This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
Following updates to the general synthesis procedure.

Supporting Information

Recyclable LaF_3.Pd Nanocatalyst in Suzuki Coupling: Green Synthesis of Biaryls from Haloarenes and Phenylboronic acids

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[#]Equal contribution in the work

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Experimental Section

General Information

All the reagents and chemicals were procured from commercial sources like Sigma Aldrich, TCI, Avra, BLD pharm, Chemscene. Unless otherwise mentioned, all the chemicals were used without further purification. The reactions were monitored by thin layer chromatography (TLC plates, Aluminium Sheet Silica gel 60 F 254). Column chromatography was performed using 60-120 mesh silica gel, using a mixture of ethyl acetate and n-hexane as eluent. The spectra (^{1}H and ^{13}C) were recorded on a Bruker 400 MHz NMR spectrometer in $CDCl_3$ or a mixture of $CDCl_3$ and few drops of CD_3OD in tetramethylsilane as internal standard. Chemical shifts were reported in δ values, coupling constants *J* values were reported in ppm and Hz respectively.

Procedure for the synthesis of Pd-nanocatalyst

To a 250 ml round bottom flask added La_2O_3 (500 mg), $Pd(OAc)_2$ (36 mg), and dissolved with a minimum amount of concentrated HCl. The mixture was then diluted with 5ml water, and heated in a heating mental till dry. This step was followed three times until reddish colour appeared. Then 50 ml of ethylene glycol was added followed by 359 mg of NH_4F. To the mixture 1.2 ml of NH_4OH (50%) was added. The whole solution was taken in a Teflon lined autoclave and heated at 120 ^oC overnight. The reaction mixture was cooled down to room temperature and centrifuged three times using distilled water. Then the catalyst was washed two times with ethanol. The catalyst was dried in oven at 40-45 ^oC.

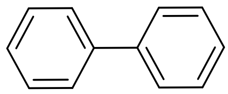
General procedure for the synthesis of Pd-nanocatalyzedbiaryls (3a-3v except 3f)

A 10 ml round bottom flask was charged with aryl bromides **1**(1.0 mmol) and phenylboronic acid **2** (1.5 mmol), 15 mg of LaF_3.Pd-nanocatalyst, K_2CO_3 (2.0 mmol), 3 ml H_2O and fitted with reflux condenser and stirred continuously at 70 ^oC for 4 hours. After completion of reaction (TLC monitor), the reaction mixture was cooled to room temperature and worked up with ethyl acetate and washed with water three times, then the organic portion was dried over Na_2SO_4 and concentrated under vacuum. The crude product was subjected to column chromatography to obtain the pure product. The aqueous layer was centrifuged to recover the catalyst.

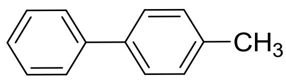
General procedure for the synthesis of 3f

A 10 ml round bottom flask was charged with aryl bromides **1**(1.0 mmol) and phenylboronic acid **2** (1.5 mmol), 15 mg of LaF_3.Pd nanocatalyst, K_2CO_3 (2.0 mmol), 2 ml H_2O and stirred continuously at room temperature for 1 hour. After completion of reaction, the reaction mixture was worked up with ethyl acetate and water three times, and then the combined organic portion was dried over Na_2SO_4 and concentrated under vacuum. The crude product was subjected to column chromatography to obtain **3f**.

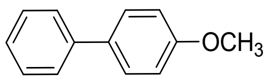
NMR data of the products



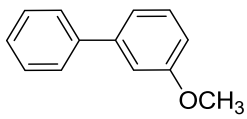
1,1'-biphenyl (3a):[1,2,3] white solid; 130 mg, (85%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 4H), 7.46 (t, J = 8.0 Hz, 4H), 7.38-7.35 (m, 2H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.4, 128.9, 127.4, 127.3 ppm.



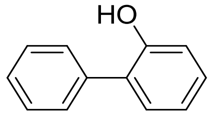
4-methyl-1,1'-biphenyl (3b):[1,2] white solid; 134 mg, (80%, **3b**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.3, 138.5, 137.2, 129.6, 129.6, 128.8, 127.1, 127.1, 21.2 ppm



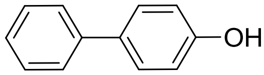
4-methoxy-1,1'-biphenyl (3c): [1,2] white solid; 142 mg, (77%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, J = 8.0 Hz, 4H), 7.42 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 6.98 (d, J = 12.0 Hz, 2H), 3.86 (s, 3H) ppm.



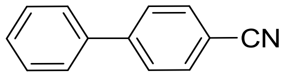
3-methoxy-1,1'-biphenyl (3d):[4] white solid; 156 mg, (85%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.38-7.31 (m, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 6.89 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 3.86 (s, 3H) ppm.



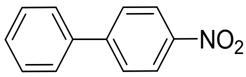
[1,1'-biphenyl]-2-ol (3e):[5] white solid; 134 mg, (79%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.56 (d, J = 4.0 Hz, 2H), 7.53-7.43 (m, 5H) ppm.



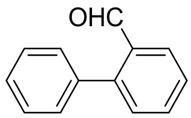
[1,1'-biphenyl]-4-ol (3f):[1] white solid; 164 mg, (97%) ^{1}H NMR (400 MHz, $CDCl_3$+ few drops of CD_3OD): δ 7.49 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H), 3.67 (s, 1H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$+ few drops of CD_3OD): δ156.3, 141.0, 132.8, 128.6, 128.1, 126.5, 126.4, 115.6 ppm.



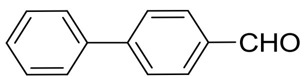
[1,1'-biphenyl]-4-carbonitrile (3g):[2] white solid; 134 mg, (75%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, J = 20.0 Hz, 8.0 Hz, 4H), 7.69 (d, J = 8.0 Hz, 2H), 7.50-7.47 (m, 2H), 7.44-7.41 (m, 1H) ppm.



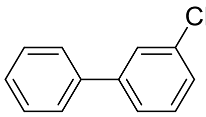
4-nitro-1,1'-biphenyl (3h):[1] white solid; 190 mg, (95%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.64-7.62 (m, 2H), 7.53-7.43 (m, 1H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ147.8, 147.2, 138.9, 129.3, 129.0, 127.9, 127.5, 124.2 ppm.



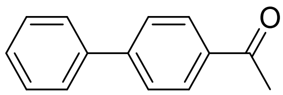
[1,1'-biphenyl]-2-carbaldehyde (3i):[6] white solid; 150 mg, (82%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.52-7.44 (m, 5H), 7.40-7.38 (m, 2H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.6, 146.1, 137.9, 133.9, 133.7, 130.9, 130.2, 128.6, 128.3, 127.9, 127.7 ppm.



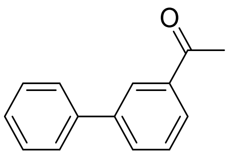
[1,1'-biphenyl]-4-carbaldehyde (3j):[7] white solid; 170 mg, (93%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.50-7.47 (m, 2H), 7.44-7.40 (m, 1H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.0, 147.3, 139.9, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5 ppm.



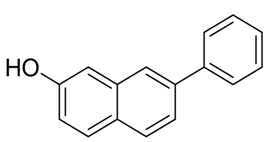
[1,1'-biphenyl]-3-carbaldehyde (3k):[8] white solid; 136 mg, (75%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.10-8.09 (m, 1H), 7.86-7.84 (m, 2H), 7.63-7.58 (m, 3H), 7.47 (t, J = 8.0 Hz, 2H), 7.41-7.37 (m, 1H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.5, 142.3, 139.8, 137.1, 133.2, 129.6, 129.1, 128.8, 128.3, 128.1, 127.3 ppm.



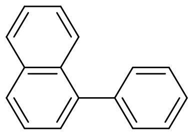
1-([1,1'-biphenyl]-4-yl)ethanone (3l):[3,8] white solid; 166 mg, (85%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.42-7.39 (m, 1H), 2.64 (s, 3H) ppm.^{13}C {^{1}H } NMR (100 MHz, $CDCl_3$): δ 197.9, 145.9, 140.0, 136.0, 129.1, 129.0, 128.4, 127.4, 127.37 ppm.



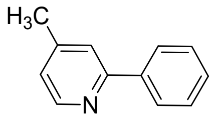
1-([1,1'-biphenyl]-3-yl)ethanone (3m):[9] white solid; 172 mg, (88%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H), 7.48-7.45 (m, 2H), 7.38 (t, J = 8.0 Hz, 1H), 2.66 (s, 3H) ppm. ^{13}C {^{1}H } NMR (100 MHz, $CDCl_3$): δ 198.3, 141.9, 140.3, 137.8, 131.9, 129.2, 129.1, 127.9, 127.3, 127.1, 26.9 ppm.



