Electronic Supplementary Information

Highly efficient heterogeneous aerobic cross-dehydrogenative coupling via C-H functionalization of tertiary amines by nanoporous gold skeleton catalyst

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General Information: GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m × 0.25 mm capillary column, HP-5MS). Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-6500F instrument operated at an accelerating voltage of 30 kV. TEM characterization was performed using a JEM-2100F TEM (JEOL, 200 kV) equipped with double spherical aberration (Cs) correctors for both the probe-forming and image-forming lenses. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (400, 700 MHz) spectrometers. ^{11}B NMR spectra were recorded on JEOL JNM AL 700 (225 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (100.5 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer and JEOL JMS-700 MStation operator. Column chromatography was carried out employing Merck silica (spherical, neutral, MercK Chemical Co.) and the florisil (particle size 150 -250 μm, Kanto Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. The commercially available chemicals were used as received. Au (99.99%) and Ag (99.99%) are purchased from Tanaka Kikinzoku Hanbai K. K. and Mitsuwa's Pure Chemical, respectively. *N*-Protected 1,2,3,4-tetrahydroisoquinolines were prepared following the reported methods.[1] Structures of the products were identified by ^{1}H, ^{13}C NMR, HRMS, and compared with reported compounds.[2-4]

References

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[2] (a) Z. Li, D. Bohle and C.-J. Li, *Proc. Natl. Acad. Sci. USA.*, 2006, **103**, 8928; (b) Z. Li and C.-J. Li, *J. Am. Chem. Soc.*, 2005, **127**, 3672; (c) J. Xie, H. Li, J. Zhou, Y. Cheng and C. Zhu, *Angew. Chem., Int. Ed.*, 2012, **51**, 1252; (d) K. Alagiri and K. Prabhu, *Tetrahedron Lett.*, 2012, **12**, 1456; (e) J. Dhineskumar, M. Lamani, K. Alagiri and K. Prabhu, *Org. Lett.*, 2013, **15**, 1092; (f) K. Jones, P. Karier and M. Klussmann, *ChemCatChem*, 2012, **4**, 51; (g) Z. Li and C. J. Li, *Eur. J. Org. Chem.*, 2005, 3173.

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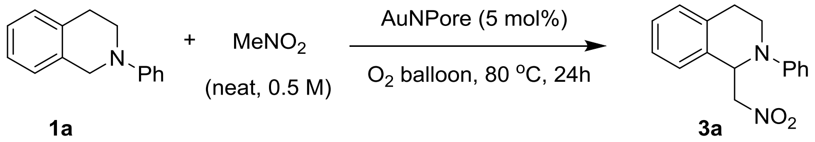
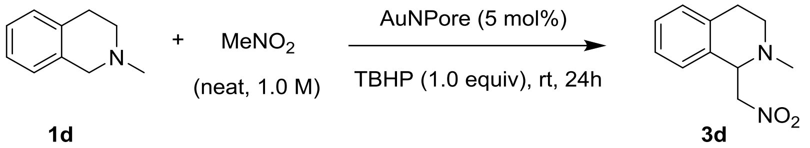
Representative procedure for AuNPore-catalyzed cross-dehydrogenative coupling of 1a with nitromethane: Method A



To a 5 mL reaction vial were added starting material **1a** (0.3 mmol, 62.7 mg) and nitromethane **2a** (0.5 M, 0.6 mL) and stirred for 5 min at room temperature before adding AuNPore catalyst (5 mol%, 2.97 mg). The vial cap was sealed under oxygen flow and oxygen balloon was attached. Reaction mixture was stirred at 80 ^{o}C for 24 hours. AuNPore catalyst was recovered by filtration, and the solvent was removed under vacuum. AuNPore catalyst was recovered and washed with acetone, and dried under vacuum. The residue was purified with short silica gel chromatography (Merck Chemical Co, hexane:ethyl acetate = 10:1, R_f = 0.3) to afford **3a** (77 mg, 95%) as a yellow oil.

Representative procedure for AuNPore-catalyzed cross-dehydrogenative coupling of 1d with nitromethane: Method B



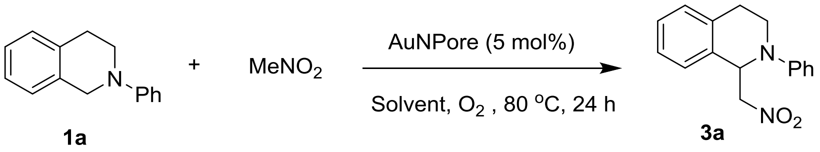
To a 5 mL reaction vial were added starting material **1d** (0.6 mmol, 88.3 µL) and nitromethane **2a** (1.0 M, 0.6 mL) and TBHP (5.5 M in decane solution; 0.6 mmol, 109 µL) and stirred for 5 min at room temperature before adding AuNPore catalyst (5 mol%, 5.9 mg). The reaction mixture was stirred at room temperature for 24 hours. The reaction was monitored by using TLC chromatography. The AuNPore catalyst was recovered by filtration, and the solvent was removed under vacuum. The recovered AuNPore catalyst was washed with acetone and dried under vacuum before being used for another cycle. The residue was purified with silica gel chromatography (MercK Chemical Co, hexane:ethyl acetate: Et_3N = 5:1:0.01, R_f = 0.4) to afford **3d** (99 mg, 80%) as a yellow oil.

Fabrication of AuNPore Catalyst

Au (99.99%) and Ag (99.99%) were melted with electric arc-melting furnace under Ar atmosphere to form Au/Ag alloy (30:70, in at.%), which was rolled down to thickness of 0.04 mm. The resulting foil was annealed at 850 ^{o}C for 20 h. The foil was cut into small pieces (5 × 2 mm square). Treatment of the resulting chips (67.1 mg) with 70 wt% nitric acid (7.5 mL) for 18 h at room temperature in a shaking apparatus resulted in the formation of the nanoporous structure by selective leaching of silver.

The material was washed with a saturated aqueous solution of $NaHCO_3$, pure water, and acetone, successively. Drying of the material under reduced pressure gave the nanoporous gold (30.2 mg), and its composition was found to be $Au_{98}Ag_2$ from EDX analysis.

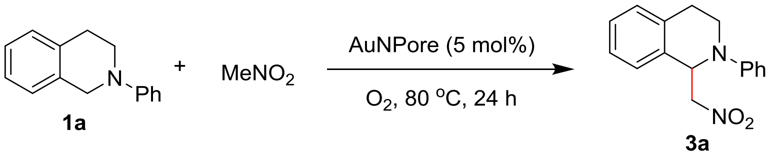
Table S1. Screening of solvents under an oxygen atmosphere (method A).[a]



Entry	Solvent	Yield (%)[b]
1	$MeNO_2$	99
2	MeOH	99
3	MeCN	93
4	Toluene	41
5	Octane	46
6	H_2O	50
7	$MeNO_2$	73[c]

[a] Reaction conditions: **1a** (0.3 mmol), nitromethane (0.5 M, neat or 5 equiv. when used with other solvents), AuNPore (5 mol%), oxygen sealed vial. [b] ^1H NMR yield determined using CH_2Br_2 as an internal standard. [c] Reaction temperature is 60 °C.

Reusability of nanoporous gold



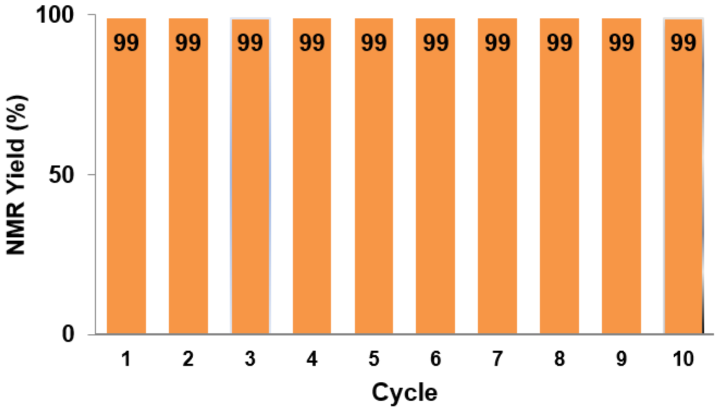


Figure S1. AuNPore was used for ten cycles and the yield was still 99% after tenth cycle. The 1H NMR yields are shown using CH_2Br_2 as an internal standard.

SEM images of nanoporous gold

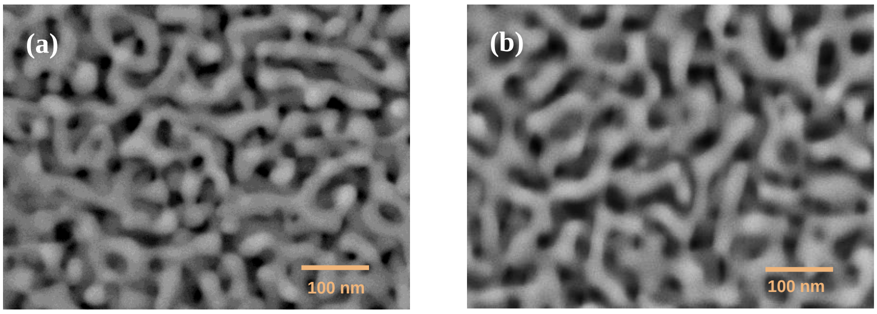
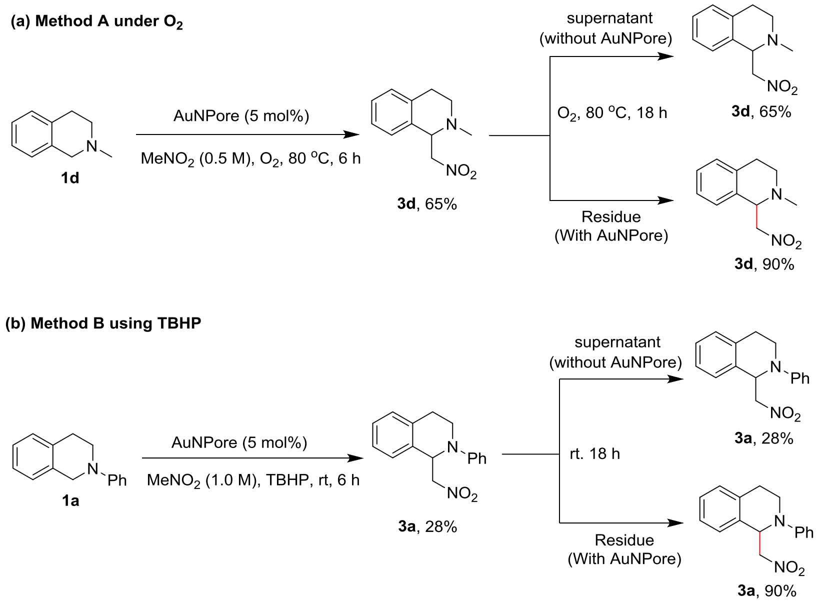


Figure S2. SEM images of nanoporous gold (AuNPore) catalyst. (a) fresh AuNPore, (b) after tenth cycle.

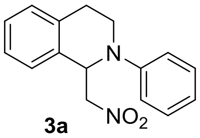
Leaching experiments



Scheme S1. Leaching experiment under methods A and B. 1,2,4-Trimethylbenzene was used as an internal standard for ^{1}H NMR yield determination.

Analytical data of products[2-4]

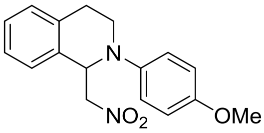
1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3a)



3a

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30-7.18 (m, 5H); 7.13 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.85 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.55 (dd, *J* = 8.0, 7.8 Hz, 1H), 4.87 (dd, *J* = 12.0, 8.0 Hz, 1H), 4.56 (dd, *J* = 12.0, 7.8 Hz, 1H), 3.70-3.59 (m, 2H), 3.13-3.05 (m, 1H), 2.80 (dt, *J* = 16.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.2, 135.1, 132.7, 129.3, 129.0, 127.9, 126.8, 126.5, 119.2, 114.9, 78.6, 58.1, 42.0, 26.4.

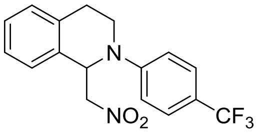
2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3b)



3b

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28-7.16 (m, 5H), 6.94 (d, *J* = 9.2 Hz, 2H), 6.84 (d, *J* = 9.2 Hz, 2H), 5.42 (dd, *J* = 8.4, 5.6 Hz, 1H), 4.85 (dd, *J* = 12.0, 8.4 Hz, 1H), 4.58 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.78 (s, 3H), 3.61-3.55 (m, 2H), 3.08-3.00 (m, 1H), 2.72 (dt, *J* = 16.4, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.7, 142.9, 135.3, 132.7, 129.3, 127.7, 126.7, 126.4, 118.7, 114.5, 78.8, 58.8, 55.5, 43.0, 25.7.

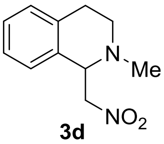
1-(Nitromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (3c)



3c

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.33-7.24 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.63 (dd, *J* = 7.2, 7.2 Hz, 1H), 4.90 (dd, *J* =12.0, 7.2 Hz, 1H), 4.62 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.75-3.68 (m, 2H), 3.17-3.11 (m, 1H), 2.90 (dt, *J* = 16.4, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.3, 134.7, 132.2, 129.0, 128.3, 126.9, 126.8, 126.7 (q, J^3 = 3.3 Hz), 124.5 (q, J^1 = 269.0 Hz), 120.3 (q, J^2 = 33.0 Hz), 113.2, 78.3, 57.7, 41.7, 26.5. HRMS (ESI positive) calcd for $C_{17}H_{15}F_3N_2O_2$ [M + H]$^+$: 337.1158, found: 337.1157.

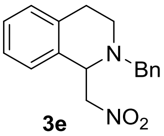
2-Methyl-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3d)



3d

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.18 (m, 2H), 7.16-7.09 (m, 2H), 4.69 (dd, *J* = 12.0, 9.6 Hz, 1H), 4.50 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.43 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.24 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.22-3.15 (m, 1H), 3.03-2.95 (m, 1H), 2.91-2.85 (m, 1H), 2.60 (dt, *J* = 16.8, 4.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 132.1, 129.3, 127.3, 127.2, 126.3, 79.3, 61.3, 45.5, 42.1, 23.7. HRMS (ESI positive) calcd for $C_{11}H_{14}N_2O_2$ [M + H]$^+$: 207.1128, found: 207.1127.

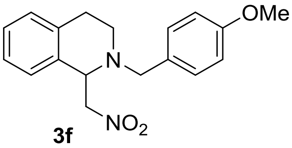
2-Benzyl-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3e)



3e

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.14 (m, 8H), 7.07 (d, *J* = 6.8 Hz, 1H), 4.71 (dd, *J* = 11.6, 10.0 Hz, 1H), 4.53 (dd, *J* = 10.0, 4.4 Hz, 1H), 4.45 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.82 (d, *J* = 13.2 Hz, 1H), 3.73 (d, *J* = 13.2 Hz, 1H), 3.06-2.89 (m, 2H), 2.50 (dd, *J* = 16.4, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.2, 132.0, 129.6, 128.6, 128.2, 127.6, 127.4, 127.2, 126.4, 79.4, 59.6, 57.5, 41.7, 22.8. HRMS (ESI positive) calcd for $C_{17}H_{18}N_2O_2$ [M + H]$^+$: 283.1441, found: 283.1440.

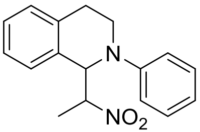
2-(4-Methoxybenzyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3f)



3f

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.30-7.12 (m, 6H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.77 (dd, *J* = 11.6, 10.0 Hz, 1H), 4.58 (dd, *J* = 10.0, 4.4 Hz, 1H), 4.51 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.85 (s, 3H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.28-3.20 (m, 1H), 3.11-2.95 (m ,2H), 2.76 (dd, J = 16.8, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 135.2, 132.0, 130.1, 129.8, 129.5, 127.6, 127.4, 126.4, 113.6, 79.4, 59.3, 56.8, 55.2, 41.6, 22.8. HRMS (ESI positive) calcd for $C_{18}H_{20}N_2O_3$ [M + H]$^+$: 313.1546, found 313.1545.

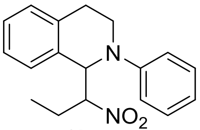
1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3g)



3g

Yellow oil. Isolated diastereomeric ratio = 1.7:1; Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, mixture of isomers), 7.18-7.10 (m, mixture of isomers), 7.02-6.98 (m, mixture of isomers), 6.85-6.80 (m, mixture of isomers), 5.25 (m, 1H, mixture of isomers), 5.05 (dq, *J* = 8.4, 6.8 Hz, 1H, major isomer), 4.89 (dq, *J* = 8.8, 6.8 Hz, 1H, minor isomer), 3.88-3.81 (m, 1H, major isomer), 3.64-3.54 (m, 3H, mixture of isomers), 3.10-3.02 (m, 1H, mixture of isomers), 2.95-2.85 (m, mixture of isomers), 1.71 (d, *J* = 6.8, 3H, minor isomer), 1.55 (d, *J* = 6.8, 3H, major isomer); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of isomers) δ 148.7 (149.0), 135.5 (134.6), 131.9 (133.7), 129.2 (129.3), 129.0 (128.6), 128.2 (128.1), 127.1 (128.1), 126.0 (126.5), 119.2 (118.7), 115.3 (114.4), 85.3 (88.9), 62.7 (61.1), 42.6 (43.5), 26.4 (26.7), 16.4 (17.4); HRMS (ESI positive) calcd for $C_{17}H_{18}N_2O_2$ $[M + H]^+$: 283.1441, found:283.14401.

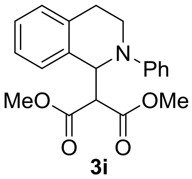
1-(1-Nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3h)



3h

Yellow oil. Isolated diastereomeric ratio = 1.3:1; Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.19 (m, mixture of isomers), 7.06-6.99 (m, mixture of isomers), 6.89-6.83 (m, mixture of isomers), 5.30 (d, *J* = 9.2 Hz, 1H, minor isomer), 5.19 (d, *J* = 9.6 Hz, 1H, major isomer), 4.96-4.90 (m, 1H, major isomer), 4.77-4.71 (m, 1H, minor isomer), 3.94-3.88 (m, 1H, major isomer), 3.76-3.55 (m, 3H, mixture of isomers), 3.16-3.09 (m, mixture of isomers), 3.00-2.91 (m, 1H, mixture of isomers), 2.27-2.16 (m, 3H, mixture of isomers), 1.92-1.86 (m, 1H, major isomer), 1.02-0.98 (m, 3H, mixture of isomers); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of isomers) δ 148.9 (149.0), 135.4 (134.6), 133.8 (132.5), 129.3 (129.1), 129.2, 128.5 (128.6), 128.0 (128.1), 127.1, 125.8 (126.5), 119.2 (118.5), 115.8 (114.1), 96.1 (93.0), 62.1 (60.7), 43.5 (42.4), 25.7 (26.8), 25.0 (24.6), 10.7; HRMS (ESI positive) calcd for $C_{18}H_{20}N_2O_2$ $[M + H]^+$: 297.1597, found:297.1598.

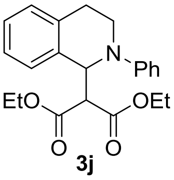
Dimethyl 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (3i)



3i

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.09 (m, 6H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.71 (d, *J* = 9.2 Hz, 1H), 3.95 (d, *J* = 9.2 Hz, 1H), 3.73-3.60 (m, 2H), 3.66 (s, 3H), 3.55 (s, 3H), 3.11-3.03 (m, 1H), 2.88 (dt, *J* = 16.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 167.2, 148.6, 135.5, 134.6, 128.9, 128.8, 127.5, 126.9, 125.9, 118.5, 115.0, 59.1, 58.1, 52.5, 52.4, 42.2, 26.1; HRMS (ESI positive) calcd for $C_{20}H_{21}NO_4$ [M + H]$^+$: 340.1543, found: 340.1542.

