Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of 1,4-benzodiazepinones and 1,4-benzoxazepinones via palladium-catalyzed amino and oxyacetoxylation

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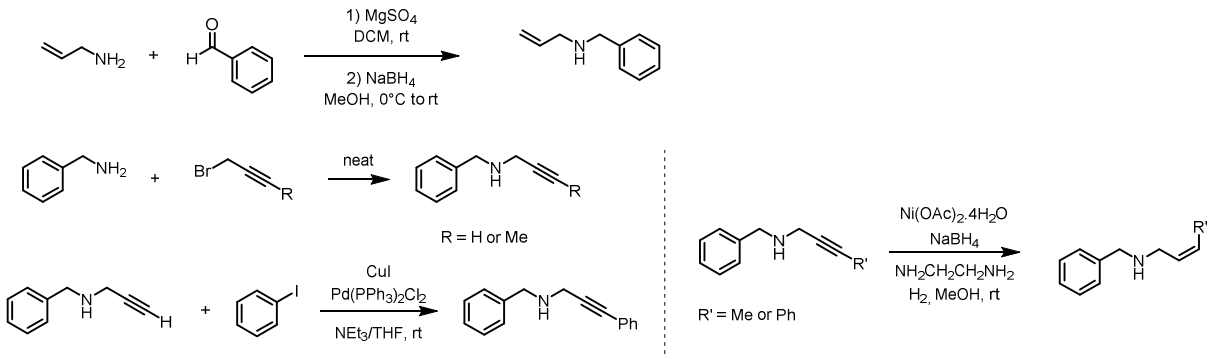
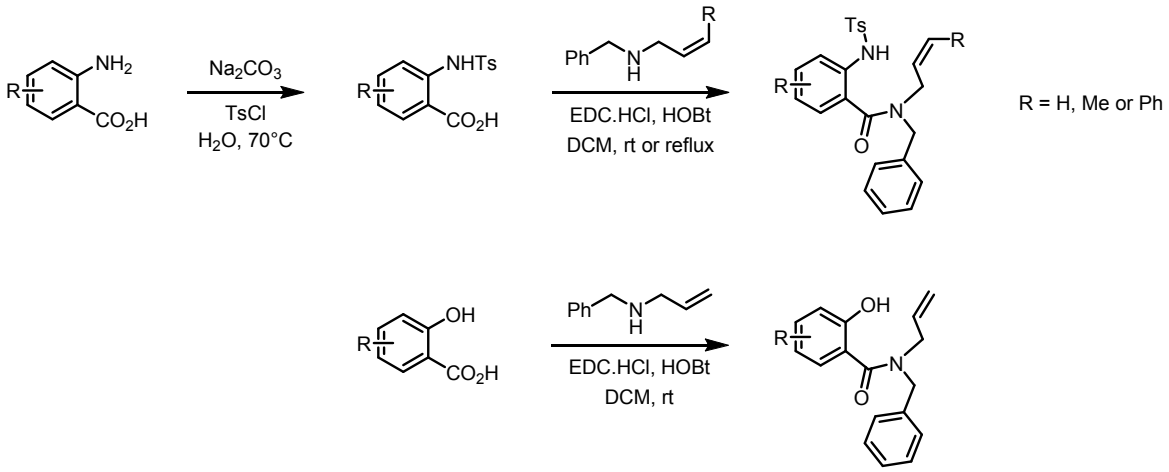
I. General Information

All reagents were purchased from chemical suppliers and used without further purification. Reactions were performed using freshly distilled solvents under an argon atmosphere. DCM was dried on calcium hydride. THF was dried on sodium/benzophenone. Dry DMF, DMSO, toluene, acetonitrile and dioxane were purchased from chemical suppliers. Analytical thin layer chromatography was performed on commercial silica gel plates $60F_{254}$. Flash column chromatography was performed on silica gel 60 (40−63 μm). NMR spectra were recorded on a 250 or 500 MHz spectrometer as specified. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (δ 0.00 ppm) or the $CHCl_3$ residual peak (δ 7.26) or the MeOH residual peak (δ 3.31) for ^1H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16) or CD_3OD (δ 49.00). Coupling constant (*J*) are reported in Hertz unit (Hz). Multiplicities are described with standard following abbreviations: s = singlet, br = broad, d = doublet, t = triplet, q = quadruplet, m = multiplet. Low resolution mass spectra (LRMS) were recorded with an ion trap mass analyzer under electrospray ionization (ESI) in positive or negative ionization mode detection or atmospheric pressure chemical ionization (APCI). High resolution mass spectra (HRMS) were recorded with a TOF mass analyzer under electrospray ionization (ESI) in positive or negative ionization mode detection, atmospheric pressure chemical ionization or atmospheric pressure photoionization (APPI). Melting points were measured on a Köfler bench. IR spectra were recorded on a FT-IR spectrophotometer, and the wavelengths reported in cm^{-1}.

II. General Procedure

Preparation of substrates:





- General procedure for the tosylation reaction:

The nitrogen tosylation of anthranilic acid derivatives was done using a reported procedure.[1] In a round bottom flask, 1.0 equiv. of Na_2CO_3 was dissolved in 70°C water (C = 1.1 mol/L). Then 1.2 equiv. of tosyl chloride was added followed by 1.0 equiv. of the desired anthranilic acid. The suspension was stirred at 70°C for 40 mn then at 85°C for 5 mn. The reaction mixture was then directly filtrated over Büchner and the solid washed with 85°C water. The filtrate was cooled to room temperature and then acidified to pH = 1 using an aqueous 6M HCl solution. The precipitated solid was collected by suction over Büchner and dried over vacuum. The resulting tosyl anthranilic acids were used without further purification.

- General procedure for the peptidic coupling:

In a round bottom flask, 1.2 equiv. of allyl benzylamine was placed in DCM (C = 0.67 mol/L) under argon. Then 1.0 equiv. of the desired tosyl anthranilic acid or salicylic acid were added, followed successively by 1.0 equiv. of EDC.HCl and 1.0 equiv. of HOBt. The clear solution was stirred at room temperature or reflux until starting material was totally consumed (monitored by TLC). The reaction mixture was then quenched with water. The aqueous layer was extracted with DCM (3 times). The combined organic phases were then dried with $MgSO_4$, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using Pentane/Et_2O as eluent (9:1 to 1:1). Rf of aniline derivatives were between 0.4 and 0.6 using Cyclohexane/AcOEt 1:1 as eluent. Rf of phenol derivatives were between 0.5 and 0.7 using Pentane/AcOEt 1:1 as eluent.

[1] M. D. Surman, M. J. Mulvihill, M. J. Miller, *Org. Lett.*, 2002, **4**, 139

- Preparation of *N*-allylbenzylamine:

The *N*-allylbenzylamine was synthesized using a reported procedure.[2] In a round bottom flask was placed at 0°C, 4.0 equiv. of $MgSO_4$ in dry DCM (C = 0.2 mol/L) under argon, then 1.0 equiv. of benzaldehyde was added, followed by 1.1 equiv. of allylamine. The suspension was stirred at room temperature for 24h, then the reaction mixture was filtrated over Büchner and the solvent was removed under vaccum. The crude imine was used directly without purification in the next step. The oily residue was dissolved in MeOH (C = 1 mol/L) and 2.0 equiv. of sodium borohydride were added by small portions at 0°C. The solution was stirred at room temperature for 2h, then the solvent was evaporated and the reaction was quenched carefully with a saturated aqueous solution of ammonium chloride. The aqueous phase was extracted with DCM (3 times) and the combined organic phases were then dried with $MgSO_4$, filtrated and the solvent was removed under vacuum. The resulting *N*-allylbenzylamine showed clean NMR spectra and was used without further purification.

- Preparation of *N*-benzylprop-2-yn-1-amine and *N*-benzylbut-2-yn-1-amine:

These two propargylic amines were prepared using a reported procedure.[3] In a round bottom flask, under argon, was placed 6.0 equiv. of benzylamine. Then, 1.0 equiv. of the appropriate propargyl bromide was added dropwise and the orange solution was stirred at room temperature for 20h. The mixture was then diluted with water and Et_2O, the layers were separated and the organic one was washed using a saturated aqueous solution of sodium bicarbonate. After drying with $MgSO_4$ and filtration, the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using Cyclohexane/AcOEt as eluent (6:4).

- Preparation of *N*-benzyl-3-phenylprop-2-yn-1-amine:

This propargylic amine was prepared using a reported procedure.[4] In a round bottom flask, under argon, was placed 1.0 equiv. of iodobenzene followed by 4 mol% of CuI and 2 mol% of $Pd(PPh_3)_2Cl_2$ in NEt_3 (C = 1.5 mol/L). Then, a solution of 1.0 equiv. of *N*-Benzylprop-2-yn-1-amine in THF (C = 0.75 mol/L) was added and the suspension was stirred at room temperature for 45 mn. The reaction mixture was then filtrated on celite® and the solids washed with AcOEt.

[2] S. Kakaei, J. Xu, *Org. Biomol. Chem.*, 2013, **11**, 5481.
[3] C. Molinaro, T. F. Jamison, *J. Am. Chem. Soc.*, 2003, **125**, 8076
[4] H. V. Wachenfeldt, F. Paulsen, A. Sundin, D. Strand, *Eur. J. Org. Chem.*, **2013**, 4578.

After evaporation the crude residue was purified by silica gel flash chromatography using Cyclohexane/AcOEt as eluent (6:4). Rf was 0.4 using Cyclohexane/AcOEt 1:1 as eluent.

- Preparation of (Z)-*N*-benzylbut-2-en-1-amine and (Z)-*N*-benzyl-3-phenylprop-2-en-1-amine:

These alkenes were prepared using a reported procedure.[5] In a dry round bottom flask were placed 0.25 equiv. (0.31 mmol) of nickel(II) acetate tetrahydrate in 0.6 mL of MeOH, followed by 0.25 equiv. (0.31 mmol) of sodium borohydride at 0°C. The suspension was stirred at room temperature for 15 mn. Then, 1.0 equiv. (1.24 mmol) of *N*-Benzylbut-2-yn-1-amine or *N*-Benzyl-3-phenylprop-2-yn-1-amine and 0.5 equiv. (0.62 mmol) of ethylene diamine in 4.0 mL of MeOH were added and the mixture was stirred under H_2 atmosphere at room temperature. After total consumption of starting material (monitored by TLC), the reaction was filtrated on celite® and the solids washed with AcOEt. The solvent was removed under vacuum and the crude residue was then purified by silica gel flash chromatography using AcOEt/MeOH as eluent (9/1).

Procedure for aminoacetoxylation reaction:

In a dry schlenk tube were placed, 1.0 equiv. (0.2 mmol) of alkenyl-amide **1**, followed by 10 mol% of $Pd(OAc)_2$ (0.02 mmol) and 2.5 equiv. (0.5 mmol) of iodosobenzene diacetate. The schlenk tube was flushed with argon, then dry DCM (C = 0.2 mol/L) was introduced and the solution was stirred for two minutes to achieve complete dissolution of starting materials. Finally, 1.0 equiv. (0.2 mmol) of DiPEA was added and the solution was stirred at room temperature. After total consumption of starting material (monitored by TLC), the reaction was quenched with a saturated aqueous solution of ammonium chloride. The aqueous phase was extracted with DCM (3 times). The combined organic phases were then dried with $MgSO_4$, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using Pentane/Et_2O as eluent (9:1 to 4:6). Rf of this set of compounds were between 0.3 and 0.5 using Cyclohexane/AcOEt 1:1 as eluent.

Procedure for oxyacetoxylation reaction:

In a dry schlenk tube were placed 1.0 equiv. (0.2 mmol) of alkenyl-amide **12**, followed by 10 mol% of $Pd(OAc)_2$ (0.02 mmol) and 2.5 equiv. (0.5 mmol) of iodosobenzene diacetate. The

[5] G. Prestat, C. Baylon, M.-P. Heck, G. A. Grasa, S. P. Nolan, C. Mioskowski, *J. Org. Chem.*, 2004, **69**, 5770

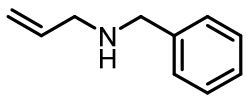
schlenk tube was flushed with argon, then dry DMF (C = 0.2 mol/L) was introduced and the solution was stirred for two minutes to achieve complete dissolution of starting materials. Finally, 1.0 equiv. (0.2 mmol) of Bu_4NOAc was added and the solution was stirred at room temperature. After total consumption of starting material (monitored by TLC), the reaction was quenched with a saturated aqueous solution of ammonium chloride. The aqueous phase was extracted with DCM (3 times). The combined organic phases were then dried with $MgSO_4$, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using Pentane/Et_2O as eluent (7:3 to 2:8). Rf of this set of compounds were between 0.4 and 0.6 using Pentane/AcOEt 1:1 as eluent.

Procedure for tosyl amine deprotection:

In a dry round bottom flask were placed 20.0 equiv. (12.5 mmol) of magnesium turnings under argon, followed by a solution of 1.0 equiv. (0.625 mmol) of tosyl amine **2a** in MeOH (C = 0.045 mol/L). The suspension was vigorously stirred at room temperature for two hours. The grey-white reaction mixture was then diluted with DCM and a saturated aqueous solution of ammonium chloride. The two phases were separated and the aqueous one was extracted with DCM (4 times). The combined organic phases were washed 1 time with a saturated aqueous solution of sodium bicarbonate then dried with $MgSO_4$ and the solvent was removed under vacuum. The crude residue was then purified by silica gel flash chromatography using Pentane/AcOEt as eluent (3:7 to 0:1).

III. Characterization of compounds

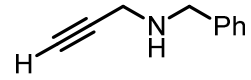
N-Allylbenzylamine:



(known compound[2]) pale yellow oil, 80% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (d, *J* = 4.5 Hz, 4H), 7.30-7.25 (m, 1H), 5.97 (ddt, *J* = 16.5 Hz, *J* = 10.0 Hz, *J* = 5.5 Hz, 1H), 5.23 (dd, *J* = 17.0 Hz, *J* = 2.0 Hz, 1H), 5.16 (dd, *J* = 10.0 Hz, *J* = 1.0 Hz, 1H), 3.82 (s, 2H), 3.30 (d, *J* = 6.5 Hz, 2H), 1.80 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.2, 136.8, 128.5, 128.3, 127.1, 116.2, 53.3, 51.8.

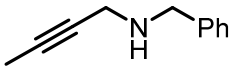
N-Benzylprop-2-yn-1-amine:

[2] S. Kakaei, J. Xu, *Org. Biomol. Chem.*, 2013, **11**, 5481.



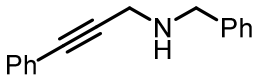
(known compound[3]) yellow oil, 83% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48-7.21 (m, 5H), 3,90 (s, 2H), 3.44 (d, *J* = 2.5 Hz, 2H), 2.27 (t, *J* = 2.5 Hz, 1H), 1.62-1.46 (br s, 1H).

N-Benzylbut-2-yn-1-amine:



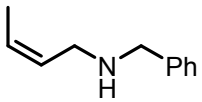
(known compound[6]) yellow oil, 84% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30-7.21 (m, 4H), 7.20-7.14 (m, 1H), 3,78 (s, 2H), 3,30 (q, *J* = 2.5 Hz, 2H), 1,77 (t, *J* = 2.5 Hz, 3H), 1.48-1.38 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.9, 128.5, 128.5, 127.2, 79.3, 77.3, 52.7, 38.0, 3.6.

N-Benzyl-3-phenylprop-2-yn-1-amine:



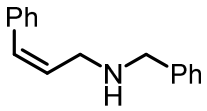
(known compound[4]) yellow oil, 96% Yield, ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.52-7.43 (m, 2H), 7.42-7.25 (m, 8H), 3.96 (s, 2H), 3.66 (s, 2H), 1.71-1.51 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.7, 131.8, 128.6, 128.4, 128.2, 127.3, 123.4, 87.7, 83.9, 52.7, 38.4; MS (ESI) : m/z = 222.2 [M+H$^+$]; IR (ν = cm^{-1}) : 3342, 3055, 3026, 2920, 2844, 1952, 1885, 1598, 1488, 1450, 1438, 1103.

(Z)-*N*-Benzylbut-2-en-1-amine:



(known compound[7]) yellow oil, 91% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32 (d, *J* = 4.5 Hz, 4H), 7.26-7.20 (br s, 1H), 5.69-5.46 (m, 2H), 3.90-3.70 (br s, 2H), 3.40-3.23 (br s, 2H), 1.62 (d, *J* = 6.0 Hz, 3H).

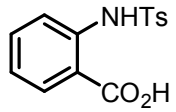
(Z)-*N*-Benzyl-3-phenylprop-2-en-1-amine:



(known compound[8]) orange oil, 80% Yield, ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.35-7.13 (m, 10H), 6.52 (d, *J* = 11.75 Hz, 1H), 5.79 (td, *J* = 11.75 Hz, *J* = 6.5 Hz, 1H), 3.75 (s, 2H), 3.53 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.8, 137.1, 131.1, 130.7, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.2, 127.0, 126.4, 53.5, 46.9.

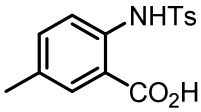
[3] C. Molinaro, T. F. Jamison, *J. Am. Chem. Soc.*, 2003, **125**, 8076
[6] Y. Hirata, T. Yukawa, N. Kashihara, Y. Nakao, T. Hiyama, *J. Am. Chem. Soc.*, 2009, **131** 10964.
[4] H. V. Wachenfeldt, F. Paulsen, A. Sundin, D. Strand, *Eur. J. Org. Chem.*, **2013**, 4578.
[7] J. Blid, P. Brandt, P. Somfai, *J. Org. Chem.*, 2004, **69**, 3043.
[8] B. C. Ranu, A. Majee, A. Sarkar, *J. Org. Chem.*, 1998, **63**, 370.

2-((4-Methylphenyl)sulfonamido)benzoic acid:



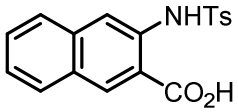
(known compound[1]) white solid, 80% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 7.93 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.67-7.64 (m, 3H), 7.48-7.44 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 171.4, 145.6, 141.8, 137.5, 135.2, 132.8, 130.7, 128.4, 124.3, 120.4, 118.4, 21.4; MS (ESI) : m/z = 291.9 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{14}H_{12}O_4NS$ [M-H$^+$] 290.04925, found 290.04883; IR (ν = cm^{-1}) : 3203, 3069, 2997, 1673, 1492; mp : 224-228°C.

5-Methyl-2-((4-methylphenyl)sulfonamido)benzoic acid:



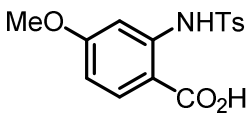
(known compound[9]) white solid, 88% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 7.73 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.5 Hz, *J* = 2.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 171.2, 145.5, 139.3, 137.4, 135.9, 134.5, 132.8, 130.6, 128.3, 120.9, 118.3, 21.4, 20.5; MS (ESI) : m/z = 305.9 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{15}H_{14}O_4NS$ [M-H$^+$] 304.06490, found 304.06415; mp : 198-202°C.

3-((4-Methylphenyl)sulfonamido)-2-naphthoic acid:



(known compound[10]) brown solid, 86% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 8.56 (s, 1H), 8.01 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 171.1, 145.6, 137.3, 137.2, 136.7, 135.0, 130.6, 130.6, 130.5, 130.1, 128.4, 128.1, 127.0, 118.4, 118.2, 21.4; MS (ESI) : m/z = 341.9 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{18}H_{14}O_4NS$ [M-H$^+$] 340.06490, found 340.06445; IR (ν = cm^{-1}) : 3204, 3008, 2889, 1677, 1282; mp : 224-228°C.

4-Methoxy-2-((4-methylphenyl)sulfonamido)benzoic acid:

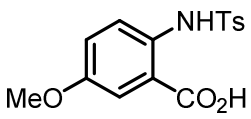


(known compound[11]) white solid, 75% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* =

[1] M. D. Surman, M. J. Mulvihill, M. J. Miller, *Org. Lett.*, 2002, **4**, 139
[9] M. R. Yadav, R. K. Rit, A. K. Sahoo, *Org. Lett.*, 2013, **15**, 1638
[10] W. F. Beech, N. Legg, *J. Chem. Soc.*, 1950, 961
[11] W. N. Speckamp, U. K. Pandit, H. O. Huisman, *Recl. Trav. Chim. Pays Bas*, **82**, 39

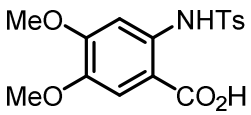
8.0 Hz, 2H), 7.14 (d, *J* = 2.5 Hz, 1H), 6.58 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 3.79 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (CD_3OD, 62.5 MHz) δ 172.0, 165.2, 145.6, 143.6, 137.4, 134.7, 134.2, 130.7, 128.3, 109.9, 104.7, 56.0, 21.4; MS (ESI) : m/z = 320.1 [M-H$^+$]; HRMS (ESI) : m/z calcd for $C_{15}H_{14}O_5NS$ [M-H$^+$] 320.05960, found 320.05982; IR (ν = cm^{-1}) : 3214, 2925, 1654, 1161; mp : 230-234°C.

5-Methoxy-2-((4-methylphenyl)sulfonamido)benzoic acid:



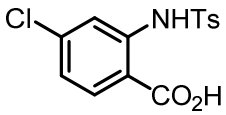
beige solid, 58% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 7.63-7.54 (m, 3H), 7.39 (s, 1H), 7.27-7.21 (m, 2H), 7.12-7.07 (m, 1H), 3.74 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 170.7, 157.3, 145.5, 137.2, 134.6, 130.6, 128.4, 123.8, 121.4, 120.5, 116.4, 56.0, 21.4; MS (ESI) : m/z = 321.9 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{15}H_{14}O_5NS$ [M-H$^+$] 320.0598, found 320.0599; IR (ν = cm^{-1}) : 3163, 2930, 1628, 1161; mp : 178-182°C.

4,5-Dimethoxy-2-((4-methylphenyl)sulfonamido)benzoic acid:



(known compound[12]) beige solid, 57% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.38 (s, 1H), 7.30-7.25 (m, 3H), 3.87 (s, 3H), 3.75 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 171.0, 155.3, 146.4, 145.6, 137.3, 137.2, 130.7, 128.4, 114.6, 104.6, 56.6, 56.5, 21.4; MS (ESI) : m/z = 351.9 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{16}H_{16}O_6NS$ [M-H$^+$] 350.07038, found 350.07004; IR (ν = cm^{-1}) : 3188, 3049, 2992, 1648, 1268; mp : 218-222°C.

4-Chloro-2-((4-methylphenyl)sulfonamido)benzoic acid:



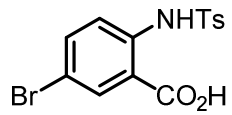
(known compound[13]) white solid, 68% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 7.85 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.00 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 170.5, 145.9, 142.9, 141.2, 137.1, 134.1, 130.8, 128.2, 124.2, 119.7, 116.2, 21.4; MS (ESI) : m/z = 325.8 [M+H$^+$]; HRMS (ESI) : m/z calcd for

[12] R. V. Coombs, R. P. Danna, M. Denzer, G. E. Hardtmann, B. Huegi, G. Koletar, J. Koletar, H. Ott, E. Jukniewicz, *J. Med. Chem.*, 1973, **16**, 1237

[13] M. M. Krayushkin, B. V. Lichitskii, D. V. Pashchenko, I. A. Antonov, B. V. Nabatov, A. A. Dudinov, *Russ. J. Organ. Chem.* 2007, **43**, 1357 and references cited.

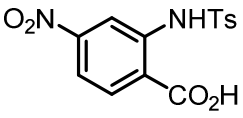
$C_{14}H_{11}O_4NClS$ [M-H$^+$] 324.01028, found 324.00980; IR (ν = cm^{-1}) : 3182, 3031, 2823, 1672, 1160; mp : 200-204°C.

5-Bromo-2-((4-methylphenyl)sulfonamido)benzoic acid:



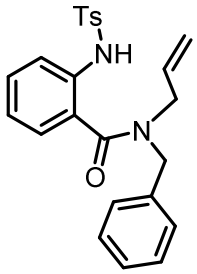
(known compound[14]) white solid, 74% Yield, ^{1}H NMR (CD_3OD, 500 MHz) δ 8.03-8.01 (m, 1H), 7.67 (td, *J* = 8.5 Hz, *J* = 1.5 Hz, 2H), 7.61-7.59 (m, 2H), 7.31-7.28 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 169.9, 145.9, 140.9, 138.0, 137.2, 135.1, 130.8, 128.4, 122.3, 119.8, 116.7, 21.4; MS (ESI) : m/z = 369.8 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{14}H_{11}O_4NBrS$ [M-H$^+$] 367.9598, found 367.9587; IR (ν = cm^{-1}) : 3065, 2872, 1662, 1162; mp : 198-200°C.

2-((4-Methylphenyl)sulfonamido)-4-nitrobenzoic acid:



(known compound[15]) brown solid, 71% Yield, ^{1}H NMR (CD_3OD, 250 MHz) δ 8.46 (d, *J* = 2.0 Hz, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), 7.85 (dd, *J* = 6.0 Hz, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.25 Hz, 2H), 2.35 (s, 3H); MS (ESI) : m/z = 335.2 [M-H$^+$]; HRMS (ESI) : m/z calcd for $C_{14}H_{11}O_6N_2S$ [M-H$^+$] 335.03433, found 335.03366; IR (ν = cm^{-1}) : 3224, 3108, 2860, 1702, 1531, 1157. mp : 200-204°C.

N-Allyl-*N*-benzyl-2-((4-methylphenyl)sulfonamido)benzamide (**1a**):

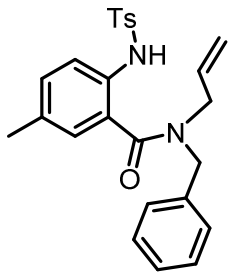


beige solid, 74% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.52-8.23 (br s, 1H), 7.68 (d, *J* = 5.0 Hz, 2H), 7.42-6.88 (m, 11H), 5.88-5.54 (br s, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.14 (d, *J* = 17.5 Hz, 1H), 4.70-3.19 (br m, 4H), 2.47-2.20 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.3, 143.6, 136.2, 132.7, 131.2, 129.6, 129.1, 128.1, 127.3, 127.0, 126.6, 124.0, 123.3, 118.8, 50.3, 47.5, 21.6; MS (ESI) : m/z = 421.0 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{24}H_{23}O_3N_2S$ [M-H$^+$] 419.14349, found 419.14264; IR (ν = cm^{-1}) : 3027, 2988, 2920, 2899, 1620, 1163; mp : 76-80°C.

N-Allyl-*N*-benzyl-5-methyl-2-((4-methylphenyl)sulfonamido)benzamide (**1b**):

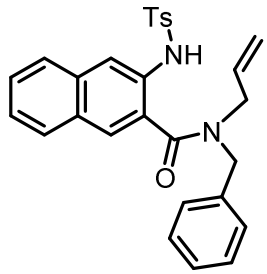
[14] P. Wangtrakuldee, M. S. Byrd, C. G. Campos, M. W. Henderson, Z. Zhang, M. Clare, A. Masoudi, P. J. Myler, J. R. Horn, P. A. Cotter, T. J. Hagen, *ACS Med. Chem. Lett.*, 2013, **4**, 699

[15] E. H. Charlesworth, P. Mathiaparanam, *Can. J. Chem.*, 1968, **46**, 463



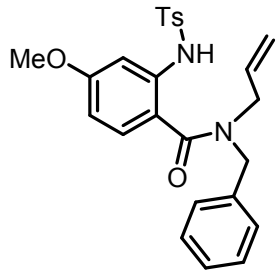
white solid, 75% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.28-8.08 (br m, 1H), 7.78-6.73 (br m, 12H), 5.89-5.54 (br m, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 5.13 (dd, *J* = 17.5 Hz, *J* = 1.5 Hz, 1H), 4.71-3.10 (br m, 4H), 2.51-1.98 (br m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.3, 143.4, 136.6, 134.1, 133.4, 132.7, 131.8, 129.5, 129.0, 128.1, 127.4, 127.3, 123.8, 118.8, 50.3, 47.4, 21.5, 20.8; MS (ESI) : m/z = 435.0 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{25}H_{27}O_3N_2S$ [M+H$^+$] 435.17369, found 435.17346; IR (ν = cm^{-1}) : 3026, 2917, 2855, 1620, 1383, 1165; mp : 138-140°C.

N-Allyl-*N*-benzyl-3-((4-methylphenyl)sulfonamido)-2-naphthamide (**1c**):



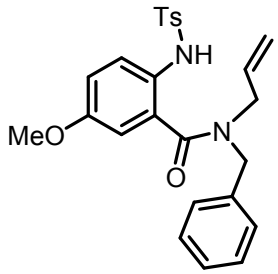
white solid, 61% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.48-8.27 (br s, 1H), 8.15-8.03 (br s, 1H), 7.86-7.60 (br m, 4H), 7.57-7.31 (br m, 8H), 7.24-7.07 (br m, 1H), 6.90-6.76 (br s, 1H), 5.97-5.61 (br s, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 5.19 (dd, *J* = 17.0 Hz, *J* = 1.0 Hz, 1H), 4.82-3.17 (br m, 4H), 2.48-2.13 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.3, 143.5, 136.7, 134.3, 132.7, 132.4, 129.7, 129.6, 129.4, 129.1, 128.2, 127.9, 127.5, 127.3, 127.2, 126.4, 121.2, 118.7, 117.2, 50.5, 47.7, 21.5; MS (ESI) : m/z = 471.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{28}H_{27}O_3N_2S$ [M+H$^+$] 471.17369, found 471.17371; IR (ν = cm^{-1}) : 3155, 3046, 2984, 1623, 1353, 1145; mp : 125-129°C.

N-Allyl-*N*-benzyl-4-methoxy-2-((4-methylphenyl)sulfonamido)benzamide (**1d**):



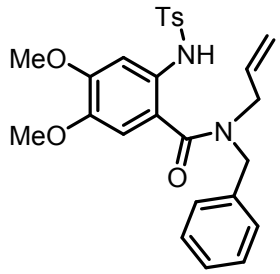
white solid, 74% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.31-8.38 (br s, 1H), 7.86-6.72 (br m, 11H), 6.53 (s, 1H), 5.89-5.51 (br s, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 5.15 (d, *J* = 17.0 Hz, 1H), 4.82-4.15 (br s, 2H), 3.80 (s, 3H), 3.71-2.90 (br s, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 170.5, 161.6, 143.5, 138.5, 136.4, 136.3, 132.4, 129.5, 128.8, 128.5, 127.8, 127.1, 118.6, 117.7, 109.8, 108.2, 55.5, 49.9, 49.7, 21.4; MS (ESI) : m/z = 451.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{25}H_{27}O_4N_2S$ [M+H$^+$] 451.16860, found 451.16904; IR (ν = cm^{-1}) : 3173, 3018, 2972, 2920, 1623, 1294, 1159; mp = 131-133°C.

N-Allyl-*N*-benzyl-5-methoxy-2-((4-methylphenyl)sulfonamido)benzamide (**1e**):



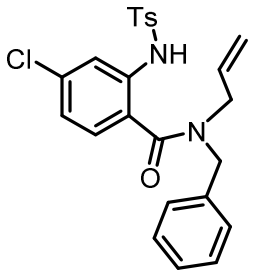
white solid, 64% Yield, ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.30-7.98 (br m, 1H), 7.70-6.55 (br m, 12H), 5.90-5.55 (br m, 1H), 5.31 (d, *J* = 10.25 Hz, 1H), 5.16 (d, *J* = 17.0 Hz, 1H), 4.68-2.95 (br m, 7H), 2.50-2.10 (br m, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 169.6, 156.2, 143.1, 136.2, 132.5, 129.6, 129.3, 128.7, 128.1, 127.9, 127.0, 126.6, 126.2, 125.9, 118.3, 116.3, 111.8, 110.7, 55.5, 49.6, 47.3, 21.3; MS (ESI) : m/z = 451.1 [M+H$^+$]; IR (ν = cm^{-1}) : 3166, 2976, 2899, 1628, 1289, 1161; mp : 136-138°C.

N-Allyl-*N*-benzyl-4,5-dimethoxy-2-((4-methylphenyl)sulfonamido)benzamide (**1f**):



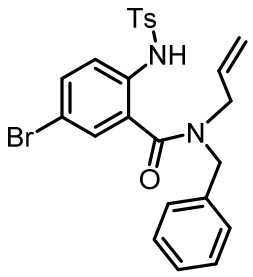
white solid, 71% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.90-8.36 (br s, 1H), 7.67-6.50 (m, 11H), 5.81-5.66 (br s, 1H), 5.30 (d, *J* = 9.0 Hz, 1H), 5.17 (d, *J* = 13.5 Hz, 1H), 4.80-2.80 (br m, 10H), 2.51-2.08 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 151.1, 145.4, 143.4, 136.7, 136.5, 132.7, 130.9, 129.6, 129.1, 127.9, 127.4, 118.5, 118.3, 109.5, 108.5, 56.3, 49.6, 49.5, 21.6; MS (ESI) : m/z = 481.2 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{26}H_{29}O_5N_2S$ [M+H$^+$] 481.17917, found 481.17935; IR (ν = cm^{-1}) : 3049, 2974, 2904, 1600, 1520, 1352, 1163; mp : 124-128°C.

N-Allyl-*N*-benzyl-4-chloro-2-((4-methylphenyl)sulfonamido)benzamide (**1g**):



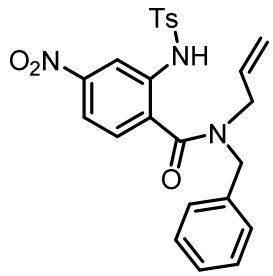
white solid, 59% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.68-8.32 (br s, 1H), 7.80-6.75 (br m, 12H), 5.87-5.48 (br s, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 5.14 (d, *J* = 17.5 Hz, 1H), 4.73-3.13 (br m, 4H), 2.54-2.13 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6, 143.9, 137.7, 137.2, 136.4, 132.3, 129.9, 129.8, 129.4, 129.1, 128.2, 128.0, 127.3, 124.1, 122.9, 118.9, 50.3, 47.7, 21.6; MS (ESI) : m/z = 455.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{24}H_{24}O_3N_2ClS$ [M+H$^+$] 455.11907, found 455.11966; IR (ν = cm^{-1}) : 3077, 2927, 2855, 1622, 1167; mp : 122-126°C.

N-Allyl-*N*-benzyl-5-bromo-2-((4-methylphenyl)sulfonamido)benzamide (**1h**):



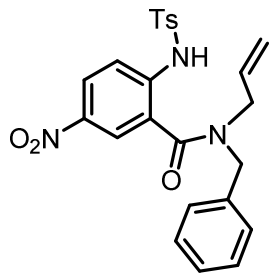
white solid, 57% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.36-8.12 (br s, 1H), 7.88-6.72 (br m, 12H), 5.92-5.53 (br s, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 5.15 (d, *J* = 17.5 Hz, 1H), 4.80-3.07 (br m, 4H), 2.56-2.14 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.7, 143.9, 136.4, 136.3, 135.2, 134.0, 132.1, 129.8, 129.6, 129.5, 129.4, 129.1, 128.2, 127.3, 125.0, 119.1, 117.2, 50.2, 47.7, 21.6; MS (ESI) : m/z = 500.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{24}H_{24}O_3N_2BrS$ [M+H$^+$] 499.06855, found 499.06860; IR (ν = cm^{-1}) : 3013, 2925, 1624, 1378, 1164; mp : 144-148°C.

N-Allyl-*N*-benzyl-2-((4-methylphenyl)sulfonamido)-4-nitrobenzamide (**1i**):



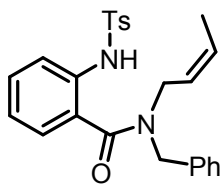
white solid, 45% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.58-8.19 (br m, 2H), 7.97-7.51 (br m, 3H), 7.51-6.92 (br m, 8H), 5.91-5.54 (br m, 1H), 5.31 (d, *J* = 10.5 Hz, 1H), 5.18 (d, *J* = 17.0 Hz, 1H), 4.80-3.27 (br m, 4H), 2.54-2.24 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.4, 149.2, 144.5, 137.5, 136.1, 131.9, 130.2, 130.0, 129.2, 128.4, 127.7, 127.4, 126.6, 119.2, 118.4, 116.8, 50.3, 47.9, 21.7; MS (ESI) : m/z = 466.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{24}H_{24}O_5N_3S$ [M+H$^+$] 466.14312, found 466.14377; IR (ν = cm^{-1}) : 3060, 2948, 2861, 1622, 1530, 1164; mp : 128-130°C.

N-Allyl-*N*-benzyl-2-((4-methylphenyl)sulfonamido)-5-nitrobenzamide (**1j**):



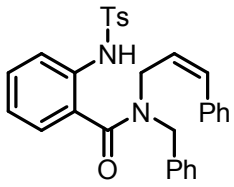
pale yellow solid, 42% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.94-8.77 (br s, 1H), 8.25-8.04 (br m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74-7.53 (br s, 2H), 7.50-7.29 (br m, 5H), 7.22-6.96 (br s, 2H), 5.95-5.56 (br m, 1H), 5.35 (d, *J* = 10.0 Hz, 1H), 5.20 (dd, *J* = 17.0 Hz, *J* = 1.0 Hz, 1H), 4.84-3.34 (br m, 4H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.3, 144.7, 142.6, 142.4, 136.2, 131.7, 130.1, 129.3, 128.4, 127.3, 126.5, 123.0, 119.5, 50.7, 48.2, 21.7; HRMS (ESI) : m/z calcd for $C_{24}H_{24}O_5N_3S$ [M+H$^+$] 466.14312, found 466.14340; IR (ν = cm^{-1}) : 3070, 2966, 2927, 2853, 1654, 1165; mp : 130-134°C.

(Z)-*N*-Benzyl-*N*-(but-2-en-1-yl)-2-((4-methylphenyl)sulfonamido)benzamide (**1k**):



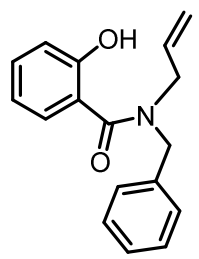
white foam, 71% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.52-8.18 (br s, 1H), 7.84-6.71 (m, 13H), 5.84-5.41 (br s, 1H), 5.46-5.16 (br s, 1H), 4.84-2.97 (br m, 4H), 2.49-2.09 (br m, 3H), 1.61-1.21 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.1, 143.5, 136.6, 136.1, 131.0, 130.9, 129.8, 129.7, 129.6, 129.2, 128.9, 128.6, 128.6, 128.0, 127.3, 125.2, 124.2, 123 .9, 123.6, 122.6, 47.7, 44.8, 21.5, 13.0; MS (ESI) : m/z = 435.3 [M+H^{+}].

(Z)-*N*-Benzyl-2-((4-methylphenyl)sulfonamido)-N-(3-phenylallyl)benzamide (**1l**):



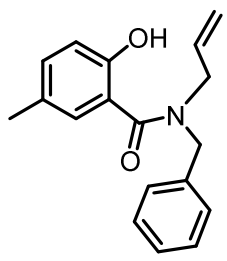
pale yellow foam, 89% Yield, ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.56-8.36 (br s, 1H), 7.83-6.74 (m, 18H), 6.66 (d, *J* = 11.5 Hz, 1H), 5.60 (td, *J* = 11.5Hz, *J* = 6.5Hz, 1H), 4.68-3.41 (m, 4H), 2.41-2.06 (br s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.8, 143.5, 136.3, 136.0, 133.3, 131.1, 129.5, 128.9, 128.8, 128.7, 128.5, 128.4, 128.0, 127.6, 127.3, 126.7, 126.2, 124.1, 123.5, 47.9, 45.9, 21.6; MS (ESI) : m/z = 495.3 [M-H^{+}].

N-Allyl-*N*-benzyl-2-hydroxybenzamide (**12a**):



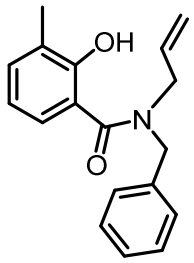
white solid, 42% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.89 (s, 1H), 7.42-7.34 (m, 3H), 7.34-7.27 (m, 4H), 7.02 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 5.95-5.86 (m, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 5.25 (d, *J* = 17.0 Hz, 1H), 4.76 (s, 2H), 4.05 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.6, 159.4, 136.5, 133.0, 132.6, 129.0, 127.8, 127.7, 127.6, 118.7, 118.5, 118.3, 117.2, 50.2, 50.1; IR (ν = cm^{-1}) : 3133, 3083, 2978, 1607, 1577, 1453, 739, mp : 94-98°C.

N-Allyl-*N*-benzyl-2-hydroxy-5-methylbenzamide (**12b**):



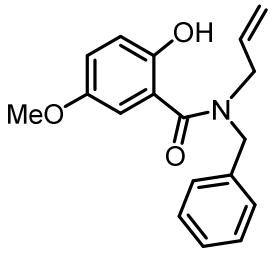
White solid, 68% Yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.59-9.33 (br s, 1H), 7.40-7.34 (m, 2H), 7.34-7.27 (m, 3H), 7.18-7.10 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.95-5.84 (m, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 5.25 (d, *J* = 17.5 Hz, 1H), 4.74 (s, 2H), 4.05 (d, *J* = 5.5 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.6, 156.8, 136.6, 133.6, 132.7, 128.9, 127.8, 127.7, 127.7, 118.5, 117.9, 117.2, 50.3, 50.1, 20.6; IR (ν = cm^{-1}) : 3059, 3033, 2921, 1602, 1577, 1483, 816; mp : 118-122°C.

N-Allyl-*N*-benzyl-2-hydroxy-3-methylbenzamide (**12c**):



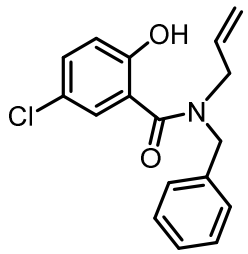
Colorless oil, 49% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.03 (s, 1H), 7.42-7.35 (m, 2H), 7.34-7.27 (m, 3H), 7.24-7.17 (m, 2H), 6.68 (t, *J* = 8.0 Hz, 1H), 5.96-5.85 (m, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 5.25 (d, *J* = 17.5 Hz, 1H), 4.76 (s, 2H), 4.05 (d, *J* = 5.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.0, 157.5, 136.5, 133.9, 132.7, 128.9, 127.7, 127.3, 125.1, 118.4, 118.0, 116.5, 50.2, 50.1, 16.1; IR (ν = cm^{-1}) : 3063, 3030, 2978, 2921, 2857, 1602, 1580, 1428, 1249, 760.

N-Allyl-*N*-benzyl-2-hydroxy-5-methoxybenzamide (**12d**):



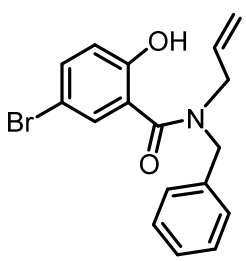
White solid, 61% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.50-8.95 (br s, 1H), 7.42-7.34 (m, 2H), 7.34-7.27 (m, 3H), 6.98-6.89 (m, 2H), 6.89-6.82 (br s, 1H), 5.98-5.87 (m, 1H), 5.35 (d, *J* = 10.5 Hz, 1H), 5.27 (d, *J* = 17.5 Hz, 1H), 4.75 (s, 2H), 4.07 (d, *J* = 5.5 Hz, 2H), 3.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.4, 153.0, 151.8, 136.6, 132.6, 129.1, 127.8, 127.5, 120.0, 119.0, 118.5, 117.3, 111.4, 55.7, 50.2, 50.1; IR (ν = cm^{-1}) : 3145, 3075, 2993, 2951, 2828, 1588, 1580, 1487, 731; mp : 96-98°C.

N-Allyl-*N*-benzyl-5-chloro-2-hydroxybenzamide (**12e**):



White solid, 72% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.60-8.20 (br s, 1H), 7.42-7.35 (m, 2H), 7.34-7.27 (m, 4H), 7.20 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 5.94-5.80 (m, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 5.25 (d, *J* = 17.5 Hz, 1H), 4.73 (s, 2H), 4.00 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.9, 156.1, 136.1, 132.3, 132.0, 128.9, 127.9, 127.8, 127.7, 127.0, 123.6, 120.4, 119.3, 118.6, 50.0, 49.9; IR (ν = cm^{-1}) : 3035, 3014, 2992, 2926, 1574, 1414, 1281, 820; mp : 113-115°C.

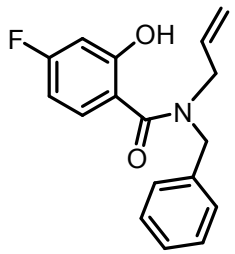
N-Allyl-*N*-benzyl-5-bromo-2-hydroxybenzamide (**12f**):



White solid, 67% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.96-9.06 (br s, 1H), 7.47 (s, 1H), 7.41-7.35 (m, 3H), 7.35-7.25 (m, 3H), 6.86 (d, *J* = 9.0 Hz, 1H), 5.95-5.82 (m, 1H), 5.34 (d, *J* = 10.5 Hz, 1H), 5.26 (d, *J* = 17.5 Hz, 1H), 4.73 (s, 2H), 4.02 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.9, 157.0; 136.1, 135.1, 132.2, 130.0, 129.0, 127.9, 127.8,

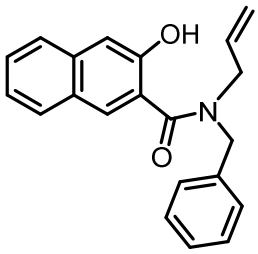
120.3, 119.9, 118.7, 110.6, 50.1, 49.8; IR (ν = cm^{-1}) : 3028, 3013, 2982, 2927, 1571, 1422, 1284, 825, 730; mp : 120-124°C.

