Nitrogen heteroaromatic cations by [2+2+2] cycloaddition†

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†Dedicated to Professor Antonín Holý on the occasion of his 74th birthday.

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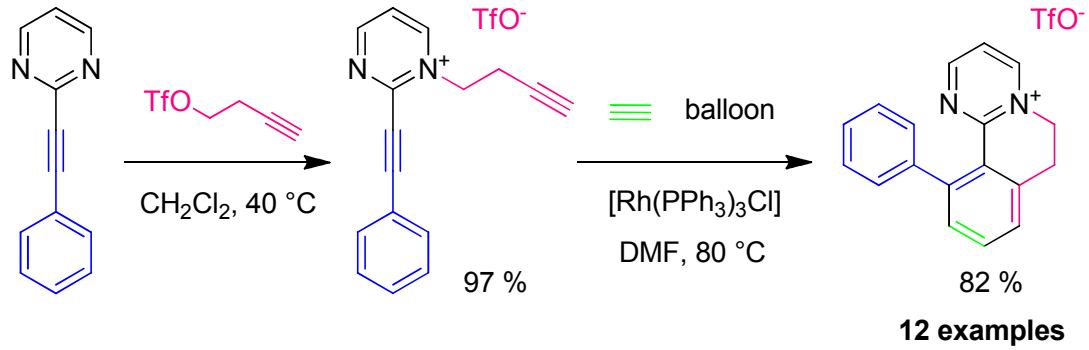
ELECTRONIC SUPPLEMENTARY INFORMATION



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1) Materials

Demineralized water obtained from the Water Purification Facility at the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., was used unless otherwise stated. Demineralization was accomplished *via* filtration through ion exchange columns (Lewatit S100 for catex column, Lewatit MP500 for anex column) in a demineralization ion exchange station type ID-PP and IDKP (Kavalier, Votice, Czech Republic). Degassed solvents were obtained *via* the freeze-pump-thaw method. The solvent was frozen under Ar, and then thawed under vacuum. This process was repeated (3×). Finally the thawed solvent was purged with argon. Unless otherwise stated, all other starting materials and reagents were obtained from commercial suppliers and used without further purification.

d_6-Acetone (Merck, 99.9%, 100021)

Acetone, cyclohexane, dichloromethane, diethyl ether, ethyl acetate, hexanes, and toluene were purchased from Penta, Czech Republic (www.pentachemicals.eu)

Acetylene (Dissolved, Messer Technogas, UN1001)

1,2-Bis(diphenylphosphino)ethane (Aldrich, 97%, 1663-45-2)

[1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), [Pd(dppf)Cl_2], (Aldrich, 72287-26-4)

Bis(triphenylphosphine)nickel(0)dicarbonyl, [Ni(PPh_3)$_2$(CO)$_2$] (Fluka, ≥98.0%, 13007-90-4)

2-Bromo-1-methyl-1*H*-imidazole (Aldrich, 95%, 16681-59-7)

2-Bromopyridine (Alfa Aesar, 99%, 109-04-6)

2-Bromopyrimidine (Alfa Aesar, 98+%, 4595-60-2)

2-Bromothiazole (Aldrich, 98%, 3034-53-5)

3-Butyn-1-ol (Alfa Aesar, 98+%, 927-74-2)

Celite (Fluka, 512 medium, 91053-39-3)

2-Chlorobenzothiazole (Aldrich, 99%, 615-20-3)

Chloro(1,5-cyclooctadiene)iridium(I) dimer, [Ir(cod)Cl]$_2$, (Strem Chemicals, 99%, 12112-67-3)

Chloro(1,5-cyclooctadiene)(pentamethylcyclopentadienyl)ruthenium(II), [(Cp*Ru(cod)Cl] (Strem, 98%, 92390-26-6)

Chloro(pentamethylcyclopentadienyl)ruthenium(II) tetramer, [Cp*RuCl]$_4$, (Aldrich, 113860-07-4)

2-Chloroquinoline (Alfa Aesar, 99%, 612-62-4)

CuI (Aldrich, 99.999%, 7681-65-4)

Dicarbonylcyclopentadienyl cobalt(I), [$CpCo(CO)_2$] (Aldrich, 12078-25-0)

1,2-Dichloroethane (Aldrich, 107-06-2)

Dichlorobis(triphenylphosphine)palladium(II), [$Pd(PPh_3)_2Cl_2$] (Aldrich, 99.99%, 13965-03-2)

N,*N*-Dimethylformamide (Aldrich, 99.8%, 68-12-2)

Et_3N (Alfa Aesar, 99%, 121-44-8)

Ethynylbenzene (Aldrich, 98%, 536-74-3)

4-Ethynyl-*N*,*N*-dimethylaniline (Aldrich, 97%, 17573-94-3)

2-Ethynylpyridine (Aldrich, 98%, 1945-84-2)

EtOH (Riedel-de Haën, absolute, 64-17-5)

1-Hexyne (Alfa Aesar, 98+%, 693-02-7)

4-Iodotoluene (Aldrich, 99%, 624-31-7)

Na_2SO_4 (Riedel-de Haën, anhydrous, 7757-82-6)

Tetrakis(triphenylphosphine)palladium(0), [$Pd(PPh_3)_4$] (Alfa Aesar, 99.8%, 14221-01-3)

3-Pentyn-1-ol (Fluka, 97+%, 10229-10-4)

4-Phenyl-3-butyn-1-ol (prepared according to literature procedure[1])

Pyridine (Alfa Aesar, anhydrous 99.5+%, 110-86-1)

3-Tetradecyn-1-ol (Alfa Aesar, 97%, 55182-74-6)

Trifluoromethanesulfonic anhydride (Alfa Aesar, 98%, 358-23-6)

Trifluoromethanesulfonic anhydride (Acros Organics, 98+%, 358-23-6)

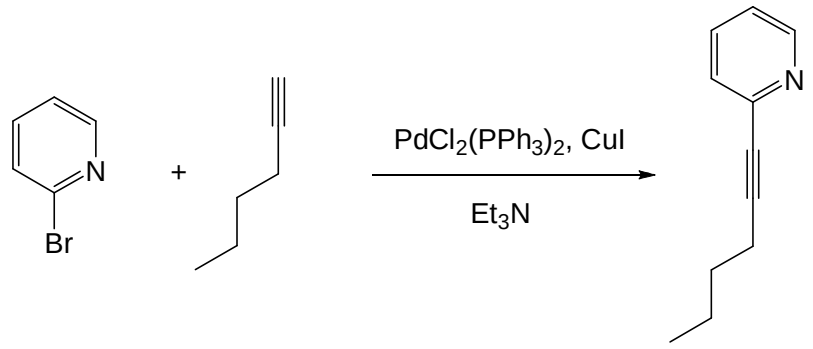
Tris(triphenylphosphine)rhodium(I)chloride, [$Rh(PPh_3)_3Cl$] (Fluka, 97+%, 14694-95-2)

2) Procedures and analytical data - Sonogashira coupling

Based on a literature procedure[2].

2-(1-Hexynyl)pyridine (3)

CAS: 16344-82-4 (ref. 2, 3)

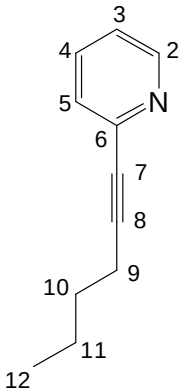


3

$C_{11}H_{13}N$
159.228

$PdCl_2(PPh_3)_2$ (308 mg, 0.44 mmol, 5 mol %) and CuI (84 mg, 0.44 mmol, 5 mol %) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed Et_3N (20 mL), 2-bromopyridine (840 µL, 8.80 mmol, 1 equiv) and 1-hexyne (1.5 mL, 13.14 mmol, 1.5 equiv) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 30 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 6 cm, plug height 8 cm, hexane:ethyl acetate 6:1). Compound **3** was obtained as a brownish liquid in 94 % yield (1.32 g, 8.30 mmol).

Analytical data for compound 3



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.98 (t, J = 7.3 Hz, 3H, H-12); 1.49 - 1.57 (m, 2H, H-11); 1.60 - 1.66 (m, 2H, H-10); 2.49 (t, J = 7.1 Hz, 2H, H-9); 7.32 (ddd, J = 1.2, 4.8, 7.6 Hz, 1H, H-3); 7.45 (dt, J = 1.1, 7.9 Hz, 1H, H-5); 7.77 (dt, J = 1.8, 7.7 Hz, 1H, H-4); 8.56 (bd, J = 4.8 Hz, 1H, H-2).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.81 (C-12), 19.15 (C-9), 22.56 (C-11), 31.25 (C-10), 81.62 (C-8), 90.61 (C-7), 123.28 (C-3), 127.61 (C-5), 136.90 (C-4), 144.82 (C-6), 150.64 (C-2).

IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 400 m, 629 w, 711 w, 886 w, 989 w, 1047 w, 1091 w,

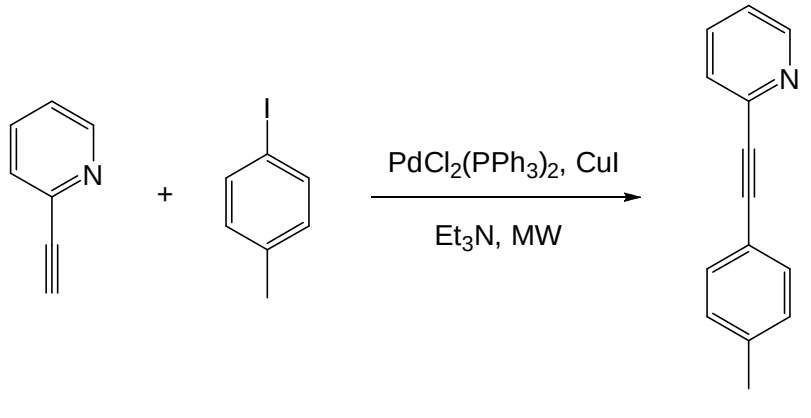
1148 m, 1269 m, 1329 w, 1380 w, 1428 s, 1465 vs, 1562 m, 1584 vs, 2231 m, 2837 w, 2864 m, 2874 m, 2934 s, 2960 s, 3056 w, 3082 w.

MS (EI^+) m/z (%): 159 [M^+] (47), 144 (35), 130 (100), 117 (93), 89 (34), 63 (26), 51 (25), 39 (23).

HRMS (EI^+) m/z: [M^+] ($C_{11}H_{13}N$) calc.: 159.1048, found: 159.1050.

2-(*p*-Tolylethynyl)pyridine

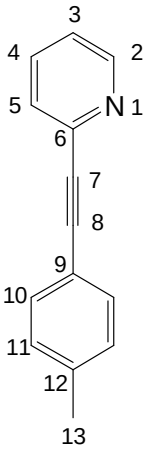
CAS: 80221-14-3 (ref. 4)



$C_{14}H_{11}N$
193.244

4-Iodotoluene (115 mg, 0.53 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (16 mg, 0.02 mmol, 5.1 mol %) and CuI (9 mg, 0.05 mmol, 11.2 mol %) were added in this order to a reaction tube. The tube was purged with Ar (3x). 2-Ethynylpyridine (44 μL, 0.44 mmol, 1.0 equiv) and freshly distilled Et_3N (1.2 mL) were added in this order. The mixture was stirred under MW (100 W, 100 psi) 5 min at 60 °C. The reaction mixture was filtered through Celite and the filtercake was washed with a mixture of hexane: ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash flash chromatography on silica gel (column diameter 1.5 cm, plug height 7 cm, hexane:ethyl acetate 7:1). 2-(*p*-Tolylethynyl)pyridine was obtained as a yellowish solid in 96 % yield (81 mg, 0.42 mmol).

Analytical data for 2-(*p*-tolylethynyl)pyridine



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 2.41 (bs, 3H, H-13); 7.31 (m, 2H, H-11); 7.40 (dddd, J = 1.2, 4.9, 7.6 Hz, 1H, H-3); 7.53 (m, 2H, H-10); 7.62 (dt, J = 1.1, 7.8 Hz, 1H, H-5); 7.85 (dt, J = 1.8, 7.7 Hz, 1H, H-4); 8.64 (ddd, J = 1.0, 1.8, 4.9 Hz, 1H, H-2).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 21.43 (C-13), 89.19 (C-8), 89.26 (C-7), 120.09 (C-9), 123.78 (C-3), 127.92 (C-5), 130.19 (C-11), 132.52 (C-10), 137.12 (C-4), 140.24 (C-12), 144.27 (C-6), 150.94 (C-2).

^{15}N NMR (61 MHz, $(CD_3)_2CO$): δ = 59.1 (N-1).

IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 400 w, 517 m, 541 w, 889 vw, 947 vw, 992 w, 1021 w, 1045 w, 1090 w, 1118 vw, 1156 m, 1184 vw, 1282 w, 1314 w, 1380 vw, 1409 vw, 1429 s, 1464 vs, 1511 s, 1584 vs, 1607 vw, 2223 m, 3033 w, 3056 w, 3084 w

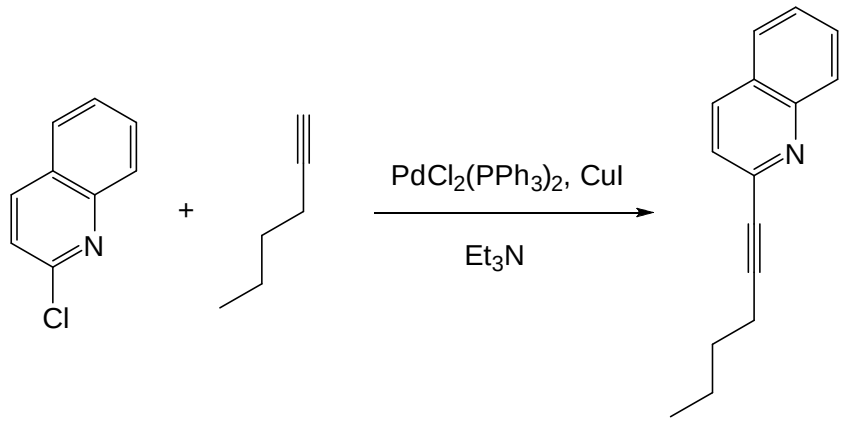
MS (ESI) m/z (%): 194 [$M+H^+$] (100).

HRMS (ESI) m/z: [$M+H^+$] ($C_{14}H_{12}N$) calc.: 194.0964, found: 194.0962.

m.p. = 66-67 °C

2-(1-Hexynyl)quinoline

CAS: 70437-01-3 (ref. 3)

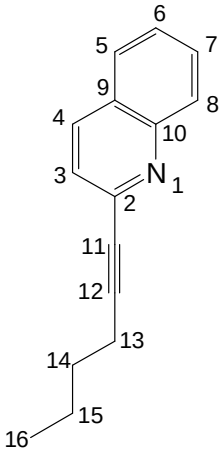


$C_{15}H_{15}N$
209.286

$PdCl_2(PPh_3)_2$ (38 mg, 0.06 mmol, 6.0 mol %), CuI (11 mg, 0.06 mmol, 6.1 mol %) and 2-chloroquinoline (150 mg, 0.91 mmol, 1 equiv) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). 1- Hexyne (150 μL, 1.31 mmol, 1.4 equiv) and freshly degassed Et_3N (3.5 mL) were added in this order. The mixture was stirred under Ar 1 min at

RT, and then 23 h at 70 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 7 cm, hexane:ethyl acetate 13:1). 2-(1-Hexynyl)quinoline was obtained as a yellow liquid in 91 % yield (174 mg, 0.83 mmol).

Analytical data for 2-(1-hexynyl)quinoline



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.01 (t, J = 7.3 Hz, 3H, H-16); 1.54 – 1.60 (m, 2H, H-15); 1.65 – 1.71 (m, 2H, H-14); 2.56 (t, J = 7.1 Hz, 2H, H-13); 7.55 (d, J = 8.4 Hz, 1H, H-3); 7.62 (ddd, J = 1.2, 6.8, 8.1 Hz, 1H, H-6); 7.80 (ddd, J = 1.4, 6.8, 8.5 Hz, 1H, H-7); 7.97 (ddt, J = 0.6, 1.4, 8.1 Hz, 1H, H-5); 8.01 (ddt, J = 0.8, 1.2, 8.5 Hz, 1H, H-8); 8.32 (dd, J = 1.1, 8.4 Hz, 1H, H-4).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.82 (C-16), 19.26 (C-13), 22.61 (C-15), 31.20 (C-14), 82.23 (C-11), 91.72 (C-12), 125.08 (C-3), 127.62 (C-6), 127.83 (C-9), 128.56 (C-5), 129.73 (C-8), 130.67 (C-7), 136.87 (C-4), 144.90 (C-2), 149.03 (C-10).

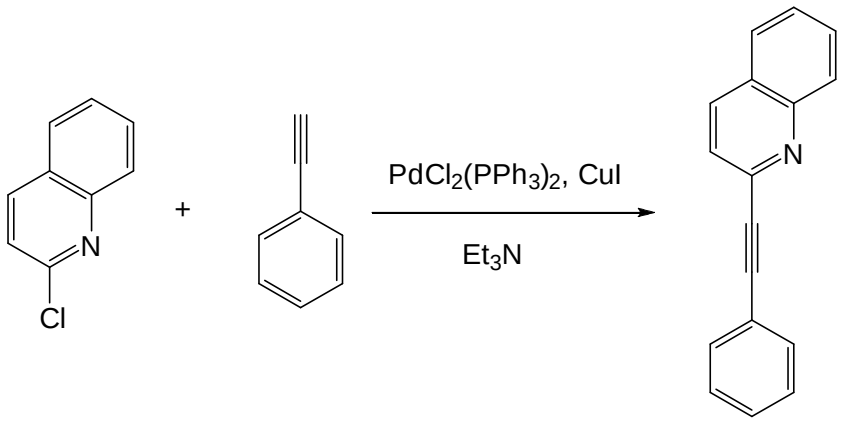
IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 477 m, 617 w, 831 vs, 870 w, 974 w, 955 w, 1024 w, 1120 m, 1142 w, 1237 m, 1260 m, 1276 m, 1307 m, 1323 m, 1335 w, 1355 w, 1379 w, 1425 s, 1460 m, 1466 m, 1501 vs, 1555 m, 1596 vs, 1618 m, 2227 m, 3042 w, 3064 w, 3088 vw, 3104 vw.

MS (EI^+) m/z (%): 209 [M^+] (61), 208 (50), 194 (30), 180 (100), 167 (90), 140 (30).

HRMS (EI^+) m/z: [M^+] ($C_{15}H_{15}N$) calc.: 209.1204, found: 209.1208.

2-(Phenylethynyl)quinoline

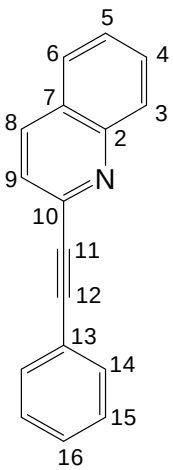
CAS: 70437-00-2 (ref. 5)



$C_{17}H_{11}N$
229.276

$PdCl_2(PPh_3)_2$ (38 mg, 0.05 mmol, 5.7 mol %), CuI (13 mg, 0.07 mmol, 7 mol %) and 2-chloroquinoline (155 mg, 0.95 mmol, 1 equiv) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Ethynylbenzene (120 µL, 1.09 mmol, 1.2 equiv) and freshly degassed Et_3N (4 mL) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 18 h at 80 °C and consequently 2 h at 100 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 8 cm, hexane:ethyl acetate 9:1). 2-(Phenylethynyl)quinoline was obtained as a yellowish liquid in 79 % yield (171 mg, 0.75 mmol).

Analytical data for 2-(phenylethynyl)quinoline



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 7.52 - 7.55 (m, 3H, H-15, H-16); 7.68 (ddd, J = 1.5, 6.9, 8.2 Hz, 1H, H-5); 7.72 - 7.74 (m, 2H, H-14); 7.74 (d, J = 8.4 Hz, 1H, H-9); 7.85 (ddd, J = 1.5, 6.9, 8.5 Hz, 1H, H-4); 8.02 (ddt, J = 0.6, 1.5, 8.2 Hz, 1H, H-6); 8.08 (ddt, J = 0.8, 1.5, 8.5 Hz, 1H, H-3); 8.41 (dd, J = 1.2, 8.4 Hz, 1H, H-8).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 89.60 (C-12), 90.37 (C-11), 122.95 (C-13), 125.16 (C-9), 128.06 (C-5), 128.06 (C-7), 128.68 (C-6), 129.60 (C-15), 129.92 (C-16), 130.24 (C-3), 130.93 (C-4), 132.79 (C-14), 137.14 (C-8), 144.23 (C-10), 149.20 (C-2).

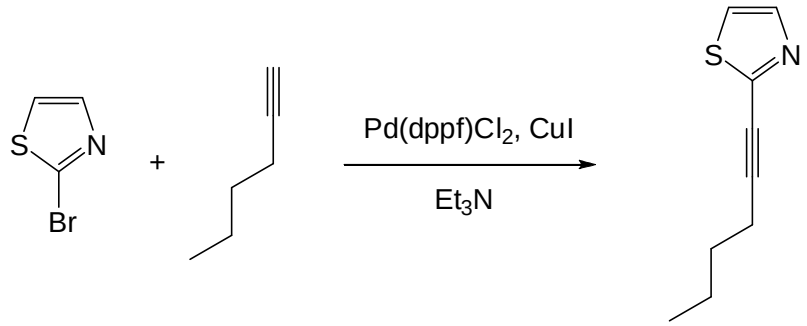
IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 477 w, 549 w, 620 w, 690 s, 831 vs, 870 w, 918 w, 955 w, 974 w, 1000 w, 1028 w, 1017 w, 1070 w, 1115 m, 1147 m, 1180 vw, 1312 m, 1338 w, 1375 w, 1425 m, 1444 m, 1459 w, 1491 m, 1501 vs, 1553 m, 1572 w, 1594 vs, 1617 m, 2195 w, 2211 m, 2222 m, 2245 w, 3040 w, 3063 w, 3085 w, 3102 w.

MS (ESI) m/z (%): 230 [$M+H^+$] (100).

HRMS (ESI) m/z: [$M+H^+$] ($C_{17}H_{12}N$) calc.: 230.0964, found: 230.0965.

2-(1-Hexynyl)thiazole

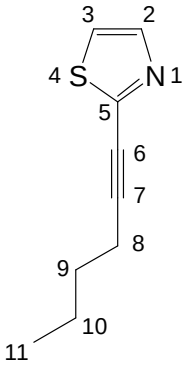
CAS: 174184-05-5 (ref. 2, 6)



$C_9H_{11}NS$
165.256

CuI (7 mg, 0.04 mmol, 3.3 mol %) and Pd(dppf)Cl_2 (20 mg, 0.03 mmol, 2.2 mol %) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed Et_3N (5.5 mL), 2-bromothiazole (100 µL, 1.12 mmol, 1 equiv) and 1-hexyne (190 µL, 1.65 mmol, 1.5 equiv) were added in this order. The mixture was stirred under Ar 5 min at RT, and then 6 h at 70 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with hexane. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 4 cm, hexane:ethyl acetate 10:1). 2-(1-Hexynyl)thiazole was obtained as a yellowish liquid in 80 % yield (148 mg, 0.89 mmol).

Analytical data for 2-(1-hexynyl)thiazole



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.95 (t, J = 7.3 Hz, 3H, H-11); 1.46-1.53 (m, 2H, H-10); 1.59-1.64 (m, 2H, H-9); 2.51 (t, J = 7.1 Hz, 2H, H-8); 7.62 (d, J = 3.3 Hz, 1H, H-3); 7.80 (d, J = 3.3 Hz, 1H, H-2).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) =13.75 (C-11), 19.30 (C-8), 22.56 (C-10), 30.85 (C-9), 74.89 (C-6), 96.34 (C-7), 121.50 (C-3), 144.10 (C-2), 149.49 (C-5).

^{15}N NMR (61 MHz, $(CD_3)_2CO$): δ = 48.7 (N-1).

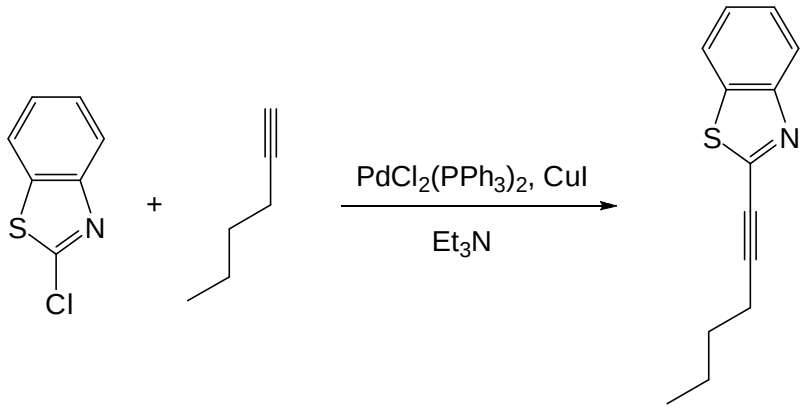
IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 620 s, 719 vs, 874 m, 885 m, 1050 m, 1059 s, 1132 vs, 1318 m, 1325 m, 1380 m, 1415 m, 1481 vs, 1602 w, 2233 s, 3088 w, 3122 w.

MS (ESI) m/z (%): 166 [$M+H^+$] (100).

HRMS (ESI) m/z: [$M+H^+$] ($C_9H_{12}NS$) calc.: 166.0685, found: 166.0682.

2-(1-Hexynyl)benzothiazole

CAS: 330436-78-7 (ref. 6)

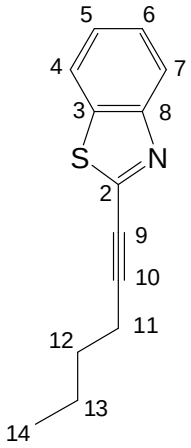


$C_{13}H_{13}NS$
215.315

$PdCl_2(PPh_3)_2$ (15 mg, 0.02 mmol, 5.4 mol %) and CuI (5 mg, 0.02 mmol, 6.3 mol %) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed (1.5 mL), 2-chlorobenzothiazole (50 µL, 0.38 mmol, 1 equiv) and 1-hexyne (66 µL, 0.58 mmol, 1.5 equiv) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 26 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with mixture hexane/EtOAc 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter

2.5 cm, plug height 7 cm, hexane:ethyl acetate 14:1). 2-(1-Hexynyl)benzothiazole was obtained as a yellow liquid in 67 % yield (56 mg, 0.26 mmol).

Analytical data for 2-(1-hexynyl)benzothiazole



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.00 (t, J = 7.4 Hz, 3H, H-14); 1.52 – 1.60 (m, 2H, H-13); 1.66 – 1.72 (m, 2H, H-12); 2.62 (t, J = 7.1 Hz, 2H, H-11); 7.54 (ddd, J = 1.3, 7.2, 8.0 Hz, 1H, H-5); 7.60 (ddd, J = 1.3, 7.2, 8.2 Hz, 1H, H-6); 8.03 (ddd, J = 0.7, 1.3, 8.2 Hz, 1H, H-7); 8.08 (ddd, J = 0.7, 1.3, 8.0 Hz, 1H, H-4).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.75 (C-14), 19.42 (C-11), 22.59 (C-13), 30.72 (C-12), 75.30 (C-10), 99.26 (C-9), 122.51 (C-4), 124.01 (C-7), 127.04 (C-5), 127.54 (C-6), 135.80 (C-3), 149.43 (C-2), 153.85 (C-8).

