Supporting Information

Palladium-Catalyzed Carbamoylation of Aryl Halides by Tungsten Carbonyl Amine Complexes

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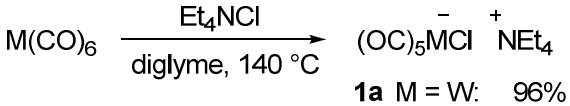
1. General

^{1}H NMR and ^{13}C NMR spectra were recorded on 3 spectrometers, (^{1}H, 300 MHz; ^{13}C, 75 MHz), (^{1}H, 400 MHz; ^{13}C, 100 MHz), and (^{1}H, 500 MHz; ^{13}C, 125 MHz). Spectra were calibrated using the residual ^{1}H chemical shift in $CDCl_3$ (7.26 ppm), which were used as the internal reference standards for ^{1}H NMR, and $CDCl_3$ (77.0 ppm) for ^{13}C NMR spectra. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. Melting points are uncorrected.

Wakogel® B-5F (Wako Pure Chemical Industries) was used for preparative thin-layer chromatography. THF was distilled from sodium for immediately use. Toluene and dichloromethane (CH_2Cl_2) were taken from a solvent purification system. Ethanol (EtOH) was distilled from sodium and stored over MS 3A. *N*,*N*-Dimethylformamide (DMF) was distilled from CaH_2 and stored over MS 4A.

2. Synthesis of chlorometalates 1a-1c:

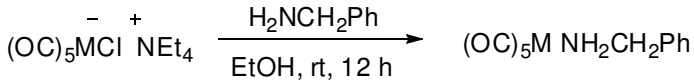


1a M = W: 96%
1b M = Mo: 93%
1c M = Cr: 84%

Typical procedure:

Complexes **1a-c** were prepared according to the literature[1] with modifications. A mixture of tetraethylammonium chloride (3.14 g, 18.9 mmol) and hexacarbonyltungsten (7.0 g, 19.9 mmol) in diglyme (45 ml) was stirred under N_2 atmosphere and heated at 140 °C till the mixture became a clear yellow solution. After the mixture was cooled to room temperature, hexane (40 ml) was added. After keeping the mixture at 0 °C for a short while, the formed solids were filtered, washed with hexane, dried under vacuum to obtain the product as yellow powder.

3. Synthesis of amine complexes 2a-2c:

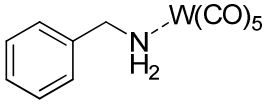


2a M = W: 73%
2b M = Mo: 50%
2c M = Cr: 38%

General procedure for preparation of group 6 metal carbonyl benzylamine complexes 2a-2c:

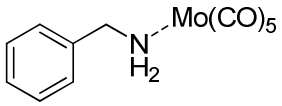
Amine complexes **2a-c** were prepared according to the literature[2]. Benzylamine were added in the suspension of $(CO)_5MClNEt_4$ in ethanol, then the mixture was stirred overnight at room temperature. The solvent was evaporated, and the residue was purified by flash column chromatography (hexane : ethyl acetate = 20 : 1) to give the corresponding product.

benzylaminepentacarbonyltungsten (2a):[3]



Yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.82 (br s, 2H), 3.92-3.96 (m, 2H), 7.26-7.28 (m, 2H), 7.36-7.44 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 58.3, 127.4, 128.9, 129.4, 139.2, 197.9 (satellite, $J_{13C\text{-}183W}$ = 129.8 Hz), 200.7.

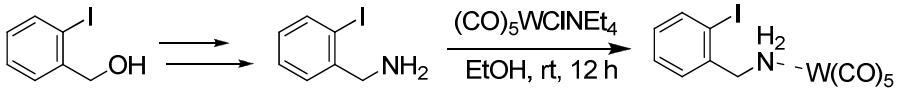
benzylaminepentacarbonylmolybdenum (2b):[3]



Dark yellow; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.46 (br s, 2H), 3.81-3.85 (m, 2H), 7.24-7.26 (m, 2H), 7.35-7.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.3, 127.3, 128.6, 129.3, 139.3, 204.0, 212.6.

4. Synthesis of amine complexes 2d and 2e

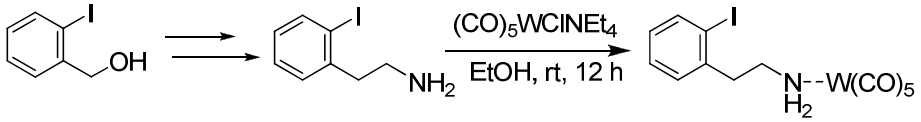
2-iodobenzylaminepentacarbonyltungsten (2d):[4]



2d: 48% (based on 2-iodobenzyl alcohol)

2-Iodobenzyl amine was prepared according to the literature.[4] **2d** was prepared according to the previous procedure, the crude product was purified by flash column chromatography (hexane : ethyl acetate = 20 : 1) to give yellow solid; mp 120 °C (decomposed); IR (KBr) 3311, 3263, 2069, 1961, 1938, 1915, 1884, 1849, 1587, 1465, 1359, 1205, 1163, 756, 597 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.01 (br s, 2H), 3.96-3.99 (m, 2H), 7.07-7.11 (m, 1H), 7.31-7.44 (m, 2H), 7.87 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 62.4, 98.5, 129.4, 129.9, 130.8, 140.1, 141.7, 197.9 (satellite, $J_{13C\text{-}183W}$ = 129.9 Hz), 200.8; ESIHRMS: Found: m/z 233.9784. Calcd for C_7H_9NI: $(M\text{-}W(CO)_5+H)^+$ 233.9780.

2-(2-iodophenyl)ethylaminepentacarbonyltungsten (2e):[5]



2e: 35% (based on 2-iodobenzyl alcohol)

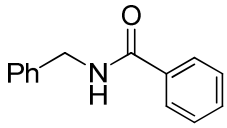
2-(2-Iodophenyl)ethylamine was prepared according to the literature.[5] **2e** was prepared according to the above mentioned procedure, the crude product was purified by flash column chromatography (hexane : ethyl acetate = 20 : 1) to give yellow solid; mp 90 °C (decomposed); IR (KBr) 3331, 3282, 2069, 1975, 1932, 1905, 1847, 1832, 1583, 1465, 1355, 1010, 750, 596 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.52 (br s, 2H), 2.97 (t, J = 6.8 Hz, 2H), 3.09-3.16 (m, 2H), 7.01 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.89 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.0, 53.9, 100.6, 129.1, 129.3, 129.8, 139.2, 140.2, 197.9 (satellite, $J_{13C\text{-}183W}$ = 130 Hz), 200.6; ESIHRMS: Found: m/z 247.9940. Calcd for $C_8H_{11}NI$: $(M\text{-}W(CO)_5+H)^+$ 247.9936.

5. Pd-catalyzed carbamoylation of aryl halide

Typical procedure for the Pd-catalyzed carbamoylation of aryl halides

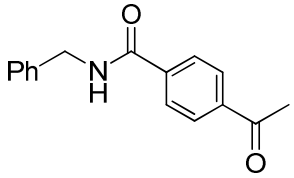
A mixture of **2a** (0.44 g, 1.0 mmol), 2-bromonaphthalene (0.32 g, 1.5 mmol), $Pd(OAc)_2$ (0.022 g, 10 mol%), P(*o*-Tol)$_3$ (0.061 g, 20 mol%) and K_2CO_3 (0.152 g, 1.1 mmol) in THF(10 ml) was refluxed for 68 hours, then THF was removed under the reduced pressure and the residue was purified by flash column chromatography (hexane : ethyl acetate = 8 : 1) to give *N*-benzylnaphthalene-2-carboxamide **3c** as a white solid. Yield: 86%.

***N*-benzylbenzamide (3a):**[6]



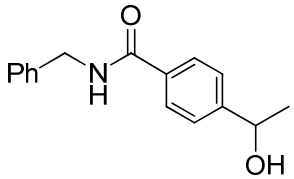
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.65 (d, J = 6.0 Hz, 2H), 6.42 (br s, 1H), 7.28-7.37 (m, 5H), 7.41-7.45 (dd, J = 7.6 Hz, 7.2 Hz, 2H), 7.48-7.52 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.1, 126.9, 127.6, 127.9, 128.6, 128.8, 131.5, 134.4, 138.1, 167.3.

4-acetyl-*N*-benzylbenzamide (3b):



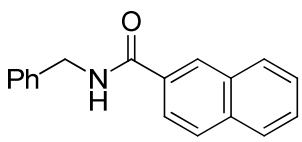
White solid; mp 112-113 °C; IR (KBr) 3292, 3091, 3066, 2918, 1685, 1639, 1606, 1552, 1421, 1361, 1323, 1300, 1263, 985, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.60 (s, 3H), 4.63 (d, J = 5.6 Hz, 2H), 6.75 (br s, 1H), 7.28-7.35 (m, 5H), 7.86 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 26.7, 44.2, 127.3, 127.7, 127.9, 128.5, 128.8, 137.8, 138.2, 139.1, 166.4, 197.4; ESIHRMS: Found: m/z 254.1179. Calcd for $C_{16}H_{16}NO_2$: $(M+H)^+$ 254.1181.

***N*-benzyl-4-(1-hydroxyethyl) benzamide (3b'):**



Sticky liquid; IR ($CHCl_3$) 3324, 2974, 2928, 1637, 1550, 1498, 1453, 1365, 1306, 1091, 1012, 898, 853, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.49 (d, J = 4.0 Hz, 3H), 2.07 (br, s, 1H), 4.64 (d, J = 8.0, 2H), 4.94 (q, J = 6.4 Hz, 1H), 6.43 (br s, 1H), 7.28-7.36 (m, 5H), 7.42 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 25.3, 44.1, 69.9, 125.5, 127.2, 127.6, 127.9, 128.8, 133.3, 138.1, 149.5, 167.1; ESIHRMS: Found: m/z 256.1335. Calcd for $C_{16}H_{18}NO_2$: $(M+H)^+$ 256.1338.

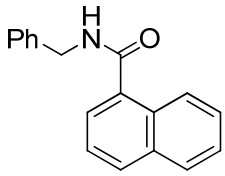
***N*-benzylnaphthalene-2-carboxamide (3c):**[7]



^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.67 (d, J = 6.0 Hz, 2H), 6.90 (br s, 1H), 7.28-7.38 (m,

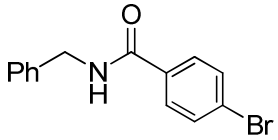
5H), 7.49-7.56 (m, 2H), 7.84-7.87 (m, 4H), 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 44.1, 123.6, 126.6, 127.4, 127.5, 127.6, 127.7, 127.8, 128.4, 128.69, 128.8, 131.5, 132.5, 134.7, 138.2, 167.5.

_N_-benzylnaphthalene-1-carboxamide (3d):[7]



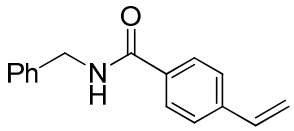
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.70 (d, J = 5.6 Hz, 2H), 6.39 (br s, 1H), 7.28-7.43 (m, 6H), 7.49-7.60 (m, 3H), 7.85-7.91 (m, 2H), 8.33-8.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.1, 124.6, 124.9, 125.4, 126.4, 127.1, 127.6, 127.8, 128.3, 128.8, 130.1, 130.6, 133.6, 134.2, 138.1, 169.4.

_N_-benzyl-4-bromobenzamide (3e):[8]



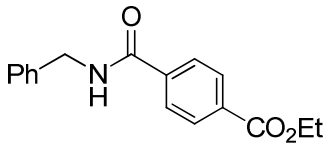
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.61 (d, J = 5.7 Hz, 2H), 6.50 (br s, 1H), 7.29-7.38 (m, 5H), 7.55 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 44.2, 126.2, 127.7, 127.9, 128.6, 128.8, 131.8, 133.2, 137.9, 166.4.

_N_-benzyl-4-vinylbenzamide (3f):



White solid; mp 116-117 °C; IR (KBr) 3280, 3261, 3082, 3030, 2922, 1641, 1564, 1502, 1454, 1427, 1357, 1323, 1246, 1078, 856, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.62 (d, J = 6.0 Hz, 2H), 5.35 (d, J = 11.0 Hz, 1H), 5.82 (d, J = 17.5 Hz, 1H), 6.62 (br s, 1H), 6.73 (dd, J = 11.0, 17.5 Hz, 1H), 7.27-7.35 (m, 5H), 7.43 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 44.0, 116.0, 126.2, 127.3, 127.5, 127.8, 128.7, 133.3, 135.9, 138.2, 140.6, 167.0; ESIHRMS: Found: m/z 238.1221. Calcd for $C_{16}H_{16}NO$: $(M+H)^+$ 238.1232.

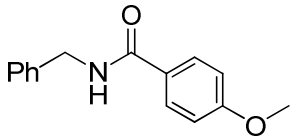
Ethyl 4-(benzylcarbamoyl)benzoate (3g):[9]



White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.39 (t, J = 7.2 Hz, 3H), 4.37 (q, J =

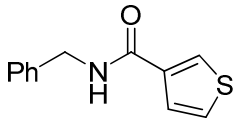
7.2Hz, 2H), 4.61 (d, *J* = 5.6 Hz, 2H), 6.81 (br s, 1H), 7.27-7.36 (m, 5H), 7.82 (d, *J* = 8.4Hz 2H), 8.04 (d, *J* = 8.4Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.2, 44.2, 61.3, 127.0, 127.6, 127.9, 128.7, 129.7, 133.0, 137.9, 138.1, 165.8, 166.6.

_N_-benzyl-4-methoxybenzamide (3h):[9]



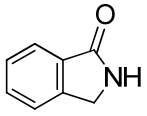
White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.74 (s, 3H), 4.51 (d, *J* = 5.5 Hz, 2H), 6.50 (br s, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 7.18-7.27 (m, 5H), 7.68 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 44.0, 55.3, 113.7, 126.6, 127.4, 127.8, 128.7, 128.8, 138.4, 162.1, 166.9.

_N_-benzylthiophene-3-carboxamide (3i):



White solid; mp 102-103 °C; IR (KBr) 3307, 3294, 3103, 3057, 1643, 1560, 1535, 1496, 1425, 1421, 1359, 1307, 1255, 1058, 1001, 819, 746 717, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.57 (d, *J* = 5.5 Hz, 2H), 6.61 (br s, 1H), 7.26-7.35 (m, 6H), 7.39-7.41 (m, 1H), 7.87-7.88 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 43.7, 126.1, 126.4, 127.5, 127.8, 128.3, 128.7, 137.2, 138.2, 163.0; ESIHRMS: Found: m/z 218.0623. Calcd for $C_{12}H_{12}NOS$: $(M+H)^+$ 218.0640.

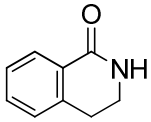
2, 3-dihydro-1*H*-isoindol-1-one (3j):[10]



A mixture of **2d** (0.56 g, 1.0 mmol), $Pd(OAc)_2$ (0.011 g, 5 mol%), P(*o*-Tol)$_3$ (0.030 g, 10 mol%) and K_2CO_3 (0.152 g, 1.1 mmol) in THF(10 ml) was refluxed for 6.5 days. The solvent was removed under reduced pressure and the residue was purify by flash column chromatography (hexane : ethyl acetate = 1 : 1) to give white solid. Yield: 36%.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.41 (s, 2H), 7.41–7.53 (m, 4H), 7.81 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 45.7, 123.2, 123.7, 128.0, 131.7, 132.1, 143.6, 172.0.

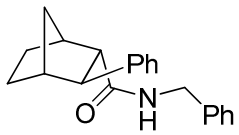
3, 4-dihydroisoquinolin-1(2*H*)-one (3k):[11]



The lactam **3k** was obtained in the same procedure to give lactam **3j** using amine complex **2e**.

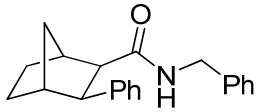
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.93 (t, J = 6.4 Hz, 2H), 3.49-3.53 (m, 2H), 6.65 (br s, 1H), 7.14-7.19 (m, 1H), 7.26-7.30 (m, 1H), 7.36-7.40 (m, 1H), 7.99 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 28.3, 40.2, 127.0, 127.2, 127.9, 128.9, 132.1, 138.8, 166.4; ESIHRMS: Found: m/z 148.0756. Calcd for $C_9H_{10}NO$: $(M+H)^+$ 148.0762.

***rac*-(1*S*,2*S*,3*S*,4*R*)-*N*-benzyl-3-phenylbicyclo[2.2.1]heptane-2-carboxamide (*trans*-4):**



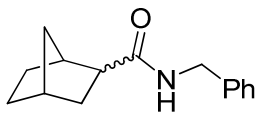
Light yellow oil; IR (NaCl) 3304, 2954, 2872, 1643, 1546, 1494, 1298, 1238, 1217, 1029, 908, 754, 731, 698 cm^{-1};
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1,40 (d, J = 10 Hz, 1H), 1.45-1.66 (m, 4H), 1.77 (d, J = 9.6 Hz, 1H), 2.50 (s, 2H), 2.64-2.67 (m, 1H), 3.29 (d, J = 6.0 Hz, 1H), 4.39 (dd, J = 5.6, 14.8 Hz, 1H), 4.47 (dd, J = 5.6, 14.4 Hz, 1H), 5.82 (br s, 1H), 7.14-7.32 (m, 10H);
^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 23.7, 30.1, 38.8, 41.6, 42.6, 43.6, 48.3, 57.1, 125.7, 126.8, 127.3, 127.6, 128.4, 128.6, 138.6, 146.2, 173.0;
ESIHRMS: Found: m/z 306.1861. Calcd for $C_{16}H_{16}NO_2$: $(M+H)^+$ 306.1858.

***rac*-(1*S*,2*R*,3*S*,4*R*)-*N*-benzyl-3-phenylbicyclo[2.2.1]heptane-2-carboxamide (*cis*-4):**



cis-**4** was obtained as an inseparable mixture with **5**.
White solid; IR (NaCl) 3313, 3009, 2955, 2972, 1651, 1512, 1236, 1215 cm^{-1} (a mixture with **5**); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1,24-1.28 (m, 1H), 1.33-1.37 (m, 1H), 1.42-1.47 (m, 1H), 1.61-1.70 (m, 2H), 2.45-2.48 (m, 2H), 2.62-2.64 (m, 2H), 3.07 (d, J = 10.0 Hz, 1H), 3.75 (dd, J = 5.0, 14.5 Hz, 1H), 4.00 (dd, J = 5.5, 14.5 Hz, 1H), 5.13 (br s, 1H), 6.80-6.83 (m, 2H), 7.17-7.28 (m, 8H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 28.7, 31.1, 37.5, 39.8, 42.1, 43.4, 52.9, 56.0, 126.2, 127.2, 127.9, 128.2 (overlapped), 128.4, 138.0, 142.4, 172.4;
ESIHRMS: Found: m/z 306.1861. Calcd for $C_{16}H_{16}NO_2$: $(M+H)^+$ 306.1858.

