Electronic Supplementary Information

Intramolecular Addition of Benzyl Anion to Alkyne Utilizing [1,2]-Phospha-Brook Rearrangement under Brønsted Base Catalysis

Azusa Kondoh,[b] Ryosuke Ozawa,[a] Takuma Aoki[a] and Masahiro Terada*[a]

[a] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

[b] Research and Analytical Center for Giant Molecules, Graduate School of Science Tohoku University, Sendai 980-8578, Japan

Contents

General Information

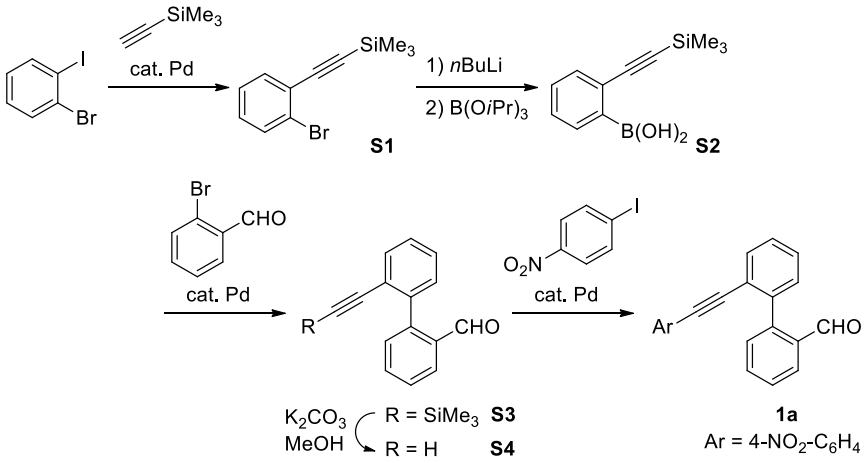
Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm; CD_3OD: 3.31 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm; CD_3OD: 49.0 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECA600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with 85% H_3PO_4 solution as an external standard (0.0 ppm in $CDCl_3$). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dichloromethane, tetrahydrofuran and toluene were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were purchased from commercial suppliers as dehydrated solvents, and used under argon atmosphere.

Experimental Procedure

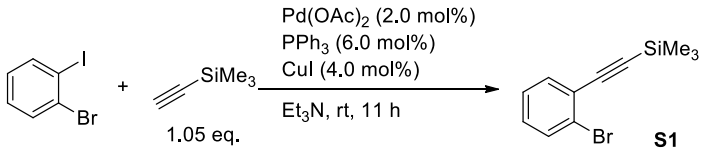
Procedure for Preparation of Biaryl Compounds 1.

Synthesis of **1a** is representative as shown in Scheme S1.



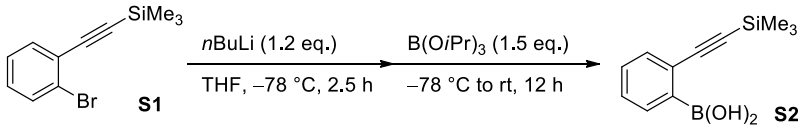
Scheme S1. Synthesis of **1a**

Synthesis of **S1**



2-Bromoiodobenzene (3.8 mL, 30 mmol) and ethynyltrimethylsilane (4.4 mL, 32 mmol) were sequentially added to a solution of palladium acetate (0.13 g, 0.60 mmol), triphenylphosphine (0.47 g, 1.8 mmol) and copper iodide (0.23 g, 1.2 mmol) in Et_3N (60 mL). The resulting mixture was stirred at ambient temperature for 11 h, and then sat. aq. NH_4Cl was added. The product was extracted with AcOEt, and the combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (hexane) afforded **S1** (7.6 g, 30 mmol, >99%) as a pale yellow oil.

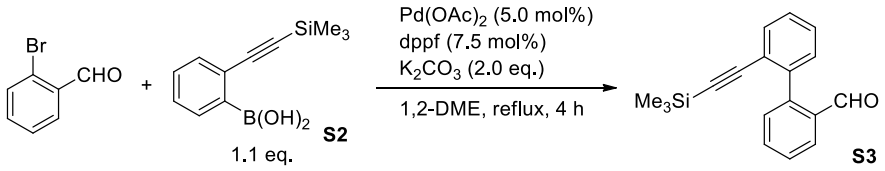
Synthesis of **S2**



To a solution of **S1** (5.1 g, 20 mmol) in THF (40 mL) was added dropwise a solution of *n*BuLi (1.6 M in hexane, 15 mL, 24 mmol) at –78 °C. After stirred for 2.5 h, triisopropyl borate (6.9 mL, 30 mmol) was added to the solution in one portion at that temperature. The resulting mixture was then allowed to warm to room temperature and was stirred for 12 h. The reaction was quenched with 2N aq. HCl, and the mixture was stirred for 10 min before the extraction of the product with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and

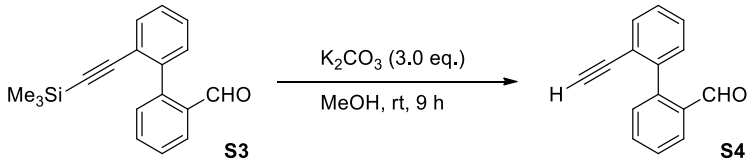
evaporated. The crude mixture was purified by recrystallization from hexane to afford **S2** (3.0 g, 14 mmol, 70%) as a white crystal.

Synthesis of **S3**



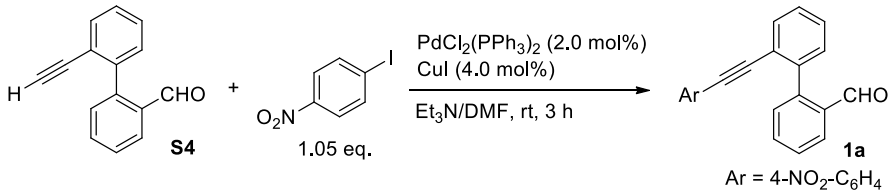
A mixture of palladium acetate (0.11 g, 0.50 mmol), DPPF (0.42 g, 0.75 mmol) and K_2CO_3 (2.8 g, 20 mmol) in 1,2-DME (30.0 mL) was stirred at room temperature for 30 min. 2-Bromobenzaldehyde (1.2 mL, 10 mmol) and **S2** (2.4 g, 11 mmol) were sequentially added, and the resulting mixture was then heated at reflux for 4 h. After cooled to room temperature, the reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography (hexane/AcOEt = 10:1) to yield **S3** (2.7 g, 9.8 mmol, 98%) as a yellow oil.

Synthesis of **S4**



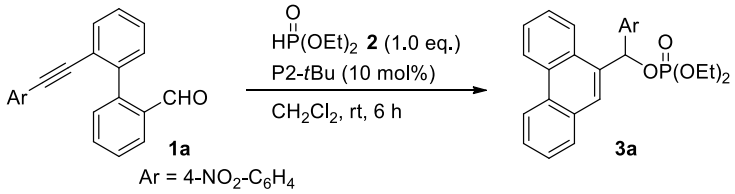
A mixture of **S3** (2.7 g, 9.8 mmol) and K_2CO_3 (4.1 g, 29 mmol) in MeOH (20 mL) was stirred at room temperature for 9 h. Sat. aq. NH_4Cl was added, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 10:1) to provide **S4** (1.9 g, 9.3 mmol, 95%) as a yellow oil.

Synthesis of **1a**



1-Iodo-4-nitrobenzene (0.52 g, 2.1 mmol) and a solution of **S4** (0.41 g, 2.0 mmol) in DMF (2.0 mL) were sequentially added to a solution of dichlorobis(triphenylphosphine)palladium (28 mg, 0.040 mmol) and copper iodide (15 mg, 0.080 mmol) in Et_3N (2.0 mL). The resulting mixture was stirred at ambient temperature for 3 h, and then sat. aq. NH_4Cl was added. The product was extracted with AcOEt, and the combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 5:1) to afford **1a** (0.47 g, 1.4 mmol, 72%) as a yellow solid.

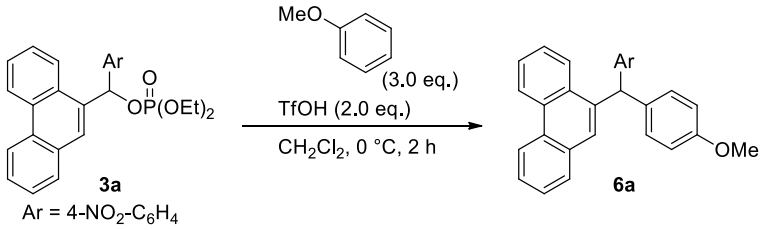
General Procedure for Intramolecular Cyclization Catalyzed by Phosphazene Base P2-*t*Bu.



The reaction of **1a** with diethyl phosphite (**2**) is representative (Table 1, entry 15).

To a solution of **1a** (82 mg, 0.25 mmol) and diethyl phosphite (**2**) (32 μL, 0.25 mmol) in CH_2Cl_2 (10 mL) was added a solution of P2-*t*Bu in THF (2.0 M, 13 μL, 0.025 mmol). The resulting mixture was then stirred at room temperature for 6 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 3:2 to 1:1) to provide **4a** (99 mg, 0.21 mmol, 86%) as a yellow solid.

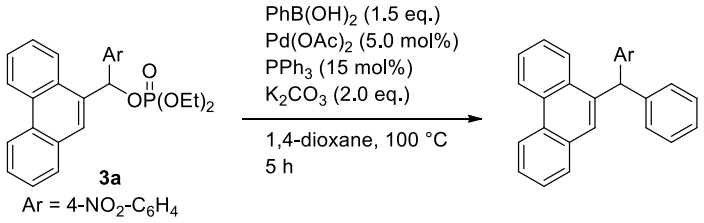
Procedure for Transformation of 3a by Friedel-Crafts Reaction (Scheme 4a).



The reaction of **3a** with anisole is representative.

To a solution of **3a** (46 mg, 0.10 mmol) and anisole (33 μL, 0.30 mmol) in CH_2Cl_2 (1.0 mL) was added TfOH (30 mg, 0.20 mmol) at 0 °C. After stirred at that temperature for 2 h, the reaction was quenched with sat. aq. $NaHCO_3$, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography (hexane/AcOEt = 10:1 to 5:1) to afford **6a** (37 mg, 0.088 mmol, 88%) as a white solid.

Procedure for Transformation of 3a by Pd-Catalyzed Cross-Coupling Reaction (Scheme 4b).



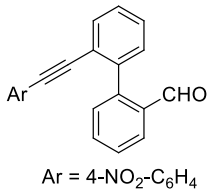
The reaction of **3a** with phenylboronic acid is representative.

A mixture of palladium acetate (1.1 mg, 5.0 μmol), triphenylphosphine (3.9 mg, 0.015 mmol) and K_2CO_3 (28 mg, 0.20 mmol) in 1,2-dioxane (0.50 mL) was stirred at room temperature for 30 min. A solution of **3a** (46 mg, 0.10 mmol) in 1,4-dioxane (0.50 mL) and phenylboronic acid (18 mg, 0.15 mmol) were sequentially added, and the

resulting mixture was then heated at 100 ℃ for 5 h. After cooled to room temperature, the reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography (hexane/AcOEt = 20:1 to 15:1) to provide **6b** (29 mg, 0.074 mmol, 74%) as a white solid.

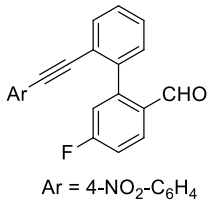
Analytical Data

2-Formyl -2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1a) :



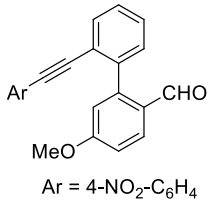
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 2H), 7.45 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.48 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.53 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.59 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.68 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.70 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 8.10 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 2H), 9.92 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.6, 93.3, 122.6, 123.5, 127.0, 128.4, 128.5, 129.5, 130.3, 131.2, 131.9, 132.2, 133.6 (2C), 134.2, 140.8, 143.8, 147.0, 191.6; IR (ATR): 2843, 2755, 2217, 1695, 1596, 1519, 1343, 1198, 1107 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{13}NO_3$ $[M+Na]^+$ 350.0788, Found 350.0788.

5-Fluoro-2-formyl-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1b):



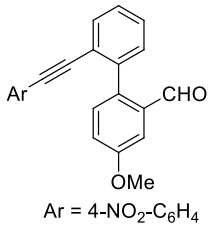
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.24-7.29 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.51 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.54 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 8.11-8.15 (m, 1H), 8.13 (d, *J* = 8.4 Hz, 2H), 9.83 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.9, 92.7, 115.9 (d, *J* = 23.1 Hz), 118.1 (d, *J* = 23.1 Hz), 122.4, 123.6, 128.9, 129.3, 129.6, 129.9 (d, *J* = 10.1 Hz), 130.1, 130.8, 131.9, 132.4, 139.4, 146.5 (d, *J* = 8.6 Hz), 147.1, 165.6 (d, *J* = 254.3 Hz), 189.9; IR (ATR): 3078, 2849, 2758, 2218, 1693, 1597, 1578, 1518, 1343, 1191, 1107 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{12}FNO_3$ $[M+Na]^+$ 368.0693, Found 368.0693.

2-Formyl-5-methoxy-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1c):



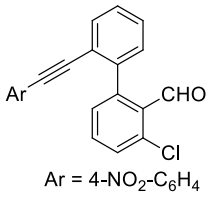
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.89 (d, *J* = 2.4 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.46 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.48 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.52 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.67 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 2H), 9.77 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.7, 91.6, 93.2, 114.3, 115.9, 122.5, 123.5, 127.8, 128.4, 129.4, 129.5, 129.6, 130.2, 131.9, 132.2, 140.8, 146.1, 147.0, 163.6, 190.3; IR (ATR): 2973, 2916, 2841, 2760, 2218, 1684, 1594, 1517, 1342, 1238, 1091, 933 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{15}NO_4$ $[M+Na]^+$ 380.0893, Found 380.0894.

2-Formyl-4-methoxy-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1d):



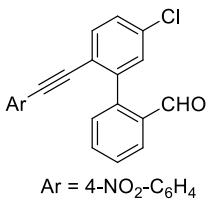
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.25 (dd, *J* = 8.4, 3.0 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.45 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.51 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.58 (d, *J* = 3.0 Hz, 1H), 7.67 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 2H), 9.88 (s,1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.7, 91.5, 93.5, 109.6, 121.0, 122.8, 123.5, 128.1, 129.5, 129.6, 130.7, 132.0, 132.3, 132.6, 135.1, 136.7, 140.5, 147.0, 159.6, 191.5; IR (ATR): 3077, 2940, 2847, 2752, 2217, 1691, 1597, 1519, 1472, 1343, 1279, 1164 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{15}NO_4$ $[M+Na]^+$ 380.0893, Found 380.0893.

3-Chloro-2-formyl-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1e):



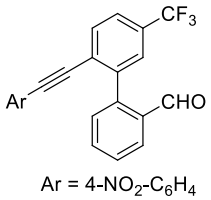
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dd, J = 4.2, 4.2 Hz, 1H), 7.34 (d, J = 9.0 Hz, 2H), 7.37 (dd, J = 7.8, 1.2 Hz, 1H), 7.45 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 7.50 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 7.54-7.58 (m, 2H), 7.63 (dd, J = 7.8, 1.2 Hz, 1H), 8.15 (d, J = 9.0 Hz, 2H), 10.2 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.7, 93.4, 121.4, 123.6, 128.2, 129.4, 129.5, 130.1, 130.6, 131.7, 131.9, 132.0, 132.2, 133.0, 135.3, 141.7, 144.1, 147.0, 190.0; IR (ATR): 3109, 3068, 2851, 2763, 2217, 1704, 1594 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{12}ClNO_3$ $[M+Na]^+$ 384.0398, Found 384.0398.

5'-Chloro-2-formyl-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1f):



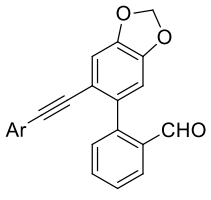
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.8 Hz, 1H), 7.47 (s, 1H), 7.45-7.48 (m, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.61 (dd, J = 7.8, 7.8 Hz, 1H), 7.72 (dd, J = 7.8, 7.8 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 2H), 9.92 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 92.1, 92.4, 121.2, 123.6, 127.3, 128.7, 129.0, 129.1, 130.3, 131.0, 131.9, 133.2, 133.8, 134.1, 135.6, 142.2, 142.5, 147.1, 191.1; IR (ATR): 2985, 2917, 2845, 2215, 1697, 1596, 1519, 1343, 1236 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{12}ClNO_3$ $[M+Na]^+$ 384.0398, Found 384.0398.

2-Formyl-2'-(4-nitrophenyl)ethynyl-5'-trifluoromethyl-1,1'-biphenyl (1g):



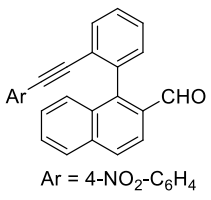
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 7.2 Hz, 1H), 7.64 (dd, J = 7.2, 7.2 Hz, 1H), 7.72-7.76 (m, 3H), 7.79 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 9.91 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.6, 93.6, 123.5 (q, J = 271.5 Hz), 123.6, 125.1, 126.3, 126.9, 127.6, 128.6, 129.2, 131.1, 131.2 (q, J = 31.7 Hz), 132.1, 132.5, 133.9, 134.1, 141.7, 142.0, 147.4, 190.9; IR (ATR): 2848, 2754, 2223, 1697, 1612, 1596, 1520, 1173, 1125 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{12}F_3NO_3$ $[M+Na]^+$ 418.0662, Found 418.0661.

4',5'-Dioxymethylene-2-formyl-2'-(4-Nitrophenyl)ethynyl-1,1'-biphenyl (1h):



^{1}H NMR (600 MHz, $CDCl_3$) δ 6.11 (s, 2H), 6.91 (s, 1H), 7.08 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.40 (dd, J = 7.8, 0.6 Hz, 1H), 7.57 (ddd, J = 7.8, 7.8, 0.6 Hz, 1H), 7.68 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 8.07 (dd, J = 7.8, 1.2 Hz, 1H), 8.09 (d, J = 8.4 Hz, 2H), 9.95 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 90.3, 93.7, 102.1, 110.5, 111.3, 115.9, 123.5, 127.0, 128.4, 129.7, 131.3, 131.6, 133.6, 134.5, 136.1, 143.5, 146.8, 147.7, 149.1, 191.6; IR (ATR): 2900, 2845, 2207, 1693, 1593, 1516, 1475, 1340, 1223, 1036 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{13}NO_5$ $[M+Na]^+$ 394.0686, Found 394.0686.

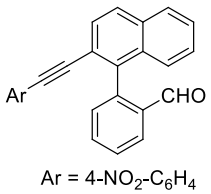
2-Formyl-1-[2-(4-nitrophenyl)ethynyl]phenylnaphthalene (1i):



^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, J = 9.0 Hz, 2H), 7.48 (ddd, J = 7.8, 6.6, 1.2 Hz, 1H), 7.51 (dd, J = 6.6, 2.4 Hz, 1H), 7.57-7.62 (m, 3H), 7.64 (ddd, J = 7.8, 6.6, 1.2 Hz, 1H), 7.77 (dd, J = 6.6, 2.4 Hz, 1H), 7.96-8.00 (m, 3H), 8.02 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 9.0 Hz, 1H), 9.90 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 92.1, 92.9, 122.0, 123.4, 123.8, 127.1, 127.3, 128.3, 128.7, 128.86, 128.91, 129.1, 129.3, 131.4, 131.5, 131.8, 132.1 (2C), 136.1, 138.5, 144.5,

146.8, 192.1; IR (ATR): 3104, 3061, 2849, 2736, 2218, 1691, 1677, 1595, 1518, 1342, 1233, 1106 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{15}NO_3$ $[M+Na]^+$ 400.0944, Found 400.0944.

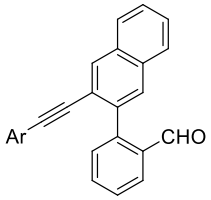
1-(2-Formyl)phenyl-2-(4-nitrophenyl)ethynylnaphthalene (1j);



Ar = 4-NO_2-C_6H_4

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.0 Hz, 2H), 7.45-7.48 (m, 3H), 7.54-7.59 (m, 1H), 7.69 (ddd, *J* = 8.4, 8.4, 0.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.71 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 2H), 8.20 (dd, *J* = 7.8, 0.6 Hz, 1H), 9.66 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 92.6, 94.1, 120.4, 123.5, 126.4, 127.2, 127.4, 127.5, 127.6, 128.3, 128.69, 128.74, 129.6, 131.9, 132.0, 132.5. 133.3, 133.7, 135.1, 139.4, 142.3, 146.9, 191.4; IR (ATR): 3057, 2839, 2746, 2206, 1697, 1596, 1517, 1341, 1195, 1108, 854 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{15}NO_3$ $[M+Na]^+$ 400.0944, Found 400.0944.

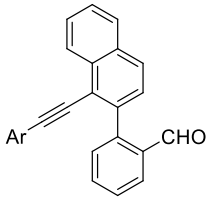
2-(2-Formyl)phenyl-3-(4-nitrophenyl)ethynylnaphthalene (1k):



Ar = 4-NO_2-C_6H_4

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.59-7.64 (m, 3H), 7.73 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.88-7.94 (m, 3H), 8.11-8.15 (m, 1H), 8.13 (d, *J* = 8.4 Hz, 2H), 8.23 (s, 1H), 9.96 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.8, 93.8, 120.2, 123.6, 127.0, 127.5, 127.8, 128.0, 128.1, 128.5, 129.6 (2C), 131.6, 131.9, 132.5, 132.7, 133.0, 133.6, 134.6, 137.0, 143.7, 147.0, 191.6; IR (ATR): 3057, 2923, 2851, 2752, 2213, 1693, 1595, 1516, 1340, 1236, 1091, 893 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{15}NO_3$ $[M+Na]^+$ 400.0944, Found 400.0944.

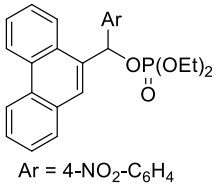
2-(2-Formyl)phenyl-1-(4-nitrophenyl)ethynylnaphthalene (1l):



Ar = 4-NO_2-C_6H_4

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.72 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.74 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 9.0 Hz, 2H), 8.46 (d, *J* = 8.4 Hz, 1H), 9.95 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.6, 96.8, 119.9, 123.6, 126.3, 127.0, 127.3, 127.5, 128.1, 128.45, 128.51, 129.6, 129.7, 131.4, 131.9, 132.6, 132.8, 133.6, 134.4, 139.8, 144.4, 147.0, 191.6; IR (ATR): 3056, 2924, 2851, 2756, 2207, 1693, 1594, 1517, 1436, 1340, 1104 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{15}NO_3$ $[M+Na]^+$ 400.0944, Found 400.0944.

9-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3a):

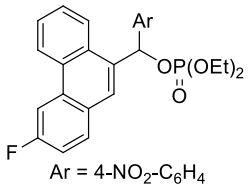


Ar = 4-NO_2-C_6H_4

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 3.86 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 3.91 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 3.99 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.09 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.73 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.62-7.68 (m, 2H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 8.70 (d, *J* = 7.8 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.77; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 63.99 (d, *J* = 5.8 Hz), 64.04 (d, *J* = 7.1 Hz), 79.1, 122.5, 123.3, 123.7 (2C), 125.0, 126.7, 126.8, 127.1,

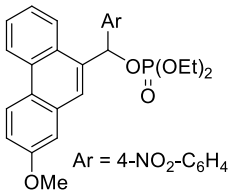
127.7, 127.8, 128.0, 128.5, 129.1, 130.7, 131.1, 132.1 (d, *J* = 2.9 Hz), 146.9 (d, *J* = 5.7 Hz), 147.5; IR (ATR): 3080, 3070, 2983, 2930, 2908, 2372, 2336, 1604, 1522, 1497, 1451, 1348, 1270, 1165, 1108, 1032, 998 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{24}NO_6P$ $[M+Na]^+$ 488.1234, Found 488.1234.

9-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]- 3-fluorophenanthrene (3b)



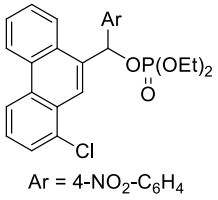
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 3.85 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 3.90 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.00 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 4.09 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.41 (ddd, *J* = 8.4, 8.4, 2.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.62-7.66 (m, 1H), 7.91-7.96 (m, 2H), 7.97 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 8.29 (dd, *J* = 10.8, 2.4 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.77; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 5.9 Hz), 16.0 (d, *J* = 7.2 Hz), 64.0 (d, *J* = 5.7 Hz), 64.1 (d, *J* = 5.7 Hz), 79.0, 107.9 (d, *J* = 21.6 Hz), 116.2 (d, *J* = 24.5 Hz), 123.6, 123.8, 125.1, 126.8, 127.4, 127.5, 127.8, 128.8, 130.5 (d, *J* = 4.4 Hz), 131.2, 131.3, 131.5, 132.4 (d, *J* = 8.6 Hz), 146.8 (d, *J* = 5.7 Hz), 147.6, 162.2 (d, *J* = 245.6 Hz); IR (ATR): 3082, 2985, 2909, 1630, 1605, 1523, 1504, 1452, 1348, 1271, 1178, 1032, 999, 899 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{23}FNO_6P$ $[M+Na]^+$ 506.1139, Found 506.1139.

9-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]-2-methoxyphenanthrene (3d):



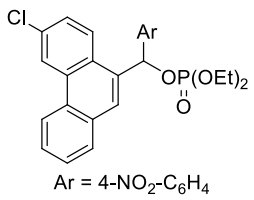
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 3.85 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 3.92 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 3.98 (s, 3H), 4.00 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.10 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 3.0 Hz, 1H), 7.34 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.43 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.59 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.93 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 2H), 8.58 (d, *J* = 9.0 Hz, 1H), 8.62 (d, *J* = 7.8 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.79; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 5.7 Hz), 16.0 (d, *J* = 7.2 Hz), 55.5, 64.0 (d, *J* = 5.9 Hz), 64.1 (d, *J* = 5.7 Hz), 79.0(d, *J* = 3.0 Hz), 109.0, 118.3, 122.9, 123.7, 124.2, 124.9, 125.0, 125.8, 126.8, 127.5, 127.6, 127.8, 131.3, 132.2, 132.8(d, *J* = 2.9 Hz), 147.0(d, *J* = 5.7 Hz), 147.6, 158.6; IR (ATR): 3080, 2983, 2937, 2909, 2840, 1605, 1522, 1347, 1269, 1231, 1033, 998 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{26}NO_7P$ $[M+Na]^+$ 518.1339, Found 518.1339.

1-Chloro-9-[diethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3e):



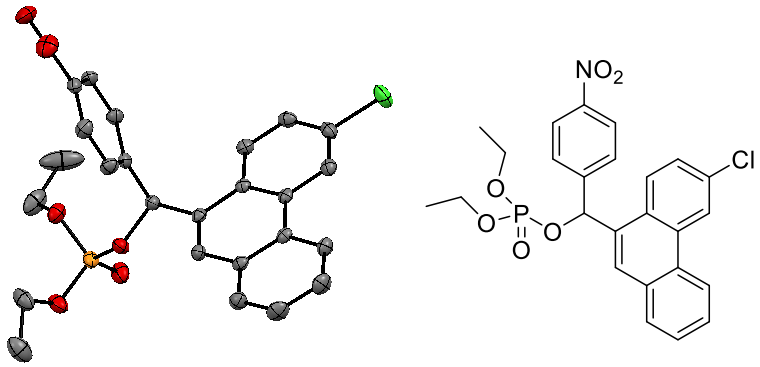
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 3.95-4.03 (m, 3H), 4.07 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.53 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.63 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.64-7.67 (m, 1H), 7.66 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 9.0 Hz, 2H), 8.53 (s, 1H), 8.63 (d, *J* = 7.8 Hz, 1H), 8.73 (d, *J* = 7.8 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.91; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 8.6 Hz), 64.16 (d, *J* = 7.1 Hz), 64.20 (d, *J* = 7.2 Hz), 79.0, 121.6, 123.1, 123.7, 123.8, 125.1, 127.3, 127.5, 127.56, 127.60, 128.1, 128.2, 128.4, 130.8, 132.3, 133.2, 133.7 (d, *J* = 4.4 Hz), 146.7 (d, *J* = 5.7 Hz); IR (ATR): 3079, 2984, 2909, 1606, 1523, 1448, 1348, 1273, 1024, 999 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{23}ClNO_6P$ $[M+Na]^+$ 522.0844, Found 522.0844.

3-Chloro-10-[diethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3f):

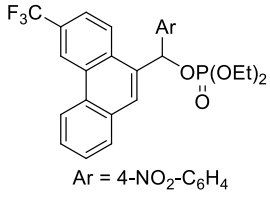


^{1}H NMR (600 MHz, $CDCl_3$) δ 1.05 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H), 3.86 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 3.91 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 4.01 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.10 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 7.05 (d, J = 9.0 Hz, 1H), 7.44 (dd, J = 9.0, 1.2 Hz, 1H), 7.62 (d, J = 9.0 Hz, 2H), 7.69 (dd, J = 7.8, 7.8 Hz, 1H), 7.74 (dd, J = 7.8, 7.8 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.97 (s, 1H), 8.18 (d, J = 9.0 Hz, 2H), 8.61 (d, J = 9.0 Hz, 1H), 8.69 (d, J = 1.2 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.73; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.1 Hz), 16.0 (d, J = 7.2 Hz), 64.1 (d, J = 5.9 Hz), 64.2 (d, J = 5.7 Hz), 79.2, 122.7, 123.1, 123.8, 126.6, 126.9, 127.3, 127.7, 127.8, 128.1, 128.5, 129.2, 129.8, 131.1, 131.9 (d, J = 4.4 Hz), 132.5, 133.1, 146.7 (d, J = 5.9 Hz), 147.7; IR (ATR): 3071, 2984, 2928, 2909, 2866, 2854, 1599, 1522, 1496, 1348, 1269, 1032, 998 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{23}ClNO_6P$ $[M+Na]^+$ 522.0844, Found 522.0844; CCDC No. 1546787. A single crystal for single-crystal X-ray diffraction analysis was obtained by recrystallization from hexane/AcOEt.

Figure S1. ORTEP diagram of **3f**.
Hydrogens are omitted for clarity.