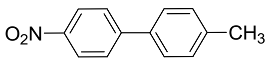
7-phenylnaphthalen-2-ol (3n):[11] white solid; 172 mg, (78%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.72-7,69 (m, 3H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.39-7.34 (m, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H) ppm.



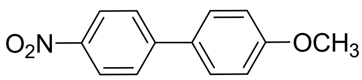
1-phenylnaphthalene (3o):[2] white solid; 138 mg, (68%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.89 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.55-7.48 (m, 6H), 7.44-7.41 (m, 3H) ppm.



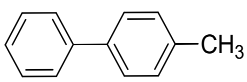
4-methyl-2-phenylpyridine (3p):[12] white solid; 112 mg, (66%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 8.0 Hz, 1H),7.97 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.42-7.39 (m, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 2.42 (s, 3H) ppm.



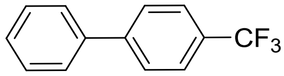
4-methyl-4'-nitro-1,1'-biphenyl (3q): [14] off white solid; 138 mg, (65%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 4.0 Hz, 2H), 2.42 (s, 3H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.6, 146.9, 139.1, 135.9, 129.9, 127.5, 127.2, 124.1, 21.2 ppm.



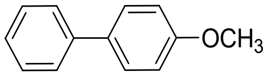
4-methoxy-4'-nitro-1,1'-biphenyl (3r):[15] off white solid, 160 mg, (70%) ^{1}H NMR (400 MHz, $CDCl_3$): δ8.27 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.5, 147.2, 146.6, 131.1, 128.6, 127.1, 124.1, 114.6, 55.4 ppm



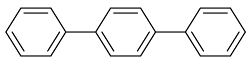
4-methyl-1,1'-biphenyl (3s):[1,2] white solid; 126 mg, (75%) ^{1}H and ^{13}C NMR spectra of **3b** and **3s** are identical.



4-(trifluoromethyl)-1,1'-biphenyl (3t):[13] white solid; 166 mg, (75%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 4H), 7.60 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 1H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.9, 139.9, 129.7, 129.3, 129.1, 128.3, 127.6, 127.4, 125.9, 125.8, 125.8, 125.8 ppm.



4-methoxy-1,1'-biphenyl (3u):[1,2] white solid; 143 mg, (78%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7. 56 (t, J = 8.0 Hz, 4H), 7.43 (t, J = 8.0 Hz, 2H), 7.33-7.30 (m, 1H) 6.99 (d, J = 4.0 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 140.9, 133.8, 128.7, 128.1, 126.8, 126.7, 114.2, 55.3 ppm.



1,1':4',1''-terphenyl (3v):[10] white solid; 154 mg, (67%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 4H), 7.66-7.44 (m, 4H), 7.46 (t, J = 8.0 Hz, 4H), 7.38-7.34 (m, 2H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.9, 140.3, 128.9, 127.6, 127.5, 127.2 ppm.

^{1}H NMR spectrum of **3a**

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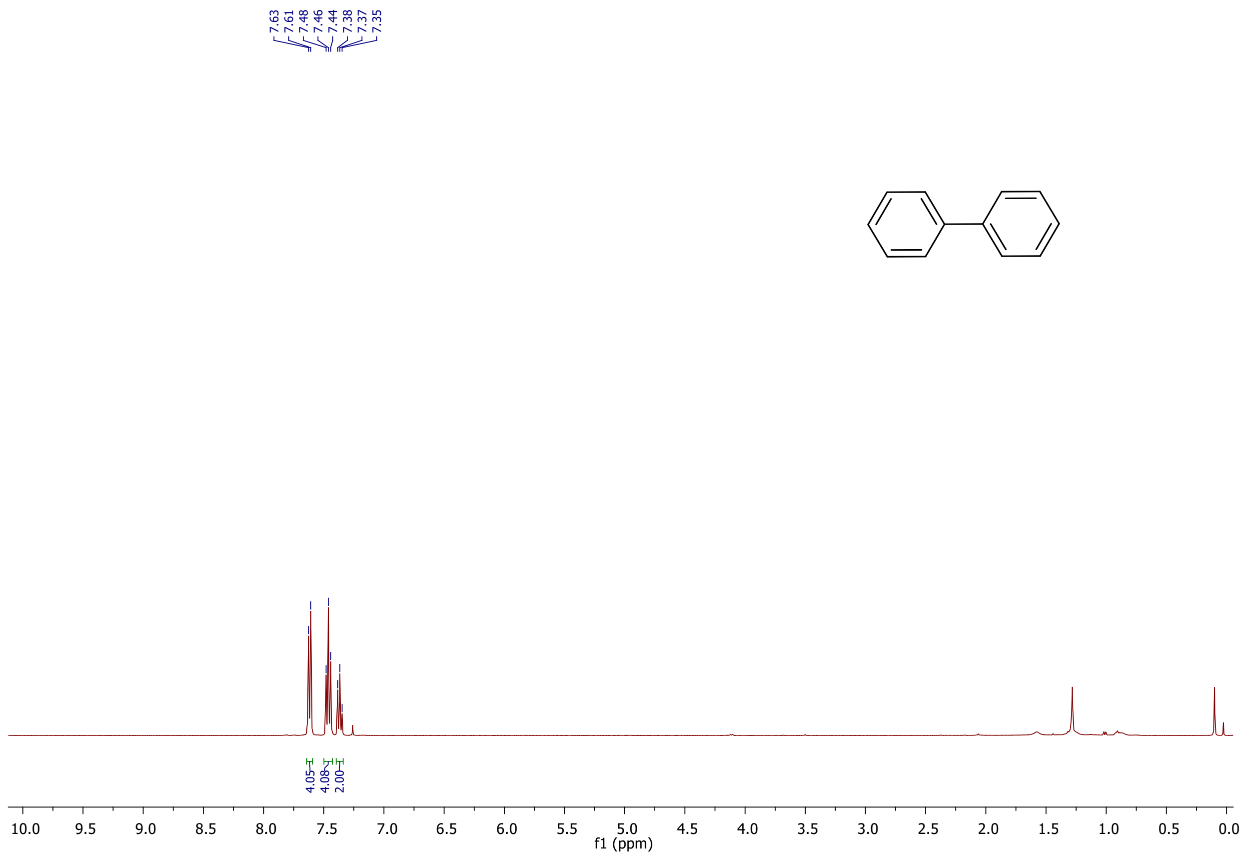

^{1}H NMR (400 MHz, $CDCl_3$)

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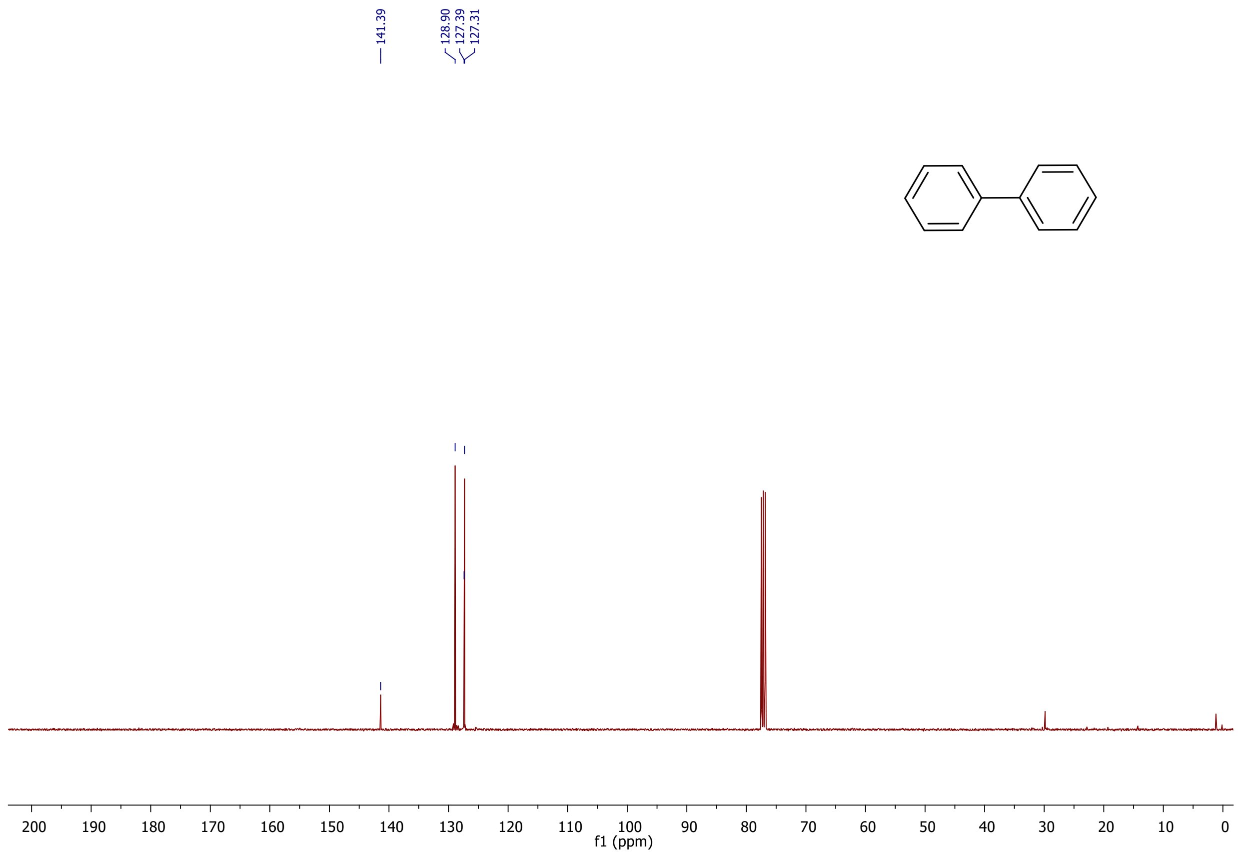
^{13}C NMR spectrum of **3a**