N-Allyl-*N*-benzyl-4-fluoro-2-hydroxybenzamide (**12g**):



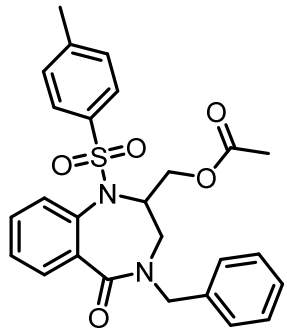
White solid, 77% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10,90-9.70 (br s, 1H), 7.41-7.27 (m, 6H), 6.70 (dd, *J* = 11.0 Hz, *J* = 2.5 Hz, 1H), 6.49 (td, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 5.95-5.84 (m, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 5.26 (d, *J* = 17.0 Hz, 1H), 4.74 (s, 2H), 4.04 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.0, 165.2 (d, *J* = 250.1 Hz), 161.3 (d, *J* = 13.0 Hz), 136.2, 132.4, 129.3 (d, *J* = 10.9 Hz), 129.0, 127.8, 127.6, 118.5, 113.9, 106.2 (d, *J* = 22.1 Hz), 105.1 (d, *J* = 24.0 Hz), 50.2, 50.1; IR (ν = cm^{-1}) : 3060, 2029, 2959, 2887, 1614, 1578, 1431, 1280, 1155, 711; mp : 108-112°C.

N-Allyl-*N*-benzyl-3-hydroxy-2-naphthamide (**12h**):



White solid, 51% Yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.35-8.95 (br s, 1H), 7.93-7.83 (br s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.64-7.54 (br s, 1H), 7.50-7.27 (m, 8H), 5.99-5.90 (m, 1H), 5.37 (d, *J* = 10.5 Hz, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 4.82 (s, 2H), 4.11 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.1, 154.4, 136.4, 136.1, 132.6, 129.1, 128.6, 128.2, 127.9, 127.8, 126.9, 126.5, 124.1, 120.2, 118.6, 112.4, 50.5, 50.1; IR (ν = cm^{-1}) : 3116, 3085, 2982, 2894, 1594, 1488, 1221, mp : 162-167°C.

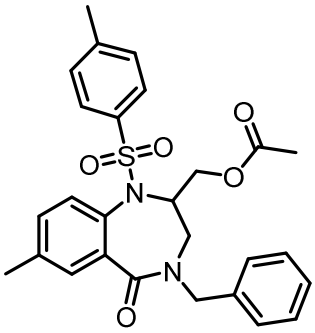
(4-Benzyl-5-oxo-1-tosyl-2,3,4,5–tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methylacetate (**2a**):



Pale yellow solid, 71 mg, 74% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.73 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.60-7.42 (m, 5H), 7.30-7.25 (m, 5H), 7.18-7.12 (m, 2H), 4.74-4.66 (m, 2H), 4.15 (dd, *J* = 11.5 Hz, *J* = 5.5 Hz, 1H), 4.06 (dd, *J* = 11.5 Hz, *J* = 5.7 Hz, 1H), 3.52 (d, *J* = 14.7 Hz, 1H), 3.13 (dd, *J* = 15.2 Hz, *J* = 5.2 Hz, 1H), 3.00 (dd, *J* = 15.0 Hz, *J* = 11.5 Hz, 1H), 2.43 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 170.5, 167.8, 143.9, 136.5, 135.8, 134.7, 133.3, 132.9, 131.9, 130.3, 129.9, 129.4, 128.8, 128.1, 127.8, 127.3, 63.8, 59.9, 49.3, 46.8, 21.6, 20.7; MS (ESI) : m/z = 479.2 [$M+H^+$]; HRMS (ESI) : m/z calcd for $C_{16}H_{27}O_5N_2S$ [$M+H^+$] 479.16352, found

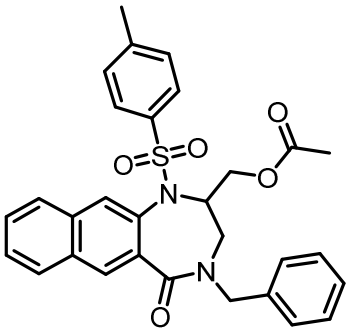
479.16263; IR (ν = cm^{-1}) : 3033, 2926, 2854, 1742, 1646, 1467, 1337, 1226, 1156; mp : 122-126°C.

(4-Benzyl-7-methyl-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methyl acetate (**2b**):



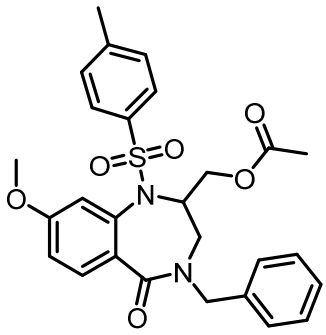
Pale yellow solid, 81 mg, 82% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.55-7.28 (m, 10H), 7.18-7.13 (m, 2H), 4.76-4.65 (m, 2H), 4.15 (dd, *J* = 11.2 Hz, *J* = 5.5 Hz, 1H), 4.07 (dd, *J* = 11.2 Hz, *J* = 5.7 Hz, 1H), 3.51 (d, *J* = 15.0 Hz, 1H), 3.12 (dd, *J* = 15.2 Hz, *J* = 5.2 Hz, 1H), 3.03 (dd, *J* = 15.0 Hz, *J* = 11.7 Hz, 1H), 2.44 (s, 6H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.7, 168.1, 144.0, 139.9, 136.6, 136.0, 134.4, 133.1, 132.8, 130.8, 130.2, 129.9, 128.8, 128.1, 127.9, 127.4, 63.9, 59.9, 49.4, 46.9, 21.7, 21.1, 20.8; MS (ESI) : m/z = 493.2 [M+H^+]; HRMS (ESI) : m/z calcd for $C_{27}H_{29}O_5N_2S$ [M+H^+] 493.17917, found 493.17819; IR (ν = cm^{-1}) : 3038, 2925, 2854, 1746, 1630, 1443, 1253, 1225, 1163; mp : 192-196°C.

(4-Benzyl-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-naphtho[2,3-*e*][1,4]diazepin-2-yl)methyl acetate (**2c**):



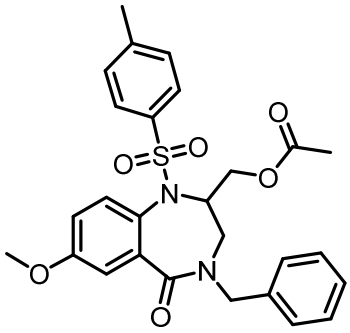
Brown solid, 73 mg, 69% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.26 (s, 1H), 8.02 (s, 1H), 7.93 (d, *J* = 9.0 Hz, 2H), 7.63-7.58 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.33-7.24 (m, 5H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.79 (d, *J* = 15.5 Hz, 1H), 4.79-4.74 (m, 1H), 4.16 (dd, *J* = 11.5 Hz, *J* = 5.5 Hz, 1H), 4.11 (dd, *J* = 11.5 Hz, *J* = 6.5 Hz, 1H), 3.63 (d, *J* = 15.0 Hz, 1H), 3.17 (dd, *J* = 15.5 Hz, *J* = 4.5 Hz, 1H), 3.02 (dd, *J* = 15.5 Hz, *J* = 12.5 Hz, 1H), 2.41 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.7, 167.9, 144.0, 136.7, 136.2, 134.7, 132.8, 132.7, 132.3, 131.6, 129.9, 129.0, 128.9, 128.7, 128.3, 128.2, 127.9, 127.4, 63.6, 59.4, 49.6, 46.8, 21.7, 20.9; MS (ESI) : m/z = 529.1 [M+H^+]; HRMS (ESI) : m/z calcd for $C_{30}H_{29}O_5N_2S$ [M+H^+] 529.17917, found 529.17798; IR (ν = cm^{-1}) : 3031, 2924, 2854, 1742, 1651, 1473, 1351, 1229, 1163; mp : 86-90°C.

(4-Benzyl-8-methoxy-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methyl acetate (**2d**):



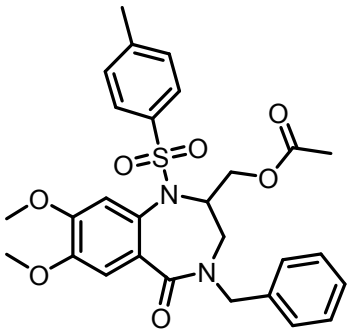
Pale yellow solid, 72 mg, 71% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.67 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.35-7.25 (m, 5H), 7.20-7.10 (m, 2H), 7.06-6.99 (m, 2H), 4.73-4.62 (m, 2H), 4.20-4.06 (m, 2H), 3.91 (s, 3H), 3.49 (d, *J* = 14.7 Hz, 1H), 3.13 (dd, *J* = 15.2 Hz, *J* = 5.5 Hz, 1H), 3.03 (dd, *J* = 15.5 Hz, *J* = 12.0 Hz, 1H), 2.44 (s, 3H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 167.9, 162.3, 144.0, 136.7, 135.8, 134.5, 131.6, 129.9, 128.8, 128.1, 127.8, 127.3, 126.8, 118.1, 115.5, 63.8, 60.0, 55.8, 49.3, 46.8, 21.6, 20.8; MS (ESI) : m/z = 509.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{27}H_{29}O_6N_2S$ [M+H$^+$] 509.1741, found 509.1738; IR (ν = cm^{-1}) : 3071, 2922, 2853, 1745, 1627, 1432, 1242, 1221, 1174, 1164; mp : dec. 125°C.

(4-Benzyl-7-methoxy-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methyl acetate (**2e**):



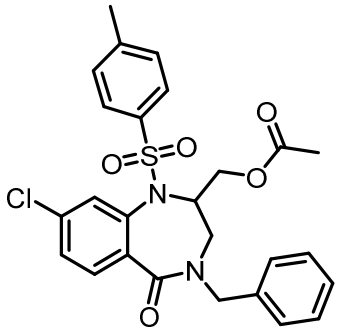
Pale yellow solid, 69 mg, 68% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.32-7.25 (m, 5H), 7.19 (d, *J* = 3.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 8.5 Hz, *J* = 3.0 Hz, 1H), 4.68 (d, *J* = 14.5 Hz, 1H), 4.68-4.64 (m, 1H), 4.11 (dd, *J* = 11.5 Hz, *J* = 5.5 Hz, 1H), 4.04 (dd, *J* = 11.5 Hz, *J* = 6.0 Hz, 1H), 3.86 (s, 3H), 3.49 (d, *J* = 15.0 Hz, 1H), 3.09 (dd, *J* = 15.0 Hz, *J* = 4.5 Hz, 1H), 2.98 (dd, *J* = 15.5 Hz, *J* = 12.5 Hz, 1H), 2.42 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.7, 167.8, 160.2, 144.0, 136.6, 136.0, 135.9, 134.6, 130.0, 128.9, 128.2, 127.9, 127.4, 125.4, 118.4, 114.4, 63.8, 59.9, 55.9, 49.5, 46.9, 21.7, 20.9; MS (ESI) : m/z = 509.2 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{27}H_{29}O_6N_2S$ [M+H$^+$] 509.17408, found 509.17313; IR (ν = cm^{-1}) : 3025, 2925, 2857, 1745, 1635, 1483, 1236, 1218, 1162, 1029; mp : 184-188°C.

(4-Benzyl-7,8-dimethoxy-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl) methyl acetate (**2f**):



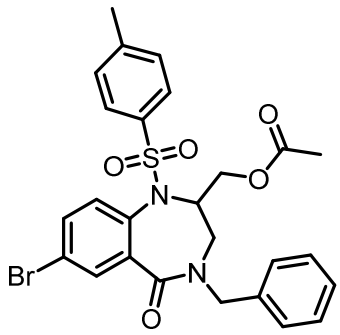
Pale yellow solid, 75 mg, 70% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.33-7.25 (m, 5H), 7.17 (s, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.99 (s, 1H), 4.72-4.67 (m, 1H), 4.64 (d, *J* = 14.5 Hz, 1H), 4.12 (d, *J* = 5.5 Hz, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 3.49 (d, *J* = 15.0 Hz, 1H), 3.11 (dd, *J* = 15.0 Hz, *J* = 5.0 Hz, 1H), 3.03 (dd, *J* = 15.5 Hz, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 167.9, 151.4, 149.6, 144.0, 136.7, 135.7, 129.9, 128.8, 128.2, 127.8, 127.4, 126.8, 126.4, 115.7, 111.8, 63.8, 60.4, 56.4, 56.3, 49.5, 46.9, 21.7, 20.9; MS (ESI) : m/z = 539.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{28}H_{31}O_7N_2S$ [M+H$^+$] 539.18465, found 539.18359; IR (ν = cm^{-1}) : 3013, 2967, 2901, 1747, 1631, 1427, 1244, 1218, 1163, 1146; mp : 136-140°C.

(4-Benzyl-8-chloro-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methyl acetate (**2g**):



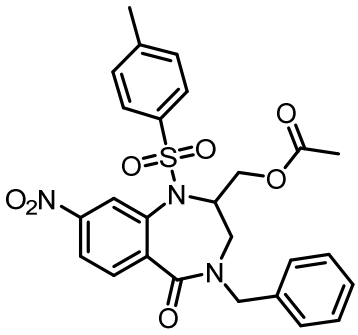
Red-yellow oil, 69 mg, 67% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 3H), 7.24-7.19 (m, 5H), 7.06-7.04 (m, 2H), 4.62-4.56 (m, 2H), 4.11 (dd, *J* = 11.5 Hz, *J* = 5.5 Hz, 1H), 3.95 (dd, *J* = 11.5 Hz, *J* = 5.0 Hz, 1H), 3.44 (d, *J* = 15.0 Hz, 1H), 3.04 (dd, *J* = 15.5 Hz, *J* = 5.0 Hz, 1H), 2.93 (dd, *J* = 15.5 Hz, *J* = 12.5 Hz, 1H), 2.34 (s, 3H), 1.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 166.9, 144.4, 137.7, 136.3, 135.6, 134.3, 133.3, 133.2, 131.4, 130.1, 129.8, 128.9, 128.2, 128.0, 127.4, 63.9, 60.2, 49.5, 46.8, 21.7, 20.7; MS (ESI) : m/z = 513.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{26}H_{26}O_5N_2ClS$ [M+H$^+$] 513.12455, found 513.12354; IR (ν = cm^{-1}) : 3030, 2922, 1746, 1635, 1351, 1219, 1159.

(4-Benzyl-7-bromo-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methyl acetate (**2h**):



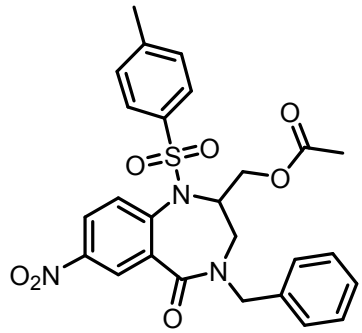
Pale yellow solid, 68 mg, 61% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (d, *J* = 2.5 Hz, 1H), 7.67 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.32-7.27 (m, 5H), 7.13-7.11 (m, 2H), 4.69 (d, *J* = 14.5 Hz, 1H), 4.68-4.64 (m, 1H), 4.13 (dd, *J* = 11.5 Hz, *J* = 5.5 Hz, 1H), 4.04 (dd, *J* = 11.5 Hz, *J* = 5.5 Hz, 1H), 3.49 (d, *J* = 15.0 Hz, 1H), 3.12 (dd, *J* = 15.5 Hz, *J* = 5.0 Hz, 1H), 2.99 (dd, *J* = 15.5 Hz, *J* = 12.5 Hz, 1H), 2.43 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 166.5, 144.4, 136.4, 136.3, 135.7, 135.2, 134.9, 133.4, 132.1, 130.1, 128.9, 128.2, 128.1, 127.4, 123.7, 63.9, 60.1, 49.6, 46.8, 21.8, 20.9; MS (ESI) : m/z = 557.0 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{26}H_{26}O_5N_2BrS$ [M+H$^+$] 557.07403, found 557.07330; IR (ν = cm^{-1}) : 3011, 2923, 2854, 1749, 1634, 1362, 1222, 1170; mp : 210-214°C.

(4-Benzyl-8-nitro-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methyl acetate (**2i**):



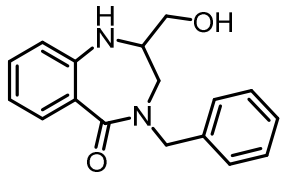
Pale yellow solid, 61 mg, 58% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.36 (d, *J* = 2.0 Hz, 1H), 8.30 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33-7.28 (m, 5H), 7.15-7.12 (m, 2H), 4.69 (d, *J* = 14.5 Hz, 1H), 4.71-4.67 (m, 1H), 4.23 (dd, *J* = 11.5 Hz, *J* = 5.0 Hz, 1H), 4.05 (dd, *J* = 11.5 Hz, *J* = 4.5 Hz, 1H), 3.58 (d, *J* = 15.0 Hz, 1H), 3.18 (dd, *J* = 15.5 Hz, *J* = 4.5 Hz, 1H), 3.02 (dd, *J* = 15.5 Hz, *J* = 12.5 Hz, 1H), 2.43 (s, 3H), 1.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 165.9, 149.8, 144.8, 140.5, 135.8, 135.4, 134.8, 131.6, 130.3, 129.0, 128.5, 128.3, 128.2, 127.4, 124.0, 64.1, 60.3, 49.6, 46.7, 21.7, 20.7; MS (ESI) : m/z = 524.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{26}H_{26}O_7N_3S$ [M+H$^+$] 524.14860, found 524.14746; IR (ν = cm^{-1}) : 3035, 2923, 2853, 1745, 1657, 1527, 1435, 1349, 1255, 1162; mp : 136-142°C.

(4-Benzyl-7-nitro-5-oxo-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepin-2-yl)methyl acetate (**2j**):



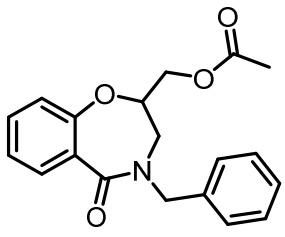
Pale yellow solid, 64 mg, 61% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.55 (d, *J* = 2.5 Hz, 1H), 8.36 (dd, *J* = 8.5 Hz, *J* = 3.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.33-7.28 (m, 5H), 7.15-7.13 (m, 2H), 4.71 (d, *J* = 15.5 Hz, 1H), 4.72-4.67 (m, 1H), 4.19 (dd, *J* = 12.0 Hz, *J* = 5.5 Hz, 1H), 4.07 (dd, *J* = 11.5 Hz, *J* = 5.0 Hz, 1H), 3.57 (d, *J* = 14.5 Hz, 1H), 3.18 (dd, *J* = 15.5 Hz, *J* = 4.5 Hz, 1H), 3.05 (dd, *J* = 15.5 Hz, *J* = 12.0 Hz, 1H), 2.44 (s, 3H), 1.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.4, 165.7, 147.9, 144.9, 138.9, 136.1, 135.8, 135.3, 134.6, 130.3, 129.0, 128.3, 127.3, 126.3, 125.9, 64.1, 60.6, 49.6, 46.6, 21.7, 20.7; MS (ESI) : m/z = 524.1 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{26}H_{26}O_7N_3S$ [M+H$^+$] 524.14860, found 524.14771; IR (ν = cm^{-1}) : 3013, 2968, 2901, 1748, 1637, 1529, 1446, 1352, 1221, 1164; mp : 128-132°C.

4-Benzyl-2-(hydroxymethyl)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (**11**):



Pale yellow oil, 133 mg, 75% yield, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.34-7.24 (m, 5H), 7.23-7.19 (m, 1H), 6.88 (td, *J* = 8.0 Hz, *J* = 0.5 Hz, 1H), 6.62 (dd, *J* = 8.0 Hz, *J* = 0.5 Hz, 1H), 4.94 (d, *J* = 15.0 Hz, 1H), 4.61 (d, *J* = 15.0 Hz, 1H), 3.65-3.54 (m, 1H), 3.47 (dd, *J* = 10.5 Hz, *J* = 5.5 Hz, 1H), 3.40 (dd, *J* = 10.5 Hz, *J* = 7.5 Hz, 1H), 3.35 (dd, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 3.30 (dd, *J* = 15.0 Hz, *J* = 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 144.4, 137.2, 132.5, 132.0, 128.8, 128.3, 127.7, 123.1, 120.0, 119.9, 63.9, 61.4, 51.8, 46.9; MS (ESI) : m/z = 283.2 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{17}H_{19}O_2N_2$ [M+H$^+$] 283.1441, found 283.1436; IR (ν = cm^{-1}) : 3338, 3030, 2923, 2852, 1615, 1480.

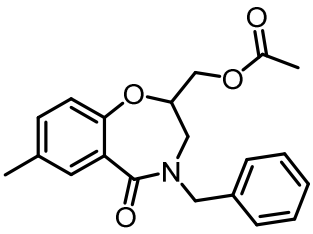
(4-Benzyl-5-oxo-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepin-2-yl)methyl acetate (**13a**):



Pale yellow oil, 46 mg, 71% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.41 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.37-7.32 (m, 4H), 7.31-7.28 (m, 1H), 7.20 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 6.99 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 5.05 (d, *J* = 15.0 Hz, 1H), 4.62 (d, *J* = 15.0 Hz, 1H), 4.45-4.40 (m, 1H), 4.14 (dd, *J* = 12.0 Hz, *J* = 6.0 Hz, 1H), 4.04 (dd, *J* = 12.0 Hz, *J* = 5.0 Hz, 1H), 3.44 (dd, *J* = 16.0 Hz, *J* = 9.0 Hz, 1H), 3.32 (dd, *J* = 16.0 Hz, *J* = 4.0 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 168.8, 152.5, 136.9, 132.9, 130.9, 128.9, 128.3, 128.0, 127.9, 124.4, 122.5, 80.9, 63.2, 51.1,

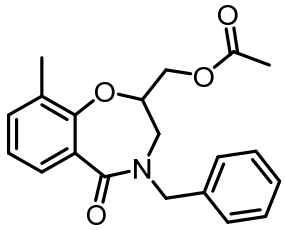
46.9, 20.8; MS (ESI) : m/z = 326.2 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{19}H_{20}O_4N$ [M+H$^+$] 326.1387, found 326.1378; IR (ν = cm^{-1}) : 3032, 2927, 2854, 1743, 1640, 1469, 1237, 1207.

(4-Benzyl-7-methyl-5-oxo-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepin-2-yl)methyl acetate (**13b**):



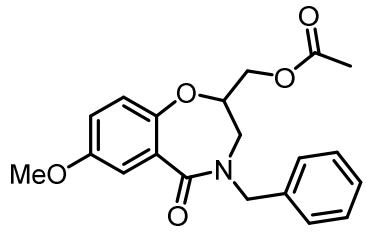
Pale yellow oil, 48 mg, 70% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.61 (d, *J* = 2.0 Hz, 1H), 7.38-7.31 (m, 4H), 7.31-7.27 (m, 1H), 7.21 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 5.03 (d, *J* = 14.5 Hz, 1H), 4.63 (d, *J* = 14.5 Hz, 1H), 4.43-4.37 (m, 1H), 4.14 (dd, *J* = 12.0 Hz, *J* = 6.0 Hz, 1H), 4.02 (dd, *J* = 12.0 Hz, *J* = 5.5 Hz, 1H), 3.41 (dd, *J* = 15.5 Hz, *J* = 8.5 Hz, 1H), 3.30 (dd, *J* = 15.5 Hz, *J* = 3.5 Hz, 1H), 2.35 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 169.1, 150.2, 137.0, 134.2, 133.6, 130.9, 128.9, 128.3, 127.9, 127.8, 122.3, 80.8, 63.2, 51.0, 46.9, 20.8, 20.7; MS (ESI) : m/z = 340.3 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{20}H_{22}O_4N$ [M+H$^+$] 340.1543, found 340.1536; IR (ν = cm^{-1}) : 3031, 2924, 2854, 1743, 1645, 1488, 1218.

(4-Benzyl-9-methyl-5-oxo-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepin-2-yl)methyl acetate (**13c**):



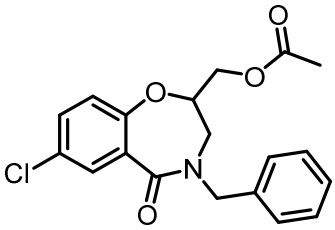
Pale yellow oil, 41 mg, 60% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.38-7.32 (m, 4H), 7.32-7.28 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 5.07 (d, *J* = 15.0 Hz, 1H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.47-4.41 (m, 1H), 4.11 (dd, *J* = 12.0 Hz, *J* = 6.0 Hz, 1H), 4.01 (dd, *J* = 12.0 Hz, *J* = 5.5 Hz, 1H), 3.43 (dd, *J* = 15.5 Hz, *J* = 8.0 Hz, 1H), 3.32 (dd, *J* = 15.5 Hz, *J* = 4.0 Hz, 1H), 2.23 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 169.2, 150.6, 137.1, 134.3, 134.2, 131.1, 128.9, 128.5, 128.3, 127.9, 124.1, 124.1, 80.9, 63.7, 51.0, 46.8, 20.8, 16.1; MS (ESI) : m/z = 340.3 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{20}H_{22}O_4N$ [M+H$^+$] 340.1543, found 340.1536; IR (ν = cm^{-1}) : 3030, 2924, 2854, 1743, 1641, 1421, 1236, 1203.

(4-Benzyl-7-methoxy-5-oxo-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepin-2-yl)methylacetate (**13d**):



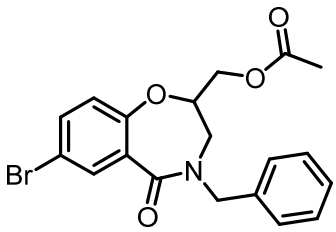
Pale yellow oil, 25 mg, 35% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.27 (m, 6H), 6.96 (dd, *J* = 9.0 Hz, *J* = 3.5 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 5.04 (d, *J* = 15.0 Hz, 1H), 4.62 (d, *J* = 15.0 Hz, 1H), 4.42-4.34 (m, 1H), 4.13 (dd, *J* = 12.0 Hz, *J* = 6.0 Hz, 1H), 4.02 (dd, *J* = 12.0 Hz, *J* = 5.5 Hz, 1H), 3.82 (s, 3H), 3.40 (dd, *J* = 15.5 Hz, *J* = 8.5 Hz, 1H), 3.30 (dd, *J* = 15.5 Hz, *J* = 4.5 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 168.9, 156.4, 145.9, 136.9, 128.9, 128.3, 127.9, 123.6, 119.7, 113.8, 80.8, 63.1, 55.9, 51.1, 46.9, 20.8; MS (ESI) : m/z = 356.3 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{20}H_{22}O_5N$ [M+H$^+$] 356.1492, found 356.1483; IR (ν = cm^{-1}) : 3030, 2936, 2852, 1742, 1645, 1488, 1197.

(4-Benzyl-7-chloro-5-oxo-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepin-2-yl)methyl acetate (**13e**):



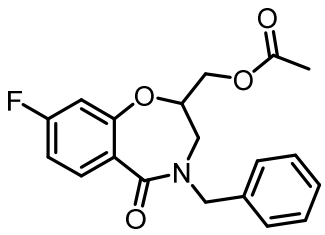
Pale yellow oil, 43 mg, 60% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, *J* = 2.5 Hz, 1H), 7.38-7.28 (m, 6H), 6.94 (d, *J* = 9.0 Hz, 1H), 5.02 (d, *J* = 15.0 Hz, 1H), 4.61 (d, *J* = 15.0 Hz, 1H), 4.45-4.38 (m, 1H), 4.13 (dd, *J* = 12.0 Hz, *J* = 5.5 Hz, 1H), 4.03 (dd, *J* = 12.0 Hz, *J* = 5.0 Hz, 1H), 3.44 (dd, *J* = 16.0 Hz, *J* = 8.5 Hz, 1H), 3.33 (dd, *J* = 16.0 Hz, *J* = 4.0 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.4, 167.4, 151.2, 136.6, 132.8, 130.7, 129.7, 129.1, 129.0, 128.3, 128.1, 123.9, 81.1, 63.1, 51.2, 46.8, 20.8; MS (ESI) : m/z = 360.2 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{19}H_{19}O_4NCl$ [M+H$^+$] 360.0997, found 360.0980; IR (ν = cm^{-1}) : 3031, 2926, 2854, 1744, 1647, 1470, 1210.

(4-Benzyl-7-bromo-5-oxo-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepin-2-yl)methyl acetate (**13f**):



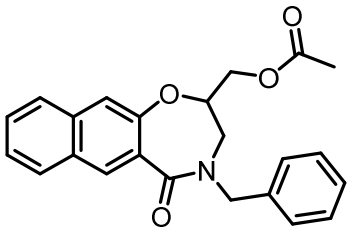
Pale yellow oil, 48 mg, 60% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 7.40-7.27 (m, 5H), 6.88 (d, *J* = 9.0 Hz, 1H), 5.01 (d, *J* = 15.5 Hz, 1H), 4.61 (d, *J* = 15.0 Hz, 1H), 4.46-4.38 (m, 1H), 4.13 (dd, *J* = 12.0 Hz, *J* = 6.0 Hz, 1H), 4.03 (dd, *J* = 12.0 Hz, *J* = 5.0 Hz, 1H), 3.44 (dd, *J* = 15.5 Hz, *J* = 8.0 Hz, 1H), 3.33 (dd, *J* = 15.5 Hz, *J* = 4.0 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 170.4, 167.3, 151.7, 136.6, 135.8, 133.7, 129.4, 129.0, 128.3, 128.1, 124.3, 117.1, 81.1, 63.2, 51.2, 46.8, 20.8; MS (ESI) : m/z = 404.2 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{19}H_{19}O_4NBr$ [M+H$^+$] 404.0492, found 404.0485; IR (ν = cm^{-1}) : 3030, 2924, 2854, 1744, 1647, 1468, 1210.

(4-Benzyl-8-fluoro-5-oxo-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepin-2-yl)methyl acetate (**13g**):



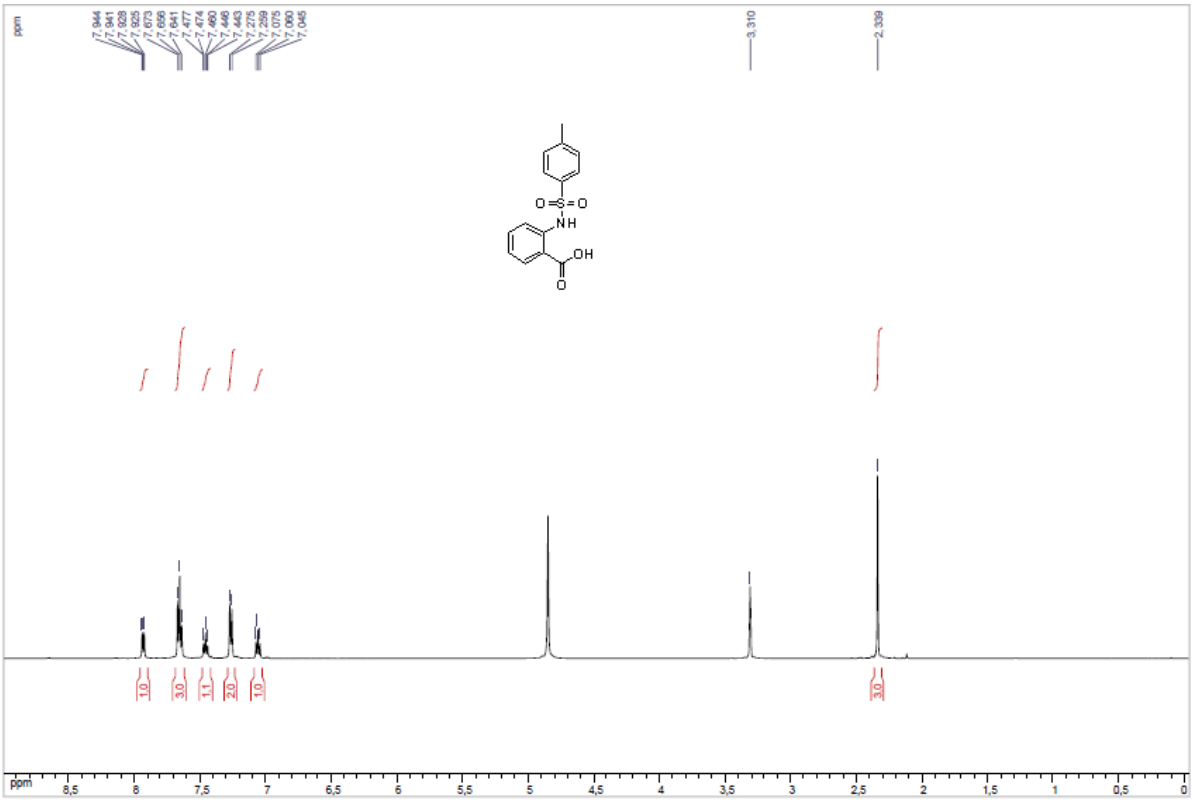
Beige solid, 43 mg, 63% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.87 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 7.38-7.28 (m, 5H), 6.91 (td, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H), 6.71 (dd, *J* = 9.5 Hz, *J* = 2.5 Hz, 1H), 5.04 (d, *J* = 15.5 Hz, 1H), 4.59 (d, *J* = 15.5 Hz, 1H), 4.45-4.39 (m, 1H), 4.14 (dd, *J* = 12.0 Hz, *J* = 5.0 Hz, 1H), 4.05 (dd, *J* = 12.0 Hz, *J* = 5.0 Hz, 1H), 3.48 (dd, *J* = 15.5 Hz, *J* = 9.0 Hz, 1H), 3.35 (dd, *J* = 15.5 Hz, *J* = 4.0 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.4, 167.8, 165.3 (d, *J* = 250.5 Hz), 154.4 (d, *J* = 12.6 Hz), 136.8, 133.1 (d, *J* = 9.9 Hz), 129.0, 128.4, 128.1, 123.5 (d, *J* = 3.1 Hz), 111.7 (d, *J* = 21.2 Hz), 109.5 (d, *J* = 23 Hz), 81.3, 63.3, 51.2, 47.0, 20.8; ^{19}F NMR ($CDCl_3$, 470 MHz) δ -106.5; MS (ESI) : m/z = 344.2 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{19}H_{19}O_4NF$ [M+H$^+$] 344.1293, found 344.1285; IR (ν = cm^{-1}) : 3031, 2923, 2853, 1732, 1643, 1434, 1260; mp : 102-106°C.

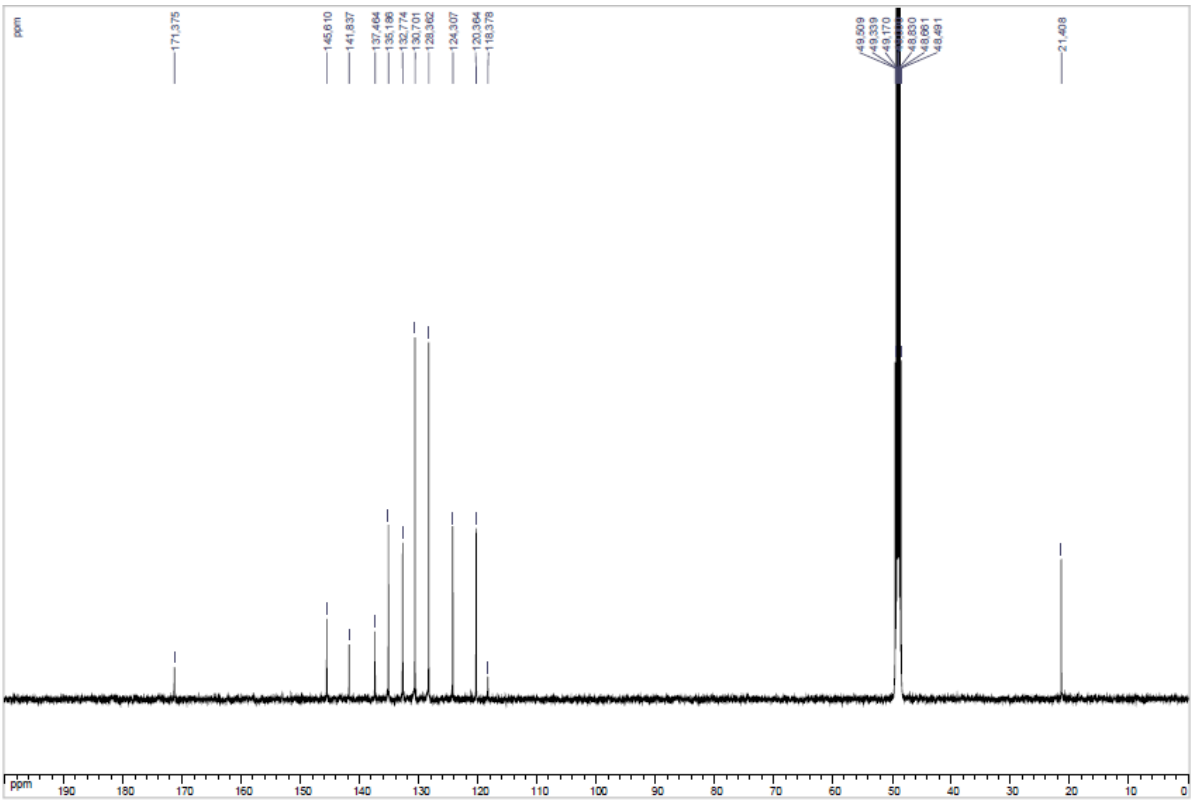
(4-Benzyl-5-oxo-2,3,4,5-tetrahydronaphtho[2,3-*f*][1,4]oxazepin-2-yl)methyl acetate (**13h**):

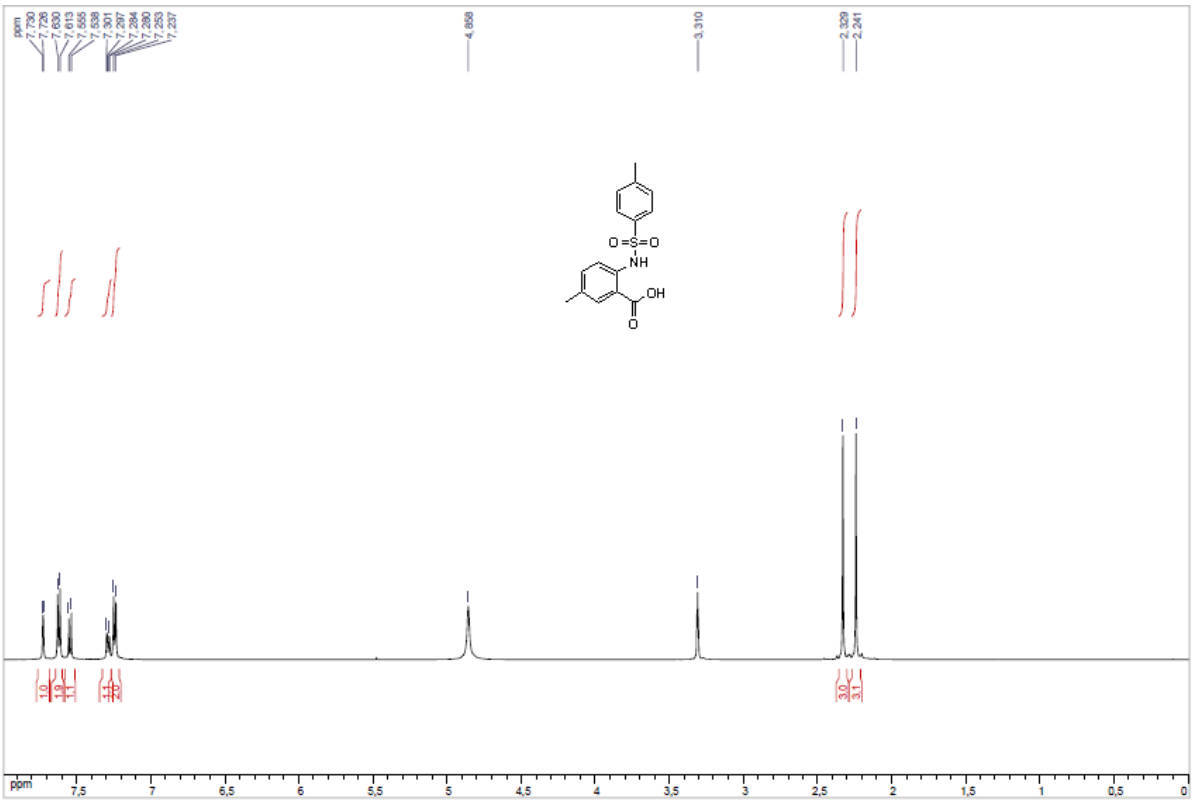


Pale yellow oil, 45 mg, 60% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.37 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.40-7.35 (m, 4H), 7.35-7.29 (m, 1H), 5.09 (d, *J* = 15.0 Hz, 1H), 4.70 (d, *J* = 15.0 Hz, 1H), 4.50-4.42 (m, 1H), 4.22 (dd, *J* = 11.5 Hz, *J* = 6.0 Hz, 1H), 4.07 (dd, *J* = 11.5 Hz, *J* = 5.0 Hz, 1H), 3.42 (dd, *J* = 16.0 Hz, *J* = 8.5 Hz, 1H), 3.35 (dd, *J* = 16.0 Hz, *J* = 4.0 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 168.9, 148.9, 137.0, 135.8, 131.7, 130.6, 129.1, 129.0, 128.9, 128.3, 128.1, 128.0, 127.0, 125.9, 119.5, 80.3, 62.9, 51.1, 46.8, 20.9; MS (ESI) : m/z = 376.3 [M+H$^+$]; HRMS (ESI) : m/z calcd for $C_{23}H_{22}O_4N$ [M+H$^+$] 376.1543, found 376.1533; IR (ν = cm^{-1}) : 3030, 2925, 2853, 1742, 1650, 1454, 1215.

