

Supporting Information

(3+2) Cycloaddition of 2-alkoxynaphthalenes with azaoxyallyl cations: access to benzo[e]indolones

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1. General considerations:

^1H and ^{13}C NMR spectra were recorded with a 300 and 400 MHz spectrometer as solutions in CDCl_3 . Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to CDCl_3 ($\delta = 7.28$ and 7.18 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals includes: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublets, dq = doublet of quadruplet, ddd = doublet of doublet of doublets, td = triplet of doublet, and brs. = broad singlet. ^{13}C NMR spectra were recorded as solutions in CDCl_3 with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to CDCl_3 ($\delta = 77.16$ ppm) as an internal standard. The molecular fragments in High Resolution Mass Spectra (HRMS) are quoted as the relation between mass and charge (m/z). The routine monitoring of reactions was performed with silica gel pre-coated Al plate, which was analysed with iodine and/or UV light and ^1H NMR analysis of the crude reaction mixture. All reactions were executed with oven-dried glassware under nitrogen atmosphere.

2. List of α -halohydroxamate derivatives used in the study

General procedure A: for the synthesis of the alpha-haloamides to a suspension of the *O*-benzyloxyamine hydrochloride and triethylamine in CH_2Cl_2 (0.25 M) was added dropwise the alpha-haloacid halide at 0°C . The reaction mixture was stirred at this temperature until TLC analysis (1:3) ethyl acetate: hexane revealed complete consumption of starting material. The mixture was warmed to room temperature and quenched with water. The organic phase was washed 3x with water, dried over sodium sulfate, filtered and evaporated. Purification via a column chromatography (SiO_2 , 3:1, Hexane: EtOAc) provided the haloamides in 45-90 % yield as a colorless solid.

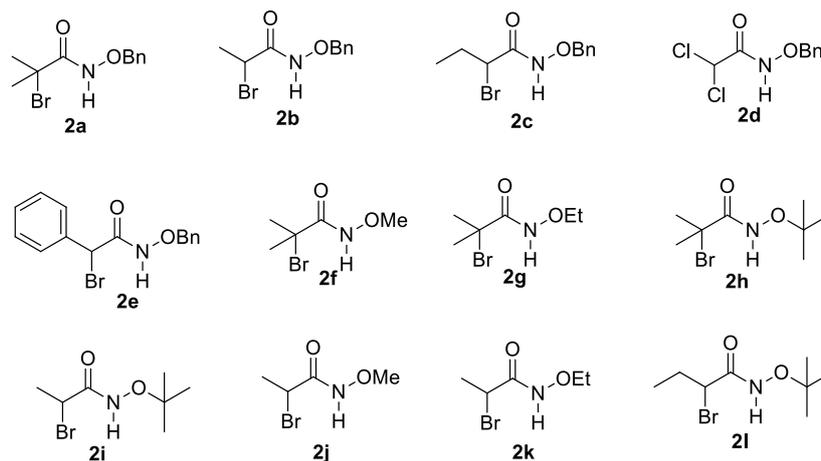
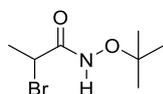


Figure 1: List of α -halo hydroxamate derivatives used in the study.

Among those following α -halo hydroxamate derivatives, i.e. **2a–2l** were prepared according to the literature procedure.¹

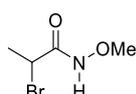
3. Experimental procedures and characterization data of unknown α -halo hydroxamate

2-bromo-*N*-(*tert*-butoxy)propanamide (**2i**):



Prepared in 75% yield (332.6 mg, 1.48 mmol., white solid) from the reaction of 2-bromo-2-methylpropanoyl bromide (500 mg, 1.98 mmol.) with *O*-(*tert*-Butyl)hydroxylamine hydrochloride (248.80 mg, 1.98 mmol.) via general procedure A. $R_f = 0.58$ (1:3, ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.16 (br s, 1H), 4.56 (q, $J = 6.6$ Hz, 1H), 1.75 (d, $J = 6.9$ Hz, 3H), 1.24 (s, 9H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 169.0, 83.0, 40.4, 26.3, 22.0 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_7\text{H}_{14}\text{BrNO}_2$ 224.0286, mass found 224.0287.

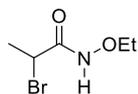
2-bromo-*N*-methoxypropanamide (**2j**):



Prepared in 70% yield (252.3 mg, 1.38 mmol, colourless oil) from the reaction of 2-bromo-2-methylpropanoyl bromide (500 mg, 1.98 mmol) with *O*-methylhydroxylamine hydrochloride (165.36 mg, 1.98 mmol) via general procedure A. $R_f = 0.58$ (1:3, ethyl acetate: hexane); ^1H

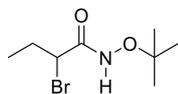
NMR (300 MHz, CDCl₃): δ 9.60–9.48 (br d, 1H), 4.39 (q, J = 6.9Hz, 1H), 3.81 (s, 3H), 1.87 (d, J = 6.9 Hz, 3H) ppm; **¹³C NMR** (75MHz, CDCl₃) δ 167.3, 64.3, 40.7, 22.3 ppm; **HRMS (ESI)** m/z: [M+H]⁺ calculated for C₄H₉BrNO₂ 181.9811, mass found 181.9823.

2-bromo-*N*-ethoxypropanamide (2k):



Prepared in 80% yield (310.2 mg, 1.60 mmol., white solid) from the reaction of 2-bromo-2-methylpropanoyl bromide (500 mg, 1.98 mmol.) with *O*-ethylhydroxylamine hydrochloride (193.12 mg, 1.98 mmol.) via general procedure A. R_f = 0.58 (1:3, ethyl acetate: hexane); **¹H NMR** (300 MHz, CDCl₃): δ 1.88 (br s, 1H), 4.46 (q, J = 6.6 Hz, 1H), 3.94 (q, J = 7.2 Hz, 2H), 1.75 (d, J = 8.7 Hz, 3H), 1.21 (t, J = 6.9 Hz, 3H) ppm; **¹³C NMR** (75MHz, CDCl₃) δ 168.1, 71.9, 39.9, 21.8, 13.3 ppm; **HRMS (ESI)** m/z: [M+H]⁺ calculated for C₅H₁₁BrNO₂ 195.9968, mass found 195.9945.

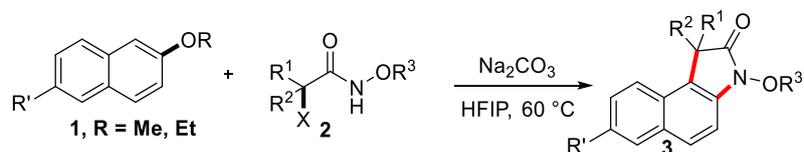
2-bromo-*N*-(*tert*-butoxy)butanamide (2l):



Prepared in 60% yield (310.0 mg, 1.34 mmol., white solid) from the reaction of 2-bromobutyryl bromide (500 mg, 2.17 mmol.) with *O*-(*tert*-Butyl)hydroxylamine hydrochloride (272.72 mg, 2.17 mmol.) via general procedure A. R_f = 0.58 (1:3 ethyl acetate: hexane); **¹H NMR** (300 MHz, CDCl₃): δ 9.99 (br s, 1H), 4.33 (t, J = 7.2 Hz, 1H), 2.16–1.90 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H) ppm; **¹³C NMR** (75MHz, CDCl₃) δ 168.2, 82.9, 47.7, 28.6, 26.3, 11.8 ppm; **HRMS (ESI)** m/z:[M+H]⁺ calculated for C₈H₁₇BrNO₂ 238.0438, mass found 238.0428.

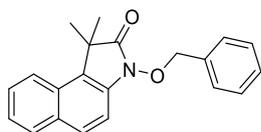
4. Experimental procedures and characterization data of all products

General Procedure B:



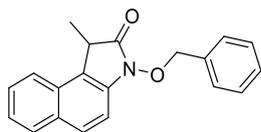
To a solution of 2-alkoxy naphthalene (**1**, 1 equiv.) and α -halo hydroxamate (**2**, 2 equiv.) in $(\text{CF}_3)_2\text{CHOH}$ (0.4 M), was added sodium carbonate (Na_2CO_3 , 4.2 equiv). The reaction mixture was allowed to stirring for 12 h at 60 °C. The reaction was monitored by TLC and stopped and allowed to cool at room temperature and extracted with ethyl acetate (3 times) and the whole solution washed with brine solution. The solution was then concentrated under rotary evaporation and purified by using column chromatography (ethyl acetate/hexane) to afforded product (**3**).

3-(benzyloxy)-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (3a):



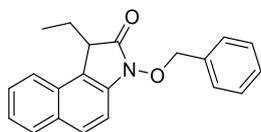
Following the general procedure **B**, reaction between 2-methoxynaphthalene (**1a**) or 2-ethoxynaphthalene (**1b**) (0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding product **3a**, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as colourless oil in 83% (from **1a**, 131.7 mg, 0.41 mmol.) and 81% (from **1b**, 128.5 mg, 0.5 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.92 – 7.84 (m, 2H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.63 – 7.44 (m, 3H), 7.44 – 7.32 (m, 4H), 7.15 (d, $J = 8.6$ Hz, 1H), 5.30 (s, 2H), 1.68 (s, 6H). $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 177.1, 137.7, 134.1, 130.8, 130.1, 129.8, 129.3, 129.1, 129.0, 128.6, 127.0, 123.6, 123.0, 122.1, 109.0, 78.1, 44.5, 23.7 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{20}\text{NO}_2$ 318.1489, mass found 318.1494.

3-(benzyloxy)-1-methyl-1,3-dihydro-2H-benzo[e]indol-2-one (3b):



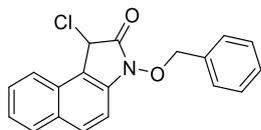
Following the general procedure **B**, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2b**, 1.0 mmol, 2 equiv.) afforded the corresponding **3b** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 81% (from **1a**, 122.8 mg, 0.40 mmol.) and 80% (from **1b**, 121.3 mg, 0.40 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane) ; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.84 (d, $J = 8.5$ Hz, 1H), 7.79–7.75 (m, 2H), 7.56–7.50 (m, 3H), 7.41–7.35 (m, 4H), 7.10 (d, $J = 8.6$ Hz, 1H), 5.31 (d, $J = 12.0$ Hz, 1H), 5.26 (d, $J = 12.0$ Hz, 1H), 3.81 (q, $J = 7.6$ Hz, 1H), 1.71 (d, $J = 7.6$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 174.6, 139.0, 134.2, 130.4, 130.0, 129.4, 129.4, 129.3, 129.0, 128.6, 127.2, 123.9, 122.1, 119.0, 109.0, 78.3, 39.1, 16.5 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{20}\text{H}_{17}\text{NO}_2\text{Na}$ 326.1157, mass found 326.1166.

3-(benzyloxy)-1-ethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3c**):



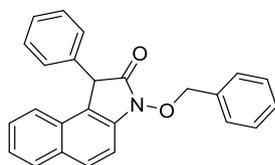
Following the general procedure **B**, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2c**, 1.0 mmol., 2 equiv.) afforded the corresponding **3c** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 78% (from **1a**, 123.7 mg, 0.39 mmol.) and 74% (from **1b**, 117.4 mg, 0.37 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane) ; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.85 (d, $J = 8.1$ Hz, 1H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.65 – 7.49 (m, 3H), 7.45 – 7.33 (m, 4H), 7.12 (d, $J = 8.6$ Hz, 1H), 5.30 (d, $J = 9.0$ Hz, 1H), 5.26 (d, $J = 9.0$ Hz, 1H), 3.88 (q, $J = 3.8$ Hz, 1H), 2.56 – 2.10 (m, 2H), 0.77 (t, $J = 7.4$ Hz, 3H).ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 173.9, 139.8, 134.3, 130.4, 129.9, 129.6, 129.5, 129.3, 129.1, 128.7, 127.2, 123.9, 122.0, 116.9, 108.8, 78.4, 45.0, 23.8, 9.0 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{20}\text{NO}_2$ 318.1489, mass found 318.1499.

3-(benzyloxy)-1-chloro-1,3-dihydro-2*H*-benzo[*e*]indol-2-one (3d):



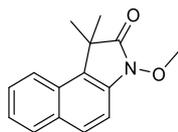
Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2d**, 1.0 mmol., 2 equiv.) afforded the corresponding **3d** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 74% (from **1a**, 119.7 mg, 0.37 mmol.) and 80% (from **1b**, 129.5 mg, 0.40 mmol.) yield respectively. R_f = 0.30 (0.5:9.5 ethyl acetate: hexane) ; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.95 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 9.0 Hz, 2H), 7.62–7.53 (m, 3H), 7.46–7.78 (m, 4H), 7.15 (d, J = 8.6 Hz, 1H), 5.44 (s, 1H), 5.29 (s, 2H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 168.6, 140.2, 133.8, 132.0, 130.6, 130.1, 129.5, 129.4, 129.2, 128.8, 128.2, 124.7, 122.1, 113.6, 109.0, 78.6, 49.5 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{Cl}$ 324.0786, mass found 324.0787.

3-(benzyloxy)-1-phenyl-1,3-dihydro-2*H*-benzo[*e*]indol-2-one (3e):



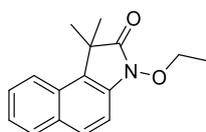
Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2e**, 1.0 mmol., 2 equiv.) afforded the corresponding **3e** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 88% (from **1a**, 160.7 mg, 0.44 mmol.) and 88% (from **1b**, 160.7 mg, 0.44 mmol.) yield respectively. R_f = 0.25 (0.5:9.5 ethyl acetate: hexane) ; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.83 (d, J = 9.0 Hz, 2H), 7.53–7.50 (m, 2H), 7.38–7.32 (m, 9H), 7.20–7.14 (m, 3H), 5.30 (d, J = 12.0 Hz, 1H), 5.25 (d, J = 12.0 Hz, 1H), 4.89 (s, 1H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 172.1, 140.2, 135.6, 134.2, 130.6, 130.1, 129.8, 129.4, 129.3, 129.2, 129.0, 128.6, 128.4, 127.8, 127.3, 124.0, 122.7, 116.6, 109.0, 78.2, 50.3 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{20}\text{NO}_2$ 366.1489, mass found 366.1499.

3-methoxy-1,1-dimethyl-1,3-dihydro-2*H*-benzo[*e*]indol-2-one (3f):



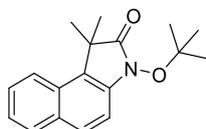
Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2f**, 1.0 mmol., 2 equiv.) afforded the corresponding **3e** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 65% (from **1a**, 78.4 mg, 0.32 mmol.) and 63% (from **1b**, 74.7 mg, 0.31 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 EtOAc: Hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.95–7.88 (m, 3H), 7.57–7.52 (m, 1H), 7.44–7.35 (m, 2H), 4.11 (s, 1H), 1.69 (s, 6H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 176.6, 136.9, 130.9, 129.8, 129.3, 129.3, 127.1, 123.7, 123.4, 122.2, 108.6, 63.8, 44.6, 23.7 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{Na}$ 264.1000, mass found 264.1000.

3-ethoxy-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3g**):



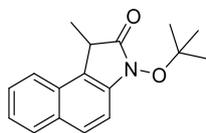
Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2g**, 1.0 mmol., 2 equiv.) afforded the corresponding **3g** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 60% (from **1a**, 76.5 mg, 0.30 mmol.) and 45% (from **1b**, 76.5 mg, 0.30 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.94–7.86 (m, 3H), 7.56–7.51 (m, 1H), 7.42–7.33 (m, 2H), 4.35 (q, $J = 7.2$ Hz, 2H), 1.6 (s, 6H), 1.46 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 177.0, 137.7, 130.9, 129.8, 129.3, 127.1, 123.7, 123.4, 122.2, 108.9, 72.0, 44.5, 23.7, 13.7 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{18}\text{NO}_2$ 256.1338, mass found 256.1331.

3-(*tert*-butoxy)-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3h**):



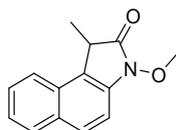
Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol, 1 equiv.) and α -halo hydroxamate (**2h**, 1.0 mmol., 2 equiv.) afforded the corresponding **3h** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 67% (from **1a**, 94.9 mg, 0.33 mmol.) and 62% (from **1b**, 87.8 mg, 0.31 mmol.) yield respectively. R_f = 0.25 (0.5:9.5 ethyl acetate:hexane) ; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.95–7.82 (m, 3H), 7.56–7.50 (m, 1H), 7.41–7.36 (m, 2H), 1.70 (s, 6H), 1.50 (s, 9H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 180.3, 140.1, 130.8, 129.7, 129.1, 128.8, 127.01, 123.7, 123.6, 122.2, 110.4, 86.2, 44.3, 27.8, 24.0 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{22}\text{NO}_2$ 284.1646, mass found 284.1647.

3-(*tert*-butoxy)-1-methyl-1,3-dihydro-2*H*-benzo[*e*]indol-2-one (**3i**):



Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2i**, 1.0 mmol., 2 equiv.) afforded the corresponding **3i** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 69% (from **1a**, 92.9 mg, 0.34 mmol.) and 66% (from **1b**, 88.8 mg, 0.33 mmol.) yield respectively. R_f = 0.25 (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.88–7.78 (m, 3H), 7.56–7.50 (m, 1H), 7.42–7.33 (m, 2H), 3.86 (q, J = 7.8 Hz, 1H), 1.73 (d, J = 7.5 Hz, 3H), 1.51 (s, 9H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 177.9, 141.4, 130.4, 129.4, 128.8, 127.2, 123.8, 122.2, 119.7, 110.4, 86.1, 39.0, 27.7, 16.8 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{NO}_2$ 270.1489, mass found 270.1494.

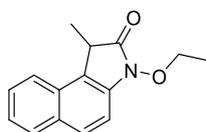
3-methoxy-1-methyl-1,3-dihydro-2*H*-benzo[*e*]indol-2-one (**3j**):



Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2j**, 1.0 mmol., 2 equiv.) afforded the corresponding **3j**

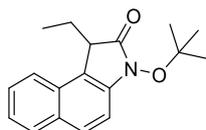
product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 62% (from **1a**, 70.4 mg, 0.31 mmol.) and 60% (from **1b**, 68.17 mg, 0.30 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.89 (d, $J = 8.5$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 15.8$ Hz, 1H), 7.33 (d, $J = 8.6$ Hz, 1H), 4.11 (s, 3H), 3.82 (q, $J = 7.5$ Hz, 1H), 1.73 (d, $J = 7.6$ Hz, 3H).ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 174.1, 138.1, 130.6, 129.6, 129.5, 129.3, 127.3, 124.0, 122.1, 119.3, 108.6, 63.8, 39.2, 16.3 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{14}\text{NO}_2$ 228.1019, mass found 228.1008.

3-ethoxy-1-methyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3k**):



Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2k**, 1.0 mmol., 2 equiv.) afforded the corresponding **3k** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 71% (from **1a**, 85.6 mg, 0.35 mmol.) and 65% (from **1b**, 78.4 mg, 0.32 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.88 (d, $J = 8.7$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.56–7.51 (m, 1H), 7.42–7.37 (m, 1H), 7.31 (d, $J = 8.7$, 1H), 4.36 (q, $J = 6.9$ Hz, 2H), 3.82 (q, $J = 7.8$ Hz, 1H), 1.73 (d, $J = 7.5$ Hz, 3H), 1.47 (t, $J = 6.9$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 174.5, 138.9, 130.5, 129.6, 129.5, 129.2, 127.3, 123.9, 122.1, 119.3, 108.8, 72.1, 39.16, 16.4, 13.7 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{16}\text{NO}_2$ 242.1176, mass found 242.1174.

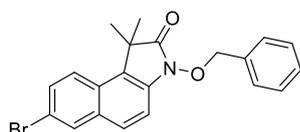
3-(tert-butoxy)-1-ethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3l**):



Following the general procedure, reaction between 2-alkoxynaphthalene (**1a/1b**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2l**, 1.0 mmol., 2 equiv.) afforded the corresponding **3l**

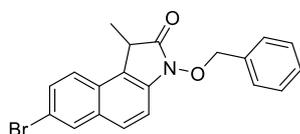
product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 78% (from **1a**, 110.5 mg, 0.39 mmol.) and 75% (from **1b**, 106.2 mg, 0.37 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.88–7.77 (m, 3H), 7.55–7.50 (m, 1H), 7.42–7.32 (m, 2H), 3.92 (q, $J = 3.9$ Hz, 1H), 2.47–2.28 (m, 2H), 1.51 (s, 9H), 0.79 (t, $J = 7.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 177.2, 142.4, 130.3, 129.5, 129.4, 128.8, 127.1, 123.8, 122.1, 117.6, 110.3, 85.9, 45.0, 27.8, 23.9, 9.23 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{22}\text{NO}_2$ 284.1686, mass found 284.1687.

3-(benzyloxy)-7-bromo-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (3m):



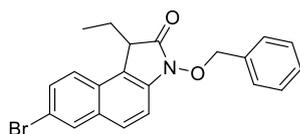
Following the general procedure, reaction between 6-bromo-2-methoxynaphthalene (**1c**) or 6-bromo-2-ethoxynaphthalene (**1d**), (0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding **3m** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white sticky liquid in 55% (from **1c**, 108.9 mg, 0.27 mmol.) and 51% (from **1d**, 101.0 mg, 0.26 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.00 (s, 1H), 7.76 (d, $J = 9.0$ Hz, 1H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.59 – 7.48 (m, 3H), 7.39 – 7.34 (m, 3H), 7.13 (d, $J = 8.6$ Hz, 1H), 5.29 (s, 2H), 1.64 (s, 6H).ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 176.8, 138.2, 134.0, 131.8, 131.6, 130.3, 130.1, 129.4, 128.6, 128.1, 127.5, 123.7, 123.3, 117.1, 110.0, 78.2, 44.4, 23.8 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{19}\text{BrNO}_2$ 396.0594, mass found 396.0583.

3-(benzyloxy)-7-bromo-1-methyl-1,3-dihydro-2H-benzo[e]indol-2-one (3n):



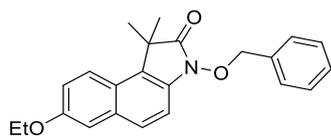
Following the general procedure, reaction between 6-bromo-2-alkoxynaphthalene (**1c/1d**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2b**, 1.0 mmol., 2 equiv.) afforded the corresponding **3n** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 71% (from **1c**, 135.7 mg, 0.35 mmol.) and 68% (from **1d**, 124.2 mg, 0.32 mmol.) yield respectively. R_f = 0.25 (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, Chloroform- d) δ 7.99 (d, J = 2.0 Hz, 1H), 7.65 (d, J = 8.9 Hz, 2H), 7.59 – 7.49 (m, 3H), 7.40 – 7.35 (m, 3H), 7.08 (d, J = 8.6 Hz, 1H), 5.29 (d, J = 9.0 Hz, 1H), 5.24 (d, J = 9.0 Hz, 1H), 3.79 (q, J = 7.6 Hz, 1H), 1.69 (d, J = 7.6 Hz, 3H); $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 174.3, 139.5, 134.1, 131.5, 131.3, 130.5, 130.0, 129.4, 128.7, 128.2, 127.8, 123.8, 119.2, 117.4, 110.0, 78.3, 39.0, 16.5 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{17}\text{BrNO}_2$ 382.0438, mass found 382.0435.

3-(benzyloxy)-7-bromo-1-ethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3o**):



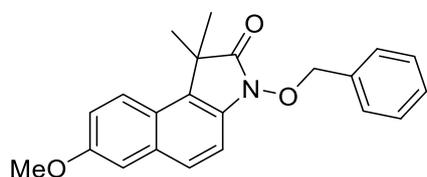
Following the general procedure, reaction between 6-bromo-2-alkoxynaphthalene (**1c/1d**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2c**, 1.0 mmol., 2 equiv.) afforded the corresponding **3o** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white solid in 73% (from **1c**, 144.6 mg, 0.36 mmol.) and 73% (from **1c**, 144.6 mg, 0.36 mmol.) yield respectively. R_f = 0.25 (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, Chloroform- d) δ 7.99 (d, J = 2.0 Hz, 1H), 7.68– 7.63 (m, 2H), 7.59 – 7.53 (m, 3H), 7.41–7.37 (m, 3H), 7.09 (d, J = 8.7 Hz, 1H), 5.28 (d, J = 9.0 Hz, 1H), 5.24 (d, J = 9.0 Hz, 1H), 3.87 (q, J = 3.8 Hz, 1H), 2.60 – 2.16 (m, 2H), 0.74 (t, J = 7.4 Hz, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 173.6, 140.3, 134.2, 131.5, 131.4, 130.5, 129.9, 129.3, 128.7, 128.2, 128.0, 123.7, 117.4, 117.1, 109.8, 78.5, 44.9, 23.8, 9.0 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{19}\text{BrNO}_2$ 396.0594, mass found 396.0572.