***N*-benzylbicyclo[2.2.1]heptane-2-carboxamide (5):**



Compound **5** was obtained as an inseparable mixture with *cis*-**4**. Compound **5** was obtained as a single isomer and the stereoconfiguration of 2-position in the

bicyclo[2.2.1]heptane is not clarified.

White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1,16-1.19 (m, 2H), 1.50-1.54 (m, 2H), 1.61-1.63 (m, 3H), 1.88-1.93 (m, 1H), 2.11-2.14 (m, 1H), 2.31 (br s, 1H), 2.41 (br s, 1H), 4.39 (dd, J = 5.5, 15.0 Hz, 1H), 4.44 (dd, J = 5.5, 14.5 Hz, 1H), 5.73 (br s, 1H), 7.32-7.35 (m, 5H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 28.6, 29.8, 34.4, 35.9, 36.5, 41.5, 43.6, 48.1, 127.4, 127.7, 128.7, 138.6, 175.6;

ESIHRMS: Found: m/z 230.1550. Calcd for $C_{16}H_{16}NO_2$: $(M+H)^+$ 230.1545.

6. Reference

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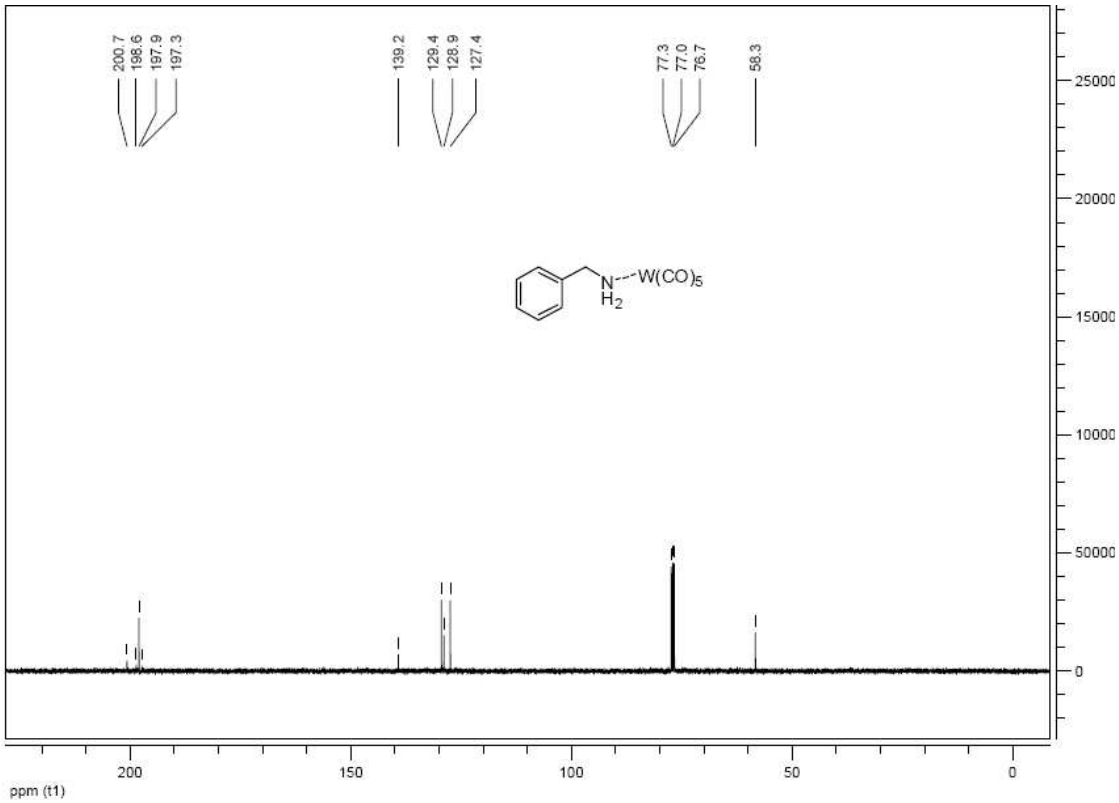
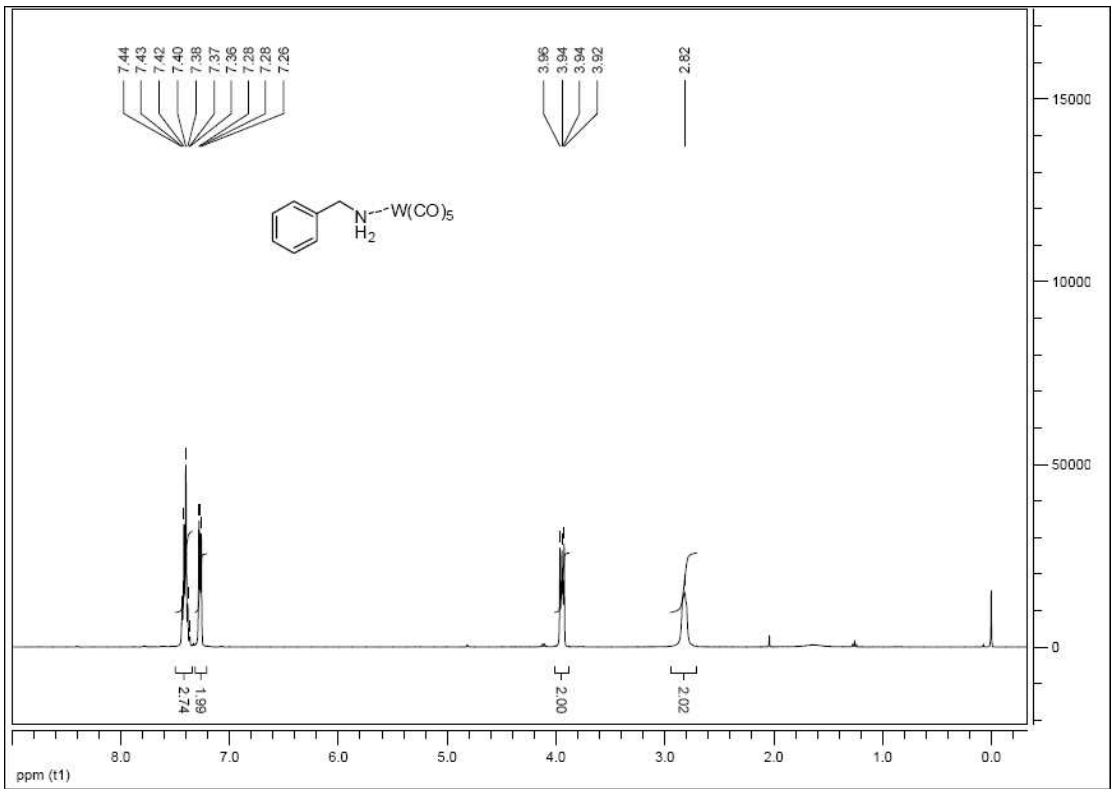
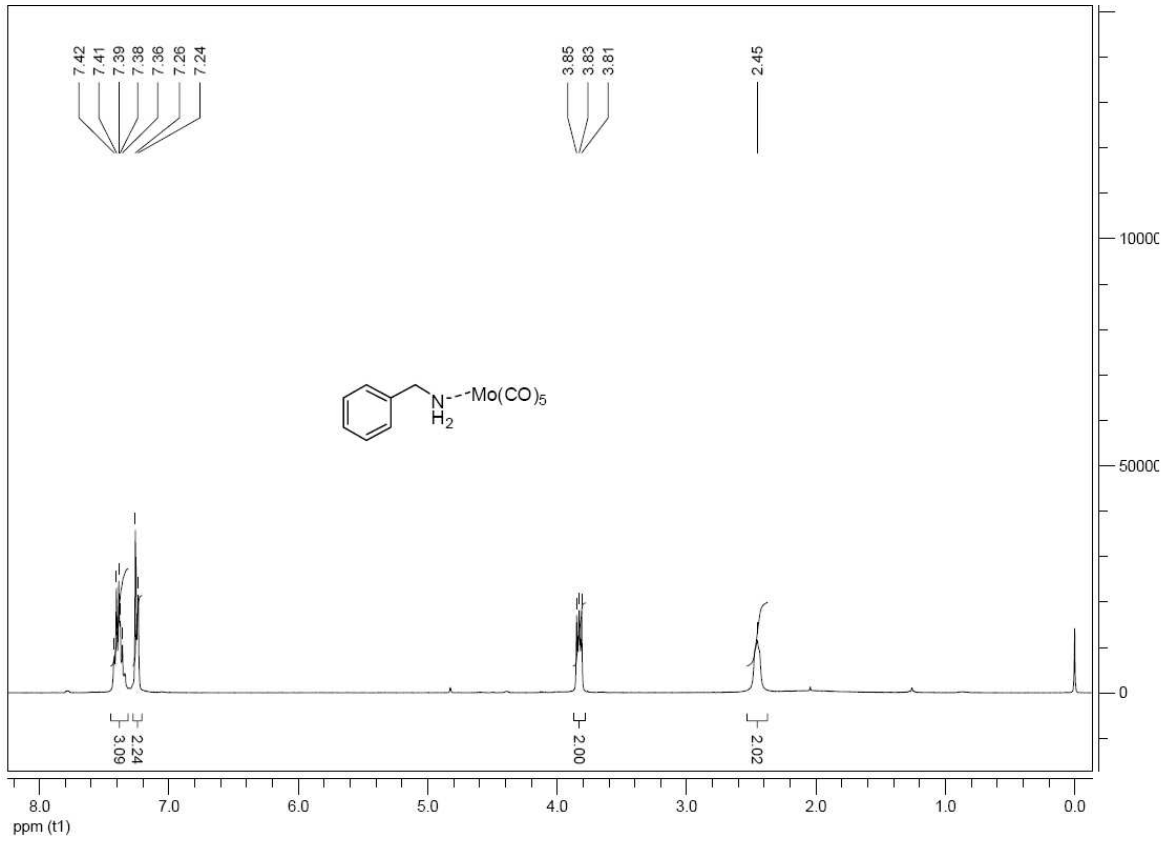
7. NMR Spectrum of 2a, 2b, 2d, 2e, 3a–k, 4, 5

2a





2b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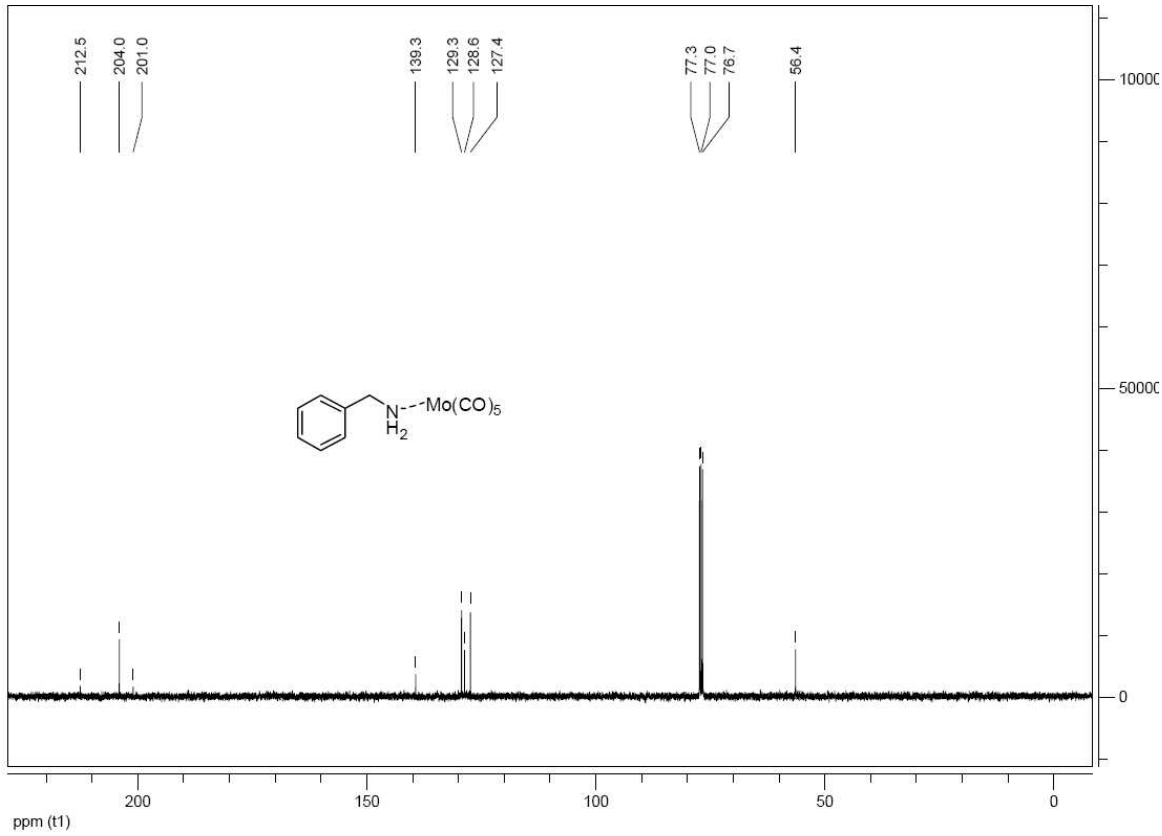
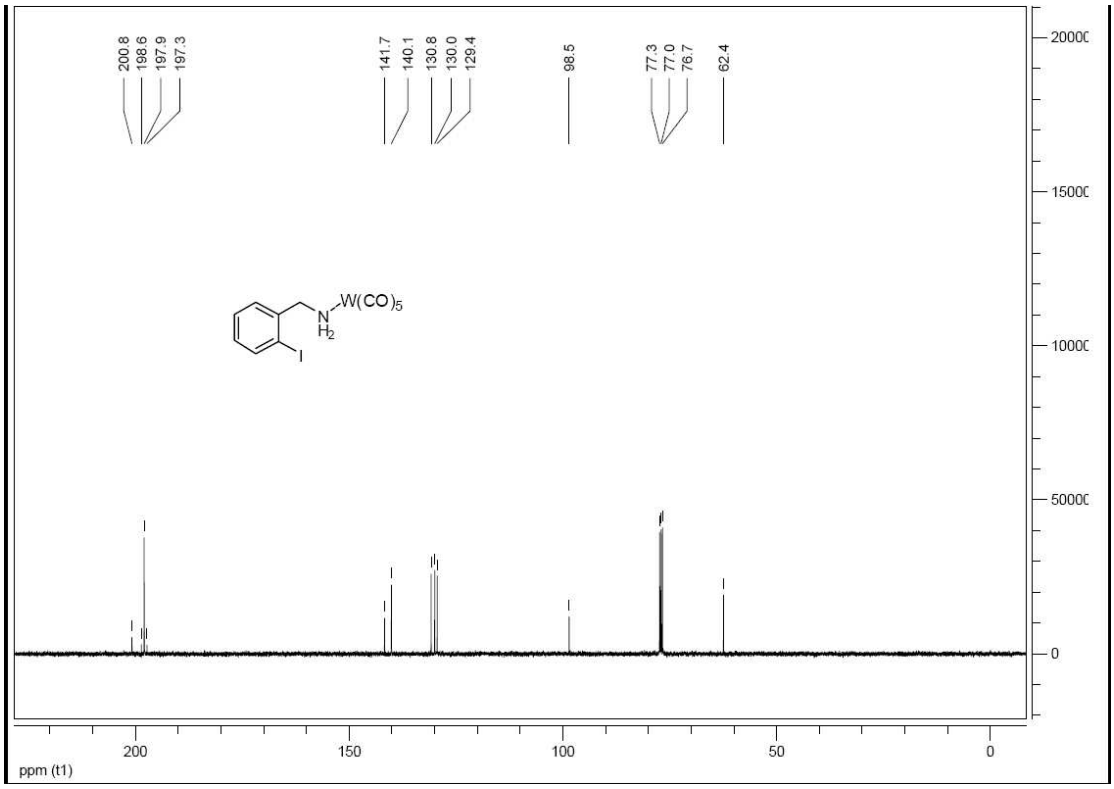
7.41
7.39
7.38
7.36
7.26
7.24
3.85
3.83
3.81
2.45
Mo(CO)5
3.09
2.24
2.00
2.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


212.5
204.0
201.0
139.3
129.3
128.6
127.4
77.3
77.0
76.7
56.4
Mo(CO)5
200
150
100
50
0
ppm (t1)