IV. ^{1}H and ^{13}C NMR spectra



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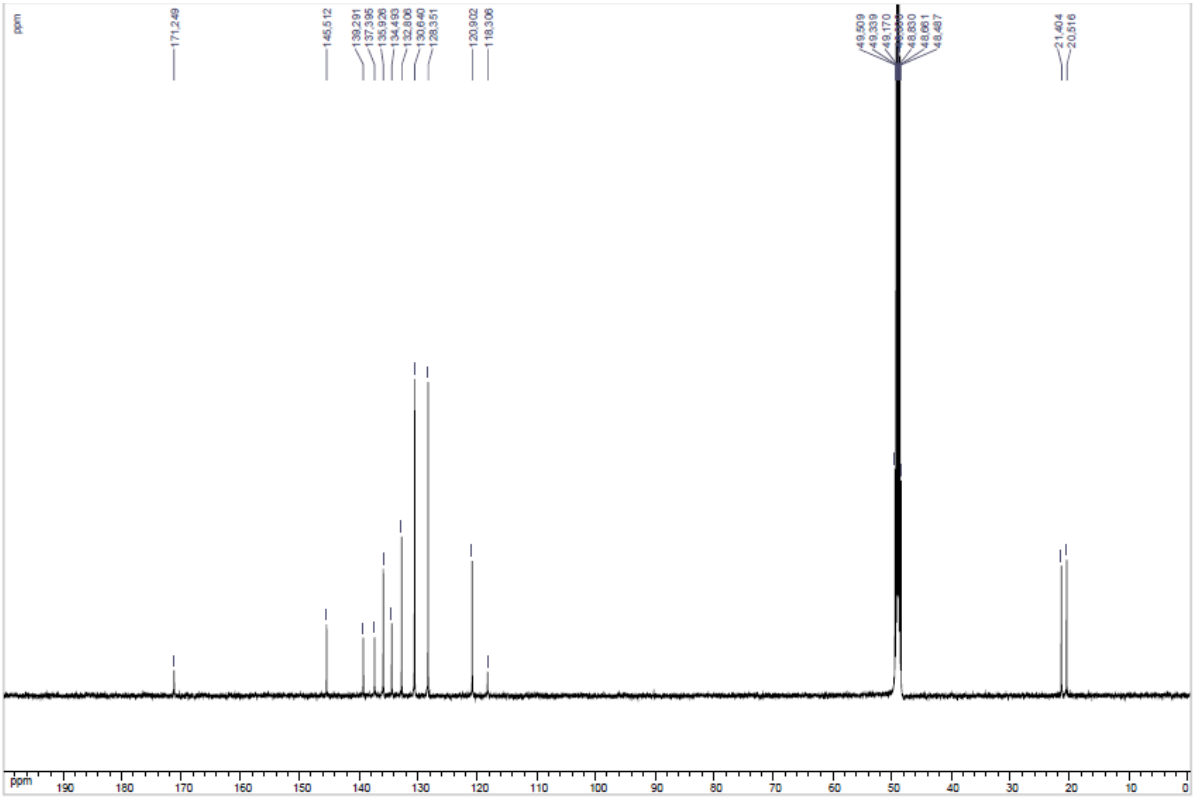
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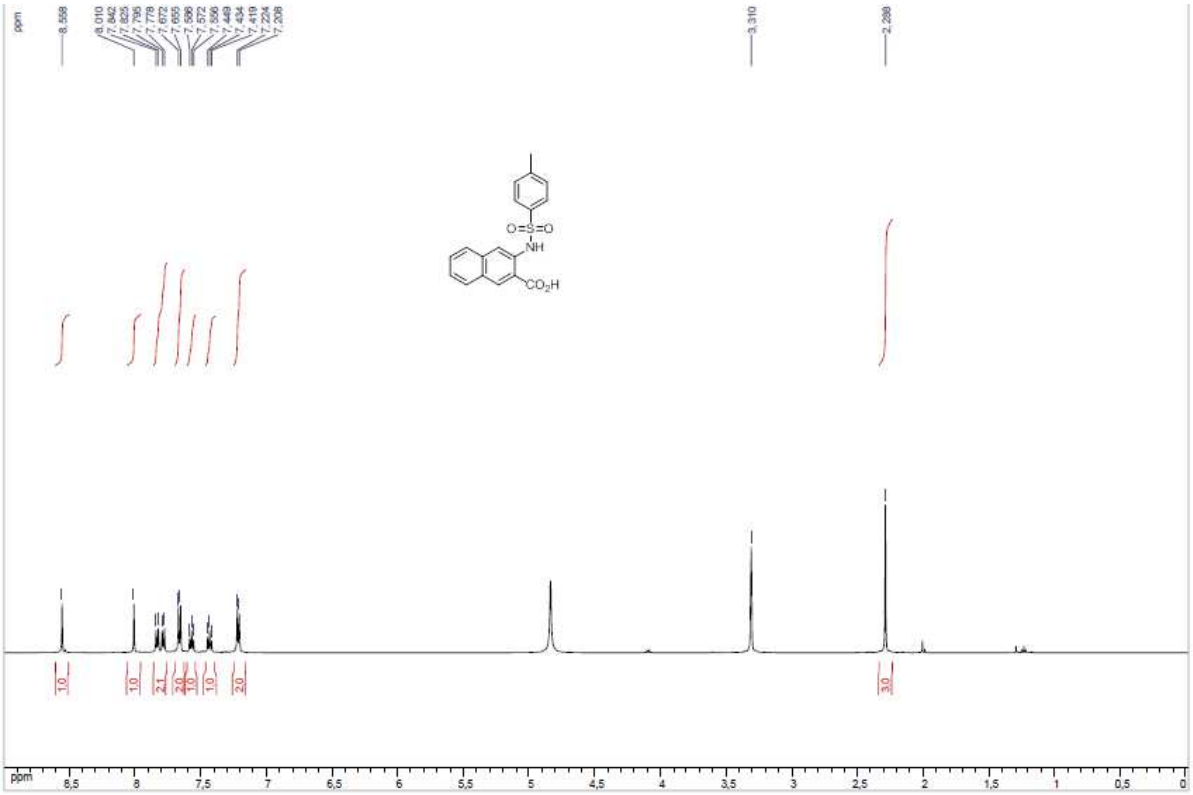
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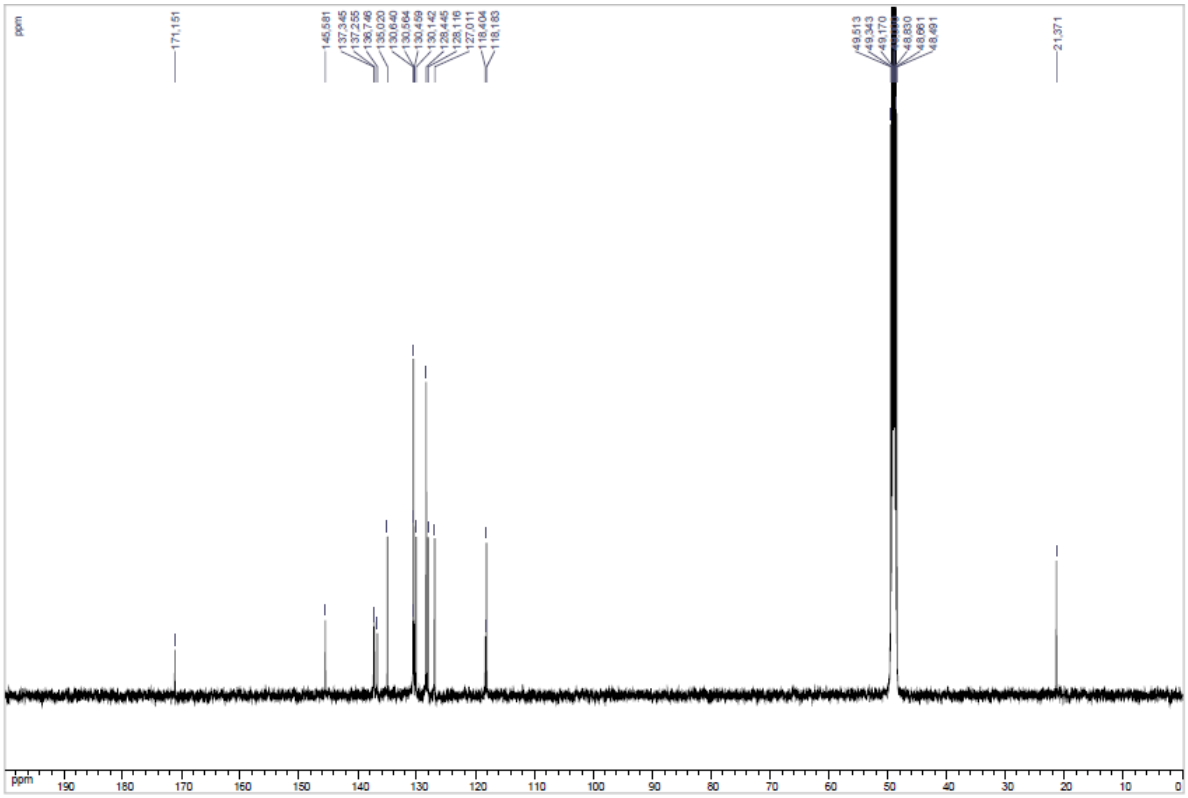
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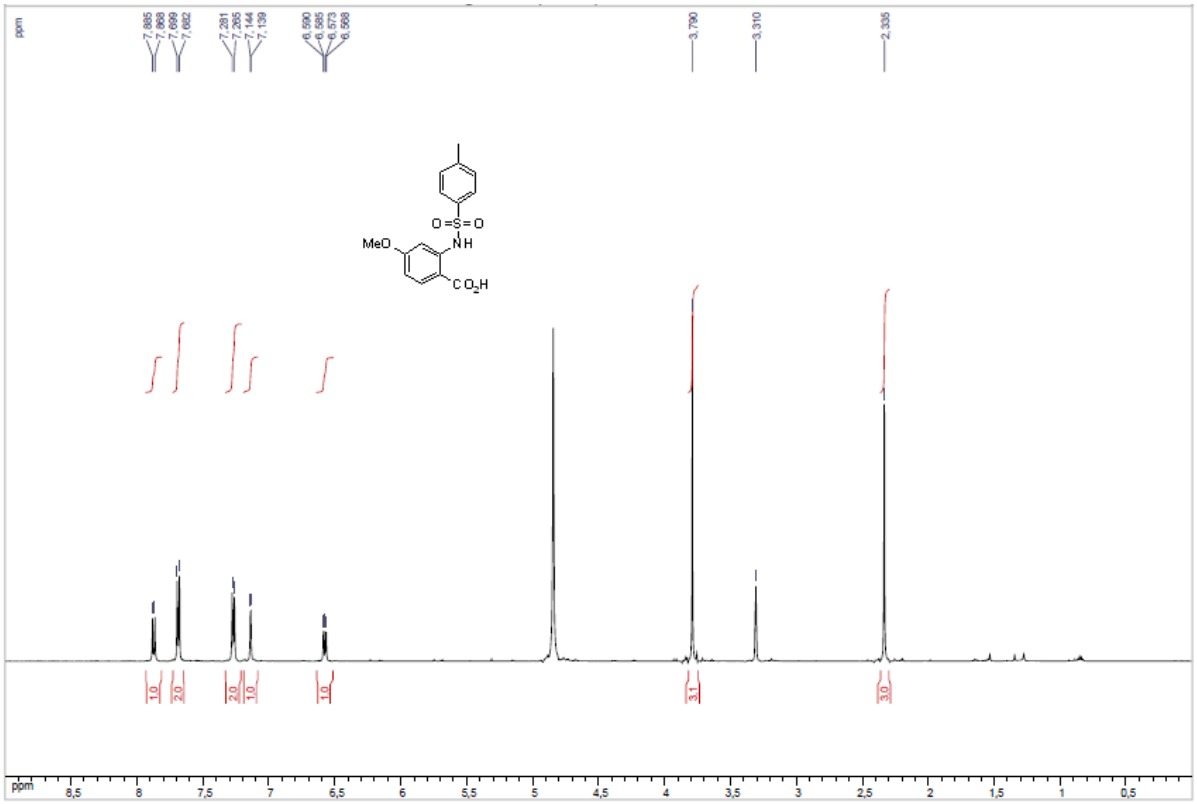
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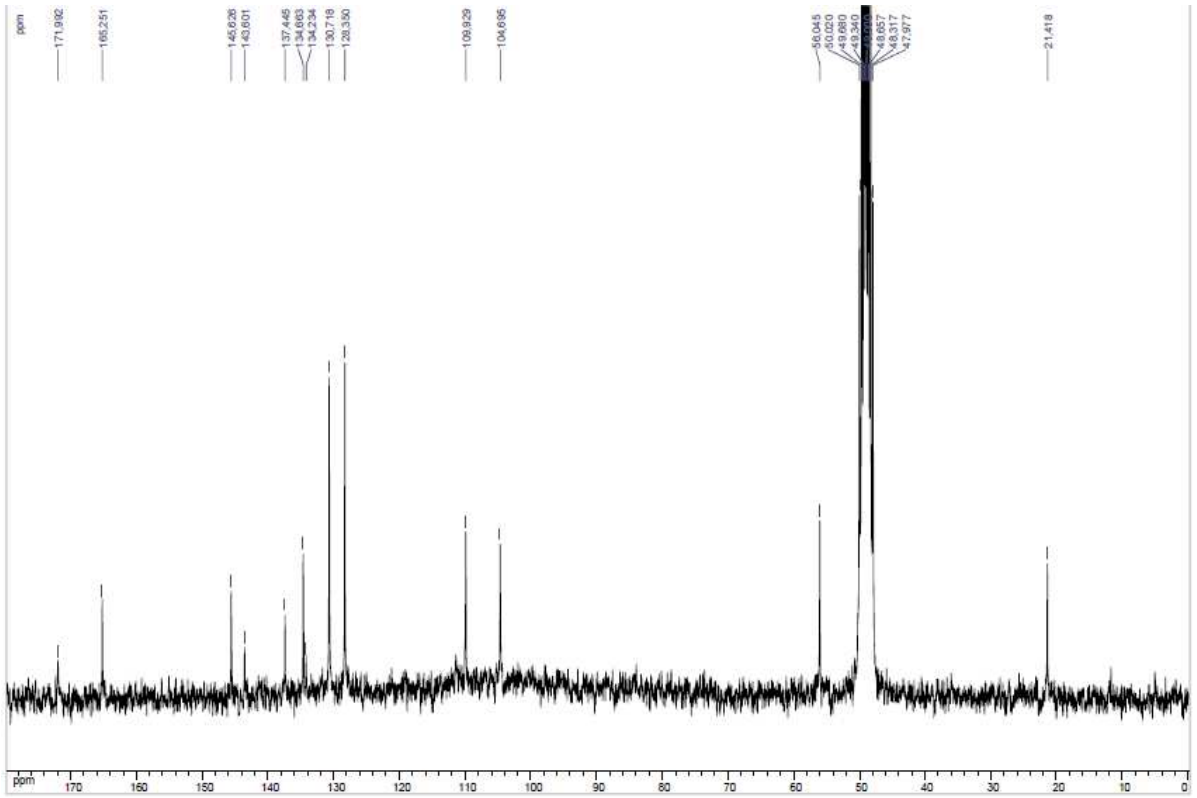
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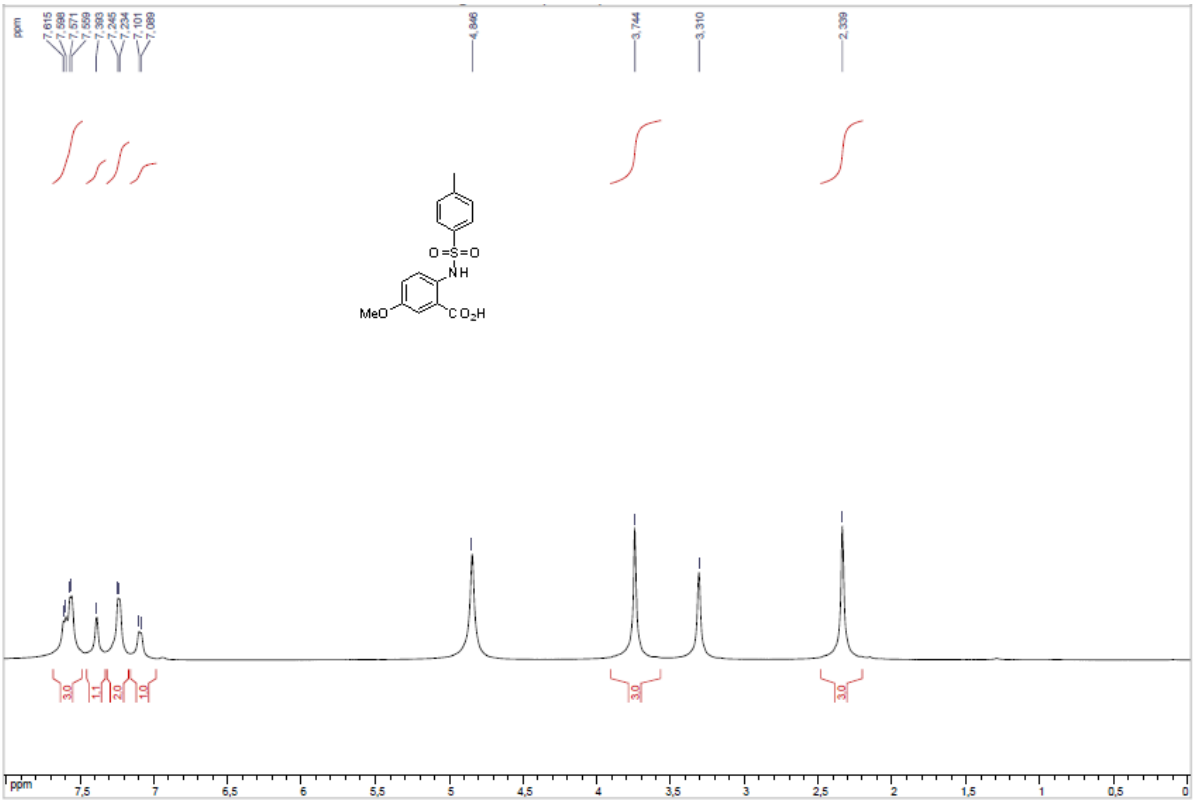
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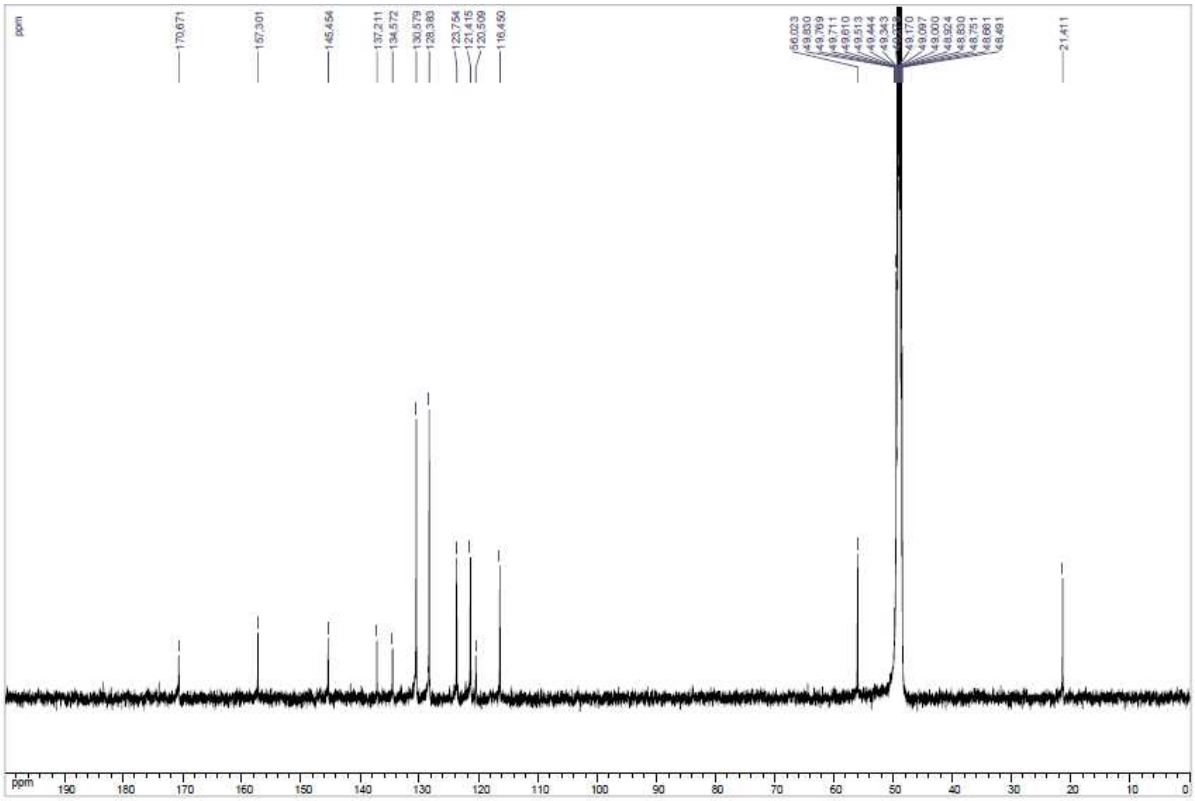
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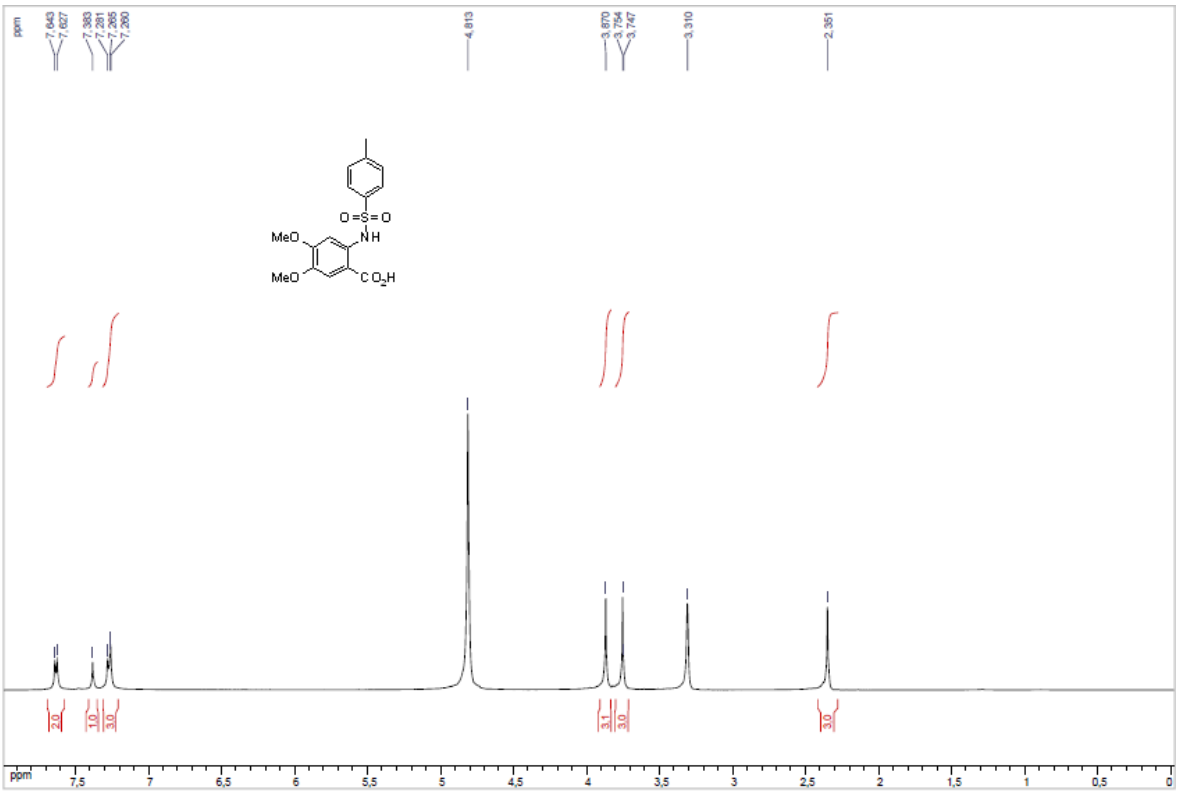
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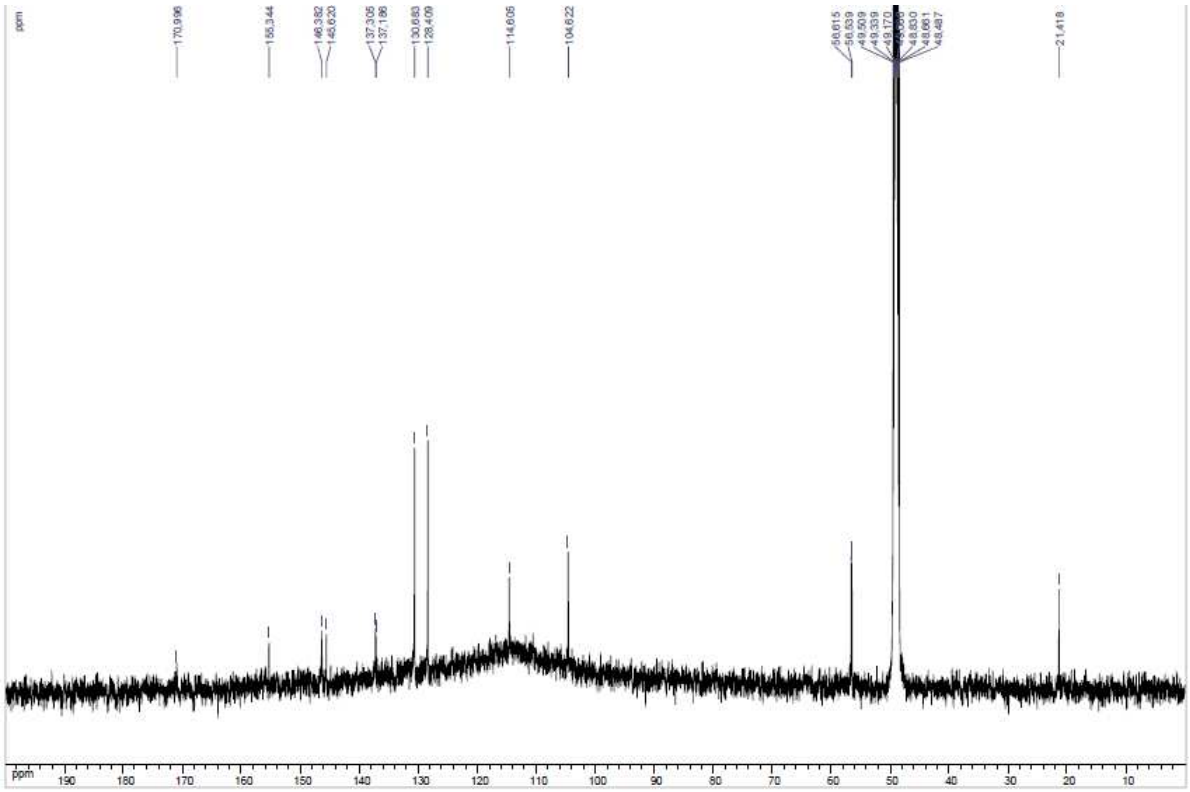
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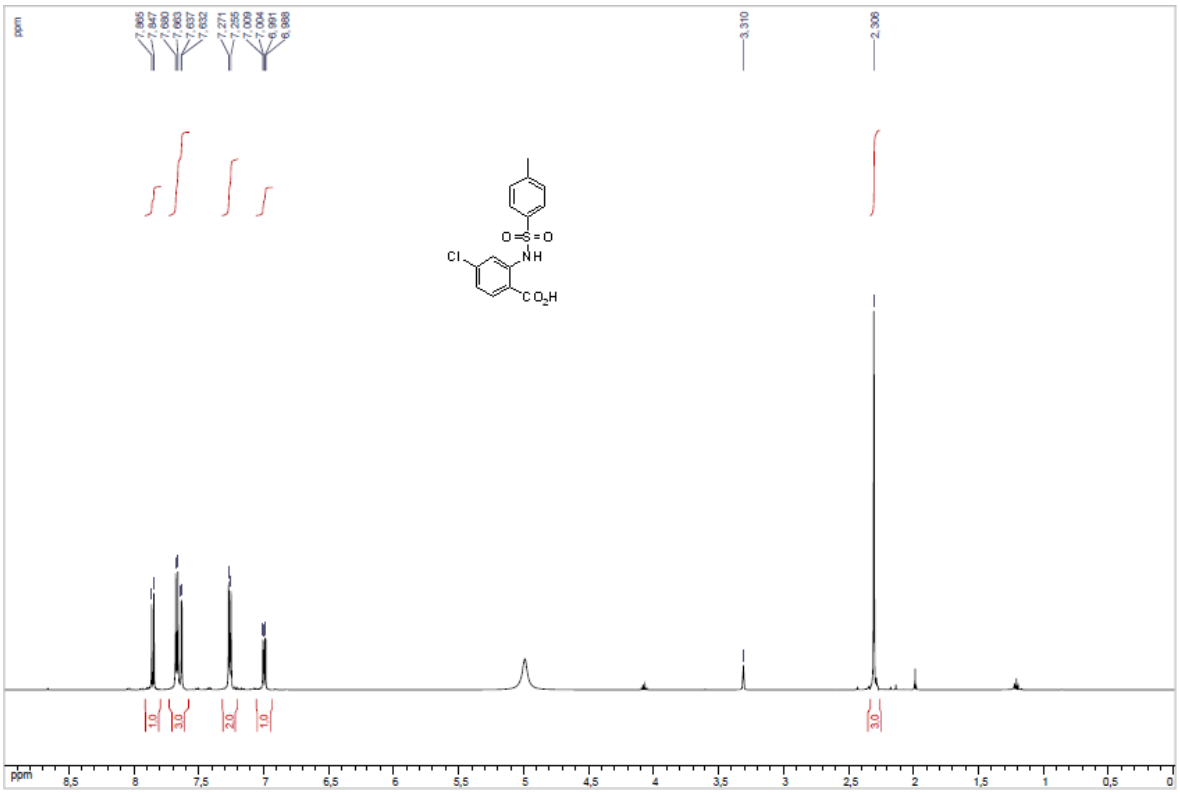
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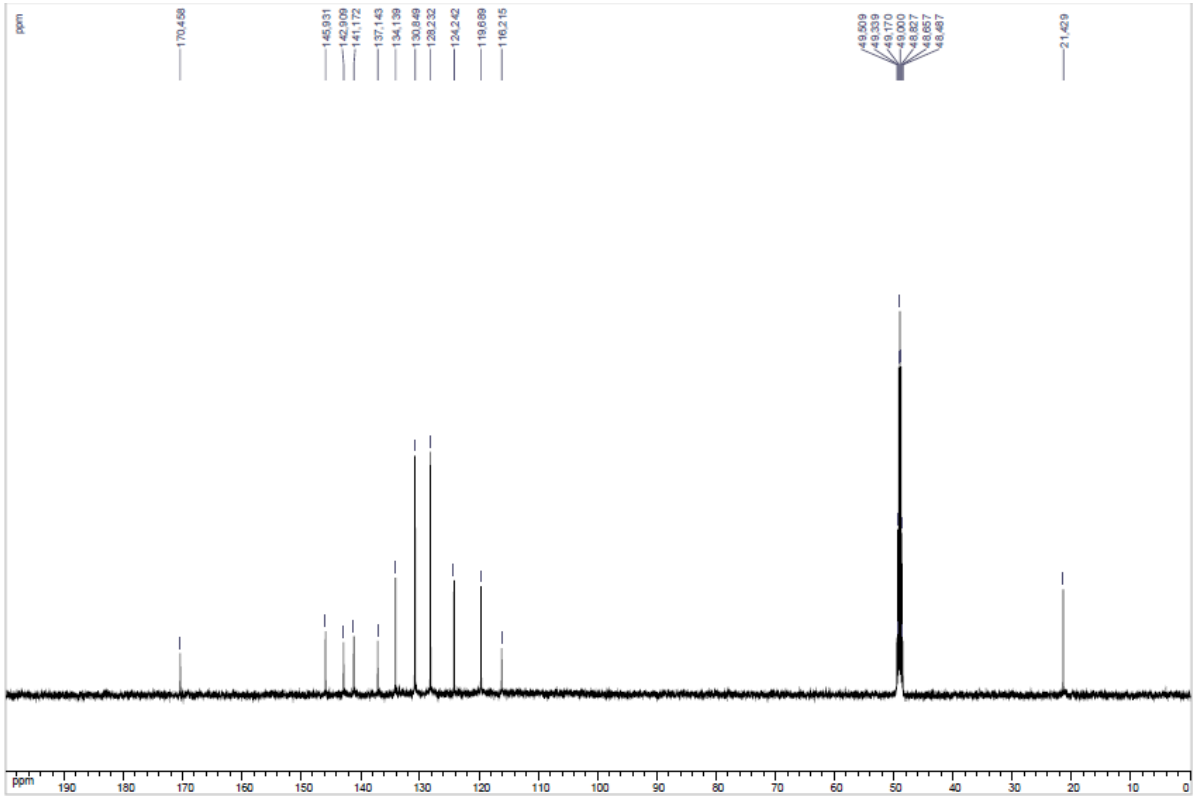
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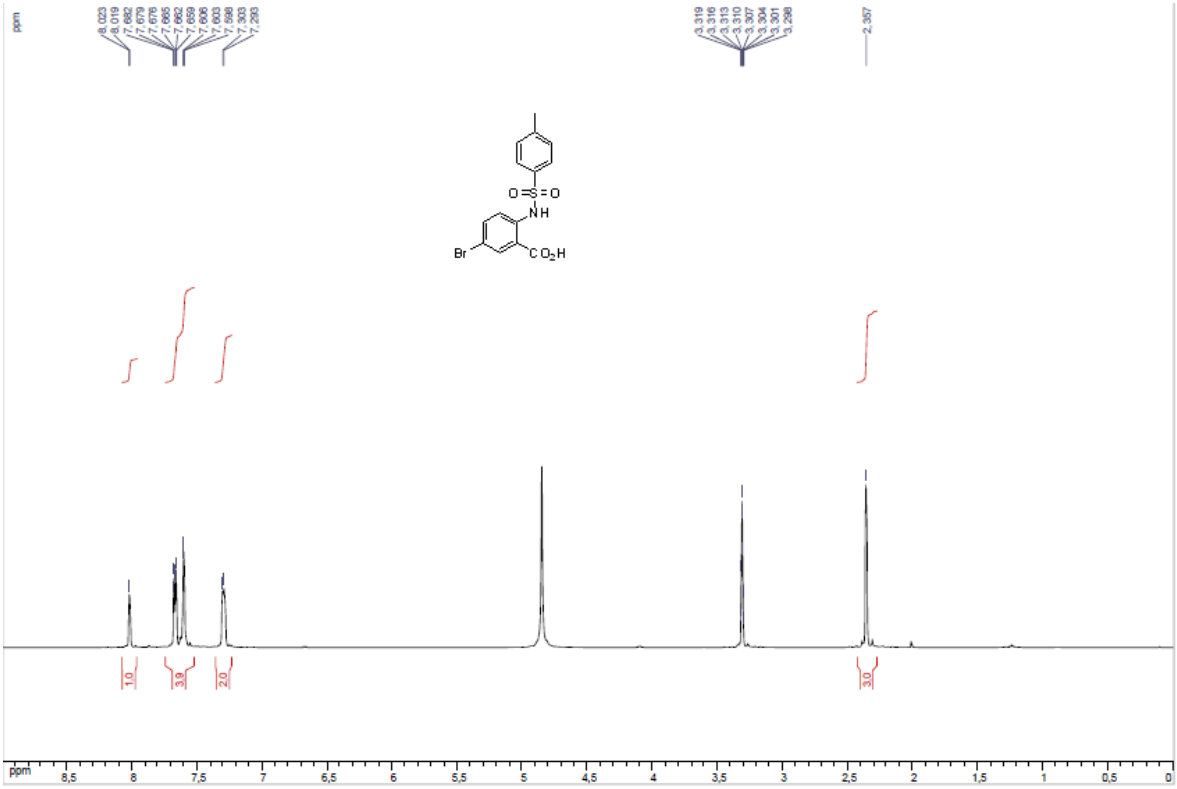
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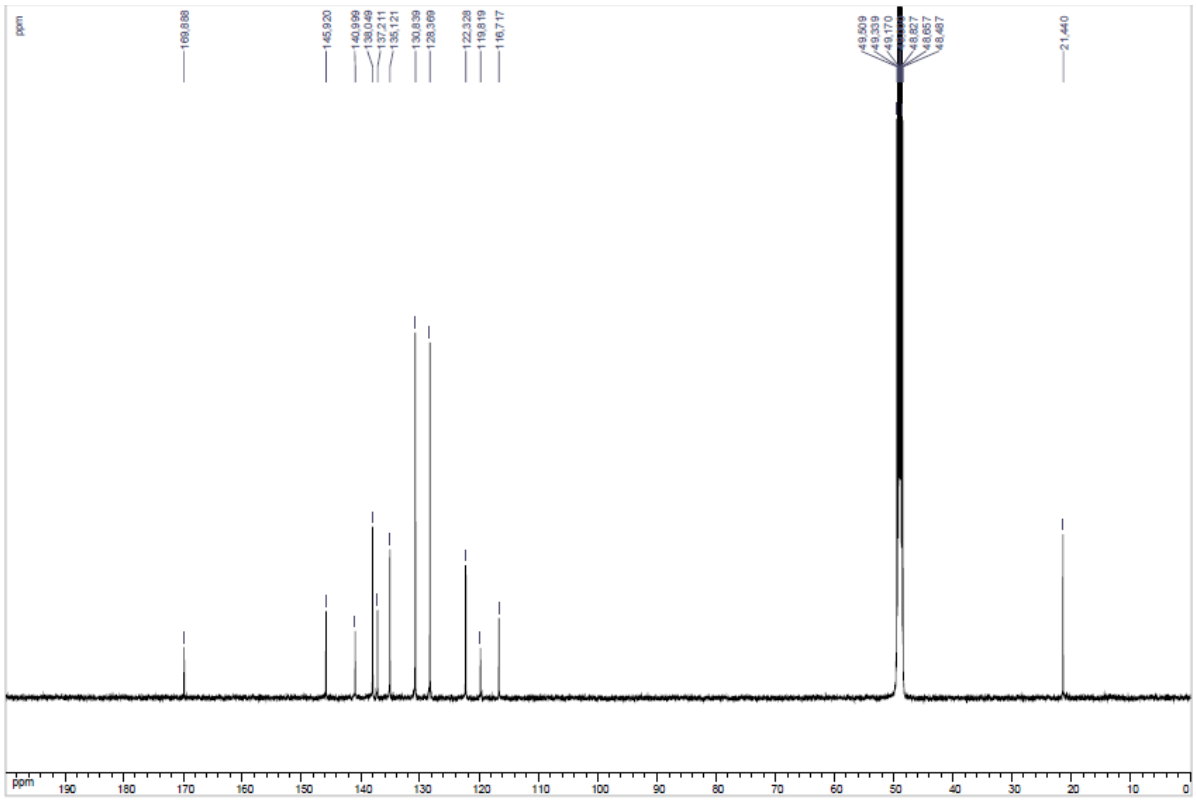
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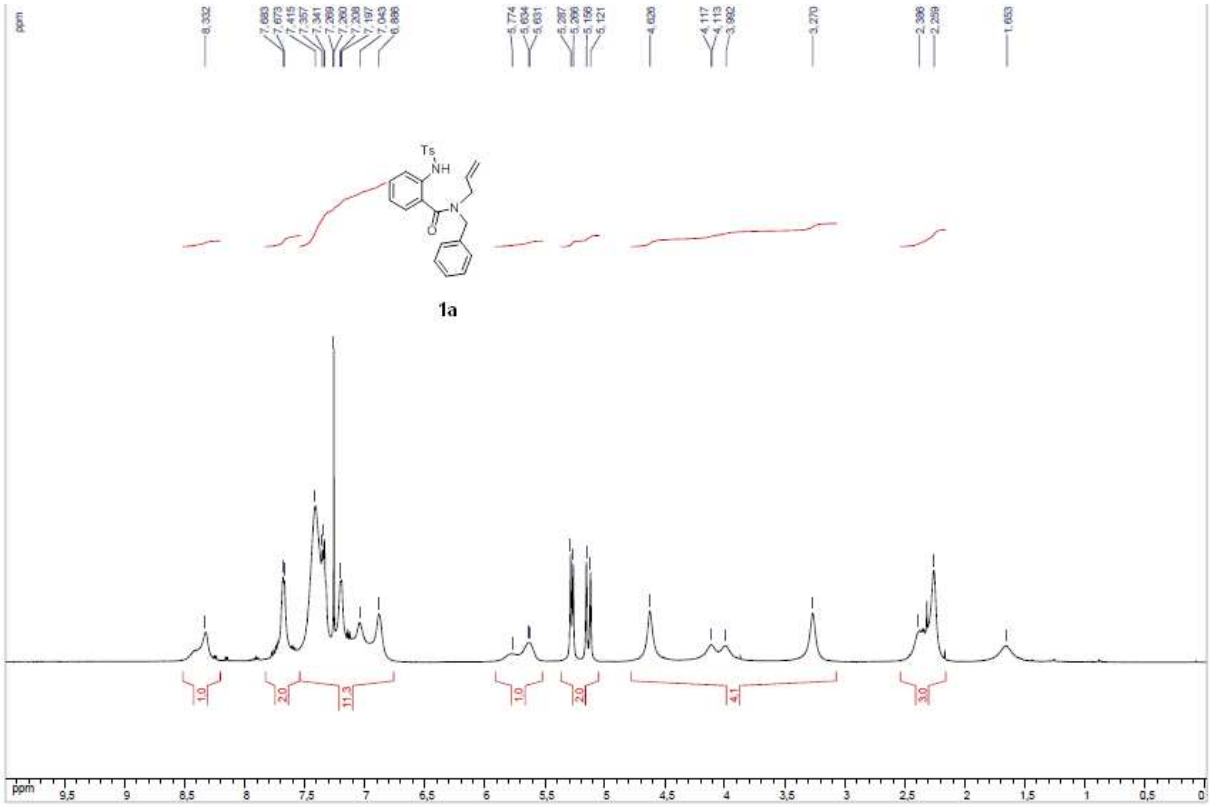
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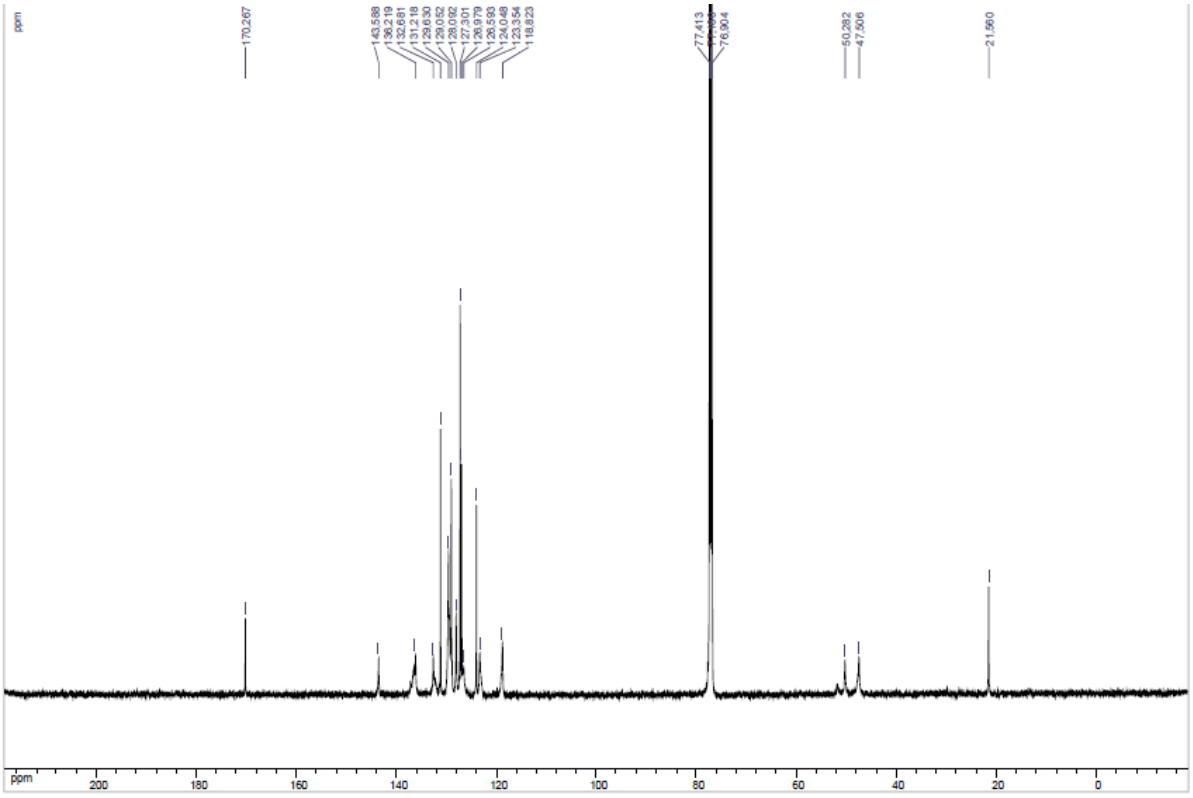
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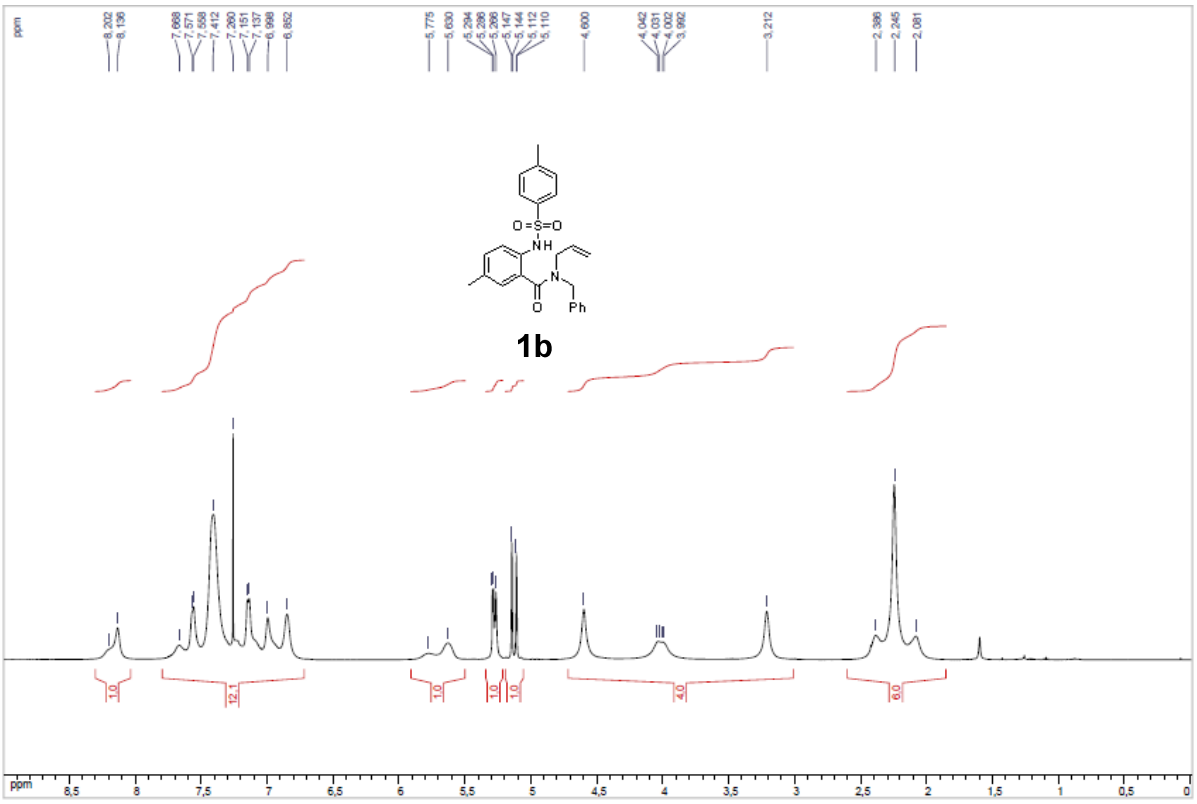
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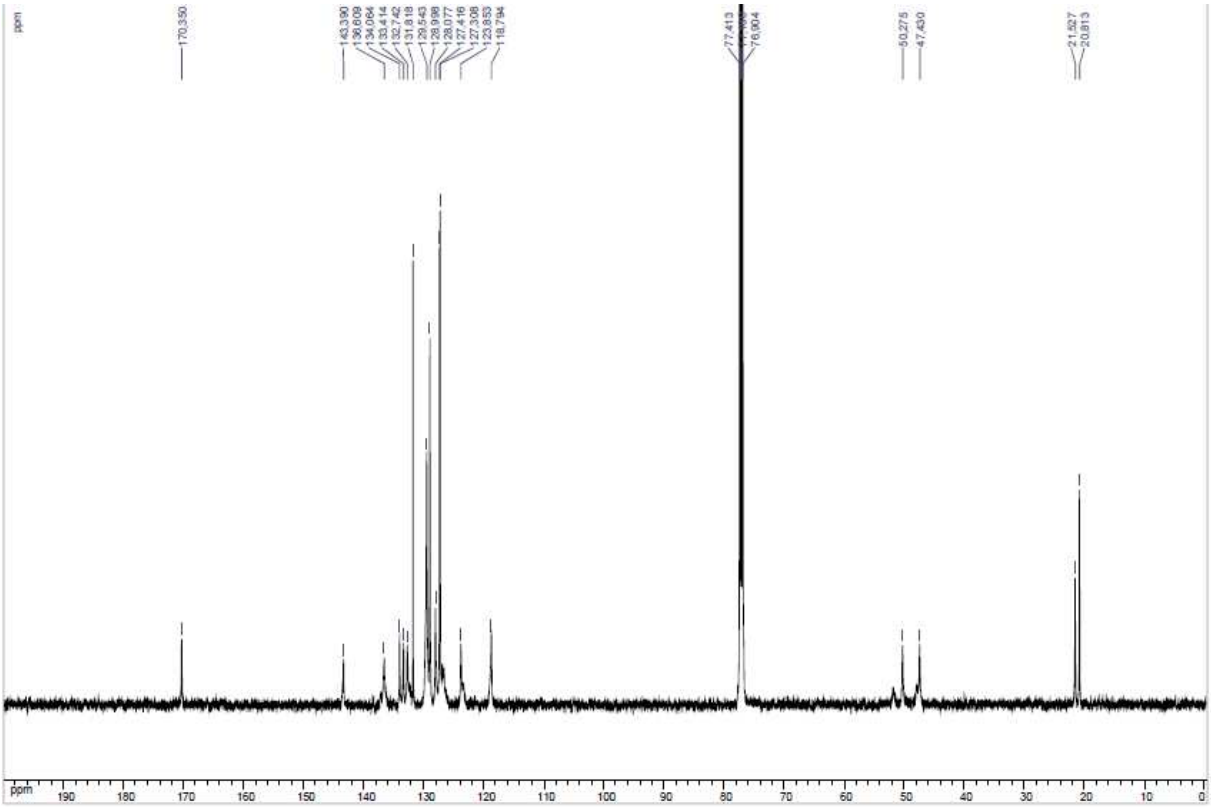

