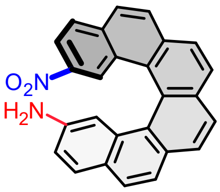
Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

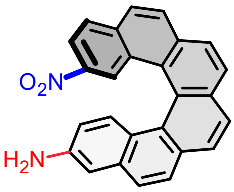
Push-pull amino-nitro helicenes: their synthesis, (chir)optical properties and self-assembly into Langmuir–Blodgett films

Michal Šámal,[a] Jiří Rybáček,[a] Jan Holec,[a] Jan Hanus,[a] Jaroslav Vacek,[a]
Miloš Buděšínský,[a] Lucie Bednárová,[a] Pavel Fiedler,[a] Michaela Šrámová Slušná,[b]
Irena G. Stará*[a] and Ivo Starý*[a]

[a]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences
Flemingovo nám. 2, 166 10 Prague 6, Czech Republic
E-mail: stara@uochb.cas.cz, stary@uochb.cas.cz
[b]Institute of Inorganic Chemistry, Czech Academy of Sciences
Husinec-Řež 1001, 250 68 Řež, Czech Republic



(-)-(*M*)/(+)-(*P*)-**3**



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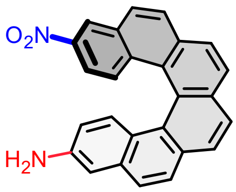
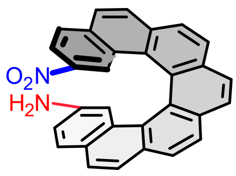
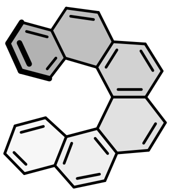


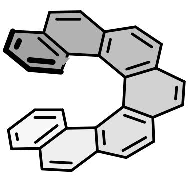
(-)-(*M*)/(+)-(*P*)-**5**



(-)-(*M*)/(+)-(*P*)-**6**

versus


(-)-(*M*)/(+)-(*P*)-**7**
[6]helicene


(-)-(*M*)/(+)-(*P*)-**8**
[7]helicene

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Experimental Section

General: Melting points were determined on Mikro-Heiztisch Polytherm A (Hund, Wetzlar) apparatus and are uncorrected. The NMR spectra were measured on Bruker Advance III HD 400 and 600 intruments, respectively. The ^{1}H NMR spectra were measured at 400.13 MHz and 600.13 MHz, the ^{13}C NMR spectra at 100.61 MHz and 150.90 MHz in $CDCl_3$, CD_2Cl_2 or DMSO-d_6 as indicated in 5 mm PFG probe with indirect detection. For referencing of ^{1}H NMR spectra, the residual solvent signal (δ 7.26 for $CDCl_3$, δ 5.32 for CD_2Cl_2 or δ 2.50 for DMSO-d_6) were used. In the case of ^{13}C spectra, the signal of solvents (δ 77.16 for $CDCl_3$, δ 54.00 for CD_2Cl_2 or δ 39.52 for DMSO-d_6) were used. The chemical shifts are given in δ-scale, the coupling constants *J* are given in Hz. For the assignment of both the ^{1}H and ^{13}C NMR spectra of key compounds, homonuclear 2D-H,H-COSY, 2D-H,H-ROESY, and heteronuclear 2D-H,C-HSQC, and 2D-H,C-HMBC experiments were performed. The IR spectra were measured in $CHCl_3$ or KBr on FT-IR spectrometer Bruker Equinox 55. The EI mass spectra were determined at an ionizing voltage of 70 eV, the *m/z* values are given along with their relative intensities (%). The standard 70 eV spectra were recorded in the positive ion mode. The sample was dissolved in chloroform, loaded into a quartz cup of the direct probe and inserted into the ion source. The source temperature was 220 °C. For exact mass measurement, the spectrum was internally calibrated using perfluorotri-*n*-butylamine (Heptacosa). The low resolution ESI mass spectra were recorded using a quadrupole orthogonal acceleration time-of-flight tandem mass spectrometer (Q-Tof micro, Waters) and high resolution ESI mass spectra using a hybrid FT mass spectrometer combining a linear ion trap MS and the Orbitrap mass analyzer (LTQ Orbitrap XL, Thermo Fisher Scientific). The conditions were optimized for suitable ionization in the ESI Orbitrap source (sheat gas flow rate 35 a.u., aux gas flow rate 10 a.u. of nitrogen, source voltage 4.3 kV, capillary voltage 40 V, capillary temperature 275 °C, tube lens voltage 155 V). The samples were dissolved in methanol and applied by direct injection. As a mobile phase was used 80% methanol (flow rate 100 µL/min). The low- and high-resolution CI mass spectra were measured using an orthogonal acceleration time-of-flight (OA-TOF) mass spectrometer (GCT premier, Waters). The spectra were recorded in positive mode and the source temperature was 150 °C. Methane was present as a reagent gas in the CI source. For exact measurement the spectra were internally calibrated using Heptacosa or 2,4,6-tris(trifluoromethyl)-1,3,5-triazine. The APCI mass spectra were recorded using an LTQ Orbitrap XL (Thermo Fisher Scientific) hybrid mass spectrometer equipped with an APCI ion source. The APCI vaporizer and heated capillary temperatures were set to 400 °C and 200 °C, respectively; the corona discharge current was 3.5 µA. Nitrogen served both as the sheath and auxiliary gas at flow rate 55 and 5 arbitary units, respectively. The ionization conditions were the same for low-resolution as well as high-resolution experiment. The HR spectra were aquired at a resolution of 100 000. The ECD, absorption, and fluorescence spectra were measured on a Jasco 1500 spectropolarimeter (JASCO International Co. Ltd.) equipped with a fluorescence emission monochromator (FMO522) and separate fluorescence emission detector (FDT-538). The ECD and absorption spectra were measured over a spectral range of

210 nm to 550 nm in tetrahydrofuran (10^{-4} M solutions). Measurements were made in quartz cell with a 0.1 cm path length using a scanning speed of 20 nm/min, a response time of 4 seconds, and standard instrument sensitivity. After a baseline correction, spectra were expressed in terms of differential molar extinction ($\Delta\varepsilon$) and molar extinction (ε), respectively. Fluorescence spectra were measured with emission and excitation slits 10 nm and 5 nm, respectively, with excitation wavelength indicated in the spectra. Optical rotations were measured in CH_2Cl_2 using an Autopol IV instrument (Rudolph Research Analytical). The procedure for chiral resolutions was as follows: Samples of racemic aminonitrohelicenes were dissolved in dichloromethane at a concentration of cca 1 mg/mL and filtered through a PTFE membrane syringe filter (0.22 µm pore size). For analytical separations (CSP screening, optimization, and determination of enantiomeric excess), isocratic HPLC systems (Waters Acquity or Knauer Smartline) were used (1 µL injection volume). Waters Acquity PDA (or Knauer Smartline 2500) and IBZ Messtechnik Chiralyser were used as detectors. For semi-preparative resolutions, Puriflash PF5.250 (Interchim) chromatograph equipped with a diode array detector was used. Due to poor solubility, concentrated samples (>10 mg/mL) had to be prepared in a mixture of 1,1,2,2-tetrachloroethane and heptane (injection volume <1.5 mL). Langmuir monolayers and Langmuir-Blodgett thin films were formed on PTFE trough (KSV NIMA mini trough) with a surface area of 273 cm^2. Surface pressure (mN m^{-1}) was measured through a Wilhelmy platinum plate hanging on a micro balance and partially immersed into a subphase. As the subphase, extra pure Milli-Q (18.2 MΩ·cm) water was used. Samples were prepared by dissolution of the compounds in dichloromethane (UV-Vis grade). The samples were applied dropwise on the subphase surface with a Hamilton syringe. The software included in the KSV NIMA package was used to determine the molecular area values in Langmuir monolayers. Langmuir-Blodgett thin films were deposited on quartz glass plates (UQG Optics, UV Fused Silica Plates 25 × 25 × 1 mm) or silicon chips with silicon dioxide layer (Ossila Ltd., 15 × 20 × 0.725 mm, 300 nm SiO_2). Tapping-mode AFM was performed on Dimension Icon device with ScanAsyst technology using Scanasyst-air probes (Bruker). The AFM pictures were processed in Gwyddion software, version 2.50.

TLC was performed on silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2 . 4 H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). The flash chromatography was performed on Silica gel 60 (0.040-0.063 mm, Merck). Diisopropylamine and triethylamine were distilled from calcium hydride under nitrogen and degassed by three freeze-pump-thaw cycles before use; dichloromethane and chloroform were distilled from calcium hydride under nitrogen; tetrahydrofuran was freshly distilled from sodium/benzophenone under nitrogen; toluene and benzene were freshly distilled form sodium under nitrogen; mesitylene and *N*,*N*-dimethylformamide were used as received. Otherwise, all commercially available solvents, catalysts, and reagent grade materials were used as received. CpCo(CO)(fum) (fum = dimethyl fumarate) was synthesized according to literature procedure.[1] The starting materials 7-nitro-3,4-dihydro-2*H*-naphthalen-1-one **13**,[2] 2-bromo-4-nitrobenzaldehyde **16**,[3] 2-bromo-5-nitrobenzaldehyde **19**,[4] and ethyl 1-amino-6-nitronaphthalene-2-carboxylate **27**[5] were synthesized according to the literature procedures.

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[1] A. Geny, N. Agenet, L. Iannazzo, M. Malacria, C. Aubert, V. Gandon *Angew. Chem. Int. Ed.* **2009**, *48*, 1810.

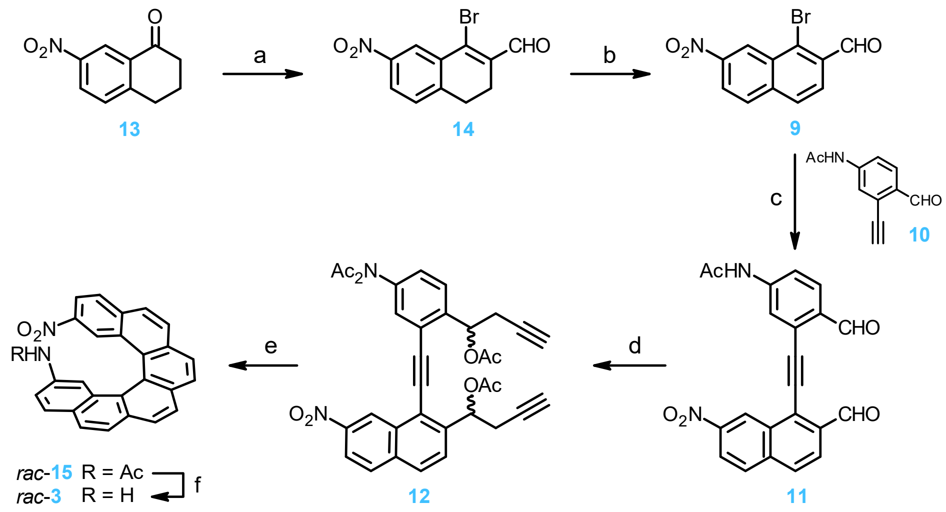
[2] D. E. Nichols, J. M. Cassady, P. E. Persons, M. C. Yeung, J. A. Clemens, E. B. Smalstig, *J. Med. Chem.* **1989**, *32*, 2128.

[3] N. R. Vautravers, D. D. Regent, B. Breit, *Chem. Comm.* **2011**, *47*, 6635.

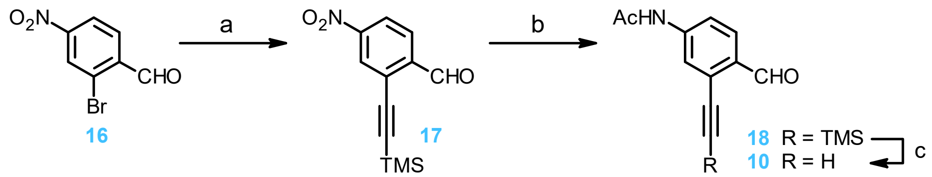
[4] T. Kawabata, C. Jiang, K. Hayashi, K. Tsubaki, T. Yoshimura, S. Majumdar, T. Sasamori, N. Tokitoh, *J. Am. Chem. Soc.* **2009**, *131*, 54.

[5] R. S. Reddy, P. K. Prasad, B. B. Ahuja, A. Sudalai, *J. Org. Chem.* **2013**, *78*, 5045.

Synthesis of 15-nitrohexahelicen-2-amine *rac*-3

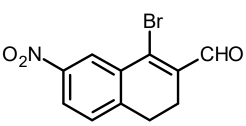


a) DMF (3.0 equiv.), PBr_3 (2.7 equiv.), $CHCl_3$, rt, 16 h, 83%;
b) DDQ (5.0 equiv.), benzene, 90 °C, 7 d, 37%;
c) 10 (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), Et_3N (3.0 equiv.), DMF, 60 °C, 3 h, 88%;
d) Zn powder (6.0 equiv.), $BrCH_2$-C≡CH (6.0 equiv.), THF, rt, 1 h, then Ac_2O (10 equiv.), Et_3N (10 equiv.), DMAP (0.1 equiv.), rt, 16 h, 64%;
e) $Ni(PPh_3)_2(CO)_2$ (0.5 equiv.), toluene, 120 °C, 30 min, then *p*-TsOH (5.0 equiv.), 90 °C, 30 min, 58%;
f) dioxane:H_2O:HCl (10:1:1), 90 °C, 6 h, 81%.



a) TMS-C≡CH (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), Et_3N:THF (2:1), rt, 2 h, 84%;
b) Zn (5.0 equiv.), NH_4Cl (10 equiv.), EtOH:H_2O (4:1), rt, 2 h, then Ac_2O (1.2 equiv.), DCM, rt, 16 h, then PCC (1.0 equiv.), DCM, rt, 1 h, 80%;
c) K_2CO_3 (1.5 equiv.), MeOH, rt, 20 min, 85%.

1-Bromo-7-nitro-3,4-dihydronaphthalene-2-carbaldehyde 14



A Schlenk flask was flushed with nitrogen, then dry chloroform (80 mL) and dry *N*,*N*-dimethylformamide (4.83 mL, 62.7 mmol, 3.0 equiv.) were injected. The solution was cooled to 0 °C and phosphorus tribromide (5.37 mL, 56.4 mmol, 2.7 equiv.) was added dropwise. The mixture was stirred at 0 °C for 1 h before a solution of 7-nitro-3,4-dihydro-2*H*-naphthalen-1-one **13**[2] (4.00 g, 20.9 mmol) in dry chloroform (40 mL) was slowly added. The resulted mixture was stirred at room temperature for 16 h. Then a saturated solution of sodium hydrogen carbonate was added until pH was slightly basic. The organic layer was separated and the water layer was extracted with chloroform (50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane-dichloromethane-ethyl acetate 10:1:1) to afford **14** (4.89 g, 83%) as a solid.

M.p.: 195.5 - 196 °C (dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$): 2.66 – 2.72 (m, 2H), 2.93 – 2.99 (m, 2H), 7.40 (d, *J* = 8.2, 1H), 8.22 (dd, *J* = 8.2, 2.1, 1H), 8.76 (d, *J* = 2.0, 1H), 10.27 (s, 1H).

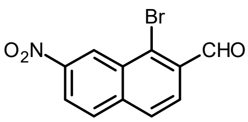
^{13}C NMR (101 MHz, $CDCl_3$): 22.51, 27.39, 123.62, 125.78, 128.86, 134.64, 135.71, 136.34, 145.81, 147.51, 192.65.

IR ($CHCl_3$): 3081 vw, 3028 w, 2954 w, 2901 w, 2871 w, 2847 w, 2740 vw, 1672 vs, 1612 m, 1595 m, 1568 s, 1527 vs, 1382 w, 1356 vs, 1348 s, 1265 m, 1155 m, 841 s, 807 m, 709 w, 642 w, 540 vw, sh cm^{-1}.

CI MS: 282 ($[M+H]^+$).

HR CI MS: calcd for $C_{11}H_9O_3N^{79}Br$ 281.9766, found 281.9772.

1-Bromo-7-nitronaphthalene-2-carbaldehyde 9



A pressure tube was charged with **14** (4.86 g, 17.2 mmol) and dry benzene (120 mL) was added followed by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (19.5 g, 86.0 mmol, 5.0 equiv.). The tube was closed and the reaction mixture was stirred at 90 °C for 7 d. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-dichloromethane 2:1 to 1:1) to afford **9** (1.78 g, 37%) as a solid.

M.p.: 149 - 151 °C (dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$): 7.97 (d, *J* = 8.6, 1H), 8.05 (d, *J* = 9.0, 1H), 8.11 (d, *J* = 8.6, 1H), 8.42 (dd, *J* = 9.0, 2.2, 1H), 9.43 (d, *J* = 2.2, 1H), 10.64 (s, 1H).

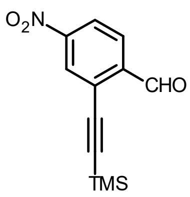
^{13}C NMR (101 MHz, $CDCl_3$): 123.08, 124.92, 128.05, 128.34, 130.58, 131.77, 132.21, 132.99, 139.53, 147.29, 191.84.

IR ($CHCl_3$): 3099 w, 3062 vw, 1692 vs, 1627 s, 1597 m, 1577 s, 1529 vs, 1497 m, 1444 w, 1421 w, 1391 m, 1358 s, 1345 vs, 1312 s, 1292 m, 1250 m, 1196 m, 1146 m, 1092 m, 978 m, 907 m, 854 s, 840 s, 812 m, 633 m, 536 w, 433 w cm^{-1}.

EI MS: 279 ($M^{+\bullet}$, 100), 249 (23), 232 (10), 222 (8), 205 (14), 193 (4), 171 (3), 141 (9), 126 (48), 113 (5), 99 (6), 75 (5).

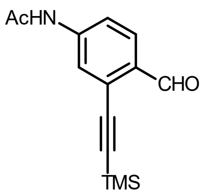
HR EI MS: calcd for $C_{11}H_6O_3N^{79}Br$ 278.9531, found 278.9530.

4-Nitro-2-[(trimethylsilyl)ethynyl]benzaldehyde 17



A Schlenk flask was charged with 2-bromo-4-nitrobenzaldehyde **16**[5] (5.00 g, 21.7 mmol), $Pd(PPh_3)_2Cl_2$ (305 mg, 0.434 mmol, 2 mol%), CuI (165 mg, 0.866 mmol, 4 mol%), flushed with nitrogen, and the degassed triethylamine (60 mL) followed by the degassed tetrahydrofuran (30 mL) were added. The mixture was stirred at room temperature for 5 min before ethynyltrimethylsilane (3.71 mL, 26.0 mmol, 1.2 equiv.) was added and stirring continued for 2 h. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 20:1) to afford alkyne **17** (4.51 g, 84%) as an amorphous solid. ^{1}H NMR and ^{13}C NMR spectra were in agreement with published spectra.[6]

***N*-{4-Formyl-3-[(trimethylsilyl)ethynyl]phenyl}acetamide 18**



Alkyne **17** (4.00 g, 16.2 mmol) was suspended in ethanol (60 mL), then water (15 mL), Zn dust (5.30 g, 81.0 mmol, 5.0 equiv.), and ammonium chloride (8.66 g, 162 mmol, 10 equiv.) were added subsequently. The suspension was stirred at room temperature for 2 h, then diluted with dichloromethane (100 mL) and water (100 mL), and the mixture was filtered (paper filter). The organic layer was separated, the water layer was extracted with dichloromethane (50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvents were evaporated under the reduced pressure, the residue was dissolved in dichloromethane (50 mL), and acetic anhydride (1.83 mL, 19.4 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature for 16 h, then celite (5 g) was added followed by pyridinium chlorochromate (3.49 g, 16.2 mmol, 1.0 equiv.) and the mixture was stirred at room temperature for 1 h. The mixture was adsorbed on silica gel and purified by flash chromatography on silica gel (hexane-ethyl acetate 3:1) to afford **18** (3.36 g, 80%) as a solid.

M.p.: 97 - 99 °C (acetone).

^{1}H NMR (400 MHz, $CDCl_3$): 0.27 (s, 9H), 2.22 (s, 3H), 7.32 (bs, 1H), 7.49 (ddd, *J* = 8.9, 2.3, 0.9, 1H), 7.85 (d, *J* = 2.2, 1H), 7.88 (d, *J* = 8.6, 1H), 10.43 (d, *J* = 0.8, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): -0.17, 24.86, 99.78, 102.81, 119.47, 123.29, 128.37, 128.41, 132.02, 143.19, 169.14, 190.99.

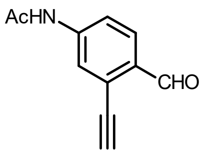
IR (KBr): 3434 m, 2900 w, 2848 w, 2756 w, 2155 w, 1707 s, sh, 1694 vs, sh, 1679 vs, 1644 s, 1592 bd, 1575 s, 1527 vs, 1489 m, 1267 s, sh, 1252 vs, 1104 m, 846 vs, 761 m, 683 m cm^{-1}.

ESI MS: 282 ([M+Na]$^+$).

HR ESI MS: calcd for $C_{14}H_{17}O_2NSiNa$ 282.0921, found 282.0921.

[6] J. Suffert, E. Abraham, S. Raeppel, R. Brückner, *Liebigs Ann.* **1996**, 447.

N-(3-Ethynyl-4-formylphenyl)acetamide 10



Amide **18** (3.33 g, 12.8 mmol) was dissolved in methanol (50 mL) and potassium carbonate (2.63 g, 19.2 mmol, 1.5 equiv.) was added, and the mixture was stirred at room temperature for 20 min. The reaction was quenched with a saturated ammonium chloride solution (100 mL), extracted with ethyl acetate (2 x 70 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvents were evaporated under the reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 1:1) to afford **10** (2.04 g, 85%) as a solid.

M.p.: 165 - 167 ^{o}C (acetone).

^{1}H NMR (400 MHz, DMSO-*d$_6$*): 2.10 (s, 3H), 4.64 (s, 1H), 7.67 (dd, *J* = 8.6, 2.1, 1H), 7.80 (d, *J* = 8.5, 1H), 7.95 (d, *J* = 2.1, 1H), 10.23 (s, 1H), 10.43 (s, 1H).

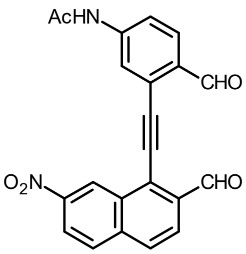
^{13}C NMR (101 MHz, DMSO-*d$_6$*): 24.26, 79.24, 87.23, 119.26, 122.44, 125.83, 128.81, 130.86, 144.41, 169.42, 189.51.

IR (KBr): 3431 w, br, 3320 s, 3286 s, 3259 s, 3233 s, 3223 s, 2104 w, 1709 s, 1689 vs, 1672 vs, 1604 vs, 1587 vs, 1537 vs, 1490 vs, 1372 vs, 1255 vs, 1241 vs, sh, 1093 s, 838 m, 824 s, br, 710 m, br, 678 s, 653 s, 596 m, 533 m cm^{-1}.

EI MS: 187 ($M^{+\bullet}$, 57), 145 (100), 117 (29), 89 (11), 63 (3).

HR EI MS: calcd for $C_{11}H_9O_2N$ 187.0633, found 187.0632.

***N*-{4-Formyl-3-[(2-formyl-7-nitronaphthalen-1-yl)ethynyl]phenyl}acetamide 11**



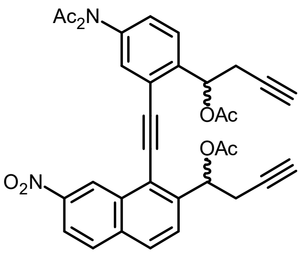
A Schlenk flask was charged with bromide **9** (500 mg, 1.79 mmol), $Pd(PPh_3)_2Cl_2$ (25.1 mg, 0.0358 mmol, 2 mol%), CuI (13.6 mg, 0.0714 mmol, 4 mol%), flushed with nitrogen, and the degassed *N*,*N*-dimethylformamide (10 mL) followed by the degassed triethylamine (750 µL, 5.37 mmol, 3.0 equiv.) were added. The mixture was heated to 60 °C before a solution of alkyne **10** (369 mg, 1.97 mmol, 1.1 equiv.) in degassed *N*,*N*-dimethylformamide (8 mL) was slowly added within 1 h. The reaction mixture was stirred at the same temperature for 2 h. Then water (30 mL) was added and the mixture was filtered (paper filter). The solid was washed with acetone – water solution (1:1, 2 x 10 mL) and dried *in vacuo* to afford **11** (608 mg, 88%) as a solid, which was used in the next reaction without further purification. Due its low solubility, the product was characterized only by IR and MS spectra.

IR (KBr): 3372 m, 3332 w, 2926 w, 2203 w, 1713 s, sh, 1700 vs, sh, 1690 vs, sh, 1678 vs, 1617 m, 1599 s, sh, 1588 s, 1574 s, 1533 vs, 1518 vs, sh, 1500 s, 1446 m, 1396 m, 1388 m, 1370 m, 1344 vs, 1320 m, 1298 s, 1264 m, 1238 s, sh, 1207 m, 1123 m, 1012 s, 879 w, 853 m, 826 m, 783 w, 741 w, 653 w, 586 w cm^{-1}.

ESI MS: 409 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{22}H_{14}O_5N_2Na$ 409.0795, found 409.0796.

1-[1-({2-[1-(Acetyloxy)but-3-yn-1-yl]-5-(diacetylamino)phenyl}ethynyl)-7-nitronaphthalen-2-yl]but-3-yn-1-yl acetate 12



A Schlenk flask was charged with zinc powder (600 mg, 9.18 mmol, 6.0 equiv.) and flushed with nitrogen. The freshly distilled tetrahydrofuran (7 mL) was added, the suspension was put to a water bath at room temperature and vigorously stirred. Then propargyl bromide (80 wt. % in toluene, 1.01 mL, 9.18 mmol, 6.0 equiv.) was slowly added within 10 min and the mixture was then stirred at room temperature for 20 min before it was transferred by a syringe to the second Schlenk flask with a suspension of dialdehyde **11** (590 mg, 1.53 mmol) in tetrahydrofuran (40 mL). The reaction mixture was stirred at room temperature for 1 h, then triethylamine (2.13 mL, 15.3 mmol, 10 equiv.), acetic anhydride (1.45 mL, 15.3 mmol, 10 equiv.), and 4-dimethylaminopyridine (18.0 mg, 0.15 mmol, 0.1 equiv.) were added, and the solution was stirred at room temperature for 16 h. After that, the mixture was evaporated under the reduced pressure to dryness. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 3:1 to 1:1) to obtain **12** (580 mg, 64%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers): 1.98 – 2.03 (m, 4H), 2.16 (s, 6H), 2.17 (s, 6H), 2.37 (s, 12H), 2.90 – 3.11 (m, 8H), 6.56 – 6.68 (m, 4H), 7.23 – 7.28 (m, 2H), 7.53 – 7.57 (m, 2H), 7.70 (d, *J* = 8.3, 1H), 7.71 (d, *J* = 8.4, 1H), 7.85 (d, *J* = 8.7, 2H), 7.98 (d, *J* = 8.4, 2H), 7.99 (d, *J* = 8.8, 2H), 8.30 (d, *J* = 8.9, 2H), 9.37 (bs, 2H).

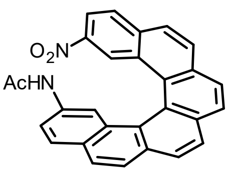
^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereomers): 21.10 (4C), 25.73, 25.80, 25.96, 26.03, 27.20 (4C), 71.06, 71.14, 71.47, 71.62, 71.69, 71.70, 71.77, 71.84, 78.70, 78.83, 78.87, 78.92, 89.60, 89.75, 98.24 (2C), 120.47 (2C), 120.65, 120.68, 122.58, 122.62, 123.28 (2C), 127.09, 127.16, 128.32, 128.40, 129.17 (2C), 130.08 (4C), 132.16, 132.19, 132.87 (2C), 135.33, 135.35, 139.43, 139.47, 141.66 (2C), 142.04, 142.10, 146.71, 146.74, 169.70 (2C), 169.77 (2C), 172.84 (4C).

IR ($CHCl_3$): 3309 m, 3287 w, sh, 2958 w, 2203 vw, 2125 vw, 1745 s, 1715 s, 1626 w, 1604 w, 1594 vw, sh, 1582 w, 1572 w, 1531 m, 1504 m, 1495 m, 1453 w, 1430 w, 1421 w, 1370 s, 1345 s, 1303 m, 1265 m, sh, 1239 vs, 1143 vw, 1031 m, 851 m, 815 w, 658 m, sh, 643 m, 603 w, 552 w cm^{-1}.

ESI MS: 615 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{34}H_{28}O_8N_2Na$ 615.1738, found 615.1738.

***N*-(15-Nitrohexahelicen-2-yl)acetamide 15**



A crimp-sealed pressure vial was charged with triyne **12** (250 mg, 0.422 mmol), $Ni(PPh_3)_2(CO)_2$ (135 mg, 0.211 mmol, 0.5 equiv.) and flushed with nitrogen. The degassed toluene (15 mL) was added and the mixture was stirred at 120 °C for 30 min. Then *p*-toluenesulfonic acid monohydrate (400 mg, 2.10 mmol, 5.0 equiv.) was added and the stirring was continued at 90 °C for 30 min. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (dichloromethane-ethyl acetate 20:1 to 4:1) to afford helicene **15** (105 mg, 58%) as a yellow solid.

M.p.: 273 - 275 °C (acetone).

UV/Vis (THF): λ_{max} (log ε) = 258 (5.02), 307 (4.75) nm.

^{1}H NMR (600 MHz, DMSO-*d6*): 1.76 (s, 3H), 7.31 (dd, *J* = 8.6, 2.1, 1H), 7.84 (d, *J* = 8.6, 1H), 8.001 (dd, *J* = 8.8, 2.3, 1H), 8.003 (d, *J* = 8.5, 1H), 8.02 (dd, *J* = 8.5, 0.5, 1H), 8.09 (dd, *J* = 2.1, 0.5, 1H), 8.13 (dd, *J* = 8.8, 0.6, 1H), 8.18 (dd, *J* = 8.8, 0.5, 1H), 8.19 (d, *J* = 8.2, 1H), 8.22 (d, *J* = 8.2, 1H), 8.23 (d, *J* = 8.4, 1H), 8.29 (d, *J* = 8.4, 1H), 8.32 (d, *J* = 8.8, 1H), 8.47 (dt, *J* = 2.3, 0.6, 1H), 9.45 (s, 1H).

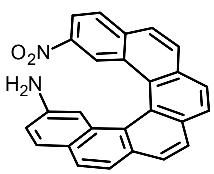
^{13}C NMR (151 MHz, DMSO-*d6*): 23.94, 115.32, 118.65, 118.82, 122.91, 123.13, 124.74, 126.32, 127.43, 127.46, 127.48, 127.86, 128.13, 128.32, 128.40, 128.45, 128.59, 128.60, 129.41, 129.46, 130.63, 131.88, 132.12, 133.11, 135.63, 137.04, 143.51, 167.60.

IR (KBr): 3372 m, 3049 m, 1683 m, 1664 s, 1622 m, 1605 m, 1570 m, 1549 m, 1522 s, 1495 s, 1433 m, 1411 w, 1394 w, 1369 w, 1338 vs, 1305 w, 1275 w, 1248 w, 1103 w, 1087 w, 904 w, 850 s, 838 m, 743 m, 733 m, 669 w, 626 w, 607 w, 582 w, 535 w cm^{-1}.

ESI MS: 453 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{28}H_{18}O_3N_2Na$ 453.1210, found 453.1212.

15-Nitrohexahelicen-2-amine 3



Helicene **15** (90 mg, 0.21 mmol) was dissolved in dioxane (5 mL), water (0.5 mL) and hydrochloric acid (35 wt%, 0.5 mL) were added, and the mixture was stirred at 90 °C for 6 h. After cooling to room temperature, a saturated solution of sodium bicarbonate (10 mL) was added and the mixture was extracted with dichloromethane (2 x 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, the solvents were evaporated under the reduced pressure, and the residue was purified by flash chromatography on silica gel (dichloromethane-acetone 20:1) to afford helicene **3** (65.7 mg, 81%) as a red solid.

M.p.: 303 – 305 °C (methanol).

Chiral HPLC separation: *Analytical*: ChiralArt Amylose-SA (150 x 3 mm, 3 µm, Alcyon YMC), heptane – dichloromethane 70:30, 0.1% DEA @ 1.0 mL/min., 35 °C, t_R(+) = 2.3 min. (>99% *ee*), t_R(-) = 3.0 min. (>99% *ee*); *Semipreparative*: ChiralArt Amylose-SA (250 x 20 mm, 5 µm, YMC), heptane – dichloromethane 60:40 @20 mL/min.

Specific rotation: $[\alpha]^{20}_D$ = + 6121 (c 0.13, CH_2Cl_2); $[\alpha]^{20}_D$ = - 6261 (c 0.08, CH_2Cl_2).

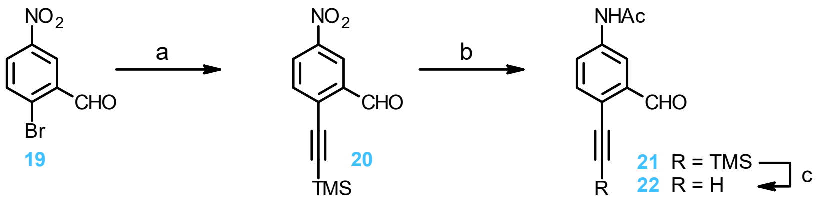
UV/Vis (THF): λ_{max} (log ε) = 238 (4.98), 261 (5.01), 318 (4.72) nm.

^{1}H NMR (600 MHz, CD_2Cl_2): 3.22 (bs, 2H), 6.66 (bd, *J* = 2.3, 1H), 6.68 (dd, *J* = 8.4, 2.3, 1H), 7.64 (bd, *J* = 8.4, 1H), 7.77 (bd, *J* = 8.4, 1H), 7.88 (bd, *J* = 8.4, 1H), 7.95 (bd, *J* = 8.7, 1H), 8.00 (bd, *J* = 8.5, 1H), 8.02 (bd, *J* = 8.1, 1H), 8.03 (d, *J* = 8.0, 1H), 8.04 (dd, *J* = 8.7, 2.3, 1H), 8.05 (dd, *J* = 8.1, 0.4, 1H), 8.13 (d, *J* = 8.0, 1H), 8.17 (d, *J* = 8.5, 1H), 8.70 (bd, *J* = 2.3, 1H).

^{13}C NMR (151 MHz, CD_2Cl_2): 110.84, 116.79, 119.48, 122.76, 124.26, 124.40, 126.28, 126.78, 126.95, 127.02, 127.21, 128.31, 128.72, 128.81, 128.84, 128.93, 129.80, 129.87, 130.87, 131.09, 132.14, 133.19, 133.67, 135.13, 144.60, 144.93.

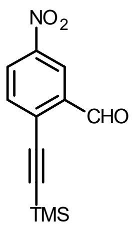
IR ($CHCl_3$): 3484 vw, 3400 vw, 3053 w, 1627 s, 1605 w, 1585 w, 1562 w, 1531 m, 1523 s, 1502 m, 1478 w, 1435 w, 1425 w, 1376 w, 1342 vs, 1249 w, 850 s, 533 w cm^{-1}.
APCI MS: 389 ($[M+H]^+$).
HR APCI MS: calcd for $C_{26}H_{17}O_2N_2$ 389.1285, found 389.1287.

Synthesis of 15-nitrohexahelicen-3-amine *rac*-4



a) TMS-C≡CH (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), Et_3N:THF (2:1), rt, 2 h, 77%;
b) Zn (5.0 equiv.), NH_4Cl (10 equiv.), EtOH:H_2O (4:1), rt, 2 h, then Ac_2O (1.2 equiv.), DCM, rt, 16 h, then PCC (1.0 equiv.), DCM, rt, 1 h, 71%;
c) K_2CO_3 (1.5 equiv.), MeOH, rt, 20 min, 86%.

5-Nitro-2-[(trimethylsilyl)ethynyl]benzaldehyde 20



A Schlenk flask was charged with 2-bromo-5-nitrobenzaldehyde 19[3] (4.00 g, 17.4 mmol), $Pd(PPh_3)_2Cl_2$ (244 mg, 0.348 mmol, 2 mol%), CuI (133 mg, 0.698 mmol, 4 mol%), flushed with nitrogen and the degassed triethylamine (60 mL) followed by the degassed tetrahydrofuran (30 mL) were added. The mixture was stirred at room temperature for 2 min before ethynyltrimethylsilane (3.00 mL, 20.9 mmol, 1.2 equiv.) was added and the stirring continued for 2 h. The solvents were evaporated under the reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 20:1) to afford alkyne 20 (3.31 g, 77%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 0.31 (s, 9H), 7.74 (dd, J = 8.5, 0.6, 1H), 8.36 (dd, J = 8.5, 2.4, 1H), 8.70 (dd, J = 2.5, 0.5, 1H), 10.54 (s, 1H).

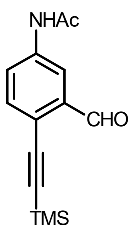
^{13}C NMR (101 MHz, $CDCl_3$): -0.34, 98.31, 108.99, 122.34, 127.69, 132.28, 134.85, 137.07, 147.57, 189.54.

IR ($CHCl_3$): 3093 w, 2963 m, 2901 w, 2158 w, 2116 w, 1701 vs, 1603 s, 1583 m, 1527 vs, 1473 m, 1414 m, 1346 vs, 1253 s, 1283 w, 1181 m, 1073 m, 941 m, 920 w, 859 vs, 848 vs, 815 m, 703 w, 643 w, 581 w cm^{-1}.

EI MS: 247 ($M^{+•}$, 5), 232(100), 217 (16), 202 (13), 186 (91), 173 (49), 157 (12), 143 (67), 115 (11), 73 (8).

HR EI MS: calcd for $C_{12}H_{13}O_3NSi$ 247.0665, found 247.0661.

N-{3-Formyl-4-[(trimethylsilyl)ethynyl]phenyl}acetamide 21



Alkyne 20 (3.29 g, 13.3 mmol) was suspended in ethanol (60 mL), then water (15 mL), Zn dust (4.35 g, 66.5 mmol, 5.0 equiv.), and ammonium chloride (7.11 g, 133 mmol, 10 equiv.) were added subsequently. The suspension was stirred at room temperature for 2 h, then diluted with dichloromethane (100 mL) and water (100 mL), and the mixture was filtered (paper filter). The organic layer was separated, the water layer was extracted with dichloromethane (50 mL) and the combined organic layers were dried over anhydrous magnesium sulfate. The solvents were evaporated under the reduced pressure, the residue was dissolved in dichloromethane (40 mL) and acetic anhydride (1.51 mL, 16.0 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature for 16 h, then celite (5 g) was added followed by pyridinium chlorochromate (2.87 g, 13.3 mmol, 1.0 equiv.) and the mixture was stirred at room temperature for 1 h. The mixture was adsorbed on silica gel and purified by flash chromatography on silica gel (hexane-ethyl acetate 4:1 to 2:1) to afford **21** (2.45 g, 71%) as a solid.

M.p.: 255 - 257 ^{o}C (acetone).