^{13}C NMR (100 MHz, $CDCl_3$)

^{1}H NMR spectrum of **3b**

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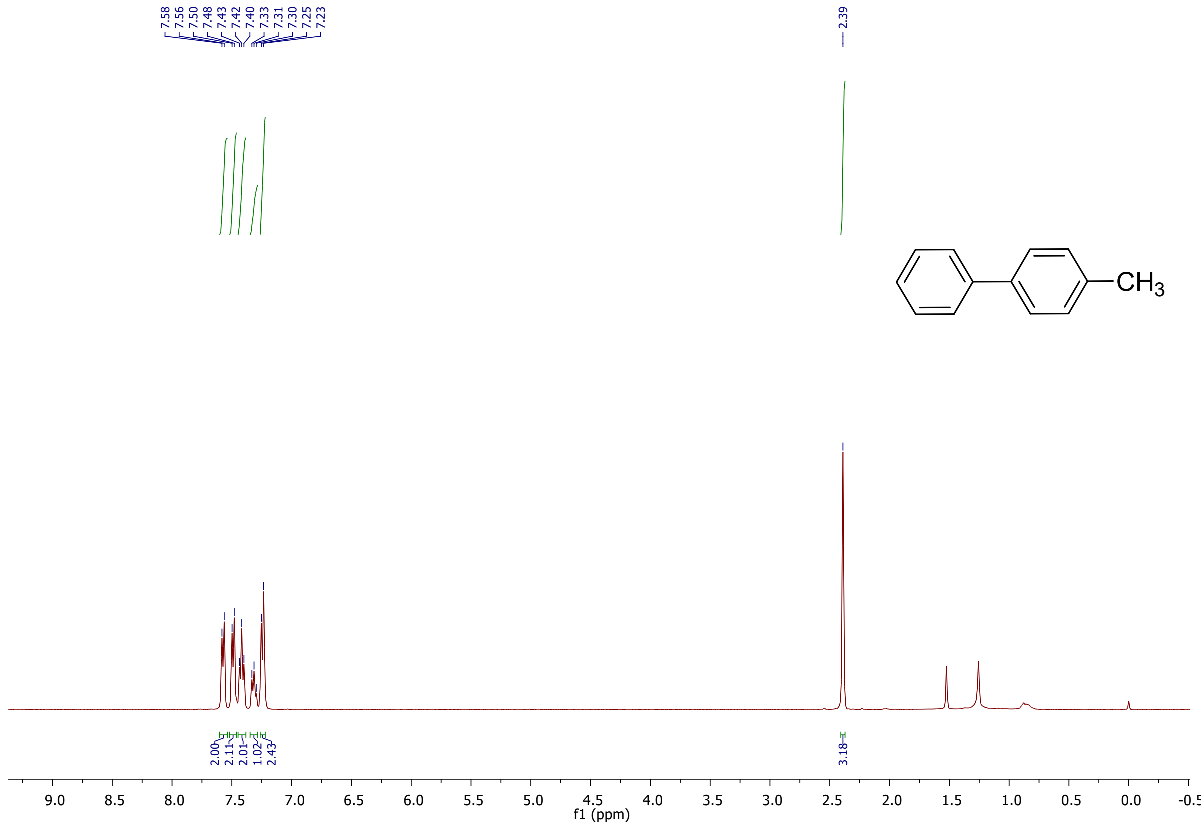

^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum of **3b**

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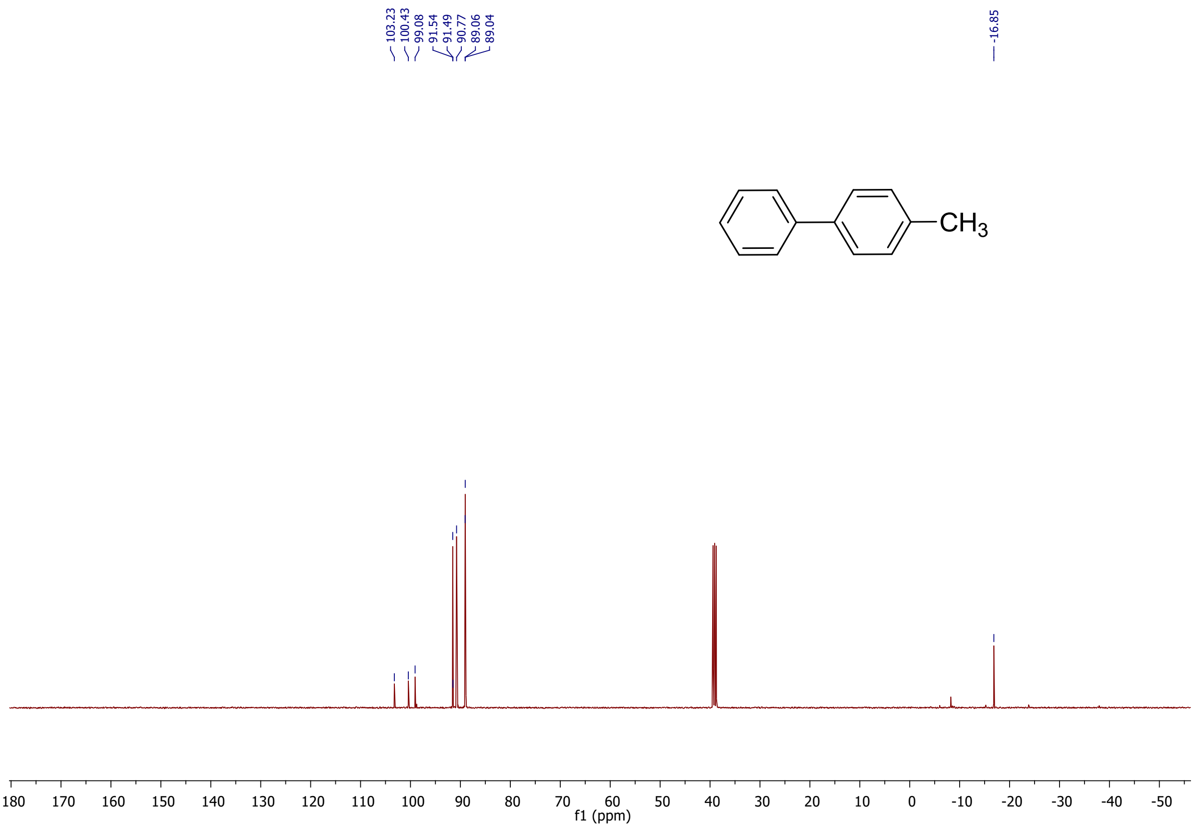

^{13}C NMR (100 MHz, $CDCl_3$)

