Supporting Information for:

Expedient Synthesis of N-Acyl Anthranilamides and β-Enamine Amides by the Rh(III)-Catalyzed Amidation of Aryl and Vinyl C–H Bonds with Isocyanates

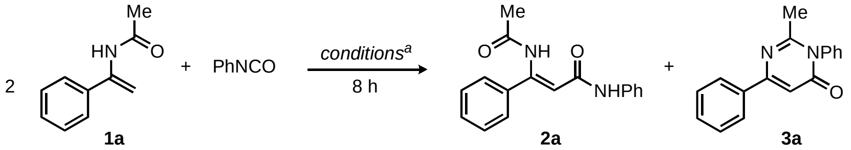
Kevin D. Hesp, Robert G. Bergman,* and Jonathan A. Ellman*

Department of Chemistry, Yale University, New Haven, Connecticut, United States 06520
Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California, United States 94720

I. General Information

Unless noted, all catalytic reactions were set up inside an inert atmosphere (N_2) glovebox utilizing glassware that was oven-dried (150 ^oC) and evacuated while hot prior to use, whereas the work-up and isolation of the products from the catalytic reactions were conducted on the bench-top using standard techniques. Dichloromethane and tetrahydrofuran were passed through a column of activated alumina under nitrogen and were stored in a glovebox over activated 4 Å molecular sieves prior to use. *tert*-Butanol was deoxygenated by sparging with nitrogen gas followed by storage over activated 4 Å molecular sieves for 48 h prior to use. Chloroform-d_1 (Cambridge Isotopes) was used as received. Unless otherwise noted, all reagents and materials were obtained from commercial suppliers and used without further purification. $[Cp^*Rh(MeCN)_3](SbF_6)_2$,[S1] acetanilides,[S2] and *N*-acyl enamides[S3] were synthesized according to published procedures. Chromatography was performed on Merck 60 230-240 mesh silica gel. ^1H and $^{13}C\{^1H\}$ NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1 and 125.8 MHz (respectively) with chemical shifts reported in parts per million relative to $CHCl_3$ (^1H NMR; 7.26 ppm, $^{13}C\{^1H\}$ NMR; 77.23 ppm). IR spectra were recorded on a Nicolet 6700 FTIR spectrometer and only partial data are provided. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectra (HRMS) were obtained by the Keck Center of Yale University using a Bruker 9.4 T APEXQe FT-ICR mass spectrometer.

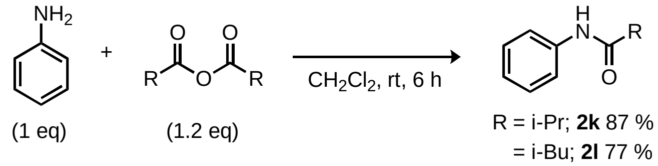
II. Reaction Optimization and Control Reactions



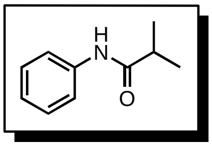
entry	catalyst	solvent	**1a**:PhNCO	[PhNCO] (mM)	temp (°C)	yield[b]	**2a**:**3a**[b]
1	$[Cp^*RhCl_2]_2$/2 $AgSbF_6$	THF	2:1	0.1	75	93	1:8
2	$[Cp^*RhCl_2]_2$/2 $AgB(C_6F_5)_4$	THF	2:1	0.1	75	94	1:3
3	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	THF	2:1	0.1	75	94	1:3
4	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	CH_2Cl_2	2:1	0.1	75	85	3:1
5	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	t-BuOH	2:1	0.1	75	75	1:8
6	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	toluene	2:1	0.1	75	30	1:1
7	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	THF	1:1	0.1	75	75	1:2
8	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	THF	1:2	0.1	75	78	1:2
9	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	THF	2:1	0.3	75	93	1:5
10	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	THF	2:1	0.03	75	89	1:2
11	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	THF	2:1	0.1	55	94	2:1
12	***$[Cp^*Rh(MeCN)_3](SbF_6)_2$***	***THF***	***2:1***	***0.1***	***rt***	***96***	***15:1***
13	***$[Cp^*Rh(MeCN)_3](SbF_6)_2$***	***THF***	***2:1***	***0.1***	***105***	***99***	***1:>50***
14	$[Cp^*RhCl_2]_2$	THF	2:1	0.1	75	0	-
15	$AgSbF_6$	THF	2:1	0.1	75	0	-
16	acid[c]	THF	2:1	0.1	75	0	-
17	base[d]	THF	2:1	0.1	75	0	-
18	-	THF	2:1	0.1	75	0	-

[a] 0.05 mmol substrate scale, 5 mol % [Rh], 8 h. [b] Determined by ^{1}H NMR relative to 2,6-dimethoxytoluene as an internal standard. [c] 20 mol % of acetic acid or trifluoroacetic acid employed. [d] 20 mol % of NEt_3, K_3PO_4, or KO(t-Bu) employed.

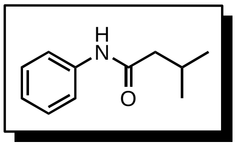
III. Substrate Preparation



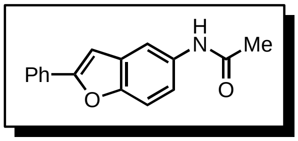
General procedure I. Preparation of anilides.[S2] To a round-bottom flask was added aniline (1 equiv) and a stir bar, and the flask was then fitted with a rubber septum. The flask was purged with nitrogen followed by the addition of anhydrous CH_2Cl_2 (0.4 M aniline). The corresponding anhydride (1.2 equiv) was added, and the reaction mixture was stirred at room temperature for 6 h (or until complete by TLC). Upon completion, the reaction mixture was diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ (aq), followed by brine, and the organic layers were dried over $MgSO_4$ followed by removal of the solvent under reduced pressure. Products were used without subsequent purification (reaction yields are unoptimized).



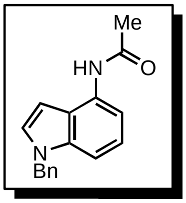
Isobutyranilide: General procedure I was employed using the following components: aniline (0.910 mL, 10.0 mmol) and isobutyric anhydride (2.00 mL, 12.0 mmol) in 25.0 mL of CH_2Cl_2. After work-up, the anilide was isolated in an 87% yield (1.42 g, 8.70 mmol) as a beige solid that was used without further purification. The analytical data for this compound are consistent with previously reported data.[S4]



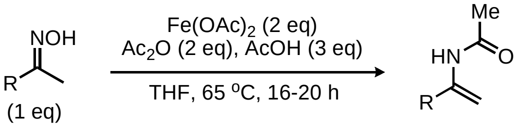
Isovaleranilide: General procedure I was employed using the following components: aniline (0.460 mL, 5.00 mmol) and isovaleric anhydride (1.20 mL, 6.00 mmol) in 13.0 mL of CH_2Cl_2. Following the work-up, the anilide was isolated in an 76% yield (680 mg, 3.80 mmol) as a white solid that was used without further purification (mp = 107-109 °C). IR (film): 3244, 2965, 1653, 1597, 1542, 1500 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.52 (d, J = 7.9 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.17 (s, 1H), 7.10 (t, J = 7.2 Hz, 1H), 2.30-2.10 (m, 3H), 1.02 (d, J = 4.6 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.0, 138.1, 129.2, 124.4, 120.0, 47.4, 26.5, 22.7. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{11}H_{15}NO$: 178.12264. Found: 178.12260.



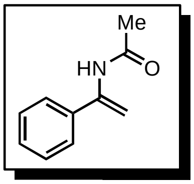
5-*N*-Acetylamino-2-phenylbenzofuran: General procedure I was employed using the following components: corresponding aniline (0.628 g, 3.00 mmol) and acetic anhydride (0.680 mL, 7.20 mmol) in 20.0 mL of CH_2Cl_2. Following the work-up, the anilide was isolated in an 47% yield (0.353 g, 1.40 mmol) as an off-white solid (hexanes:EtOAc (1:1), R_f = 0.26) that was used without further purification (mp = 217-219 °C). IR (film): 3255, 3072, 2918, 1651, 1601, 1566, 1471 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.97 (s, 1H), 8.01 (d, J = 1.9 Hz, 1H), 7.95-7.84 (m, 2H), 7.58-7.46 (m, 3H), 7.46-7.35 (m, 3H), 3.33 (s, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6): δ 168.0, 155.7, 150.5, 135.1, 129.7, 129.0, 128.8, 128.7, 124.6, 116.9, 111.0, 110.9, 102.3, 23.9. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{16}H_{13}NO_2$: 252.1019. Found: 252.1016.



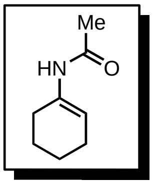
4-*N*-Acetylamino-1-benzylindole: The indicated compound was prepared using the Pd-catalyzed C-N cross-coupling method described by Buchwald.[S5] A 4 dram scintillation vial containing a stir bar was charged with Pd_2dba_3 (0.0382 g, 0.0420 mmol), Xantphos (0.0734 g, 0.125 mmol), Cs_2CO_3 (0.762 g, 2.34 mmol), acetamide (0.118 g, 2.00 mmol), and 4-bromo-1-benzylindole (0.477 g, 1.67 mmol). Following addition of 4.00 mL of 1,4-dioxane, the vial was sealed and was heated in a temperature-controlled aluminum-heating block set at 100 ^{o}C for 24 h. The reaction mixture was left to cool to room temperature, diluted with CH_2Cl_2 (5 mL), filtered through a Celite plug, and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel using hexanes:EtOAc (1:1; $R_f = 0.27$) in a 57% isolated yield (0.250 mg, 0.95 mmol) as a white solid (mp: 155-157 ^{o}C). IR (film): 3245, 3043, 1647, 1619, 1578, 1539, 1512 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.38-7.20 (m, 3H), 7.19-7.05 (m, 5H), 6.51 (d, *J* = 3.0 Hz, 1H), 5.30 (s, 2H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.6, 137.4, 137.3, 130.3, 129.0, 128.0, 127.9, 127.0, 122.6, 121.0, 111.9, 106.7, 97.9, 50.4, 24.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{16}N_2O$: 265.1335. Found: 265.1333.



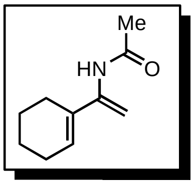
General procedure II. Preparation of *N*-acyl enamides.[S3a] To a round-bottom flask was added ketoxime (1 equiv; prepared by condensation of H_2NOH with the respective ketone), $Fe(OAc)_2$ (2 equiv), and a stir bar, and the flask was then fitted with a rubber septum. The flask was purged with nitrogen followed by the addition of anhydrous THF (0.2 M ketoxime), acetic anhydride (2 equiv), and acetic acid (3 equiv). The reaction mixture was stirred at 65 ^{o}C for 15-20 h. Upon completion, the reaction was quenched with sat. $NaHCO_3$ (aq), and the combined organic extracts were washed with brine and dried over $MgSO_4$ followed by removal of the solvent under reduced pressure. *N*-Acetyl enamides were purified by flash column chromatography (reaction yields are unoptimized).



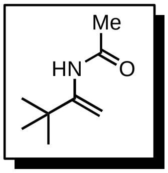
2a. General procedure II was employed using the following components: ketoxime (0.270 g, 2.00 mmol), acetic anhydride (0.380 mL, 4.00 mmol), acetic acid (0.340 mL, 6.00 mmol), and $Fe(OAc)_2$ (0.696 g, 4.00 mmol) in 10.0 mL of THF. Following the work-up, the enamide was isolated by flash column chromatography (hexanes:EtOAc = 2:1) in an 80% yield (0.258 g, 1.60 mmol) as a beige solid. The analytical data for this compound are consistent with previously reported data.[S3]



2b. General procedure II was employed using the following components: ketoxime (0.566 g, 5.00 mmol), acetic anhydride (0.950 mL, 10.0 mmol), acetic acid (0.860 mL, 15.0 mmol), and $Fe(OAc)_2$ (1.74 g, 10.0 mmol) in 25.0 mL of THF. Following the work-up, the enamide was isolated by flash column chromatography (hexanes:EtOAc = 2:1) in a 34% yield (0.240 g, 1.72 mmol) as a yellow solid. The analytical data for this compound are consistent with previously reported data.[S3b]



2c. General procedure II was employed using the following components: ketoxime (0.696 g, 5.00 mmol), acetic anhydride (0.950 mL, 10.0 mmol), acetic acid (0.860 mL, 15.0 mmol), and $Fe(OAc)_2$ (1.74 g, 10.0 mmol) in 25.0 mL of THF. Following the work-up, the enamide was isolated by flash column chromatography (hexanes:EtOAc = 2:1) in a 40% yield (0.328 g, 2.00 mmol) as a waxy yellow solid. The analytical data for this compound are consistent with previously reported data.[S6]



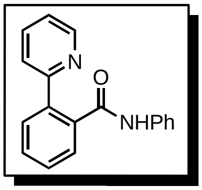
2d. General procedure II was employed using the following components: ketoxime (0.576 g, 5.00 mmol), acetic anhydride (0.950 mL, 10.0 mmol), acetic acid (0.860 mL, 15.0 mmol), and $Fe(OAc)_2$ (1.74 g, 10.0 mmol) in 25.0 mL of THF. Following the work-up, the enamide was isolated by flash column chromatography (hexanes:EtOAc = 2:1) in a 39% yield (0.276 g, 1.95 mmol) as a white solid. The analytical data for this compound are consistent with previously reported data.[S7]

IV. General Procedures for the Rh-Catalyzed Addition of Isocyanates to C-H Bonds

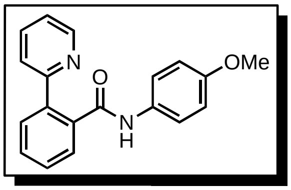
General procedure I. Rh-catalyzed coupling of 2-phenylpyridine with isocyanates (Equation 1). In a N_2-filled glovebox, $[Cp^*RhCl_2]_2$ (7.70 mg, 0.0125 mmol), $AgSbF_6$ (17.2 mg, 0.0500 mmol), 2-phenylpyridine (0.500 mmol) and the corresponding isocyanate (0.250 mmol) were added to a screw-capped vial followed by addition of a stir bar and CH_2Cl_2 (2.00 mL, [isocyanate] = 0.125 mM). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled aluminum-heating block set at 75 ^{o}C. After 24 h of stirring, the vial was removed from the heating block and was left to cool to ambient temperature. After filtration through a pad of silica and removal of the solvent, the residue was purified by column chromatography on silica gel.

General procedure II. Rh-catalyzed coupling of acetanilides or enamides with isocyanates (Table 2 and Equations 2-3). In a N_2-filled glovebox, $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.4 mg, 0.0125 mmol), the acetanilide or enamide (0.500 mmol) and the corresponding isocyanate (0.250 mmol) were added to a screw-capped vial followed by addition of a stir bar and THF (1.00 mL, [isocyanate] = 0.250 mM). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled aluminum-heating block set at the indicated temperature. After 16 h of stirring, the vial was removed from the heating block and was left to cool to ambient temperature. After filtration through a pad of silica and removal of the solvent, the residue was purified by column chromatography on silica gel.

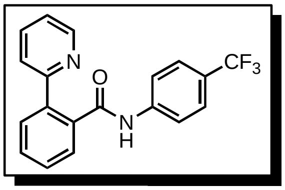
V. Preparation and Characterization of Amide Products



Equation 1, 1a. Following general procedure I, the indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; $R_f = 0.11$) in a 85% isolated yield (58 mg, 0.21 mmol) as a waxy white solid. IR (film): 3288, 3056, 1653, 1597, 1587, 1532 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.80-8.59 (m, 2H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.60-7.42 (m, 6H), 7.36-7.24 (m, 3H), 7.09 (t, *J* = 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.7, 158.7, 149.0, 138.5, 138.4, 137.2, 136.5, 130.6, 130.5, 129.6, 129.1, 129.0, 124.5, 124.4, 122.8, 120.1. HRMS (ESI/$[M+H]^+$) calcd. for $C_{18}H_{14}N_2O$: 275.1179. Found: 275.1171.



Equation 1, 1b. Following general procedure I, the indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; $R_f = 0.10$) in a 72% isolated yield (56 mg, 0.18 mmol) as a waxy off-white solid. IR (film): 3283, 3054, 1649, 1598, 1587 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.68-8.62 (m, 1H), 8.45 (s, 1H), 7.81 (d, *J* = 7.0 Hz, 1H). 7.75 (dt, *J* = 7.5 Hz, 1H), 7.58-7.46 (m, 4H), 7.36-7.30 (m, 2H), 7.29-7.23 (m, 1H), 6.84-6.78 (m, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.6, 158.7, 156.6, 149.1, 138.5, 137.2, 136.5, 131.5, 130.5, 130.4, 129.5, 129.0, 124.5, 122.8, 121.8, 114.3, 55.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{16}N_2O_2$: 305.1285. Found: 305.1272.



Equation 1, 1c. Following general procedure I, the indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; $R_f = 0.13$) in a 84% isolated yield (73 mg, 0.21 mmol) as an off-white solid (mp: 183-185 °C). IR (film): 3240, 2921, 1677, 1604, 1594, 1539 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.59 (s, 1H), 8.62 (d, *J* = 4.0 Hz, 1H), 7.84-7.70 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.54-7.39 (m, 6H), 7.33-7.27 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.0, 158.7, 148.7, 141.7, 138.5, 137.6, 135.9, 130.9, 130.7, 129.7, 129.0, 126.3 (q, *J* = 3.8 Hz), 126.0 (q, *J* = 32.5 Hz), 124.6, 124.3 (q, *J* = 270.0 Hz), 123.0, 119.6. HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{13}F_3N_2O$: 343.1053. Found: 343.1035.

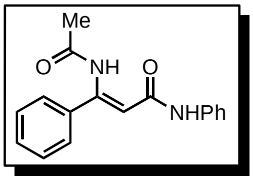


Table 2, 3a. General procedure II was followed and the reaction was conducted at room temperature. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; $R_f = 0.30$) in a 96% isolated yield (68 mg, 0.24 mmol) as a pale yellow solid (mp: 162-164 °C). IR (film): 3317, 2059, 1695, 1624, 1596, 1576 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.47 (s, 1H), 7.54-7.43 (m, 2H), 7.42-7.28 (m, 8H), 7.21-7.09 (m, 1H), 5.17 (s, 1H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.9, 166.4, 153.2, 137.7, 136.5, 129.5, 129.3, 128.2, 127.2, 124.8, 120.5, 103.8, 25.1. HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{16}N_2O_2$: 281.1285. Found: 281.1271.

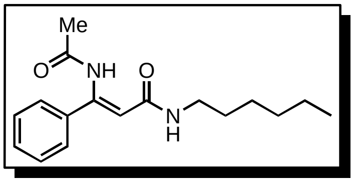


Table 2, 3b. General procedure II was followed and the reaction was conducted at room temperature. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.17) in a 96% isolated yield (70 mg, 0.24 mmol) as a colorless oil. IR (film): 3321, 2929, 2858, 1698, 1627, 1577, 1552 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.57 (s, 1H), 7.39-7.28 (m, 5H), 5.68 (s, 1H), 5.01 (s, 1H), 3.38-3.17 (m, 2H), 2.13 (s, 3H), 1.61-1.42 (m, 2H), 1.41-1.20 (m, 6H), 0.98-0.81 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 168.8, 168.1, 151.5, 136.7, 129.1, 128.1, 127.1, 103.7, 39.6, 31.7, 29.7, 26.8, 25.0, 22.7, 14.2. HRMS (ESI/[M+H]$^+$) calcd. for $C_{17}H_{24}N_2O_2$: 289.1911. Found: 289.1904.

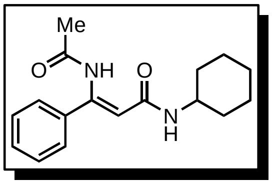


Table 2, 3c. General procedure II was followed and the reaction was conducted at room temperature. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.18) in a 84% isolated yield (59 mg, 0.21 mmol) as a waxy off-white solid. IR (film): 3310, 2930, 2854, 1696, 1623, 1576, 1546 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.58 (s, 1H), 7.40-7.29 (m, 5H), 5.40 (d, *J* = 6.4 Hz, 1H), 5.00 (s, 1H), 3.88-3.74 (m, 1H), 2.14 (s, 3H), 2.01-1.90 (m, 2H), 1.79-1.69 (m, 2H), 1.68-1.60 (m, 1H), 1.47-1.32 (m, 2H), 1.24-1.09 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 168.7, 167.3, 151.8, 136.8, 129.2, 128.1, 127.1, 103.7, 48.4, 33.4, 25.7, 25.1, 25.0. HRMS (ESI/[M+H]$^+$) calcd. for $C_{17}H_{22}N_2O_2$: 287.1754. Found: 287.1747.

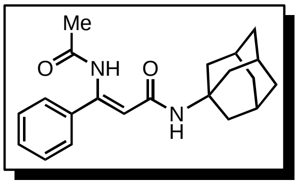


Table 2, 3d. General procedure II was followed and the reaction was conducted at room temperature. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.36) in a 40% isolated yield (34 mg, 0.10 mmol) as a white solid (mp: 185-187 ^{o}C). IR (film): 3326, 2905, 2850, 1696, 1624, 1576, 1544 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.49 (s, 1H), 7.42-7.28 (m, 5H), 5.19 (s, 1H), 4.94 (s, 1H), 2.14 (s, 3H), 2.15-2.08 (m, 3H), 2.07-1.98 (m, 6H), 1.79-1.64 (m, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 168.7, 167.7, 151.3, 137.0, 129.0, 128.1, 127.1, 104.8, 52.5, 42.0, 36.5, 29.6, 25.1. HRMS (ESI/[M+H]$^+$) calcd. for $C_{21}H_{26}N_2O_2$: 339.2067. Found: 339.2059.

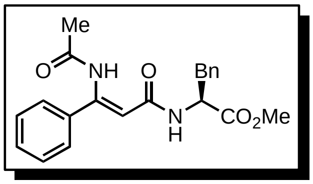


Table 2, 3e. General procedure II was followed and the reaction was conducted at room temperature. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.12) in a 65% isolated yield (59 mg, 0.16 mmol) as a waxy pale yellow solid. IR (film): 3308, 3058, 1741, 1711, 1622, 1577, 1538 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.60 (s, 1H), 7.62-7.46 (m, 8H), 7.39-7.31 (m, 2H), 6.17 (d, *J* = 7.4 Hz, 1H), 5.30 (s, 1H), 5.16 (m, 1H), 4.00 (s, 3H), 3.41 (m, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.1, 168.7, 167.6, 152.9, 136.5, 135.8, 129.4 (x 2), 128.9, 128.2, 127.5, 127.2, 102.6, 53.2, 52.7, 38.1, 25.0. HRMS (ESI/[M+H]$^+$) calcd. for $C_{21}H_{22}N_2O_4$: 367.1652. Found: 367.1635.

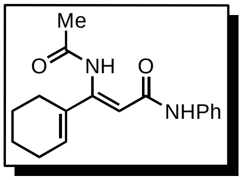


Table 2, 3f. General procedure II was followed and the reaction was conducted at room temperature. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (5:1; R_f = 0.16) in a 80% isolated yield (58 mg, 0.20 mmol) as a white solid (mp: 141-143 °C). IR (film): 3314, 2936, 1694, 1614, 1595, 1546 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.38 (s, 1H), 7.55-7.41 (m, 2H), 7.39-7.28 (m, 3H), 7.12 (t, *J* = 7.2 Hz, 1H), 5.84 (s, 1H), 5.03 (s, 1H), 2.19-2.04 (m, 7H), 1.74-1.56 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.5, 167.42, 156.0, 137.8, 137.1, 129.3, 127.4, 124.7, 120.4, 100.0, 27.6, 25.6, 25.0, 22.5, 22.1. HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{20}N_2O_2$: 285.1598. Found: 285.1586.

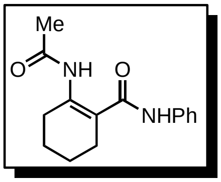


Table 2, 3g. General procedure II was followed and the reaction was conducted at room temperature. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.29) in a 76% isolated yield (50 mg, 0.19 mmol) as a white solid (mp: 190-192 °C). IR (film): 3289, 2943, 1674, 1641, 1594, 1541, 1521 cm^{-1}. ^1H NMR ($CDCl_3$): δ 12.46 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41-7.29 (m, 3H), 7.15 (t, *J* = 6.9 Hz, 1H), 3.11-2.94 (m, 2H), 2.49-2.34 (m, 2H), 2.11 (s, 3H), 1.81-1.62 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.3, 168.8, 151.6, 137.5, 129.3, 125.1, 121.6, 104.3, 28.8, 25.9, 25.3, 22.1, 21.9. HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{18}N_2O_2$: 259.1441. Found: 259.1439.

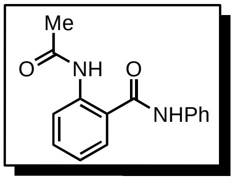


Table 2, 3h. General procedure II was followed and the reaction was conducted at 75 °C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.27) in a 60% isolated yield (38 mg, 0.15 mmol) as a white solid (mp: 179-181 °C). IR (film): 3294, 3030, 1674, 1650, 1596, 1583 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.63 (s, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.28 (s, 1H), 7.63 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.56 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.46-7.38 (m, 3H), 7.24-7.19 (m, 1H), 7.09 (td, *J* = 7.7, 1.1 Hz, 1H), 2.18 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.5, 167.6, 139.4, 137.6, 132.9, 129.5, 127.0, 125.4, 123.1, 122.1, 121.5, 121.0, 25.5. HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{14}N_2O_2$: 255.1128. Found: 255.1122.

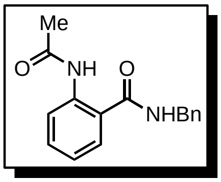


Table 2, 3i. General procedure II was followed and the reaction was conducted at 75 °C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.23) in a 68% isolated yield (46 mg, 0.17 mmol) as a white solid (mp: 146-148 °C). IR (film): 3235, 3031, 1660, 1630, 1602, 1538 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.05 (s, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 7.50-7.42 (m, 2H), 7.41- 7.30 (m, 5H), 7.04 (m, 1H), 6.60 (s, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.3, 169.1, 139.9, 137.7, 132.9, 129.1, 128.1, 128.0, 126.6, 122.9, 121.8, 120.3, 44.3, 25.5. HRMS (ESI/$[M+H]^+$) calcd. for $C_{16}H_{16}N_2O_2$: 269.1285. Found: 269.1284.

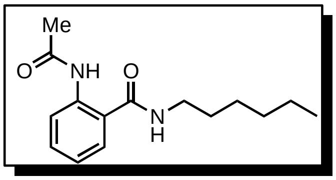


Table 2, 3j. General procedure II was followed and the reaction was conducted at 75 ^{o}C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.30) in a 76% isolated yield (50 mg, 0.19 mmol) as a white solid (mp: 118-120 ^{o}C). IR (film): 3243, 2956, 2927, 2857, 1660, 1630, 1601, 1519 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.03 (s, 1H), 8.56 (d, *J* = 8.3 Hz, 1H), 7.49-7.38 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.27 (s, 1H), 3.43 (m, 2H), 2.19 (s, 3H), 1.67-1.58 (m, 2H), 1.44-1.27 (m, 6H), 0.90 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 169.3, 169.2, 139.7, 132.7. 126.5, 122.9, 121.7, 120.8, 40.3, 31.7, 29.7, 26.9, 25.5, 22.8, 14.2. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{15}H_{22}N_2O_2$: 263.1573. Found: 263.1747.

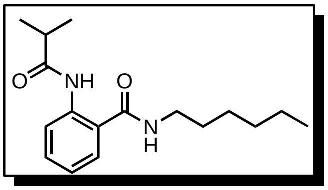


Table 2, 3k. General procedure II was followed and the reaction was conducted at 120 ^{o}C for 24 h. The indicated compound was observed in a 77% ^{1}H NMR yield relative to 2,6-dimethoxytoluene as an internal standard, and a pure fraction for characterization purposes (28 mg, 0.095 mmol) was obtained by flash column chromatography on silica gel using CH_2Cl_2:1% NH_4OH in MeOH (100:1; R_f = 0.05) as a colorless oil. IR (film): 3320, 2961, 2930, 1678, 1638, 1599, 1586 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.11 (s, 1H), 8.61 (d, *J* = 7.9 Hz, 1H), 7.50-7.39 (m, 2H), 7.04 (dt, *J* = 7.9, 1.2 Hz, 1H), 6.28 (s, 1H), 3.49-3.36 (m, 2H), 2.58 (sept, *J* = 6.9 Hz, 1H), 1.70-1.56 (m, 2H), 1.50-1.29 (m, 6H), 1.26 (d, *J* = 6.9 Hz, 6H), 0.97-0.84 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 176.3, 169.3, 140.0, 132.7, 126.5, 122.7, 121.8, 120.9, 40.3, 37.5, 31.8, 29.7, 26.9, 22.8, 19.8, 14.2. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{17}H_{26}N_2O_2$: 291.2067. Found: 291.2063.

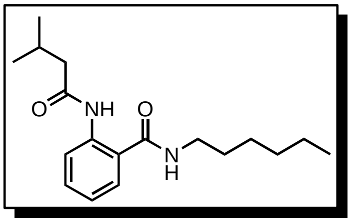


Table 2, 3l. General procedure II was followed and the reaction was conducted at 120 ^{o}C for 24 h. The indicated compound was observed in 72% ^{1}H NMR yield relative to 2,6-dimethoxytoluene as an internal standard, and a pure fraction for characterization purposes (24 mg, 0.079 mmol) was obtained by flash column chromatography on silica gel using 30% Et_2O in hexanes (R_f = 0.11) as a white solid (mp: 121-123 ^{o}C). IR (film): 3284, 2957, 2927, 1653, 1627, 1601, 1534 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.01 (s, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 7.54-7.35 (m, 2H), 7.04 (dt, *J* = 7.9, 1.2 Hz, 1H), 6.29 (s, 1H), 3.51-3.35 (m, 2H), 2.31-2.13 (m, 3H), 1.68-1.54 (m, 2H), 1.49-1.24 (m, 6H), 1.00 (d, *J* = 6.4 Hz, 6H), 0.90 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 171.8, 169.2, 139.8, 132.6,. 126.5, 122.8, 121.8, 120.8, 48.1, 40.3, 31.7, 29.7, 26.9, 26.5, 22.8, 22.7, 14.2. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{18}H_{28}N_2O_2$: 305.2223. Found: 305.2213.