^{1}H NMR (400 MHz, $CDCl_3$): 0.27 (s, 9H), 2.23 (s, 3H), 7.54 (d, *J* = 8.5, 1H), 7.76 (d, *J* = 2.3, 1H), 8.09 – 8.21 (m, 2H), 10.48 (s, 1H).

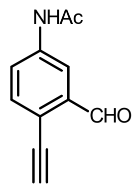
^{13}C NMR (101 MHz, $CDCl_3$): -0.07, 24.75, 99.95, 101.84, 116.97, 122.20, 125.14, 134.79, 136.63, 138.98, 169.13, 191.97.

IR ($CHCl_3$): 3433 w, 3372 w, 3095 vw, 2963 w, 2900 w, 2854 w, 2750 vw, 2154 w, 1691 vs, 1681 s, sh, 1603 m, 1583 m, sh, 1576 m, 1520 s, sh, 1509 vs, 1491 s, 1412 m, 1406 m, sh, 1389 w, 1370 m, 1252 s, 1234 m, 1168 m, 1098 w, 989 w, 916 w, 862 vs, 846 vs, 817 w, 702 w, 647 m, 542 m, 480 vw, 427 vw cm^{-1}.

EI MS: 259 ($M^{+\bullet}$, 37), 244 (100), 217 (21), 202 (98), 185 (12), 174 (9), 159 (11), 143 (9), 116 (9), 75 (6).

HR EI MS: calcd for $C_{14}H_{17}O_2NSi$ 259.1029, found 259.1027.

***N*-(4-Ethynyl-3-formylphenyl)acetamide 22**



Amide **21** (2.42 g, 9.33 mmol) was dissolved in methanol (40 mL) and potassium carbonate (1.93 g, 14.0 mmol, 1.5 equiv.) was added, and the mixture was stirred at room temperature for 20 min. The reaction was quenched with a saturated ammonium chloride solution (100 mL), extracted with ethyl acetate (2 x 60 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvents were evaporated under the reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 1:1) to afford **22** (1.50 g, 86%) as a solid.

M.p.: 156 - 157 ^{o}C (acetone).

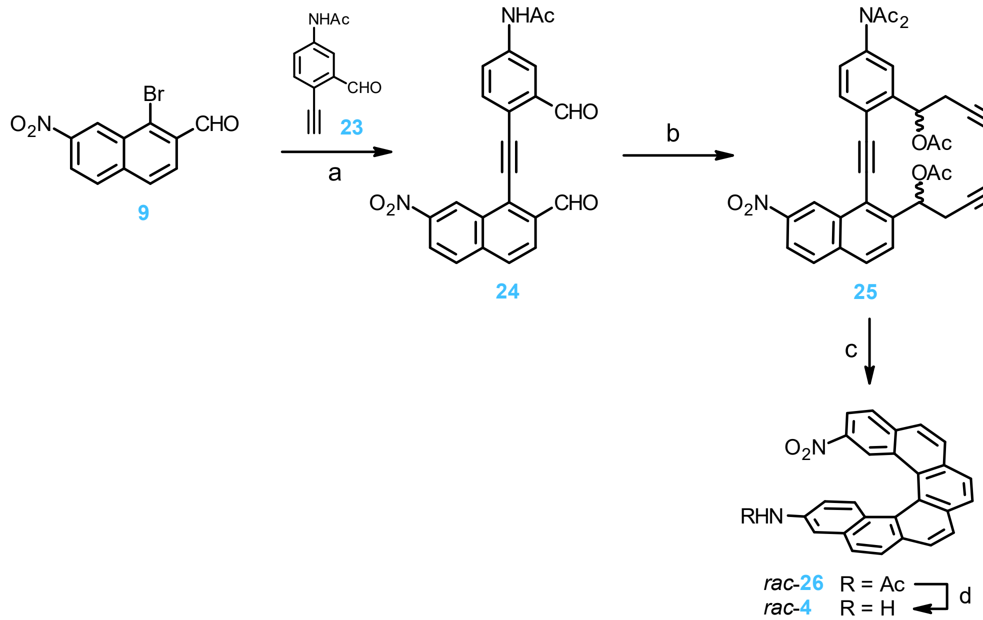
^{1}H NMR (400 MHz, DMSO-*d*$_6$): 2.07 (s, 3H), 4.58 (s, 1H), 7.61 (d, *J* = 8.4, 1H), 7.85 (dd, *J* = 8.5, 2.3, 1H), 8.11 (d, *J* = 2.3, 1H), 10.33 (bs, 1H), 10.34 (s, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$): 24.08, 79.23, 86.49, 116.46, 118.86, 124.05, 134.53, 136.56, 140.21, 168.94, 190.89.

IR (KBr): 3336 w, sh, 3305 m, 3247 s, 2860 m, 2101 w, 1692 vs, 1671 vs, 1605 s, 1588 s, 1541 s, 1526 s, 1489 s, 1415 m, 1397 m, 1370 m, 1323 s, 1282 m, 1271 m, 1264 m, sh, 1163 m, 1099 w, 999 w, 899 w, 837 m, 804 w, 726 m, 709 m, 670 w, 647 w, 569 w, 485 w cm^{-1}.

EI MS: 187 ($M^{+\bullet}$, 75), 145 (100), 117 (49), 89 (12), 63 (4).

HR EI MS: calcd for $C_{11}H_9O_2N$ 187.0633, found 187.0632.



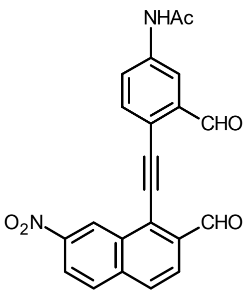
a) **23** (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), THF:Et_3N (2:1), 55 °C, 3 h, 78%;

b) Zn powder (6.0 equiv.), $BrCH_2$-C≡CH (6.0 equiv.), THF, rt, 1 h, then Ac_2O (10 equiv.), Et_3N (10 equiv.), DMAP (0.1 equiv.), rt, 4 h, 67%;

c) $Ni(PPh_3)_2(CO)_2$ (0.3 equiv.), PhMe, 120 °C, 30 min, then *p*-TsOH (5.0 equiv.), 90 °C, 30 min, 51%;

d) dioxane:HCl:H_2O (10:1:1), 90 °C, 6 h, 83%.

***N*-{3-Formyl-4-[(2-formyl-7-nitronaphthalen-1-yl)ethynyl]phenyl}acetamide 24**



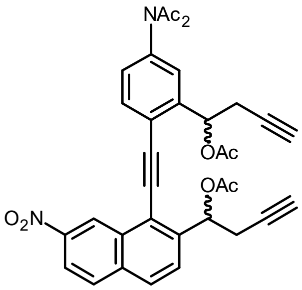
A Schlenk flask was charged with bromide **9** (440 mg, 1.57 mmol), $Pd(PPh_3)_2Cl_2$ (22.0 mg, 0.0313 mmol, 2 mol%), CuI (12.0 mg, 0.0630 mmol, 4 mol%), flushed with nitrogen, and the degassed tetrahydrofuran (10 mL) followed by the degassed triethylamine (10 mL) were added. The mixture was heated to 55 °C before a solution of alkyne **23** (323 mg, 1.73 mmol, 1.1 equiv.) in degassed tetrahydrofuran (10 mL) was slowly added within 1 h. The reaction mixture was stirred at the same temperature for 2 h. Then water (30 mL) was added and the mixture was filtered (paper filter). The solid was washed with acetone – water solution (1:1, 2 x 10 mL) and dried *in vacuo* to afford **24** (473 mg, 78%) as a solid, which was used in the next reaction without further purification. Due its low solubility, the product was characterized only by IR and MS spectra.

IR (KBr): 3370 m, 3284 m, 3092 m, 2853 m, 2732 w, 2195 m, 1695 vs, 1670 s, 1622 s, 1602 s, 1579 s, 1524 s, 1501 s, 1414 m, 1372 m, 1343 s, 1317 s, 1279 m, 1249 m, sh, 1171 m, 1092 m, 903 w, 853 m, 828 s, 739 m, 648 m, 568 w, 523 w cm^{-1}.

ESI MS: 385 ($[M-H]^-$).

HR ESI MS: calcd for $C_{22}H_{13}O_5N_2$ 385.0830, found 385.0826.

1-[2-({2-[1-(Acetyloxy)but-3-yn-1-yl]-4-(diacetylamino)phenyl}ethynyl)-7-nitronaphthalen-2-yl]but-3-yn-1-yl acetate 25



A Schlenk flask was charged with zinc powder (467 mg, 7.14 mmol, 6.0 equiv.) and flushed with nitrogen. The freshly distilled tetrahydrofuran (5 mL) was added, the suspension was put to a water bath at room temperature and vigorously stirred. Then propargyl bromide (80 wt. % in toluene, 0.80 mL, 7.14 mmol, 6.0 equiv.) was slowly added within 10 min and the mixture was then stirred at room temperature for 20 min before it was transferred by a syringe to the second Schlenk flask with a suspension of dialdehyde **24** (461 mg, 1.19 mmol) in tetrahydrofuran (50 mL). The reaction mixture was stirred at room temperature for 1 h, then triethylamine (1.66 mL, 11.9 mmol, 10 equiv.), acetic anhydride (1.12 mL, 11.9 mmol, 10 equiv.), and 4-dimethylaminopyridine (15.0 mg, 0.12 mmol, 0.1 equiv.) were added, and the solution was stirred at room temperature for 4 h. After that, the mixture was evaporated under the reduced pressure to dryness. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 3:1 to 1:1) to obtain **25** (472 mg, 67%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers): 1.97 – 2.00 (m, 2H), 2.00 – 2.03 (m, 2H), 2.15 (s, 6H), 2.17 (s, 3H), 2.18 (s, 3H), 2.35 (s, 12H), 2.91 – 3.18 (m, 8H), 6.55 (t, *J* = 5.5, 1H), 6.57 (t, *J* = 5.5, 1H), 6.64 – 6.70 (m, 2H), 7.22 (dd, *J* = 8.1, 2.4, 1H), 7.23 (dd, *J* = 8.1, 2.5, 1H), 7.42 (t, *J* = 2.3, 2H), 7.86 (d, *J* = 8.7, 2H), 7.87 (d, *J* = 8.1, 1H), 7.89 (d, *J* = 8.2, 1H), 7.99 (d, *J* = 8.6, 2H), 8.00 (d, *J* = 8.9, 2H), 8.31 (dd, *J* = 9.0, 2.2, 2H), 9.37 (d, *J* = 2.2, 1H), 9.39 (d, *J* = 2.2, 1H).

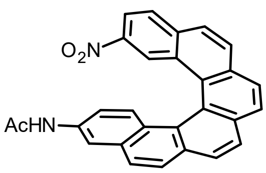
^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereomers): 21.13 (4C), 25.73, 25.74, 25.77, 25.80, 27.17 (4C), 70.88, 70.94, 71.69 (4C), 71.80, 71.83, 78.73, 78.75, 78.78, 78.93, 89.65, 89.75, 98.36, 98.41, 120.50 (2C), 120.76 (2C), 121.20, 121.22, 123.28 (2C), 127.23, 127.25, 127.68, 127.71, 128.88, 128.91, 129.16 (2C), 130.11 (2C), 132.18 (2C), 134.51, 134.53, 135.37, 135.38, 140.23 (2C), 141.92, 141.96, 142.61 (2C), 146.71, 146.73, 169.66 (2C), 169.81 (2C), 172.75 (4C).

IR ($CHCl_3$): 3308 w, 3078 vw, 2959 w, 2928 w, 2872 w, 2857 w, 2208 vw, 2125 vw, 1744 s, 1715 s, 1660 vw, sh, 1626 vw, 1606 vw, 1593 vw, 1582 w, 1531 m, 1503 w, 1494 w, 1452 vw, 1430 vw, sh, 1422 w, 1370 s, 1345 s, 1301 w, 1239 vs, 1047 w, sh, 1032 m, 910 vw, 851 w, 828 w, 650 w, 638 w, 559 vw cm^{-1}.

ESI MS: 615 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{34}H_{28}O_8N_2Na$ 615.1738, found 615.1738.

***N*-(15-Nitrohexahelicen-3-yl)acetamide 26**



A crimp-sealed pressure vial was charged with triyne **25** (300 mg, 0.507 mmol), $Ni(PPh_3)_2(CO)_2$ (97.9 mg, 0.153 mmol, 0.3 equiv.) and flushed with nitrogen. The degassed toluene (15 mL) was added and the mixture was stirred at 120 °C for 30 min. Then *p*-toluenesulfonic acid monohydrate (485 mg, 2.55 mmol, 5.0 equiv.) was added and the stirring was continued at 90 °C for 30 min. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (dichloromethane-ethyl acetate 20:1 to 3:1) to afford helicene **26** (111 mg, 51%) as a yellow solid.

M.p.: > 350 °C (acetone).

UV/Vis (THF): λ_{max} (log ε) = 251 (4.78), 276 (4.56) nm.

^{1}H NMR (600 MHz, DMSO-*d6*): 2.01 (s, 3H), 6.81 (dd, *J* = 9.1, 2.3, 1H), 7.30 (d, *J* = 9.1, 1H), 8.01 (dt, *J* = 8.5, 0.6, 1H), 8.05 (dd, *J* = 8.8, 2.3, 1H), 8.10 (d, *J* = 8.6, 1H), 8.18 (d, *J* = 8.3, 1H), 8.20 (d, *J* = 8.8, 1H), 8.21 (d, *J* = 8.3, 1H), 8.22 (d, *J* = 8.8, 1H), 8.23 (d, *J* = 8.3, 1H), 8.26 (bd, *J* = 2.3, 1H), 8.29 (d, *J* = 8.3, 1H), 8.36 (d, *J* = 8.7, 1H), 8.48 (dd, *J* = 2.2, 0.7, 1H), 9.96 (bs, 1H).

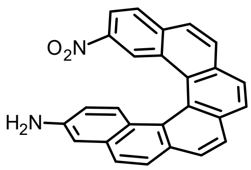
^{13}C NMR (151 MHz, DMSO-*d_6*): 24.25, 115.61, 117.69, 119.10, 122.55, 123.36, 124.45, 126.64, 126.75, 126.90, 127.35, 127.42, 127.51, 127.57, 128.38, 128.47, 128.52, 128.66, 129.82, 130.98, 130.99, 131.75, 133.07, 133.45, 134.92, 137.05, 143.88, 168.67.

IR (KBr): 3305 m, 3045 w, 1665 s, 1621 s, 1553 m, 1528 m, 1508 vs, 1466 m, 1385 w, 1367 w, 1333 vs, 1305 m, 1281 m, 1249 m, 1104 m, 1082 m, 956 w, 912 w, 855 m, 847 m, 837 m, 789 w, 742 m, 632 w, 618 w, 532 w cm^{-1}.

ESI MS: 453 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{28}H_{18}O_3N_2Na$ 453.1210, found 453.1211.

15-Nitrohexahelicen-3-amine 4



Helicene **26** (75 mg, 0.17 mmol) was dissolved in dioxane (5 mL), water (0.5 mL) and hydrochloric acid (35 wt%, 0.5 mL) were added, and the mixture was stirred at 90 °C for 6 h. After cooling to room temperature, a saturated solution of sodium bicarbonate (10 mL) was added and the mixture was extracted with dichloromethane (2 x 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, the solvents were evaporated under the reduced pressure, and the residue was purified by flash chromatography on silica gel (dichloromethane-acetone 20:1) to afford helicene **4** (55 mg, 83%) as a red solid.

M.p.: 278 - 280 °C (methanol).

Chiral HPLC separation: *Analytical*: Chiralpak IC (250 x 4.6 mm, 5 μm, DAICEL), heptane – toluene 1:2, 0.7% isopropyl alcohol @1.0 mL/min., t_R(-) = 14.0 min. (>99% *ee*), t_R(+) = 18.2 min. (97% *ee*); *Semipreparative*: ChiralArt Cellulose-SC (250 x 20 mm, 5 μm, YMC), heptane – toluene 30:70 @20 mL/min.

Specific rotation: $[\alpha]^{20}_D$ = - 5408 (c 0.07, CH_2Cl_2); $[\alpha]^{20}_D$ = + 5550 (c 0.07, CH_2Cl_2).

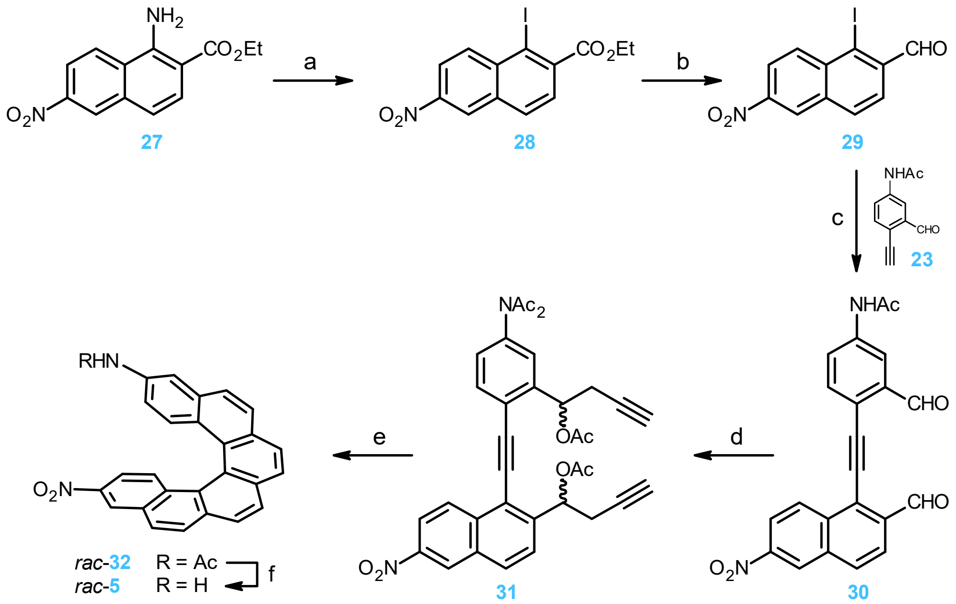
UV/Vis (THF): λ_{max} (log ε) = 247 (5.00), 283 (4.93) nm.

^{1}H NMR (600 MHz, DMSO-*d_6*): 5.30 (s, 2H), 6.08 (dd, *J* = 9.0, 2.5, 1H), 6.85 (d, *J* = 2.5, 1H), 7.07 (dt, *J* = 9.0, 0.5, 1H), 7.76 (dt, *J* = 8.5, 0.6, 1H), 7.92 (d, *J* = 8.5, 1H), 8.02 (dd, *J* = 8.1, 0.5, 1H), 8.04 (dd, *J* = 8.8, 2.3, 1H), 8.09 (dd, *J* = 8.1, 0.5, 1H), 8.15 (dd, *J* = 8.1, 0.5, 1H), 8.17 (dt, *J* = 8.6, 0.6, 1H), 8.18 (dt, *J* = 8.8, 0.5, 1H), 8.21 (dd, *J* = 8.1, 0.5, 1H), 8.31 (dd, *J* = 8.6, 0.5, 1H), 8.59 (ddd, *J* = 2.3, 0.4, 0.4, 1H).

^{13}C NMR (151 MHz, DMSO-*d_6*): 107.76, 115.59, 118.92, 119.96, 122.24, 123.59, 124.95, 126.24, 126.96, 127.02, 127.58, 127.62, 127.89, 127.91, 128.42, 128.49, 128.57, 129.46, 129.62, 130.97, 131.46, 133.43, 134.52, 134.82, 143.79, 146.84.

IR ($CHCl_3$): 3489 w, 3458 w, 3402 w, 3378 w, 3053 m, 1629 s, 1564 w, 1535 m, 1512 s, 1500 m, 1481 w, 1446 w, 1413 w, 1339 vs, 1276 w, 1245 w, 1170 w, 1106 w, 1086 w, 917 w, 855 m, 848 s, 818 w, 633 w, 532 w cm^{-1}.
ESI MS: 389 ($[M+H]^+$).
HR ESI MS: calcd for $C_{26}H_{17}O_2N_2$ 389.1285, found 389.1286.

Synthesis of 14-nitrohexahelicen-3-amine *rac*-5



a) $NaNO_2$ (1.05 equiv.), H_2SO_4:H_2O (1:1), 0 °C, 1 h, then KI (1.5 equiv.), 0 °C to rt, 5 h, 77%;

b) DIBAL (1.6 equiv.), PhMe, -78 °C, 2 h, then PCC (1.0 equiv.), DCM, rt, 1 h, 75%.

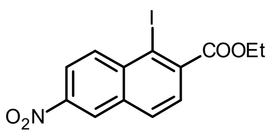
c) **23** (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), Et_3N (3.0 equiv.), DMF, 60 °C, 3 h, 69%;

d) Zn powder (6.0 equiv.), $BrCH_2$-C≡CH (6.0 equiv.), THF, rt, 1 h, then Ac_2O (10 equiv.), Et_3N (10 equiv.), DMAP (0.1 equiv.), rt, 16 h, 53%;

e) $Ni(PPh_3)_2(CO)_2$ (0.5 equiv.), PhMe, 120 °C, 30 min, then *p*-TsOH (5.0 equiv.), 90 °C, 30 min, 50%;

f) dioxane:HCl:H_2O (10:1:1), 90 °C, 5 h, 82%.

Ethyl 1-iodo-6-nitronaphthalene-2-carboxylate 28

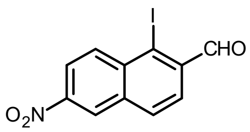


A flask was charged with ethyl 1-amino-6-nitronaphthalene-2-carboxylate **27**[5] (500 mg, 1.92 mmol), then a concentrated sulfuric acid (10 mL) was added, and the mixture was stirred until all solids dissolved. Then ice (~10 g) was added and the mixture was cooled to 0 °C, before sodium nitrite (139 mg, 2.02 mmol, 1.05 equiv) was very slowly added in several portions. The reaction mixture was stirred at 0 °C for 1 h and then potassium iodide (478 mg, 2.88 mmol, 1.5 equiv.) was added in one portion. The reaction mixture was slowly warmed to room temperature and stirred for 5 h. The mixture was poured on ice, it was extracted with diethyl ether (2 x 30 mL), the combined organic layers were washed with brine (30 mL), and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 6:1) to afford **28** (549 mg, 77%) as a solid.

M.p.: 136 - 138 °C (dichloromethane).

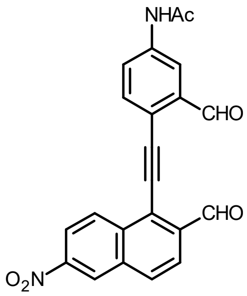
^{1}**H NMR** (400 MHz, $CDCl_3$): 1.47 (t, *J* = 7.1, 3H), 4.51 (q, *J* = 7.1, 2H), 7.68 (d, *J* = 8.4, 1H), 8.03 (d, *J* = 8.2, 1H), 8.32 (dd, *J* = 9.4, 2.4, 1H), 8.51 (dd, *J* = 9.4, 0.7, 1H), 8.74 (d, *J* = 2.3, 1H).
^{13}**C NMR** (101 MHz, $CDCl_3$): 14.32, 62.65, 99.41, 121.57, 124.67, 127.37, 130.91, 132.99, 136.19, 137.36, 141.00, 146.70, 168.11.
IR ($CHCl_3$): 3067 vw, 2985 w, 2872 w, 1728 s, 1625 w, 1605 w, 1529 vs, 1504 w, 1492 w, 1461 m, 1371 m, 1346 s, 1314 m, 1271 s, 1241 m, 1146 m, 1123 m, 1091 w, 1017 m, 972 w, 907 m, 879 w, 808 w, 522 w cm^{-1}.
CI MS: 372 ($[M+H]^+$).
HR CI MS: calcd for $C_{13}H_{11}O_4NI$ 371.9733, found 371.9735.

1-Iodo-6-nitronaphthalene-2-carbaldehyde 29



A Schlenk flask was charged with ester **28** (510 mg, 1.37 mmol) and flushed with nitrogen. Dry toluene (15 mL) was injected and the solution was cooled to -78 °C before diisobutylaluminum hydride (1M in hexanes, 2.19 mL, 2.19 mmol, 1.6 equiv.) was added, and the reaction mixture was stirred at -78 °C for 2 h. The reaction was quenched with a saturated ammonium chloride solution (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was dried over anhydrous magnesium sulfate and the solvents were evaporated under the reduced pressure. The residue was dissolved in dichloromethane (1 x 20 mL), celite (1 g) was added followed with pyridinium chlorochromate (295 mg, 1.37 mmol, 1.0 equiv.), and the mixture was stirred at room temperature for 1 h. The suspension was adsorbed on silica gel and purified by flash chromatography on silica gel (hexane-dichloromethane 2:1 to 1:2) to afford **29** (336 mg, 75%) as a solid.
M.p.: 278 - 280 °C (dichloromethane).
^{1}**H NMR** (600 MHz, CD_2Cl_2): 8.00 (d, *J* = 8.4, 1H), 8.09 (dq, *J* = 8.4, 0.8, 1H), 8.38 (dd, *J* = 9.4, 2.3, 1H), 8.66 (dt, *J* = 9.4, 0.7, 1H), 8.80 (dt, *J* = 2.3, 0.7, 1H), 10.42 (d, *J* = 0.8, 1H).
^{13}**C NMR** (151 MHz, CD_2Cl_2): 109.63, 121.82, 125.04, 126.99, 131.48, 135.72, 136.00, 137.17, 137.62, 148.02, 197.08.
IR ($CHCl_3$): 3069 vw, 2872 w, 2786 w, 1689 vs, 1621 w, 1603 w, 1558 w, 1531 vs, 1492 w, 1357 m, 1343 vs, 1308 w, 1294 w, 1255 m, 1144 w, 1089 w, 976 w, 909 w, 825 w, 807 w, 527 w cm^{-1}.
CI MS: 328 ($[M+H]^+$).
HR CI MS: calcd for $C_{11}H_7O_3NI$ 327.9471, found 327.9468.

_N_-{3-Formyl-4-[(2-formyl-6-nitronaphthalen-1-yl)ethynyl]phenyl}acetamide 30



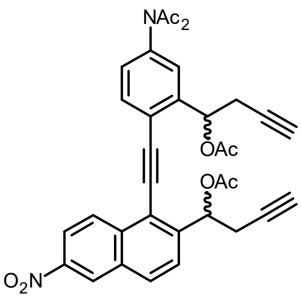
A Schlenk flask was charged with iodide **29** (320 mg, 0.979 mmol), $Pd(PPh_3)_2Cl_2$ (13.8 mg, 0.0197 mmol, 2 mol%), CuI (7.50 mg, 0.0394 mmol, 4 mol%), flushed with nitrogen, and the degassed *N*,*N*-dimethylformamide (8 mL) followed by the degassed triethylamine (410 µL, 2.94 mmol, 3.0 equiv.) were added. The mixture was heated to 60 °C, before a solution of alkyne **23** (2.03 g, 1.08 mmol, 1.1 equiv.) in degassed *N*,*N*-dimethylformamide (5 mL) was slowly added within 1 h. The reaction mixture was stirred at the same temperature for 2 h. Then water (20 mL) was added and the mixture was filtered (paper filter). The solid was washed with acetone – water solution (1:1, 2 x 10 mL) and dried *in vacuo* to afford **30** (261 mg, 69%) as a solid, which was used in the following reaction without further purification. Due its low solubility, the product was characterized only by IR and MS spectra.

IR (KBr): 3379 w, 3284 w, 3243 w, 3093 w, 3055 w, 2194 w, 1690 vs, 1675 s, 1662 s, 1619 w, 1602 m, 1587 m, 1527 s, 1494 m, 1435 m, 1382 m, 1370 m, 1346 s, 1318 m, 1278 w, 1174 m, 905 w, 835 w, 812 w, 774 m, 735 w, 693 w, 521 w cm^{-1}.

ESI MS: 409 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{22}H_{14}O_5N_2Na$ 409.0795, found 409.0798.

1-[1-({2-[1-(Acetyloxy)but-3-yn-1-yl]-4-(diacetylamino)phenyl}ethynyl)-6-nitronaphthalen-2-yl]but-3-yn-1-yl acetate 31



A Schlenk flask was charged with zinc powder (259 mg, 3.96 mmol, 6.0 equiv.) and flushed with nitrogen. The freshly distilled tetrahydrofuran (5 mL) was added, the suspension was put to a water bath at room temperature and vigorously stirred. Then propargyl bromide (80 wt. % in toluene, 436 µL, 3.96 mmol, 6.0 equiv.) was slowly added within 10 min and the mixture was then stirred at room temperature for 20 min before it was transferred by a syringe to the second Schlenk flask with a suspension of dialdehyde **30** (255 mg, 0.66 mmol) in tetrahydrofuran (20 mL). The reaction mixture was stirred at room temperature for 1 h, then triethylamine (920 µL, 6.60 mmol, 10 equiv.), acetic anhydride (1.45 mL, 6.60 mmol, 10 equiv.), and 4-dimethylaminopyridine (8.00 mg, 0.07 mmol, 0.1 equiv.) were added, and the solution was stirred at room temperature for 16 h. After that, the mixture was evaporated under the reduced pressure to dryness. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 3:1 to 2:1) to obtain **31** (207 mg, 53%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers): 2.00 – 2.05 (m, 4H), 2.169 (s, 3H), 2.172 (s, 3H), 2.179 (s, 3H), 2.181 (s, 3H), 2.34 (s, 12H), 2.88 – 3.08 (m, 8H), 6.58 (q, *J* = 5.9, 2H), 6.65 – 6.71 (m, 2H), 7.21 (ddd, *J* = 8.2, 2.2, 0.9, 2H), 7.40 (d, *J* = 2.2, 2H), 7.82 (d, *J* = 8.6, 2H), 7.83 (dd, *J* = 8.1, 3.0, 2H), 8.08 (d, *J* = 8.7, 2H), 8.38 (dd, *J* = 9.2, 2.3, 2H), 8.63 (d, *J* = 9.3, 2H), 8.81 (d, *J* = 2.3, 2H).

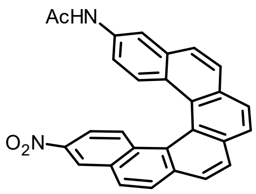
^{13}**C NMR** (101 MHz, $CDCl_3$, mixture of diastereomers): 21.11 (2C), 21.14 (2C), 25.71, 25.77, 25.89, 25.95, 27.13 (4C), 70.94, 70.95, 71.63, 71.65 (2C), 71.70, 71.78, 71.84, 78.74, 78.77, 78.89, 78.99, 90.05, 90.07, 97.58, 97.61, 118.95, 118.99, 120.91, 120.95, 121.33, 121.34, 124.79 (2C), 125.46, 125.50, 127.44 (2C), 128.57, 128.58, 128.90 (2C), 131.13 (2C), 131.71, 131.73, 134.33, 134.35, 135.71, 135.72, 140.24, 140.25, 142.55, 142.57, 143.64, 143.70, 146.33 (2C), 169.77 (2C), 169.86 (2C), 172.73 (4C).

IR ($CHCl_3$): 3283 m, 2955 w, 2204 vw, 2123 vw, 1745 vs, 1716 vs, 1660 m, 1623 m, 1604 m, 1564 w, 1534 m, 1494 m, 1457 w, 1424 m, 1369 s, 1347 s, 1302 m, 1233 vs, 1092 m, 1031 m, 970 m, 903 m, 818 m, 738 m, 651 m, 635 m, 572 w, 459 w cm^{-1}.

ESI MS: 615 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{34}H_{28}O_8N_2Na$ 615.1749, found 615.1744.

***N*-(14-Nitrohexahelicen-3-yl)acetamide 32**



A crimp-sealed pressure vial was charged with triyne **31** (130 mg, 0.22 mmol), $Ni(PPh_3)_2(CO)_2$ (70.5 mg, 0.110 mmol, 0.5 equiv.) and flushed with nitrogen. The degassed toluene (10 mL) was added and the mixture was heated to 120 °C while stirred for 30 min. Then *p*-toluenesulfonic acid monohydrate (209 mg, 1.10 mmol, 5.0 equiv.) was added and stirring continued at 90 °C for 30 min. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (dichloromethane-ethyl acetate 20:1 to 8:1) to afford helicene **32** (47.1 mg, 50%) as a yellow solid.

M.p.: 235 - 237 °C (acetone).

UV/Vis (THF): λ_{max} (log ε) = 274 (4.95), 351 (4.38) nm.

^{1}**H NMR** (600 MHz, DMSO-*d*$_6$): 2.02 (s, 3H), 6.74 (dd, *J* = 9.2, 2.3, 1H), 7.28 (dt, *J* = 9.2, 0.6, 1H), 7.47 (dd, *J* = 9.3, 2.6, 1H), 7.65 (dt, *J* = 9.3, 0.6, 1H), 8.02 (dt, *J* = 8.6, 0.6, 1H), 8.09 (d, *J* = 8.6, 1H), 8.17 (dd, *J* = 8.2, 0.5, 1H), 8.20 (dd, *J* = 8.2, 0.5, 1H), 8.21 (dd, *J* = 8.1, 0.5, 1H), 8.29 (bd, *J* = 8.5, 1H), 8.30 (d, *J* = 8.1, 1H), 8.36 (dt, *J* = 8.5, 0.6, 1H), 8.39 (bd, *J* = 2.3, 1H), 9.00 (dt, *J* = 2.5, 0.6, 1H), 9.98 (bs, 1H).

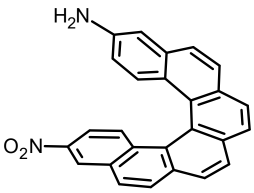
^{13}**C NMR** (151 MHz, DMSO-*d*$_6$): 24.25, 115.78, 117.86, 117.97, 122.98, 124.23, 125.06, 126.51, 126.56, 126.92 (2C), 127.14, 127.45, 128.39, 128.44, 128.64, 128.73, 128.85, 129.36, 130.86, 130.91, 132.60, 132.80, 132.93, 133.31, 137.12, 144.24, 168.72.

IR (KBr): 3399 m, 3052 w, 1670 m, 1617 m, 1580 m, 1567 m, 1550 m, 1531 s, 1505 m, 1492 m, 1464 w, 1450 w, 1371 m, 1340 vs, 1272 w, 900 w, 884 w, 840 s, 811 vw, 793 w, 752 w, 733 w, 638 w, 605 w, 525 w cm^{-1}.

ESI MS: 431 ($[M+H]^+$).

HR ESI MS: calcd for $C_{28}H_{19}O_3N_2$ 431.1390, found 431.1393.

14-Nitrohexahelicen-3-amine 5



Helicene **32** (40 mg, 0.09 mmol) was dissolved in dioxane (5 mL), water (0.5 mL), and hydrochloric acid (35 wt%, 0.5 mL) were added, and the mixture was heated to 90 °C while stirred for 5 h. After cooling to room temperature, a saturated solution of sodium bicarbonate (10 mL) was added and the mixture was extracted with dichloromethane (2 x 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, the solvents were evaporated under the reduced pressure and the residue was purified by flash chromatography on silica gel (dichloromethane-acetone 20:1) to afford helicene **5** (29 mg, 82%) as a dark orange solid.

M.p.: 263 - 265 °C (methanol).

Chiral HPLC separation: *Analytical*: Chiralpak IC (250 x 4.6 mm, 5 µm, DAICEL), heptane – toluene 40:60, 0.6% isopropyl alcohol @ 1.0 mL/min., $t_R(+)$ = 15.7 min. (>99% *ee*), $t_R(-)$ = 18.3 min. (>99% *ee*); *Semipreparative*: ChiralArt Cellulose-SC (250 x 20 mm, 5 µm, YMC), heptane – toluene 50:50 to 30:70 over 30 min. @20 mL/min.

Specific rotation: $[\alpha]^{20}_D$ = + 4624 (c 0.10, CH_2Cl_2); $[\alpha]^{20}_D$ = - 4746 (c 0.11, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 240 (4.91), 255 (4.93), 279 (4.96), 372 (4.44) nm.

^{1}H NMR (600 MHz, CD_2Cl_2): 3.80 (bs, 2H), 6.13 (dd, *J* = 8.9, 2.5, 1H), 7.02 (dd, *J* = 2.5, 0.6, 1H), 7.27 (dt, *J* = 8.9, 0.6, 1H), 7.47 (dd, *J* = 9.3, 2.5, 1H), 7.77 (dt, *J* = 8.6, 0.6, 1H), 7.80 (dt, *J* = 9.3, 0.6, 1H), 7.88 (d, *J* = 8.6, 1H), 7.94 (dd, *J* = 8.1, 0.6, 1H), 7.999 (d, *J* = 8.1, 1H), 8.001 (d, *J* = 8.2, 1H), 8.05 (dt, *J* = 8.6, 0.6, 1H), 8.10 (d, *J* = 8.6, 1H), 8.11 (dd, *J* = 8.2, 0.6, 1H), 8.76 (dd, *J* = 2.5, 0.7, 1H).

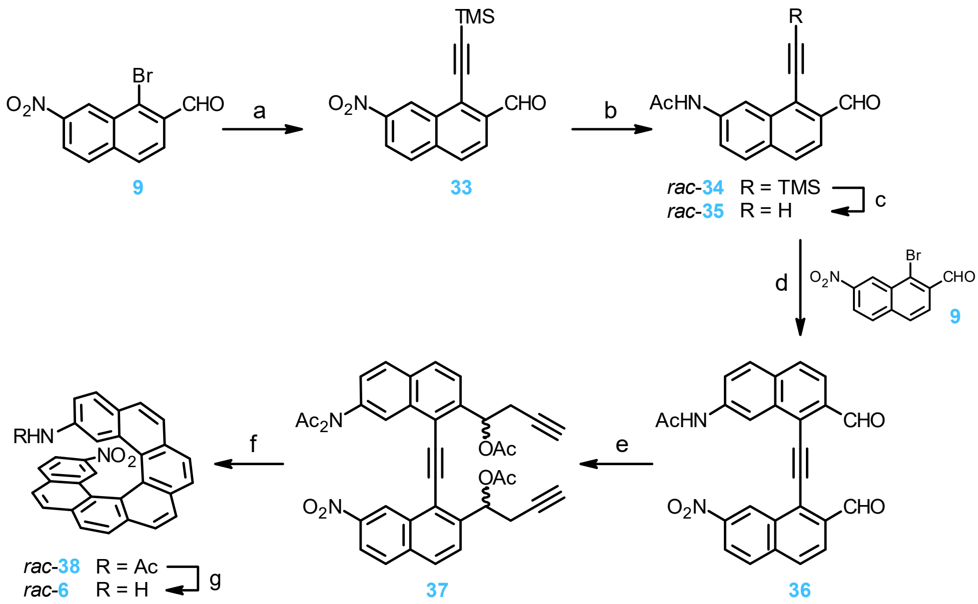
^{13}C NMR (151 MHz, CD_2Cl_2): 109.71, 116.23, 118.11, 123.12, 123.97, 124.05, 125.61, 126.91, 127.19, 127.82, 127.85, 128.32, 128.50, 128.52, 128.91, 129.01, 129.40, 129.45, 130.49, 131.27, 133.12, 133.84, 133.93, 134.34, 144.96, 145.19.

