Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Preparation of phenanthrenes from *ortho*-amino-biphenyls and alkynes *via* base-promoted homolytic aromatic substitution

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General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard *Schlenk* techniques. Acetonitrile (MeCN), dioxane and benzotrifluoride (BTF) were used as extra dry over molecular sieve. All other solvents and reagents were purified according to standard procedures or were used as received from *Aldrich*, *Fluka*, *Acros* or *ABCR*. IR spectra were recorded on a *Digilab FTS 4000* with a *Specac MKII Golden Gate Single Refelxtion ART System.* ^{1}H NMR and ^{13}C NMR spectra were recorded on a *DPX 300, AV 400 or DD2 600* at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$), followed by heating. Flash column chromatography (FC) was performed using *Merck* or *Fluka* silica gel 60 (40-63 μm) applying a pressure of about 0.2 – 0.4 bar. Mass spectra were recorded on a *Finnigan MAT 4200S*, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quatro LCZ* (ESI) or *Orbitrap LTQ XL* (APCI); peaks are given in *m/z* (% of basis peak).

General procedure for the synthesis of *ortho*-amino-biaryls (GP1)

In a Schlenk-tube, 2-bromo-4-methylaniline (467 mg, 2.50 mmol, 1.0 equiv), boronic acid (3.00 mmol, 1.2 equiv.), K_2CO_3 (1.55 g, 11.3 mmol, 4.5 equiv.) were dissolved in a 1:1 mixture of H_2O/DME and stirred at room temperature for 30 min. Then $Pd(PPh_3)_2Cl$ (35 mg, 0.05 mmol, 2 mol%) was added and the resulting mixture was stirred at 80 °C for 20 h. After cooling to room temperature the reaction mixture was extracted with EtOAc three times, the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Crude product was purified by flash chromatography on silica gel.

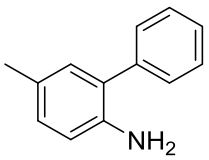
Genreral procedure for the base-promoted homolytic aromatic substitution (GP2)

The reactions were carried out under argon atmosphere. A flame-dried Schlek-tube containing *ortho*-amino-biphenyl (0.25 mmol, 1.0 equiv.), phenyl acetylene (256 mg, 2.50 mmol, 10.0 equiv.), isoamyl nitrite (44.0 mg, 0.375 mmol, 1.5 equiv.) and Bu_4NI (9.0 mg, 0.025 mmol, 10 mol%) in BTF (0.125M) was heated to 70 °C and stirred for 24h. After cooling to room temperature most of the solvent was removed *in vacuo* and the residue was adsorbed on silica gel and afterwards purified by flash chromatography on silica gel.

Genreral procedure for the base-promoted homolytic aromatic substitution (GP3)

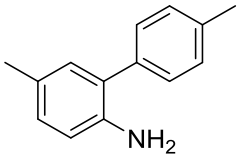
The reactions were carried out under argon atmosphere. A flame-dried Schlenk-tube containing 5-methyl-[1,1'-biphenyl]-2-amine (46 mg, 0.25 mmol, 1.0 equiv.), alkyne (2.5 mmol, 10 equiv.), isoamyl nitrite (44.0 mg, 0.375 mmol, 1.5 equiv.) and Bu_4NI (9.0 mg, 0.025 mmol, 10 mol%) in BTF (0.125 M) was heated to 70 °C and stirred for 24 h. After cooling to room temperature most of the solvent was removed *in vacuo* and the residue was adsorbed on silica gel and afterwards purified by flash chromatography on silica gel.

5-Methyl-[1,1'-biphenyl]-2-amine (1a)



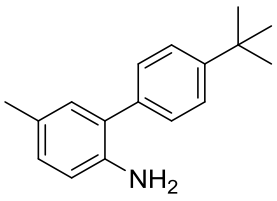
According to **GP1** with phenylboronic acid (366 mg, 3.00 mmol, 1.2 eq.). The crude mixture was purified by flash chromatography on silica gel using a 80:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1a** as pale yellow solid (375 mg, 2.46 mmol, 82%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.47 – 7.40 (*m*, 4H, CH_{arom}), 7.40 – 7.29 (*m*, 1H, CH_{arom}), 6.98 (*d*, *J* = 8.1 Hz, 2H, CH_{arom}), 6.71 (*d*, *J* = 7.8 Hz, 1H, CH_{arom}), 3.00 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.8 (C), 139.7 (C), 131.0 (CH), 129.1 (2 × CH), 129.0 (CH), 128.8 (2 × CH), 128.0 (C), 127.9 (C), 127.1 (CH), 115.9 (CH), 20.4 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{13}H_{13}NH$: 184.1121, found: 184.1128 ($[M+H]^+$). Analytical data are in accordance with the literature values.[1]

4',5-Dimethyl-[1,1'-biphenyl]-2-amine (1c)



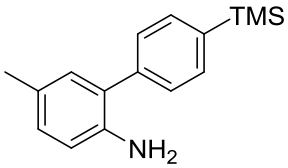
According to **GP1** with *p*-tolylboronic acid (408 mg, 3.00 mmol, 1.2 equiv). The crude mixture was purified by flash chromatography on silica gel using a 80:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1c** as pale yellow oil (355 mg, 1.80 mmol, 72%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.44 – 7.37 (*m*, 2H, CH_{arom}), 7.31 (*dd*, *J* = 8.4, 0.8 Hz, 2H, CH_{arom}), 7.07 – 7.01 (*m*, 2H, CH_{arom}), 6.79 – 6.70 (*m*, 1H, CH_{arom}), 3.66 (*s*, 2H, NH_2), 2.46 (*s*, 3H, CH_3), 2.34 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 141.0 (C), 136.8 (C), 136.8 (C), 131.1 (CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.9 (CH), 128.1 (C), 128.0 (C), 116.0 (CH), 21.3 (CH_3), 20.6 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{14}H_{15}NH$: 198.1277, found: 198.1276 ($[M+H]^+$). **IR** (neat): 3456*w*, 3363*w*, 3019*w*, 2919*w*, 2861*w*, 1619*m*, 1500*s*, 1454*w*, 1399*w*, 1296*m*, 1153*w*, 1110*w*, 1039*w*, 884*w*, 821*s*.

4'-(*tert*-butyl)-5-Methyl-[1,1'-biphenyl]-2-amine (1d)



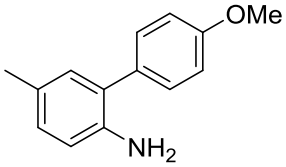
According to **GP1** with (4-(*tert*-butyl)phenyl)boronic acid (534 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 5:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1d** as white solid (413 mg, 1.73 mmol, 69%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.52 – 7.44 (*m*, 2H, CH_{arom}), 7.43 – 7.37 (*m*, 2H, CH_{arom}), 7.03 – 6.93 (*m*, 2H, CH_{arom}), 6.73 (*d*, *J* = 8.6 Hz, 1H, CH_{arom}), 3.63 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3), 1.38 (*s*, 9H, 3 × CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 150.1 (C), 140.8 (C), 136.7 (C), 131.2 (CH), 128.9 (CH), 128.8 (2 × CH), 128.2 (C), 128.1 (C), 125.8 (2 × CH), 116.1 (CH), 34.7 (C), 31.5 (3 × CH_3), 20.6 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NH$: 240.1747, found: 240.1747 ($[M+H]^+$). **IR** (neat): 3455*w*, 3368*w*, 3023*w*, 2961*s*, 2866*m*, 1620*m*, 1499*s*, 1462*m*, 1394*m*, 1363*m*, 1272*m*, 1201*w*, 1153*w*, 1112*w*, 1018*w*, 884*w*, 840*m*. **MP**: 93 °C.

5-Methyl-4'-(trimethylsilyl)-[1,1'-biphenyl]-2-amine (1e)



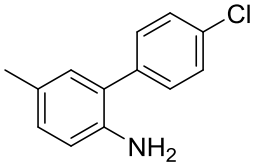
According to **GP1** with (4-(trimethylsilyl)phenyl)boronic acid (582 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 100:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1e** as yellow oil (485 mg, 1.90 mmol, 76%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.63 – 7.58 (*m*, 2H, CH_{arom}), 7.46 (*d*, *J* = 8.2 Hz, 2H, CH_{arom}), 7.02 – 6.96 (*m*, 2H, CH_{arom}), 6.76 – 6.71 (*m*, 1H, CH_{arom}), 3.64 (*s*, 3H, CH_3), 2.30 (*s*, 2H, NH_2), 0.32 (*s*, 9H, 3 × CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.7 (C), 140.1 (C), 139.3 (C), 133.9 (2 × CH), 131.1 (CH), 129.2 (CH), 128.5 (2 × CH), 128.3 (C), 128.1 (C), 116.2 (CH), 20.6 (CH_3), -0.9 (3 × CH_3). **HRMS** (ESI) exact mass calculated for $C_{16}H_{21}NSiH$: 256.1516, found: 256.1505 ($[M+H]^+$). **IR** (neat): 3454*w*, 3368*w*, 3015*w*, 2954*m*, 2920*w*, 1620*m*, 1504*m*, 1381*w*, 1294*w*, 1249*m*, 1153*w*, 1113*m*, 842*s*.

4'-Methoxy-5-methyl-[1,1'-biphenyl]-2-amine (1f)



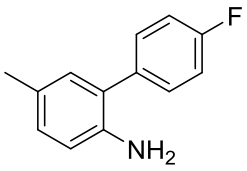
According to **GP1** with (4-methoxyphenyl)boronic acid (457 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 5:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1f** as brown solid (432 mg, 2.03 mmol, 81%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.43 – 7.35 (*m*, 2H, CH_{arom}), 7.04 – 6.90 (*m*, 4H, CH_{arom}), 6.71 (*dd*, *J* = 7.5, 0.9 Hz, 1H, CH_{arom}), 3.86 (*s*, 3H, OCH_3), 3.62 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 158.9 (C), 140.9 (C), 132.0 (C), 131.1 (CH), 130.3 (2 × CH), 128.8 (CH), 128.2 (C), 127.8 (C), 116.1 (CH), 114.3 (2 × CH), 55.4 (OCH_3), 20.6 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{14}H_{15}NOH$: 214.1226, found: 214.1223 ($[M+H]^+$). **IR** (neat): 3449*w*, 3365*w*, 3006*w*, 2931*w*, 2836*w*, 1609*m*, 1500*s*, 1462*m*, 1297*m*, 1244*s*, 1178*m*, 1106*w*, 1029*m*, 836*m*. **MP**: 41 °C.

4'-Chloro-5-methyl-[1,1'-biphenyl]-2-amine (1g)



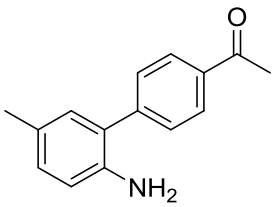
According to **GP1** with (4-chlorophenyl)boronic acid (469 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 30:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1g** as yellow oil (407 mg, 1.88 mmol, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.41 (*s*, 4H, CH_{arom}), 7.00 (*ddd*, *J* = 8.1, 2.1, 0.7 Hz, 1H, CH_{arom}), 6.96 – 6.90 (*m*, 1H, CH_{arom}), 6.71 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 3.61 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.7 (C), 138.2 (C), 133.2 (C), 130.9 (CH), 130.6 (2 × CH), 129.5 (CH), 129.0 (2 × CH), 128.3 (C), 126.7 (C), 116.2 (CH), 20.5 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{13}H_{12}NClH$: 218.0731, found: 218.0730 ($[M+H]^+$). **IR** (neat): 3456*w*, 3378*w*, 3043*w*, 2921*w*, 2361*w*, 2158*w*, 2087*w*, 1620*m*, 1503*s*, 1413*w*, 1284*w*, 1284*w*, 843*s*.

4'-Fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1h)



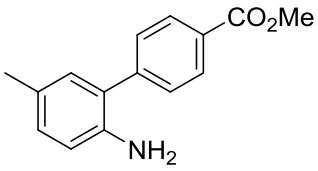
According to **GP1** with (4-fluorophenyl)boronic acid (420 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 50:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1h** as brown solid (387 mg, 1.93 mmol, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.48 – 7.32 (*m*, 2H, CH_{arom}), 7.19 – 7.07 (*m*, 2H, CH_{arom}), 7.05 – 6.94 (*m*, 1H, CH_{arom}), 6.97 – 6.90 (*m*, 1H, CH_{arom}), 6.72 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 3.63 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 162.1 (*d*, *J* = 248.3 Hz, C), 140.6 (C), 135.6 (*d*, *J* = 3.3 Hz, C), 131.1 (CH), 130.9 (*d*, *J* = 8.0 Hz, 2 × CH), 129.3 (CH), 128.4 (C), 127.1 (C), 116.2 (CH), 115.8 (*d*, *J* = 21.3 Hz, 2 × CH), 20.5 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{13}H_{12}NFH$: 202.1207, found: 202.1205 ($[M+H]^+$). **IR** (neat): 3454*w*, 3367*w*, 3016*w*, 2920*w*, 2862*w*, 1621*m*, 1500*s*, 1395*w*, 1296*w*, 1223*m*, 1157*m*, 1093*w*, 883*w*, 841*m*. **MP**: 57 °C.

1-(2'-Amino-5'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (1i)



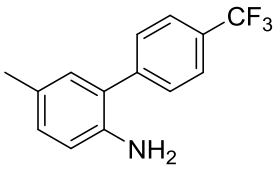
According to **GP1** with (4-acetylphenyl)boronic acid (492 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 5:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1i** as yellow solid (400 mg, 1.78 mmol, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.94 (*d*, *J* = 8.5 Hz, 2H, CH_{arom}), 7.51 (*d*, *J* = 0.6 Hz, 2H, CH_{arom}), 6.97 (*ddd*, *J* = 8.1, 2.1, 0.7 Hz, 1H, CH_{arom}), 6.92 – 6.90 (*m*, 1H, CH_{arom}), 6.73 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 2.53 (*s*, 3H, CH_3), 2.23 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 197.8 (C), 144.4 (C), 136.1 (C), 131.0 (CH), 123.0 (CH), 129.5 (2 × CH), 129.2 (C), 129.0 (2 × CH), 127.9 (C), 127.6 (C), 117.5 (CH), 26.7 (CH_3), 20.6 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{15}H_{15}NOH$: 226.1226, found: 226.1229 ($[M+H]^+$). **IR** (neat): 3451*w*, 2255*w*, 1681*m*, 1604*m*, 1499*w*, 1360*w*, 1269*m*, 905*s*. **MP**: 105 °C.

Methyl 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carboxylate (1j)



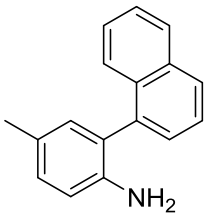
According to **GP1** with (4-(methoxycarbonyl)phenyl)boronic acid (540 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 10:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1j** as yellow solid (452 mg, 1.88 mmol, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.22 - 7.98 (*m*, 2H, CH_{arom}), 7.65 – 7.45 (*m*, 2H, CH_{arom}), 7.01 (*ddd*, *J* = 8.0, 2.1, 0.7 Hz, 1H, CH_{arom}), 6.97 – 6.95 (*m*, 1H, CH_{arom}), 6.72 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 3.94 (*s*, 3H, CO_2CH_3), 3.65 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 166.9 (C), 144.5 (C), 140.5 (C), 130.7 (CH), 130.0 (2 × CH), 129.7 (CH), 129.1 (2 × CH), 128.8 (C), 128.3 (C), 126.7 (C), 116.3 (CH), 52.1 (CO_2CH_3), 20.4 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{15}H_{15}NO_2H$: 242.1176, found: 242.1173 ($[M+H]^+$). **IR** (neat): 3448*w*, 3371*w*, 3017*w*, 2950*w*, 1718*s*, 1609*m*, 1499*m*, 1435*m*, 1397*w*, 1191*m*, 1113*m*, 1018*w*, 966*w*, 818*w*, 862*w*. **MP**: 104 °C.

5-Methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1k)



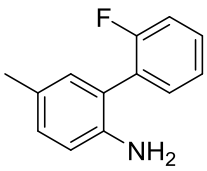
According to **GP1** with (4-(trifluoromethyl)phenyl)boronic acid (570 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 25:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1k** as pale yellow solid (452 mg, 1.80 mmol, 72%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.75 - 7.66 (*m*, 2H, CH_{arom}), 7.60 (*dt*, *J* = 7.8, 0.8 Hz, 2H, CH_{arom}), 7.03 (*ddd*, *J* = 8.0, 2.1, 0.8 Hz, 1H, CH_{arom}), 6.99 – 6.92 (*m*, 1H, CH_{arom}), 6.73 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 3.68 (*s*, 2H, NH_2), 2.30 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 143.6 (C), 140.7 (C), 130.9 (CH), 129.9 (CH), 129.6 (2 × CH), 128.5 (C), 126.5 (C), 125.8 (*q*, *J* = 3.7 Hz, 2 × CH), 122.5 (*q*, *J* = 272.0 Hz, CF_3), 119.0 (CH), 20.5 (CH_3). Quaternary carbon next to CF_3 could not be detected. **HRMS** (ESI) exact mass calculated for $C_{14}H_{12}NF_3H$: 252.0995, found: 252.0991 ($[M+H]^+$). **IR** (neat): 3460*w*, 3369*w*, 3018*w*, 2924*w*, 1619*m*, 1502*m*, 1398*w*, 1325*s*, 1166*m*, 1124*m*, 1069*m*, 1018*w*, 909*w*, 848*m*, 816*w*. **MP**: 91 °C.

4-Methyl-2-(naphthalen-1-yl)aniline (1l)



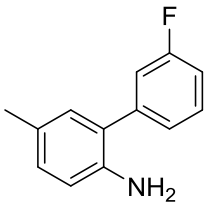
According to **GP1** with naphthalen-1-ylboronic acid (516 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 30:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1l** as red oil (379 mg, 1.63 mmol, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.95 – 7.82 (*m*, 2H, CH_{arom}), 7.68 – 7.62 (*m*, 1H, CH_{arom}), 7.57 – 7.39 (*m*, 4H, CH_{arom}), 7.14 – 7.04 (*m*, 1H, CH_{arom}), 7.00 (*d*, *J* = 2.2 Hz, 1H, CH_{arom}), 6.81 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 3.39 (*s*, 2H, NH_2), 2.32 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 170.6 (C), 167.4 (C), 143.9 (C), 134.0 (2 × C), 131.9 (2 × CH), 129.5 (CH), 128.5 (CH), 128.1 (CH), 127.8 (CH), 126.4 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 116.3 (CH), 20.7 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{17}H_{15}NH$: 234.1277, found: 234.1279 ($[M+H]^+$). **IR** (neat): 3453*w*, 3367*w*, 3017*w*, 2919*w*, 2859*w*, 2362*w*, 1620*m*, 1485*s*, 1391*m*, 1294*m*, 1190*w*, 1153*m*, 1091*m*, 1014*m*, 880*m*, 834*s*.

2'-Fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1m)



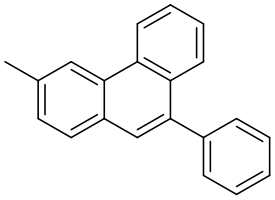
According to **GP1** with (2-fluorophenyl)boronic acid (420 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 50:1 to 25.1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1m** as brown solid (397 mg, 1.97 mmol, 79%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.41 – 7.29 (*m*, 2H, CH_{arom}), 7.24 – 7.13 (*m*, 2H, CH_{arom}), 7.03 (*ddd*, *J* = 8.1, 2.1, 0.8 Hz, 1H, CH_{arom}), 6.98 – 6.93 (*m*, 1H), 6.74 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 3.29 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 160.0 (*d*, *J* = 244.6 Hz, C), 141.6 (C), 132.1 (*d*, *J* = 3.7 Hz, CH), 131.6 (CH), 129.9 (CH), 129.4 (*d*, *J* = 8.0 Hz, CH), 128.0 (C), 127.0 (*d*, *J* = 16.4 Hz, C), 124.6 (*d*, *J* = 3.6 Hz, CH), 121.9 (C), 116.2 (CH), 116.1 (*d*, *J* = 22.4 Hz, CH), 20.53 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{13}H_{12}NFH$: 202.1207, found: 202.1207 ($[M+H]^+$). **IR** (neat): 3462*w*, 3374*w*, 3018*w*, 2919*w*, 2859*w*, 1622*m*, 1486*s*, 1447*m*, 1285*m*, 1213*s*, 1153*m*, 1105*m*, 1040*w*, 988*w*, 944*w*, 886*w*, 812*s*. **MP**: 49 °C.

3'-Fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1n)



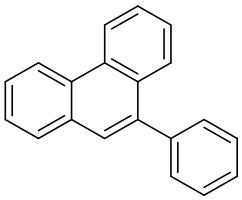
According to **GP1** with (3-fluorophenyl)boronic acid (420 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 50:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **1n** as pale yellow oil (385 mg, 1.93 mmol, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.39 (*td*, *J* = 7.9, 6.0 Hz, 1H, CH_{arom}), 7.25 – 7.22 (*m*, 1H, CH_{arom}), 7.18 (*ddd*, *J* = 9.9, 2.6, 1.6 Hz, 1H, CH_{arom}), 7.07 – 6.97 (*m*, 2H, CH_{arom}), 6.95 (*d*, *J* = 2.0 Hz, 1H, CH_{arom}), 6.74 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 3.81 (*s*, 2H, NH_2), 2.29 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 163.2 (*d*, *J* = 246.0 Hz, C), 141.9 (*d*, *J* = 7.7 Hz, C), 140.3 (C), 131.0 (CH), 130.4 (*d*, *J* = 8.5 Hz, CH), 129.6 (CH), 128.7 (C), 127.0 (*d*, *J* = 1.9 Hz, C), 125.0 (*d*, *J* = 2.9 Hz, CH), 116.5 (CH), 116.2 (*d*, *J* = 21.3 Hz, CH), 114.2 (*d*, *J* = 21.0 Hz, CH), 20.6 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{13}H_{12}NFH$: 202.1207, found: 202.1207 ($[M+H]^+$). **IR** (neat): 3460*w*, 3371*w*, 3018*w*, 2920*w*, 2860*w*, 1612*s*, 1581*s*, 1505*s*, 1433*m*, 1300*m*, 1266*m*, 1211*m*, 115*m*, 1078*w*, 1041*w*, 926*m*, 875*m*.

3-Methyl-9-phenylphenanthrene (2a)



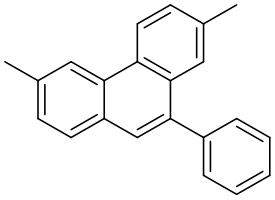
According to **GP2** with 5-methyl-[1,1'-biphenyl]-2-amine (**1a**, 46 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product **2a** as yellow oil (52 mg, 0.20 mmol, 78%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.80 (*d*, *J* = 8.3 Hz, 1H, CH_{arom}), 8.54 (*s*, 1H, CH_{arom}), 7.94 (*dd*, *J* = 8.3, 1.4 Hz, 1H, CH_{arom}), 7.81 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.70 – 7.64 (*m*, 2H, CH_{arom}), 7.60 – 7.45 (*m*, 7H, CH_{arom}), 2.67 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 141.1 (C), 138.0 (C), 136.4 (C), 131.4 (C), 130.5 (C), 130.2 (2 × CH), 130.2 (C), 129.7 (C), 128.7 (CH), 128.7 (CH), 128.4 (2 × CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 126.5 (CH), 126.3 (CH), 123.0 (CH), 122.4 (CH), 22.3 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{21}H_{16}$: 268.1246, found: 268.1246 [$M^{+\cdot}$]. Analytical data are in accordance with the literature values.[2]

9-Phenylphenanthrene (2b)



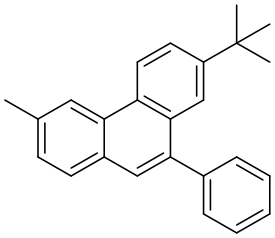
According to **GP2** with [1,1'-biphenyl]-2-amine (**1b**, 42 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product **2b** as white solid (46 mg, 0.18 mmol, 72%). **^{1}H NMR** (300 MHz, C_6D_6, 300 K): δ = 8.59 – 8.47 (*m*, 2H, CH_{arom}), 8.01 (*dd*, *J* = 8.2, 1.1 Hz, 1H, CH_{arom}), 7.69 – 7.62 (*m*, 1H, CH_{arom}), 7.55 (*s*, 1H, CH_{arom}), 7.48 – 7.35 (*m*, 5H, CH_{arom}), 7.35 – 7.21 (*m*, 4H, CH_{arom}). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.9 (C), 138.9 (C), 131.7 (C), 131.2 (C), 130.7 (C), 130.1 (2 × CH), 130.1 (C), 128.7 (C), 128.4 (2 × CH), 127.6 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.6 (CH), 126.6 (CH), 126.5 (CH), 123.0 (CH), 122.6 (CH). **HRMS** (APCI) exact mass calculated for $C_{20}H_{14}$: 254.1090, found: 254.1079 [$M^{+\cdot}$]. Analytical data are in accordance with the literature values.[3]

2,6-Dimethyl-10-phenylphenanthrene (2c)



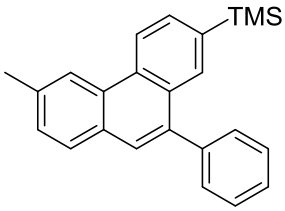
According to **GP2** with 4',5-dimethyl-[1,1'-biphenyl]-2-amine (**1c**, 49 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2c** as yellowish solid (60 mg, 0.18 mmol, 72%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.68 (*d*, *J* = 8.4 Hz, 1H, CH_{arom}), 8.58 – 8.47 (*m*, 1H, CH_{arom}), 7.81 (*s*, 1H, CH_{arom}), 7.72 (*dt*, *J* = 1.7, 0.8 Hz, 1H, CH_{arom}), 7.65 (*s*, 1H, CH_{arom}), 7.62 – 7.41 (*m*, 7H, CH_{arom}), 2.67 (*s*, 3H, CH_3), 2.50 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 141.3 (C), 137.7 (C), 136.3 (2 × C) , 136.2 (2 × C), 131.5 (C), 130.2 (2 × CH), 129.3 (C), 128.6 (CH), 128.4 (2 × CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 127.3 (CH), 126.5 (CH), 123.0 (CH), 122.2 (CH), 22.3 (CH_3), 21.8 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{22}H_{18}$: 283.1470, found: 283.1470 [$M^{+\cdot}$]. **IR** (neat): 3024*w*, 2918*m*, 1620*w*, 1496*s*, 1443*m*, 1370*w*, 1147*w*, 1032*w*, 892*m*, 817*m*, 779*m*, 702*s*, 587*s*. **MP**: 173 °C.

2-(*tert*-Butyl)-6-Methyl-10-phenylphenanthrene (2d)



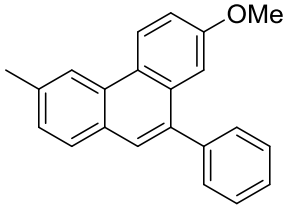
According to **GP2** with 4'-(*tert*-butyl)-5-methyl-[1,1'-biphenyl]-2-amine (**1d**, 60 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2d** as yellowish solid (69 mg, 0.21 mmol, 85%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.76 – 8.70 (*m*, 1H, CH_{arom}), 8.55 – 8.49 (*m*, 1H. CH_{arom}), 7.98 (*d*, *J* = 2.1 Hz, 1H, CH_{arom}), 7.85 - 7.72 (*m*, 2H, CH_{arom}), 7.71 – 7.41 (*m*, 7H, CH_{arom}), 2.67 (*s*, 3H, CH_3), 1.39 (*s*, 9H, 3 × CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 149.3 (C), 141.3 (C), 138.1 (C), 136.3 (C), 131.1 (C), 130.2 (2 × CH), 130.1 (C), 129.5 (C), 128.6 (CH), 128.4 (2 × CH), 128.4 (C), 128.3 (CH), 127.5 (CH), 127.3 (CH), 124.5 (CH), 122.8 (2 × CH), 122.3 (CH), 35.1 (C), 31.5 (3 × CH), 22.3 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{25}H_{24}$: 324.1870, found: 324.1873 [$M^{+\cdot}$]. **IR** (neat): 2964*w*, 1616*w*, 1372*w*, 1268*w*, 906*s*, 828*w*, 730*s*, 650*w*. **MP**: 132 °C.

Trimethyl(6-methyl-10-phenylphenanthren-2-yl)silane (2e)



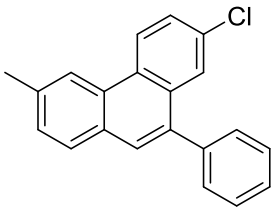
According to **GP2** with 5-methyl-4'-(trimethylsilyl)-[1,1'-biphenyl]-2-amine (**1e**, 64 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2e** as yellow oil (59 mg, 0.18 mmol, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.76 (*dd*, *J* = 8.2, 0.6 Hz, 1H, CH_{arom}), 8.59 – 8.50 (*m*, 1H, CH_{arom}), 8.15 (*dd*, *J* = 1.3, 0.6 Hz, 1H, CH_{arom}), 7.81 (*dd*, *J* = 8.2, 1.5 Hz, 2H, CH_{arom}), 7.68 (*s*, 1H, CH_{arom}), 7.65 – 7.41 (*m*, 6H, CH_{arom}), 2.67 (*s*, 3H, CH_3), 0.30 (*s*, 9H, 3 × CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 141.1 (C), 138.4 (C), 138.1 (C), 136.4 (C), 132.5 (CH), 130.8 (C), 130.7 (CH), 130.5 (C), 130.3 (2 × CH), 130.1 (C), 129.9 (C), 128.8 (CH), 128.6 (CH), 128.3 (2 × CH), 127.5 (CH), 127.4 (CH), 122.5 (CH), 122.1 (CH), 22.3 (CH_3), -0.98 (3 × CH_3). **HRMS** (APCI) exact mass calculated for $C_{24}H_{24}Si$: 340.1639, found: 340.1642 [$M^{+\cdot}$]. **IR** (neat): 3026*w*, 2953*m*, 1599*w*, 1492*w*, 1444*w*, 1364*w*, 1248*s*, 1124*m*, 892*w*, 852*s*, 753*m*, 701*m*, 664*w*, 587*m*.

2-Methoxy-6-methyl-10-phenylphenanthrene (2f)



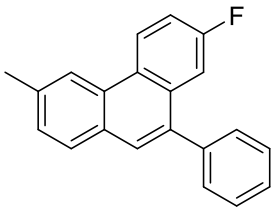
According to **GP2** with 4'-methoxy-5-methyl-[1,1'-biphenyl]-2-amine (**1f**, 53 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide analytically pure product **2f** as yellow solid (57 mg, 0.19 mmol, 76%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.68 (*d*, *J* = 8.9 Hz, 1H, CH_{arom}), 8.46 – 8.38 (*m*, 1H, CH_{arom}), 7.77 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.65 (*s*, 1H, CH_{arom}), 7.62 – 7.45 (*m*, 5H, CH_{arom}), 7.39 (*dd*, *J* = 7.9, 1.5 Hz, 1H, CH_{arom}), 7.37 – 7.27 (*m*, 2H, CH_{arom}). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 158.3 (C), 141.2 (C), 137.4 (C), 136.5 (C), 132.8 (C), 130.3 (C), 130.1 (2 × CH), 128.7 (C), 128.7 (CH), 128.5 (2 × CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 124.9 (C), 124.6 (CH), 121.9 (CH), 116.3 (CH), 108.0 (CH), 55.4 (CH_3), 22.3 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{22}H_{18}O$: 299.1419, found: 299.1419 [$M^{+\cdot}$]. **IR** (neat): 2935*w*, 2362*w*, 2250*w*, 1614*m*, 1498*m*, 1462*m*, 1259*m*, 1221*m*, 1097*w*, 1045*m*, 905*s*, 822*w*, 729*s*, 649*m*, 587*m*. **MP**: 104 °C.

2-Chloro-6-methyl-10-phenylphenanthrene (2g)



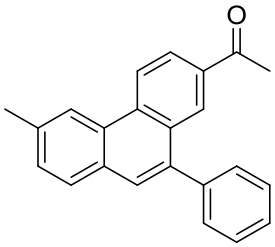
According to **GP2** with 4'-chloro-5-methyl-[1,1'-biphenyl]-2-amine (**1g**, 54 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2g** as white solid (50 mg, 0.17 mmol, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.67 (*d*, *J* = 8.9 Hz, 1H, CH_{arom}), 8.45 – 8.41 (*m*, 1H, CH_{arom}), 7.89 (*d*, *J* = 2.2 Hz, 1H, CH_{arom}), 7.79 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.68 (*s*, 1H, CH_{arom}), 7.59 (*dd*, *J* = 8.9, 2.3 Hz, 1H, CH_{arom}), 7.56 – 7.44 (*m*, 6H, CH_{arom}), 2.65 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.3 (C), 137.0 (C), 136.8 (C), 132.5 (C), 132.5 (C), 130.0 (2 × CH), 129.6 (C), 129.4 (C), 128.9 (CH), 128.7 (C), 128.6 (CH), 128.5 (CH), 128.5 (2 × CH), 127.6 (CH), 126.7 (CH), 126.0 (CH), 124.5 (CH), 122.2 (CH), 22.2 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{21}H_{15}Cl$: 302.0855, found: 302.0857 [$M^{+\cdot}$]. **IR** (neat): 3042*w*, 2257*w*, 2064*w*, 1598*m*, 1493*m*, 1438*m*, 902*s*, 820*s*, 722*m*, 730*s*, 649*w*, 582*m*. **MP**: 118 °C.

2-Fluoro-6-methyl-10-phenylphenanthrene (2h)



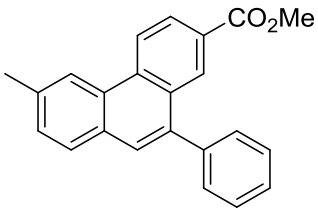
According to **GP2** with 4'-fluoro-5-methyl-[1,1'-biphenyl]-2-amine (**1h**, 50 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide analytically pure product **2h** as white solid (50 mg, 0.18 mmol, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.74 (*dd*, *J* = 9.2, 5.7 Hz, 1H, CH_{arom}), 8.43 (*s*, 1H, CH_{arom}), 7.79 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.69 (*s*, 1H, CH_{arom}), 7.62 – 7.34 (*m*, 8H, CH_{arom}), 2.65 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 161.4 (*d*, *J* = 244.6 Hz, C), 140.6 (C), 137.4 (*d*, *J* = 3.9 Hz, C), 136.9 (C), 133.1 (*d*, *J* = 8.9 Hz, C), 130.1 (2 × CH), 129.9 (C), 129.2 (C), 128.8 (CH), 128.6 (3 × CH), 128.6 (CH), 127.7 (CH), 127.1 (*d*, *J* = 1.9 Hz, C), 125.4 (*d*, *J* = 9.0 Hz, CH), 122.2 (CH), 115.4 (*d*, *J* = 23.6 Hz, CH), 111.6 (*d*, *J* = 21.5 Hz, CH), 22.3 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{21}H_{15}F$: 286.1152, found: 286.1146 [$M^{+\cdot}$]. **IR** (neat): 3056*m*, 2374*m*, 1619*s*, 1499*s*, 1452*s*, 1370*w*, 1311*w*, 1254*m*, 1207*s*, 1138*w*, 972*m*, 872*s*, 821*s*, 770*s*, 702*s*, 584*s*. **MP**: 82 °C.

1-(6-Methyl-10-phenylphenanthren-2-yl)ethan-1-one (2i)



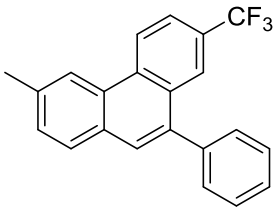
According to **GP2** with 1-(2'-amino-5'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (**1i**, 56 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2i** as white solid (62 mg, 0.20 mmol, 82%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.81 (*d*, *J* = 8.7 Hz, 1H, CH_{arom}), 8.68 – 8.49 (*m*, 2H, CH_{arom}), 8.20 (*dd*, *J* = 8.7, 1.9 Hz, 1H, CH_{arom}), 7.82 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.72 (*s*, 1H, CH_{arom}), 7.63 – 7.46 (*m*, 6H, CH_{arom}), 2.66 (*s*, 3H, CH_3), 2.59 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 198.1 (C), 140.2 (C), 138.3 (C), 136.9 (C), 134.8 (C), 133.5 (C), 130.7 (C), 130.5 (C), 130.0 (2 × CH), 129.8 (CH), 129.4 (C), 128.7 (CH), 128.5 (2 × CH), 128.3 (CH), 128.3 (CH), 127.7 (CH), 124.7 (CH), 123.4 (CH), 122.9 (CH), 26.6 (CH_3), 22.2 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{23}H_{18}O$: 310.1350, found: 310.1352 [$M^{+\cdot}$]. **IR** (neat): 2920*w*, 1680*s*, 1602*m*, 1495*w*, 1417*w*, 1372*w*, 1268*s*, 1149*w*, 899*w*, 829*w*, 767*w*, 703*m*, 595*w*. **MP**: 133 °C.

Methyl 6-methyl-10-phenylphenanthrene-2-carboxylate (2j)



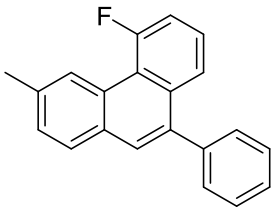
According to **GP2** with methyl 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carboxylate (**1j**, 60 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 50:1 mixture of pentane/Et_2O as eluent to provide analytically pure product **2j** as yellow solid (54 mg, 0.17 mmol, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.80 (*d*, *J* = 8.7 Hz, 1H, CH_{arom}), 8.66 (*d*, *J* = 1.8 Hz, 1H, CH_{arom}), 8.62 – 8.50 (*m*, 1H, CH_{arom}), 8.25 (*dd*, *J* = 8.7, 1.8 Hz, 1H, CH_{arom}), 7.81 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.70 (*s*, 1H, CH_{arom}), 7.59 – 7.45 (*m*, 6H, CH_{arom}), 3.92 (*s*, 3H, CH_3), 2.66 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 167.3 (C), 140.3 (C), 138.2 (C), 136.8 (C), 133.5 (C), 130.7 (C), 130.4 (C), 130.1 (2 × CH), 129.7 (CH), 129.4 (C), 129.1 (CH), 128.6 (CH), 128.5 (2 × CH), 128.2 (CH), 127.8 (C), 127.6 (CH), 126.1 (CH), 123.1 (CH), 122.9 (CH), 52.2 (CH_3), 22.2 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{23}H_{19}O_2Na$: 349.1199, found: 349.1203 ([M+Na]$^+$). **IR** (neat): 30324*w*, 2950*w*, 1717*s*, 1616*w*, 1496*w*, 1435*m*, 1370*w*, 1273*s*, 1240*m*, 1118*m*, 996*w*, 909*w*, 809*w*, 763*m*, 585*w*. **MP**: 174 °C.

6-Methyl-10-phenyl-2-(trifluoromethyl)phenanthrene (2k)



According to **GP2** with 5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (**1k**, 63 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2k** as yellowish solid (60 mg, 0.18 mmol, 72%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.90 – 8.78 (*m*, 1H, CH_{arom}), 8.55 – 8.49 (*m*, 1H, CH_{arom}), 8.23 (*dt*, *J* = 1.9, 0.9 Hz, 1H, CH_{arom}), 7.89 – 7.79 (*m*, 2H, CH_{arom}), 7.75 (*s*, 1H, CH_{arom}), 7.63 – 7.46 (*m*, 6H, CH_{arom}), 2.67 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.1 (C), 137.9 (C), 137.1 (C), 132.6 (C), 130.9 (C), 130.4 (C), 130.1 (2 × CH), 129.8 (CH), 129.4 (C), 128.9 (CH), 128.7 (CH), 128.4 (*q*, *J* = 32.2 Hz, C) 127.9 (2 × CH), 124.3 (*q*, *J* = 4.4 Hz, CH), 123.9 (CH), 122.8 (CH), 122.7 (*q*, *J* = 272.5 Hz, CF_3), 122.2 (*q*, *J* = 4.4 Hz, CH), 22.3 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{22}H_{15}F_3$: 336.1116, found: 3369.1120 [$M^{+\cdot}$]. **IR** (neat): 2253*w*, 1374*w*, 1325*m*, 1127*m*, 903*s*, 723*s*, 649*m*. **MP**: 127 °C.

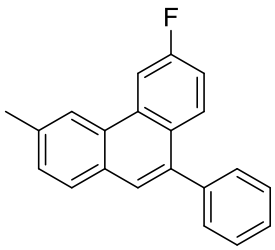
5-Fluoro-3-methyl-9-phenylphenanthrene (2m)



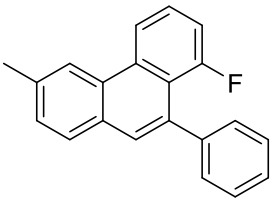
According to **GP2** with 2'-fluoro-5-methyl-[1,1'-biphenyl]-2-amine (**1m**, 50 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide analytically pure product **2m** as colorless oil (25 mg, 90 µmol, 35%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.98 (*dt*, *J* = 1.8, 0.9 Hz, 1H, CH_{arom}), 7.81 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.75 – 7.67 (*m*, 2H, CH_{arom}), 7.59 - 7.32 (*m*, 8H, CH_{arom}), 2.66 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 161.7 (*d*, *J* = 252.1 Hz, C), 140.9 (C), 137.3 (*d*, *J* = 3.0 Hz, C), 136.9 (*d*, *J* = 2.5 Hz, C), 134.2 (*d*, *J* = 4.5 Hz, C), 130.1 (2 × CH), 130.0 (C), 128.8 (*d*, *J* = 1.4 Hz, CH), 128.7 (*d*, *J* = 2.2 Hz, CH), 128.4 (CH), 128.3 (2 × CH), 128.1 (*d*, *J* = 5.4 Hz, CH), 127.4 (CH), 127.4 (*d*, *J* = 25.4 Hz, CH), 126.3 (*d*, *J* = 10.3 Hz, CH), 122.9 (*d*, *J* = 3.5 Hz, CH), 119.8 (*d*, *J* = 8.9 Hz, C), 113.2 (*d*, *J* = 25.4 Hz, CH), 22.2 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{21}H_{15}F$: 286.1152, found: 286.1146 [$M^{+\cdot}$]. **IR** (neat): 2919*w*, 2371*w*, 1617*w*, 1568*w*, 1492*w*, 1447*s*, 1384*w*, 1324*w*, 1221*m*, 896*m*, 809*m*, 766*s*, 702*s*.

6-Fluoro-3-methyl-9-phenylphenanthrene (2n) and 1-fluoro-6-methyl-10-phenyl-phenanthrene (2n')

According to **GP2** with 3'-fluoro-5-methyl-[1,1'-biphenyl]-2-amine (**1n**, 50 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide the analytically pure product **2n** (20 mg, 70 µmol, 28%) along with **2n'** (35 mg, 0.12 mmol, 49%).

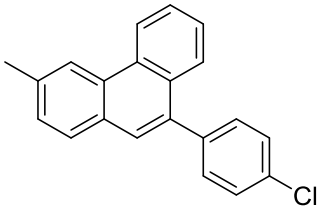


2n Minor regioisomer (white solid): **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.40 – 8.32 (*m*, 2H, CH_{arom}), 7.89 (*dd*, *J* = 9.1, 6.0 Hz, 1H, CH_{arom}), 7.79 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.60 (*s*, 1H, CH_{arom}), 7.57 - 7.43 (*m*, 6H, CH_{arom}), 7.30 – 7.21 (*m*, 1H, CH_{arom}), 2.65 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 161.6 (*d*, *J* = 245.6 Hz, C), 140.9 (C), 137.6 (C), 136.6 (C), 132.3 (*d*, *J* = 8.5 Hz, C), 130.2 (CH), 130.1 (*d*, *J* = 8.5 Hz, CH), 129.6 (*d*, *J* = 8.1 Hz, C), 129.4 (CH), 129.3 (*d*, *J* = 8.1 Hz, CH), 128.7 (CH), 128.5 (2 × CH), 128.2 (*d*, *J* = 1.5 Hz, C), 127.6 (CH), 126.7 (*d*, *J* = 2.3 Hz, CH), 122.6 (CH), 115.3 (*d*, *J* = 23.5 Hz, CH), 108.1 (*d*, *J* = 23.5 Hz, CH), 22.3 (CH_3). **IR** (neat): 3014*w*, 2362*s*, 1601*m*, 1524*m*, 1439*m*, 1273*w*, 1201*m*, 948*w*, 863*w*, 823*w*, 767*w*, 701*m*, 513*s*. **HRMS** (APCI) exact mass calculated for $C_{21}H_{15}F$: 286.1152, found: 286.1154 [$M^{+\cdot}$]. **MP**: 93 °C.