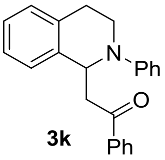
Diethyl 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (3j)



3j

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.13 (m, 7H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.80 (dd, *J* = 8.0, 8.0 Hz, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 4.24-3.99 (m, 4H), 3.95 (d, *J* = 9.6 Hz, 1H), 3.79-3.65 (m, 2H), 3.16-3.08 (m, 1H), 2.93 (dt, *J* = 16.4, 5.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.9, 148.6, 135.8, 134.6, 128.9, 128.7, 127.3, 127.0, 125.8, 118.3, 114.9, 61.5(4), 61.5(3), 59.5, 57.8, 42.2, 26.1, 14.0, 13.9(7), 13.9(1); HRMS (ESI positive) calcd for $C_{22}H_{25}NO_4$ [M + H]$^+$: 368.1856, found: 368.1856.

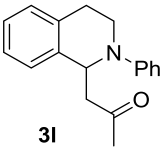
1-Phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3k)



3k

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.57-7.54 (m, 1H), 7.46-7.42 (m, 2H), 7.29-7.15 (m, 6H), 7.01 (d, *J* = 8.0, 2H), 6.79 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.70 (dd, *J* = 7.2, 7.2 Hz, 1H), 3.72-3.59 (m, 3H), 3.42 (dd, *J* = 16.8, 7.6 Hz, 1H), 3.19-3.12 (m, 1H), 2.97 (dt, *J* = 16.0, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 148.6, 138.4, 137.1, 134.4, 132.9, 129.2, 128.4, 128.0, 127.0, 126.7, 126.1, 117.8, 114.2, 55.0, 45.3, 42.1, 27.6; HRMS (ESI positive) calcd for $C_{23}H_{21}NO$ [M + H]$^+$: 328.1696, found: 328.1695.

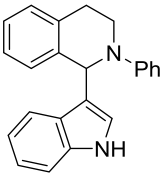
1-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3l)



3l

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 3H), 7.17-7.13 (m, 4H), 6.93 (d, *J* = 8.8, 2H), 6.78 (dd, H = 6.8, 6.8 Hz, 1H), 5.40 (dd, *J* = 6.4, 6.4 Hz, 1H), 3.68-3.62 (m, 1H), 3.57-3.50 (m, 1H), 3.09-3.03 (m ,2H), 2.83 (dt, *J* = 16.4, 3.6 Hz, 2H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 148.7, 138.1, 134.3, 129.2, 128.5, 126.8, 126.7, 126.2, 118.1, 114.7, 54.8, 50.2, 42.0, 31.1, 27.2; HRMS (ESI positive) calcd for $C_{18}H_{19}NO$ [M + H]$^+$: 266.1539, found: 266.1539.

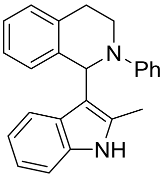
1-(1*H*-Indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3m)



3m

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (bs, 1H), 7.55 (d, *J* =8.0 Hz, 1H), 7.33-7.14 (m, 8H), 7.05-7.02 (m, 3H), 6.78 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.63 (s, 1H), 6.18 (s, 1H), 3.64 (dd, *J* = 7.6, 4.8 Hz, 2H), 3.12-3.04 (m, 1H), 2.82 (dt, *J* = 16.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 137.3, 136.5, 135.4, 129.1, 128.7, 127.9, 126.5, 126.3, 125.4, 124.0, 122.0, 119.5, 119.2, 118.0, 115.7, 110.9, 56.6, 42.3, 26.6; HRMS (ESI positive) calcd for $C_{23}H_{20}N_2$ [M + Na]$^+$: 347.1518, found: 347.1518.

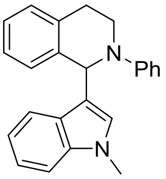
1-(2-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3n):



3n

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (bs, 1H), 7.22-7.02 (m, 11H), 6.92 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.87 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.99 (s, 1H), 3.74-3.61 (m, 2H), 3.15-2.99 (m, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 137.8, 135.1, 134.7, 133.2, 128.7, 128.5, 128.1, 126.1, 125.9, 120.6, 120.0, 119.5, 119,3, 119.0, 113.2, 109.9, 57.0, 45.7, 27.9 12.2; HRMS (ESI positive) calcd for $C_{24}H_{22}N_2$ [M + H]$^+$: 339.1069, found: 339.1069.

1-(1-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3o)

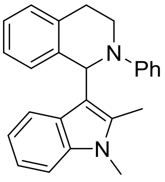


3o

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.32-7.17 (m, 9H), 7.04-7.02

(m, 3H), 6.78 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.51 (s, 1H), 6.19 (s, 1H), 3.66 (s, 3H), 3.75-3.60 (m, 2H), 3.12-3.04 (m, 1H), 2.83 (dt, *J* = 16.4, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 137.5, 137.2, 135.4, 129.1, 128.7, 128.6, 127.9, 126.7, 126.5, 125.6, 121.5, 120.0, 119.0, 117.8, 117.5, 115.5, 109.0, 56.5, 42.1, 32.7, 26.6; HRMS (ESI positive) calcd for $C_{24}H_{24}N_2$ $[M + H]^+$: 339.1855, found: 339.1854.

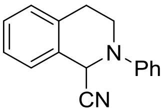
1-(1,2-Dimethyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3p)



3p

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.16 (m, 5H), 7.09-7.01 (m, 5H), 6.94-6.81 (m, 3H), 6.00 (s, 1H), 3.73-3.55 (m, 2H), 3.59 (s, 3H), 3.13-2.96 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 138.0, 136.2, 135.2, 128.6, 128.5, 128.2, 127.6, 126.1, 120.1, 120.0, 119.4, 118.99, 118.97, 112,6, 108.3, 57.1, 45.9, 29.4,27.8, 10.6; HRMS (ESI positive) calcd for $C_{25}H_{24}N_2$ $[M + H]^+$: 353.2012, found: 353.2011.

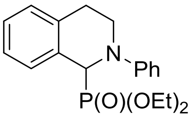
2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3q)



3q

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.19 (m, 6H), 7.07-6.96 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.48 (s, 1H), 3.77-3.71 (m, 1H), 3.48-3.42 (m, 1H), 3.17-3.08 (m, 1H), 2.93 (dt, *J* = 16.4, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 134.4, 129.4, 129.2, 128.6, 126.9, 126.7, 121.7, 117.6, 117.4, 53.1, 44.1, 28.5; HRMS (ESI positive) calcd for $C_{16}H_{14}N_2$ $[M + H]^+$: 235.1229, found: 235.1229.

Diethyl 2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-ylphosphonate (3r)

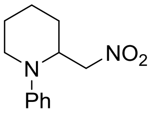


3r

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.8, 1H), 7.28-7.14 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.80 (dd, *J* = 6.8, 6.8 Hz, 1H), 5.20 (d, *J* = 20.0 Hz, 1H), 4,15-3.86 (m, 5H), 3.64 (dt, *J* = 12.4, 6.0 Hz, 1H), 3.12-2.97 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2 (d, *J* = 5.8 Hz), 136.2 (d, *J* = 5.7 Hz), 130.5, 129.0, 128.6 (d, *J* = 2.4 Hz), 128.0

(d, *J* = 4.9 Hz), 127.3 (d, *J* = 3.3 Hz), 125.7 (d, *J* = 3.3 Hz), 118.3, 114.6, 63.3 (d, *J* = 7.4 Hz), 62.2 (d, *J* = 7.4 Hz), 58.7 (d, *J* = 158.4 Hz), 43.4, 26.7, 16.5 (d, *J* = 5.0 Hz), 16.4 (d, *J* = 5.7 Hz); HRMS (ESI positive) calcd for $C_{19}H_{24}NO_3P$ $[M + H]^+$: 346.1566, found: 346.1566.

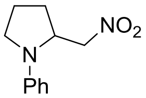
2-(Nitromethyl)-1-phenylpiperidine (3s)



3s

Pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.55-4.51 (m, 2H), 4.45-4.38 (m, 1H), 3.39 (dt, *J* = 12.8, 3.2 Hz, 1H), 2.90-2.84 (m, 1H), 1.93-1.87 (m, 1H), 1.80-1.57 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 129.4, 120.3, 116.8, 73.2, 54.9, 44.5, 26.4, 25.0, 19.1; HRMS (ESI positive) calcd for $C_{12}H_{16}N_2O_2$ $[M + H]^+$: 221.1284, found: 221.1283.

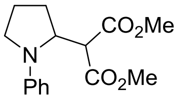
2-(Nitromethyl)-1-phenylpyrrolidine (3t)



3t

Pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2H), 6.75 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 2H), 4.60 (dd, J = 11.2, 2.8 Hz, 1H), 4.42-4.37 (m, 1H), 4.18-4.13 (m, 1H), 3.48-3.44 (m, 1H), 3.21-3.15 (m, 1H), 2.13-2.04 (m,4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 129.5, 117.2, 111.9, 75.7, 57.4, 48.1, 29.3, 22.8; HRMS (ESI positive) calcd for $C_{11}H_{14}N_2O_2$ $[M + H]^+$: 207.1128, found: 207.1127.

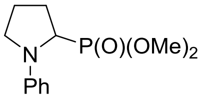
Dimethyl 2-(1-phenylpyrrolidin-2-yl)malonate (3u)



3u

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 6.73 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.65-4.61 (m, 1H), 3.85 (d, *J* = 6.0 Hz, 1H), 3.74 (s, 3H), 3.61 (s, 3H), 3.55-3.50 (m, 1H), 3.25 (m, 1H), 2.19-2.14 (m, 2H), 2.108-2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4(9), 168.4(4), 146.4, 129.1, 116.4, 112.3, 57.7, 53.1, 52.4, 52.3, 48.6, 29.5, 23.0; HRMS (ESI positive) calcd for $C_{15}H_{19}NO_4$ $[M + H]^+$: 278.1386, found: 278.1386.

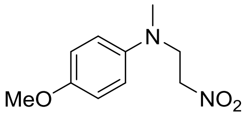
Dimethyl 1-phenylpyrrolidin-2-ylphosphonate (3v)



3v

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28-7.24 (m ,2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.77 (dd, *J* = 7.2, 7.2 Hz, 1H), 4.09 (d, *J* = 9.6 Hz, 1H), 3.77 (dd, *J* = 9.6, 0.8 Hz, 3H), 3.64 (dd, *J* = 9.6, 0.8 Hz, 3H), 3.63-3.59 (m, 1H), 3.23-3.16 (m, 1H), 2.44-2.33 (m, 2H), 2.18-2.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.5, 128.8, 117.1, 112.9, 56.2 (d, *J* = 167.5 Hz), 53.2 (d, *J* = 6.6 Hz), 52.5 (d, *J* = 7.4 Hz), 49.6 (d, *J* = 2.5 Hz), 27.8, 24.3; HRMS (ESI positive) calcd for $C_{12}H_{18}NO_3P$ [M + H]$^+$: 256.1097, found: 256.1096.

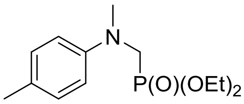
4-Methoxy-*N*-methyl-*N*-(2-nitroethyl)aniline (3w)



3w

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.85 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.54 (t, *J* = 6.4 Hz, 2H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.7, 142.6, 115.4, 114.8, 72.7, 55.7, 51.9, 39.5; HRMS (ESI positive) calcd for $C_{10}H_{14}N_2O_3$ [M + H]$^+$: 211.1077, found: 211.1076.

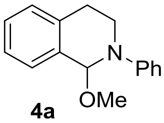
Diethyl ((methyl(*p*-tolyl)amino)methyl)phosphonate (3x)



3x

White solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6,74 (d, *J* = 8.4 Hz, 2H), 4.14-4.04 (m, 4H), 3.66 (d, *J* =7.6 Hz, 2H), 3.00 (s, 3H), 2.25 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.4, 129.4, 126.7, 113.2, 62.1 (d, *J* = 6.6 Hz), 50.4 (d, *J* = 161.7 Hz), 39.4, 20.2, 16.5 (d, *J* = 5.8 Hz); HRMS (ESI positive) calcd for $C_{13}H_{22}NO_3P$ [M + H]$^+$: 272.1410, found: 272.1408.

1-Methoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4a): crude NMR using CH_2Br_2 as an internal standard

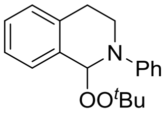


4a

Crude product was pure enough for characterization; product decomposes when subject to silica column chromatography. Colourless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30-7.18 (m, 6H), 7.00 (d, *J*

= 8.4 Hz, 2H), 6.84 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.63 (s, 1H), 3.73-3.67 (m, 1H), 3.57-3.51 (m, 1H), 3.28 (s, 3H), 3.10-3.03 (m, 1H), 2.97-2.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.8, 135.9, 135.35, 129.0, 128.2, 128.1, 127.9, 127.8, 125.9, 114.6, 88.2, 53.4, 43.8, 27.82; HRMS (ESI positive) calcd for $C_{16}H_{17}NO$ [M +Na]$^+$: 262.1201; found: 262.1202.

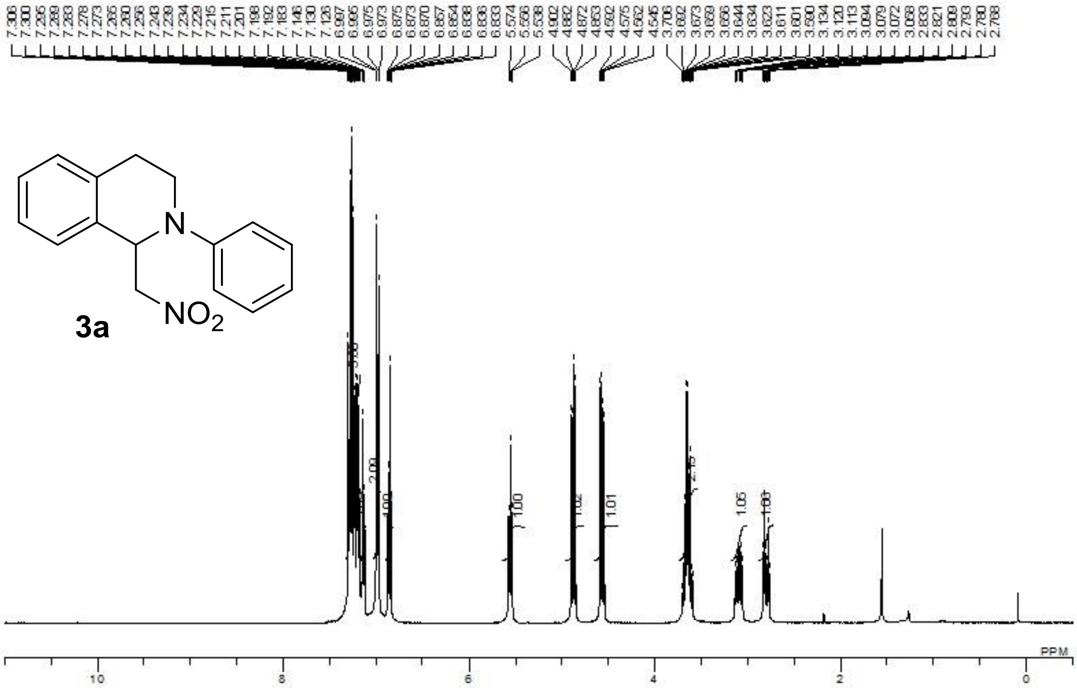
1-(*Tert*-butylperoxy)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4b)



4b

Colourless oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, *J* = 7.2 Hz, 1H), 7.32-7.21 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.77 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.24 (s, 1H), 3.62-3.56 (m, 1H), 3.52-3.46 (m, 1H), 3.03-2.90 (m, 2H), 3.02-2.97 (m, 1H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.1, 136.1, 132.4, 128.7, 128.6, 128.4, 127.4, 125.7, 118.2, 114.2, 89.6, 79.2, 41.8, 27.4, 26.2. HRMS (ESI positive) calcd for $C_{19}H_{23}NO_2$ [M + H]$^+$: 298.1801, found: 298.1801.

