Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information

# Palladium and copper-catalyzed ligand-free coupling of phenylhydrazines in water

Parul Chauhan,‡[a] Makthala Ravi,‡[a] Shikha Singh,[a] Kanumuri S. R. Raju,[c] Vikas Bajpai,[b] Brijesh Kumar,[b] Wahajuddin,[c] Prem. P. Yadav*[a]

[a]*Division of Medicinal and Process Chemistry, CSIR-Central Drug Research Institute, Lucknow-226031, India*
[b]*Sophisticated Analytical Instrument Facility, CSIR-Central Drug Research Institute, Lucknow-226031, India*
[c]*Division of Pharmacokinetics and Metabolism, CSIR-Central Drug Research Institute, Lucknow-226031, India.*

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## General Experimental Details:

All glass apparatus were oven dried prior to use. Melting points were determined in open capillary tubes on an electrically heated block and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR RX1 spectrophotometer. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on Bruker DRX-300 and Bruker Ascend-400 using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Direct Analysis in Real Time Mass spectrometry (DARTMS) was obtained on JMS-T100LC, AccuTOF. Column chromatography was performed over silica gel (60-120 Mesh) by using Smart flash EPCLC AI-700X YAMAZEN with minimal amount of solvent. HPLC analyses was carried out using system consists of Shimazdu LC-10ATVp pumps and SIL-HTc auto sampler with temperature controller on a Zorbax SB100 C18 column (4.6 × 150 mm, 5.0 μm). The system was run in gradient mode with mobile phase consisting of acetonitrile (A) and water (B) at a flow rate of 0.80 mL/min. Data acquisition was carried out on Class Vp software. All chemicals and reagents were obtained from Aldrich (USA), Alfa Aesar (England) and used without further purification. All reactions were performed in a 25 ml RB flask equipped with a guard tube and reaction mixture was stirred at 600 rpm at rt for the duration of reaction.

**Representative procedure for the synthesis of 4,4′-difluorobiphenyl (2a):**

To a solution of phenylhydrazine **1a** (100 mg, 0.62 mmol) in water (10 mL) added $Pd(TFA)_2$ (5.1 mg, 0.015 mmol) and $Cu(OAc)_2$ (11.2 mg, 0.062 mmol) and stirred the reaction mixture at rt for 15 min. The reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was removed under reduced pressure to give the crude product. Crude product was further purified by column chromatography over silica gel using 100% hexane as eluent to furnish 53mg (90%) of **2a** as white solid.

**Representative procedure for the synthesis of 4-fluoro-4′-methoxybiphenyl (3c):**

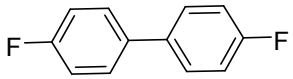
To a solution of phenylhydrazine **1a** (110mg, 0.68 mmol) and phenylhydrazine **1h** (100mg, 0.57 mmol) in water (10 mL) added $Pd(TFA)_2$ (4.7 mg, 0.014 mmol) and $Cu(OAc)_2$ (10.3mg, 0.057 mmol) and stirred the reaction mixture at rt for 2 h. The reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was removed under reduced pressure to give the crude product. Crude product was further purified by column chromatography over silica gel using 100% hexane as eluent. Quantitative yields of cross coupling products were carried out using system consists of Shimazdu LC-10ATVp pumps and SIL-HTc auto sampler with temperature controller to give 71% of 3c, 13% of 2a and 15% of 2h by using Zorbax SB100 C18 column (4.6 × 150 mm, 5.0 μm) eluted with gradient of $H_2O$:Acetonotrile.

**Representative procedure for the synthesis of 4-chloro-4′-methoxybiphenyl (3a):**

To a solution of 4-Chlorophenylhydrazine hydrochloride **1c** (100mg, 0.56 mmol) and 4-Methoxyphenylboronic acid **6** (100mg, 0.66 mmol) in water (10 mL) added $Pd(TFA)_2$ (3.3 mg, 0.010 mmol) and $Cu(OAc)_2$ (10.8mg, 0.06 mmol) and stirred the reaction mixture at rt for 6 h. The reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was removed under reduced pressure to give the crude product. Crude product was further purified by column chromatography over silica gel using 100% hexane as eluent and to furnish 62.3mg (51%) of **3a** as white solid, 17mg (28%) of **2c** as white solid and 12.5mg (18 %) of **2h** as white solid.

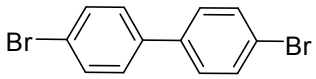
## Compound Characterization Data:

**4,4′-difluorobiphenyl (2a)[1]**



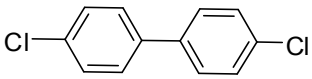

White solid, Yield 90%, mp 78-81°C, lit[1] mp 88-90°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1601, 1497, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.10-7.14 (4H, m), 7.47-7.51 (4H, m);**$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 115.9 (d, *J*= 21.37 Hz, 4×CH), 128.8 (d, *J*= 8.0 Hz, 4×CH), 136.6 (d, *J*= 2.95 Hz, 2×C), 164.2 (d, *J*= 244.93 Hz, 2xC-F); **HRMS** (**DART**) *m/z* calcd for $C_{12}H_8F_2$ $(M)^+$ 190.0594, found 190.0603.

**4,4′-dibromobiphenyl (2b)[1]**



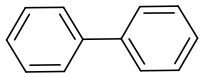

White solid, Yield 85%, mp 158-162°C, lit[1] mp 162-164°C, ; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1634, 1473, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.43 (4H, m), 7.55-7.58 (4H, m); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 122.1 (2×C), 128.6 (4×CH), 132.2 (4×CH), 139.0 (2×C); **HRMS** (DART) *m/z* calcd for $C_{12}H_8Br_2$ $(M)^+$ 309.8992, found 309.9020.

**4,4′-dichlorobiphenyl (2c)[1]**



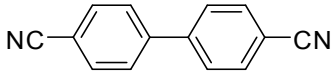

White solid, Yield 90%, mp 142-145°C, lit[1] mp 148-150°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1634, 1478, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.42 (4H, m), 7.46-7.49 (4H, m); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 128.3 (4×CH), 129.2 (4×CH), 133.9 (2×C), 138.5 (2×C); **HRMS** (DART) *m/z* calcd for $C_{12}H_8Cl_2$ $(M)^+$ 222.0003, found 221.9995.

**Biphenyl (2d)[1]**



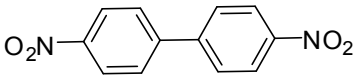
White solid, Yield 82%, mp 65-68°C, lit[1] mp 68-70°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1631, 1521, 927; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, t, *J* = 6.9 Hz), 7.45 (4H, t, *J* = 7.5Hz,), 7.61 (4H, d, *J* = 8 Hz); **$^{13}$C NMR** (100 MHz, $CDCl_3$), δ 127.3 (4×CH), 127.4 (2×CH), 128.9 (4×CH), 141.4 (2×C), **HRMS** (DART) *m/z* calcd for $C_{12}H_{10}$ $(M)^+$ 154.0783, found 154.0786.

**Biphenyl-4,4′-dicarbonitrile (2e)[1]**



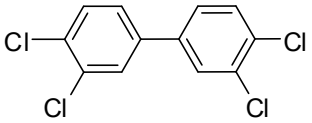

Light Yellow solid, Yield 69%, mp 223-225°C, lit[1] mp 235-237°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3019, 2231, 1605, 1493, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.69 (4H, d, *J* = 8.5 Hz) 7.78 (4H, d, *J* = 8.4 Hz). **$^{13}$C NMR** (100 MHz, $CDCl_3$), δ 112.5 (2×C), 118.5 (2×C), 128.1 (4×CH), 133.0 (4×CH), 143.6 (2×C); **HRMS** (DART) *m/z* calcd for $C_{14}H_9N_2$ $(M+H)^+$ 205.0766, found 205.0766.

**4,4′-dinitrobiphenyl (2f)[2]**



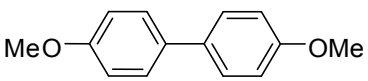

White solid, Yield 81%, mp 236-240°C, lit[2] mp 235°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3019, 1638, 1480, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.79 (4H, d, *J* = 8.7 Hz), 8.36 (4H, d, *J* = 8.7 Hz); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 124.5 (4×CH), 128.5 (4×CH), 145.1 (2×C), 148.2 (2×C); **HRMS** (DART) *m/z* calcd for $C_{12}H_9N_2O_4$ $(M+H)^+$ 245.0562, found 245.0564.

**3,3,4,4′-tetrachlorobiphenyl (2g)[3]**



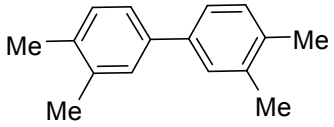

White solid, Yield 79%, mp 165-168°C, lit[3] mp 175-177°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3019, 1635, 1545, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.37 (2H, dd, *J* = 8.3, 2.1 Hz), 7.51-7.53 (2H, m), 7.62 (2H, d, *J* = 2.1 Hz); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 126.3 (2×CH), 128.9 (2×CH), 131.1 (2×CH), 132.6 (2×C), 133.4 (2×C), 138.9 (2×C); **HRMS** (DART) *m/z* calcd for $C_{12}H_6Cl_4$ $(M)^+$ 289.9223, found 289.9207.

**4,4′-dimethoxybiphenyl (2h)[1]**



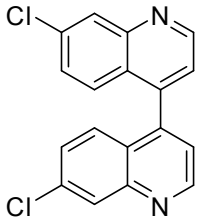
White solid, Yield 68%, mp 165-168°C, lit[1] mp 172-174°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1610, 1499, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.85 (6H, s), 6.95-6.97 (4H, m), 7.47-7.49 (4H, m); **$^{13}$C NMR** (75 MHz, $CDCl_3$), δ 55.5 (2×$CH_3$), 114.3 (4×CH), 127.9 (4×CH), 133.6 (2×C), 158.8 (2×C), **HRMS** (DART) *m/z* calcd for $C_{14}H_{15}O_2$ $(M+H)^+$ 215.1072, found 215.1075.

**3,3,4,4′-tetramethylbiphenyl (2i)[1]**



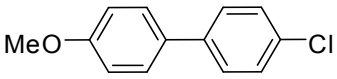

White solid, Yield 80%, mp 68-70°C, lit[1] mp 72-74°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3019, 1637, 1495, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.31 (6H, s), 2.34 (6H, s), 7.19 (2H, d, *J* = 7.7 Hz), 7.33 (2H, d, *J* = 7.8 Hz), 7.37 (2H, s); **$^{13}$C NMR** (100 MHz, $CDCl_3$), δ 19.5 (2×$CH_3$), 20.0 (2×$CH_3$), 124.5 (2×CH), 128.4 (2×CH), 130.1 (2×CH), 135.4 (2×C), 136.9 (2×C), 139.0 (2×C); **HRMS** (DART) *m/z* calcd for $C_{16}H_{19}$ $(M+H)^+$ 211.1487, found 211.1480.