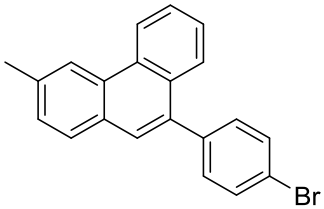
2n' Major regioisomer (colorless oil): **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.58 (*dd*, *J* = 8.5, 1.1 Hz, 1H, CH_{arom}), 8.52 – 8.45 (*m*, 1H, CH_{arom}), 7.77 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.64 – 7.52 (*m*, 2H, CH_{arom}), 7.54 – 7.38 (*m*, 6H, CH_{arom}), 7.20 (*ddd*, *J* = 12.5, 7.8, 1.1 Hz, 1H, CH_{arom}), 2.66 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 159.7 (*d*, *J* = 256.8 Hz, C), 143.6 (*d*, *J* = 3.5 Hz, C), 136.9 (C), 134.0 (C), 132.9 (*d*, *J* = 3.2 Hz, C), 130.0 (CH), 129.5 (C), 129.3 (C), 129.2 (CH), 128.8 (CH), 128.8 (CH), 128.5 (CH), 127.5 (2 × CH), 126.7 (CH), 126.5 (*d*, *J* = 9.2 Hz, C), 122.7 (CH), 120.6 (*d*, *J* = 8.9 Hz, C), 118.9 (*d*, *J* = 3.9 Hz, CH), 112.7 (*d*, *J* = 23.0 Hz, CH), 22.2 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{21}H_{15}F$: 286.1152, found: 286.1145 [$M^{+\cdot}$]. **IR** (neat): 3055*m*, 2919*w*, 1599*m*, 1519*w*, 1456*s*, 1369*m*, 1241*s*, 1143*m*, 895*m*, 810*s*, 752*s*, 701*s*.

9-(4-Chlorophenyl)-3-methylphenanthrene (2o)



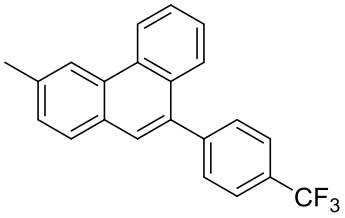
According to **GP3** with 1-chloro-4-ethynylbenzene (344 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product **2o** as yellowish solid (56 mg, 0.19 mmol, 74%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.88 - 8.66 (*m*, 1H, CH_{arom}), 8.61 – 8.42 (*m*, 1H, CH_{arom}), 7.88 – 7.77 (*m*, 2H, CH_{arom}), 7.70 – 7.59 (*m*, 2H, CH_{arom}), 7.56 – 7.40 (*m*, 6H, CH_{arom}), 2.65 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 139.4 (C), 136.6 (C), 136.5 (C), 133.3 (C), 131.4 (2 × CH), 131.0 (C), 130.4 (C), 130.1 (C), 129.4 (C), 128.7 (CH), 128.5 (CH), 128.5 (2 × CH), 127.5 (CH), 126.5 (CH), 126.5 (CH), 126.4 (CH), 123.0 (CH), 122.3 (CH), 22.2 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{21}H_{15}Cl$: 302.0857, found: 302.0850 [$M^{+\cdot}$]. **IR** (neat): 3064*w*, 2919*w*, 1606*w*, 1489*s*, 1448*w*, 1400*w*, 1149*w*, 1091*s*, 1015*m*, 949*w*, 894*m*, 834*s*. **MP**: 88 °C.

9-(4-Bromophenyl)-3-methylphenanthrene (2p)



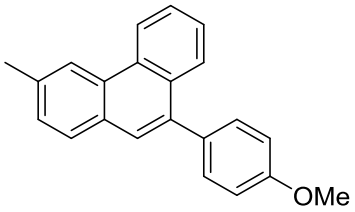
According to **GP3** with 1-bromo-4-ethynylbenzene (453 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product **2p** as yellow solid (60 mg, 0.17 mmol, 69%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.70 – 8.63 (*m*, 1H, CH_{arom}), 8.42 (*s*, 1H, CH_{arom}), 7.78 – 7.67 (*m*, 2H, CH_{arom}), 7.60 – 7.50 (*m*, 4H, CH_{arom}), 7.50 – 7.37 (*m*, 1H, CH_{arom}), 7.38 – 7.30 (*m*, 3H, CH_{arom}), 2.56 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.0 (C), 136.7 (C), 136.6 (C), 131.9 (2 × CH), 131.6 (2 × CH), 131.1 (C), 130.5 (C), 130.3 (C), 129.5 (C), 128.8 (CH), 128.7 (CH), 127.6 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 123.1 (CH), 122.5 (CH), 121.6 (CH), 22.4 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{21}H_{15}Br$: 346.0352, found: 346.0346 [$M^{+\cdot}$]. **IR** (neat): 2254*w*, 1067*w*, 1488*m*, 1387*w*, 1170*w*, 1074*w*, 1011*m*, 904*s*, 833*m*. **MP**: 100 °C.

3-Methyl-9-(4-(trifluoromethyl)phenyl)phenanthrene (2q)



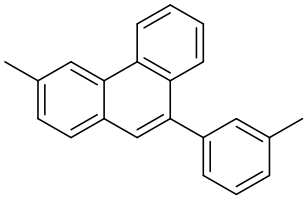
According to **GP3** with 1-ethynyl-4-(trifluoromethyl)benzene (426 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 50:1 mixture of pentane/DCM as eluent to provide analytically pure product **2q** as yellowish solid (61 mg, 0.18 mmol, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.79 (*dd*, *J* = 8.4, 1.1 Hz, 1H, CH_{arom}), 8.53 (*s*, 1H, CH_{arom}), 7.85 – 7.75 (*m*, 4H, CH_{arom}), 7.73 – 7.62 (*m*, 4H, CH_{arom}), 7.57 – 7.50 (*m*, 1H, CH_{arom}), 7.48 (*dd*, *J* = 8.1, 1.6 Hz, 1H, CH_{arom}), 2.67 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 144.9 (C), 137.0 (C), 136.5 (C), 130.9 (C), 130.6 (2 × CH), 130.6 (C), 130.4 (C), 129.7 (*q*, *J* = 32.7 Hz, C), 129.4 (C), 128.9 (CH), 128.8 (CH), 127.8 (CH), 126.8 (CH), 126.6 (CH), 126.5 (CH), 125.4 (*q*, *J* = 3.9 Hz, 2 × CH), 124.5 (*q*, *J* = 271.2 Hz, CF_3) 123.2 (CH), 122.5 (CH), 22.4 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{22}H_{15}F_3$: 336.1120, found: 336.1114 [$M^{+\cdot}$]. **IR** (neat): 3071*w*, 2923*w*, 16116*w*, 1504*w*, 1450*w*, 1410*w*, 1323*s*, 1164*m*, 1123*s*, 1066*m*, 1019*w*, 957*w*, 895*w*, 847*m*. **MP**: 92 °C.

9-(4-Methoxyphenyl)-3-methylphenanthrene (2r)



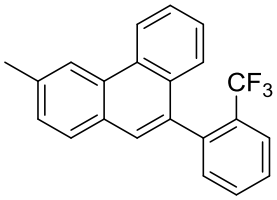
According to **GP3** with 1-ethynyl-4-methoxybenzene (330 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/Et_2O as eluent to provide analytically pure product **2r** as yellow foam (60 mg, 0.20 mmol, 80%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.81 - 8.73 (*m*, 1H, CH_{arom}), 8.52 (*d*, *J* = 1.6 Hz, 1H, CH_{arom}), 7.95 (*dd*, *J* = 8.2, 1.4 Hz, 1H, CH_{arom}), 7.79 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.70 – 7.62 (*m*, 2H, CH_{arom}), 7.58 – 7.40 (*m*, 4H, CH_{arom}), 7.06 (*d*, *J* = 8.6 Hz, 2H, CH_{arom}), 3.92 (*s*, 3H, OCH_3), 2.66 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 159.0 (C), 137.4 (C), 136.1 (C), 133.3 (C), 131.6 (C), 131.2 (2 × CH), 130.4 (C), 129.9 (C), 129.6 (C), 128.5 (CH), 128.4 (CH), 127.3 (CH), 126.9 (CH), 126.3 (CH), 126.1 (CH), 122.9 (CH), 122.3 (CH), 113.8 (2 × CH), 55.4 (OCH_3), 22.2 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{22}H_{18}O$: 298.1352, found: 298.1346 [$M^{+\cdot}$]. **IR** (neat): 3017*w*, 2955*w*, 2930*w*, 2835*w*, 1609*m*, 1507*s*, 1459*m*, 1377*w*, 1284*w*, 1245*s*, 1175*m*, 1107*w*, 1034*m*, 905*m*, 836*m*. **MP**: 103 °C.

3-Methyl-9-(*m*-tolyl)phenanthrene (2s)



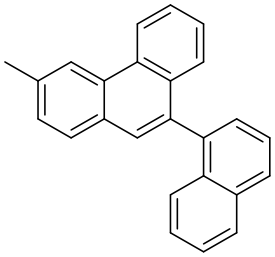
According to **GP3** with 1-ethynyl-3-methylbenzene (290 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product **2s** as yellowish oil (52 mg, 0.19 mmol, 74%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.77 (*dd*, *J* = 8.3, 1.2 Hz, 1H, CH_{arom}), 8.52 (*d*, *J* = 1.6 Hz, 1H, CH_{arom}), 7.93 (*dd*, *J* = 8.3, 1.4 Hz, 1H, CH_{arom}), 7.80 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 7.69 – 7.61 (*m*, 2H, CH_{arom}), 7.53 (*ddd*, *J* = 8.2, 6.9, 1.3 Hz, 1H, CH_{arom}), 7.49 – 7.33 (*m*, 4H, CH_{arom}), 7.31 – 7.25 (*m*, 1H, CH_{arom}), 2.66 (*s*, 3H, CH_3), 2.47 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.9 (C), 138.0 (C), 137.9 (C), 136.2 (C), 131.4 (C), 130.8 (CH), 130.4 (C), 130.0 (C), 129.6 (C), 128.6 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.2 (CH), 127.2 (CH), 127.0 (CH), 126.3 (CH), 126.2 (CH), 122.8 (CH), 122.3 (CH), 22.2 (CH_3), 21.5 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{22}H_{18}$: 282.1403, found: 282.1396 [$M^{+\cdot}$]. **IR** (neat): 3020*m*, 2918*m*, 2858*w*, 1600*s*, 1503*m*, 1449*s*, 1377*m*, 1168*w*, 1199*w*, 1091*w*, 1043*m*, 954*w*, 891*s*.

3-Methyl-9-(2-(trifluoromethyl)phenyl)phenanthrene (2t)



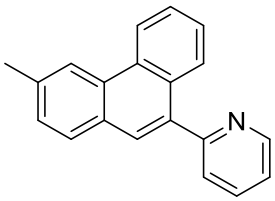
According to **GP3** with 1-ethynyl-2-(trifluoromethyl)benzene (425 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically product **2t** as brown oil (68 mg, 0.20 mmol, 81%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.78 (*dd*, *J* = 8.4, 1.2 Hz, 1H, CH_{arom}), 8.62 – 8.46 (*m*, 1H, CH_{arom}), 7.89 (*dd*, *J* = 7.6, 1.6 Hz, 1H, CH_{arom}), 7.81 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.70 – 7.57 (*m*, 4H, CH_{arom}), 7.51 – 7.35 (*m*, 4H, CH_{arom}), 2.68 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 139.5 (C), 136.7 (C), 134.4 (C), 132.9 (CH), 132.0 (C), 131.2 (CH), 130.3 (C), 130.1 (*q*, *J* = 29.9 Hz, C), 130.0 (C), 129.0 (C), 128.7 (CH), 128.6 (CH), 127.7 (CH), 127.7 (CH), 127.0 (CH), 126.4 (CH), 126.2 (2 × CH), 124.1 (*q*, *J* = 271.2 Hz, CF_3), 122.7 (CH), 122.4 (CH), 22.2 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{22}H_{15}F_3$: 336.1120, found: 336.1114 [$M^{+\cdot}$]. **IR** (neat): 3068*w*, 2922*w*, 1602*w*, 1503*w*, 1451*w*, 1314*s*, 1264*w*, 1168*m*, 1126*s*, 1035*m*, 899*w*.

3-Methyl-9-(naphthalen-1-yl)phenanthrene (2u)



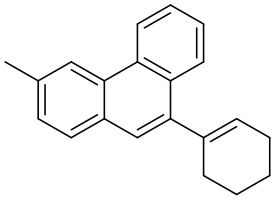
According to **GP3** with 1-ethynylnaphthalene (381 mg, 2,50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product **2u** as white solid (68 mg, 0.21 mmol, 85%) along with small amounts of another unidentified isomer. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.81 (*d*, *J* = 8.2 Hz, 1H, CH_{arom}), 8.60 (*s*, 1H, CH_{arom}), 8.00 – 7.94 (*m*, 2H, CH_{arom}), 7.81 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 7.75 (*s*, 1H, CH_{arom}), 7.66 – 7.30 (*m*, 9H, CH_{arom}), 2.70 (*s*, 3H, CH_{arom}). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 138.8 (C), 136.6 (C), 136.2 (C), 133.7 (C), 133.2 (C), 132.5 (C), 130.5 (C), 130.2 (C), 129.7 (C), 128.8 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 126.1 (CH), 126.0 (CH), 125.6 (CH), 122.9 (CH), 122.5 (CH), 22.4 (CH_3). **HRMS** (APCI) exact mass calculated for $C_{25}H_{18}$: 318.1403, found: 318.1394 [$M^{+\cdot}$]. **IR** (neat): 3058*m*, 2165*w*, 1920*w*, 1591*m*, 1504*s*, 1449*m*, 1378*m*, 1038*w*, 906*s*. **MP**: 82 °C.

2-(3-Methylphenanthren-9-yl)pyridine (2v)



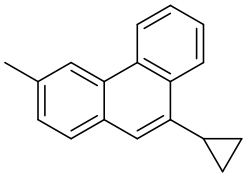
According to **GP3** with 2-ethynylpyridine (258 mg, 2.50 mmol, 10.0 equiv.) Crude product was purified by flash column chromatography on silica gel using a 10:1 mixture of pentane/Et_2O as eluent to provide analytically pure product **2v** as green oil (44 mg, 0.17 mmol, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.84 (*d*, *J* = 4.9 Hz, 1H, CH_{arom}), 8.77 (*dd*, *J* = 8.3, 1.3 Hz, 1H, CH_{arom}), 8.56 – 8.50 (*m*, 1H, CH_{arom}), 8.08 (*dd*, *J* = 8.2, 1.4 Hz, 1H, CH_{arom}), 7.88 – 7.82 (*m*, 3H, CH_{arom}), 7.72 – 7.62 (*m*, 2H, CH_{arom}), 7.59 – 7.53 (*m*, 1H, CH_{arom}), 7.46 (*dd*, *J* = 8.1, 1.6 Hz, 1H, CH_{arom}), 7.40 – 7.34 (*m*, 1H, CH_{arom}), 2.65 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 159.5 (C), 149.5 (CH), 137.0 (2 × C), 136.7 (CH), 136.1 (C), 130.7 (C), 130.5 (C), 129.4 (C), 129.0 (CH), 128.7 (CH), 128.6 (CH), 126.7 (CH), 126.5 (CH), 126.5 (CH), 125.3 (CH), 123.0 (CH), 122.5 (CH), 122.2 (CH), 22.4 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{20}H_{15}NH$: 270.1227, found: 270.1282 ([M+H]$^+$). **IR** (neat): 3051*w*, 2918*w*, 1584*s*, 1521*w*, 1468*s*, 1450*m*, 1382*w*, 1254*w*, 1150*m*, 1046*m*, 933*m*, 895*m*, 786*s*, 763*s*, 725*s*, 586*m*.

9-(Cyclohex-1-en-1-yl)-3-methylphenanthrene (2w)



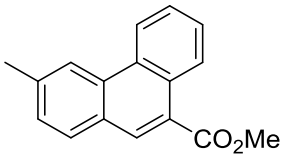
According to **GP3** with 1-ethynylcyclohex-1-ene (256 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2w** as colorless oil (31 mg, 0.12 mmol, 46%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.75 – 8.66 (*m*, 1H, CH_{arom}), 8.46 (*s*, 1H, CH_{arom}), 8.04 (*dd*, *J* = 8.0, 1.6 Hz, 1H, CH_{arom}), 7.75 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.66 – 7.56 (*m*, 2H, CH_{arom}), 7.51 (*s*, 1H, CH_{arom}), 7.46 – 7.38 (*m*, 2H, CH_{arom}), 5.86 (*dt*, *J* = 3.7, 1.9 Hz, 1H, C=C*H*), 2.63 (*s*, 3H, CH_3), 2.48 – 2.40 (*m*, 2H, CH_2), 2.37 – 2.24 (*m*, 2H, CH_2), 1.95 - 1.77 (*m*, 4H, 2 × CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 140.6 (C), 138.2 (C), 135.7 (C), 130.3 (C), 129.8 (C), 129.7 (C), 128.7 (C), 128.3 (CH), 128.2 (CH), 127.1 (CH), 126.5 (CH), 126.1 (CH), 125.9 (CH), 125.0 (CH), 122.9 (CH), 122.2 (CH), 31.0 (CH_2), 25.6 (CH_2), 23.3 (CH_2), 22.4 (CH_3), 22.1 (CH_2). **HRMS** (APCI) exact mass calculated for $C_{21}H_{20}$: 272.1560, found: 272.1553 [$M^{+\cdot}$]. **IR** (neat): 3066*w*, 2924*s*, 2855*m*, 1602*m*, 1502*m*, 1446*m*, 1378*w*, 1342*w*, 1133*w*, 1042*w*, 886*m*.

9-Cyclopropyl-3-methylphenanthrene (2x)



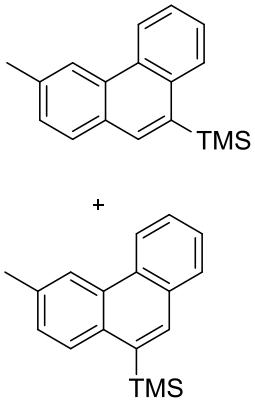
According to **GP3** with ethynylcyclopropane (165 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product **2x** as colorless oil (33 mg, 0.14 mmol, 57%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.73 (*dd*, *J* = 6.3, 3.3 Hz, 1H, CH_{arom}), 8.54 – 8.48 (*m*, 1H, CH_{arom}), 8.48 – 8.44 (*m*, 1H, CH_{arom}), 7.76 – 7.64 (*m*, 3H, CH_{arom}), 7.53 (*t*, *J* = 0.9 Hz, 1H, CH_{arom}), 7.41 (*dd*, *J* = 8.1, 1.6 Hz, 1H, CH_{arom}), 2.63 (*s*, 3H, CH_3), 2.41 – 2.28 (*m*, 1H, CH), 1.15 – 1.06 (*m*, 2H, CH_2), 0.90 – 0.78 (*m*, 2H, CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 136.3 (C), 135.7 (C), 132.9 (C), 130.2 (C), 129.9 (C), 129.7 (C), 128.3 (CH), 128.1 (CH), 126.3 (CH), 126.0 (CH), 125.0 (CH), 124.4 (CH), 122.9 (CH), 122.2 (CH), 22.1 (CH_3), 13.8 (CH), 6.2 (2 × CH_2). **HRMS** (APCI) exact mass calculated for $C_{18}H_{16}$: 232.1247, found: 232.1237 [$M^{+\cdot}$]. **IR** (neat): 3077*m*, 3007*m*, 2917*w*, 1610*m*, 1504*m*, 1433*m* 1327*m*, 1221*w*, 1164*m*, 1124*m*, 1022*m*, 950*w*, 890*s*.

Methyl 3-methylphenanthrene-9-carboxylate (2y)



According to **GP3** with methyl propiolate (210 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 50:1 mixture of pentane/EtOAc as eluent to provide analytically pure product **2y** as brown oil (30 mg, 0.12 mmol, 48%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 9.05 – 8.85 (*m*, 1H, CH_{arom}), 8.78 – 8.66 (*m*, 1H, CH_{arom}), 8.49 – 8.43 (*m*, 2H, CH_{arom}), 7.86 (*d*, *J* = 8.1 Hz, 1H, CH_{arom}), 7.73 – 7.62 (*m*, 2H, CH_{arom}), 7.47 (*dd*, *J* = 8.2, 1.6 Hz, 1H, CH_{arom}), 4.04 (*s*, 3H, CO_2CH_3), 2.64 (*s*, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 168.1 (C), 139.1 (C), 132.4 (CH), 132.3 (C), 130.4 (C), 129.8 (CH), 129.3 (C), 128.8 (CH), 127.9 (C), 127.3 (CH), 126.7 (CH), 126.6 (CH), 125.1 (C), 122.8 (CH), 122.4 (CH), 52.2 (CO_2CH_3), 22.4 (CH_3). **HRMS** (ESI) exact mass calculated for $C_{17}H_{14}O_2Na$: 273.0886, found: 273.0897 ($[M+Na]^+$). **IR** (neat): 2950*w*, 1714*s*, 1621*m*, 1520*w*, 1449*m*, 1296*m*, 1250*s*, 1193*s*, 1161*s*, 1109*m*, 1030*m* 913*w*, 874*w*.

Trimethyl(3-methylphenanthren-9-yl)silane (2z) and trimethyl(6-methylphenanthren-9-yl)silane (2z')



According to **GP3** with ethynyltrimethylsilane (246 mg, 2.50 mmol, 10.0 equiv). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide an inseparable mixture of two isomers as yellow oil (31 mg, 0.12 mmol, 47%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.79 – 8.66 (*m*, 1H, CH_{arom}), 8.51 (*m*, 1H, CH_{arom}), 8.17 – 8.03 (*m*, 1H, CH_{arom}), 7.96 – 7.86 (*m*, 1H, CH_{arom}), 7.79 (*m*, 1H, CH_{arom}), 7.69 – 7.56 (*m*, 2H, CH_{arom}), 7.43 (*dd*, *J* = 7.9, 1.6 Hz, 1H, CH_{arom}), 2.64 (*s*, 3H, CH_3), 0.53 (*s*, 9H, 2 × CH_3). For the major isomer: **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 134.8 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 125.7 (CH), 125.4 (CH), 123.0 (CH), 121.9 (CH), 21.9 (CH_3), 0.0 (3 × CH_3). For the minor isomer: **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 134.8 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 125.7 (CH), 125.4 (CH), 123.0 (CH), 121.9 (CH), 21.9 (CH_3), 0.0 (3 × CH_3). Other signals cannot be clearly identified. **HRMS** (APCI) exact mass calculated for $C_{18}H_{20}Si$: 264.1324, found: 264.1329 [$M^{+\cdot}$]. **IR** (neat): 2932*w*, 2311*w*, 1289*w*, 931*s*, 822*m*, 750*s*, 686*m*.

X-ray crystallographic data

X-Ray diffraction: For the compound **2c** data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014);[4] cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013);[4] data reduction: SAINT V8.34A (Bruker AXS Inc., 2013);[4] absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014);[4] structure solution SHELXT-2014 (Sheldrick, 2014);[5] structure refinement SHELXL-2014 (Sheldrick, 2014) [5] and graphics, XP (Bruker AXS Inc., 2014).[5] For the compound **2g** data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326);[6] absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234);[7] structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473);[8] structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122)[5] and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

X-ray crystal structure analysis of 2c: formula $C_{22}H_{18}$, M = 282.36, colourless crystal, 0.18 x 0.15 x 0.05 mm, a = 11.2196(4), b = 12.1534(4), c = 11.8670(4) Å, β = 112.497(1)°, V = 1495.0(1) $Å^3$, ρ_{calc} = 1.255 gcm^{-3}, μ = 0.532 mm^{-1}, empirical absorption correction (0.911 ≤ T ≤ 0.972), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 100(2) K, ω and φ scans, 15233 reflections collected (±h, ±k, ±l) to a maximum θ angle of 66.60° (0.84 Å resolution), 2634 independent (R_{int} = 0.030) and 2283 observed reflections [I>2σ(I)], 201 refined parameters, R = 0.038, wR^2 = 0.104, max. (min.) residual electron density 0.32 (-0.31) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 2g: formula $C_{21}H_{15}Cl$, M = 302.78, colourless crystal, 0.15 x 0.15 x 0.08 mm, a = 11.2081(2), b = 12.3535(3), c = 11.9376(3) Å, β = 113.383(3) °, V = 1517.1(1) $Å^3$, ρ_{calc} = 1.326 gcm^{-3}, μ = 0.245 mm^{-1}, empirical absorption correction (0.964 ≤ T ≤ 0.980), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 8277 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 $Å^{-1}$, 3609 independent (R_{int} = 0.039) and 2653 observed reflections [I>2σ(I)], 200 refined parameters, R = 0.061,

wR^2 = 0.151, max. (min.) residual electron density 0.22 (-0.23) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

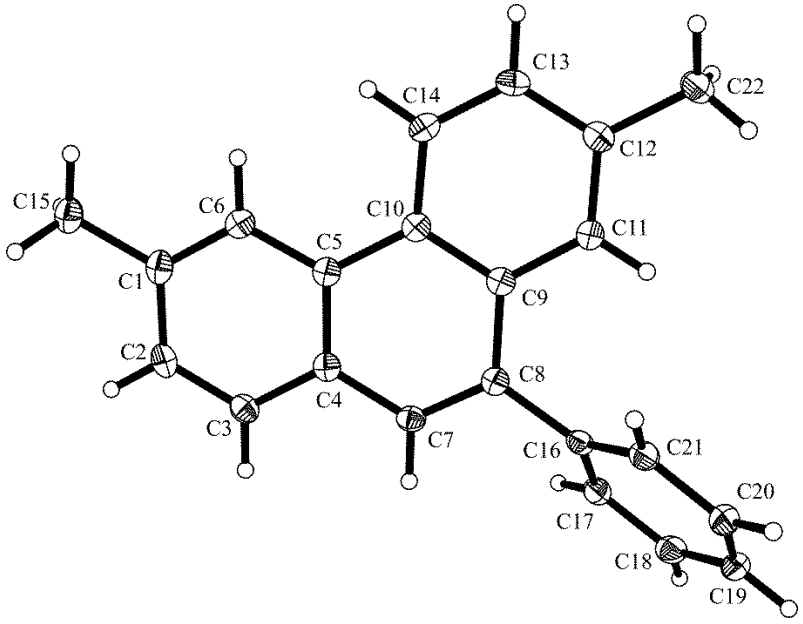


Figure 1. Crystal structure of compound **2c**.

(Thermals ellipsoids are shown with 50% probability.)

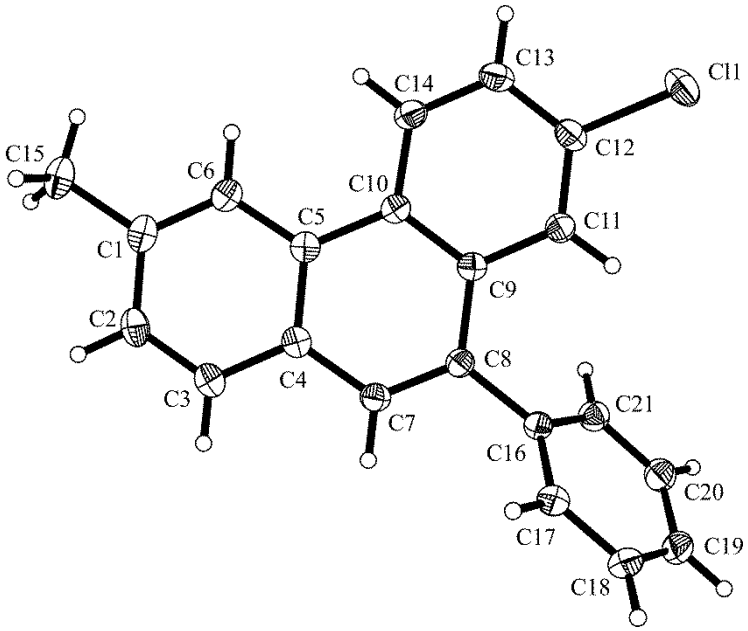
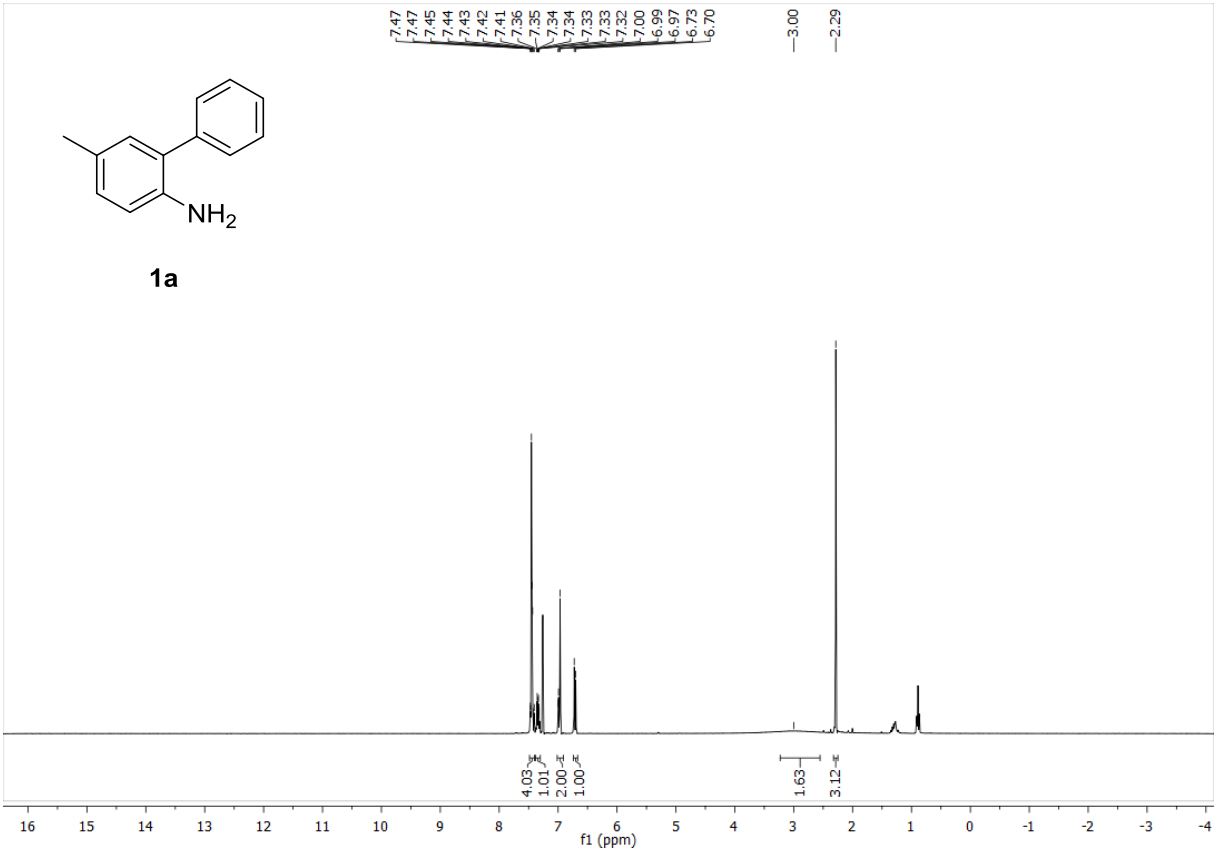
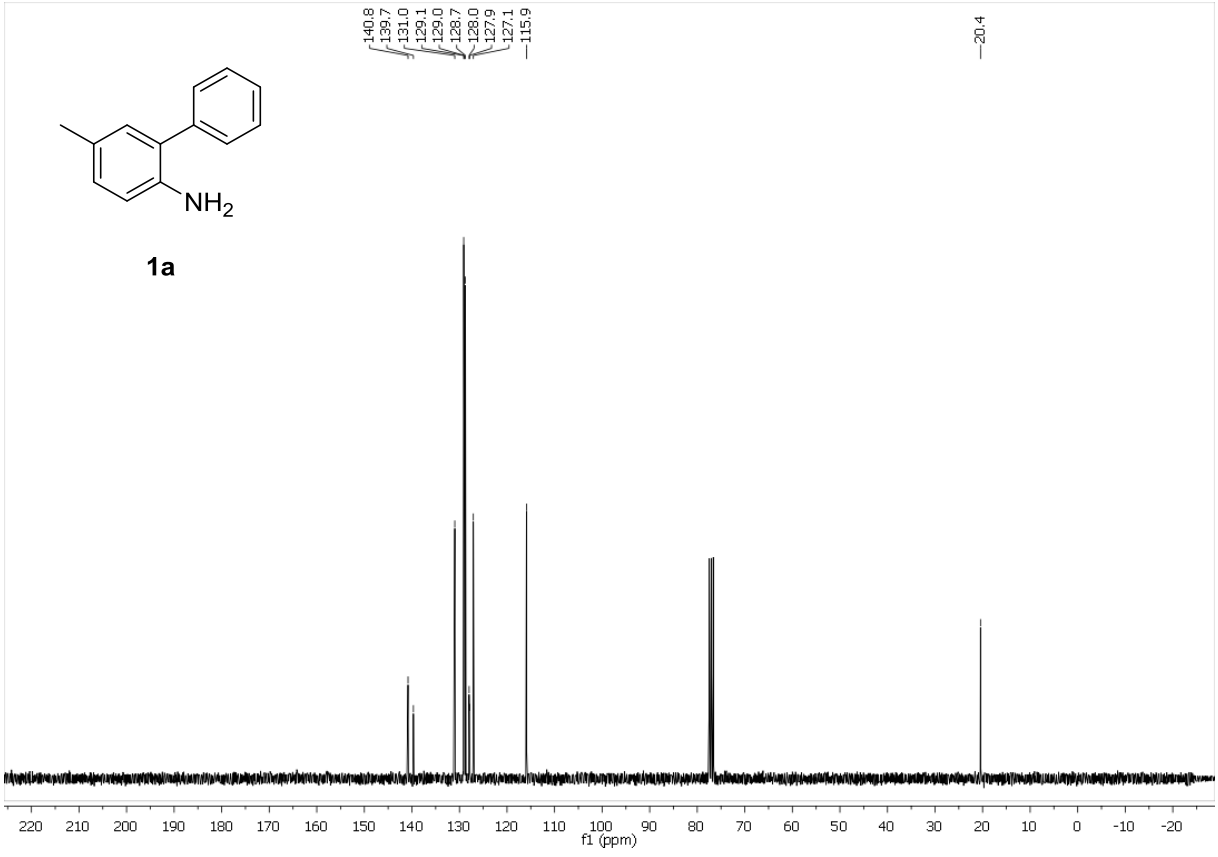


Figure 2. Crystal structure of compound **2g**.

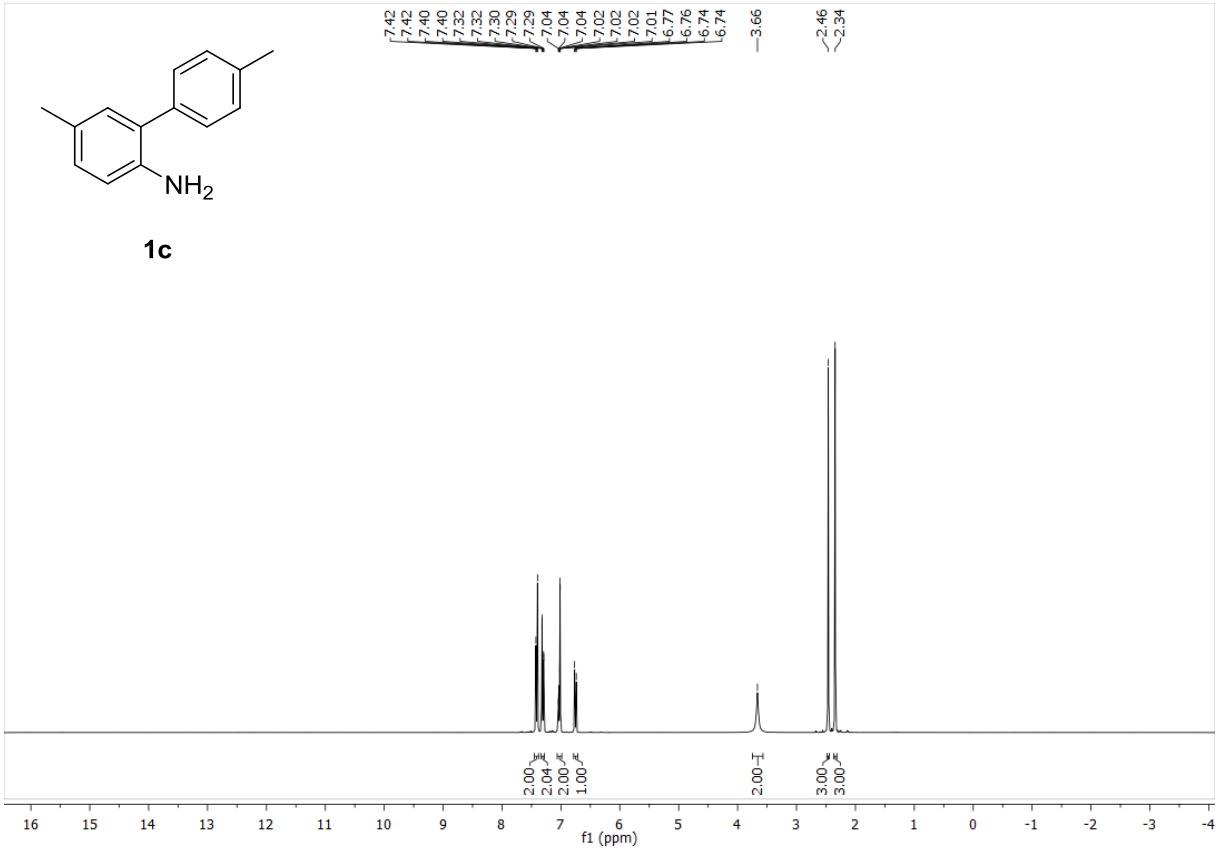
(Thermals ellipsoids are shown with 30% probability.)