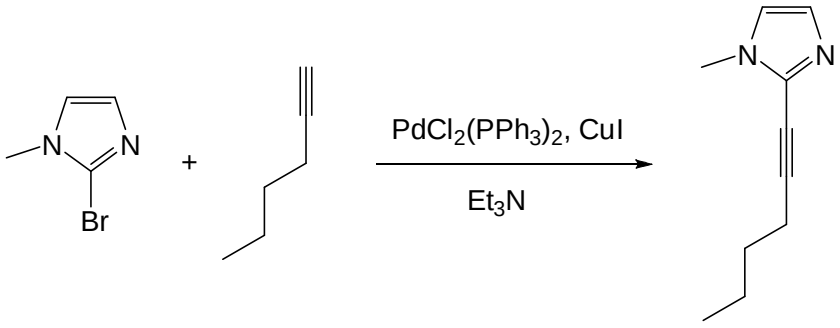
IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 441 m, 611 w, 689 w, 854 vw, 874 w, 927 m, 938 m, 972 w, 997 m, 1015 w, 1106 w, 1127 w, 1161 w, 1245 m, 1283 w, 1313 s, 1365 w, 1381 w, 1433 vs, 1487 s, 1520 vw, 1557 w, 1581 vw, 1592 w, 2230 vs, 3067 w.

MS (ESI) m/z (%): 216 [$M+H^+$] (100).

HRMS (ESI) m/z: [$M+H^+$] ($C_{13}H_{14}NS$) calc.: 216.0841, found: 216.0841.

2-(1-Hexynyl)-1-methylimidazole

CAS: 192063-28-8 (ref. 7)

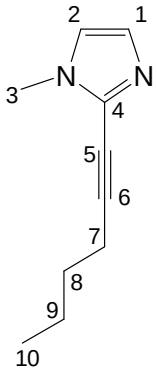


$C_{10}H_{14}N_2$
162.232

$PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol, 4.8 mol %) and CuI (7 mg, 0.04 mmol, 6.2 mol %) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). 2-Bromo-1-methylimidazole (60 µL, 0.62 mmol, 1 equiv), 1-hexyne (85 µL, 0.74 mmol, 1.2 equiv) and freshly degassed Et_3N (2 mL) were added in this order. The mixture was stirred under Ar 1

min at RT, and then 40 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 8 cm, hexane:ethyl acetate 3:1). 2-(1-Hexynyl)-1-methylimidazole was obtained as a yellow liquid in 69 % yield (69 mg, 0.42 mmol).

Analytical data for 2-(1-hexynyl)-1-methylimidazole



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.95 (t, J = 7.3 Hz, 3H, H-10); 1.47-1.52 (m, 2H, H-9); 1.58-1.63 (m, 2H, H-8); 2.48 (t, J = 7.0 Hz, 2H, H-7); 3.71 (s, 3H, H-3); 6.90 (bs, 1H, H-2); 7.10 (bs, 1H, H-1).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) =13.77 (C-10), 19.18 (C-7), 22.53 (C-9), 31.18 (C-8), 33.41 (C-3), 71.63 (C-5), 93.98 (C-6), 122.25 (C-1), 129.29 (C-2), 133.46 (C-4).

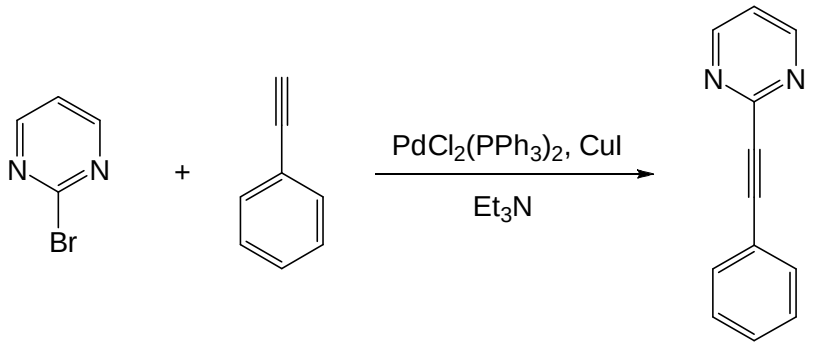
IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 704 vs, 809 w, 913 w, 1140 m, 1286 s, 1324 w, 1380 w, 1409 m, 1474 s, 1513 m, 1582 w, 2243 w, 3115 w.

MS (ESI) m/z (%): 163 [M+H$^+$] (100).

HRMS (ESI) m/z: [M+H$^+$] ($C_{10}H_{15}N_2$) calc.: 163.1230, found: 163.1228.

2-(Phenylethynyl)pyrimidine (24)

CAS: 69696-00-0 (ref. 8)

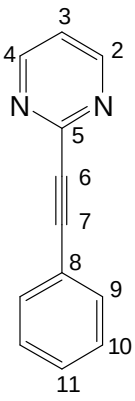


24

$C_{12}H_8N_2$
180.205

$PdCl_2(PPh_3)_2$ (75 mg, 0.11 mmol, 5.1 mol %), CuI (21 mg, 0.11 mmol, 5.4 mol %) and 2-bromopyrimidine (334 mg, 2.10 mmol, 1 equiv) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Ethynylbenzene (230 µL, 2.09 mmol, 1 equiv) and freshly degassed Et_3N (3 mL) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 8 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 9 cm, hexane:ethyl acetate 3:1). Compound **24** was obtained as a yellowish solid in 76 % yield (288 mg, 1.60 mmol).

Analytical data for compound 24



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 7.51 (t, J = 4.9 Hz, 1H, H-3); 7.51 - 7.57 (m, 3H, H-10, H-11); 7.70 - 7.72 (m, 2H, H-9); 8.87 (d, J = 4.9 Hz, 2H, H-2, H-4).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 86.86 (C-7), 89.31 (C-6), 121.19 (C-3), 122.26 (C-8), 129.65 (C-10), 130.64 (C-11), 133.01 (C-9), 153.86 (C-5), 158.35 (C-2,4).

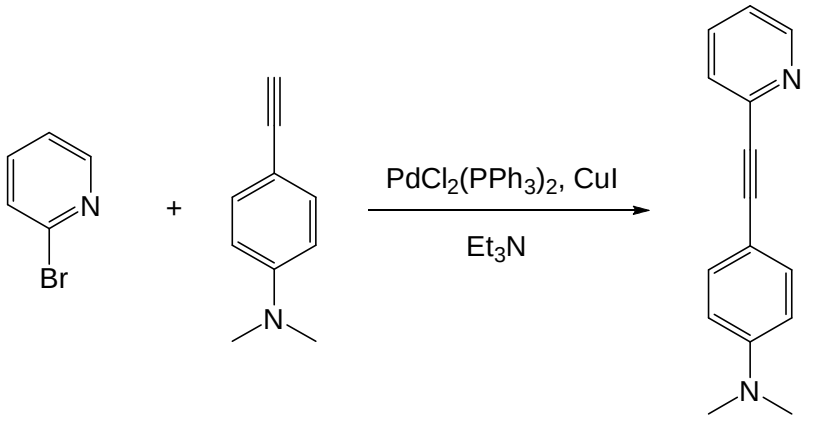
IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 544 w, 641 w, 689 s, 807 m, 919 w, 1000 w, 1027 w, 1070 w, 1174 m, 1255 m, 1280 vw, 1329 vw, 1401 w, 1415 vs, 1444 w, 1493 s, 1555 vs, 1566 s, 1578 w, 1600 w, 2188 w, 2204 w, 2230 s, 2279 w, 3041 w, 3086 w.

MS (EI^+) m/z (%): 180 [M^+] (100), 127 (90).

HRMS (EI^+) m/z: [M^+] ($C_{12}H_8N_2$) calc.: 180.0687, found: 180.0694.

m.p. = 74-76 °C

N,*N*-Dimethyl-4-(2-pyridinylethynyl)aniline (27)

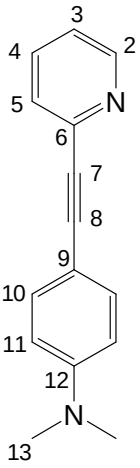


27

$C_{15}H_{14}N_2$
222.285

$PdCl_2(PPh_3)_2$ (48 mg, 0.07 mmol, 9.4 mol %), CuI (13 mg, 0.07 mmol, 9.4 mol %) and 4-ethynyl-*N*,*N*-dimethylaniline (115 mg, 0.79 mmol, 1.1 equiv) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed Et_3N (20 mL) and 2-bromopyridine (70 µL, 0.73 mmol, 1 equiv) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 18 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 8 cm, hexane:ethyl acetate 3:1). Compound **27** was obtained as a yellow solid in 41 % yield (66 mg, 0.30 mmol).

Analytical data for compound 27



^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 3.05 (s, 6H, H-13); 6.78 - 6.80 (m, 2H, H-11); 7.33 (ddd, J = 1.2, 4.8, 7.5 Hz, 1H, H-3); 7.45 - 7.47 (m, 2H, H-10); 7.55 (dt, J = 1.1, 7.9 Hz, 1H, H-5); 7.80 (dt, J = 1.8, 7.8 Hz, 1H, H-4); 8.60 (ddd, J = 1.0, 1.8, 4.8 Hz, 1H, H-2).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 40.10 (C-13), 88.21 (C-7), 91.01 (C-8), 109.29 (C-9), 112.64 (C-11), 123.00 (C-3), 127.39 (C-5), 133.73 (C-10), 136.91 (C-4), 145.06 (C-6), 150.78 (C-2), 151.68 (C-12).

IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 400 w, 497 vw, 524 m, 540 w, 628 w, 819 s, 887 vw, 946 m, 991 w, 1006 w, 1046 w, 1064 w, 1091 w, 1130 m, 1152 vs, 1175 w, 1235

m, 1281 w, 1324 w, 1364 s, 1412 vw, 1428 m, 1446 m, 1464 s, 1523 vs, 1561 m, 1583 vs, 1607 vs, 2213 s, 2810 w, 3054 w, 3084 w.

MS (ESI) m/z (%): 223 [$M+H^+$] (100).

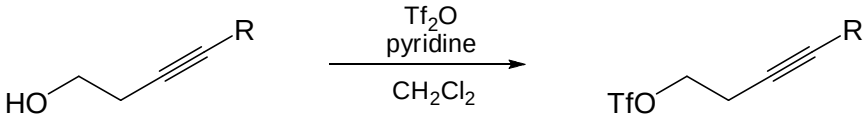
HRMS (ESI) m/z: [$M+H^+$] ($C_{15}H_{15}N_2$) calc.: 223.1230, found: 223.1230.

m.p. = 92-93 °C

3) Procedures and analytical data - Preparation of triflates from alcohols

The preparation of alkynyl trifluoromethanesulfonates is based on literature procedures[9,10].

General procedure for preparation of alkynyl trifluoromethanesulfonates

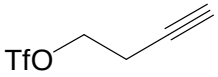


R = H, Me, Ph, *n*-$C_{10}H_{21}$

A solution of alkyn-1-ol (1 equiv) and dry pyridine (1 equiv) in freshly distilled CH_2Cl_2 (1 mL per 1 mmol of the alcohole used) was added dropwise *via* syringe and needle to a stirring solution of triflic anhydride (1 equiv) in freshly distilled CH_2Cl_2 (1 mL per 1 mmol of the alcohole used) prepared in a separate Schlenk tube prepurged with Ar (3x) and cooled to 0 °C. The reaction mixture was stirred for a further 1 h at 0 °C. The reaction mixture was warmed to RT and extracted with H_2O (3x). CH_2Cl_2 layer was dried with Na_2SO_4 and filtered through a plug of anhydrous Na_2SO_4. The filtercake was washed with CH_2Cl_2. The filtrate was concentrated *in vacuo* at 100 mbar at 25 °C. The triflates were obtained as brownish liquids.

But-3-ynyl trifluoromethanesulfonate

CAS: 32264-79-2 (ref. 11)



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.11 (t, J = 2.7 Hz, 1H); 2.73 (td, J = 2.7, 6.7 Hz, 2H); 4.57 (tq, J = 0.5, 6.7 Hz, 2H).

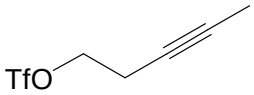
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 19.89, 71.77, 73.50, 76.86, 118.61.

B.p. = 55 °C at 2 mbar

d = 1.33

Pent-3-ynyl trifluoromethanesulfonate

CAS: 54106-83-1 (ref. 12)



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =1.78 (t, J = 2.5 Hz, 3H); 2.67 (tq, J = 2.5, 6.9 Hz, 2H); 4.53 (t, J = 6.9 Hz, 2H).

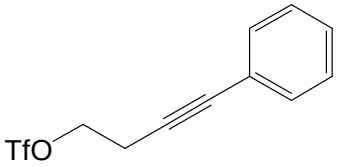
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 3.28, 20.19, 71.67, 74.41, 79.41, 118.62.

B.p. = 65 °C at 2 mbar

d = 1.28

4-Phenylbut-3-ynyl trifluoromethanesulfonate

CAS: 87639-40-5 (ref. 13)

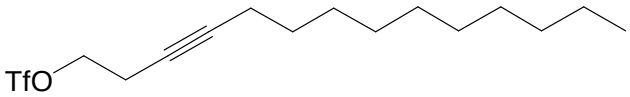


^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.97 (t, J = 6.8 Hz, 2H); 4.66 (tq, J = 0.5, 6.8 Hz, 2H); 7.38 - 7.45 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 20.85, 73.84, 82.04, 83.69, 118.64, 122.56, 128.31, 128.41, 131.68.

d = 1.34

Tetradec-3-ynyl trifluoromethanesulfonate



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.88 (t, J = 6.8 Hz, 3H); 1.17 - 1.40 (m, 14 H); 1.42-1.53 (m, 2H); 2.14 (tt, J = 2.3, 7.1 Hz, 2H); 2.69 (tt, J = 2.3, 6.9 Hz, 2H); 4.53 (tq, J = 0.5, 6.9 Hz, 2H).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 14.31, 18.94, 20.51, 23.28, 29.42, 29.45, 29.83, 30.01, 30.22, 30.25, 32.57, 74.54, 77.28, 83.67, 118.92.

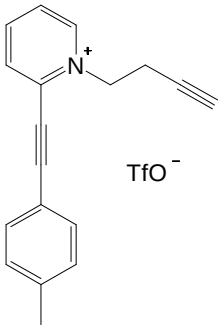
d = 1.09

4) X-ray analysis

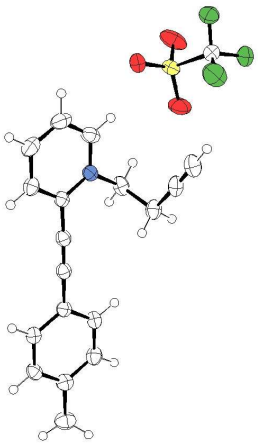
X-ray analysis of

1-(3-Butynyl)-2-(p-tolylethynyl)pyridinium trifluoromethanesulfonate (8)

CCDC 736009



8



Crystallization is effected *via* the slow diffusion of diethylether into a solution of the compound **8** in CH_2Cl_2.

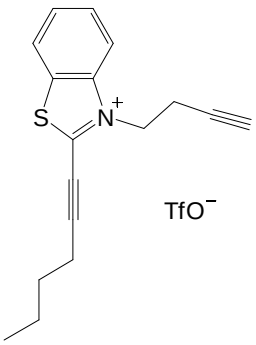
$C_{19}H_{16}F_3NO_3S$, MW = 395.40, m.p. = 166-168 °C.

Unit cell parameters: Space group P21/c, a = 7.4866 (2) Å, b = 14.3369 (2) Å, c = 17.3851 (3) Å, β = 100.0166 (9)°.

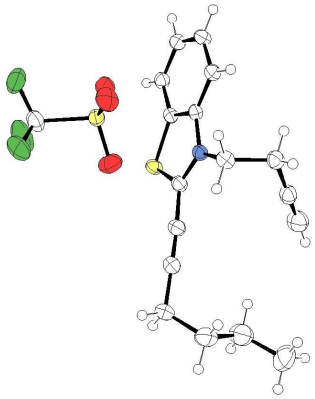
X-ray analysis of

3-(3-Butynyl)-2-(1-hexynyl)benzothiazolium trifluoromethanesulfonate (12)

CCDC 736010



12



Crystallization is effected *via* the slow diffusion of cyclohexane into a solution of the compound **12** in ethylacetate.

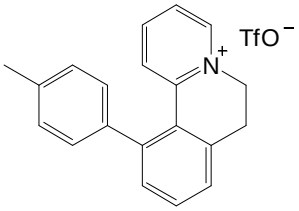
$C_{18}H_{18}F_3NO_3S_2$, MW = 417.47, m.p. = 90-92 °C.

Unit cell parameters: Space group Pca21, a = 12.1750 (2) Å, b = 10.9843 (2) Å, c = 14.5988 (2) Å.

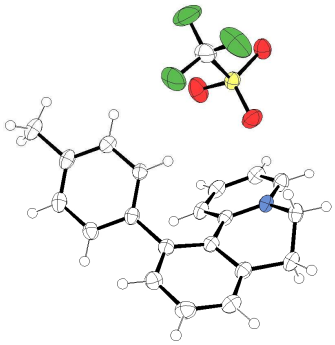
X-ray analysis of

11-*p*-Tolyl-6,7-dihydropyrido[2,1-*a*]isoquinolinium trifluoromethanesulfonate (16)

CCDC 736011



16



Crystallization is effected *via* the slow diffusion of CCl_4 into a solution of the compound **16** in CH_2Cl_2.

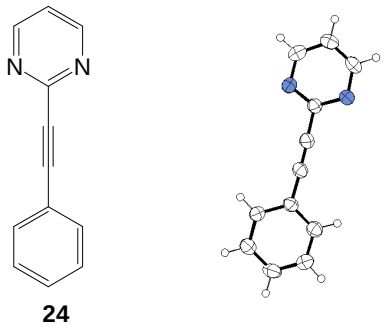
$C_{21}H_{18}F_3NO_3S$, MW = 421.43, m.p. = 125-127 °C.

Unit cell parameters: Space group C2/c, a = 23.1671 (5) Å, b = 10.5994 (2) Å, c = 15.6896 (3) Å, β = 92.5160 (13)°.

X-ray analysis of

2-(Phenylethynyl)pyrimidine (24)

CCDC 736012



24

Crystallization is effected *via* the slow diffusion of hexane into a solution of the compound **24** in diethylether.

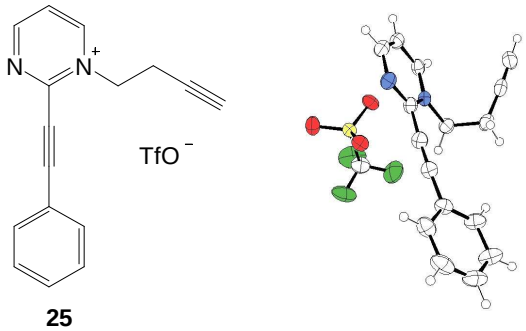
$C_{12}H_8N_2$, MW = 180.21, m.p. = 74-76 °C.

Unit cell parameters: Space group Pna21, a = 23.3925 (2) Å, b = 6.2169 (4) Å, c = 13.0456 (8) Å.

X-ray analysis of

1-(3-Butynyl)-2-(phenylethynyl)pyrimidinium trifluoromethanesulfonate (25)

CCDC 736013



25

Crystallization is effected *via* the slow diffusion of diethylether into a solution of the compound **25** in THF.

$C_{17}H_{13}F_3N_2O_3S$, MW = 382.36, m.p. = 97-99 °C.

Unit cell parameters: Space group P-1, a = 7.4977 (2) Å, b = 10.5242 (2) Å, c = 11.7581 (3) Å, α = 81.4639 (15)°, β = 79.5813 (13)°, γ = 75.5501 (15)°.

5) Electrochemical experiments

Tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) and acetonitrile were supplied by Sigma-Aldrich. The indifferent electrolyte n-Bu_4NPF_6 was re-crystallized and dried under vacuum. Acetonitrile was dried over activated 4Å molecular sieves. Electrochemical measurements were performed using a system for DC polarography, cyclic voltammetry, phase-sensitive AC polarography, AC voltammetry and electrochemical impedance spectroscopy (EIS). It consisted of a fast rise-time potentiostat, a lock-in amplifier (Stanford Research, model SRS830) and a frequency response analyzer (Stanford Research, model SRS760). The instruments were interfaced to a personal computer *via* an IEEE–interface card (PC–Lab, AdvanTech Model PCL–848) and a data acquisition card (PCL–818) using 12–bit precision for both A/D and D/A conversion. A three-electrode electrochemical cell was used. The reference electrode, Ag|AgCl|1M LiCl, was separated from the test solution by a salt bridge. The potential of the ferrocene/ferrocenium redox couple measured vs our reference electrode was 0.471 V. The working electrode was a valve–operated static mercury electrode (SMDE2, Laboratorní Přístroje, Prague) with an area 2.30×10^{-3} cm^2 and a computer controlled drop time. The auxiliary electrode was the cylindrical platinum net. Oxygen was removed from the solution by passing a stream of argon saturated with vapors of the solvent. Numerical simulations of voltammograms by the finite difference method were done by means of a freeware program[14].

6) References

[1] Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett*. **1993**, *34*, 6403.

