Electronic Supplementary Material (ESI) for ChemComm.

Brønsted Acid-Catalysed Hydroarylation of Unactivated Alkynes in Fluoroalcohol–Hydrocarbon Biphasic System: Construction of Phenanthrene Frameworks

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Supporting Information

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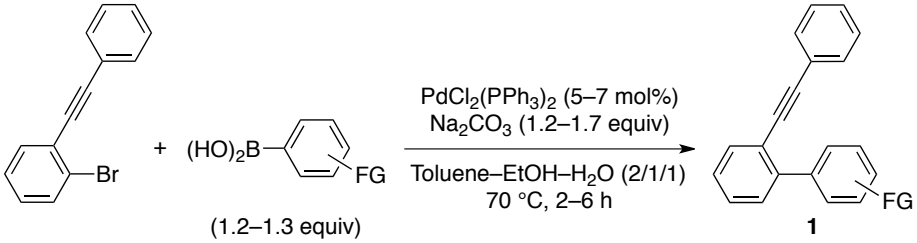
1. General Statement

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz (^{1}H NMR), at 126 MHz (^{13}C NMR), and 470 MHz (^{19}F NMR). Chemical shift values are given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00 ppm), $CDCl_3$ (for ^{13}C NMR: δ = 77.0 ppm), and C_6F_6 (for ^{19}F NMR: δ = 0.00 ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL JMS-T100GCV spectrometer. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 apparatus equipped with a JAIGEL-1H and -2H assembly.

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc.). Toluene, dichloromethane, and tetrahydrofuran (THF) were purified by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) was distilled and stored over activated molecular sieves 4A. Cyclohexane was distilled from $MgSO_4$ and stored over activated molecular sieves 4A. 1-Bromo-2-(2-phenylethynyl)benzene,[1] [2-(phenylethynyl)phenyl]boronic acid,[2] 1-bromonaphthalen-2-yl trifluoromethanesulfonate,[3] [2,2'-binaphthalen]-1-yl trifluoromethanesulfonate,[4] 2-[(4-methylphenyl)ethynyl]-1,1'-biphenyl (**1r**),[5] 2-[(4-methoxyphenyl)ethynyl]-1,1'-biphenyl (**1s**),[6] 2-[(4-chlorophenyl)ethynyl]-1,1'-biphenyl (**1t**),[5] and 2-[(4-bromophenyl)ethynyl]-1,1'-biphenyl (**1u**)[5] were prepared according to the literature procedures. Unless otherwise noted, materials were obtained from commercial sources and used directly without further purifications.

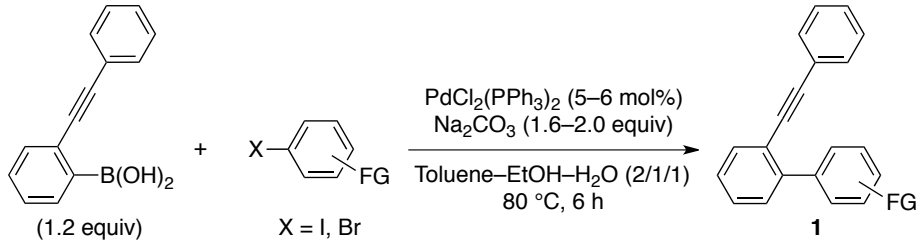
2. Preparation of 2-(Phenylethynyl)biaryls

[*Procedure A*]



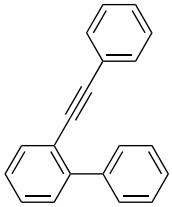
A toluene (3.0 mL), ethanol (1.5 mL), and H_2O (1.5 mL) solution of 1-bromo-2-(phenylethynyl)benzene (1.2 mmol) was degassed by using the freeze-pump-thaw method three times. To the mixture were added $PdCl_2(PPh_3)_2$ (5–7 mol%), Na_2CO_3 (1.2–1.7 equiv), and an arylboronic acid (1.2–1.3 equiv). After stirring at 70 °C for 2–6 h under nitrogen, the reaction was quenched with an aqueous NH_4Cl solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding 2-(phenylethynyl)biaryl **1**.

[*Procedure B*]



A toluene (3.0 mL), ethanol (1.5 mL), and H_2O (1.5 mL) solution of an aryl halide (1.5 mmol) was degassed by using the freeze-pump-thaw method three times. To the mixture was added $PdCl_2(PPh_3)_2$ (5 mol%), Na_2CO_3 (1.5 equiv), and [2-(phenylethynyl)phenyl]boronic acid (1.2 equiv). After stirring at 80 °C for 2–6 h under nitrogen, the reaction was quenched with an aqueous NH_4Cl solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding 2-(phenylethynyl)biaryl **1**.

2-(Phenylethynyl)-1,1'-biphenyl (1a)

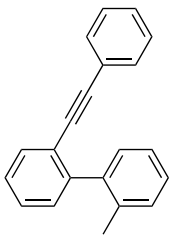


Compound **1a** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (316 mg, 1.23 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 61 μmol), Na_2CO_3 (162 mg, 1.5 mmol), and phenylboronic acid (176 mg, 1.4 mmol) at 70 °C for 2 h. Purification by silica gel column chromatography (hexane) gave **1a** (235 mg, 75%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.29 (m, 3H), 7.32–7.35 (m, 3H), 7.38–7.48 (m, 5H), 7.64–7.68 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.7, 92.6, 121.9, 123.8, 127.4, 127.8, 128.2, 128.4, 128.6, 128.9, 129.7, 129.8, 131.7, 133.2, 140.9, 144.3.

Spectral data for this compound showed good agreement with literature data.[7]

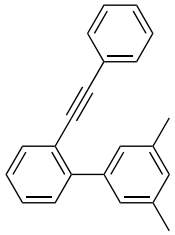
2-Methyl-2'-(phenylethynyl)-1,1'-biphenyl (1b)



Compound **1b** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene

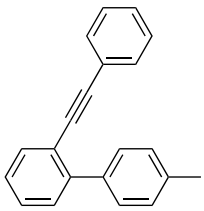
(312 mg, 1.21 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 61 μmol), Na_2CO_3 (160 mg, 1.5 mmol), and (2-methylphenyl)boronic acid (201 mg, 1.48 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane/chloroform = 100/3) gave **1b** (182 mg, 56%) as a pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.20 (s, 3H), 7.11–7.13 (m, 2H), 7.15–7.17 (m, 3H), 7.22–7.33 (m, 7H), 7.58–7.60 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.0, 88.9, 92.3, 122.8, 123.3, 125.2, 127.0, 127.5, 127.9, 128.06, 128.10, 129.4, 129.6, 129.8, 131.3, 131.6, 136.2, 140.7, 144.7. IR (neat): ν 3059, 3020, 1491, 1442, 752, 746, 687 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{21}H_{16}$ $[M]^+$: 268.1247; Found: 268.1247.

3',5'-Dimethtyl-2-(phenylethynyl)-1,1'-biphenyl (1c)



Compound **1c** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (312 mg, 1.21 mmol), $PdCl_2(PPh_3)_2$ (47 mg, 66 μmol), Na_2CO_3 (177 mg, 1.7 mmol), and (3,5-dimethylphenyl)boronic acid (228 mg, 1.52 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave **1c** (219 mg, 64%) as a pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 6H), 7.04 (s, 1H), 7.28–7.29 (m, 3H), 7.30–7.31 (m, 3H), 7.32–7.35 (m, 2H), 7.38 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.42 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.5, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.4, 89.6, 92.2, 121.4, 123.6, 126.8, 127.2, 128.0, 128.2, 128.4, 129.1, 129.4, 131.3, 132.8, 137.3, 140.4, 144.0. IR (neat): ν 3059, 3032, 3022, 2916, 1603, 1493, 850, 750, 687 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{22}H_{18}$ $[M]^+$: 282.1403; Found: 282.1411.

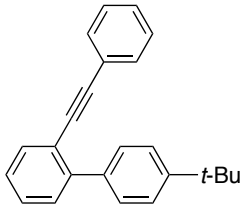
4'-Methyl-2-(phenylethynyl)-1,1'-biphenyl (1d)



Compound **1d** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (312 mg, 1.21 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 61 μmol), Na_2CO_3 (163 mg, 1.5 mmol), and (4-methylphenyl)boronic acid (210 mg, 1.54 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave **1d** (232 mg, 71%) as a pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.25–7.32 (m, 6H), 7.35–7.42 (m, 4H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.63–7.65 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 89.5, 92.1, 121.4, 123.5, 126.8, 128.0, 128.2, 128.5, 128.6, 129.2, 129.4, 131.3, 133.0, 137.2, 137.6, 143.7.

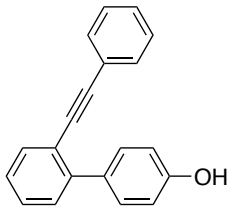
Spectral data for this compound showed good agreement with the literature data.[7]

4'-(*tert*-Butyl)-2-(phenylethynyl)-1,1'-biphenyl (1e)



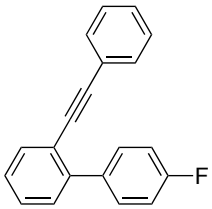
Compound **1e** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (310 mg, 1.20 mmol), $PdCl_2(PPh_3)_2$ (44 mg, 62 μmol), Na_2CO_3 (168 mg, 1.6 mmol), and [4-(*tert*-butyl)phenyl]boronic acid (262 mg, 1.47 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave **1e** (279 mg, 75%) as a pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38 (s, 9H), 7.24–7.27 (m, 3H), 7.28–7.32 (m, 3H), 7.35 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.60–7.63 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 31.4, 34.6, 89.7, 92.2, 121.6, 123.6, 124.8, 126.8, 128.0, 128.2, 128.4, 129.0, 129.3, 131.3, 132.7, 137.6, 143.9, 150.3. IR (neat): ν 3057, 2962, 2902, 2866, 1493, 1475, 833, 750, 733, 688 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{24}H_{22}$ $[M]^+$: 310.1716; Found: 310.1716.

2'-(Phenylethynyl)-[1,1'-biphenyl]-4-ol (1f)



Compound **1f** was prepared according to *Procedure B* using 4-bromophnol (262 mg, 1.52 mmol), $PdCl_2(PPh_3)_2$ (56 mg, 80 μmol), Na_2CO_3 (292 mg, 2.75 mmol), and [2-(phenylethynyl)phenyl]boronic acid (403 mg, 1.82 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 5/1) and GPC (chloroform) gave **1f** (74 mg, 18%) as a red oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.61 (br s, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.24–7.28 (m, 4H), 7.31–7.36 (m, 4H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.5, 92.1, 114.8, 121.3, 123.4, 126.6, 128.1, 128.2, 128.5, 129.3, 130.7, 131.3, 132.9, 133.2, 143.3, 155.0. IR (neat): ν 3355, 3059, 3022, 1610, 1516, 1491, 1250, 1215, 1173, 748, 688 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{20}H_{14}O$ $[M]^+$: 270.1039; Found: 270.1040.

4'-Fluoro-2-(phenylethynyl)-1,1'-biphenyl (1g)

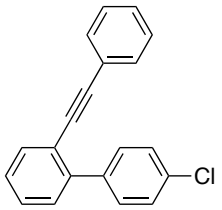


Compound **1g** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (315 mg, 1.22 mmol), $PdCl_2(PPh_3)_2$ (57 mg, 80 μmol), Na_2CO_3 (178 mg, 1.7 mmol), and (4-fluorophenyl)boronic acid (213 mg, 1.52 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave **1g** (244 mg, 73%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12–7.17 (m, 2H), 7.28–7.32 (m, 3H), 7.32–7.36 (m, 3H), 7.38–7.40 (m, 2H), 7.61–7.65 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.1, 92.4, 114.8 (d, J_{CF} = 21 Hz), 121.6, 123.3, 127.2, 128.2, 128.3, 128.6, 129.4, 131.0 (d, J_{CF} = 8 Hz), 131.3, 132.9, 136.6 (d, J_{CF} = 3 Hz), 142.8, 162.4 (d, J_{CF} = 247 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 46.5–46.6 (m).

Spectral data for this compound showed good agreement with literature data.[7]

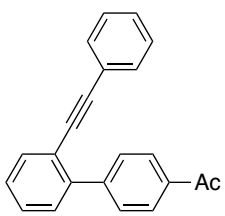
4'-Chloro-2-(phenylethynyl)-1,1'-biphenyl (1h)



Compound **1h** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (313 mg, 1.22 mmol), $PdCl_2(PPh_3)_2$ (44 mg, 63 μmol), Na_2CO_3 (164 mg, 1.5 mmol), and (4-chlorophenyl)boronic acid (231 mg, 1.48 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave **1h** (256 mg, 73%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.29 (m, 4H), 7.31–7.33 (m, 4H), 7.38 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.0, 92.5, 121.4, 123.1, 127.3, 128.0, 128.2, 128.3, 128.5, 129.2, 130.6, 131.3, 133.0, 133.5, 138.9, 142.4. IR (neat): ν 3059, 1489, 1471, 1088, 827, 750, 687 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{20}H_{13}Cl$ $[M]^+$: 288.0700; Found: 288.0695.

1-{2'-(Phenylethynyl)-[1,1'-biphenyl]-4-yl}ethan-1-one (1i)

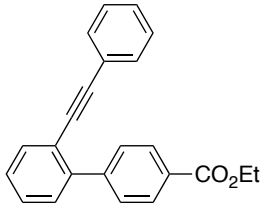


Compound **1i** was prepared according to *Procedure B* using 4'-bromoacetophenone (302 mg,

1.52 mmol), $PdCl_2(PPh_3)_2$ (62 mg, 88 μmol), Na_2CO_3 (290 mg, 2.74 mmol), and [2-(phenylethynyl)phenyl]boronic acid (406 mg, 1.83 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 10/1) gave **1i** (402 mg, 89%) as an orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.54 (s, 3H), 7.20–7.22 (m, 3H), 7.25–7.34 (m, 5H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 26.3, 88.6, 92.5, 121.2, 122.8, 127.5, 127.7, 128.07, 128.07, 128.4, 129.1, 129.3, 131.0, 132.8, 135.6, 142.1, 144.9, 197.4.

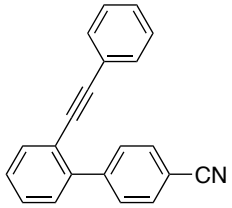
Spectral data for this compound showed good agreement with literature data.[5]

Ethyl 2'-(phenylethynyl)-[1,1'-biphenyl]-4-carboxylate (1j)



Compound **1j** was prepared according to *Procedure B* using ethyl 4-bromobenzoate (344 mg, 1.50 mmol), $PdCl_2(PPh_3)_2$ (59 mg, 84 μmol), Na_2CO_3 (283 mg, 2.67 mmol), and [2-(phenylethynyl)phenyl]boronic acid (407 mg, 1.83 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 30/1) gave **1j** (429 mg, 87%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.45 (t, *J* = 7.2 Hz, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.31–7.33 (m, 3H), 7.35–7.44 (m, 5H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.1, 60.7, 88.7, 92.5, 121.3, 122.9, 127.5, 128.06, 128.08, 128.4, 128.9, 129.1, 129.2, 131.1, 132.8, 142.3, 144.8, 166.2. IR (neat): ν 3059, 2981, 1711, 1269, 1109, 1097, 752, 687 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{23}H_{18}O_2$ $[M]^+$: 326.1301; Found: 326.1304.

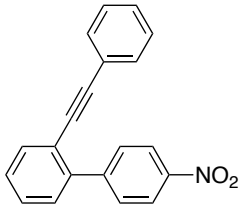
2'-(Phenylethynyl)-[1,1'-biphenyl]-4-carbonitrile (1k)



Compound **1k** was prepared according to *Procedure B* using 4-bromobenzonitrile (275 mg, 1.51 mmol), $PdCl_2(PPh_3)_2$ (55 mg, 78 μmol), Na_2CO_3 (253 mg, 2.38 mmol), and [2-(phenylethynyl)phenyl]boronic acid (401 mg, 1.80 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 15/1) gave **1k** (412 mg, 98%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–7.30 (m, 5H), 7.31–7.37 (m, 3H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.2, 92.8, 110.9, 118.7, 121.2, 122.6, 128.0, 128.2, 128.3, 128.5, 129.0, 129.8, 131.0, 131.4, 132.9, 141.4, 144.8. IR (neat): ν 3059, 3020, 2227, 1493, 837, 750, 725, 688 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{21}H_{13}N$

$[M]^+$: 279.1043; Found: 279.1041.

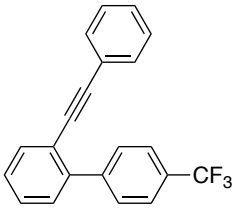
4'-Nitro-2-(phenylethynyl)-1,1'-biphenyl (1l)



Compound **1l** was prepared according to *Procedure B* using 1-iodo-4-nitrobenzene (377 mg, 1.51 mmol), $PdCl_2(PPh_3)_2$ (53 mg, 75 μmol), Na_2CO_3 (326 mg, 3.07 mmol), and [2-(phenylethynyl)phenyl]boronic acid (408 mg, 1.84 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 50/1) gave **1l** (398 mg, 88%) as a yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.35 (m, 3H), 7.37–7.44 (m, 5H), 7.71 (ddd, J = 6.2, 1.7, 1.7 Hz, 1H), 7.83 (d, J = 8.8 Hz, 2H), 8.31 (d, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.2, 93.0, 121.4, 122.6, 122.9, 128.22, 128.24, 128.4, 128.6, 129.1, 130.0, 131.1, 133.1, 141.0, 146.8, 146.9.

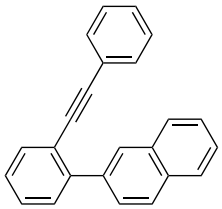
Spectral data for this compound showed good agreement with literature data.[8]

2-(Phenylethynyl)-4'-(trifluoromethyl)-1,1'-biphenyl (1m)



Compound **1m** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (314 mg, 1.22 mmol), $PdCl_2(PPh_3)_2$ (61 mg, 86 μmol), Na_2CO_3 (217 mg, 2.05 mmol), and [4-(trifluoromethyl)phenyl]boronic acid (285 mg, 1.50 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane/dichloromethane = 25/1) gave **1m** (260 mg, 66%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.31 (m, 5H), 7.35–7.38 (m, 1H), 7.39–7.41 (m, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.7, 92.8, 121.7, 123.0, 124.3 (q, J_{CF} = 272 Hz), 124.8 (q, J_{CF} = 4 Hz), 127.8, 128.3, 128.4, 128.6, 129.3, 129.5 (q, J_{CF} = 33 Hz), 129.7, 131.3, 133.0, 142.3, 144.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ 99.6 (s). IR (neat): ν 3060, 1321, 1165, 1119, 1109, 1066, 839, 750, 733 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{21}H_{13}F_3$ $[M]^+$: 322.0964; Found: 322.0963.

2-[2-(Phenylethynyl)phenyl]naphthalene (1n)

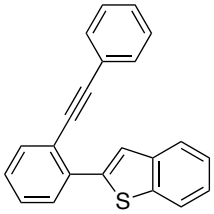


Compound **1n** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (313 mg, 1.22 mmol), $PdCl_2(PPh_3)_2$ (45 mg, 64 μmol), Na_2CO_3 (164 mg, 1.55 mmol), and naphthalen-2-ylboronic acid (252 mg, 1.47 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave **1n** (281 mg, 76%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20–7.21 (m, 3H), 7.27–7.29 (m, 2H), 7.33 (dd, *J* = 7.6 Hz, 1H), 7.40 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.47–7.49 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.82–7.91 (m, 4H), 8.12 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.4, 92.4, 121.7, 123.3, 126.0, 126.1, 127.1, 127.2, 127.6, 127.7, 128.1, 128.19, 128.19, 128.3, 128.6, 129.8, 131.3, 132.7, 133.0, 133.2, 138.0, 143.7.

Spectral data for this compound showed good agreement with literature data.[6]

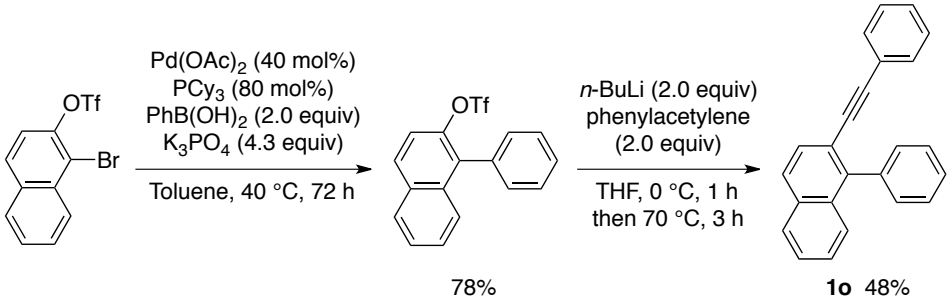
2-[2-(Phenylethynyl)phenyl]benzo[*b*]thiophene (1o)



Compound **1o** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (315 mg, 1.22 mmol), $PdCl_2(PPh_3)_2$ (45 mg, 65 μmol), Na_2CO_3 (165 mg, 1.6 mmol), and benzo[*b*]thiophen-2-ylboronic acid (266 mg, 1.49 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave **1o** (313 mg, 82%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.37 (m, 7H), 7.48–7.50 (m, 2H), 7.65 (dd, *J* = 6.9, 6.9 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.93 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.3, 93.9, 121.2, 122.1, 123.3, 123.6, 123.7, 124.3, 124.4, 127.7, 128.37, 128.37, 128.6, 129.5, 131.4, 133.7, 135.8, 140.0, 140.2, 142.2. IR (neat): ν 3055, 1491, 1441, 1425, 748, 737, 721, 687, 667 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{22}H_{14}S$ $[M]^+$: 310.0811; Found: 310.0810.

1-Phenyl-2-(phenylethynyl)naphthalene (1p)



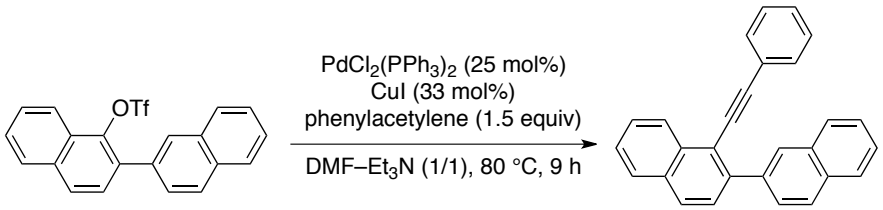
A toluene (15 mL) solution of 1-bromonaphthalen-2-yl trifluoromethanesulfonate (1.18 g, 3.31 mmol) was degassed by using the freeze-pump-thaw method three times. To the solution were added $Pd(OAc)_2$ (295 mg, 1.32 mmol), PCy_3 (743 mg, 2.65 mmol), K_3PO_4 (3.03 g, 14.3 mmol), and phenylboronic acid (806 mg, 6.61 mmol). After stirring at 40 °C for 72 h, the reaction was quenched with an aqueous NH_4Cl solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane/chloroform = 100/3–25/2) to give 1-phenylnaphthalen-2-yl trifluoromethanesulfonate (906 mg, 78%) as a colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.41 (m, 2H), 7.46–7.58 (m, 6H), 7.64 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 8.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 118.3 (q, J_{CF} = 321 Hz), 119.4, 126.8, 126.9, 127.4, 128.1, 128.4, 128.5, 129.9, 130.7, 132.5, 132.6, 133.0, 133.3, 144.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ 87.4 (s). IR (neat): ν 3060, 1419, 1201, 1136, 943, 831, 808, 750 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{17}H_{11}F_3O_3S$ $[M]^+$: 352.0376; Found: 352.0362.

To a THF (15 mL) solution of phenylacetylene (0.43 mL, 4.0 mmol) was added *n*-BuLi (1.6 M in hexane, 2.5 mL, 4.0 mmol) at 0 °C. After stirring at 0 °C for 1 h, a THF (15 mL) solution of 1-phenylnaphthalen-2-yl trifluoromethanesulfonate (702 mg, 1.99 mmol) was added to the reaction mixture. After being refluxed for 3 h, the reaction was quenched with an aqueous $NaHCO_3$ solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane/chloroform = 20/1) to give **1p** (293 mg, 48%) as a colourless hard oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.41 (m, 5H), 7.53 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.62–7.65 (m, 1H), 7.66–7.69 (m, 4H), 7.85 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 90.0, 93.2, 120.1, 123.4, 126.3, 126.4, 126.6, 127.41, 127.43, 127.89, 127.94, 127.94, 128.1, 128.2, 130.6, 131.3, 132.1, 133.0, 138.9, 143.0. IR (neat): ν 3057, 818, 744, 731, 696, 688, 679 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{24}H_{16}$ $[M]^+$: 304.1247; Found: 304.1246.

1-(Phenylethynyl)-2,2'-binaphthalene (1q)

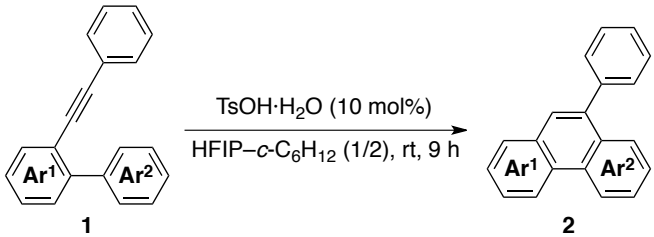


1p 83%

A DMF (7.5 mL) and Et_3N (7.5 mL) solution of [2,2'-binaphthalen]-1-yl trifluoromethanesulfonate (1.23 g, 3.05 mmol), $PdCl_2(PPh_3)_2$ (527 mg, 0.751 mmol), and CuI (190 mg, 1.0 mmol) was degassed by using the freeze-pump-thaw method three times. To the mixture was added phenylacetylene (0.49 mL, 4.5 mmol). After stirring at 80 °C for 9 h, the reaction was quenched with aqueous $NaHCO_3$ solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane/chloroform = 20/1–10:1) to give **1q** (902 mg, 83%) as a pale yellow hard oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.53 (m, 3H), 7.75–7.82 (m, 5H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.95–7.98 (m, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 8.17–8.19 (m, 2H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.29 (dd, *J* = 8.5, 1.8 Hz, 1H), 8.57 (d, *J* = 1.3 Hz, 1H), 9.06 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 87.6, 97.8, 118.4, 123.4, 125.99, 125.99, 126.2, 126.6, 127.1, 127.2, 127.56, 127.56, 128.0, 128.06, 128.06, 128.15, 128.15, 128.6, 128.8, 131.2, 132.1, 132.6, 133.1, 133.6, 138.4, 142.1. IR (neat): ν 3055, 1489, 904, 814, 808, 725, 646 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{28}H_{19}$ $[M + H]^+$: 355.1481; Found: 355.1488.

3. Synthesis of Phenacenes 2

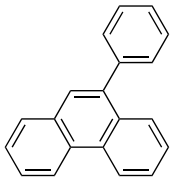
[*Procedure C*]



1 **2**

To a cyclohexane (3.0 mL) solution of a 2-(phenylethynyl)biaryl **1** (0.3 mmol) was added HFIP (0.8 mL). To the reaction mixture was added a HFIP (0.7 mL) solution of $TsOH·H_2O$ (5.7 mg, 30 μmol). After stirring vigorously at room temperature for 9 h under air, dichloromethane (5 mL) was added and the resulting mixture was filtered through a pad of $NaHCO_3$ (dichloromethane). After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding phenacene **2**.

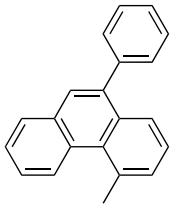
9-Phenylphenanthrene (2a)



Compound **2a** was synthesised according to *Procedure C* using **1a** (76 mg, 0.30 mmol), $TsOH·H_2O$ (6.1 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 100/3) gave **2a** (58 mg, 77%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.44 (m, 1H), 7.46–7.53 (m, 5H), 7.55–7.58 (m, 1H), 7.60–7.63 (m, 2H), 7.65 (s, 1H), 7.84 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.90 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.72 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.5, 122.9, 126.4, 126.46, 126.54, 126.8, 126.9, 127.3, 127.5, 128.3, 128.6, 129.9, 130.0, 130.6, 131.1, 131.5, 138.7, 140.8.

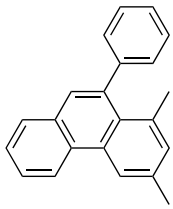
Spectral data for this compound showed good agreement with literature data.[7]

4-Methyl-10-phenylphenanthrene (2b)



Compound **2b** was synthesised according to *Procedure C* using **1b** (81 mg, 0.30 mmol), $TsOH·H_2O$ (5.9 mg, 31 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) and GPC (chloroform) gave **2b** (67 mg, 82%) as a colourless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.15 (s, 3H), 7.36–7.39 (m, 1H), 7.40–7.43 (m, 1H), 7.45–7.50 (m, 5H), 7.55–7.62 (m, 2H), 7.63 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 7.5, 1.6 Hz, 1H), 8.87 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.6, 125.4, 125.59, 125.62, 126.1, 127.2, 127.5, 127.9, 128.2, 128.7, 130.1, 130.6, 131.10. 131.10, 132.84, 132.84, 135.5, 139.2, 141.5. IR (neat): ν 3057, 2960, 1597, 1489, 1450, 1390, 1215, 891, 808, 744, 723, 698 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{21}H_{16}$ $[M]^+$: 268.1247; Found: 268.1250.

1,3-Dimethtyl-10-phenylphenanthrene (2c)

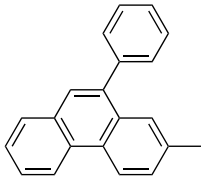


Compound **2c** was synthesised according to *Procedure C* using **1c** (86 mg, 0.30 mmol), $TsOH·H_2O$ (6.1 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel

column chromatography (hexane/chloroform = 20/1) gave **2c** (69 mg, 80%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.93 (s, 3H), 2.47 (s, 3H), 7.10 (s, 1H), 7.28–7.31 (m, 5H), 7.43 (s, 1H), 7.44–7.47 (m, 1H), 7.49–7.53 (m, 1H), 7.70 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.40 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.6, 25.2, 121.1, 122.9, 126.3, 126.6, 126.7, 127.7, 128.0, 128.1, 129.1, 129.3, 130.1, 130.9, 131.9, 132.5, 135.6, 135.9, 138.6, 145.4.

Spectral data for this compound showed good agreement with literature data.[9]

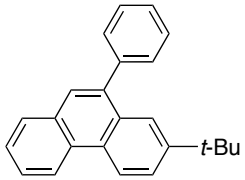
2-Methyl-10-phenylphenanthrene (2d)



Compound **2d** was synthesised according to *Procedure C* using **1d** (82 mg, 0.30 mmol), TsOH·H_2O (6.1 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) **2d** (76 mg, 93%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.43–7.55 (m, 7H), 7.58–7.61 (m, 1H), 7.62 (s, 1H), 7.67 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 8.61 (d, *J* = 8.7 Hz, 1H), 8.62 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.7, 122.3, 122.8, 126.36, 126.36, 126.5, 127.3, 127.6, 128.2, 128.3, 128.4, 128.6, 129.98, 130.02, 131.16, 131.19, 136.2, 138.5, 141.0.

Spectral data for this compound showed good agreement with literature data.[7]

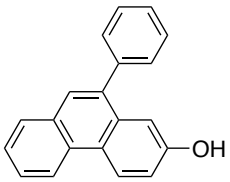
2-(*tert*-Butyl)-10-phenylphenanthrene (2e)



Compound **2e** was synthesised according to *Procedure C* using **1e** (94 mg, 0.30 mmol), TsOH·H_2O (5.7 mg, 30 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave **2e** (84 mg, 90%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (s, 9H), 7.41–7.45 (m, 1H), 7.48–7.62 (m, 6H), 7.65 (s, 1H), 7.71 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 8.65 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 31.3, 34.9, 122.4, 122.6, 122.7, 124.6, 126.39, 126.44, 127.3, 127.5, 128.2, 128.4, 128.6, 129.9, 130.0, 130.8, 131.3, 138.9, 140.9, 149.2. IR (neat): ν 3057, 2962, 2902, 1614, 1485, 1454, 1373, 1269, 1215, 897, 827, 787, 744, 700, 592 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{24}H_{22}$ $[M]^+$: 310.1716; Found: 310.1718.

Spectral data for this compound showed good agreement with literature data.[10]

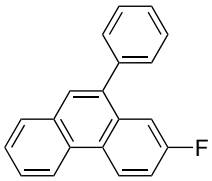
10-Phenylphenanthren-2-ol (2f)



Compound **2f** was synthesised according to *Procedure C* using **1f** (66 mg, 0.24 mmol), TsOH·H_2O (4.6 mg, 24 μmol), cyclohexane (2.4 mL), and HFIP (1.2 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 10/1/1) gave **2f** (34 mg, 52%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.07 (s, 1H), 7.20–7.23 (m, 2H), 7.42–7.44 (m, 1H), 7.47–7.55 (m, 5H), 7.61–7.64 (m, 2H), 7.84 (d, J = 7.8 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.64 (d, J = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 110.5, 116.4, 122.0, 124.9, 125.0, 125.9, 126.7, 127.4, 128.2, 128.4, 128.7, 129.9, 130.0, 130.5, 132.7, 137.8, 140.7, 154.1. IR (neat): ν 3511, 3354, 3057, 3024, 1614, 1454, 1214, 744, 698, 590 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{20}H_{14}O$ $[M]^+$: 270.1039; Found: 270.1046.

2-Fluoro-10-phenylphenanthrene (2g)

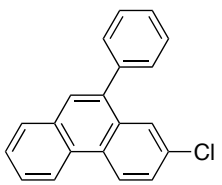


Compound **2g** was synthesised according to *Procedure C* using **1g** (82 mg, 0.30 mmol), TsOH·H_2O (5.7 mg, 30 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave **2g** (74 mg, 91%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.37 (m, 1H), 7.42–7.46 (m, 1H), 7.48–7.49 (m, 4H), 7.53–7.58 (m, 2H), 7.60–7.64 (m, 1H), 7.68 (s, 1H), 7.84 (dd, J = 7.8, 1.1 Hz, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.66–8.69 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.3 (d, J_{CF} = 22 Hz), 115.3 (d, J_{CF} = 24 Hz), 122.3, 125.2 (d, J_{CF} = 9 Hz), 126.6, 126.9, 127.21, 127.22, 128.5, 128.6, 128.8, 129.6, 129.9, 131.0, 132.7 (d, J_{CF} = 8 Hz), 138.1 (d, J_{CF} = 4 Hz), 140.2, 161.4 (d, J_{CF} = 246 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 47.5–47.6 (m).

Spectral data for this compound showed good agreement with literature data.[7,10]

2-Chloro-10-phenylphenanthrene (2h)

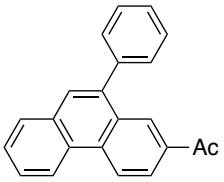


Compound **2h** was synthesised according to *Procedure C* using **1h** (87 mg, 0.30 mmol), TsOH·H_2O (6.0 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel

column chromatography (hexane/chloroform = 20/1) gave **2h** (77 mg, 89%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.50 (m, 5H), 7.52 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.54–7.61 (m, 2H), 7.64 (s, 1H), 7.81 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.85 (d, *J* = 2.2 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.57 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.4, 124.5, 125.9, 126.8, 126.9, 127.1, 127.6, 128.5, 128.6, 128.7, 128.9, 129.4, 129.9, 131.3, 132.2, 132.5, 137.8, 140.0.

Spectral data for this compound showed good agreement with literature data.[10]

1-(10-Phenylphenanthren-2-yl)ethan-1-one (2i)

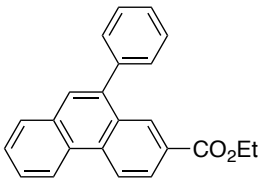


Compound **2i** was synthesised according to *Procedure C* using **1i** (91 mg, 0.31 mmol), $TsOH·H_2O$ (6.1 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 10/1/1) gave **2i** (71 mg, 78%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.59 (s, 3H), 7.49–7.56 (m, 5H), 7.66–7.70 (m, 2H), 7.74 (s, 1H), 7.89–7.91 (m, 1H), 8.20 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.56 (d, *J* = 1.7 Hz, 1H), 8.69–8.71 (m, 1H), 8.77 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 26.5, 123.1, 123.3, 124.8, 126.9, 127.7, 127.9, 128.2, 128.3, 128.5, 128.7, 129.2, 129.9, 130.4, 132.4, 133.7, 134.7, 139.1, 139.9, 197.9.