3-(benzyloxy)-7-ethoxy-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3p**):



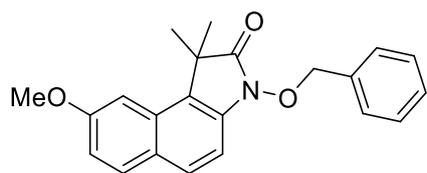
Following the general procedure, reaction between 2-ethoxy-6-methoxynaphthalene (**1e**, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding **3m** product, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as white sticky liquid in 45% (81.3 mg, 0.22 mmol.) yield. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.71 (d, $J = 9$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.45–7.41 (m, 2H), 7.28–7.26 (m, 3H), 7.12 (dd, $J = 2.4, 9.0$ Hz, 1H), 7.05 (d, $J = 2.4$ Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 5.18 (s, 2H), 4.05 (q, $J = 6.9$ Hz, 2H), 1.52 (s, 6H), 1.40 (t, $J = 6.9$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 176.8, 155.1, 135.8, 134.2, 132.0, 130.0, 129.2, 128.6, 127.4, 124.6, 123.6, 123.5, 120.4, 109.3, 108.3, 78.0, 63.5, 44.5, 23.8, 14.8 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{24}\text{NO}_3$ 362.1751, mass found 362.1750.

3-(benzyloxy)-7-methoxy-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**3q**):



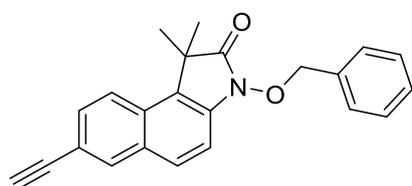
Following the general procedure **B**, reaction between 2,6-dimethoxynaphthalene (**1f**) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding product **3q**, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as colourless oil in 45% (78.1 mg, 0.22 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 12$ Hz, 1H), 7.64 (d, $J = 8$ Hz, 1H), 7.54–7.52 (m, 2H), 7.38–7.36 (m, 3H), 7.23–7.16 (m, 2H), 7.10 (d, $J = 8$ Hz, 1H) 5.28 (s, 2H), 3.92 (s, 3H), 1.64 (s, 6H) ppm; $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ 176.8, 155.8, 135.9, 134.2, 131.9, 130.0, 129.3, 128.6, 127.4, 124.6, 123.6, 123.6, 120.1, 109.4, 107.4, 78.0, 55.3, 44.5, 23.8 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{23}\text{NO}_3$ 348.1595, mass found 348.1588.

3-(benzyloxy)-8-methoxy-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (3r):



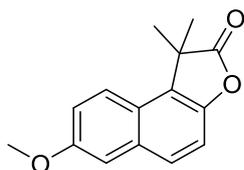
Following the general procedure **B**, reaction between 2,7-dimethoxynaphthalene (**1h**) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding product **3s**, which was purified by silica gel column chromatography (using 3:95 ethyl acetate: hexane as eluent) to give the title compound as colourless oil in 80% (138.8 mg, 0.4 mmol.) yield respectively. $R_f = 0.25$ (0.3:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.75 (d, $J = 9.0$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.62 – 7.47 (m, 2H), 7.47 – 7.31 (m, 3H), 7.14 (s, 1H), 7.04 (m, 2H), 5.29 (s, 2H), 3.96 (s, 3H), 1.67 (s, 6H) ppm; $^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 177.02, 158.3, 138.2, 134.1, 131.3, 130.2, 130.1, 129.3, 128.8, 128.6, 126.3, 121.8, 116.2, 106., 100.78, 78.1, 55.2, 44.3, 23.3 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{23}\text{NO}_3$ 348.1595, mass found 348.1586.

3-(benzyloxy)-7-ethynyl-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (3s):



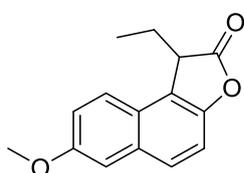
Following the general procedure **B**, reaction between 2-ethynyl-6-methoxynaphthalene (**1g**) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding product **3r**, which was purified by silica gel column chromatography (using 5:95 ethyl acetate: hexane as eluent) to give the title compound as colourless oil in 45% (78.1 mg, 0.22 mmol.) yield respectively. $R_f = 0.25$ (0.5:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.6$ Hz, 1H), 7.59 – 7.46 (m, 3H), 7.36 (dd, $J = 4.8, 2.4$ Hz, 3H), 7.13 (d, $J = 8.6$ Hz, 1H), 5.29 (s, 2H), 3.16 (s, 1H), 1.64 (s, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 176.9, 138.8, 134.1, 134.0, 130.1, 130.1, 129.7, 129.4, 129.0, 128.6, 128.6, 123.1, 122.2, 117.1, 109.7, 83.7, 78.2, 77.4, 44.4, 23.7 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{20}\text{NO}_2$ 342.1489, mass found 342.1477.

7-methoxy-1,1-dimethylnaphtho[2,1-b]furan-2(1H)-one (4a):



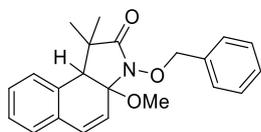
Following the general procedure **B**, reaction between 6-methoxy-2-naphthol (**1i**) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding product **4a**, which was purified by silica gel column chromatography (using 3:95 ethyl acetate: hexane as eluent) to give the title compound as yellow oil in 66% (79.9 mg, 0.33 mmol.) yield respectively. R_f = 0.3 (0.3:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.82 (dt, J = 9.0, 0.7 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 7.26 – 7.20 (m, 1H), 3.95 (s, 3H), 1.77 (s, 6H) ppm; $^{13}\text{C NMR}$ (75 MHz, Chloroform- d) δ 181.8, 156.5, 148., 132.5, 128.2, 125.5, 124.4, 123.4, 120.3, 112.0, 107.7, 55.3, 44.5, 24.8 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{15}\text{O}_3$ 243.1016, mass found 243.1002.

1-ethyl-7-methoxynaphtho[2,1-b]furan-2(1H)-one (4b):



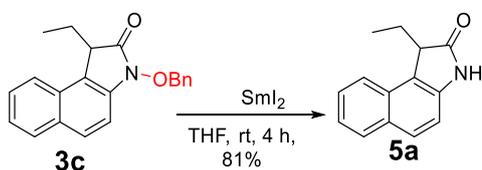
Following the general procedure **B**, reaction between 6-methoxy-2-naphthol (**1i**) and α -halo hydroxamate (**2a**, 1.0 mmol., 2 equiv.) afforded the corresponding product **4b**, which was purified by silica gel column chromatography (using 3:95 ethyl acetate: hexane as eluent) to give the title compound as yellow oil in 62% (75.1 mg, 0.31 mmol.) yield respectively. R_f = 0.3 (0.3:9.5 ethyl acetate: hexane); $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.71 (dd, J = 17.5, 8.9 Hz, 2H), 7.32 (d, J = 8.8 Hz, 1H), 7.29 – 7.19 (m, 2H), 4.13 (q, J = 4.0 Hz, 1H), 3.94 (s, 3H), 2.47 – 2.26 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, Chloroform- d) δ 178.0, 156.7, 150.2, 132.0, 128.3, 124.8, 123.7, 120.4, 119.6, 111.76, 107.4, 55.3, 44.8, 24.1, 9.4 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{15}\text{O}_3$ 243.1016, mass found 243.1024.

3-(benzyloxy)-3a-methoxy-1,1-dimethyl-1,3,3a,9b-tetrahydro-2H-benzo[e]indol-2-one (3a')

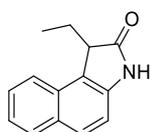


To the solution of 2-Methoxy naphthalene (**1a**, 79 mg, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2a**, 272 mg, 1 mmol., 2 equiv.) in $(\text{CF}_3)_2\text{CHOH}$ (0.4 M), was added sodium carbonate (Na_2CO_3 , 106 mg, 1.5 mmol., 3 equiv.). The reaction mixture was allowed to stirring for 12h at room temperature. The reaction was monitored by TLC and stopped and extract with ethyl acetate (3 times) and the whole solution washed with brine solution. The solution was then concentrated under rotary evaporation and purified by using column chromatography (5:95 ethyl acetate: hexane) to afforded product **3a'** as colourless sticky liquid with 33% (57.65 mg, 0.17 mmol.) yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.58–7.55 (m, 2H), 7.41–7.40 (m, 2H), 7.39–7.27 (m, 3H), 7.22–7.17 (m, 2H), 6.72 (d, $J = 9.9$ Hz, 1H), 5.29 (d, $J = 9.3$ Hz, 1H), 5.19 (d, $J = 9.3$ Hz, 1H), 3.32 (s, 1H), 3.24 (s, 3H), 1.43 (s, 3H), 0.61 (s, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 174.4, 135.1, 132.1, 131.7, 131.1, 129.5, 128.7, 128.4, 127.9, 127.8, 121.2, 89.8, 79.6, 50.3, 49.8, 43.2, 25.5, 20.2 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{24}\text{NO}_3$ 350.1751, mass found 350.1743.

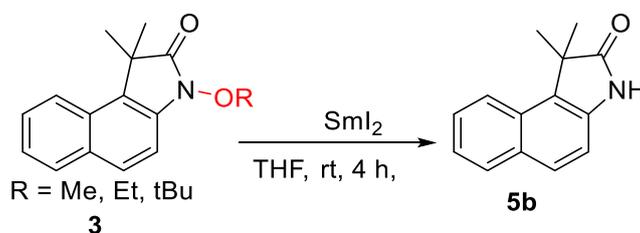
Selective deprotection of N–O bond: Preparation and characterization of compound 5a and 5b:



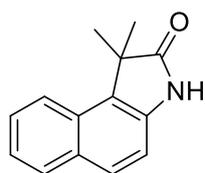
1-ethyl-1,3-dihydro-2H-benzo[e]indol-2-one (5a):



To a solution of **3c** (0.06 g, 0.18 mmol.) in dry THF (0.25M) was added dry methanol (0.5 ml) and 13 ml of Sml_2 solution in THF (0.1 M). The mixture was stirred under nitrogen for 4 h at room temperature and quenched with saturated ammonium chloride solution. The mixture was extracted with ethyl acetate, washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and purified by column chromatography (1:5 ethyl acetate: hexane) to afford **4a** white solid 81% (30.8 mg, 0.14 mmol.) yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.16 (br s, 1H), 7.88–7.79 (m, 3H), 7.55–7.50 (m, 1H), 7.41–7.36 (m, 1H), 7.20 (d, $J = 8.7$ Hz, 1H), 3.95 (t, $J = 5.1$ Hz, 1H), 2.44–2.31 (m, 2H), 0.76 (t, $J = 7.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75MHz, CDCl_3) δ 180.8, 139.3, 130.1, 130.0, 129.4, 129.0, 127.1, 123.7, 122.1, 121.3, 110.9, 47.0, 23.6, 9.0 ppm; **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{14}\text{NO}$ 212.1070, mass found 212.1055.



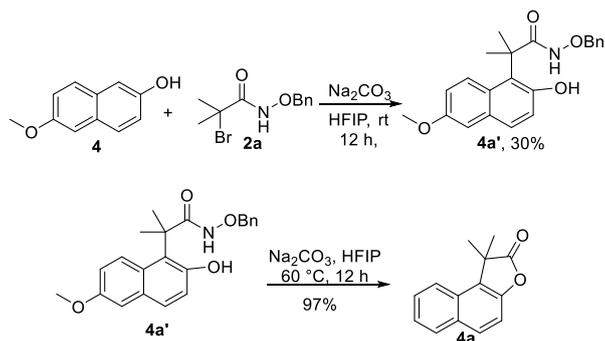
1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**5b**):



To a solution of **3f** (0.043 g, 0.18 mmol.), **3g** (0.046 g, 0.18 mmol.) and **3h** (0.051 g, 0.18 mmol.), in dry THF (0.25M) was added dry methanol (0.5 ml) and 13 ml of Sml_2 solution in THF (0.1 M). The mixture was stirred under nitrogen for 4 h at room temperature and quenched with saturated ammonium chloride solution. The mixture was extracted with ethyl acetate, washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and purified by column chromatography (1:5 ethyl acetate: hexane) to afford **4** white solid 95% (from **3f**, 36.1 mg, 0.17 mmol.), 91% (from **3g**, 34.6 mg, 0.16 mmol.) and 95% (from **3h**, 36.1 mg, 0.17 mmol.) yield respectively. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 9.78 (br s, 1H), 7.96 (d, $J = 8.5$ Hz,

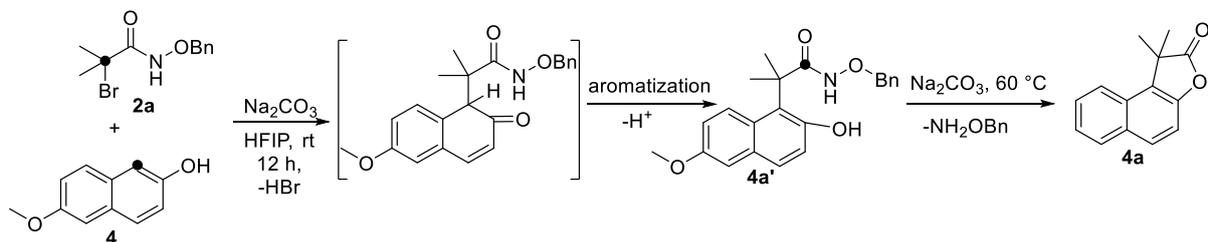
1H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.55 (t, $J = 8.3$ Hz, 1H), 7.42-7.38 (m, 1H), 7.34 (d, $J = 8.5$ Hz, 1H), 1.74 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-d) δ 185.7, 137.5, 130.6, 129.7, 129.6, 129.0, 127.4, 126.9, 123.4, 121.9, 111.7, 46.5, 23.9 ppm; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{14}\text{NO}$ 212.1070, mass found 212.1053.

5. Possible mechanism of lactone formation as described in Scheme 3 of the manuscript:



Scheme SI 1 Controlled experiments

To understand the mechanism of 5-membered lactone formation as described in the Scheme 3 of the manuscript, a controlled reaction was performed between 6-methoxy-2-naphthol (**4**) and α -halohydroxamate (**2a**) at room temperature under basic medium in HFIP solvent (Scheme SI 1). Formation of an intermediate **4a'** was observed via C-1 centre of compound **4** in 30% yield. When the compound **4a'** was subjected to heat at 60 °C in presence of base, formation of the lactone **4a** was observed in 97% yield, thus, proving the intermediacy of **4a'**. Mentionable that, no conversion of **4a'** to **4a** was observed when the reaction was carried out without the base.

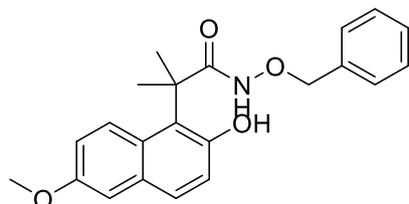


Scheme SI 2 Possible mechanism of lactone formation as described in Scheme 3 of the manuscript

Based on the above results, a possible mechanism was drawn. In presence of base, the nucleophilic attack by 6-methoxy-2-naphthol (**4**) takes place by the most reactive C-1 carbon atom of naphthol derivative forming the intermediate **4a'** (followed by aromatization). The

–OH group of **4a'** deprotonated in presence of base and attacked the carbonyl carbon to break the stable amide C–N bond and furnished the final 5-membered cyclic lactam derivative **4a**.

N-(benzyloxy)-2-(2-hydroxy-6-methoxynaphthalen-1-yl)-2-methylpropanamide (4a'):

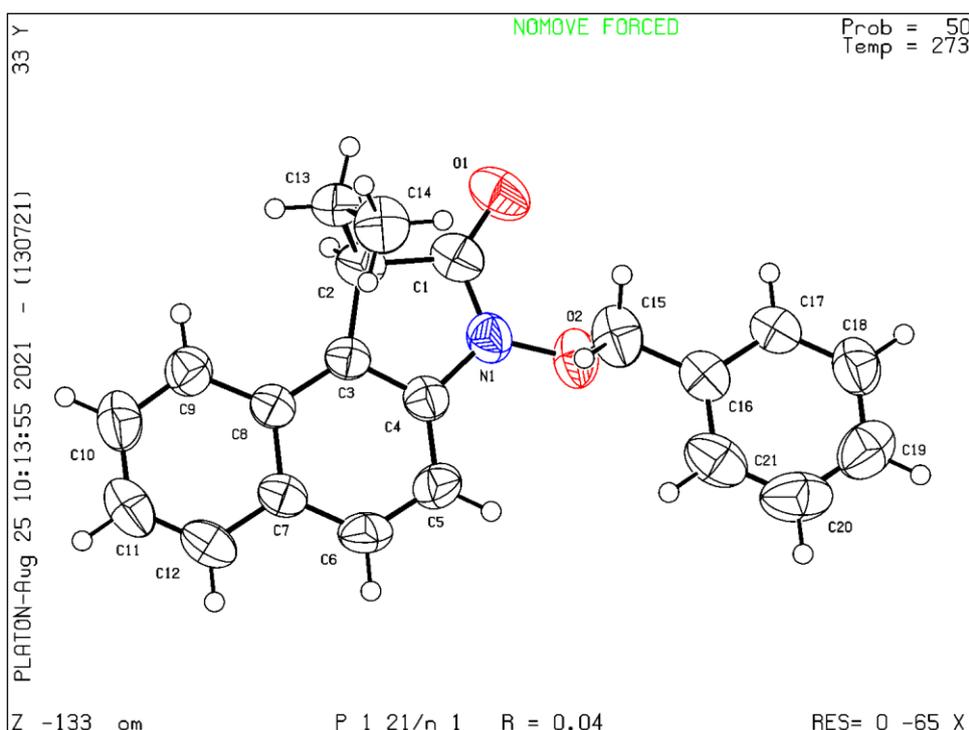


To the solution of 6-Methoxy-2-naphthol (**4**, 87 mg, 0.5 mmol., 1 equiv.) and α -halo hydroxamate (**2a**, 272 mg, 1 mmol., 2 equiv.) in $(\text{CF}_3)_2\text{CHOH}$ (0.4 M), was added sodium carbonate (Na_2CO_3 , 106 mg, 1.5 mmol., 3 equiv.). The reaction mixture was allowed to stir for 12 h at room temperature. The reaction was monitored by TLC and stopped and extracted with ethyl acetate (3 times) and the whole organic solution washed with brine solution. The solution was then concentrated under rotary evaporation and purified by using column chromatography (15:85 ethyl acetate: hexane) to afforded product **4a'** as colourless sticky liquid with 30% (53 mg, 0.14 mmol.) yield. $^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 9.20 (s, 1H), 7.64 (dd, J = 8.9, 4.6 Hz, 2H), 7.46 – 7.33 (m, 5H), 7.19 (dd, J = 6.0, 2.5 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.03 (dd, J = 8.9, 2.5 Hz, 1H), 5.00 (s, 2H), 3.92 (s, 3H), 1.57 (s, 6H) ppm; $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ 172.1, 157.0, 149.7, 135.0, 131.3., 129.3, 129.3, 129.1, 128.8, 128.7, 128.6, 127.9, 122.8, 119.3, 117.6, 105.7, 78.2, 55.3, 44.5, 25.2; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{24}\text{NO}_4$ 366.1700, mass found 366.1723.

6. X-ray Crystallography:

Single-crystal X-ray data of compound **3c** were collected on a Bruker SMART Apex-II CCD diffractometer in the presence of graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. The Bruker Apex-II suite program was used to perform data processing, structure solution, and refinement. Reflections available in $2\theta_{\max}$ range were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus.² Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS.³ The structures were solved using direct methods and refined by means of full-matrix least-squares techniques based on F^2 with SHELX2017/1 software package.⁴ Non-hydrogen atoms present in the structures were refined with anisotropic thermal parameters. C-H hydrogen atoms were introduced at geometrical positions with $U_{\text{iso}} = 1/2U_{\text{eq}}$ to those of the atoms to which they are attached.

7. X-ray structure data for **3c**:



8. Crystal data and structure refinement for 3c:

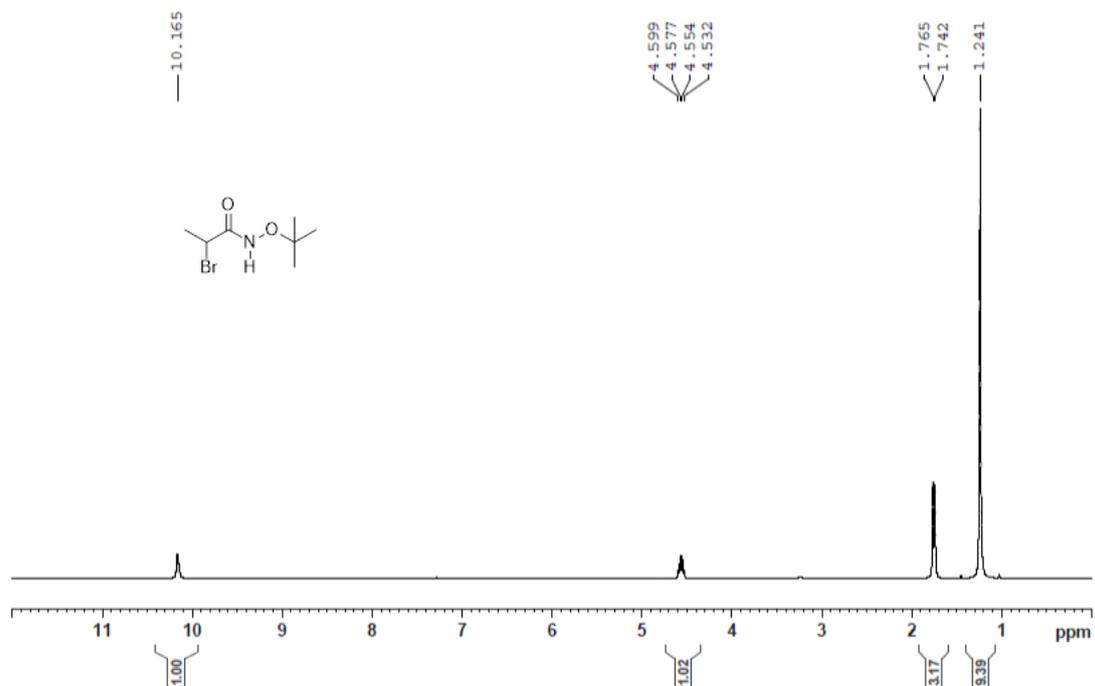
Identification code	3c
Empirical formula	C ₂₁ H ₁₉ NO ₂
Formula weight	317.37
Temperature/K	273.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.729(6)
b/Å	5.448(2)
c/Å	23.303(10)
α/°	90
β/°	104.322(7)
γ/°	90
Volume/Å ³	1688.8(12)
Z	4
ρ _{calc} /cm ³	1.248
μ/mm ⁻¹	0.080
F(000)	672.0
Crystal size/mm ³	0.4 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	1.804 to 27.095
Index ranges	-17 ≤ h ≤ 17, -6 ≤ k ≤ 6, -29 ≤ l ≤ 29
Reflections collected	32688
Independent reflections	3695 [R _{int} = 0.0332, R _{sigma} = 0.0181]
Data/restraints/parameters	3695/0/218
Goodness-of-fit on F ²	1.013
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0435, wR ₂ = 0.1025
Final R indexes [all data]	R ₁ = 0.0657, wR ₂ = 0.1191
Largest diff. peak/hole / e Å ⁻³	0.13/-0.15
CCDC Number	2141571

9. References:

1. (a) J. Xuan, X. Cao and X. Cheng, *Chem. Commun.*, 2018, **54**, 5154; (b) C. S. Jeffrey, K. L. Barnes, J. A. Eickhoff and C. R. Carson, *J. Am. Chem. Soc.*, 2011, **133**, 7688; (c) A. Acharya, D. Anumandla and C. S. Jeffrey, *J. Am. Chem. Soc.*, 2015, **137**, 14858; (d) A. Acharya, K. Montes and C. S. Jeffrey, *Org. Lett.*, 2016, **18**, 6082; (e) V. Jaiswal, B. Mondal, K. Singh, D. Das and j. Saha, *Org. Lett.*, 2019, **21**, 5848.
2. G. M. Sheldrick, *SAINT, Ver. 6.02 and SADABS, Ver. 2.03, Bruker AXS Inc.: Madison, WI*, 2002.
3. G. M. Sheldrick, *SADABS, software for empirical absorption correction, Universitat: Göttingen, Germany, 1999–2003*.
4. G. M. Sheldrick, *SHELXS-2013 and SHELXL-2013, Program for Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 2013*.