2d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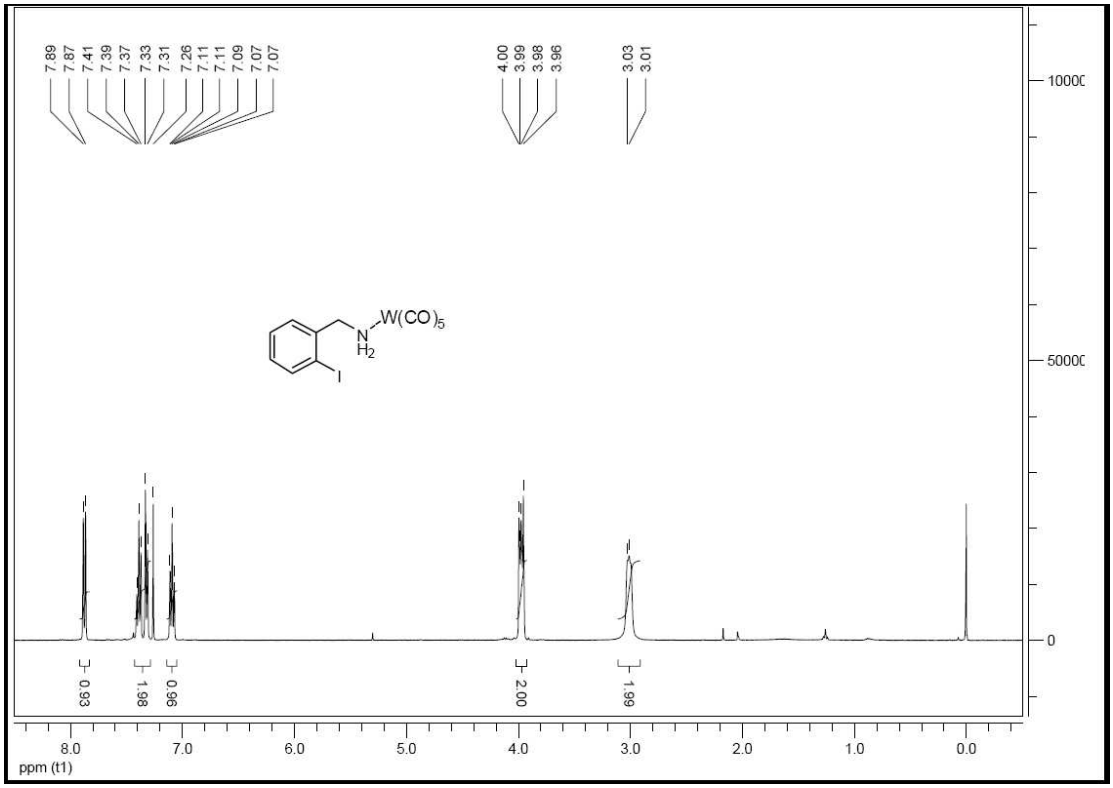
197.9
197.3
141.7
140.1
130.8
130.0
129.4
98.5
77.3
77.0
76.7
62.4
W(CO)5
N
H2
I
200
150
100
50
0
ppm (t1)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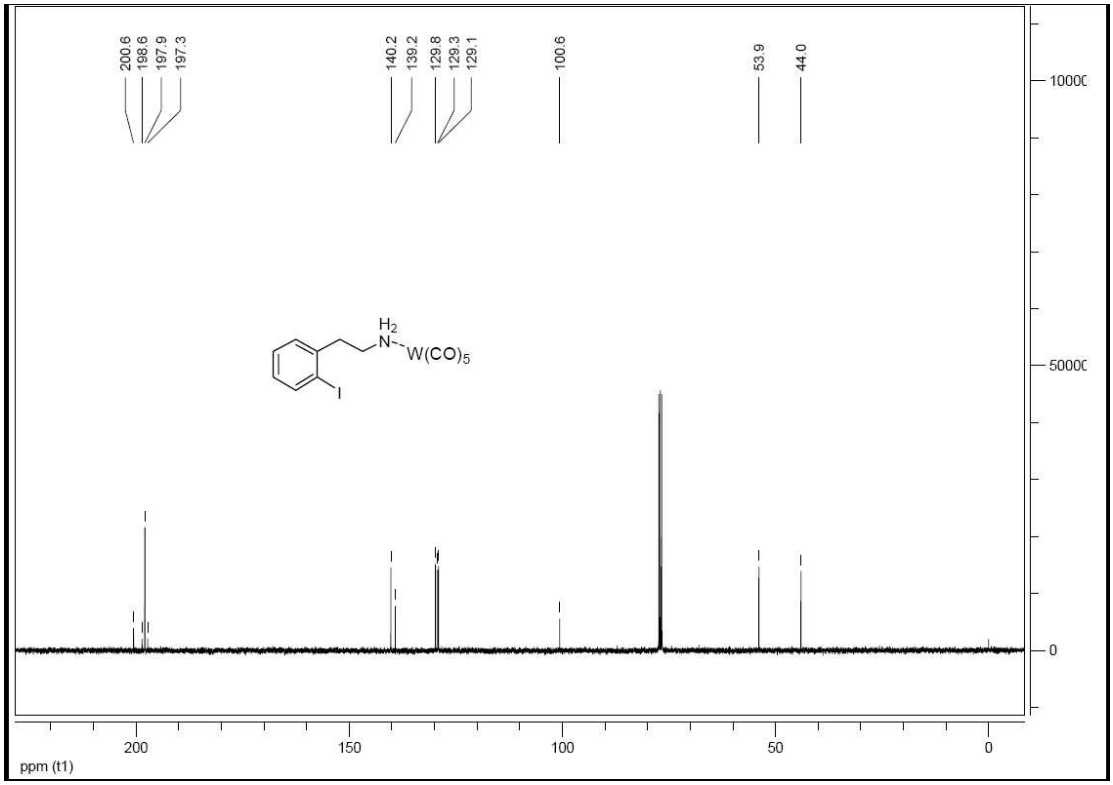
7.87
7.41
7.39
7.37
7.33
7.31
7.26
7.11
7.11
7.09
7.07
7.07
4.00
3.99
3.98
3.96
3.03
3.01
W(CO)5
N
H2
I
0.93
1.98
0.96
2.00
1.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

2e


200.6
198.6
197.9
197.3
140.2
139.2
129.8
129.3
129.1
100.6
53.9
44.0
H2
N
W(CO)5
I
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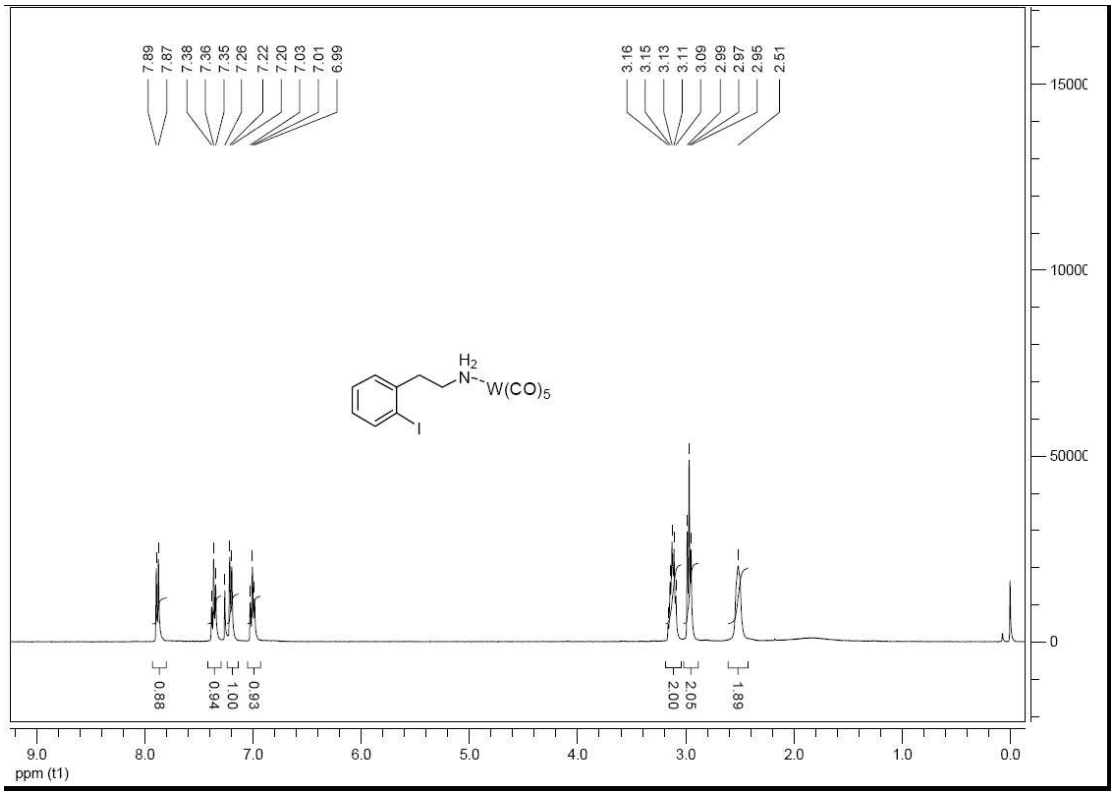
5000
0
200
150
100
50
0
ppm (t1)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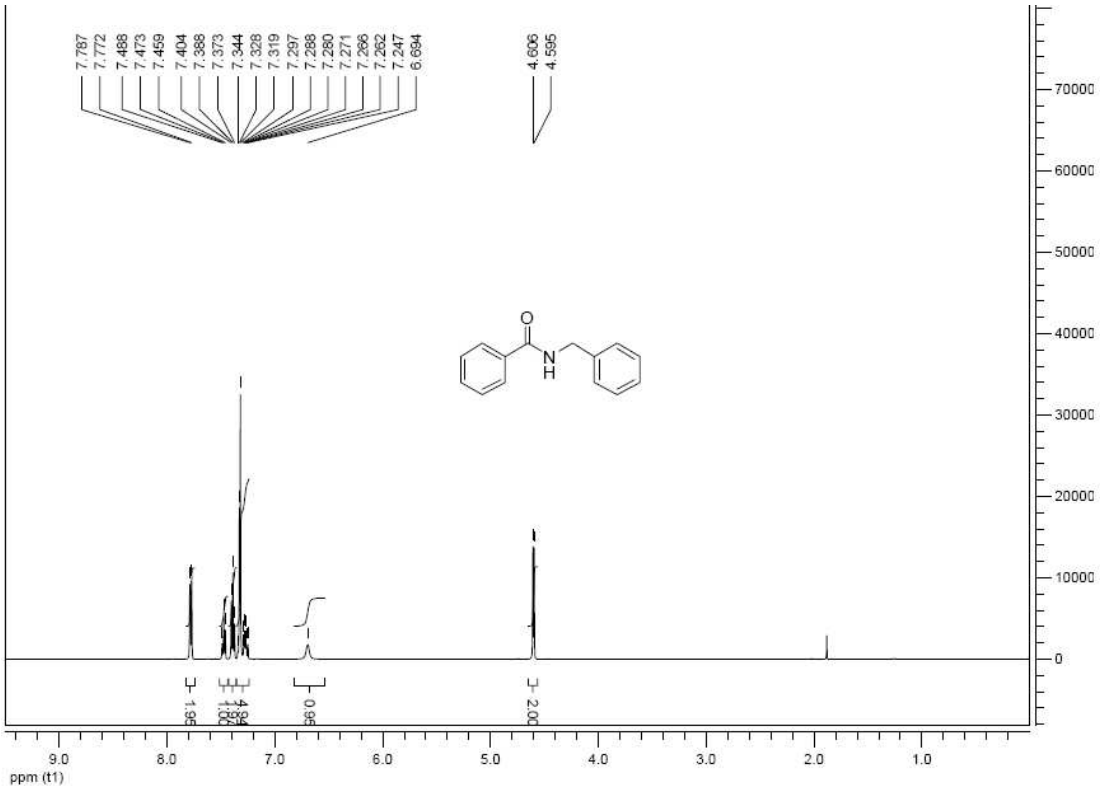
7.87
7.38
7.36
7.35
7.26
7.22
7.20
7.03
7.01
6.99
3.16
3.15
3.13
3.11
3.09
2.99
2.97
2.95
2.51
H2
N
W(CO)5
I
15000
10000
5000
0
0.88
0.64
1.00
0.93
2.00
2.05
1.89
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

3a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7.459
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7.388
7.373
7.344
7.328
7.319
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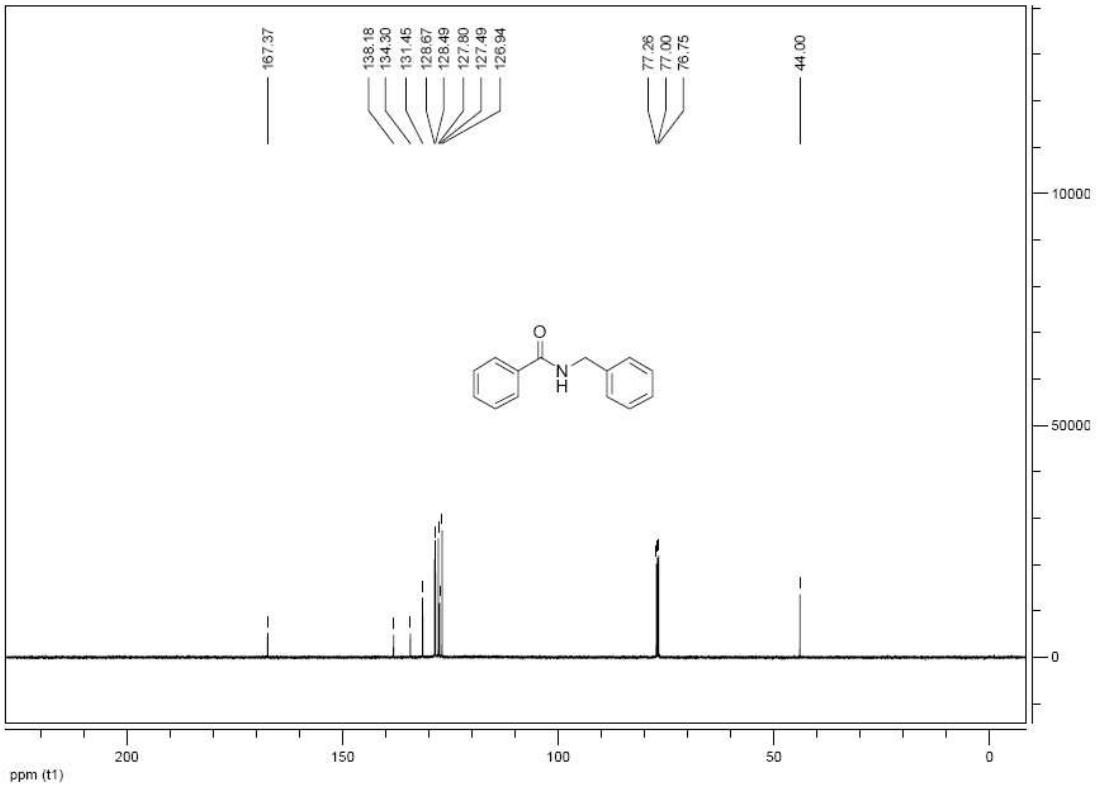
7.288
7.280
7.271
7.266
7.262
7.247
6.694
4.606
4.595
1.96
1.00
4.84
0.96
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
70000
60000
50000
40000
30000
20000
10000
0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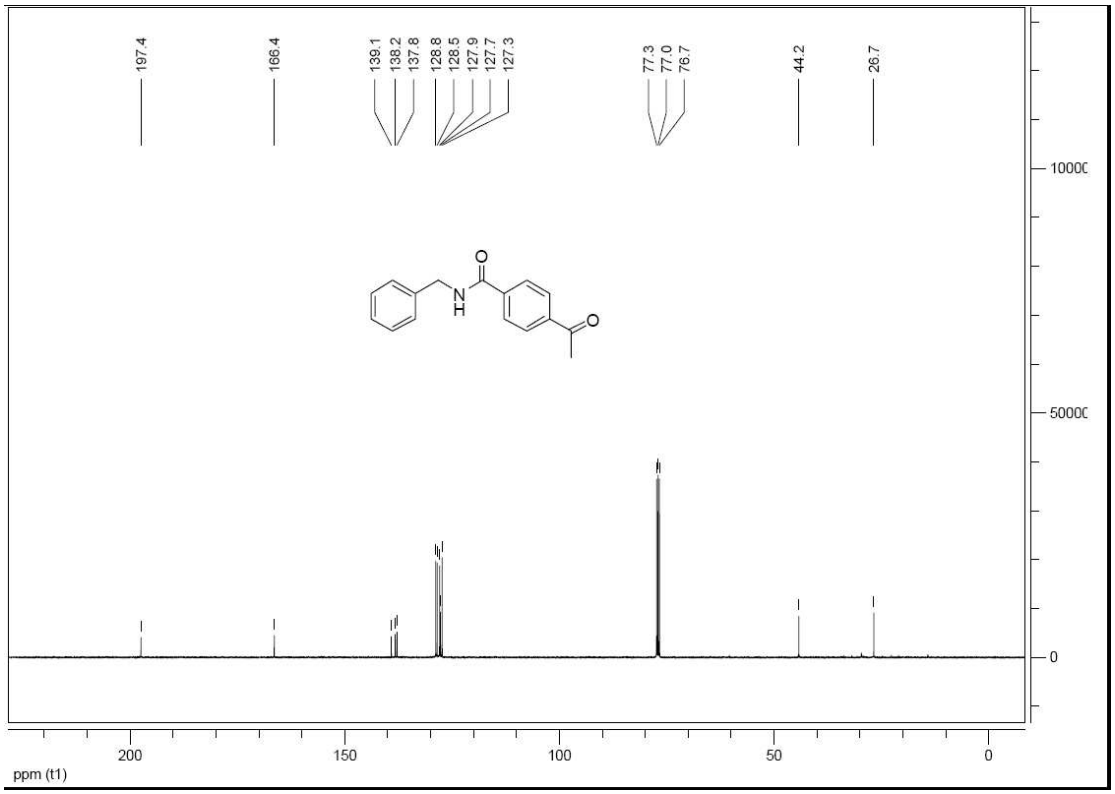
134.30
131.45
128.67
128.49
127.80
127.49
126.94
77.26
77.00
76.75
44.00
200
150
100
50
0
ppm (t1)
10000
50000
0

3b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166.4
139.1
138.2
137.8
128.8
128.5
127.9
127.7
127.3
77.3
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76.7
44.2
26.7
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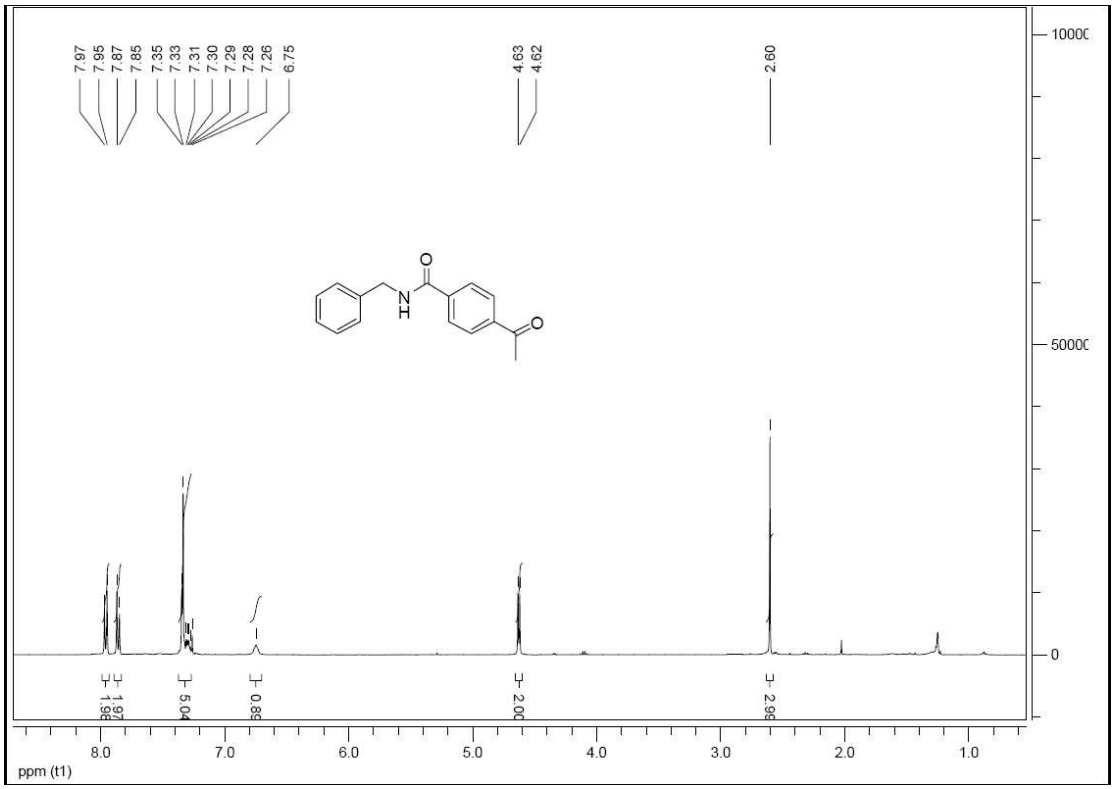
0
200
150
100
50
0
ppm (t1)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7.95
7.87
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7.33
7.31
7.30
7.29
7.28
7.26
6.75
4.63
4.62
2.60
10000
5000
0
1.98
1.97
5.04
0.88
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2.96
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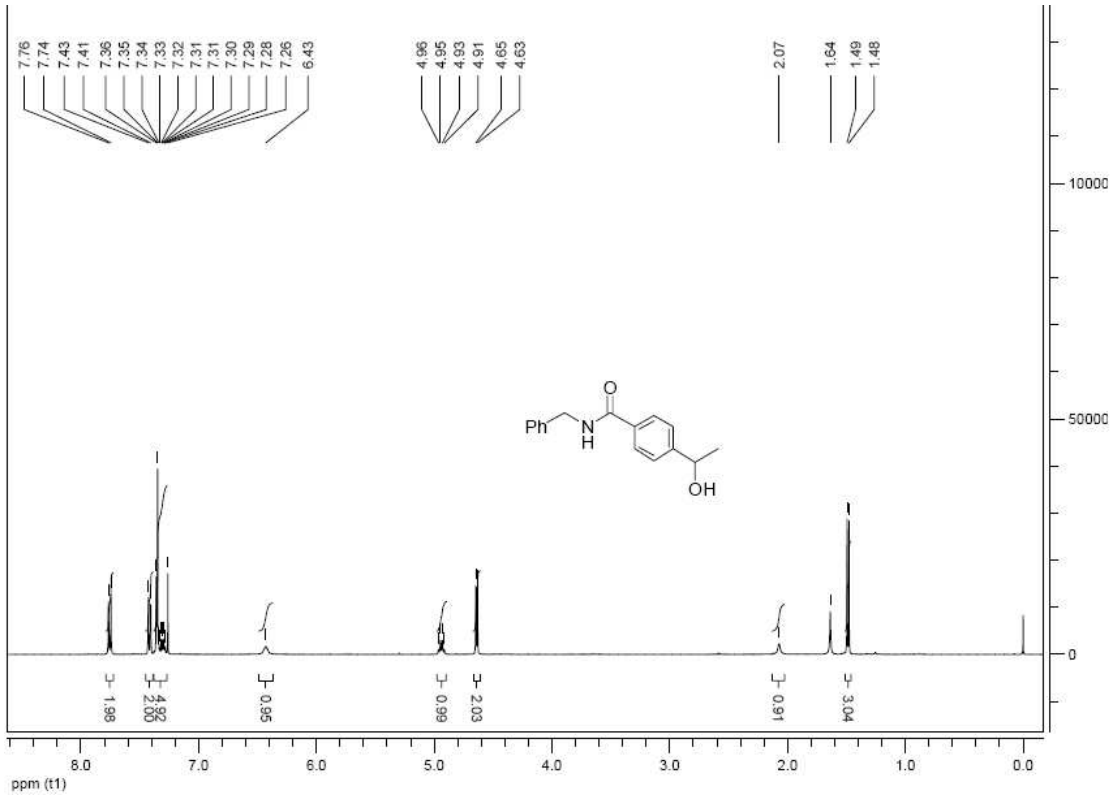
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