NMR spectra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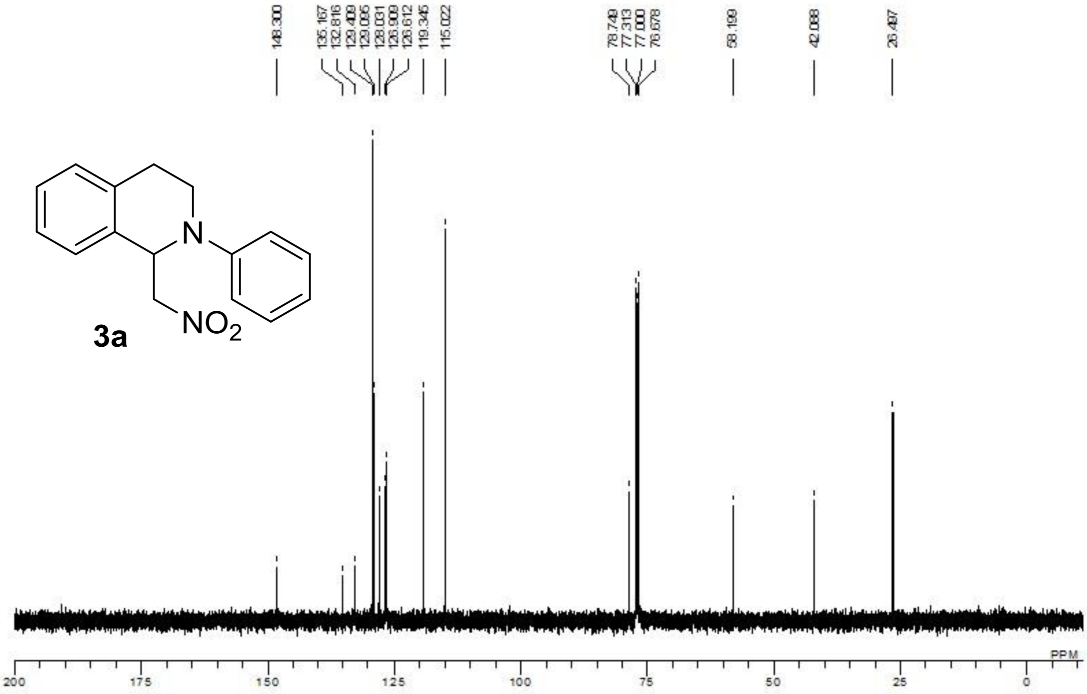
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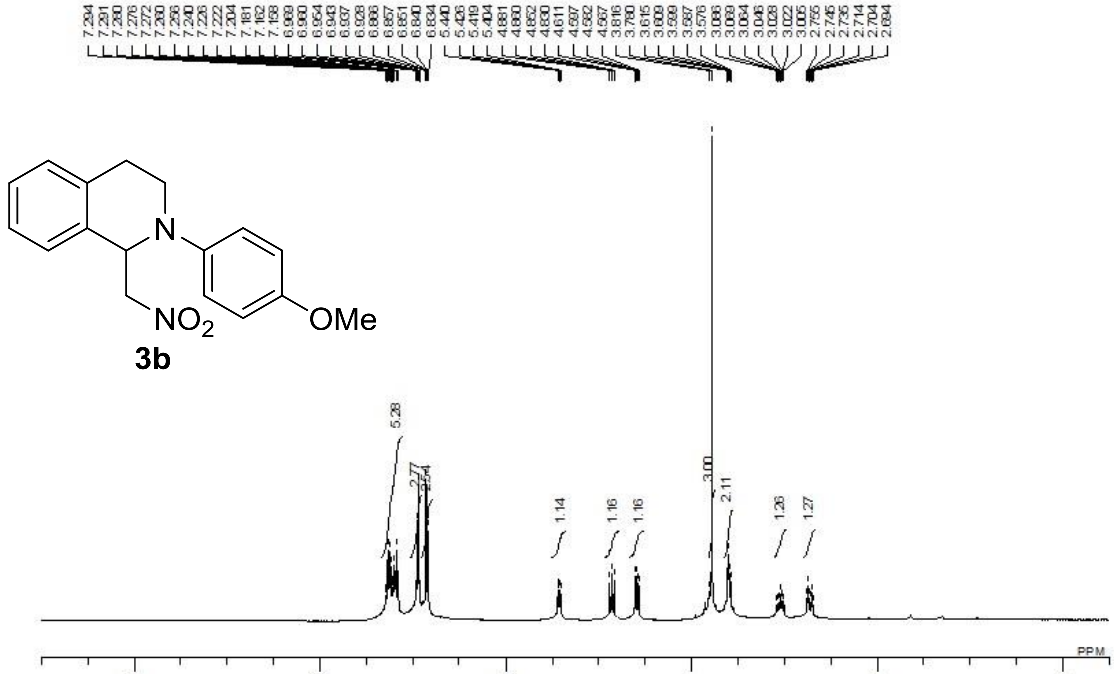
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6
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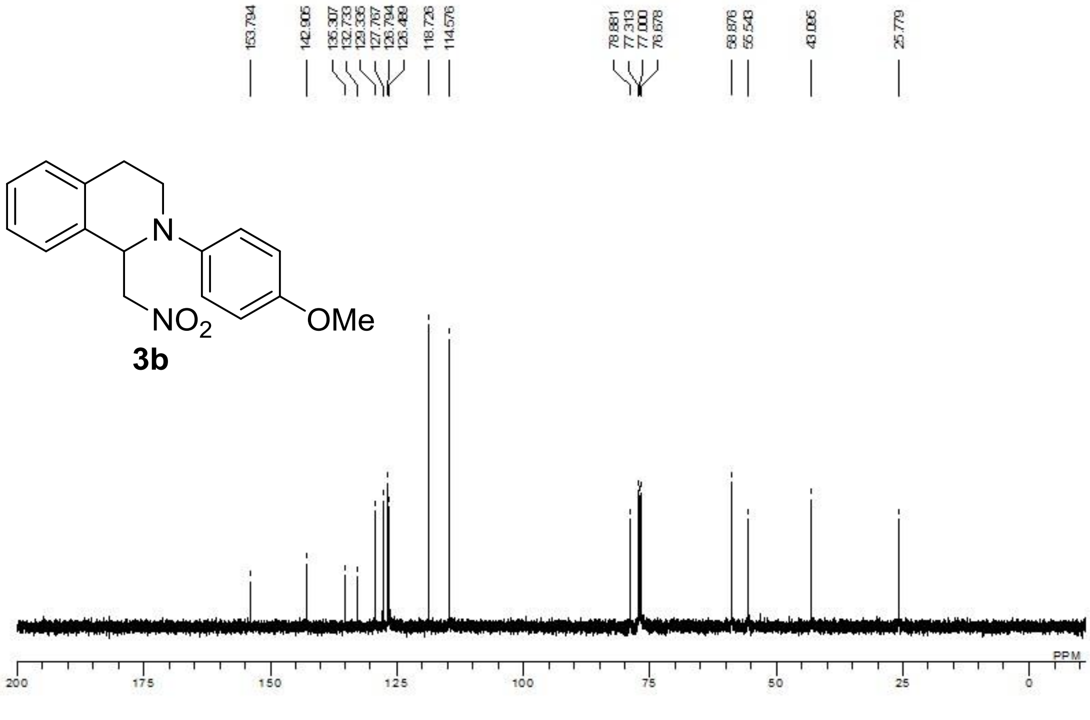
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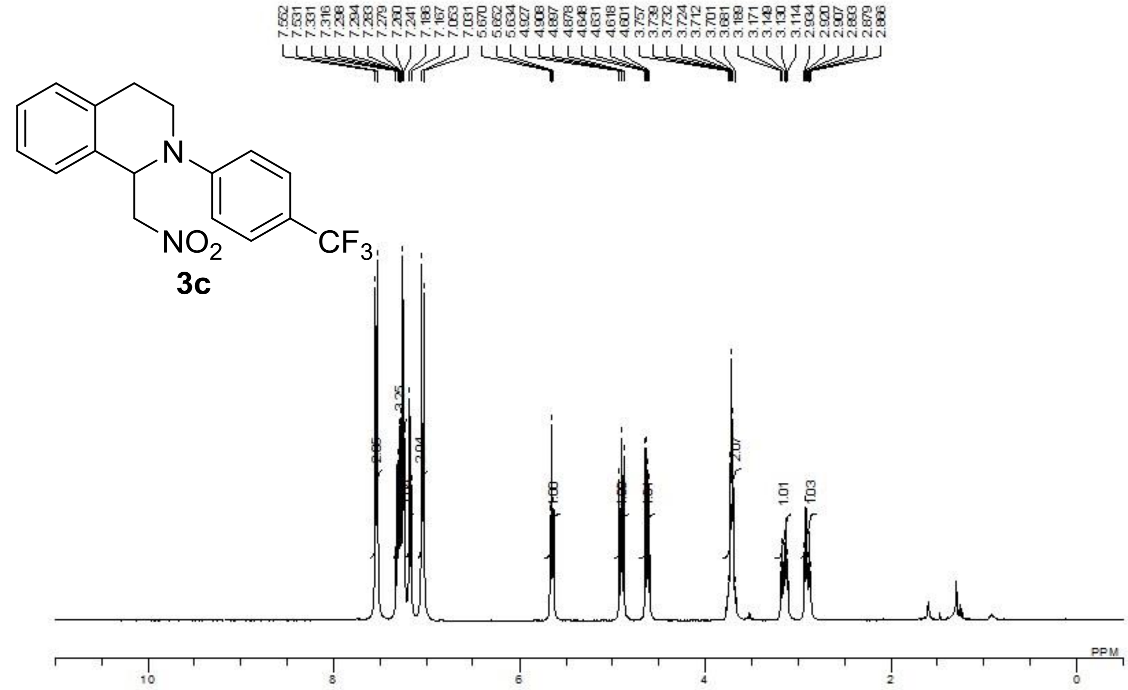
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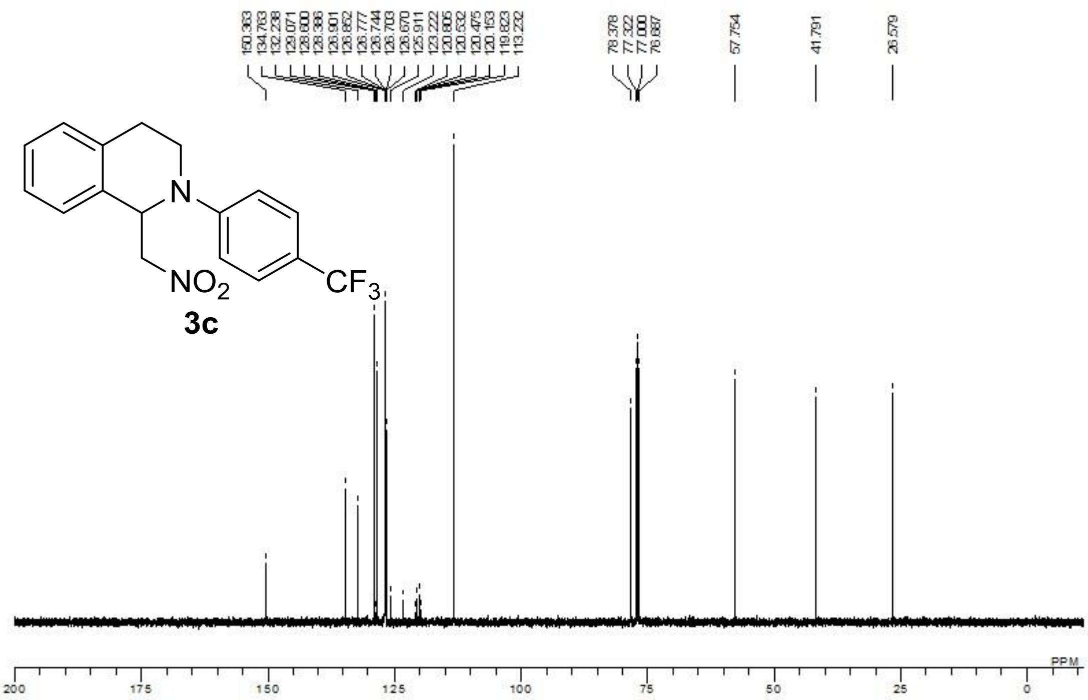
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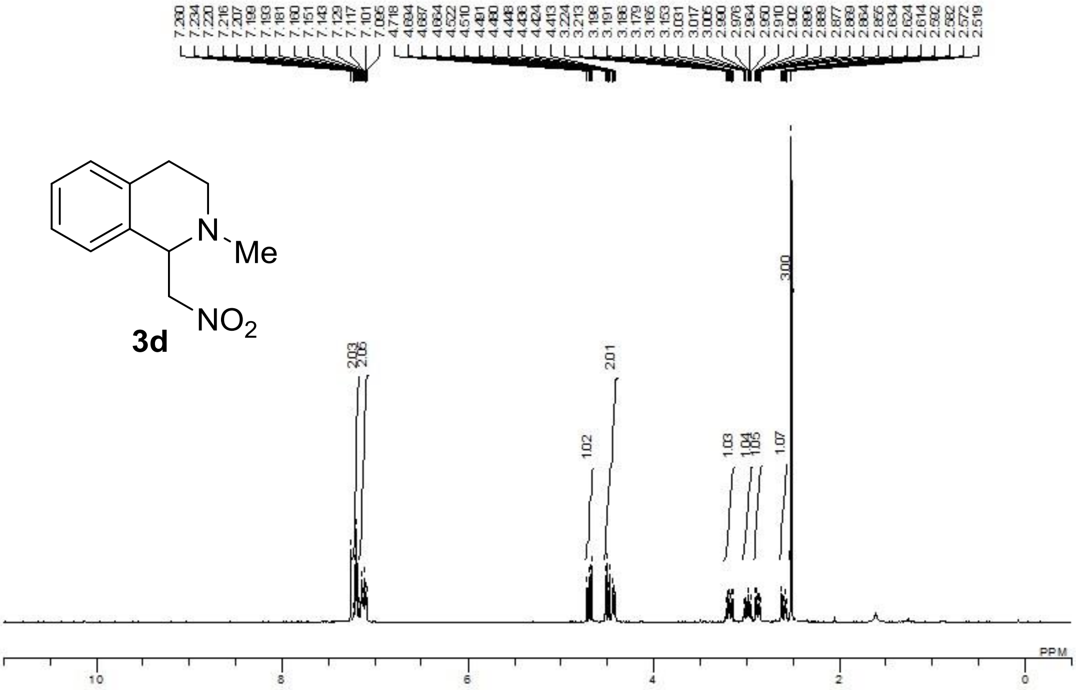
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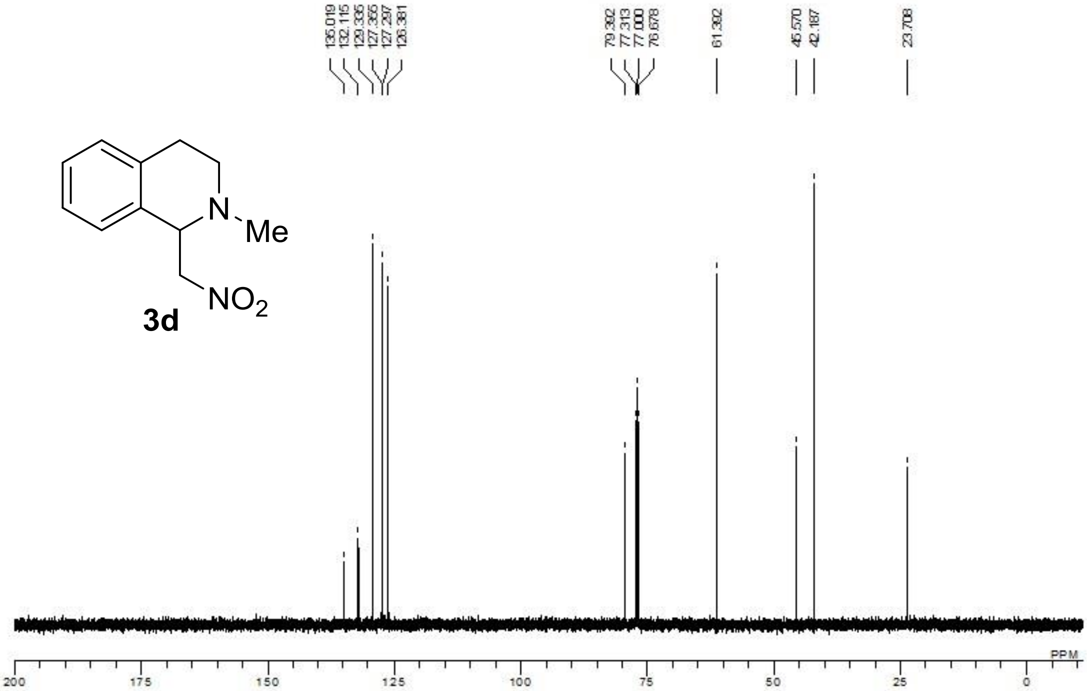
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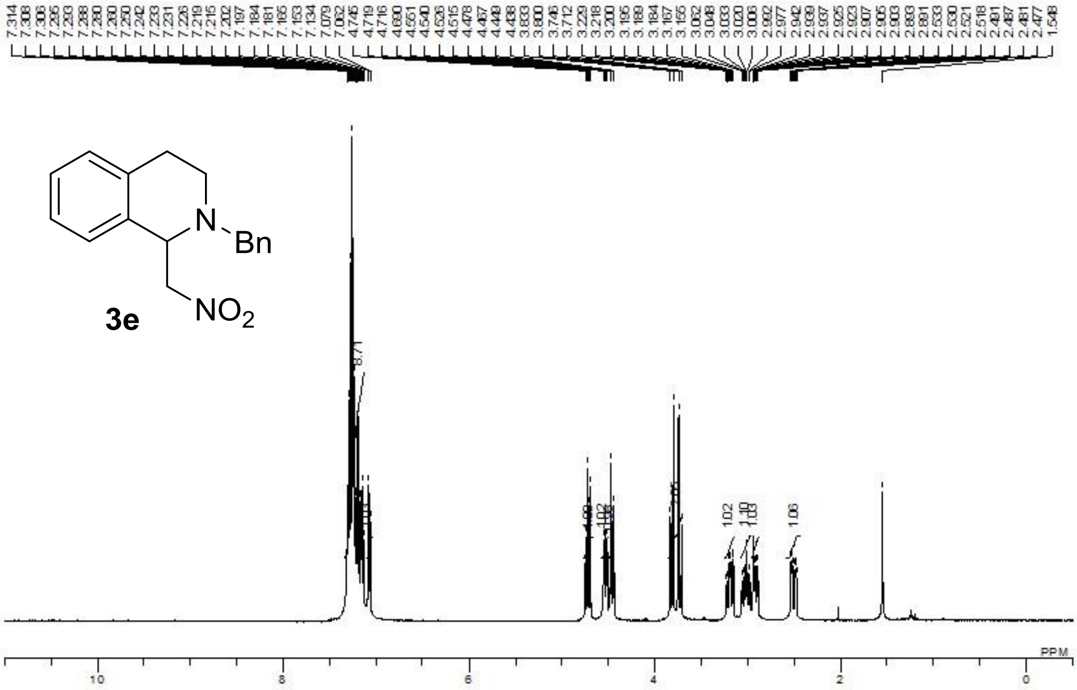
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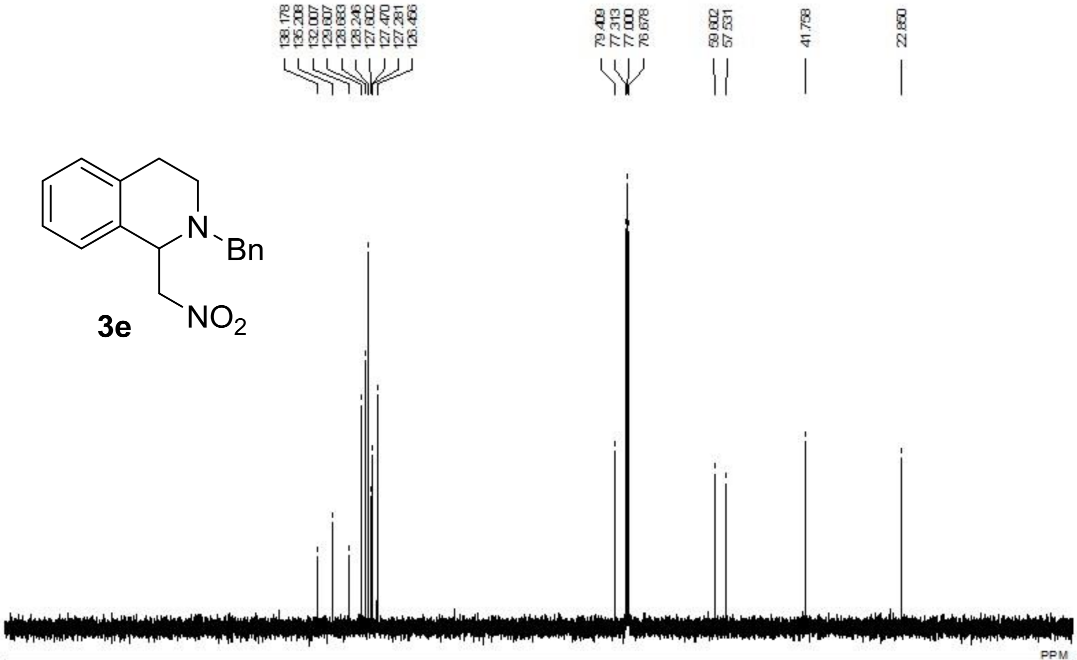
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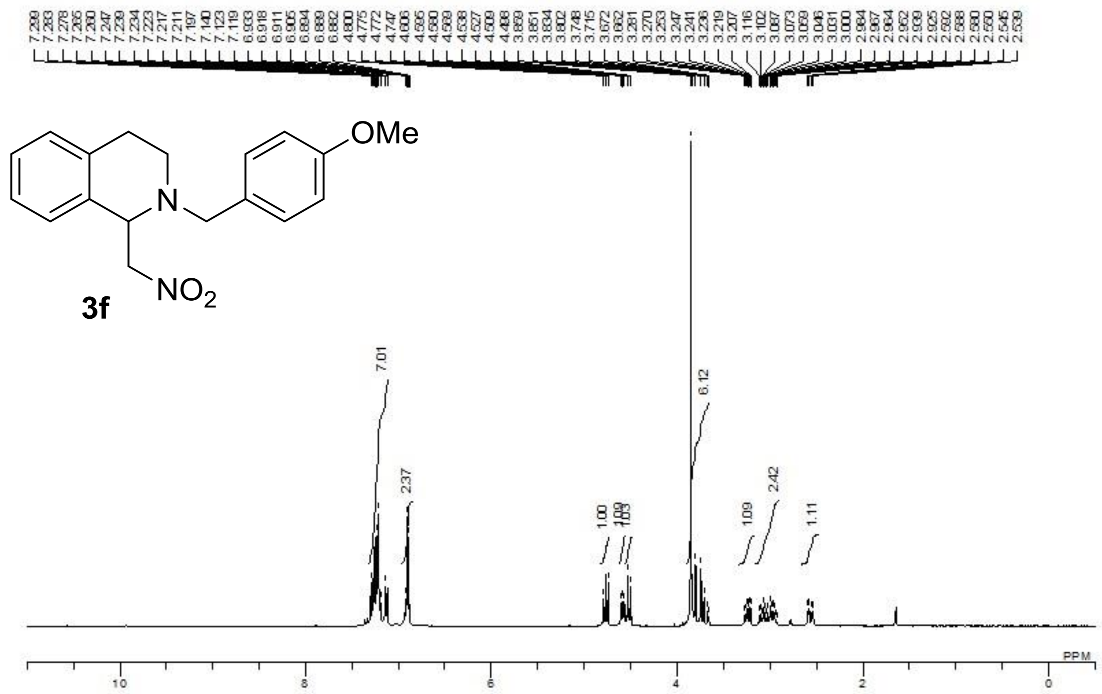
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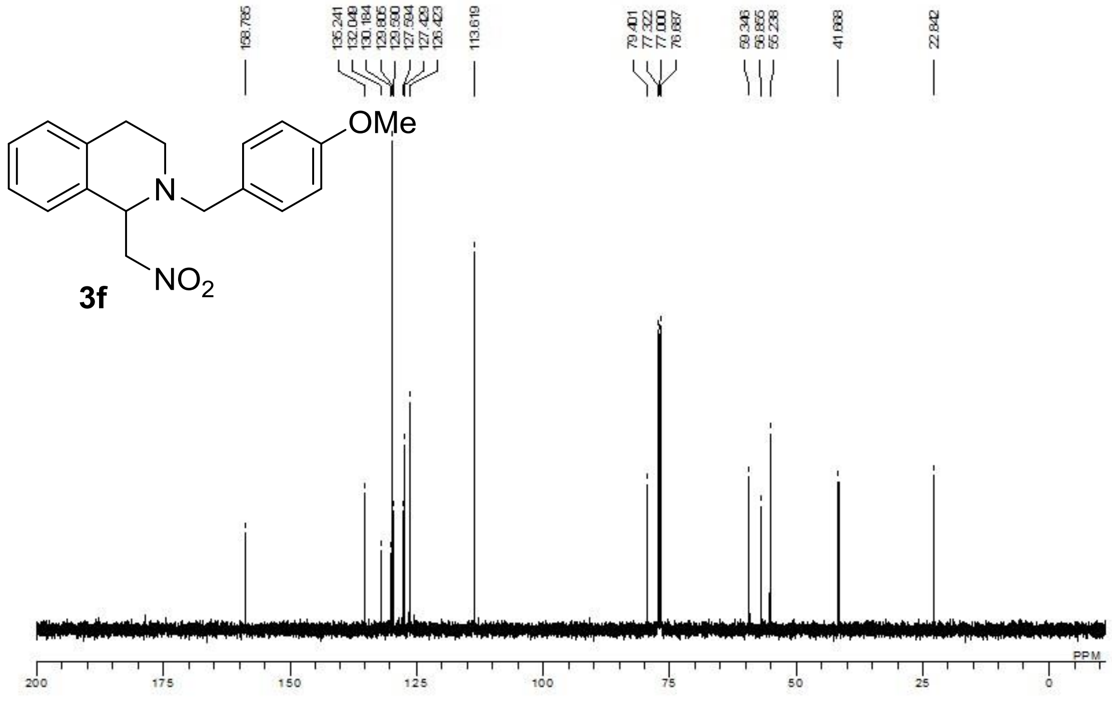
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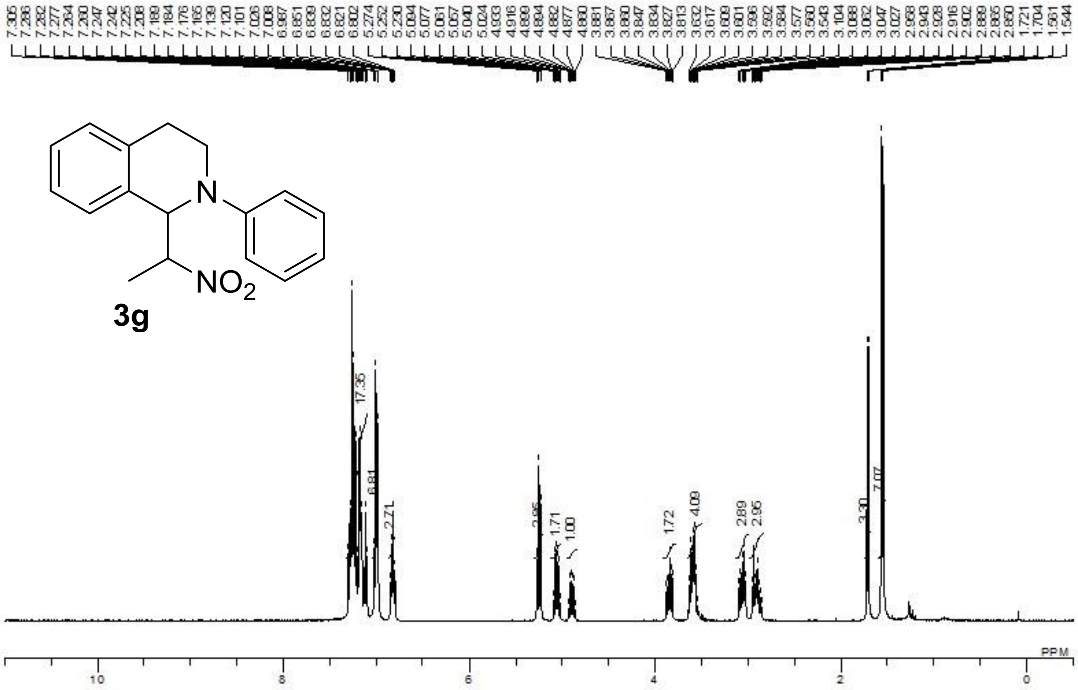
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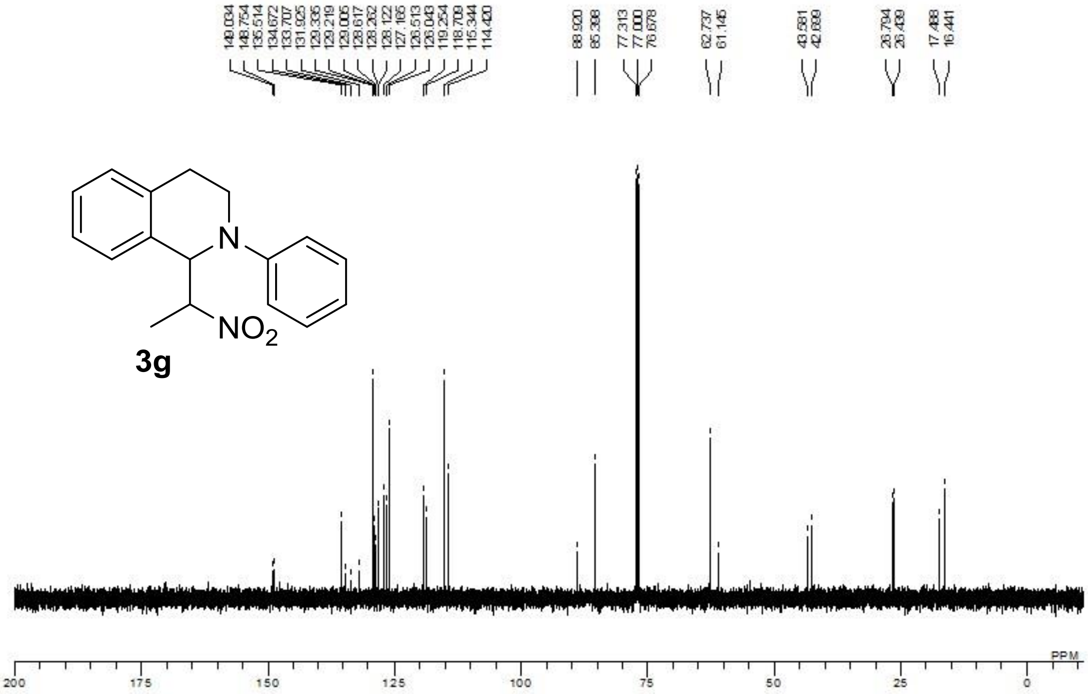
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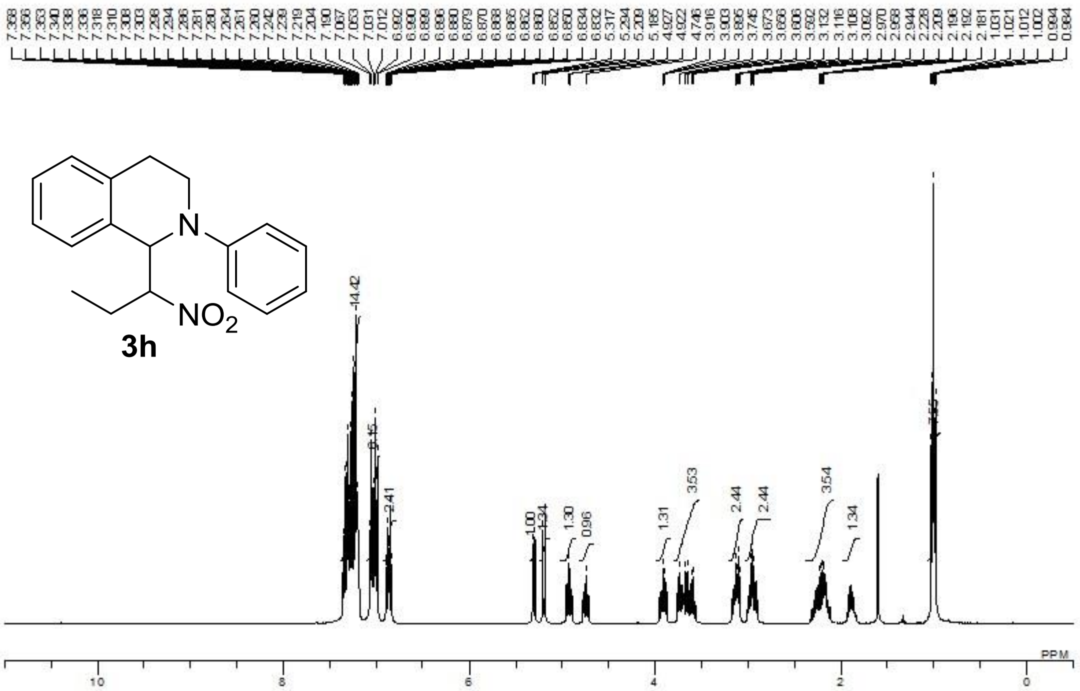
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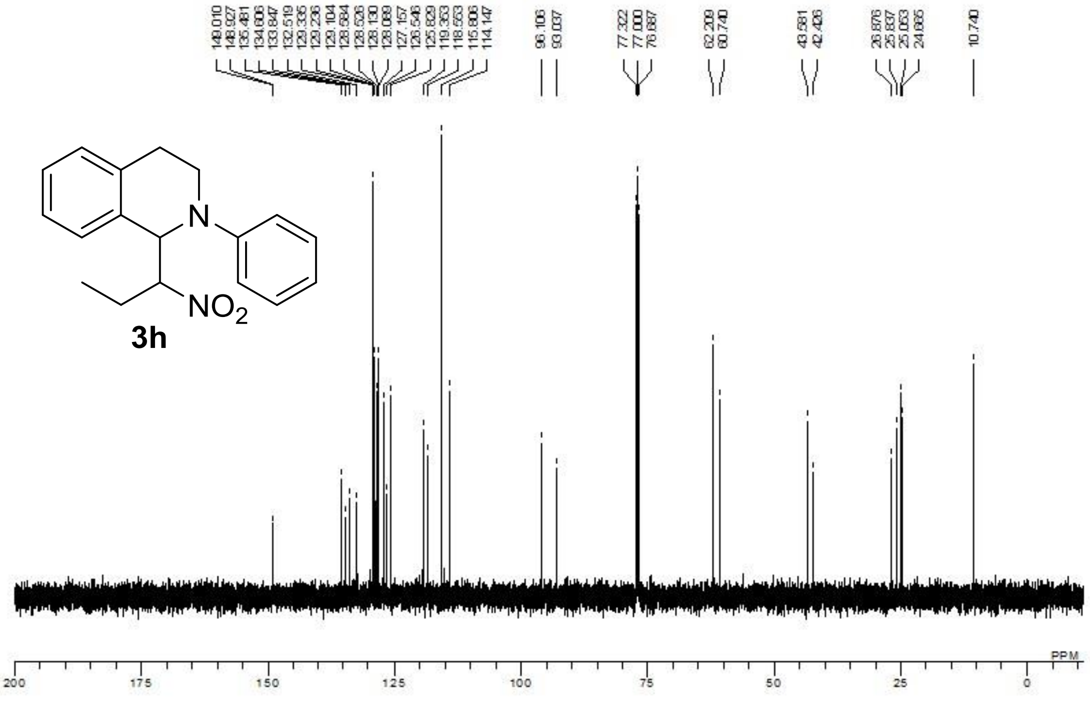
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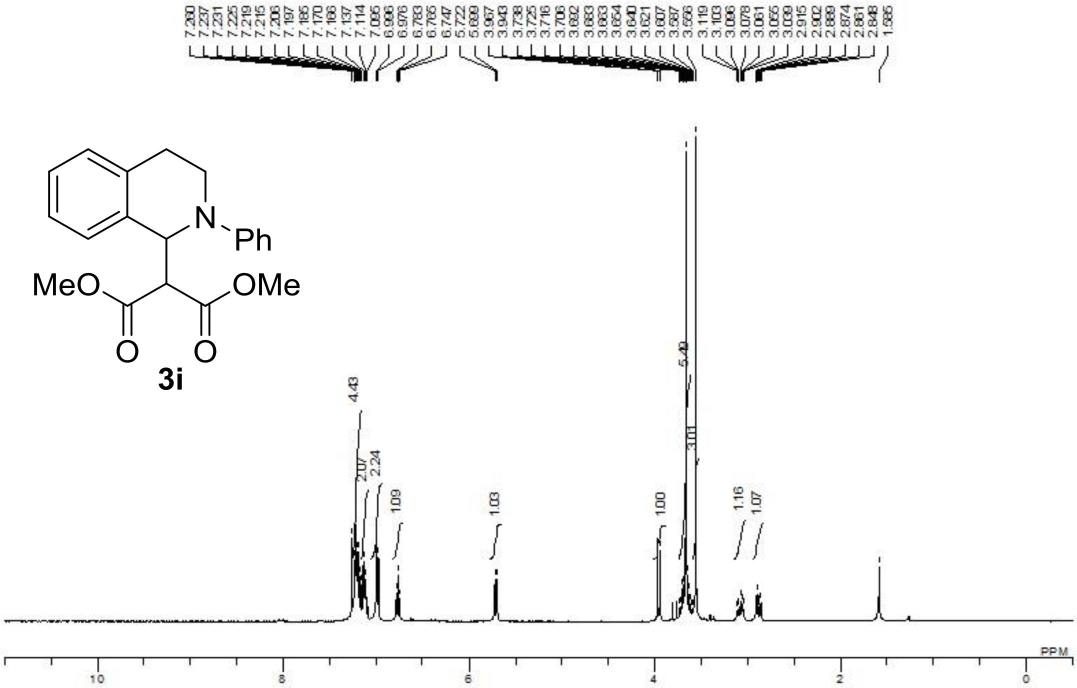