10. Copies of ^1H and ^{13}C NMR spectra of all unknown starting materials:

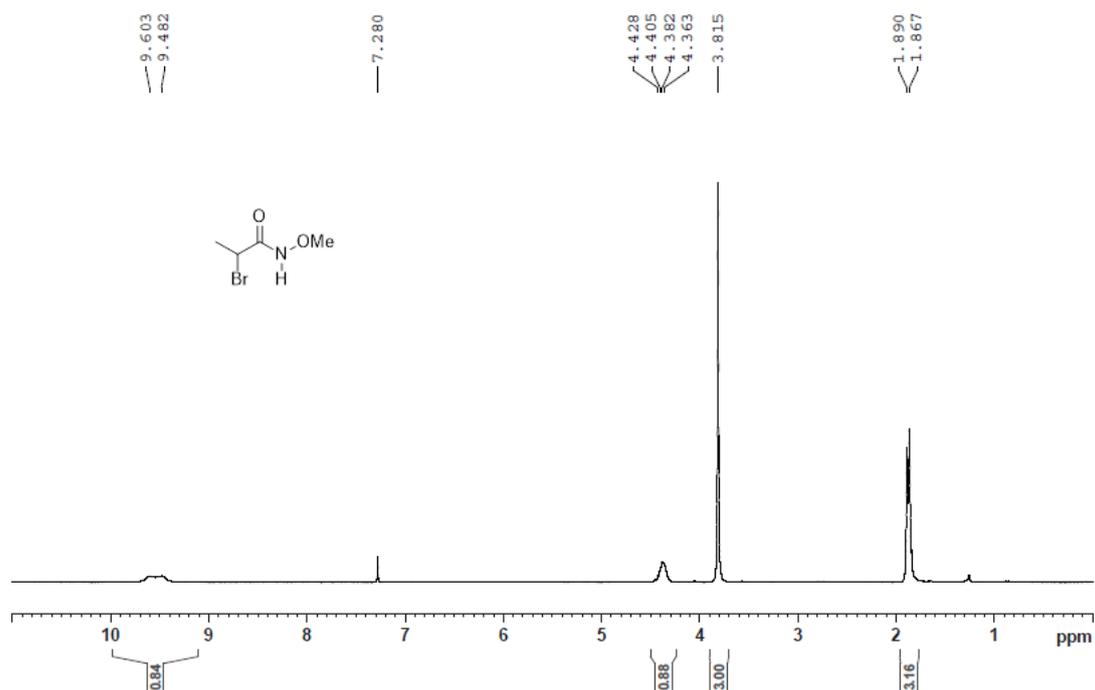
^1H NMR spectra of **2i** (300 MHz, CDCl_3);



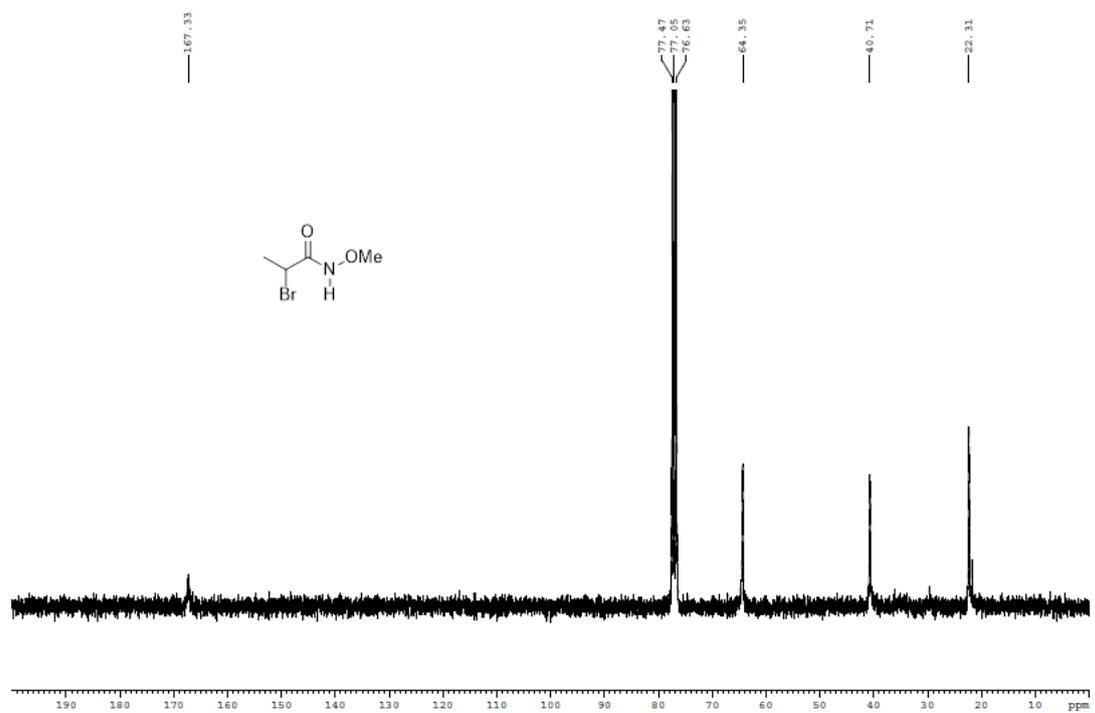
^{13}C NMR spectra of **2i** (75 MHz, CDCl_3);



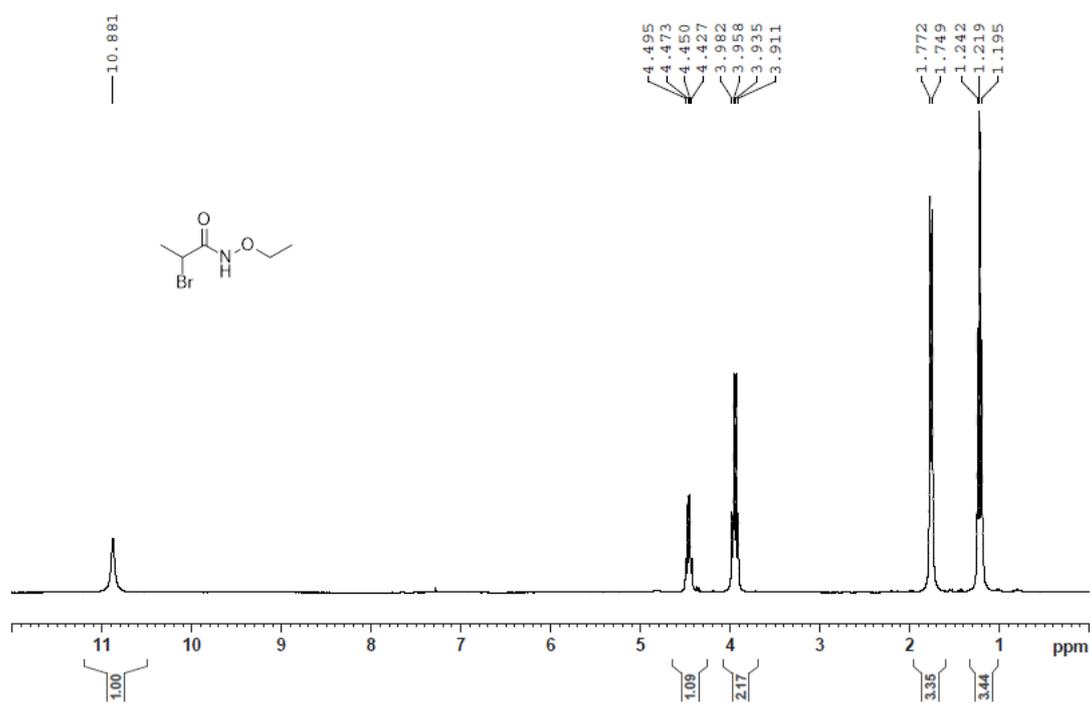
¹H NMR spectra of **2j** (300 MHz, CDCl₃);



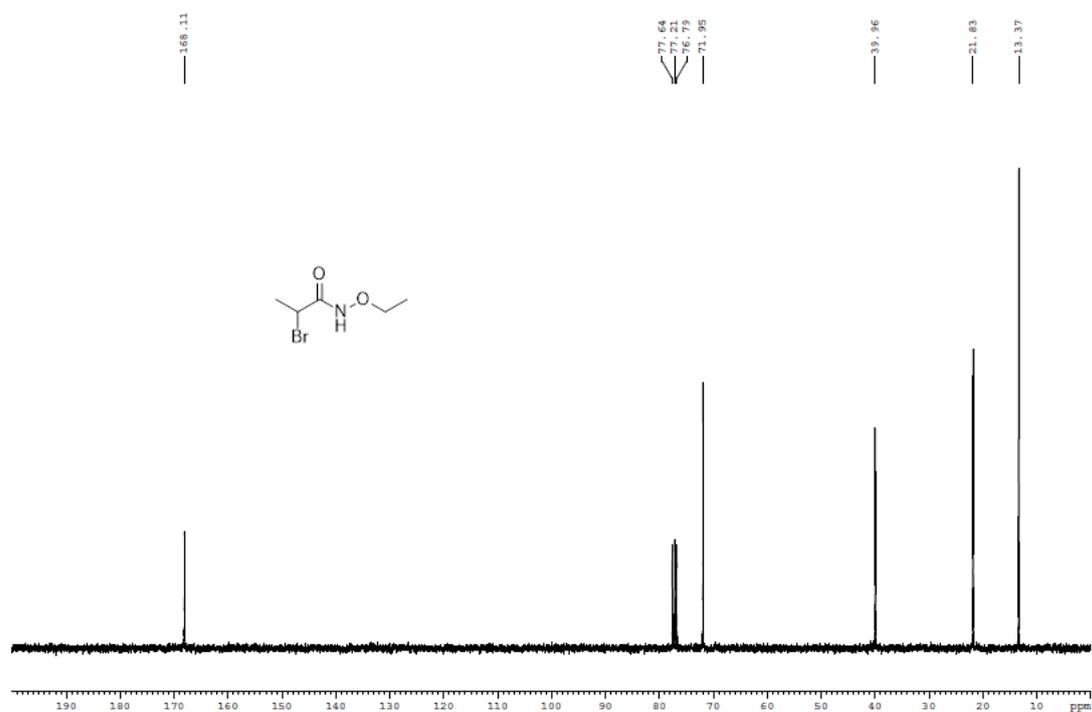
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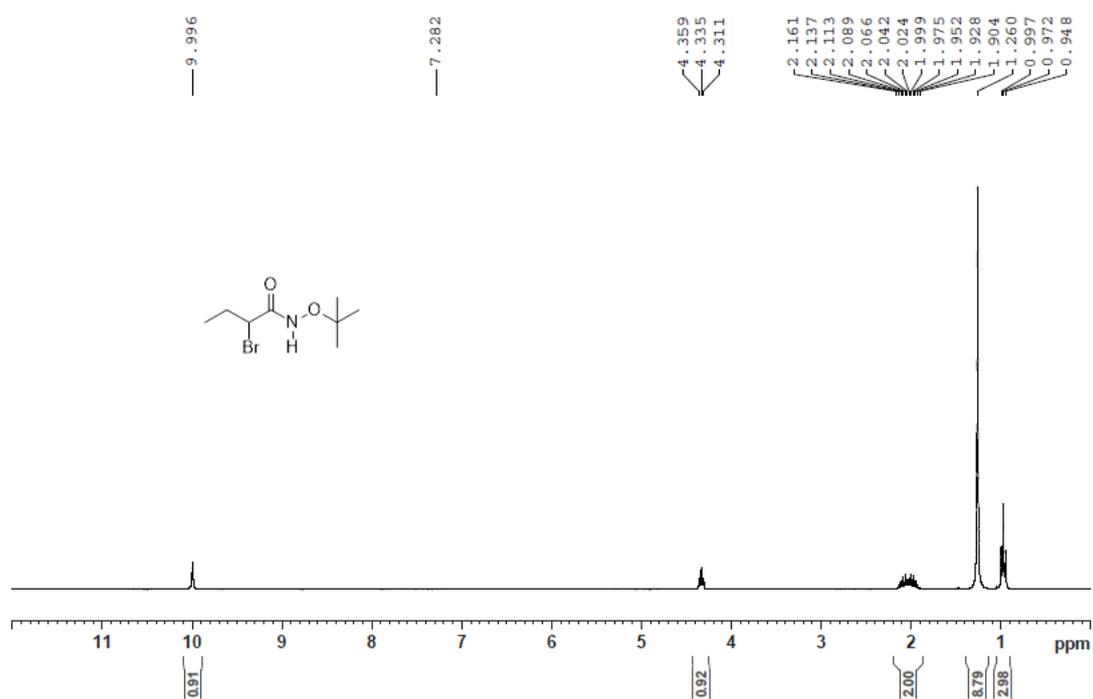
^1H NMR spectra of **2k** (300 MHz, CDCl_3);



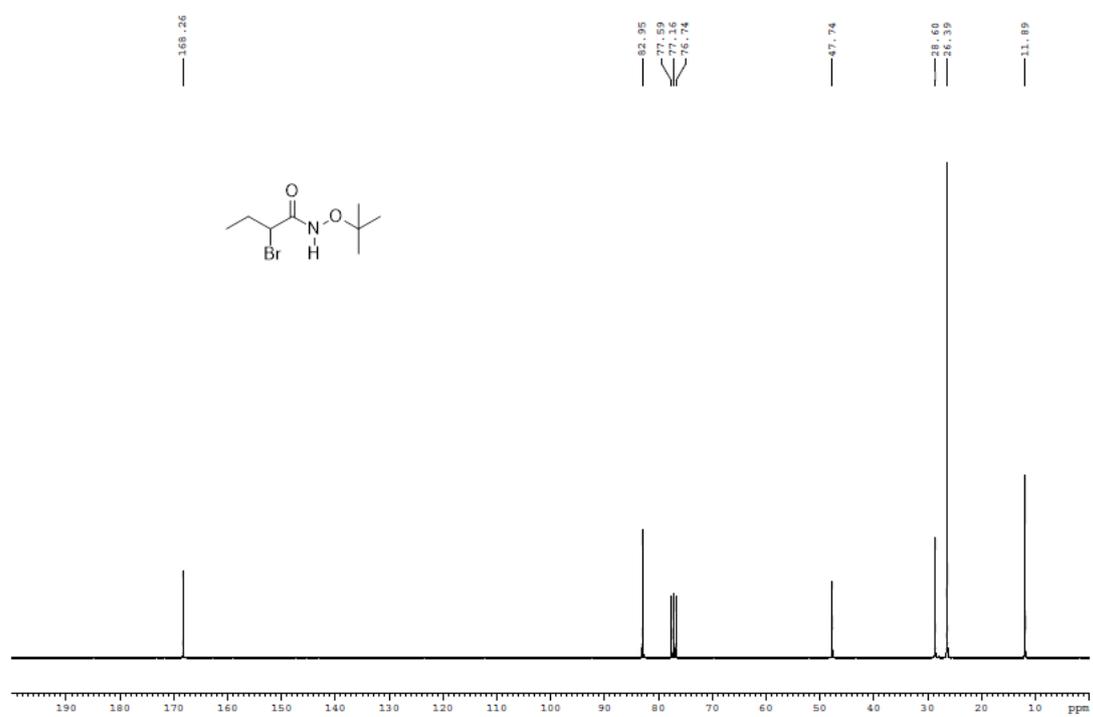
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¹H NMR spectra of **2l** (300 MHz, CDCl₃);

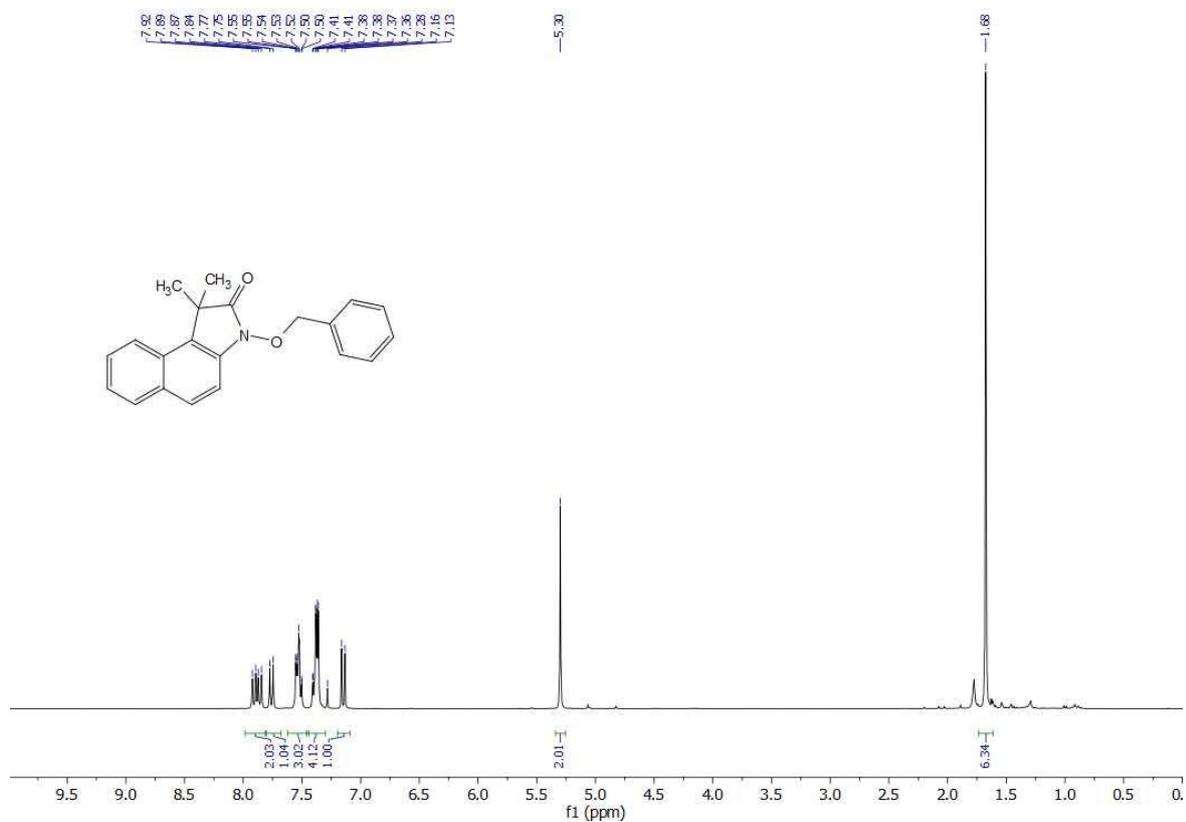


¹³C NMR spectra of **2k** (75 MHz, CDCl₃);

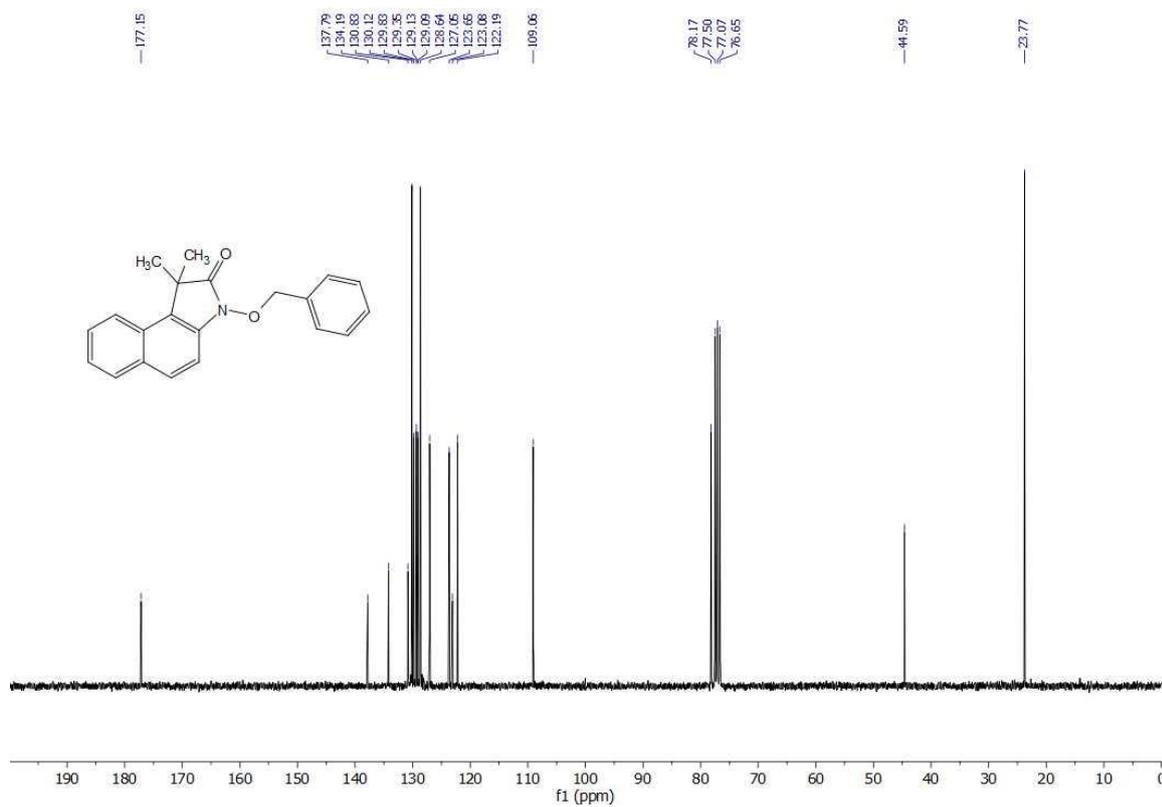


11. Copies of ^1H and ^{13}C NMR spectra of all products:

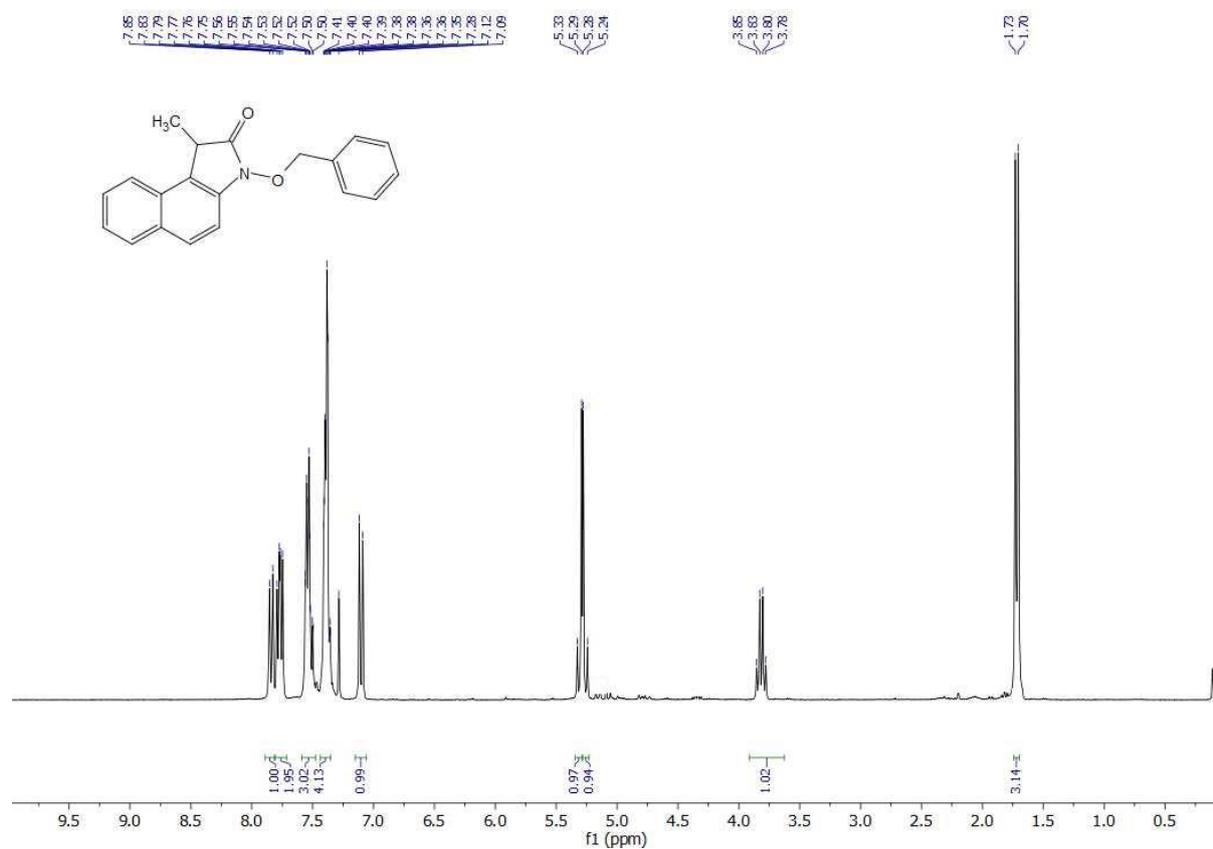
^1H NMR spectra of **3a** (300 MHz, CDCl_3);