7.47
7.47
7.45
7.44
7.43
7.42
7.41
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.00
6.99
6.97
6.73
6.70
3.00
2.29
NH2
4.03
1.01
2.00
1.00
1.63
3.12
f1 (ppm)

1a


140.8
139.7
131.0
129.1
129.0
128.7
128.0
127.9
127.1
115.9
20.4
NH2
f1 (ppm)

1a


7.42
7.42
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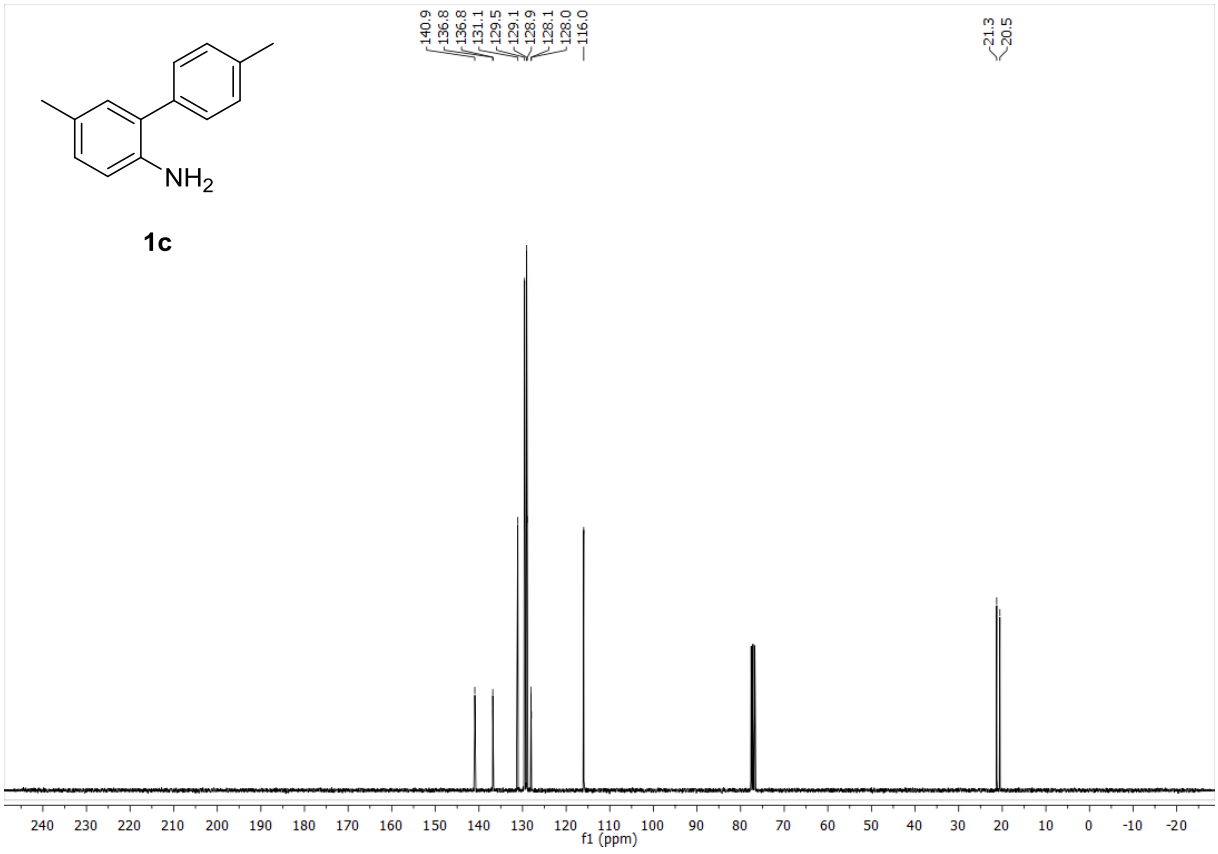
7.32
7.30
7.29
7.29
7.04
7.04
7.04
7.02
7.02
7.02
7.01
6.77
6.76
6.74
6.74
3.66
2.46
2.34
NH2
1c
2.00
2.04
2.00
1.00
2.00
3.00
3.00
f1 (ppm)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128.9
128.1
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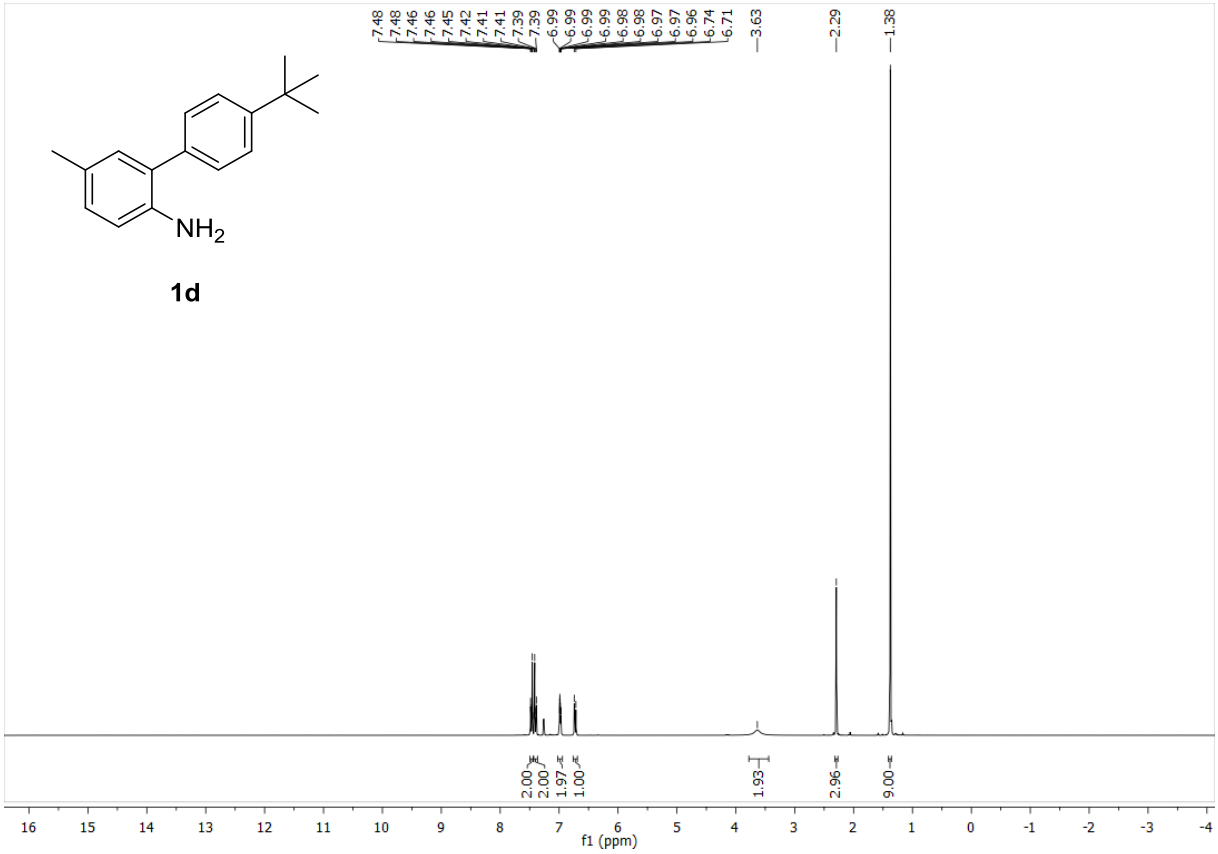
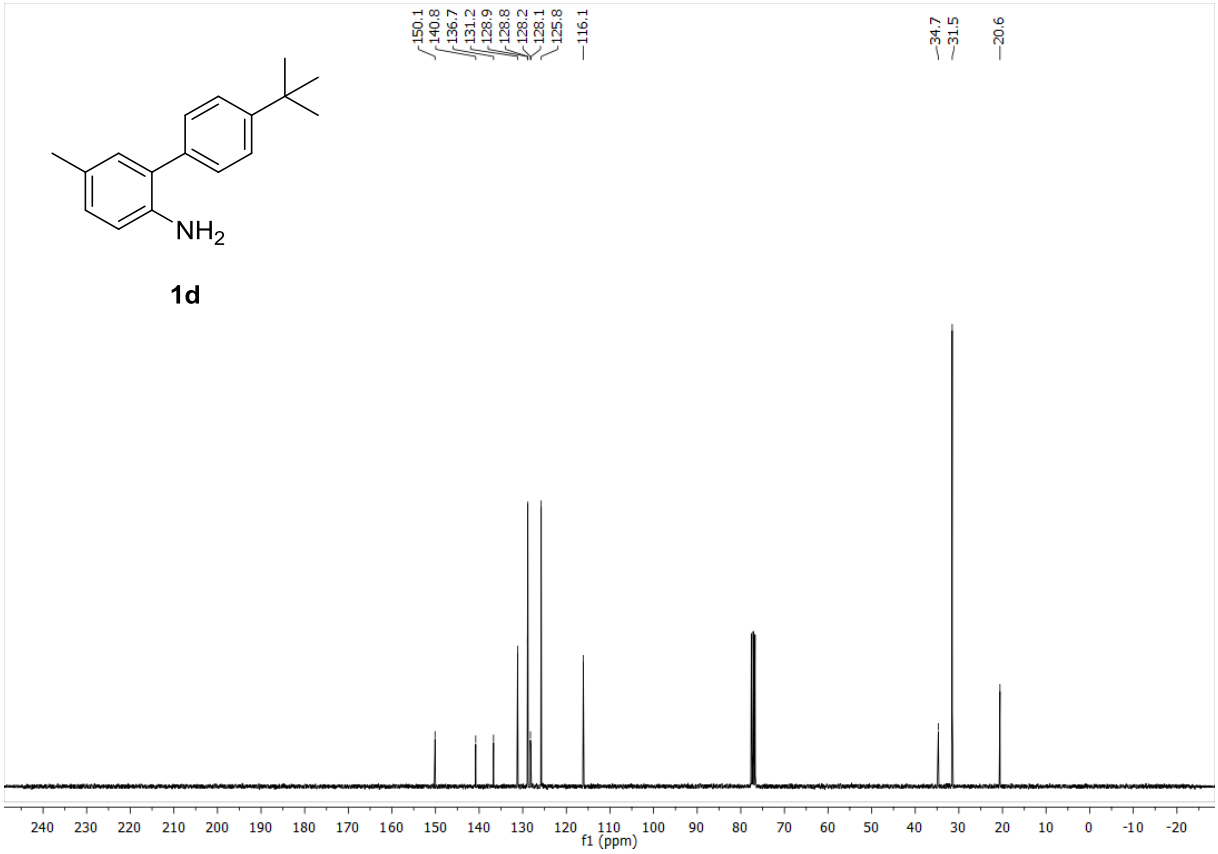
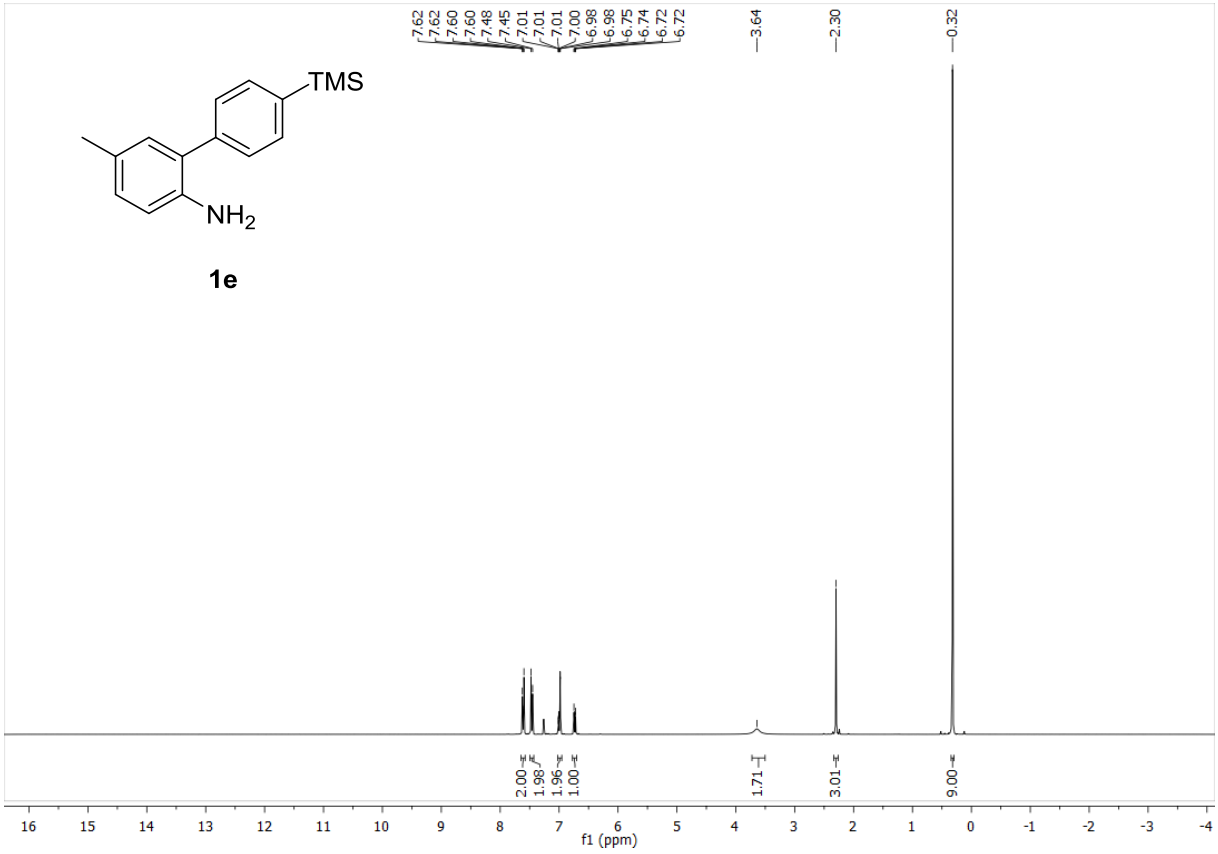
21.3
20.5
NH2
1c
f1 (ppm)


7.48
7.48
7.46
7.46
7.45
7.42
7.41
7.41
7.39
7.39
6.99
6.99
6.99
6.99
6.98
6.98
6.97
6.97
6.96
6.74
6.71
3.63
2.29
1.38
NH2
1d
2.00
2.00
1.97
1.00
1.93
2.96
9.00
f1 (ppm)


150.1
140.8
136.7
131.2
128.9
128.8
128.2
128.1
125.8
116.1
34.7
31.5
20.6
NH2
1d
f1 (ppm)


TMS
NH2
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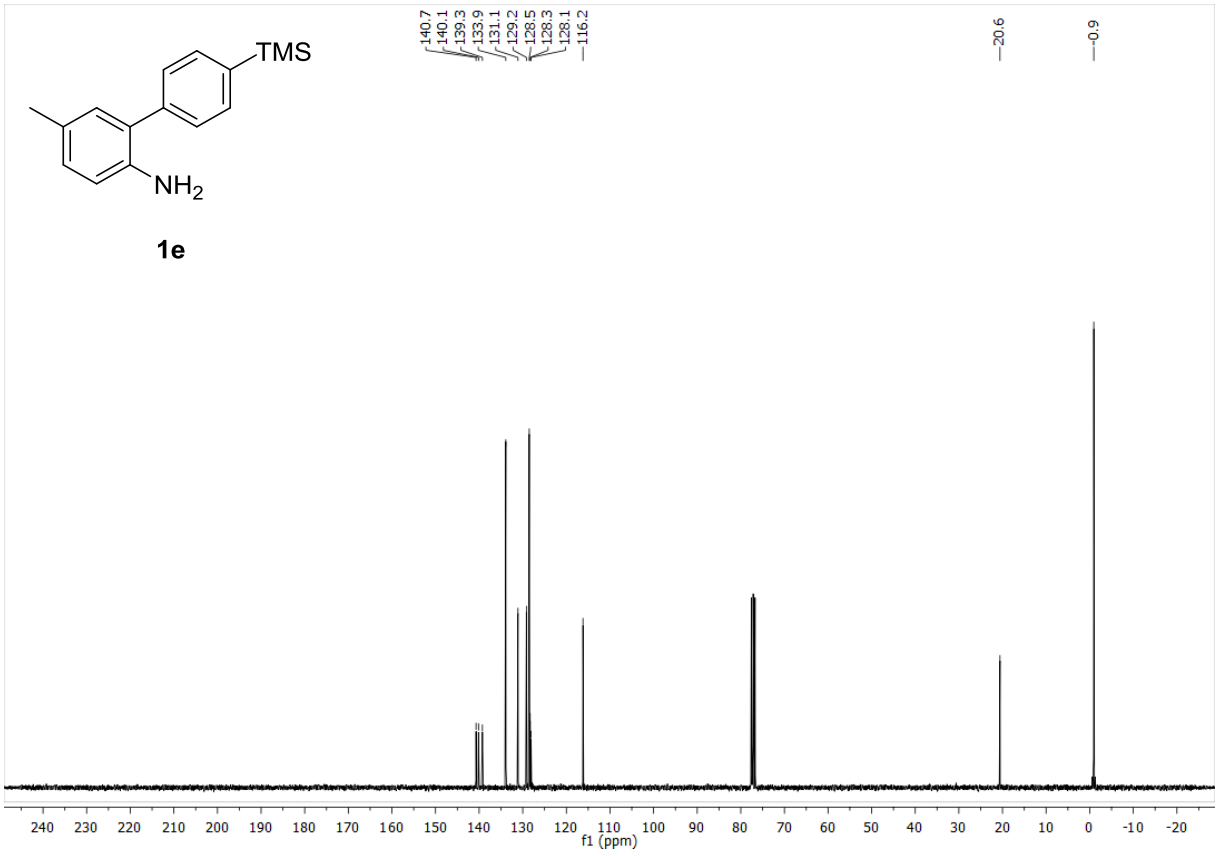
7.62
7.60
7.60
7.48
7.45
7.01
7.01
7.01
7.00
6.98
6.98
6.75
6.74
6.72
6.72
3.64
2.30
0.32
2.00
1.98
1.96
1.00
1.71
3.01
9.00
f1 (ppm)


TMS
NH2
1e
140.7
140.1
139.3
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131.1
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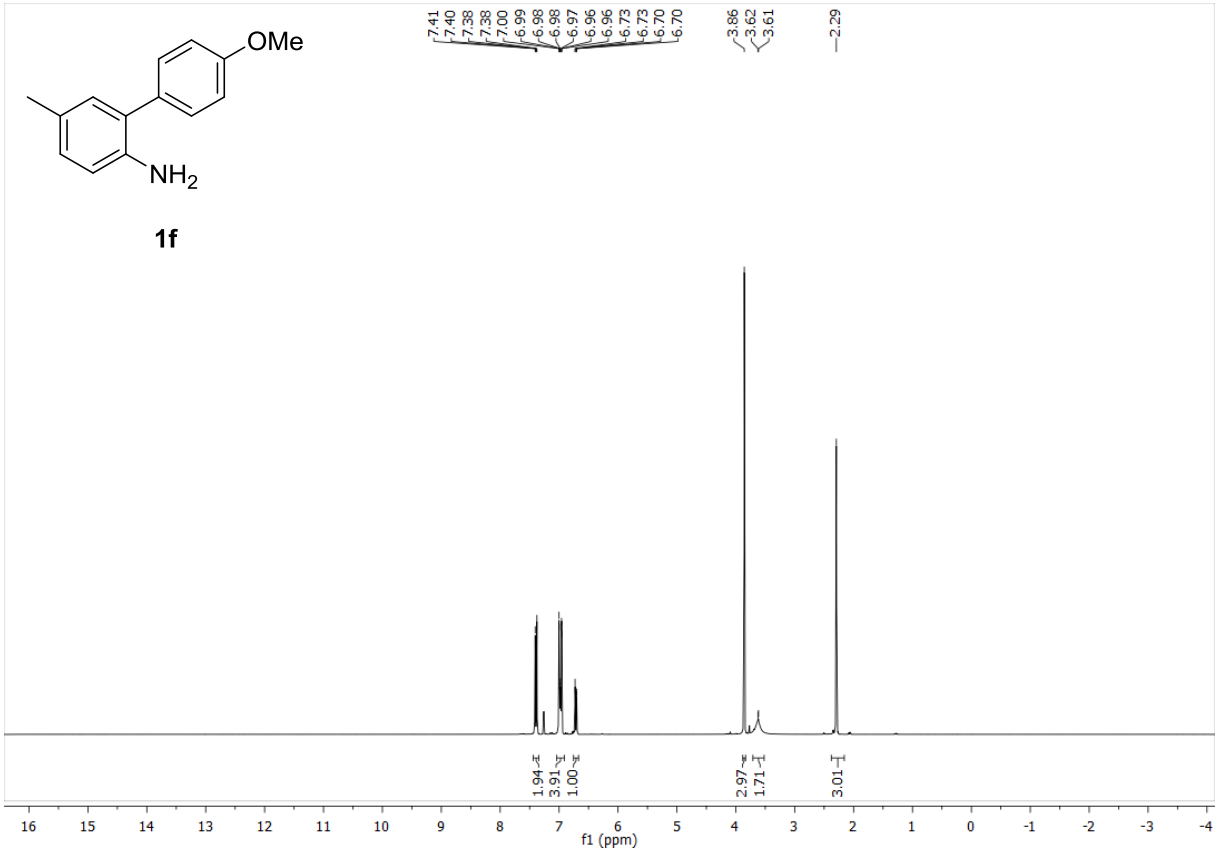
128.3
128.1
116.2
20.6
0.9
f1 (ppm)


OMe
NH2
1f
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7.40
7.38
7.38
7.00
6.99
6.98
6.98
6.97
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6.96
6.73
6.73
6.70
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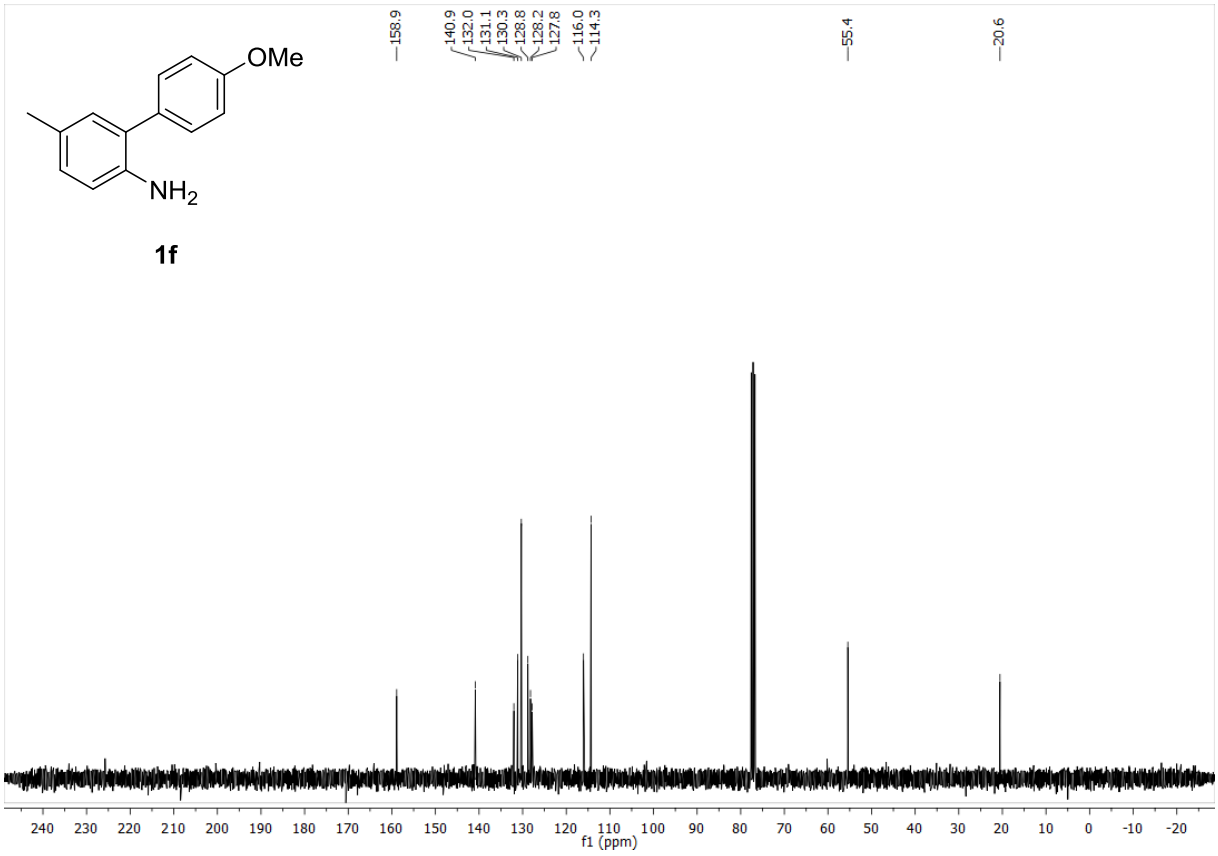
1.00
2.97
1.71
3.01
f1 (ppm)


OMe
NH2
1f
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131.1
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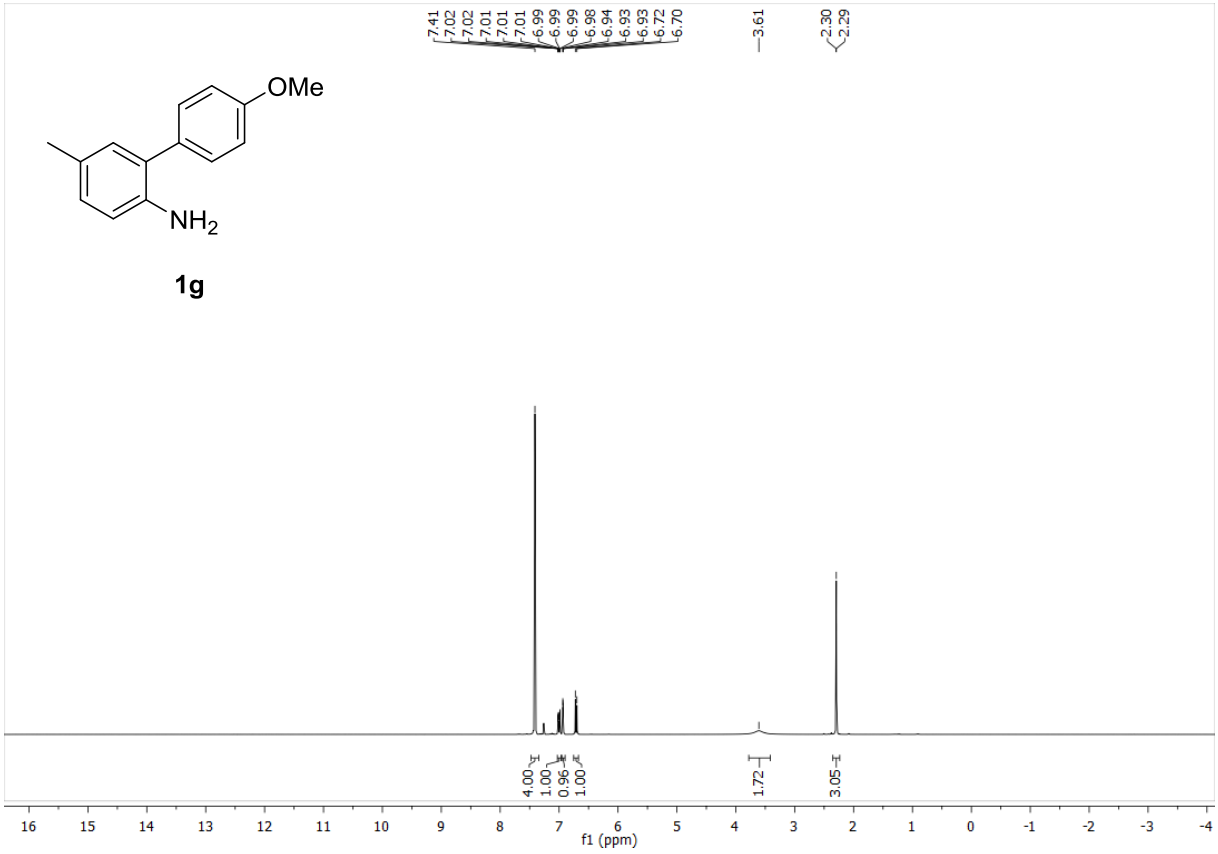
128.2
127.8
116.0
114.3
55.4
20.6
f1 (ppm)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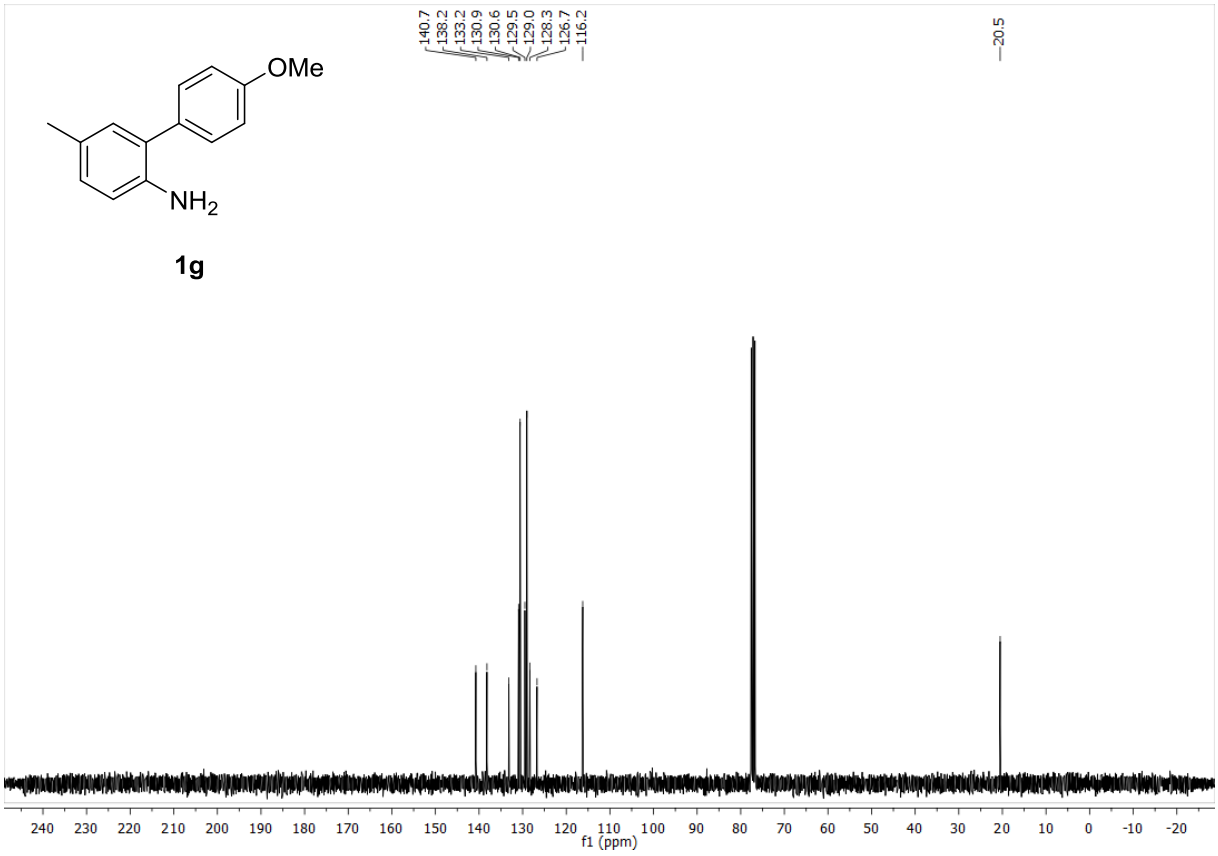
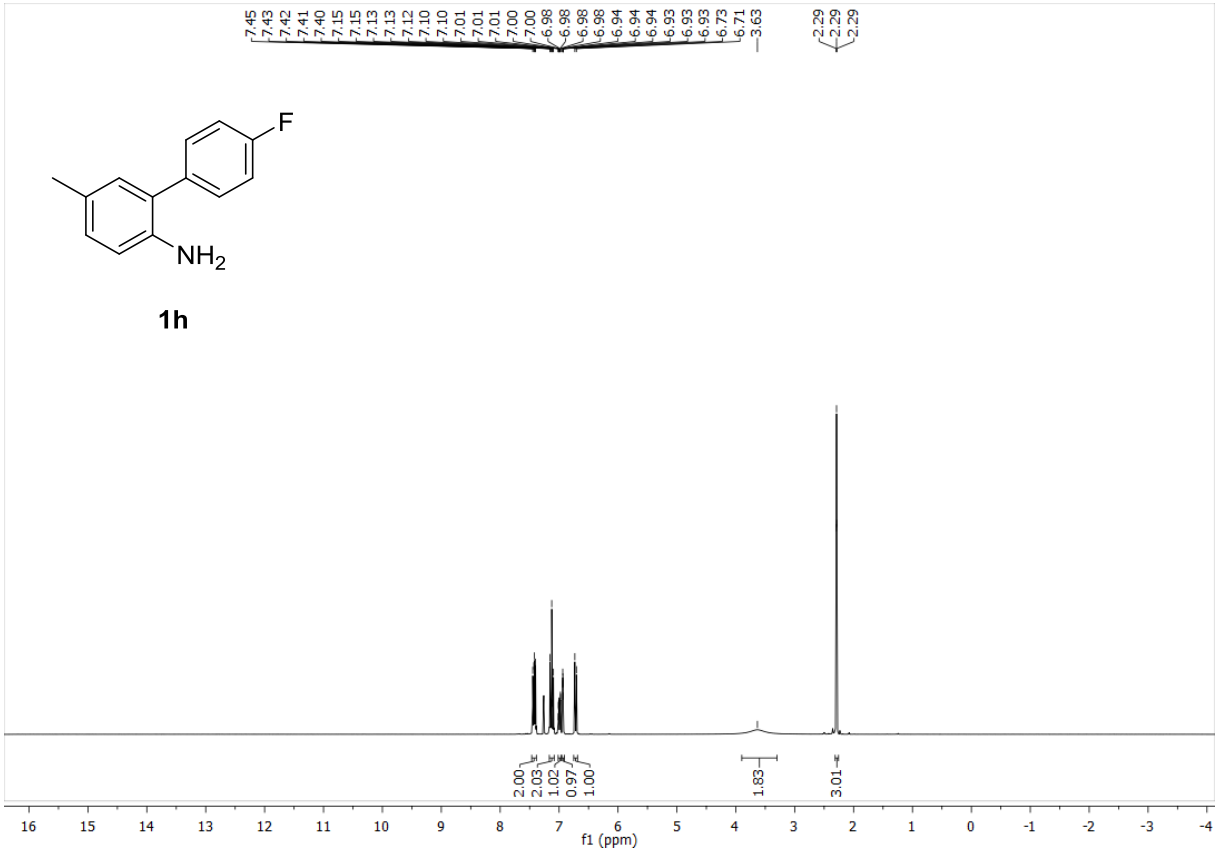
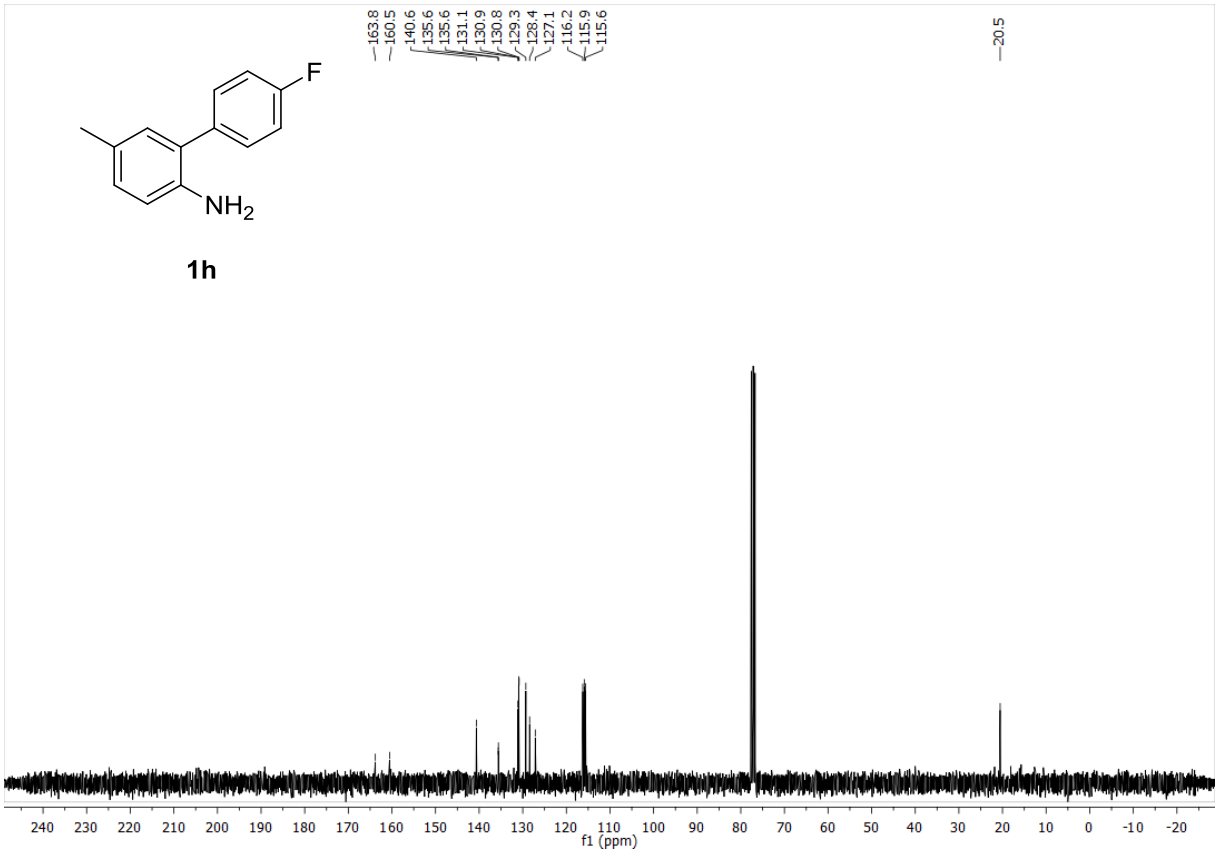
7.02
7.01
7.01
7.01
6.99
6.99
6.99
6.98
6.94
6.93
6.93
6.72
6.70
3.61
2.30
2.29
OMe
NH2
4.00
1.00
0.96
1.00
1.72
3.05
f1 (ppm)

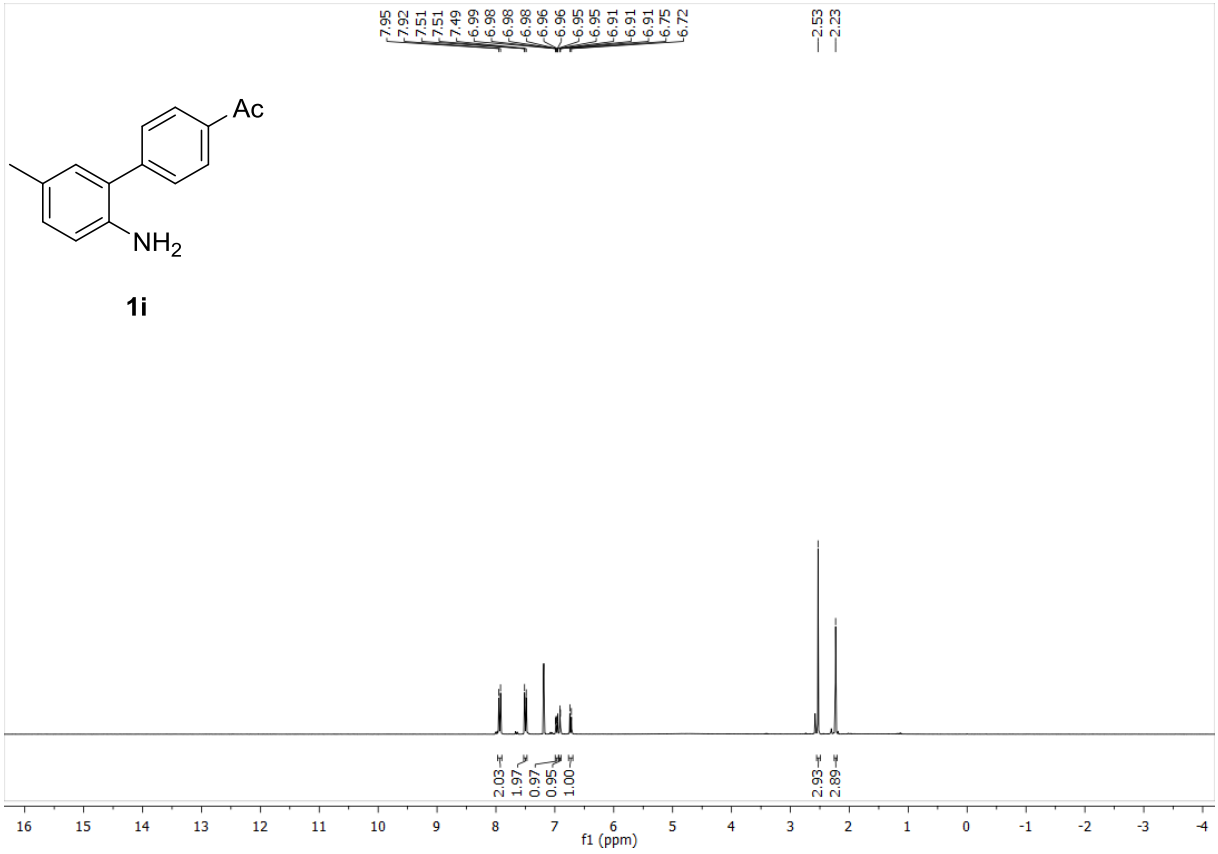
1g


140.7
138.2
133.2
130.9
130.6
129.5
129.0
128.3
126.7
116.2
20.5
OMe
NH2
f1 (ppm)

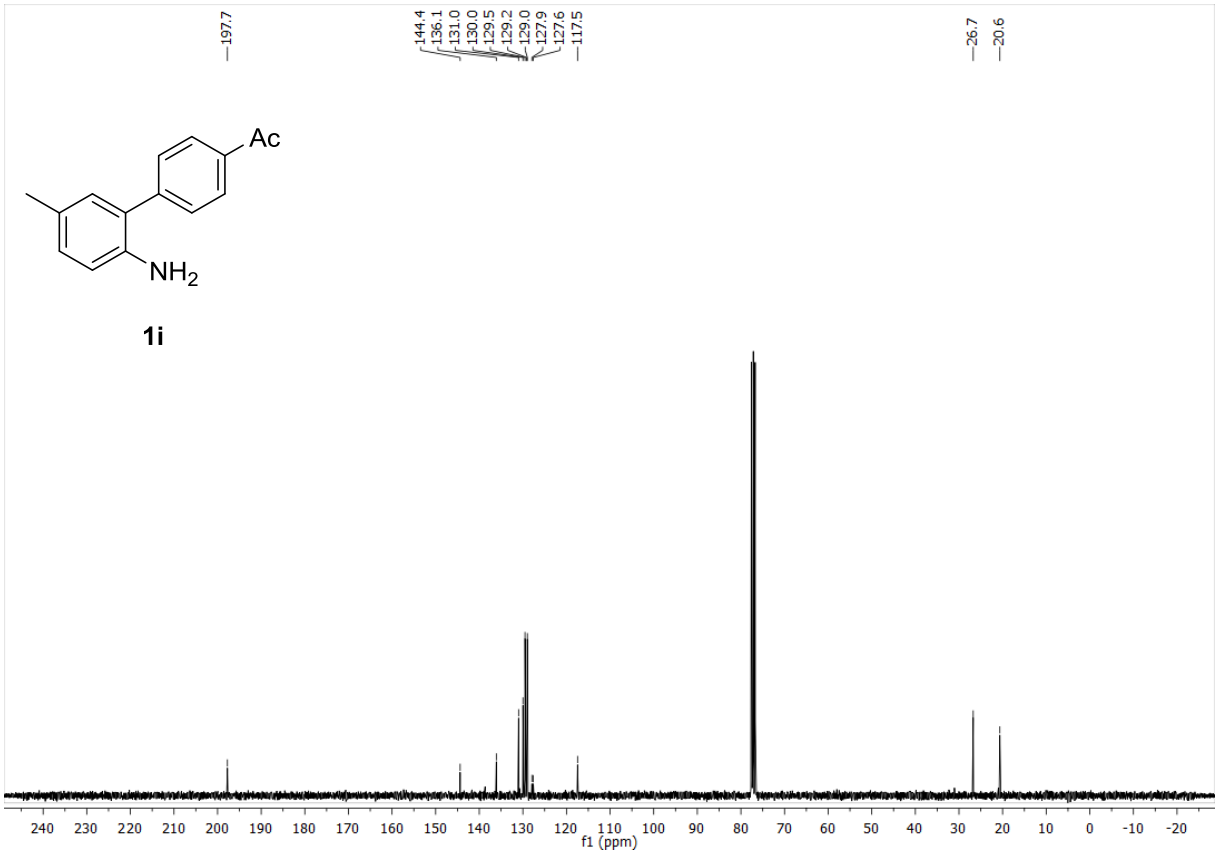
1g


7.45
7.43
7.42
7.41
7.40
7.15
7.15
7.13
7.13
7.12
7.10
7.10
7.01
7.01
7.01
7.00
7.00
6.98
6.98
6.98
6.98
6.94
6.94
6.94
6.93
6.93
6.93
6.73
6.71
3.63
2.29
2.29
2.29
F
NH2
1h
2.00
2.03
1.02
0.97
1.00
1.83
3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

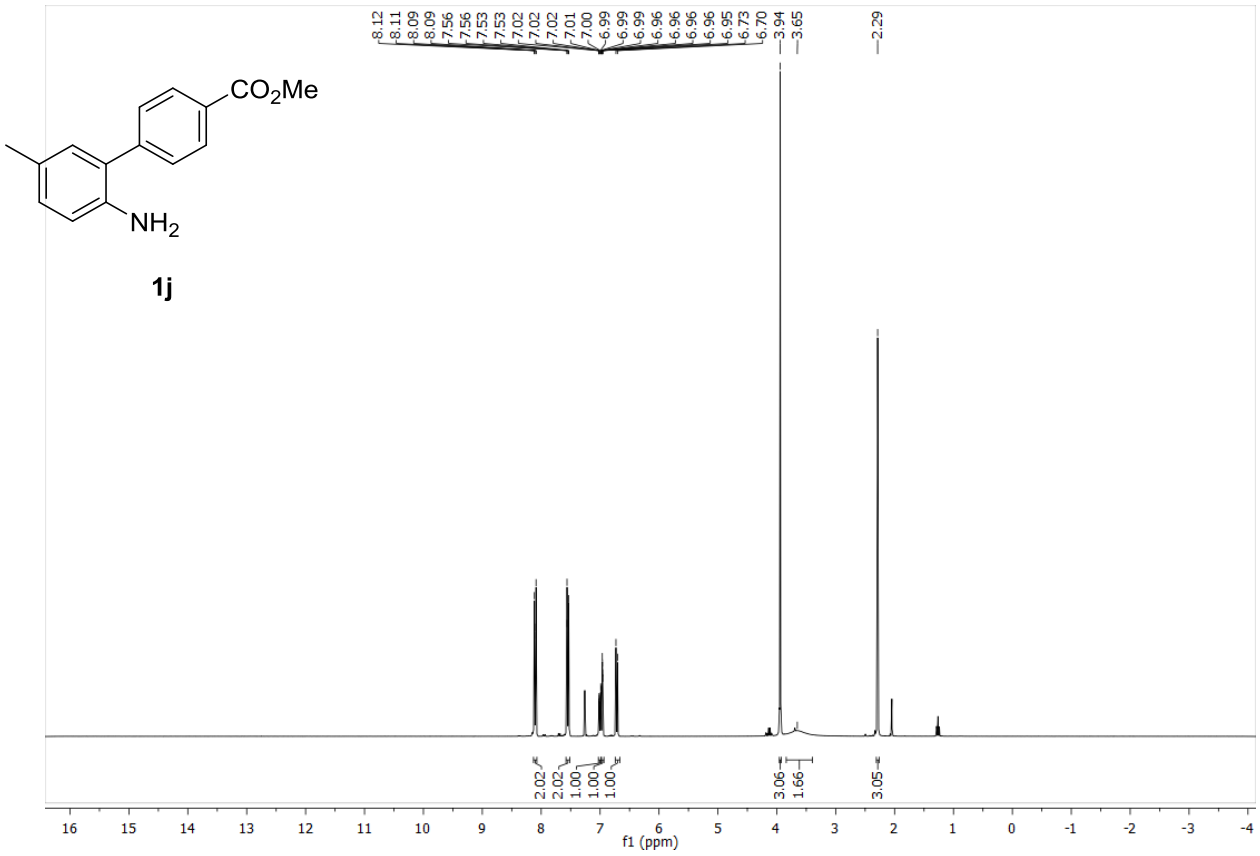

163.8
160.5
140.6
135.6
135.6
131.1
130.9
130.8
129.3
128.4
127.1
116.2
115.9
115.6
20.5
F
NH2
1h
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