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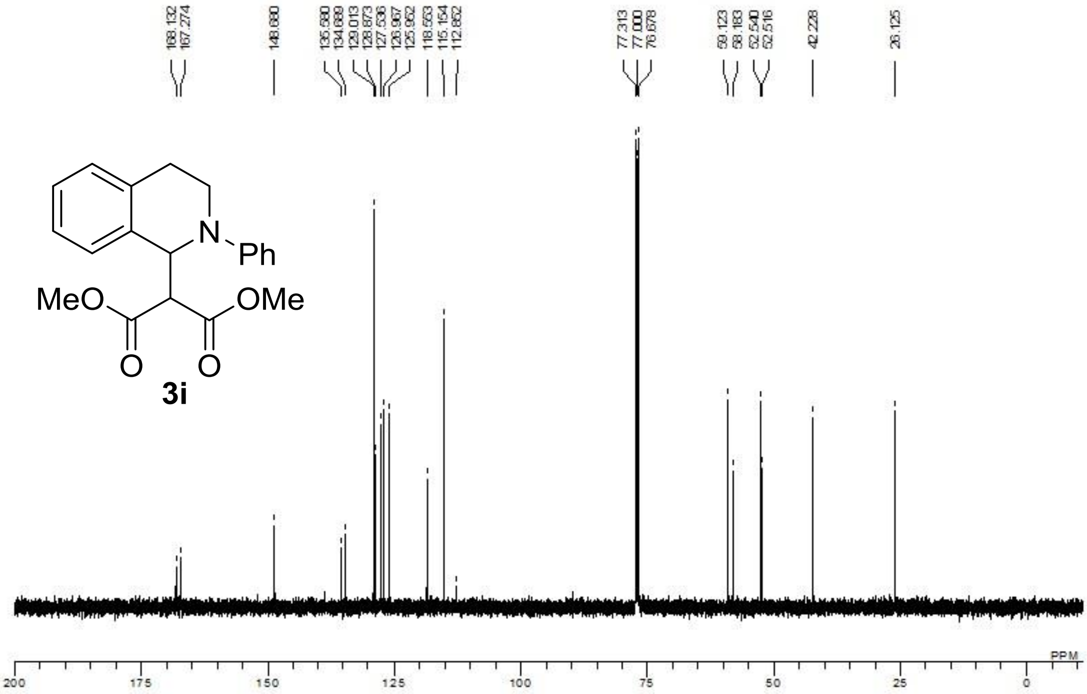