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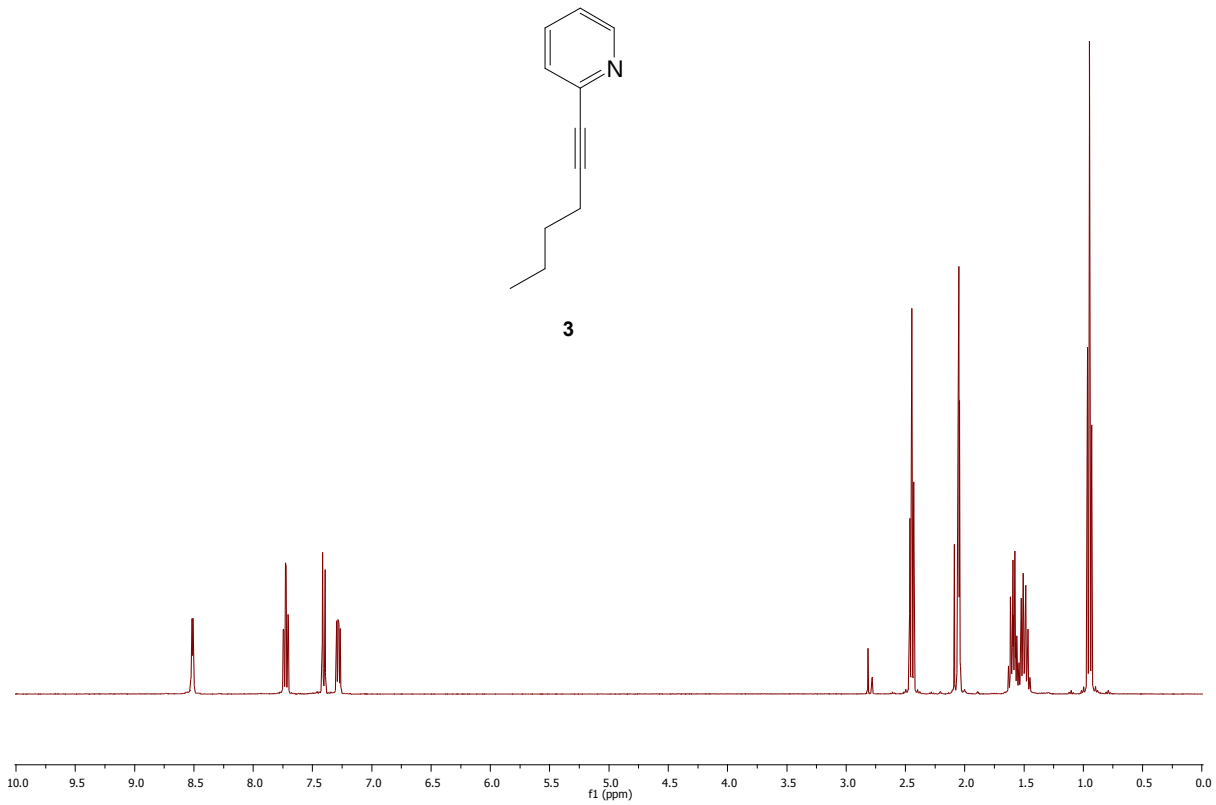
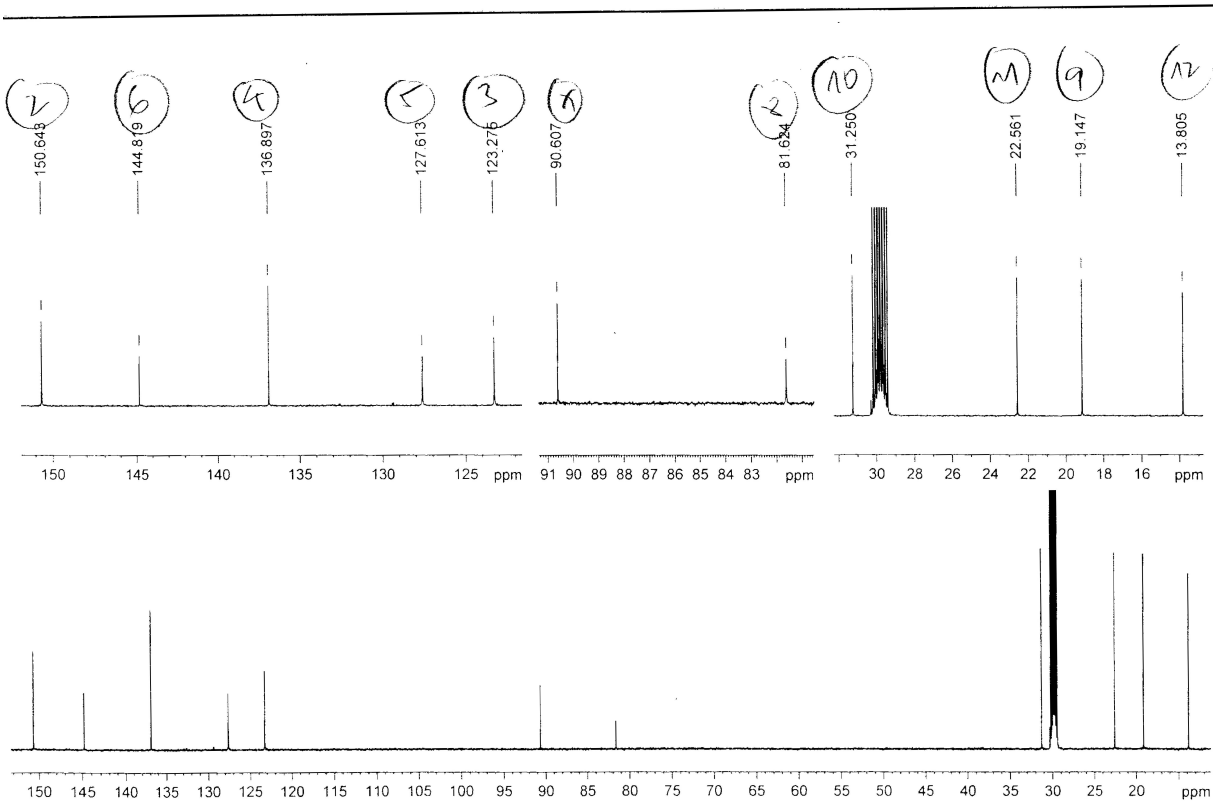
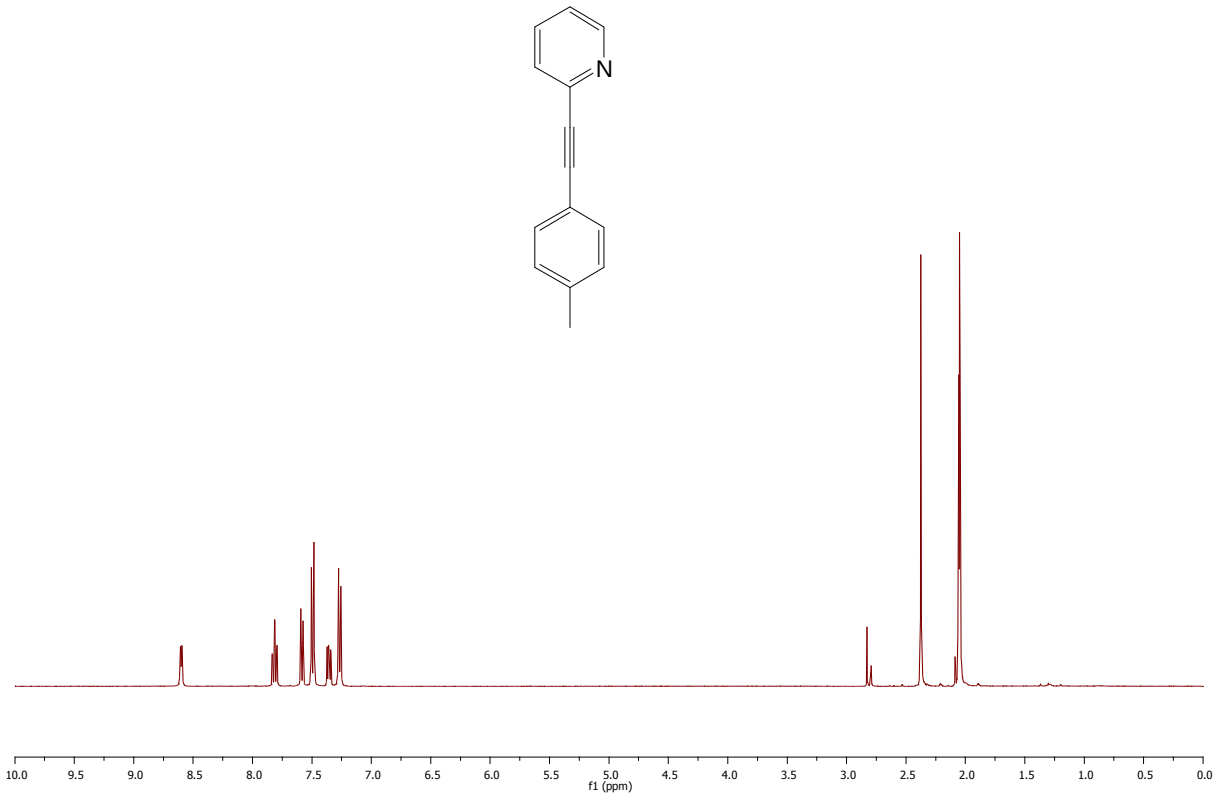
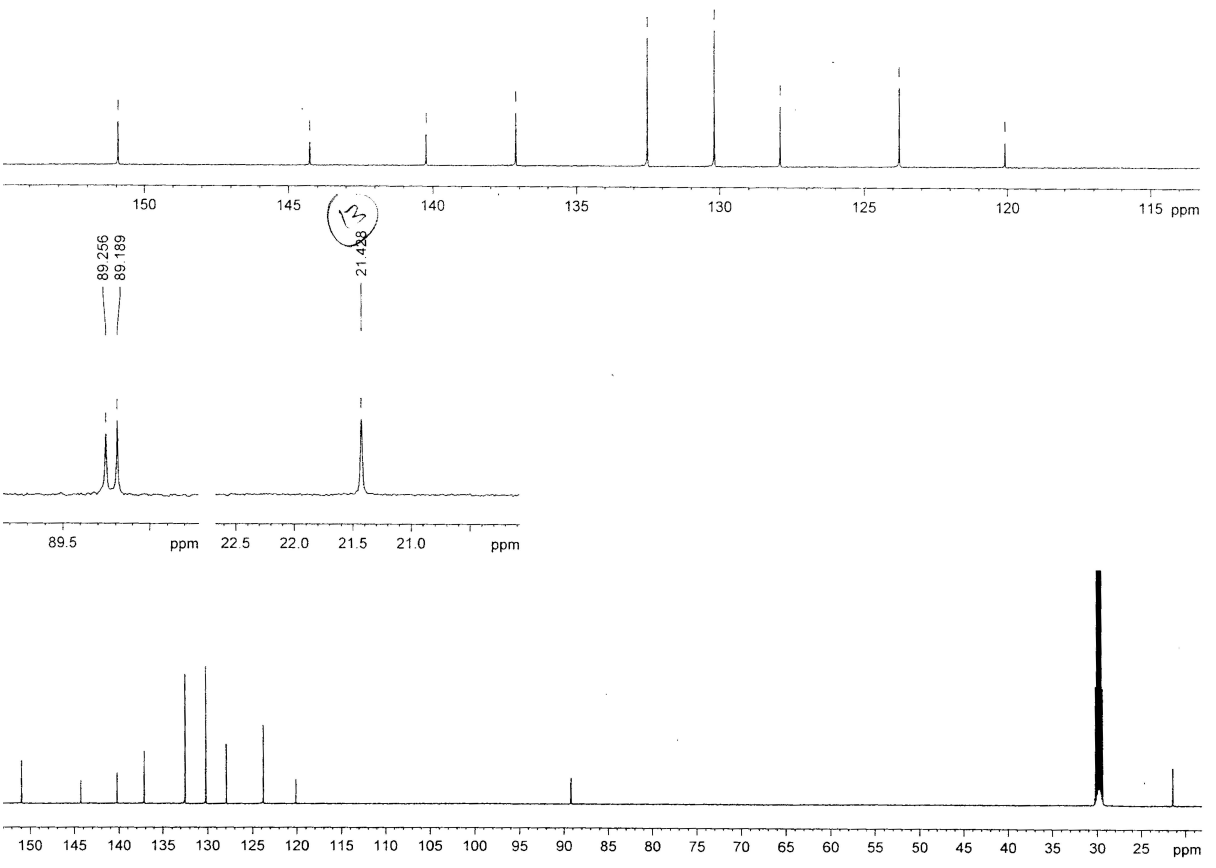
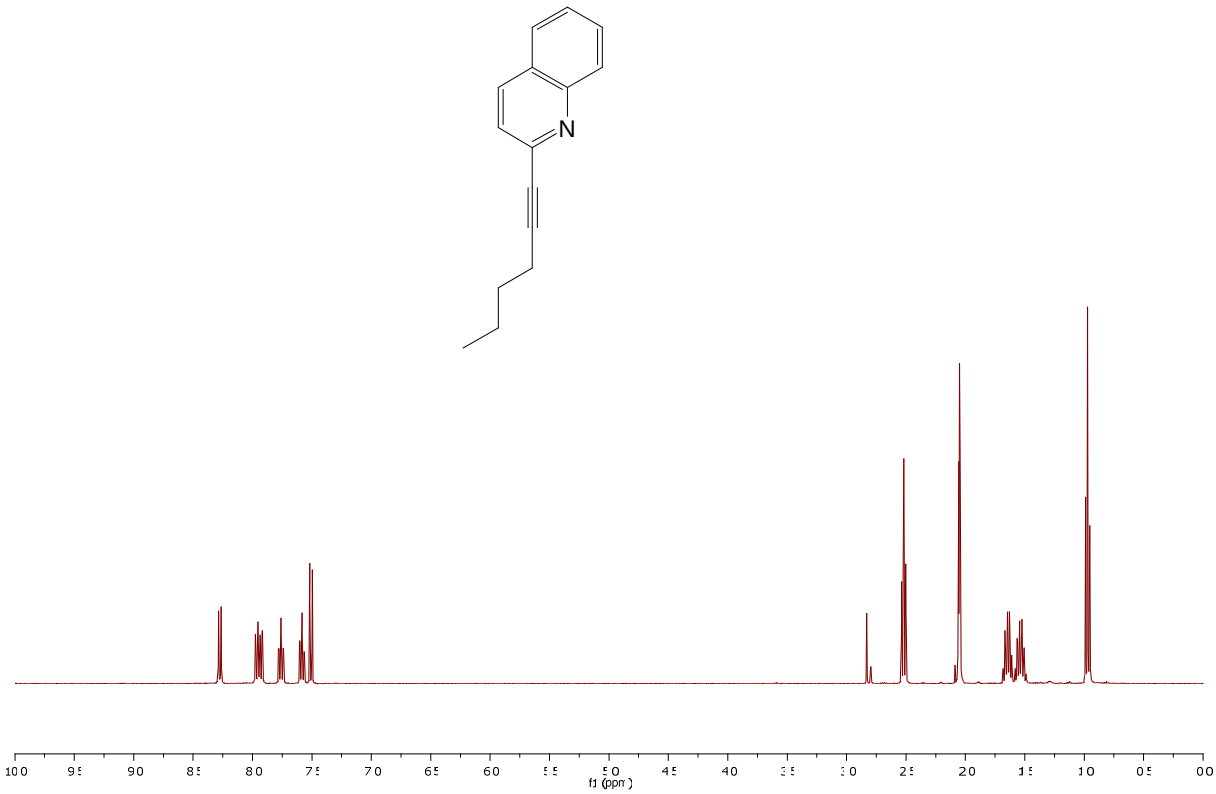
7) ^{1}H and ^{13}C NMR spectra