Spectral data for this compound showed good agreement with literature data.[11]

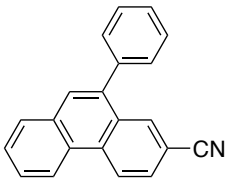
Ethyl 10-phenylphenanthrene-2-carboxylate (2j)



Compound **2j** was synthesised according to *Procedure C* using **1j** (98 mg, 0.30 mmol), $TsOH·H_2O$ (6.0 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 15/1/1) gave **2j** (77 mg, 79%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.42 (t, *J* = 7.1 Hz, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 7.50–7.60 (m, 5H), 7.65–7.70 (m, 2H), 7.75 (s, 1H), 7.90–7.92 (m, 1H), 8.29 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.71–8.74 (m, 2H), 8.78 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.2, 61.0, 123.0, 123.1, 126.2, 126.8, 127.6, 127.8, 128.16, 128.23, 128.4, 128.7, 129.1, 129.2, 130.0, 130.5, 132.3, 133.5, 139.1, 140.0, 166.6. IR (neat): ν 3053, 2978, 1716, 1371, 1275, 1238, 1120, 1024, 742, 700 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{23}H_{18}O_2$ $[M]^+$: 326.1301; Found: 326.1304.

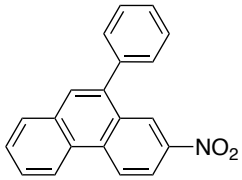
10-Phenylphenanthrene-2-carbonitrile (2k)



Compound **2k** was synthesised according to *Procedure C* using **1k** (84 mg, 0.30 mmol), TfOH (4.8 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 20/2/1) gave **2k** (60 mg, 72%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.57 (m, 5H), 7.69–7.75 (m, 2H), 7.78 (s, 1H), 7.81 (dd, J = 8.6, 1.2 Hz, 1H), 7.91–7.93 (m, 1H), 8.25 (d, J = 1.6 Hz, 1H), 8.68 (d, J = 9.0 Hz, 1H), 8.79 (d, J = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 109.8, 119.3, 123.0, 124.0, 127.3, 127.7, 128.0, 128.5, 128.7, 128.86, 128.88, 129.2, 129.9, 130.8, 132.2, 132.4, 133.1, 138.0, 139.2.

Spectral data for this compound showed good agreement with literature data.[10,12]

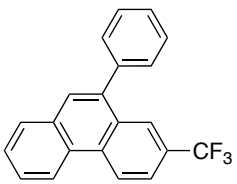
2-Nitro-10-phenylphenanthrene (2l)



Compound **2l** was synthesised according to *Procedure C* using **1l** (90 mg, 0.30 mmol), TfOH (5.1 mg, 34 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 20/4/1) gave **2l** (72 mg, 80%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51–7.54 (m, 3H), 7.56–7.59 (m, 2H), 7.72–7.76 (m, 2H), 7.82 (s, 1H), 7.94–7.95 (m, 1H), 8.41 (dd, J = 9.1, 2.4 Hz, 1H), 8.70–8.72 (m, 1H), 8.83 (d, J = 2.4 Hz, 1H), 8.85 (d, J = 10.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.1, 122.8, 123.4, 124.3, 127.5, 128.1, 128.76, 128.81, 128.81, 129.0, 129.6, 129.9, 130.8, 132.8, 134.6, 139.0, 139.2, 145.9.

Spectral data for this compound showed good agreement with literature data.[12]

10-Phenyl-2-(trifluoromethyl)phenanthrene (2m)

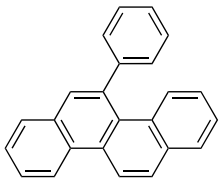


Compound **2m** was synthesised according to *Procedure C* using **1m** (97 mg, 0.30 mmol), $TsOH{\cdot}H_2O$ (6.0 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave **2m** (91 mg, 94%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.51 (m, 5H), 7.59–7.64 (m, 2H), 7.70 (s, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 8.21 (s, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.2 (q, J_{CF} = 3 Hz), 122.9, 123.8, 124.1 (q, J_{CF} = 4 Hz), 124.4 (q,

J_{CF} = 273 Hz), 127.1, 127.8, 127.9, 128.2 (q, J_{CF} = 32 Hz), 128.6, 128.8, 128.9, 129.1, 129.9, 130.5, 132.2, 132.7, 138.6, 139.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ 99.9 (s).

Spectral data for this compound showed good agreement with literature data.[10,12]

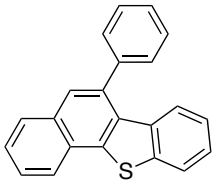
5-Phenylchrysene (2n)



Compound **2n** was synthesised according to *Procedure C* using **1n** (93 mg, 0.30 mmol), TsOH·H_2O (5.9 mg, 31 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave **2n** (61 mg, 65%) as a yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1H), 7.42–7.47 (m, 6H), 7.62 (dd, *J* = 7.8, 7.0 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.83 (s, 1H), 7.90–7.94 (m, 2H), 8.00 (d, *J* = 9.0 Hz, 1H), 8.76 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.2, 123.1, 124.6, 125.7, 126.67, 126.74, 127.0, 127.4, 128.0, 128.1, 128.4, 128.8, 128.9, 129.0, 129.9, 130.0, 130.6, 130.8, 131.4, 133.3, 138.4, 145.5.

Spectral data for this compound showed good agreement with literature data.[6]

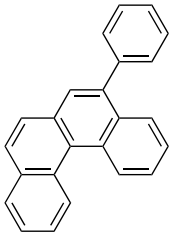
6-Phenylbenzo[*b*]naphtho[2,1-*d*]thiophene (2o)



Compound **2o** was synthesised according to *Procedure C* using **1o** (93 mg, 0.30 mmol), TsOH·H_2O (5.9 mg, 31 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 25/1) gave **2o** (65 mg, 69%) as a pale yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09–7.13 (m, 2H), 7.34 (ddd, *J* = 7.9, 6.3, 1.8 Hz, 1H), 7.52–7.62 (m, 7H), 7.65 (s, 1H), 7.91 (dd, *J* = 8.0, 7.4 Hz, 2H), 8.18 (dd, *J* = 8.0, 0.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.7, 123.9, 124.3, 124.8, 125.5, 126.6, 126.7, 126.8, 127.8, 128.1, 128.5, 128.6, 129.3, 130.7, 131.3, 136.6, 137.3, 138.2, 139.2, 141.3.

Spectral data for this compound showed good agreement with literature data.[13]

5-Phenylbenzo[*c*]phenanthrene (2p)

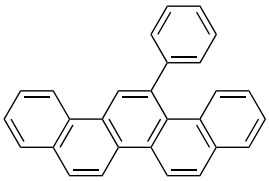


Compound **2p** was synthesised according to *Procedure C* using **1p** (91 mg, 0.30 mmol), TsOH·H_2O (5.9 mg, 31 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) and GPC (chloroform) gave **2p** (53 mg, 58%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.47 (m, 1H), 7.51–7.55 (m, 3H), 7.57–7.63 (m, 3H), 7.65–7.70 (m, 2H), 7.77 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 8.00–8.05 (m, 1H), 9.13 (d, *J* = 8.4 Hz, 1H), 9.17 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 125.8, 125.88, 125.92, 126.2, 126.7, 126.8, 126.9, 127.39, 127.39, 127.8, 127.9, 128.2, 128.4, 128.6, 130.05, 130.05, 130.3, 130.7, 132.2, 133.5, 139.1, 140.6.

Spectral data for this compound showed good agreement with literature data.[14]

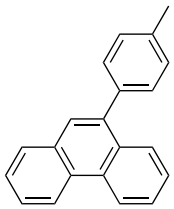
13-Phenylpicene (2q)



Compound **2q** was synthesised according to *Procedure C* using **1q** (104 mg, 0.29 mmol), TsOH·H_2O (6.0 mg, 32 μmol), cyclohexane (4.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) and GPC (chloroform) gave **2q** (45 mg, 43%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.17–7.20 (m, 4H), 7.34–7.36 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.43 (ddd, *J* = 8.1, 6.9, 1.0 Hz, 1H), 7.61 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.80–7.85 (m, 2H), 7.86–7.89 (m, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 8.24 (s, 1H), 8.63 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 118.16, 118.22, 124.3, 124.5, 124.7, 125.3, 127.2, 127.82, 127.82, 128.36, 128.38, 128.60, 128.62, 128.7, 129.9, 130.1, 130.7, 133.1, 133.9, 134.7, 135.0, 137.1, 137.7, 137.9, 140.3, 140.6. IR (neat): ν 3051, 2922, 2852, 1585, 1518, 1491, 1444, 1365, 1309, 1215, 1024, 862, 806, 737, 688 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{28}H_{19}$ $[M + H]^+$: 355.1481; Found: 355.1477.

9-(4-Methylphenyl)phenanthrene (2r)

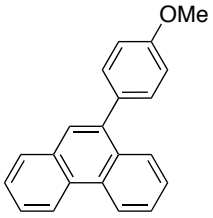


Compound **2r** was synthesised according to *Procedure C* using **1r** (81 mg, 0.30 mmol), TsOH·H_2O (5.7 mg, 30 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at room temperature for 3 h. Purification by silica gel column chromatography (hexane/dichloromethane = 100/1) gave **2r** (69 mg, 86%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.49 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.55 (dd, *J* = 7.5, 6.8 Hz, 1H), 7.58–7.62 (m, 2H), 7.64 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 8.71 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 122.5, 122.8, 126.3, 126.40, 126.43, 126.8, 126.9, 127.4, 128.6, 129.0, 129.85, 129.90, 130.6, 131.2, 131.6, 137.0, 137.8, 138.7.

Spectral data for this compound showed good agreement with literature data.[10,11]

9-(4-Methoxyphenyl)phenanthrene (2s)

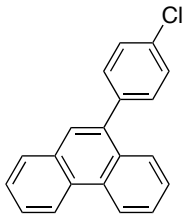


Compound **2s** was synthesised according to *Procedure C* using **1s** (85 mg, 0.30 mmol), $TsOH·H_2O$ (5.8 mg, 30 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at room temperature for 1 h. Purification by silica gel column chromatography (hexane/dichloromethane = 5/1) gave **2s** (82 mg, 96%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 3H), 7.02 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.45 (ddd, *J* = 7.8, 6.8, 1.1 Hz, 1H), 7.58 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.61–7.64 (m, 2H), 7.64 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.3, 113.7, 122.5, 122.9, 126.3, 126.40, 126.41, 126.8, 126.9, 127.4, 128.5, 129.8, 130.6, 131.1, 131.4, 131.6, 133.1, 138.4, 159.0.

Spectral data for this compound showed good agreement with literature data.[10,11]

9-(4-Chlorophenyl)phenanthrene (2t)

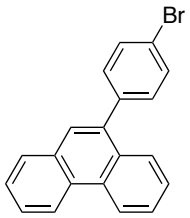


Compound **2t** was synthesised according to *Procedure C* using **1t** (87 mg, 0.30 mmol), $TsOH·H_2O$ (12 mg, 60 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at 60 °C for 3 h. Purification by silica gel column chromatography (hexane/dichloromethane = 100/1) gave **2t** (64 mg, 73%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.51 (ddd, *J* = 8.1, 7.0, 0.6 Hz, 1H), 7.57–7.66 (m, 4H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.5, 123.0, 126.55, 126.57, 126.60, 126.8, 126.9, 127.6, 128.5, 128.6, 130.0, 130.6, 130.8, 131.35, 131.35, 133.4, 137.4, 139.2.

Spectral data for this compound showed good agreement with literature data.[10,11]

9-(4-Bromophenyl)phenanthrene (2u)



Compound **2u** was synthesised according to *Procedure C* using **1u** (99 mg, 0.30 mmol), $TsOH·H_2O$ (11 mg, 60 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at 60 °C for 3 h. Purification by silica gel column chromatography (hexane/dichloromethane = 100/1) gave **2u** (71 mg, 71%) as a white solid.

^1H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.51 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.57–7.66 (m, 6H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 121.5, 122.5, 123.0, 126.5, 126.58, 126.60, 126.8, 126.9, 127.5, 128.6, 130.0, 130.6, 130.7, 131.3, 131.4, 131.7, 137.4, 139.6.

Spectral data for this compound showed good agreement with literature data.[10]

4. Recycling of HFIP Solution Containing TsOH for Sequential Hydroarylation

To a cyclohexane (3.0 mL) solution of **1a** (76 mg, 0.30 mmol) was added HFIP (0.8 mL). To the reaction mixture was added a HFIP (0.7 mL) solution of $TsOH·H_2O$ (5.7 mg, 30 μmol). After stirring vigorously at room temperature for 9 h under air, the cyclohexane (upper) and HFIP (lower) layers were separated by extracting the cyclohexane layer. The combined extracts were filtered through a pad of silica gel (hexane/chloroform = 20/1). After the solvent was removed under reduced pressure, the yield of **2a** was determined by ^1H NMR measurement using CH_2Br_2 as an internal standard. The second cycle was conducted by adding another cyclohexane (3.0 mL) solution of **1a** (0.3 mmol) to the remained HFIP solution containing TsOH. Thus, the same experiment was continuously conducted up to the fifth cycle.

5. References

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(2) W.-J. Yoo, T. V. Q. Nguyen and S. Kobayashi, *Angew. Chem. Int. Ed.*, 2014, **53**, 10213–10217.

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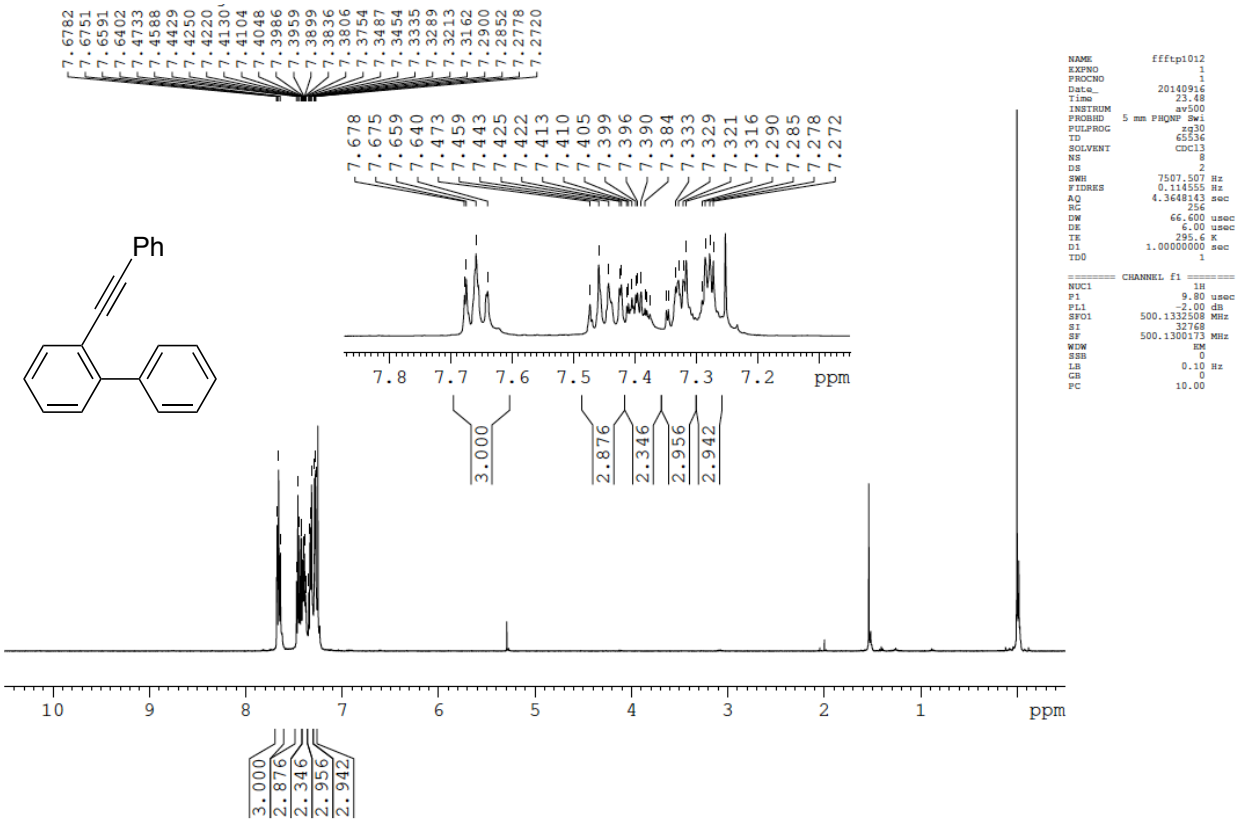
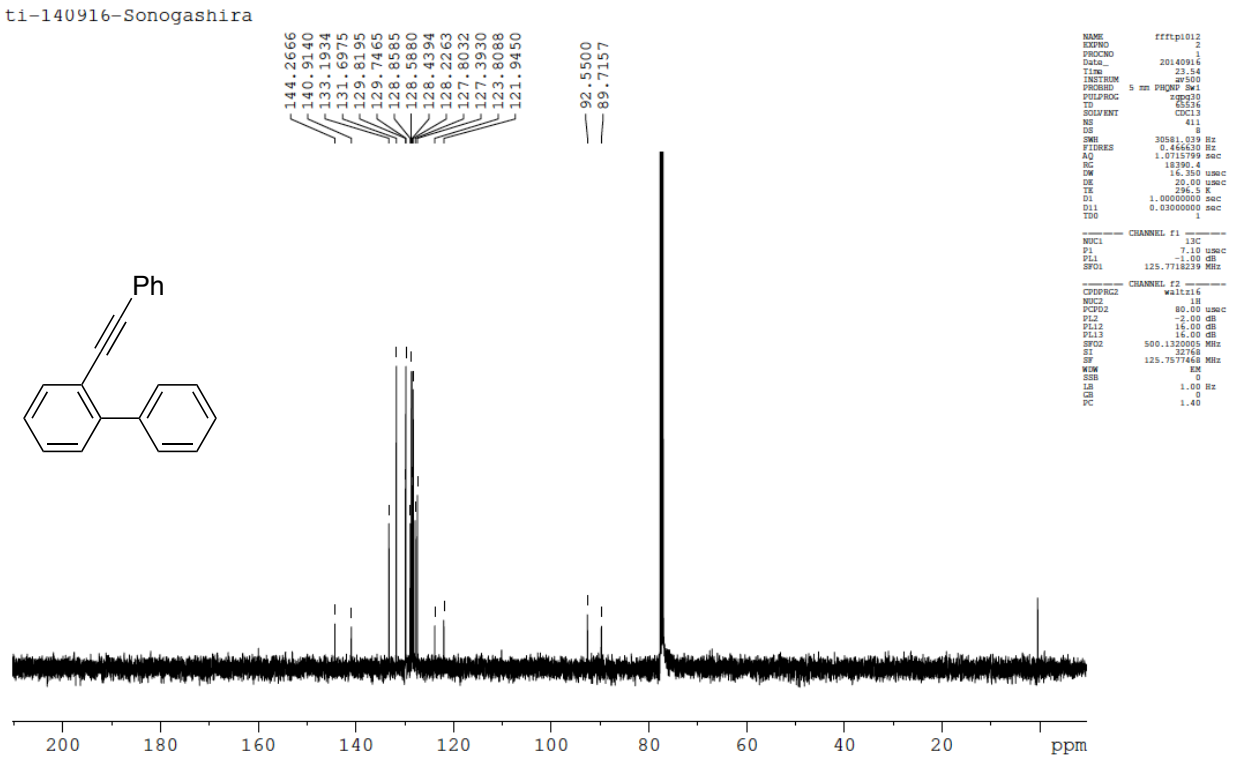
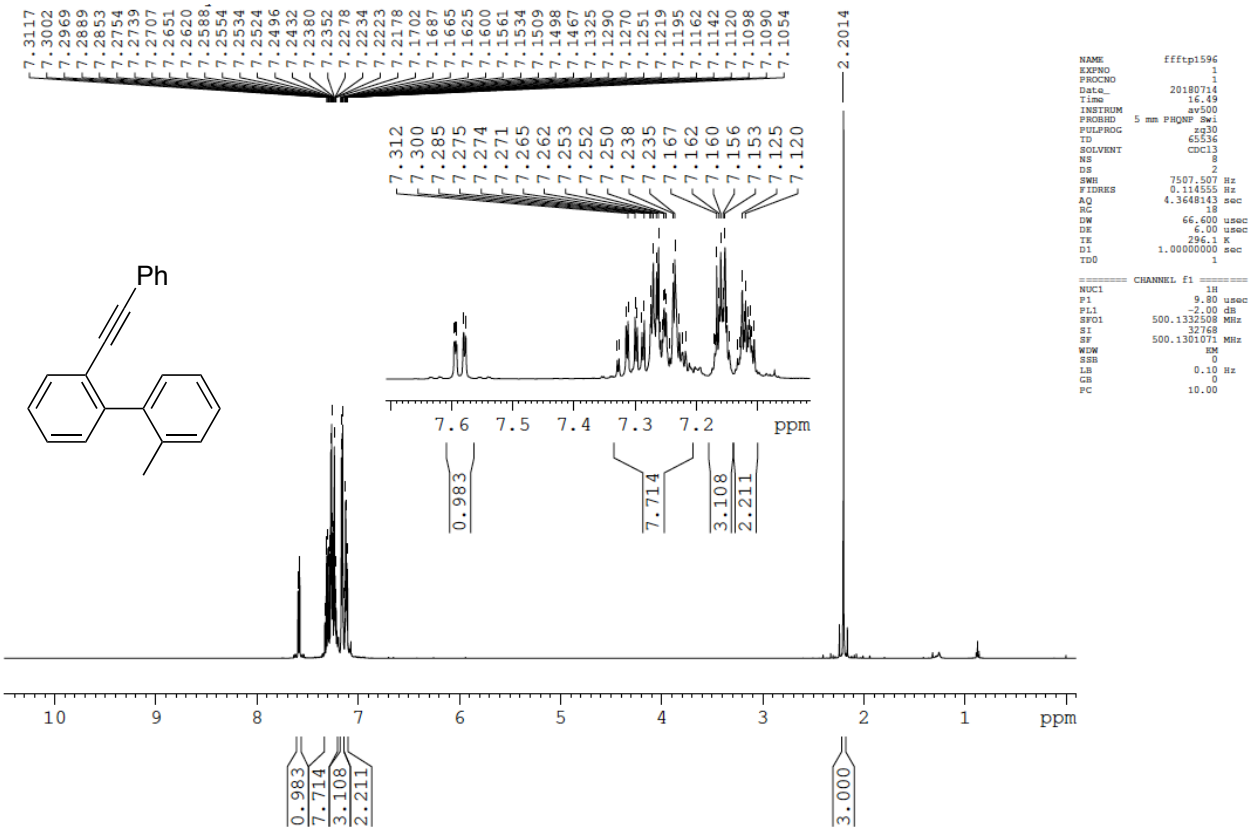
6. ^{1}H, ^{13}C, and ^{19}F NMR Charts

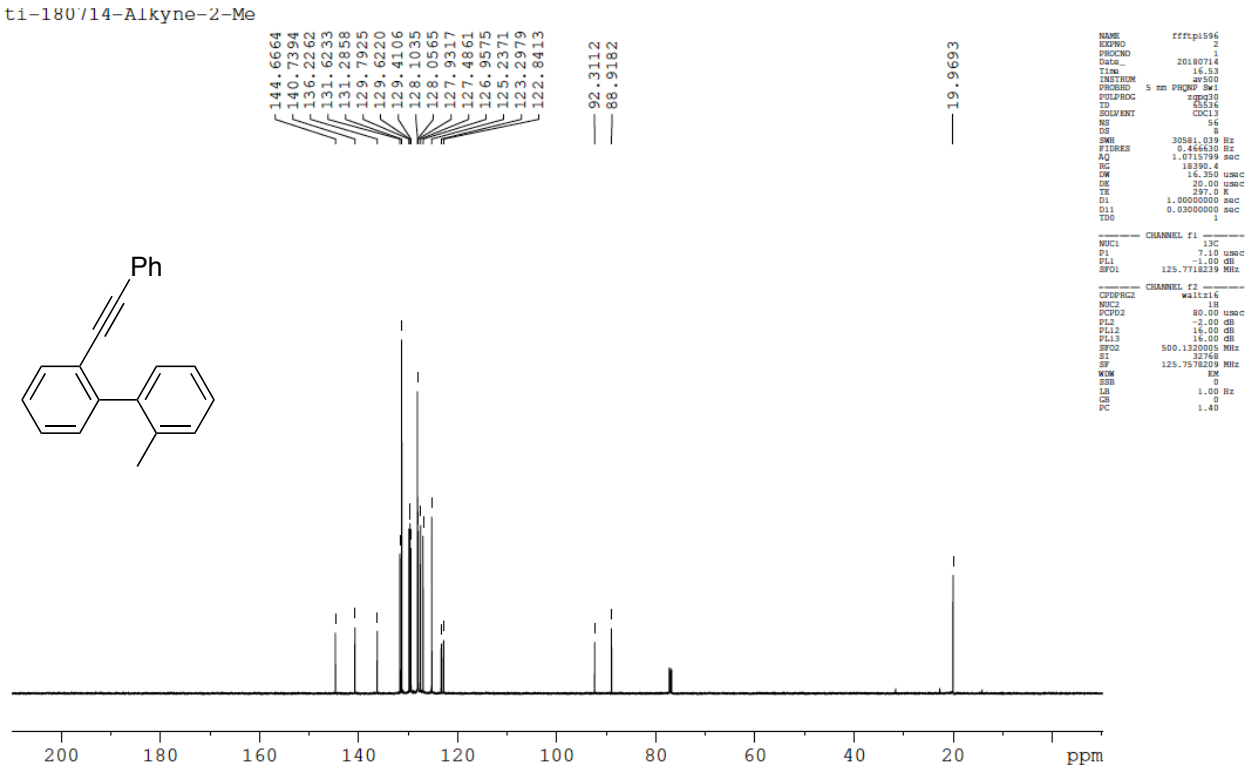
2-(Phenylethynyl)-1,1'-biphenyl (1a)



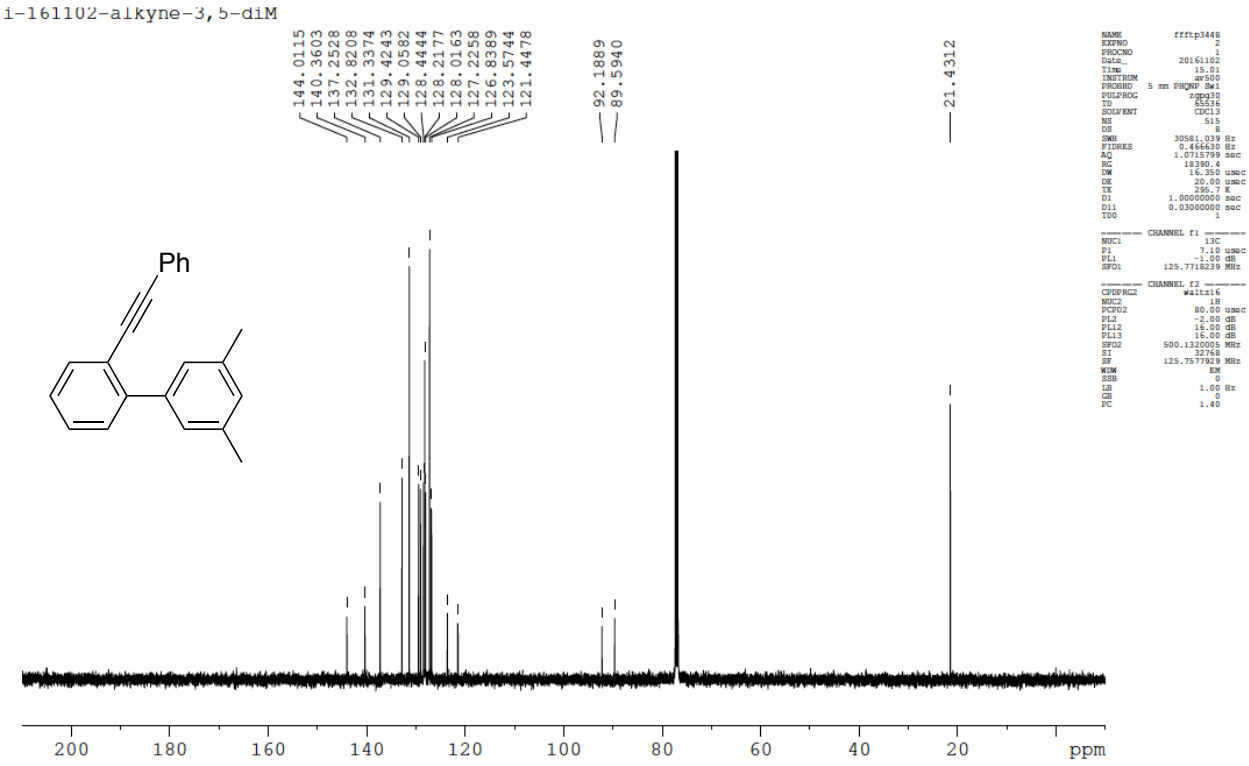


2-Methyl-2'-(phenylethynyl)-1,1'-biphenyl (1b)

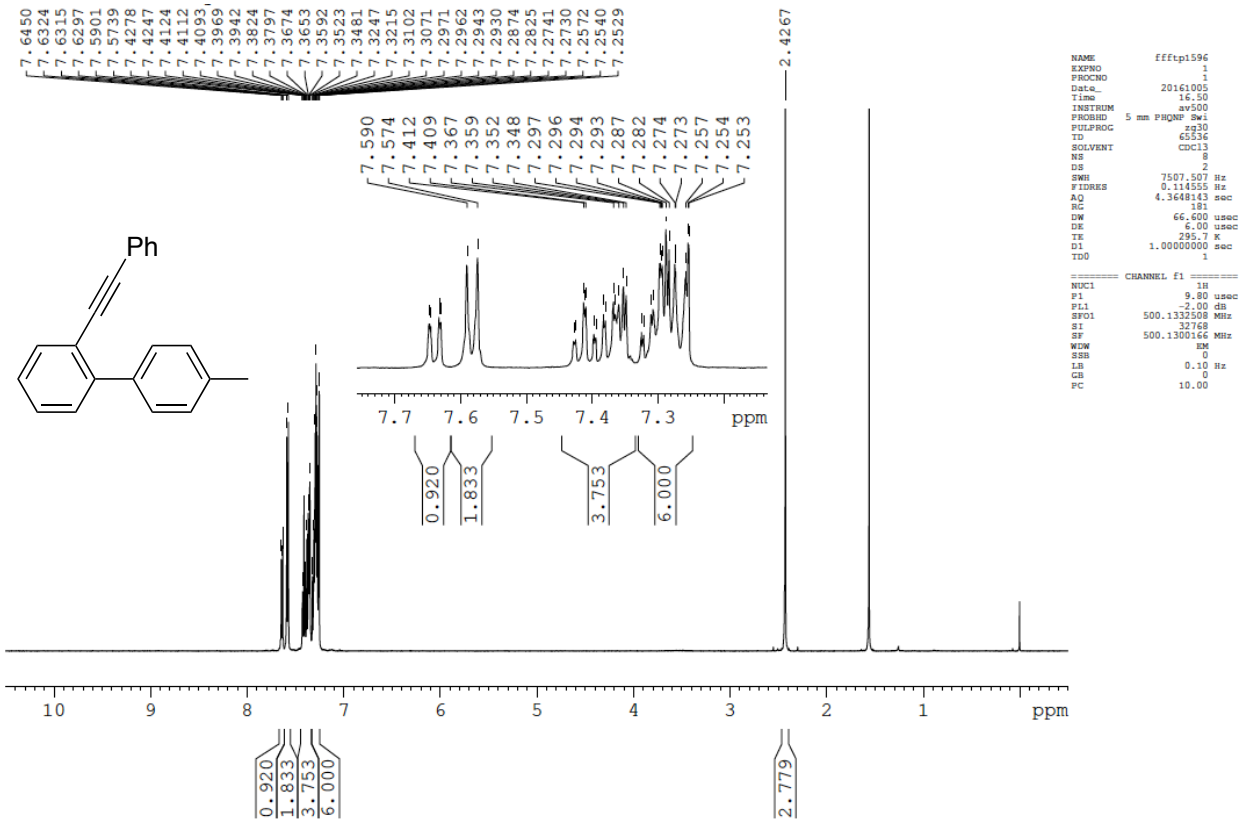


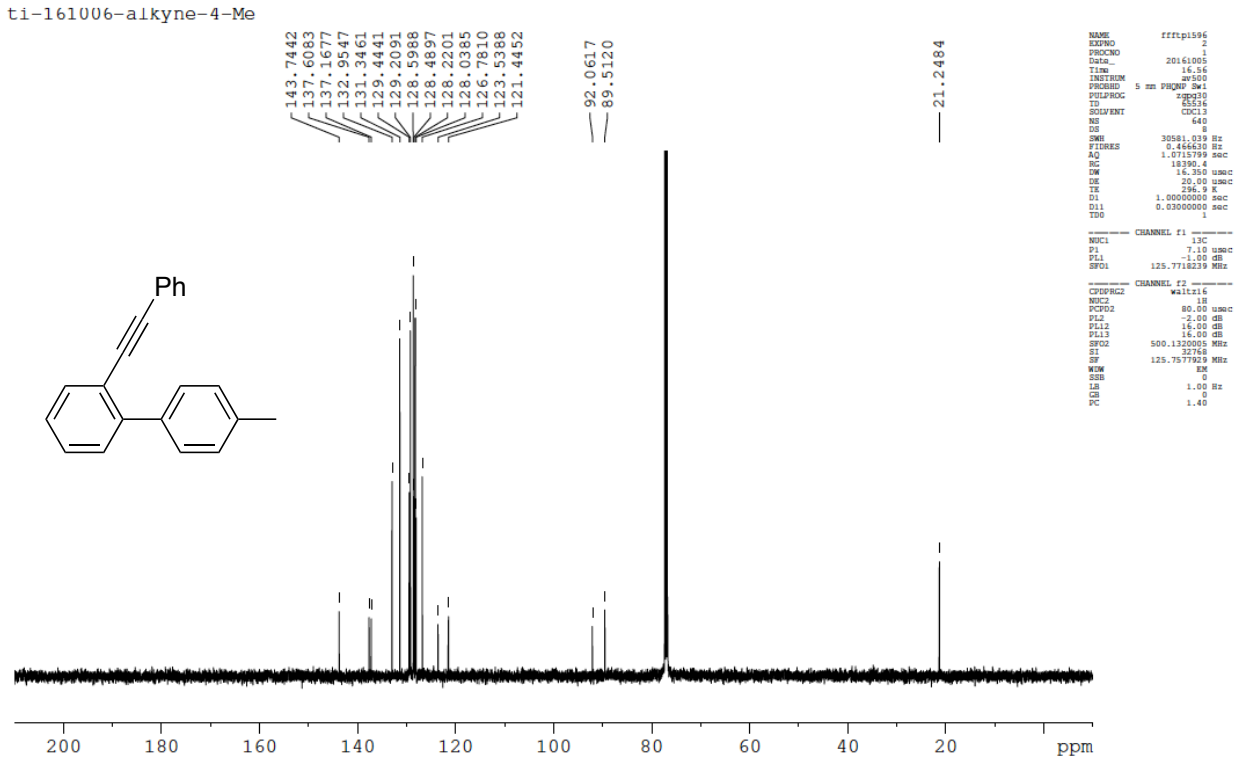


3',5'-Dimethtyl-2-(phenylethynyl)-1,1'-biphenyl (1c)