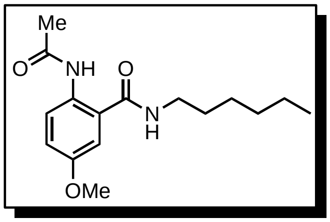


Table 2, 3m. General procedure II was followed and the reaction was conducted at 75 ^{o}C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.14) in a 60% isolated yield (44 mg, 0.15 mmol) as a yellow solid (mp: 96-98 ^{o}C). IR (film): 3307, 2929, 2857, 1668, 1643, 1597, 1511 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 10.53 (s, 1H), 8.39 (d, *J* = 9.1 Hz, 1H), 6.98 (dd, *J* = 9.2, 1.8 Hz, 1H), 6.94 (s, 1H), 6.33 (s, 1H), 3.80 (s, 3H), 3.49-3.30 (m, 2H), 2.15 (s, 3H), 1.67-1.57 (m, 2H), 1.45-1.26 (m, 6H), 0.97-0.80 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 168.9, 168.8, 155.0, 132.6, 123.5, 122.9, 116.7, 112.8, 55.9, 40.3, 31.7, 29.6, 26.9, 25.2, 22.8, 14.2. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{16}H_{24}N_2O_3$: 293.1860. Found: 293.1856.

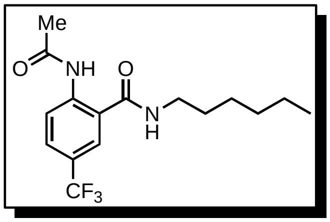


Table 2, 3n. General procedure II was followed and the reaction was conducted at 75 ^{o}C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.53) in a 44% isolated yield (35 mg, 0.11 mmol) as a yellow solid (mp: 84-86 ^{o}C). IR (film): 3315, 2930, 2859, 1685, 1646, 1594, 1518 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.19 (s, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 7.73-7.60 (m, 2H), 6.41 (s, 1H), 3.50-3.36 (m, 2H), 2.21 (s, 3H), 1.73-1.57 (m, 2H), 1.43-1.27 (m, 6H), 0.96-0.83 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.6, 168.1, 142.7, 129.4 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 33.9 Hz), 123.9 (q, *J* = 271.5 Hz), 123.7 (q, *J* = 3.8 Hz), 121.7, 120.5, 40.5, 31.7, 29.6, 26.9, 25.5, 22.8, 14.2. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{16}H_{21}N_2O_2$: 331.1628. Found: 331.1617.

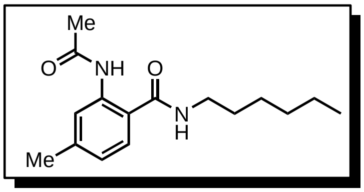


Table 2, 3o. General procedure II was followed and the reaction was conducted at 75 ^{o}C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.31) to provide the product in a 97% isolated yield (67 mg, 0.24 mmol) as a white solid (mp: 83-85 ^{o}C). IR (film): 3320, 2928, 2858, 1676, 1637, 1607, 1579, 1522 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.16 (s, 1H), 8.35 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.58 (s, 1H), 3.44-3.31 (m, 2H), 2.32 (s, 3H), 2.13 (s, 3H), 1.65-1.54 (m, 2H), 1.42-1.21 (m, 6H), 0.90-0.82 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.3, 169.2, 143.2, 139.6, 126.6, 121.9, 121.8, 117.8, 40.2, 31.6, 29.6, 26.8, 25.5, 22.7, 21.9, 14.1. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{16}H_{24}N_2O_2$: 277.1911. Found: 277.1901.

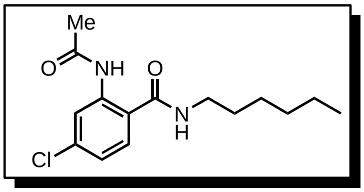


Table 2, 3p. General procedure II was followed and the reaction was conducted at 75 ^{o}C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.44) to provide the product in a 68% isolated yield (50 mg, 0.17 mmol) as a white solid (mp: 74-76 ^{o}C). IR (film): 3318, 2930, 2859, 1679, 1641, 1592, 1577, 1508 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.14 (s, 1H), 8.59 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.51 (s, 1H), 3.44-3.34 (m, 2H), 2.16 (s, 3H), 1.66-1.57 (m, 2H), 1.43-1.26 (m, 6H), 0.92-0.84 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.4, 168.4, 140.6, 138.5, 127.8, 122.8, 121.3, 118.8, 40.4, 31.6, 29.5, 26.9, 25.5, 22.7, 14.2. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{15}H_{21}ClN_2O_2$: 297.1364. Found: 297.1359.

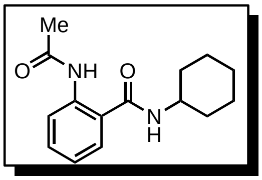


Table 2, 3q. General procedure II was followed and the reaction was conducted at 75 ^{o}C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.24) in a 76% isolated yield (49 mg, 0.19 mmol) as a white solid (mp: 168-170 ^{o}C). IR (film): 3287, 2931, 2850, 1688, 1625, 1586, 1518 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.04 (s, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 7.52-7.37 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 4.00-3.86 (m, 1H), 2.19 (s, 3H), 2.09-1.98 (m, 2H), 1.83-1.73 (m, 2H), 1.67 (m, 1H), 1.52-1.38 (m, 2H), 1.33-1.17 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.2, 168,4, 139.8, 132.7, 126.5, 122.8, 121.7, 120.9, 49.1, 33.3, 25.7, 25.5, 25.1. HRMS (ESI/[M+H]$^{+}$) calcd. for $C_{15}H_{20}N_2O_2$: 261.1598. Found: 261.1590.

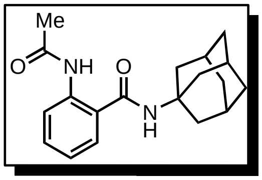


Table 2, 3r. General procedure II was followed and the reaction was conducted at 75 °C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R$_f$ = 0.38) in a 48% isolated yield (36 mg, 0.12 mmol) as a white solid (mp: 177-179 °C). IR (film): 3321, 2906, 2851, 1670, 1640, 1586, 1520 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.88 (s, 1H), 8.52 (d, *J* = 8.3 Hz, 1H), 7.49-7.33 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 2.18 (s, 3H), 2.16-2.07 (m, 9H), 1.79-1.68 (m, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.2, 168.7, 139.5, 132.3, 126.6, 122.8, 122.3, 121.8, 53.1, 41.8, 36.5, 29.7, 25.5. HRMS (ESI/[M+H]$^+$) calcd. for C$_{19}$H$_{24}$N$_2$O$_2$: 313.1911. Found: 313.1898.

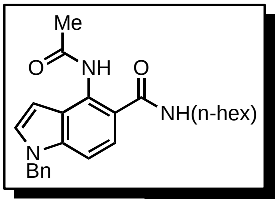
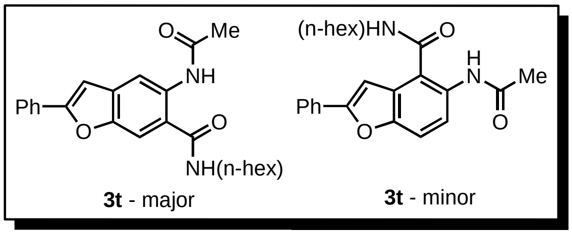


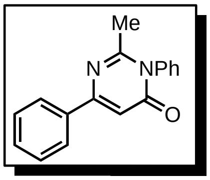
Table 2, 3s. General procedure II was followed and the reaction was conducted at 75 °C and on a 0.15 mmol scale. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (1:1; R$_f$ = 0.15) to provide the product in a 47% isolated yield (27 mg, 0.069 mmol) as a white solid (mp: 161-163 °C). IR (film): 3289, 2955, 2928, 2857, 1676, 1616, 1505 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.43 (s, 1H), 7.33-7.24 (m, 3H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.13 (d, *J* = 3.2 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 6.17 (s, 1H), 5.29 (s, 2H), 3.43-3.32 (m, 2H), 2.26 (s, 3H), 1.65-1.53 (m, 2H), 1.42-1.23 (m, 6H), 0.95-0.85 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 170.2, 168.8, 138.9, 137.1, 131.7, 129.0, 128.8, 128.0, 127.0, 124.0, 120.3, 107.0, 104.6, 50.5, 40.2, 31.7, 29.8, 26.9, 24.8, 22.8, 14.2. HRMS (ESI/[M+H]$^+$) calcd. for C$_{24}$H$_{29}$N$_3$O$_2$: 392.2333. Found: 392.2315.



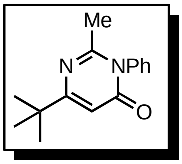
3t - major

3t - minor

Table 2, 3t. General procedure II was followed and the reaction was conducted at 120 °C. The indicated regioisomers were purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R$_f$(**3t**-major) = 0.30 and R$_f$(**3t**-minor) = 0.22) to provide the product isomers in a combined 68% isolated yield (**3t**-major - 42 mg, 0.11 mmol and **3t**-minor - 21 mg, 0.056 mmol) as pale yellow solids. **3t**-major – mp = 154-156 °C; IR (film): 3373, 2957, 2929, 2855, 1658, 1641, 1593, 1543, 1514 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 10.92 (s, 1H), 8.66 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.56 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 6.94 (s, 1H), 6.57 (s, 1H), 3.47-3.39 (m, 2H), 2.18 (s, 3H), 1.72-1.59 (m, 2H), 1.49-1.30 (m, 6H), 0.92 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.5, 169.1, 159.1, 150.1, 134.7, 132.6, 129.9, 129.4, 129.1, 125.3, 118.6, 113.6, 109.4, 101.8, 40.4, 31.7, 29.7, 26.9, 25.4, 22.8, 14.2; HRMS (ESI/[M+H]$^+$) calcd. for C$_{23}$H$_{26}$N$_2$O$_3$: 379.2016. Found: 379.2012. **3t**-minor – mp = 189-191 °C; IR (film): 3264, 2922, 1659, 1633, 1608, 1555, 1531 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.40 (s, 1H), 8.37 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.52-7.36 (m, 3H), 7.06 (s, 1H), 6.35 (s, 1H), 3.58-3.50 (m, 2H), 2.18 (s, 3H), 1.77-1.67 (m, 2H), 1.57-1.32 (m, 6H), 0.98-0.90 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.1, 168.2, 158.0, 151.4, 134.9, 129.8, 129.6, 129.2, 126.7, 125.4, 119.0, 114.8, 114.3, 100.3, 40.3, 31.7, 29.8, 27.1, 25.3, 22.9, 14.2. HRMS (ESI/[M+H]$^+$) calcd. for C$_{23}$H$_{26}$N$_2$O$_3$: 379.2016. Found: 379.2011.

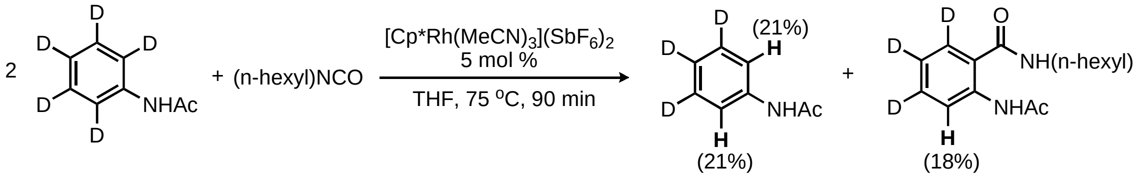


Equation 2, 4a. General procedure II was followed and the reaction was conducted at 105 °C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.20) in a 96% isolated yield (63 mg, 0.24 mmol) as a white solid (mp: 162-164 °C). IR (film): 3056, 1670, 1601, 1590, 1571, 1538 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.10-8.00 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.57-7.46 (m, 4H), 7.30 (d, *J* = 6.9 Hz, 2H), 6.92 (s, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.4, 160.4, 159.1, 137.6, 136.6, 130.8, 130.3, 129.6, 129.0, 127.7, 127.2, 107.9, 24.5. HRMS (ESI/[M+H]$^+$) calcd. for $C_{17}H_{14}N_2O$: 263.1179. Found: 263.1169.



Equation 2, 4b. General procedure II was followed and the reaction was conducted at 105 °C. The indicated compound was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1; R_f = 0.27) in a 92% isolated yield (56 mg, 0.23 mmol) as a white solid (mp: 108-109 °C). IR (film): 2960, 1668, 1601, 1586, 1549 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.58-7.45 (m, 3H), 7.25-7.18 (m, 2H), 6.41 (s, 1H), 2.15 (s, 3H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 174.1, 163.7, 157.7, 137.9, 130.2, 129.4, 127.8, 107.3, 37.2, 28.8, 24.3. HRMS (ESI/[M+H]$^+$) calcd. for $C_{15}H_{18}N_2O$: 243.1492. Found: 243.1489.

VI. Mechanistic Studies



Reversibility of acetanilide cyclorhodation. In a N_2-filled glovebox, $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.4 mg, 0.0125 mmol), acetanilide-d_5 (70.2 mg, 0.500 mmol) and hexyl isocyanate (0.0364 mL, 0.250 mmol) were added to a screw-capped vial followed by addition of a stir bar and THF (1.0 mL, [isocyanate] = 0.250 mM). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled aluminum-heating block set at 75 ^{o}C. After 90 min of stirring, the vial was removed from the heating block and was left to cool to ambient temperature. After removal of the solvent, the residue was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1). A combined 88% yield of material (relative to 0.500 mmol acetanilide-d_5), consisting of acetanilide-d_n (51 mg, 0.36 mmol) and product *N*-acyl anthranilamide-d_n (20 mg, 0.078 mmol, 31%), was recovered. Each isolated compound showed modest deuterium loss at the *ortho*-positions (acetanilide, 21% H; *N*-acyl anthranilamide, 18% H) as determined by ^{1}H NMR integration (Figure S1 and S2).

Figure S1.

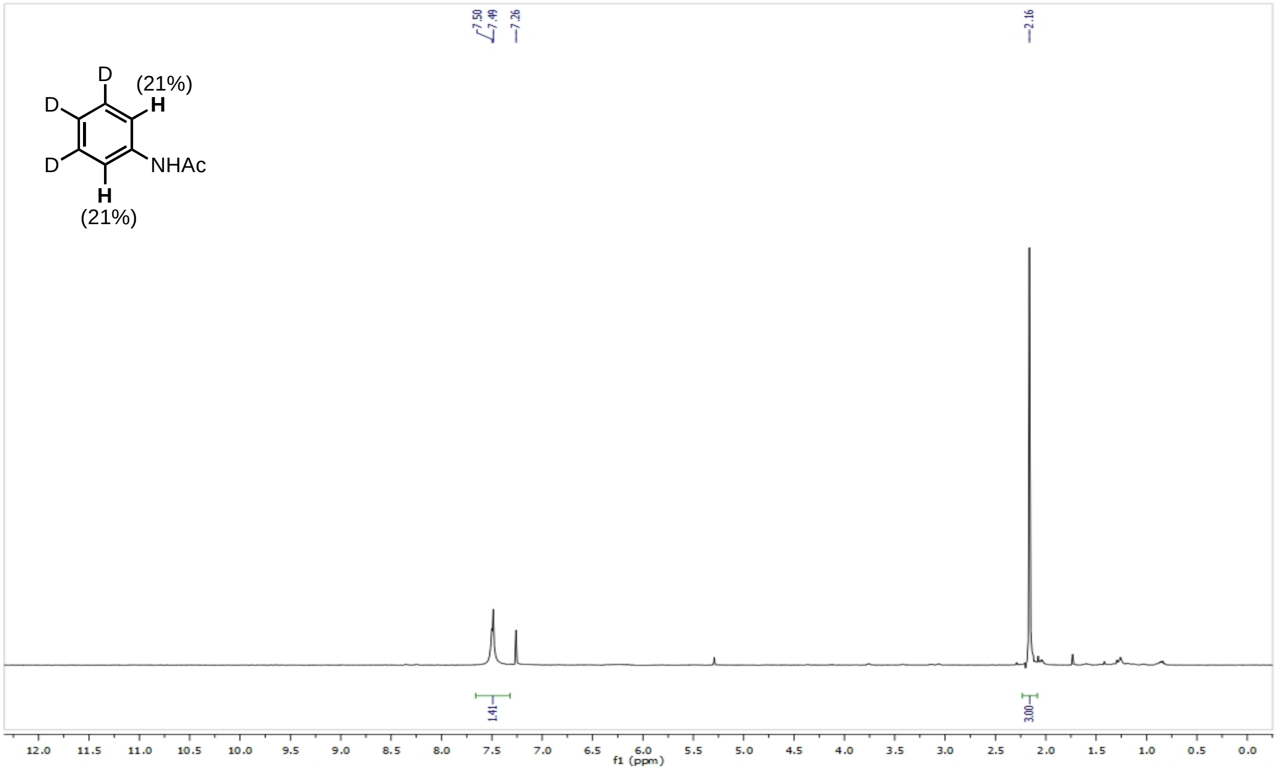
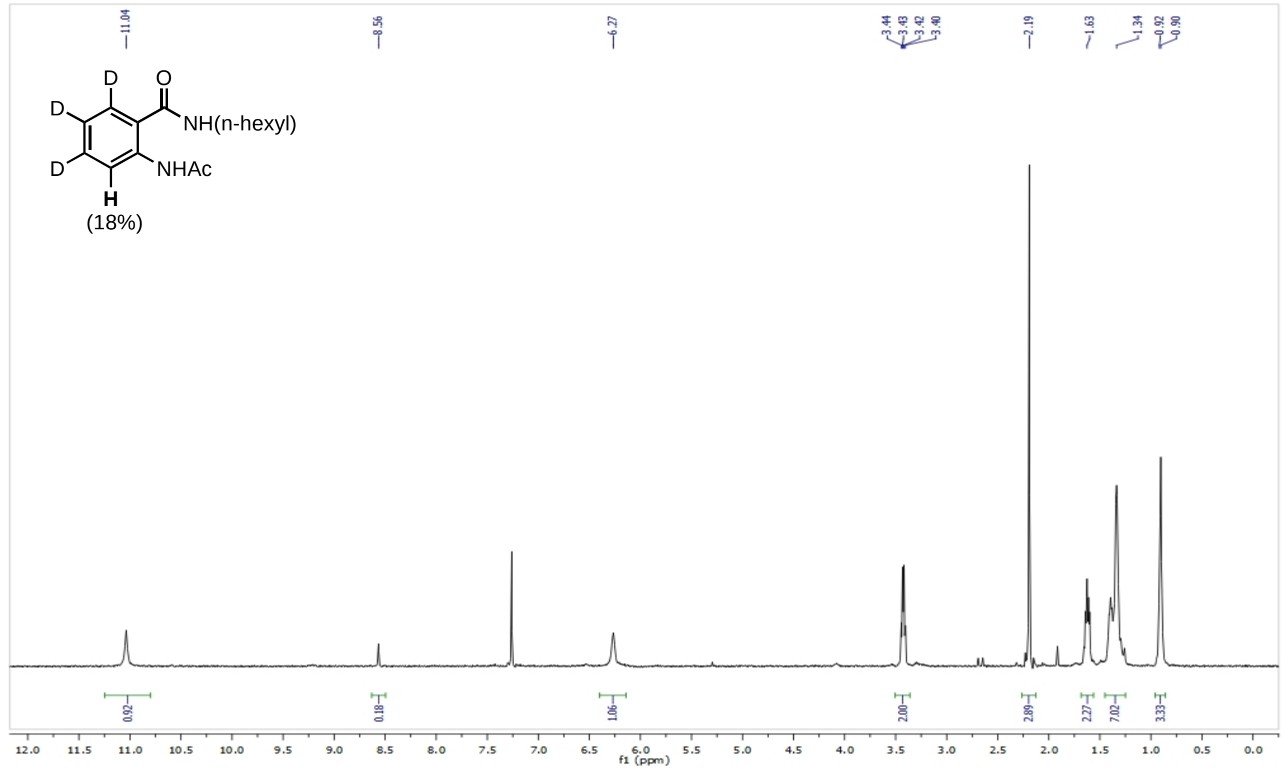
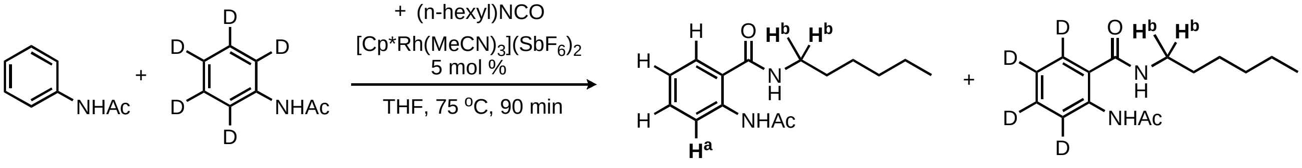


Figure S2.



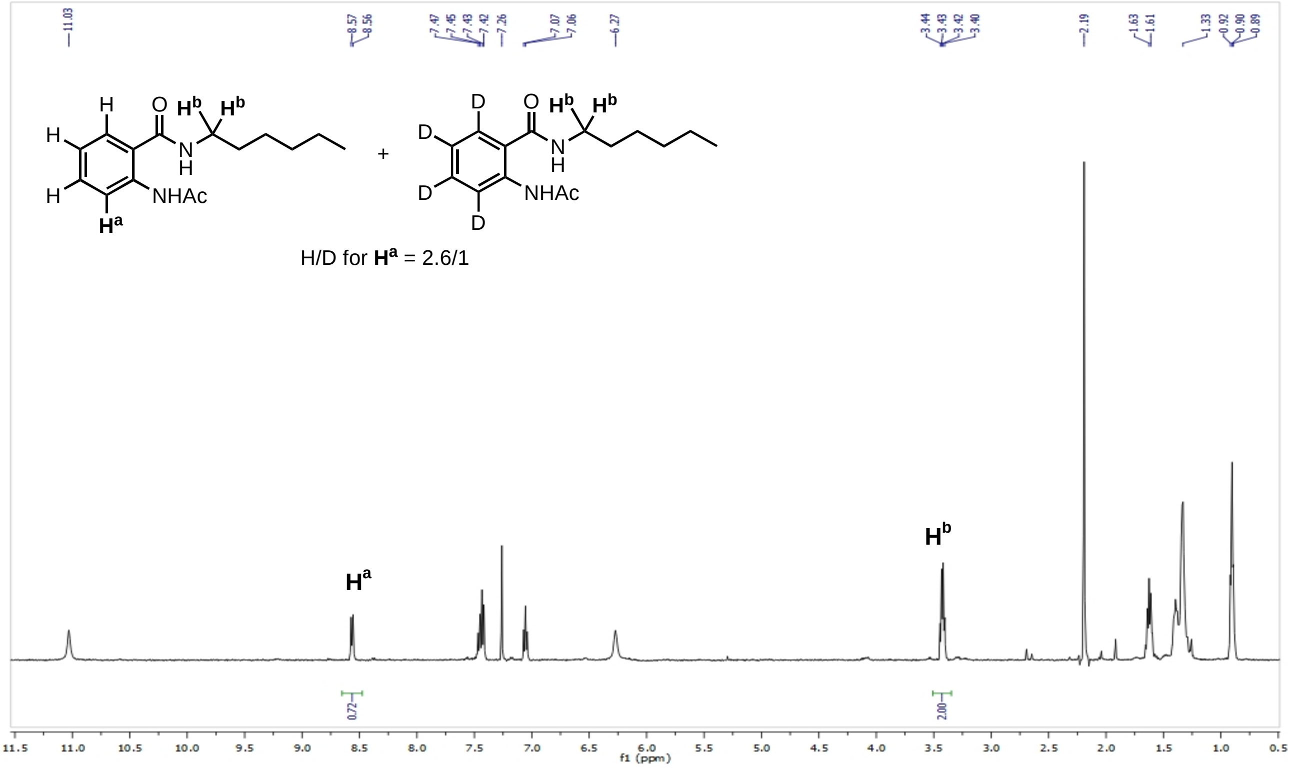
D
O
D
NH(n-hexyl)
D
NHAc
H
(18%)
11.04
8.56
6.27
3.44
3.43
3.42
3.40
2.19
1.63
1.34
0.92
0.90
0.92
0.18
1.06
2.00
2.89
2.27
7.02
3.33
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

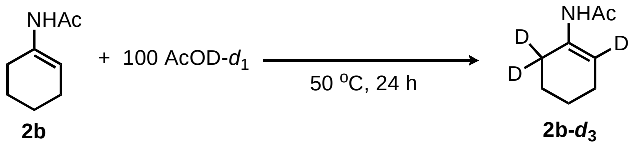


H/D for $\mathbf{H^a}$ = 2.6/1

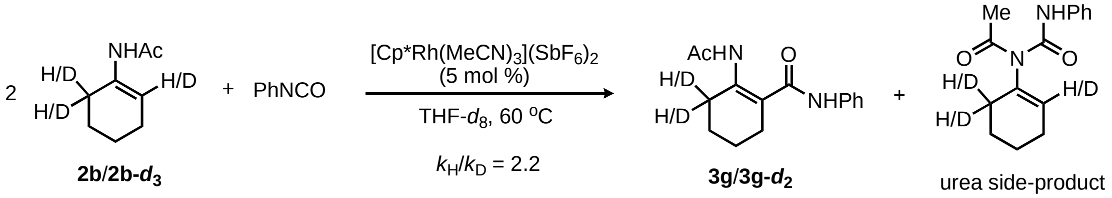
Intermolecular competition between protio- and deutero-acetanilide at early reaction conversion. In a N_2-filled glovebox, $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.4 mg, 0.0125 mmol), acetanilide-*d*$_5$ (35.0 mg, 0.250 mmol), acetanilide (33.8 mg, 0.250 mmol), and hexyl isocyanate (0.0364 mL, 0.250 mmol) were added to a screw-capped vial followed by addition of a stir bar and THF (1.0 mL, [isocyanate] = 0.250 mM). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled aluminum-heating block set at 75 ^{o}C. After 90 min of stirring, the vial was removed from the heating block and was left to cool to ambient temperature. After removal of the solvent, the residue was purified by flash column chromatography on silica gel using hexanes:EtOAc (2:1). Relative to 0.500 mmol acetanilide, an 85% mass recovery (0.34 mmol of acetanilide and 0.084 mmol of *N*-acyl anthranilamide) was achieved. Based upon the initial amount of isocyanate (0.250 mmol), 34% conversion to the *N*-acyl anthranilamide was observed. The amount of product derived from acetanilide (N_H) was determined by integration of $\mathbf{H^a}$, which appeared as a doublet at 8.56 ppm, and the total amount of product (N_{total}) was determined by integration of $\mathbf{H^b}$, which appeared as a multiplet at 3.43 ppm for both the deuterio- and protio-anthranilamide products (Figure S3). The amount of product derived from acetanilide-*d*$_5$ (N_D) was then calculated by subtraction: $N_D = N_{total} - N_H$ (H/D for H_a = 2.6:1). Even upon completely subtracting the 18% background deuterium loss observed for the deuterated anthranilimide shown in Figure S2, the minimum relative rate of protio- versus deutero-acetanilide conversion to product is 2.0:1. These results are consistent with a primary rather than a secondary isotope effect. However, a much more thorough kinetic examination of this reaction is required before precise kinetic isotope effect values can be assigned unambiguously.

Figure S3.

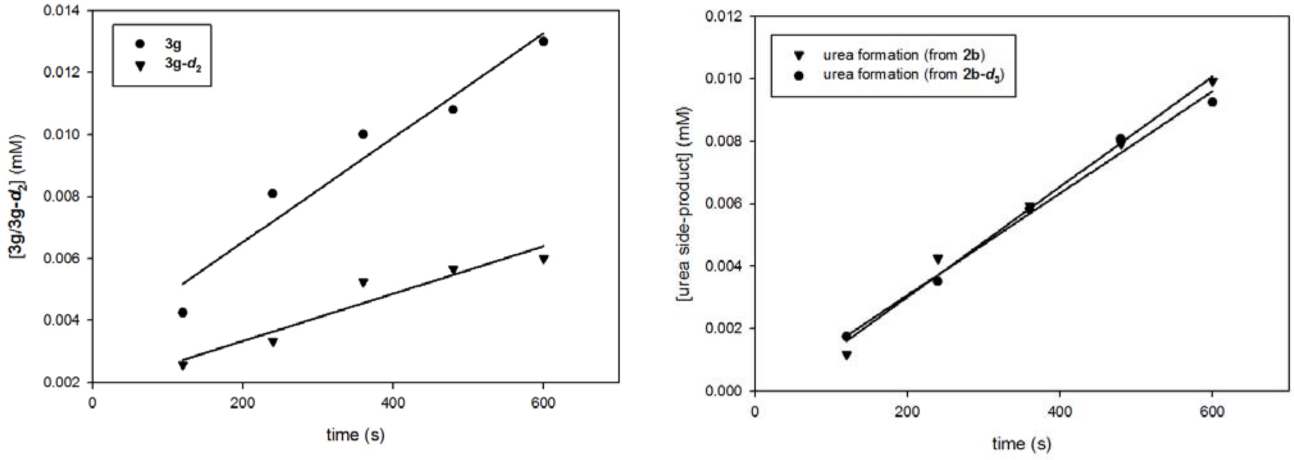




Preparation of 2b-*d*$_3$. A 4-dram scintillation vial containing a stir bar was charged with **2b** (0.0790 g, 0.560 mmol) followed by the addition of AcOD-d_1 (3.30 mL, 56.0 mmol) to afford a homogenous solution. The vial was capped and heated in a temperature-controlled aluminum-heating block set at 50 °C for 24 h. The reaction mixture was then left to cool to room temperature, and the solvent was removed *in vacuo* to afford a brown oil. The crude residue was dissolved in EtOAc (50 mL) and was washed with a saturated solution of $NaHCO_3$ (aq) (2 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The crude residue was then purified by flash column chromatography on silica gel using hexanes:EtOAc (1:1; $R_f = 0.26$) to provide the product in a 47% isolated yield (0.0370 g, 0.260 mmol) as an off-white solid that had 96% deuterium incorporation. IR (film): 3279, 3184, 2929, 2859, 2836, 1653, 1536 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.52 (s, 1H), 2.13-2.04 (m, 2H), 2.00 (s, 3H), 1.69-1.60 (m, 2H), 1.60-1.49 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.5, 132.6, 113.1 (t, *J* = 23.8 Hz), 27.5 (pent, *J* = 18.8 Hz), 24.6, 24.0, 22.5, 22.1. HRMS (ESI/[M+H]$^+$) calcd. for 2($C_8H_{10}D_3NO$): 285.2444. Found: 285.2443.