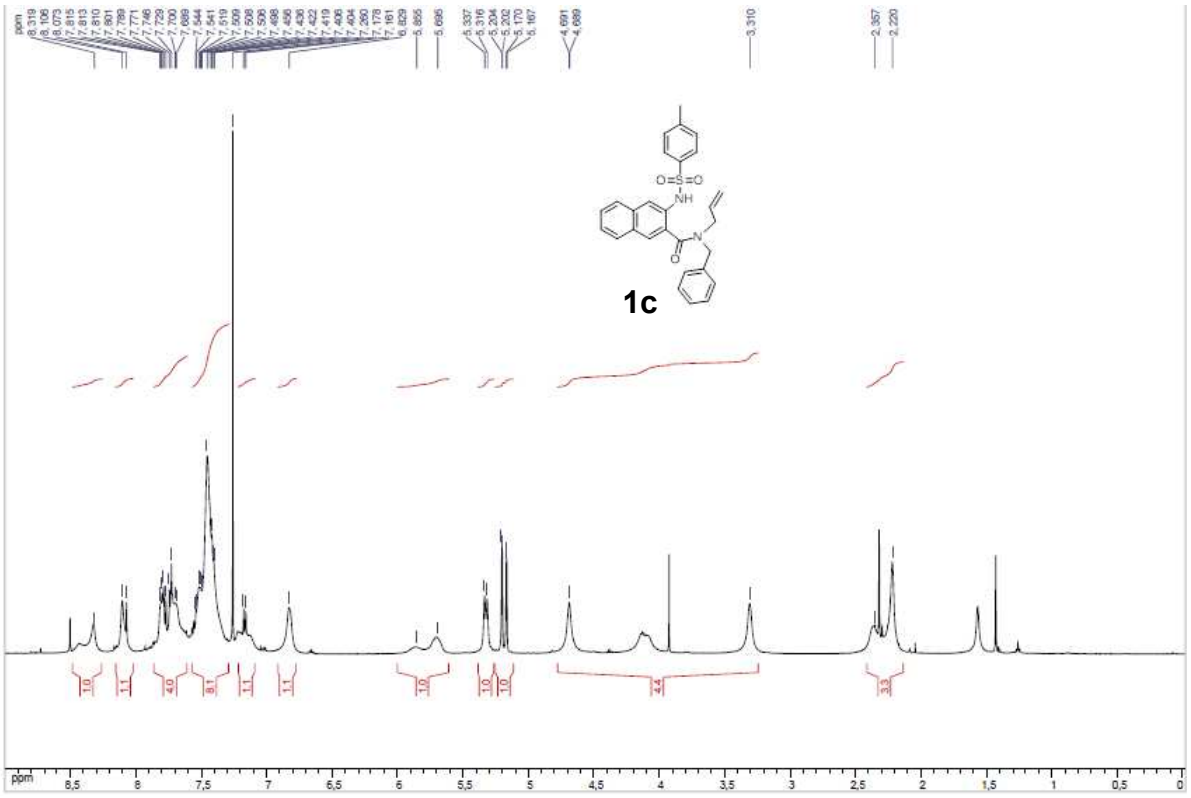
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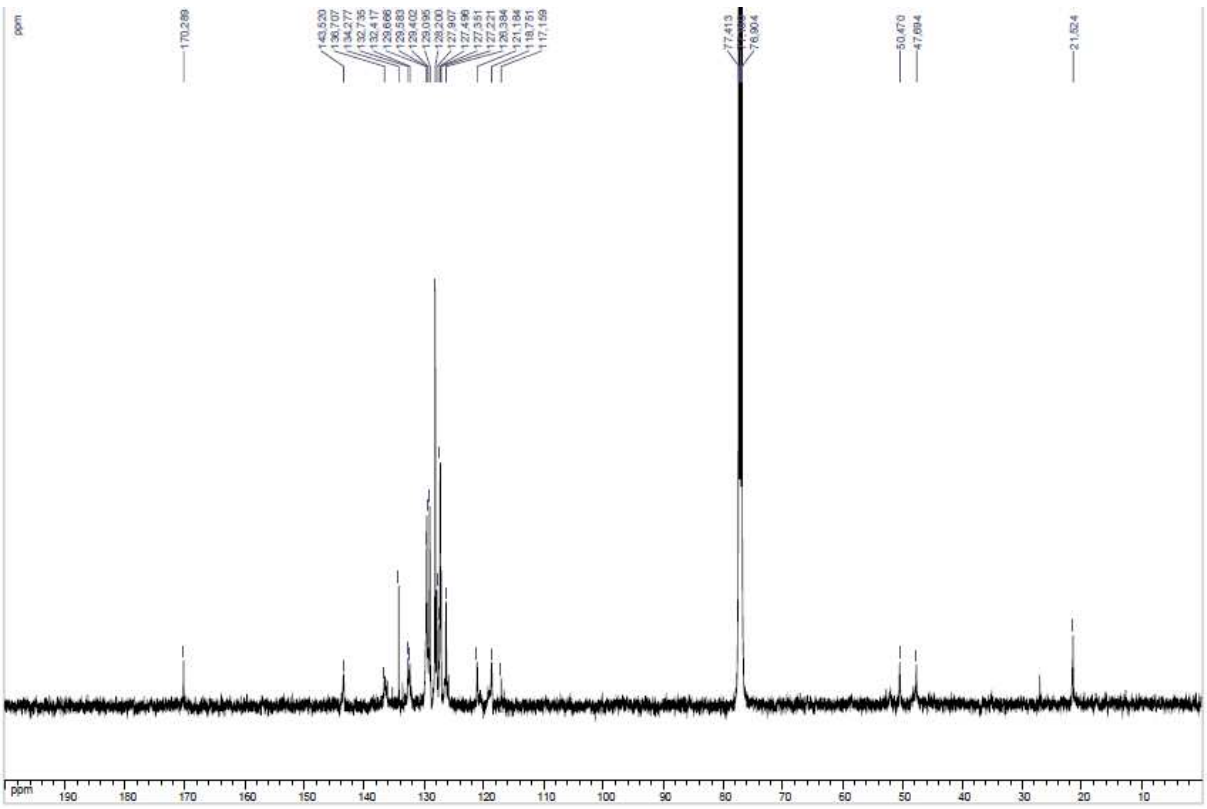

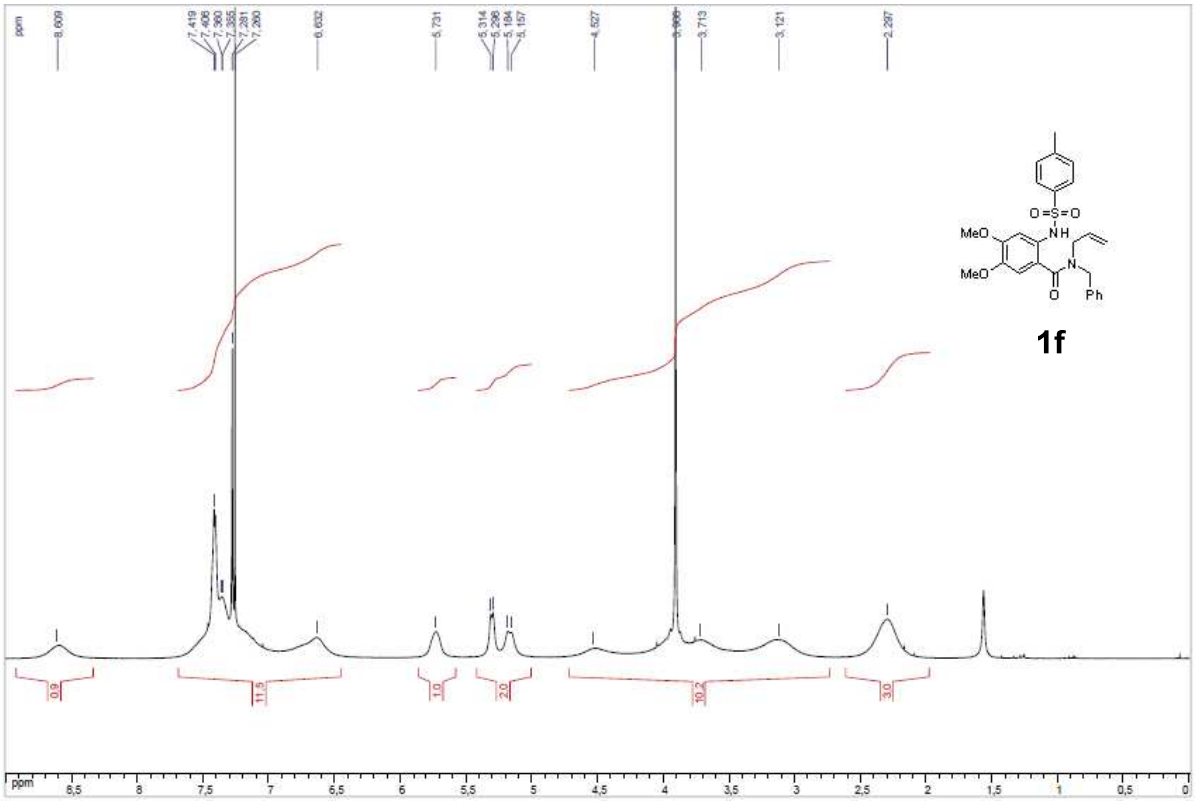
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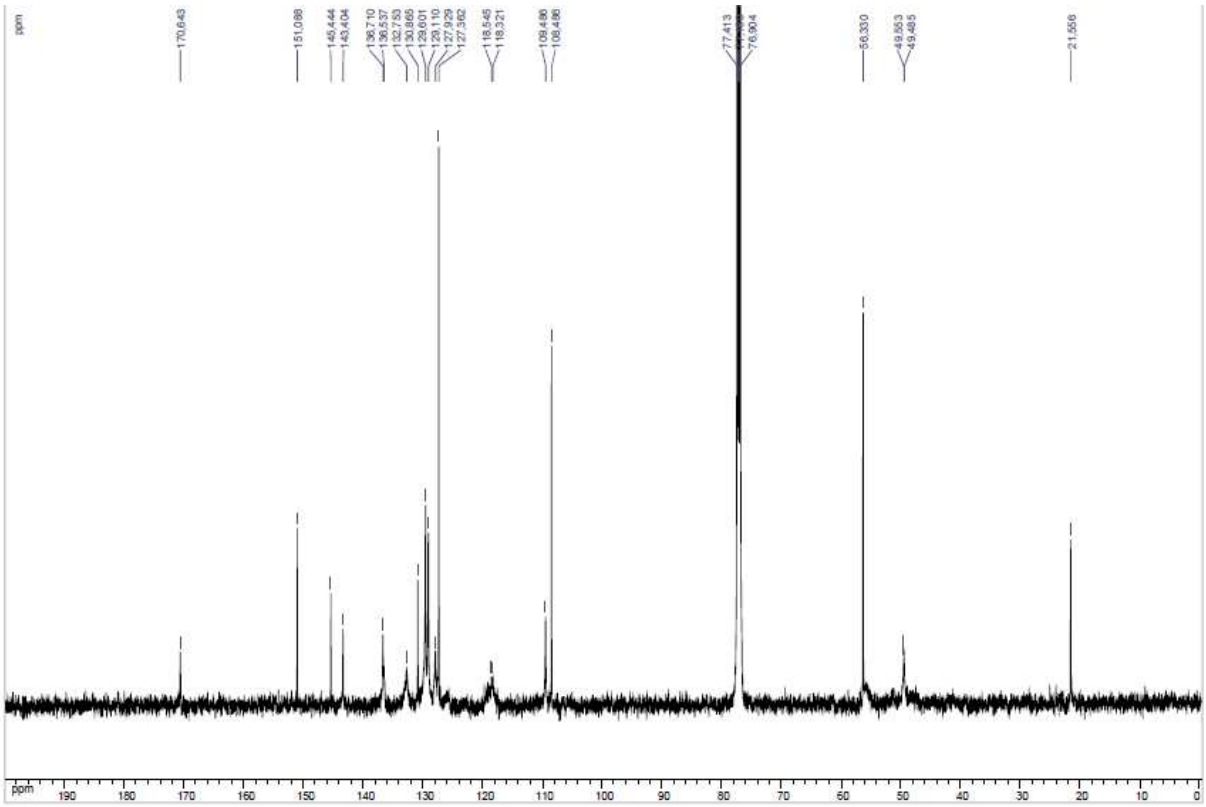
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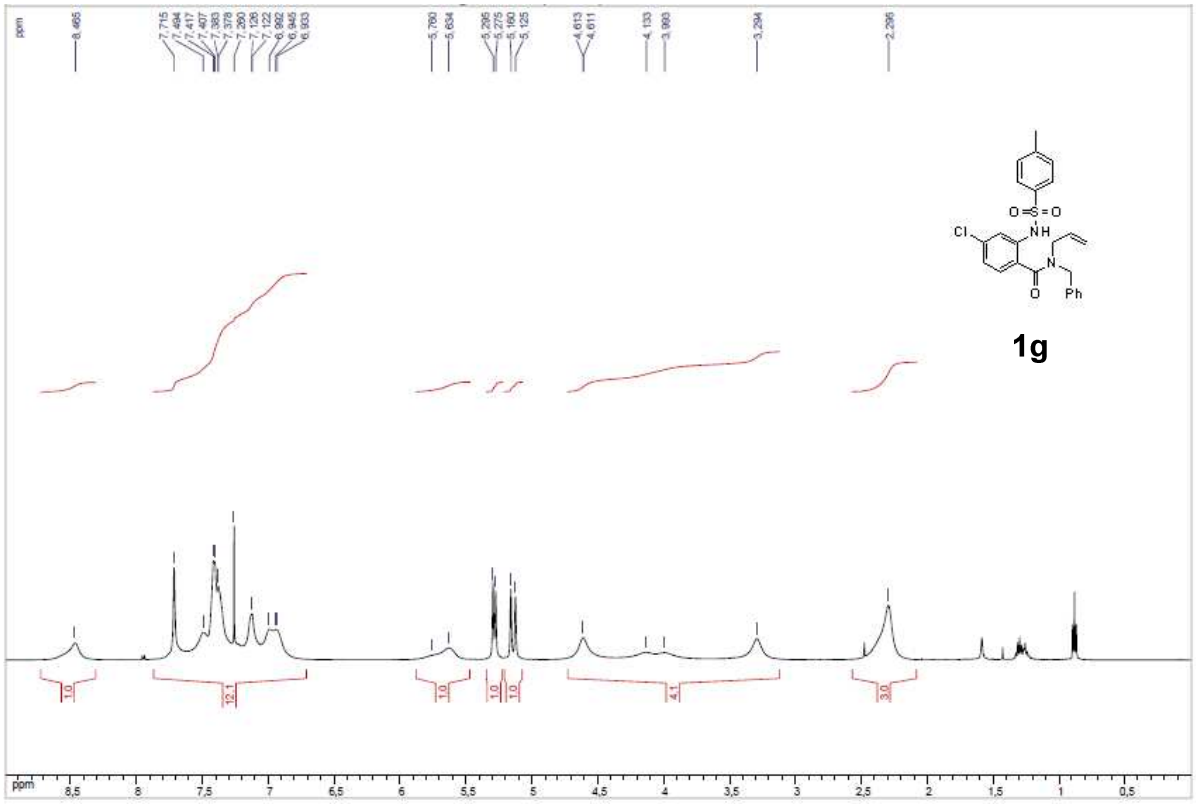
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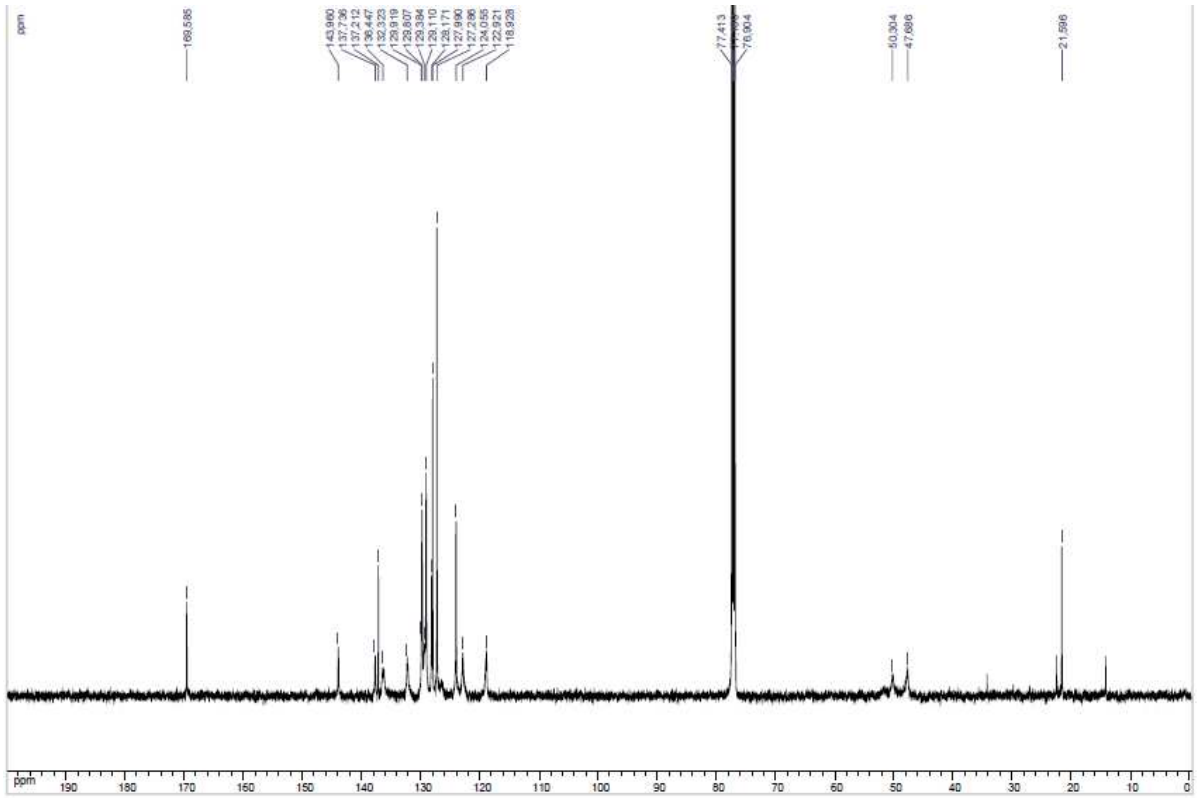
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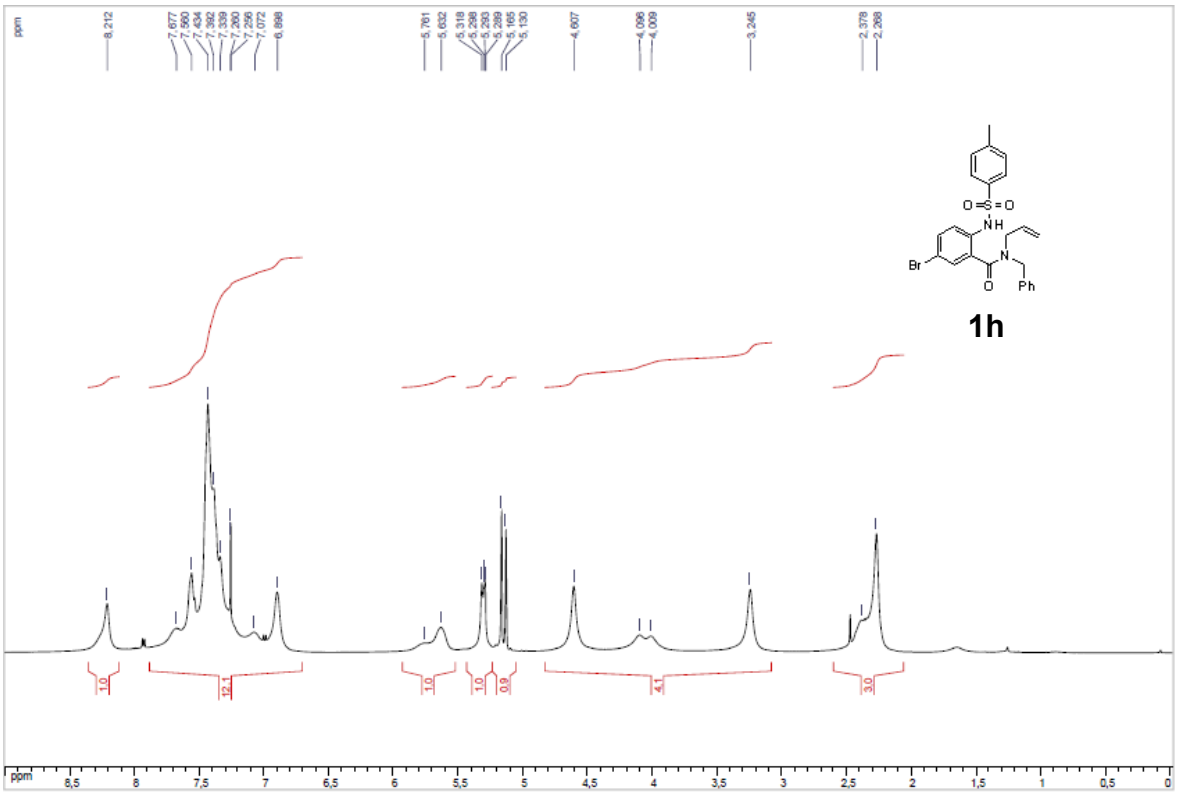
S
O
NH
Cl
N
O
Ph

1g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7.434
7.392
7.339
7.260
7.259
7.072
6.898
5.761
5.632
5.318
5.298
5.289
5.165
5.130
4.607
4.096
4.009
3.245
2.378
2.268
1.0
12.1
1.0
1.0
0.9
4.1
3.0
ppm
8,5
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7,5
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6,5
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5,5
5
4,5
4
3,5
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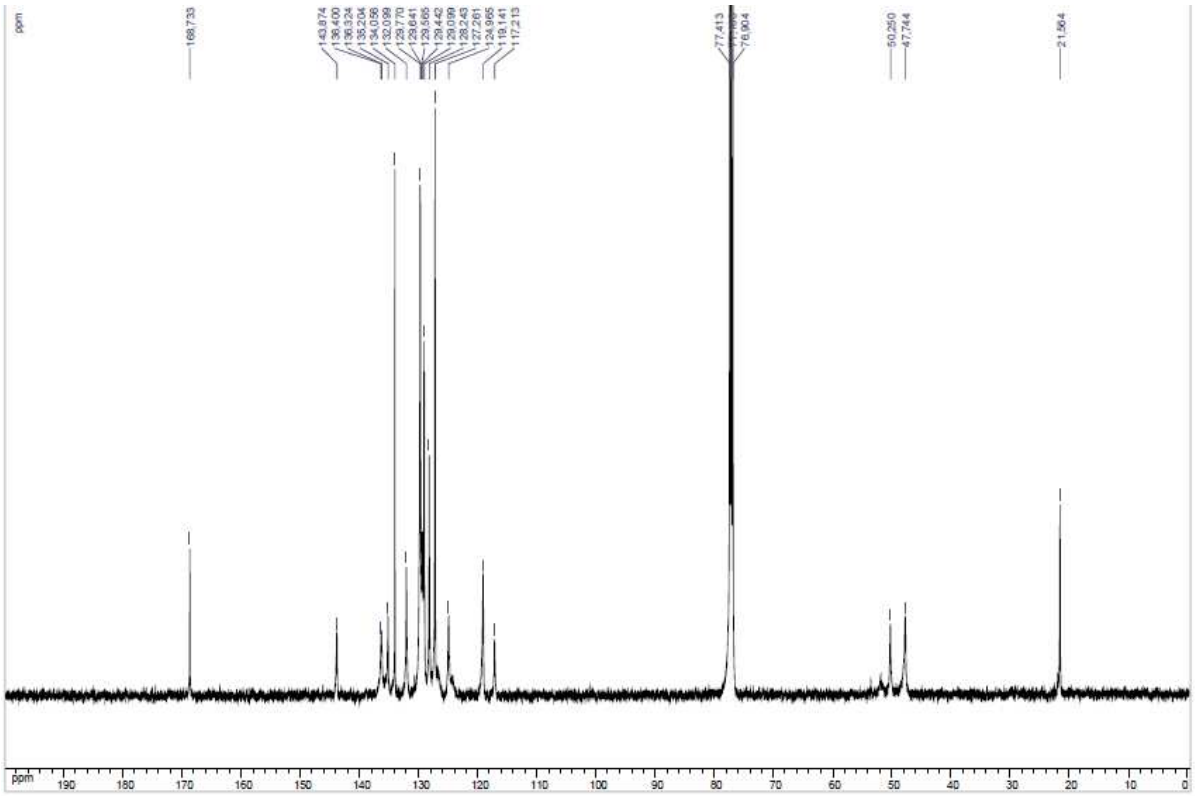
2,5
2
1,5
1
0,5
0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143.874
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136.324
135.204
134.086
133.098
131.770
129.641
129.565
129.442
129.099
128.243
127.261
124.966
119.141
117.213
77.413
77.000
76.904
50.250
47.744
21.564
ppm
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
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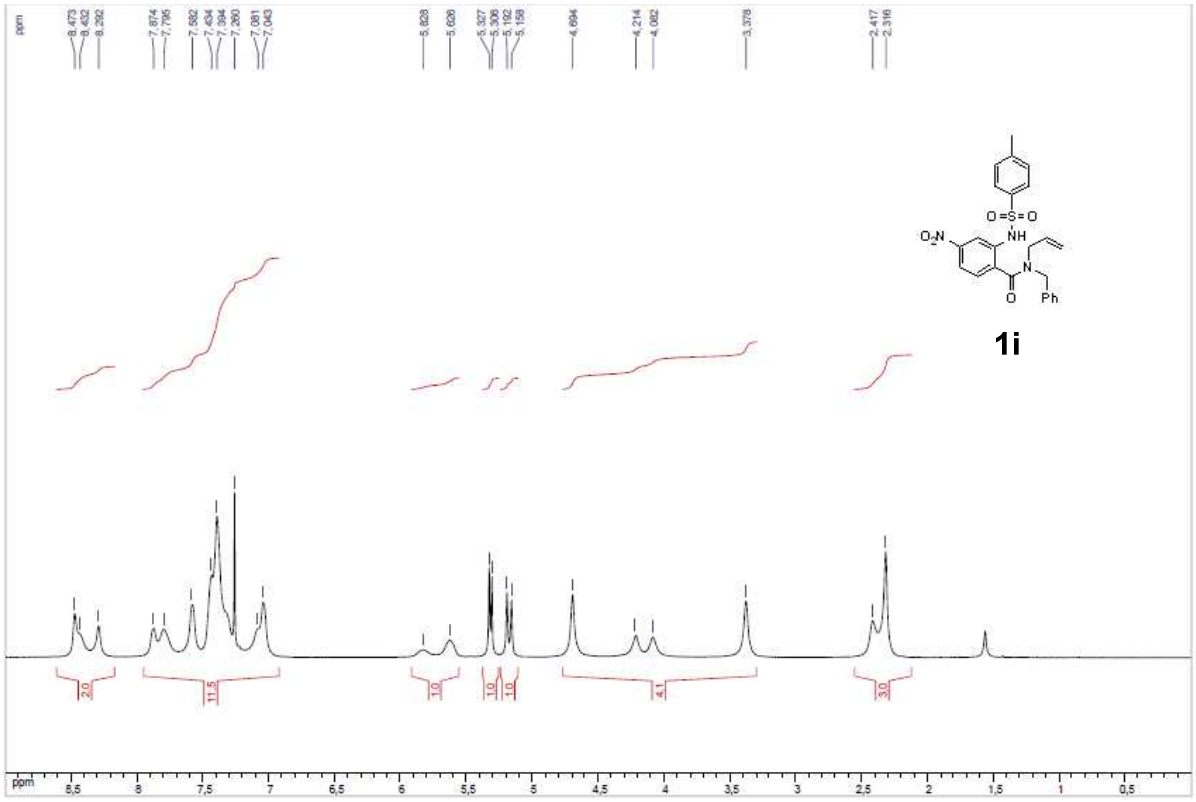
20
10
0

1h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8.292
7.874
7.795
7.582
7.434
7.394
7.260
7.081
7.043
5.828
5.626
5.327
5.306
5.192
5.159
4.694
4.214
4.082
3.378
2.417
2.316
O=S=O
NH
O2N
N
O
Ph
2.0
11.5
1.0
1.0
1.0
4.1
3.0
ppm
8,5
8
7,5
7
6,5
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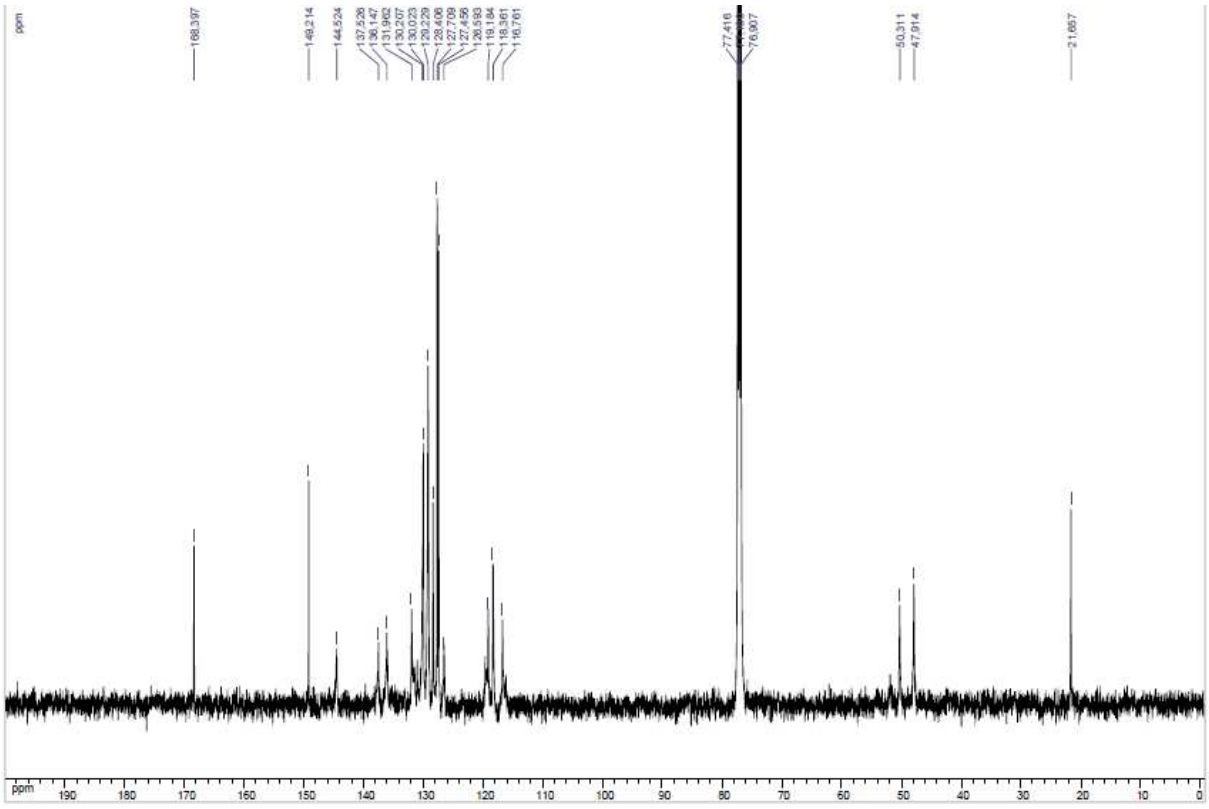
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5

1i


ppm
168.397
149.214
144.524
137.528
136.147
131.960
130.207
130.023
129.229
128.406
127.709
127.456
126.593
119.184
118.361
116.761
77.416
77.000
76.907
50.311
47.914
21.667
ppm
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180
170
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150
140
130
120
110
100
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10
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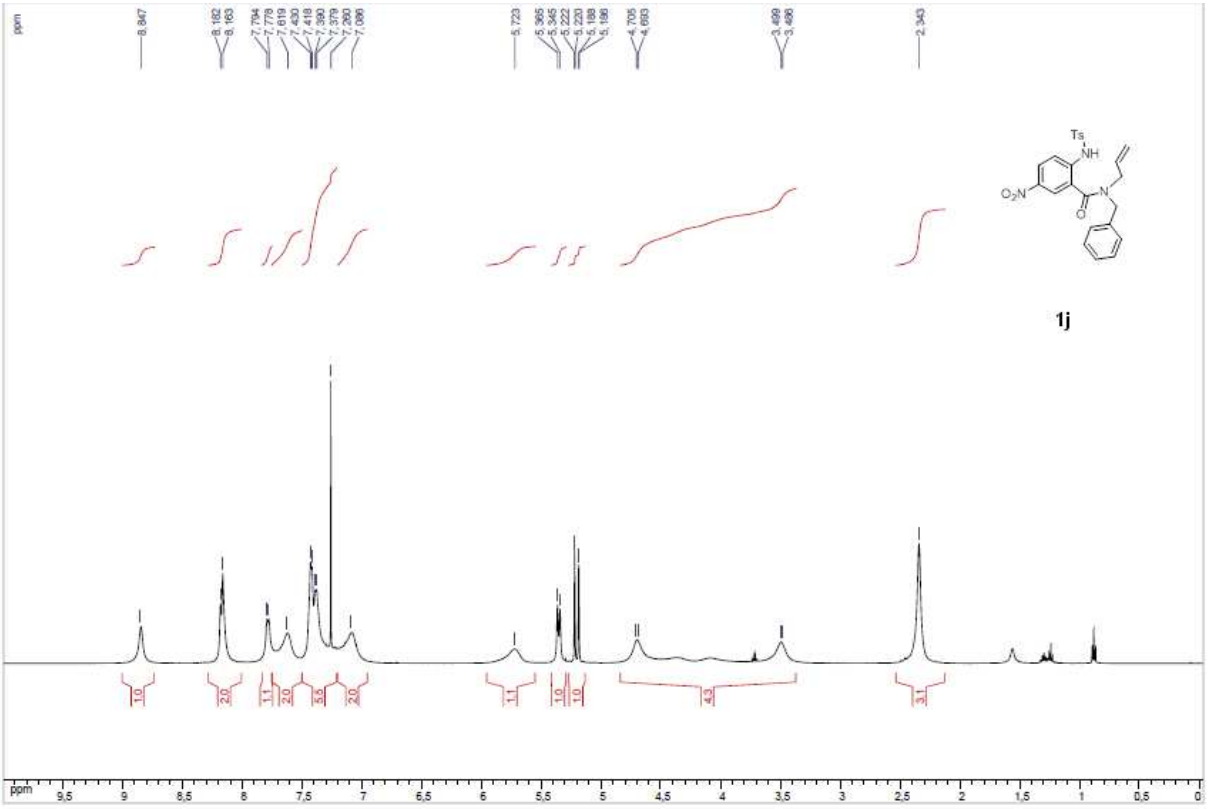
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8.163
7.794
7.778
7.619
7.430
7.418
7.390
7.379
7.260
7.086
5.723
5.365
5.345
5.222
5.203
5.189
5.186
4.705
4.693
3.499
3.486
2.343
Ts
NH
O2N
N
O
1j
1.0
2.0
1.1
2.0
3.5
2.0
1.1
1.0
1.0
4.3
3.1
ppm
9,5
9
8,5
8
7,5
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6,5
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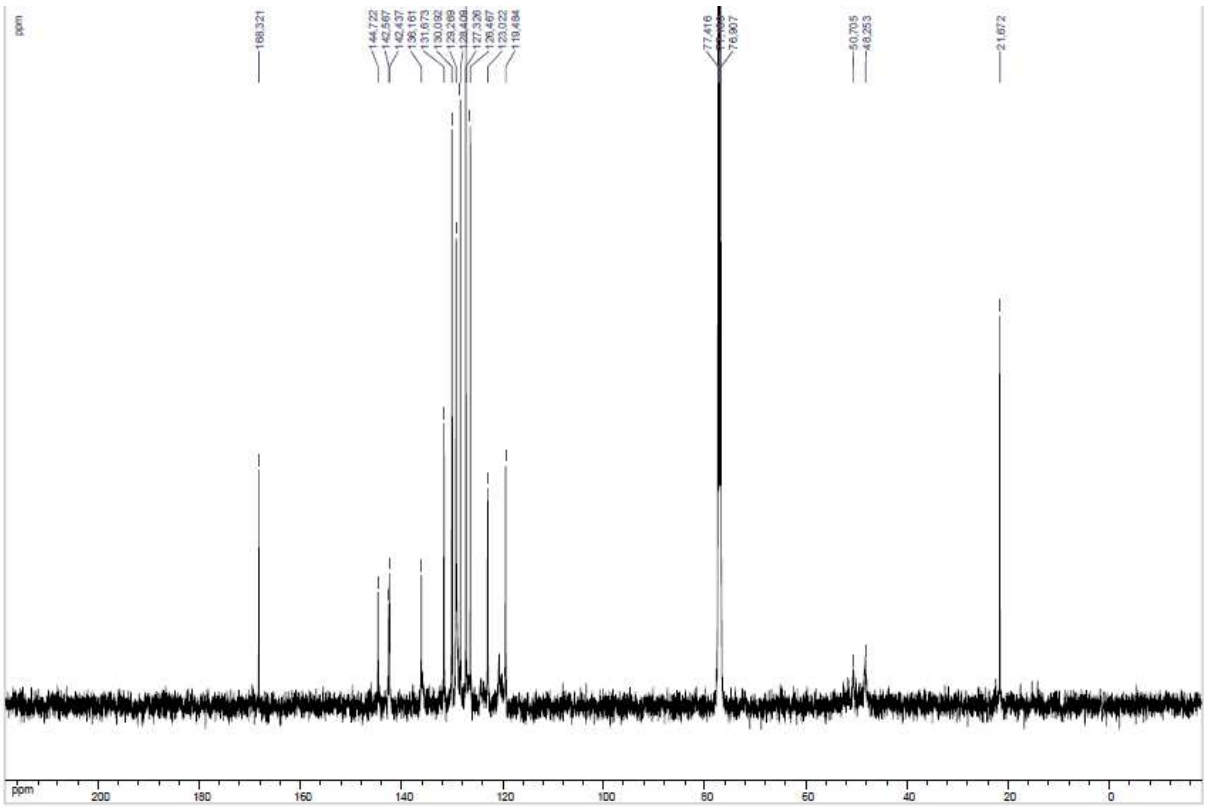
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


ppm
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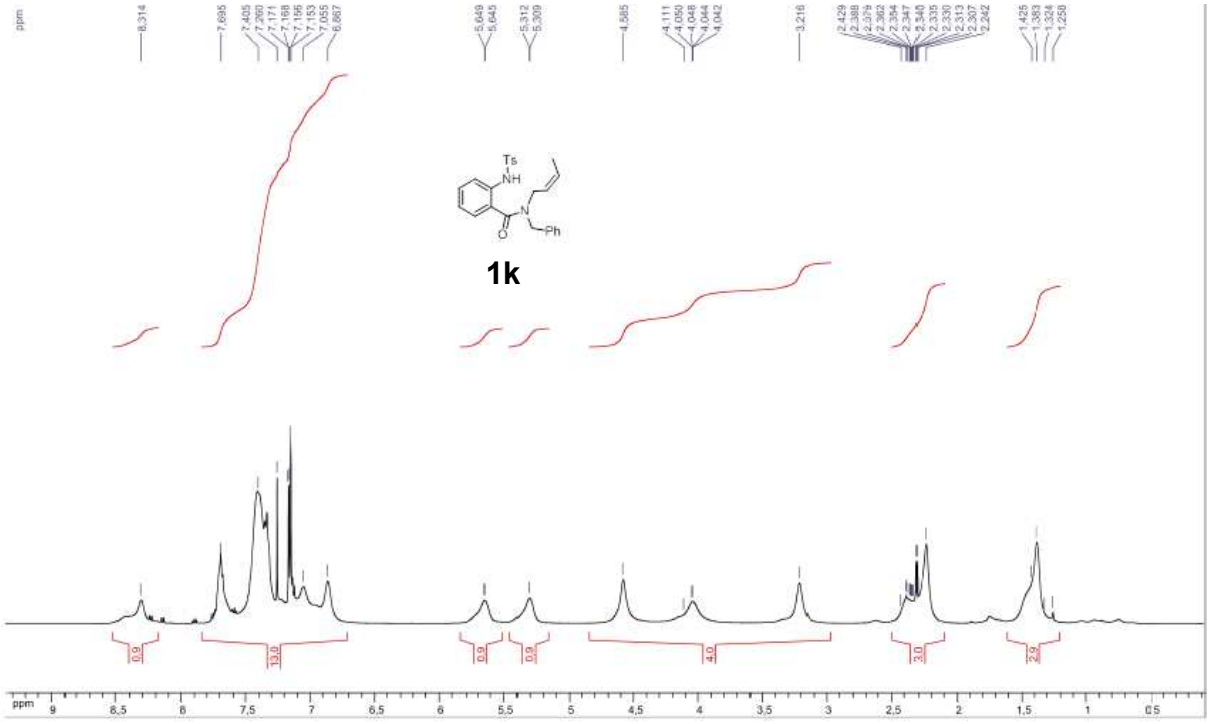
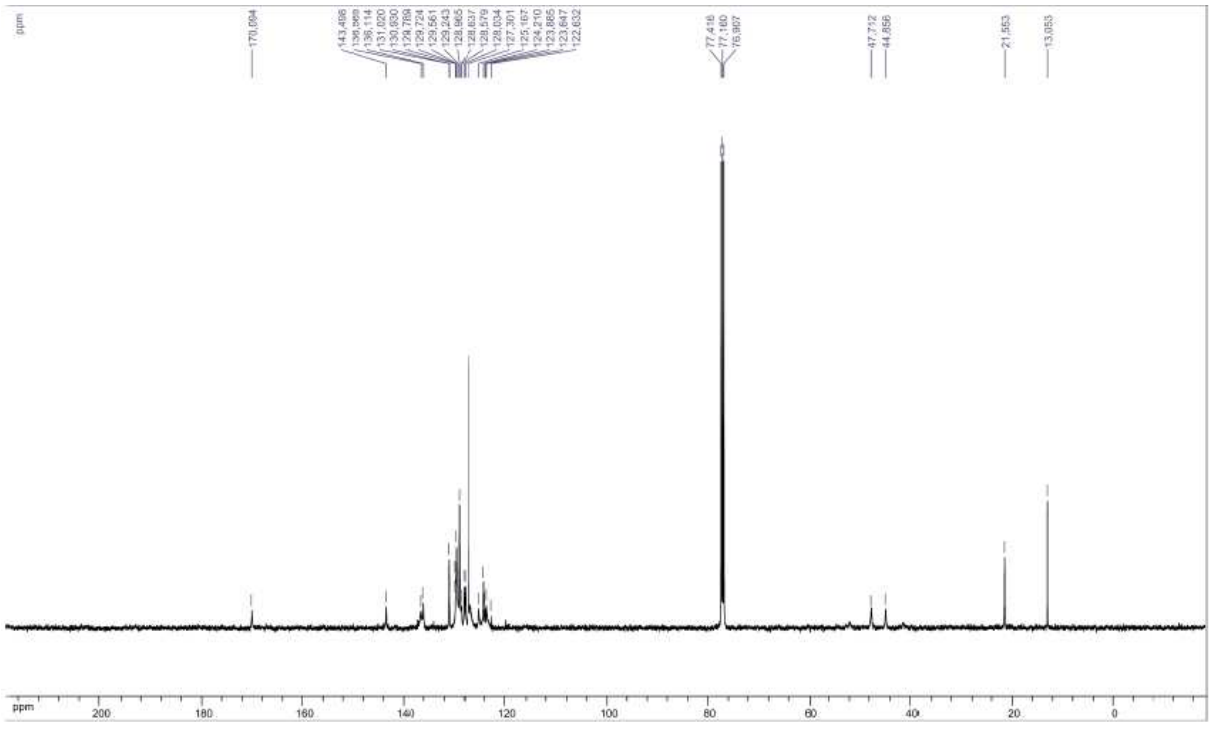
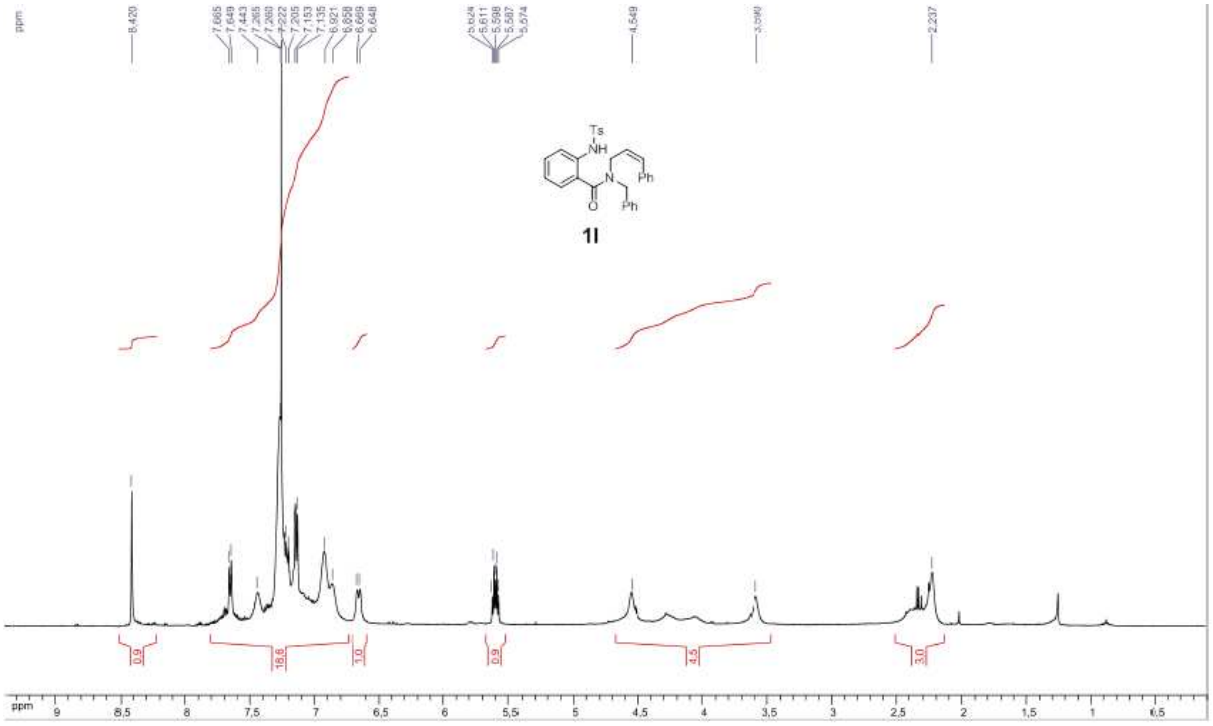
144.722
142.567
142.437
136.651
131.673
130.092
129.269
128.469
127.326
126.467
123.022
119.484
77.416
77.000
76.807
50.705
48.253
21.672
ppm
200
180
160
140
120
100
80
60
40
20
0



