Supporting Information

6-Aroylated Phenanthridines
via Base Promoted Homolytic Aromatic Substitution (BHAS)

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1. General

All reactions containing air- or moisture-sensitive compounds were performed under argon atmosphere in oven-dried glassware using *Schlenk* techniques.

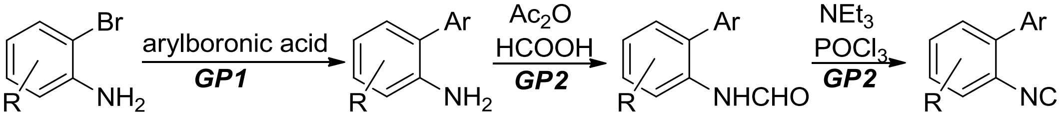
Iron(III)chloride (≥ 99.9%, trace metal basis), 1,2-dimethoxyethane (≥ 99%), $PdCl_2(PPh_3)_2$ (≥ 98%), *tert*-butylhydroperoxide (TBHP, 5.5 M in decane) and acetonitrile (99.9%, extra dry, Aeroseal) were purchased by *Sigma Aldrich* and used as received. Other chemicals were purchased by *ABCR*, *Acros Organics*, *Alfa Aesar*, *Fluka* and *Sigma Aldrich* and used as received. Solvents for extraction and flash chromatography (FC) were distilled.

^{1}H-NMR (300 MHz and 400 MHz), **^{13}C-NMR** (75 MHz, 76 MHz and 101 MHz), **^{19}F-NMR** (282 MHz) measurements were carried out on a *Bruker DPX 300*, *Bruker AV 300* or *Bruker AV 400* spectrometer. The chemical shifts were refered to the solvent ($CDCl_3$) residual peak (^{1}H: $\delta = 7.26$ ppm, ^{13}C: $\delta = 77.0$ ppm) and to an external standard ($CFCl_3$: $\delta = 0$ ppm) for ^{19}F-NMR spectra. The multiplicity was described by s (singlet), d (doublet), t (triplet), q (quintet), sext (sextet) and m (multiplet). All melting points (**MP**) were determined by a *Stuart SMP10* and are uncorrected. Infrared spectra (**IR**) were recorded by a *Digilab 3100 FT-IR Excalibur Series* spectrometer. The intensity of the IR signals was mentioned with w (weak), m (medium) and s (strong). **HRMS ESI** (*m/z*) spectra were measured on a *Bruker MicroTof.*

For thin layer chromatography (TLC) *Merck* silica gel 60 F_{254} plates were used and UV light was used for detection. For FC *Merck* silica gel 60 (40-63 µm) was used with an argon excess pressure up to 0.5 bar.

2. General procedures

According to a literature procedure by *Chatani et al.*[1] 2-isocyanobiphenyls **1** were synthesized *via* a three step route (see scheme below).



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2.1. *General procedure for the synthesis of 2-aminobiphenyls (**GP1**)*

Phenylboronic acid (1.2 equiv.) and an aq. solution of K_2CO_3 (2 M, 4.5 equiv.) were added to a mixture of 2-bromoaniline (1.0 equiv.) in 1,2-dimethoxyethane (0.5 M) and the reaction mixture was stirred for 30 min. After adding bis(triphenylphosphine)palladium(II)chloride (2 mol%), the mixture was heated to 80 °C and stirred overnight at this temperature. The reaction mixture was cooled to room temperature, filtered through a short pad of silica and eluted with EtOAc. The filtrate was washed with water and the organic phase dried over MgSO. Filtration, concentration *in vacuo* and FC (P/EtOAc) afforded the desired 2-aminobiphenyl.

2.2. *General procedure for the synthesis of 2-isocyanobiphenyls **1** (**GP2**)*

An equimolar mixture of acetic anhydride and formic acid was stirred at 55 °C to form *in situ* acetic formic anhydride (2.0 equiv.). After cooling to room temperature it was added dropwise to a stirred solution of 2-aminobiphenyl in THF (0.3 – 0.6 M) at 0 °C. After stirring 2 h at room temperature, the reaction was stopped by the addition of a saturated aq. solution of $NaHCO_3$. The aqueous phase was extracted three times with EtOAc and the combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*.

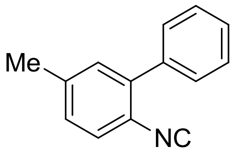
Without further purification the residue was dissolved in THF (0.6 M) and triethylamine (6.0 equiv.) was added. The reaction mixture was cooled to 0 °C and phosphoryl chloride (1.5 equiv.) was added dropwise. After stirring two hours at this temperature a saturated solution of aq. Na_2CO_3 was added to the mixture and stirred for 1 h at room temperature. The aqueous phase was extracted three times with DCM. The combined organic phases were dried over $MgSO_4$ and filtered. Purification *via* FC (P/EtOAc) afforded the desired 2-isocyanobiphenyl **1**.

*2.3. General procedure for the synthesis of phenanthridines (**GP3**)*

To a solution of 2-isocyanobiphenyl **1** (0.25 mmol, 1.0 equiv.) in MeCN (0.90 mL) a solution of iron(III)chloride in MeCN (10.0 mᴍ, 0.10 mL, 0.4 mol%), an arylaldehyde (0.50 mmol, 2.0 equiv.) and TBHP in decane (5.5 ᴍ, 0.10 mL, 0.55 mmol, 2.2 equiv.) were added. After stirring 5 min at room temperature the mixture was heated to 90 °C and stirred for 24 h at this temperature. The reaction mixture was cooled to room temperature, filtered through a short pad of silica and eluted with DCM (180 mL). After concentration *in vacuo* the crude product was quantified by ^{1}H-NMR analysis using dibromomethane as internal standard. Purification by FC (P/EtOAc) or recrystallization from hot MeCN afforded the desired phenanthridine.

3. Analytic data of starting materials

2-Isocyano-5-methyl-1,1'-biphenyl (1a)

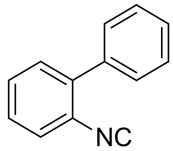


According to ***GP1*** with 2-bromo-4-methylaniline (1.25 mL, 10.0 mmol, 1.0 equiv.), phenylboronic acid (1.464 g, 12.01 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (140 mg, 200 µmol, 2.0 mol%) and K_2CO_3 (6.221 g, 45.01 mmol, 4.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 5-methyl-[1,1'-biphenyl]-2-amine (1.586 g, 8.652 mmol, 86%) as an orange oil.

According to ***GP2*** with 5-methyl-[1,1'-biphenyl]-2-amine (1.533 g, 8.363 mmol, 1.0 equiv.), formic acid (0.63 mL, 17 mmol, 2.0 equiv.), acetic anhydride (1.6 mL, 17 mmol, 2.0 equiv.), triethylamine (7.9 mL, 57 mmol, 6.8 equiv.) and phosphoryl chloride (1.3 mL, 14 mmol, 1.7 equiv.). FC (P/EtOAc = 20/1) afforded the desired 2-isocyanobiphenyl **1a** (1.433 g, 7.421 mmol, 89%) as a green liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.35 (m, 6H, $C_{arom}H$), 7.25 – 7.21 (m, 1H, $C_{arom}H$), 7.17 (ddd, J = 8.1 Hz, J = 1.3 Hz, J = 0.6 Hz, 1H, $C_{arom}H$), 2.42 (s, 3H, CH_3). **^{13}C-NMR** (76 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.8 (C), 139.8 (C), 138.5 (C), 137.1 (C), 131.1 (CH), 128.9 (2 × CH), 128.7 (CH), 128.4 (2 × CH), 128.2 (CH), 127.6 (CH), 122.1 (C), 21.3 (CH_3). **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa$ $[M+Na]^+$, found: 216.0788. Spectroscopic data are in accordance with those described in the literature.[1]

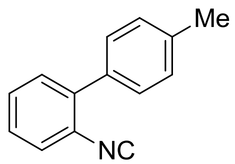
2-Isocyano-1,1'-biphenyl (1l)



According to ***GP2*** with [1,1'-biphenyl]-2-amine (508 mg, 3.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.80 mL), triethylamine (2.5 mL, 18 mmol, 6.0 equiv.) and phosphoryl chloride (0.41 mL, 4.5 mmol, 1.5 equiv.). FC (P/EtOAc = 40/1) afforded the desired 2-isocyanobiphenyl **1p** (456 mg, 2.54 mmol, 85%) as a green liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57 – 7.34 (m, 9H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): 166.5 (C), 138.8 (C), 137.0 (C), 130.6 (CH), 129.6 (CH), 129.0 (2 × CH), 128.6 (2 × CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 124.6 (C). **HRMS (ESI)** *m/z* = 202.06272 calcd. for $C_{13}H_9NNa$ $[M+Na]^+$, found: 202.06247. Spectroscopic data are in accordance with those described in the literature.[2]

2-Isocyano-4'-methyl-1,1'-biphenyl (1m)

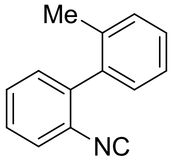


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 4-methylphenylboronic acid (491 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.867 g, 13.51 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 4'-methyl-[1,1'-biphenyl]-2-amine (425 mg, 2.32 mmol, 77%) as a yellow liquid.

According to ***GP2*** with 4'-methyl-[1,1'-biphenyl]-2-amine (425 mg, 2.32 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.61 mL), triethylamine (1.9 mL, 14 mmol, 6.0 equiv.) and phosphoryl chloride (0.32 mL, 3.5 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1m** (419 mg, 2.17 mmol, 94%) as a green liquid.

IR (neat): 3064*w*, 3028*w*, 2921*w*, 2865*w*, 2120*s*, 1616*w*, 1518*w*, 1479*s*, 1444*w*, 1410*w*, 1186*w*, 1107*w*, 1046*w*, 1007*w*, 946*w*, 820*m*, 759*s*, 680*w*, 562*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 – 7.40 (m, 5H, $C_{arom}H$), 7.38 – 7.28 (m, 3H, $C_{arom}H$), 2.44 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.5 (C), 138.8 (C), 138.2 (C), 134.0 (C), 130.4 (CH), 129.4 (CH), 129.2 (2 × CH), 128.8 (2 × CH), 127.8 (CH), 127.7 (CH), 124.5 (C), 21.2 (CH_3). **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa$ $[M+Na]^+$, found: 216.0790.

2-Isocyano-2'-methyl-1,1'-biphenyl (1n)

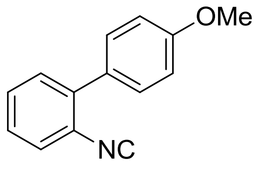


According to ***GP1*** with 2-bromoaniline (688 mg, 4.00 mmol, 1.0 equiv.), 2-methylphenylboronic acid (652 mg, 4.79 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (56 mg, 80 µmol, 2.0 mol%) and K_2CO_3 (2.488 g, 18.00 mmol, 4.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2'-methyl-[1,1'-biphenyl]-2-amine (642 mg, 3.50 mmol, 88%) as a yellow liquid.

According to ***GP2*** with 2'-methyl-[1,1'-biphenyl]-2-amine (636 mg, 3.47 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.92 mL), triethylamine (2.9 mL, 21 mmol, 6.1 equiv.) and phosphoryl chloride (0.48 mL, 5.3 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1n** (606 mg, 3.14 mmol, 90%) as a green liquid.

IR (neat): 3062*w*, 3020*w*, 2957*w*, 2925*w*, 2866*w*, 2120*s*, 1633*w*, 1476*m*, 1440*m*, 1380*w*, 1280*w*, 1185*w*, 1160*w*, 1124*w*, 1102*w*, 1048*w*, 1041*w*, 1008*m*, 949*w*, 873*w*, 755*s*, 739*s*, 725*s*, 696*w*, 622*m*, 573*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 – 7.24 (m, 7H, $C_{arom}H$), 7.19 (d, *J* = 7.4 Hz, 1H, $C_{arom}H$), 2.20 (s, 3H, CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7 (C), 139.3 (C), 136.8 (C), 135.9 (C), 130.6 (CH), 130.2 (CH), 129.3 (CH), 129.1 (CH), 128.4 (CH), 128.1 (CH), 126.8 (CH), 125.7 (CH), 19.6 (CH_3).[*] **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa$ $[M+Na]^+$, found: 216.0788.

2-Isocyano-4'-methoxy-1,1'-biphenyl (1o)

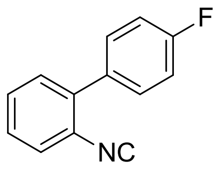


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 4-methoxyphenylboronic acid (548 mg, 3.61 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.866 g, 13.50 mmol, 4.5 equiv.). FC (P/EtOAc = 15/1) afforded the desired 4'-methoxy-[1,1'-biphenyl]-2-amine (545 mg, 2.74 mmol, 91%) as a yellow oil.

According to ***GP2*** with 4'-methoxy-[1,1'-biphenyl]-2-amine (545 mg, 2.74 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.73 mL), triethylamine (2.3 mL, 17 mmol, 6.2 equiv.) and phosphoryl chloride (0.38 mL, 4.2 mmol, 1.5 equiv.). FC (P/EtOAc = 20/1) afforded the desired 2-isocyanobiphenyl **1o** (510 mg, 2.44 mmol, 89%) as a light green solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 – 7.38 (m, 5H, $C_{arom}H$), 7.33 (ddd, J = 7.7 Hz, J = 6.4 Hz, J = 2.7 Hz, 1H, $C_{arom}H$), 7.07 – 6.98 (m, 2H, $C_{arom}H$), 3.87 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.1 (C), 159.6 (C), 138.4 (C), 130.4 (CH), 130.1 (2 × CH), 129.4 (CH), 129.2 (C), 127.8 (CH), 127.6 (CH), 124.4 (C), 113.9 (2 × CH), 55.2 (CH_3). **HRMS (ESI)** *m/z* = 232.0733 calcd. for $C_{14}H_{11}NONa$ $[M+Na]^+$, found: 232.0740. Spectroscopic data are in accordance with those described in the literature.[3]

4'-Fluoro-2-isocyano-1,1'-biphenyl (1p)



According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 4-fluorophenylboronic acid (506 mg, 3.62 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.867 g, 13.51 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 4'-fluoro-[1,1'-biphenyl]-2-amine (345 mg, 1.84 mmol, 61%) as an orange liquid.

According to ***GP2*** with 4'-fluoro-[1,1'-biphenyl]-2-amine (339 mg, 1.81 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.48 mL), triethylamine (1.5 mL, 11 mmol, 6.1 equiv.) and phosphoryl chloride (0.25 mL, 2.7 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1p** (322 mg, 1.63 mmol, 90%) as a green liquid.

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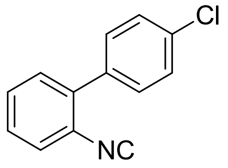
[*] The signal of the isonitrile carbon could not be identified.

IR (neat): 3069*w*, 2120*s*, 1609*m*, 1598*w*, 1514*s*, 1479*s*, 1447*m*, 1405*w*, 1226*s*, 1186*w*, 1160*m*, 1110*w*, 1096*m*, 1047*w*, 1010*m*, 953*w*, 874*w*, 836*s*, 822*m*, 784*m*, 757*s*, 715*w*, 682*w*, 579*m*, 561*s*, 508*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.43 (m, 4H, $C_{arom}H$), 7.43 – 7.34 (m, 2H, $C_{arom}H$), 7.22 – 7.13 (m, 2H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.6 (C), 162.7 (d, *J* = 248.1 Hz, C), 137.7 (C), 132.9 (d, *J* = 3.4 Hz, C), 130.7 (d, *J* = 8.3 Hz, 2 × CH), 130.4 (CH), 129.6 (CH), 128.2 (CH), 127.8 (CH), 124.5 (C), 115.6 (d, *J* = 21.7 Hz, 2 × CH). **^{19}F-NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -113.4 (s, CF). **HRMS (ESI)** *m/z* = 220.0533 calcd. for $C_{13}H_8FNNa$ $[M+Na]^+$, found: 220.0539.

4'-Chloro-2-isocyano-1,1'-biphenyl (1q)

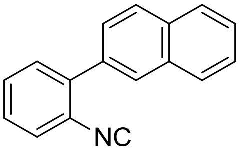


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 4-chlorophenylboronic acid (563 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.862 g, 13.47 mmol, 4.5 equiv.). FC (P/EtOAc = 40/1) afforded the desired 4'-chloro-[1,1'-biphenyl]-2-amine (512 mg, 2.51 mmol, 84%) as a yellow liquid.

According to ***GP2*** with 4'-chloro-[1,1'-biphenyl]-2-amine (511 mg, 2.51 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.66 mL), triethylamine (2.1 mL, 15 mmol, 6.0 equiv.) and phosphoryl chloride (0.34 mL, 3.7 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1q** (491 mg, 2.30 mmol, 92%) as a light green solid.

MP: 97 °C. **IR** (neat): 3059*m*, 2292*w*, 2127*s*, 1980*w*, 1947*w*, 1906*w*, 1835*w*, 1729*w*, 1654*w*, 1594*w*, 1499*m*, 1475*s*, 1443*m*, 1397*m*, 1352*w*, 1298*w*, 1284*m*, 1267*w*, 1181*m*, 1100*m*, 1090*s*, 1049*m*, 1019*m*, 1006*m*, 909*m*, 878*m*, 829*s*, 819*s*, 796*m*, 762*s*, 739*s*, 653*w*, 632*m*, 562*s*, 535*m*, 506*m*. **^{1}H-NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 – 7.37 (m, 8H, CH_{arom}). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8 (C), 137.5 (C), 135.3 (C), 134.5 (C), 130.3 (CH), 130.2 (2 × CH), 129.6 (CH), 128.8 (2 × CH), 128.5 (CH), 127.8 (CH), 124.4 (C). **HRMS (ESI)** *m/z* = 236.0237 calcd. for $C_{13}H_8ClNNa$ $[M+Na]^+$, found: 236.0247.

2-(2-Isocyanophenyl)naphthalene (1r)

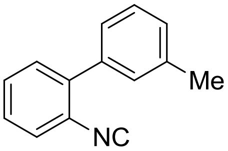


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 2-naphtylboronic acid (619 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.872 g, 13.55 mmol, 4.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-(naphthalene-2-yl)aniline (585 mg, 2.67 mmol, 89%) as an orange solid.

According to ***GP2*** with 2-(naphthalene-2-yl)aniline (577 mg, 2.63 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.69 mL), triethylamine (2.2 mL, 16 mmol, 6.1 equiv.) and phosphoryl chloride (0.36 mL, 3.9 mmol, 1.5 equiv.). FC (P/EtOAc = 40/1) afforded the desired 2-isocyanobiphenyl **1r** (564 mg, 2.46 mmol, 94%) as a brown solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 – 7.96 (m, 2H, $C_{arom}H$), 7.96 – 7.89 (m, 2H, $C_{arom}H$), 7.67 (dd, *J* = 8.5 Hz, *J* = 1.8 Hz, 1H, $C_{arom}H$), 7.60 – 7.46 (m, 5H, $C_{arom}H$), 7.40 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 1H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.6 (C), 138.7 (C), 134.3 (C), 133.1 (C), 132.8 (C), 130.7 (CH), 129.5 (CH), 128.3 (CH), 128.2 (CH), 128.1 (2 × CH), 127.8 (CH), 127.7 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 124.7 (C). **HRMS (ESI)** *m/z* = 252.0784 calcd. for $C_{17}H_{11}NNa$ $[M+Na]^+$, found: 252.0788. Spectroscopic data are in accordance with those described in the literature.[1]

2-Isocyano-3'-methyl-1,1'-biphenyl (1s)

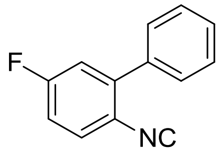


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 3-methylphenylboronic acid (490 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.862 g, 13.47 mmol, 4.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 3'-methyl-[1,1'-biphenyl]-2-amine (460 mg, 2.51 mmol, 84%) as a yellow liquid.

According to ***GP2*** with 3'-methyl-[1,1'-biphenyl]-2-amine (460 mg, 2.51 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.66 mL), triethylamine (2.1 mL, 15 mmol, 6.0 equiv.) and phosphoryl chloride (0.34 mL, 3.7 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1s** (130 mg, 673 µmol, 27%) as a green liquid.

IR (neat): 3062*w*, 3036*w*, 2921*w*, 2865*w*, 2121*s*, 1609*w*, 1588*w*, 1473*m*, 1443*w*, 1271*w*, 1109*w*, 1051*w*, 949*w*, 888*w*, 791*m*, 758*s*, 736*m*, 703*m*, 623*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 – 7.31 (m, 7H, $C_{arom}H$), 7.28 – 7.23 (m, 1H, $C_{arom}H$), 2.45 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.5 (C), 138.9 (C), 138.1 (C), 136.9 (C), 130.5 (CH), 129.6 (CH), 129.4 (CH), 129.0 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 126.0 (CH), 124.5 (C), 21.4 (CH_3). **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa$ $[M+Na]^+$, found: 216.0789.

5-Fluoro-2-isocyano-1,1'-biphenyl (1t)



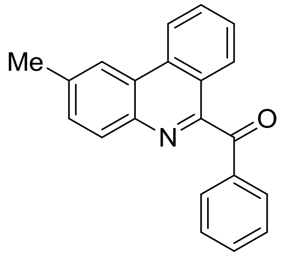
According to ***GP1*** with 2-bromo-4-fluoroaniline (760 mg, 4.00 mmol, 1.0 equiv.), phenylboronic acid (585 mg, 4.80 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (56 mg, 80 µmol, 2.0 mol%) and K_2CO_3 (2.492 g, 18.03 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 5-fluoro-[1,1'-biphenyl]-2-amine (727 mg, 3.88 mmol, 97%) as an orange liquid.

According to ***GP2*** with 5-fluoro-[1,1'-biphenyl]-2-amine (721 mg, 3.85 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.97 mL), triethylamine (3.1 mL, 22 mmol, 5.7 equiv.) and phosphoryl chloride (0.50 mL, 5.5 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1t** (617 mg, 3.13 mmol, 81%) as a green liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 – 7.41 (m, 6H, $C_{arom}H$), 7.14 (dd, J = 9.0 Hz, J = 2.8 Hz, 1H, $C_{arom}H$), 7.07 (ddd, J = 8.7 Hz, J = 7.6 Hz, J = 2.8 Hz, 1H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.6 (C), 162.1 (d, J = 252.1 Hz, C), 141.2 (d, J = 8.7 Hz, C), 135.9 (d, J = 1.6 Hz, C), 129.7 (d, J = 9.2 Hz, CH), 128.8 (CH), 128.7 (2 × CH), 128.6 (2 × CH), 120.7 (C), 117.4 (d, J = 23.5 Hz, CH), 115.2 (d, J = 23.3 Hz, CH). **^{19}F-NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -108.7 (s, CF). **HRMS (ESI)** *m/z* = 220.0533 calcd. for $C_{13}H_8FNNa$ $[M+Na]^+$, found: 220.0544. Spectroscopic data are in accordance with those described in the literature.[1]

4. Analytic data of products

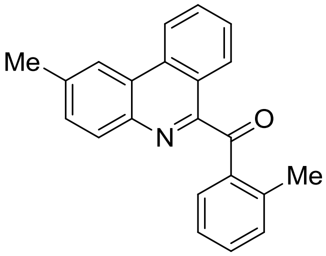
(2-Methylphenanthridin-6-yl)(phenyl)methanone (2a)



According to ***GP3*** with **1a** (48.3 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 20/1) afforded phenanthridine **2a** (48.3 mg, 0.162 mmol, 65%) as a colorless solid.

MP: 172 °C. **IR** (neat): 3300*w*, 3066*w*, 3031*w*, 2921*w*, 2860*w*, 2252*w*, 1967*w*, 1919*w*, 1819*w*, 1667*s*, 1612*w*, 1596*m*, 1580*m*, 1521*w*, 1496*m*, 1448*s*, 1364*m*, 1324*m*, 1293*w*, 1244*s*, 1199*m*, 1178*m*, 1164*m*, 1139*w*, 1120*w*, 1058*w*, 1039*w*, 1025*w*, 904*m*, 887*s*, 824*m*, 783*w*, 765*s*, 747*m*, 728*s*, 720*s*, 700*m*, 686*s*, 650*m*, 624*m*, 587*m*, 547*w*, 535*w*. **^{1}H-NMR** (300 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.69 (d, *J* = 8.4 Hz, 1H, C$_{arom}$H), 8.42 (s, 1H, C$_{arom}$H), 8.15 (d, *J* = 8.2 Hz, 1H, C$_{arom}$H), 8.11 (d, *J* = 8.4 Hz, 1H, C$_{arom}$H), 8.08 – 8.00 (m, 2H, C$_{arom}$H), 7.90 – 7.82 (m, 1H, C$_{arom}$H), 7.65 (dd, *J* = 7.4 Hz, *J* = 1.2 Hz, 1H, C$_{arom}$H), 7.61 (d, *J* = 7.5 Hz, 2H, C$_{arom}$H), 7.52 – 7.43 (m, 2H, C$_{arom}$H), 2.66 (s, 3H, CH$_3$). **^{13}C-NMR** (76 MHz, CDCl$_3$, 300 K): δ (ppm) = 194.8 (CO), 156.4 (C), 140.9 (C), 138.3 (C), 136.3 (C), 133.8 (CH), 133.0 (C), 131.0 (CH), 130.8 (3 × CH), 130.3 (CH), 128.5 (2 × CH), 127.6 (CH), 127.2 (CH), 124.3 (C), 123.9 (C), 122.2 (CH), 121.7 (CH), 22.1 (CH$_3$). **HRMS (ESI)** *m/z* = 320.1046 calcd. for C$_{21}$H$_{15}$NONa [M+Na]$^+$, found: 320.1044.

(2-Methylphenanthridin-6-yl)(o-tolyl)methanone (2b)

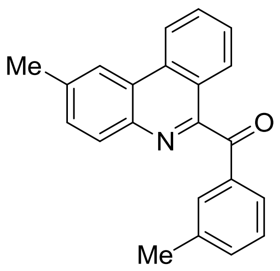


According to ***GP3*** with **1a** (48.4 mg, 0.250 mmol, 1.0 equiv.) and *o*-tolualdehyde (58 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 25/1) afforded phenanthridine **2b** (38.7 mg, 0.124 mmol, 50%) as a yellow solid.

MP: 127 °C. **IR** (neat): 3064*w*, 2966*w*, 2926*w*, 1671*s*, 1613*w*, 1570*m*, 1520*w*, 1495*w*, 1453*m*, 1362*w*, 1321*w*, 1286*w*, 1242*m*, 1196*m*, 1165*w*, 1138*w*, 1037*w*, 901*m*, 889*m*, 825*m*, 779*m*, 743*m*, 667*w*, 568*w*. **^{1}H-NMR** (300 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.70 (d, *J* = 8.8 Hz, 1H, C$_{arom}$H), 8.41 (s, 1H, C$_{arom}$H), 8.25 (d, *J* = 8.2 Hz, 1H, C$_{arom}$H), 8.06 (d, *J* = 8.4 Hz, 1H, C$_{arom}$H), 7.87 (ddd, *J* = 8.4 Hz, *J* = 7.1 Hz, *J* = 1.3 Hz, 1H, C$_{arom}$H), 7.67 (ddd, *J* = 8.2 Hz, *J* = 7.0 Hz, *J* = 1.2 Hz, 1H, C$_{arom}$H), 7.58 (dd, *J* = 8.4 Hz, *J* = 1.8 Hz, 1H, C$_{arom}$H), 7.53 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H, C$_{arom}$H), 7.45 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H, C$_{arom}$H), 7.35

(d, $J = 7.6$ Hz, 1H, $C_{arom}H$), 7.18 (t, $J = 7.5$ Hz, 1H, $C_{arom}H$), 2.66 (s, 6H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 197.5 (CO), 157.3 (C), 141.0 (C), 140.6 (C), 138.3 (C), 136.3 (C), 133.1 (C), 132.9 (CH), 132.4 (CH), 132.0 (CH), 130.9 (CH), 130.7 (CH), 130.4 (CH), 127.7 (CH), 127.3 (CH), 125.5 (CH), 124.4 (C), 123.9 (C), 122.2 (CH), 121.7 (CH), 22.1 (CH_3), 21.8 (CH_3). **HRMS (ESI)** *m/z* = 334.1202 calcd. for $C_{22}H_{17}NONa$ $[M+Na]^+$, found: 334.1211.

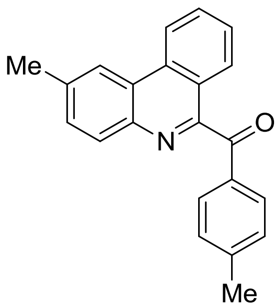
(2-Methylphenanthridin-6-yl)(m-tolyl)methanone (2c)



According to ***GP3*** with **1a** (48.3 mg, 0.250 mmol, 1.0 equiv.) and *m*-tolualdehyde (59 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 30/1) afforded phenanthridine **2c** (49.4 mg, 0.159 mmol, 64%) as a yellow solid.

MP: 125 °C. **IR** (neat): 3064*w*, 2920*w*, 2861*w*, 1668*s*, 1602*w*, 1583*w*, 1571*w*, 1522*w*, 1496*w*, 1447*m*, 1363*w*, 1323*w*, 1294*w*, 1259*s*, 1178*m*, 1159*m*, 1118*w*, 1088*w*, 1040*w*, 997*w*, 934*w*, 918*w*, 825*m*, 798*w*, 778*m*, 757*m*, 729*m*, 683*w*, 658*w*, 624*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.70 (d, $J = 8.4$ Hz, 1H, $C_{arom}H$), 8.43 (s, 1H, $C_{arom}H$), 8.12 (d, $J = 8.3$ Hz, 2H, $C_{arom}H$), 7.92 – 7.83 (m, 2H, $C_{arom}H$), 7.80 (d, $J = 7.6$ Hz, 1H, $C_{arom}H$), 7.68 – 7.58 (m, 2H, $C_{arom}H$), 7.43 (d, $J = 7.5$ Hz, 1H, $C_{arom}H$), 7.35 (t, $J = 7.6$ Hz, 1H, $C_{arom}H$), 2.67 (s, 3H, CH_3), 2.38 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.1 (CO), 156.7 (C), 141.0 (C), 138.3 (C), 138.2 (C), 136.3 (C), 134.7 (CH), 132.9 (C), 131.0 (CH), 130.9 (CH), 130.8 (CH), 130.3 (CH), 128.4 (CH), 128.2 (CH), 127.6 (CH), 127.2 (CH), 124.3 (C), 123.9 (C), 122.2 (CH), 121.7 (CH), 22.0 (CH_3), 21.3 (CH_3). **HRMS (ESI)** *m/z* = 334.1202 calcd. for $C_{22}H_{17}NONa$ $[M+Na]^+$, found: 334.1200.

(2-Methylphenanthridin-6-yl)(*p*-tolyl)methanone (2d)

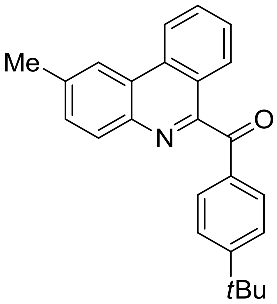


According to ***GP3*** with **1a** (48.3 mg, 0.250 mmol, 1.0 equiv.) and *p*-tolualdehyde (59 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 30/1) afforded phenanthridine **2d** (45.1 mg, 0.145 mmol, 58%) as a yellow solid.

MP: 171 °C. **IR** (neat): 3066*w*, 3031*w*, 2948*w*, 2920*w*, 2860*w*, 1925*w*, 1663*s*, 1604*s*, 1571*m*, 1522*w*, 1496*m*, 1446*m*, 1408*w*, 1365*m*, 1323*m*, 1293*w*, 1250*s*, 1201*m*, 1178*s*, 1163*s*, 1139*w*, 1119*w*, 1058*w*, 1039*m*, 1019*w*, 956*w*, 901*m*, 888*s*, 823*m*, 796*m*, 771*m*, 757*m*, 726*s*, 695*w*, 649*w*, 626*m*, 617*m*, 586*m*, 544*w*, 529*w*. **^{1}H-NMR**

(300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.69 (d, J = 8.4 Hz, 1H, $C_{arom}H$), 8.42 (s, 1H, $C_{arom}H$), 8.16 – 8.08 (m, 2H, $C_{arom}H$), 7.93 (d, J = 8.2 Hz, 2H, $C_{arom}H$), 7.86 (ddd, J = 8.4 Hz, J = 7.0 Hz, J = 1.3 Hz, 1H, $C_{arom}H$), 7.67 – 7.58 (m, 2H, $C_{arom}H$), 7.27 (d, J = 8.3 Hz, 2H, $C_{arom}H$), 2.67 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.6 (CO), 156.8 (C), 144.9 (C), 141.0 (C), 138.2 (C), 133.9 (C), 132.9 (C), 130.9 (3 × CH), 130.8 (CH), 130.3 (CH), 129.2 (2 × CH), 127.5 (CH), 127.3 (CH), 124.3 (C), 123.9 (C), 122.2 (CH), 121.7 (CH), 22.0 (CH_3), 21.8 (CH_3). **HRMS (ESI)** *m/z* = 334.1202 calcd. for $C_{22}H_{17}NONa$ $[M+Na]^+$, found: 334.1200.