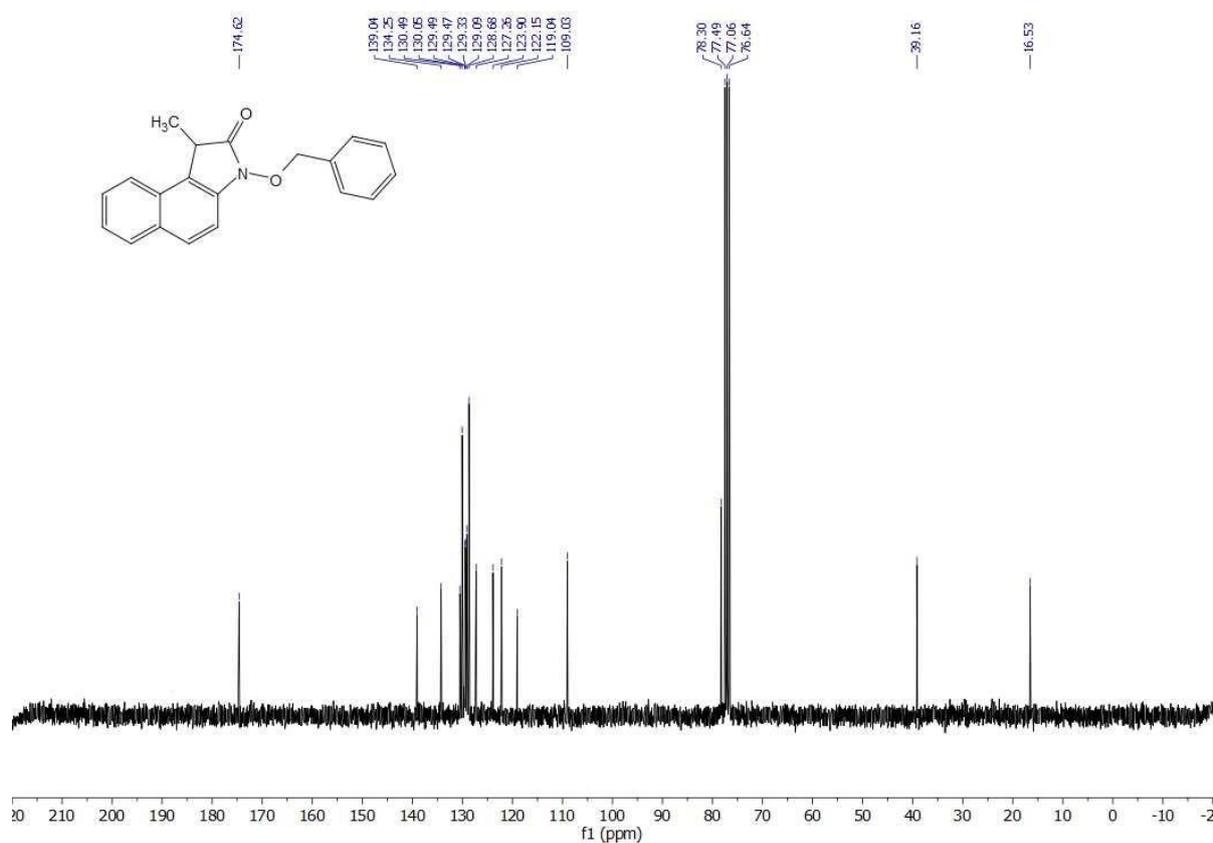
^{13}C NMR spectra of **3a** (75 MHz, CDCl_3);



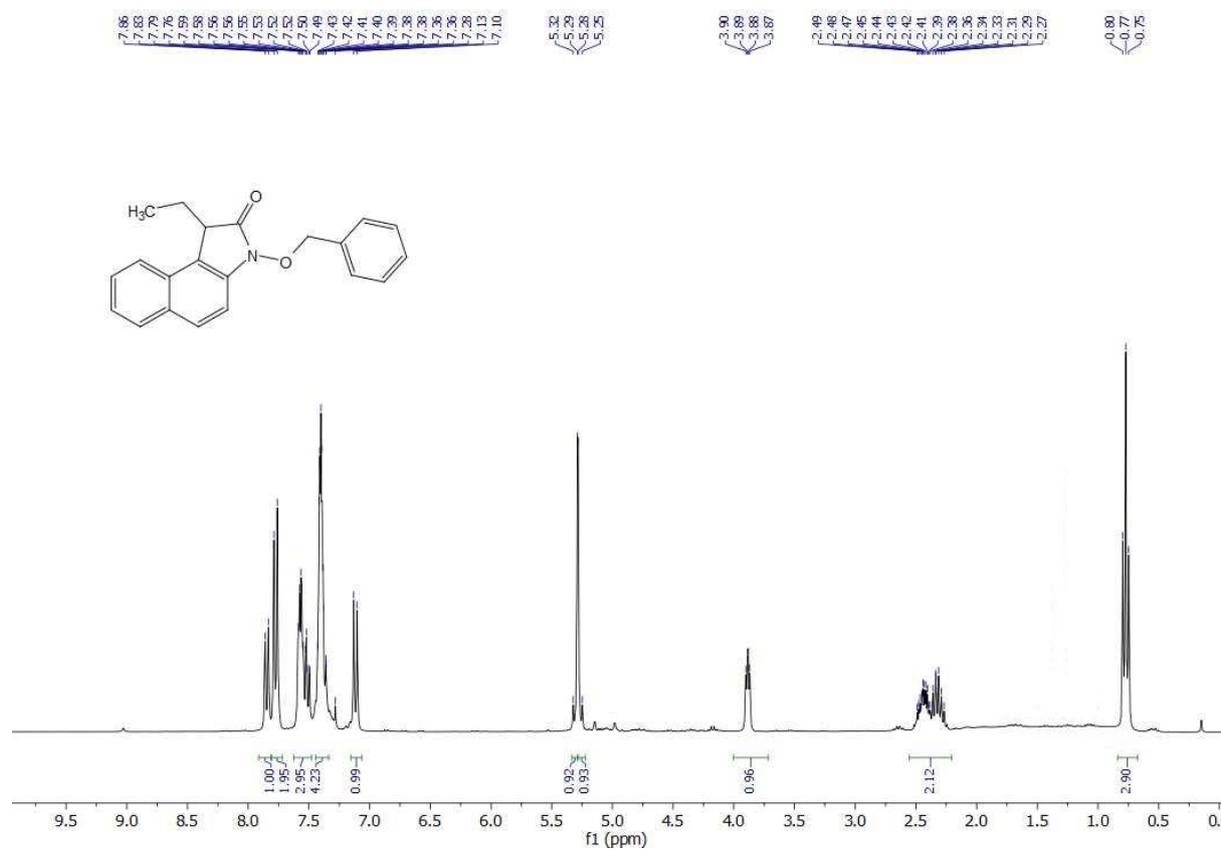
¹H NMR spectra of **3b** (300 MHz, CDCl₃);



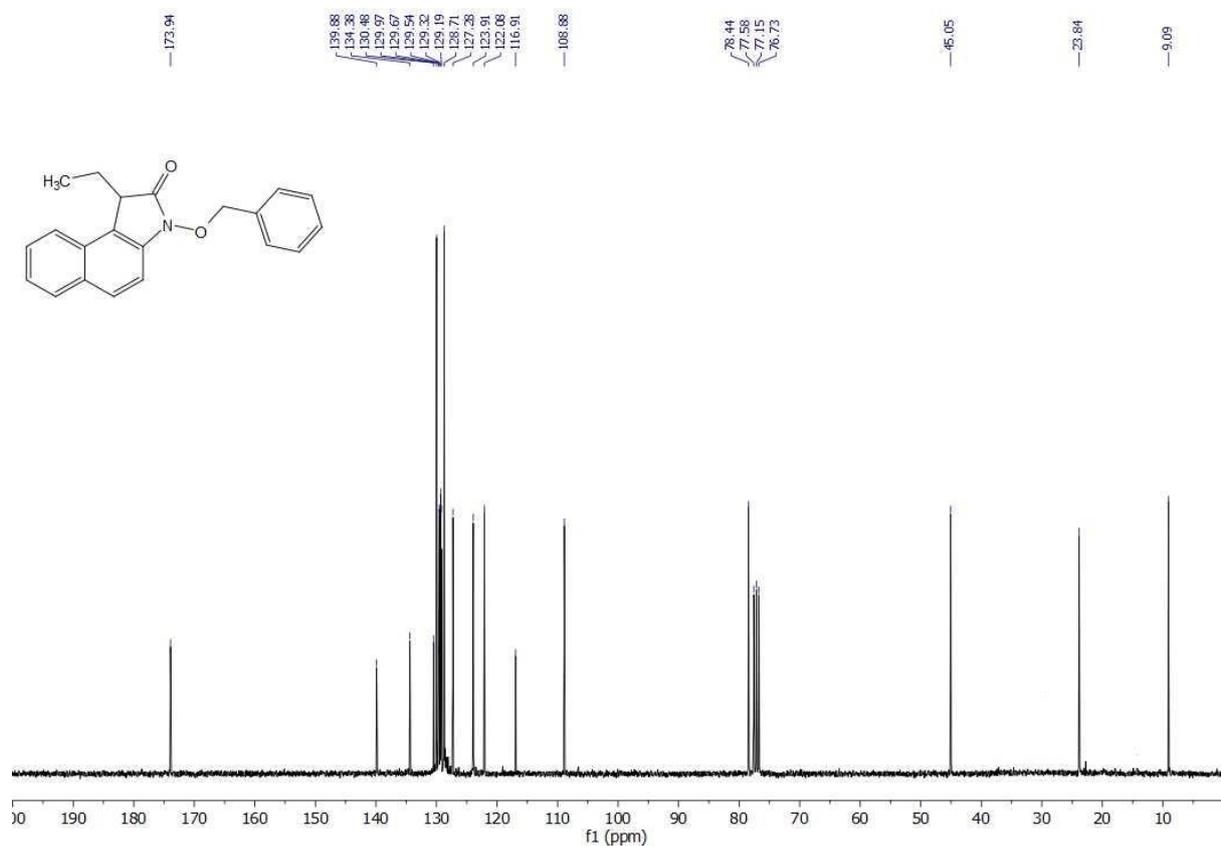
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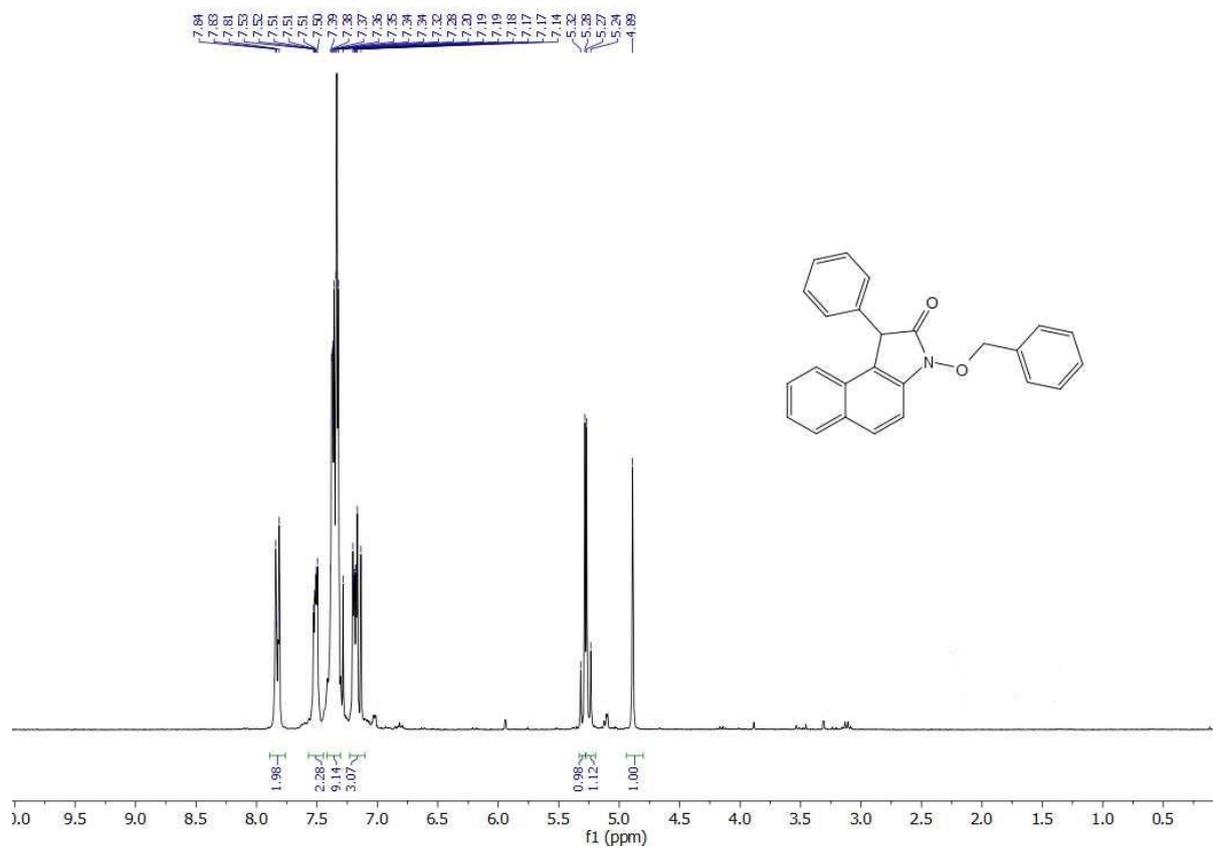
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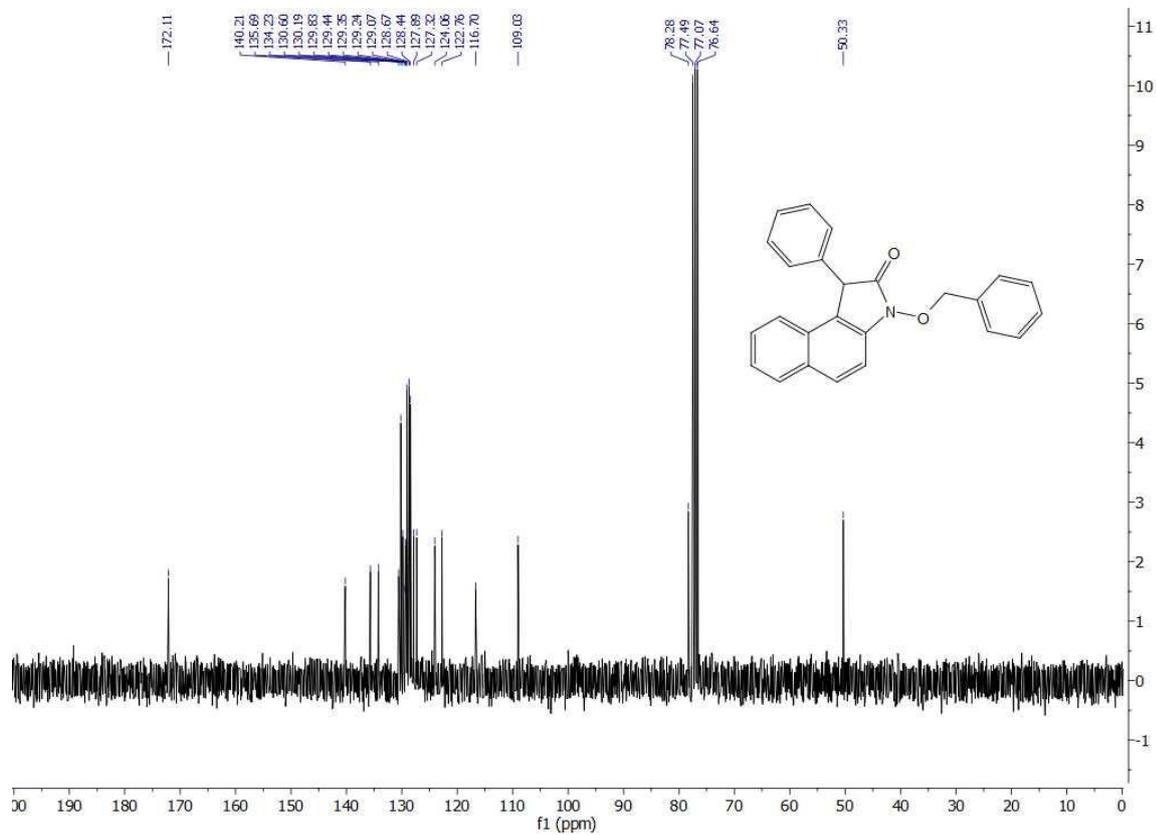
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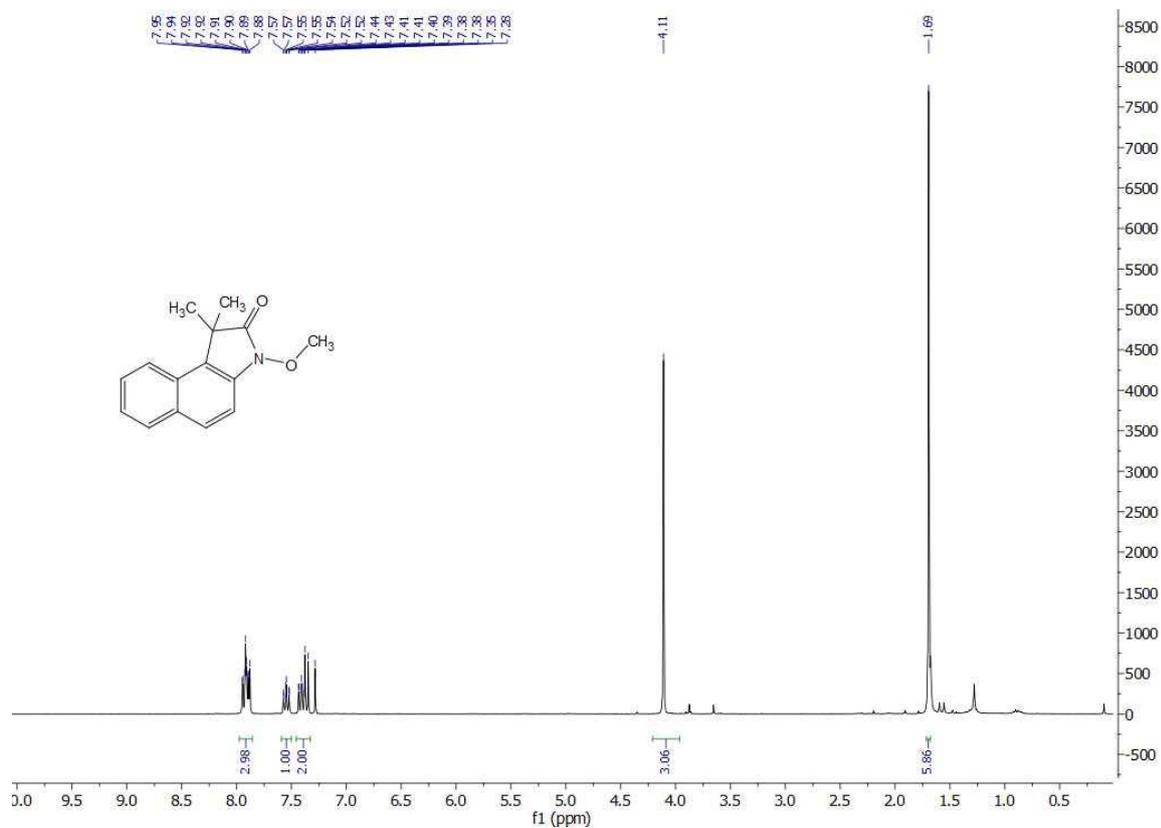
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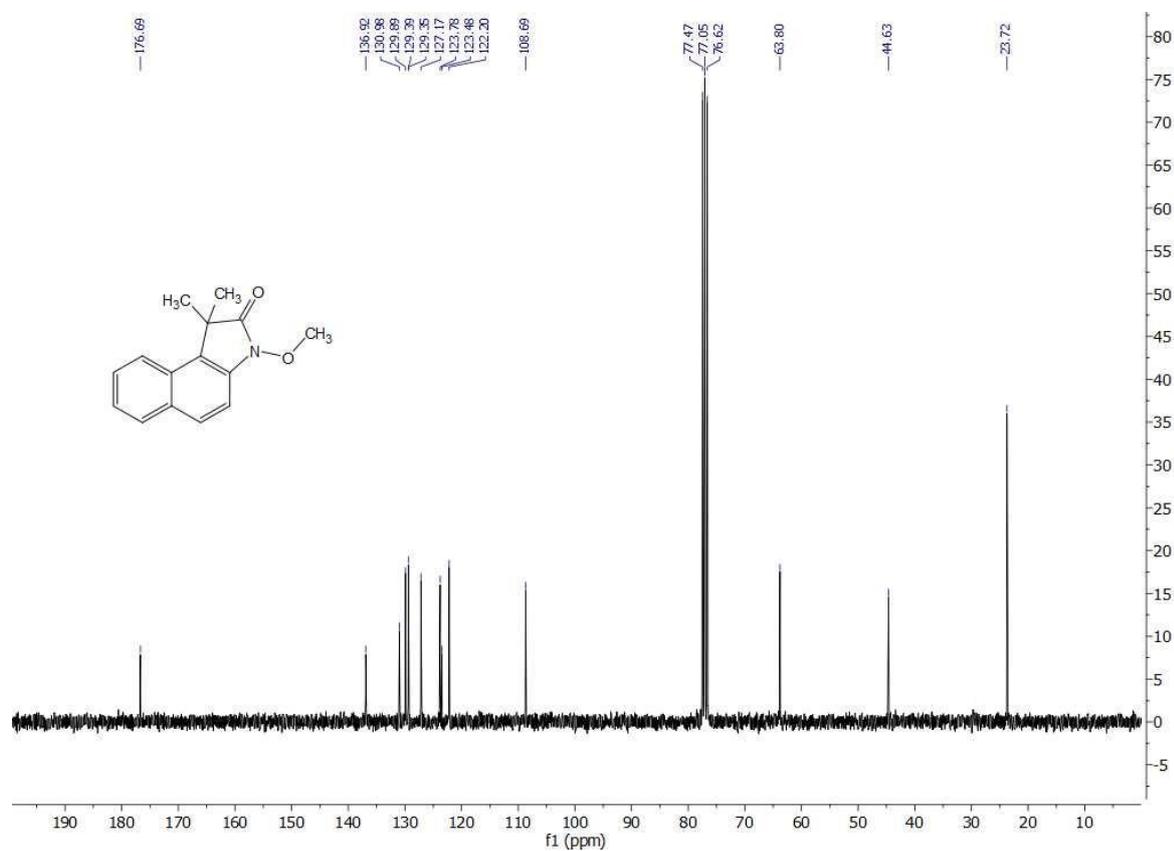
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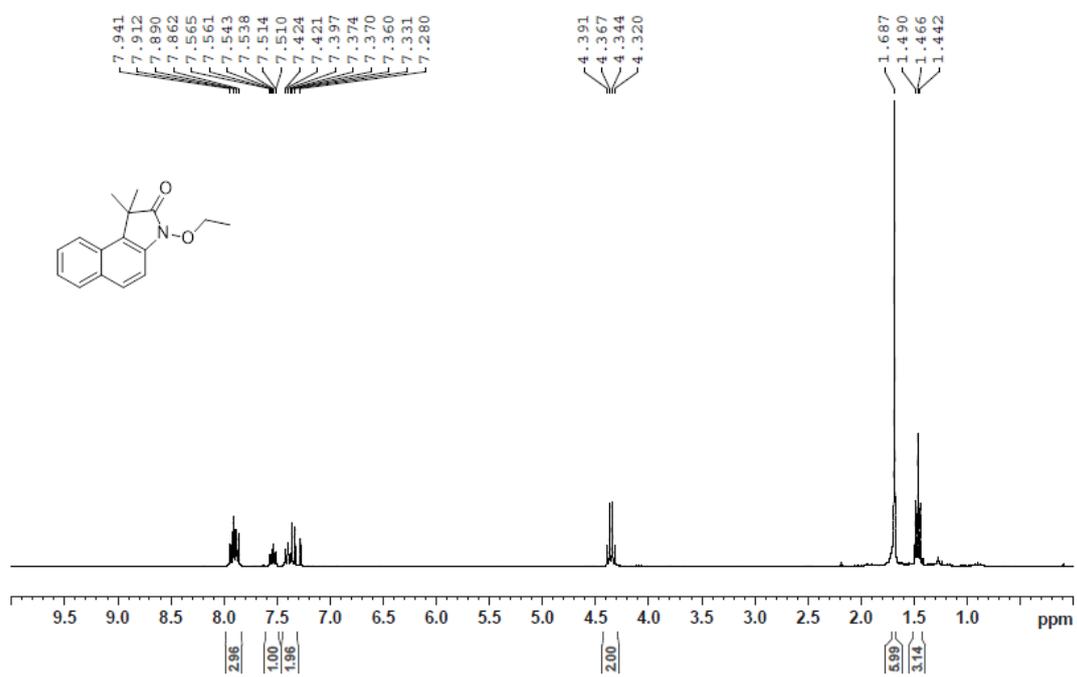
^1H NMR spectra of **3f** (300 MHz, CDCl_3);