Initial Rate Measurements for Deuterium Kinetic Isotope Effect Study. A sample experimental set-up is as follows: In a N_2-filled glovebox, cyclohexenylacetamide (**2b**: 0.0139 g, 0.100 mmol; or **2b-*d*$_3$**: 0.0142 g, 0.100 mmol) and 2,6-dimethoxytoluene (as internal standard; 5.10 mg, 0.0335 mmol) were weighed into a vial followed by the addition of phenyl isocyanate (5.40 μL, 0.0500 mmol) and THF-d_8 (0.600 mL). This homogeneous solution was then transferred to a J. Young NMR tube. In a separate vial, [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (3.30 mg, 0.00396 mmol) was weighed out and 0.0793 mL of acetone was added to provide a homogenous, bright yellow solution of the catalyst ([Rh] = 0.0500 mM). 0.0500 mL of the catalyst stock solution (0.00250 mmol, 5.00 mol%) was added directly to the J. Young NMR tube containing the other reaction components. The J. Young NMR tube was sealed, removed from the glovebox, and placed in an NMR instrument that had been previously equilibrated to 60 °C [Note: Although this reaction can take place at room temperature over the course of 16 h, the reaction rates were measured at 60 °C to prevent long data acquisitions and to suppress urea side-product formation for these specific reaction parameters. While urea byproduct formation is further reduced at higher temperatures, the reactions rates are too fast to be conveniently measured]. Measurements of β-enamide amide formation, urea side-product formation, and enamide deuterium incorporation (for **2b-*d*$_3$**) were monitored as a function of time to early conversions (approx. 15%). The rate of enamine amide formation was slowed by deuterium incorporation, which translated into a deuterium kinetic isotope effect of 2.2 (Figure S4a, **2b**: rate = 1.69 x 10^{-5} mmol/s; **2b-*d*$_3$**: rate = 7.65 x 10^{-6} mmol/s). These results are consistent with a primary isotope effect; however, a much more thorough kinetic examination of this reaction is required before precise kinetic isotope effect values can be assigned unambiguously. Notably, the rate of urea side-product formation was consistent for both experiments using **2b** and **2b-*d*$_3$** (Figure S4b, **2b**: rate = 1.76 x 10^{-5} mmol/s; **2b-*d*$_3$**: rate = 1.63 x 10^{-5} mmol/s) and serves as an internal control for reagent concentrations, stoichiometry, temperature, etc. Moreover, background H/D exchange at the alkene position of **2b-*d*$_3$** was not observed during the course rate measurements.



(a) (b)

Figure S4. (a) Plot of enamide amide product concentration versus time for the Rh-catalyzed addition of phenyl isocyanate to **3g** and **3g-*d*$_2$**. For **3g**: y = 1.69e-5 + 3.20e-3 (R^2 = 0.9422); and for **3g-*d*$_2$**: y = 7.65e-6 + 1.80e-3 (R^2 = 0.9145). (b) Plot of urea side-product concentration versus time for the addition of phenyl isocyanate to *N*-acyl enamides **2b** and **2b-*d*$_3$**. For **2b**: y = 1.76e-5 – 5.00e-4 (R^2 = 0.9890); and for **2b-*d*$_3$**: y = 1.63e-5 – 2.00e-4 (R^2 = 0.9900).

VII. References

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[S2] Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 16474.

[S3] a) Tang, W.; Capacci, A.; Sarvestani, M.; Wei, X.; Yee, N. K.; Senanayake, C. H. *J. Org. Chem.* **2009**, *74*, 9528. b) Guan, Z. –H.; Zhang, Z. –Y.; Ren, Z. –H.; Wang, Y. –Y.; Zhang, X. *J. Org. Chem.* **2011**, *76*, 339.

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[S6] Wang, Q. –S.; Xie, J. –H.; Li, W.; Zhu, S. –F.; Wang, L. –X.; Zhou, Q. –L. *Org. Lett.* **2011**, doi: 10.1021/ol201142v

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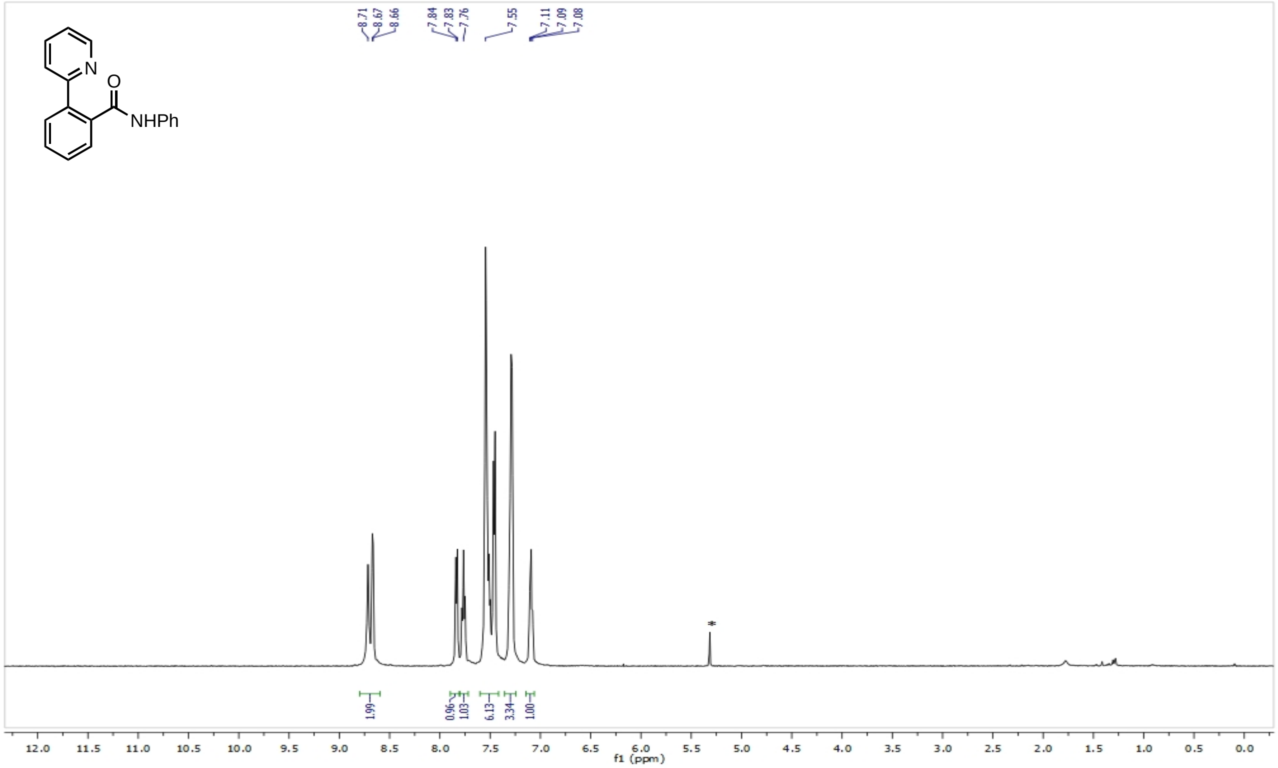
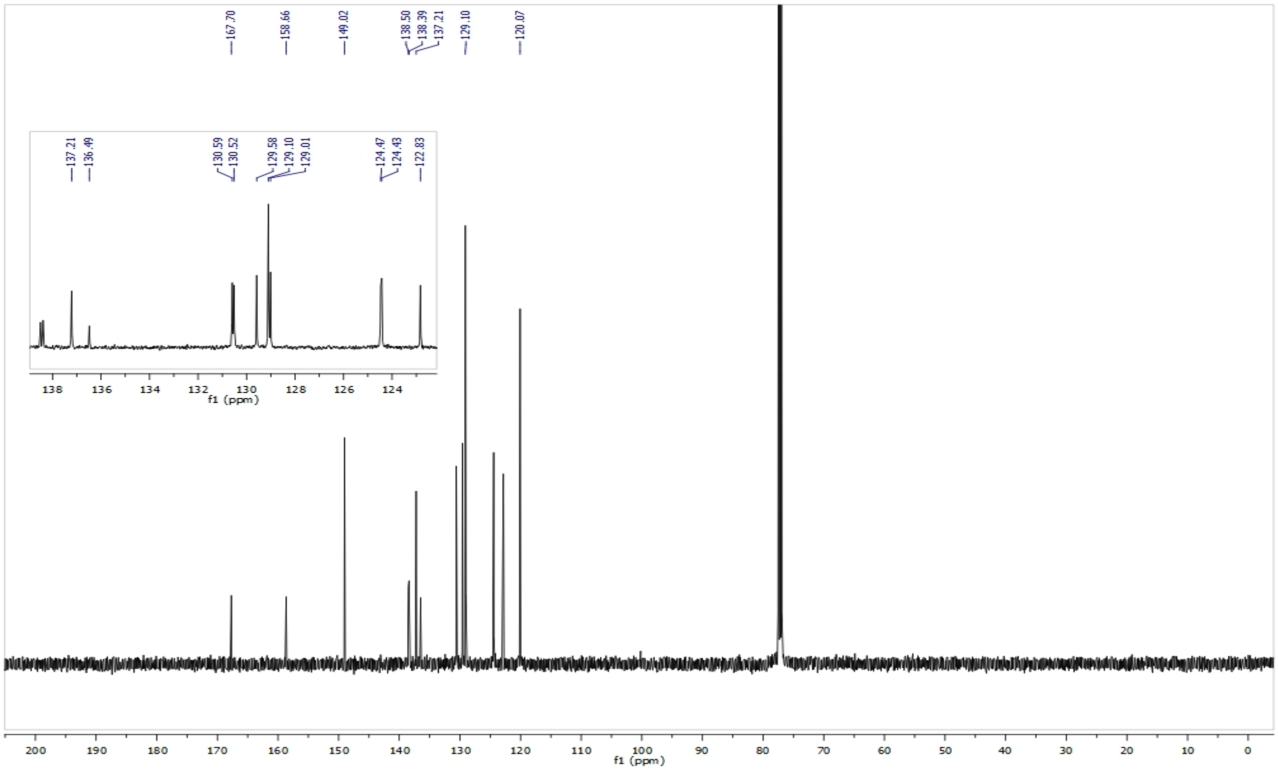
VIII. ^{1}H and ^{13}C{^{1}H} NMR Spectra

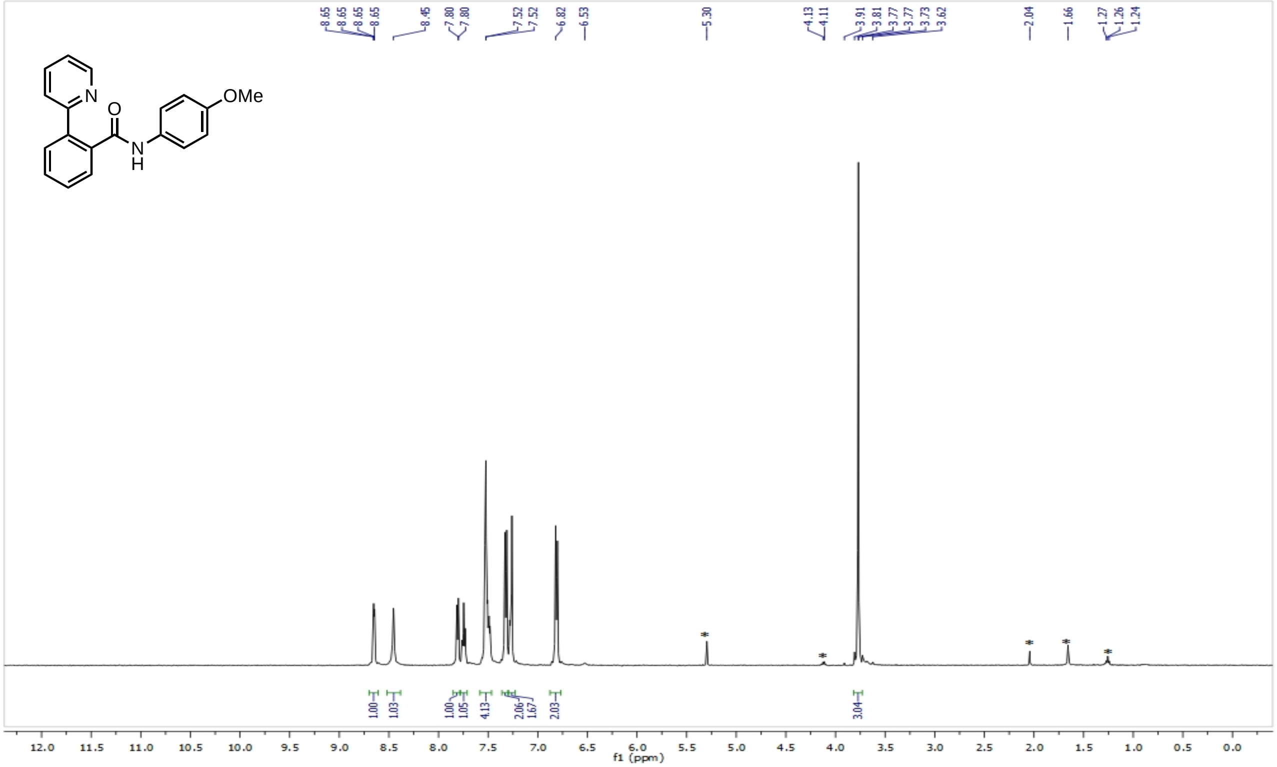
(common solvent impurities are indicated with *)

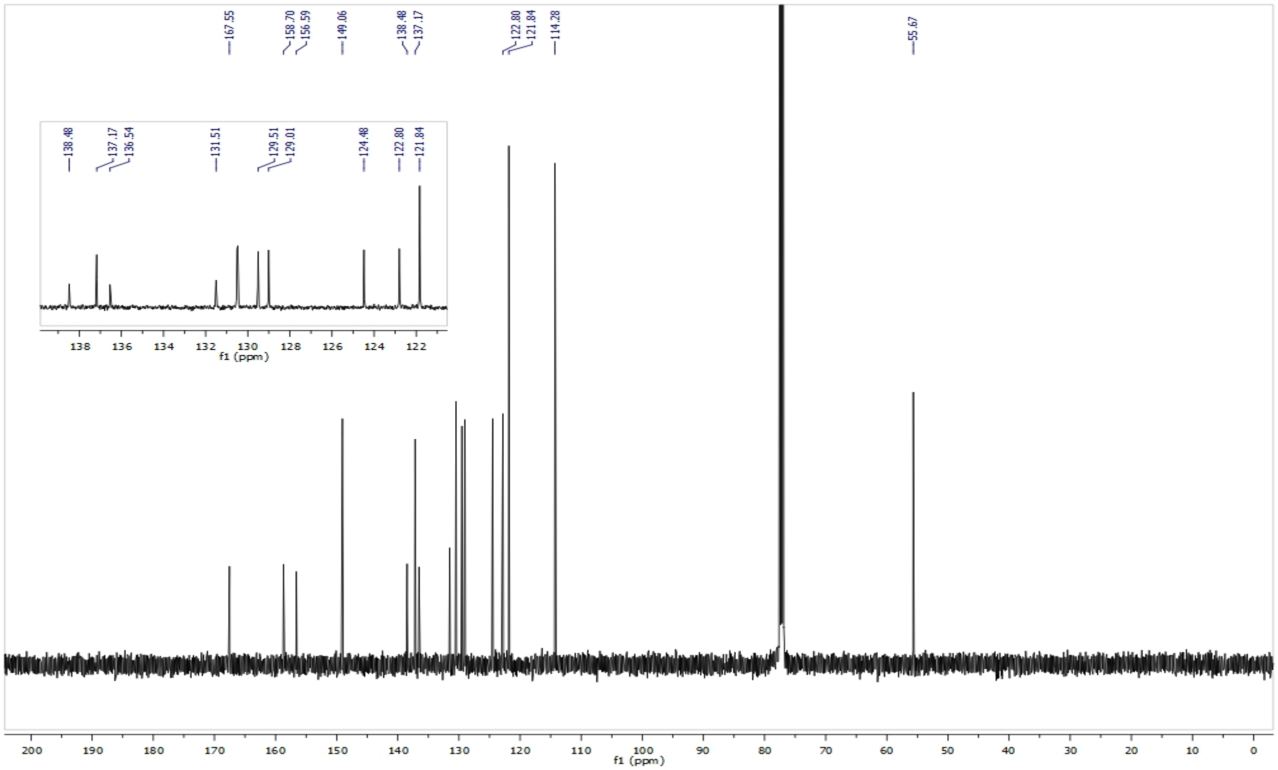
Equation 1, **1a**:



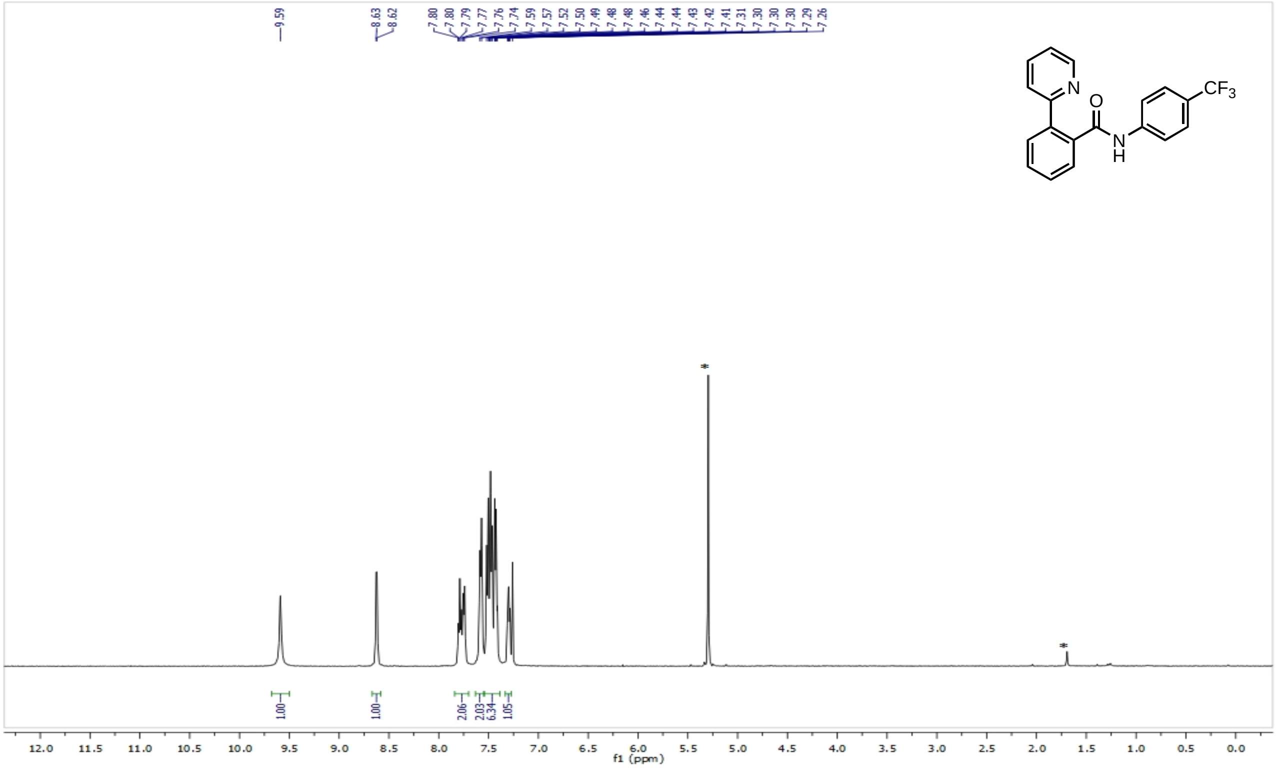


Equation 1, **1b**:





Equation 1, **1c**:



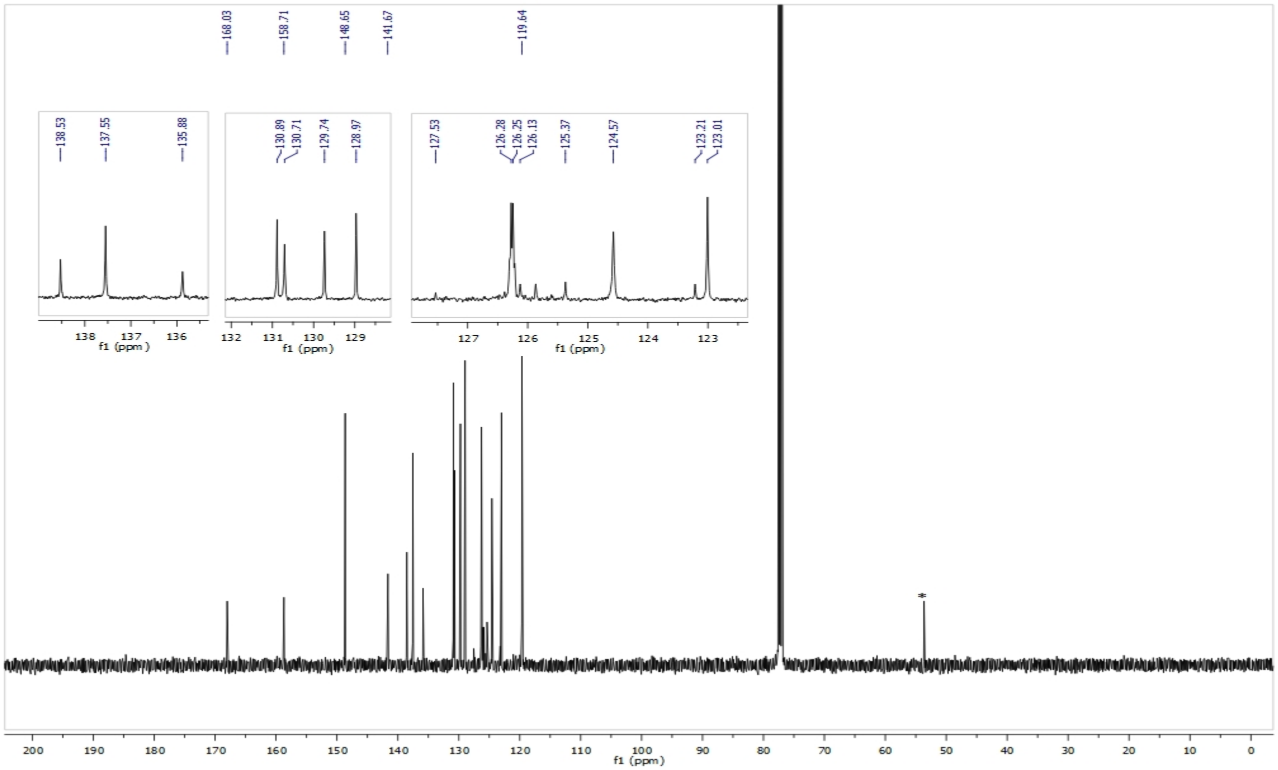
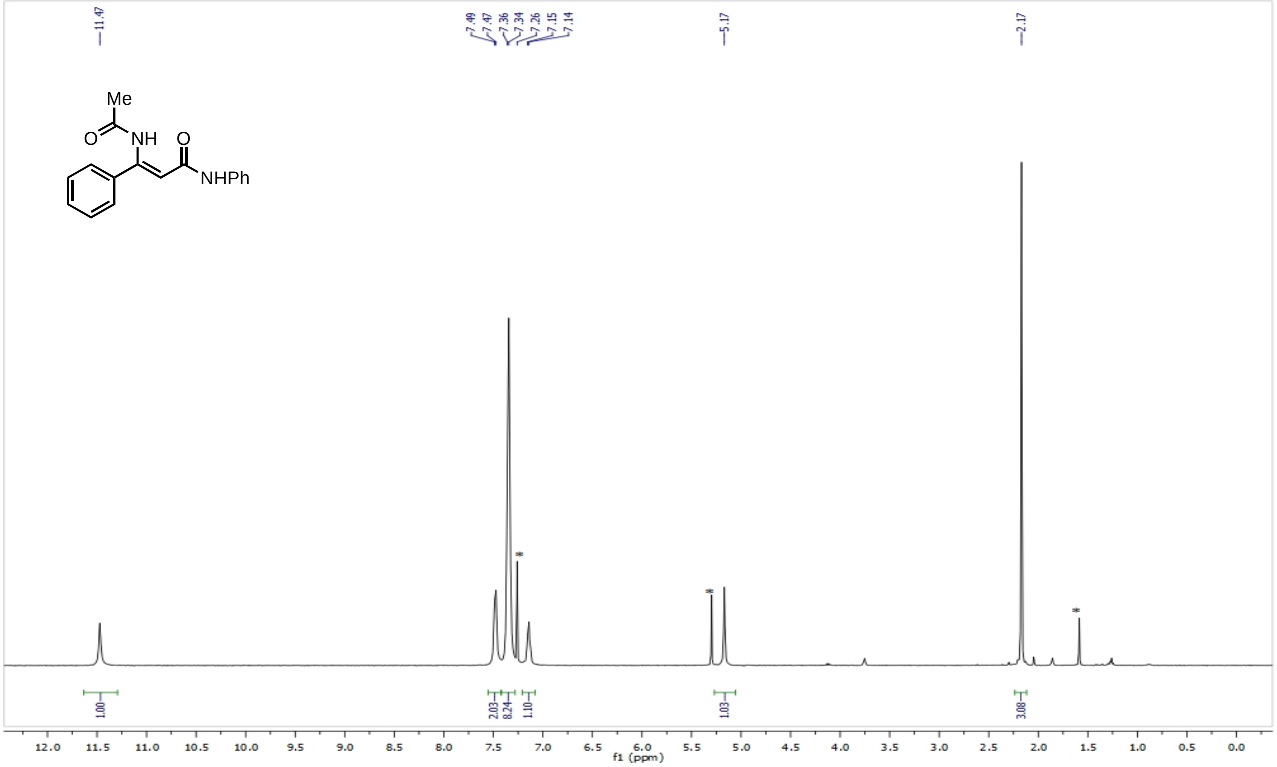

168.03
158.71
148.65
141.67
119.64
138.53
137.55
135.88
130.89
130.71
129.74
128.97
127.53
126.28
126.25
126.13
125.37
124.57
123.21
123.01
*
f1 (ppm)

Table 2, **3a**:


11.47
7.49
7.47
7.36
7.34
7.26
7.15
7.14
5.17
2.17
Me
O
NH
O
NHPh
*
1.00
2.03
8.24
1.10
1.03
3.08
f1 (ppm)

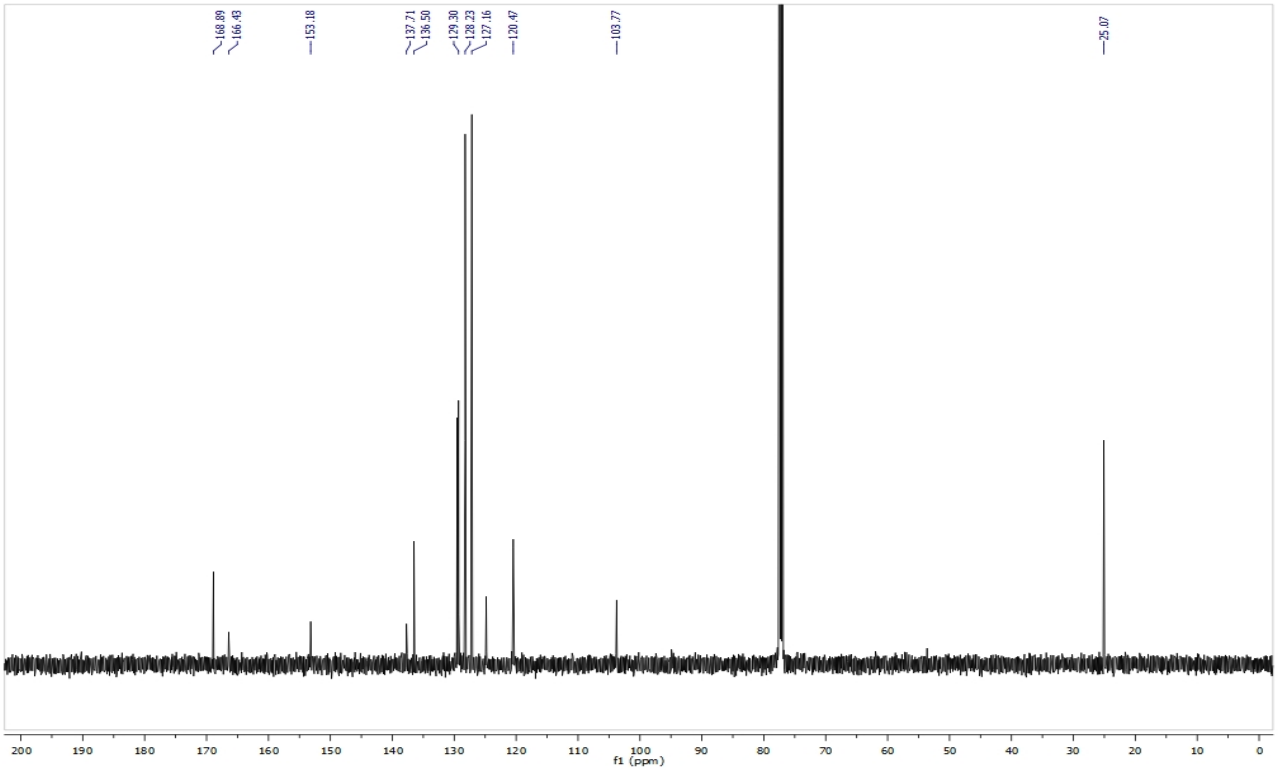
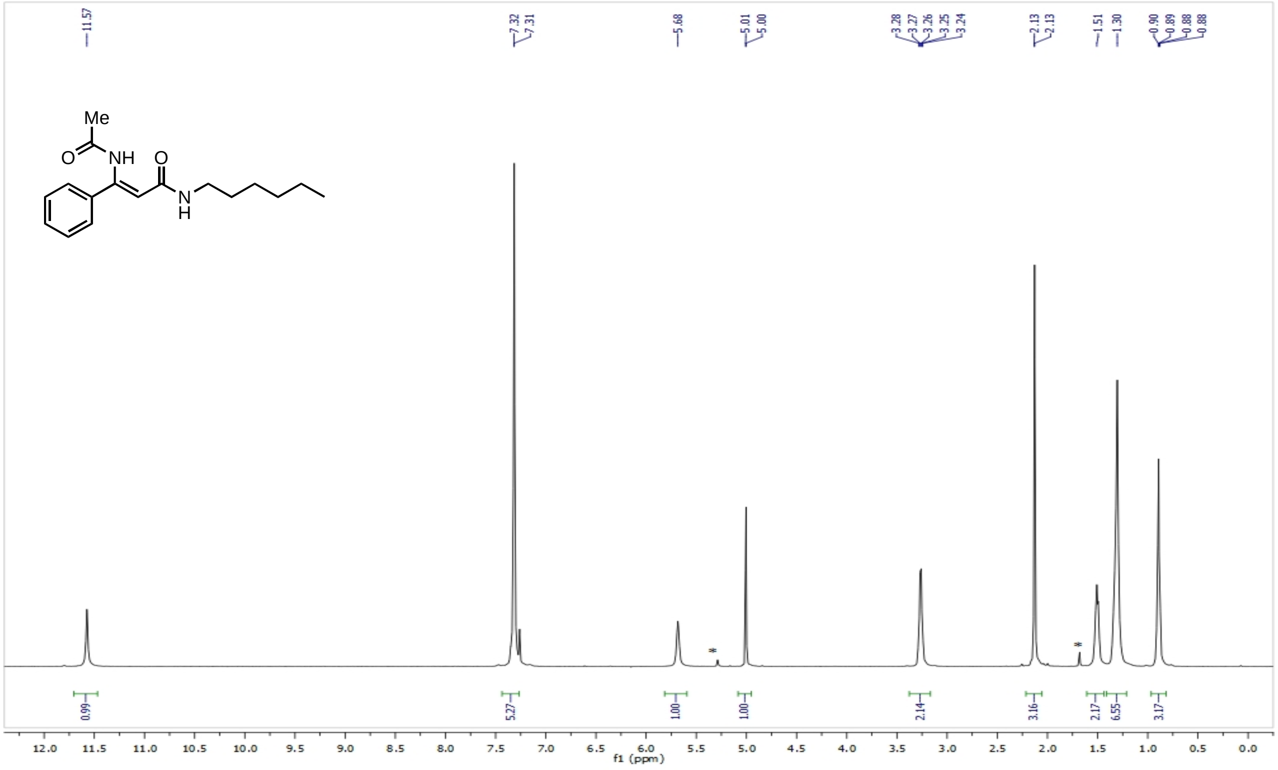

