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Supporting Information

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A Straightforward Route to Helically Chiral *N*-Heteroaromatics: The First Practical Synthesis of Racemic 1,14-Diaza[5]helicene and Optically Pure 1- and 2-Aza[6]helicenes

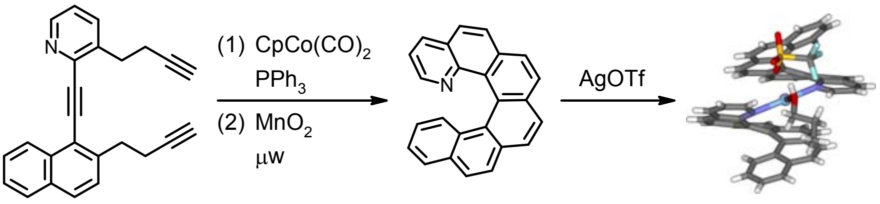
Jiří Míšek,[a] Filip Teplý,[a] Irena G. Stará,*[,a] Miloš Tichý,[a] David Šaman,[a]
Ivana Císařová,[b] Pavel Vojtíšek,[b] and Ivo Starý*[,a]

[a]Institute of Organic Chemistry and Biochemistry
Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6,
Czech Republic

[b]Department of Inorganic Chemistry, Charles University
Albertov 2030, 128 40 Prague 2, Czech Republic

stara@uochb.cas.cz, stary@uochb.cas.cz

Supporting Information



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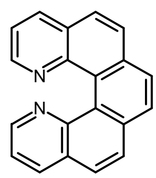
Experimental Section

General. ^1H NMR spectra were measured at 200.04 MHz, 499.8 MHz and 500.13 MHz, ^{13}C NMR spectra at 125.7 MHz, in $CDCl_3$ with TMS as an internal standard and DMSO. Chemical shifts are given in δ-scale, coupling constants *J* are given in Hz. HMBC experiments were set up for $J_{C\text{-}H}$ = 5 Hz. For correct assignment of both ^1H and ^{13}C NMR spectra of key compounds, the COSY, ROESY, HMQC, HMBC, and CIGAR-HMBC experiments were performed. For all the other compounds, the general semiempirical equations were applied to the chemical shift assignments. IR spectra were measured in $CHCl_3$ or CCl_4. EI mass spectra were determined at an ionizing voltage of 70 eV, *m/z* values are given along with their relative intensities (%). FAB mass spectra were measured using the thioglycerol-glycerol 3:1 matrix, *m/z* values are given. Accurate mass measurements were obtained by the EI or FAB-MS. Commercially available reagent grade materials were used as received. Decane, piperidine, and diisopropylamine were degassed by three freeze-pump-thaw cycles before use; toluene was distilled from calcium hydride under argon; THF and diethyl ether were freshly distilled from sodium/benzophenone under nitrogen. Commercial pure solvents were used directly when growing crystals for the X-ray analysis. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2 \cdot 4\,H_2O$ (1 %) and $H_3P(Mo_3O_{10})_4$ (2 %) in sulfuric acid (10 %). Flash chromatography was performed on Silica gel 60 (0.040-0.063 mm or <0.063 mm, Merck) or on Biotage KP-Sil® Silica cartridges (0.040-0.063 mm) used in Horizon® HPFC system (Biotage, Inc.). The HPLC analyses of chiral azahelicenes **2** and **3** were performed on a Chiralcel OD-H column (250 × 4.6 mm, 5 μm) in heptane–isopropanol 3:1, flow rate 0.8 ml/min, simultaneous UV detection at 254 nm (Varian) and polarimetric detection (Chiralizer, Knauer).

Cyclization procedure. A Schlenk flask was charged with the starting triyne, triphenylphosphine (40 mol %), and filled with argon. Degassed decane was added and the mixture was warmed to 140 ^oC to dissolve. $CpCo(CO)_2$ (20 mol %) was added via Hamilton syringe and the reaction mixture was heated to 140 ^oC with simultaneous irradiation with two 250 W halogen lamps (Halo Star 64480, Osram, or KANDOlite JDD E27, placed outside the reaction vessel) for 1 h. Solvent was removed *in vacuo* (80 °C, 20 mbar) and the crude product was chromatographed on silica gel (hexane-acetone 85:15) to provide the cyclized product.

Aromatization procedure. A glass vial was charged with a solution of the starting tetrahydroazahelicene in toluene and MnO_2 (30 equiv.). The vial was tightly capped and heated by microwave irradiation (Biotage microwave oven system). The resulting reaction mixture was directly chromatographed on silica gel (hexane-acetone-triethylamine 80:20:1) to provide the desired product.



Benzo[1,2-*h*:4,3-*h'*]diquinoline (1,14-diaza[5]helicene) 1. Tetrahydroazahelicene **8** (60 mg, 0.21 mmol), MnO_2 (0.55 g, 6.33 mmol, 29.98 equiv.), toluene (18 ml), 150 °C, 20 min. The aromatization procedure afforded azahelicene **1** (24 mg, 41%) as an amorphous yellowish solid.

Mp 260-264 °C (hexane).

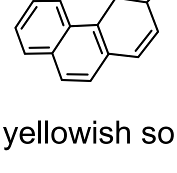
^{1}H NMR (500 MHz, DMSO): 7.59 (2 H, dd, *J* = 8.1, 4.1), 8.10 (2 H, d, *J* = 8.5), 8.12 (2 H, d, *J* = 8.5), 8.19 (2 H, s), 8.44 (2 H, dd, *J* = 8.1, 1.8), 8.56 (2 H, dd, *J* = 4.1, 1.8).

^{13}C NMR (125 MHz, DMSO): 122.11 (d), 126.08 (s), 126.31 (d), 127.11 (d), 127.64 (s), 127.98 (d), 133.70 (s), 134.95 (d), 145.95 (d), 146.70 (s).

IR ($CHCl_3$): 3360 w, 3204 w, 2937 vs, 2463 w, 1636 w, 1616 w, 1596 w, 1589 w, 1553 w, 1507 w, 1475 m, 1439 w, 1399 m, 1389 m, 1362 m, 1343 w, 1330 w, 1280 w (sh), 1270 w, 1246 m, 1187 w, 1174 w, 1157 m, 1129 w, 1099 w, 1087 w, 1031 w, 1008 w, 975 w, 938 w, 899 w, 864 vw, 846 s, 830 w, 820 w, 810 w, 719 w, 661 s, 652 m, 639 w, 618 w, 537 vw, 514 w.

EI MS: 280 ($M^{+\cdot}$, 100), 279 (48), 252 (49), 227 (5), 149 (13), 129 (10), 111 (10), 97 (19), 83 (25), 71 (51), 57 (50), 43 (45).

Accurate mass (EI MS): calculated for $C_{20}H_{12}N_2$ 280.1000; found 280.0996.



Benzo[5,6]phenanthro[3,4-*h*]quinoline (1-aza[6]helicene) 2. Tetrahydroazahelicene **12** (200 mg, 0.60 mmol) in toluene (18 ml), MnO_2 (1.57 g, 18.08 mmol, 30.13 equiv.), 150 °C, 80 min. The aromatization procedure afforded azahelicene **2** (128 mg, 65%) as an amorphous yellowish solid.

Mp 184-186 °C (heptane).

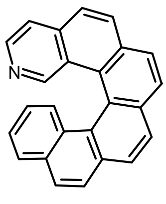
^{1}H NMR (500 MHz, $CDCl_3$): 6.59 (1 H, ddd, *J* = 8.5, 6.8, 1.4), 7.10 (1 H , dd, *J* = 8.0, 4.2), 7.18 (1 H, ddd, *J* = 8.0, 6.8, 1.2), 7.56 (1 H, ddt, *J* = 8.5, 1.2, 0.6, 0.6), 7.84 (1 H, ddd, *J* = 8.0, 1.4, 0.7), 7.86 (1 H, dd, *J* = 8.5, 0.5), 7.92 (1 H, dd, *J* = 4.2, 1.8), 7.98 (1 H, dd, *J* = 8.2, 0.5), 8.00 (2 H, s), 8.01 (1 H, d, *J* = 8.2), 8.03 (2 H, bd, *J* = 8.5), 8.11 (1 H, dd, *J* = 9.0, 0.5), 8.11 (1 H, ddd, *J* = 8.0, 1.8, 0.6).

^{13}C NMR (125 MHz, $CDCl_3$): 120.56 (d), 124.12 (d), 124.20 (s), 124.66 (d), 125.98 (d), 126.05 (d), 126.23 (d), 126.29 (s), 126.34 (d), 126.53 (d), 127.20 (d), 127.48 (d), 127.83 (d), 128.12 (d), 128.57 (d), 128.69 (s), 129.78 (s), 130.96 (s), 131.15 (s), 131.83 (s), 133.07 (s), 133.27 (s), 135.08 (d), 145.83 (s), 146.72 (d).

IR (CCl_4): 3049 m, 1622 w, 1606 w, 1599 w, 1583 w, 1553 w, 1519 w, 1512 w, 1497 w, 1438 w, 1426 w, 1411 w, 1391 w, 1368 w, 1308 w, 1262 w, 1133 m, 1114 m, 1104 m, 1097 m, 1072 m, 1054 m, 1040 m, 1027 m, 1019 m, 844 vs, 828 m, 819 m, 631 m, 618 m, 517 m.

FAB MS : 330 ($(M+H)^+$), 302, 289, 279.

Accurate mass (FAB MS): calculated for $C_{25}H_{16}N$ 330.1283; found 330.1297.



Benzo[5,6]phenanthro[3,4-*h*]isoquinoline (2-aza[6]helicene) 3. Tetrahydroazahelicene **18** (200 mg, 0.60 mmol) in toluene (18 ml), MnO_2 (1.57 g, 18.08 mmol, 30.13 equiv.), 130 °C, 30 min. The aromatization procedure afforded azahelicene **3** (105 mg, 53%) as an amorphous yellowish solid.

Mp 233-235 °C (heptane-dichloromethane).

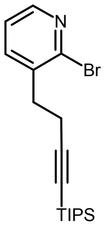
^{1}H NMR (500 MHz, $CDCl_3$): 6.73 (1 H, ddd, *J* = 8.4, 6.8, 1.4), 7.26 (1 H, ddd, *J* = 8.0, 6.8, 1.1), 7.54 (1 H, ddt, *J* = 8.4, 1.1, 0.6, 0.6), 7.61 (1 H, dd, *J* = 5.4, 1.1), 7.86 (1 H, dt, *J* = 8.5, 0.6, 0.6), 7.87 (1 H, ddd, *J* = 8.0, 1.4, 0.6), 7.93 (1 H, d, *J* = 8.5), 7.95 (1 H, bd, *J* = 8.5), 8.02 (1 H, d, *J* = 8.1), 8.02 (1 H, d, *J* = 8.2), 8.04 (1 H, d, *J* = 8.1), 8.08 (1 H, d, *J* = 8.2), 8.14 (1 H, d, *J* = 8.5), 8.24 (1 H, d, *J* = 5.4), 8.91 (1 H, t, *J* = 0.9).

^{13}C NMR (125 MHz, $CDCl_3$): 119.88 (d), 123.39 (s), 124.50 (s), 124.82 (d), 125.82 (d), 125.88 (d), 126.04 (d), 126.84 (d), 126.88 (s), 127.08 (d), 127.76 (d), 127.82 (d), 127.90 (s), 128.15 (d), 128.29 (d), 128.56 (d), 128.99 (s), 130.95 (d), 131.35 (s), 131.63 (s), 132.31 (s), 133.48 (s), 134.64 (s), 143.15 (d), 150.51 (d).

IR ($CHCl_3$): 3058 w, 3033 w, 1618 w (sh), 1607 m, 1599 w (sh), 1582 w, 1568 w, 1551 w, 1509 w, 1496 w, 1431 w, 1418 w, 1408 w, 1396 w, 1309 w, 1300 w, 852 vs, 523 s.

FAB MS : 330 ($(M+H)^+$), 314, 300, 287, 277, 250, 224, 181, 149, 93, 73, 69, 57, 55.

Accurate mass (FAB MS): calculated for $C_{25}H_{16}N$ 330.1283; found 330.1293.



2-Bromo-3-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}pyridine 5. A 250 ml flask was charged with tris(1-methylethyl)(prop-1-yn-1-yl)silane (6.56 g, 33.40 mmol, 1.10 equiv.) and flushed with argon. THF (30 ml) was added and the solution was cooled to –78°C. n-BuLi (1.6 M solution in hexanes, 21 ml, 33.60 mmol, 1.11 equiv.) was added and the mixture was stirred for 2 h at –78°C. The resulting organolithium was added dropwise to the solution of bromopyridine **4** (7.63 g, 30.39 mmol) in THF (30 ml) precooled to –78 °C. The reaction mixture was stirred at –78°C for 30 min. Solvents were removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-ether 93:7) to provide alkyne **5** (9.0 g, 81%) as an amorphous solid.

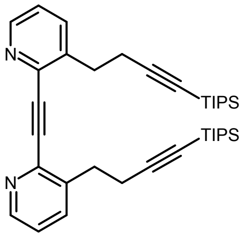
^{1}H NMR (500 MHz, $CDCl_3$): 0.97-1.07 (21 H, m), 2.65 (2 H, t, *J* = 6.9), 2.94 (2 H, t, *J* = 6.9), 7.19 (1 H, dd, *J* = 7.5, 4.7), 7.64 (1 H, dd, *J* = 7.5, 2.0), 8.24 (1 H, dd, *J* = 4.7, 2.0).

^{13}C NMR (125 MHz, $CDCl_3$): 11.24 (d), 18.59 (q), 19.49 (t), 34.36 (t), 82.28 (s), 106.60 (s), 122.58 (d), 136.82 (s), 139.07 (d), 144.23 (s), 148.04 (d).

IR ($CHCl_3$): 2866 vs, 2171 m, 1581 w, 1560 m, 1464 m, 1451 m, 1429 m, 1407 vs, 1383 m, 1367 w, 1119 m, 1069 m, 996 m, 884 m, 800 w, 679 s, 660 s, 618 w.

EI MS: 324 ($(M\text{-}C_3H_7)^{+\cdot}$ with ^{81}Br, 100), 322 ($(M\text{-}C_3H_7)^{+\cdot}$ with ^{79}Br, 100), 282 (with ^{81}Br, 40), 280 (with ^{79}Br, 40), 254 (with ^{81}Br, 12), 252 (with ^{79}Br, 10), 240 (with ^{81}Br, 12), 238 (with ^{79}Br, 12), 172 (with ^{81}Br, 16), 170 (with ^{79}Br, 15), 158 (with ^{81}Br, 44), 156 (with ^{79}Br, 40), 130 (23), 109 (7), 83 (10), 66 (20), 59 (25), 43 (27).

Accurate mass (EI MS): calculated for $C_{15}H_{21}{}^{79}BrNSi$ 322.0627; found 322.0622; calculated for $C_{15}H_{21}{}^{81}BrNSi$ 324.0606; found 324.0605.



2,2'-Ethyne-1,2-diylbis(3-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}pyridine) 6. A Schlenk flask was charged with $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 5%), CuI (52 mg, 0.27 mmol, 15%) and filled with acetylene. A solution of bromopyridine **5** (666 mg, 1.85 mmol) in piperidine (10 ml) was added and reaction mixture was stirred for 30 min at 80°C. The solvent was removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-ether 90:10) to provide triyne **6** (467 mg, 86%) as a pale yellow amorphous solid.

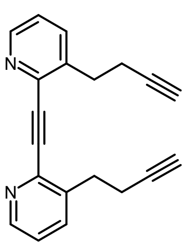
^{1}H NMR (500 MHz, $CDCl_3$): 0.95 – 1.03 (42 H, m), 2.74 (4 H, t, *J* = 6.9), 3.12 (4 H, t, *J* = 6.9), 7.21 (2 H, dd, *J* = 7.8, 4.7), 7.71 (2 H, bdd, *J* = 7.8, 1.7), 8.52 (2 H, dd, *J* = 4.7, 1.7).

^{13}C NMR (125 MHz, $CDCl_3$): 11.26 (d), 18.56 (q), 20.34 (t), 32.39 (t), 82.13 (s), 89.87 (s), 107.03 (s), 123.03 (d), 137.05 (d), 138.66 (s), 142.11 (s), 148.21 (d).

IR ($CHCl_3$): 3055 w, 2866 vs, 2171 m, 1581 w, 1567 m, 1463 m, 1442 s, 1383 w, 1367 w, 1341 w, 1326 w, 1104 w, 1073 w, 997 m, 884 s, 799 w, 678 s, 662 s, 620 w.

EI MS: 596 ($M^{+\cdot}$, 12), 581 (4), 553 (76), 511 (4), 439 (12), 425 (5), 397 (7), 357 (5), 298 (5), 273 (19), 255 (8), 234 (6), 213 (6), 183 (9), 149 (20), 98 (12), 87 (25), 73 (47), 59 (100), 41 (59).

Accurate mass (EI MS): calculated for $C_{38}H_{56}N_2Si_2$ 596.3982; found 596.4000.



2,2'-Ethyne-1,2-diylbis(3-but-3-yn-1-ylpyridine) 7. A Schlenk flask was charged with triyne **6** (467 mg, 0.782 mmol) and filled with argon. THF (20 ml) was added and the resulting solution was treated with a solution of n-$Bu_4NF \cdot 3\ H_2O$ (608 mg, 1.93 mmol, 2.47 equiv.) in THF (10 ml). After stirring at room temperature for 1 h, the solvent was removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-acetone 60:40) to provide the unprotected triyne **7** (171 mg, 77%) as a pale yellow solid.

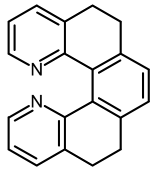
^{1}H NMR (500 MHz, $CDCl_3$): 1.98 (2 H, t, *J* = 2.6), 2.65 (4 H, dt, *J* = 7.1, 7.1, 2.6), 3.15 (4 H, t, *J* = 7.1), 7.25 (2 H, dd, *J* = 7.8, 4.8), 7.68 (2 H, dd, *J* = 7.8, 1.7), 8.54 (2 H, dd, *J* = 4.8, 1.7).

^{13}C NMR (125 MHz, $CDCl_3$): 19.03 (t), 32.02 (t), 69.82 (d), 82.89 (s), 89.77 (s), 123.22 (d), 136.76 (d), 138.45 (s), 142.17 (s), 148.37 (d).

IR ($CHCl_3$): 3309 s, 3055 w, 2965 m, 2934 w, 2857 w, 2120 vw, 1582 w, 1568 m, 1443 vs, 1343 vw, 1328 vw, 1311 w, 1105 w, 1061 vw, 803 w, 643 m.

EI MS: 284 ($M^{+\cdot}$, 26), 283 (100), 268 (23), 257 (9), 243 (25), 231 (9), 205 (9), 191 (6), 178 (5), 167 (3), 151 (5), 141 (5), 127 (3), 116 (5), 101 (8), 83 (9), 69 (12), 59 (50).

Accurate mass (EI MS): calculated for $C_{20}H_{16}N_2$ 284.1313; found 284.1316.