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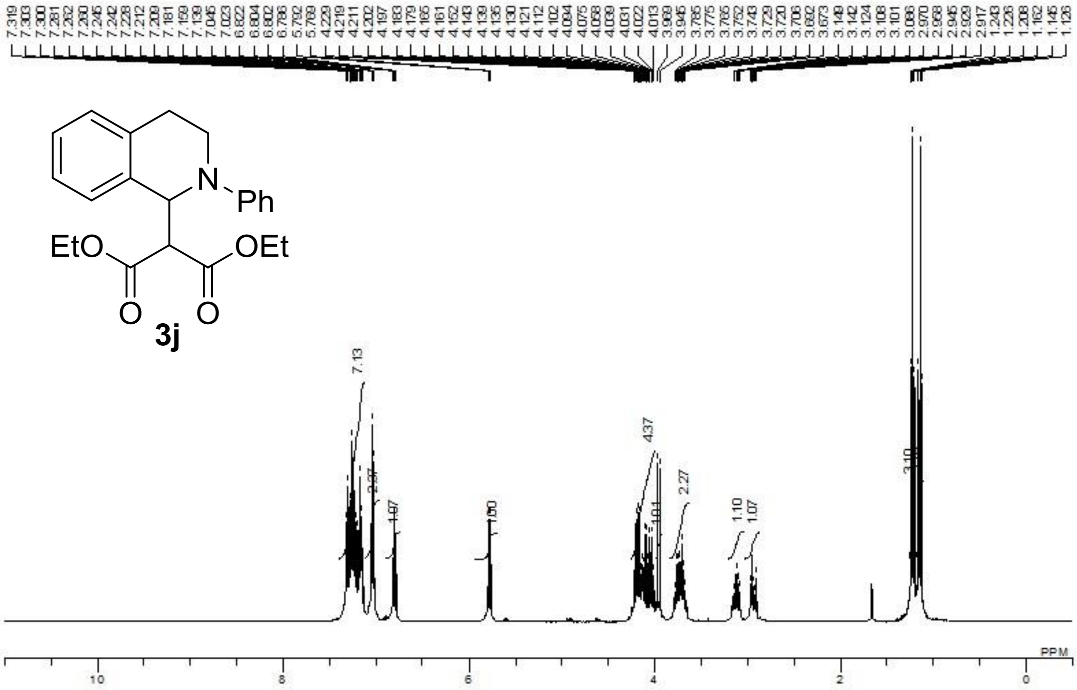
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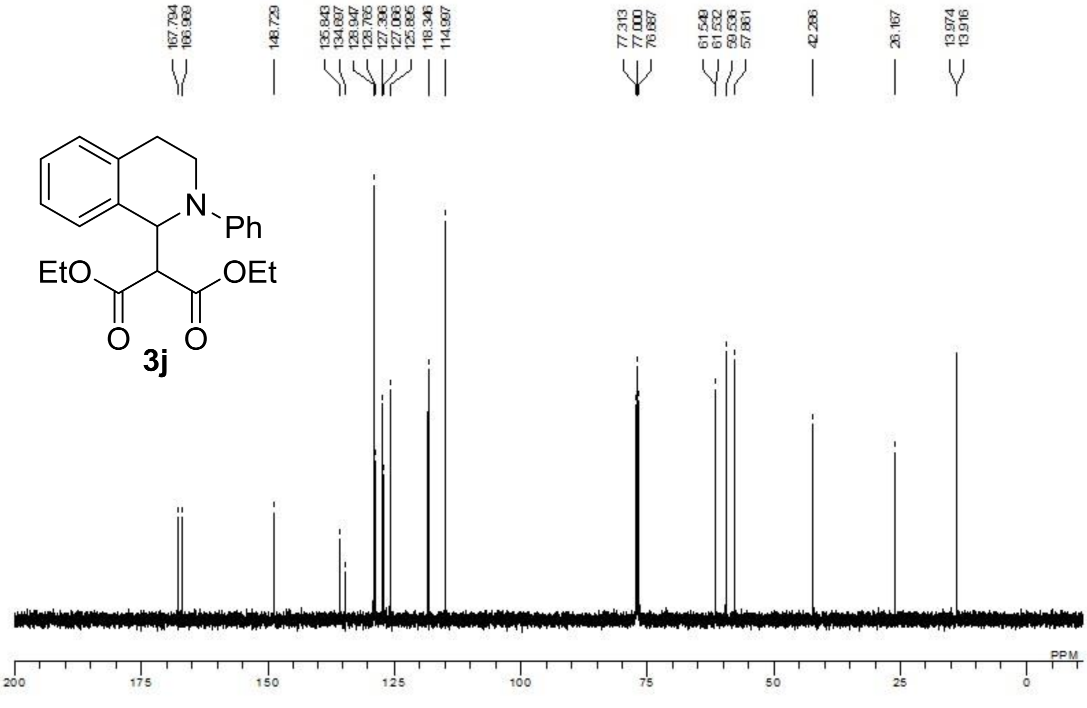
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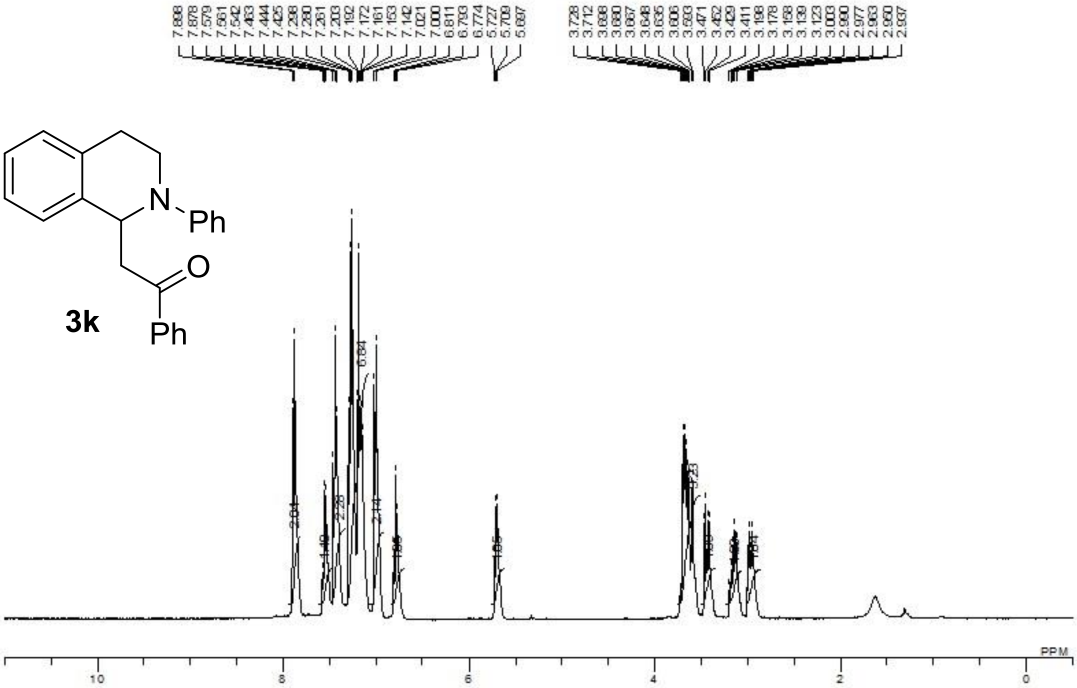
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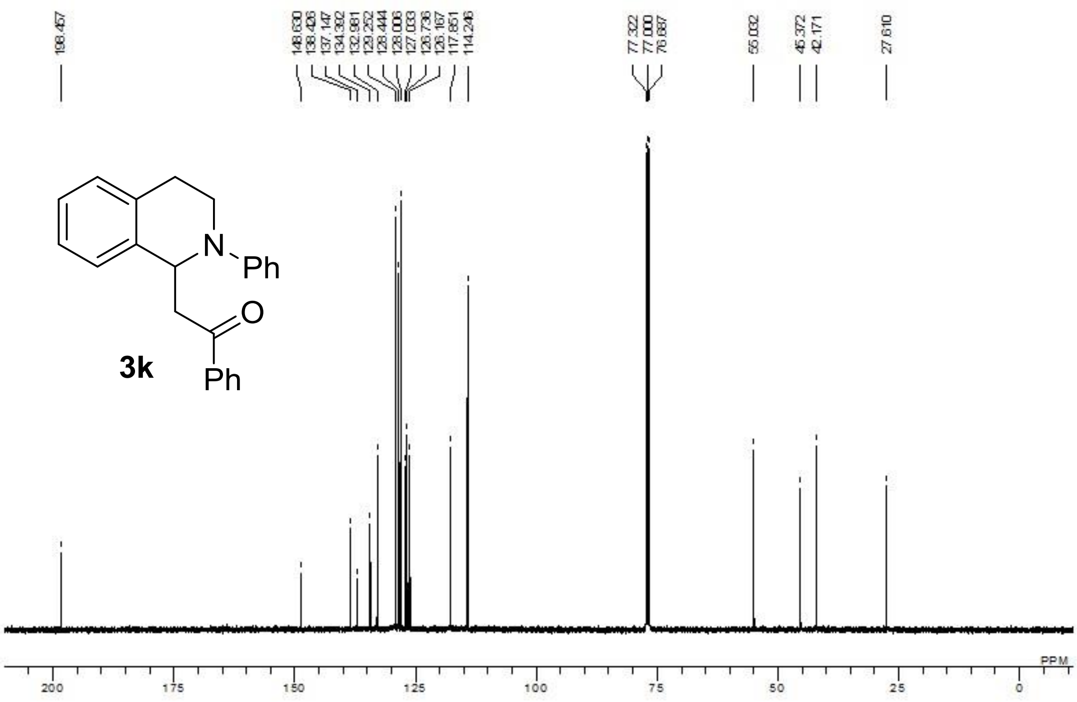
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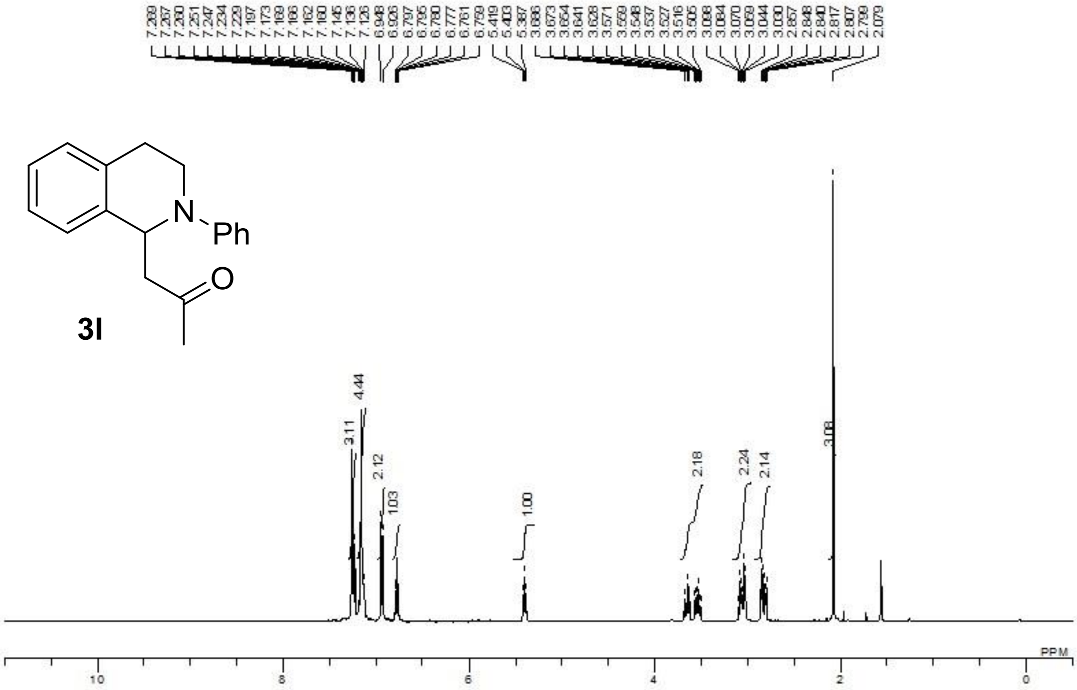
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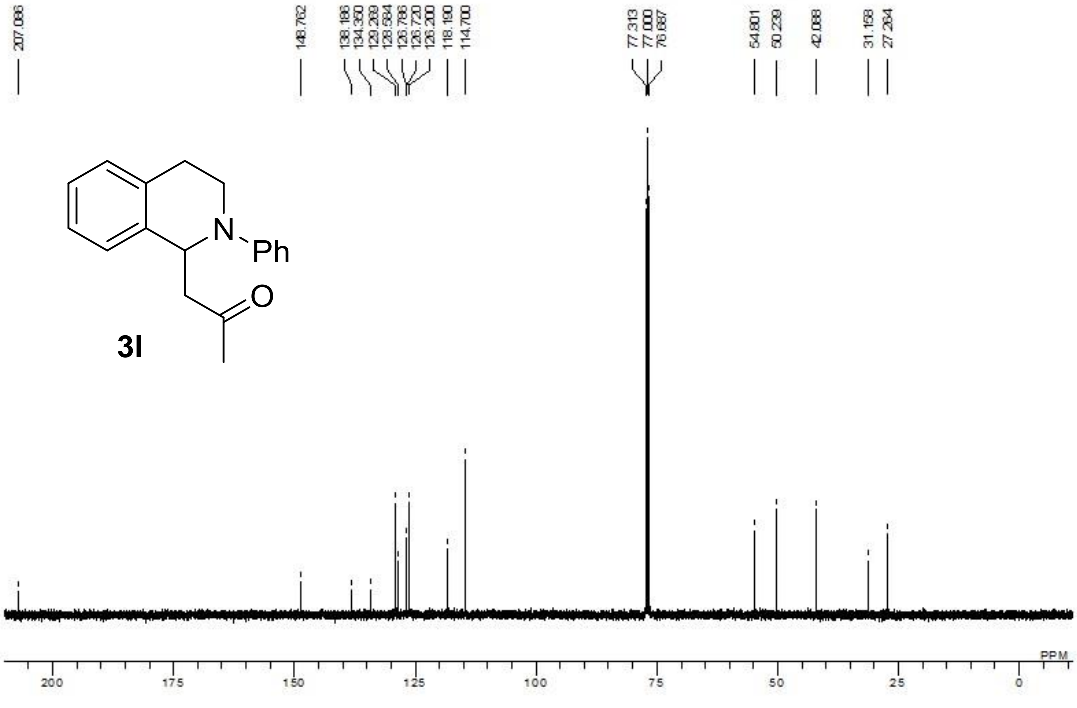
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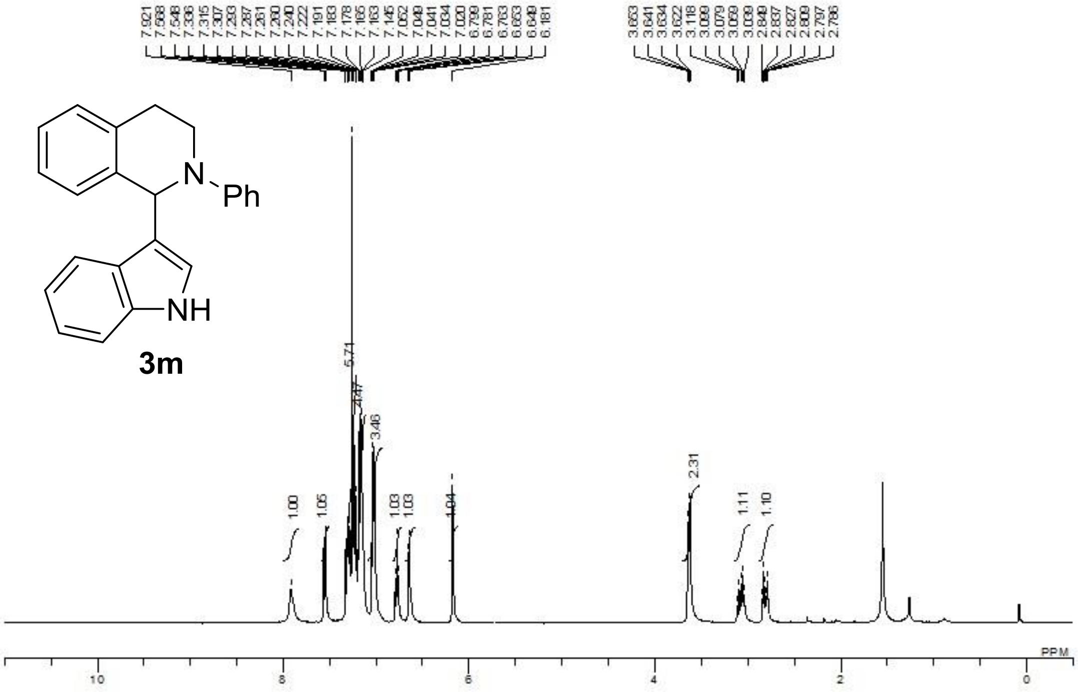

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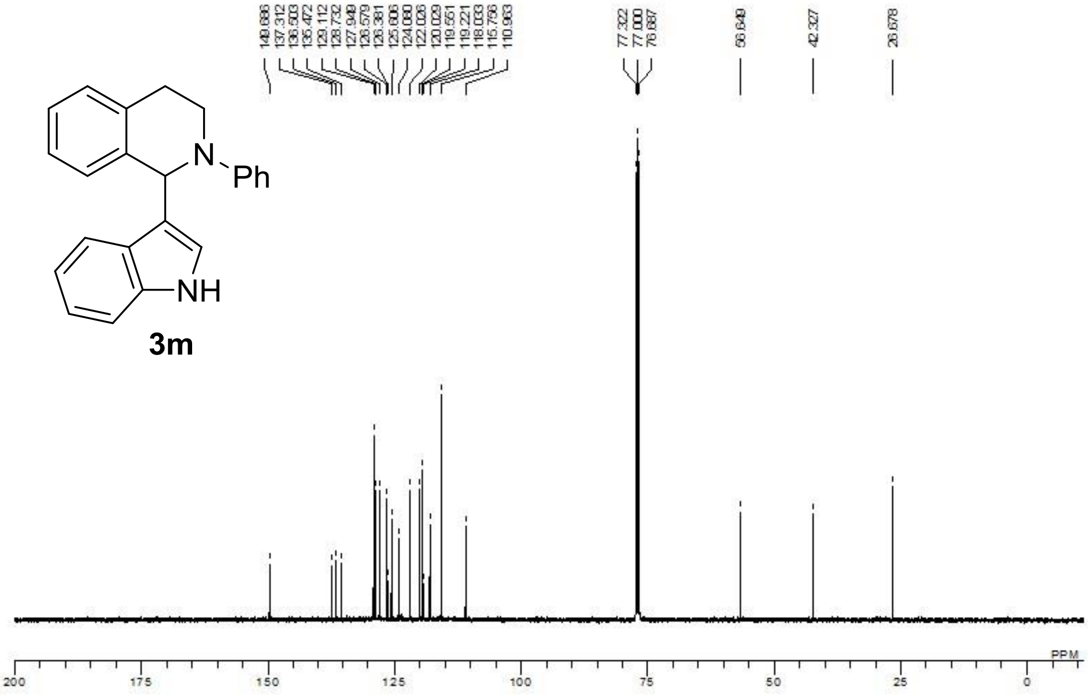