IR ($CHCl_3$): 3491 w, 3376 w, sh, 3050 w, 1627 s, 1604 w, 1585 w, 1560 w, 1538 m, 1516 m, 1496 m, 1449 w, 1411 vw, 1364 m, 1345 vs, 1306 w, 1280 w, 1246 w, 1101 w, 903 w, 859 m, 841 m, 635 w, 530 vw, 523 w cm^{-1}.

ESI MS: 389 ($[M+H]^+$).

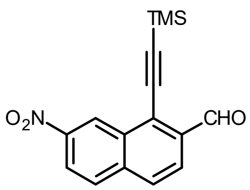
HR ESI MS: calcd for $C_{26}H_{17}O_2N_2$ 389.1285, found 389.1283.

Synthesis of 17-nitroheptahelicen-2-amine *rac*-6



a) TMS-C≡CH (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), Et_3N:THF (3:1), 40 °C, 3 h, 84%;
b) Zn (5.0 equiv.), NH_4Cl (10 equiv.), THF:EtOH:H_2O (4:4:1), rt, 2 h, then Ac_2O (1.2 equiv.), DCM, rt, 16 h, then PCC (1.0 equiv.), DCM, rt, 1 h, 71%;
c) K_2CO_3 (1.5 equiv.), MeOH:DCM (4:1), rt, 20 min, 89%;
d) 9 (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), Et_3N (3.0 equiv.), DMF, 60 °C, 3 h, 90%;
e) Zn powder (6.0 equiv.), $BrCH_2$-C≡CH (6.0 equiv.), THF, rt, 1 h, then Ac_2O (10 equiv.), Et_3N (10 equiv.), DMAP (0.1 equiv.), rt, 16 h, 55%;
f) $Ni(PPh_3)_2(CO)_2$ (0.5 equiv.), PhMe, 125 °C, 40 min., then *p*-TsOH (10 equiv.), 90 °C, 1 h, 42%;
g) dioxane:HCl:H_2O (10:1:1), 90 °C, 5 h, 75%.

7-Nitro-1-[(trimethylsilyl)ethynyl]naphthalene-2-carbaldehyde 33

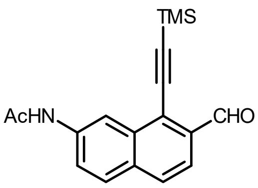


A Schlenk flask was charged with bromide **9** (1.00 g, 3.57 mmol), $Pd(PPh_3)_2Cl_2$ (50.1 mg, 0.0714 mmol, 2 mol%), CuI (27.2 mg, 0.143 mmol, 4 mol%), and flushed with nitrogen. The degassed tetrahydrofuran (6 mL) and trimethylamine (18 mL) were added. The mixture was heated to 40 °C before ethynyltrimethylsilane (610 µL, 4.28 mmol, 1.2 equiv.) was added and the stirring was continued for 3 h. The solvents were evaporated under the reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 8:1) to afford **33** (892 mg, 84%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 0.41 (s, 9H), 7.94 (d, *J* = 8.6, 1H), 8.01 (d, *J* = 9.0, 1H), 8.11 (d, *J* = 8.6, 1H), 8.39 (dd, *J* = 9.0, 2.3, 1H), 9.40 (d, *J* = 2.6, 1H), 10.76 (s, 1H).

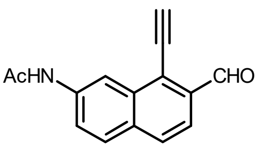
^{13}**C NMR** (101 MHz, $CDCl_3$): -0.16, 96.55, 111.96, 122.71, 124.02, 125.77, 128.78, 129.15, 130.20, 132.65, 135.83, 138.07, 146.85, 191.39.
IR ($CHCl_3$): 3063 vw, 2963 w, 2901 w, 2149 w, 1692 vs, 1625 m, 1591 w, 1582 m, 1533 s, 1501 s, 1431 w, 1395 m, 1345 vs, 1323 m, 1253 s, 1143 vw, 915 m, 897 m, 854 vs, 847 vs, sh, 702 w, 621 w, 543 vw, 443 w cm^{-1}.
CI MS: 298 ($[M+H]^+$).
HR CI MS: calcd for $C_{16}H_{16}O_3NSi$ 298.0899, found 298.0894.

_N_-{7-Formyl-8-[(trimethylsilyl)ethynyl]naphthalen-2-yl}acetamide 34



Nitro derivate **33** (870 mg, 2.93 mmol) was suspended in ethanol (8 mL) and tetrahydrofuran (8 mL), then water (2 mL), Zn dust (960 mg, 14.6 mmol, 5.0 equiv.), and ammonium chloride (1.57 g, 29.3 mmol, 10 equiv.) were added subsequently. The suspension was stirred at room temperature for 2 h, then diluted with dichloromethane (20 mL) and water (10 mL), and the mixture was filtered (paper filter). The organic layer was separated, the water layers was extracted with dichloromethane (20 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvents were evaporated under the reduced pressure, the residue was dissolved in dichloromethane (20 mL), and acetic anhydride (330 µL, 3.52 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature for 16 h, then celite (2 g) was added followed by pyridinium chlorochromate (630 mg, 2.93 mmol, 1.0 equiv.), and the mixture was stirred at room temperature for 1 h. The mixture was adsorbed on silica gel and purified by flash chromatography on silica gel (hexane-ethyl acetate 2:1) to afford **34** (644 mg, 71%) as a solid.
M.p.: 194.5 – 196.5 °C (methanol).
^{1}**H NMR** (400 MHz, $CDCl_3$): 0.38 (s, 9H), 2.27 (s, 3H), 7.73 – 7.87 (m, 5H), 8.65 (bs, 1H), 10.76 (d, J = 0.8, 1H).
^{13}**C NMR** (101 MHz, $CDCl_3$): 0.04, 24.93, 97.97, 109.41, 115.61, 121.00, 123.26, 126.80, 128.78, 129.45, 132.82, 134.16, 135.24, 137.62, 168.70, 192.63.
IR (KBr): 3437 vs, br, 2900 w, sh, 2854 w, 2148 w, 1702 w, sh, 1683 vs, 1676 s, sh, 1642 s, 1622 s, 1594 m, 1541 m, 1500 m, 1447 m, 1390 w, 1373 w, 1318 m, 1267 w, sh, 1251 m, 1238 m, 1066 w, 1019 w, 849 s, 838 m, sh, 737 w, 647 vw cm^{-1}.
ESI MS: 332 ($[M+Na]^+$).
HR ESI MS: calcd for $C_{18}H_{19}O_2NSiNa$ 332.1077, found 332.1077.

_N_-(8-Ethynyl-7-formylnaphthalen-2-yl)acetamide 35



TMS-alkyne **34** (625 mg, 2.02 mmol) was dissolved in dichloromethane (3 mL) and methanol (12 mL). Potassium carbonate (420 mg, 3.03 mmol, 1.5 equiv.) was added, and the mixture was stirred at room temperature for 20 min. The reaction was quenched with a saturated ammonium chloride solution (40 mL), extracted with ethyl acetate (2 x 20 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvents were evaporated under the reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 1:1 to 1:2) to afford **35** (426 mg, 89%) as a solid.

M.p.: 211 - 213 °C (methanol).

^{1}H NMR (600 MHz, DMSO-d_6): 2.13 (s, 3H), 5.24 (s, 1H), 7.75 (d, J = 8.5, 1H), 7.93 (dd, J = 8.8, 2.1, 1H), 8.00 (d, J = 8.5, 1H), 8.01 (d, J = 8.8, 1H), 8.86 (bd, J = 2.1, 1H), 10.41 (bs, 1H), 10.64 (d, J = 0.9, 1H).

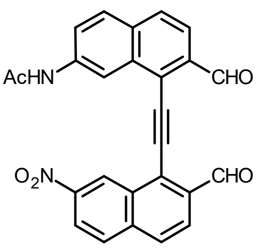
^{13}C NMR (151 MHz, DMSO-d_6): 21.62, 74.33, 91.39, 110.92, 117.39, 120.54, 121.99, 126.62, 126.76, 129.10, 131.21, 132.46, 136.72, 166.38, 188.99.

IR (KBr): 3286 m, 3231 s, 3050 m, 2926 w, 2847 m, 2093 w, 1682 vs, 1670 vs, 1622 m, 1598 s, 1580 s, 1550 vs, 1501 m, 1451 s, 1431 m, 1398 m, 1382 w, 1369 m, 1343 w, 1319 s, 1278 s, 1237 m, 1208 w, 1194 m, 968 w, 847 m, 822 w, 762 w, 706 m, 647 w, 607 w, 567 m, 523 w cm^{-1}.

ESI MS: 238 ($[M+H]^+$).

HR ESI MS: calcd for $C_{15}H_{12}O_2N$ 238.0863, found 238.0861.

***N*-{7-Formyl-8-[(2-formyl-7-nitronaphthalen-1-yl)ethynyl]naphthalen-2-yl}acetamide 36**



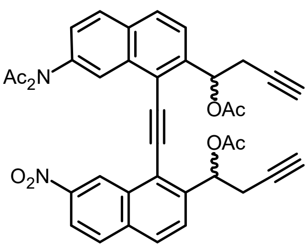
A Schlenk flask was charged with bromide **9** (435 mg, 1.55 mmol), $Pd(PPh_3)_2Cl_2$ (21.8 mg, 0.0311 mmol, 2 mol%), CuI (11.8 mg, 0.0620 mmol, 4 mol%), flushed with nitrogen, and the degassed *N*,*N*-dimethylformamide (7 mL) followed by the degassed triethylamine (650 µL, 4.65 mmol, 3.0 equiv.) were added. The mixture was heated to 60 °C, before a solution of alkyne **35** (405 mg, 1.71 mmol, 1.1 equiv.) in degassed *N*,*N*-dimethylformamide (5 mL) was slowly added within 1 h. The reaction mixture was stirred at the same temperature for 2 h. Then water (20 mL) was added and the mixture was filtered (paper filter). The solid was washed with acetone – water solution (1:1, 2 x 10 mL) and dried *in vacuo* to afford **36** (609 mg, 90%) as a solid, which was used in the following reaction without further purification. Due to its low solubility, the product was characterized only by IR and MS spectra.

IR (KBr): 3402 w, 3346 m, 3078 w, 2926 w, 2854 w, 2181 w, 1692 vs, 1682 vs, 1621 m, 1590 m, 1575 m, 1528 m, 1498 s, 1451 m, 1436 m, 1420 w, 1394 m, 1380 m, 1341 s, 1314 m, 1269 w, 1253 m, 1241 m, 1182 w, 891 w, 851 m, 824 m, 777 w, 739 m, 657 w, 628 vw, 555 w cm^{-1}.

ESI MS: 459 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{26}H_{16}O_5N_2Na$ 459.0951, found 459.0953.

1-[1-({2-[1-(Acetyloxy)but-3-yn-1-yl]-7-(diacetylamino)naphthalen-1-yl}ethynyl)-7-nitronaphthalen-2-yl]but-3-yn-1-yl acetate 37



A Schlenk flask was charged with zinc powder (530 mg, 8.11 mmol, 6.0 equiv.) and flushed with nitrogen. The freshly distilled tetrahydrofuran (5 mL) was added, the suspension was put to a water bath at room temperature and vigorously stirred. Then propargyl bromide (80 wt. % in toluene, 890 µL, 8.11 mmol, 6.0 equiv.) was slowly added within 10 min and the mixture was stirred at room temperature for 20 min before it was transferred by a syringe to the second Schlenk flask with a suspension of dialdehyde 36 (590 mg, 1.35 mmol) in tetrahydrofuran (40 mL). The reaction mixture was stirred at room temperature for 1 h, then triethylamine (1.88 mL, 13.5 mmol, 10 equiv.), acetic anhydride (1.28 mL, 13.5 mmol, 10 equiv.), and 4-dimethylaminopyridine (16.5 mg, 0.14 mmol, 0.1 equiv.) were added, and the solution was stirred at room temperature for 16 h. After that, the mixture was evaporated under the reduced pressure to dryness. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 2:1 to 1:1) to obtain 37 (477 mg, 55%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers): 1.97 – 2.03 (m, 4H), 2.155 (s, 3H), 2.158 (s, 6H), 2.19 (s, 3H), 2.35 (s, 6H), 2.37 (s, 6H), 2.88 – 3.02 (m, 4H), 3.05 (dd, *J* = 6.6, 2.6, 2H), 3.13 (dd, *J* = 6.4, 2.7, 2H), 6.82 – 6.91 (m, 4H), 7.359 (dd, *J* = 8.6, 2.1, 1H), 7.361 (dd, *J* = 8.6, 2.1, 1H), 7.79 (d, *J* = 8.6, 1H), 7.80 (d, *J* = 8.6, 1H), 7.89 (d, *J* = 8.7, 2H), 7.98 – 8.04 (m, 8H), 8.307 (dd, *J* = 9.0, 2.1, 1H), 8.310 (dd, *J* = 9.0, 2.4, 1H), 8.62 (d, *J* = 2.3, 1H), 8.63 (d, *J* = 2.4, 1H), 9.49 (d, *J* = 2.3, 1H), 9.55 (d, *J* = 2.3, 1H).

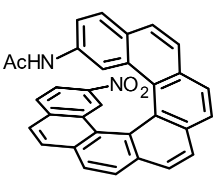
^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereomers): 21.01, 21.02, 21.09, 21.11, 25.96, 25.98, 26.08, 26.13, 27.35 (4C), 71.43, 71.58, 71.65, 71.71, 71.75, 72.02, 72.05, 72.22, 78.48, 78.69, 78.80, 79.05, 94.18, 94.30, 96.37, 96.50, 118.83, 118.85, 120.52 (2C), 121.37, 121.41, 123.51, 123.57, 124.52, 124.65, 126.71, 126.78, 127.32, 127.33, 127.83, 127.87, 129.14, 129.19, 129.74, 129.82, 130.08, 130.11, 130.34, 130.38, 132.13, 132.19, 132.60 (2C), 133.85, 133.89, 135.48 (2C), 139.11, 139.14, 141.31, 141.45, 141.78, 141.82, 146.76 (2C), 169.73, 169.76, 169.86, 169.89, 173.27 (2C), 173.31 (2C).

IR ($CHCl_3$): 3308 m, 3062 w, 3026 w, 3014 w, 2195 w, sh, 2126 vw, 1744 vs, 1712 vs, 1625 w, 1596 w, 1583 w, 1531 m, 1504 w, 1469 w, sh, 1370 s, 1431 w, sh, 1346 s, 1238 vs, 1143 w, 1113 w, 1031 m, 851 m, 846 m, sh, 829 w, 639 w, 622 m cm^{-1}.

ESI MS: 665 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{38}H_{30}O_8N_2Na$ 665.1894, found 665.1895.

***N*-(17-Nitroheptahelicen-2-yl)acetamide 38**



A crimp-sealed pressure vial was charged with triyne 37 (200 mg, 0.31 mmol), $Ni(PPh_3)_2(CO)_2$ (100 mg, 0.16 mmol, 0.5 equiv.), and flushed with nitrogen. The degassed toluene (15 mL) was added and the mixture was heated to 125 °C and stirred for 40 min. Then *p*-toluenesulfonic acid monohydrate (590 mg, 3.10 mmol, 10 equiv.) was added and the stirring was continued at 90 °C for 1 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (dichloromethane-ethyl acetate 20:1 to 3:1) to afford helicene **38** (62 mg, 42%) as a yellow solid.

M.p.: 313 – 314.5 °C (methanol).

UV/Vis (THF): λ_{max} (log ε) = 261 (5.27), 298 (4.96) nm.

^{1}H NMR (600 MHz, DMSO-*d*$_6$): 1.88 (s, 3H), 7.10 (dd, *J* = 8.6, 2.1, 1H), 7.32 (d, *J* = 8.6, 1H), 7.45 (d, *J* = 8.2, 1H), 7.62 – 7.64 (m, 1H), 7.63 (d, *J* = 8.2, 1H), 7.64 (d, *J* = 8.8, 1H), 7.69 (dd, *J* = 8.8, 2.3, 1H), 7.72 (d, *J* = 8.8, 1H), 8.05 (dt, *J* = 2.3, 0.6, 1H), 8.06 (d, *J* = 8.8, 1H), 8.08 (d, *J* = 8.5, 1H), 8.10 (d, *J* = 8.5, 1H), 8.18 (d, *J* = 8.5, 1H), 8.23 (d, *J* = 8.5, 1H), 8.24 (d, *J* = 8.3, 1H), 8.26 (d, *J* = 8.3, 1H), 9.25 (s, 1H).

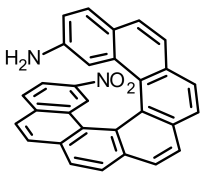
^{13}C NMR (151 MHz, DMSO-*d*$_6$): 23.98, 112.64, 118.14, 118.52, 119.86, 123.85, 124.06, 124.77, 126.13, 126.21, 126.38, 127.06, 127.28, 127.36, 127.62, 127.69, 127.80, 127.86, 128.11, 128.22, 128.33, 128.49, 129.08, 130.05, 131.85, 132.01, 132.03, 132.18, 134.70, 136.58, 142.87, 167.45.

IR (KBr): 3419 s, 3046 w, 1676 s, 1619 m, 1607 m, 1569 m, 1545 m, 1534 s, 1521 m, 1508 m, 1496 m, 1463 w, 1430 w, 1365 m, 1335 s, 1255 m, 1095 m, 891 w, 850 m, 837 m, 801 w, 741 w, 610 w, 528 w cm^{-1}.

ESI MS: 503 ([M+Na]$^+$).

HR ESI MS: calcd for $C_{32}H_{20}O_3N_2Na$ 503.1366, found 503.1367.

17-Nitroheptahelicen-2-amine 6



Helicene **38** (40 mg, 0.08 mmol) was dissolved in dioxane (5 mL), water (0.5 mL), and hydrochloric acid (35 wt%, 0.5 mL) were added, and the mixture was heated to 90 °C while stirred for 5 h. After cooling to room temperature, a saturated solution of sodium bicarbonate (10 mL) was added and the mixture was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate, the solvents were evaporated under the reduced pressure, and the residue was purified by flash chromatography on silica gel (dichloromethane-acetone 20:1) to afford helicene **6** (26 mg, 75%) as a red solid.

M.p.: 325.5 - 327 °C (methanol).

Chiral HPLC separation: *Analytical*: ChiralArt Amylose-SA (250 x 4.6 mm, 5 µm, YMC), heptane – toluene 1:2, 0.7% isopropyl alcohol @ 1.0 mL/min., t_R(+) = 8.2 min. (>99% *ee*), t_R(-) = 11.4 min. (82% *ee*); *Semipreparative*: ChiralArt Amylose-SA (250 x 20 mm, 5 µm, YMC), heptane – toluene 35:65 @20 mL/min.

Specific rotation: $[\alpha]^{20}_D$ = + 6165 (c 0.05, CH_2Cl_2); $[\alpha]^{20}_D$ = - 5131 (c 0.06, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 261 (5.07), 306 (4.69) nm.

^{1}H NMR (600 MHz, DMSO-*d*$_6$): 4.48 (bs, 2H), 6.03 (dt, *J* = 2.2, 0.6, 1H), 6.38 (dd, *J* = 8.5, 2.2, 1H), 7.11 (dt, *J* = 8.5, 0.6, 1H), 7.32 (dt, *J* = 8.2, 0.6, 1H), 7.37 (dd, *J* = 8.2, 0.5, 1H), 7.67 (dt, *J* = 8.7, 0.6, 1H), 7.70 (dd, *J* = 8.7, 2.2, 1H), 7.82 (dt, *J* = 8.4, 0.7, 1H), 8.00 (dd, *J* = 8.1, 0.5, 1H), 8.09 (dt, *J* = 2.2, 0.7, 1H), 8.10 (dd, *J* = 8.1, 0.5, 1H), 8.12 (dd, *J* = 8.4, 0.6, 1H), 8.15 (dd, *J* = 8.1, 0.6, 1H), 8.19 (dd, *J* = 8.1, 0.5, 1H), 8.23 (dd, *J* = 8.1, 0.5, 1H), 8.25 (dd, *J* = 8.1, 0.5, 1H).

^{13}C NMR (151 MHz, DMSO-d_6): 106.27, 116.39, 118.17, 120.07, 121.15, 123.59, 124.10, 124.27, 125.27, 126.46, 126.52, 126.63, 126.95, 127.73, 127.81, 127.88, 127.99, 128.20, 128.29, 128.36, 128.45, 130.24, 130.32, 131.14, 131.75, 131.83, 132.28, 134.86, 142.68, 146.33.

IR ($CHCl_3$): 3488 vw, 3449 vw, 3398 vw, 3372 vw, 3054 w, 1625 m, 1605 w, 1560 vw, 1531 m, 1522 w, 1512 w, 1499 m, 1467 w, 1434 vw, 1364 w, 1340 vs, 1291 vw, 1242 m, 1195 w, 919 w, 871 w, 848 s, 837 w, 832 m, 611 vw, 587 w, 569 w, 528 w cm^{-1}.

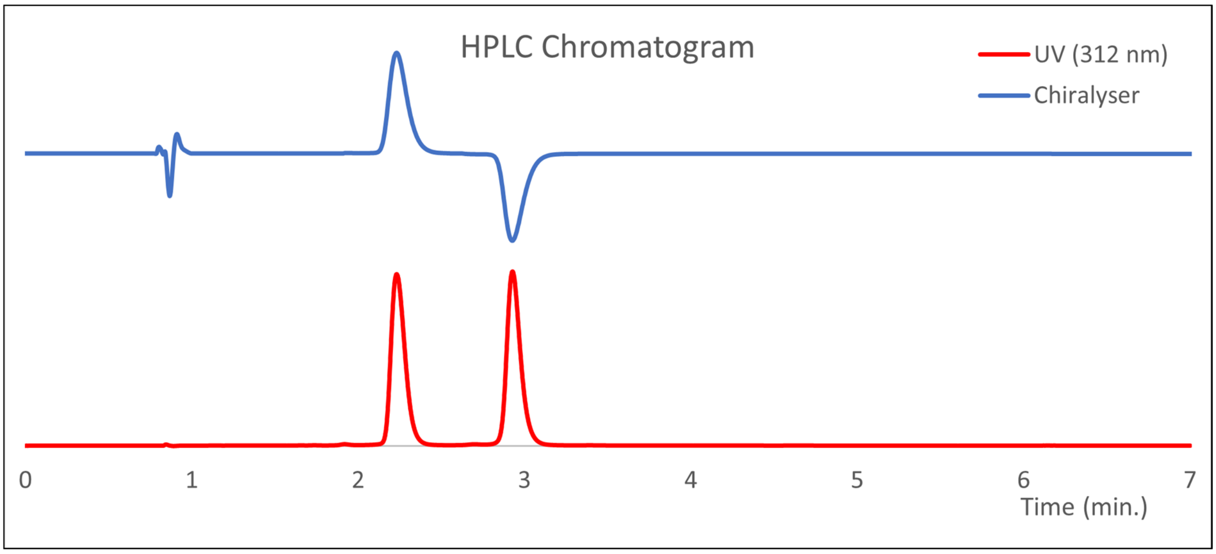
ESI MS: 439 ($[M+H]^+$).

HR ESI MS: calcd for $C_{30}H_{19}O_2N_2$ 439.1441, found 439.1445.

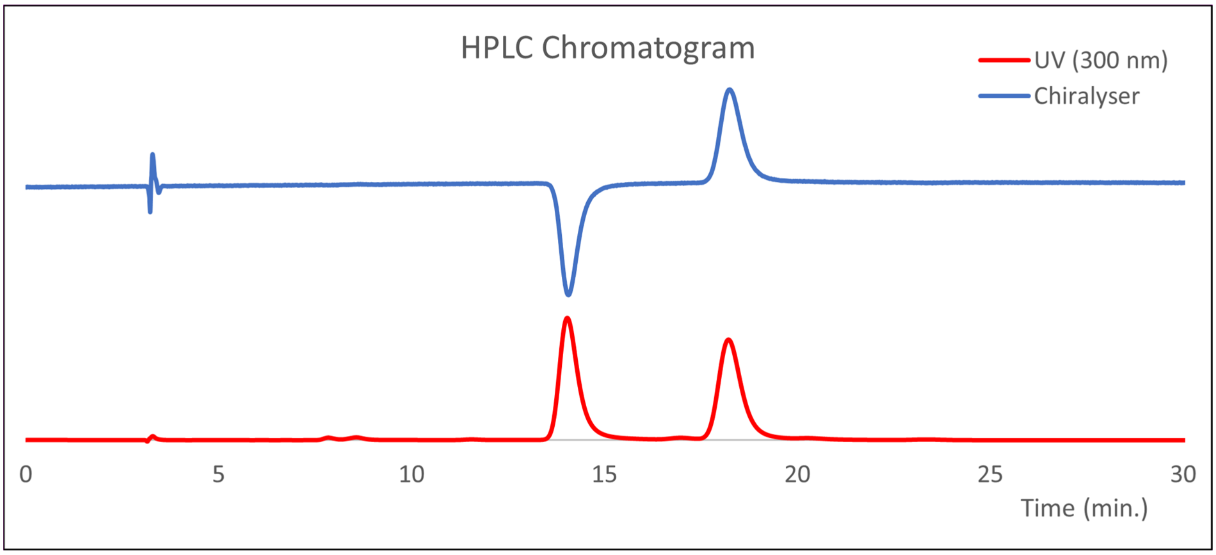
HPLC Resolution of Amino-Nitro Helicenes *rac*-3–6 into Enantiomers

Detailed experimental conditions for all separations are given as part of the helicene characterization data, *vide supra*. Below are illustrative chromatograms for each of the racemic mixtures.

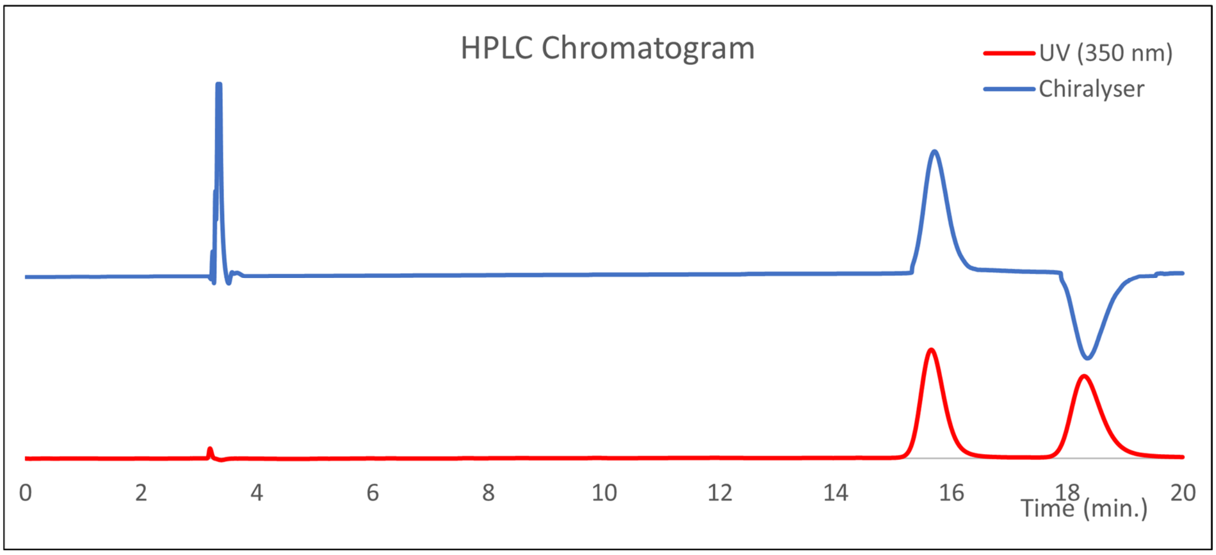
rac-3



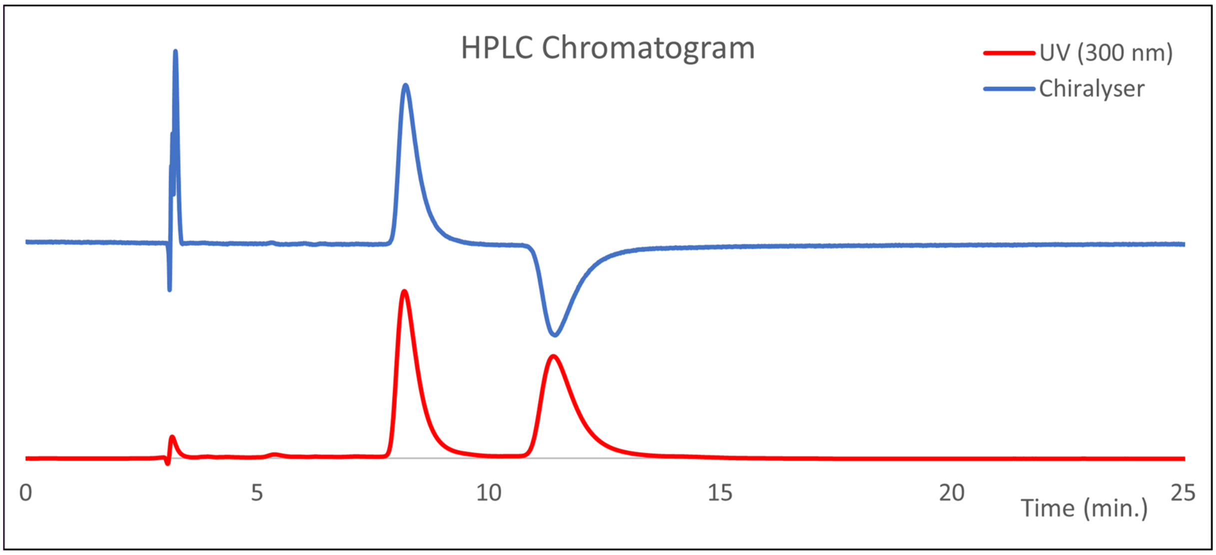
rac-4



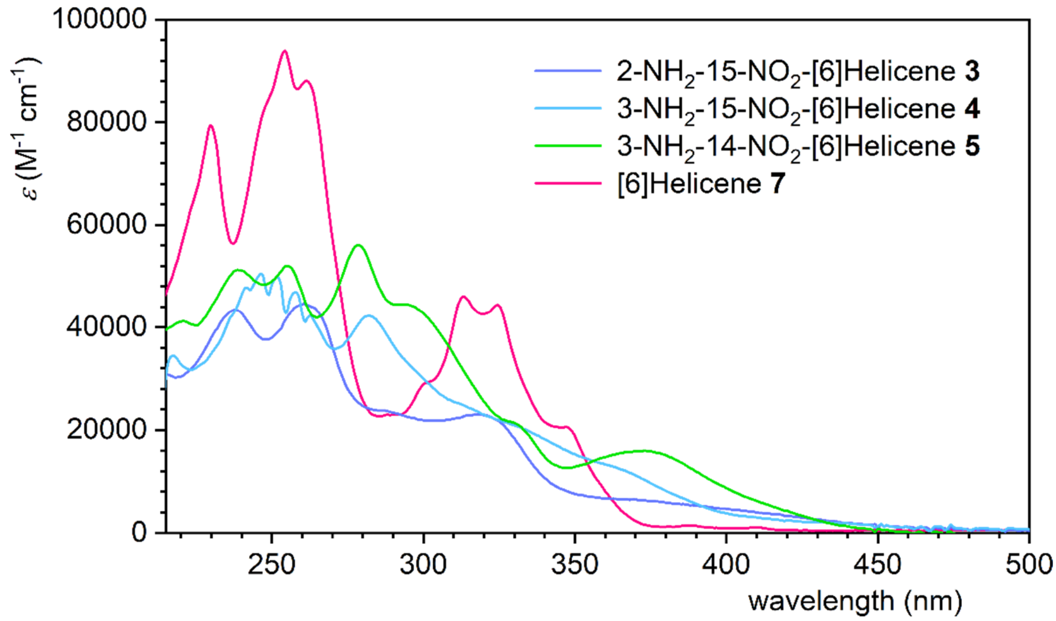
rac-**5**

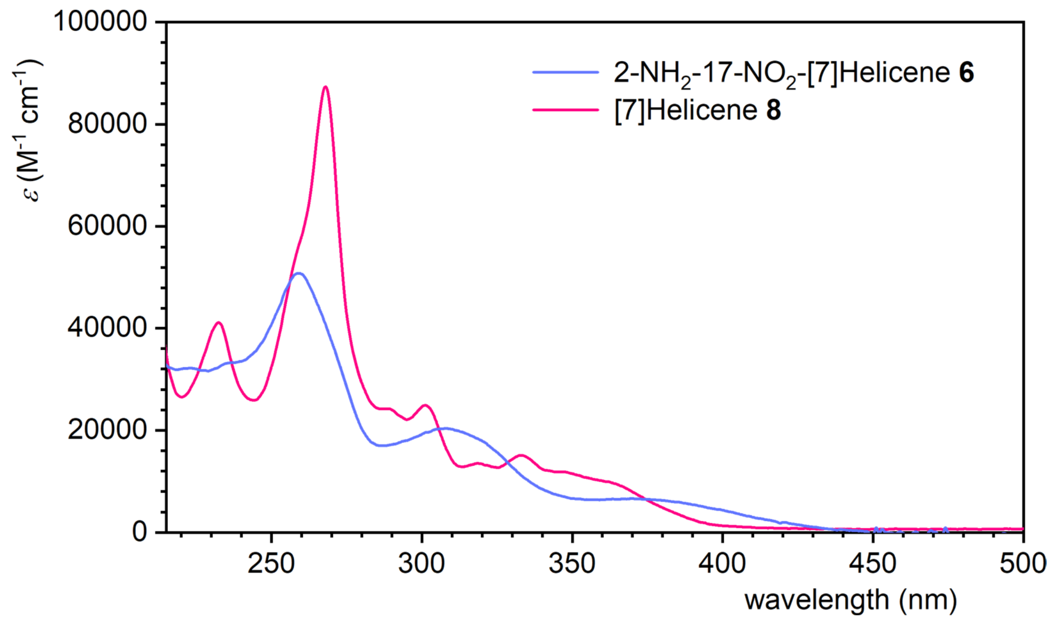

HPLC Chromatogram
UV (350 nm)
Chiralyser
0
2
4
6
8
10
12
14
16
18
20
Time (min.)

rac-**6**


HPLC Chromatogram
UV (300 nm)
Chiralyser
0
5
10
15
20
25
Time (min.)

UV-Vis spectra of push-pull helicenes 3–6 and the parent [6]helicene 7 and [7]helicene 8

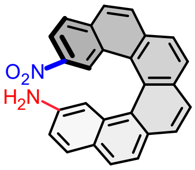




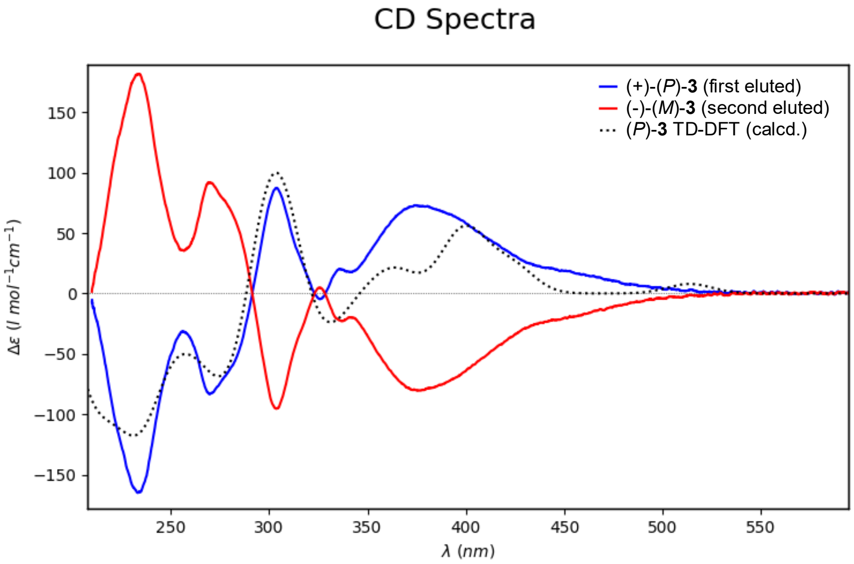
The UV-Vis spectra of push-pull helicenes **3**–**6** and the parent [6]helicene **7** and [7]helicene **8** (in THF, 10^{-4} M).