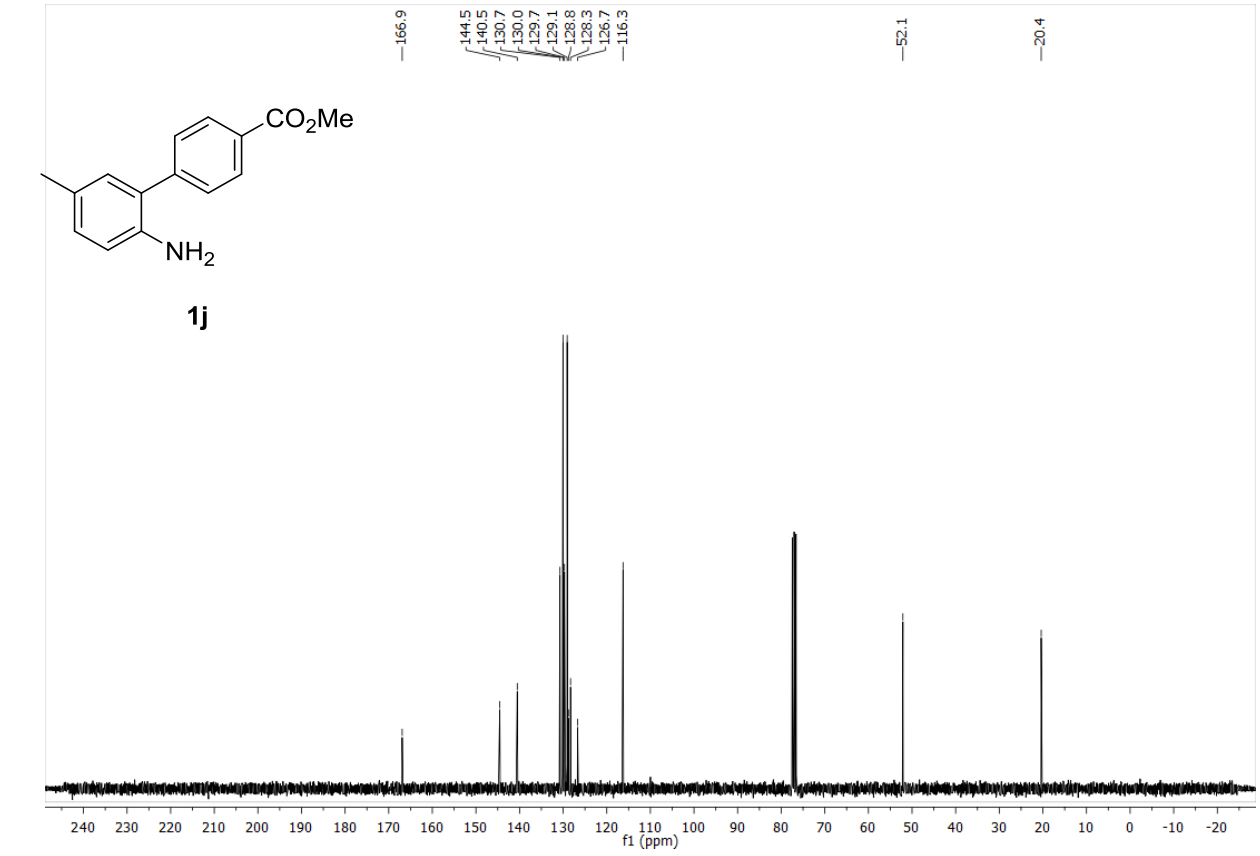

7.95
7.92
7.51
7.51
7.49
6.99
6.98
6.98
6.98
6.96
6.96
6.95
6.95
6.91
6.91
6.91
6.75
6.72
2.53
2.23
Ac
NH2
2.03
1.97
0.97
0.95
1.00
2.93
2.89
f1 (ppm)

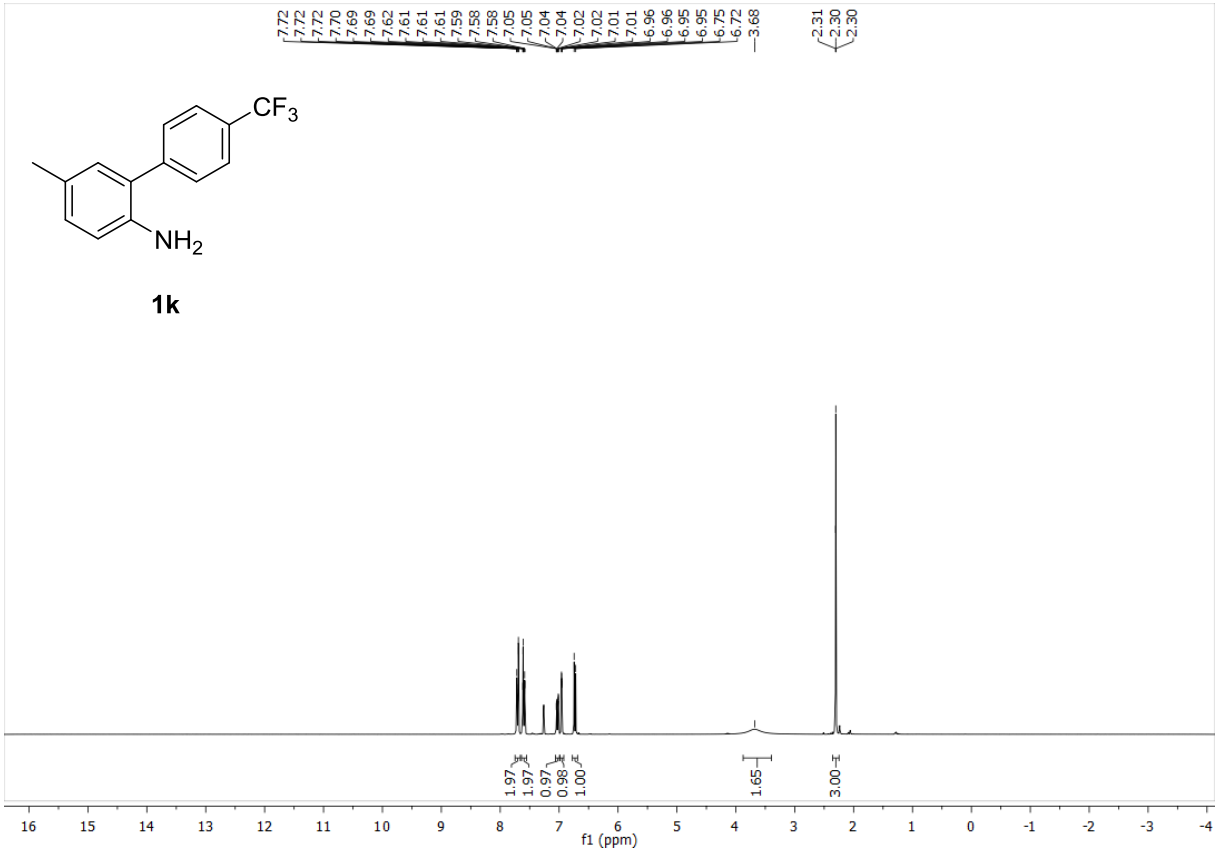
1i


197.7
144.4
136.1
131.0
130.0
129.5
129.2
129.0
127.9
127.6
117.5
26.7
20.6
Ac
NH2
f1 (ppm)

1i


8.12
8.11
8.09
8.09
7.56
7.56
7.53
7.53
7.02
7.02
7.02
7.01
7.00
6.99
6.99
6.96
6.96
6.96
6.96
6.95
6.73
6.70
3.94
3.65
2.29
CO2Me
NH2
1j
2.02
2.02
1.00
1.00
1.00
3.06
1.66
3.05
f1 (ppm)


166.9
144.5
140.5
130.7
130.0
129.7
129.1
128.8
128.3
126.7
116.3
52.1
20.4
CO2Me
NH2
1j
f1 (ppm)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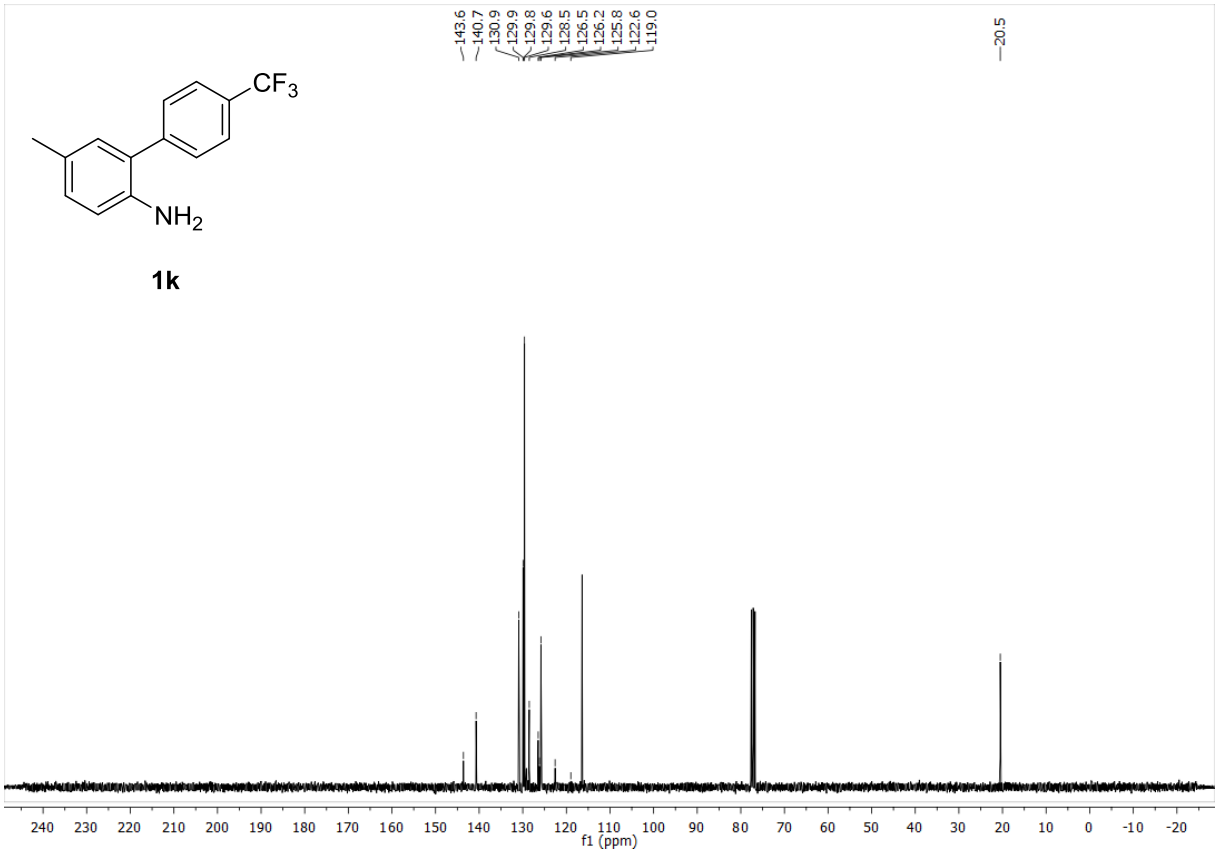
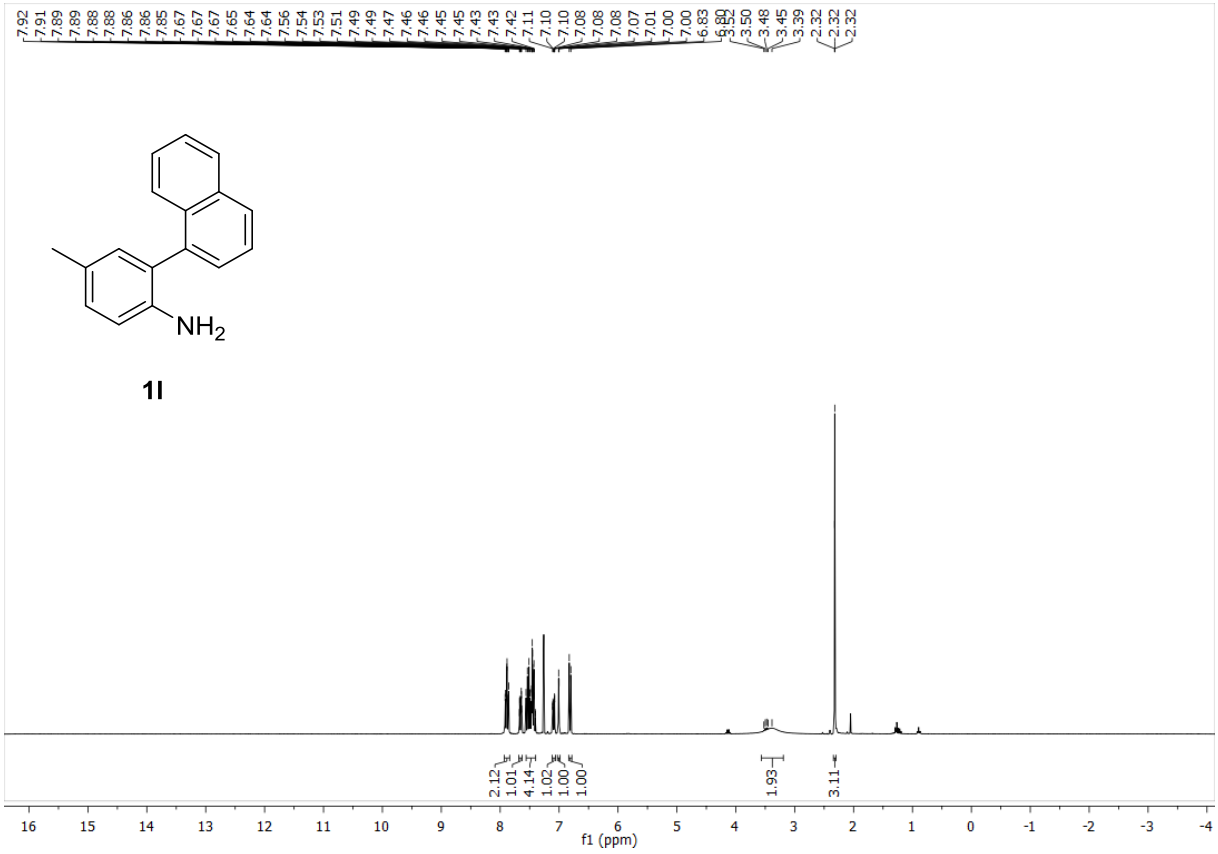
7.72
7.72
7.70
7.69
7.69
7.62
7.61
7.61
7.61
7.59
7.58
7.58
7.05
7.05
7.04
7.04
7.02
7.02
7.01
7.01
6.96
6.96
6.95
6.95
6.75
6.72
3.68
2.31
2.30
2.30
CF3
NH2
1k
1.97
1.97
0.97
0.98
1.00
1.65
3.00
f1 (ppm)


143.6
140.7
130.9
129.9
129.8
129.6
128.5
126.5
126.2
125.8
122.6
119.0
20.5
CF3
NH2
1k
f1 (ppm)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7.91
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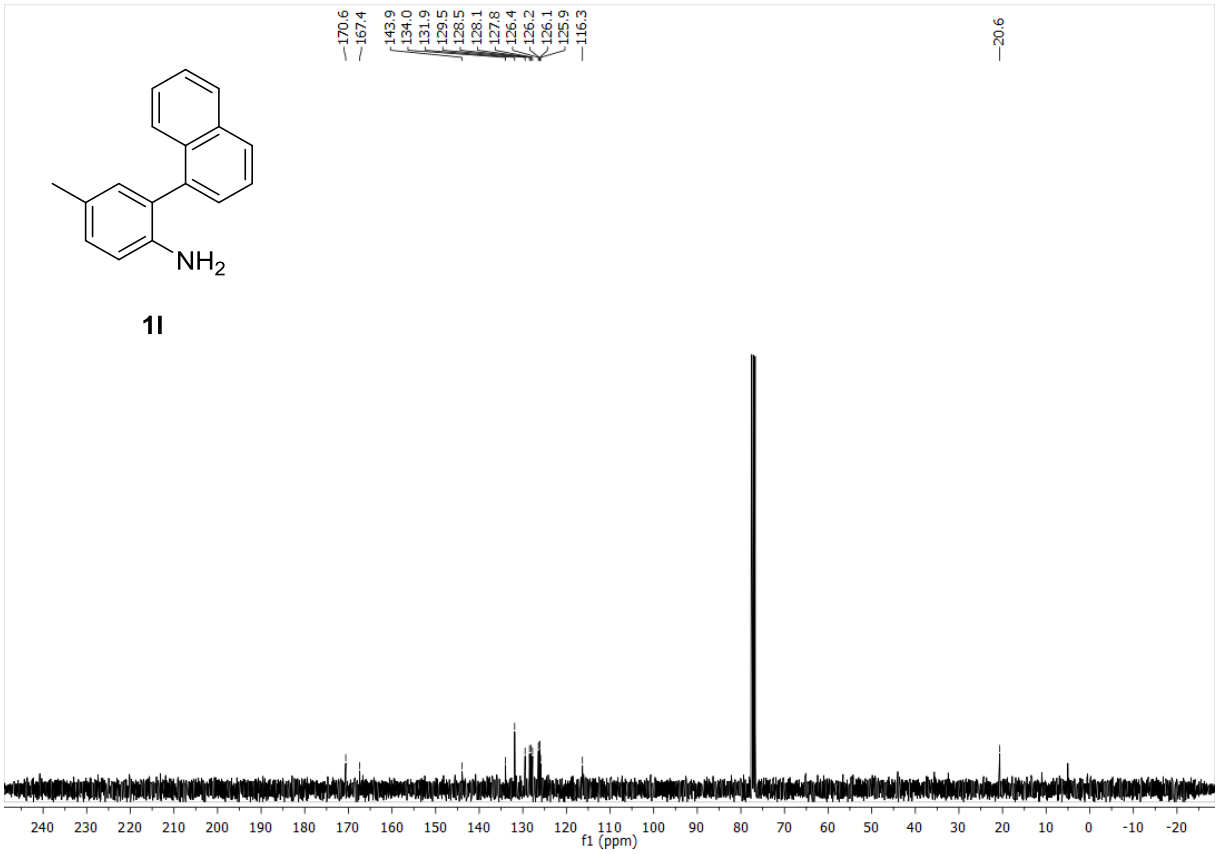
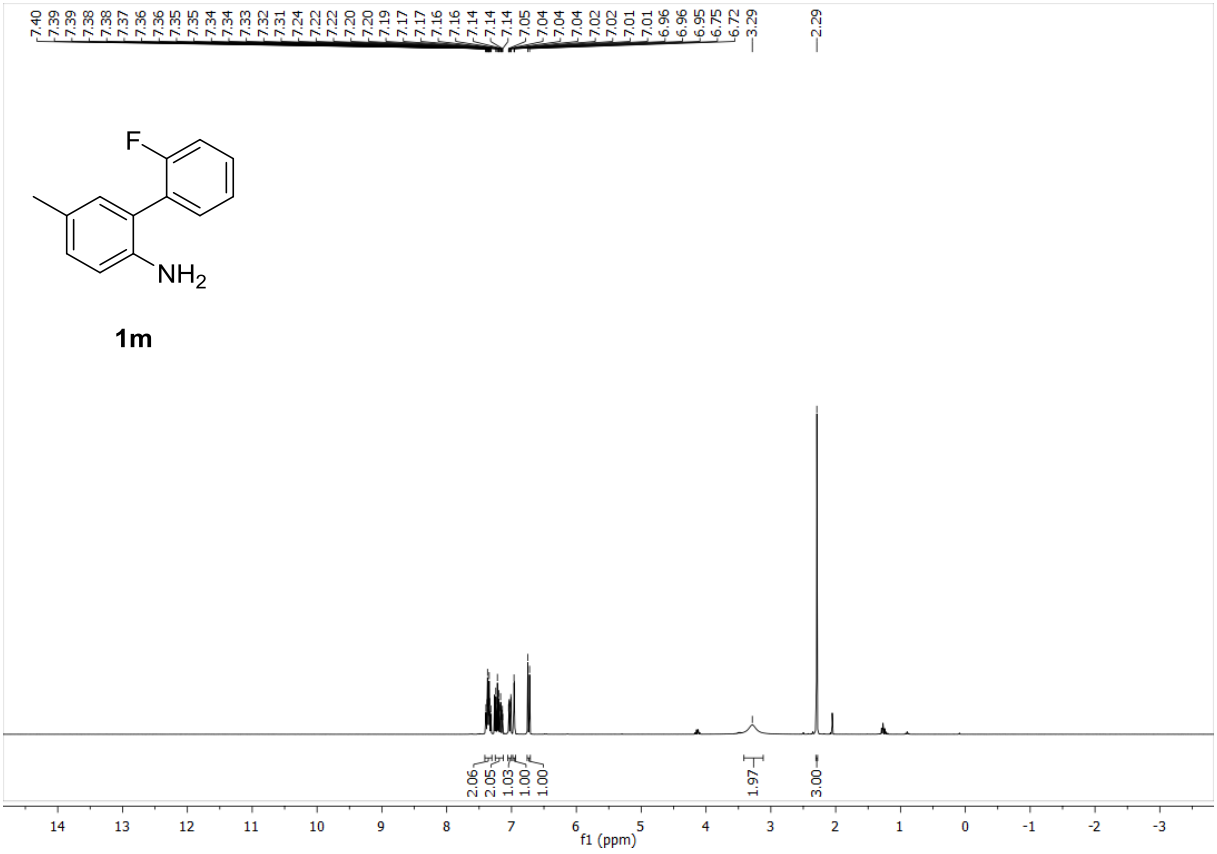
7.89
7.88
7.88
7.86
7.86
7.85
7.67
7.67
7.67
7.65
7.64
7.64
7.56
7.54
7.53
7.51
7.49
7.49
7.47
7.46
7.46
7.45
7.45
7.43
7.43
7.42
7.11
7.10
7.10
7.08
7.08
7.08
7.07
7.01
7.00
7.00
6.83
6.80
3.52
3.50
3.48
3.45
3.39
2.32
2.32
2.32
NH2
2.12
1.01
4.14
1.02
1.00
1.00
1.93
3.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

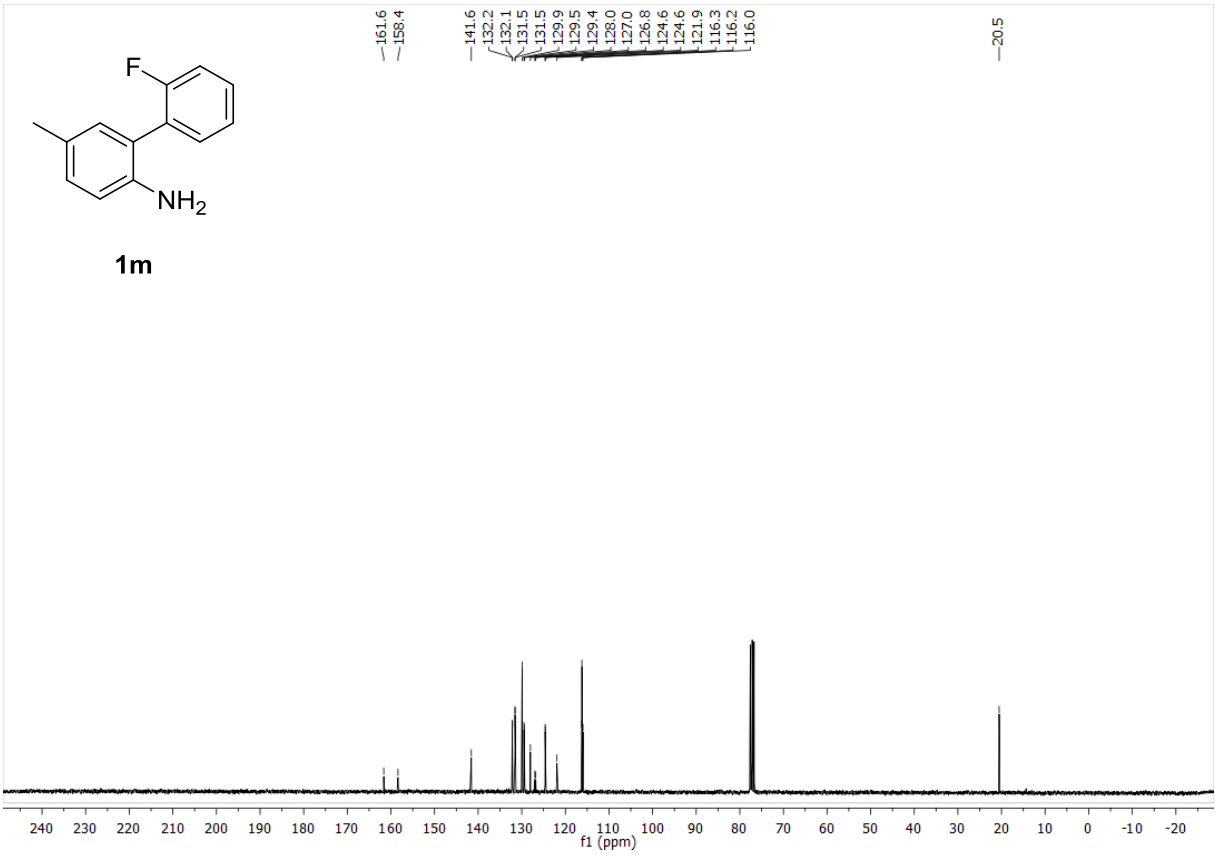
1l


170.6
167.4
143.9
134.0
131.9
129.5
128.5
128.1
127.8
126.4
126.2
126.1
125.9
116.3
20.6
NH2
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

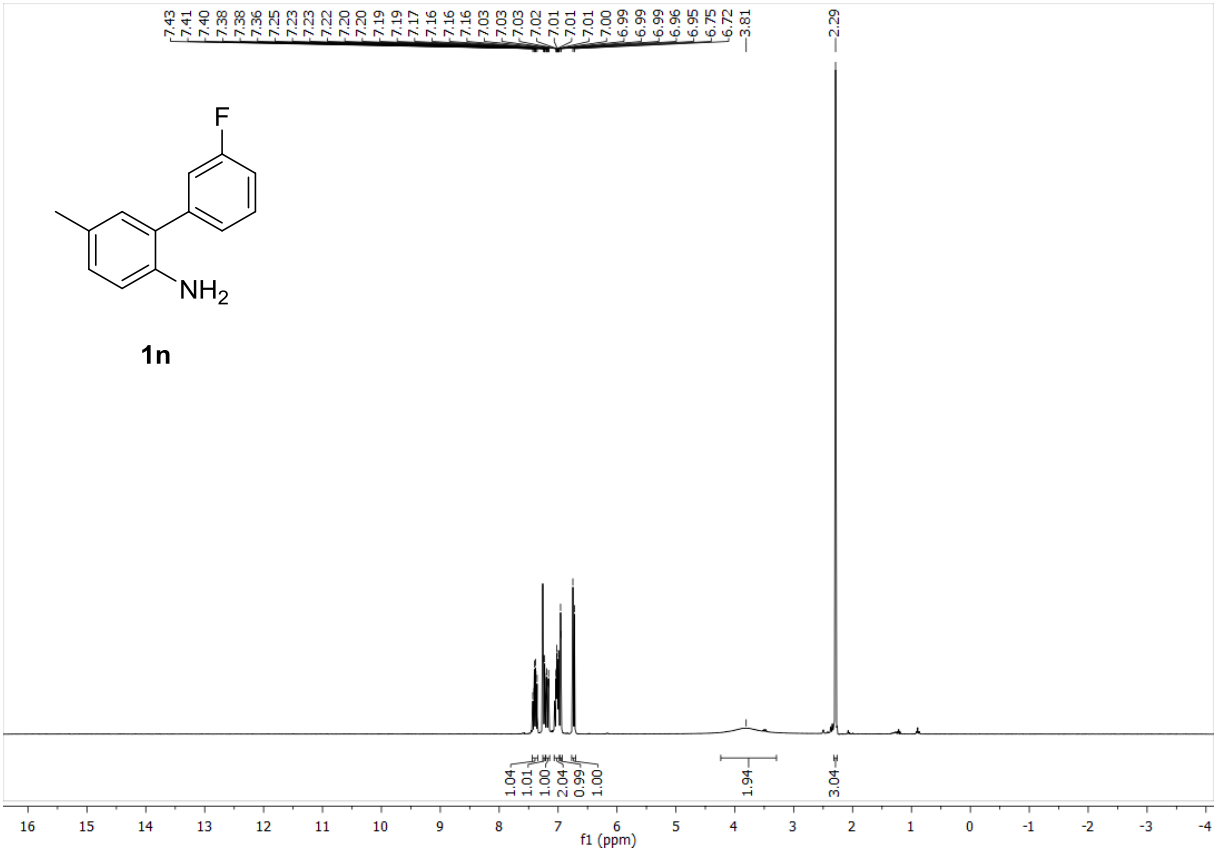
1l

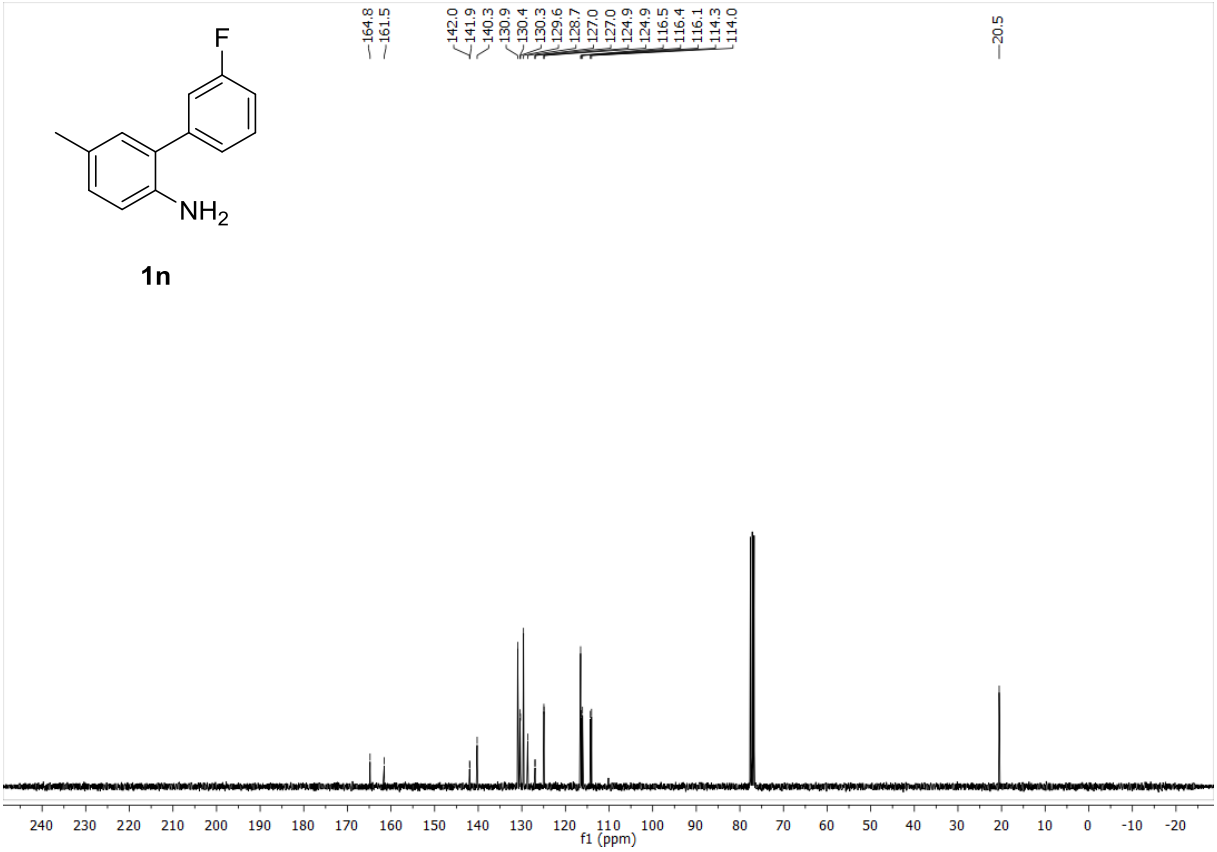

7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.24
7.22
7.22
7.20
7.20
7.19
7.17
7.17
7.16
7.16
7.14
7.14
7.14
7.05
7.04
7.04
7.04
7.02
7.02
7.01
7.01
6.96
6.96
6.95
6.75
6.72
3.29
2.29
F
NH2
2.06
2.05
1.03
1.00
1.00
1.97
3.00
f1 (ppm)

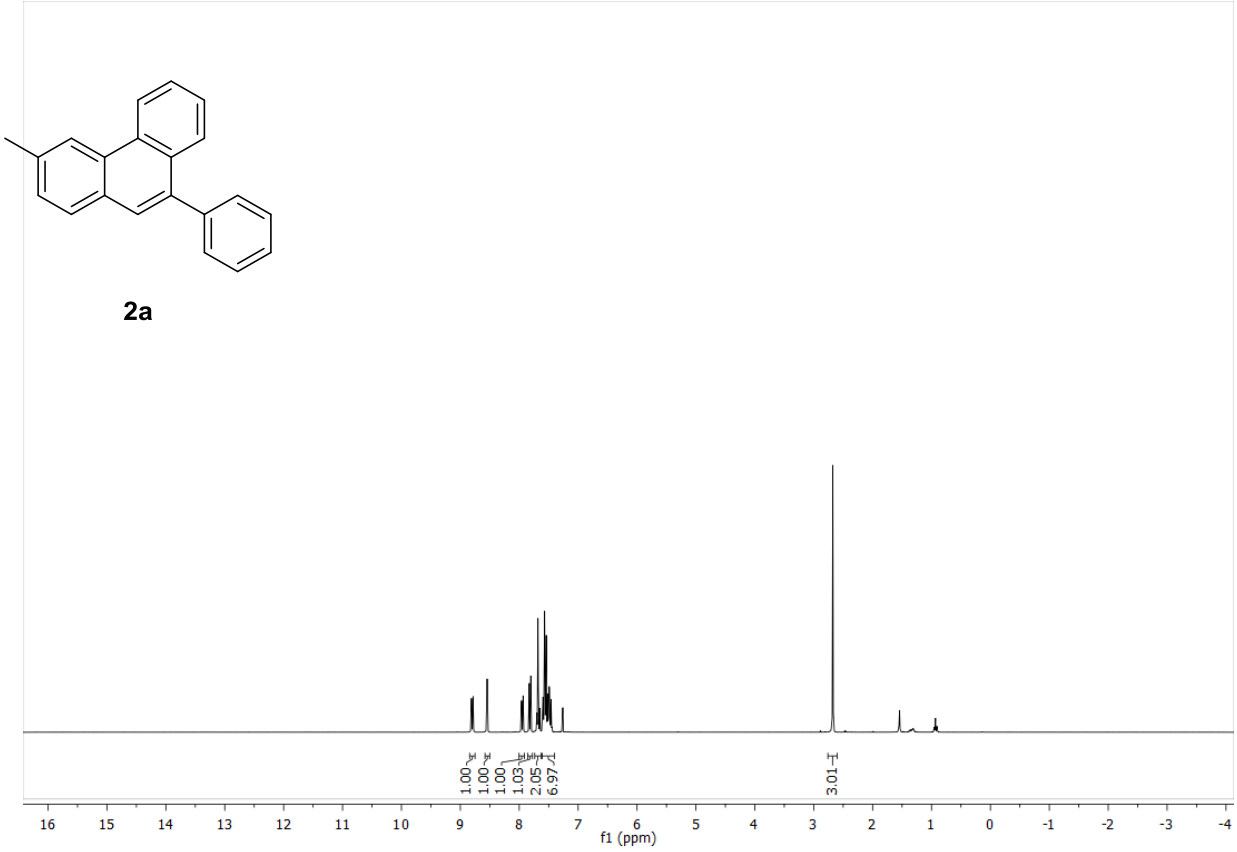
1m

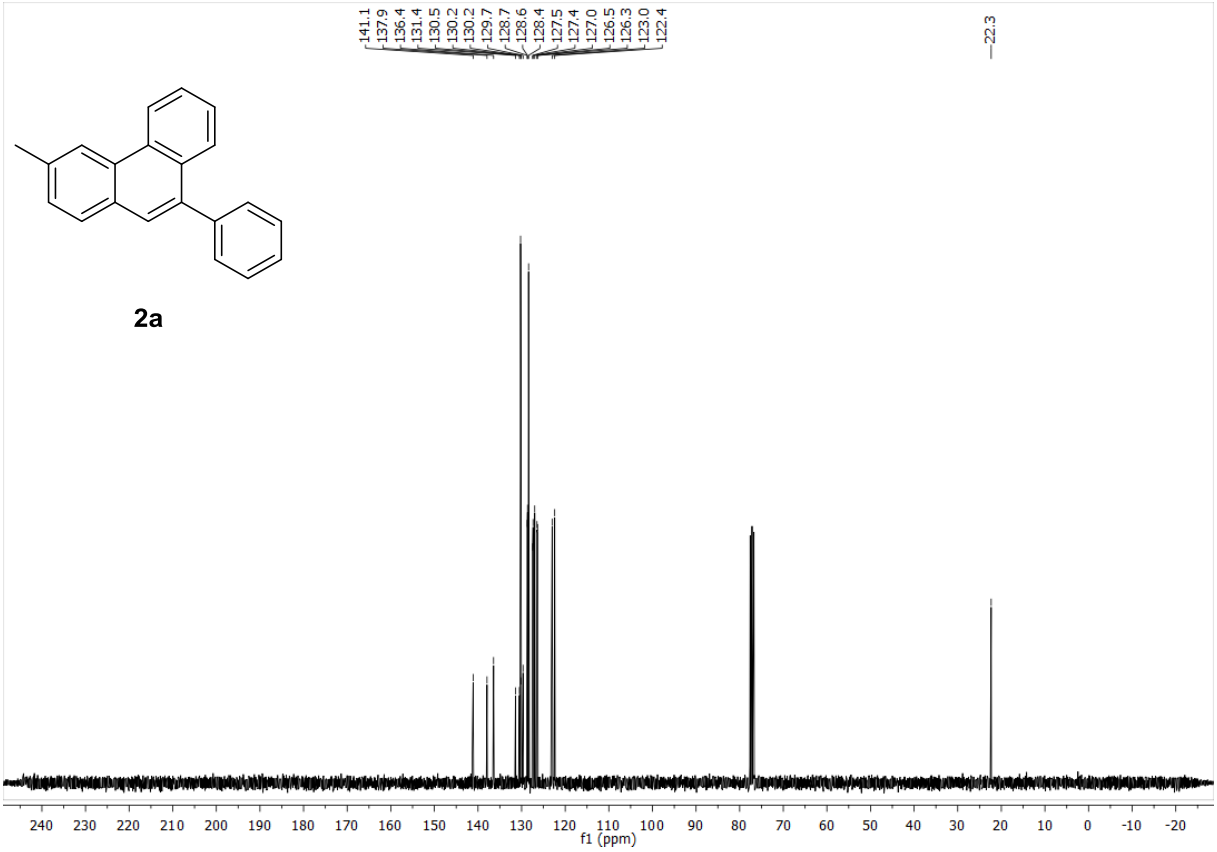

161.6
158.4
141.6
132.2
132.1
131.5
131.5
129.9
129.5
129.4
128.0
127.0
126.8
124.6
124.6
121.9
116.3
116.2
116.0
20.5
F
NH2
f1 (ppm)

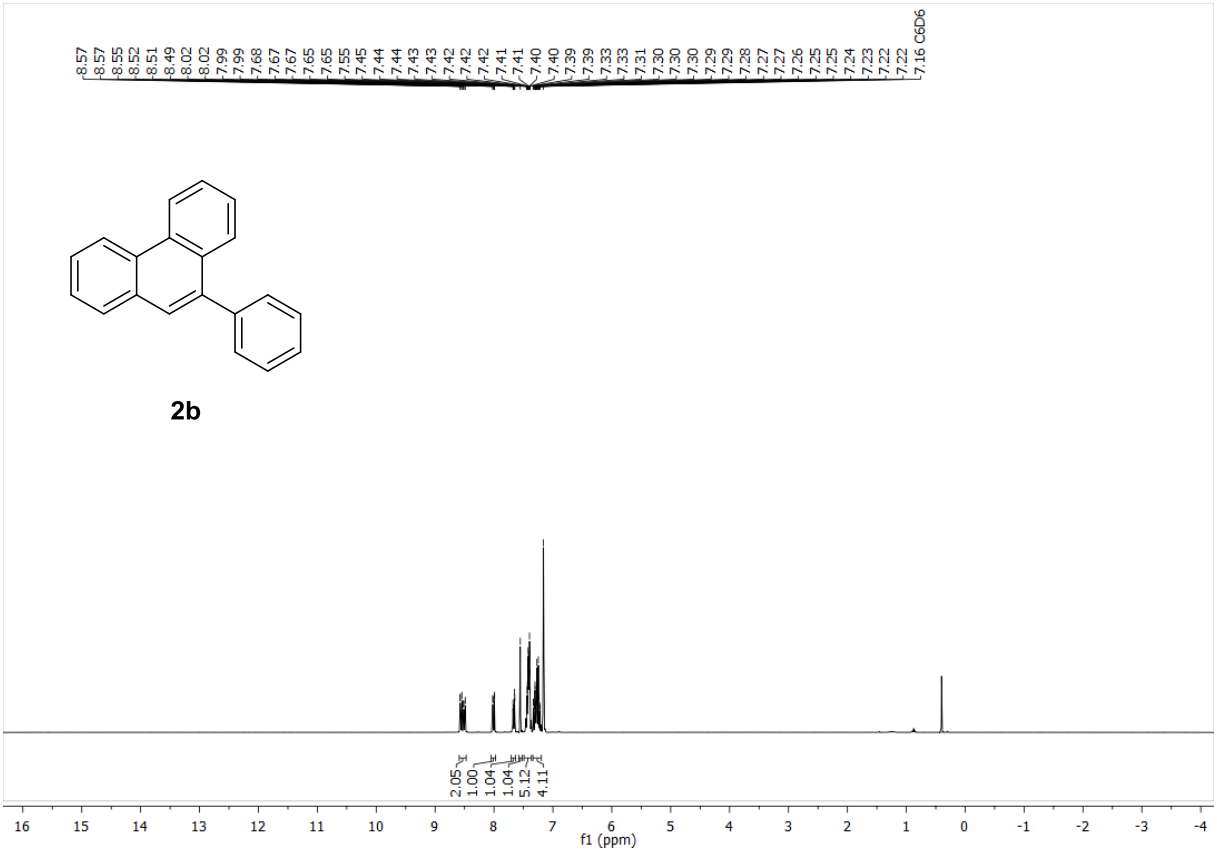
1m


7.43
7.41
7.40
7.38
7.38
7.36
7.25
7.23
7.23
7.22
7.20
7.20
7.19
7.19
7.17
7.16
7.16
7.16
7.03
7.03
7.03
7.02
7.01
7.01
7.01
7.00
6.99
6.99
6.96
6.95
6.75
6.72
3.81
2.29
F
NH2
1n
1.04
1.01
1.00
2.04
0.99
1.00
1.94
3.04
f1 (ppm)