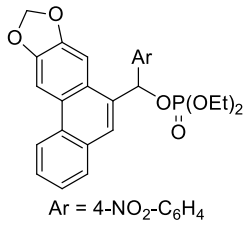


10-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]-3-trifluoromethylphenanthrene (3g):



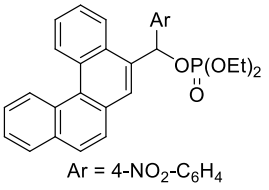
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.05 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 3.86 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 3.91 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 4.02 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 4.11 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 9.0 Hz, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.73 (dd, J = 7.8, 7.8 Hz, 1H), 7.80 (dd, J = 7.8, 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H), 8.20 (d, J = 9.0 Hz, 2H), 8.72 (d, J = 7.8 Hz, 1H), 9.00 (s, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.71; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz), 16.0 (d, J = 7.2 Hz), 64.1 (d, J = 5.7 Hz), 64.2 (d, J = 5.9 Hz), 79.0, 120.8 (q, J = 2.9 Hz), 122.6, 122.7 (q, J = 2.9 Hz), 123.8, 124.2 (q, J = 270.0 Hz), 126.0, 127.7, 128.0, 128.45, 128.47 (q, J = 33.0 Hz), 129.4, 130.4, 130.47, 130.54, 130.9, 131.0, 131.8 (d, J = 4.4 Hz), 146.5 (d, J = 7.2 Hz), 147.7; IR (ATR): 2984, 2908, 1734, 1605, 1524, 1349, 1321, 1277, 1124, 1034, 1000 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{23}F_3NO_6P$ $[M+Na]^+$ 556.1107, Found 556.1107.

10-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]-2,3-dioxymethylenephenanthrene (3h):



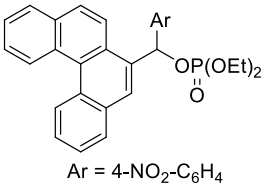
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.05 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H), 3.86 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 3.91 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 4.01 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 4.11 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 6.05 (s, 1H), 6.06 (s, 1H), 6.97 (d, J = 8.4 Hz, 1H), 7.25 (s, 1H), 7.59 (dd, J = 7.8, 7.8 Hz, 1H), 7.61 (d, J = 9.0 Hz, 2H), 7.66 (dd, J = 7.8, 7.8 Hz, 1H), 7.91 (s, 1H), 7.92 (d, J = 7.8 Hz, 1H), 8.05 (s, 1H), 8.17 (d, J = 9.0 Hz, 2H), 8.46 (d, J = 7.8 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.74; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz), 16.0 (d, J = 5.9 Hz), 64.0 (d, J = 5.7 Hz), 64.1 (d, J = 4.4 Hz), 79.8, 101.4, 101.6, 103.0, 122.3, 123.8, 124.9, 126.3, 126.8, 127.4, 127.7, 127.8, 129.1, 130.2, 130.6, 131.6 (d, J = 3.0 Hz), 146.9 (d, J = 5.7 Hz), 147.6, 147.7, 148.0; IR (ATR): 2985, 2907, 1605, 1523, 1503, 1474, 1348, 1266, 1244, 1217, 1033, 999 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{24}NO_8P$ $[M+Na]^+$ 532.1131, Found 532.1131.

5-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]benzo[c]phenanthrene (3i):



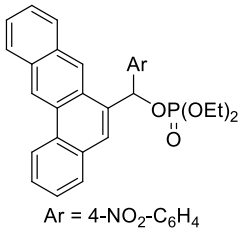
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.04 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 3.86 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.91 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.00 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 4.10 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.54 (dd, J = 7.8, 7.2 Hz, 1H), 7.64-7.72 (m, 3H), 7.67 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 8.07 (s, 1H), 8.19 (d, J = 8.4 Hz, 2H), 9.05 (d, J = 8.4 Hz, 1H), 9.13 (d, J = 8.4 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.73; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 5.7 Hz), 16.0 (d, J = 7.2 Hz), 64.06 (d, J = 5.9 Hz), 64.11 (d, J = 7.2 Hz), 78.7 (d, J = 3.0 Hz), 123.8, 124.5, 126.1, 126.2, 126.4, 126.5, 126.7, 127.7 (2C), 128.0, 128.1 (2C), 128.3, 128.6, 128.8, 129.7, 129.8, 131.1, 132.5 (d, J = 2.9 Hz), 133.9, 147.0 (d, J = 4.4 Hz), 147.6; IR (ATR): 2976, 2911, 1526, 1347, 1236, 1090, 1034, 932, 887 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{26}NO_6P$ $[M+Na]^+$ 538.1390, Found 538.1390.

6-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]benzo[c]phenanthrene (3j):



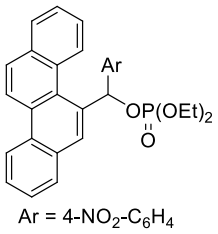
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 3.83 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 3.88 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 3.99 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 4.10 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.61-7.65 (m, 1H), 7.64 (d, J = 9.0 Hz, 2H), 7.66-7.70 (m, 2H), 7.73 (dd, J = 7.8, 7.8 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 8.12 (s, 1H), 8.17 (d, J = 9.0 Hz, 1H), 9.06 (d, J = 8.4 Hz, 1H), 9.07 (d, J = 7.8 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.73; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz), 16.0 (d, J = 7.2 Hz), 64.06 (d, J = 5.7 Hz), 64.13 (d, J = 5.9 Hz), 79.3, 122.2, 123.8, 126.3, 126.5, 126.6, 127.0, 127.6 (2C), 127.9, 128.2, 128.27, 128.31, 128.4, 128.8, 129.0, 130.2, 130.5, 132.0 (d, J = 4.4 Hz), 132.2, 132.9, 147.2 (d, J = 5.7 Hz), 147.6; IR (ATR): 3054, 2985, 2907, 1601, 1522, 1490, 1347, 1270, 1093, 1029, 1004 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{26}NO_6P$ $[M+Na]^+$ 538.1390, Found 538.1390.

6-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]benzo[a]anthracene (3k):



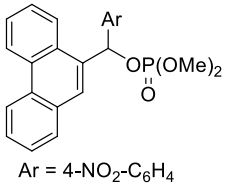
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.05 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 3.90 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.95 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.01 (ddq, J =10.2, 7.2, 7.2 Hz, 1H), 4.10 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.52 (ddd, J = 8.4, 8.4, 1.2 Hz, 1H), 7.56 (ddd, J = 8.4, 8.4, 1.2 Hz, 1H), 7.67 (dd, J = 8.4, 8.4 Hz, 1H), 7.72-7.78 (m, 1H), 7.75 (d, J = 9.0 Hz, 2H), 7.89 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 3.6 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 9.0 Hz, 2H), 8.41 (s, 1H), 8.84 (d, J = 8.4 Hz, 1H), 9.22 (s, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −0.61; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 5.7 Hz), 16.0 (d, J = 7.2 Hz), 64.05 (d, J = 5.7 Hz), 64.09 (d, J = 4.4 Hz), 79.0, 122.3, 122.8, 123.7, 124.0, 126.2, 126.3, 126.9, 127.4, 127.9, 127.98, 128.02, 128.1, 128.3, 129.2, 129.3, 130.5, 131.0, 131.47, 131.52, 132.3 (d, J = 4.4 Hz), 146.9 (d, J = 5.9 Hz), 147.6; IR (ATR): 3057, 2984, 2932, 2908, 2867, 1606, 1522, 1347, 1269, 1031, 1000, 970 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{26}NO_6P$ $[M+Na]^+$ 538.1390, Found 538.1390.

5-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]chrysene (3l):



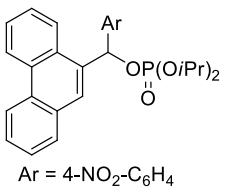
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.81 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 6.6 Hz, 3H), 3.62-3.77 (m, 3H), 3.89-3.97 (m, 1H), 7.44 (dd, J = 7.2, 7.2 Hz, 1H), 7.58 (dd, J = 7.2, 7.2 Hz, 1H), 7.70-7.73 (m, 1H), 7.77 (dd, J = 7.8, 7.8 Hz, 1H), 7.79-7.83 (m, 2H), 7.99 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 9.0 Hz, 2H), 8.10-8.23 (m, 1H), 8.22 (d, J = 9.0 Hz, 2H), 8.31 (s, 1H), 8.75 (d, J = 9.0 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −1.1; ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.6 (d, J = 7.2 Hz), 15.8 (d, J = 7.2 Hz), 63.9 (d, J = 5.7 Hz), 63.9 (d, J = 7.2 Hz), 78.7, 121.4, 123.2, 123.8, 126.0, 126.4, 127.0, 127.4, 127.5, 127.7, 128.1, 128.7, 129.2, 129.3 (2C), 129.8, 130.3 (2C), 131.2, 133.2, 133.7, 147.5 (d, J = 7.2 Hz), 147.8; IR (ATR): 3593, 3056, 2983, 2907, 1604, 1522, 1347, 1270, 1166, 1106, 1032, 1004, 982 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{26}NO_6P$ $[M+Na]^+$ 538.1390, Found 538.1390.

9-[Dimethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3m):



^{1}H NMR (600 MHz, $CDCl_3$) δ 3.52 (d, J = 10.8 Hz, 3H), 3.70 (d, J = 11.4 Hz, 3H), 7.12 (d, J = 9.0 Hz, 1H), 7.50 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.62-7.68 (m, 4H), 7.73 (ddd, J = 7.8, 7.2, 1.2 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.96 (dd, J = 7.8, 1.2 Hz, 1H), 8.01 (s, 1H), 8.18 (d, J = 9.0 Hz, 2H), 8.69 (d, J = 7.8 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ 1.65; ^{13}C NMR (150 MHz, $CDCl_3$) δ 54.39 (d, J = 5.7 Hz), 54.44 (d, J = 5.7 Hz), 79.4, 122.6, 123.4, 123.8, 124.9, 126.86, 126.90, 127.2, 127.8, 127.9, 128.0, 128.5, 129.2, 130.7, 130.8, 131.2, 132.0 (d, J = 3.0 Hz), 146.8 (d, J = 5.7 Hz), 147.7; IR (ATR): 2956, 2918, 2853, 1606, 1523, 1451, 1348, 1272, 1187, 1042, 1000, 854 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{20}NO_6P$ $[M+Na]^+$ 460.0920, Found 460.0920.

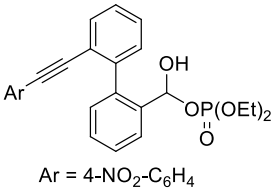
9-[Diisopropoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3n):



δ 1.00 (d, J = 6.0 Hz, 3H), 1.139 (d, J = 6.0 Hz, 3H), 1.143 (d, J = 6.0 Hz, 3H), 1.29 (d, J = 6.0 Hz, 3H), 4.47 (dsep, J = 7.2, 6.0 Hz, 1H), 4.61 (dsep, J = 7.2, 6.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.49 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.62 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.65 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.66 (d, J = 9.0 Hz, 2H), 7.71 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.93 (dd,

J = 8.4, 1.2 Hz, 1H), 7.95 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.01 (s, 1H), 8.16 (d, *J* = 9.0 Hz, 2H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H); ^{31}P NMR (243 MHz, $CDCl_3$) δ −2.42; ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.2 (d, *J* = 5.9 Hz), 23.4 (d, *J* = 5.9 Hz), 23.4 (d, *J* = 5.9 Hz), 23.5 (d, *J* = 4.4 Hz), 72.8 (d, *J* = 5.7 Hz), 72.9 (d, *J* = 5.7 Hz), 78.9, 122.5, 123.3, 123.6, 125.0, 126.6, 126.7, 127.0, 127.6, 127.85, 127.90, 128.6, 129.0, 130.66, 130.72, 131.1, 132.4 (d, *J* = 4.4 Hz), 147.2 (d, *J* = 5.7 Hz), 147.5; IR (ATR): 3064, 2980, 2936, 2871, 1604, 1522, 1452, 1347, 1258, 1107, 989 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{28}NO_6P$ $[M+Na]^+$ 516.1546, Found 516.1546.

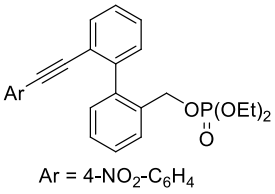
2-Diethoxyphosphoryl(hydroxy)methyl-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (4a):



Mixture of diastereomers. The ratio is 74:26.

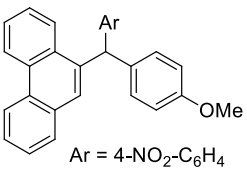
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.2 Hz, 0.78H), 1.14 (t, *J* = 7.2 Hz, 0.78H), 1.18 (t, *J* = 7.2 Hz, 2.22H), 1.21 (t, *J* = 7.2 Hz, 2.22H), 3.00 (dd, *J* = 12.6, 5.4 Hz, 0.74H), 3.20 (dd, *J* = 6.0, 6.0 Hz, 0.26H), 3.78 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 0.26H), 3.86 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 0.26H), 3.88-4.03 (m, 3.48H), 4.97 (dd, *J* = 11.4, 6.0 Hz, 0.26H), 5.03 (dd, *J* = 10.8, 5.4 Hz, 0.74H), 7.23 (d, *J* = 8.4 Hz, 0.52H), 7.24 (d, *J* = 6.6 Hz, 0.74 H), 7.31 (d, *J* = 8.4 Hz, 1.48H), 7.39-7.53 (m, 5.26H), 7.63 (d, *J* = 6.6 Hz, 0.74H), 7.68 (d, *J* = 7.2 Hz, 0.26H), 7.89 (d, *J* = 7.8 Hz, 0.74H), 8.02 (d, *J* =7.8 Hz, 0.26H), 8.08 (d, *J* = 8.4 Hz, 1.48H), 8.10 (d, *J* = 8.4 Hz, 0.52H); ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.9, 22.6; ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.2 (d, *J* = 4.2 Hz), 16.27 (d, *J* = 7.2 Hz), 16.32 (d, *J* = 5.7 Hz), 62.66 (d, *J* = 7.2 Hz), 62.70 (d, *J* = 4.2 Hz), 63.0 (d, *J* = 7.2 Hz), 63.1 (d, *J* = 7.1 Hz), 67.0 (d, *J* = 159.5 Hz), 67.7 (d, *J* = 158.0 Hz), 91.0, 91.4, 93.5, 94.6, 121.3, 122.1, 123.3, 123.5, 127.5, 127.56, 127.59, 127.8 (d, *J* = 2.9 Hz), 128.0, 128.1, 128.2, 128.7 (d, *J* = 2.9 Hz), 129.1, 129.2, 129.8, 129.9, 130.0, 130.1, 130.9, 131.0, 131.7, 131.8, 132.2, 132.6, 134.7, 135.2, 139.7 (d, *J* = 8.6 Hz), 140.1 (d, *J* = 10.1 Hz), 143.1, 143.6, 146.8 (2C); IR (ATR): 3283, 3061, 2982, 2218, 1594, 1518, 1342, 1228, 1106, 1041, 1023, 971 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{24}NO_6P$ $[M+Na]^+$ 488.1234, Found 488.1234.

2-Diethoxyphosphoryloxymethyl-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (5a):



^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 3.91-4.03 (m, 4H), 4.90 (dd, *J* = 12.0, 6.6 Hz, 1H), 5.00 (dd, *J* = 12.0, 6.6 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.32 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.42 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.43 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.46 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.48 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.0 (d, *J* = 7.2 Hz), 63.7 (d, *J* = 5.9 Hz), 66.6 (d, *J* = 5.7 Hz), 91.0, 93.7, 121.8, 123.5, 127.8, 128.0, 128.18, 128.23, 129.3, 129.8, 129.9, 130.2, 131.9, 132.0, 134.3 (d, *J* = 7.2 Hz), 139.7, 143.1, 146.8; IR (ATR): 2983, 2908, 2217, 1594, 1519, 1441, 1343, 1273, 1096, 1029, 981 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{24}NO_6P$ $[M+Na]^+$ 488.1234, Found 488.1234.

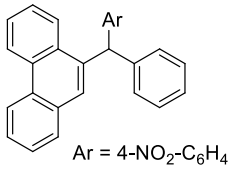
9-[(4-Methoxyphenyl)(4-nitrophenyl)methyl]phenanthrene (6a):



^{1}H NMR (600 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.29 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.10 (s, 1H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.51 (dd, *J* = 8.4, 7.8 Hz, 1H), 7.55 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.64 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.65 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.68

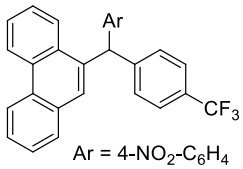
(d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 9.0 Hz, 2H), 8.68 (d, *J* = 7.8 Hz, 1H), 8.75 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 52.5, 55.2, 114.2, 122.4, 123.3, 123.7, 124.8, 126.5, 126.81, 126.84, 126.9, 128.68, 128.74, 129.9, 130.4, 130.6, 130.7, 130.9, 131.1, 133.8, 137.0, 146.6, 151.7, 158.5; IR (ATR):3076, 2933, 2836, 1606, 1510, 1346, 1249, 1179, 1111, 1036 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{21}NO_3$ $[M+Na]^+$ 442.1414, Found 442.1413.

9-[(4-Nitrophenyl)(phenyl)methyl]phenanthrene (6b):



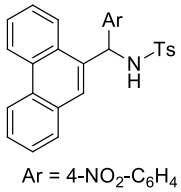
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.34 (s, 1H), 7.10 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.32-7.36 (m, 5H), 7.51 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.55 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.63 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.65 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.75 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 53.3, 122.4, 123.3, 123.7, 124.8, 126.5, 126.8, 126.89, 126.94, 127.2, 128.78, 128.85 (2c), 129.7, 130.0, 130.5, 130.7, 131.0, 131.1, 136.7, 141.8, 146.7, 151.3; IR (ATR):3077, 3061, 3028, 2927, 2853, 1600, 1518, 1494, 1345, 1110 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{19}NO_2$ $[M+Na]^+$ 412.1308, Found 412.1308.

9-[(4-Nitrophenyl)(4-trifluoromethylphenyl)methyl]phenanthrene (6c):



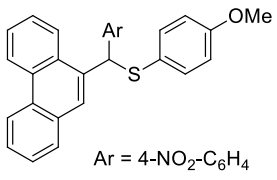
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.40 (s, 1H), 7.07 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.52 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.57 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 8.4, 7.8 Hz, 1H), 7.67 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 2H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.77 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 53.0, 122.5, 123.4, 123.9, 124.0 (q, *J* = 270 Hz), 124.5, 125.8 (q, *J* = 2.9 Hz), 126.7, 126.99, 127.03, 127.2, 128.8, 129.0, 129.5 (q, *J* = 31.7 Hz), 129.99, 130.02, 130.4, 130.5, 130.96, 131.04, 135.8, 145.9, 146.9, 150.1; IR (ATR): 3077, 2921, 1597, 1519, 1346, 1324, 1165, 1124, 1112, 1068, 1018 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{18}F_3NO_2$ $[M+Na]^+$ 480.1182, Found 480.1182.

9-[(4-Nitrophenyl)(tosylamido)methyl]phenanthrene (7):

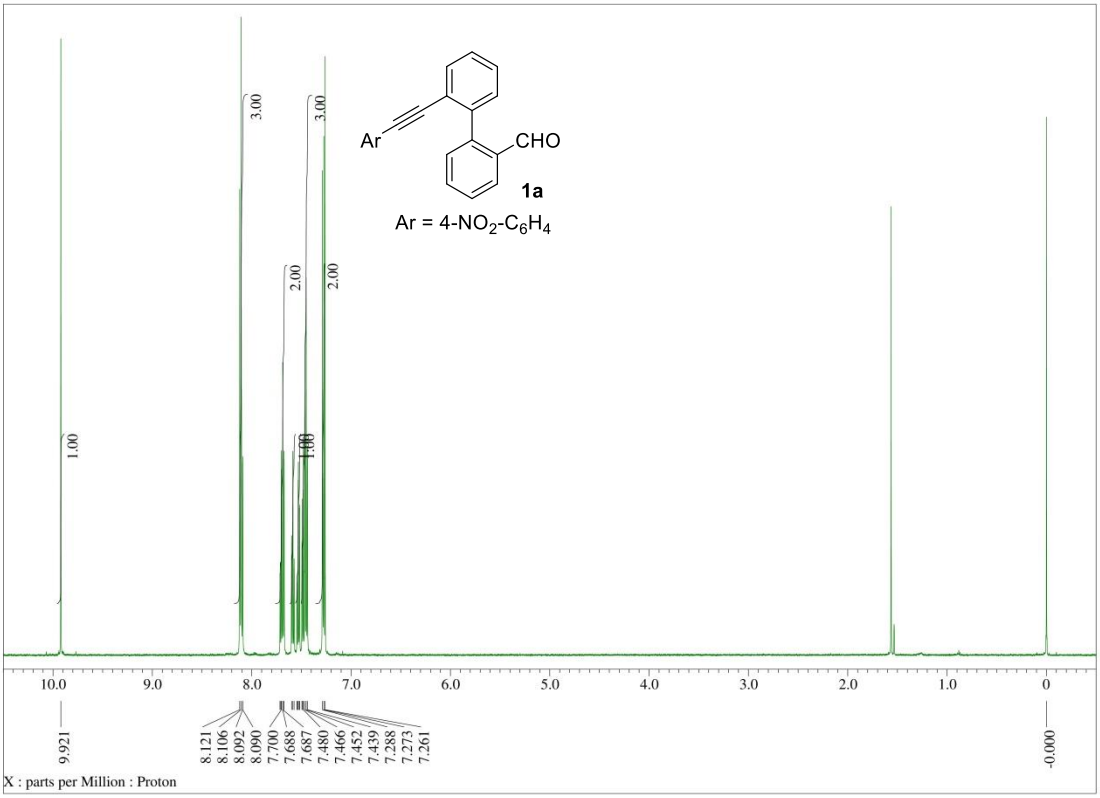


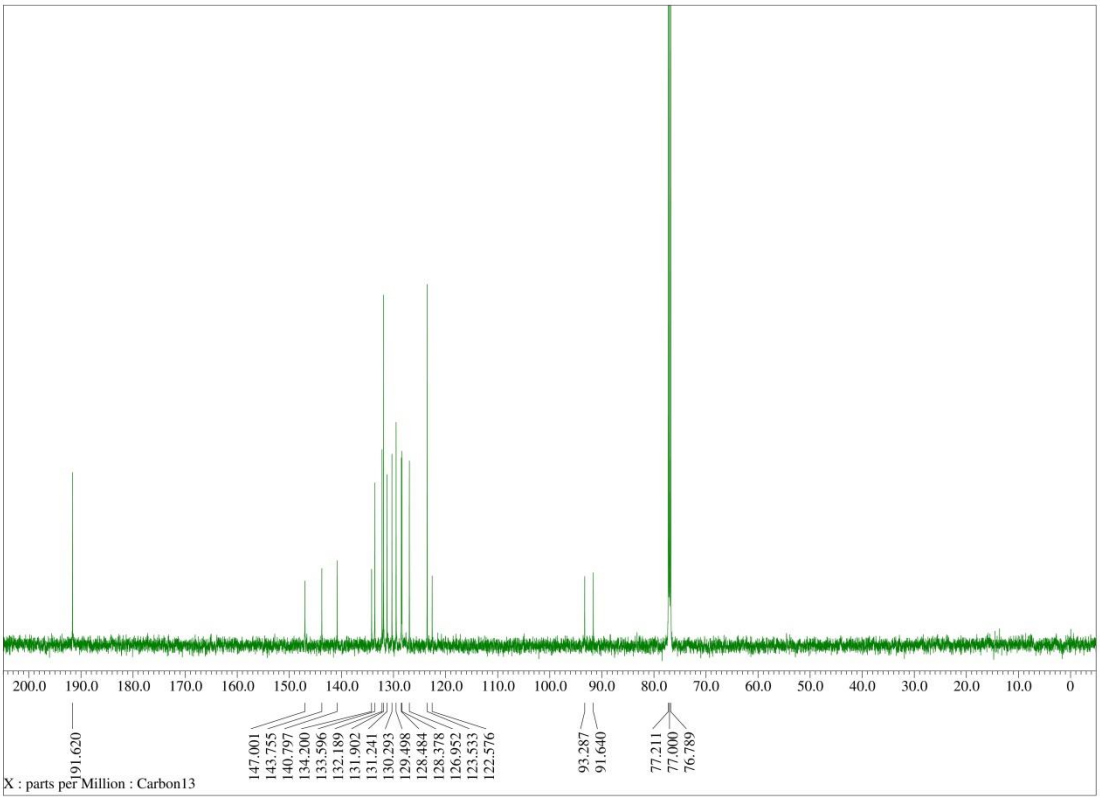
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.24 (s, 3H), 5.46 (d, *J* = 7.2 Hz, 1H), 6.30 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 7.24 (s, 1H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.45-7.51 (m, 3H), 7.57 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.60-7.69 (m, 4H), 8.08 (d, *J* = 9.0 Hz, 2H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.70 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 59.0, 122.4, 123.6, 123.8, 123.9, 126.9, 127.0, 127.1, 127.2, 127.6, 128.36, 128.44, 128.5, 128.8, 129.4, 130.3, 130.6, 131.2, 131.9, 136.7, 143.8, 147.36, 147.38; IR (ATR): 3269, 2959, 2925, 2853, 1599, 1520, 1450, 1346, 1158, 1090 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{22}N_2O_4S$ $[M+Na]^+$ 505.1193, Found 505.1193.

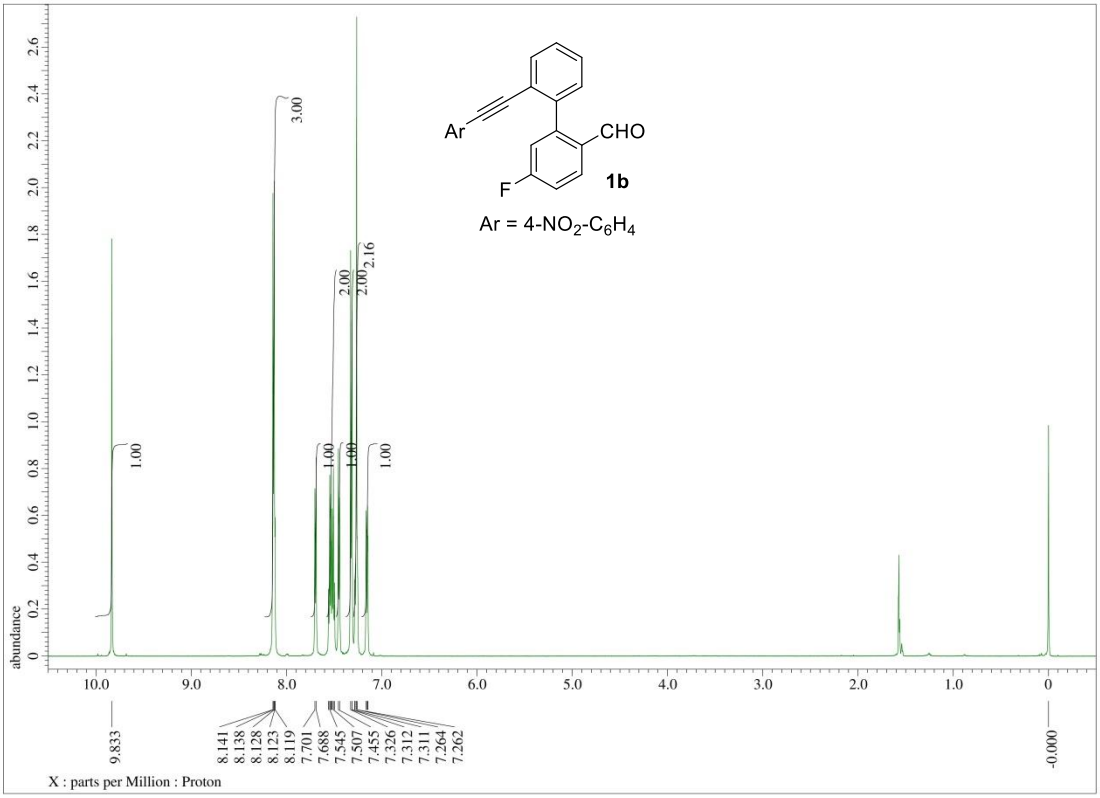
9-[(4-Methoxyphenylsulfanyl)(4-nitrophenyl)methyl]phenanthrene (8):

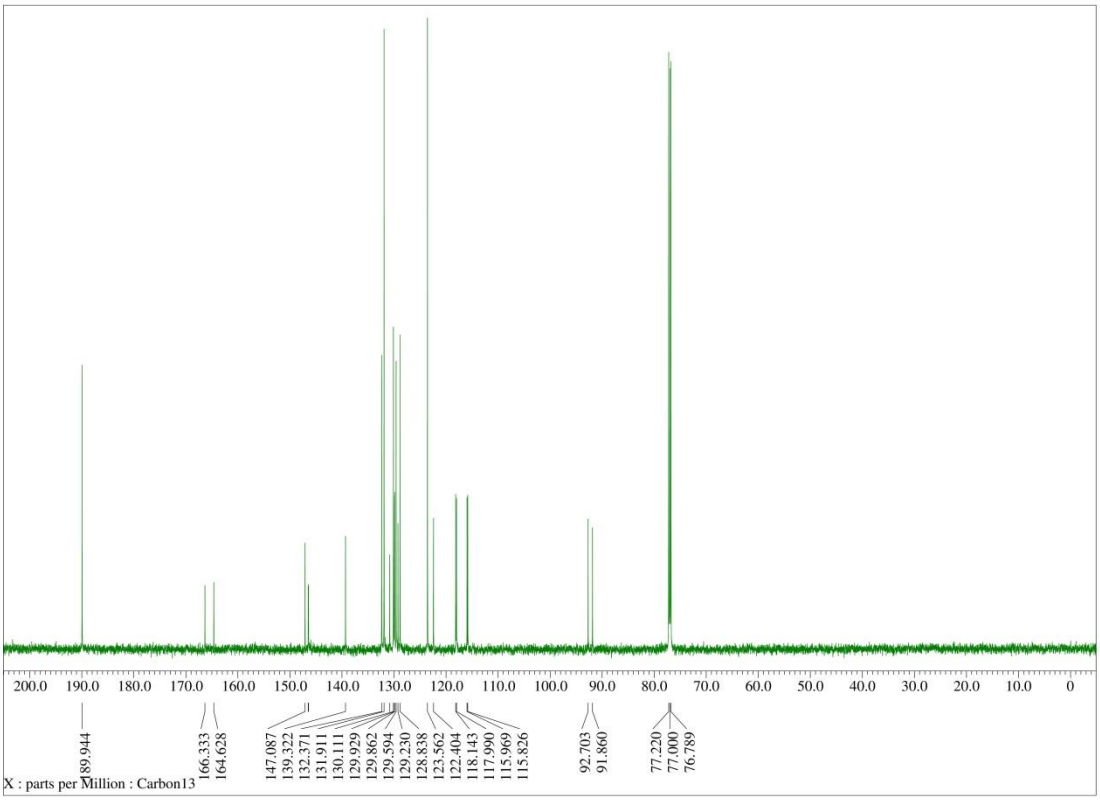


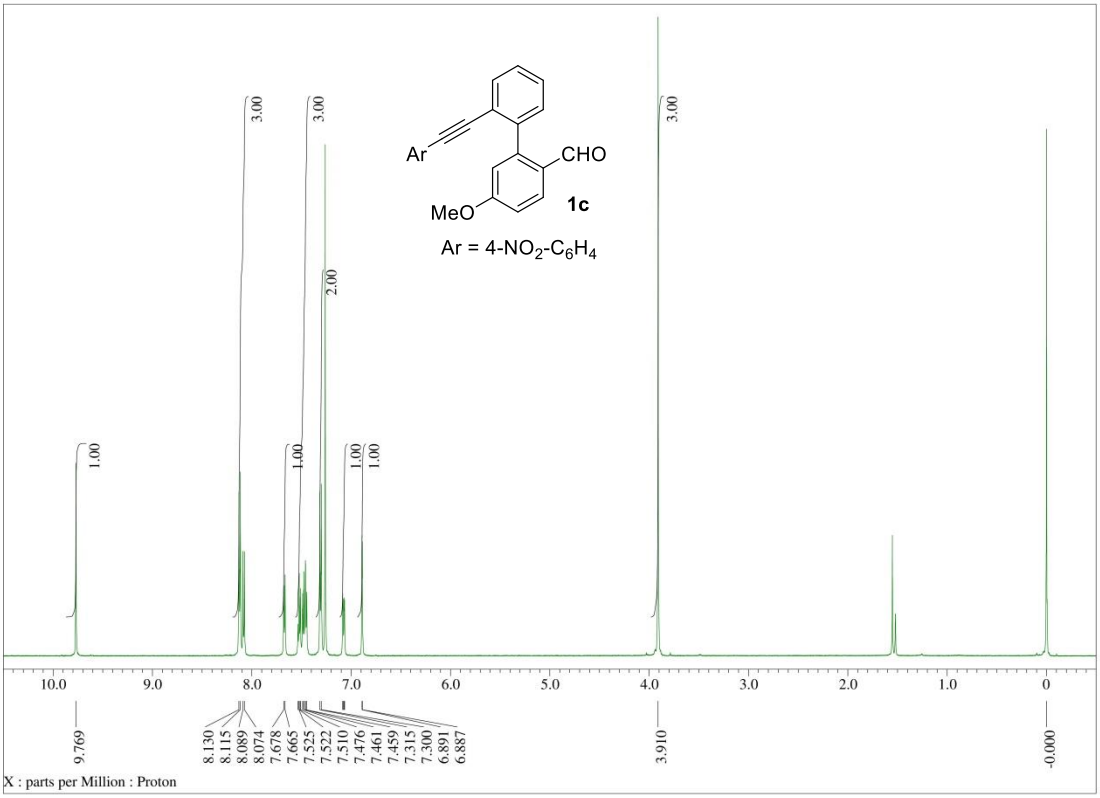
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, 3H), 6.10 (s, 1H), 6.76 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.55 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.63 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.64 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.68 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 8.06 (s, 1H), 8.09 (d, *J* = 9.0 Hz, 2H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.74 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.3, 55.9, 114.7, 122.5, 123.5, 123.7, 124.1, 125.1, 126.6, 126.8, 127.0, 127.3, 128.0, 128.9, 129.4, 129.8, 130.2, 131.1 (2C), 133.0, 134.8, 146.9, 148.7, 159.8; IR (ATR): 3075, 2938, 2836, 1592, 1519, 1493, 1345, 1287, 1248, 1173, 1105, 1031 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{21}NO_3S$ $[M+Na]^+$ 474.1134, Found 474.1134.