Calculated *vs* Experimental ECD Spectra of Nonracemic Amino-Nitro Helicenes 3–6, Parent [6]Helicene 7 and [7]Helicene 8

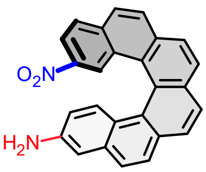
15-Nitro[6]helicen-2-amine **3**



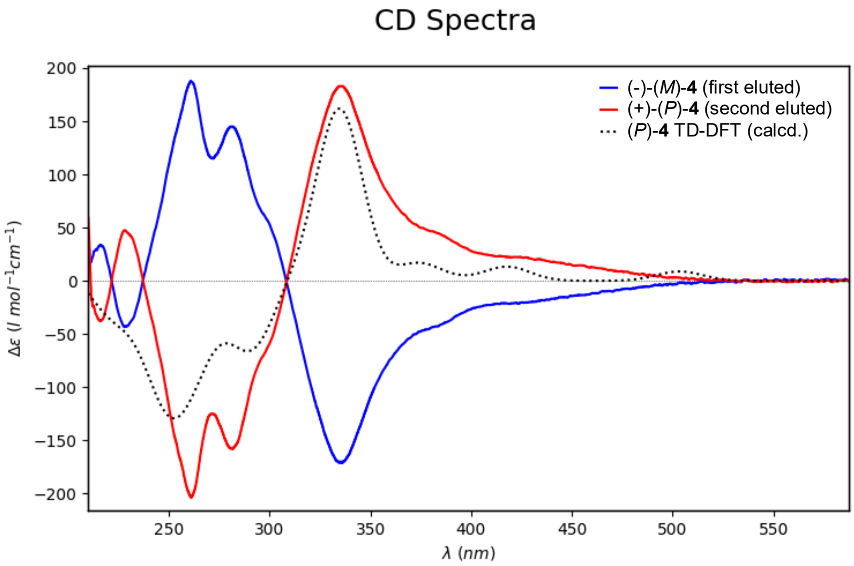
3



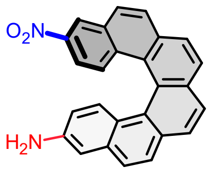
15-Nitro[6]helicen-3-amine **4**



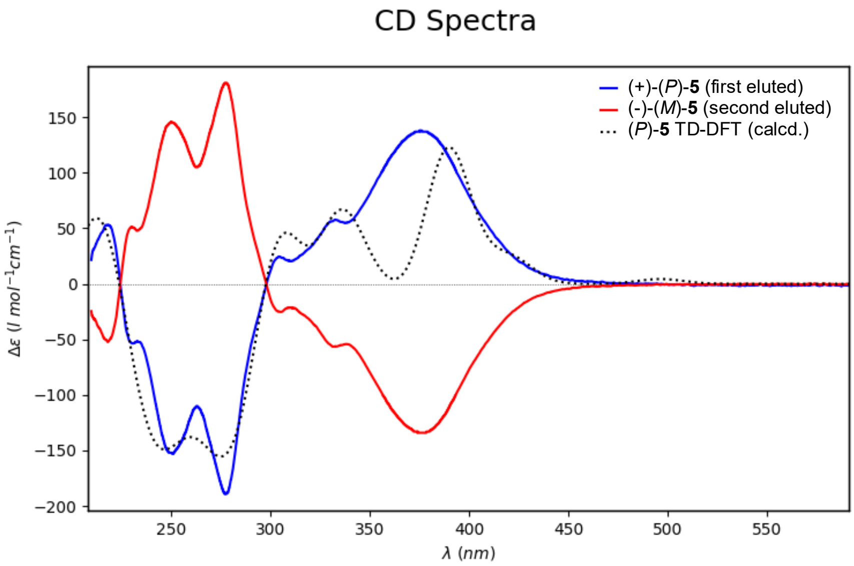
4



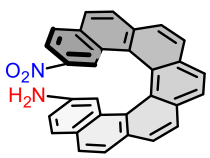
14-Nitro[6]helicen-3-amine **5**



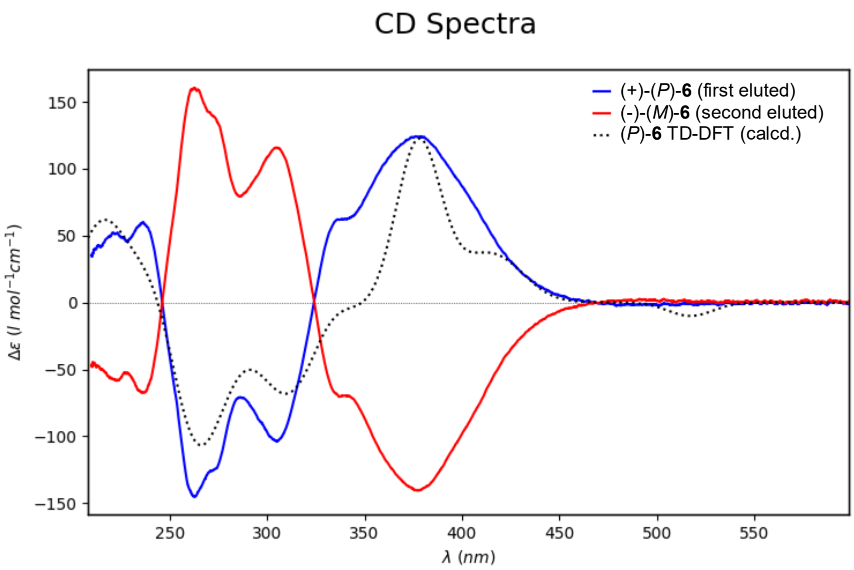
5



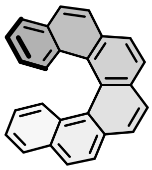
17-Nitro[7]helicen-2-amine **6**



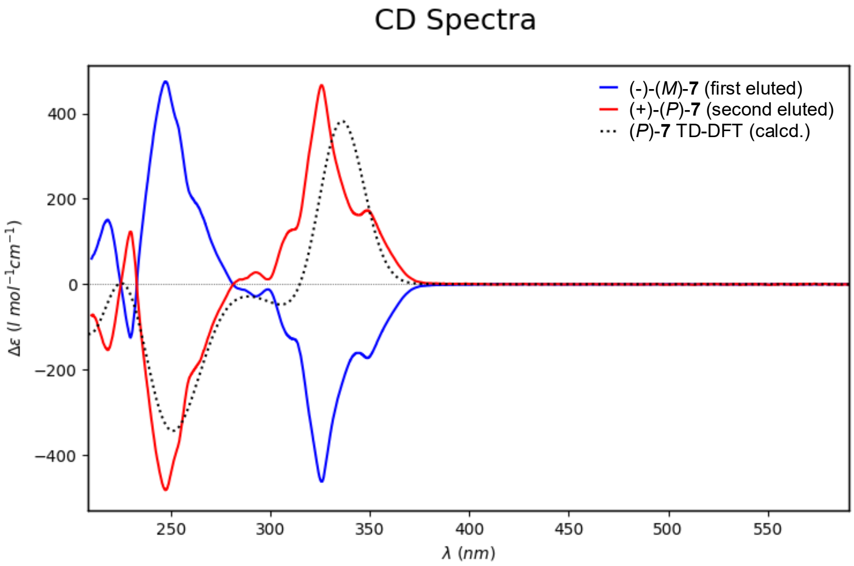
6



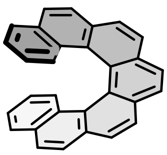
[6]Helicene **7**



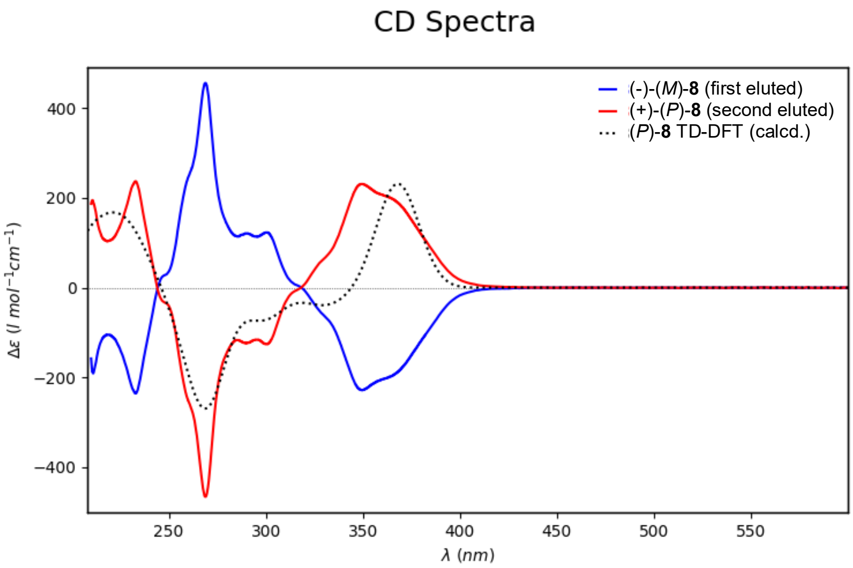
7



[7]Helicene **8**



8



Langmuir-Blodgett Films Formation

The samples of both the racemic and enantiopure amino-nitro [6]helicene *rac*-, (-)-(*M*)- and (+)-(*P*)-**3** were prepared in CH_2Cl_2 (UV-Vis grade at a concentration of 1 mg mg mL^{-1}. The water subphase temperature was 22 °C. After the samples (20 - 50 µL) were spread on the subphase surface, 10 min delay was applied to evaporate the organic solvent from the subphase surface before the compression. The layers were compressed at a constant compression rate with a barrier speed of 10 mm min^{-1}. In order to deposit the LB films on quartz glass plates and silicon chips, the Langmuir layers were compressed to surface pressure of 20 mN m^{-1} and this value was kept constant during the deposition of the LB films on both sides of hydrophilic substrates. The vertically oriented substrates were pulled up from the subphase at a constant speed of 1 mm min^{-1}. Maximal forward/backward rate of the barriers was 2 mm min^{-1}.

Computational Details

DFT calculations were performed using Gaussian 16 software package.[7] The geometries of (*P*)-enantiomers of the amino-nitro- substituted as well as parent hexa- and heptahelicenes **3** – **8** were optimized at PBE0[8]/cc-pVTZ[9]/GD3[10]/PCM[11,12] (tetrahydrofuran) level and subsequent vibrational analyses confirmed absence of negative vibrational frequencies in all cases.
ECD spectra and HOMO-LUMO gaps were extracted from TD-DFT calculations performed at the same level of theory for 100 lowest-energy singlet states.

Cartesian coordinates for the optimized geometries and their respective calculated CD spectra states:

Compound **3**:

C	4.202180	0.766547	0.133456
C	3.321120	-0.323996	0.338031
C	1.932505	-0.176577	0.094885
C	1.431210	1.172938	0.013050
C	2.334278	2.210289	-0.296861
C	3.730184	1.972698	-0.271941
C	1.148702	-1.381880	-0.030425
C	1.656379	-2.565273	0.546930
C	3.004461	-2.621182	0.984235
C	3.833947	-1.565876	0.789277
C	0.839061	-3.725064	0.655253
C	-0.414134	-3.740267	0.139589
C	-0.885028	-2.646145	-0.630234
C	-0.081817	-1.486639	-0.787858
C	-0.495726	-0.517108	-1.712929
C	-1.699540	-0.608996	-2.387868
C	-2.533072	-1.722742	-2.147477
C	-2.119402	-2.715643	-1.304708
H	5.264742	0.603783	0.272427
H	4.404598	2.788066	-0.504892

[7] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
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H	3.374829	-3.548802	1.405125
H	4.891830	-1.638814	1.013425
H	1.242038	-4.591711	1.166096
H	-1.051182	-4.610190	0.253181
H	-3.485452	-1.798123	-2.660163
H	-2.741523	-3.591237	-1.156366
C	1.850078	3.515017	-0.598256
C	0.533481	3.821416	-0.512240
C	-0.380140	2.868377	0.010686
C	0.075745	1.563012	0.331372
H	2.569467	4.265555	-0.905759
H	0.172266	4.809543	-0.770836
C	-0.804990	0.723581	1.030176
C	-2.090136	1.123901	1.283913
C	-2.585951	2.368663	0.880249
C	-1.720254	3.229358	0.265918
H	-0.483648	-0.241324	1.387537
N	-2.973486	0.210235	2.000103
H	-3.612610	2.634911	1.083272
H	-2.052181	4.221156	-0.016812
O	-2.515669	-0.842574	2.400545
O	-4.131154	0.550735	2.157276
H	0.140904	0.332927	-1.915650
N	-2.065291	0.336478	-3.324723
H	-1.635622	1.241120	-3.221078
H	-3.051263	0.400413	-3.517072

[Wavelength (nm), R (length)]: [518.697205, 28.1745], [427.782469, 85.1895], [403.817845, 190.770], [376.462601, -33.745], [370.478076, 101.459], [349.566350, 10.0241], [333.255008, -98.648], [324.906166, -31.614], [315.521550, 42.8997], [309.712712, 6.01470], [307.241396, 368.021], [295.024850, -7.2448], [286.814548, -2.1227], [284.380460, -185.16], [281.673428, -75.851], [274.398444, 18.7107], [271.710445, 15.6354], [263.359091, -131.07], [256.425292, 18.1697], [255.959440, -3.1638], [252.719513, -22.830], [249.179398, 74.8043], [243.670046, 22.6963], [243.130097, -1.2337], [240.465851, -276.11], [238.656028, -199.27], [234.379087, 8.54980], [232.842911, 38.7311], [229.455885, 42.9940], [224.495171, -7.3990], [222.313418, -71.262], [221.266005, 15.4185], [219.188885, -50.568], [217.653594, -110.20], [216.294255, -39.230], [214.286789, -51.396], [211.569900, 34.8811], [210.485184, 3.52360], [209.616881, 1.30650], [208.625743, 7.66460], [208.090015, -45.030], [207.661323, -25.794], [207.030229, -1.2674], [205.302434, -86.087], [205.241260, 18.1130], [202.900195, 49.6130], [202.119580, -19.778], [200.245806, 9.14660], [199.665346, 12.7958], [198.476329, 12.9971], [197.379914, 9.78840], [196.819051, -8.1459], [196.572532, -25.054], [194.662113, -13.460], [194.335637, 32.4902], [193.740438, 43.2884], [192.113351, -16.274], [191.914112, 9.30770], [191.679720, -13.386], [191.077093, 46.8357], [190.610019, 8.70460], [190.002441, 23.5228], [189.671082, 3.24270], [187.974458, -6.5376], [187.692740, 0.96920], [187.383540, 19.5386], [187.292959, 138.210], [185.939102, -16.511], [185.266718, 25.3944], [184.481070, -12.319], [183.129541, 8.29100], [183.091680, 0.73720], [182.646641, 1.59290], [181.348281, 28.1818], [181.006749, 13.0175], [180.243641, -23.935], [180.178156, 101.535], [179.757576, 112.861], [179.167909, -13.534], [178.384256, 21.0597], [177.974554, -11.608], [177.523508, 16.0539], [177.206347, 4.30800], [176.902938, 4.35340], [176.598050, -0.4301], [176.474882, -18.145], [176.229060, 21.0155], [175.600081, -54.578], [175.257538, -12.887], [174.684672, 15.6248], [174.326078, -2.8268], [173.890874, -0.5242], [173.773887, -6.2586], [173.302666, 9.54030], [173.111508, -3.4929], [172.578983, 6.49890], [172.526151, 2.20710], [171.897061, 6.89000], [171.343550, -0.3120], [170.723040, 0.53870].

Compound 4:

C	-4.347240	0.327732	-0.097391
C	-3.219192	1.122781	0.227185
C	-1.910875	0.618797	0.018063
C	-1.783662	-0.805902	-0.159564
C	-2.912401	-1.536117	-0.581823
C	-4.193132	-0.929738	-0.583553
C	-0.826228	1.570283	0.015973
C	-1.026980	2.797550	0.681152
C	-2.329020	3.190920	1.076083
C	-3.403144	2.421173	0.763572
C	0.076540	3.667534	0.913651
C	1.311236	3.380359	0.439501
C	1.510275	2.260840	-0.418926
C	0.423102	1.388105	-0.681895
C	0.619349	0.420263	-1.687728
C	1.823863	0.255647	-2.313870
C	2.938621	1.051018	-1.968252
C	2.751934	2.057660	-1.039741
H	-5.333882	0.761426	0.017846
H	-5.047890	-1.513584	-0.904080
H	-2.456138	4.150816	1.563497
H	-4.412530	2.765088	0.956668
H	-0.096748	4.569322	1.490095
H	2.150940	4.032697	0.649928
N	4.140172	0.871774	-2.619848
H	3.570002	2.728667	-0.799427
C	-2.778787	-2.899501	-0.970181
C	-1.598153	-3.555360	-0.865487
C	-0.492490	-2.922598	-0.238158
C	-0.600445	-1.568121	0.172030
H	-3.654639	-3.404934	-1.361006
H	-1.500268	-4.583915	-1.191349
C	0.430701	-1.048896	0.969765
C	1.549116	-1.796209	1.228953
C	1.717403	-3.096652	0.740293
C	0.687465	-3.648042	0.031144
H	0.356776	-0.063124	1.398858
N	2.604601	-1.205993	2.044655
H	2.624484	-3.642609	0.953048
H	0.758328	-4.670366	-0.320343
O	2.421134	-0.101351	2.518542
O	3.622951	-1.852792	2.205232
H	-0.209055	-0.202177	-1.995149
H	1.926944	-0.489923	-3.094471

H	4.298683	-0.046480	-3.000181
H	4.951772	1.240621	-2.152541

[Wavelength (nm), R (length)]: [513.434, 31.4210], [427.782, 47.6891], [395.483, 6.85550], [382.266, 59.8701], [361.269, -29.675], [344.956, 587.360], [332.682, 2.86430], [319.728, 1.69560], [315.401, 27.9511], [309.805, -6.9788], [300.291, -253.52], [293.224, -5.6447], [288.415, 64.5550], [285.677, -16.192], [282.289, -1.6728], [273.388, -248.30], [271.591, 18.8928], [265.269, 43.2944], [261.586, -7.2163], [258.391, -395.01], [253.504, 23.9183], [250.089, -7.6804], [245.693, 9.46420], [240.237, 18.2432], [239.010, 13.2793], [235.836, -38.396], [233.518, -5.2307], [231.443, -154.15], [228.981, 47.4237], [225.988, -1.3345], [220.978, 24.8105], [219.569, 4.44960], [218.709, -1.3490], [217.710, -49.138], [216.207, 2.48820], [214.331, 55.4357], [212.622, 1.08500], [212.530, -31.976], [210.660, 9.14930], [209.016, -4.7162], [207.682, 1.77160], [207.151, -13.235], [204.966, 10.4374], [204.186, 130.090], [203.122, -29.990], [201.810, 15.7058], [201.449, -16.928], [200.628, -95.078], [199.270, 77.7078], [198.289, -21.144], [197.222, -59.026], [196.800, -2.9636], [195.567, -2.6120], [194.546, 1.89830], [193.577, -88.082], [192.749, -10.808], [192.369, 60.4727], [191.549, -4.5842], [191.183, -9.9179], [190.504, 15.4859], [189.618, -9.4989], [188.721, 41.6303], [188.603, 22.3881], [187.928, 25.9623], [187.465, 18.4926], [187.273, 12.2298], [186.889, 15.4882], [186.100, 29.5970], [185.691, -2.3104], [185.349, 5.95300], [184.163, 12.3588], [182.810, 3.14430], [182.019, 6.75010], [181.893, 3.57030], [180.642, 2.46820], [180.248, -9.5471], [179.908, -21.233], [179.611, -3.1771], [179.079, -3.4586], [177.831, 7.24670], [177.434, -4.9718], [177.246, -0.3605], [176.608, -4.4412], [176.191, -19.478], [176.058, -7.6422], [175.894, -0.5101], [175.381, 5.63460], [175.091, 9.62100], [174.684, -3.9108], [174.304, -49.605], [173.917, 12.7648], [173.567, -1.8219], [172.954, -1.1208], [172.677, 49.3773], [172.040, 22.1962], [171.801, -3.9155], [171.402, -9.8172], [171.182, -1.4975], [170.202, -25.349], [169.988, -0.1250].

Compound 5:

C	3.429902	2.768939	-0.256823
C	3.254209	1.446223	0.222505
C	2.002020	0.800312	0.073940
C	0.864330	1.640256	-0.211211
C	1.091482	2.906578	-0.789355
C	2.403443	3.438781	-0.839902
C	1.973952	-0.633221	0.222567
C	3.013827	-1.238176	0.959991
C	4.176944	-0.501593	1.291510
C	4.333192	0.771325	0.844669
C	2.916586	-2.610407	1.328274
C	1.881586	-3.378547	0.914694
C	0.924705	-2.863274	-0.006890
C	1.003885	-1.501832	-0.398823
C	0.161934	-1.099993	-1.455477
C	-0.755677	-1.944276	-2.016623
C	-0.908568	-3.268399	-1.549918
C	-0.046500	-3.709508	-0.563618
H	4.413952	3.217437	-0.182914
H	2.553375	4.418363	-1.278122
H	4.968642	-0.999434	1.839641
H	5.265550	1.304414	0.989294
H	3.696972	-3.027874	1.954629
H	1.804185	-4.415130	1.222553

N	-1.831501	-4.103412	-2.141629
H	-0.092643	-4.740308	-0.228095
C	0.001409	3.677986	-1.285757
C	-1.277968	3.267139	-1.131894
C	-1.558119	2.112743	-0.348390
C	-0.492959	1.327019	0.167039
H	0.225193	4.607548	-1.796287
H	-2.103637	3.840350	-1.535913
C	-0.813982	0.325206	1.108121
C	-2.107811	0.034112	1.443138
C	-3.140132	0.752351	0.831316
C	-2.884505	1.784824	-0.031524
H	-0.018628	-0.219666	1.593477
N	-4.523018	0.420607	1.149948
H	-3.701120	2.358613	-0.447707
H	0.252705	-0.101093	-1.857804
H	-1.371291	-1.599233	-2.839867
H	-2.614290	-3.649410	-2.582151
H	-2.103896	-4.910173	-1.605064
H	-2.341058	-0.731759	2.167980
O	-4.722177	-0.491044	1.930312
O	-5.407258	1.065992	0.619532

[Wavelength (nm), R (length)]: [496.274239, 10.4115], [420.114506, 58.4133], [388.982221, 317.783], [379.760454, -32.622], [369.671705, -14.154], [338.181750, 47.8443], [334.198208, 126.107], [316.181351, -69.586], [309.906249, -3.9715], [303.629801, 301.743], [300.822984, -96.758], [295.116141, -8.8555], [290.130091, -63.395], [289.297415, -50.654], [277.692602, -221.78], [275.520429, -38.530], [272.349075, 37.4257], [267.138225, -79.253], [265.576080, -14.971], [256.940757, -140.29], [255.300620, 79.1060], [250.169881, -92.307], [244.366425, -55.758], [240.218924, -136.67], [237.276698, -27.092], [234.224115, -28.674], [233.333697, -17.928], [228.517017, 14.2369], [227.815800, 89.1159], [226.608289, -39.495], [225.102476, -130.82], [222.305445, 50.1832], [218.478199, 11.7876], [218.074705, 19.8160], [214.992792, 124.645], [212.972710, -0.2010], [210.968696, -32.490], [210.882576, 18.9183], [208.769773, -10.333], [208.485418, 57.5844], [207.144373, 9.34070], [205.122416, 38.5930], [203.881130, 30.0651], [202.525675, -31.552], [202.373611, 9.46030], [201.711829, 57.2724], [201.282843, -48.046], [200.368779, -57.019], [198.384231, -100.41], [197.896591, 2.89970], [197.323370, 18.6109], [196.084443, -10.803], [195.481581, 78.5253], [194.195619, -35.312], [193.386875, -10.156], [192.695585, 8.78440], [191.976516, 2.20720], [191.000559, 3.79860], [190.739043, -30.568], [189.920948, -6.7310], [189.277285, 5.17710], [188.609275, -15.097], [188.285613, -20.904], [187.225081, 15.8222], [187.196813, 36.4356], [186.641667, -1.9367], [186.277127, 5.33490], [184.954416, 20.6682], [184.357630, 36.1279], [183.281140, -11.983], [183.091680, -17.528], [182.781273, 27.8869], [182.297525, 0.44400], [181.160147, 22.1938], [180.729706, -10.516], [180.123187, 12.2677], [179.979377, -28.227], [178.992021, -31.650], [178.829374, 0.96640], [178.520386, -42.596], [177.910708, -1.2184], [177.378742, 14.9504], [176.769262, 6.12790], [176.306746, -12.069], [176.056392, -26.777], [175.649836, 3.54380], [174.664985, 19.5388], [173.942105, -0.1355], [173.771452, 1.89980], [173.406891, 12.2462], [173.029367, 6.15190], [172.535754, 0.07960], [172.052112, -24.699], [171.336447, 0.48890], [171.220506, -14.678], [170.887755, -52.161], [170.671337, 6.09710], [170.441407, -2.1640], [170.251830, -6.0183], [170.086005, 2.98840].

Compound 6:

C	4.221021	0.257318	-0.804251
C	3.209436	1.203367	-0.495441
C	1.872213	0.775639	-0.329372
C	1.531667	-0.528807	-0.828895
C	2.560987	-1.471868	-1.003857
C	3.916787	-1.056955	-0.957417
C	0.950887	1.679895	0.318664
C	1.250928	3.059268	0.254766
C	2.559334	3.484758	-0.092055
C	3.533684	2.577006	-0.355423
C	0.239607	4.013675	0.538483
C	-1.012584	3.609341	0.869673
C	-1.280701	2.240982	1.136916
C	-0.252421	1.286107	1.006266
C	-0.464301	-0.014269	1.601908
C	-1.784892	-0.394245	1.954539
C	-2.840994	0.549612	1.871802
C	-2.583143	1.840710	1.545659
C	-2.007946	-1.694644	2.448260
C	-0.978023	-2.570445	2.648878
C	0.351604	-2.166761	2.399190
C	0.582586	-0.900155	1.895121
H	5.246241	0.601917	-0.874658
H	4.694820	-1.795234	-1.112173
H	2.775426	4.546943	-0.088373
H	4.558172	2.889345	-0.520614
H	0.477261	5.066363	0.437959
H	-1.812559	4.329076	0.998677
H	-3.844300	0.234379	2.135580
H	-3.368084	2.587450	1.566672
H	-3.023136	-1.991207	2.687823
H	-1.170376	-3.565975	3.033115
N	1.399844	-3.010597	2.713170
H	1.605295	-0.591651	1.729539
C	2.238813	-2.840387	-1.229890
C	0.953165	-3.257449	-1.334904
C	-0.100276	-2.305514	-1.376902
C	0.198057	-0.929917	-1.205488
H	3.053964	-3.552311	-1.294057
H	0.716752	-4.307536	-1.457975
C	-0.813594	-0.002008	-1.493929
C	-2.083453	-0.433914	-1.775230
C	-2.425483	-1.790350	-1.817763
C	-1.425675	-2.706796	-1.646943
H	-0.608919	1.055914	-1.509399
N	-3.113871	0.562783	-2.034143
H	-3.444877	-2.084795	-2.018694

H	-1.639768	-3.765086	-1.735697
H	1.171939	-3.990914	2.739169
H	2.257084	-2.833846	2.214970
O	-2.778521	1.726112	-2.149789
O	-4.265291	0.176726	-2.117615

[Wavelength (nm), R (length)]: [517.268943, -48.074], [442.927240, 7.83980], [425.112954, 91.9942], [409.350875, 123.340], [387.595952, 52.0641], [377.230027, 555.713], [365.024416, -16.322], [343.332391, -34.088], [333.317722, 42.6155], [323.642468, -22.188], [318.627141, -68.831], [313.455511, -160.44], [309.133550, 12.7143], [307.553873, -29.312], [300.073075, -138.23], [289.290665, 31.0366], [287.046959, -69.407], [284.139322, 13.1230], [275.557170, 0.42150], [273.153102, -250.07], [271.051097, 14.5369], [270.082763, -12.459], [265.360086, 34.2990], [261.184312, -213.34], [261.079814, -103.31], [255.859080, -110.53], [248.879284, 14.7922], [248.032875, 26.9464], [246.484549, 68.3089], [244.351977, -31.552], [242.417036, 32.3702], [239.425678, 68.8801], [236.936617, 5.18860], [235.264123, -35.436], [231.141299, -17.079], [230.792787, 25.7423], [228.272992, -54.796], [226.513068, -5.8389], [223.984162, 5.05570], [223.725492, 155.102], [220.463375, 2.76310], [219.406100, 7.50360], [218.593757, 12.2663], [216.653316, 35.7893], [215.801077, -7.1651], [214.680091, -2.9362], [214.016766, 19.5452], [213.287791, 15.0030], [212.830131, 12.7021], [212.443572, 6.54840], [210.613904, -28.567], [210.317370, 78.7389], [209.577905, 19.6050], [208.868250, 26.6633], [207.619594, 11.4020], [206.053070, 7.35630], [204.584250, 11.8847], [203.049726, 3.22880], [202.648153, -61.148], [202.525675, 42.8550], [201.931942, -10.512], [200.933802, 3.30250], [200.045489, 8.04020], [199.104227, 34.1436], [198.711724, -12.236], [197.842907, 4.62780], [197.678879, -40.091], [196.616174, 23.8259], [196.404380, 6.54520], [194.738551, 59.6174], [194.116568, -62.541], [193.616392, 23.6740], [193.305466, -43.265], [192.680611, -9.3605], [191.931938, 0.65350], [191.516873, -5.2804], [190.686240, 3.72160], [190.583649, 23.2314], [190.066521, -12.215], [189.688493, 51.7221], [189.430556, -40.027], [188.022919, -38.724], [187.772332, -3.4966], [187.326917, 4.28360], [187.095118, -4.0352], [186.551802, -47.287], [186.095391, -10.652], [185.241806, -14.722], [185.006854, 5.31410], [184.703681, -24.877], [184.163203, 17.5593], [183.528026, -2.4597], [182.482659, -24.481], [181.880344, 10.3174], [181.515545, -6.6208], [181.337672, 1.42310], [180.677032, 9.85990], [180.414122, 1.39710], [180.170302, -5.4711], [179.937584, 7.29570].

Compound 7:

C	-3.611525	0.832639	-0.830636
C	-2.379858	1.496188	-0.562952
C	-1.283620	0.776570	-0.045250
C	-1.551830	-0.534538	0.505650
C	-2.788133	-1.169337	0.219772
C	-3.789523	-0.469929	-0.509916
C	0.000047	1.433161	0.000016
C	0.000088	2.849993	0.000011
C	-1.157960	3.560666	-0.403421
C	-2.280298	2.894251	-0.774191
C	1.158180	3.560601	0.403433
C	2.280486	2.894123	0.774189
C	2.379966	1.496055	0.562945
C	1.283677	0.776499	0.045266
C	1.551798	-0.534623	-0.505639
C	2.788073	-1.169492	-0.219796
C	3.789522	-0.470140	0.509866

C	3.611603	0.832437	0.830596
C	3.044114	-2.461310	-0.719385
C	2.144122	-3.093972	-1.537332
C	0.964857	-2.431309	-1.903978
C	0.679024	-1.187881	-1.398438
H	-4.406388	1.400818	-1.300462
H	-4.719681	-0.977393	-0.738735
H	-1.112045	4.642773	-0.445960
H	-3.142980	3.425650	-1.158981
H	1.112329	4.642711	0.445965
H	3.143205	3.425475	1.158962
H	4.719657	-0.977657	0.738661
H	4.406510	1.400570	1.300404
H	3.985488	-2.936118	-0.465843
H	2.355403	-4.083833	-1.923235
H	0.274161	-2.898771	-2.595318
H	-0.229199	-0.692641	-1.709522
C	-3.044264	-2.461140	0.719354
C	-2.144336	-3.093852	1.537333
C	-0.965050	-2.431252	1.904022
C	-0.679129	-1.187841	1.398488
H	-3.985658	-2.935894	0.465785
H	-2.355687	-4.083698	1.923234
H	-0.274405	-2.898748	2.595390
H	0.229106	-0.692649	1.709612

[Wavelength (nm), R (lenght)]: [370.988010, 1.52110], [355.326836, -4.1718], [334.938523, 733.076], [318.537094, -144.68], [308.196060, 44.3972], [305.034181, -74.755], [289.277165, 16.3363], [288.248188, -31.255], [280.990375, -10.387], [280.082664, 2.88630], [268.387291, 57.1119], [263.196962, -231.41], [257.875981, -34.367], [247.468500, -471.76], [245.790681, -22.170], [237.964364, -138.95], [237.013617, 147.760], [231.902202, -62.326], [227.364605, 20.8040], [223.612511, -7.0966], [222.680759, 289.376], [221.392438, 7.85580], [218.328156, -6.5565], [216.918650, 2.68600], [212.687743, -288.73], [211.551850, 21.4740], [208.833069, 1.79630], [205.346638, -0.5876], [204.929163, -32.162], [202.900195, -198.88], [202.267963, 17.1123], [200.491903, 16.0723], [200.135905, 1.38980], [199.142603, -9.8361], [198.581233, -12.760], [197.395627, -3.8665], [196.488420, -11.957], [195.914029, 9.79040], [194.457556, -19.802], [191.928966, 201.690], [191.310013, 6.93950], [190.947611, -0.3696], [188.706878, 5.27990], [187.917477, 37.7321], [186.274328, 130.035], [185.911221, 6.30210], [184.695427, -35.079], [184.237091, 25.0159], [183.473708, 89.5234], [182.678935, -17.034], [181.944402, 132.475], [181.210455, -0.4842], [180.650707, 62.5488], [180.440379, -4.7665], [179.460959, 1.22140], [179.307831, 4.77910], [178.094708, -4.9053], [177.711802, 17.2931], [177.688880, 9.17410], [176.852471, -17.661], [176.525134, -56.850], [176.314268, -38.918], [175.779331, -14.969], [174.788103, 7.60360], [174.785639, -8.3594], [173.394765, 3.27350], [173.022123, -0.5915], [172.846040, -31.627], [172.571777, -5.9693], [171.012680, -4.1129], [170.100006, 0.41270], [168.892784, -8.8116], [168.431611, -28.834], [168.342421, 0.49450], [168.171167, 33.0452], [168.102763, -23.384], [167.936546, -7.3724], [167.099104, -10.897], [166.759732, -28.100], [166.229846, 1.07240], [165.856266, -50.463], [165.329893, -7.8582], [165.184515, -0.0281], [164.642710, -2.8083], [164.393844, 64.0553], [164.065361, -1.6060], [163.991579, -89.306], [163.515764, -0.2250], [163.259541, 0.66600], [162.421161, 5.68870], [161.890962, 0.22720], [161.768450, -6.5679], [161.211048, 22.0333], [160.995433, -7.8684], [160.845054, 0.17090], [160.690790, 1.37960], [160.590885, 1.16200], [160.347887, -4.6447], [160.206994, -3.1017], [159.395497, -1.9103].

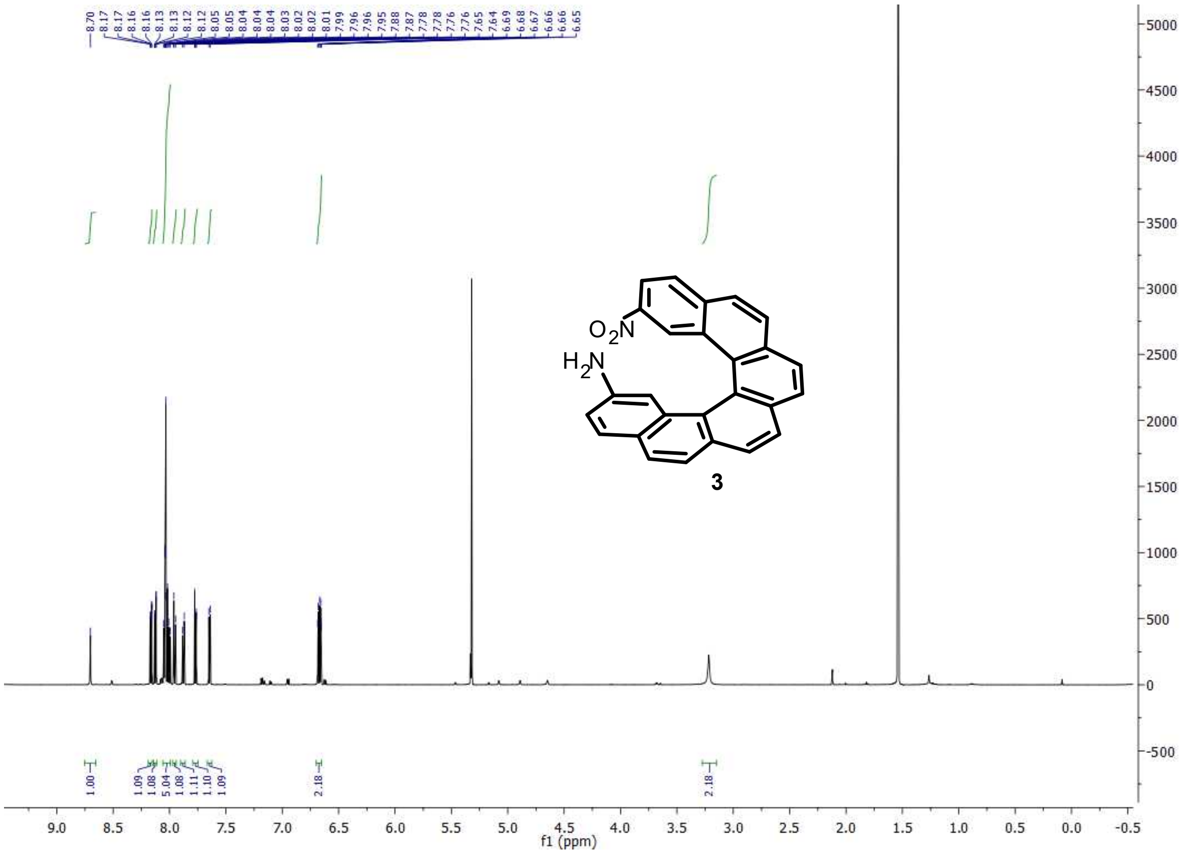
Compound 8:

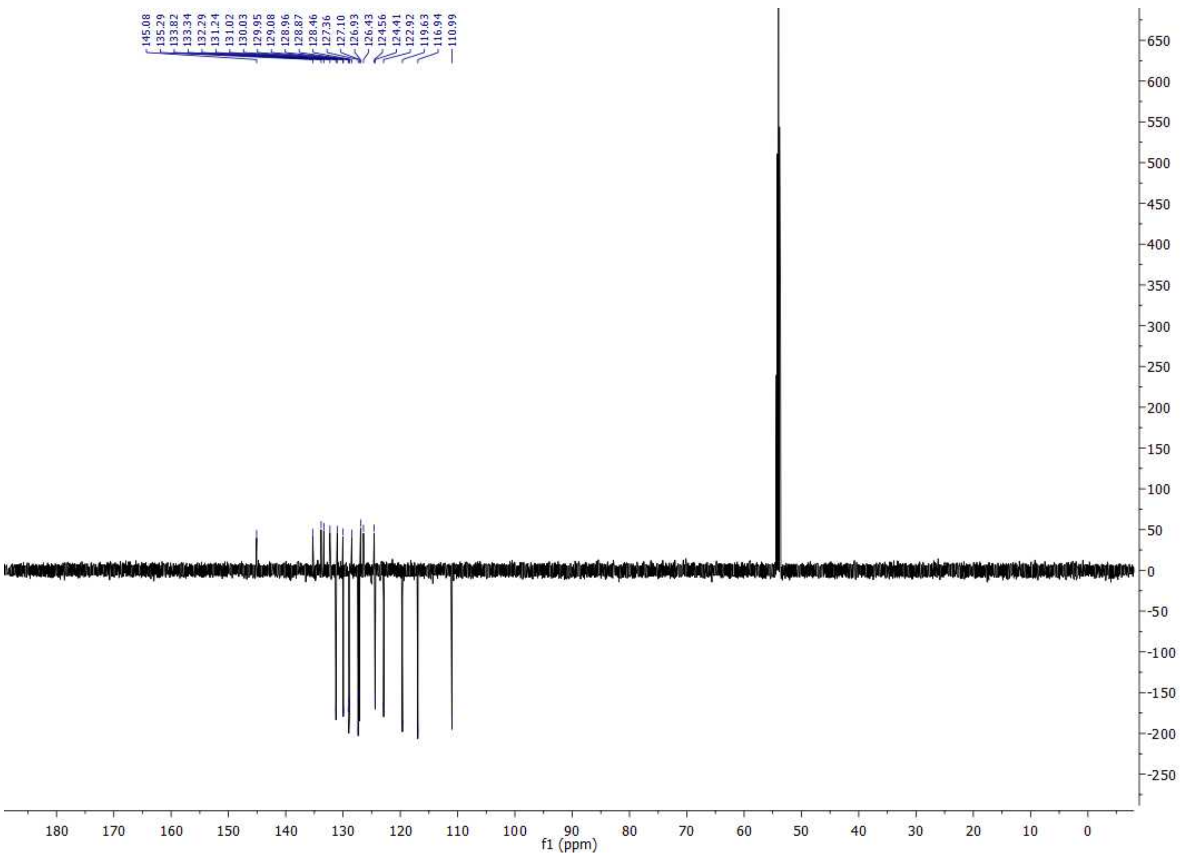
C	2.839903	-2.753597	0.592467
C	2.832150	-1.376128	0.253932
C	1.606596	-0.722356	-0.011355
C	0.459129	-1.547506	-0.288164
C	0.471834	-2.876822	0.177008
C	1.679063	-3.454524	0.647751
C	1.606605	0.722340	0.011349
C	2.832166	1.376100	-0.253940
C	4.051629	0.655498	-0.174987
C	4.051621	-0.655538	0.174981
C	2.839932	2.753570	-0.592472
C	1.679098	3.454508	-0.647755
C	0.471863	2.876818	-0.177014
C	0.459148	1.547502	0.288160
C	-0.685499	1.122123	1.060605
C	-1.868624	1.903887	1.034524
C	-1.870363	3.156930	0.361349
C	-0.722586	3.651619	-0.159496
C	-3.009262	1.469465	1.737695
C	-2.973448	0.338915	2.512185
C	-1.772001	-0.372802	2.634892
C	-0.660256	0.011656	1.927850
H	3.785589	-3.220070	0.843385
H	1.666471	-4.484956	0.983794
H	4.980566	1.188528	-0.341691
H	4.980552	-1.188578	0.341687
H	3.785621	3.220034	-0.843389
H	1.666514	4.484940	-0.983799
H	-2.786719	3.735555	0.337041
H	-0.693190	4.646873	-0.588455
H	-3.912408	2.066567	1.677149
H	-3.854453	0.017853	3.054565
H	-1.715078	-1.228754	3.296458
H	0.259851	-0.538596	2.058407
C	-0.722620	-3.651615	0.159487
C	-1.870393	-3.156920	-0.361359
C	-1.868649	-1.903873	-1.034524
C	-0.685519	-1.122116	-1.060602
H	-0.693228	-4.646871	0.588442
H	-2.786750	-3.735545	-0.337057
C	-0.660272	-0.011643	-1.927840
C	-1.772018	0.372825	-2.634876
C	-2.973471	-0.338881	-2.512166
C	-3.009287	-1.469439	-1.737687
H	0.259840	0.538601	-2.058399
H	-1.715092	1.228781	-3.296437
H	-3.854476	-0.017807	-3.054537

