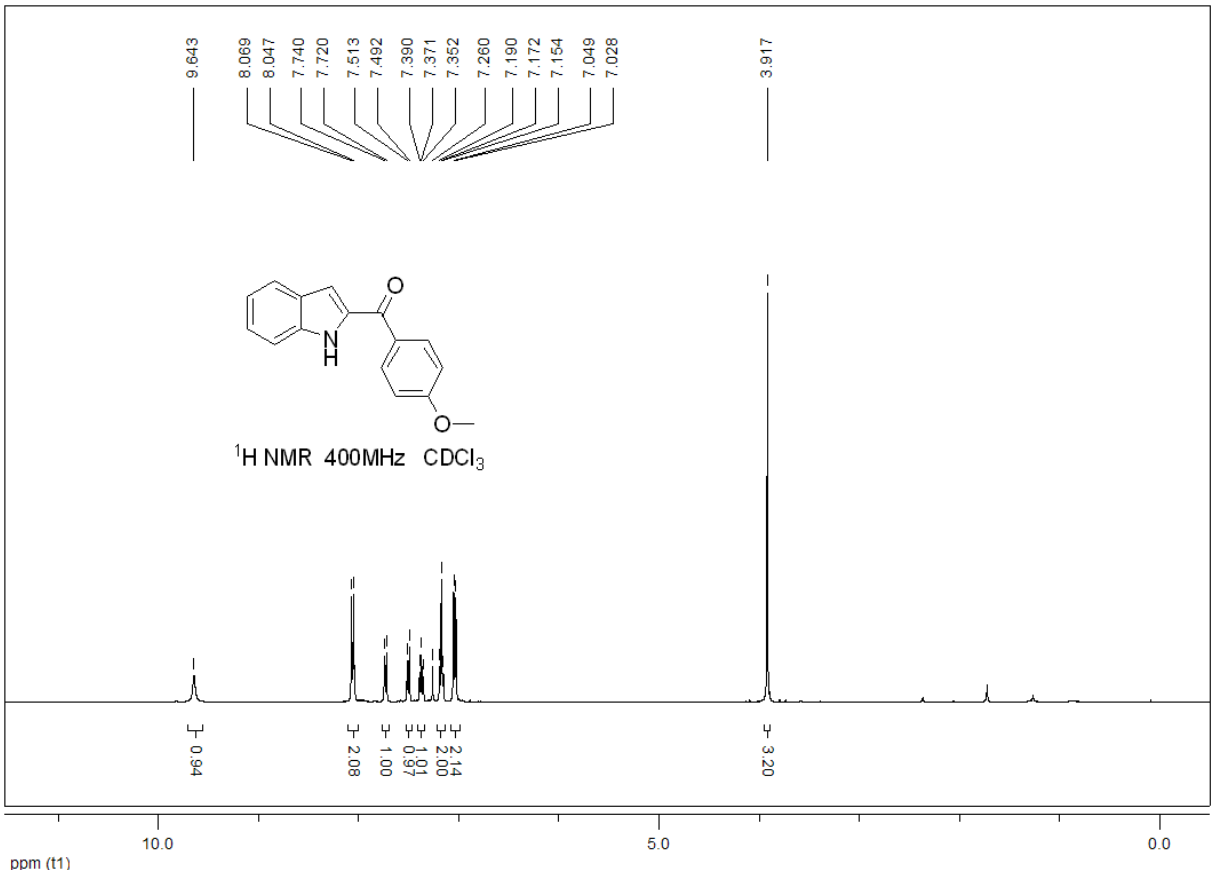

188.611
140.280
139.364
134.930
132.144
129.680
128.167
125.909
125.807
122.978
120.732
114.836
110.327
77.318
77.000
76.682
31.944
O
N
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

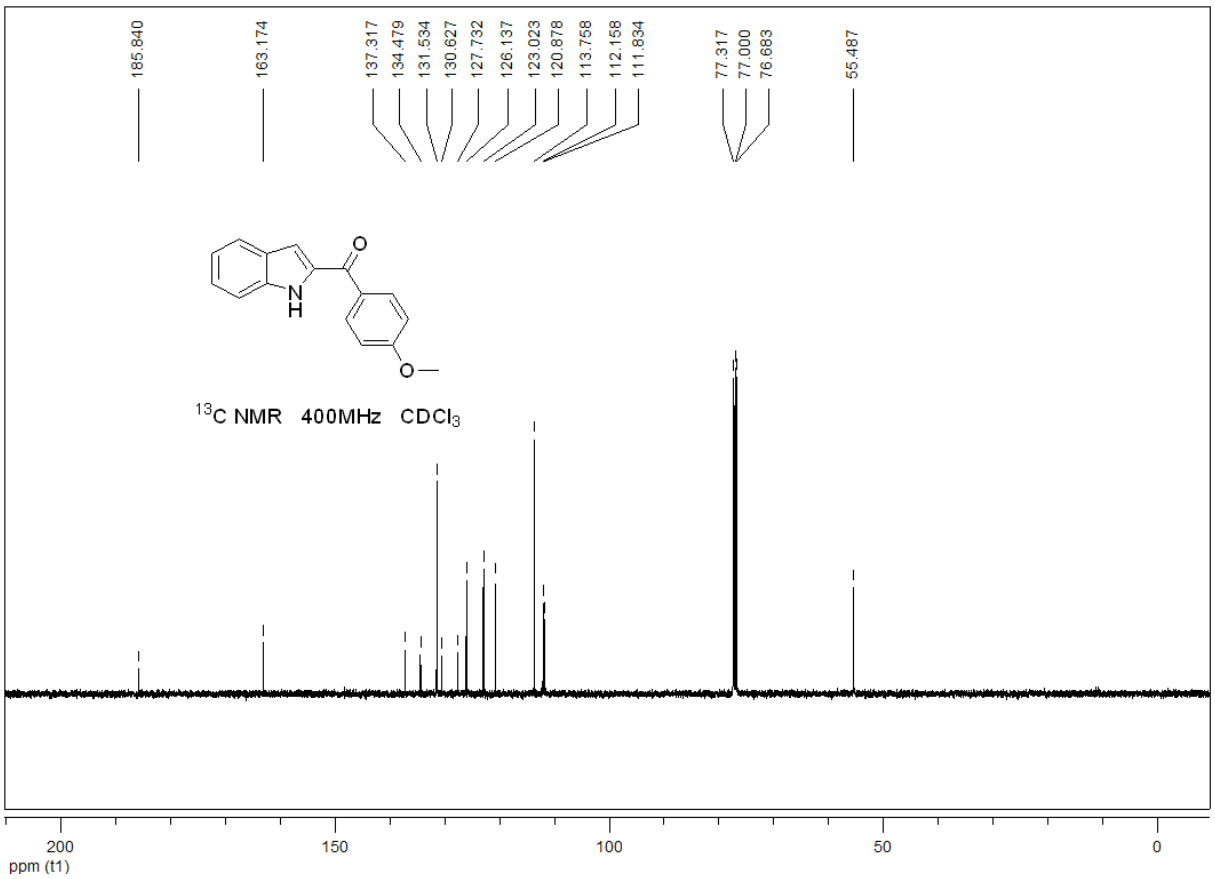
Compound **2a**:


9.585
8.027
8.007
7.741
7.720
7.656
7.638
7.620
7.569
7.550
7.532
7.520
7.499
7.407
7.389
7.369
7.260
7.197
7.182
7.160
O
N
H
1H NMR 400MHz CDCl3
1.08
1.97
2.00
10.0
5.0
0.0
ppm (t1)

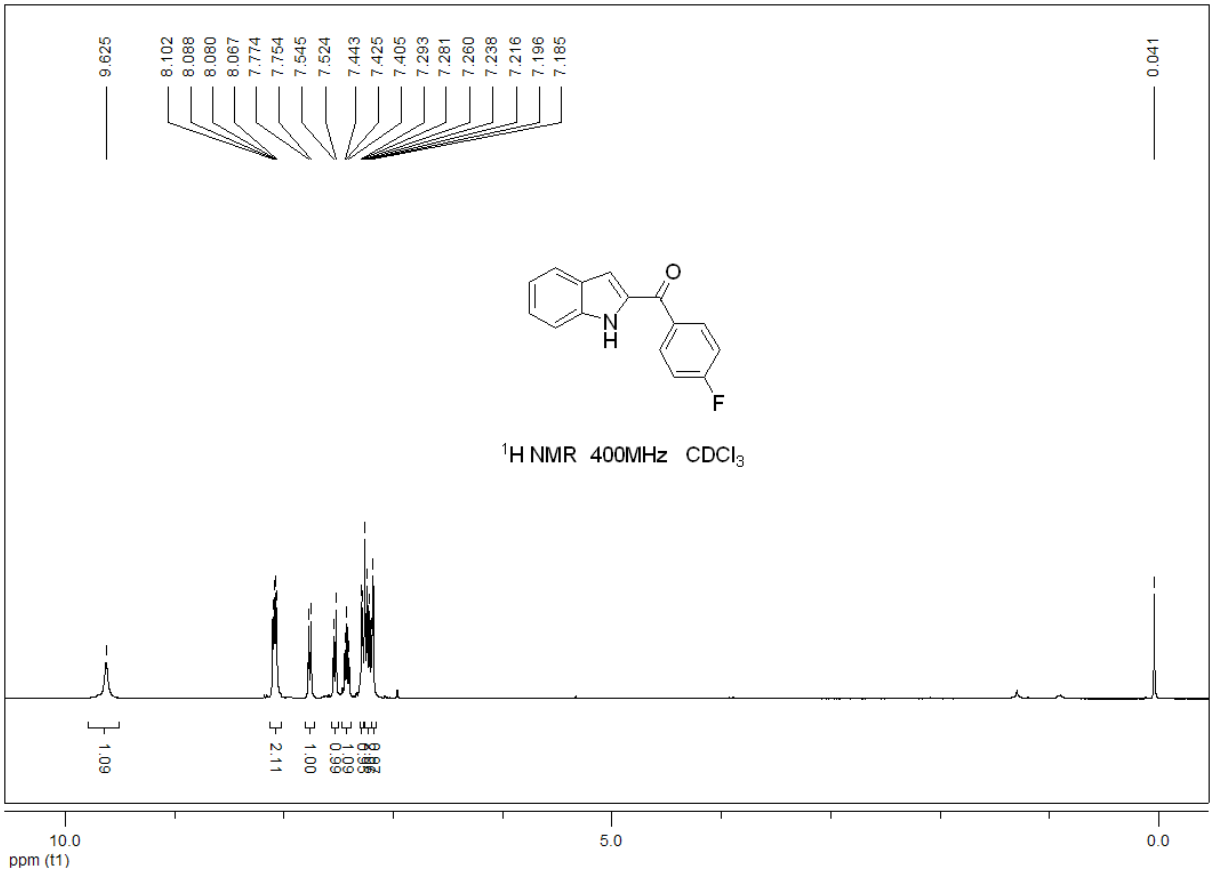

187.235
137.980
137.568
134.308
132.346
129.217
128.452
127.694
126.508
123.203
121.012
112.856
112.212
77.317
77.000
76.683
O
N
H
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

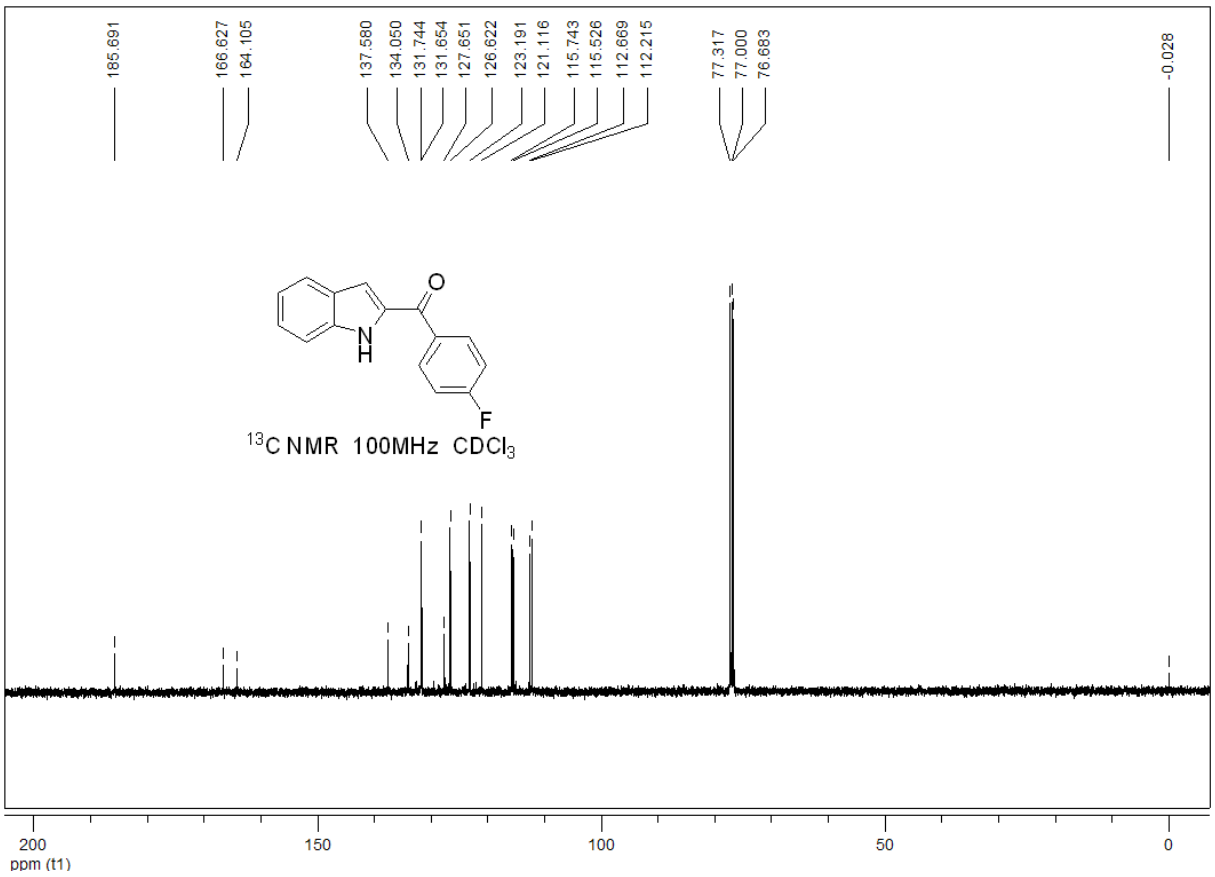
Compound **2b**:

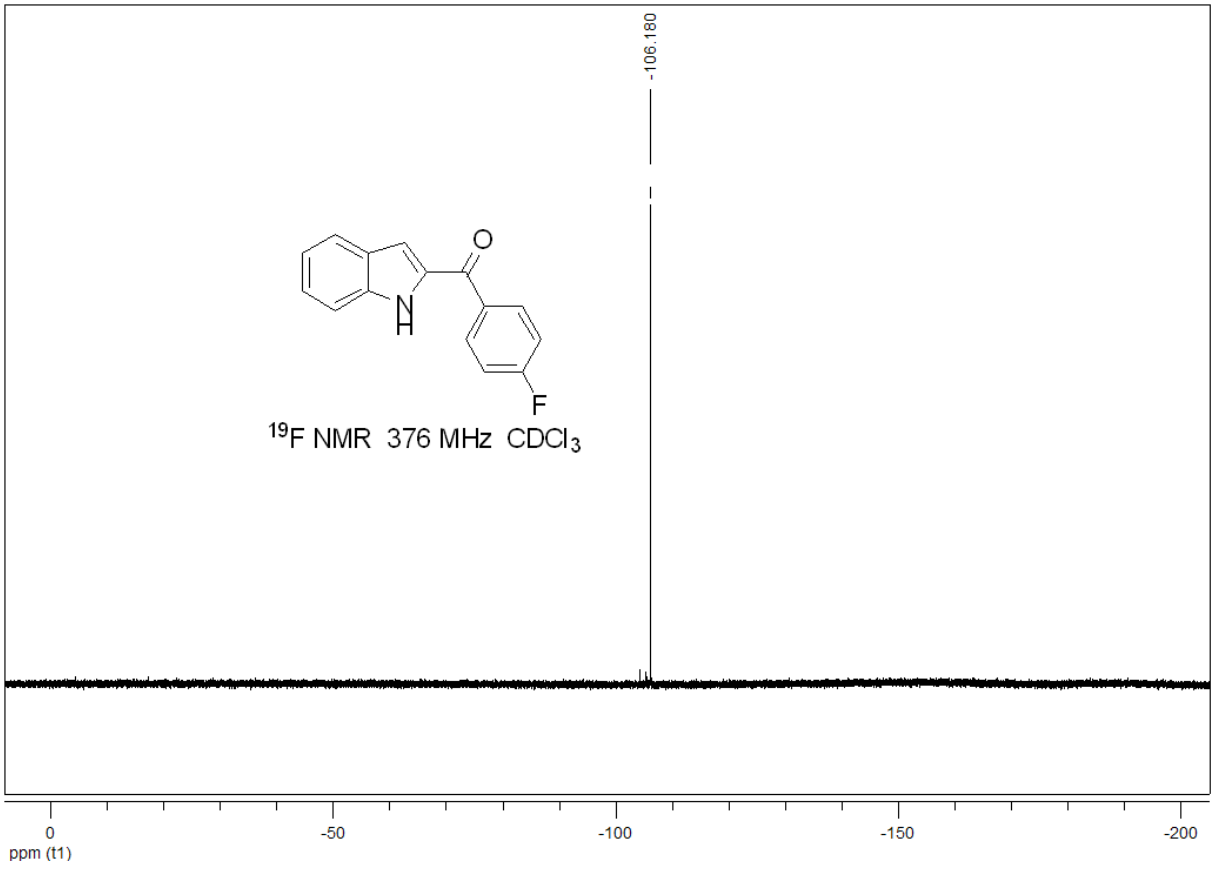

9.643
8.069
8.047
7.740
7.720
7.513
7.492
7.390
7.371
7.352
7.260
7.190
7.172
7.154
7.049
7.028
3.917
O
N
H
O
^{1}H NMR 400MHz CDCl$_3$
0.94
2.08
1.00
1.01
0.97
2.00
2.14
3.20
10.0
5.0
0.0
ppm (t1)


185.840
163.174
137.317
134.479
131.534
130.627
127.732
126.137
123.023
120.878
113.758
112.158
111.834
77.317
77.000
76.683
55.487
O
N
H
O
^{13}C NMR 400MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

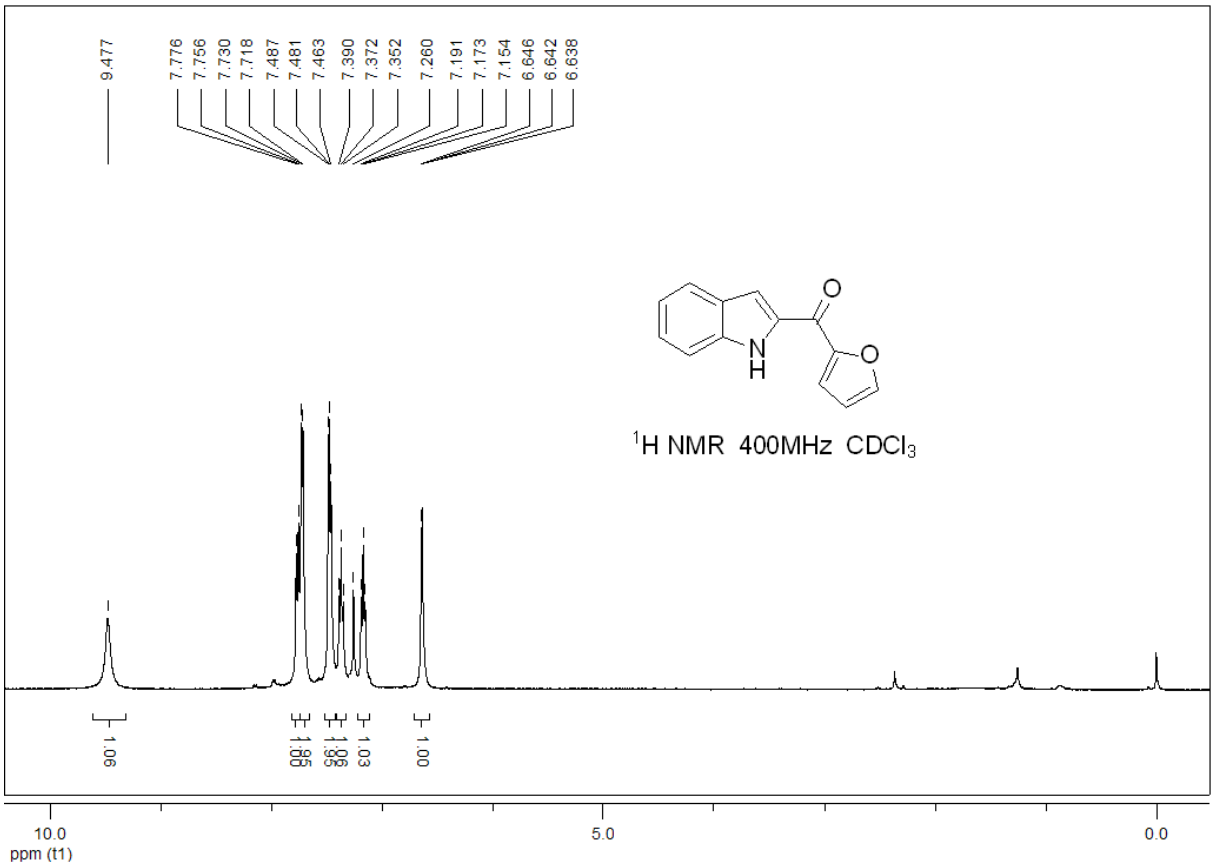
Compound **2c**:

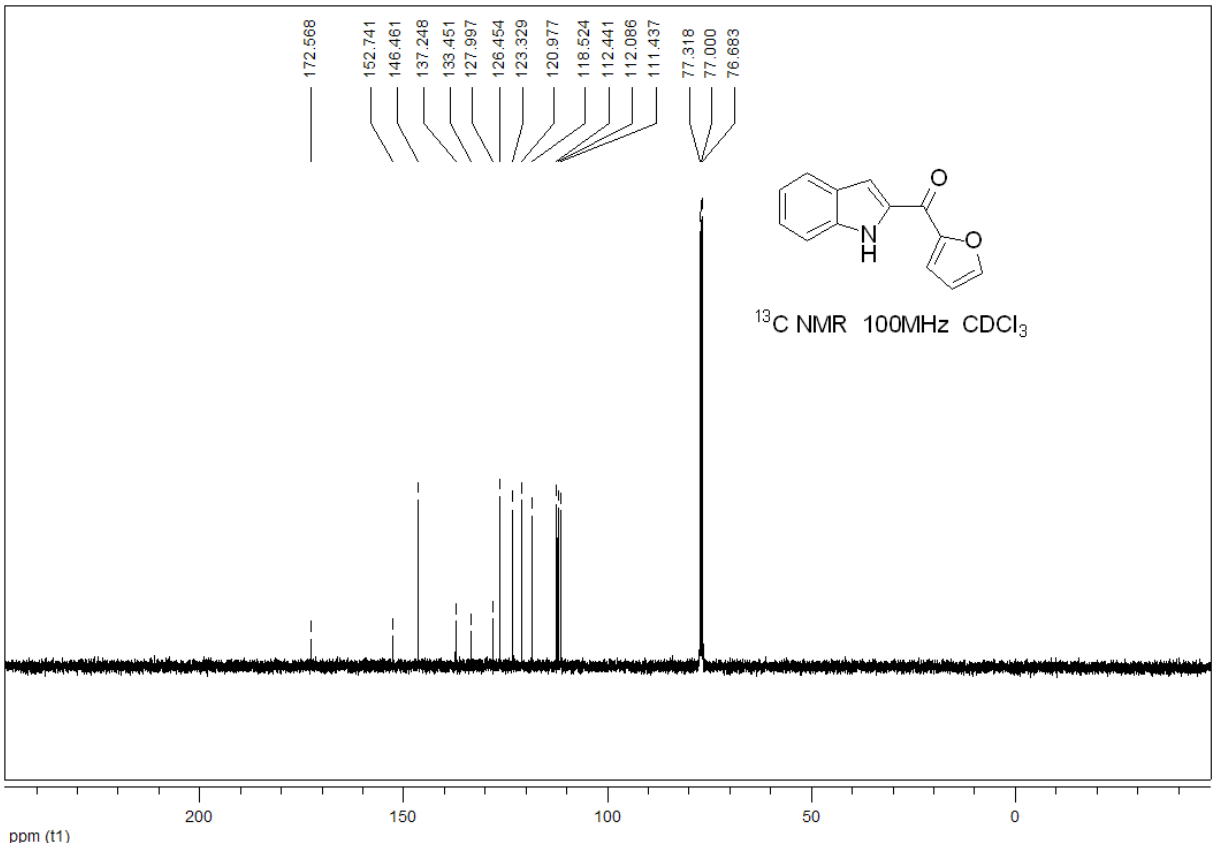

9.625
8.102
8.088
8.080
8.067
7.774
7.754
7.545
7.524
7.443
7.425
7.405
7.293
7.281
7.260
7.238
7.216
7.196
7.185
0.041
O
N
H
F
^{1}H NMR 400MHz CDCl$_3$
1.09
2.11
1.00
0.99
10.0
5.0
0.0
ppm (t1)


185.691
166.627
164.105
137.580
134.050
131.744
131.654
127.651
126.622
123.191
121.116
115.743
115.526
112.669
112.215
77.317
77.000
76.683
-0.028
O
N
H
F
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

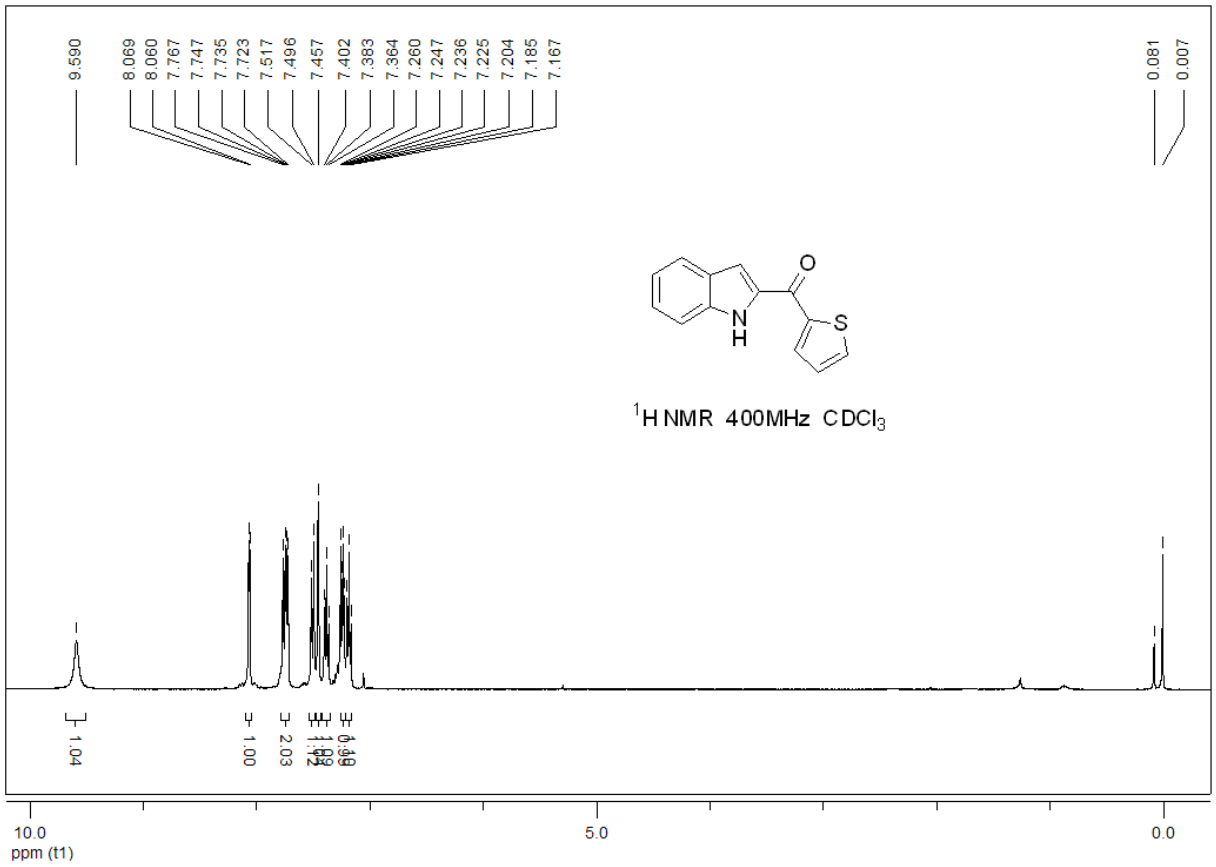

-106.180
O
N
H
F
^{19}F NMR 376 MHz CDCl$_3$
0
-50
-100
-150
-200
ppm (t1)

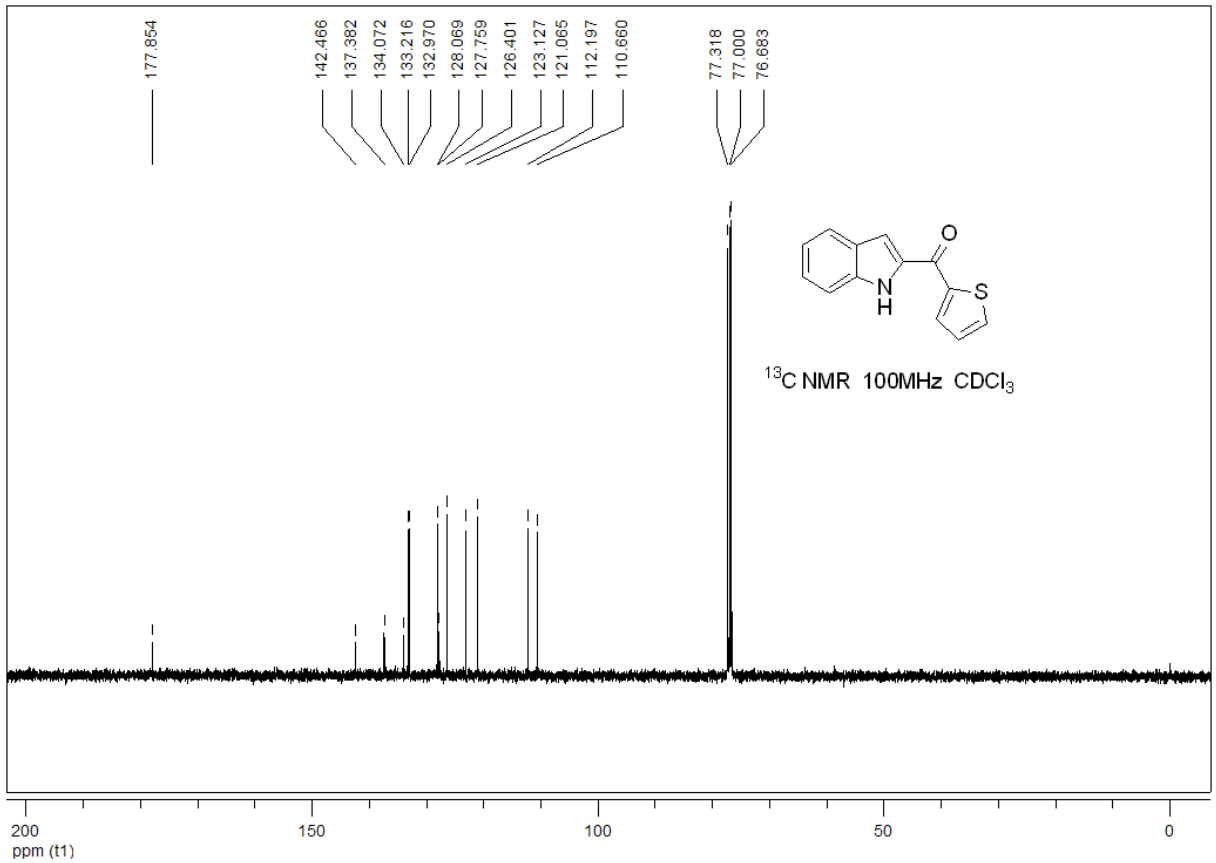
Compound **2d**:


9.477
7.776
7.756
7.730
7.718
7.487
7.481
7.463
7.390
7.372
7.352
7.260
7.191
7.173
7.154
6.646
6.642
6.638
O
N
H
O
^{1}H NMR 400MHz CDCl$_3$
1.06
1.86
1.96
1.03
1.00
10.0
ppm (t1)
5.0
0.0

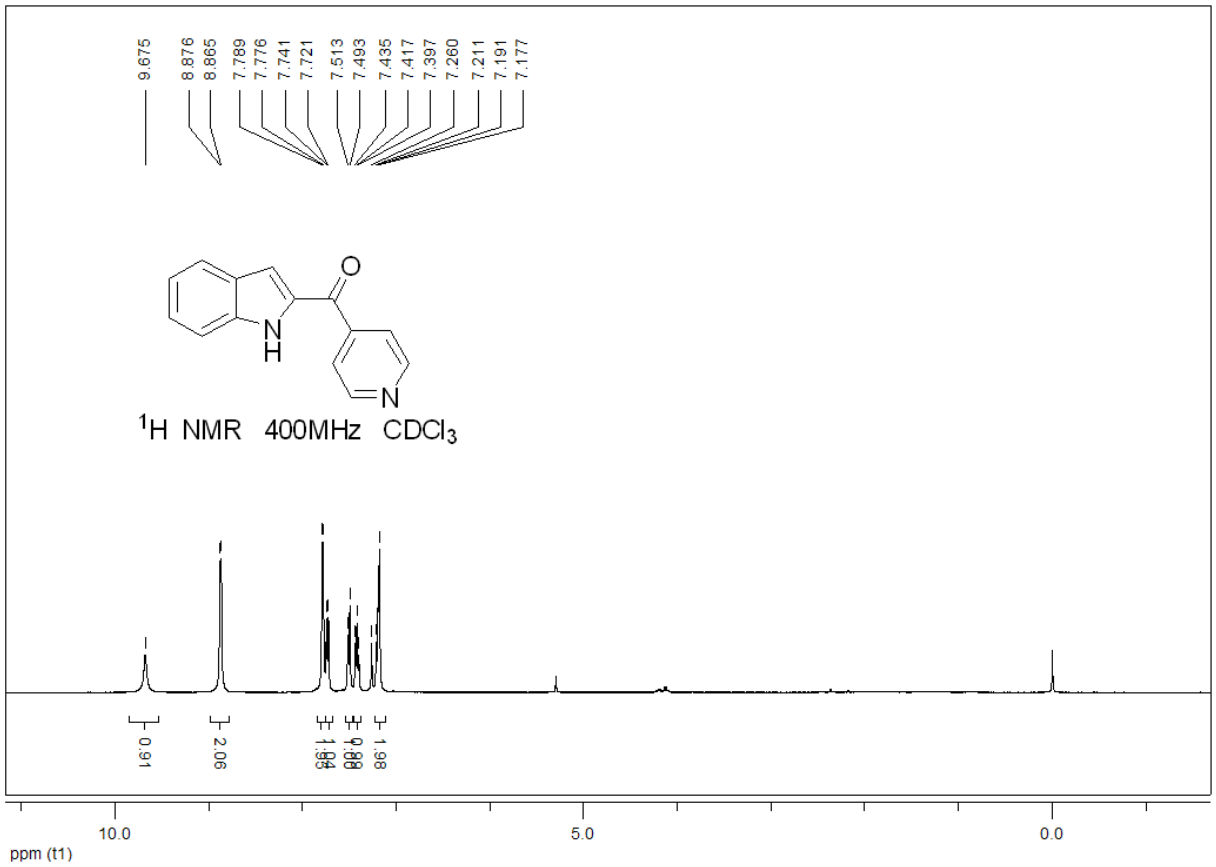

172.568
152.741
146.461
137.248
133.451
127.997
126.454
123.329
120.977
118.524
112.441
112.086
111.437
77.318
77.000
76.683
O
N
H
O
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

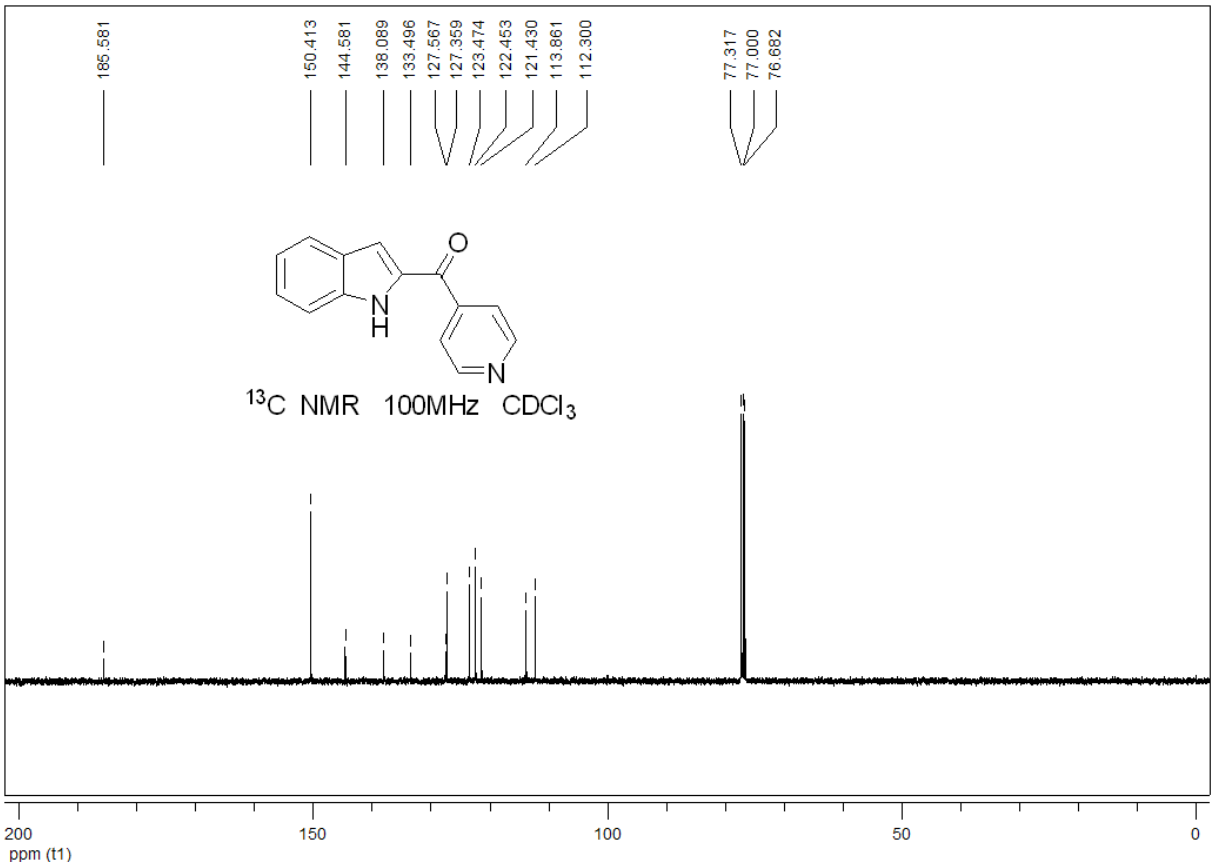
Compound **2e**:


9.590
8.069
8.060
7.767
7.747
7.735
7.723
7.517
7.496
7.457
7.402
7.383
7.364
7.260
7.247
7.236
7.225
7.204
7.185
7.167
0.081
0.007
O
N
H
S
^{1}H NMR 400MHz CDCl$_3$
1.04
1.00
2.03
10.0
ppm (t1)
5.0
0.0