168.89
166.43
153.18
137.71
136.50
129.30
128.23
127.16
120.47
103.77
25.07
f1 (ppm)

Table 2, **3b**: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5.68
5.01
5.00
3.28
3.27
3.26
3.25
3.24
2.13
2.13
1.51
1.30
0.90
0.89
0.88
0.88
Me
O
NH
O
N
H
*
*
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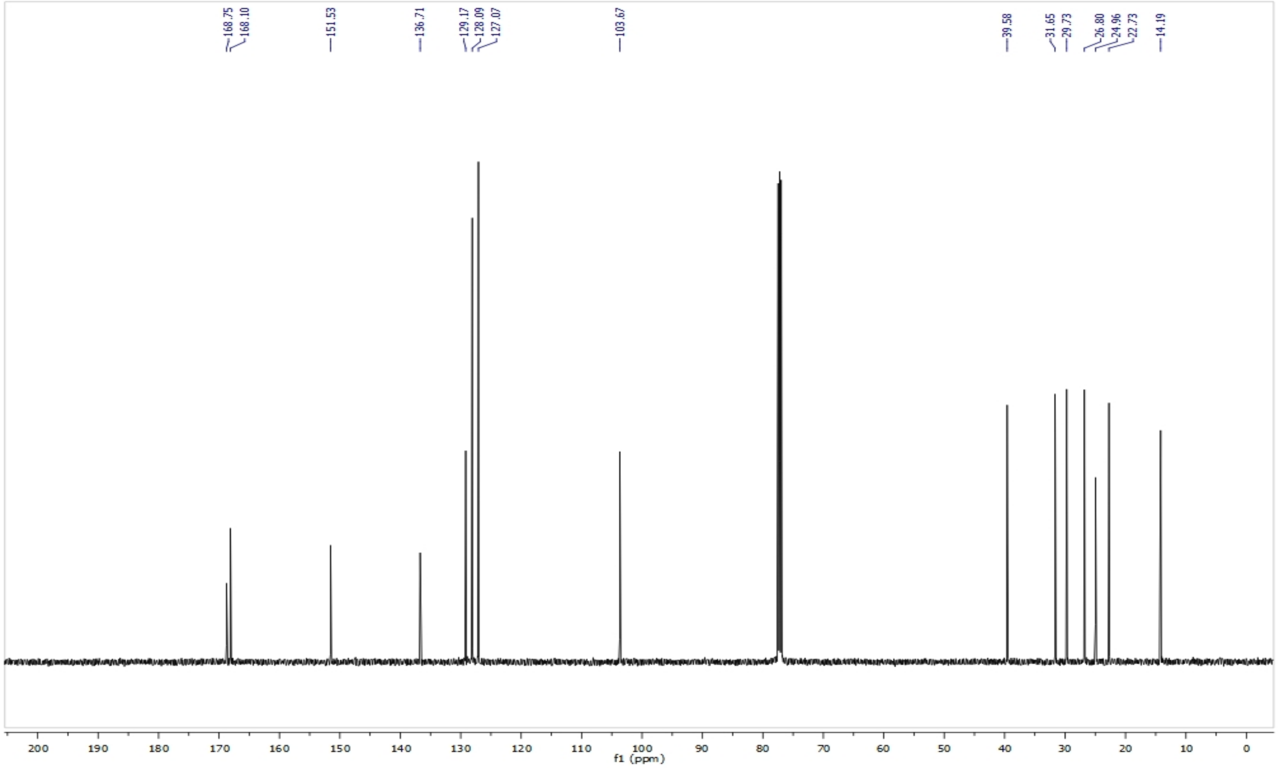
1.00
1.00
2.14
3.16
2.17
6.55
3.17
f1 (ppm)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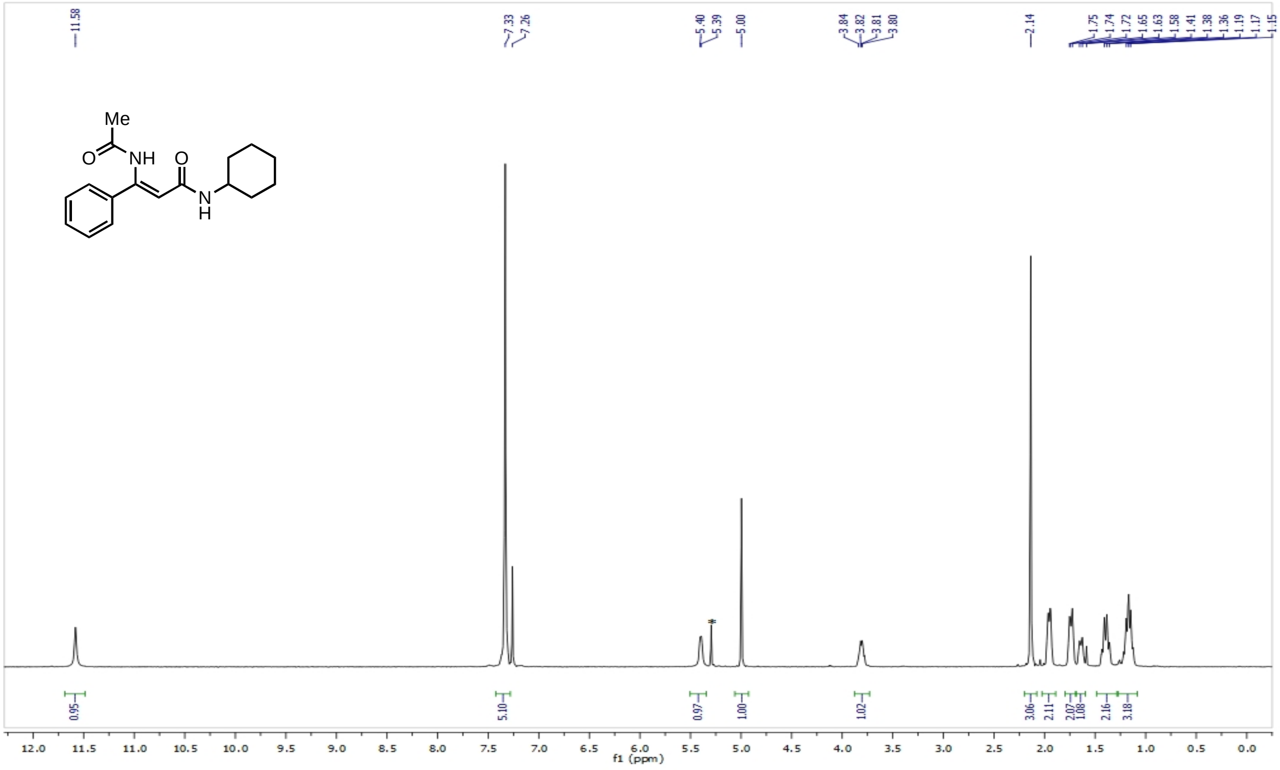
129.17
128.09
127.07
103.67
39.58
31.65
29.73
26.80
24.96
22.73
14.19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3c**:


Me
O
NH
O
N
H
11.58
7.33
7.26
5.40
5.39
5.00
3.84
3.82
3.81
3.80
2.14
1.75
1.74
1.72
1.65
1.63
1.58
1.41
1.38
1.36
1.19
1.17
1.15
0.95
5.10
0.97
1.00
1.02
3.06
2.11
2.07
1.08
2.16
3.18
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

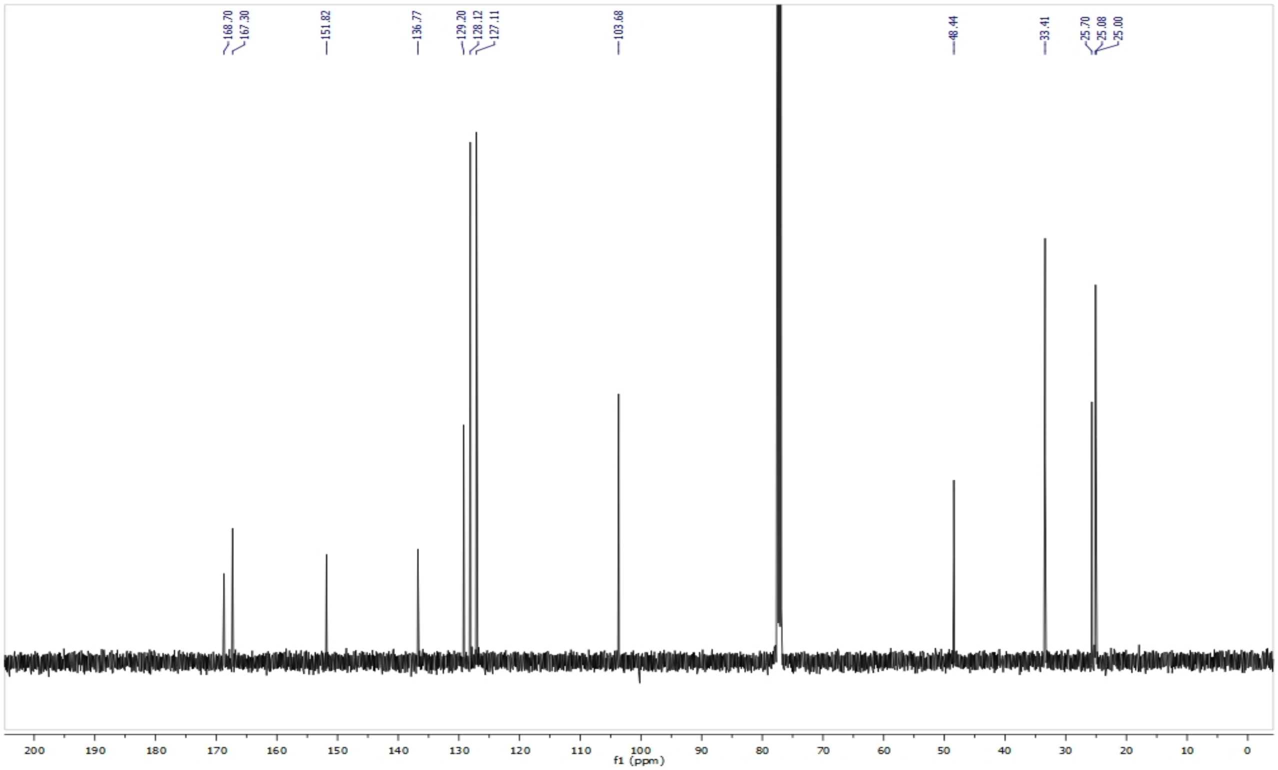
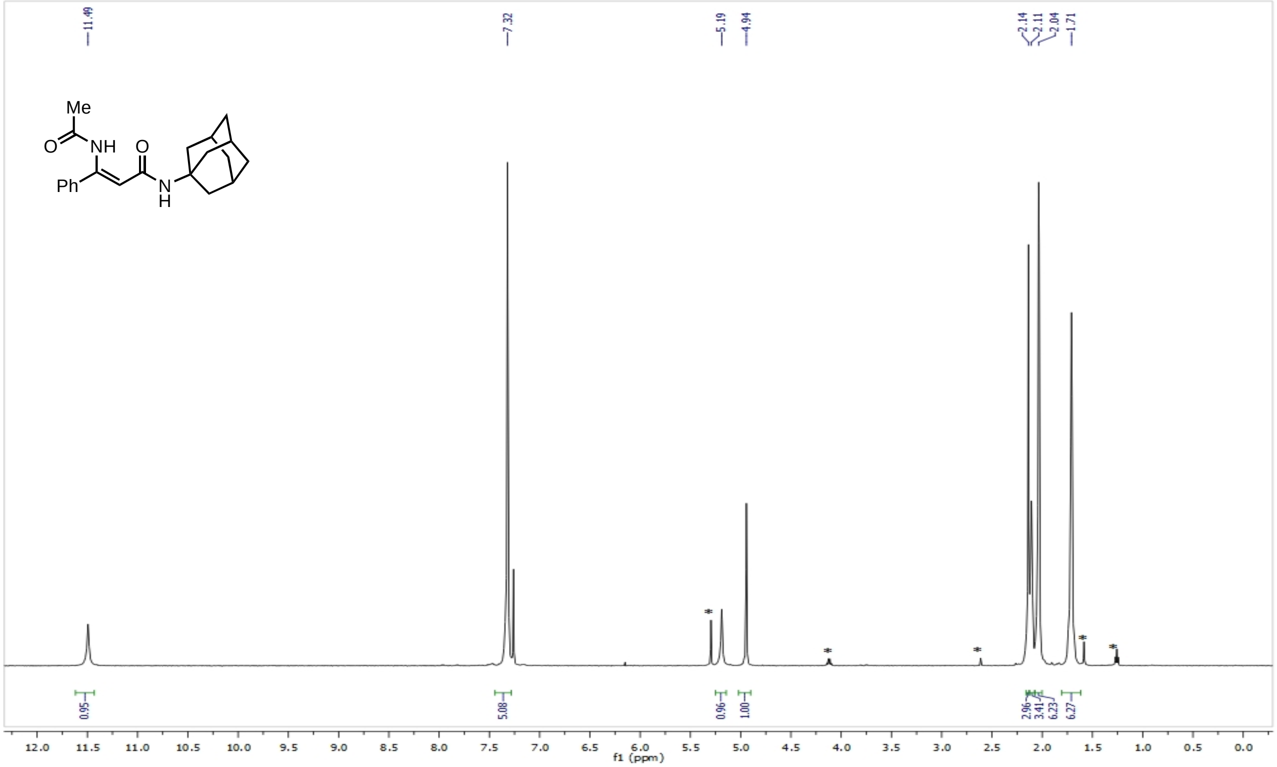

168.70
167.30
151.82
136.77
129.20
128.12
127.11
103.68
48.44
33.41
25.70
25.08
25.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3d**:


11.49
7.32
5.19
4.94
2.14
2.11
2.04
1.71
Me
O
NH
O
Ph
N
H
*
*
*
*
*
0.95
5.08
0.96
1.00
2.96
3.41
6.23
6.27
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

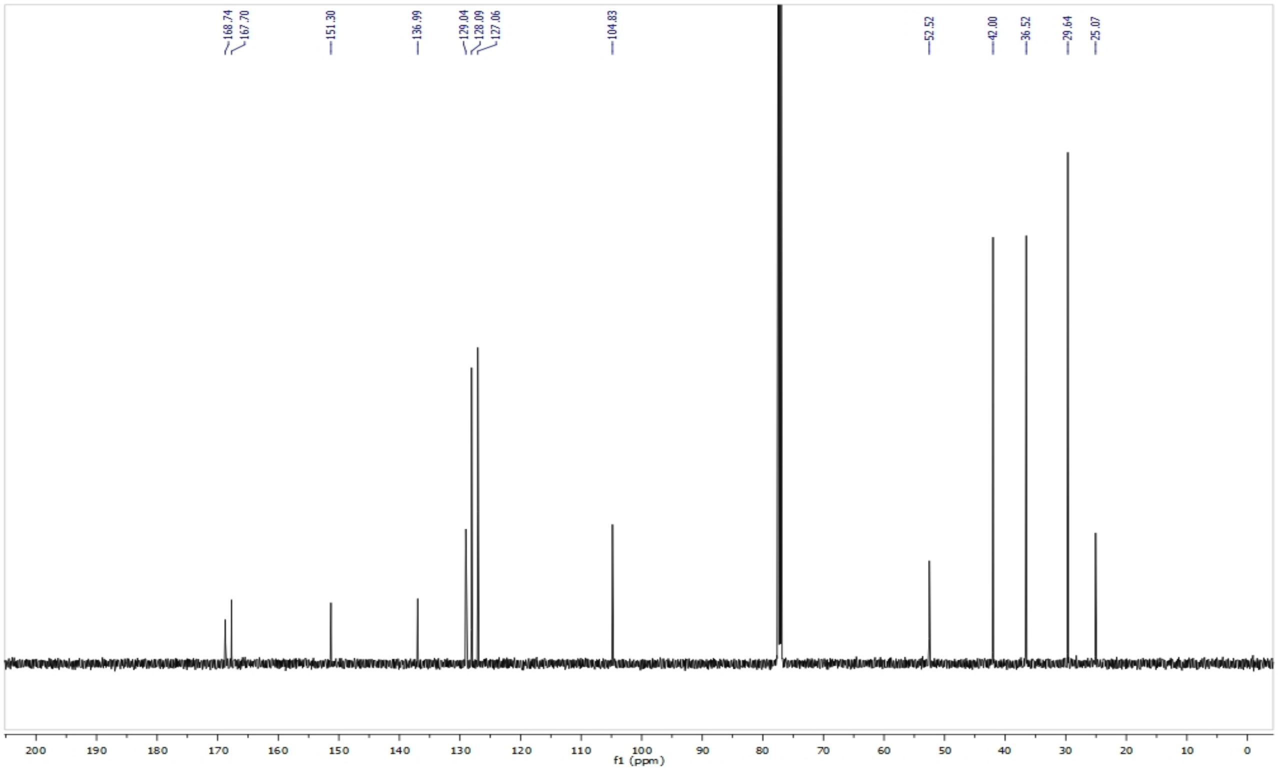
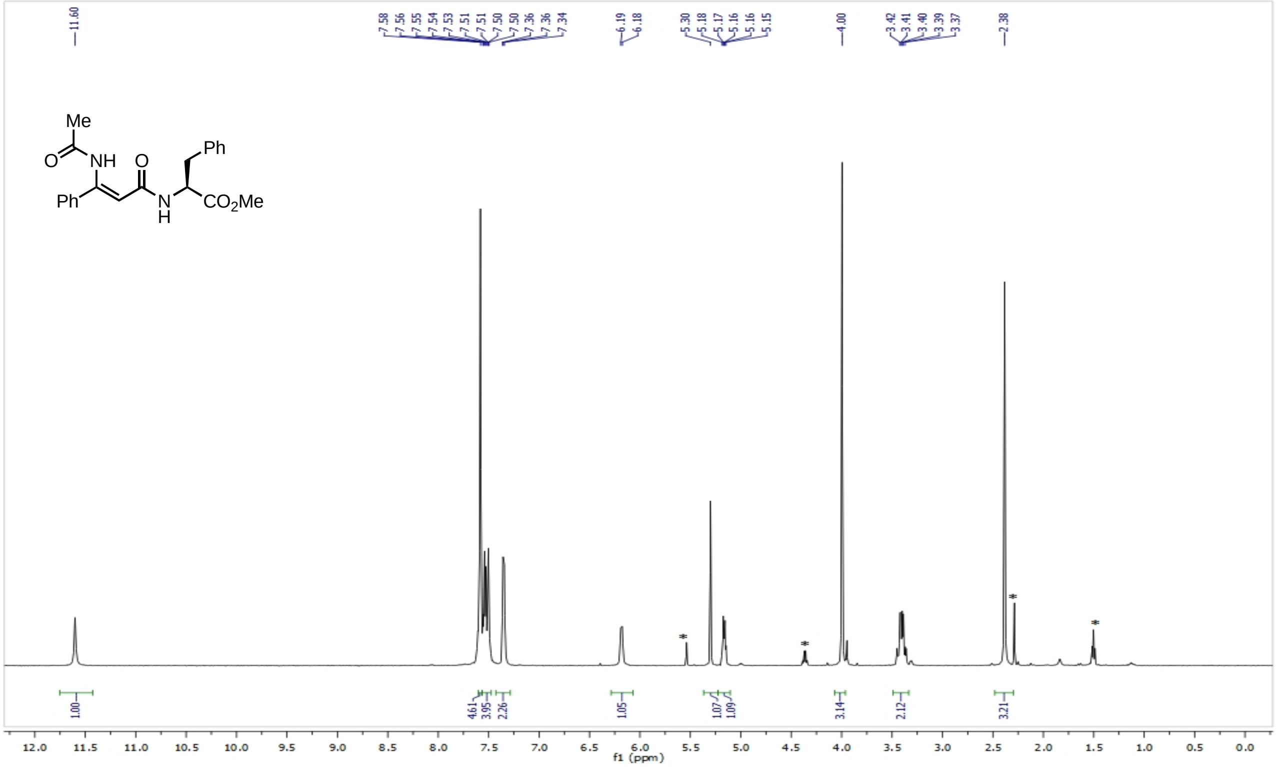

168.74
167.70
151.30
136.99
129.04
128.09
127.06
104.83
52.52
42.00
36.52
29.64
25.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3e**:


11.60
7.58
7.56
7.55
7.54
7.53
7.51
7.51
7.50
7.50
7.36
7.36
7.34
6.19
6.18
5.30
5.18
5.17
5.16
5.16
5.15
4.00
3.42
3.41
3.40
3.39
3.37
2.38
Me
O
NH
O
Ph
Ph
N
H
CO2Me
*
*
*
*
1.00
4.61
3.95
2.26
1.05
1.07
1.09
3.14
2.12
3.21
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

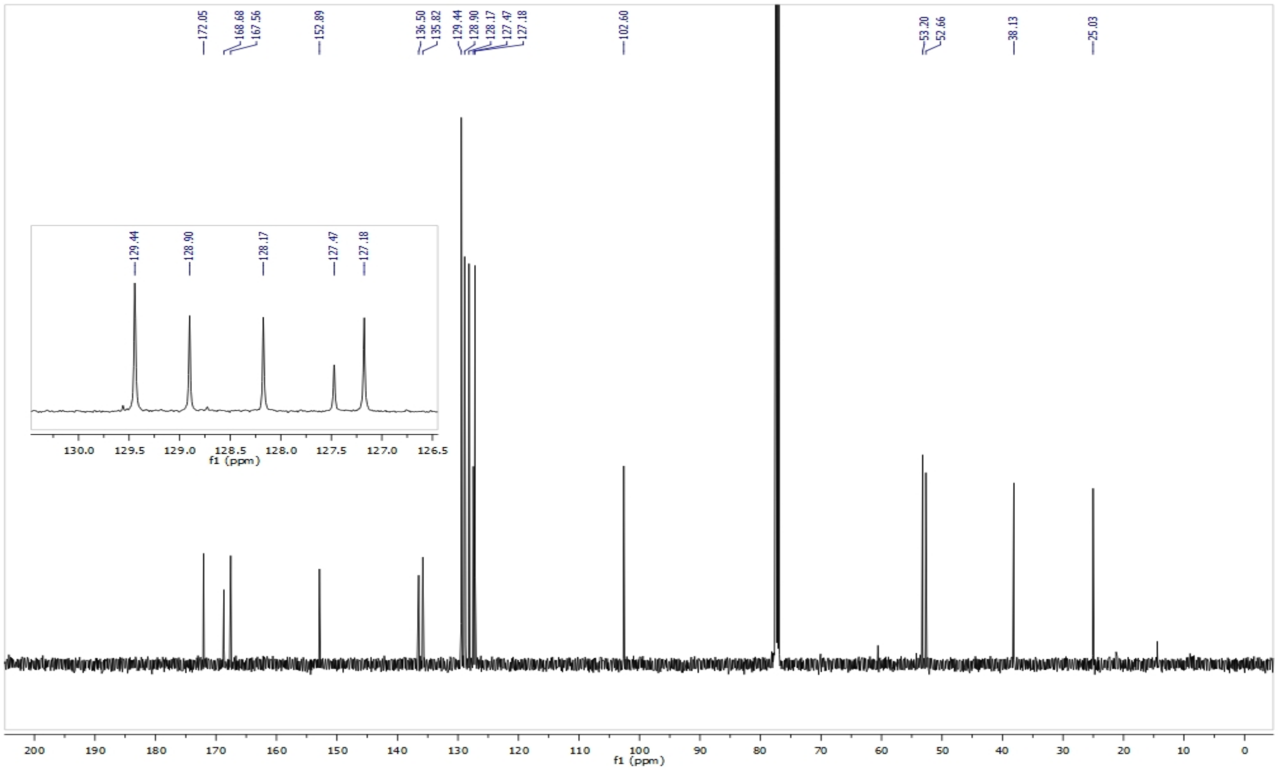
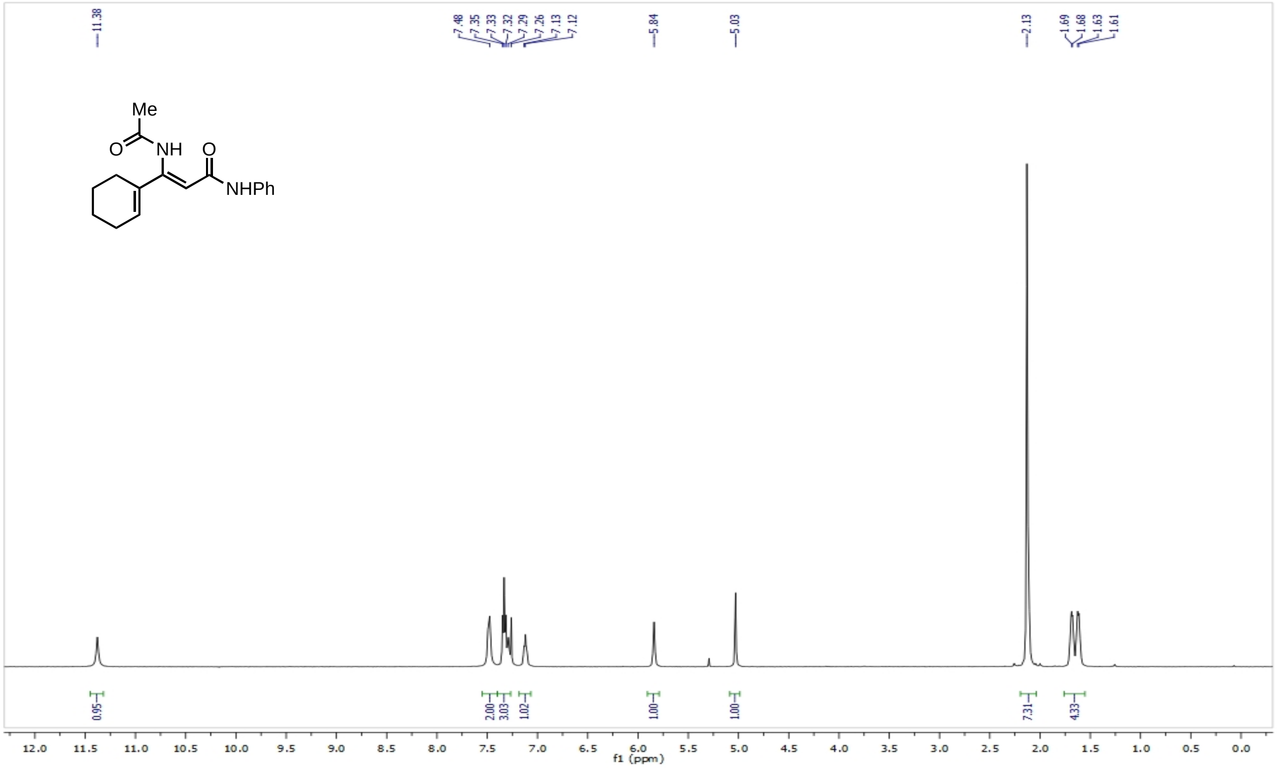

172.05
168.68
167.56
152.89
136.50
135.82
129.44
128.90
128.17
127.47
127.18
102.60
53.20
52.66
38.13
25.03
129.44
128.90
128.17
127.47
127.18
130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Table 2, **3f**:


Me
O
NH
O
NHPh
11.38
7.48
7.35
7.33
7.32
7.29
7.26
7.13
7.12
5.84
5.03
2.13
1.69
1.68
1.63
1.61
0.95
2.00
3.03
1.02
1.00
1.00
7.31
4.33
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