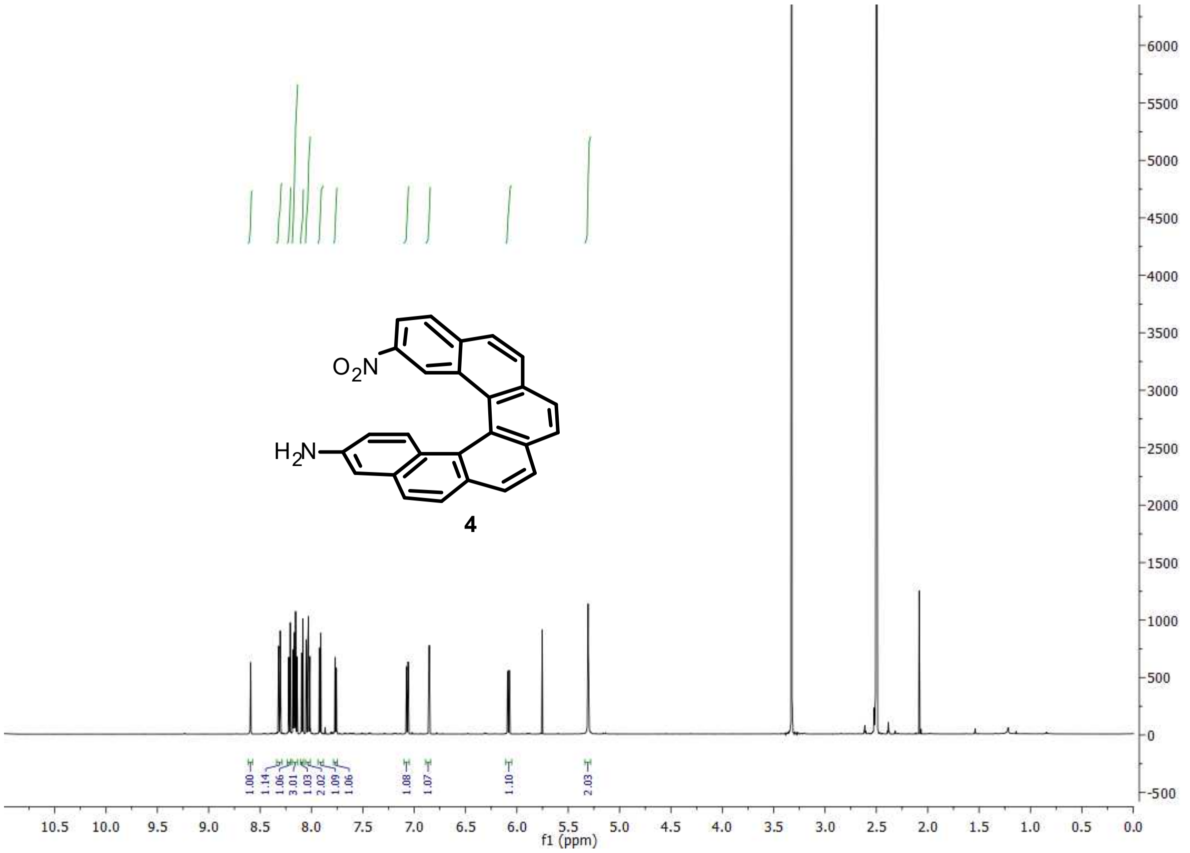
H -3.912434 -2.066540 -1.677148

[Wavelength (nm), R (length)]: [391.463100, -1.0686], [373.210298, 313.323], [364.831076, 469.444], [341.121975, 24.4926], [337.592422, -77.613], [326.600793, -78.853], [309.643098, -5.4211], [304.592048, -38.738], [298.440673, 7.89470], [297.681136, -190.12], [281.136920, -8.5823], [275.587795, -61.007], [275.453096, 146.812], [270.365461, -533.50], [268.917022, -344.37], [267.253391, 15.1224], [255.648054, 1.96720], [253.567149, -182.35], [249.500318, 65.6041], [249.119317, 40.5402], [247.993185, -33.752], [238.738746, 55.1429], [237.740778, 11.7733], [231.681198, 83.4719], [230.569604, 37.0271], [226.079380, 40.8057], [224.690455, 200.916], [224.101569, 4.36190], [222.078477, 1.48110], [219.997858, 36.9003], [218.860005, 17.3712], [216.301802, -8.8503], [215.336320, 2.70610], [212.512758, -48.483], [211.526586, 280.828], [210.628216, -5.4285], [208.006229, 12.9577], [207.418140, -56.530], [206.265606, -8.4888], [203.673478, 110.654], [203.599897, 41.6249], [203.282768, -31.804], [200.953342, 0.09420], [200.615179, 43.3406], [199.678208, 147.822], [198.947678, -77.501], [198.301734, 18.9006], [198.127446, -4.7210], [196.149588, 37.1179], [195.176930, 43.9824], [194.769142, -4.4118], [193.852517, -295.80], [193.151882, 47.5869], [193.010559, 67.2594], [190.891752, -59.383], [190.037389, -2.7049], [189.034874, 19.6785], [189.008938, 3.72360], [188.037177, 34.1762], [187.451533, -138.28], [186.686632, -10.902], [186.184817, -28.649], [186.106564, -3.9570], [185.758024, -40.772], [185.280561, -0.3596], [184.387789, -12.918], [183.538893, -9.5670], [183.189068, -10.514], [182.155576, 23.9034], [181.488975, -24.469], [180.419373, -4.3727], [179.963702, -8.2850], [179.757576, -4.9950], [179.596137, -116.32], [178.484407, -2.3249], [177.620150, -40.285], [177.498093, 43.5604], [177.069684, 7.81950], [176.978693, -9.7959], [176.472370, -66.293], [175.923993, 4.34330], [175.692150, -0.8059], [175.446019, 32.1935], [175.190676, -14.803], [174.778247, 72.6849], [174.679750, 1.67750], [173.256652, -13.988], [172.911125, 1.10900], [172.838811, -7.9023], [172.329515, 6.07470], [171.959048, -1.5872], [171.725637, -2.6362], [171.312773, -55.252], [170.657242, -0.8676], [170.378168, -90.327], [170.072006, 6.17360], [169.967089, -5.4704], [169.750672, 8.91260], [169.259386, 23.0083], [168.610274, -37.272].

^{1}H and ^{13}C NMR spectra of 3–6, 9, 10, 12, 14, 15, 18, 20–22, 25, 26, 28, 29, 31–35, 37, 38



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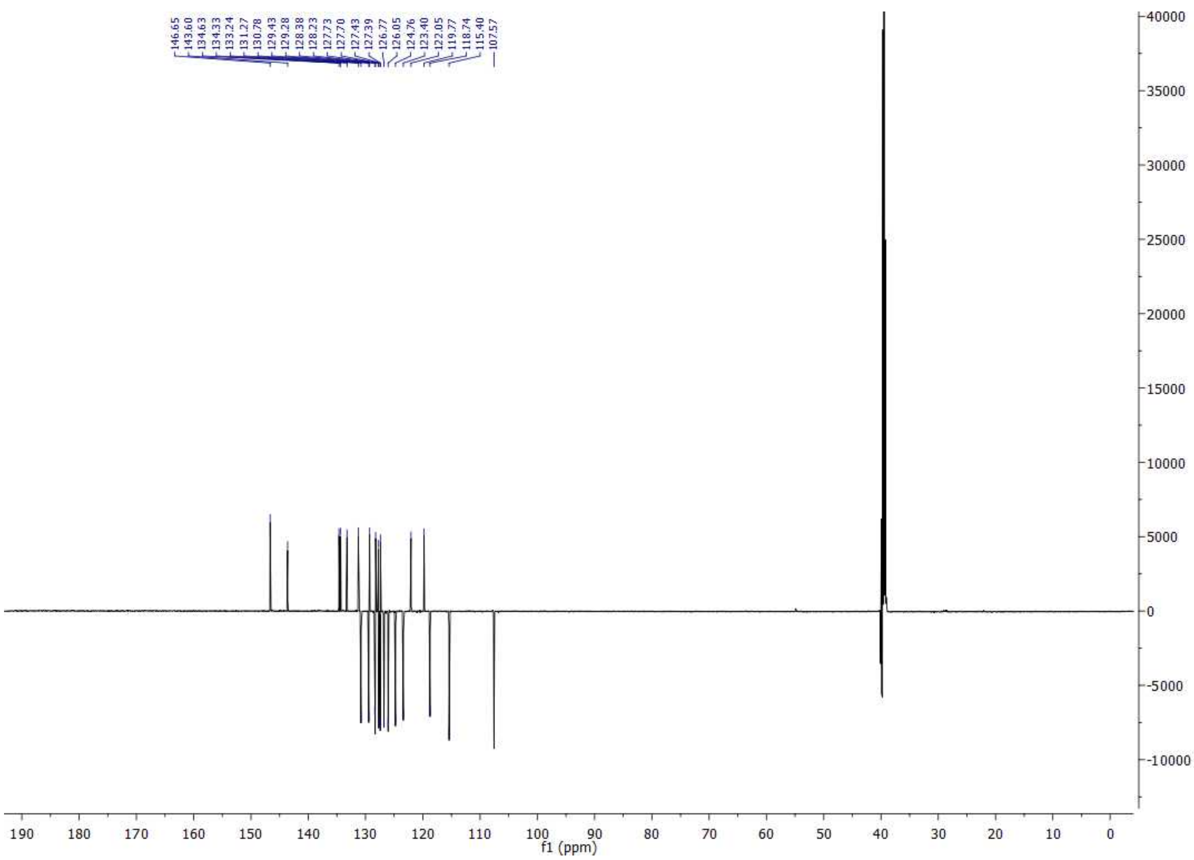
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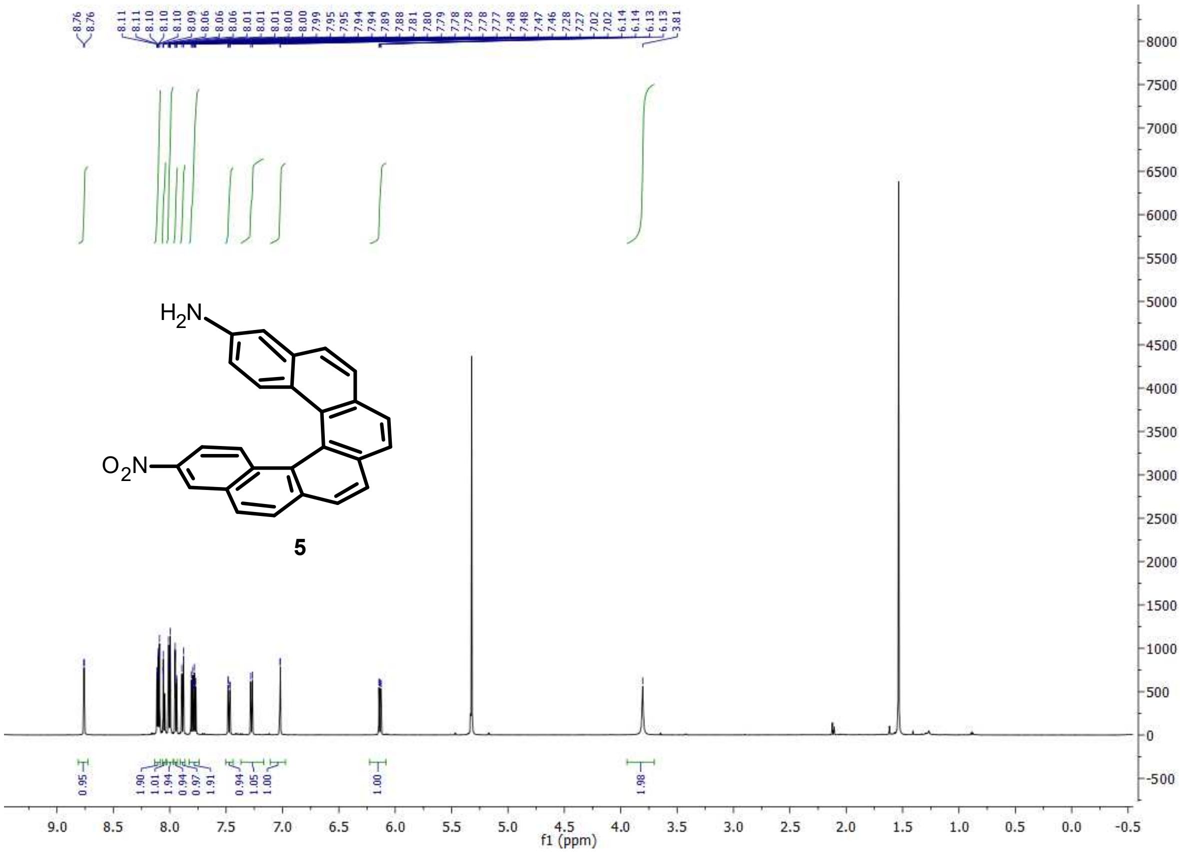
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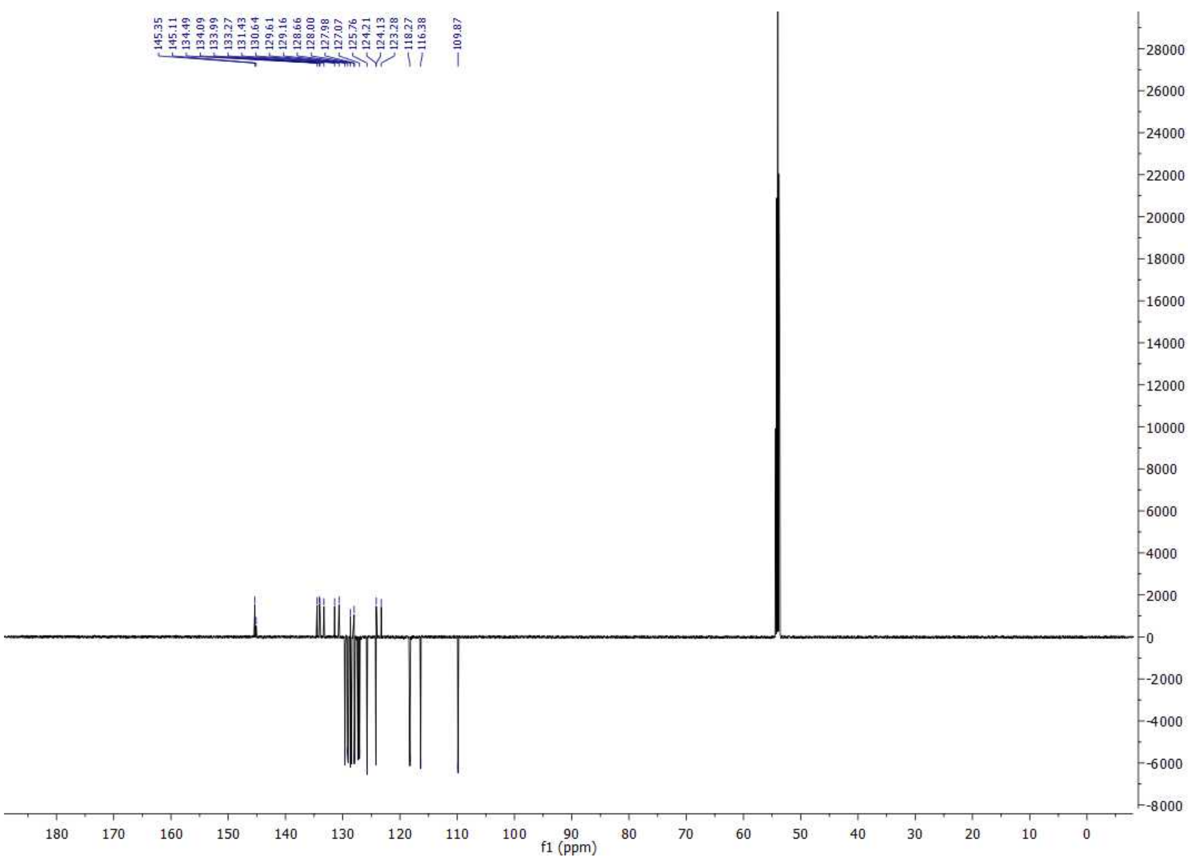
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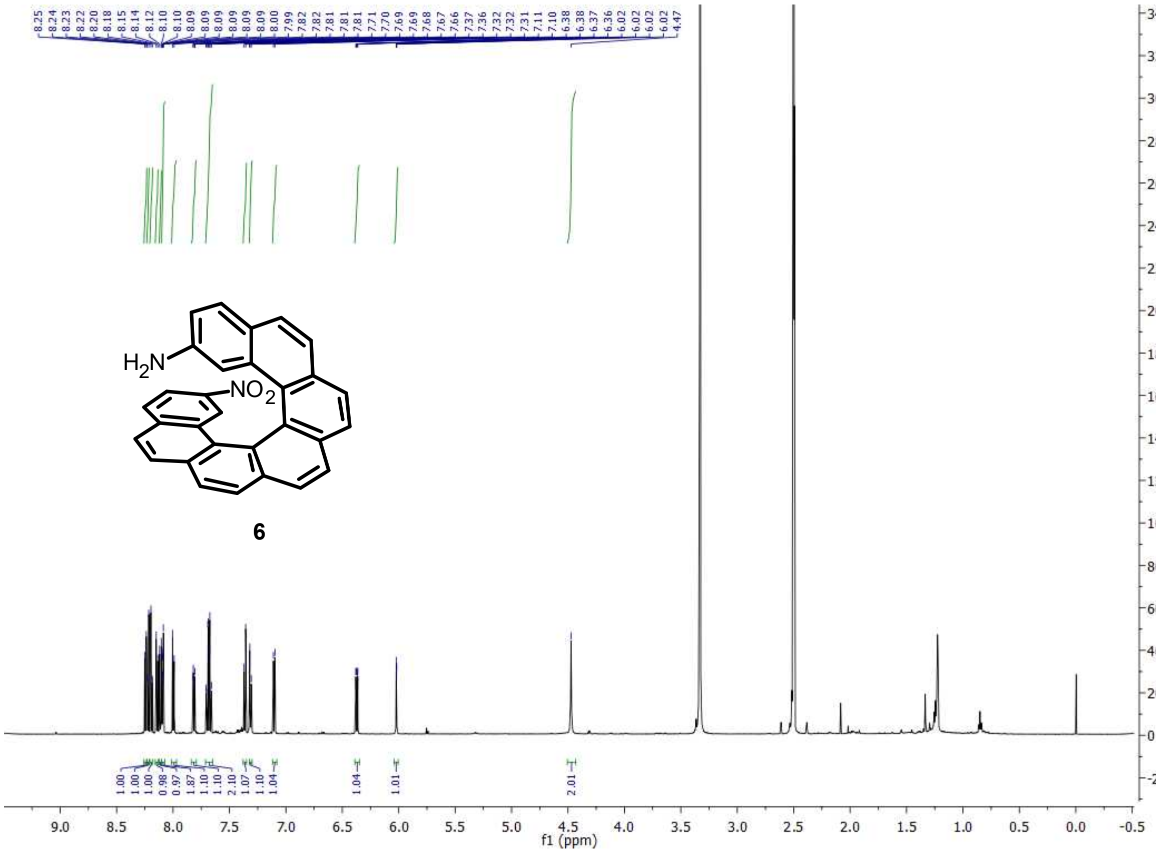

H_2N
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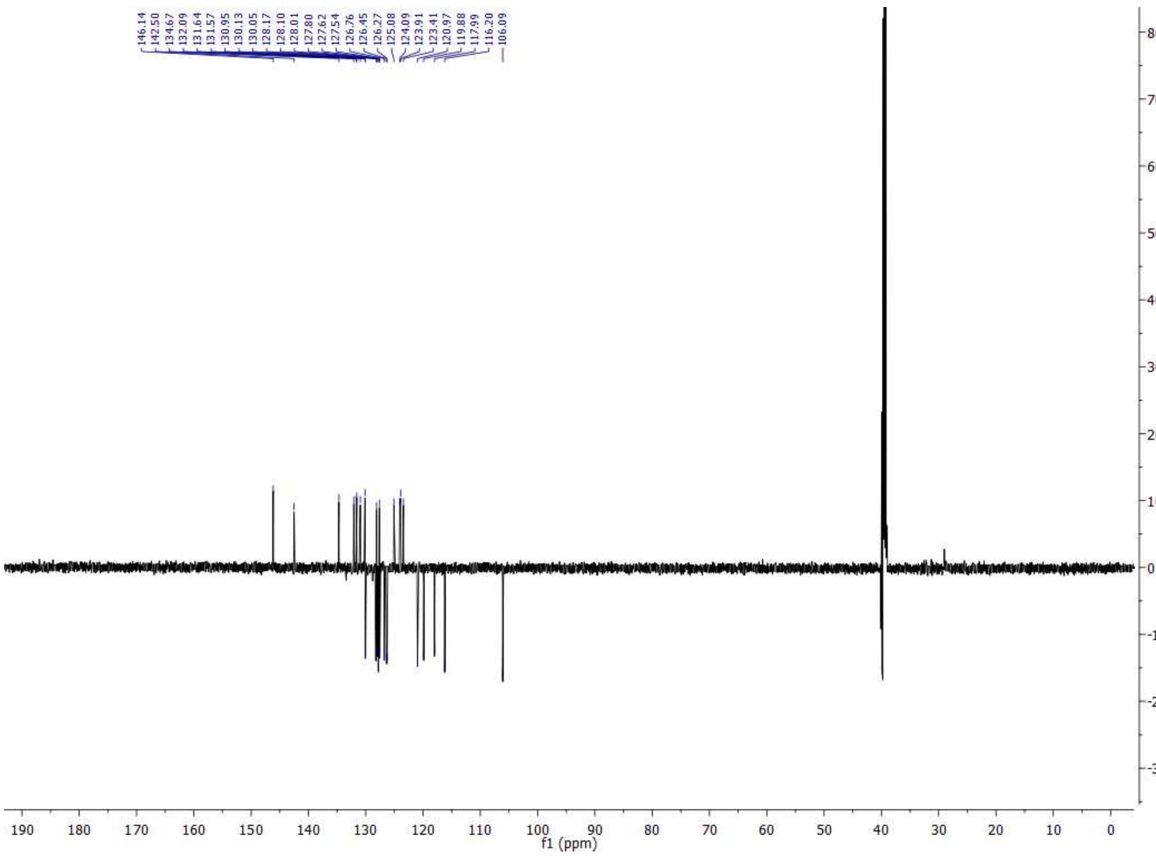

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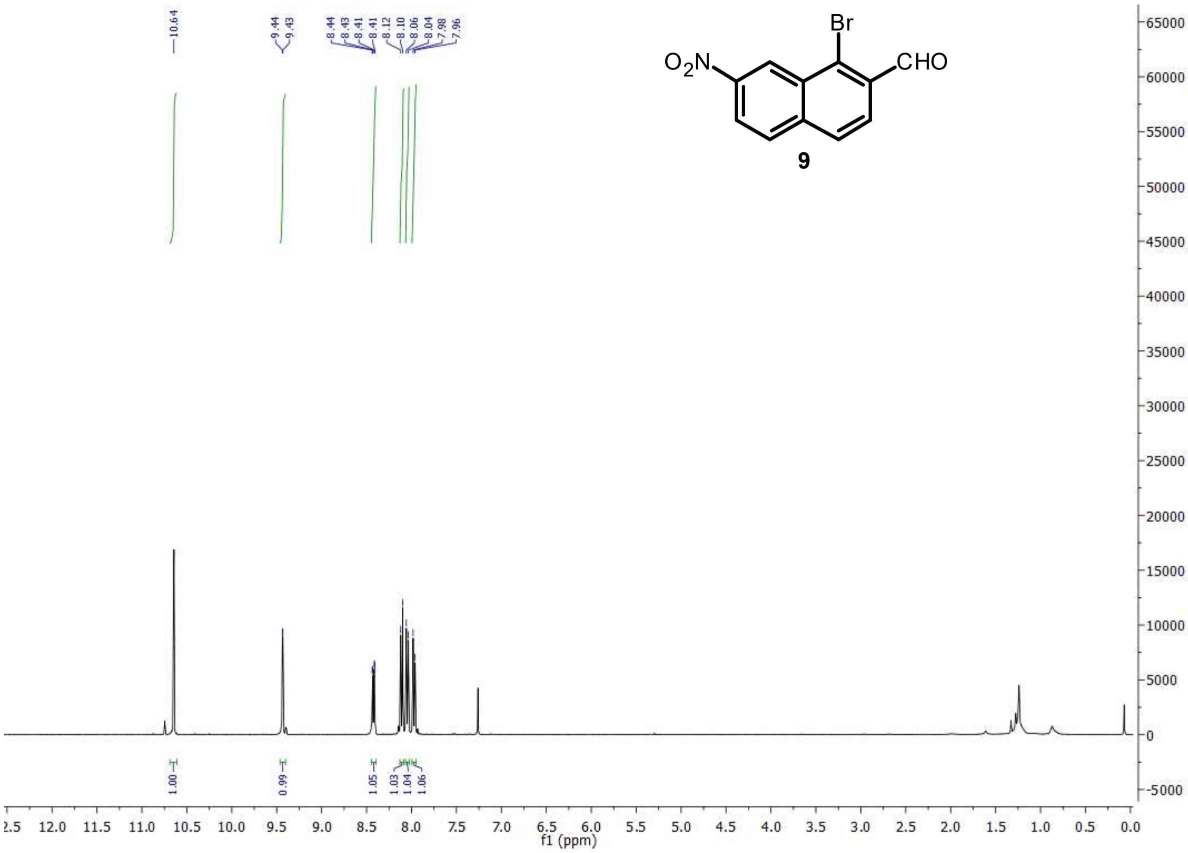
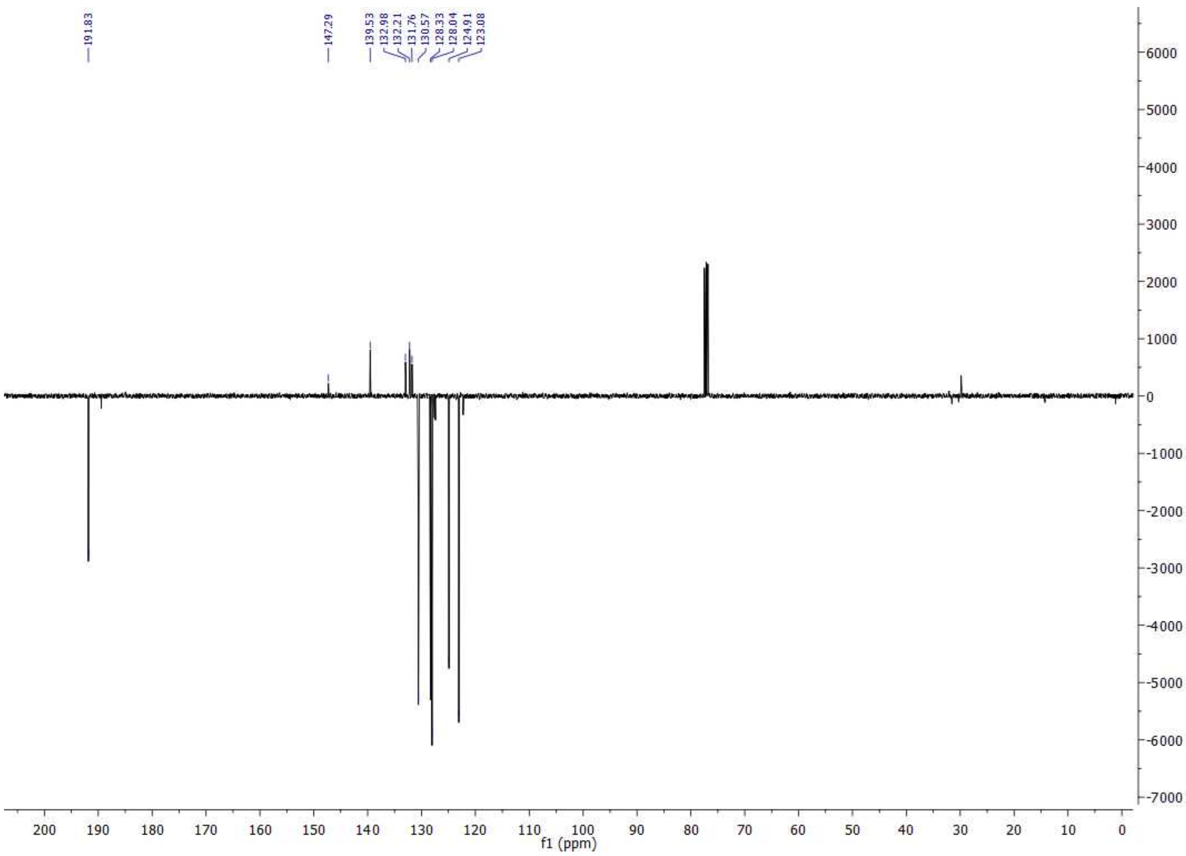
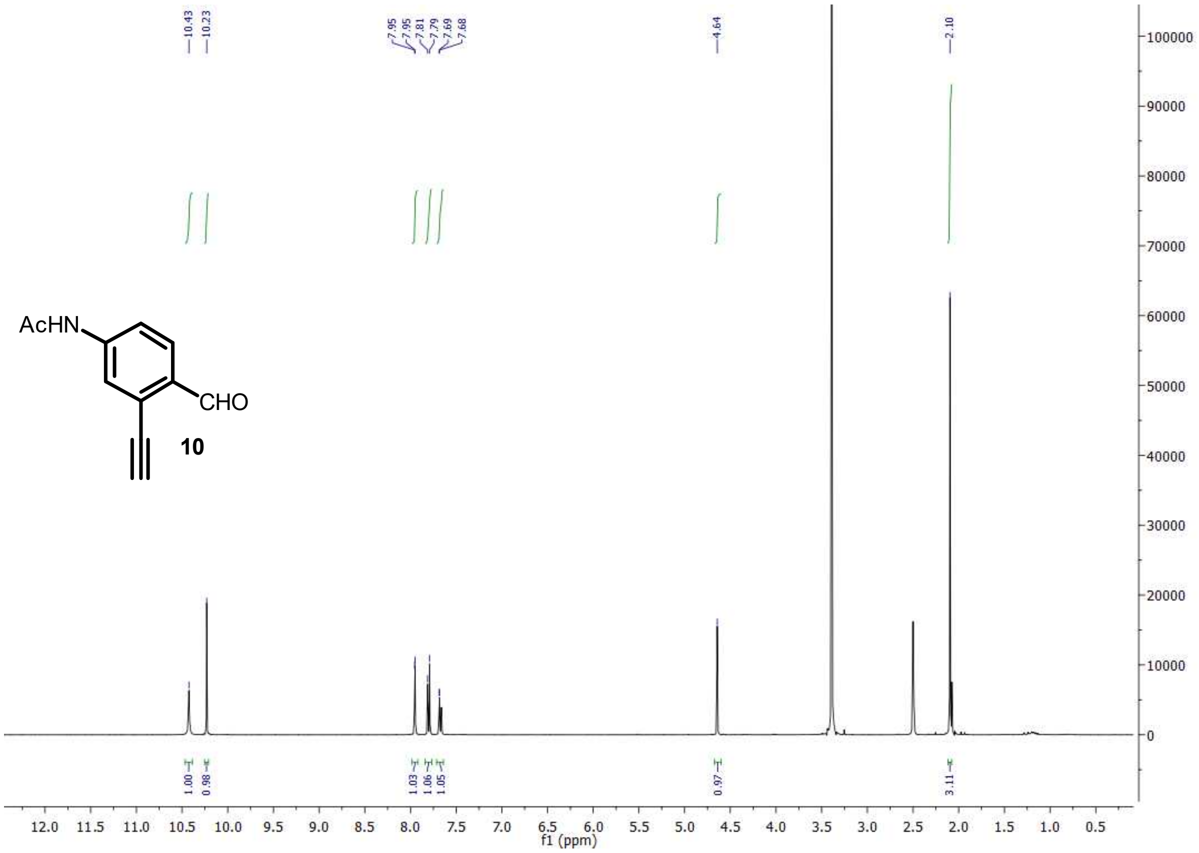


9

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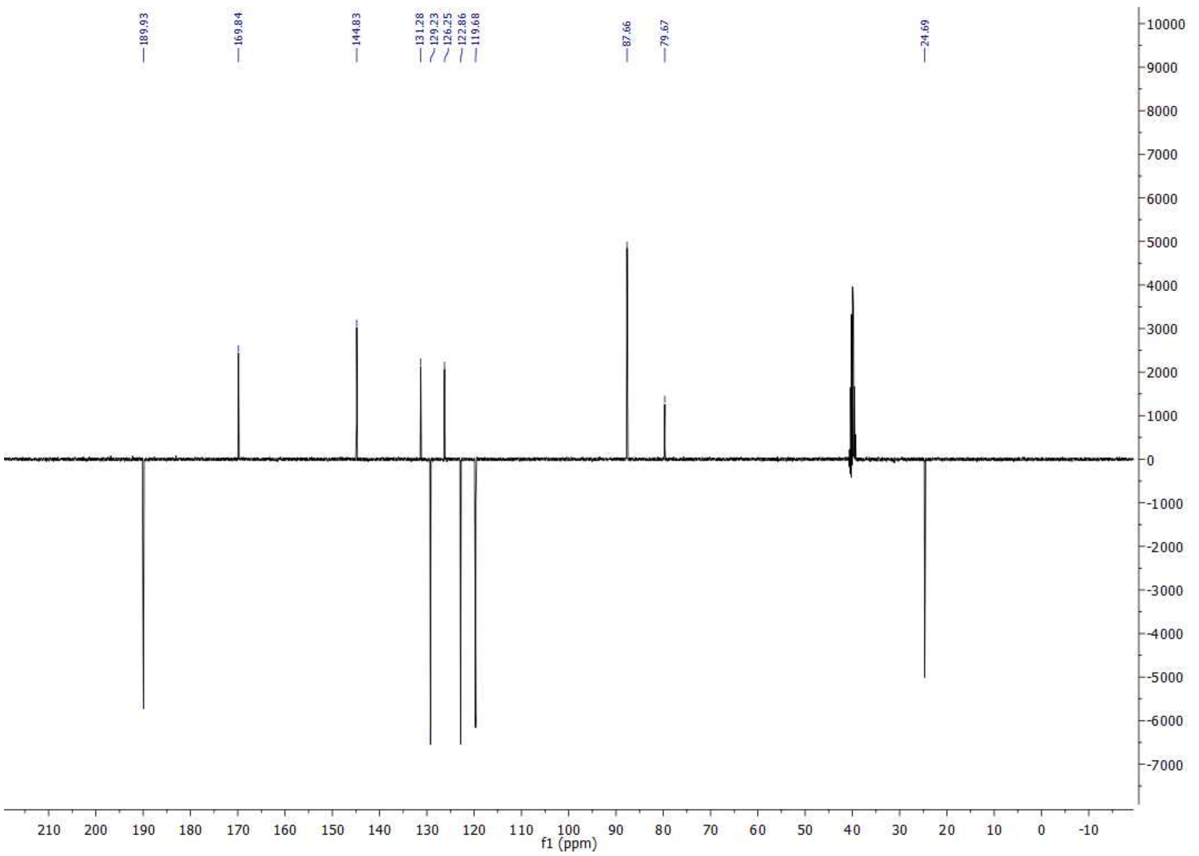
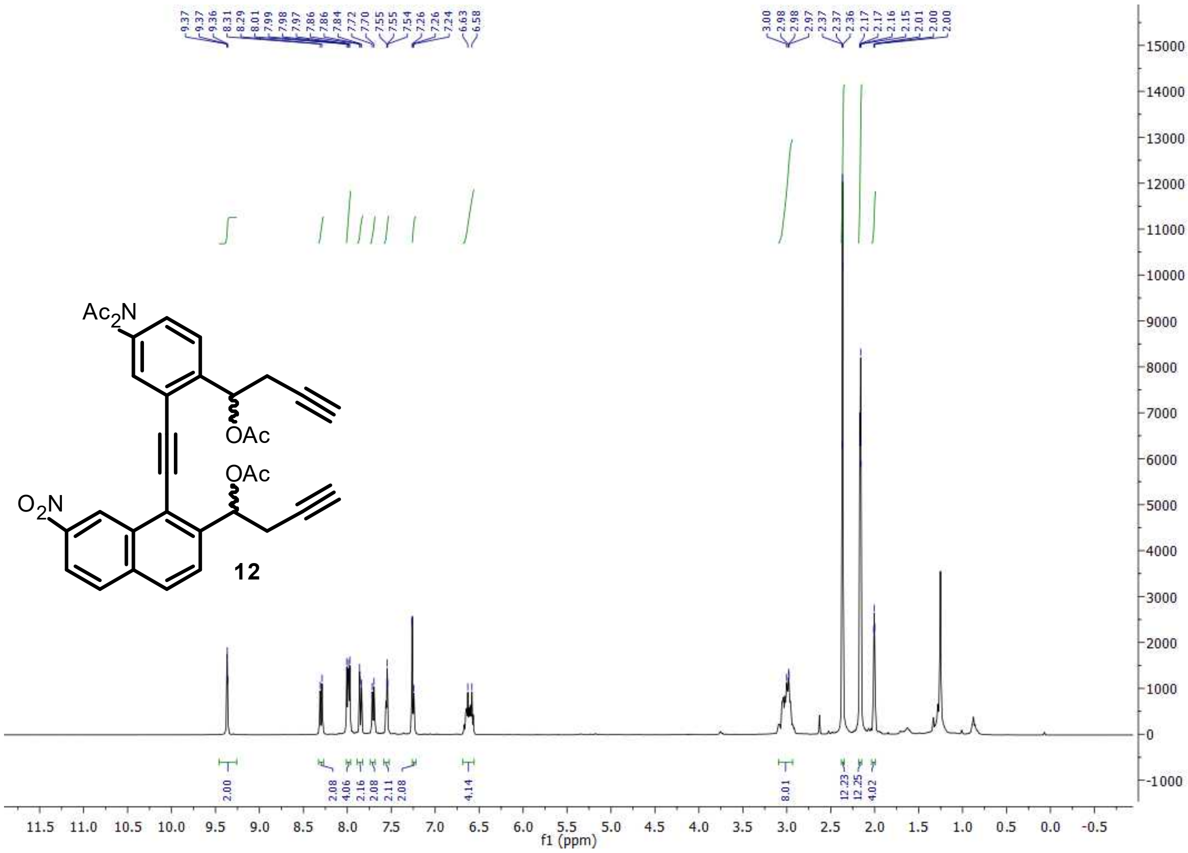
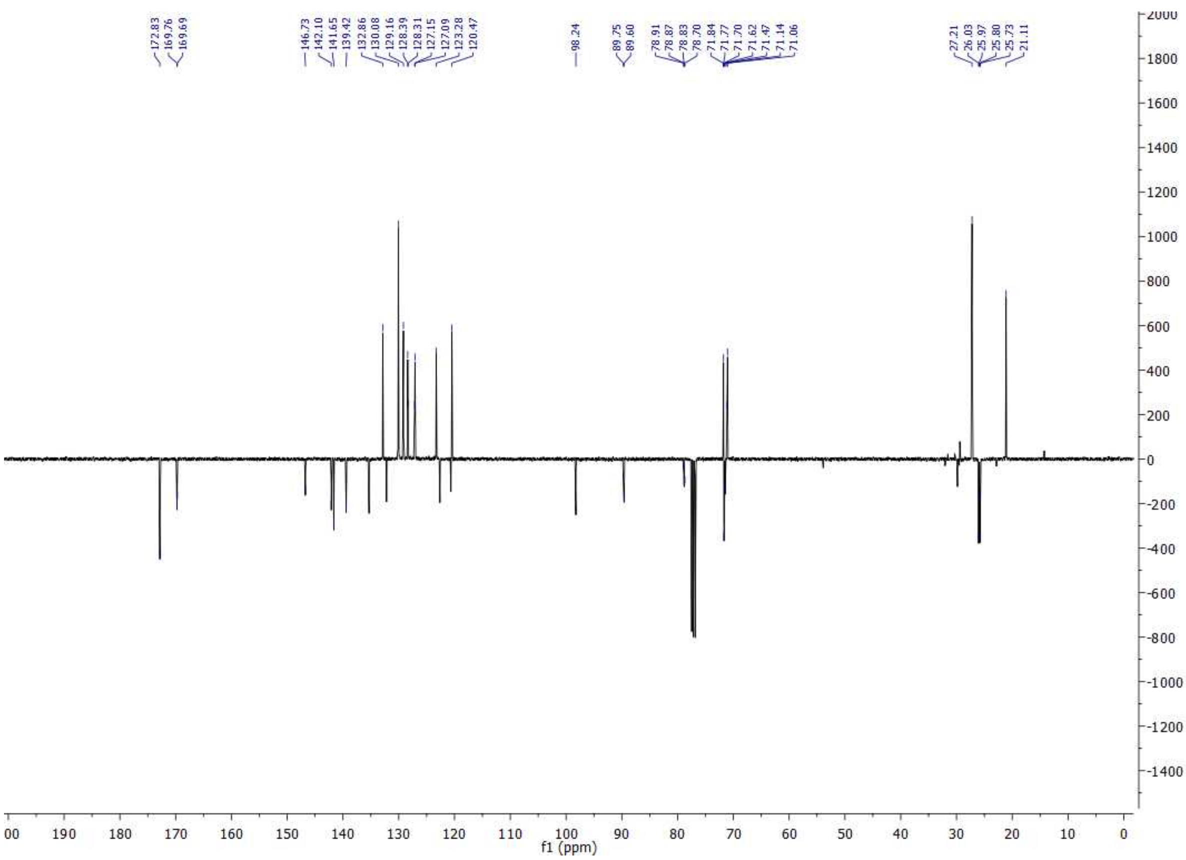
3.11
f1 (ppm)