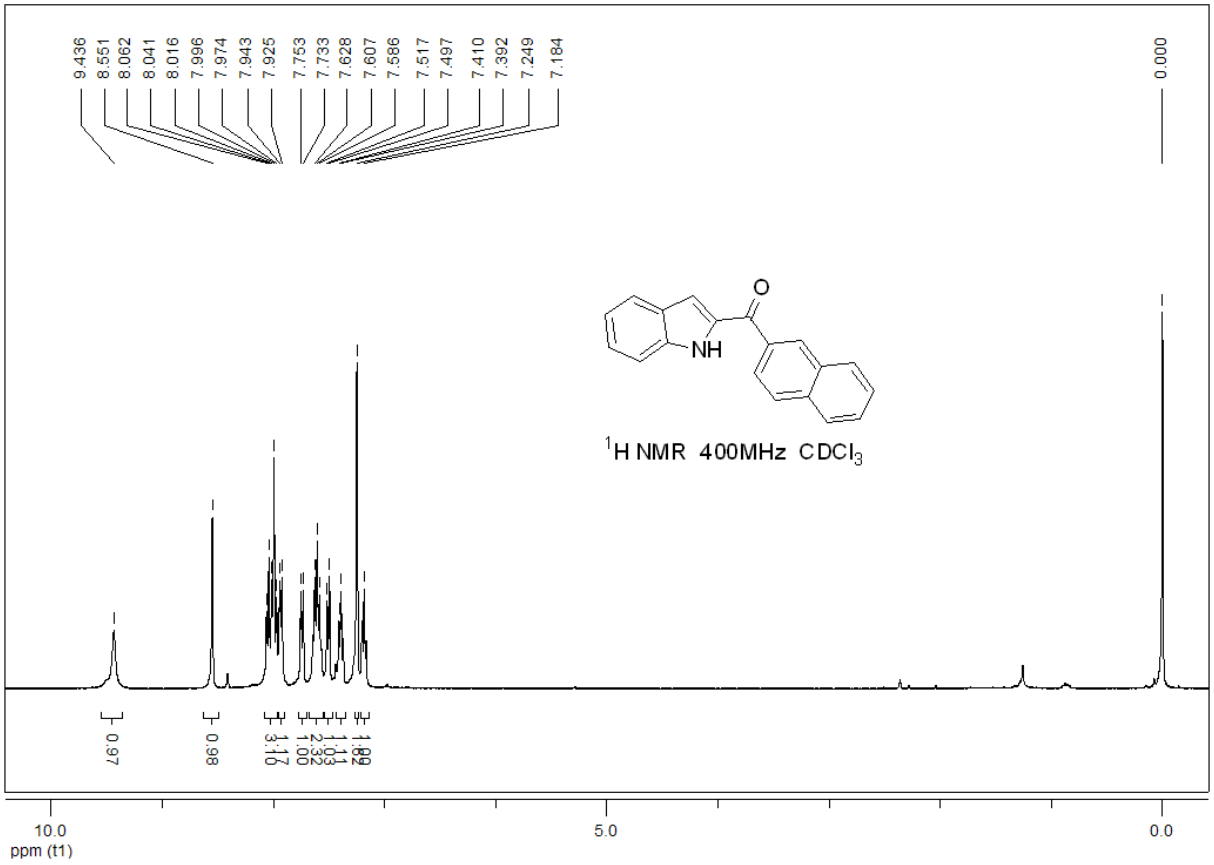

177.854
142.466
137.382
134.072
133.216
132.970
128.069
127.759
126.401
123.127
121.065
112.197
110.660
77.318
77.000
76.683
O
N
H
S
^{13}C NMR 100MHz CDCl$_3$
200
ppm (t1)
150
100
50
0

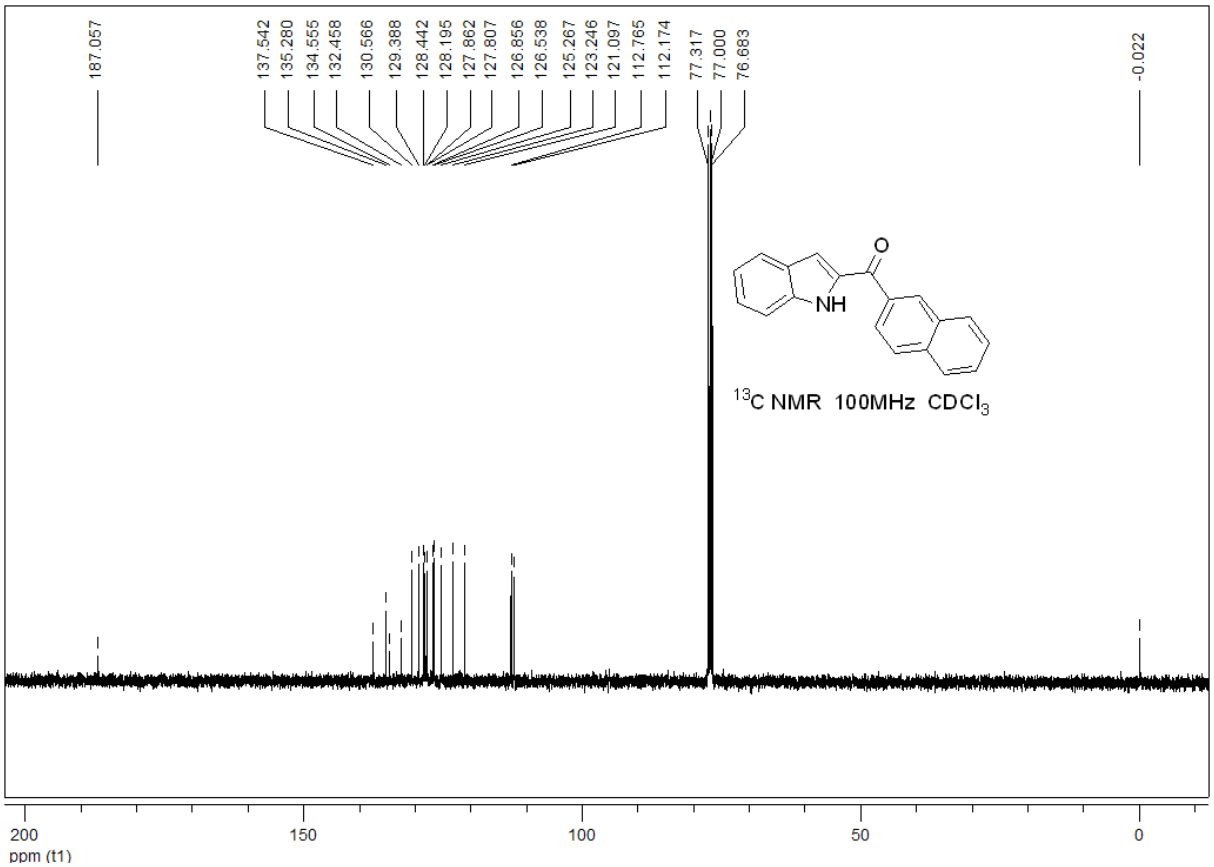
Compound **2f**:


9.675
8.876
8.865
7.789
7.776
7.741
7.721
7.513
7.493
7.435
7.417
7.397
7.260
7.211
7.191
7.177
O
N
H
N
^{1}H NMR 400MHz CDCl$_3$
0.91
2.06
1.98
1.98
0.98
1.98
10.0
5.0
0.0
ppm (t1)

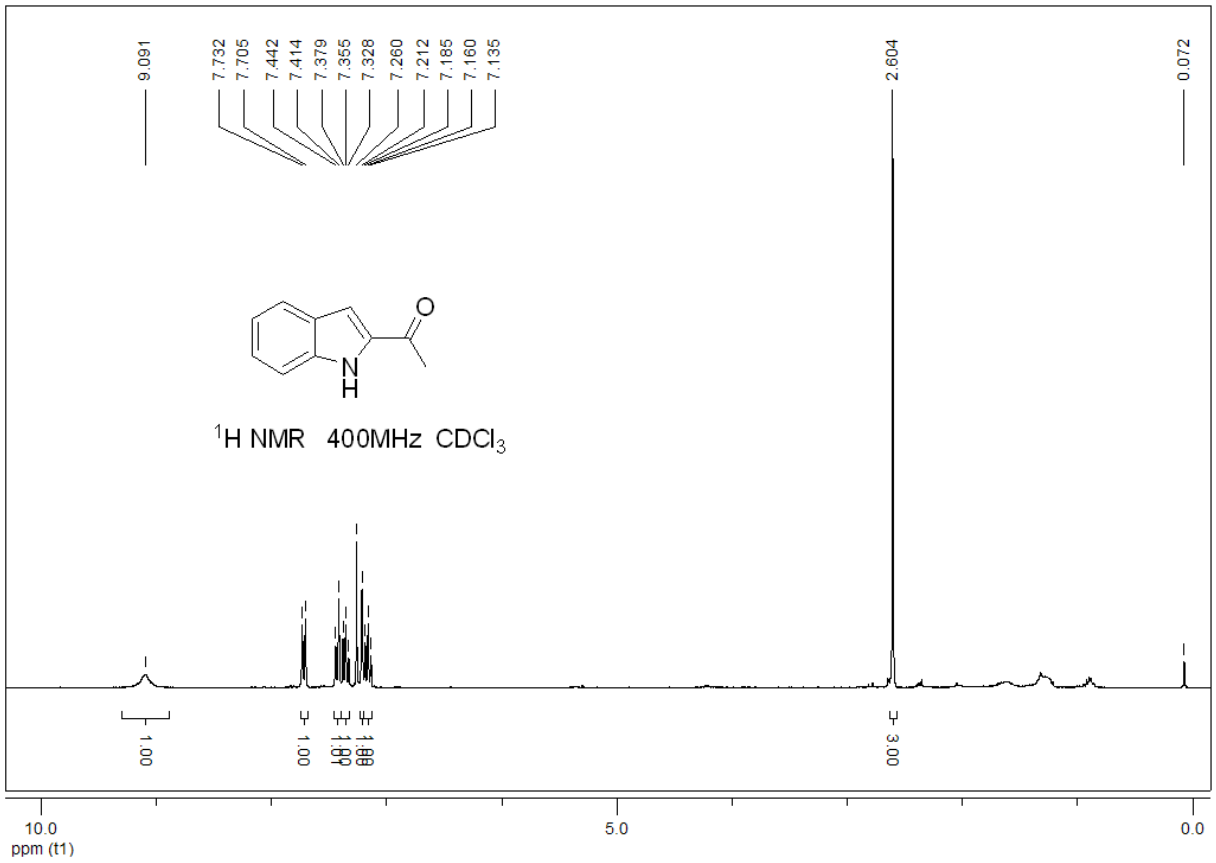

185.581
150.413
144.581
138.089
133.496
127.567
127.359
123.474
122.453
121.430
113.861
112.300
77.317
77.000
76.682
O
N
H
N
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

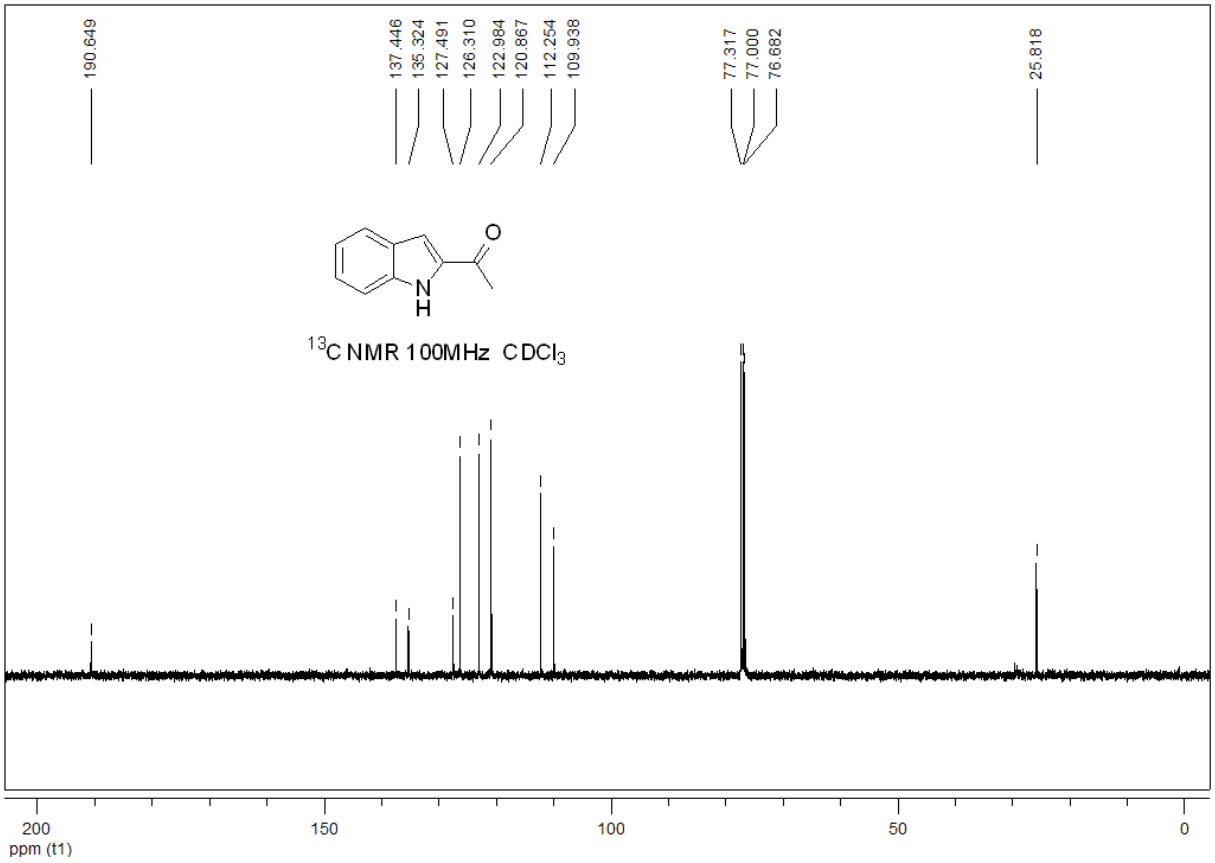
Compound **2g**:


9.436
8.551
8.062
8.041
8.016
7.996
7.974
7.943
7.925
7.753
7.733
7.628
7.607
7.586
7.517
7.497
7.410
7.392
7.249
7.184
0.000
O
NH
^{1}H NMR 400MHz CDCl$_3$
0.97
0.98
3.10
2.00
2.33
1.13
1.02
1.00
10.0
ppm (t1)
5.0
0.0

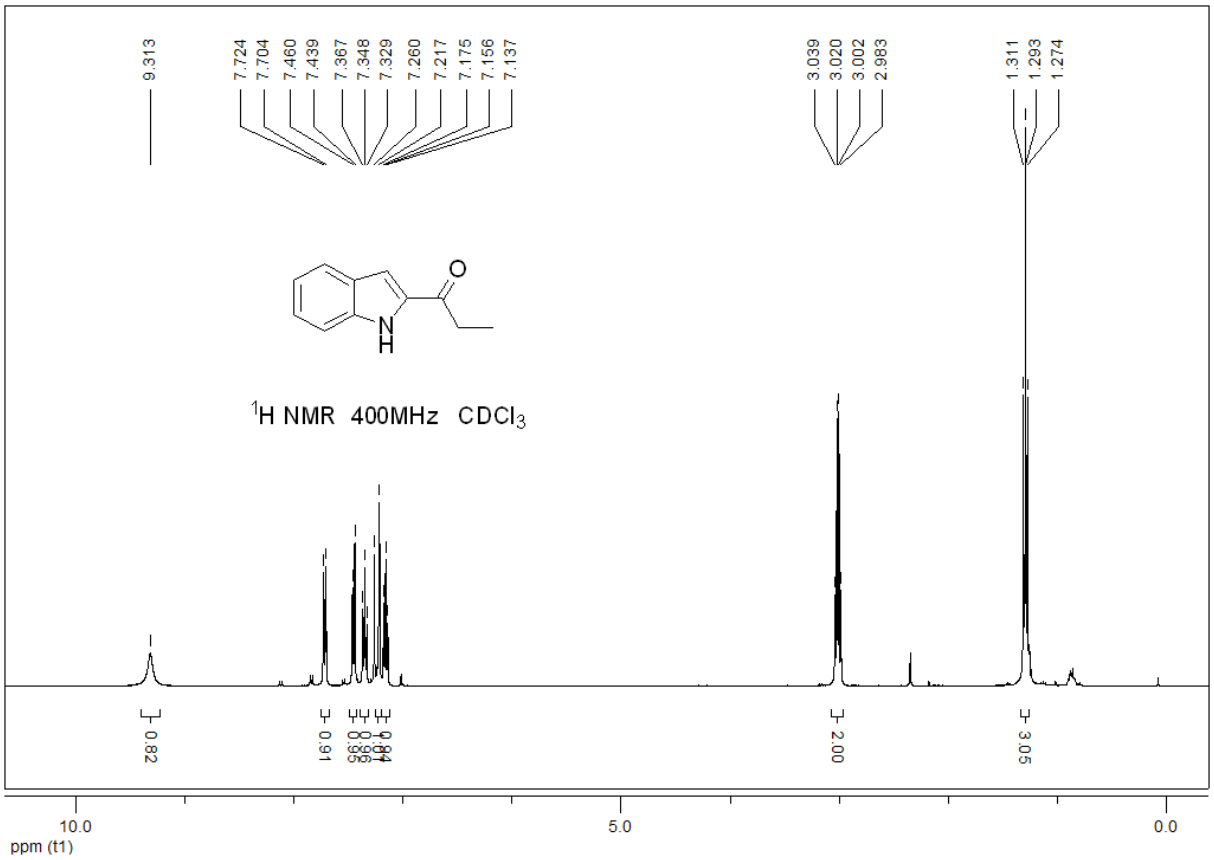

187.057
137.542
135.280
134.555
132.458
130.566
129.388
128.442
128.195
127.862
127.807
126.856
126.538
125.267
123.246
121.097
112.765
112.174
77.317
77.000
76.683
-0.022
O
NH
^{13}C NMR 100MHz CDCl$_3$
200
ppm (t1)
150
100
50
0

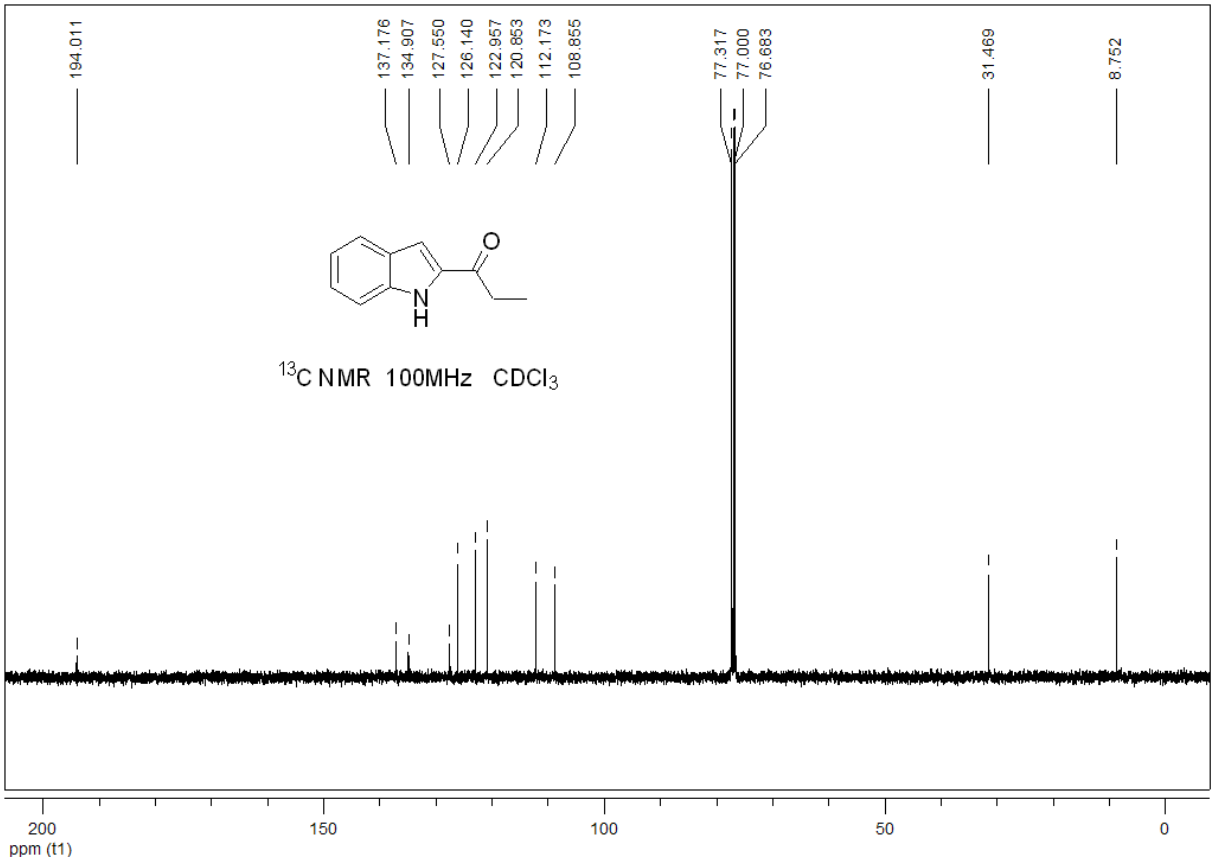
Compound **2h**:


9.091
7.732
7.705
7.442
7.414
7.379
7.355
7.328
7.260
7.212
7.185
7.160
7.135
2.604
0.072
O
N
H
^{1}H NMR 400MHz CDCl$_3$
1.00
1.00
3.00
10.0
ppm (t1)
5.0
0.0

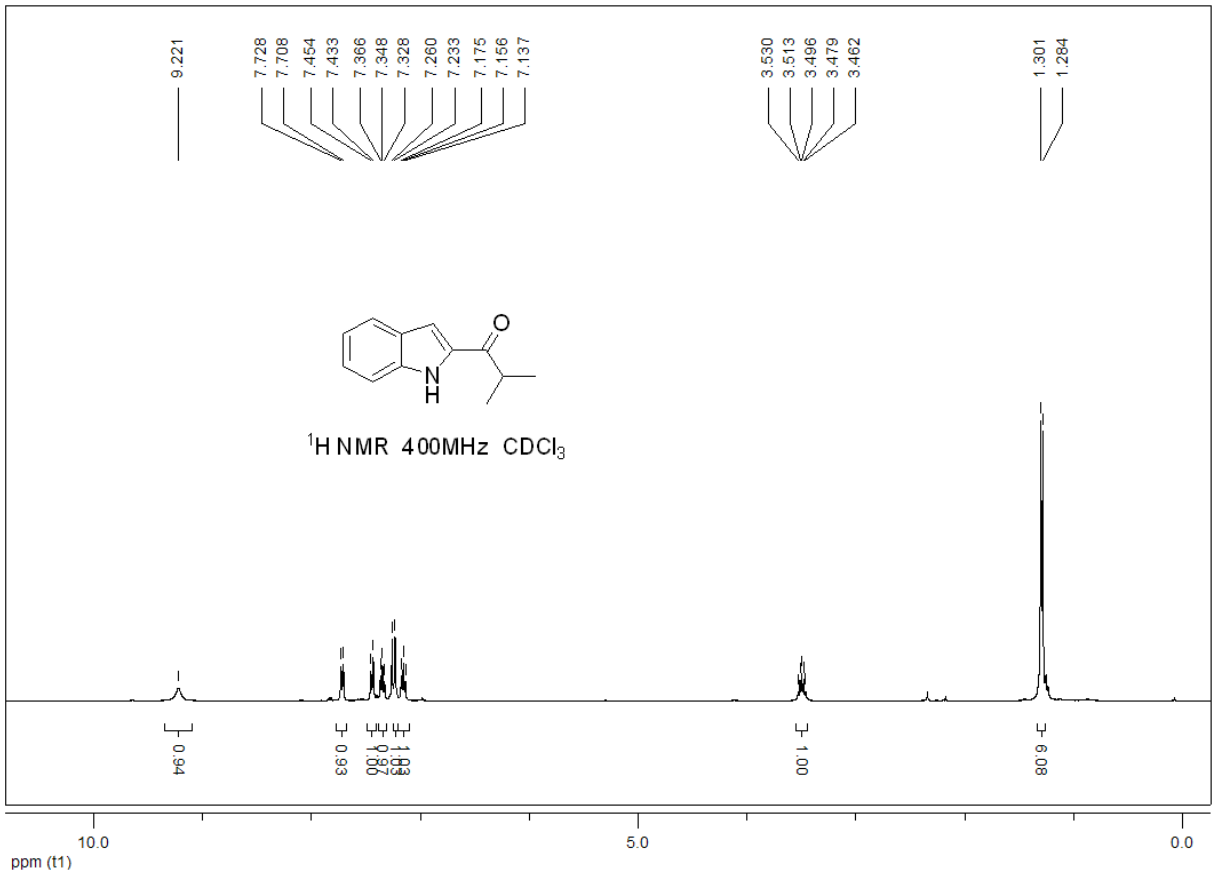

190.649
137.446
135.324
127.491
126.310
122.984
120.867
112.254
109.938
77.317
77.000
76.682
25.818
O
N
H
^{13}C NMR 100MHz CDCl$_3$
200
ppm (t1)
150
100
50
0

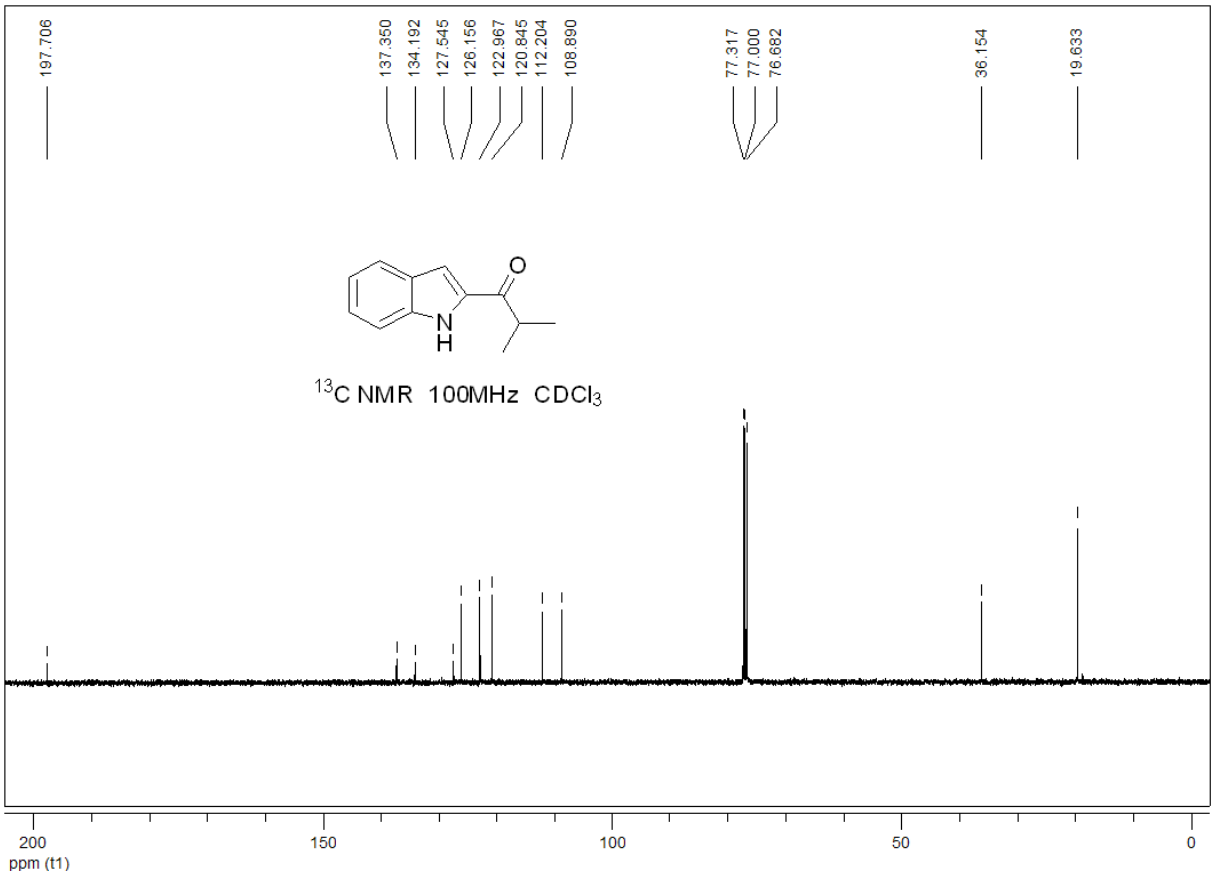
Compound **2i**:


9.313
7.724
7.704
7.460
7.439
7.367
7.348
7.329
7.260
7.217
7.175
7.156
7.137
3.039
3.020
3.002
2.983
1.311
1.293
1.274
O
N
H
^{1}H NMR 400MHz CDCl$_3$
0.82
0.91
2.00
3.05
10.0
5.0
0.0
ppm (t1)

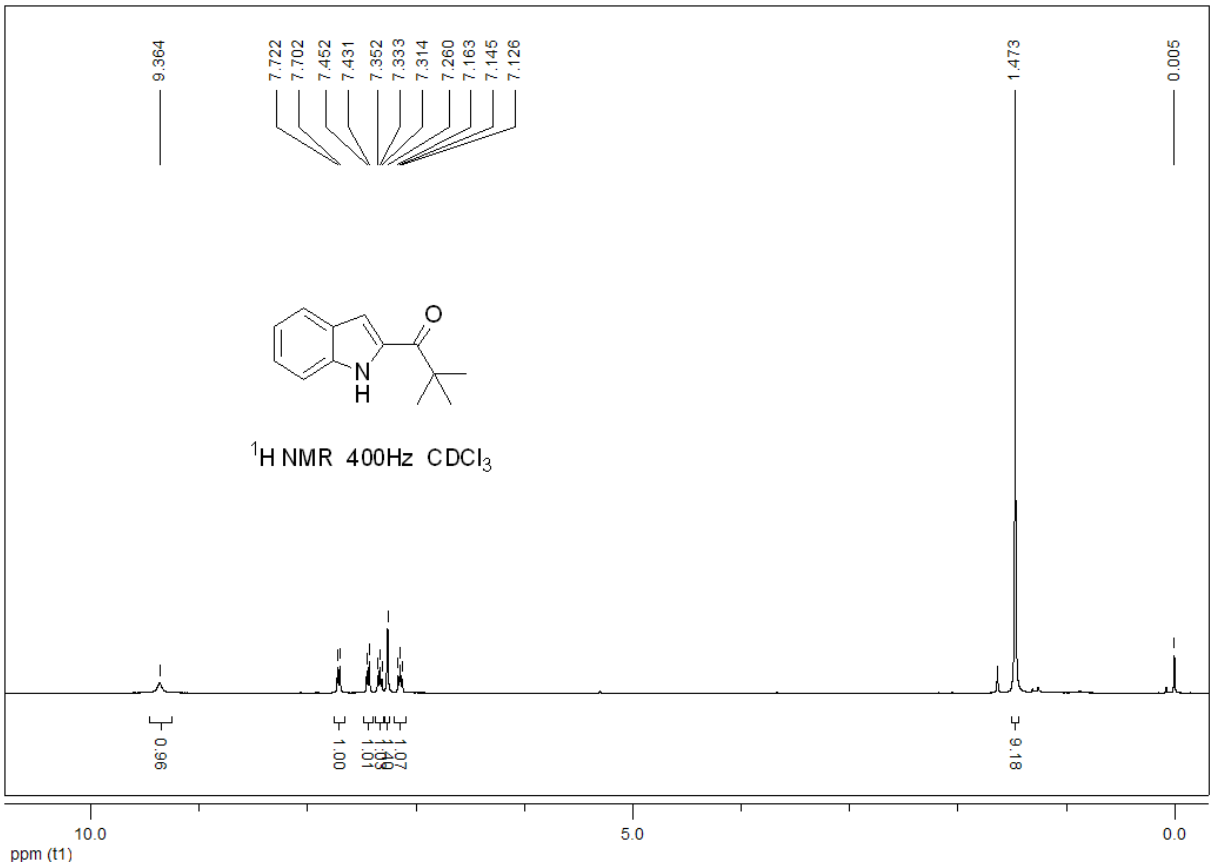

194.011
137.176
134.907
127.550
126.140
122.957
120.853
112.173
108.855
77.317
77.000
76.683
31.469
8.752
O
N
H
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

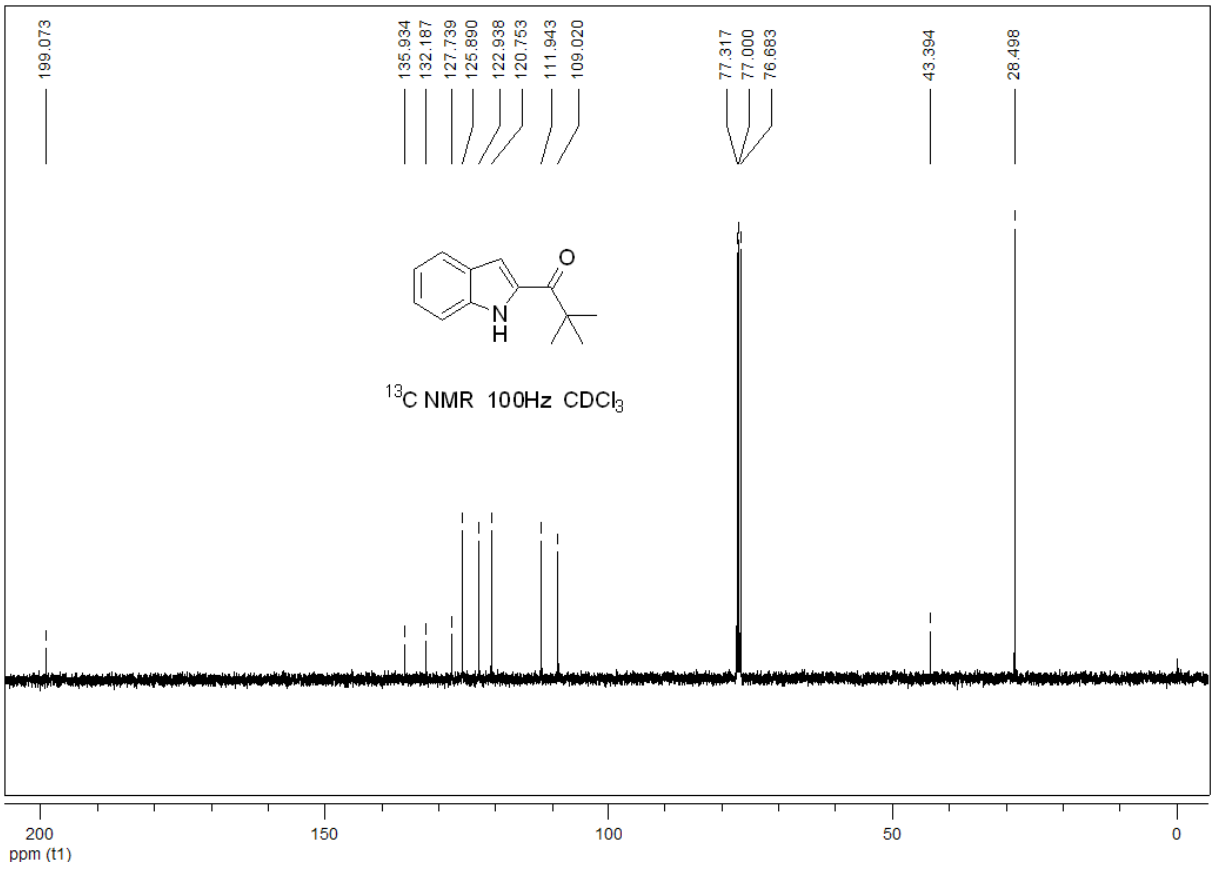
Compound **2j**:


9.221
7.728
7.708
7.454
7.433
7.366
7.348
7.328
7.260
7.233
7.175
7.156
7.137
3.530
3.513
3.496
3.479
3.462
1.301
1.284
O
N
H
^{1}H NMR 400MHz CDCl$_3$
0.94
0.93
1.00
1.00
1.00
1.00
1.00
6.08
10.0
5.0
0.0
ppm (t1)

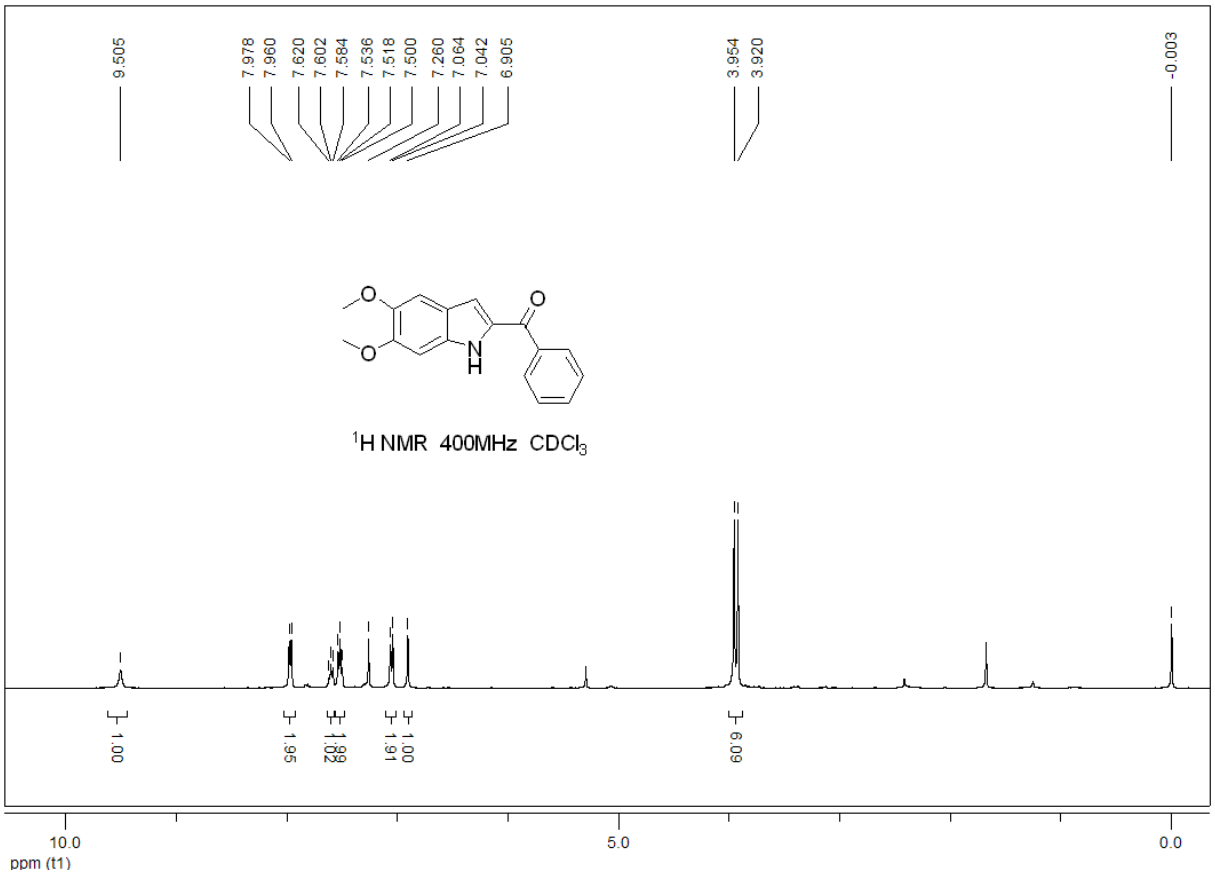

197.706
137.350
134.192
127.545
126.156
122.967
120.845
112.204
108.890
77.317
77.000
76.682
36.154
19.633
O
N
H
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