5,6,9,10-Tetrahydrobenzo[1,2-*h*:4,3-*h'*]diquinoline 8. Triyne **7** (148 mg, 0.52 mmol), PPh_3 (55 mg, 0.21 mmol, 40 mol %), $CpCo(CO)_2$ (14 μl, 0.11 mmol, 21 mol %), decane (6 ml). The cyclization procedure afforded tetrahydrohelicene **8** (89 mg, 60%) as an amorphous yellowish solid.

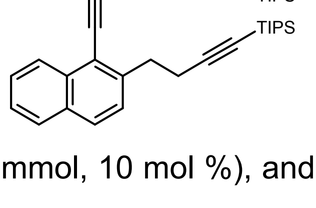
^{1}H NMR (500 MHz, $CDCl_3$): 2.81 (4 H, m), 2.96 (4 H, m), 7.00 (2 H, dd, *J* = 7.5, 4.8), 7.19 (2 H, s), 7.52 (2 H, ddt, *J* = 7.5, 1.8, 0.8, 0.8), 8.14 (2 H, dd, *J* = 4.8, 1.8).

^{13}C NMR (125 MHz, $CDCl_3$): 29.13 (t), 29.23 (t), 121.51 (d), 127.55 (d), 133.10 (s), 133.96 (s), 134.63 (d), 140.23 (s), 146.39 (d), 154.19 (s).

IR ($CHCl_3$): 3057 w, 2945 vs, 2845 m, 1587 m, 1575 s, 1568 s,1507 vw, 1455 s, 1448 s, 1435 vs, 1426 vs, 1402 s, 1349 w, 1319 w, 1292 w, 1239 m, 1181 w, 1170 w, 1154 w, 1133 w, 1110 m, 1092 w, 971 w, 943 w, 920 w, 872 w, 829 s, 814 w, 807 m, 641 m, 624 s, 600 w, 585 w, 532 w, 523 w, 512 w, 499 w, 468 w.

EI MS: 284 ($M^{+\cdot}$, 13), 97 (12), 83 (16), 69 (34), 55 (62), 43 (100).

Accurate mass (EI MS): calculated for $C_{20}H_{16}N_2$ 284.1313; found 284.1309.



3-{4-[Tris(1-methylethyl)silyl]but-3-yn-1-yl}-2-[(2-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}naphthalen-1-yl)ethynyl]-pyridine 10. A 100 ml flask was charged with bromopyridine **5** (2.0 g, 5.46 mmol), diyne **9** (2.0 g, 5.55 mmol, 1.02 equiv.), $Pd(PPh_3)_4$ (315 mg, 0.27 mmol, 5 mol %), CuI (105 mg, 0.55 mmol, 10 mol %), and filled with argon. Diisopropylamine (40 ml) and toluene (20 ml) were added and the reaction mixture was stirred at room temperature for 80 min. Solvents were removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-ether 80:20) to provide triyne **10** (3.19 g, 90 %) as a white solid.

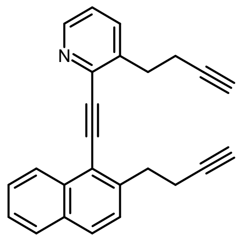
^{1}H NMR (500 MHz, $CDCl_3$): 0.96-1.05 (21 H, m), 2.79 (2 H, t, *J* = 7.0), 3.19 (2 H, t, *J* = 7.0), 7.21 (1 H, dd, *J* = 7.8, 4.8), 7.49 (1 H, ddd, *J* = 8.1, 6.8, 1.2), 7.51 (1 H, d, *J* = 8.4), 7.51 (1 H, ddd, *J* = 8.4, 6.8, 1.5), 7.73 (1 H, dd, *J* = 7.8, 1.7), 7.80 (1 H, bd, *J* = 8.4), 7.83 (1 H, ddt, *J* = 8.1, 1.5, 0.8, 0.8), 8.53 (1 H, dq, *J* = 8.4, 1.0, 1.0, 1.0), 8.58 (1 H, dd, *J* = 4.8, 1.7).

^{13}C NMR (125 MHz, $CDCl_3$): 11.28 (d), 18.57 (q), 20.69 (t), 32.80 (t), 82.12 (s), 89.08 (s), 96.48 (s), 107.00 (s), 118.45 (s), 122.55 (d), 125.94 (d), 126.31 (d), 127.18 (d), 127.41 (d), 128.03 (d), 129.08 (d), 137.10 (d), 137.90 (s), 142.35 (s), 143.08 (s), 148.31 (d).

IR ($CHCl_3$): 2866 vs, 2205 w, 2171 m, 1621 vw, 1593 w, 1582 w, 1566 w, 1508 w, 1464 m, 1436 s, 1430 m, 1383 w, 1367 w, 1103 w, 1072 w, 1040 w, 1026 w, 997 m, 884 s, 868 w (sh), 817 m, 678 s, 661 s, 619 m.

EI MS: 645 ($M^{+\cdot}$, 11), 602 (47), 560 (3), 488 (15), 450 (26), 436 (5), 408 (7), 394 (3), 322 (8), 157 (13), 129 (8), 115 (39), 87 (45), 73 (64), 59 (100), 41 (43).

Accurate mass (EI MS): calculated for $C_{43}H_{59}NSi_2$ 645.4186; found 645.4205.



3-But-3-yn-1-yl-2-[(2-but-3-yn-1-ylnaphthalen-1-yl)ethynyl]-pyridine 11. A 100 ml flask was charged with triyne **10** (3.02 g, 4.67 mmol) and filled with argon. THF (30 ml) was added and the solution was treated with n-Bu_4NF (0.964 M in THF, 23.2 ml, 23.28 mmol, 2.40 equiv.). The reaction mixture was stirred at room temperature for 30 h. The solvent was removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-ether 50:50) to provide unprotected triyne **11** (1.43 g, 92%) as a pale yellow solid.

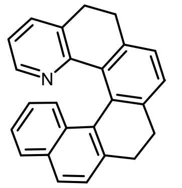
^{1}H NMR (500 MHz, $CDCl_3$): 1.99 (1 H, t, *J* = 2.6), 2.02 (1 H, t, *J* = 2.6), 2.70 (2 H, dt, *J* = 7.5, 7.5, 2.6), 2.70 (2 H, dt, *J* = 7.3, 7.3, 2.6), 3.22 (2 H, t, *J* = 7.3), 3.36 (2 H, t, *J* = 7.5), 7.26 (1 H, dd, *J* = 7.8, 4.8), 7.47 (1 H, d, *J* = 8.4), 7.50 (1 H, ddd, *J* = 8.1, 6.8, 1.2), 7.61 (1 H, ddd, *J* = 8.4, 6.8, 1.3), 7.70 (1 H, ddt, *J* = 7.8, 1.7, 0.6, 0.6), 7.84 (1 H, bd, *J* = 8.4), 7.84 (1 H, ddt, *J* = 8.1, 1.3, 0.6, 0.6), 8.52 (1 H, ddt, *J* = 8.4, 1.2, 0.9, 0.9), 8.60 (1 H, dd, *J* = 4.8, 1.7).

^{13}C NMR (125 MHz, $CDCl_3$): 19.32 (t), 19.88 (t), 32.46 (t), 34.37 (t), 69.31 (d), 69.81 (d), 82.90 (s), 83.55 (s), 89.02 (s), 96.35 (s), 118.52 (s), 122.78 (d), 126.07 (d), 126.29 (d), 127.12 (d), 127.29 (d), 128.11 (d), 129.26 (d), 131.96 (s), 133.81 (s), 136.76 (d), 137.72 (s), 142.07 (s), 143.10 (s), 148.44 (d).

IR ($CHCl_3$): 3309 vs, 3058 w, 2205 w, 2119 w, 1620 vw, 1592 w, 1582 m, 1566 m, 1556 w (sh), 1508 w, 1453 w (sh), 1436 vs, 1430 s, 1103 m, 1067 w, 1026 w, 867 w, 820 m, 642 s.

EI MS: 333 ($M^{+\cdot}$, 33), 332 (100), 318 (19), 317 (19), 294 (32), 278 (21), 254 (12), 226 (8), 142 (11), 73 (5).

Accurate mass (EI MS): calculated for $C_{25}H_{19}N$ 333.1518; found 333.1512.



5,6,9,10-Tetrahydrobenzo[5,6]phenanthro[3,4-*h*]quinoline 12. Triyne **11** (50 mg, 0.15 mmol), PPh_3 (16 mg, 59 μmol, 39 mol %), $CpCo(CO)_2$ (4 μl, 30 μmol, 20 mol %), decane (7 ml). The cyclization procedure afforded tetrahydrohelicene **12** (41 mg, 82%) as an amorphous yellowish solid.

Mp 225-227 °C (dioxane).

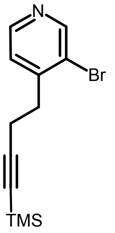
^{1}H NMR (500 MHz, $CDCl_3$): 2.65-2.74 (1 H, m), 2.83-2.91 (2 H, m), 2.96 (1 H, ddd, *J* = 15.1, 4.6, 1.9), 3.07-3.12 (2 H, m), 6.65 (1 H, dd, *J* = 7.5, 4.8), 6.75 (1 H, ddd, *J* = 8.7, 6.7, 1.4), 7.07 (1 H, ddd, *J* = 8.0, 6.8, 1.2), 7.20 (1 H, ddt, *J* = 7.4, 1.3, 0.6, 0.6), 7.33 (1 H, bdd, *J* = 7.4, 1.3), 7.37 (1 H, dq, *J* = 8.7, 1.0, 1.0, 1.0), 7.40 (1 H, ddt, *J* = 7.5, 1.8, 0.8, 0.8), 7.46 (1 H, bdd, *J* = 8.2, 0.2), 7.65 (1 H, ddt, *J* = 8.0, 1.4, 0.6, 0.6), 7.67 (1 H, bdd, *J* = 8.2, 0.8).

^{13}C NMR (125 MHz, $CDCl_3$): 29.24 (t), 29.25 (t), 30.46 (t), 30.93 (t), 120.86 (d), 123.52 (d), 124.47 (d) (two carbon atoms), 125.94 (d), 126.41 (d), 127.17 (d), 127.64 (d), 127.72 (d), 130.29 (s), 132.11 (s), 132.55 (s), 132.78 (s), 133.02 (s), 133.88 (s), 134.29 (d), 137.19 (s), 138.64 (s), 140.90 (s), 146.50 (d), 154.18 (s).

IR ($CHCl_3$): 3056 m, 3009 s, 2944 vs, 2839 m, 1586 m, 1569 m, 1509 w, 1451 s, 1436 vs, 1410 m, 1377 m, 1159 w, 1111 w, 1028 w, 865 w, 834 s, 822 s, 813 m.

EI MS: 333 ($M^{+\cdot}$, 100), 300 (8), 277 (8), 167 (6), 149 (42), 83 (7), 71 (10), 57 (23).

Accurate mass (EI MS): calculated for $C_{25}H_{19}N$ 333.1518; found 333.1526.



3-Bromo-4-[4-(trimethylsilyl)but-3-yn-1-yl]pyridine 14. A 100 ml flask was charged with diisopropylamine (1.23 g, 12.13 mmol, 1.05 equiv.) in THF (20 ml) under argon and cooled to 0°C. n-BuLi (1.6 M solution in hexanes, 7.30 ml, 11.68 mmol, 1.01 equiv.) was added dropwise and the mixture was stirred at 0°C for 30 min. Bromopyridine **13** (1.99 g, 11.57 mmol) in THF (10 ml) was added and the reaction mixture was stirred at 50°C for 45 min. After cooling it to 0°C, a solution of (3-bromoprop-1-yn-1-yl)(trimethyl)silane (2.55 g, 13.34 mmol, 1.15 equiv.) in THF (10 ml) was added. The mixture was stirred at 0°C for 3 h and then allowed to reach room temperature. Solvents were removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-acetone 90:10) to provide alkyne **14** (3.02 g, 93%) as a yellowish oil.

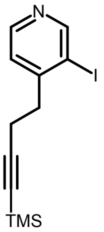
^{1}H NMR (500 MHz, $CDCl_3$): 0.13 (9 H, s), 2.57 (2 H, t, J = 7.2), 2.94 (2 H, t, J = 7.2), 7.23 (1 H, d, J = 4.9), 8.43 (1 H, bd, J = 4.9), 8.67 (1 H, bs).

^{13}C NMR (125 MHz, $CDCl_3$): -0.02 (q), 19.23 (t), 34.26 (t), 86.55 (s), 104.71 (s), 123.00 (s), 125.66 (d), 148.03 (d), 148.21 (s), 151.90 (d).

IR ($CHCl_3$): 3057 w, 2902 m, 2175 m, 1587 m, 1477 w, 1468 w, 1402 s, 1339 w, 1320 w, 1252 s, 845 vs, 698 m, 604 w.

EI MS: 283 ($M^{+\cdot}$ with ^{81}Br, 3), 281 ($M^{+\cdot}$ with ^{79}Br, 3), 268 (with ^{81}Br, 98), 266 (with ^{79}Br, 100), 202 (60), 196 (8), 186 (62), 144 (99).

Accurate mass (EI MS): calculated for $C_{12}H_{16}{}^{79}BrNSi$ 281.0235; found 281.0244; calculated for $C_{12}H_{16}{}^{81}BrNSi$ 283.0214; found 283.0188.



3-Iodo-4-[4-(trimethylsilyl)but-3-yn-1-yl]pyridine 15. A Schlenk flask was charged with bromopyridine **14** (709 mg, 2.51 mmol) and filled with argon. Diethyl ether (30 ml) was added, the solution was cooled to -78°C, and n-BuLi (1.6 M solution in hexanes, 2.77 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was stirred at -78°C for 30 min. Then, a solution of iodine (959 mg, 3.79 mmol, 1.51 equiv.) in diethyl ether (7 ml) was added and the mixture was stirred at -78°C for 1.5 h. After reaching room temperature, the resulting mixture was poured into cold water (50 ml) and the product was extracted with diethyl ether (2 × 50 ml). The combined organic fractions were washed with aqueous sodium thiosulfate (2 × 50 ml), solvents were evaporated *in vacuo*, and the crude product was chromatographed on silica gel (hexane-acetone 90:10) to provide iodopyridine **15** (678 mg, 82%) as an yellowish oil.

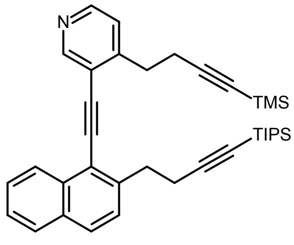
^{1}H NMR (500 MHz, $CDCl_3$): 0.13 (9 H, s), 2.55 (2 H, t, *J* = 7.2), 2.91 (2 H, t, *J* = 7.2), 7.25 (1 H, d, *J* = 5.0), 8.48 (1 H, bd, *J* = 5.0), 8.93 (1 H, bs).

^{13}C NMR (125 MHz, $CDCl_3$): -0.01 (q), 19.44 (t), 38.72 (t), 86.66 (s), 99.85 (s), 104.53 (s), 125.42 (d), 148.90 (d), 151.69 (s), 157.61 (d).

IR ($CHCl_3$): 2174 w, 1580 w, 1468 w, 1399 w, 1252 m, 845 vs, 700 w, 602 vw.

EI MS: 329 ($M^{+\cdot}$, 14), 314 (57), 202 (100), 186 (44), 144 (54).

Accurate mass (EI MS): calculated for $C_{12}H_{16}INSi$ 329.0097; found 329.0104.



4-[4-(Trimethylsilyl)but-3-yn-1-yl]-3-[(2-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}naphthalen-1-yl)ethynyl]pyridine 16. A Schlenk flask was charged with diyne **9** (420 mg, 1.16 mmol, 1.14 equiv.), $Pd(PPh_3)_4$ (59 mg, 0.051 mmol, 5%), CuI (23 mg, 0.121 mmol, 12%) and filled with argon. A solution of iodopyridine **15** (335 mg, 1.02 mmol) in diisopropylamine (30 ml) was added and the reaction was stirred at room temperature for 40 min. The solvent was removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-acetone 80:20) to provide triyne **16** (520 mg, 91%) as an off-white solid.

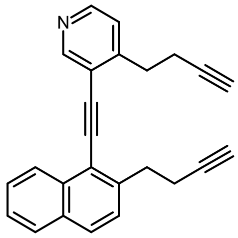
^{1}H NMR (500 MHz, $CDCl_3$): 0.12 (9 H, s), 0.96-1.04 (21 H, m), 2.72 (2 H, t, *J* = 7.3), 2.76 (2 H, t, *J* = 7.3), 3.16 (2 H, t, *J* = 7.3), 3.32 (2 H, t, *J* = 7.3), 7.29 (1 H, d, *J* = 5.1), 7.51 (1 H, d, *J* = 8.3), 7.51 (1 H, ddd, *J* = 8.1, 6.8, 1.2), 7.61 (1 H, ddd, *J* = 8.4, 6.8, 1.3), 7.80 (1 H, bd, *J* = 8.3), 7.85 (1 H, ddt, *J* = 8.1, 1.3, 0.6, 0.6), 8.40 (1 H, dq, *J* = 8.4, 1.0, 1.0, 1.0), 8.51 (1 H, bd, *J* = 5.1), 8.86 (1 H, bs).

^{13}C NMR (125 MHz, $CDCl_3$): -0.02 (q), 11.28 (d), 18.57 (q), 20.24 (t), 21.32 (t), 33.41 (t), 34.81 (t), 81.60 (s), 86.40 (s), 92.94 (s), 93.62 (s), 105.08 (s), 107.59 (t), 118.65 (s), 120.59 (s), 123.92 (d), 125.88 (d), 125.94 (d), 127.14 (d), 127.49 (d), 128.22 (d), 128.95 (d), 132.02 (s), 133.49 (s), 142.00 (s), 148.51 (d), 150.17 (s), 152.75 (d).

IR ($CHCl_3$): 3059 w, 2960 vs, 2944 vs, 2866 s, 2200 w, 2172 m, 1620 w, 1600 m (sh), 1589 m, 1568 w, sh, 1508 w, 1487 w, 1464 m, 1450 m (sh), 1406 m, 1383 m, 1366 m, 1252 s, 1173 w, 1074 m, 1026 m, 996 m, 884 s, 845 vs, 821 m, 698 w, 679 m, 662 m.

EI MS: 561 ($M^{+\cdot}$, 11), 518 (86), 451 (20), 408 (64), 366 (6), 266 (36), 254 (8), 223 (5), 202 (22), 186 (20), 149 (59), 144 (36), 115 (10), 87 (17), 73 (100), 59 (56).

Accurate mass (EI MS): calculated for $C_{37}H_{47}NSi_2$ 561.3247; found 561.3225.



4-But-3-yn-1-yl-3-[(2-but-3-yn-1-ylnaphthalen-1-yl)ethynyl]-pyridine 17. A Schlenk flask was charged with triyne **16** (520 mg, 0.926 mmol) and filled with argon. THF (20 ml) was added and the resulting solution was treated with a solution of n-Bu_4NF • 3 H_2O (731 mg, 2.32 mmol, 2.50 equiv.) in THF (10 ml). After stirring at room temperature for 1 h, the solvent was removed *in vacuo* and the crude product was chromatographed on silica gel (hexane-acetone 80:20) to provide unprotected triyne **17** (260 mg, 84%) as a pale yellow solid.