**7,7′-dichloro-4,4′-biquinoline (2j)**



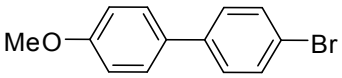

Brown solid, Yield 45%, mp 168-170°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3020,1605, 1492, 878; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.23 (2H, d, *J* = 3.8 Hz,), 7.34-7.37 (4H, m), 8.21 (2H, t, *J* = 2.04 Hz), 9.04 (2H, s); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 121.9 (2× CH), 125.1 (2×C) , 126.8 (2×CH), 128.4 (2×CH), 128.9 (2×CH), 136.0 (2×C), 143.8 (2×C), 148.8 (2×C), 150.9 (2×CH), **HRMS** (ESI) *m/z* calcd for $C_{18}H_{10}Cl_2N_2$ $(M+H)^+$ 325.0297, found 325.0299.

**4-chloro-4′-methoxybiphenyl (3a)[4]**



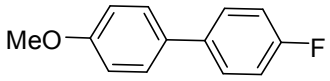

White solid, Yield 76%, mp 105-107°C, lit[4] mp 115-116.4°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1611, 1485, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.85 (3H, s), 6.96-6.99 (2H, m), 7.37-7.39 (2H, m), 7.46-7.50 (4H, m); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 55.5 ($CH_3$), 114.5 (2×CH), 128.1 (2×CH), 128.2 (2×CH), 128.9 (2×CH), 132.6 (C), 132.8 (C), 139.4 (C), 159.5 (C); **HRMS** (DART) *m/z* calcd for $C_{13}H_{11}ClO$ $(M)^+$ 218.0498, found 218.0512;

**4-bromo-4′-methoxybiphenyl (3b)[5]**



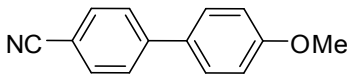

White solid, Yield 75%, mp 136-140°C, lit[5] 143-145°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1612, 1481, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.85 (3H, s), 6.96-6.98 (2H, m), 7.40-7.42 (2H, m), 7.47-7.54 (4H, m); **$^{13}$C NMR** (100MHz, $CDCl_3$), δ 55.5 ($CH_3$), 114.5 (2×CH), 120.9 (C), 128.1 (2×CH), 128.4 (2×CH), 131.9 (2×CH), 132.6 (C), 139.9 (C), 159.6 (C); HRMS (DART) *m/z* calcd for $C_{13}H_{12}BrO$ $(M+H)^+$ 263.0072, found 263.0064;

**4-fluoro-4′-methoxybiphenyl (3c)[6]**



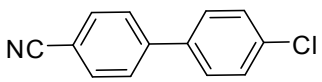

White solid, Yield 71%, mp 90-94°C, lit[6] mp 84-86°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 1611, 1500, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.85 (3H, s), 6.95-6.99 (2H, m), 7.07-7.13 (2H, m), 7.45-7.52 (4H, m); **$^{13}$C NMR** (100 MHz, $CDCl_3$), δ 55.4 ($CH_3$), 114.3 (2×CH), 115.6 (d, *J*= 21.22 Hz, 2×CH), 128.0 (2xCH), 128.3 (d, *J*= 7.86 Hz, 2×CH), 132.9 (C), 137.0 (C), 159.1 (C), 163.3 (d, *J*= 243.84 Hz, C-F); **HRMS** (DART) *m/z* calcd for $C_{13}H_{12}FO$ $(M+H)^+$ 203.0872, found 203.0867.

**4′-methoxybiphenyl-4-carbonitrile (3d)[4]**



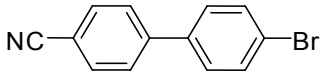

White solid, Yield 41%, mp 97-99°C, lit[4] mp 114.115.4°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3019, 2228, 1606, 1495, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.87 (3H, s), 6.99-7.02 (2H, m), 7.52-7.56 (2H, m), 7.62-7.65 (2H, m), 7.68-7.71 (2H, m); **$^{13}$C NMR** (100 MHz, $CDCl_3$), δ 55.5 ($CH_3$), 110.2 (C), 114.7 (2×CH), 119.2 (C), 127.2 (2×CH), 128.5 (2×CH), 131.6 (C), 132.7 (2×CH), 145.4 (C), 160.3 (C); **HRMS** (DART) *m/z* calcd for $C_{14}H_{12}NO$ $(M+H)^+$ 210.0919, found 210.0918.

**4′-chlorobiphenyl-4-carbonitrile (3e)[4]**



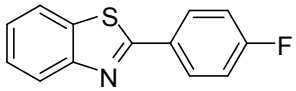

White solid, Yield 59%, mp 117-120°C, lit[4] mp 124-125°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3020, 2230 1637, 1485, 929; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.47 (2H, m), 7.50-7.54 (2H, m), 7.63-7.66 (2H, m), 7.72-7.74 (2H, m); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 111.4 (C), 118.9 (C), 127.7 (2×CH), 128.6 (2×CH), 129.5 (2×CH), 132.8 (2×CH), 135.1 (C), 137.7 (C), 144.5 (C); **HRMS** (DART) *m/z* calcd for $C_{13}H_9ClN$ $(M+H)^+$ 214.0424, found 214.0427.

**4′-bromobiphenyl-4-carbonitrile (3f)[7]**




White solid, Yield 64%, mp 116-118°C, lit[7] mp 115-115.5°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3021, 2230, 1610, 1482, 928; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.47 (2H, m), 7.60-7.67 (4H, m), 7.72-7.74 (2H, m); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 111.5 (C), 118.9 (C), 123.3 (C), 127.7 (2×CH), 128.9 (2×CH), 132.4 (2×CH), 132.8 (2×CH), 138.2 (C), 144.6 (C); **HRMS** (DART) *m/z* calcd for $C_{13}H_9BrN$ $(M+H)^+$ 257.9918, found 257.9926.

**2-(4-fluorophenyl)benzo[d]thiazole (5)[8]**




Off yellow solid, Yield 47%, mp 95-98°C, lit[8] mp 98-100°C; **FT-IR** (KBr, $\nu_{max}$/cm$^{-1}$) 3019,1607, 1485, 839; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.17-7.21 (2H, m), 7.39 (1H, td, *J* = 8.24, 1.08), 7.50 (1H, td, *J* = 8.24, 1.2), 7.91 (1H, d, *J*= 7.96), 8.05-8.12 (3H, m); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ116.3 (d, *J*= 21.99, 2XCH), 121.6 (CH), 123.2 (CH), 125.3 (CH), 126.4 (CH), 129.6 (d, *J*= 8.6 Hz, 2XCH), 130.0 (C), 135.1 (C), 154.1 (C), 165.8 (d, *J*= 251.0 Hz, C-F), 166.8 (C); **HRMS** (ESI) *m/z* calcd for $C_{13}H_8FNS$ $(M+H)^+$ 230.0439, found 230.0440..

References:

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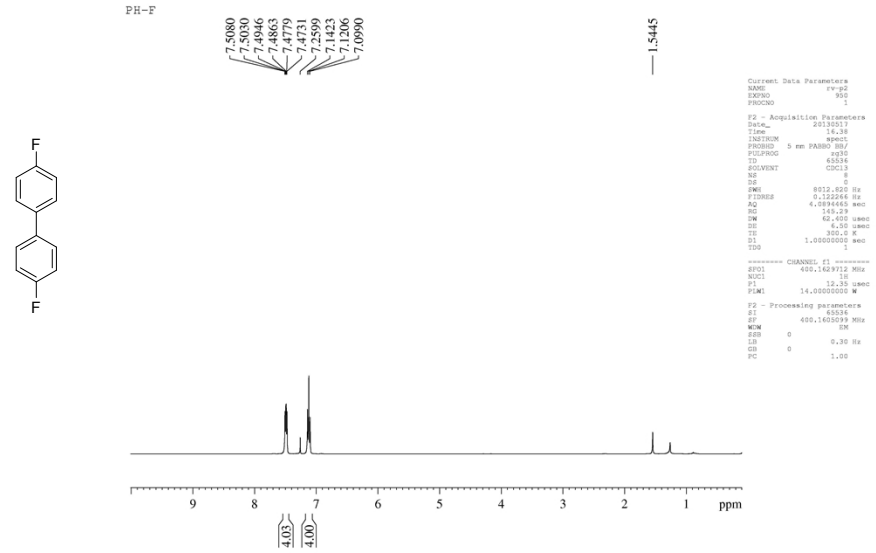
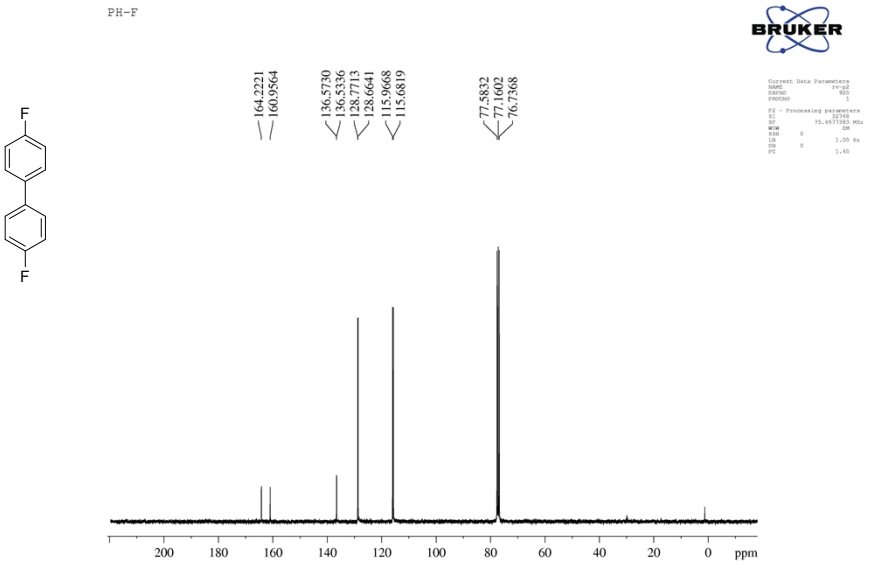
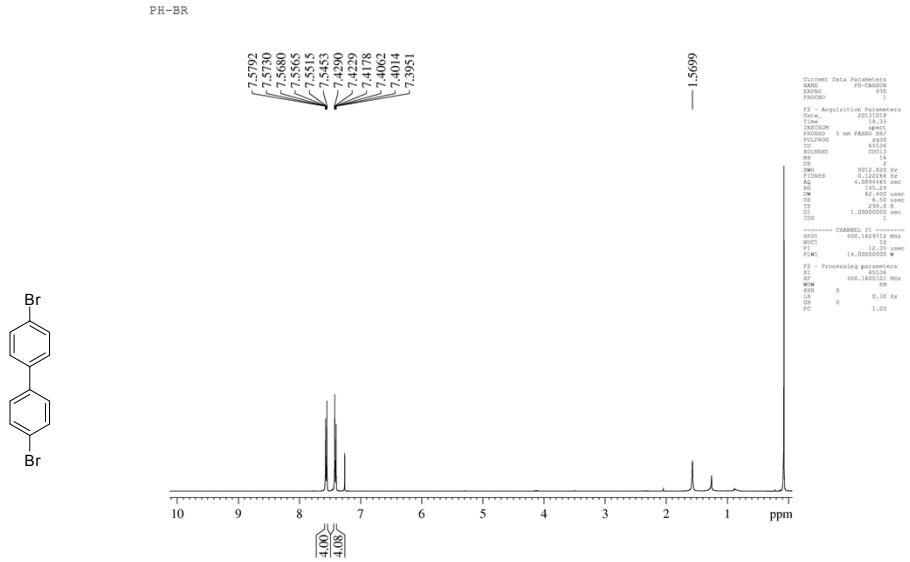


