Supporting Information

A novel alternative for the *N–N* bond formation through a PIFA-mediated oxidative cyclization and its application to the synthesis of indazol-3-ones

Arkaitz Correa, Imanol Tellitu, Esther Domínguez,* and Raul SanMartin*

Departamento de Química Orgánica II, Facultad de Ciencia y Tecnología,

Universidad del País Vasco – Euskal Herriko Unibertsitatea

P. O. Box 644, 48080 Bilbao, Spain.

imanol.tellitu@ehu.es

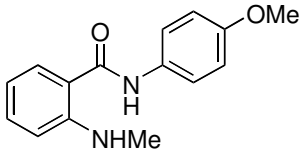
Supporting Information Available. Experimental details for compounds **2a-o** and ^{1}H NMR and ^{13}C NMR spectra of all new compounds are included

General Methods and Materials. All reagents were purchased and used as received. Melting points were measured using open glass capillaries and are uncorrected. Infrared spectra were recorded as KBr plates or as thin films and peaks are reported in cm^{-1}. Only representative absorptions are given. NMR spectra were recorded on a 250 instrument (250 MHz for ^{1}H and 62.83 MHz for ^{13}C) at 20 ºC. Chemical shifts (δ) were

measured in ppm relative to chloroform (δ= 7.26 for ^{1}H or 77.00 for ^{13}C) as internal standard. Coupling constants, *J*, are reported in hertz. DEPT experiments were used to assist with the assignation of the signals. HRMS spectra were recorded at the University of Vigo.

Typical procedure 1 for the synthesis of benzamides 2a-e, h-k, m-o. Synthesis of *N*-(4-methoxyphenyl)-2-methylaminobenzamide (2a).[1] A solution of $AlMe_3$ (9.0 mmol, 2.0 M in toluene) was added dropwise to a cooled (0 ºC) suspension of *p*-anisidine (2.23 g, 18.1 mmol) in CH_2Cl_2 (50 mL). When the addition was complete, the reaction mixture was allowed to warm to room temperature and was stirred for 45 minutes until the gas evolution ceased. Then, a solution of commercially available methyl *N*-methylanthranilate (**1a**) (1.32 mL, 9.0 mmol) was added and the mixture was heated under reflux overnight. The reaction mixture was cooled to room temperature and was carefully quenched with 5% aq HCl (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x15 mL). The combined organic extracts were washed with a saturated aqueous solution of $NaHCO_3$ (15 mL) and brine (15 mL). Then, the organic layer was dried over sodium sulfate, filtered and the solvent was evaporated at reduced pressure. The resulting residue was purified by crystallization from Et_2O to afford amide **2a** as a white solid (69% yield).

2a

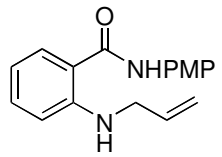


Mp 127-128 ºC (Et_2O) (lit.[1] mp 122-123 ºC); ^{1}H-NMR ($CDCl_3$) δ 2.86 (s, 3H) 3.81 (s, 3H), 6.60-6.72 (m, 2H), 6.90 (d, *J*=8.7, 2H), 7.33-7.48 (m, 5H), 7.66 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 29.6, 55.4, 111.2, 114.0, 114.5, 115.2, 122.6, 127.2, 130.7, 133.0, 150.6, 156.5, 168.1; IR (KBr) 3378, 1631 cm^{-1}; MS (EI) *m/z* (%) 256 (M^{+}, 29), 134 (100), 123 (88), 77 (25); HRMS calc. for $C_{15}H_{16}N_2O_2$ 256.1212, found 256.1208.

[1] Lee, C. –M. *J. Heterocycl. Chem.* **1964**, *1*, 235-8.

2-Allylamino-*N*-(4-methoxyphenyl)benzamide (2b). According to the general procedure 1 benzamide **2b** was obtained as a white solid from methyl *N*-allylanthranilate (**1b**)[2] in 77% yield after purification by crystallization from Et_2O.

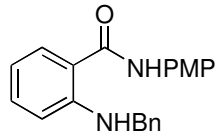
2b



Mp 107-108 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 3.80-3.82 (m, 2H), 3.81 (s, 3H), 5.13-5.33 (m, 2H), 5.86-6.00 (m, 1H), 6.61-6.88 (m, 2H), 6.90-6.91 (m, 2H), 7.27-7.29 (m, 1H), 7.32-7.29 (m, 3H), 7.62 (bs, 1H), 7.71 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 45.4, 55.4, 112.0, 114.0, 114.8, 115.3, 116.0, 122.7, 127.3, 130.7, 132.9, 134.6 149.5, 156.5, 168.1; IR (KBr) 3342, 1631 cm^{-1}; MS (EI) *m/z* (%) 282 (M^+, 2), 280 (26), 254 (29), 251 (24), 123 (24), 121 (100), 92 (27), 77 (67); HRMS calc. for $C_{17}H_{18}N_2O_2$ 282.1368, found 282.1362.

2-Benzylamino-*N*-(4-methoxyphenyl)benzamide (2c). According to the general procedure 1 benzamide **2c** was obtained as a white solid from commercially available methyl *N*-benzylanthranilate (**1c**) in 67% yield after purification by crystallization from Et_2O.

2c



Mp 112-114 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 3.81 (s, 3H), 4.41 (d, *J*=5.5, 2H), 6.60-6.71 (m, 2H), 6.90 (d, *J*=8.7, 2H), 7.29-7.94 (m, 9H), 7.97 (bs, 1H), 7.99 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 47.2, 55.3, 112.0, 114.0, 115.0, 115.2, 122.7, 126.9, 127.0, 127.3, 128.4, 130.6, 132.9, 138.8, 149.5, 156.4, 168.1; IR (KBr) 3343, 1637 cm^{-1}; MS (EI) *m/z* (%) 332 (M^+, 6), 253 (11), 210 (34), 208 (30), 180 (10), 132 (25), 123 (100), 91 (36); HRMS calc. for $C_{21}H_{20}N_2O_2$ 332.1525, found 332.1523.

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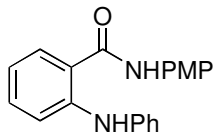
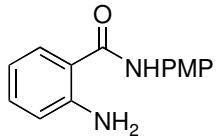
[2] Anderson, W. K.; Lai, G. *Synthesis* **1995**, 1287-1290.

***N*-(4-methoxyphenyl)-2-phenylaminobenzamide (2d).** According to the general procedure 1 benzamide **2d** was obtained as a white solid from methyl *N*-phenylanthranilate (**1d**)[3] in 68% yield after purification by crystallization from Et_2O.

2d 

Mp 140-142 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 3.80 (s, 3H), 6.79-6.93 (m, 3H), 6.98-7.04 (m, 1H), 7.17-7.47 (m, 8H), 7.55-7.58 (m, 1H), 7.85 (bs, 1H), 9.16 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 55.3, 114.0, 115.6, 118.1, 118.7, 120.5, 122.3, 122.8, 127.6, 129.2, 129.3, 132.3, 141.3, 145.3, 156.7, 167.8; IR (KBr) 3308, 1584 cm^{-1}; MS (EI) *m/z* (%) 318 (M^+, 34), 196 (87), 195 (44), 167 (42), 123 (100); HRMS calc. $C_{20}H_{18}N_2O_2$ 318.1368, found 318.1371.

***N*-(4-methoxyphenyl)benzamide (2e).[4]** According to the general procedure 1 benzamide **2e** was obtained as a white solid from commercially available methyl anthranilate (**1e**) in 71% yield after purification by crystallization from Et_2O.

2e 

Mp 122-123 ºC (Et_2O) (lit.[4] 123-125 ºC); ^{1}H-NMR ($CDCl_3$) δ 3.79 (s, 3H), 5.32 (bs, 2H), 6.63-6.70 (m, 2H), 6.87 (d, *J*=8.7, 2H), 7.19-7.26 (m, 1H), 7.41-7.45 (m, 3H), 7.80 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 55.4, 114.1, 116.2, 116.7, 117.4, 122.6, 127.1, 130.7, 132.5, 149.0, 156.5, 167.5; IR (KBr) 3283, 1637 cm^{-1}; MS (EI) *m/z* (%) 242 (M^+, 45), 123 (82), 120 (100), 92 (33); HRMS calc. for $C_{14}H_{14}N_2O_2$ 242.1055, found 242.1054.

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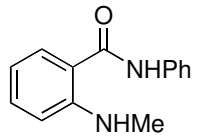
[3] Gujadhur, R.; Venkataraman, D.; Kintigh, J. T. *Tetrahedron Lett.* **2001**, *42*, 4791-4793.

[4] Waisser, K.; Machacek, M.; Dostal, H.; Gregor, J.; Kubicova, L.; Klimesova, V.; Kunes, J.; Palat, K.; Hladuvkova, J.; Kaustova, J.; Möllmann, U. *Collect. Czech. Chem. Commun.* **1999**, 1902-1924.

2-Methylaminobenzanilide (2h).[5] According to the general procedure 1 benzanilide **2h** was obtained as a white solid from commercially available methyl *N*-methylanthranilate (**1a**) and aniline in 88% yield after purification by crystallization from Et_2O.

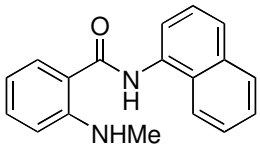
2h



Mp 121-122 ºC (Et_2O) (lit.[5] 124-125 ºC); ^{1}H-NMR ($CDCl_3$) δ 2.87 (s, 3H), 6.62-6.74 (m, 2H), 7.12-7.18 (m, 1H), 7.38-7.57 (m, 6H), 7.76 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 29.5, 111.1, 114.4, 115.0, 120.5, 124.2, 127.3, 128.8, 133.1, 137.7, 150.6, 168.2; IR (KBr) 3367, 1637 cm^{-1}; MS (EI) *m/z* (%) 226 (M^+, 33), 134 (100), 93 (32), 77 (21); HRMS calc. for $C_{14}H_{14}N_2O$ 226.1106, found 226.1105.

2-Methylamino-*N*-(1-naphthyl)benzamide (2i). According to the general procedure 1 benzamide **2i** was obtained as a white solid from commercially available methyl *N*-methylanthranilate (**1a**) and 1-naphthylamine in 91% yield after purification by crystallization from Et_2O.