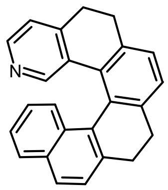
^{1}H NMR (500 MHz, $CDCl_3$): 2.02 (1 H, t, J = 2.6), 2.04 (1 H, t, J = 2.6), 2.68 (2 H, dt, J = 7.6, 7.6, 2.6), 2.71 (2 H, dt, J = 7.4, 7.4, 2.6), 3.20 (2 H, t, J = 7.4), 3.33 (2 H, t, J = 7.6), 7.31 (1 H, dd, J = 5.1, 0.8), 7.46 (1 H, d, J = 8.4), 7.52 (1 H, ddd, J = 8.1, 6.8, 1.2), 7.62 (1 H, ddd, J = 8.5, 6.8, 1.4), 7.84 (1 H, bd, J = 8.4), 7.86 (1 H, ddt, J = 8.1, 1.4, 0.7, 0.7), 8.41 (1 H, ddt, J = 8.5, 1.2, 0.9, 0.9), 8.52 (1 H, d, J = 5.1), 8.88 (1 H, d, J = 0.8).

^{13}C NMR (125 MHz, $CDCl_3$): 18.72 (t), 19.88 (t), 33.16 (t), 34.55 (t), 69.32 (d), 69.83 (d), 82.59 (s), 83.43 (s), 92.72 (s), 93.68 (s), 118.71 (s), 120.42 (s), 123.63 (d), 125.84 (d), 126.08 (d), 127.20 (d), 127.25 (d), 128.27 (d), 129.11 (d), 131.98 (s), 133.42 (s), 141.66 (s), 148.72 (d), 149.86 (s), 152.87 (d).

IR ($CHCl_3$): 3309 vs, 3059 w, 2203 w, 2119 w, 1620 vw, 1588 m, 1568 w, 1552 w, 1510 w, 1488 w, 1432 w, 1260 w, 1046 w, 1026 w, 962 vw, 891 vw, 867 w, 820 m, 642 vs, 435 w.

EI MS: 333 ($M^{+\cdot}$, 50), 332 (100), 318 (45), 305 (31), 292 (41), 278 (50), 265 (19), 254 (26), 239 (17), 226 (36), 215 (13), 202 (33), 189 (24), 178 (13), 165 (17), 139 (13), 115 (8), 97 (11), 83 (15), 71 (28), 55 (34), 43 (35).

Accurate mass (EI MS): calculated for $C_{25}H_{19}N$ 333.1518; found 333.1514.



5,6,9,10-Tetrahydrobenzo[5,6]phenanthro[3,4-*h*]isoquinoline 18. Triyne **17** (108 mg, 0.32 mmol), PPh_3 (31 mg, 0.118 mmol, 37 mol %), $CpCo(CO)_2$ (8 μl, 0.060 mmol, 19 mol %), decane (8 ml). The cyclization procedure afforded tetrahydroazahelicene **17** (96 mg, 89%) as an amorphous yellowish solid.

Mp 201-205 °C (hexane-acetone).

^{1}H NMR (500 MHz, $CDCl_3$): 2.65-2.78 (5 H, m), 2.85-3.05 (3 H, m), 6.87 (1 H, ddd, *J* = 8.6, 6.7, 1.4), 7.07 (1 H, bd, *J* = 4.5), 7.12 (1 H, ddd, *J* = 8.0, 6.7, 1.2), 7.22 (1 H, dd, *J* = 7.4, 1.1), 7.31 (1 H, dd, *J* = 7.4, 1.2), 7.42 (1 H, dq, *J* = 8.6, 1.0, 1.0, 1.0), 7.47 (1 H, d, *J* = 8.1), 7.52 (1 H, bd, *J* = 4.5), 7.67 (1 H,ddt, *J* = 8.0, 1.4, 0.7, 0.7), 7.72 (1 H, bd, *J* = 8.1), 7.97 (1 H, bs).

^{13}C NMR (125 MHz, $CDCl_3$): 29.04 (t), 29.13 (t), 30.50 (t), 30.96 (t), 121.99 (d), 124.34 (d), 124.98 (d), 125.36 (d), 126.26 (d), 126.51 (d), 127.01 (s), 128.25 (d) (two carbon atoms), 128.44 (s), 128.88 (s), 130.88 (s), 131.10 (s), 131.20 (s), 133.30 (s), 137.71 (s), 138.42 (s), 140.97 (s), 145.74 (s), 146.71 (d), 148.18 (d).

IR ($CHCl_3$): 3056 m, 3011 s, 1622 w (sh), 1600 m, 1583 w, 1571 w (sh), 1555 w, 1509 m, 1491 m, 1467 m, 1458 m, 1437 s, 1406 s, 1378 m, 1351 w, 1328 w, 1322 w, 1240 m, 1159 w, 1051 w, 1027 w, 885 m, 866 w, 835 vs, 820 s, 813 s, 688 m.

EI MS: 333 ($M^{+\cdot}$, 100), 305 (8), 277 (11), 159 (7), 85 (7), 71 (10), 57 (15), 43 (9).

Accurate mass (EI MS): calculated for $C_{25}H_{19}N$ 333.1518; found 333.1510.

X-Ray Analysis of 1-Aza[6]helicene 2. Racemic azahelicene **2** (4 mg) was refluxed in heptane (2 ml) until dissolved. The resulting solution in a capped vial was placed in a Dewar flask filled with hot water. The sample was allowed to cool to room temperature over the period of 3 days. Single crystals of **2** were separated; $C_{25}H_{15}N$, M_r = 329.38; orthorhombic, space group *Pbca*, *a* = 9.8414 (4) Å, *b* = 15.8948 (7) Å, *c* = 21.6929 (9) Å; Z = 8, D_{calc} 1.289 Mgm^{-3}; dimensions of yellow crystal 0.61 × 0.58 × 0.47 mm^3; X-ray data were measured on CCD detector with MoK_α radiation, T=150(2) K; θ_{max} = 26.7°; 36819 diffractions collected, 3574 independent (R_{int} = 0.110); an absorption neglected (μ = 0.08 mm^{-1}). Refinement method: full matrix least squares based on F^2, 235 parameters, goodness of fit 1.08, final R indices [$I > 2\sigma(I)$] R1=0.059, wR2(all data) = 0.191, maximal/minimal residual electron density 0.33/−0.27 $eÅ^{-3}$.

X-Ray Analysis of 2-Aza[6]helicene 3. Dichloromethane was added dropwise to a slurry of racemic azahelicene **3** (4 mg) in refluxing heptane (2 ml) until the solid was dissolved. The resulting solution in a capped vial was placed in a Dewar flask filled with hot water. The sample was allowed to cool to room temperature over a period of 3 days. Single crystals of **3** were separated; $C_{25}H_{15}N$, M_r = 329.38; monoclinic, space group *$P2_1/c$*, *a* = 16.542 (2) Å, *b* = 15.035 (5) Å, *c* = 14.245 (2) Å, β = 112.793 (14)° ; Z = 8, D_{calc} 1.340 Mgm^{-3}; dimensions of yellow crystal 0.34 × 0.14 × 0.03 mm^3; X-ray data were measured on CCD detector with MoKα radiation, T=150(2) K; θ_{max} = 25.1°; 20975 diffractions collected, 5809 independent (R_{int} = 0.066); an absorption neglected (μ = 0.08 mm^{-1}). Refinement method: full matrix least squares based on F^2, 469 parameters, goodness of fit 0.64, final R indices [$I > 2\sigma(I)$] R1=0.034, wR2(all data) = 0.067, maximal/minimal residual electron density 0.13/−0.16 $eÅ^{-3}$.

X-Ray Analysis of 5,6,9,10-Tetrahydrobenzo[5,6]phenanthro[3,4-*h*]quinoline 12. Racemic azahelicene **12** (2 mg) was dissolved in 3 ml of a hexane-diethyl ether-acetone mixture (80:10:10). The vial was capped and pierced with a needle and set aside to allow slow evaporation of solvents. After three days single crystals of **12** were separated; $C_{25}H_{19}N$, M_r = 333.41; triclinic, space group *P-1 (No 2)*, *a* = 7.5486 (2) Å, *b* = 10.4213 (2) Å, *c* = 11.3060 (3) Å, α = 94.4738 (9)°, β = 100.3361 (10)°, γ = 103.2240 (10)°; Z = 2, D_{calc} 1.310 Mgm^{-3}; dimensions of colorless crystal 0.28 × 0.2

× 0.18 mm^3; X-ray data were measured on CCD detector with MoKα radiation, T=150(2) K; θ_{max} = 27.5°; 15083 diffractions collected, 3852 independent (R_{int} = 0.036); an absorption neglected (μ = 0.08 mm^{-1}). Refinement method: full matrix least squares based on F^2, 236 parameters, goodness of fit 1.03, final R indices [$I > 2\sigma(I)$] R1= 0.043, wR2(all data) = 0.116, maximal/minimal residual electron density 0.26/−0.20 eÅ^{-3}.

X-Ray Analysis of [Ag(1-aza[6]helicene)$_2$(PrOH)][OTf] 20. A solution of racemic azahelicene **2** (2 mg, 6.08 μmol) in toluene (1 ml) was added to a solution of AgOTf (1 mg, 3.89 μmol) in toluene (1 ml) at room temperature. Immediate precipitation of a complex occurred. The solvent was removed *in vacuo* and heptane (2 ml) was added. Propanol was added dropwise to a refluxing mixture of the complex in heptane until the solid was dissolved. The resulting solution in a capped vial was placed in a Dewar flask filled with hot water. The sample was allowed to cool to room temperature over a period of 3 days. Single crystals of **20** were separated; $C_{53}H_{38}AgN_2O\cdot CF_3O_3S$, M_r = 975.79; monoclinic, space group $P\ 2_1/n$,, a = 18.174 (2) Å, b = 12.728 (2) Å, c = 18.724 (3) Å, β = 103.738 (12)°; Z = 4, D_{calc} 1.541 Mgm^{-3}; dimensions of colorless crystal 0.3 × 0.19 × 0.08 mm^3; X-ray data were measured on CCD detector with MoKα radiation, T=150(2) K; θ_{max} = 26.6°; 55741 diffractions collected, 8781 independent (R_{int} = 0.025); an absorption neglected (μ = 0.60 mm^{-1}). Refinement method: full matrix least squares based on F^2, 587 parameters, goodness of fit 1.10, final R indices [$I > 2\sigma(I)$] R1= 0.027, wR2(all data) = 0.077, maximal/minimal residual electron density 1.21/−0.50 eÅ^{-3}.

X-Ray Analysis of Ag(2-aza[6]helicene)$_2$][OTf] 21. A solution of racemic azahelicene **3** (2 mg, 6.08 μmol) in toluene (1 ml) was added to a solution of AgOTf (1 mg, 3.89 μmol) in toluene (1 ml) at room temperature. Immediate precipitation of a complex occurred. The heterogeneous mixture was refluxed until the solid dissolved. The resulting solution in a capped vial was placed in a Dewar flask filled with hot water. The sample was allowed to cool to room temperature over a period of 3 days. Single crystals of **21** were separated; $C_{51}H_{30}AgF_3N_2O_3S\cdot C_7H_8$, M_r = 1007.83; monoclinic, space group $P\ 2_1/n$,, a = 12.5583 (3) Å, b = 12.9296 (4) Å, c = 28.3045 (14) Å, β = 101.716 (3)°; Z = 4, D_{calc} 1.488 Mgm^{-3}; dimensions of colorless crystal

$0.31 \times 0.19 \times 0.07$ mm^3; X-ray data were measured on CCD detector with MoKα radiation, T=150(2) K; θ_{max} = 26.0°; 27399 diffractions collected, 8920 independent (R_{int} = 0.038); an absorption neglected (μ = 0.56 mm^{-1}). Refinement method: full matrix least squares based on F^2, 587 parameters, goodness of fit 1.07, final R indices [I > 2σ(I)] R1= 0.056, wR2(all data) = 0.159, maximal/minimal residual electron density 1.15/−0.66 eÅ^{-3}. The correction for twinning (matrix -1 0 0, 0 -1 0, 1 0 1) were applied during refinement. The solvating toluene molecule is disordered over two positions.

Optical resolution of 1-aza[6]helicene 2. Optical resolution of racemic azahelicene **2** via diastereoisomeric salts was attempted using mandelic, malic, tartaric, di-O-toluoyltartaric, 10-camphorsulfonic, and Mosher acids without success. Eventually, we succeeded with (+)-di-O-benzoyltartaric acid, applied in large excess. Under these conditions, the acid formed with racemic **2** a yellow, diastereoisomerically enriched solid. It contained the respective components in a 2:1 ratio. Crystallization of this adduct was not practical and thus it was purified only by boiling in diethyl ether (liberated (+)-**2** exhibited about 95% ee). After basification, (+)-**2** was crystallized from diethyl ether-pentane to give optically pure (+)-**2**. The laevorotatory enantiomer was obtained from the mother liquors using the enantiomeric (-)-di-O-benzoyltartaric acid and the above-mentioned procedure.

(+)-1-Aza[6]helicene 2. A saturated solution of racemic azahelicene **2** (50.3 mg) in diethyl ether (10 ml) was mixed with a solution of (+)-di-O-benzoyltartaric acid (unnatural isomer, 400 mg) in diethyl ether (3 ml) and the solvent was slowly evaporated under stirring and heating. After concentration to about 4 ml, a yellow solid separated from the clear solution (about 75 % ee, analyzed as a free base). This was collected, washed with a small amount of cold diethyl ether and then boiled in ether (6 ml) under stirring for 2 h. After cooling, the product was collected on a filter, washed with cold diethyl ether and dried to yield a yellow solid material (36 mg, 93 % ee after basification). Calculated for $C_{25}H_{15}N \cdot 2\ C_{18}H_{14}O_8$ 70.04 % C, 4.14 % H, 1.34 % N; found 69.88 % C, 4.05 % H, 1.27 % N. Azahelicene (+)-**2** was liberated with aqueous sodium hydroxide and taken up in ether. The solvent was evaporated and the crude product was crystallized from diethyl ether-pentane to afford (+)-1-aza[6]helicene **2** (10 mg, >99 % ee) as yellowish crystals. **Mp** 209-211 °C (the pure enantiomer completely racemized at the melting point), **[α]$^{25}_{D}$** +3 615 (c 0.001, dichloromethane), retention time 10.5 min (Chiralcel OD-H column).

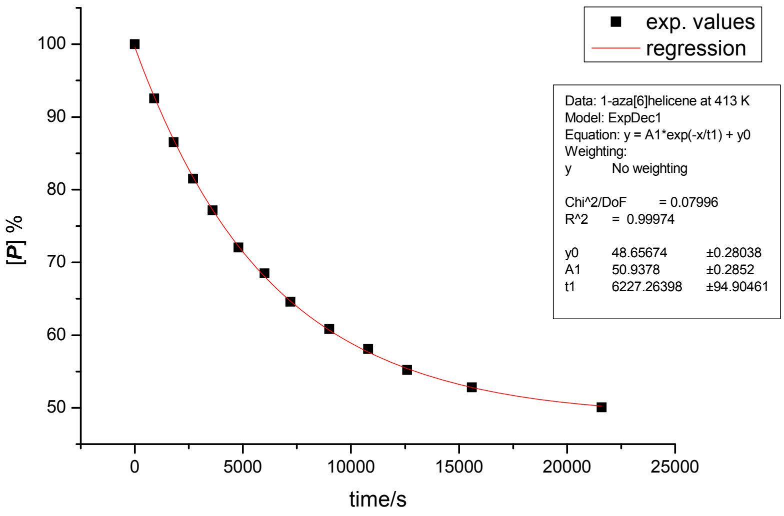
(-)-1-Aza[6]helicene 2. Mother liquors from the preparation and purification of the addition salt to resolve racemic **2** (100 mg) were evaporated and basified to afford (-)-**2** (45.8 mg, 62 % ee). This was dissolved in diethyl ether (5 ml), mixed with a solution of (-)-di-O-benzoyltartaric acid (natural isomer, 250 mg) in diethyl ether (2 ml), and the precipitated adduct was purified as described above. Basification of the adduct (85.4 mg) gave (-)-**2** (17 mg, 95 % ee), which on crystallization from diethyl ether-pentane afforded optically pure (-)-1-aza[6]helicene **2** (10 mg, >99 % ee) as yellowish crystals. **Mp** 212-213 °C (the pure enantiomer completely racemized at the melting point). **[α]$^{25}_{D}$** -3 631 (c 0.001, dichloromethane), retention time 9.1 min (Chiralcel OD-H column).

Optical resolution of 2-aza[6]helicene 3. In HPLC on a Chiralcel OD-H column both enantiomers of racemic azahelicene **3** differed significantly in their retention times and, therefore, they were separated in a semipreparative way on an overloaded analytical column. Racemic azahelicene **3** (55 mg) was resolved by the repeated HPLC separation using an Agilent 1100 Series preparative instrument (heptane-isopropanol 3:1, 0.8 ml/min flow rate, 1.5 mg injections of a racemate in 900 μl of the eluent). Evaporation of the solvents and crystallization from diethyl ether afforded (-)-2-aza[6]helicene **3** (21 mg, >99 % ee) and (+)-2-aza[6]helicene **3** (19 mg, >99 % ee) as yellowish crystals.

(-)-2-Aza[6]helicene 3: **Mp** 251-252 °C (the pure enantiomer completely racemized at the melting point). **[α]$^{25}_{D}$** -3 840 (c 0.001, dichloromethane), retention time 9.4 min (Chiralcel OD-H column).

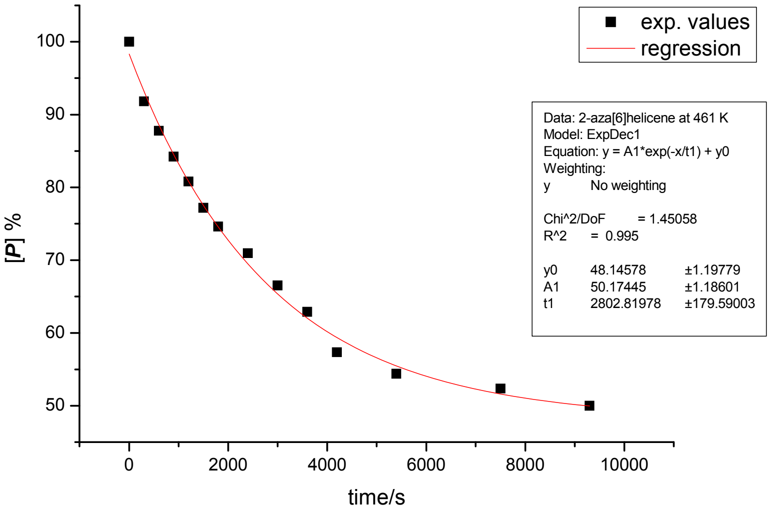
(+)-2-Aza[6]helicene 3: **Mp** 250-252 °C (the pure enantiomer completely racemized at the melting point). **[α]$^{25}_{D}$** +3 825 (c 0.001, dichloromethane), retention time 20.1 min (Chiralcel OD-H column).

Racemization of 1-aza[6]helicene 2. Optically pure (+)-**2** (2 mg, >99 % ee) in 1-decanol (2 ml) was distributed in 20 vials, that were heated to a constant temperature (413 K) using a thermostat (Block-Heater H 250, Rotilabo). The content of (+)-**2** (*P*, %) was monitored by HPLC (Chiralcel OD-H column) in the course of time (seconds).