1k




ppm
8,420
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7,649
7,443
7,265
7,260
7,222
7,205
7,193
7,135
6,921
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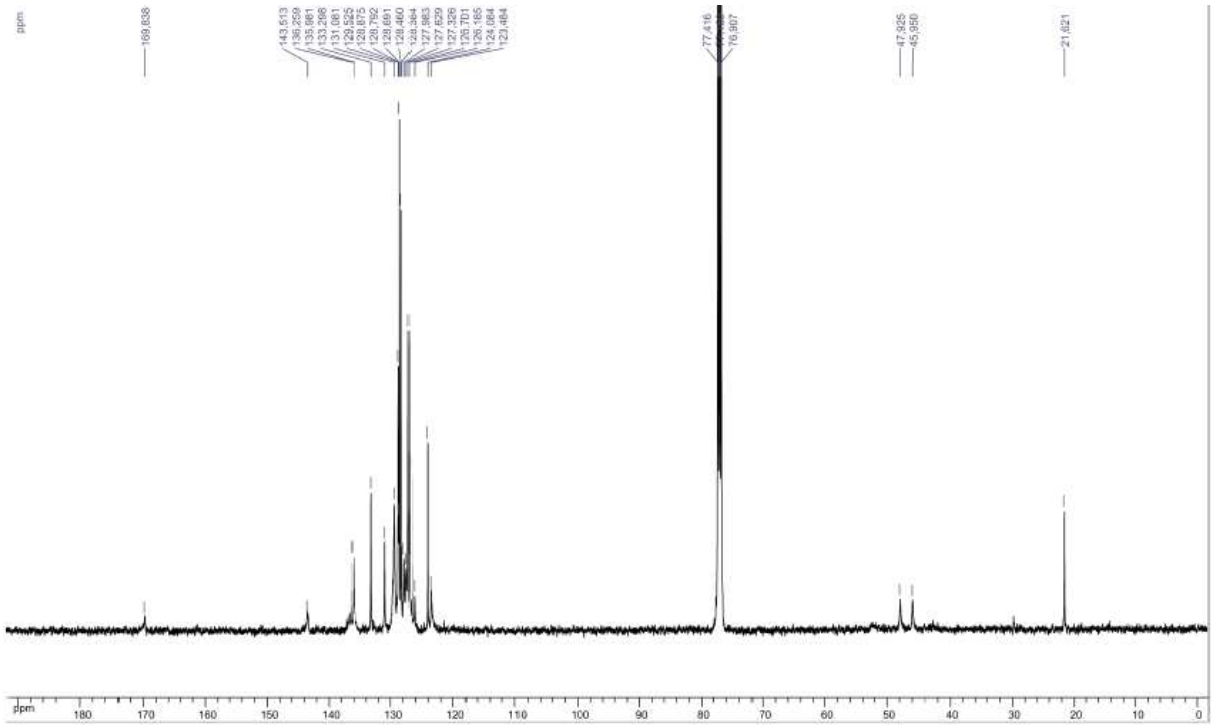
6,648
5,611
5,598
5,587
5,574
4,549
3,590
2,237
Ts
NH
N
Ph
Ph
O
1l
0,9
18,6
3,0
0,9
4,5
3,0


ppm
169,838
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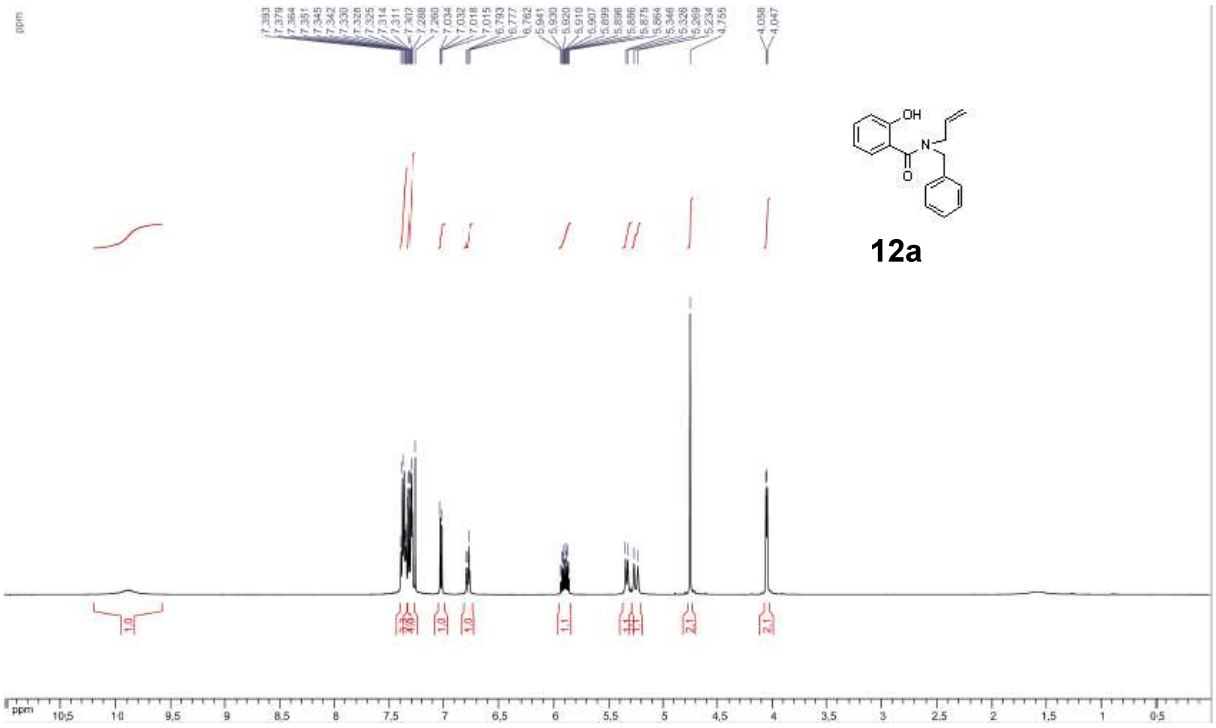
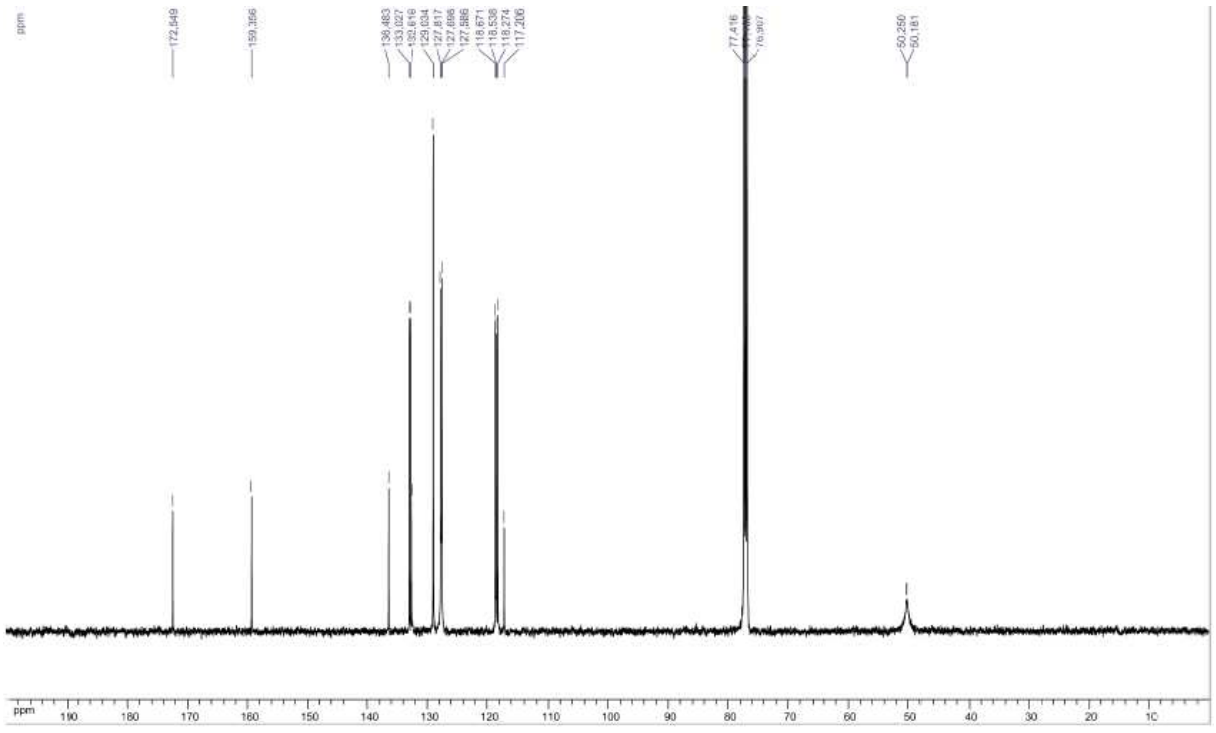
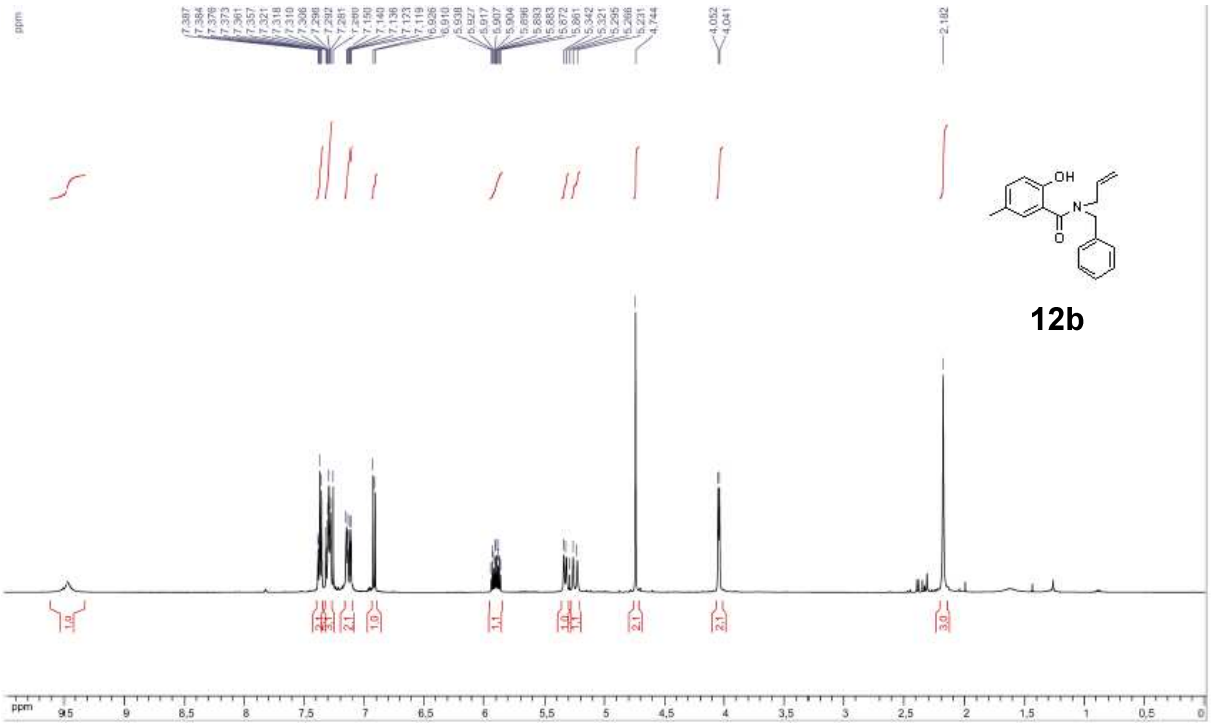
136,259
135,861
133,298
131,081
129,525
129,455
129,075
128,792
128,691
128,460
128,364
127,983
127,829
127,326
126,701
126,165
124,084
123,484
77,416
77,095
76,907
47,925
45,950
21,621

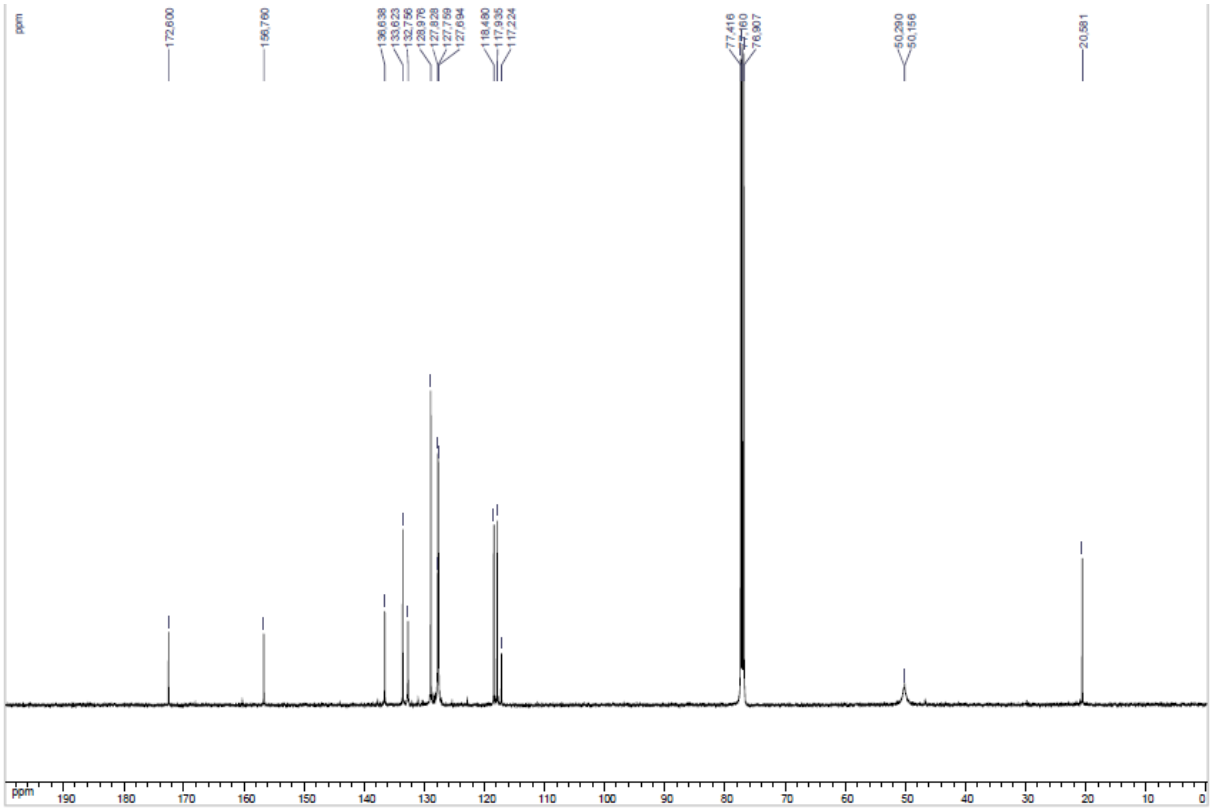


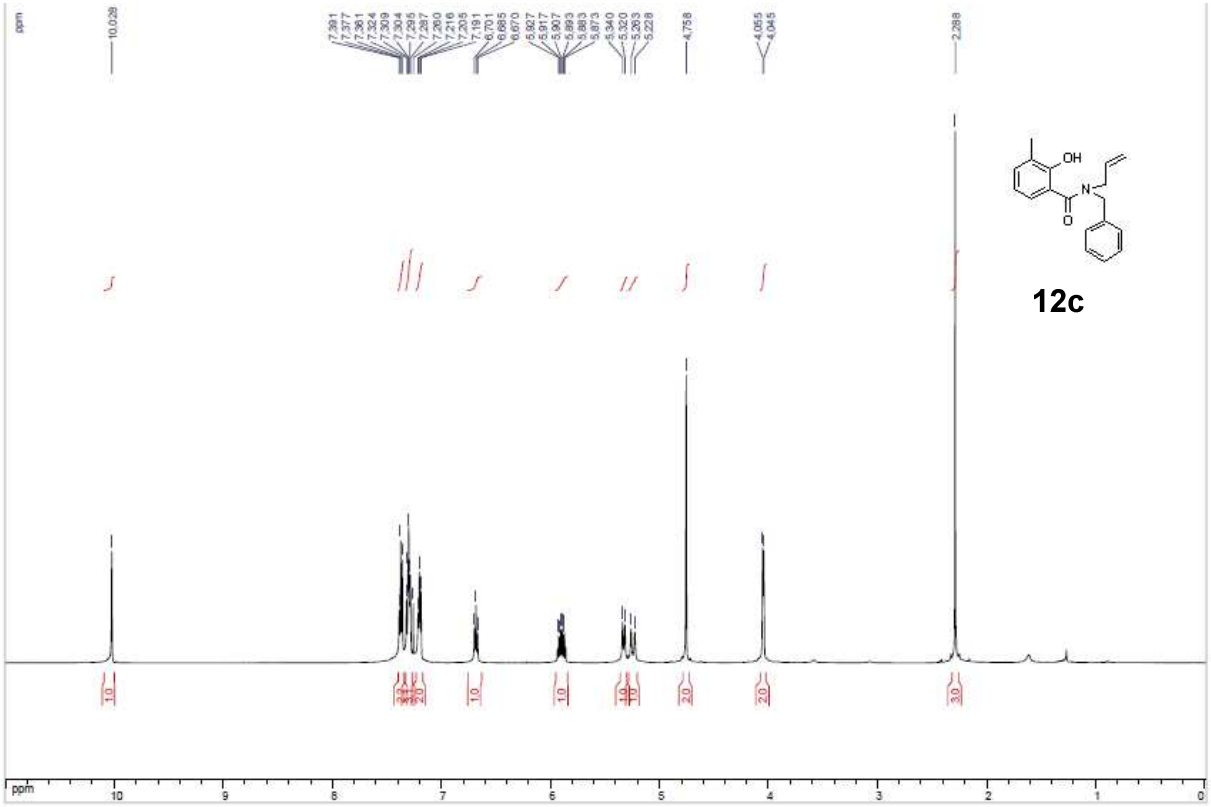
12a





12b

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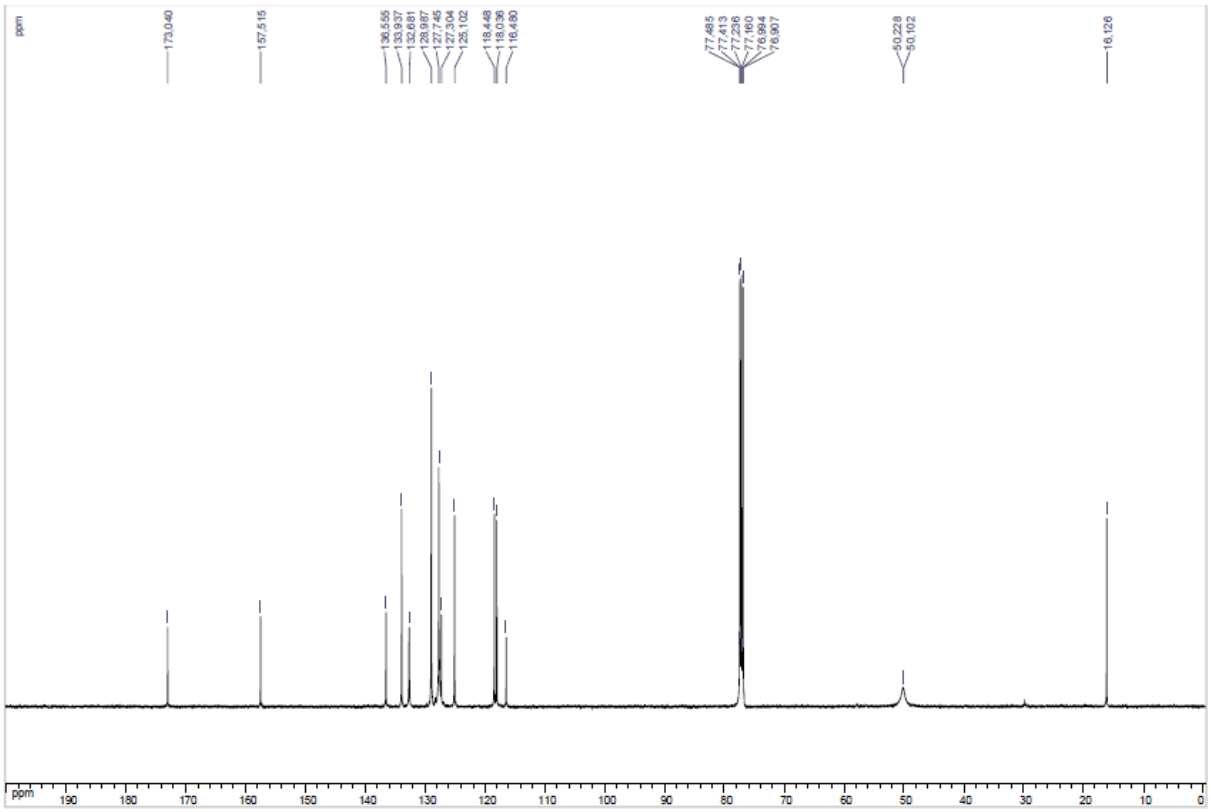
7.377
7.364
7.324
7.309
7.304
7.295
7.287
7.260
7.216
7.205
7.191
6.701
6.685
6.670
5.927
5.917
5.907
5.893
5.883
5.873
5.340
5.320
5.263
5.228
4.758
4.055
4.045
2.288
OH
N
O
12c
1.0
3.3
2.0
1.0
1.0
1.0
1.0
2.0
2.0
3.0
ppm
10
9
8
7
6
5
4
3
2
1
0


ppm
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133.937
132.681
128.987
127.745
127.304
125.102
118.448
118.036
116.460
77.485
77.443
77.236
77.160
76.984
76.907
50.228
50.102
16.126
ppm
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170
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150
140
130
120
110
100
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70
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20
10
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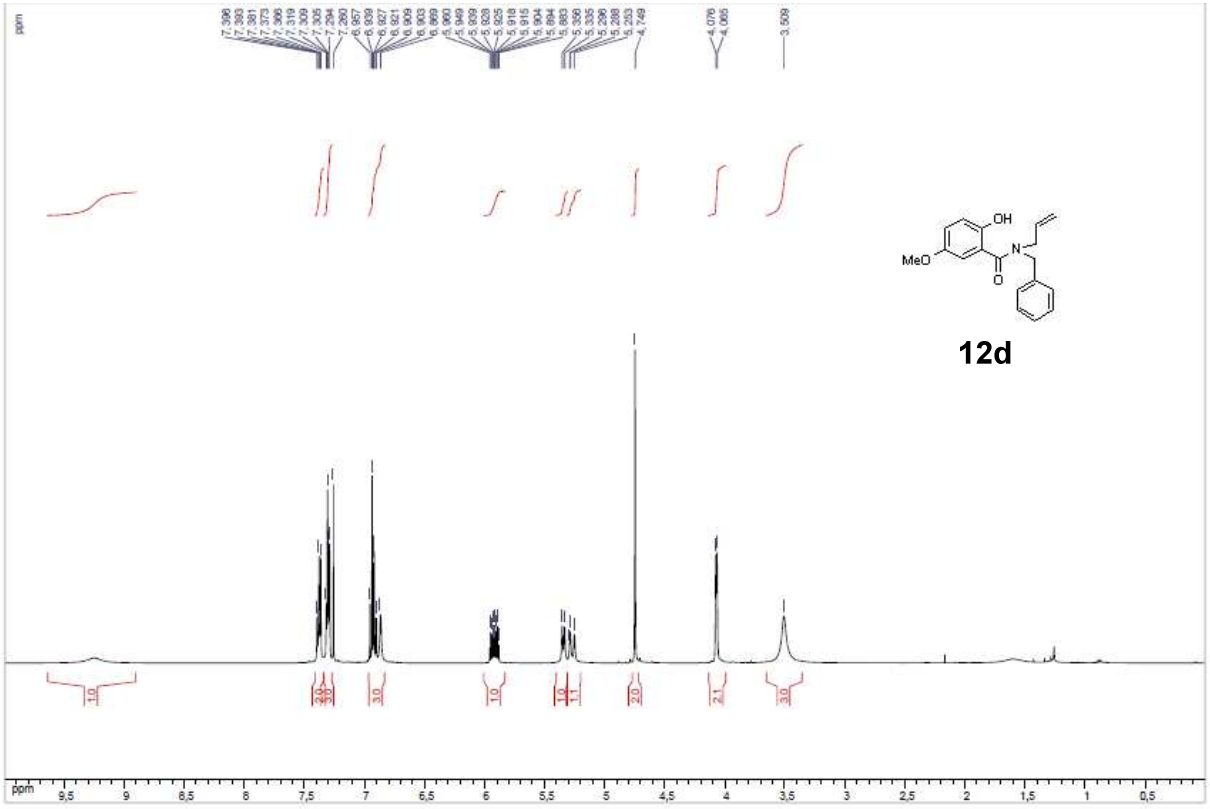
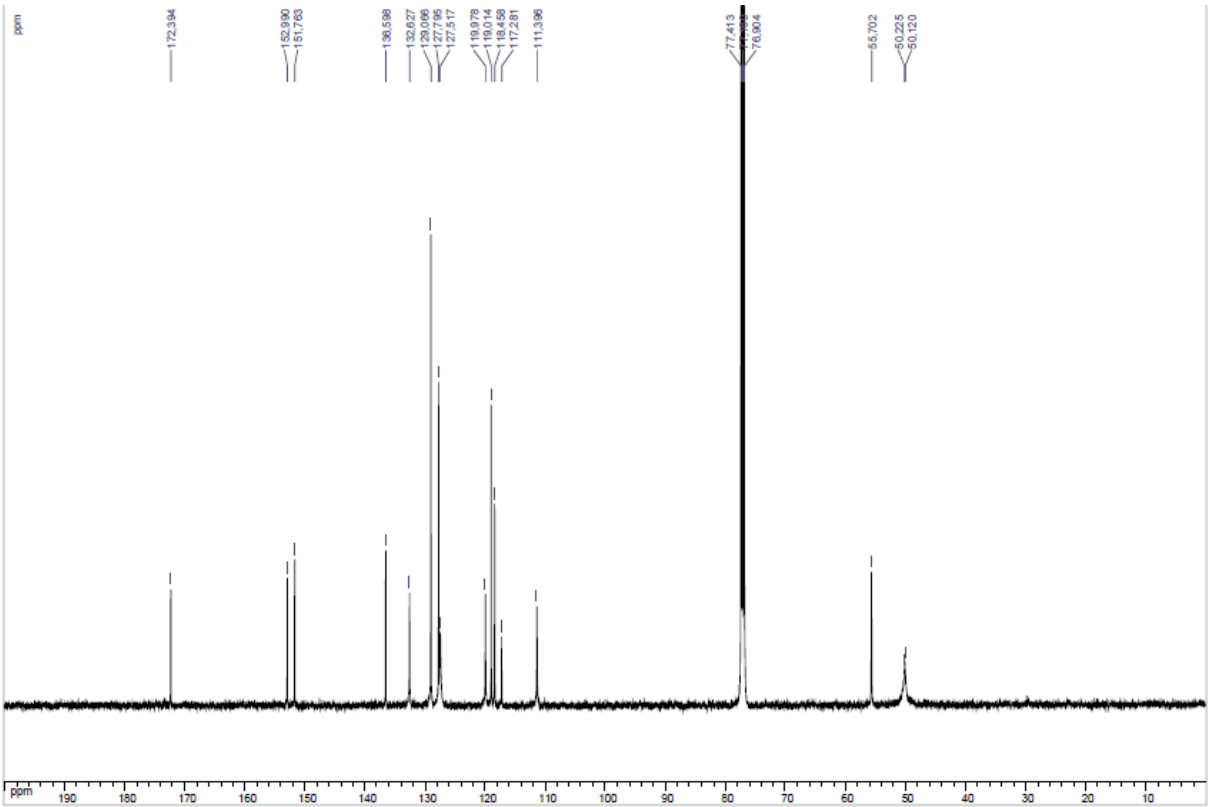
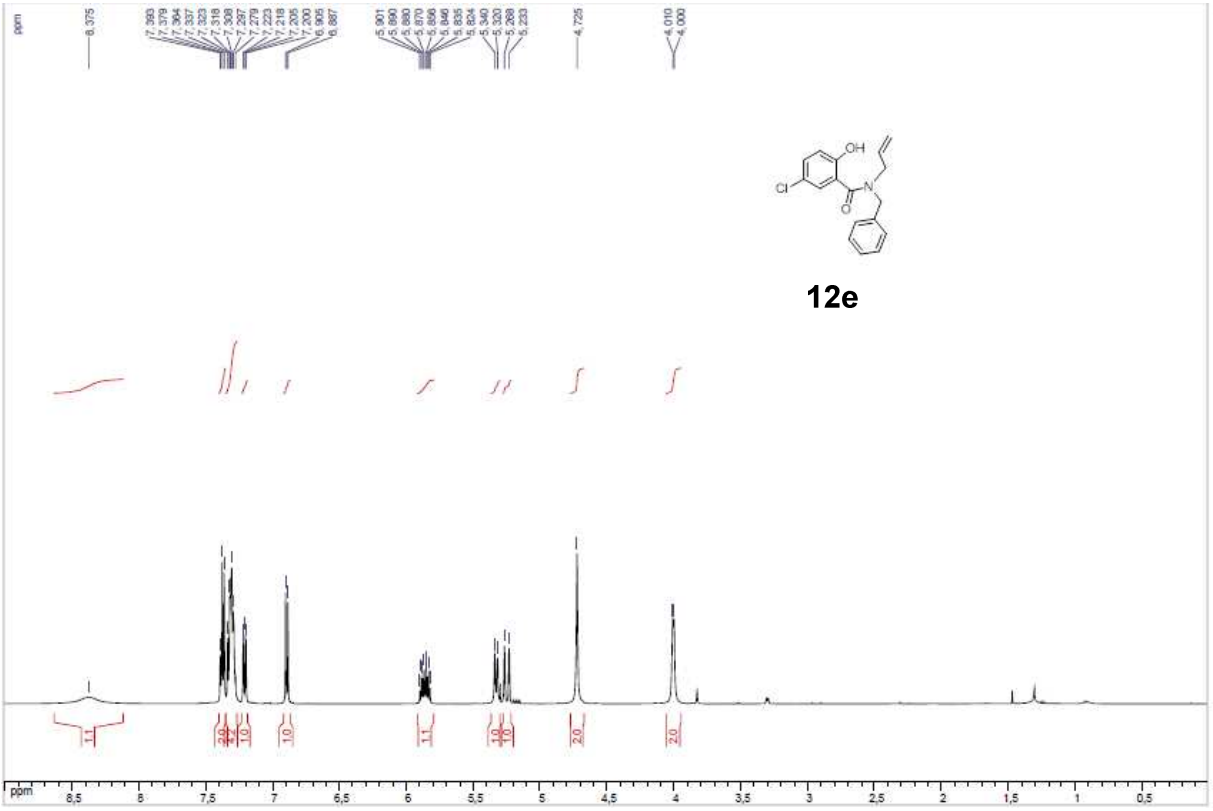


12d

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7.308
7.297
7.279
7.223
7.218
7.205
7.200
6.905
6.887
5.901
5.890
5.880
5.870
5.856
5.846
5.835
5.824
5.340
5.330
5.269
5.233
4.725
4.010
4.000
OH
Cl
N
O
1.1
2.0
1.0
1.0
1.1
1.0
1.0
2.0
2.0
ppm
8.5
8
7.5
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6.5
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5.5
5
4.5
4
3.5
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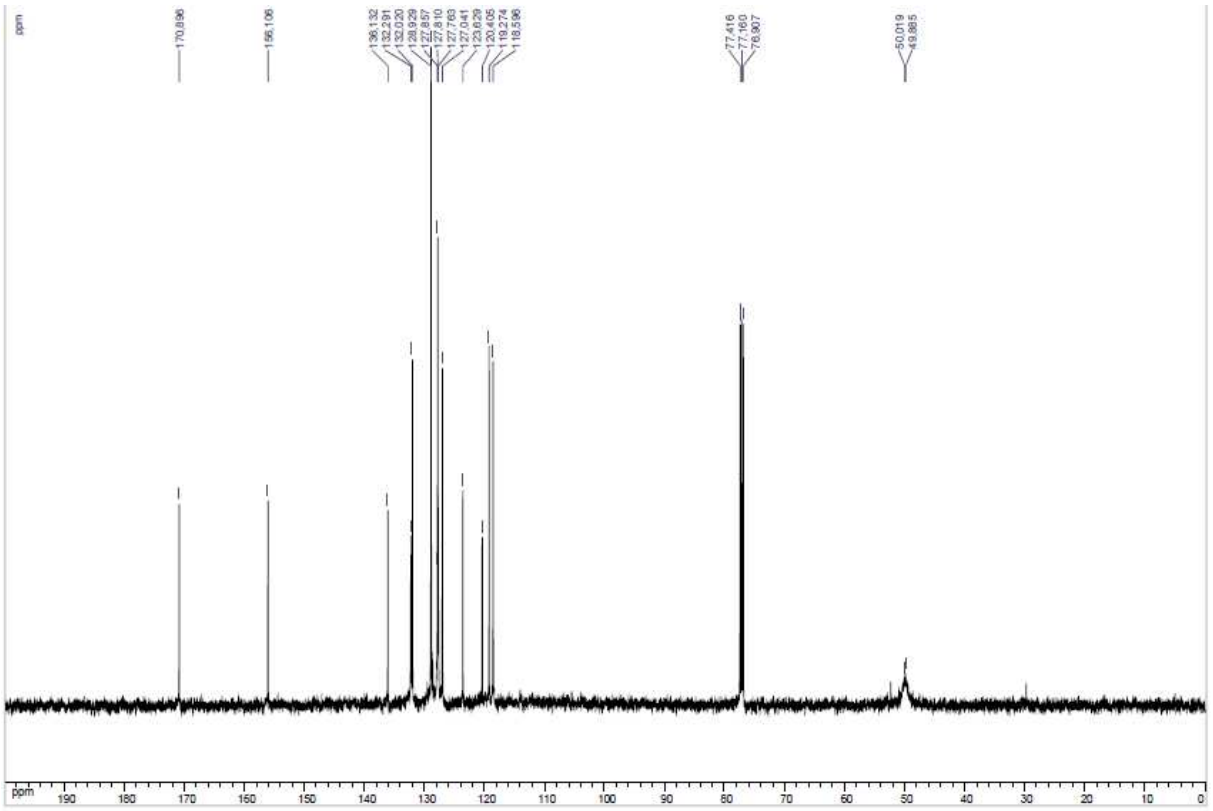
2.5
2
1.5
1
0.5

12e


ppm
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132.291
132.030
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127.857
127.810
127.763
127.041
123.629
120.405
119.274
118.596
77.416
77.160
76.907
50.019
49.885
ppm
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150
140
130
120
110
100
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80
70
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30
20
10
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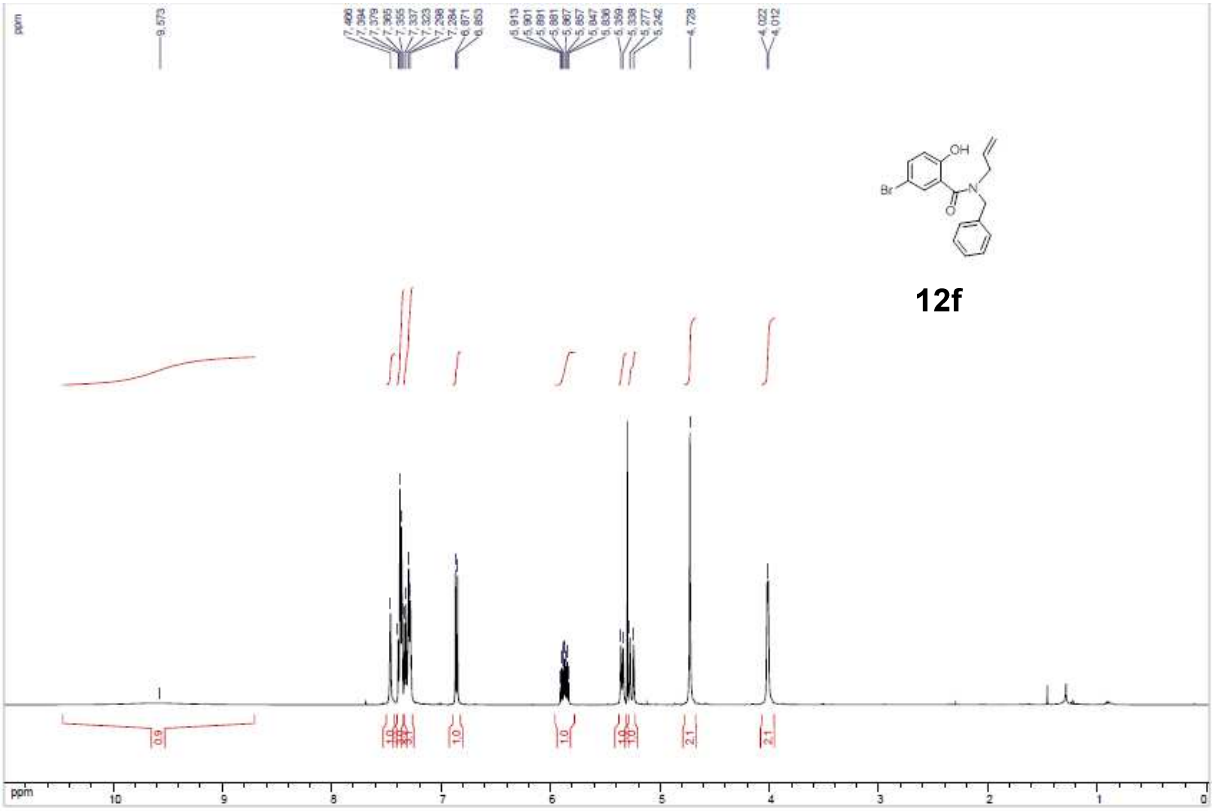
ppm
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7.365
7.355
7.337
7.323
7.298
7.284
6.871
6.853
5.913
5.901
5.891
5.881
5.867
5.857
5.847
5.836
5.359
5.338
5.277
5.242
4.728
4.022
4.012
OH
Br
O
N
12f
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1.0
3.1
1.0
1.0
1.9
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2.1
2.1
ppm
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9
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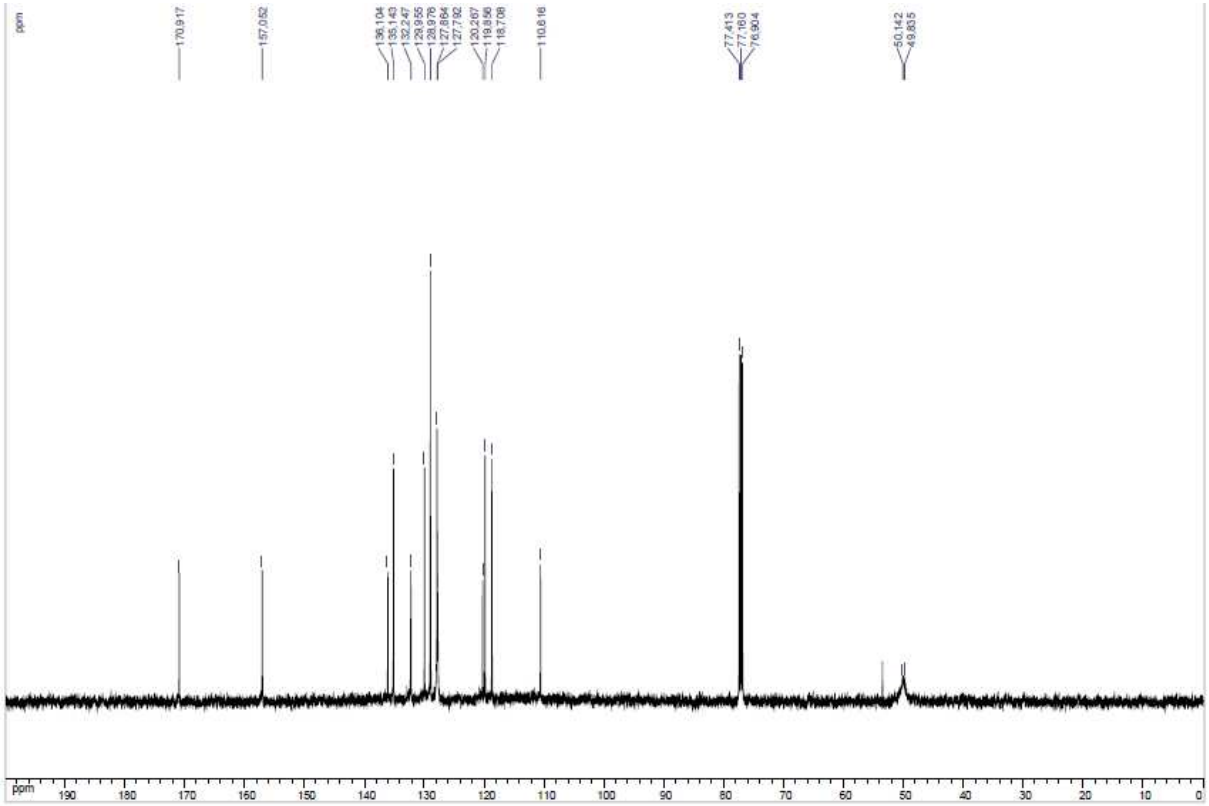
7
6
5
4
3
2
1
0


ppm
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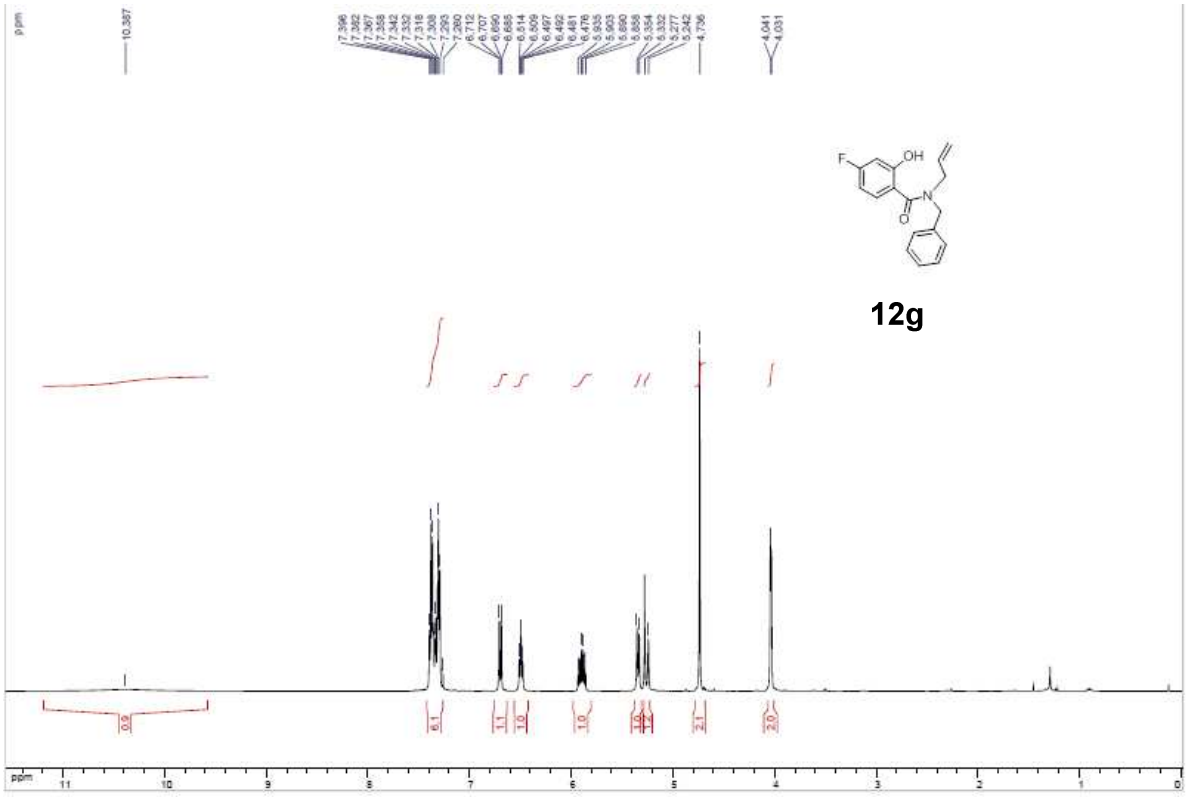
135.143
132.247
129.955
128.976
127.864
127.782
120.267
119.856
118.708
110.616
77.413
77.160
76.904
50.142
49.835
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


ppm
10.387
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7.382
7.367
7.358
7.342
7.332
7.318
7.308
7.293
7.280
6.712
6.707
6.690
6.685
6.514
6.509
6.497
6.492
6.481
6.476
5.918
5.903
5.890
5.858
5.354
5.332
5.277
5.242
4.706
4.041
4.031
F
OH
O
N
0.9
6.1
1.1
1.0
1.0
1.0
1.2
2.1
2.0
ppm
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10
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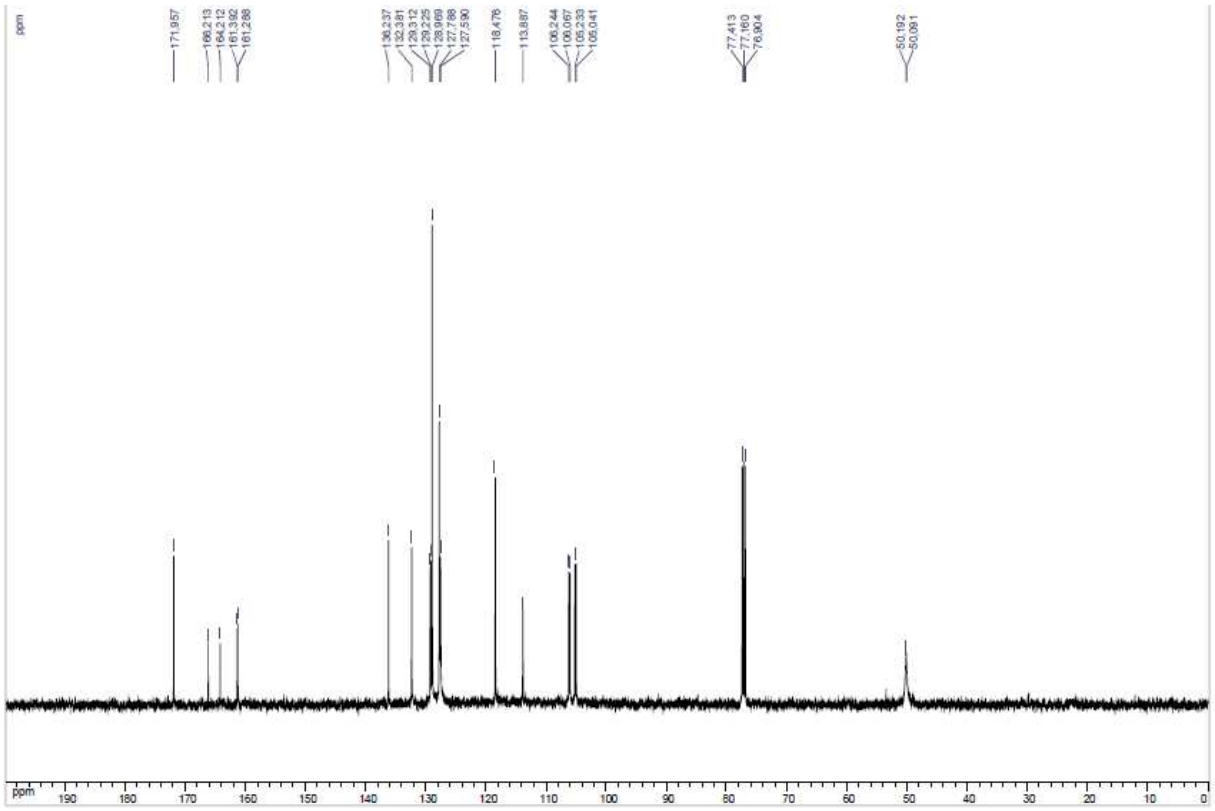
8
7
6
5
4
3
2
1
0