3b'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7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.26
6.43
4.96
4.95
4.93
4.91
4.65
4.63
2.07
1.64
1.49
1.48
Ph
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H
O
OH
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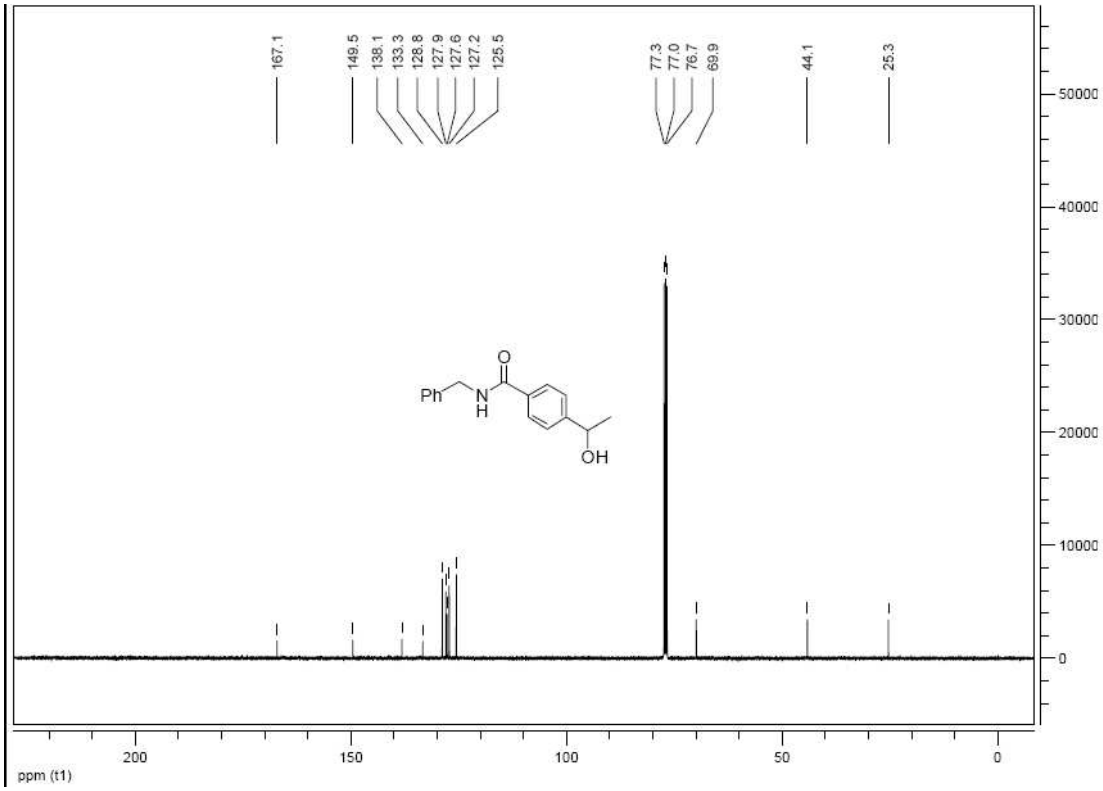
4.00
2.92
0.96
0.99
2.03
0.91
3.04
ppm (t1)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138.1
133.3
128.8
127.9
127.6
127.2
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77.3
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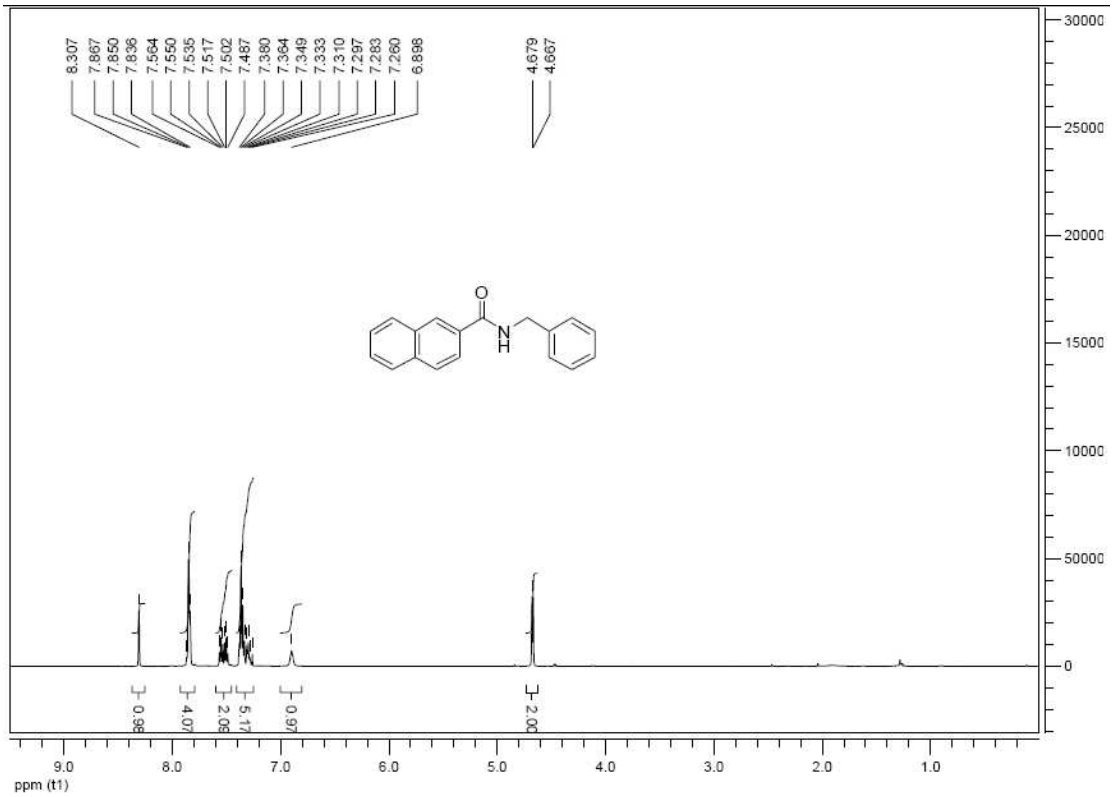
76.7
69.9
44.1
25.3
Ph
N
H
O
OH
ppm (t1)

3c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7.380
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7.349
7.333
7.310
7.297
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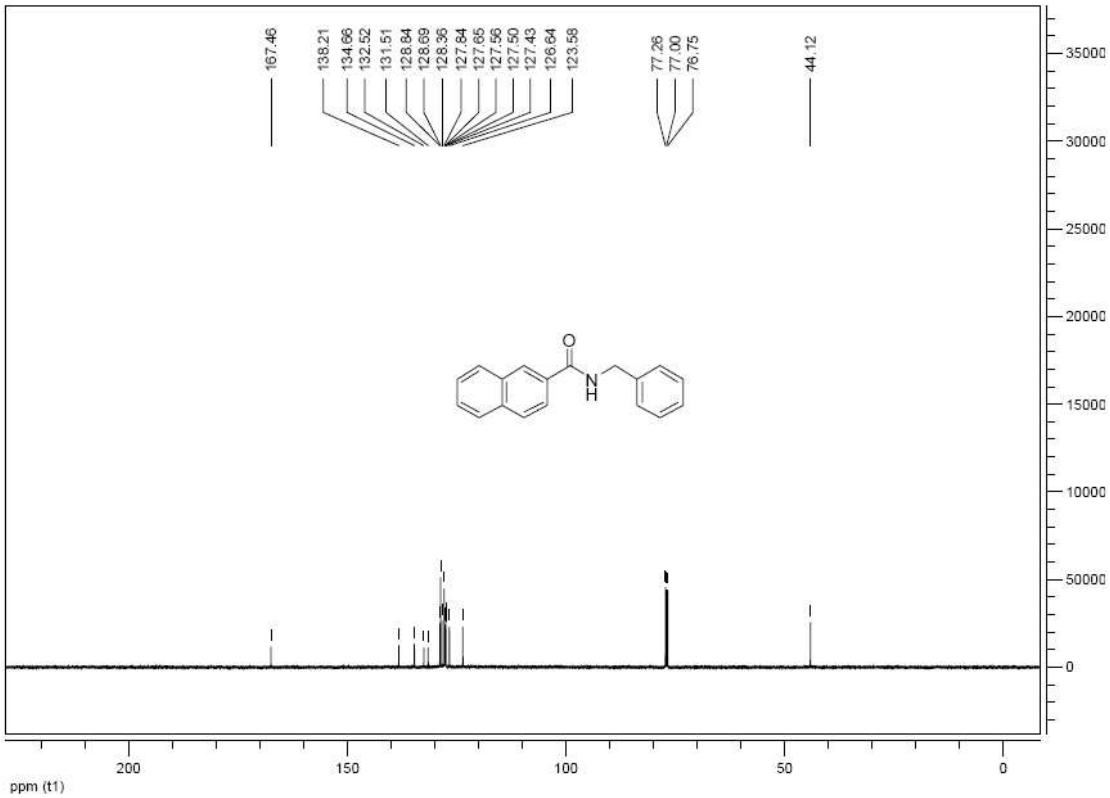
ppm (t1)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127.43
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123.58
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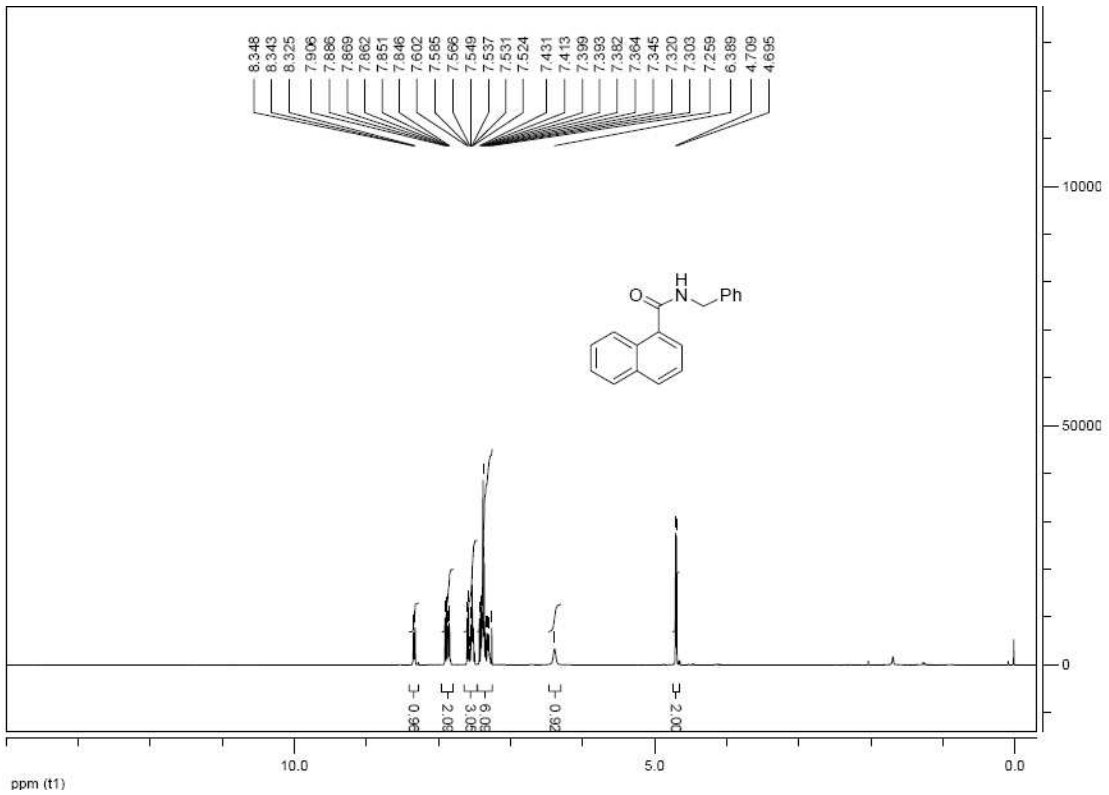
77.00
76.75
44.12
ppm (t1)

3d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7.869
7.862
7.851
7.846
7.602
7.585
7.566
7.549
7.537
7.531
7.524
7.431
7.413
7.399
7.393
7.382
7.364
7.345
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7.303
7.259
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4.695
10000
50000
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H
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Ph
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3.06
6.09
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10.0
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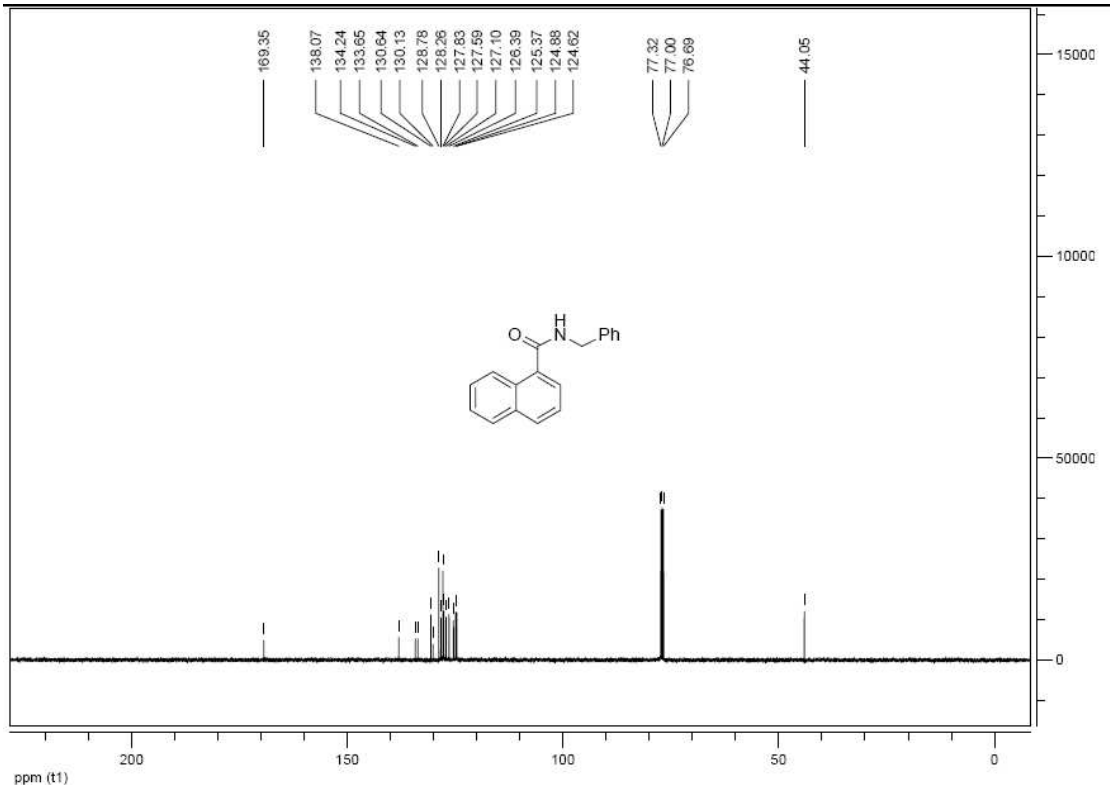
0.0
ppm (t1)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130.64
130.13
128.78
128.26
127.83
127.59
127.10
126.39
125.37
124.88
124.62
77.32
77.00
76.69
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10000
50000
0
O
H
N
Ph
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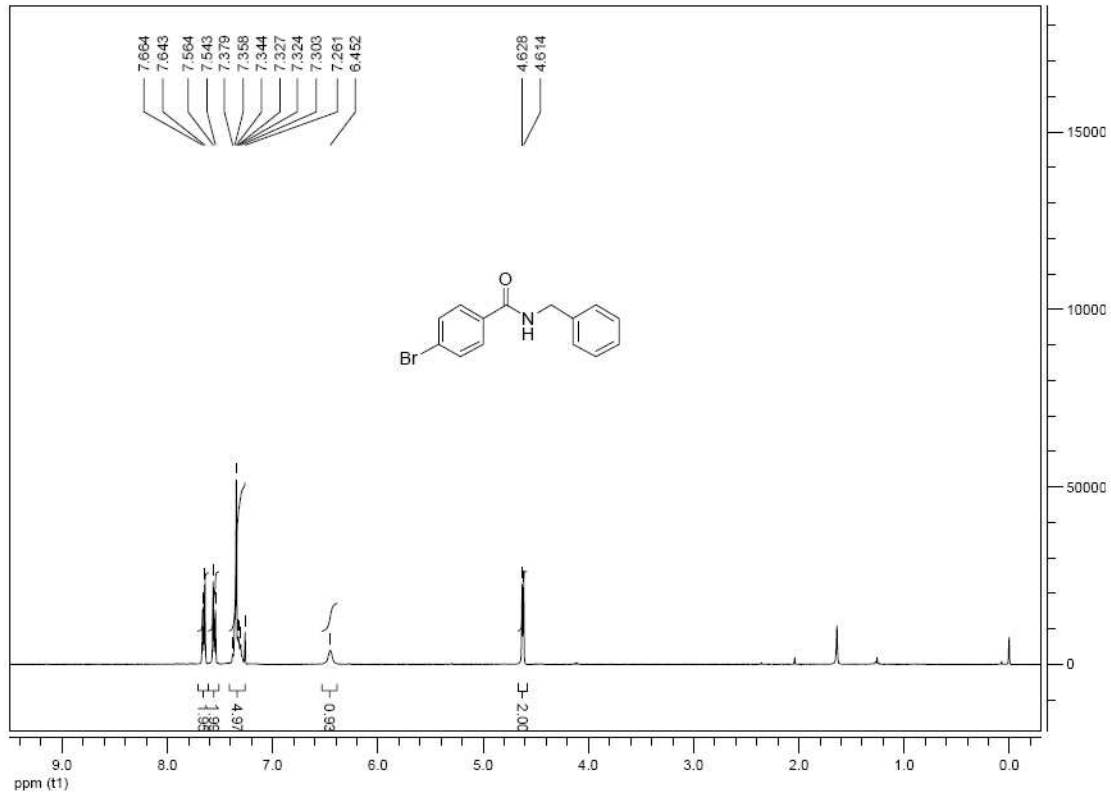
150
100
50
0
ppm (t1)