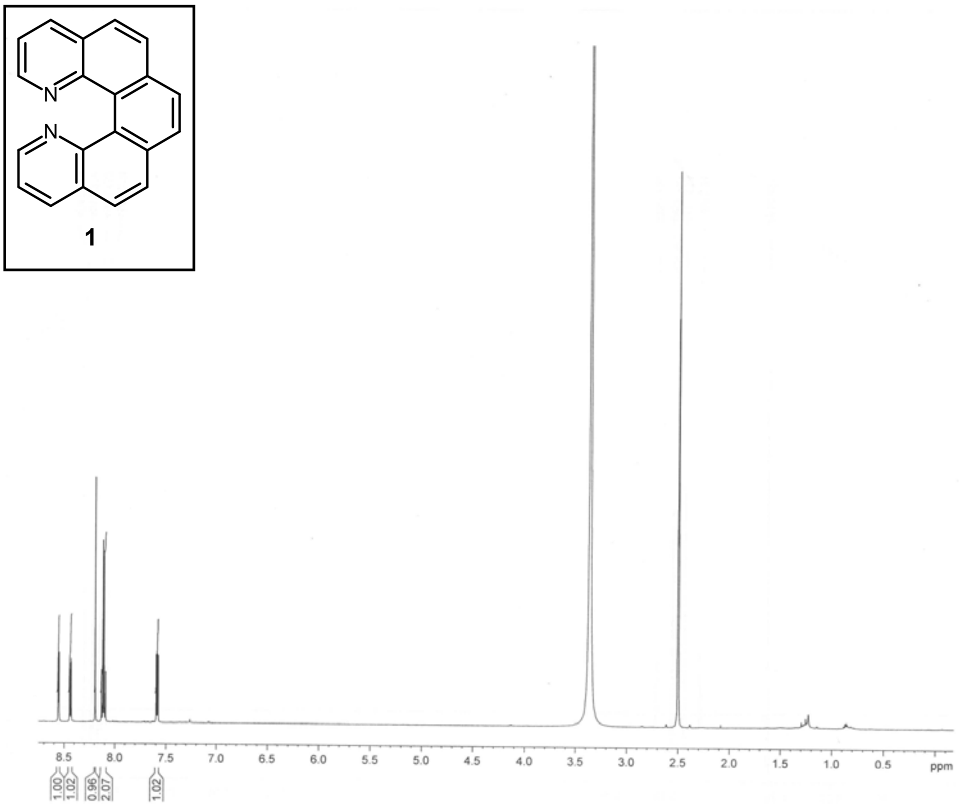


T (in K)	413
solvent	1-decanol
$\Delta G^{\neq}$ (in kJ/mol)	134.8
$t_{1/2}$ (in min)	71.9
k_i (in s^{-1})	8.03×10^{-5}

Racemization of 2-aza[6]helicene 3. Optically pure (+)-**3** (2 mg, >99 % ee) in 1-decanol (2 ml) was distributed in 20 vials that were heated to a constant temperature (461 K) using a thermostat (Block-Heater H 250, Rotilabo). The content of (+)-**2** (*P*, %) was monitored by HPLC (Chiralcel OD-H column) in the course of time (seconds).



T (in K)	461
solvent	1-decanol
$\Delta G^{\neq}$ (in kJ/mol)	147.8
$t_{1/2}$ (in min)	32.4
k_i (in s^{-1})	1.78×10^{-4}



1

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J.Misek   JIM-64
in DMSO, rfp=2.50 ppm
26.7.2007  DA
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Current Data Parameters
NAME             Misek-JIM64
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070726
Time                    7.17
INSTRUM                spect
PROBHD       5 mm CPTCI 1H
PULPROG                 zg30
TD                     48076
SOLVENT                 DMSO
NS                         8
DS                         0
SWH              6009.615 Hz
FIDRES           0.125002 Hz
AQ             3.9999733 sec
RG                         9
DW               83.200 usec
DE                 6.00 usec
TE                   300.0 K
D1            3.00000000 sec
TD0                        1

======== CHANNEL f1 =====
NUC1                      1H
P1                10.00 usec
PL1                  8.10 dB
SFO1          600.1326735 MH

F2 - Processing parameters
SI                    131072
SF           600.1300040 MHz
WDW                       no
SSB                        0
LB                   0.00 Hz
GB                         0
PC                      1.00
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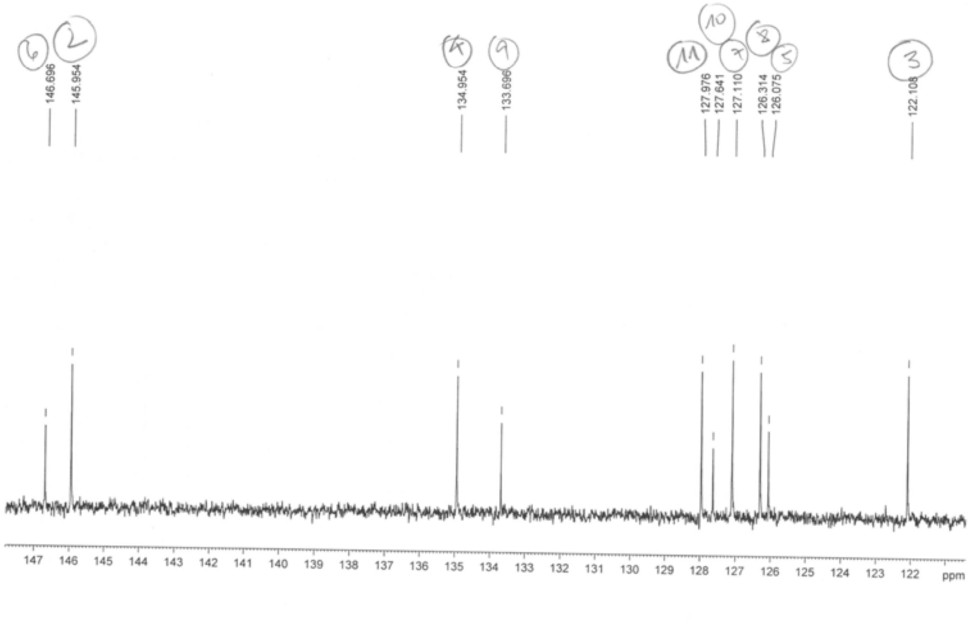
36737



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J.Misek   JIM-64
in DMSO, rfp=2.50 ppm
26.7.2007  DA
********************

Current Data Parameters
NAME             Misek-JIM64
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070726
Time                    7.20
INSTRUM                spect
PROBHD       5 mm CPTCI 1H
PULPROG               zgpg30
TD                     59520
SOLVENT                 DMSO
NS                      1024
DS                         4
SWH             29761.904 Hz
FIDRES           0.500032 Hz
AQ             0.9999860 sec
RG                     32800
DW               16.800 usec
DE                 6.50 usec
TE                   300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 se
TD0                        1

======== CHANNEL f1 =====
NUC1                     13C
P1                11.50 usec
PL1                 -1.40 dB
SFO1          150.9171448 MH

======== CHANNEL f2 =====
CPDPRG2              waltz16
NUC2                      1H
PCPD2             80.00 usec
PL12                25.00 dB
PL13                25.00 dB
PL2                  7.00 dB
SFO2          600.1324005 MH

F2 - Processing parameters
SI                     32768
SF           150.9028748 MHz
WDW                       EM
SSB                        0
LB                   1.00 Hz
GB                         0
PC                      1.40
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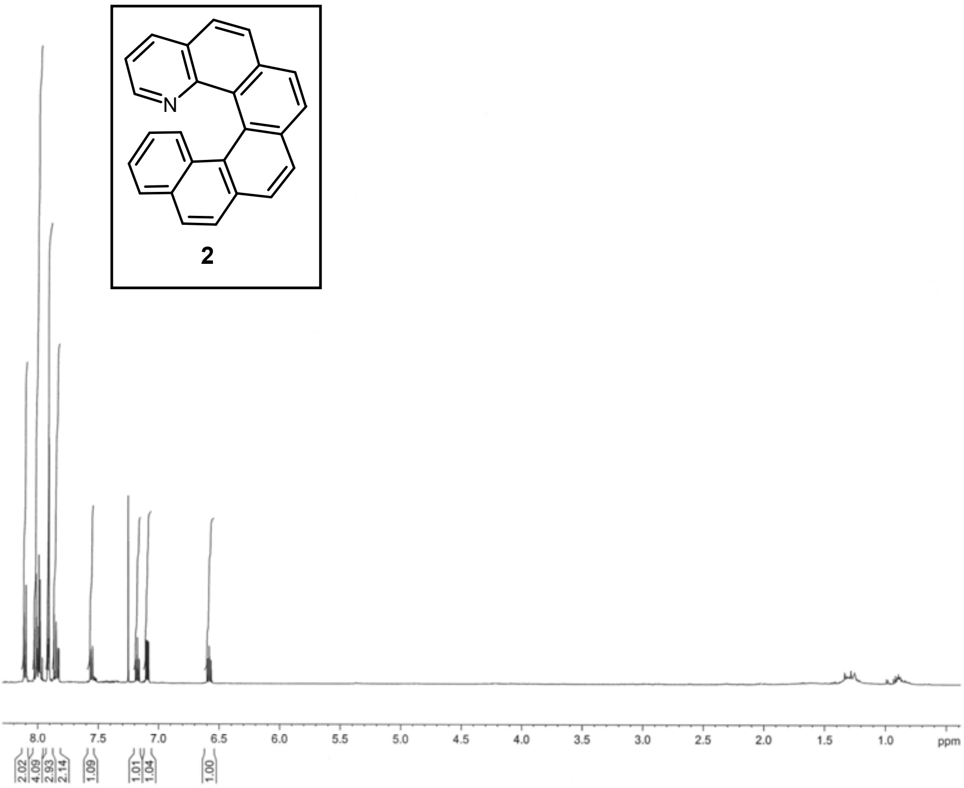
36737



2

J.Misek JIM-90
in CDCl3, ref=TMS
7.2.2006 DA
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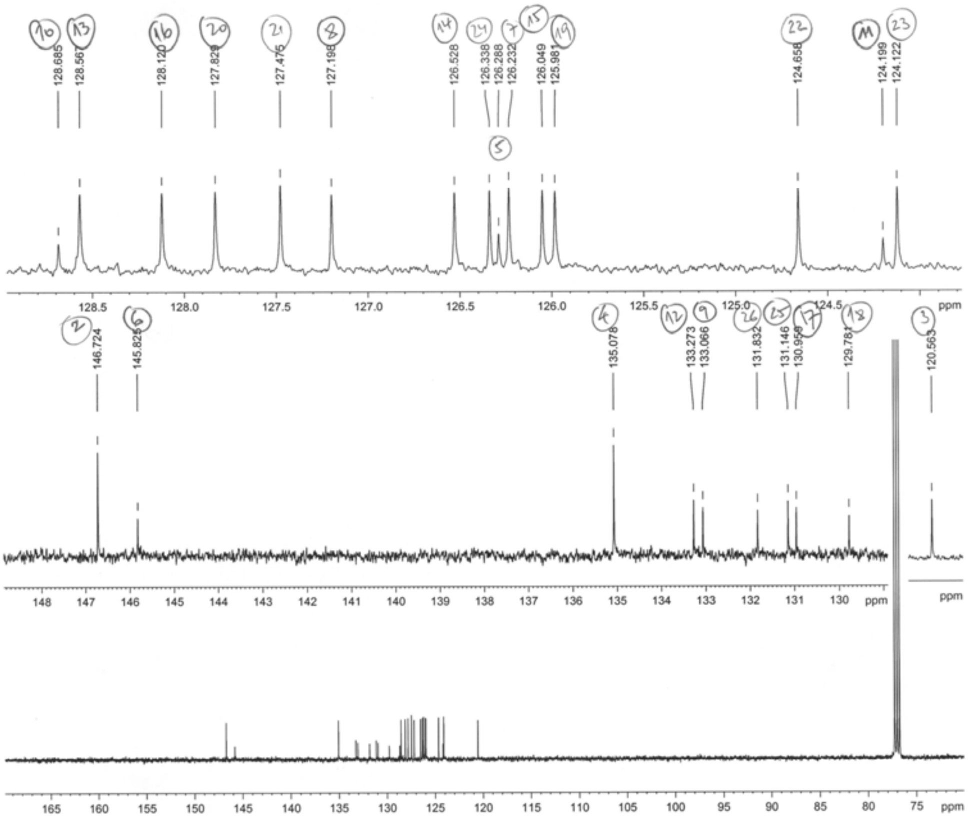
Current Data Parameters
NAME Misek-JIM90
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060207
Time 10.02
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG zg30
TD 39998
SOLVENT CDCl3
NS 64
DS 0
SWH 5000.000 Hz
FIDRES 0.125006 Hz
AQ 3.9999499 sec
RG 12.7
DW 100.000 usec
DE 6.00 usec
TE 300.0 K
D1 0.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.20 usec
PL1 1.00 dB
SFO1 500.1323006 MHz

F2 - Processing parameters
SI 131072
SF 500.1300168 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.35

33449



J.Misek JIM-90
in CDCl3, ref=TMS
7.2.2006 DA
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Current Data Parameters
NAME Misek-JIM90
EXPNO 3
PROCNO 1

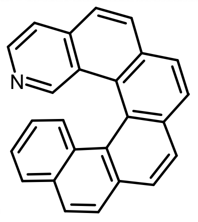
F2 - Acquisition Parameters
Date_ 20060207
Time 10.18
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG zgpg30
TD 25060
SOLVENT CDCl3
NS 1648
DS 8
SWH 12531.328 Hz
FIDRES 0.500053 Hz
AQ 0.9999839 sec
RG 32768
DW 39.900 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 15.50 usec
PL1 0.20 dB
SFO1 125.7728799 MHz

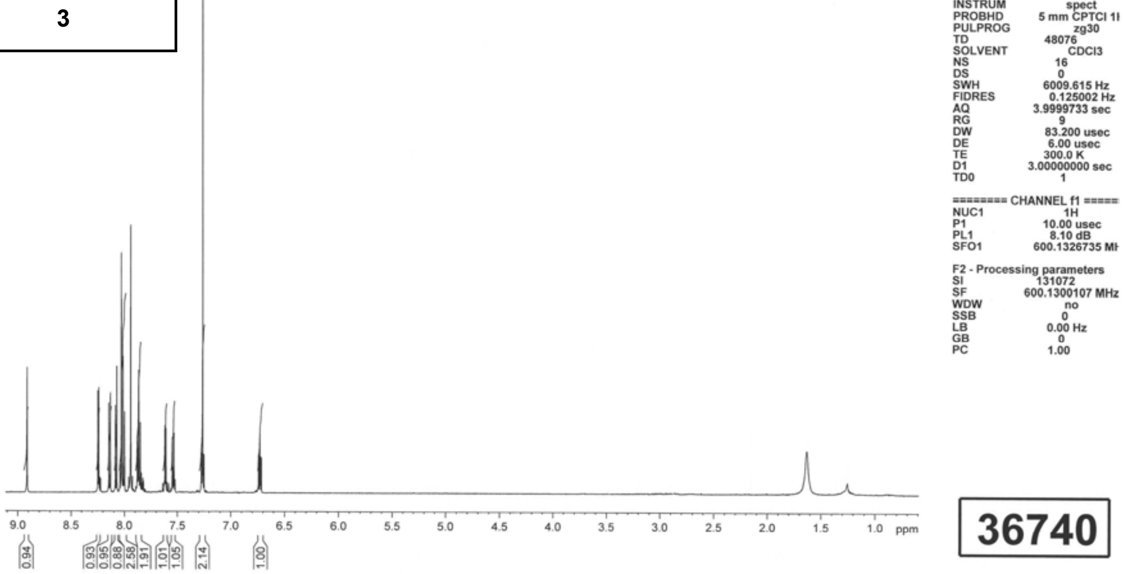
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 19.79 dB
PL13 19.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 131072
SF 125.7577933 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

33449



3



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J.Misek   JIM-140
in CDCl3, rfp=TMS
27.7.2007  DA
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Current Data Parameters
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EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070727
Time                  7.06
INSTRUM              spect
PROBHD      5 mm CPTCI 1I
PULPROG               zg30
TD                   48076
SOLVENT              CDCl3
NS                      16
DS                       0
SWH            6009.615 Hz
FIDRES         0.125002 Hz
AQ           3.9999733 sec
RG                       9
DW             83.200 usec
DE               6.00 usec
TE                 300.0 K
D1          3.00000000 sec
TD0                      1

======== CHANNEL f1 =====
NUC1                    1H
P1              10.00 usec
PL1                8.10 dB
SFO1        600.1326735 MI

F2 - Processing parameters
SI                  131072
SF        600.1300107 MHz
WDW                     no
SSB                      0
LB                 0.00 Hz
GB                       0
PC                    1.00
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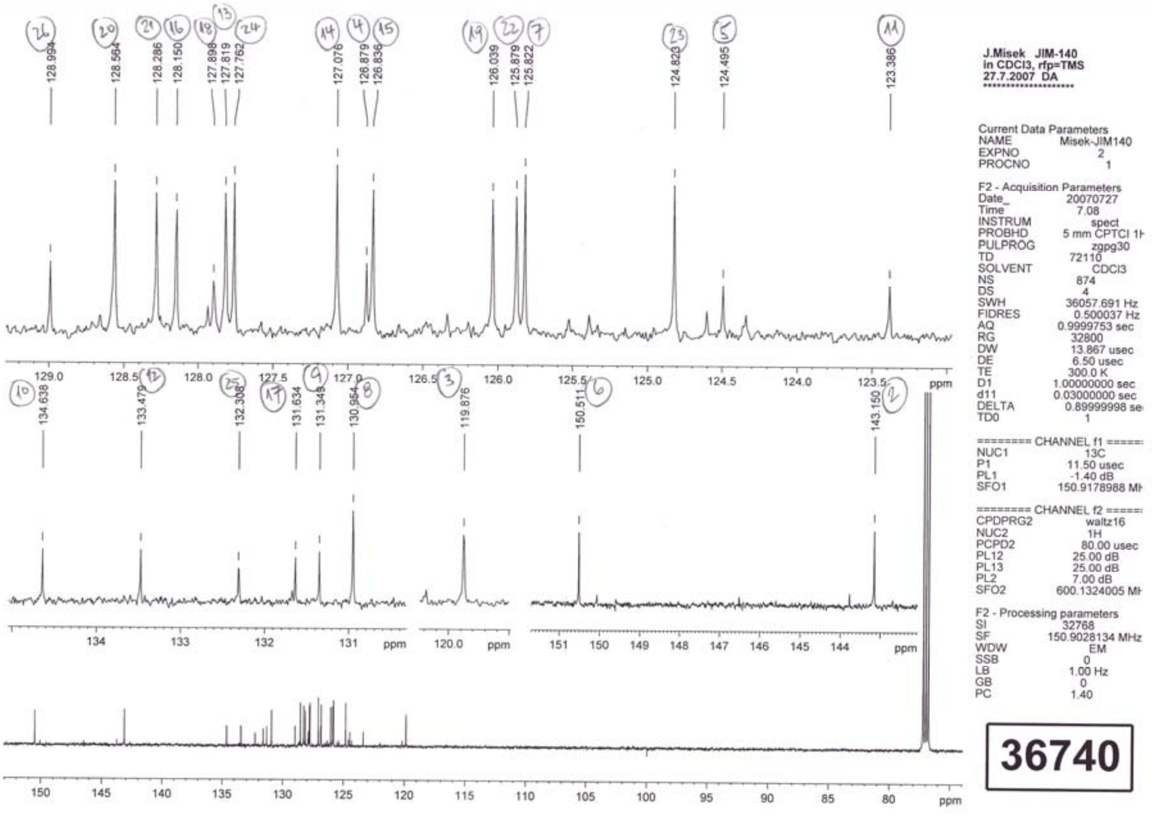
36740