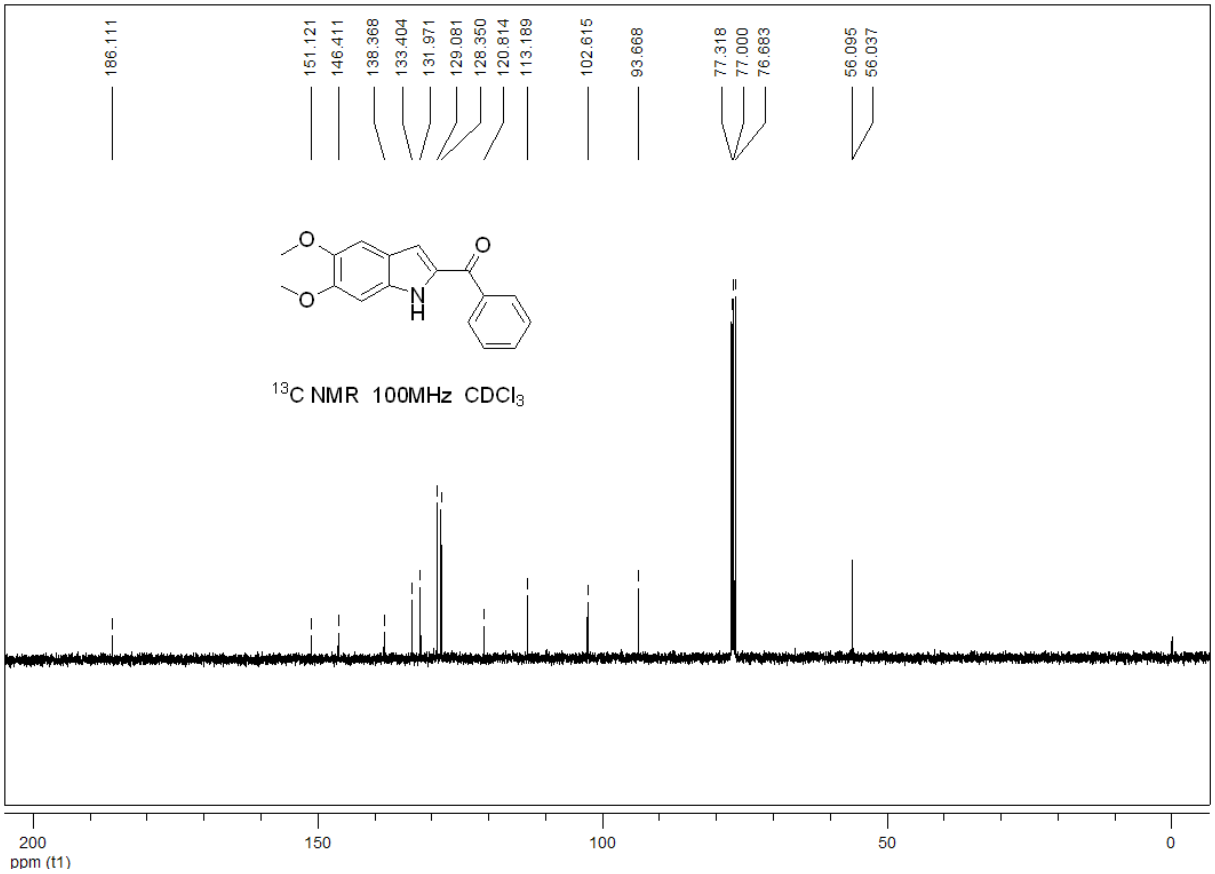
Compound **2k**:


9.364
7.722
7.702
7.452
7.431
7.352
7.333
7.314
7.260
7.163
7.145
7.126
1.473
0.005
O
N
H
^{1}H NMR 400Hz CDCl$_3$
0.96
1.00
1.07
9.18
10.0
5.0
0.0
ppm (t1)

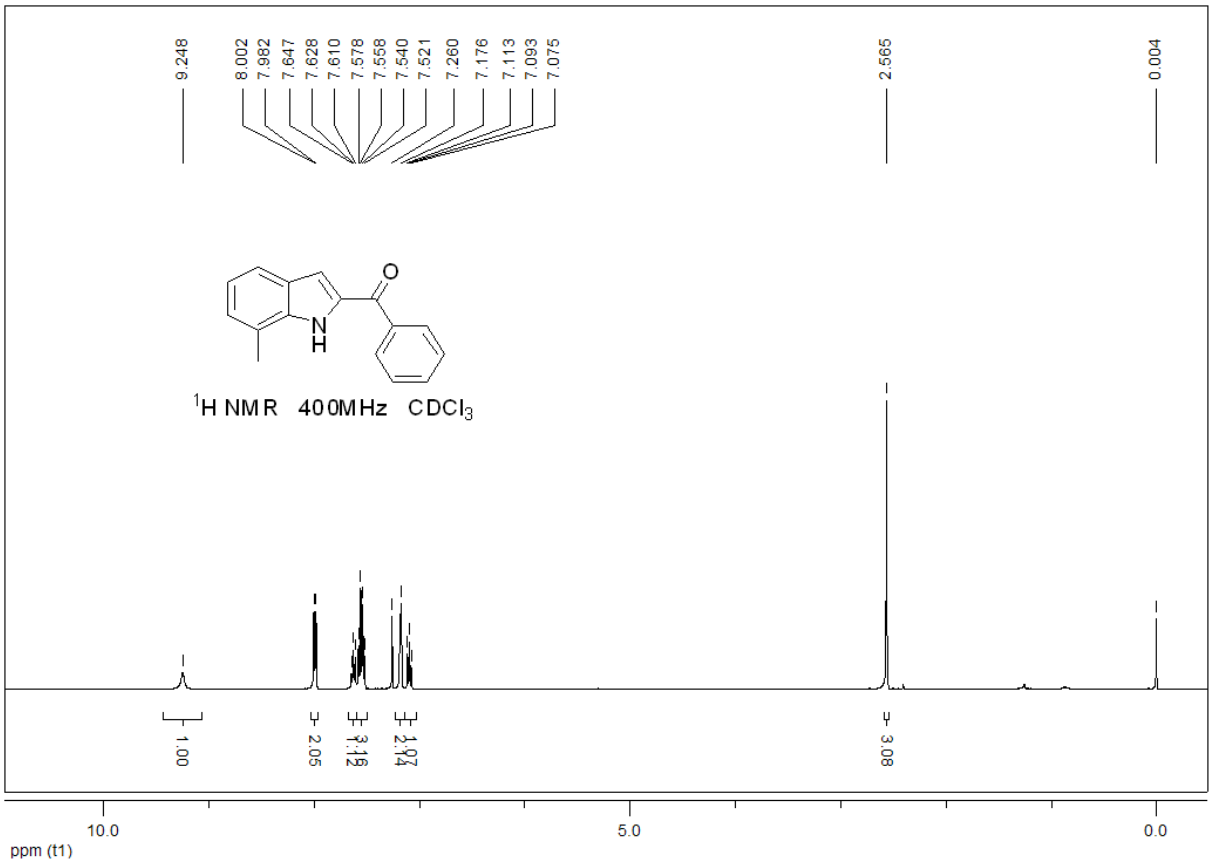

199.073
135.934
132.187
127.739
125.890
122.938
120.753
111.943
109.020
77.317
77.000
76.683
43.394
28.498
O
N
H
^{13}C NMR 100Hz CDCl$_3$
200
150
100
50
0
ppm (t1)

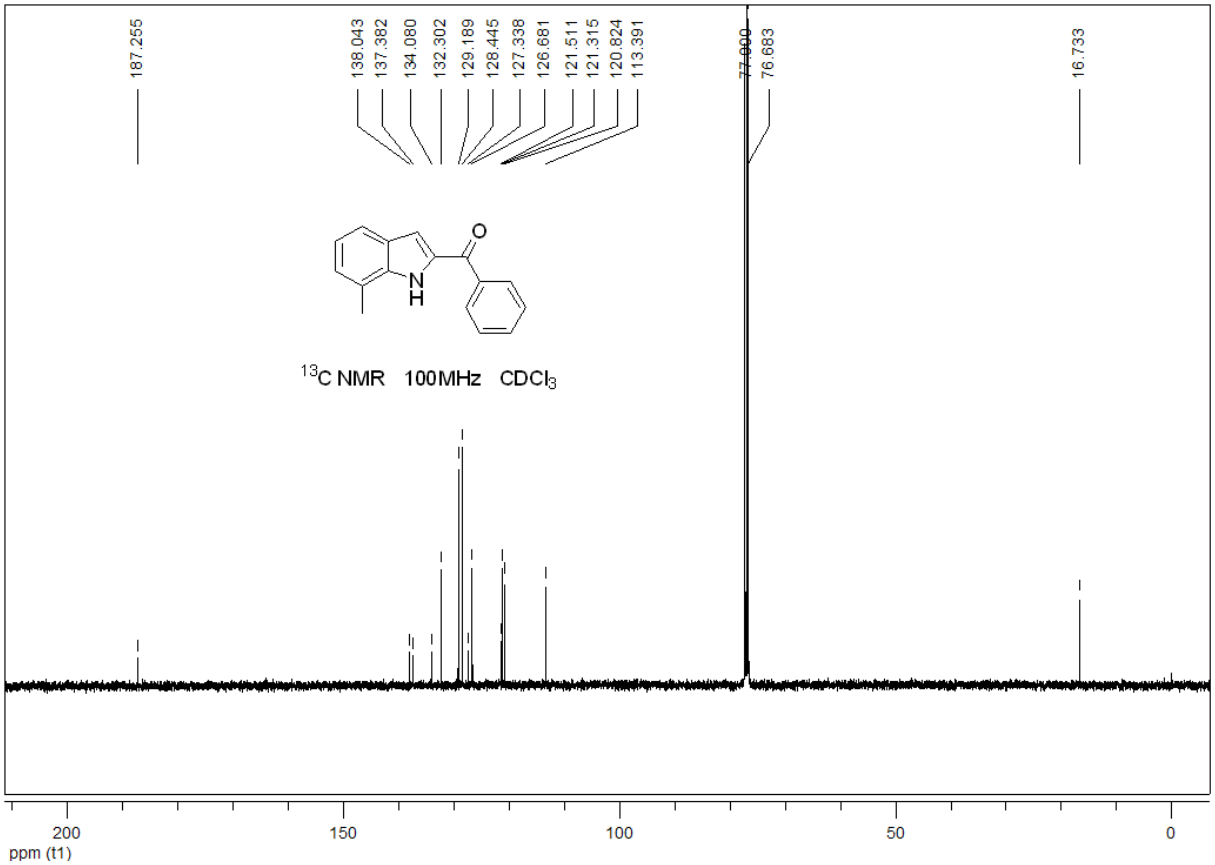
Compound **2l**:


9.505
7.978
7.960
7.620
7.602
7.584
7.536
7.518
7.500
7.260
7.064
7.042
6.905
3.954
3.920
-0.003
O
O
O
N
H
^{1}H NMR 400MHz CDCl$_3$
1.00
1.95
1.82
1.89
1.91
1.00
6.09
10.0
5.0
0.0
ppm (t1)

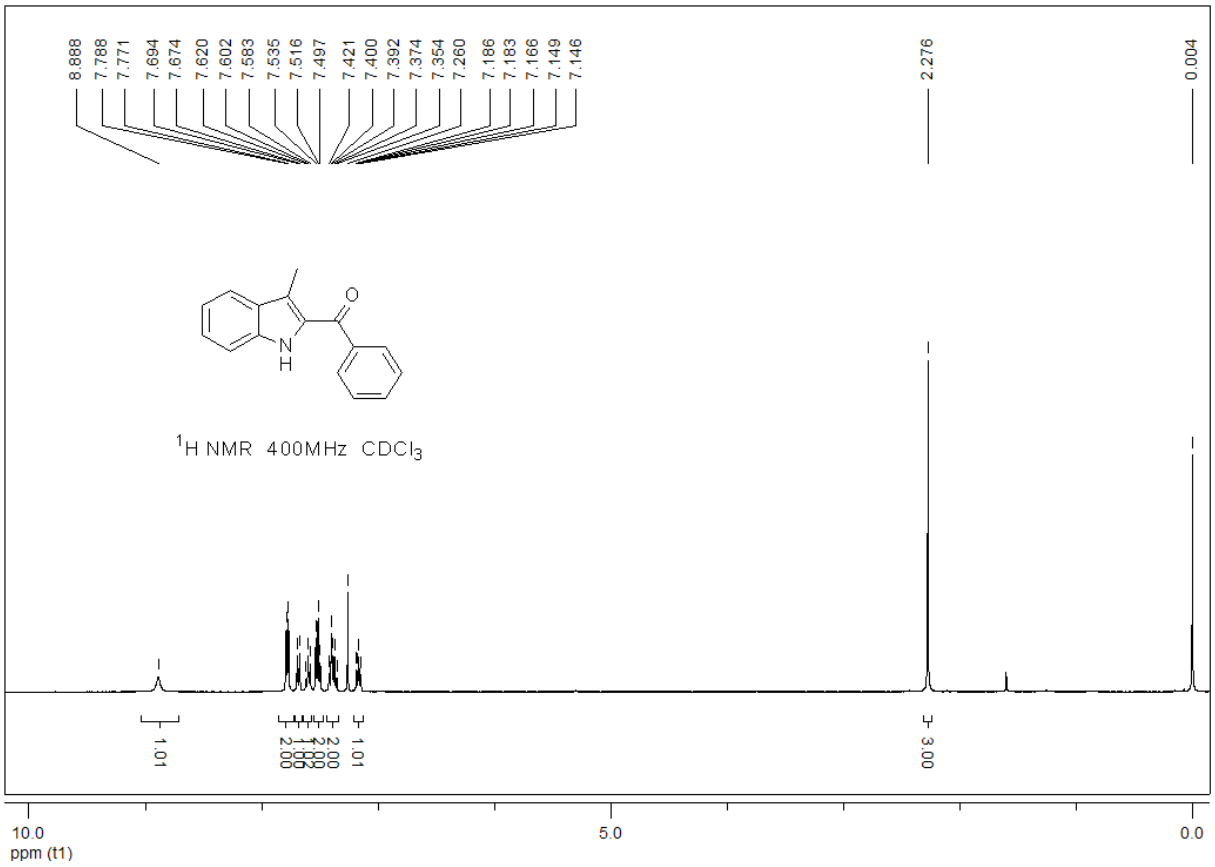

186.111
151.121
146.411
138.368
133.404
131.971
129.081
128.350
120.814
113.189
102.615
93.668
77.318
77.000
76.683
56.095
56.037
O
O
O
N
H
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

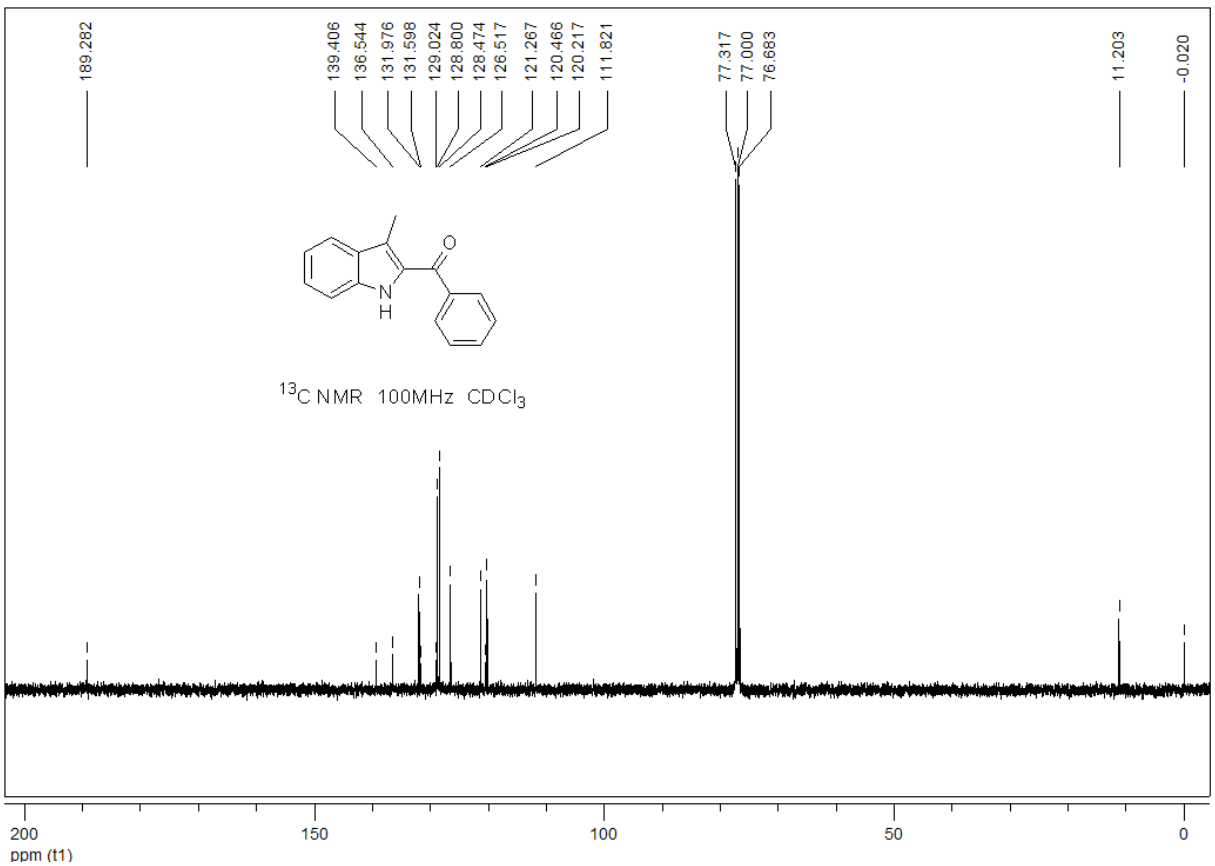
Compound **2m**:


9.248
8.002
7.982
7.647
7.628
7.610
7.578
7.558
7.540
7.521
7.260
7.176
7.113
7.093
7.075
2.565
0.004
O
N
H
^{1}H NMR 400MHz CDCl$_3$
1.00
2.05
3.18
2.14
3.08
10.0
5.0
0.0
ppm (t1)

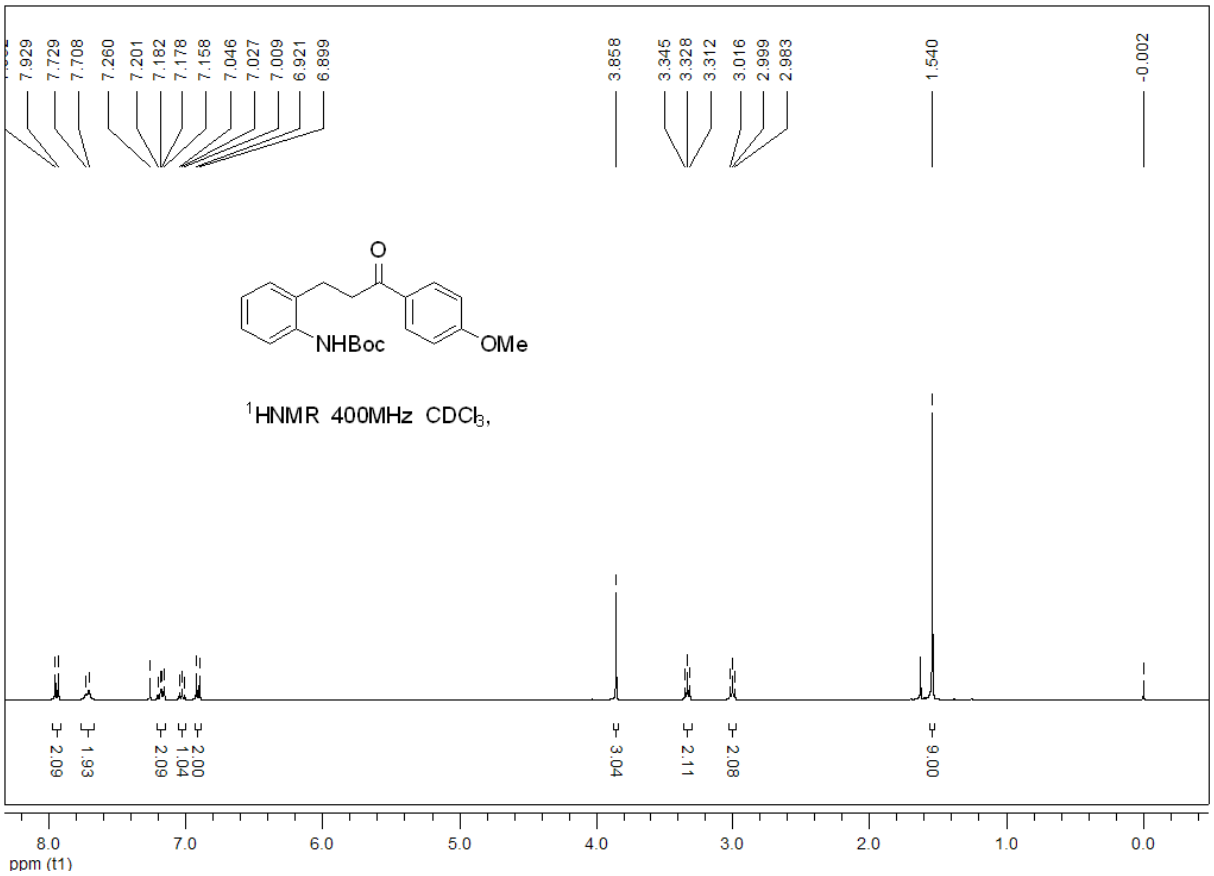

187.255
138.043
137.382
134.080
132.302
129.189
128.445
127.338
126.681
121.511
121.315
120.824
113.391
77.000
76.683
16.733
O
N
H
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

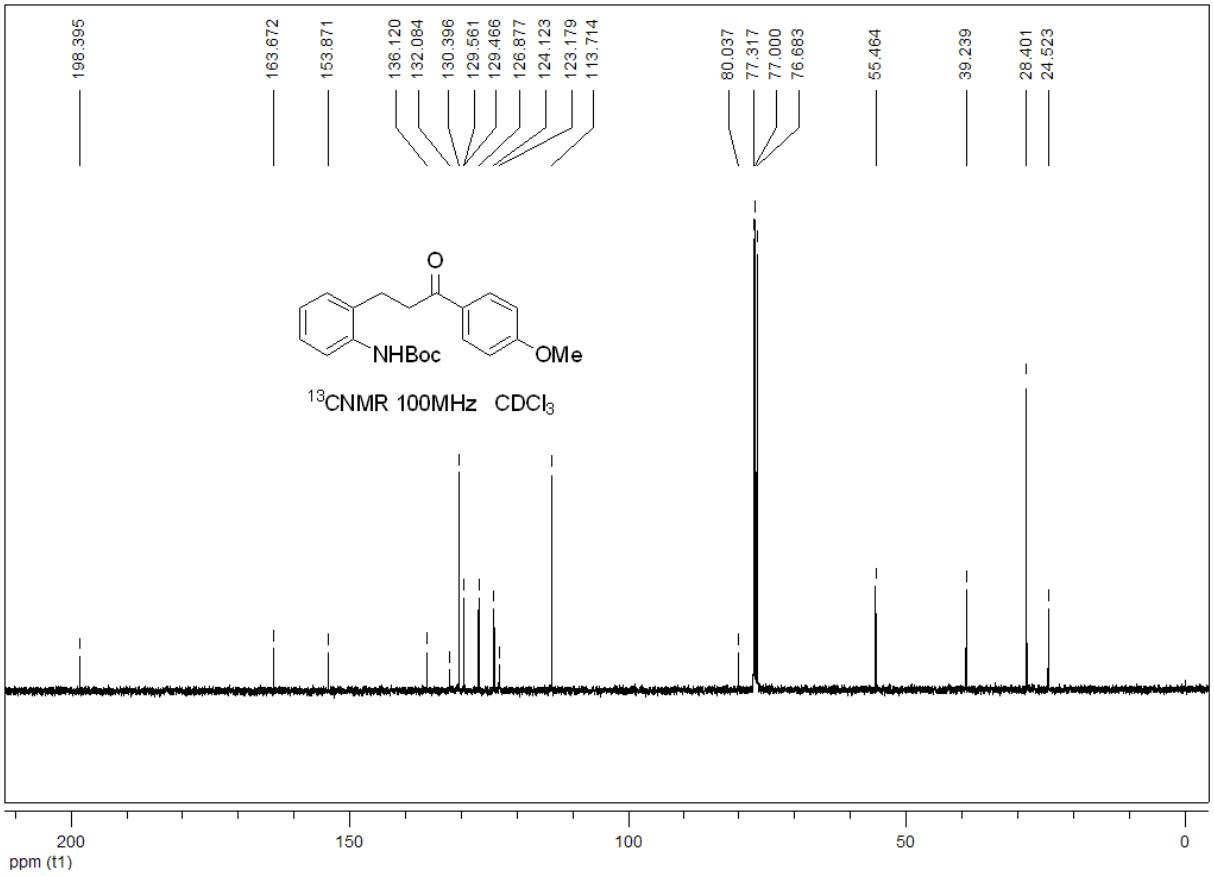
Compound **2n**:


8.888
7.788
7.771
7.694
7.674
7.620
7.602
7.583
7.535
7.516
7.497
7.421
7.400
7.392
7.374
7.354
7.260
7.186
7.183
7.166
7.149
7.146
2.276
0.004
O
N
H
^{1}H NMR 400MHz CDCl$_3$
1.01
2.00
2.00
2.00
2.00
1.01
3.00
10.0
ppm (t1)
5.0
0.0

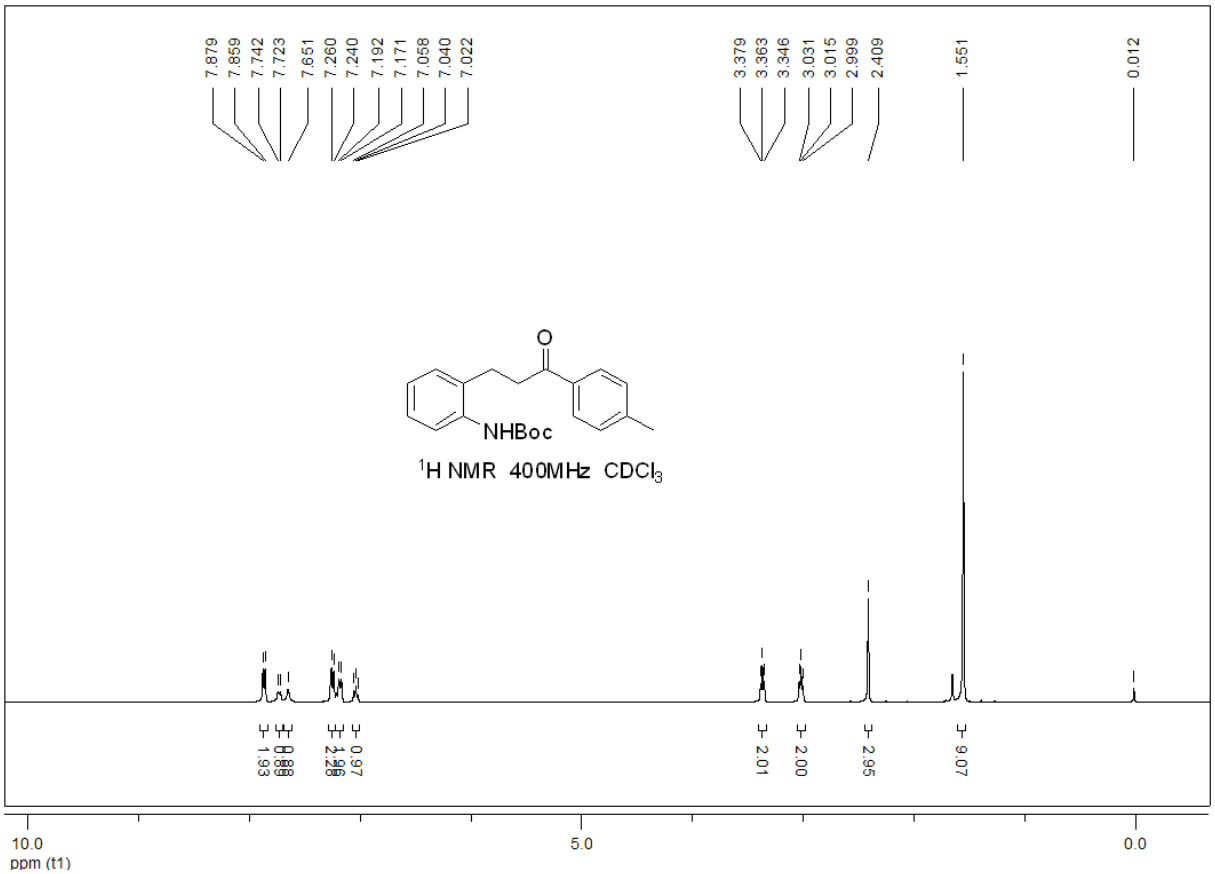

189.282
139.406
136.544
131.976
131.598
129.024
128.800
128.474
126.517
121.267
120.466
120.217
111.821
77.317
77.000
76.683
11.203
-0.020
O
N
H
^{13}C NMR 100MHz CDCl$_3$
200
ppm (t1)
150
100
50
0

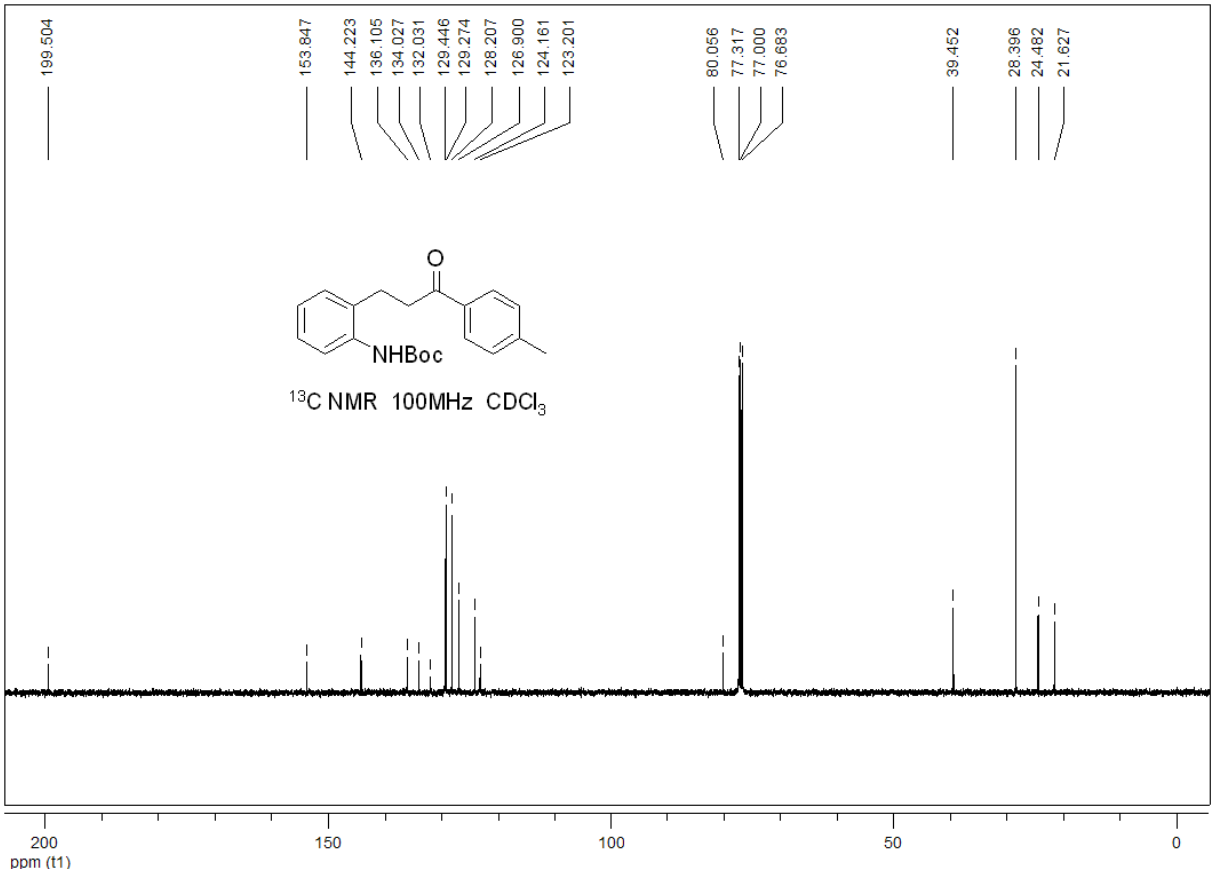
Compound **3b**:


7.929
7.729
7.708
7.260
7.201
7.182
7.178
7.158
7.046
7.027
7.009
6.921
6.899
3.858
3.345
3.328
3.312
3.016
2.999
2.983
1.540
-0.002
O
NHBoc
OMe
1HNMR 400MHz CDCl3,
2.09
1.93
2.09
1.04
2.00
3.04
2.11
2.08
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

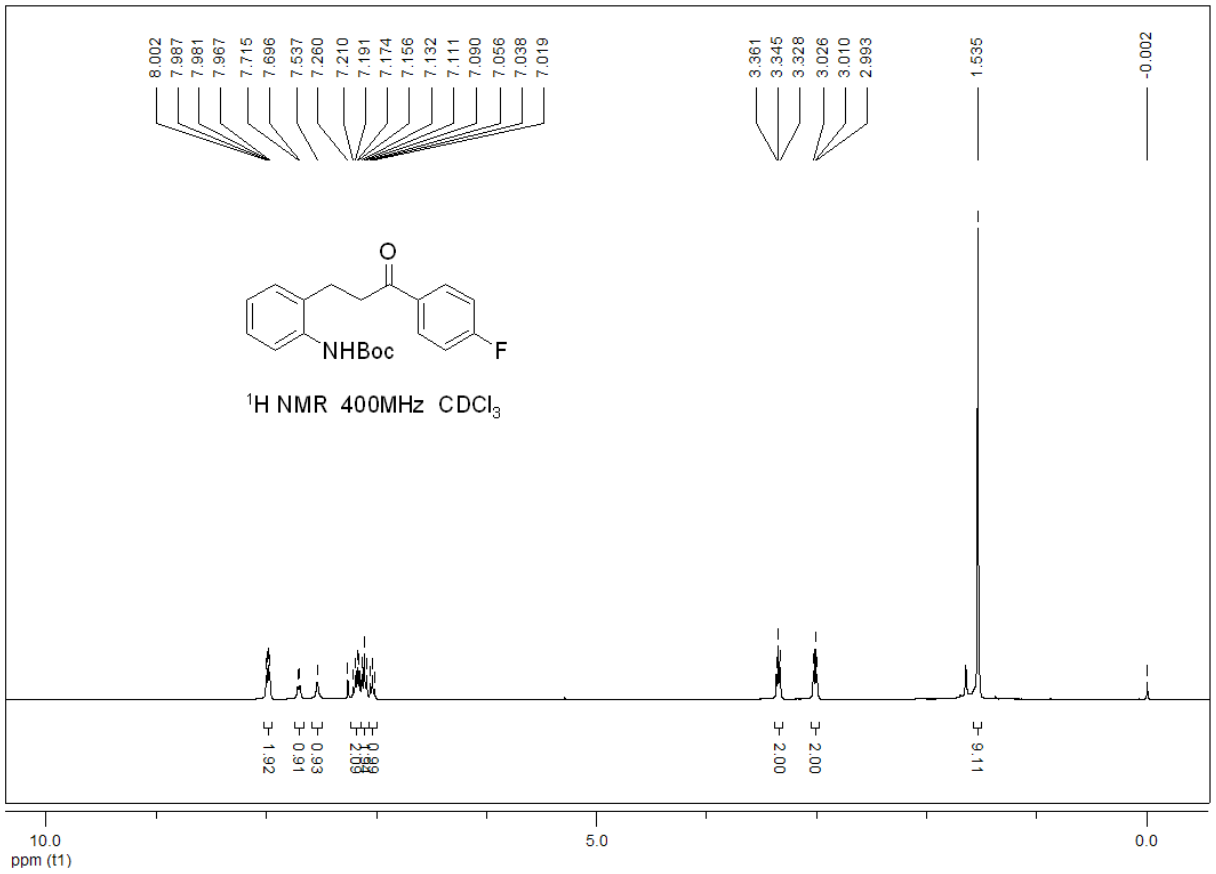

198.395
163.672
153.871
136.120
132.084
130.396
129.561
129.466
126.877
124.123
123.179
113.714
80.037
77.317
77.000
76.683
55.464
39.239
28.401
24.523
O
NHBoc
OMe
13CNMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

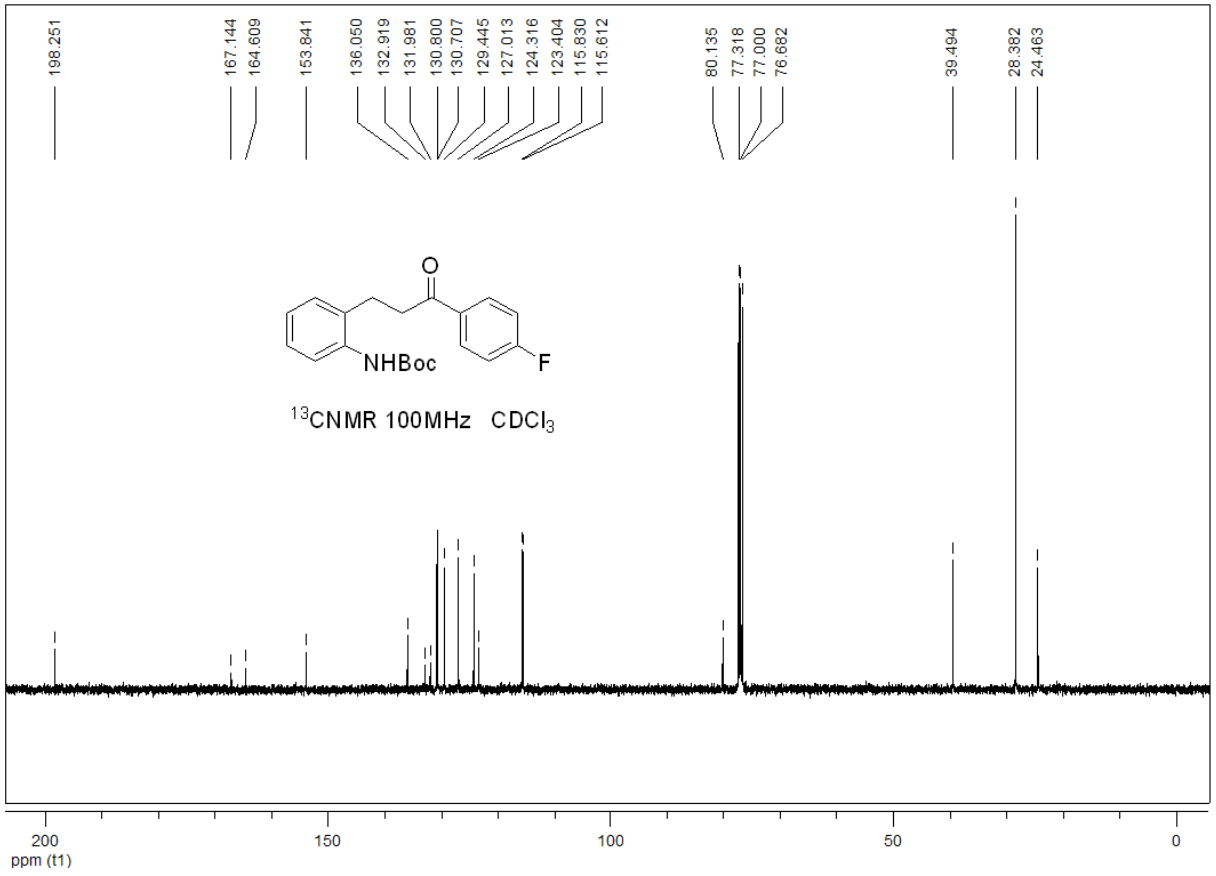
Compound **3c**:

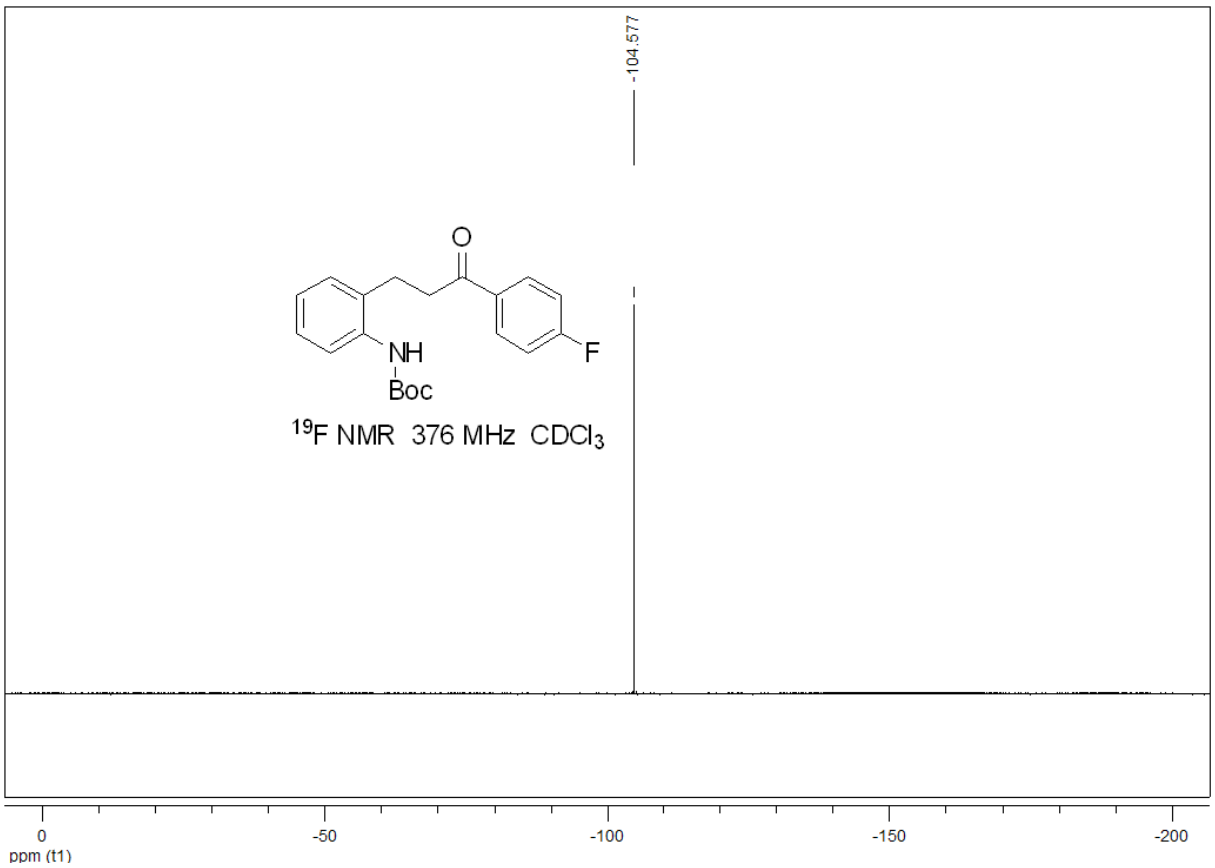

7.879
7.859
7.742
7.723
7.651
7.260
7.240
7.192
7.171
7.058
7.040
7.022
3.379
3.363
3.346
3.031
3.015
2.999
2.409
1.551
0.012
O
NHBoc
^{1}H NMR 400MHz CDCl$_3$
1.93
0.97
2.01
2.00
2.95
9.07
10.0
5.0
0.0
ppm (t1)


199.504
153.847
144.223
136.105
134.027
132.031
129.446
129.274
128.207
126.900
124.161
123.201
80.056
77.317
77.000
76.683
39.452
28.396
24.482
21.627
O
NHBoc
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

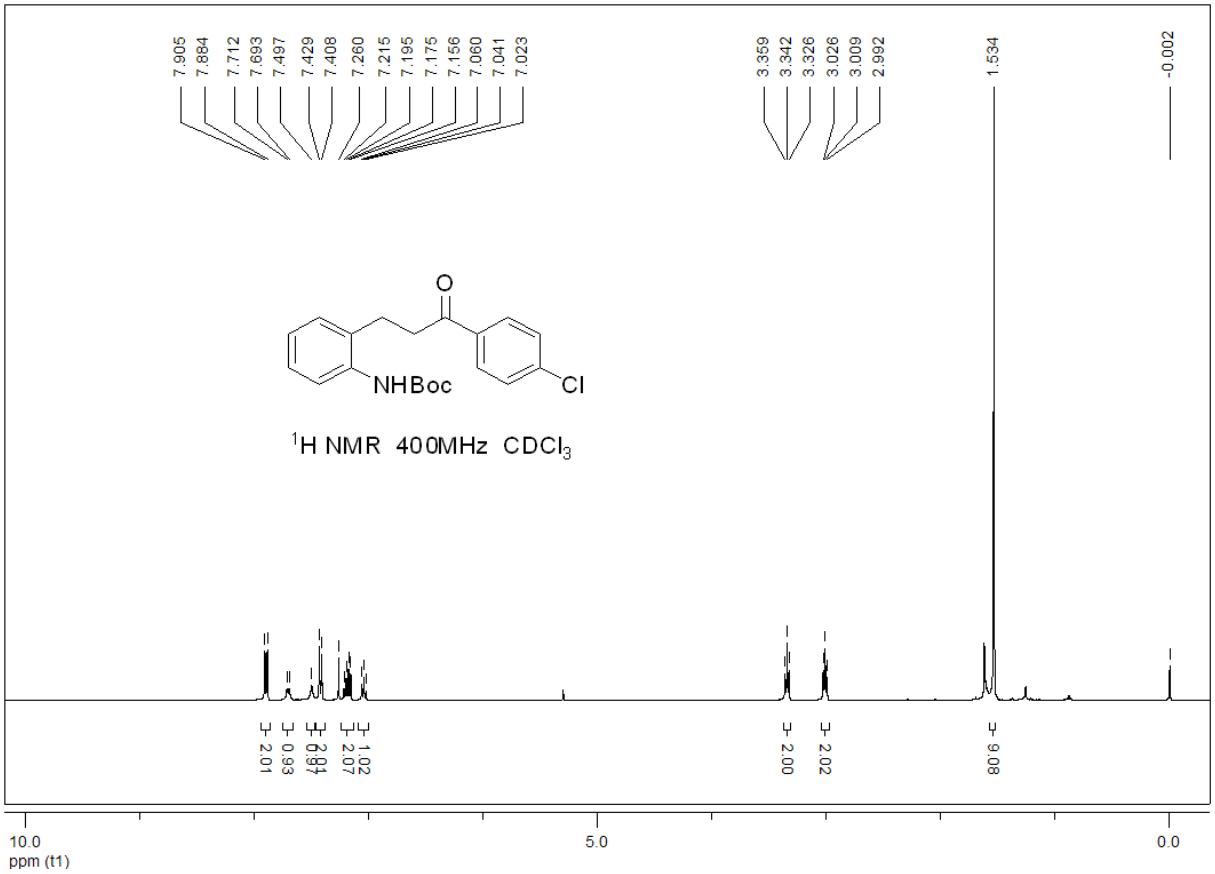
Compound **3d**:

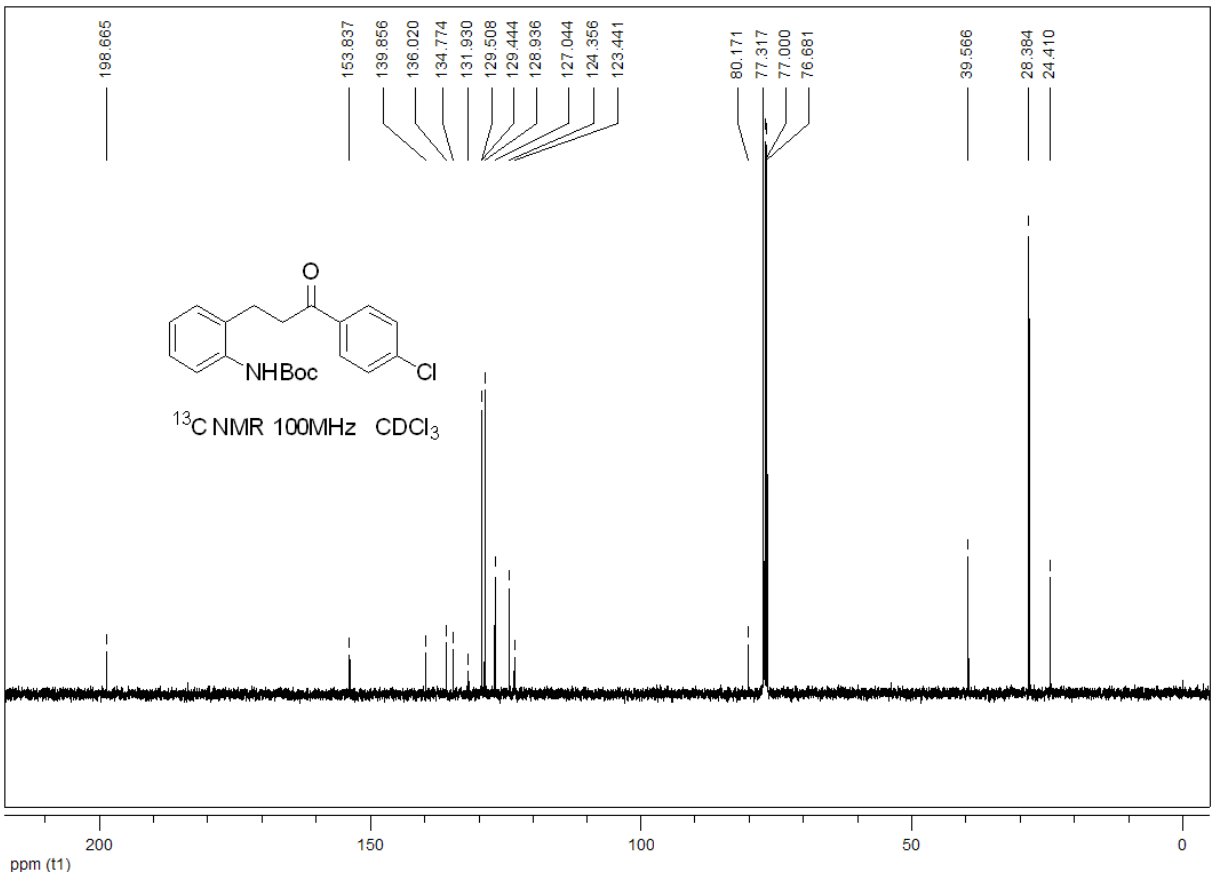

8.002
7.987
7.981
7.967
7.715
7.696
7.537
7.260
7.210
7.191
7.174
7.156
7.132
7.111
7.090
7.056
7.038
7.019
3.361
3.345
3.328
3.026
3.010
2.993
1.535
-0.002
O
NHBoc
F
1H NMR 400MHz CDCl3
1.92
0.93
0.91
2.09
2.00
2.00
9.11
10.0
ppm (t1)
5.0
0.0


198.251
167.144
164.609
153.841
136.050
132.919
131.981
130.800
130.707
129.445
127.013
124.316
123.404
115.830
115.612
80.135
77.318
77.000
76.682
39.494
28.382
24.463
O
NHBoc
F
13CNMR 100MHz CDCl3
200
ppm (t1)
150
100
50
0

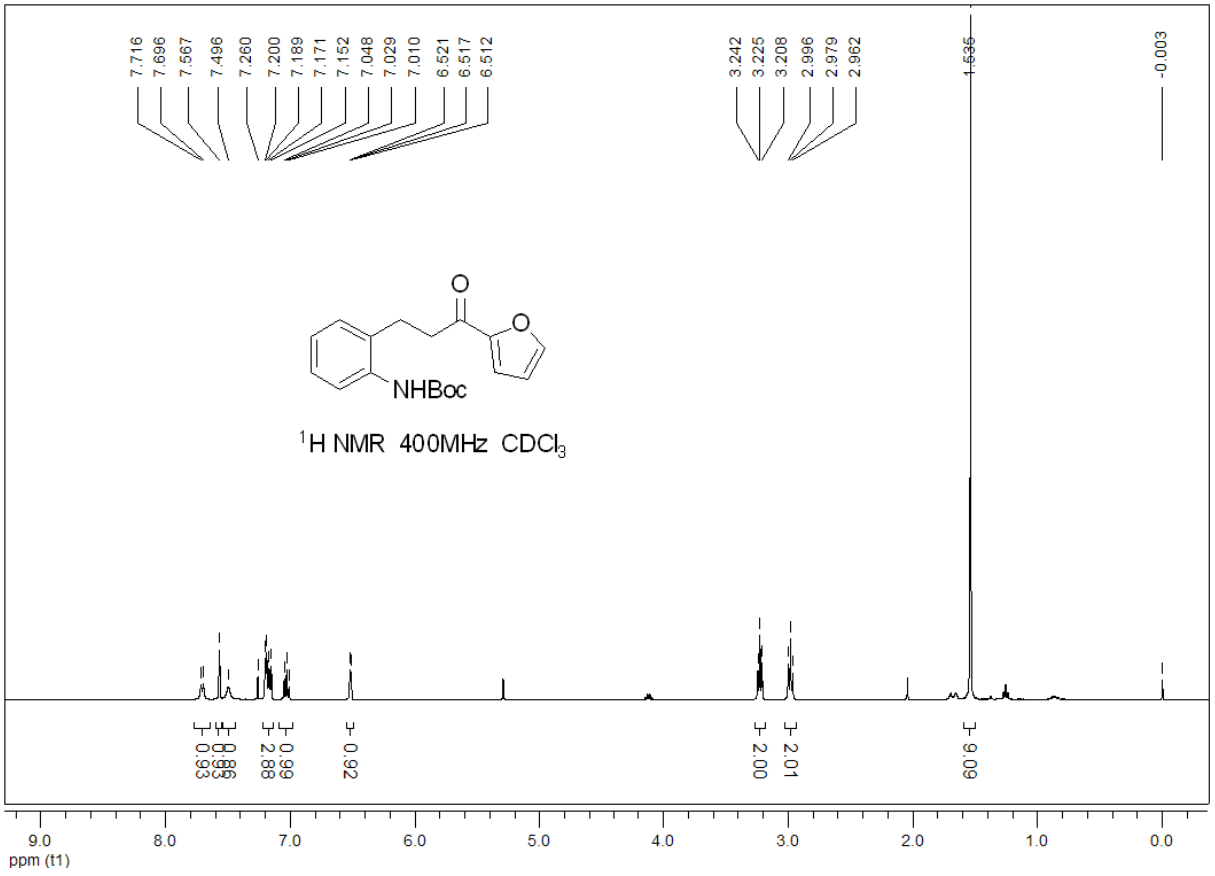

-104.577
O
NH
Boc
F
19F NMR 376 MHz CDCl3
0
-50
-100
-150
-200
ppm (t1)

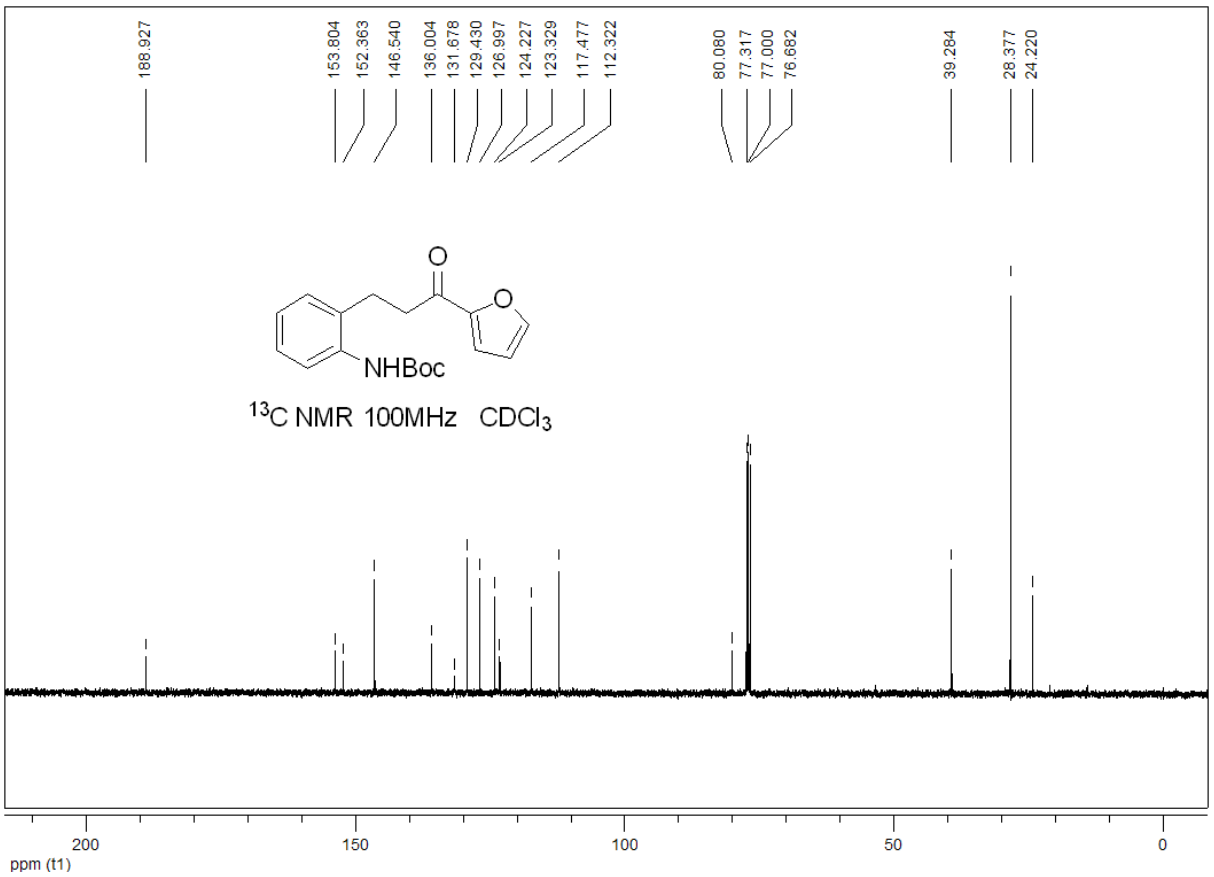
Compound **3e**:


7.905
7.884
7.712
7.693
7.497
7.429
7.408
7.260
7.215
7.195
7.175
7.156
7.060
7.041
7.023
3.359
3.342
3.326
3.026
3.009
2.992
1.534
-0.002
O
NHBoc
Cl
1H NMR 400MHz CDCl3
2.01
0.93
2.01
2.07
1.02
2.00
2.02
9.08
10.0
5.0
0.0
ppm (t1)

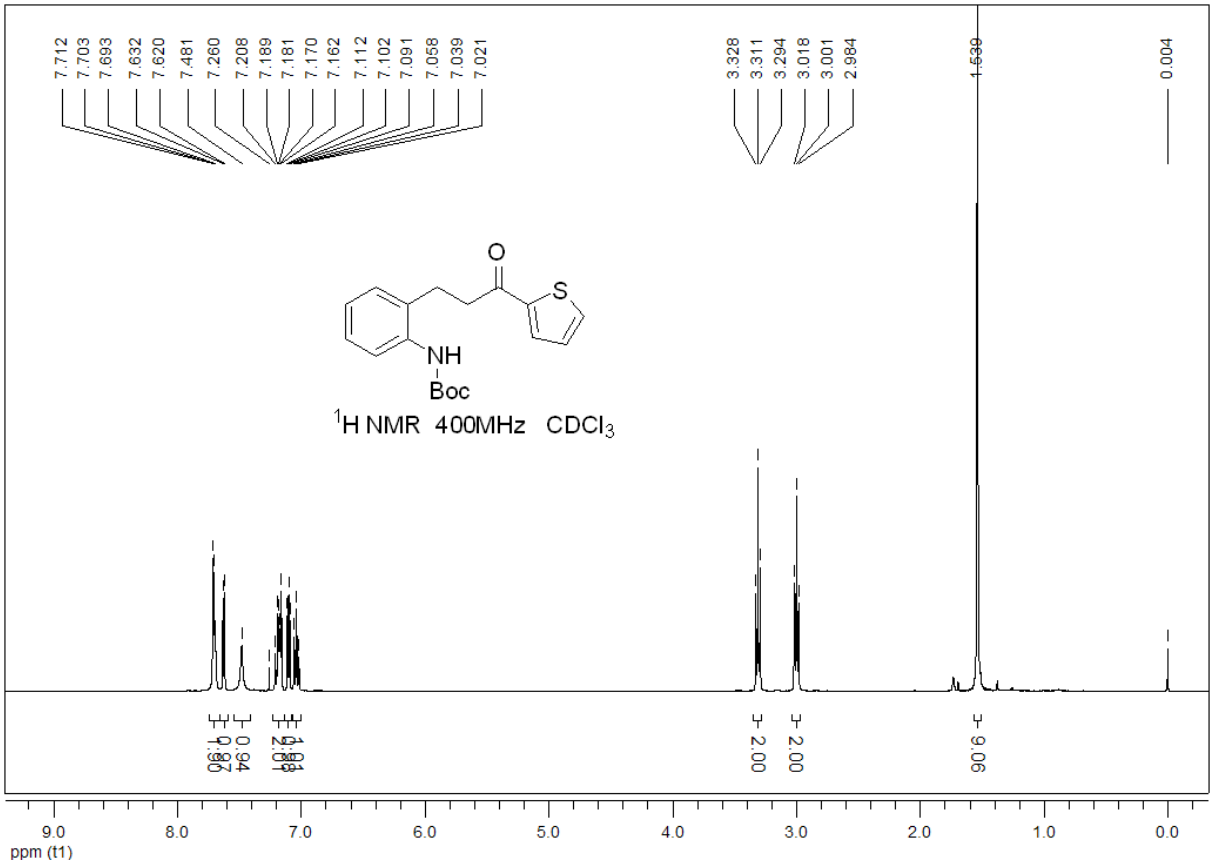

198.665
153.837
139.856
136.020
134.774
131.930
129.508
129.444
128.936
127.044
124.356
123.441
80.171
77.317
77.000
76.681
39.566
28.384
24.410
O
NHBoc
Cl
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

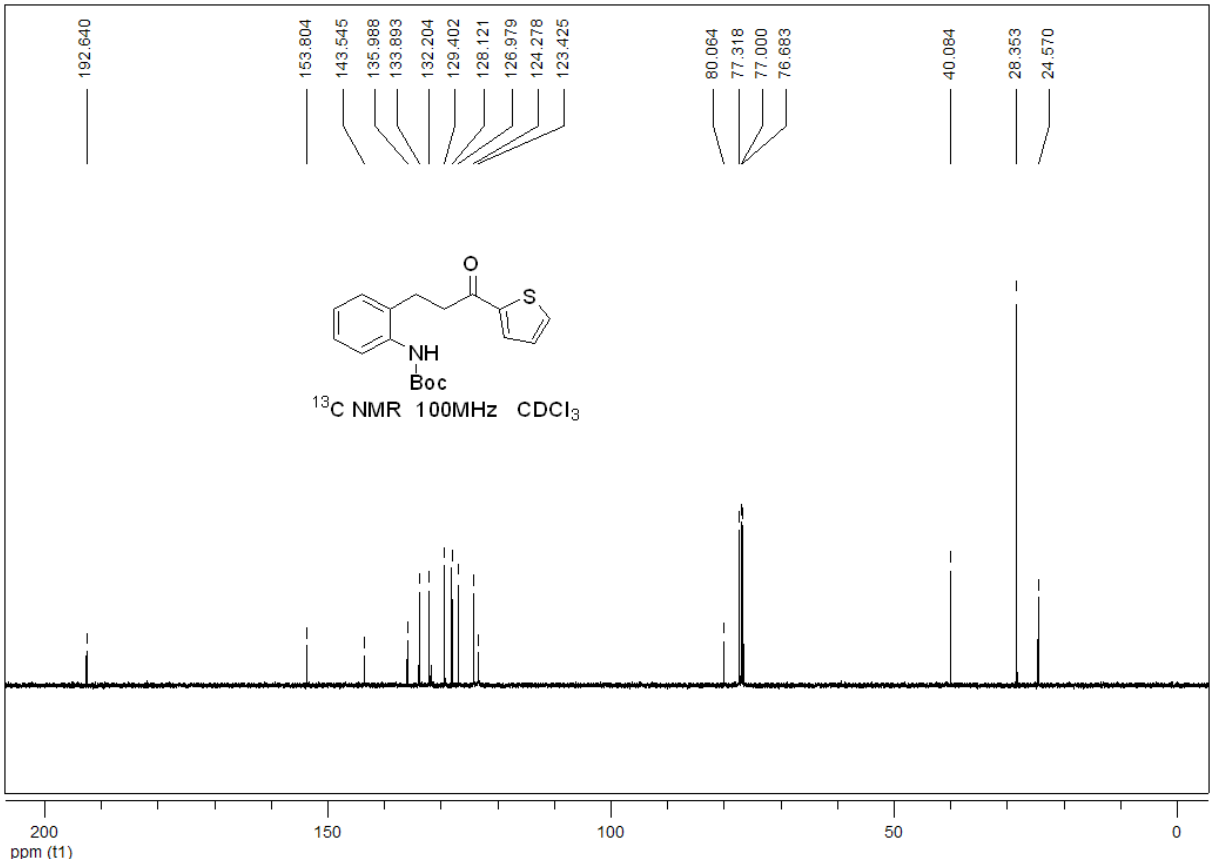
Compound **3f**:


7.716
7.696
7.567
7.496
7.260
7.200
7.189
7.171
7.152
7.048
7.029
7.010
6.521
6.517
6.512
3.242
3.225
3.208
2.996
2.979
2.962
1.535
-0.003
O
O
NHBoc
1H NMR 400MHz CDCl3
0.93
0.88
0.99
2.88
0.92
2.00
2.01
9.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

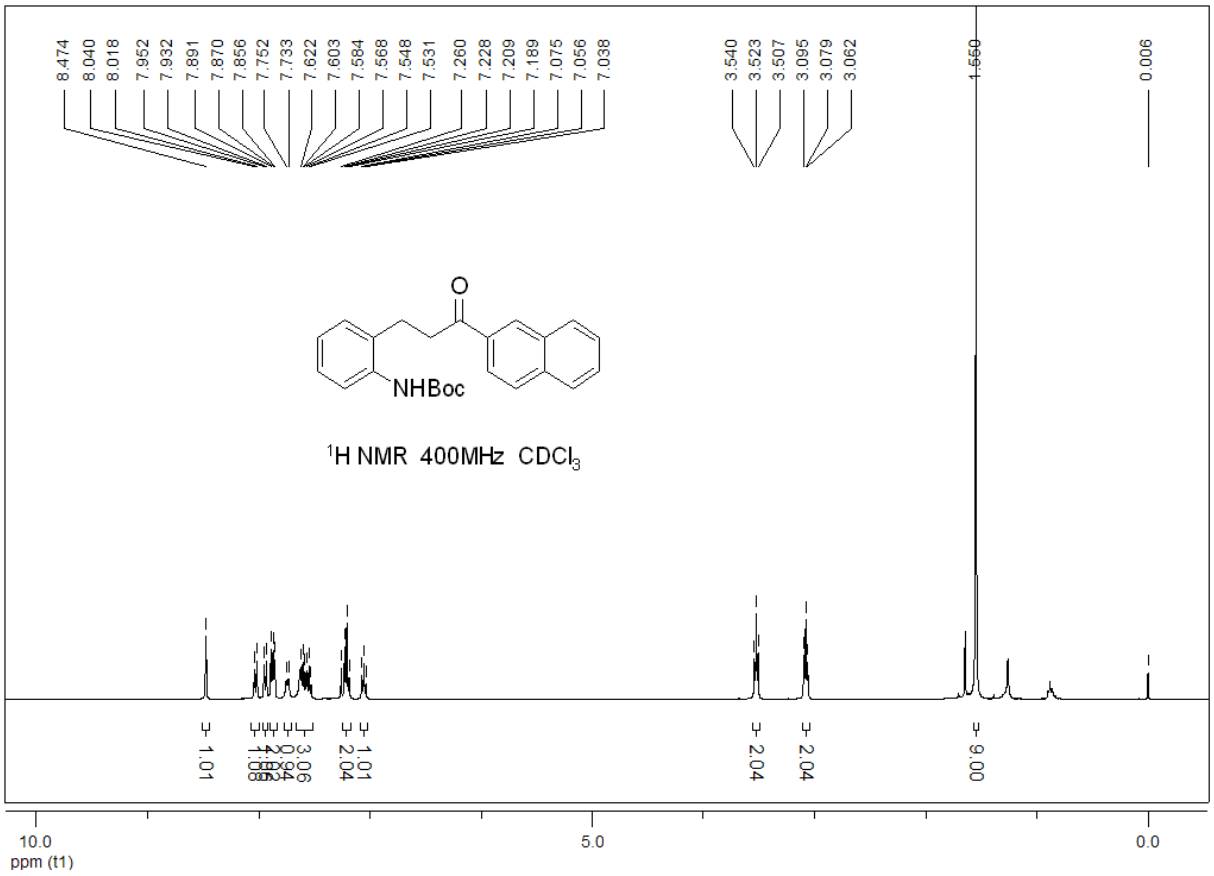

188.927
153.804
152.363
146.540
136.004
131.678
129.430
126.997
124.227
123.329
117.477
112.322
80.080
77.317
77.000
76.682
39.284
28.377
24.220
O
O
NHBoc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

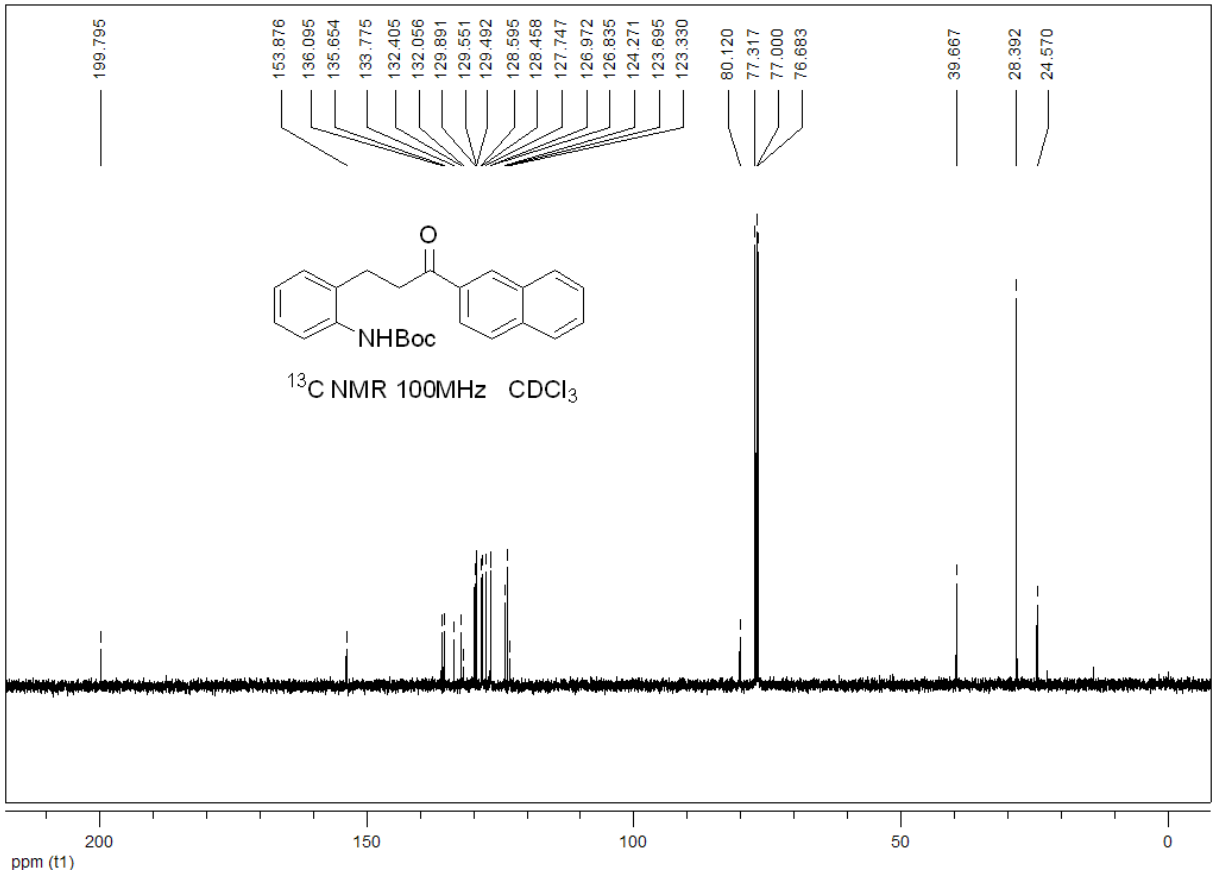
Compound **3g**:


7.712
7.703
7.693
7.632
7.620
7.481
7.260
7.208
7.189
7.181
7.170
7.162
7.112
7.102
7.091
7.058
7.039
7.021
3.328
3.311
3.294
3.018
3.001
2.984
1.539
0.004
O
S
NH
Boc
1H NMR 400MHz CDCl3
1.90
0.94
2.00
2.00
9.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

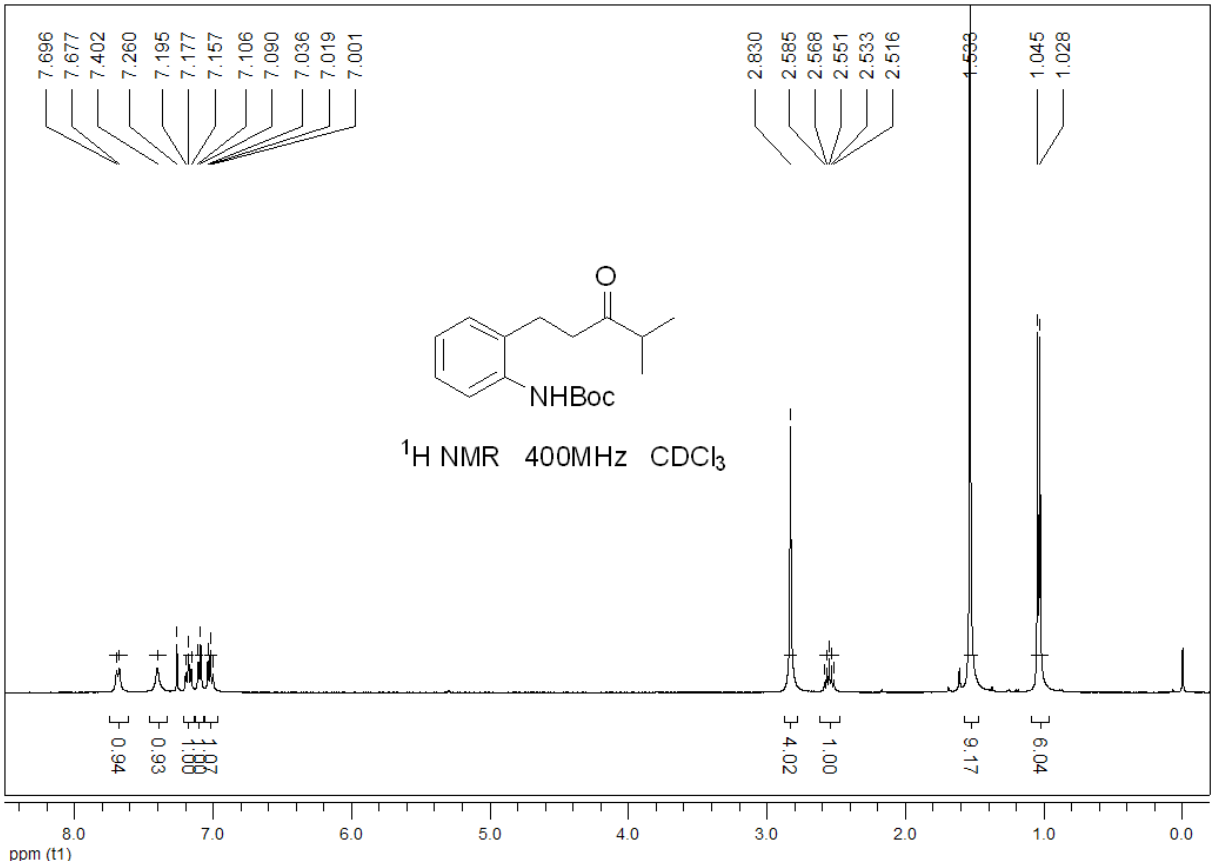

192.640
153.804
143.545
135.988
133.893
132.204
129.402
128.121
126.979
124.278
123.425
80.064
77.318
77.000
76.683
40.084
28.353
24.570
O
S
NH
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

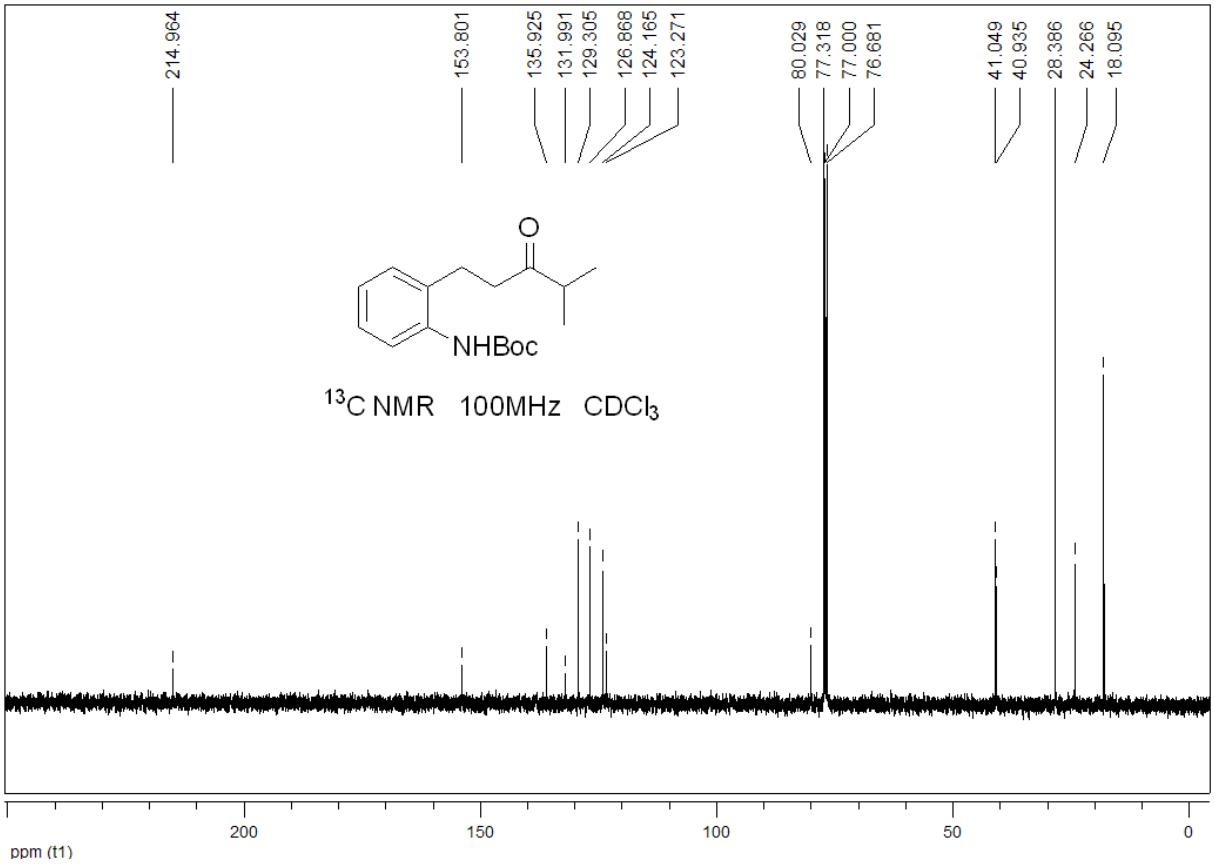
Compound **3h**:


8.474
8.040
8.018
7.952
7.932
7.891
7.870
7.856
7.752
7.733
7.622
7.603
7.584
7.568
7.548
7.531
7.260
7.228
7.209
7.189
7.075
7.056
7.038
3.540
3.523
3.507
3.095
3.079
3.062
1.560
0.006
O
NHBoc
1H NMR 400MHz CDCl3
1.01
3.06
2.04
1.01
2.04
2.04
9.00
10.0
5.0
0.0
ppm (t1)

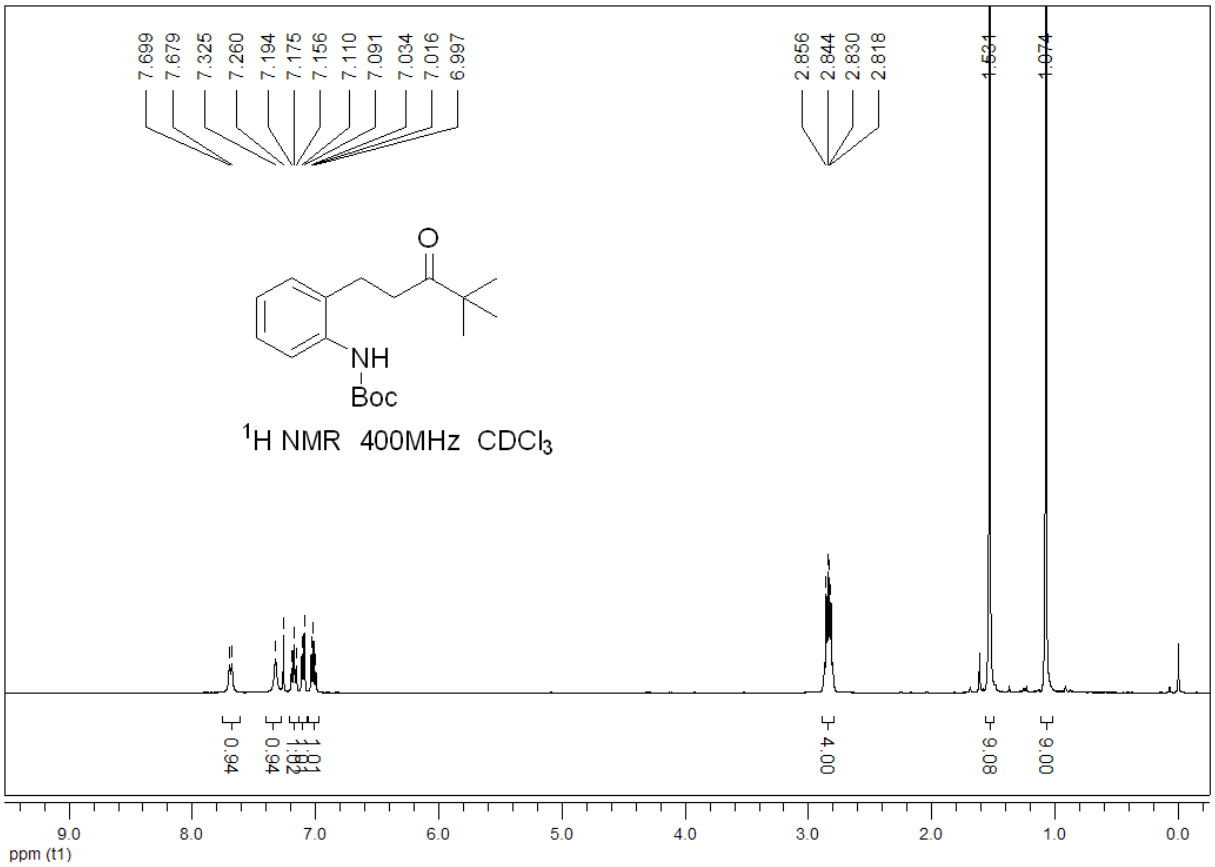

199.795
153.876
136.095
135.654
133.775
132.405
132.056
129.891
129.551
129.492
128.595
128.458
127.747
126.972
126.835
124.271
123.695
123.330
80.120
77.317
77.000
76.683
39.667
28.392
24.570
O
NHBoc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

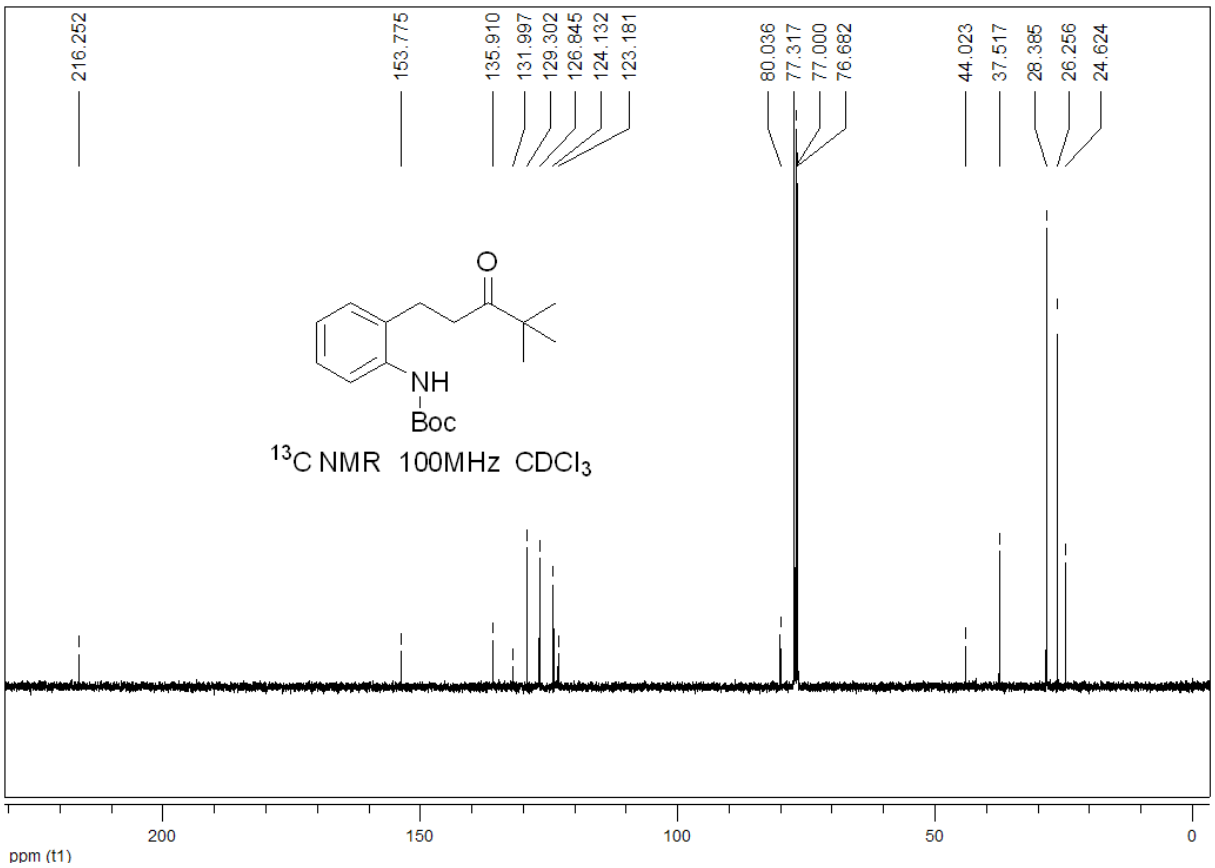
Compound **3i**:


7.696
7.677
7.402
7.260
7.195
7.177
7.157
7.106
7.090
7.036
7.019
7.001
2.830
2.585
2.568
2.551
2.533
2.516
1.533
1.045
1.028
O
NHBoc
1H NMR 400MHz CDCl3
0.94
0.93
1.88
1.02
4.02
1.00
9.17
6.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

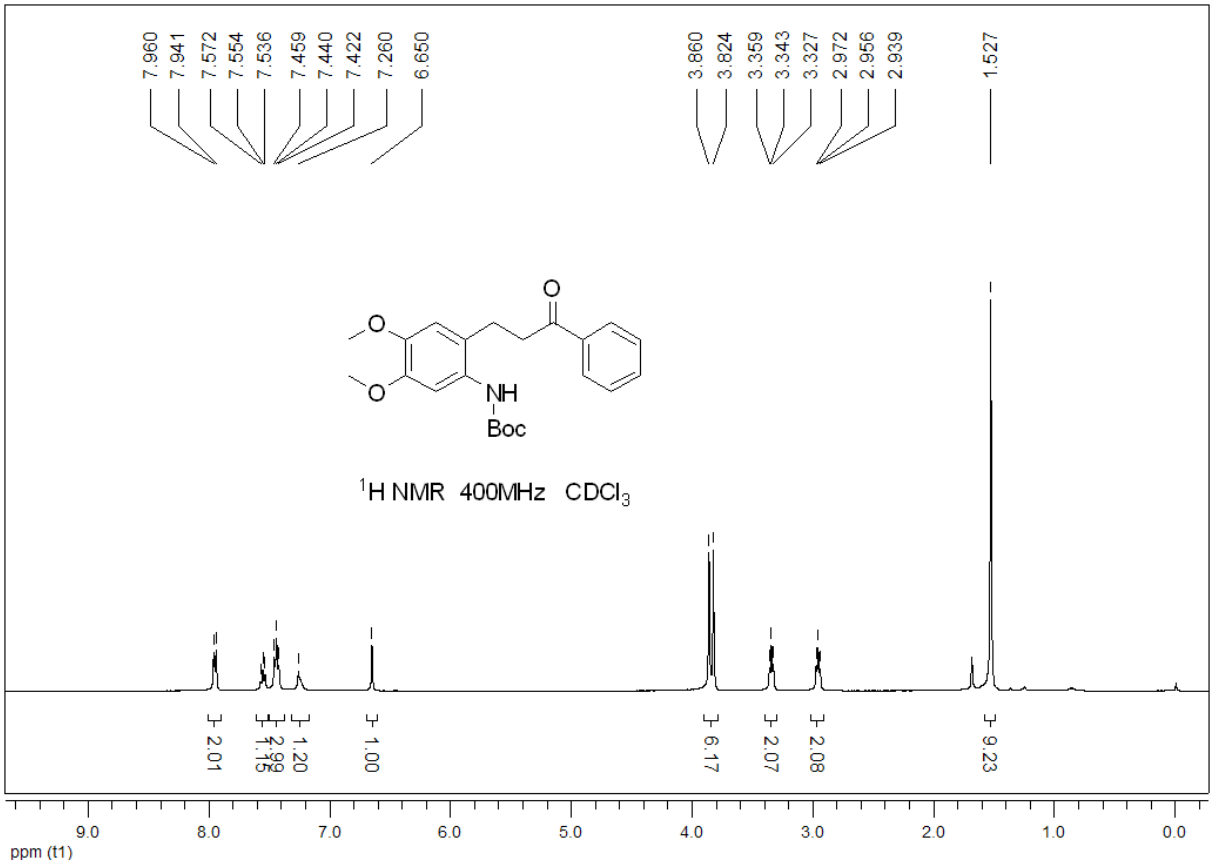

214.964
153.801
135.925
131.991
129.305
126.868
124.165
123.271
80.029
77.318
77.000
76.681
41.049
40.935
28.386
24.266
18.095
O
NHBoc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

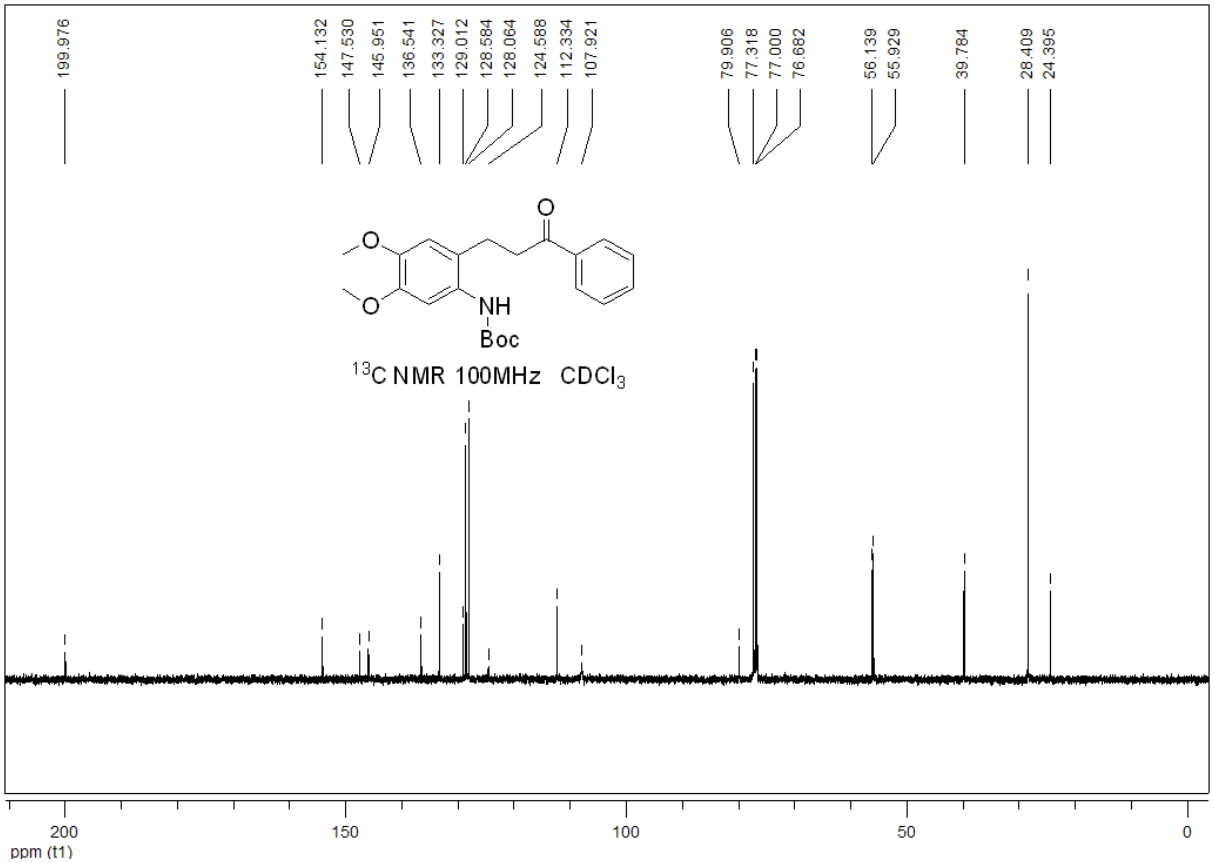
Compound **3j**:


7.699
7.679
7.325
7.260
7.194
7.175
7.156
7.110
7.091
7.034
7.016
6.997
2.856
2.844
2.830
2.818
1.531
1.074
O
NH
Boc
1H NMR 400MHz CDCl3
0.94
0.94
4.00
9.08
9.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

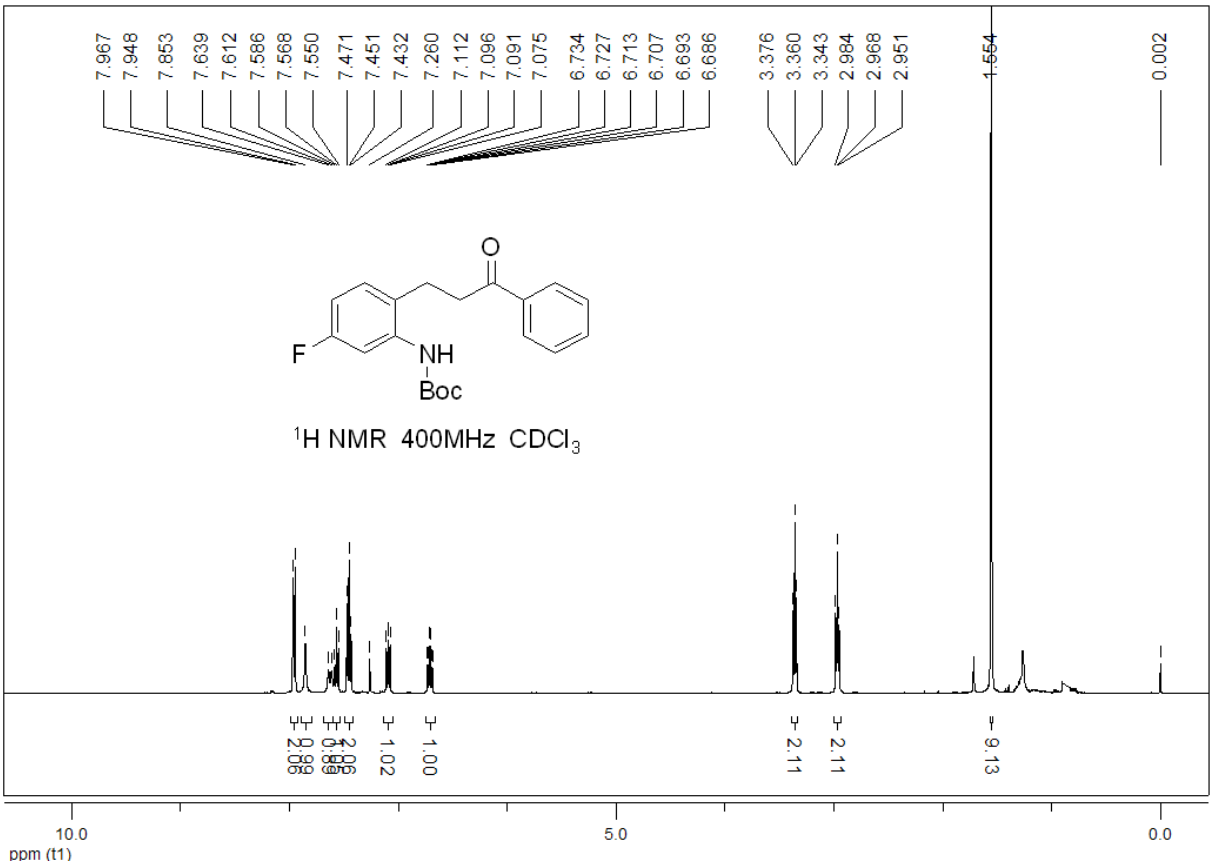

216.252
153.775
135.910
131.997
129.302
126.845
124.132
123.181
80.036
77.317
77.000
76.682
44.023
37.517
28.385
26.256
24.624
O
NH
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

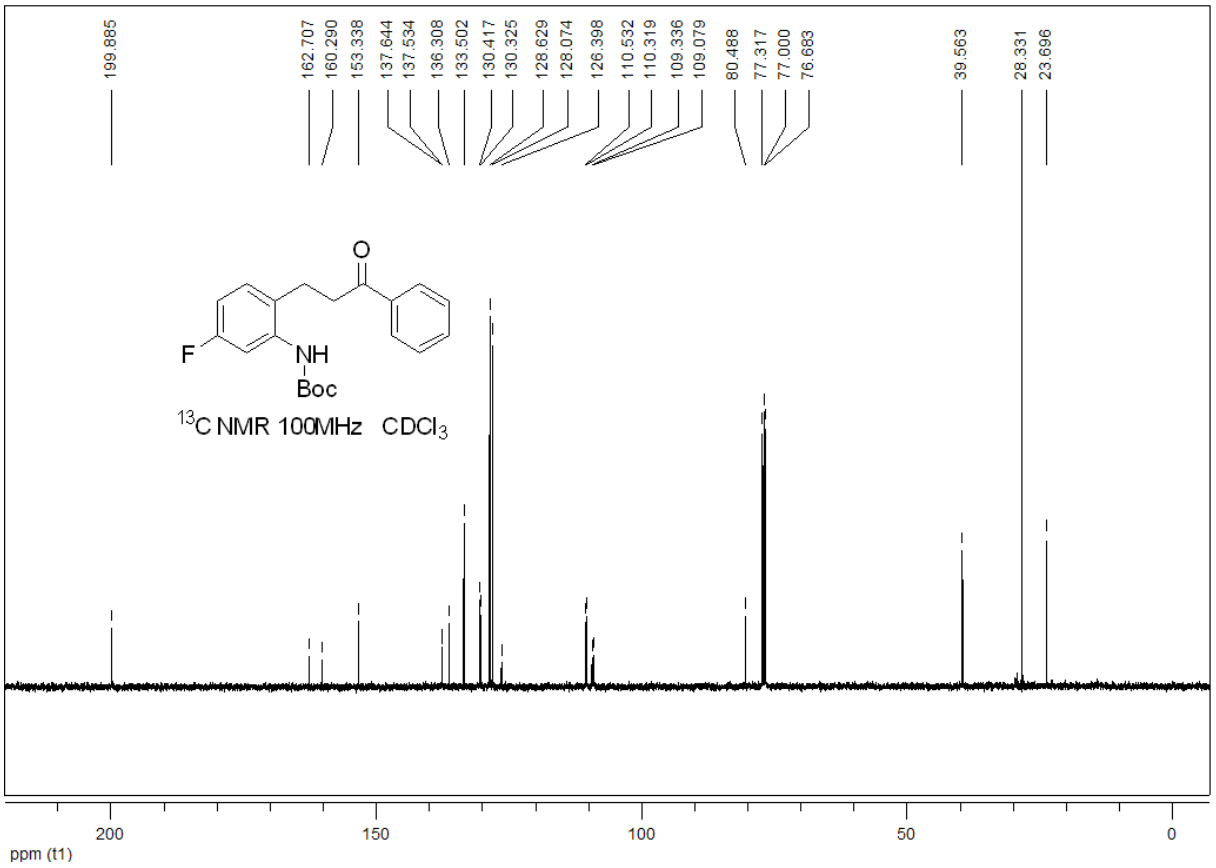
Compound **3k**:

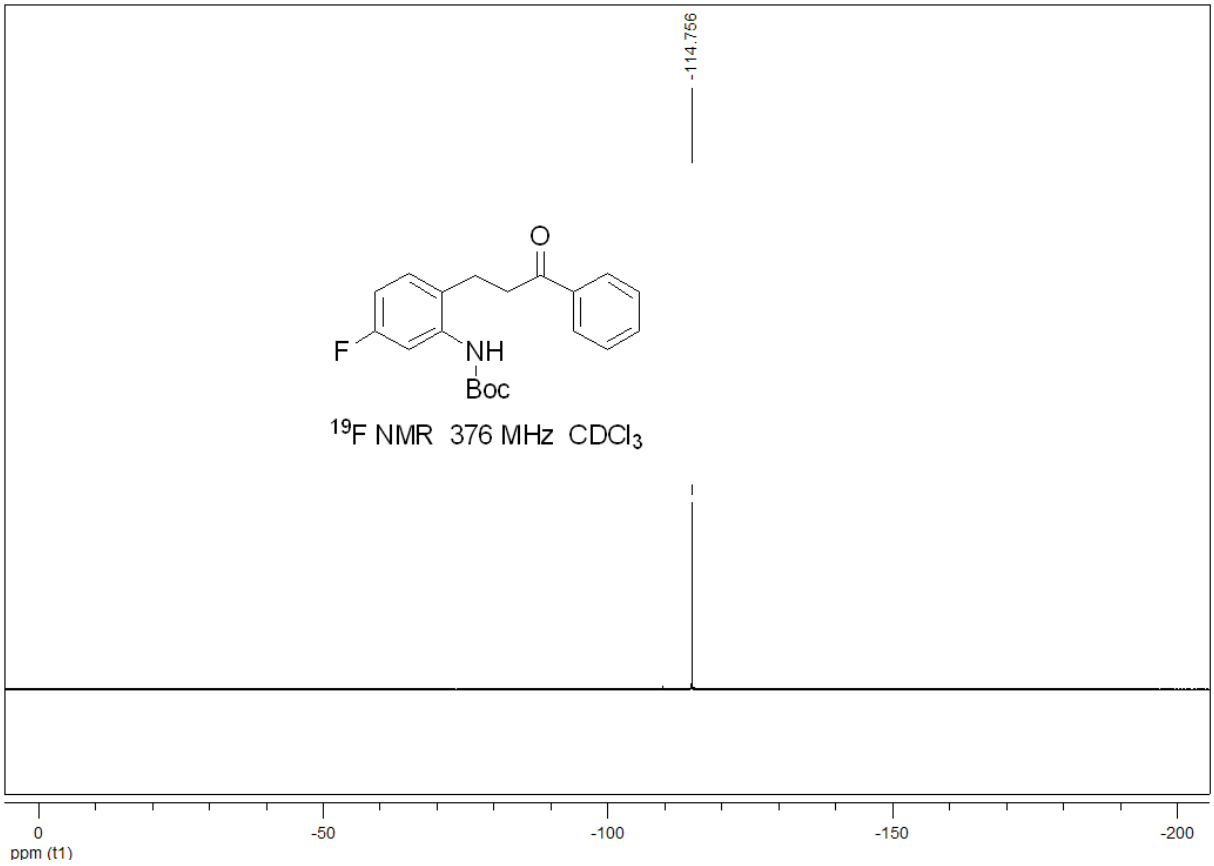

7.960
7.941
7.572
7.554
7.536
7.459
7.440
7.422
7.260
6.650
3.860
3.824
3.359
3.343
3.327
2.972
2.956
2.939
1.527
O
O
O
NH
Boc
1H NMR 400MHz CDCl3
2.01
1.15
2.99
1.20
1.00
6.17
2.07
2.08
9.23
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


199.976
154.132
147.530
145.951
136.541
133.327
129.012
128.584
128.064
124.588
112.334
107.921
79.906
77.318
77.000
76.682
56.139
55.929
39.784
28.409
24.395
O
O
O
NH
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

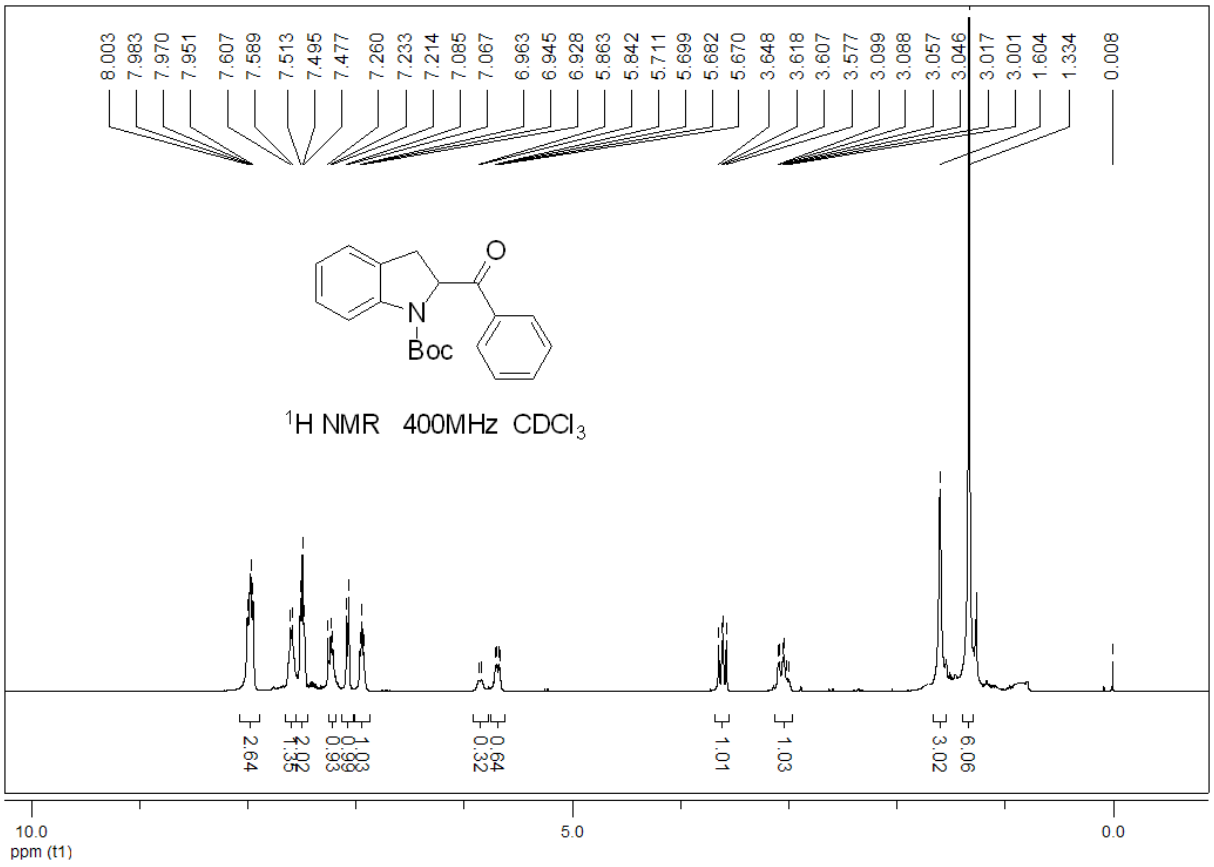
Compound **3l**:

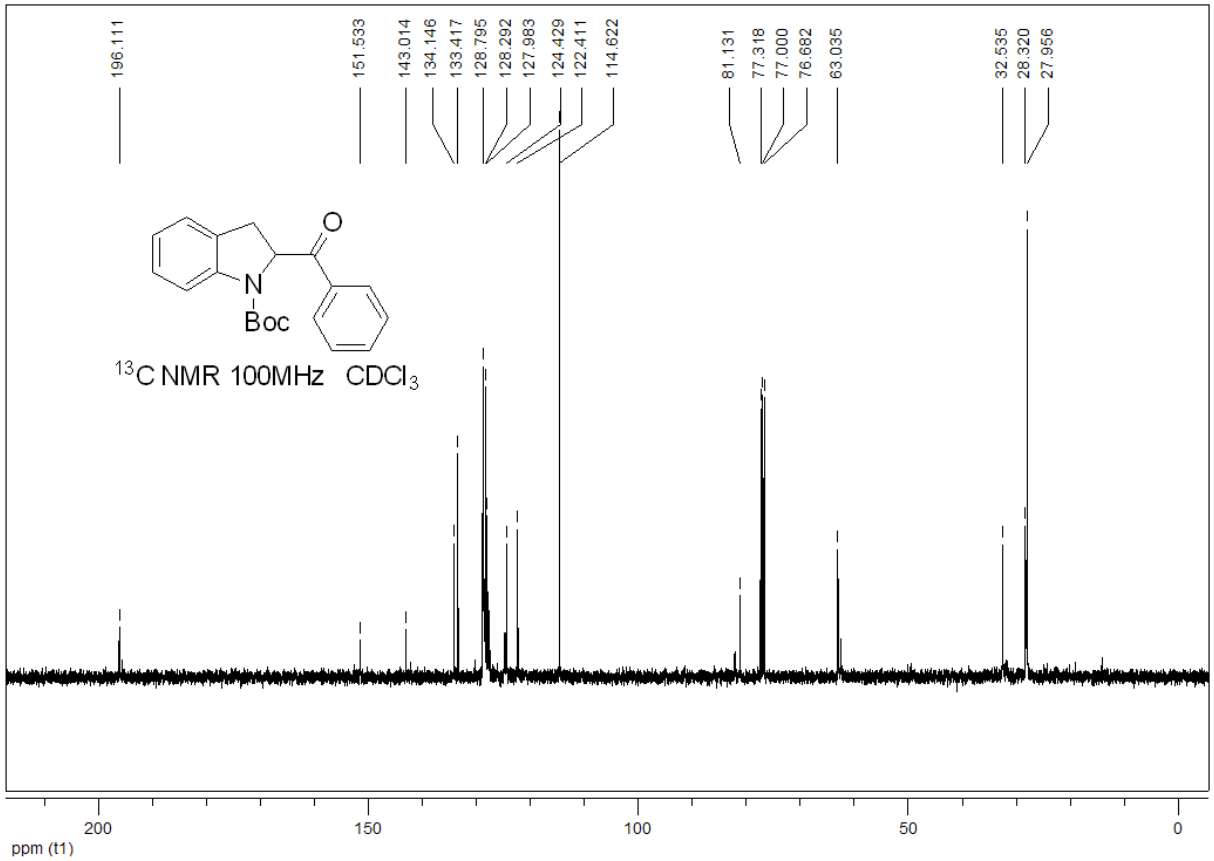

7.967
7.948
7.853
7.639
7.612
7.586
7.568
7.550
7.471
7.451
7.432
7.260
7.112
7.096
7.091
7.075
6.734
6.727
6.713
6.707
6.693
6.686
3.376
3.360
3.343
2.984
2.968
2.951
1.554
0.002
O
F
NH
Boc
1H NMR 400MHz CDCl3
2.06
0.99
1.08
1.02
1.00
2.11
2.11
9.13
10.0
5.0
0.0
ppm (t1)


199.885
162.707
160.290
153.338
137.644
137.534
136.308
133.502
130.417
130.325
128.629
128.074
126.398
110.532
110.319
109.336
109.079
80.488
77.317
77.000
76.683
39.563
28.331
23.696
O
F
NH
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

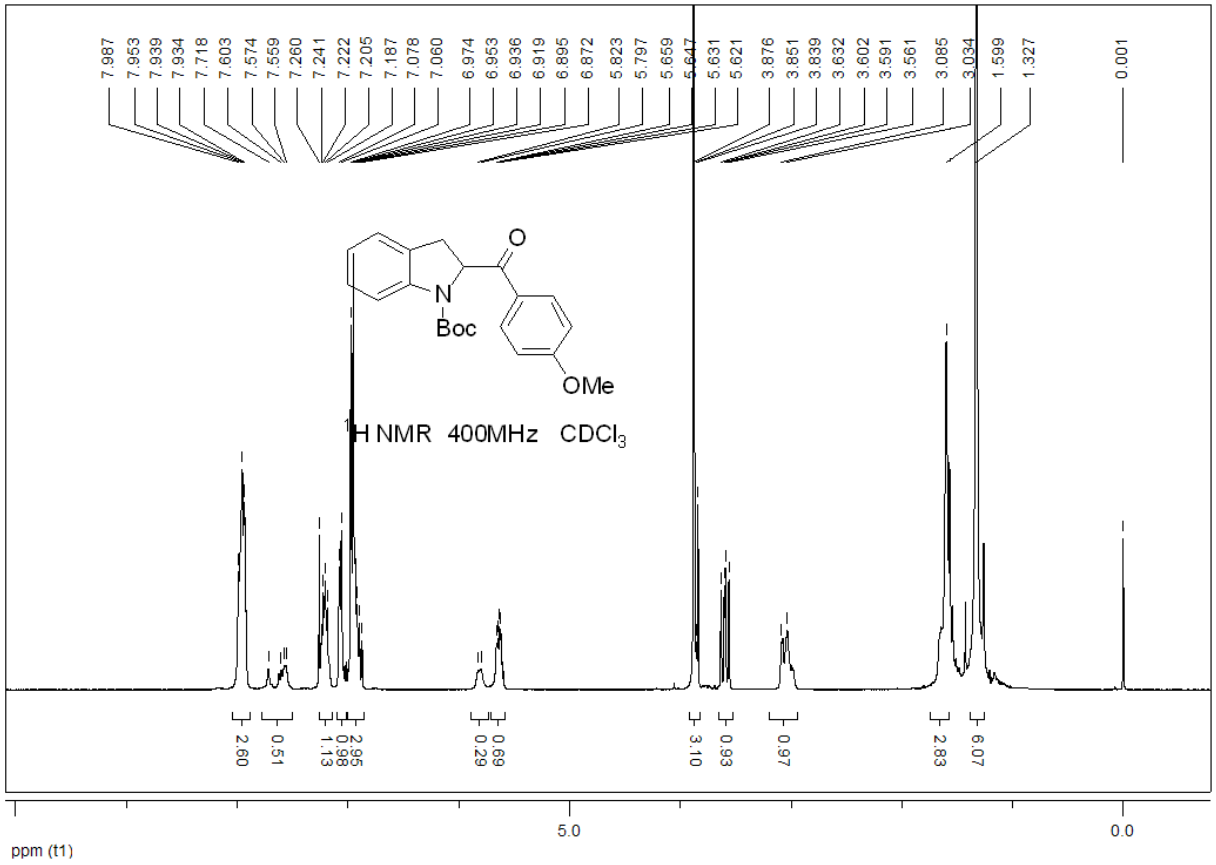

-114.756
O
F
NH
Boc
19F NMR 376 MHz CDCl3
0
-50
-100
-150
-200
ppm (t1)

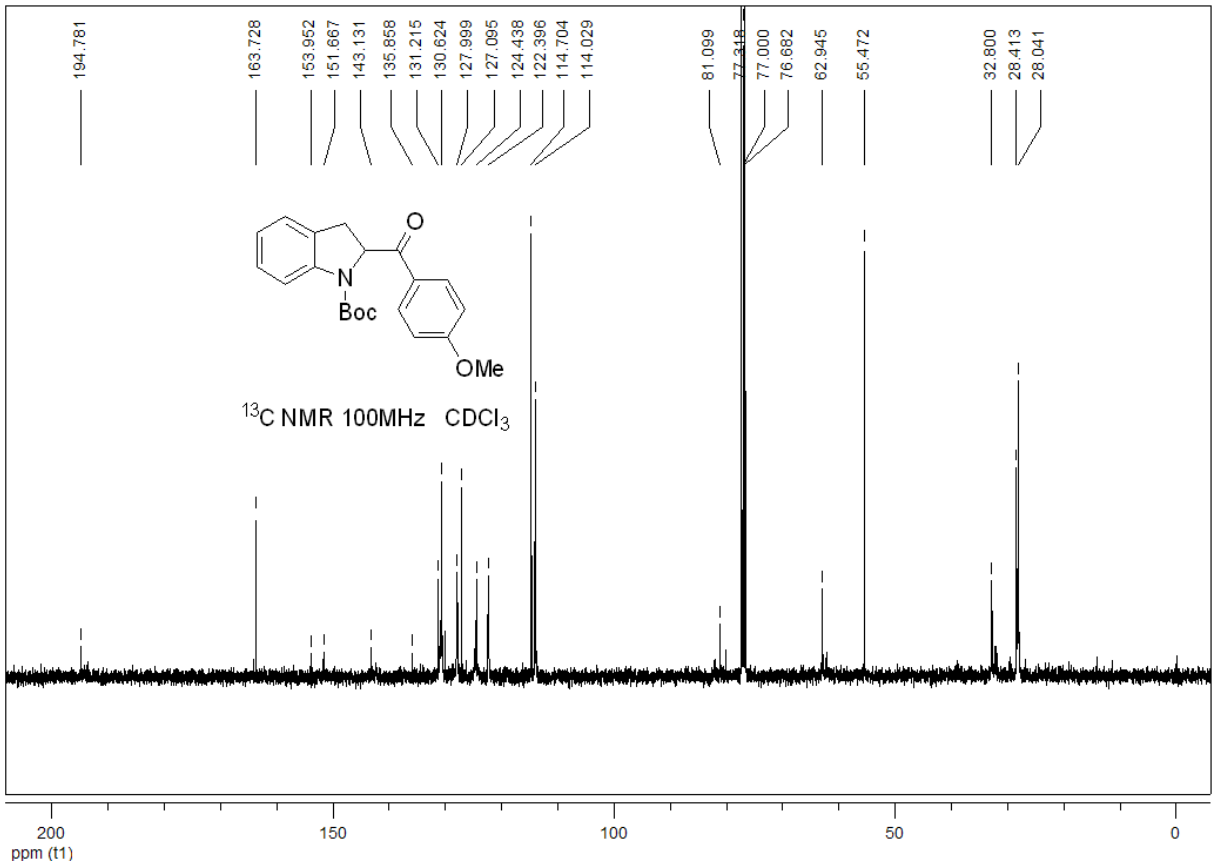
Compound **4a**:


8.003
7.983
7.970
7.951
7.607
7.589
7.513
7.495
7.477
7.260
7.233
7.214
7.085
7.067
6.963
6.945
6.928
5.863
5.842
5.711
5.699
5.682
5.670
3.648
3.618
3.607
3.577
3.099
3.088
3.057
3.046
3.017
3.001
1.604
1.334
0.008
O
N
Boc
1H NMR 400MHz CDCl3
2.64
2.35
1.03
0.93
0.98
0.64
0.32
1.01
1.03
3.02
6.06
10.0
5.0
0.0
ppm (t1)

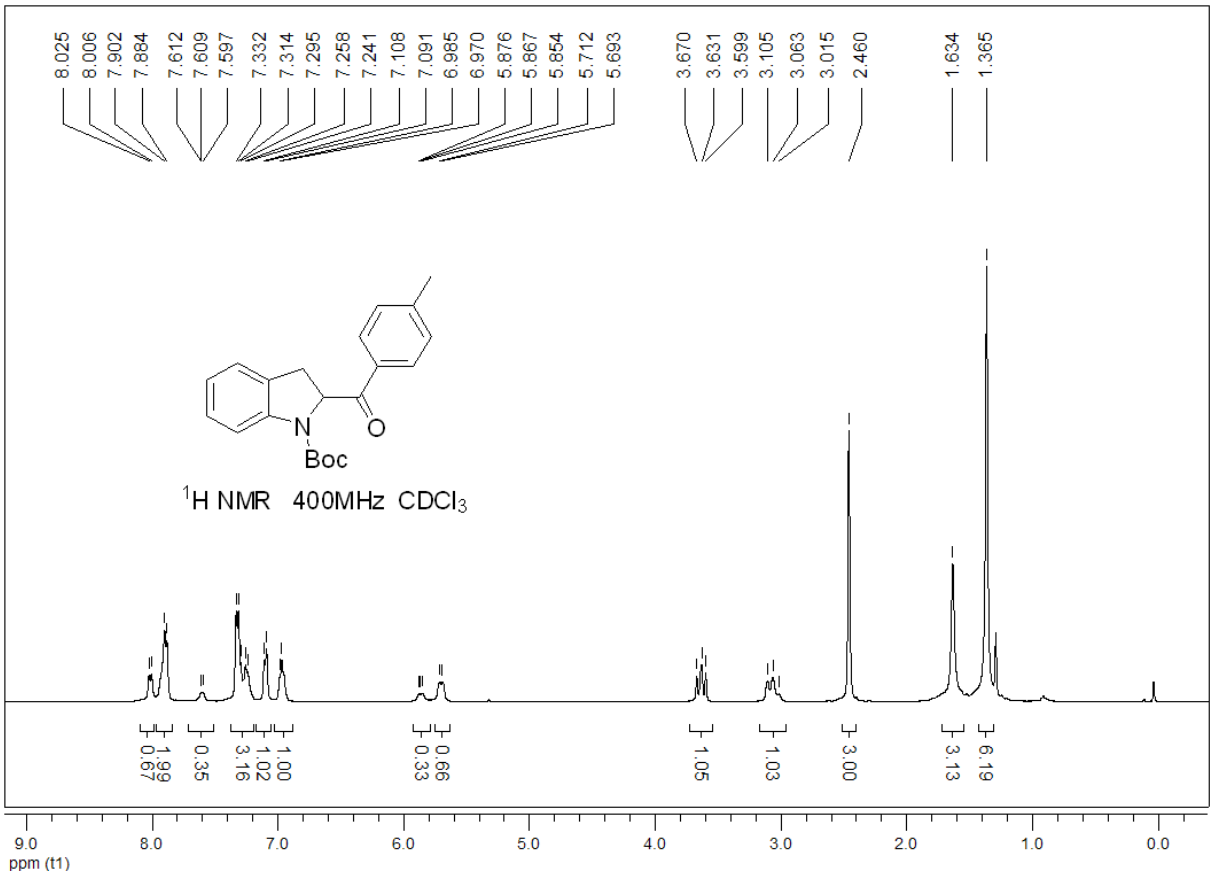

196.111
151.533
143.014
134.146
133.417
128.795
128.292
127.983
124.429
122.411
114.622
81.131
77.318
77.000
76.682
63.035
32.535
28.320
27.956
O
N
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

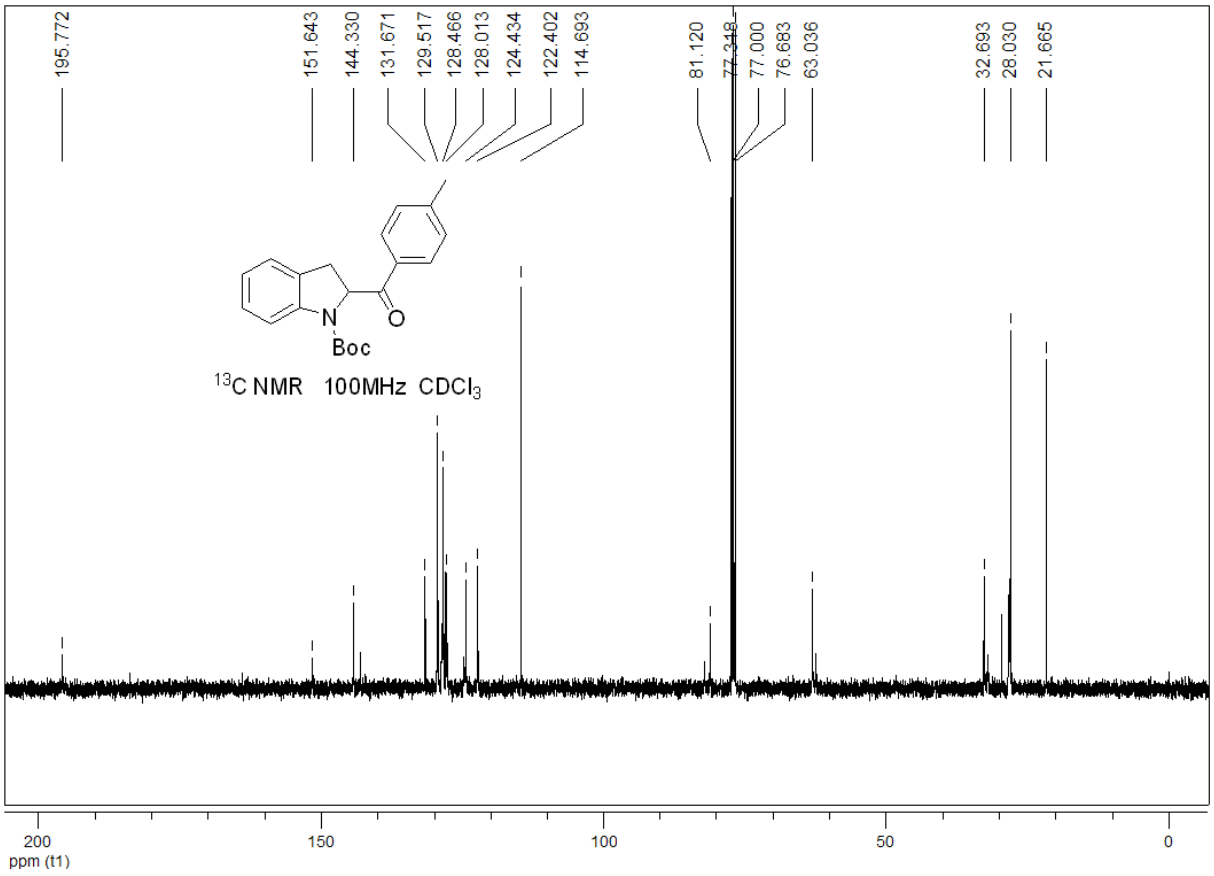
Compound **4b**:


7.987
7.953
7.939
7.934
7.718
7.603
7.574
7.559
7.260
7.241
7.222
7.205
7.187
7.078
7.060
6.974
6.953
6.936
6.919
6.895
6.872
5.823
5.797
5.659
5.647
5.631
5.621
3.876
3.851
3.839
3.632
3.602
3.591
3.561
3.085
3.034
1.599
1.327
0.001
O
N
Boc
OMe
^{1}H NMR 400MHz CDCl$_3$
2.60
0.51
1.13
0.98
2.95
0.69
0.29
3.10
0.93
0.97
2.83
6.07
5.0
0.0
ppm (t1)

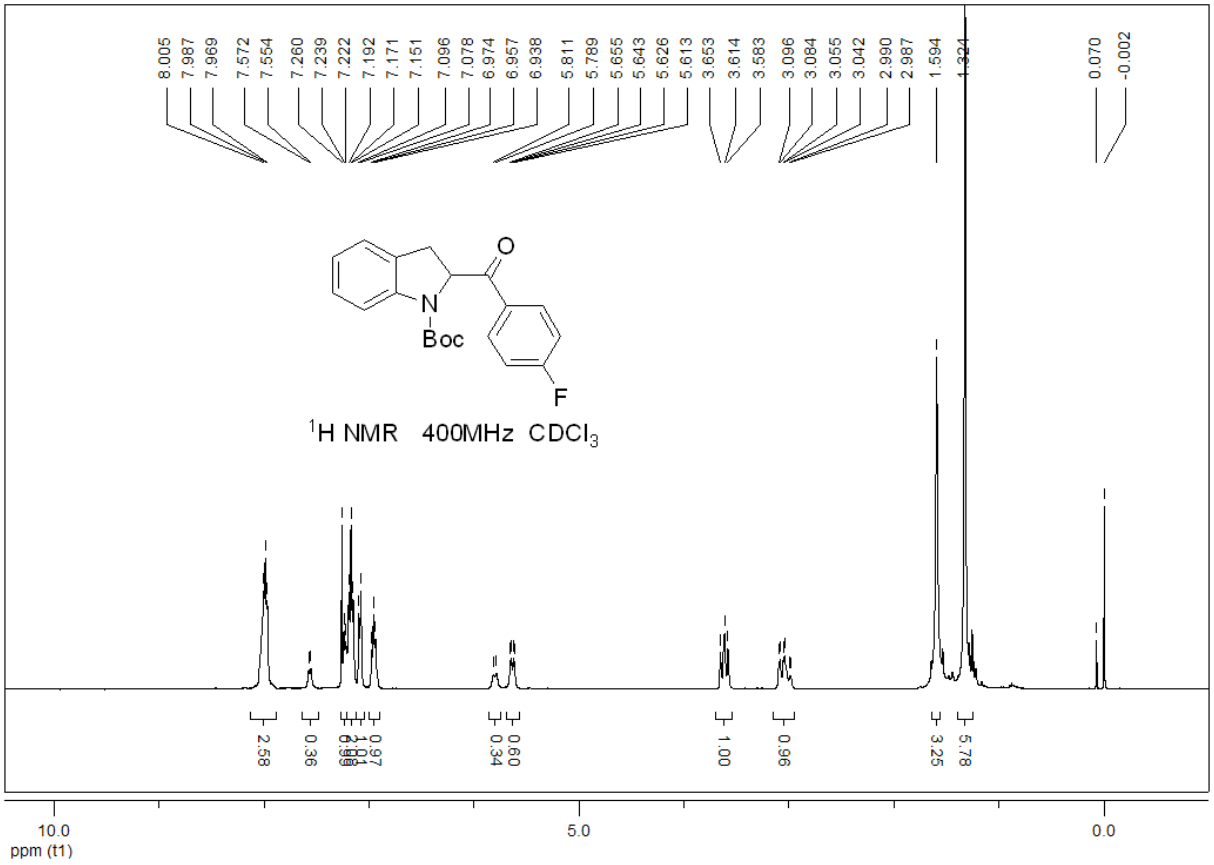

194.781
163.728
153.952
151.667
143.131
135.858
131.215
130.624
127.999
127.095
124.438
122.396
114.704
114.029
81.099
77.318
77.000
76.682
62.945
55.472
32.800
28.413
28.041
O
N
Boc
OMe
^{13}C NMR 100MHz CDCl$_3$
200
150
100
50
0
ppm (t1)

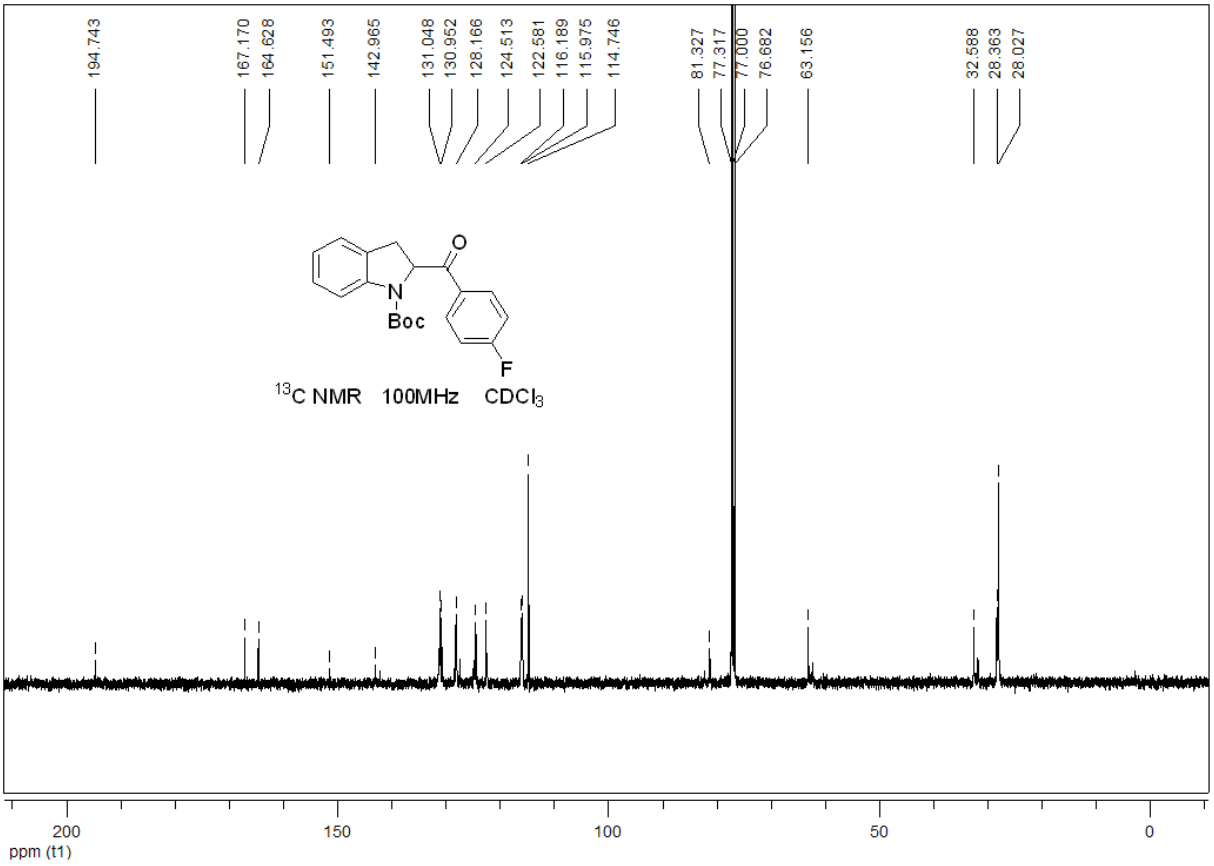
Compound **4c**:

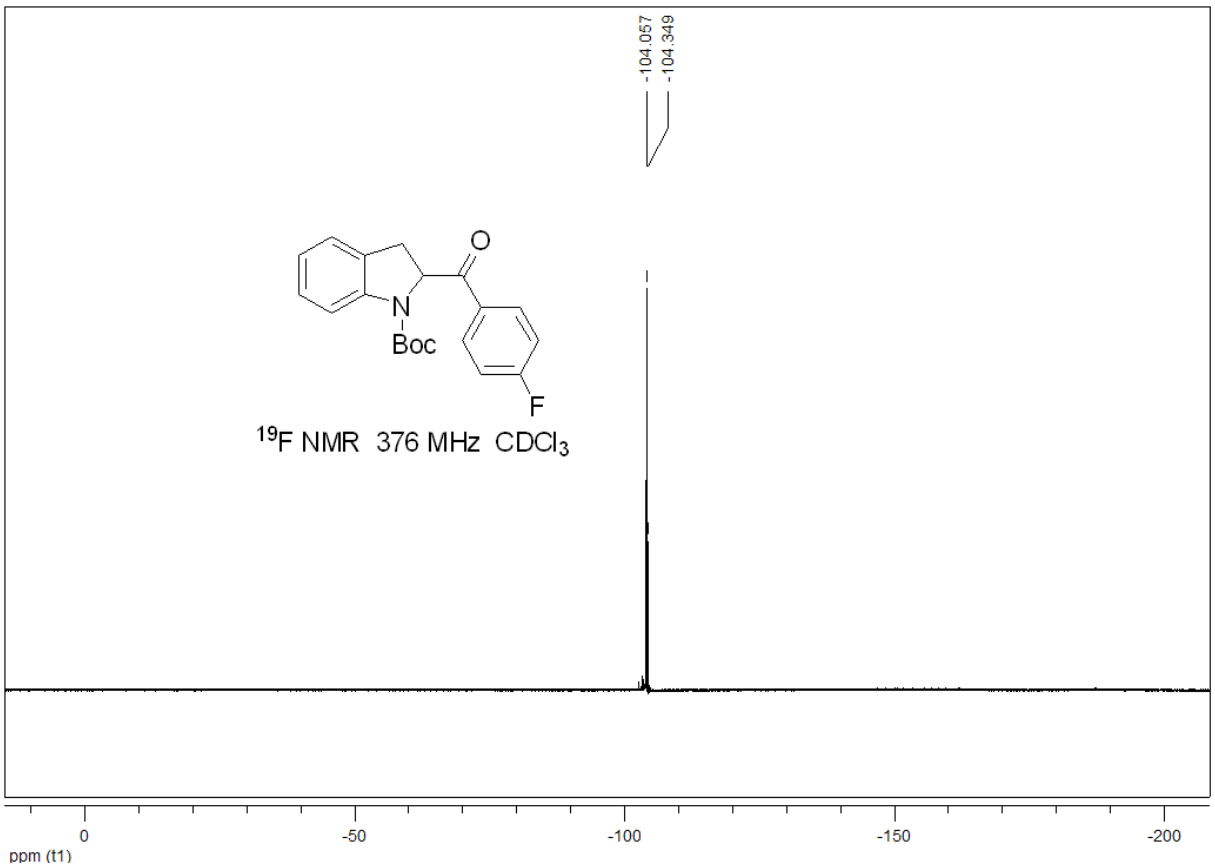

8.025
8.006
7.902
7.884
7.612
7.609
7.597
7.332
7.314
7.295
7.258
7.241
7.108
7.091
6.985
6.970
5.876
5.867
5.854
5.712
5.693
3.670
3.631
3.599
3.105
3.063
3.015
2.460
1.634
1.365
N
O
Boc
1H NMR 400MHz CDCl3
0.67
1.99
0.35
3.16
1.02
1.00
0.33
0.66
1.05
1.03
3.00
3.13
6.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


195.772
151.643
144.330
131.671
129.517
128.466
128.013
124.434
122.402
114.693
81.120
77.348
77.000
76.683
63.036
32.693
28.030
21.665
N
O
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

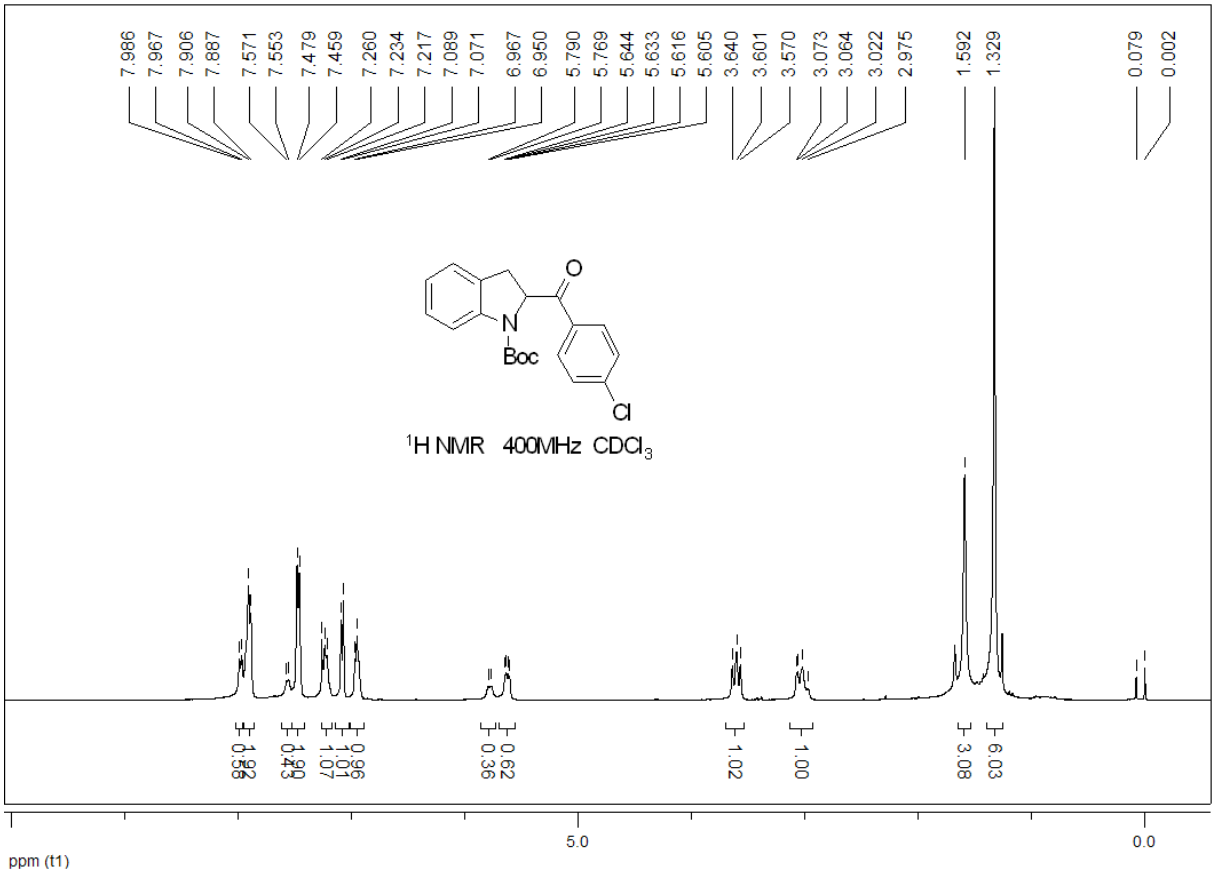
Compound **4d**:

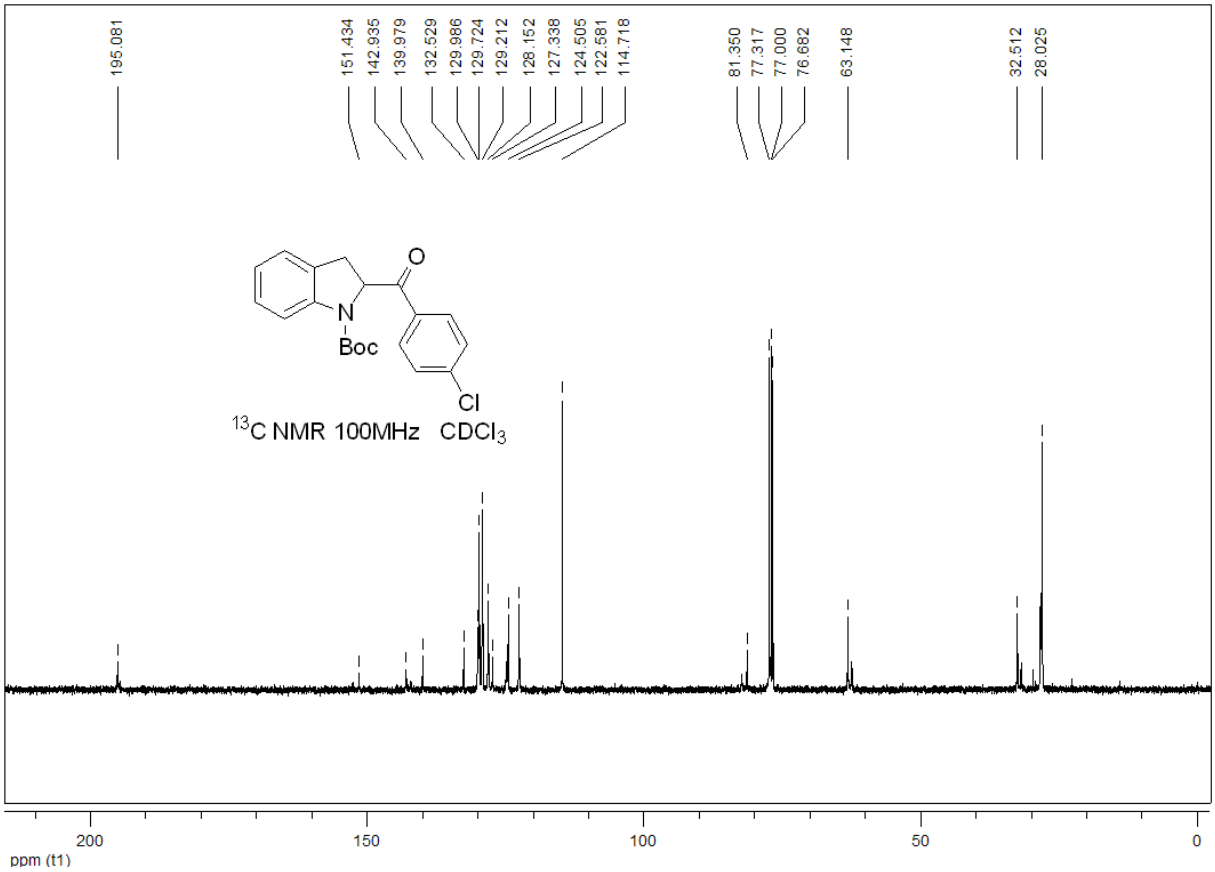

8.005
7.987
7.969
7.572
7.554
7.260
7.239
7.222
7.192
7.171
7.151
7.096
7.078
6.974
6.957
6.938
5.811
5.789
5.655
5.643
5.626
5.613
3.653
3.614
3.583
3.096
3.084
3.055
3.042
2.990
2.987
1.594
1.324
0.070
-0.002
O
N
Boc
F
1H NMR 400MHz CDCl3
2.58
0.36
0.97
0.60
0.34
1.00
0.96
3.25
5.78
10.0
5.0
0.0
ppm (t1)


194.743
167.170
164.628
151.493
142.965
131.048
130.952
128.166
124.513
122.581
116.189
115.975
114.746
81.327
77.317
77.000
76.682
63.156
32.588
28.363
28.027
O
N
Boc
F
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

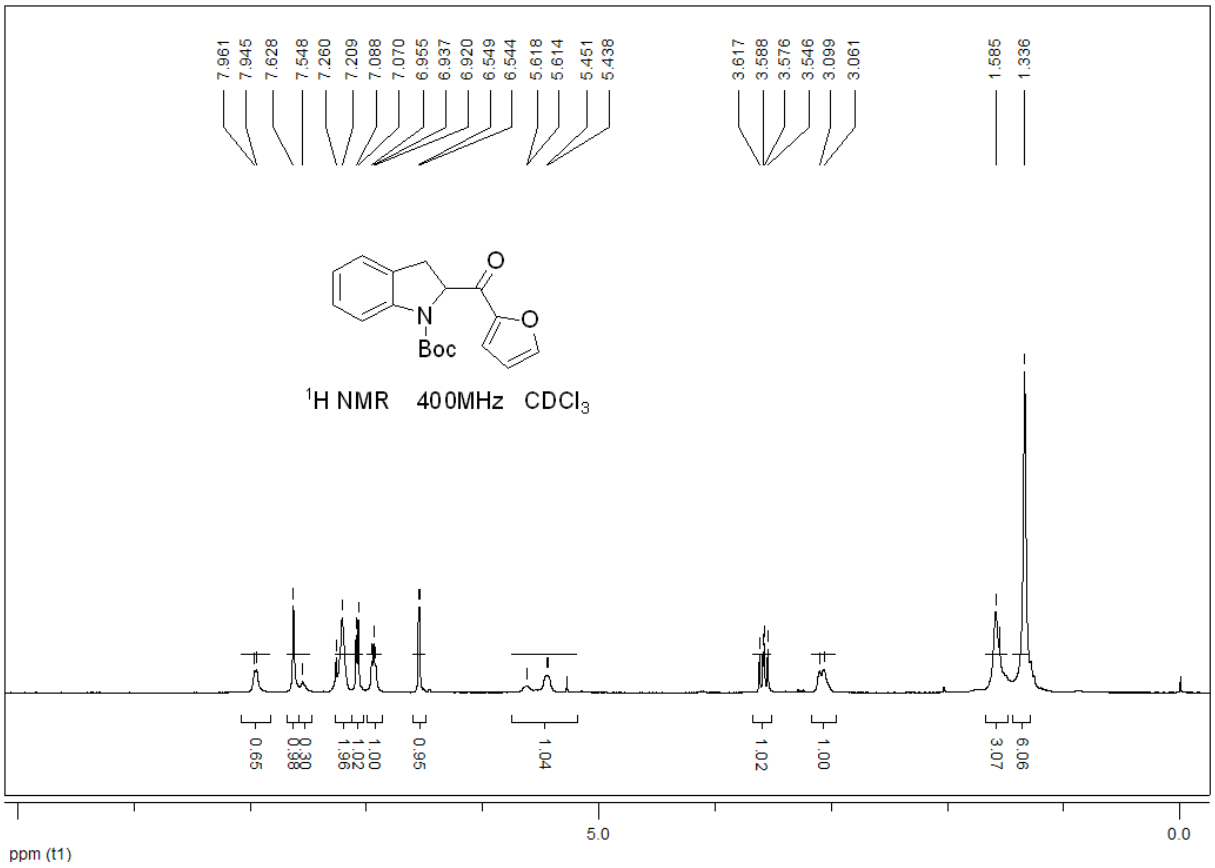

-104.057
-104.349
O
N
Boc
F
^{19}F NMR 376 MHz $CDCl_3$
0
-50
-100
-150
-200
ppm (t1)

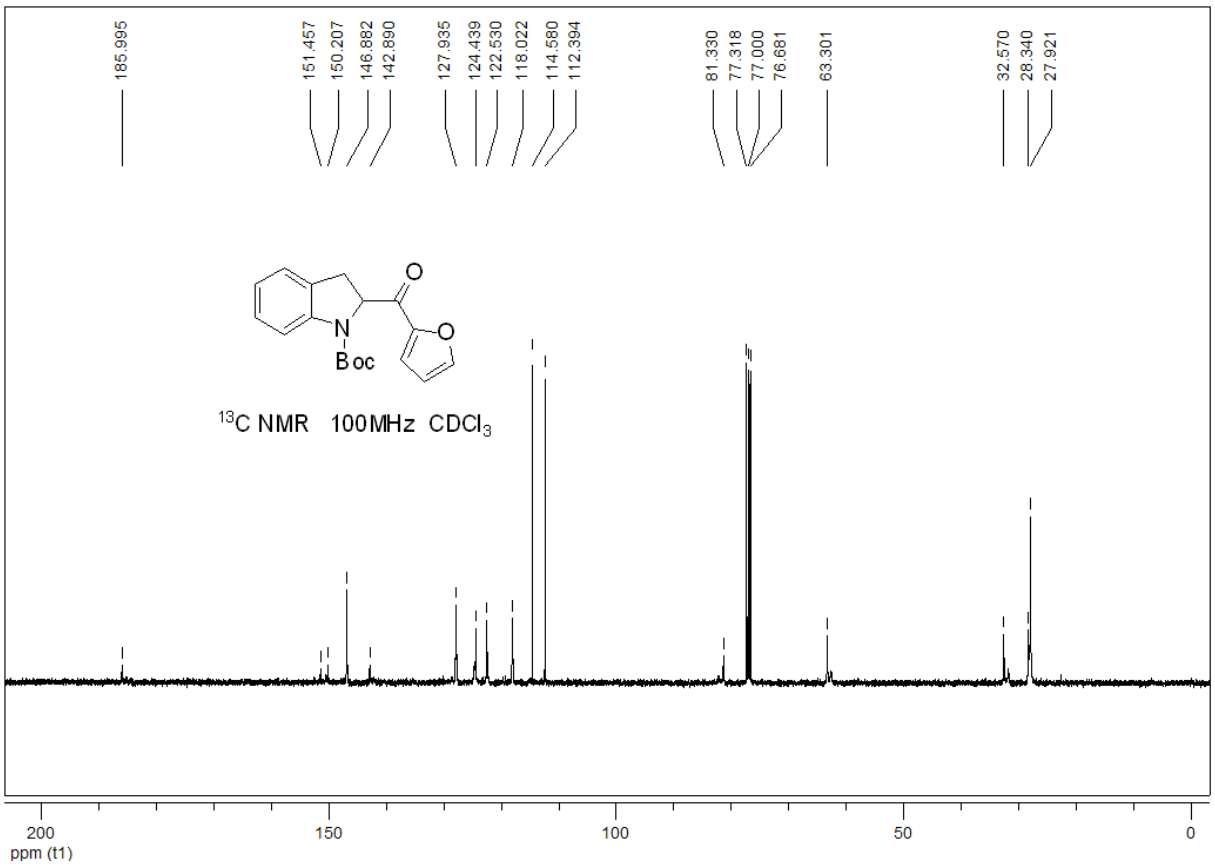
Compound **4e**:


7.986
7.967
7.906
7.887
7.571
7.553
7.479
7.459
7.260
7.234
7.217
7.089
7.071
6.967
6.950
5.790
5.769
5.644
5.633
5.616
5.605
3.640
3.601
3.570
3.073
3.064
3.022
2.975
1.592
1.329
0.079
0.002
O
N
Boc
Cl
^{1}H NMR 400MHz $CDCl_3$
0.96
1.07
1.01
0.90
0.36
0.62
1.02
1.00
3.08
6.03
5.0
0.0
ppm (t1)

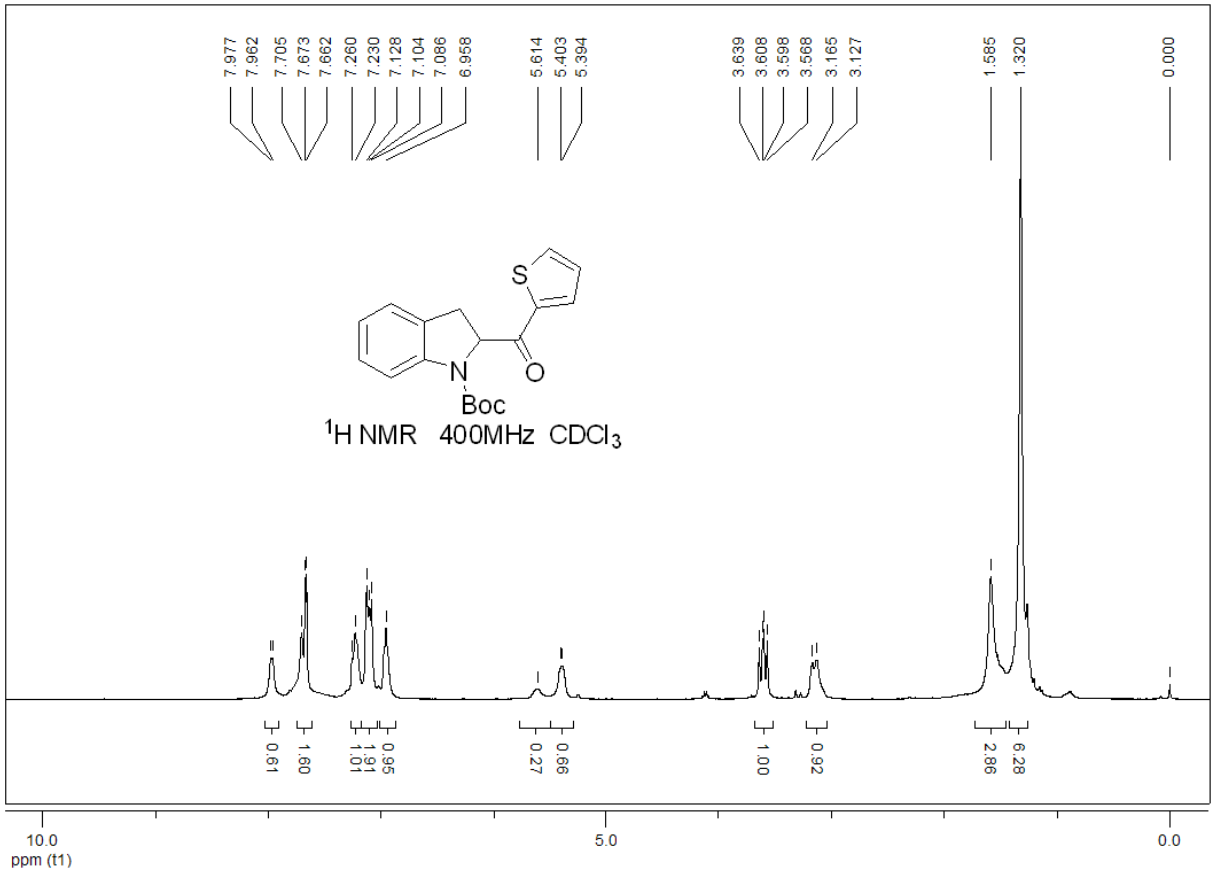

195.081
151.434
142.935
139.979
132.529
129.986
129.724
129.212
128.152
127.338
124.505
122.581
114.718
81.350
77.317
77.000
76.682
63.148
32.512
28.025
O
N
Boc
Cl
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

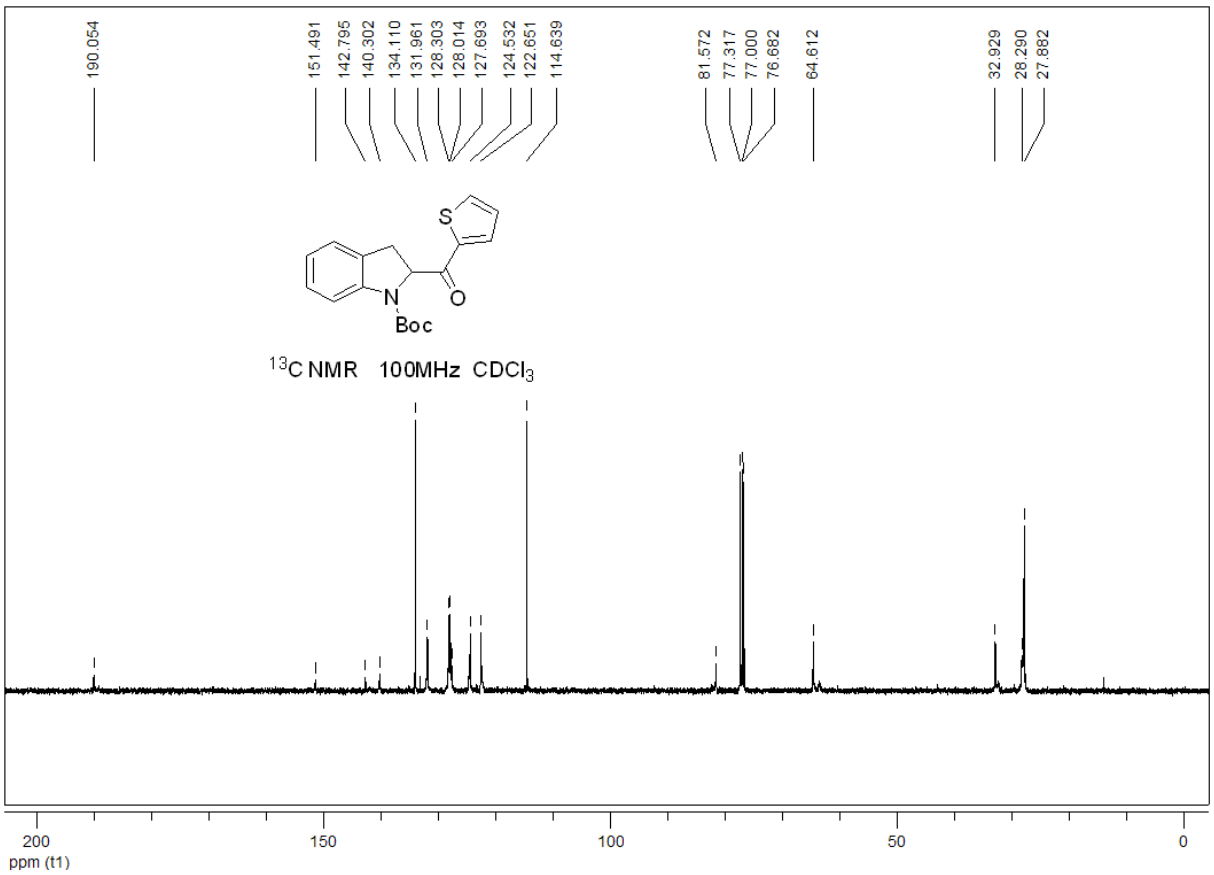
Compound **4f**:


7.961
7.945
7.628
7.548
7.260
7.209
7.088
7.070
6.955
6.937
6.920
6.549
6.544
5.618
5.614
5.451
5.438
3.617
3.588
3.576
3.546
3.099
3.061
1.585
1.336
O
N
O
Boc
1H NMR 400MHz CDCl3
0.66
0.38
1.96
1.02
1.00
0.95
1.04
1.02
1.00
3.07
6.06
5.0
0.0
ppm (t1)

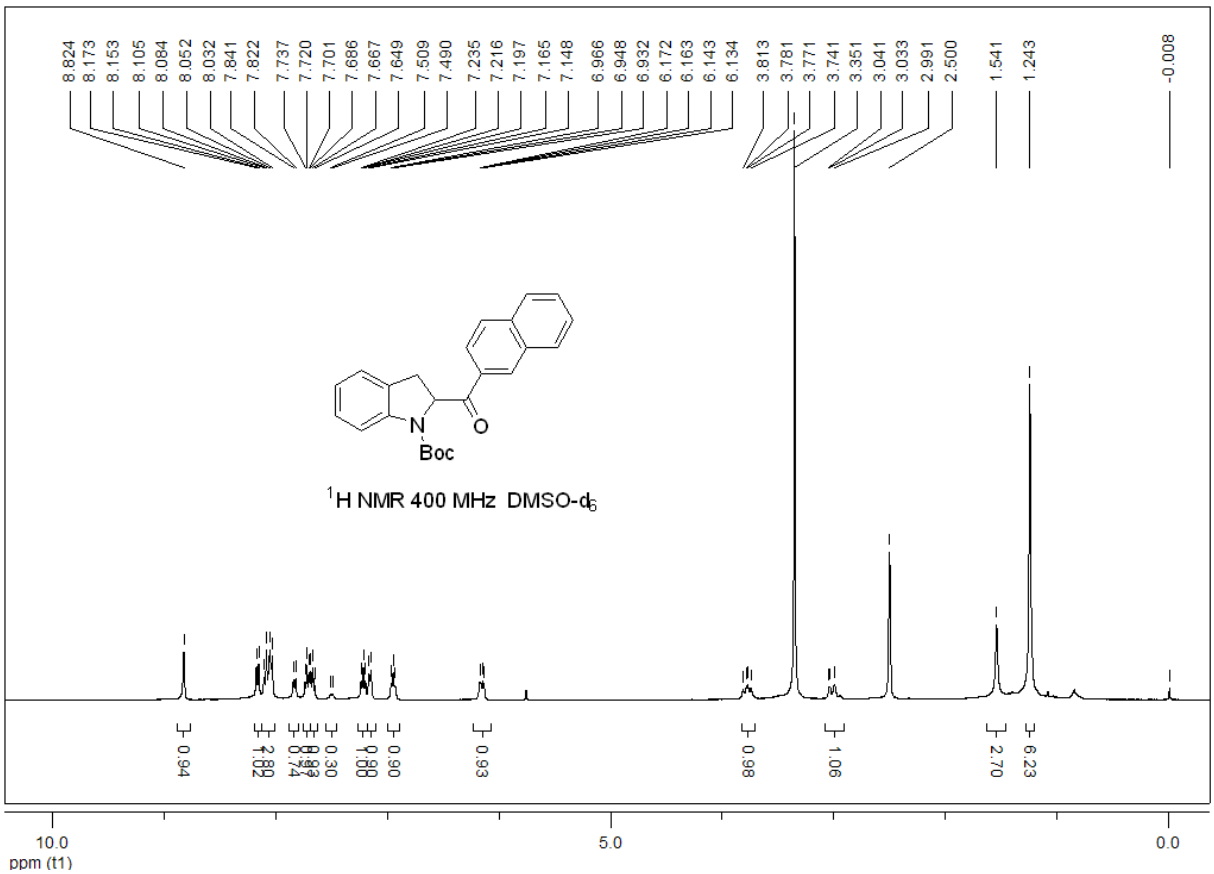

185.995
151.457
150.207
146.882
142.890
127.935
124.439
122.530
118.022
114.580
112.394
81.330
77.318
77.000
76.681
63.301
32.570
28.340
27.921
O
N
O
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

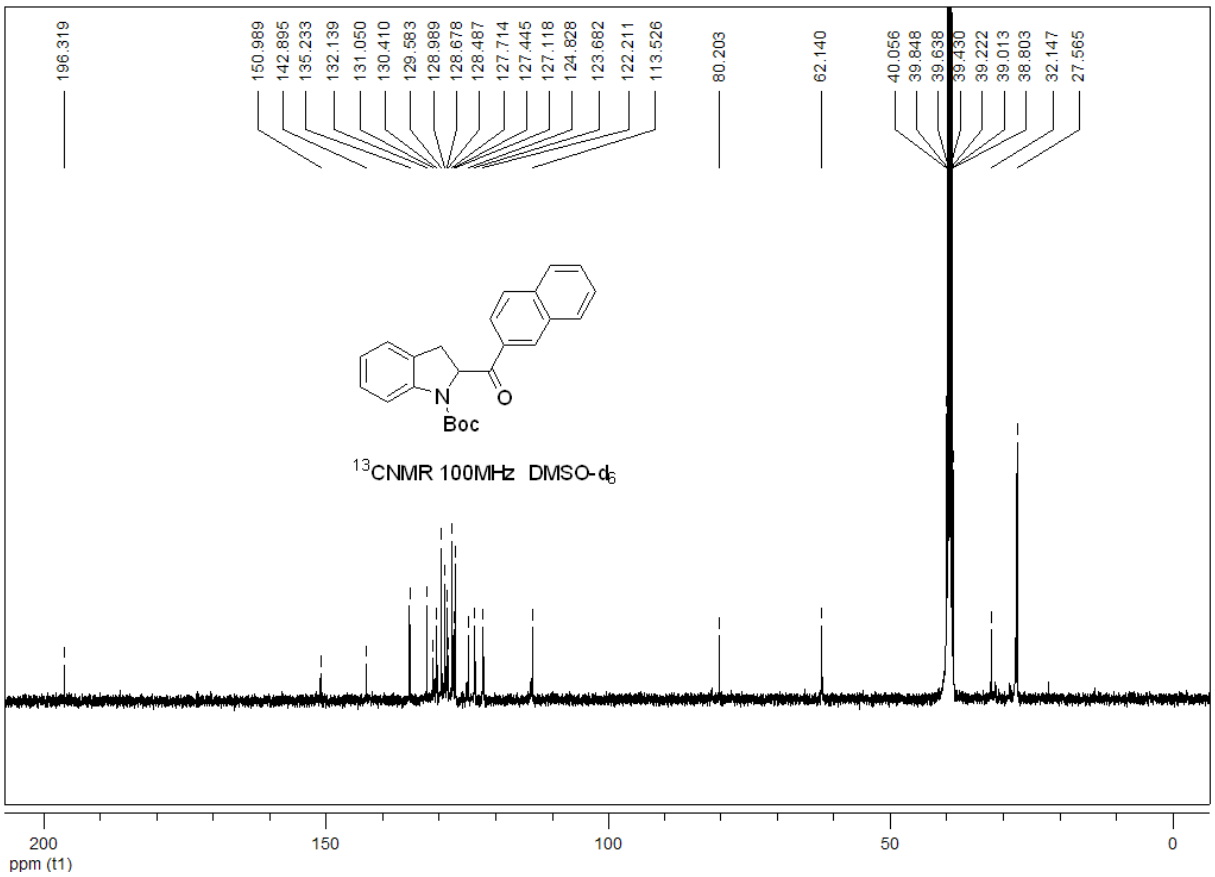
Compound **4g**:


7.977
7.962
7.705
7.673
7.662
7.260
7.230
7.128
7.104
7.086
6.958
5.614
5.403
5.394
3.639
3.608
3.598
3.568
3.165
3.127
1.585
1.320
0.000
S
N
O
Boc
1H NMR 400MHz CDCl3
0.61
1.60
1.01
1.91
0.96
0.27
0.66
1.00
0.92
2.86
6.28
10.0
5.0
0.0
ppm (t1)

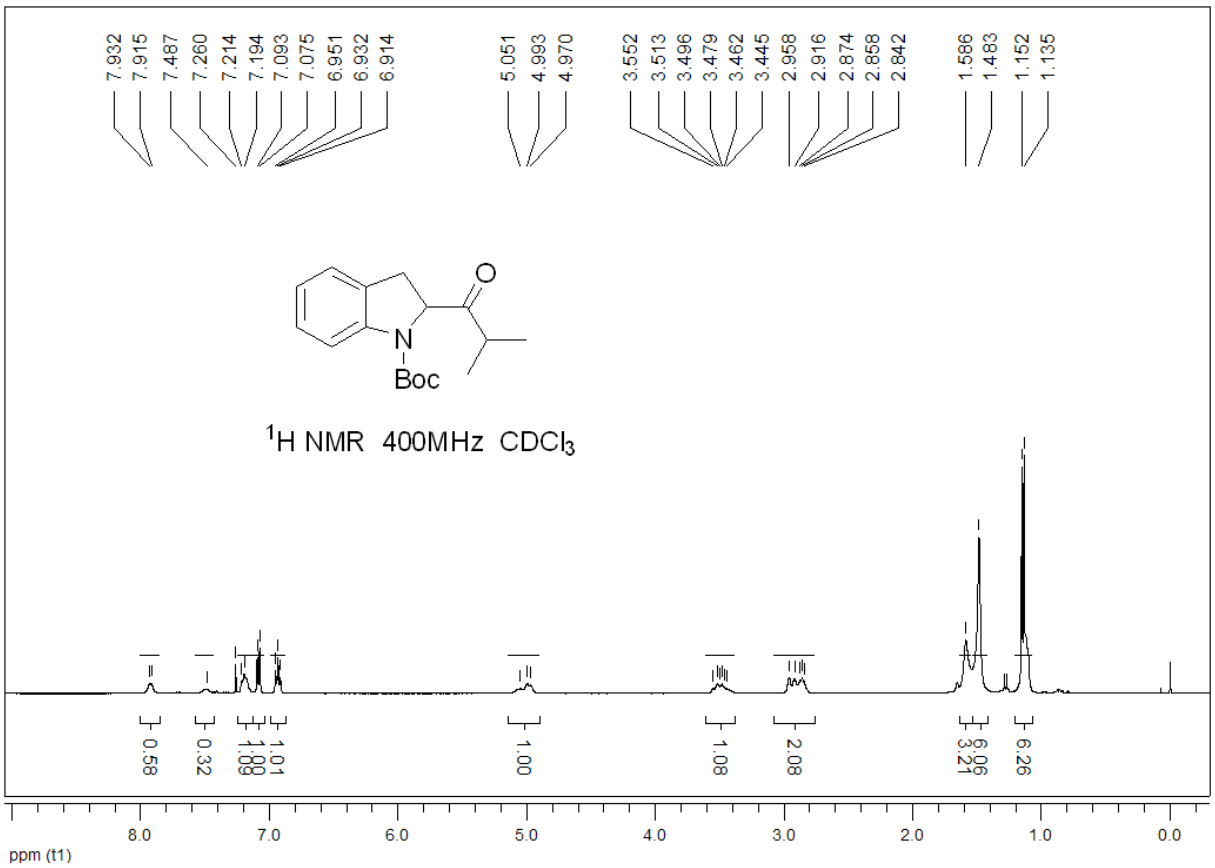

190.054
151.491
142.795
140.302
134.110
131.961
128.303
128.014
127.693
124.532
122.651
114.639
81.572
77.317
77.000
76.682
64.612
32.929
28.290
27.882
S
N
O
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

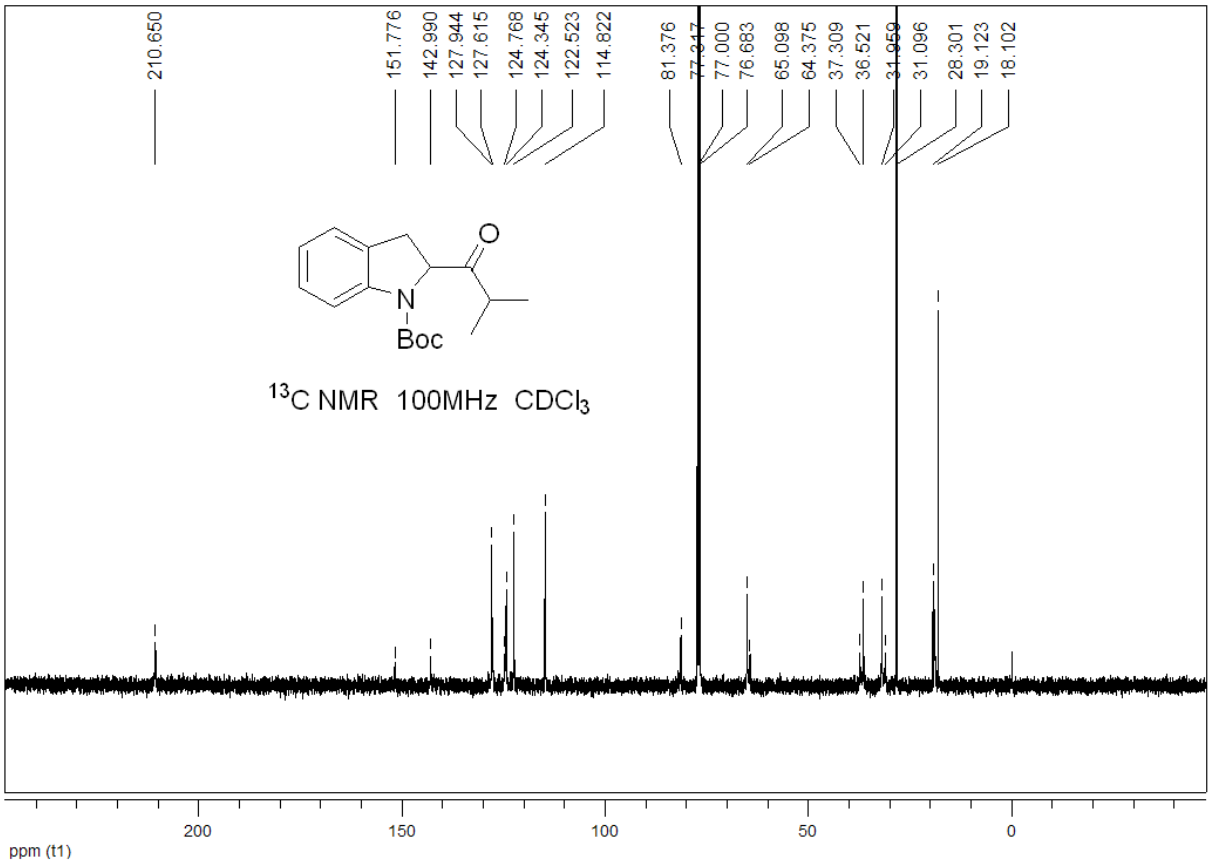
Compound **4h**:


8.824
8.173
8.153
8.105
8.084
8.052
8.032
7.841
7.822
7.737
7.720
7.701
7.686
7.667
7.649
7.509
7.490
7.235
7.216
7.197
7.165
7.148
6.966
6.948
6.932
6.172
6.163
6.143
6.134
3.813
3.781
3.771
3.741
3.351
3.041
3.033
2.991
2.500
1.541
1.243
-0.008
N
O
Boc
1H NMR 400 MHz DMSO-d6
0.94
2.02
0.74
0.30
0.88
0.90
0.93
0.98
1.06
2.70
6.23
10.0
5.0
0.0
ppm (t1)

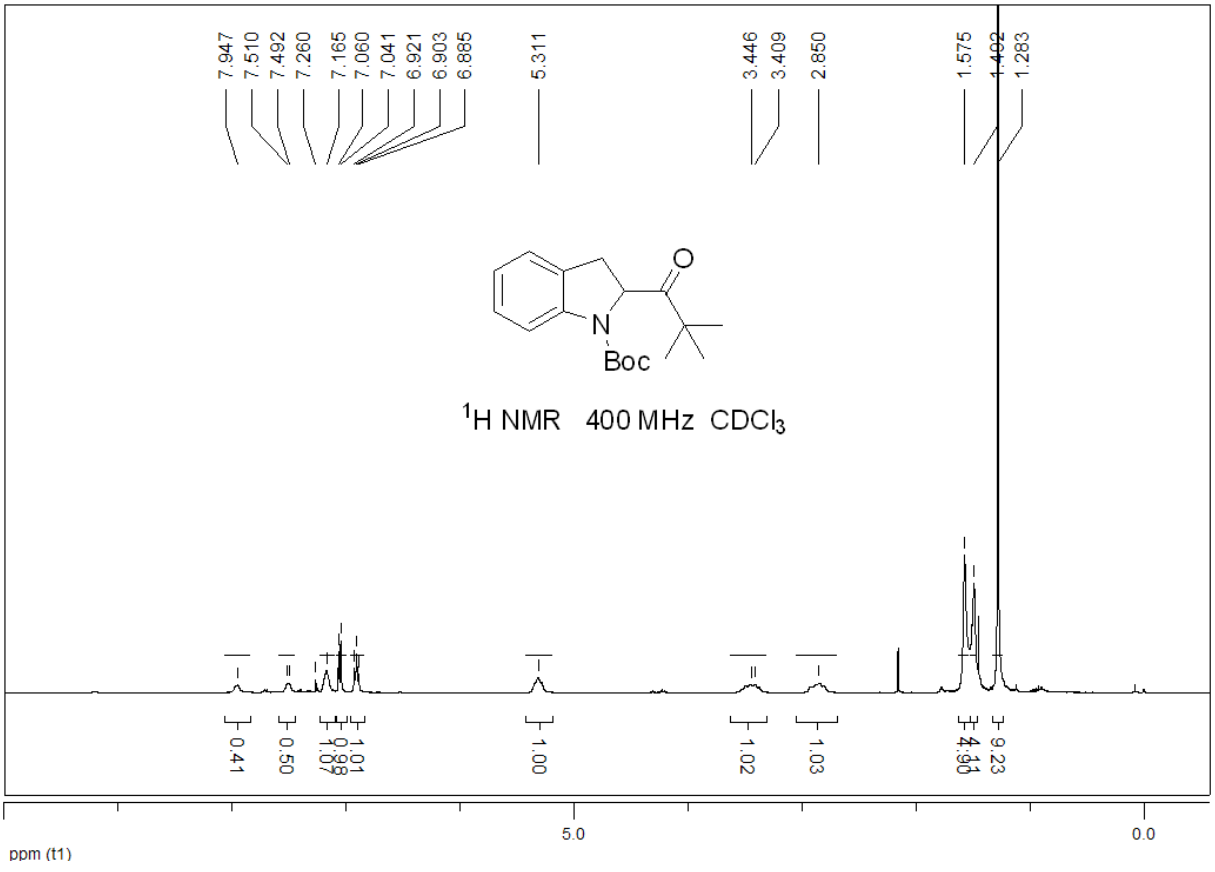

196.319
150.989
142.895
135.233
132.139
131.050
130.410
129.583
128.989
128.678
128.487
127.714
127.445
127.118
124.828
123.682
122.211
113.526
80.203
62.140
40.056
39.848
39.638
39.430
39.222
39.013
38.803
32.147
27.565
N
O
Boc
13CNMR 100MHz DMSO-d6
200
150
100
50
0
ppm (t1)

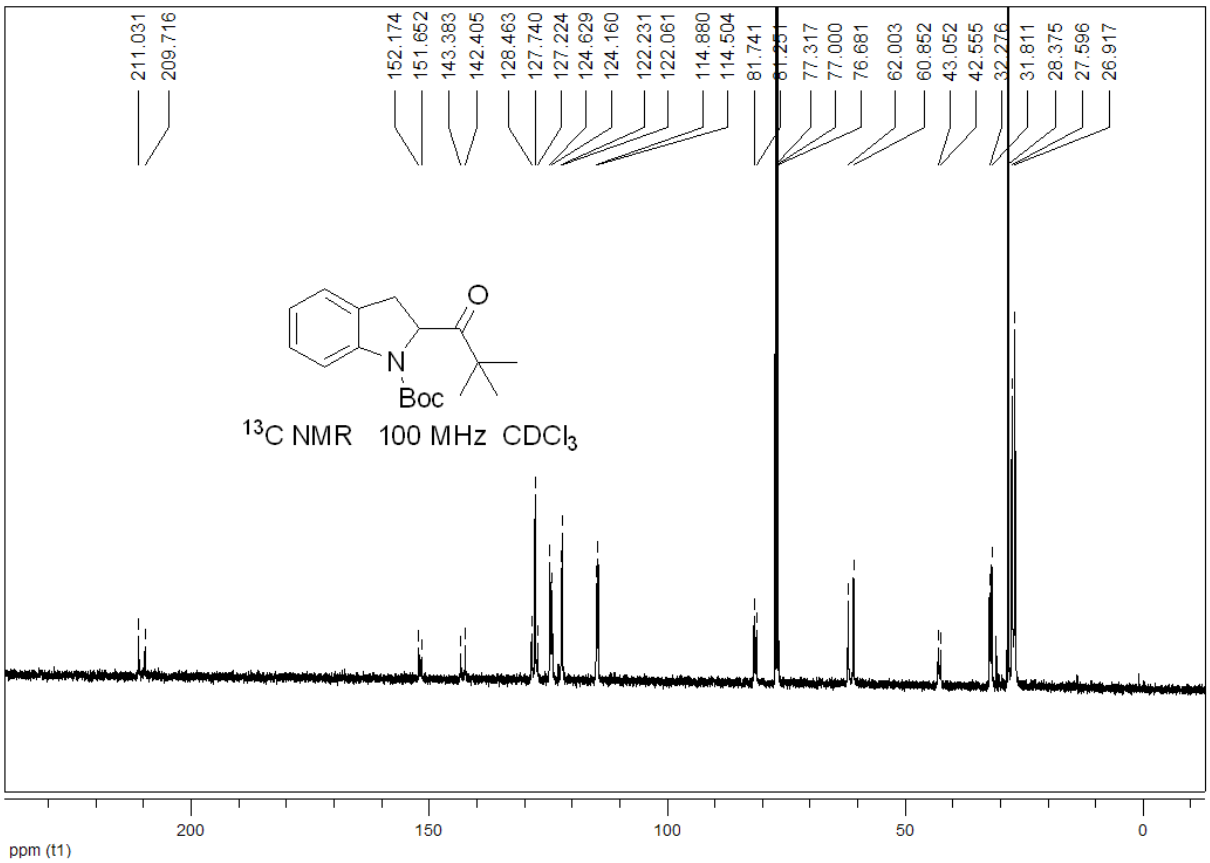
Compound **4i**:


7.932
7.915
7.487
7.260
7.214
7.194
7.093
7.075
6.951
6.932
6.914
5.051
4.993
4.970
3.552
3.513
3.496
3.479
3.462
3.445
2.958
2.916
2.874
2.858
2.842
1.586
1.483
1.152
1.135
O
N
Boc
1H NMR 400MHz CDCl3
0.58
0.32
1.88
1.01
1.00
1.08
2.08
3.21
6.06
6.26
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

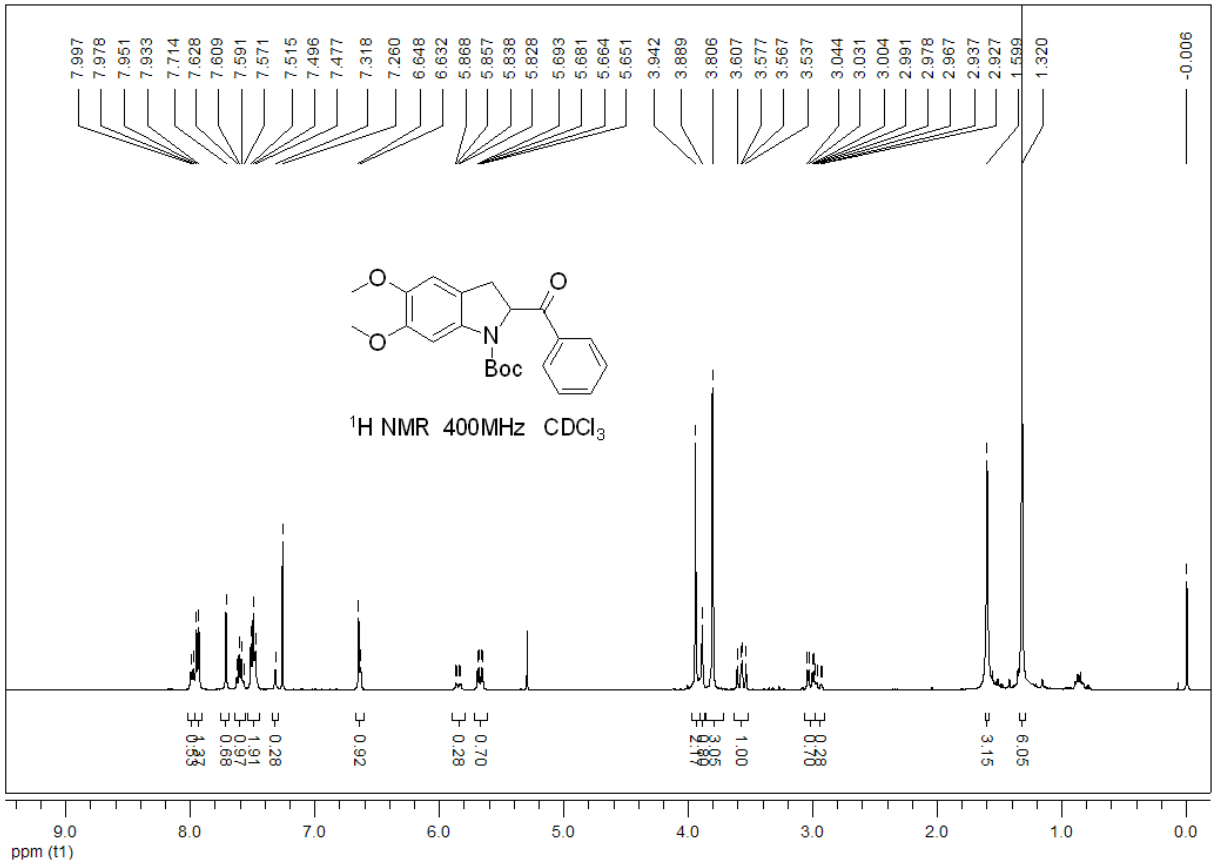

210.650
151.776
142.990
127.944
127.615
124.768
124.345
122.523
114.822
81.376
77.317
77.000
76.683
65.098
64.375
37.309
36.521
31.959
31.096
28.301
19.123
18.102
O
N
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

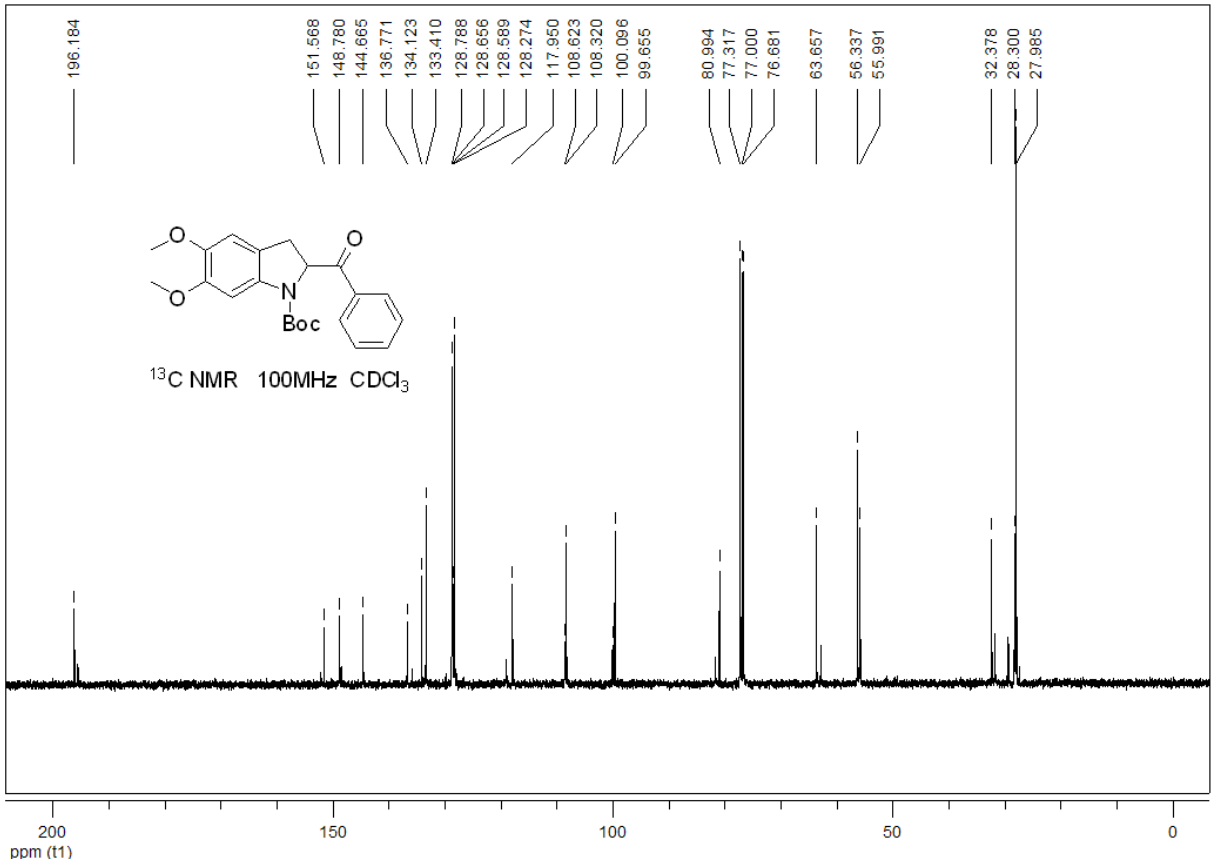
Compound **4j**:


7.947
7.510
7.492
7.260
7.165
7.060
7.041
6.921
6.903
6.885
5.311
3.446
3.409
2.850
1.575
1.492
1.283
O
N
Boc
1H NMR 400 MHz CDCl3
0.41
0.50
1.07
1.00
1.02
1.03
4.90
9.23
5.0
0.0
ppm (t1)

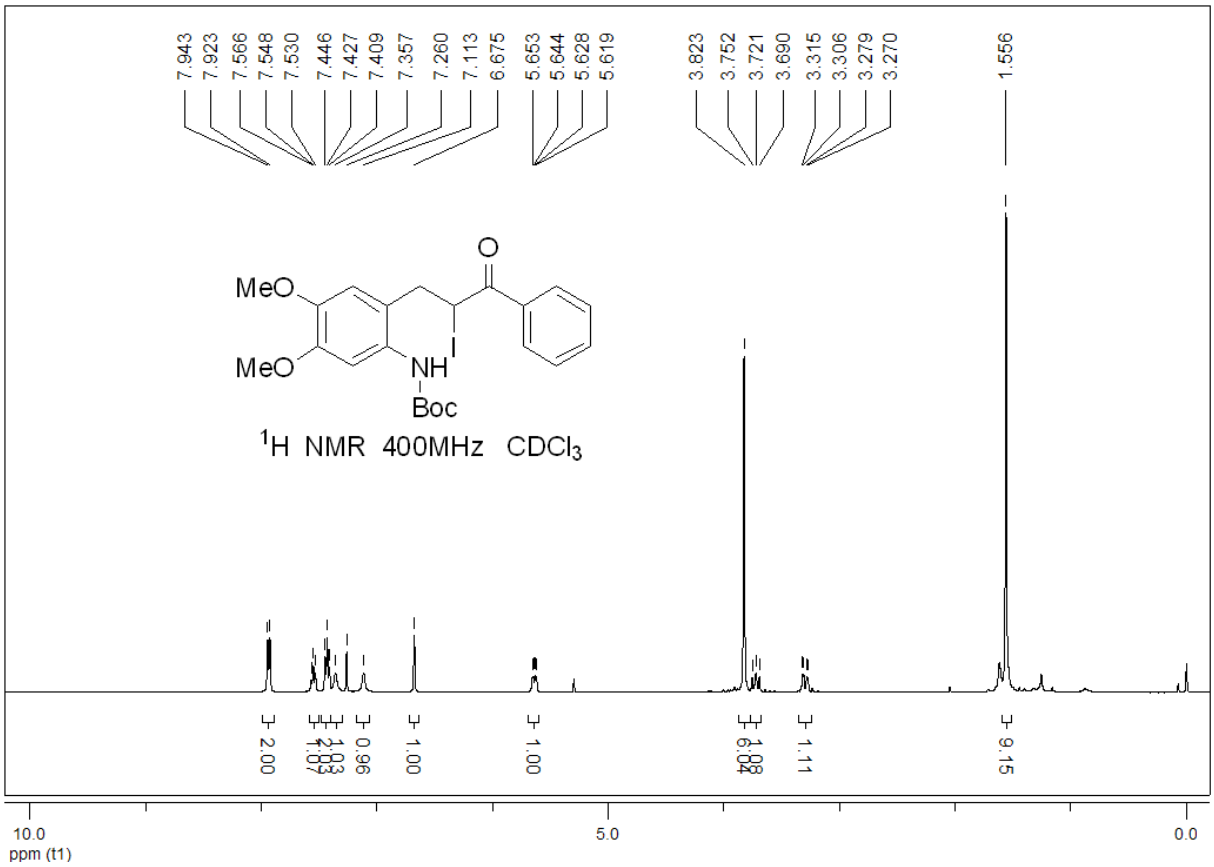

211.031
209.716
152.174
151.652
143.383
142.405
128.463
127.740
127.224
124.629
124.160
122.231
122.061
114.880
114.504
81.741
81.251
77.317
77.000
76.681
62.003
60.852
43.052
42.555
32.276
31.811
28.375
27.596
26.917
O
N
Boc
13C NMR 100 MHz CDCl3
200
150
100
50
0
ppm (t1)

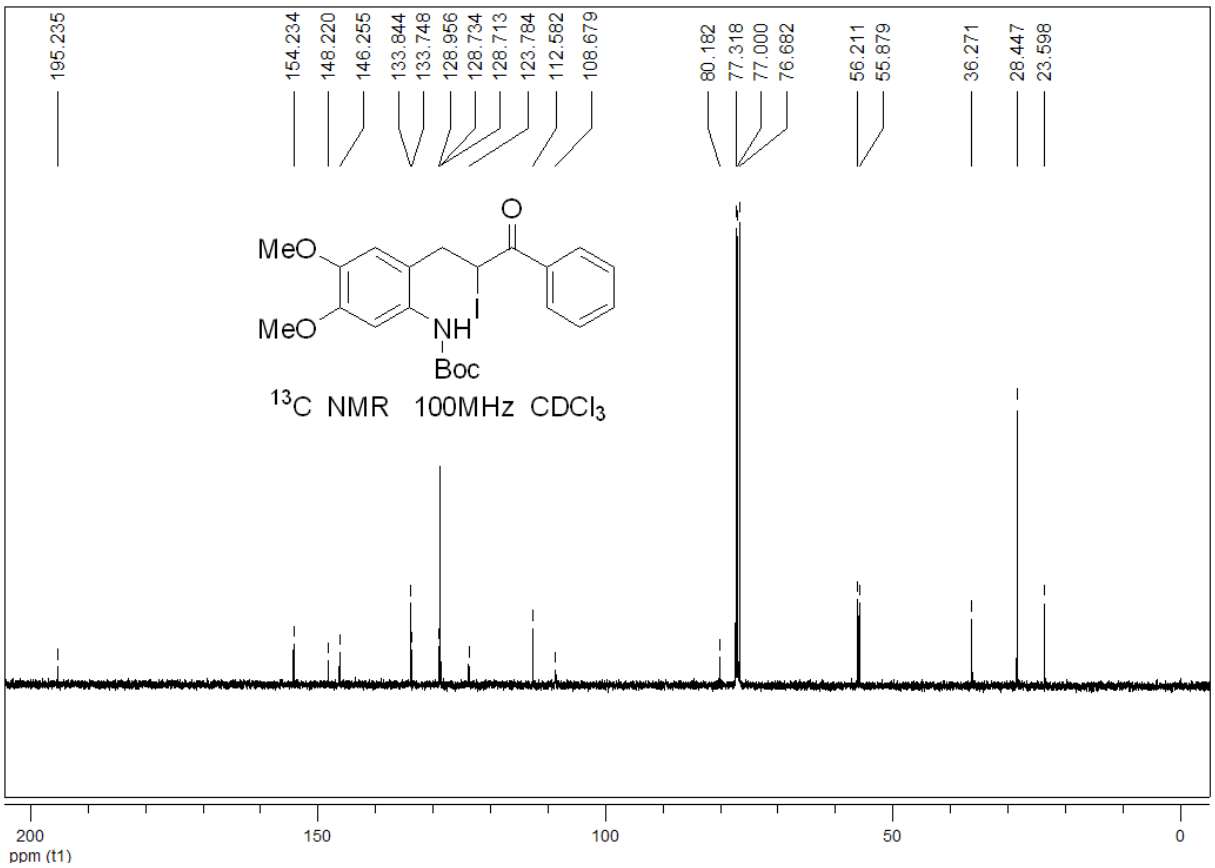
Compound **4k**:


7.997
7.978
7.951
7.933
7.714
7.628
7.609
7.591
7.571
7.515
7.496
7.477
7.318
7.260
6.648
6.632
5.868
5.857
5.838
5.828
5.693
5.681
5.664
5.651
3.942
3.889
3.806
3.607
3.577
3.567
3.537
3.044
3.031
3.004
2.991
2.978
2.967
2.937
2.927
1.599
1.320
-0.006
O
O
N
Boc
1H NMR 400MHz CDCl3
0.83
2.43
0.68
1.97
1.91
0.28
0.92
0.28
0.70
2.17
3.08
1.00
8.78
3.15
6.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