164.8
161.5
142.0
141.9
140.3
130.9
130.4
130.3
129.6
128.7
127.0
127.0
124.9
124.9
116.5
116.4
116.1
114.3
114.0
20.5
F
NH2
1n
f1 (ppm)


2a
1.00
1.00
1.00
1.03
2.05
6.97
3.01
f1 (ppm)


141.1
137.9
136.4
131.4
130.5
130.2
130.2
129.7
128.7
128.6
128.4
127.5
127.4
127.0
126.5
126.3
123.0
122.4
22.3
2a
f1 (ppm)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8.57
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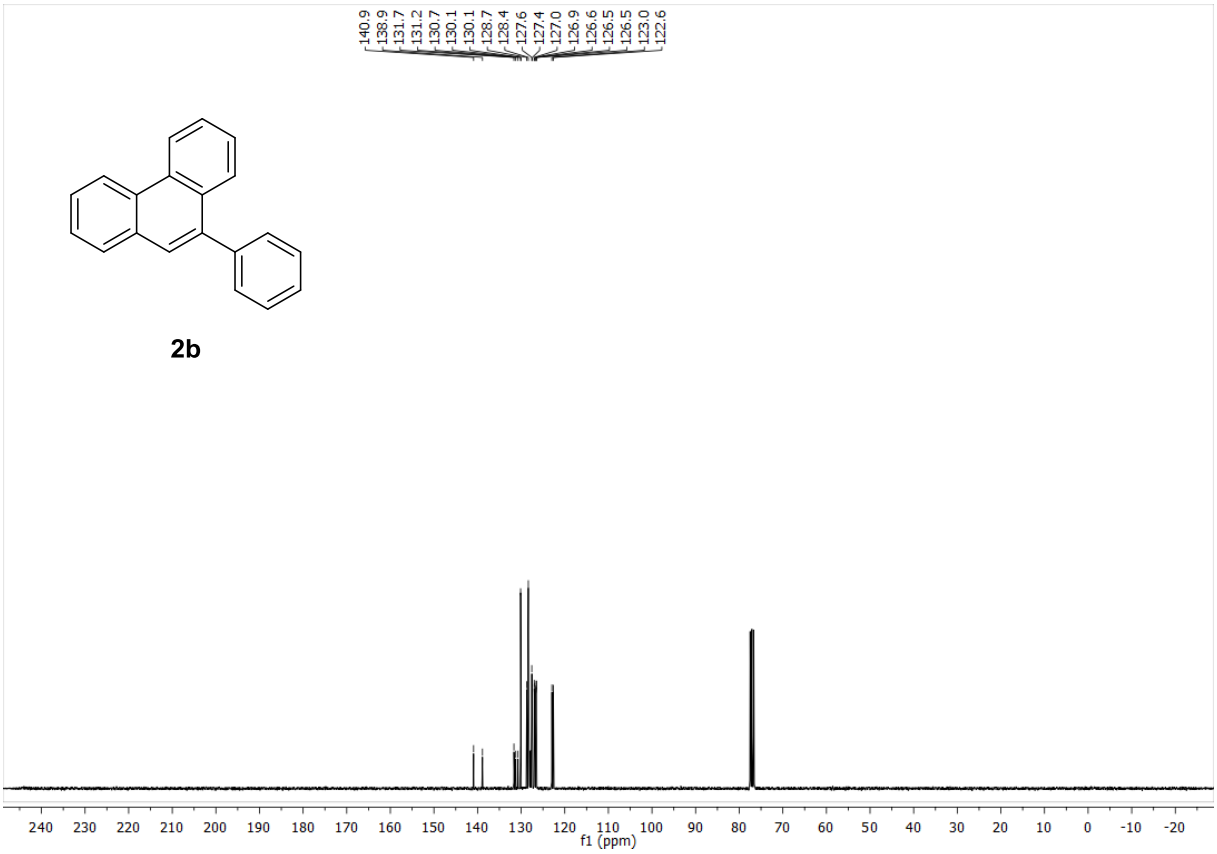
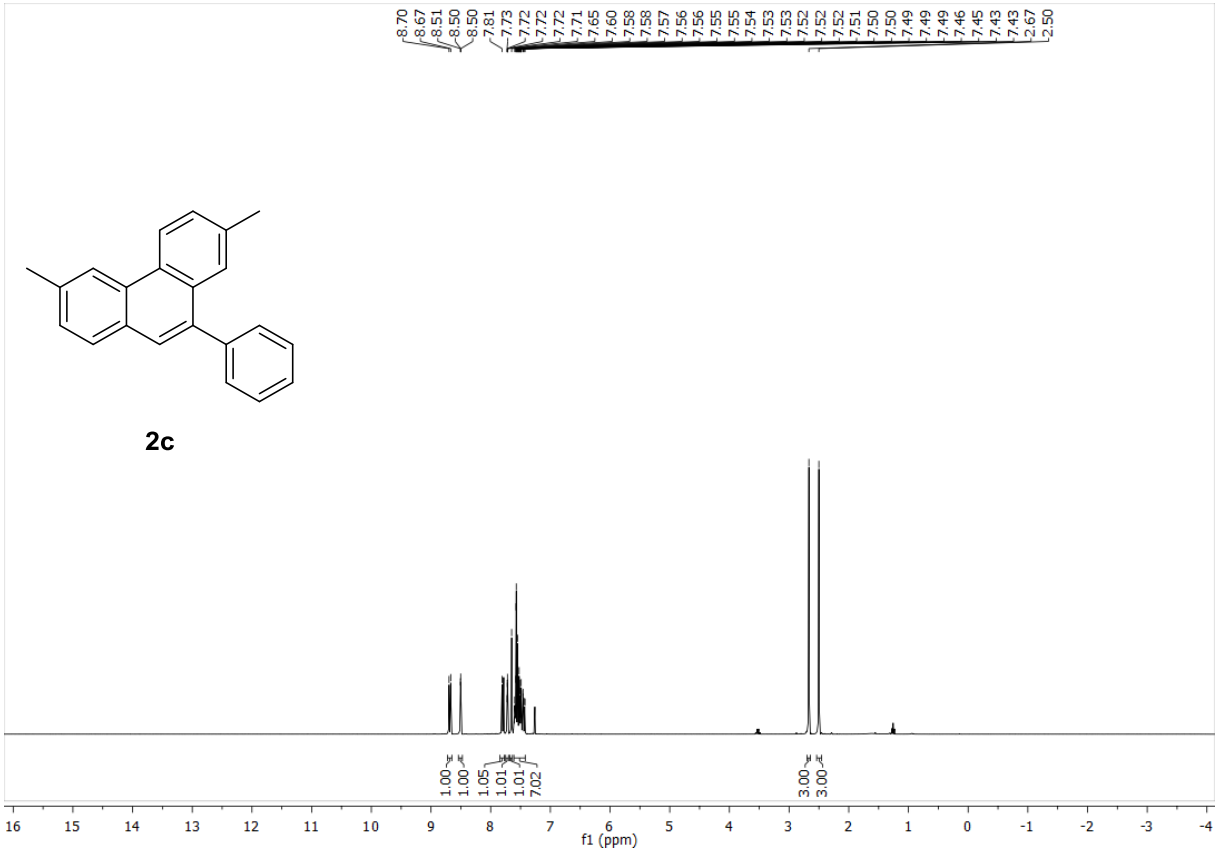
8.52
8.51
8.49
8.02
8.02
7.99
7.99
7.68
7.67
7.67
7.65
7.65
7.55
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.33
7.33
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.16 C6D6
2.05
1.00
1.04
1.04
5.12
4.11
f1 (ppm)

2b


140.9
138.9
131.7
131.2
130.7
130.1
130.1
128.7
128.4
127.6
127.4
127.0
126.9
126.6
126.5
126.5
123.0
122.6
f1 (ppm)

2b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8.50
8.50
7.81
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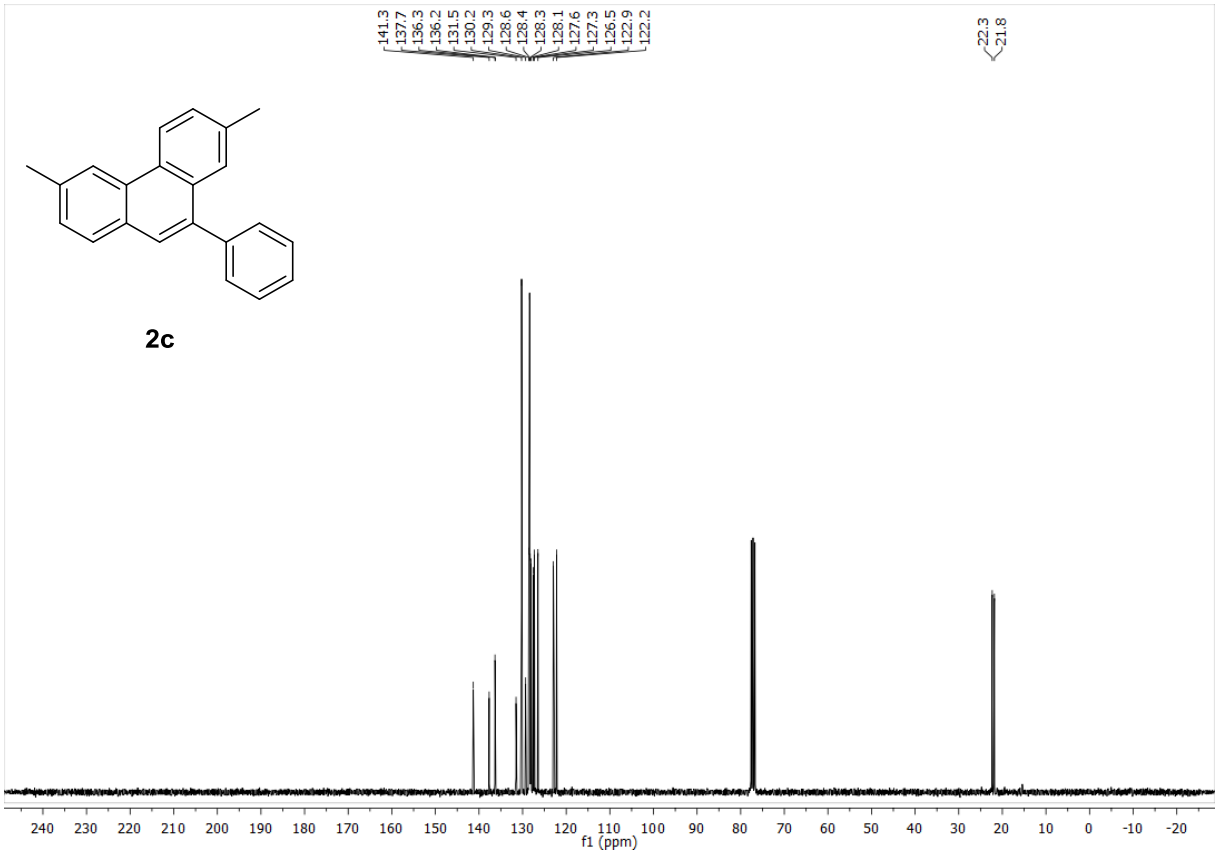
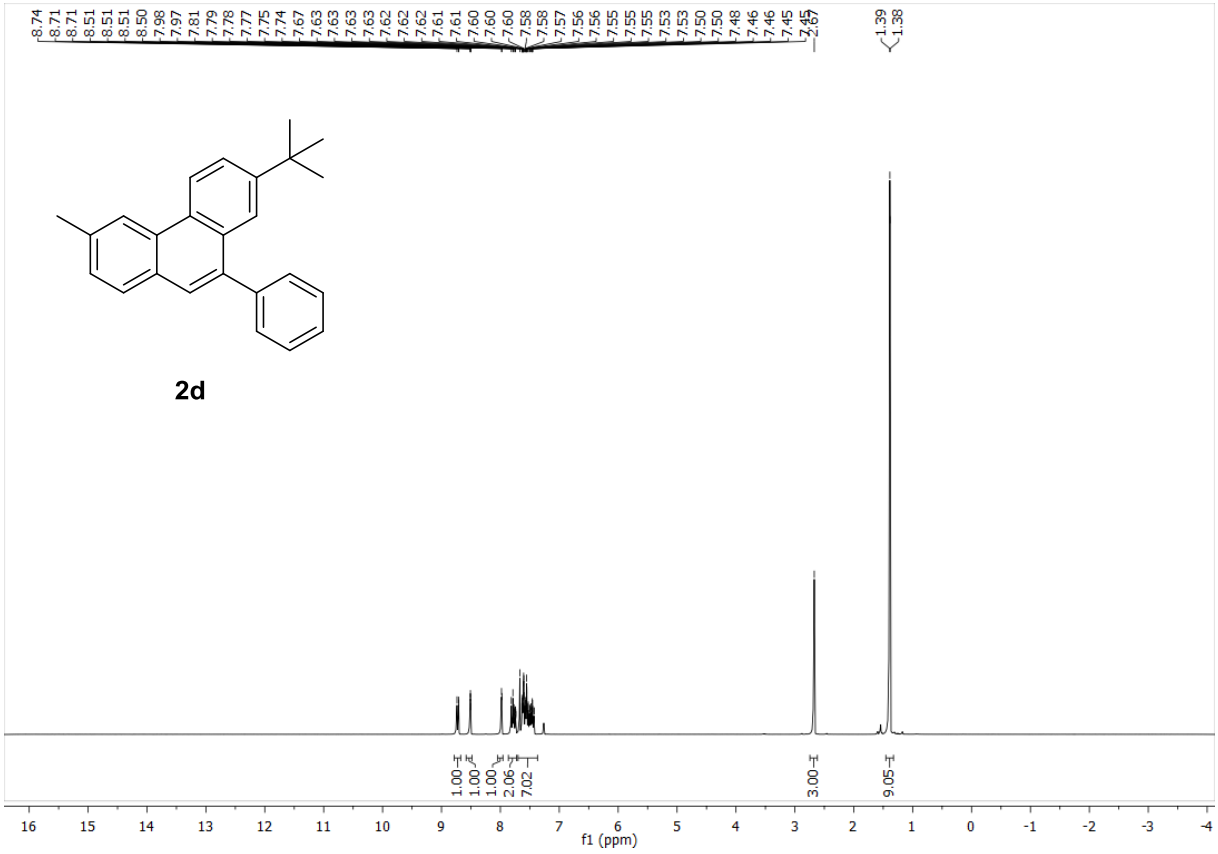
7.72
7.72
7.72
7.71
7.65
7.60
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.49
7.46
7.45
7.43
7.43
2.67
2.50
1.00
1.00
1.05
1.01
1.01
7.02
3.00
3.00
f1 (ppm)

2c


141.3
137.7
136.3
136.2
131.5
130.2
129.3
128.6
128.4
128.3
128.1
127.6
127.3
126.5
122.9
122.2
22.3
21.8
f1 (ppm)

2c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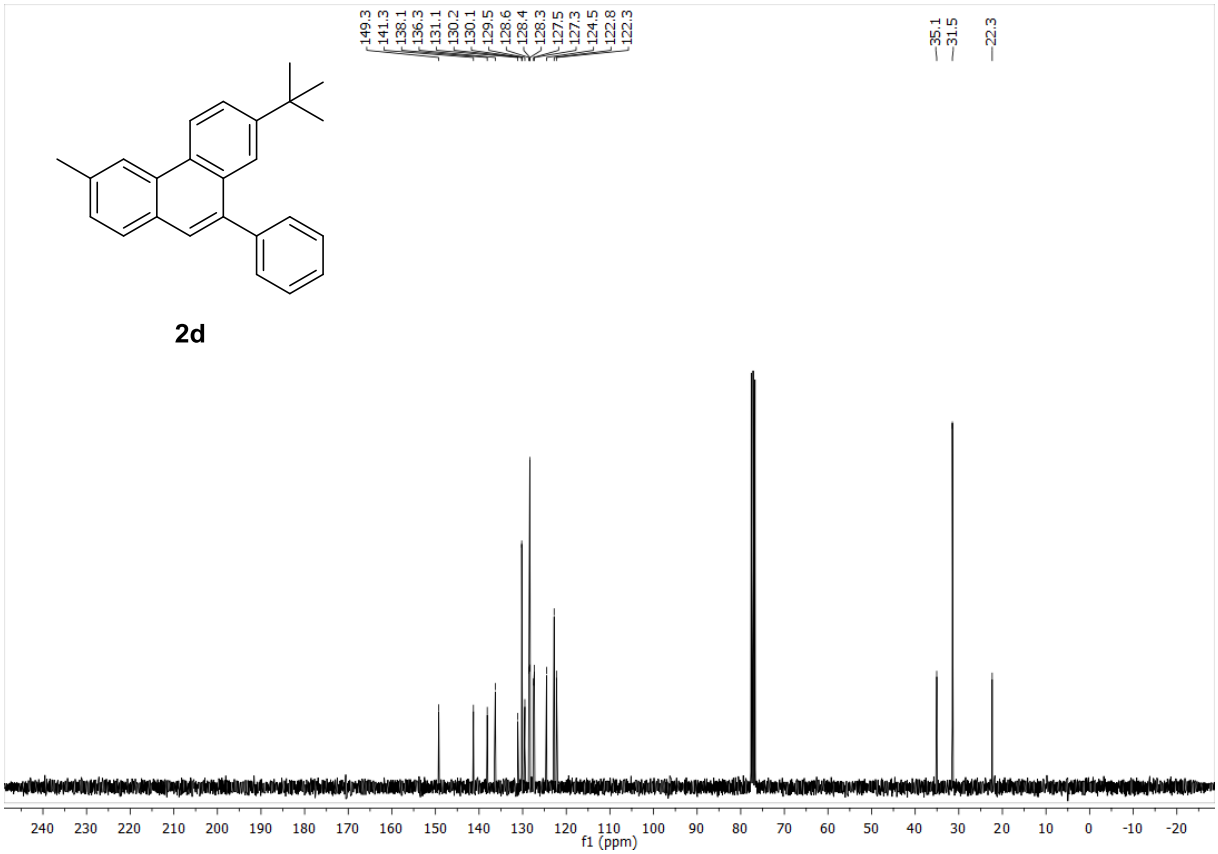
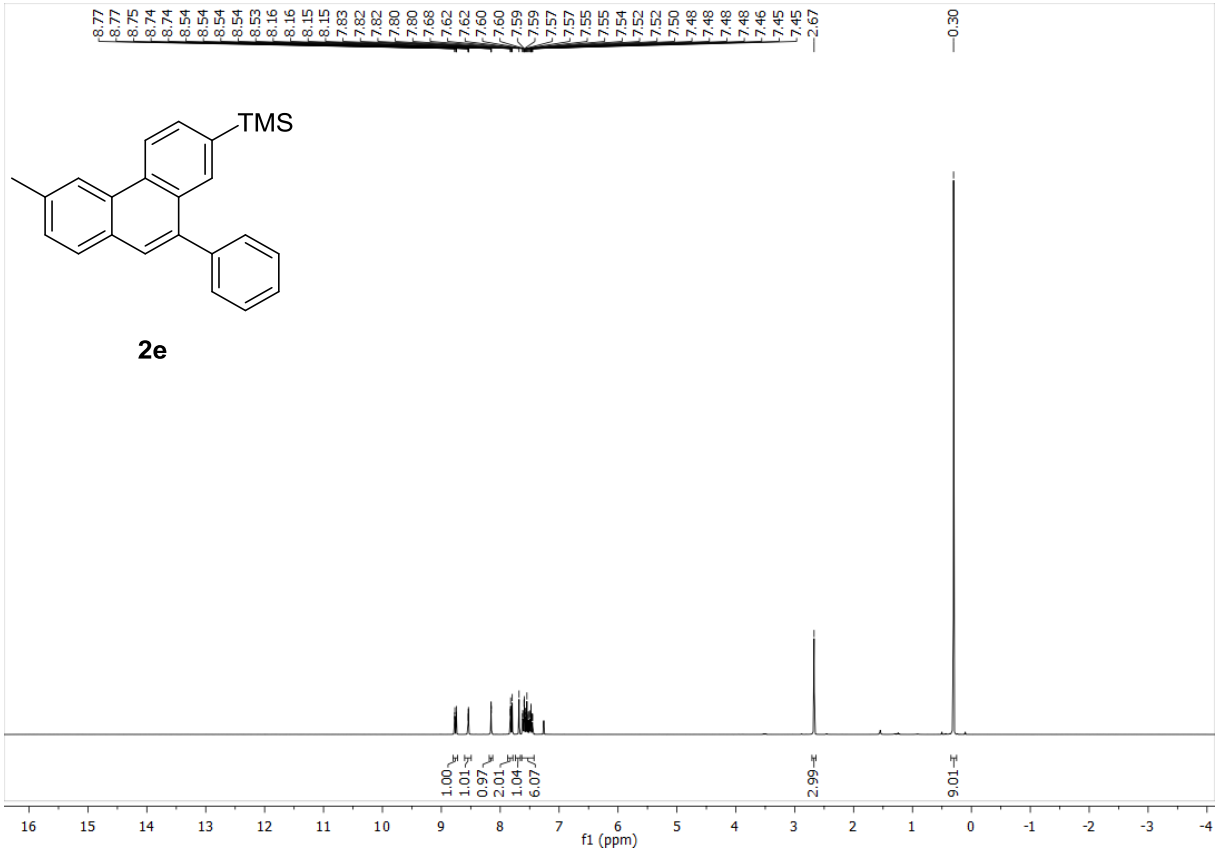
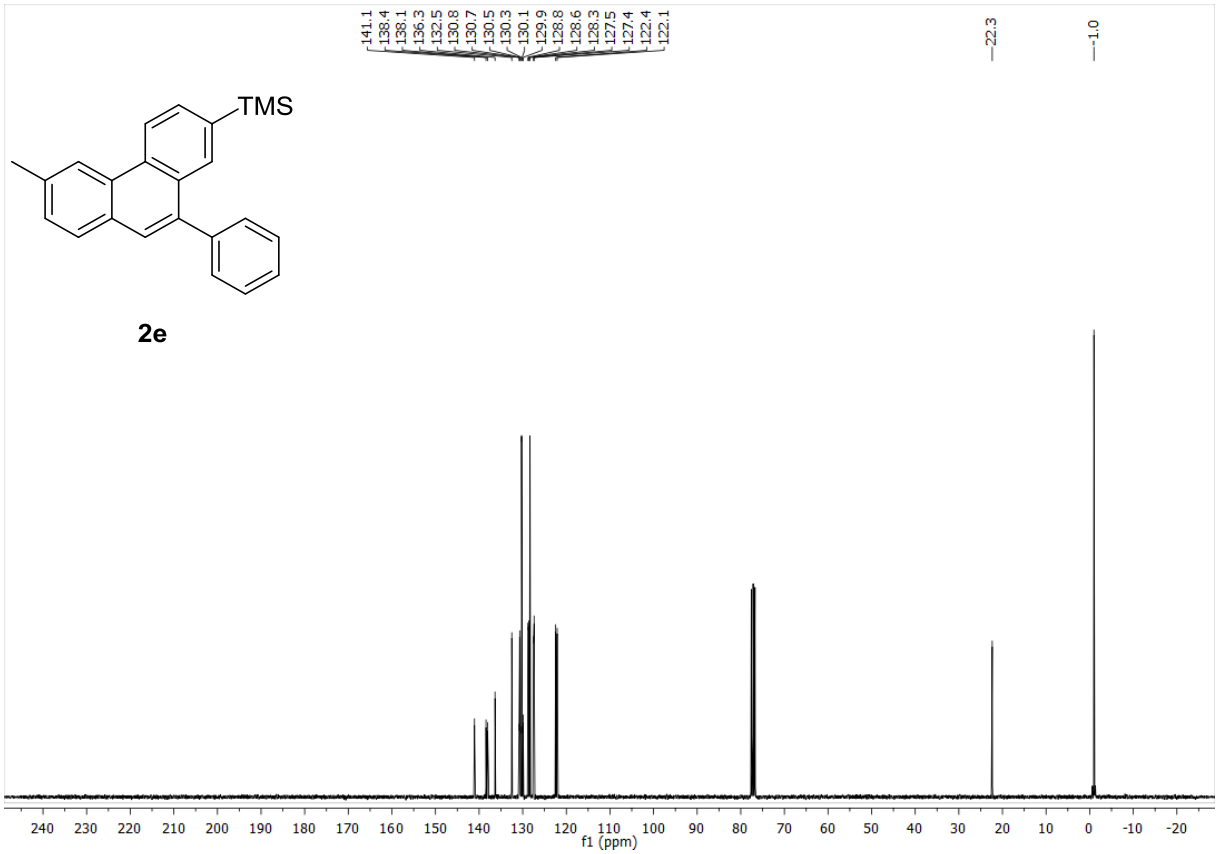
8.71
8.51
8.51
8.51
8.50
7.98
7.97
7.81
7.79
7.78
7.77
7.75
7.74
7.67
7.63
7.63
7.63
7.62
7.62
7.62
7.61
7.61
7.60
7.60
7.60
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.55
7.53
7.53
7.50
7.50
7.48
7.46
7.46
7.45
7.45
2.87
1.39
1.38
1.00
1.00
1.00
2.06
7.02
3.00
9.05
f1 (ppm)

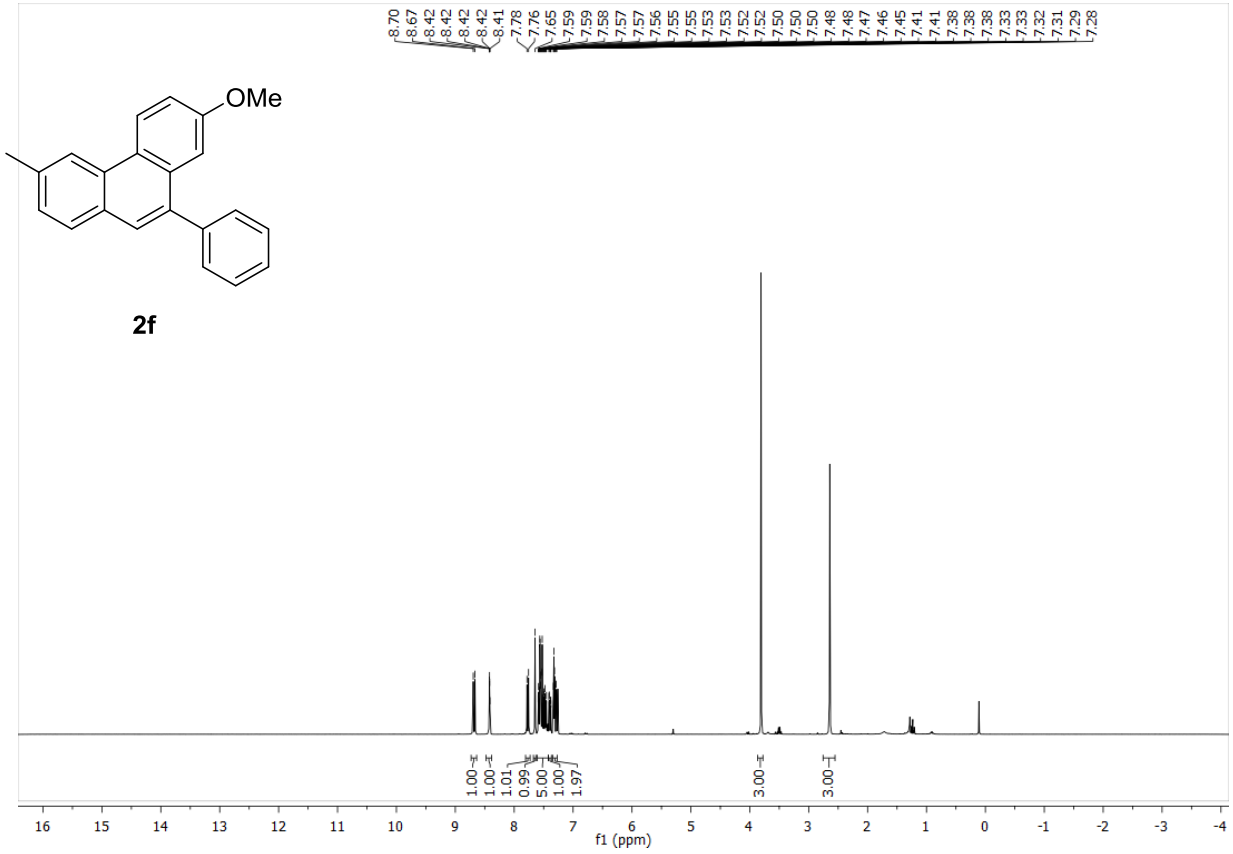
2d

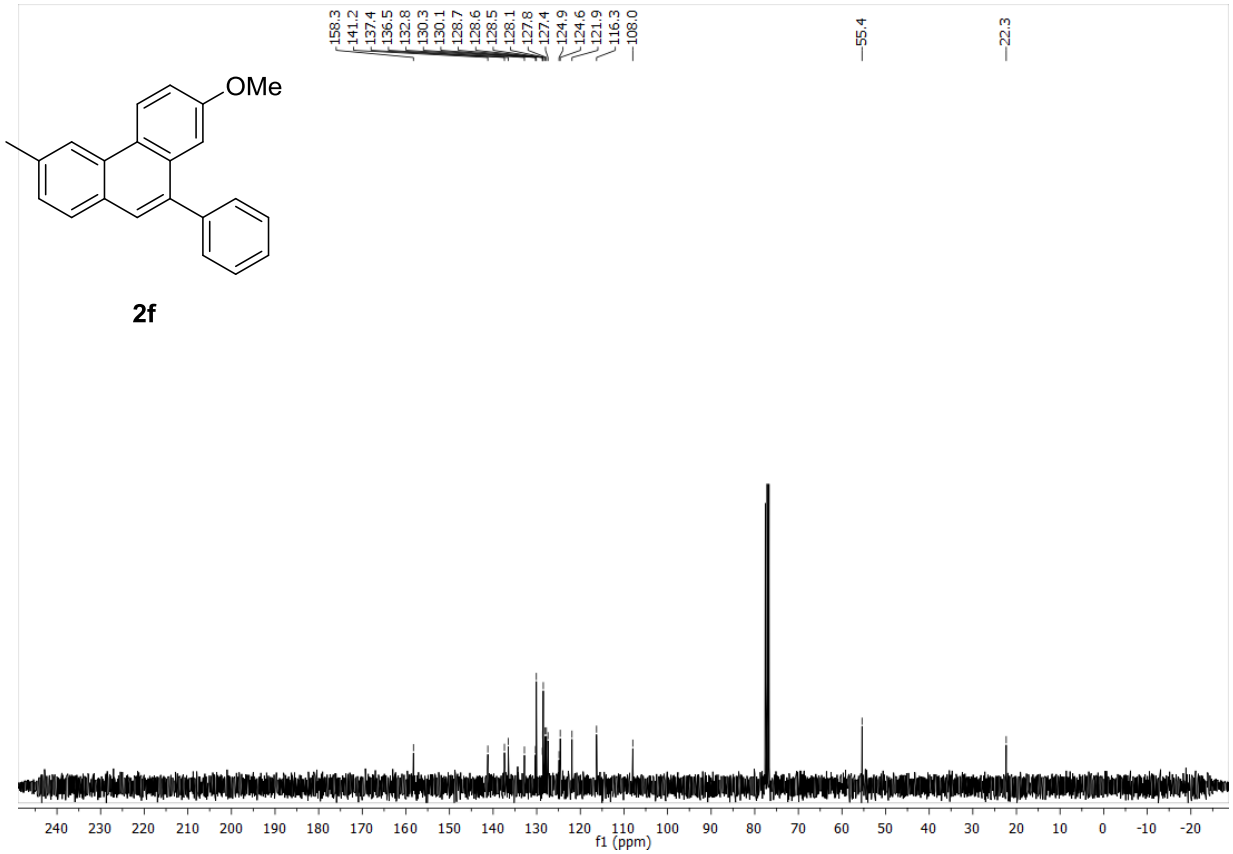

149.3
141.3
138.1
136.3
131.1
130.2
130.1
129.5
128.6
128.4
128.3
127.5
127.3
124.5
122.8
122.3
35.1
31.5
22.3
f1 (ppm)

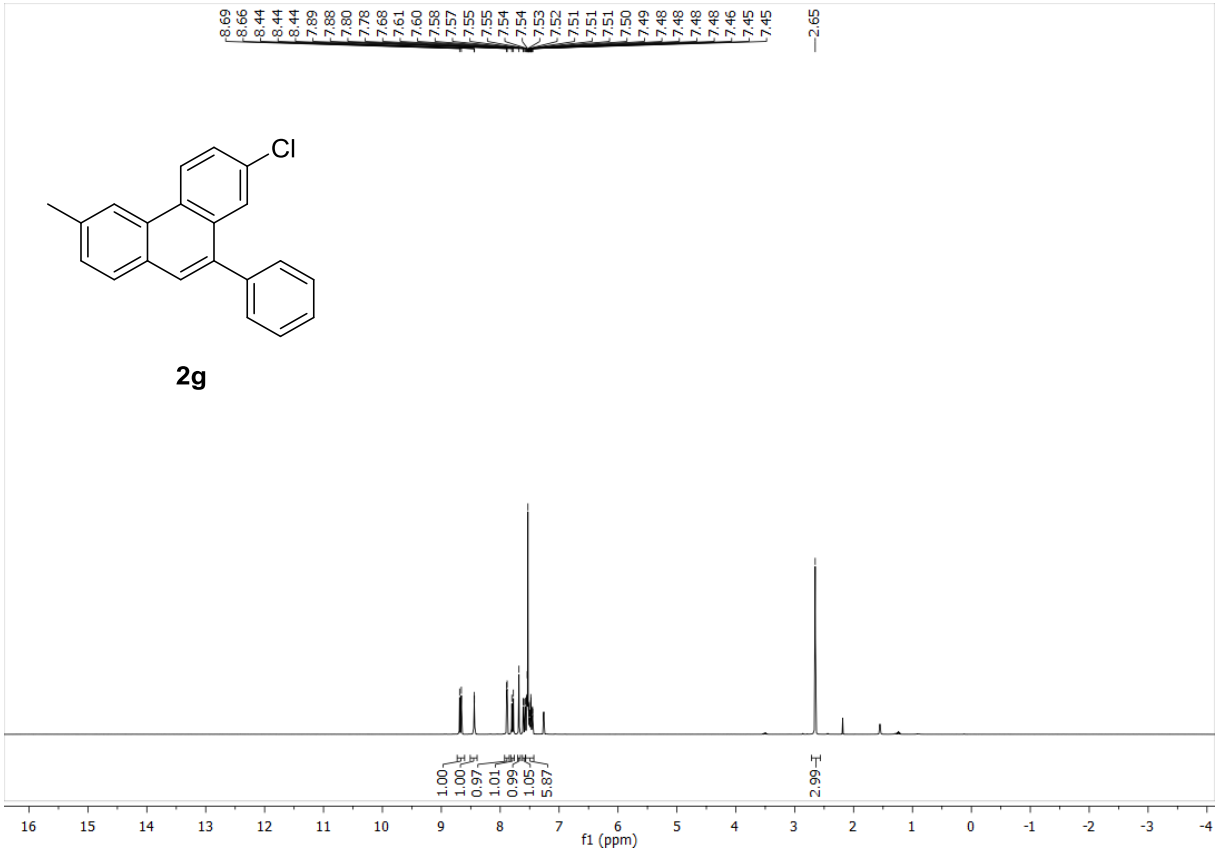
2d


8.77
8.77
8.75
8.74
8.74
8.54
8.54
8.54
8.54
8.53
8.16
8.15
8.15
7.83
7.82
7.82
7.80
7.80
7.68
7.62
7.62
7.60
7.60
7.59
7.59
7.57
7.57
7.55
7.55
7.54
7.52
7.52
7.50
7.48
7.48
7.48
7.46
7.45
2.67
0.30
TMS
2e
1.00
1.01
0.97
2.01
1.04
6.07
2.99
9.01
f1 (ppm)


141.1
138.4
138.1
136.3
132.5
130.8
130.7
130.5
130.3
130.1
129.9
128.8
128.6
128.3
127.5
127.4
122.4
122.1
22.3
1.0
TMS
2e
f1 (ppm)


OMe
2f
8.70
8.67
8.42
8.42
8.42
8.42
8.41
7.78
7.76
7.65
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.53
7.53
7.52
7.52
7.50
7.50
7.50
7.48
7.48
7.47
7.46
7.45
7.41
7.41
7.38
7.38
7.38
7.33
7.33
7.32
7.31
7.29
7.28
1.00
1.00
1.01
0.99
5.00
1.00
1.97
3.00
3.00
f1 (ppm)


OMe
2f
158.3
141.2
137.4
136.5
132.8
130.3
130.1
128.7
128.6
128.5
128.1
127.8
127.4
124.9
124.6
121.9
116.3
108.0
55.4
22.3
f1 (ppm)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7.80
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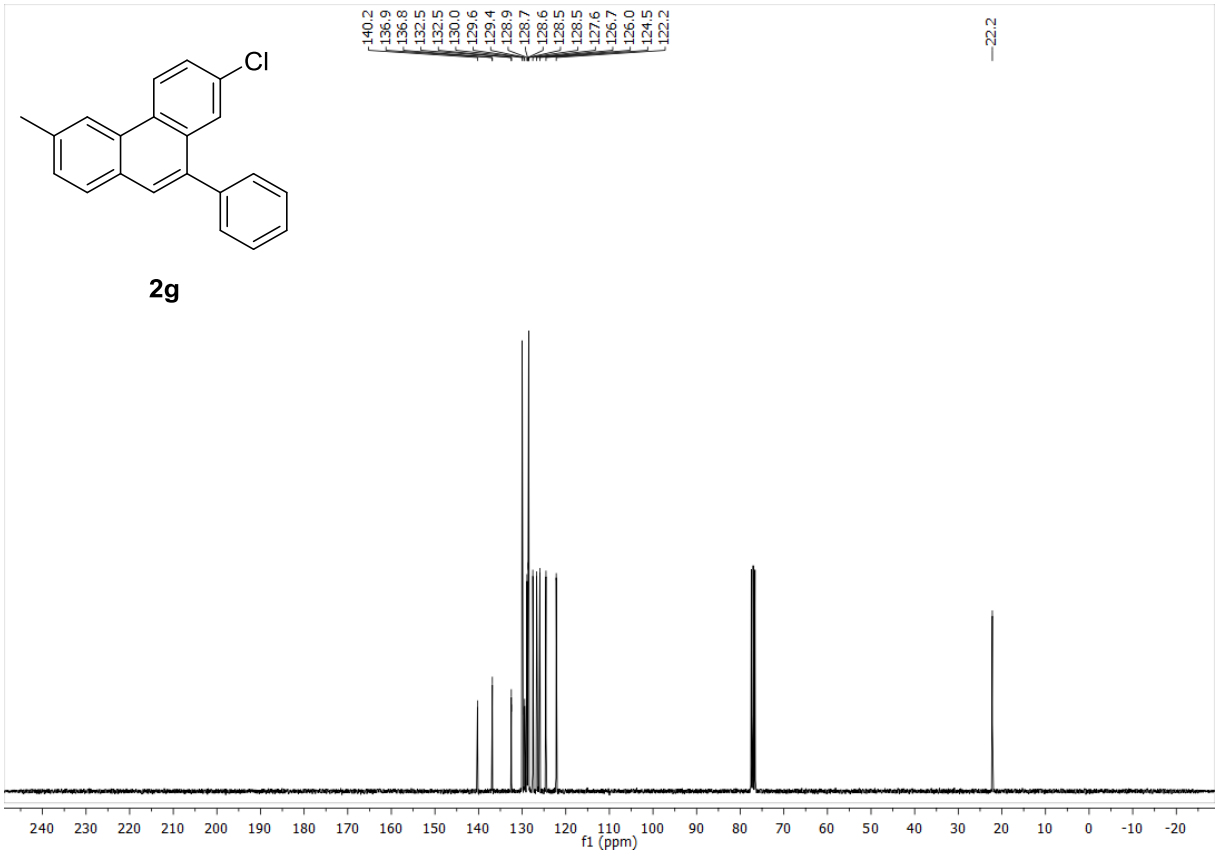
7.57
7.55
7.55
7.54
7.54
7.53
7.52
7.51
7.51
7.51
7.50
7.49
7.48
7.48
7.48
7.48
7.46
7.45
7.45
2.65
Cl
1.00
1.00
0.97
1.01
0.99
1.05
5.87
2.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