12g


ppm
171.957
169.213
164.212
161.392
161.288
136.237
132.381
129.312
129.225
128.969
127.788
127.590
118.476
113.887
106.244
106.067
105.233
105.041
77.413
77.160
76.904
50.192
50.091
ppm
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180
170
160
150
140
130
120
110
100
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70
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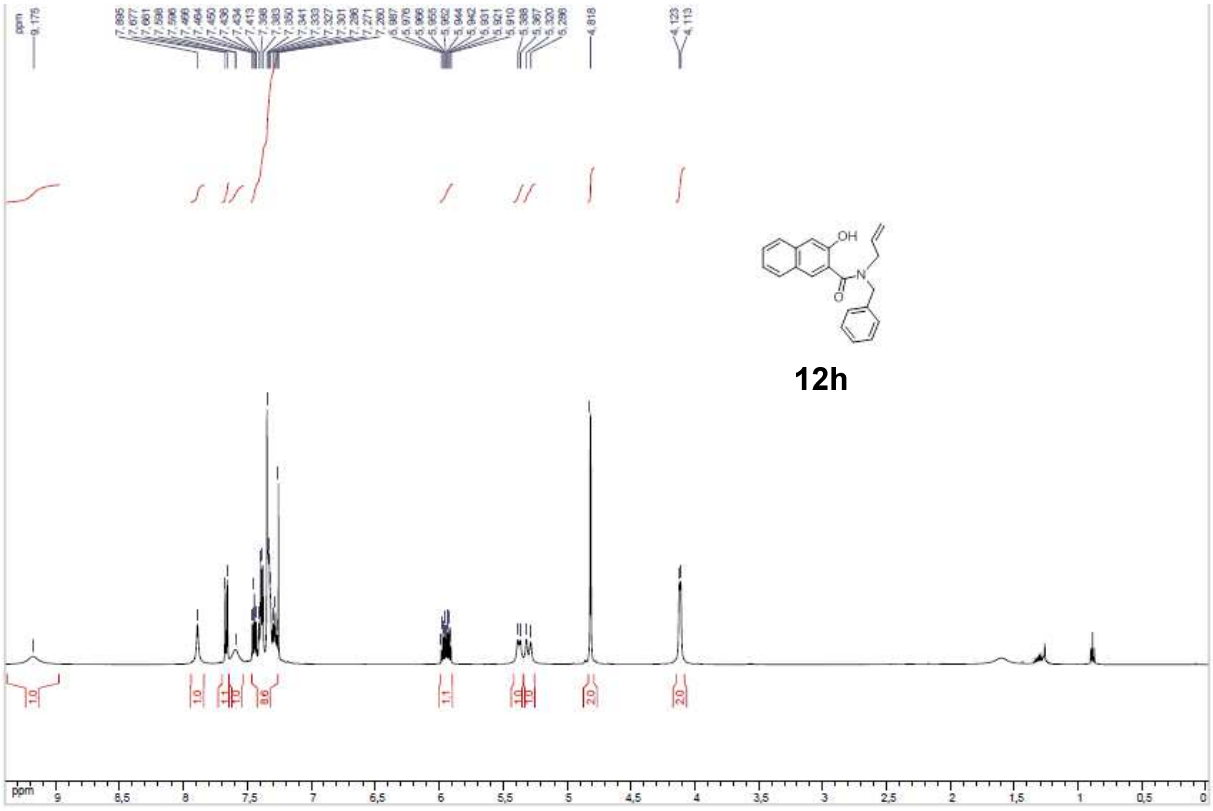
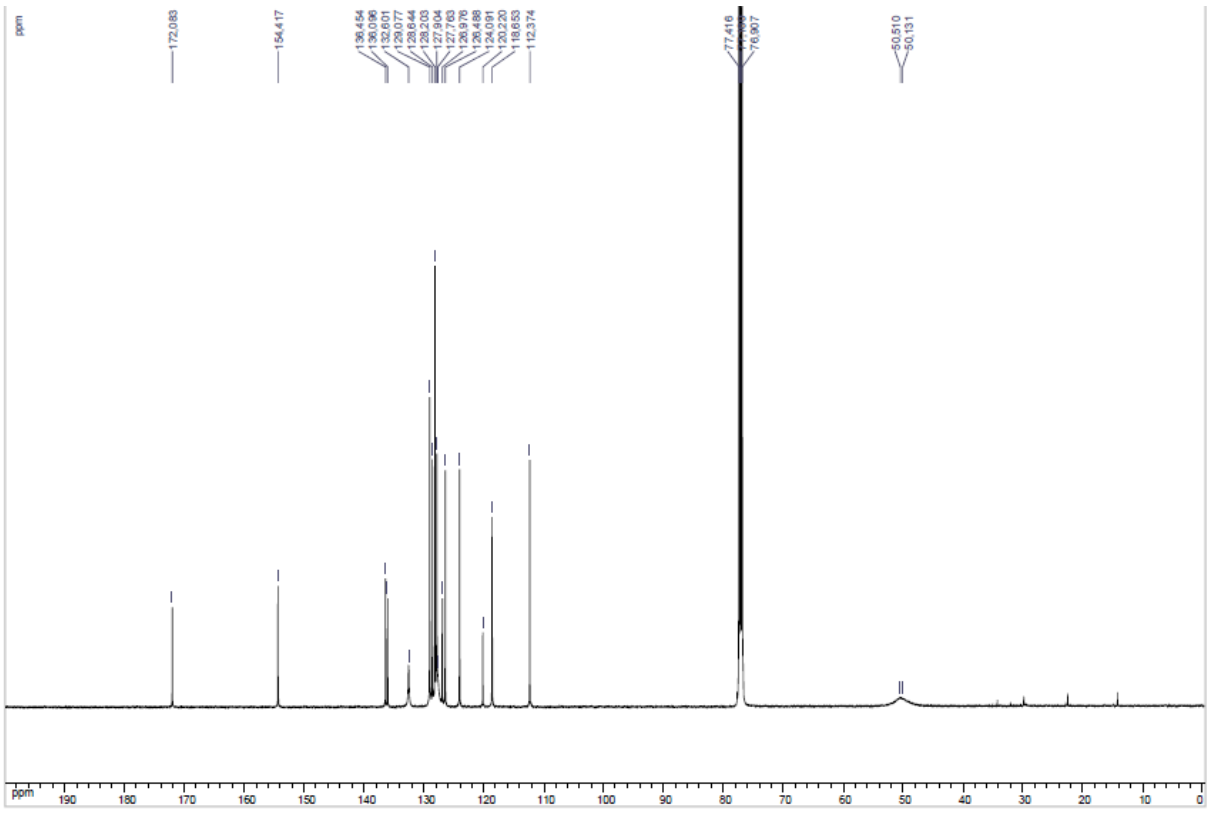
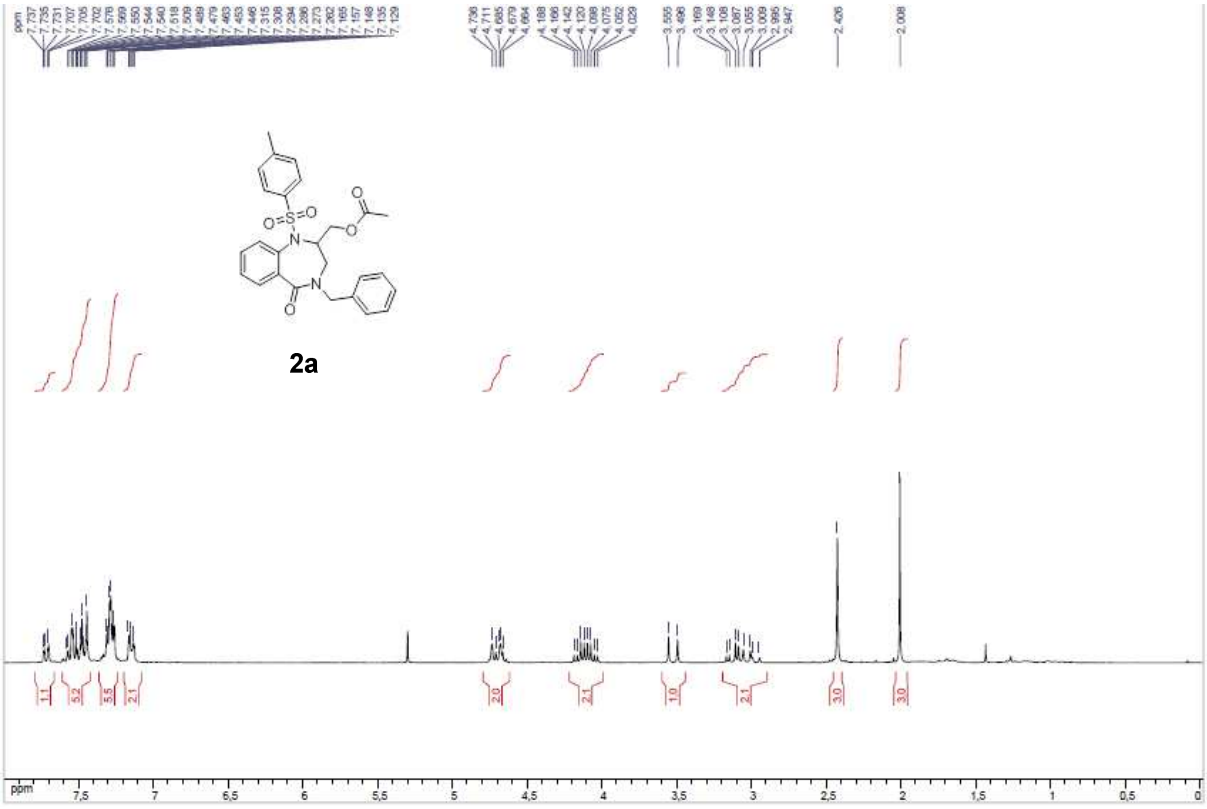
10
0

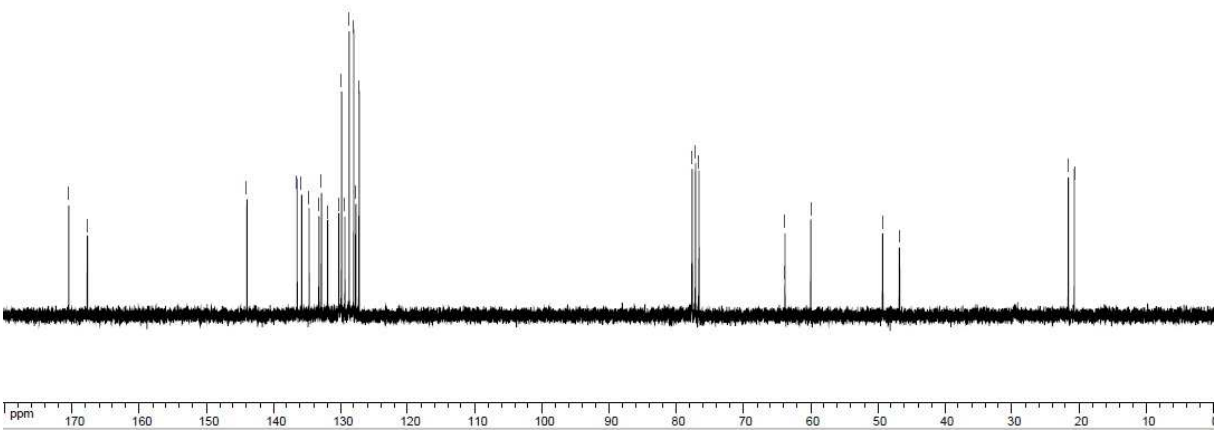


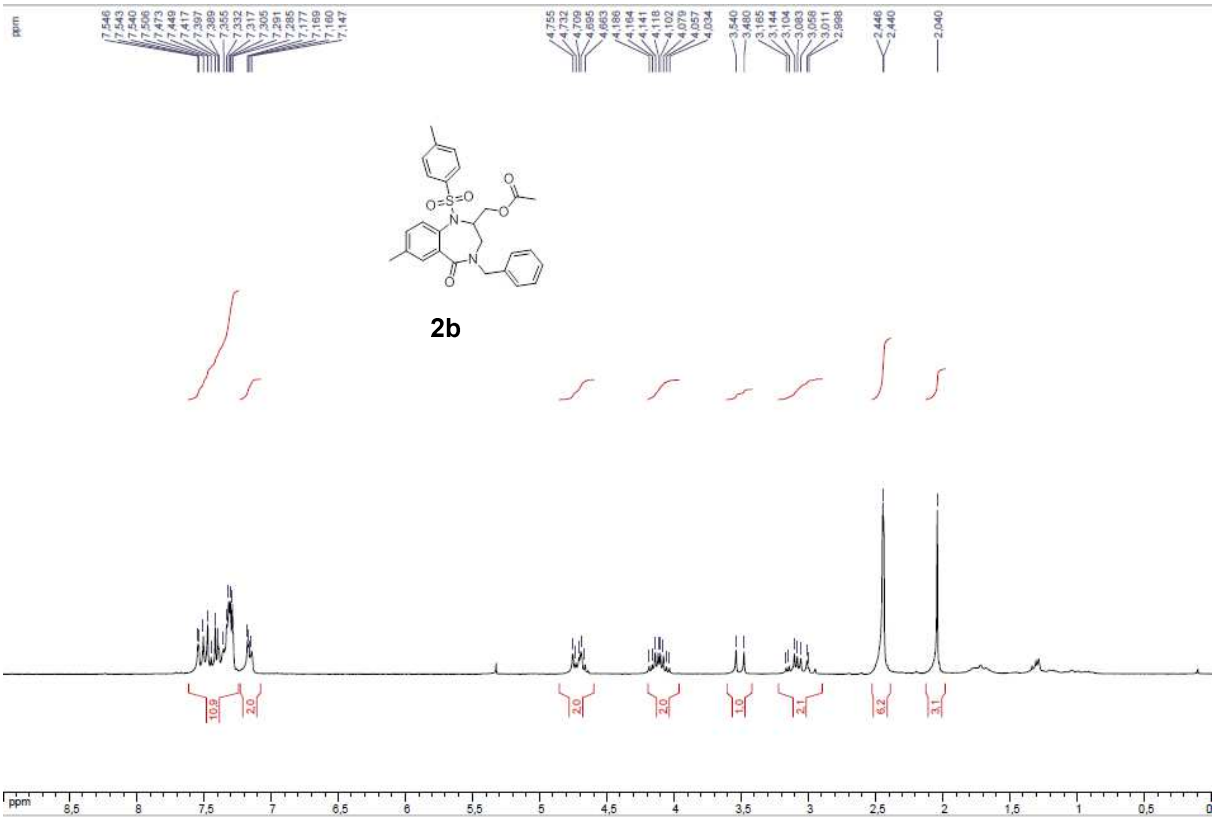
12h





2a

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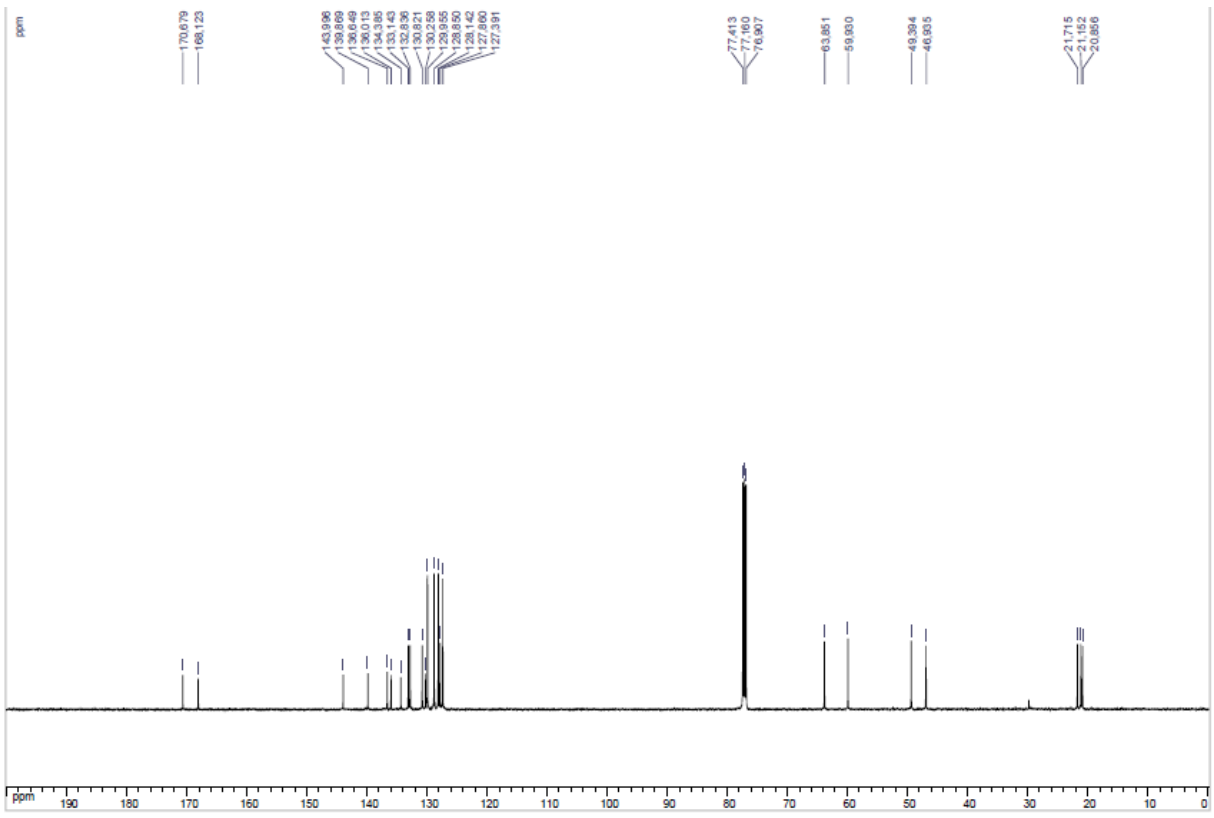
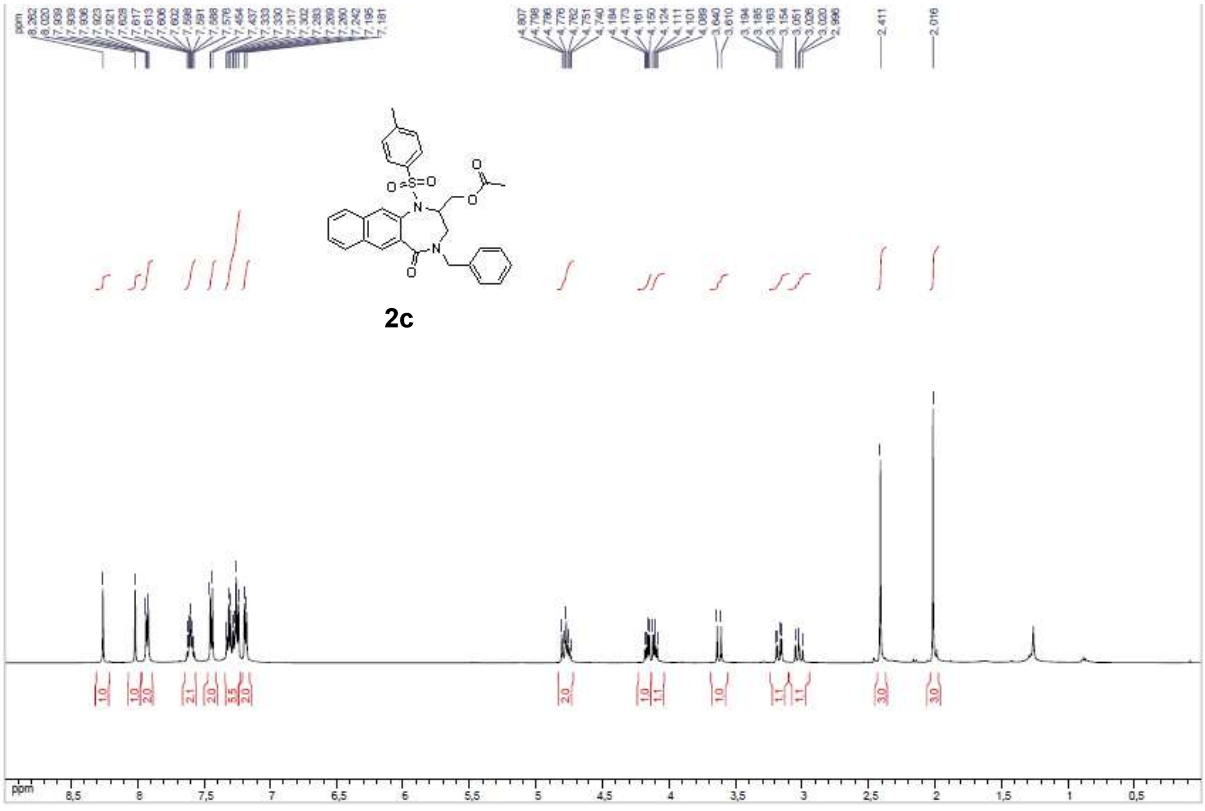
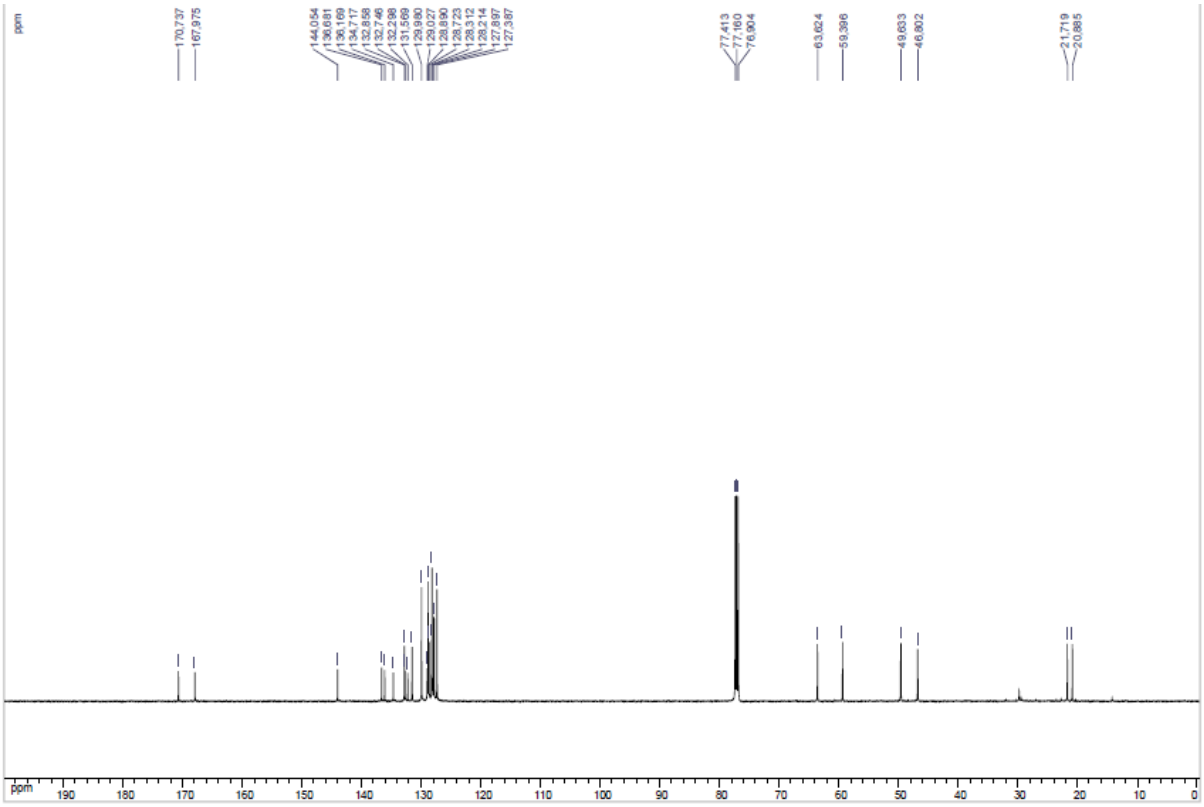
7.540
7.506
7.473
7.449
7.417
7.397
7.389
7.355
7.332
7.317
7.305
7.291
7.285
7.177
7.169
7.160
7.147
4.755
4.732
4.709
4.695
4.663
4.186
4.164
4.141
4.118
4.102
4.079
4.057
4.034
3.540
3.480
3.165
3.144
3.104
3.083
3.058
3.011
2.998
2.446
2.440
2.040
10.8
2.0
2.0
2.0
1.0
2.1
6.2
3.1
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

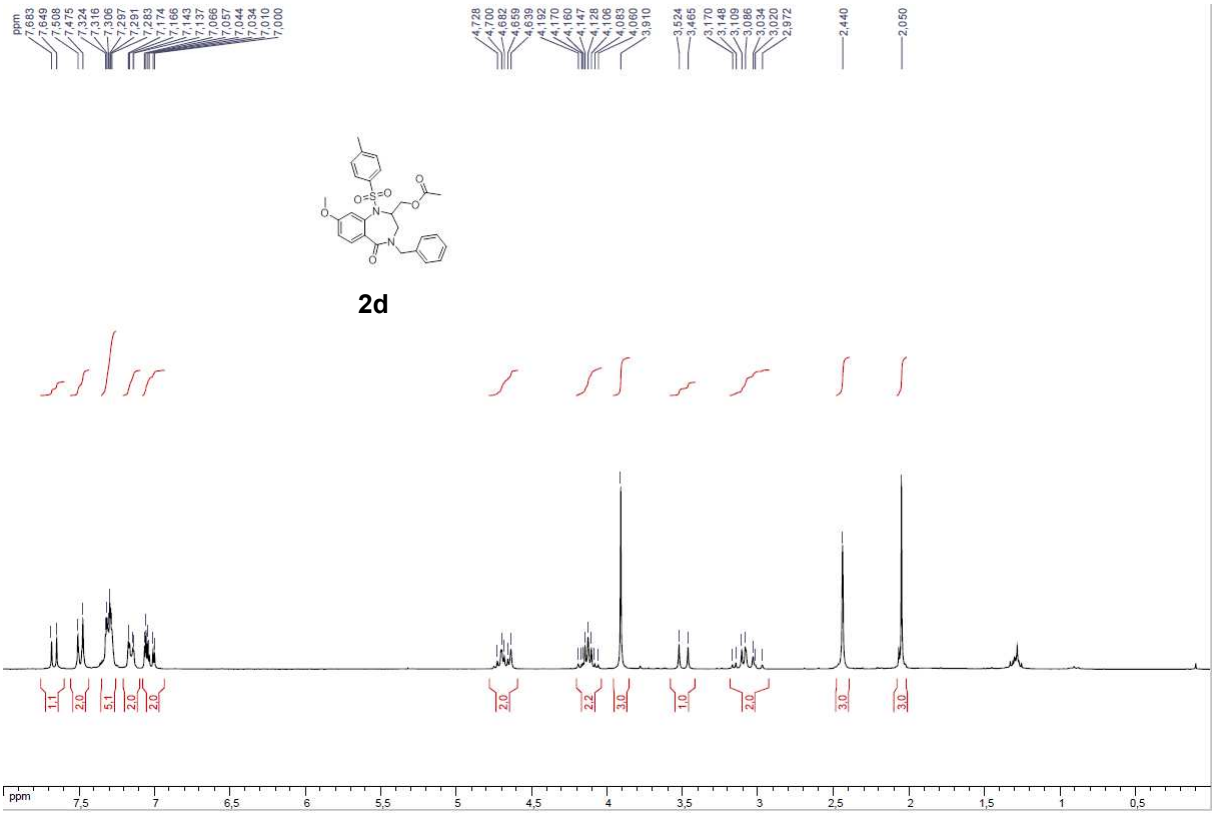
2b


ppm
170.679
168.123
143.996
139.869
136.649
136.013
134.385
133.143
132.836
130.821
130.298
129.955
128.850
128.142
127.960
127.391
77.413
77.160
76.907
63.851
59.930
49.394
46.935
21.715
21.152
20.856
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



2c

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7.475
7.324
7.316
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7.291
7.283
7.174
7.166
7.145
7.137
7.066
7.057
7.044
7.034
7.010
7.000
4.728
4.700
4.682
4.659
4.639
4.192
4.170
4.160
4.147
4.128
4.106
4.083
4.060
3.910
3.524
3.465
3.170
3.148
3.109
3.086
3.034
3.020
2.972
2.440
2.050
1.1
2.0
5.1
2.0
2.0
2.0
2.2
3.0
1.0
2.0
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3.0
ppm
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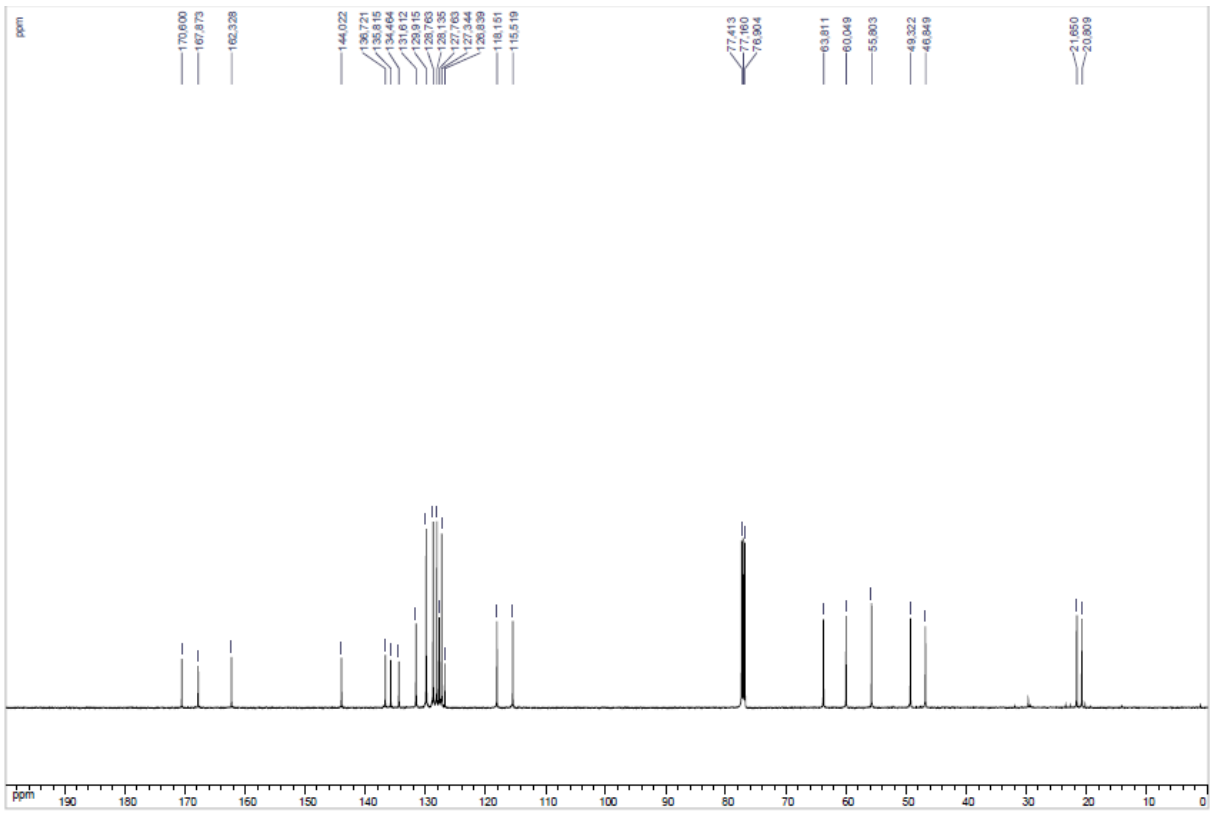
2d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144.022
136.721
135.815
134.464
131.612
128.915
128.763
128.135
127.763
127.344
126.839
118.151
115.519
77.413
77.160
76.904
63.811
60.049
55.803
49.322
46.849
21.650
20.909
ppm
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180
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150
140
130
120
110
100
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70
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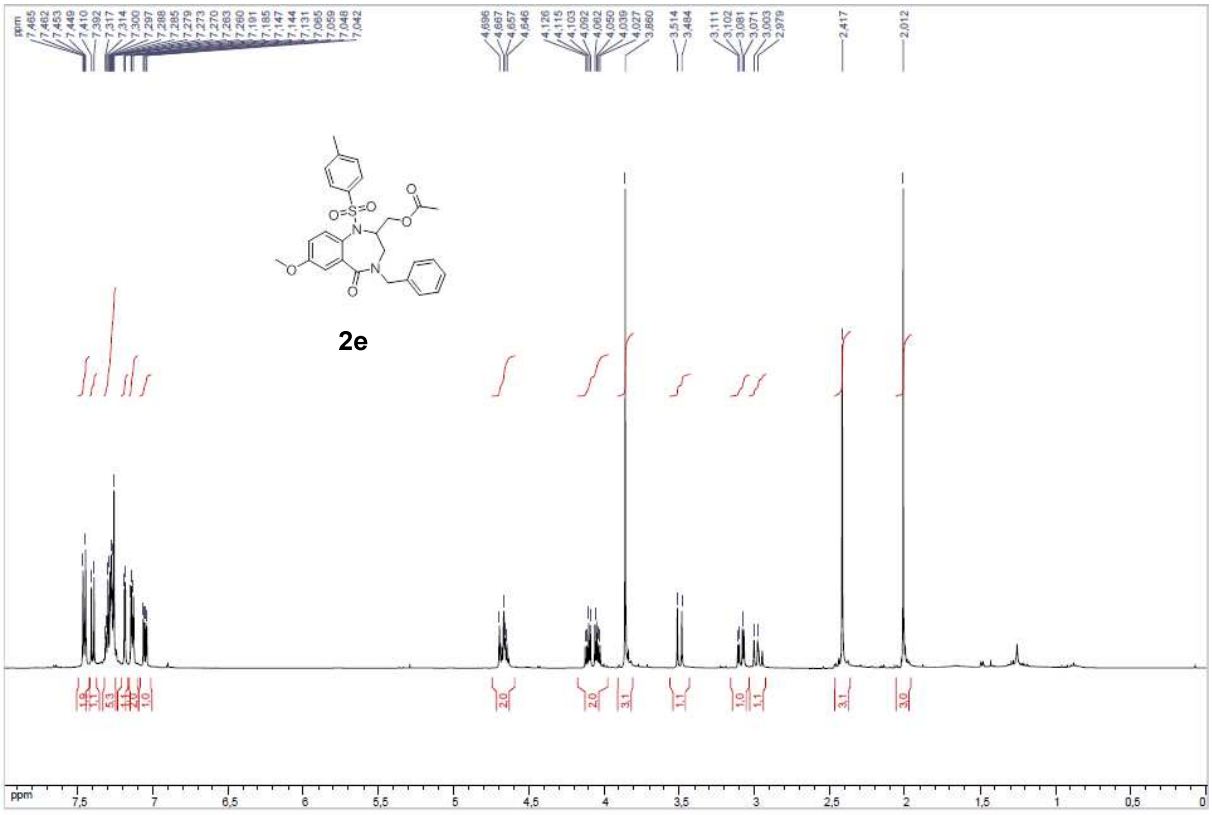
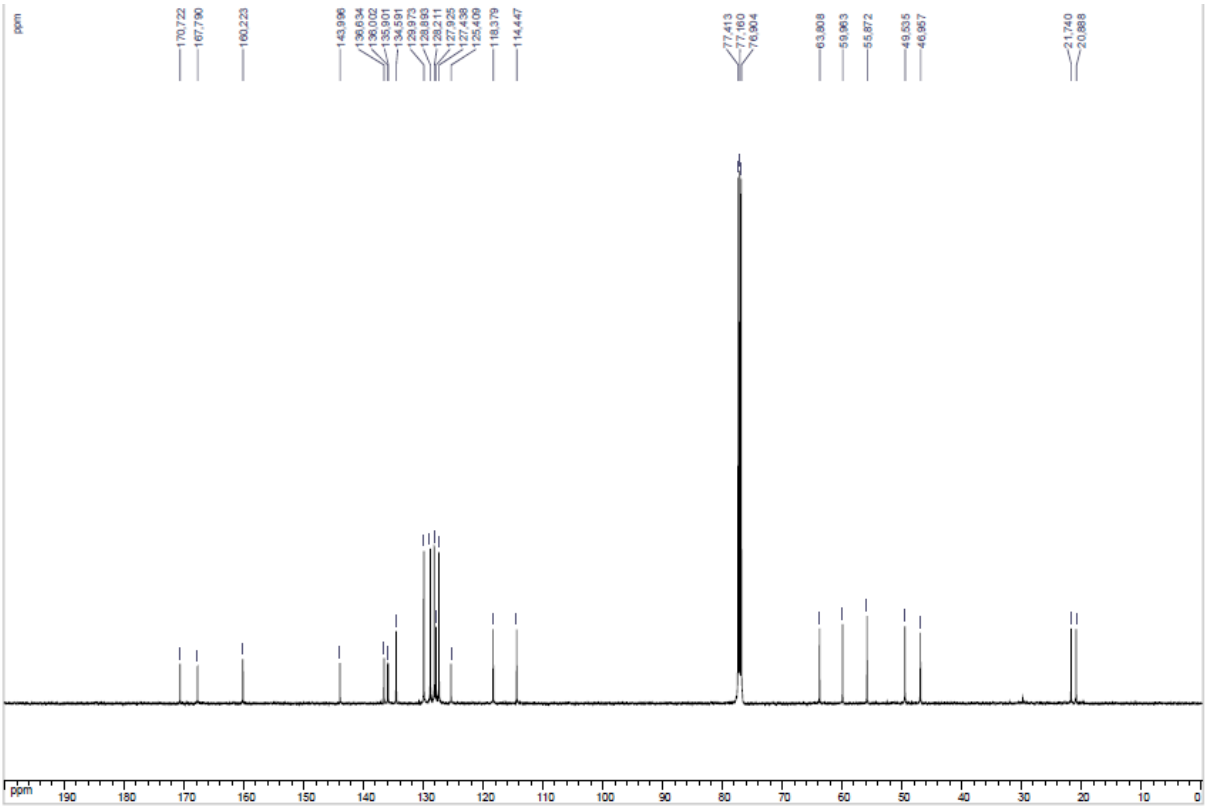
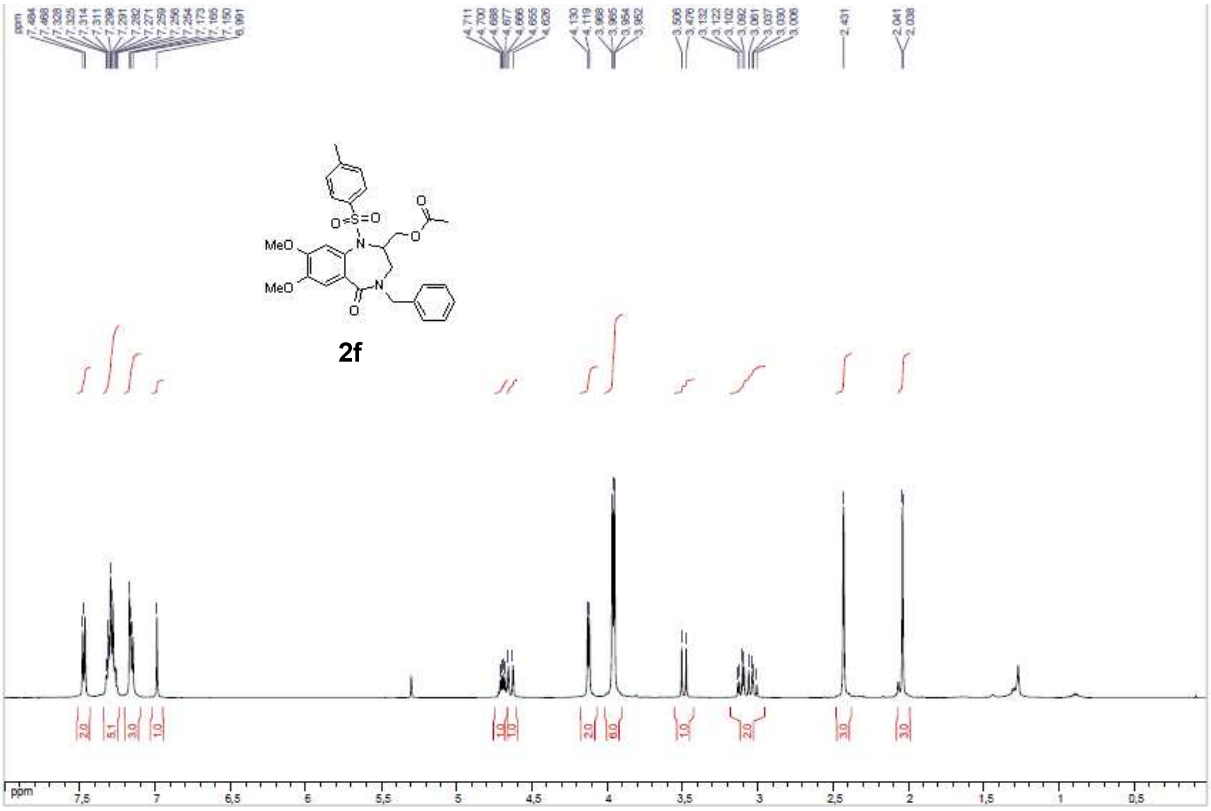
30
20
10
0