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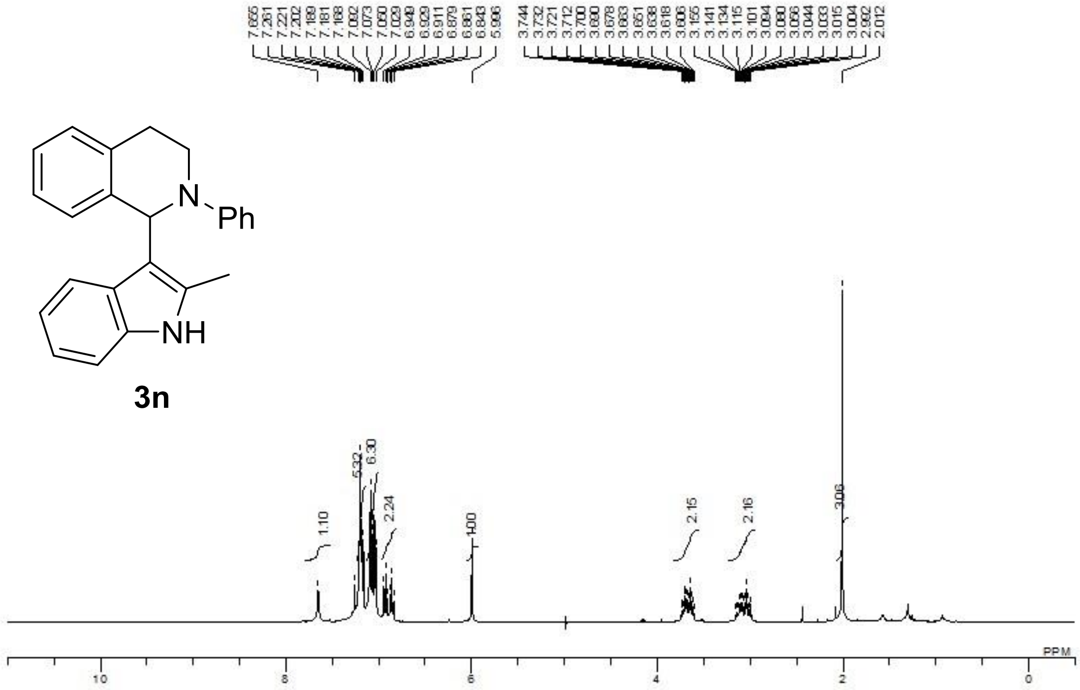
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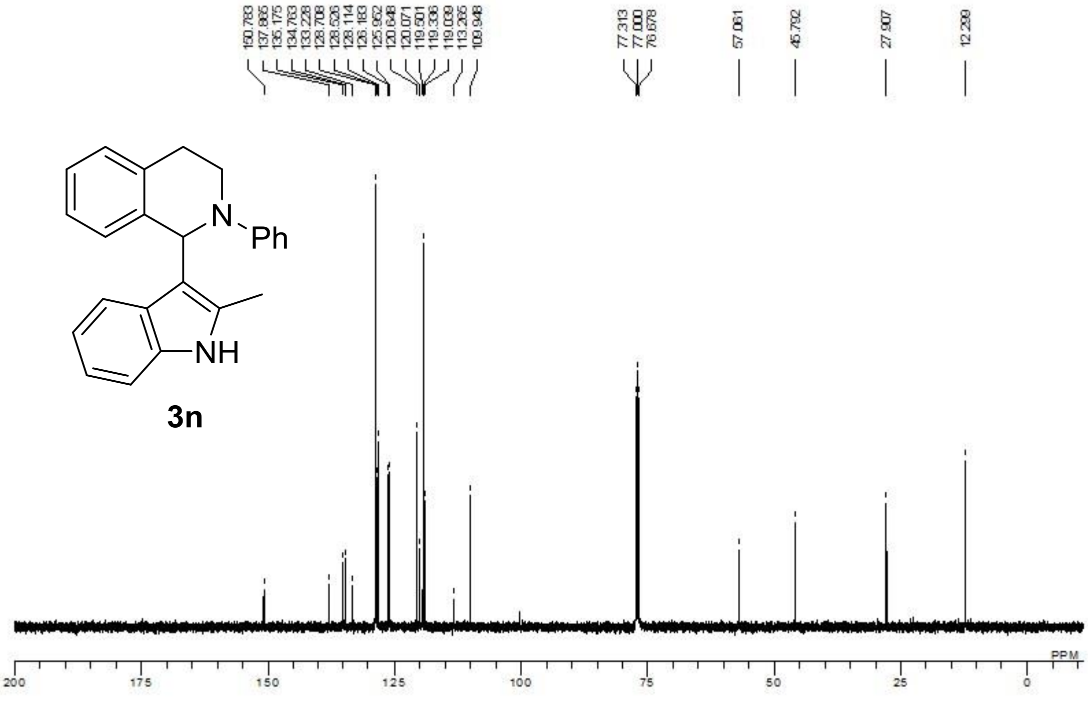
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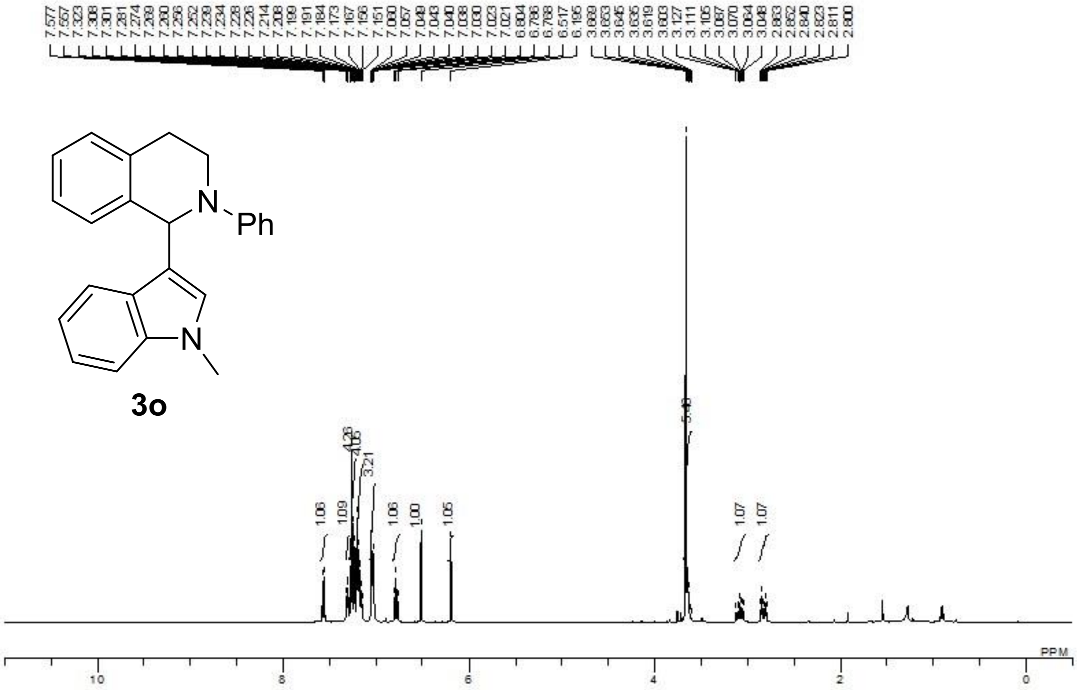
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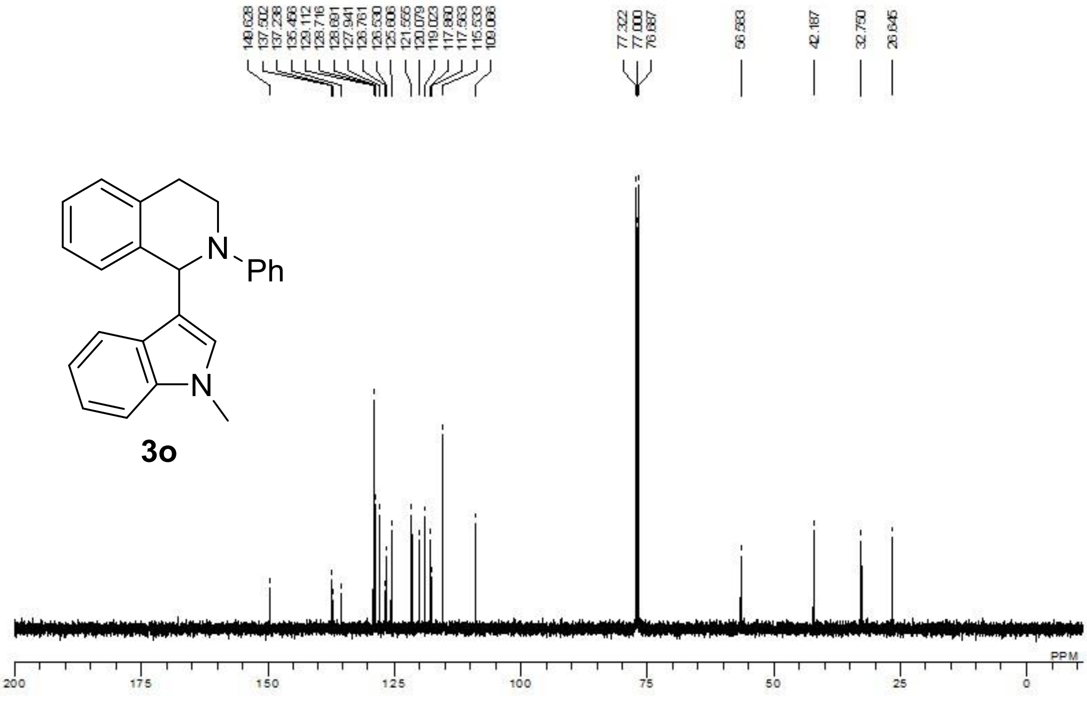
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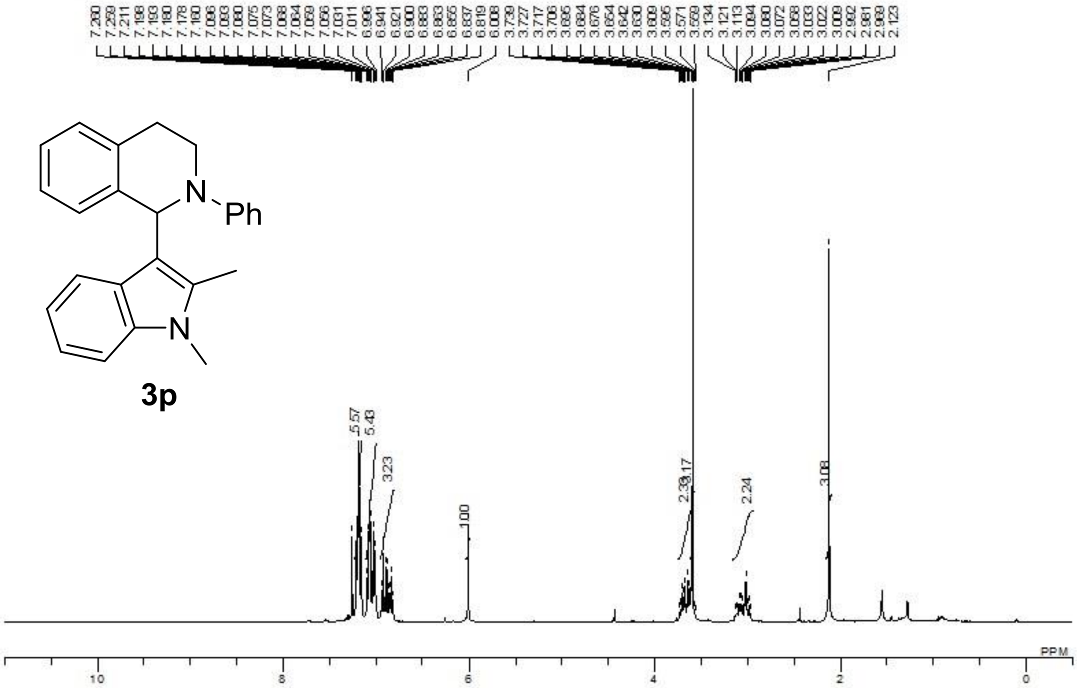
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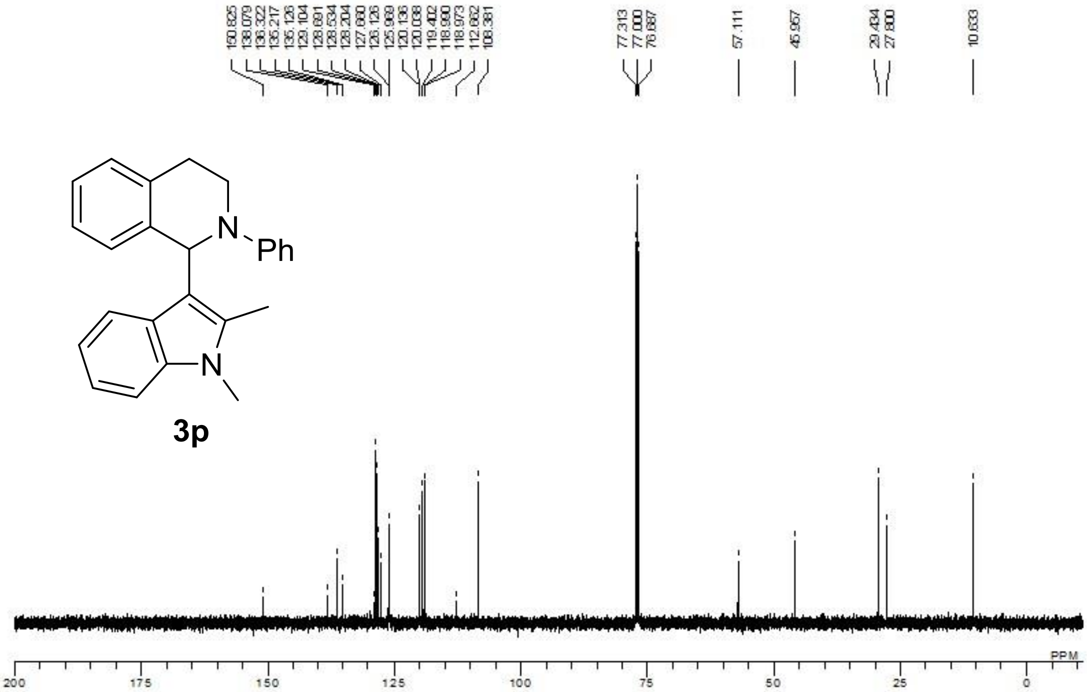
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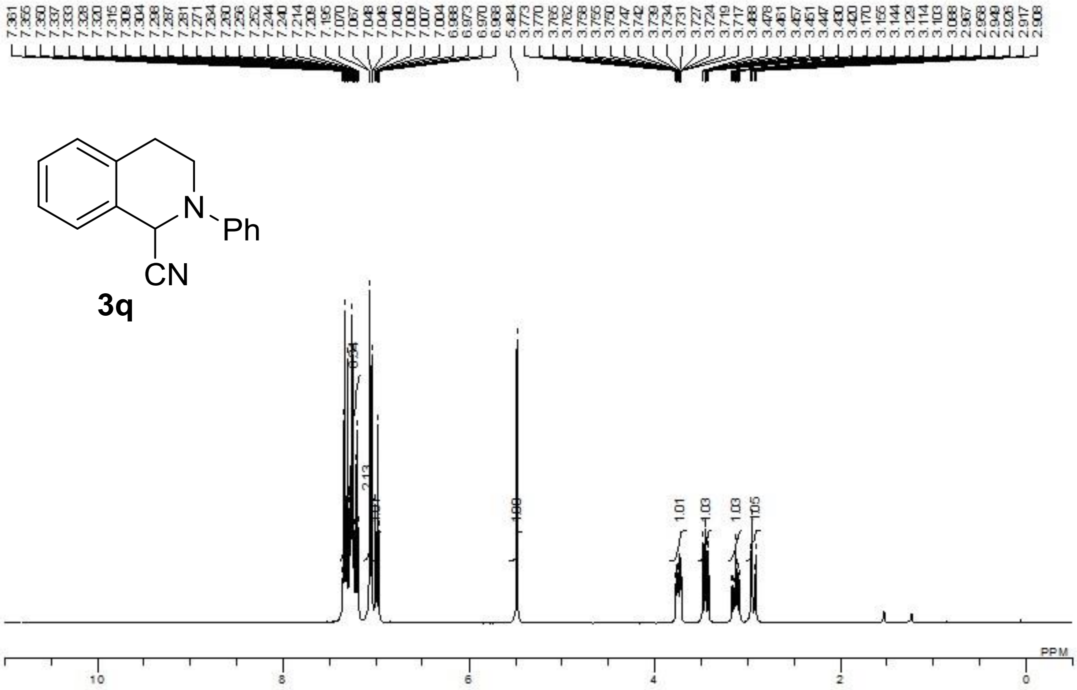
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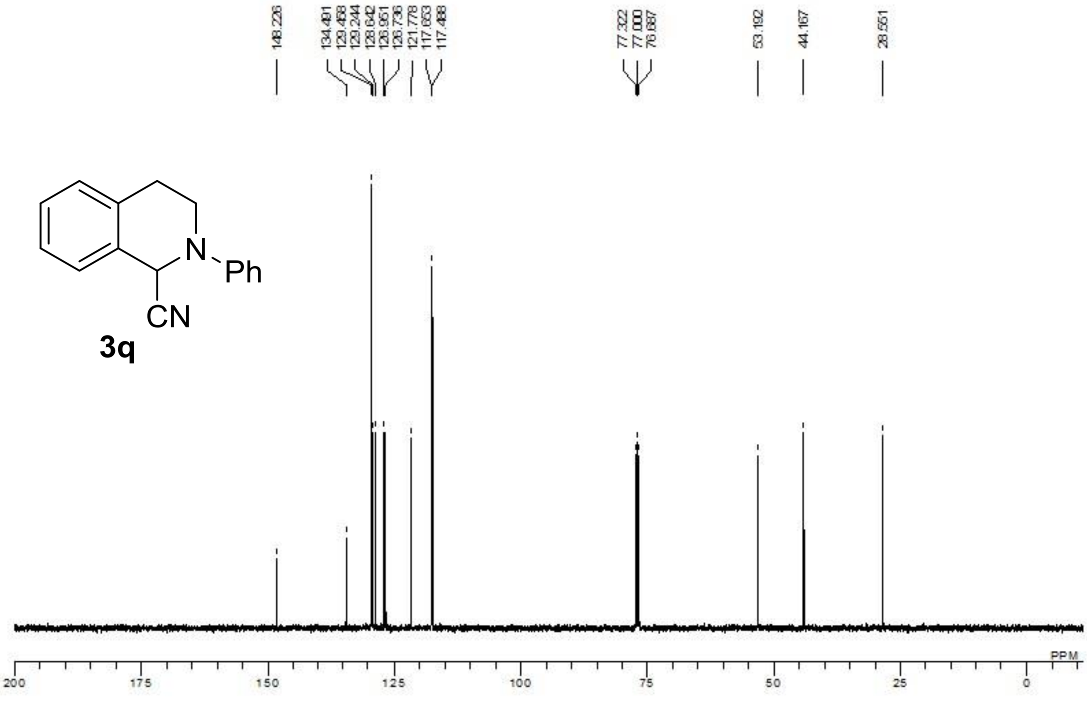
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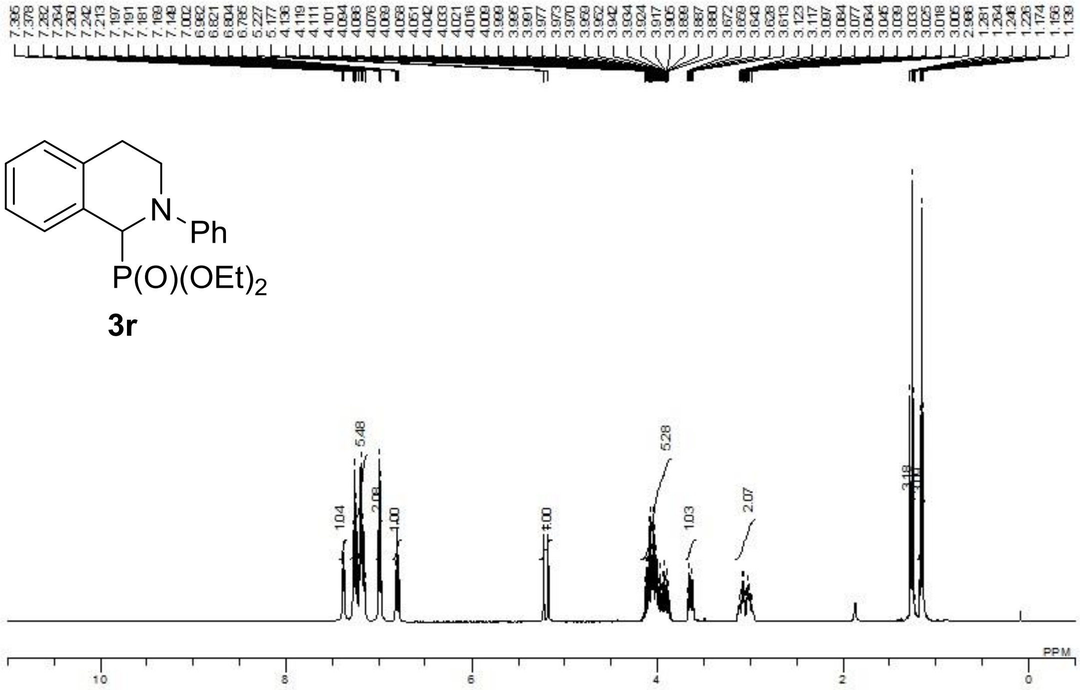
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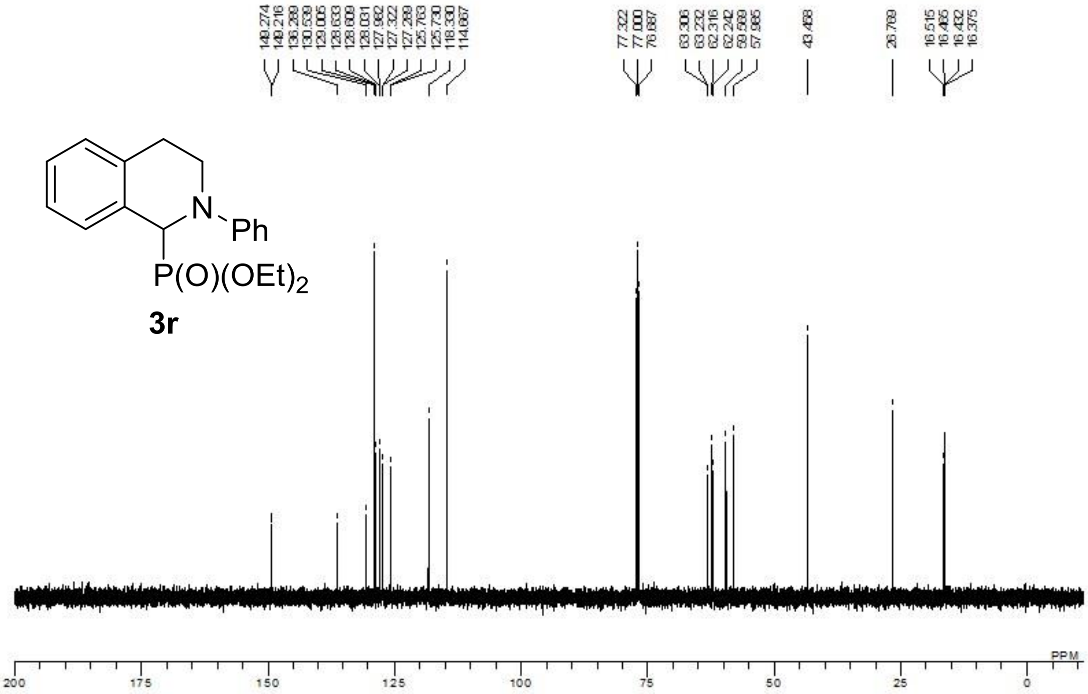
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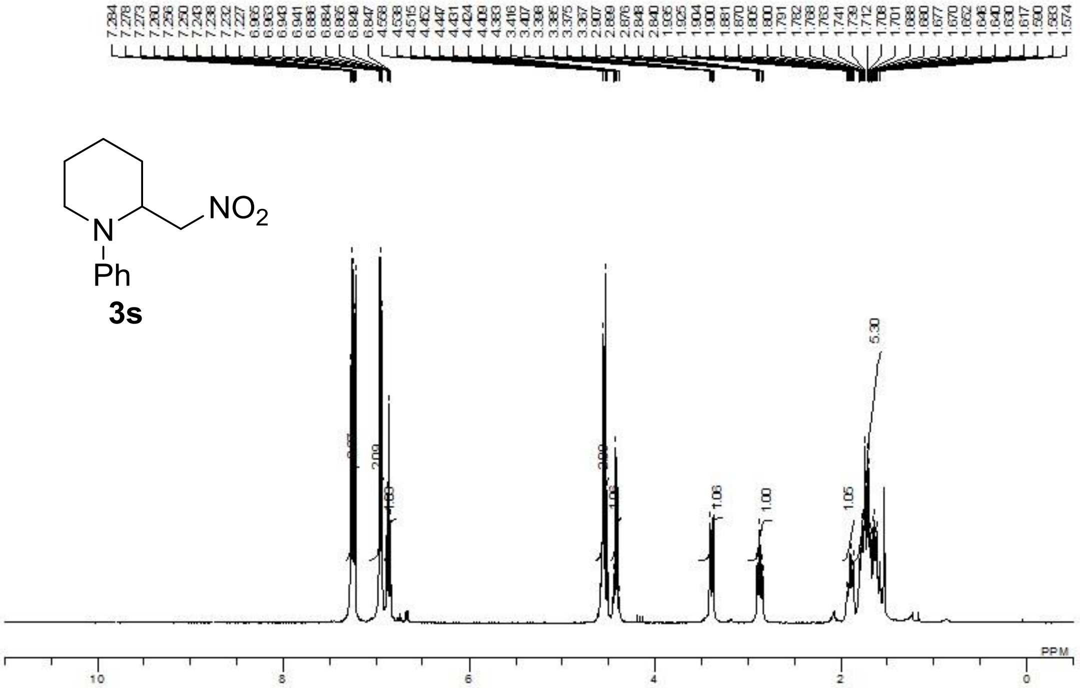
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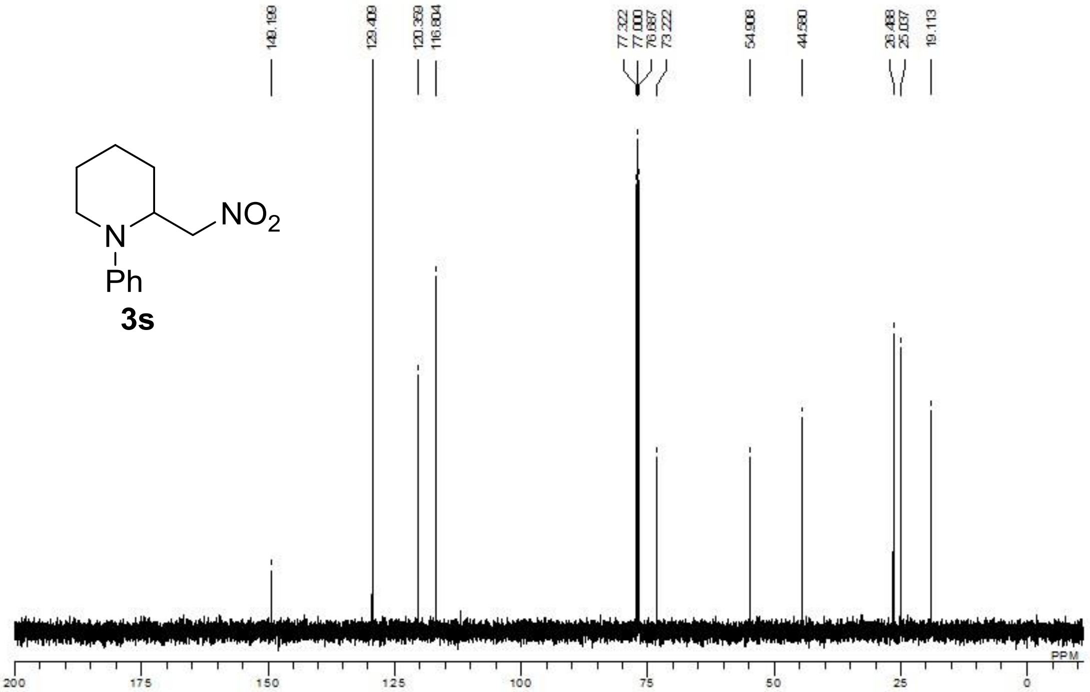