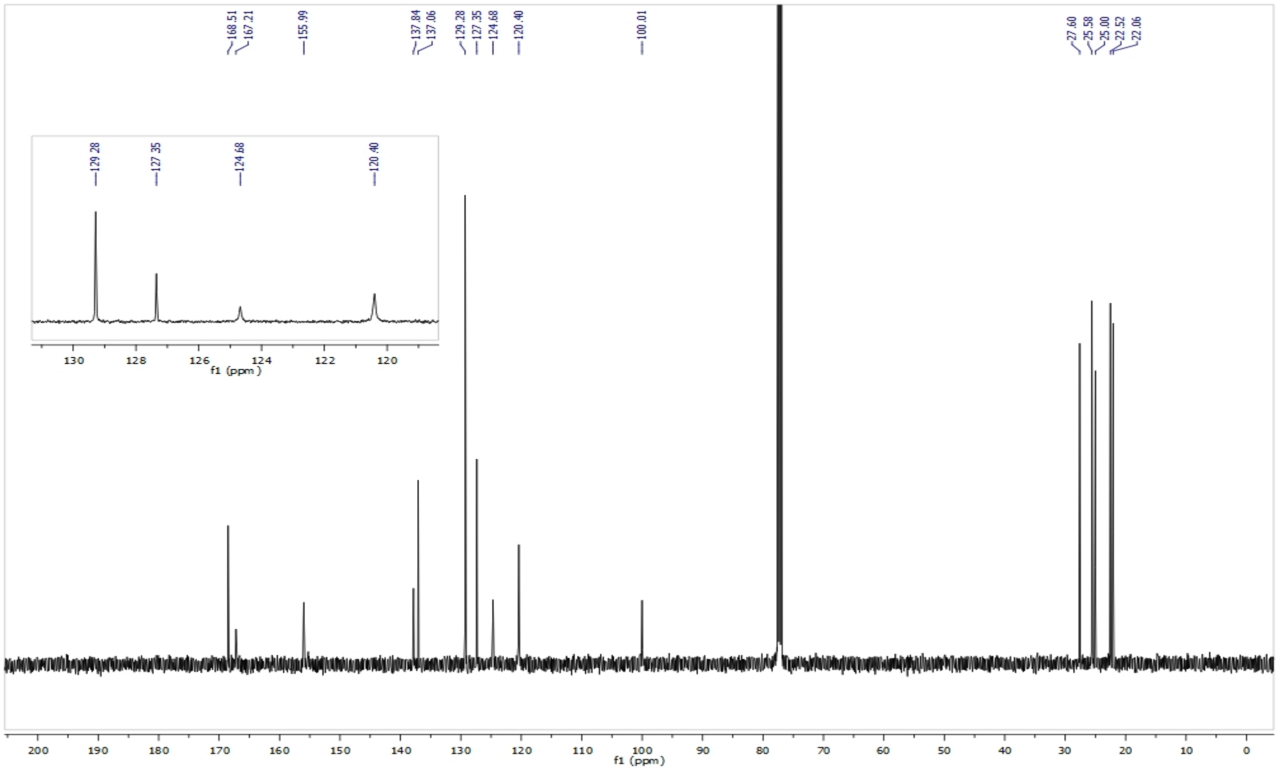
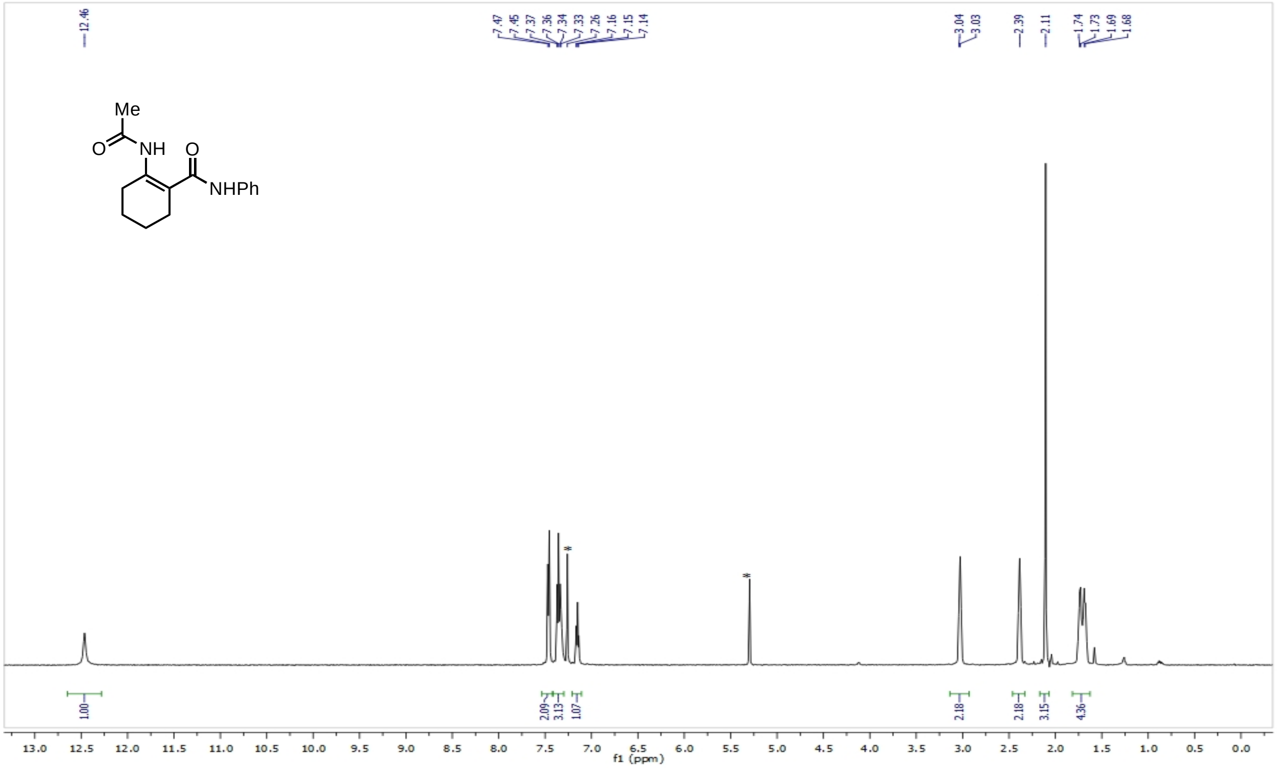

168.51
167.21
155.99
137.84
137.06
129.28
127.35
124.68
120.40
100.01
27.60
25.58
25.00
22.52
22.06
129.28
127.35
124.68
120.40
130
128
126
124
122
120
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3g**:


12.46
7.47
7.45
7.37
7.36
7.34
7.33
7.26
7.16
7.15
7.14
3.04
3.03
2.39
2.11
1.74
1.73
1.69
1.68
Me
O
NH
O
NHPh
*
*
1.00
2.09
3.13
1.07
2.18
2.18
3.15
4.36
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

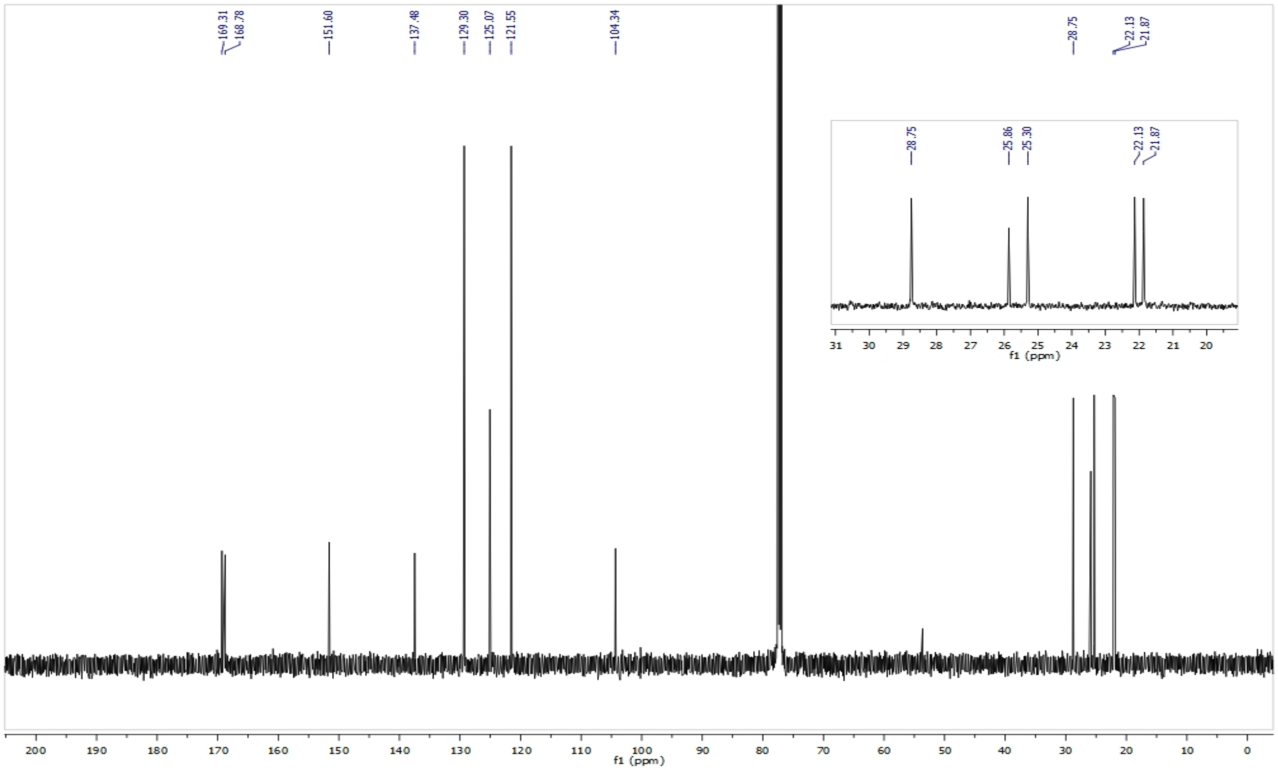
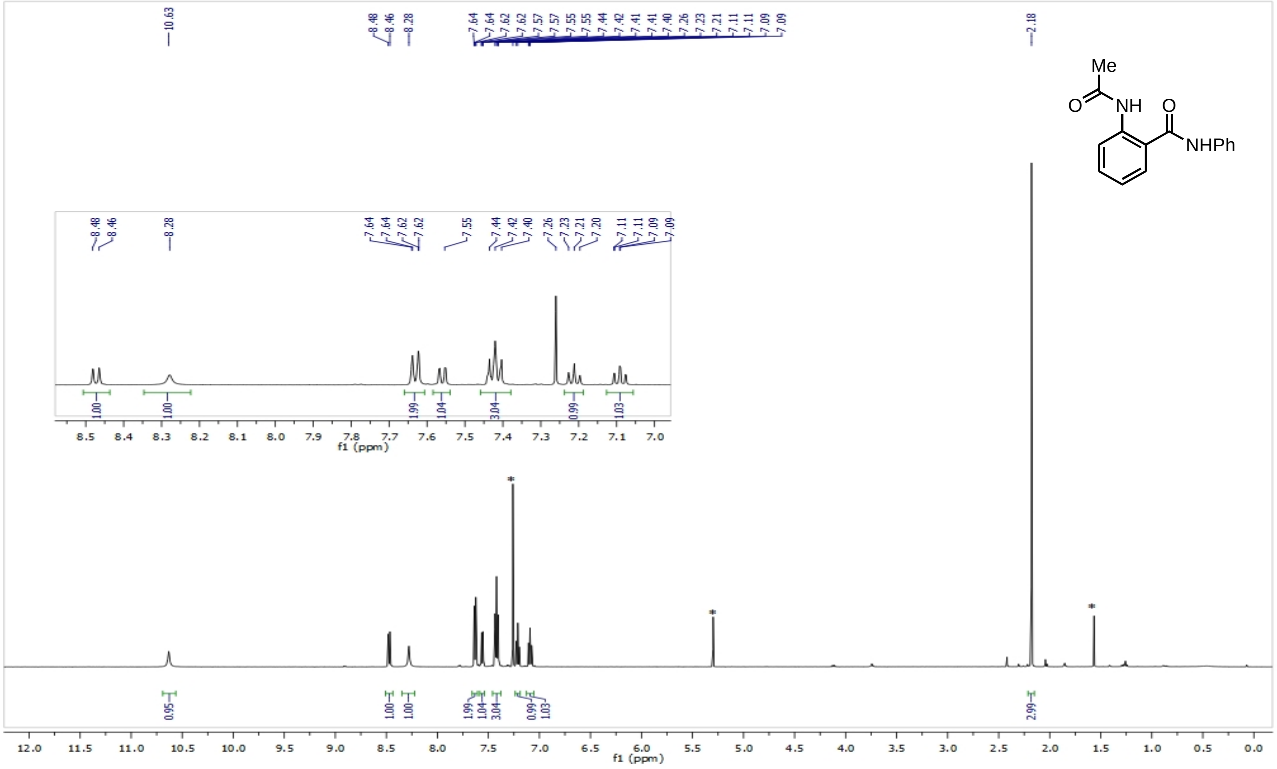

169.31
168.78
151.60
137.48
129.30
125.07
121.55
104.34
28.75
22.13
21.87
28.75
25.86
25.30
22.13
21.87
f1 (ppm)
f1 (ppm)

Table 2, **3h**:


10.63
8.48
8.46
8.28
7.64
7.64
7.62
7.62
7.57
7.55
7.55
7.44
7.42
7.41
7.41
7.40
7.26
7.23
7.21
7.11
7.11
7.09
7.09
2.18
Me
O
NH
O
NHPh
1.00
1.00
1.99
1.04
3.04
0.99
1.03
0.95
1.00
1.00
1.99
1.04
3.04
0.99
1.03
2.99
*
*
*
f1 (ppm)
f1 (ppm)

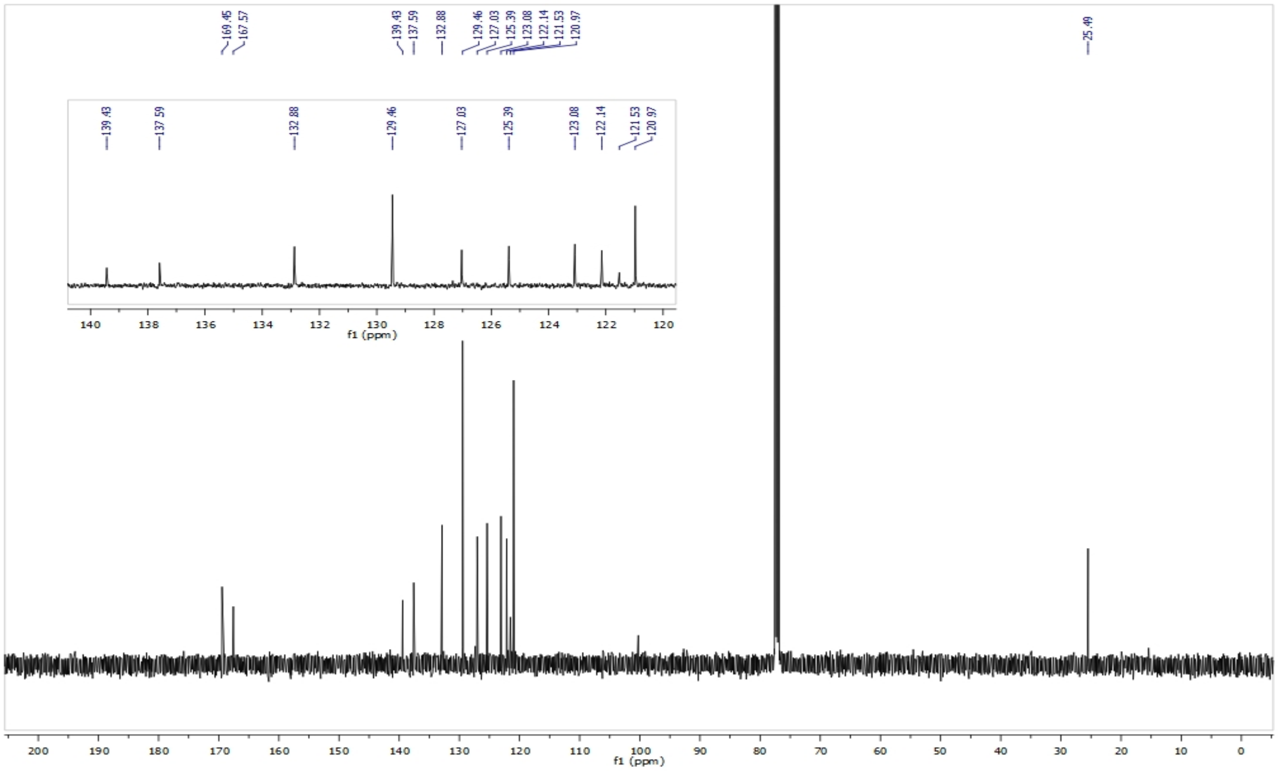
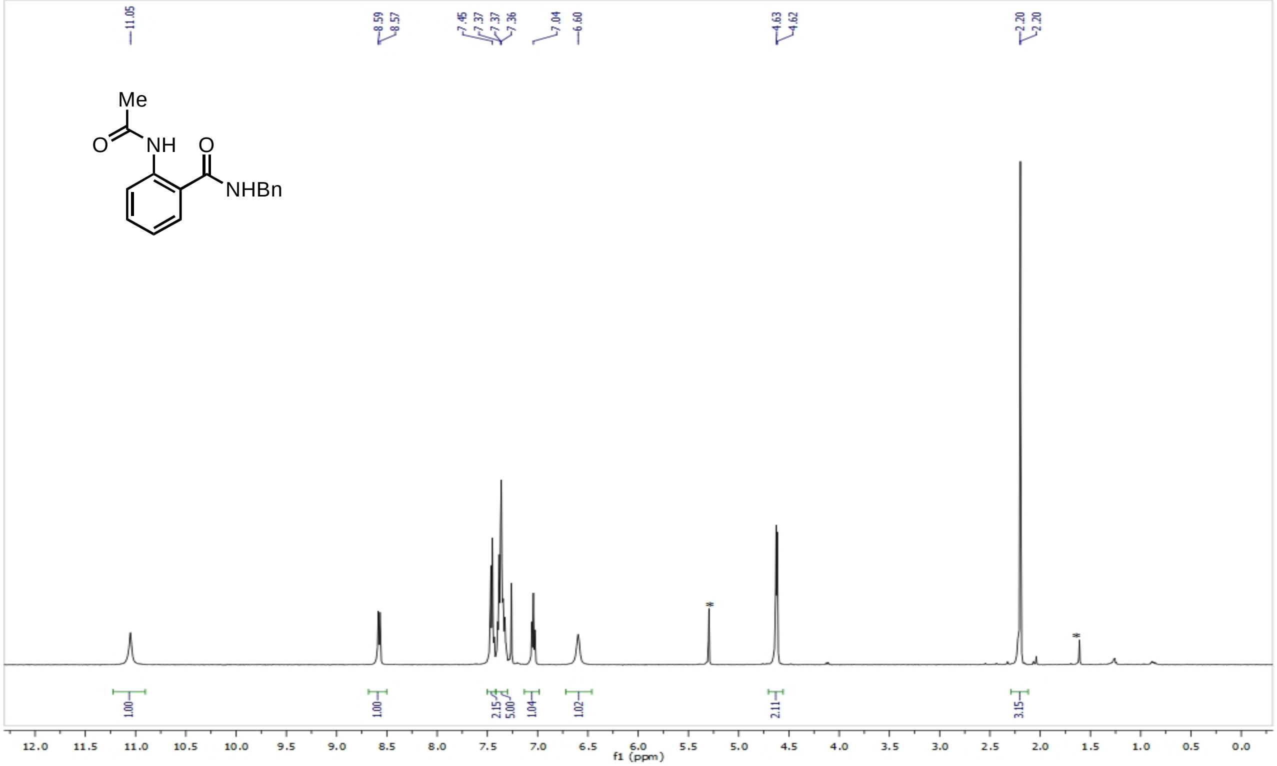

169.45
167.57
139.43
137.59
132.88
129.46
127.03
125.39
123.08
122.14
121.53
120.97
25.49
140
138
136
134
132
130
128
126
124
122
120
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3i**:


11.05
8.59
8.57
7.45
7.37
7.37
7.36
7.04
6.60
4.63
4.62
2.20
2.20
Me
O
NH
O
NHBn
*
*
1.00
1.00
2.15
5.00
1.04
1.02
2.11
3.15
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

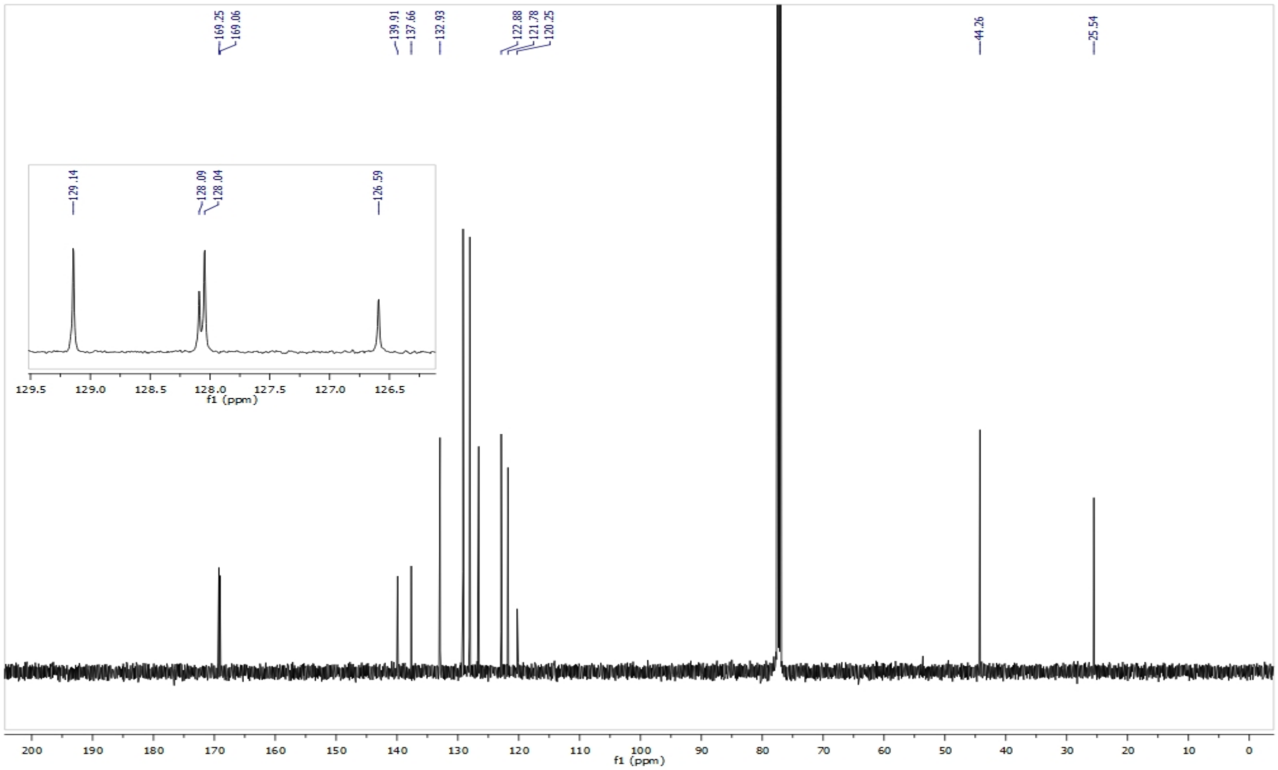
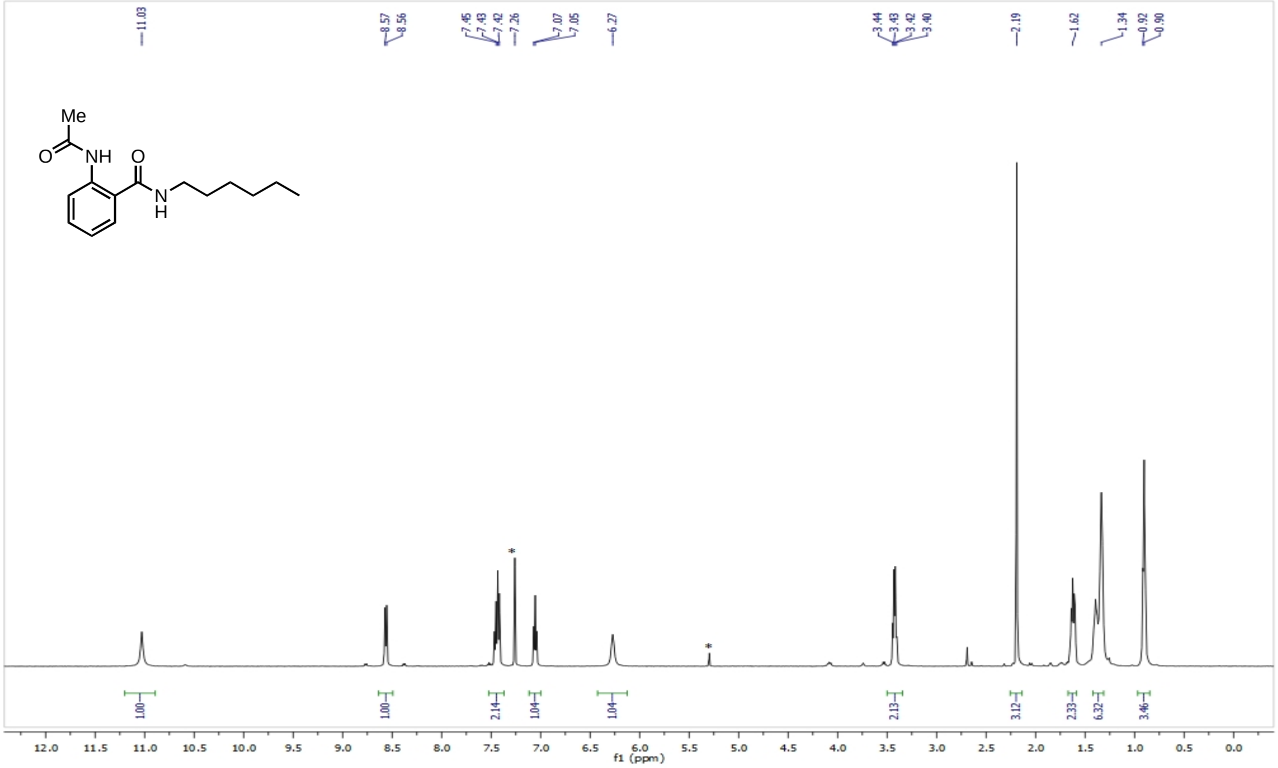

169.25
169.06
139.91
137.66
132.93
122.88
121.78
120.25
44.26
25.54
129.14
128.09
128.04
126.59
129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Table 2, **3j**:


11.03
8.57
8.56
7.45
7.43
7.42
7.26
7.07
7.05
6.27
3.44
3.43
3.42
3.40
2.19
1.62
1.34
0.92
0.90
Me
O
NH
O
N
H
*
*
1.00
1.00
2.14
1.04
1.04
2.13
3.12
2.33
6.32
3.46
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

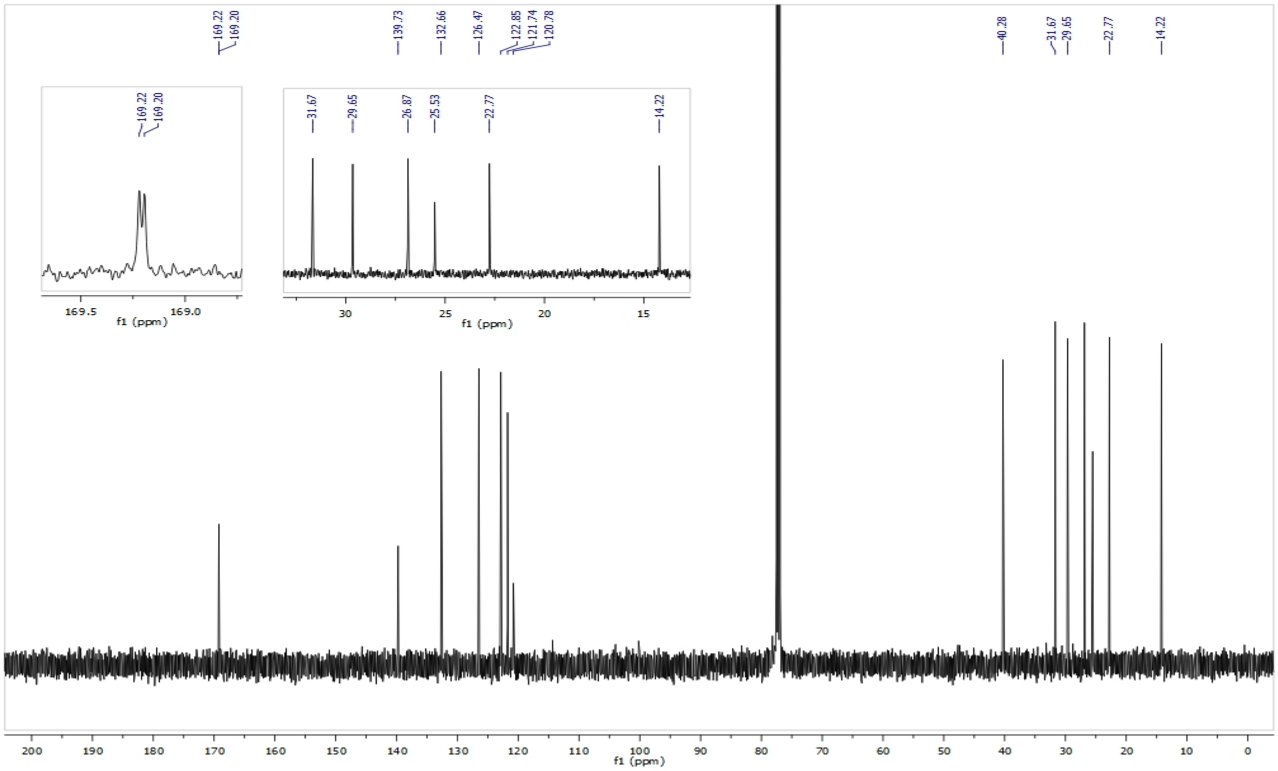
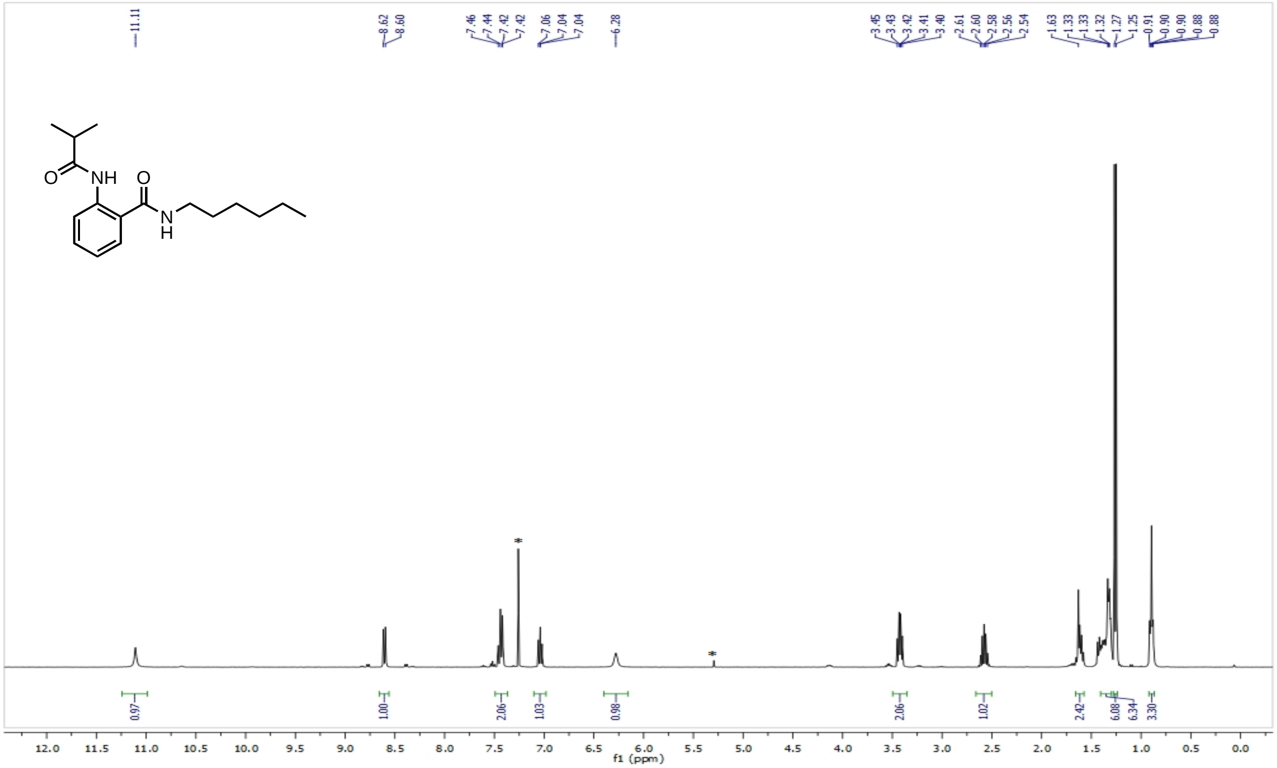
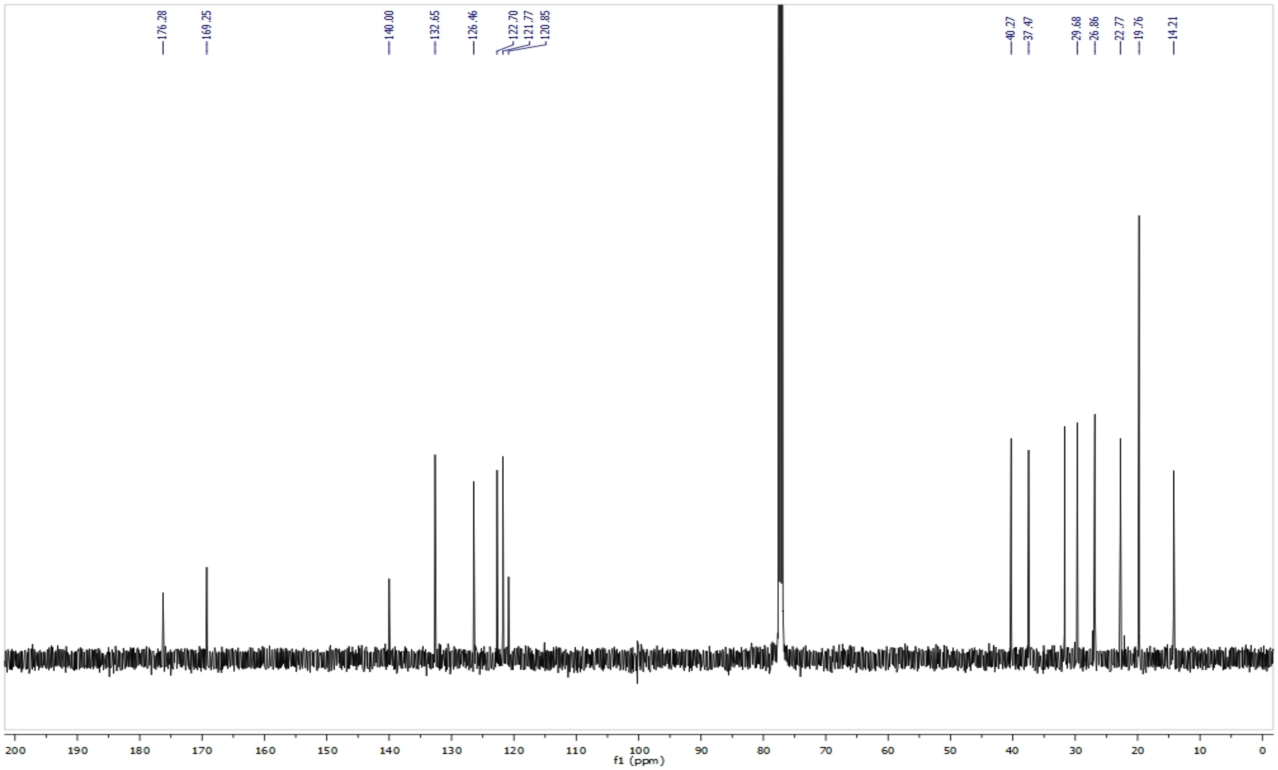