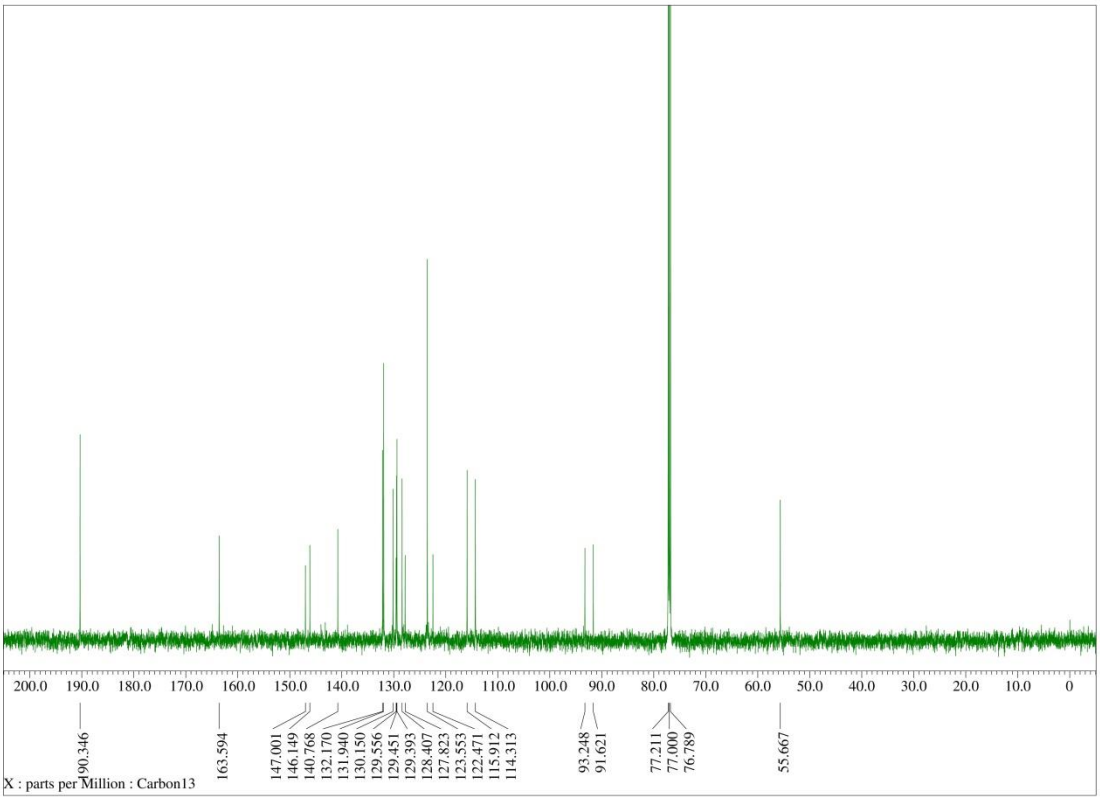

Ar
CHO
1a
Ar = 4-NO2-C6H4
3.00
3.00
2.00
2.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.921
8.121
8.106
8.092
8.090
7.700
7.688
7.687
7.480
7.466
7.452
7.439
7.288
7.273
7.261
-0.000
X : parts per Million : Proton

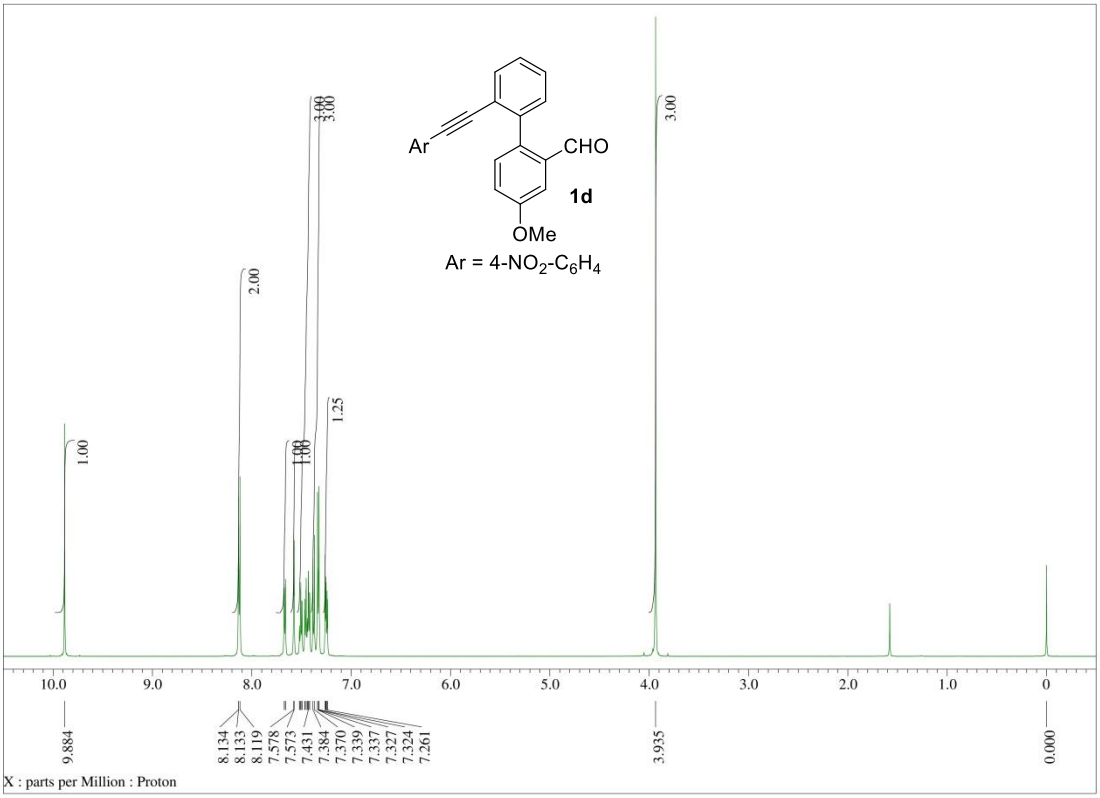

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.620
147.001
143.755
140.797
134.200
133.596
132.189
131.902
131.241
130.293
129.498
128.484
128.378
126.952
123.533
122.576
93.287
91.640
77.211
77.000
76.789
X : parts per Million : Carbon13

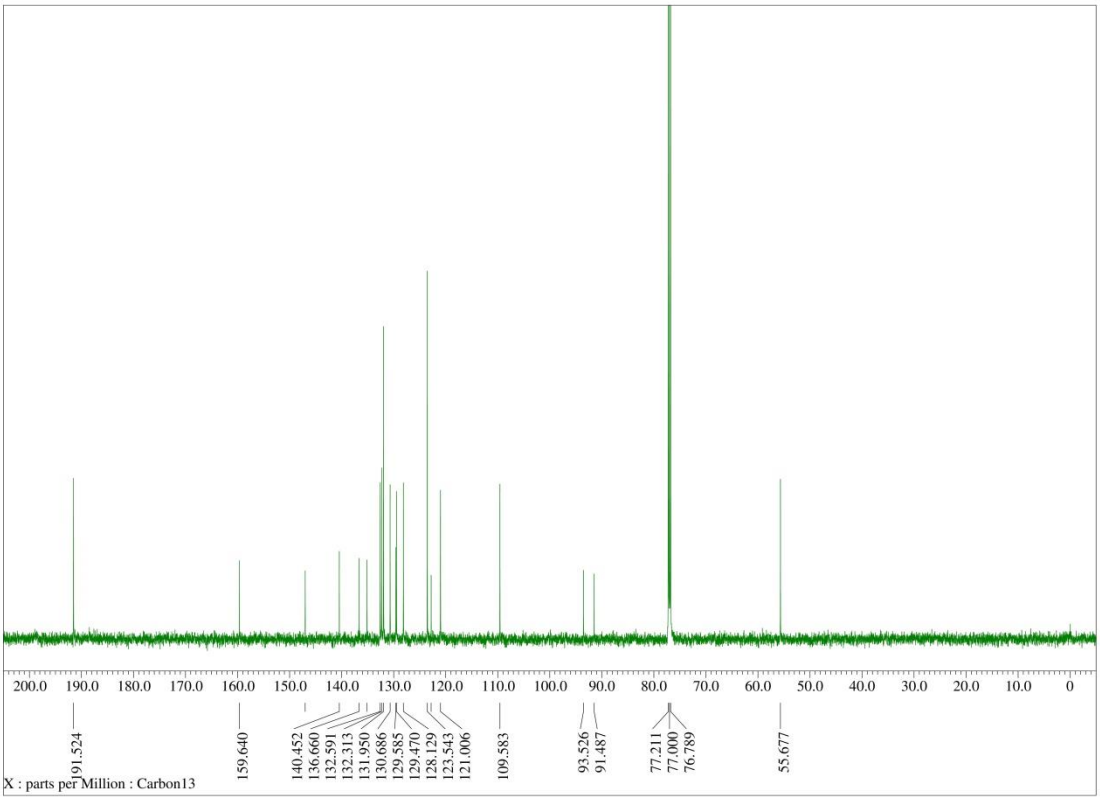

Ar
CHO
F
1b
Ar = 4-NO2-C6H4
abundance
X : parts per Million : Proton

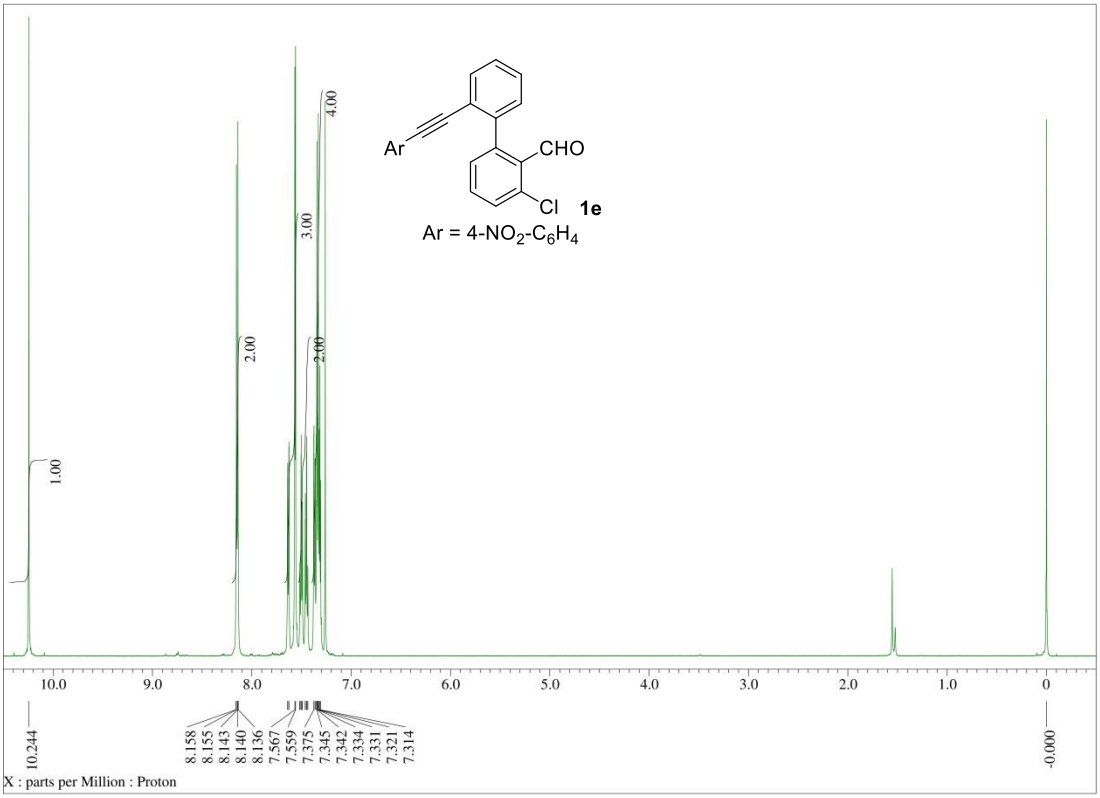

X : parts per Million : Carbon13

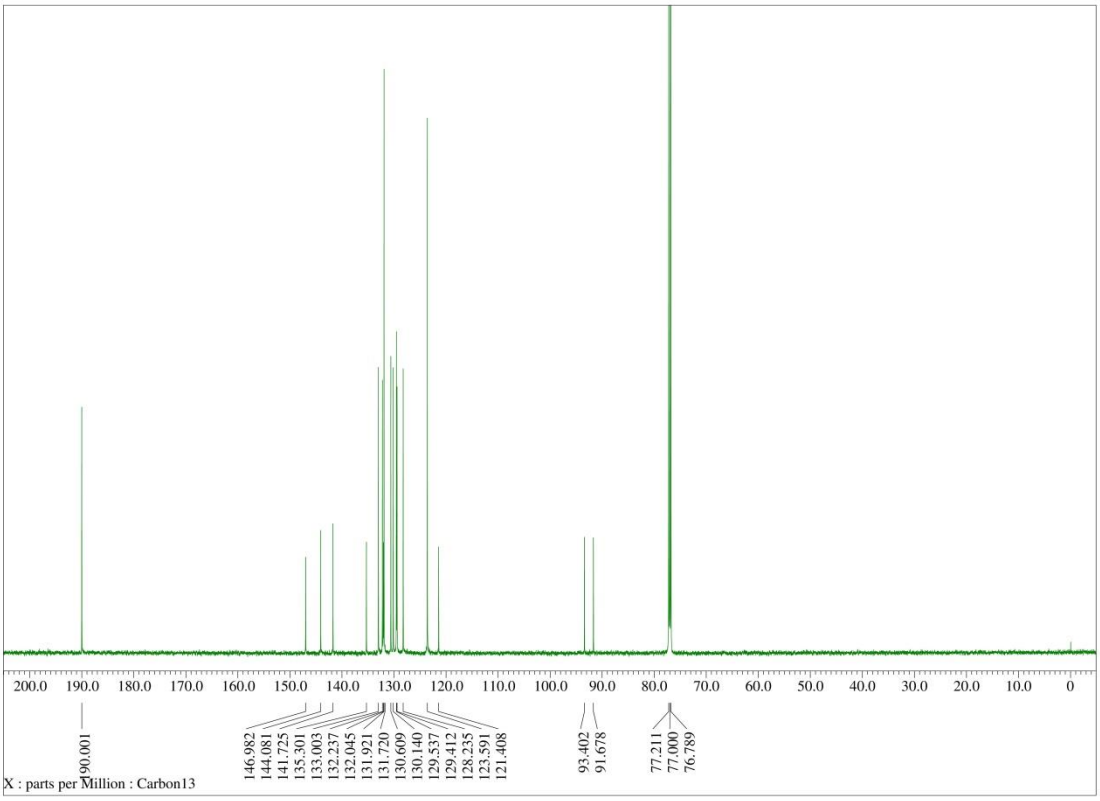

Ar
CHO
MeO
1c
Ar = 4-NO2-C6H4
3.00
3.00
3.00
2.00
1.00
1.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.769
8.130
8.115
8.089
8.074
7.678
7.665
7.525
7.522
7.510
7.476
7.461
7.459
7.315
7.300
6.891
6.887
3.910
-0.000
X : parts per Million : Proton

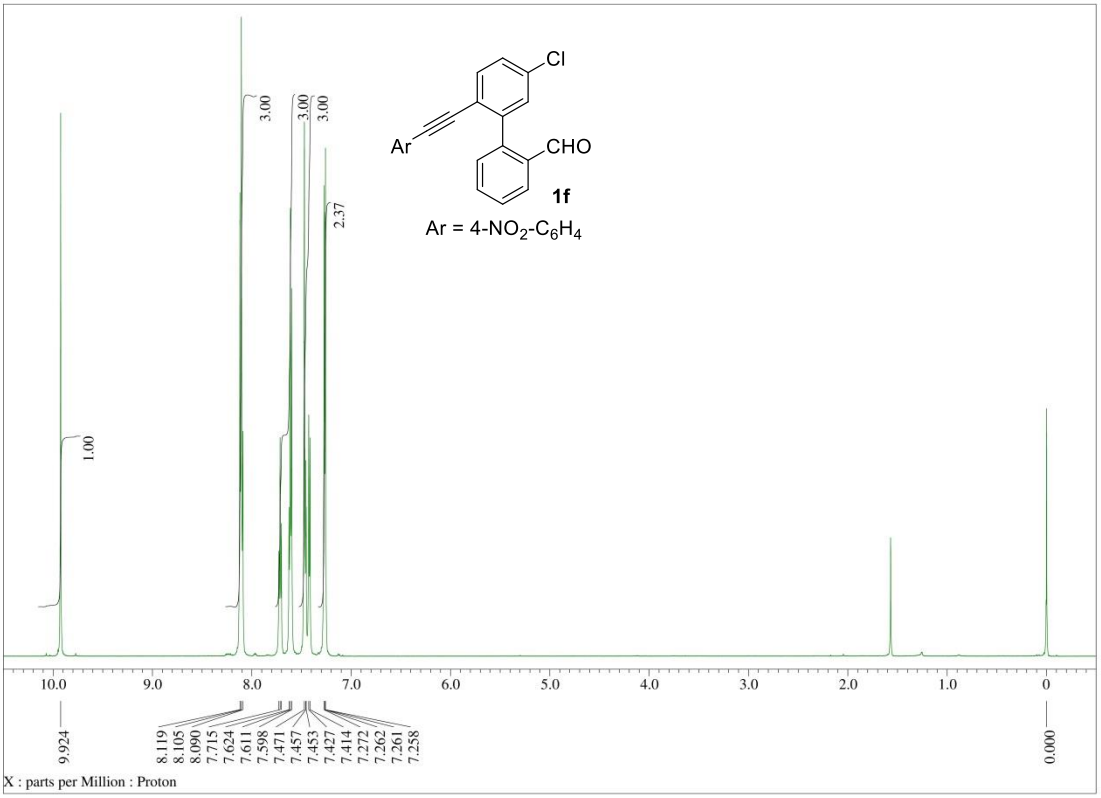

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.346
163.594
147.001
146.149
140.768
132.170
131.940
130.150
129.556
129.451
129.393
128.407
127.823
123.553
122.471
115.912
114.313
93.248
91.621
77.211
77.000
76.789
55.667
X : parts per Million : Carbon13

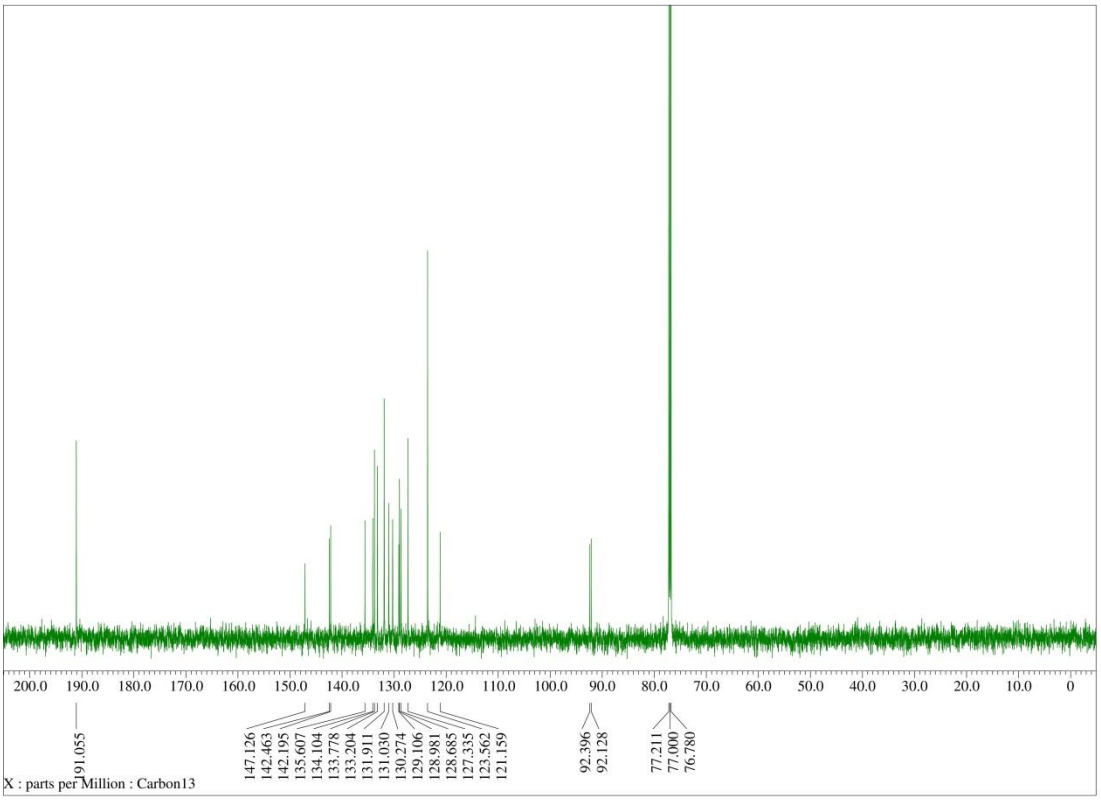

Ar
CHO
1d
OMe
Ar = 4-NO2-C6H4
X : parts per Million : Proton

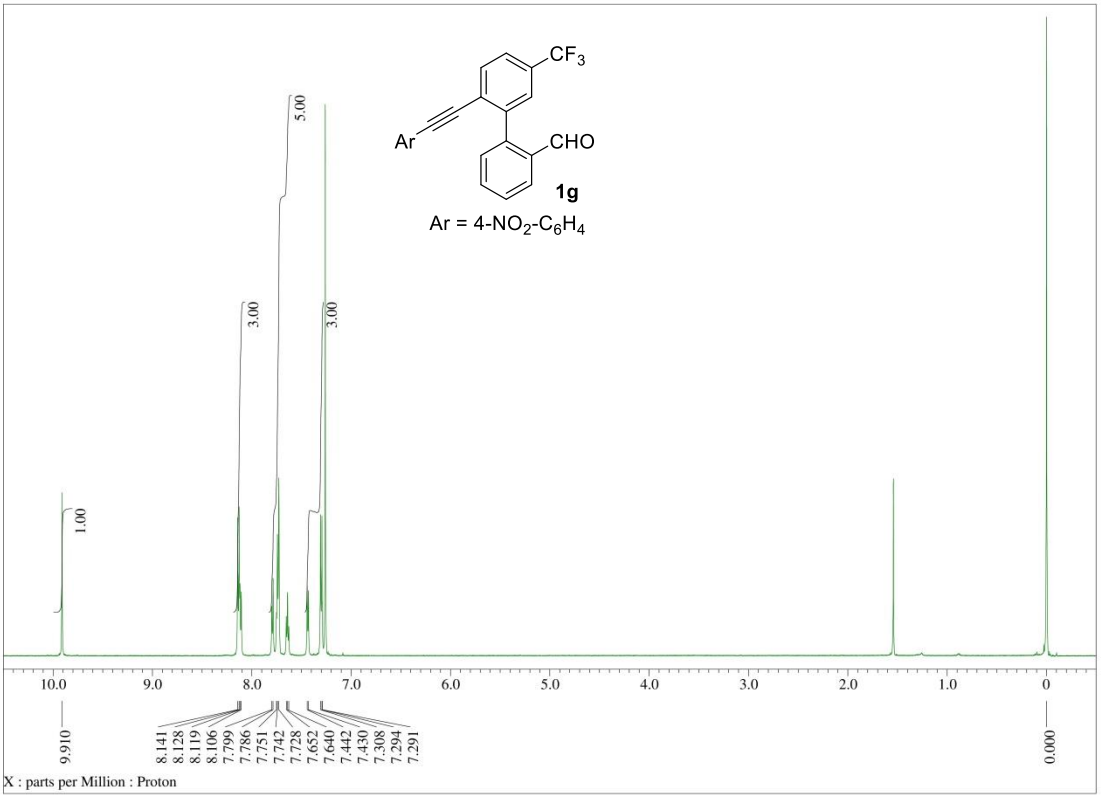

X : parts per Million : Carbon13

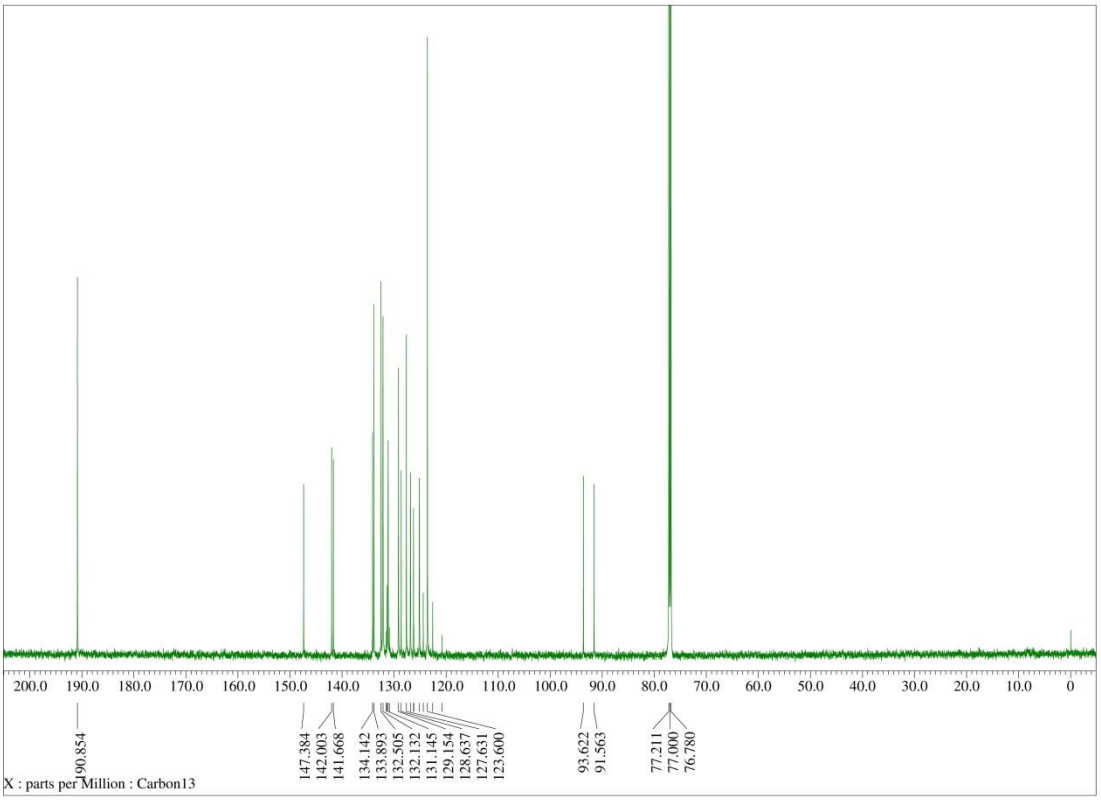

Ar
CHO
Cl
1e
Ar = 4-NO2-C6H4
4.00
3.00
2.00
2.00
1.00
10.244
8.158
8.155
8.143
8.140
8.136
7.567
7.559
7.375
7.345
7.342
7.334
7.331
7.321
7.314
-0.000
X : parts per Million : Proton