2g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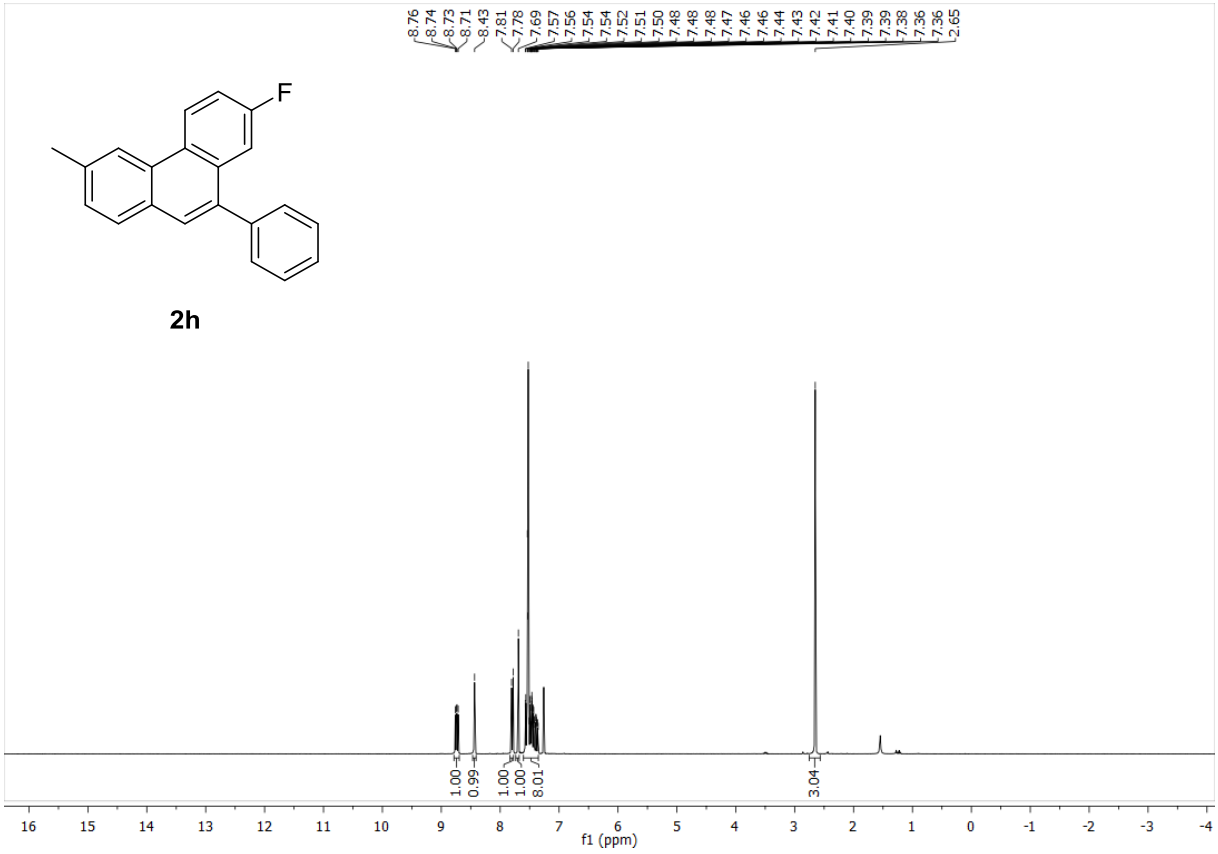
136.8
132.5
132.5
130.0
129.6
129.4
128.9
128.7
128.6
128.5
128.5
127.6
126.7
126.0
124.5
122.2
22.2
Cl
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2g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7.51
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7.48
7.48
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7.47
7.46
7.46
7.44
7.43
7.42
7.41
7.40
7.39
7.39
7.38
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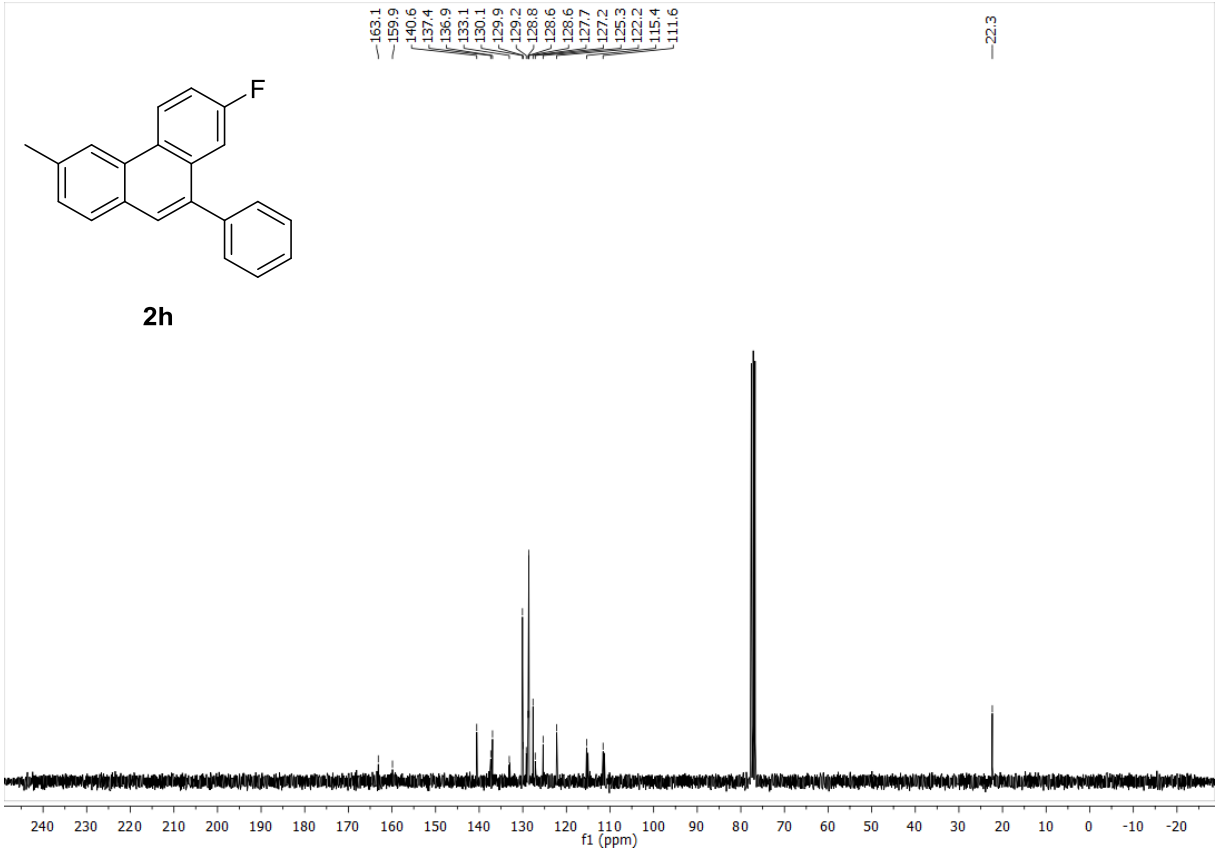
2.65
F
2h
1.00
0.99
1.00
1.00
8.01
3.04
f1 (ppm)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129.2
128.8
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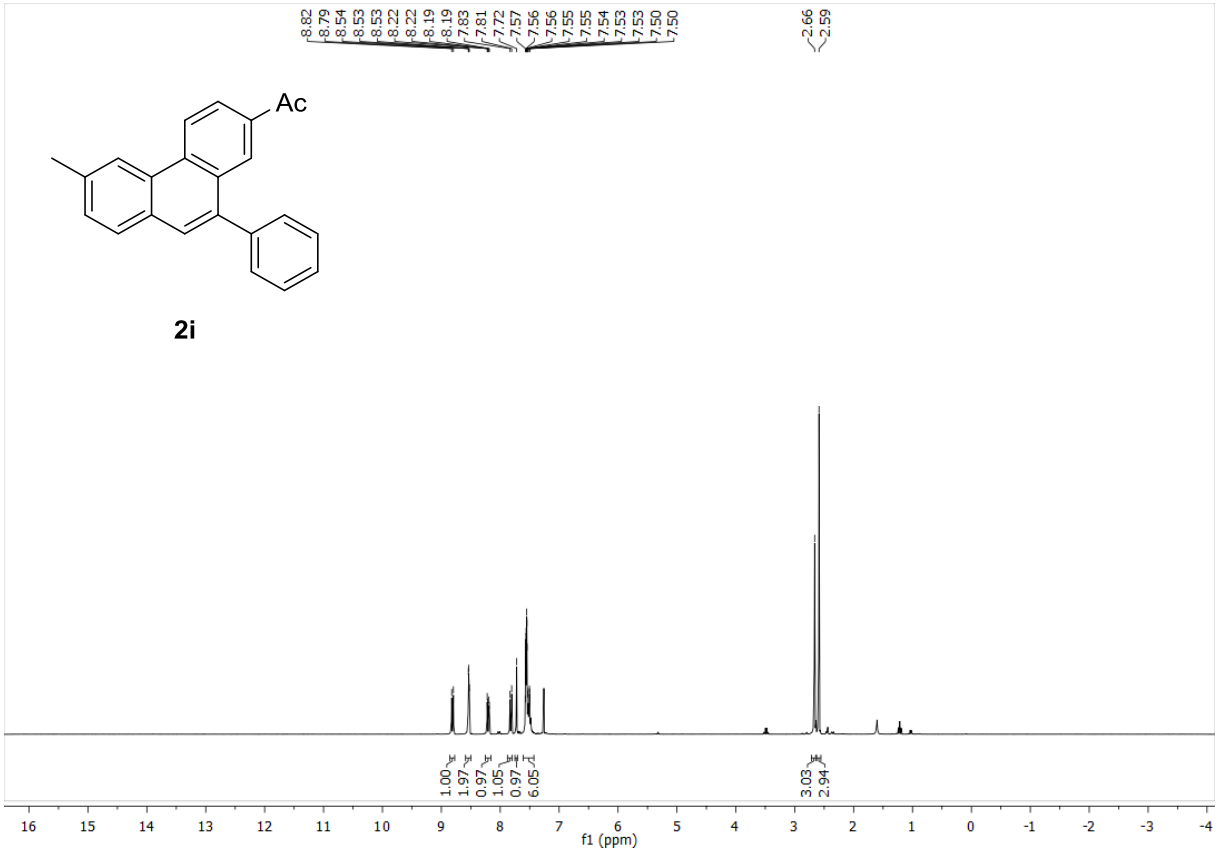
127.7
127.2
125.3
122.2
115.4
111.6
22.3
F
2h
f1 (ppm)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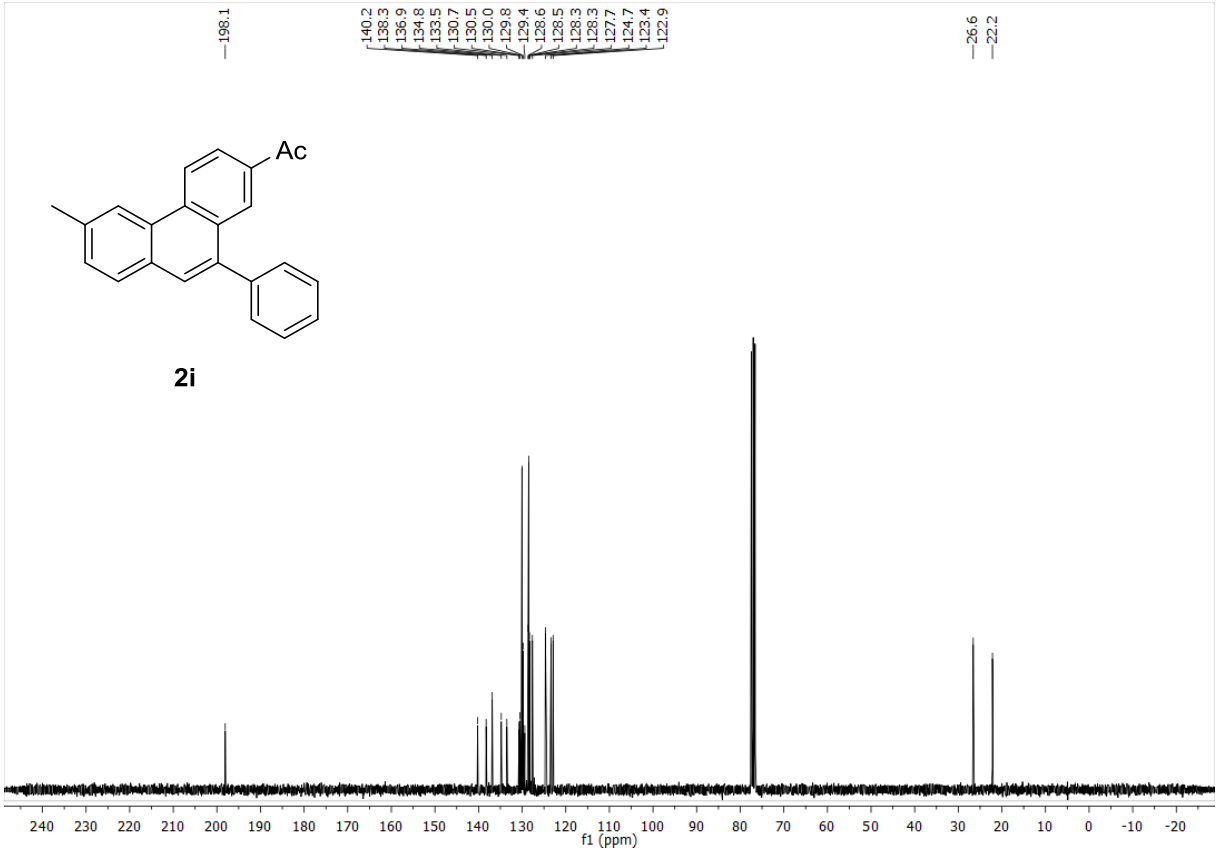
8.22
8.19
8.19
7.83
7.81
7.72
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.50
7.50
2.66
2.59
Ac
1.00
1.97
0.97
1.05
0.97
6.05
3.03
2.94
f1 (ppm)

2i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129.4
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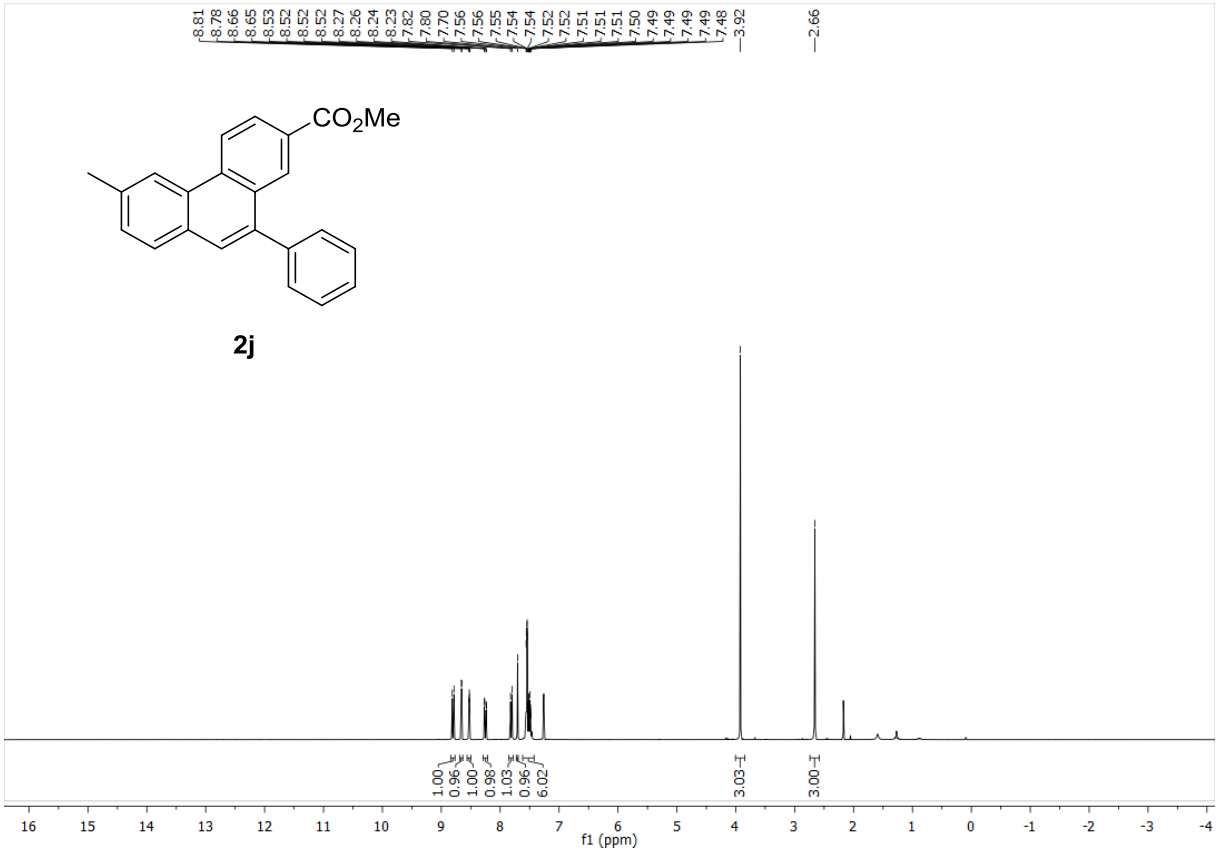
128.3
127.7
124.7
123.4
122.9
26.6
22.2
Ac
f1 (ppm)

2i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7.80
7.70
7.56
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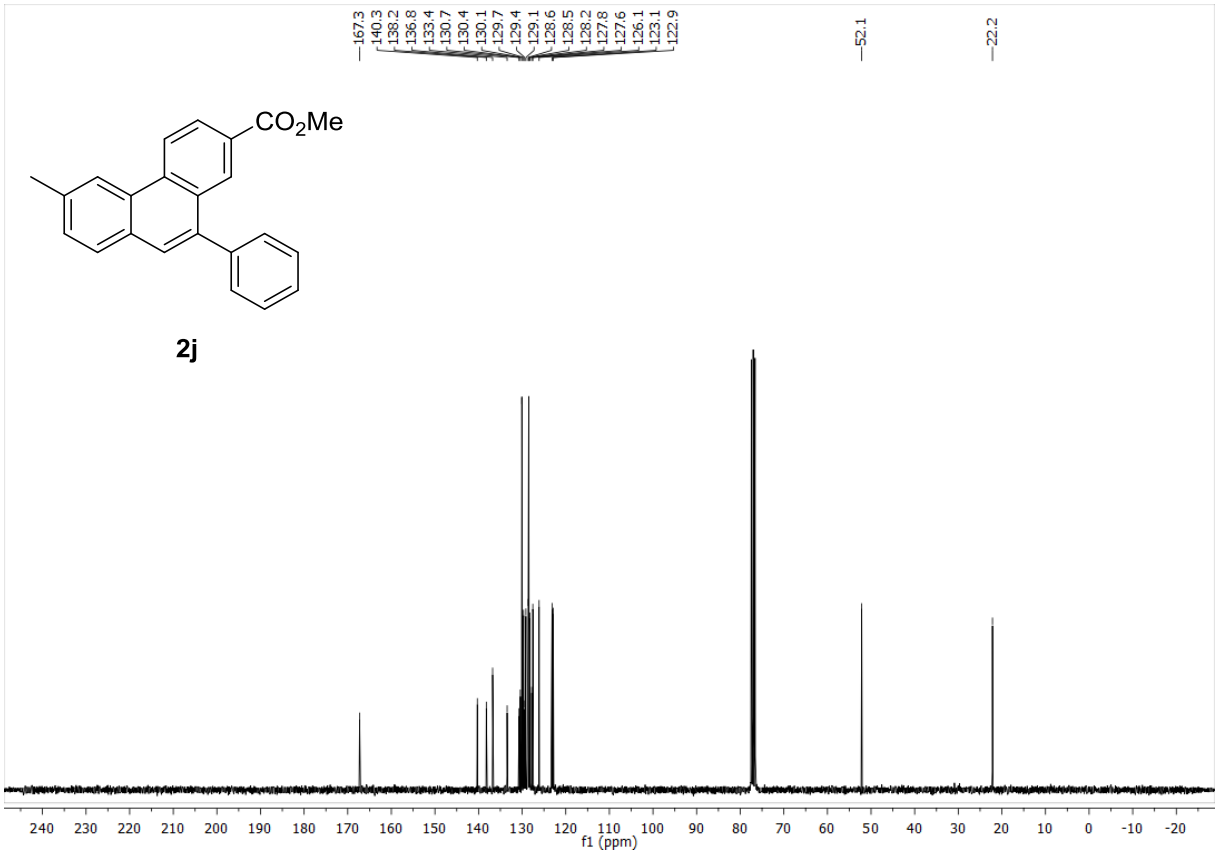
7.55
7.54
7.54
7.52
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.49
7.49
7.48
3.92
2.66
CO2Me
2j
1.00
0.96
1.00
0.98
1.03
0.96
6.02
3.03
3.00
f1 (ppm)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128.6
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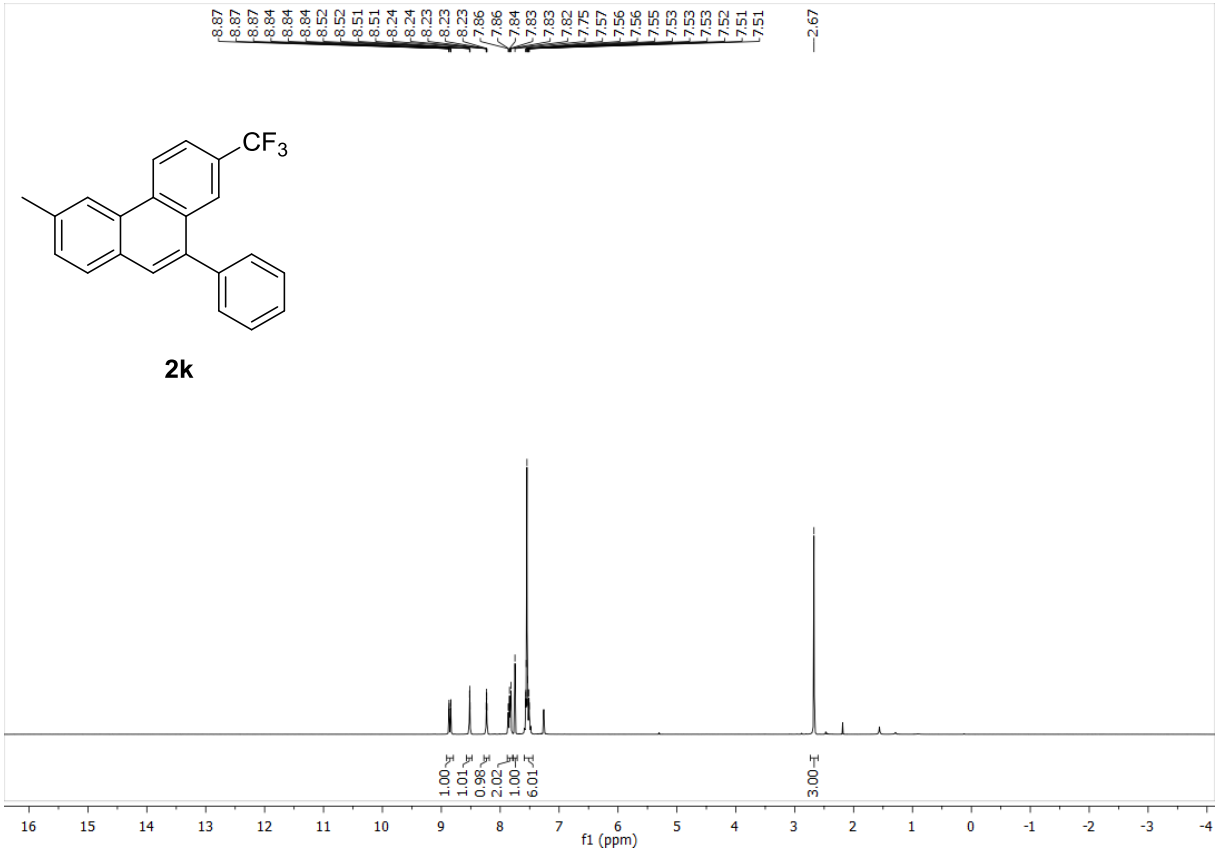
127.8
127.6
126.1
123.1
122.9
52.1
22.2
CO2Me
2j
f1 (ppm)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8.23
8.23
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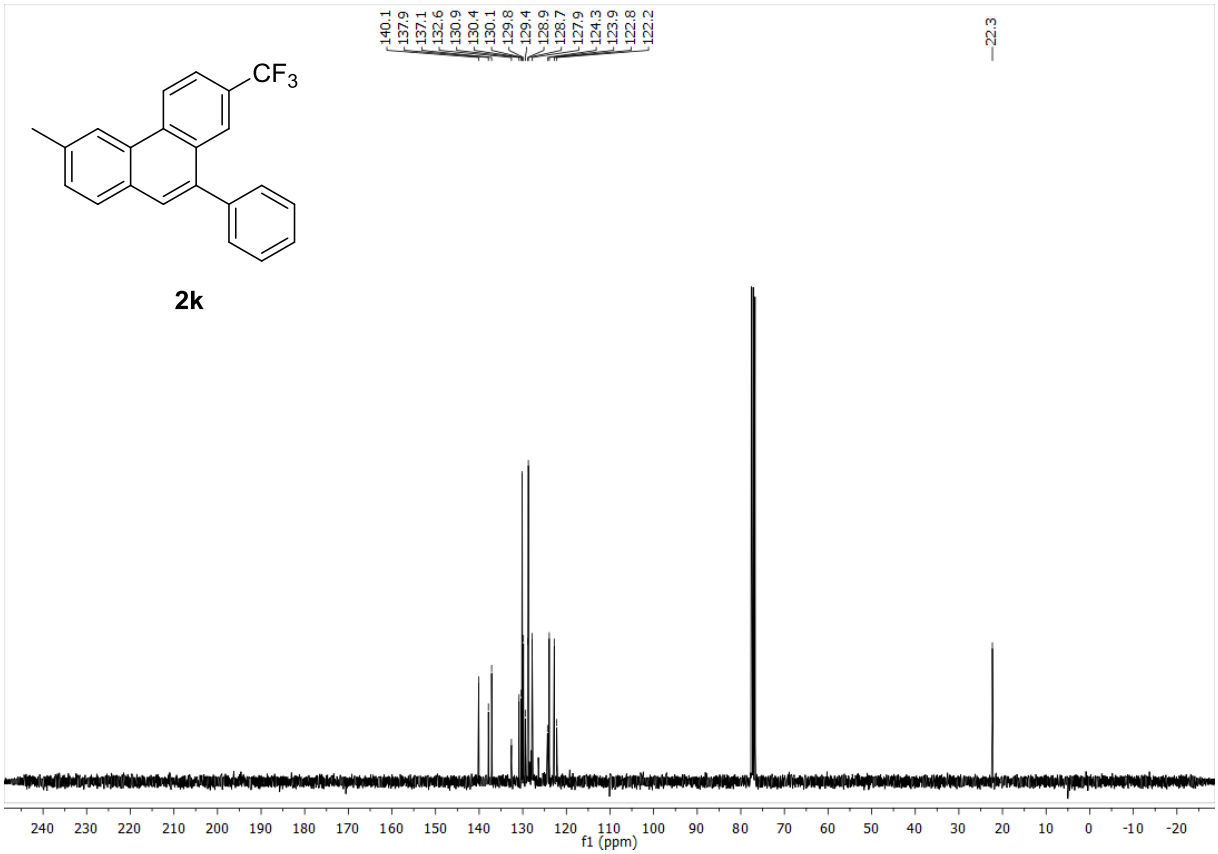
7.86
7.84
7.83
7.83
7.82
7.75
7.57
7.56
7.56
7.55
7.53
7.53
7.53
7.52
7.51
7.51
2.67
CF3
2k
1.00
1.01
0.98
2.02
1.00
6.01
3.00
f1 (ppm)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137.9
137.1
132.6
130.9
130.4
130.1
129.8
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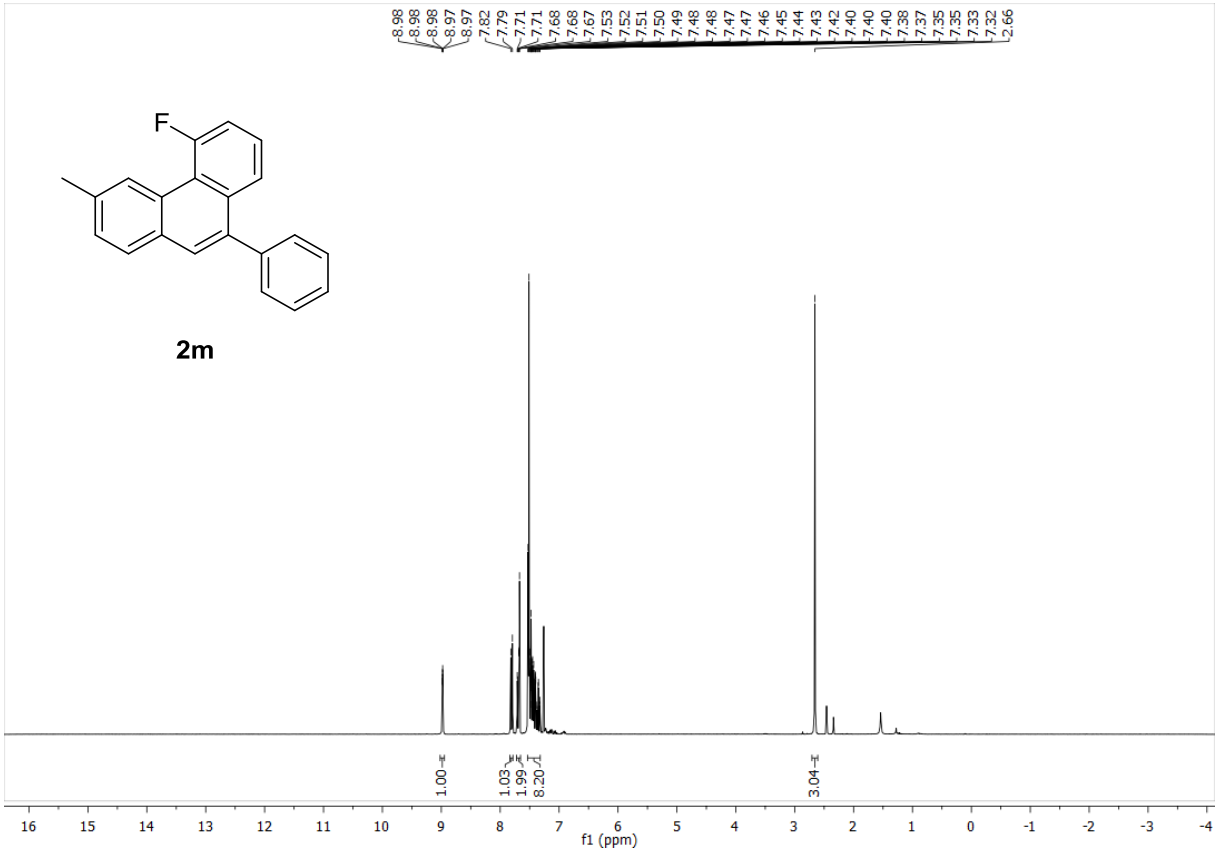
128.9
128.7
127.9
124.3
123.9
122.8
122.2
22.3
CF3
2k
f1 (ppm)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8.98
8.97
8.97
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7.79
7.71
7.71
7.68
7.68
7.67
7.53
7.52
7.51
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.42
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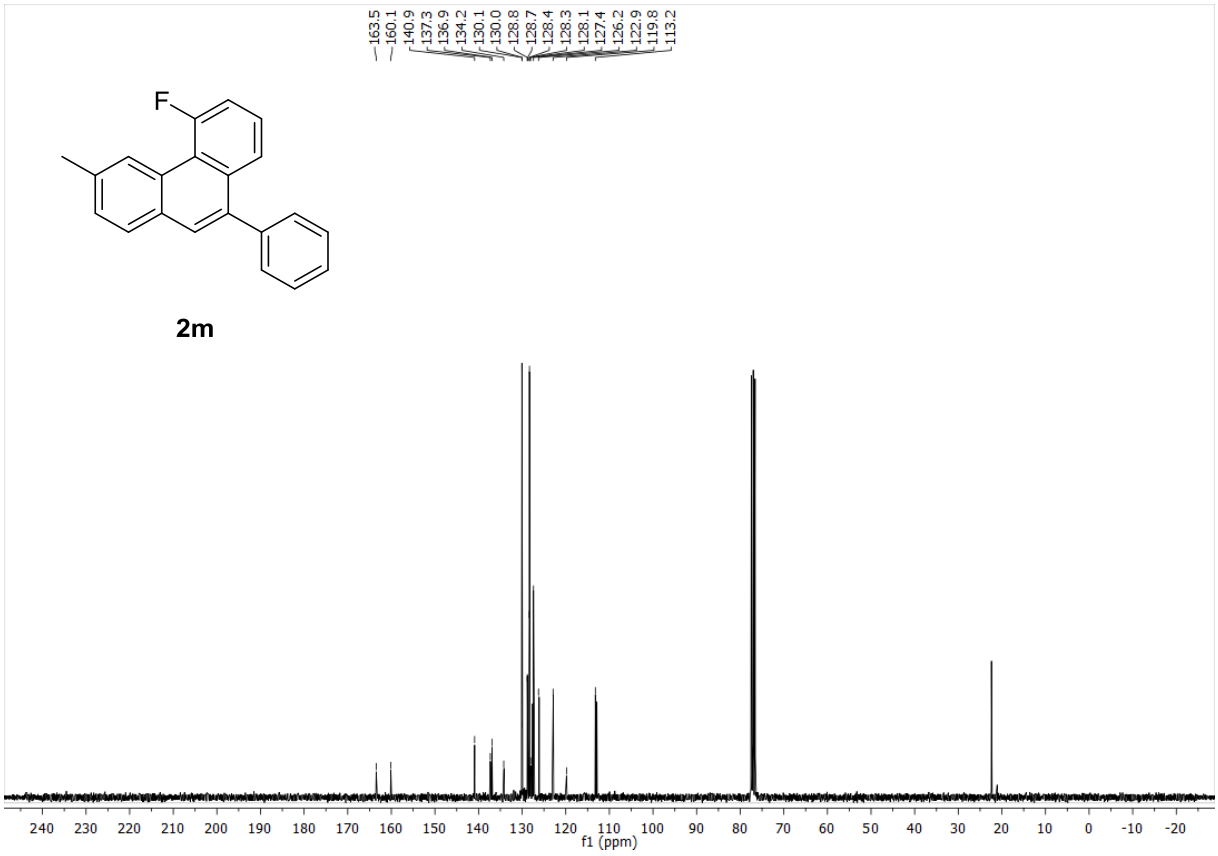
7.40
7.40
7.38
7.37
7.35
7.35
7.33
7.32
2.66
F
2m
1.00
1.03
1.99
8.20
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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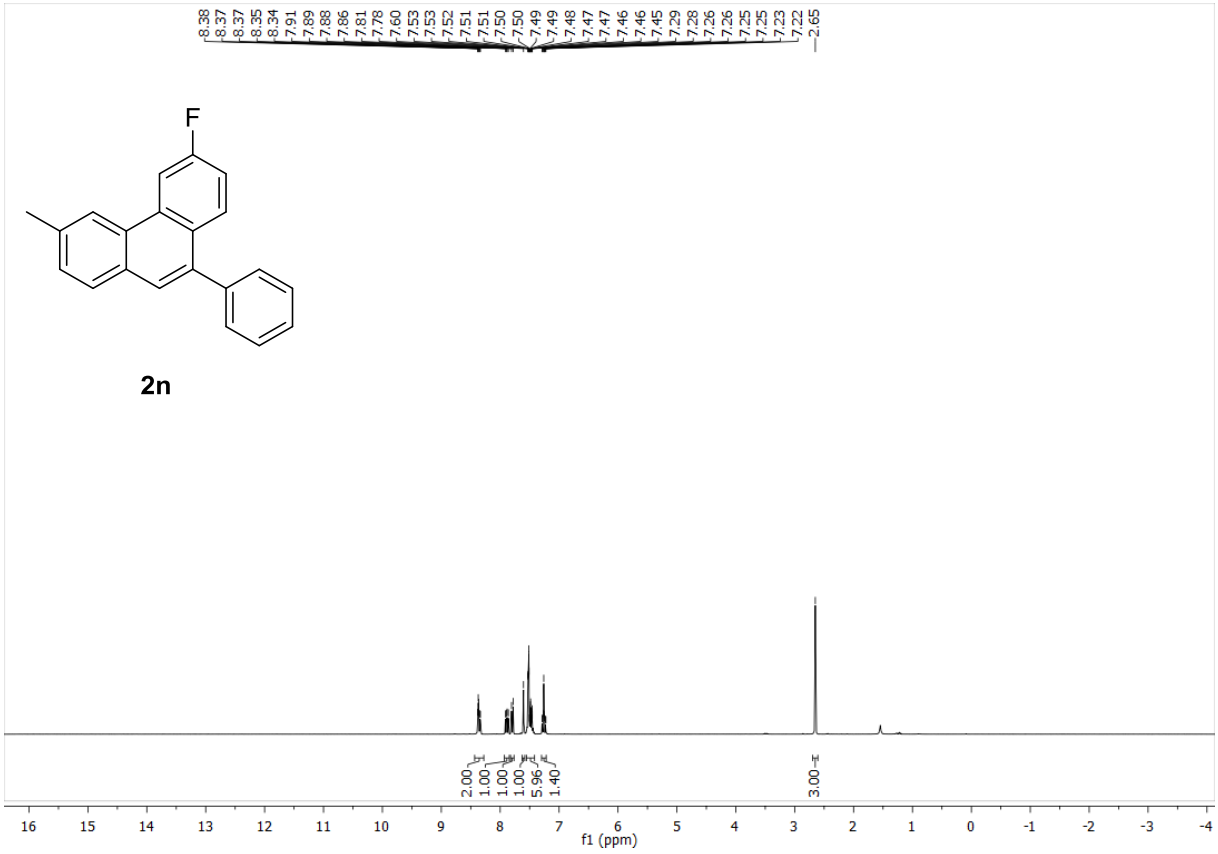
140.9
137.3
136.9
134.2
130.1
130.0
128.8
128.7
128.4
128.3
128.1
127.4
126.2
122.9
119.8
113.2
F
2m
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.88
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7.81
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7.53
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7.52
7.51
7.51
7.50
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7.48
7.47
7.47
7.46
7.46
7.45
7.29
7.28
7.26
7.26
7.25
7.25
7.23
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F
2n
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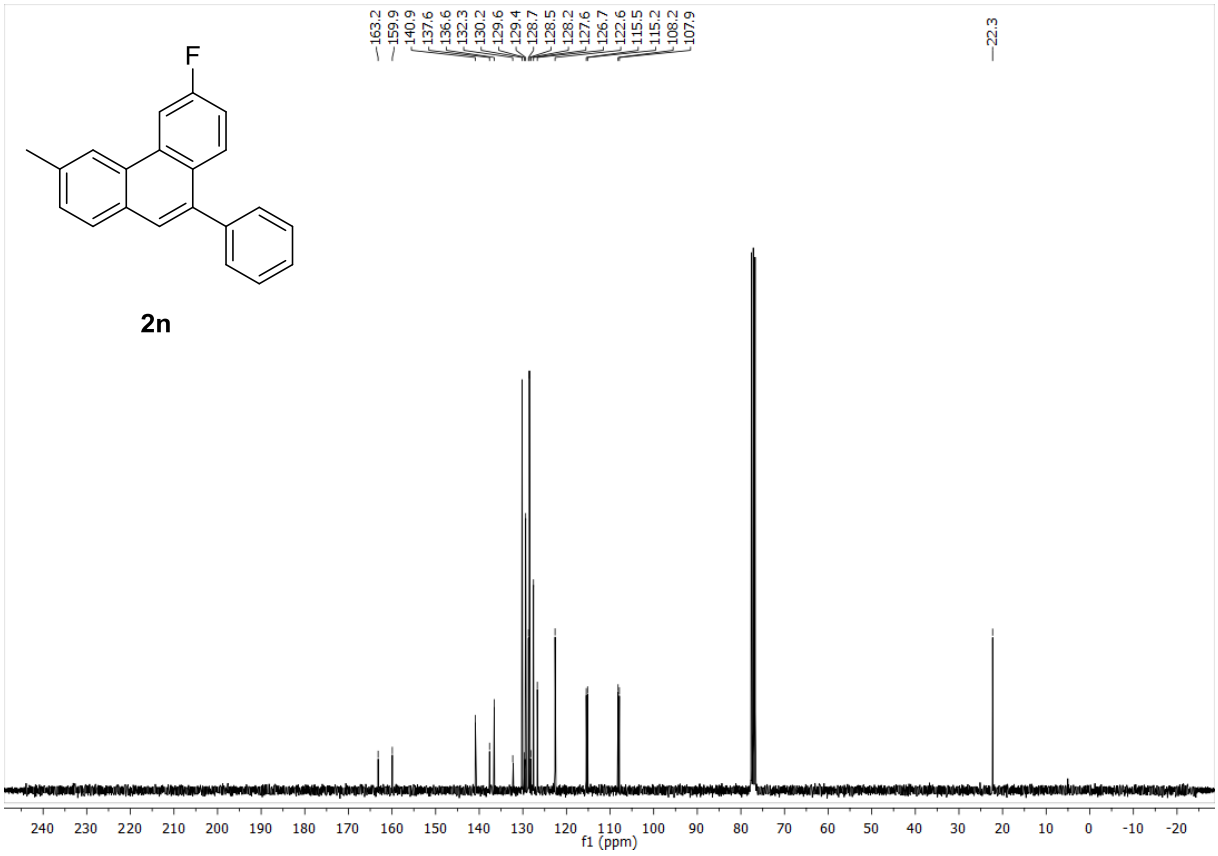
1.00
1.00
5.96
1.40
3.00
f1 (ppm)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140.9
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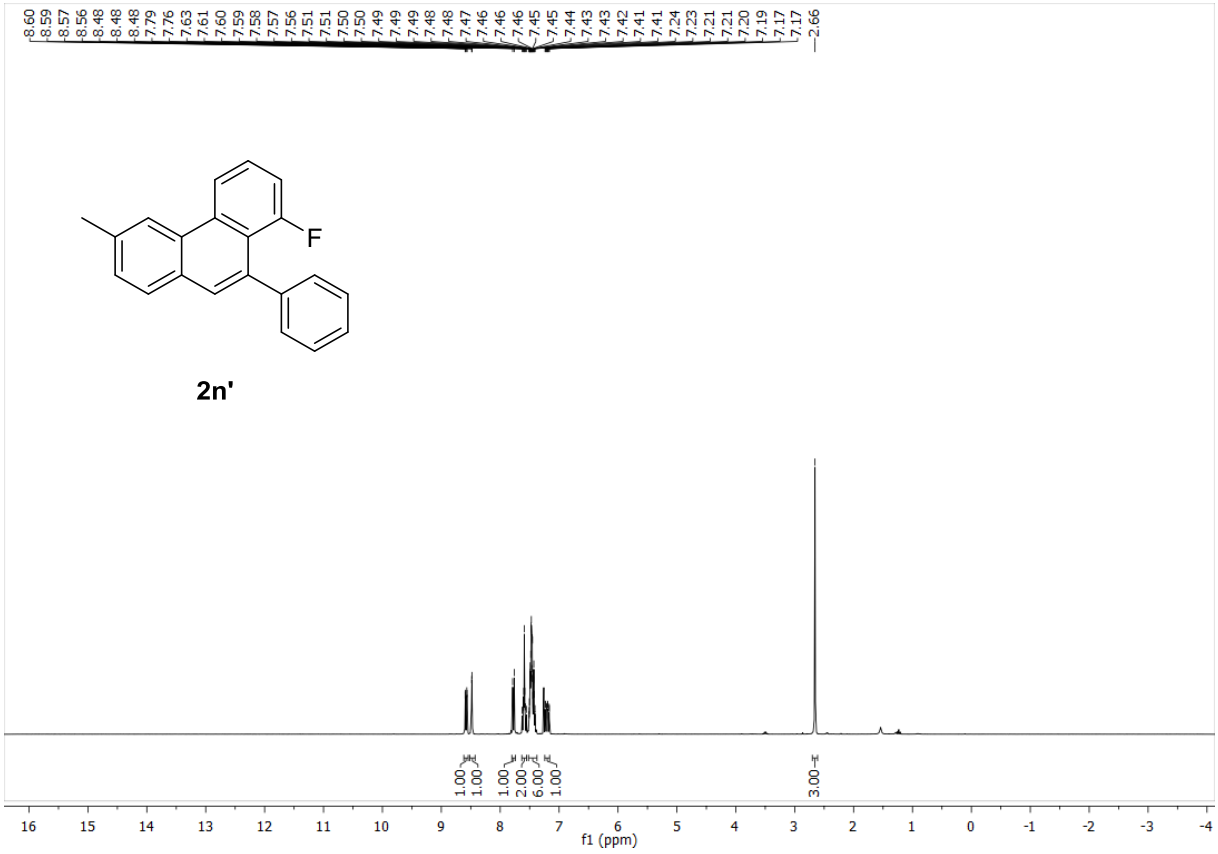
130.2
129.6
129.4
128.7
128.5
128.2
127.6
126.7
122.6
115.5
115.2
108.2
107.9
22.3
F
2n
f1 (ppm)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7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.24
7.23
7.21
7.21
7.20
7.19
7.17
7.17
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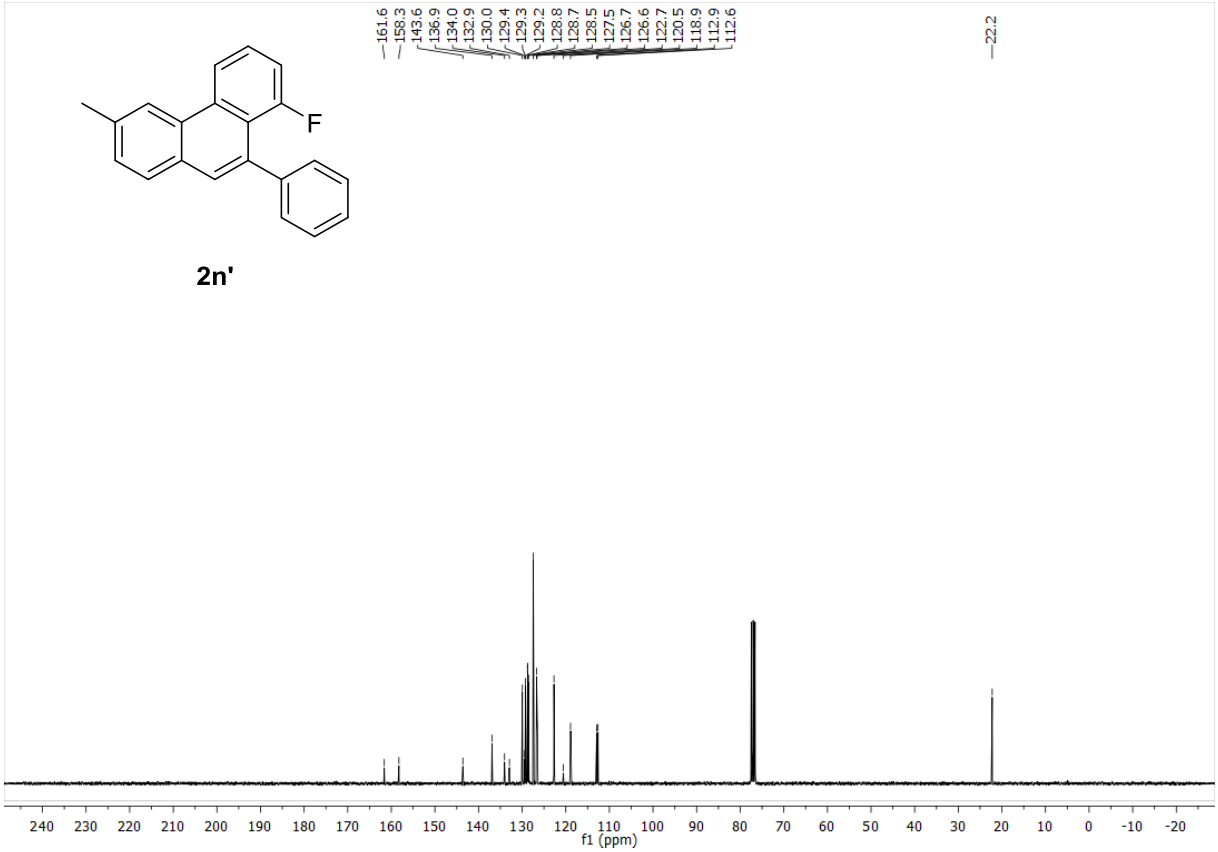
F
2n'
1.00
1.00
1.00
2.00
6.00
1.00
3.00
f1 (ppm)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129.4
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129.2
128.8
128.7
128.5
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126.6
122.7
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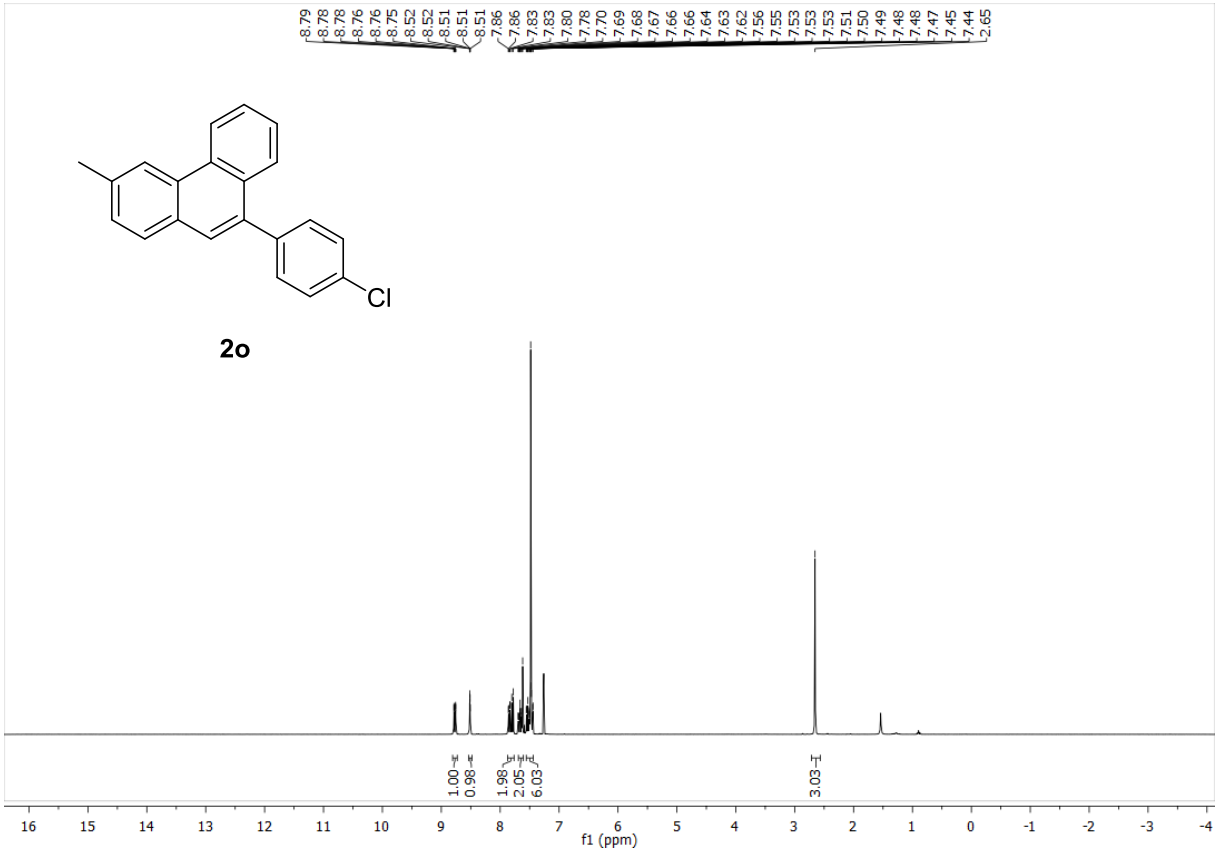
112.9
112.6
22.2
F
2n'
f1 (ppm)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7.69
7.68
7.67
7.66
7.66
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7.63
7.62
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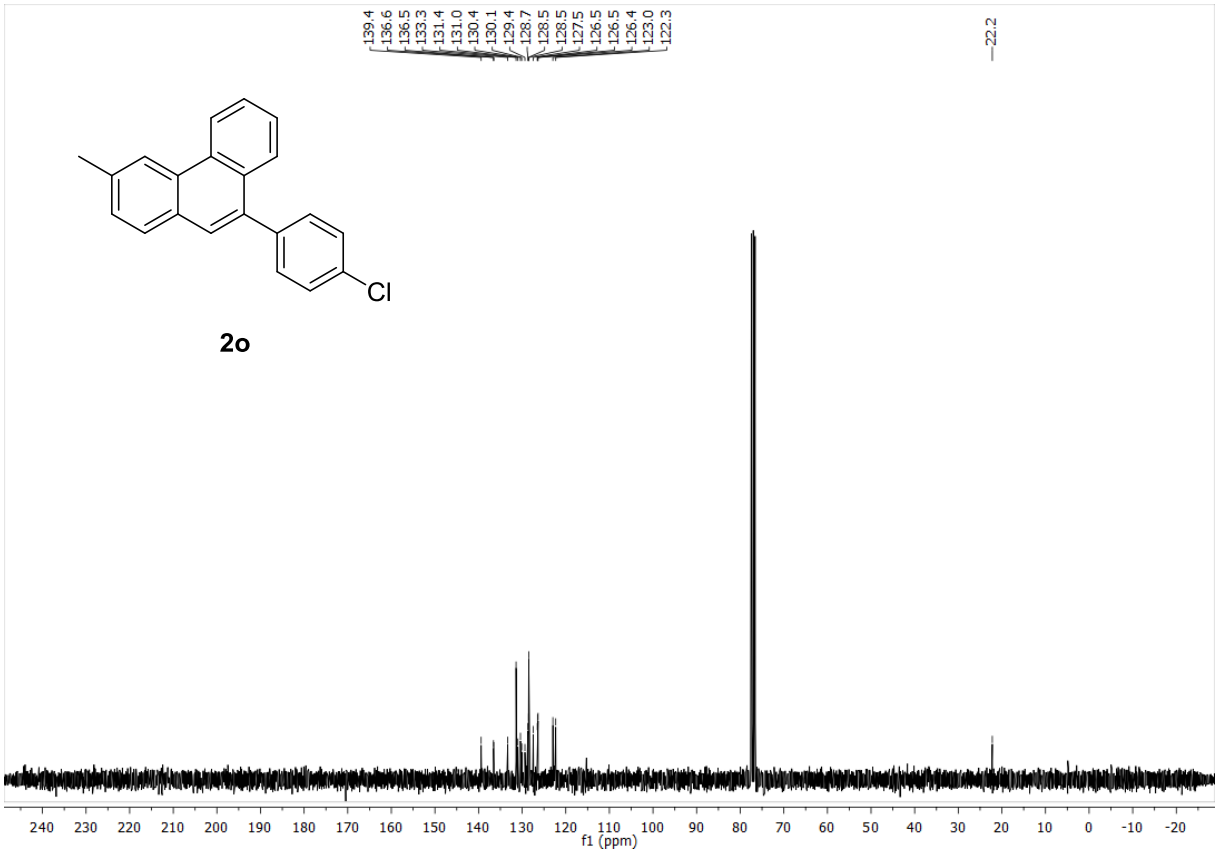
7.53
7.53
7.53
7.51
7.50
7.49
7.48
7.48
7.47
7.45
7.44
2.65
Cl
2o
1.00
0.98
1.98
2.05
6.03
3.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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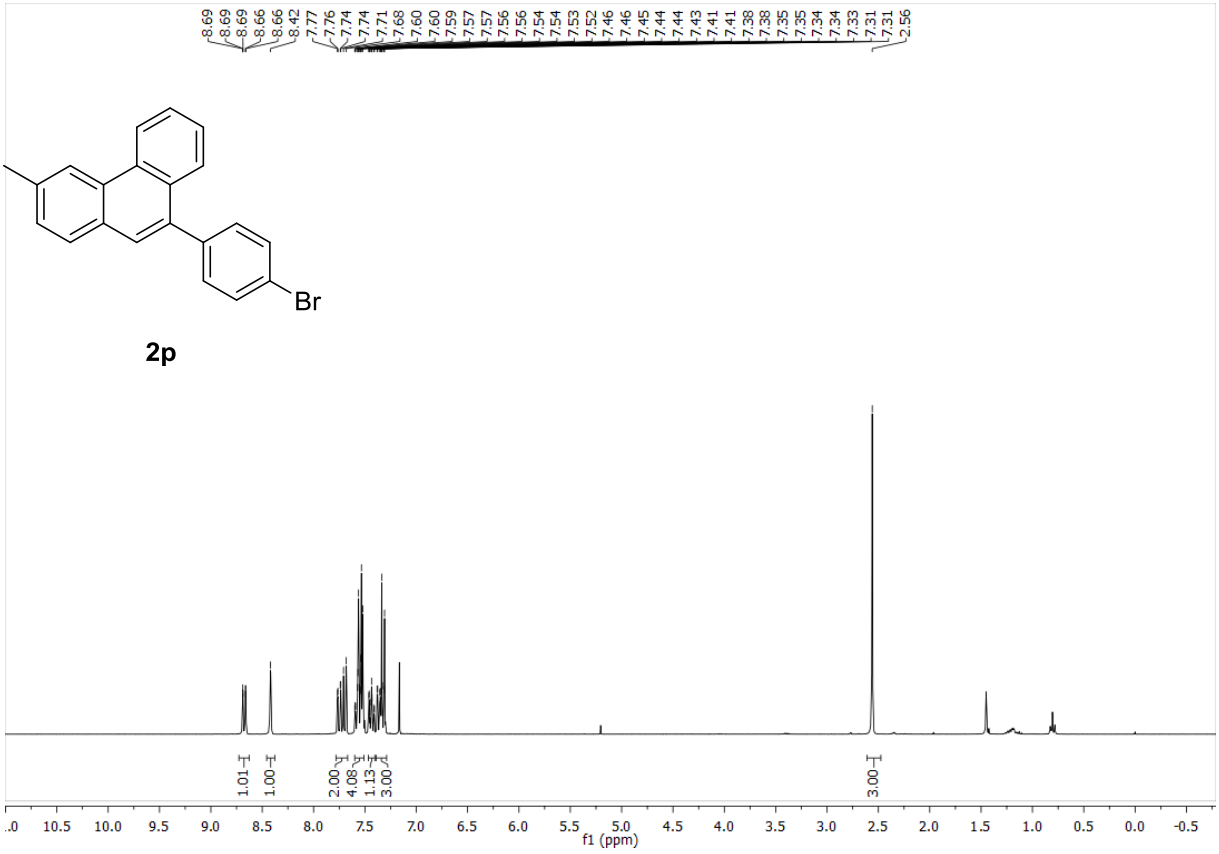
128.7
128.5
128.5
127.5
126.5
126.5
126.4
123.0
122.3
22.2
Cl
2o
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.60
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7.41
7.41
7.38
7.35
7.35
7.34
7.34
7.33
7.31
7.31
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Br
2p
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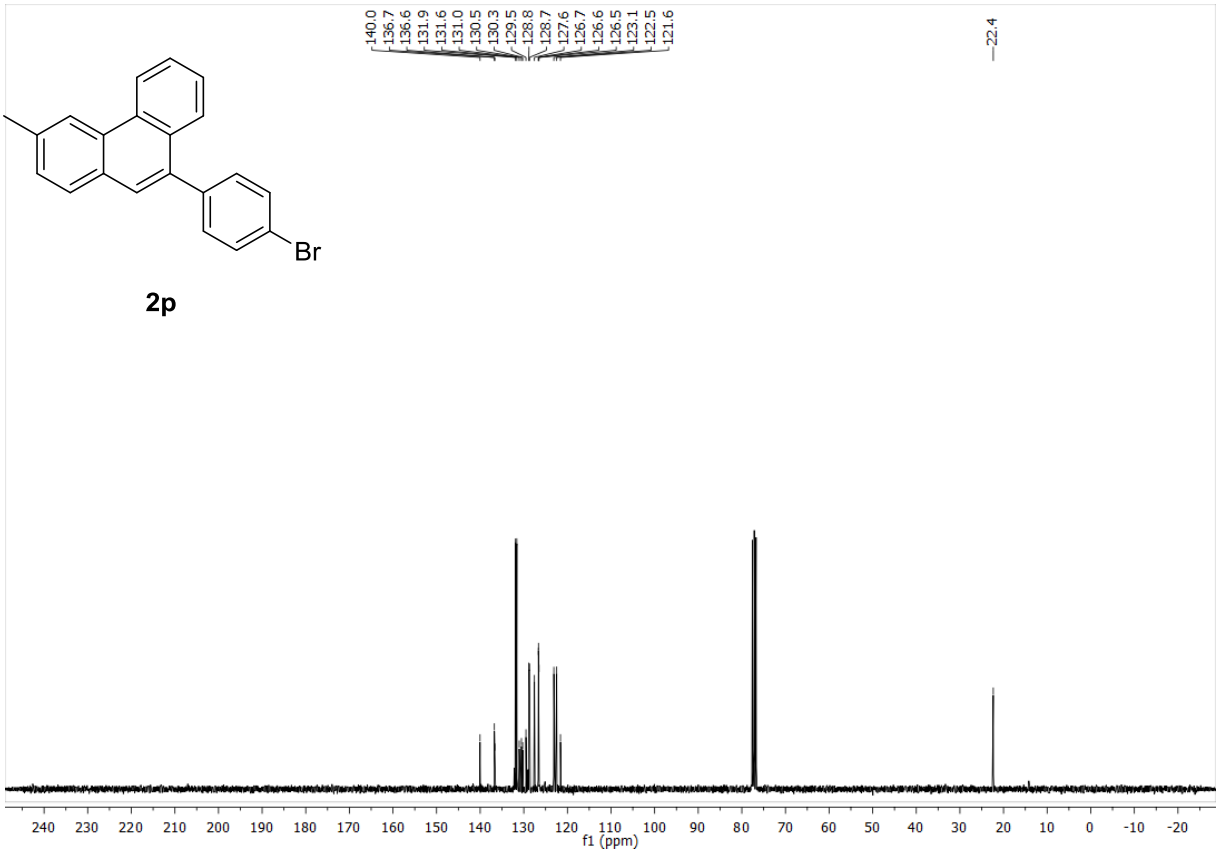
1.13
3.00
3.00
f1 (ppm)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130.3
129.5
128.8
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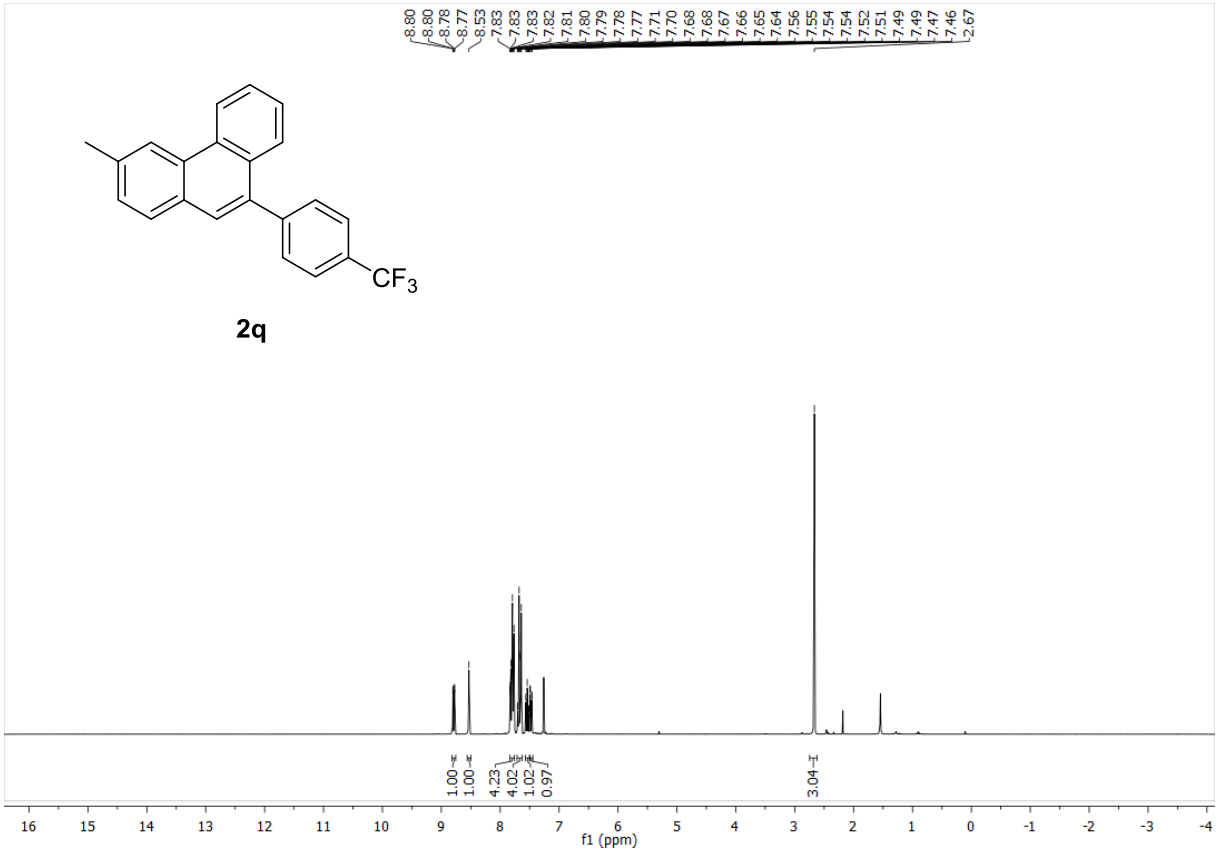
122.5
121.6
22.4
Br
2p
f1 (ppm)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7.77
7.71
7.70
7.68
7.68
7.67
7.66
7.65
7.64
7.56
7.55
7.54
7.54
7.52
7.51
7.49
7.49
7.47
7.46
2.67
CF3
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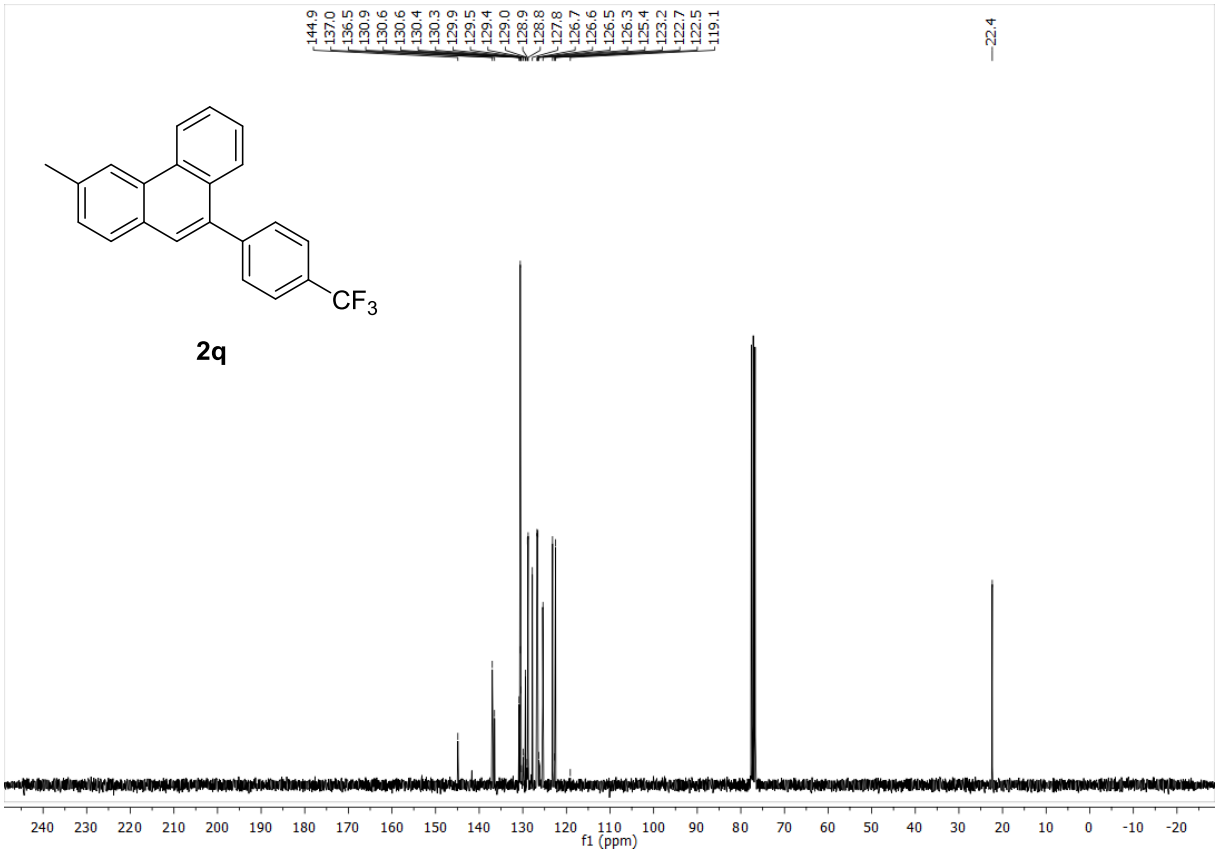
1.00
4.23
4.02
1.02
0.97
3.04
f1 (ppm)