2i

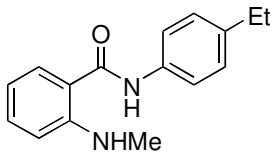


Mp 185-187 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 2.88 (d, *J*=4.8, 3H), 6.68-6.77 (m, 2H), 7.40-7.54 (m, 5H), 7.66-7.77 (m, 2H), 7.84-7.92 (m, 3H), 8.11 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 29.6, 111.5, 114.6, 121.1, 121.7, 125.6, 126.1, 126.2, 126.4, 127.4, 128.0, 128.7, 132.5, 133.5, 134.2, 151.1, 168.8; IR (KBr) 3300, 1627 cm^{-1}; MS (EI) *m/z* (%) 276 (M^+, 11), 143 (45), 134 (100), 77 (26); HRMS calc. for $C_{18}H_{16}N_2O$ 276.1263, found 276.1262.

***N*-(4-ethylphenyl)-2-methylaminobenzamide (2j).** According to the general procedure 1 benzamide **2j** was obtained as a white solid from commercially available methyl *N*-

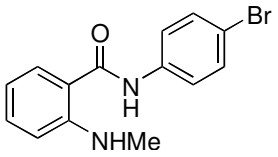
[5] Katritzky, A. R.; Fan, W.-Q.; Akutagawa, K. *Tetrahedron* **1986**, *42*, 4027-4034.

methylanthranilate (**1a**) and 4-ethylaniline in 89% yield after purification by crystallization from Et_2O.

2j 

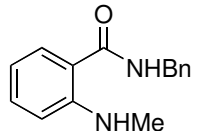
Mp 120-121 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 1.25 (t, *J*=7.5, 3H), 2.65 (q, *J*= 7.5, 2H), 2.85 (s, 3H), 6.59-6.72 (m, 2H), 7.19 (d, *J*=7.9, 2H), 7.18-7.50 (m, 5H), 7.82 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 15.6, 28.2, 29.5, 111.1, 114.5, 115.2, 120.8, 127.2, 128.2, 133.1, 135.3, 140.4, 150.6, 168.1; IR (KBr) 3354, 1637 cm^{-1}; MS (EI) *m/z* (%) 254 (M^+, 27), 134 (100), 121 (48), 106 (25), 77 (21); HRMS calc. for $C_{16}H_{18}N_2O$ 254.1419, found 254.1423.

***N*-(4-bromophenyl)-2-methylaminobenzamide (2k).** According to the general procedure 1 benzamide **2k** was obtained as a white solid from commercially available methyl *N*-methylanthranilate (**1a**) and 4-bromoaniline in 22% yield after purification by crystallization from Et_2O.

2k 

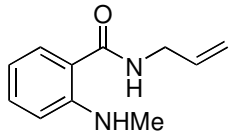
Mp 130-132 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 2.84 (s, 3H), 6.57-6.70 (m, 2H), 7.33-7.49 (m, 7H), 7.89 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 29.6, 111.3, 114.6, 116.9, 122.0, 127.2, 131.8, 133.4, 136.9, 150.7, 168.1; IR (KBr) 3350, 1637 cm^{-1}; MS (EI) *m/z* (%) 306 (M+2, 12), 304 (M^+, 11), 134 (100), 91 (14), 79 (13), 77 (27); HRMS calc. for $C_{12}H_{13}BrN_2O$ 304.0211, found 304.0217.

***N*-benzyl-2-methylaminobenzamide (2m).** According to the general procedure 1 benzamide **2m** was obtained as a white solid from commercially available methyl *N*-methylanthranilate (**1a**) and benzylamine in 88% yield after purification by crystallization from Et_2O.

2m 

Mp 93-95 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 2.86 (s, 3H), 4.58 (d, *J*=5.5, 2H), 6.39 (bs, 1H), 6.53-6.70 (m, 2H), 7.30-7.35 (m, 7H), 7.60 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 29.3, 43.1, 110.7, 114.2, 114.5, 127.0, 127.2, 127.3, 128.3, 132.6, 138.2, 150.3, 169.6; IR (KBr) 3354, 1631 cm^{-1}; MS (EI) *m/z* (%) 240 (M^+, 61), 134 (34), 132 (32), 106 (100), 91 (39), 77 (25) ; HRMS calc. for $C_{15}H_{16}N_2O$ 240.1263, found 240.1264.

***N*-allyl-2-(methylamino)benzamide (2n)**[6]. According to the general procedure 1 benzamide **2n** was obtained as a white solid from commercially available methyl *N*-methylanthranilate (**1a**) and allylamine in 65% yield after purification by crystallization from Et_2O.

2n 

Mp 75-76 ºC (Et_2O) (lit.[6] 70-73 ºC); ^{1}H-NMR ($CDCl_3$) δ 2.85 (s, 3H), 4.01-4.02 (m, 2H), 5.25-5.28 (m, 2H), 5.84-5.99 (m, 1H), 6.16 (bs, 1H), 6.55-6.69 (m, 2H), 7.29-7.36 (m, 2H), 7.53 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 29.4, 41.7, 110.8, 114.2, 114.7, 115.8, 127.1, 132.5, 134.1, 150.2, 169.6; IR (KBr) 3354, 1631 cm^{-1}; MS (EI) *m/z* (%) 190 (M^+, 83), 134 (100), 132 (38), 106 (25), 105 (69), 104 (53), 78 (22), 77 (52); HRMS calc. for $C_{11}H_{14}N_2O$ 190.1106, found 190.1109.

***N*-methoxy-2-methylaminobenzamide (2o)** According to the general procedure 1 benzamide **2o** was obtained as a white solid from commercially available methyl *N*-methylanthranilate (**1a**) and $NH_2OMe{\cdot}HCl$ in 18% yield after purification by crystallization from Et_2O.

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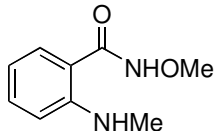
[6] Coppola, G. M.; Mansukhani, R. I. *J. Heterocycl. Chem.* **1978**, *15*, 1169-1173.

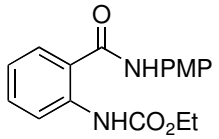
2o



Mp 90-91 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 2.81 (s, 3H), 3.78 (s, 3H), 6.47-6.86 (m, 2H), 7.29-7.39 (m, 2H), 9.35 (bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 29.5, 64.2, 110.9, 111.7, 114.4, 127.3, 133.2, 150.4, 169.0; IR (KBr) 3367, 1637 cm^{-1}; MS (EI) *m/z* (%) 180 (M^+, 25), 150 (93), 148 (38), 134 (100), 133 (78), 105 (98), 77 (68); HRMS calc. for $C_9H_{12}N_2O_2$ 180.0899, found 180.0894.

Typical procedure 2 for the synthesis of benzamides 2f-g. Synthesis of 2-ethoxycarbonylamino-*N*-(4-methoxyphenyl)benzamide (2f). $LiOH·H_2O$ (658 mg, 15.7 mmol) was added to a solution of methyl *N*-ethoxycarbonylanthranilate[7] (**1f**) (700 mg, 3.14 mmol) in THF/H_2O (50 mL, 4/1). The mixture was stirred at rt until conversion was complete. Then, the solution was treated with HCl (5% aq.) and extracted with Et_2O (3x15 mL). The organic extracts were dried over sodium sulfate and the solvent was evaporated under reduced pressure. The resulting residue, *p*-anisidine (423 mg, 3.44 mmol), and Et_3N (0.6 mL, 4.31 mmol) were dissolved in CH_2Cl_2 (11 mL). Then, the obtained suspension was treated with a solution of EDC·HCl (826 mg, 4.31 mmol) and HOBt (543 mg, 4.02 mmol) in the same solvent (5 mL). The mixture was cooled (0 ºC) and Et_3N (0.48 mL, 3.44 mmol) was added dropwise. After stirring for 2 h, temperature was raised to rt and stirring was continued until the conversion was complete. Then, the solution was washed with water, extracted with CH_2Cl_2 (3x15 mL), dried over sodium sulfate, and the solvent was evaporated at reduced pressure. The resulting residue was crystallized from Et_2O to afford benzamide **2f** as a white solid in 85% yield.

2f



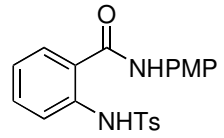
Mp 62-63 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 1.29 (t, *J*= 7.1, 3H), 3.81 (s, 3H), 4.19 (t, *J*= 7.1, 2H), 6.81-7.00 (m, 4H), 7.36-7.55 (m, 4H), 8.25-8.28 (m, 1H), 8.37 (bs, 1H), 10.09

[7] Schmidt, R. R.; Wagner, A. *Synthesis* **1982**, 958-962.

(bs, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.4, 55.4, 61.1, 114.1, 119.9, 120.7, 121.7, 122.6, 127.0, 130.6, 132.3, 139.4, 154.0, 167.2; IR (KBr) 3308, 1737, 1630 cm^{-1}; MS (EI) *m/z* (%) 314 (M^+, 2), 269 (11), 268 (98), 149 (15), 146 (100), 123 (45), 119 (76), 92 (38), 64 (13); HRMS calc. for $C_{17}H_{18}N_2O_4$ 314.1267, found 314.1276.

***N*-(4-methoxyphenyl)-2-(methylphenylsulfonyl)benzamide (2g).** According to the general procedure 2 benzamide **2g** was obtained as a white solid from methyl *N*-tosylanthranilate[8] (**1g**) in 86% yield after purification by crystallization from Et_2O.