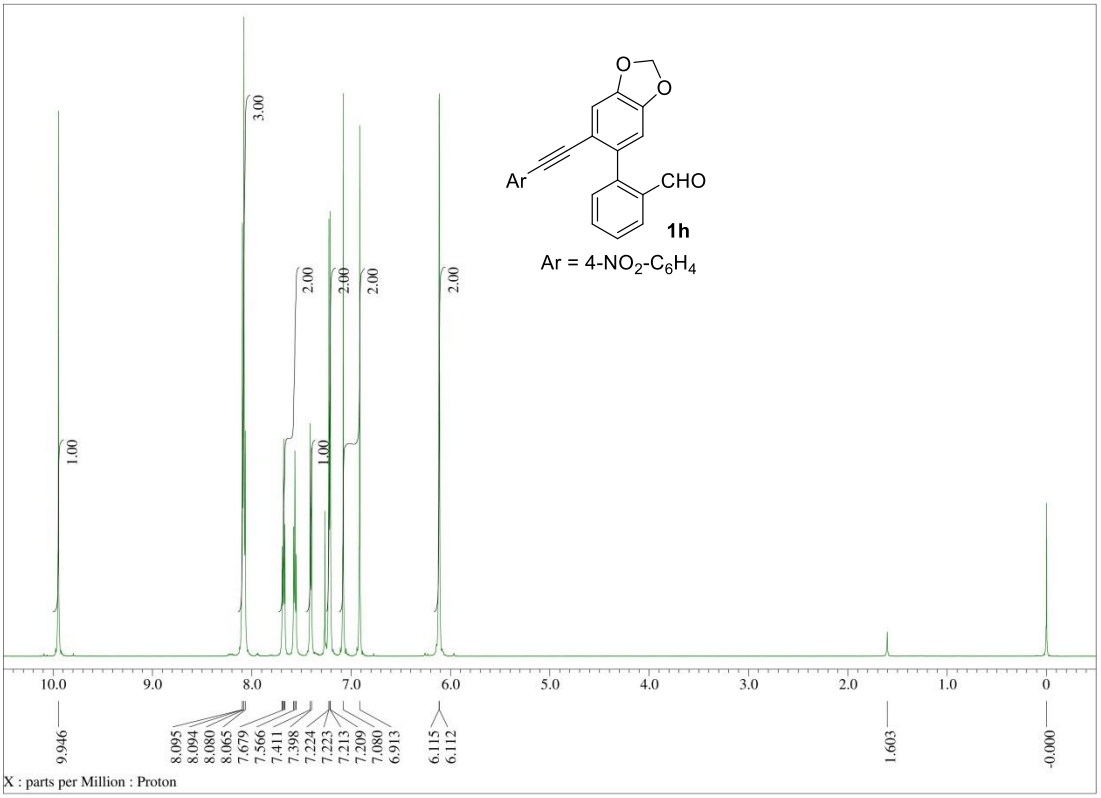

190.001
146.982
144.081
141.725
135.301
133.003
132.237
132.045
131.921
131.720
130.609
130.140
129.537
129.412
128.235
123.591
121.408
93.402
91.678
77.211
77.000
76.789
X : parts per Million : Carbon13

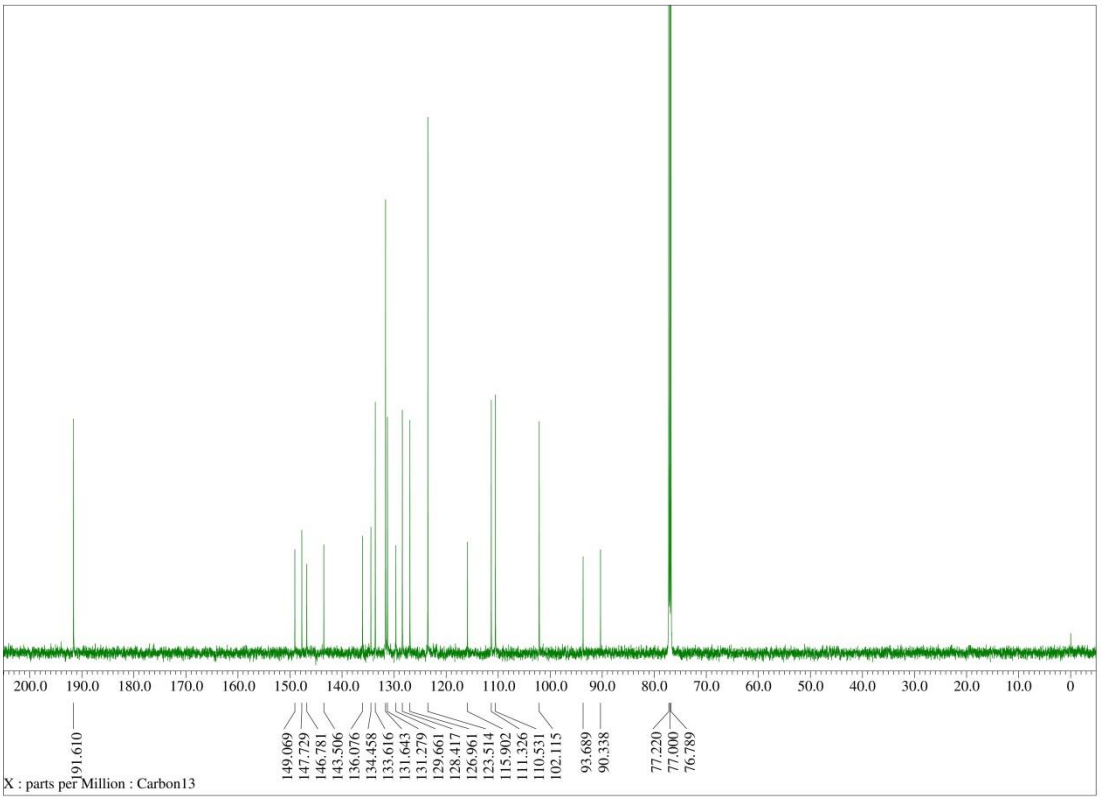

Cl
Ar
CHO
1f
Ar = 4-NO2-C6H4
3.00
3.00
3.00
2.37
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.924
8.119
8.105
8.090
7.715
7.624
7.611
7.598
7.471
7.457
7.453
7.427
7.414
7.272
7.262
7.261
7.258
0.000
X : parts per Million : Proton

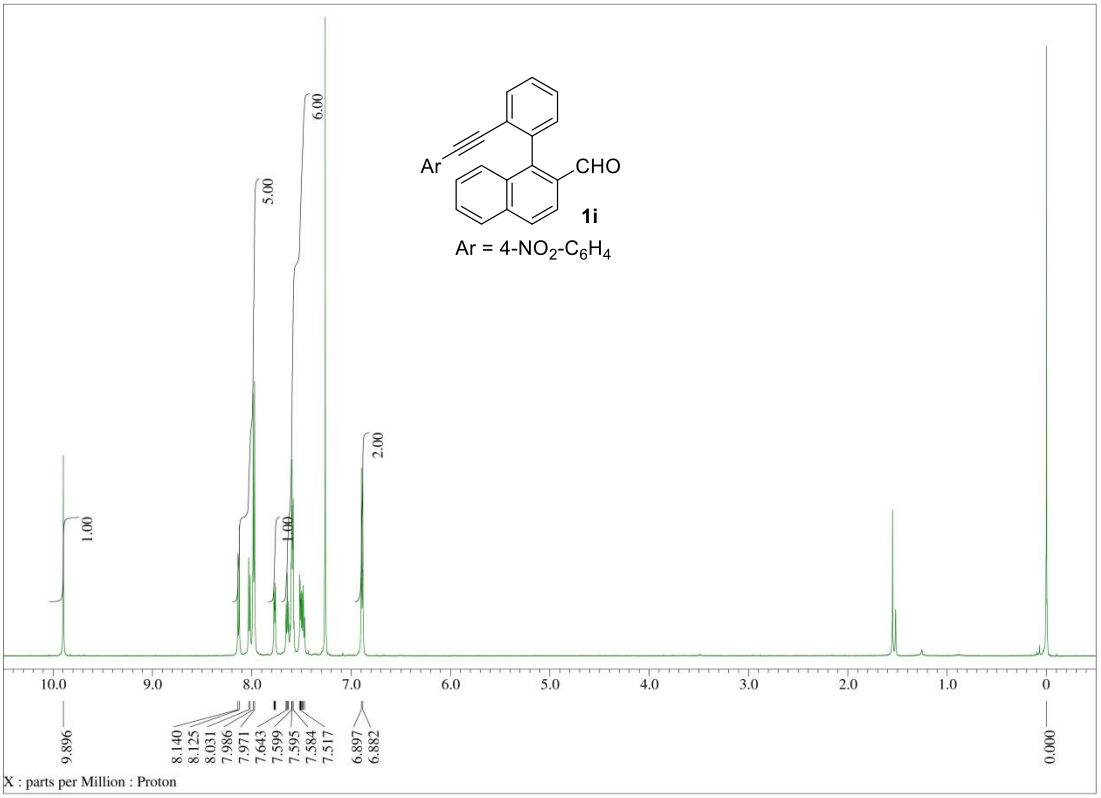

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.055
147.126
142.463
142.195
135.607
134.104
133.778
133.204
131.911
131.030
130.274
129.106
128.981
128.685
127.335
123.562
121.159
92.396
92.128
77.211
77.000
76.780
X : parts per Million : Carbon13

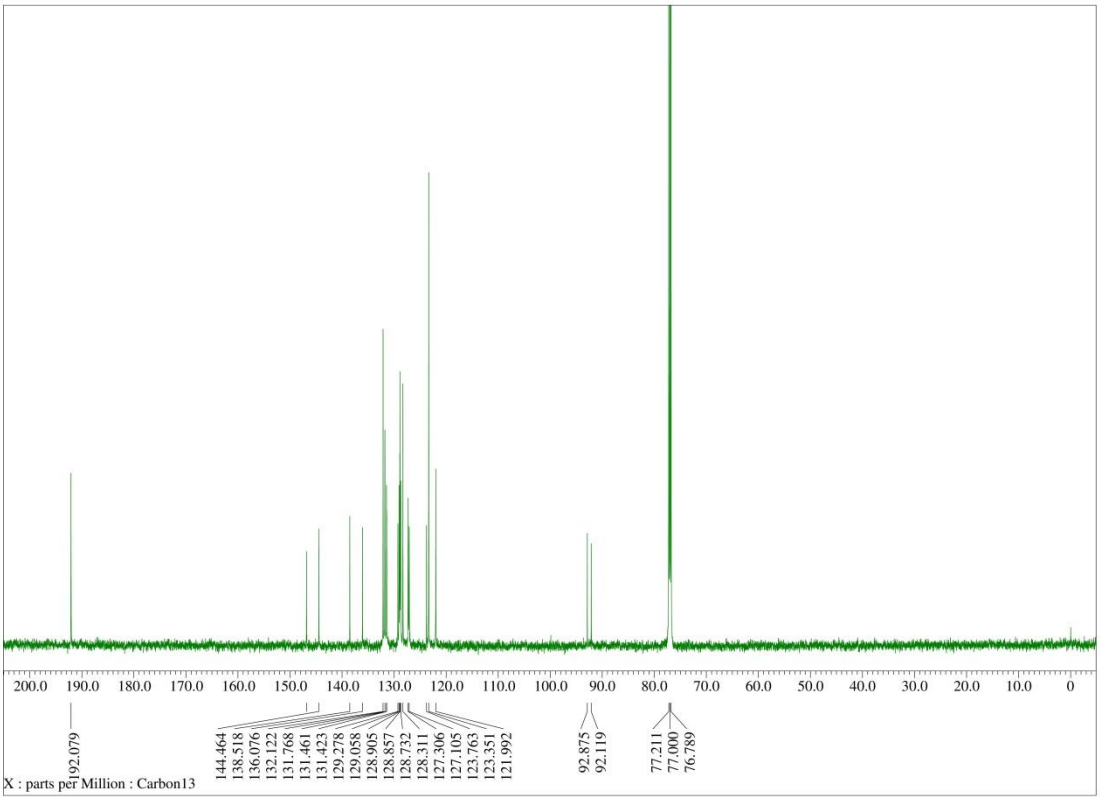

CF3
Ar
CHO
1g
Ar = 4-NO2-C6H4
5.00
3.00
3.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.910
8.141
8.128
8.119
8.106
7.799
7.786
7.751
7.742
7.728
7.652
7.640
7.442
7.430
7.308
7.294
7.291
0.000
X : parts per Million : Proton

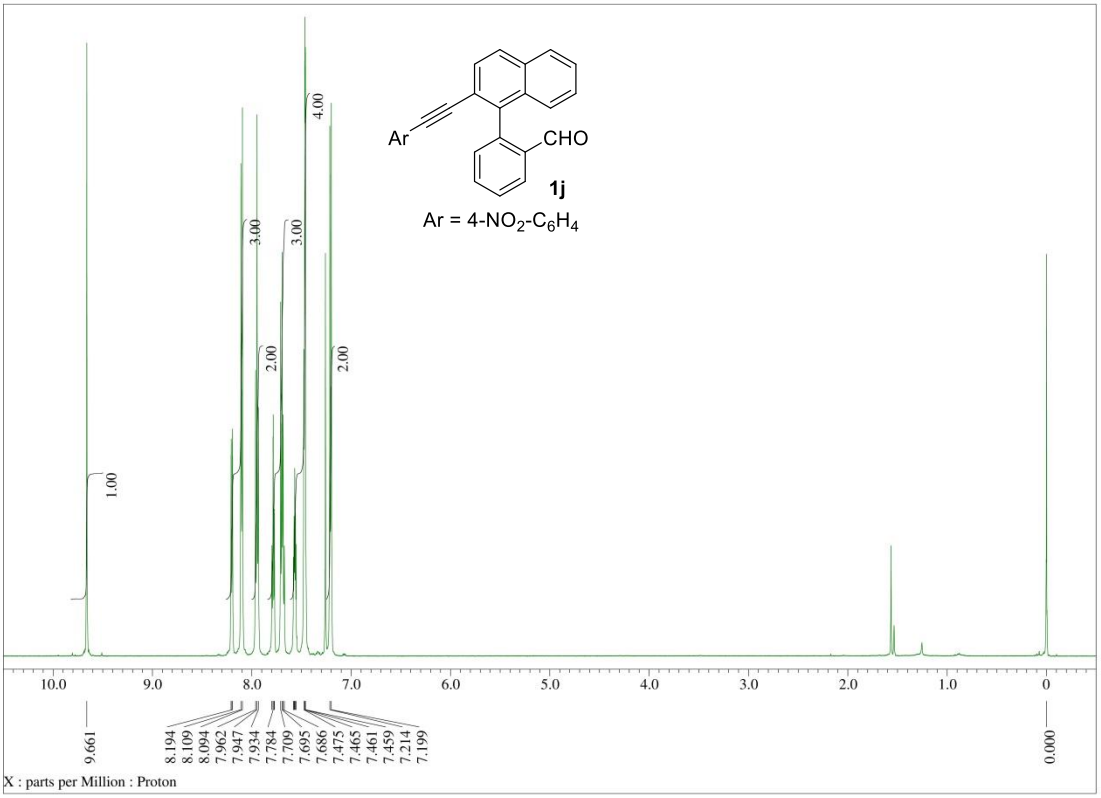

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.854
147.384
142.003
141.668
134.142
133.893
132.505
132.132
131.145
129.154
128.637
127.631
123.600
93.622
91.563
77.211
77.000
76.780
X : parts per Million : Carbon13

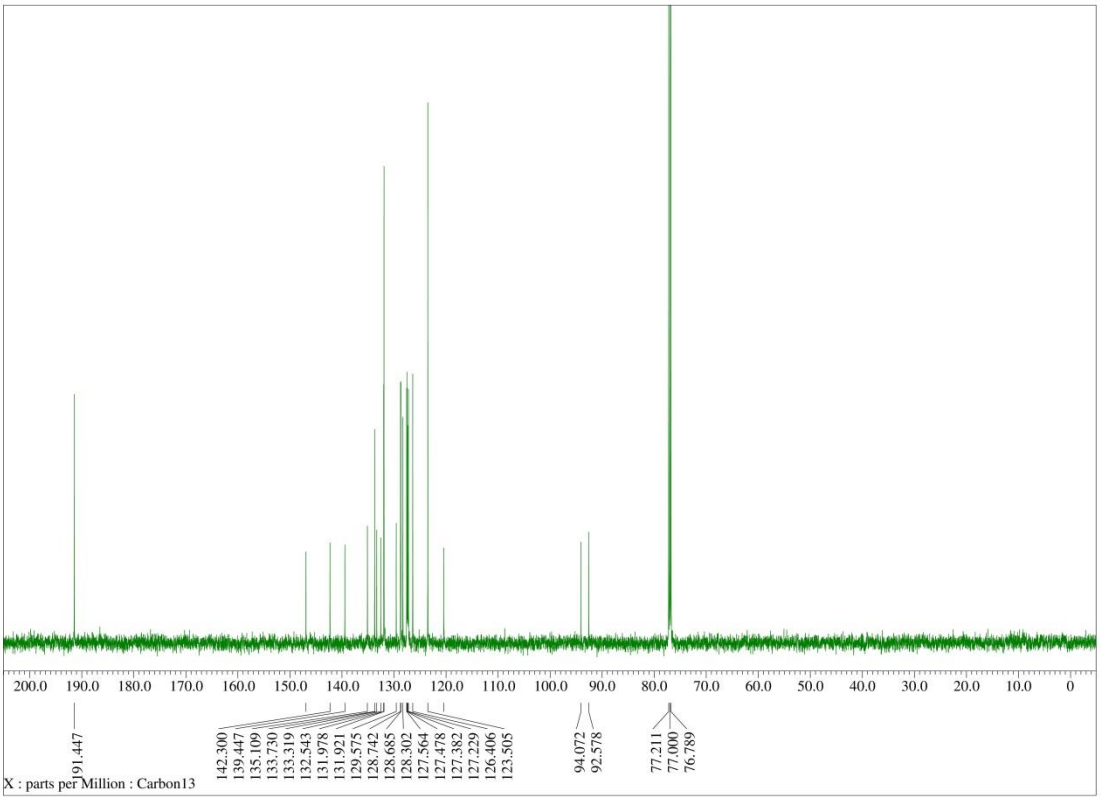

Ar
CHO
1h
Ar = 4-NO2-C6H4
3.00
2.00
2.00
2.00
2.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.946
8.095
8.094
8.080
8.065
7.679
7.566
7.411
7.398
7.224
7.223
7.213
7.209
7.080
6.913
6.115
6.112
1.603
-0.000
X : parts per Million : Proton

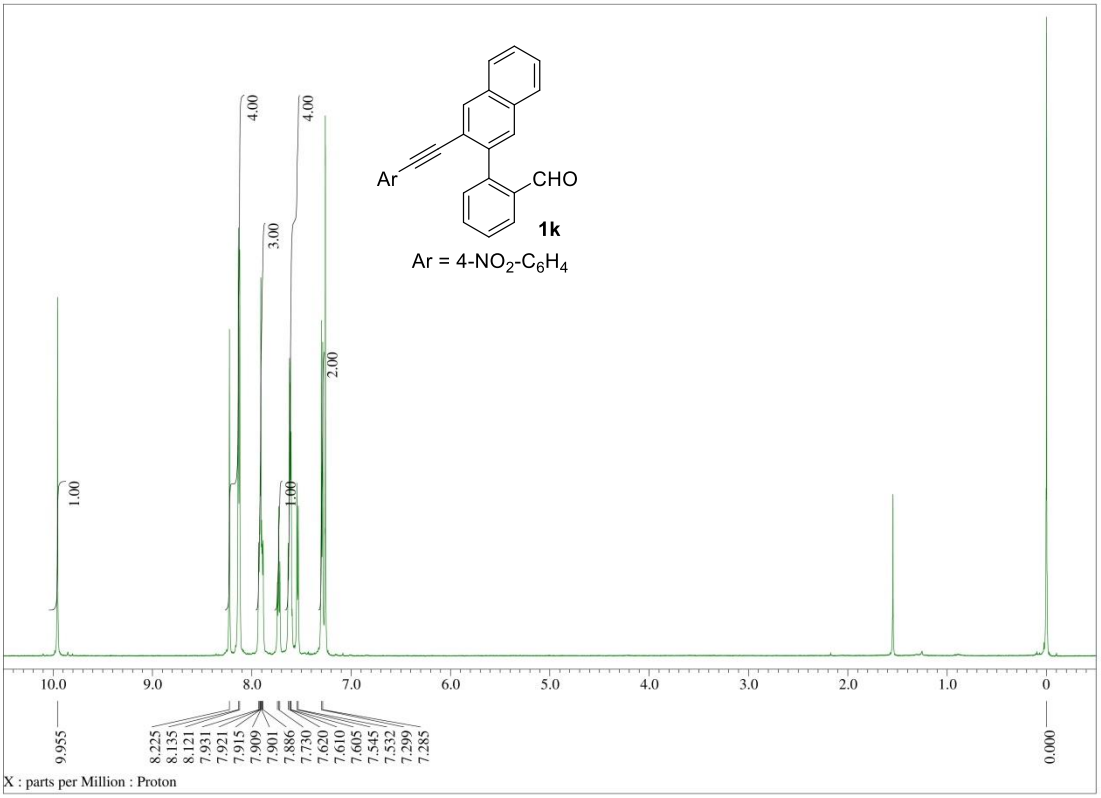

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.610
149.069
147.729
146.781
143.506
136.076
134.458
133.616
131.643
131.279
129.661
128.417
126.961
123.514
115.902
111.326
110.531
102.115
93.689
90.338
77.220
77.000
76.789
X : parts per Million : Carbon13

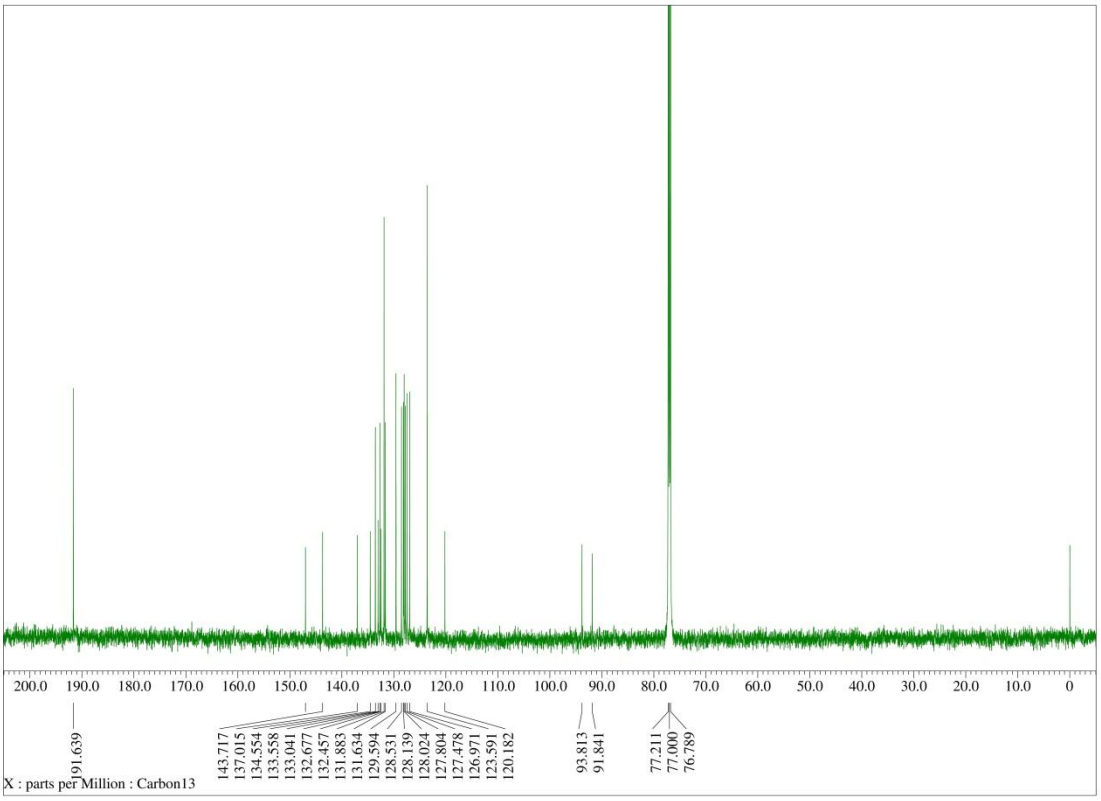

Ar
CHO
1i
Ar = 4-NO2-C6H4
6.00
5.00
2.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.896
8.140
8.125
8.031
7.986
7.971
7.643
7.599
7.595
7.584
7.517
6.897
6.882
0.000
X : parts per Million : Proton

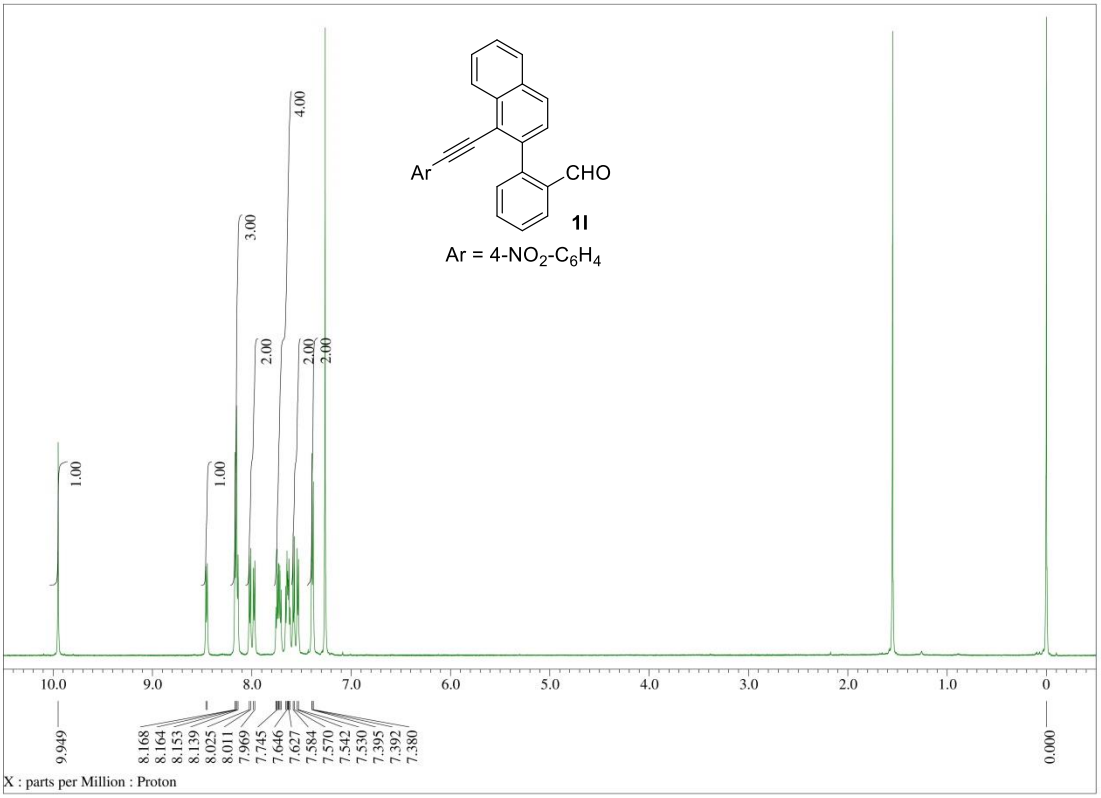

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.079
144.464
138.518
136.076
132.122
131.768
131.461
131.423
129.278
129.058
128.905
128.857
128.732
128.311
127.306
127.105
123.763
123.351
121.992
92.875
92.119
77.211
77.000
76.789
X : parts per Million : Carbon13

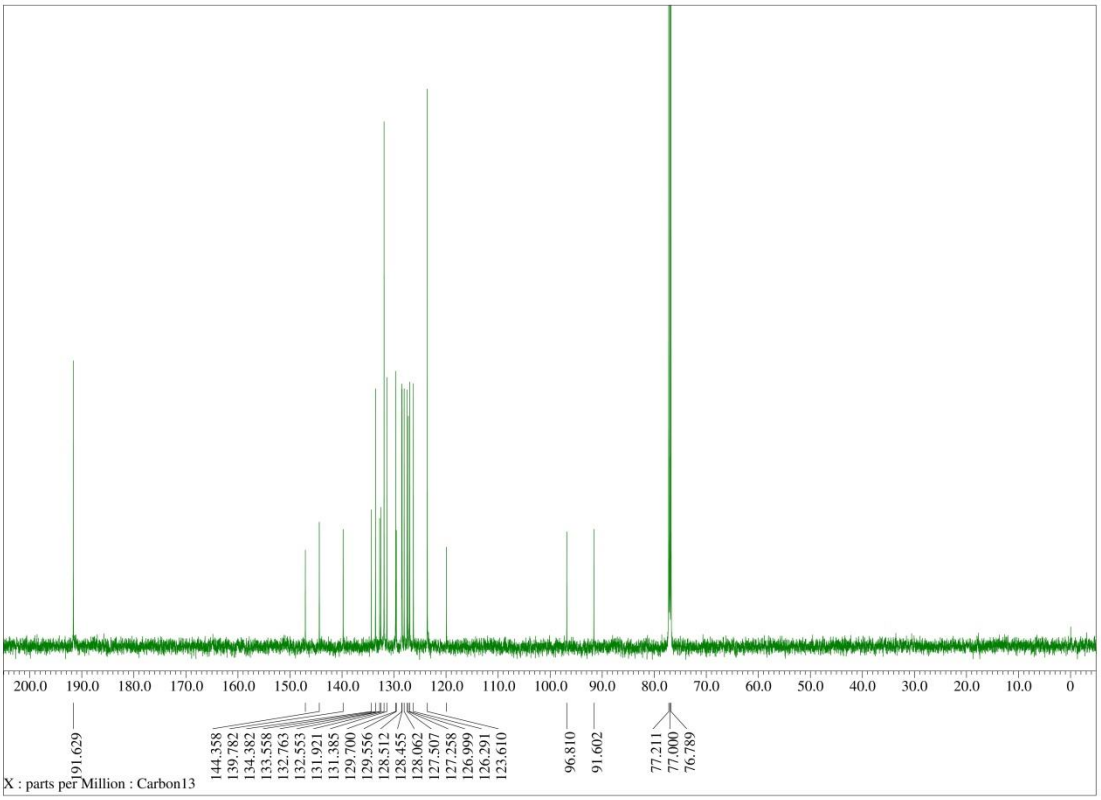

Ar
CHO
1j
Ar = 4-NO2-C6H4
4.00
3.00
3.00
2.00
2.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.661
8.194
8.109
8.094
7.962
7.947
7.934
7.784
7.709
7.695
7.686
7.475
7.465
7.461
7.459
7.214
7.199
0.000
X : parts per Million : Proton