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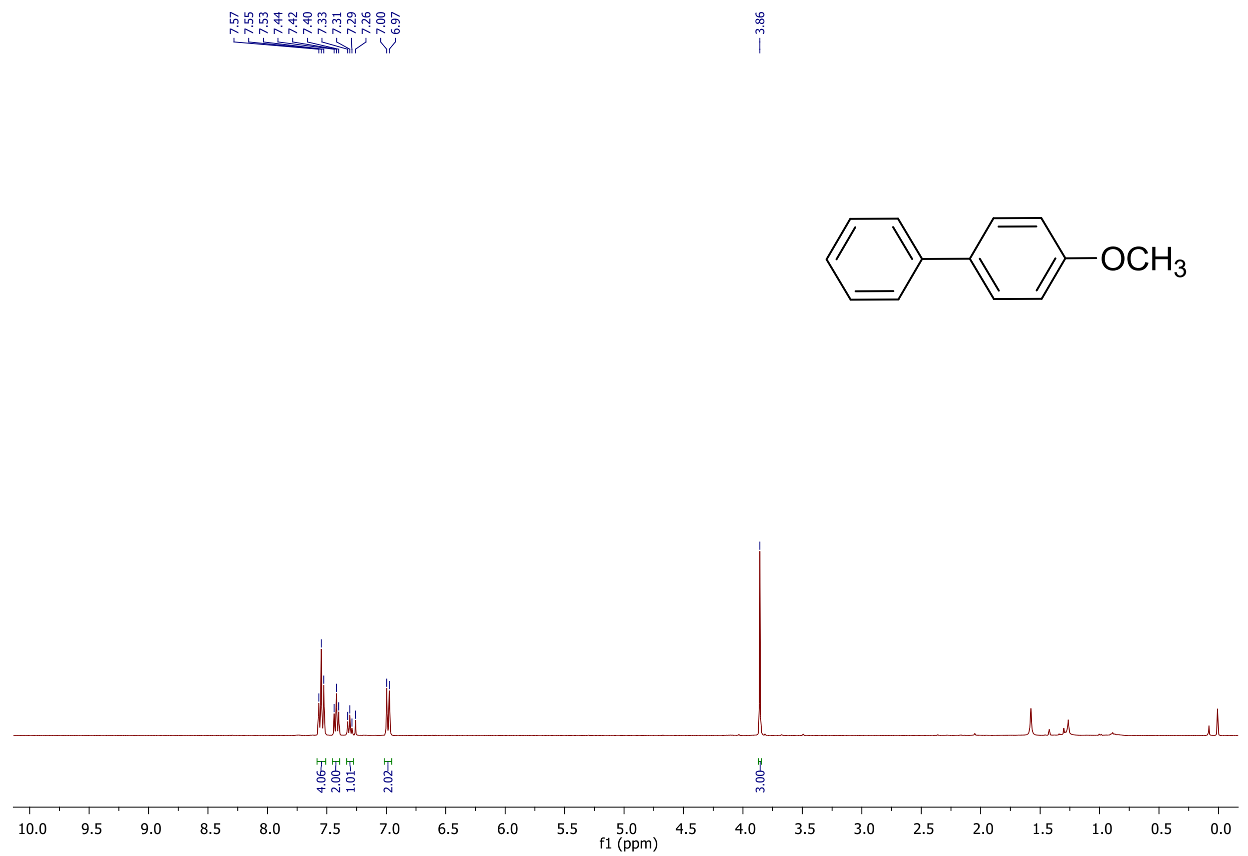
^{1}H NMR spectrum of **3c**



^{1}H NMR (400 MHz, $CDCl_3$)

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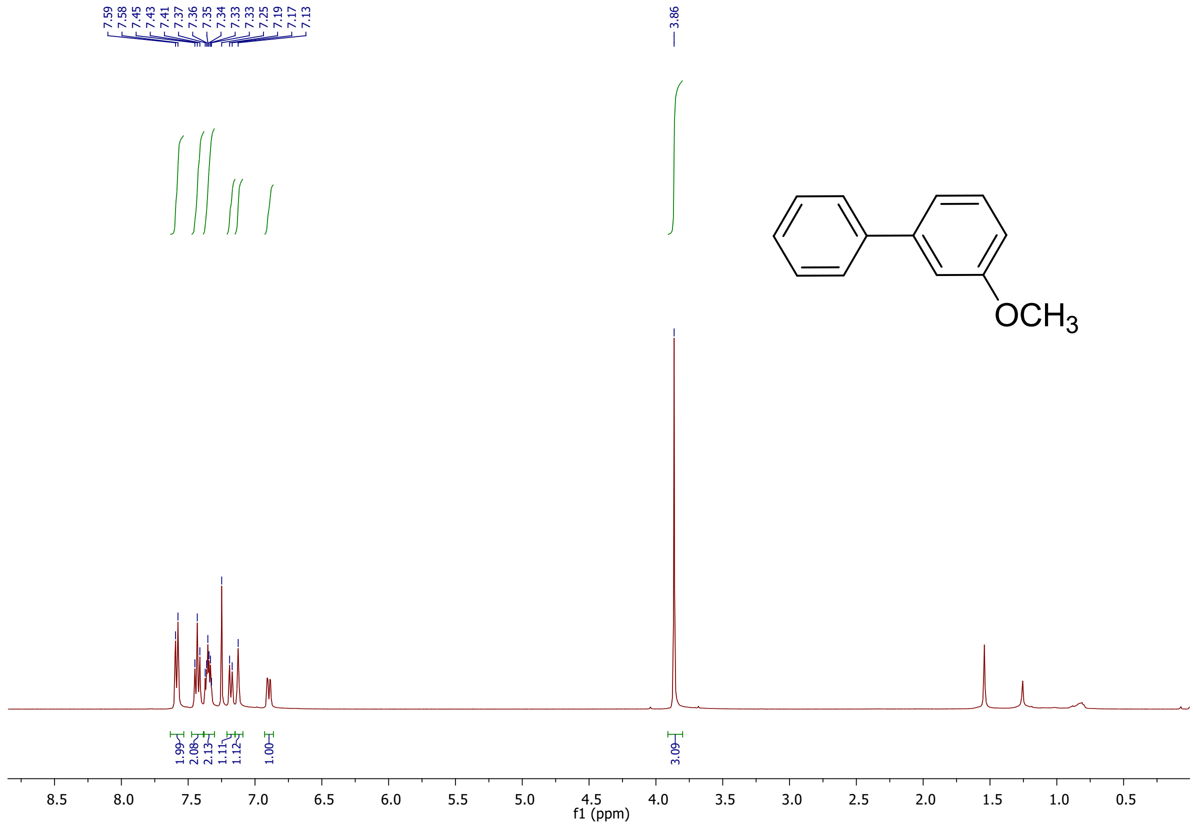
^{1}H NMR spectrum of **3d**



^{1}H NMR (400 MHz, $CDCl_3$)

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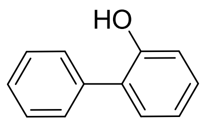
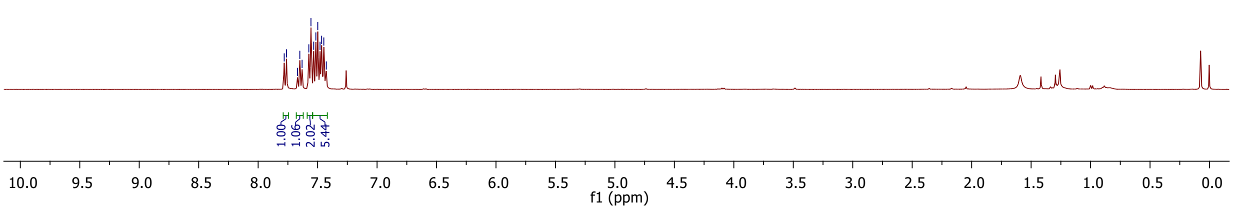
^{1}H NMR spectrum of **3e**





^{1}H NMR (400 MHz, $CDCl_3$)