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J.Misek   JIM-140
in CDCl3, rfp=TMS
27.7.2007  DA
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Current Data Parameters
NAME          Misek-JIM140
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070727
Time                  7.08
INSTRUM              spect
PROBHD      5 mm CPTCI 1H
PULPROG            zgpg30
TD                   72110
SOLVENT              CDCl3
NS                     874
DS                       4
SWH           36057.691 Hz
FIDRES         0.500037 Hz
AQ           0.9999753 sec
RG                   32800
DW             13.867 usec
DE               6.50 usec
TE                 300.0 K
D1          1.00000000 sec
d11         0.03000000 sec
DELTA       0.89999998 se
TD0                      1

======== CHANNEL f1 =====
NUC1                   13C
P1              11.50 usec
PL1               -1.40 dB
SFO1        150.9178988 MI

======== CHANNEL f2 =====
CPDPRG2           waltz16
NUC2                    1H
PCPD2           80.00 usec
PL12              25.00 dB
PL13              25.00 dB
PL2                7.00 dB
SFO2        600.1324005 MI

F2 - Processing parameters
SI                   32768
SF        150.9028134 MHz
WDW                     EM
SSB                      0
LB                 1.00 Hz
GB                       0
PC                    1.40
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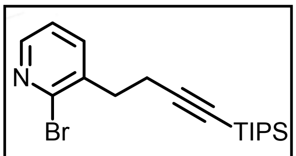
36740



5

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TEPLY   FT516
1H NMR in CDCl3, ref=TMS
Bruker 400 MHz
28-07-03 RA
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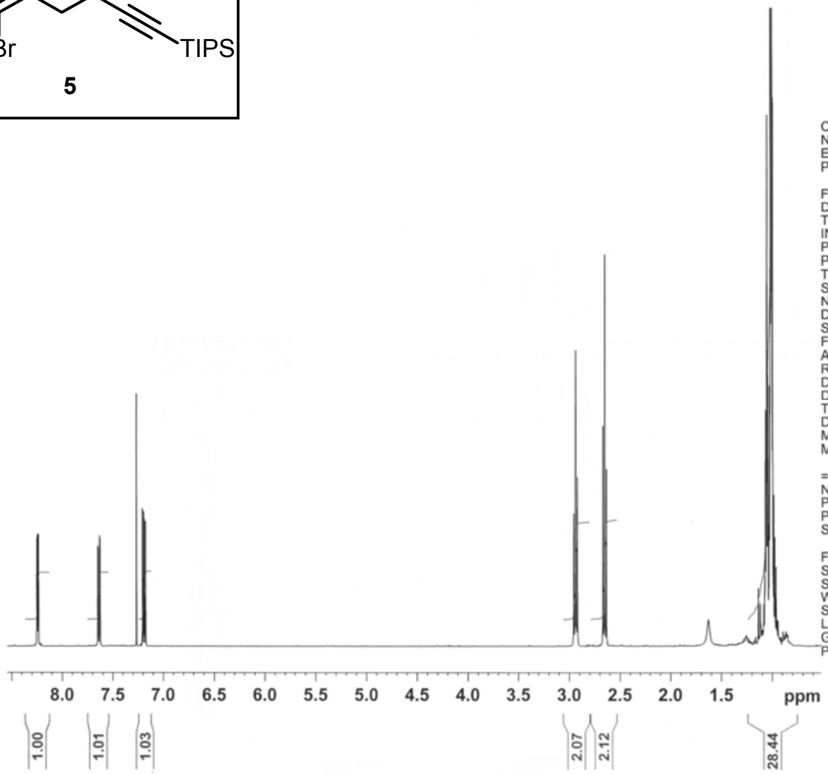

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Current Data Parameters
NAME       TEPLY_FT516
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20030728
Time            18.51
INSTRUM          spect
PROBHD   5 mm BBI 1H-BB
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                128
DS                  0
SWH          8278.146 Hz
FIDRES       0.126314 Hz
AQ          3.9584243 sec
RG               71.8
DW             60.400 usec
DE               6.00 usec
TE              297.2 K
D1         2.00000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1               1H
P1               8.00 usec
PL1              3.00 dB
SFO1      400.1324710 MHz

F2 - Processing parameters
SI             131072
SF        400.1300075 MHz
WDW                no
SSB                 0
LB               0.00 Hz
GB                  0
PC               1.00
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27627.

```
F.Teply           FT-516
in CDCl3, rfp=77.00 ppm
29.7.2003   DA
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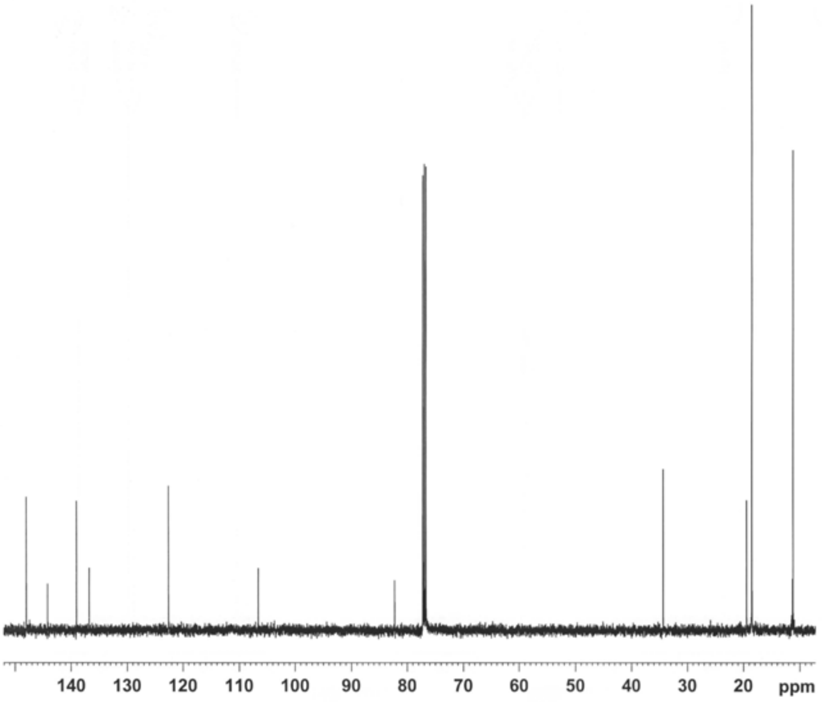

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Current Data Parameters
NAME       Teply-FT516
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
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Time            10.29
INSTRUM          spect
PROBHD   5 mm BBO BB-1H
PULPROG        zgpg30
TD              45450
SOLVENT          CDCl3
NS                193
DS                  8
SWH         22727.273 Hz
FIDRES       0.500050 Hz
AQ          0.9999720 sec
RG             1149.4
DW             22.000 usec
DE               6.00 usec
TE              303.0 K
D1         1.00000000 sec
d11        0.03000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1              13C
P1               4.90 usec
PL1             -3.00 dB
SFO1      125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2           81.00 usec
PL2             -5.00 dB
PL12            13.00 dB
PL13            13.00 dB
SFO2      500.1320005 MHz

F2 - Processing parameters
SI              32768
SF        125.7577894 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
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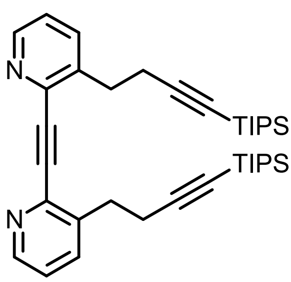
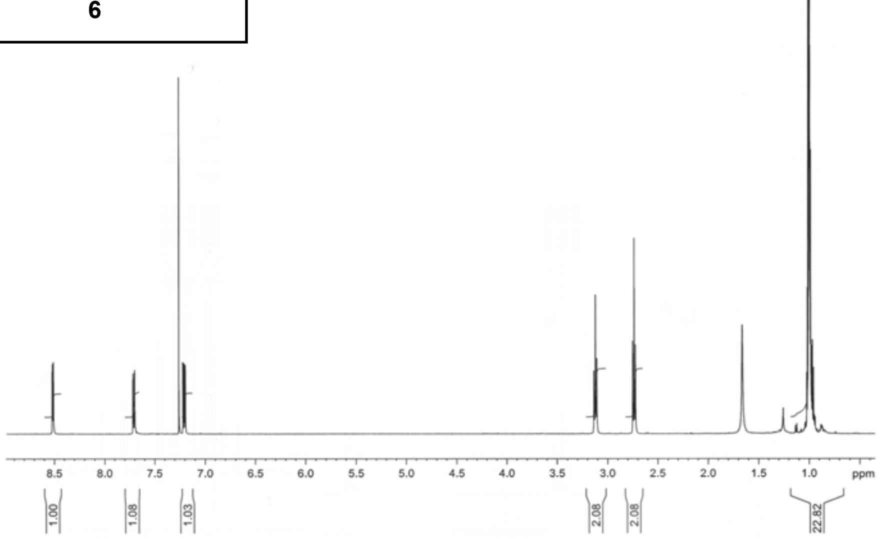
27628.



6



F.Teply FT-549
in CDCl3, ref=TMS
12.8.2003 DA
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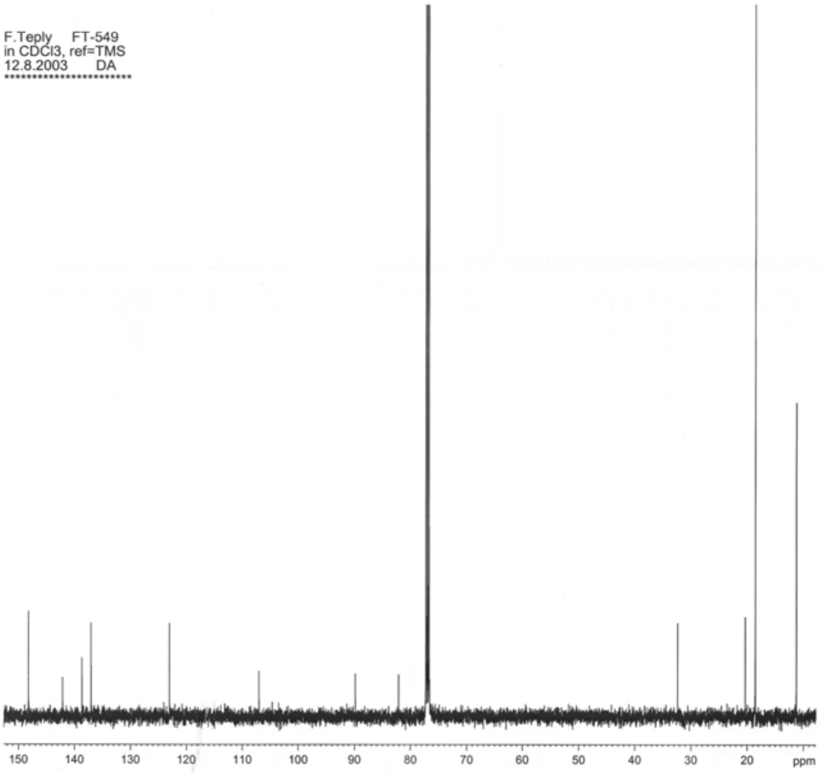
Current Data Parameters
NAME Teply-FT549
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030812
Time 11.41
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 37876
SOLVENT CDCl3
NS 40
DS 0
SWH 4734.849 Hz
FIDRES 0.125009 Hz
AQ 3.9998612 sec
RG 287.4
DW 105.600 usec
DE 6.00 usec
TE 303.0 K
D1 0.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ======
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 500.1321341 MHz

F2 - Processing parameters
SI 131072
SF 500.1300131 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.75

27783



F.Teply FT-549
in CDCl3, ref=TMS
12.8.2003 DA
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Current Data Parameters
NAME Teply-FT549
EXPNO 2
PROCNO 1

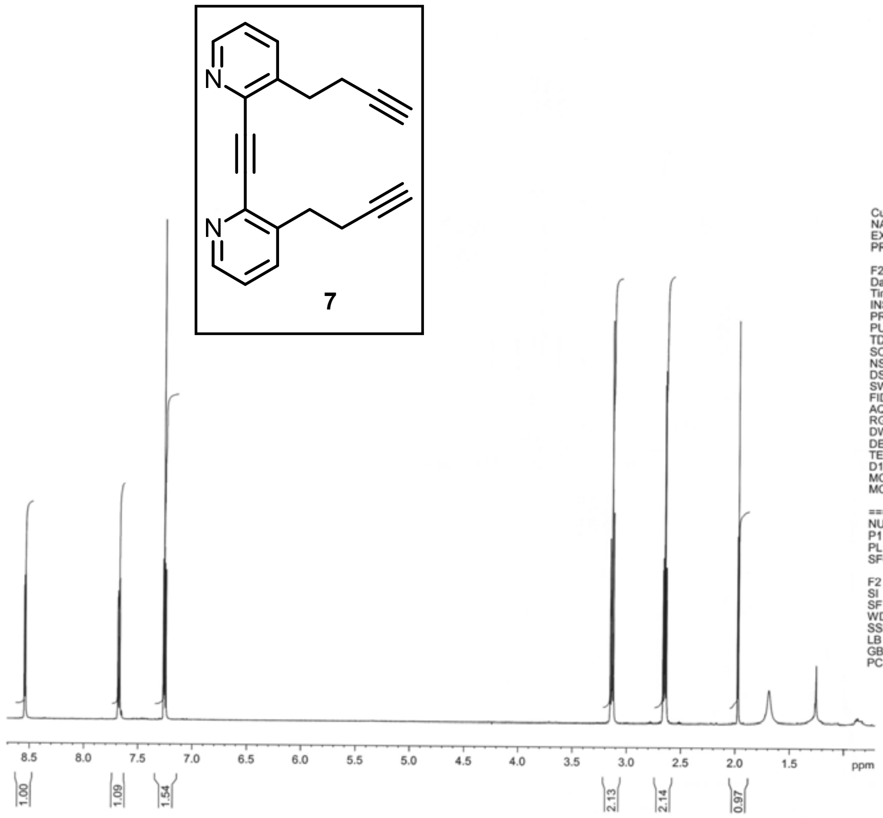
F2 - Acquisition Parameters
Date_ 20030812
Time 12.00
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 45450
SOLVENT CDCl3
NS 376
DS 8
SWH 22727.273 Hz
FIDRES 0.500050 Hz
AQ 0.9999720 sec
RG 181
DW 22.000 usec
DE 6.00 usec
TE 303.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 85.00 usec
PL2 -3.00 dB
PL12 13.31 dB
PL13 14.72 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577887 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.75

27784



7

F.Teply FT-553
in CDCl3, ref=TMS
15.8.2003 DA
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Current Data Parameters
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EXPNO 1
PROCNO 1

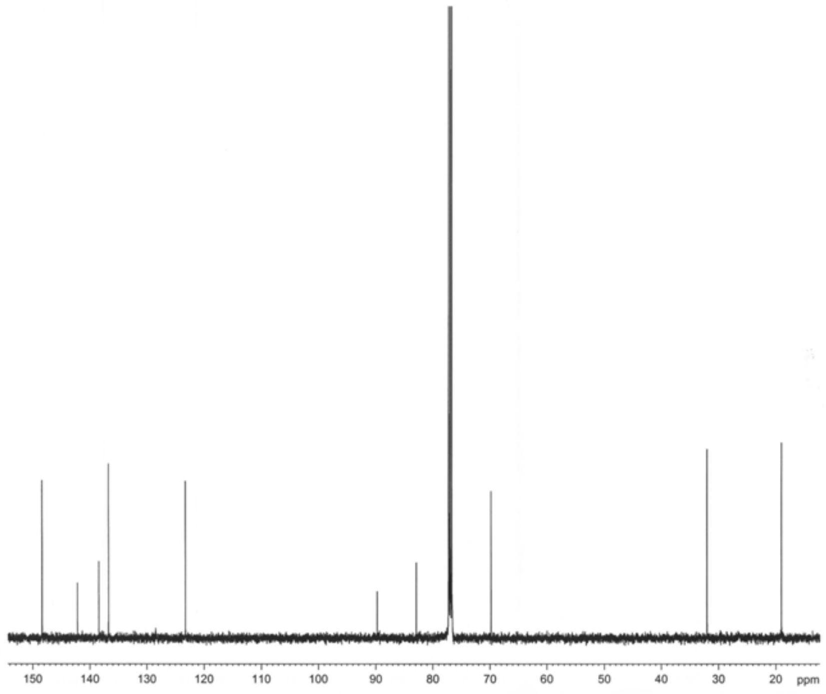
F2 - Acquisition Parameters
Date_ 20030815
Time 10.33
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 37876
SOLVENT CDCl3
NS 40
DS 0
SWH 4734.849 Hz
FIDRES 0.125009 Hz
AQ 3.9998612 sec
RG 406.4
DW 105.600 usec
DE 6.00 usec
TE 303.0 K
D1 0.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 500.1321341 MHz

F2 - Processing parameters
SI 131072
SF 500.1300128 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.75

27795

F.Teply FT-553
in CDCl3, ref=TMS
15.8.2003 DA
****



Current Data Parameters
NAME Teply-FT553
EXPNO 2
PROCNO 1

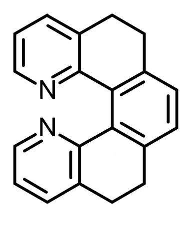
F2 - Acquisition Parameters
Date_ 20030815
Time 12.21
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 45450
SOLVENT CDCl3
NS 1220
DS 8
SWH 22727.273 Hz
FIDRES 0.500050 Hz
AQ 0.9999720 sec
RG 724.1
DW 22.000 usec
DE 6.00 usec
TE 303.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 85.00 usec
PL2 -3.00 dB
PL12 13.31 dB
PL13 14.72 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577894 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.75

27796



8

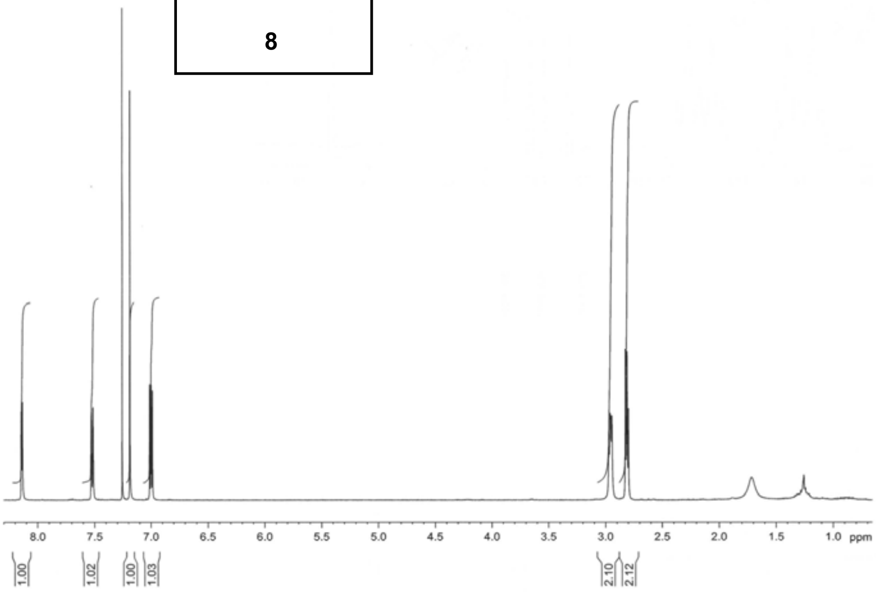
F.Teply FT-596
in CDCl3, ref=TMS
15.8.2003 DA
****

Current Data Parameters
NAME Teply-FT596
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030815
Time 12.33
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 37876
SOLVENT CDCl3
NS 40
DS 0
SWH 4734.849 Hz
FIDRES 0.125009 Hz
AQ 3.9998612 sec
RG 362
DW 105.600 usec
DE 6.00 usec
TE 303.0 K
D1 0.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

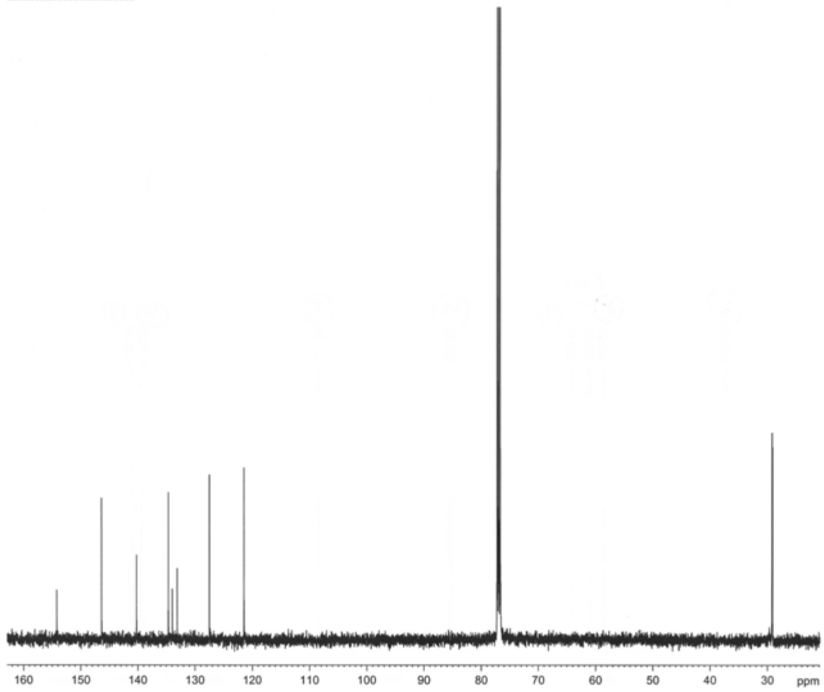
======== CHANNEL f1 ======
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 500.1321341 MHz

F2 - Processing parameters
SI 131072
SF 500.1300150 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.75



27797

F.Teply FT-596
in CDCl3, ref=TMS
15.8.2003 DA
****



Current Data Parameters
NAME Teply-FT596
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030815
Time 12.48
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 45450
SOLVENT CDCl3
NS 1329
DS 8
SWH 22727.273 Hz
FIDRES 0.500050 Hz
AQ 0.9999720 sec
RG 512
DW 22.000 usec
DE 6.00 usec
TE 303.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

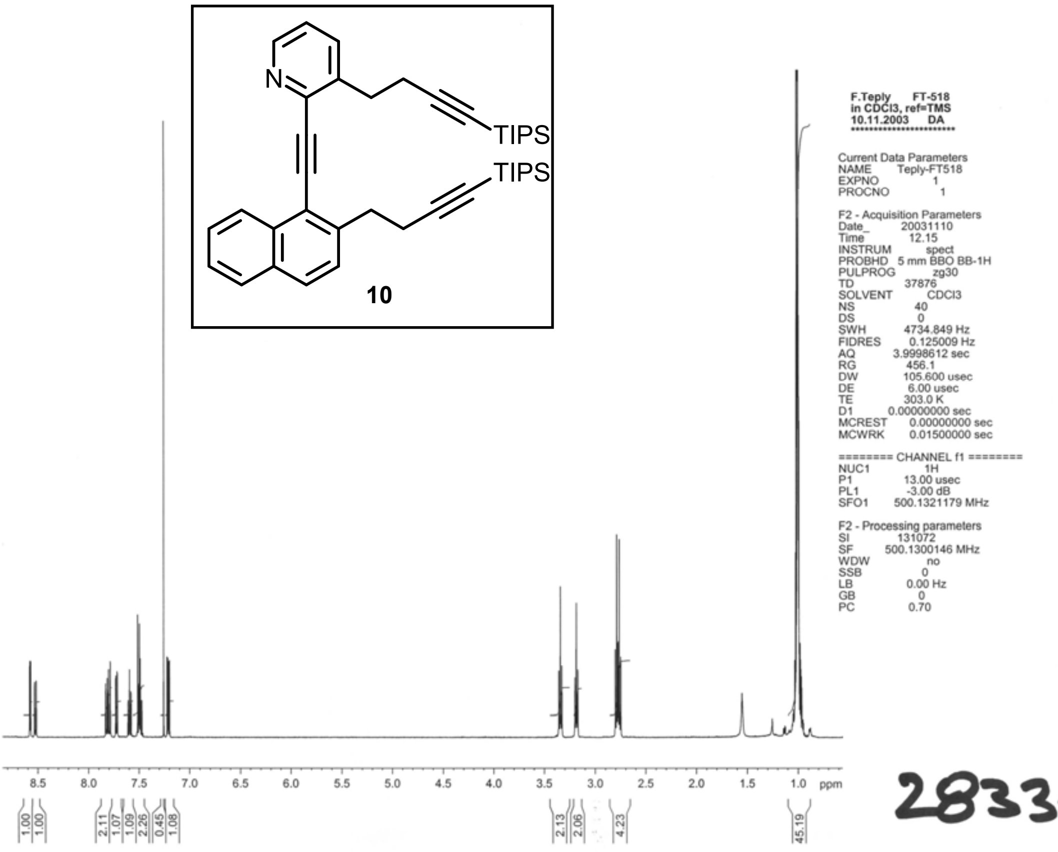
======== CHANNEL f1 ========
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 85.00 usec
PL2 -3.00 dB
PL12 13.31 dB
PL13 14.72 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577894 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.75

27798

10



F.Teply FT-518
in CDCl3, ref=TMS
10.11.2003 DA
****

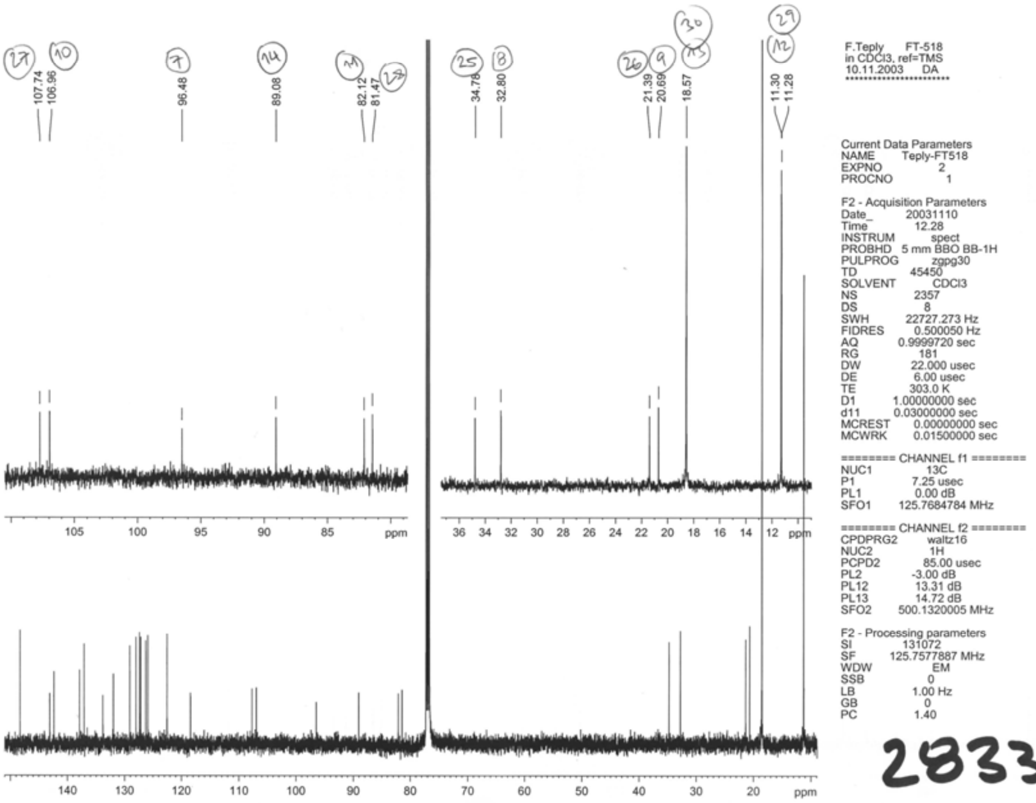
Current Data Parameters
NAME Teply-FT518
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20031110
Time 12.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 37876
SOLVENT CDCl3
NS 40
DS 0
SWH 4734.849 Hz
FIDRES 0.125009 Hz
AQ 3.9998612 sec
RG 456.1
DW 105.600 usec
DE 6.00 usec
TE 303.0 K
D1 0.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 500.1321179 MHz

F2 - Processing parameters
SI 131072
SF 500.1300146 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.70

28334



F.Teply FT-518
in CDCl3, ref=TMS
10.11.2003 DA
****

Current Data Parameters
NAME Teply-FT518
EXPNO 2
PROCNO 1

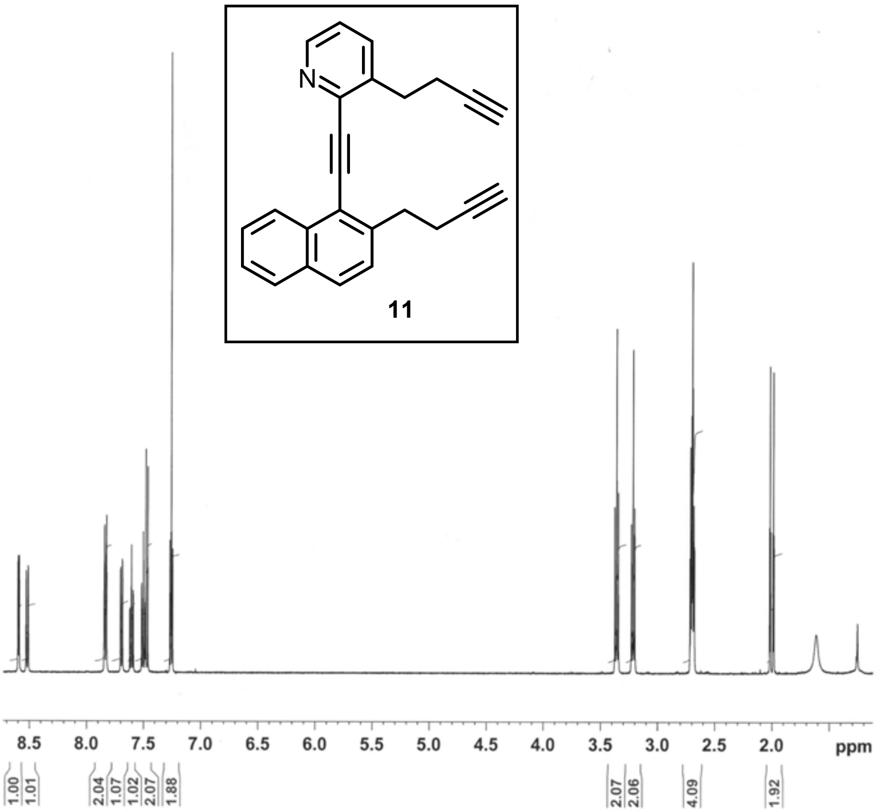
F2 - Acquisition Parameters
Date_ 20031110
Time 12.28
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 45450
SOLVENT CDCl3
NS 2357
DS 8
SWH 22727.273 Hz
FIDRES 0.500050 Hz
AQ 0.9999720 sec
RG 181
DW 22.000 usec
DE 6.00 usec
TE 303.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 85.00 usec
PL2 -3.00 dB
PL12 13.31 dB
PL13 14.72 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 131072
SF 125.7577887 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

28335


11