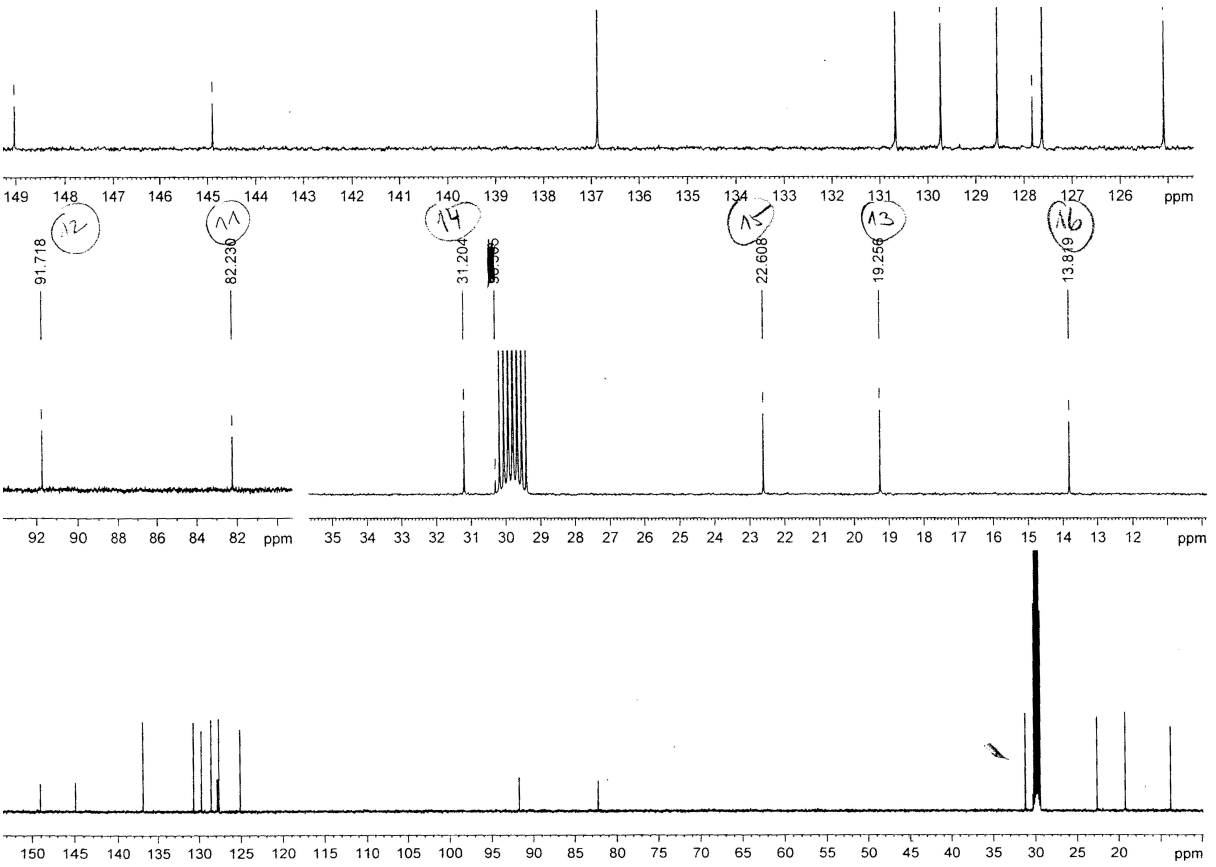


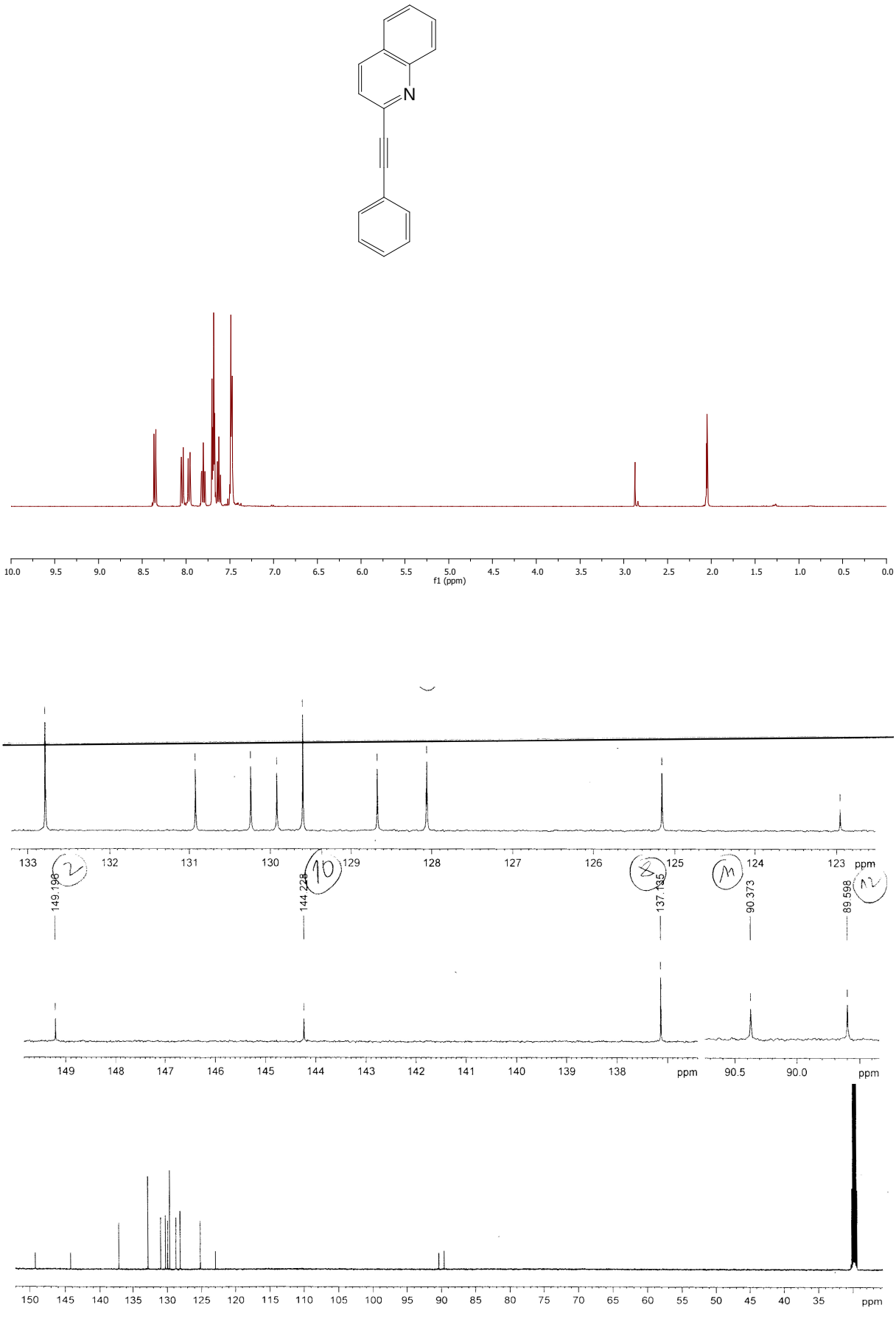


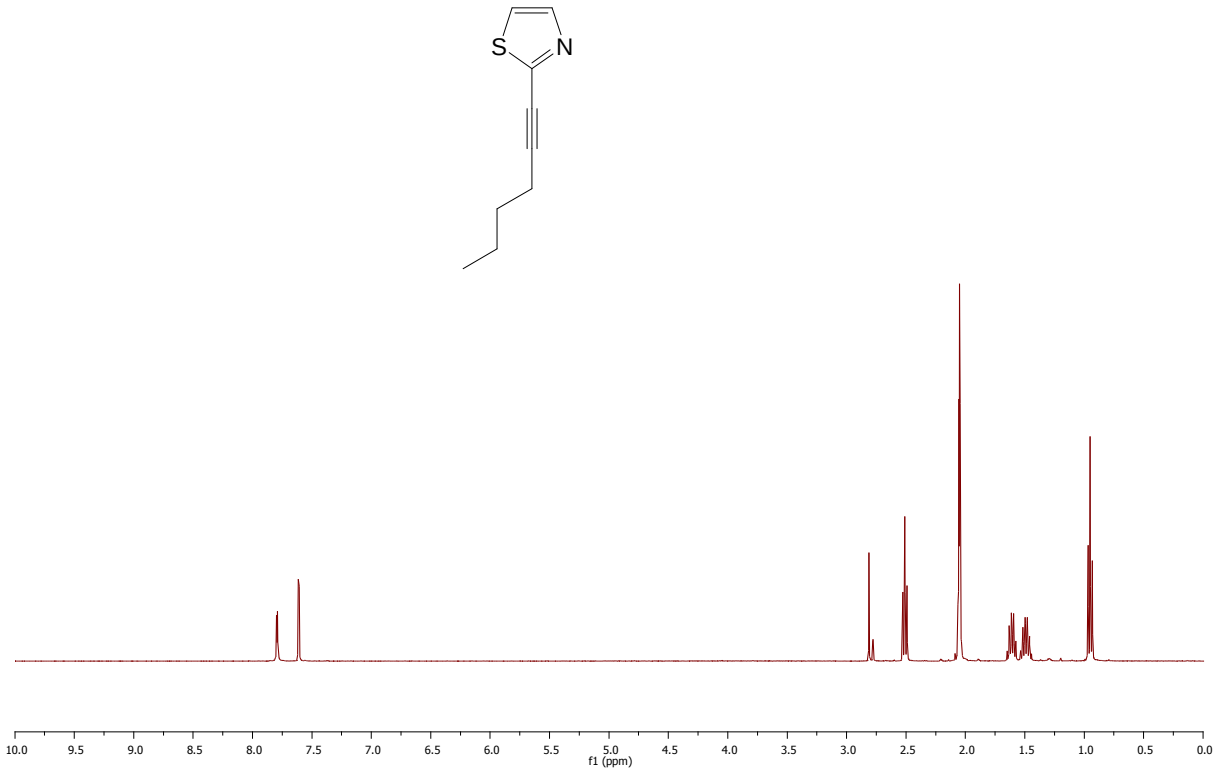


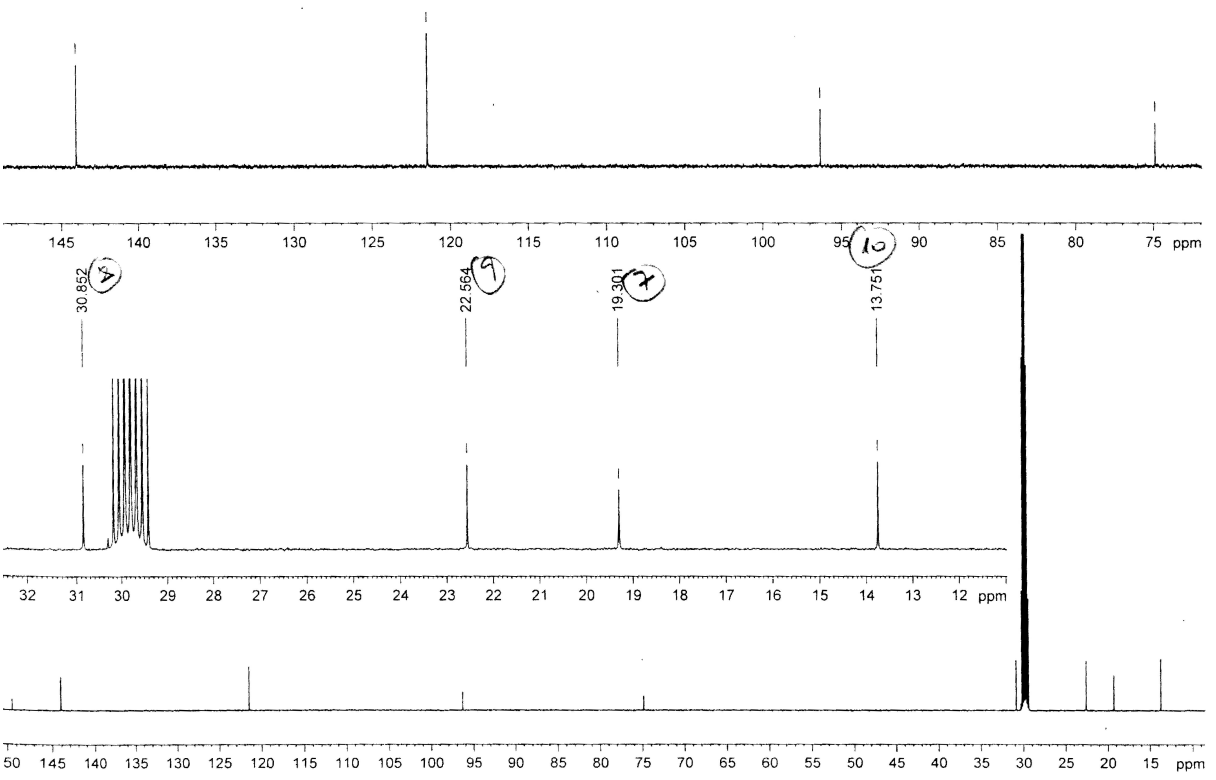


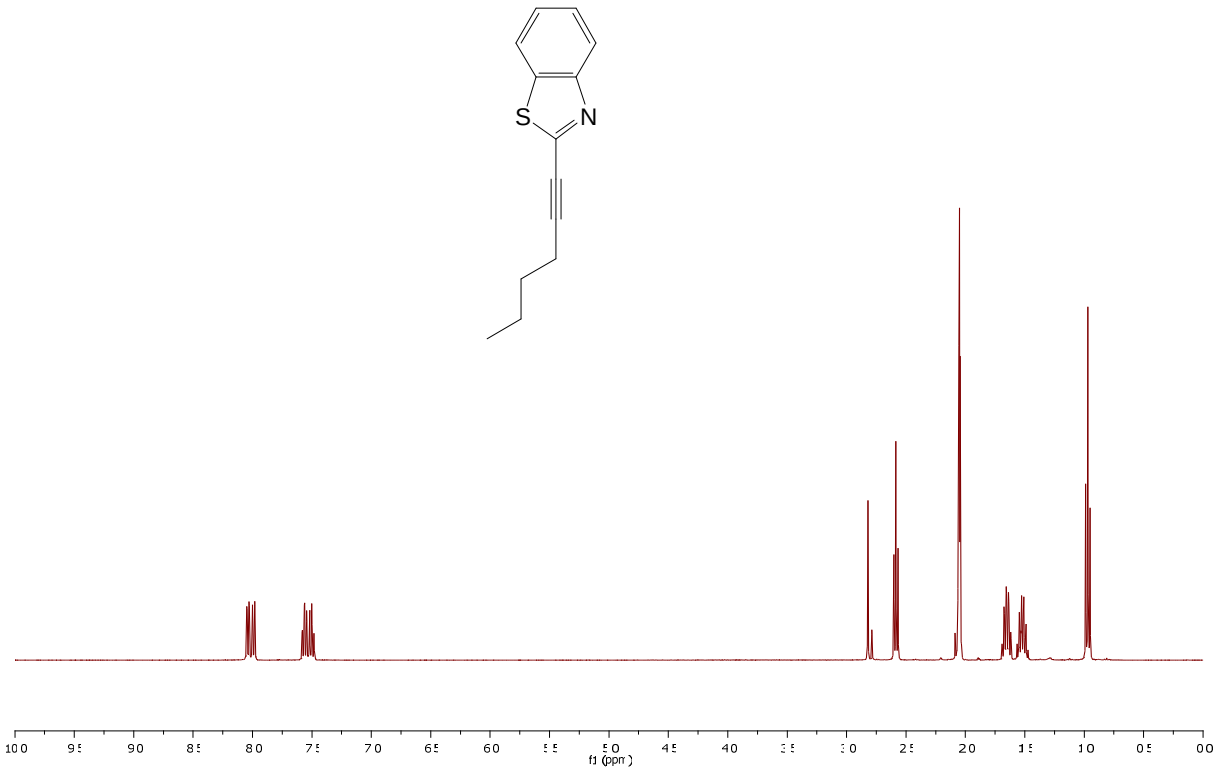


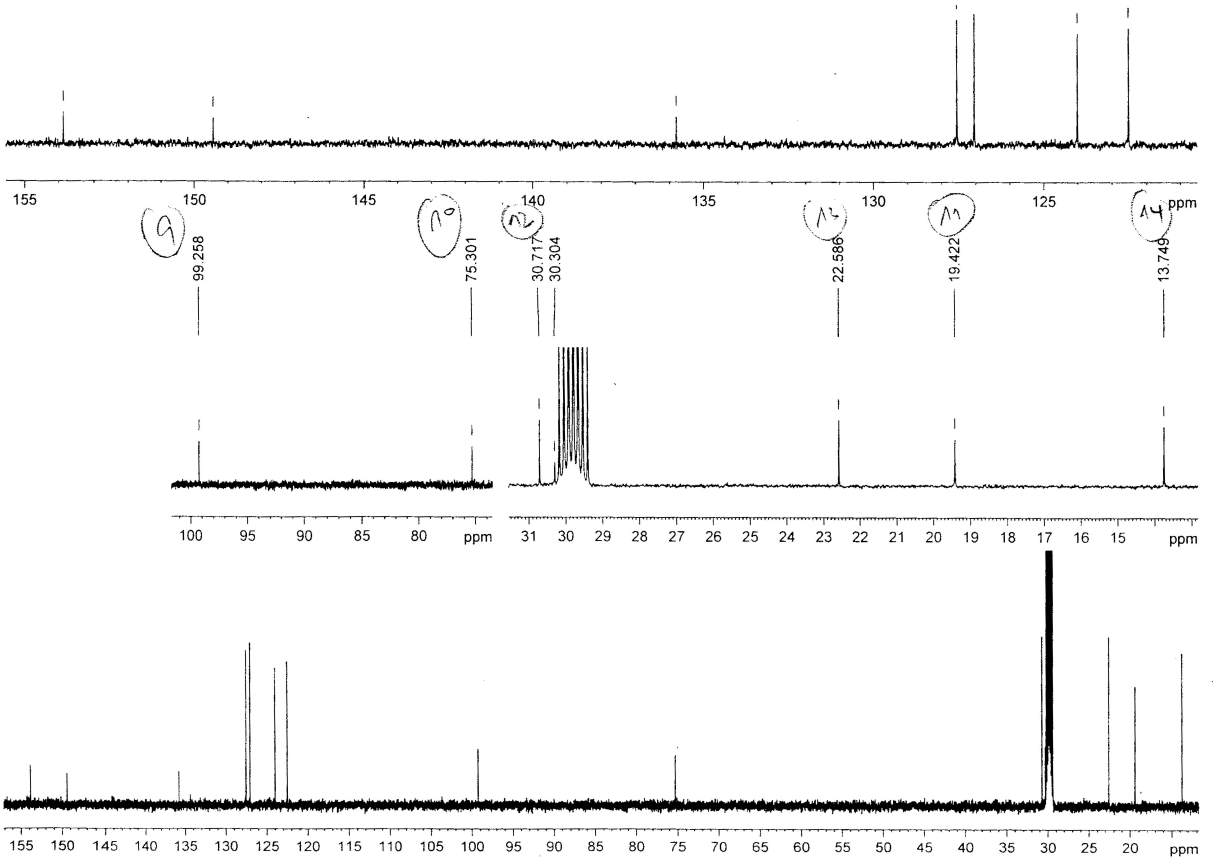


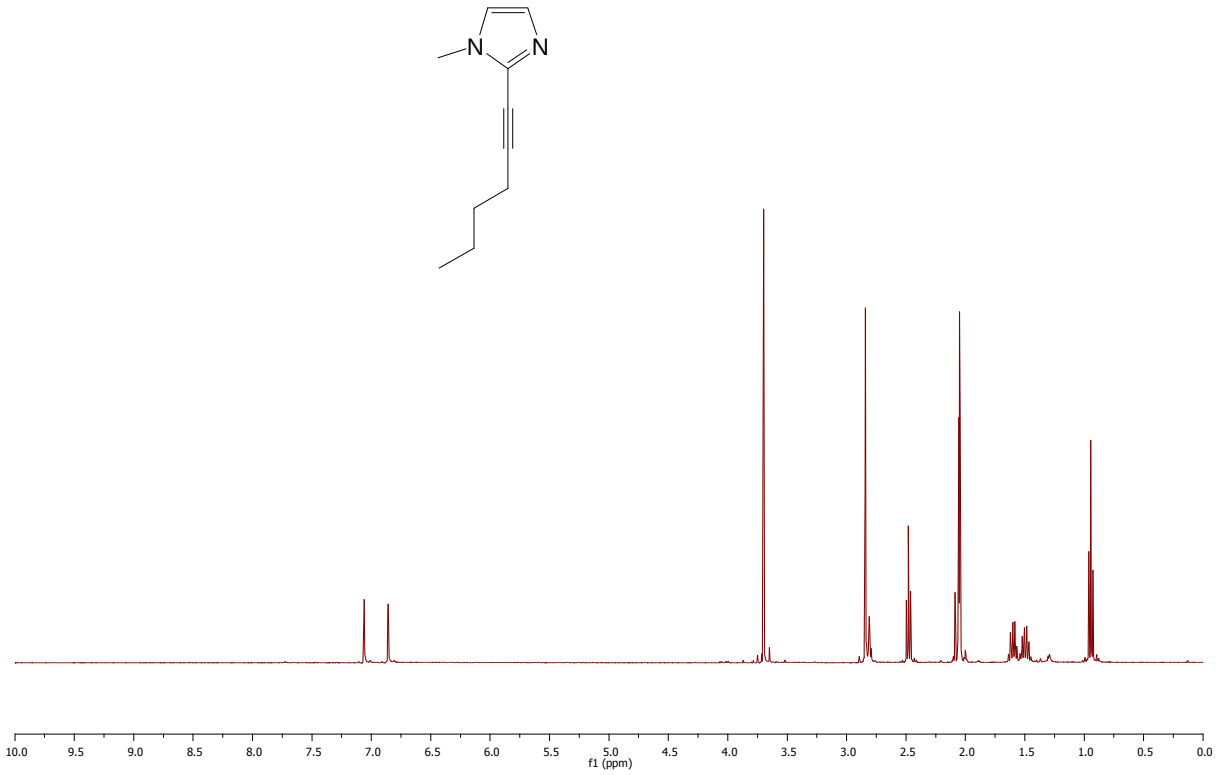


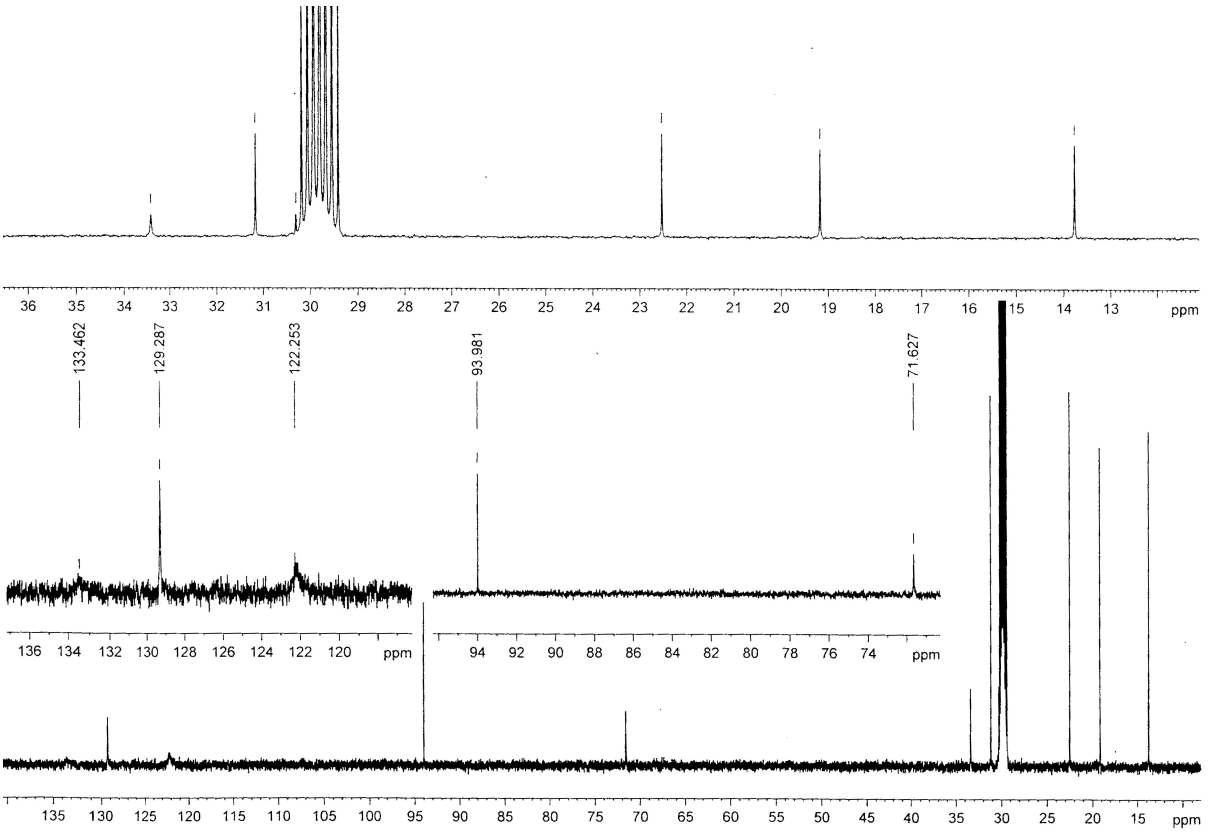


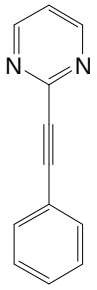












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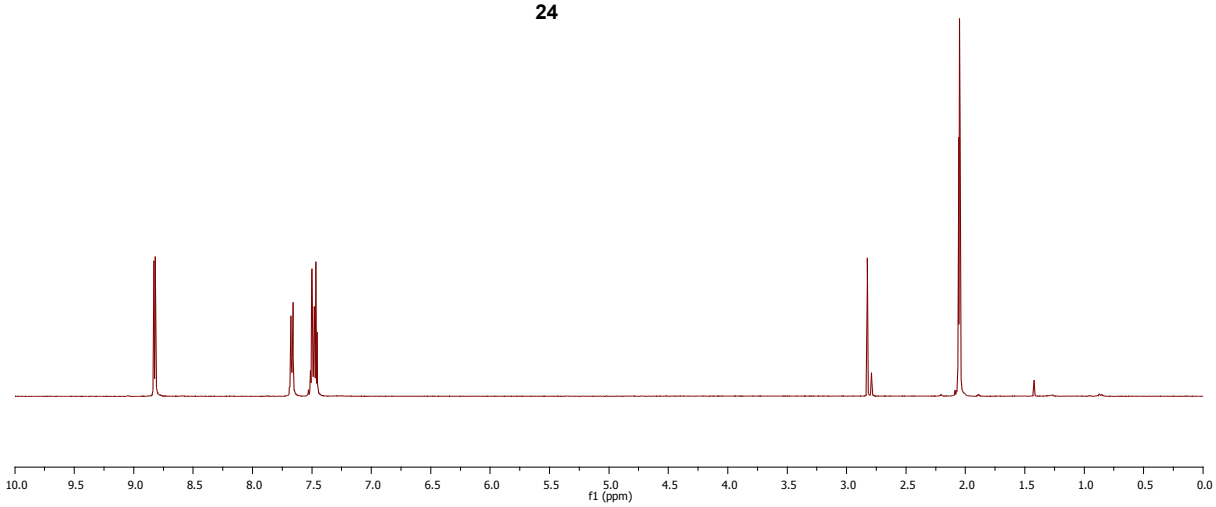

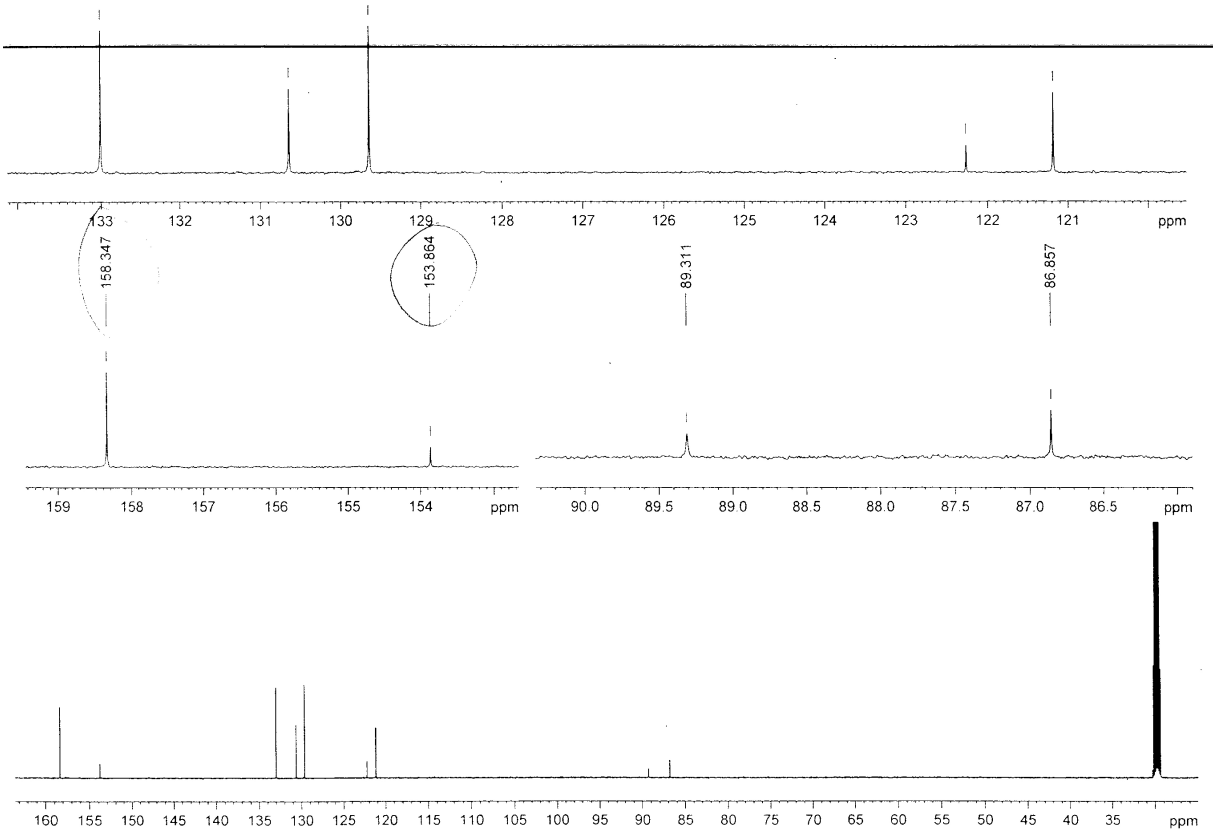

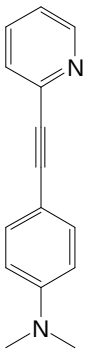

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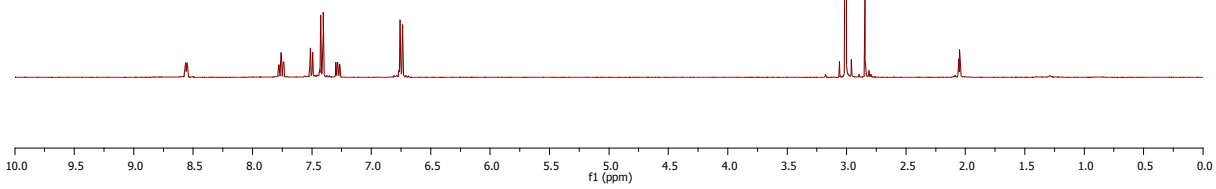

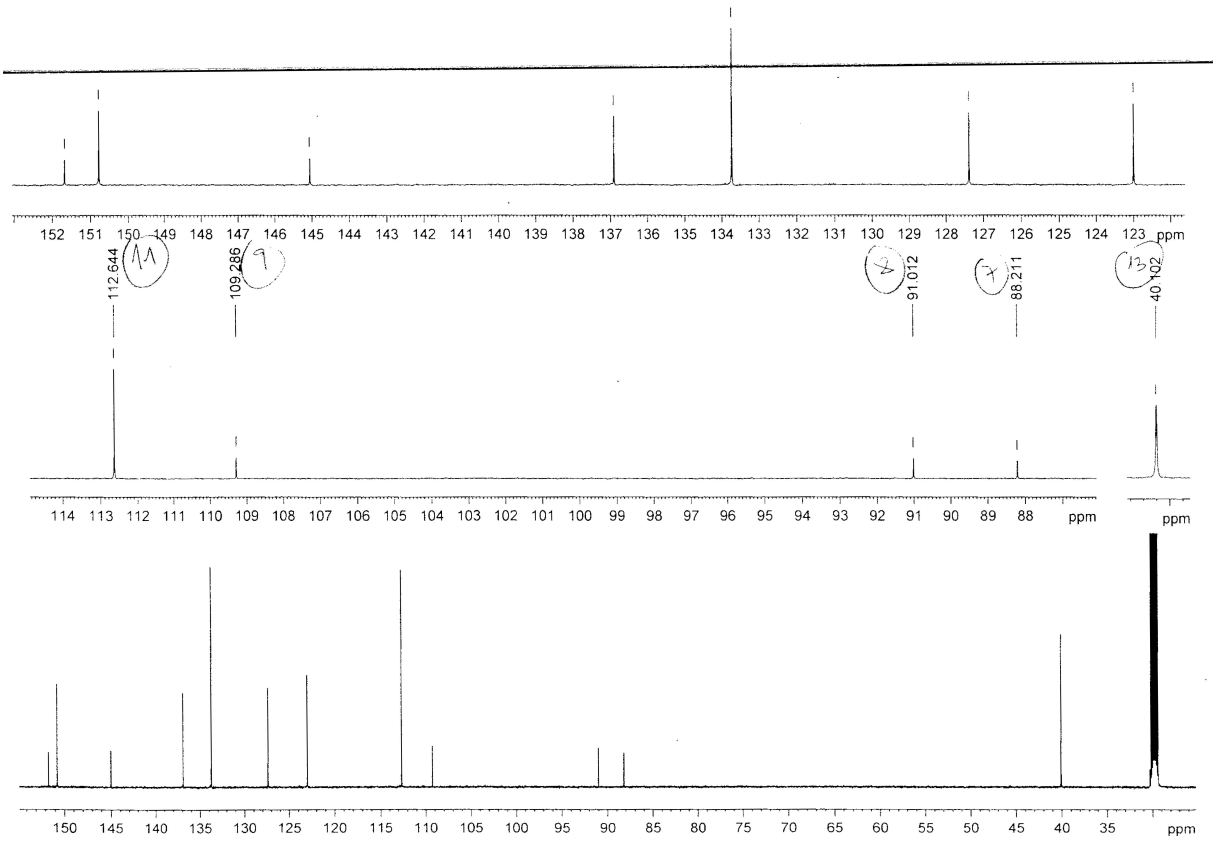

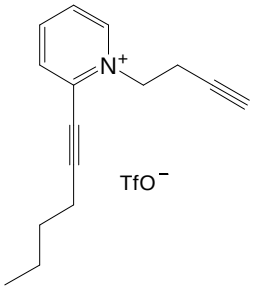

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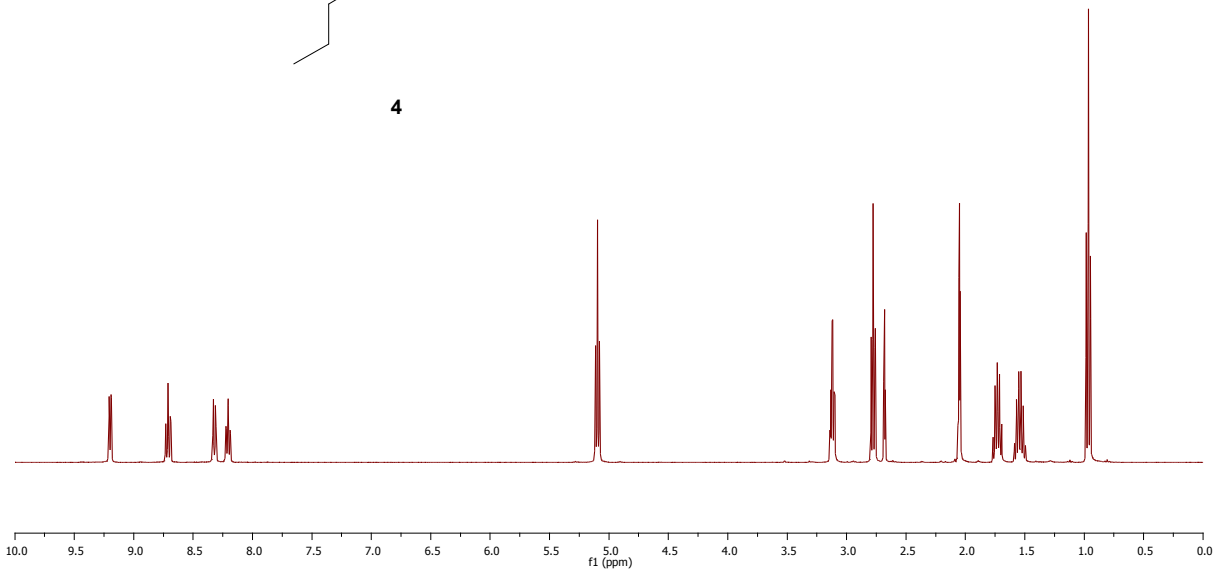

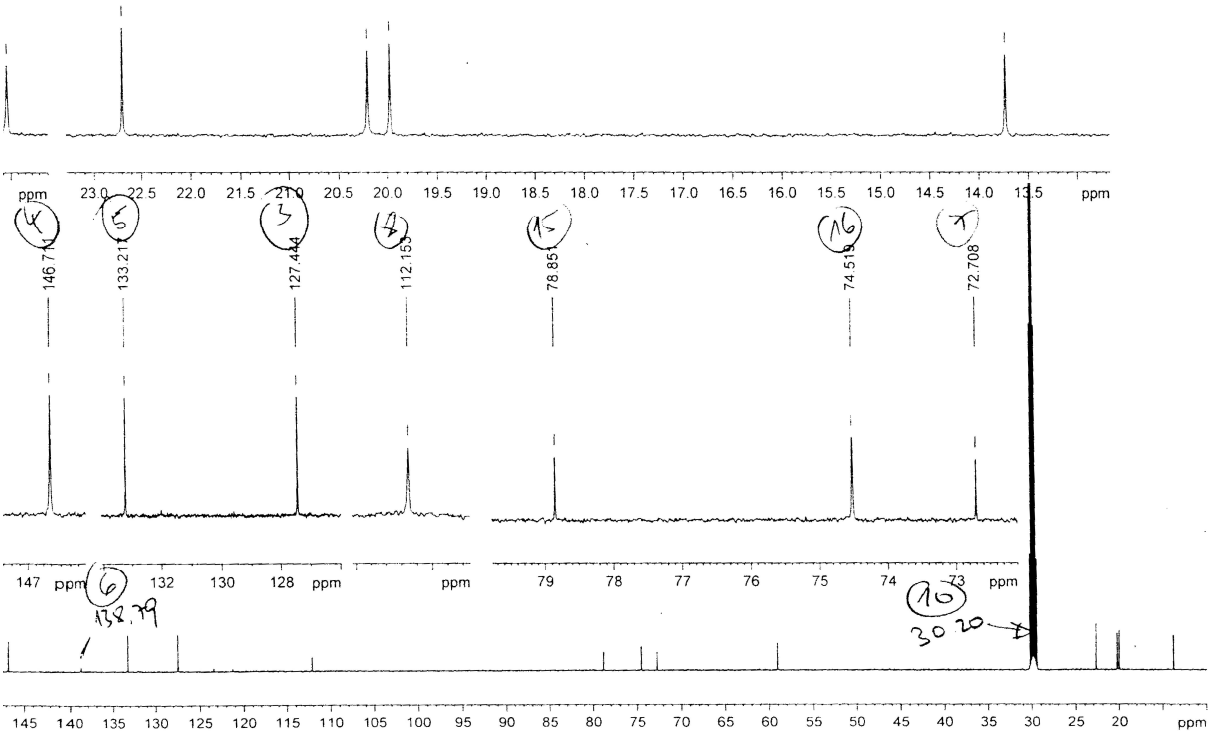

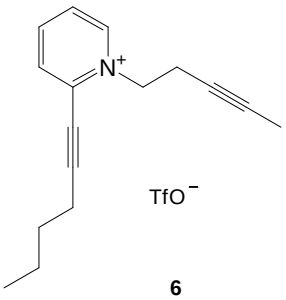

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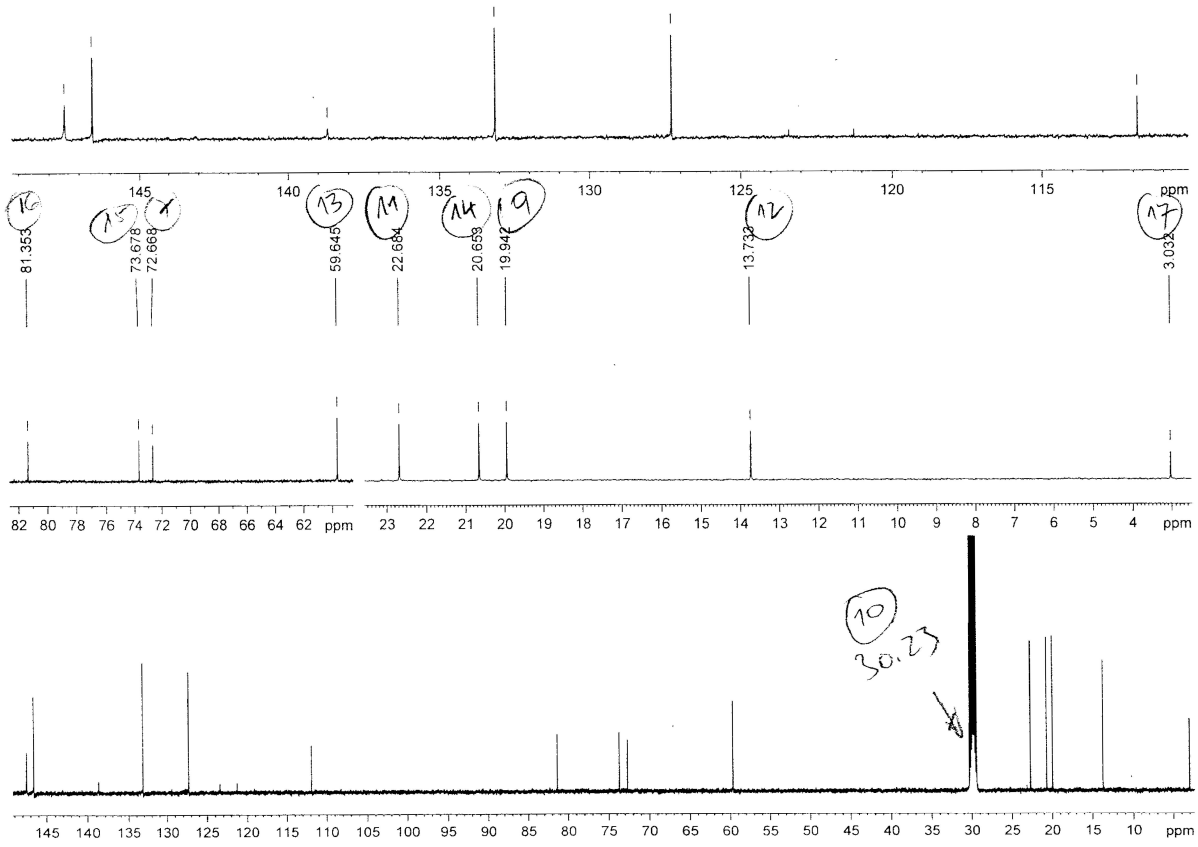