3e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7.379
7.358
7.344
7.327
7.324
7.303
7.261
6.452
4.628
4.614
O
N
H
Br
15000
10000
50000
0
1.98
4.97
0.99
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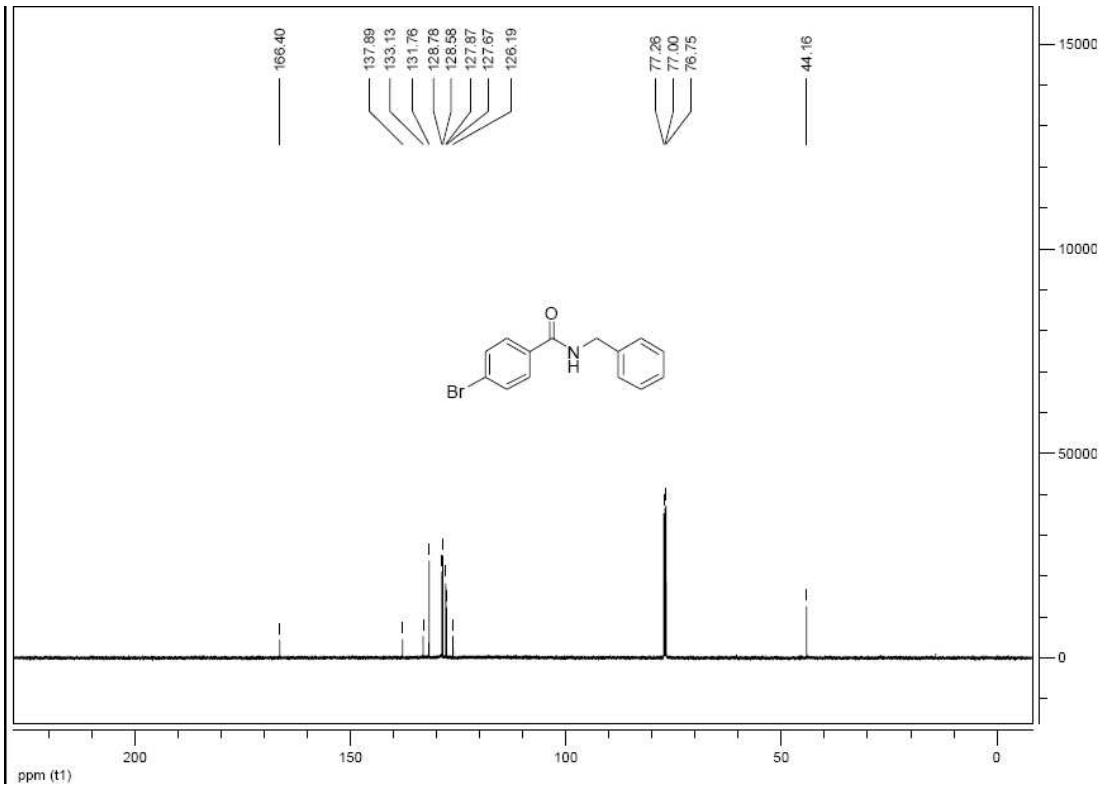
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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77.00
76.75
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H
Br
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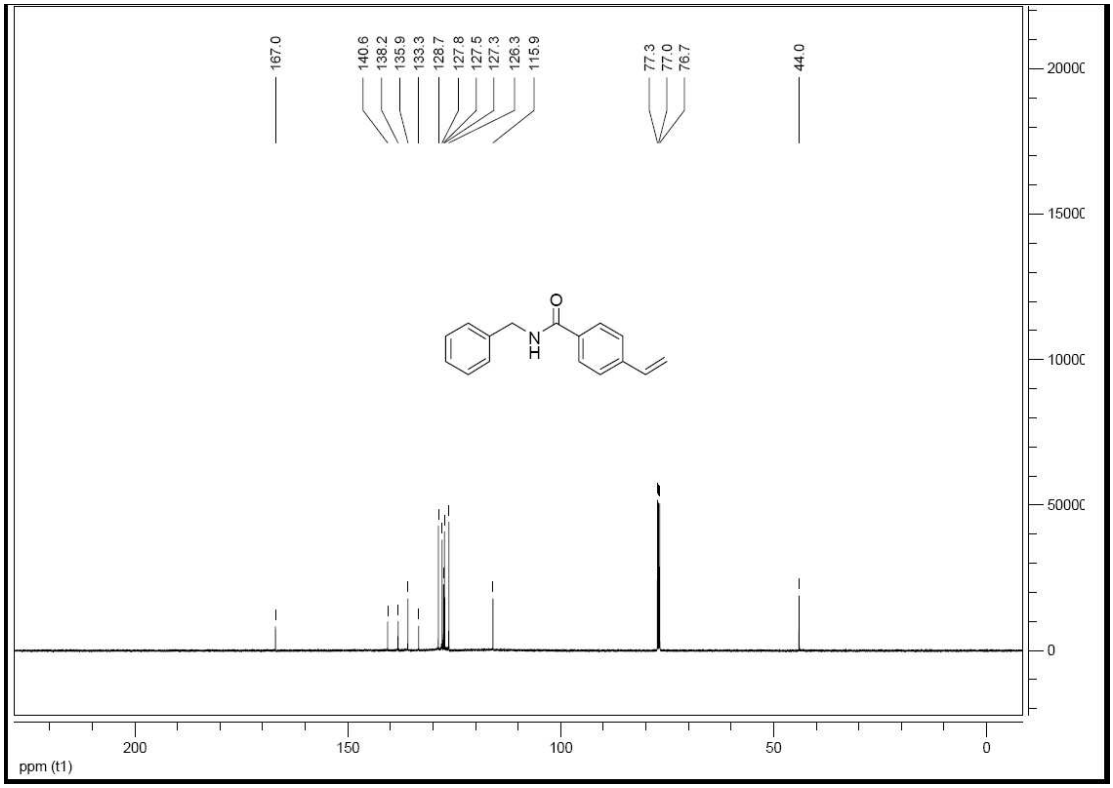
150
100
50
0
ppm (t1)

3f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127.8
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127.3
126.3
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76.7
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200
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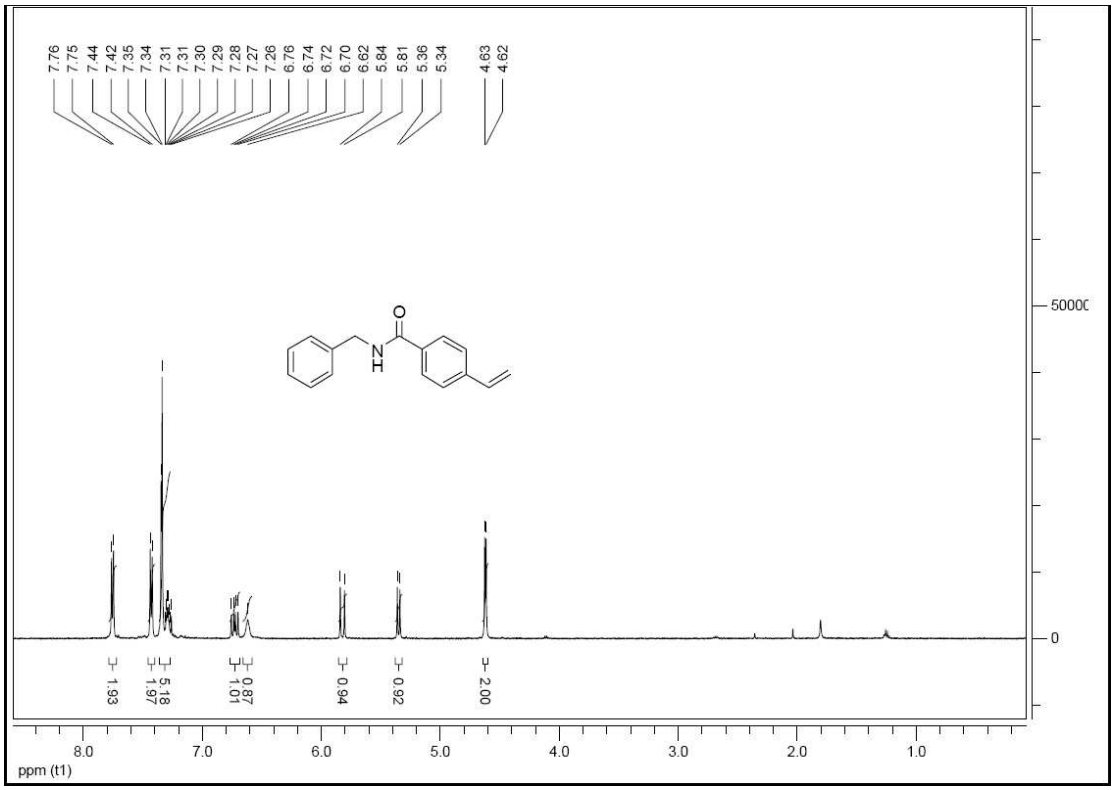
50
0
ppm (t1)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7.34
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7.31
7.30
7.29
7.28
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6.76
6.74
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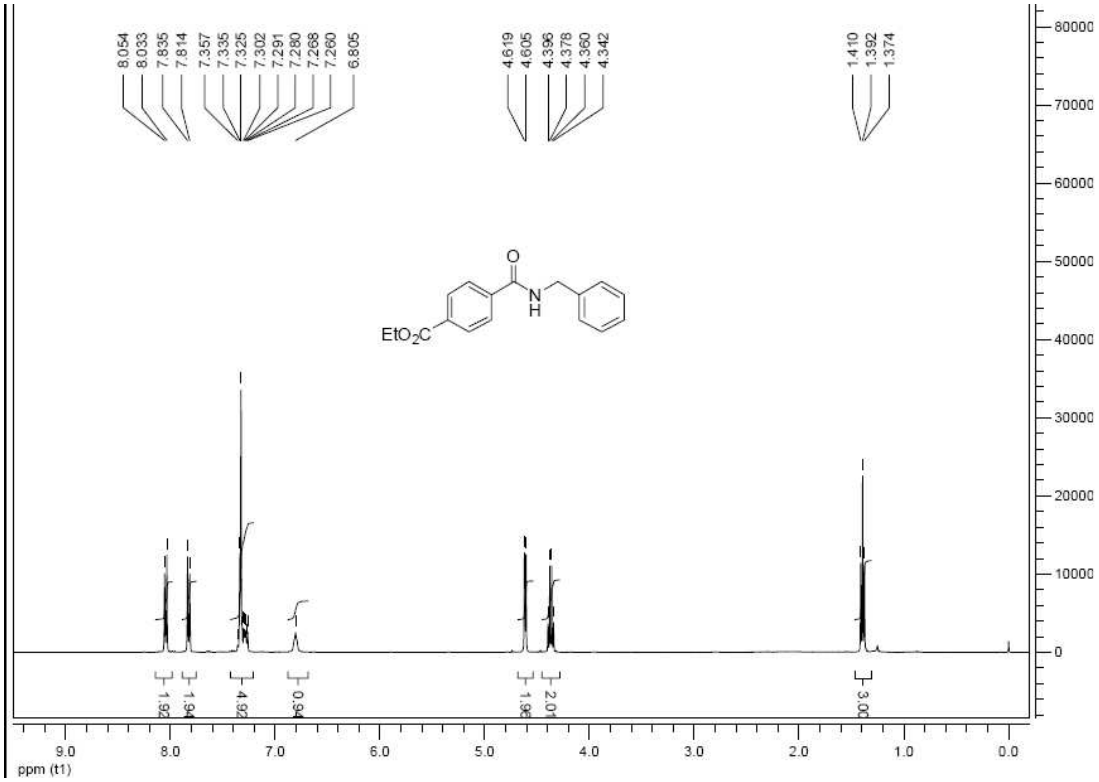
6.70
6.62
5.84
5.81
5.36
5.34
4.63
4.62
1.93
1.67
5.18
1.01
0.87
0.94
0.92
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

3g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7.302
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7.280
7.268
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4.619
4.605
4.396
4.378
4.360
4.342
1.410
1.392
1.374
EtO2C
O
N
H
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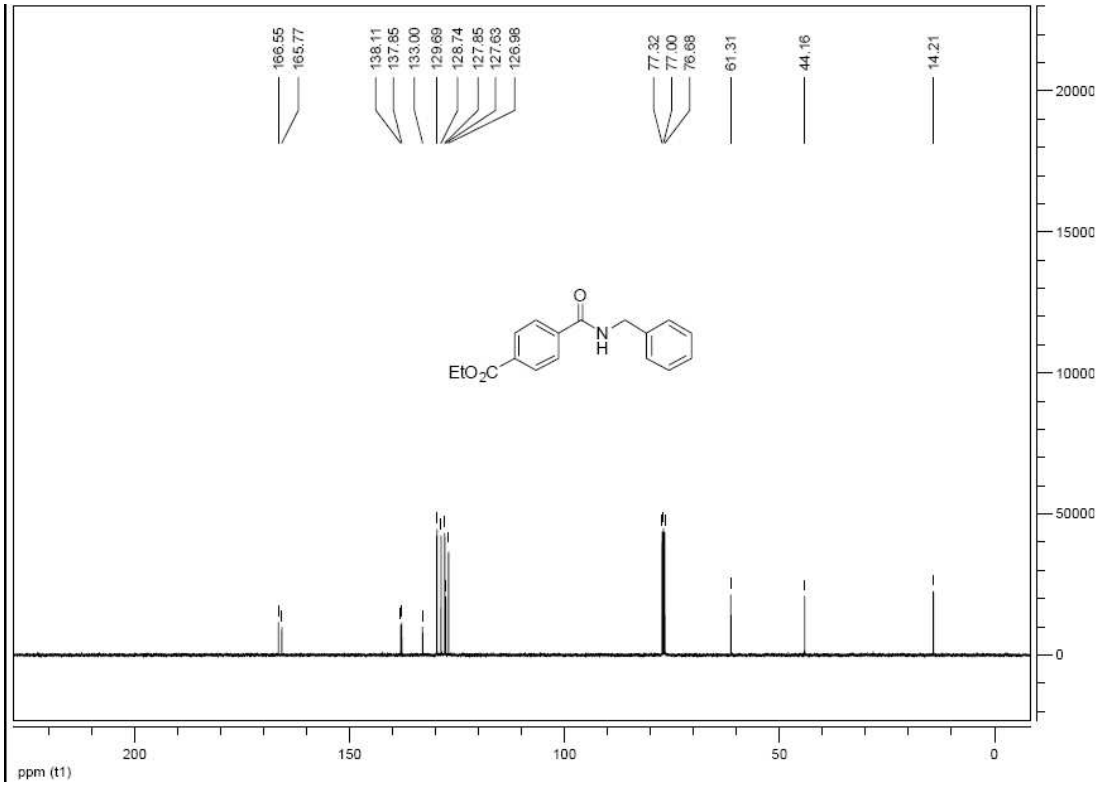
1.94
4.22
0.94
1.96
2.01
3.00
ppm (t1)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129.69
128.74
127.85
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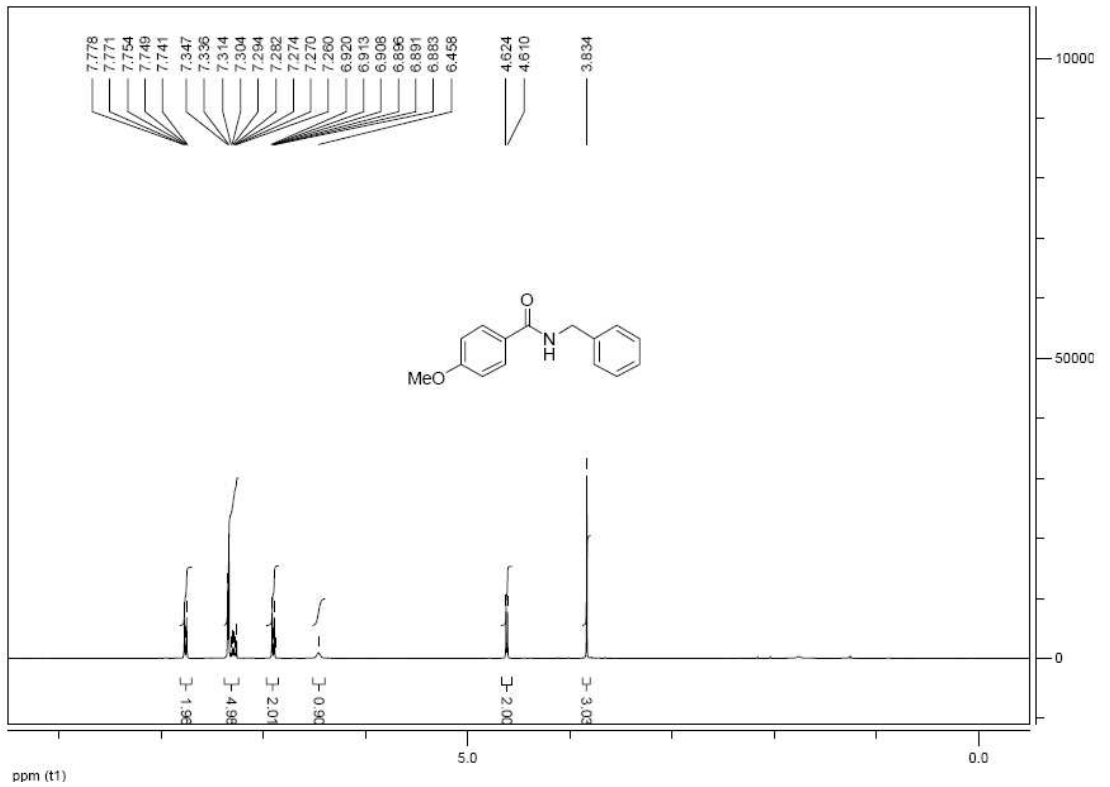
126.98
77.32
77.00
76.68
61.31
44.16
14.21
EtO2C
O
N
H
ppm (t1)