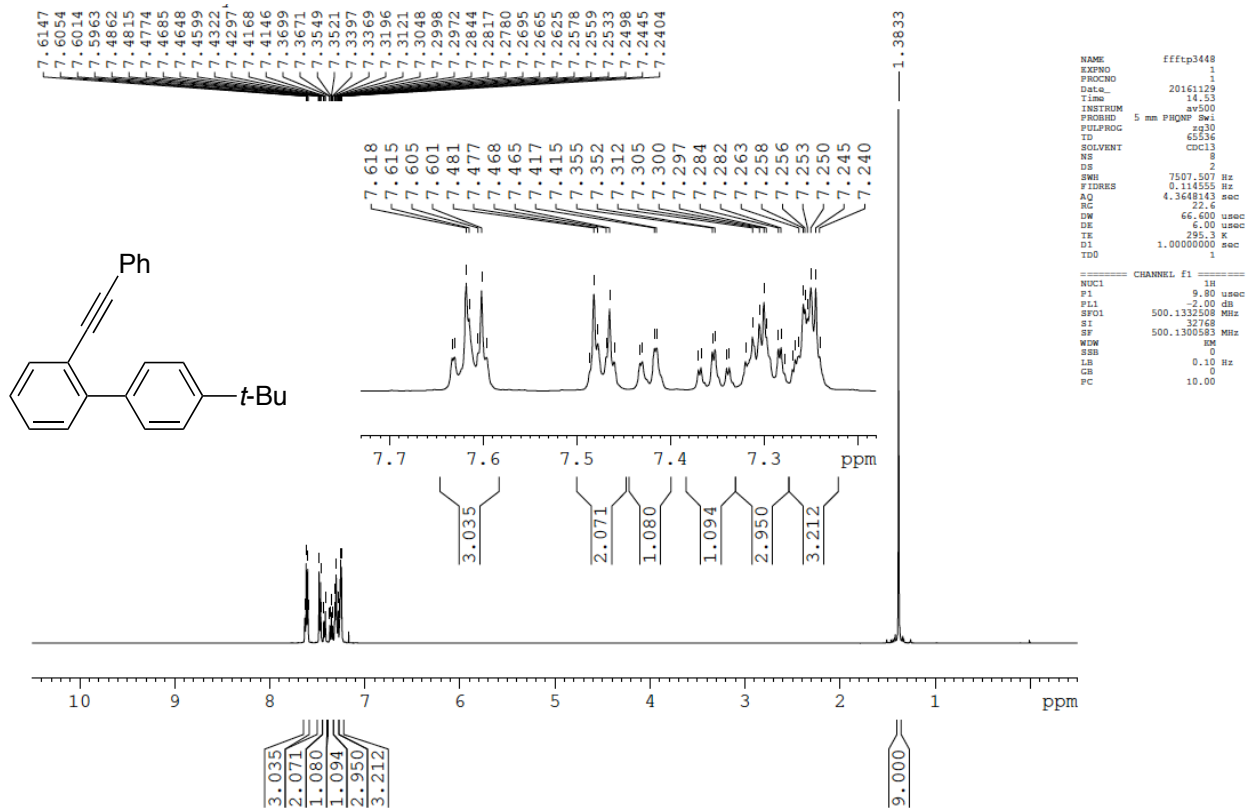


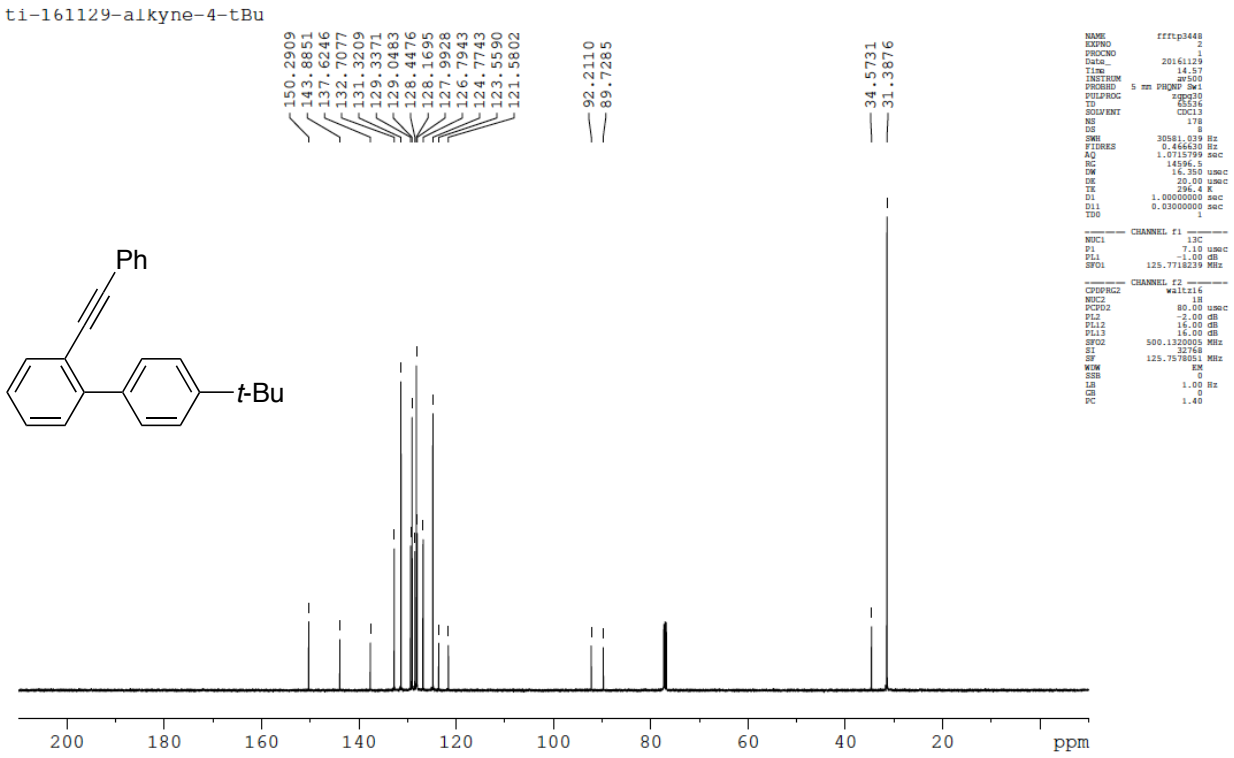
4'-Methyl-2-(phenylethynyl)-1,1'-biphenyl (1d)



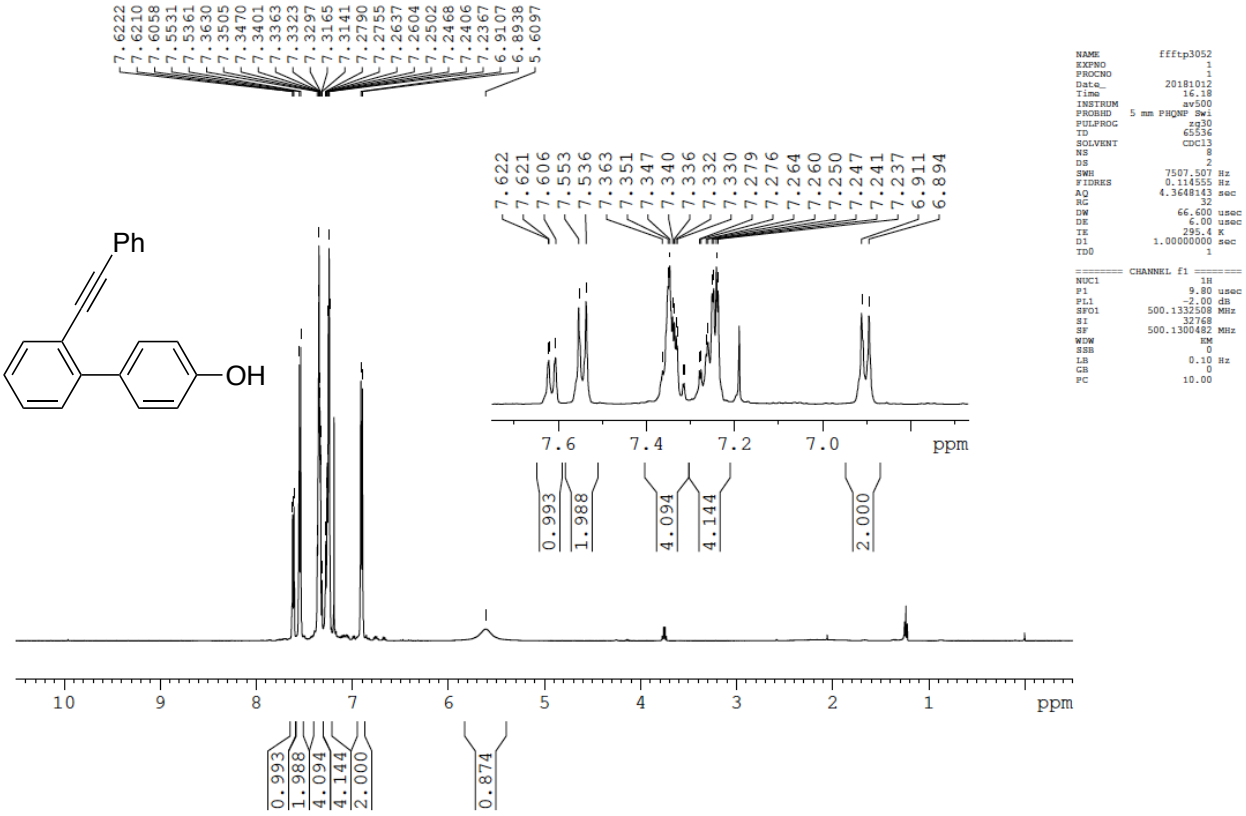


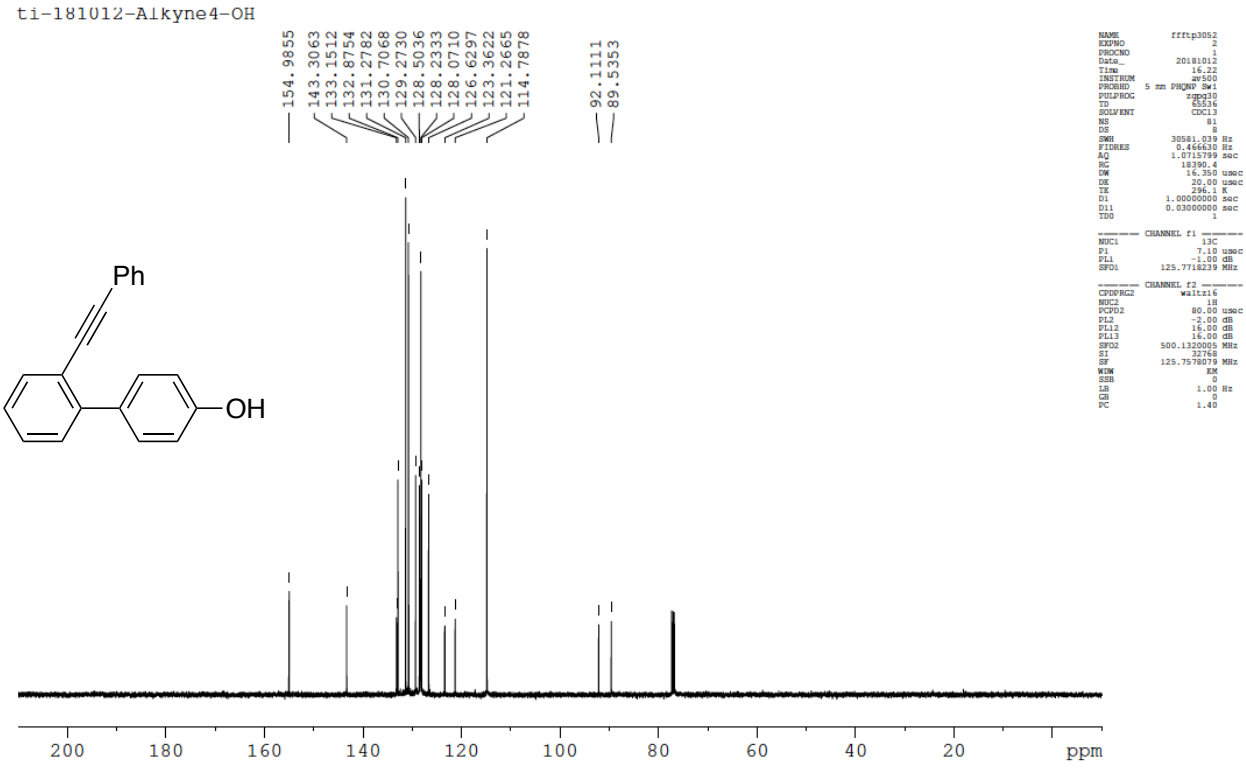
4'-(*tert*-Butyl)-2-(phenylethynyl)-1,1'-biphenyl (1e)



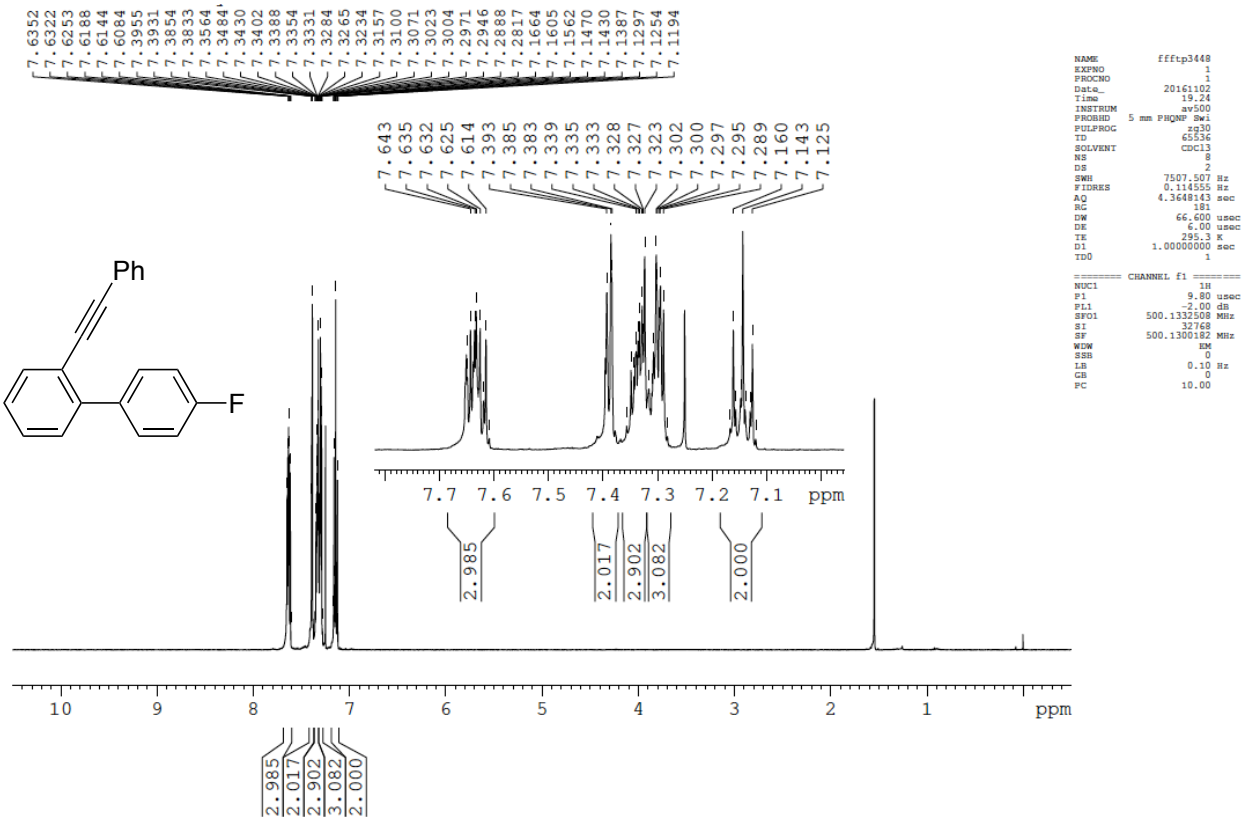


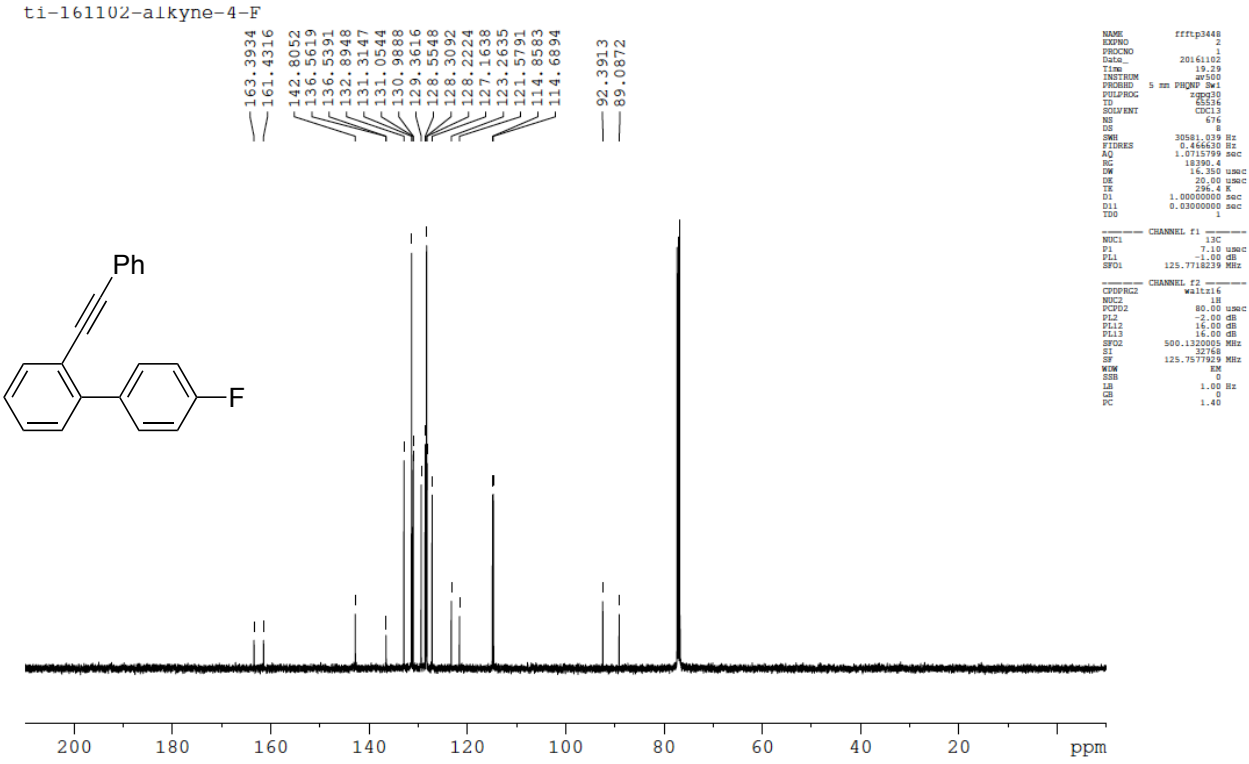
2'-(Phenylethynyl)-[1,1'-biphenyl]-4-ol (1f)

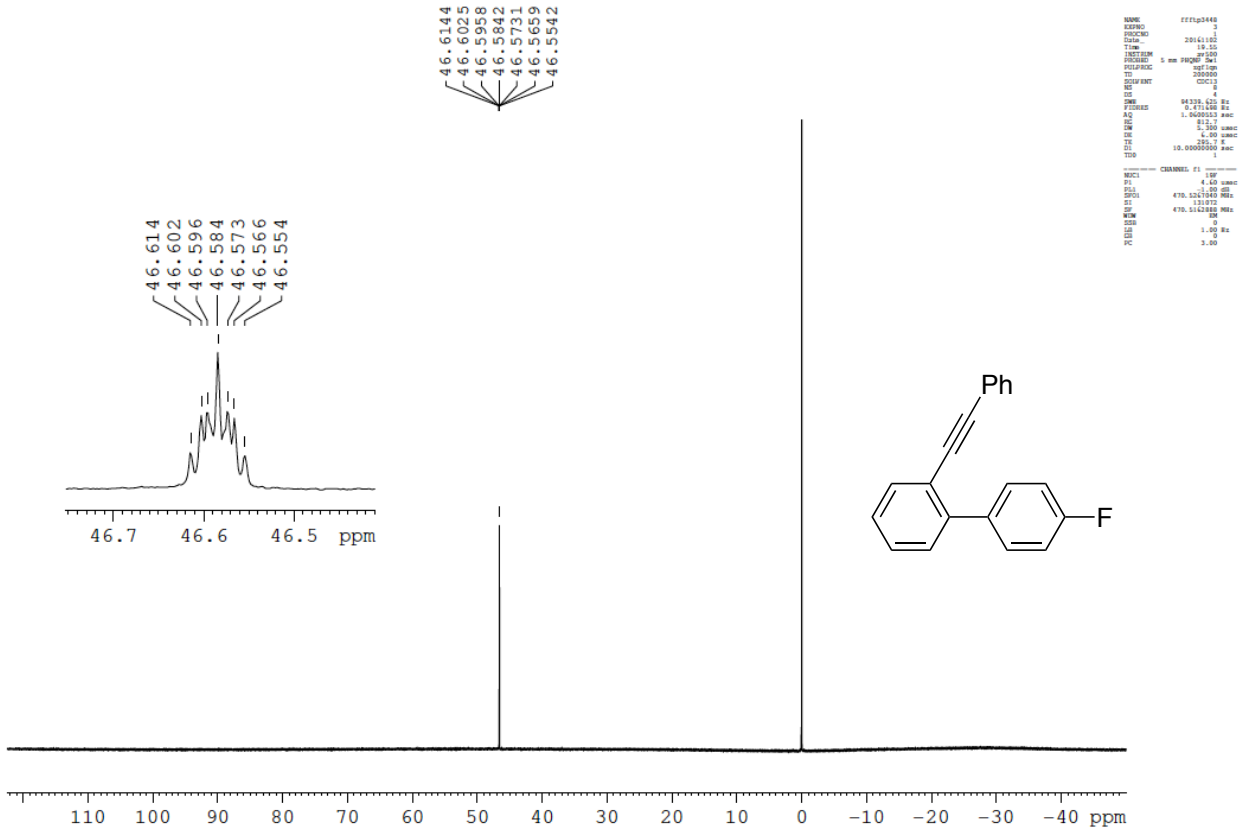




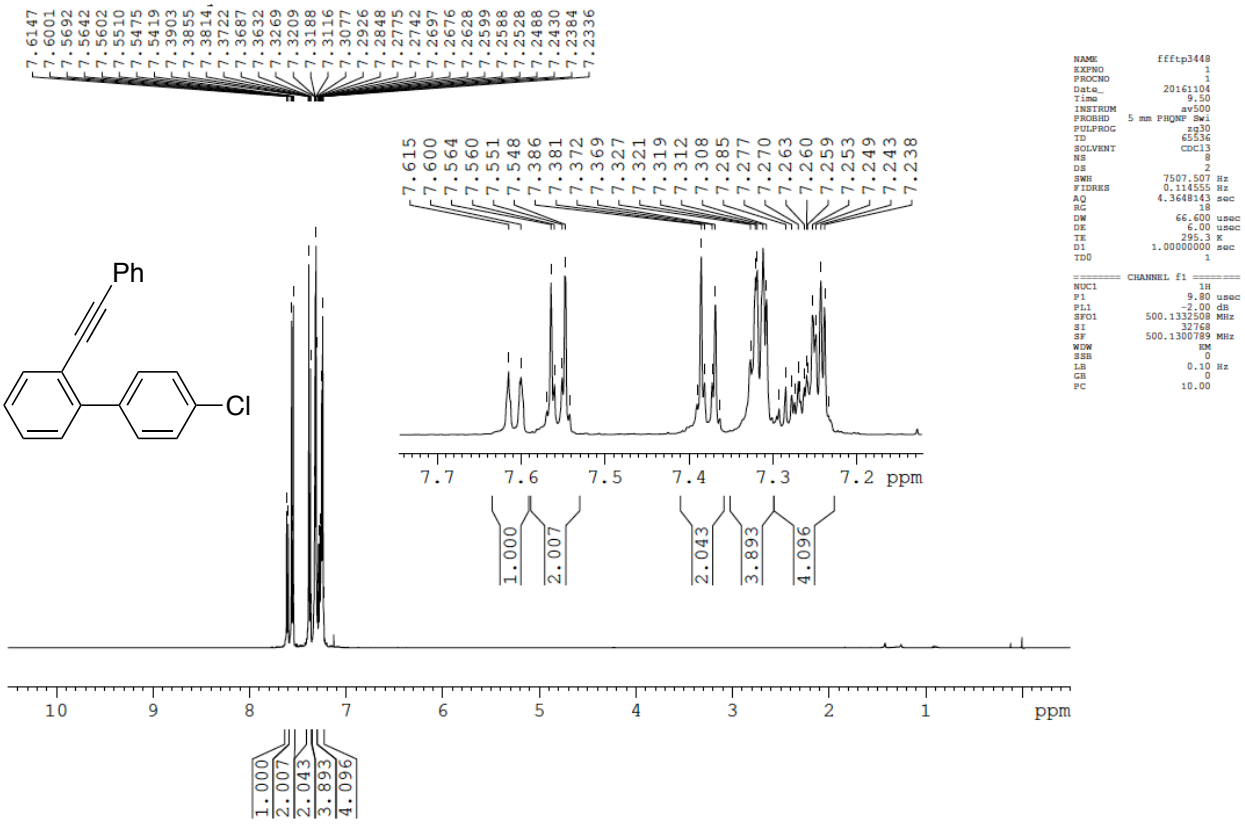
4'-Fluoro-2-(phenylethynyl)-1,1'-biphenyl (1g)

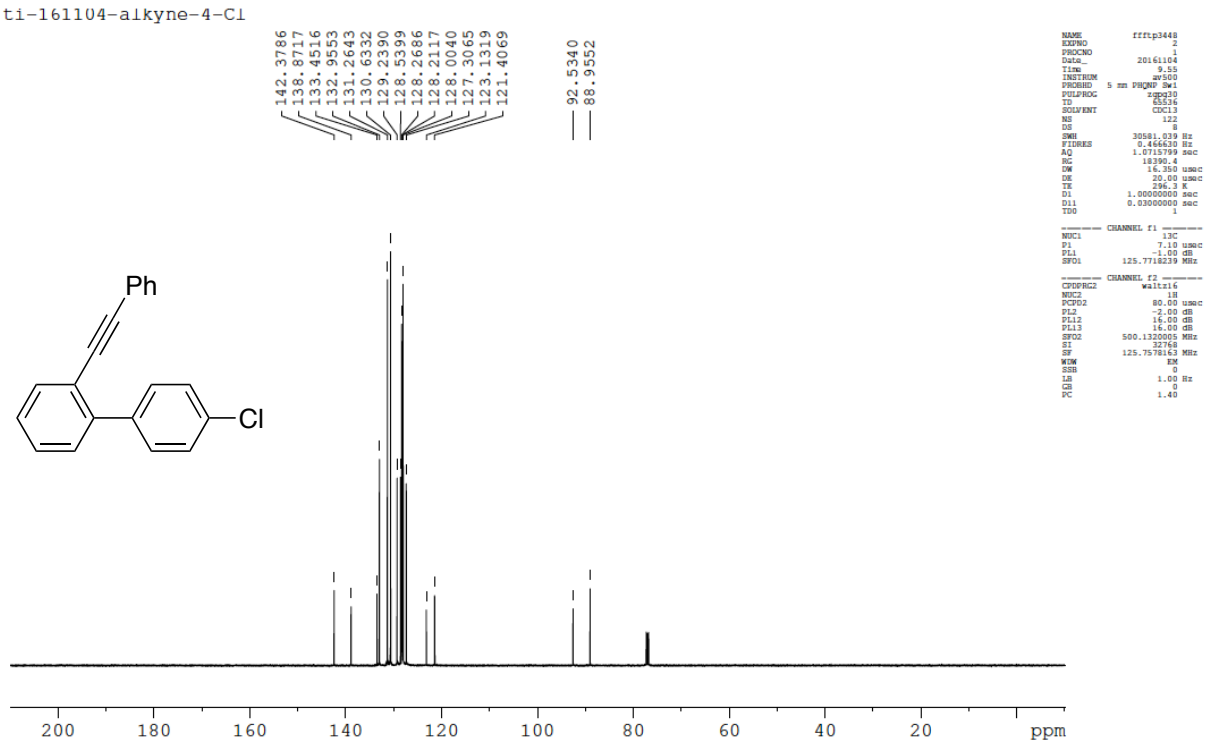




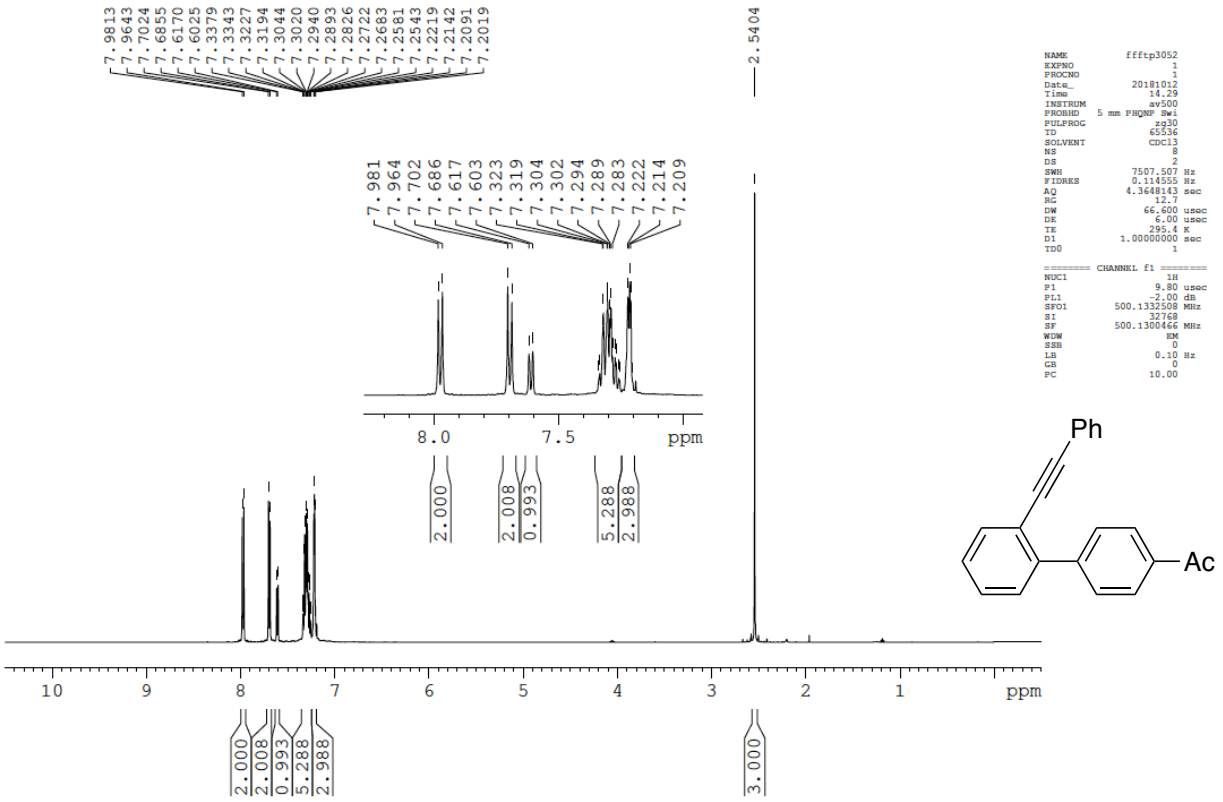


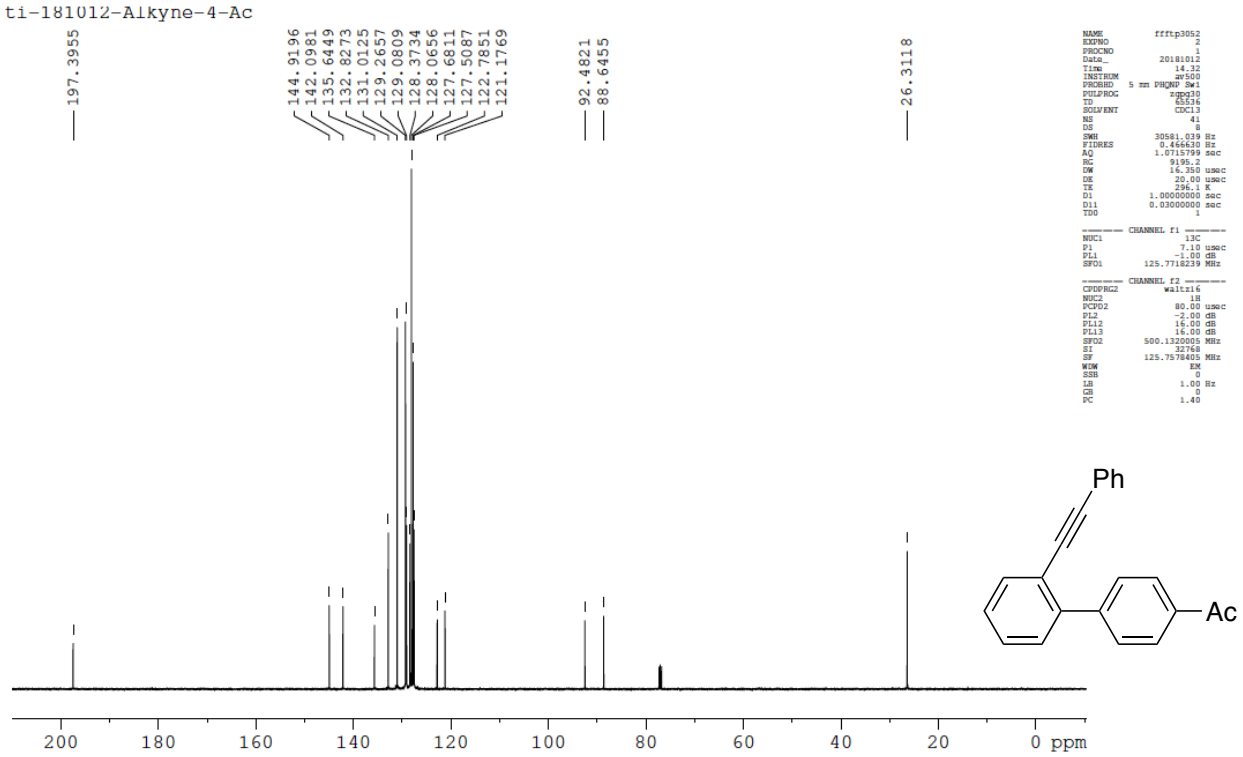
4'-Chloro-2-(phenylethynyl)-1,1'-biphenyl (1h)



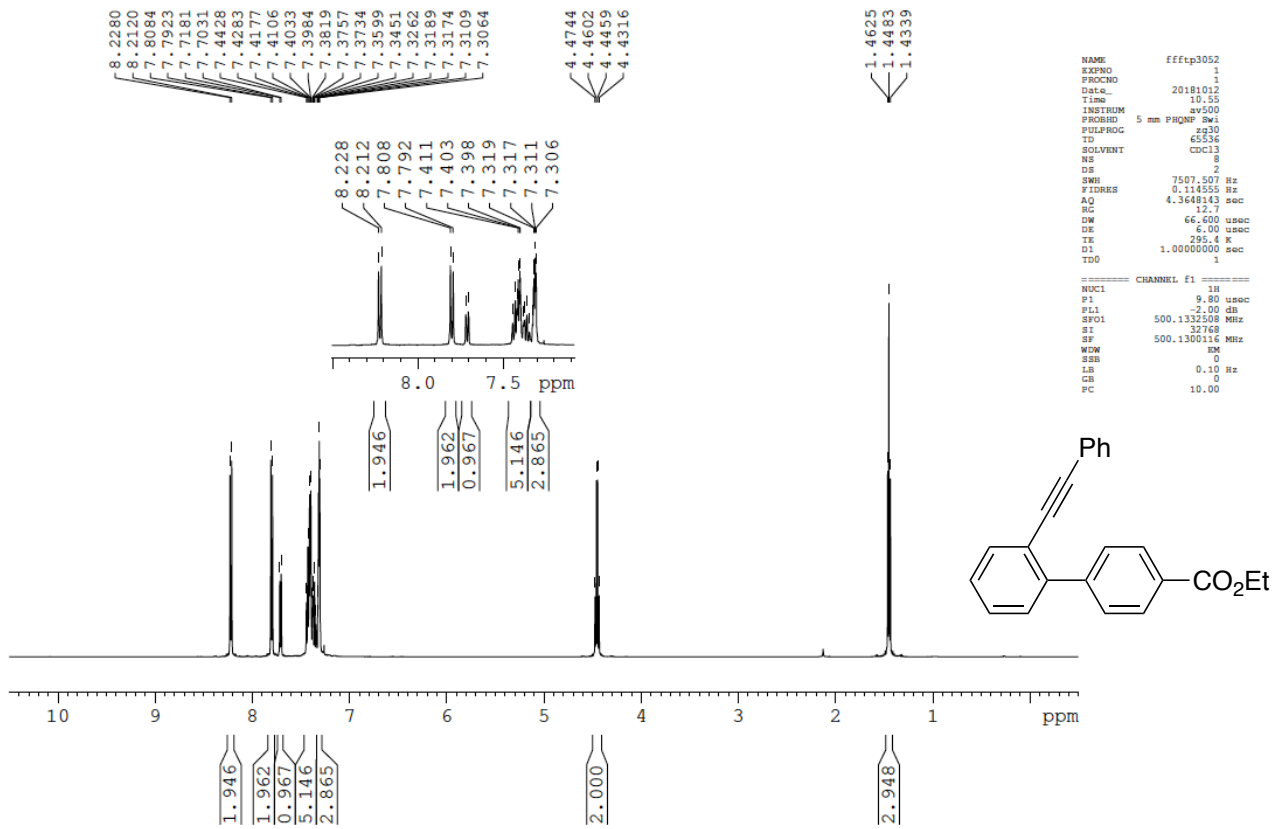


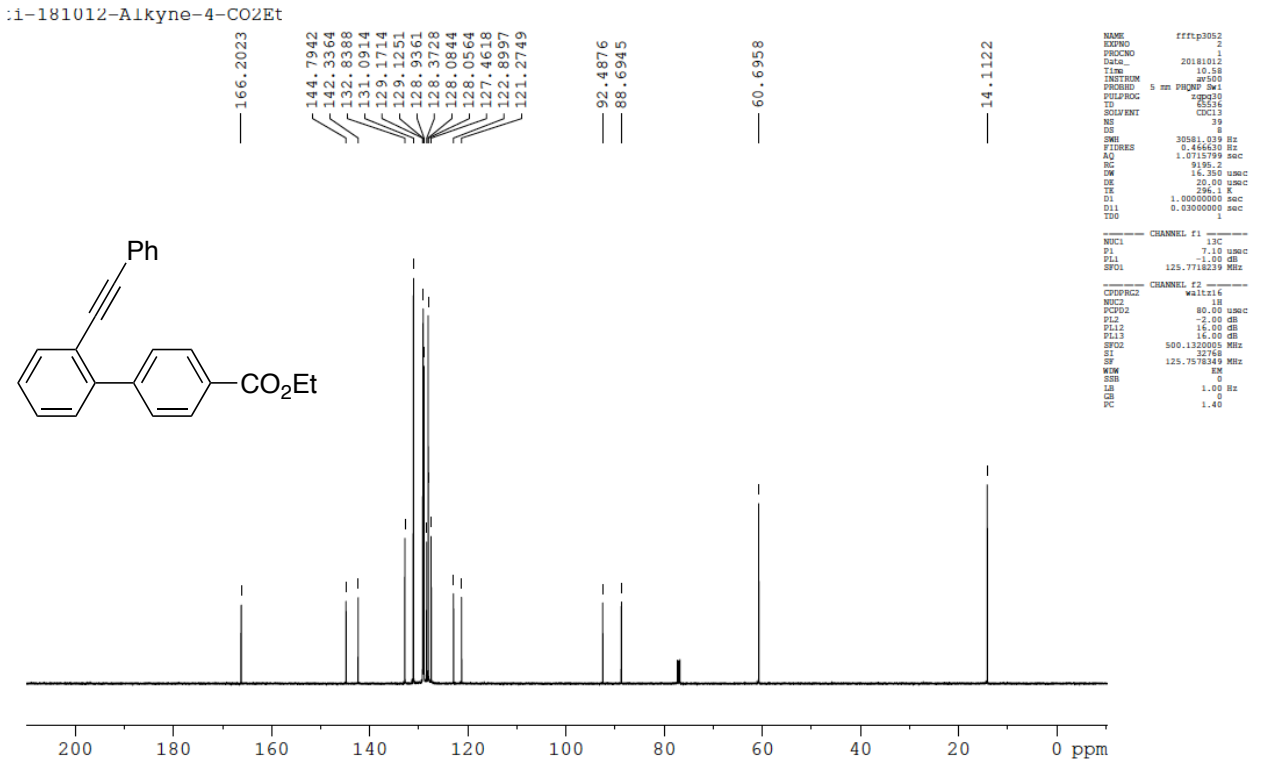
1-{2'-(Phenylethynyl)-[1,1'-biphenyl]-4-yl}ethan-1-one (1i)