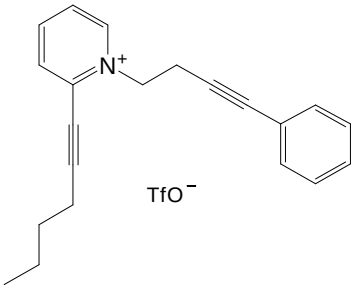

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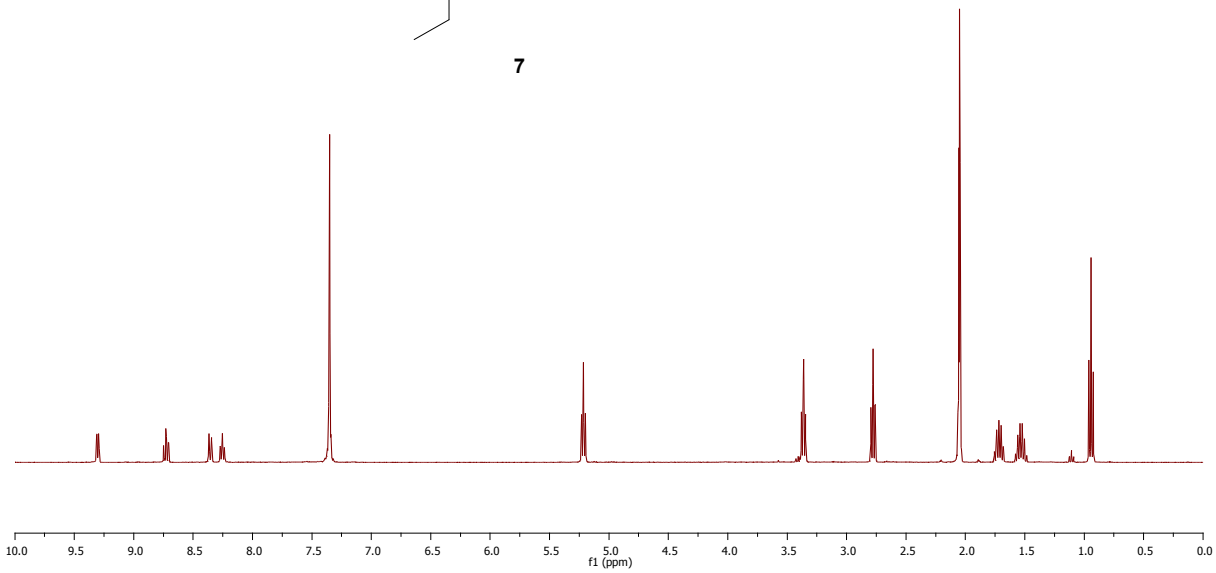

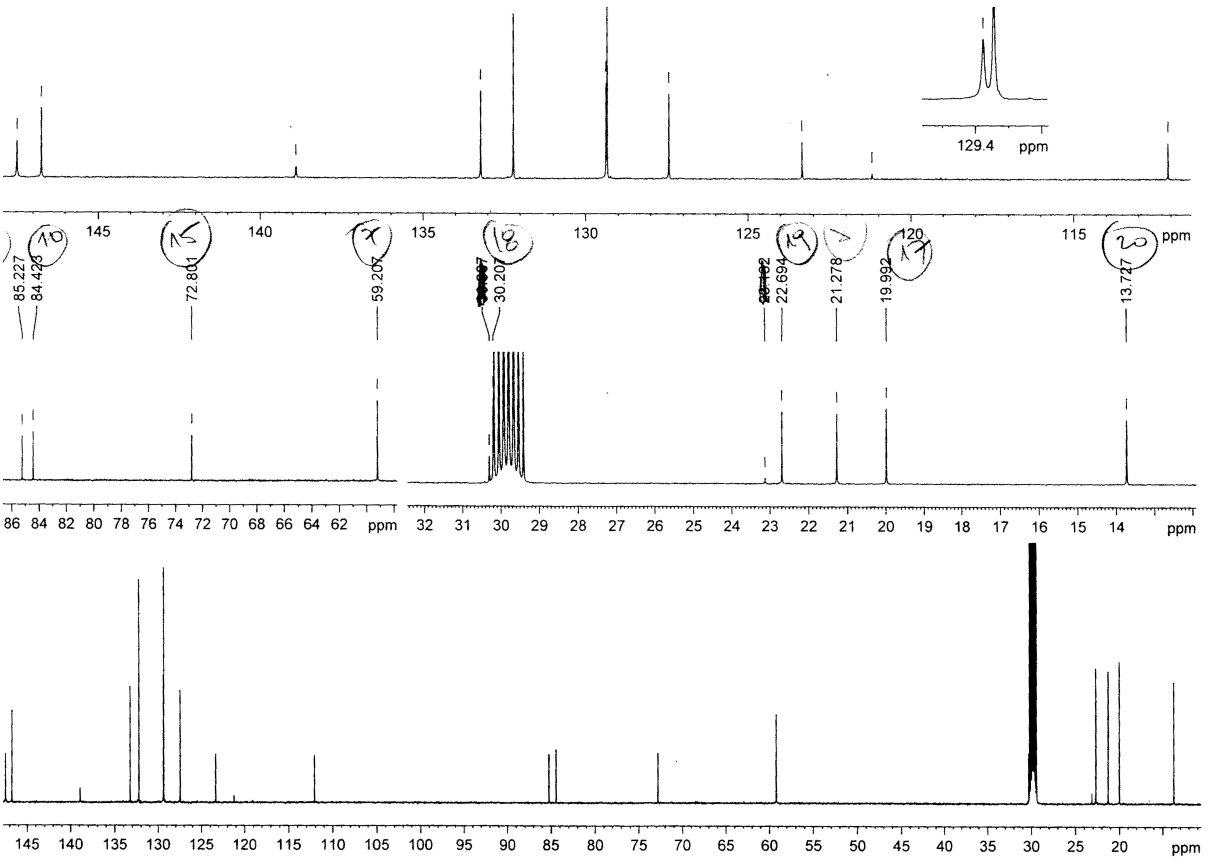

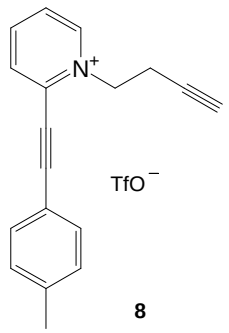

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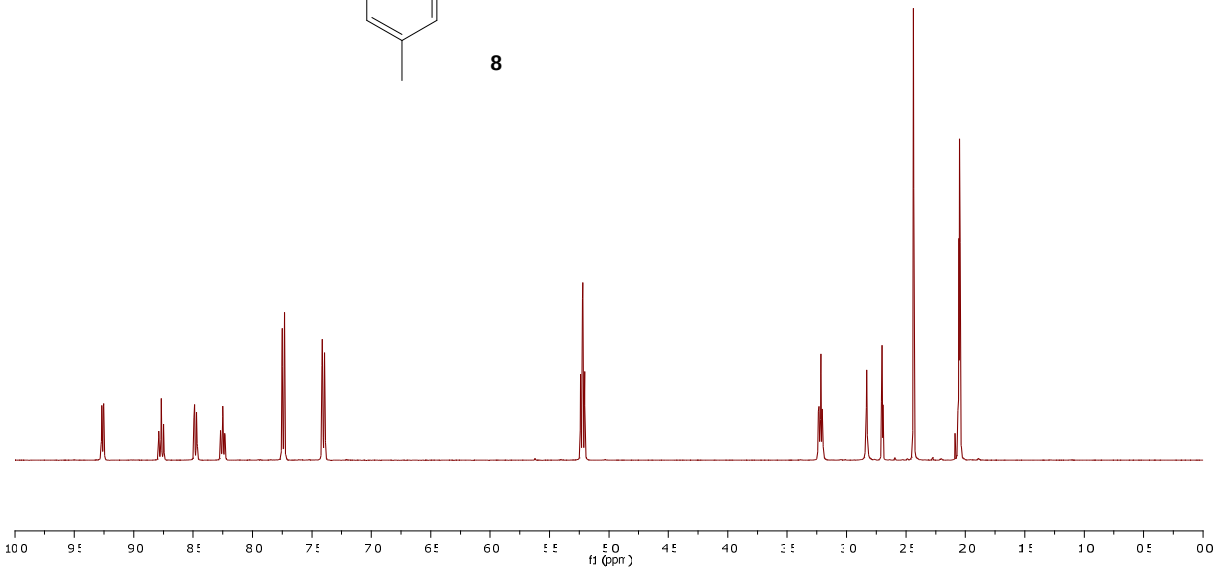

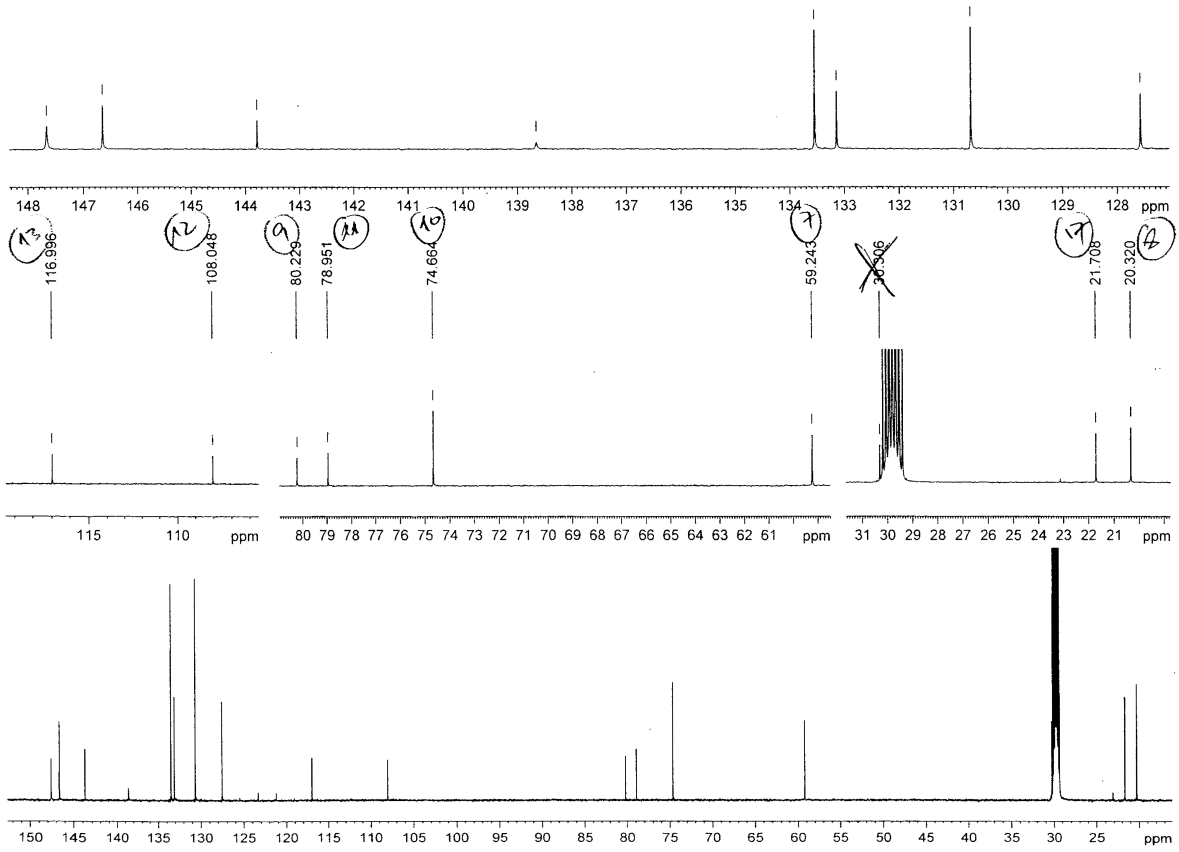

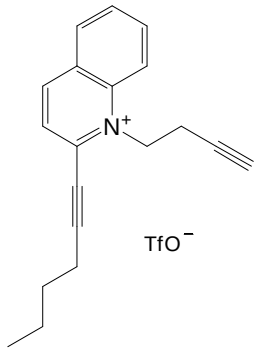

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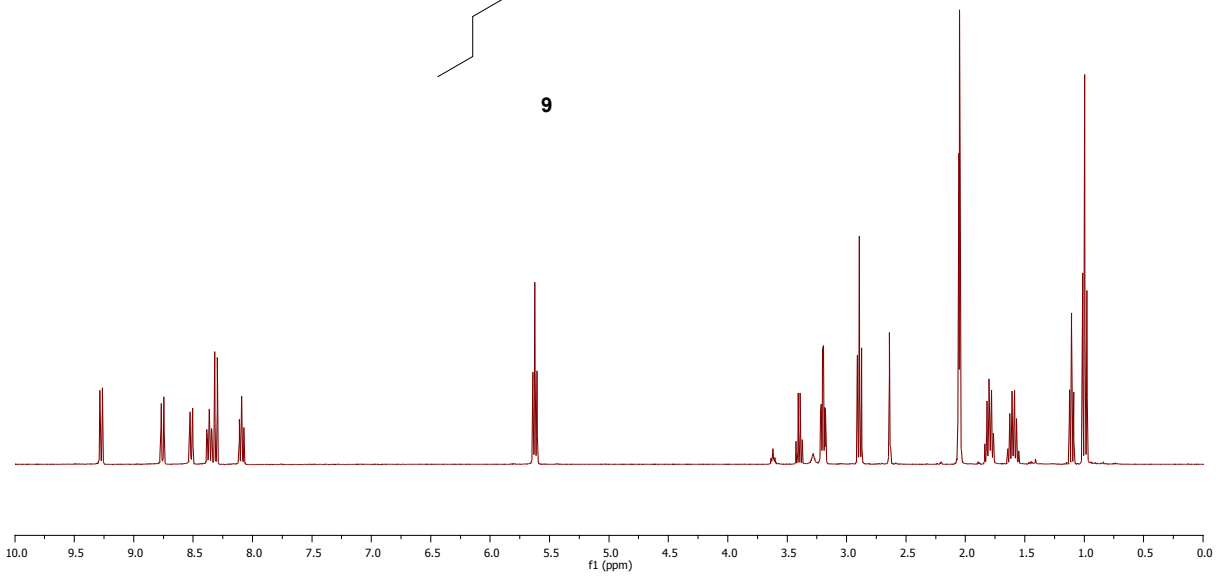

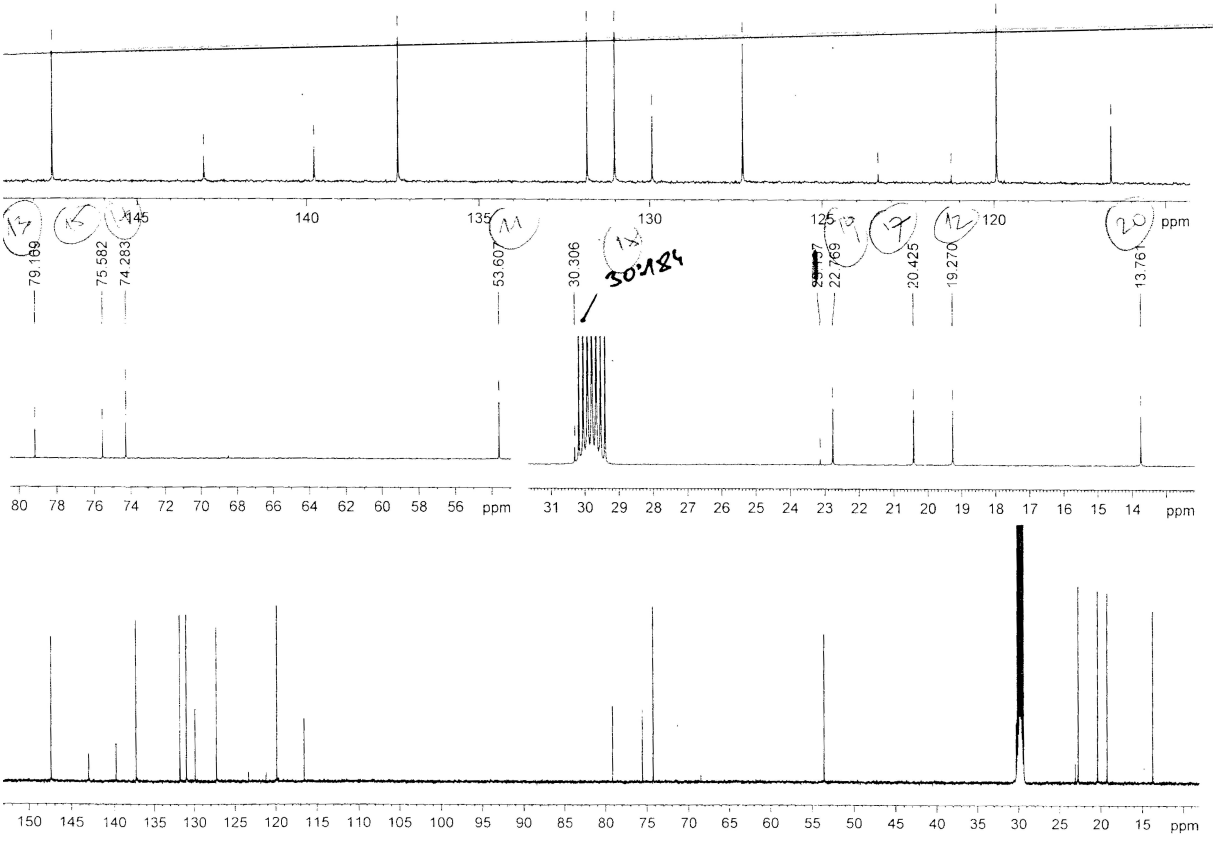

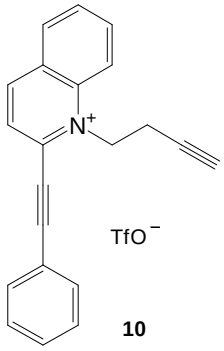

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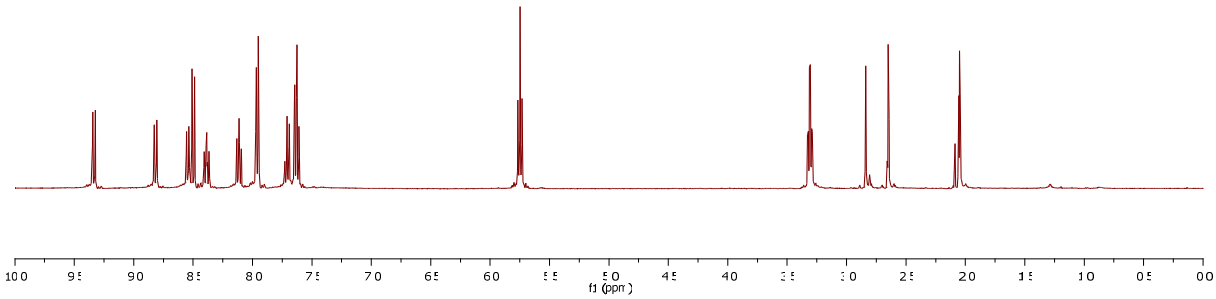

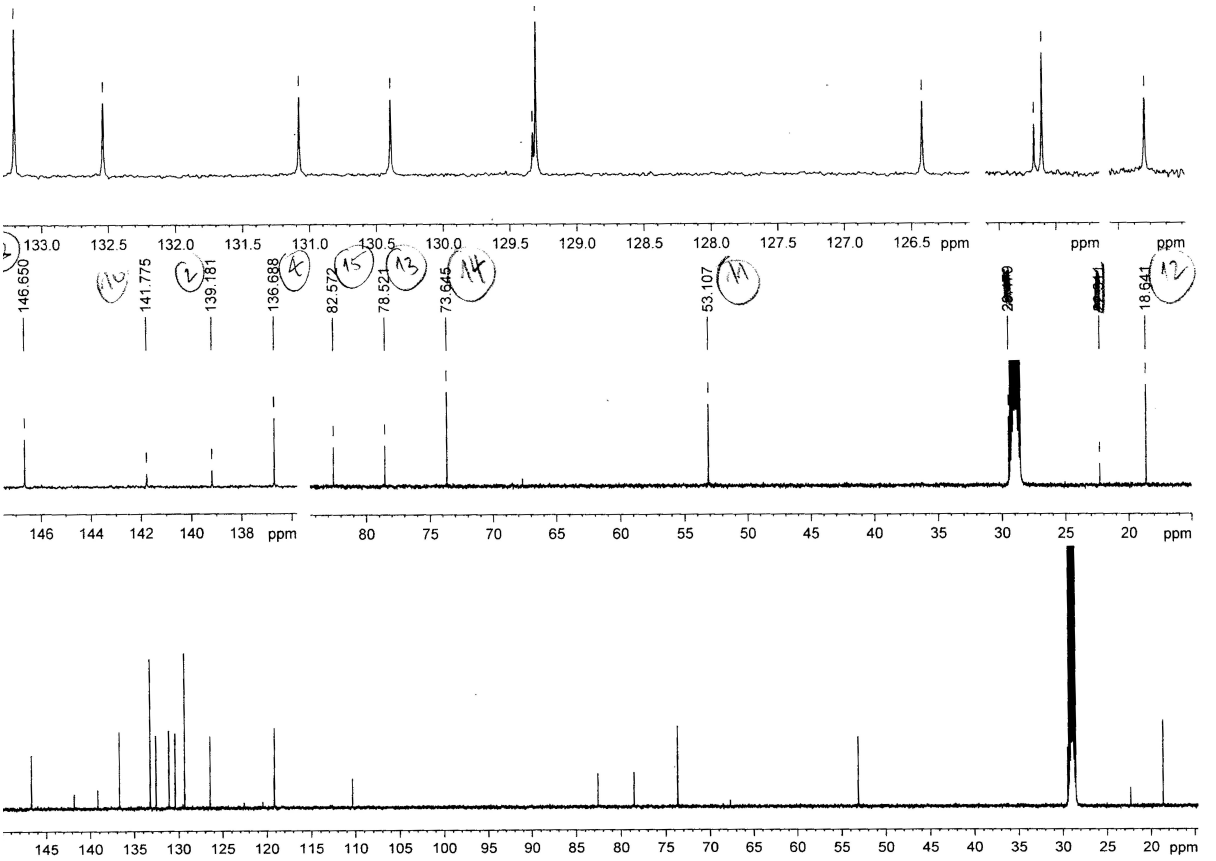

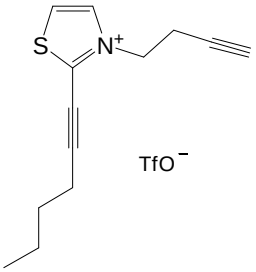

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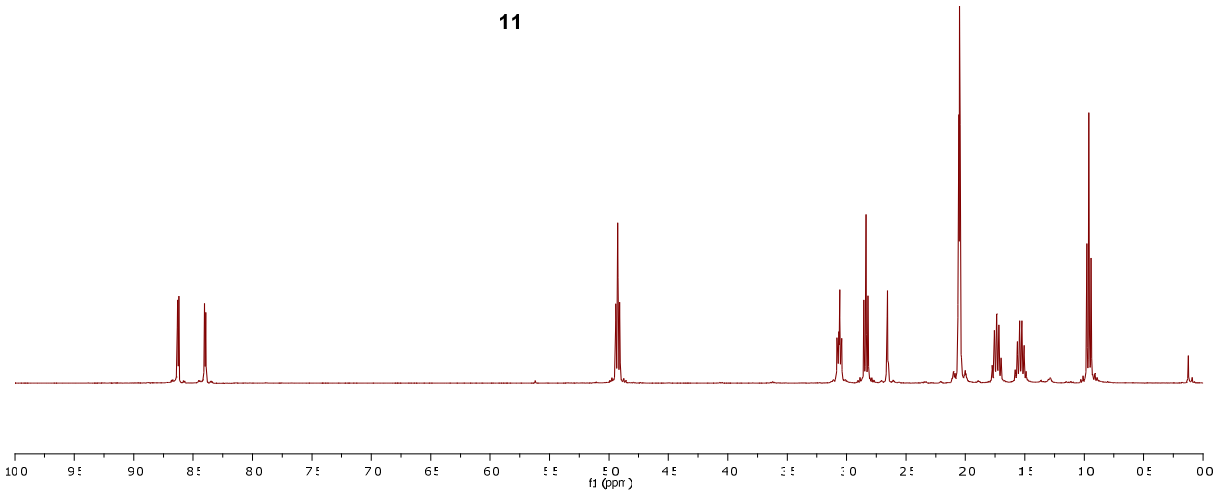