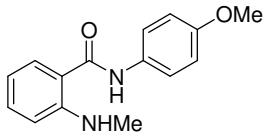
2g

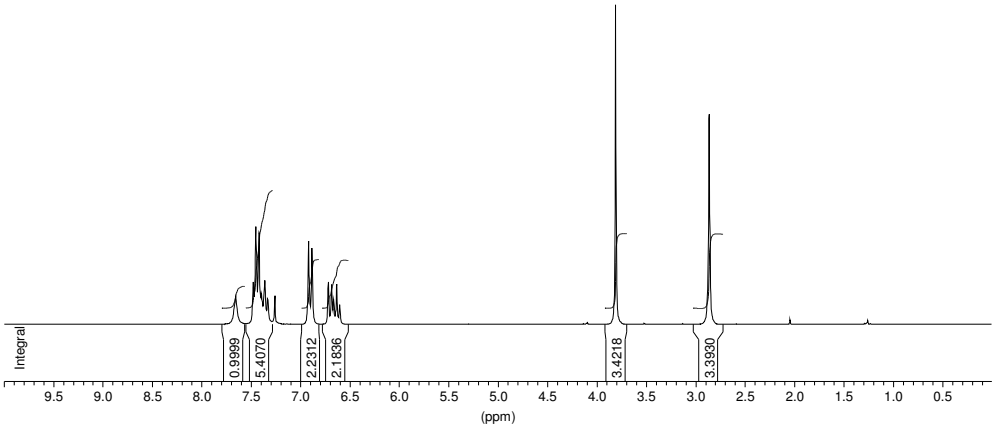


Mp 150-151 ºC (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 2.33 (s, 3H), 3.82 (s, 3H), 6.68-6.93 (m, 3H), 7.09-7.88 (m, 9H), 9.14 (bs, 1H), 10.3 (bs, 1H); ^{13}C-NMR (CD_3COCD_3) δ 20.0, 54.3, 113.3, 120.8, 122.3, 123.5, 126.4, 127.6, 128.9, 129.1, 130.7, 131.9, 135.9, 138.2, 143.4, 156.3, 166.3; IR (KBr) 3343, 1643 cm^{-1}; MS (EI) *m/z* (%) 396 (M^+, 16), 123 (100), 92 (20), 91 (30), 65 (12); HRMS calc. for $C_{21}H_{20}N_2O_4S$ 396.1144, found 396.1148.

[8] Tsunoda, T.; Tanaka, A.; Mase, T.; Sakamoto, S. *Heterocycles* **2004**, 1113-1122.

2a


O
N
H
OMe
NHMe


Integral
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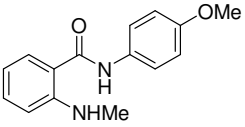
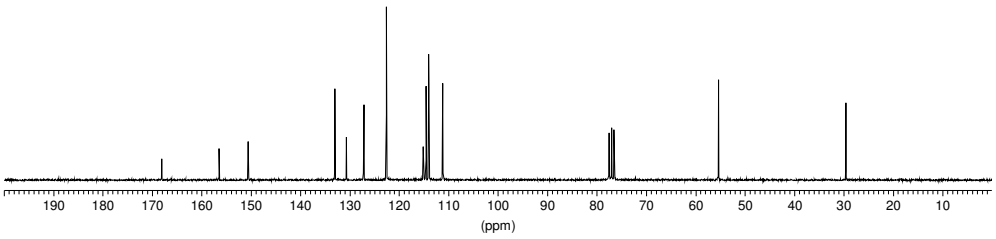
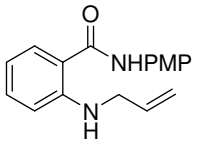
5.4070
2.2312
2.1836
3.4218
3.3930
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

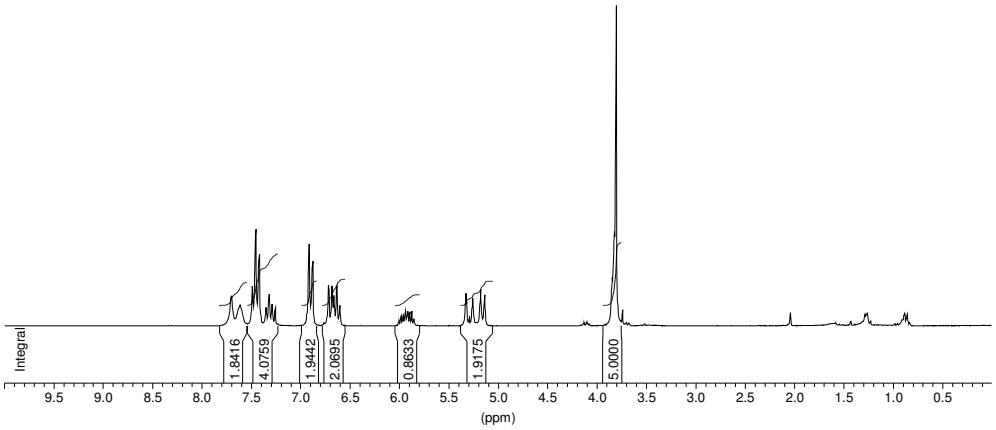
2a


O
N
H
OMe
NHMe

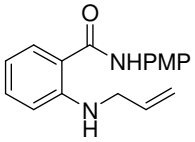

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

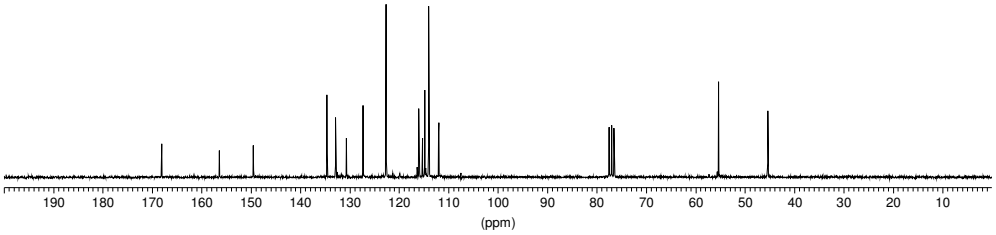
2b


O
NHPMP
N
H

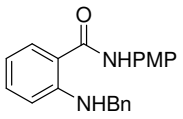

Integral
1.8416
4.0759
1.9442
2.0695
0.8633
1.9175
5.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

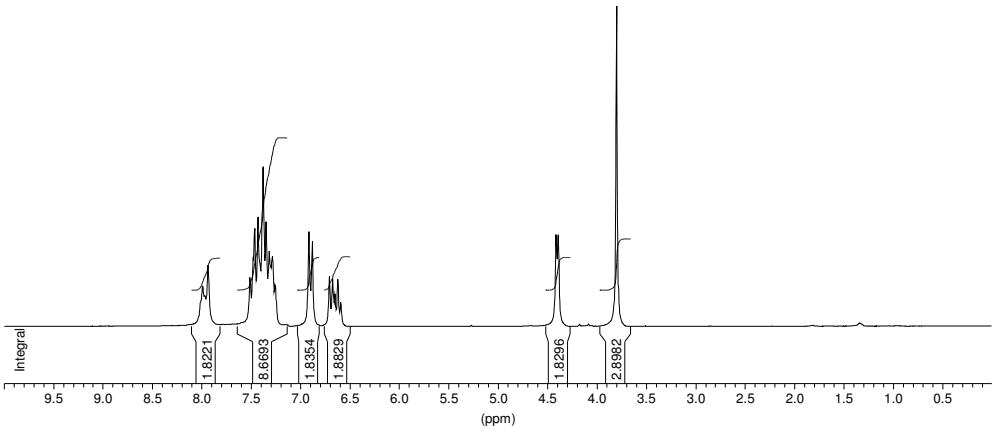
2b


O
NHPMP
N
H

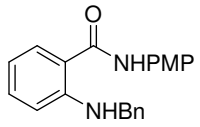

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

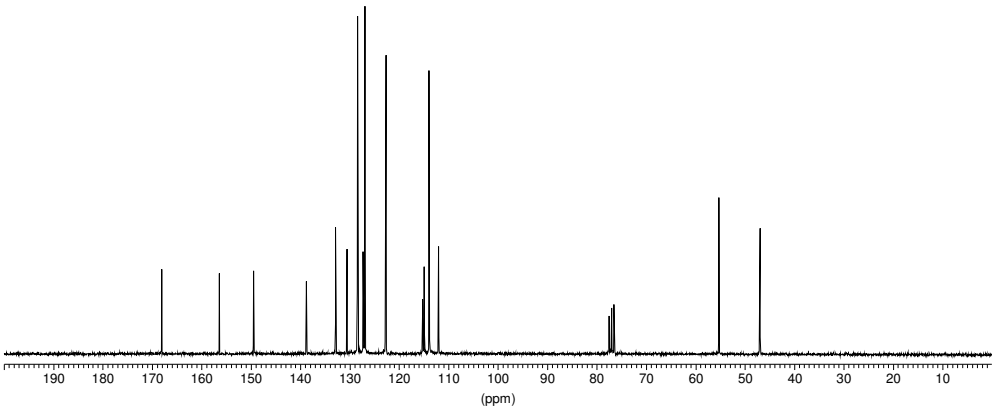
2c


O
NHPMP
NHBn

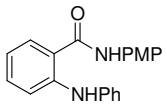

Integral
1.8221
8.6693
1.8354
1.8829
1.8296
2.8982
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

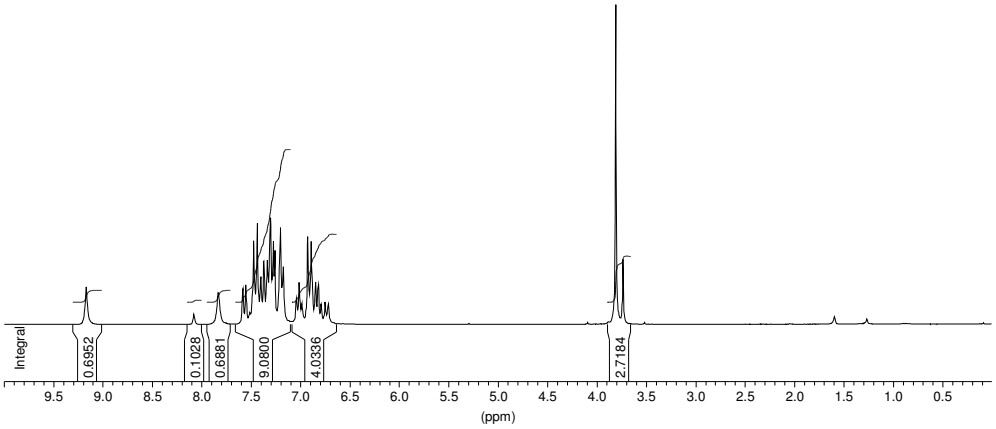
2c


O
NHPMP
NHBn

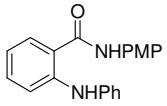

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

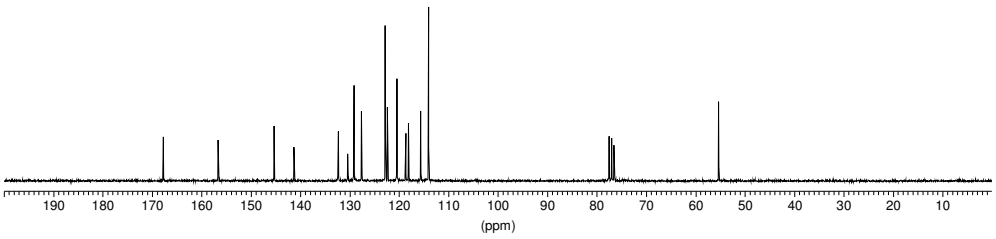
2d


O
NHPMP
NHPh

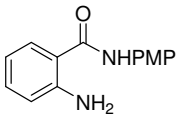

Integral
0.6952
0.1028
0.6881
9.0800
4.0336
2.7184
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