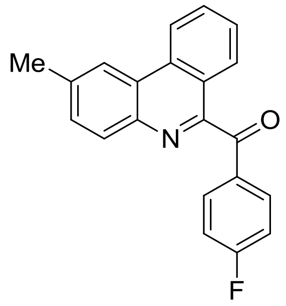
(4-(*tert*-Butyl)phenyl)(2-methylphenanthridin-6-yl)methanone (2e)



According to ***GP3*** with **1a** (48.3 mg, 0.250 mmol, 1.0 equiv.) and *p-tert*-butylbenzaldehyde (84 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 30/1) afforded phenanthridine **2e** (57.7 mg, 0.163 mmol, 65%) as a yellow solid.

IR (neat): 3286*w*, 3063*w*, 3032*w*, 2963*m*, 2905*w*, 2867*w*, 1667*s*, 1602*s*, 1569*w*, 1521*w*, 1497*w*, 1475*m*, 1446*m*, 1432*w*, 1408*w*, 1364*w*, 1323*w*, 1294*w*, 1253*s*, 1205*w*, 1185*s*, 1165*m*, 1139*w*, 1107*m*, 1075*w*, 1039*w*, 1008*w*, 952*w*, 902*m*, 889*s*, 851*w*, 825*m*, 795*w*, 778*m*, 758*s*, 737*m*, 730*m*, 699*s*, 650*w*, 634*w*, 625*m*, 585*w*, 568*w*, 550*m*, 528*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.69 (d, J = 8.3 Hz, 1H, $C_{arom}H$), 8.42 (s, 1H, $C_{arom}H$), 8.13 (t, J = 7.7 Hz, 2H, $C_{arom}H$), 8.01 – 7.96 (m, 2H, $C_{arom}H$), 7.86 (t, J = 7.7 Hz, 1H, $C_{arom}H$), 7.67 – 7.57 (m, 2H, $C_{arom}H$), 7.49 (d, J = 8.5 Hz, 2H, $C_{arom}H$), 2.67 (s, 3H, CH_3), 1.34 (s, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.5 (CO), 157.8 (C), 156.8 (C), 141.0 (C), 138.2 (C), 133.7 (C), 133.0 (C), 130.9 (CH), 130.8 (2 × CH), 130.8 (CH), 130.3 (CH), 127.6 (CH), 127.3 (CH), 125.5 (2 × CH), 124.3 (C), 123.9 (C), 122.2 (CH), 121.7 (CH), 35.2 (C), 31.0 (3 × CH_3), 22.1 (CH_3). **HRMS (ESI)** *m/z* = 376.1672 calcd. for $C_{25}H_{23}NONa$ $[M+Na]^+$, found: 376.1673.

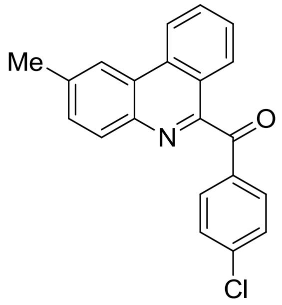
(4-Fluorophenyl)(2-methylphenanthridin-6-yl)methanone (2f)



According to ***GP3*** with **1a** (48.4 mg, 0.250 mmol, 1.0 equiv.) and *p*-fluorobenzaldehyde (54 µL, 0.50 mmol, 2.0 equiv.). Recrystallization from hot MeCN and FC (P/EtOAc = 30/1) of the remaining liquid afforded phenanthridine **2f** (50.7 mg, 0.161 mmol, 64%) as a colorless solid.

MP: 189 °C. **IR** (neat): 3056*w*, 2922*w*, 1661*s*, 1598*s*, 1568*w*, 1507*m*, 1446*w*, 1410*w*, 1368*w*, 1325*w*, 1299*w*, 1253*m*, 1236*s*, 1199*m*, 1157*s*, 1099*w*, 1040*w*, 951*w*, 899*m*, 891*m*, 847*m*, 818*m*, 773*m*, 740*w*, 724*w*, 615*m*, 586*w*, 531*w*. **^{1}H-NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.69 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.41 (s, 1H, $C_{arom}H$), 8.16 (dd, *J* = 8.3 Hz, *J* = 0.6 Hz, 1H, $C_{arom}H$), 8.13 – 8.06 (m, 3H, $C_{arom}H$), 7.87 (ddd, *J* = 8.4 Hz, *J* = 7.0 Hz, *J* = 1.3 Hz, 1H, $C_{arom}H$), 7.65 (ddd, *J* = 8.1 Hz, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H, $C_{arom}H$), 7.61 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1H, $C_{arom}H$), 7.18 – 7.11 (m, 2H, $C_{arom}H$), 2.66 (s, 3H, CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.1 (CO), 166.2 (d, *J* = 256.3 Hz, C), 155.9 (C), 140.8 (C), 138.5 (C), 133.6 (d, *J* = 9.6 Hz, 2 × CH), 133.0 (C), 132.7 (d, *J* = 2.9 Hz, C), 131.0 (CH), 130.9 (CH), 130.3 (CH), 127.7 (CH), 127.1 (CH), 124.3 (C), 123.8 (C), 122.3 (CH), 121.7 (CH), 115.7 (d, *J* = 22.0 Hz, 2 × CH), 22.1 (CH_3). **^{19}F-NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -103.6. **HRMS (ESI)** *m/z* = 338.0952 calcd. for $C_{21}H_{14}FNONa$ $[M+Na]^+$, found: 338.0966.

(4-Chlorophenyl)(2-methylphenanthridin-6-yl)methanone (2g)

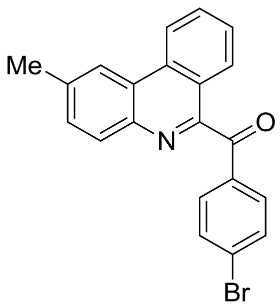


According to ***GP3*** with **1a** (48.4 mg, 0.250 mmol, 1.0 equiv.) and *p*-chlorobenzaldehyde (70 mg, 0.50 mmol, 2.0 equiv.). Recrystallization from hot MeCN and FC (P/EtOAc = 20/1) of the remaining liquid afforded phenanthridine **2g** (52.7 mg, 0.159 mmol, 64%) as a colorless solid.

MP: 218 °C. **IR** (neat): 2363*w*, 2337*w*, 1659*s*, 1617*w*, 1590*w*, 1489*w*, 1446*w*, 1402*w*, 1368*w*, 1323*w*, 1254*m*, 1200*w*, 1169*w*, 1139*w*, 1093*m*, 1043*w*, 1017*w*, 952*w*, 898*m*, 890*s*, 842*m*, 816*m*, 788*m*, 772*s*, 755*w*, 743*w*, 727*m*, 640*m*, 587*m*, 554*w*, 520*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.70 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.43 (s, 1H, $C_{arom}H$), 8.18 (d, *J* = 7.8 Hz, 1H, $C_{arom}H$), 8.09 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.04 – 7.97 (m, 2H, $C_{arom}H$), 7.88 (ddd, *J* = 8.3 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H, $C_{arom}H$), 7.70 – 7.59 (m, 2H, $C_{arom}H$), 7.49 – 7.41

(m, 2H, C$_{\text{arom}}$H), 2.67 (s, 3H, CH$_3$). ^{13}**C-NMR** (75 MHz, CDCl$_3$, 300 K): δ (ppm) = 193.4 (CO), 155.6 (C), 140.8 (C), 140.4 (C), 138.6 (C), 134.8 (C), 133.1 (C), 132.2 (2 × CH), 131.1 (CH), 130.9 (CH), 130.4 (CH), 128.8 (2 × CH), 127.7 (CH), 127.2 (CH), 124.5 (C), 123.9 (C), 122.3 (CH), 121.8 (CH), 22.1 (CH$_3$). **HRMS (ESI)** *m/z* = 354.0656 calcd. for $C_{21}H_{14}ClNONa$ [M+Na]$^+$, found: 354.0655.

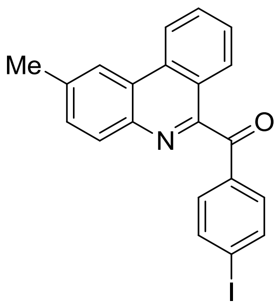
(4-Bromophenyl)(2-methylphenanthridin-6-yl)methanone (2h)



According to ***GP3*** with **1a** (48.3 mg, 0.250 mmol, 1.0 equiv.) and *p*-bromobenzaldehyde (93 mg, 0.50 mmol, 2.0 equiv.). Recrystallization from hot MeCN and FC (P/EtOAc = 40/1) of the remaining liquid afforded phenanthridine **2h** (64.4 mg, 0.171 mmol, 68%) as a colorless solid.

MP: 219 °C. **IR** (neat): 3054*w*, 2961*w*, 2921*w*, 2857*w*, 1664*s*, 1614*w*, 1584*s*, 1496*w*, 1446*m*, 1397*m*, 1366*w*, 1324*w*, 1250*s*, 1199*m*, 1166*m*, 1071*m*, 1039*w*, 1012*m*, 954*w*, 899*m*, 887*s*, 840*m*, 820*m*, 773*m*, 725*m*, 643*w*, 586*w*. ^{1}**H-NMR** (300 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.70 (d, *J* = 8.4 Hz, 1H, C$_{\text{arom}}$H), 8.43 (s, 1H, C$_{\text{arom}}$H), 8.18 (d, *J* = 8.2 Hz, 1H, C$_{\text{arom}}$H), 8.09 (d, *J* = 8.4 Hz, 1H, C$_{\text{arom}}$H), 7.96 – 7.85 (m, 3H, C$_{\text{arom}}$H), 7.70 – 7.59 (m, 4H, C$_{\text{arom}}$H), 2.67 (s, 3H, CH$_3$). ^{13}**C-NMR** (75 MHz, CDCl$_3$, 300 K): δ (ppm) = 193.6 (CO), 155.5 (C), 140.8 (C), 138.7 (C), 135.2 (C), 133.1 (C), 132.3 (2 × CH), 131.8 (2 × CH), 131.1 (CH), 130.9 (CH), 130.4 (CH), 129.2 (C), 127.7 (CH), 127.1 (CH), 124.5 (C), 123.9 (C), 122.3 (CH), 121.8 (CH), 22.1 (CH$_3$). **HRMS (ESI)** *m/z* = 398.0156 calcd. for $C_{21}H_{14}BrNONa$ [M+Na]$^+$, found: 398.0152.

(4-Iodophenyl)(2-methylphenanthridin-6-yl)methanone (2i)

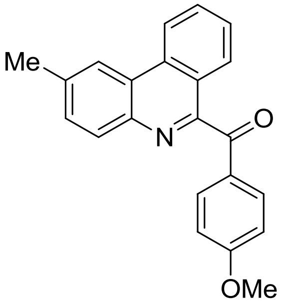


According to ***GP3*** with **1a** (48.2 mg, 0.250 mmol, 1.0 equiv.) and *p*-iodobenzaldehyde (116 mg, 0.50 mmol, 2.0 equiv.). Recrystallization from hot MeCN and FC (P/EtOAc = 40/1) of the remaining liquid afforded phenanthridine **2i** (58.5 mg, 0.138 mmol, 55%) as a colorless solid.

MP: 202 °C. **IR** (neat): 3068*w*, 2921*w*, 1666*s*, 1612*w*, 1579*s*, 1519*w*, 1497*w*, 1445*w*, 1393*m*, 1365*w*, 1324*w*, 1250*s*, 1199*w*, 1178*w*, 1164*m*, 1139*w*, 1062*m*, 1039*w*, 1007*m*, 900*m*, 887*s*, 839*w*, 824*m*, 774*m*, 726*m*, 649*w*, 624*w*, 587*w*, 552*w*, 536*w*, 510*m*. ^{1}**H-NMR**

(300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.69 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.41 (s, 1H, $C_{arom}H$), 8.18 (d, *J* = 8.2 Hz, 1H, $C_{arom}H$), 8.08 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 7.90 – 7.82 (m, 3H, $C_{arom}H$), 7.80 – 7.72 (m, 2H, $C_{arom}H$), 7.69 – 7.58 (m, 2H, $C_{arom}H$), 2.66 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.9 (CO), 155.4 (C), 140.8 (C), 138.6 (C), 137.8 (2 × CH), 135.8 (C), 133.1 (C), 132.1 (2 × CH), 131.0 (CH), 130.9 (CH), 130.4 (CH), 127.7 (CH), 127.1 (CH), 124.4 (C), 123.8 (C), 122.3 (CH), 121.7 (CH), 102.2 (C), 22.1 (CH_3). **HRMS (ESI)** *m/z* = 446.0018 calcd. for $C_{21}H_{14}INONa$ $[M+Na]^+$, found: 446.0003.

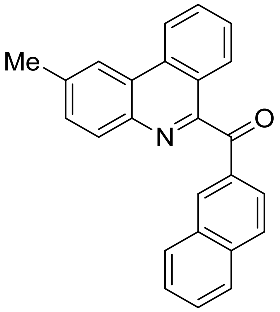
(4-Methoxyphenyl)(2-methylphenanthridin-6-yl)methanone (2j)



According to ***GP3*** with **1a** (48.3 mg, 0.250 mmol, 1.0 equiv.) and *p*-anisaldehyde (61 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 10/1) afforded phenanthridine **2j** (56.6 mg, 0.173 mmol, 69%) as a colorless solid.

MP: 142 °C. **IR** (neat): 3070*w*, 2934*w*, 2840*w*, 1658*m*, 1594*s*, 1572*m*, 1508*m*, 1446*w*, 1366*w*, 1315*w*, 1248*s*, 1160*s*, 1117*w*, 1026*m*, 904*m*, 889*m*, 845*m*, 825*m*, 778 *m*, 729*s*, 616*m*, 532*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.67 (d, *J* = 8.7 Hz, 1H, $C_{arom}H$), 8.41 (s, 1H, $C_{arom}H$), 8.17 – 8.07 (m, 2H, $C_{arom}H$), 8.05 – 7.97 (m, 2H, $C_{arom}H$), 7.84 (ddd, *J* = 8.4 Hz, *J* = 7.1 Hz, *J* = 1.3 Hz, 1H, $C_{arom}H$), 7.66 – 7.56 (m, 2H, $C_{arom}H$), 6.97 – 6.90 (m, 2H, $C_{arom}H$), 3.86 (s, 3H, CH_3), 2.66 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.5 (CO), 164.2 (C), 157.0 (C), 141.0 (C), 138.1 (C), 133.2 (2 × CH), 132.9 (C), 130.9 (CH), 130.7 (CH), 130.3 (CH), 129.4 (C), 127.5 (CH), 127.3 (CH), 124.2 (C), 123.9 (C), 122.2 (CH), 121.7 (CH), 113.8 (2 × CH), 55.5 (CH_3), 22.0 (CH_3). **HRMS (ESI)** *m/z* = 350.1151 calcd. for $C_{22}H_{17}NO_2Na$ $[M+Na]^+$, found: 350.1143.

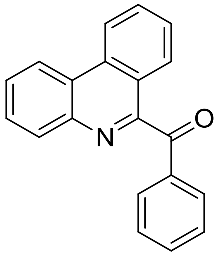
(2-Methylphenanthridin-6-yl)(naphthalen-2-yl)methanone (2k)



According to ***GP3*** with **1a** (48.4 mg, 0.250 mmol, 1.0 equiv.) and 2-naphthaldehyde (78 mg, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 30/1) afforded phenanthridine **2k** (39.1 mg, 0.113 mmol, 45%) as a yellow solid.

MP: 159 °C. **IR** (neat): 3059*w*, 3020*w*, 2963*w*, 2922*w*, 2858*w*, 1664*s*, 1625*m*, 1596*w*, 1570*w*, 1523*w*, 1497*w*, 1466*w*, 1446*w*, 1368*w*, 1322*w*, 1294*w*, 1273*m*, 1262*m*, 1229*w*, 1182*m*, 1162*m*, 1129*w*, 1114*m*, 1038*w*, 959*w*, 912*w*, 898*w*, 867*w*, 849*w*, 824*m*, 801*w*, 779*s*, 758*s*, 735*m*, 707*w*, 667*w*, 624*w*, 585*w*, 546*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.71 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.43 (d, *J* = 8.5 Hz, 2H, $C_{arom}H$), 8.25 (dd, *J* = 8.6 Hz, *J* = 1.7 Hz, 1H, $C_{arom}H$), 8.18 (dd, *J* = 8.2 Hz, *J* = 0.6 Hz, 1H, $C_{arom}H$), 8.14 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 7.95 (d, *J* = 8.7 Hz, 1H, $C_{arom}H$), 7.90 – 7.84 (m, 2H, $C_{arom}H$), 7.80 (d, *J* = 8.2 Hz, 1H, $C_{arom}H$), 7.66 – 7.57 (m, 3H, $C_{arom}H$), 7.48 (ddd, *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 1.2 Hz, 1H, $C_{arom}H$), 2.68 (s, 3H, CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.9 (CO), 156.6 (C), 140.9 (C), 138.3 (C), 136.0 (C), 133.9 (CH), 133.6 (C), 133.0 (C), 132.3 (C), 131.0 (CH), 130.8 (CH), 130.3 (CH), 129.8 (CH), 128.9 (CH), 128.5 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 126.7 (CH), 125.1 (CH), 124.3 (C), 123.9 (C), 122.2 (CH), 121.7 (CH), 22.1 (CH_3). **HRMS (ESI)** *m/z* = 370.1202 calcd. for $C_{25}H_{17}NONa$ $[M+Na]^+$, found: 370.1200.

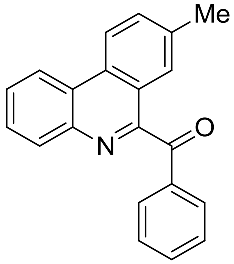
Phenanthridin-6-yl(phenyl)methanone (2l)



According to ***GP3*** with **1l** (45.0 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 40/1) afforded phenanthridine **2l** (45.0 mg, 0.159 mmol, 64%) as a colorless solid.

MP: 151 °C. **IR** (neat): 3064*w*, 1671*s*, 1611*w*, 1597*m*, 1579*w*, 1526*w*, 1486*w*, 1461*w*, 1449*m*, 1367*w*, 1329*w*, 1244*m*, 1201*m*, 1178*w*, 1167*w*, 1155*m*, 1059*w*, 1038*w*, 1025*w*, 1001*w*, 894*m*, 848*w*, 765*m*, 753*s*, 727*s*, 719*s*, 704*w*, 687*m*, 631*w*, 614*w*, 526s. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.72 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.68 – 8.61 (m, 1H, $C_{arom}H$), 8.28 – 8.19 (m, 1H, $C_{arom}H$), 8.15 (d, *J* = 8.2 Hz, 1H, $C_{arom}H$), 8.05 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 2H, $C_{arom}H$), 7.89 (t, *J* = 7.7 Hz, 1H, $C_{arom}H$), 7.83 – 7.72 (m, 2H, $C_{arom}H$), 7.70 – 7.59 (m, 2H, $C_{arom}H$), 7.48 (t, *J* = 7.7 Hz, 2H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.7 (CO), 157.5 (C), 142.7 (C), 136.2 (C), 133.9 (CH), 133.3 (C), 131.2 (CH), 130.8 (2 × CH), 130.6 (CH), 129.1 (CH), 128.5 (2 × CH), 128.1 (CH), 127.8 (CH), 127.3 (CH), 124.5 (C), 123.8 (C), 122.3 (CH), 122.1 (CH). **HRMS (ESI)** *m/z* = 306.0889 calcd. for $C_{20}H_{13}NONa$ [M+Na]$^+$, found: 306.0885.

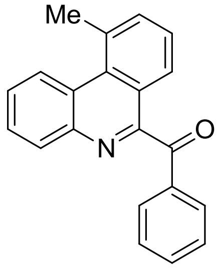
(8-Methylphenanthridin-6-yl)(phenyl)methanone (2m)



According to ***GP3*** with **1m** (48.2 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 20/1) afforded phenanthridine **2m** (47.7 mg, 0.160 mmol, 64%) as a yellow solid.

MP: 167 °C. **IR** (neat): 3062*w*, 2920*w*, 1672*s*, 1596*w*, 1577*w*, 1530*w*, 1479*w*, 1462*m* 1450*m*, 1370*w*, 1328*w*, 1250*s*, 1187*w* 1174*s*, 1159*w* 1058*w*, 1028*w*, 1001*w*, 922*m*, 878*w*, 833*m*, 824*w*, 764*s*, 729*m*, 710*s*, 687*m*, 584*w*, 500*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.62 – 8.55 (m, 2H, $C_{arom}H$), 8.23 – 8.17 (m, 1H, $C_{arom}H$), 8.09 – 8.01 (m, 2H, $C_{arom}H$), 7.91 (s, 1H, $C_{arom}H$), 7.78 – 7.68 (m, 3H, $C_{arom}H$), 7.66 – 7.59 (m, 1H, $C_{arom}H$), 7.52 – 7.44 (m, 2H, $C_{arom}H$), 2.51 (s, 3H, CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.9 (CO), 157.1 (C), 142.3 (C), 137.9 (C), 136.1 (C), 133.9 (CH), 133.1 (CH), 131.1 (C), 130.8 (2 × CH), 130.4 (CH), 128.6 (CH), 128.5 (2 × CH), 128.0 (CH), 126.5 (CH), 124.5 (C), 123.9 (C), 122.1 (CH), 121.9 (CH), 21.6 (CH_3). **HRMS (ESI)** *m/z* = 320.1046 calcd. for $C_{21}H_{15}NONa$ [M+Na]$^+$, found: 320.1049.

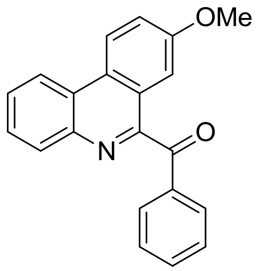
(10-Methylphenanthridin-6-yl)(phenyl)methanone (2n)



According to ***GP3*** with **1n** (48.2 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 20/1) afforded a mixture of phenanthridine **2n** and **2l** (42.3 mg, **2n**: 0.142 mmol, 49%, **2l**: 0.020 mmol, 8%) as a yellow solid.

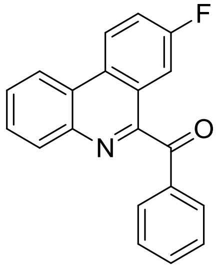
2n: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.95 – 8.85 (m, 1H, $C_{arom}H$), 8.31 – 8.24 (m, 1H, $C_{arom}H$), 8.04 – 7.93 (m, 3H, $C_{arom}H$), 7.82 – 7.69 (m, 3H, $C_{arom}H$), 7.66 – 7.53 (m, 2H, $C_{arom}H$), 7.52 – 7.43 (m, 2H, $C_{arom}H$), 3.17 (s, 3H, CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.3 (CO), 158.5 (C), 143.9 (C), 136.0 (C), 135.6 (C), 135.4 (CH), 134.0 (CH), 132.6 (C), 130.8 (CH), 130.6 (2 × CH), 128.6 (2 × CH), 128.3 (CH), 127.2 (CH), 127.1 (CH), 126.6 (CH), 125.9 (CH), 125.8 (C), 125.1 (C), 26.8 (CH_3). **HRMS (ESI)** *m/z* = 320.1046 calcd. for $C_{21}H_{15}NONa$ [M+Na]$^+$, found: 320.1047.

(8-Methoxyphenanthridin-6-yl)(phenyl)methanone (2o)



According to ***GP3*** with **1o** (52.3 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 20/1) afforded phenanthridine **2o** (54.1 mg, 0.173 mmol, 69%) as a yellow solid. **MP:** 182 °C. **IR** (neat): 3064*w*, 2965*w*, 2916*w*, 2843*w*, 1663*s*, 1618*m*, 1597*m*, 1580*w*, 1569*w*, 1530*m*, 1482*m*, 1461*s*, 1419*w*, 1384*m*, 1326*w*, 1291*m*, 1254*m*, 1242*m*, 1218*s*, 1192*m*, 1176*m*, 1155*m*, 1113*w*, 1053*w*, 1036*s*, 1001*w*, 927*w*, 881*m*, 855*m*, 836*m*, 822*m*, 759*s*, 737*m*, 710*s*, 684*m*, 595*w*, 571*w*, 534*w*. **^{1}H-NMR** (400 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.60 (d, *J* = 8.9 Hz, 1H, C$_{arom}$H), 8.56 – 8.51 (m, 1H, C$_{arom}$H), 8.21 – 8.15 (m, 1H, C$_{arom}$H), 8.09 – 8.00 (m, 2H, C$_{arom}$H), 7.75 – 7.68 (m, 2H, C$_{arom}$H), 7.66 – 7.60 (m, 1H, C$_{arom}$H), 7.55 – 7.45 (m, 4H, C$_{arom}$H), 3.87 (s, 3H, CH$_3$). **^{13}C-NMR** (101 MHz, CDCl$_3$, 300 K): δ (ppm) = 194.8 (CO), 158.9 (C), 156.0 (C), 141.7 (C), 136.2 (C), 133.9 (2 × CH), 130.9 (CH), 130.5 (CH), 128.5 (2 × CH), 128.3 (CH), 128.0 (CH), 127.8 (C), 125.1 (C), 124.6 (C), 123.9 (CH), 122.4 (CH), 121.6 (CH), 106.5 (CH), 55.5 (CH$_3$). **HRMS (ESI)** *m/z* = 336.0995 calcd. for C$_{21}$H$_{15}$NO$_2$Na [M+Na]$^+$, found: 336.0999.

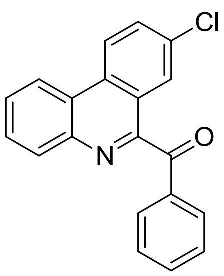
(8-Fluorophenanthridin-6-yl)(phenyl)methanone (2p)



According to ***GP3*** with **1p** (49.6 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 20/1) afforded phenanthridine **2p** (51.7 mg, 0.172 mmol, 69%) as a colorless solid. **MP:** 213 °C. **IR** (neat): 3062*w*, 1660*s*, 1624*w*, 1600*w*, 1574*w*, 1530*w*, 1482*w*, 1463*w*, 1449*w*, 1424*w*, 1376*w*, 1333*w*, 1280*w*, 1254*m*, 1201*m*, 1174*m*, 1157*w*, 1053*w*, 1033*w*, 959*w*, 945*m*, 928*w*, 882*m*, 870*m*, 840*w*, 828*m*, 764*s*, 738*m*, 705*m*, 681*s*, 592*w*, 569*w*, 504*w*. **^{1}H-NMR** (300 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.72 (dd, *J* = 9.1 Hz, *J* = 5.2 Hz, 1H, C$_{arom}$H), 8.64 – 8.55 (m, 1H, C$_{arom}$H), 8.28 – 8.18 (m, 1H, C$_{arom}$H), 8.13 – 7.99 (m, 2H, C$_{arom}$H), 7.87 (dd, *J* = 9.5 Hz, *J* = 2.6 Hz, 1H, C$_{arom}$H), 7.82 – 7.74 (m, 2H, C$_{arom}$H), 7.71 – 7.58 (m, 2H, C$_{arom}$H), 7.55 – 7.45 (m, 2H, C$_{arom}$H). **^{13}C-NMR** (101 MHz, CDCl$_3$, 300 K): δ (ppm) = 194.1 (CO), 161.5 (d, *J* = 249.7 Hz, C), 156.0 (d, *J* = 4.2 Hz, C), 142.1 (C), 135.9 (C), 134.1 (CH), 130.9 (2 × CH, C), 130.8 (CH), 130.1 (d, *J* = 1.9 Hz, C), 129.0 (CH), 128.7 (CH), 128.6 (2 × CH), 124.9 (d, *J* = 8.5 Hz, CH), 124.2 (C), 121.9 (CH), 120.7 (d, *J* = 24.1 Hz, CH), 111.9 (d, *J* = 22.3 Hz, CH). **^{19}F-NMR** (282 MHz, CDCl$_3$, 300 K):

δ (ppm) = -110.9 (s, CF). **HRMS (ESI)** *m/z* = 324.0795 calcd. for $C_{20}H_{12}FNONa$ $[M+Na]^+$, found: 324.0800.

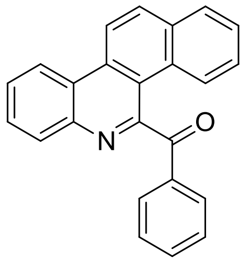
(8-Chlorophenanthridin-6-yl)(phenyl)methanone (2q)



According to ***GP3*** with **1q** (53.5 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). Recrystallization from hot MeCN and FC (P/EtOAc = 20/1) of the remaining liquid afforded phenanthridine **2q** (56.5 mg, 0.178 mmol, 71%) as a colorless solid.

MP: 224 °C. **IR** (neat): 3059*w*, 1662*s*, 1599*w*, 1581*w*, 1567*w*, 1521*w*, 1475*w*, 1460*m*, 1449*w*, 1409*w*, 1366*w*, 1328*w*, 1250*m*, 1190*w*, 1181*w*, 1160*w*, 1099*w*, 1055*w*, 1026*w*, 900*m*, 861*w*, 827*w*, 820*w*, 762*s*, 734*m*, 704*m*, 681*m*, 585*w*, 567*w*, 512*w*. **^{1}H-NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.65 (d, *J* = 8.9 Hz, 1H, $C_{arom}H$), 8.63 – 8.56 (m, 1H, $C_{arom}H$), 8.25 – 8.16 (m, 2H, $C_{arom}H$), 8.08 – 8.03 (m, 2H, $C_{arom}H$), 7.88 – 7.75 (m, 3H, $C_{arom}H$), 7.69 – 7.62 (m, 1H, $C_{arom}H$), 7.54 – 7.47 (m, 2H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.0 (CO), 155.9 (C), 142.4 (C), 135.9 (C), 134.1 (CH), 133.9 (C), 131.9 (CH), 131.7 (C), 130.9 (2 × CH), 130.8 (CH), 129.4 (CH), 128.7 (CH), 128.6 (2 × CH), 126.5 (CH), 124.6 (C), 124.0 (CH), 124.0 (C), 122.0 (CH). **HRMS (ESI)** *m/z* = 340.0500 calcd. for $C_{20}H_{12}ClNONa$ $[M+Na]^+$, found: 340.0492.

Benzo[i]phenanthridin-5-yl(phenyl)methanone (2r)

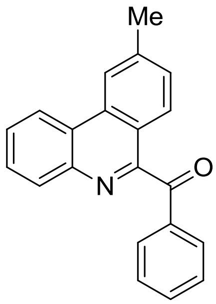


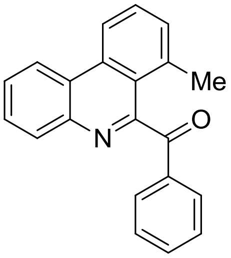
According to ***GP3*** with **1r** (57.5 mg, 0.251 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 15/1) afforded phenanthridine **2r** with traces of the other regioisomer (59.9 mg, 0.180 mmol, 72%) as a yellow solid, which was separated *via* recrystallization.

MP: 193 °C **IR** (neat): 3057*w*, 3026*w*, 1675*s*, 1596*m*, 1580*w*, 1563*w*, 1513*w*, 1468*m*, 1450*m*, 1388*w*, 1365*w*, 1326*w*, 1267*m*, 1246*m*, 1218*s*, 1191*m*, 1176*m*, 1157*w*, 1035*w*, 1008*w*, 940*w*, 909*w*, 884*m*, 854*w*, 831*w*, 817*w*, 758*s*, 716*s*, 687*m*, 672*m*, 631*s* 530*s*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.75 – 8.63 (m, 2H, $C_{arom}H$), 8.38 (d, *J* = 8.5 Hz, 1H, $C_{arom}H$), 8.28 – 8.23 (m, 1H, $C_{arom}H$), 8.18 (d, *J* = 9.0 Hz, 1H, $C_{arom}H$), 8.14 – 8.06 (m, 2H, $C_{arom}H$), 7.95 (dd, *J* = 7.9 Hz, *J* = 1.0 Hz, 1H, $C_{arom}H$), 7.85 – 7.71 (m, 2H, $C_{arom}H$), 7.66 – 7.59 (m, 1H, $C_{arom}H$), 7.59 – 7.53 (m, 1H, $C_{arom}H$), 7.52 – 7.42 (m, 3H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K):

δ (ppm) = 196.2 (CO), 156.7 (C), 143.3 (C), 135.9 (C), 134.0 (CH, C), 132.9 (CH), 132.8 (C), 130.8 (2 × CH), 130.1 (CH), 129.3 (CH), 129.1 (CH), 128.8 (2 × CH), 128.7 (C), 127.9 (CH), 127.6 (CH), 126.9 (CH), 126.5 (CH), 124.3 (C), 122.7 (CH), 120.6 (C), 120.0 (CH). **HRMS (ESI)** *m/z* = 356.1046 calcd. for $C_{24}H_{15}NONa$ $[M+Na]^+$, found: 356.1054.