189.93
169.84
144.83
131.28
129.23
126.25
122.86
119.68
87.66
79.67
24.69
f1 (ppm)


9.37
9.37
9.36
8.31
8.29
8.01
7.99
7.98
7.97
7.86
7.86
7.84
7.72
7.70
7.55
7.55
7.54
7.26
7.26
7.24
6.63
6.58
3.00
2.98
2.98
2.97
2.37
2.37
2.36
2.17
2.17
2.16
2.15
2.01
2.00
2.00
Ac2N
OAc
OAc
O2N
12
2.00
2.08
4.06
2.16
2.08
2.11
2.08
4.14
8.01
12.23
12.25
4.02
f1 (ppm)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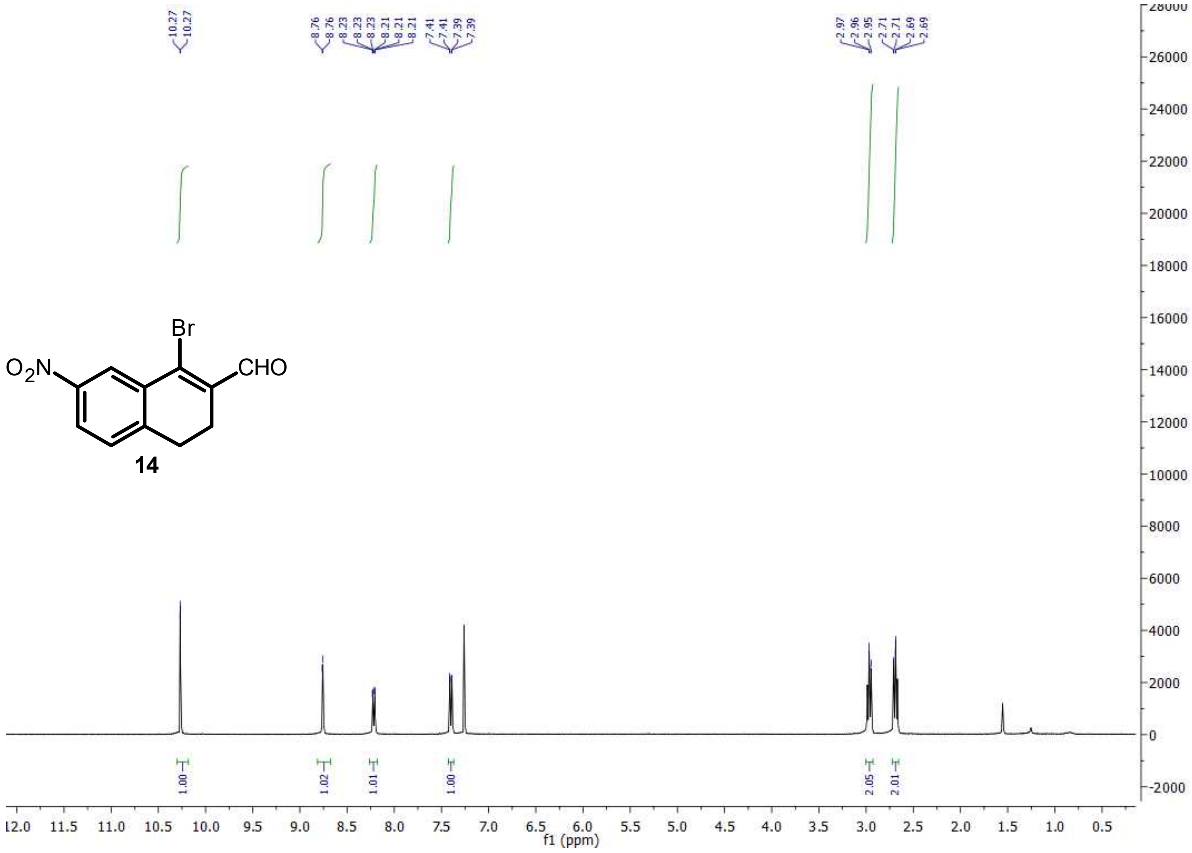
169.76
169.69
146.73
142.10
141.65
139.42
132.86
130.08
129.16
128.39
128.31
127.15
127.09
123.28
120.47
98.24
89.75
89.60
78.91
78.87
78.83
78.70
71.84
71.77
71.70
71.62
71.47
71.14
71.06
27.21
26.03
25.97
25.80
25.73
21.11
f1 (ppm)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10.27
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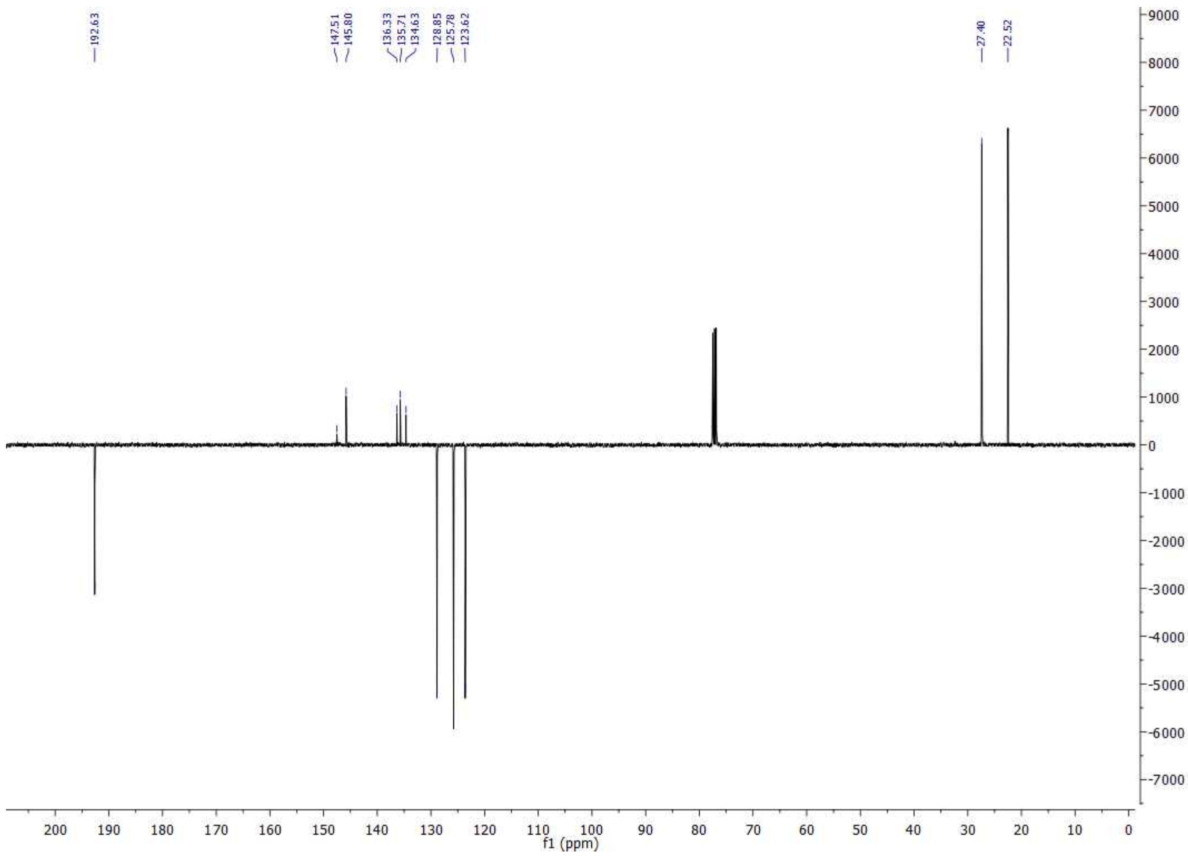
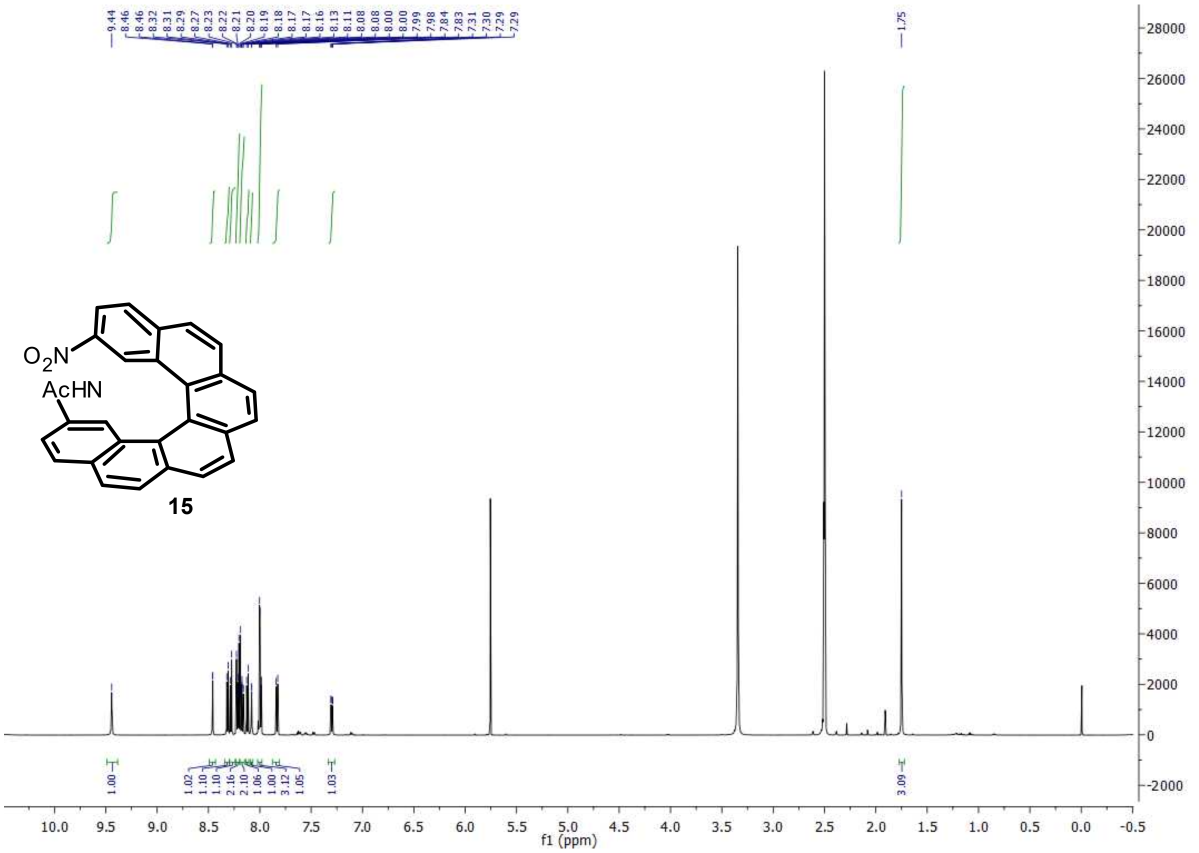
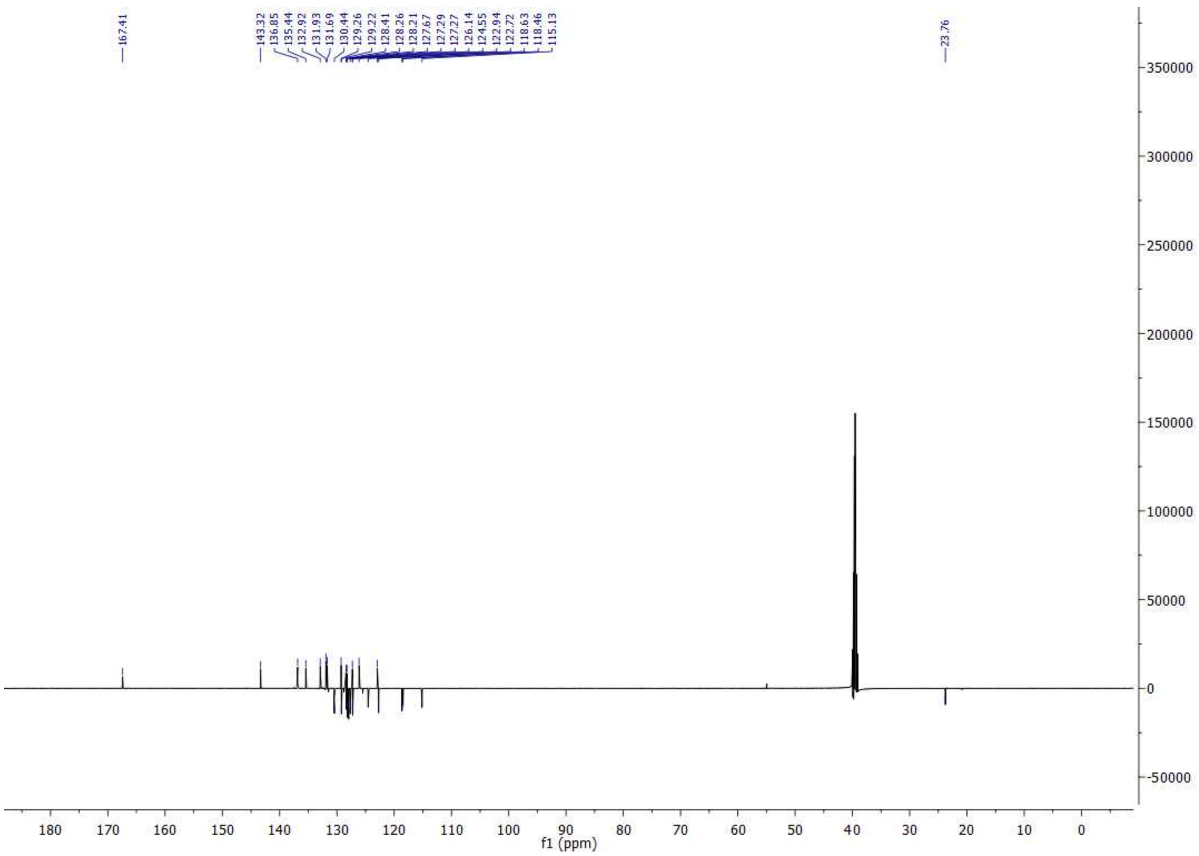
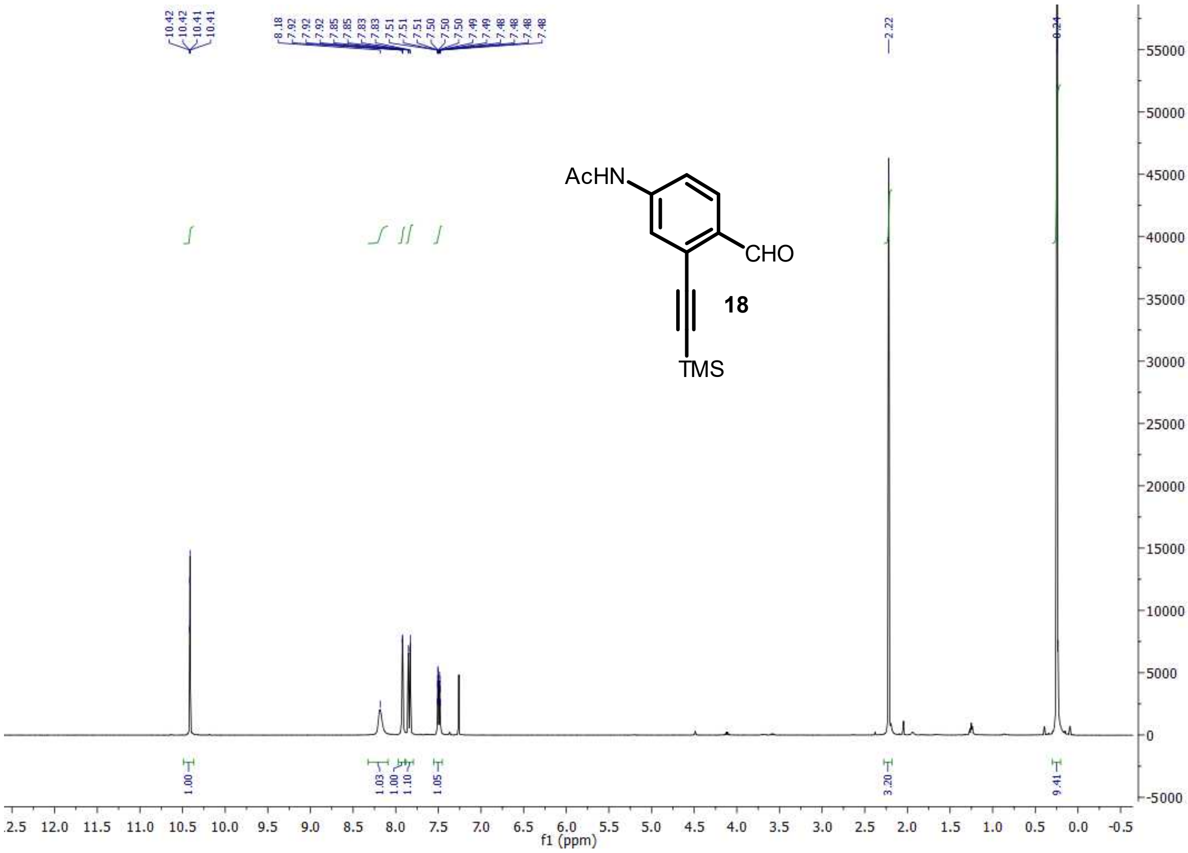
8.76
8.23
8.23
8.23
8.21
8.21
8.21
7.41
7.41
7.39
7.39
2.97
2.96
2.95
2.71
2.71
2.69
2.69
Br
O_2N
CHO
14
1.00
1.02
1.01
1.00
2.05
2.01
f1 (ppm)

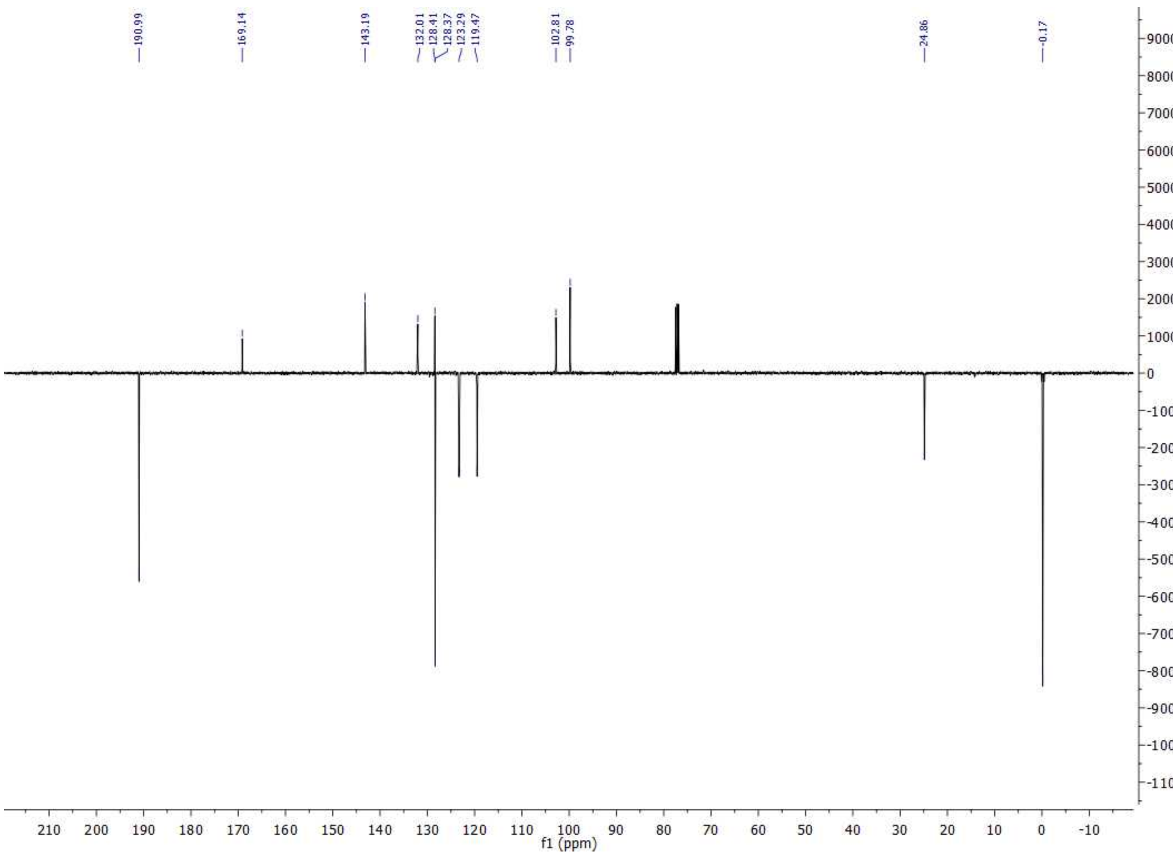

192.63
147.51
145.80
136.33
135.71
134.63
128.85
125.78
123.62
27.40
22.52
f1 (ppm)


O2N
AcHN
15
f1 (ppm)

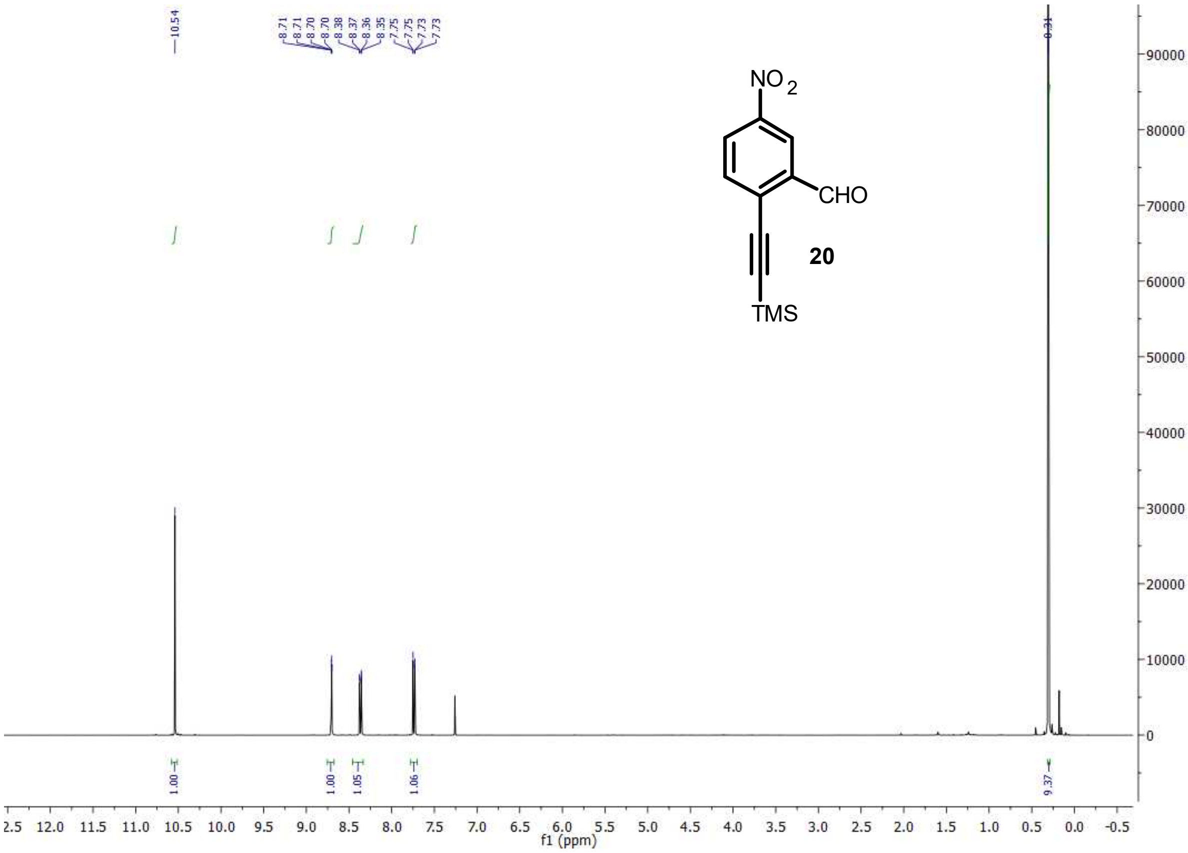

f1 (ppm)

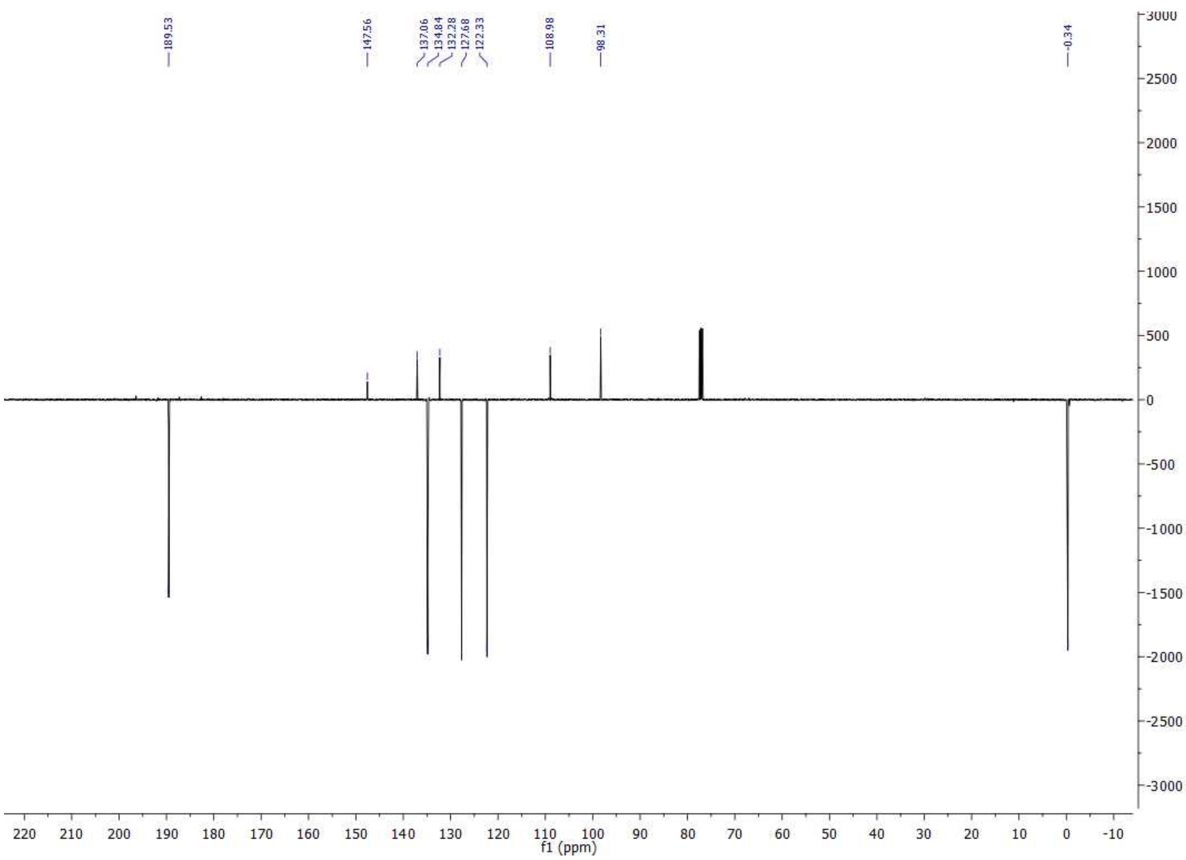


AcHN
CHO
18
TMS
f1 (ppm)



f1 (ppm)


10.54
8.71
8.71
8.70
8.70
8.38
8.37
8.36
8.35
7.75
7.75
7.73
7.73
0.31
NO2
CHO
20
TMS
1.00
1.00
1.05
1.06
9.37
f1 (ppm)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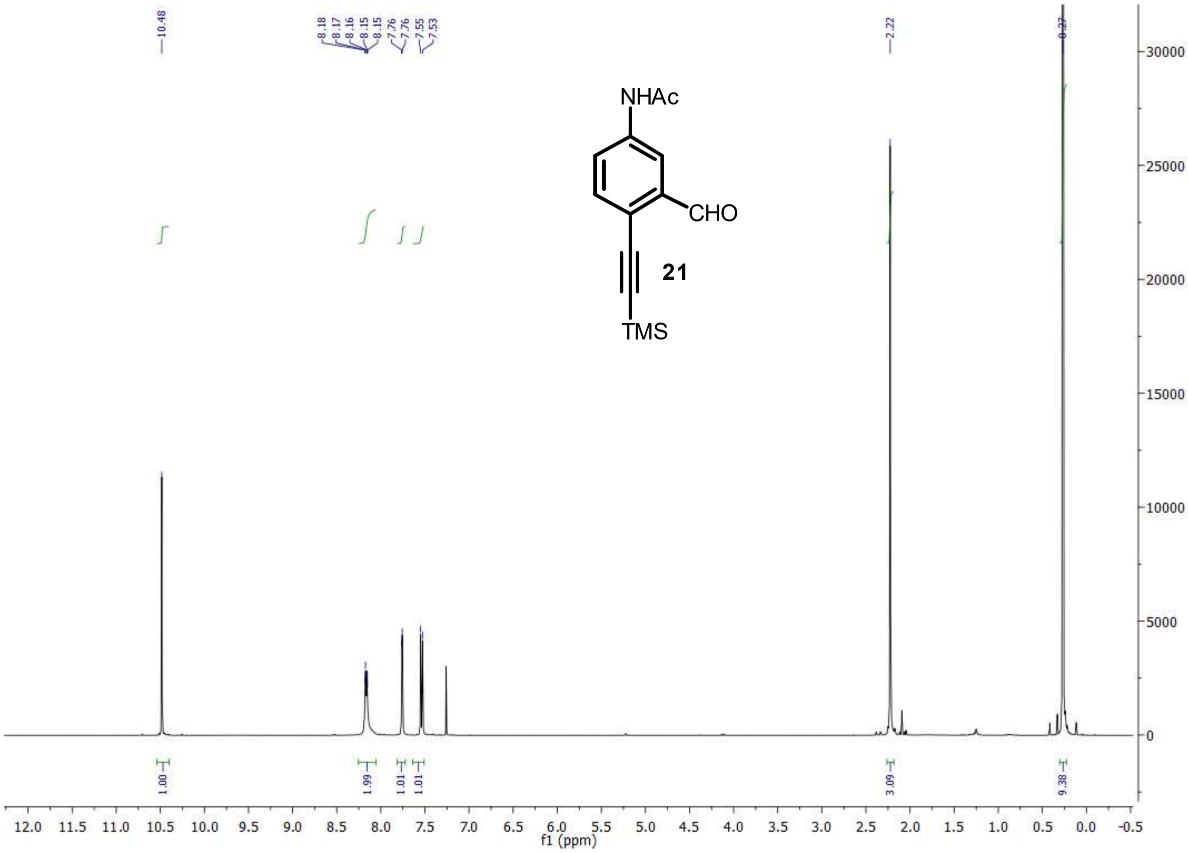
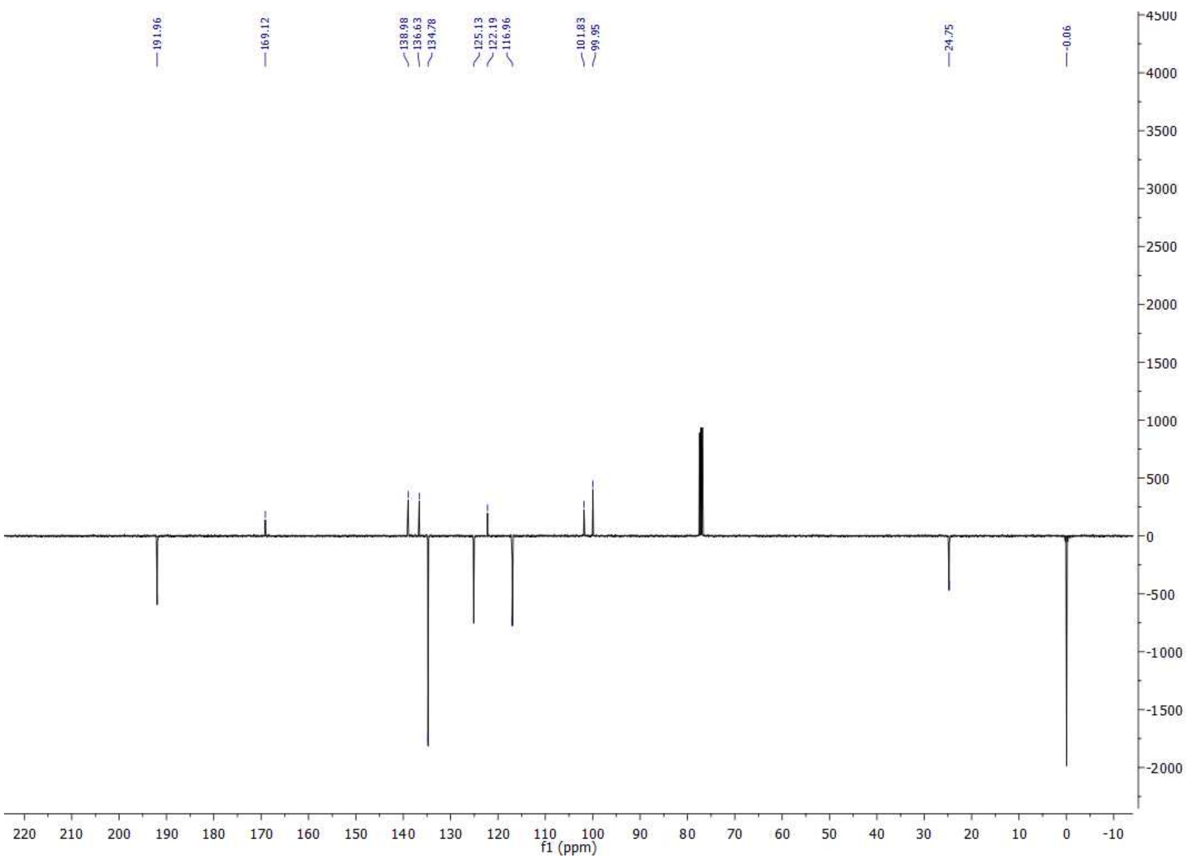
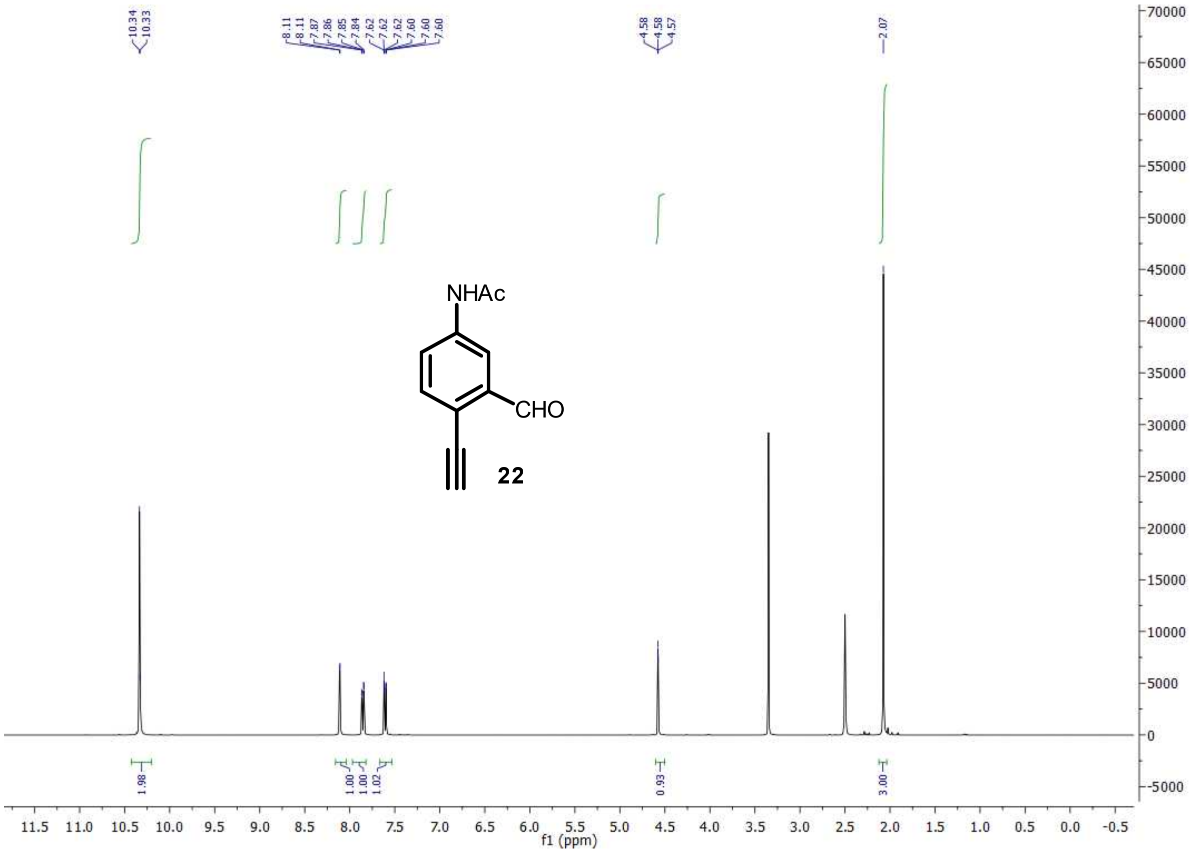
132.28
127.68
122.33
108.98
98.31
-0.34
f1 (ppm)