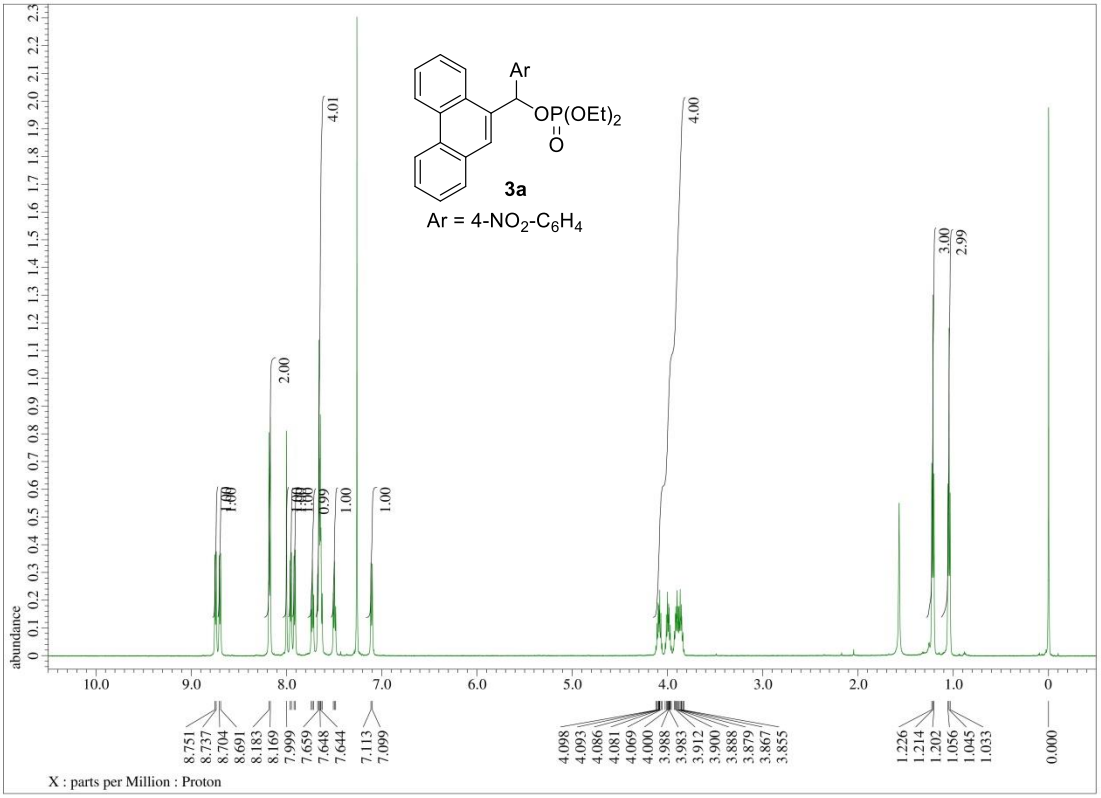

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.447
142.300
139.447
135.109
133.730
133.319
132.543
131.978
131.921
129.575
128.742
128.685
128.302
127.564
127.478
127.382
127.229
126.406
123.505
94.072
92.578
77.211
77.000
76.789
X : parts per Million : Carbon13

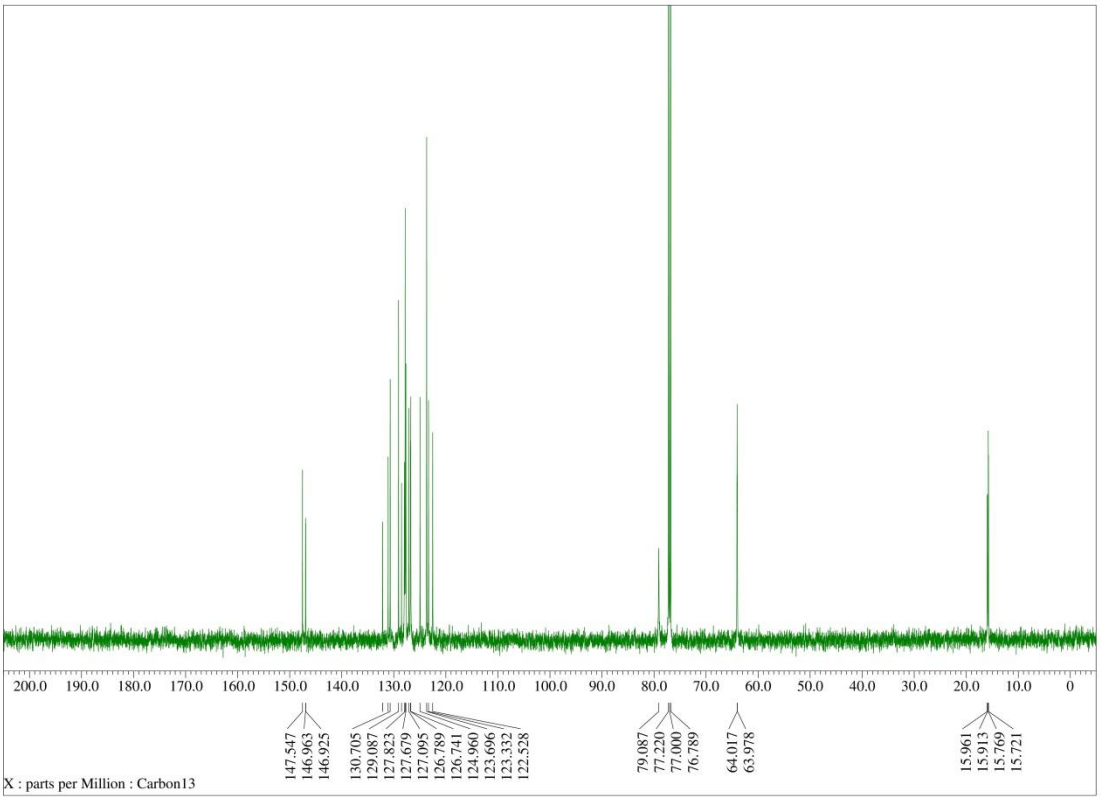

Ar
CHO
1k
Ar = 4-NO2-C6H4
4.00
4.00
3.00
2.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.955
8.225
8.135
8.121
7.931
7.921
7.915
7.909
7.901
7.886
7.730
7.620
7.610
7.605
7.545
7.532
7.299
7.285
0.000
X : parts per Million : Proton

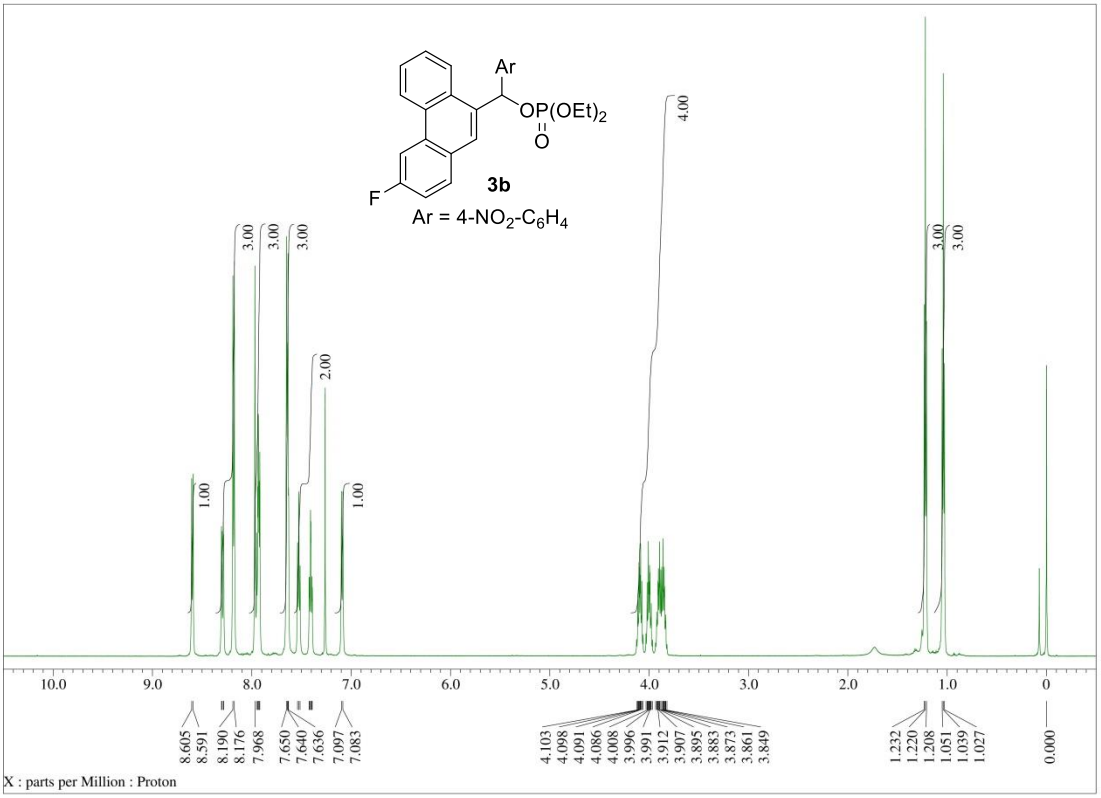

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.639
143.717
137.015
134.554
133.558
133.041
132.677
132.457
131.883
131.634
129.594
128.531
128.139
128.024
127.804
127.478
126.971
123.591
120.182
93.813
91.841
77.211
77.000
76.789
X : parts per Million : Carbon13

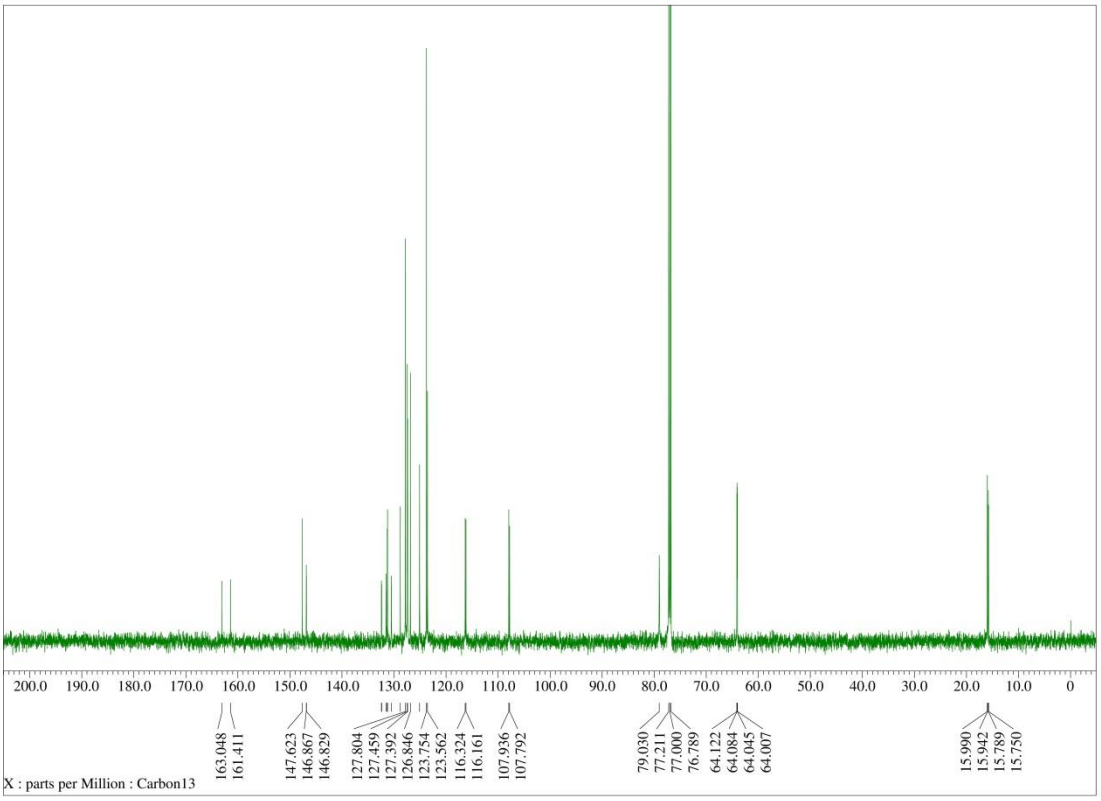

Ar
CHO
1l
Ar = 4-NO2-C6H4
4.00
3.00
2.00
2.00
2.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.949
8.168
8.164
8.153
8.139
8.025
8.011
7.969
7.745
7.646
7.627
7.584
7.570
7.542
7.530
7.395
7.392
7.380
0.000
X : parts per Million : Proton

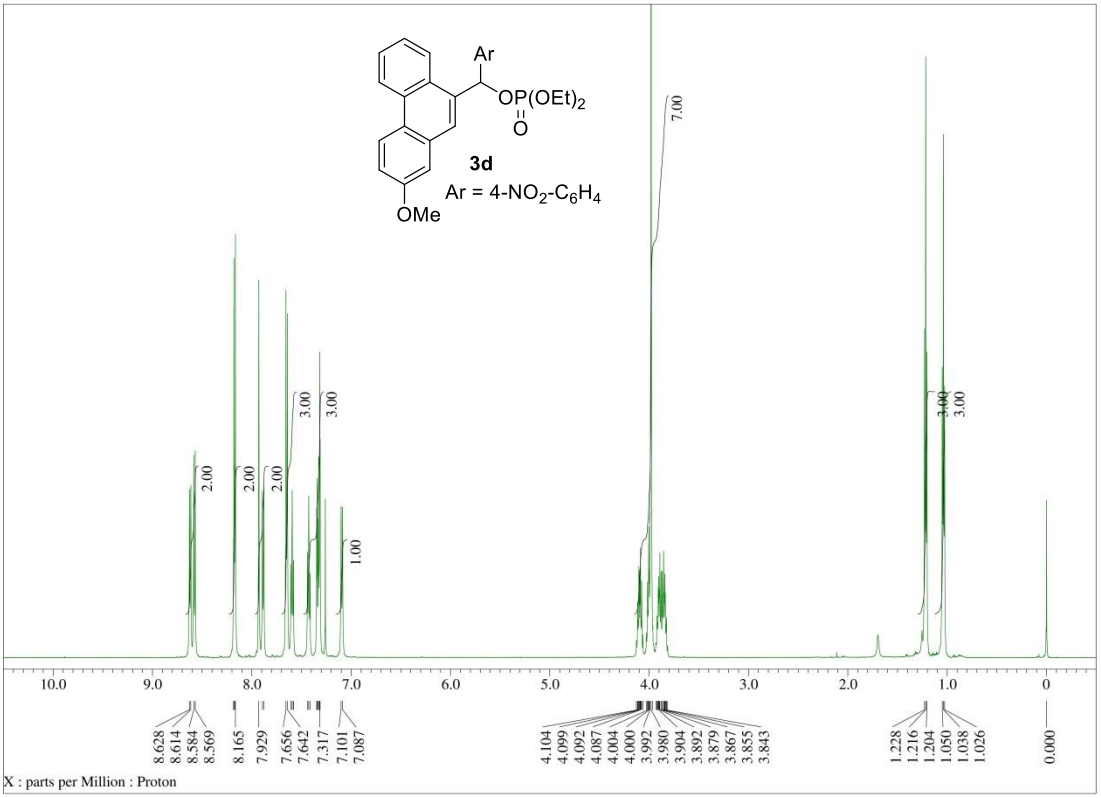

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.629
144.358
139.782
134.382
133.558
132.763
132.553
131.921
131.385
129.700
129.556
128.512
128.455
128.062
127.507
127.258
126.999
126.291
123.610
96.810
91.602
77.211
77.000
76.789
X : parts per Million : Carbon13

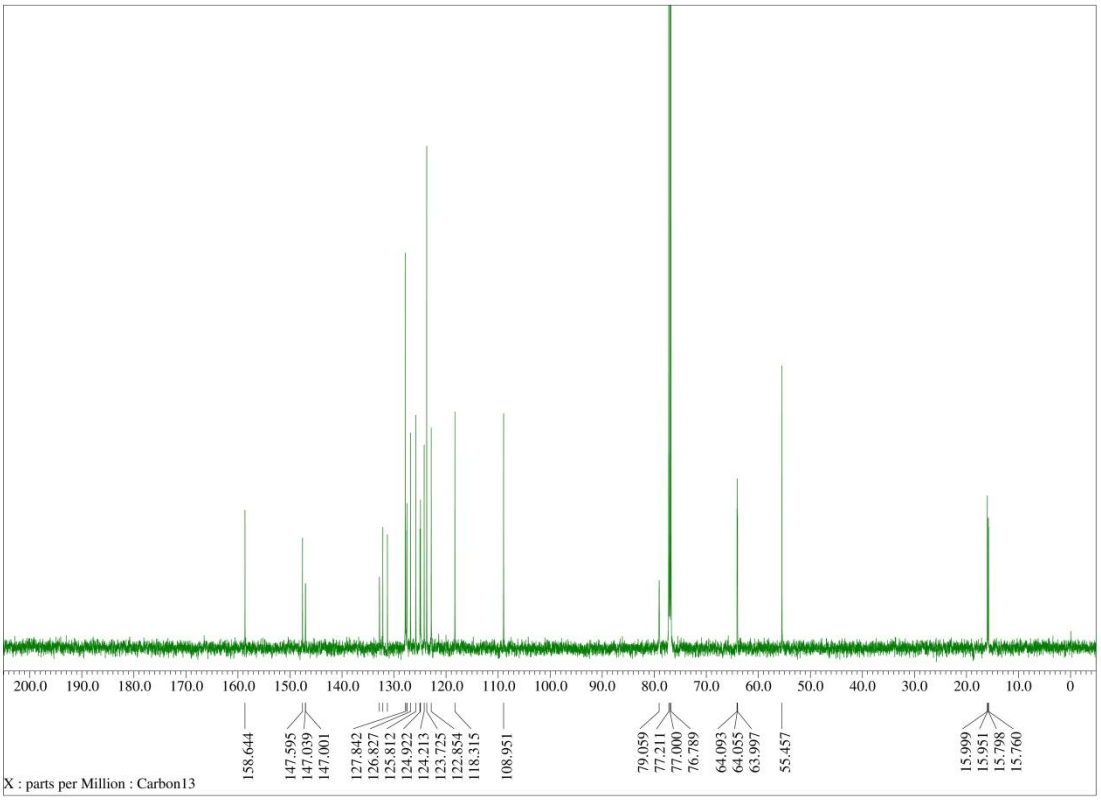

Ar
OP(OEt)2
O
3a
Ar = 4-NO2-C6H4
4.01
4.00
3.00
2.99
2.00
1.00
0.99
abundance
X : parts per Million : Proton

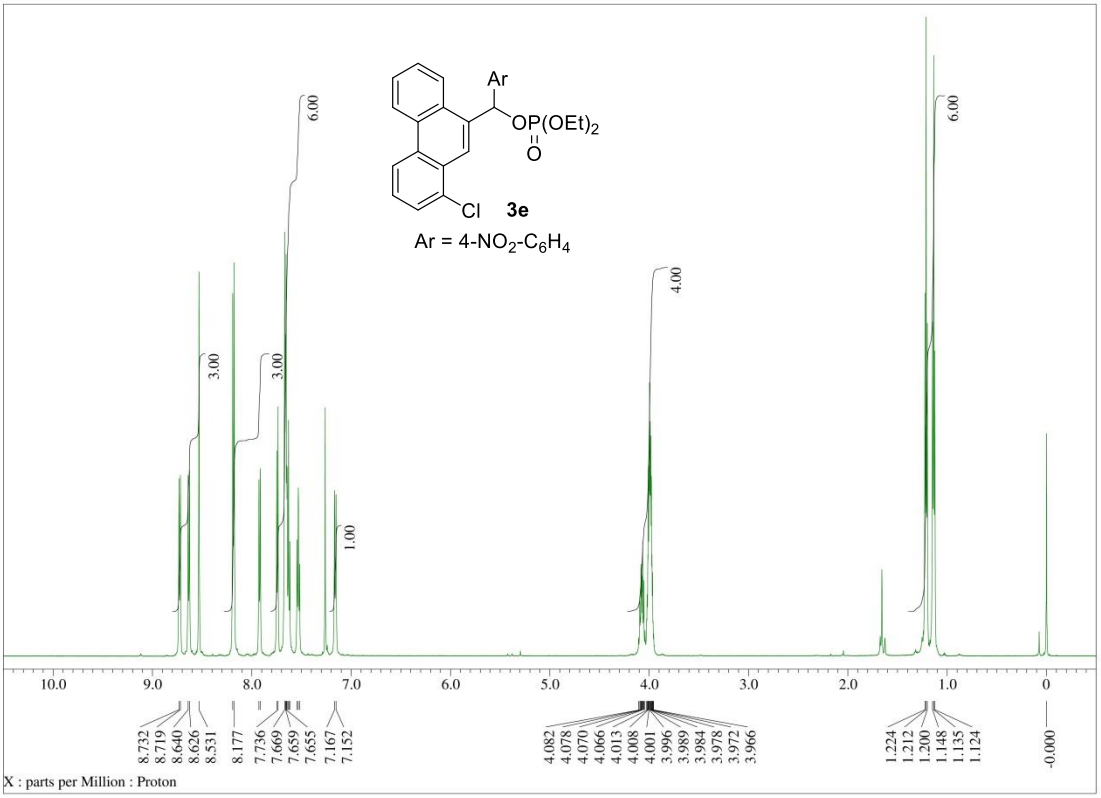

X : parts per Million : Carbon13

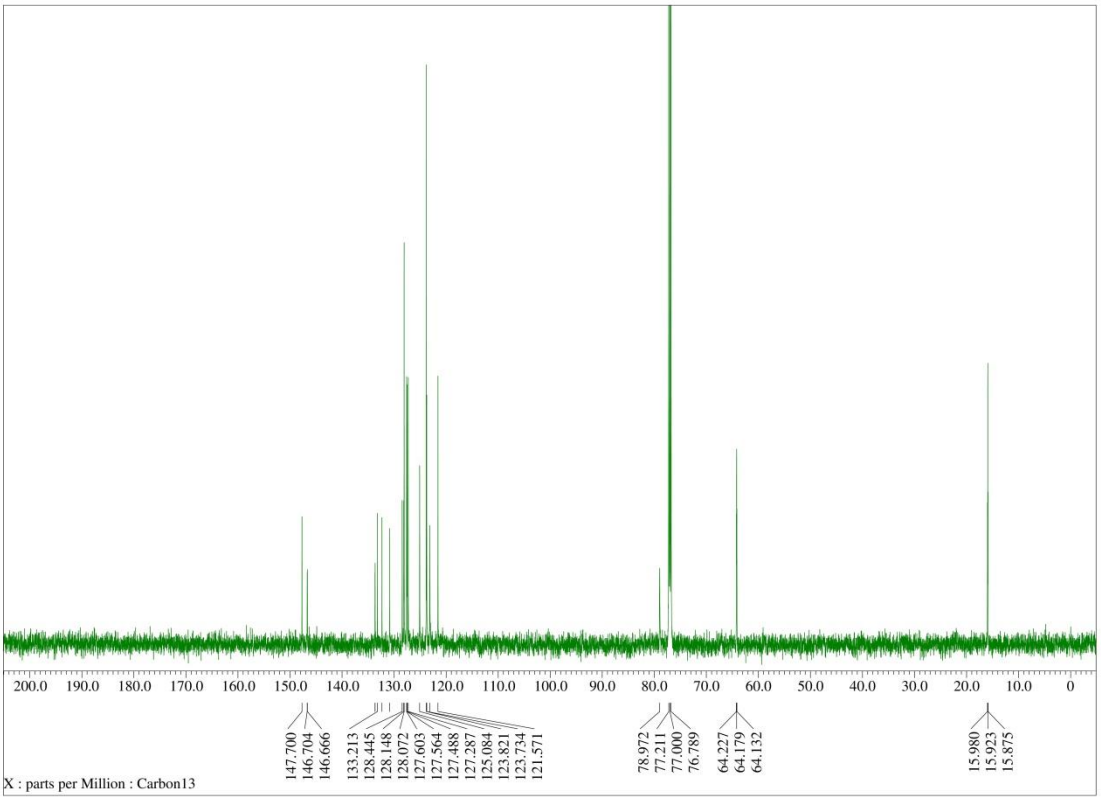

Ar
OP(OEt)2
O
F
3b
Ar = 4-NO2-C6H4
X : parts per Million : Proton

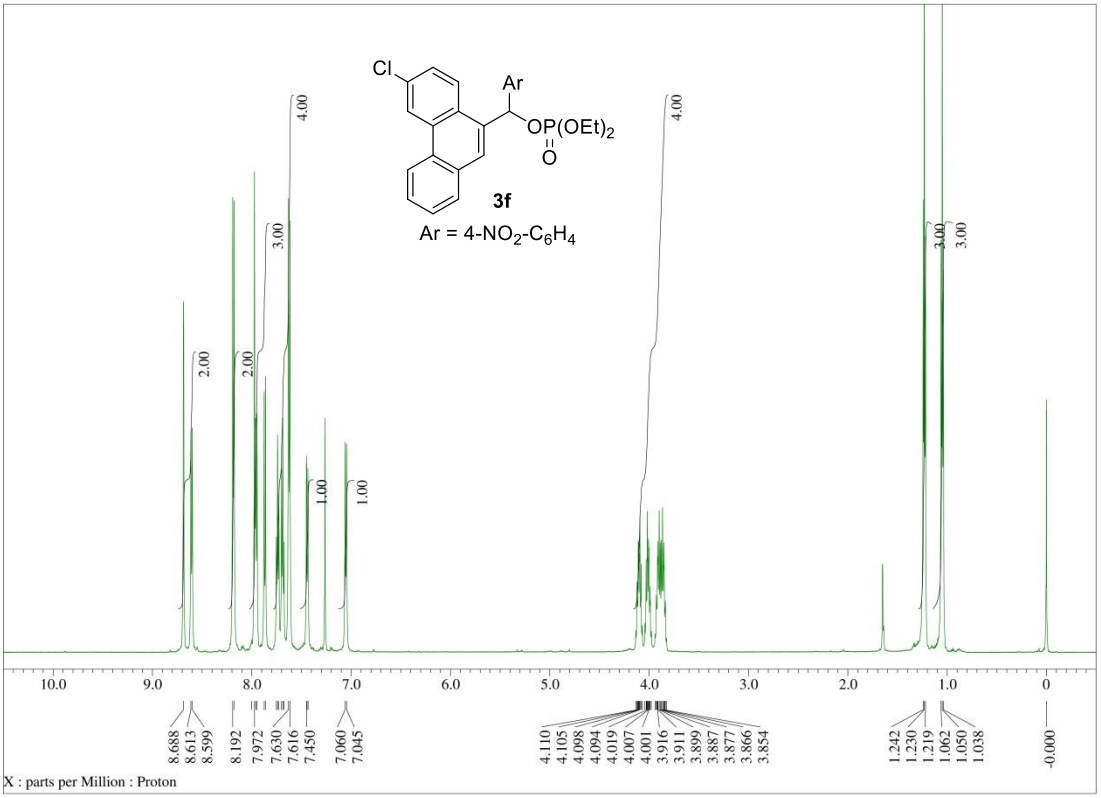

X : parts per Million : Carbon13

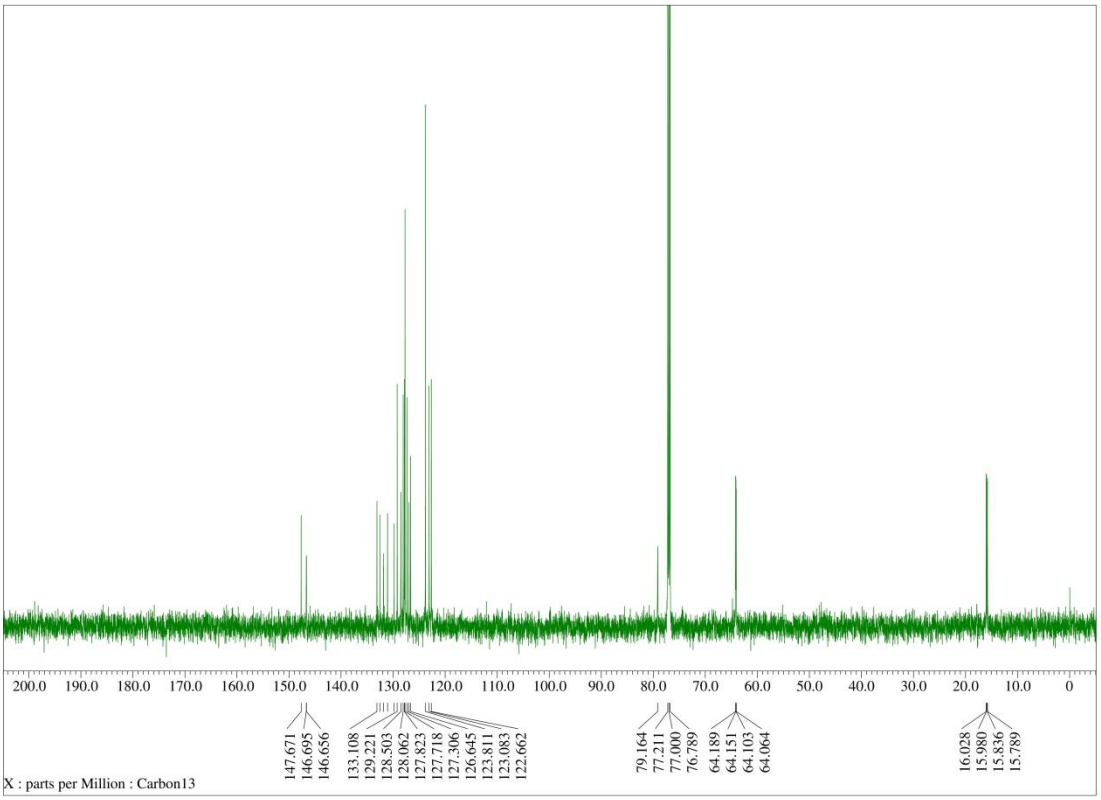

Ar
OP(OEt)2
O
3d
Ar = 4-NO2-C6H4
OMe
X : parts per Million : Proton

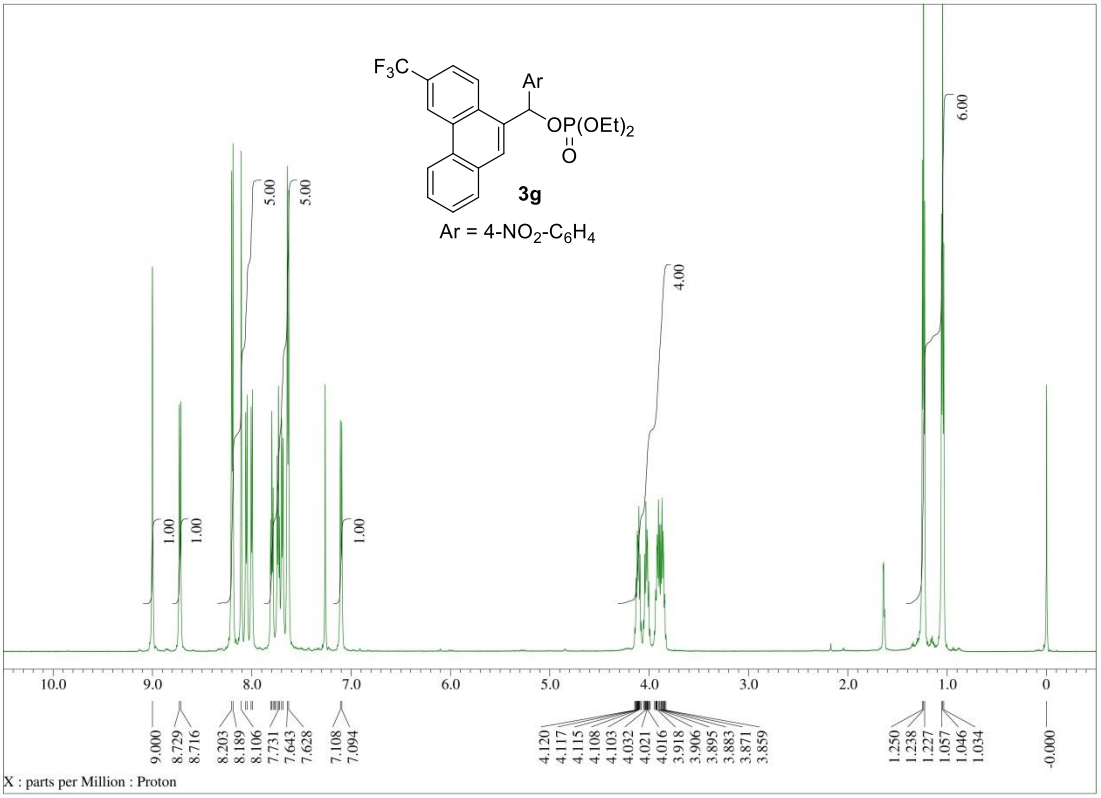

X : parts per Million : Carbon13

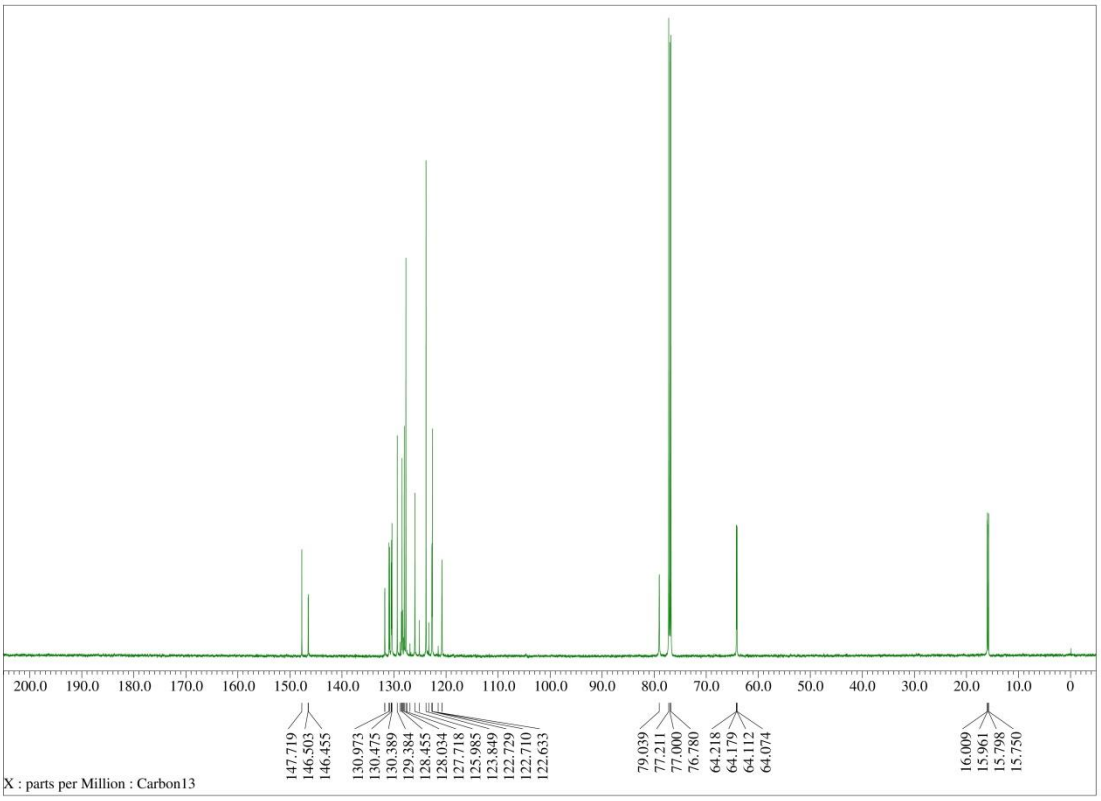

Ar
OP(OEt)2
O
Cl
3e
Ar = 4-NO2-C6H4
6.00
3.00
3.00
1.00
4.00
6.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.732 8.719 8.640 8.626 8.531 8.177 7.736 7.669 7.659 7.655 7.167 7.152
4.082 4.078 4.070 4.066 4.013 4.008 4.001 3.996 3.989 3.984 3.978 3.972 3.966
1.224 1.212 1.200 1.148 1.135 1.124
-0.000
X : parts per Million : Proton