(9-Methylphenanthridin-6-yl)(phenyl)methanone (2s) and (7-methylphenanthridin-6-yl)(phenyl)methanone (2s')

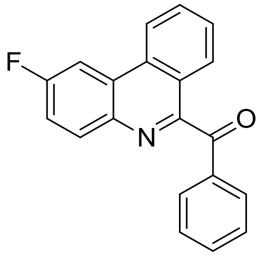




According to ***GP3*** with **1s** (48.3 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 20/1) afforded a mixture of phenanthridine **2s** and **2s'** (50.0 mg, 0.168 mmol, 67%) in a ratio of 1/1.8 as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.67 – 8.57 (m, 1H, 2H', $C_{arom}H$), 8.48 (s, 1H, $C_{arom}H$), 8.24 – 8.13 (m, 1H, 1H', $C_{arom}H$), 8.08 – 7.98 (m, 3H, 2H', $C_{arom}H$), 7.81 – 7.67 (m, 2H, 3H', $C_{arom}H$), 7.67 – 7.57 (m, 1H, 1H', $C_{arom}H$), 7.53 – 7.42 (m, 3H, 3H', $C_{arom}H$), 2.64 (s, 3H, CH_3), 2.54 (s, 3H', CH_3). **HRMS (ESI)** *m/z* = 320.1046 calcd. for $C_{21}H_{15}NONa$ $[M+Na]^+$, found: 320.1047.

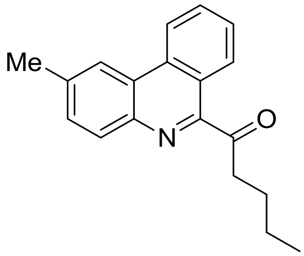
(2-Fluorophenanthridin-6-yl)(phenyl)methanone (2t)



According to ***GP3*** with **1t** (49.3 mg, 0.250 mmol, 1.0 equiv.) and benzaldehyde (51 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 20/1) afforded phenanthridine **2t** (48.0 mg, 0.159 mmol, 64%) as a colorless solid.

MP: 181 °C. **IR** (neat): 3085*w*, 3068*w*, 1663*s*, 1621*m*, 1598*m*, 1579*m*, 1524*m*, 1495*m*, 1450*s*, 1416*w*, 1364*w*, 1324*w*, 1279*m*, 1252*w*, 1205*s*, 1182*m*, 1168*w*, 1139*w*, 1103*w*, 1057*w*, 1026*w*, 890*s*, 868*w*, 831*m*, 806*w*, 766*m*, 748*m*, 719*m*, 706*w*, 684*m*, 642*w*, 623*w*, 607*m*, 551*w*, 535*m*, 518*w*. **^{1}H-NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.60 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.30 – 8.13 (m, 3H, $C_{arom}H$), 8.08 – 7.99 (m, 2H, $C_{arom}H$), 7.92 (ddd, *J* = 8.3 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H, $C_{arom}H$), 7.71 (ddd, *J* = 8.2 Hz, *J* = 7.1 Hz, *J* = 1.1 Hz, 1H, $C_{arom}H$), 7.67 – 7.60 (m, 1H, $C_{arom}H$), 7.56 – 7.45 (m, 3H, $C_{arom}H$). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.5 (CO), 162.1 (d, *J* = 249.1 Hz, C), 156.6 (d, *J* = 2.8 Hz, C), 139.3 (C), 136.1 (C), 134.0 (CH), 132.9 (d, *J* = 9.4 Hz, CH), 132.7 (d, *J* = 4.3 Hz, C), 131.4 (CH), 130.8 (2 × CH), 128.6 (2 × CH), 128.5 (CH), 127.4 (CH), 126.0 (d, *J* = 9.4 Hz, C), 123.8 (C), 122.5 (CH), 118.1 (d, *J* = 24.4 Hz, CH), 107.2 (d, *J* = 23.5 Hz, CH). **^{19}F-NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -110.6. **HRMS (ESI)** *m/z* = 324.0795 calcd. for $C_{20}H_{12}FNONa$ [M+Na]$^+$, found: 324.0798.

1-(2-methylphenanthridin-6-yl)pentan-1-one (2u)



According to ***GP3*** with **1a** (48.2 mg, 0.250 mmol, 1.0 equiv.) and pentanal (53 µL, 0.50 mmol, 2.0 equiv.). FC (P/EtOAc = 60/1) afforded phenanthridine **2u** (26.9 mg, 97.0 µmol, 39%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.76 (dd, *J* = 8.4 Hz, *J* = 0.7 Hz, 1H, $C_{arom}H$), 8.62 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 8.35 (s, 1H, $C_{arom}H$), 8.10 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 7.83 (ddd, *J* = 8.3 Hz, *J* = 7.0 Hz, *J* = 1.3 Hz, 1H, $C_{arom}H$), 7.69 (ddd, *J* = 8.3 Hz, *J* = 7.0 Hz, *J* = 1.2 Hz, 1H, $C_{arom}H$), 7.59 (dd, *J* = 8.3 Hz, *J* = 1.8 Hz, 1H, $C_{arom}H$), 3.41 (t, *J* = 7.5 Hz, 2H, CH_2), 2.64 (s, 3H, CH_3), 1.81 (q, *J* = 7.5 Hz, 2H, CH_2), 1.50 (sext, *J* = 7.4 Hz, 2H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3H, CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 205.2 (CO), 153.7 (C), 140.8 (C), 138.8 (C), 133.1 (C), 130.6 (CH), 130.6 (CH), 130.5 (CH), 127.8 (CH), 127.6 (CH), 125.0 (C), 123.2 (C), 121.9 (CH), 121.7 (CH), 40.1 (CH_2), 26.3 (CH_2), 22.5 (CH_2), 22.2 (CH_3), 14.0 (CH_3). **HRMS (ESI)** *m/z* = 300.1364 calcd. for $C_{19}H_{19}NONa$ [M+Na]$^+$, found: 300.1350.

5. X-ray crystallographic data

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN;[4] absorption correction, Denzo;[5] structure solution SHELXS-97;[6] structure refinement SHELXL-97[7] 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 2s': formula $C_{21}H_{15}NO$, M = 297.34, pale yellow crystal, 0.25 x 0.20 x 0.12 mm, a = 9.6987(2), b = 17.9944(5), c = 8.8383(2) Å, β = 100.696(1)°, V = 1515.68(6) Å^3, ρ_{calc} = 1.303 gcm^{-3}, μ = 0.080 mm^{-1}, empirical absorption correction ($0.980 \leq T \leq 0.990$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 11250 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.67 Å^{-1}, 3681 independent (R_{int} = 0.042) and 2924 observed reflections [$I > 2\sigma(I)$], 209 refined parameters, R = 0.060, wR^2 = 0.151, max. (min.) residual electron density 0.20 (-0.15) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.

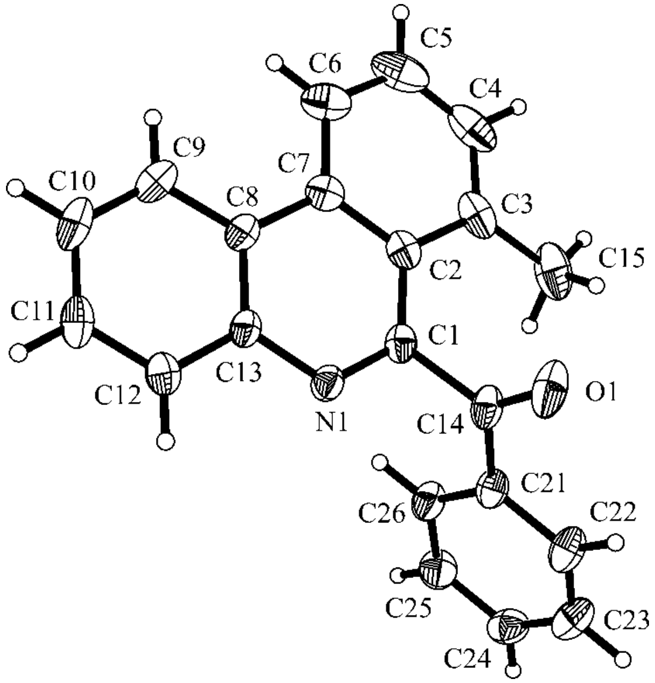
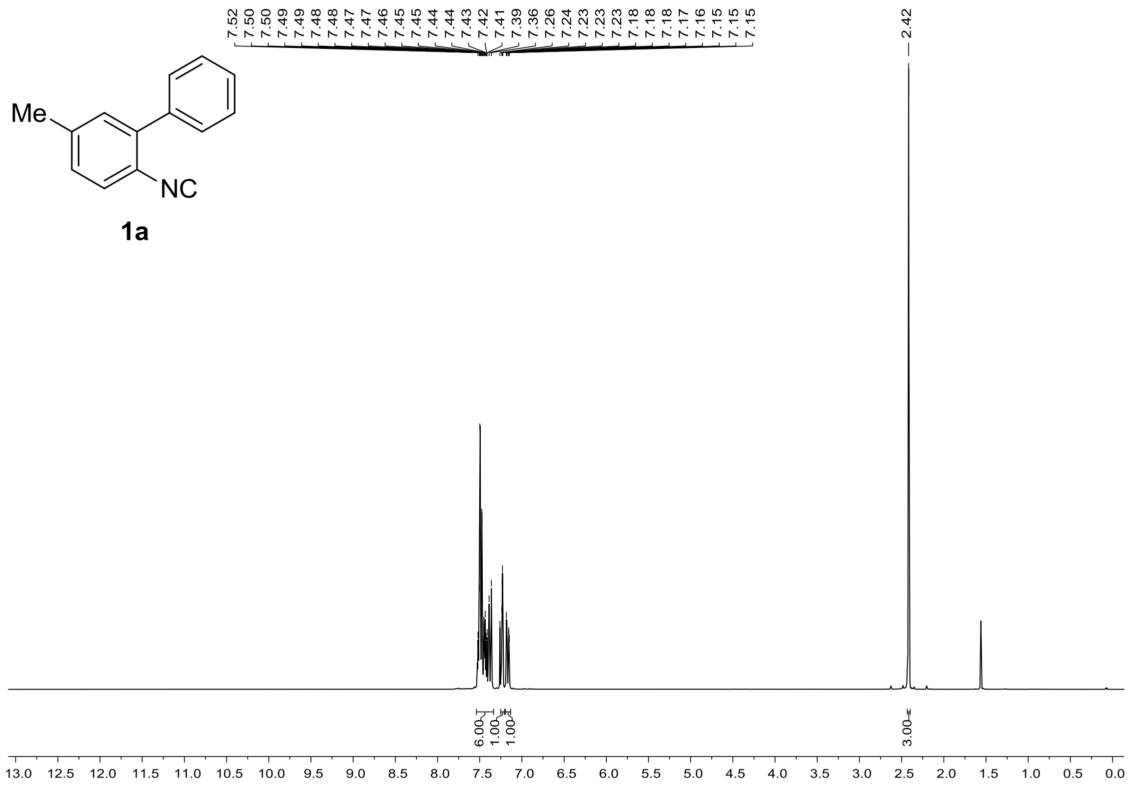
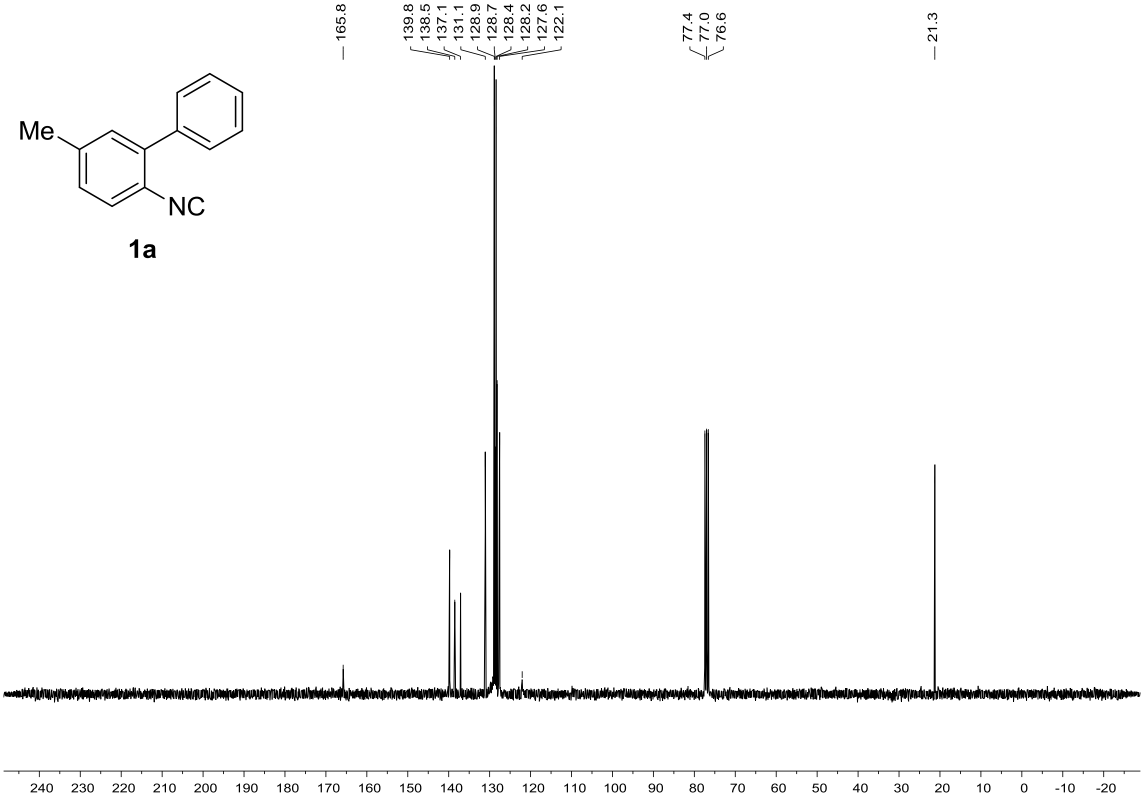


Figure 1. Crystal structure of compound **2s'**.
Thermals ellipsoids are shown with 30% probability.)

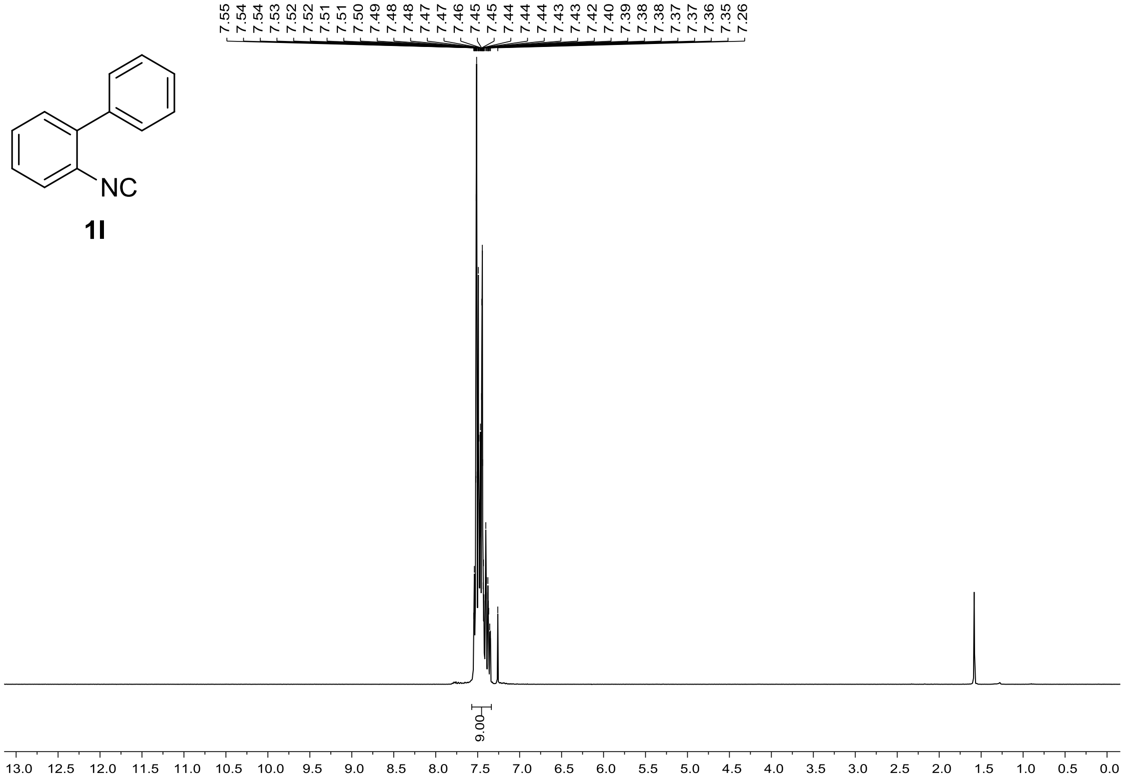
6. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra

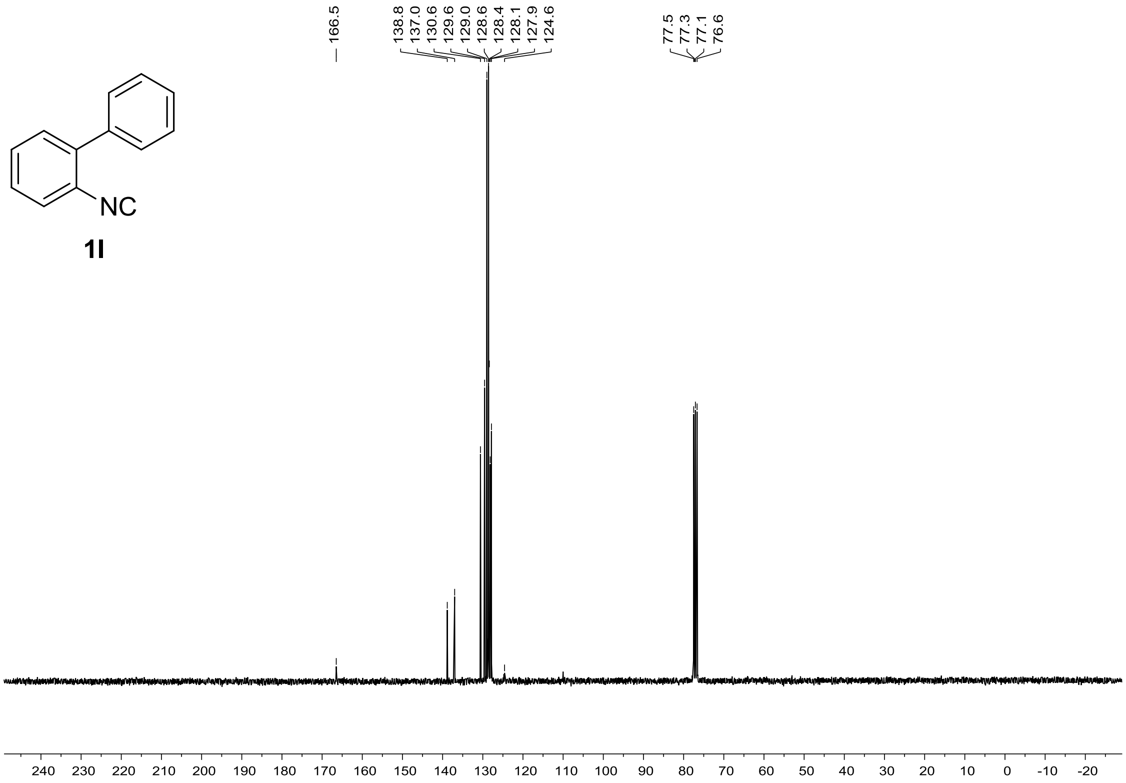
2-Isocyano-5-methyl-1,1'-biphenyl (1a)



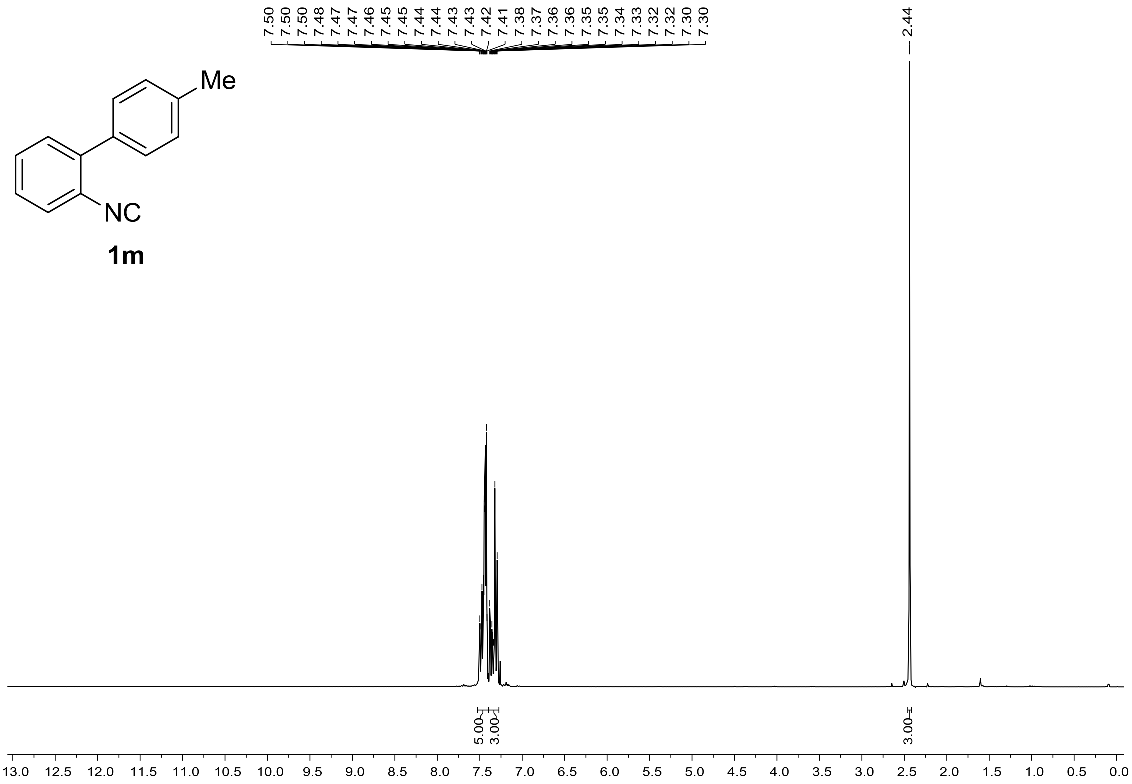


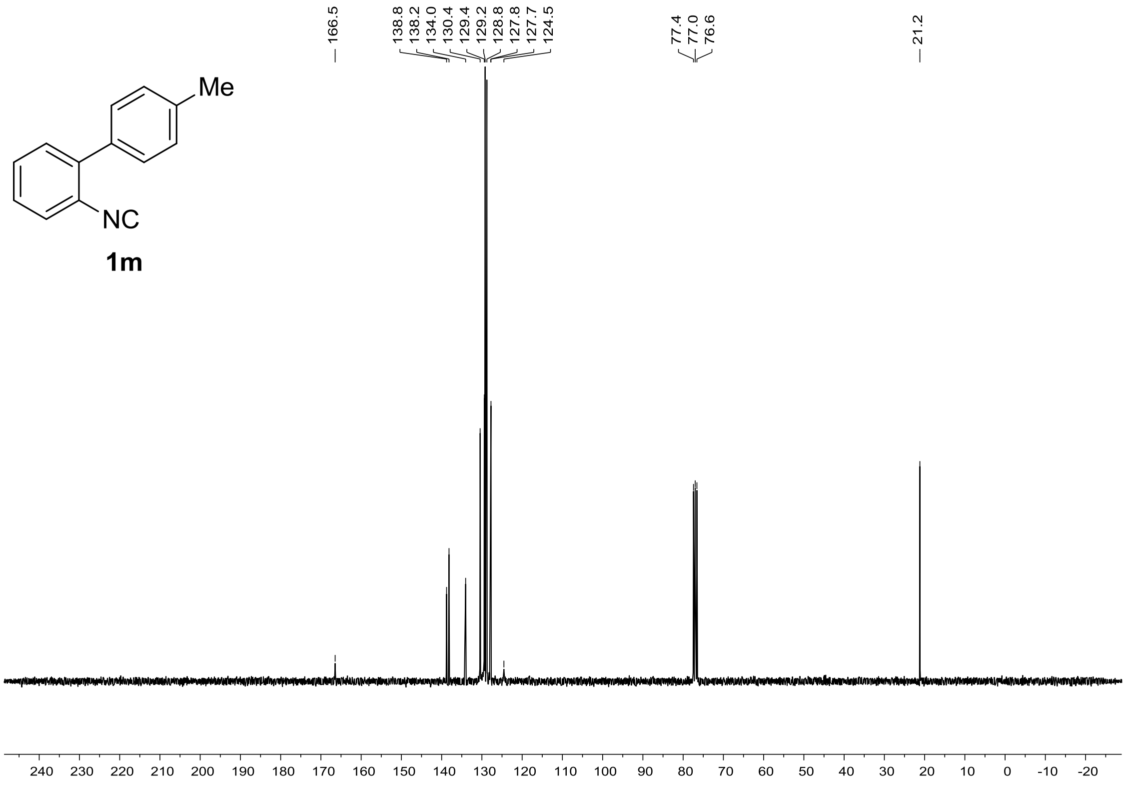
2-Isocyano-1,1'-biphenyl (1l)



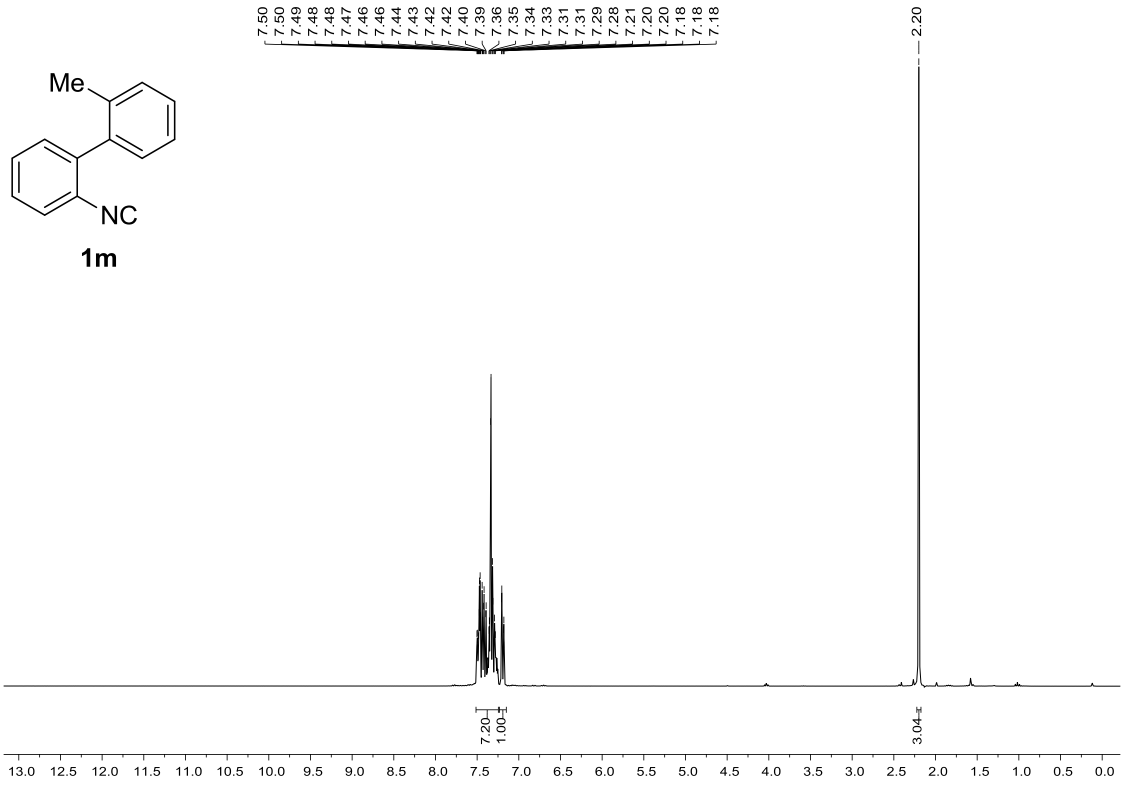


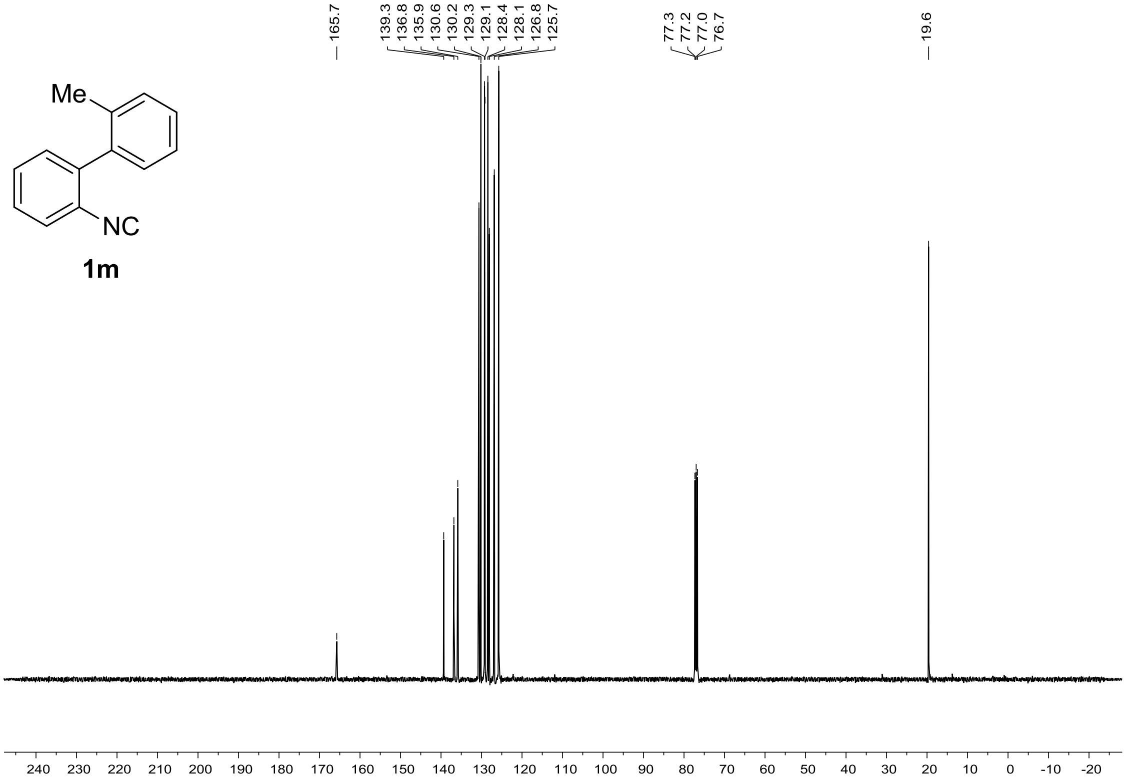
2-Isocyano-4'-methyl-1,1'-biphenyl (1m)