2e

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MeO
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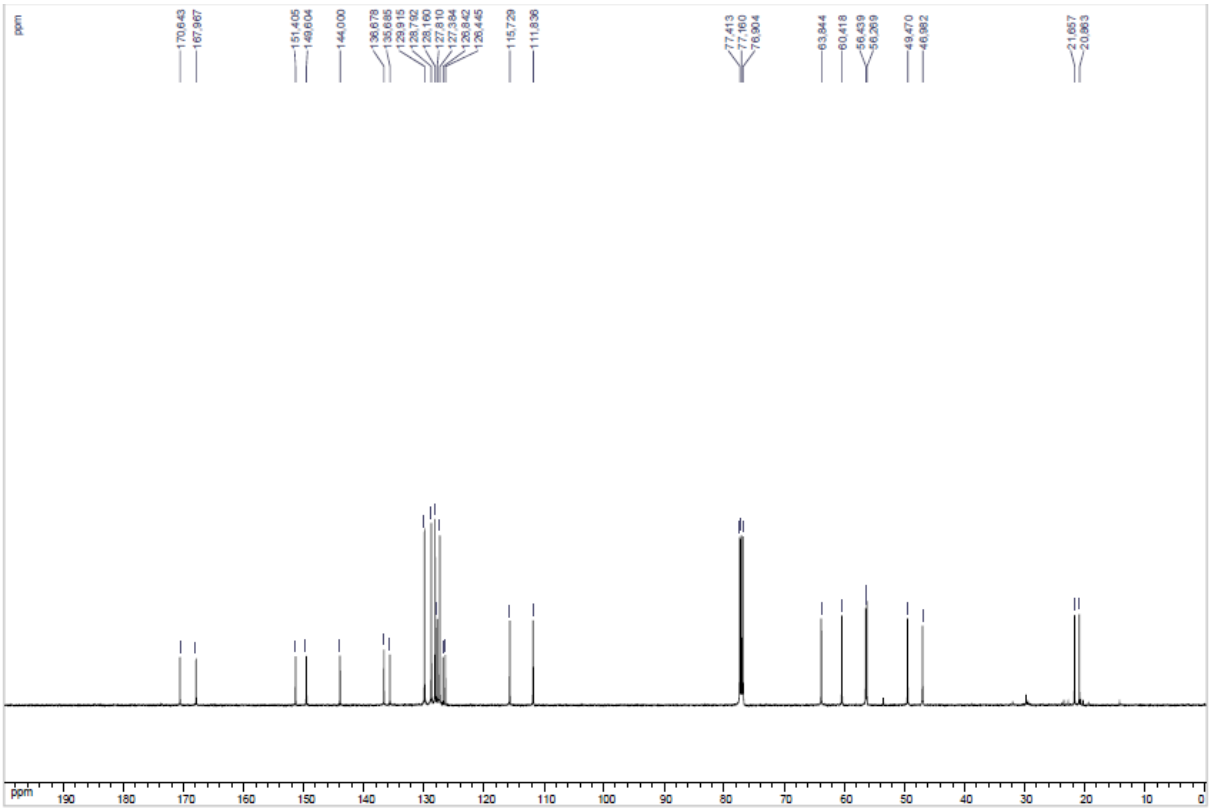

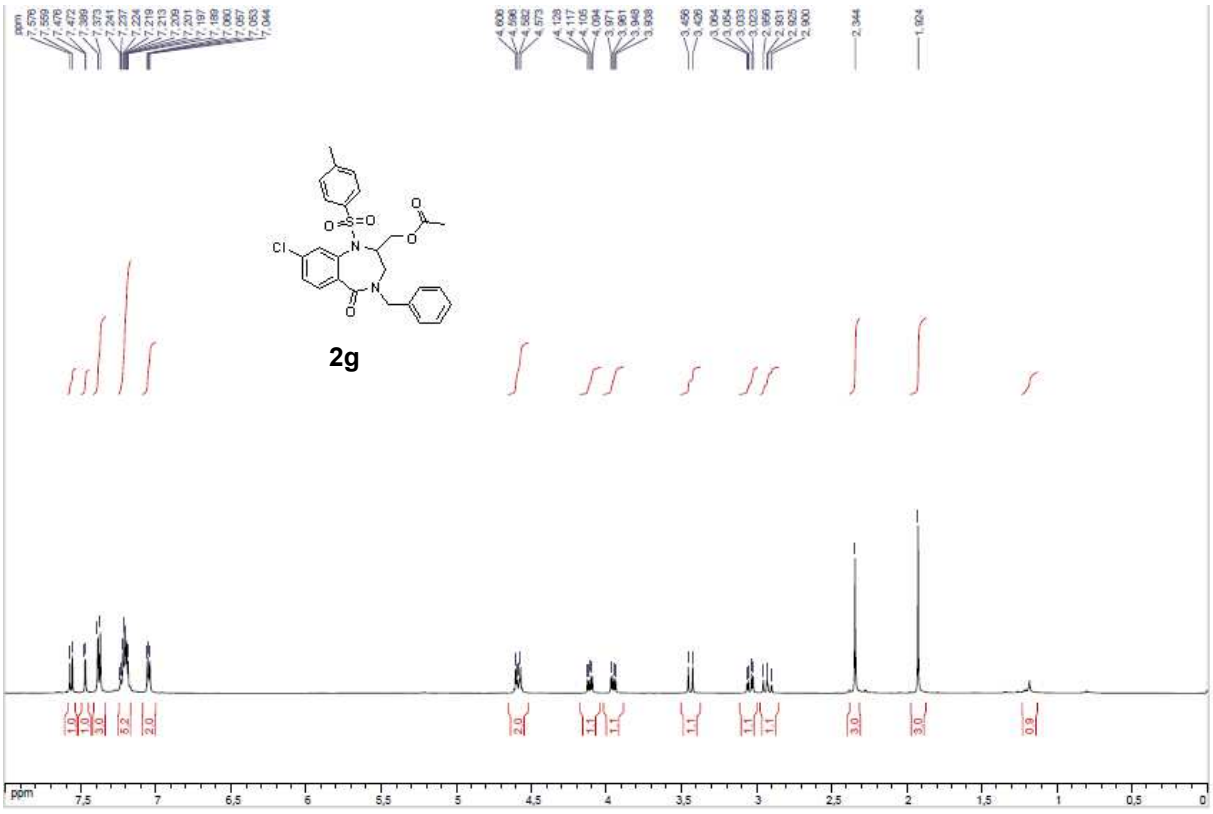

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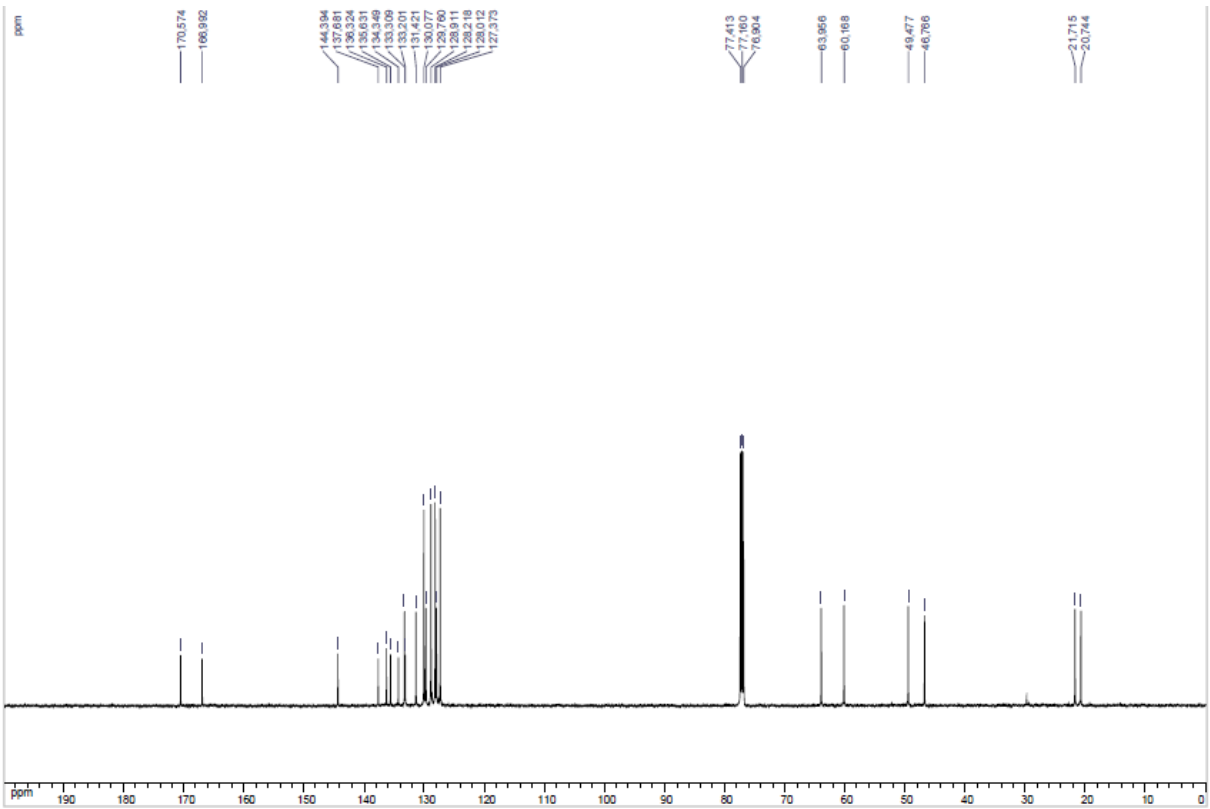

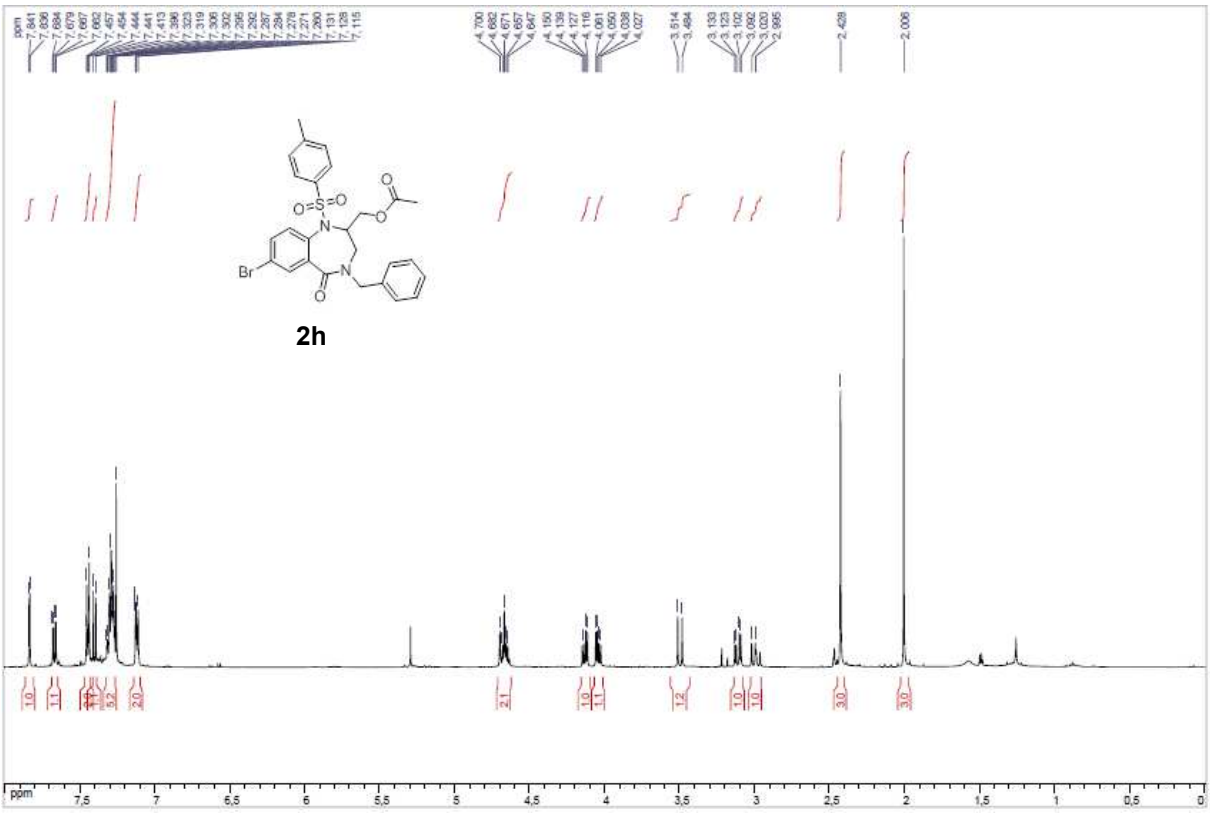
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7.667
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7.444
7.441
7.413
7.396
7.323
7.319
7.305
7.302
7.295
7.292
7.287
7.284
7.278
7.271
7.200
7.131
7.128
7.115
4.700
4.682
4.671
4.657
4.647
4.150
4.139
4.127
4.116
4.061
4.050
4.038
4.027
3.514
3.494
3.133
3.123
3.102
3.092
3.020
2.995
2.428
2.006
O=S=O
N
O
O
Br
N
O
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1.1
2.1
1.0
1.1
1.2
1.0
1.0
3.0
3.0
ppm
7,5
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0,5
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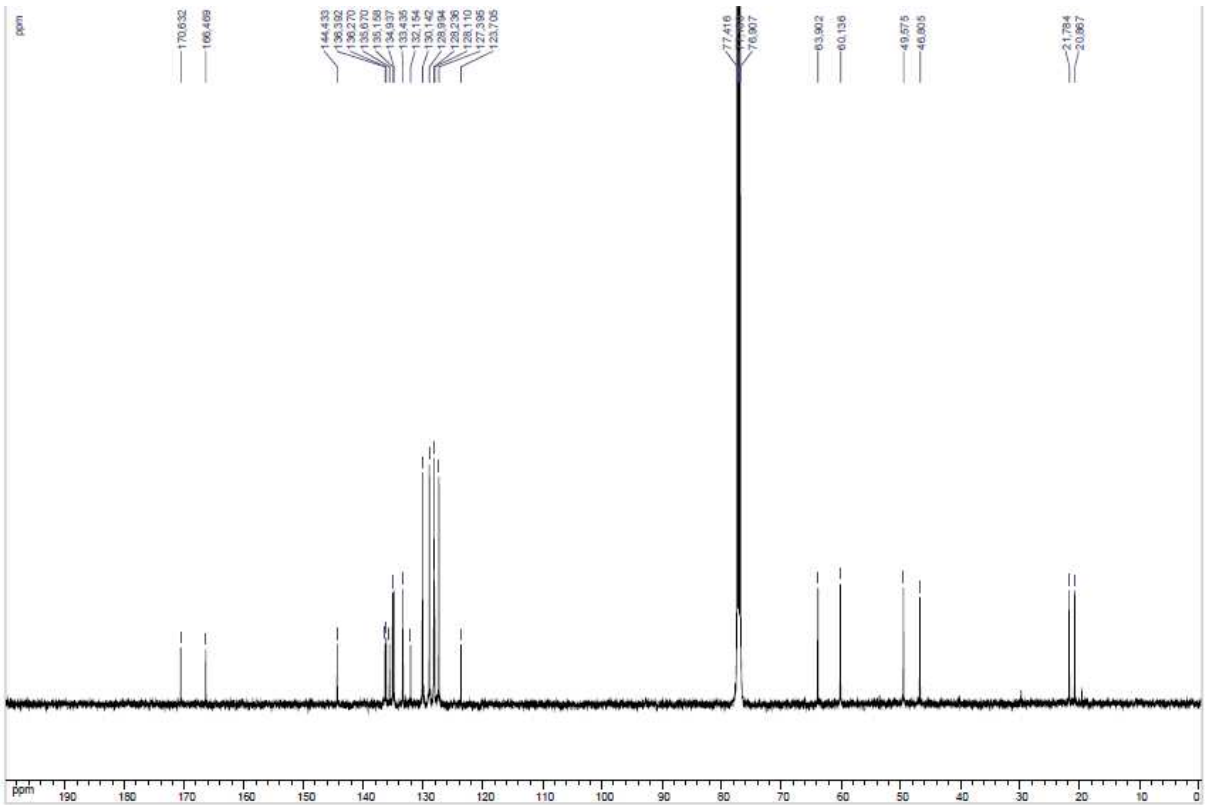
2h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136.392
136.270
135.670
135.158
134.937
133.435
132.154
130.142
128.994
128.236
128.110
127.395
123.705
77.416
77.000
76.907
63.902
60.136
49.575
46.805
21.784
20.867
ppm
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150
140
130
120
110
100
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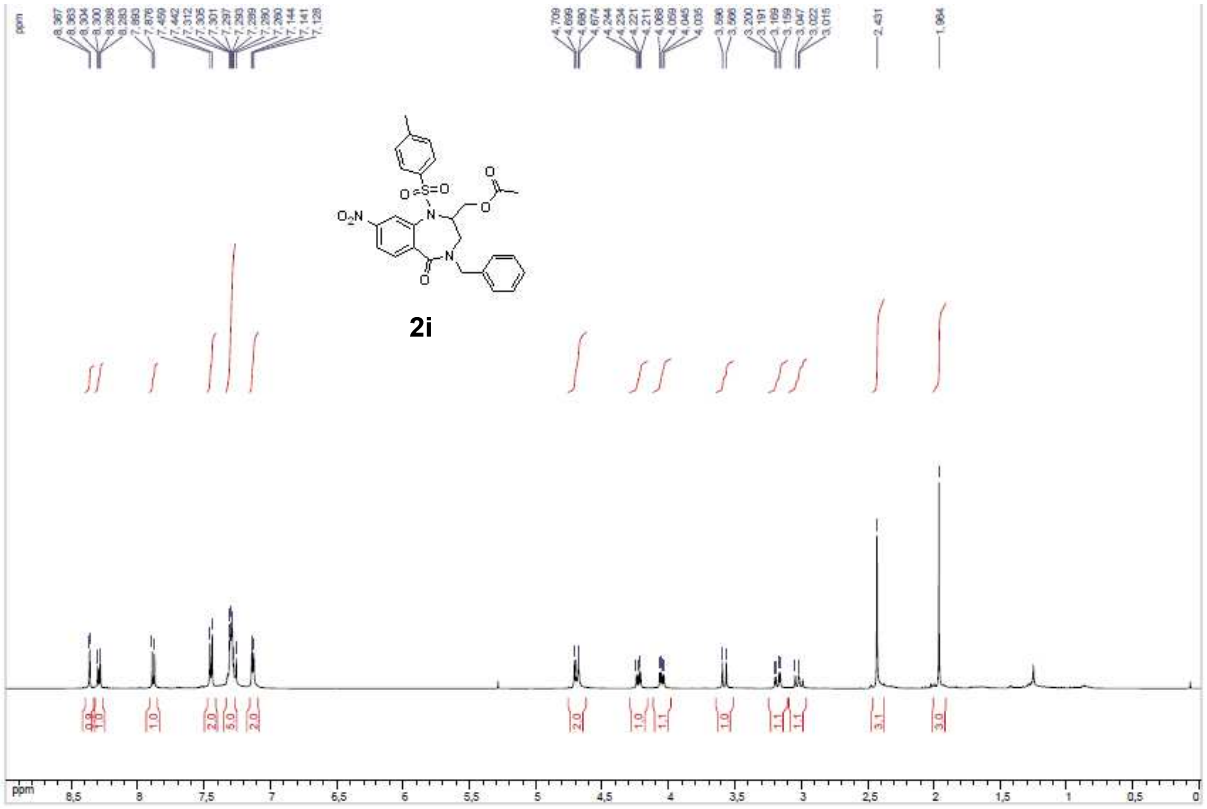
70
60
50
40
30
20
10
0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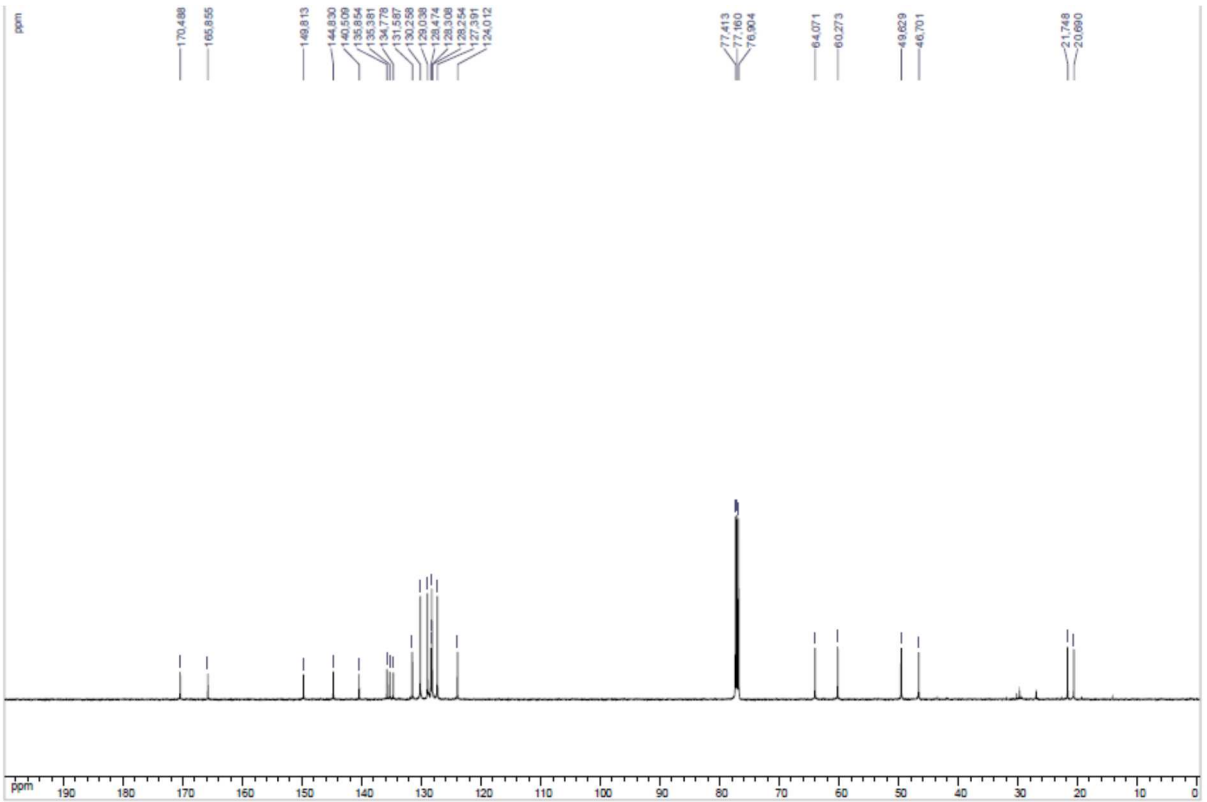
8.300
8.288
8.283
7.880
7.876
7.459
7.442
7.312
7.305
7.301
7.297
7.293
7.289
7.280
7.144
7.141
7.128
4.709
4.699
4.680
4.674
4.244
4.234
4.221
4.211
4.068
4.059
4.045
4.035
3.996
3.966
3.200
3.191
3.169
3.159
3.047
3.022
3.015
2.431
1.964
O2N
2i
ppm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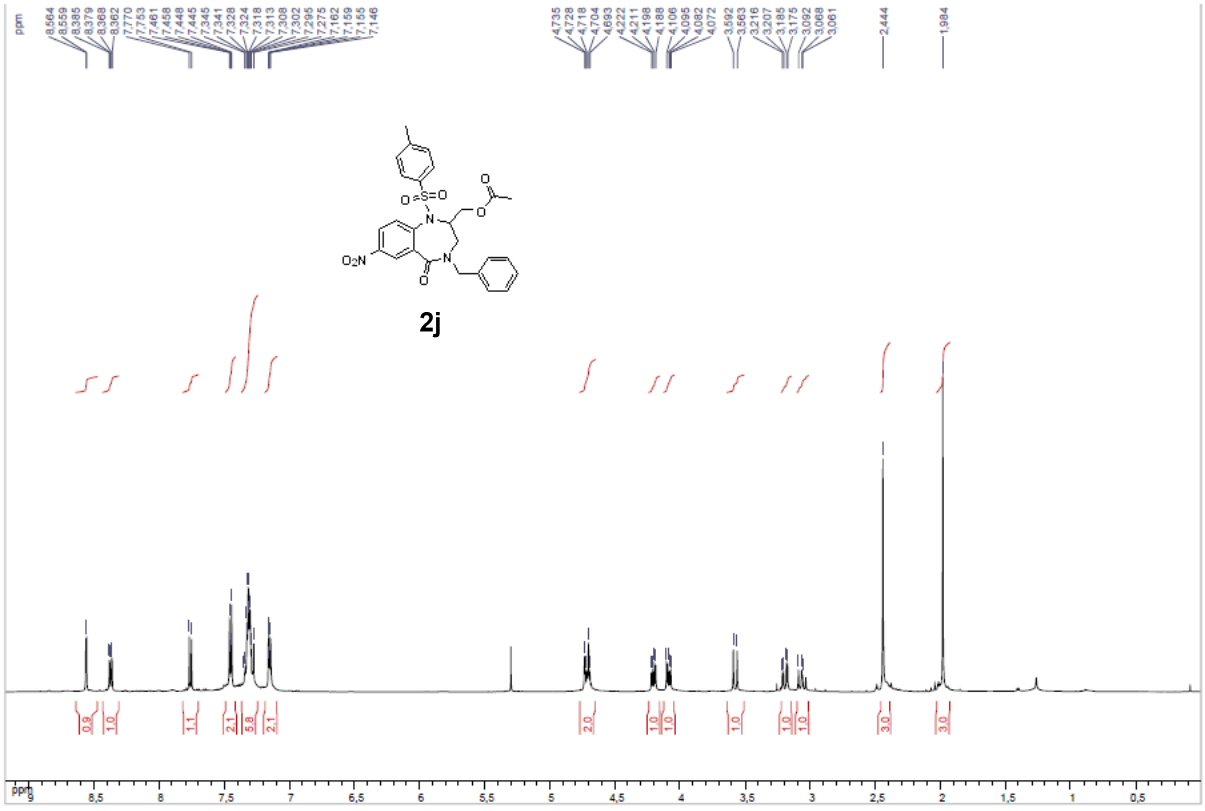
144.830
140.509
135.854
135.381
134.778
131.567
130.238
129.939
128.474
128.308
128.254
127.391
124.012
77.413
77.160
76.904
64.071
60.273
49.629
46.701
21.748
20.690
ppm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8.379
8.368
8.362
7.770
7.753
7.461
7.458
7.448
7.445
7.345
7.341
7.328
7.324
7.318
7.313
7.308
7.302
7.295
7.275
7.162
7.159
7.155
7.146
4.735
4.728
4.718
4.704
4.693
4.222
4.211
4.198
4.188
4.106
4.095
4.082
4.072
3.592
3.563
3.216
3.207
3.185
3.175
3.092
3.068
3.061
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2.1
5.8
2.1
2.0
1.0
1.0
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1.0
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4,5
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3,5
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1,5
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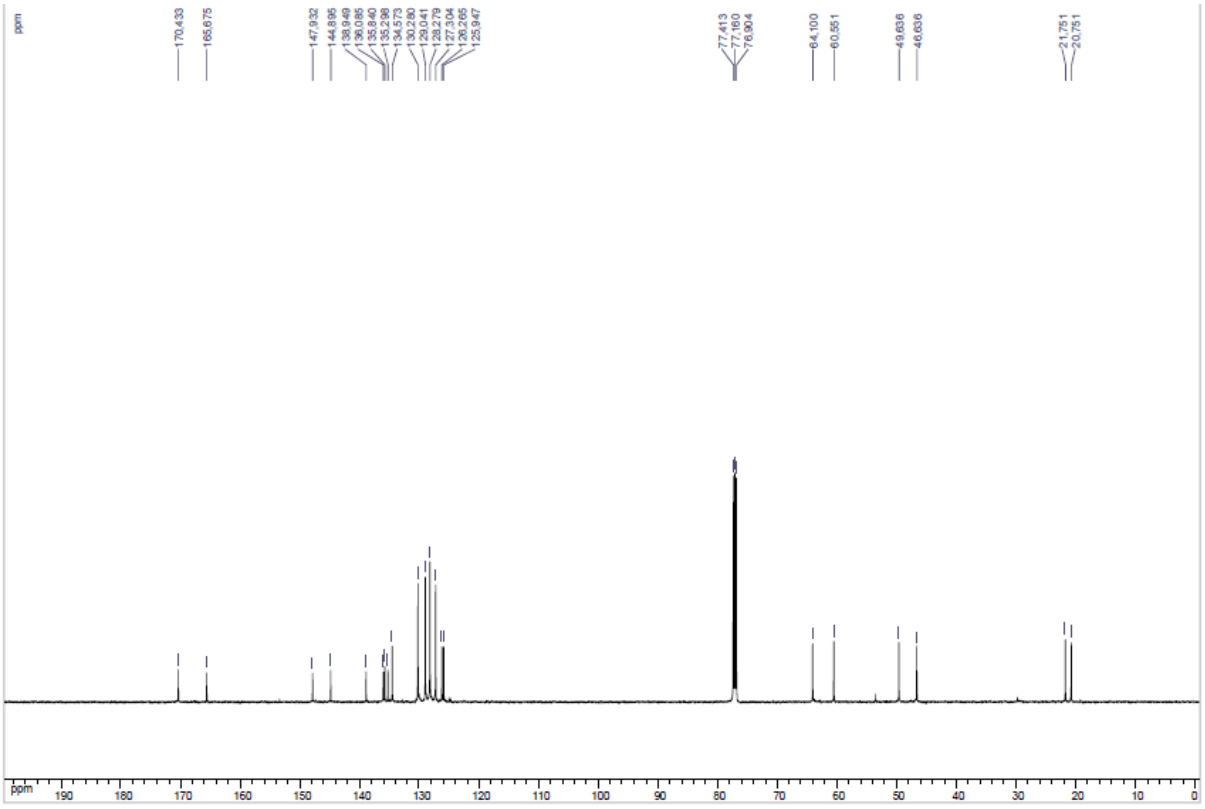
0,5

O2N

2j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144.895
138.949
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135.840
135.298
134.573
130.280
129.041
128.779
127.304
126.265
125.947
77.413
77.160
76.904
64.100
60.551
49.636
46.636
21.751
20.751
ppm
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150
140
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120
110
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90
80
70
60
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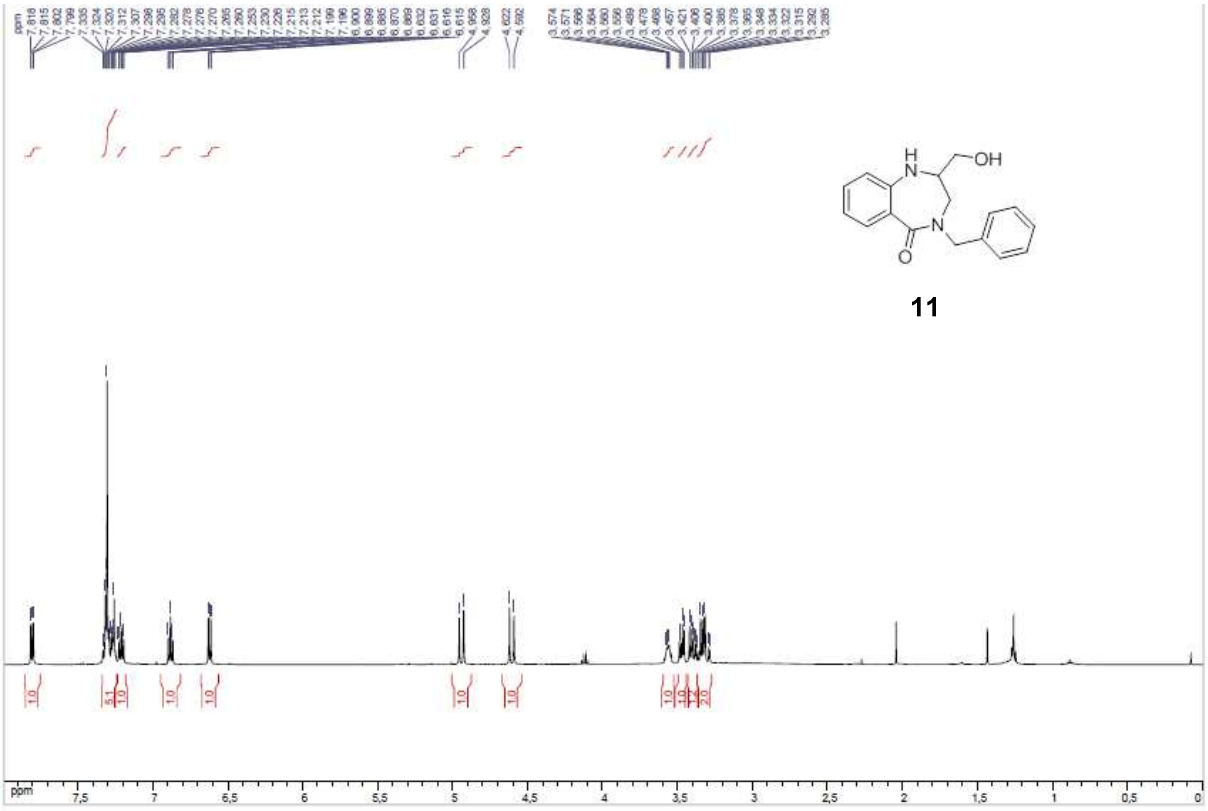
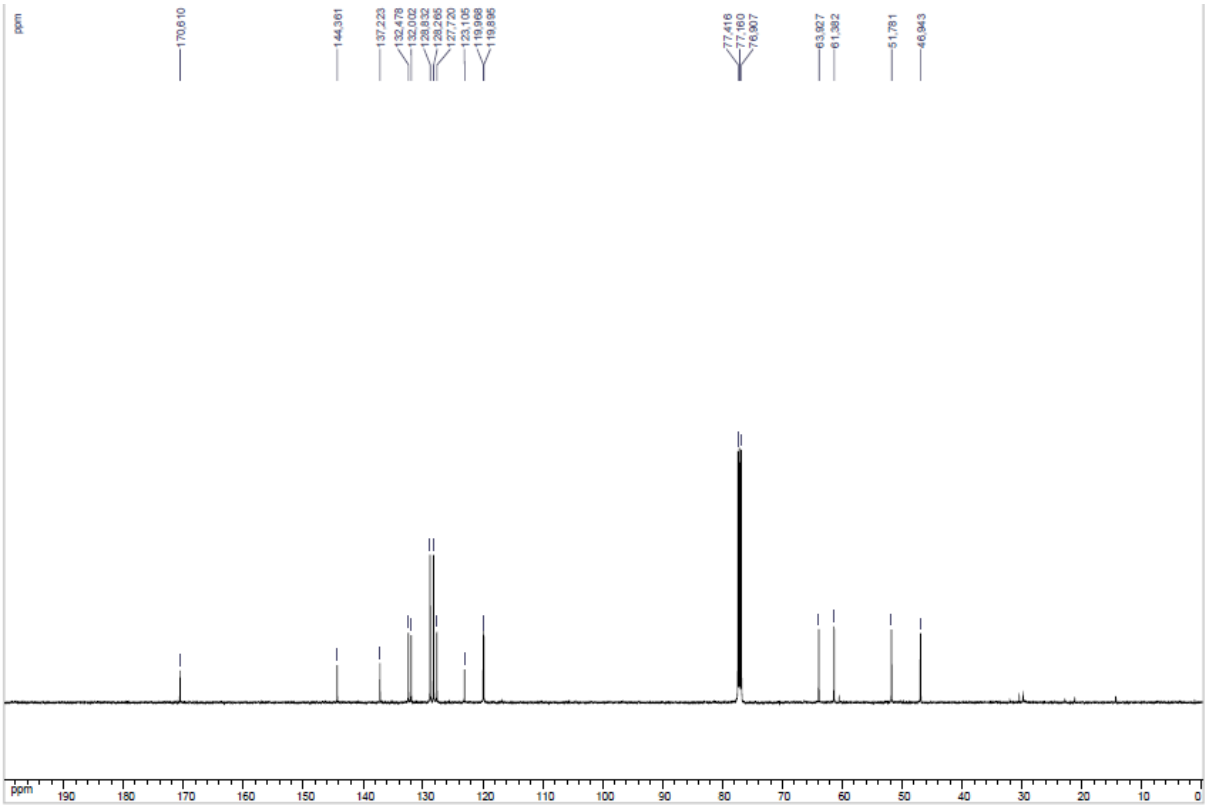
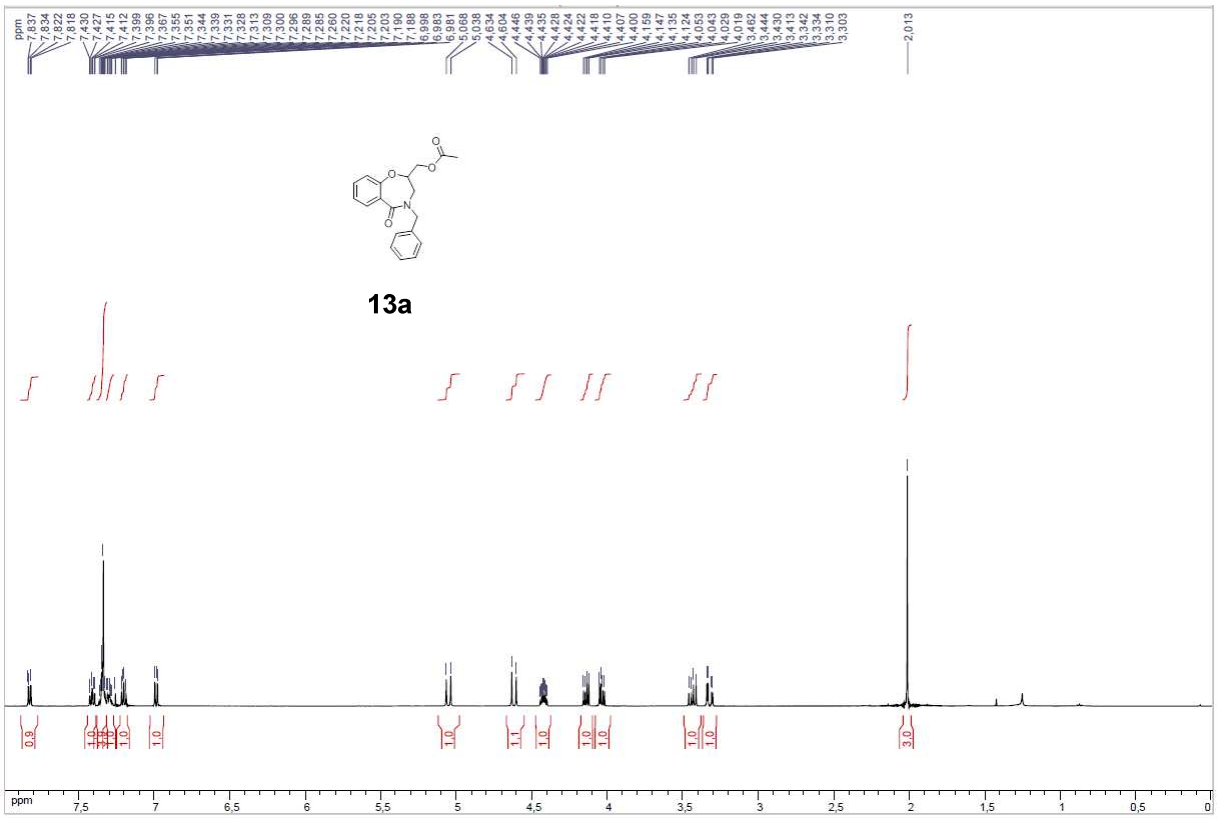
30
20
10
0