```
F.Teply    FT-520
in CDCl3, ref=TMS
22.5.2003    DA
**********************
```

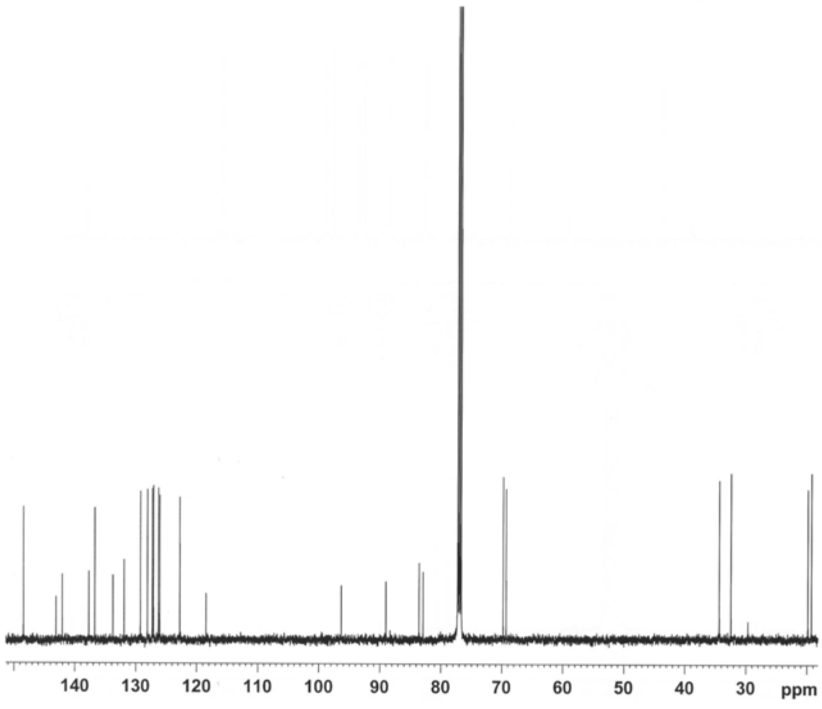
```
Current Data Parameters
NAME        Teply-FT520
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20030522
Time             10.13
INSTRUM          spect
PROBHD   5 mm BBO BB-1H
PULPROG           zg30
TD               39998
SOLVENT          CDCl3
NS                  11
DS                   0
SWH        5000.000 Hz
FIDRES     0.125006 Hz
AQ        3.9999499 sec
RG                 256
DW         100.000 usec
DE           6.00 usec
TE             300.0 K
D1       1.00000000 sec

======== CHANNEL f1 ======
NUC1                1H
P1          10.60 usec
PL1           -5.00 dB
SFO1   500.1321005 MHz

F2 - Processing parameters
SI              131072
SF     500.1300150 MHz
WDW                 no
SSB                  0
LB             0.00 Hz
GB                   0
PC                1.00
```

27314



```
F.Teply    FT-520
in CDCl3, ref=TMS
22.5.2003    DA
**********************
```

```
Current Data Parameters
NAME        Teply-FT520
EXPNO              2
PROCNO             1

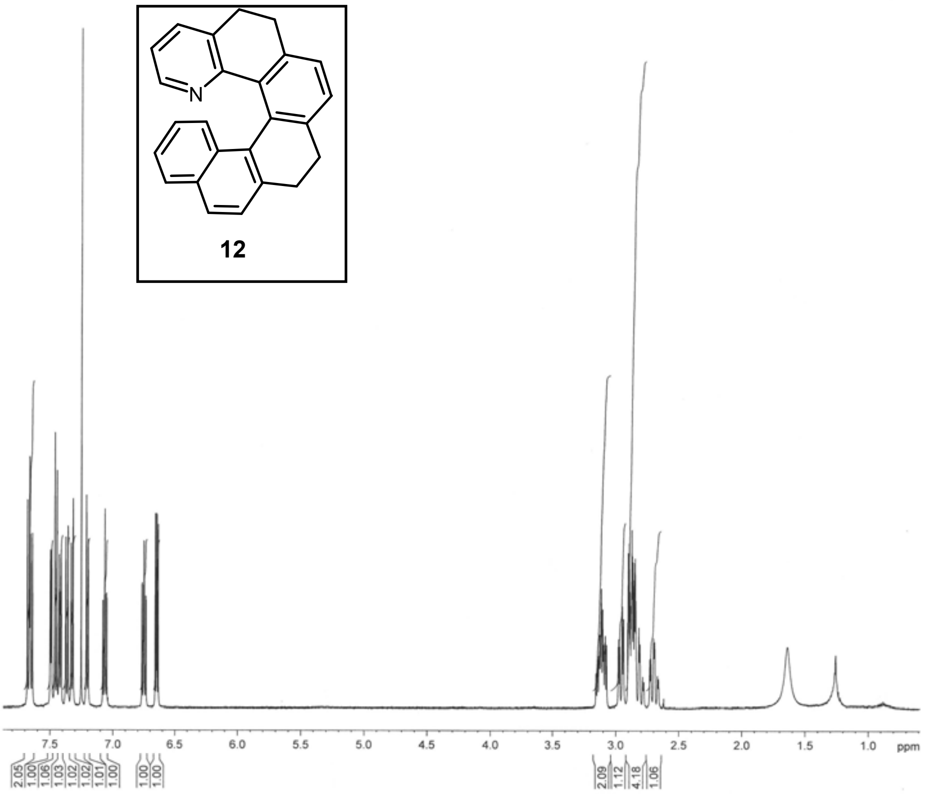
F2 - Acquisition Parameters
Date_         20030522
Time             10.29
INSTRUM          spect
PROBHD   5 mm BBO BB-1H
PULPROG         zgpg30
TD               45450
SOLVENT          CDCl3
NS                2224
DS                   8
SWH       22727.273 Hz
FIDRES     0.500050 Hz
AQ        0.9999720 sec
RG               16384
DW          22.000 usec
DE           6.00 usec
TE             300.0 K
D1       2.00000000 sec
d11      0.03000000 sec
d12      0.00002000 sec

======== CHANNEL f1 ========
NUC1               13C
P1           4.90 usec
PL1           -3.00 dB
SFO1   125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2       81.00 usec
PL2           -5.00 dB
PL12          13.00 dB
PL13          13.00 dB
SFO2   500.1320005 MHz