^{13}C NMR spectra of **3f** (75 MHz, CDCl_3);

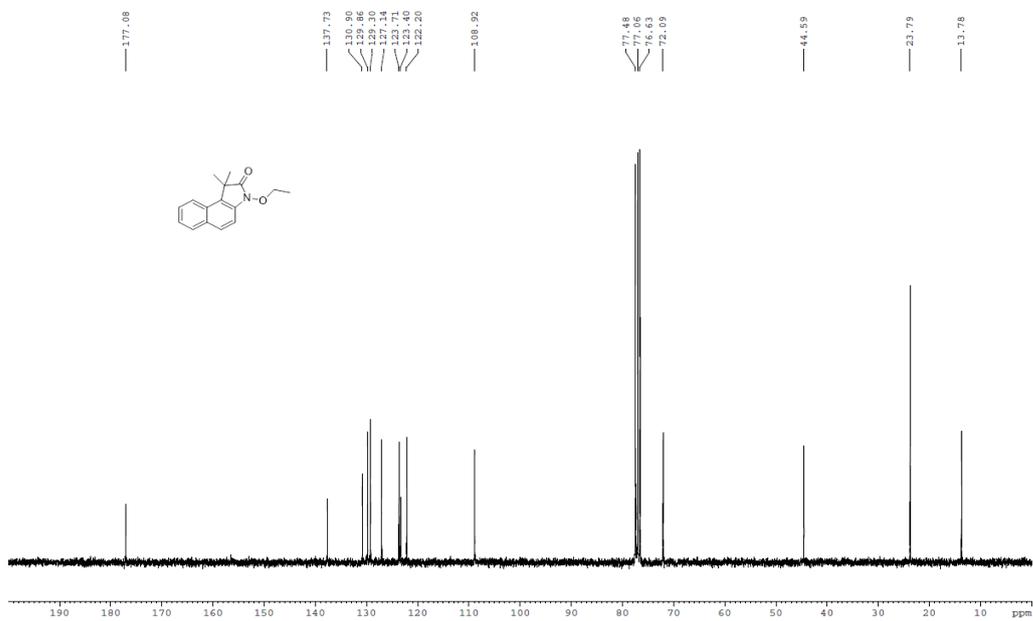


^1H NMR spectra of **3g** (300 MHz, CDCl_3);