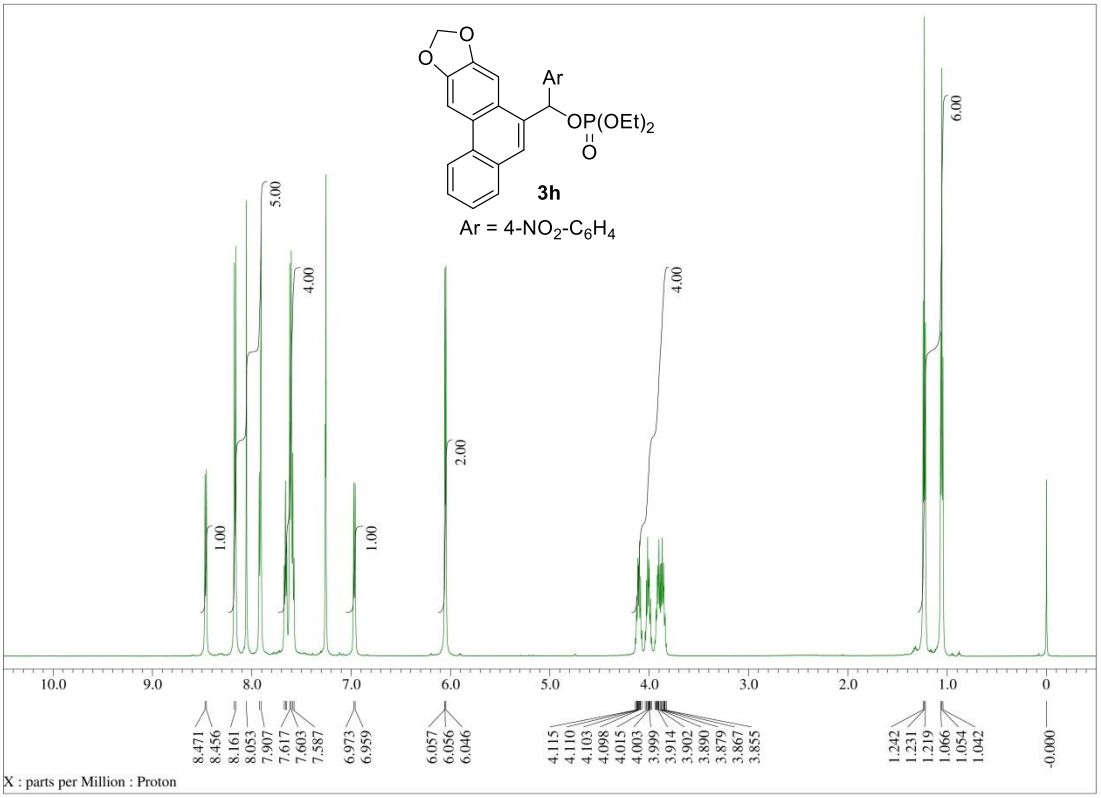

200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.700 146.704 146.666
133.213 128.445 128.148 128.072 127.603 127.564 127.488 127.287 125.084 123.821 123.734 121.571
78.972 77.211 77.000 76.789
64.227 64.179 64.132
15.980 15.923 15.875
X : parts per Million : Carbon13

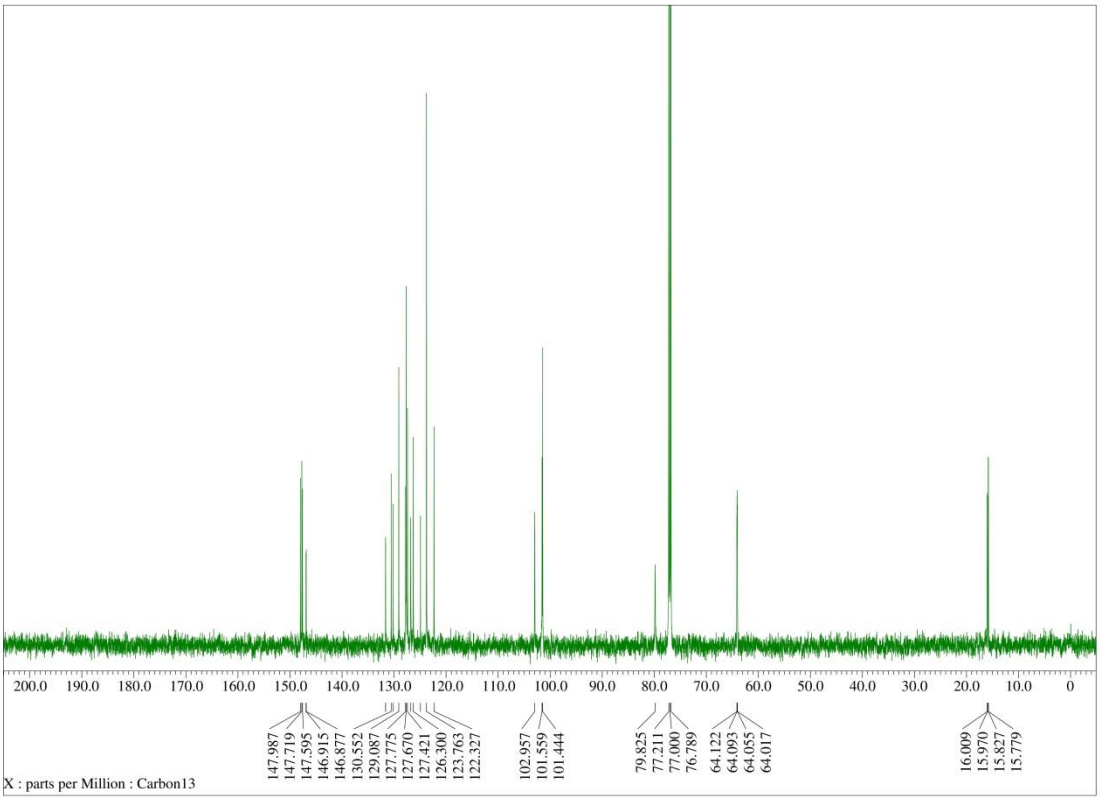

Cl
Ar
OP(OEt)2
O
3f
Ar = 4-NO2-C6H4
4.00
3.00
2.00
2.00
3.00
1.00
1.00
4.00
3.00
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.688 8.613 8.599 8.192 7.972 7.630 7.616 7.450 7.060 7.045
4.110 4.105 4.098 4.094 4.019 4.007 4.001 3.916 3.911 3.899 3.887 3.877 3.866 3.854
1.242 1.230 1.219 1.062 1.050 1.038
-0.000
X : parts per Million : Proton

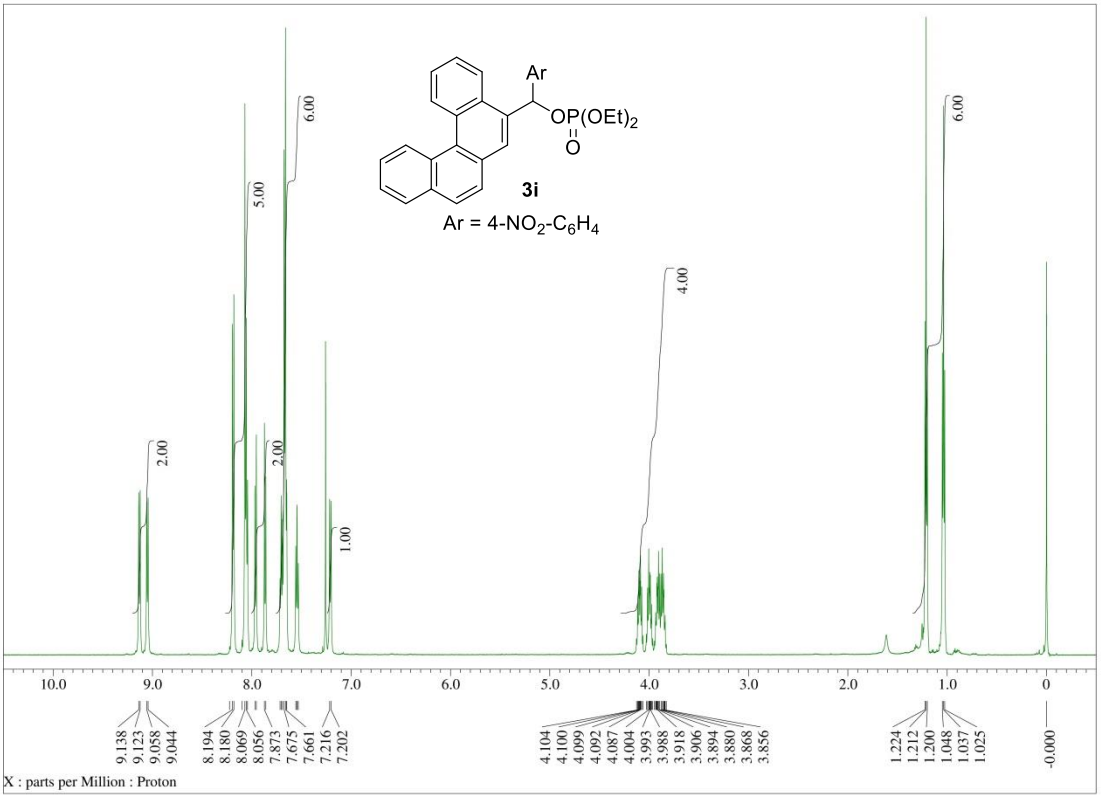

200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.671 146.695 146.656
133.108 129.221 128.503 128.062 127.823 127.718 127.306 126.645 123.811 123.083 122.662
79.164 77.211 77.000 76.789
64.189 64.151 64.103 64.064
16.028 15.980 15.836 15.789
X : parts per Million : Carbon13

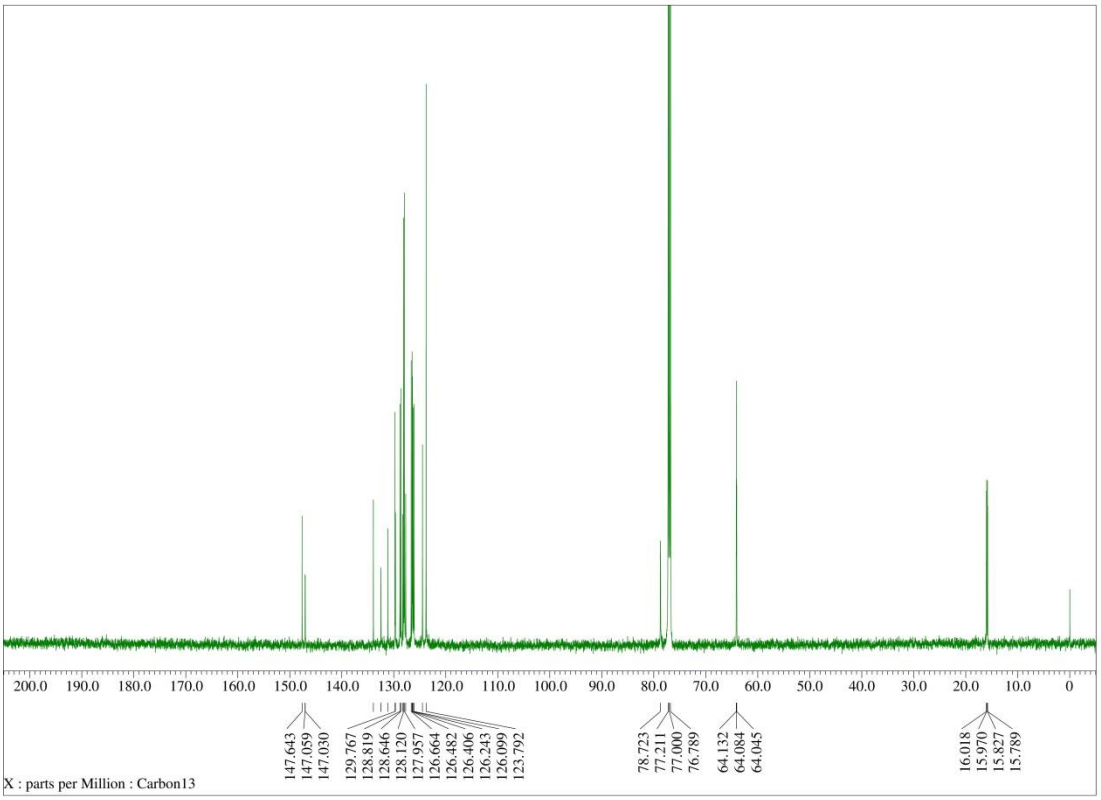

F3C
Ar
OP(OEt)2
O
3g
Ar = 4-NO2-C6H4
1.00
1.00
5.00
5.00
1.00
4.00
6.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.000
8.729
8.716
8.203
8.189
8.106
7.731
7.643
7.628
7.108
7.094
4.120
4.117
4.115
4.108
4.103
4.032
4.021
4.016
3.918
3.906
3.895
3.883
3.871
3.859
1.250
1.238
1.227
1.057
1.046
1.034
-0.000
X : parts per Million : Proton

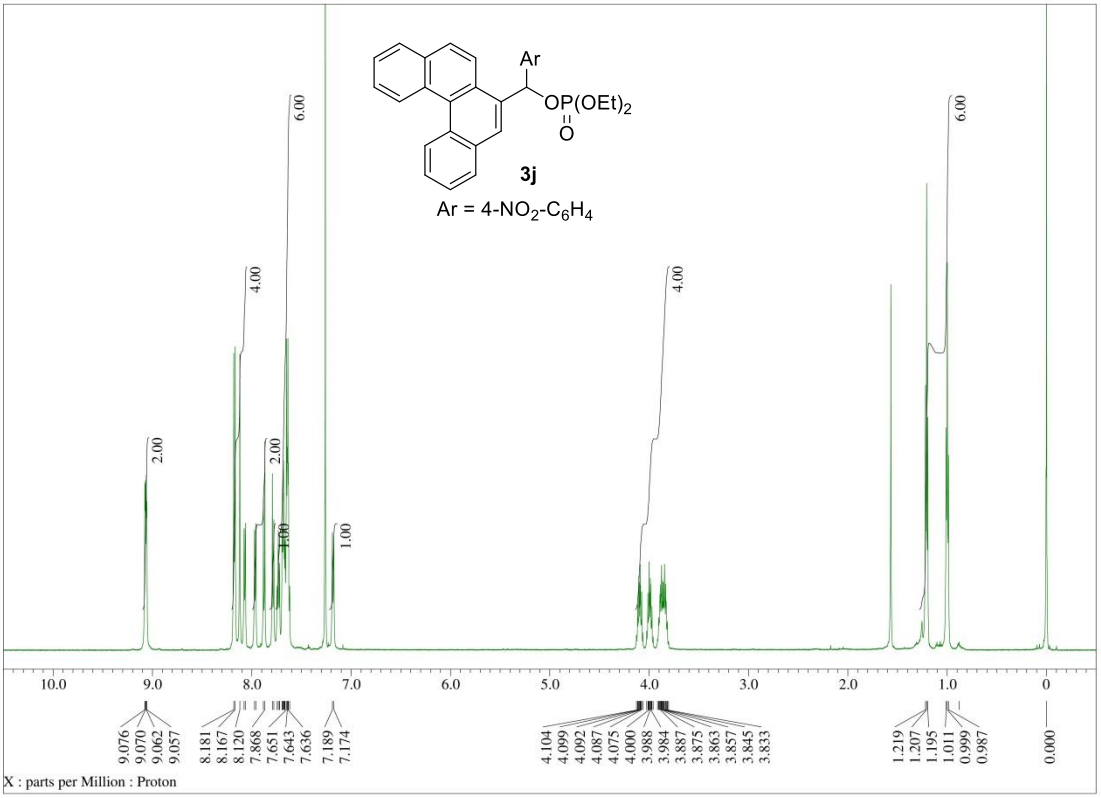

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.719
146.503
146.455
130.973
130.475
130.389
129.384
128.455
128.034
127.718
125.985
123.849
122.729
122.710
122.633
79.039
77.211
77.000
76.780
64.218
64.179
64.112
64.074
16.009
15.961
15.798
15.750
X : parts per Million : Carbon13

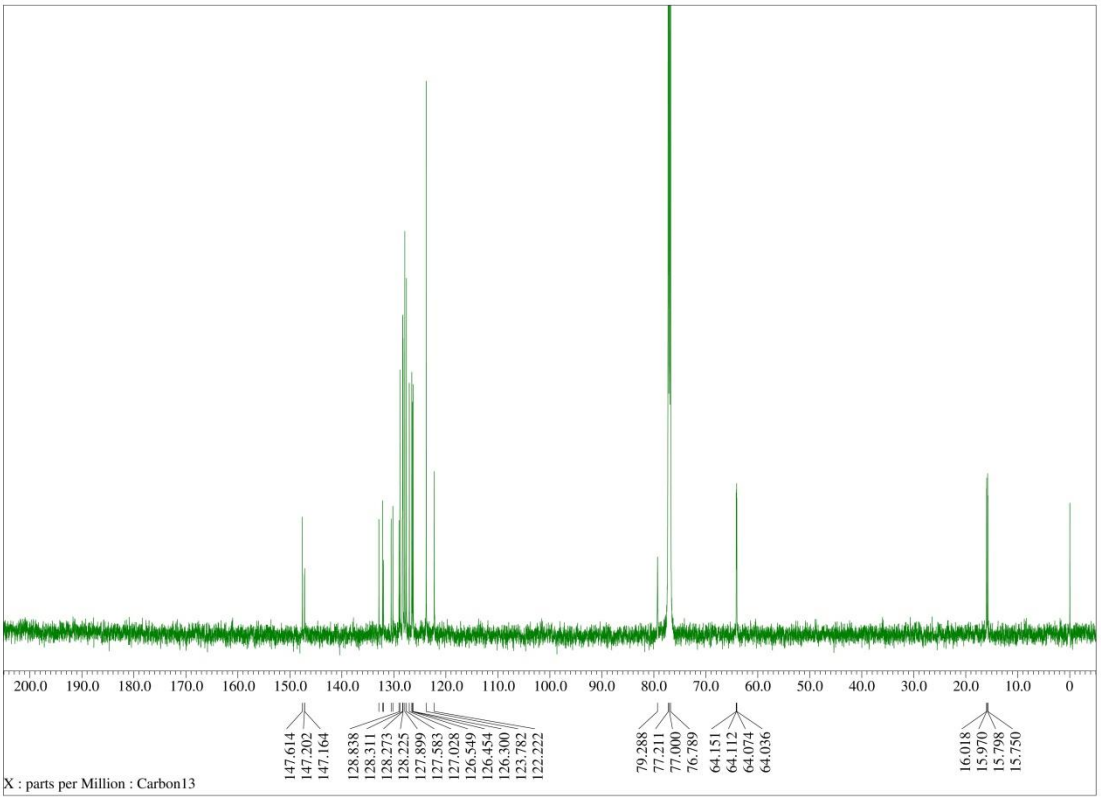

Ar
OP(OEt)2
O
3h
Ar = 4-NO2-C6H4
1.00
5.00
4.00
1.00
2.00
4.00
6.00
X : parts per Million : Proton

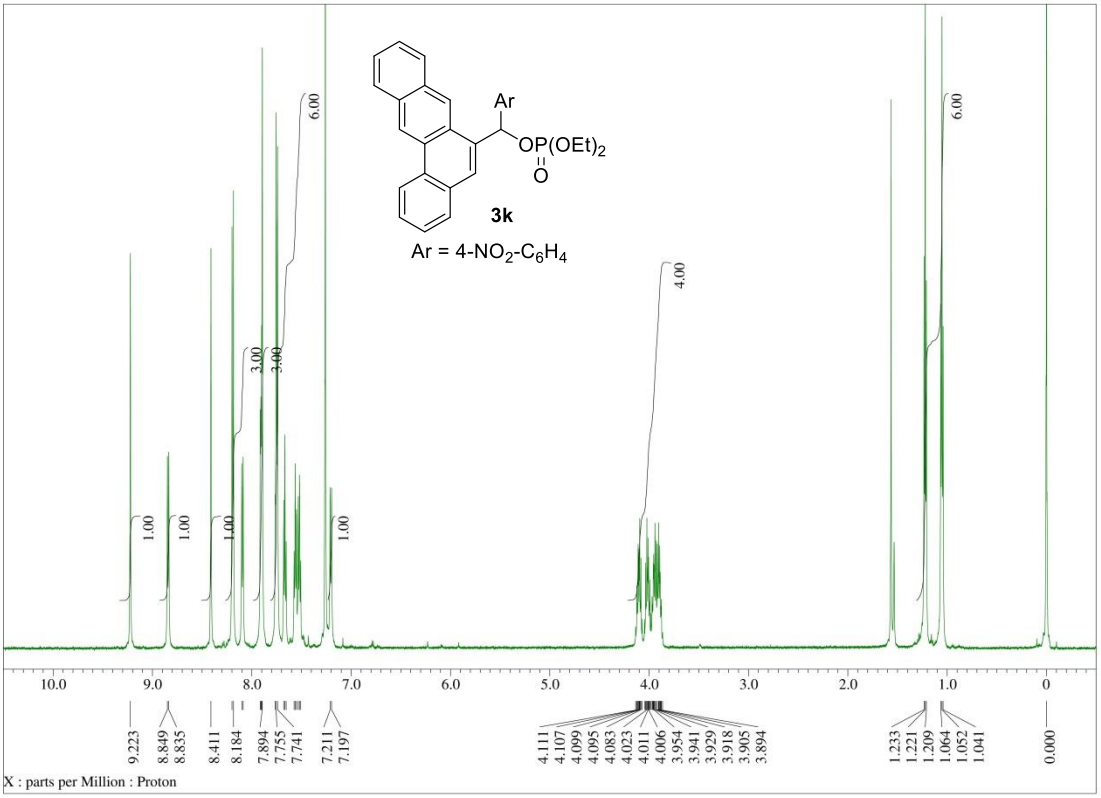

X : parts per Million : Carbon13

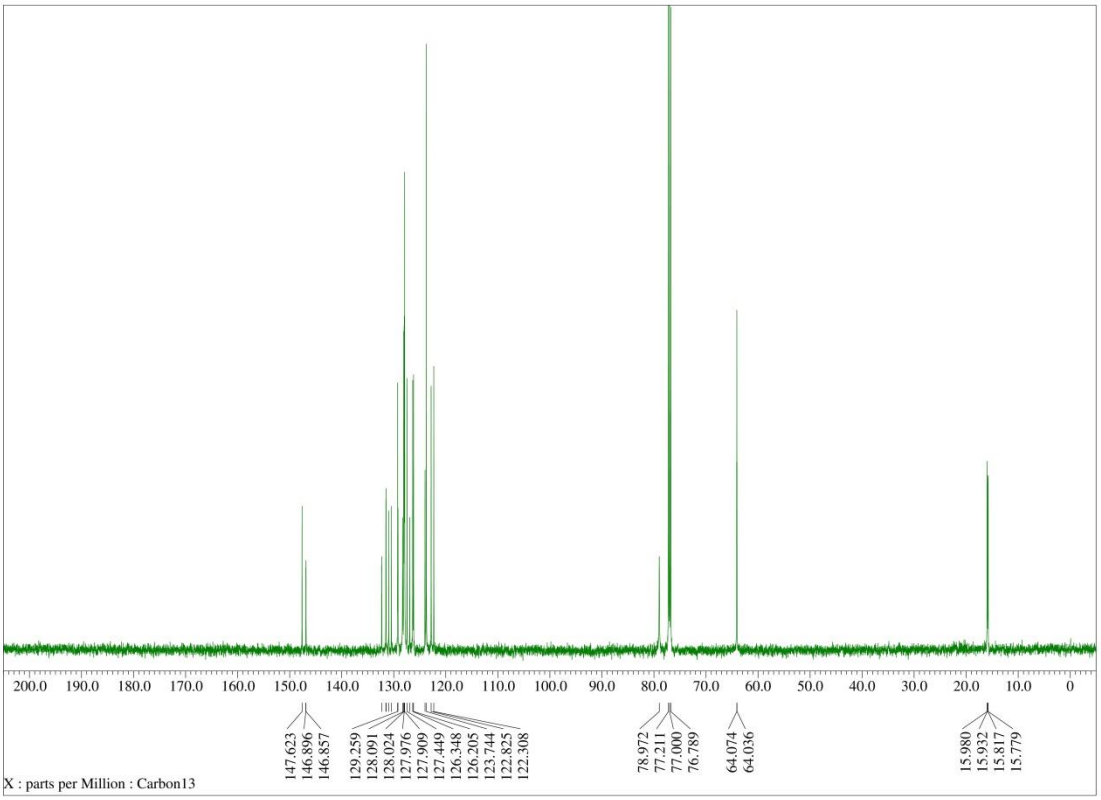

Ar
OP(OEt)2
O
3i
Ar = 4-NO2-C6H4
6.00
5.00
2.00
2.00
1.00
4.00
6.00
9.138
9.123
9.058
9.044
8.194
8.180
8.069
8.056
7.873
7.675
7.661
7.216
7.202
4.104
4.100
4.099
4.092
4.087
4.004
3.993
3.988
3.918
3.906
3.894
3.880
3.868
3.856
1.224
1.212
1.200
1.048
1.037
1.025
-0.000
X : parts per Million : Proton