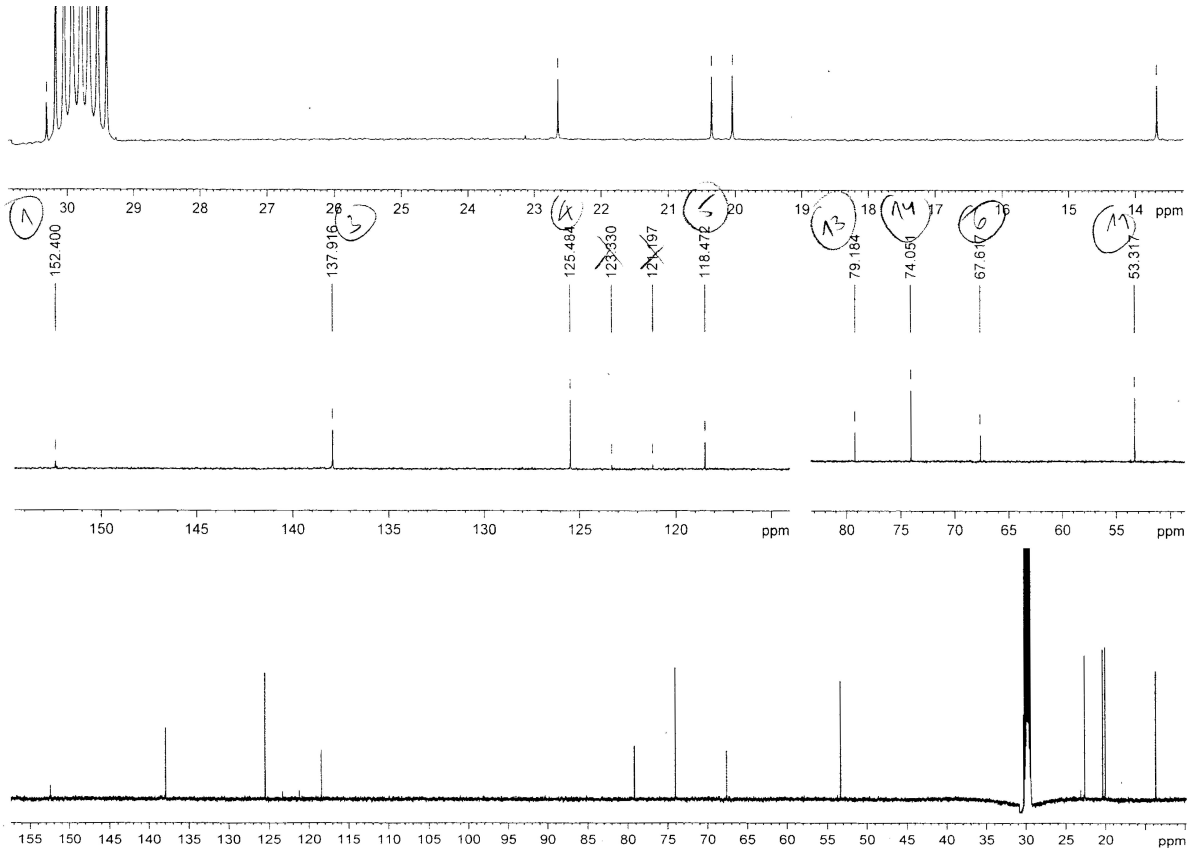

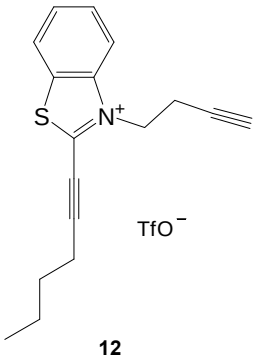

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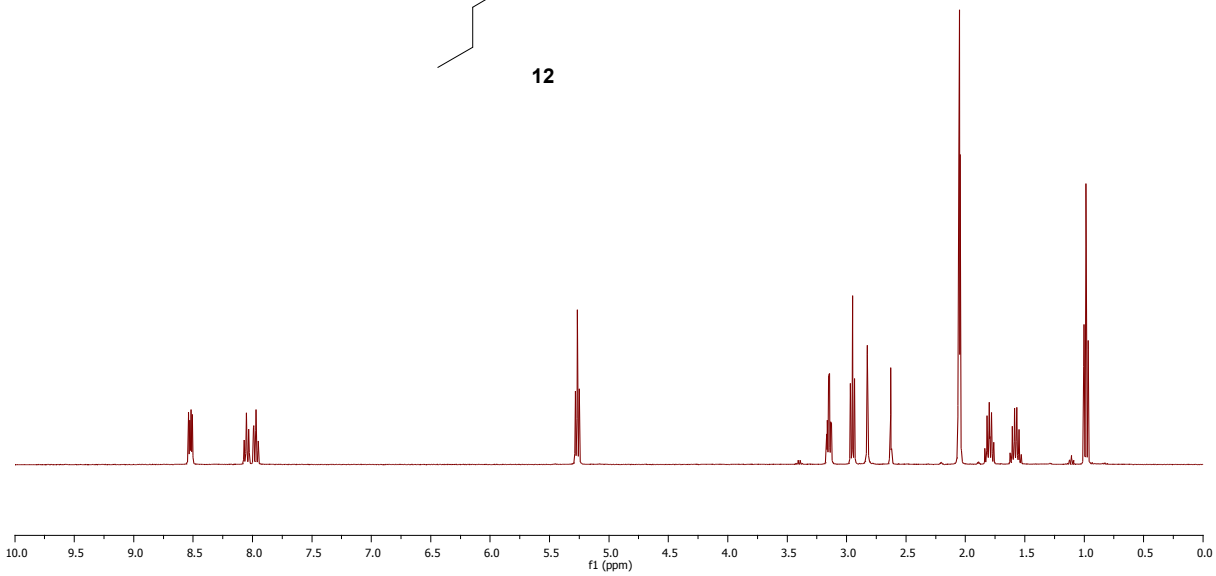

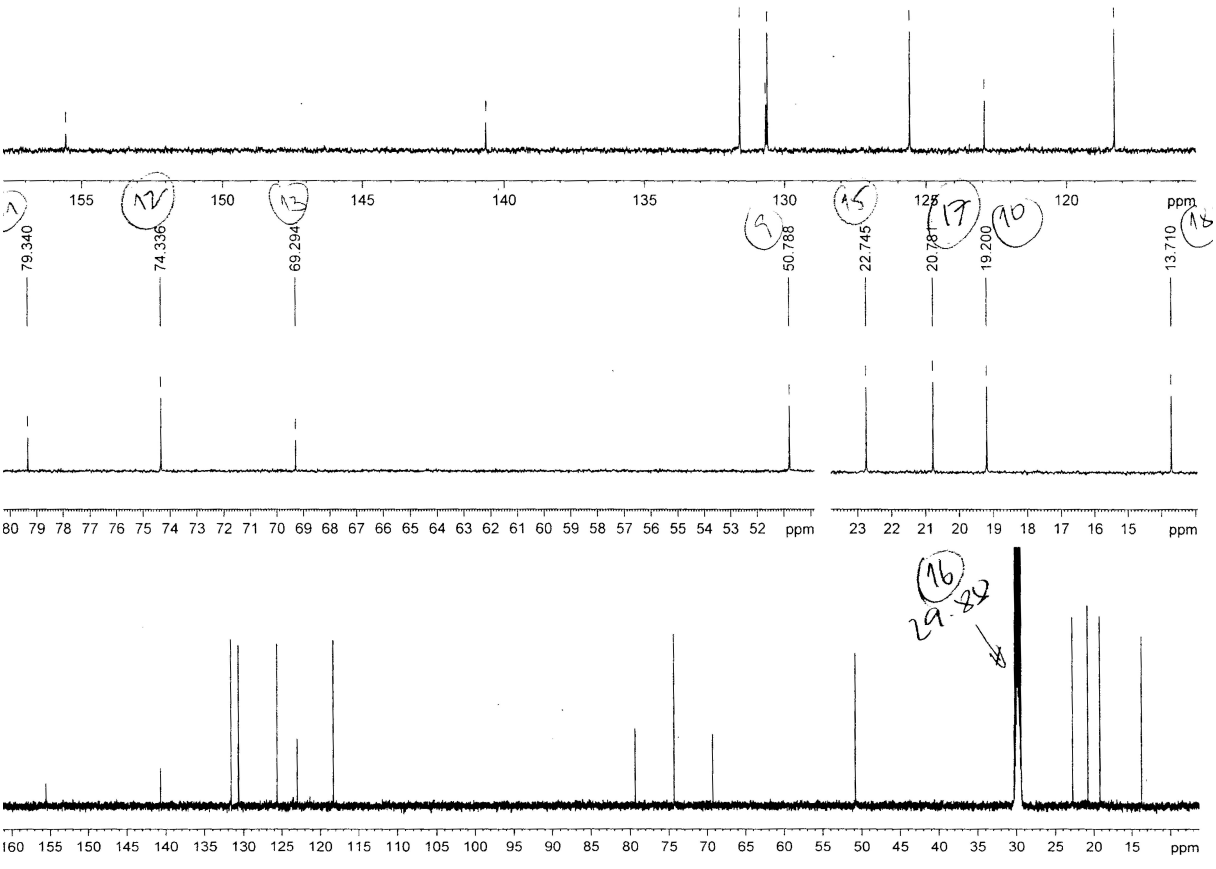

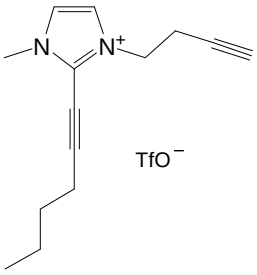

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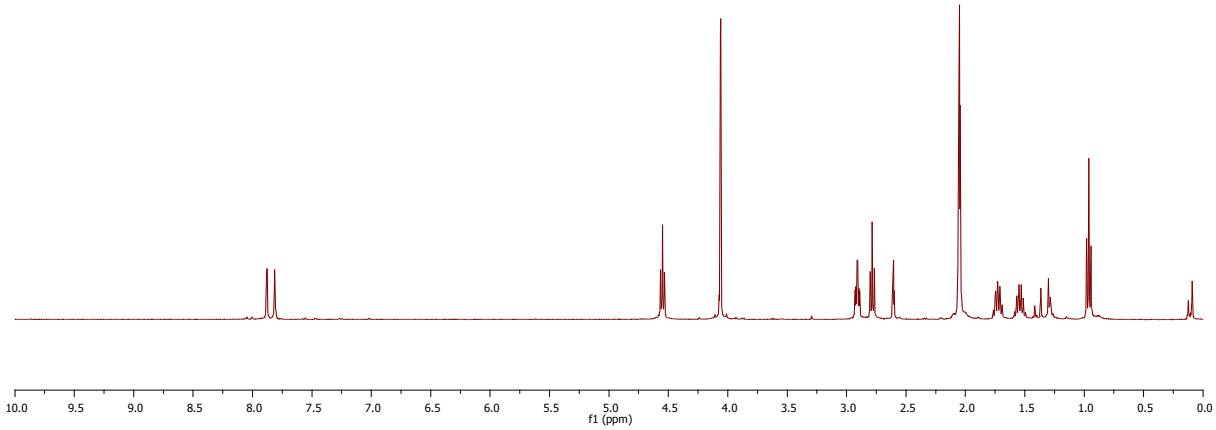

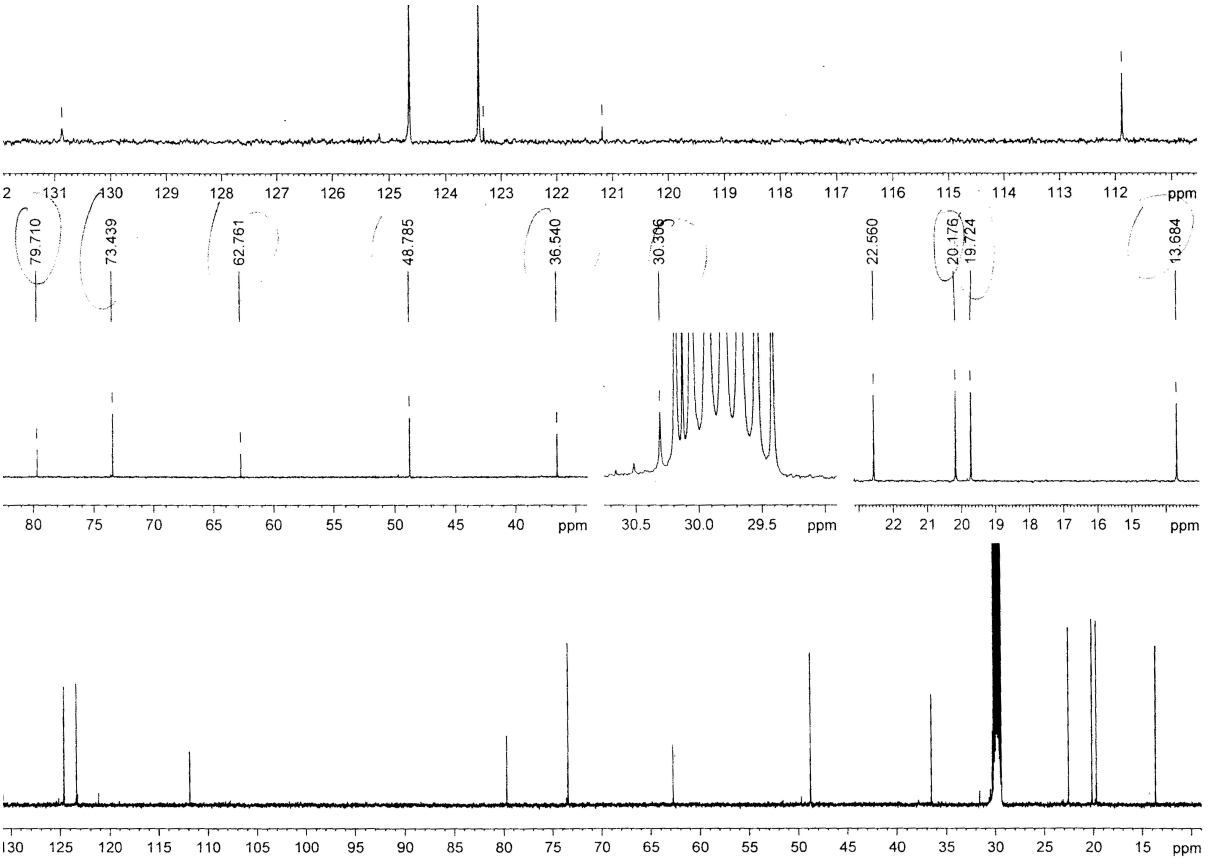

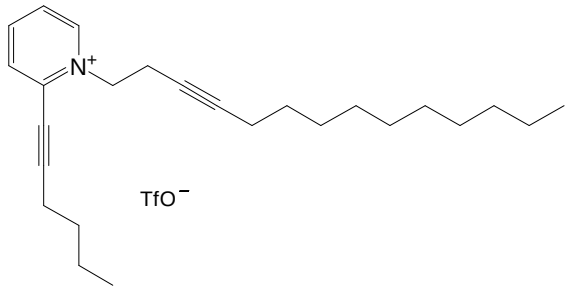

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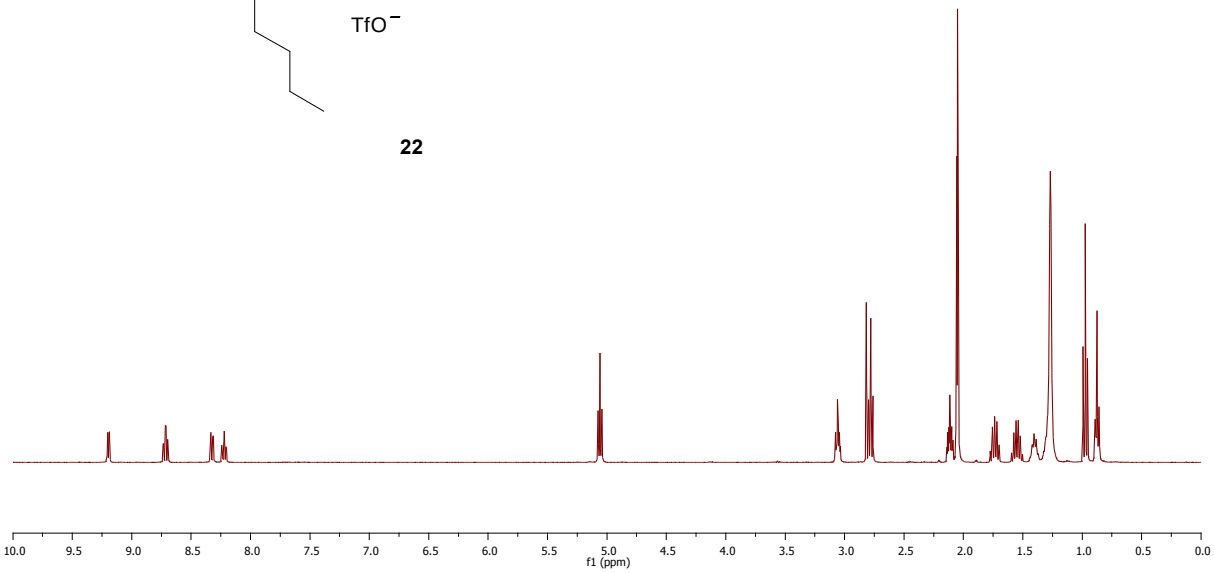

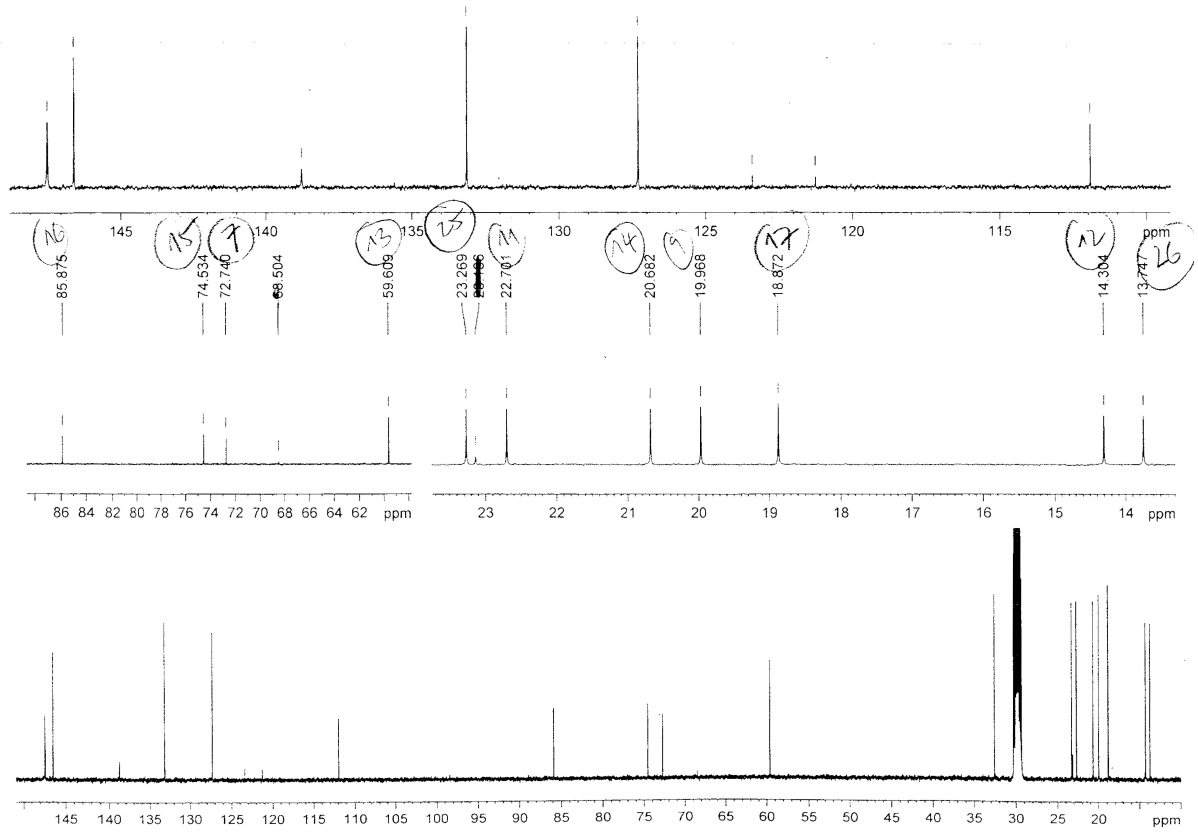

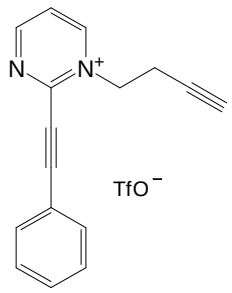

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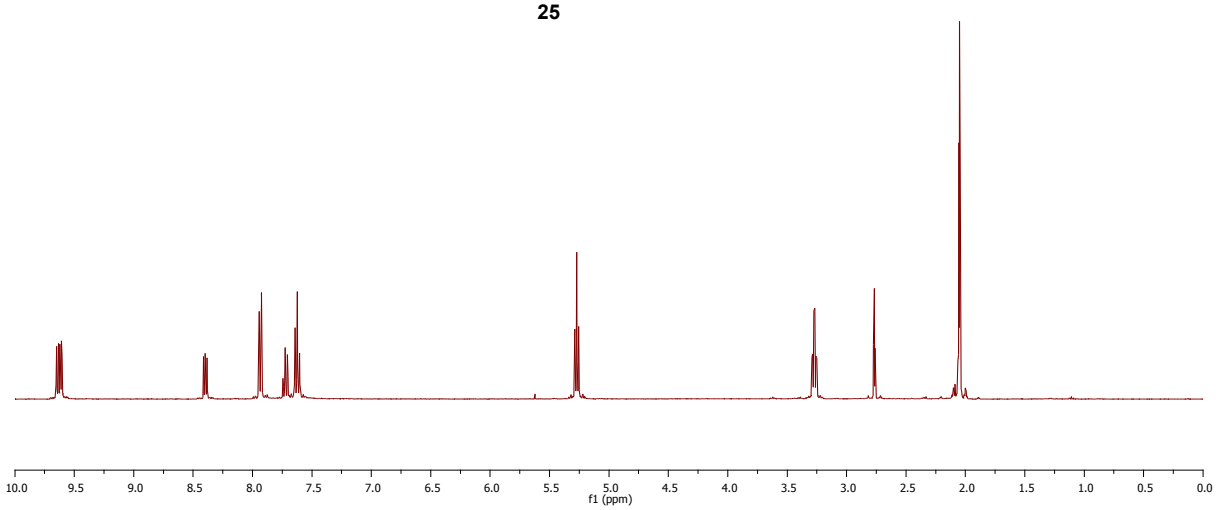

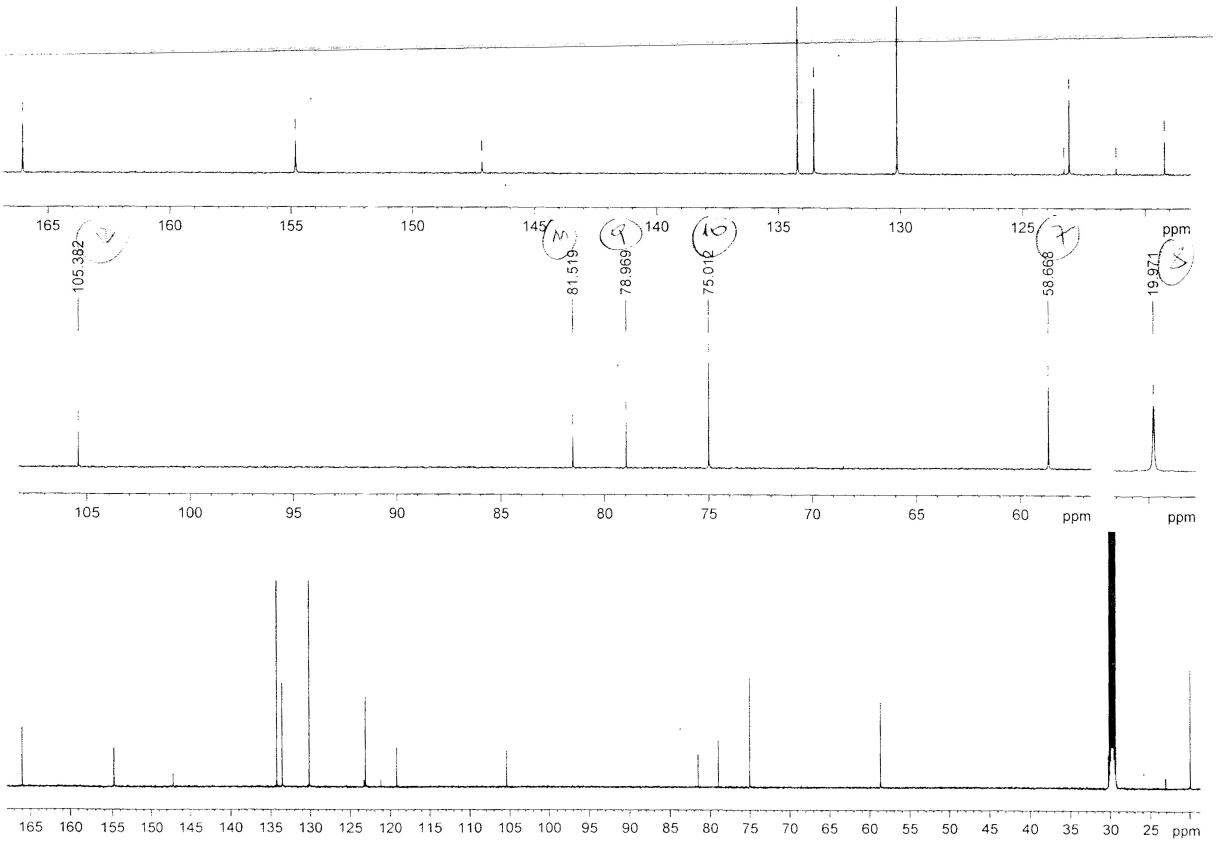

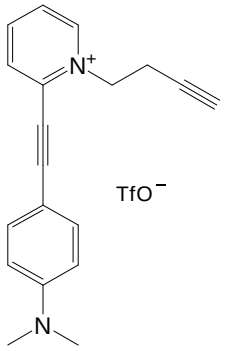

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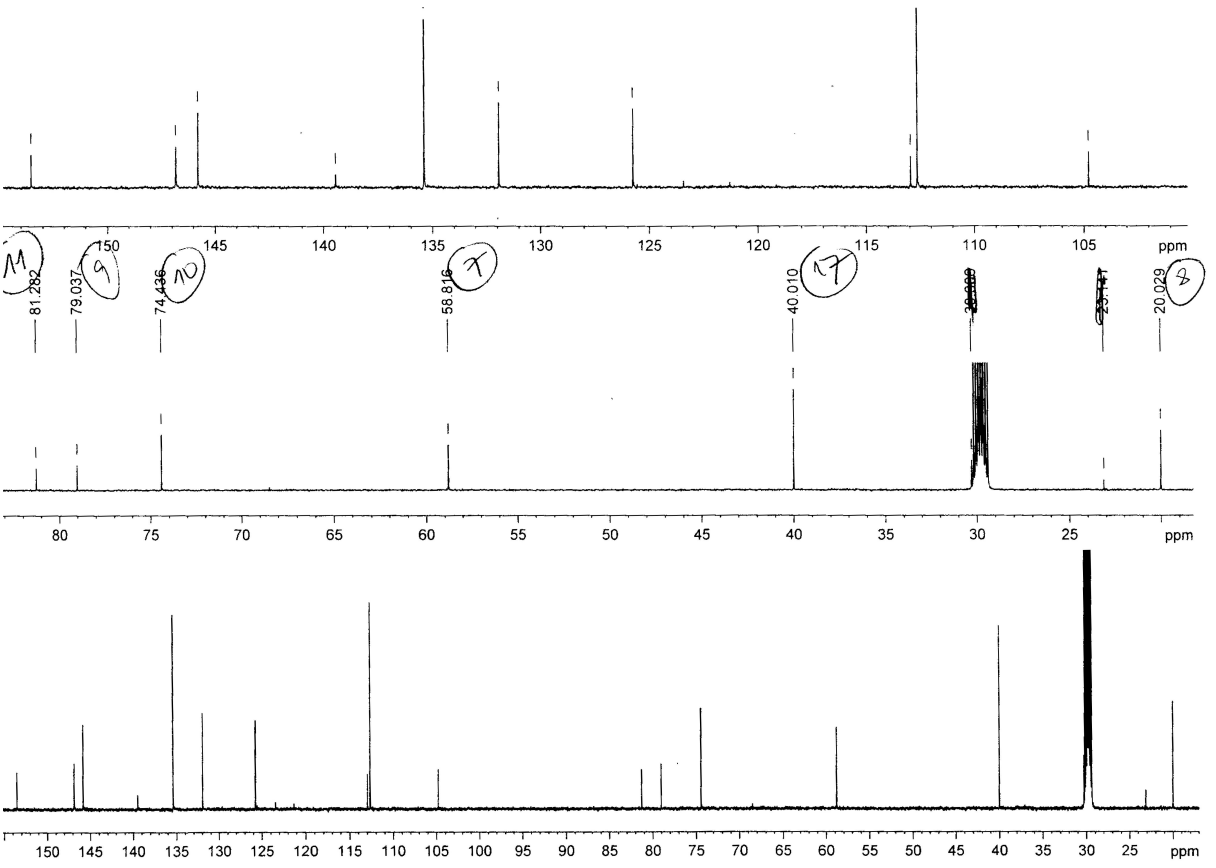