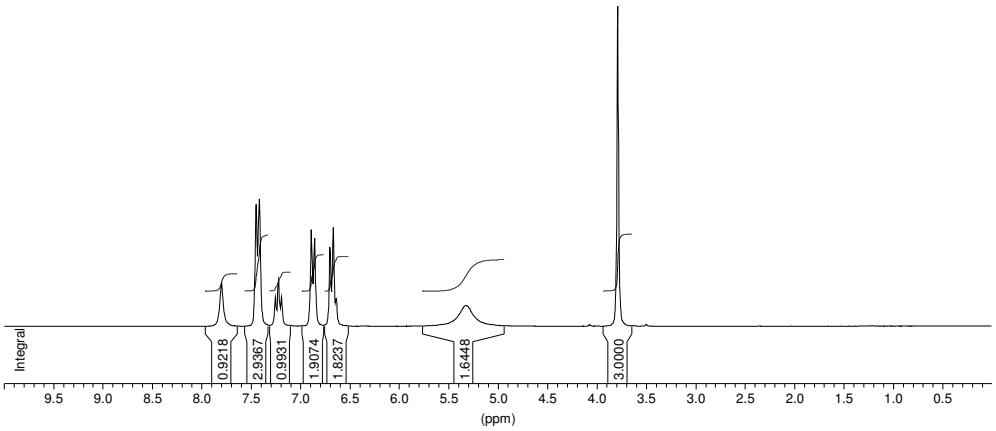
2d


O
NHPMP
NHPh

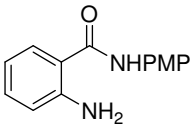

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

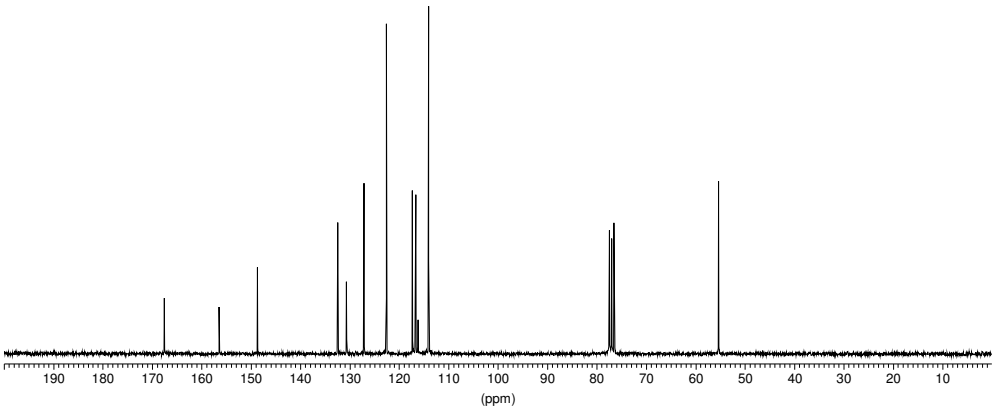
2e


O
NHPMP
NH2

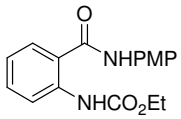

Integral
0.9218
2.9367
0.9931
1.9074
1.8237
1.6448
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

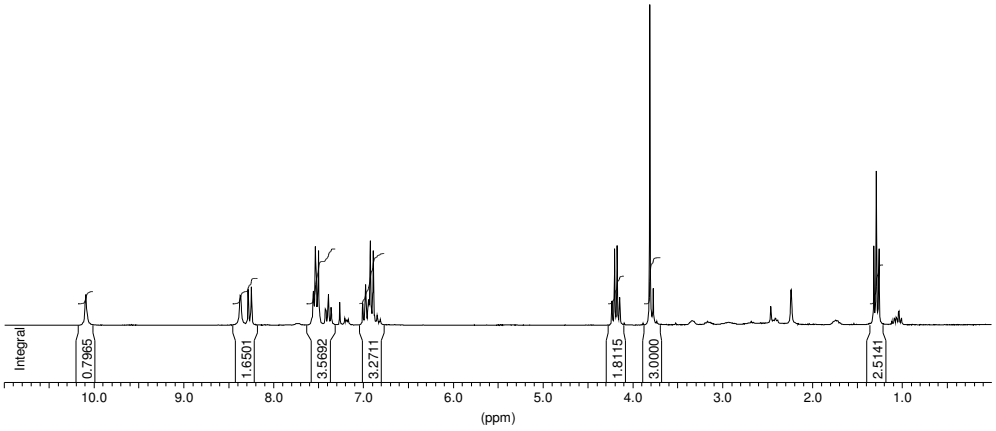
2e


O
NHPMP
NH2

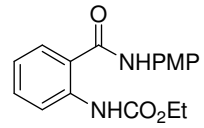

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

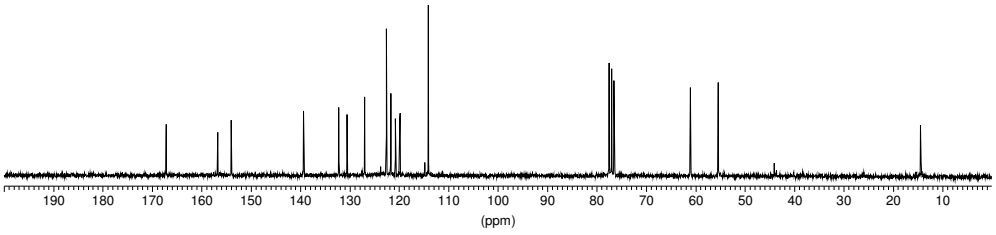
2f


O
NHPMP
NHCO2Et

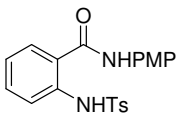

Integral
0.7965
1.6501
3.5692
3.2711
1.8115
3.0000
2.5141
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

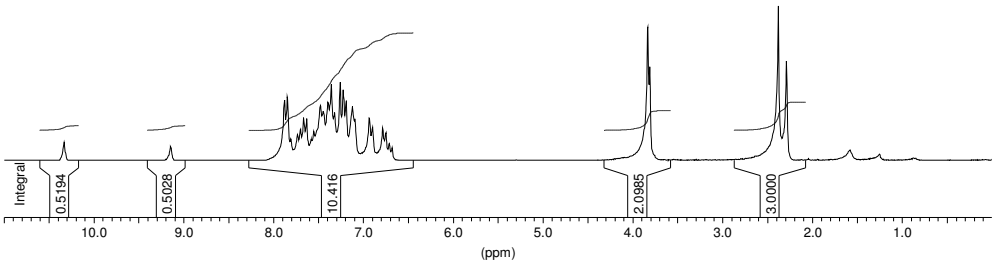
2f


O
NHPMP
NHCO2Et

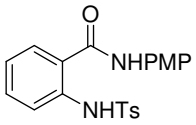

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

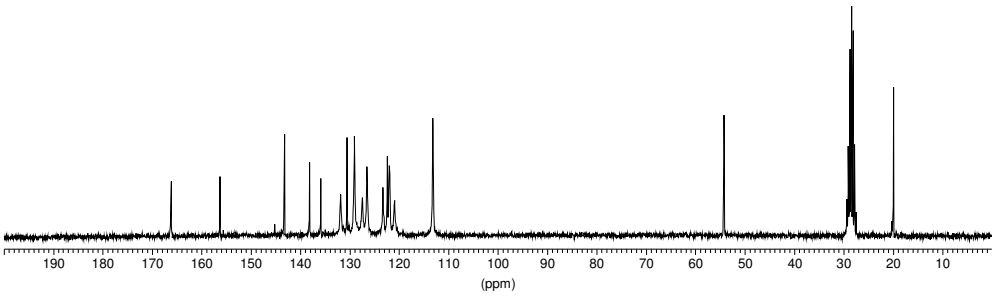
2g


O
NHPMP
NHTs

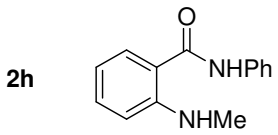

Integral
0.5194
0.5028
10.416
2.0985
3.0000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

2g


O
NHPMP
NHTs

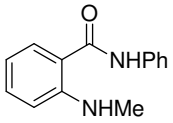

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

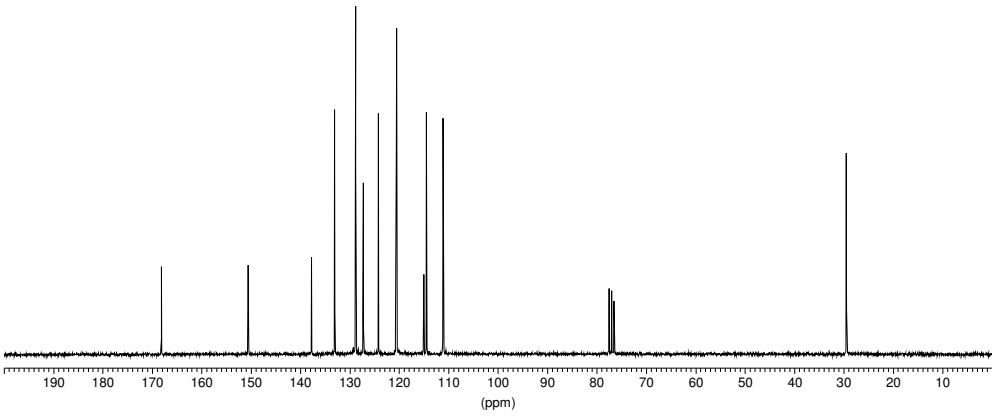
2h


O
NHPh
NHMe

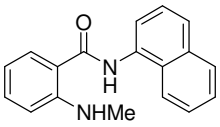
Integral
1.0001
7.0608
1.0485
2.1189
3.4050
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