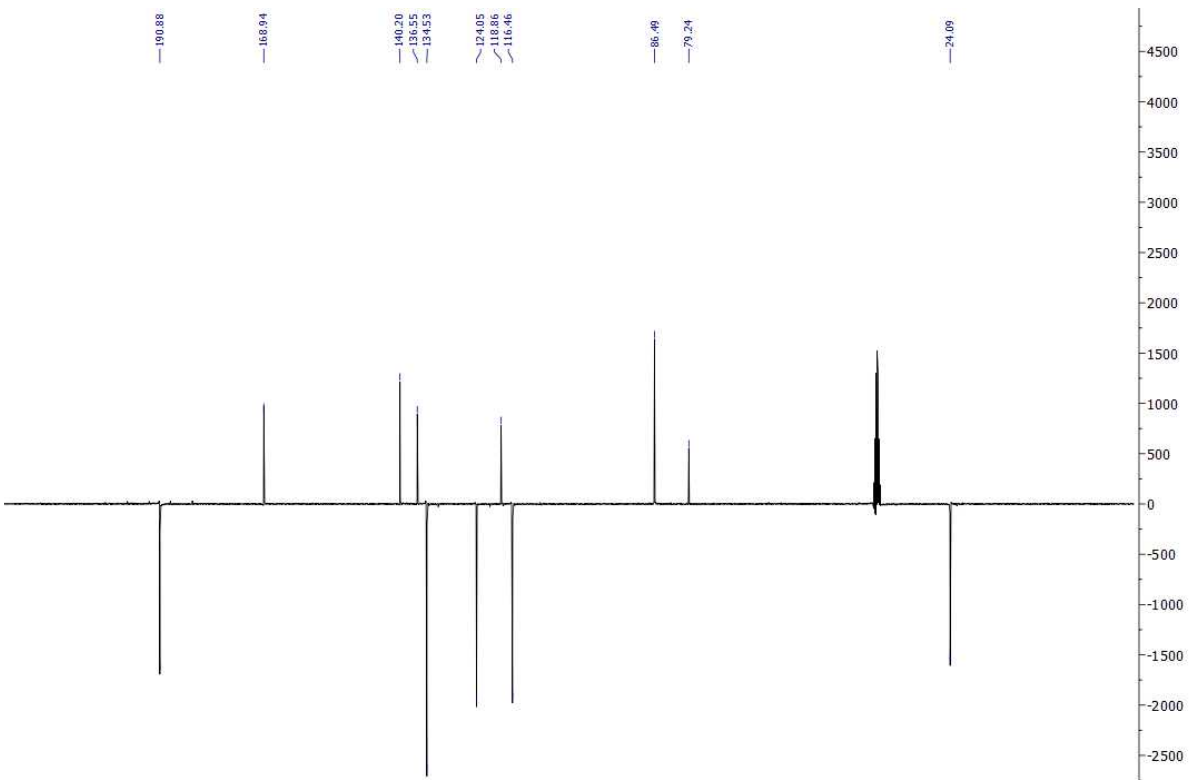


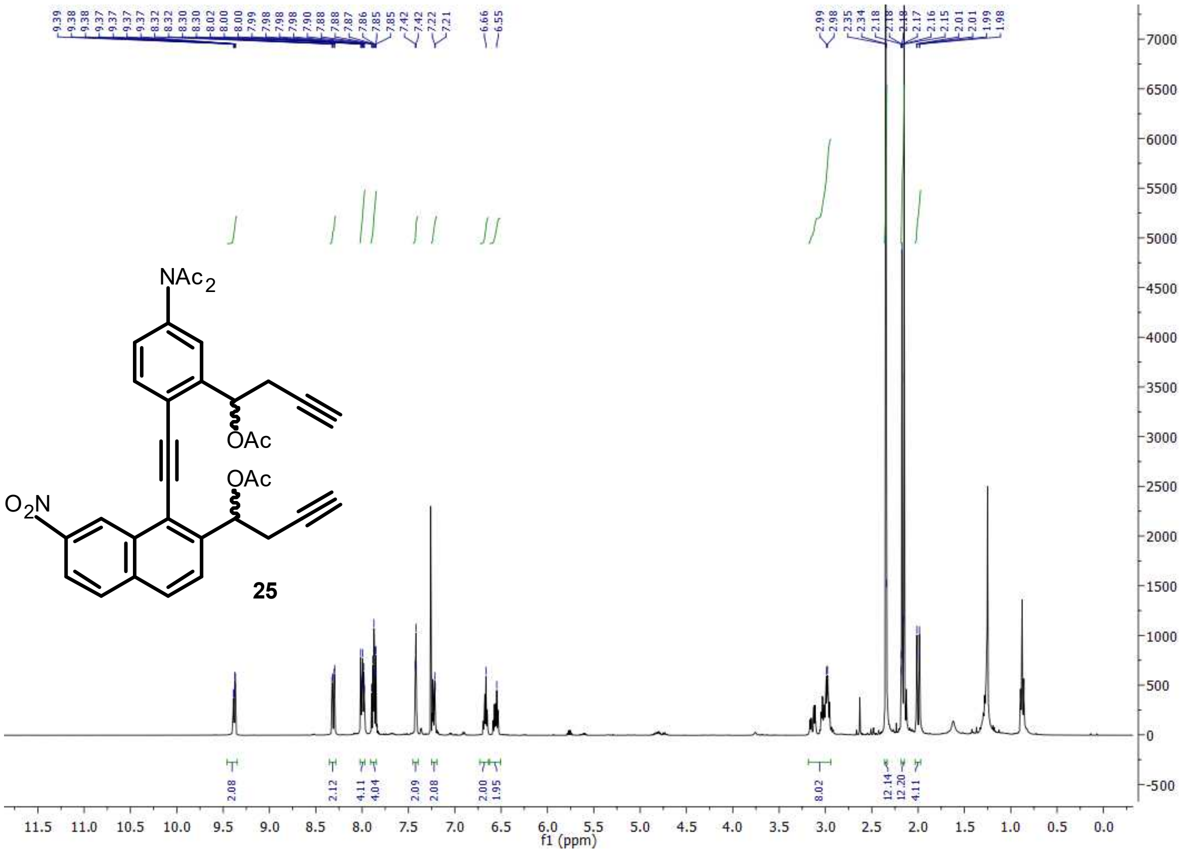
NHAc
CHO
21
TMS
10.48
8.18
8.17
8.16
8.15
8.15
7.76
7.76
7.55
7.53
2.22
0.27
1.00
1.99
1.01
1.01
3.09
9.38
f1 (ppm)

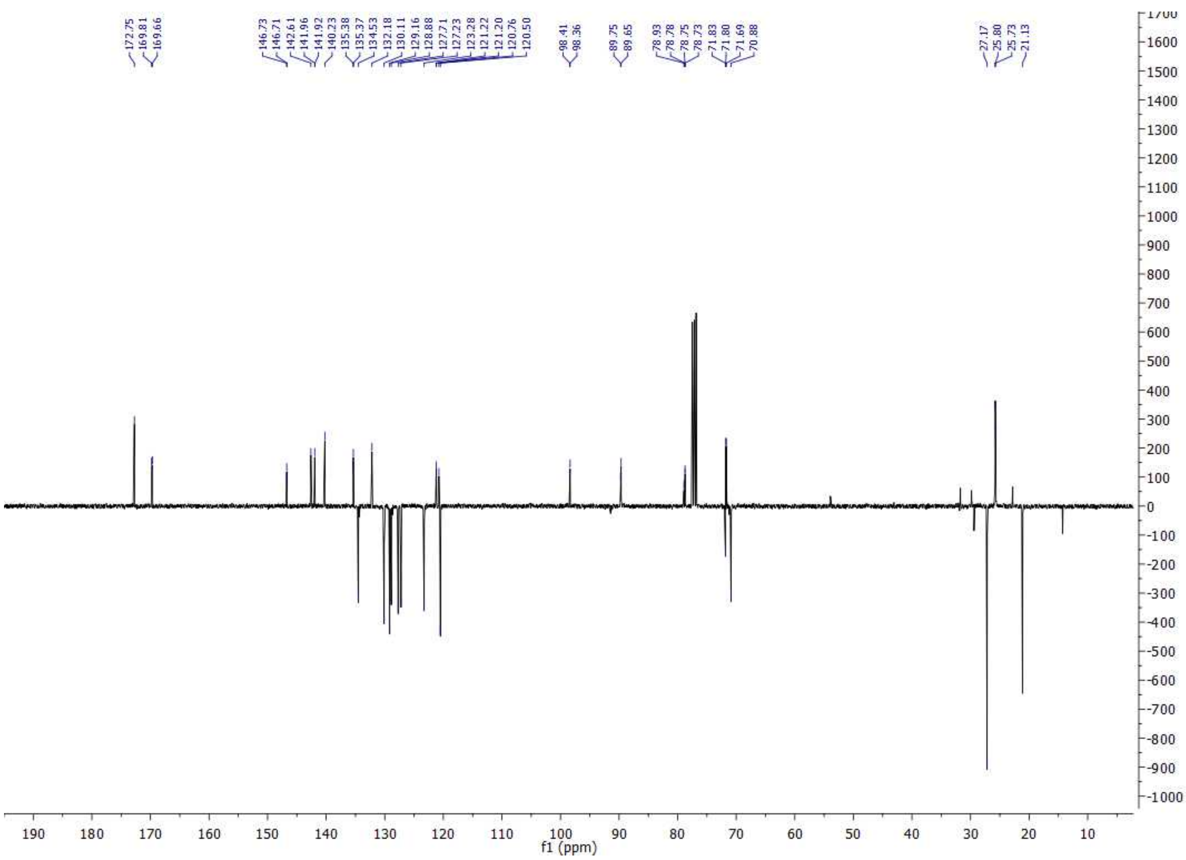


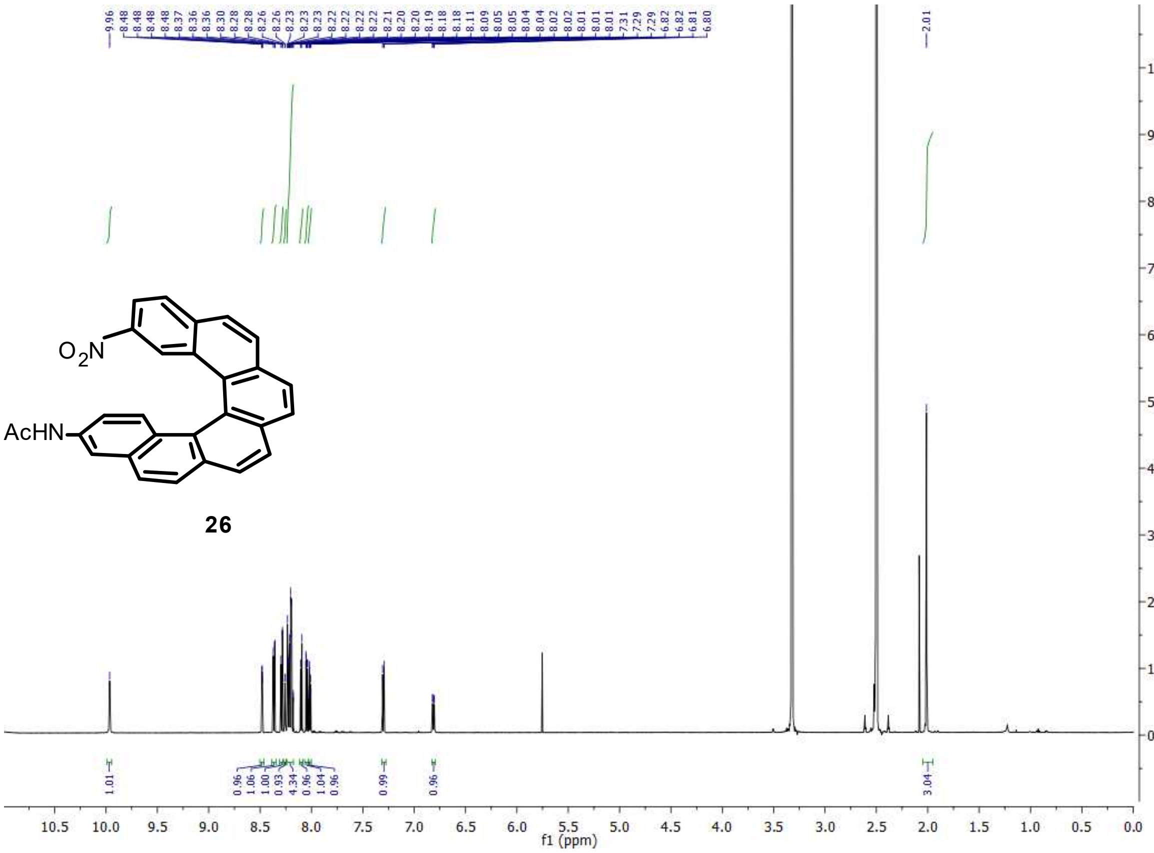
191.96
169.12
138.98
136.63
134.78
125.13
122.19
116.96
101.83
99.95
24.75
-0.06
f1 (ppm)


NHAc
CHO
22
f1 (ppm)

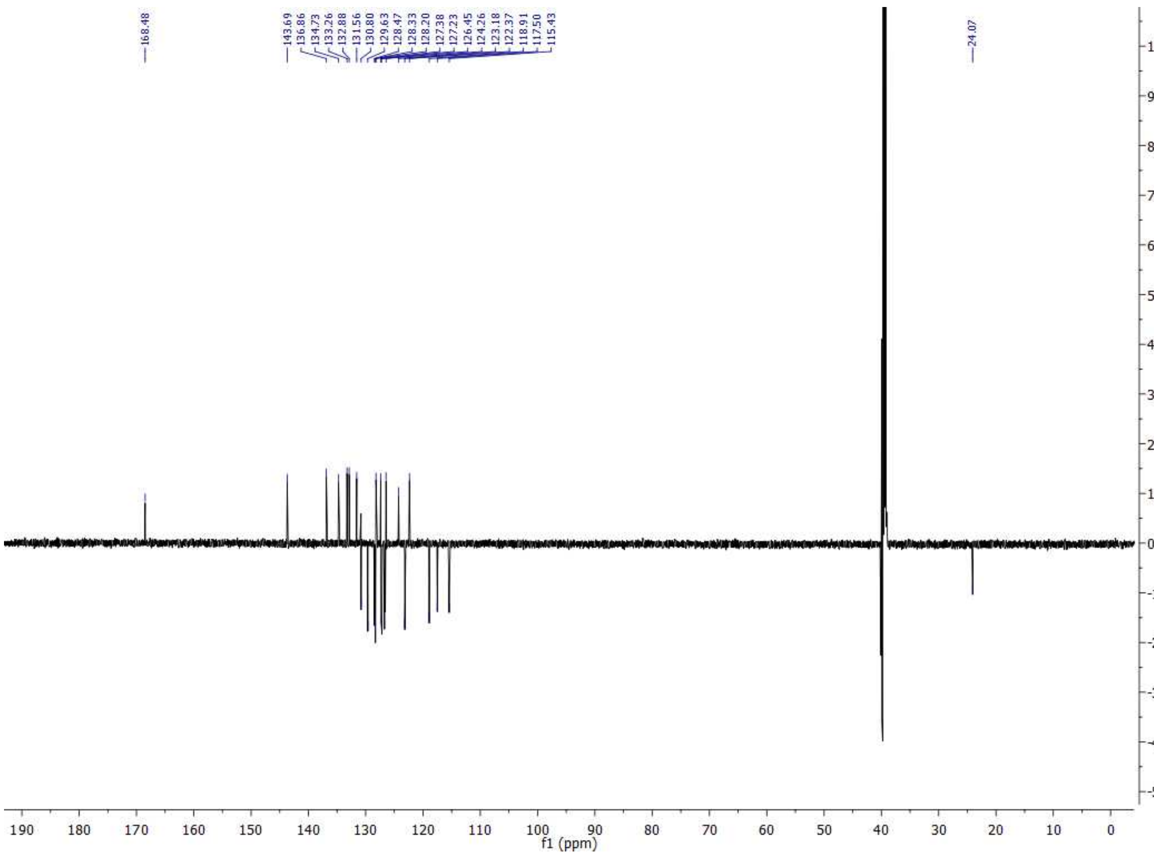

f1 (ppm)

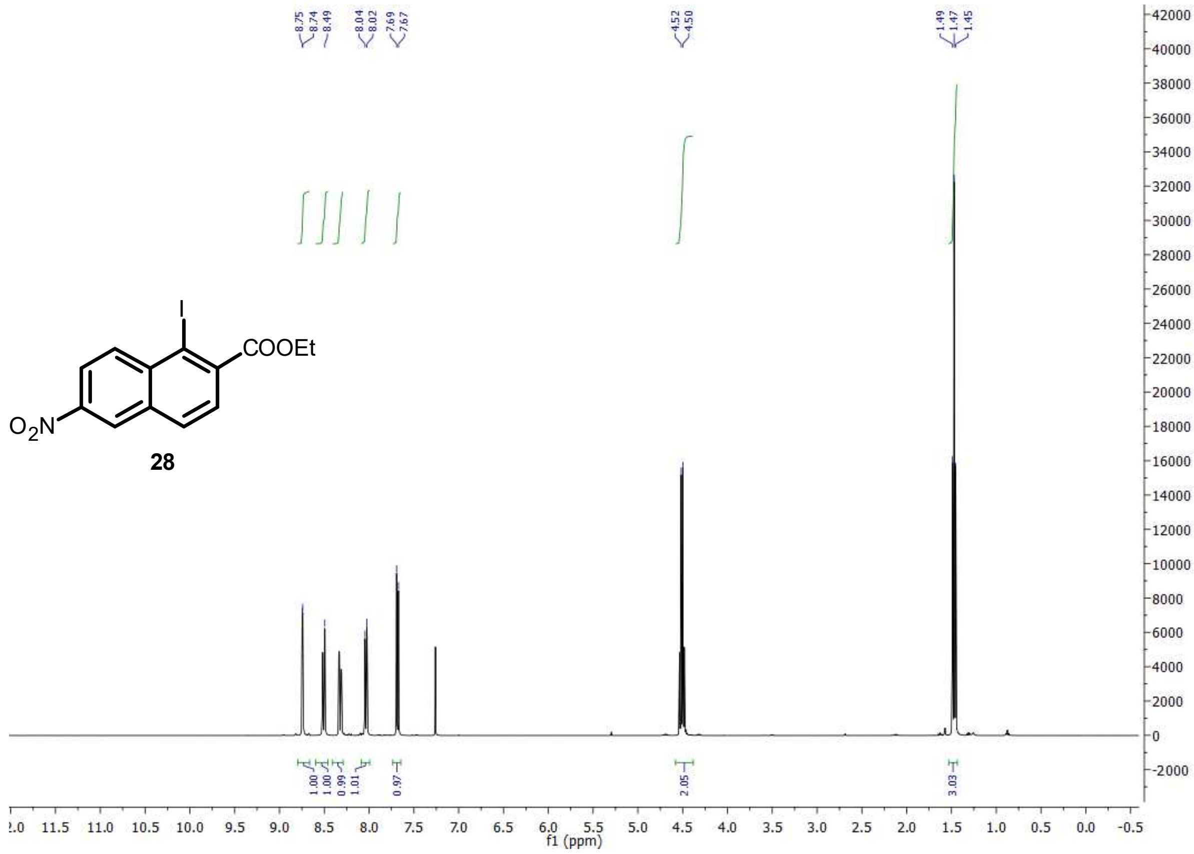

NAc2
OAc
OAc
O2N
25
f1 (ppm)

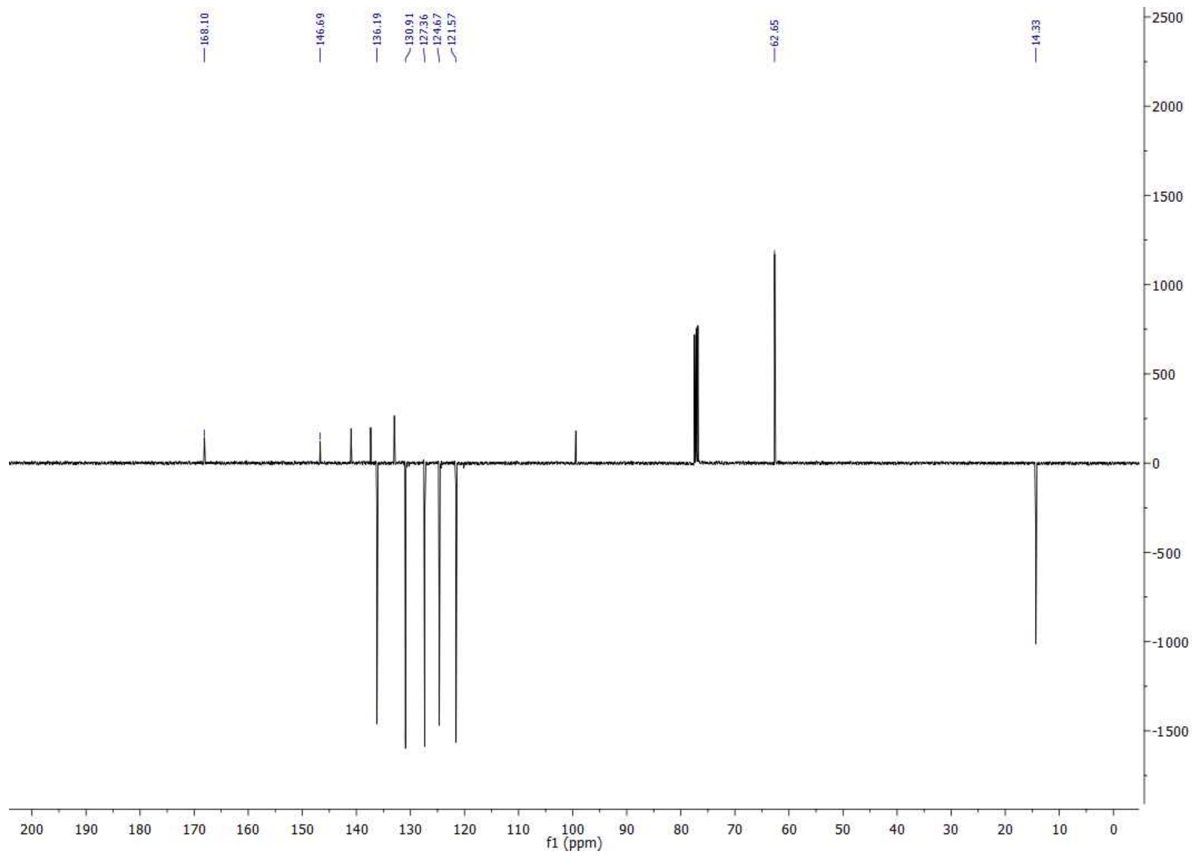

f1 (ppm)


9.96
8.48
8.48
8.48
8.48
8.37
8.36
8.36
8.30
8.28
8.28
8.26
8.26
8.23
8.23
8.23
8.22
8.22
8.22
8.22
8.21
8.20
8.19
8.18
8.18
8.11
8.09
8.05
8.05
8.04
8.04
8.02
8.02
8.01
8.01
8.01
7.31
7.29
6.82
6.81
6.80
2.01
O_2N
AcHN
1.01
0.96
1.06
1.00
0.93
4.34
0.96
1.04
0.96
0.99
0.96
3.04
f1 (ppm)

26


168.48
143.69
136.86
134.73
133.26
132.88
131.56
130.80
129.63
128.47
128.33
128.20
127.38
127.23
126.45
124.26
123.18
122.37
118.91
117.50
115.43
24.07
f1 (ppm)


8.75
8.74
8.49
8.04
8.02
7.69
7.67
4.52
4.50
1.49
1.47
1.45
I
COOEt
O_2N
28
1.00
1.00
0.99
1.01
0.97
2.05
3.03
f1 (ppm)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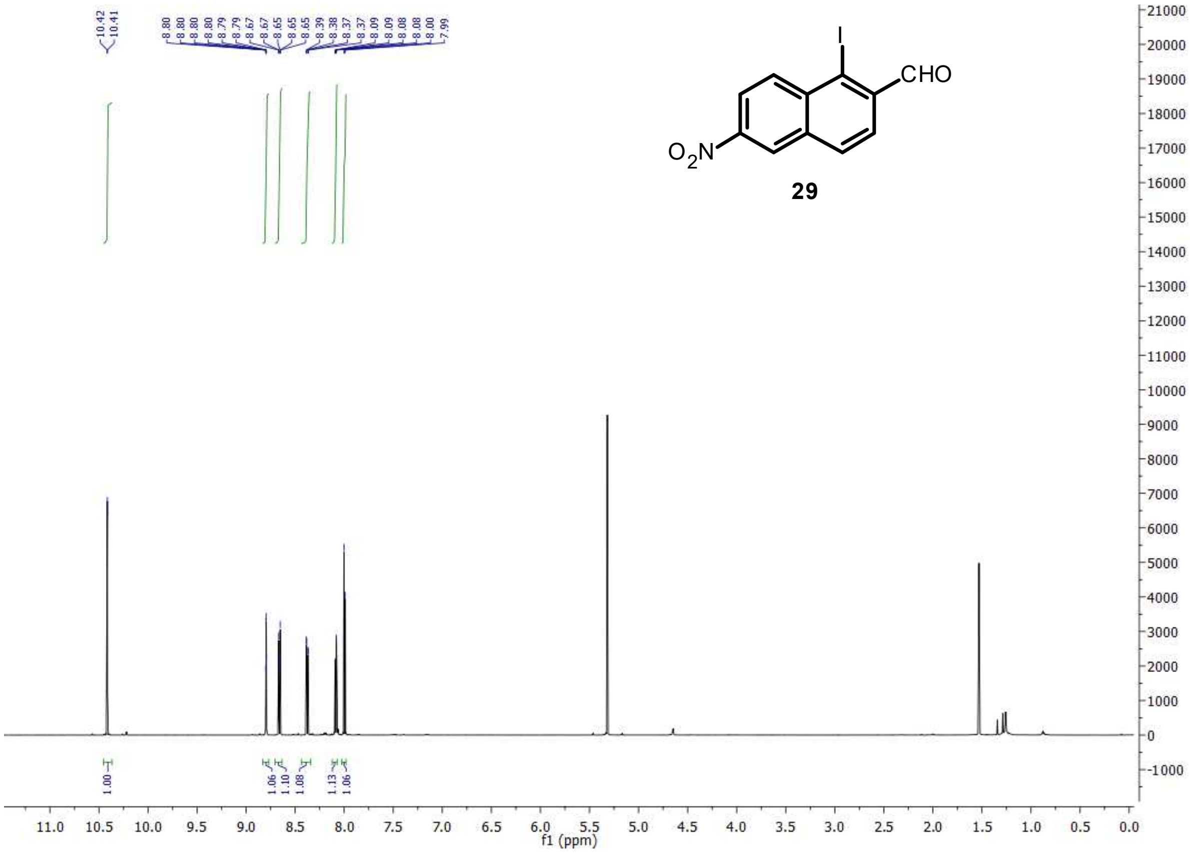
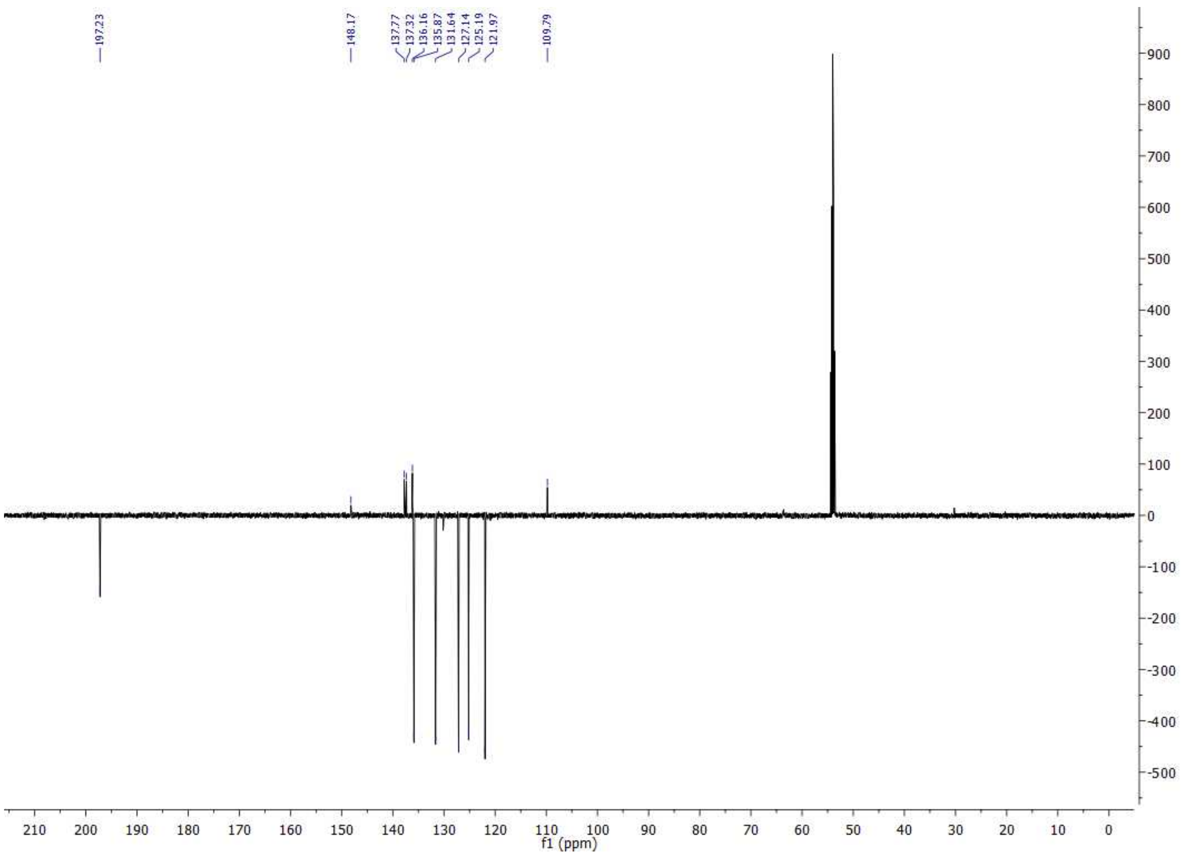
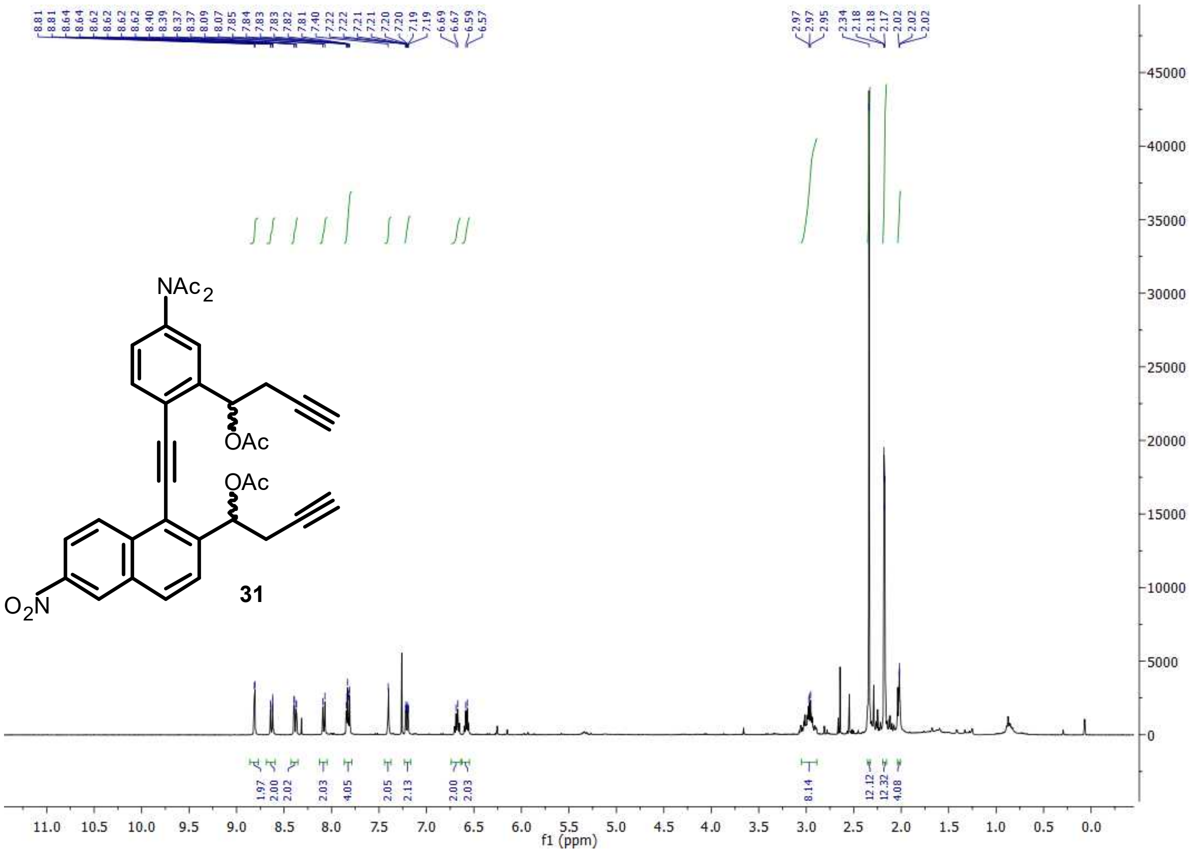
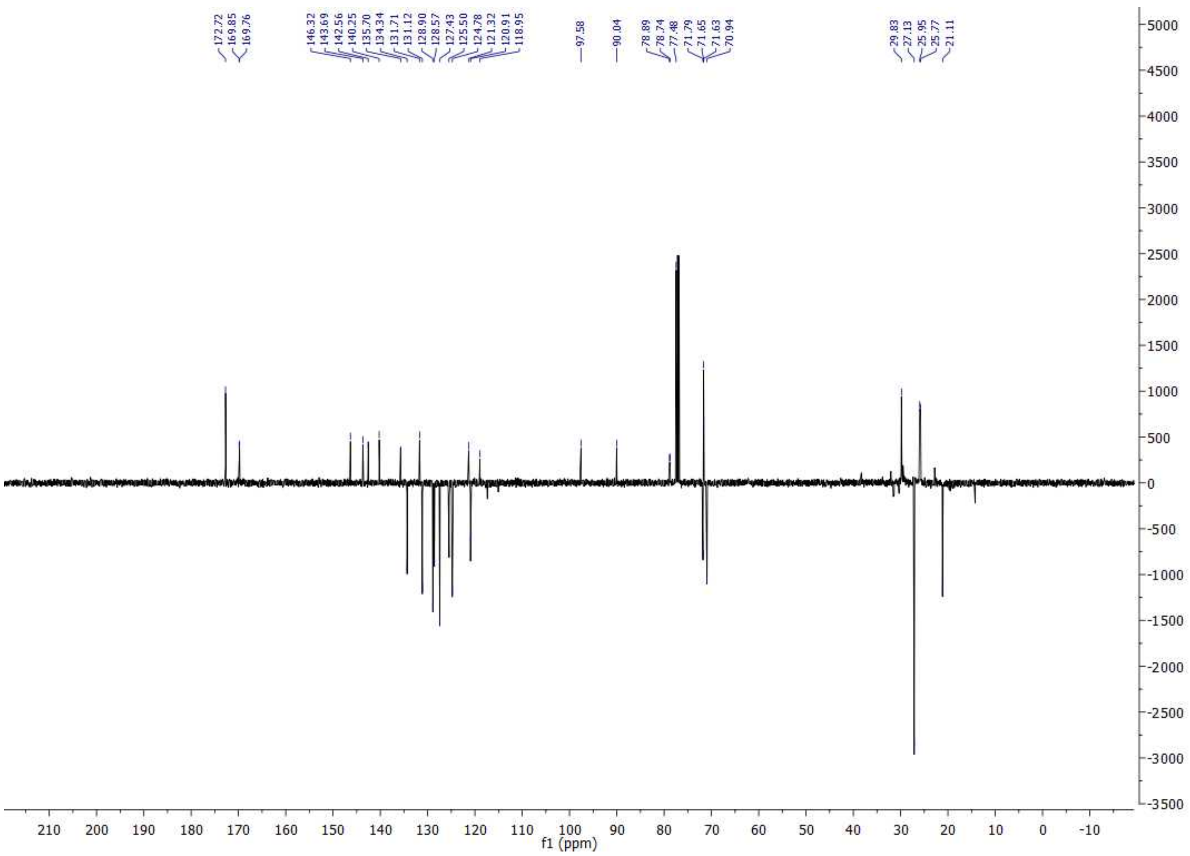
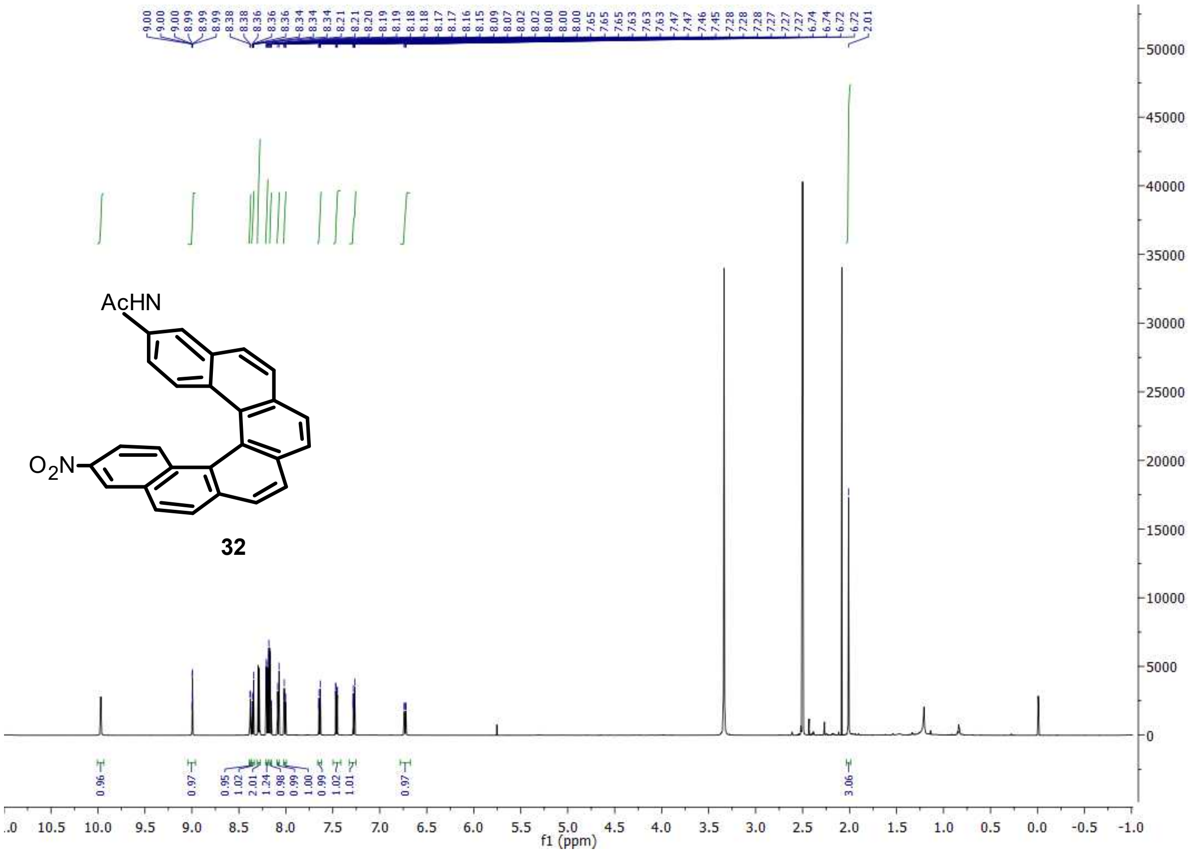
146.69
136.19
130.91
127.36
124.67
121.57
62.65
14.33
f1 (ppm)