3h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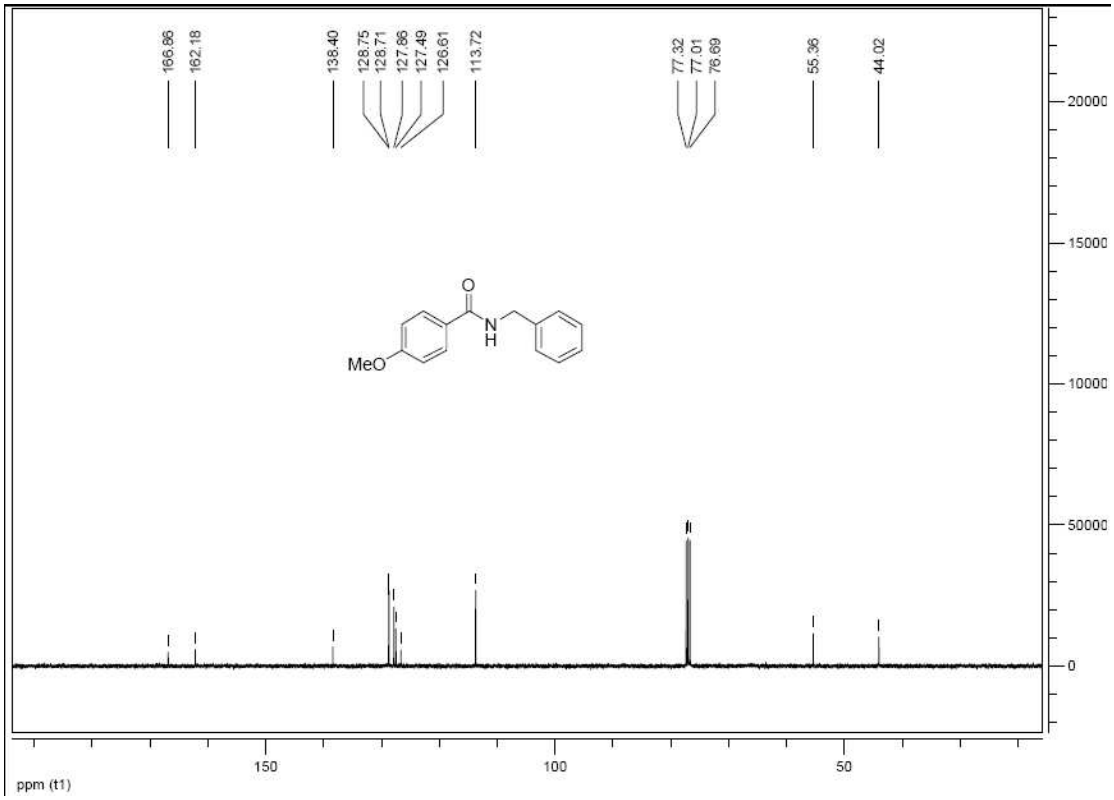
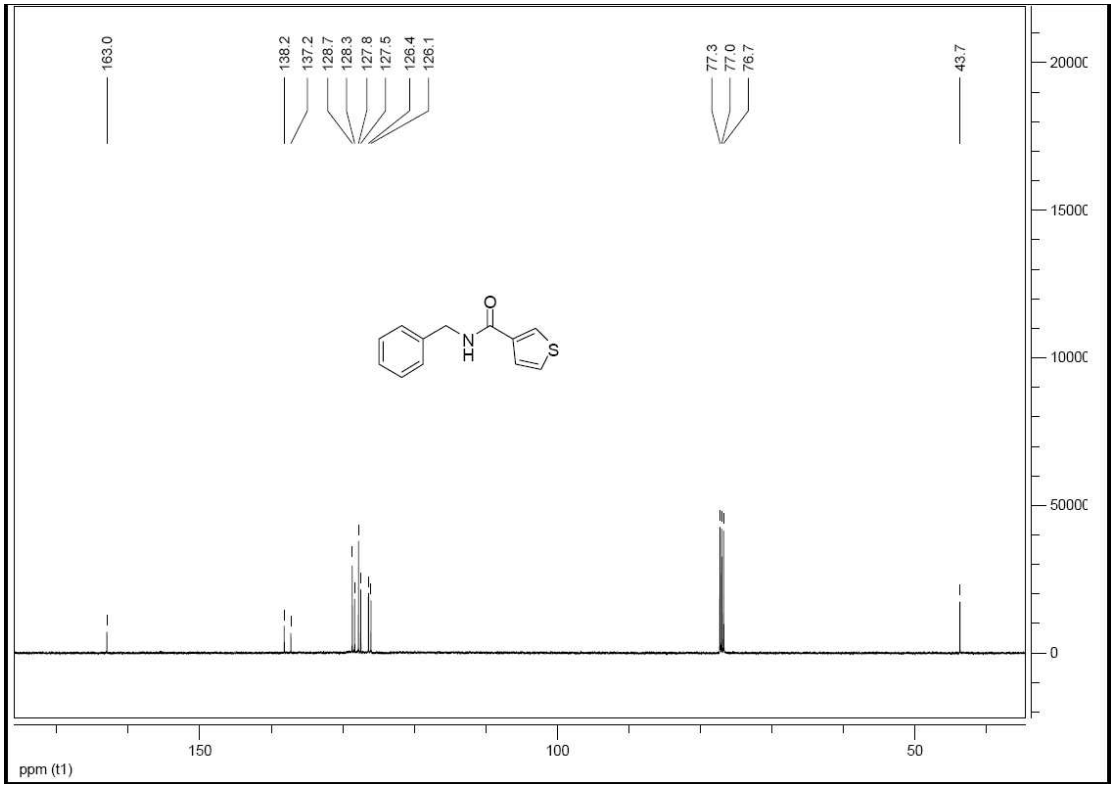
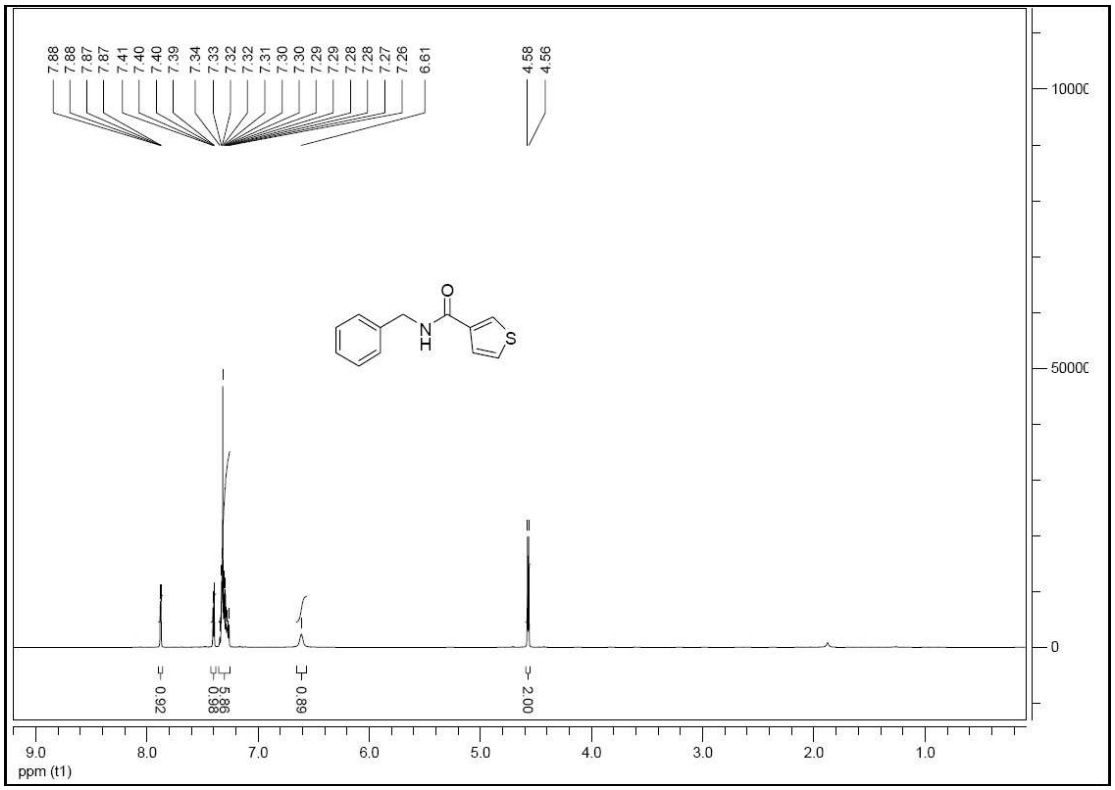
7.314
7.304
7.294
7.282
7.274
7.270
7.260
6.920
6.913
6.908
6.896
6.891
6.883
6.458
4.624
4.610
3.834
MeO
1.96
4.98
2.07
0.90
2.00
3.02
10000
50000
0
5.0
0.0
ppm (t1)

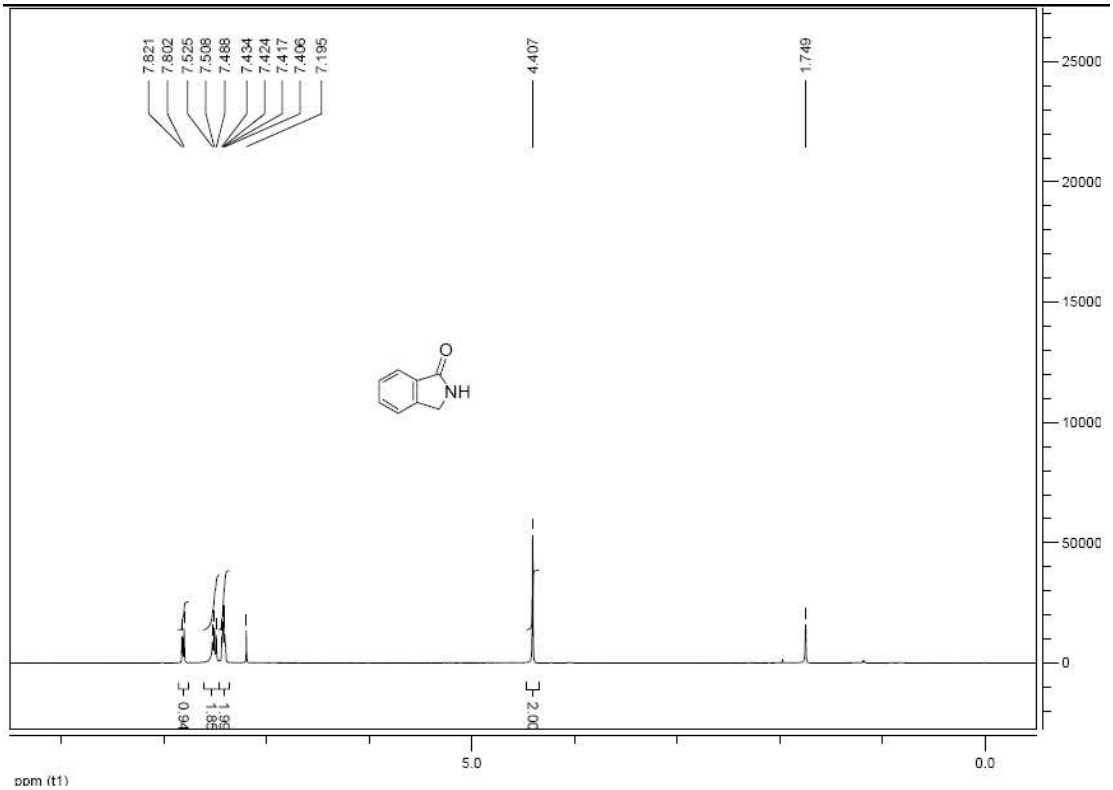

166.86
162.18
138.40
128.75
128.71
127.86
127.49
126.61
113.72
77.32
77.01
76.69
55.36
44.02
MeO
20000
15000
10000
50000
0
150
100
50
ppm (t1)

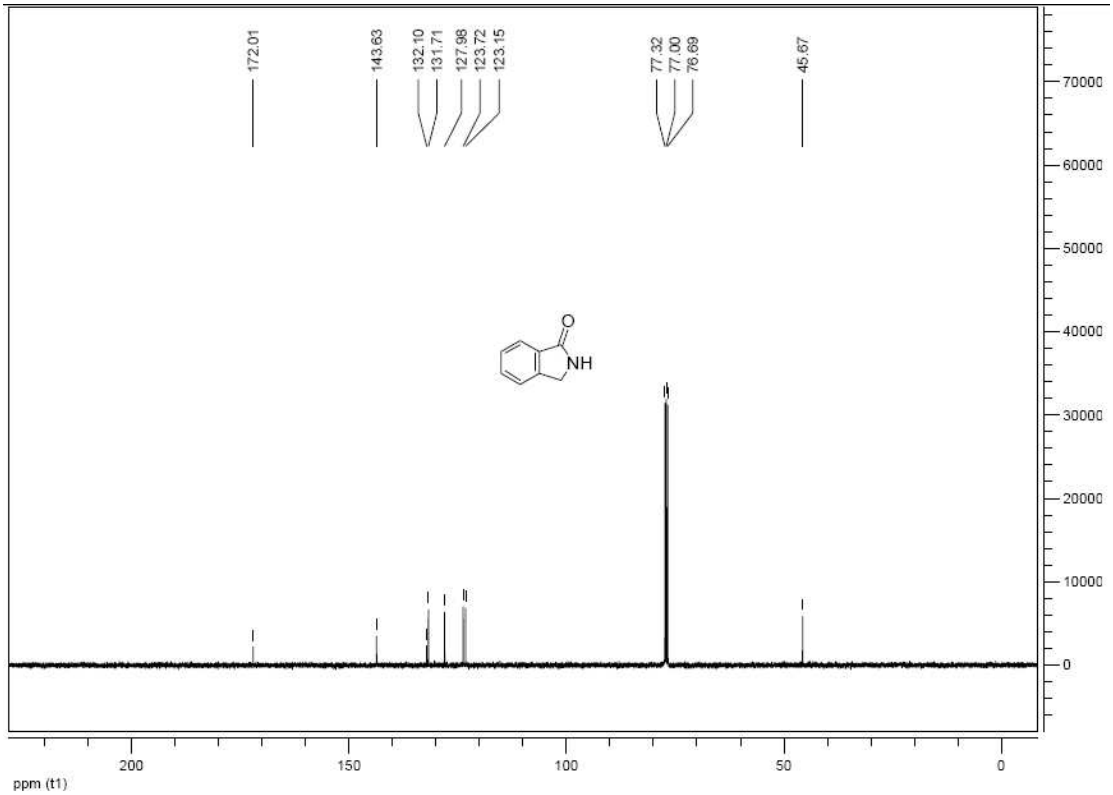
3i


163.0
138.2
137.2
128.7
128.3
127.8
127.5
126.4
126.1
77.3
77.0
76.7
43.7
O
N
H
S
150
100
50
ppm (t1)

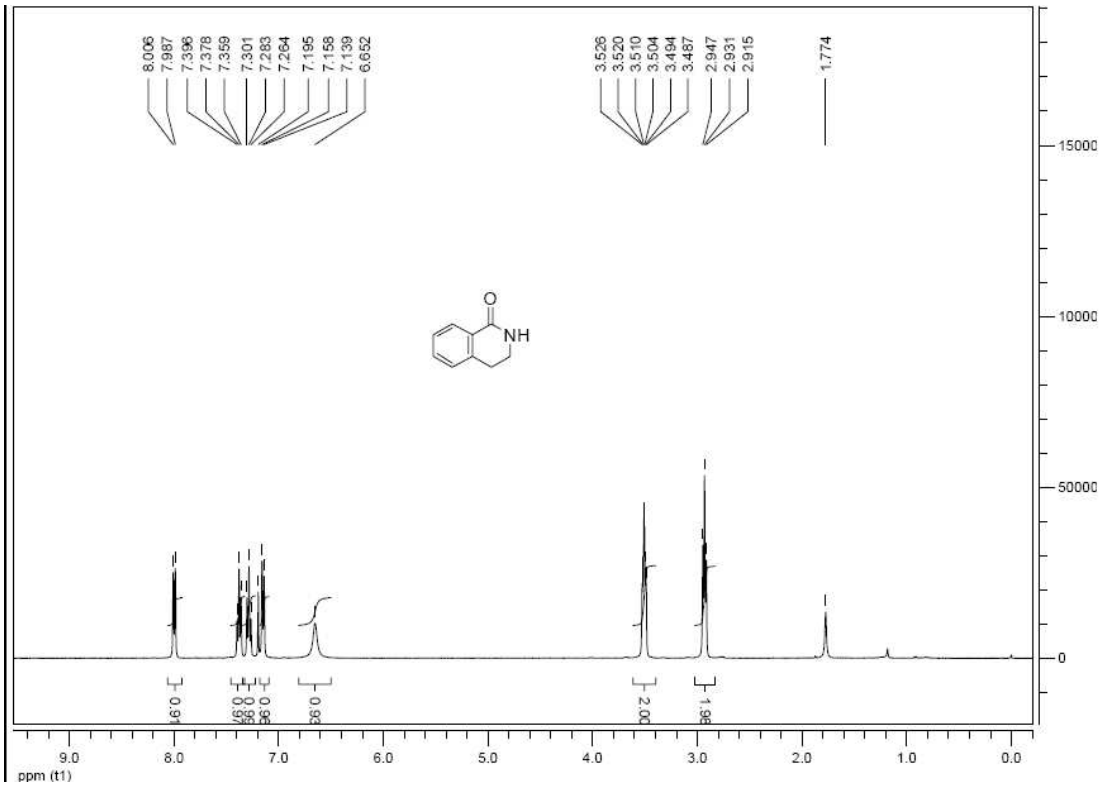

7.88
7.88
7.87
7.87
7.41
7.40
7.40
7.39
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
6.61
4.58
4.56
O
N
H
S
0.92
5.88
0.89
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