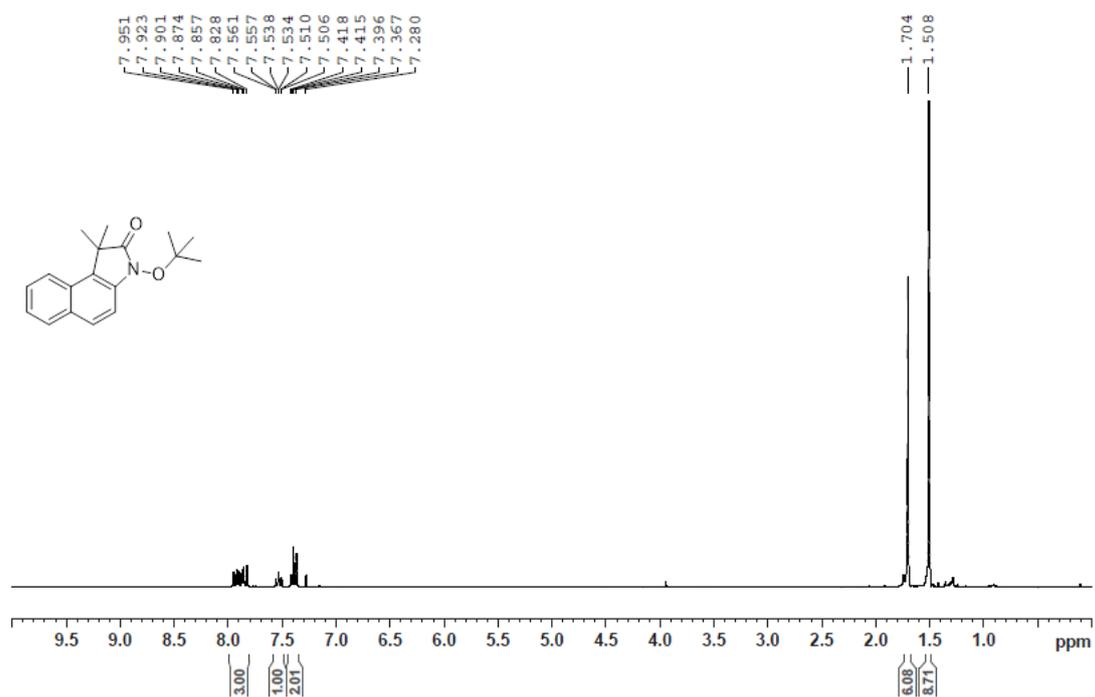


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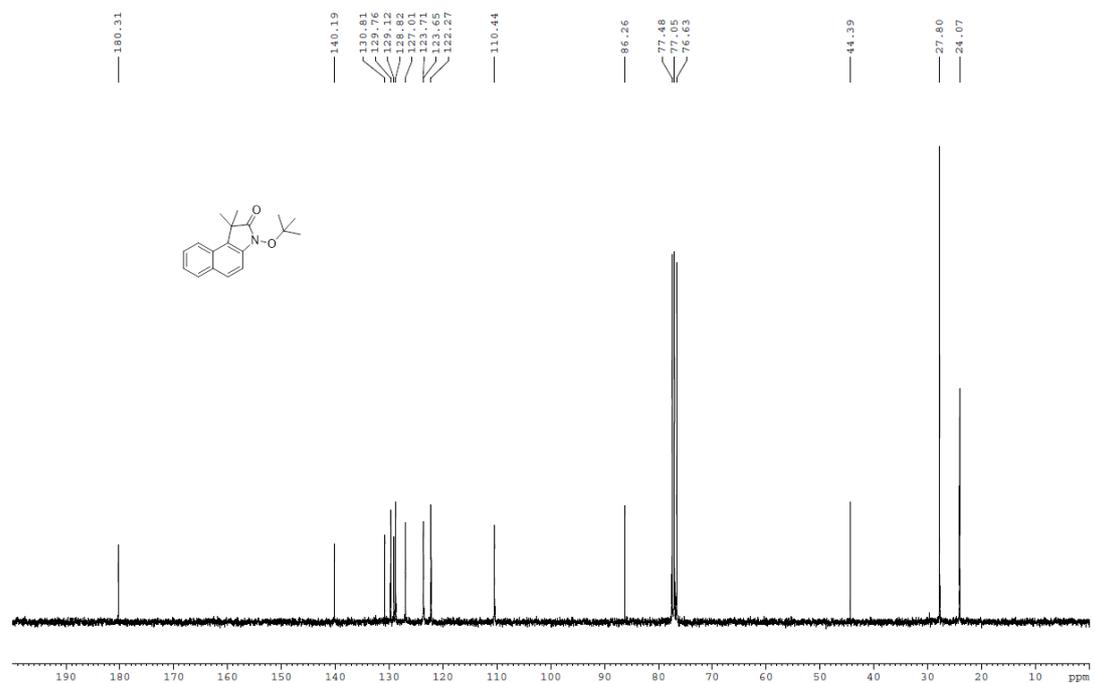
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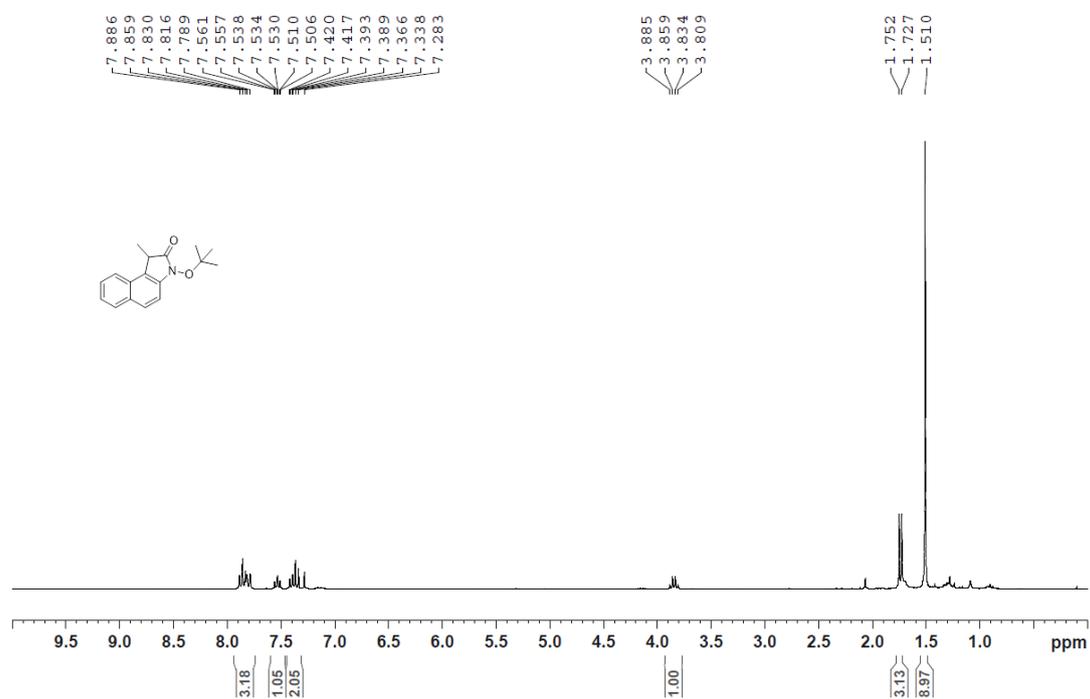
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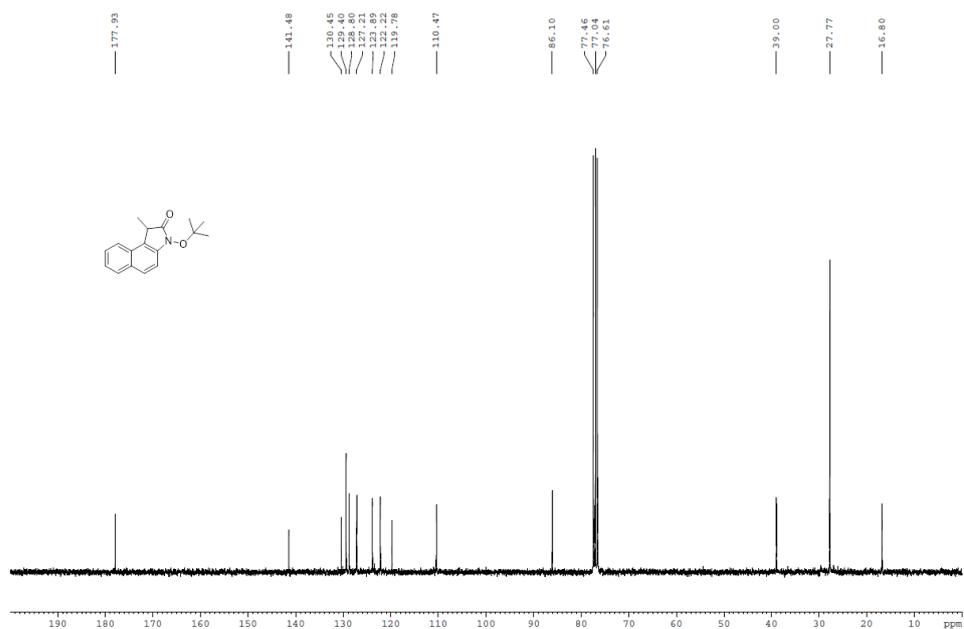
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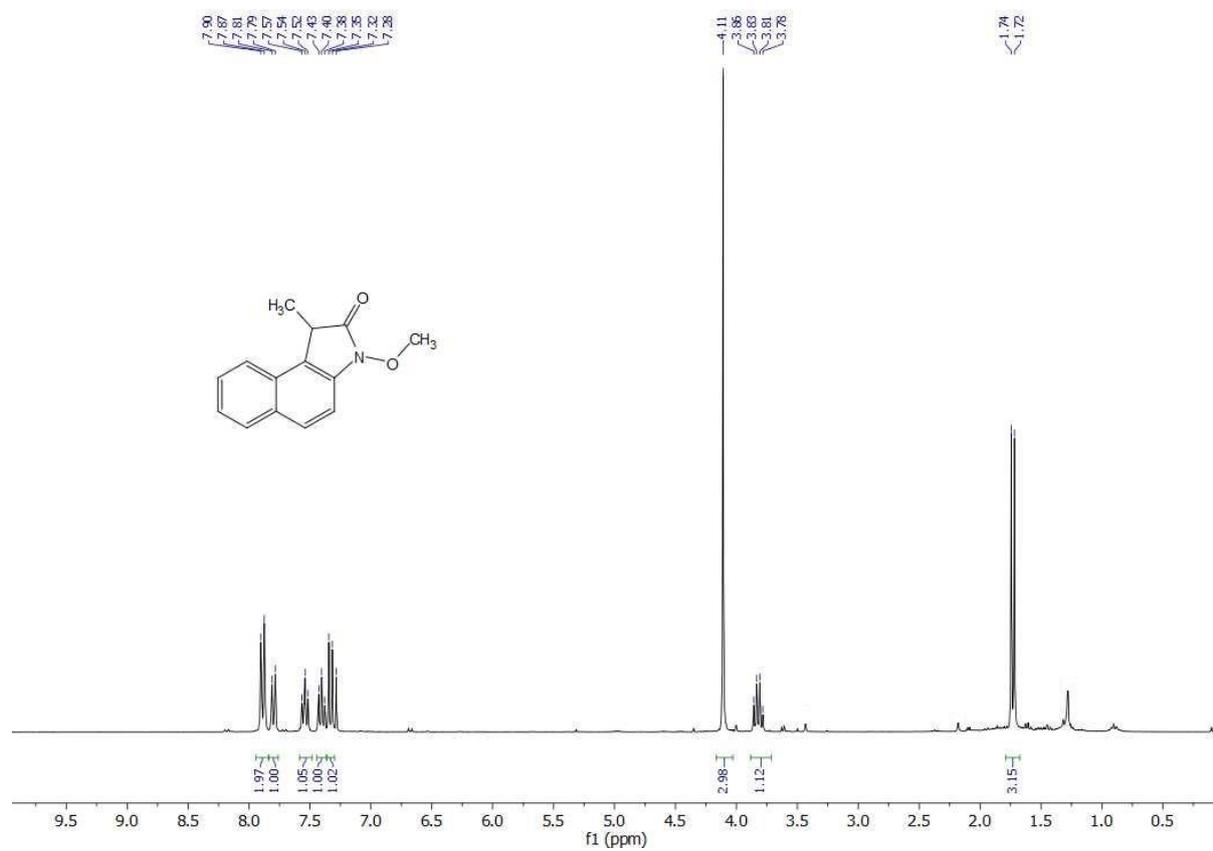
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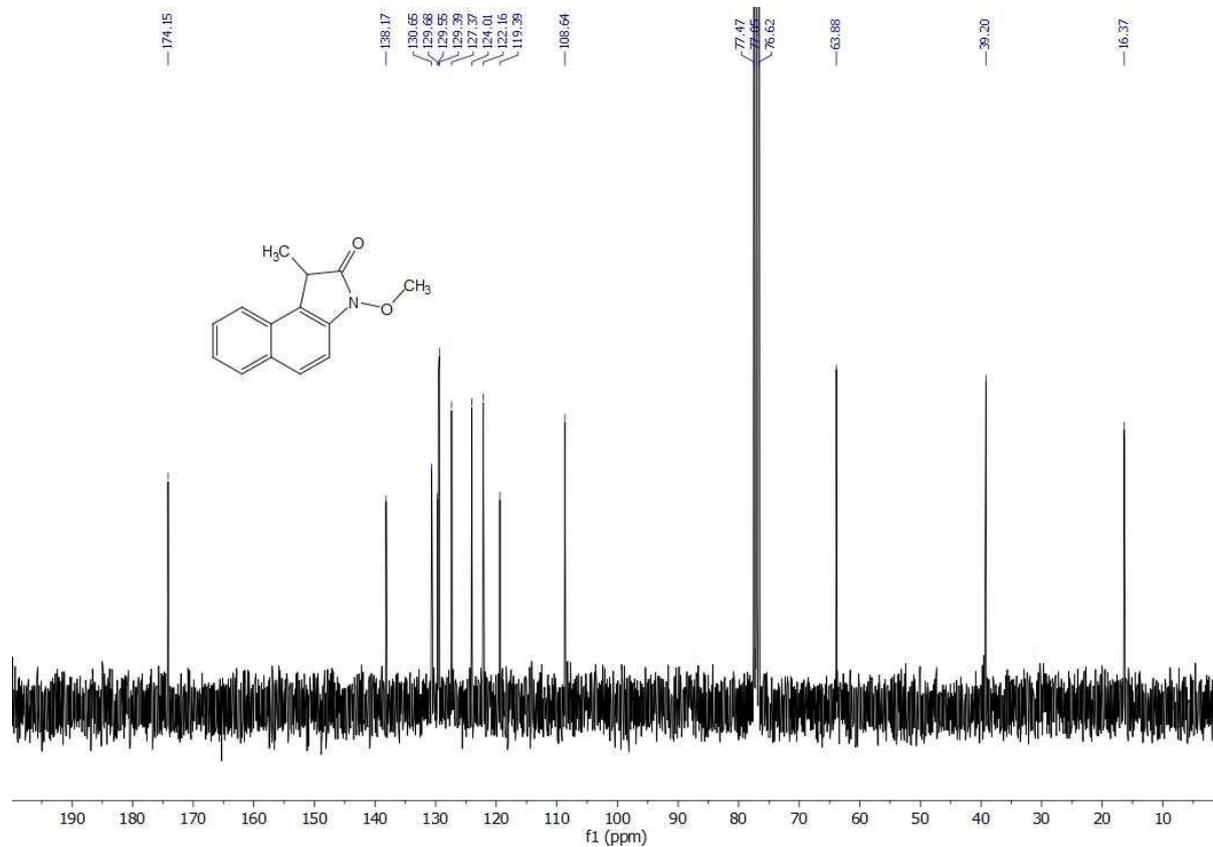
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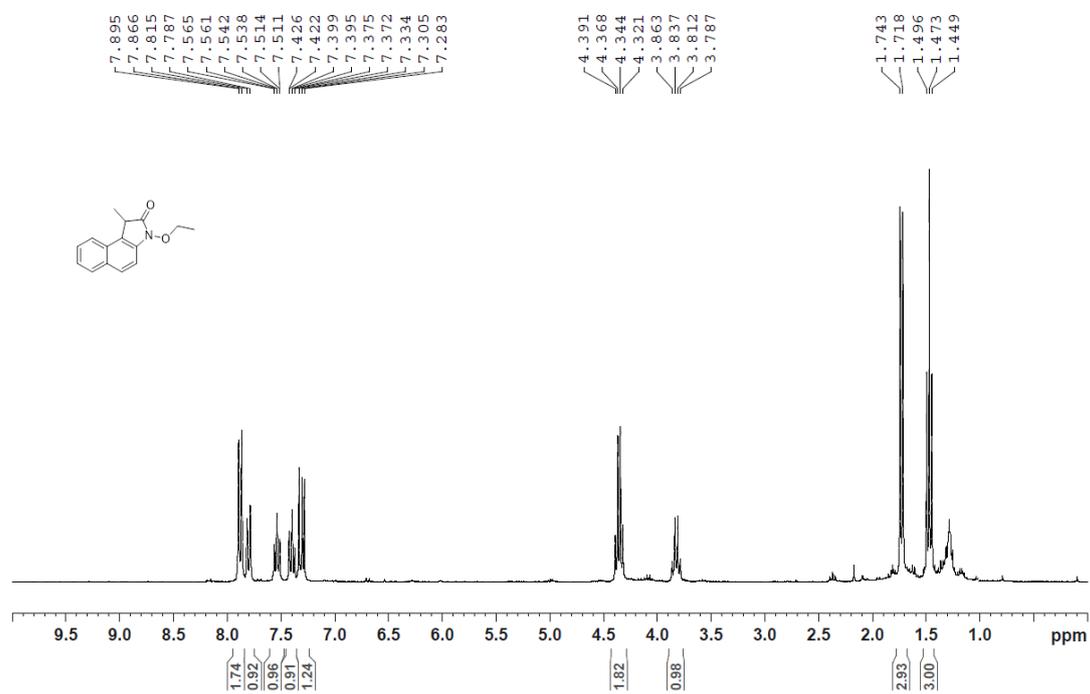
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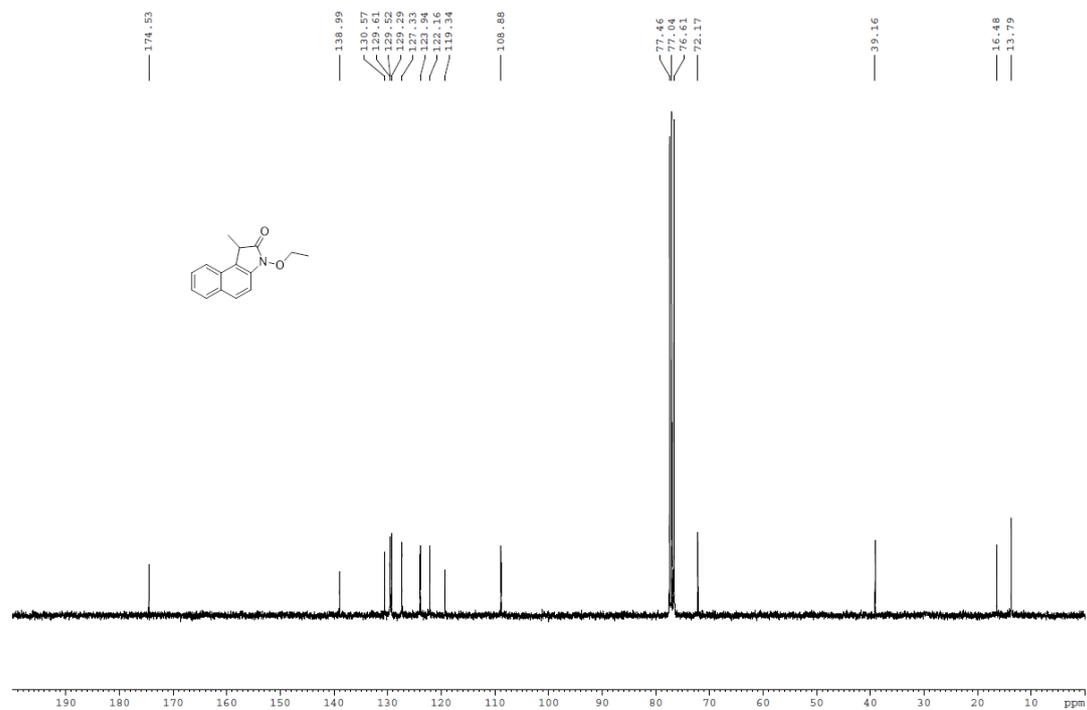
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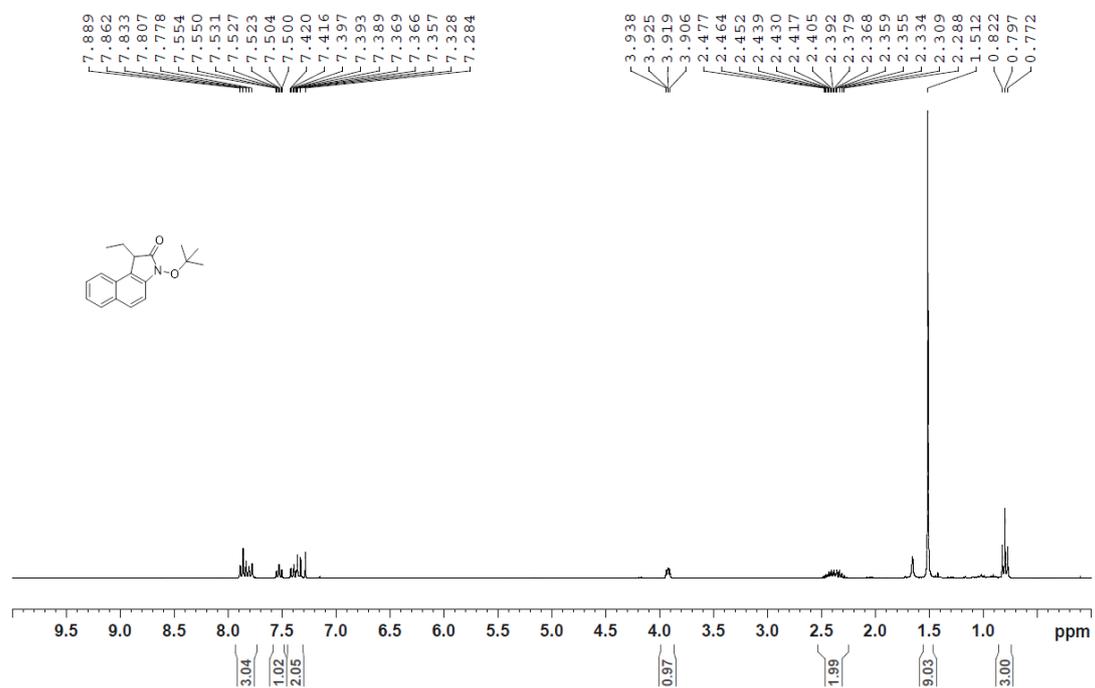
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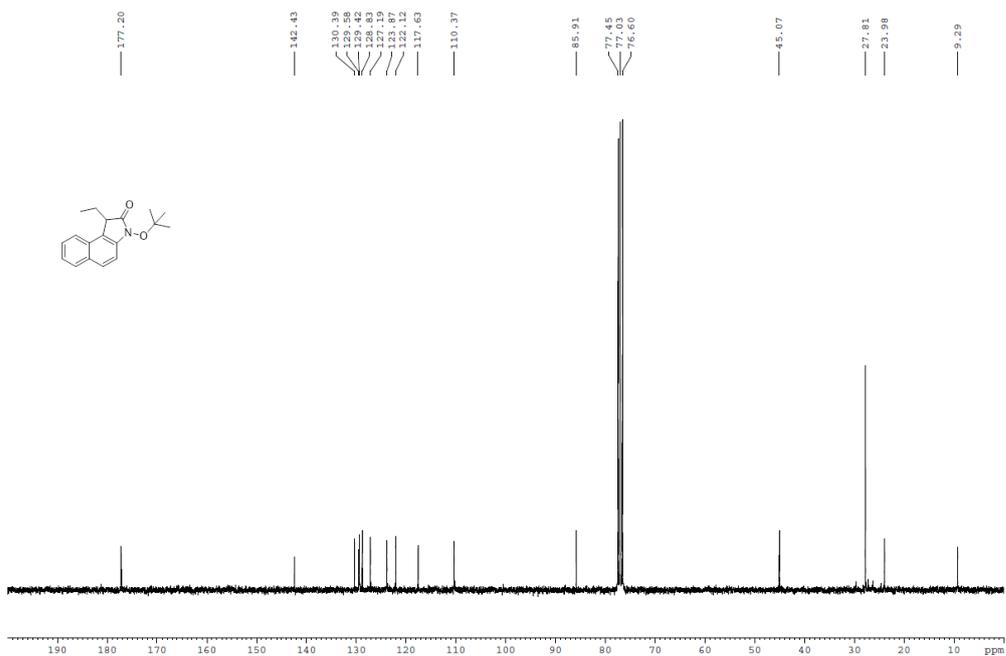
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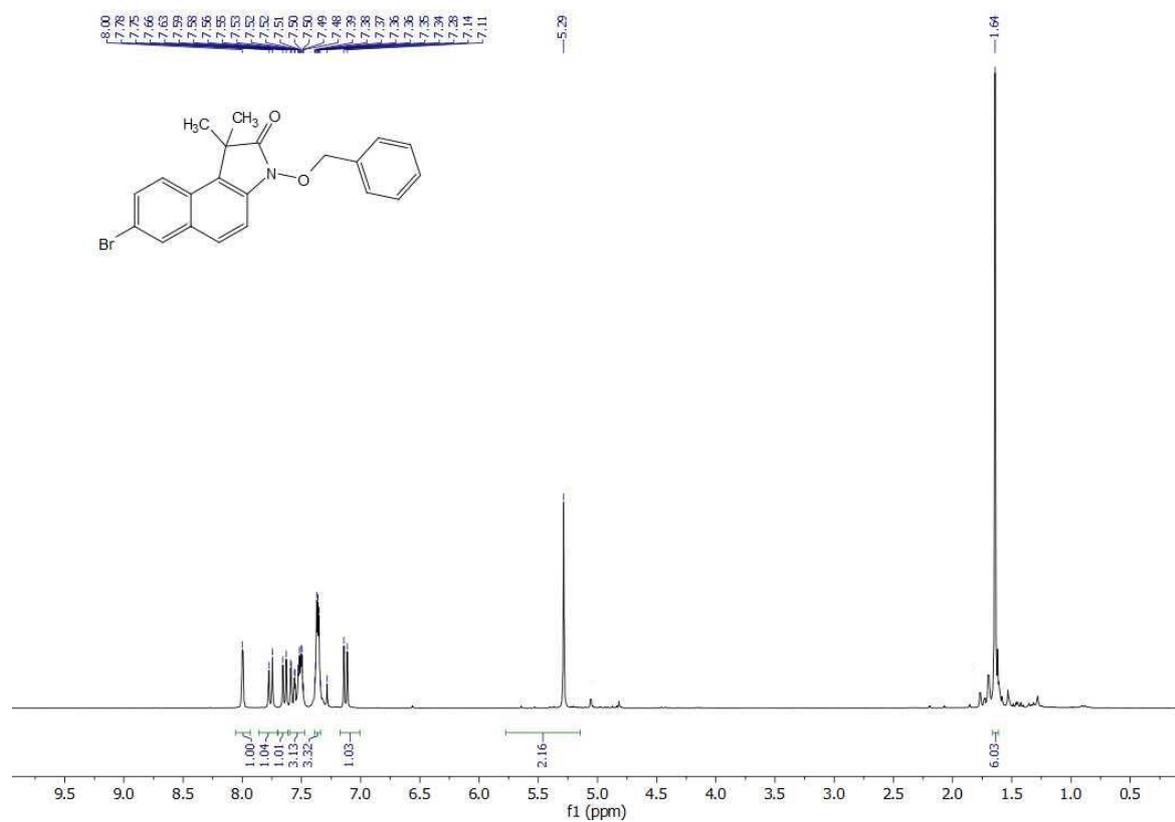
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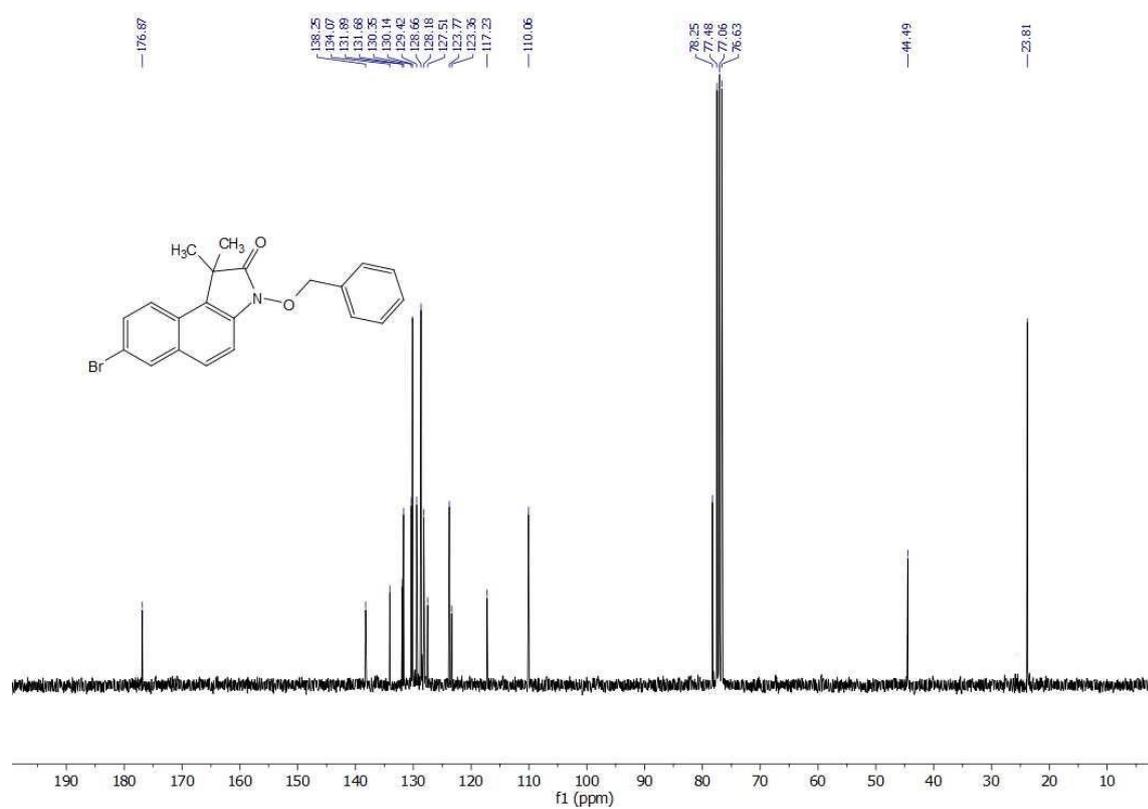
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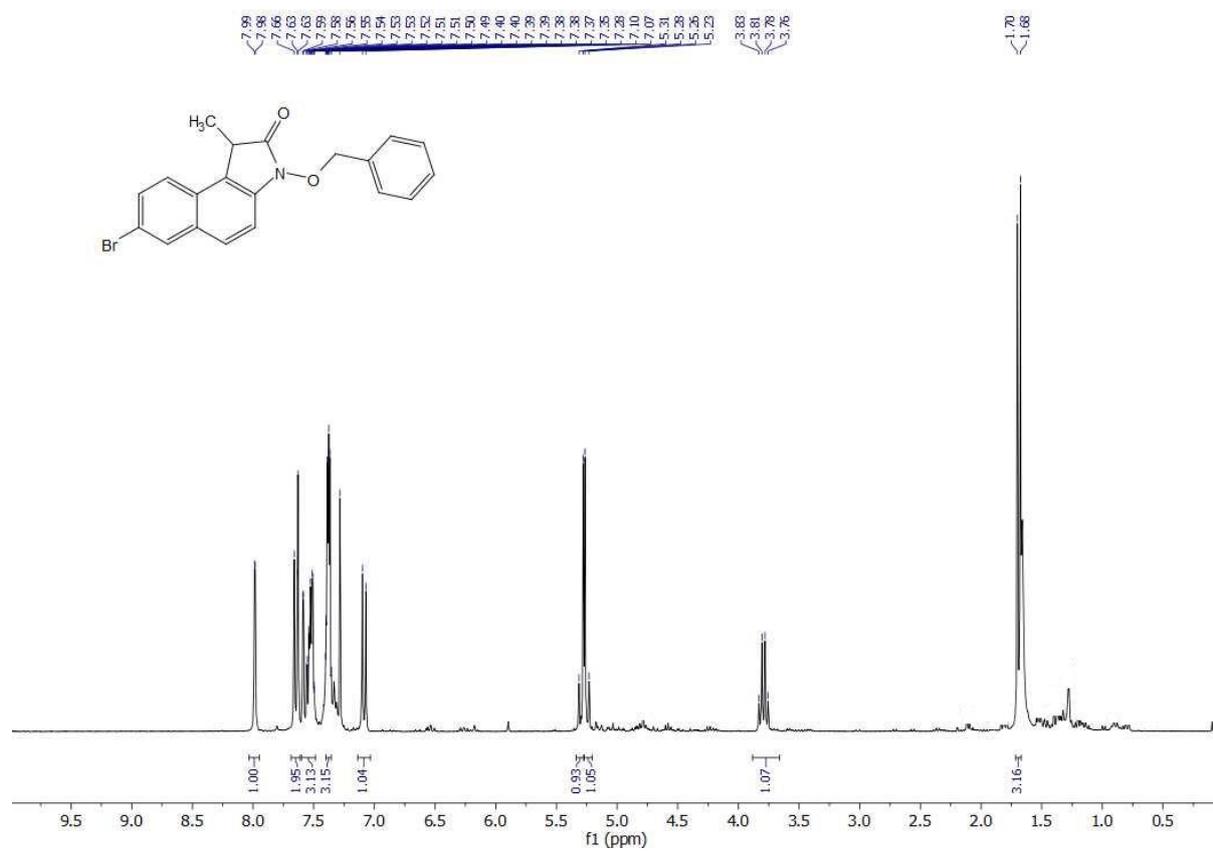
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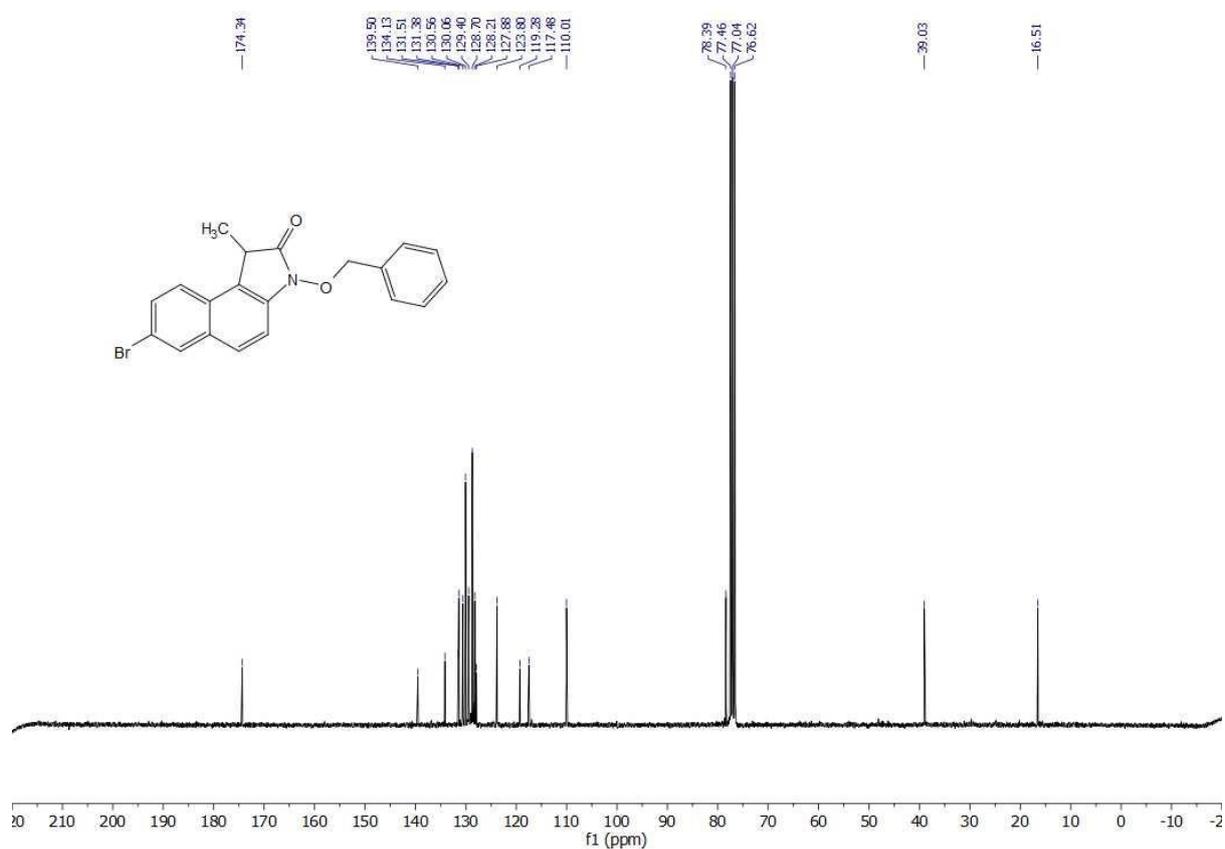
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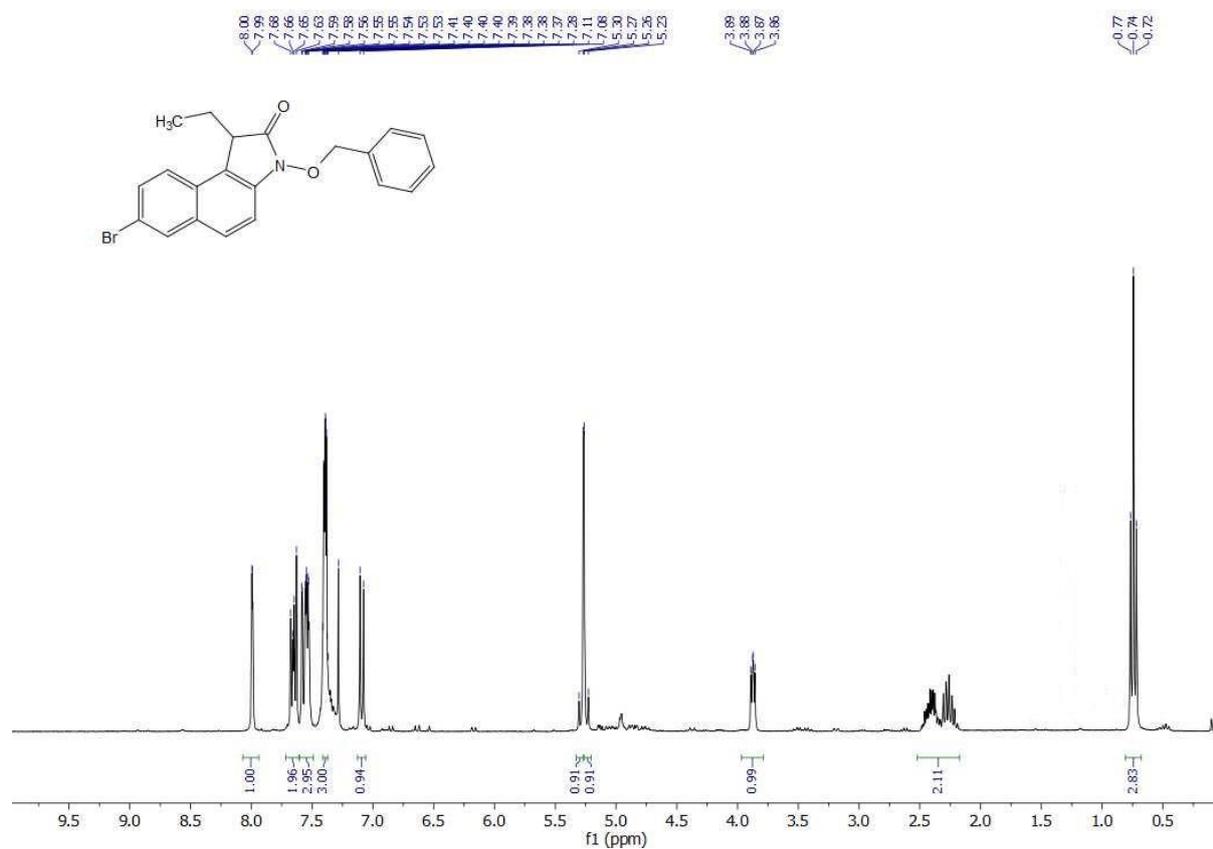
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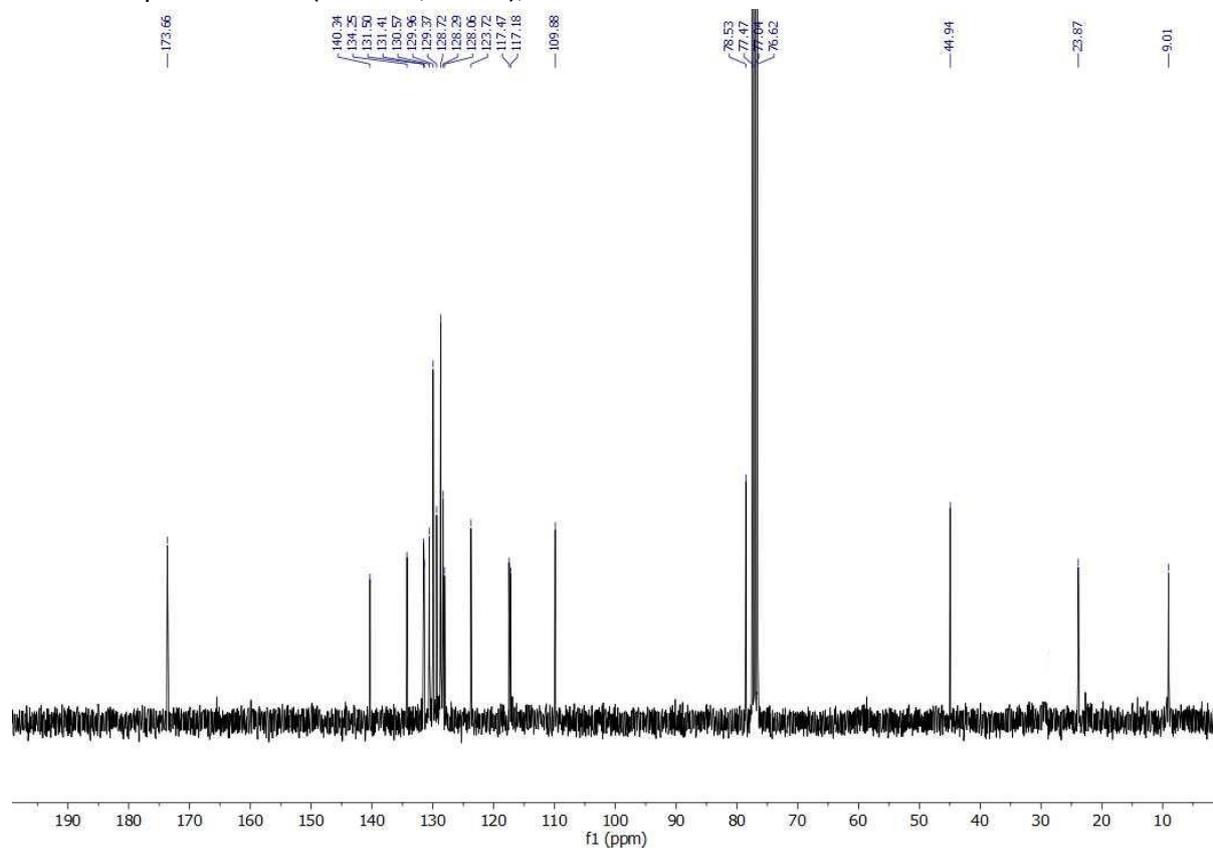
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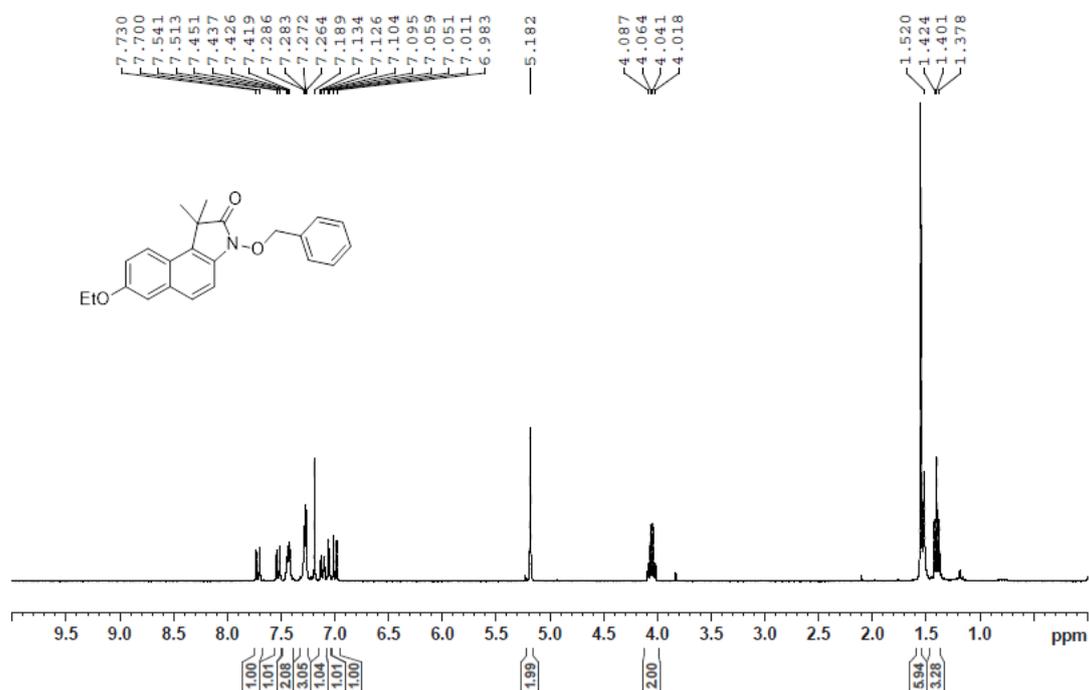
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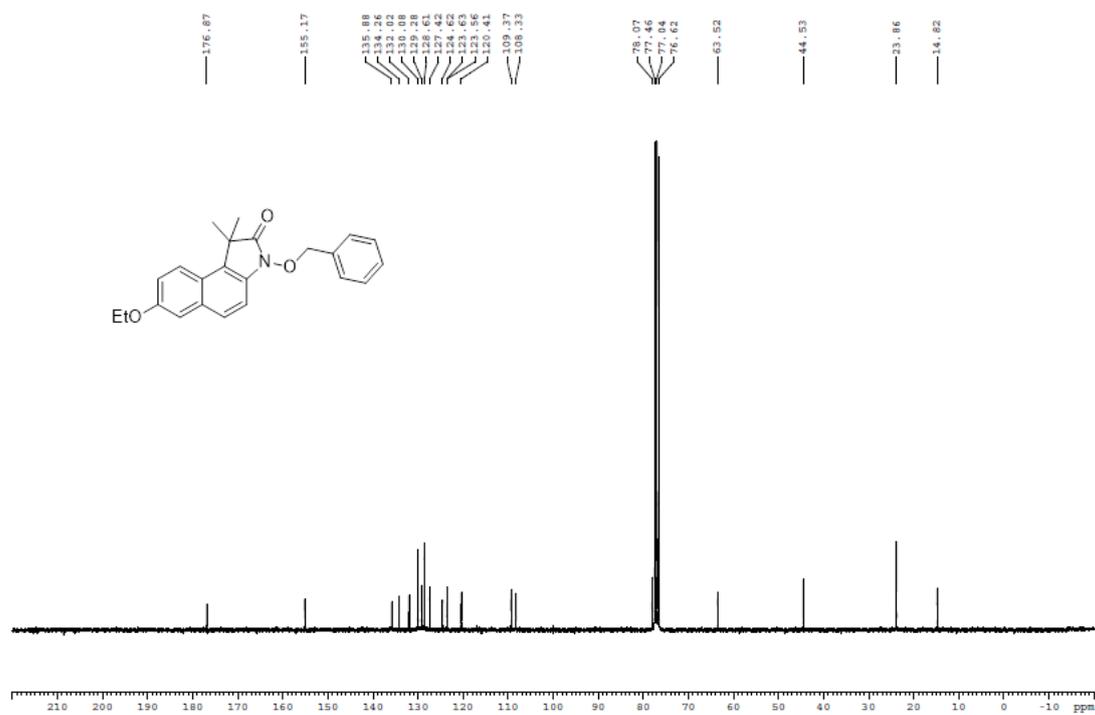
^{13}C NMR spectra of **3o** (75 MHz, CDCl_3);