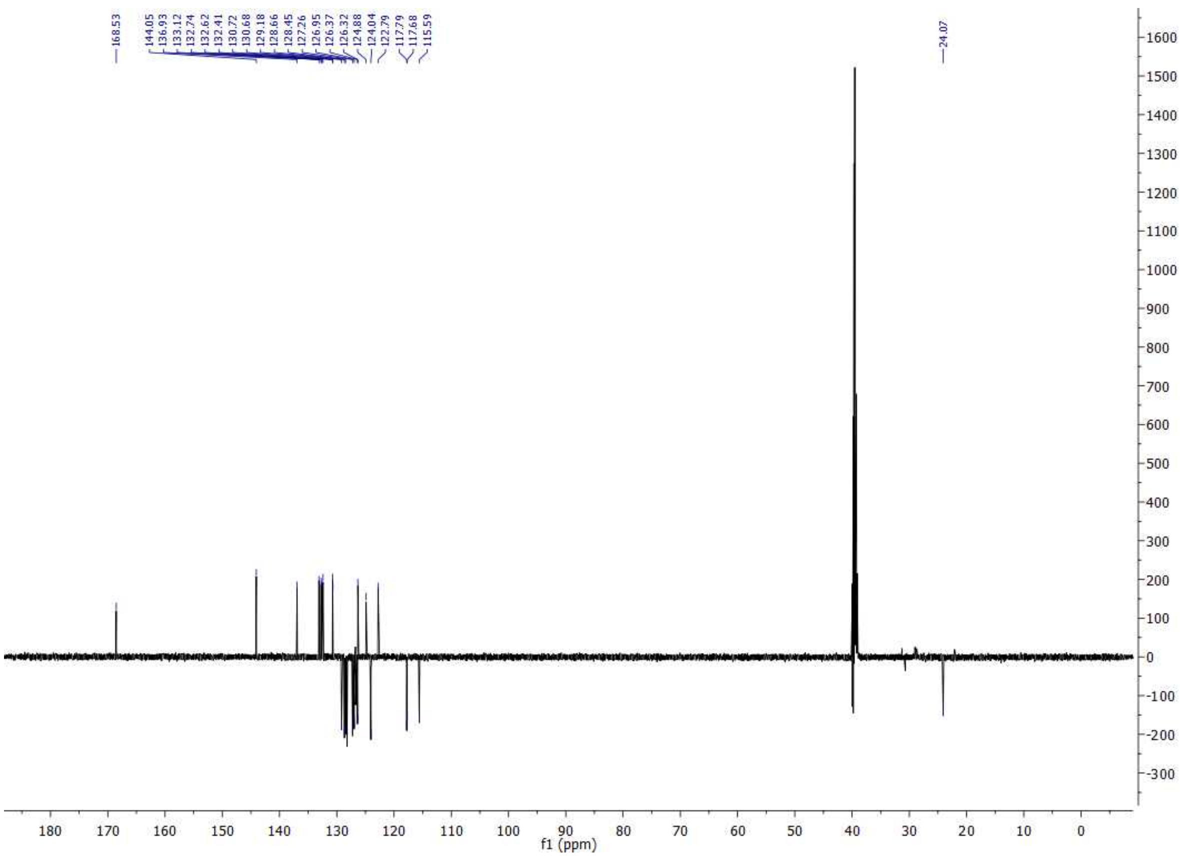

CHO
O2N
I
29
f1 (ppm)

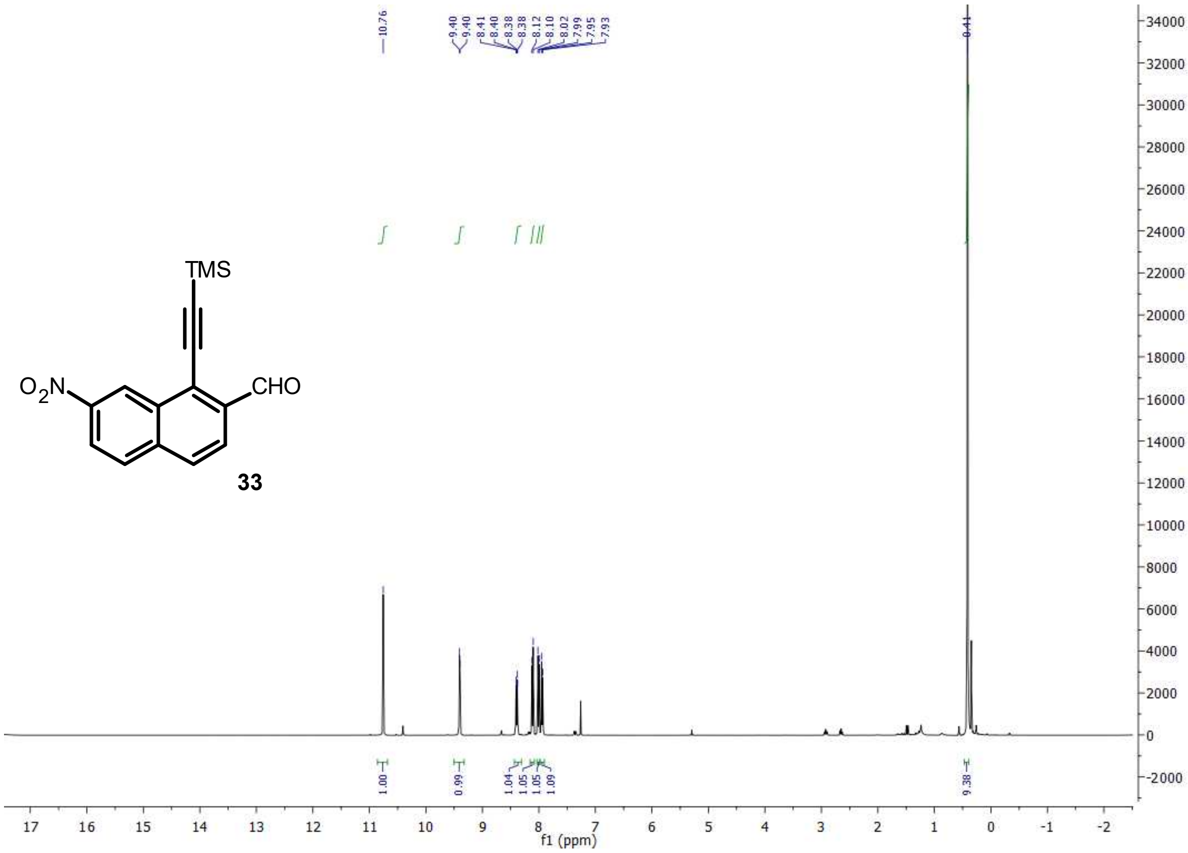

197.23
148.17
137.77
137.32
136.16
135.87
131.64
127.14
125.19
121.97
109.79
f1 (ppm)

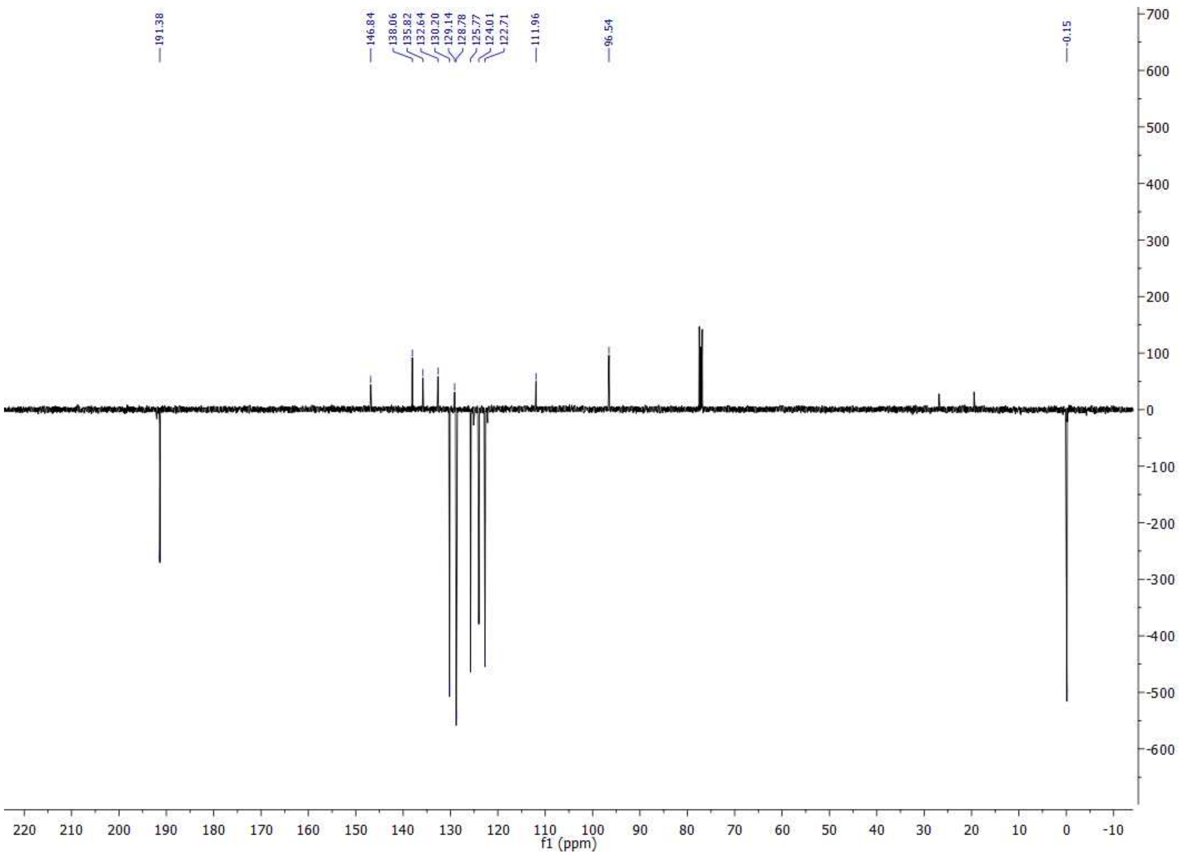

NAc2
OAc
OAc
O2N
31

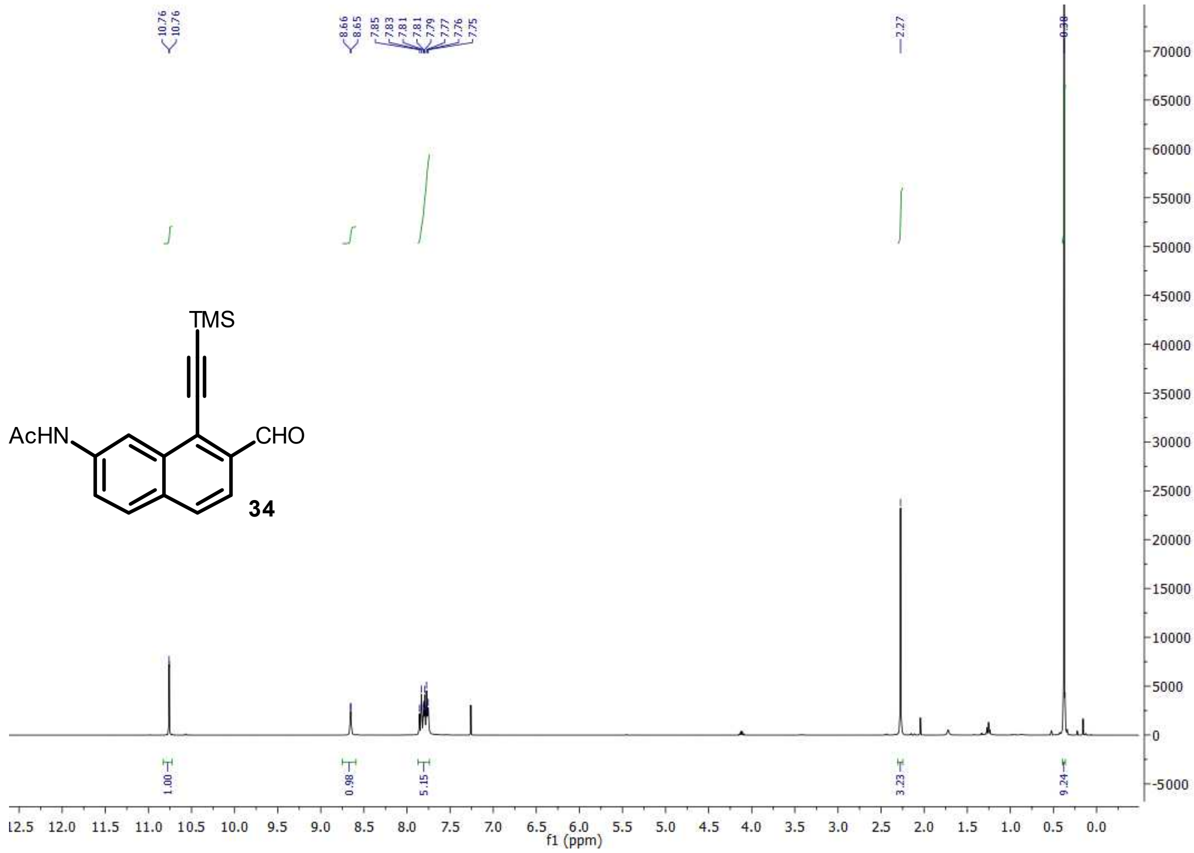



32

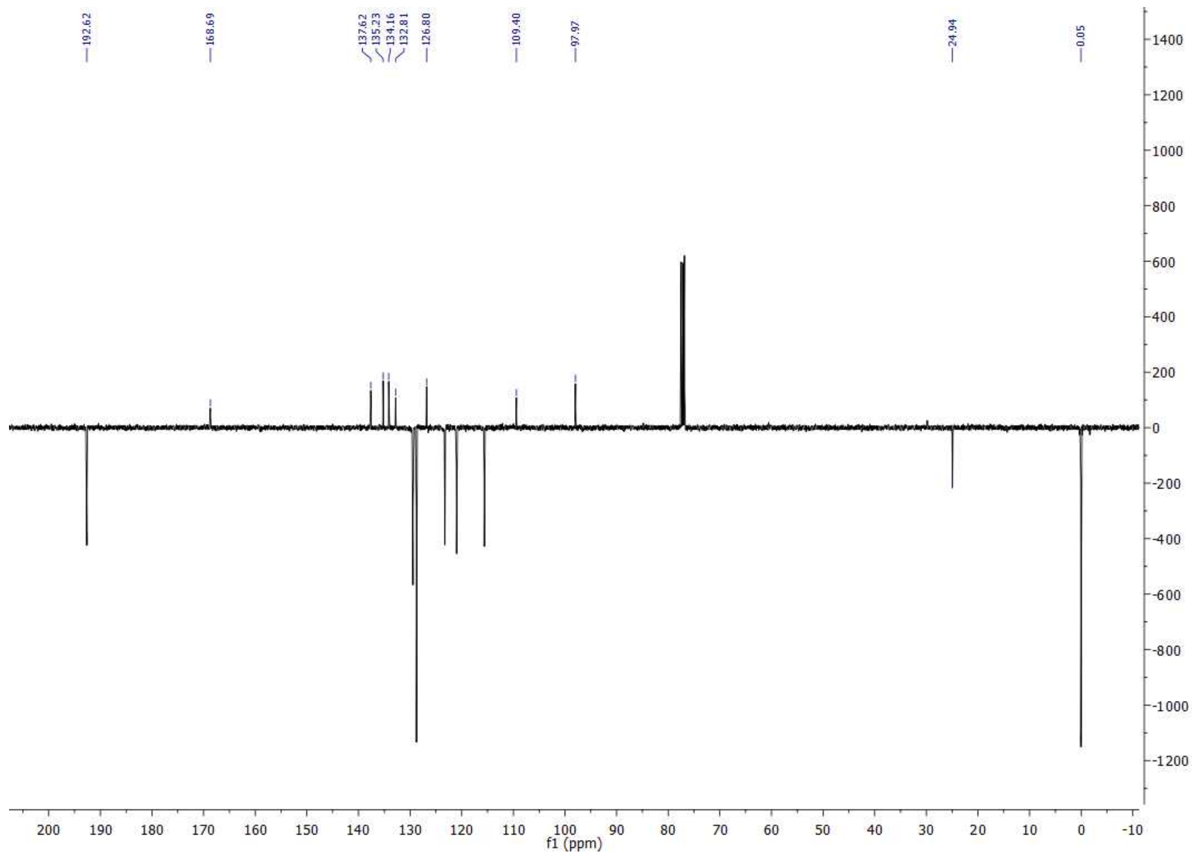



TMS
O_2N
CHO
33
f1 (ppm)


f1 (ppm)



10.76
10.76
8.66
8.65
7.85
7.83
7.81
7.81
7.79
7.77
7.76
7.75
2.27
0.38
TMS
AcHN
CHO
34
1.00
0.98
5.15
3.23
9.24
f1 (ppm)



192.62
168.69
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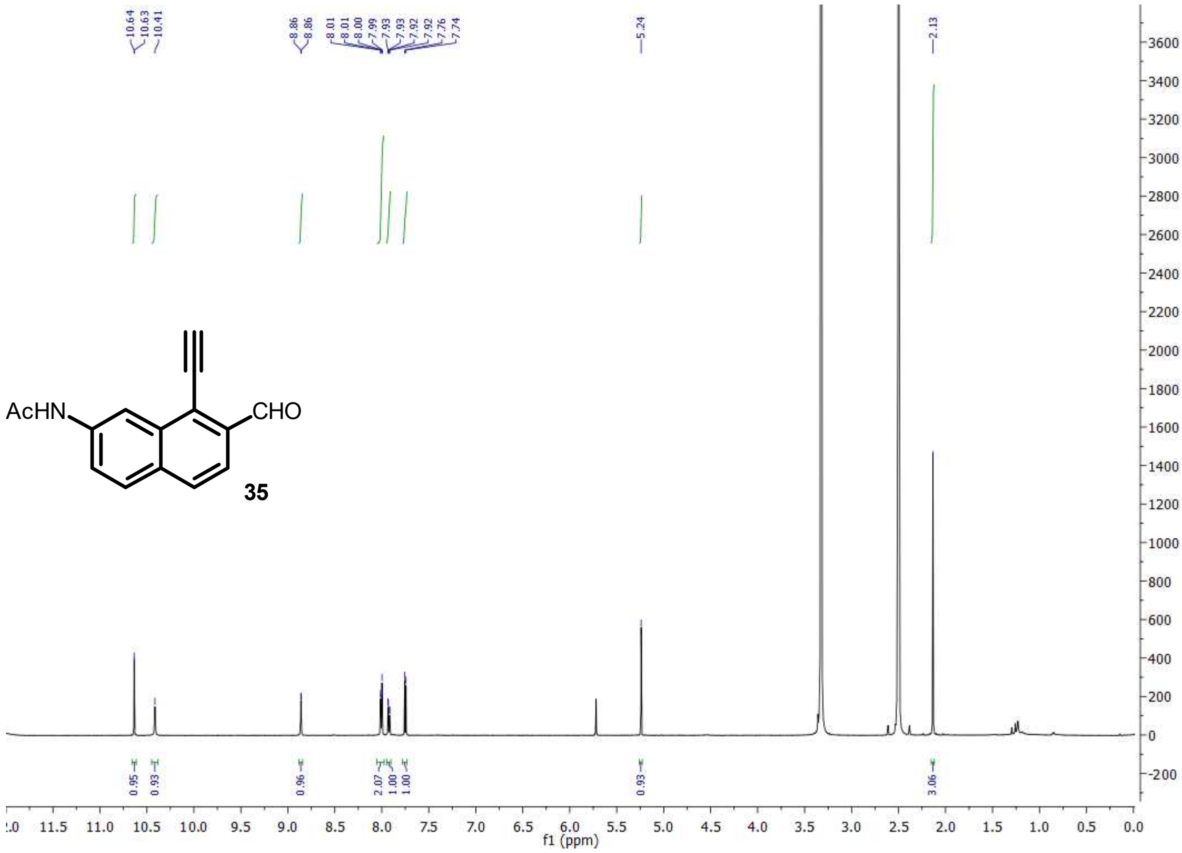
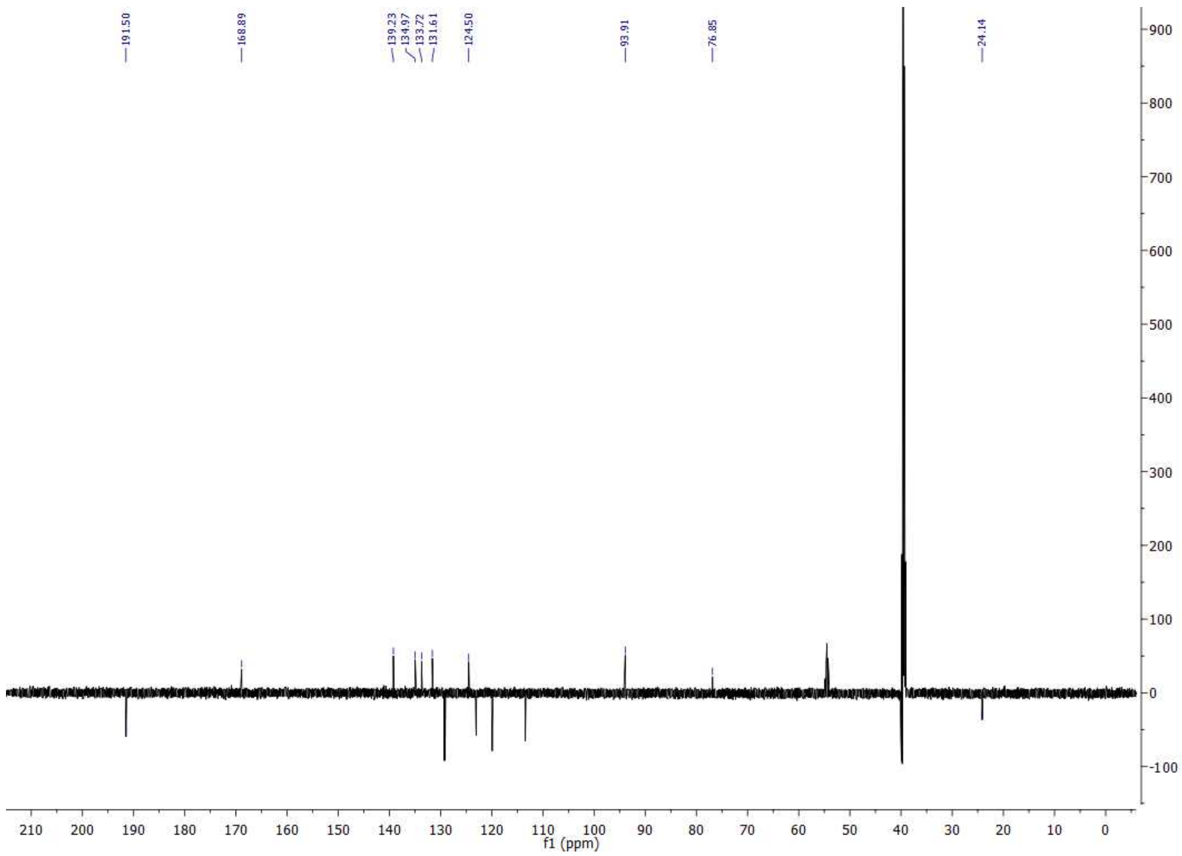
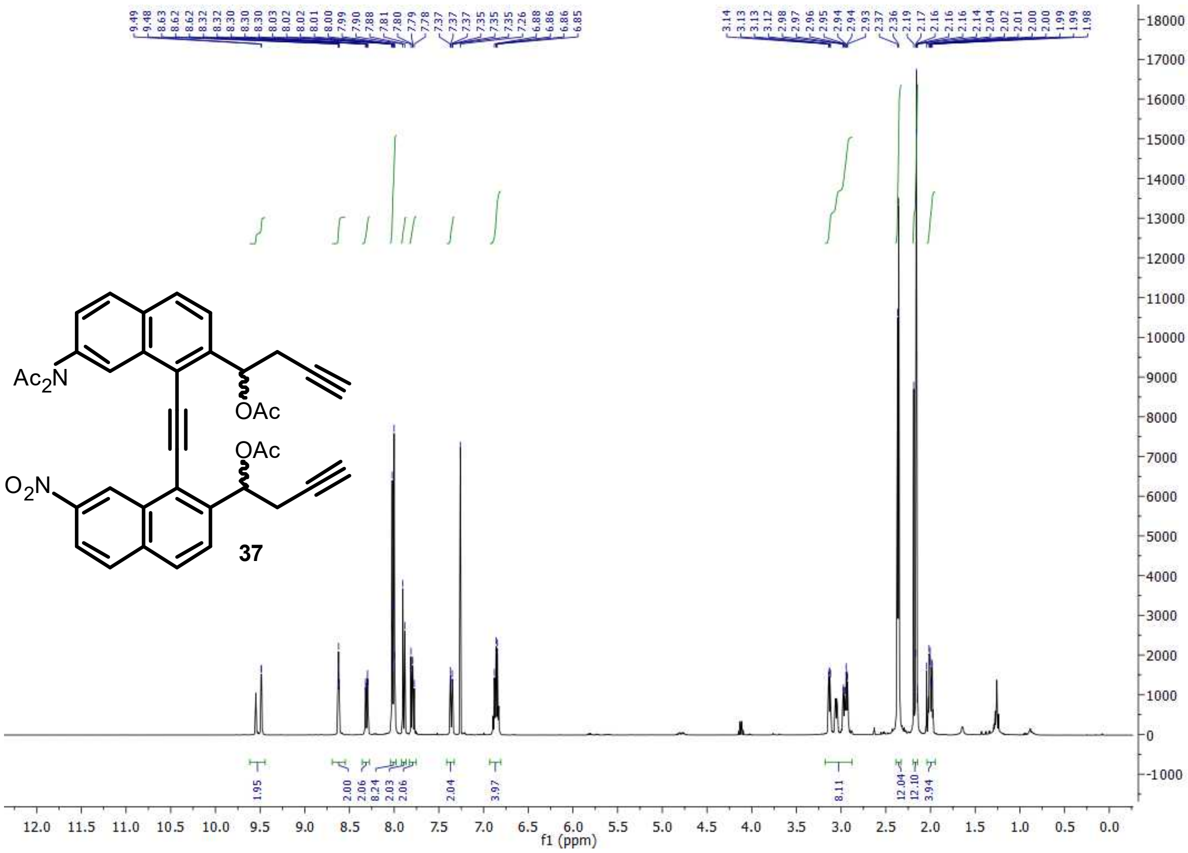
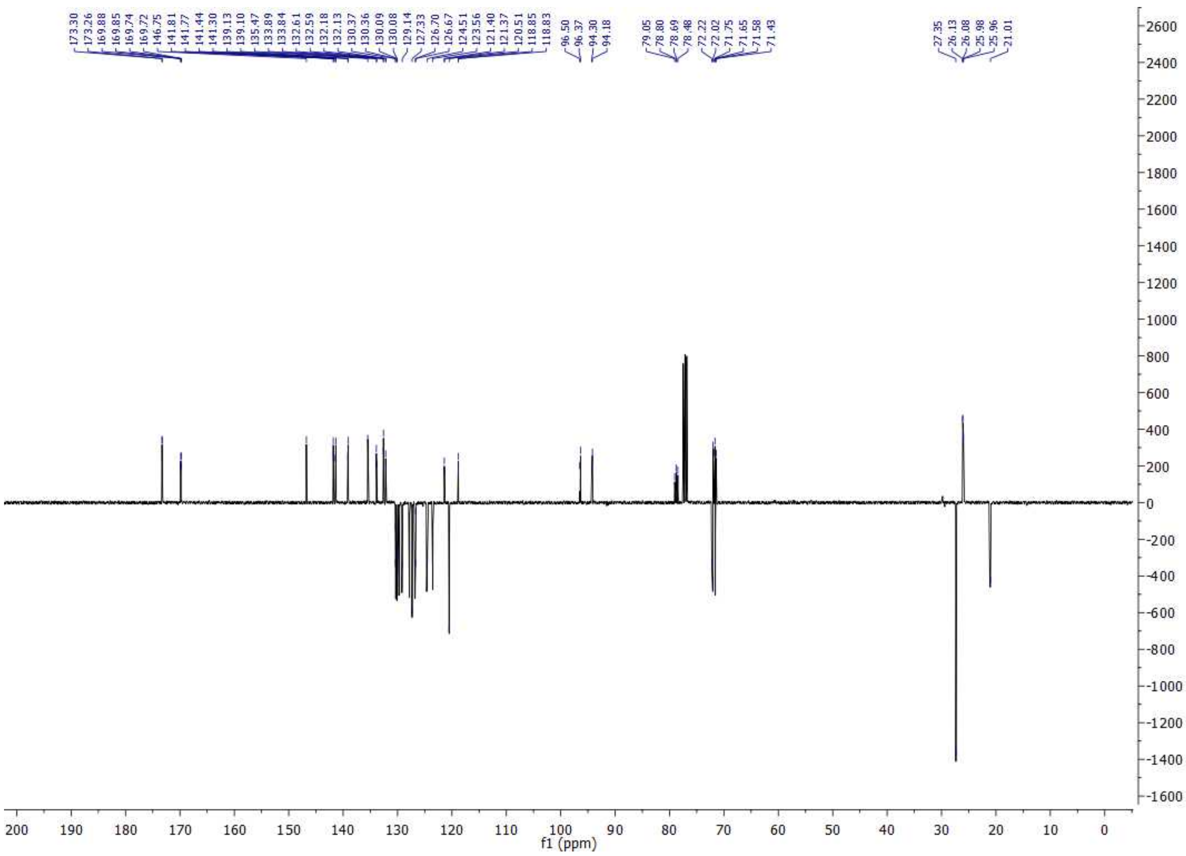
134.16
132.81
126.80
109.40
97.97
24.94
0.05
f1 (ppm)



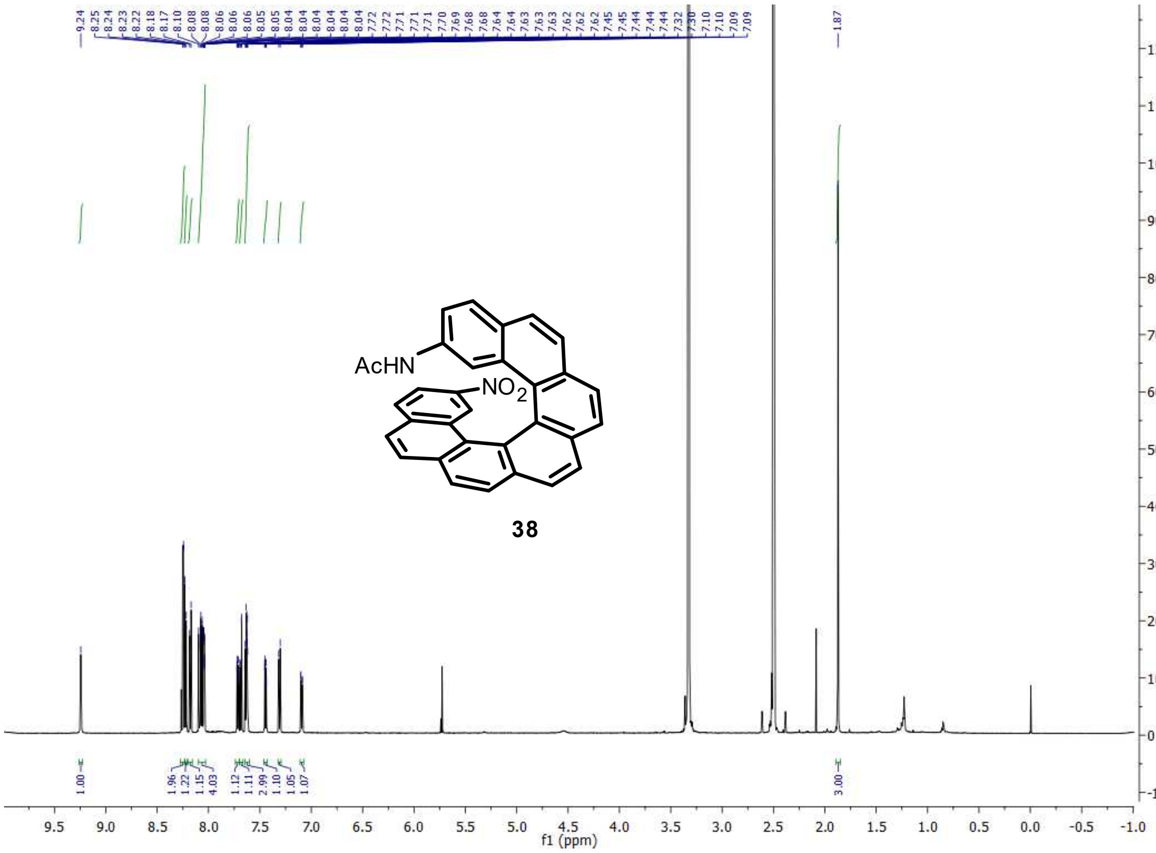


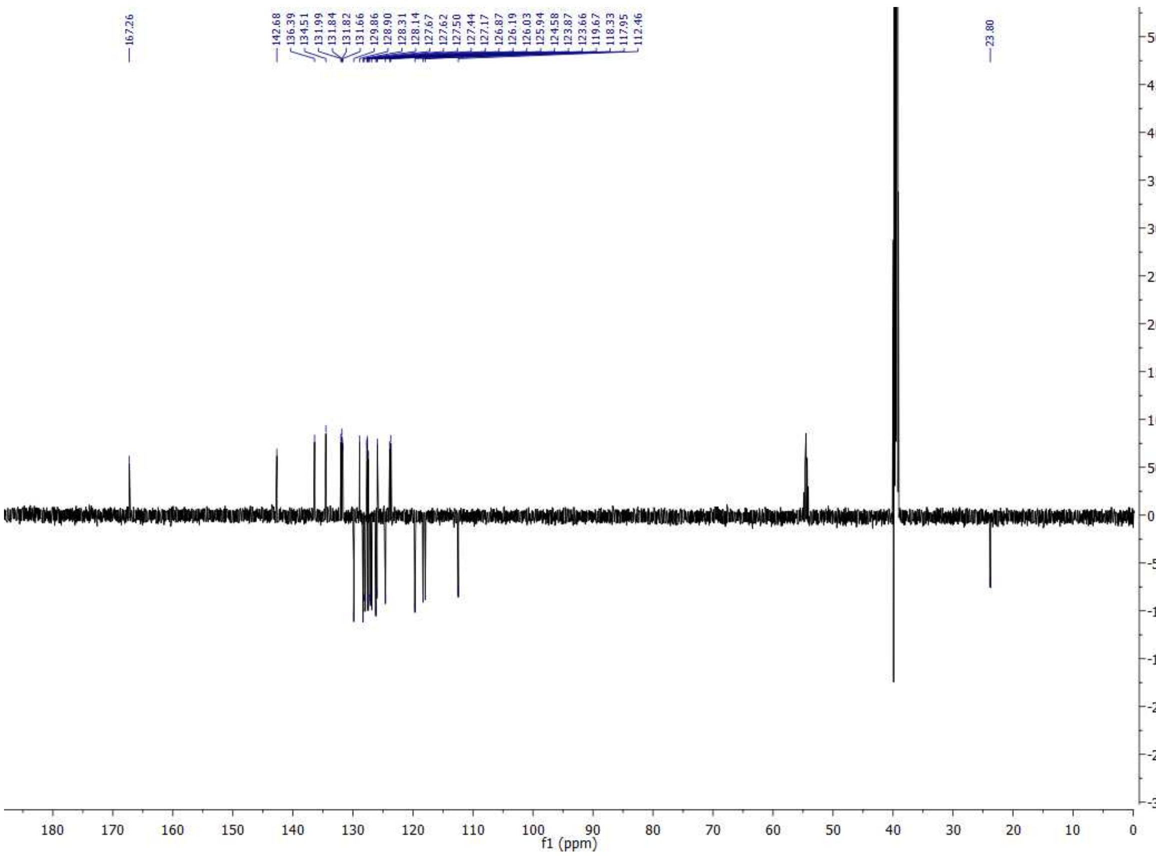


Ac2N
OAc
OAc
O2N
37
f1 (ppm)



f1 (ppm)


AcHN
NO2
38
f1 (ppm)


f1 (ppm)