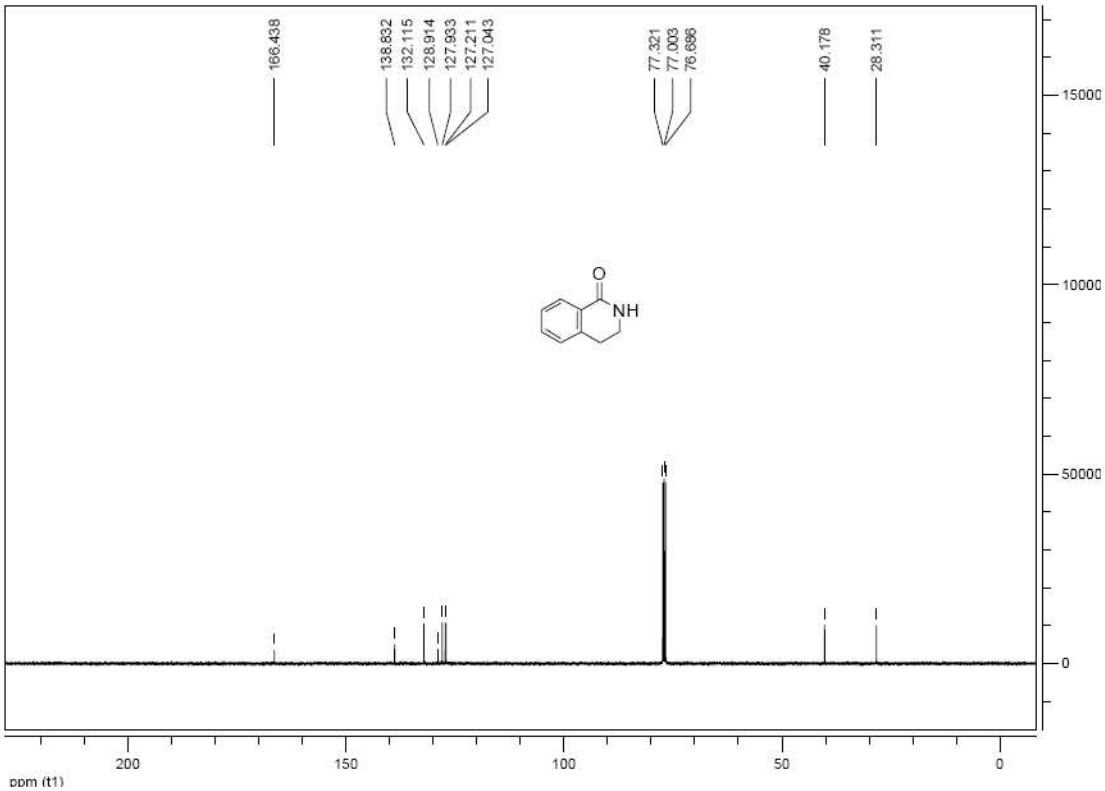
3j


7.821
7.802
7.525
7.508
7.488
7.434
7.424
7.417
7.406
7.195
4.407
1.749
O
NH
25000
20000
15000
10000
50000
0
0.94
1.68
1.68
2.00
5.0
0.0
ppm (t1)

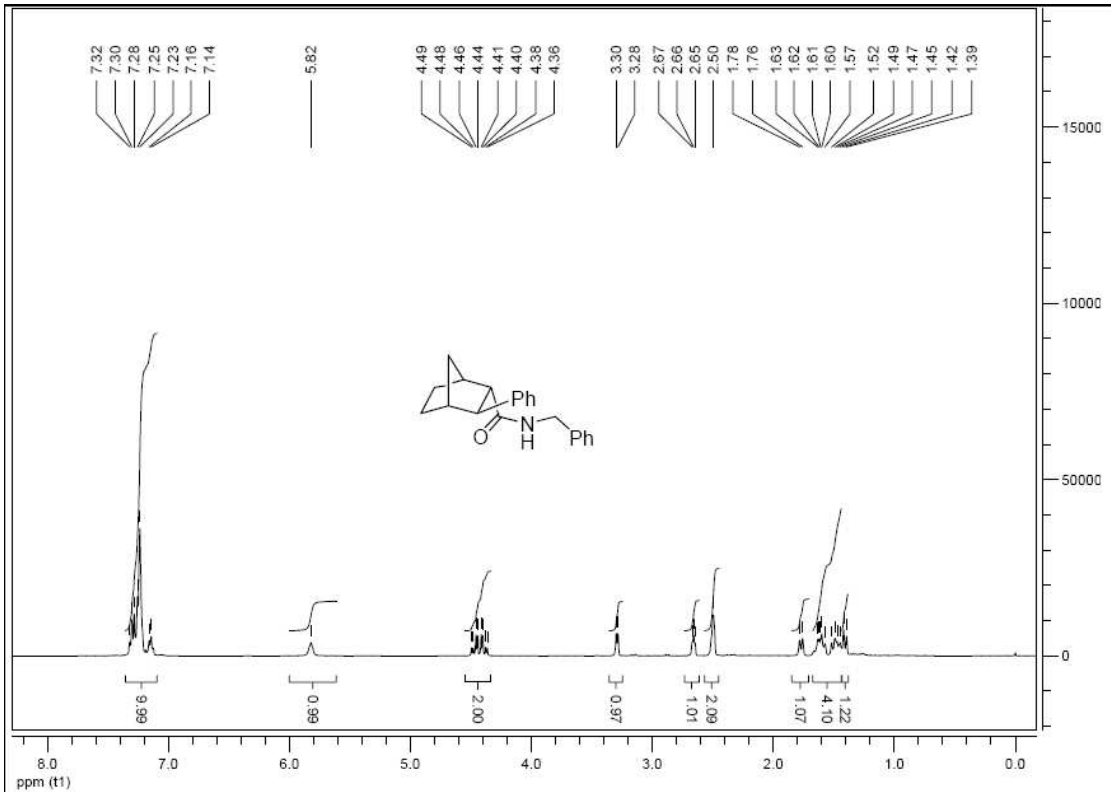

172.01
143.63
132.10
131.71
127.98
123.72
123.15
77.32
77.00
76.69
45.67
O
NH
70000
60000
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

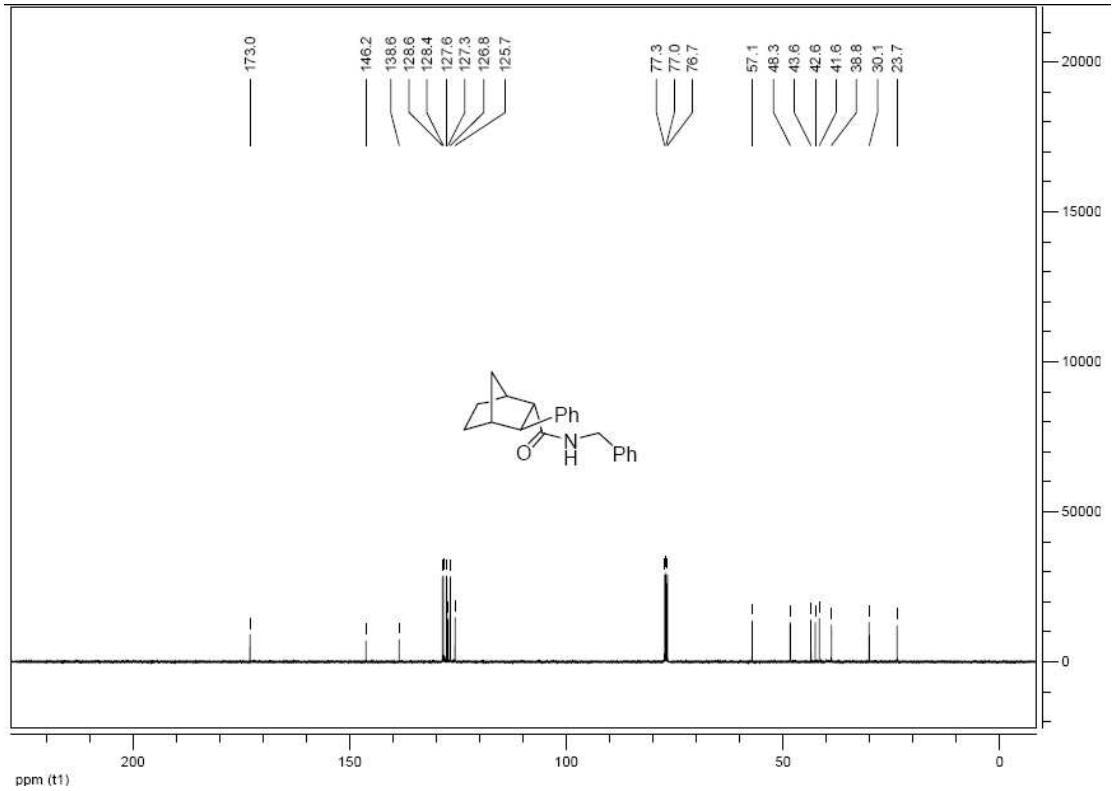
3k


8.006
7.987
7.396
7.378
7.359
7.301
7.283
7.264
7.195
7.158
7.139
6.652
3.526
3.520
3.510
3.504
3.494
3.487
2.947
2.931
2.915
1.774
NH
15000
10000
50000
0
0.97
0.97
0.96
0.96
0.92
2.00
1.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

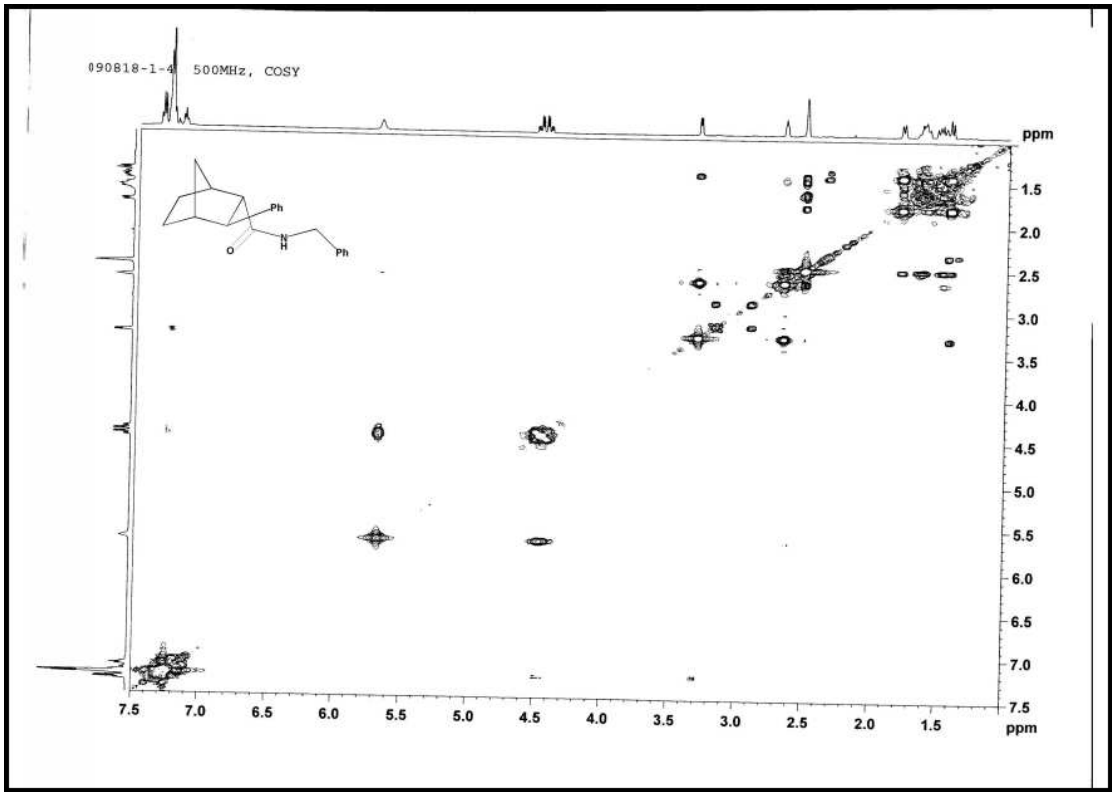

166.438
138.832
132.115
128.914
127.933
127.211
127.043
77.321
77.003
76.686
40.178
28.311
NH
15000
10000
50000
0
200
150
100
50
0
ppm (t1)

***trans*-4**

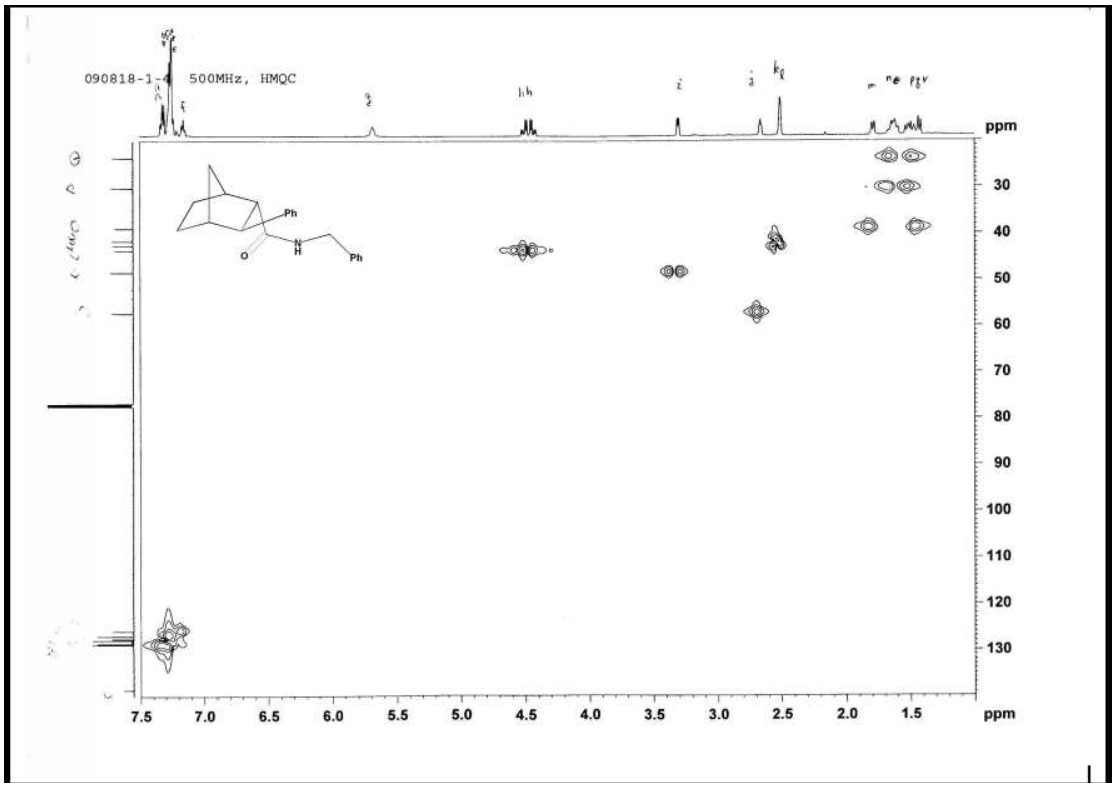

7.32
7.30
7.28
7.25
7.23
7.16
7.14
5.82
4.49
4.48
4.46
4.44
4.41
4.40
4.38
4.36
3.30
3.28
2.67
2.66
2.65
2.50
1.78
1.76
1.63
1.62
1.61
1.60
1.57
1.52
1.49
1.47
1.45
1.42
1.39
Ph
N
H
O
Ph
9.99
0.99
2.00
0.97
1.01
2.09
1.07
4.10
1.22
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
15000
10000
50000
0


173.0
146.2
138.6
128.6
128.4
127.6
127.3
126.8
125.7
77.3
77.0
76.7
57.1
48.3
43.6
42.6
41.6
38.8
30.1
23.7
Ph
N
H
O
Ph
200
150
100
50
0
ppm (t1)
20000
15000
10000
50000
0

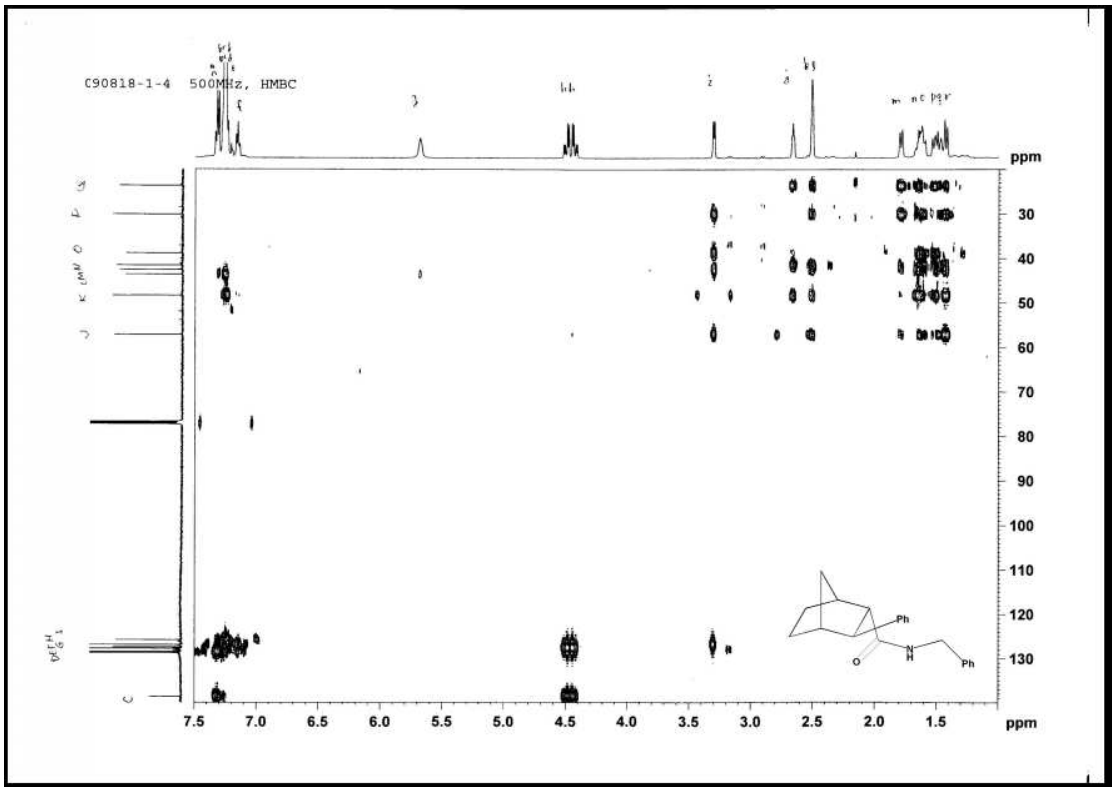
***trans*-4** (^{1}H-^{1}H COSY)