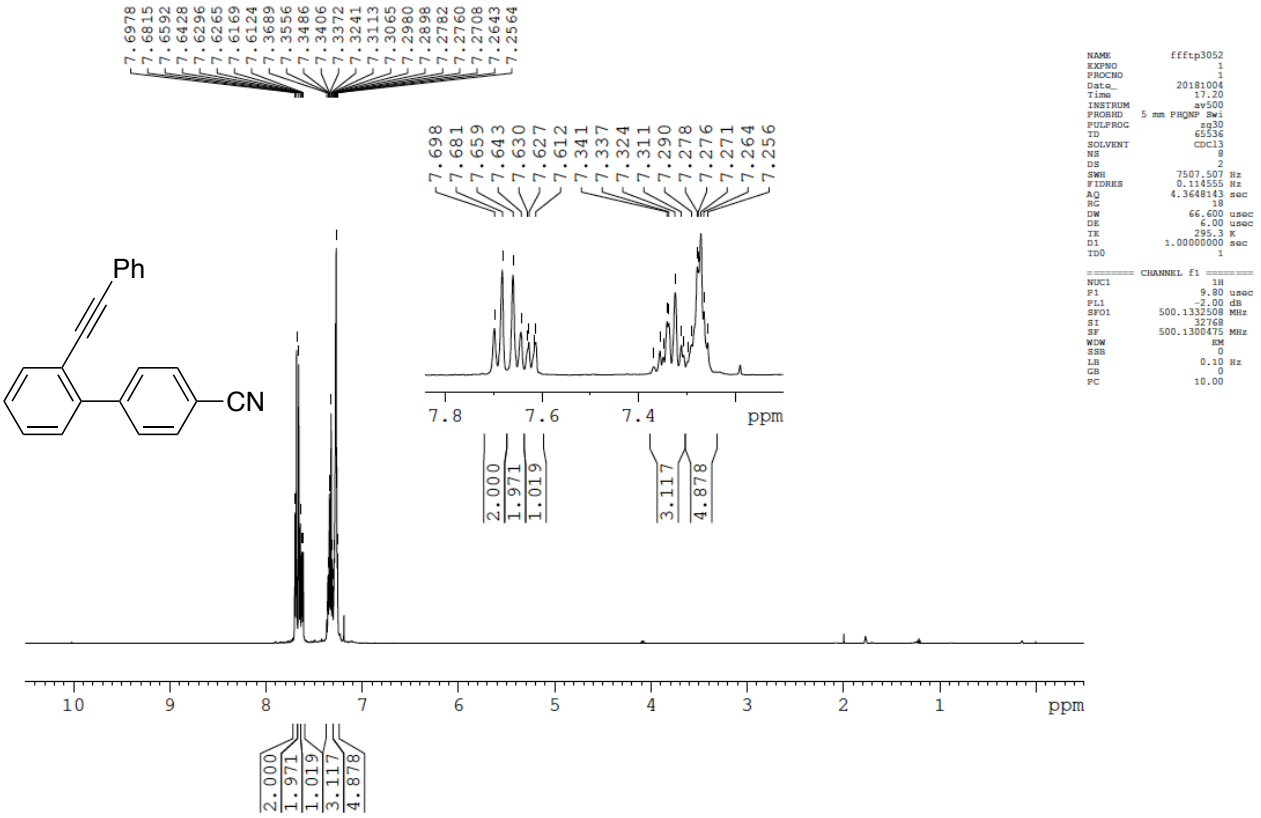


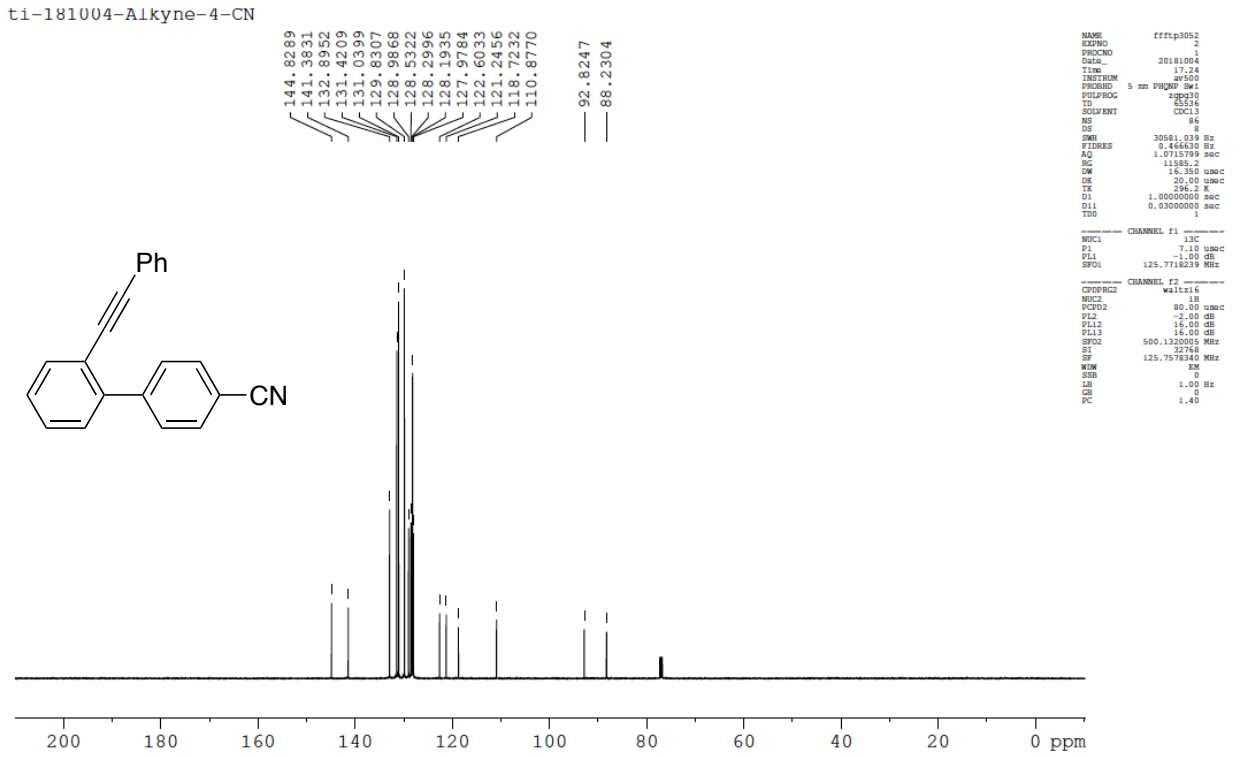
Ethyl 2'-(phenylethynyl)-[1,1'-biphenyl]-4-carboxylate (1j)



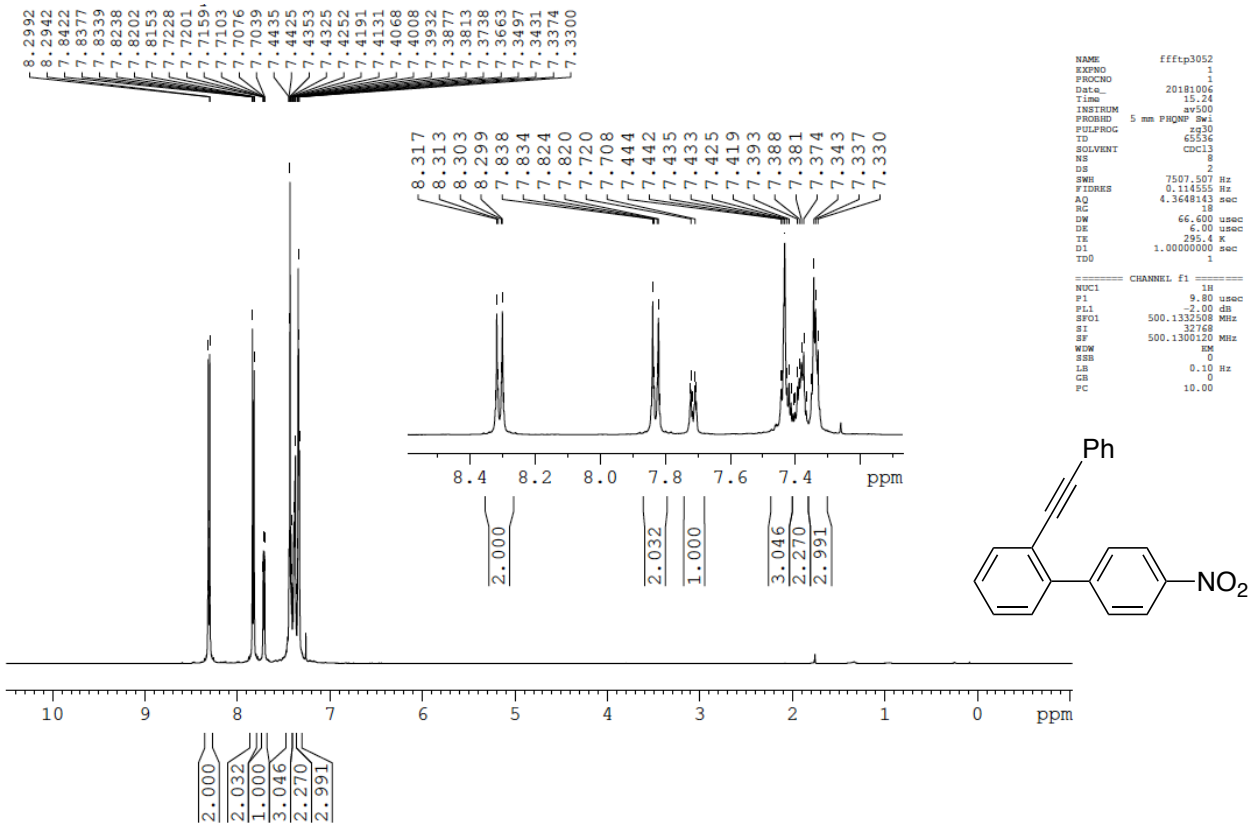


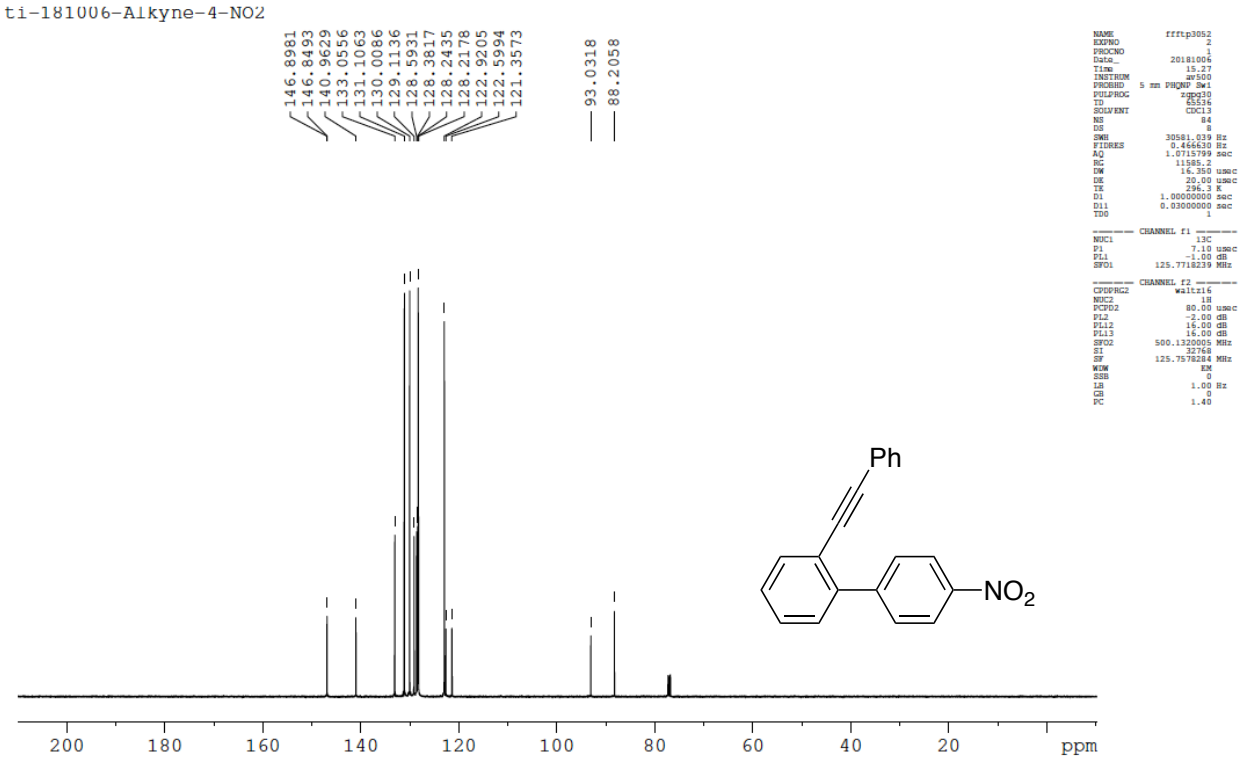
2'-(Phenylethynyl)-[1,1'-biphenyl]-4-carbonitrile (1k)



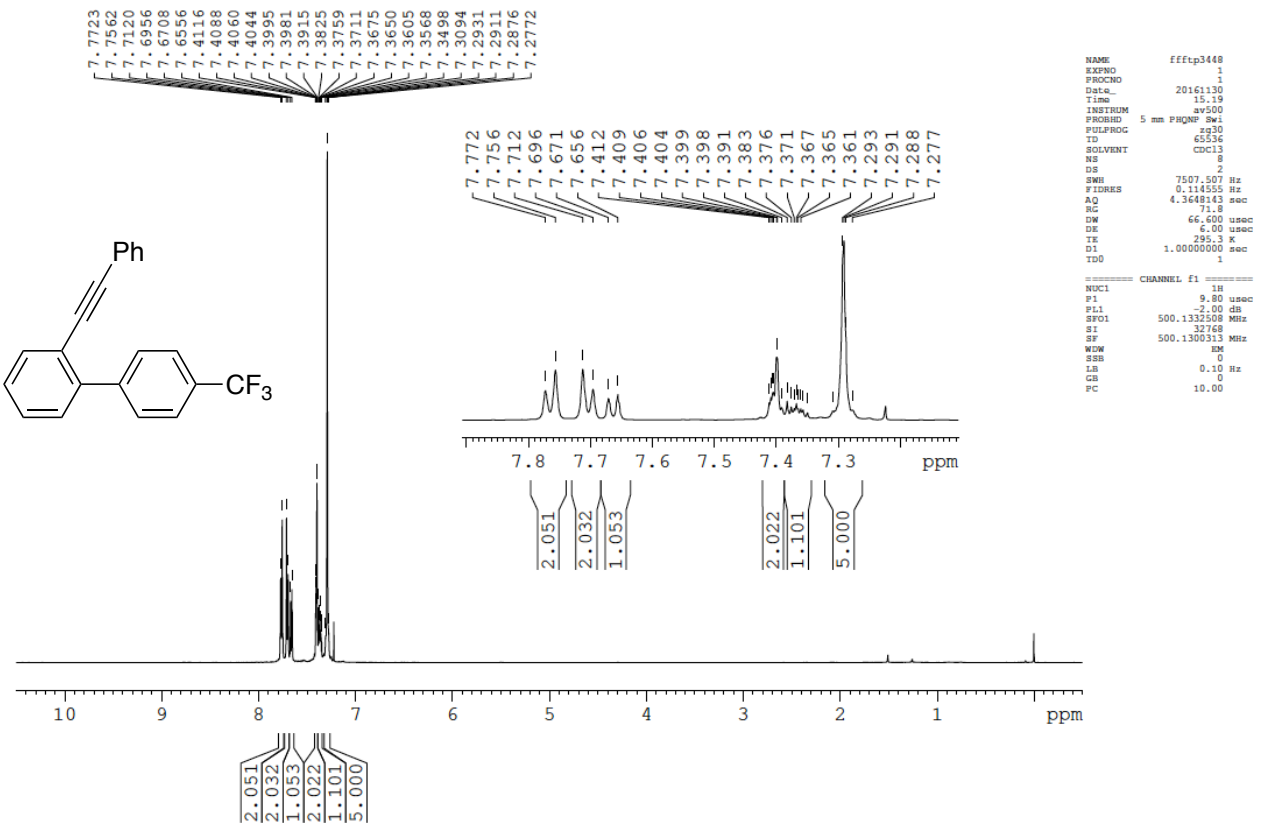


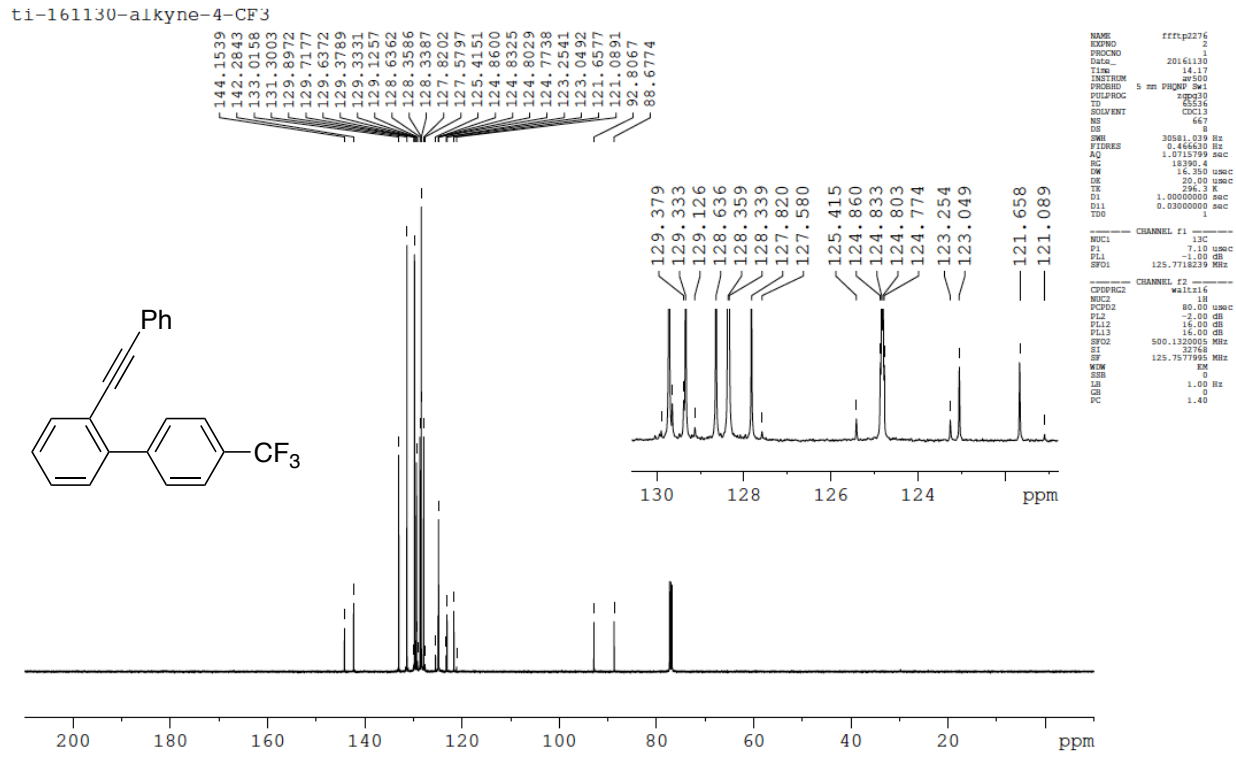
4'-Nitro-2-(phenylethynyl)-1,1'-biphenyl (1l)





2-(Phenylethynyl)-4'-(trifluoromethyl)-1,1'-biphenyl (1m)

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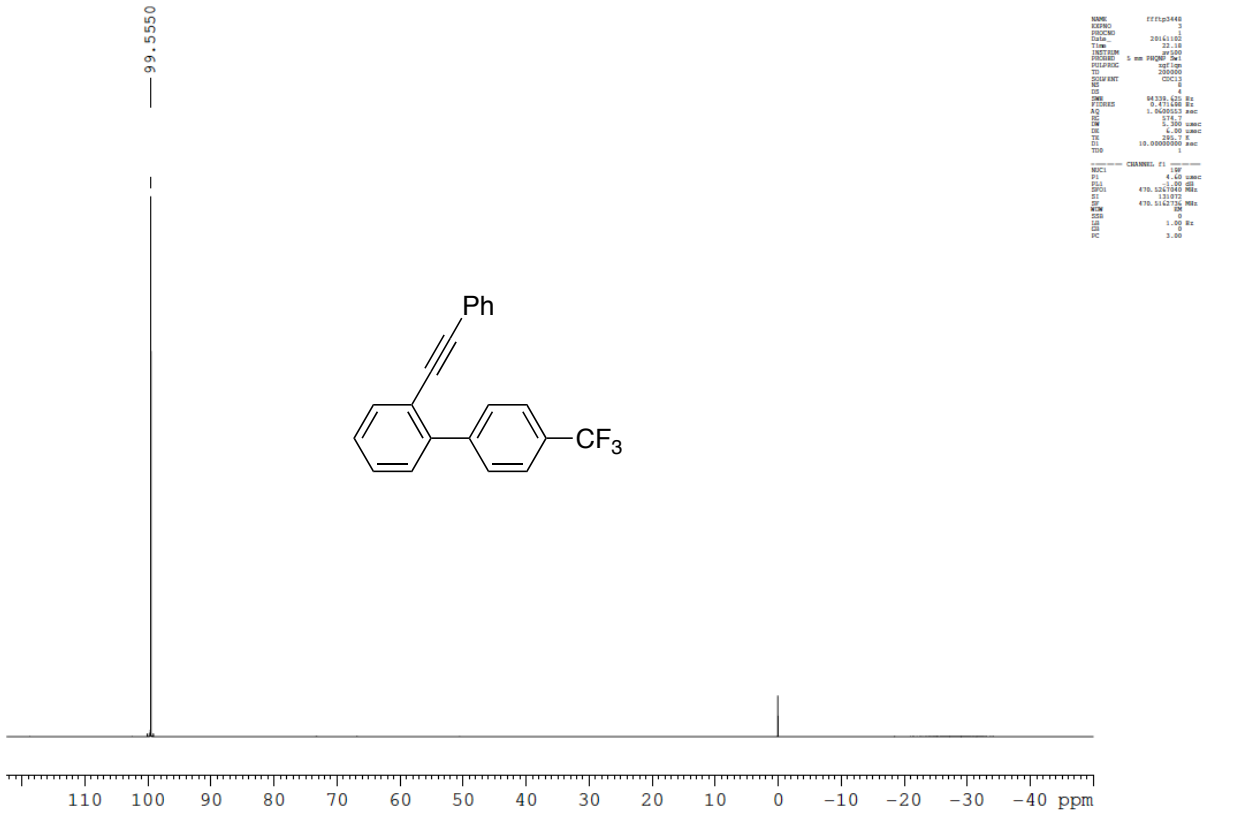
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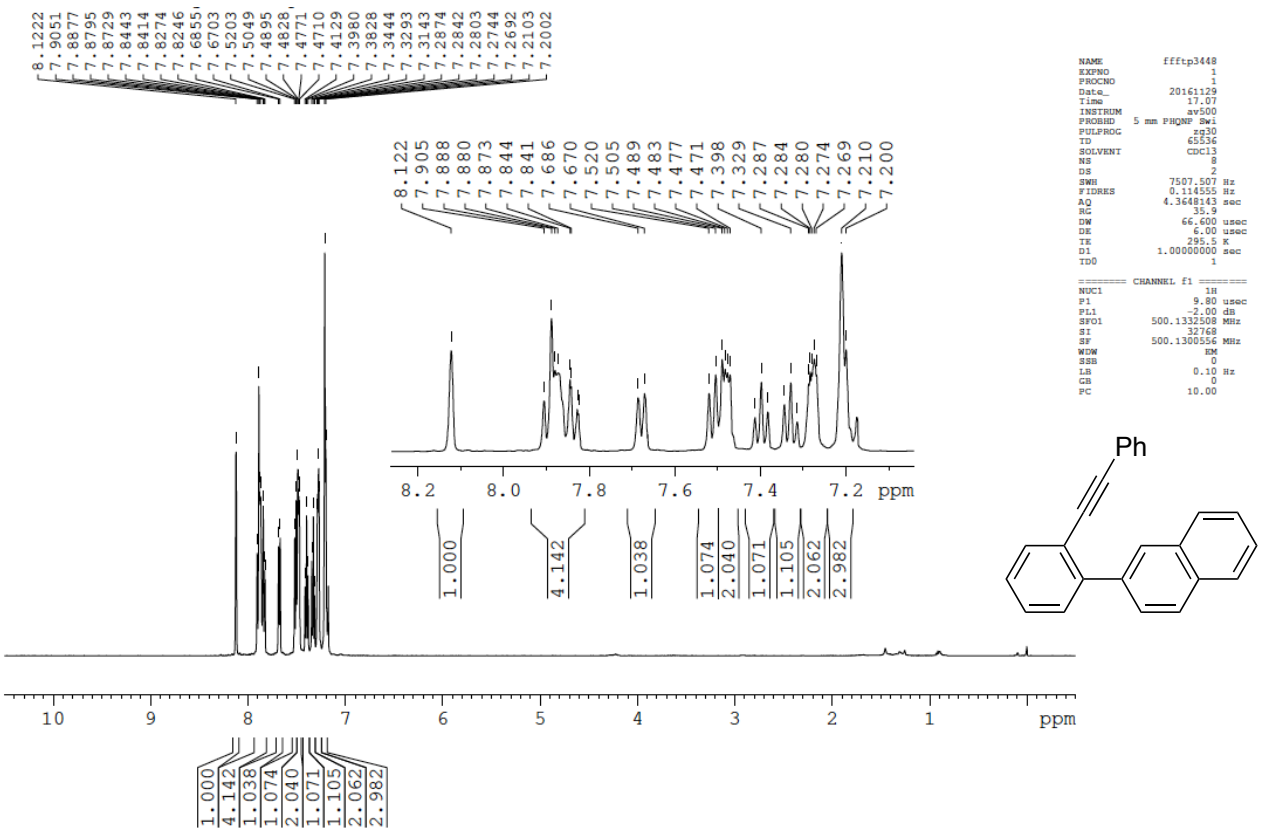
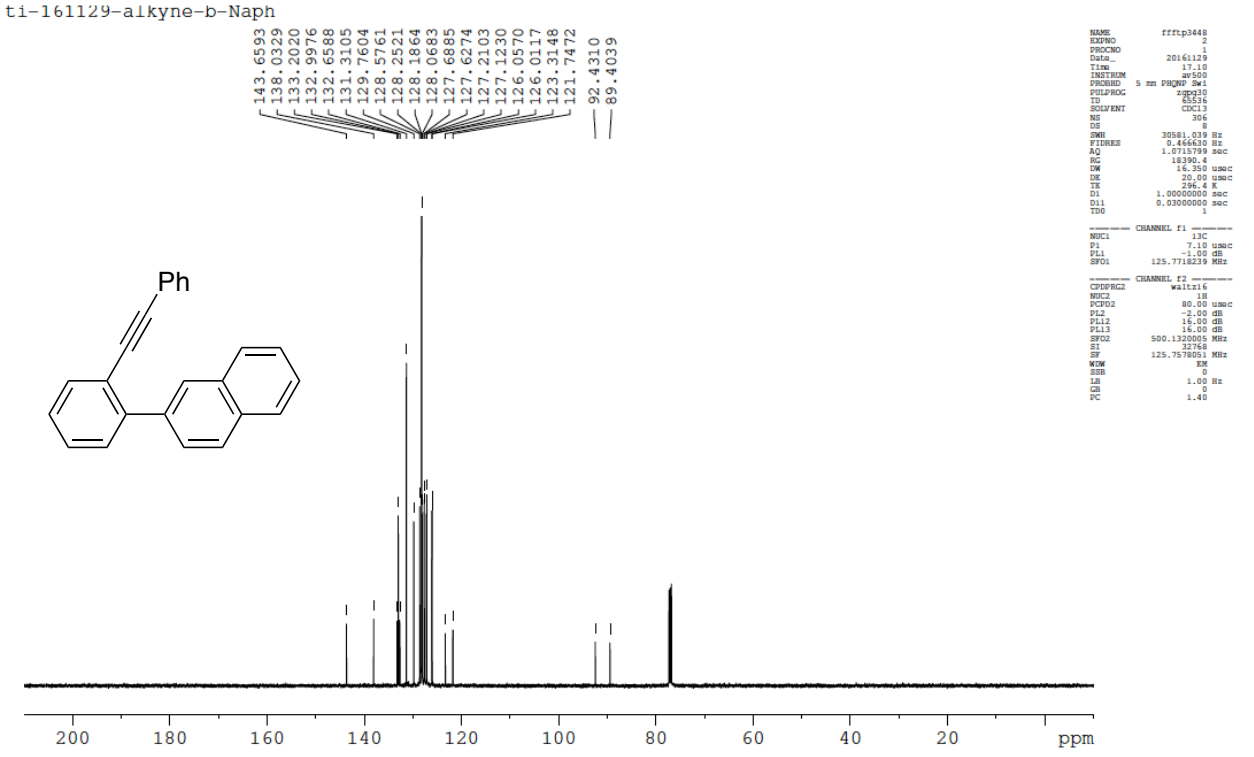
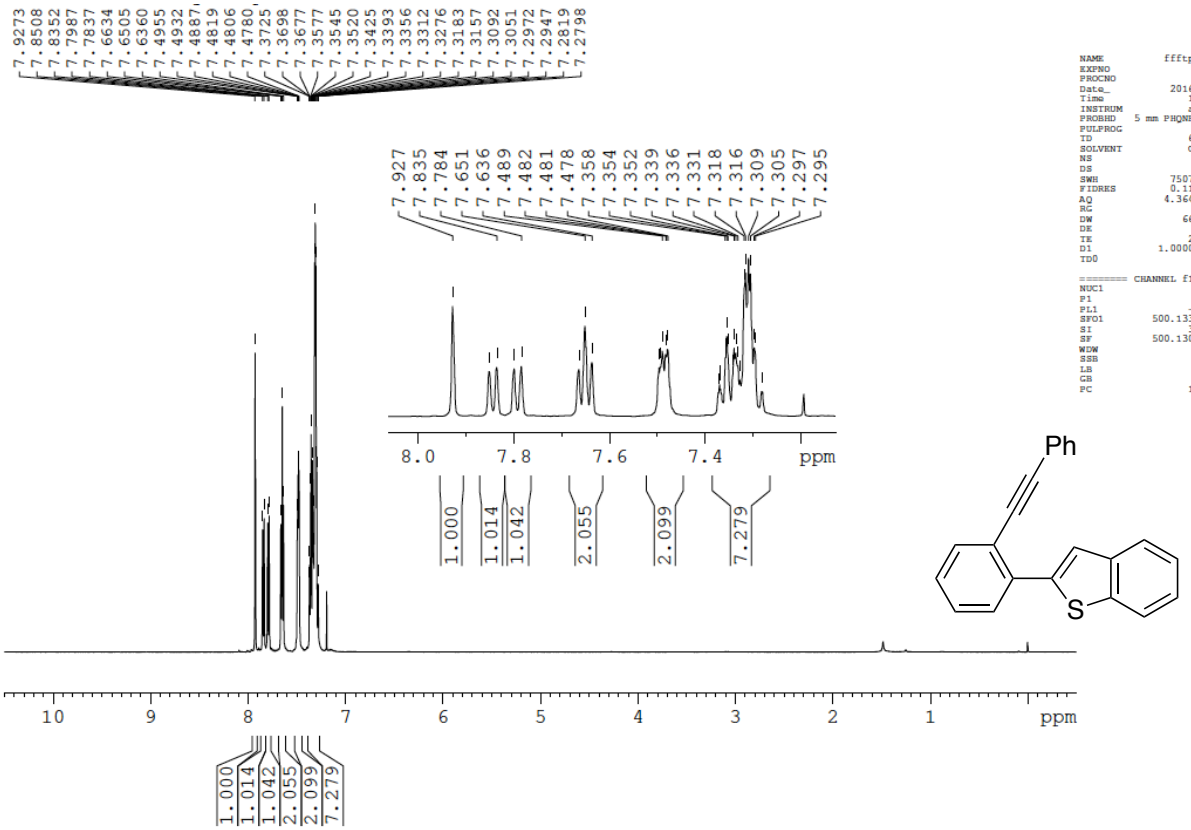
ppm

2-[2-(Phenylethynyl)phenyl]naphthalene (1n)





2-[2-(Phenylethynyl)phenyl]benzo[*b*]thiophene (1o)