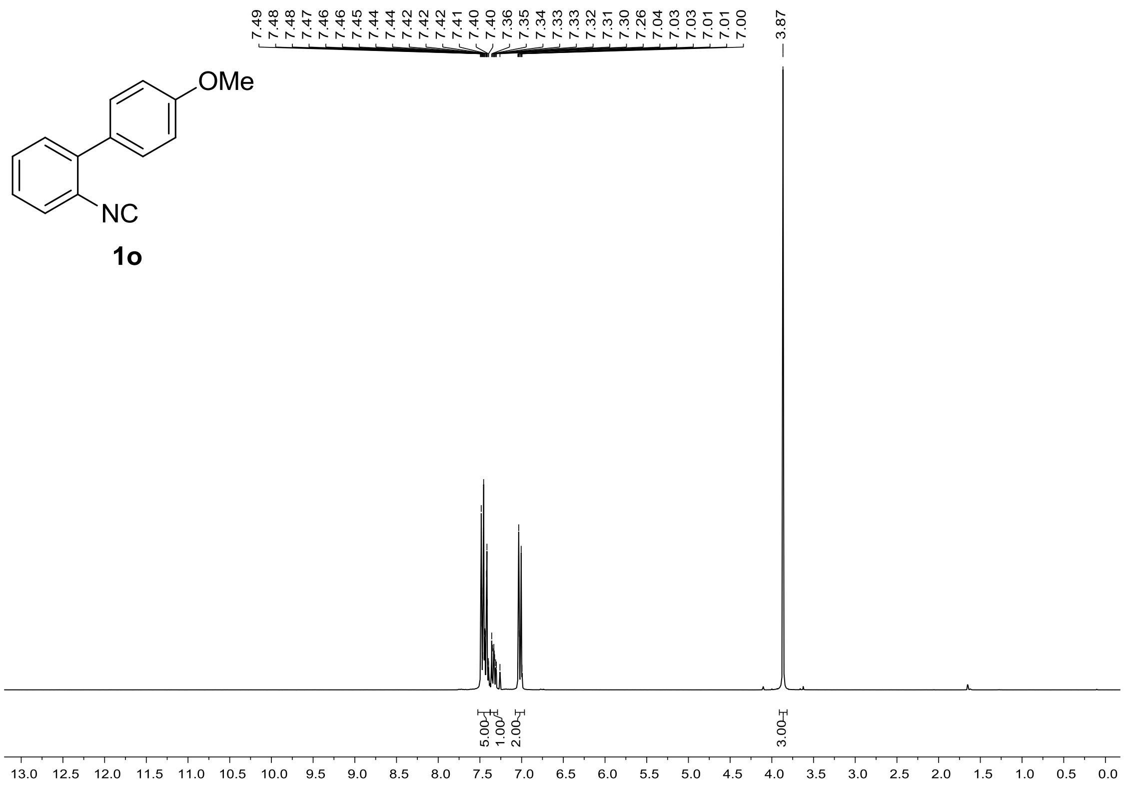


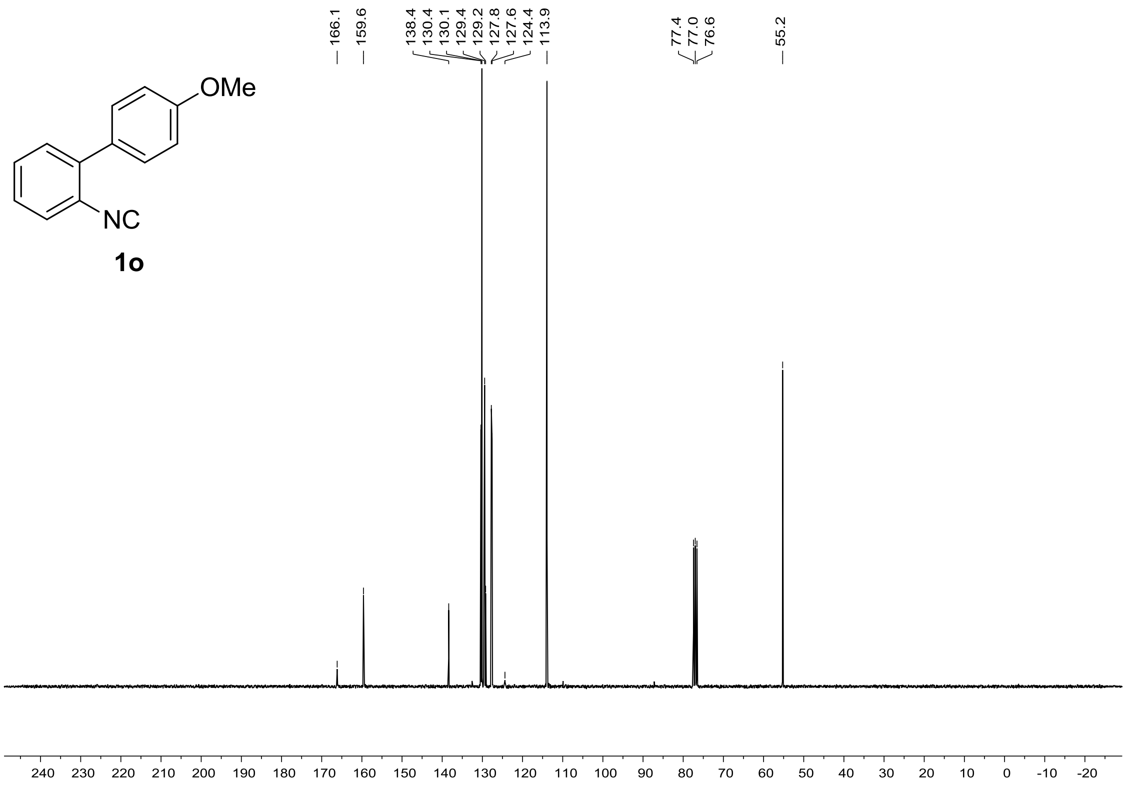
2-Isocyano-2'-methyl-1,1'-biphenyl (1n)



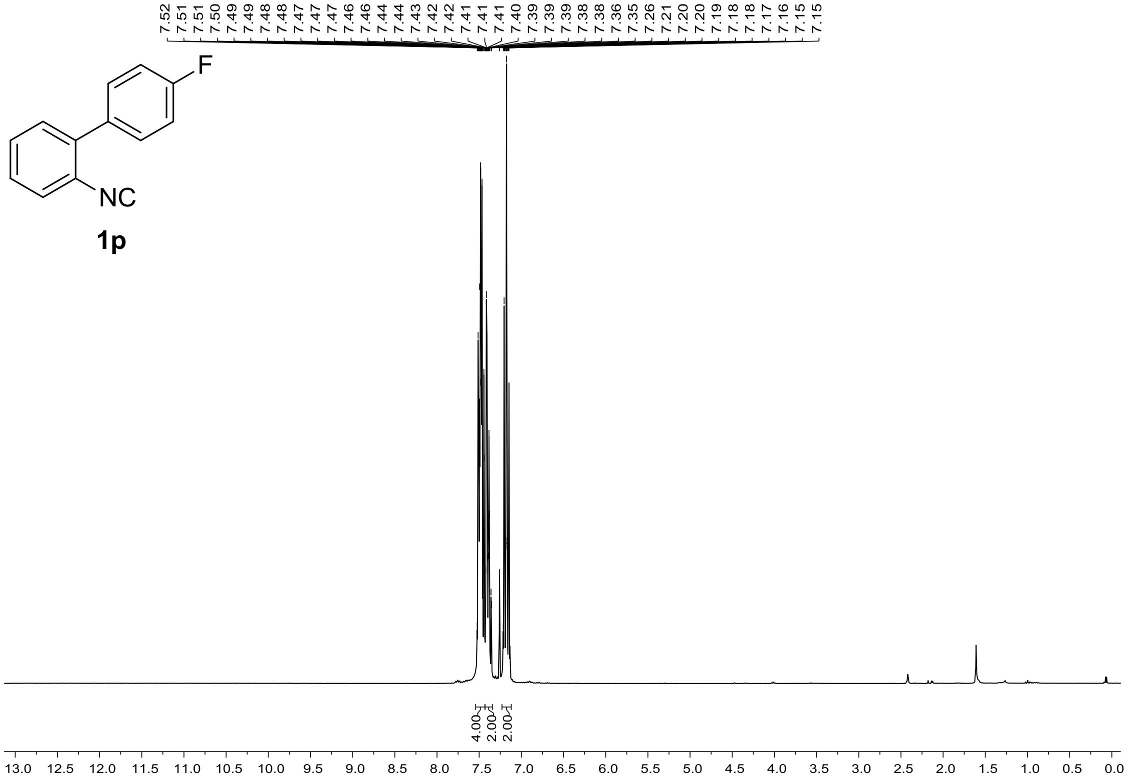


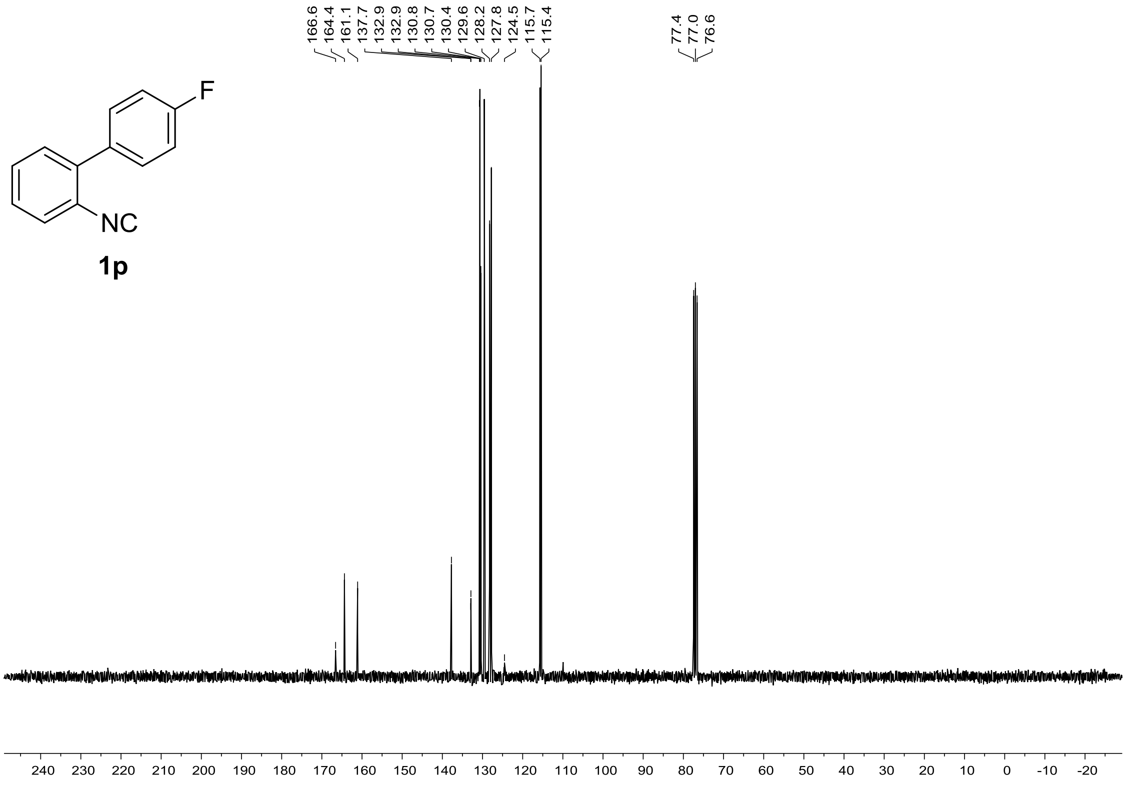
2-Isocyano-4'-methoxy-1,1'-biphenyl (1o)

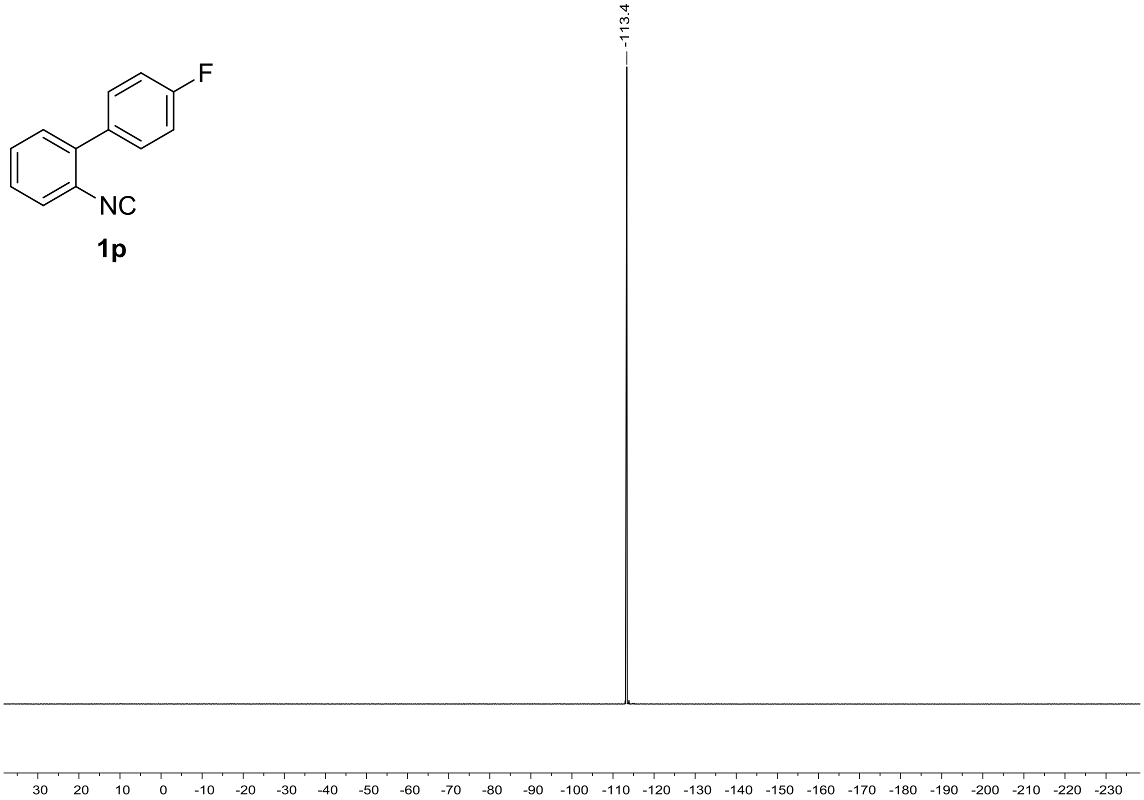




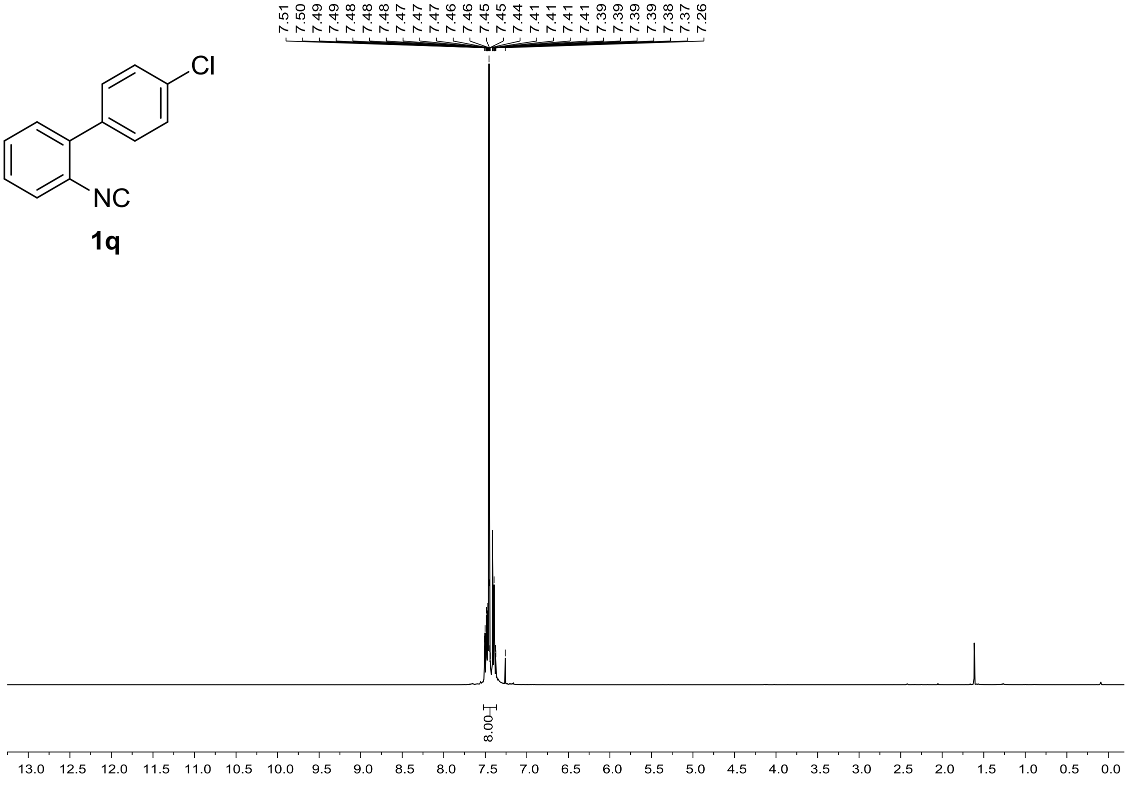
4'-Fluoro-2-isocyano-1,1'-biphenyl (1p)

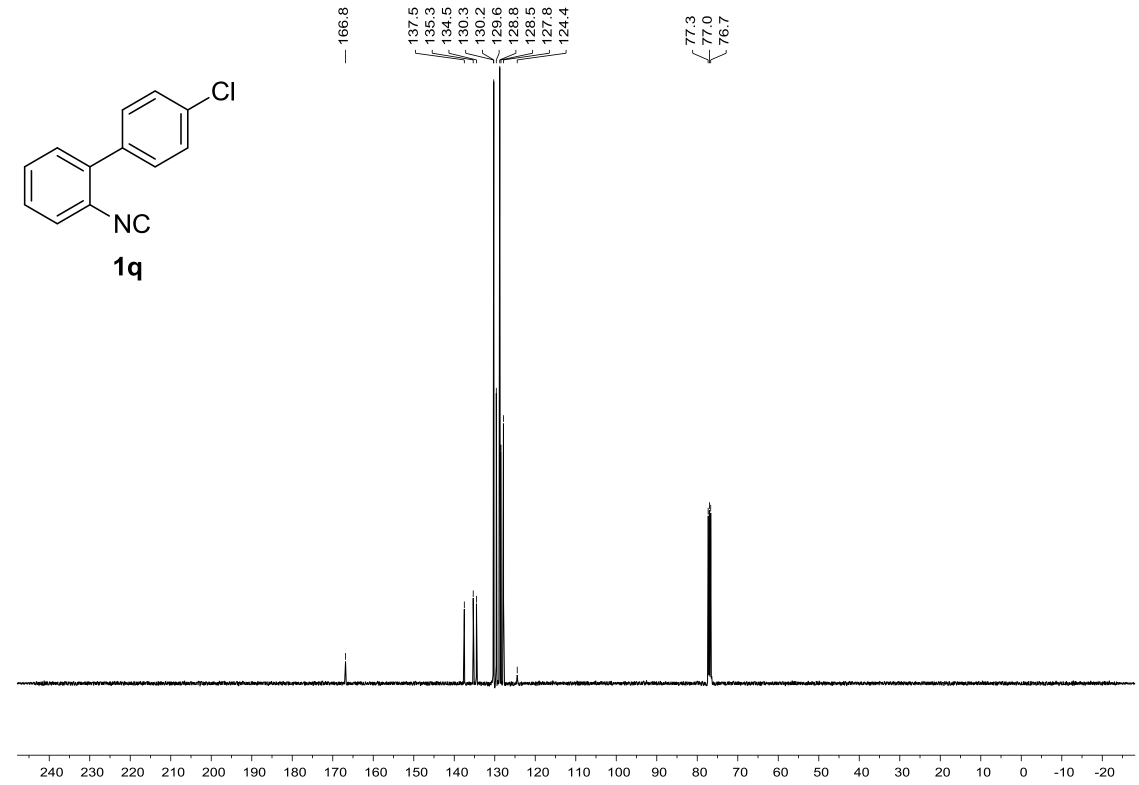




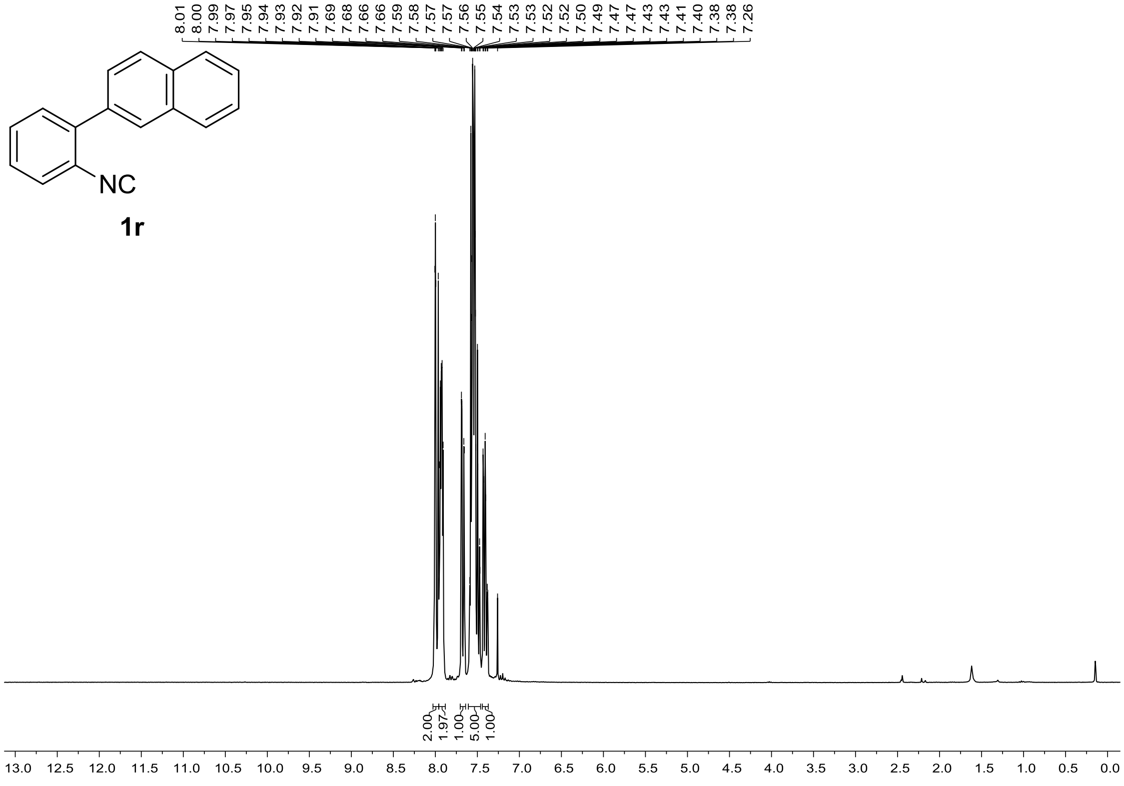


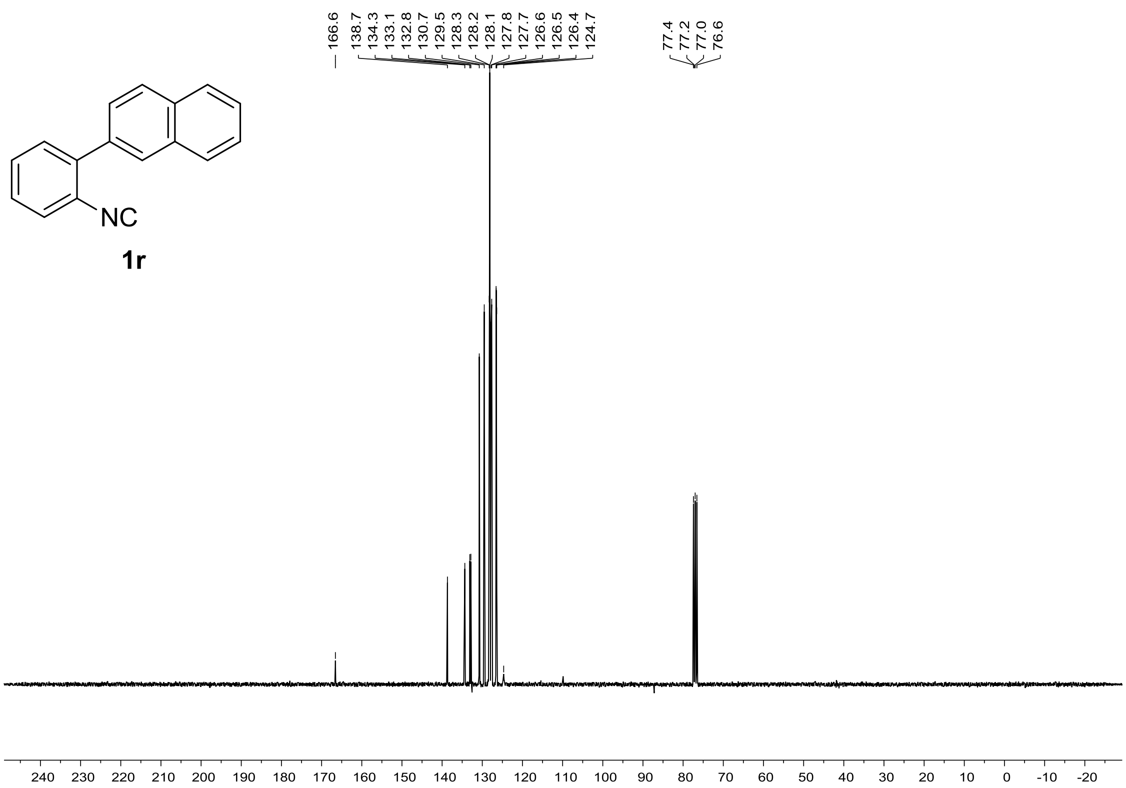
4'-Chloro-2-isocyano-1,1'-biphenyl (1q)





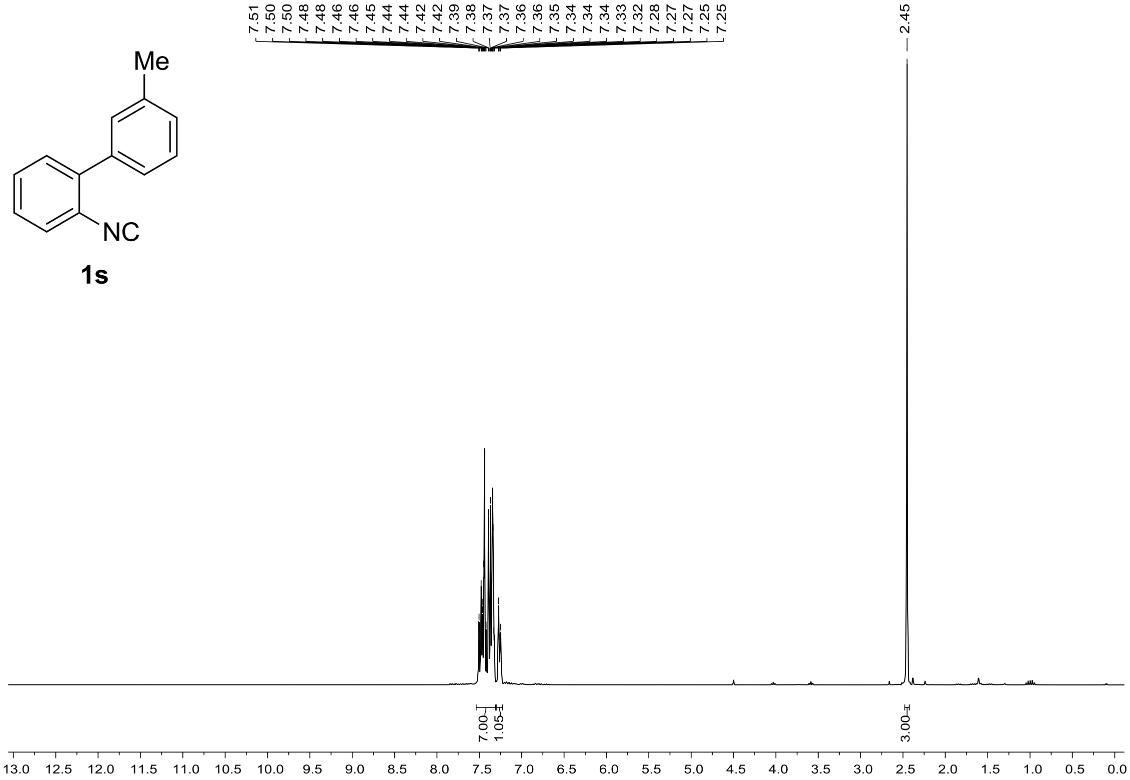
2-(2-Isocyanophenyl)naphthalene (1r)



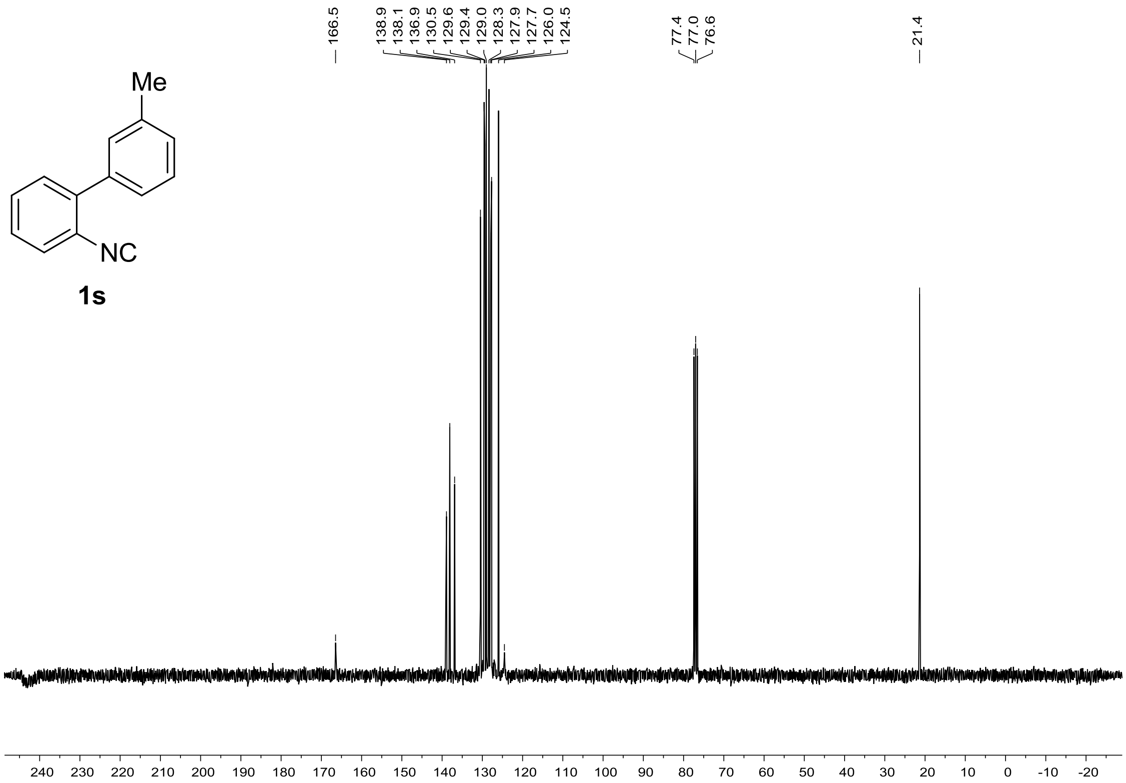


1r

2-Isocyano-3'-methyl-1,1'-biphenyl (1s)

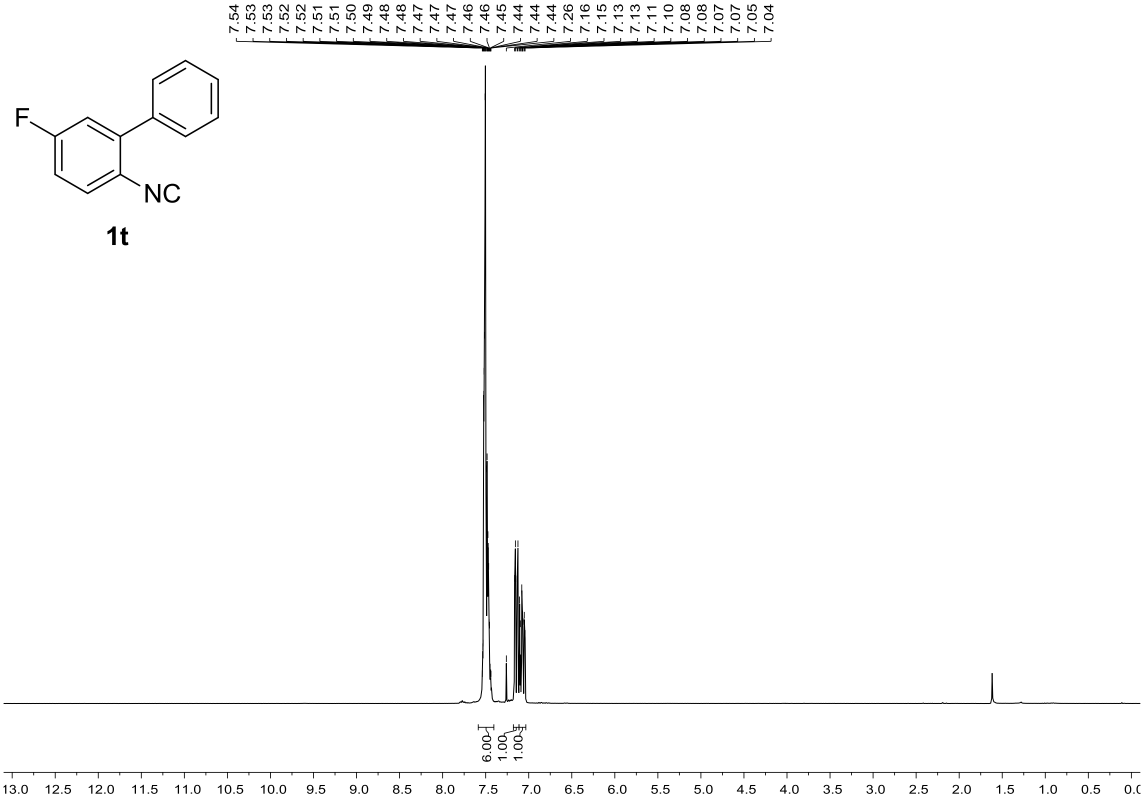


1s



1s

5-Fluoro-2-isocyano-1,1'-biphenyl (1t)