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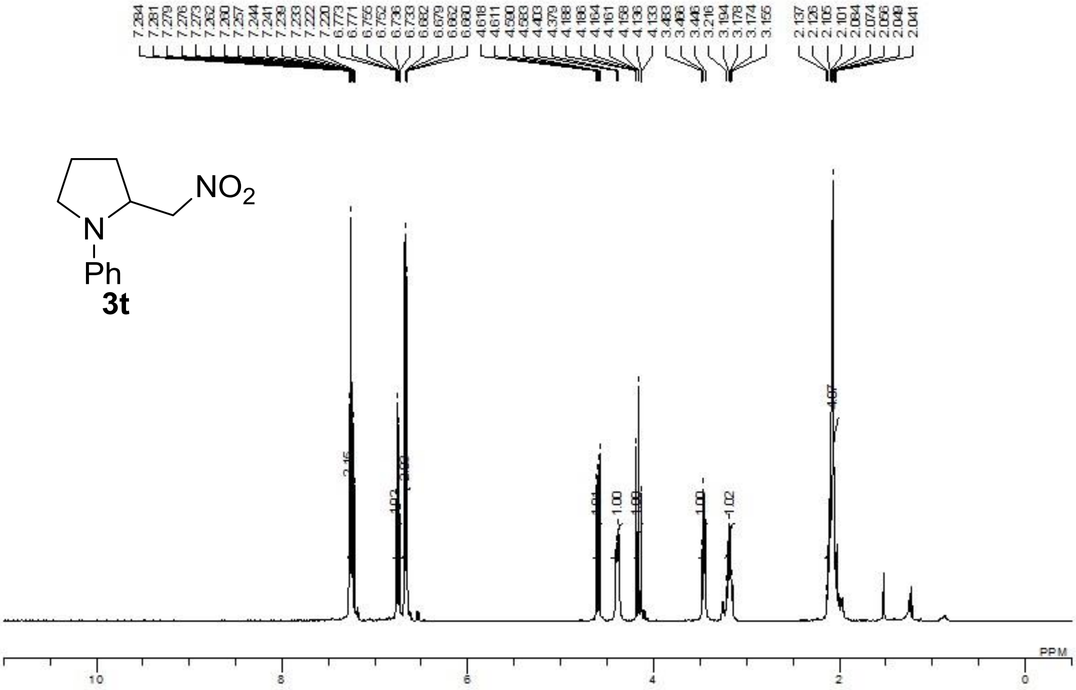
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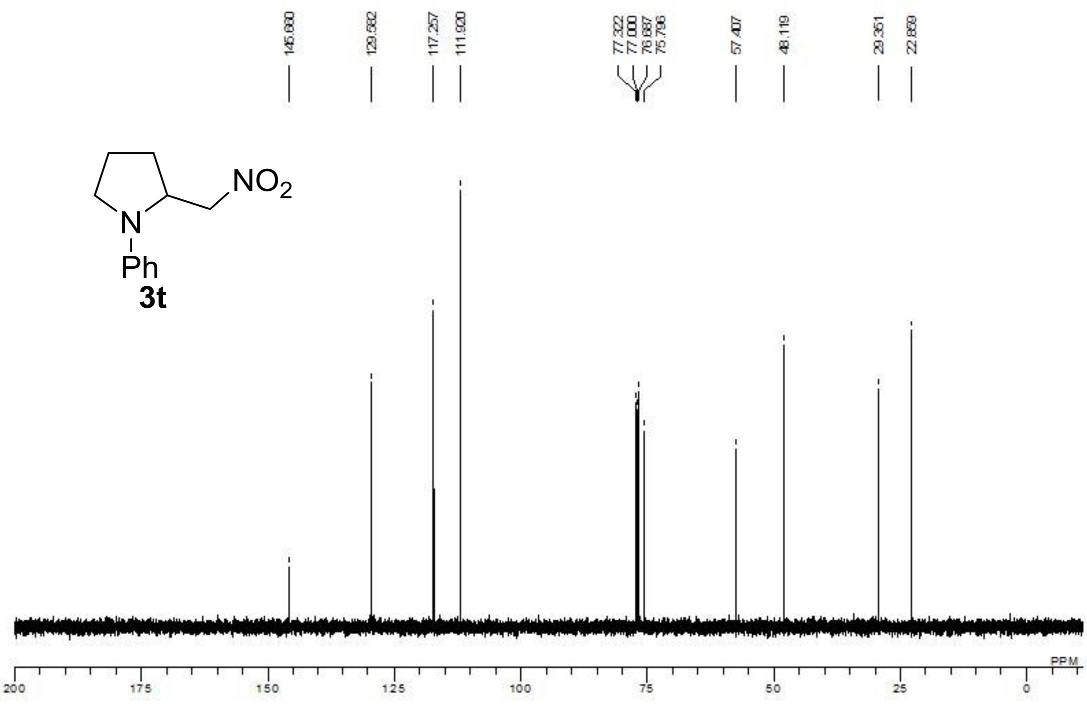
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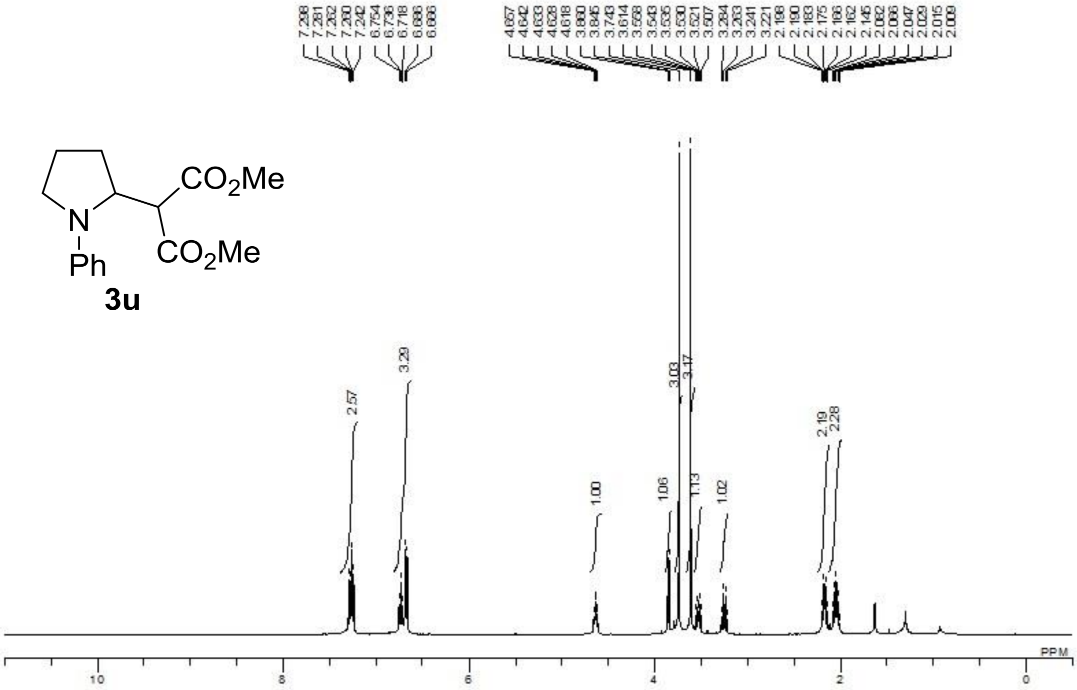
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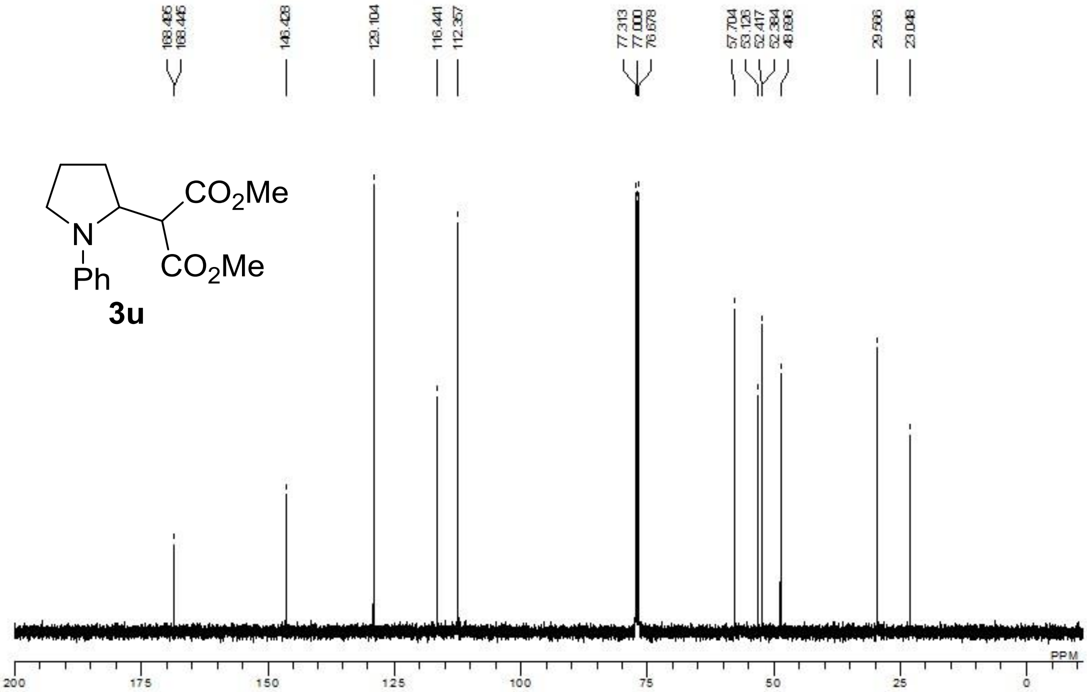
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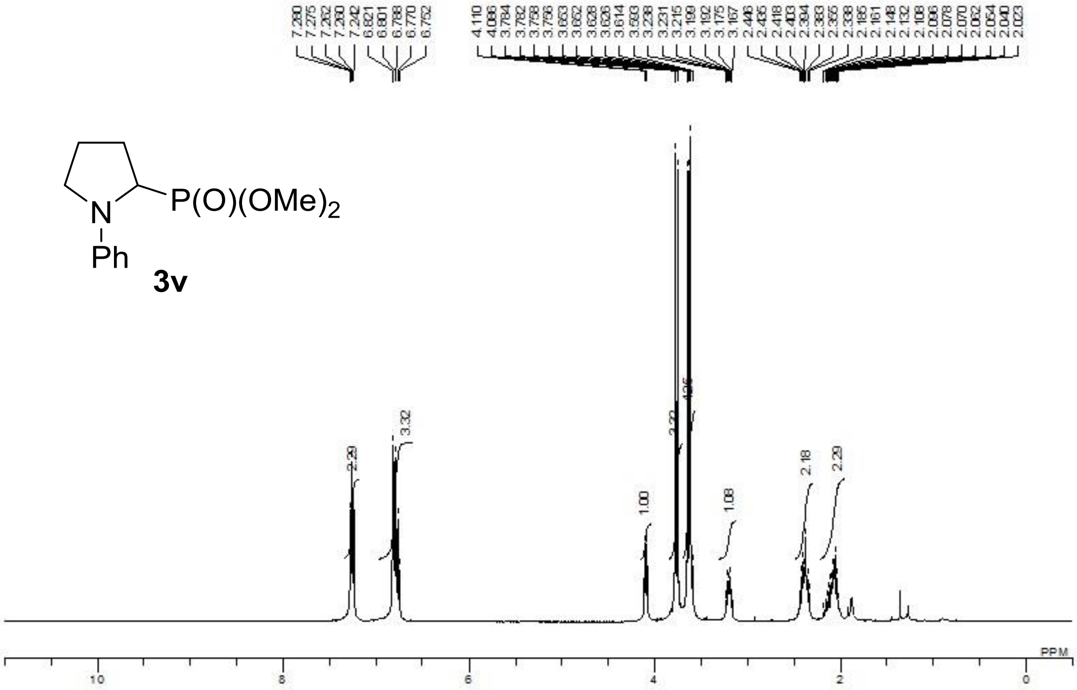
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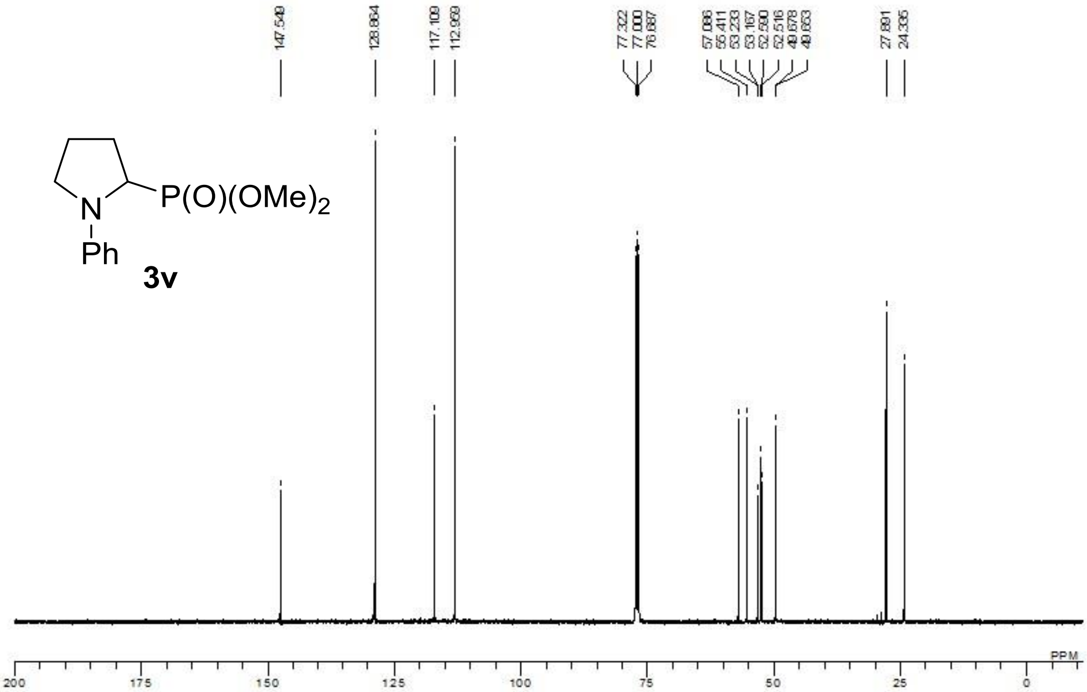
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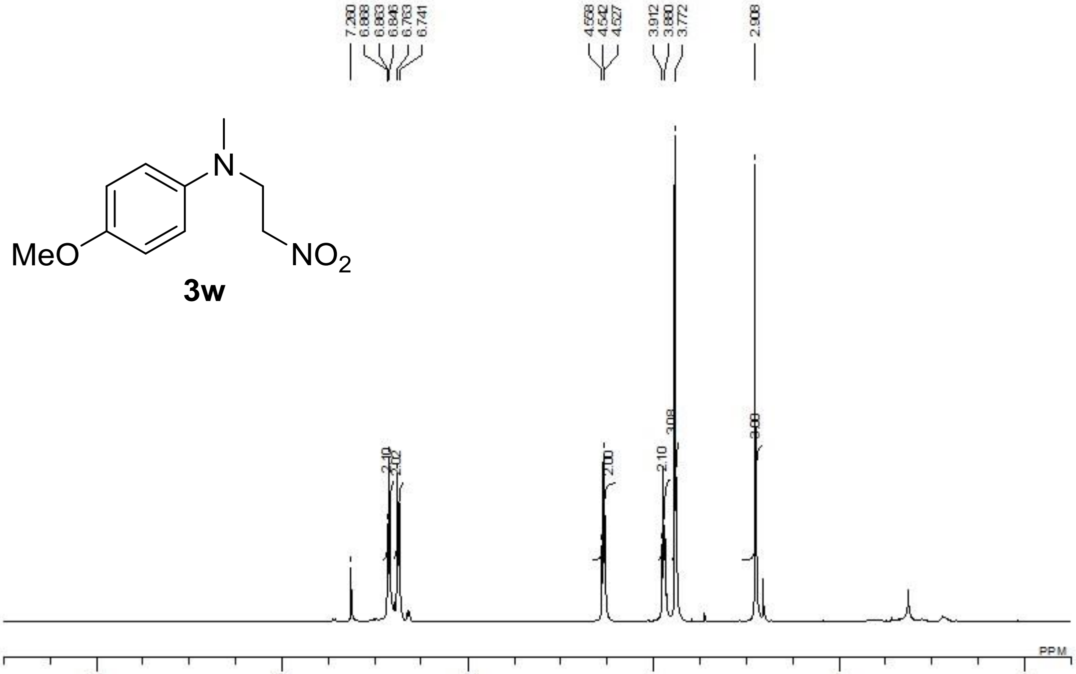
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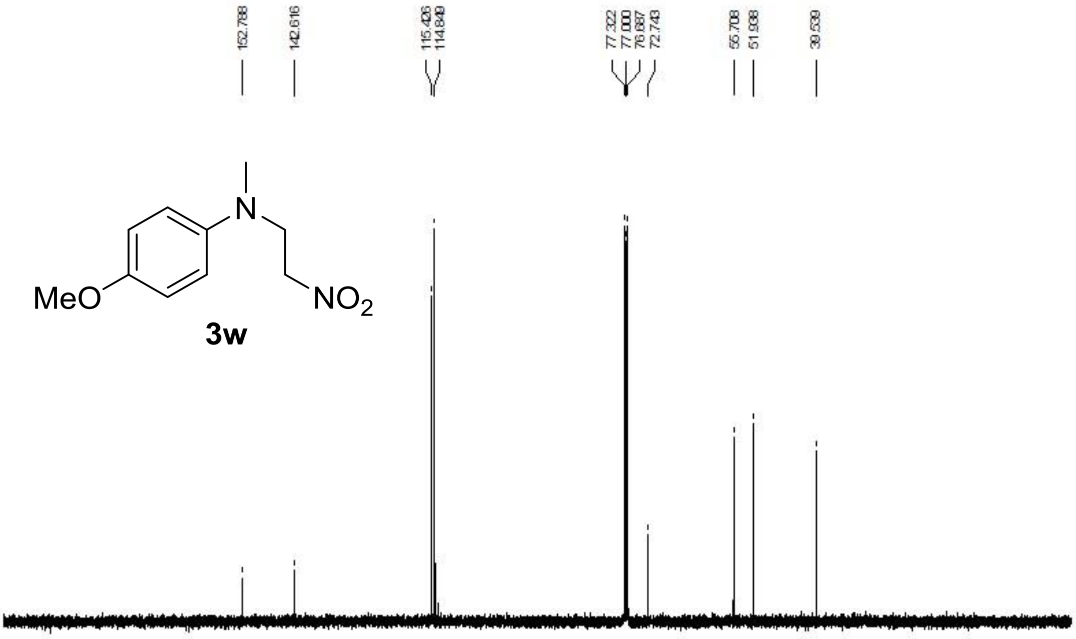
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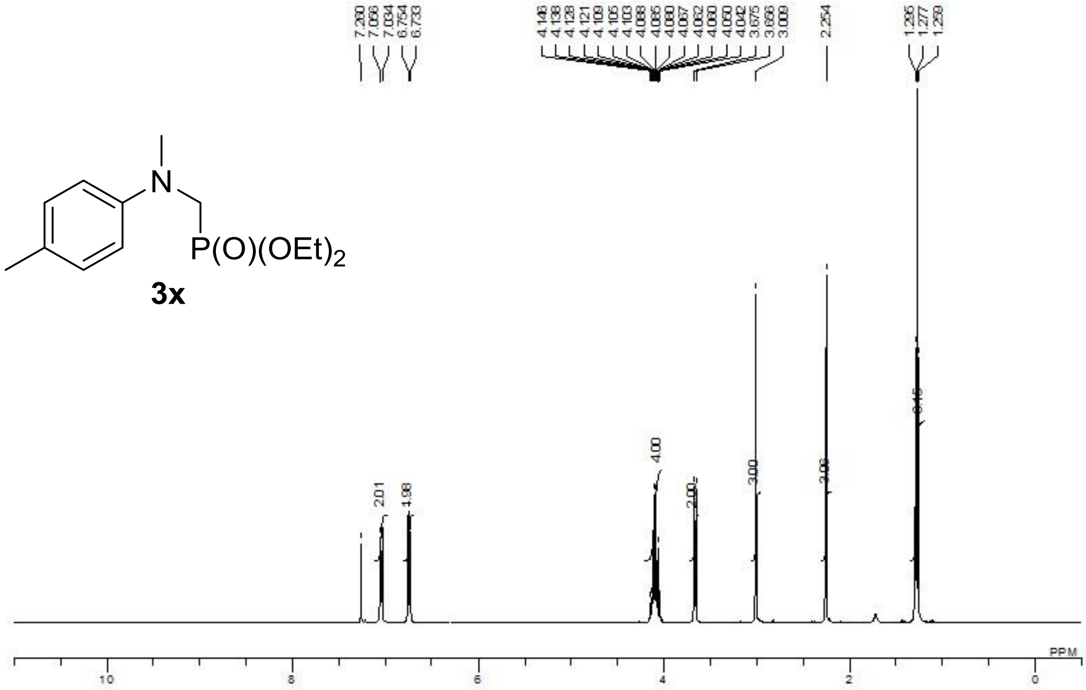
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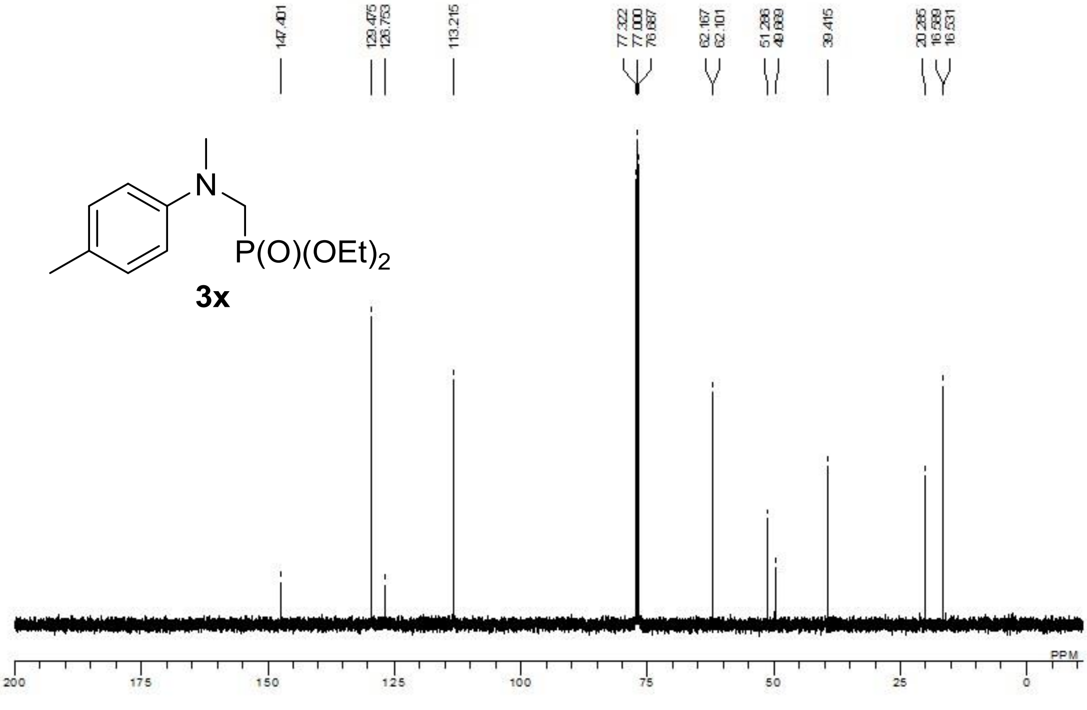
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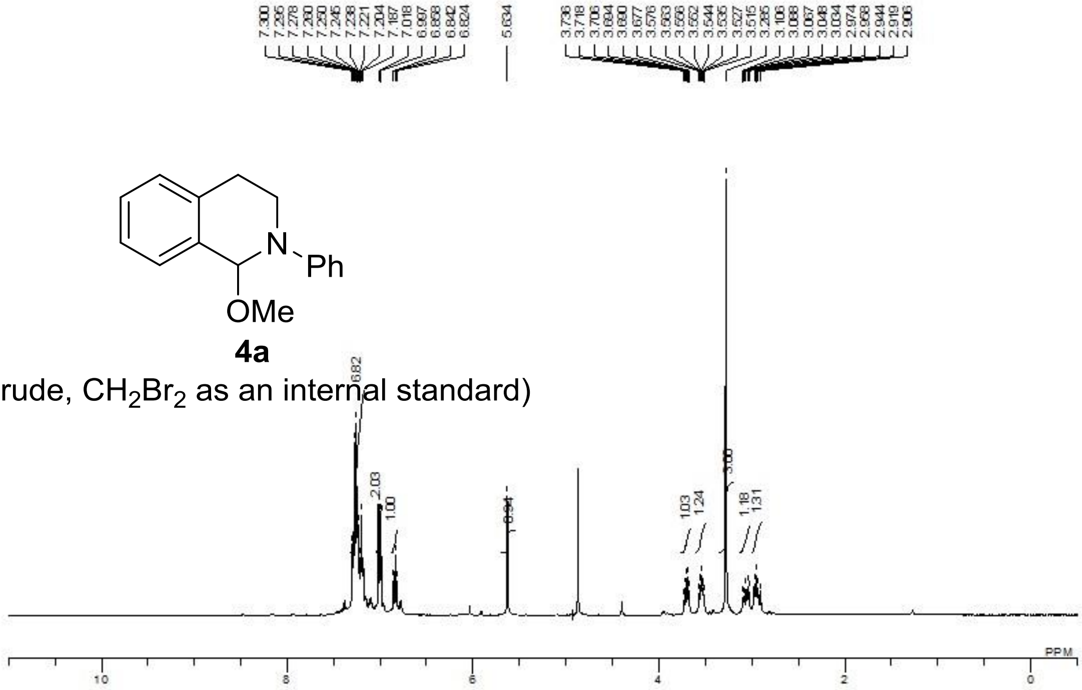
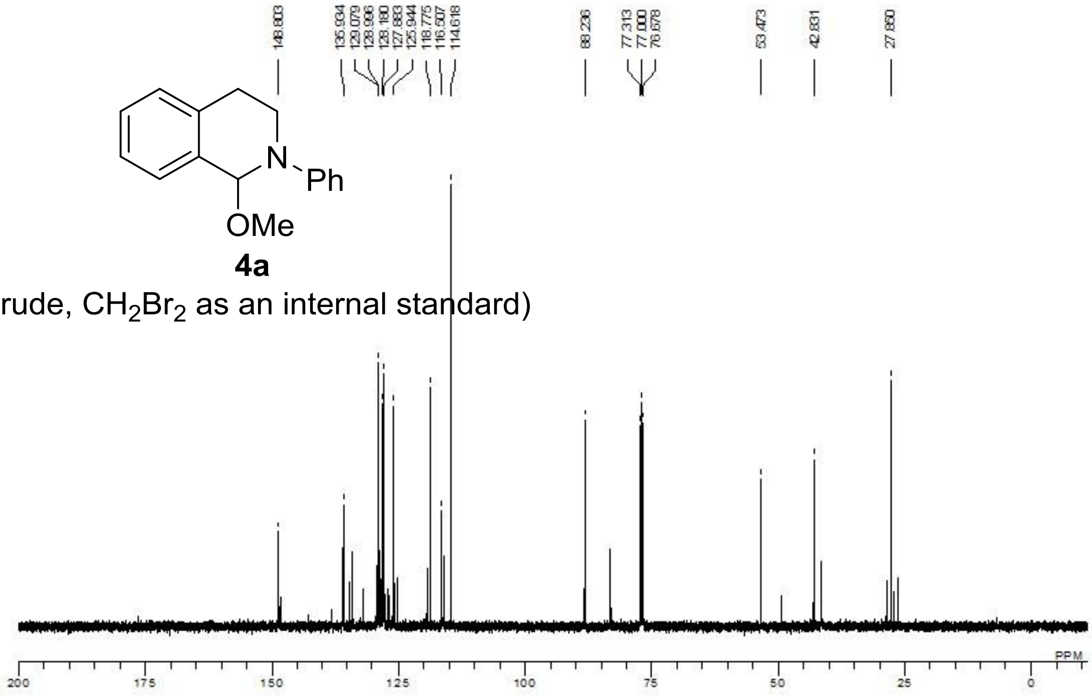