F2 - Processing parameters
SI               32768
SF     125.7577901 MHz
WDW                 EM
SSB                  0
LB             1.00 Hz
GB                   0
PC                1.00
```

27315



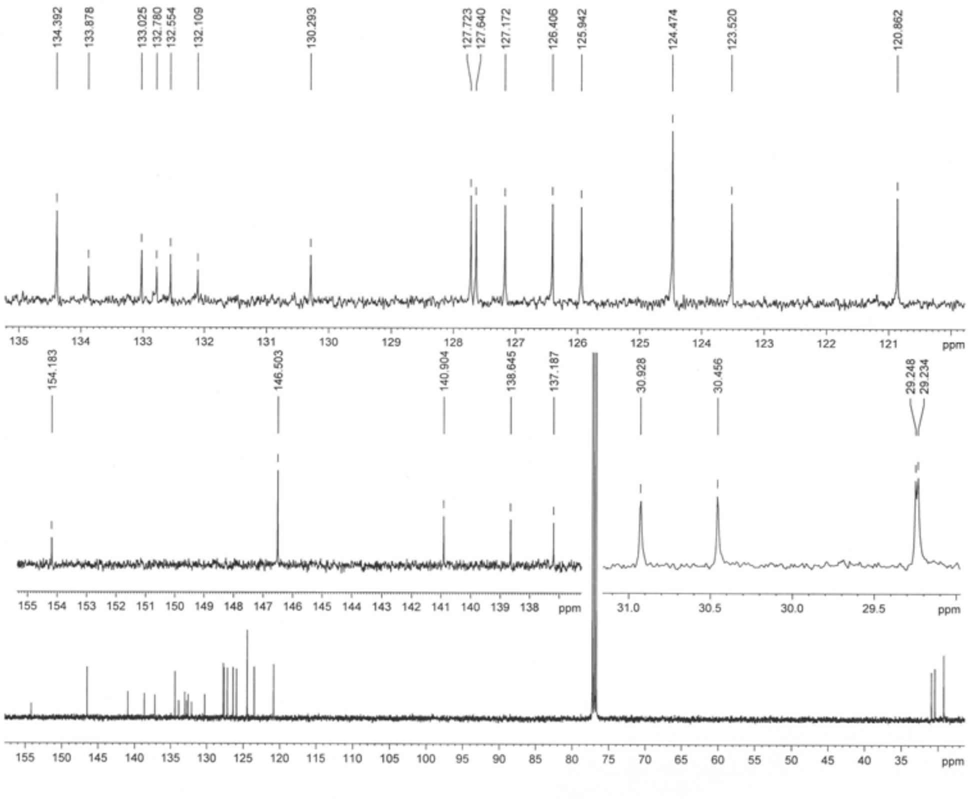
```
F.Teply  FT-521
in CDCl3, ref=TMS
10.6.2003  DA
**********************

Current Data Parameters
NAME             Teply-FT521
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_            20030610
Time               11.36
INSTRUM            spect
PROBHD        5 mm BBO BB-
PULPROG             zg30
TD                39998
SOLVENT            CDCl3
NS                   33
DS                    0
SWH          5000.000 Hz
FIDRES       0.125006 Hz
AQ          3.9999499 sec
RG                406.4
DW          100.000 usec
DE             6.00 usec
TE              300.0 K
D1         1.00000000 sec

======== CHANNEL f1 =====
NUC1                 1H
P1            10.60 usec
PL1             -5.00 dB
SFO1        500.1321005 MH

F2 - Processing parameters
SI               131072
SF        500.1300175 MHz
WDW                  no
SSB                   0
LB              0.00 Hz
GB                    0
PC                 0.28
```



```
F.Teply  FT-521
in CDCl3, ref=TMS
10.6.2003  DA
**********************

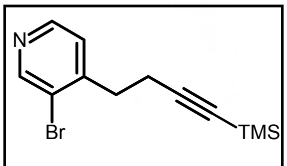
Current Data Parameters
NAME             Teply-FT521
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_            20030610
Time               13.54
INSTRUM            spect
PROBHD        5 mm BBO BB-'
PULPROG           zgpg30
TD                45450
SOLVENT            CDCl3
NS                  539
DS                    8
SWH          22727.273 Hz
FIDRES        0.500050 Hz
AQ          0.9999720 sec
RG                16384
DW           22.000 usec
DE             6.00 usec
TE              300.0 K
D1         2.00000000 sec
d11        0.03000000 sec
d12        0.00002000 sec

======== CHANNEL f1 =====
NUC1                13C
P1             4.90 usec
PL1             -3.00 dB
SFO1        125.7684784 MH

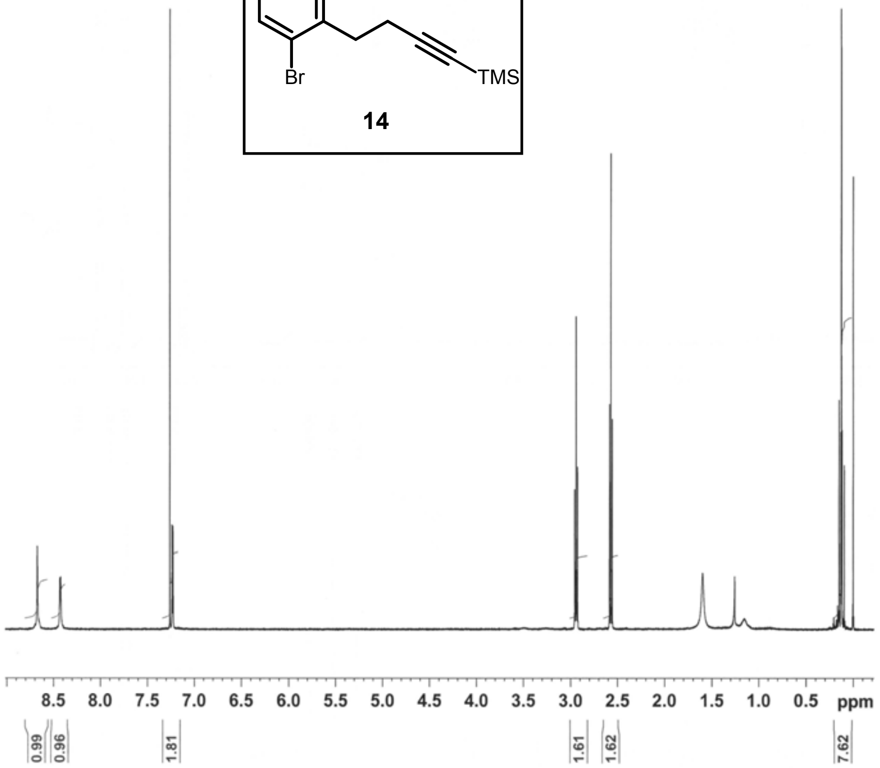
======== CHANNEL f2 =====
CPDPRG2         waltz16
NUC2                 1H
PCPD2         81.00 usec
PL2             -5.00 dB
PL12            13.00 dB
PL13            13.00 dB
SFO2        500.1320005 MH

F2 - Processing parameters
SI                32768
SF        125.7577897 MHz
WDW                  EM
SSB                   0
LB              1.00 Hz
GB                    0
PC                 1.40
```



14

```
I.Stara   IR-1484
in CDCl3, ref=TMS
26.6.2003   DA
************************
```



```
Current Data Parameters
NAME      Stara-IR1484
EXPNO            1
PROCNO           1

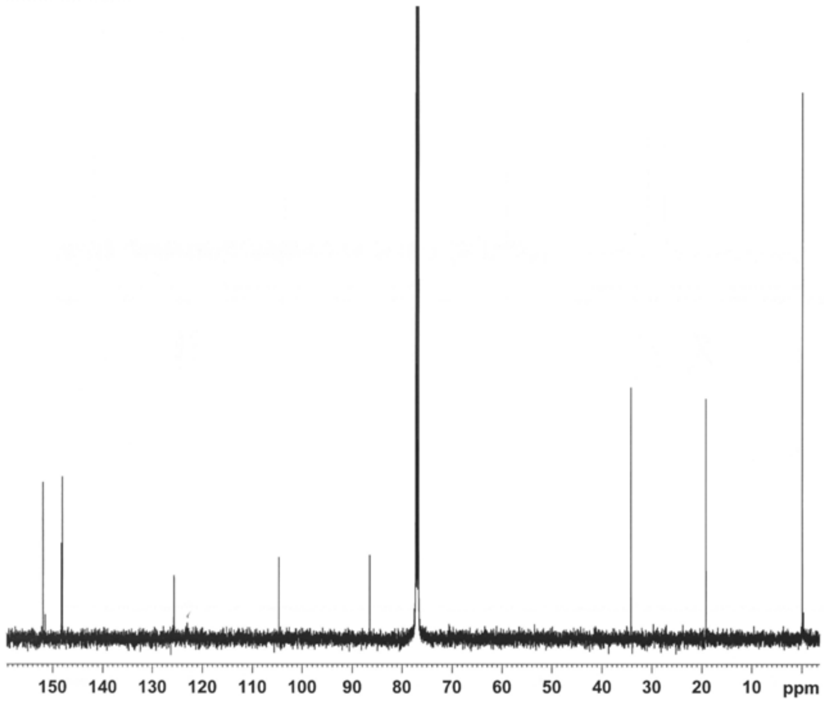
F2 - Acquisition Parameters
Date_        20030626
Time            10.09
INSTRUM         spect
PROBHD   5 mm BBO BB-1H
PULPROG          zg30
TD             48074
SOLVENT          CDCl3
NS                 20
DS                  0
SWH         6009.615 Hz
FIDRES      0.125008 Hz
AQ         3.9998901 sec
RG                256
DW            83.200 usec
DE              6.00 usec
TE             300.0 K
D1         1.00000000 sec

======== CHANNEL f1 ======
NUC1               1H
P1             10.10 usec
PL1            -5.00 dB
SFO1     500.1320505 MHz

F2 - Processing parameters
SI             131072
SF       500.1300133 MHz
WDW                no
SSB                 0
LB               0.00 Hz
GB                  0
PC               0.50
```

27442

```
I.Stara   IR-1484
in CDCl3, ref=TMS
26.6.2003   DA
************************
```



```
Current Data Parameters
NAME      Stara-IR1484
EXPNO            3
PROCNO           1

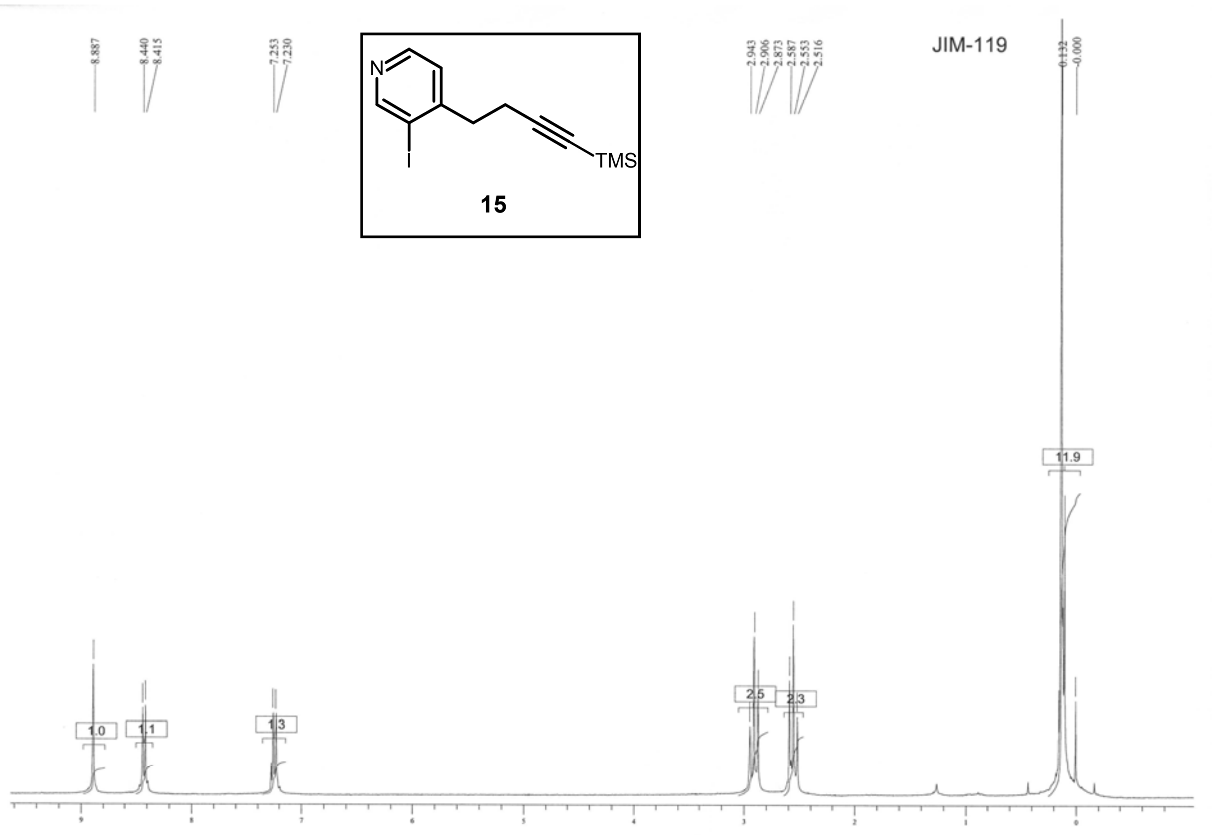
F2 - Acquisition Parameters
Date_        20030626
Time            11.00
INSTRUM         spect
PROBHD   5 mm BBO BB-1H
PULPROG        zgpg30
TD             50120
SOLVENT          CDCl3
NS               2123
DS                  8
SWH        25062.656 Hz
FIDRES      0.500053 Hz
AQ         0.9999639 sec
RG              32768
DW            19.950 usec
DE              6.00 usec
TE             300.0 K
D1         3.00000000 sec
d11        0.03000000 sec
d12        0.00002000 sec

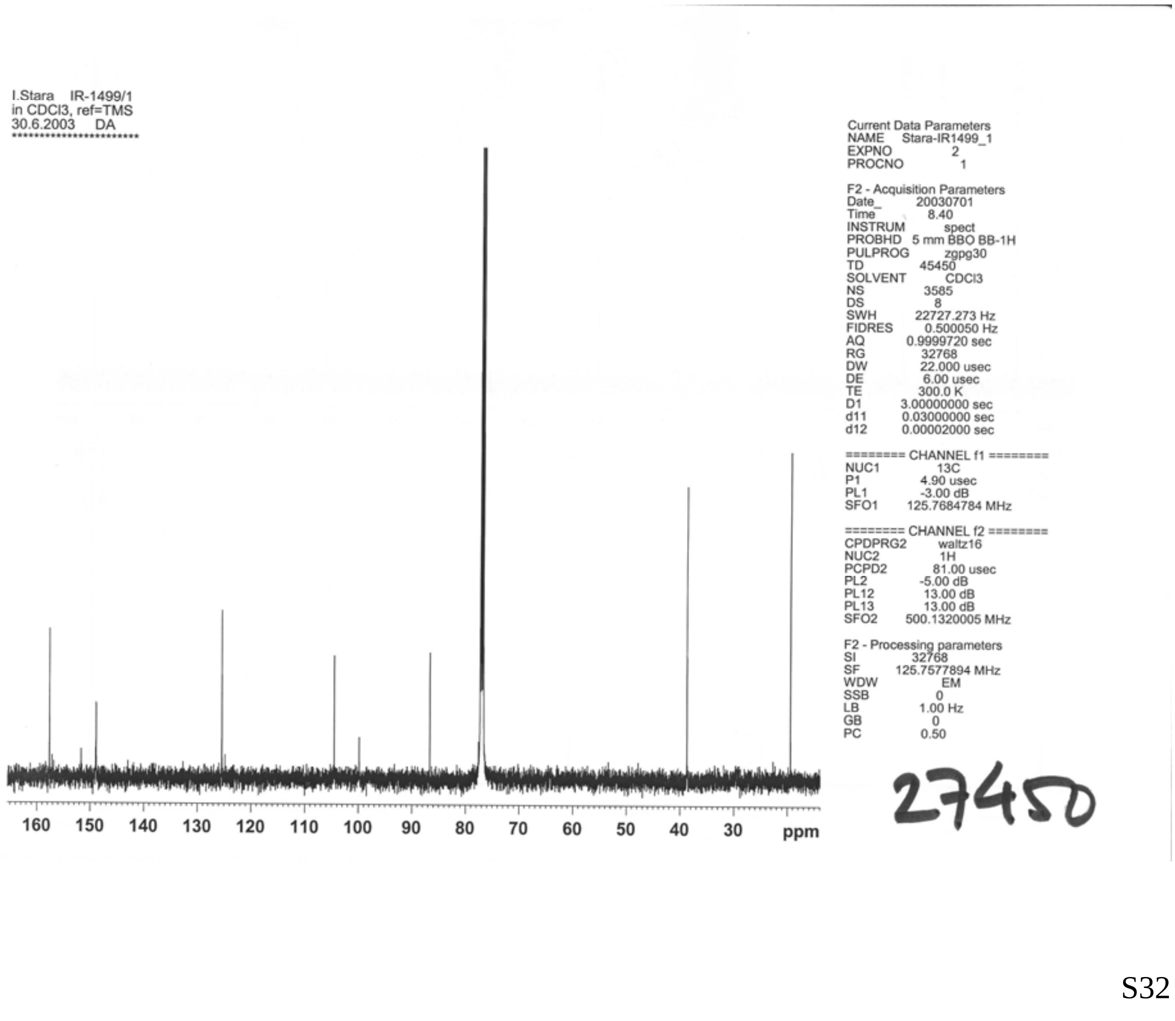
======== CHANNEL f1 ========
NUC1              13C
P1              4.90 usec
PL1            -3.00 dB
SFO1     125.7691072 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2          81.00 usec
PL2            -5.00 dB
PL12           13.00 dB
PL13           13.00 dB
SFO2     500.1320005 MHz

F2 - Processing parameters
SI              32768
SF       125.7577886 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