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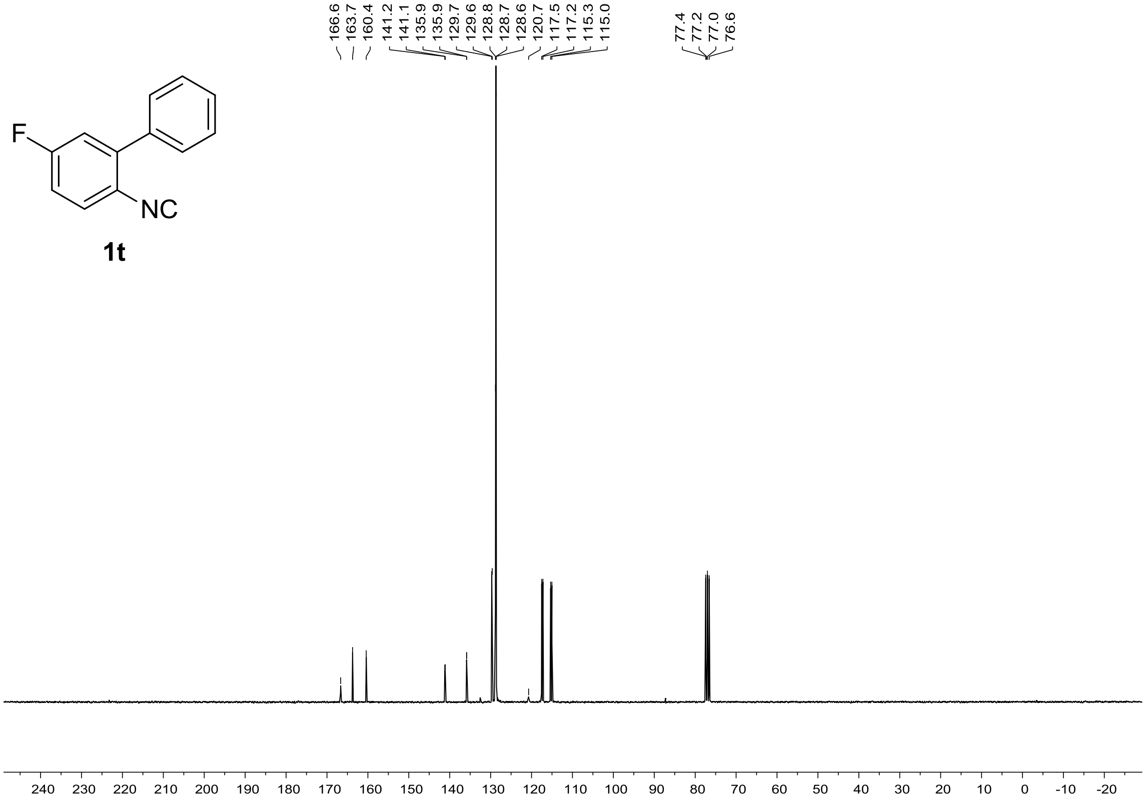
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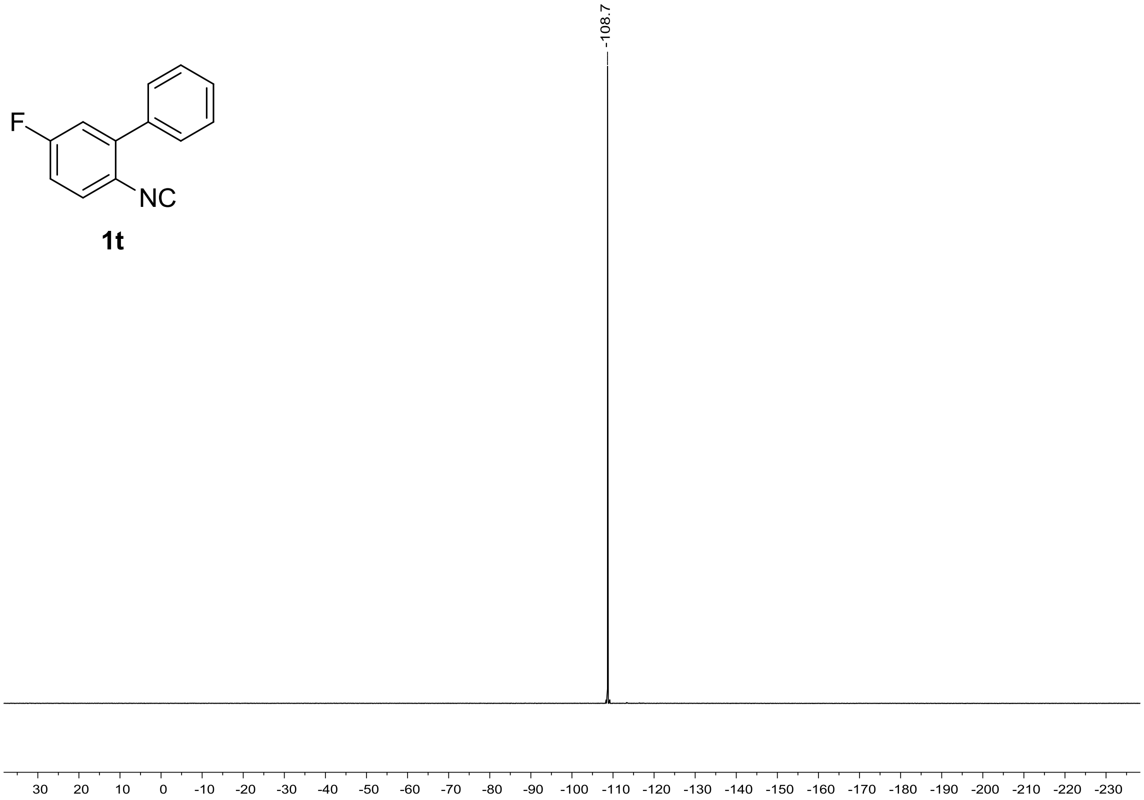
1t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-150
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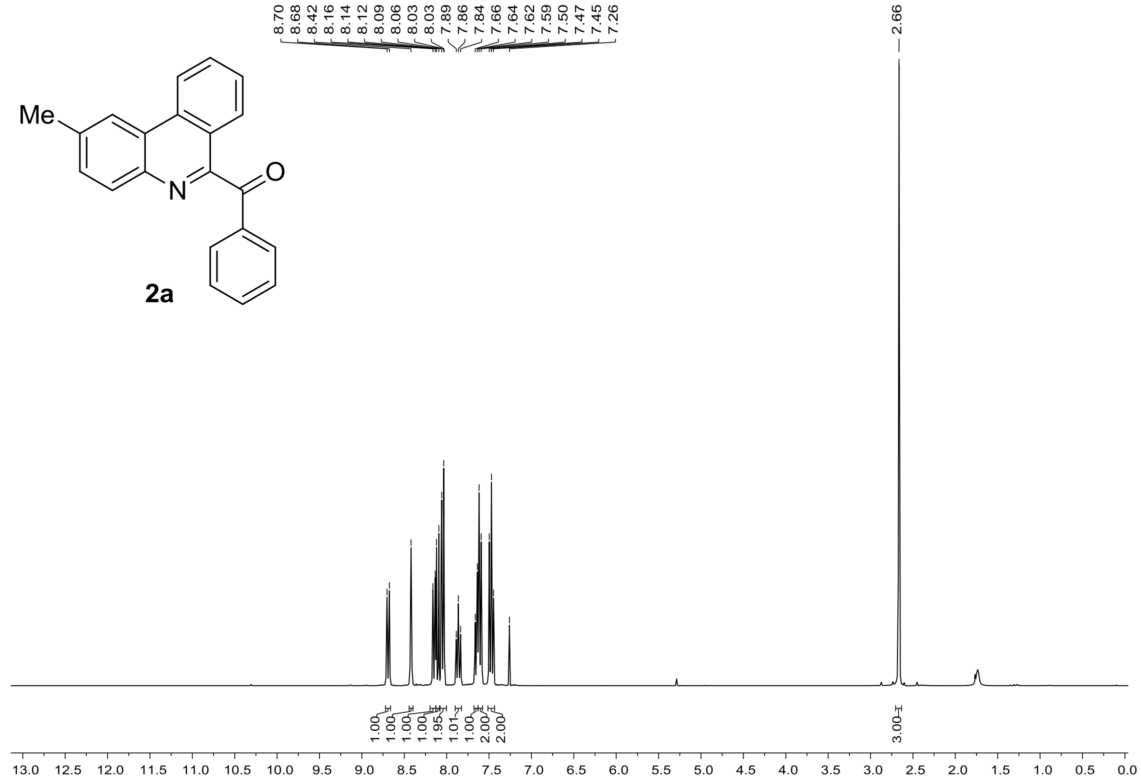
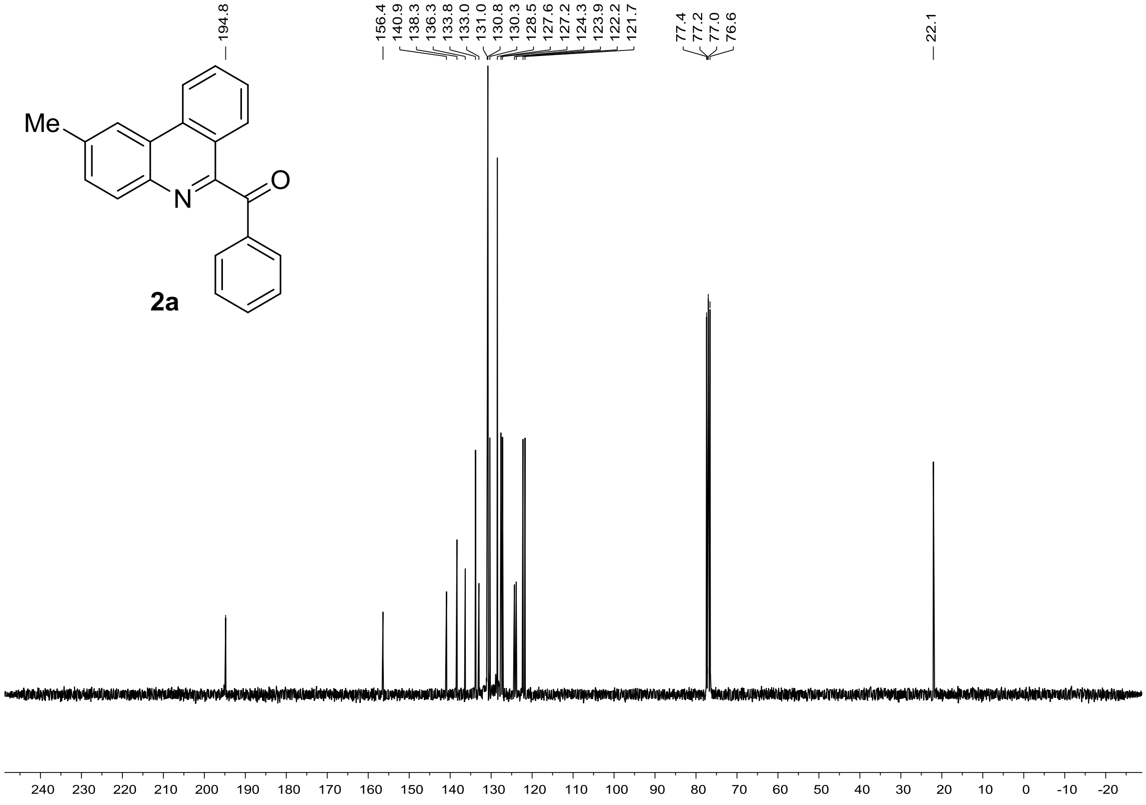
-230

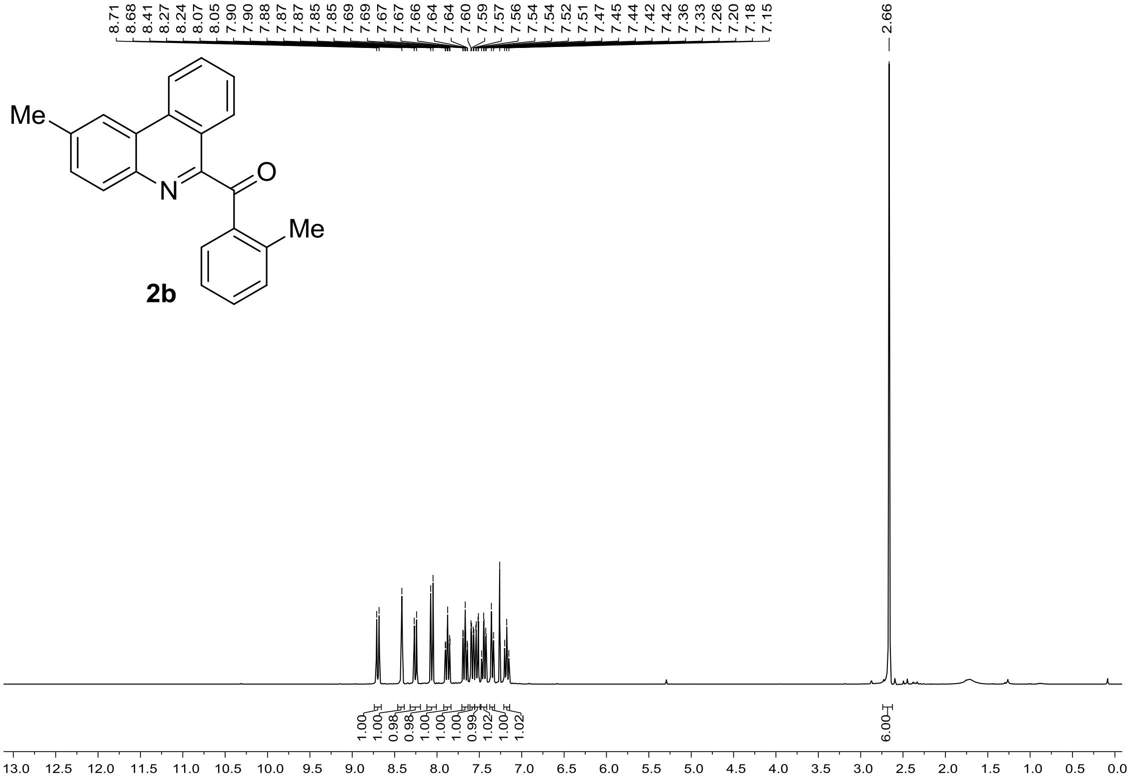
1t

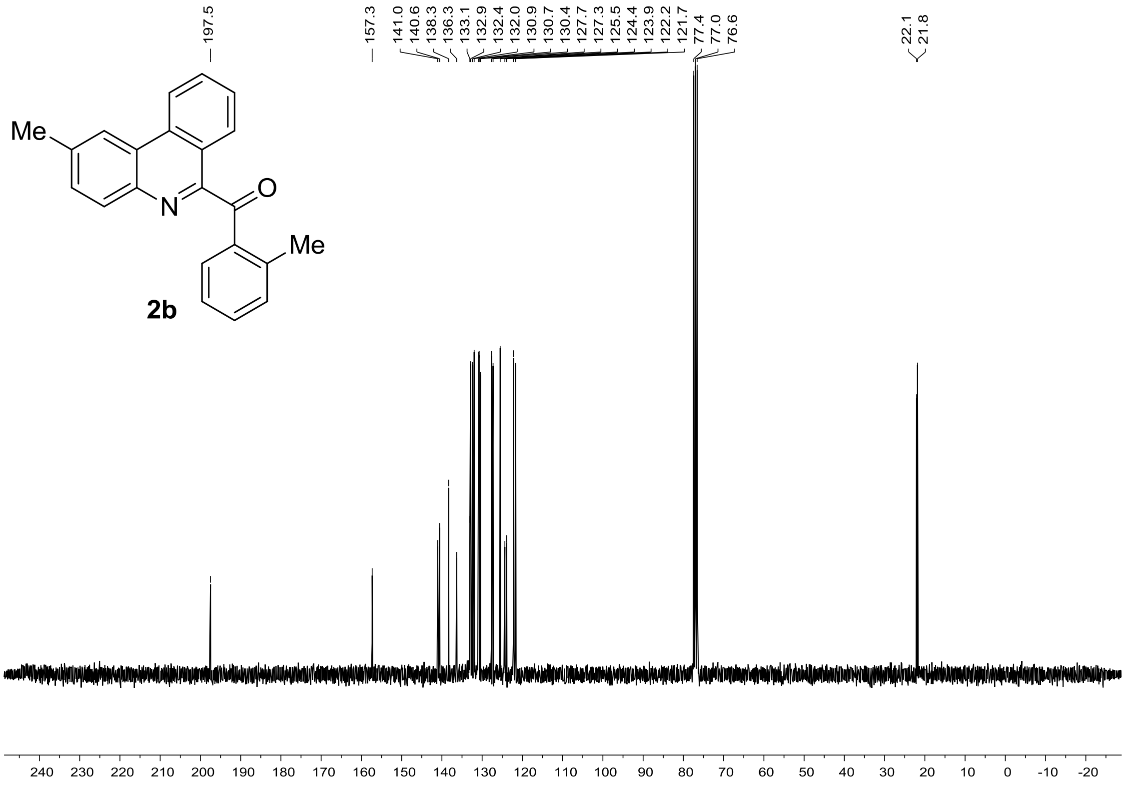
(2-Methylphenanthridin-6-yl)(phenyl)methanone (2a)



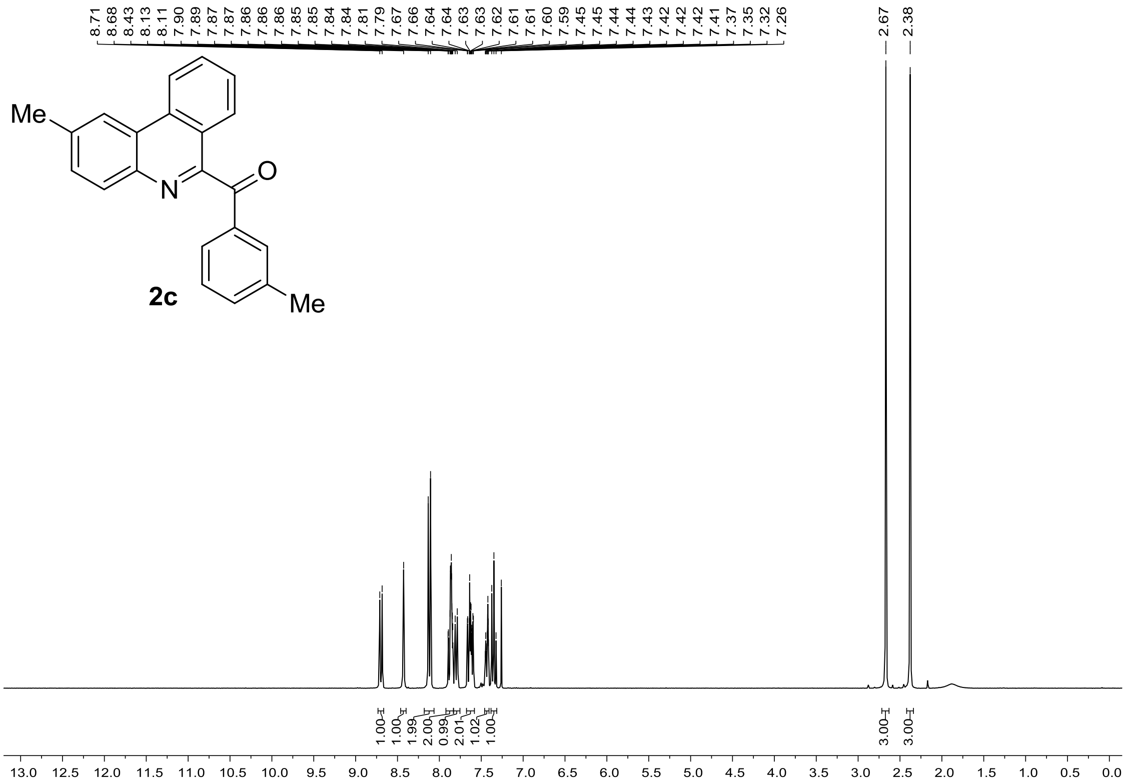


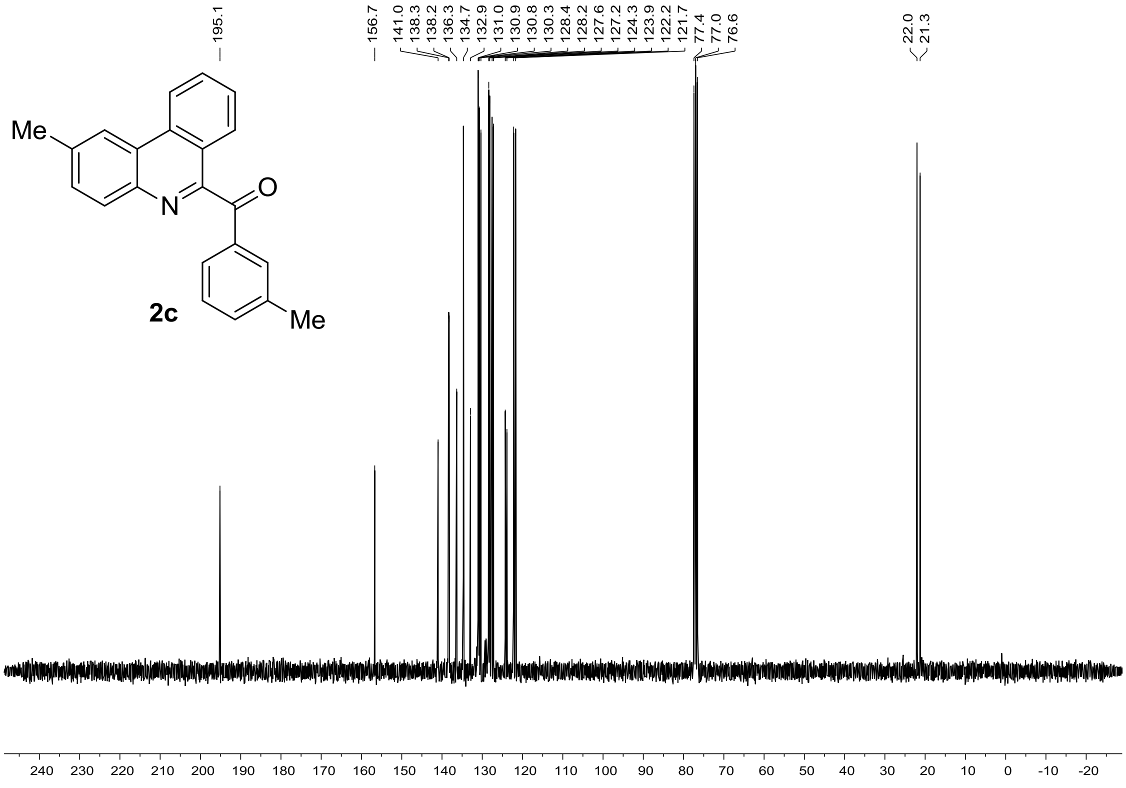
(2-Methylphenanthridin-6-yl)(o-tolyl)methanone (2b)



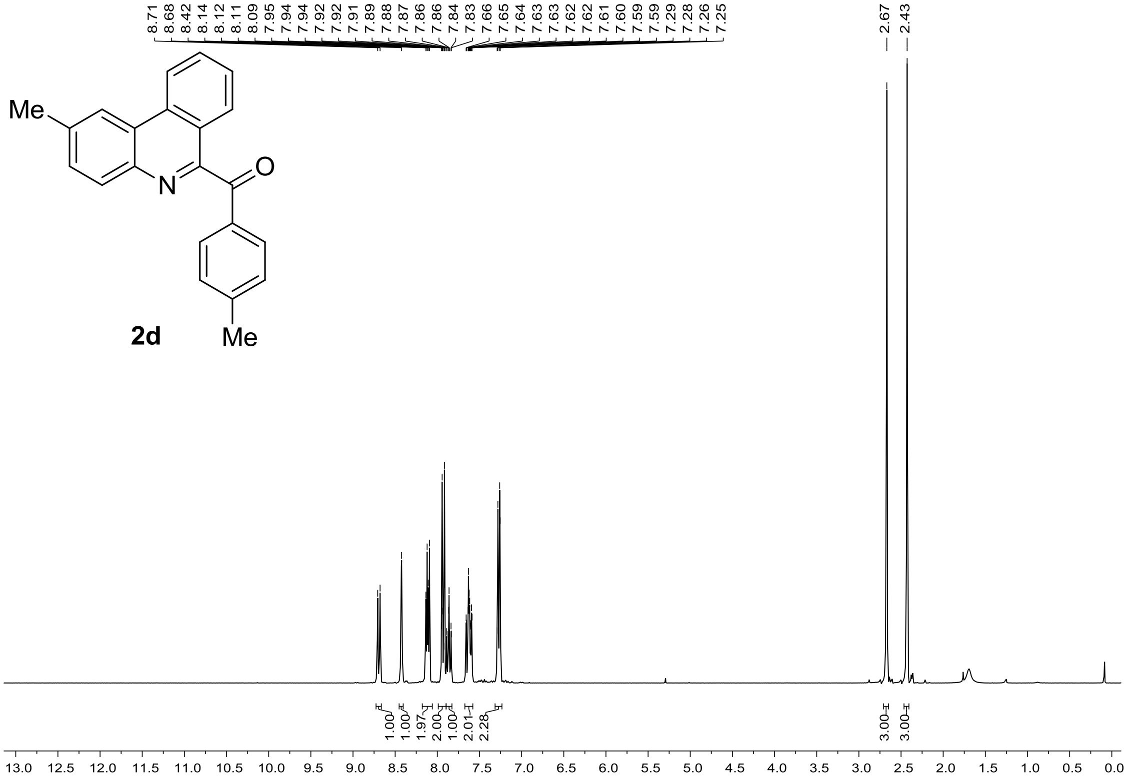


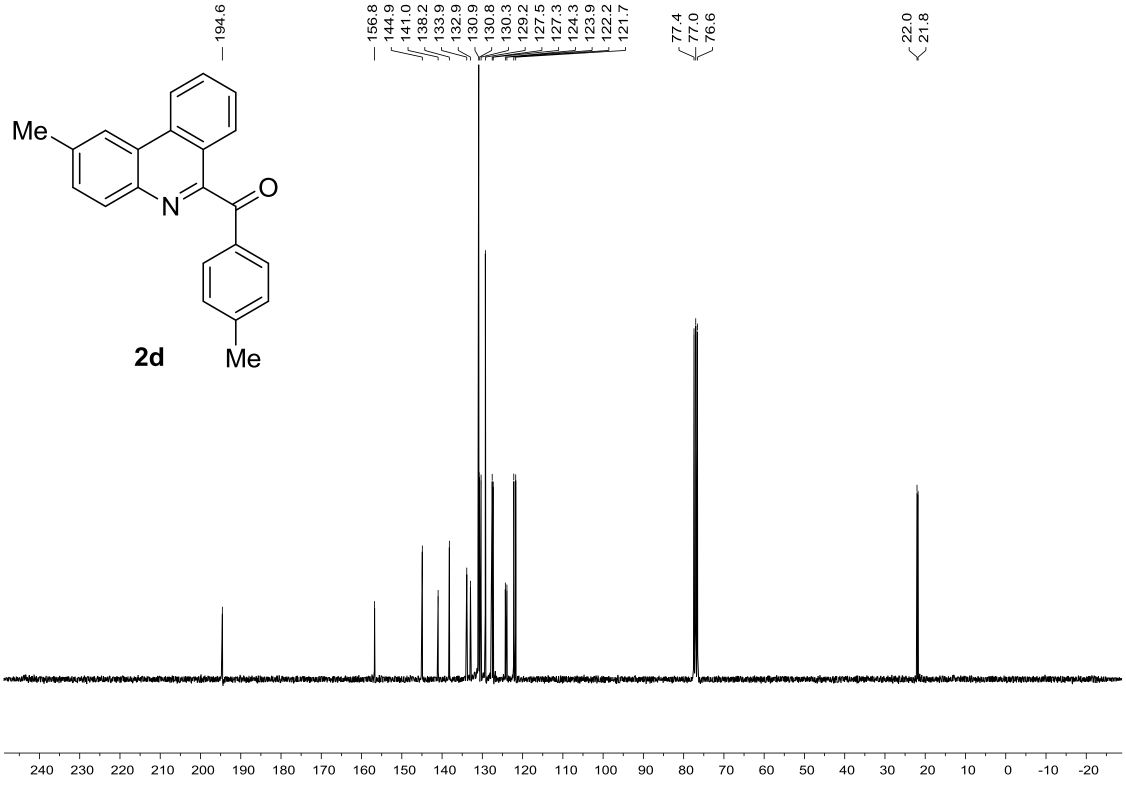
(2-Methylphenanthridin-6-yl)(m-tolyl)methanone (2c)



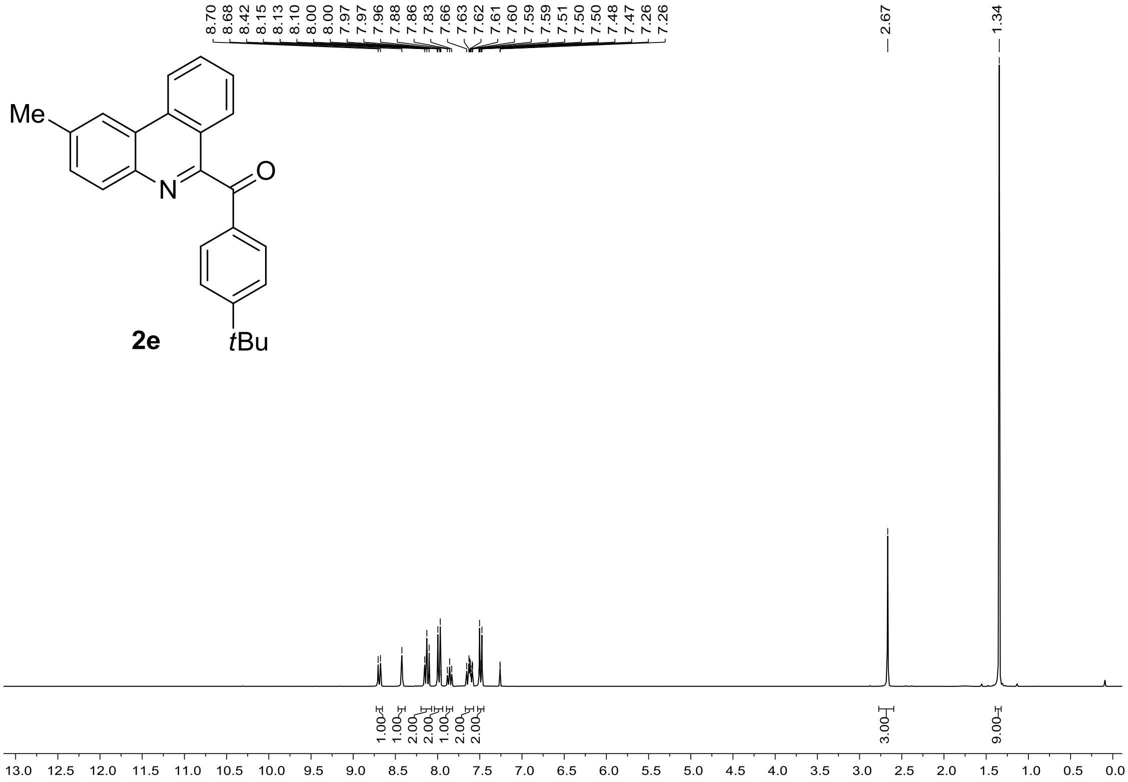


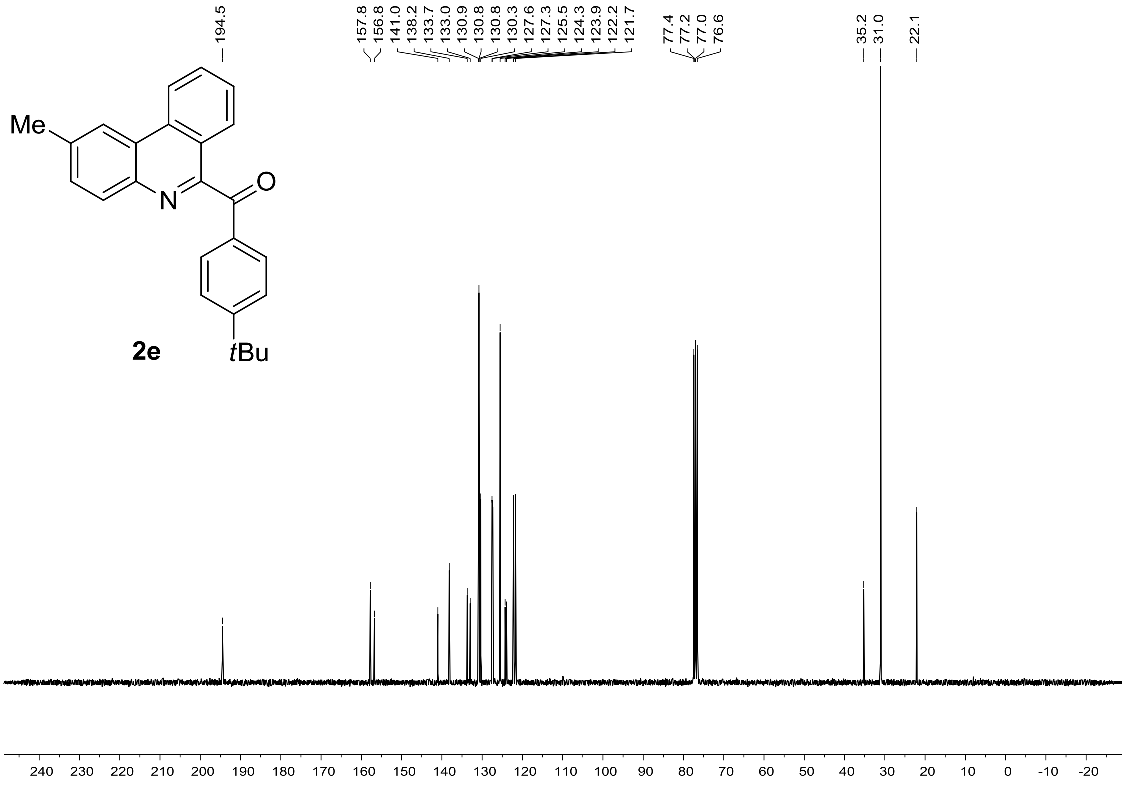
(2-Methylphenanthridin-6-yl)(*p*-tolyl)methanone (2d)