169.22
169.20
139.73
132.66
126.47
122.85
121.74
120.78
40.28
31.67
29.65
22.77
14.22
169.22
169.20
169.5
169.0
f1 (ppm)
31.67
29.65
26.87
25.53
22.77
14.22
30
25
20
15
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

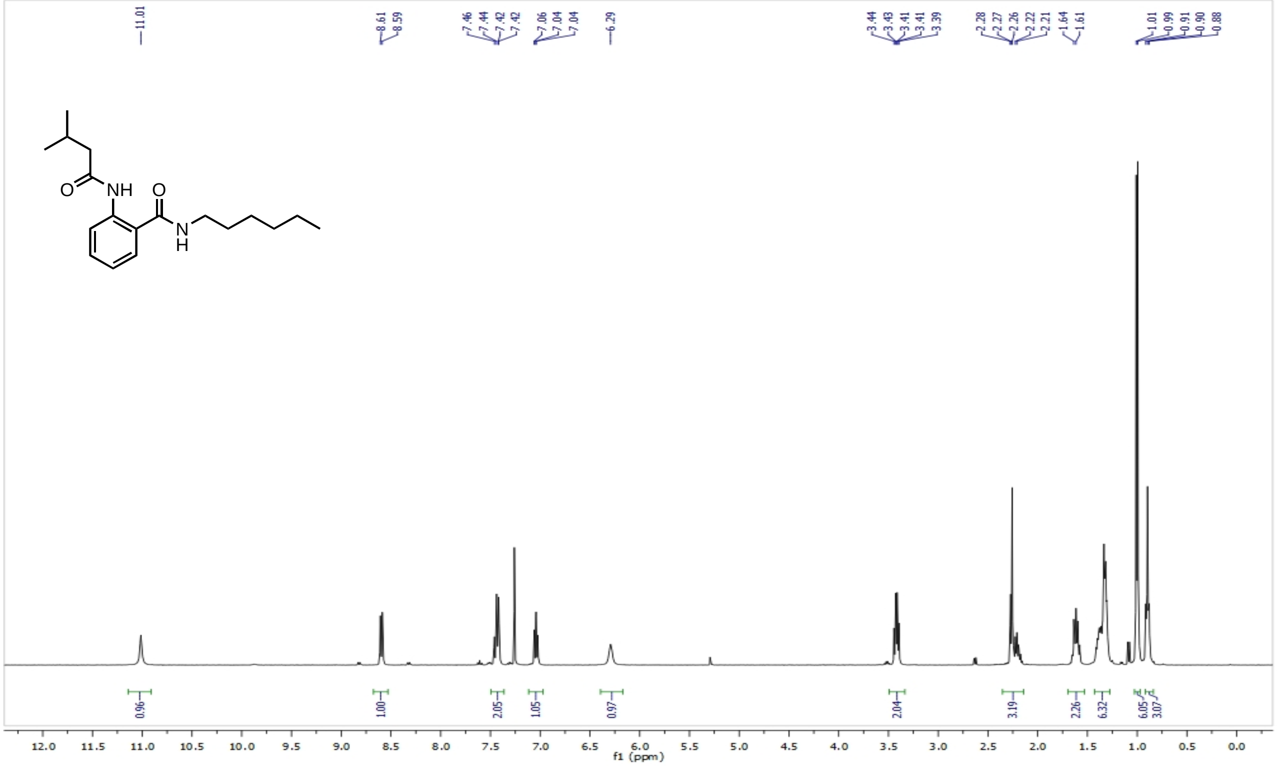
Table 2, **3k**:


11.11
8.62
8.60
7.46
7.44
7.42
7.42
7.06
7.04
7.04
6.28
3.45
3.43
3.42
3.41
3.40
2.61
2.60
2.58
2.56
2.54
1.63
1.33
1.33
1.32
1.27
1.25
0.91
0.90
0.90
0.88
0.88
O
NH
O
N
H
*
*
0.97
1.00
2.06
1.03
0.98
2.06
1.02
2.42
6.08
6.34
3.30
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



176.28
169.25
140.00
132.65
126.46
122.70
121.77
120.85
40.27
37.47
29.68
26.86
22.77
19.76
14.21
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Table 2, **3l**:



11.01
8.61
8.59
7.46
7.44
7.42
7.42
7.06
7.04
7.04
6.29
3.44
3.43
3.41
3.41
3.39
2.28
2.27
2.26
2.22
2.21
1.64
1.61
1.01
0.99
0.91
0.90
0.88
O
NH
O
N
H
0.96
1.00
2.05
1.05
0.97
2.04
3.19
2.26
6.32
6.05
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

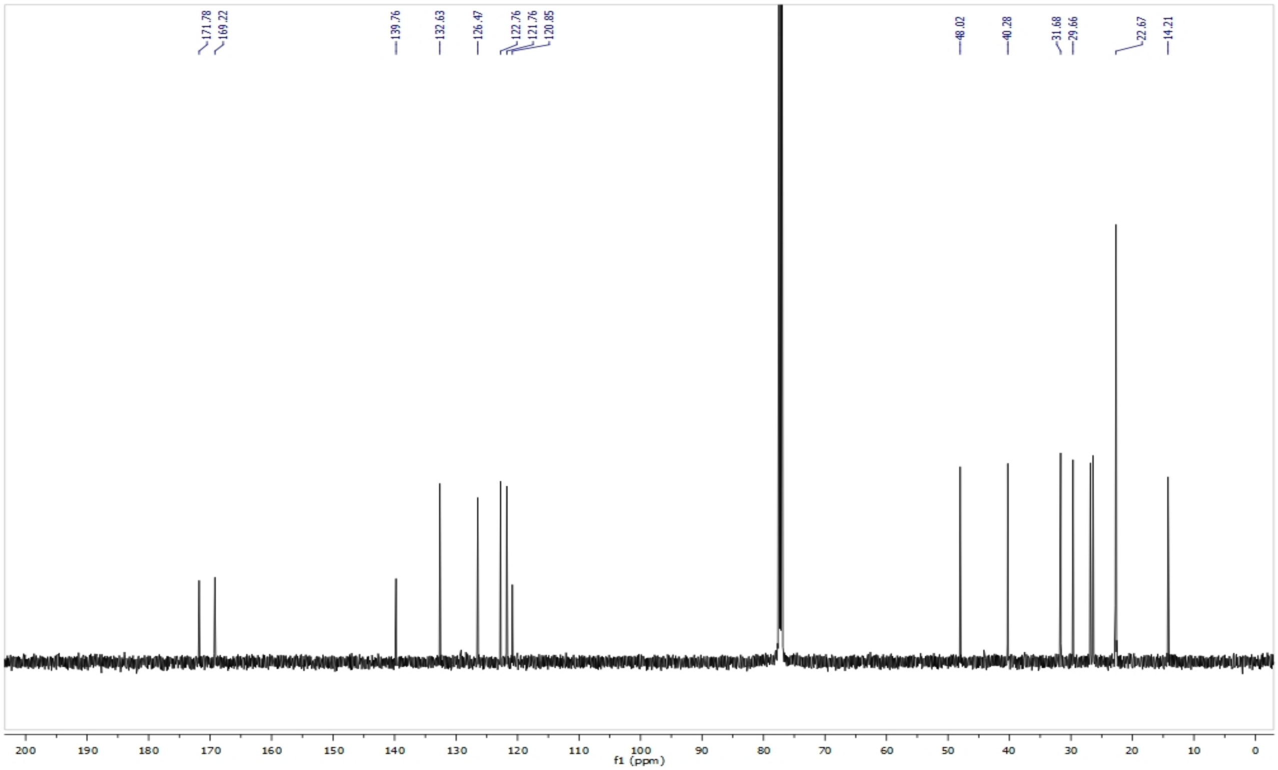
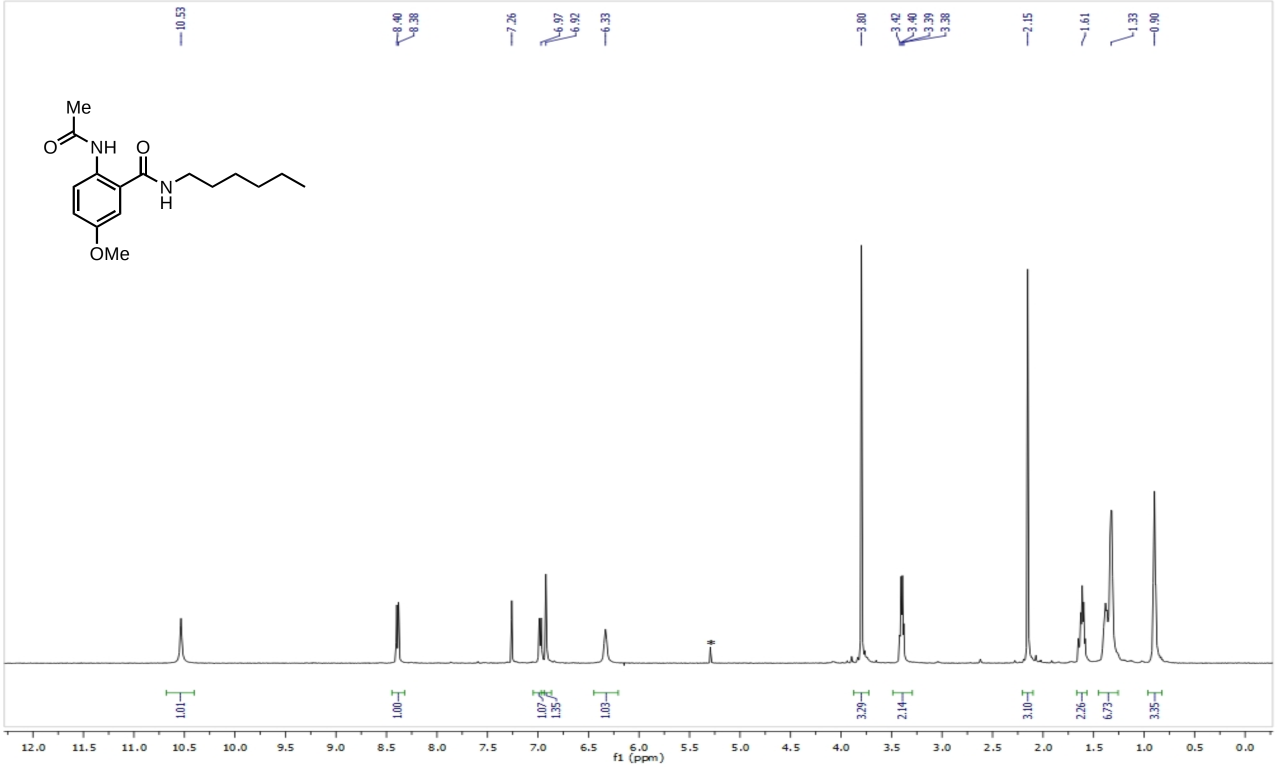

171.78
169.22
139.76
132.63
126.47
122.76
121.76
120.85
48.02
40.28
31.68
29.66
22.67
14.21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3m**:


10.53
8.40
8.38
7.26
6.97
6.92
6.33
3.80
3.42
3.40
3.39
3.38
2.15
1.61
1.33
0.90
Me
O
NH
O
N
H
OMe
*
1.01
1.00
1.07
1.35
1.03
3.29
2.14
3.10
2.26
6.73
3.35
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

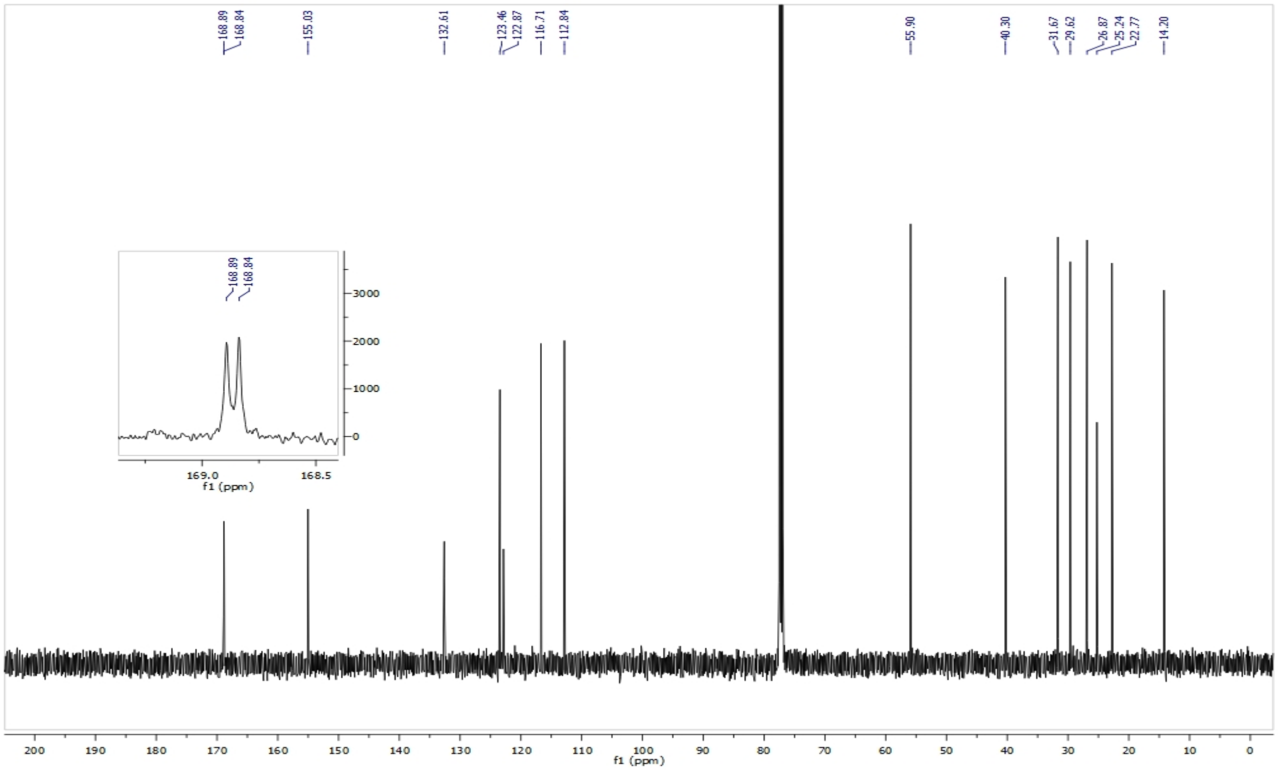
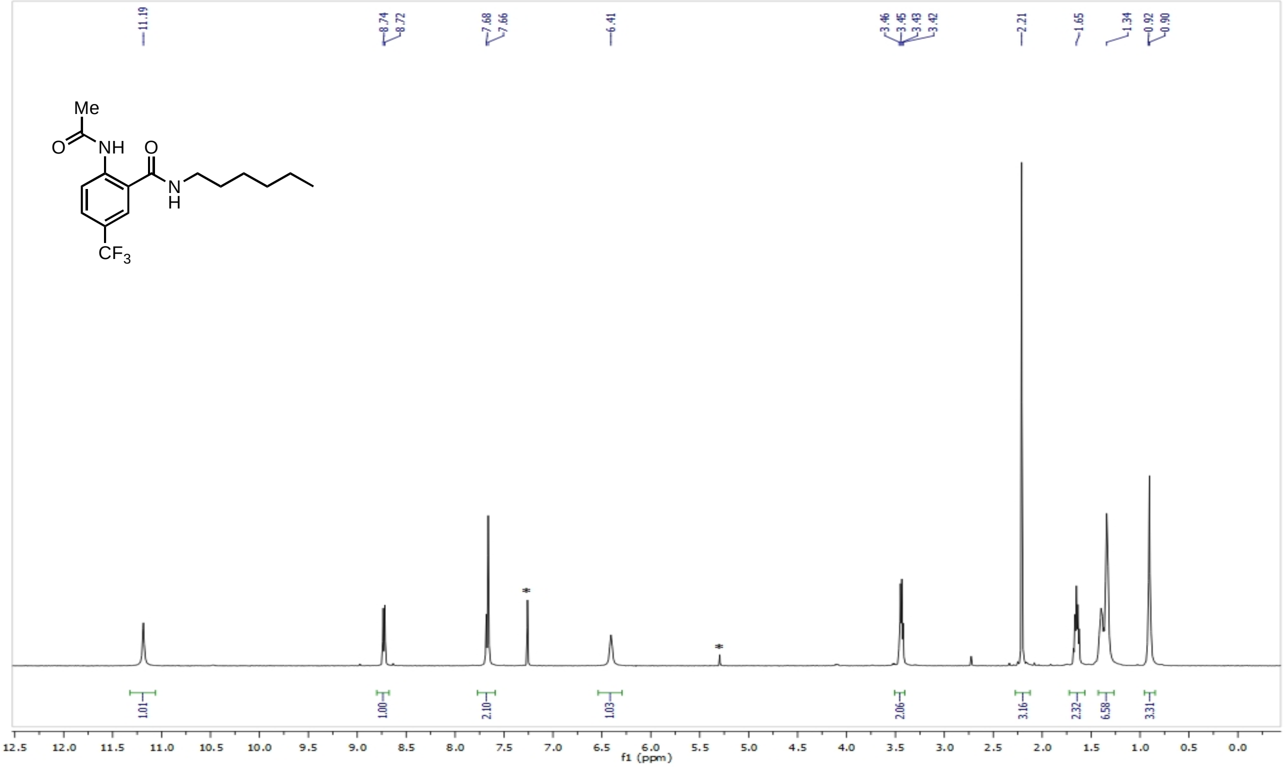

168.89
168.84
155.03
132.61
123.46
122.87
116.71
112.84
55.90
40.30
31.67
29.62
26.87
25.24
22.77
14.20
3000
2000
1000
0
169.0
168.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Table 2, **3n**:


11.19
8.74
8.72
7.68
7.66
6.41
3.46
3.45
3.43
3.42
2.21
1.65
1.34
0.92
0.90
Me
O
NH
O
N
H
CF3
*
*
1.01
1.00
2.10
1.03
2.06
3.16
2.32
6.58
3.31
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

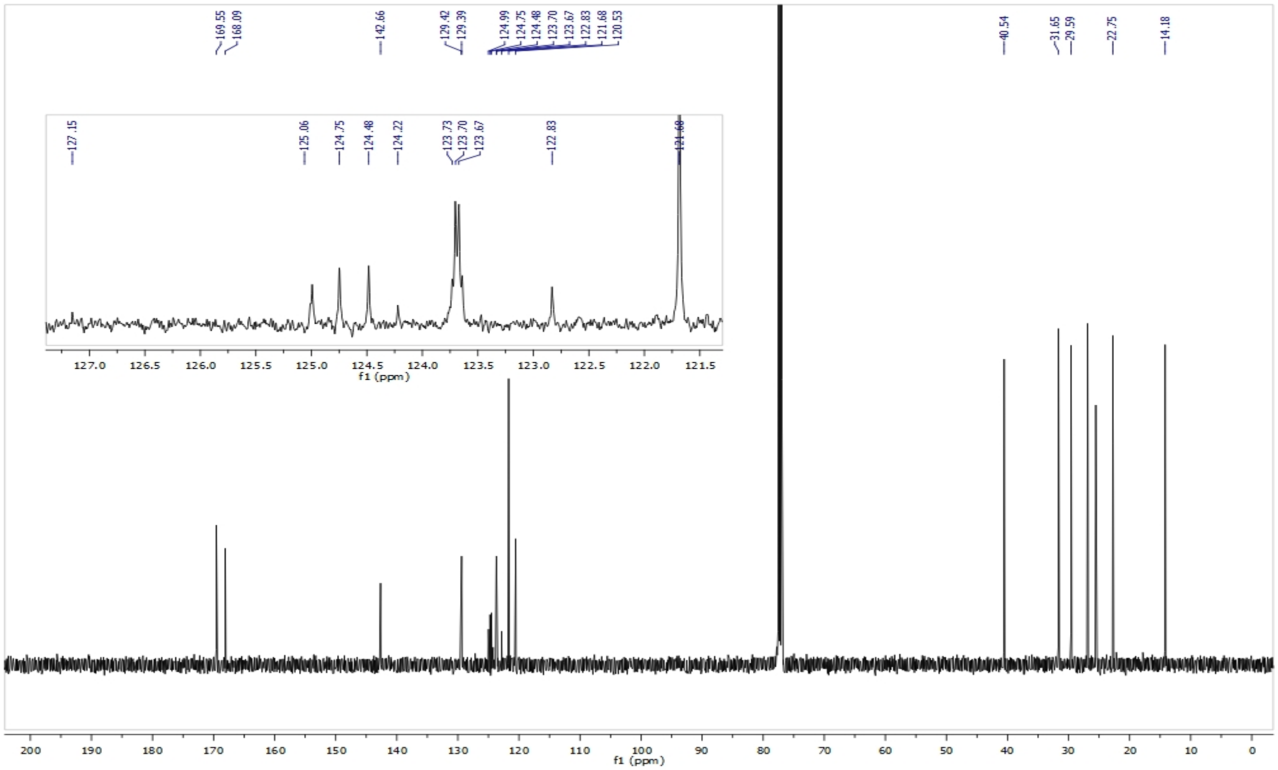
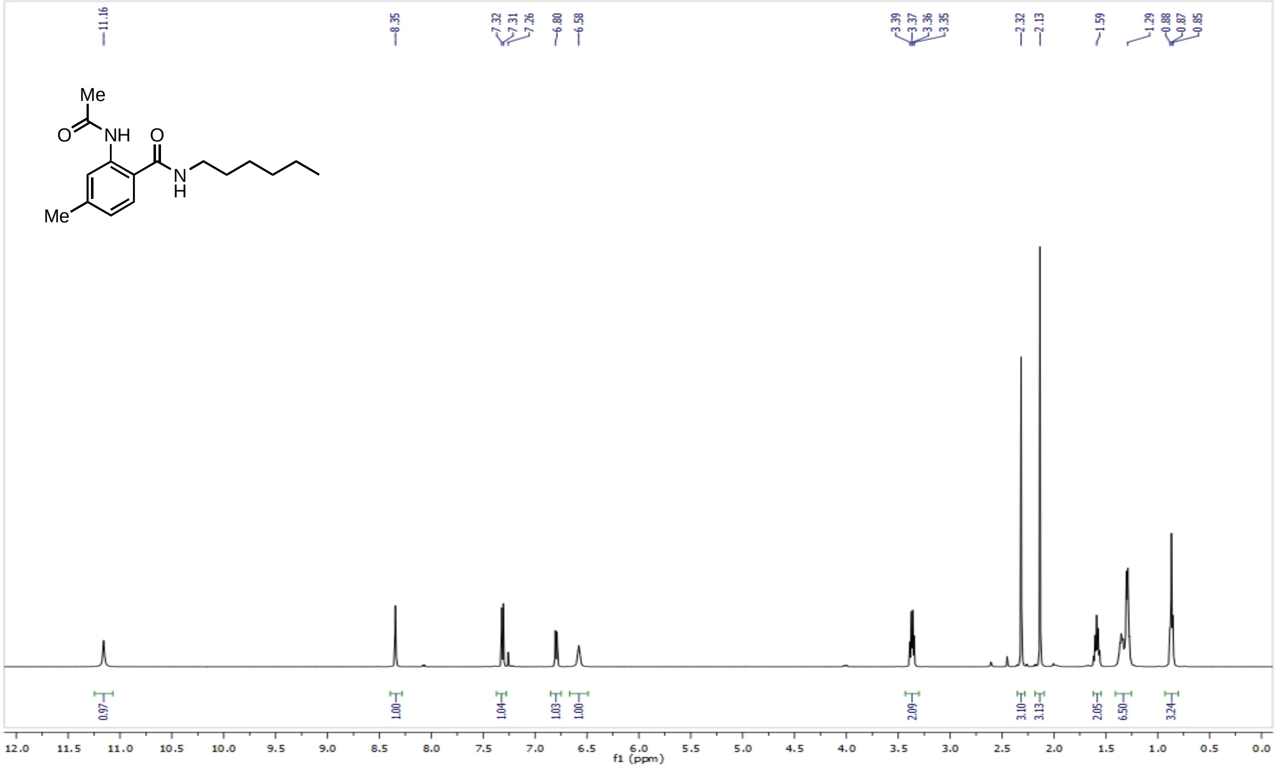

169.55
168.09
142.66
129.42
129.39
124.99
124.75
124.48
123.70
123.67
122.83
121.68
120.53
40.54
31.65
29.59
22.75
14.18
127.15
125.06
124.75
124.48
124.22
123.73
123.70
123.67
122.83
121.68
f1 (ppm)
f1 (ppm)

Table 2, **3o**:


11.16
8.35
7.32
7.31
7.26
6.80
6.58
3.39
3.37
3.36
3.35
2.32
2.13
1.59
1.29
0.88
0.87
0.85
Me
O
NH
O
N
H
Me
0.97
1.00
1.04
1.03
1.00
2.09
3.10
3.13
2.05
6.50
3.24
f1 (ppm)