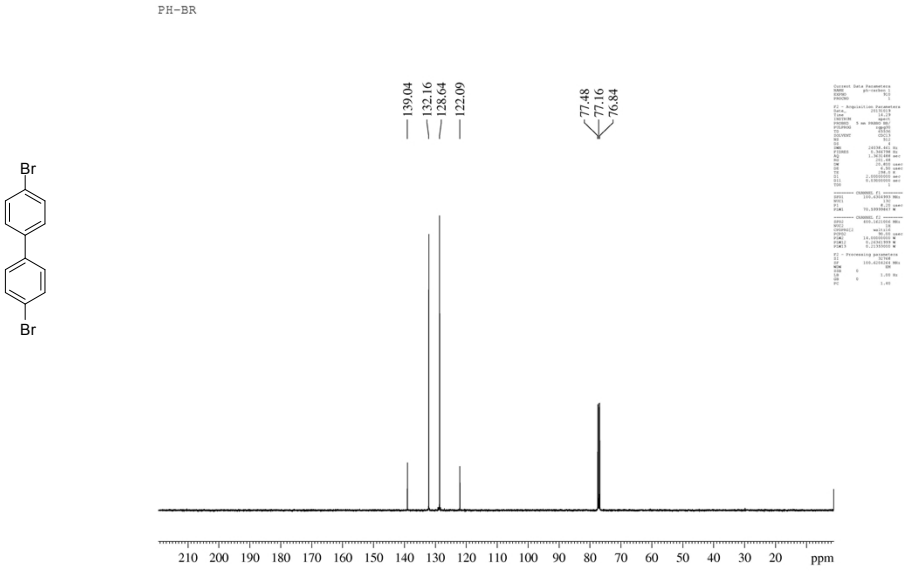

$^{1}$H NMR Spectra of (**2a**) (400 MHz, $CDCl_3$)



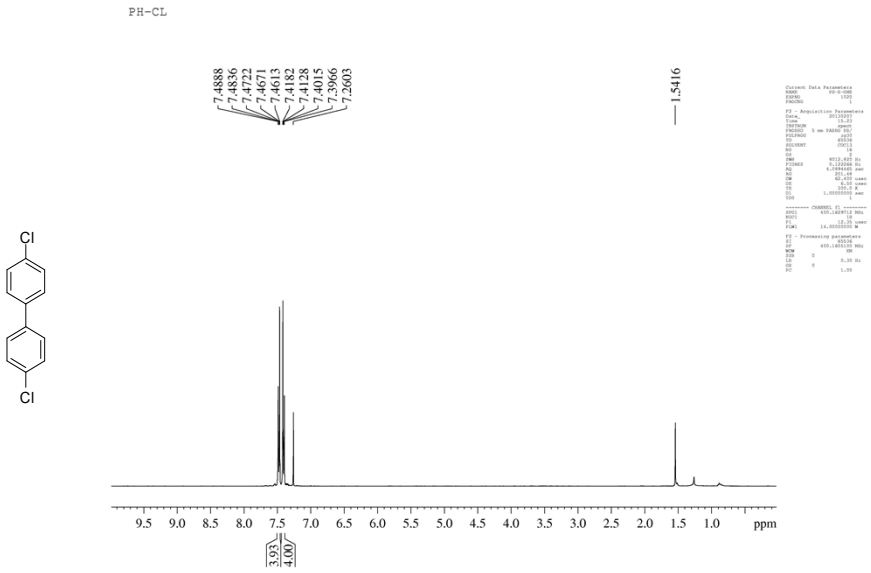

$^{13}$C NMR Spectra of (**2a**) (75 MHz, $CDCl_3$)



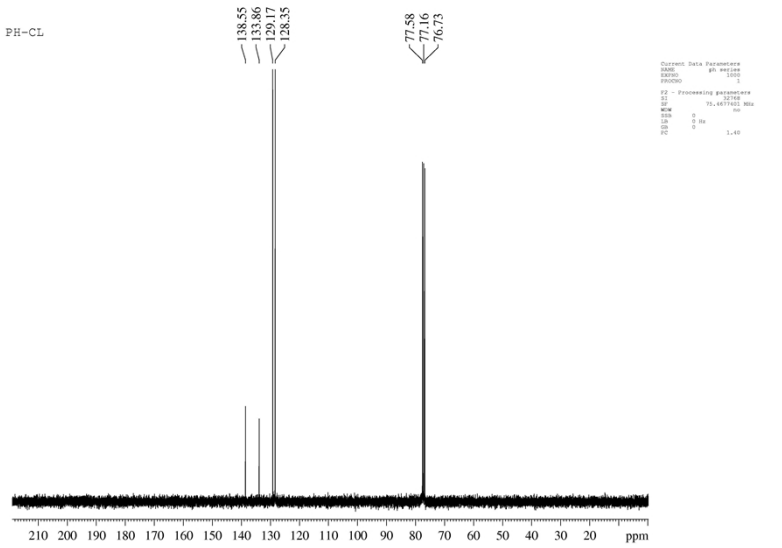

$^{1}$H NMR Spectra of (**2b**) (400 MHz, $CDCl_3$)



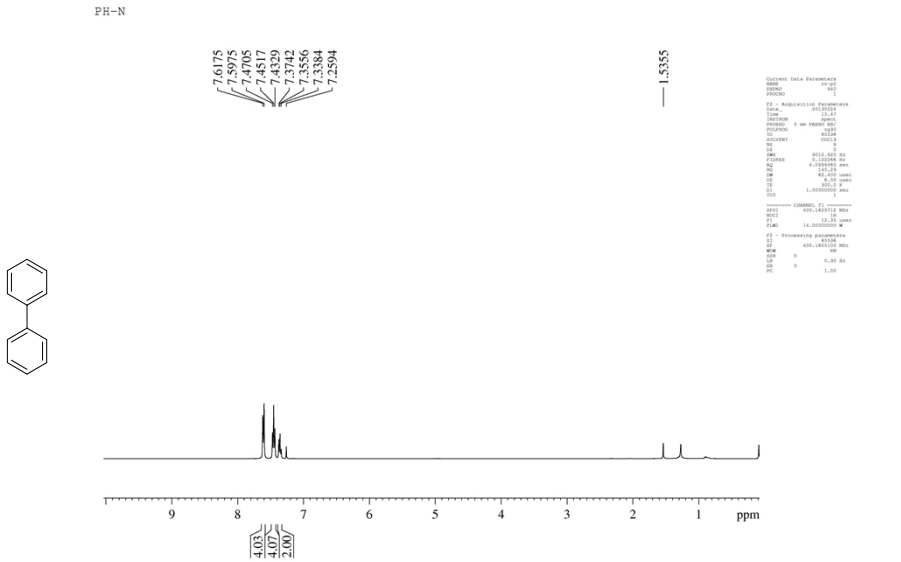

$^{13}$C NMR Spectra of (**2b**) (100 MHz, $CDCl_3$)



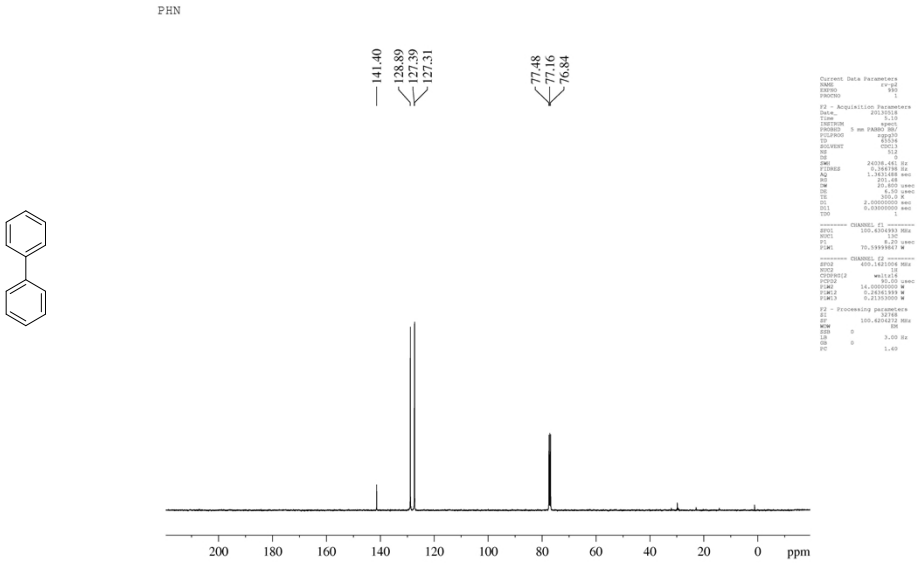

$^{1}$H NMR Spectra of (**2c)** (400 MHz, $CDCl_3$)



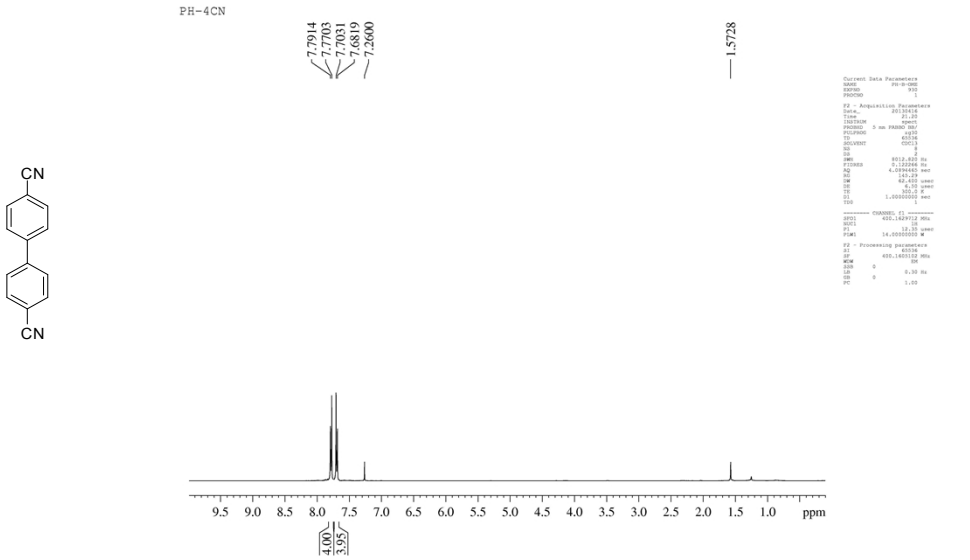

$^{13}$C NMR Spectra of (**2c)** (75 MHz, $CDCl_3$)