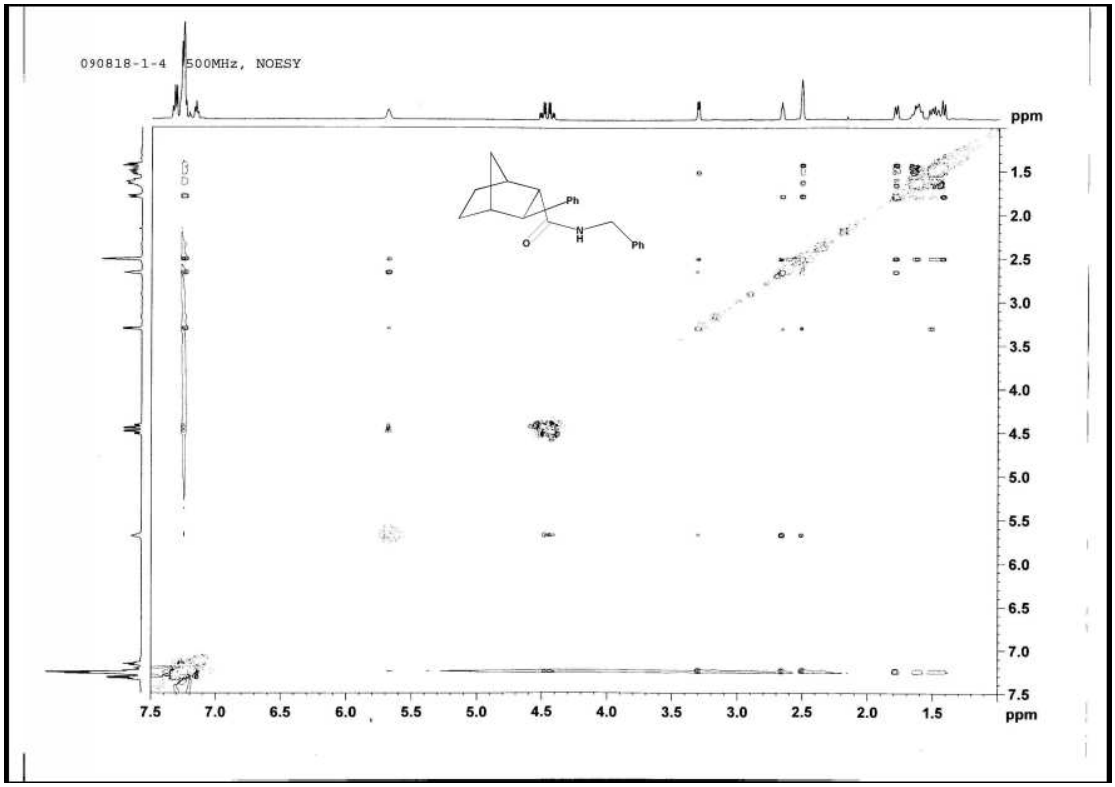
***trans*-4** (HMQC)



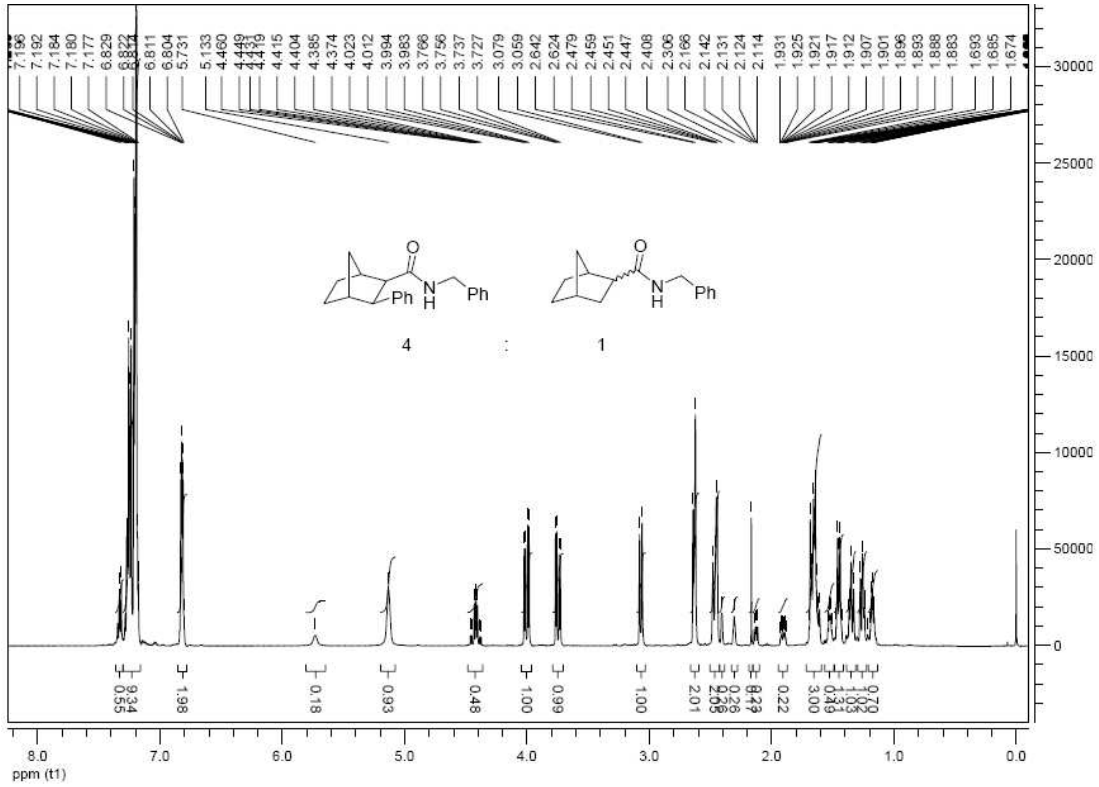
***trans*-4** (HMBC)

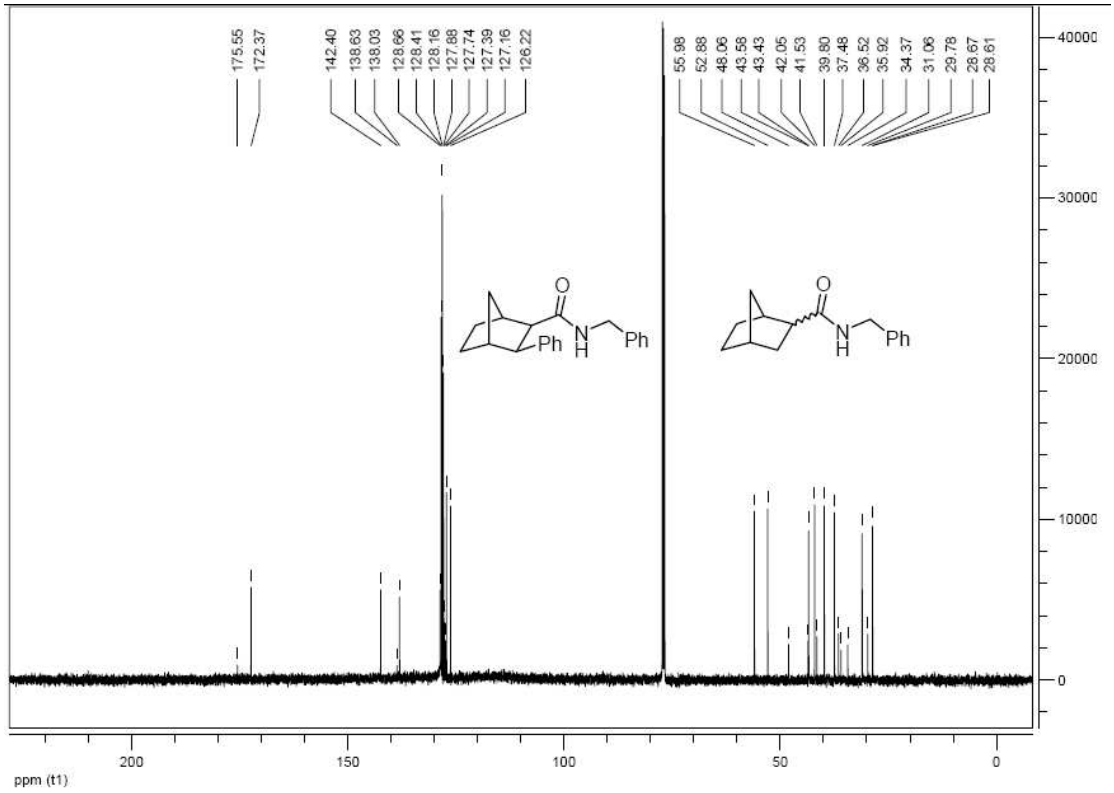


***trans*-4** (NOESY)

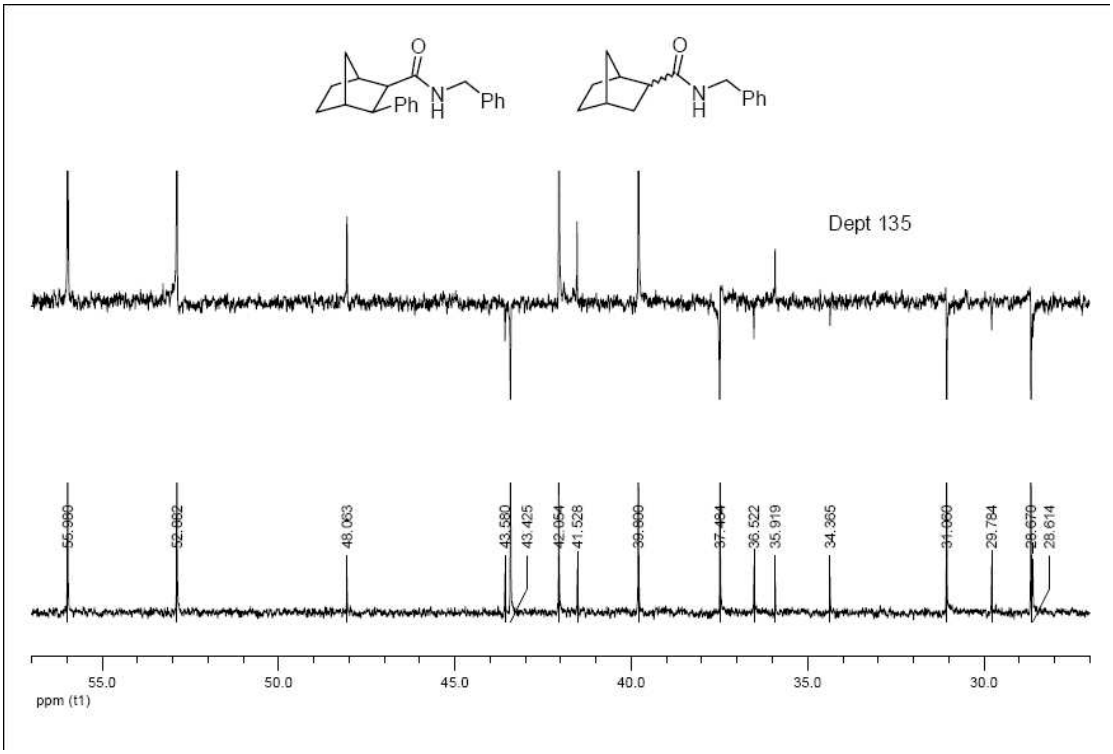


A mixture of ***cis*-4** and **5**

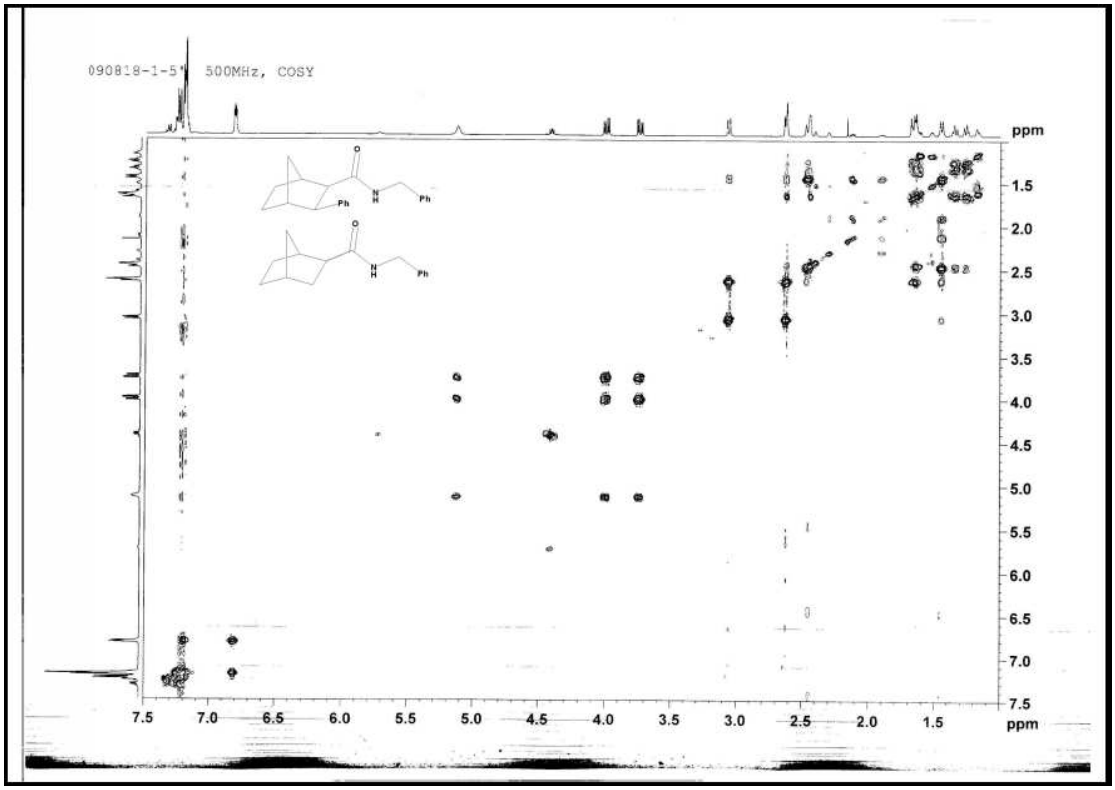




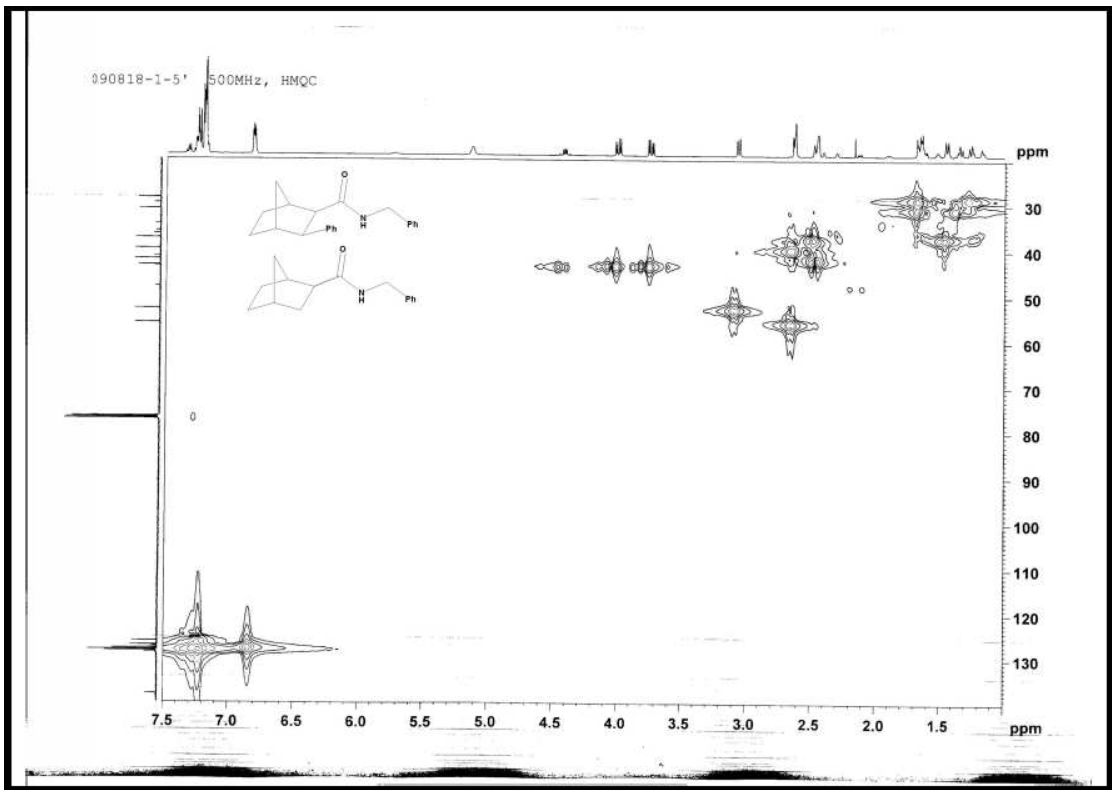
A mixture of ***cis*-4** and **5** (DEPT135)



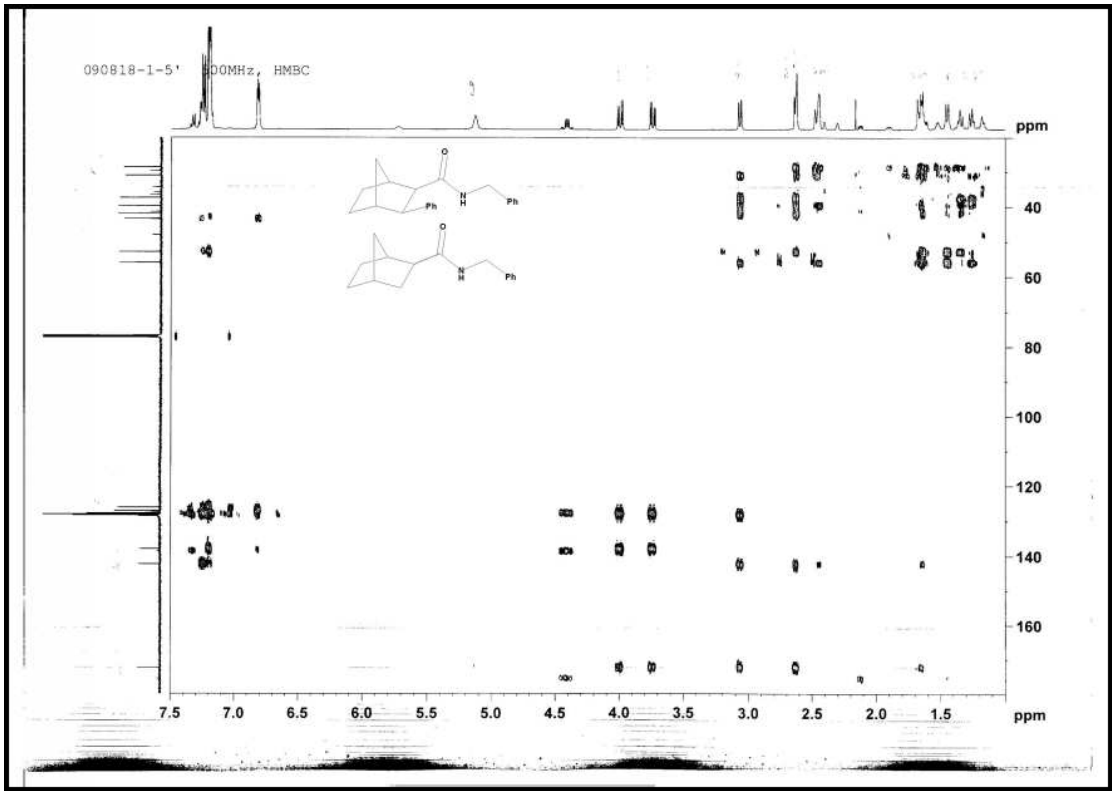
A mixture of ***cis*-4** and **5** (^{1}H-^{1}H COSY)



A mixture of ***cis*-4** and **5** (HMQC)



A mixture of ***cis*-4** and **5** (HMBC)



A mixture of ***cis*-4** and **5** (NOESY)