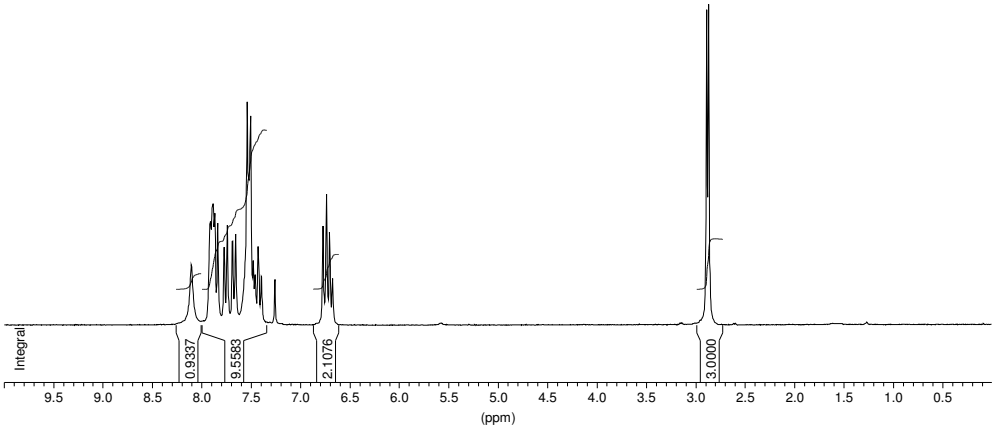
2h


O
NHPh
NHMe

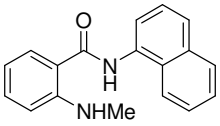

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

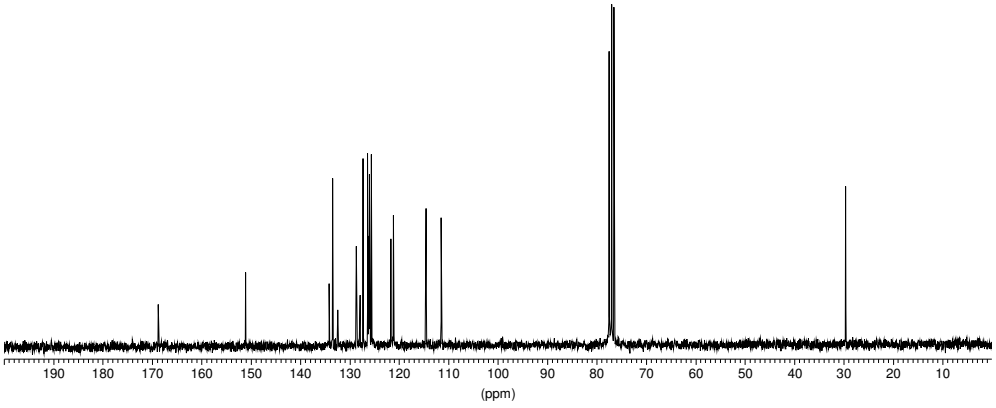
2i


O
N
H
NHMe

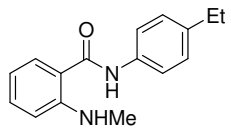

Integral
0.9337
9.5583
2.1076
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

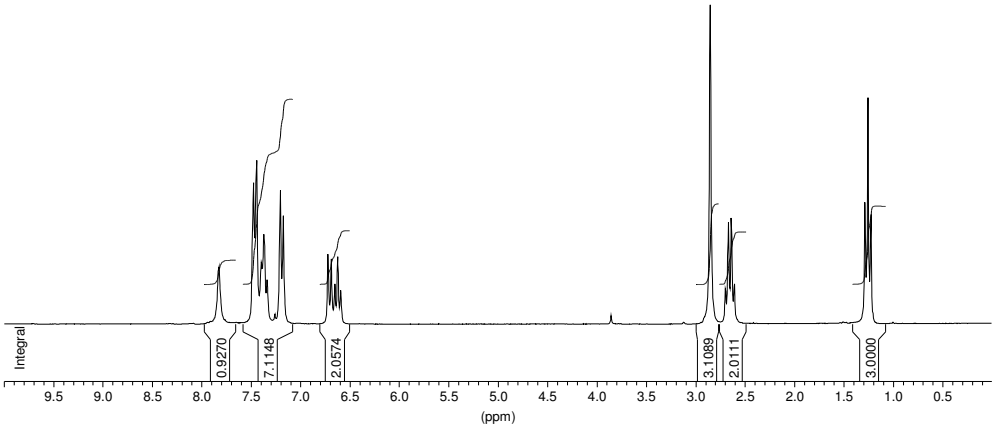
2i


O
N
H
NHMe

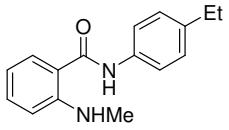

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

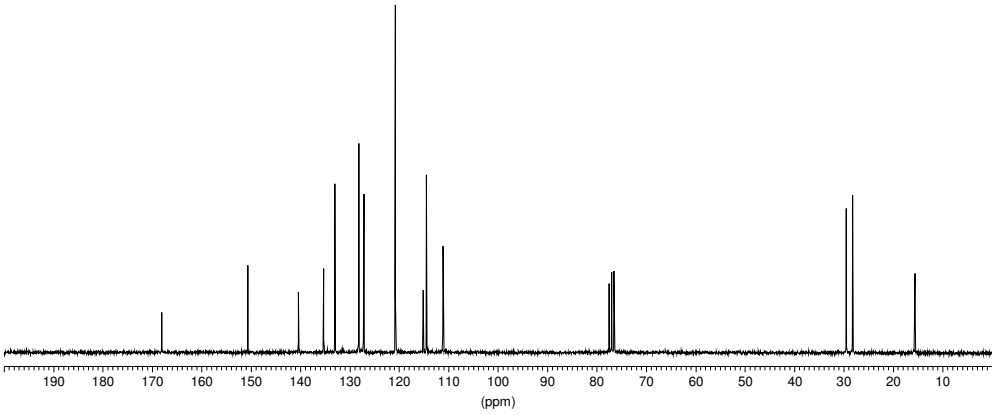
2j


O
N
H
Et
NHMe

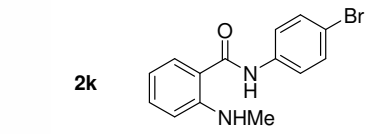

Integral
0.9270
7.1148
2.0574
3.1089
2.0111
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

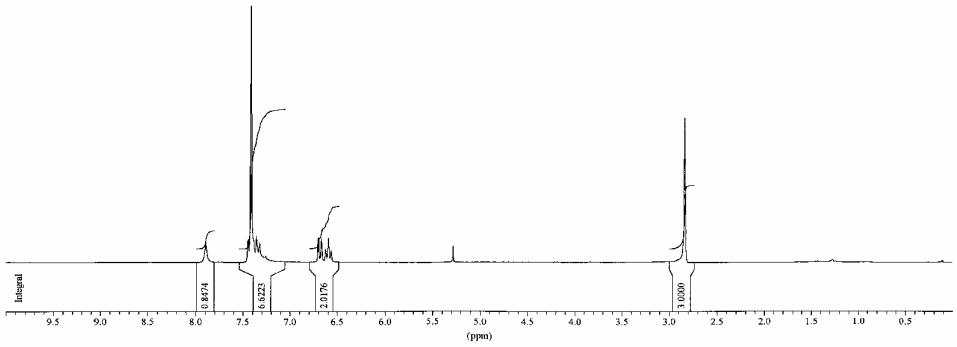
2j


O
N
H
Et
NHMe

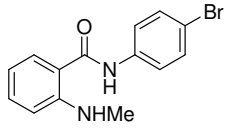

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

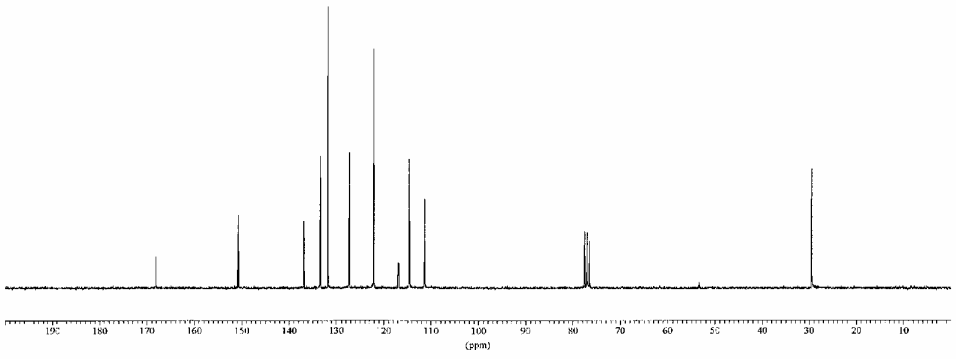
2k


O
N
H
Br
NHMe

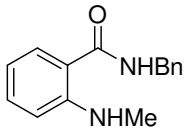

Integral
0.8474
6.8223
2.0176
3.0000
(ppm)

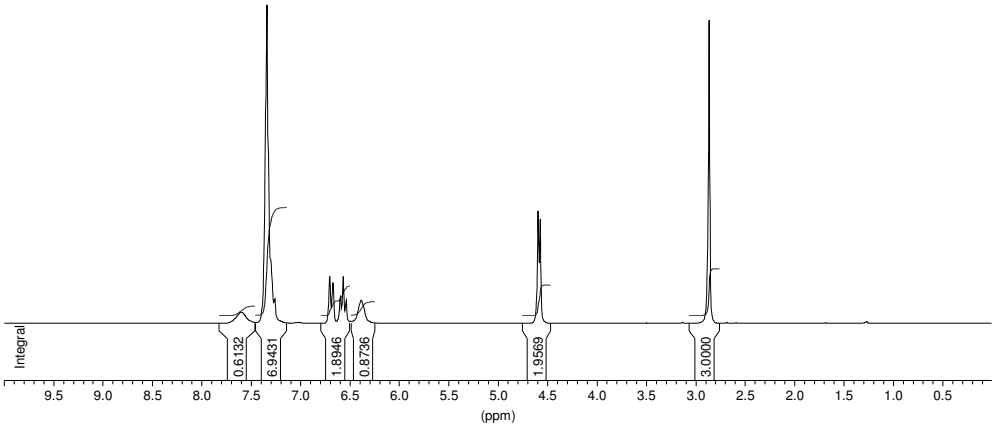
2k


O
N
H
Br
NHMe

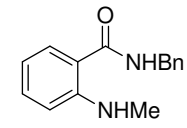

(ppm)