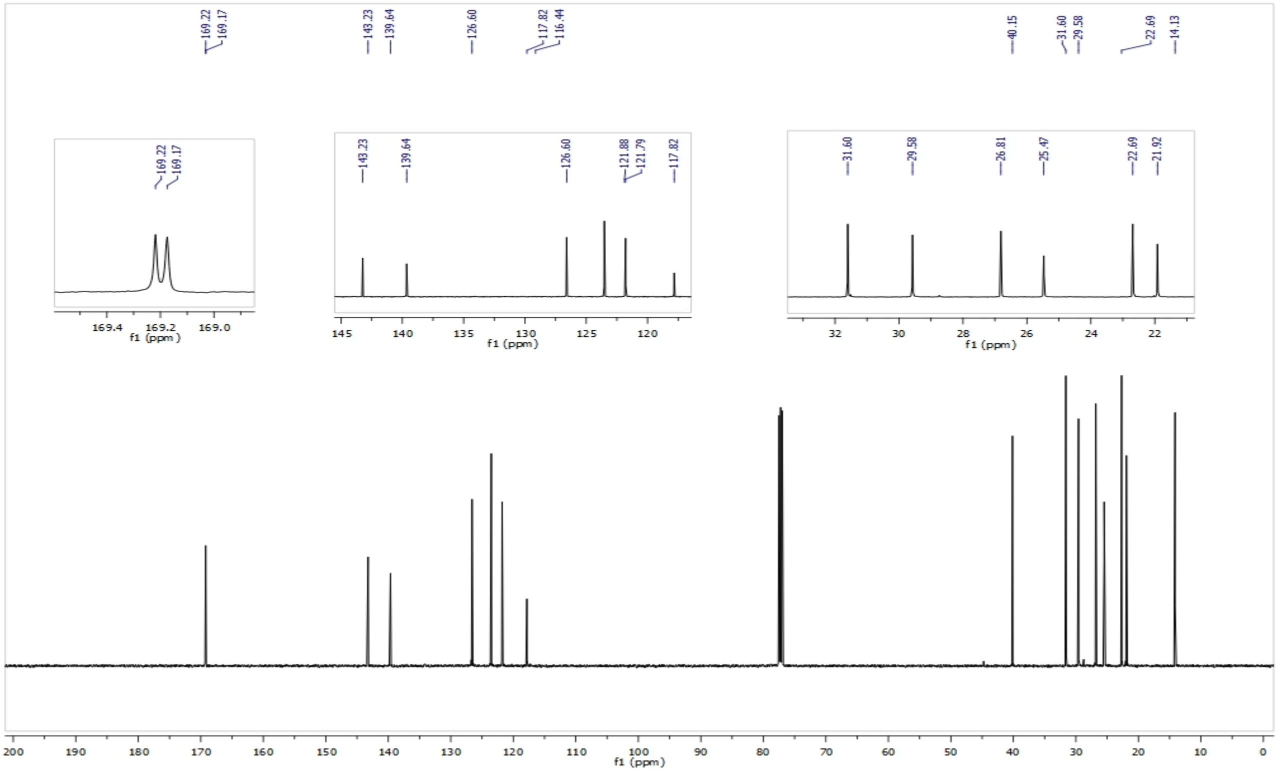
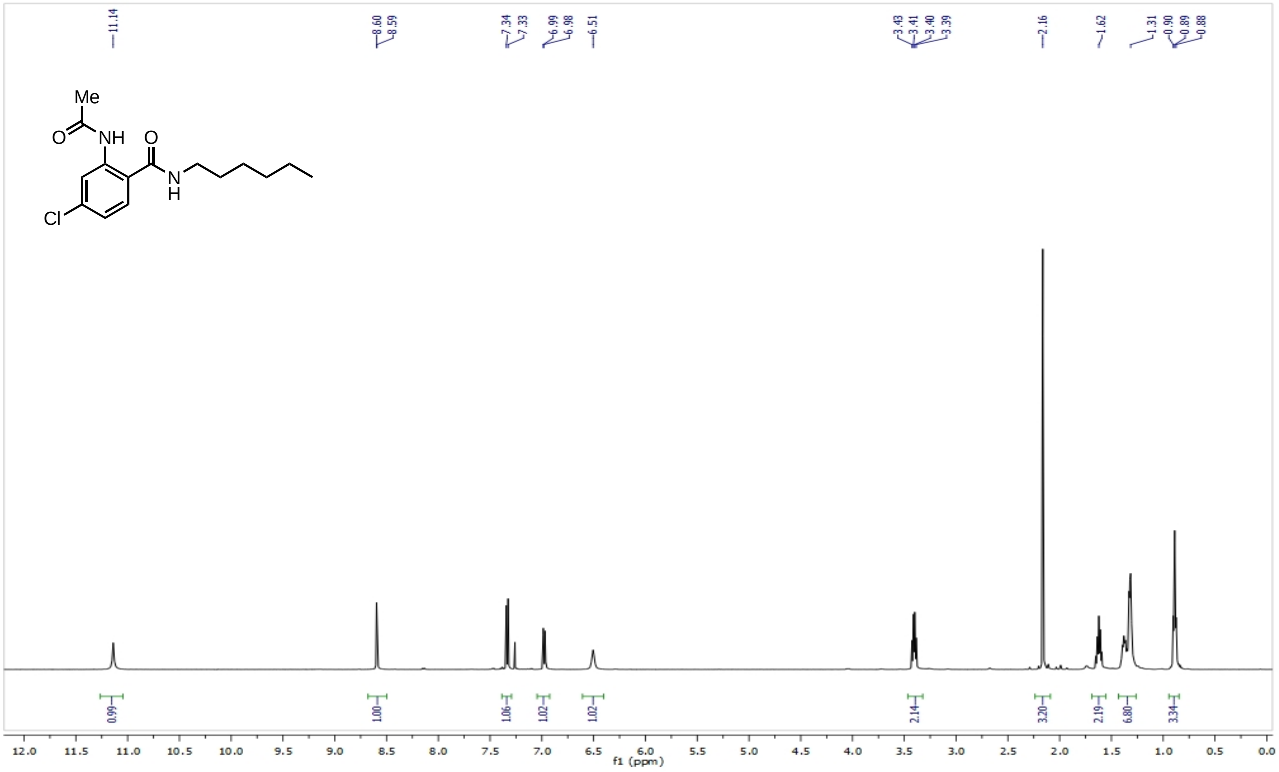

169.22
169.17
143.23
139.64
126.60
117.82
116.44
40.15
31.60
29.58
22.69
14.13
169.22
169.17
169.4
169.2
169.0
f1 (ppm)
143.23
139.64
126.60
121.88
121.79
117.82
145
140
135
130
125
120
f1 (ppm)
31.60
29.58
26.81
25.47
22.69
21.92
32
30
28
26
24
22
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3p**:


11.14
8.60
8.59
7.34
7.33
6.99
6.98
6.51
3.43
3.41
3.40
3.39
2.16
1.62
1.31
0.90
0.89
0.88
Me
O
NH
O
N
H
Cl
0.99
1.00
1.06
1.02
1.02
2.14
3.20
2.19
6.80
3.34
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

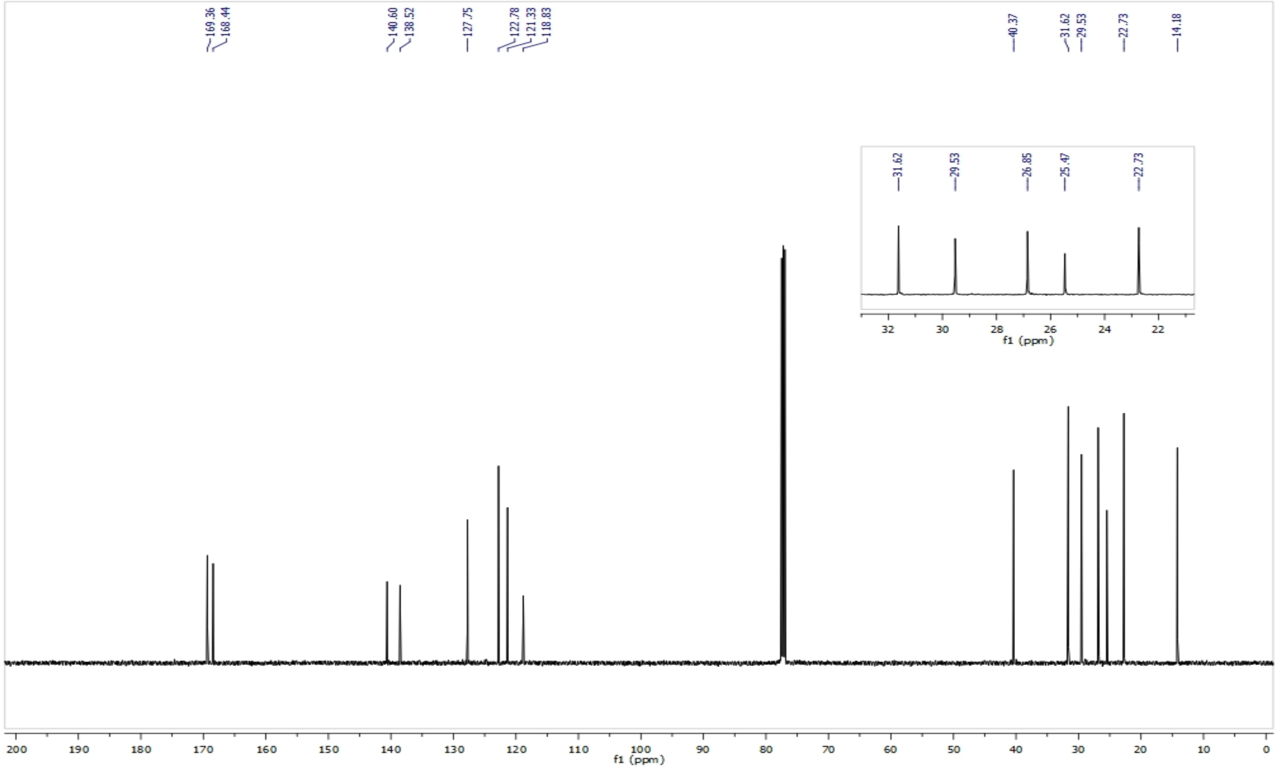
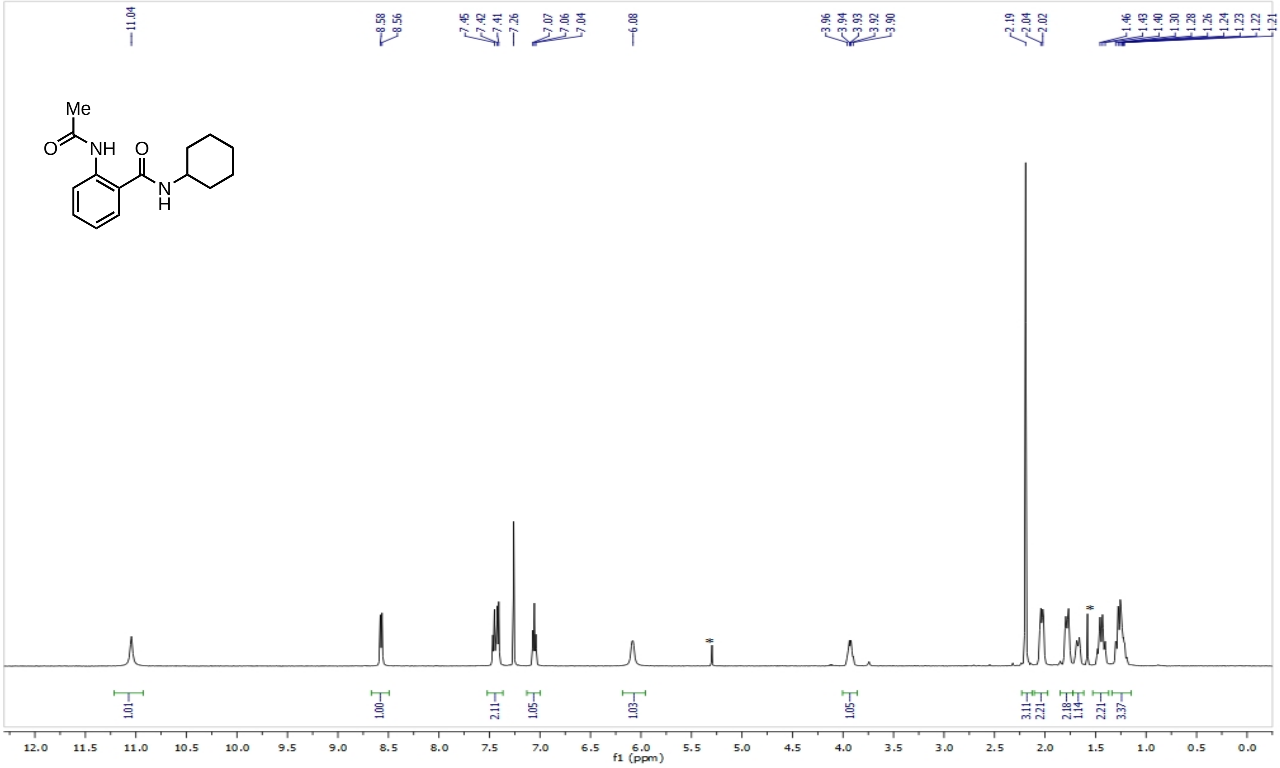

169.36
168.44
140.60
138.52
127.75
122.78
121.33
118.83
40.37
31.62
29.53
22.73
14.18
31.62
29.53
26.85
25.47
22.73
32
30
28
26
24
22
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3q**:


11.04
8.58
8.56
7.45
7.42
7.41
7.26
7.07
7.06
7.04
6.08
3.96
3.94
3.93
3.92
3.90
2.19
2.04
2.02
1.46
1.43
1.40
1.30
1.28
1.26
1.24
1.23
1.22
1.21
Me
O
NH
O
N
H
*
*
1.01
1.00
2.11
1.05
1.03
1.05
3.11
2.21
2.18
1.14
2.21
3.37
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

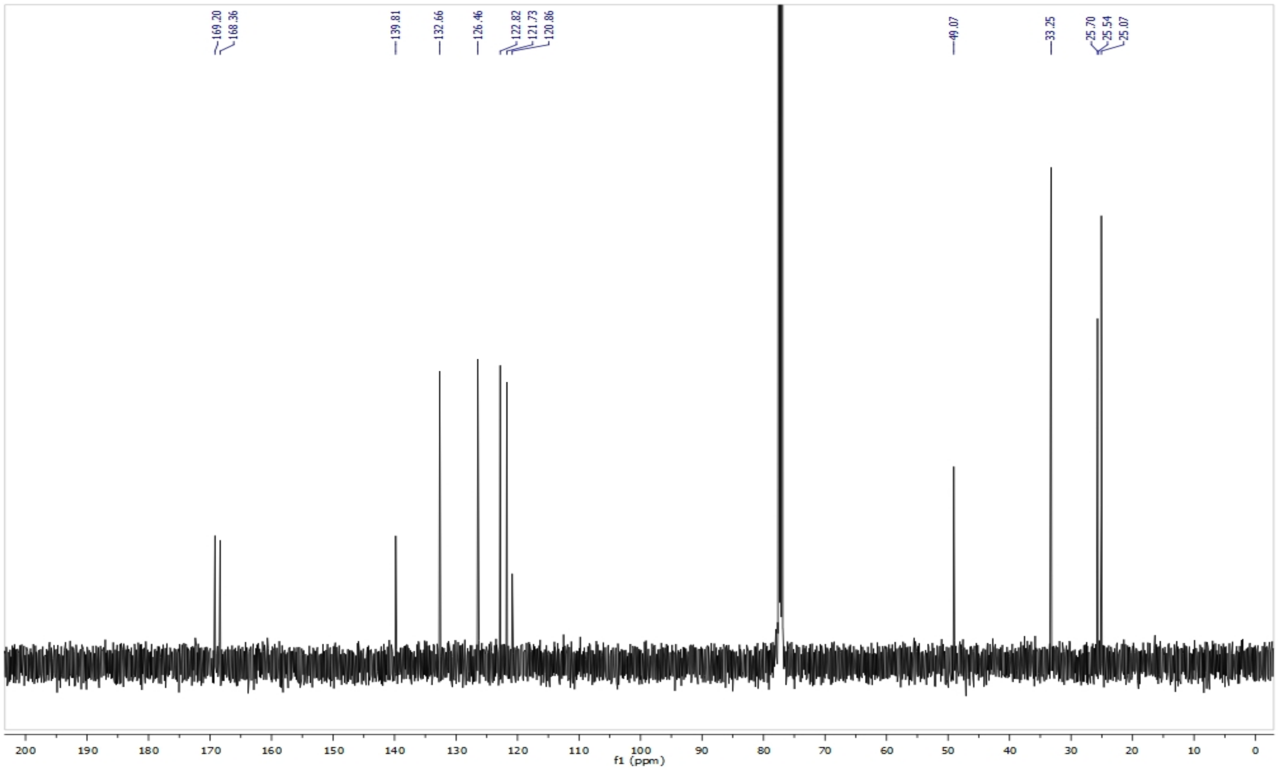
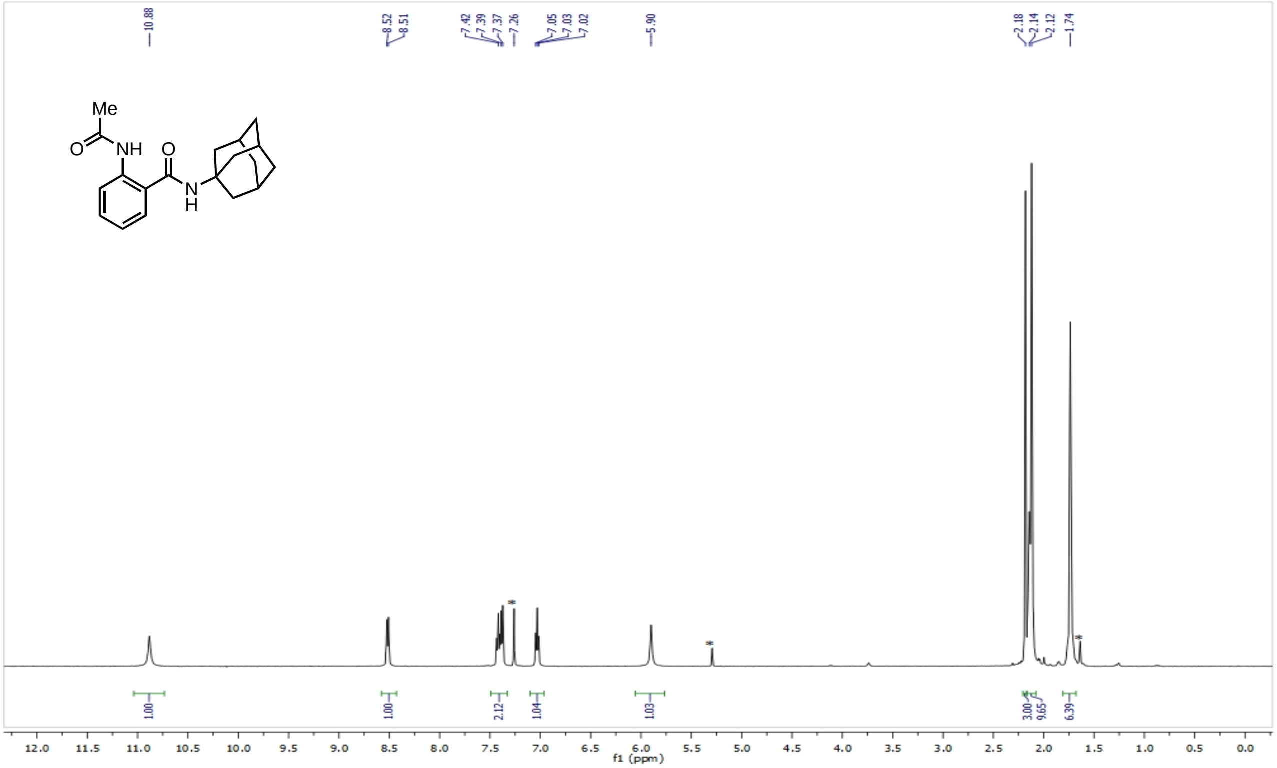

169.20
168.36
139.81
132.66
126.46
122.82
121.73
120.86
49.07
33.25
25.70
25.54
25.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3r**:


Me
O
NH
O
N
H
10.88
8.52
8.51
7.42
7.39
7.37
7.26
7.05
7.03
7.02
5.90
2.18
2.14
2.12
1.74
*
*
*
1.00
1.00
2.12
1.04
1.03
3.00
9.65
6.39
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

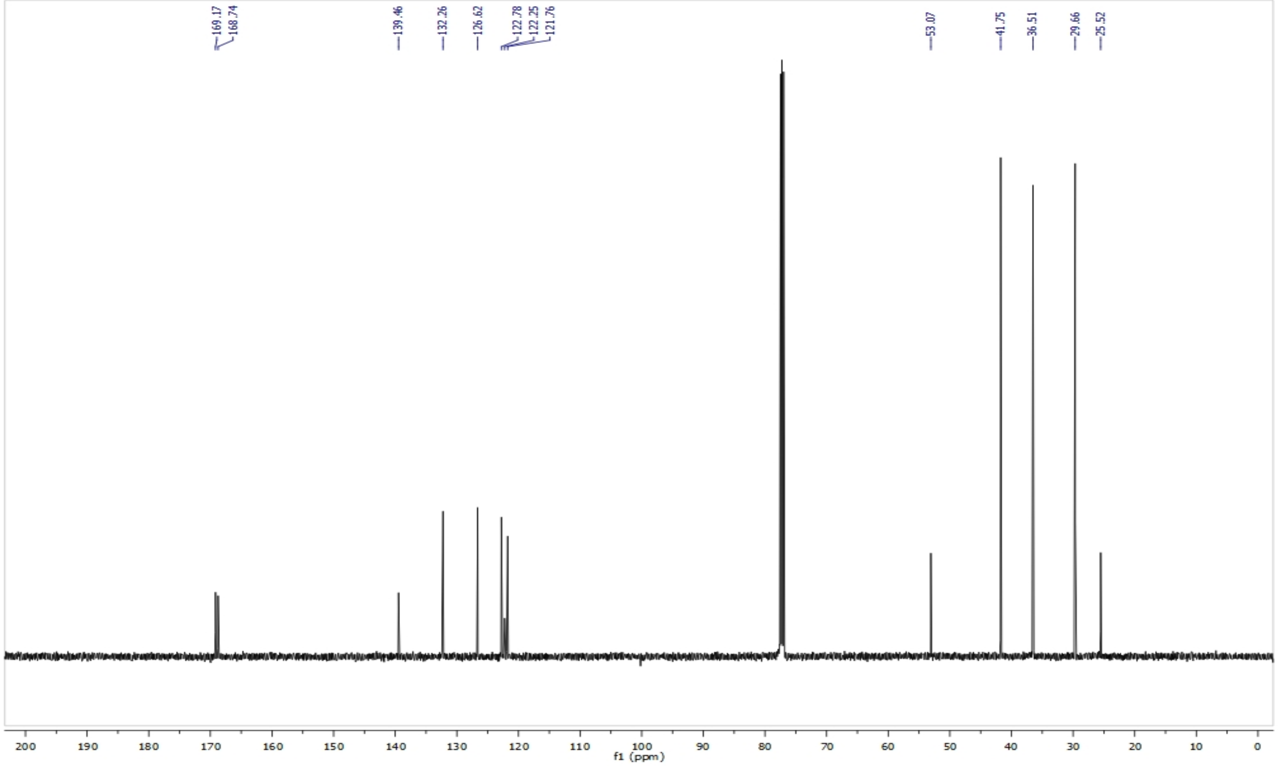
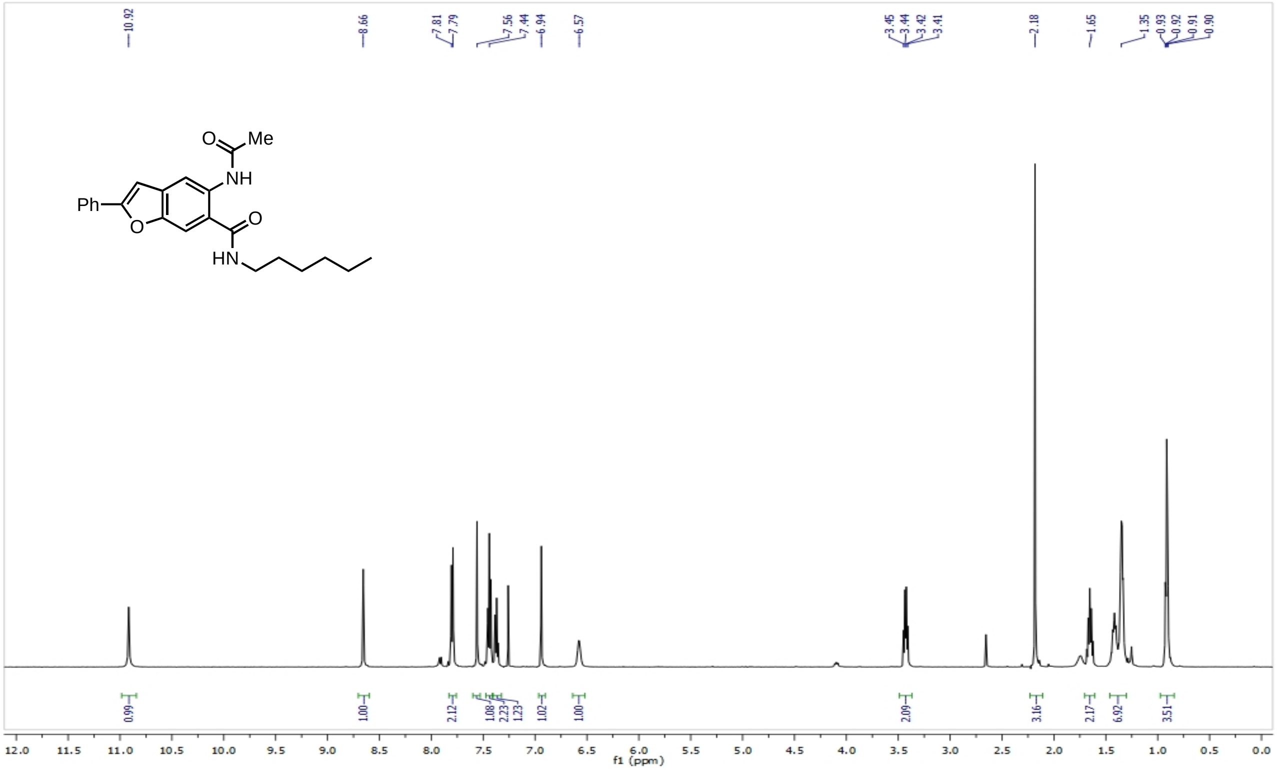

169.17
168.74
139.46
132.26
126.62
122.78
122.25
121.76
53.07
41.75
36.51
29.66
25.52
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3sa**:


10.92
8.66
7.81
7.79
7.56
7.44
6.94
6.57
3.45
3.44
3.42
3.41
2.18
1.65
1.35
0.93
0.92
0.91
0.90
O
Me
NH
Ph
O
O
HN
0.99
1.00
2.12
1.08
2.23
1.23
1.02
1.00
2.09
3.16
2.17
6.92
3.51
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

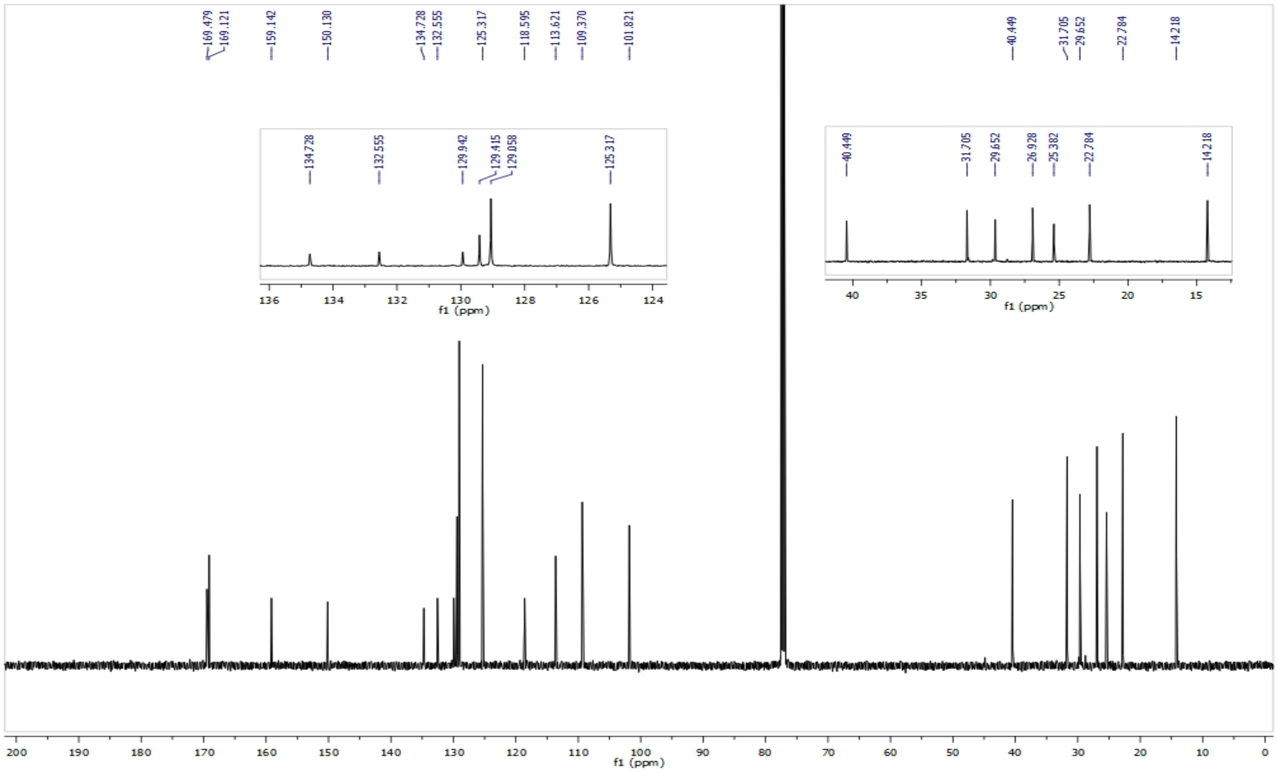
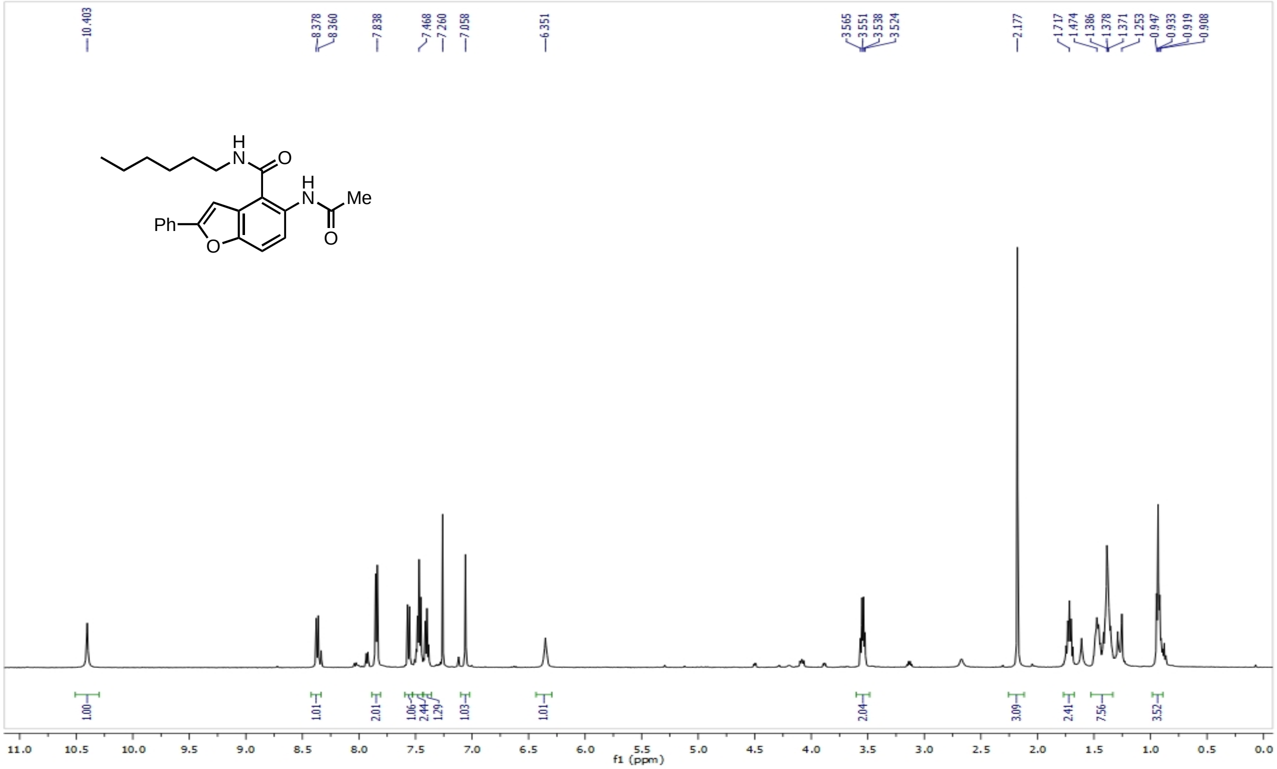