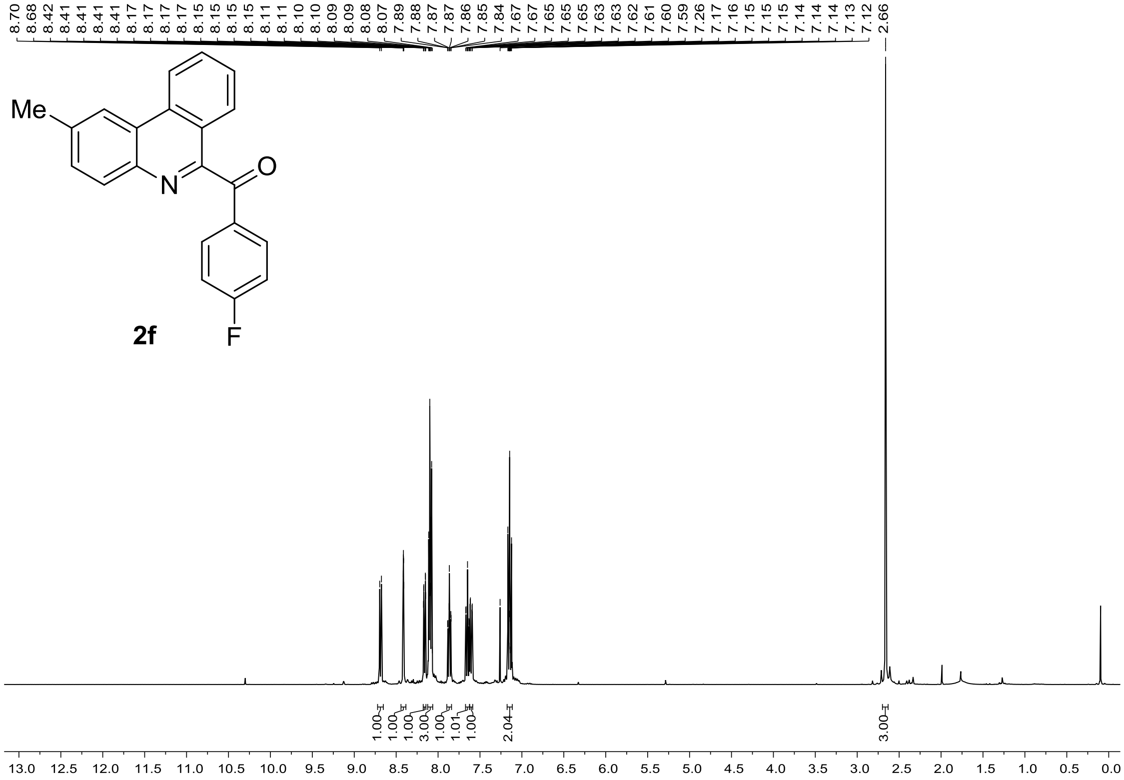


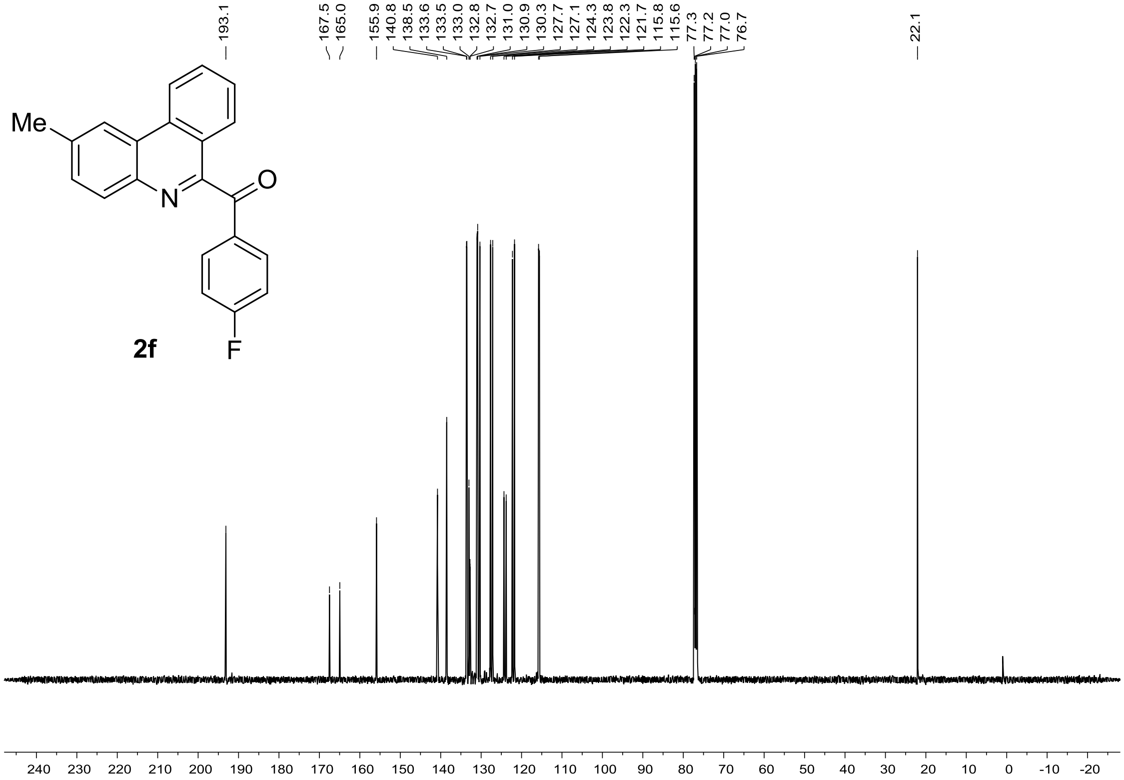
(4-(*tert*-Butyl)phenyl)(2-methylphenanthridin-6-yl)methanone (2e)

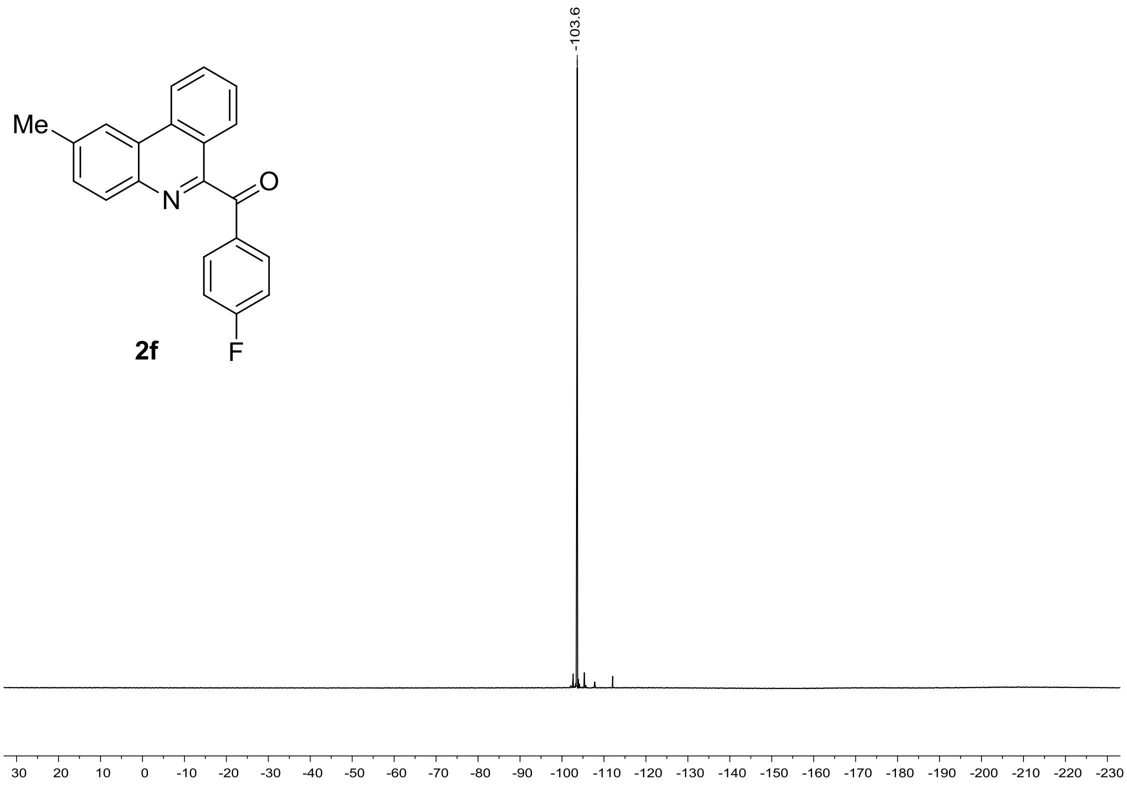




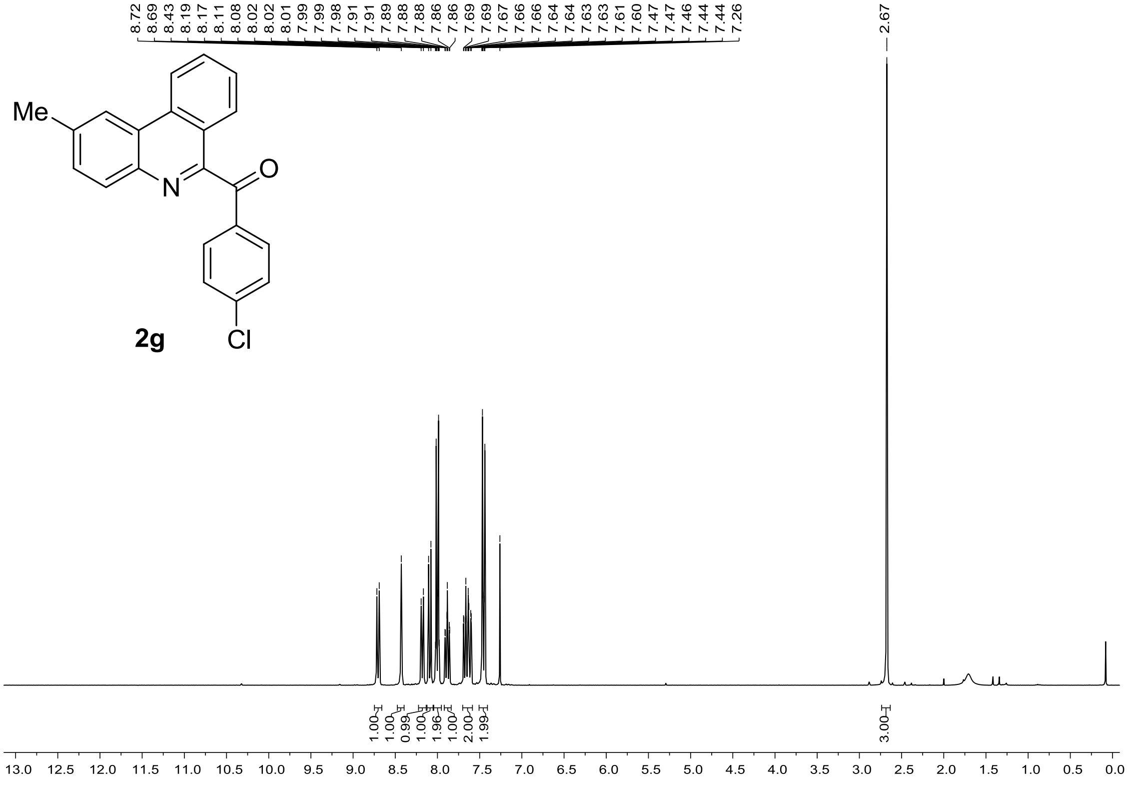
(4-Fluorophenyl)(2-methylphenanthridin-6-yl)methanone (2f)

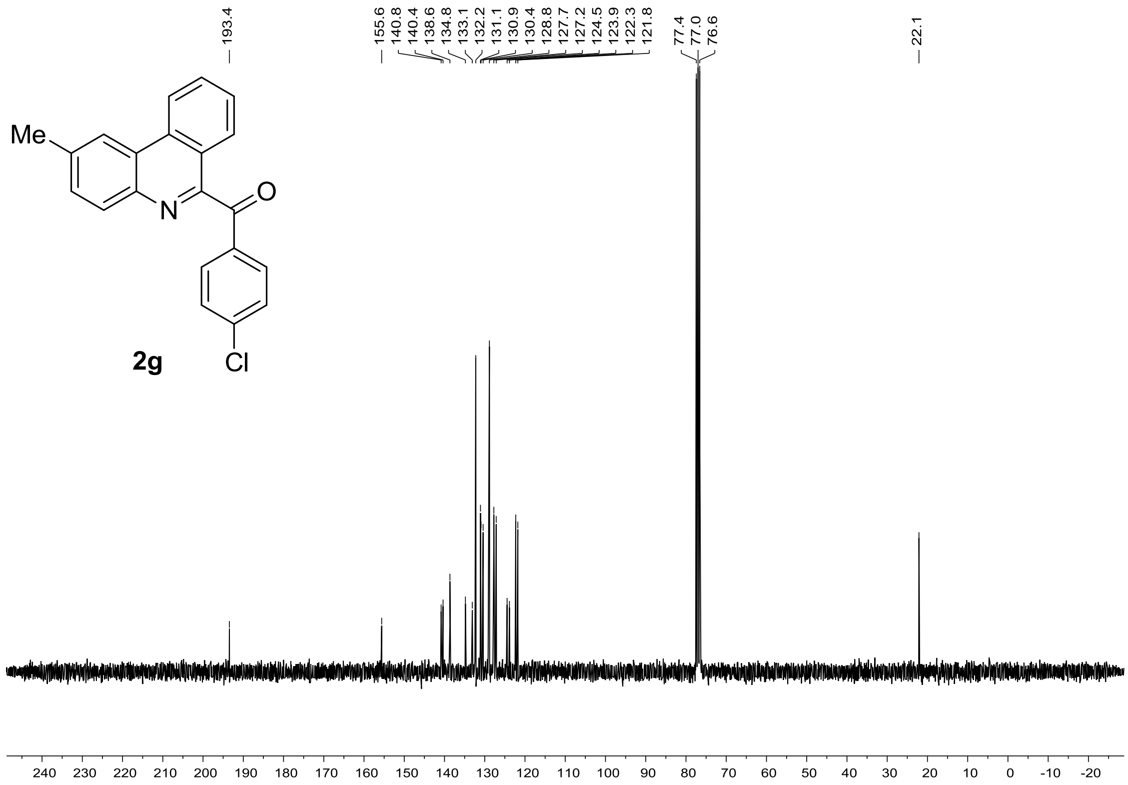




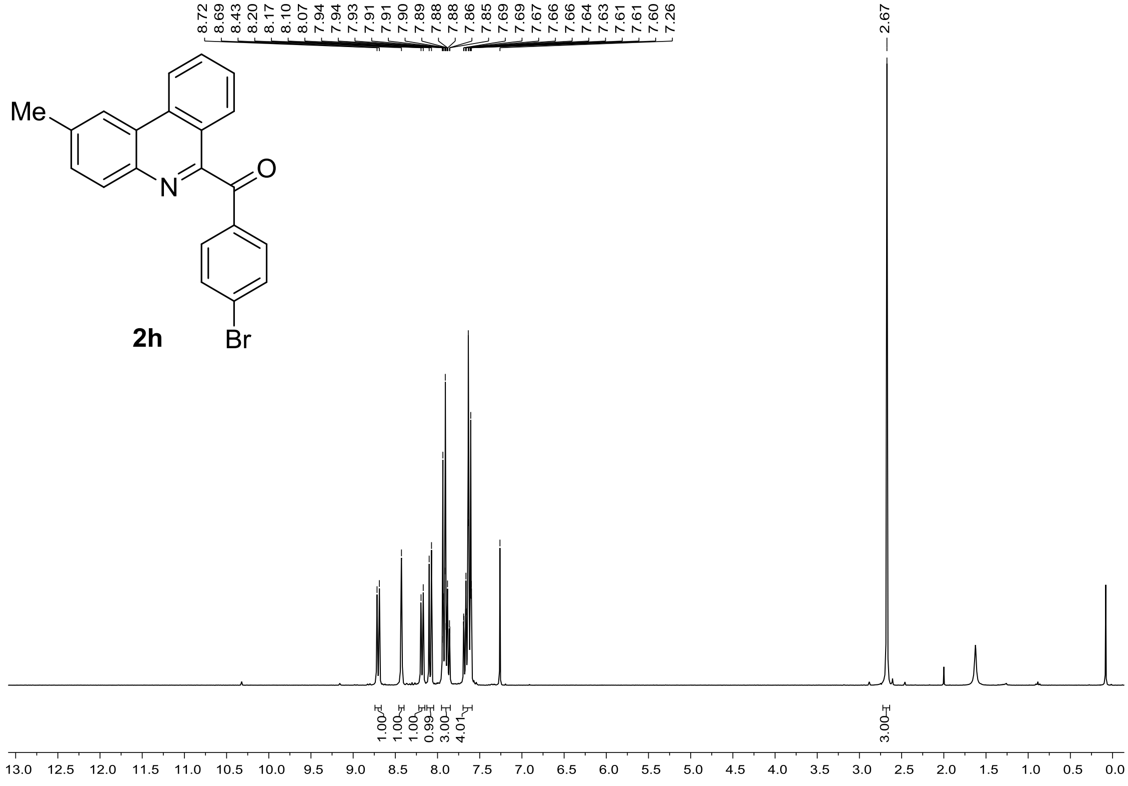


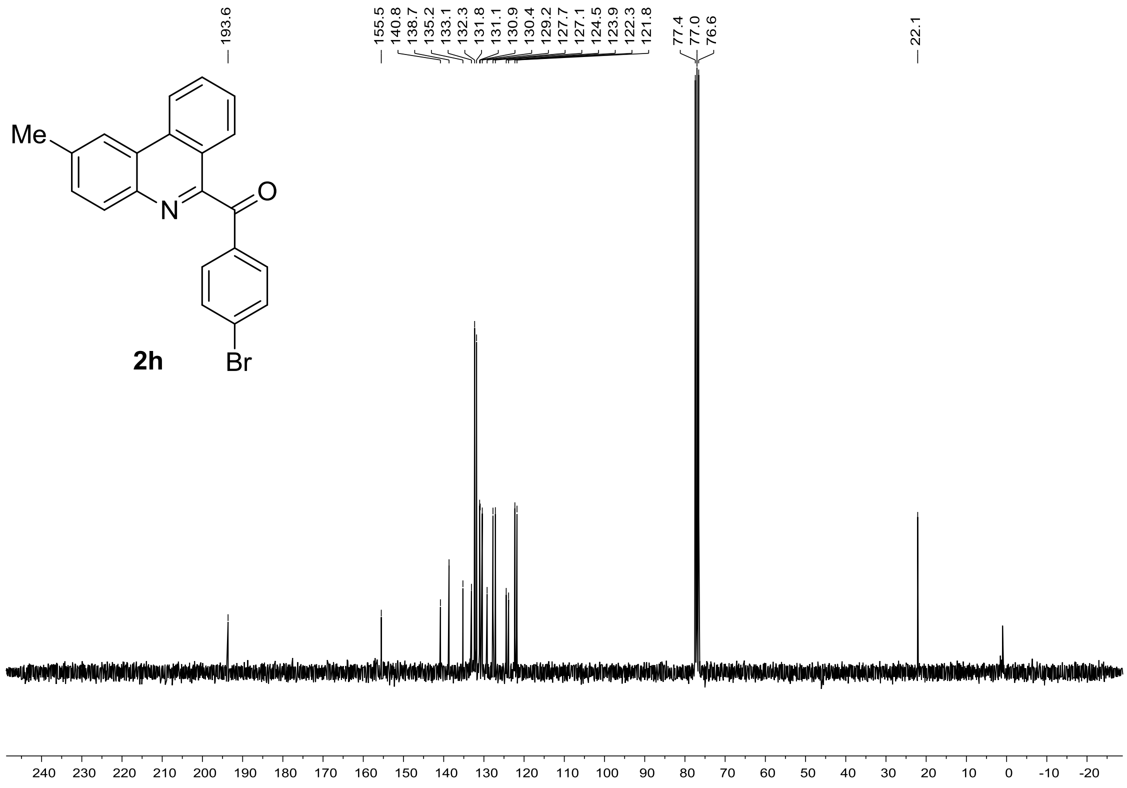
(4-Chlorophenyl)(2-methylphenanthridin-6-yl)methanone (2g)





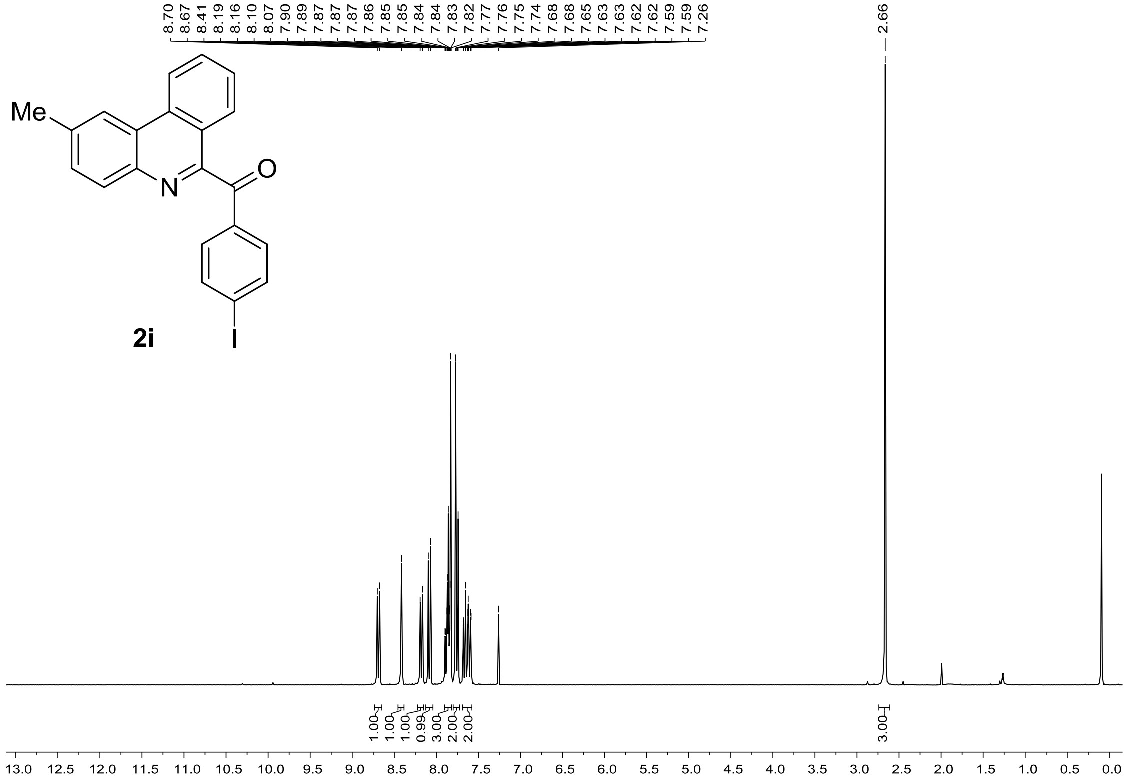
(4-Bromophenyl)(2-methylphenanthridin-6-yl)methanone (2h)



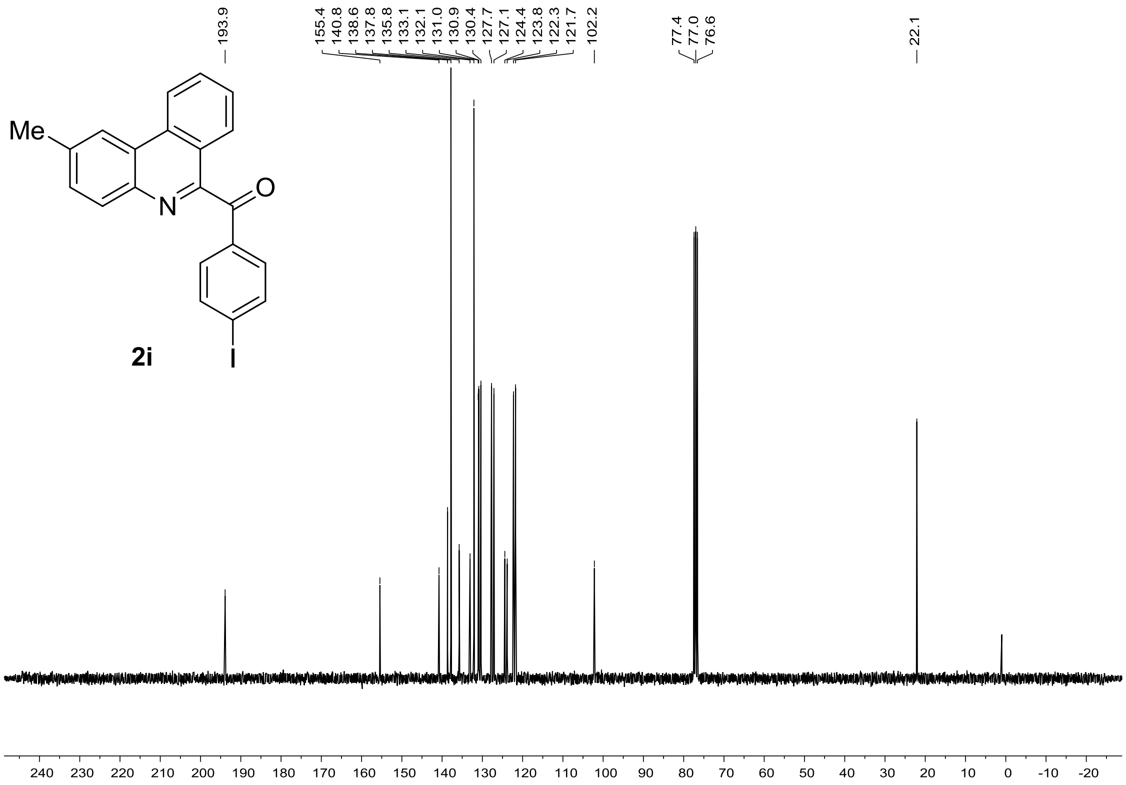


2h

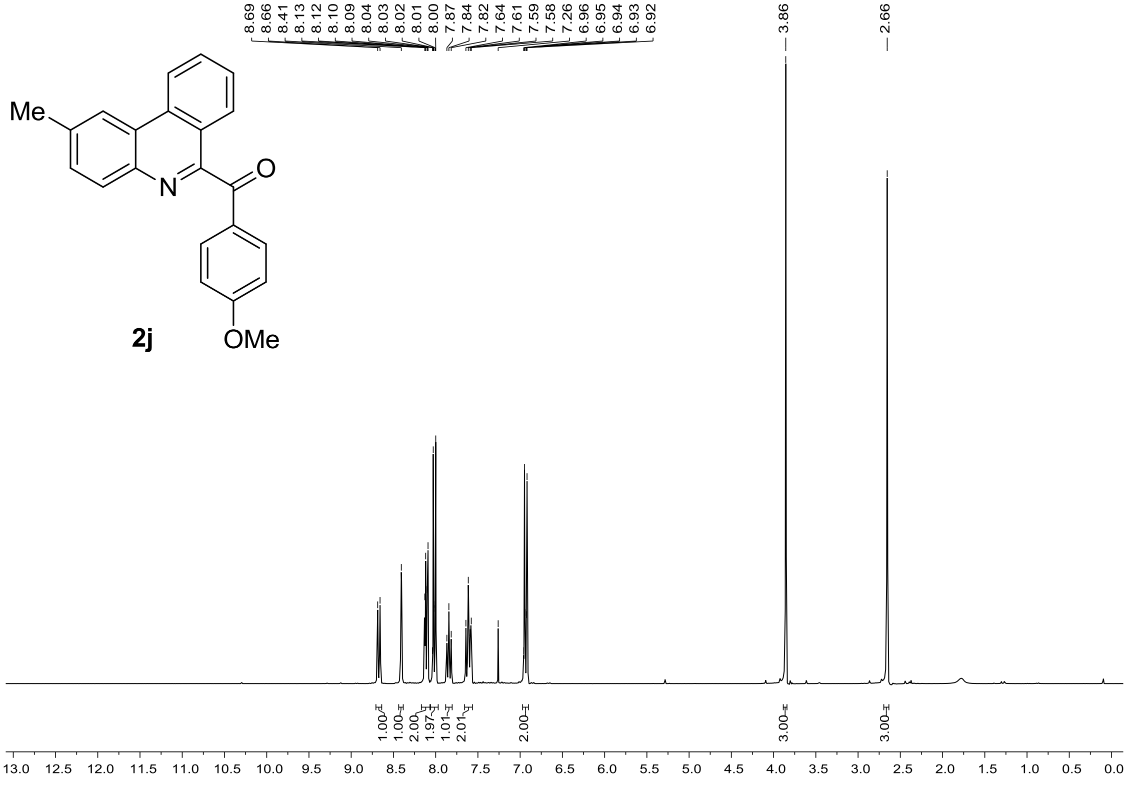
(4-Iodophenyl)(2-methylphenanthridin-6-yl)methanone (2i)