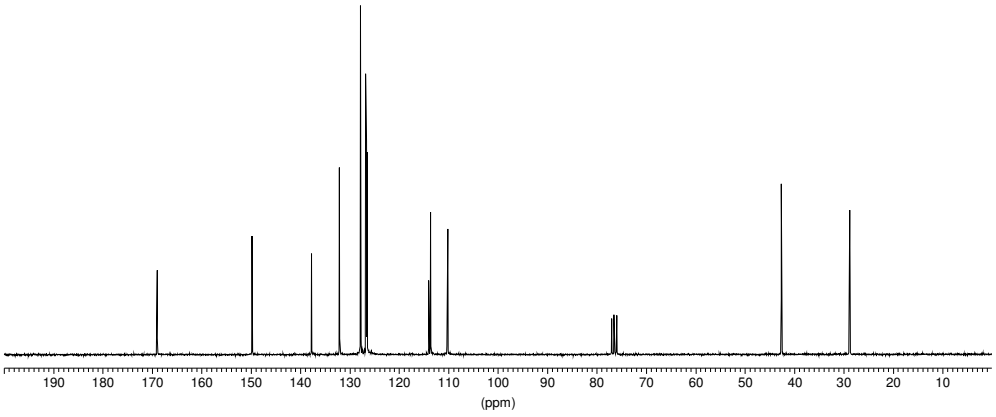
2m


O
NHBn
NHMe

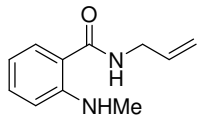

Integral
0.6132
6.9431
1.8946
0.8736
1.9569
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

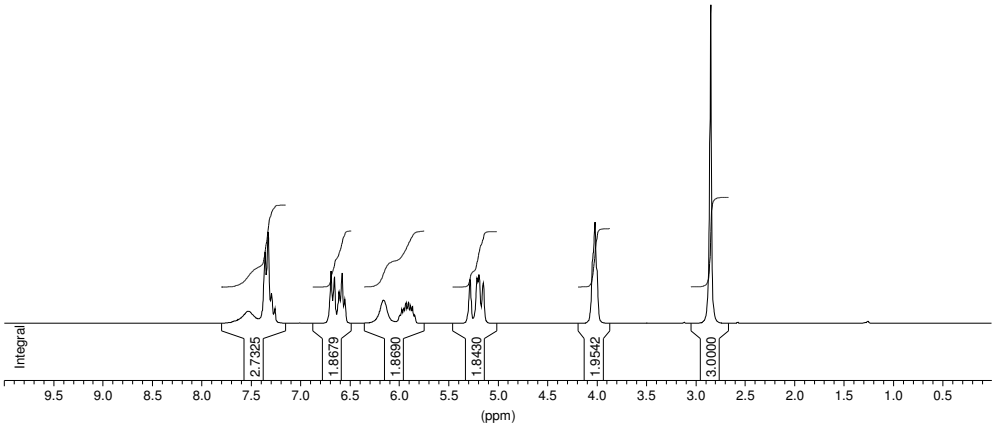
2m


O
NHBn
NHMe

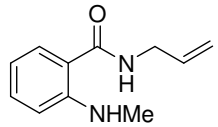

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

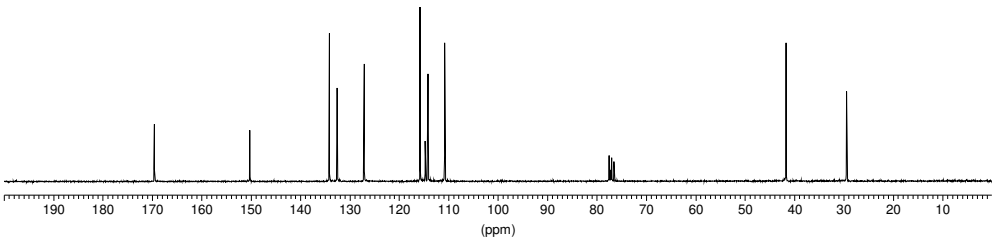
2n


O
N
H
NHMe

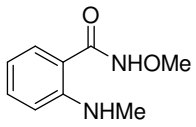

Integral
2.7325
1.8679
1.8690
1.8430
1.9542
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

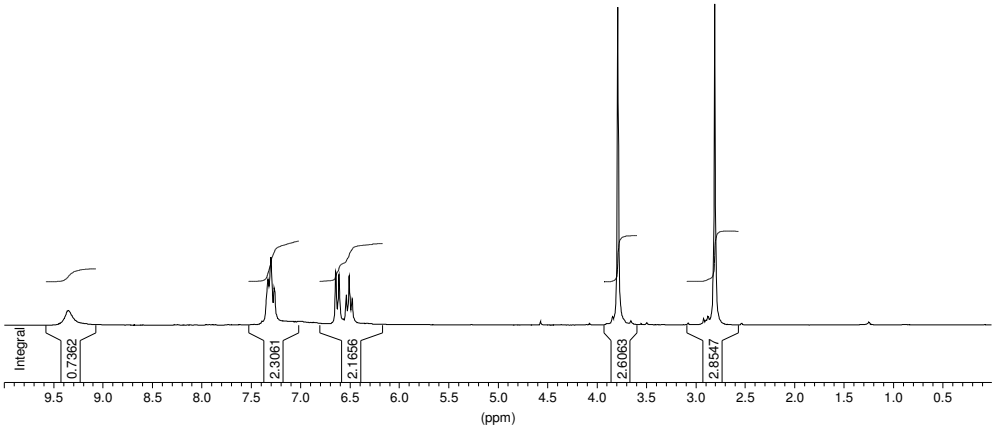
2n


O
N
H
NHMe

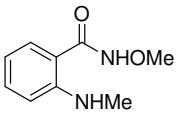

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

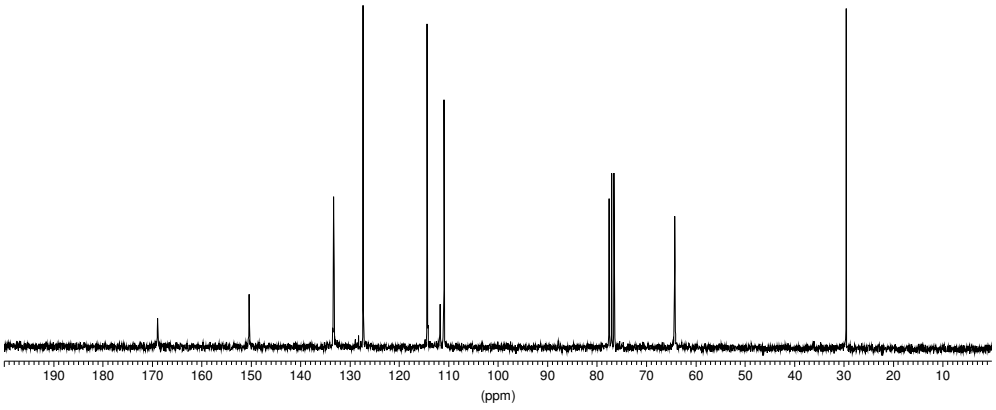
2o


O
NHOMe
NHMe

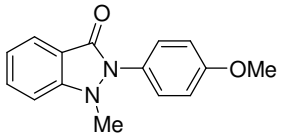

Integral
0.7362
2.3061
2.1656
2.6063
2.8547
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

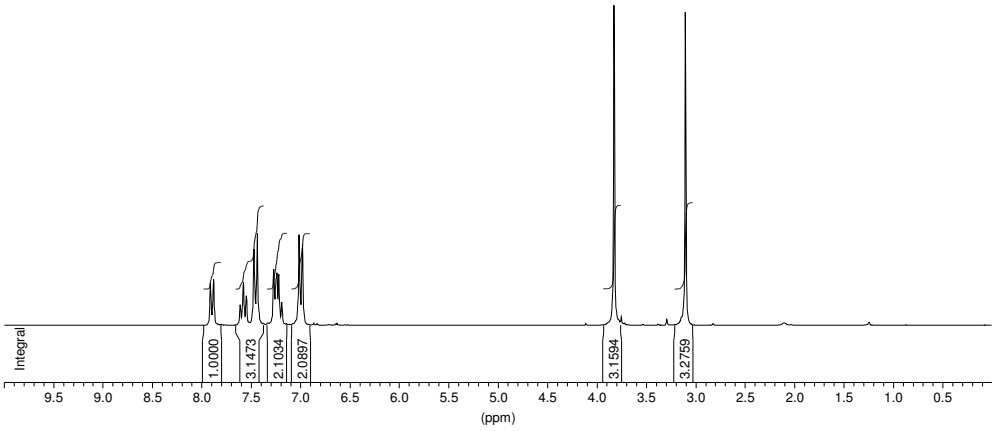
2o


O
NHOMe
NHMe

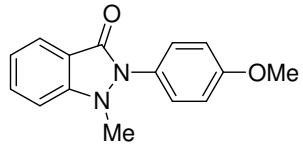

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

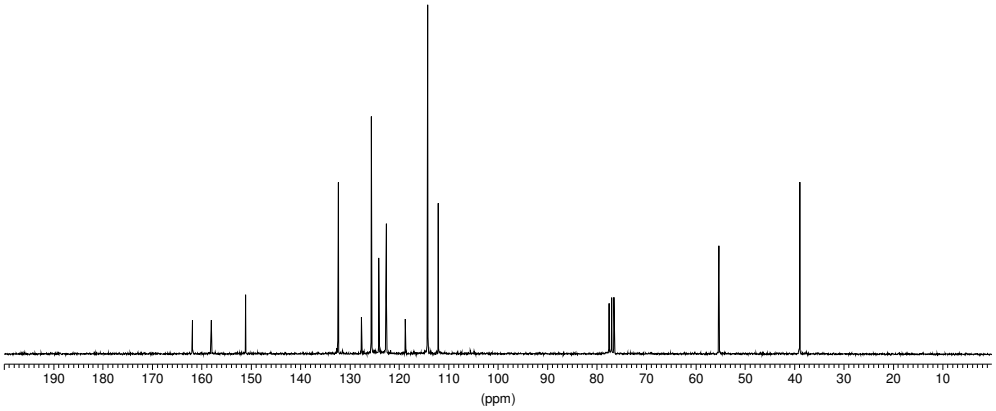
3a


O
N
N
Me
OMe

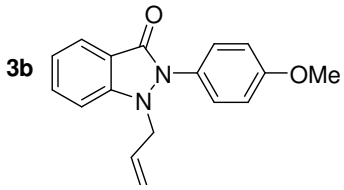

Integral
1.0000
3.1473
2.1034
2.0897
3.1594
3.2759
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