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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                      8
DS                      2
SWH           7507.507 Hz
FIDRES        0.114555 Hz
AQ            4.3648143 sec
RG                     64
DW               66.600 usec
DE                6.00 usec
TE               295.7 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.80 usec
PL1                 -2.00 dB
SFO1         500.1332508 MHz
SI                  32768
SF           500.1300464 MHz
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GB                      0
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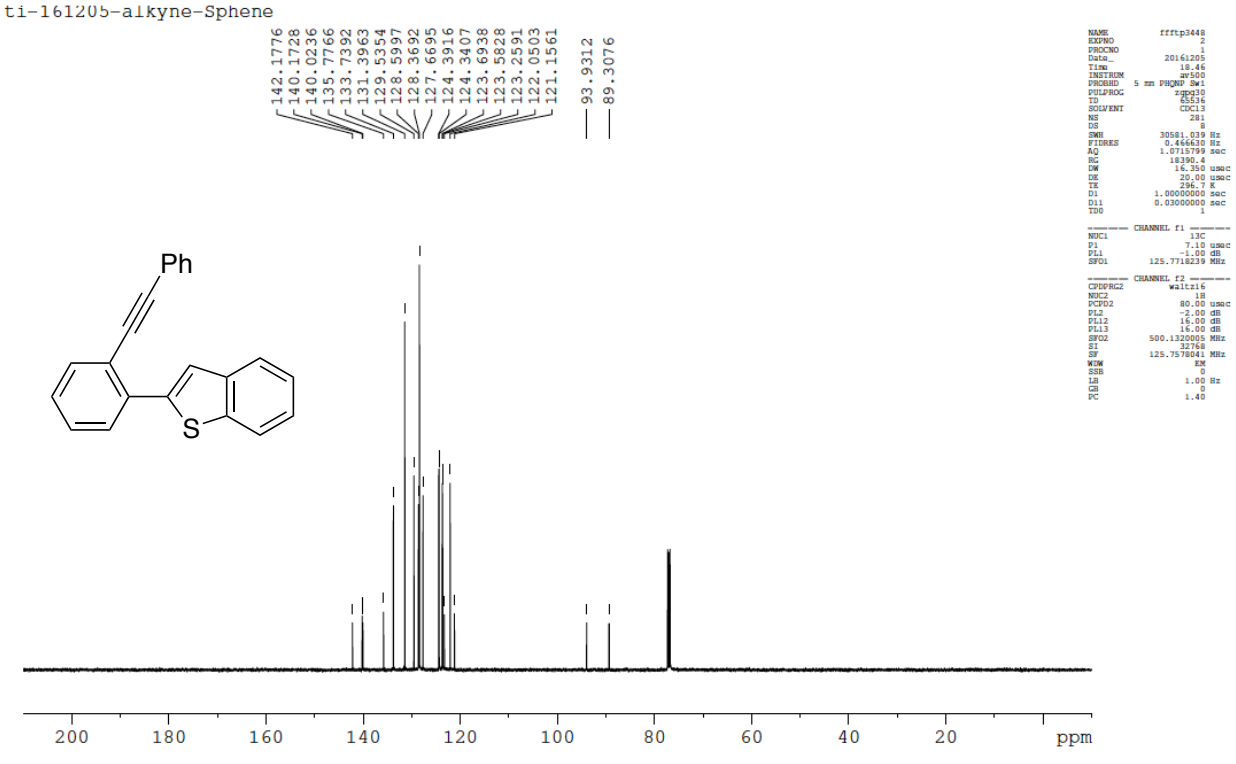


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FIDRES        0.466630 Hz
AQ            1.0715799 sec
RG                18390.4
DW               16.350 usec
DE                20.00 usec
TE               296.7 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                   7.10 usec
PL1                 -1.00 dB
SFO1         125.7718239 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                16.00 dB
PL13                16.00 dB
SFO2         500.1320005 MHz
SI                  32768
SF           125.7578041 MHz
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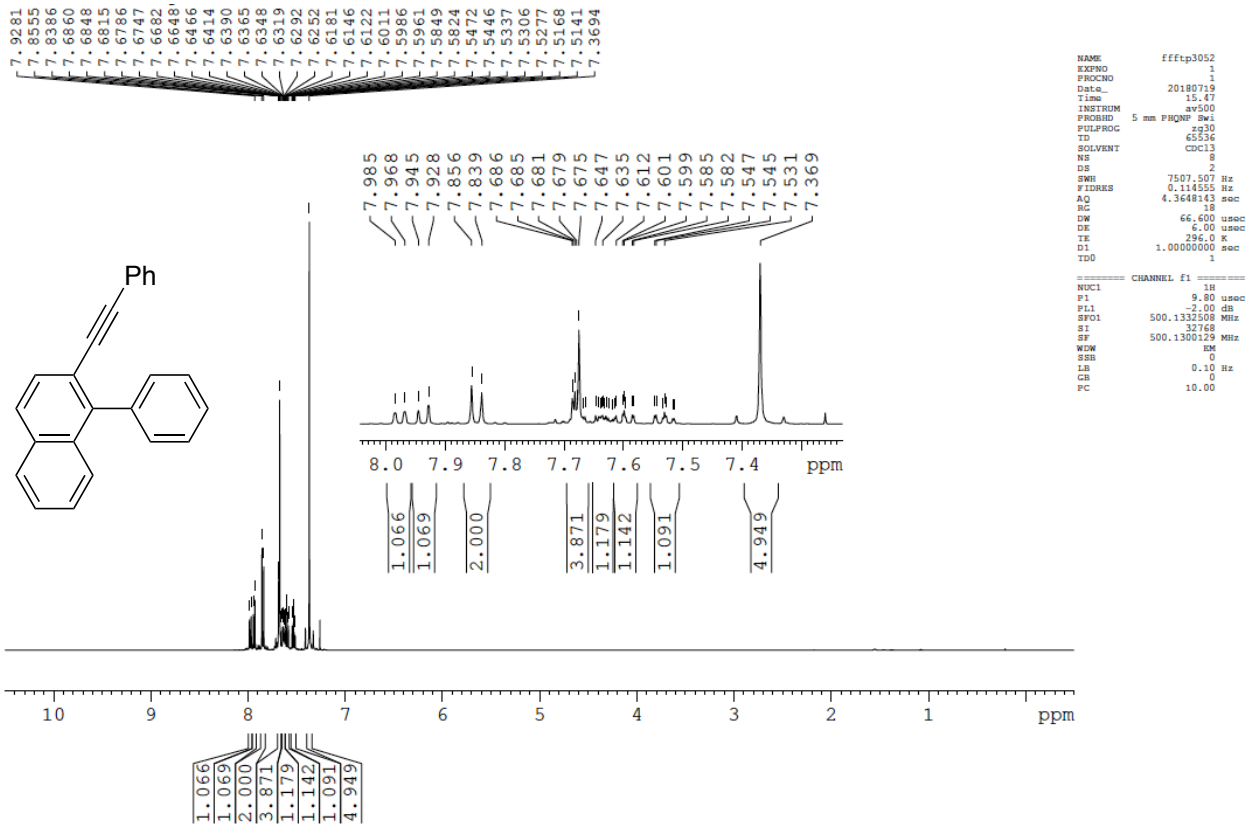
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

1-Phenyl-2-(phenylethynyl)naphthalene (1p)

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PROCNO                      1
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TD                     65536
SOLVENT                CDCl3
NS                          8
DS                          2
SWH                7507.507 Hz
FIDRES             0.114555 Hz
AQ                 4.3648143 sec
RG                         18
DW                    66.600 usec
DE                     6.00 usec
TE                    296.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.80 usec
PL1                     -2.00 dB
SFO1          500.1332508 MHz
SI                      32768
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LB                       0.10 Hz
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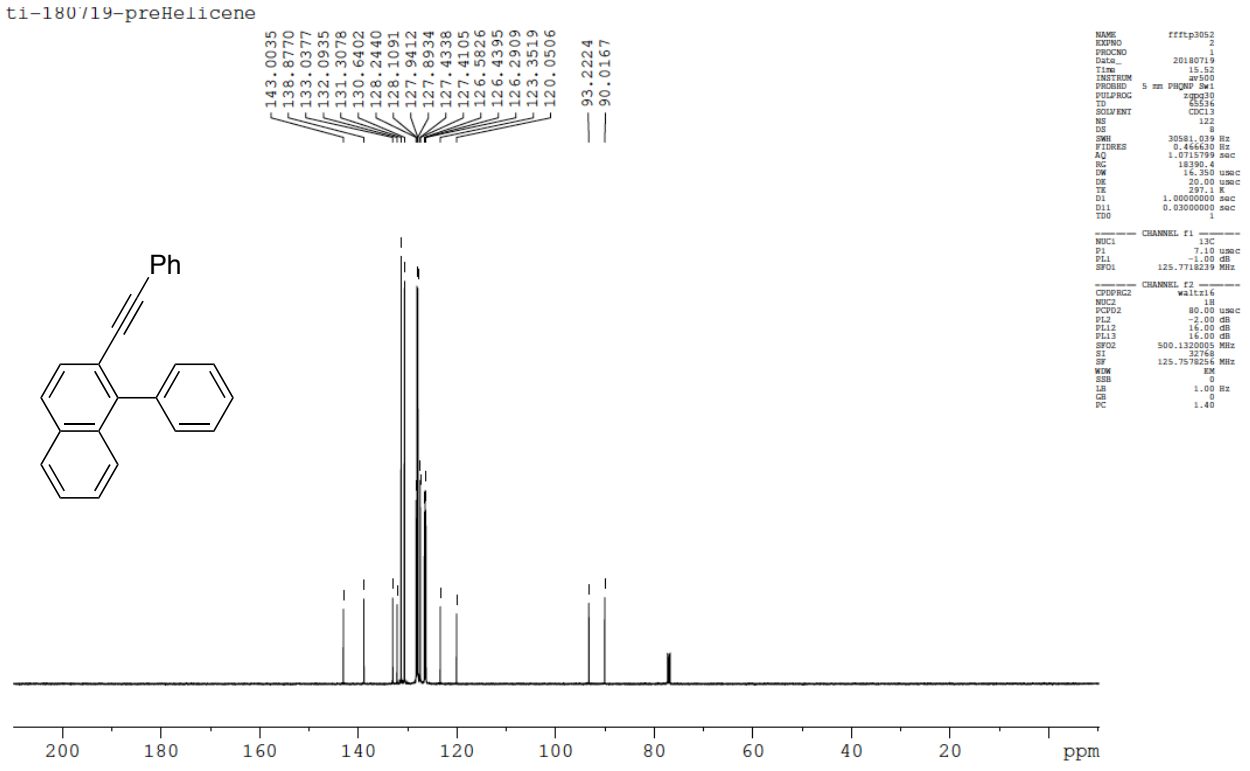


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PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        122
DS                          8
SWH               30581.039 Hz
FIDRES             0.466630 Hz
AQ                 1.0715799 sec
RG                    18390.4
DW                    16.350 usec
DE                     20.00 usec
TE                    297.1 K
D1                 1.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       7.10 usec
PL1                     -1.00 dB
SFO1          125.7718239 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -2.00 dB
PL12                    16.00 dB
PL13                    16.00 dB
SFO2          500.1320005 MHz
SI                      32768
SF            125.7578256 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
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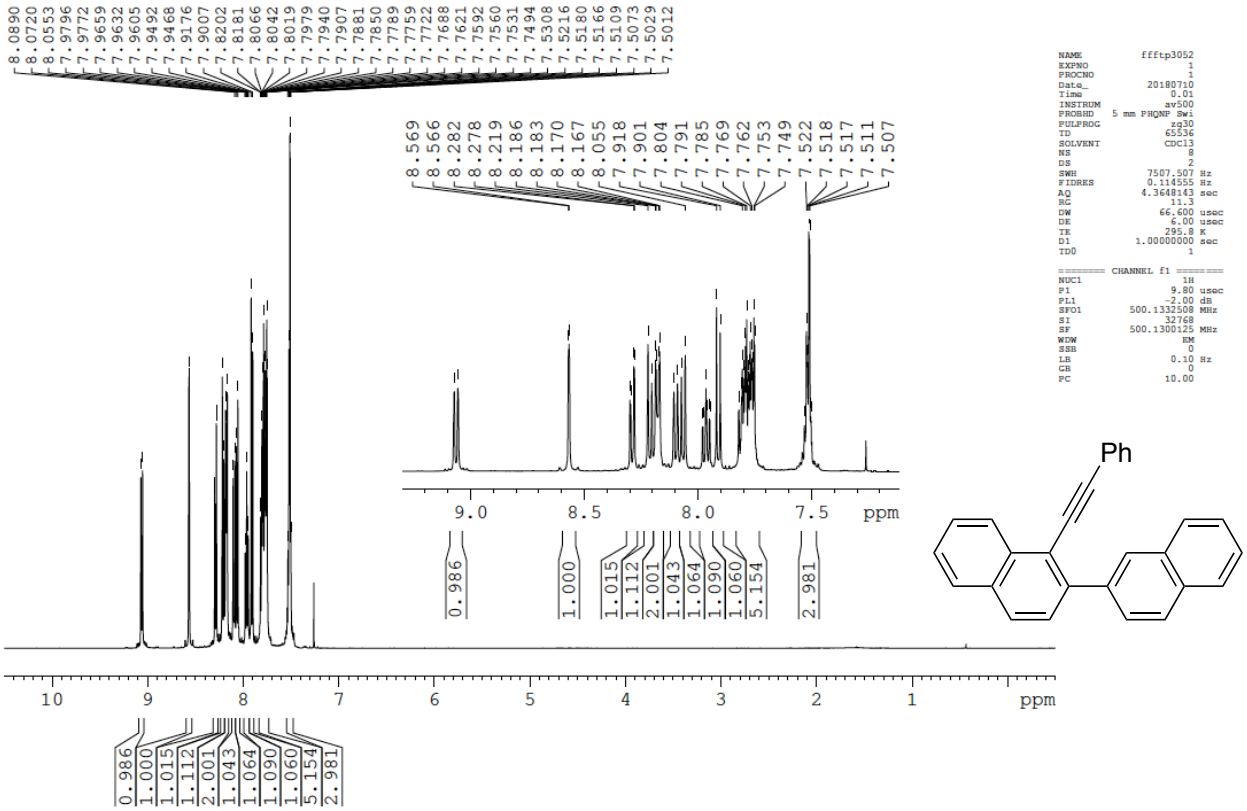
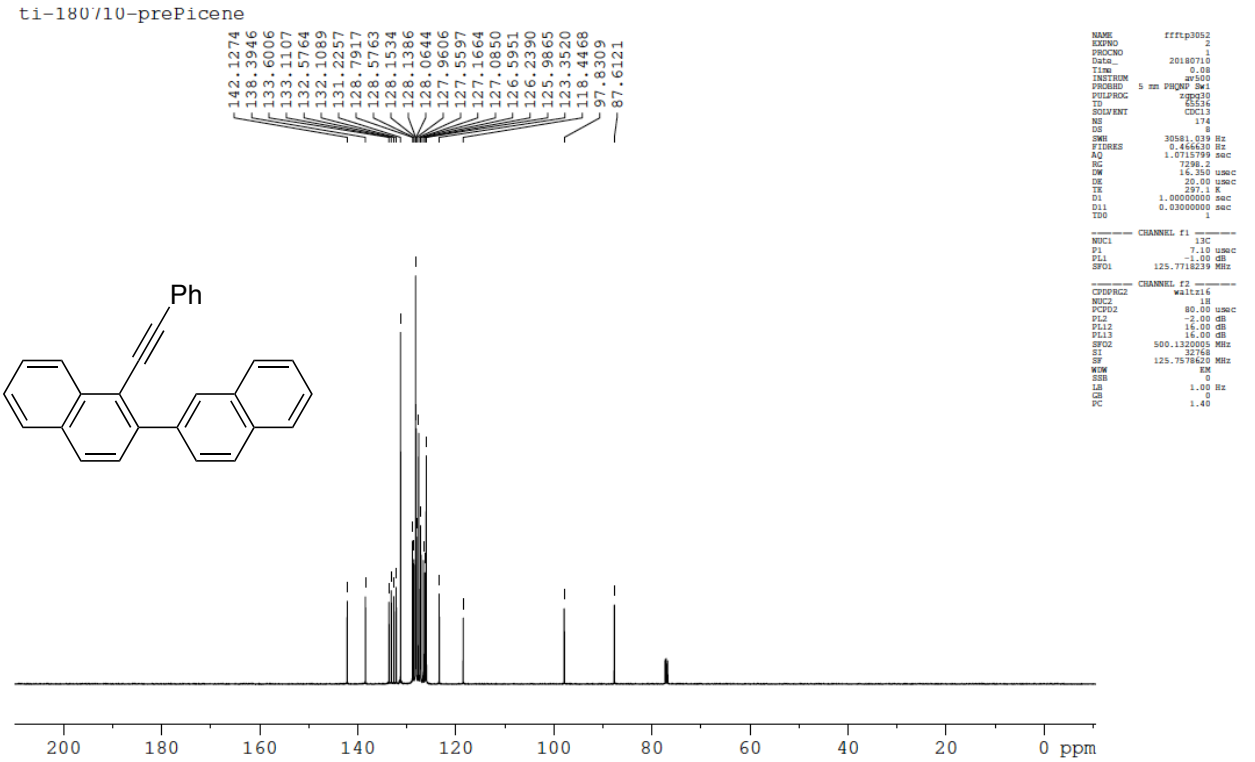
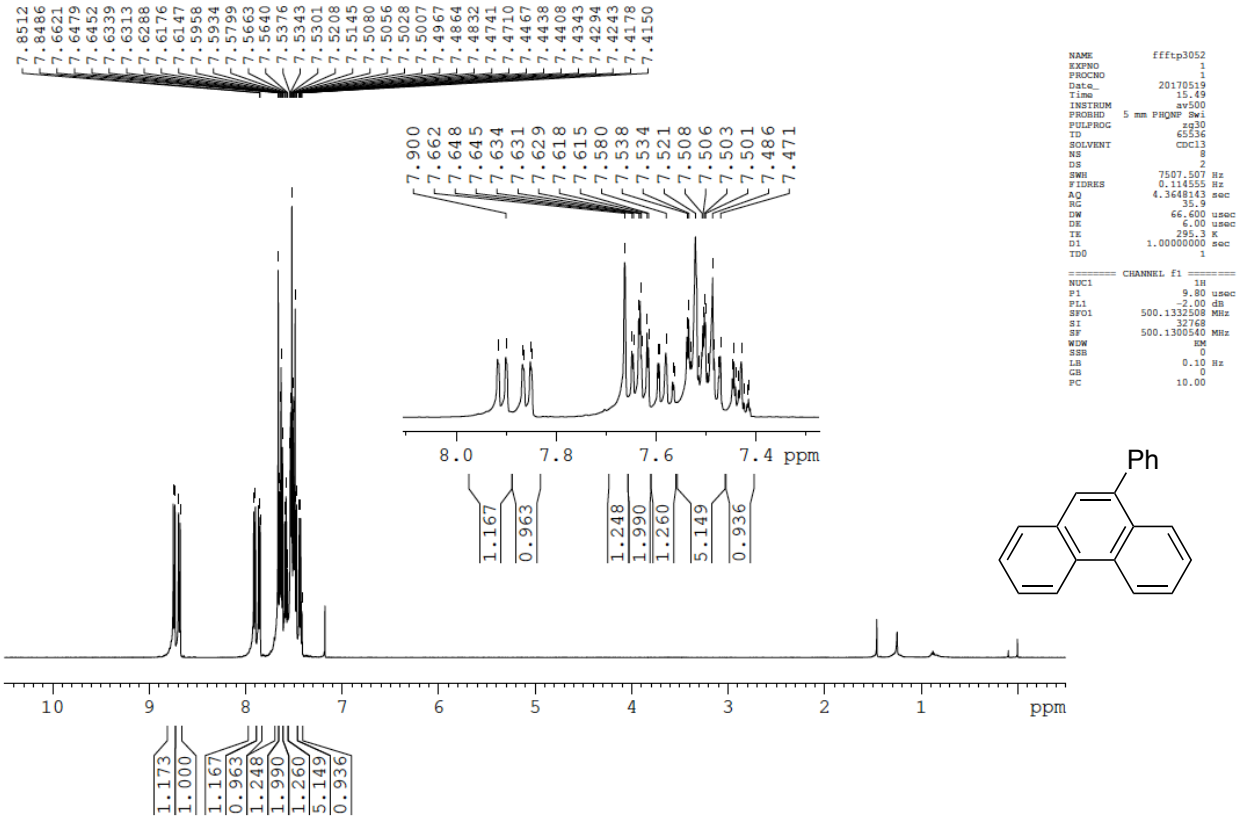
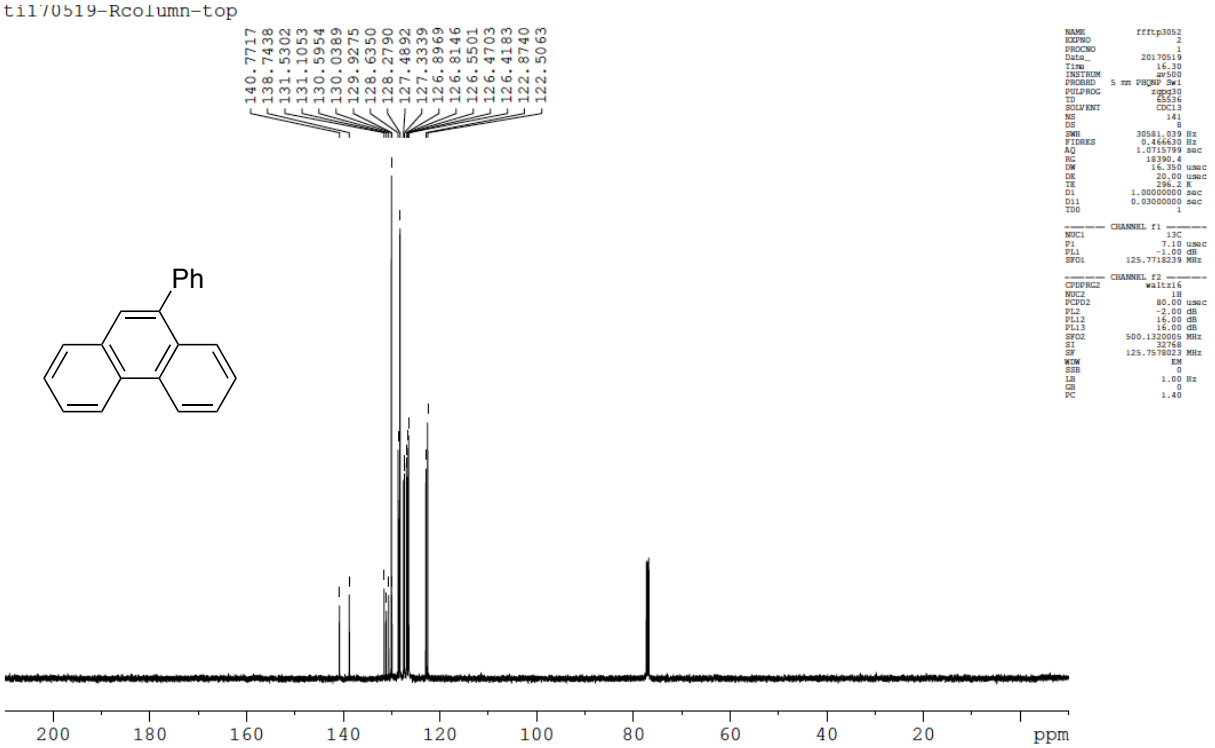
1-(Phenylethynyl)-2,2'-binaphthalene (1q)



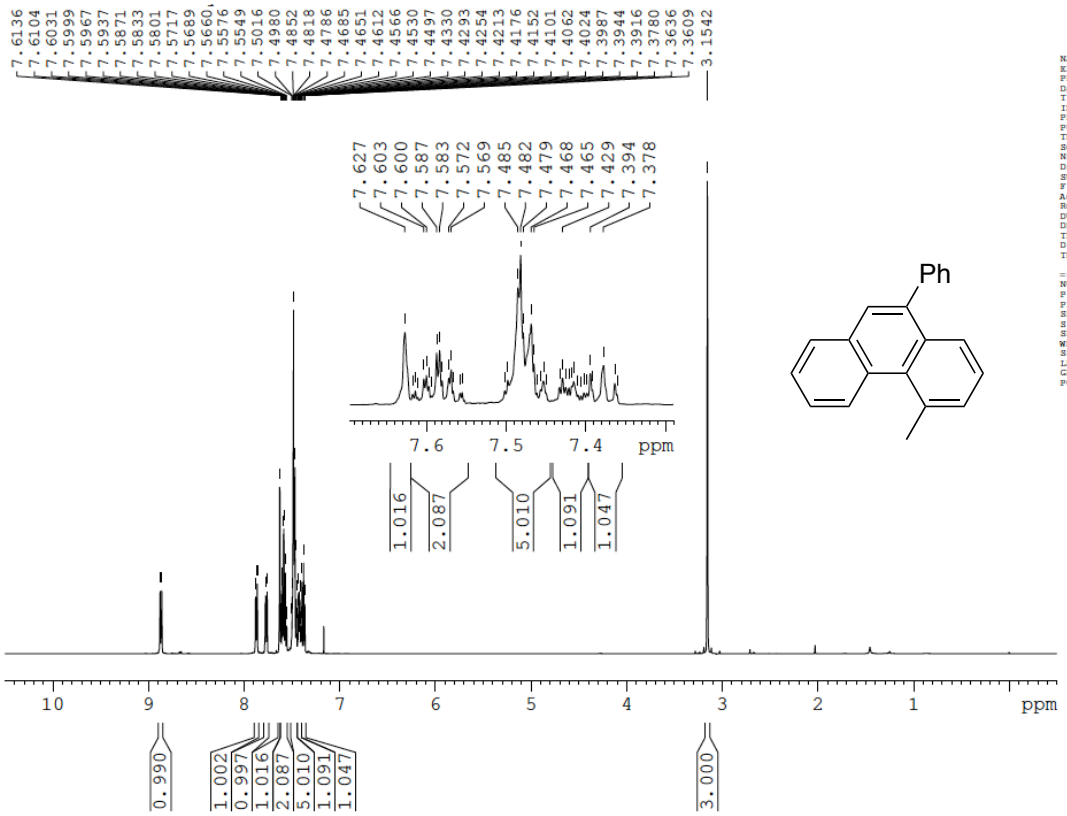


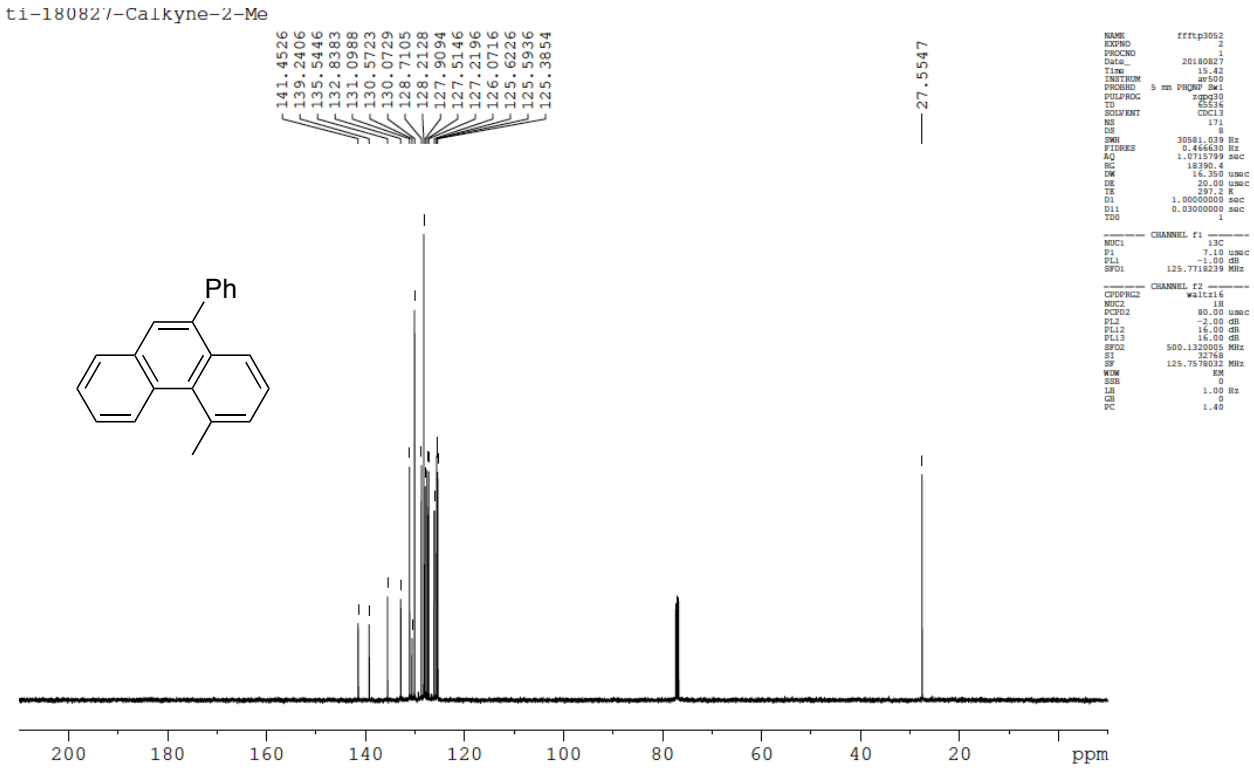
9-Phenylphenanthrene (2a)



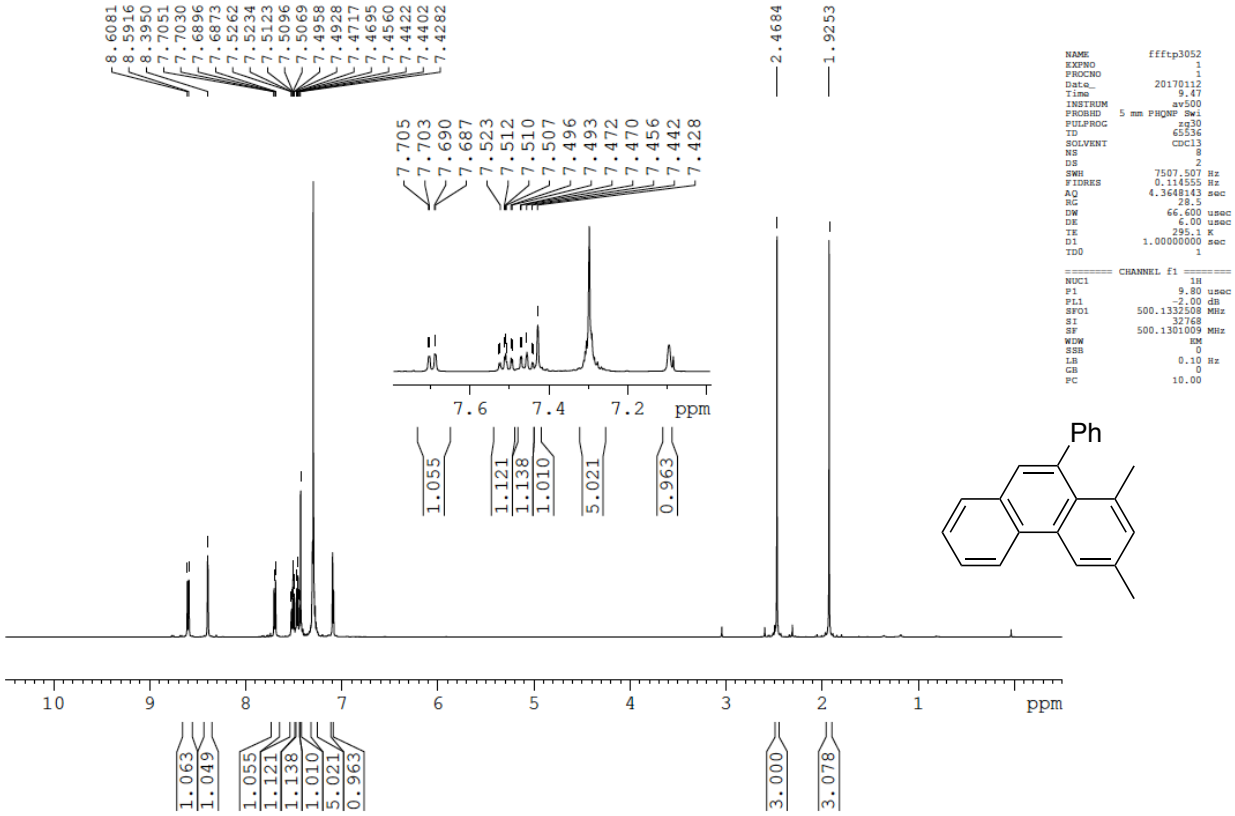


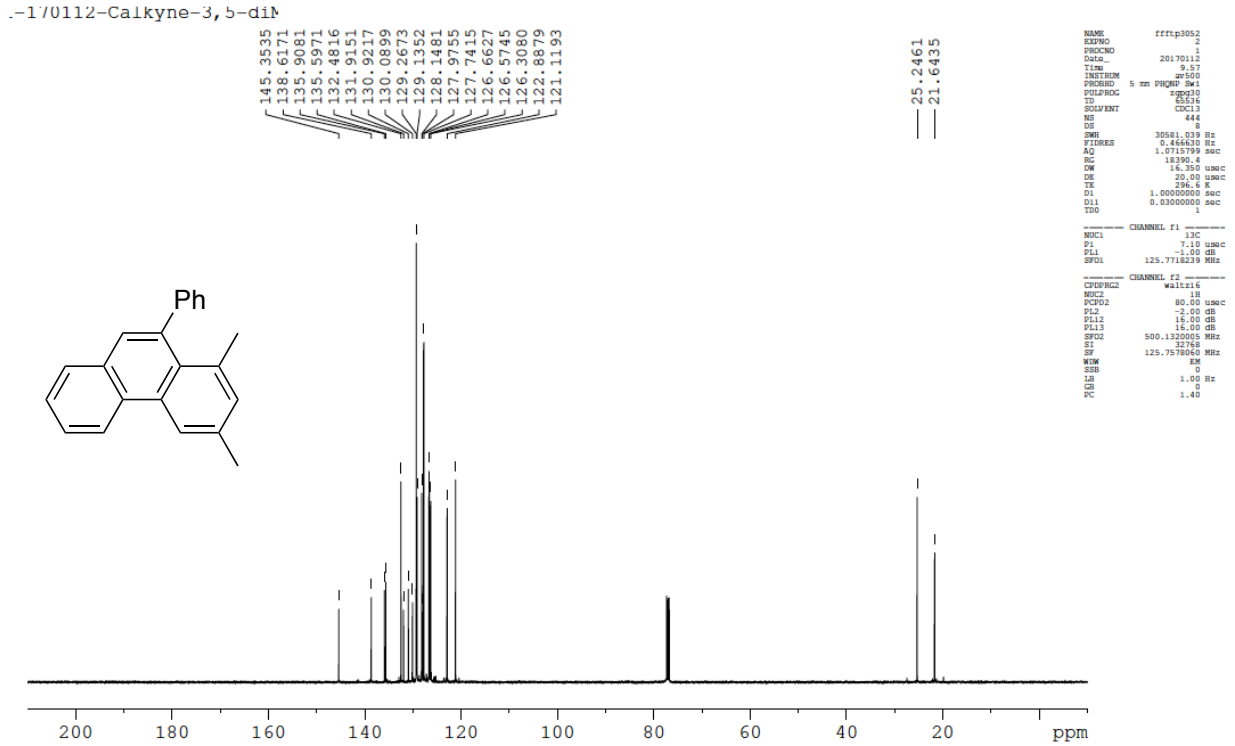
4-Methyl-10-phenylphenanthrene (2b)