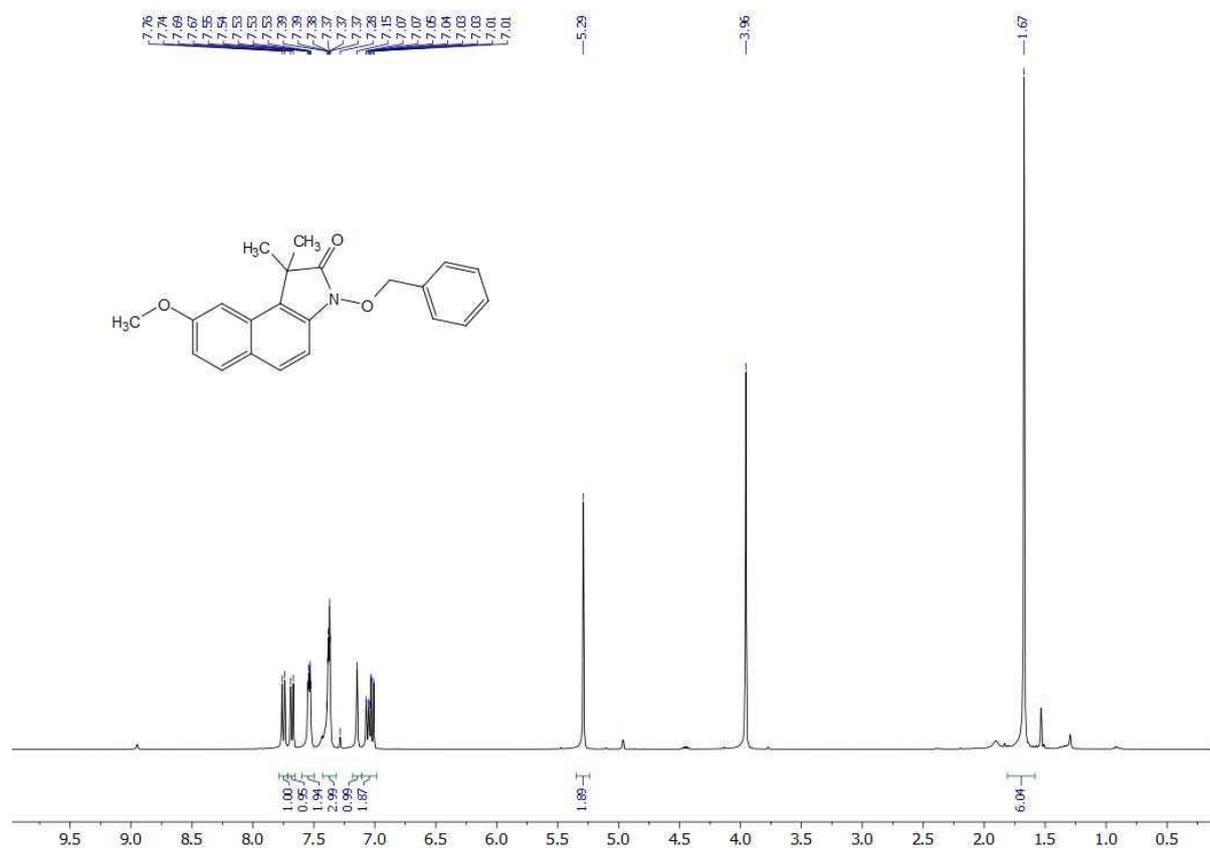
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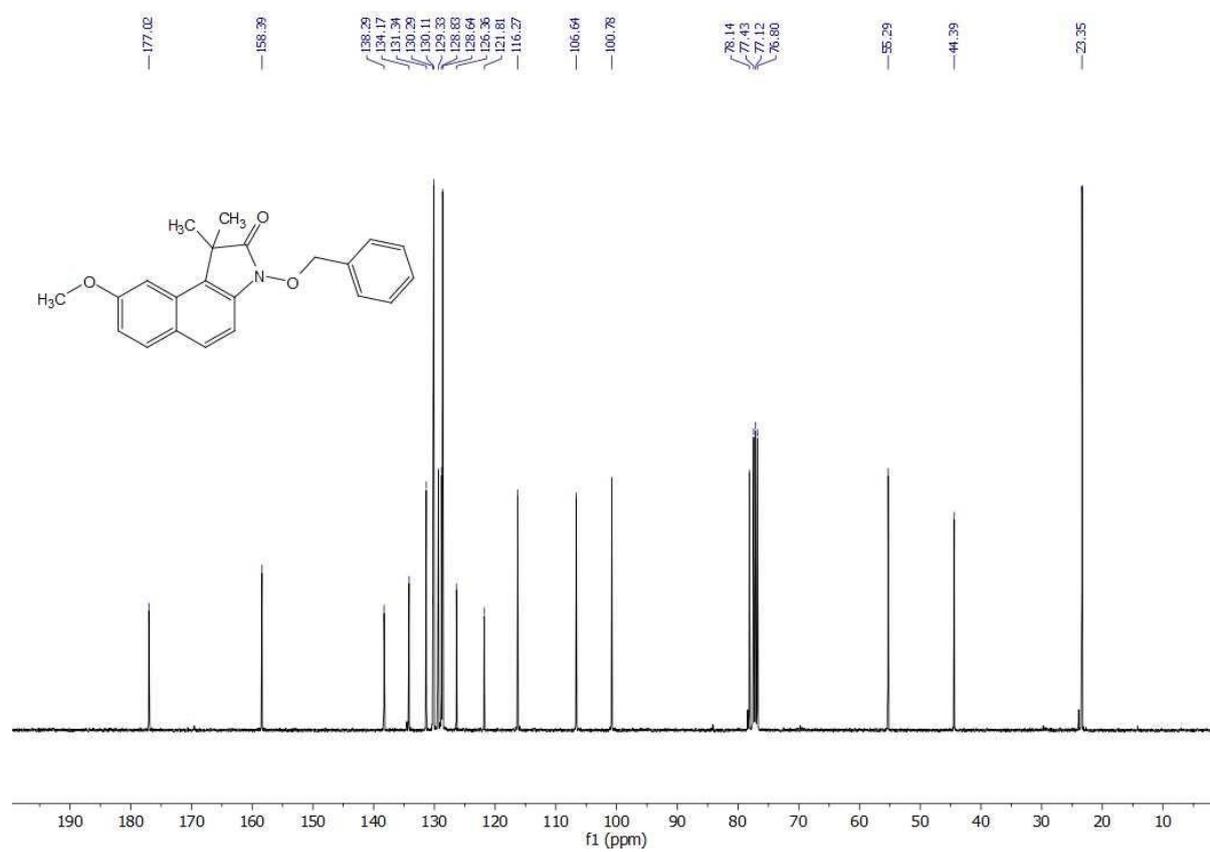
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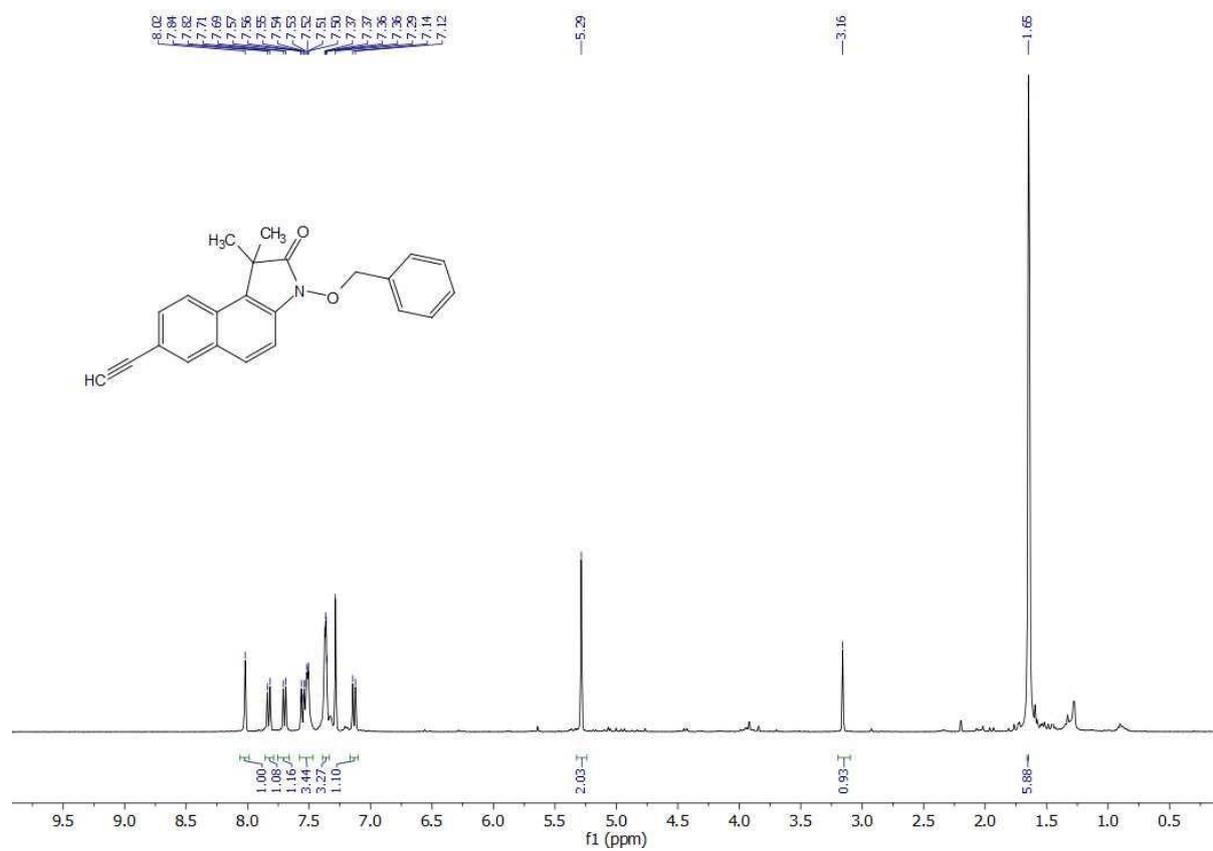
^1H NMR spectra of **3r** (400 MHz, CDCl_3);



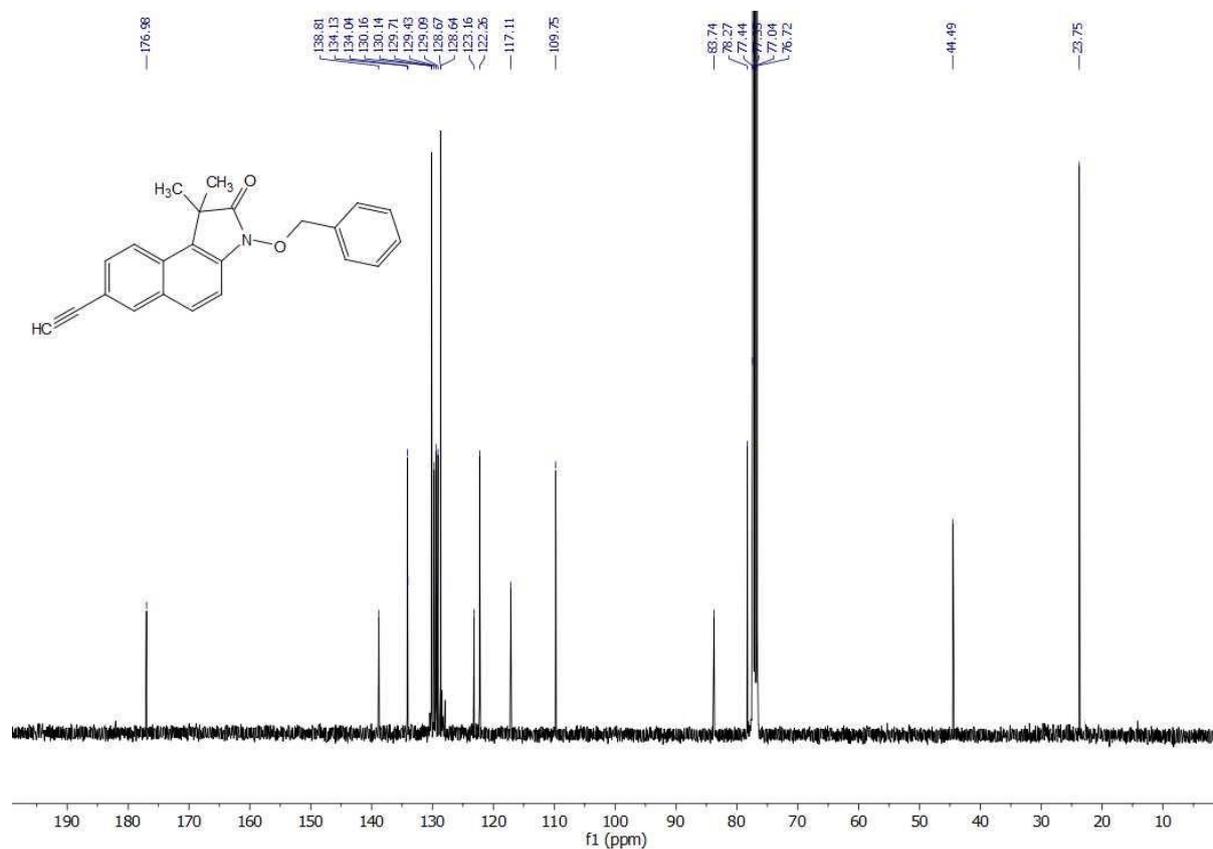
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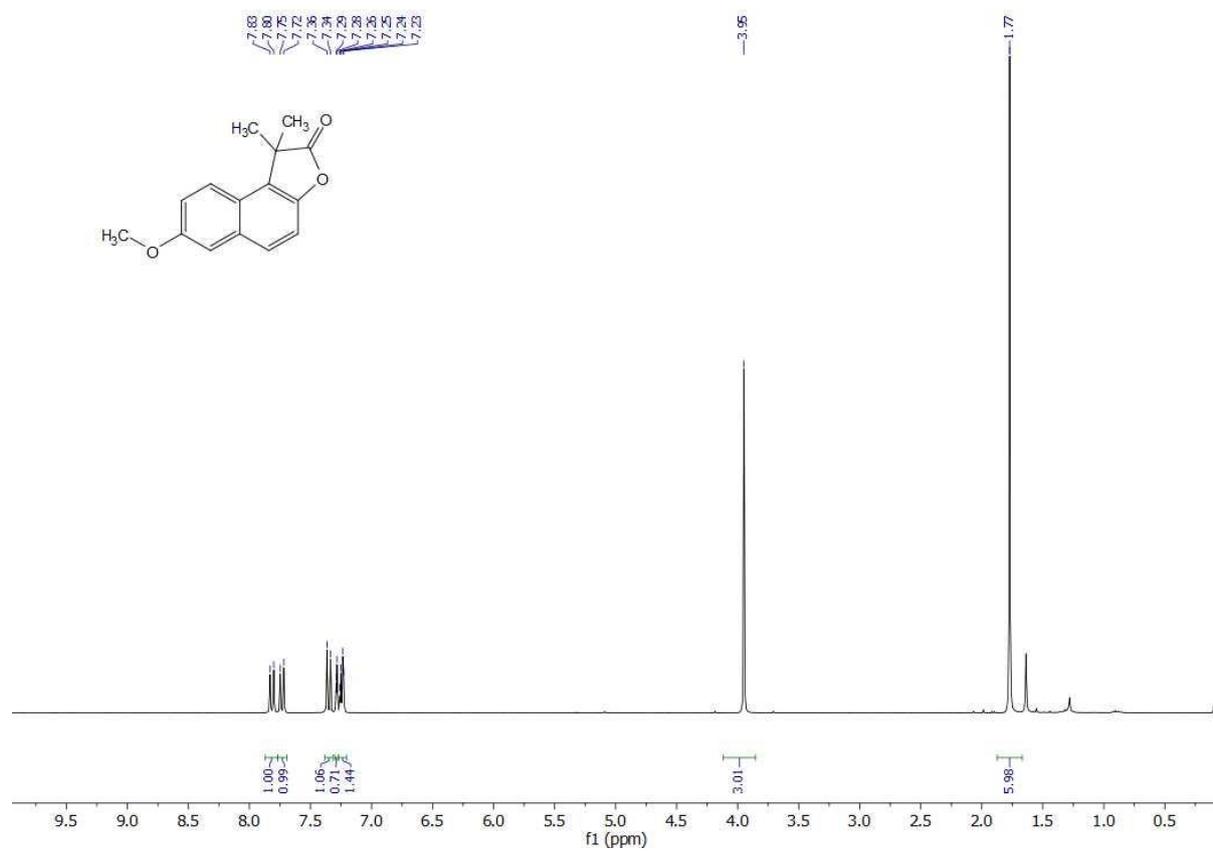
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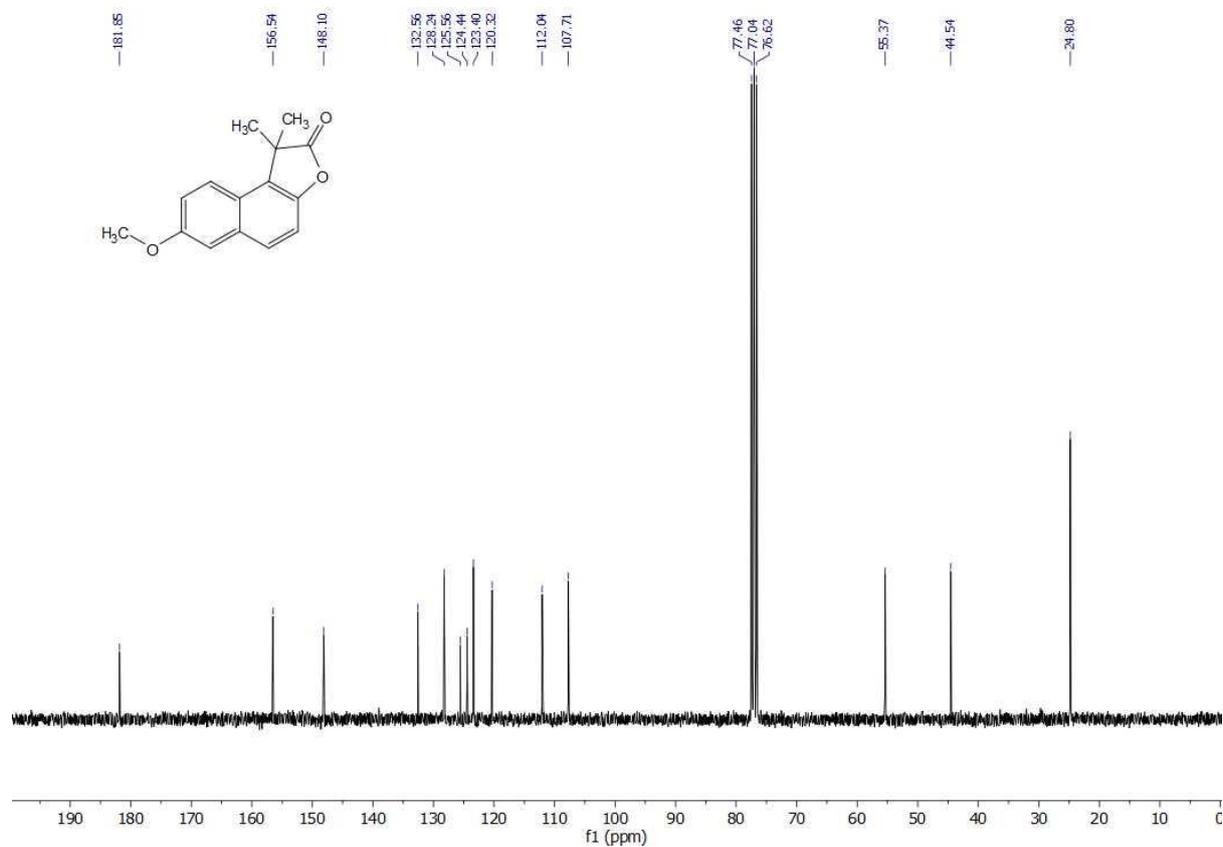
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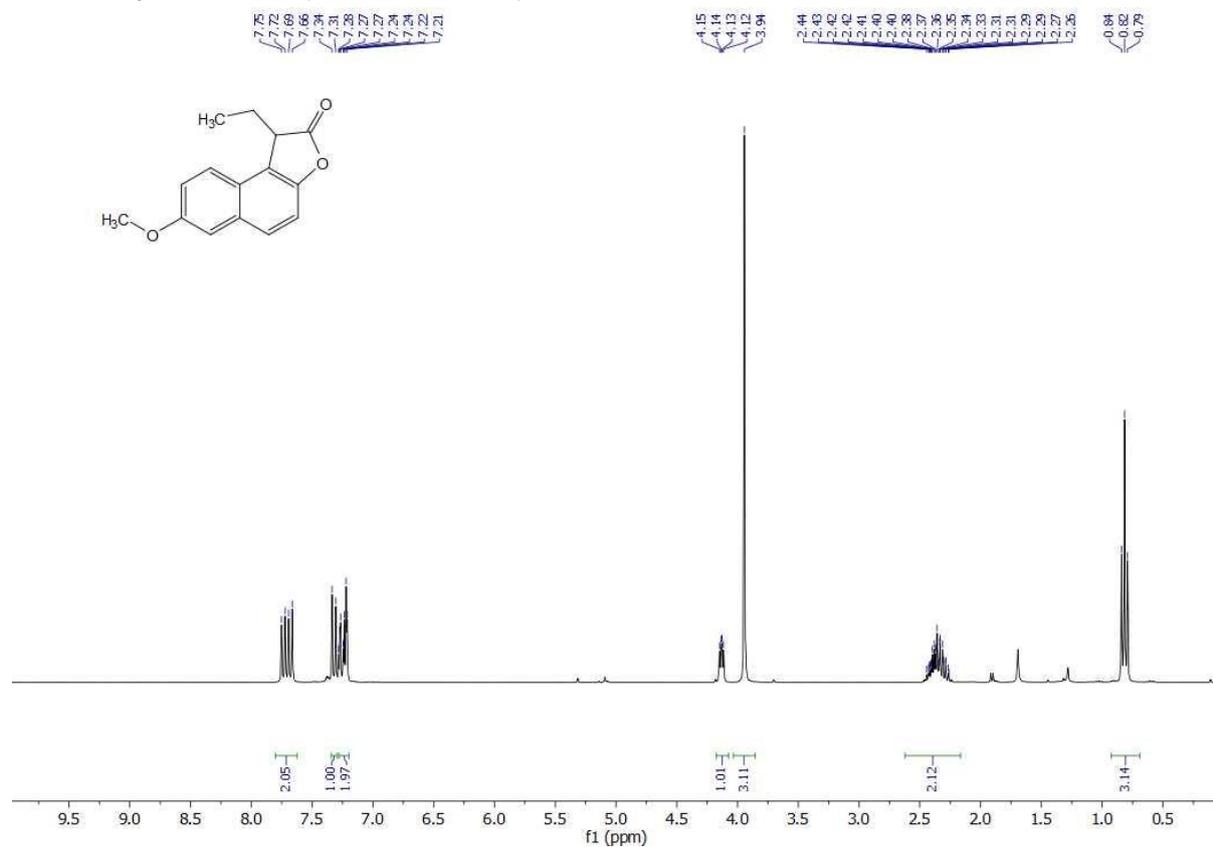
^1H NMR spectra of **4a** (300 MHz, CDCl_3);