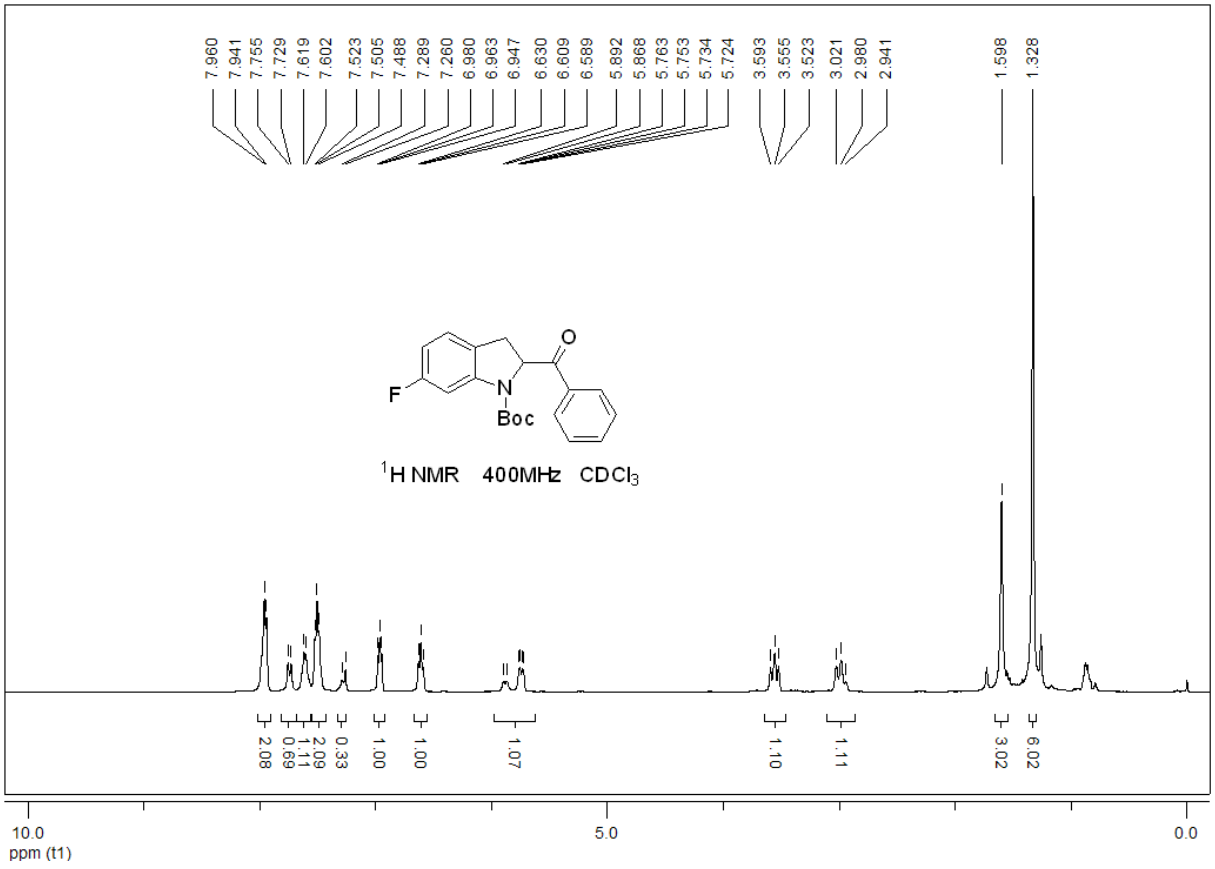

196.184
151.568
148.780
144.665
136.771
134.123
133.410
128.788
128.656
128.589
128.274
117.950
108.623
108.320
100.096
99.655
80.994
77.317
77.000
76.681
63.657
56.337
55.991
32.378
28.300
27.985
O
O
O
N
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

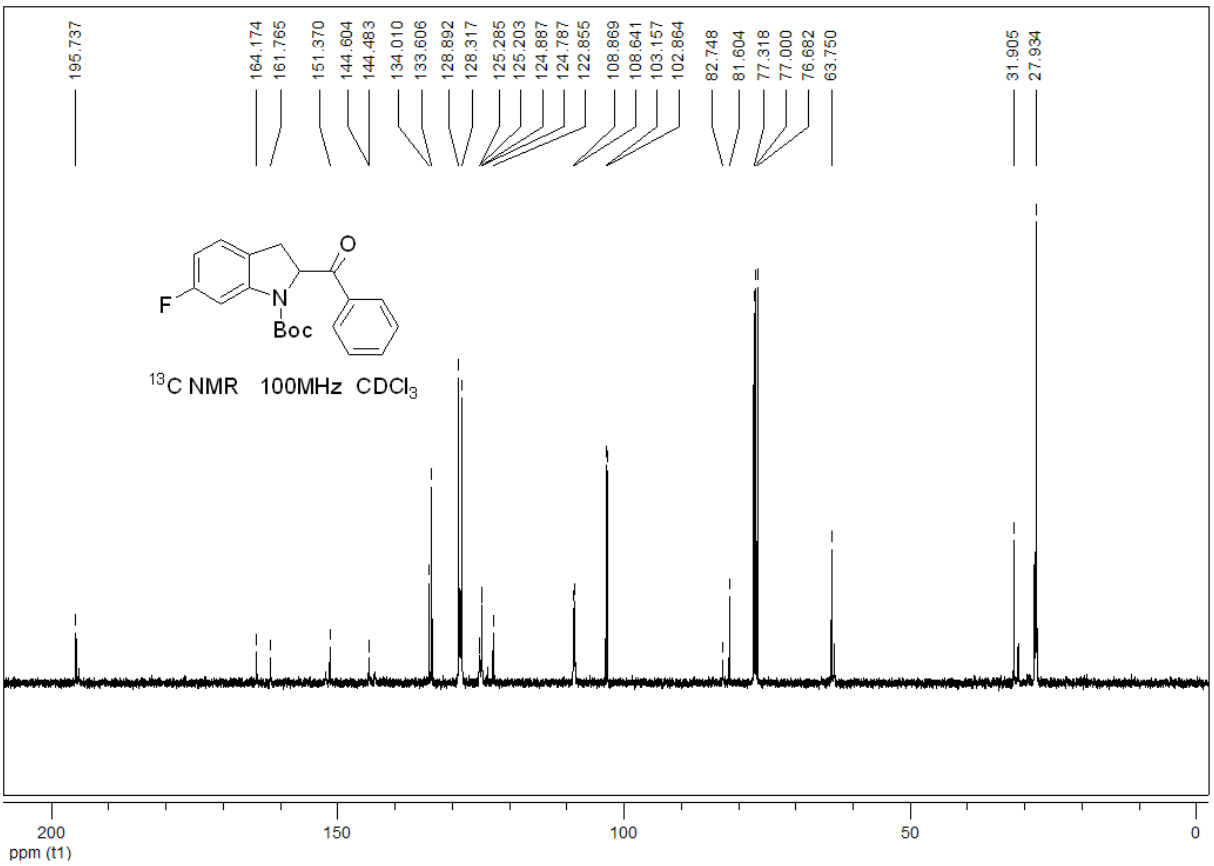
Compound **7**:

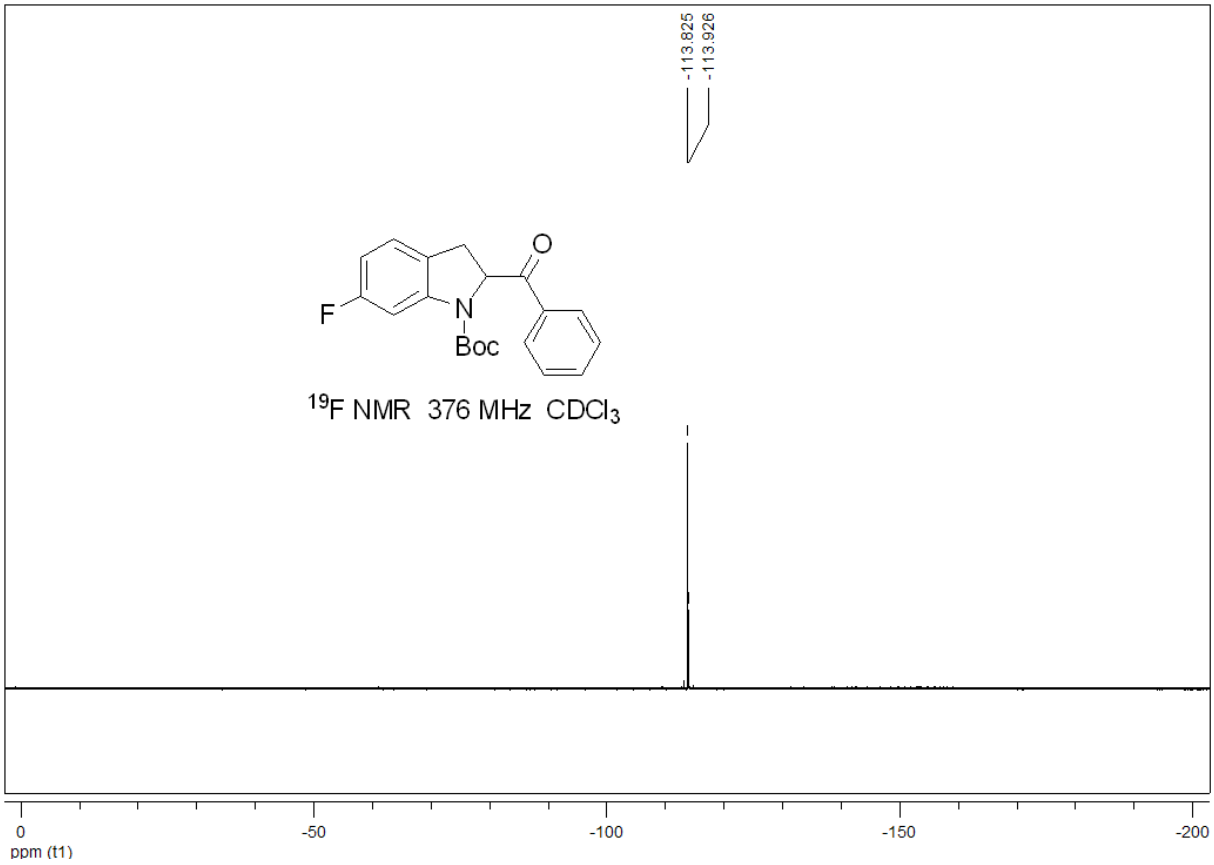

7.943
7.923
7.566
7.548
7.530
7.446
7.427
7.409
7.357
7.260
7.113
6.675
5.653
5.644
5.628
5.619
3.823
3.752
3.721
3.690
3.315
3.306
3.279
3.270
1.556
O
MeO
MeO
NH
Boc
1H NMR 400MHz CDCl3
2.00
1.07
1.03
2.03
0.96
1.00
1.00
6.08
1.04
1.11
9.15
10.0
5.0
0.0
ppm (t1)


195.235
154.234
148.220
146.255
133.844
133.748
128.956
128.734
128.713
123.784
112.582
108.679
80.182
77.318
77.000
76.682
56.211
55.879
36.271
28.447
23.598
MeO
MeO
NH
Boc
O
I
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

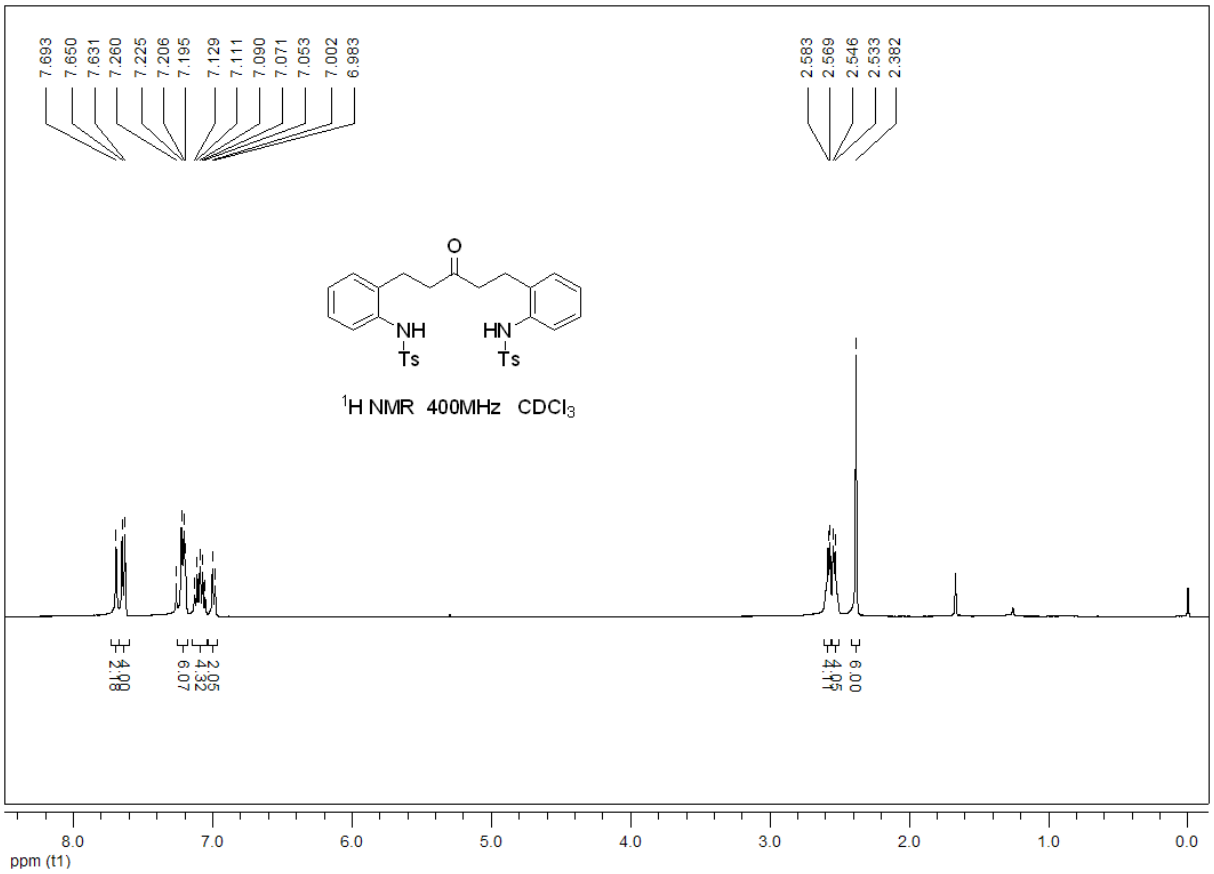
Compound **4l**:

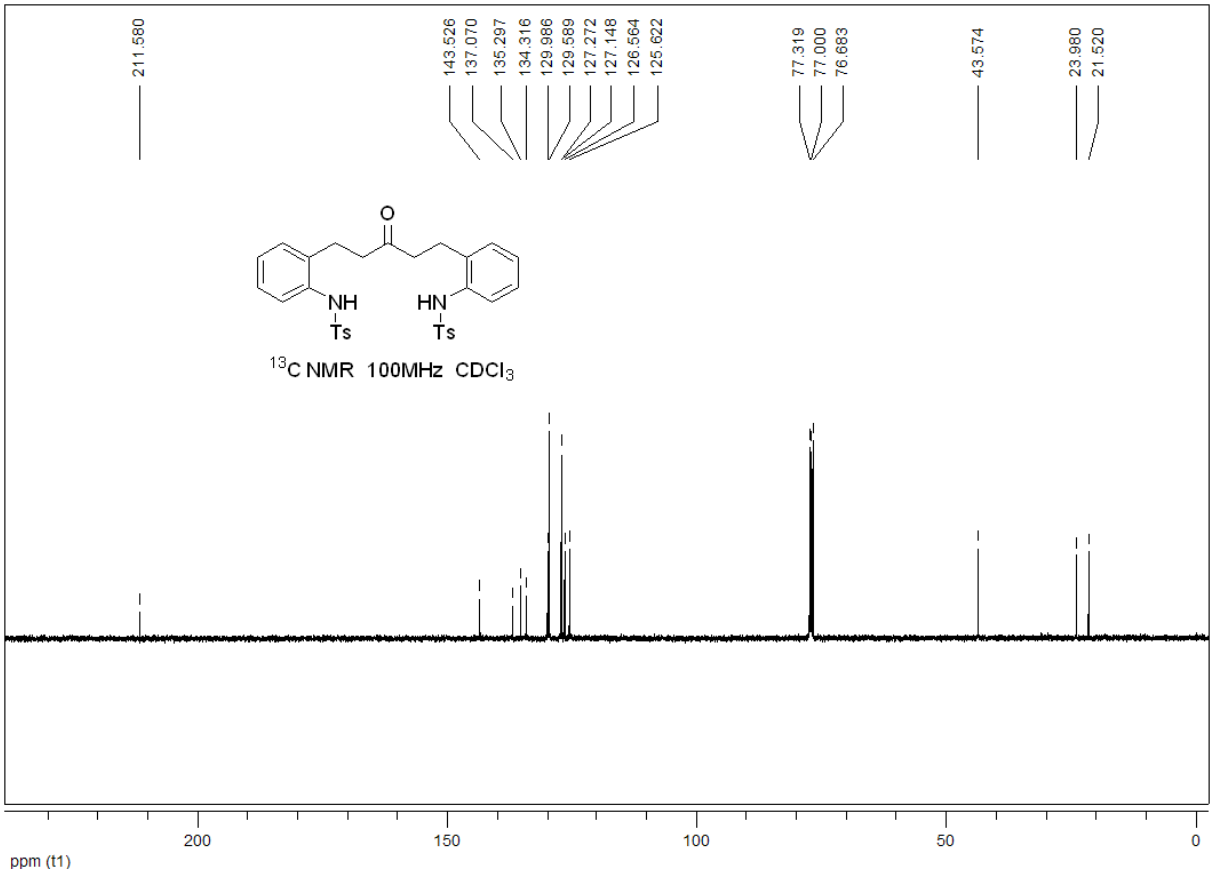

7.960
7.941
7.755
7.729
7.619
7.602
7.523
7.505
7.488
7.289
7.260
6.980
6.963
6.947
6.630
6.609
6.589
5.892
5.868
5.763
5.753
5.734
5.724
3.593
3.555
3.523
3.021
2.980
2.941
1.598
1.328
F
N
Boc
O
1H NMR 400MHz CDCl3
2.08
0.69
1.11
2.09
0.33
1.00
1.00
1.07
1.10
1.11
3.02
6.02
10.0
5.0
0.0
ppm (t1)


195.737
164.174
161.765
151.370
144.604
144.483
134.010
133.606
128.892
128.317
125.285
125.203
124.887
124.787
122.855
108.869
108.641
103.157
102.864
82.748
81.604
77.318
77.000
76.682
63.750
31.905
27.934
O
F
N
Boc
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

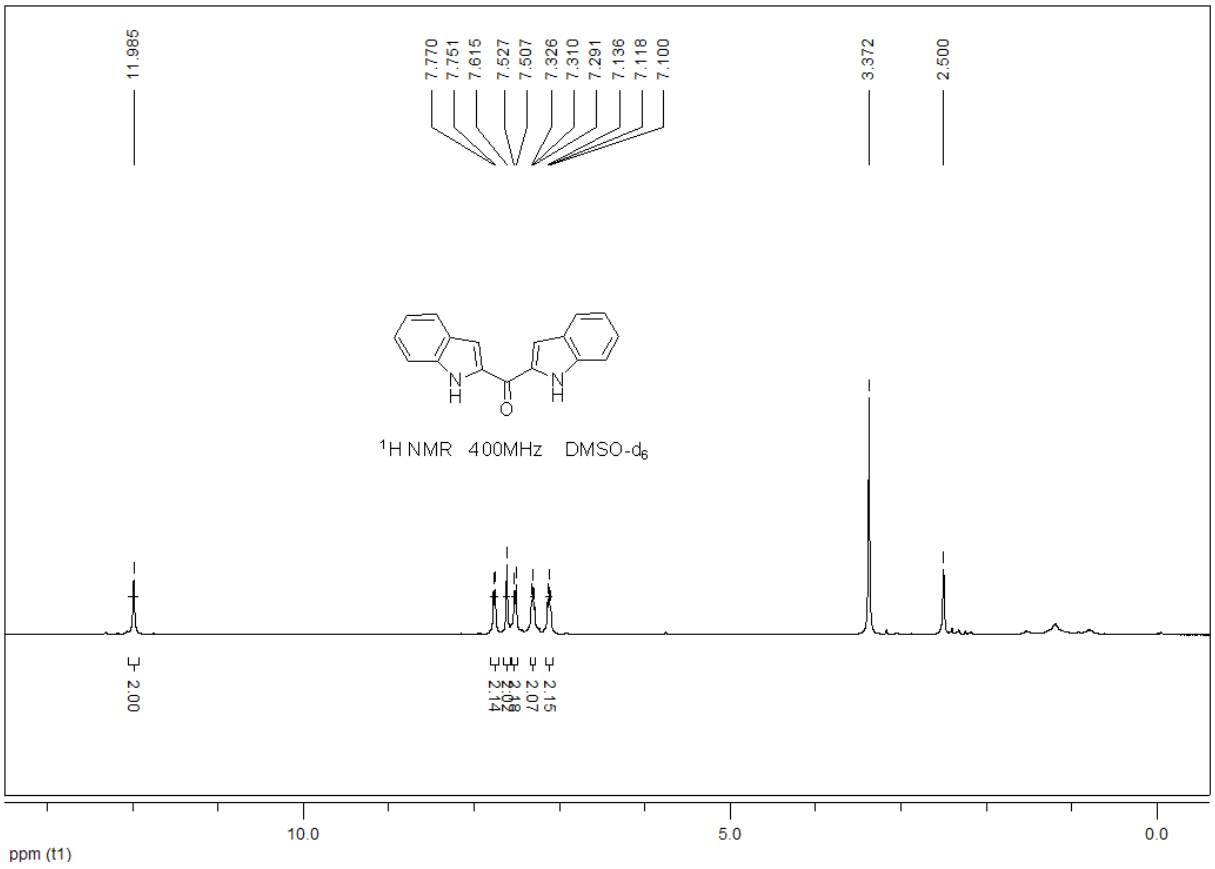

-113.825
-113.926
O
F
N
Boc
19F NMR 376 MHz CDCl3
0
-50
-100
-150
-200
ppm (t1)

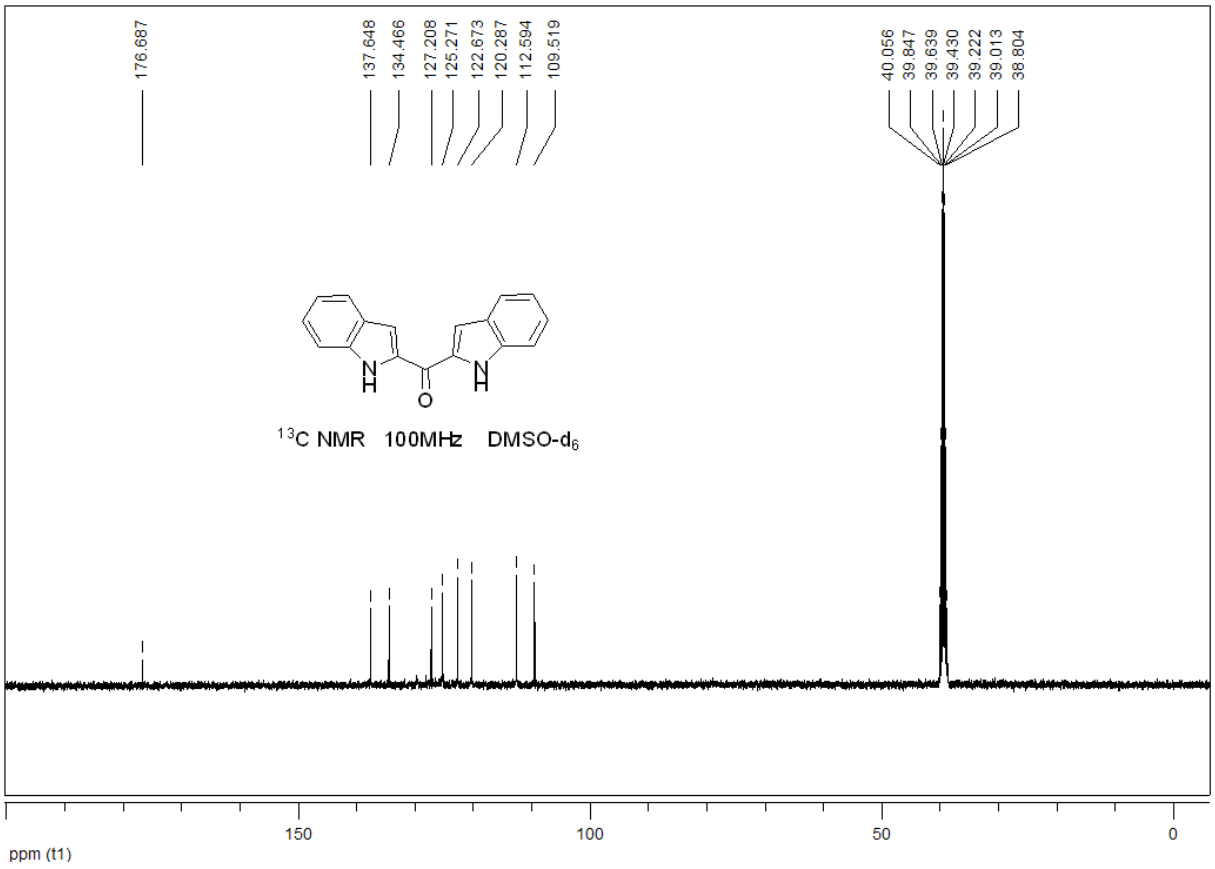
Compound **S12**:



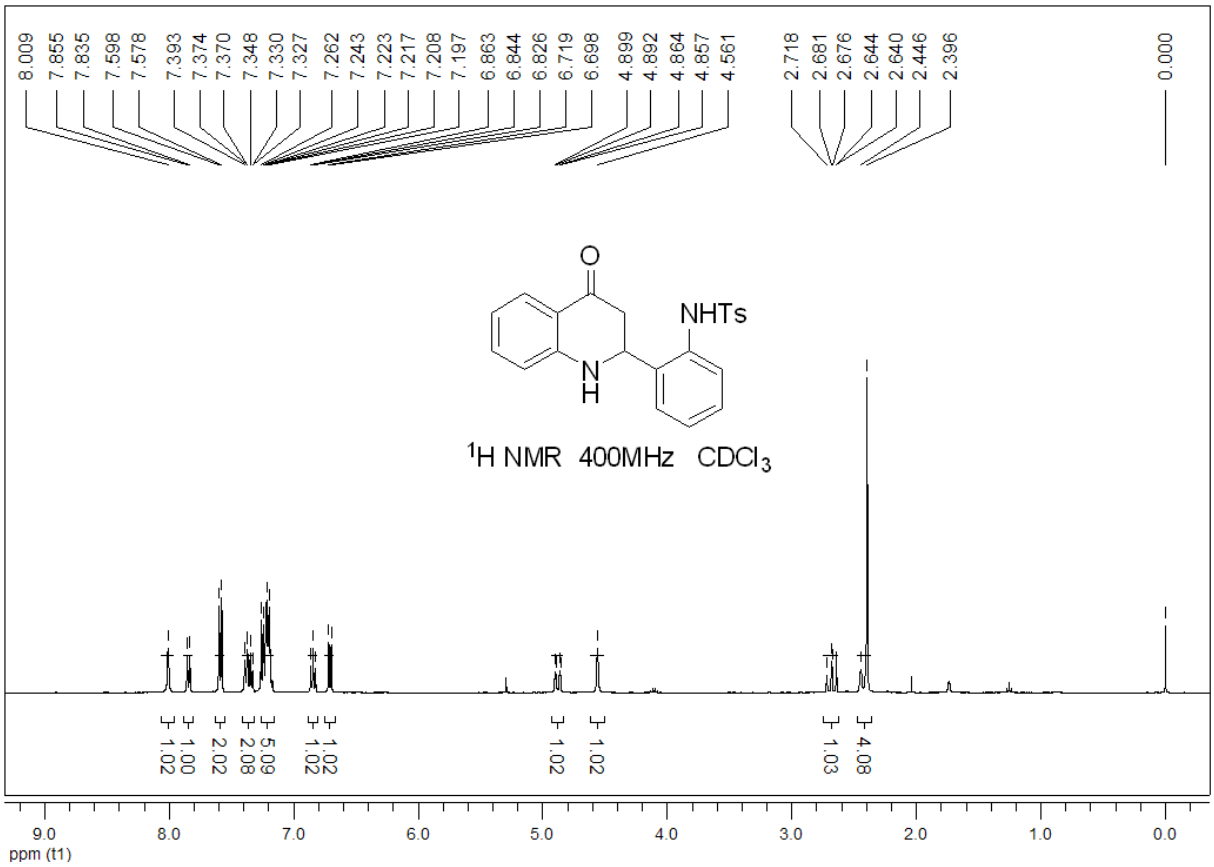


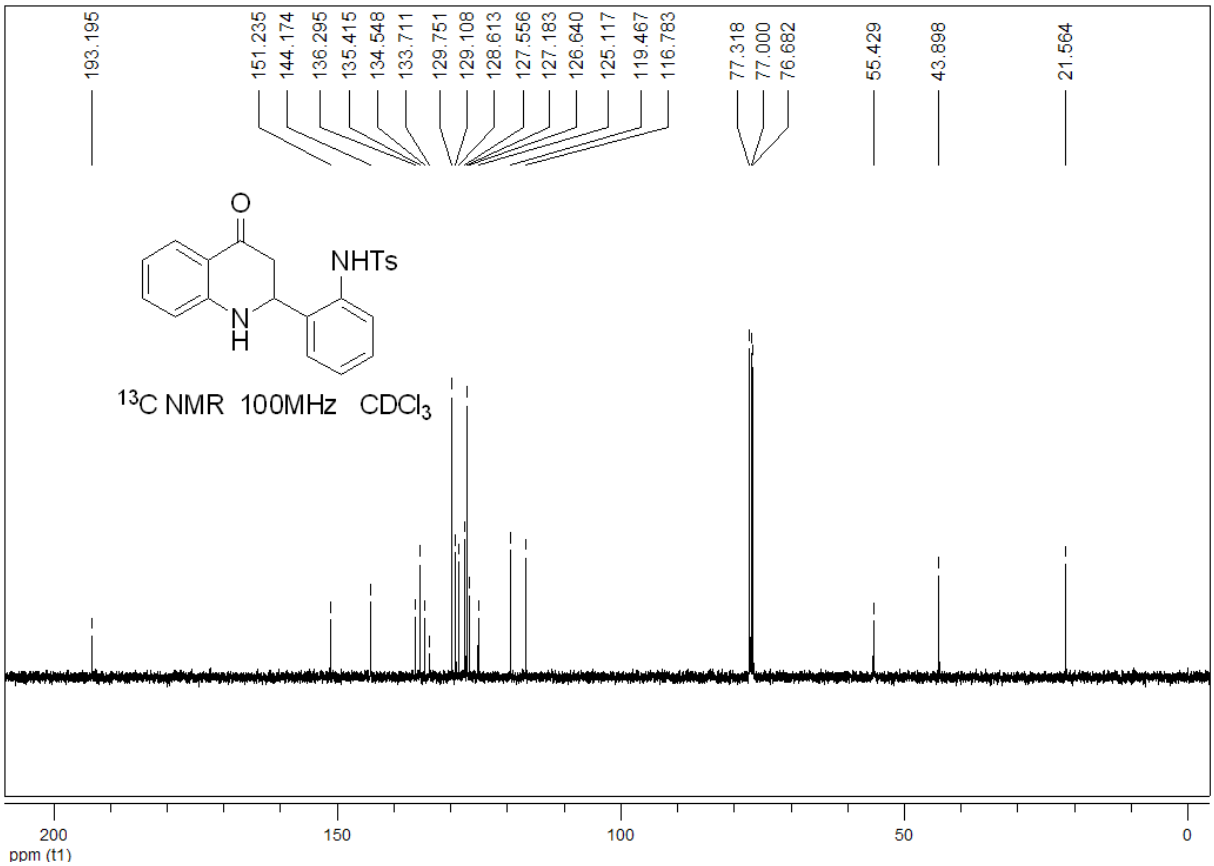
Compound **5**:


11.985
7.770
7.751
7.615
7.527
7.507
7.326
7.310
7.291
7.136
7.118
7.100
3.372
2.500
^{1}H NMR 400MHz DMSO-d$_6$
2.00
2.14
2.18
2.07
2.15
10.0
5.0
0.0
ppm (t1)

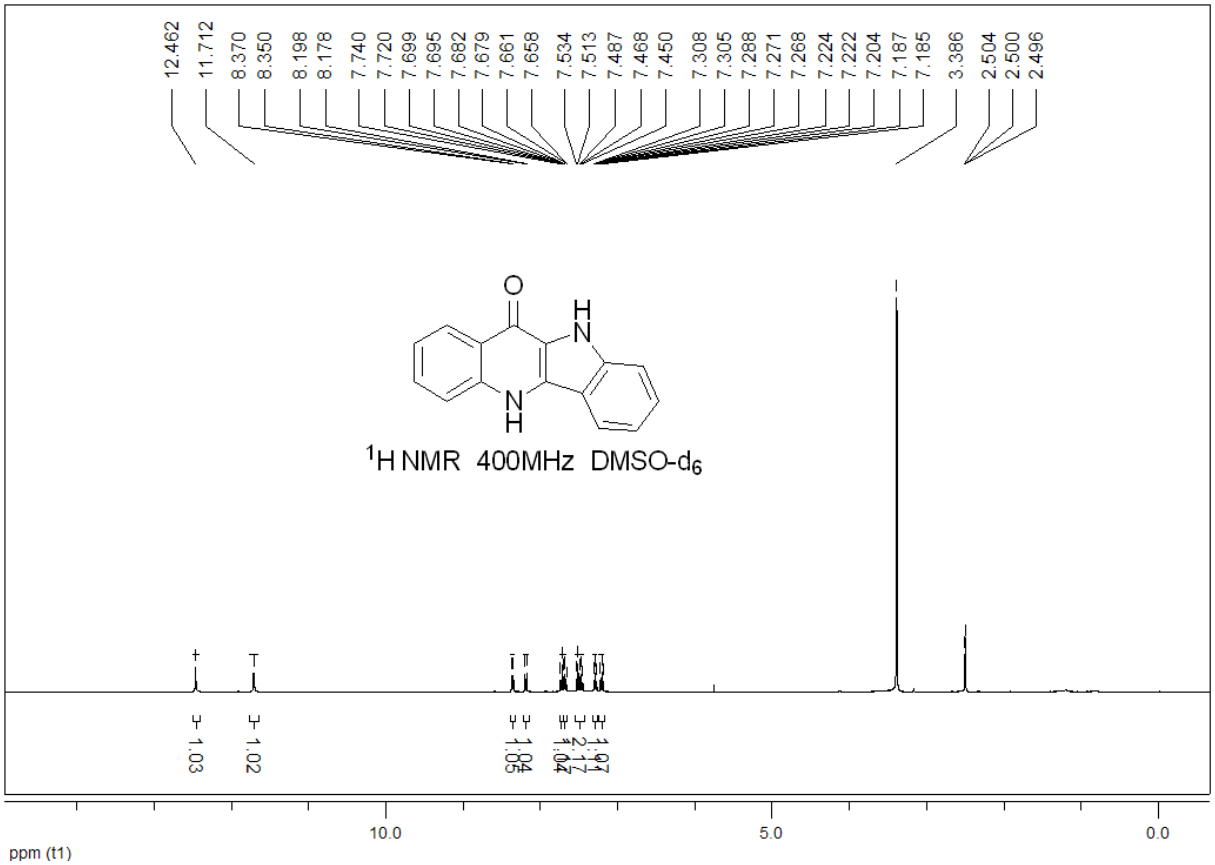

176.687
137.648
134.466
127.208
125.271
122.673
120.287
112.594
109.519
40.056
39.847
39.639
39.430
39.222
39.013
38.804
^{13}C NMR 100MHz DMSO-d$_6$
150
100
50
0
ppm (t1)

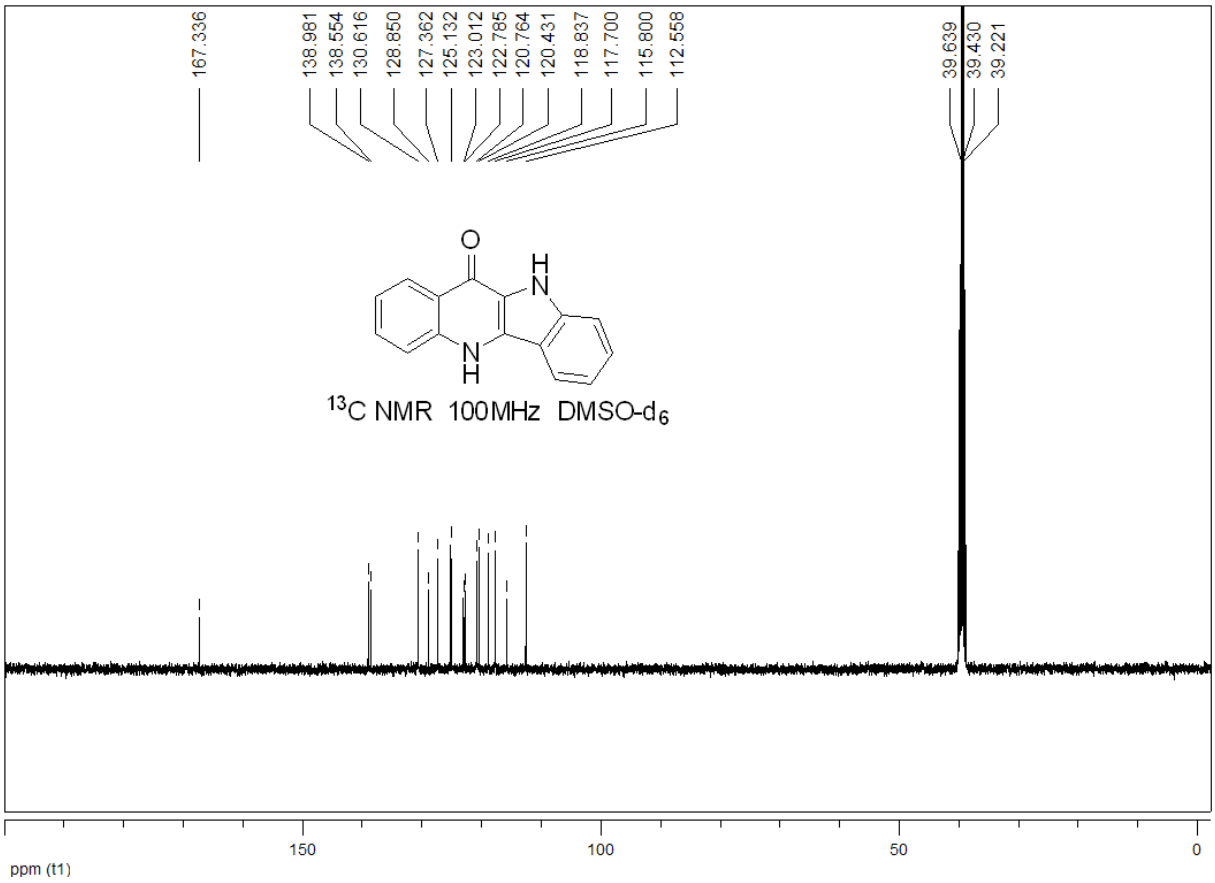
Compound **10**:


8.009
7.855
7.835
7.598
7.578
7.393
7.374
7.370
7.348
7.330
7.327
7.262
7.243
7.223
7.217
7.208
7.197
6.863
6.844
6.826
6.719
6.698
4.899
4.892
4.864
4.857
4.561
2.718
2.681
2.676
2.644
2.640
2.446
2.396
0.000
O
NHTs
N
H
1H NMR 400MHz CDCl3
1.02
1.00
2.02
2.08
5.09
1.02
1.02
1.02
1.03
4.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


193.195
151.235
144.174
136.295
135.415
134.548
133.711
129.751
129.108
128.613
127.556
127.183
126.640
125.117
119.467
116.783
77.318
77.000
76.682
55.429
43.898
21.564
O
NHTs
N
H
13C NMR 100MHz CDCl3
200
150
100
50
0
ppm (t1)

Compound **12**:


12.462
11.712
8.370
8.350
8.198
8.178
7.740
7.720
7.699
7.695
7.682
7.679
7.661
7.658
7.534
7.513
7.487
7.468
7.450
7.308
7.305
7.288
7.271
7.268
7.224
7.222
7.204
7.187
7.185
3.386
2.504
2.500
2.496
O
H
N
N
H
1H NMR 400MHz DMSO-d6
1.03
1.02
1.05
1.04
1.12
1.17
1.07
10.0
5.0
0.0
ppm (t1)


167.336
138.981
138.554
130.616
128.850
127.362
125.132
123.012
122.785
120.764
120.431
118.837
117.700
115.800
112.558
39.639
39.430
39.221
O
H
N
N
H
13C NMR 100MHz DMSO-d6
150
100
50
0
ppm (t1)