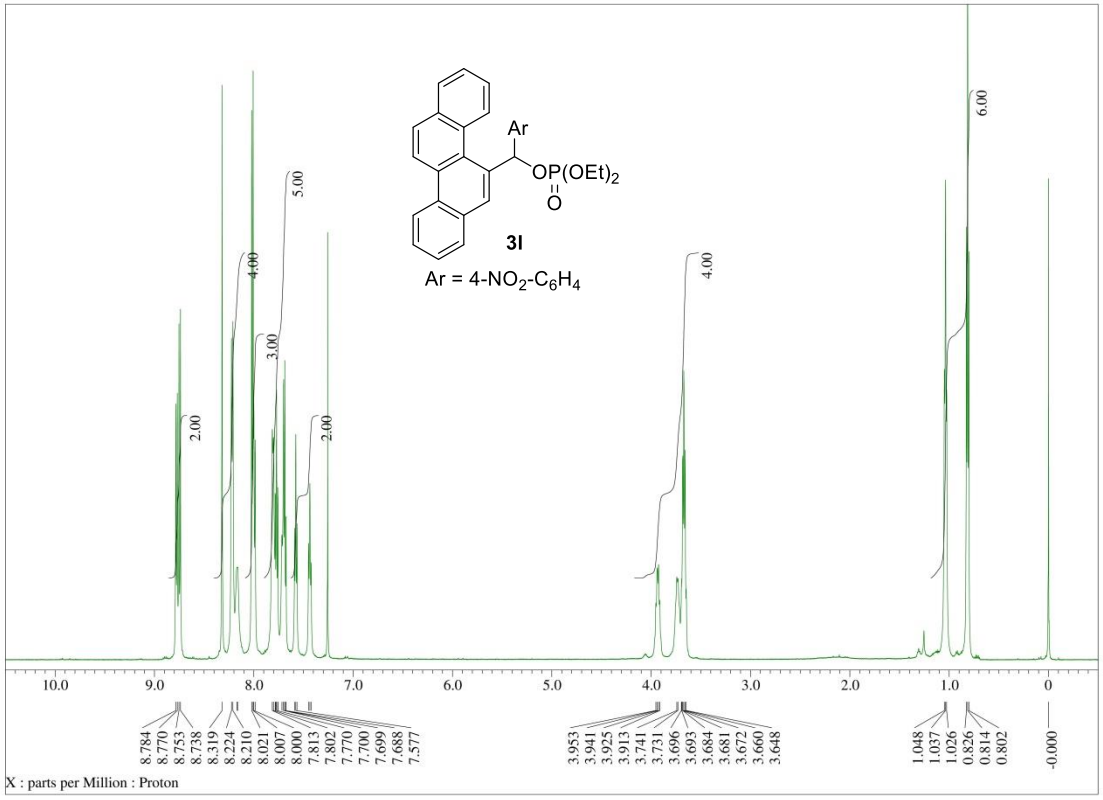

147.643
147.059
147.030
129.767
128.819
128.646
128.120
127.957
126.664
126.482
126.406
126.243
126.099
123.792
78.723
77.211
77.000
76.789
64.132
64.084
64.045
16.018
15.970
15.827
15.789
X : parts per Million : Carbon13

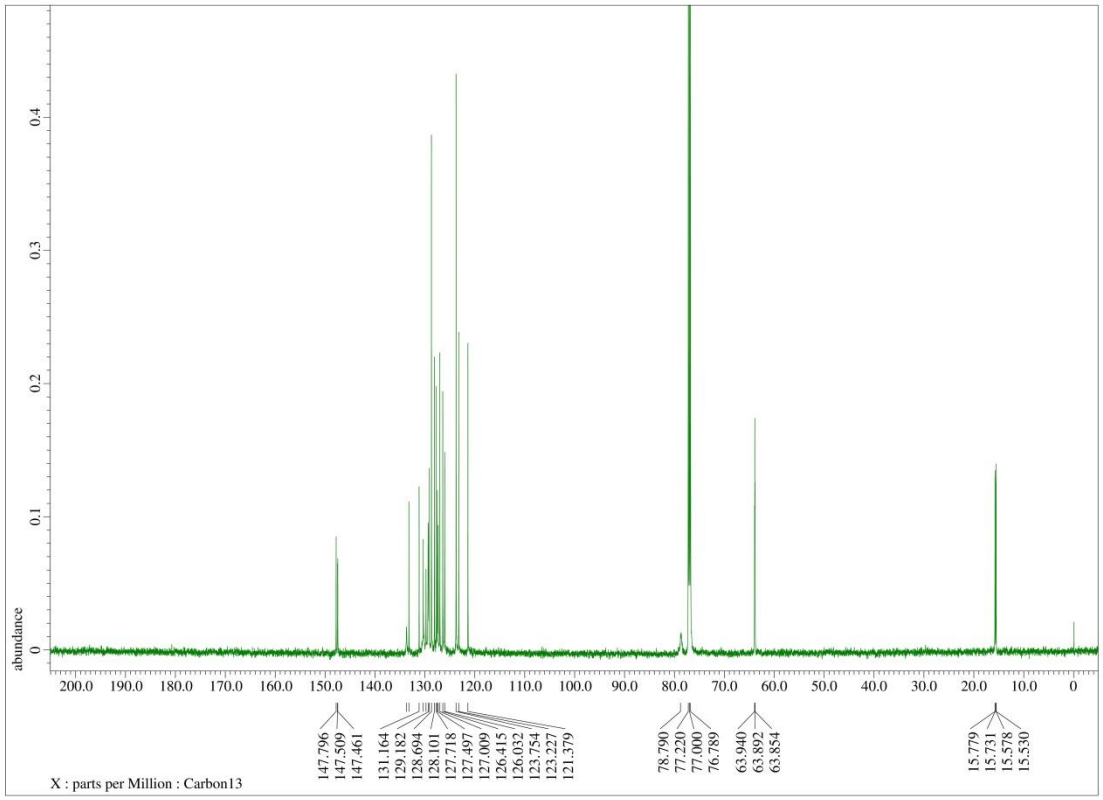

Ar
OP(OEt)2
O
3j
Ar = 4-NO2-C6H4
6.00
4.00
2.00
2.00
1.00
1.00
4.00
6.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.076 9.070 9.062 9.057
8.181 8.167 8.120 7.868 7.651 7.643 7.636
7.189 7.174
4.104 4.099 4.092 4.087 4.075 4.000 3.988 3.984 3.887 3.875 3.863 3.857 3.845 3.833
1.219 1.207 1.195 1.011 0.999 0.987
0.000
X : parts per Million : Proton

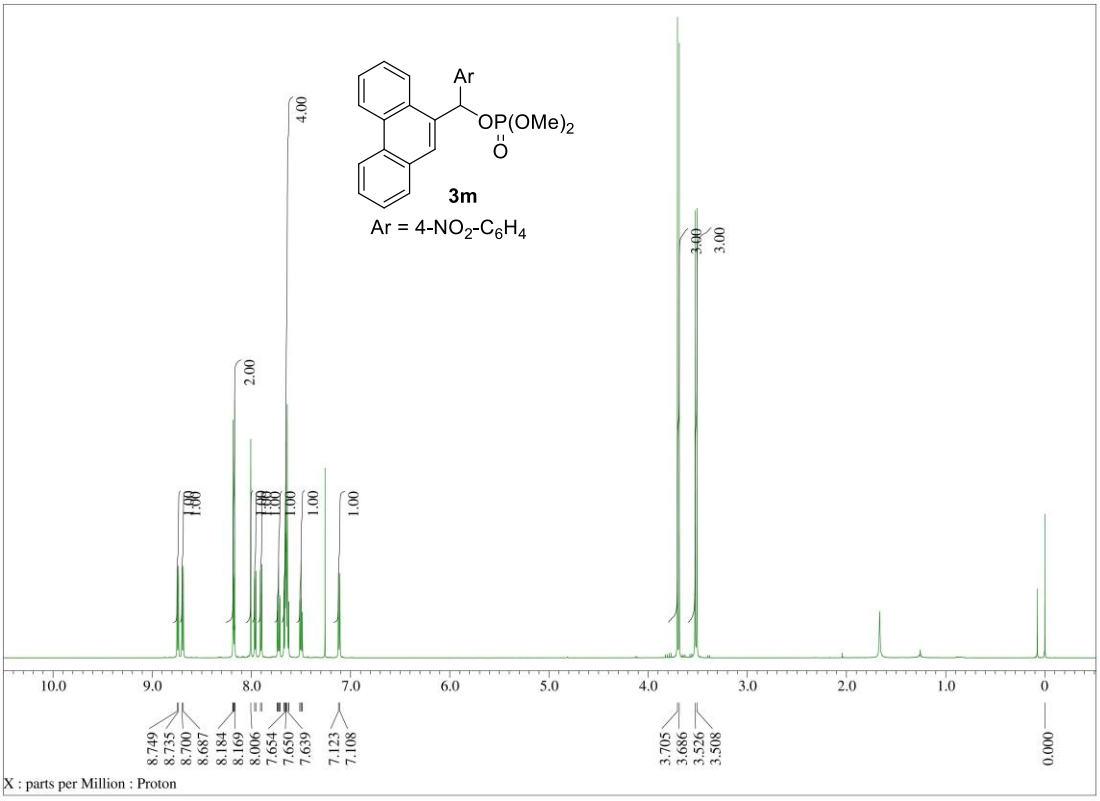

200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.614 147.202 147.164
128.838 128.311 128.273 128.225 127.899 127.583 127.028 126.549 126.454 126.300 123.782 122.222
79.288 77.211 77.000 76.789
64.151 64.112 64.074 64.036
16.018 15.970 15.798 15.750
X : parts per Million : Carbon13

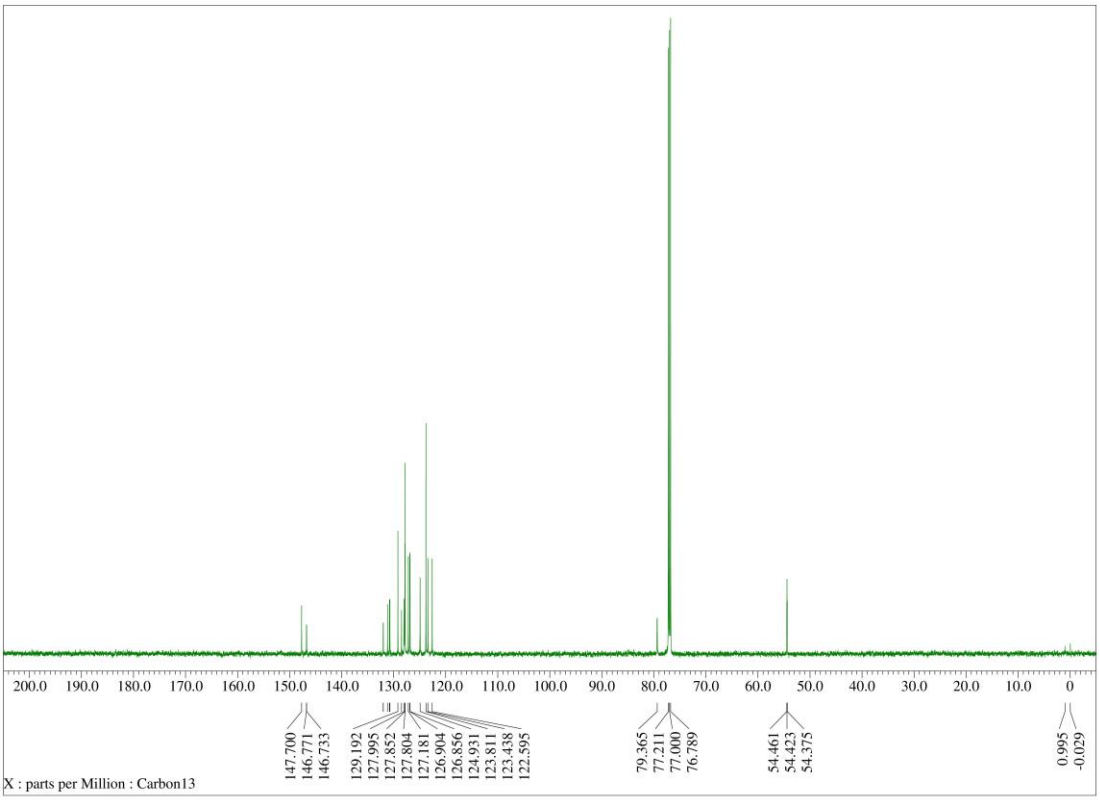

Ar
OP(OEt)2
O
3k
Ar = 4-NO2-C6H4
6.00
6.00
4.00
3.00
3.00
1.00
1.00
1.00
1.00
1.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.223
8.849
8.835
8.411
8.184
7.894
7.755
7.741
7.211
7.197
4.111
4.107
4.099
4.095
4.083
4.023
4.011
4.006
3.954
3.941
3.929
3.918
3.905
3.894
1.233
1.221
1.209
1.064
1.052
1.041
0.000
X : parts per Million : Proton

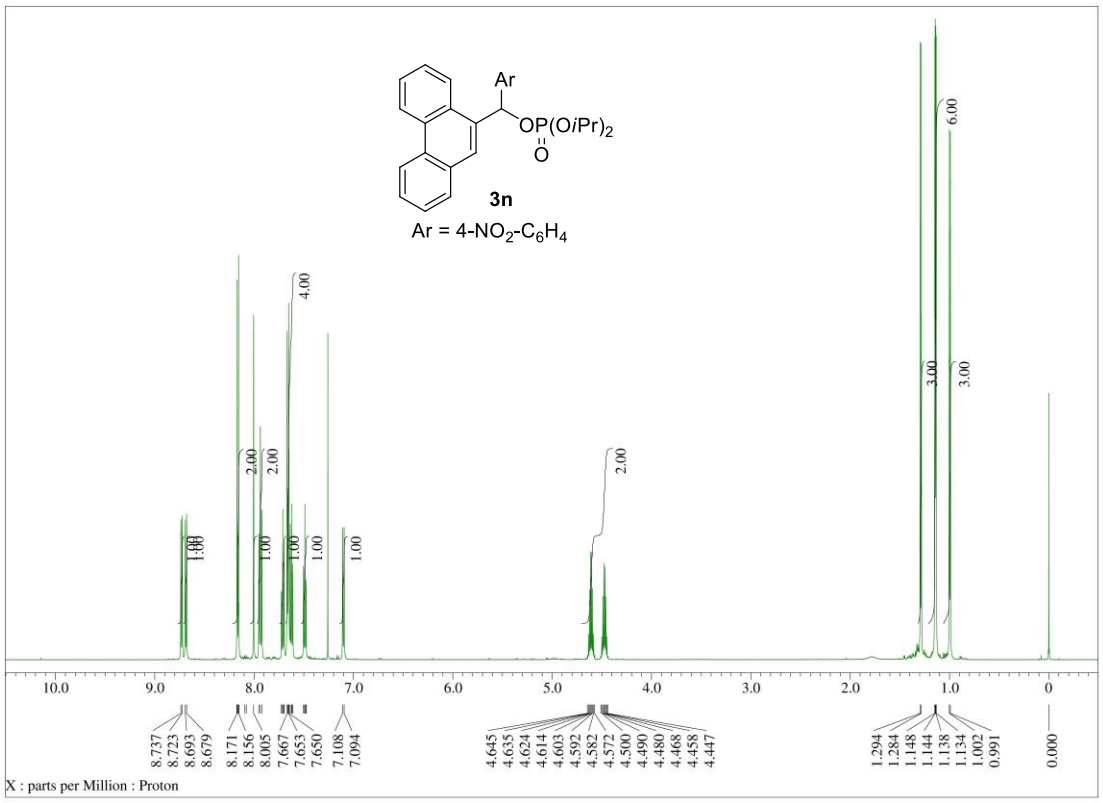

200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.623
146.896
146.857
129.259
128.091
128.024
127.976
127.909
127.449
126.348
126.205
123.744
122.825
122.308
78.972
77.211
77.000
76.789
64.074
64.036
15.980
15.932
15.817
15.779
X : parts per Million : Carbon13

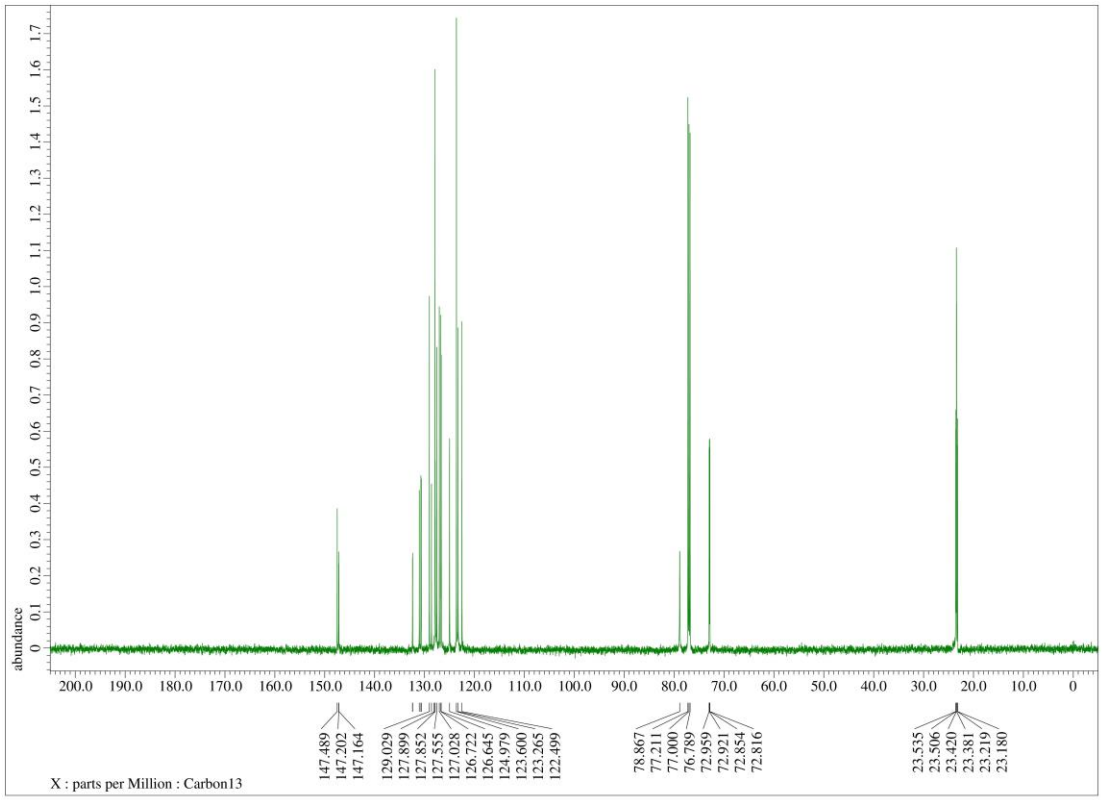

Ar
OP(OEt)2
O
3l
Ar = 4-NO2-C6H4
6.00
5.00
4.00
4.00
3.00
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.784
8.770
8.753
8.738
8.319
8.224
8.210
8.021
8.007
8.000
7.813
7.802
7.770
7.700
7.699
7.688
7.577
3.953
3.941
3.925
3.913
3.741
3.731
3.696
3.693
3.684
3.681
3.672
3.660
3.648
1.048
1.037
1.026
0.826
0.814
0.802
-0.000
X : parts per Million : Proton

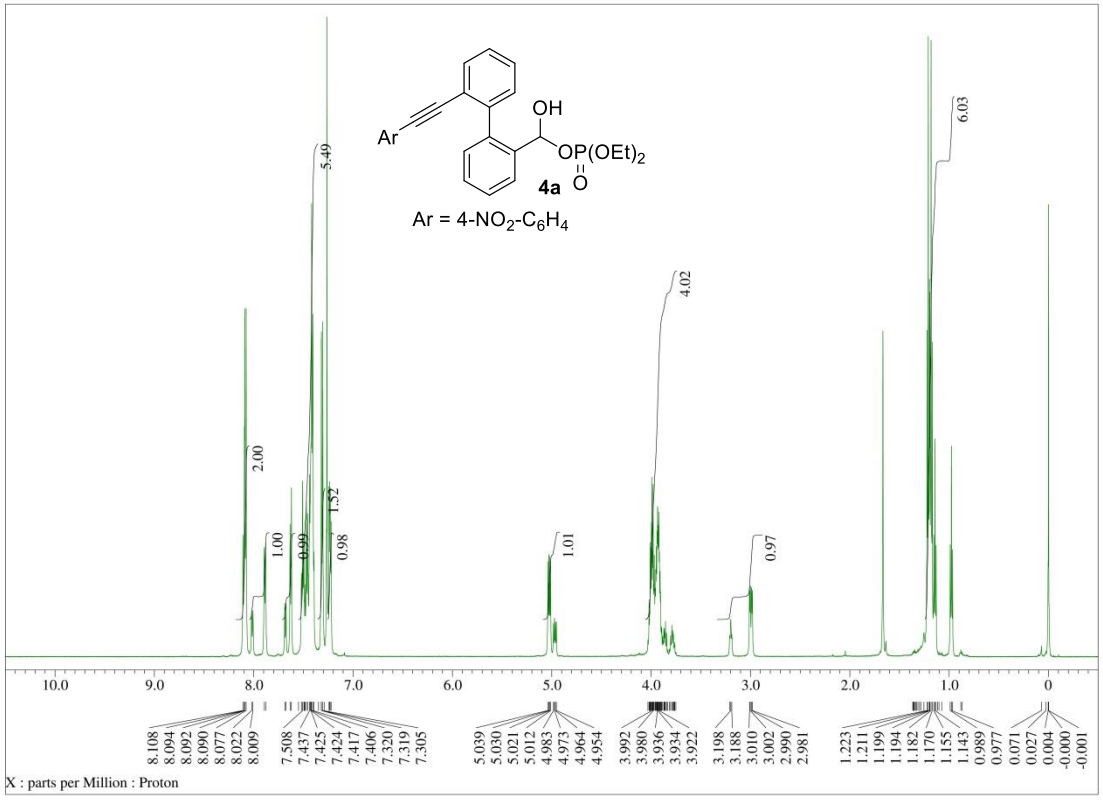

abundance
0
0.1
0.2
0.3
0.4
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.796
147.509
147.461
131.164
129.182
128.694
128.101
127.718
127.497
127.009
126.415
126.032
123.754
123.227
121.379
78.790
77.220
77.000
76.789
63.940
63.892
63.854
15.779
15.731
15.578
15.530
X : parts per Million : Carbon13

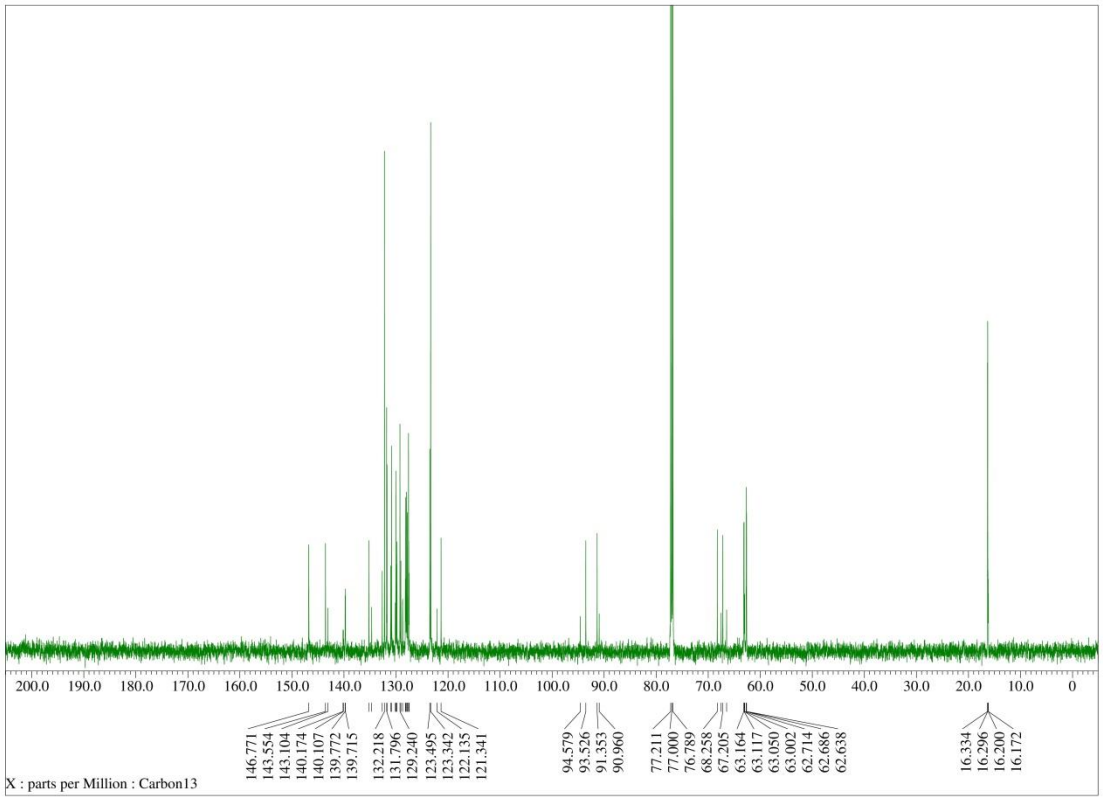

Ar
OP(OMe)2
O
3m
Ar = 4-NO2-C6H4
4.00
2.00
1.00
1.00
1.00
3.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.749
8.735
8.700
8.687
8.184
8.169
8.006
7.654
7.650
7.639
7.123
7.108
3.705
3.686
3.526
3.508
0.000
X : parts per Million : Proton

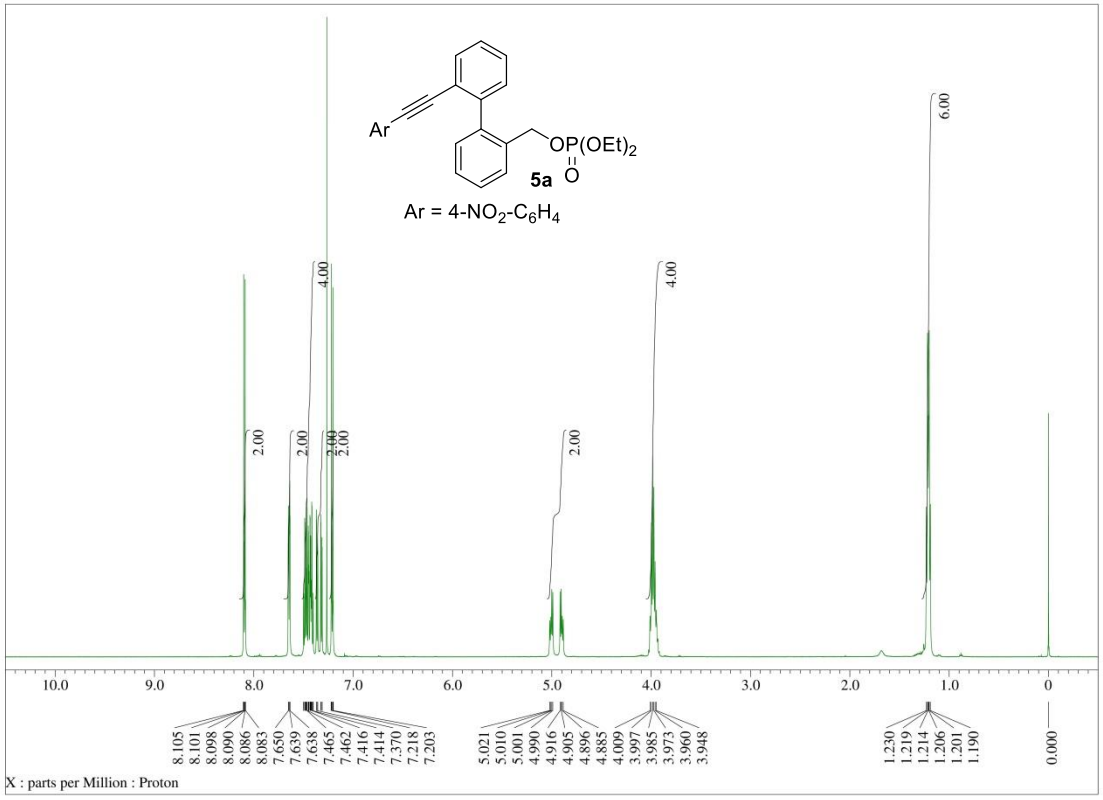

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.700
146.771
146.733
129.192
127.995
127.852
127.804
127.181
126.904
126.856
124.931
123.811
123.438
122.595
79.365
77.211
77.000
76.789
54.461
54.423
54.375
0.995
-0.029
X : parts per Million : Carbon13