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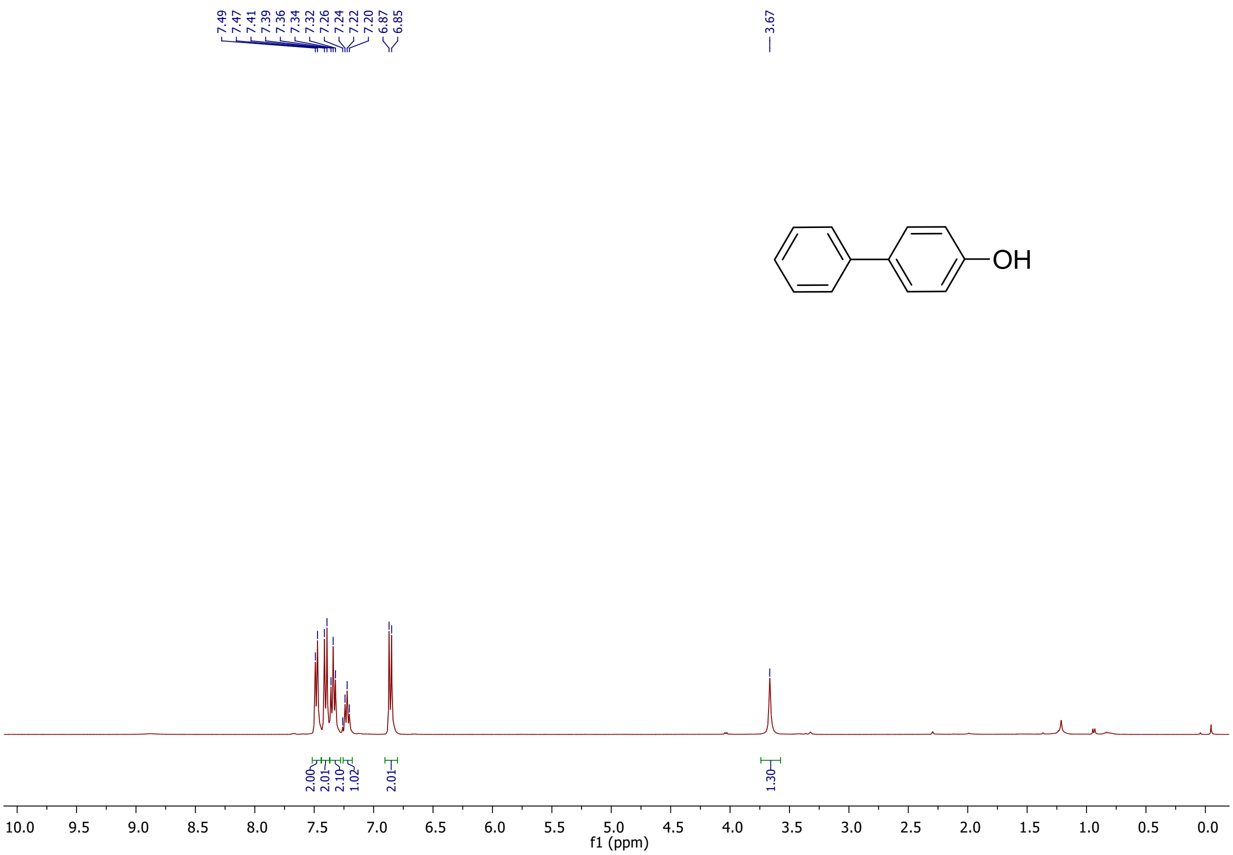
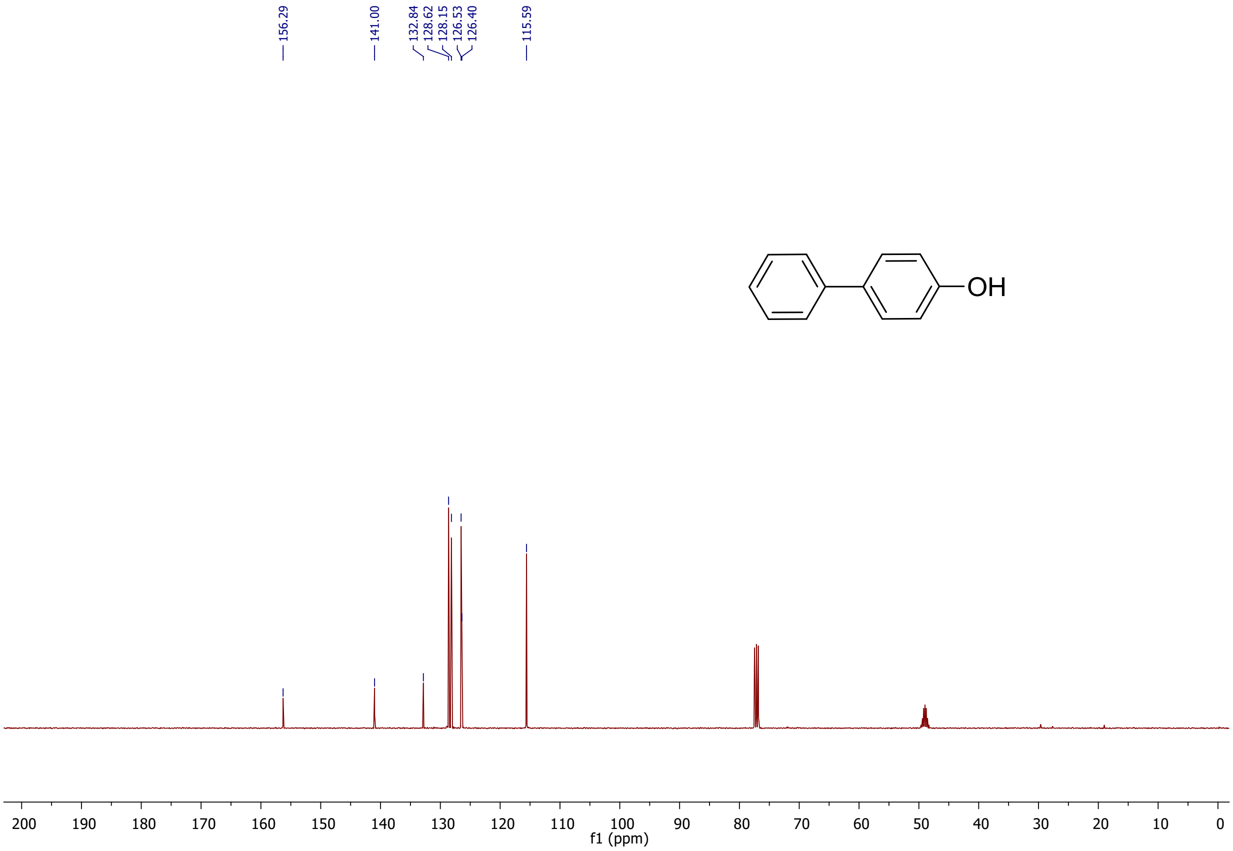
^{1}H NMR spectrum of **3f**



^{1}H NMR (400 MHz, $CDCl_3$+ few drops of CD_3OD)

This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
Following updates to the general synthesis procedure.

^{13}C NMR spectrum of **3f**



^{13}C NMR (100 MHz, $CDCl_3$+ few drops of CD_3OD)

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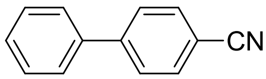
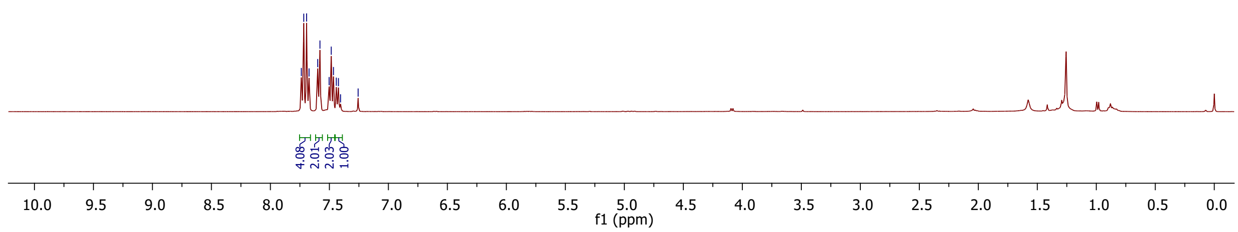
the original version published 5th of July 2024.
Following updates to the general synthesis procedure.

^{1}H NMR spectrum of **3g**





^{1}H NMR (400 MHz, $CDCl_3$)

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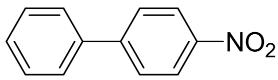
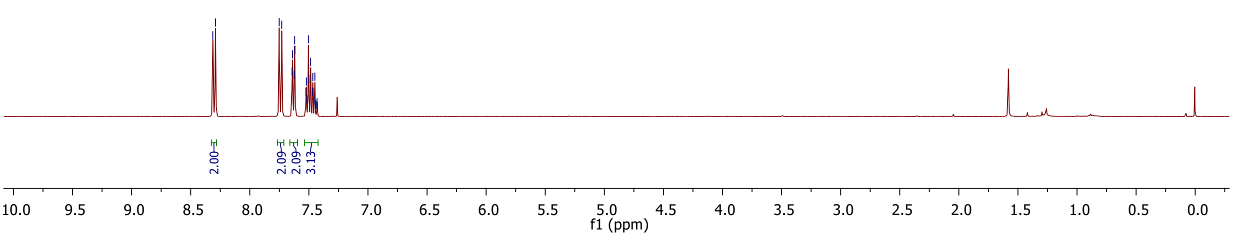
the original version published 5th of July 2024.
Following updates to the general synthesis procedure.