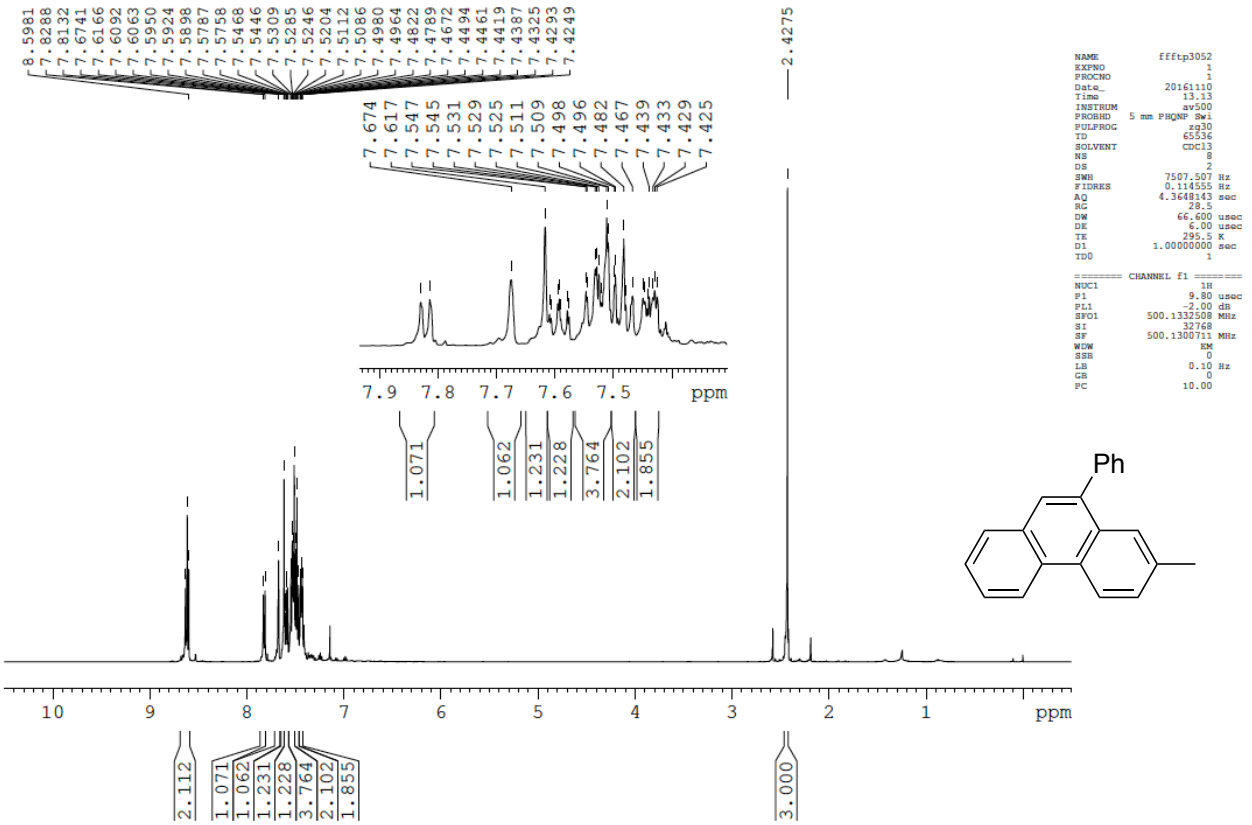


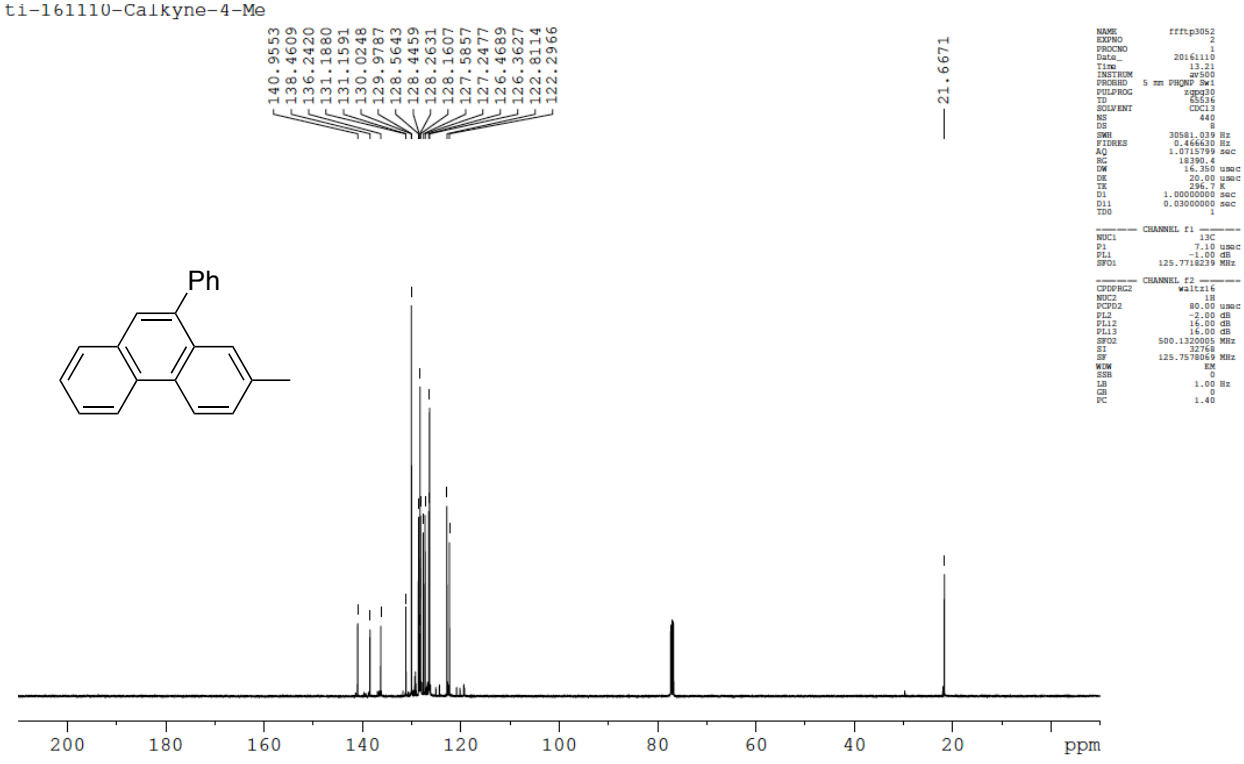
1,3-Dimethtyl-10-phenylphenanthrene (2c)



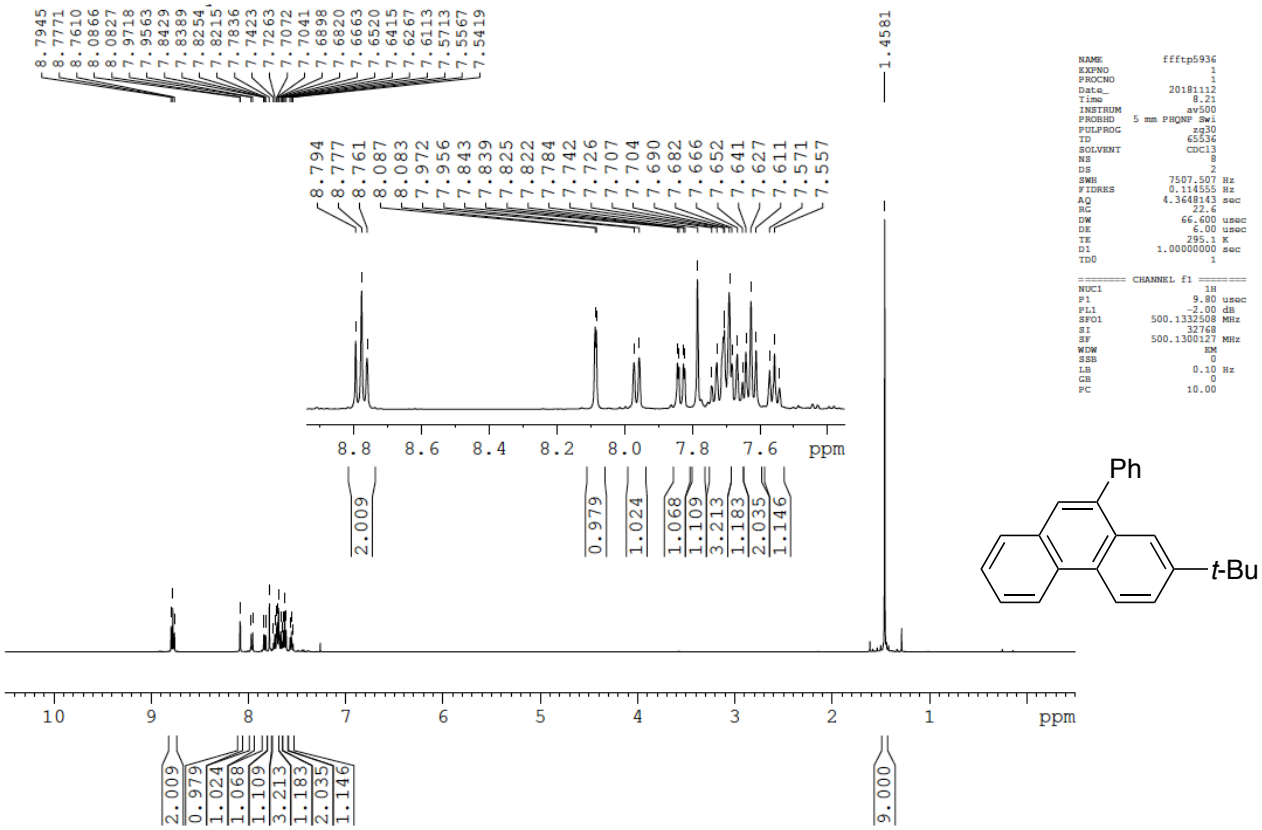


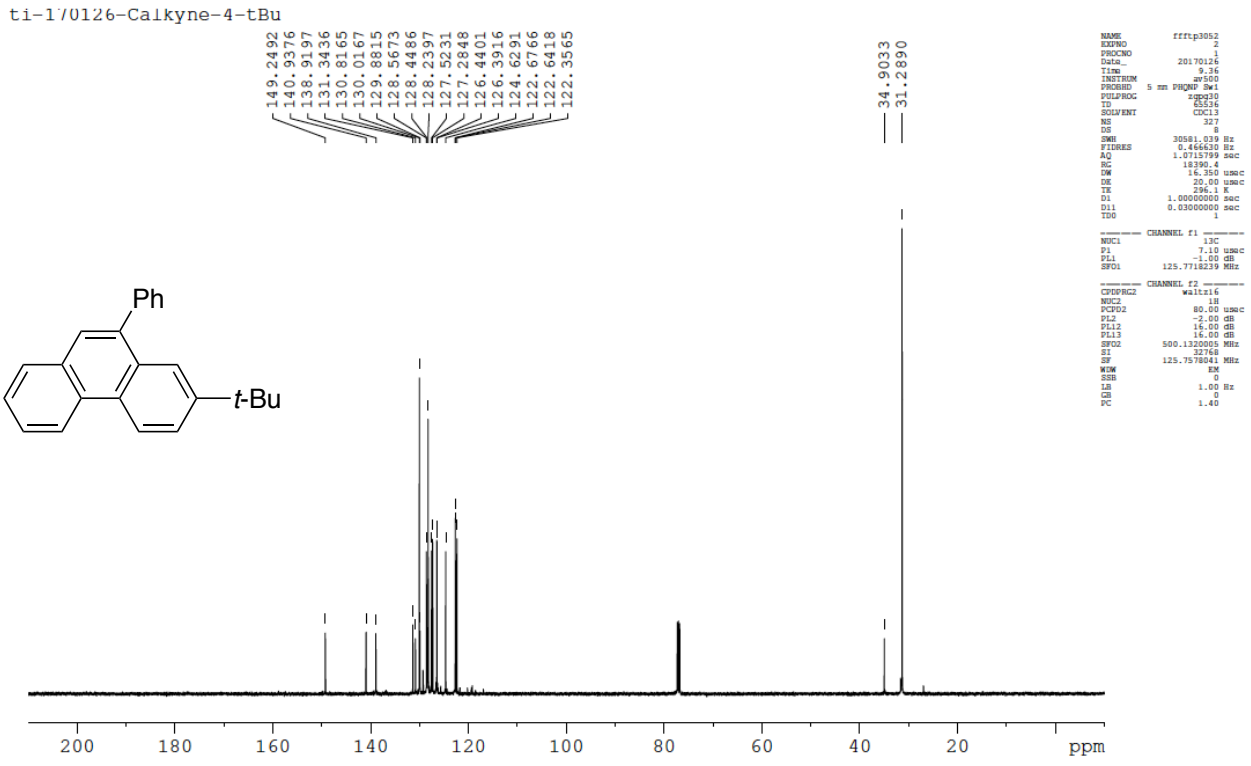
2-Methyl-10-phenylphenanthrene (2d)



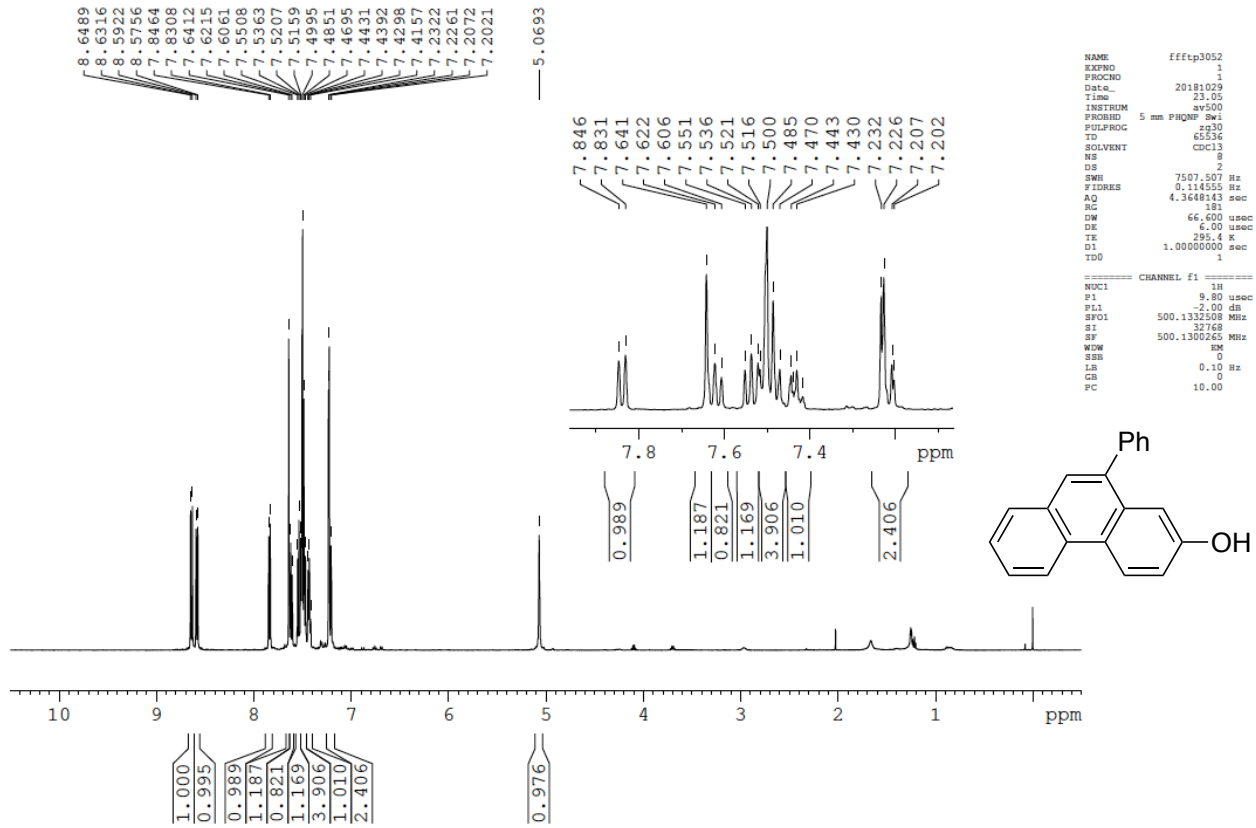


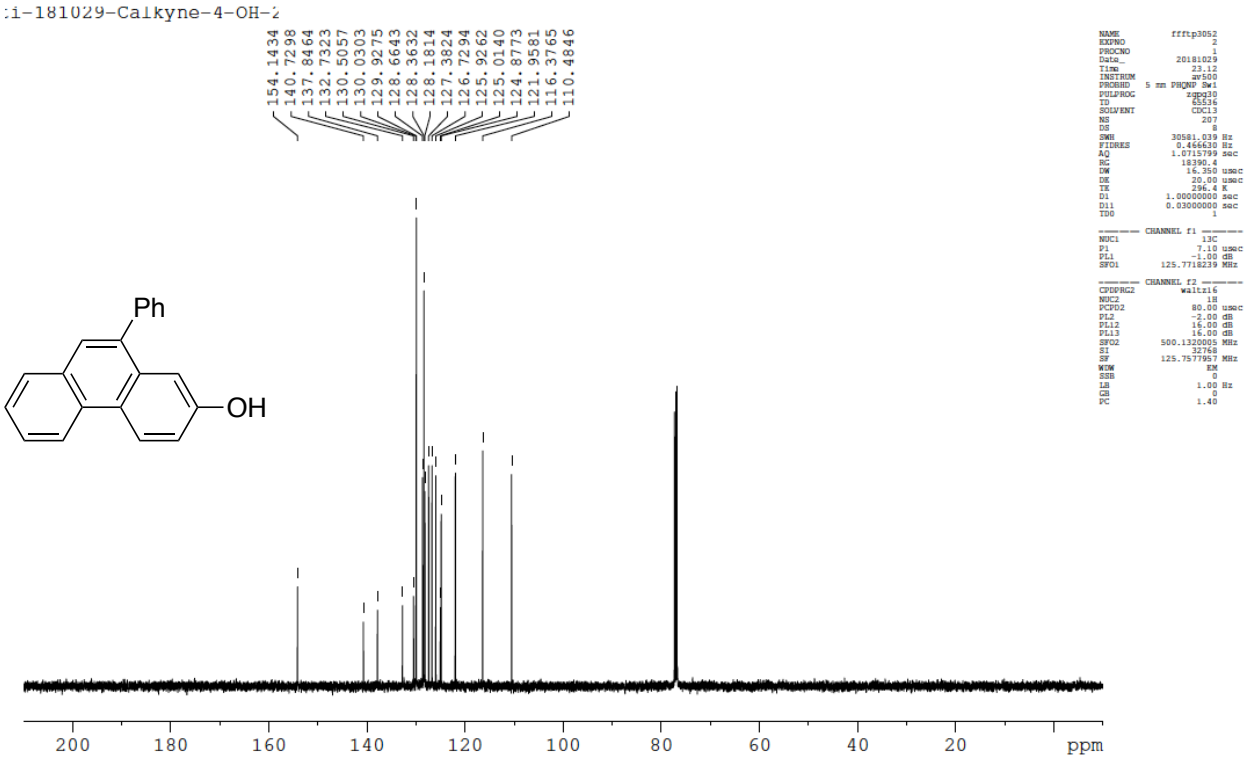
2-(*tert*-Butyl)-10-phenylphenanthrene (2e)



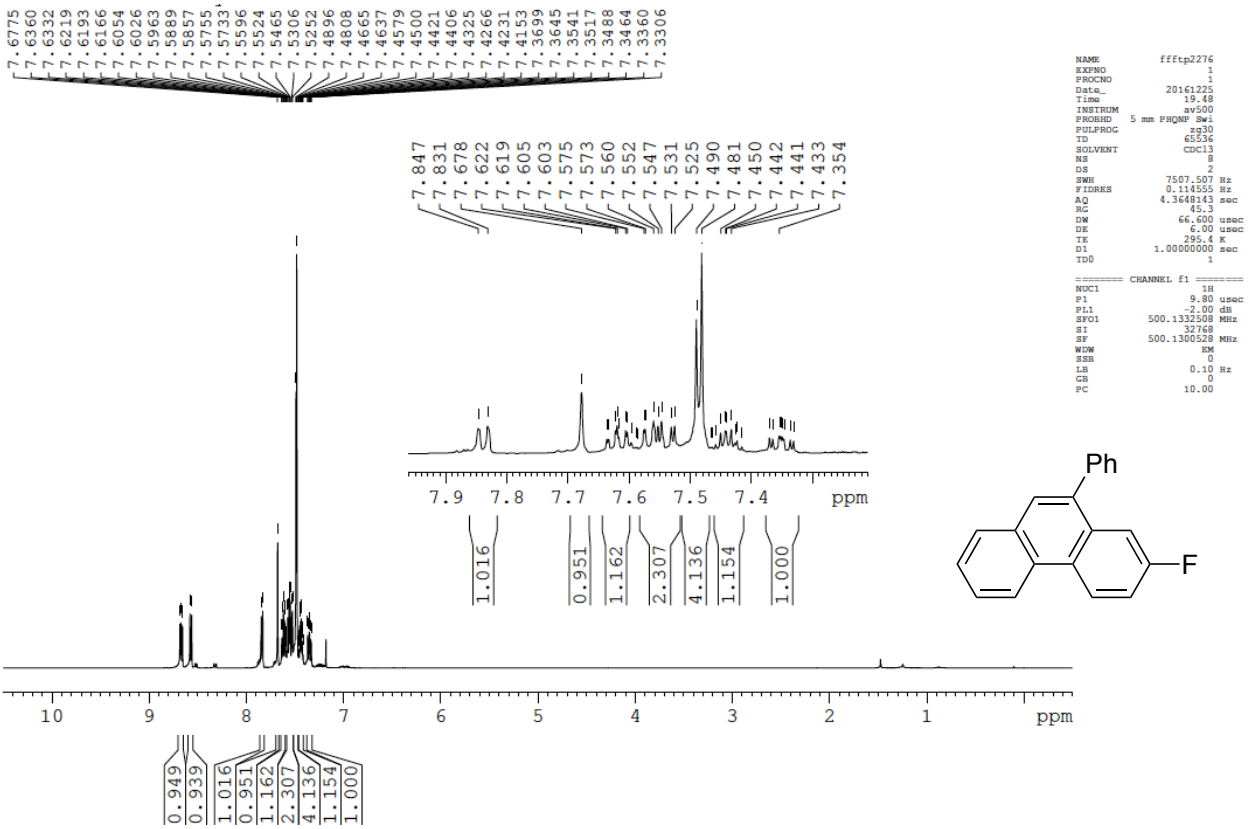


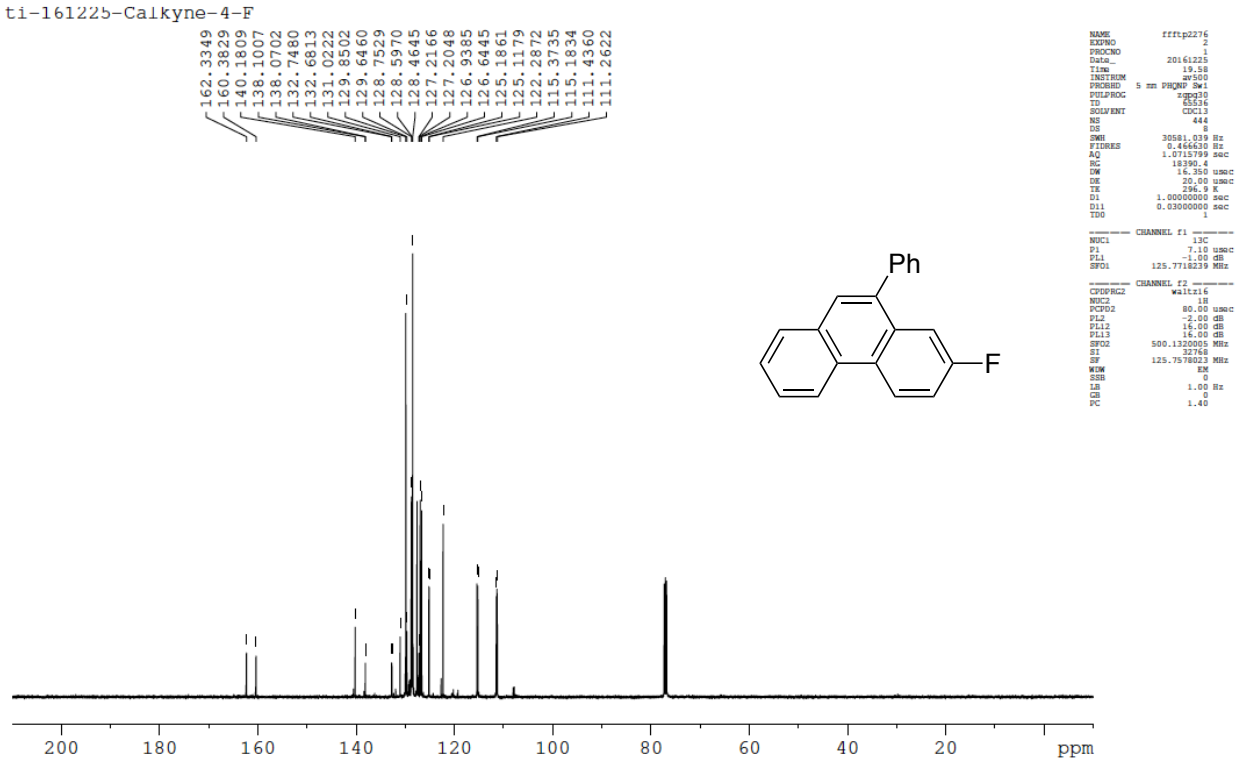
10-Phenylphenanthren-2-ol (2f)

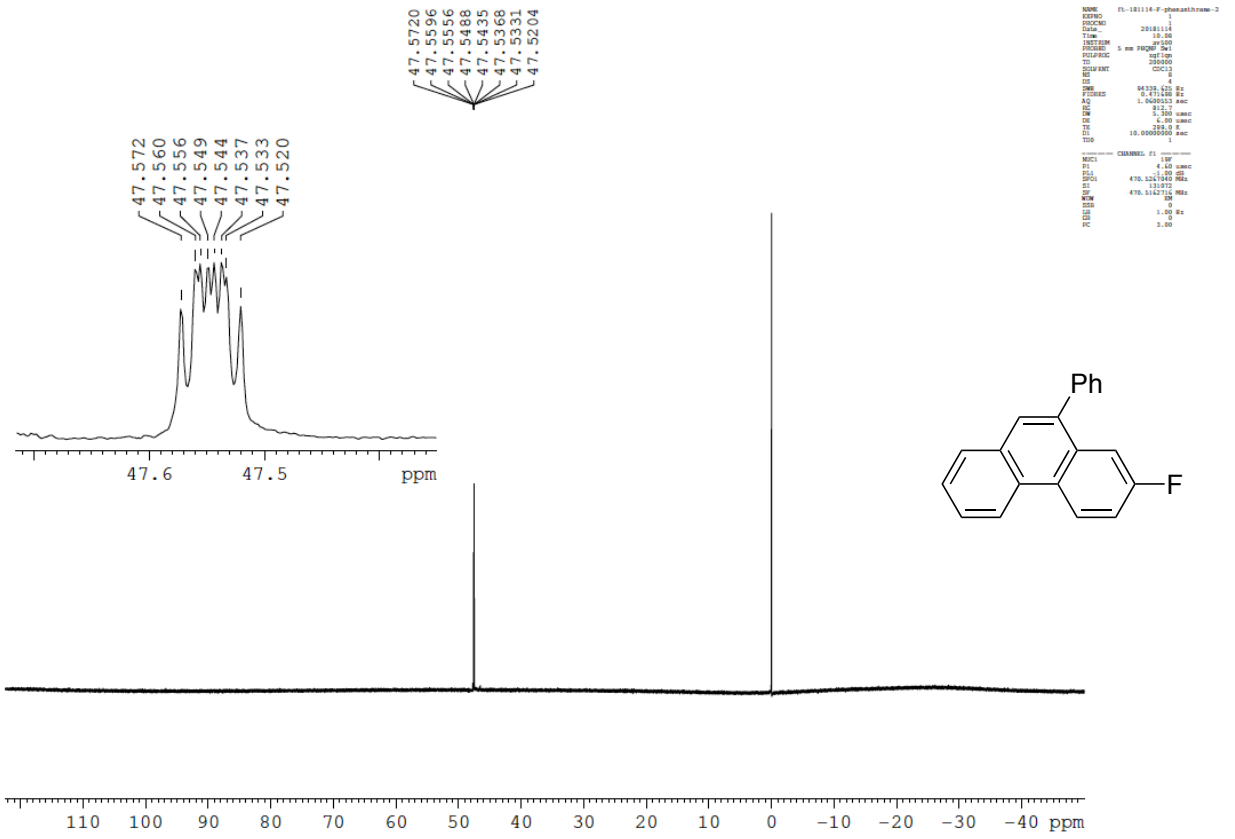




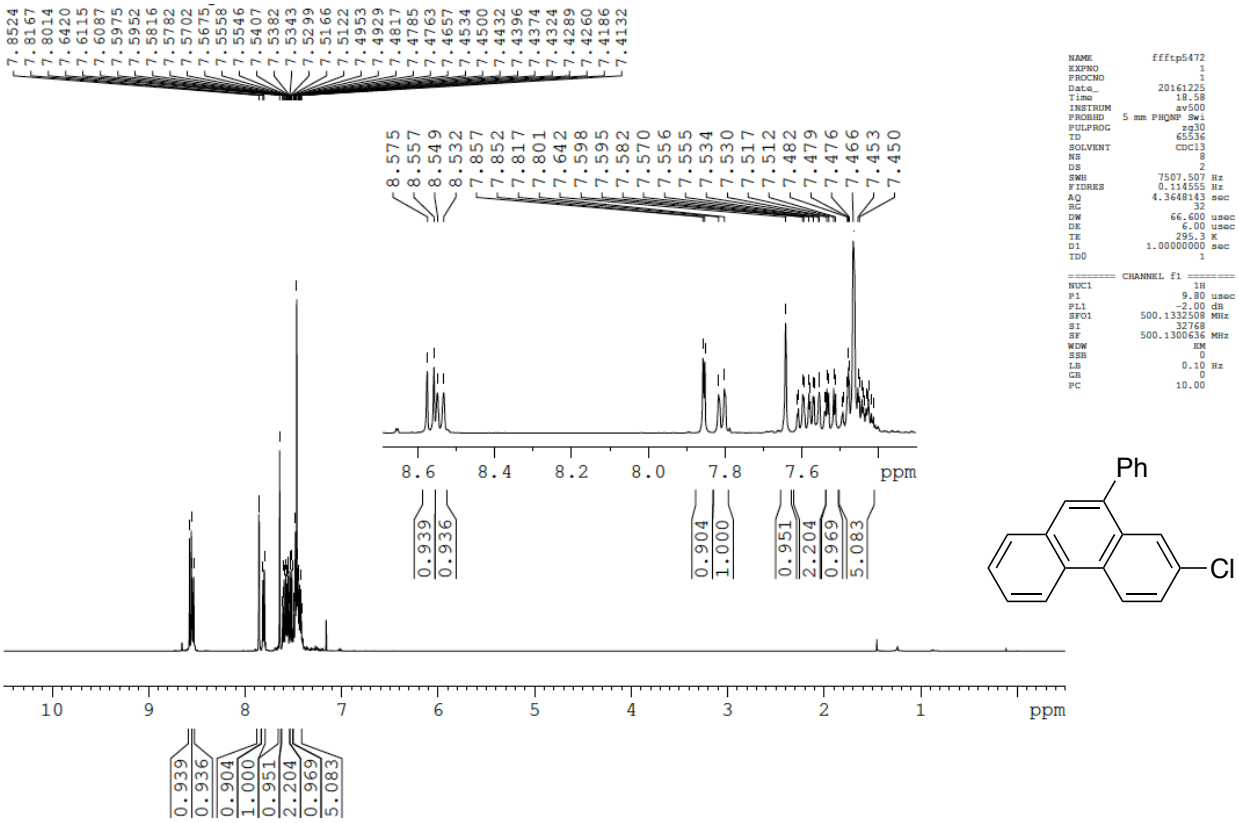
2-Fluoro-10-phenylphenanthrene (2g)

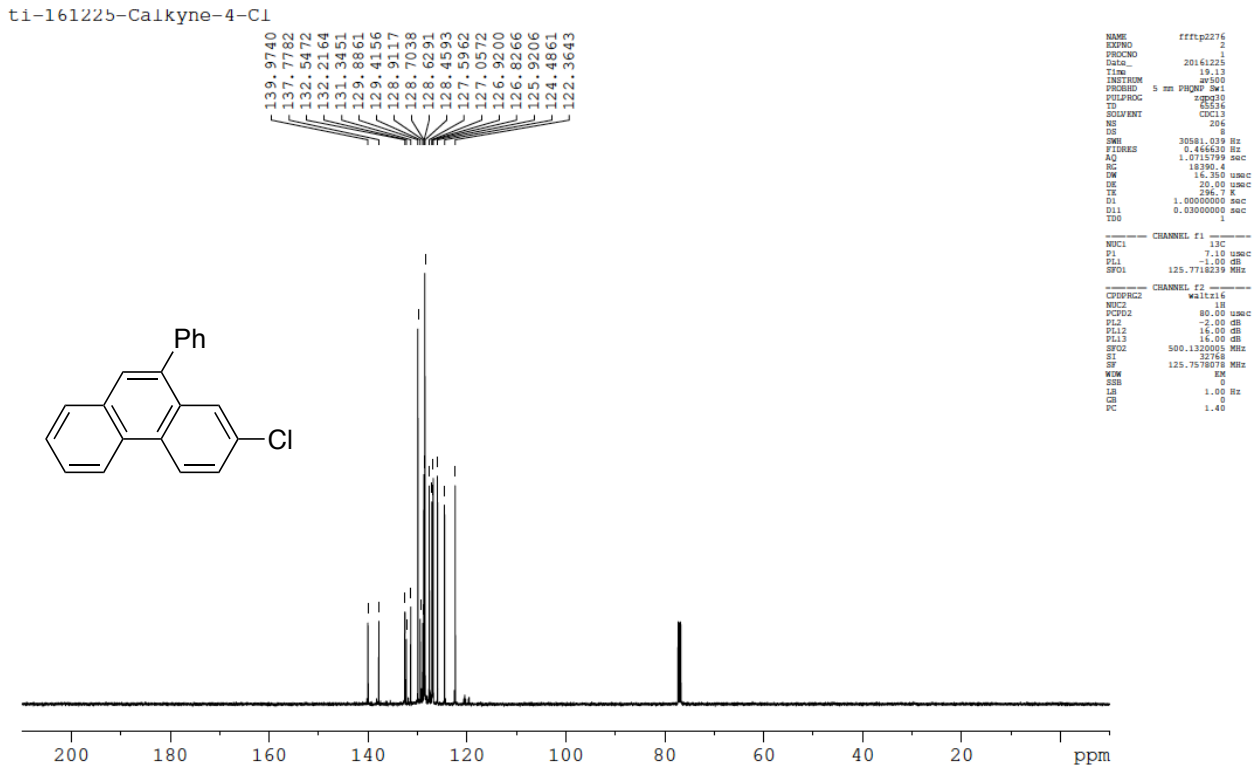




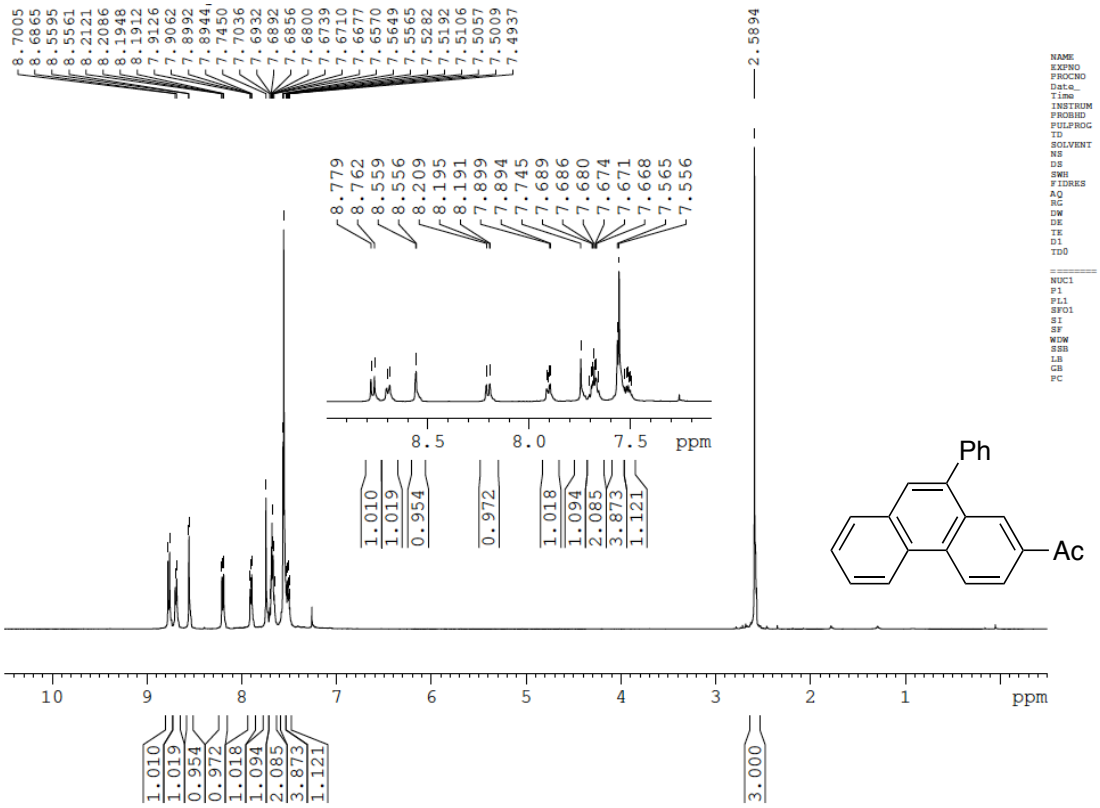


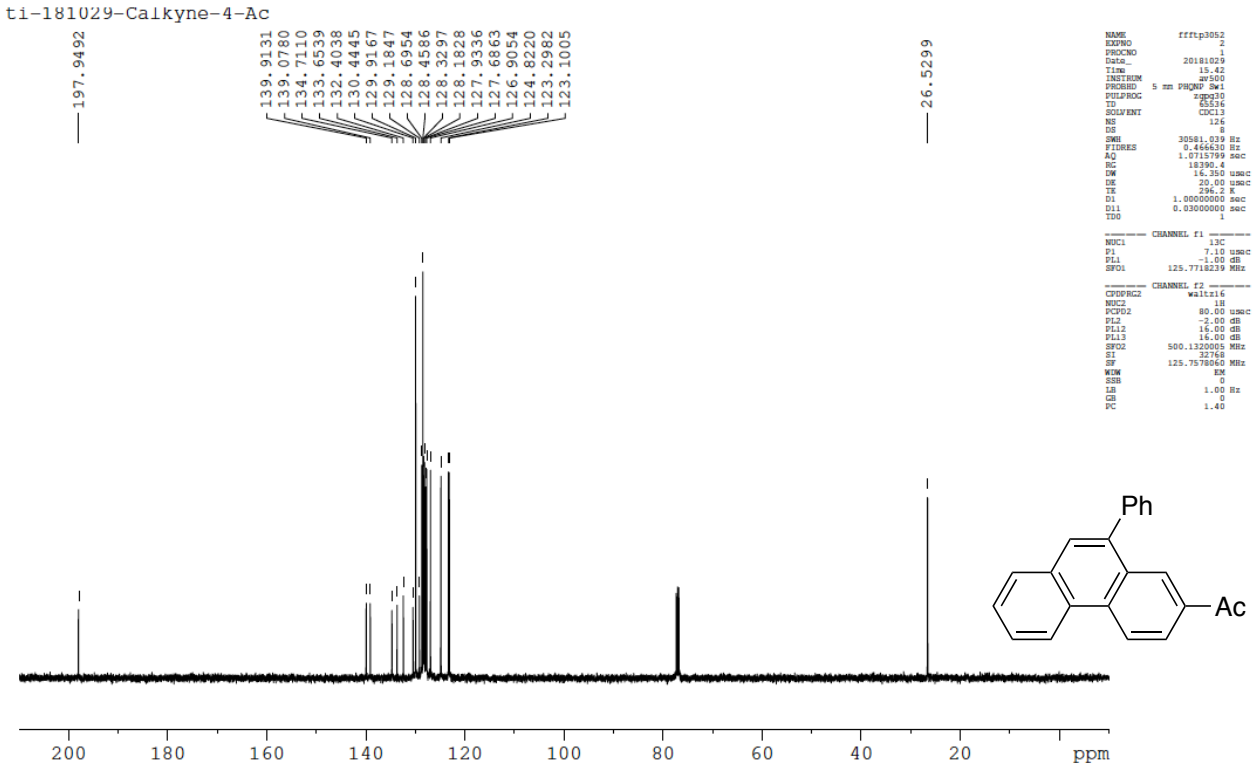
2-Chloro-10-phenylphenanthrene (2h)