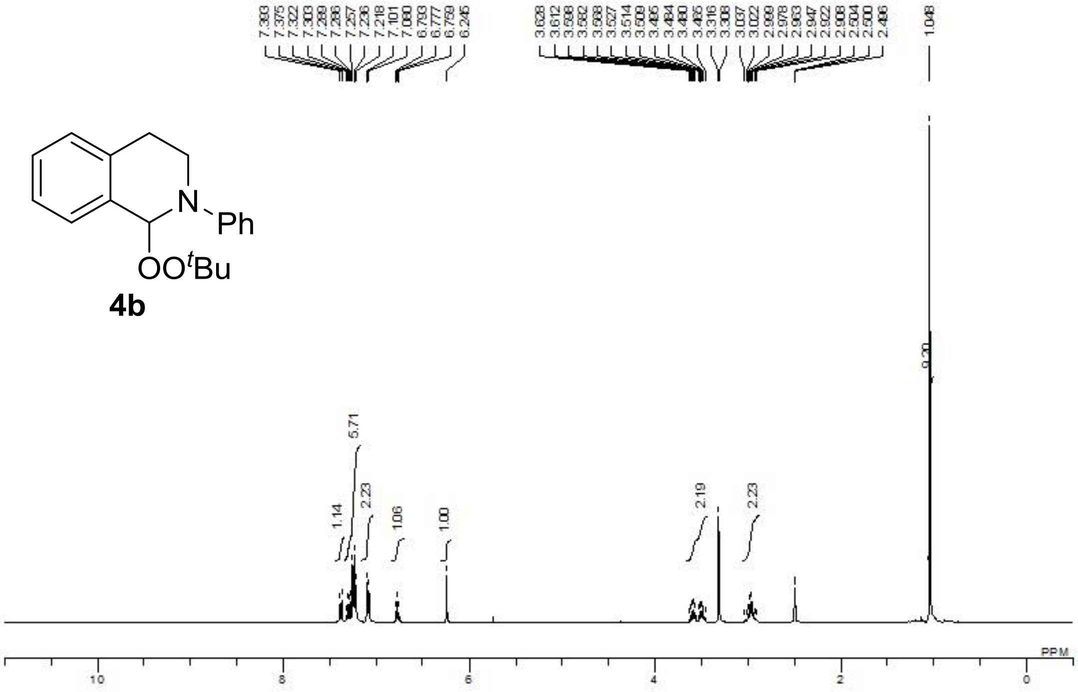
4a

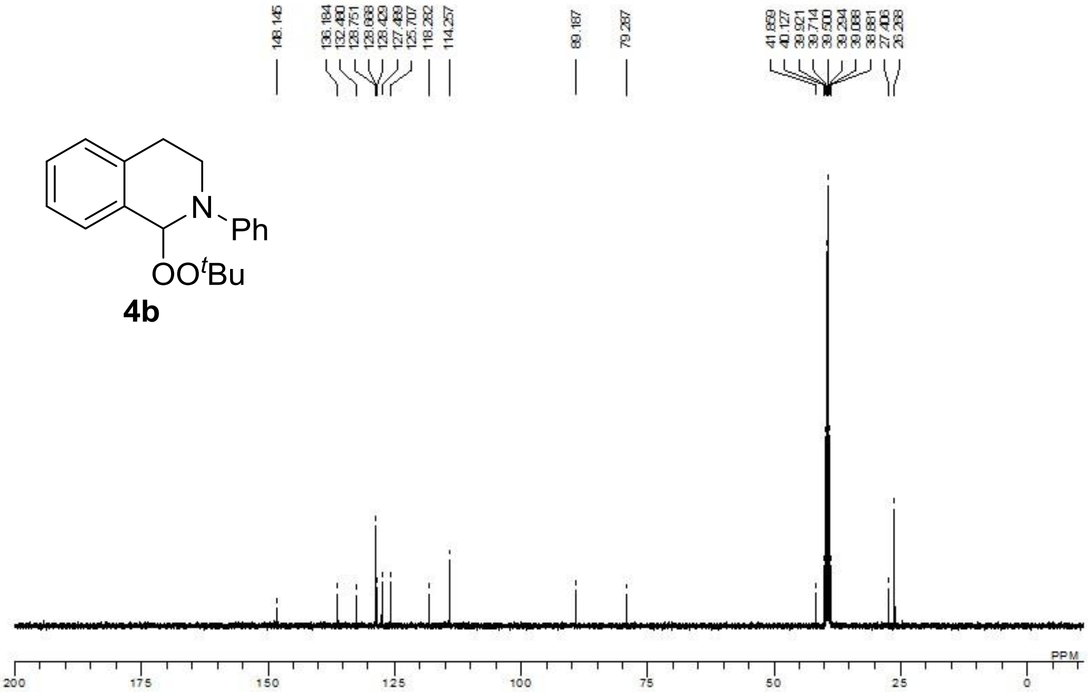
(crude, CH_2Br_2 as an internal standard)



4a

(crude, CH_2Br_2 as an internal standard)


4b
7.393
7.375
7.322
7.303
7.289
7.286
7.257
7.236
7.218
7.101
7.080
6.793
6.777
6.759
6.245
3.628
3.612
3.598
3.582
3.568
3.527
3.514
3.509
3.495
3.484
3.480
3.465
3.316
3.308
3.037
3.022
2.999
2.978
2.963
2.947
2.922
2.908
2.504
2.500
2.496
1.048
N
Ph
OO^{t}Bu
1.14
5.71
2.23
1.06
1.00
2.19
2.23
9.30
PPM
10
8
6
4
2
0


4b
148.145
136.184
132.480
128.751
128.683
128.429
127.489
125.707
118.282
114.257
89.187
79.287
41.859
40.127
39.921
39.714
39.500
39.294
39.088
38.881
27.406
26.208
N
Ph
OO^{t}Bu
PPM
200
175
150
125
100
75
50
25
0