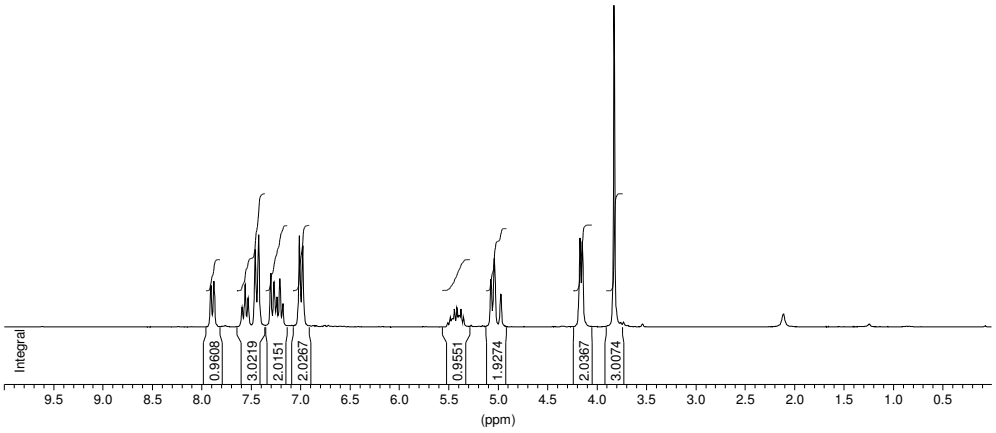
3a


O
N
N
Me
OMe

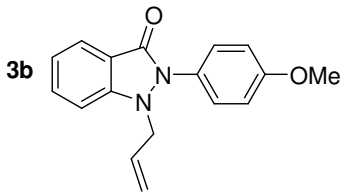

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

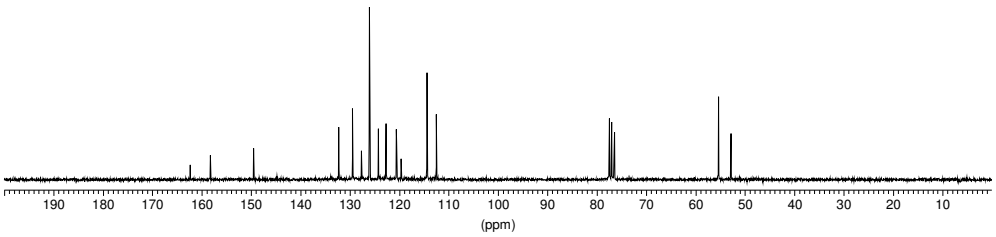
3b


O
N
N
OMe

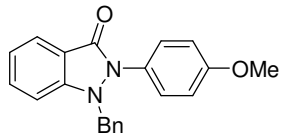

Integral
0.9608
3.0219
2.0151
2.0267
0.9551
1.9274
2.0367
3.0074
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

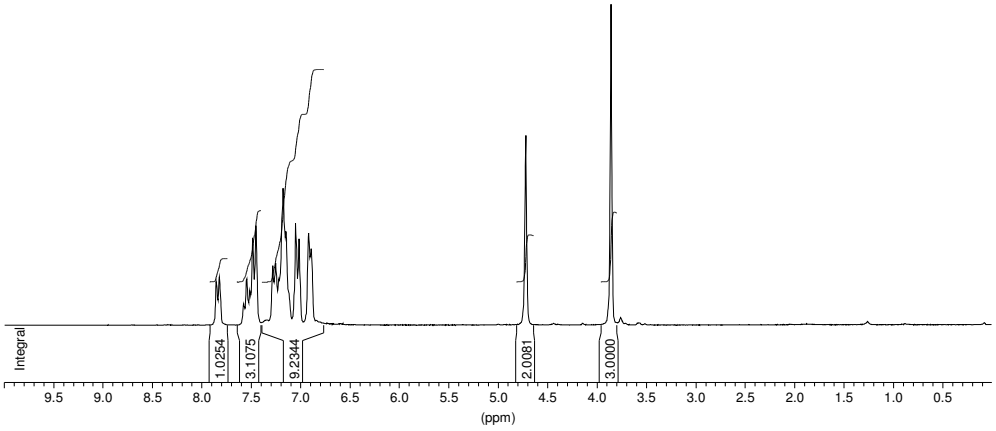
3b


O
N
N
OMe

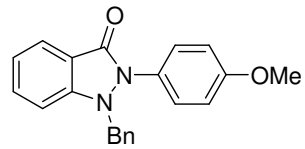

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

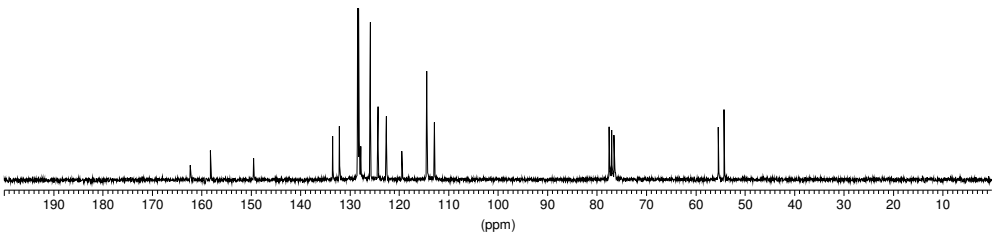
3c


O
N
N
Bn
OMe

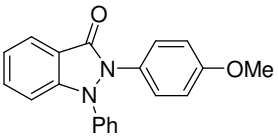

Integral
1.0254
3.1075
9.2344
2.0081
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

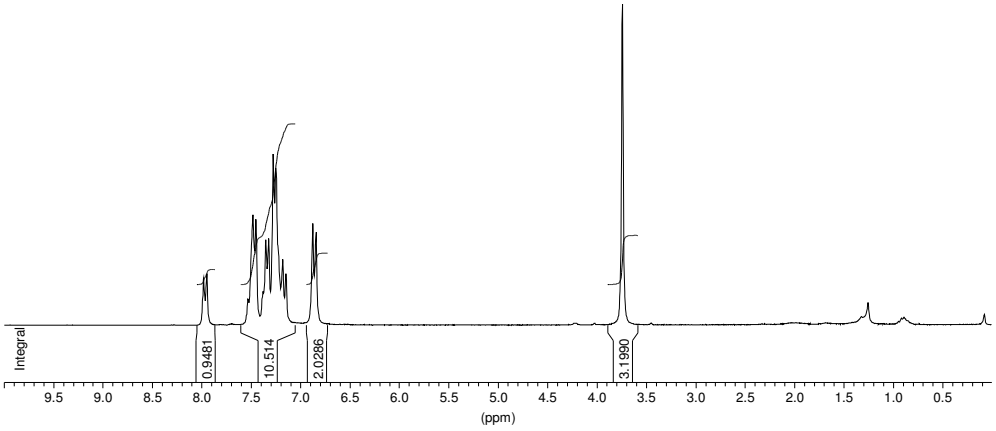
3c


O
N
N
Bn
OMe

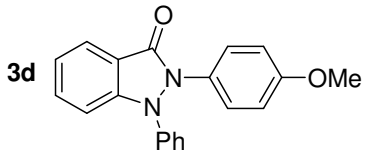

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

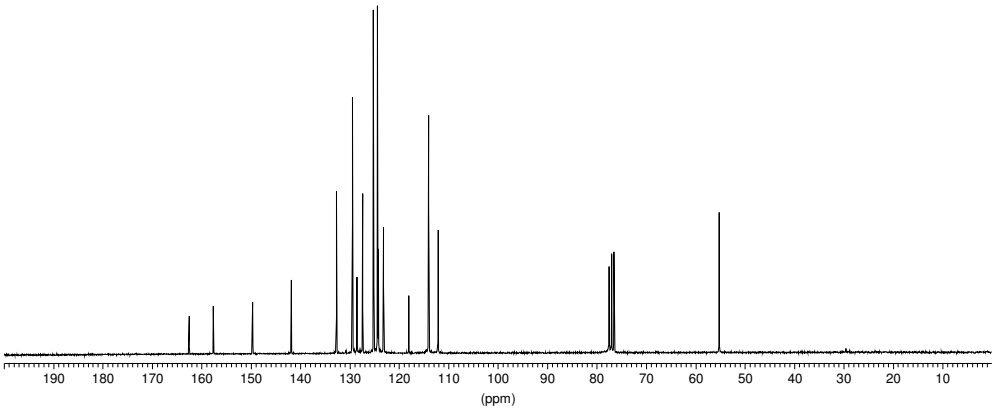
3d


O
N
N
Ph
OMe

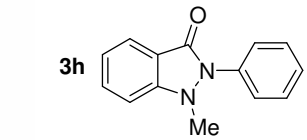

Integral
0.9481
10.514
2.0286
3.1990
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