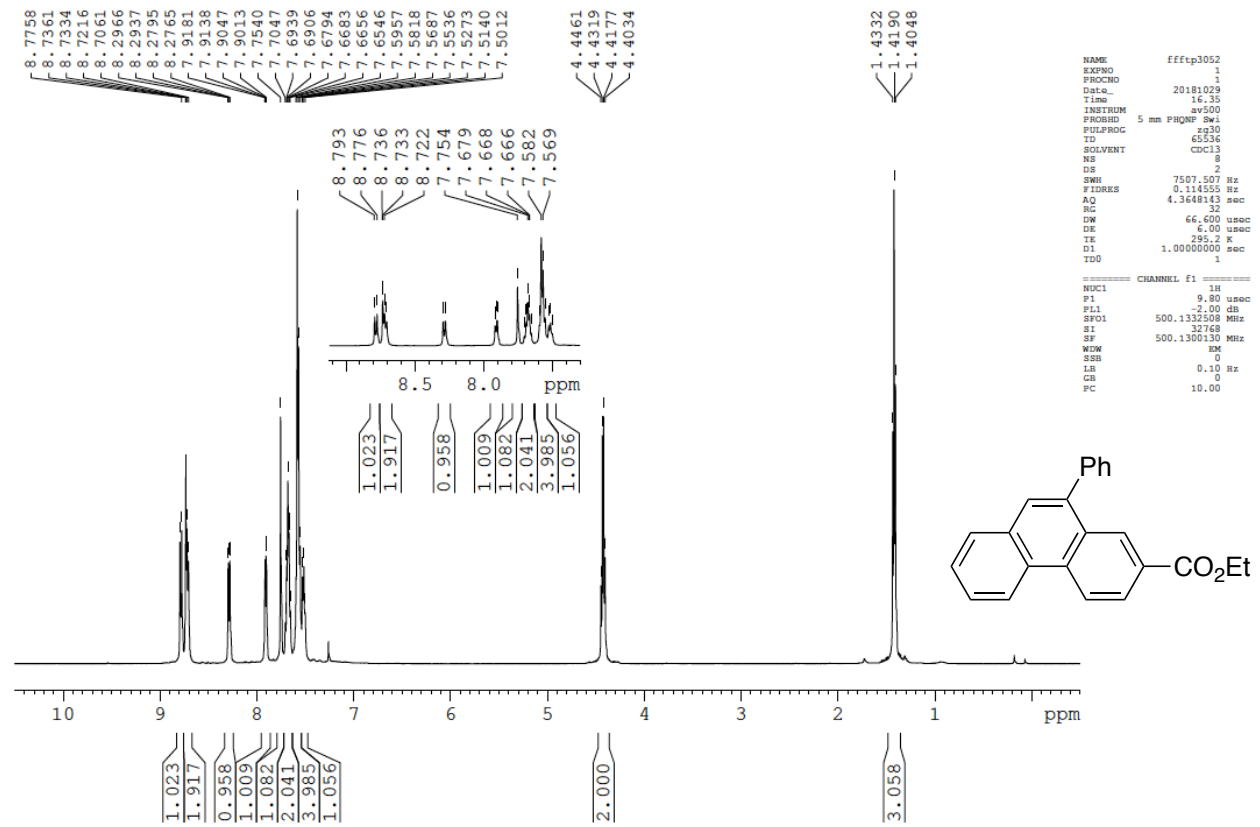


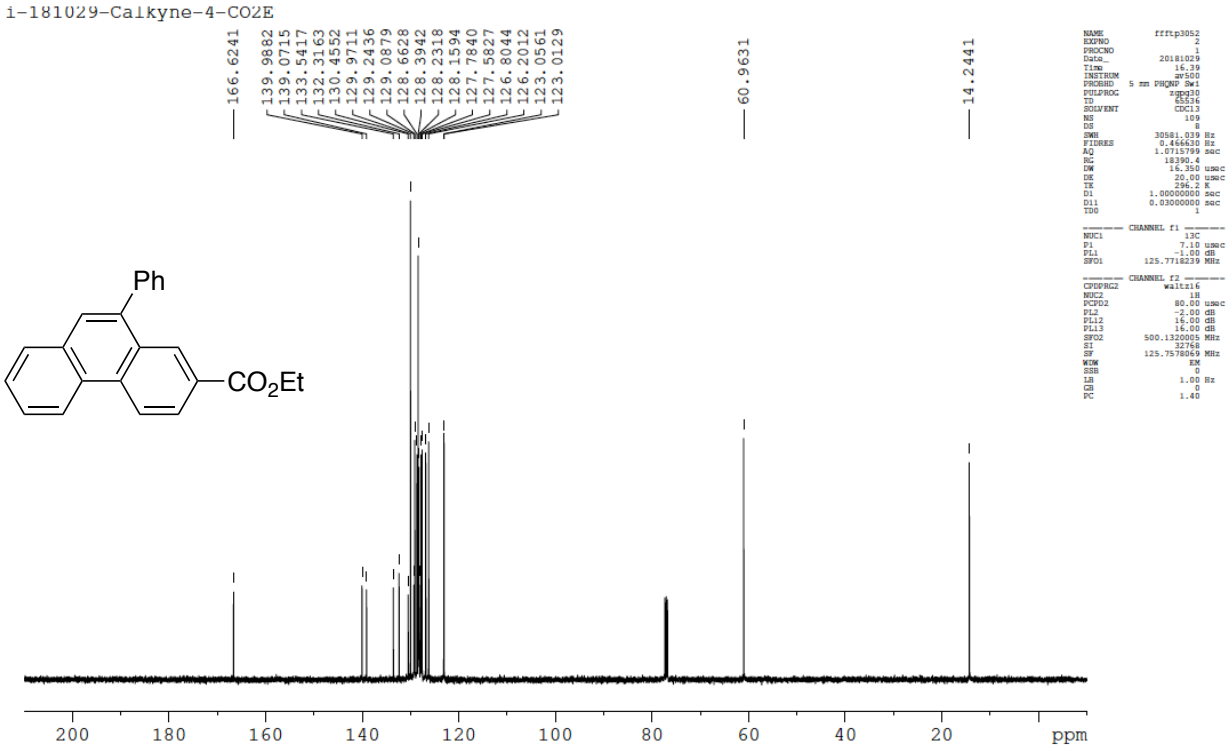
1-(10-Phenylphenanthren-2-yl)ethan-1-one (2i)



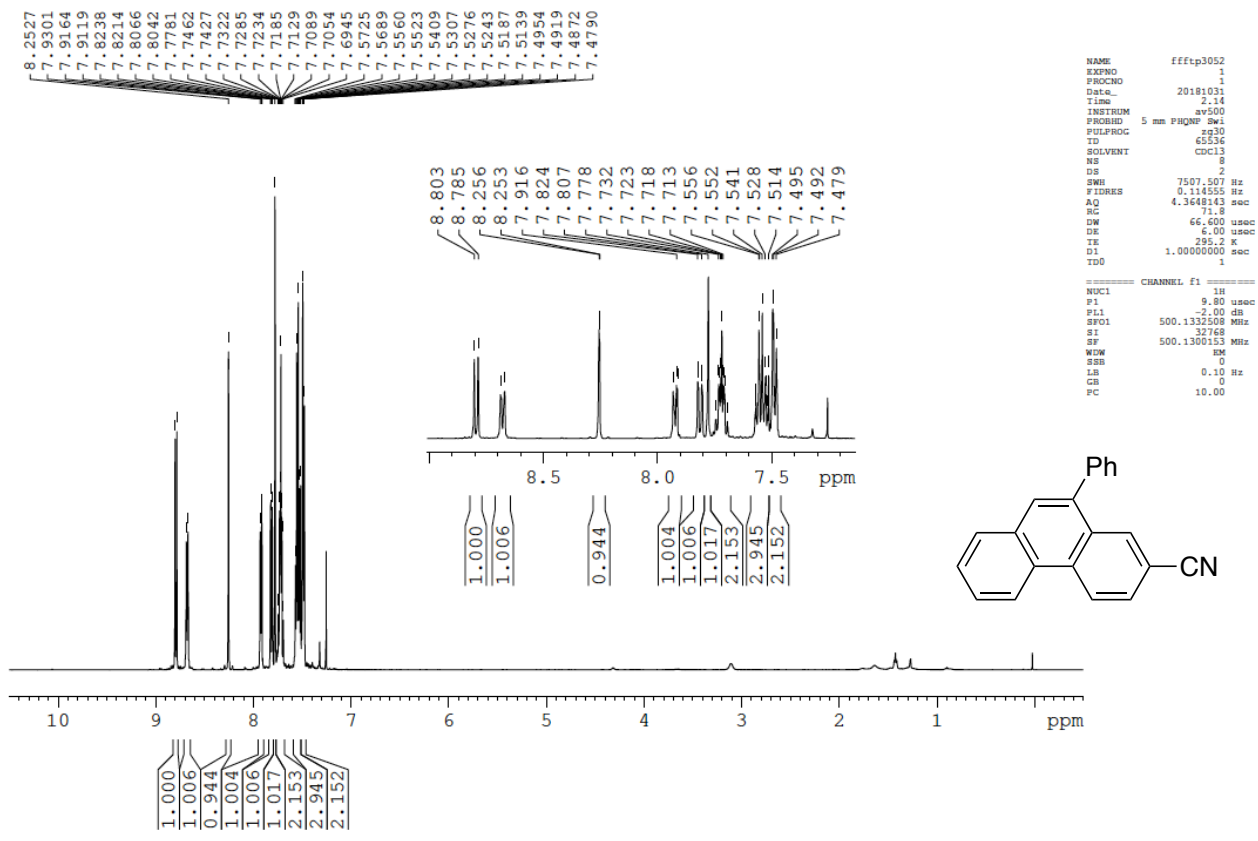


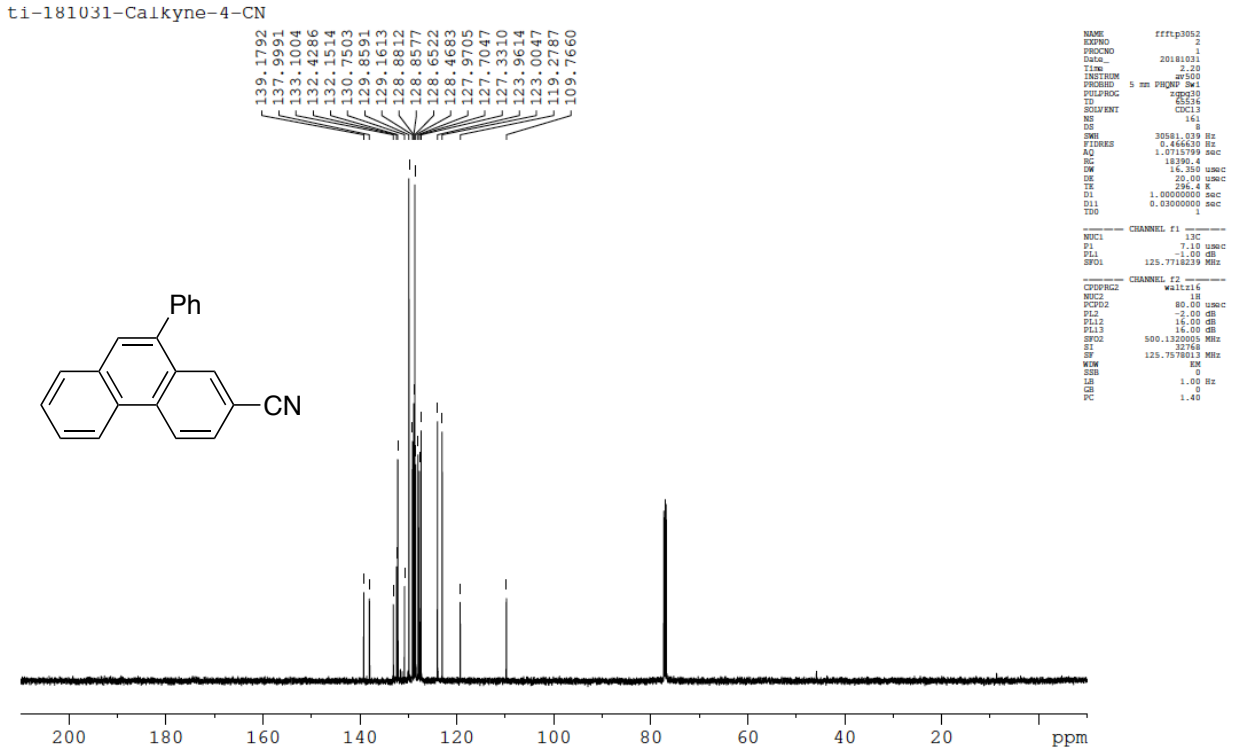
Ethyl 10-phenylphenanthrene-2-carboxylate (2j)



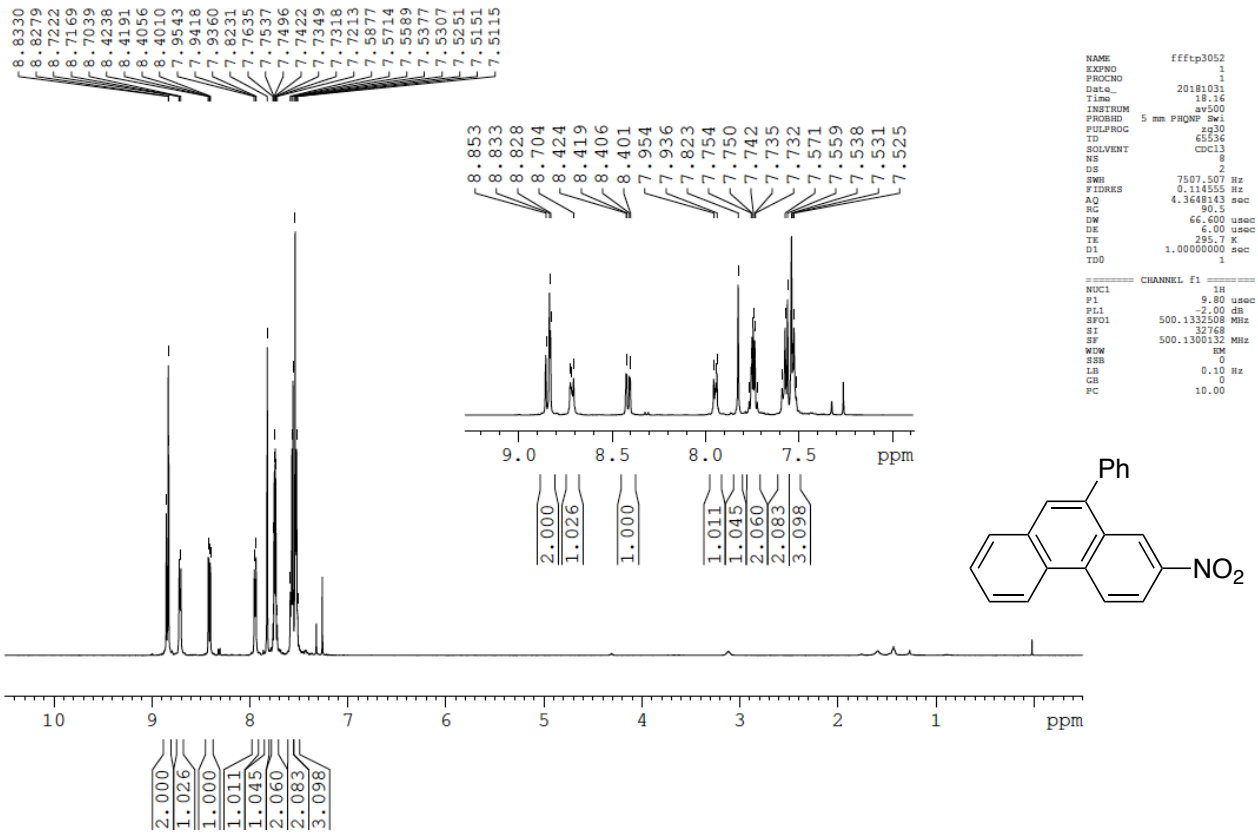


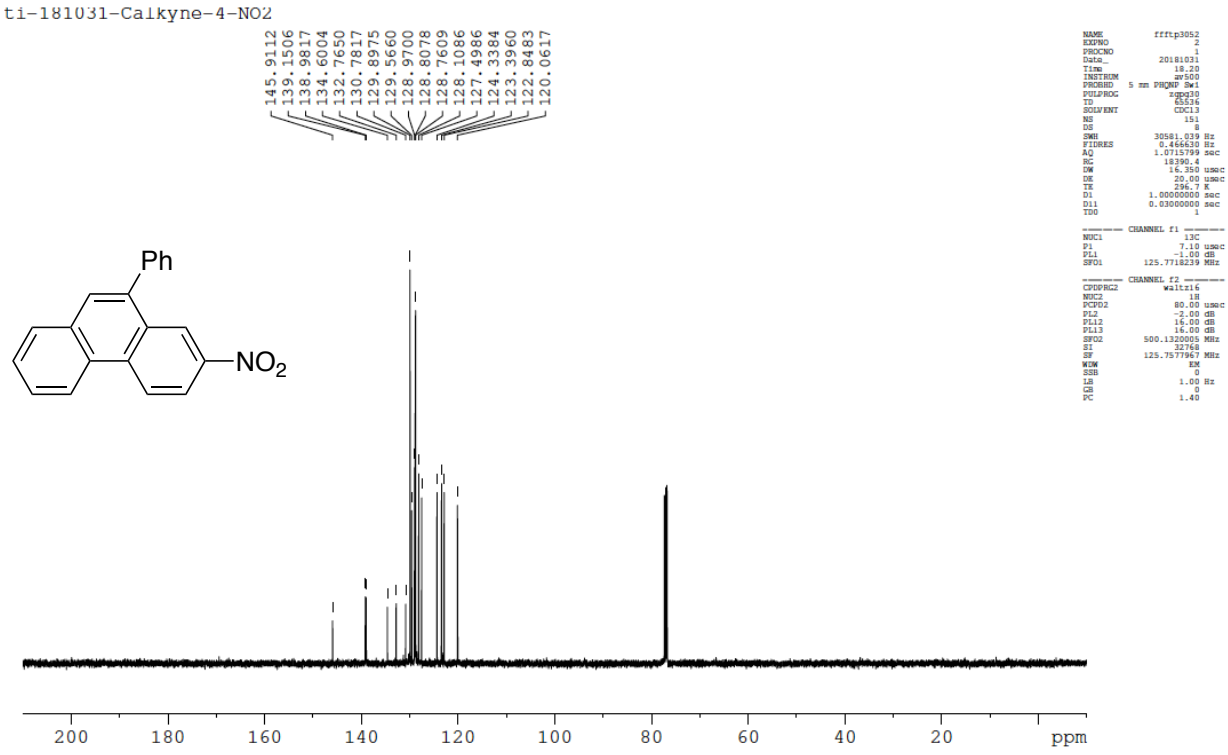
10-Phenylphenanthrene-2-carbonitrile (2k)



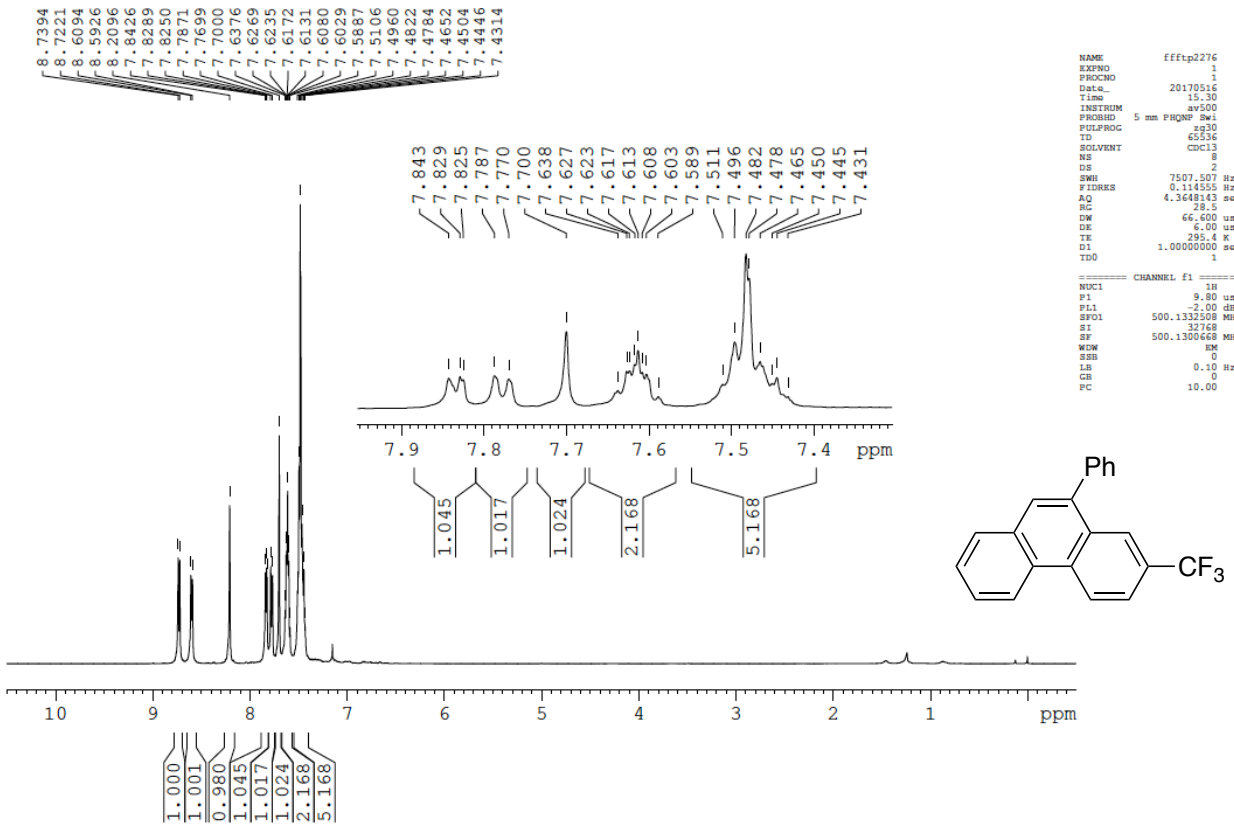


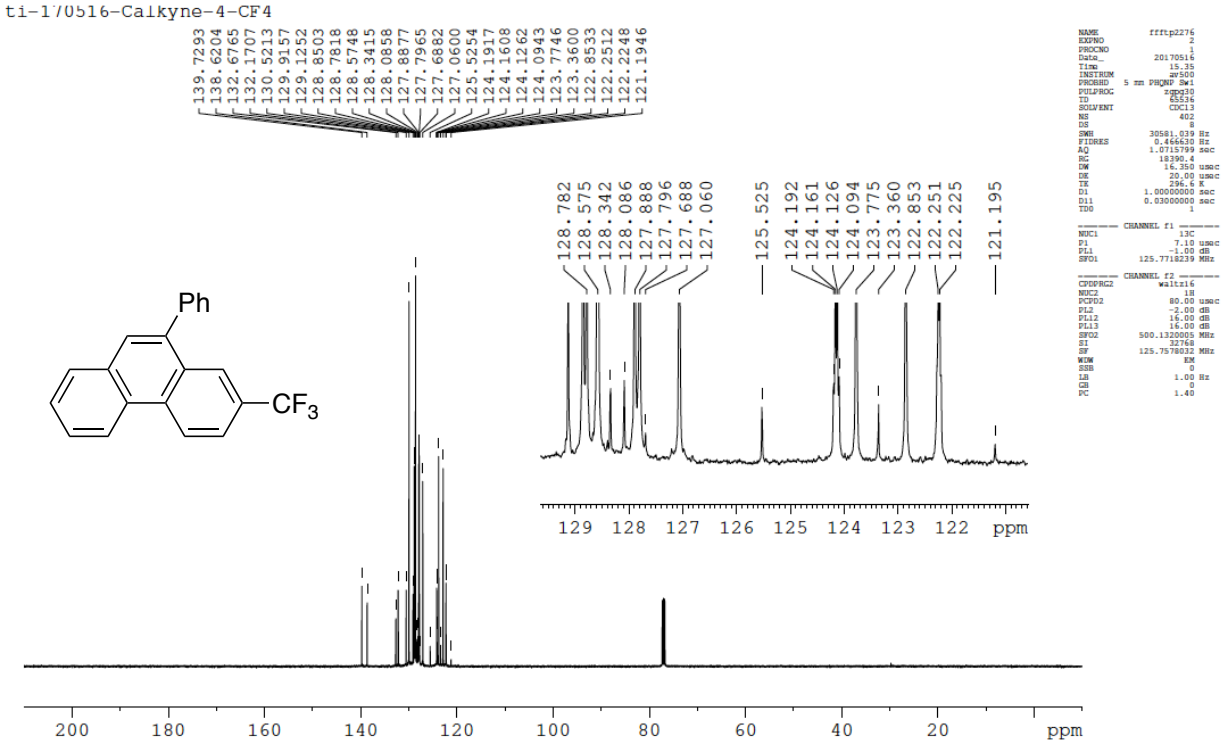
2-Nitro-10-phenylphenanthrene (2l)





10-Phenyl-2-(trifluoromethyl)phenanthrene (2m)

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122.2248
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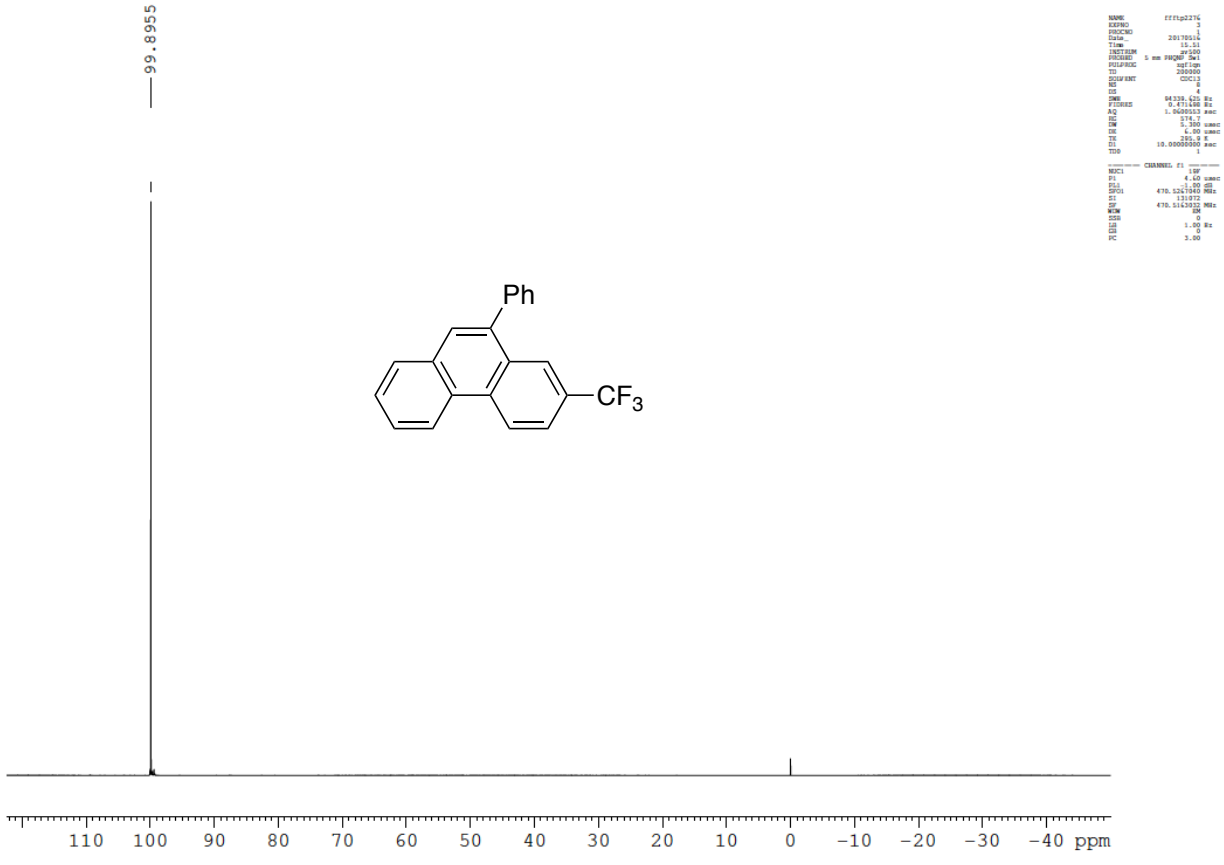
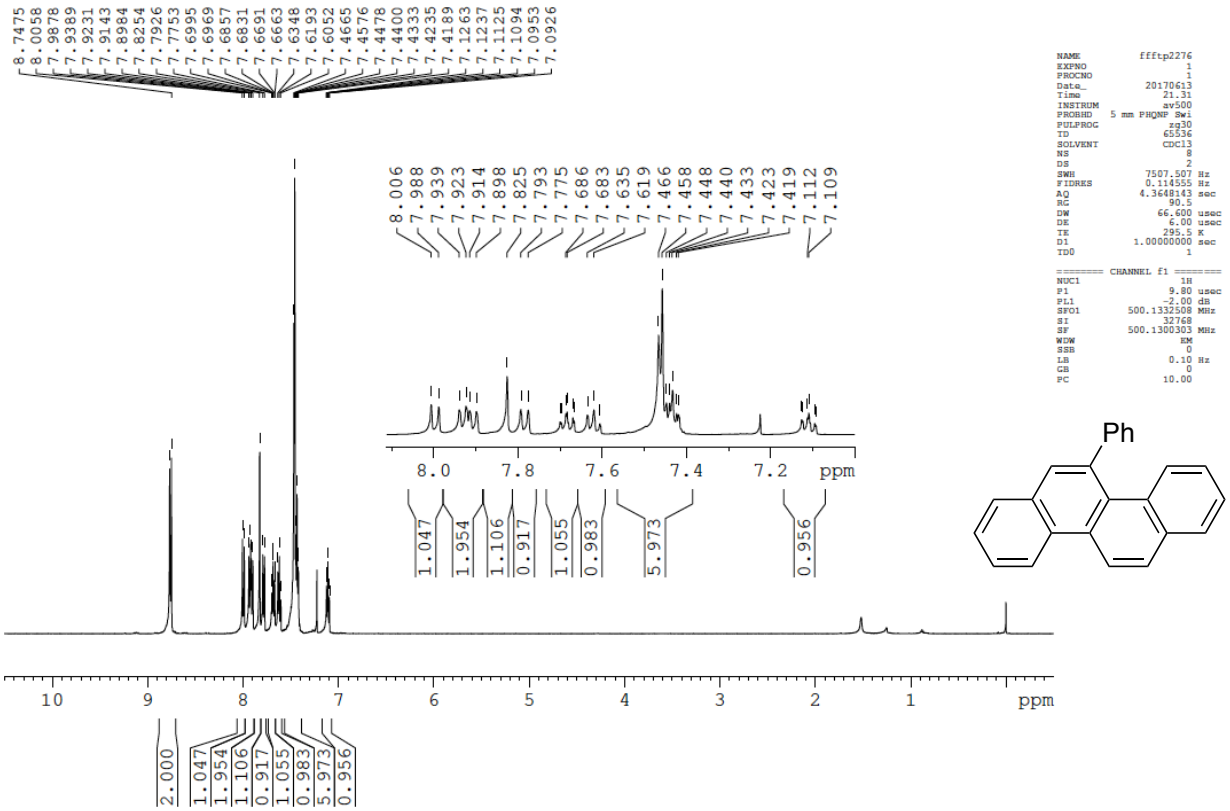
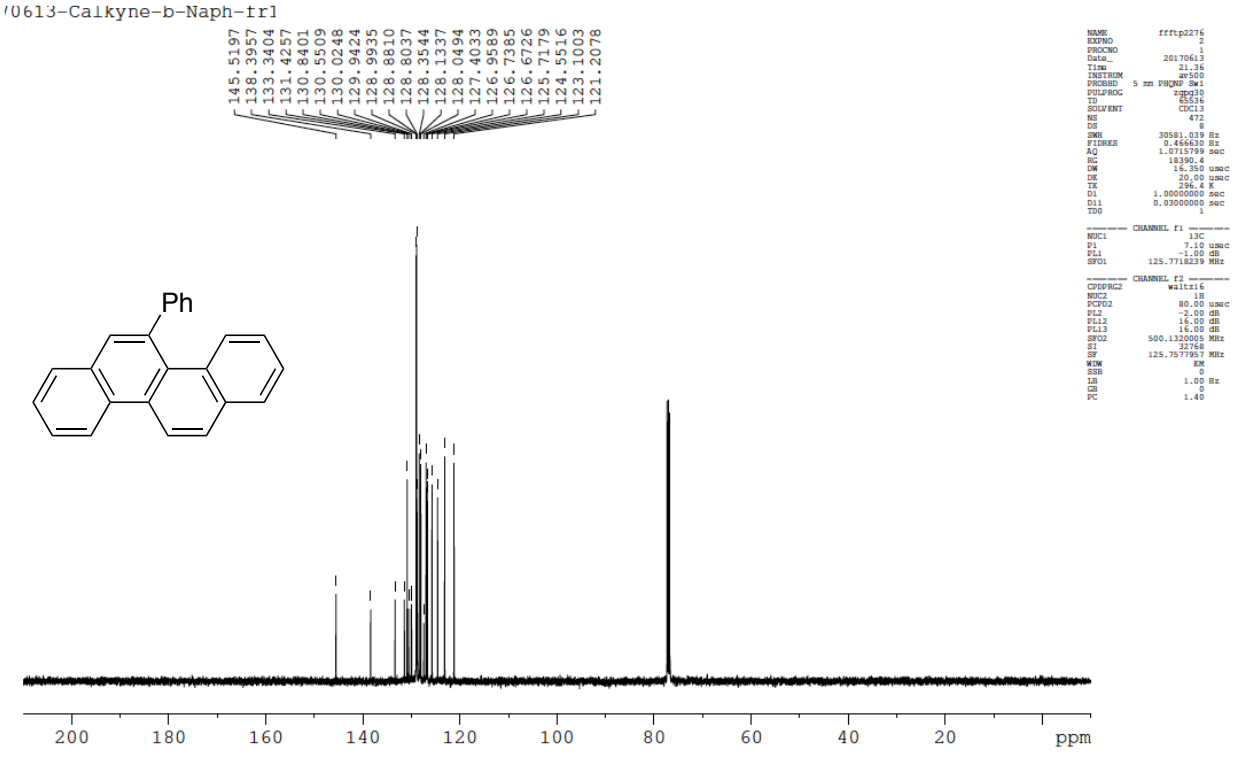
128.575
128.342
128.086
127.888
127.796
127.688
127.060
125.525
124.192
124.161
124.126
124.094
123.775
123.360
122.853
122.251
122.225
121.195
Ph
CF3
129 128 127 126 125 124 123 122 ppm
200 180 160 140 120 100 80 60 40 20 ppm