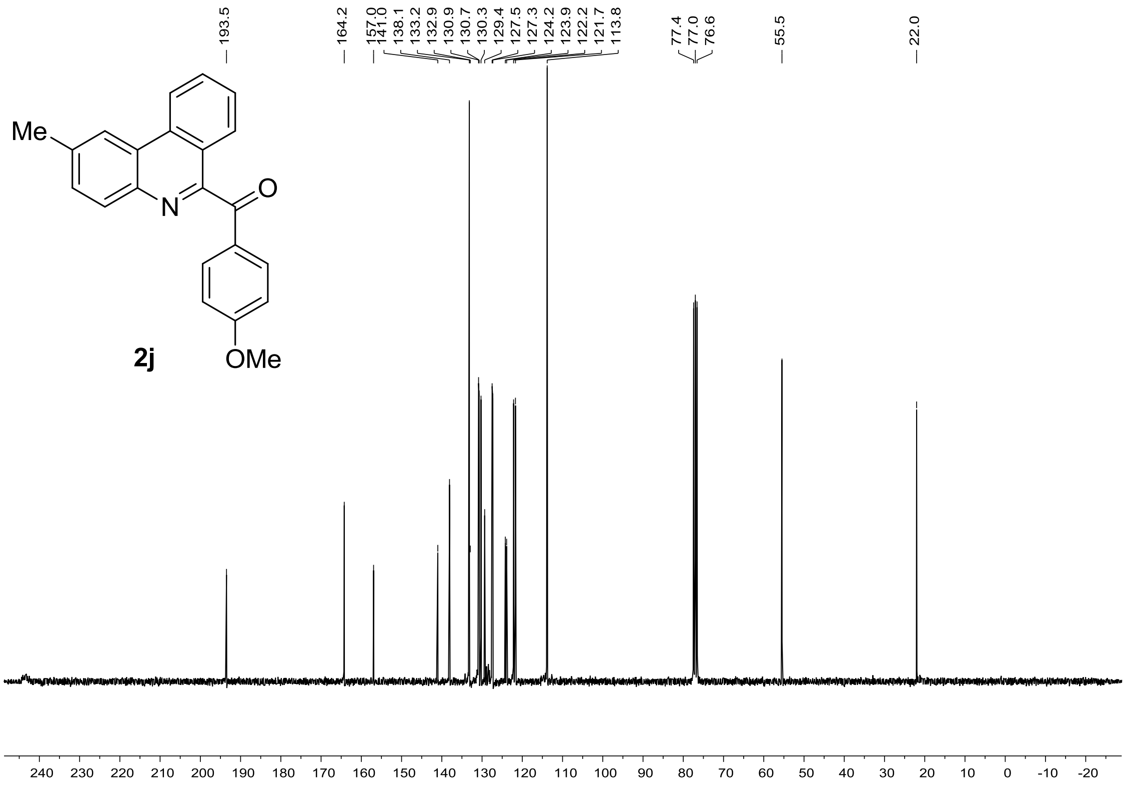


2i



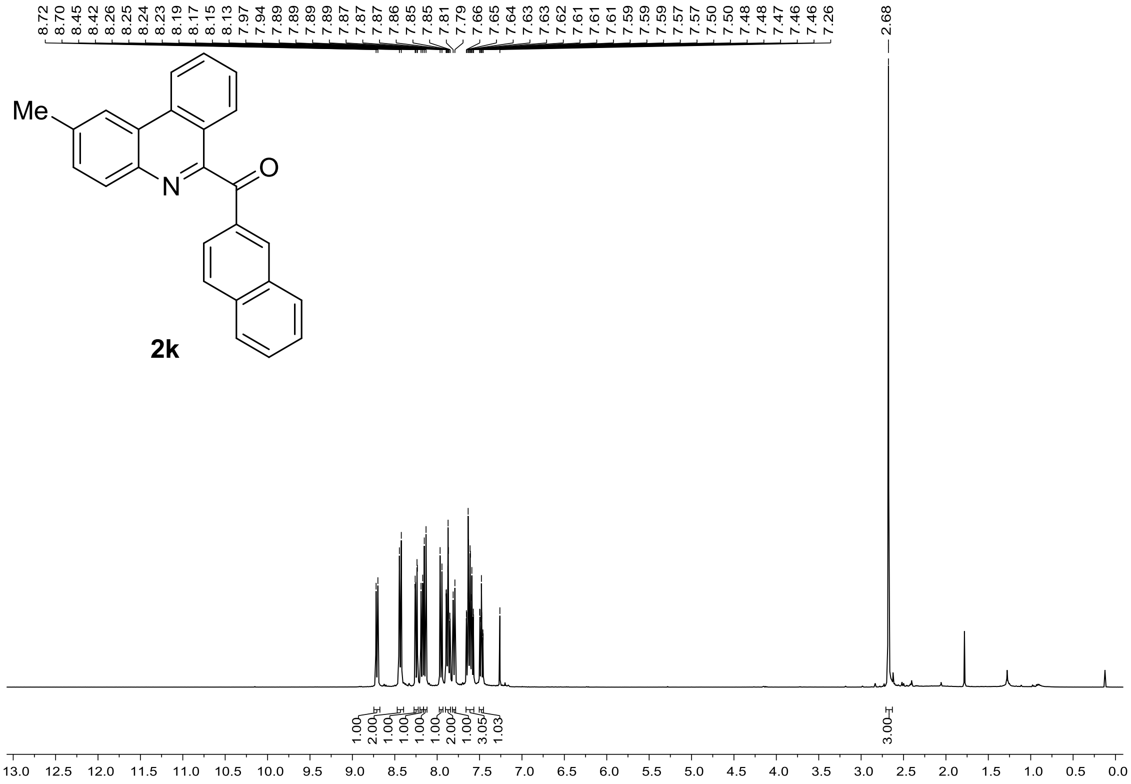
(4-Methoxyphenyl)(2-methylphenanthridin-6-yl)methanone (2j)



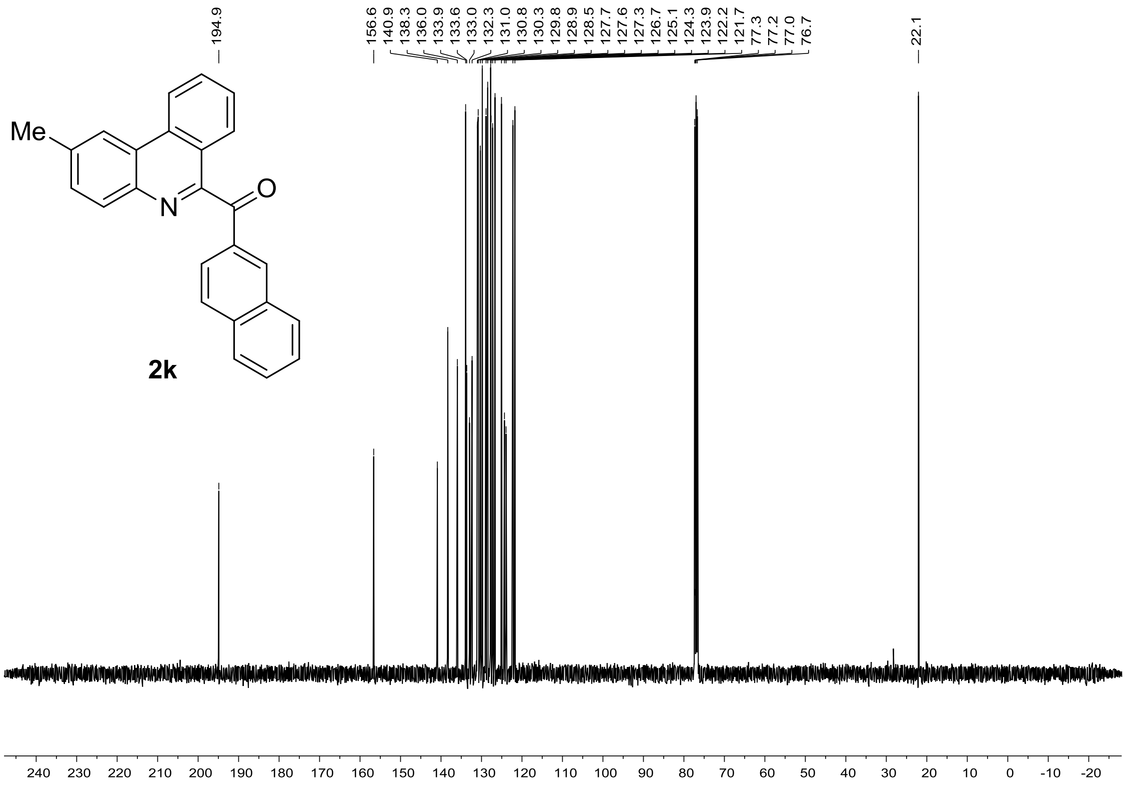


2j

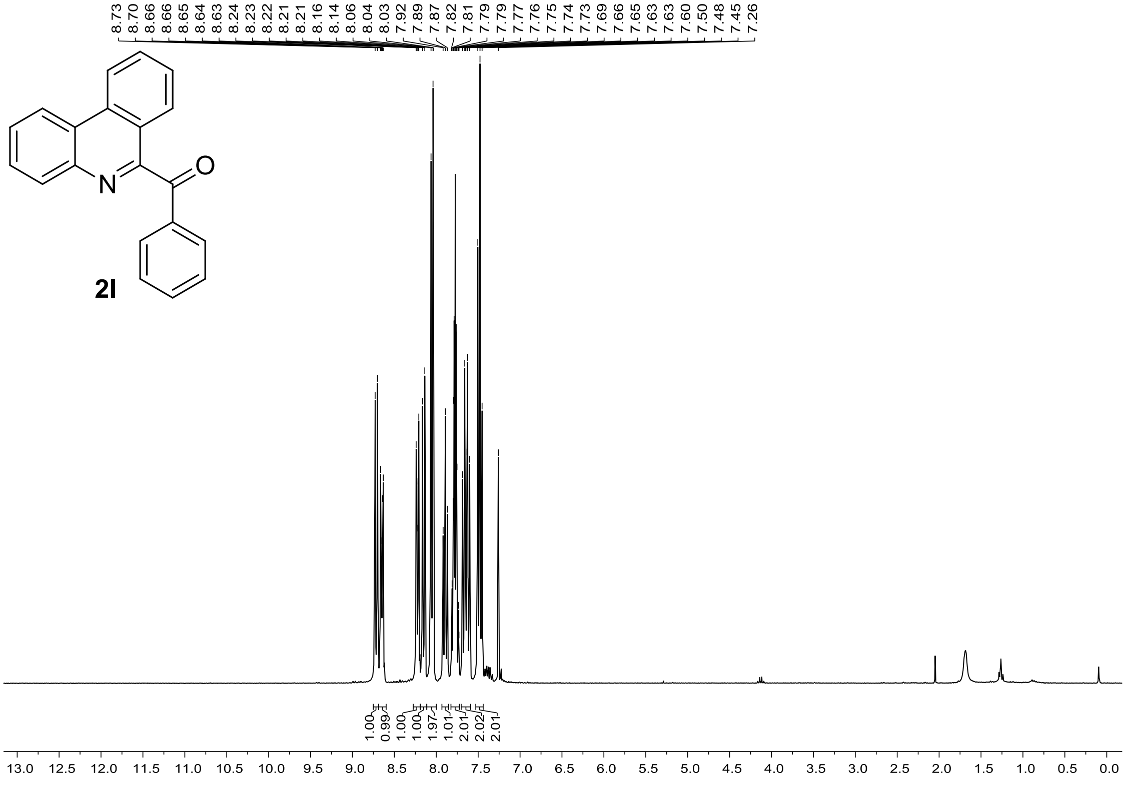
(2-Methylphenanthridin-6-yl)(naphthalen-2-yl)methanone (2k)

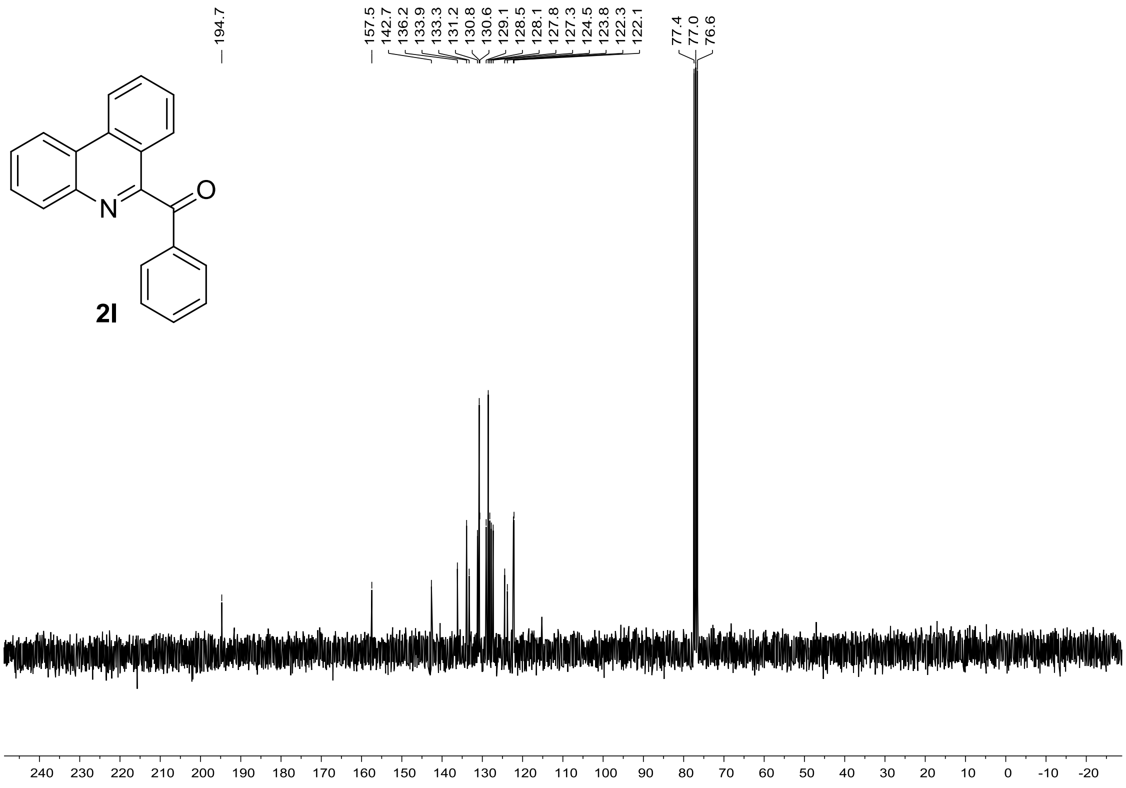


2k

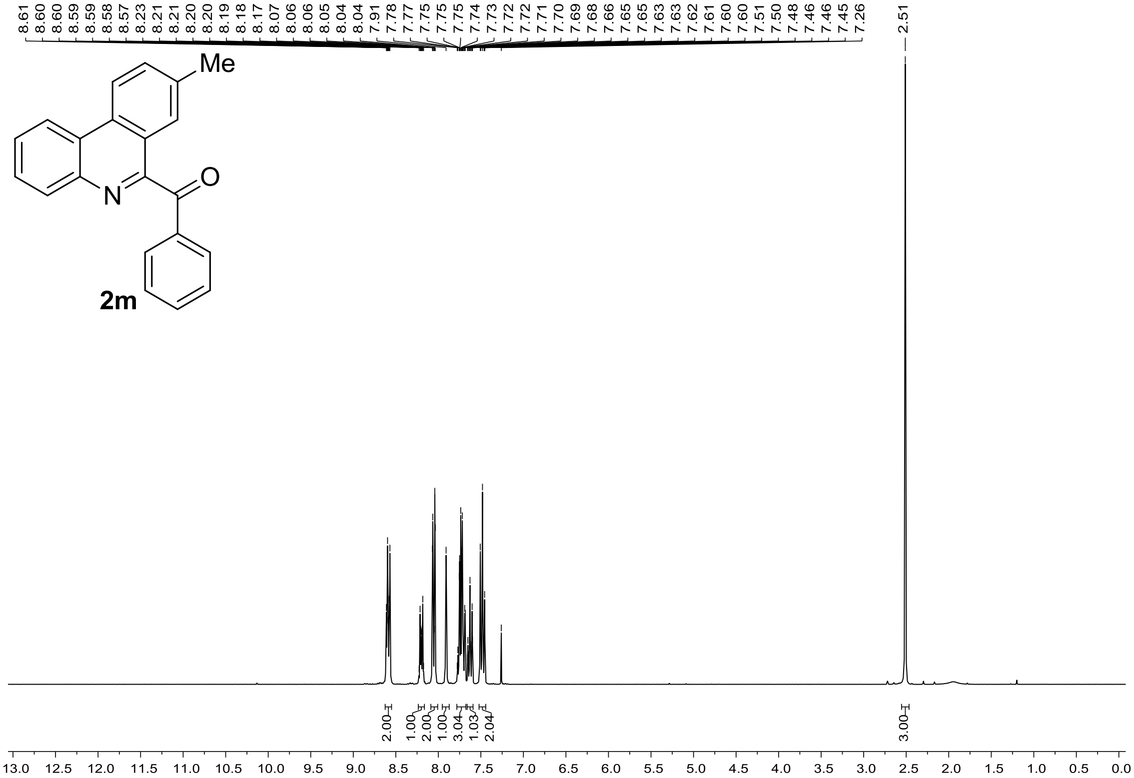


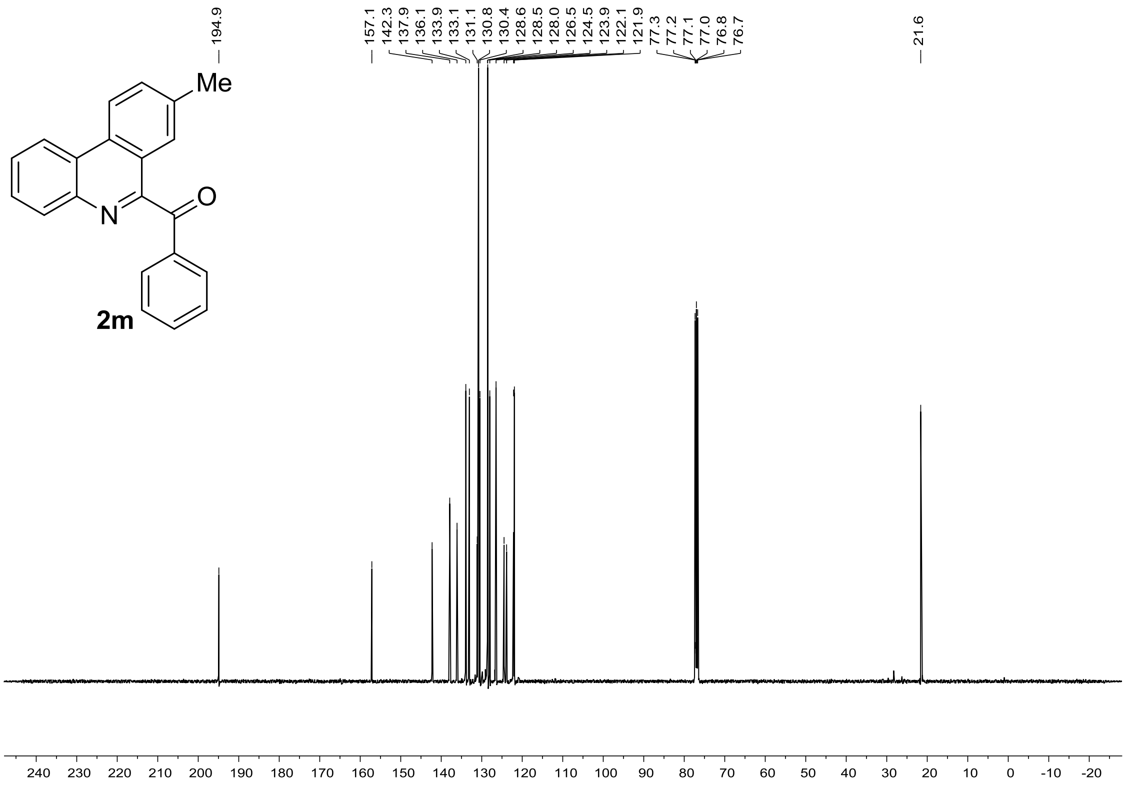
Phenanthridin-6-yl(phenyl)methanone (2l)



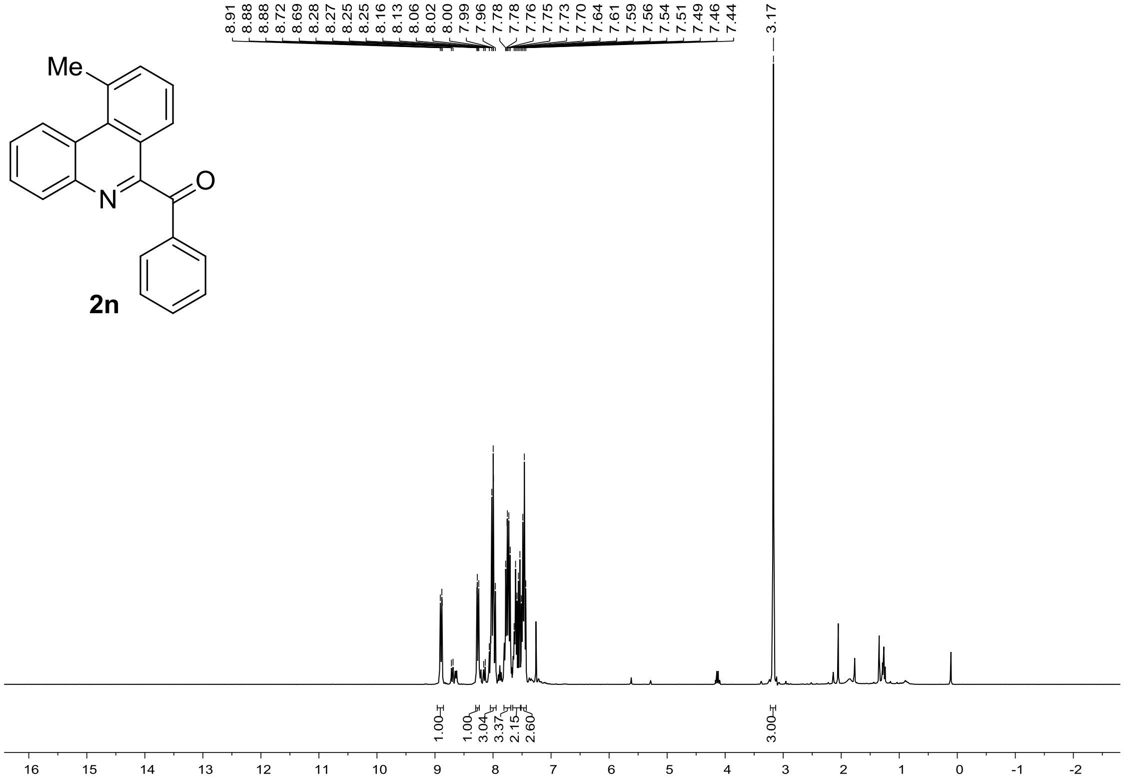


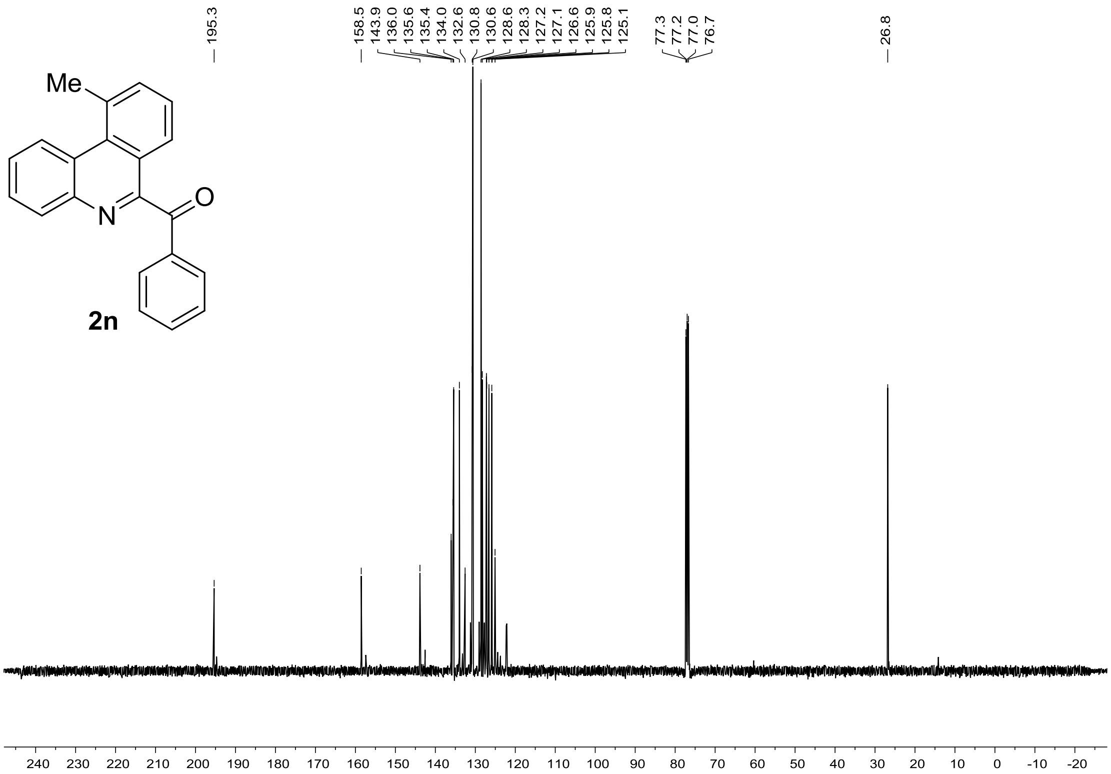
(8-Methylphenanthridin-6-yl)(phenyl)methanone (2m)



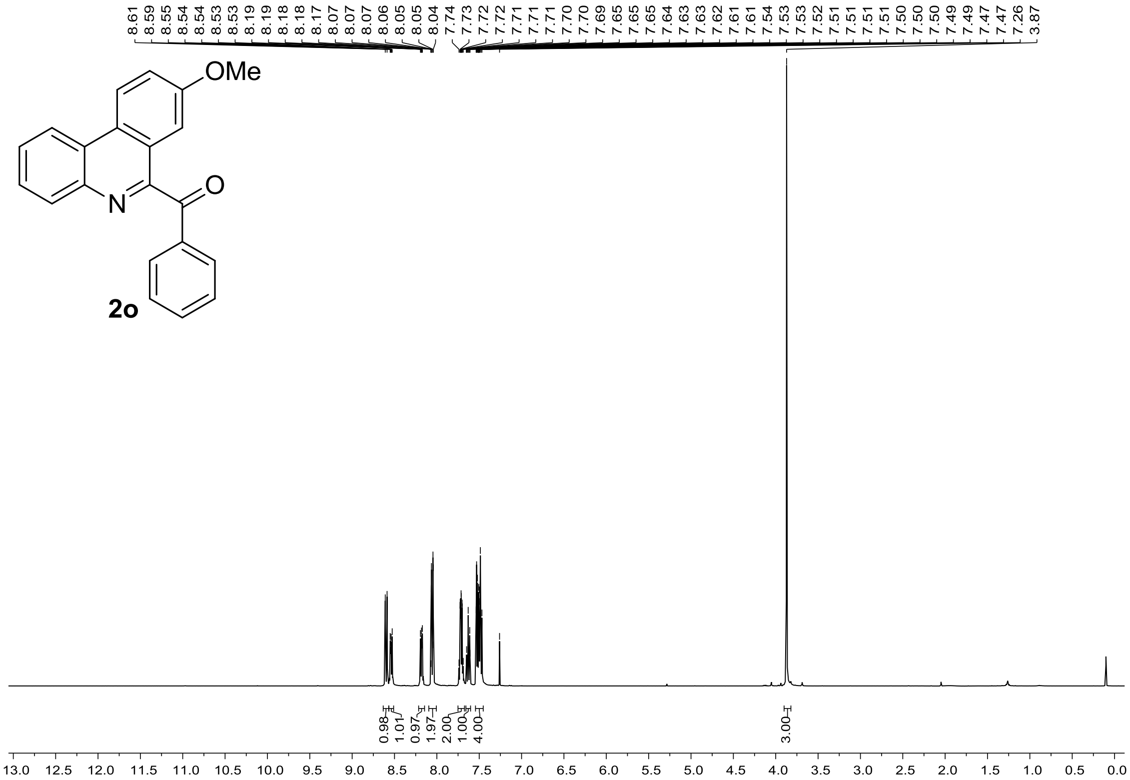


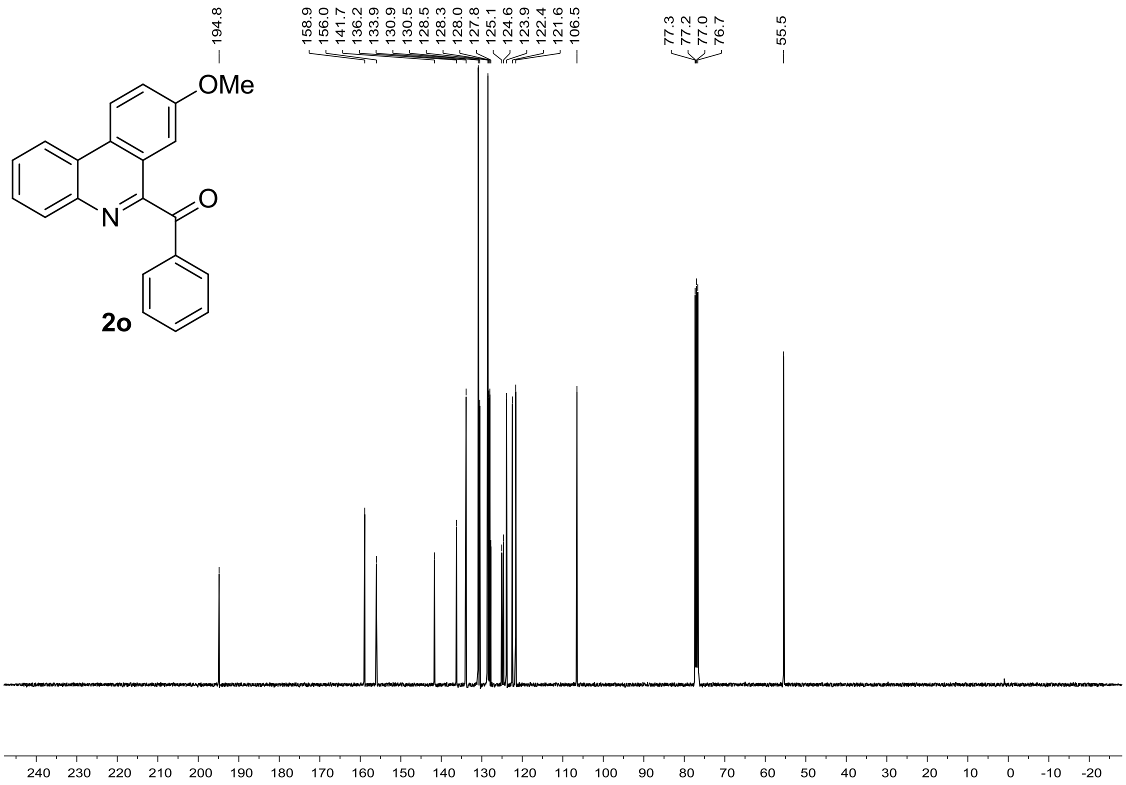
(10-Methylphenanthridin-6-yl)(phenyl)methanone (2n)