$^{1}$H NMR Spectra of (**2d)** (400 MHz, $CDCl_3$)




$^{13}$C NMR Spectra of (**2d)** (100 MHz, $CDCl_3$)

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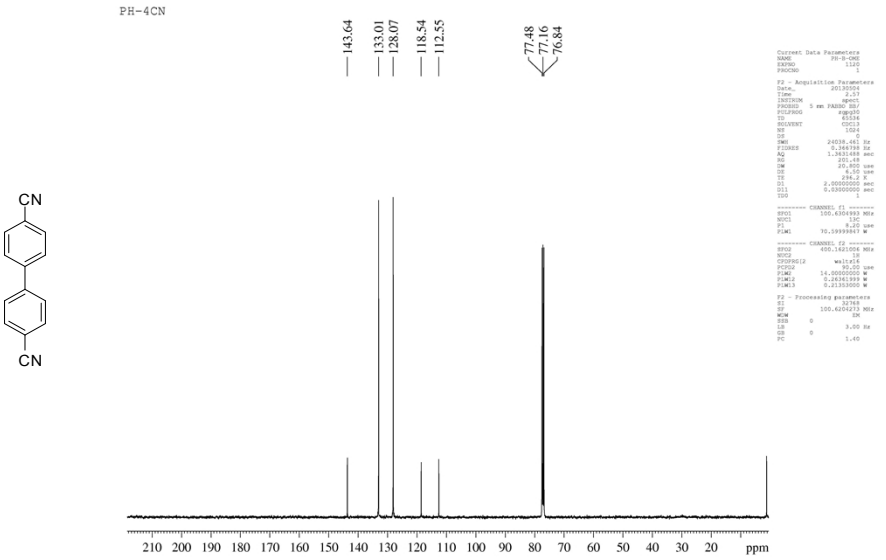


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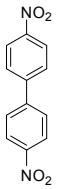


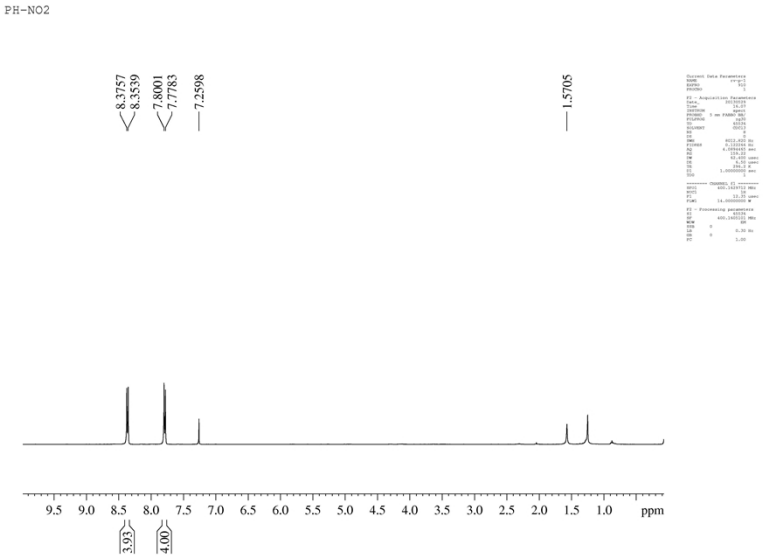


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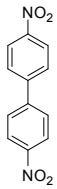


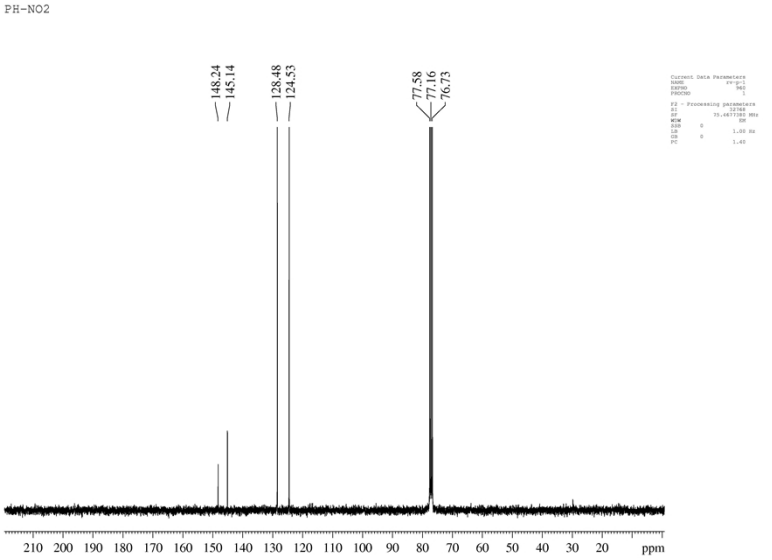


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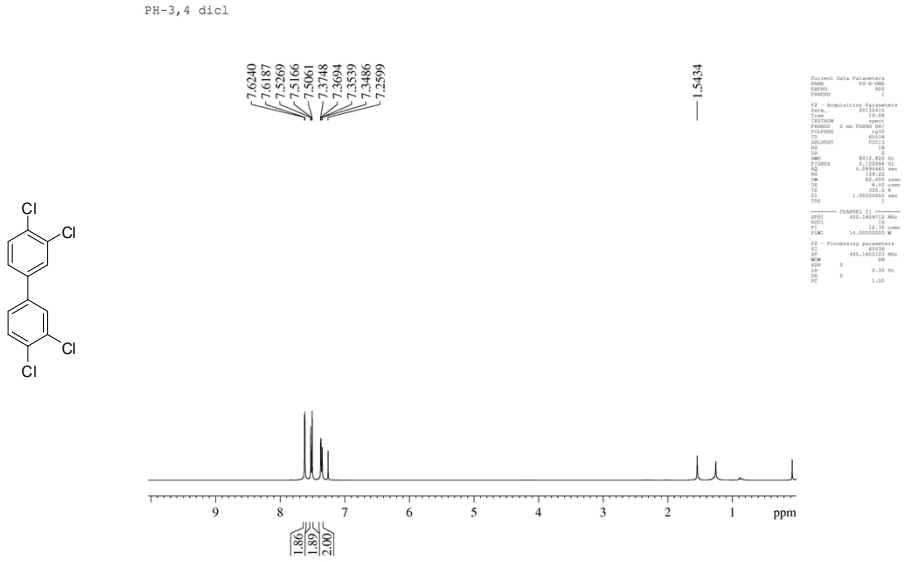
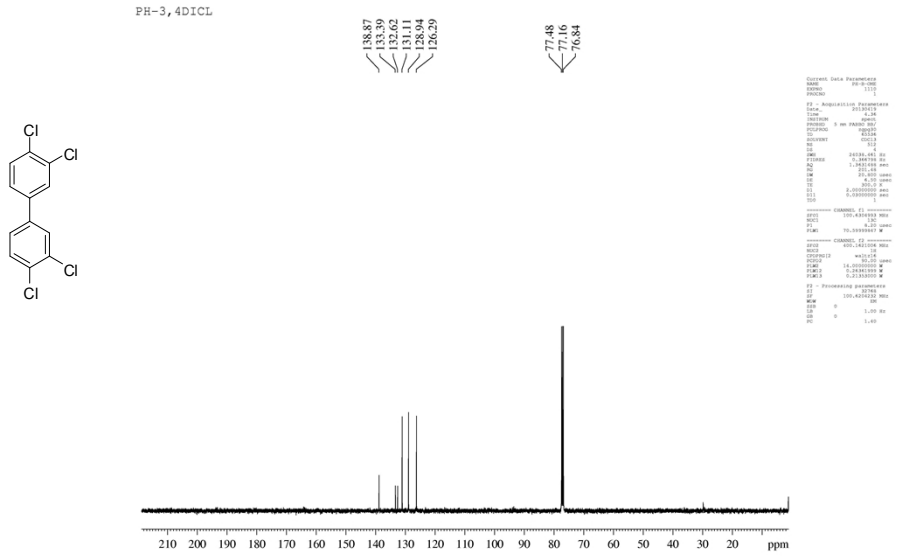
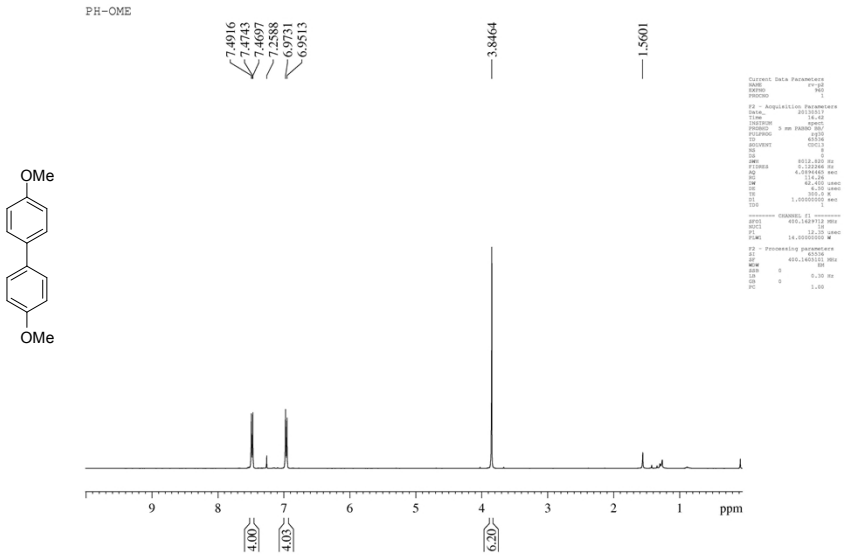