^{1}H NMR spectrum of **3h**





^{1}H NMR (400 MHz, $CDCl_3$)

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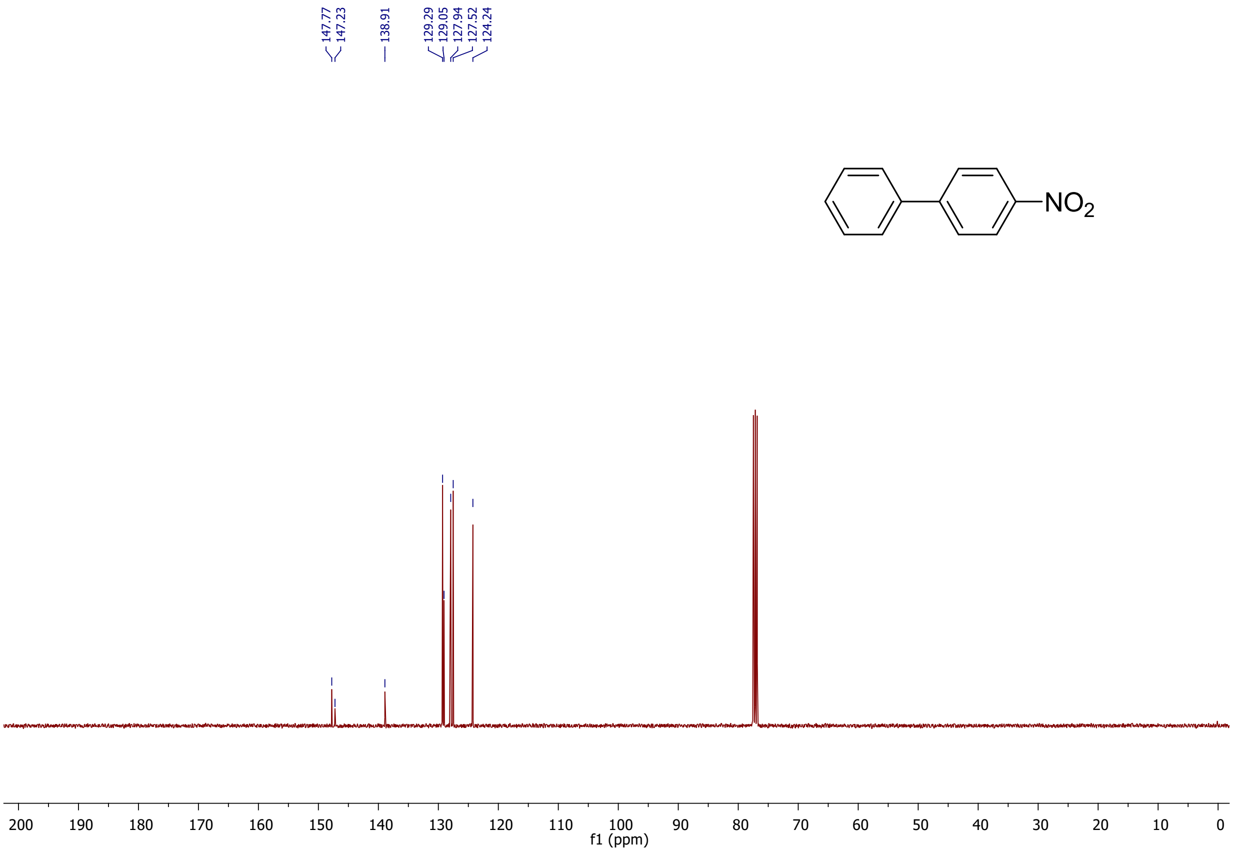
the original version published 5th of July 2024.
Following updates to the general synthesis procedure.

^{13}C NMR spectrum of **3h**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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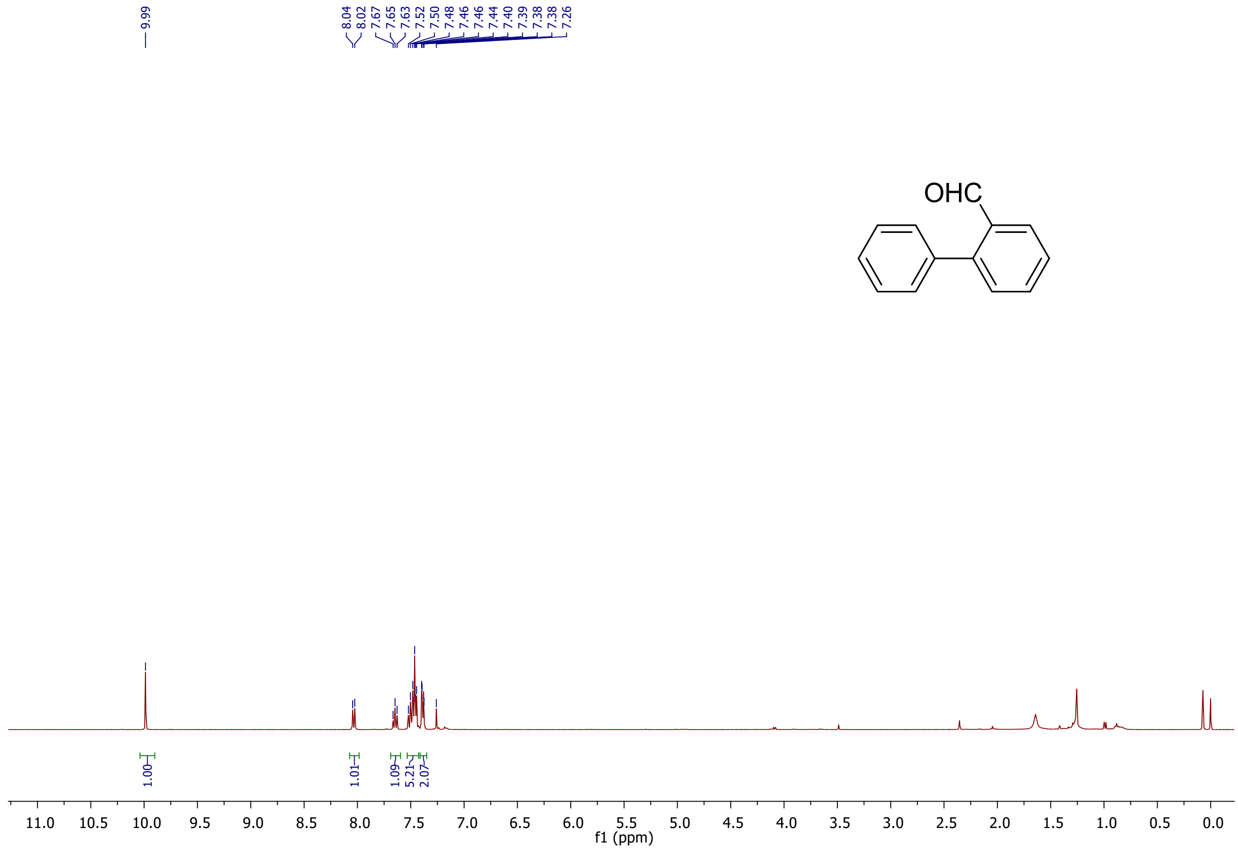
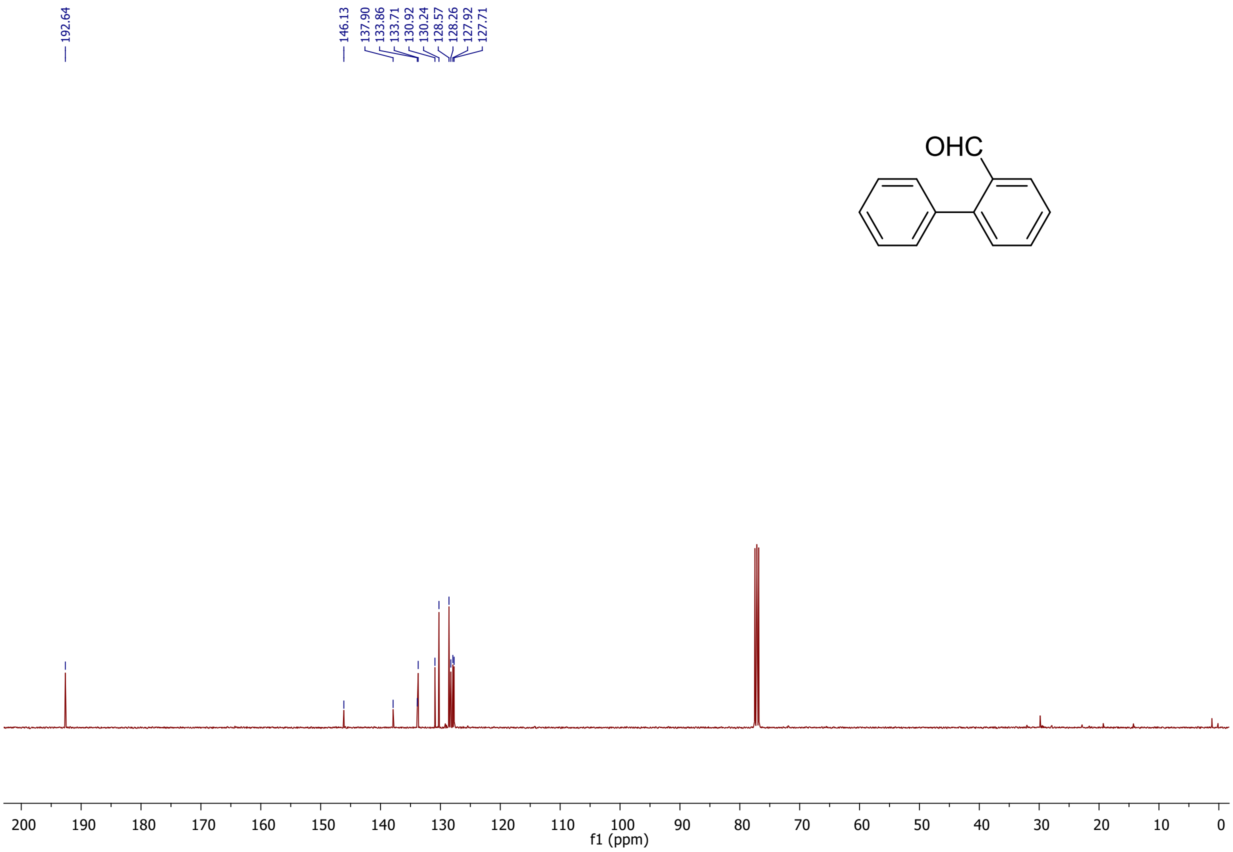
^{1}H NMR spectrum of **3i**