2q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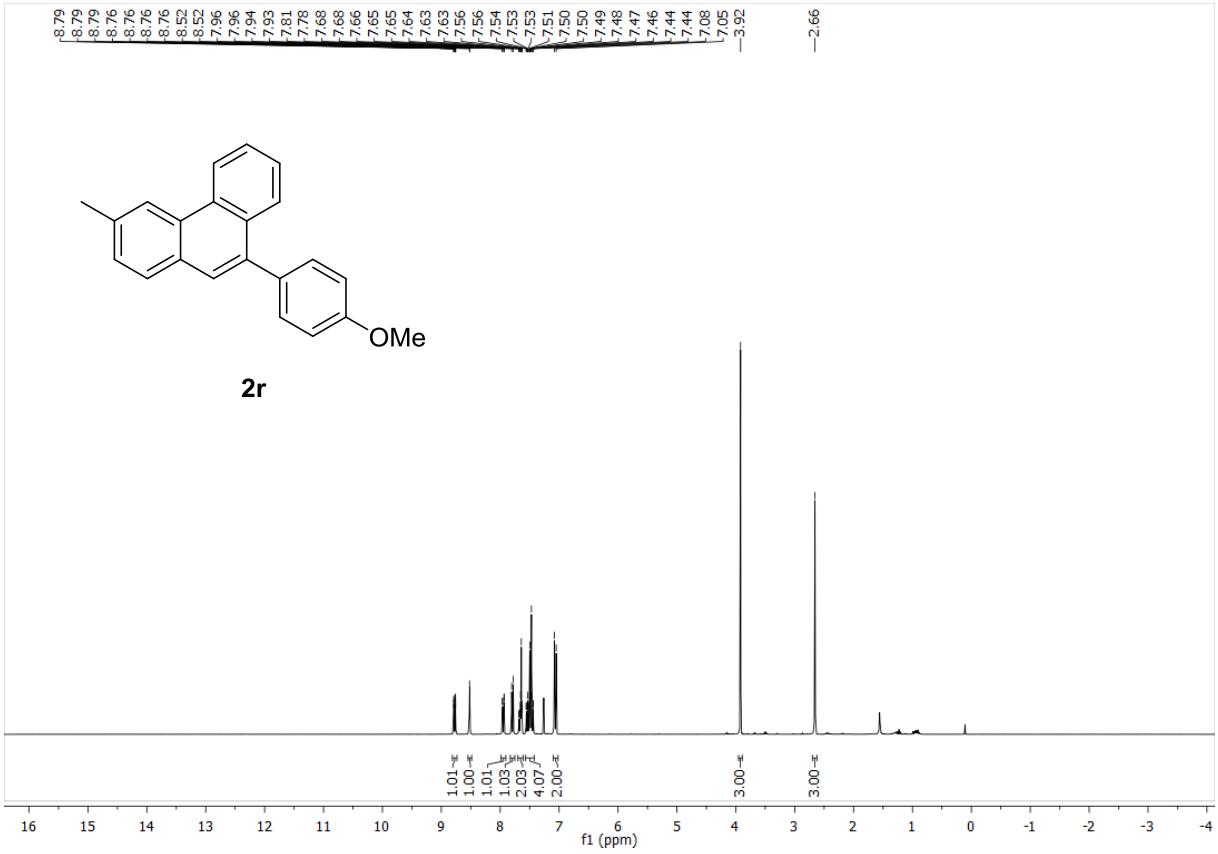
129.0
128.9
128.8
127.8
126.7
126.6
126.5
126.3
125.4
123.2
122.7
122.5
119.1
22.4
CF3
f1 (ppm)

2q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7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.44
7.44
7.08
7.05
3.92
2.66
OMe
2r
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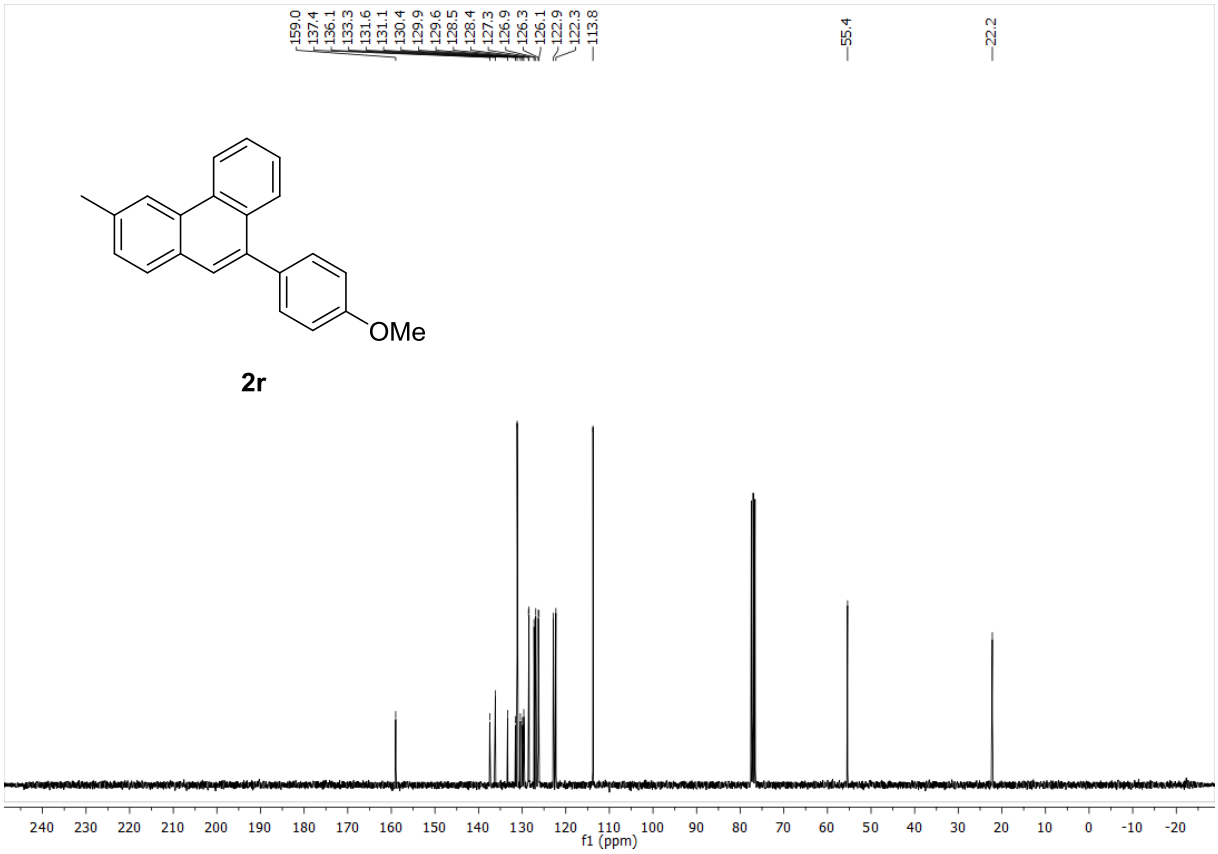
1.00
1.01
1.03
2.03
4.07
2.00
3.00
3.00
f1 (ppm)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128.5
128.4
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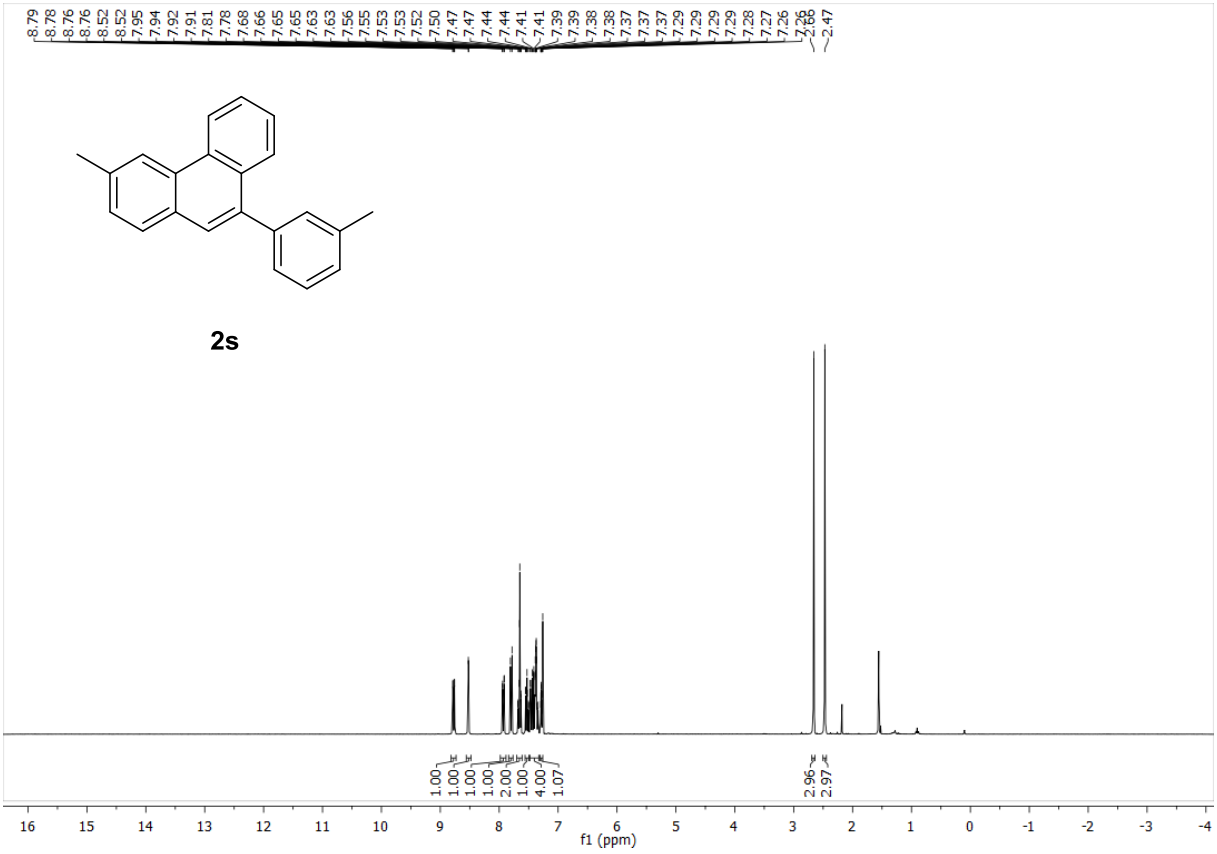
113.8
55.4
22.2
OMe
2r
f1 (ppm)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7.94
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7.91
7.81
7.78
7.68
7.66
7.65
7.65
7.63
7.63
7.56
7.55
7.53
7.53
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2.88
2.47
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1.00
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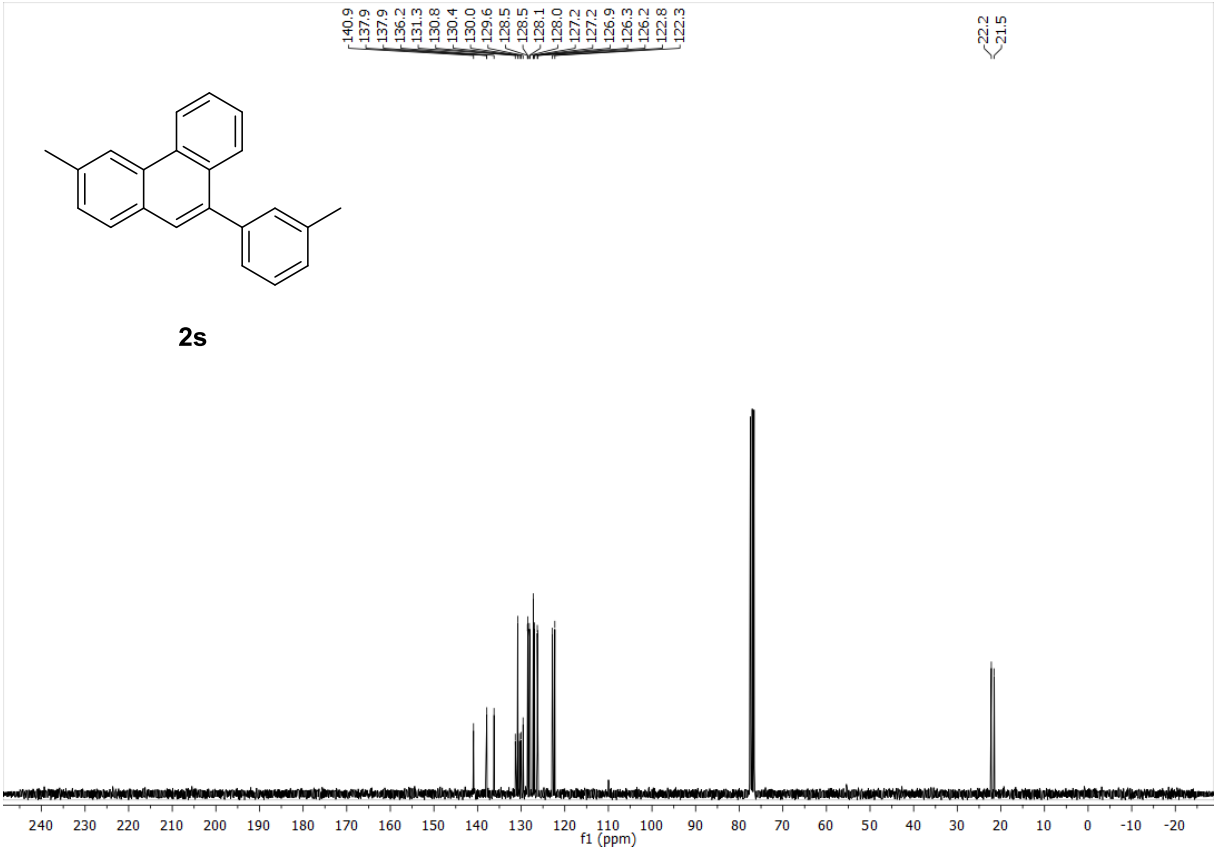
4.00
1.07
2.96
2.97
f1 (ppm)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137.9
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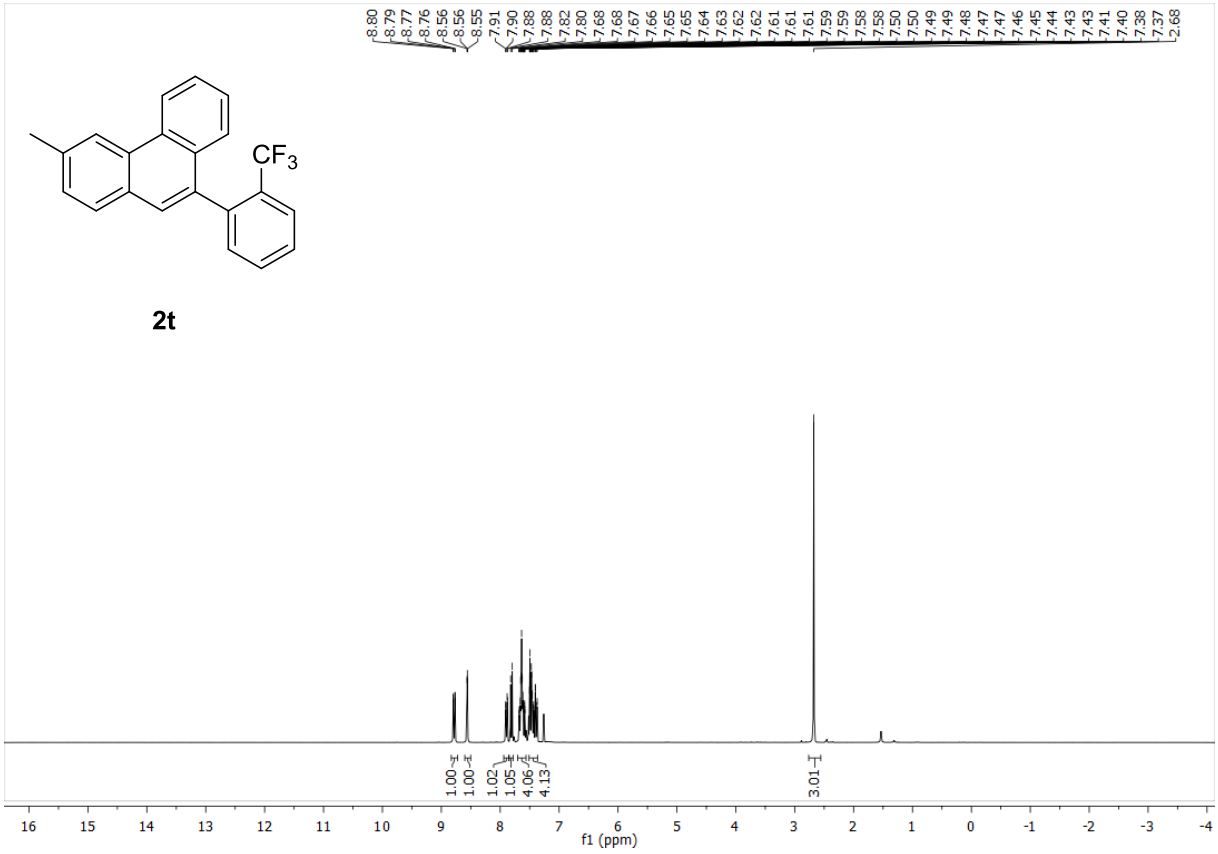
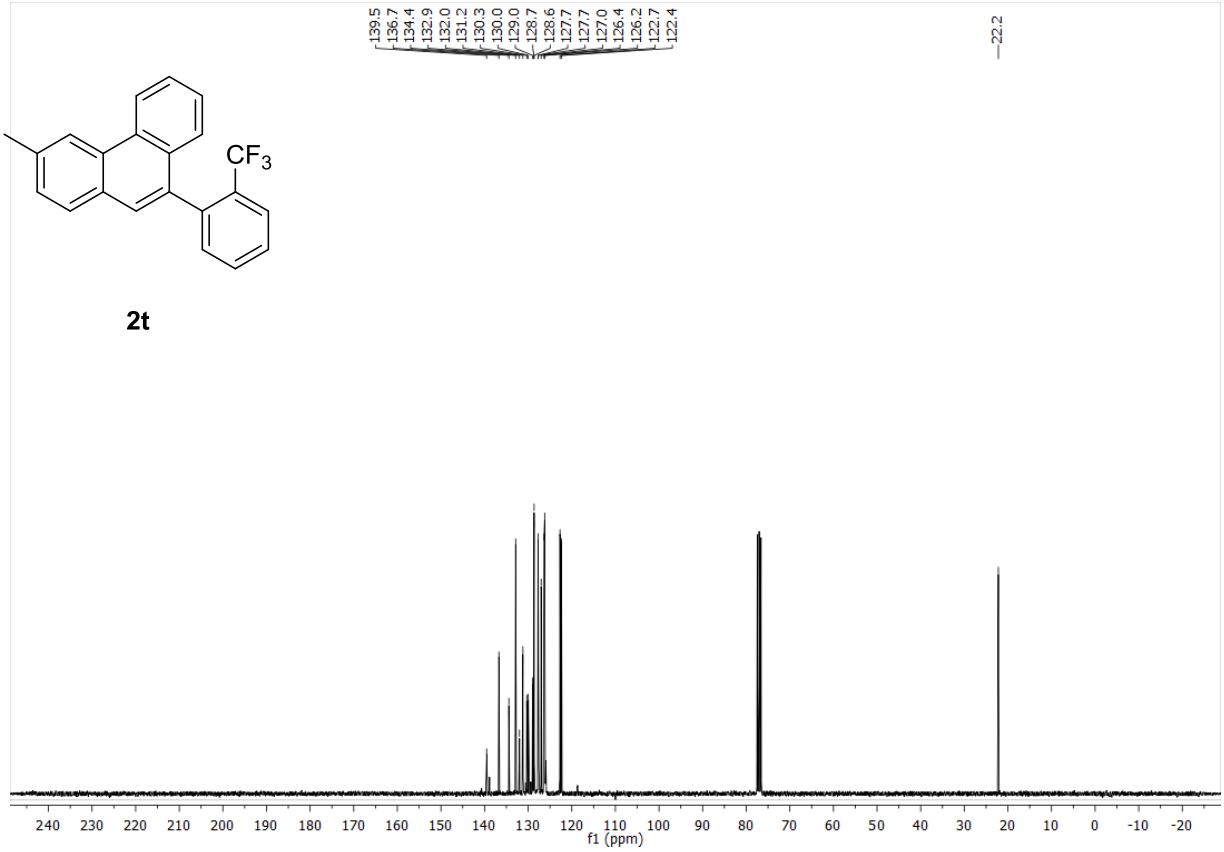
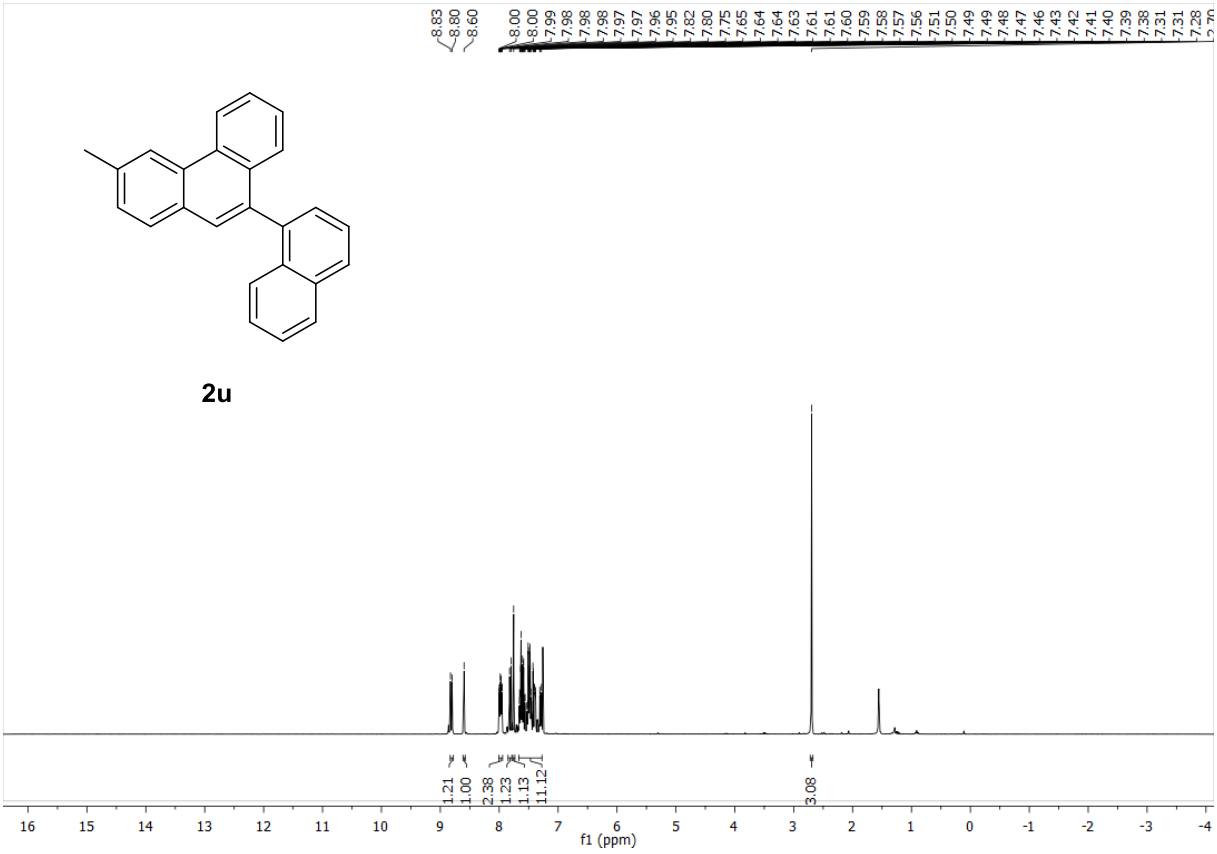
128.0
127.2
127.2
126.9
126.3
126.2
122.8
122.3
22.2
21.5
2s
f1 (ppm)