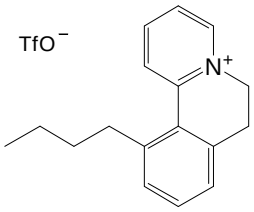

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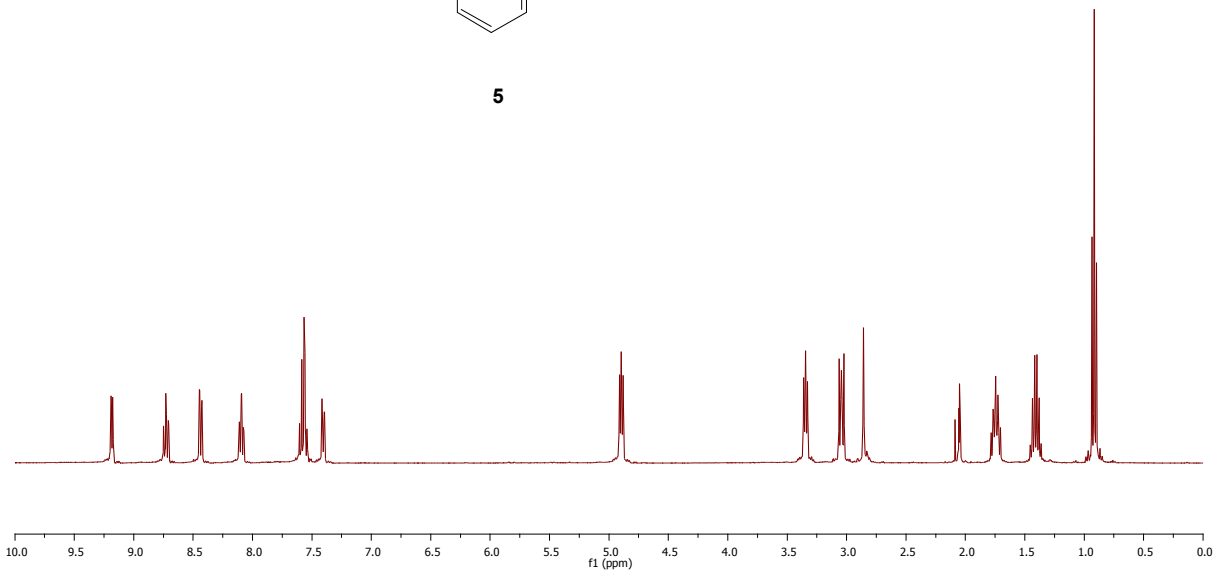

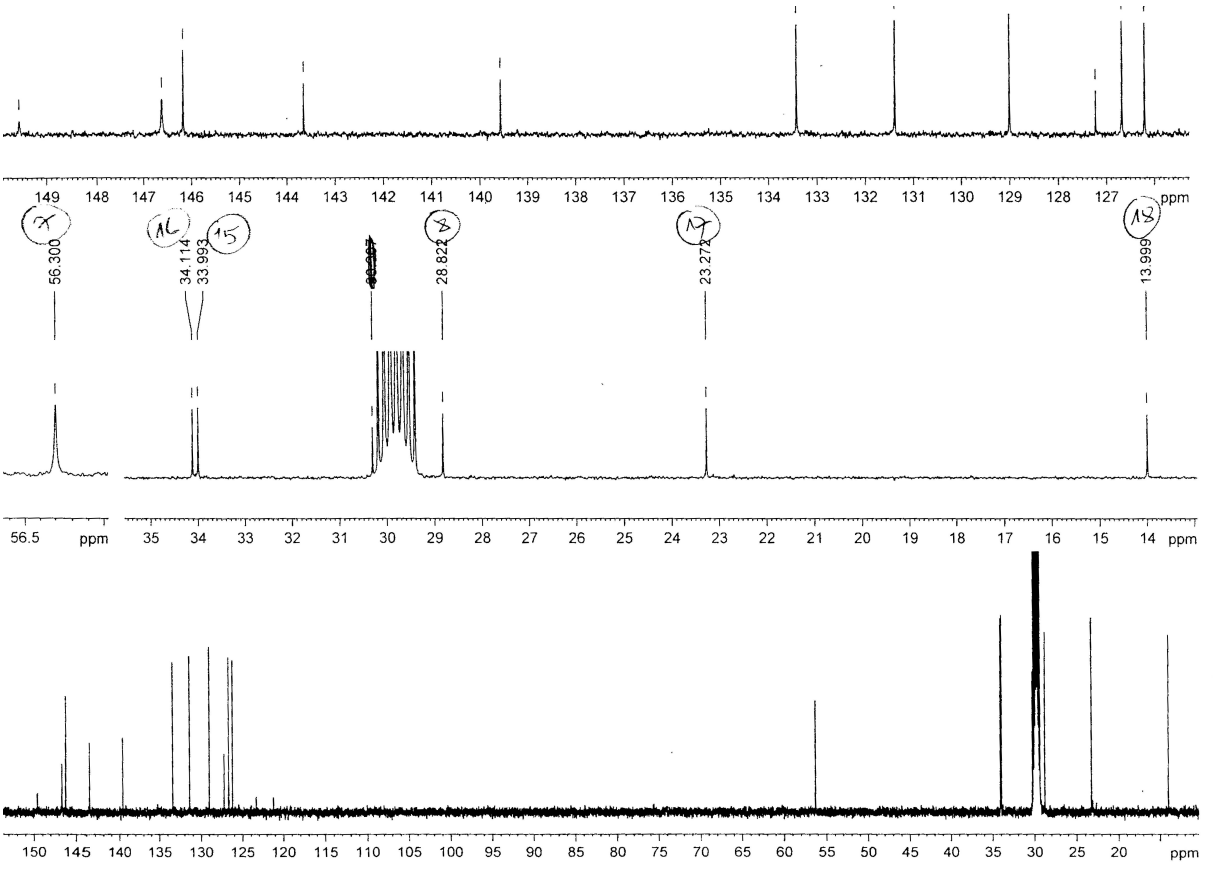

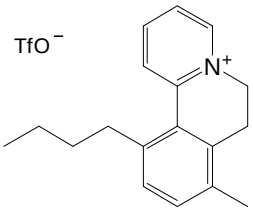

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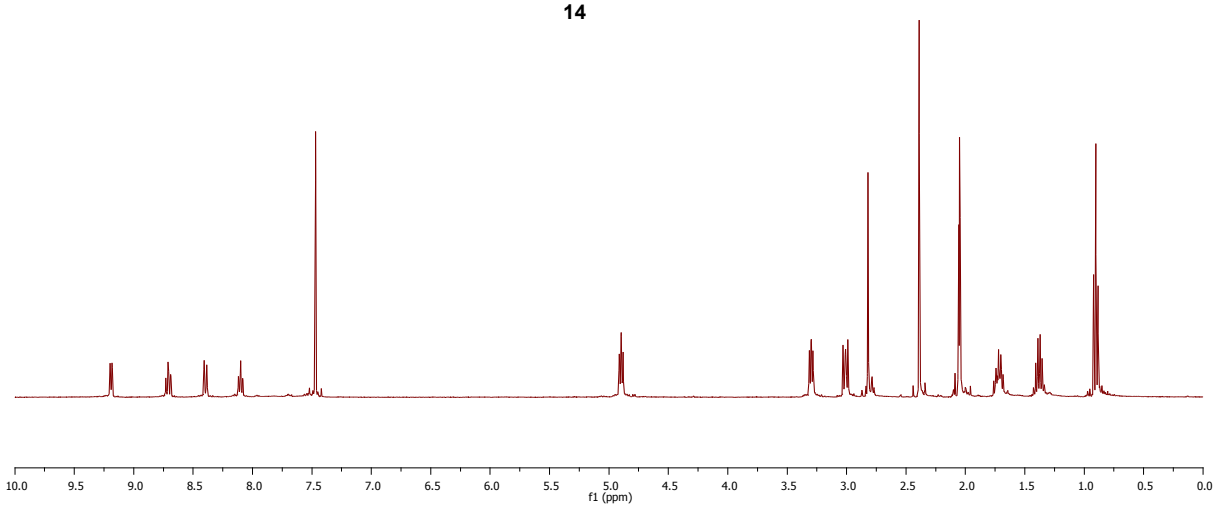

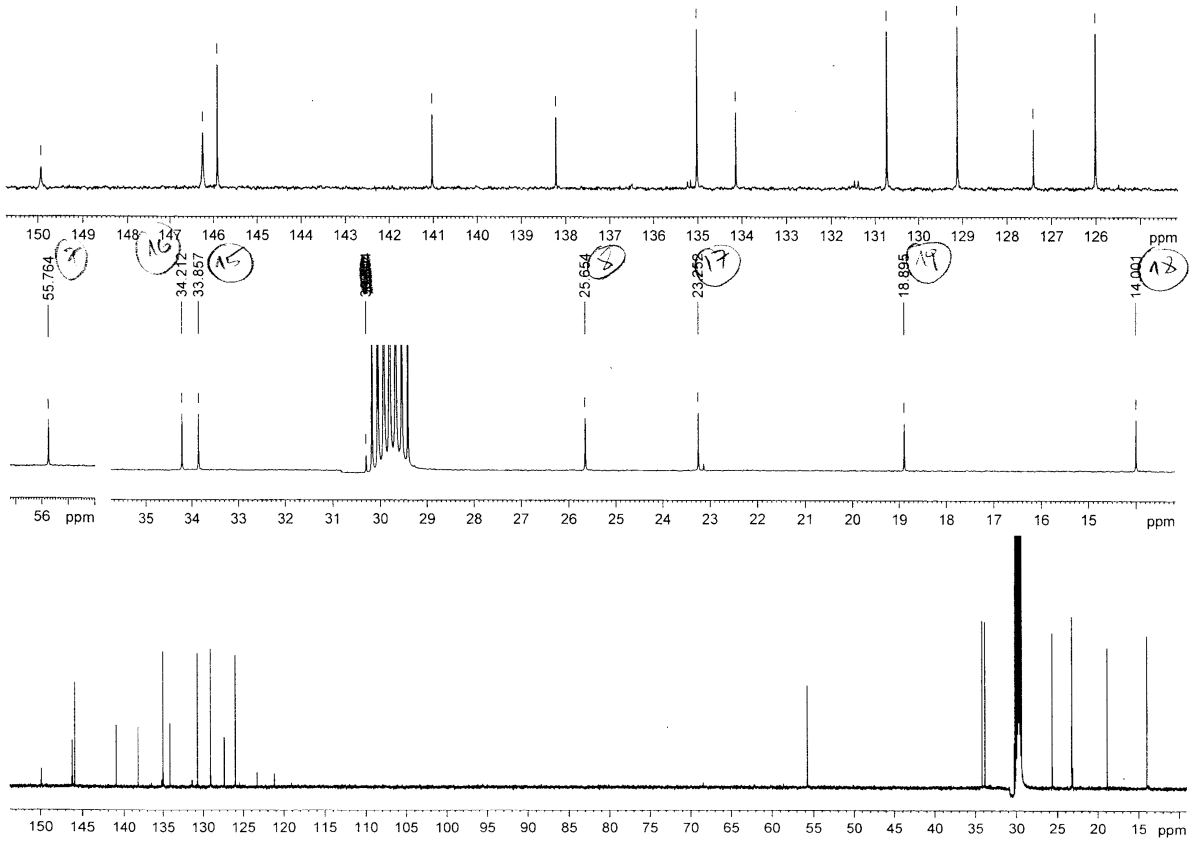

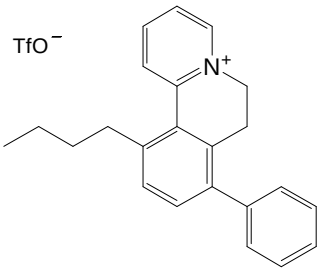

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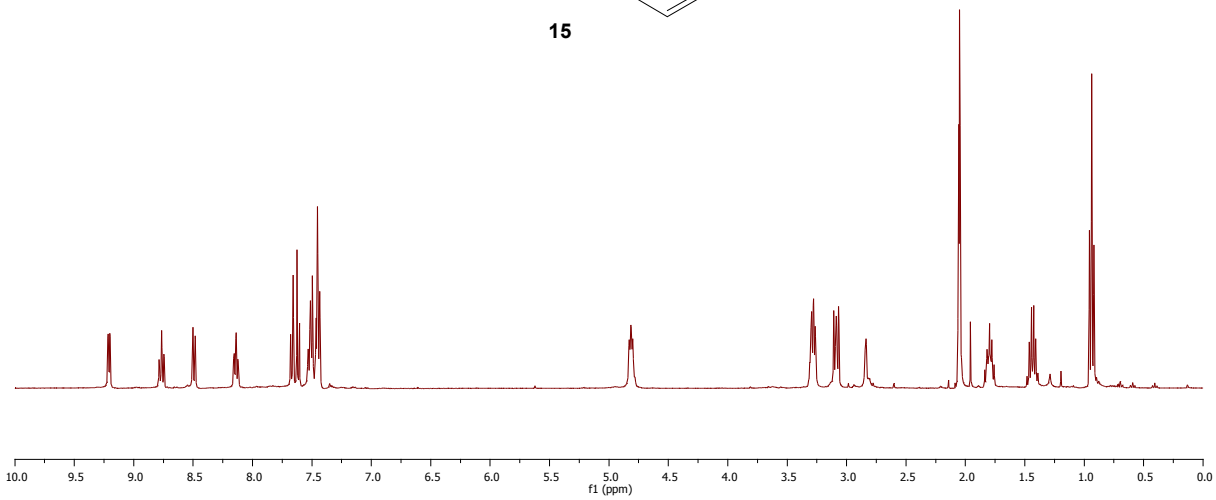

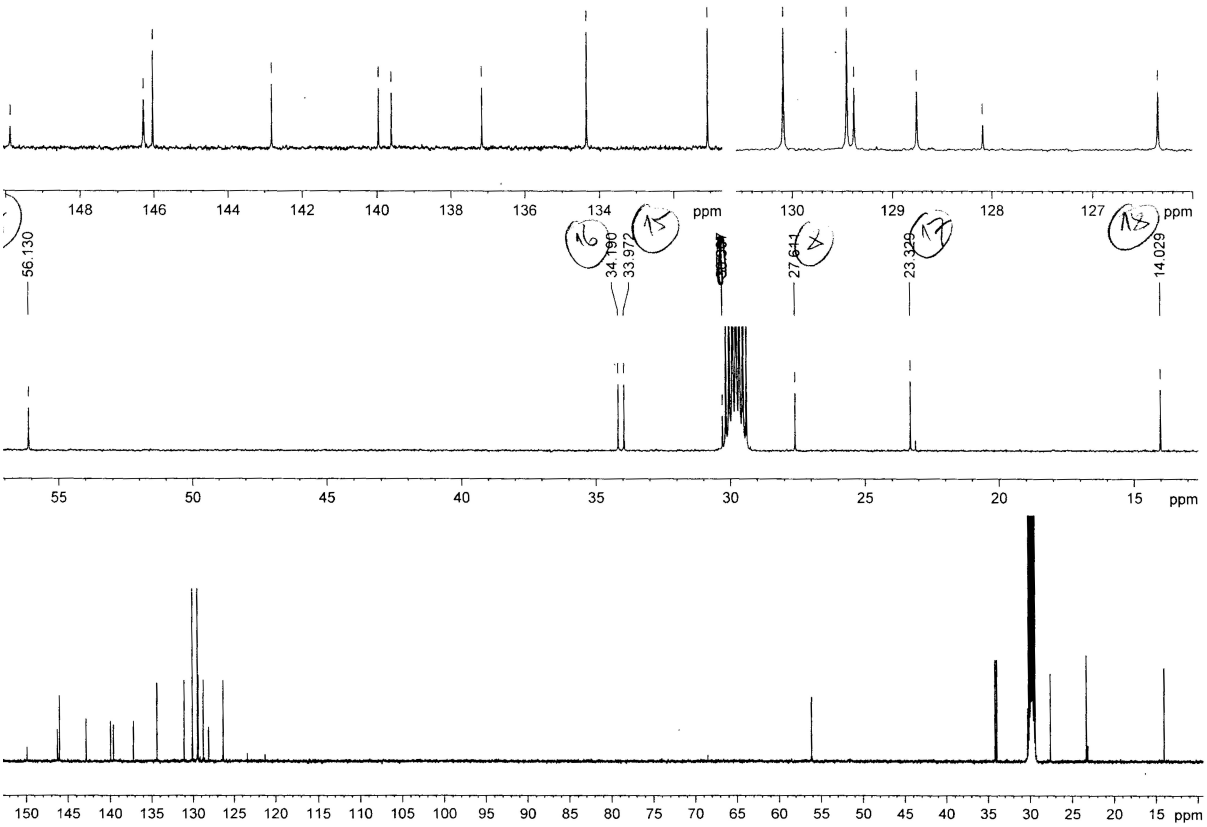

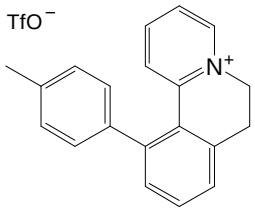

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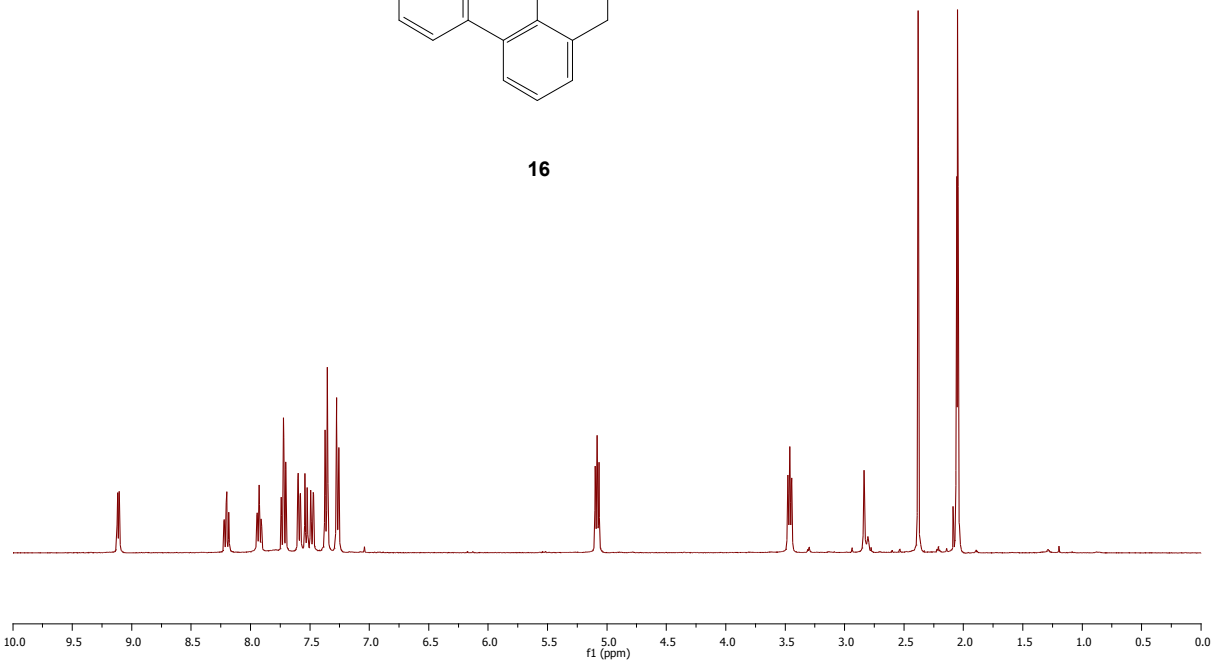

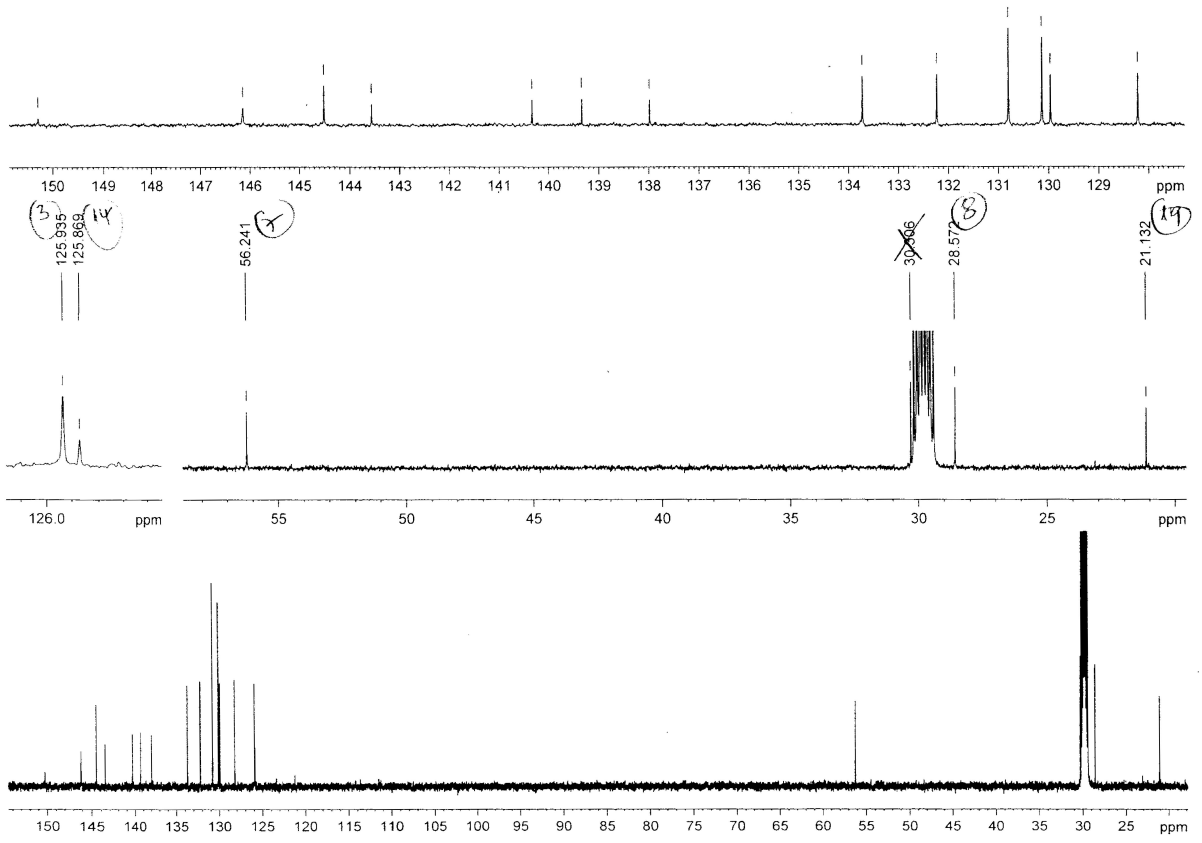

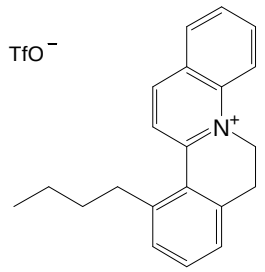

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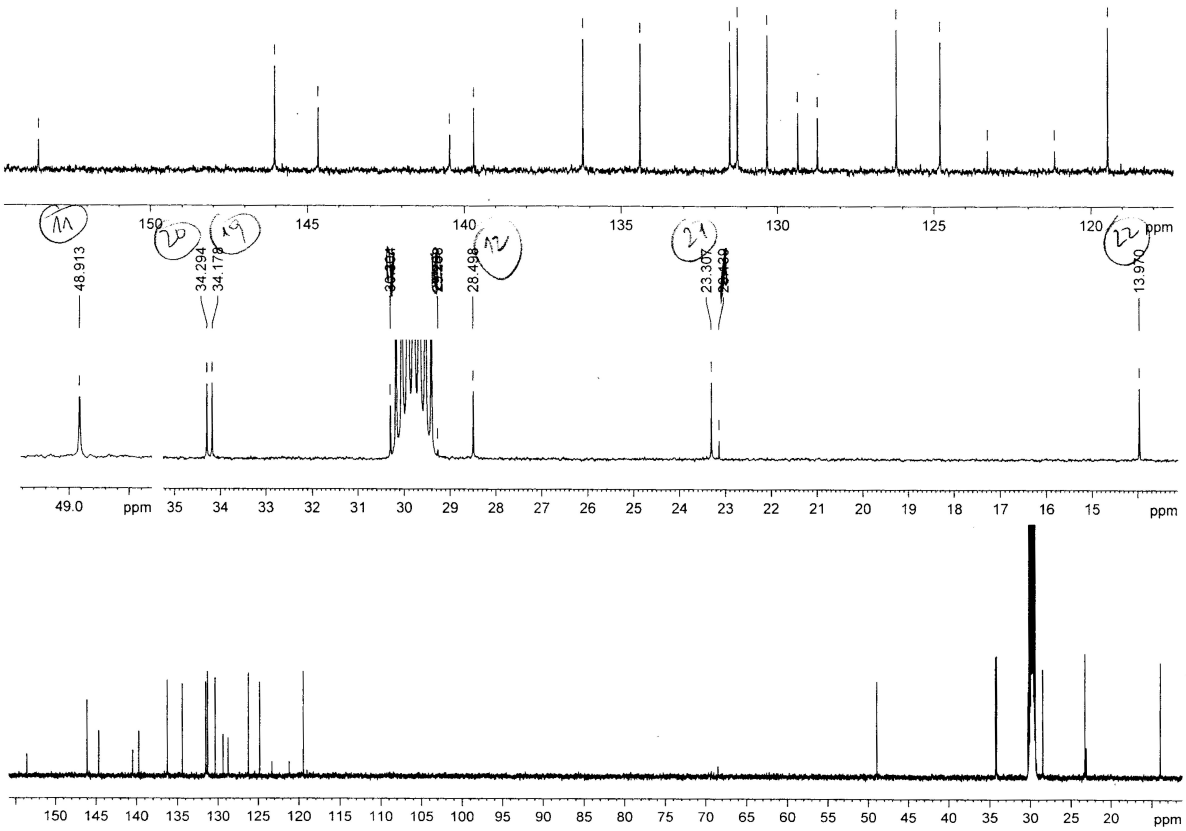