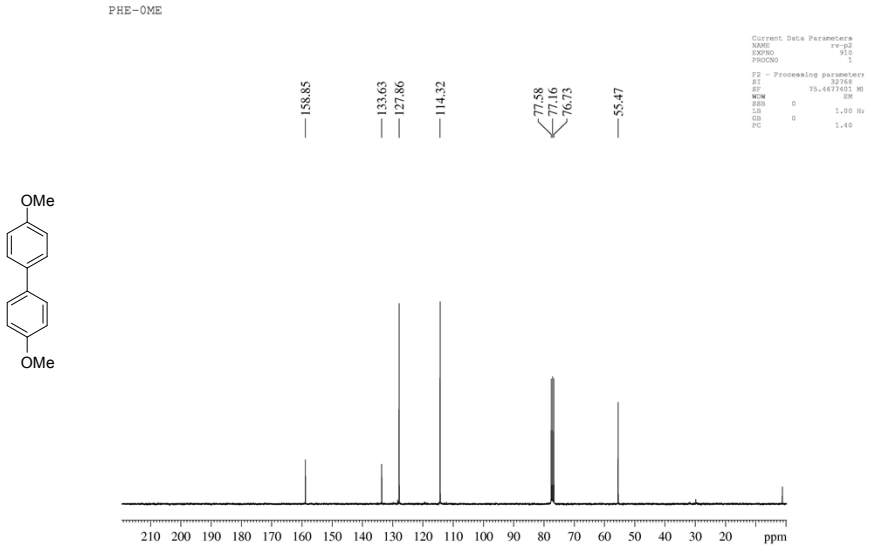

$^{1}$H NMR Spectra of (**2g)** (400 MHz, $CDCl_3$)



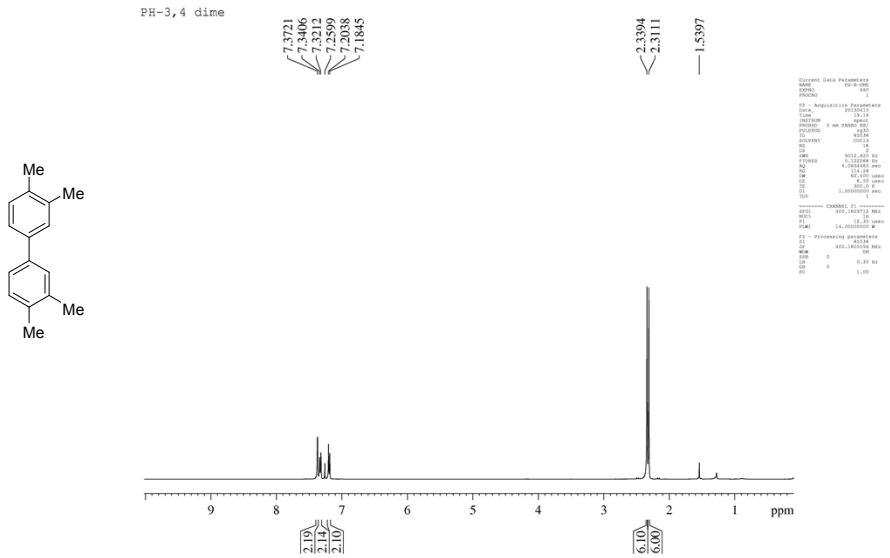

$^{13}$C NMR Spectra of (**2g)** (100 MHz, $CDCl_3$)



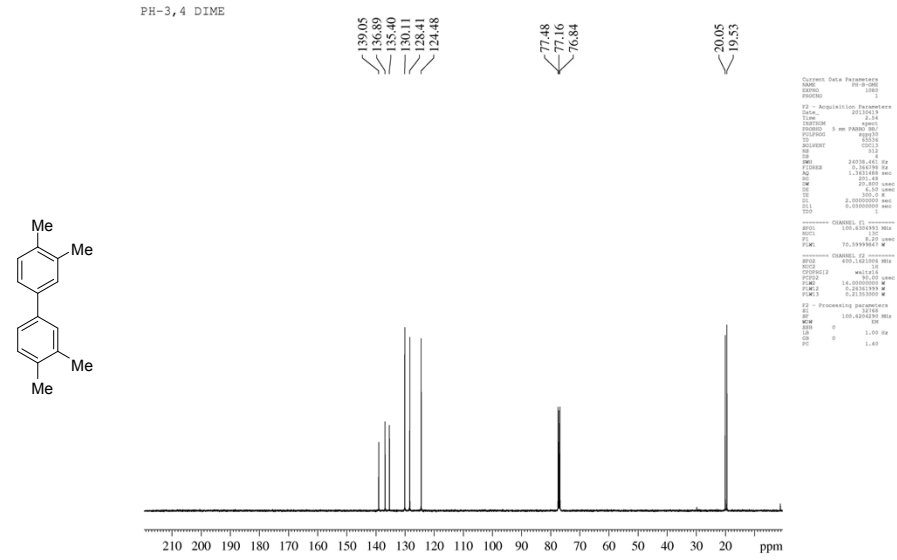

$^{1}$H NMR Spectra of (**2h)** (400 MHz, $CDCl_3$)



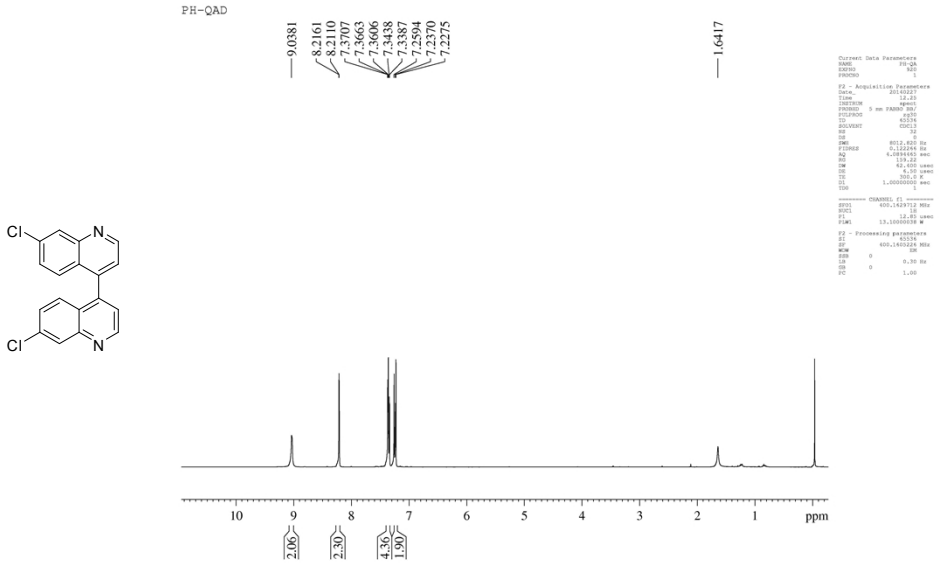

$^{13}$C NMR Spectra of (**2h)** (75 MHz, $CDCl_3$)



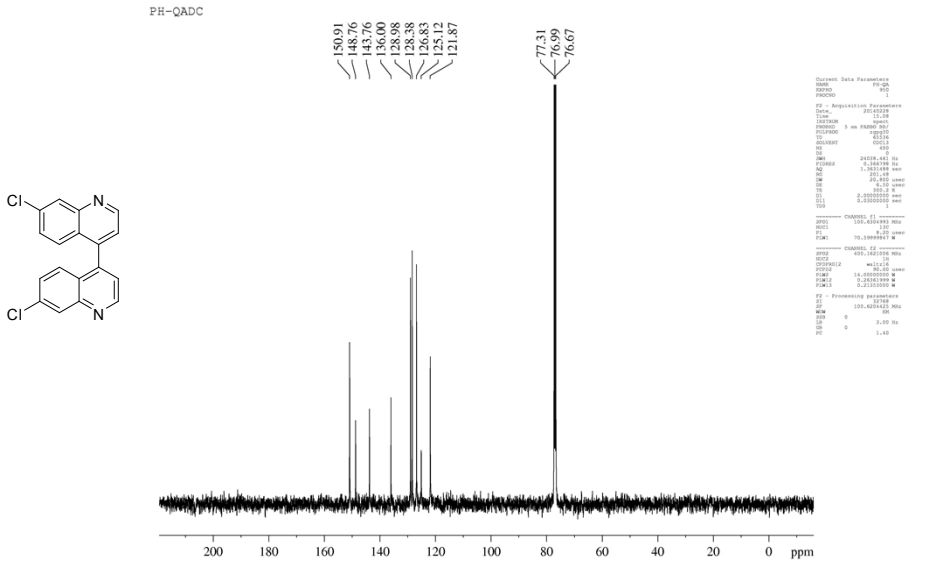

$^{1}$H NMR Spectra of (**2i)** (400 MHz, $CDCl_3$)



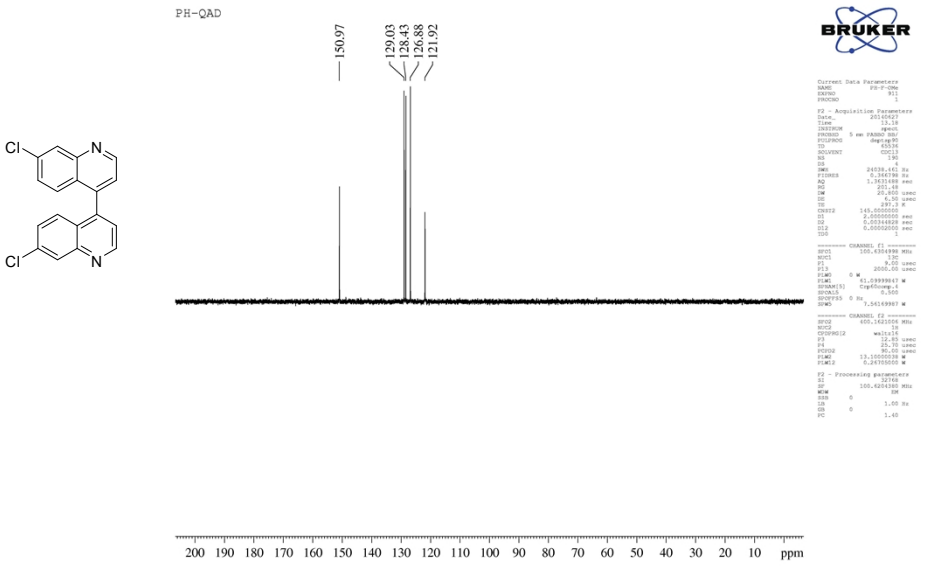

$^{13}$C NMR Spectra of (**2i)** (100 MHz, $CDCl_3$)