169.479
169.121
159.142
150.130
134.728
132.555
125.317
118.595
113.621
109.370
101.821
40.449
31.705
29.652
22.784
14.218
134.728
132.555
129.942
129.415
129.058
125.317
136
134
132
130
128
126
124
f1 (ppm)
40.449
31.705
29.652
26.928
25.382
22.784
14.218
40
35
30
25
20
15
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, **3sb**:


10.403
8.378
8.360
7.838
7.468
7.260
7.058
6.351
3.565
3.551
3.538
3.524
2.177
1.717
1.474
1.386
1.378
1.371
1.253
0.947
0.933
0.919
0.908
H
N
O
H
N
Me
O
Ph
O
1.00
1.01
2.01
1.06
2.44
1.29
1.03
1.01
2.04
3.09
2.41
7.56
3.52
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

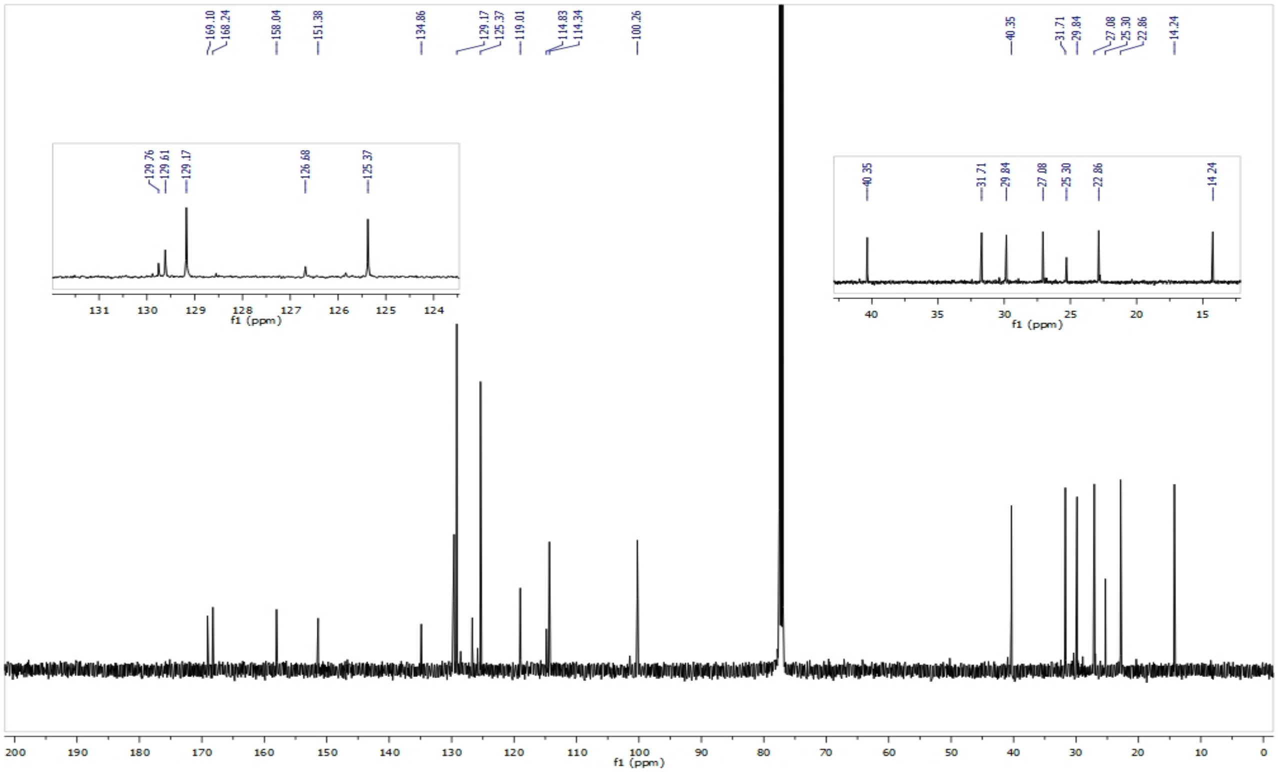
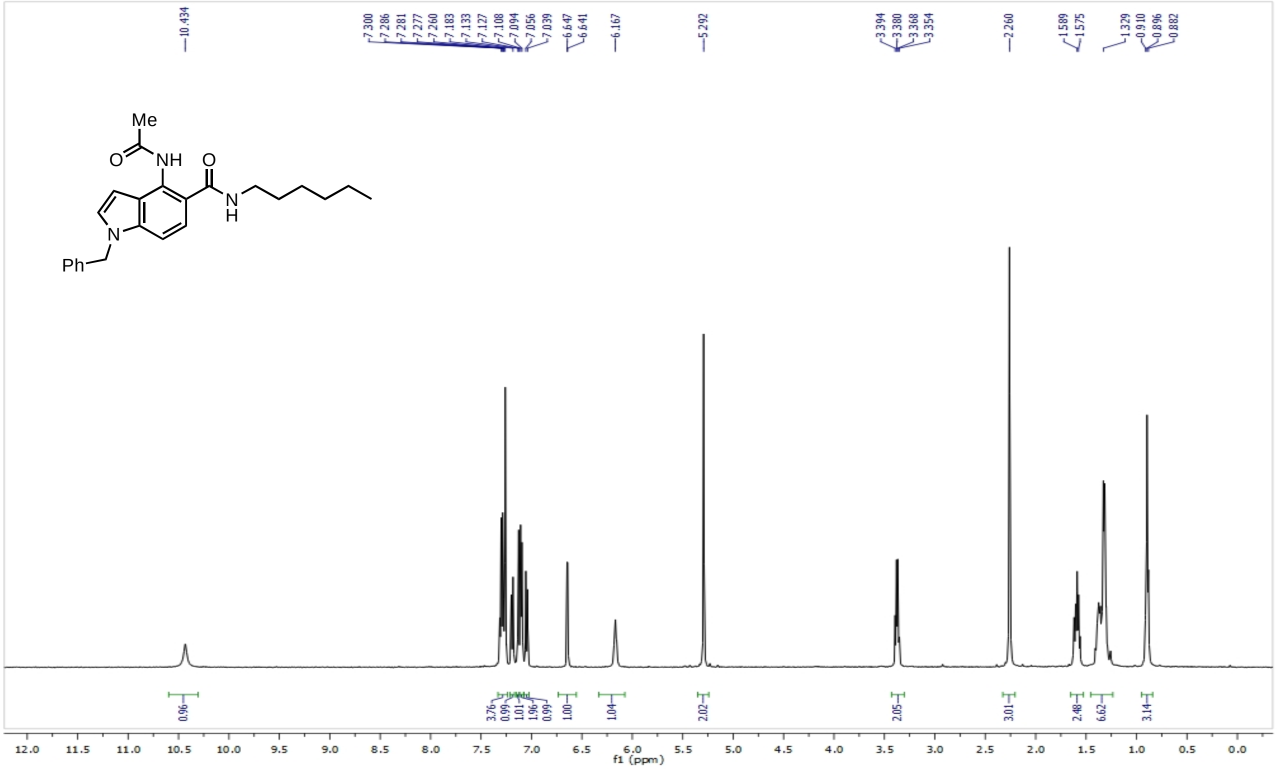
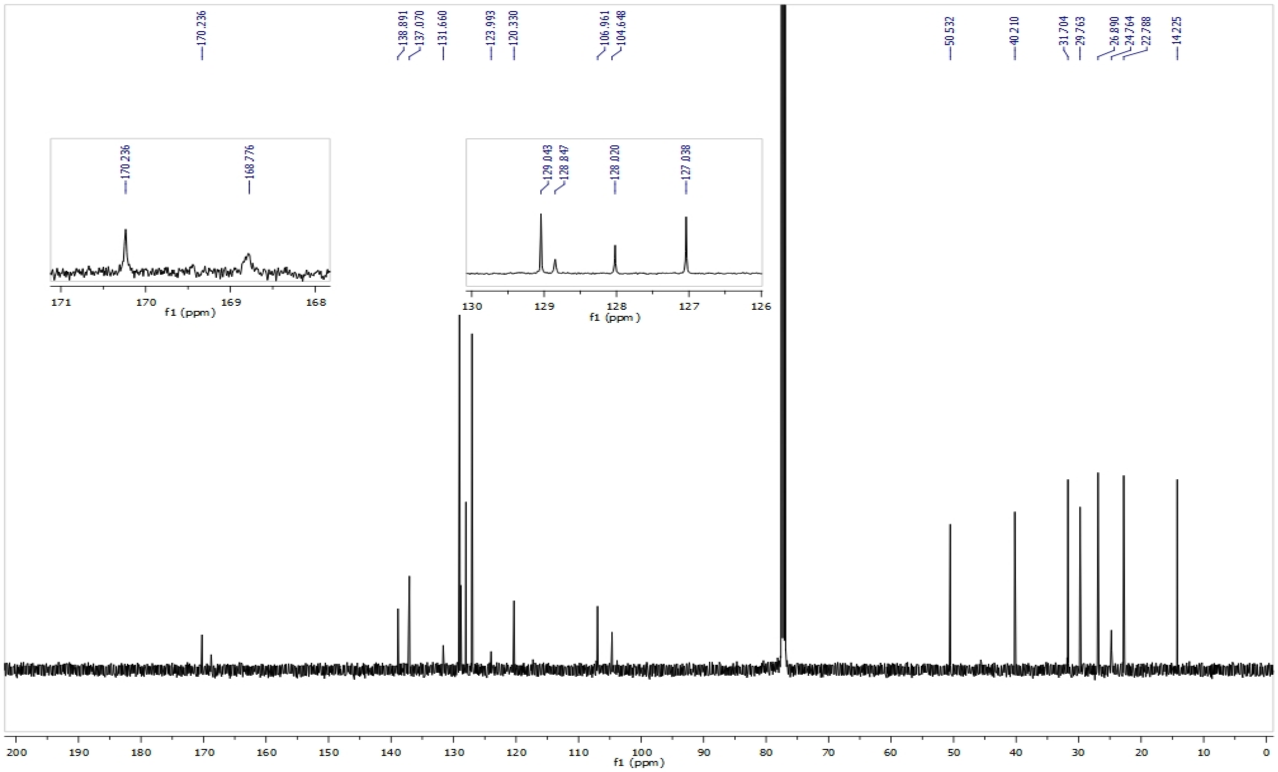
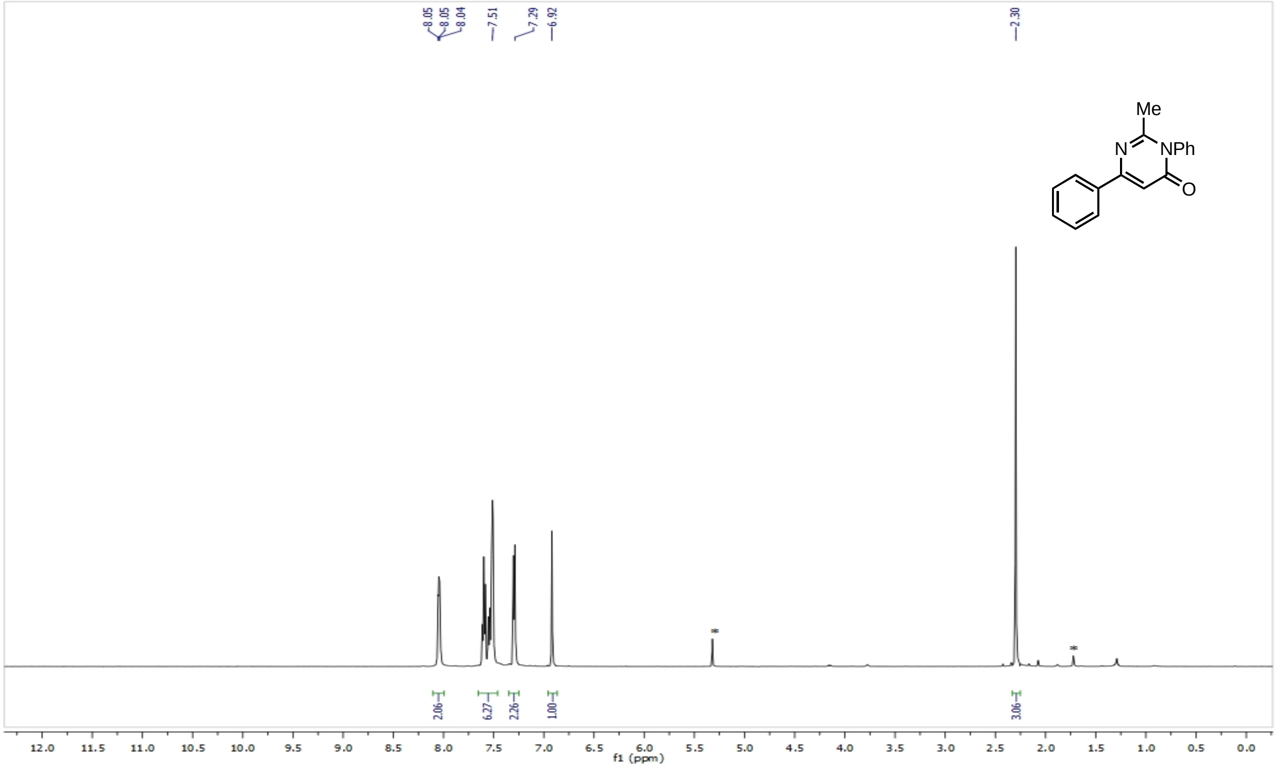

169.10
168.24
158.04
151.38
134.86
129.17
125.37
119.01
114.83
114.34
100.26
40.35
31.71
29.84
27.08
25.30
22.86
14.24
129.76
129.61
129.17
126.68
125.37
131
130
129
128
127
126
125
124
f1 (ppm)
40.35
31.71
29.84
27.08
25.30
22.86
14.24
40
35
30
25
20
15
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

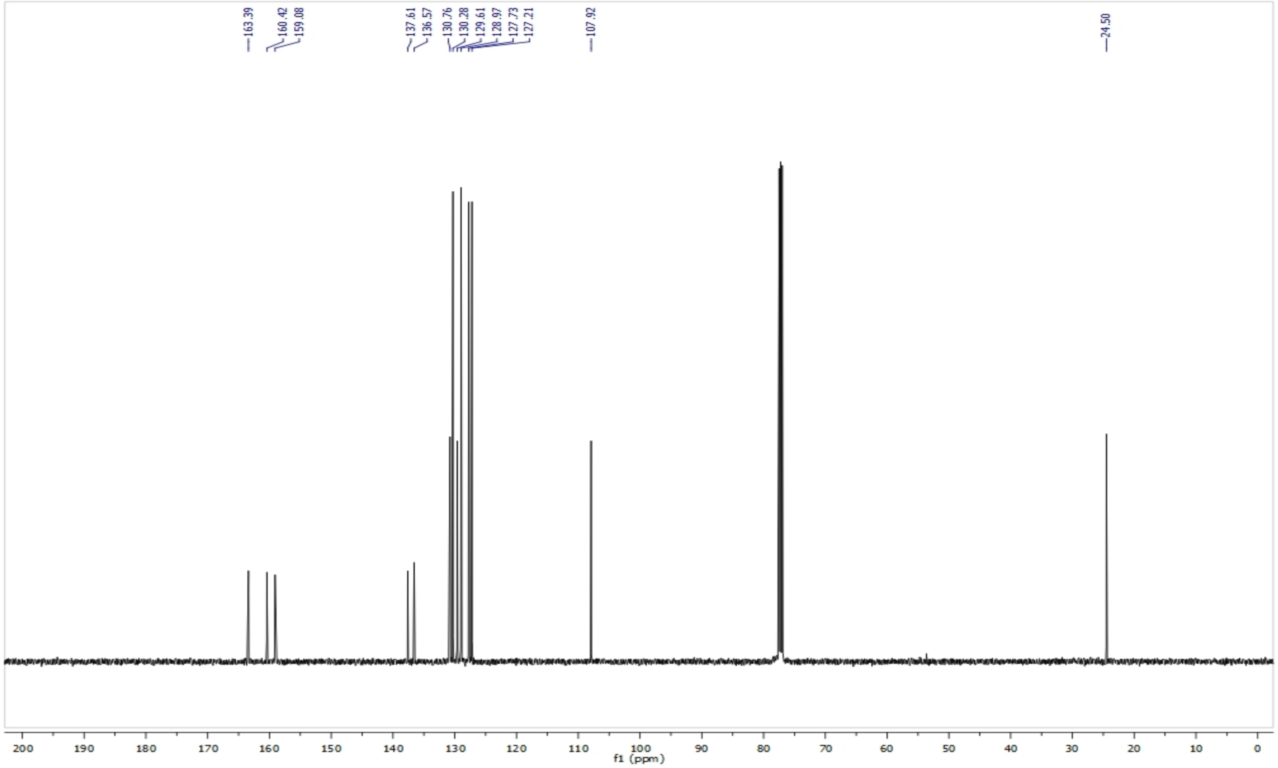
Table 2, **3t**:


10.434
7.300
7.286
7.281
7.277
7.260
7.183
7.133
7.127
7.108
7.094
7.056
7.039
6.647
6.641
6.167
5.292
3.394
3.380
3.368
3.354
2.260
1.589
1.575
1.329
0.910
0.896
0.882
Me
O
NH
O
N
H
N
Ph
0.96
3.76
0.99
1.01
1.96
0.99
1.00
1.04
2.02
2.05
3.01
2.48
6.62
3.14
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

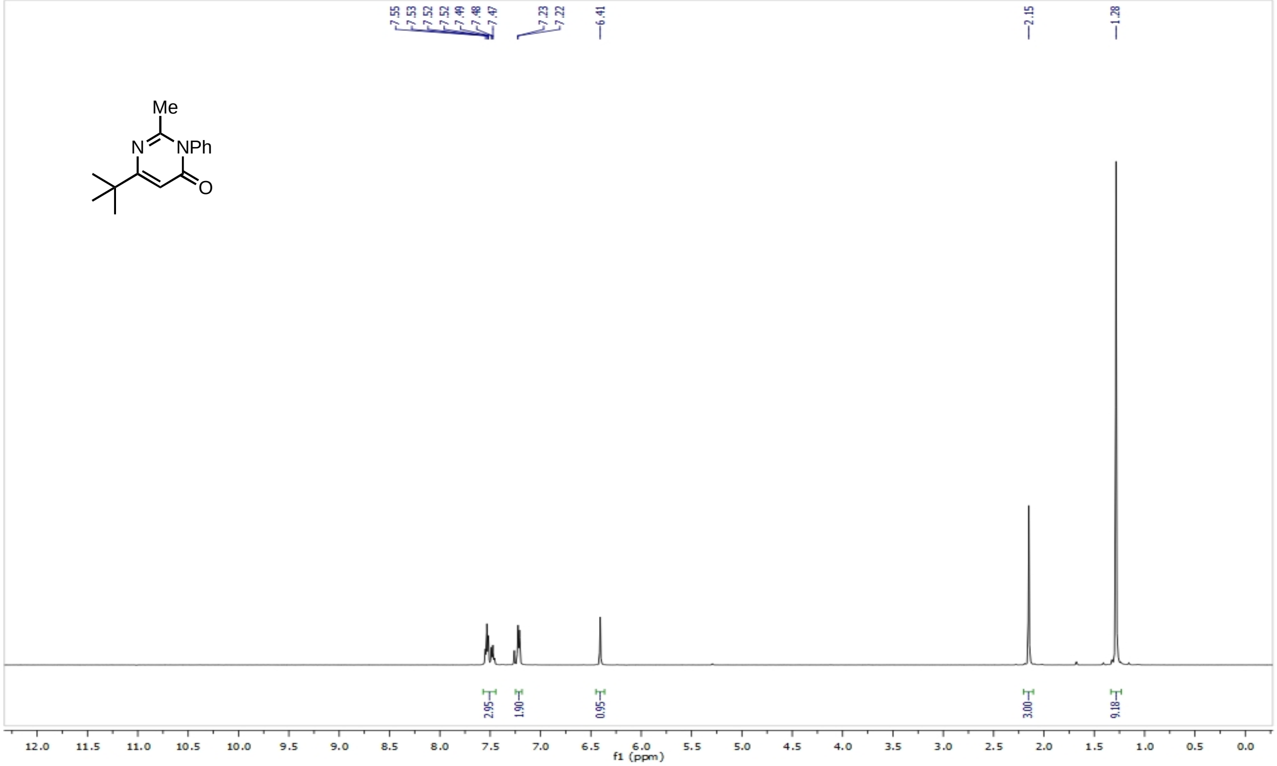


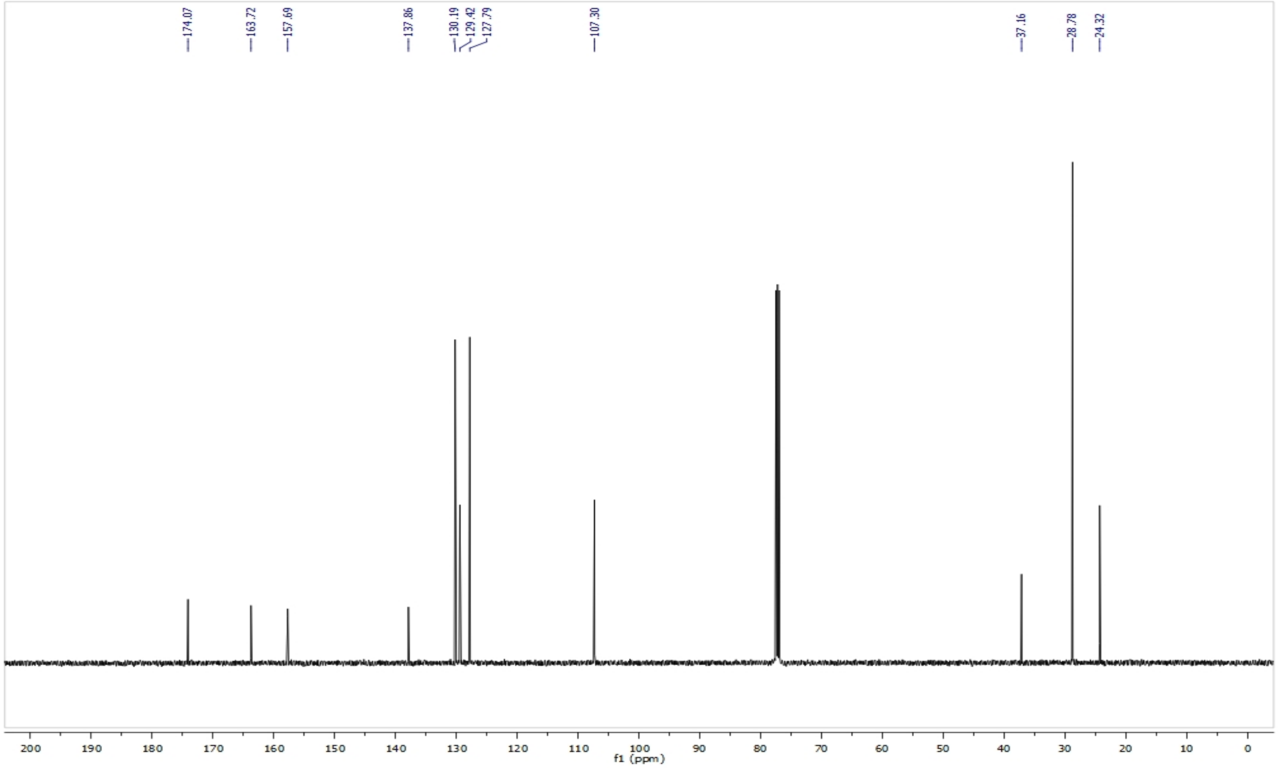
Equation 2, **4a**:



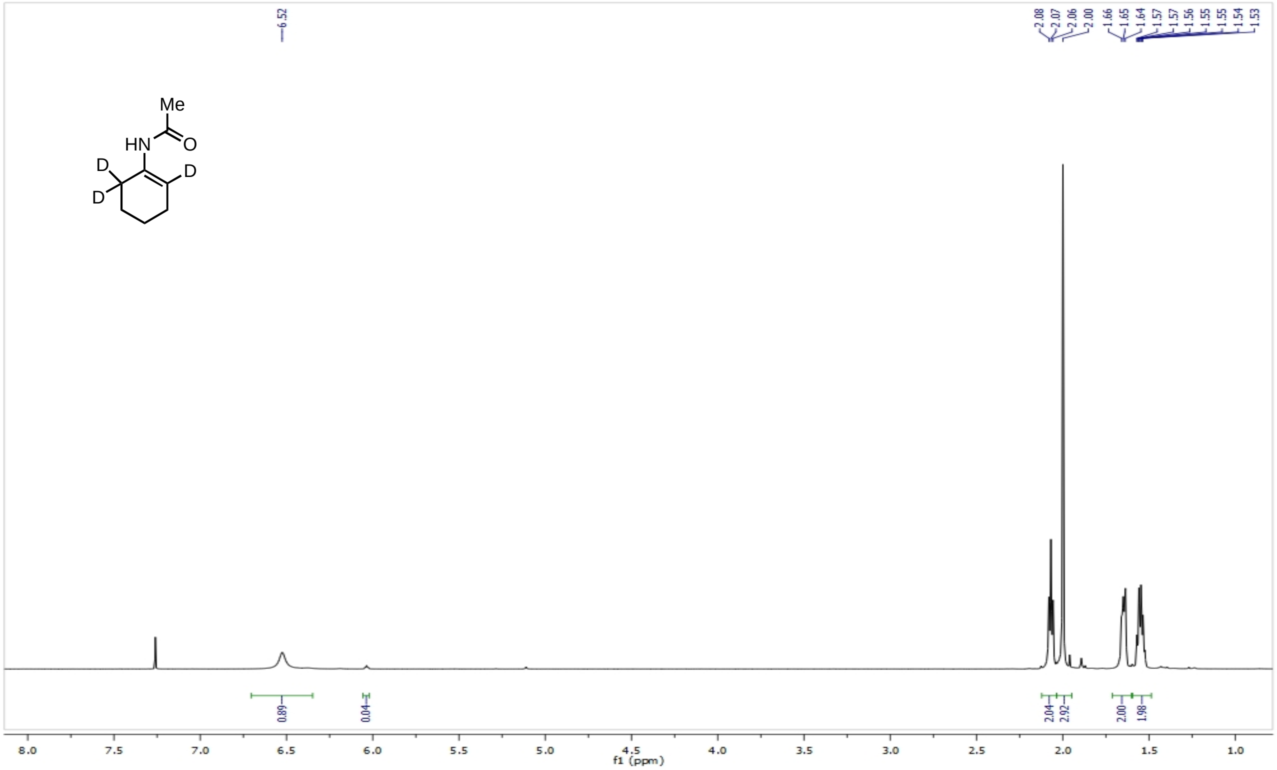


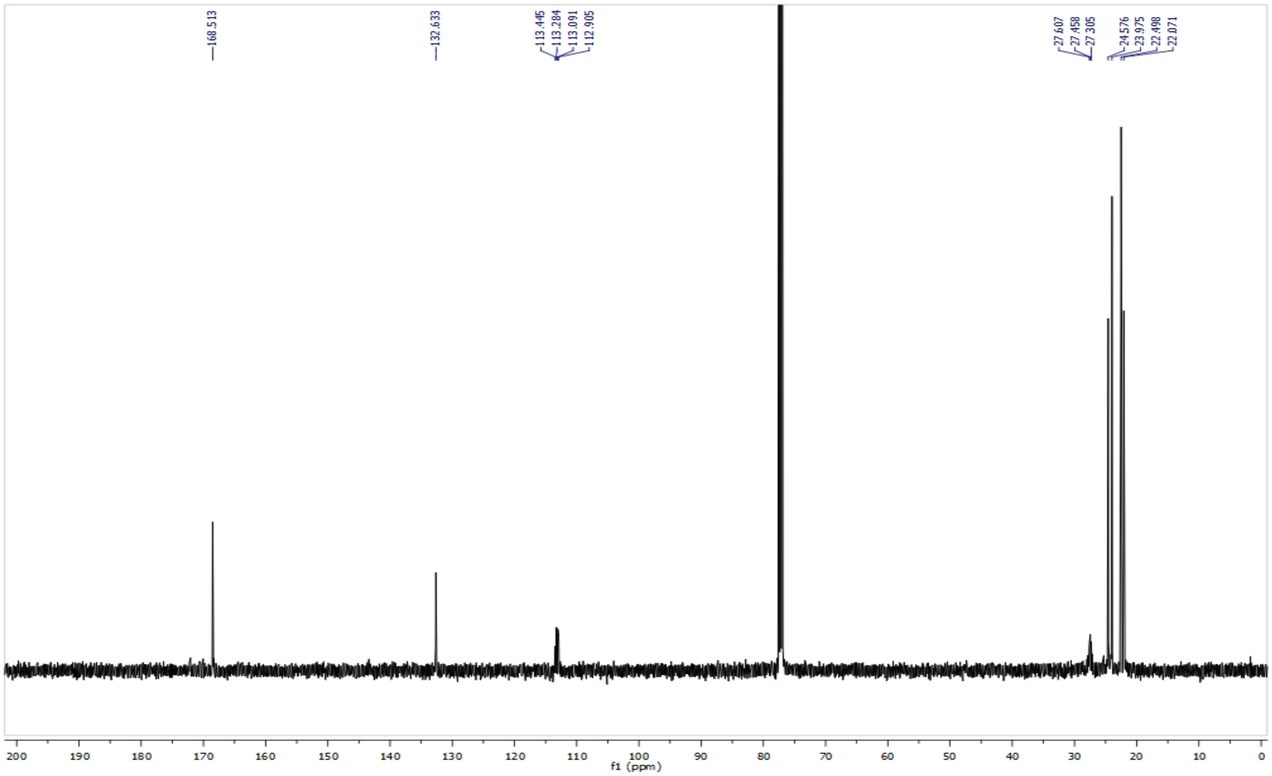
Equation 2, **4b**:




174.07
163.72
157.69
137.86
130.19
129.42
127.79
107.30
37.16
28.78
24.32
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2c-*d*$_3$:


6.52
2.08
2.07
2.06
2.00
1.66
1.65
1.64
1.57
1.57
1.56
1.55
1.55
1.54
1.53
Me
HN
O
D
D
D
0.89
0.04
2.04
2.92
2.00
1.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


168.513
132.633
113.445
113.284
113.091
112.905
27.607
27.458
27.305
24.576
23.975
22.498
22.071
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)