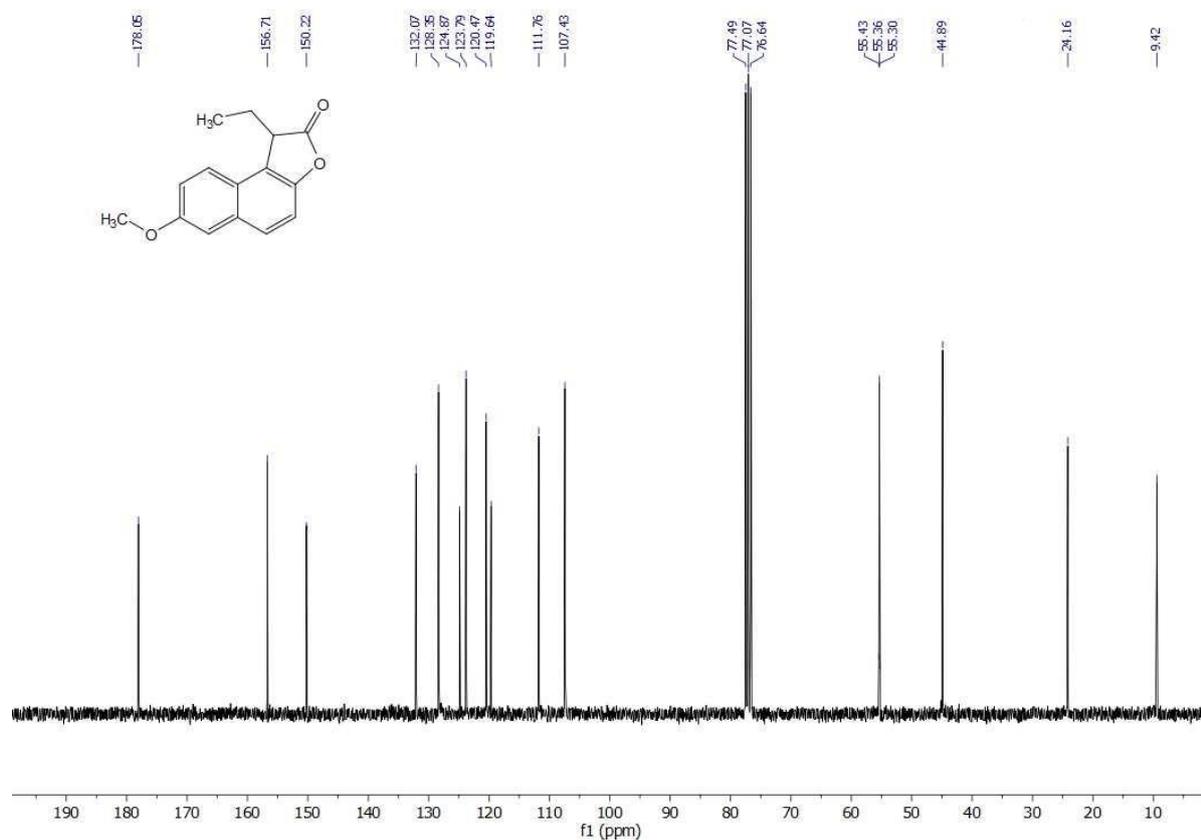
^{13}C NMR spectra of **4a** (75 MHz, CDCl_3);



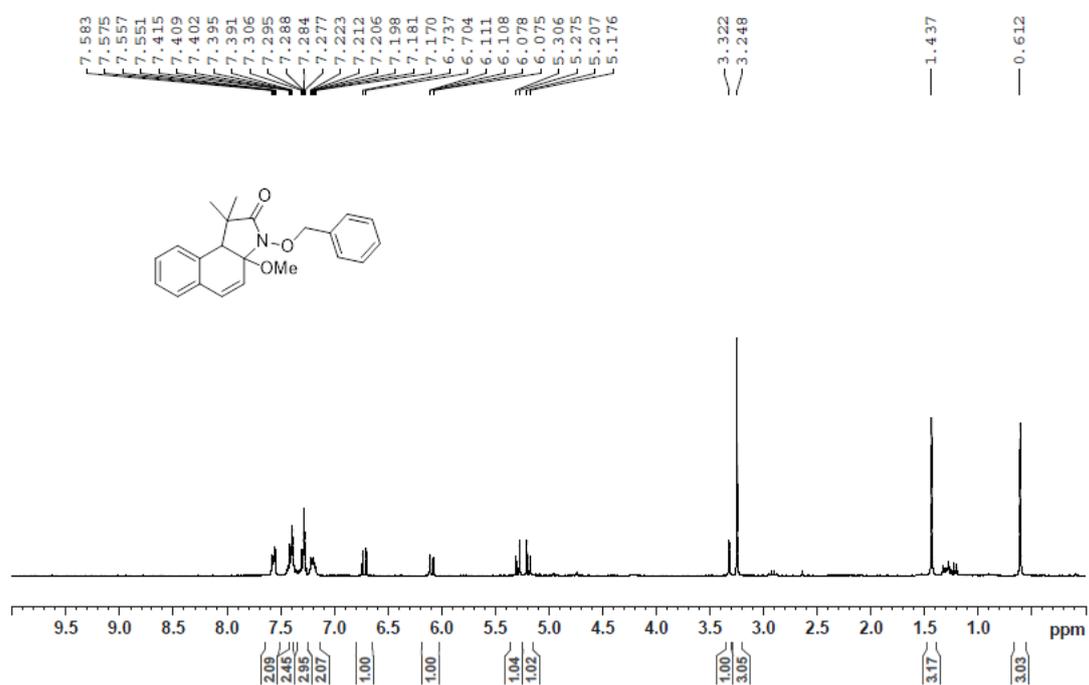
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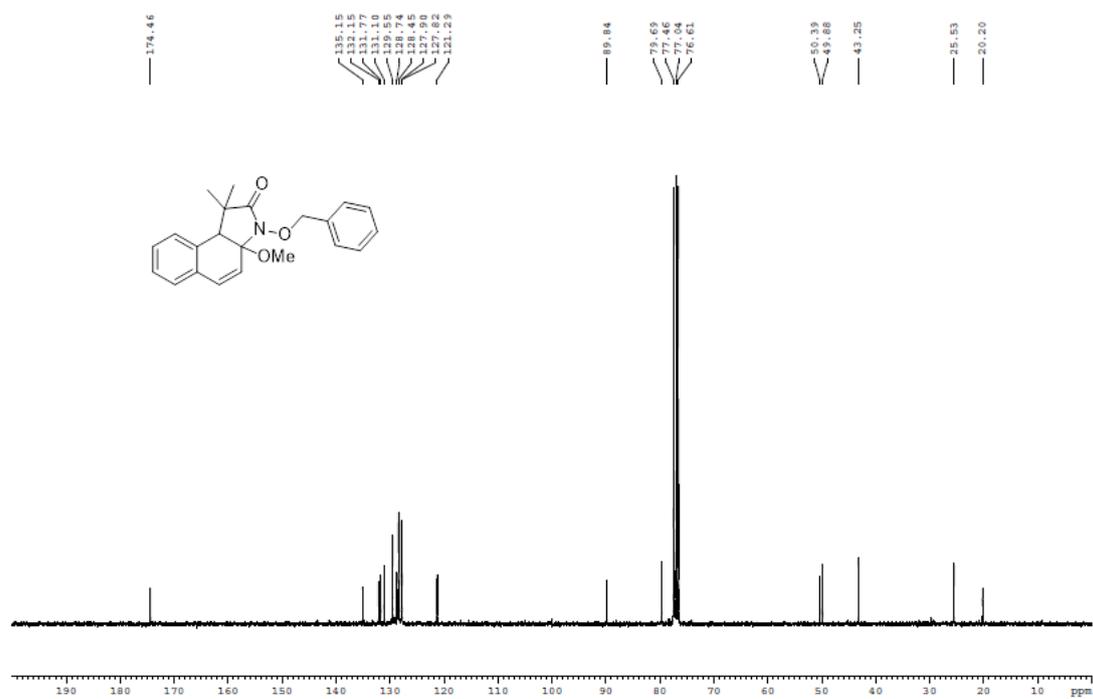
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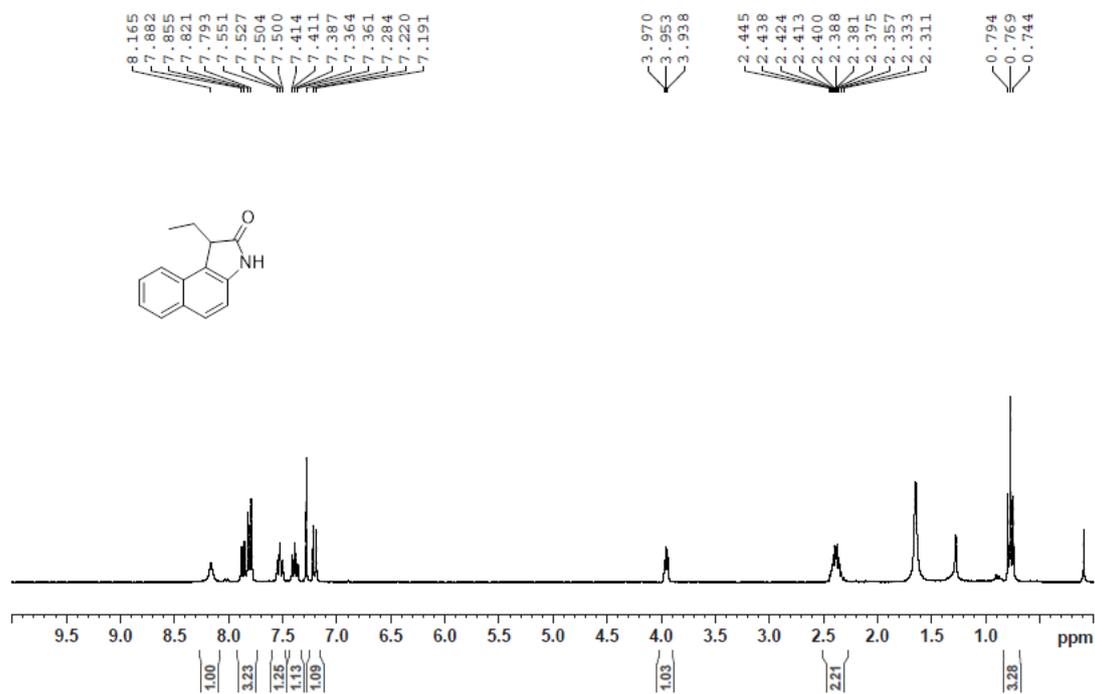
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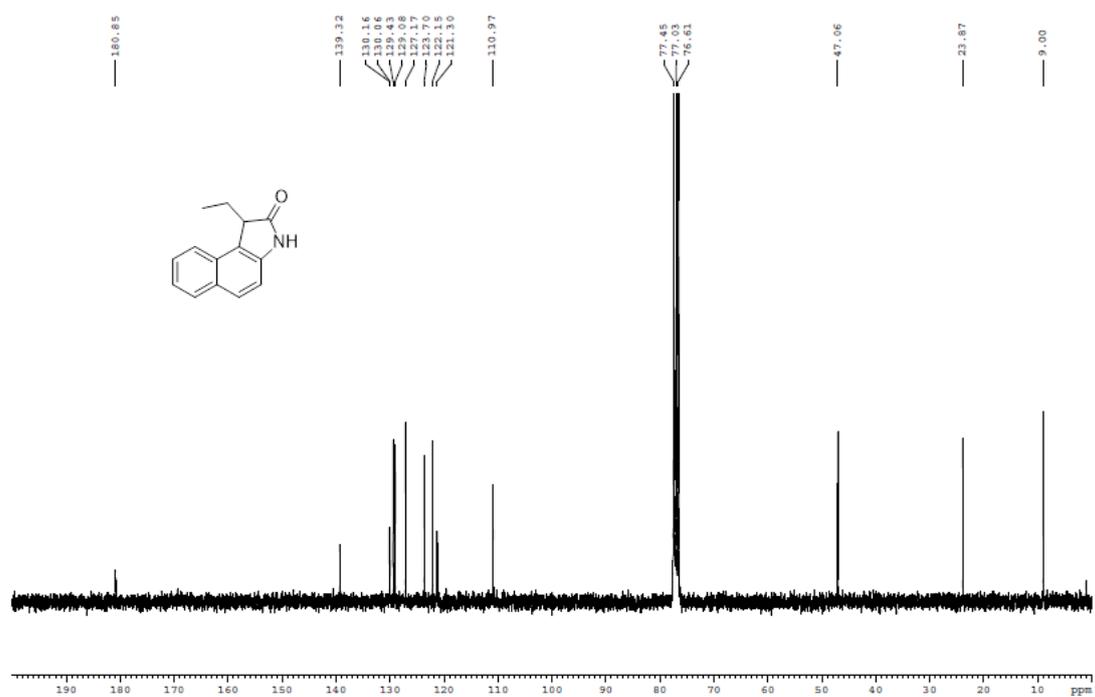
^{13}C NMR spectra of **3a'** (75 MHz, CDCl_3);



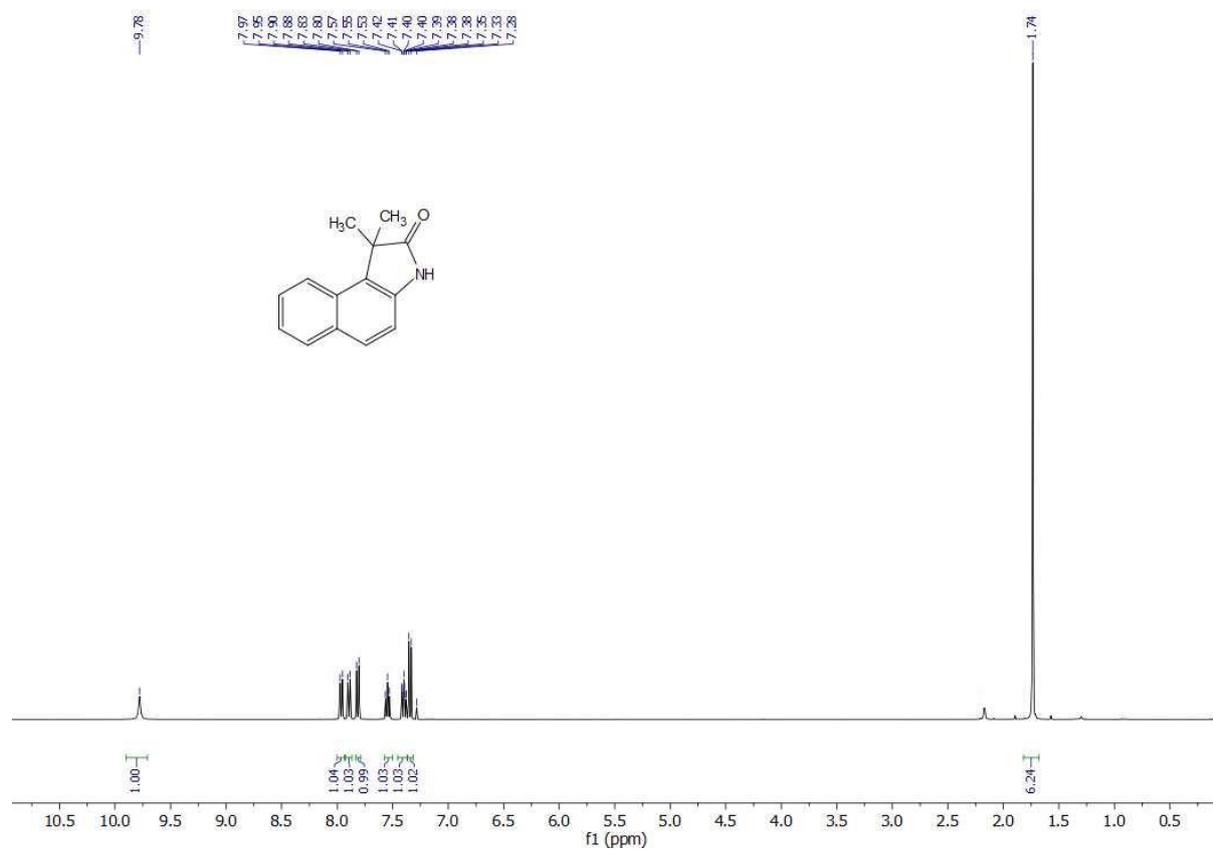
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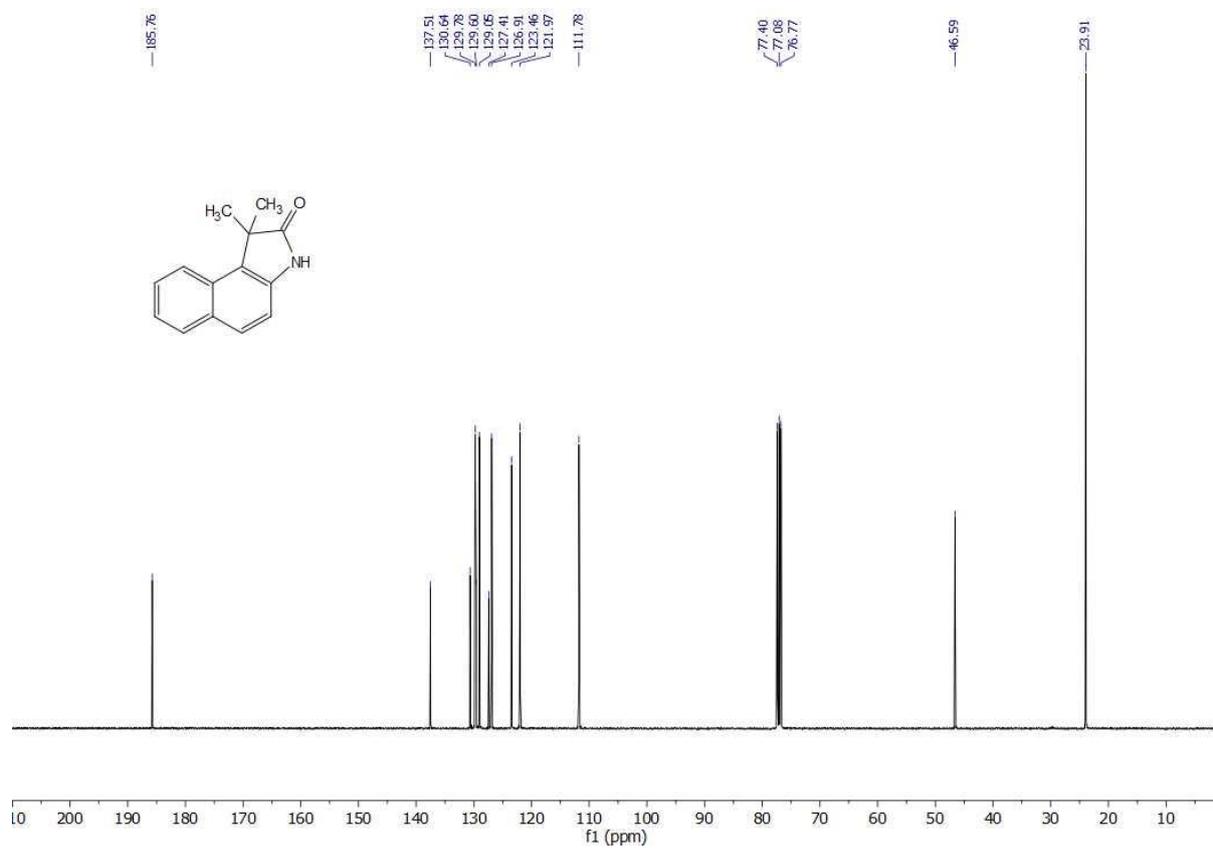
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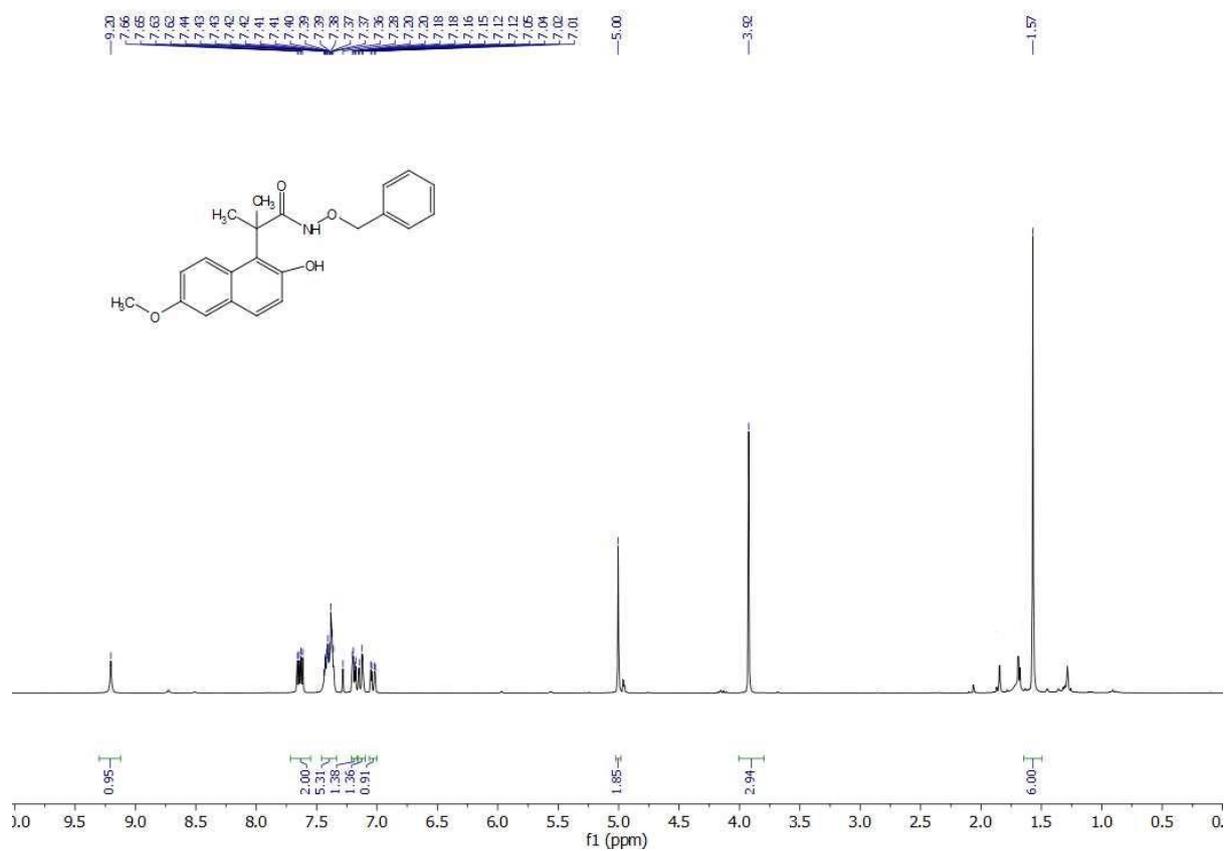
^1H NMR spectra of **5b** (400 MHz, CDCl_3);



^{13}C NMR spectra of **5b** (100 MHz, CDCl_3);



¹H NMR spectra of **4a'** (300 MHz, CDCl₃);



¹³C NMR spectra of **4a'** (100 MHz, CDCl₃);