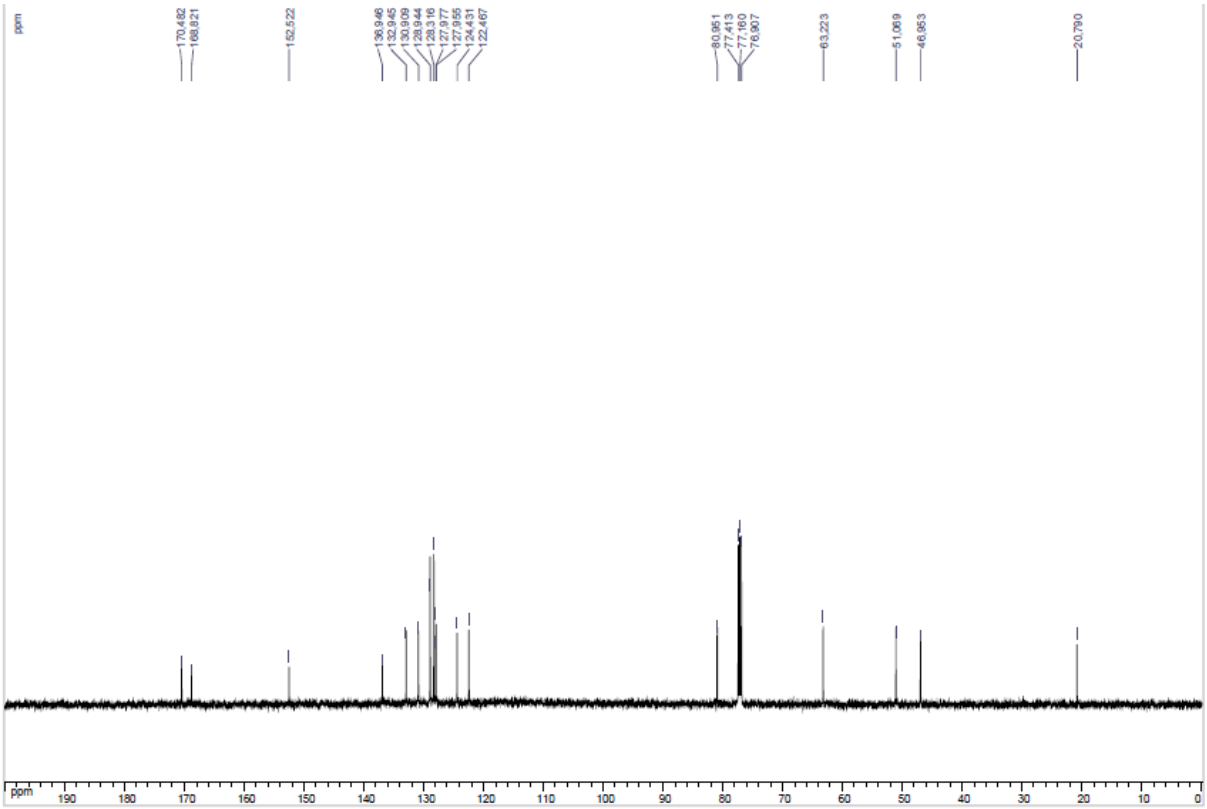


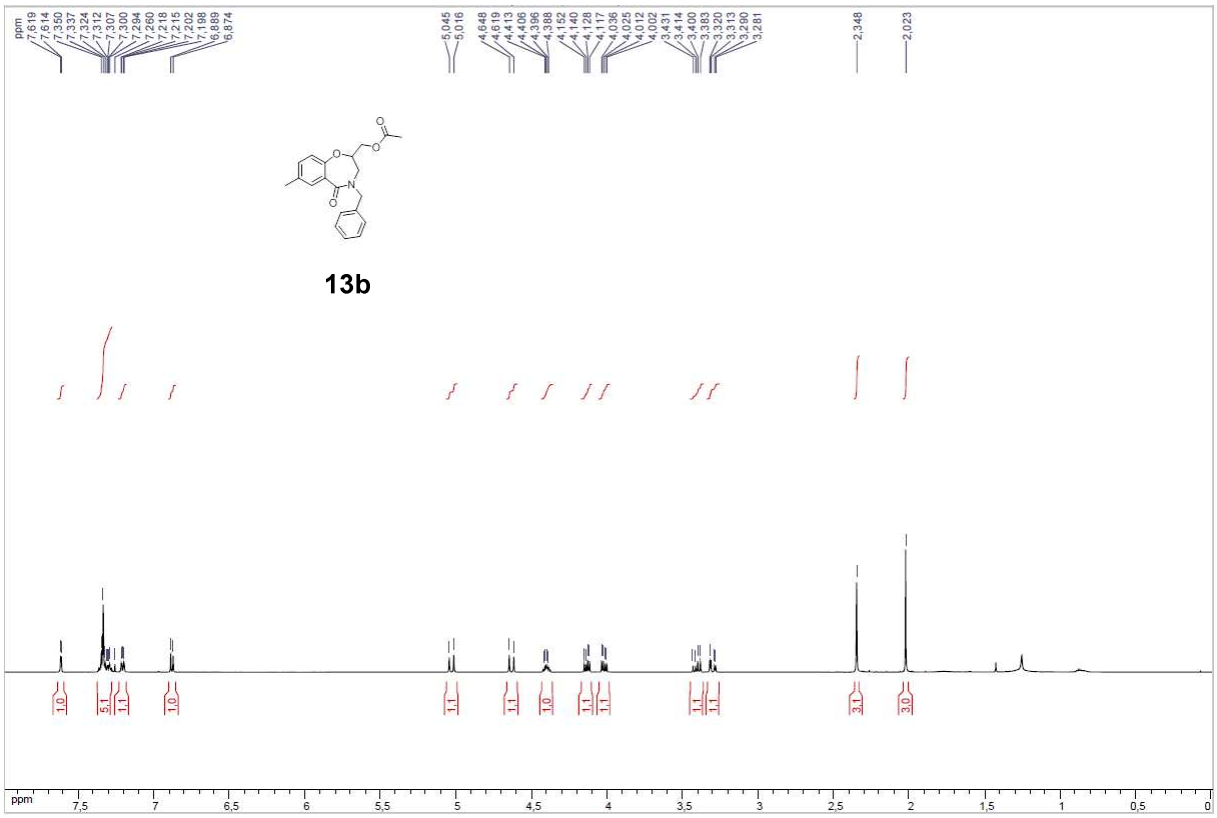
11





13a

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7.324
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7.294
7.260
7.218
7.215
7.202
7.189
6.889
6.874
5.045
5.016
4.648
4.619
4.613
4.406
4.396
4.388
4.152
4.140
4.128
4.117
4.036
4.025
4.012
4.002
3.431
3.414
3.400
3.383
3.320
3.313
3.290
3.281
2.348
2.023
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1.1
1.1
1.1
1.1
3.1
3.0
ppm
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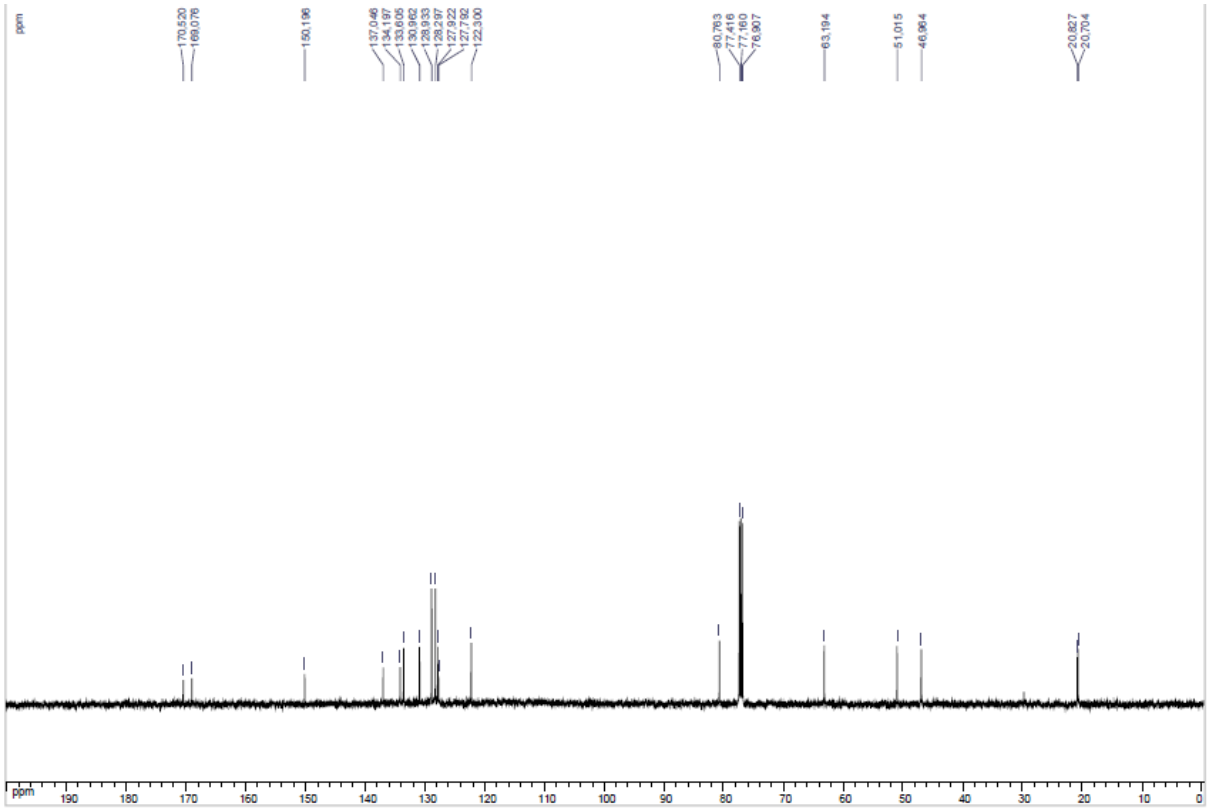
13b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130.962
128.933
128.297
127.922
127.792
122.300
80.783
77.416
77.160
76.907
63.194
51.015
46.964
20.827
20.704
ppm
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150
140
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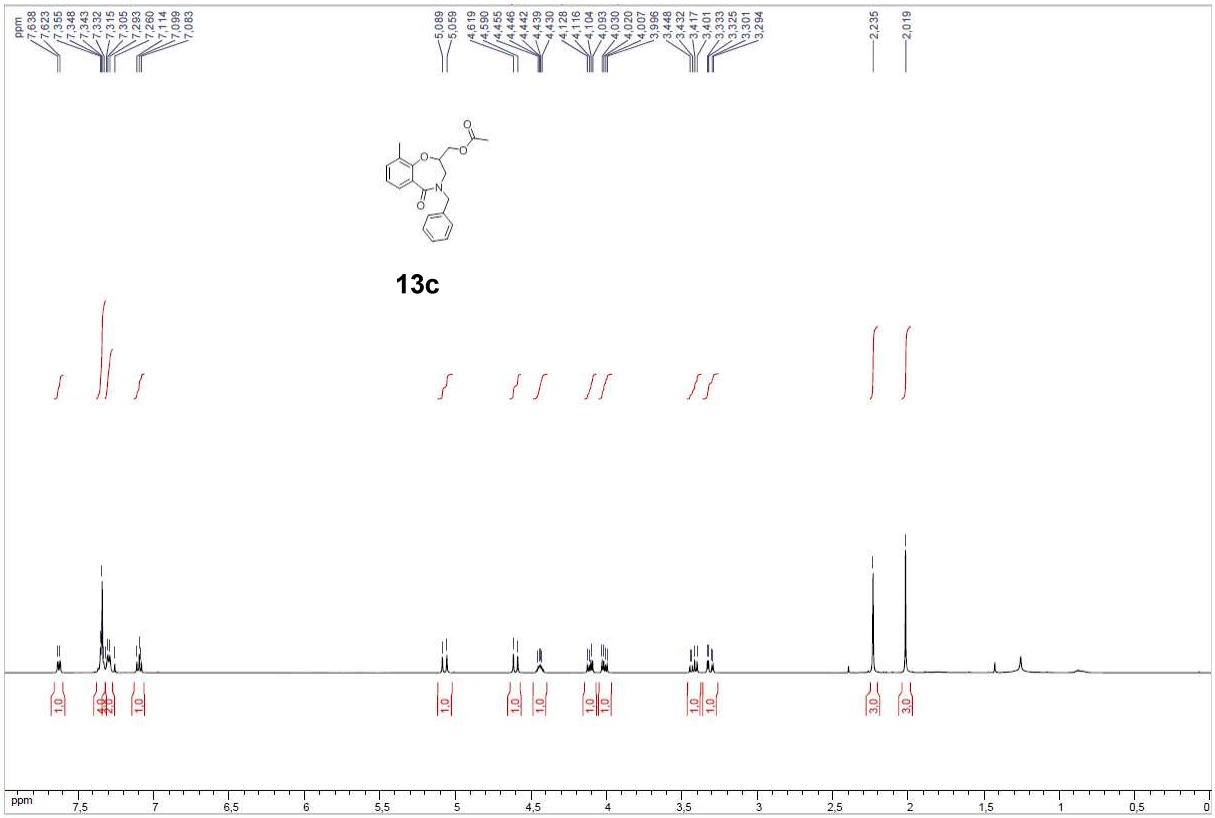
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7.293
7.260
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7.099
7.083
5.089
5.059
4.619
4.590
4.455
4.446
4.422
4.439
4.430
4.128
4.116
4.104
4.093
4.030
4.020
4.007
3.996
3.448
3.432
3.417
3.401
3.333
3.325
3.301
3.294
2.235
2.019
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2.0
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1.0
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1.0
1.0
1.0
1.0
1.0
3.0
3.0
ppm
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2
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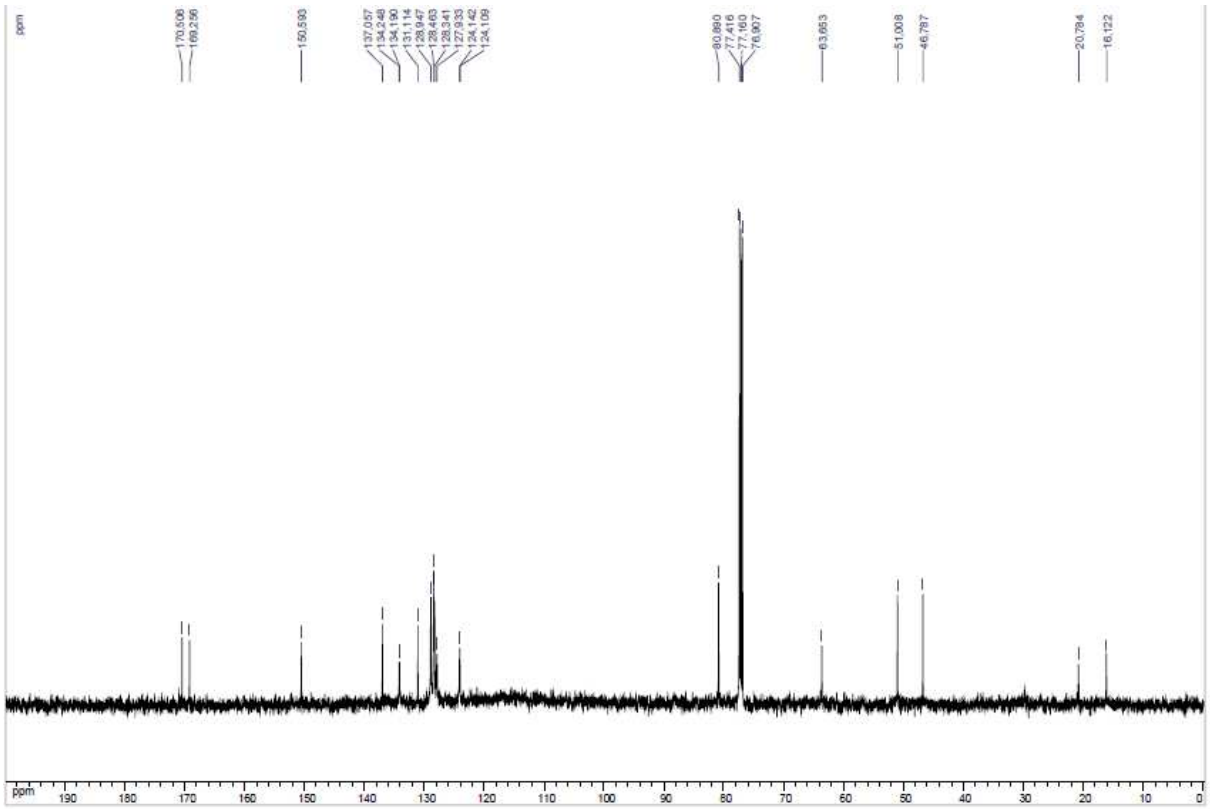
13c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128.463
128.341
127.933
124.142
124.109
80.880
77.416
77.160
76.907
63.653
51.008
46.787
20.784
16.122
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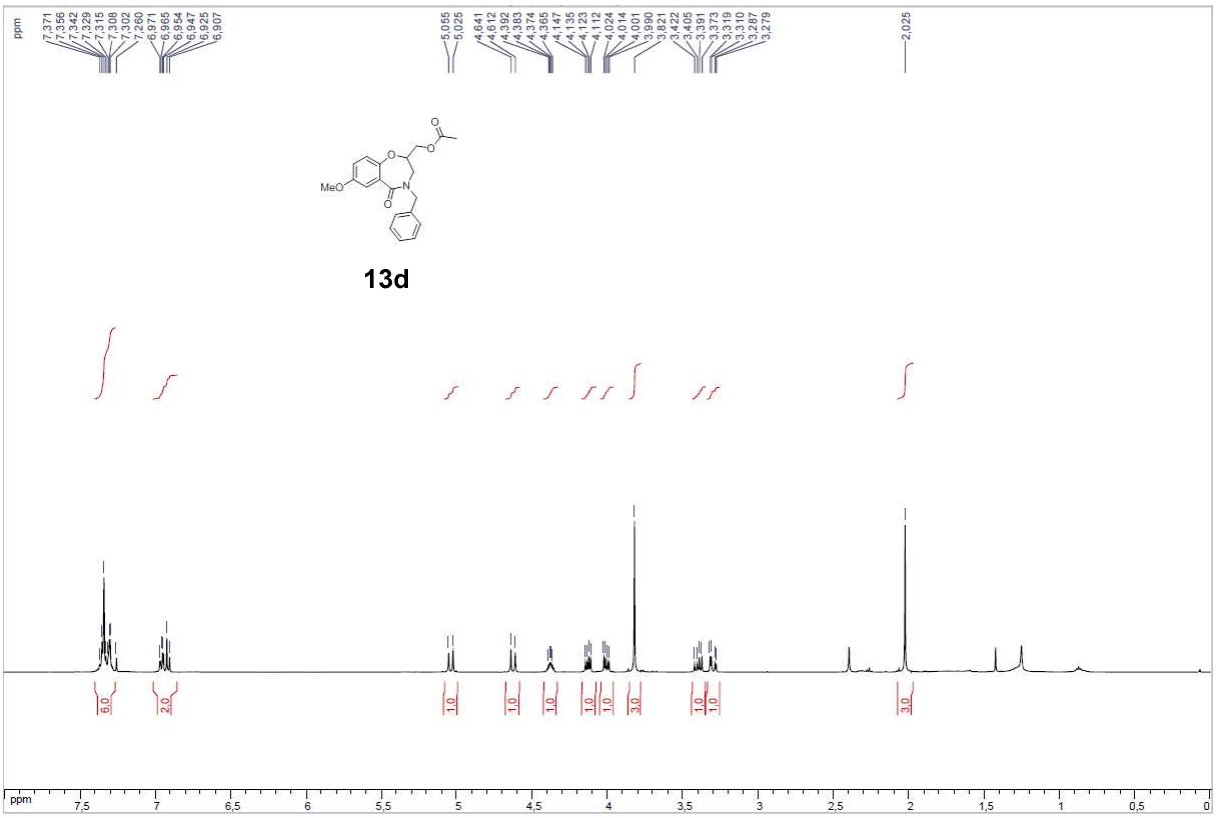
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6.965
6.954
6.947
6.925
6.907
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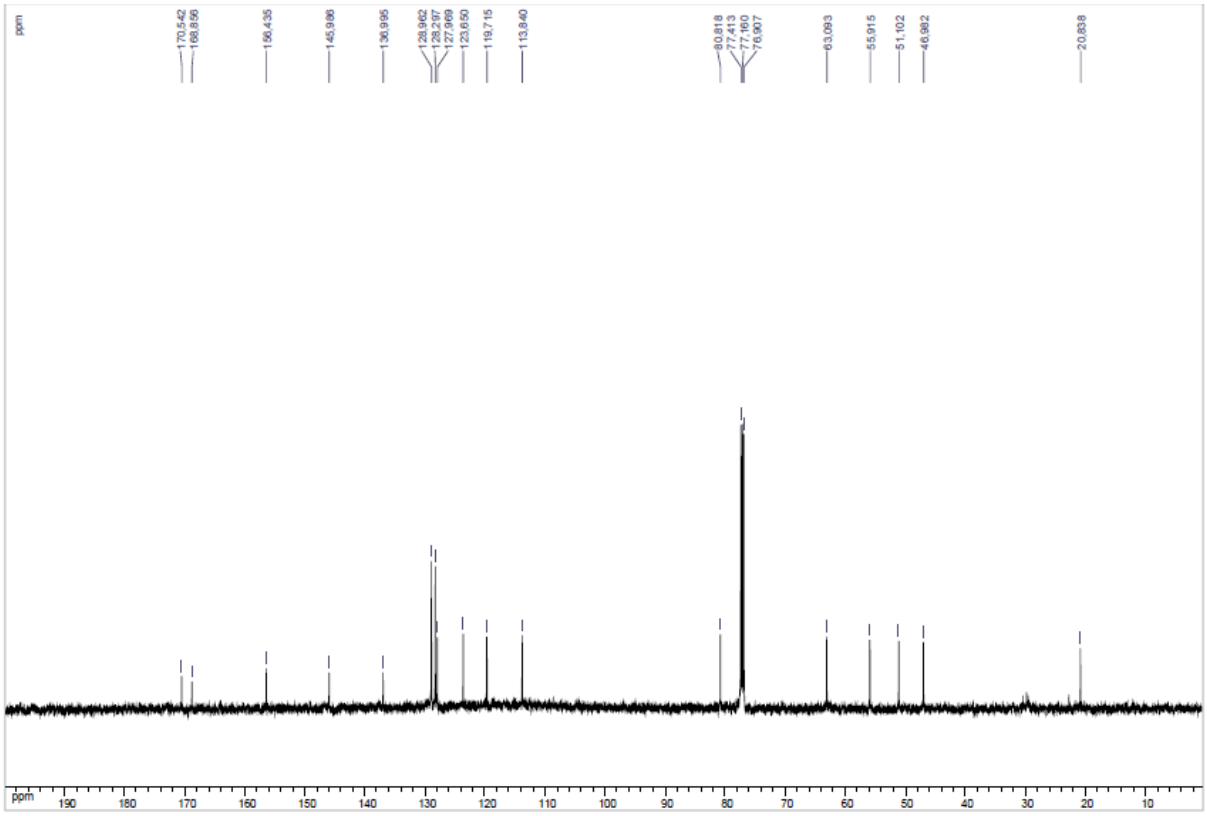
13d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119,715
113,840
80,818
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77,160
76,907
63,093
55,915
51,102
46,982
20,838
ppm
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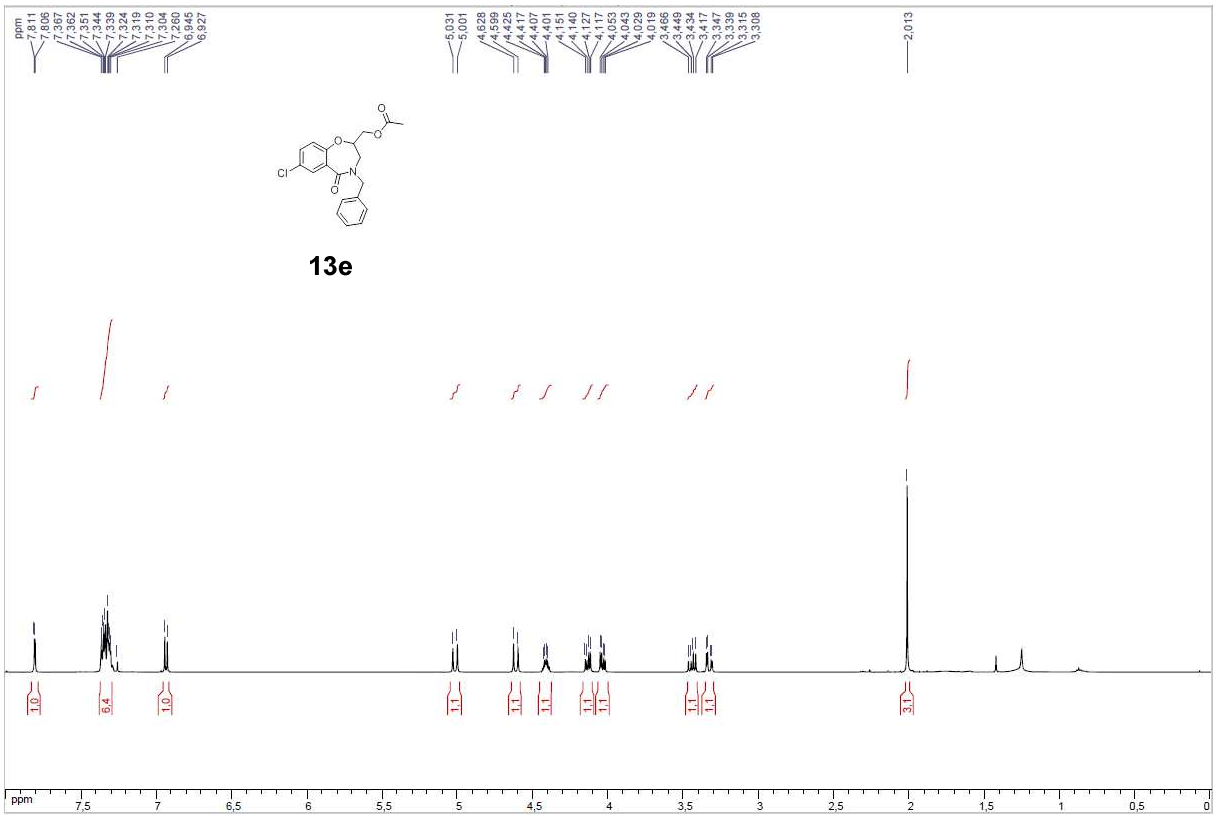
20
10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7.319
7.310
7.304
7.260
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6.927
5.031
5.001
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4.599
4.425
4.417
4.407
4.401
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4.053
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4.029
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3.434
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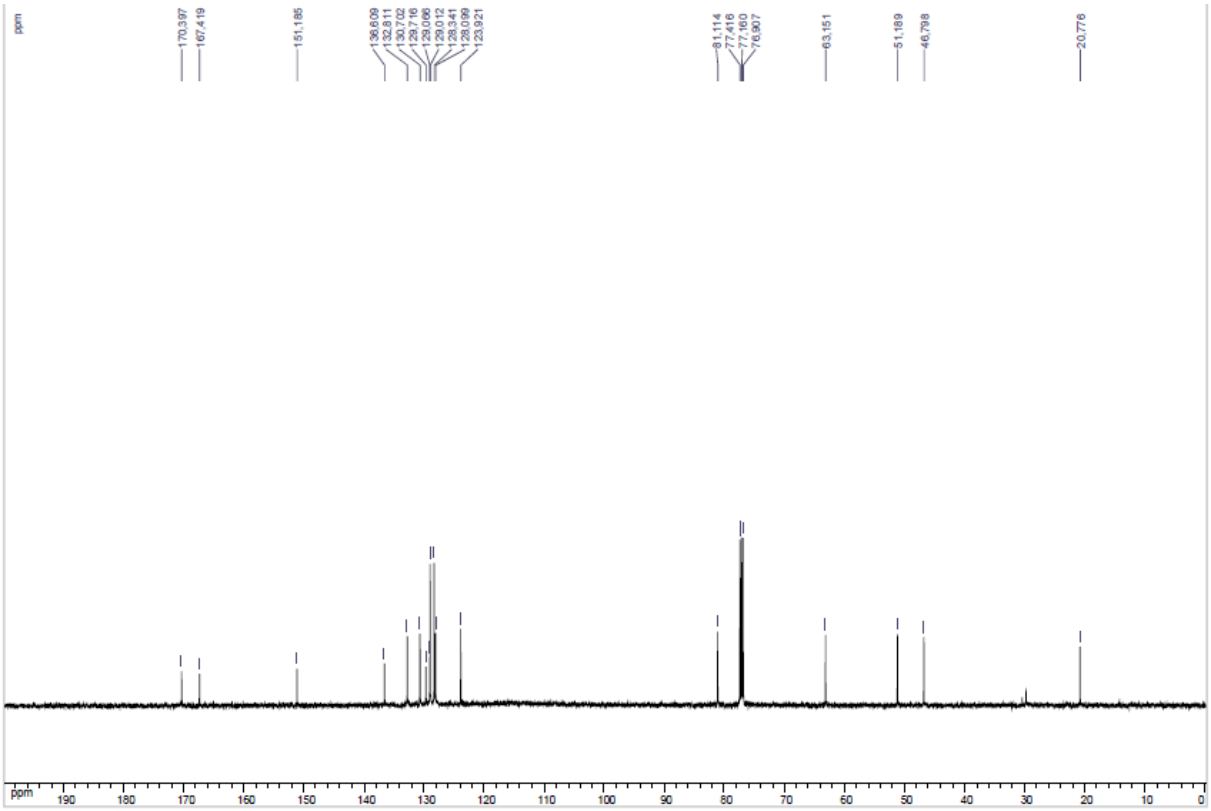
13e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128.341
128.099
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46.798
20.776
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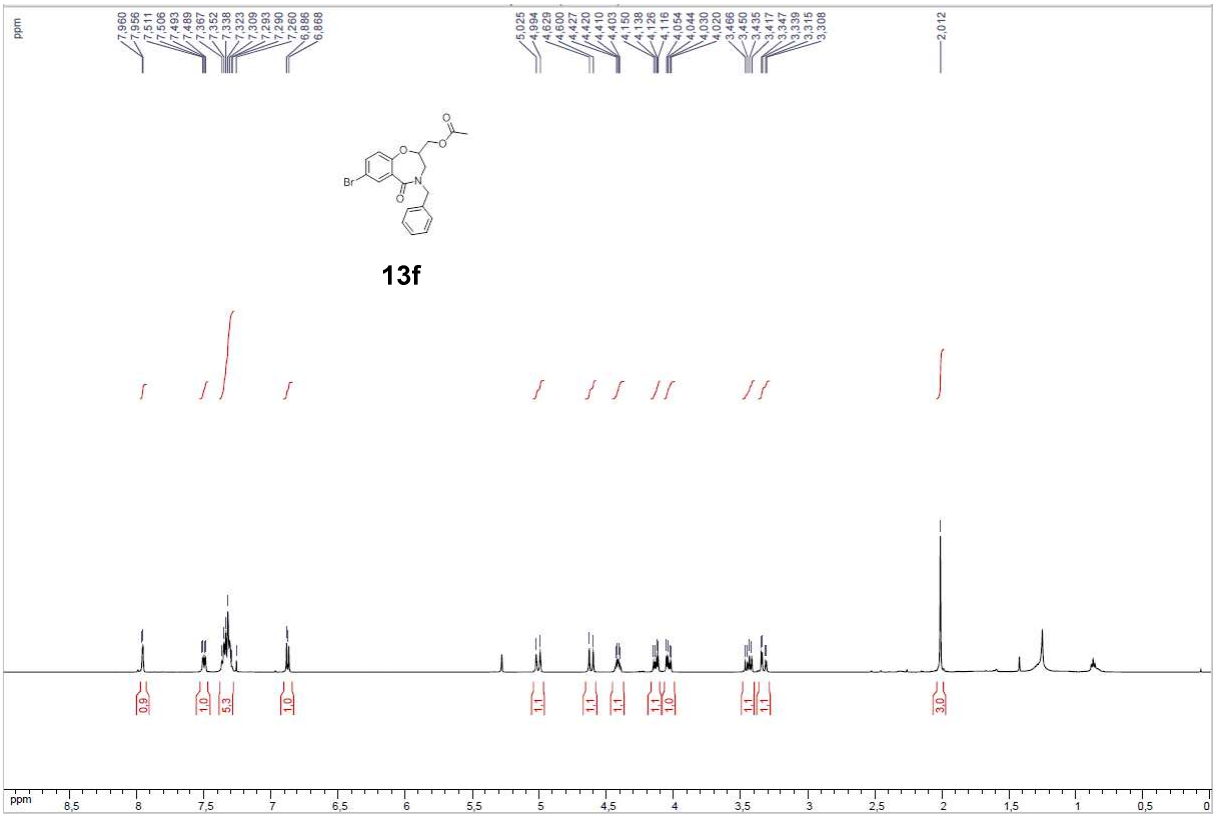
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7.290
7.260
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6.868
5.025
4.994
4.629
4.600
4.427
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4.150
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4.030
4.020
3.466
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3.308
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Br
O
N
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3.0
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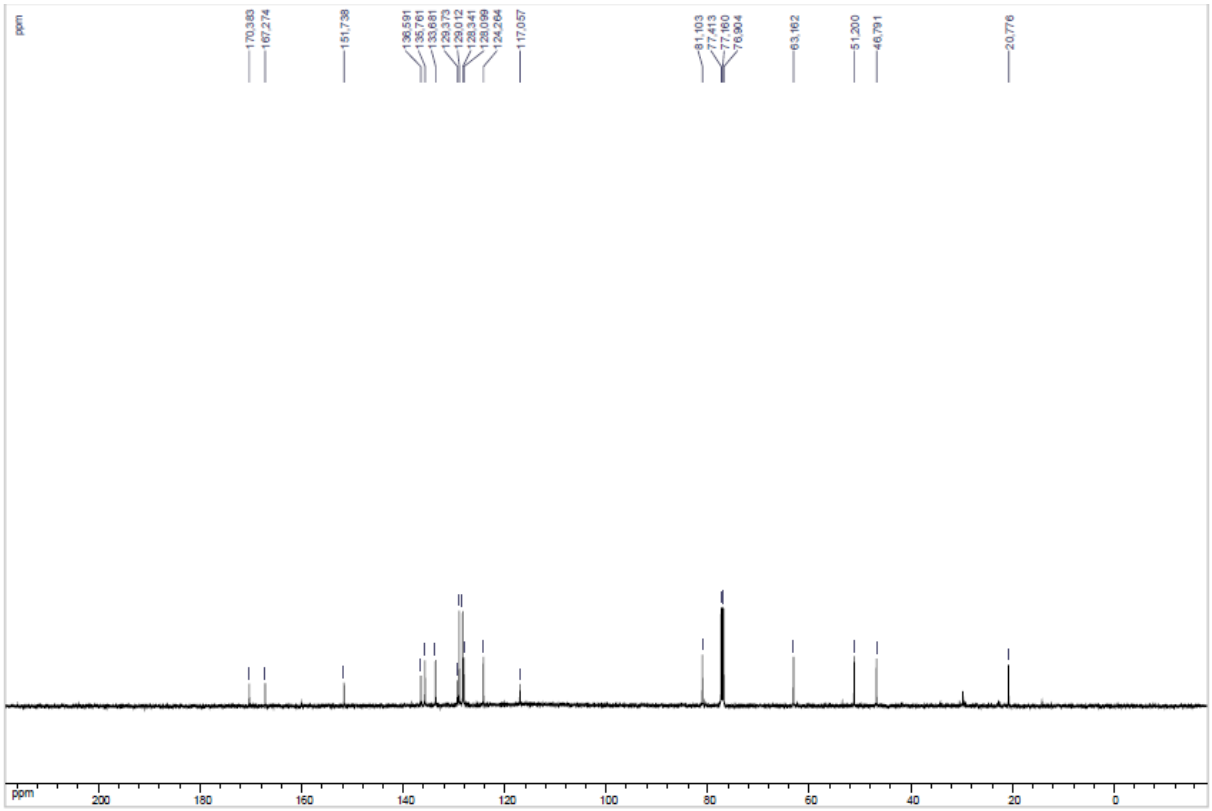
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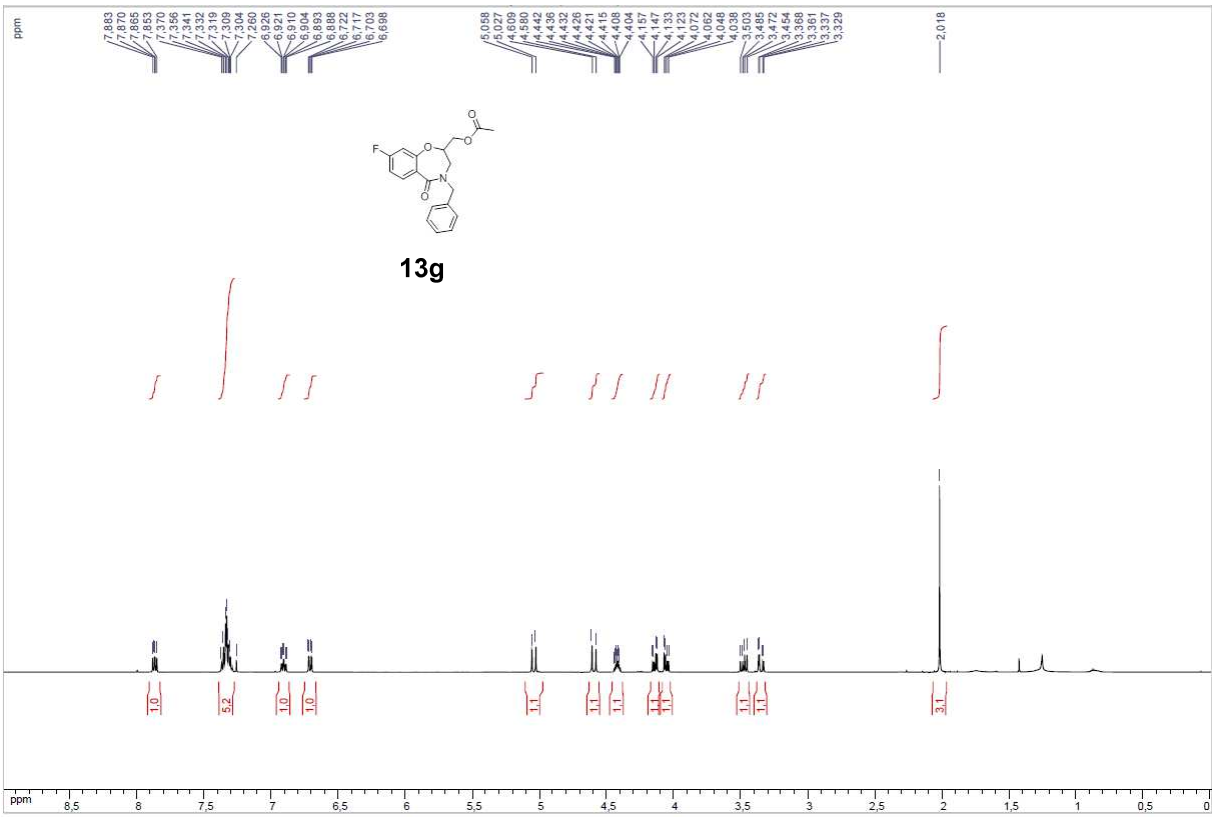
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F
O
O
O
N
O
13g
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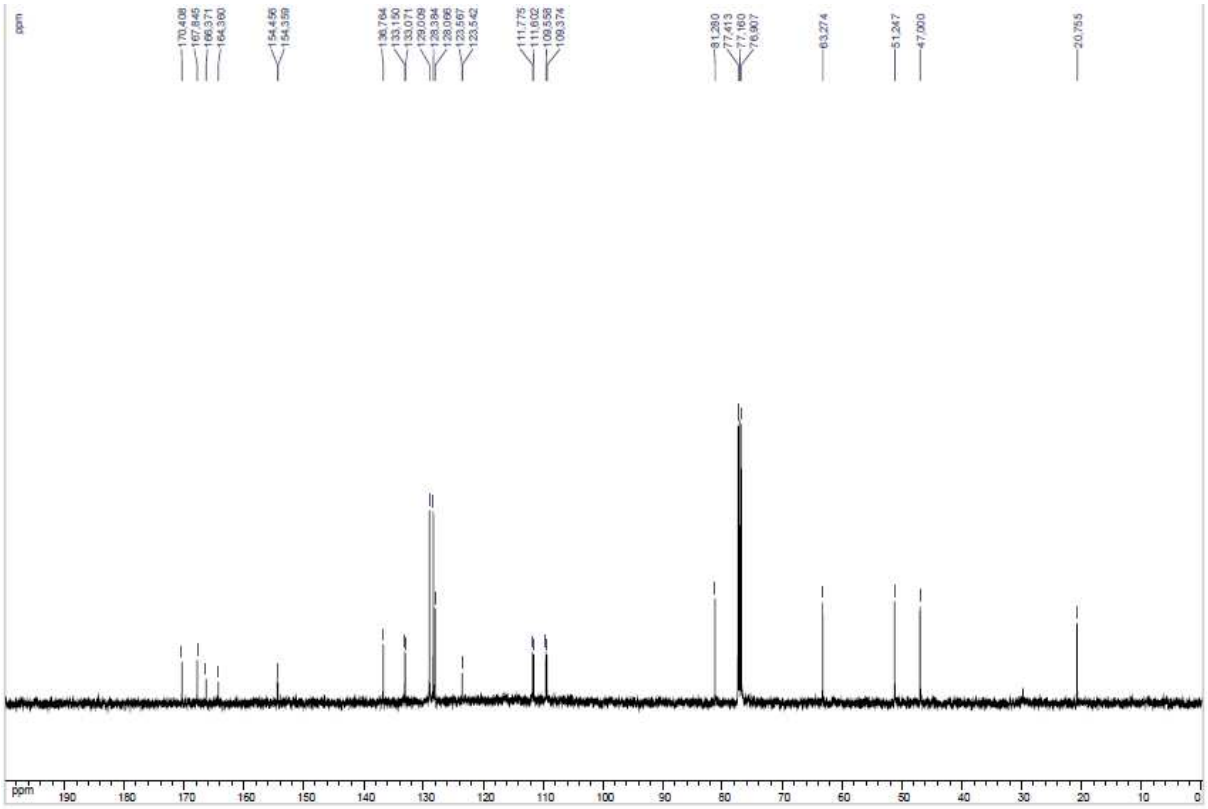
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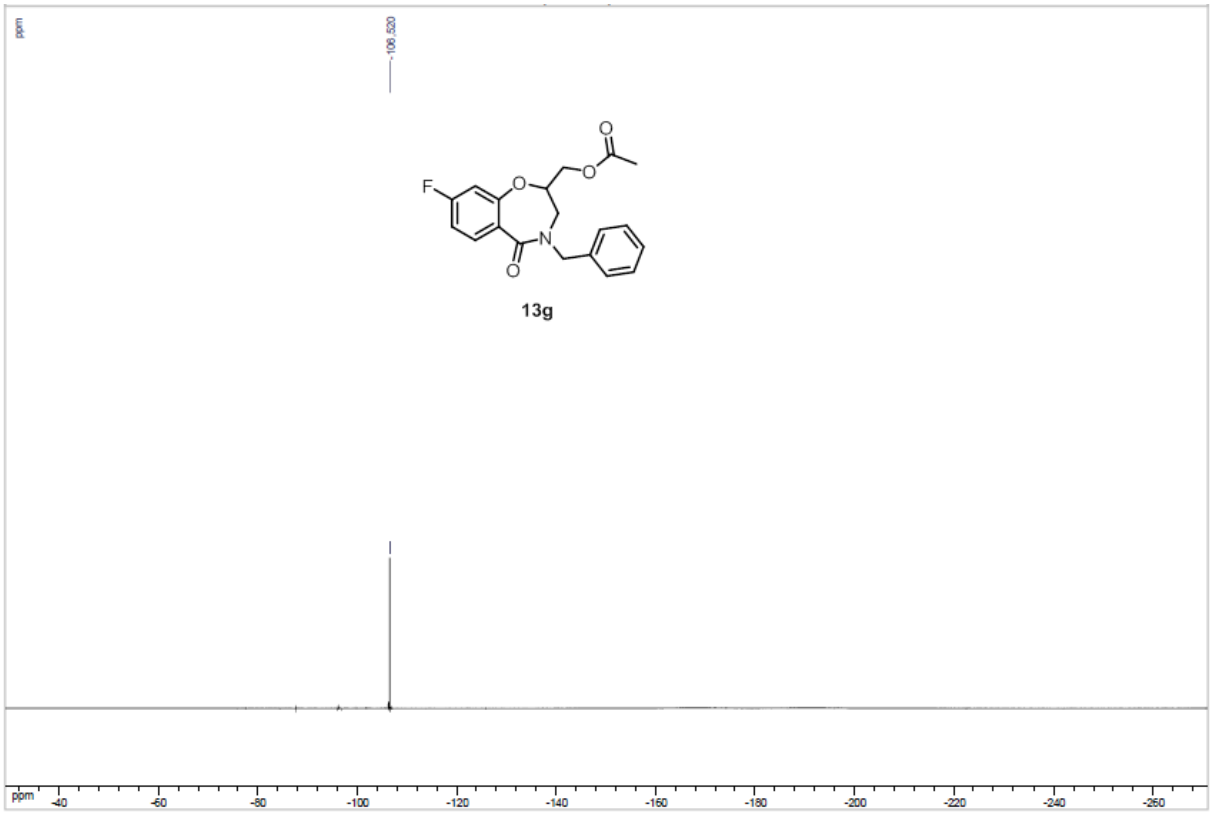
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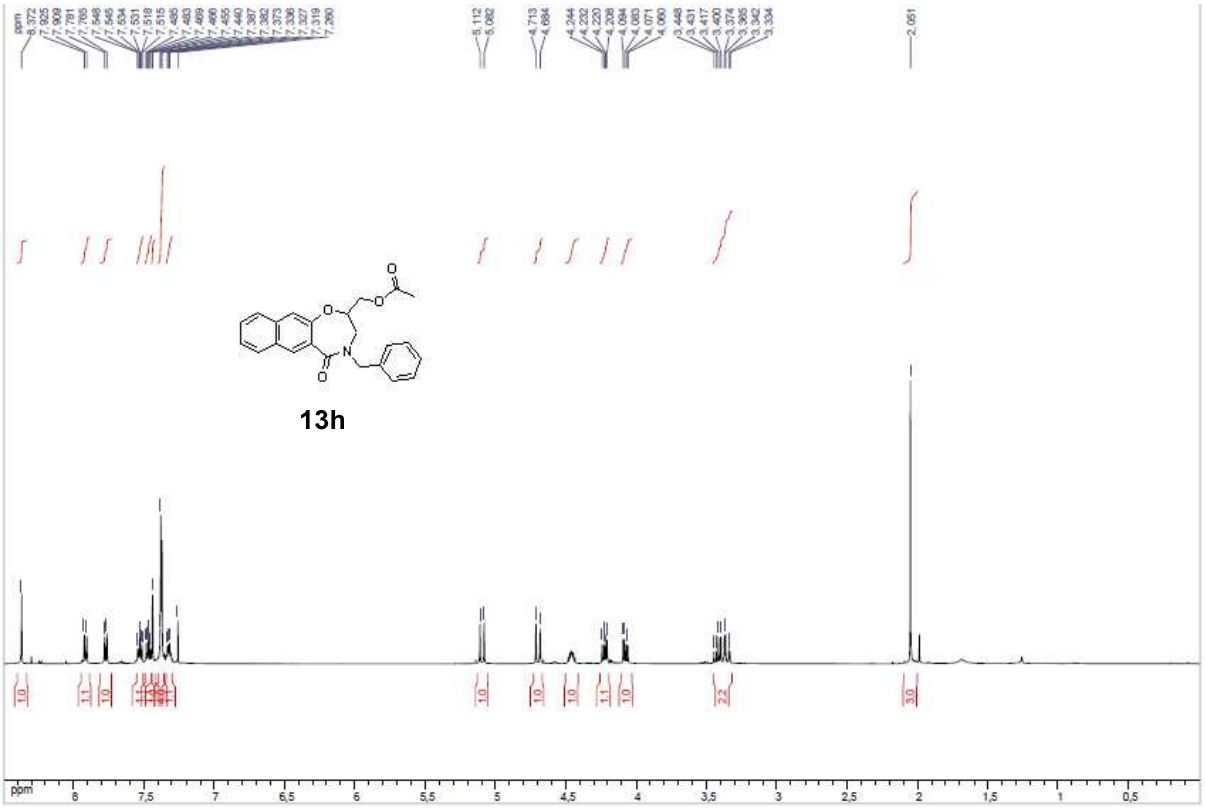
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