27443





```
Current Data Parameters
NAME     Stara-IR1499_1
EXPNO              2
PROCNO             1

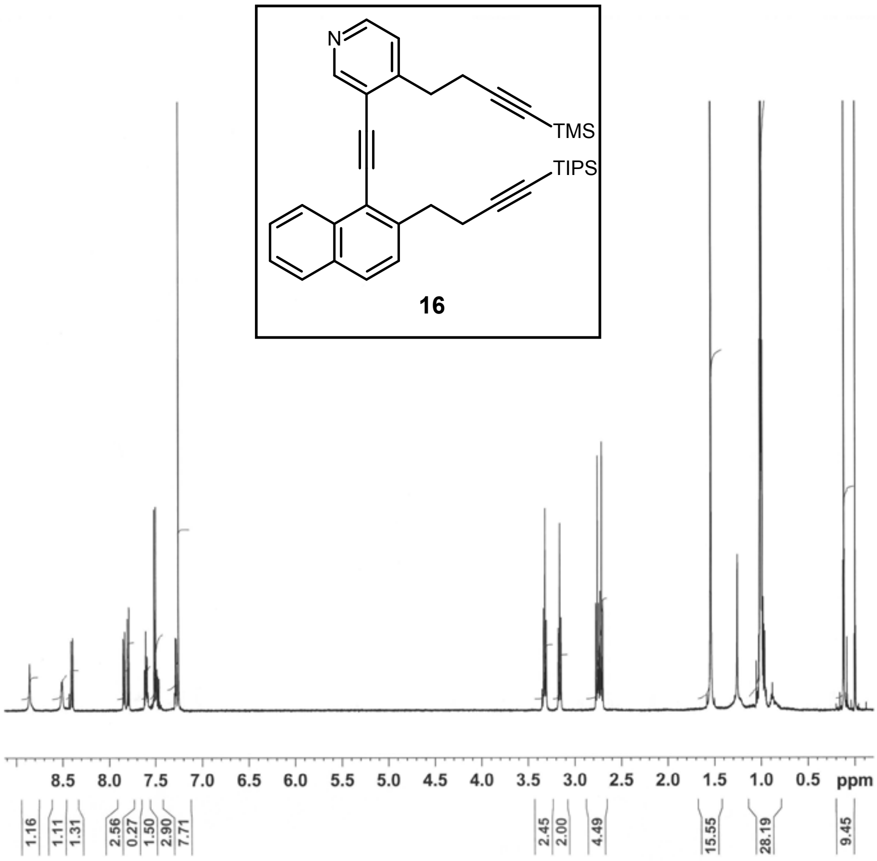
F2 - Acquisition Parameters
Date_       20030701
Time            8.40
INSTRUM        spect
PROBHD  5 mm BBO BB-1H
PULPROG       zgpg30
TD             45450
SOLVENT        CDCl3
NS              3585
DS                 8
SWH       22727.273 Hz
FIDRES     0.500050 Hz
AQ        0.9999720 sec
RG             32768
DW            22.000 usec
DE              6.00 usec
TE             300.0 K
D1       3.00000000 sec
d11      0.03000000 sec
d12      0.00002000 sec

======== CHANNEL f1 ========
NUC1             13C
P1              4.90 usec
PL1            -3.00 dB
SFO1     125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2               1H
PCPD2          81.00 usec
PL2            -5.00 dB
PL12           13.00 dB
PL13           13.00 dB
SFO2     500.1320005 MHz

F2 - Processing parameters
SI             32768
SF       125.7577894 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              0.50
```

27450



16

```
I.Stara    IR-1504/2
in CDCl3, ref=TMS
13.6.2003     DA
************************

Current Data Parameters
NAME     Stara-IR1504_2
EXPNO              1
PROCNO             1

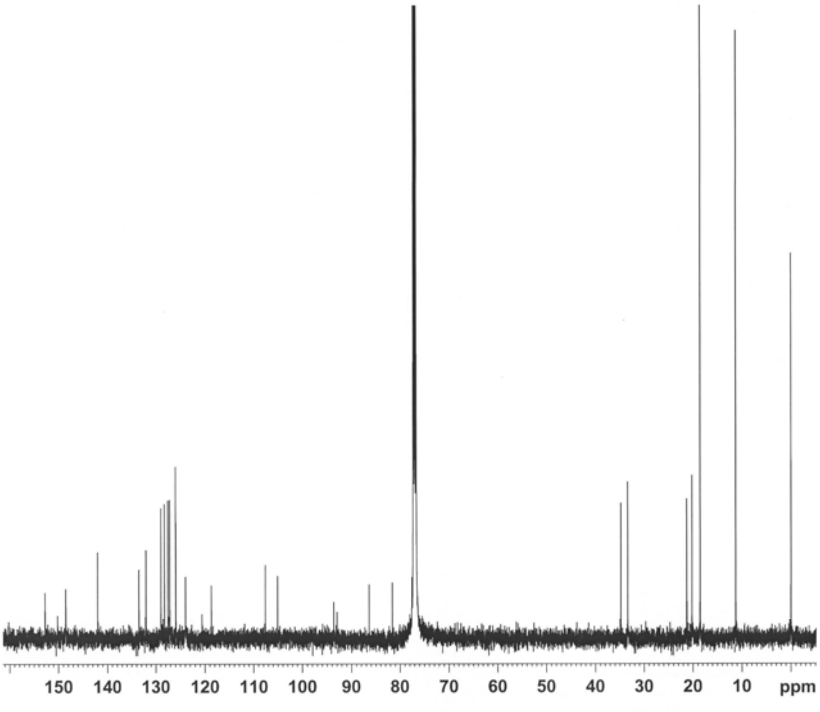
F2 - Acquisition Parameters
Date_          20030613
Time             7.43
INSTRUM          spect
PROBHD   5 mm BBO BB-1H
PULPROG           zg30
TD               39998
SOLVENT          CDCl3
NS                 146
DS                   0
SWH        5000.000 Hz
FIDRES     0.125006 Hz
AQ        3.9999499 sec
RG                 512
DW         100.000 usec
DE            6.00 usec
TE             300.0 K
D1       1.00000000 sec

======== CHANNEL f1 ======
NUC1                1H
P1          10.60 usec
PL1           -5.00 dB
SFO1    500.1323006 MHz

F2 - Processing parameters
SI              131072
SF      500.1300144 MHz
WDW                 no
SSB                  0
LB             0.00 Hz
GB                   0
PC                0.20
```

27327

```
I.Stara    IR-1504/2
in CDCl3, ref=TMS
13.6.2003     DA
************************
```



```
Current Data Parameters
NAME     Stara-IR1504_2
EXPNO              3
PROCNO             1

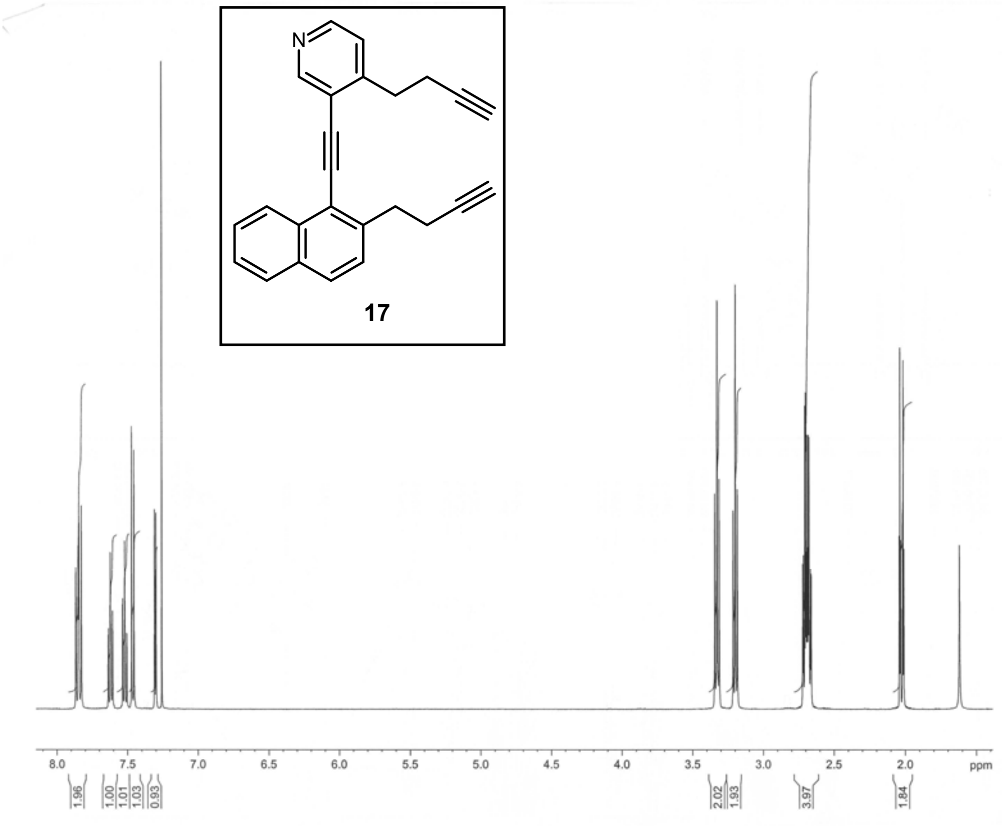
F2 - Acquisition Parameters
Date_          20030613
Time            10.49
INSTRUM          spect
PROBHD   5 mm BBO BB-1H
PULPROG        zgpg30
TD               50120
SOLVENT          CDCl3
NS               32768
DS                   8
SWH       25062.656 Hz
FIDRES     0.500053 Hz
AQ        0.9999639 sec
RG               32768
DW          19.950 usec
DE            6.00 usec
TE             300.0 K
D1       1.00000000 sec
d11      0.03000000 sec
d12      0.00002000 sec

======== CHANNEL f1 ========
NUC1               13C
P1           4.90 usec
PL1           -3.00 dB
SFO1    125.7678496 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2       81.00 usec
PL2           -5.00 dB
PL12          13.00 dB
PL13          13.00 dB
SFO2    500.1320005 MHz

F2 - Processing parameters
SI               32768
SF      125.7577884 MHz
WDW                 EM
SSB                  0
LB             1.00 Hz
GB                   0
PC                1.40
```

27328



```
J.Misek    JIM-123
in CDCl3, ref=TMS
19.7.2006        DA
*************************

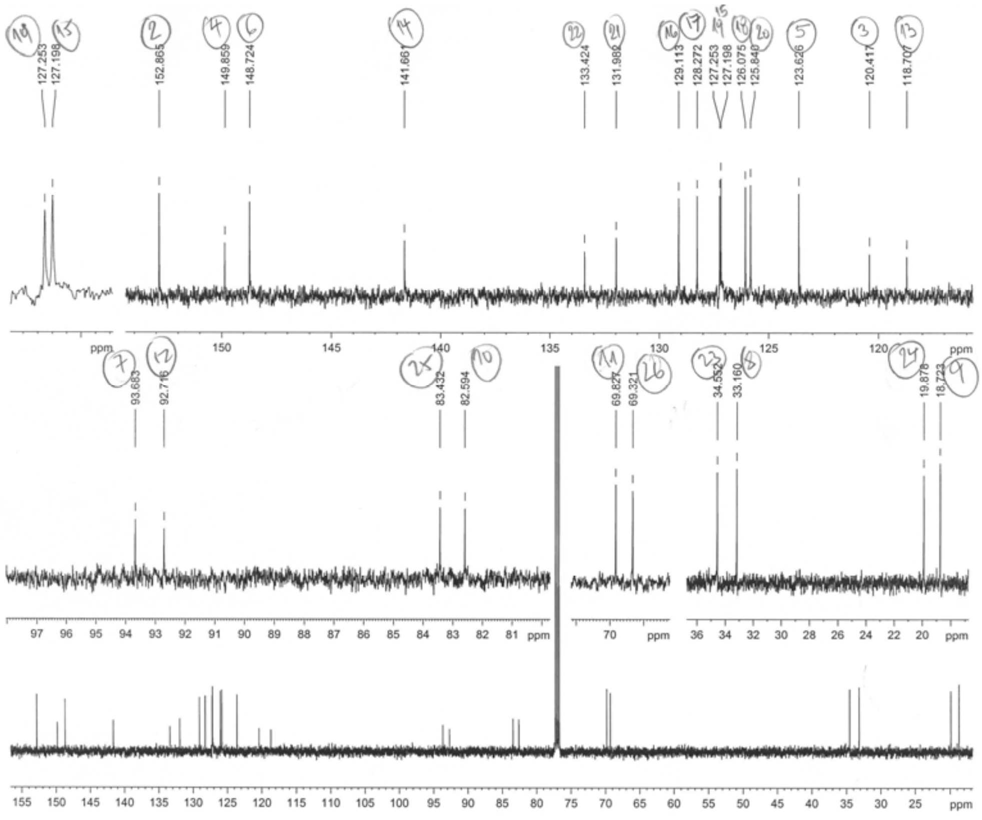
Current Data Parameters
NAME      Misek-JIM123
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20060719
Time             7.30
INSTRUM         spect
PROBHD   5 mm TXI 1H-13
PULPROG          zg30
TD             35968
SOLVENT         CDCl3
NS                32
DS                 0
SWH         4496.403 Hz
FIDRES      0.125011 Hz
AQ         3.9998028 sec
RG              10.1
DW           111.200 usec
DE             6.00 usec
TE            300.0 K
D1        0.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1              9.20 usec
PL1             1.00 dB
SFO1      500.1318755 MHz

F2 - Processing parameters
SI            131072
SF        500.1300143 MHz
WDW               no
SSB                0
LB              0.00 Hz
GB                 0
PC              0.30
```

34683



```
J.Misek    JIM-123
in CDCl3, ref=TMS
19.7.2006        DA
*************************

Current Data Parameters
NAME      Misek-JIM123
EXPNO              2
PROCNO             1

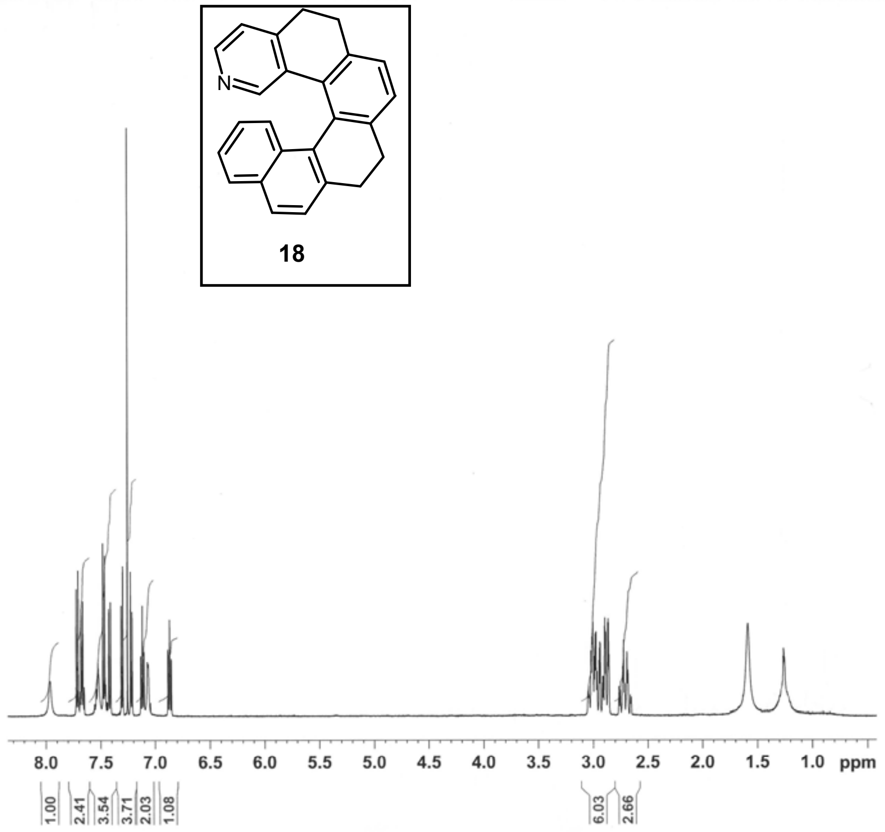
F2 - Acquisition Parameters
Date_         20060719
Time             7.43
INSTRUM         spect
PROBHD   5 mm TXI 1H-13
PULPROG        zgpg30
TD             45450
SOLVENT         CDCl3
NS               360
DS                 8
SWH        25062.656 Hz
FIDRES      0.551434 Hz
AQ         0.9067975 sec
RG             32768
DW            19.950 usec
DE             6.00 usec
TE            300.0 K
D1        1.00000000 sec
d11       0.03000000 sec
DELTA     0.89999998 sec
TD0                1

======== CHANNEL f1 =======
NUC1             13C
P1             15.50 usec
PL1             0.20 dB
SFO1      125.7697360 MHz

======== CHANNEL f2 =======
CPDPRG2        waltz16
NUC2              1H
PCPD2          80.00 usec
PL2             1.00 dB
PL12           19.79 dB
PL13           19.00 dB
SFO2      500.1320005 MHz

F2 - Processing parameters
SI            131072
SF        125.7577930 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

34683



```
I.Stara     IR-1508
in CDCl3, ref=TMS
1.7.2003    DA
**********************

Current Data Parameters
NAME       Stara-IR1508
EXPNO                 1
PROCNO                1

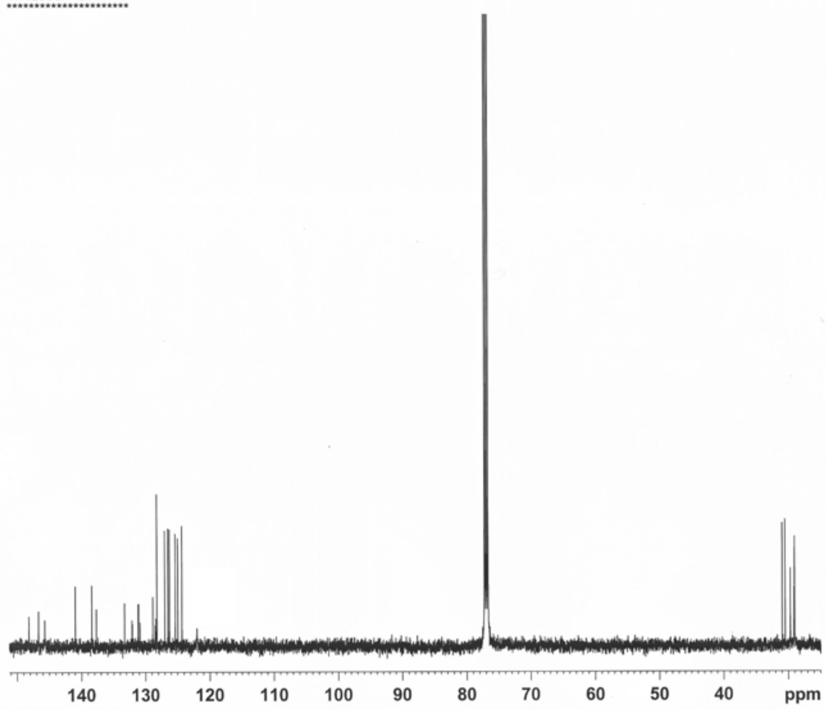
F2 - Acquisition Parameters
Date_          20030701
Time              16.22
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                36230
SOLVENT           CDCl3
NS                  100
DS                    0
SWH          4496.403 Hz
FIDRES       0.124107 Hz
AQ          4.0289373 sec
RG                  512
DW           111.200 usec
DE              6.00 usec
TE               300.0 K
D1         1.00000000 sec

======== CHANNEL f1 ======
NUC1                 1H
P1             10.10 usec
PL1             -5.00 dB
SFO1      500.1321005 MHz

F2 - Processing parameters
SI               131072
SF        500.1300152 MHz
WDW                  no
SSB                   0
LB               0.00 Hz
GB                    0
PC                 0.20
```

27459

```
I.Stara     IR-1508
in CDCl3, ref=TMS
1.7.2003    DA
**********************
```



```
Current Data Parameters
NAME       Stara-IR1508
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20030701
Time              16.54
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                45450
SOLVENT           CDCl3
NS                 4096
DS                    8
SWH         22727.273 Hz
FIDRES       0.500050 Hz
AQ          0.9999720 sec
RG                16384
DW            22.000 usec
DE              6.00 usec
TE               300.0 K
D1         1.00000000 sec
d11        0.03000000 sec
d12        0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1              4.90 usec
PL1             -3.00 dB
SFO1      125.7684784 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2          81.00 usec
PL2             -5.00 dB
PL12            13.00 dB
PL13            13.00 dB
SFO2      500.1320005 MHz

F2 - Processing parameters
SI                32768
SF        125.7577894 MHz
WDW                  EM
SSB                   0
LB               1.00 Hz
GB                    0
PC                 0.20
```

27460