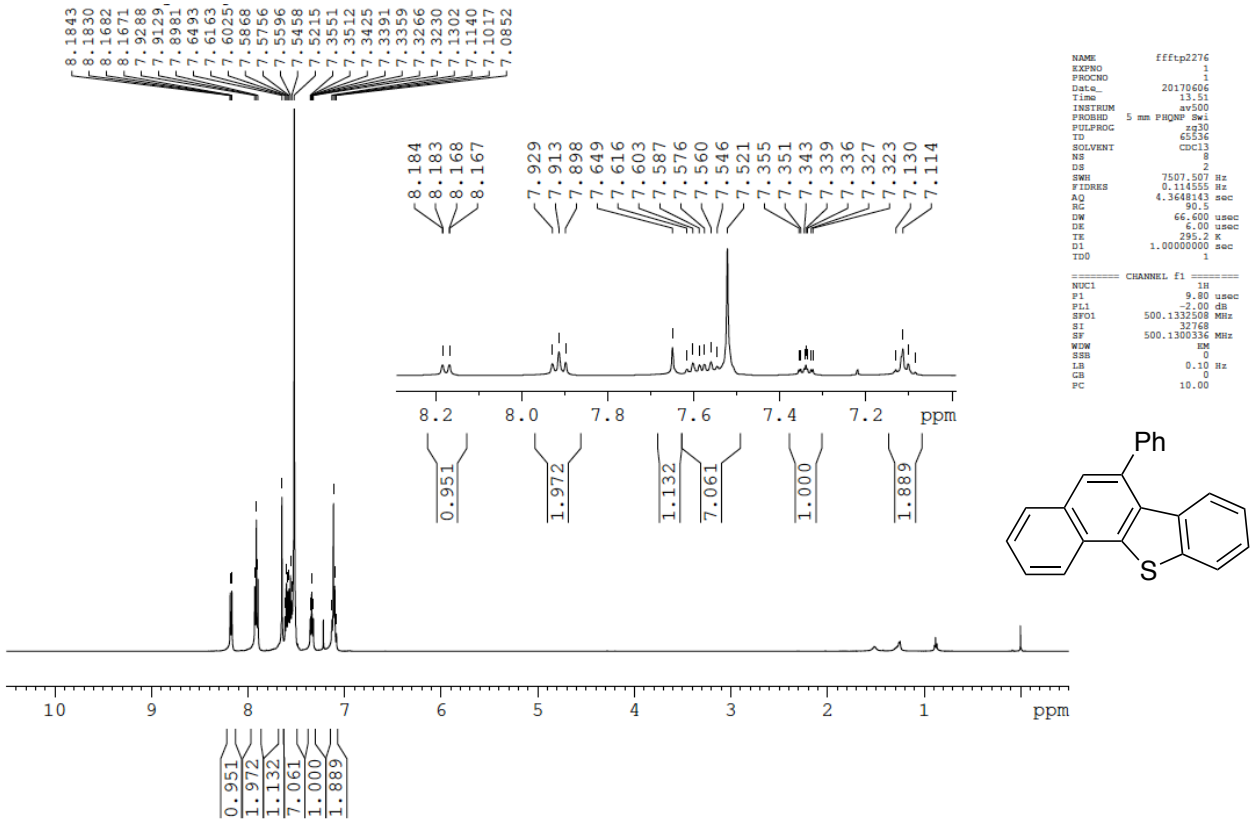

99.8955
Ph
CF3
110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 ppm

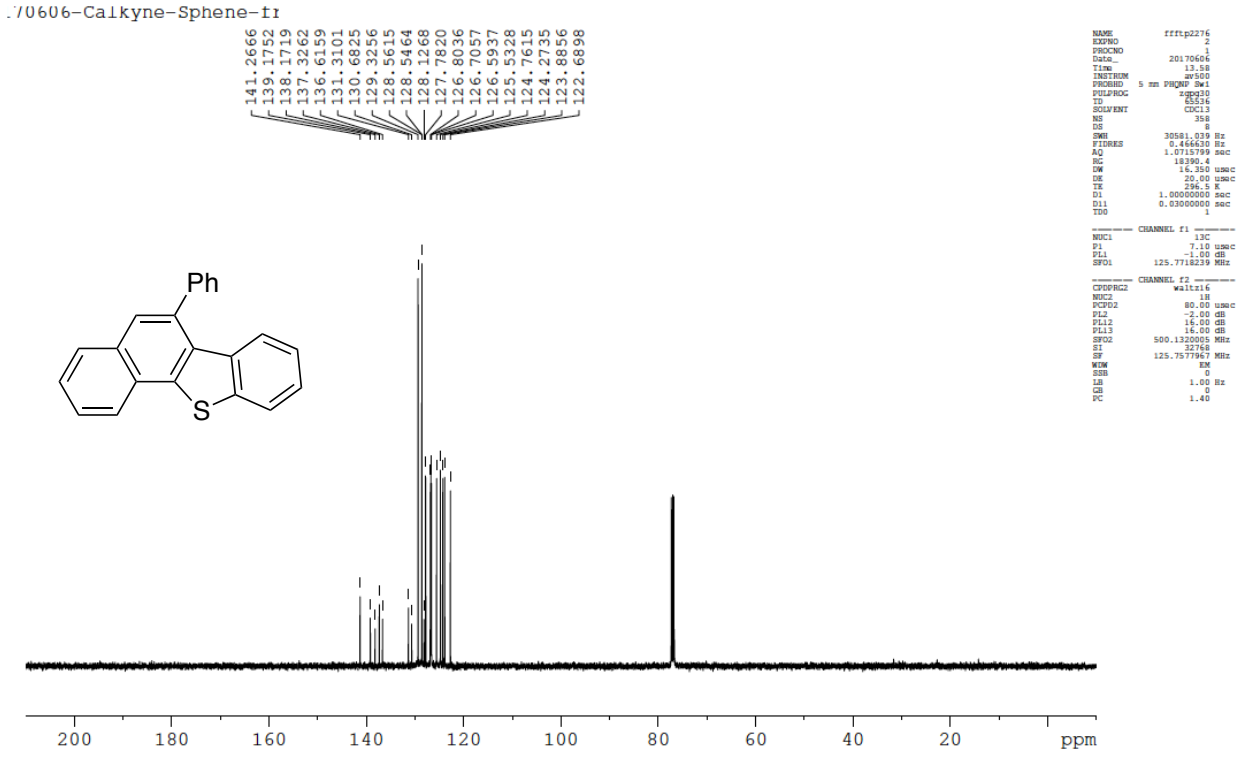
5-Phenylchrysene (2n)



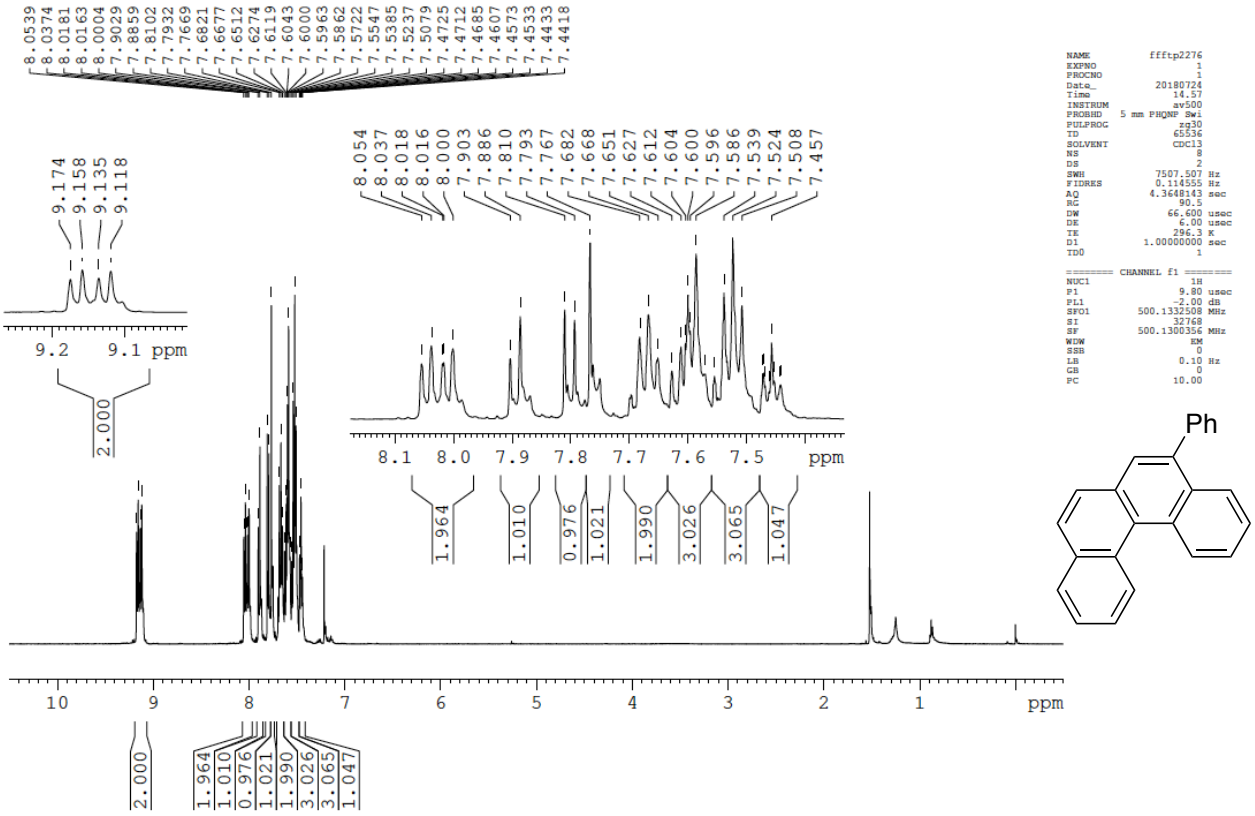


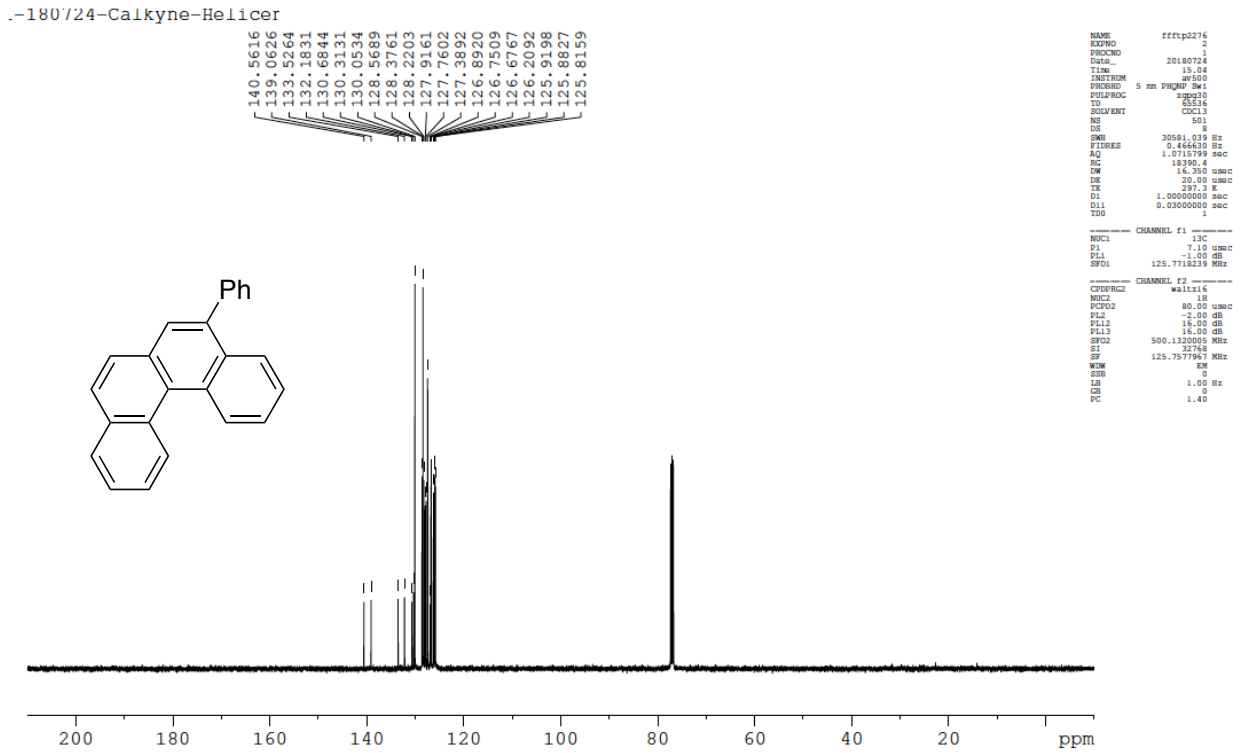
6-Phenylbenzo[*b*]naphtho[2,1-*d*]thiophene (2o)



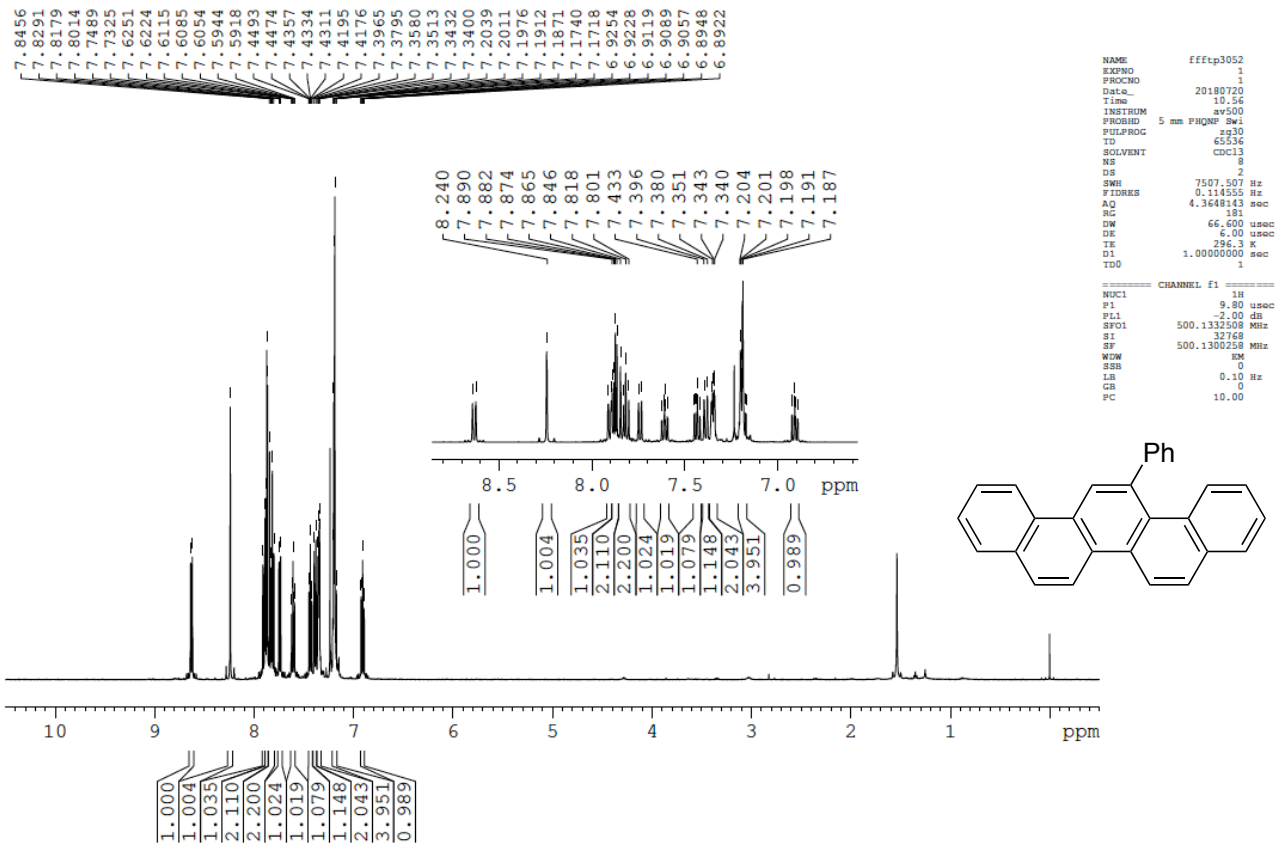


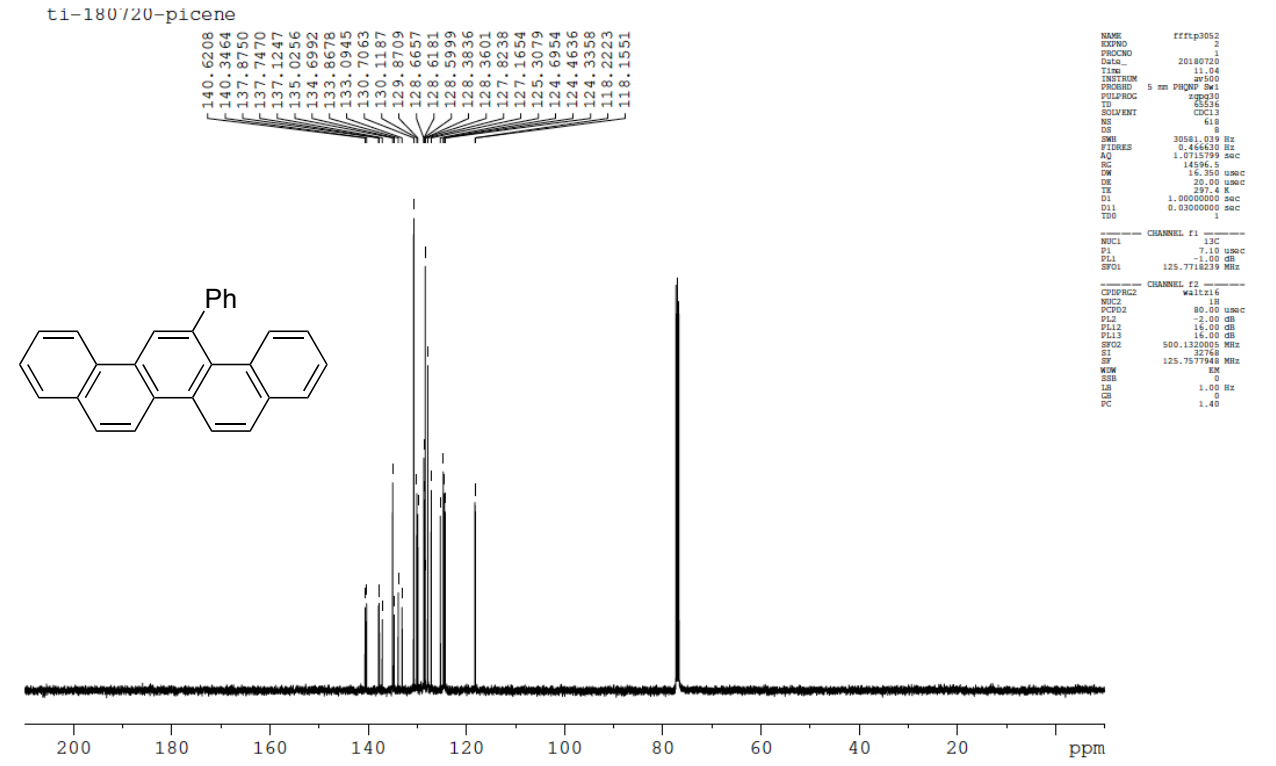
5-Phenylbenzo[*c*]phenanthrene (2p)



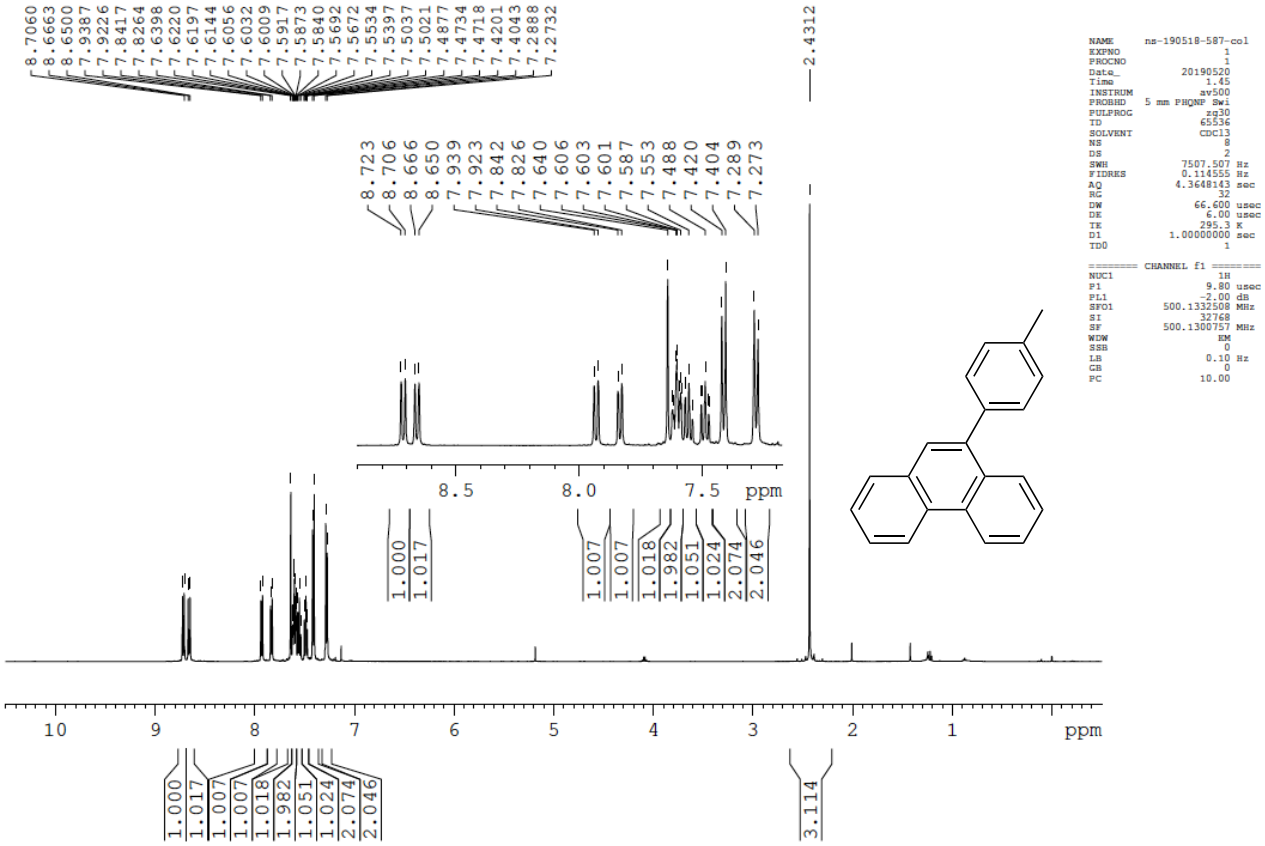


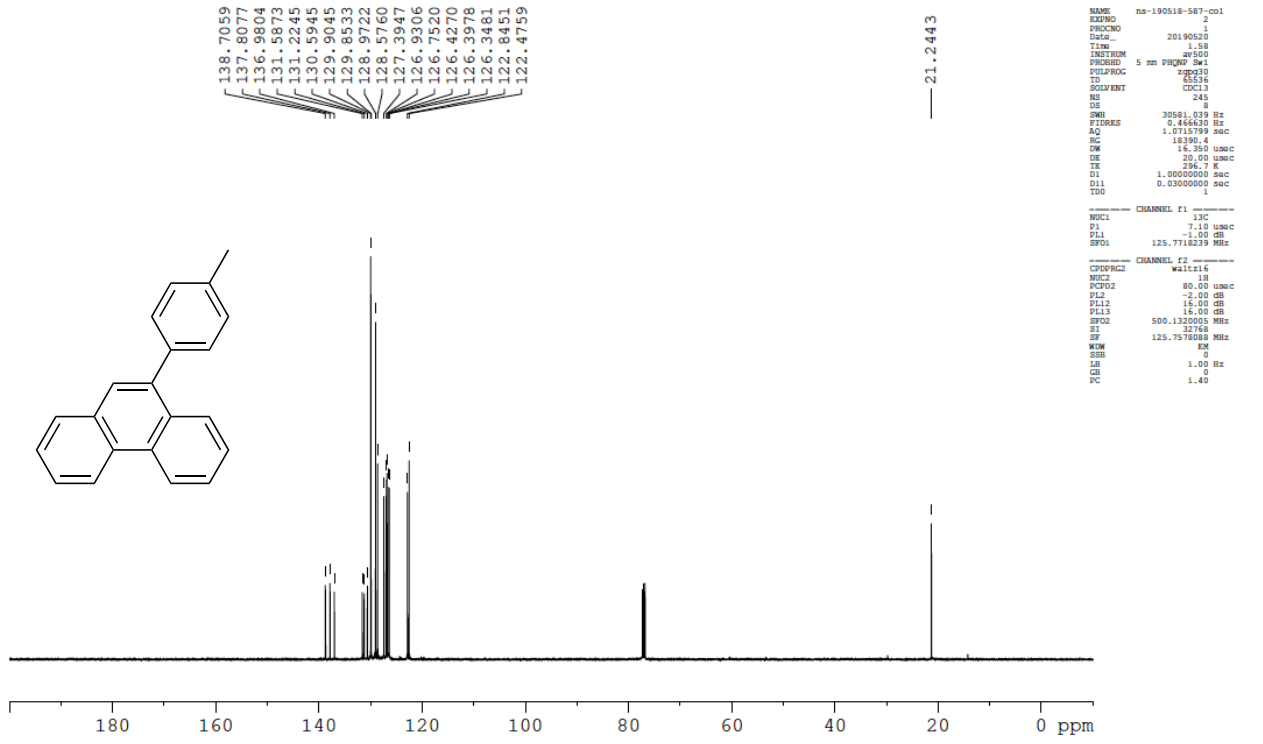
13-Phenylpicene (2q)



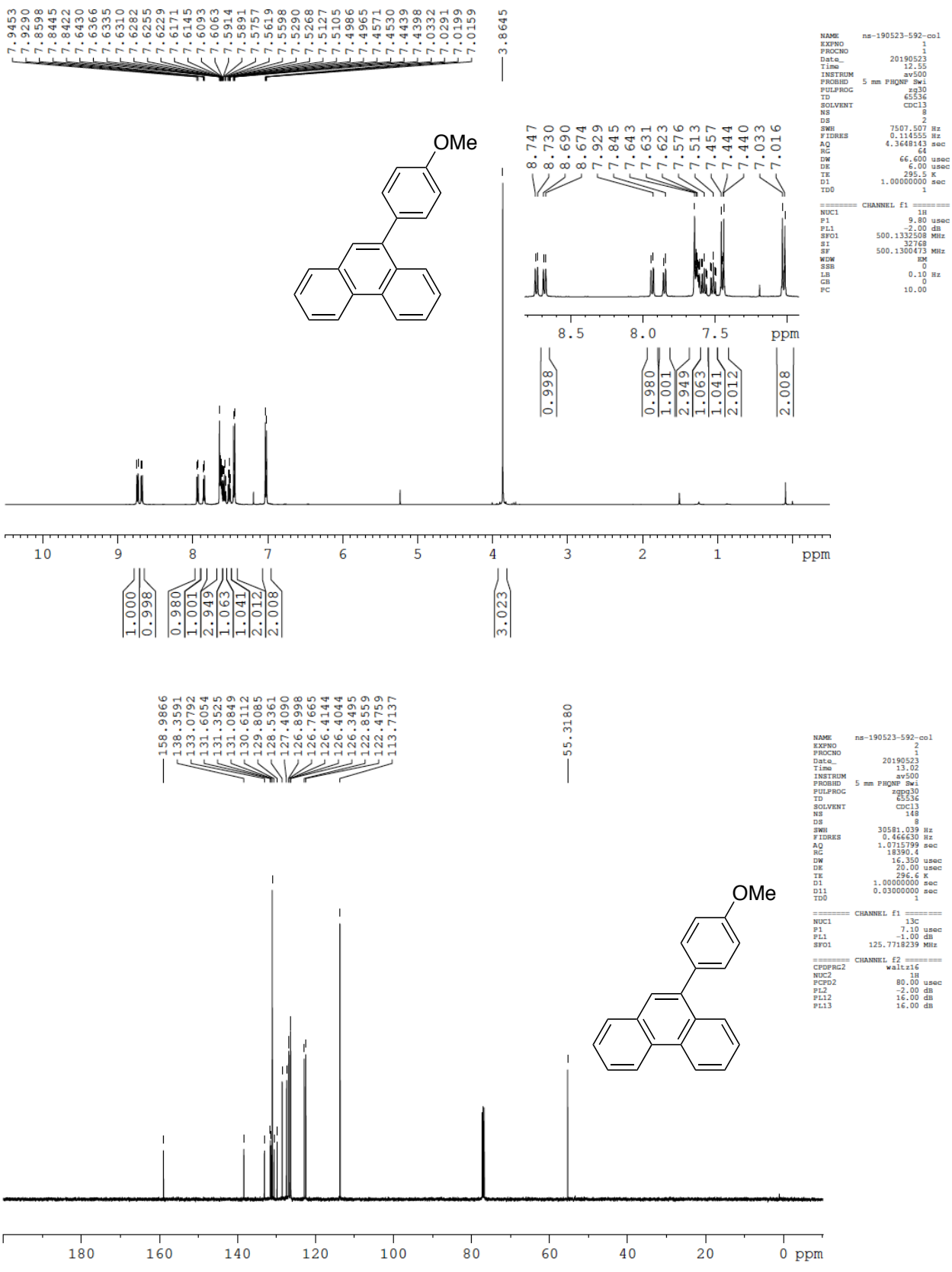


9-(4-Methylphenyl)phenanthrene (2r)

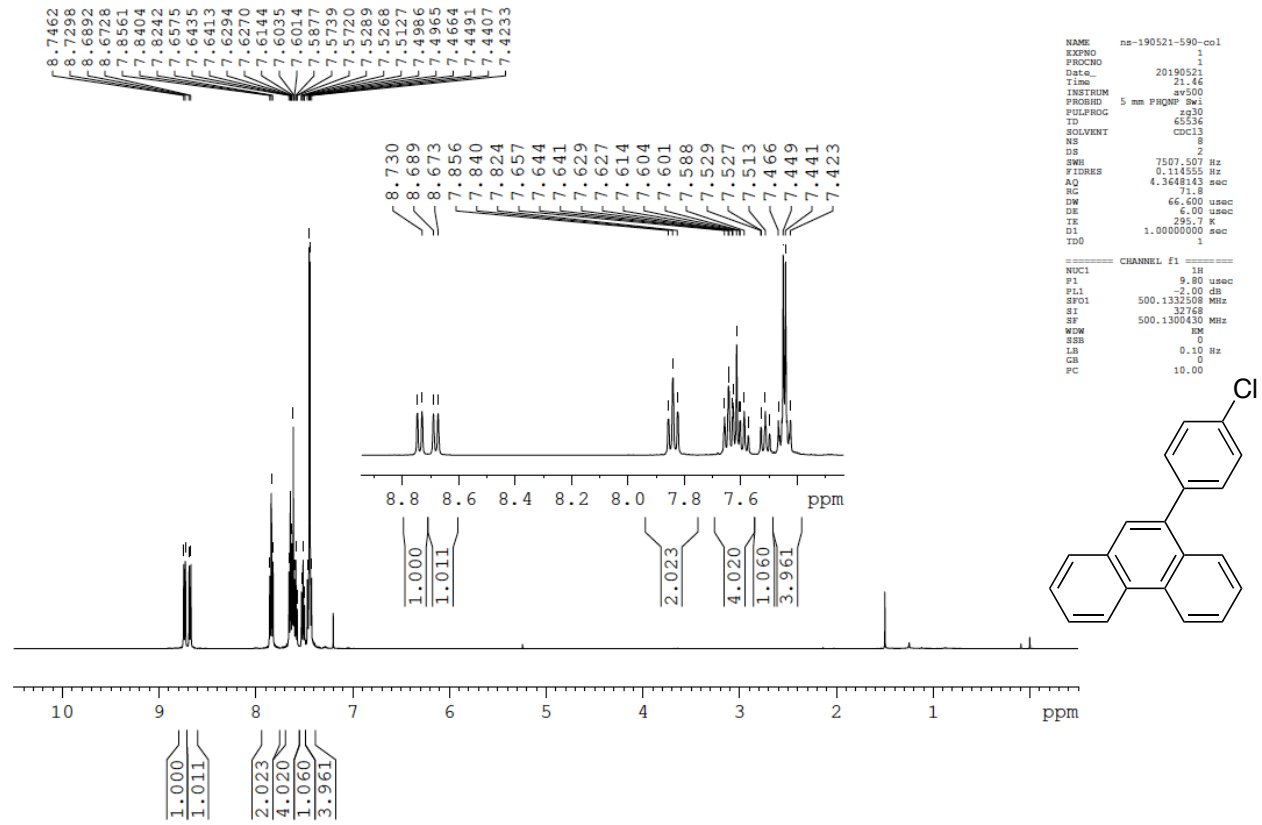


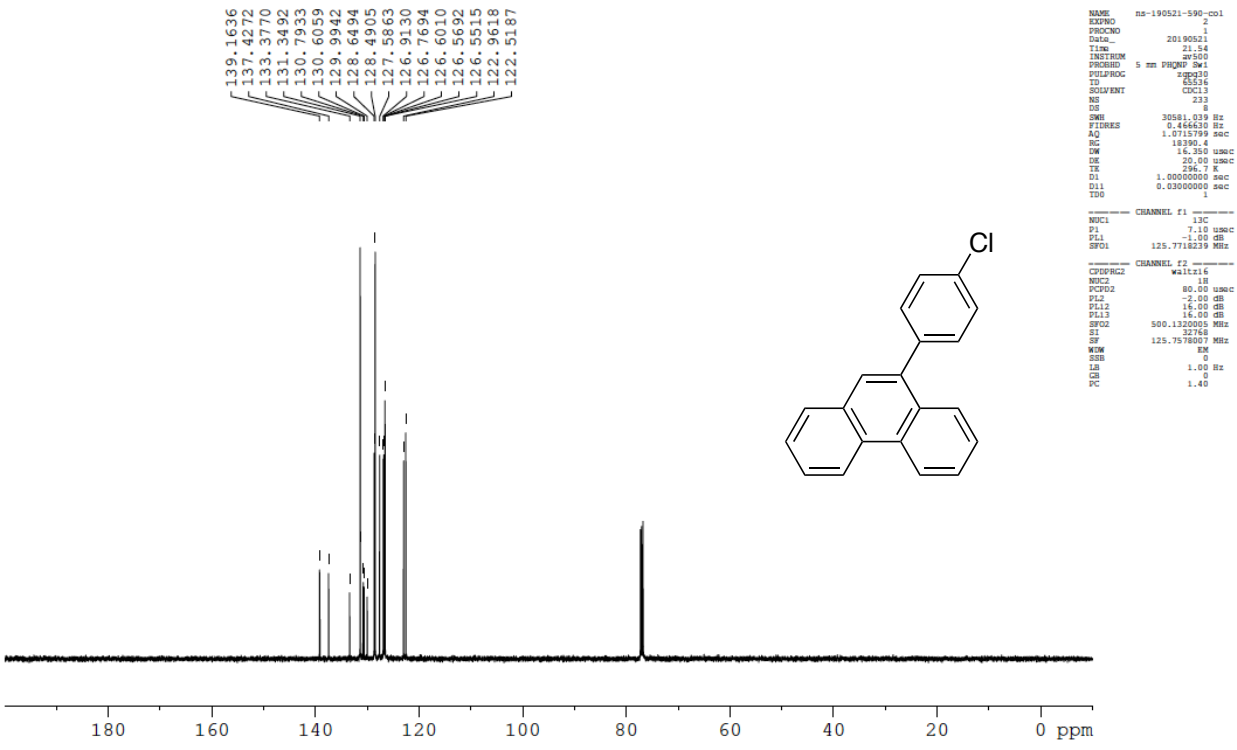


9-(4-Methoxyphenyl)phenanthrene (2s)



9-(4-Chlorophenyl)phenanthrene (2t)





9-(4-Bromophenyl)phenanthrene (2u)