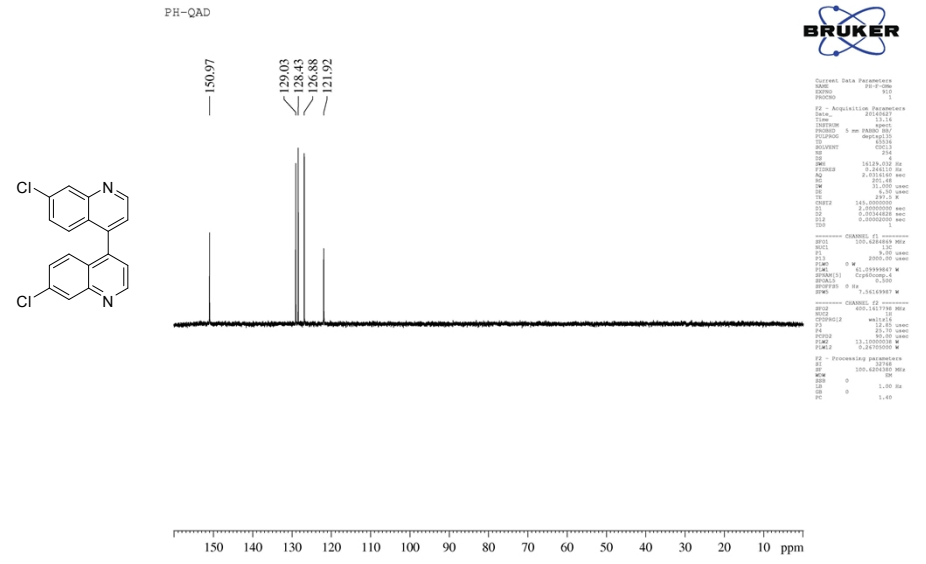

$^{1}$H NMR Spectra of (**2j**) (400 MHz, $CDCl_3$)



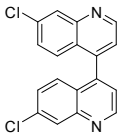

$^{13}$C NMR Spectra of (**2j**) (100 MHz, $CDCl_3$)

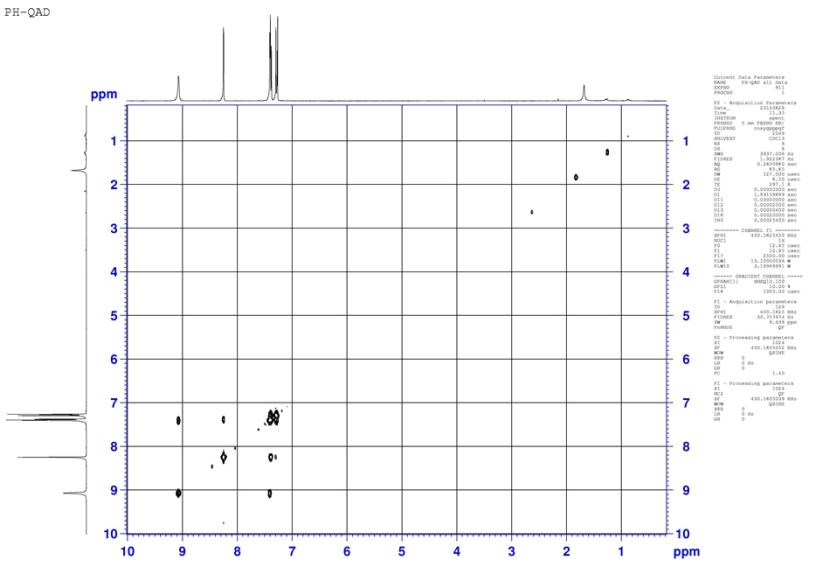



Dept 90$^{o}$ NMR Spectra of (**2j)** (400 MHz, $CDCl_3$)

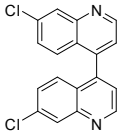


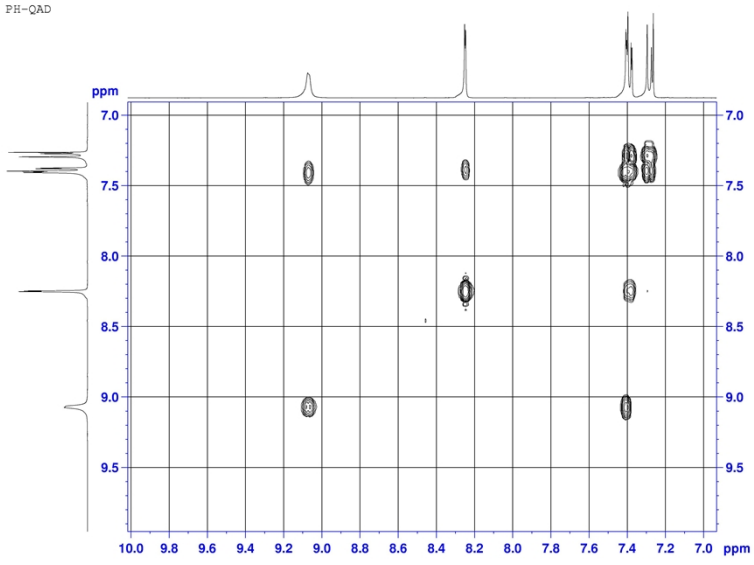

Dept 135$^{o}$ NMR Spectra of (**2j)** (400 MHz, $CDCl_3$)



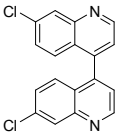



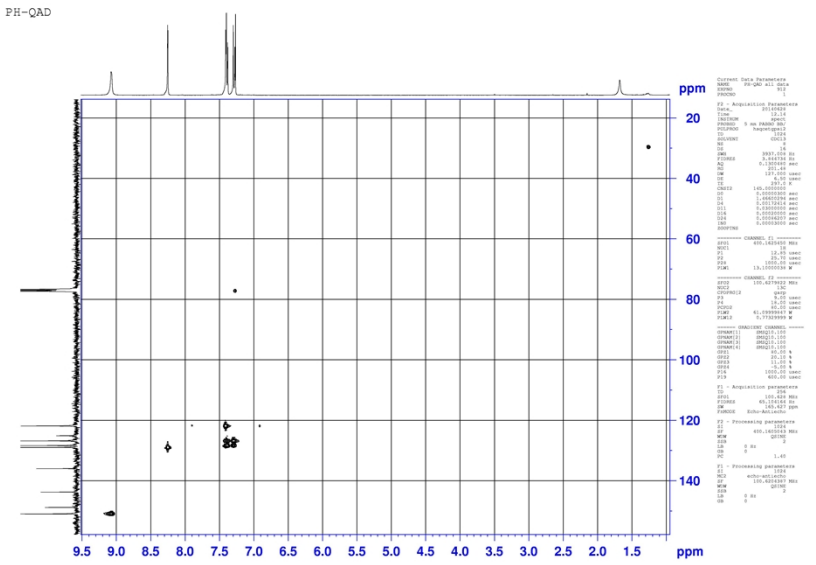

$^{1}$H-$^{1}$H-COSY of (**2j**) (400 MHz, $CDCl_3$)



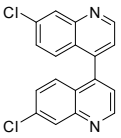



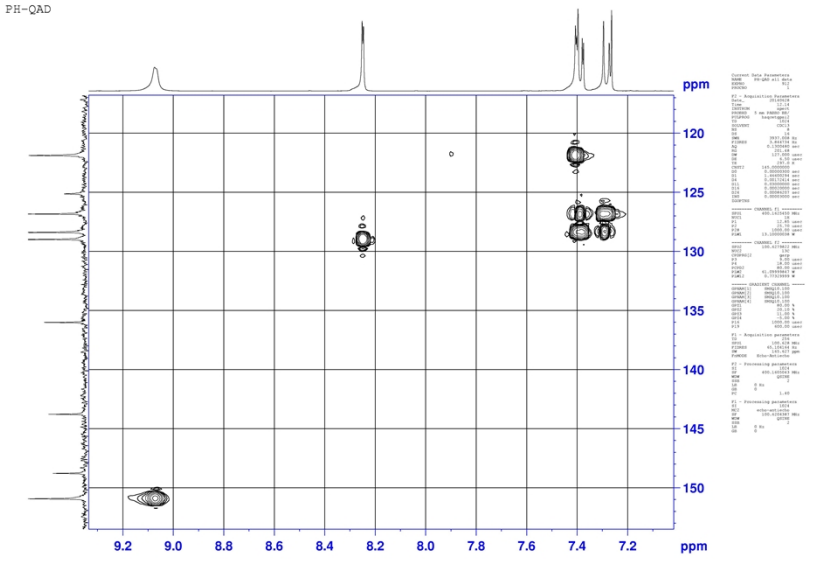

$^{1}$H-$^{1}$H-COSY of (**2j**) (400 MHz, $CDCl_3$)



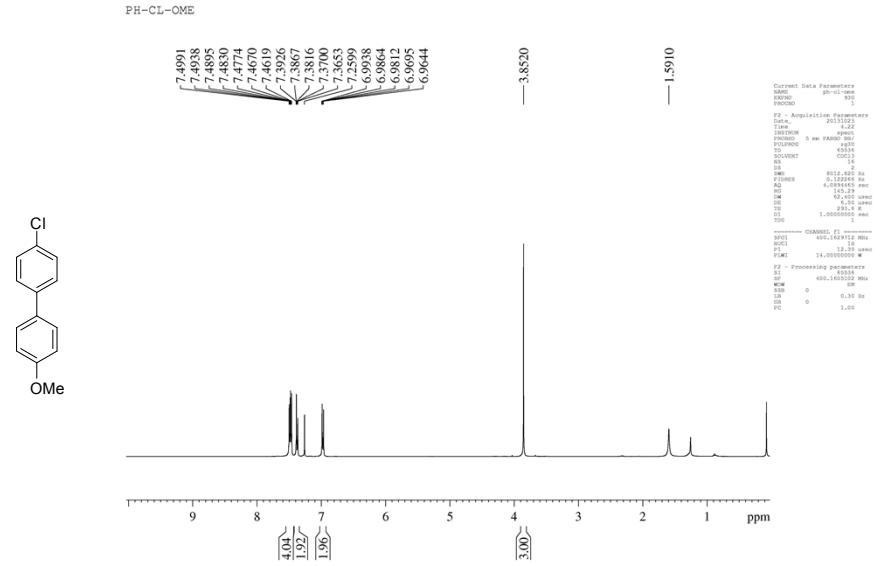



HSQC Spectrum of (**2j**) (400 MHz, $CDCl_3$)