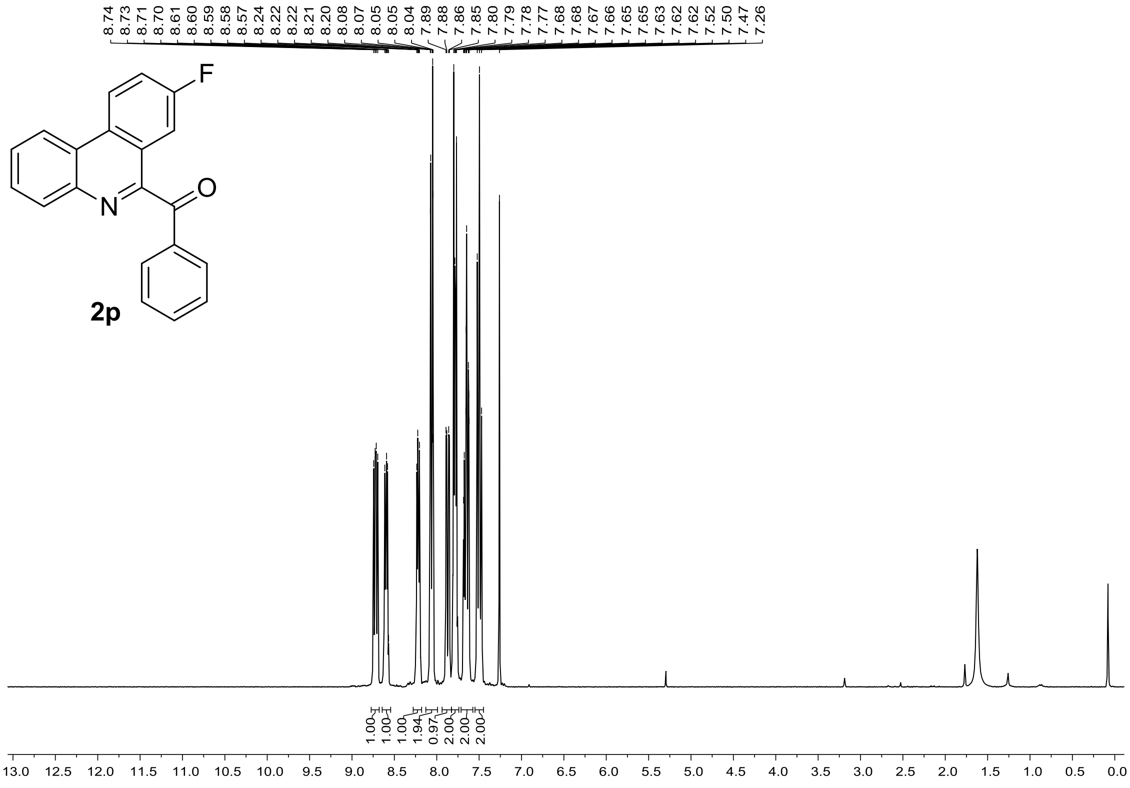


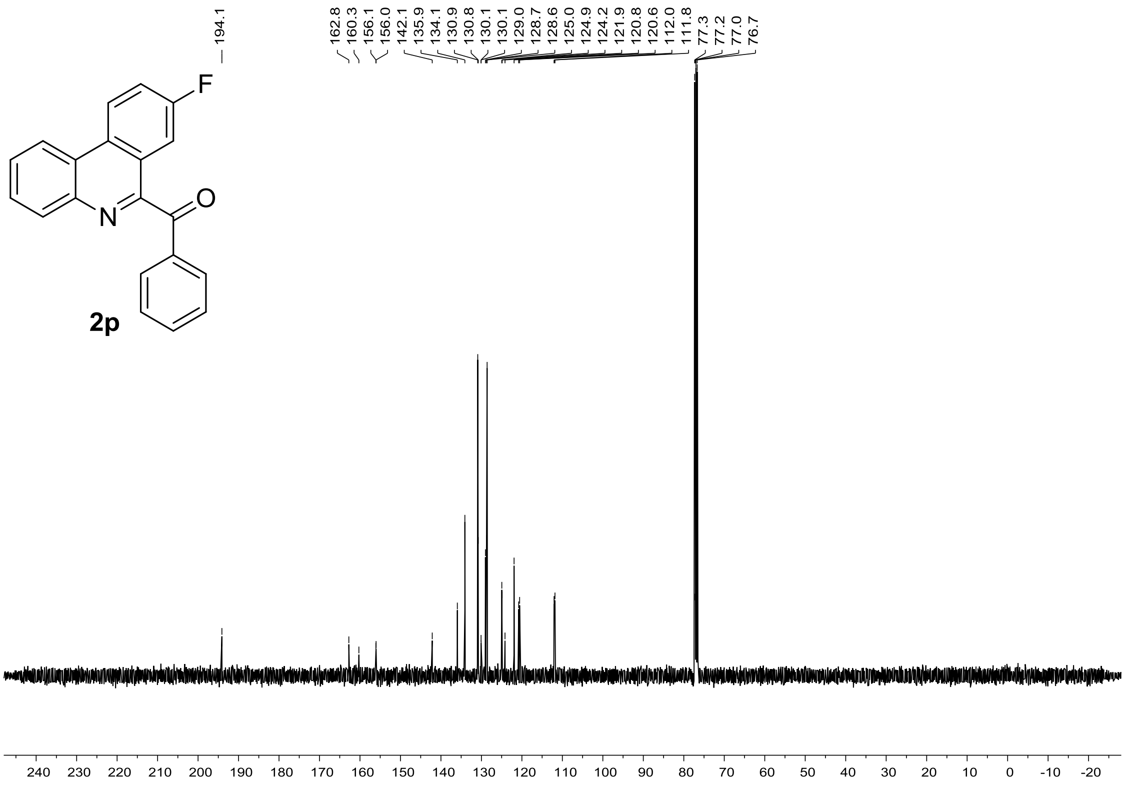
(8-Methoxyphenanthridin-6-yl)(phenyl)methanone (2o)





(8-Fluorophenanthridin-6-yl)(phenyl)methanone (2p)

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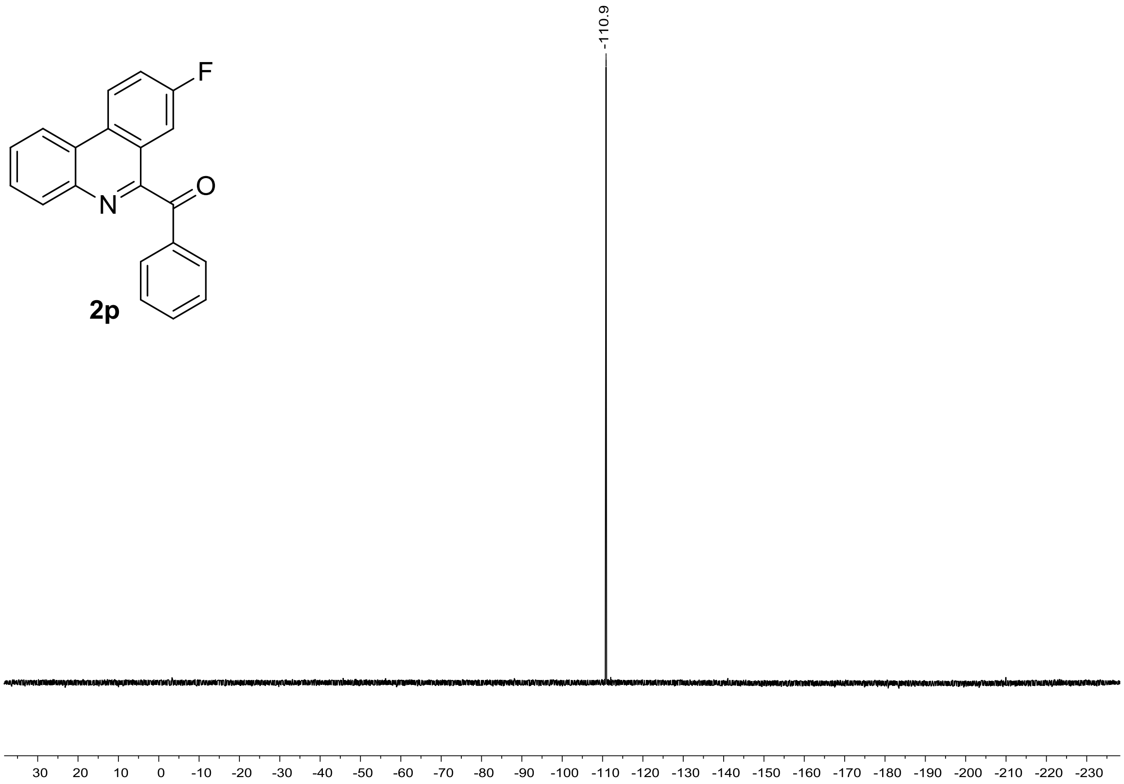
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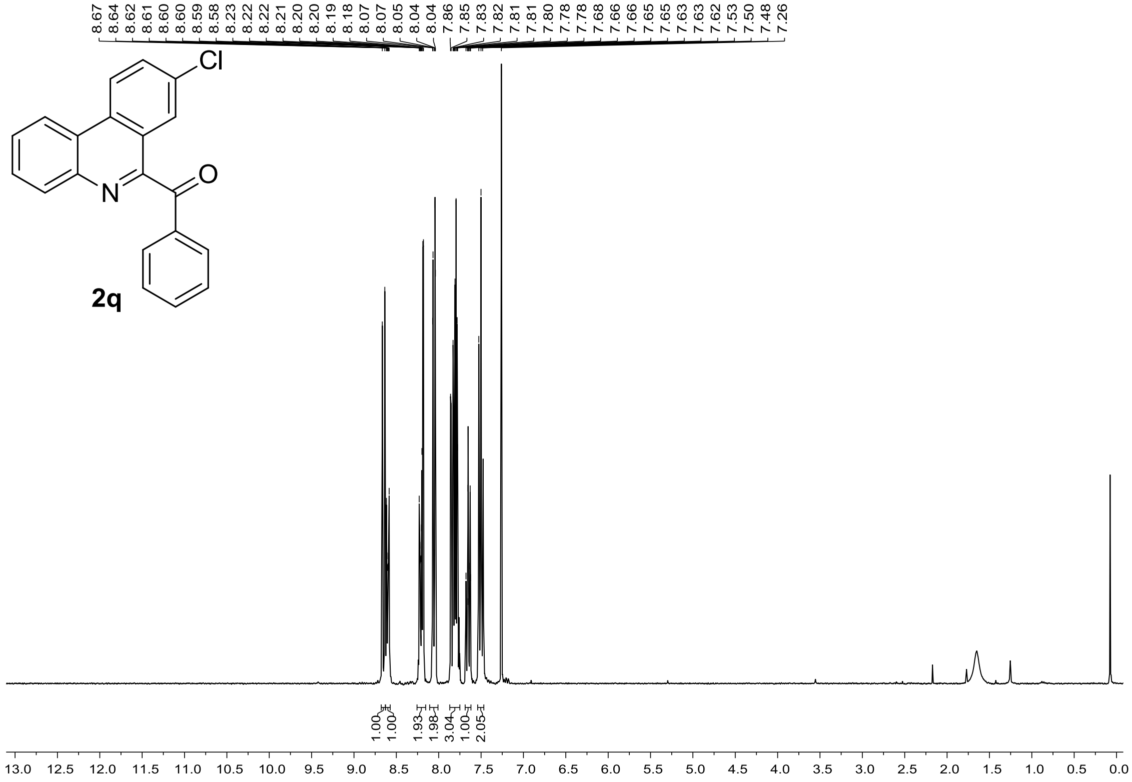
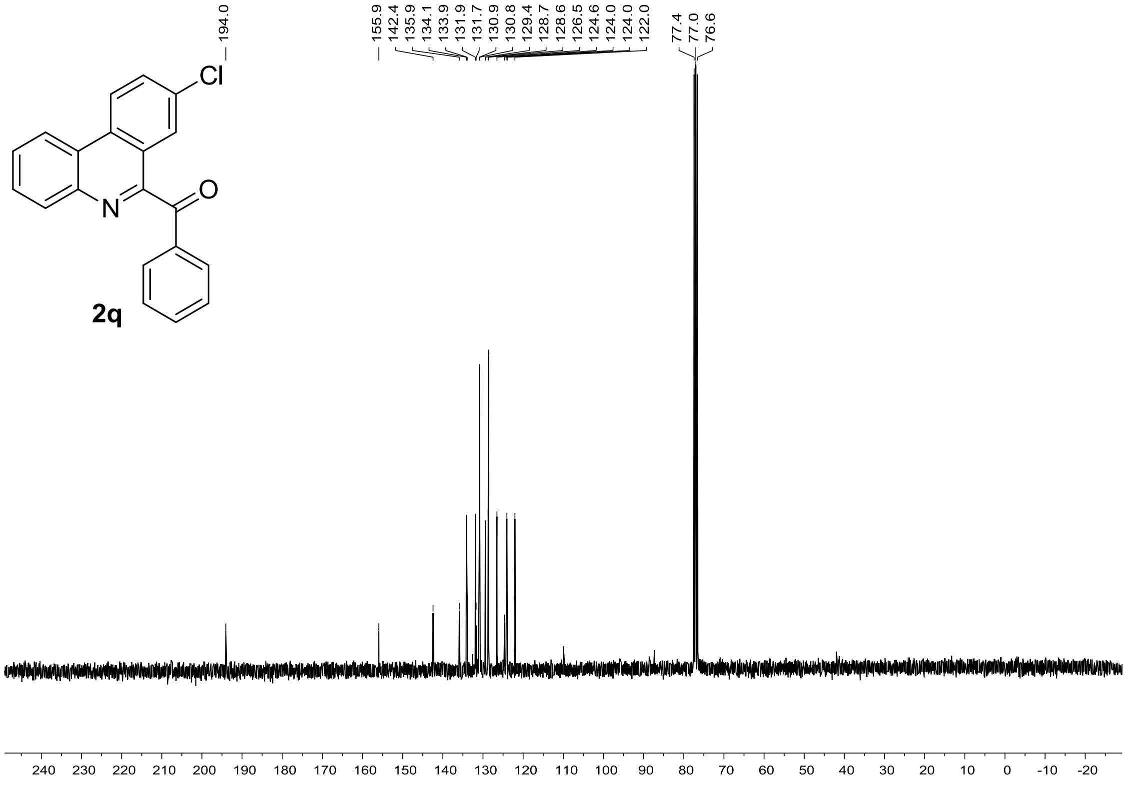
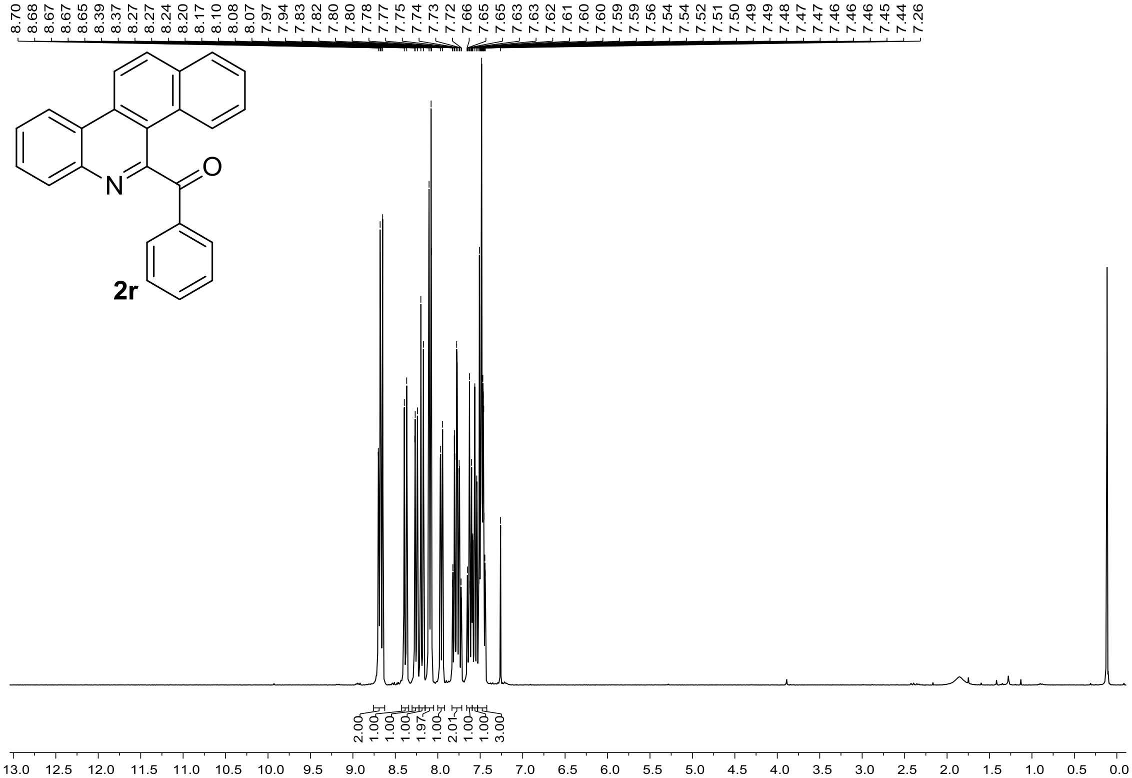
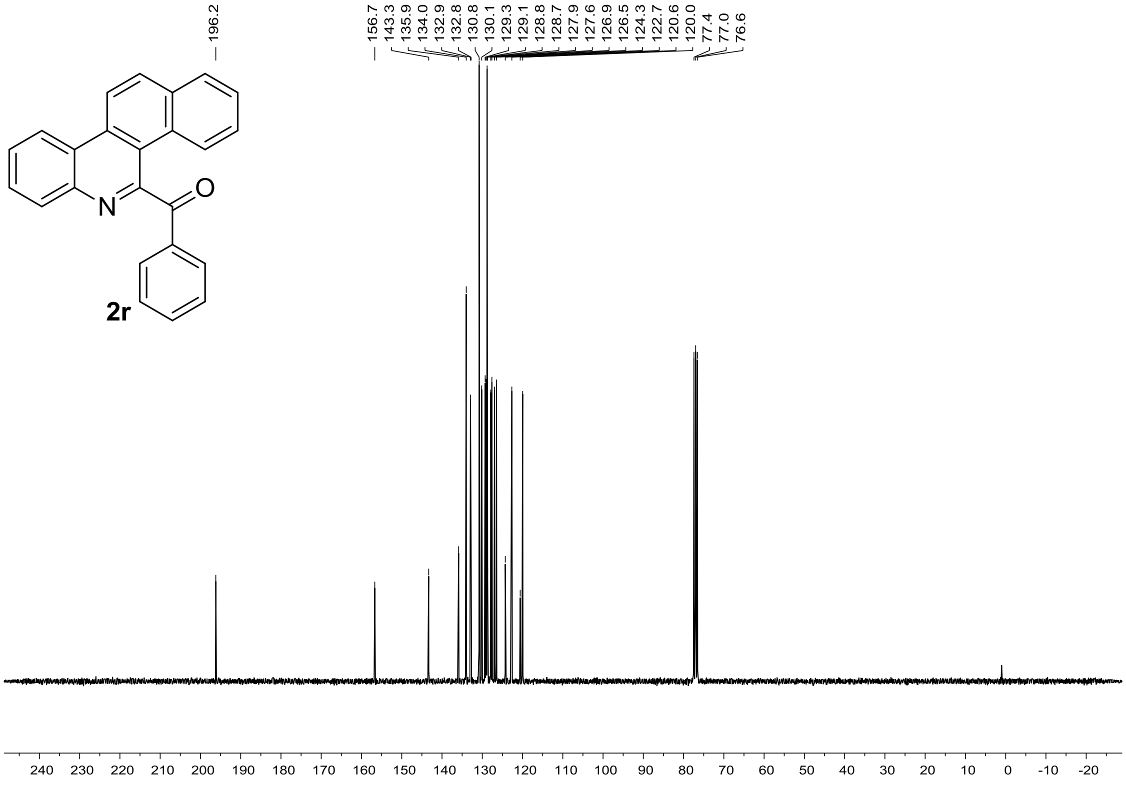
(8-Chlorophenanthridin-6-yl)(phenyl)methanone (2q)



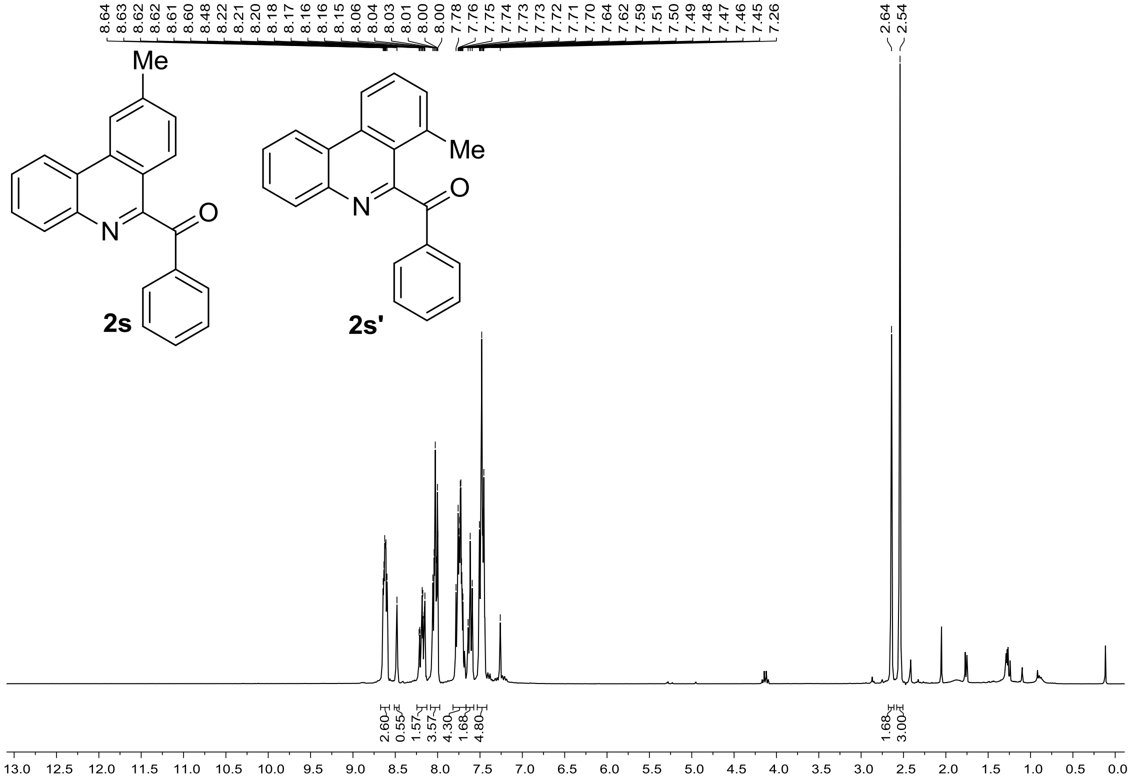


Benzo[i]phenanthridin-5-yl(phenyl)methanone (2r)

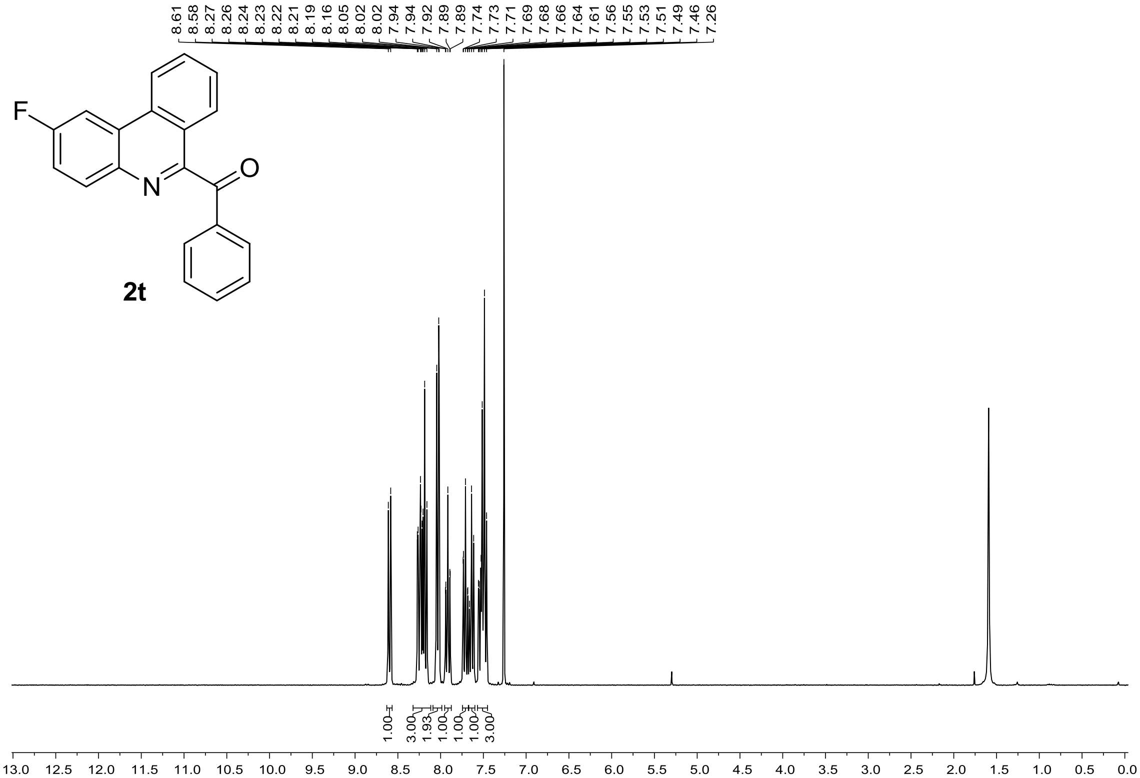


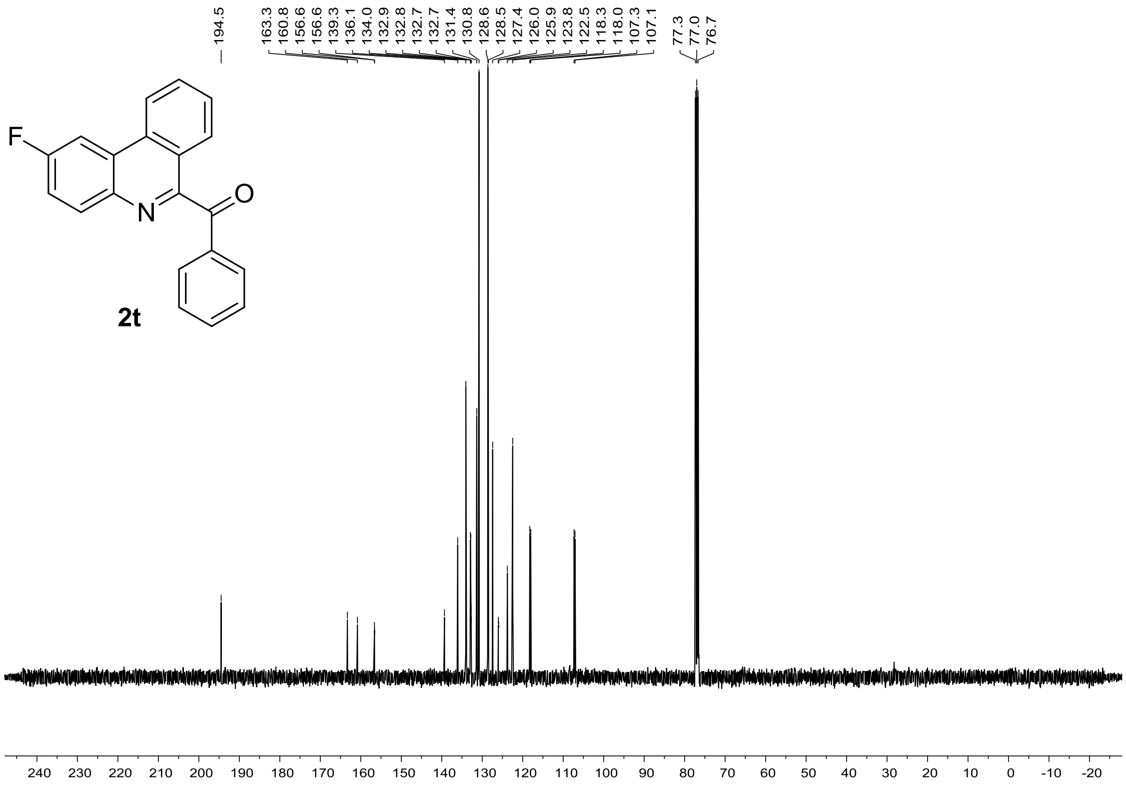


(9-Methylphenanthridin-6-yl)(phenyl)methanone (2s) and (7-methylphenanthridin-6-yl)(phenyl)methanone (2s')



(2-Fluorophenanthridin-6-yl)(phenyl)methanone (2t)

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118.0
107.3
107.1
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N
O
2t
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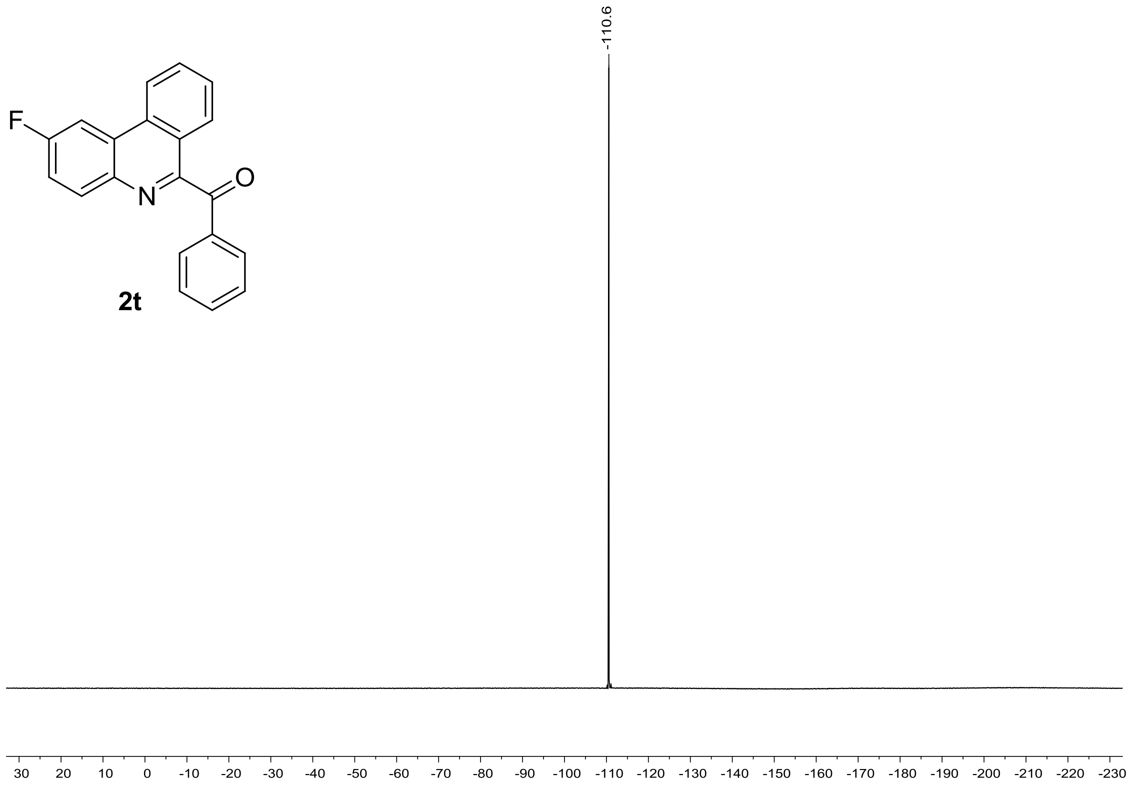
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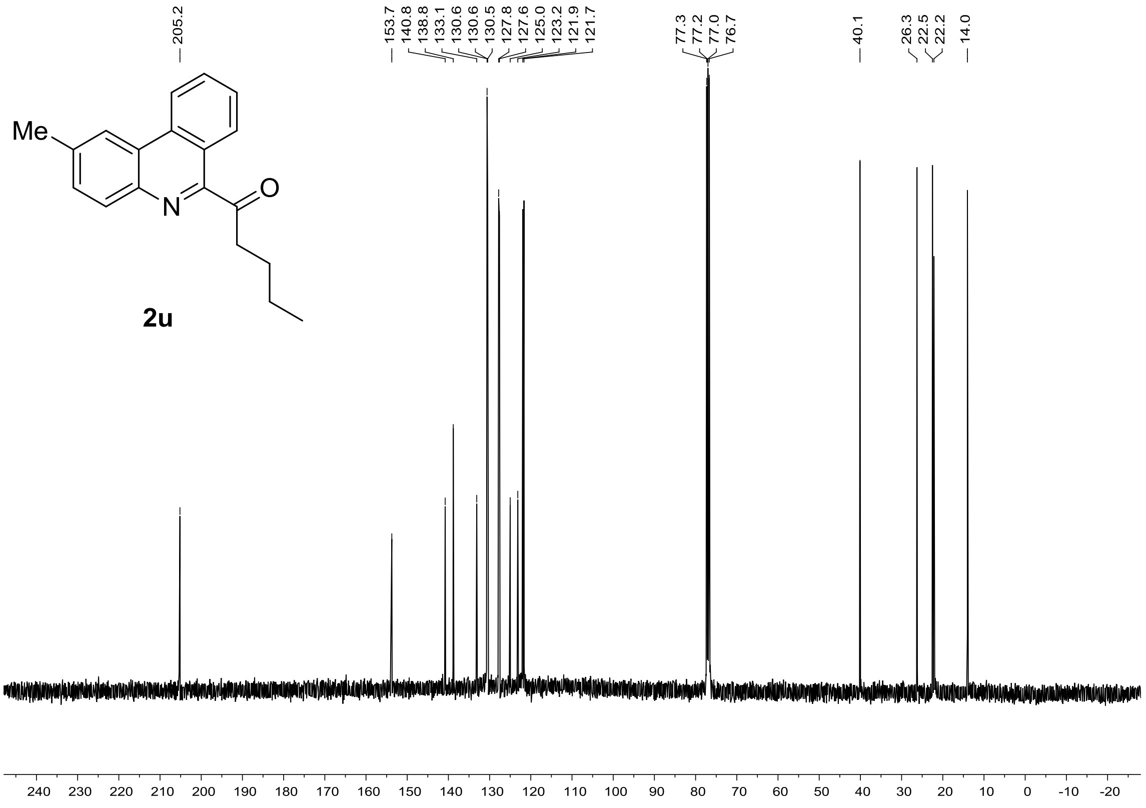
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7. Literature

[1] Tobisu, M.; Koh, K.; Furukawa, T.; Chatani, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 11363–11366.

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