^{1}H NMR (400 MHz, $CDCl_3$)

This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
Following updates to the general synthesis procedure.

^{13}C NMR spectrum of **3i**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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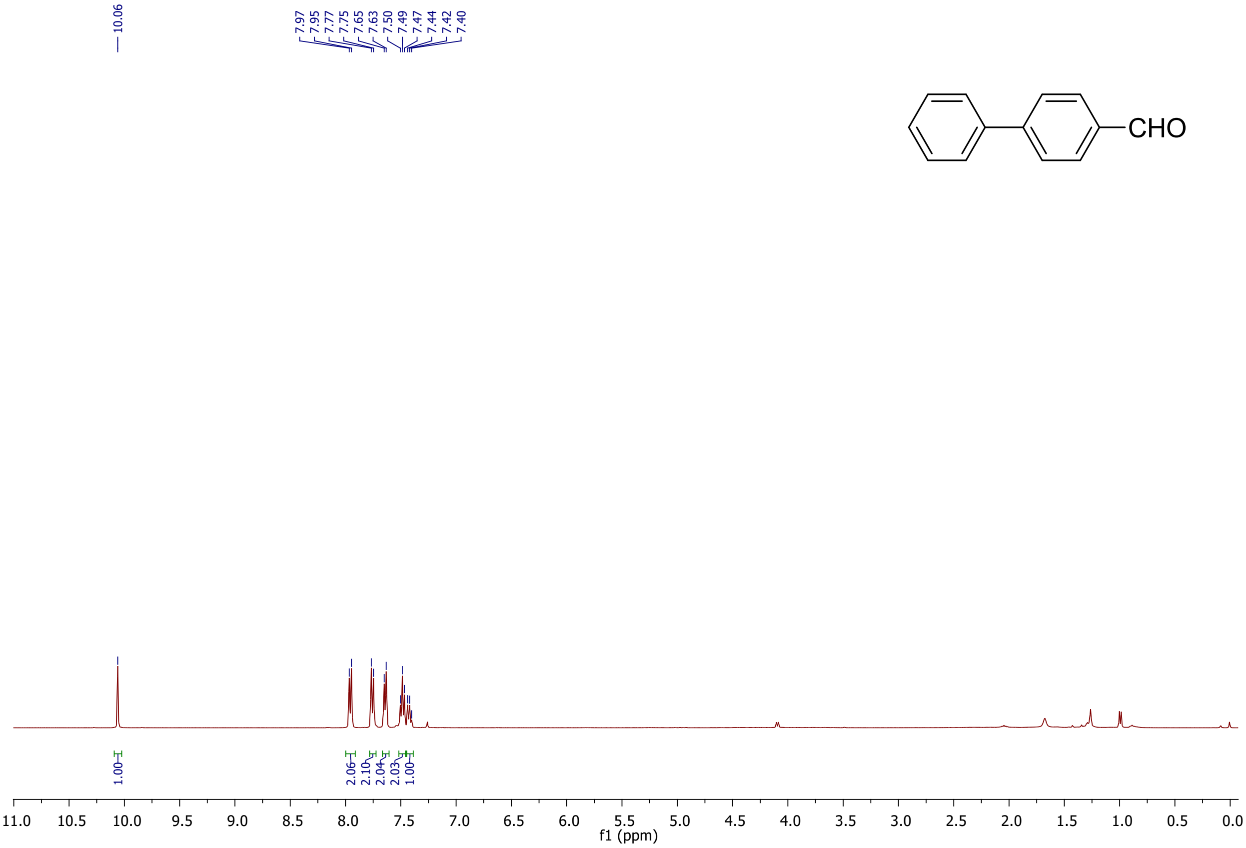
^{1}H NMR spectrum of **3j**