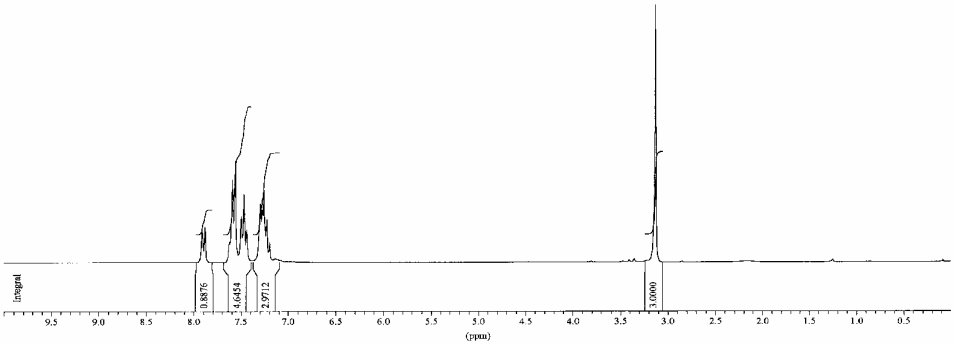
3d


O
N
N
Ph
OMe

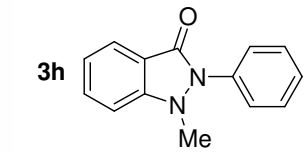

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

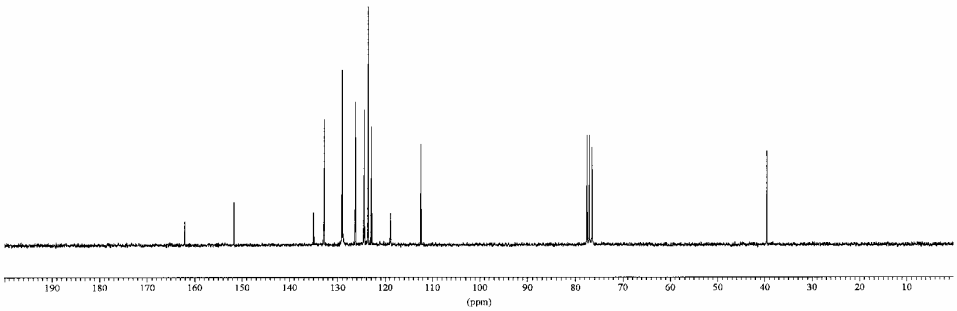
3h


O
N
N
Me

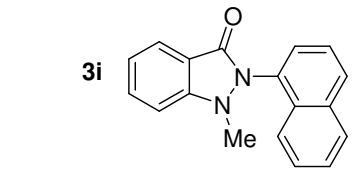

Integral
0.8876
5.6454
2.9712
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

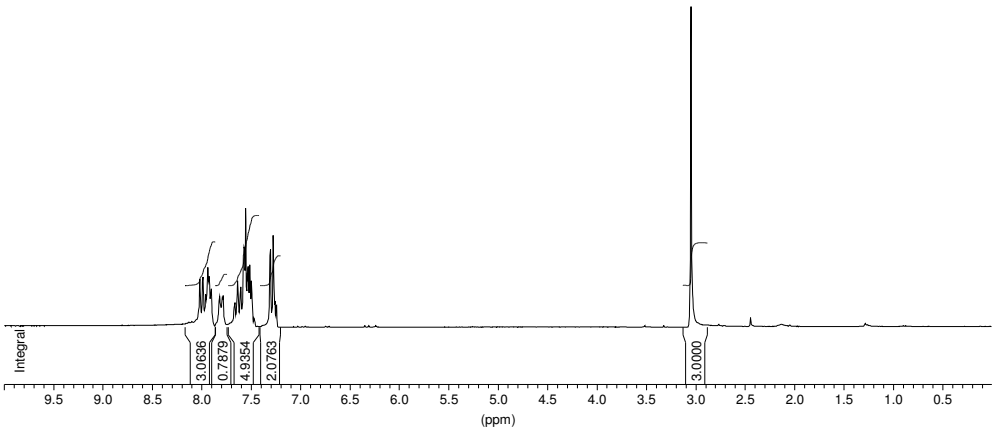
3h


O
N
N
Me

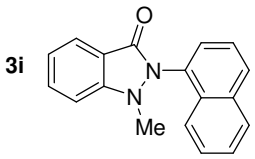

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

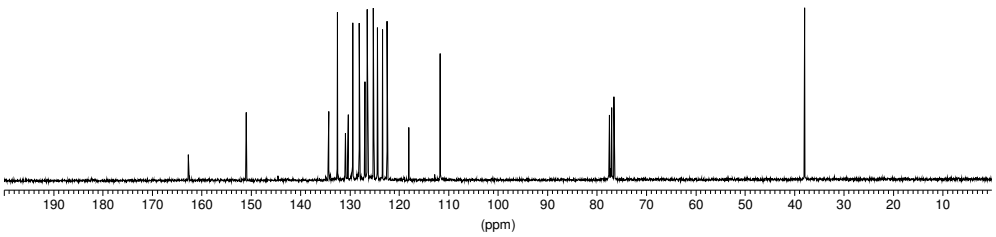
3i


O
N
N
Me

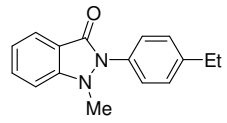

Integral
3.0636
0.7879
4.9354
2.0763
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

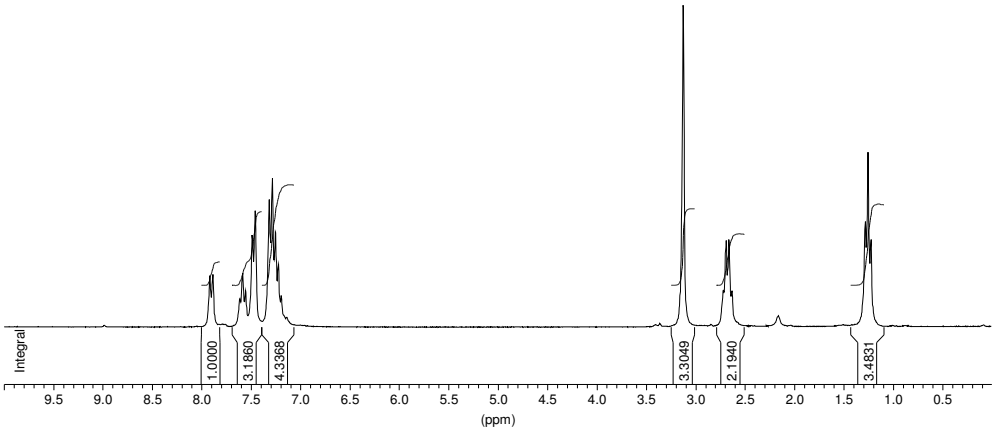
3i


O
N
N
Me

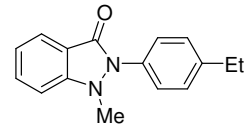

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

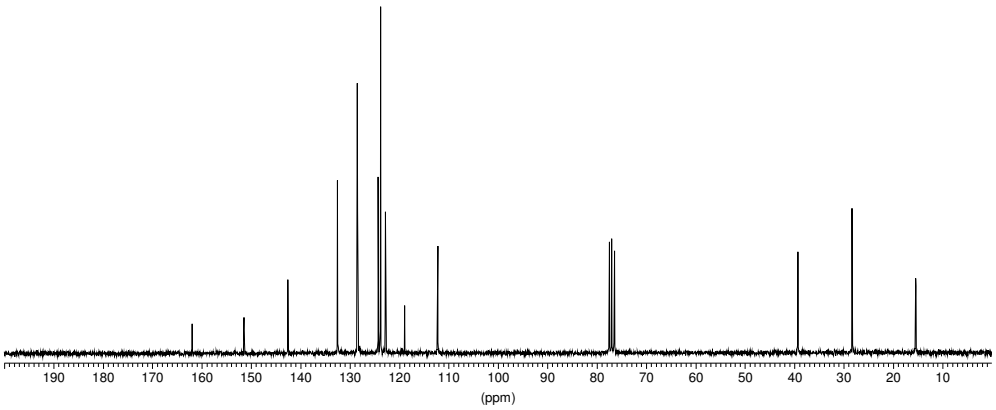
3j


O
N
N
Me
Et

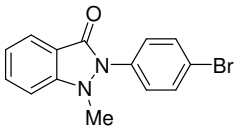

Integral
1.0000
3.1860
4.3368
3.3049
2.1940
3.4831
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

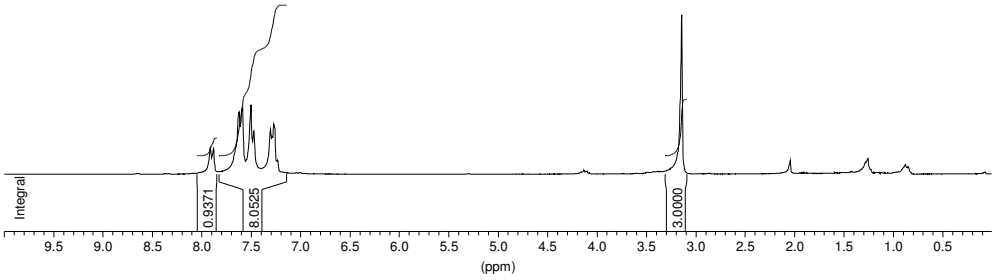
3j


O
N
N
Me
Et

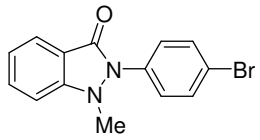

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

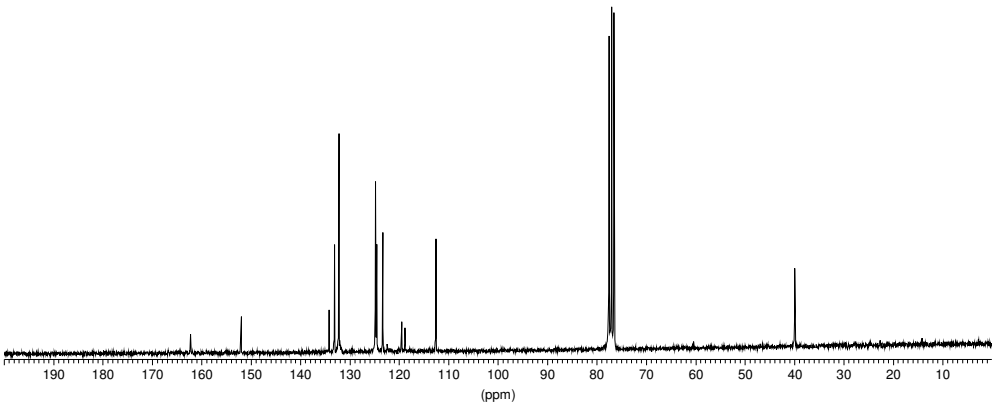
3k


O
N
N
Me
Br


Integral
0.9371
8.0525
3.0000
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
(ppm)

3k


O
N
N
Me
Br


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)