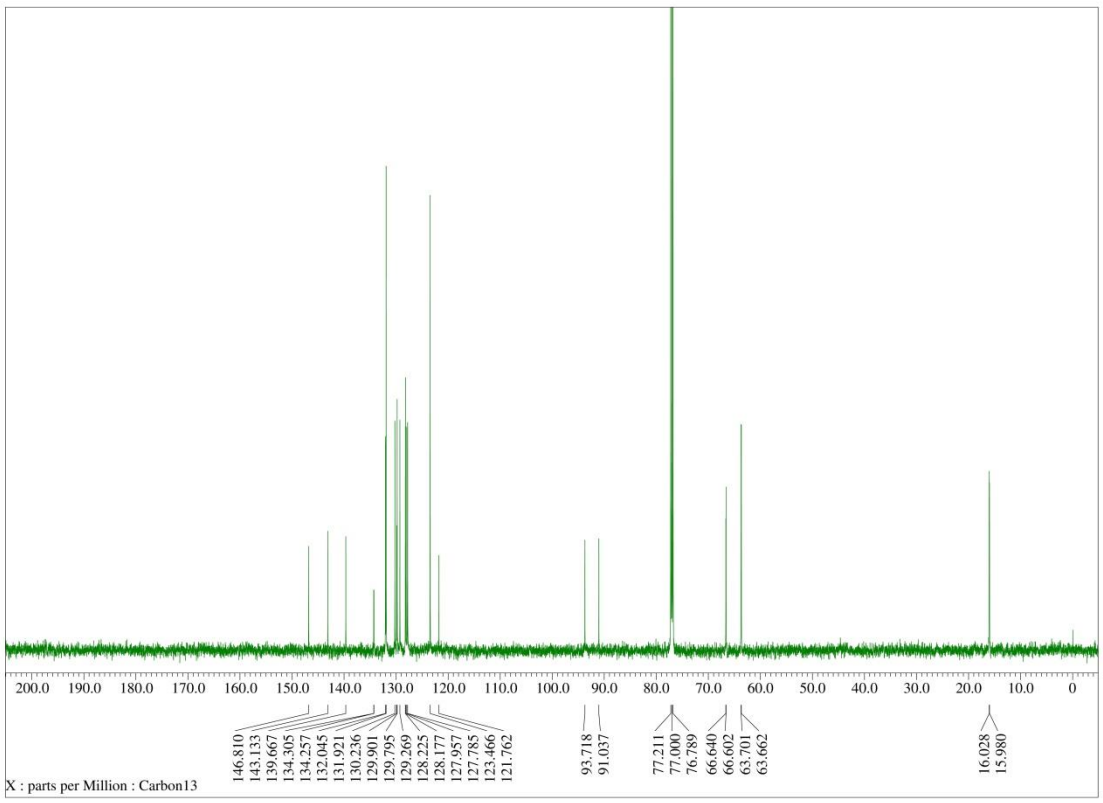

Ar
OP(O*i*Pr)$_2$
O
3n
Ar = 4-NO$_2$-C$_6$H$_4$
X : parts per Million : Proton

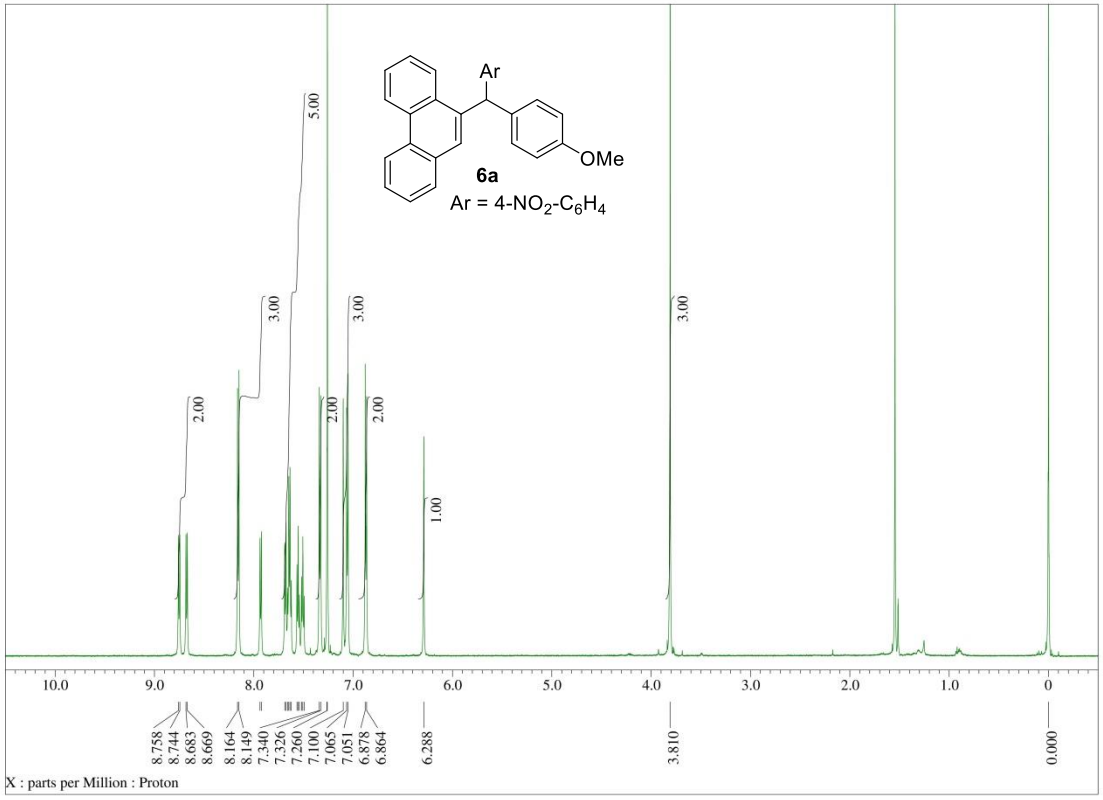

abundance
X : parts per Million : Carbon13

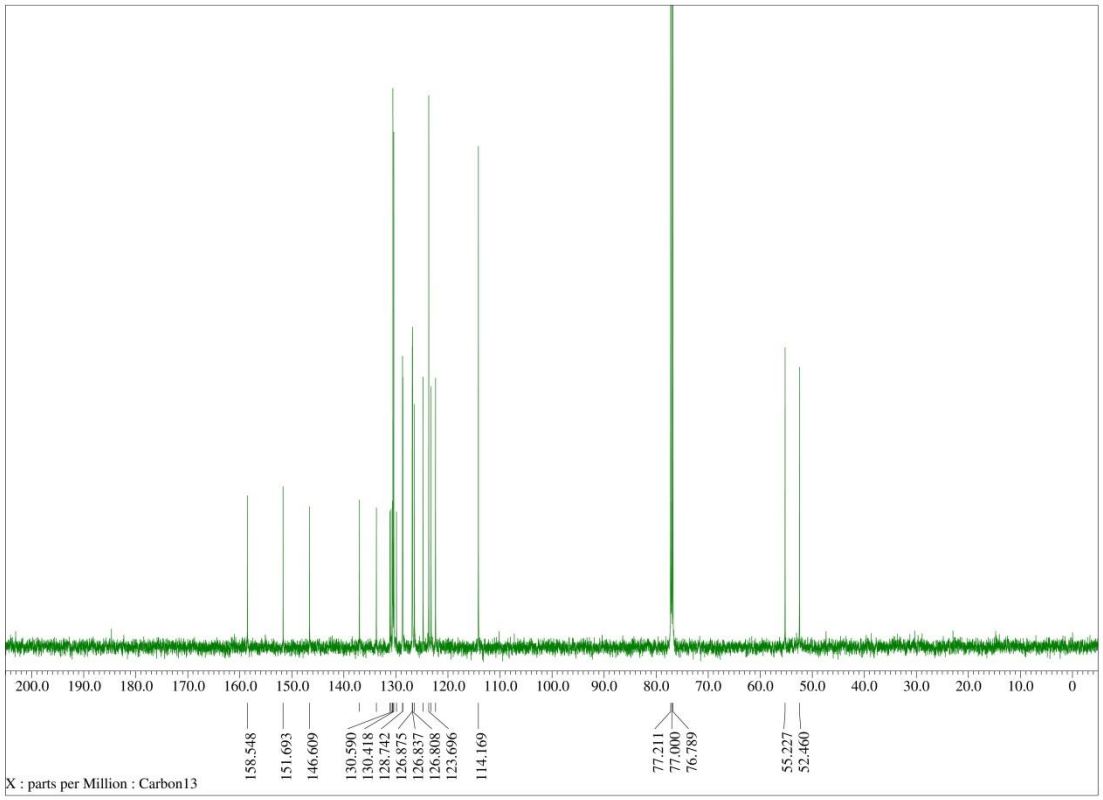

OH
Ar
OP(OEt)2
O
4a
Ar = 4-NO2-C6H4
X : parts per Million : Proton

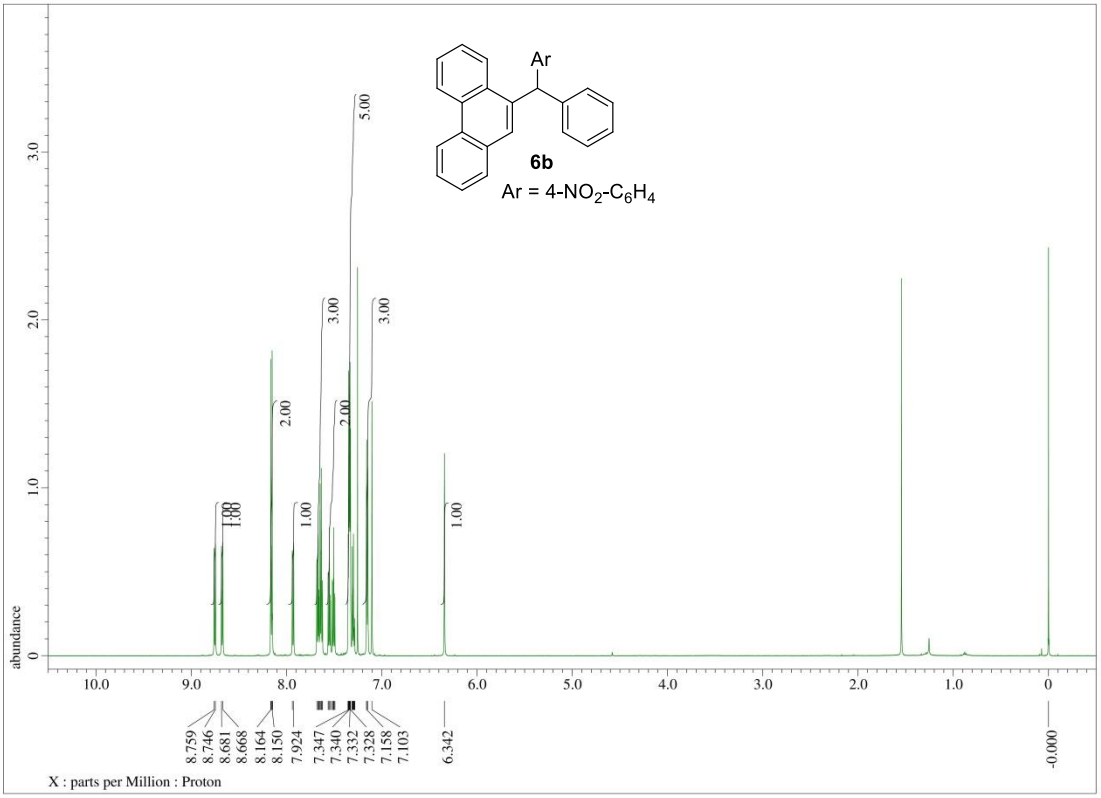

X : parts per Million : Carbon13

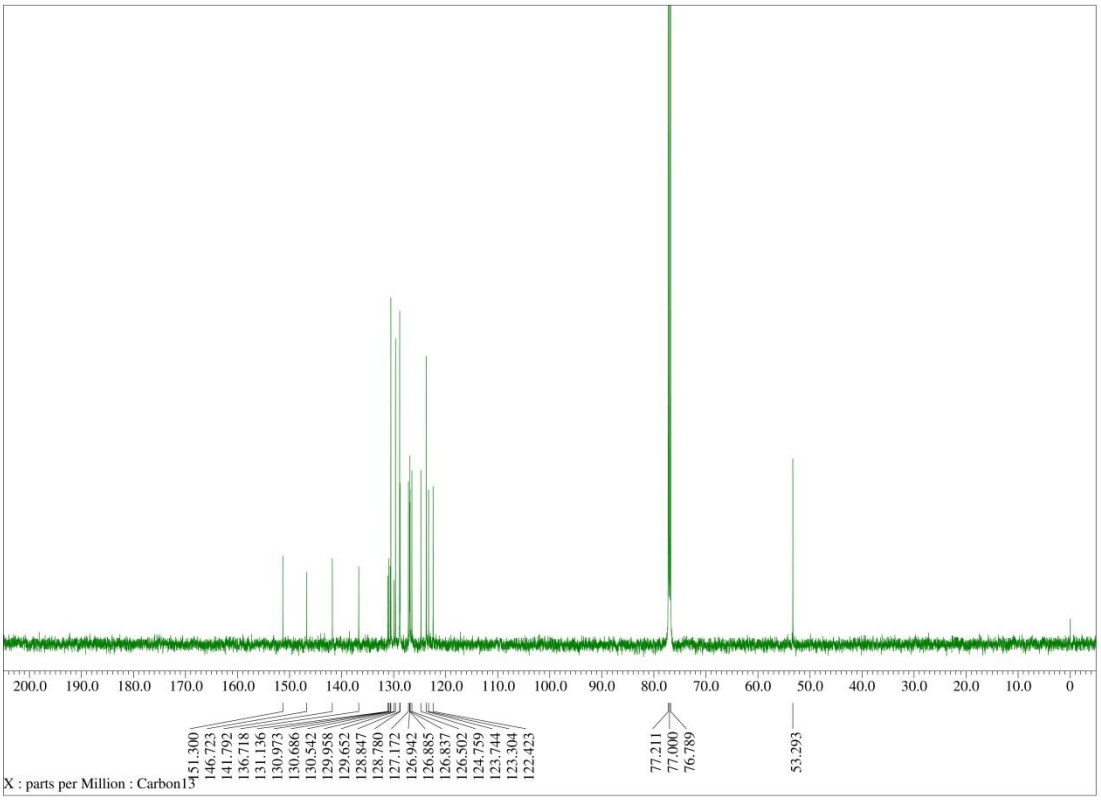

Ar
OP(OEt)2
O
5a
Ar = 4-NO2-C6H4
6.00
4.00
4.00
2.00
2.00
2.00
2.00
2.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.105 8.101 8.098 8.090 8.086 8.083 7.650 7.639 7.638 7.465 7.462 7.416 7.414 7.370 7.218 7.203
5.021 5.010 5.001 4.990 4.916 4.905 4.896 4.885 4.009 3.997 3.985 3.973 3.960 3.948
1.230 1.219 1.214 1.206 1.201 1.190
0.000
X : parts per Million : Proton

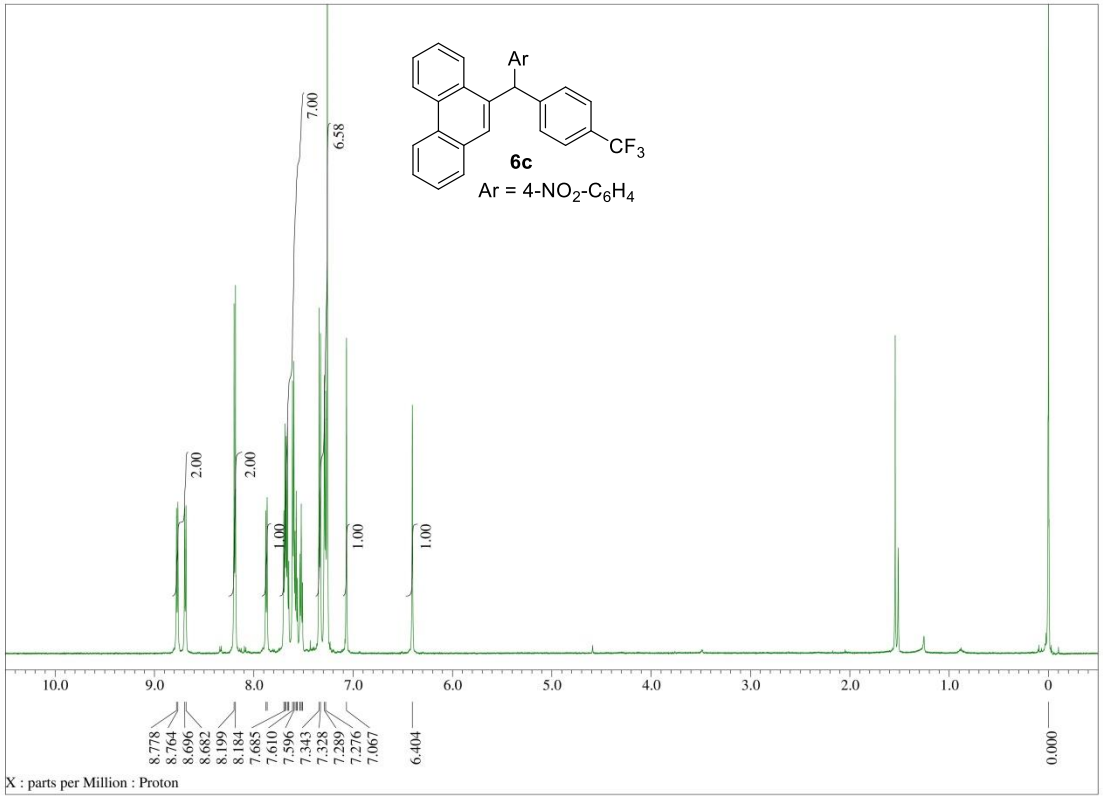

200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
146.810 143.133 139.667 134.305 134.257 132.045 131.921 130.236 129.901 129.795 129.269 128.225 128.177 127.957 127.785 123.466 121.762
93.718 91.037
77.211 77.000 76.789
66.640 66.602
63.701 63.662
16.028 15.980
X : parts per Million : Carbon13

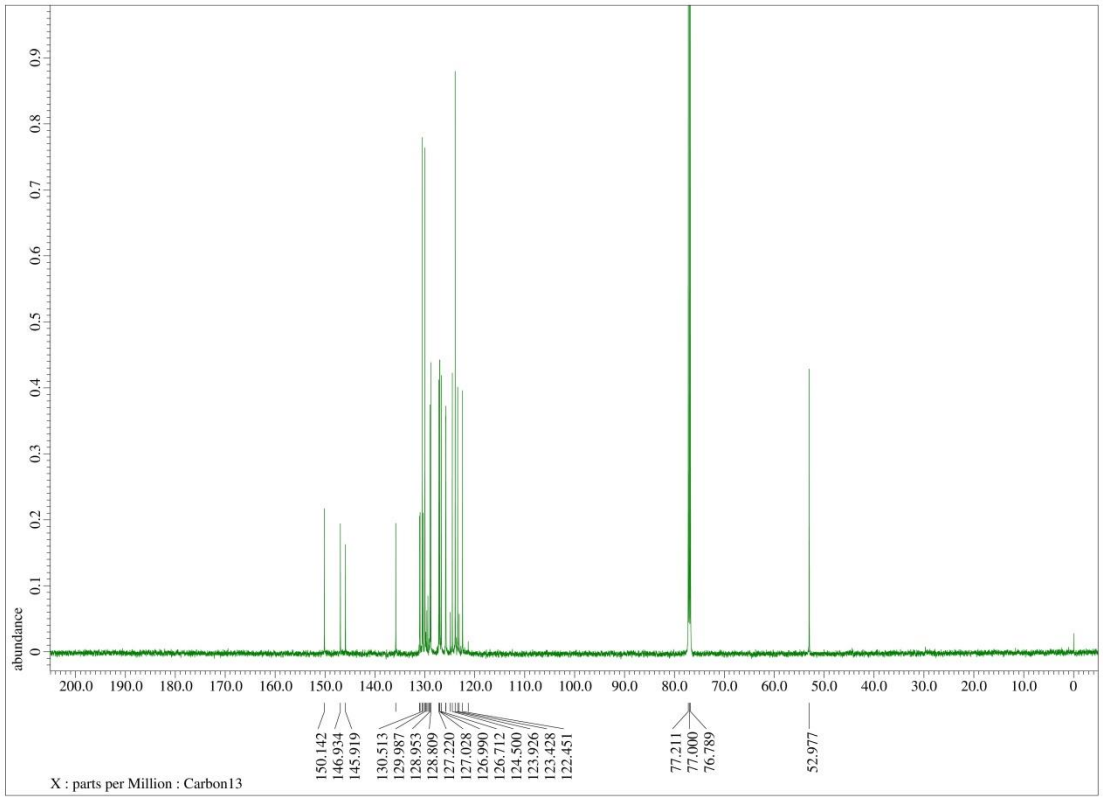

Ar
OMe
6a
Ar = 4-NO2-C6H4
5.00
3.00
3.00
3.00
2.00
2.00
2.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.758
8.744
8.683
8.669
8.164
8.149
7.340
7.326
7.260
7.100
7.065
7.051
6.878
6.864
6.288
3.810
0.000
X : parts per Million : Proton

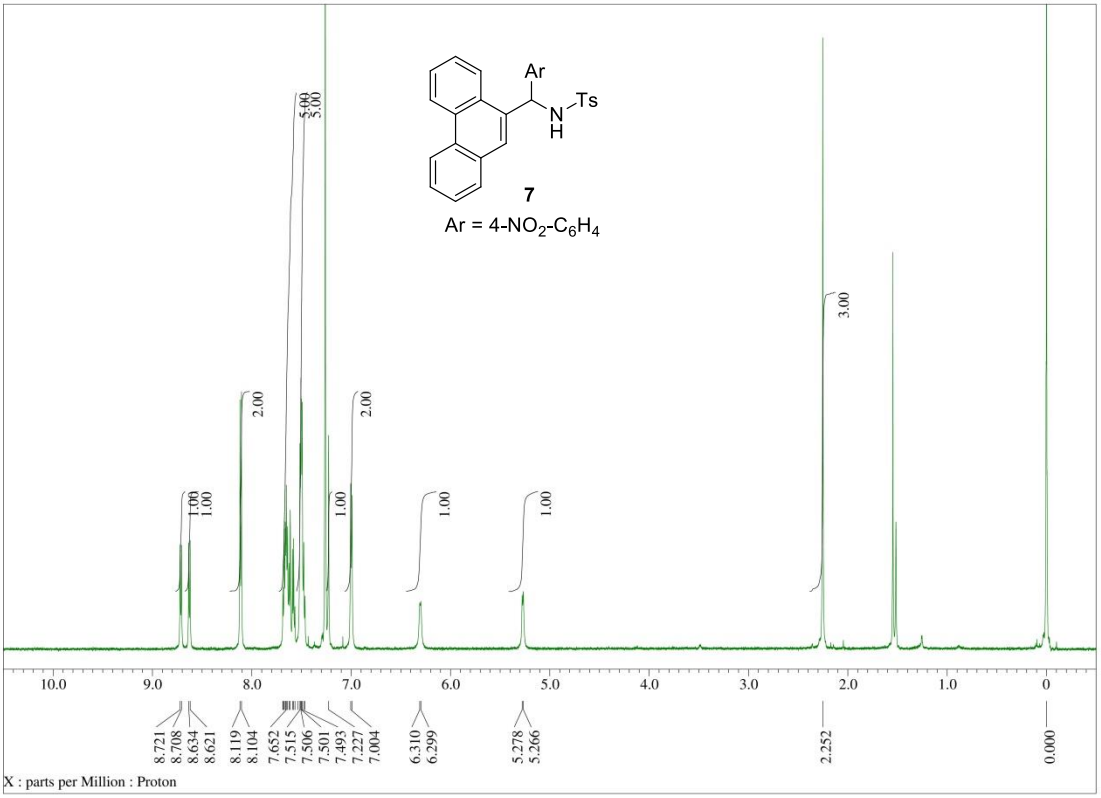

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.548
151.693
146.609
130.590
130.418
128.742
126.875
126.837
126.808
123.696
114.169
77.211
77.000
76.789
55.227
52.460
X : parts per Million : Carbon13

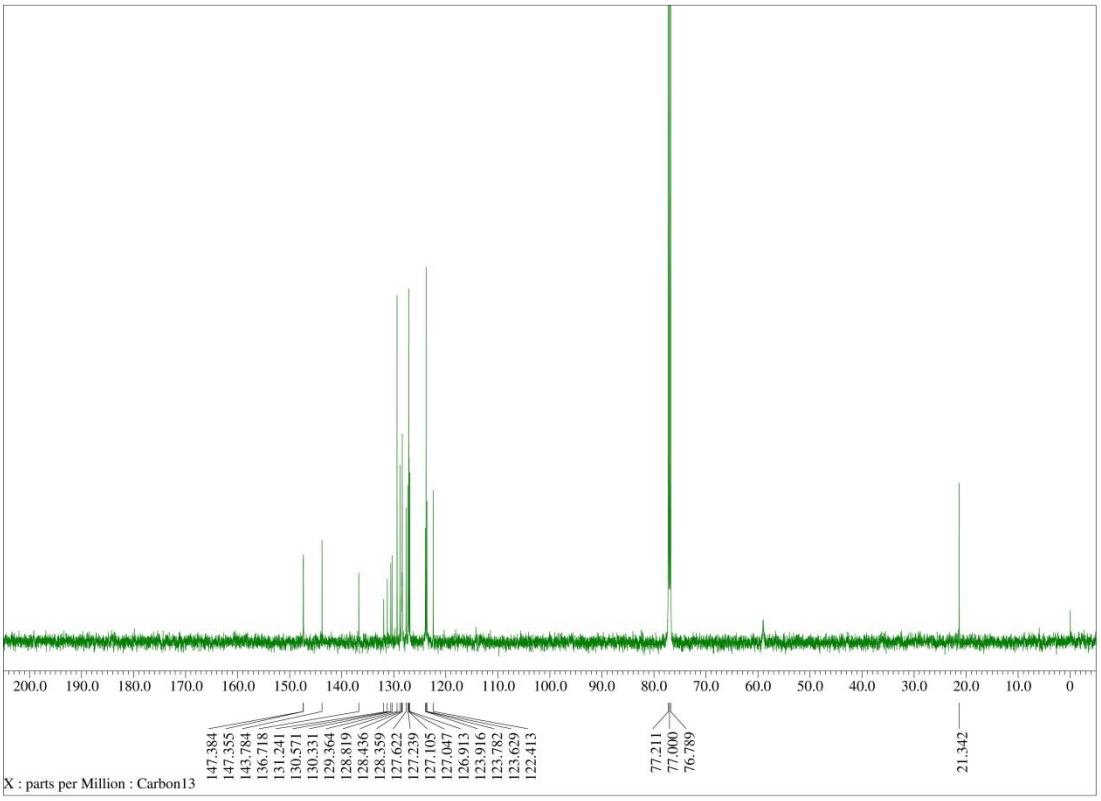

Ar
6b
Ar = 4-NO2-C6H4
abundance
X : parts per Million : Proton

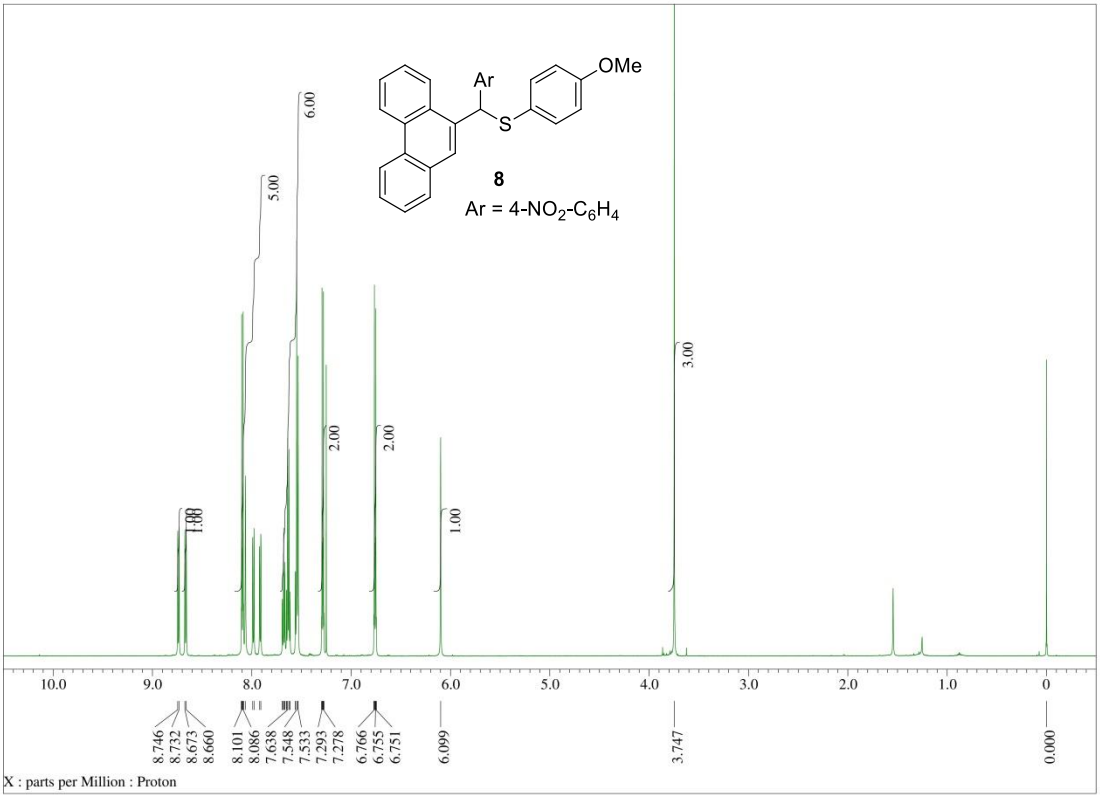

X : parts per Million : Carbon13

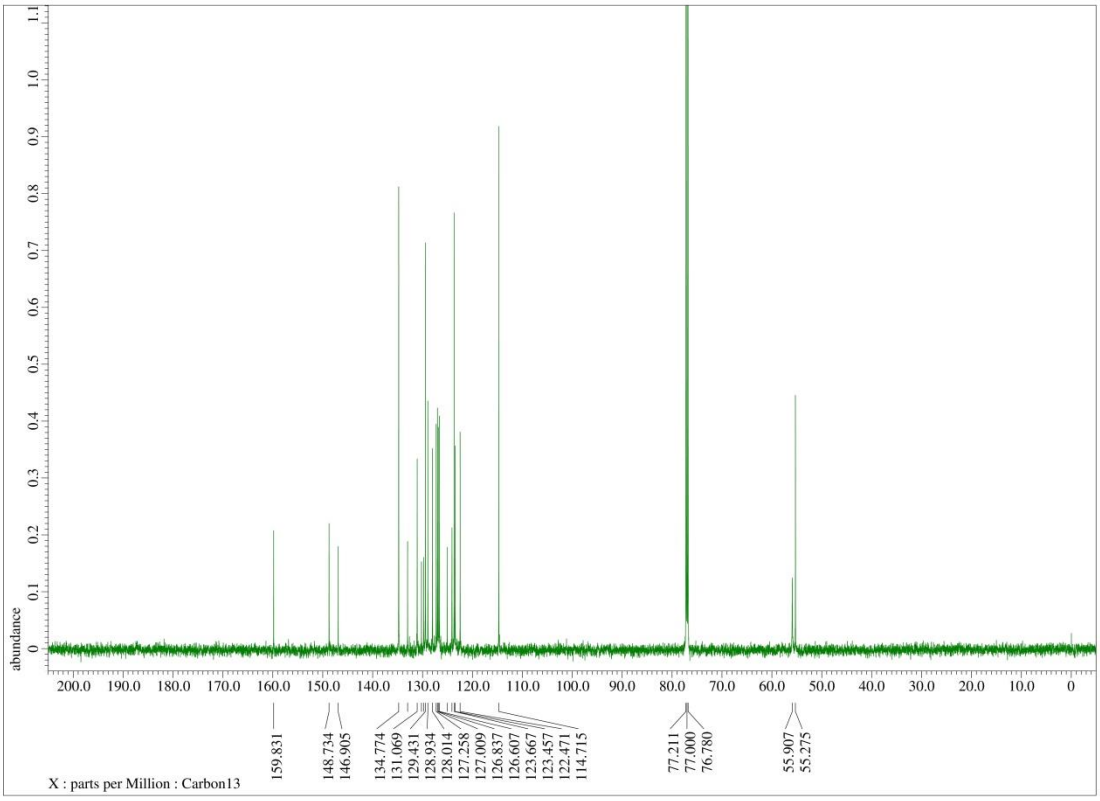

Ar
CF3
6c
Ar = 4-NO2-C6H4
7.00
6.58
2.00
2.00
1.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.778
8.764
8.696
8.682
8.199
8.184
7.685
7.610
7.596
7.343
7.328
7.289
7.276
7.067
6.404
0.000
X : parts per Million : Proton


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
150.142
146.934
145.919
130.513
129.987
128.953
128.809
127.220
127.028
126.990
126.712
124.500
123.926
123.428
122.451
77.211
77.000
76.789
52.977
X : parts per Million : Carbon13


Ar
Ts
N
H
7
Ar = 4-NO2-C6H4
5.00
5.00
2.00
2.00
1.06
1.00
1.00
1.00
1.00
1.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.721
8.708
8.634
8.621
8.119
8.104
7.652
7.515
7.506
7.501
7.493
7.227
7.004
6.310
6.299
5.278
5.266
2.252
0.000
X : parts per Million : Proton


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.384
147.355
143.784
136.718
131.241
130.571
130.331
129.364
128.819
128.436
128.359
127.622
127.239
127.105
127.047
126.913
123.916
123.782
123.629
122.413
77.211
77.000
76.789
21.342
X : parts per Million : Carbon13


Ar
OMe
S
8
Ar = 4-NO2-C6H4
6.00
5.00
3.00
2.00
2.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.746
8.732
8.673
8.660
8.101
8.086
7.638
7.548
7.533
7.293
7.278
6.766
6.755
6.751
6.099
3.747
0.000
X : parts per Million : Proton


abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.831
148.734
146.905
134.774
131.069
129.431
128.934
128.014
127.258
127.009
126.837
126.607
123.667
123.457
122.471
114.715
77.211
77.000
76.780
55.907
55.275
X : parts per Million : Carbon13