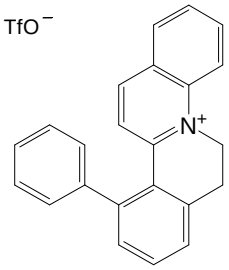

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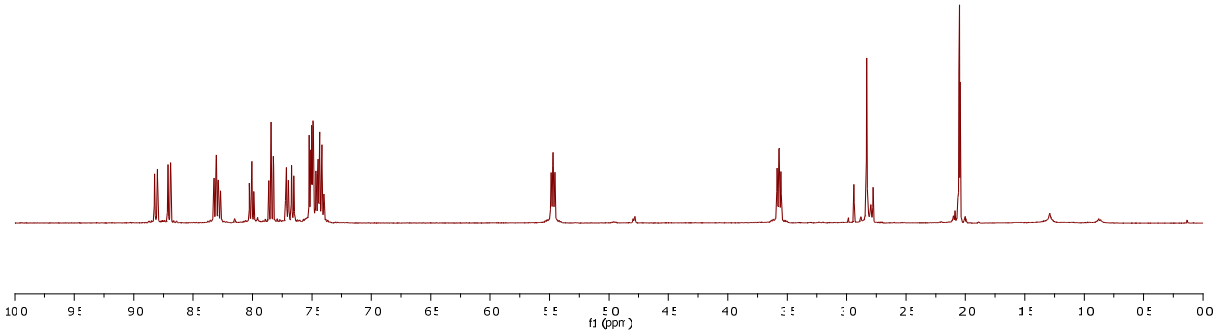

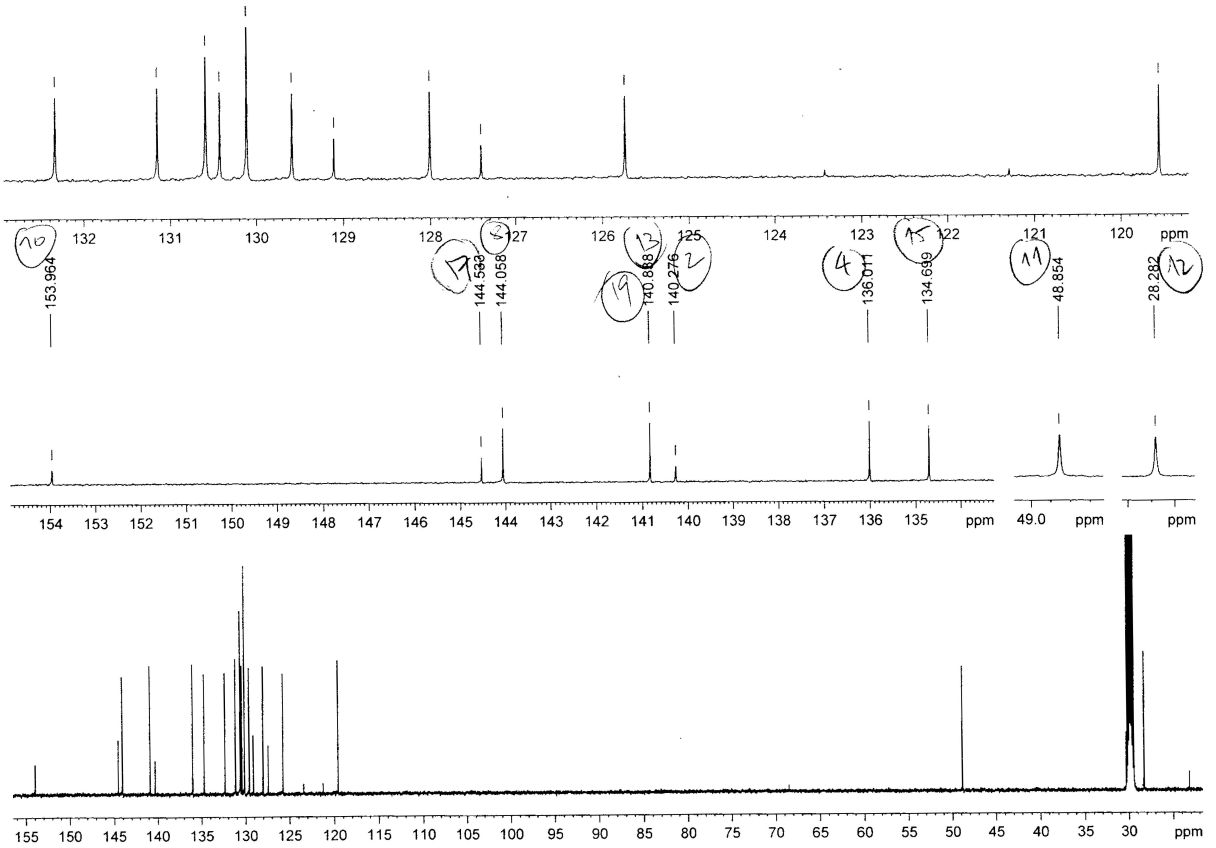

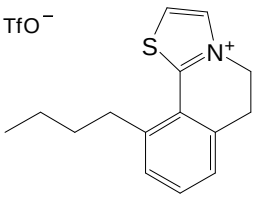
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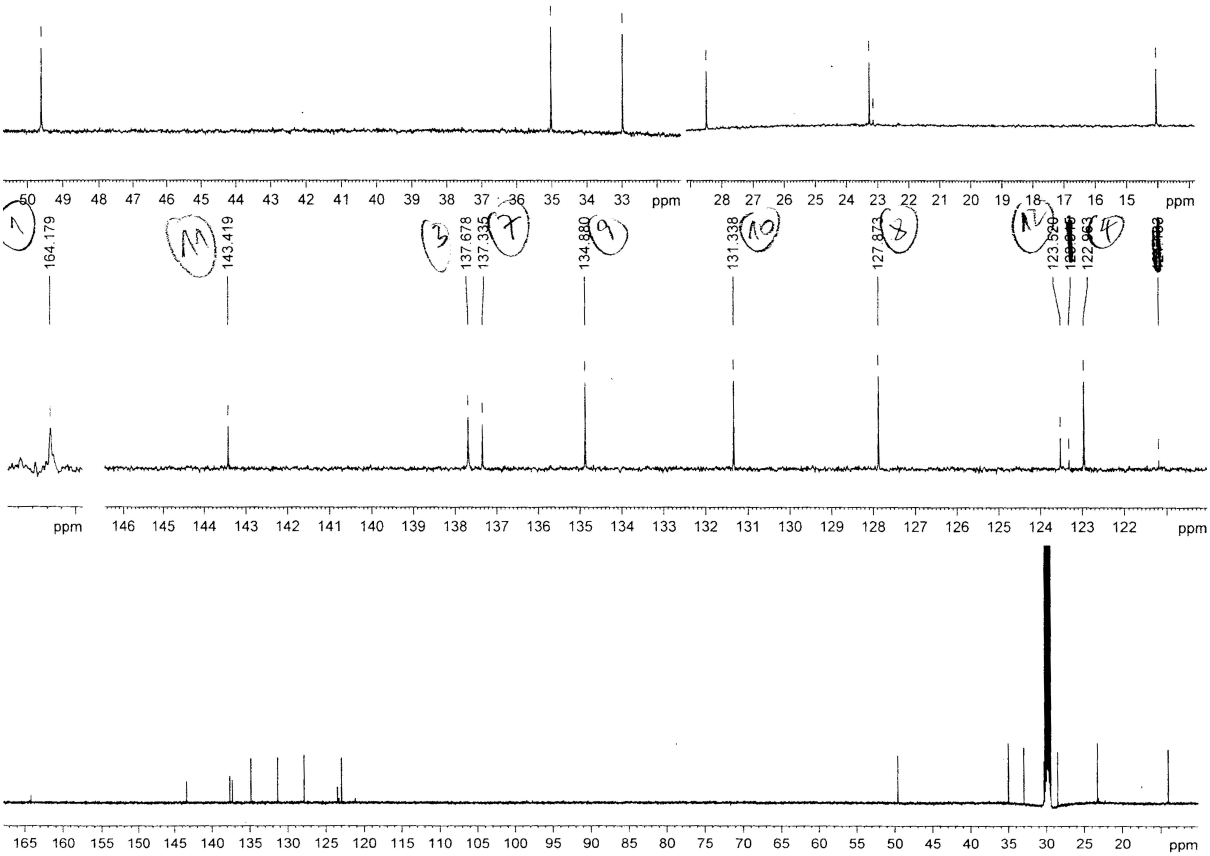
S
N⁺

19

f1 (ppm)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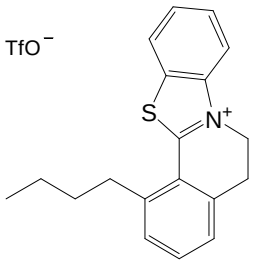
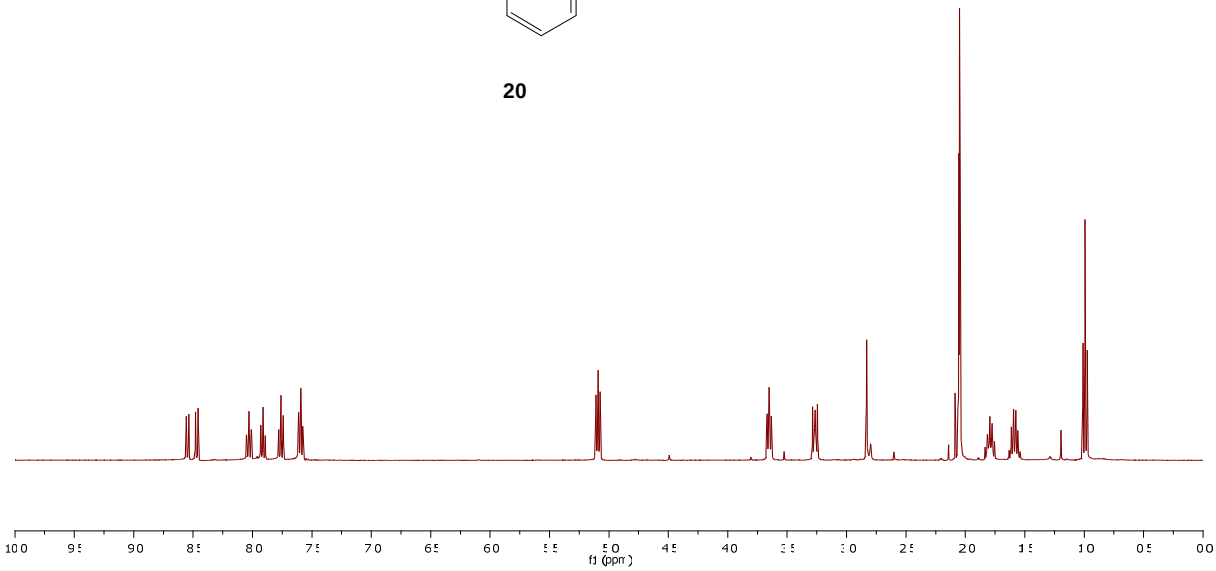
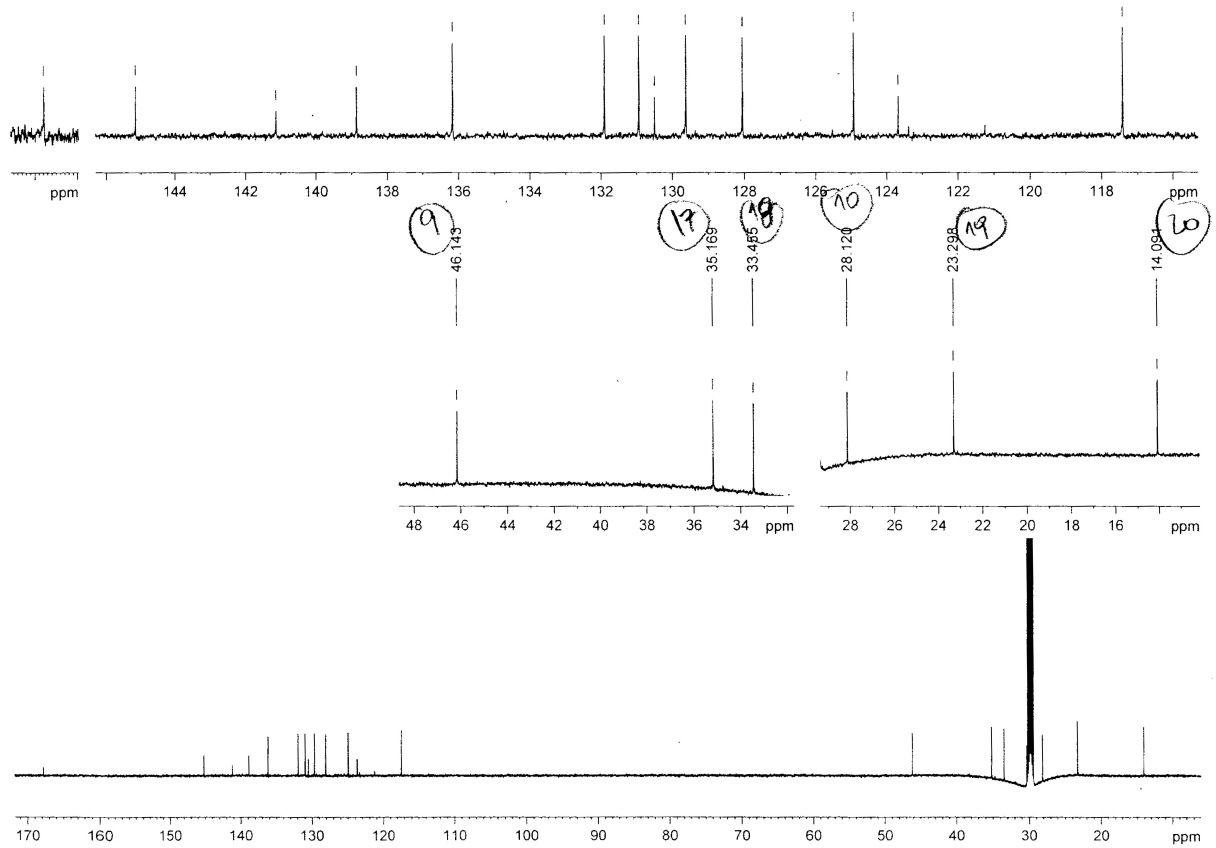

TfO⁻
S
N+

20


f1 (ppm)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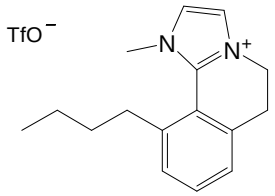
ppm
ppm
ppm



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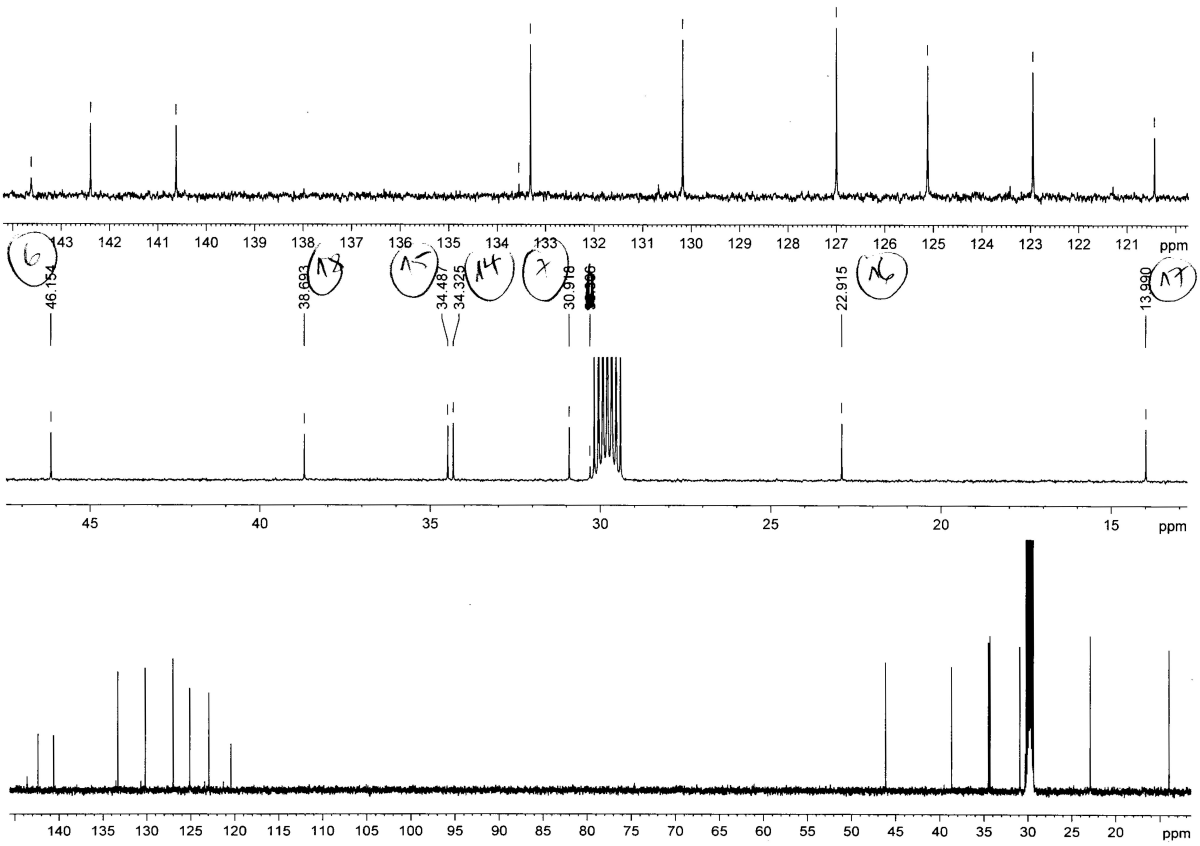

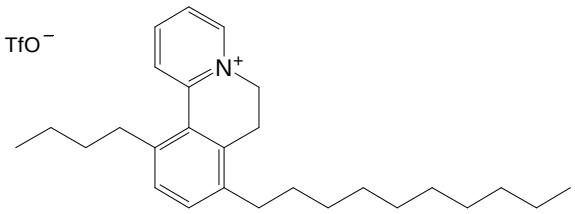

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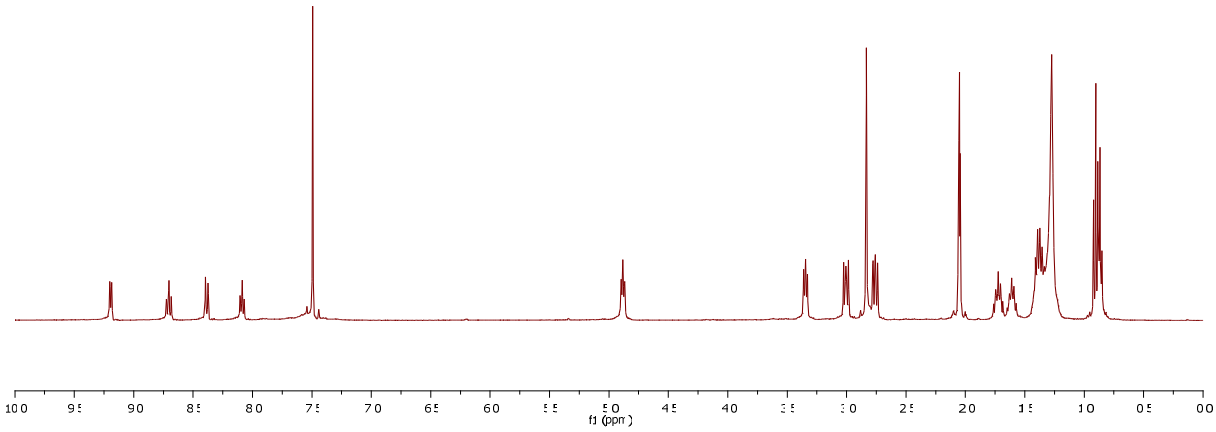

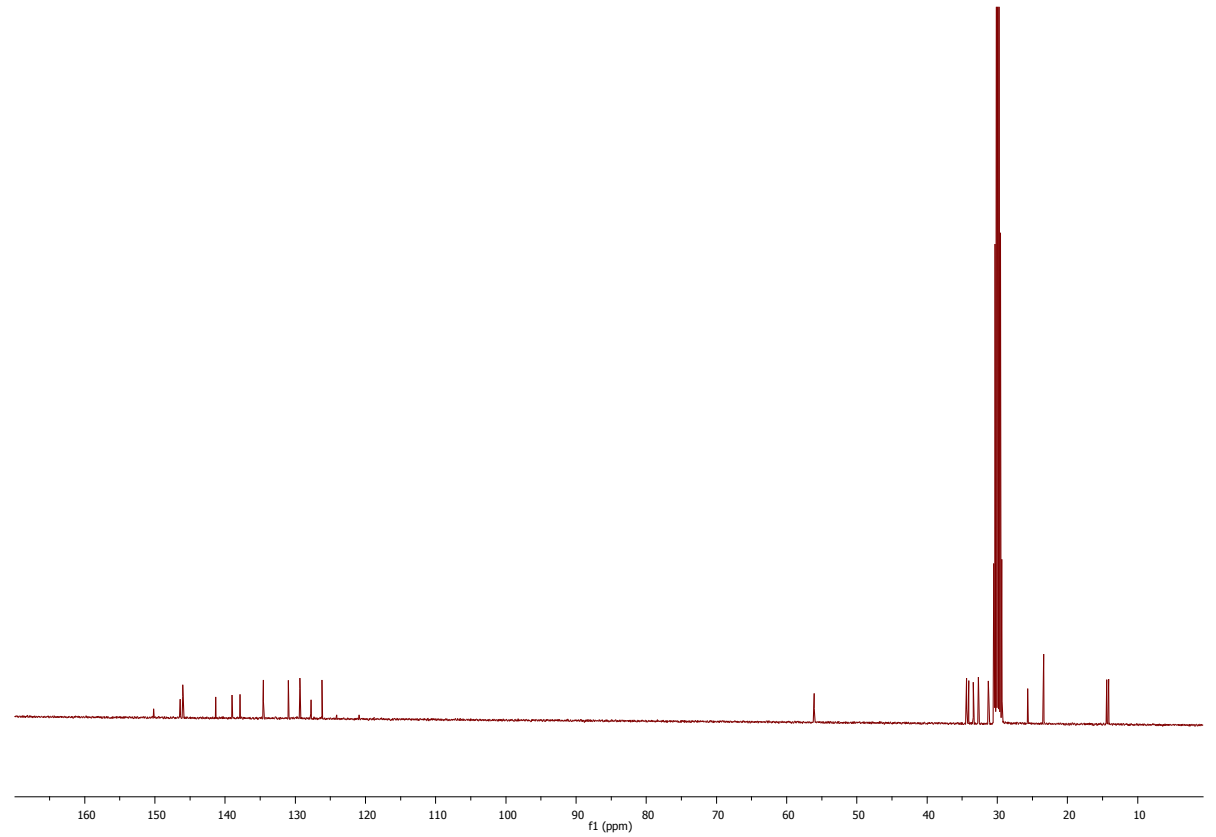

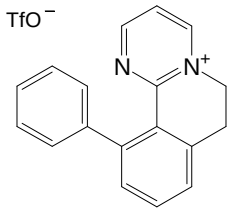

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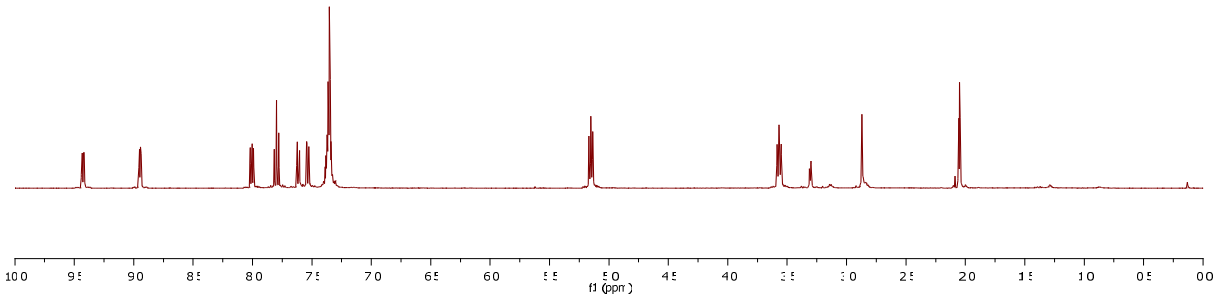

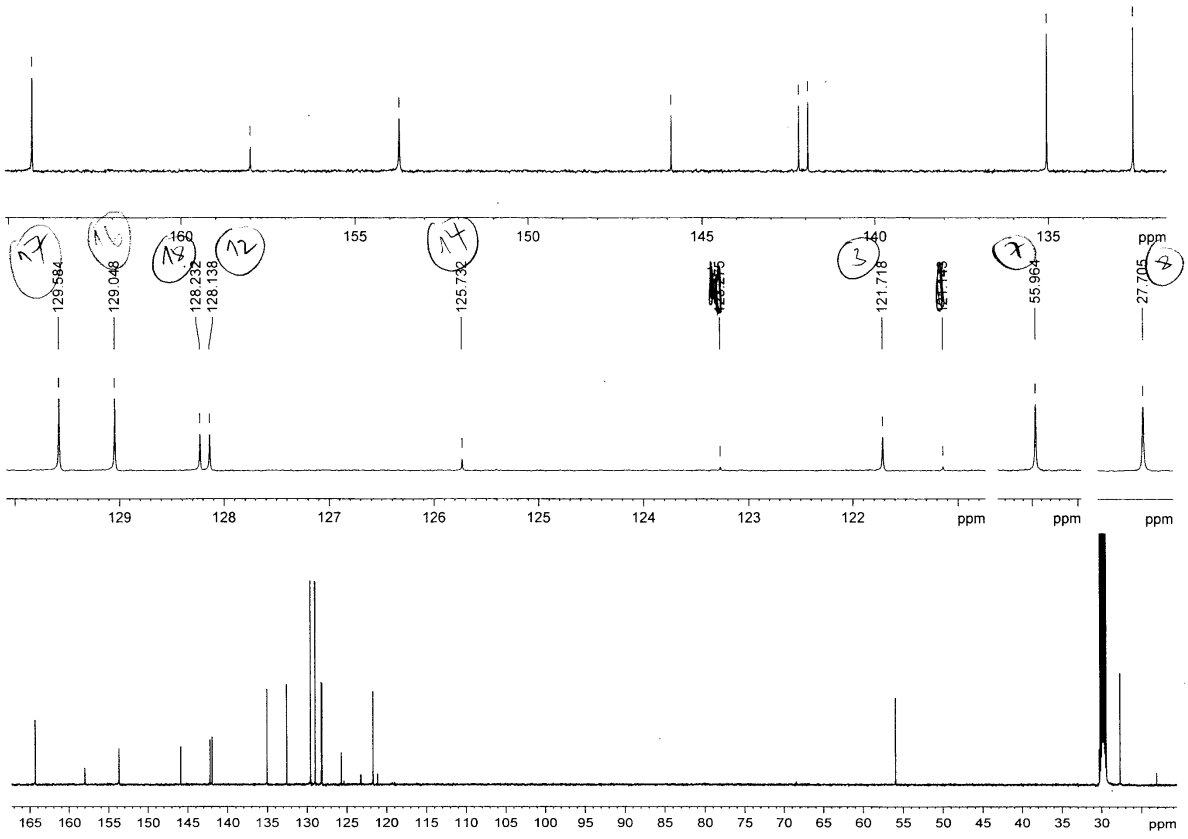

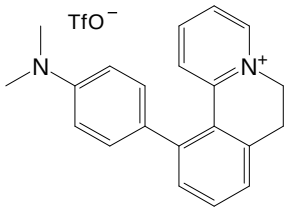

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