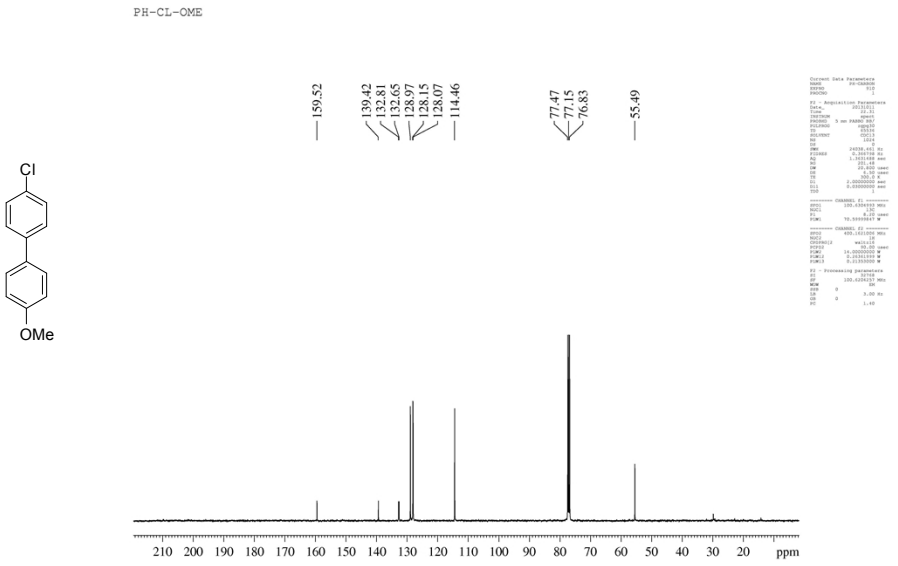




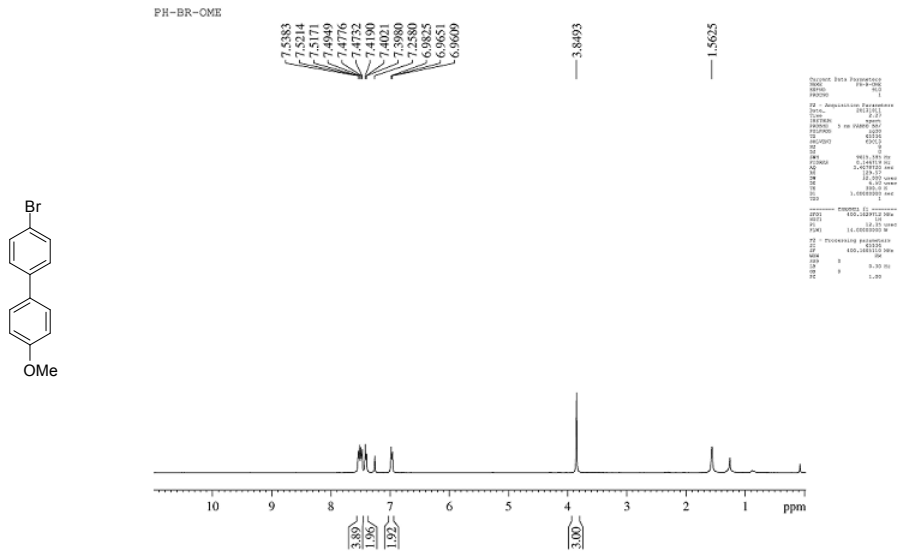

HSQC Spectrum of (**2j**) (400 MHz, $CDCl_3$)



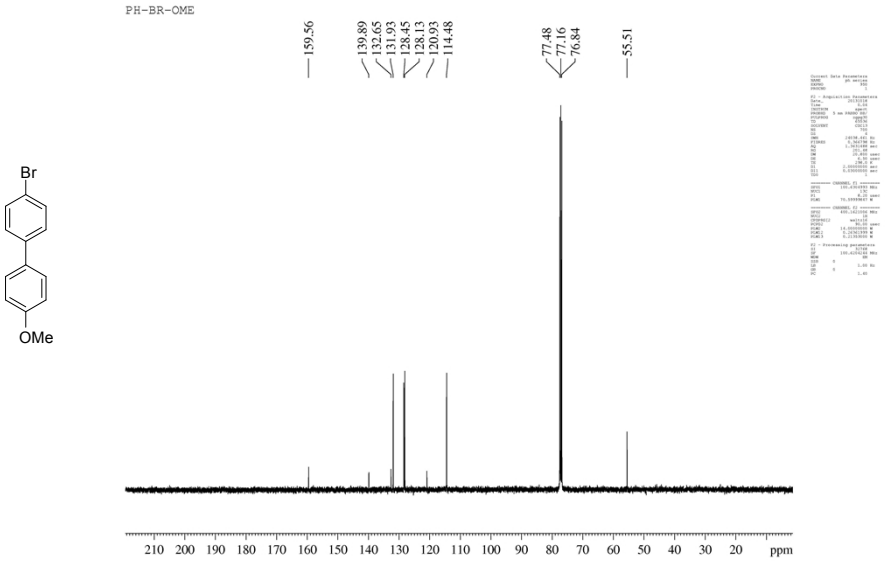

$^{1}$H NMR Spectra of (**3a)** (400 MHz, $CDCl_3$)



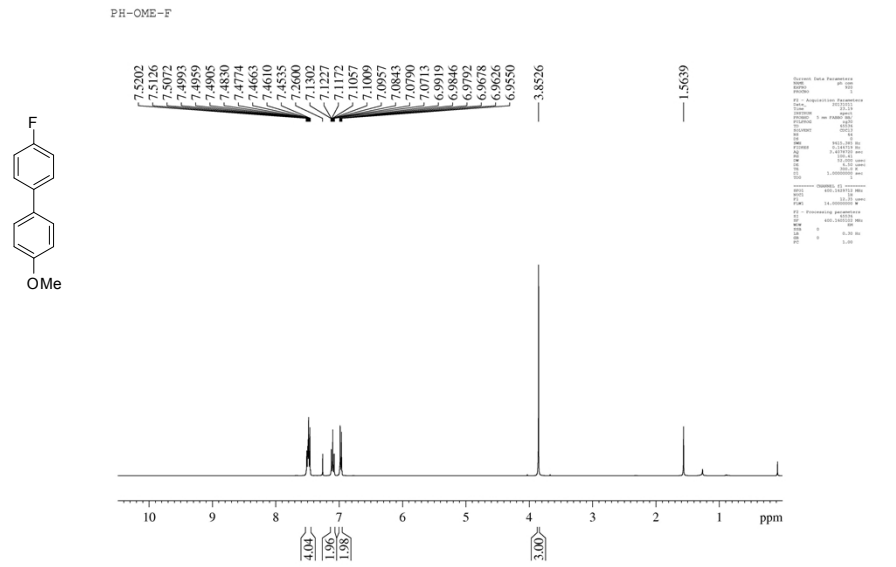

$^{13}$C NMR Spectra of (**3a)** (100 MHz, $CDCl_3$)



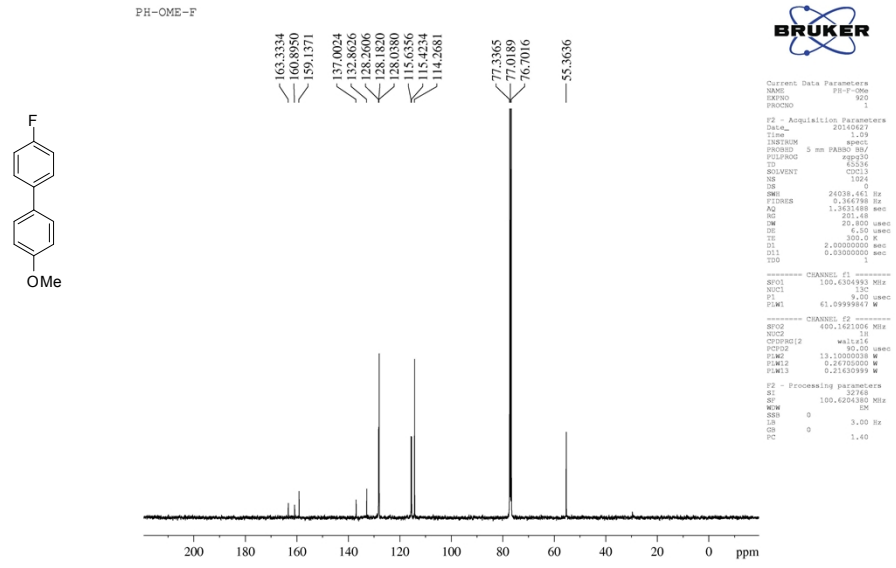

$^{1}$H NMR Spectra of (**3b)** (400 MHz, $CDCl_3$)



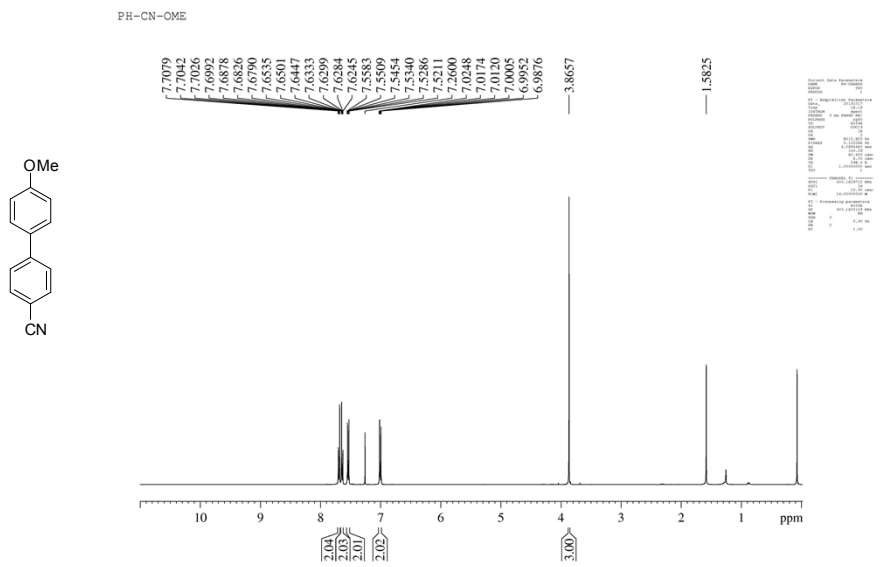

$^{13}$C NMR Spectra of (**3b)** (100 MHz, $CDCl_3$)



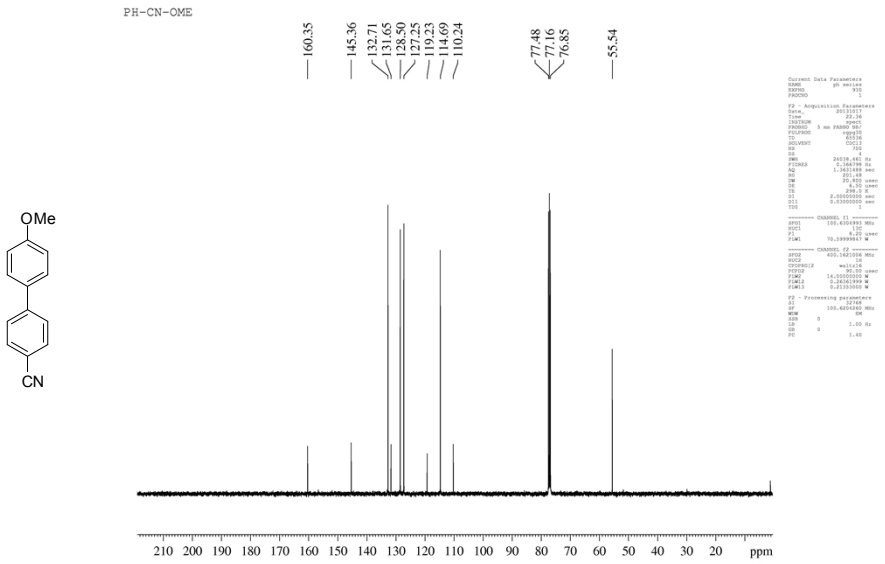

$^{1}$H NMR Spectra of (**3c)** (400 MHz, $CDCl_3$)