CF3
8.80
8.79
8.77
8.76
8.56
8.56
8.55
7.91
7.90
7.88
7.88
7.82
7.80
7.68
7.68
7.67
7.66
7.65
7.65
7.64
7.63
7.62
7.62
7.61
7.61
7.61
7.59
7.59
7.58
7.58
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.43
7.41
7.40
7.38
7.37
2.68
1.00
1.00
1.02
1.05
4.06
4.13
3.01
f1 (ppm)

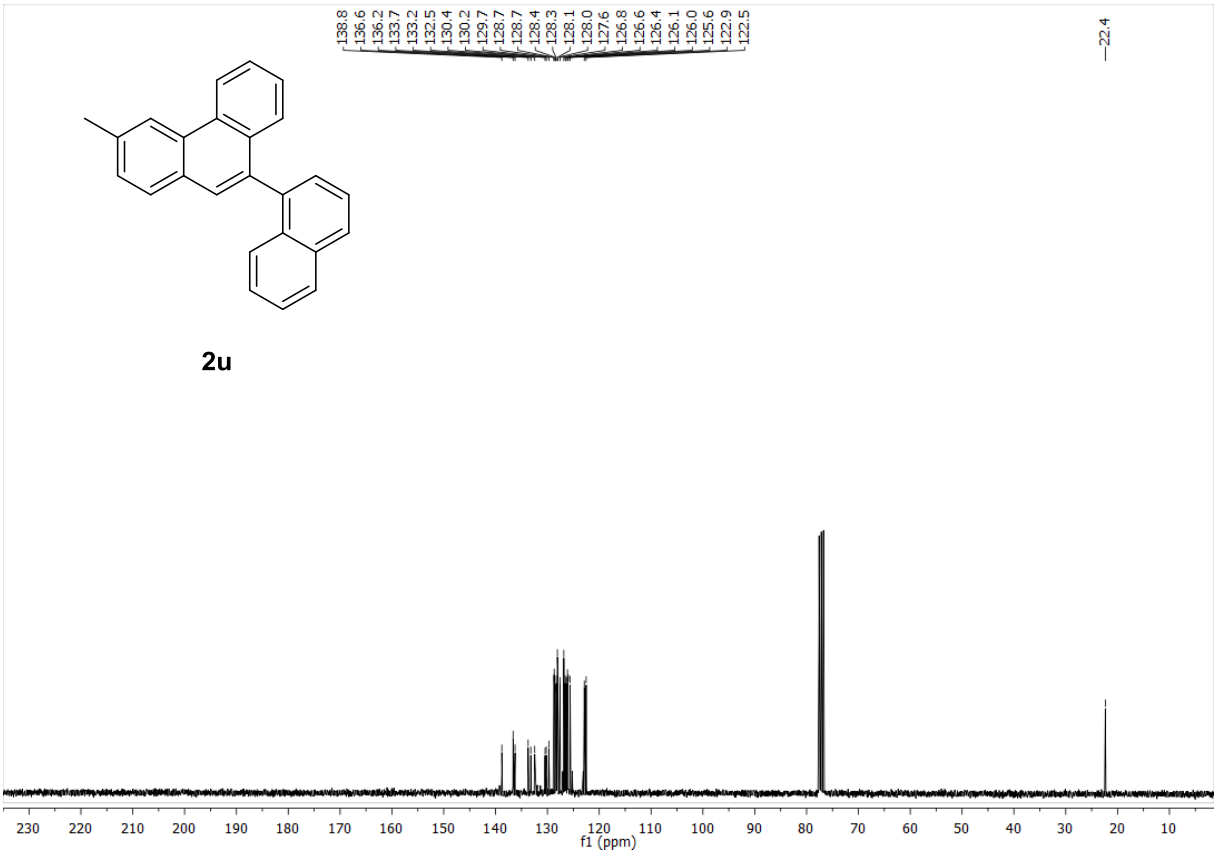
2t


CF3
139.5
136.7
134.4
132.9
132.0
131.2
130.3
130.0
129.0
128.7
128.6
127.7
127.7
127.0
126.4
126.2
122.7
122.4
22.2
f1 (ppm)

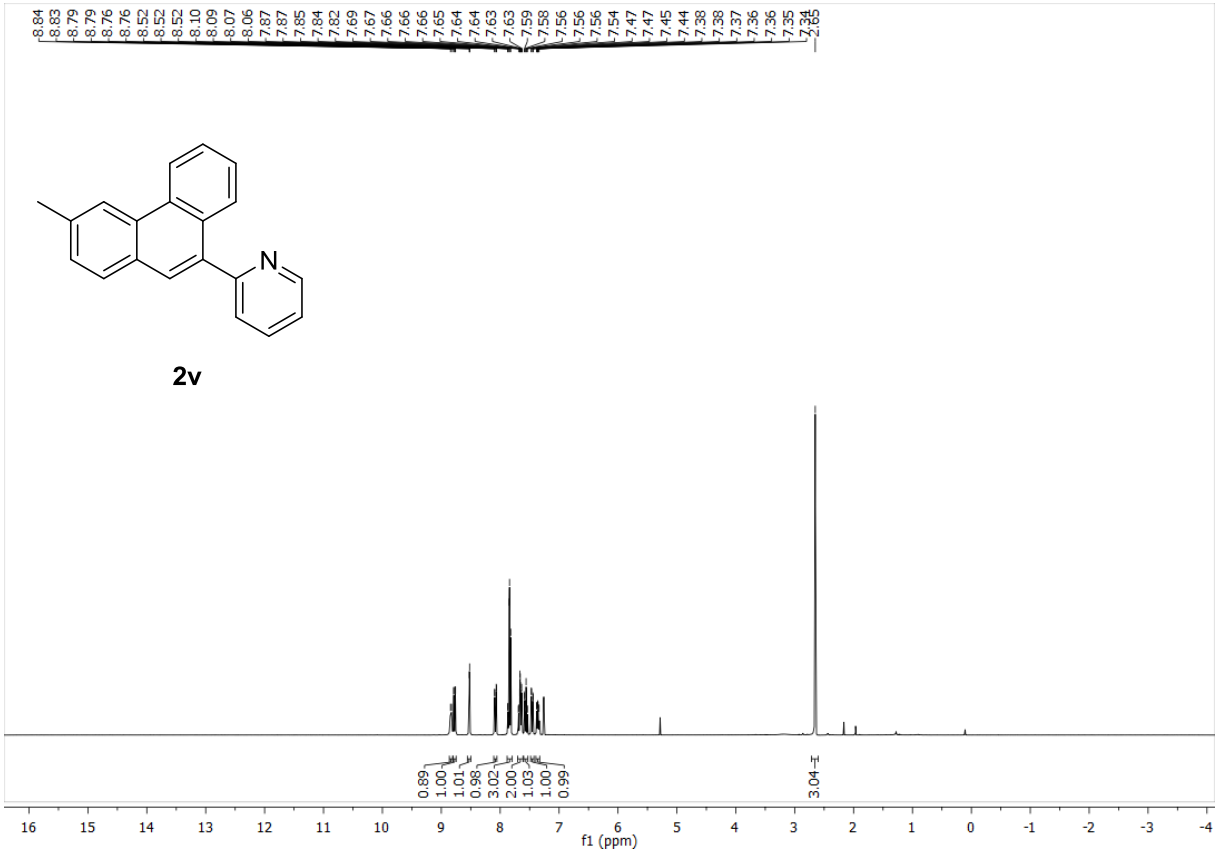
2t

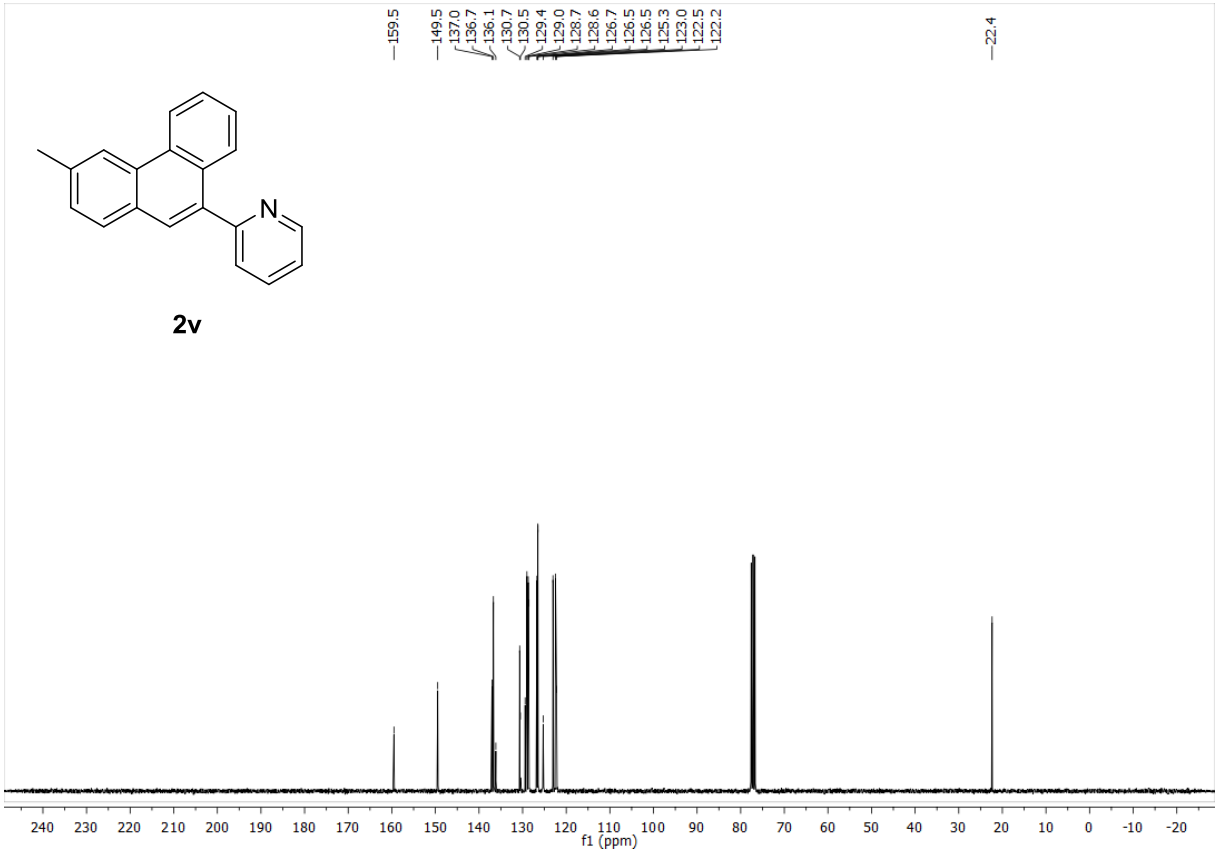


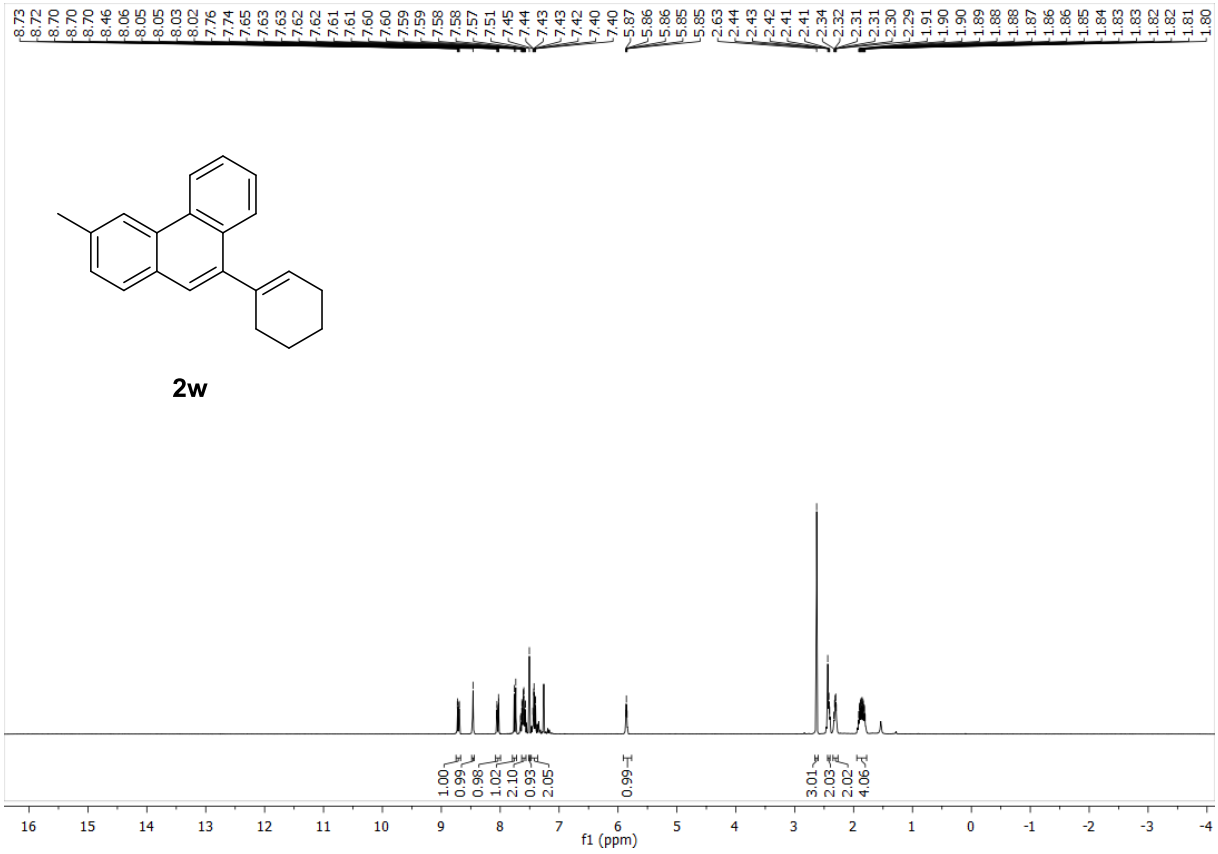
2u



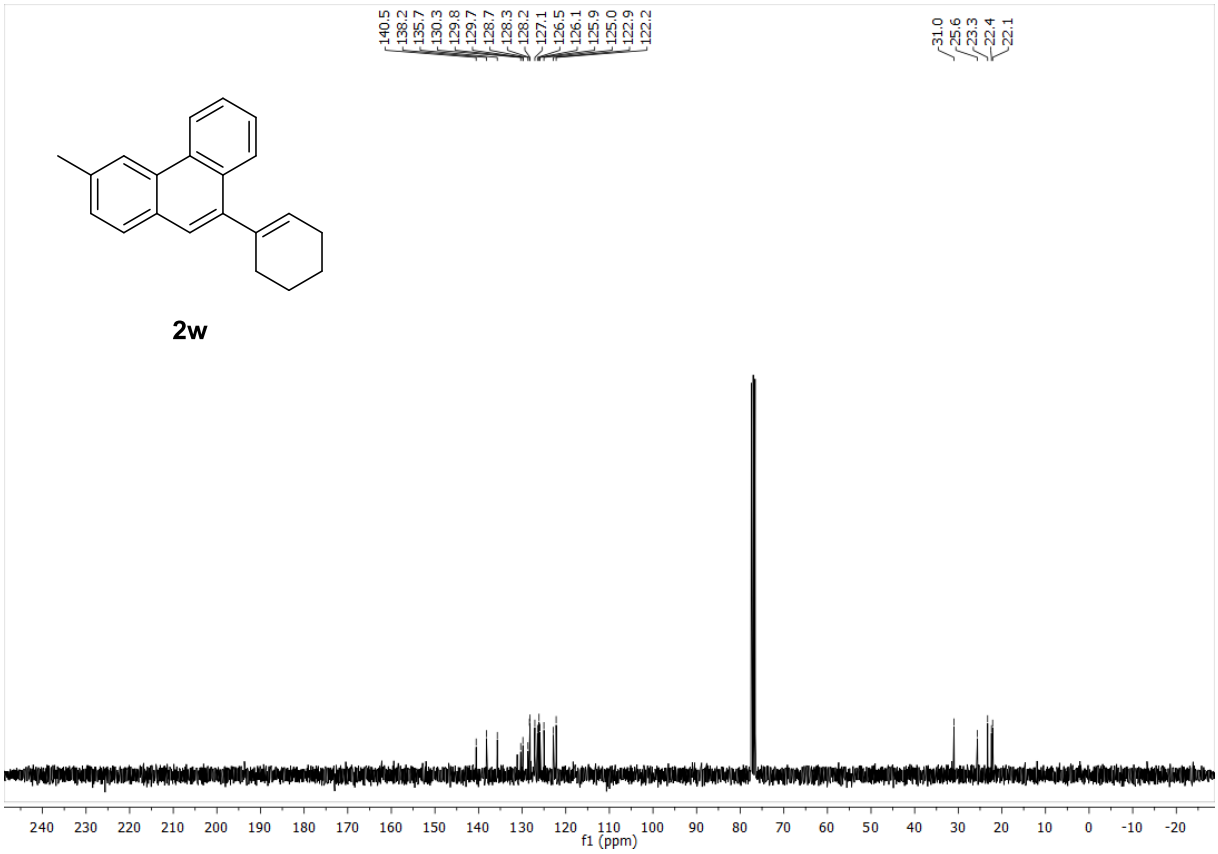
2u


8.84
8.83
8.79
8.79
8.76
8.76
8.52
8.52
8.52
8.10
8.09
8.07
8.06
7.87
7.87
7.85
7.84
7.82
7.69
7.67
7.66
7.66
7.66
7.65
7.64
7.64
7.63
7.63
7.59
7.58
7.56
7.56
7.55
7.54
7.47
7.47
7.45
7.44
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.85
N
2v
0.89
1.00
1.01
0.98
3.02
2.00
1.03
1.00
0.99
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

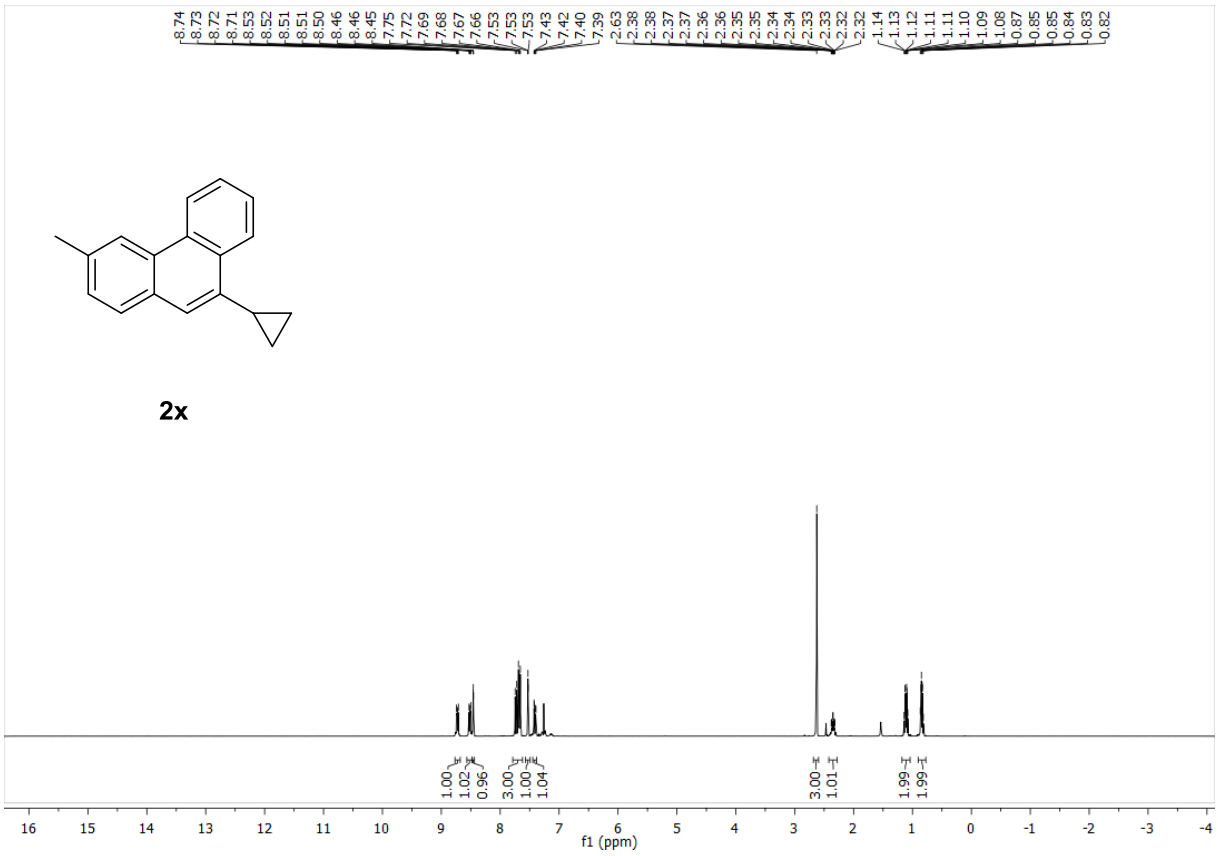

159.5
149.5
137.0
136.7
136.1
130.7
130.5
129.4
129.0
128.7
128.6
126.7
126.5
126.5
125.3
123.0
122.5
122.2
22.4
N
2v
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.73 8.72 8.70 8.70 8.70 8.46 8.06 8.05 8.05 8.03 8.02 7.76 7.74 7.65 7.63 7.63 7.62 7.62 7.61 7.61 7.60 7.60 7.59 7.59 7.58 7.58 7.57 7.51 7.45 7.44 7.43 7.43 7.42 7.40 7.40 5.87 5.86 5.86 5.85 5.85 2.63 2.44 2.43 2.42 2.41 2.41 2.34 2.32 2.31 2.31 2.30 2.29 1.91 1.90 1.90 1.89 1.88 1.88 1.87 1.86 1.86 1.85 1.84 1.83 1.83 1.82 1.82 1.81 1.80
1.00 0.99 0.98 1.02 2.10 0.93 2.05 0.99 3.01 2.03 2.02 4.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

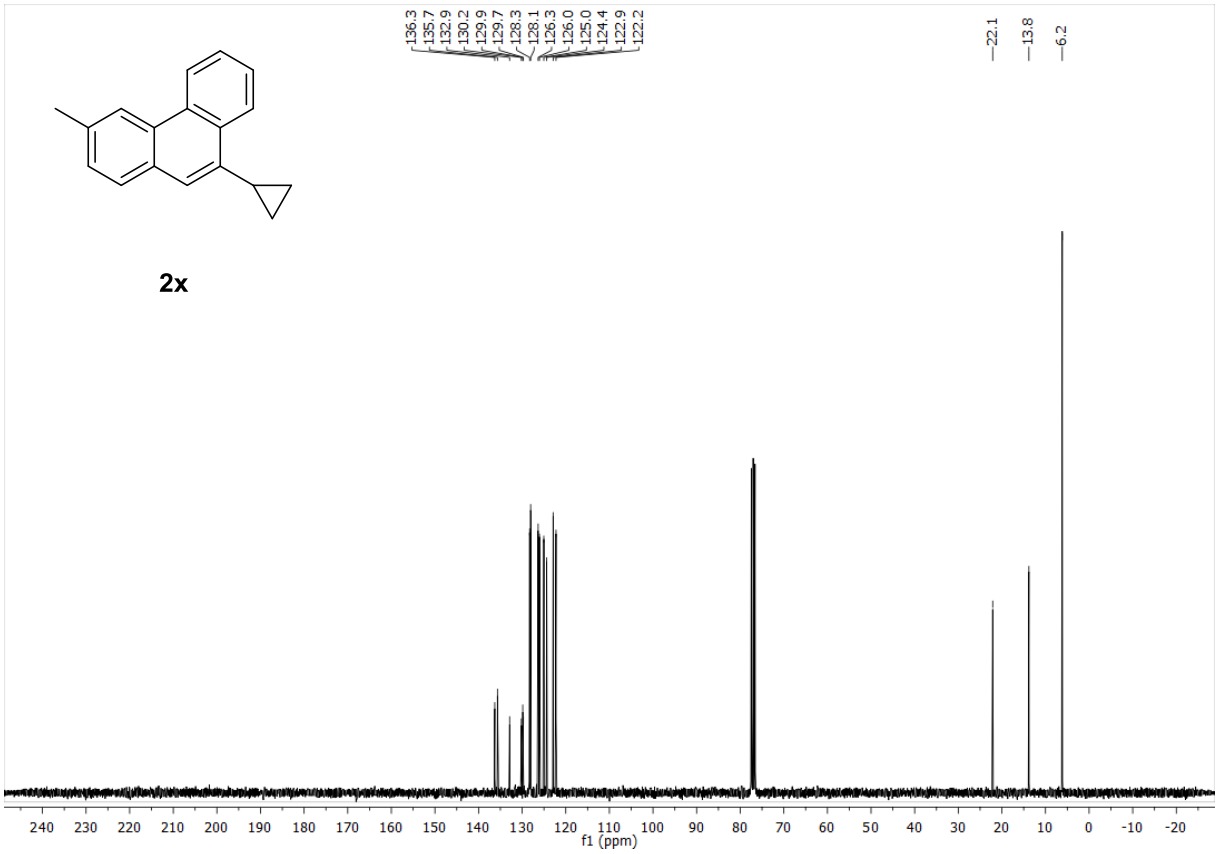
2w


140.5 138.2 135.7 130.3 129.8 129.7 128.7 128.3 128.2 127.1 126.5 126.1 125.9 125.0 122.9 122.2
31.0 25.6 23.3 22.4 22.1
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

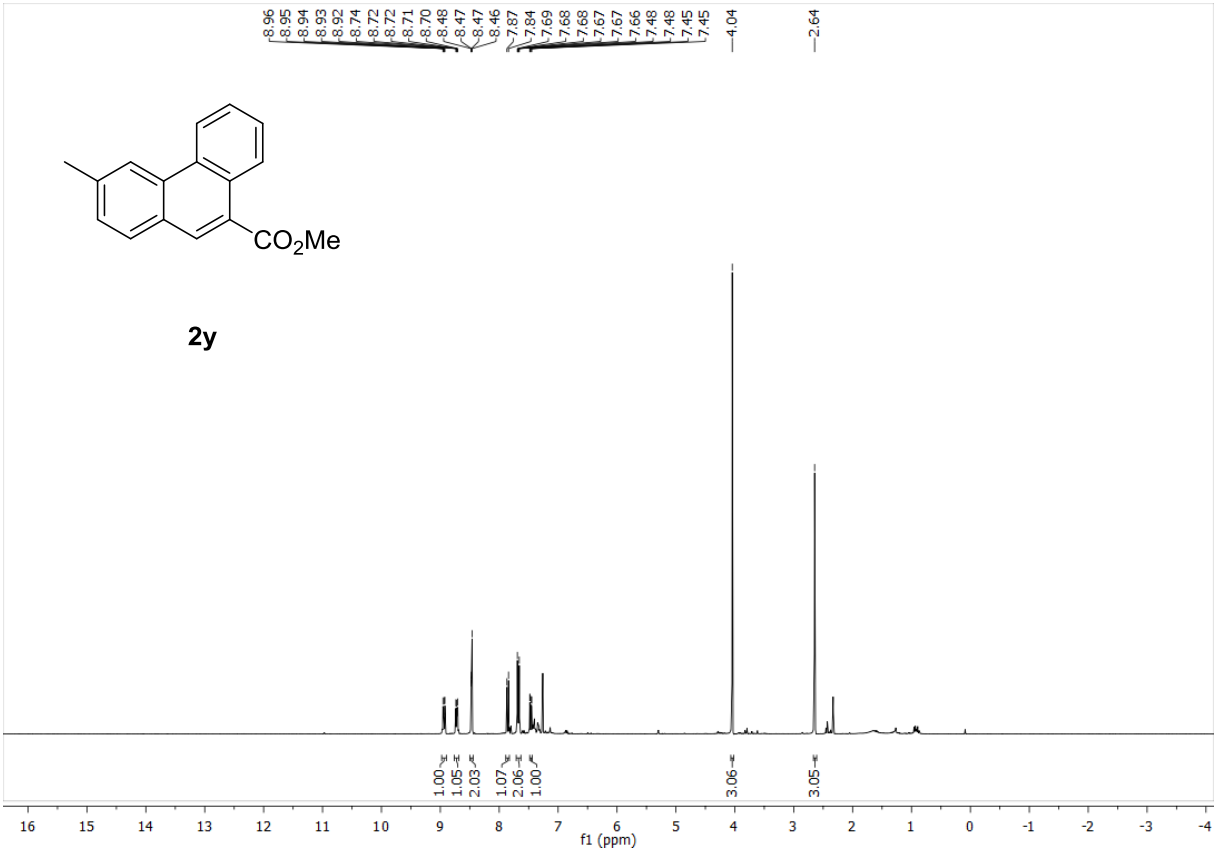
2w

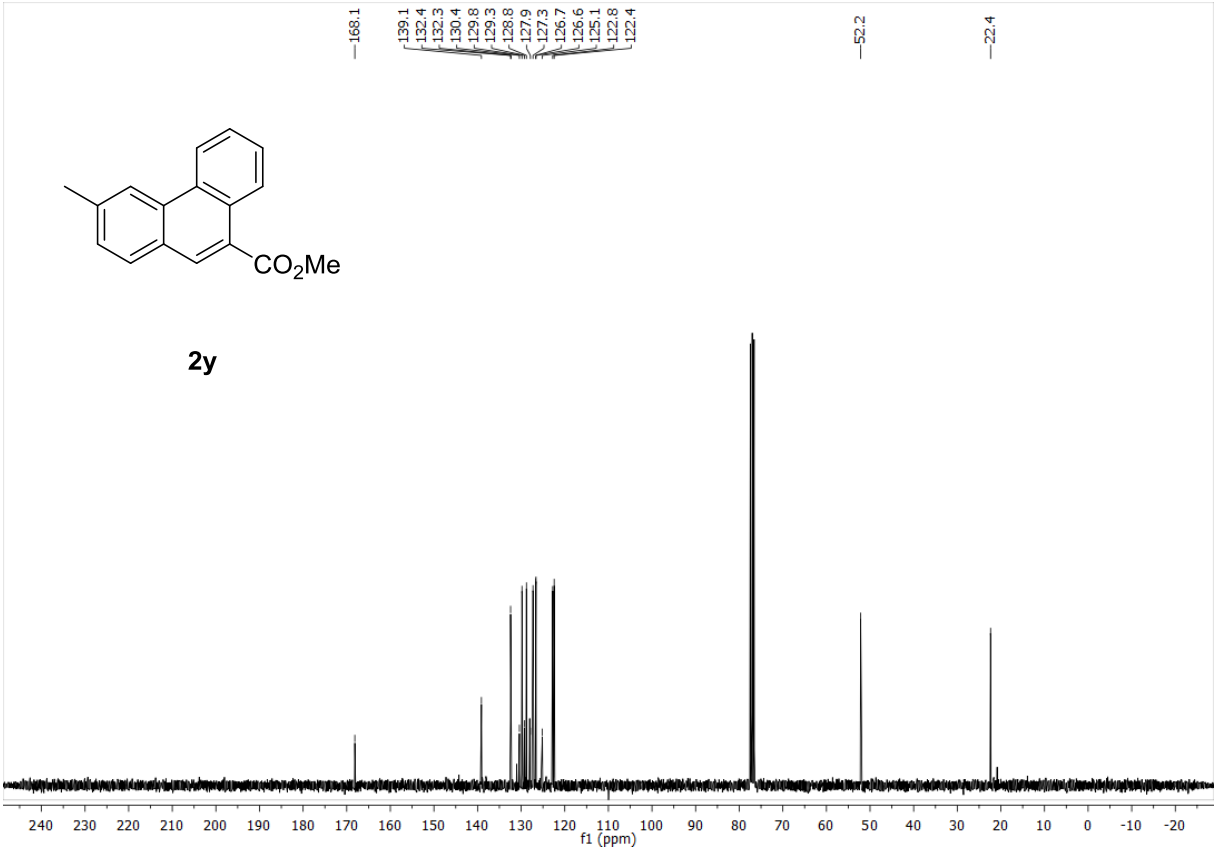

8.74
8.73
8.72
8.71
8.53
8.52
8.51
8.51
8.50
8.46
8.46
8.45
7.75
7.72
7.69
7.68
7.67
7.66
7.53
7.53
7.53
7.43
7.42
7.40
7.39
2.63
2.38
2.38
2.37
2.37
2.36
2.36
2.35
2.35
2.34
2.34
2.33
2.33
2.32
2.32
1.14
1.13
1.12
1.11
1.11
1.10
1.09
1.08
0.87
0.85
0.85
0.84
0.83
0.82
1.00
1.02
0.96
3.00
1.00
1.04
3.00
1.01
1.99
1.99
f1 (ppm)

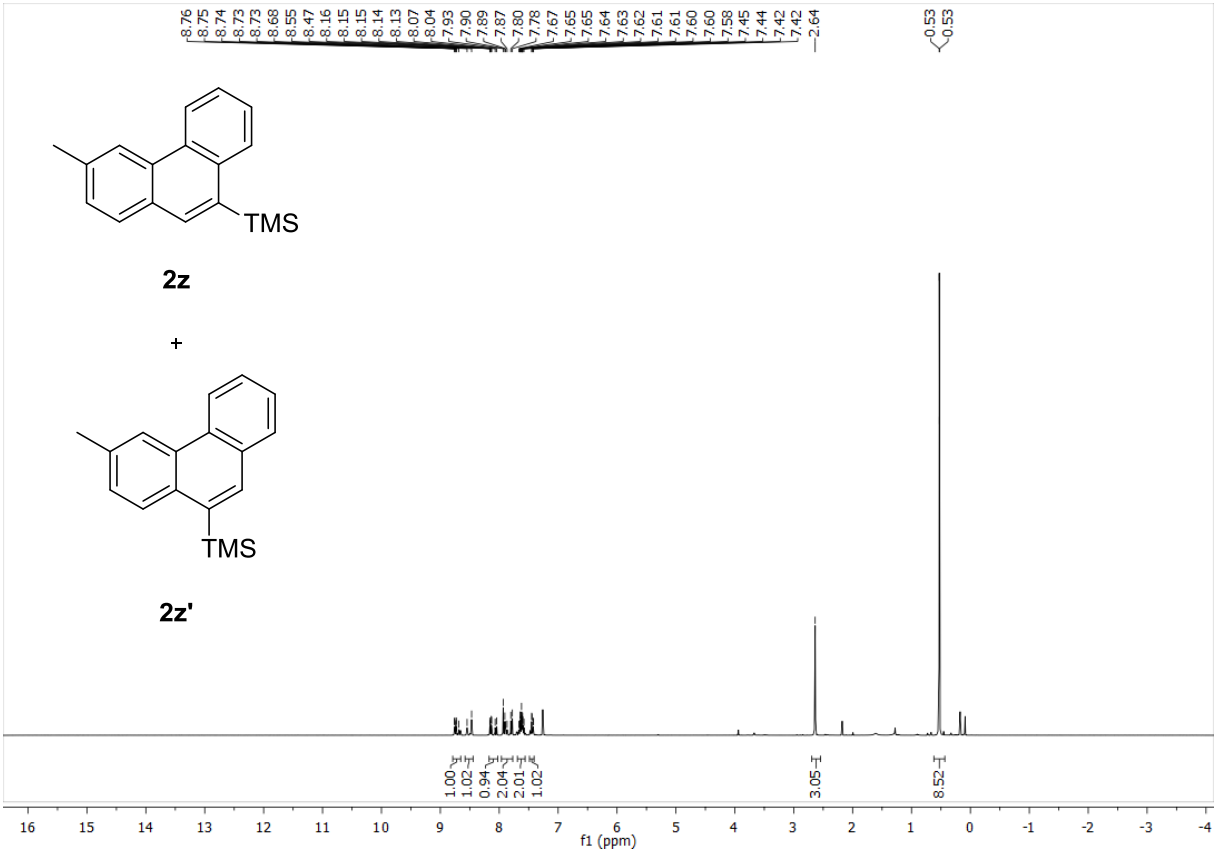
2x

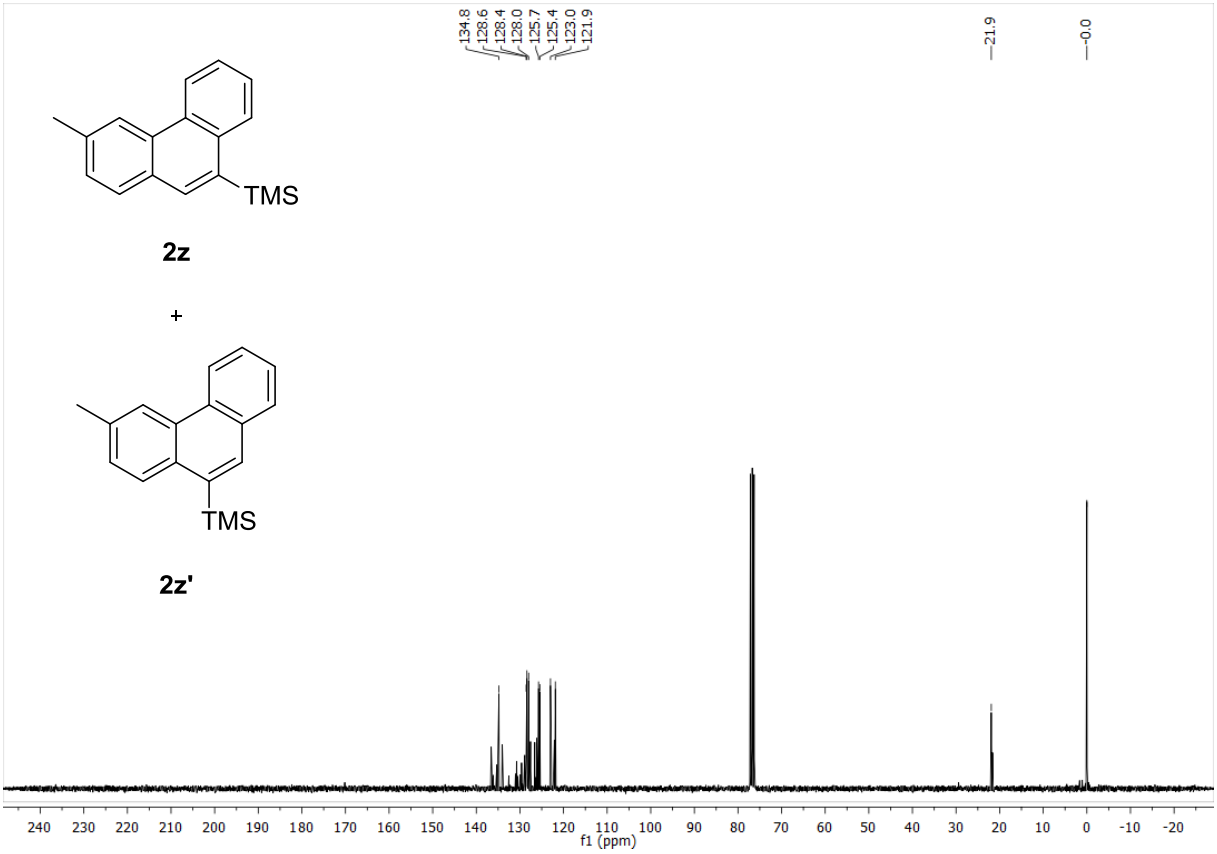

136.3
135.7
132.9
130.2
129.9
129.7
128.3
128.1
126.3
126.0
125.0
124.4
122.9
122.2
22.1
13.8
6.2
f1 (ppm)

2x


8.96
8.95
8.94
8.93
8.92
8.74
8.72
8.72
8.71
8.70
8.48
8.47
8.47
8.46
7.87
7.84
7.69
7.68
7.68
7.67
7.67
7.66
7.48
7.48
7.45
7.45
4.04
2.64
CO2Me
2y
1.00
1.05
2.03
1.07
2.06
1.00
3.06
3.05
f1 (ppm)


168.1
139.1
132.4
132.3
130.4
129.8
129.3
128.8
127.9
127.3
126.7
126.6
125.1
122.8
122.4
52.2
22.4
CO2Me
2y
f1 (ppm)


8.76
8.75
8.74
8.73
8.73
8.68
8.55
8.47
8.16
8.15
8.15
8.14
8.13
8.07
8.04
7.93
7.90
7.89
7.87
7.80
7.78
7.67
7.65
7.65
7.64
7.63
7.62
7.61
7.61
7.60
7.60
7.58
7.45
7.44
7.42
7.42
2.64
0.53
0.53
TMS
2z
+
TMS
2z'
1.00
1.02
0.94
2.04
2.01
1.02
3.05
8.52
f1 (ppm)


134.8
128.6
128.4
128.0
125.7
125.4
123.0
121.9
21.9
0.0
TMS
2z
+
TMS
2z'
f1 (ppm)

Literature

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[3] J. Monot, M. M. Brahmi, S.-H. Ueng, C. Robert, M. Desage-El Murr, D. P. Curran, M. Malacria, L. Fensterbank and E. Lacote, *Org. Lett*., 2009, **11**, 4914.

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