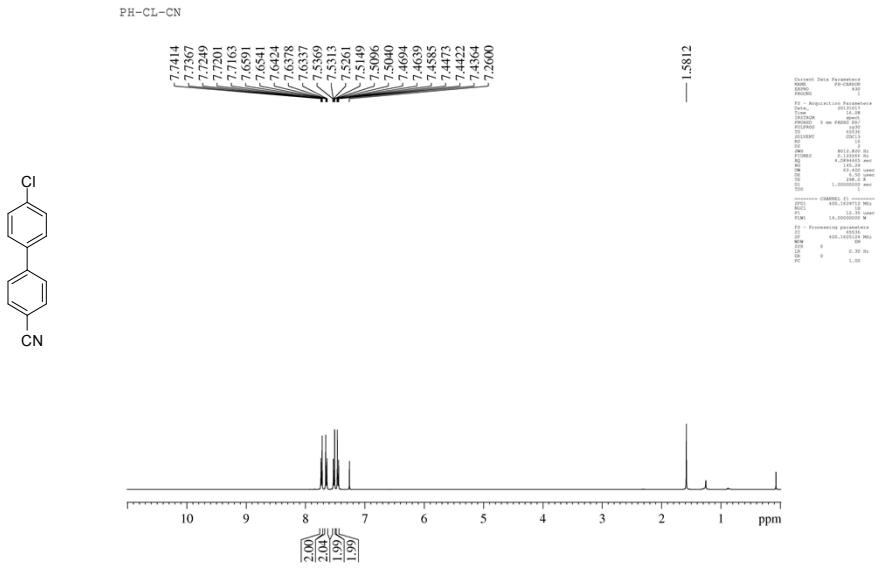

$^{13}$C NMR Spectra of (**3c)** (100 MHz, $CDCl_3$)




$^{1}$H NMR Spectra of (**3d)** (400 MHz, $CDCl_3$)




$^{13}$C NMR Spectra of (**3d)** (100 MHz, $CDCl_3$)

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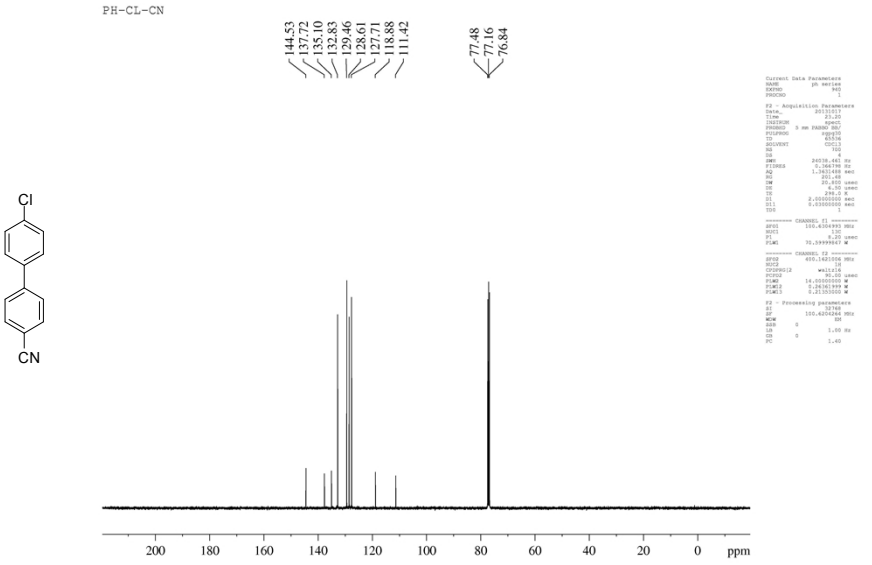


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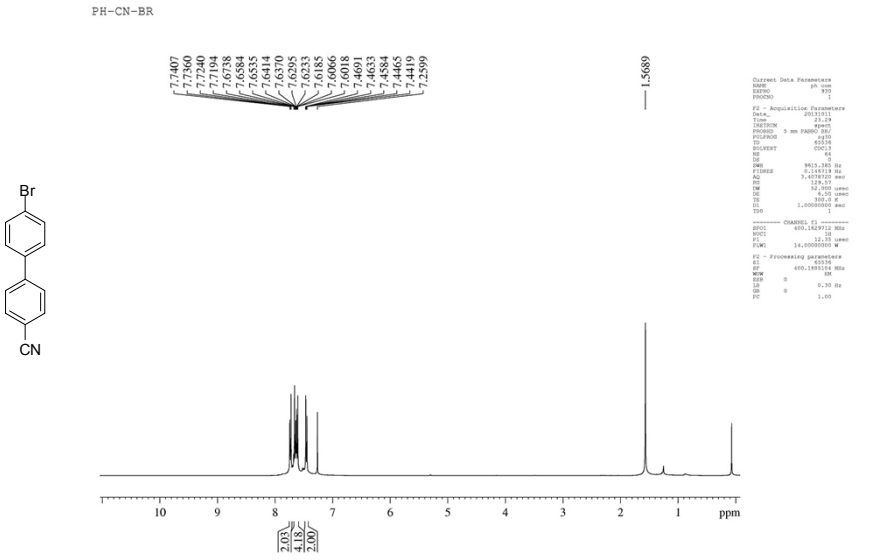
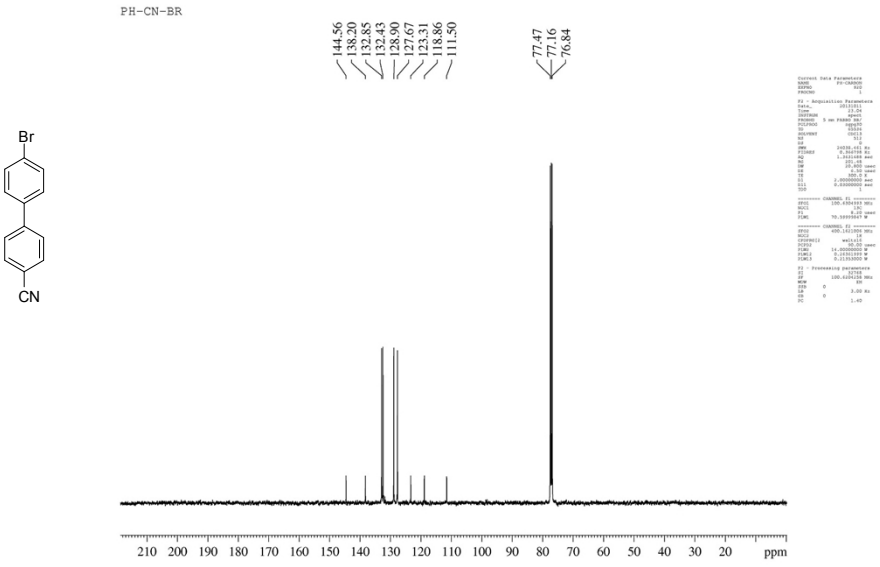



$^{1}$H NMR Spectra of (**3f)** (400 MHz, $CDCl_3$)

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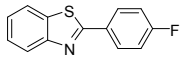
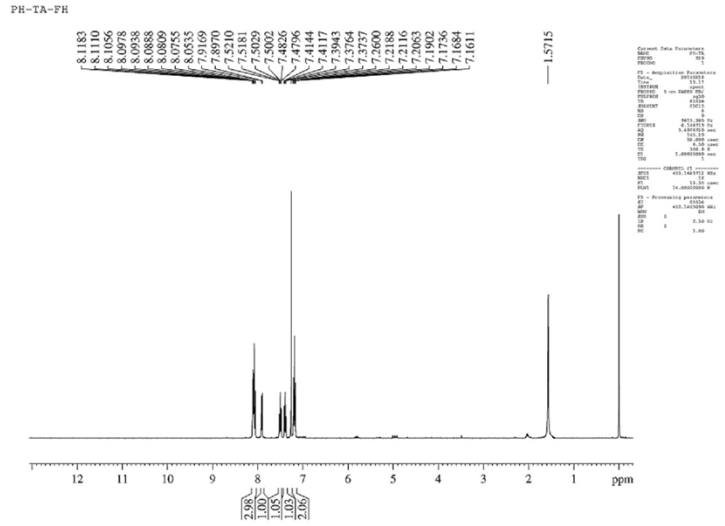
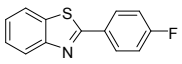
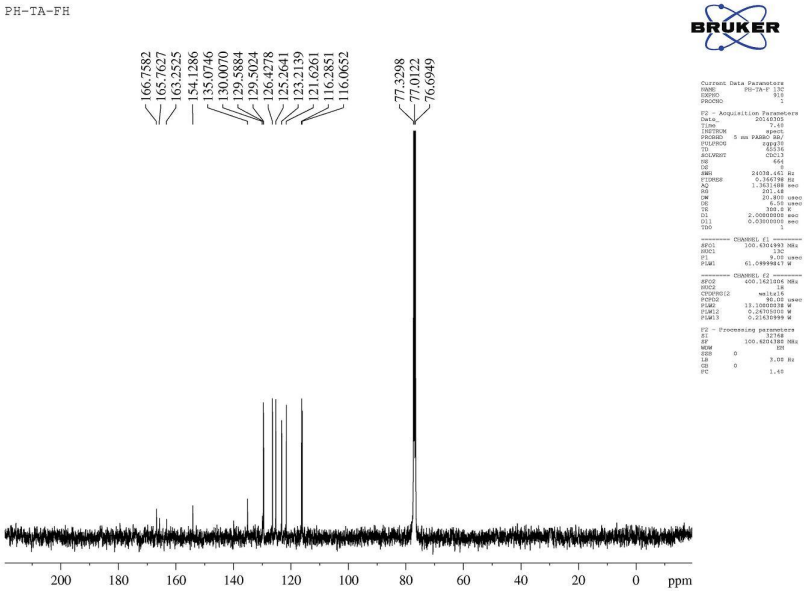



$^{1}H$ NMR Spectra of (**5**) (400 MHz, $CDCl_3$)




$^{13}C$ NMR Spectra of (**5**) (100 MHz, $CDCl_3$)