^{1}H NMR (400 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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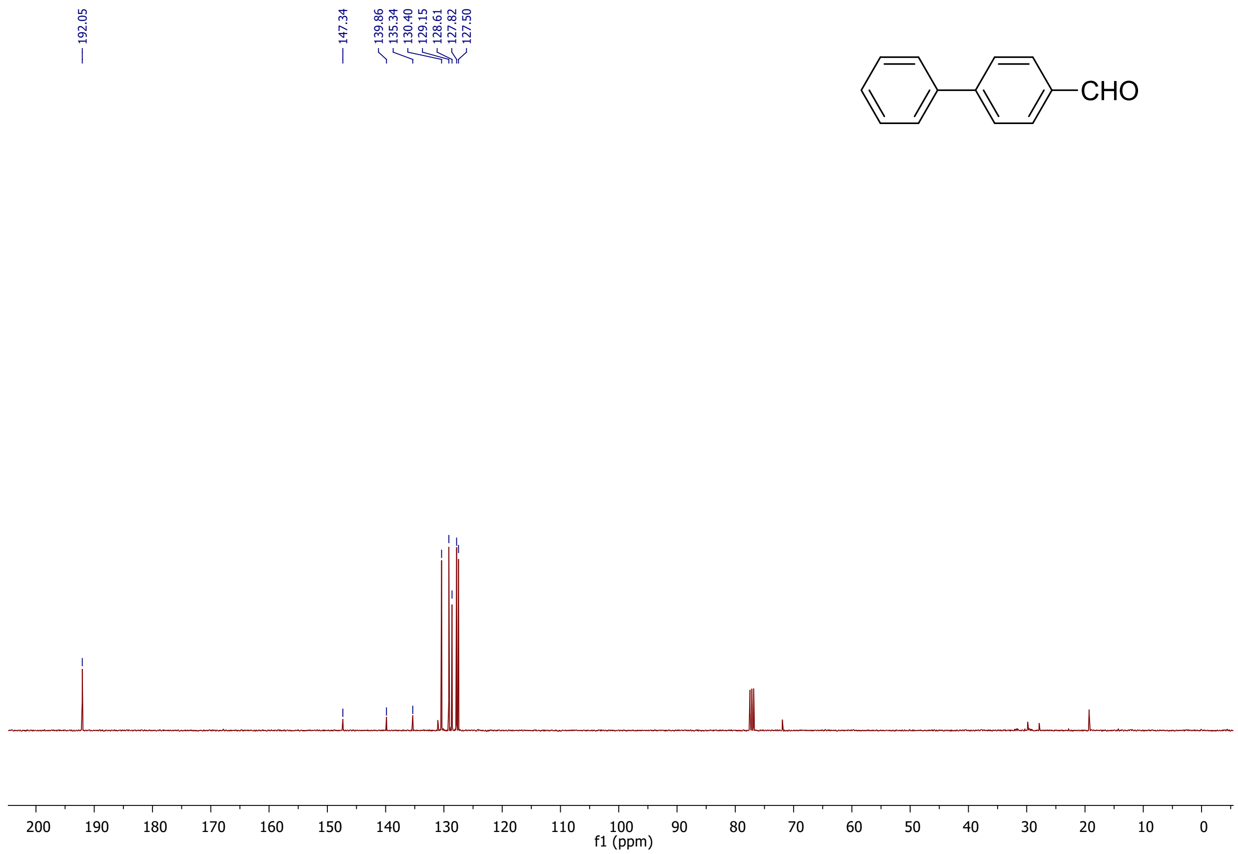
^{13}C NMR spectrum of **3j**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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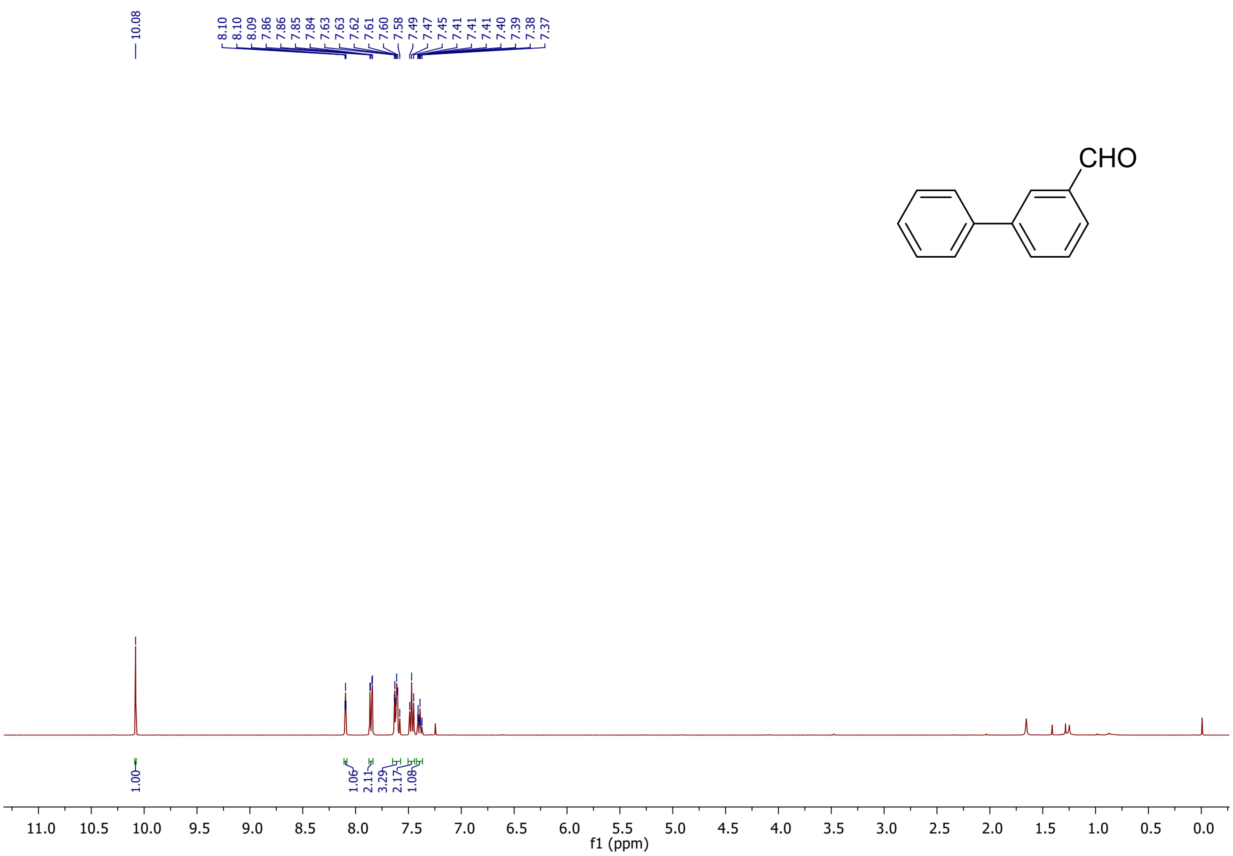
^{1}H NMR spectrum of **3k**



^{1}H NMR (400 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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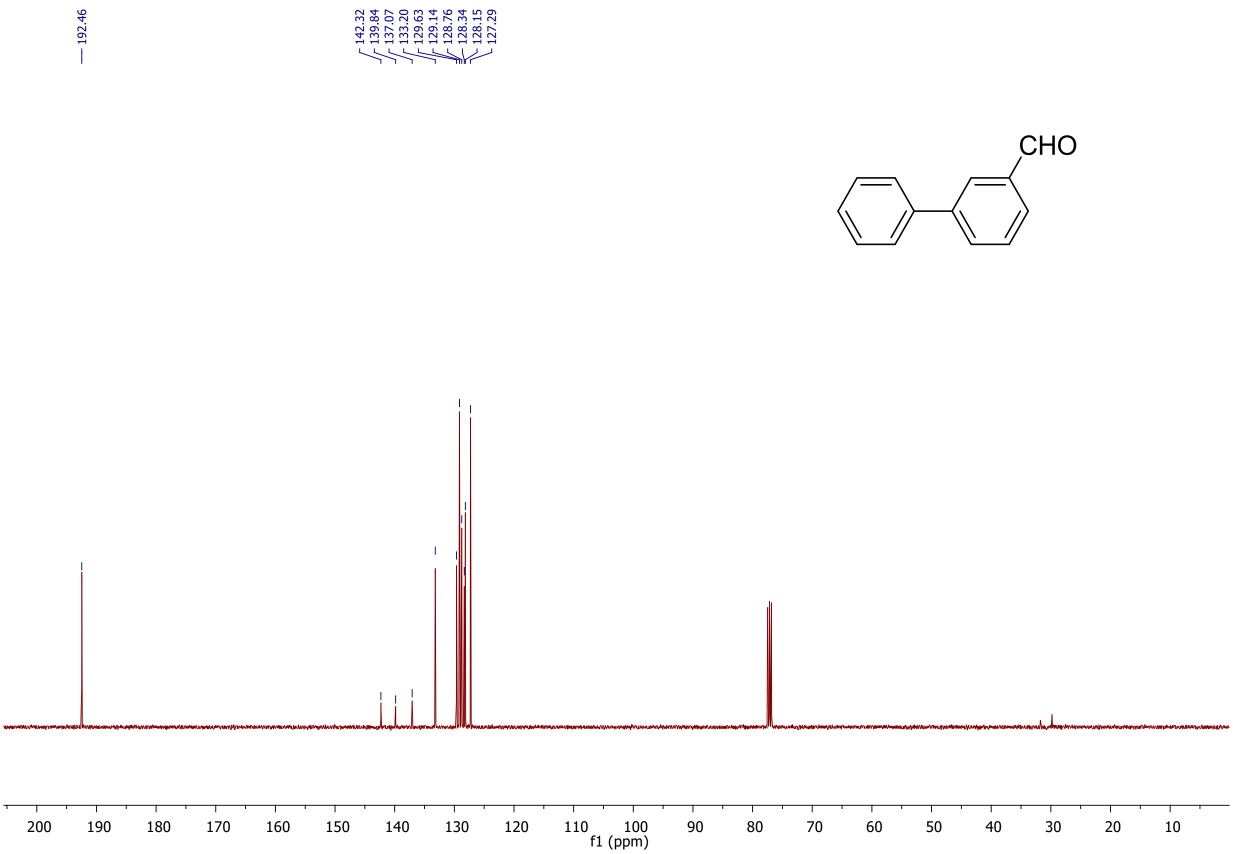
^{13}C NMR spectrum of **3k**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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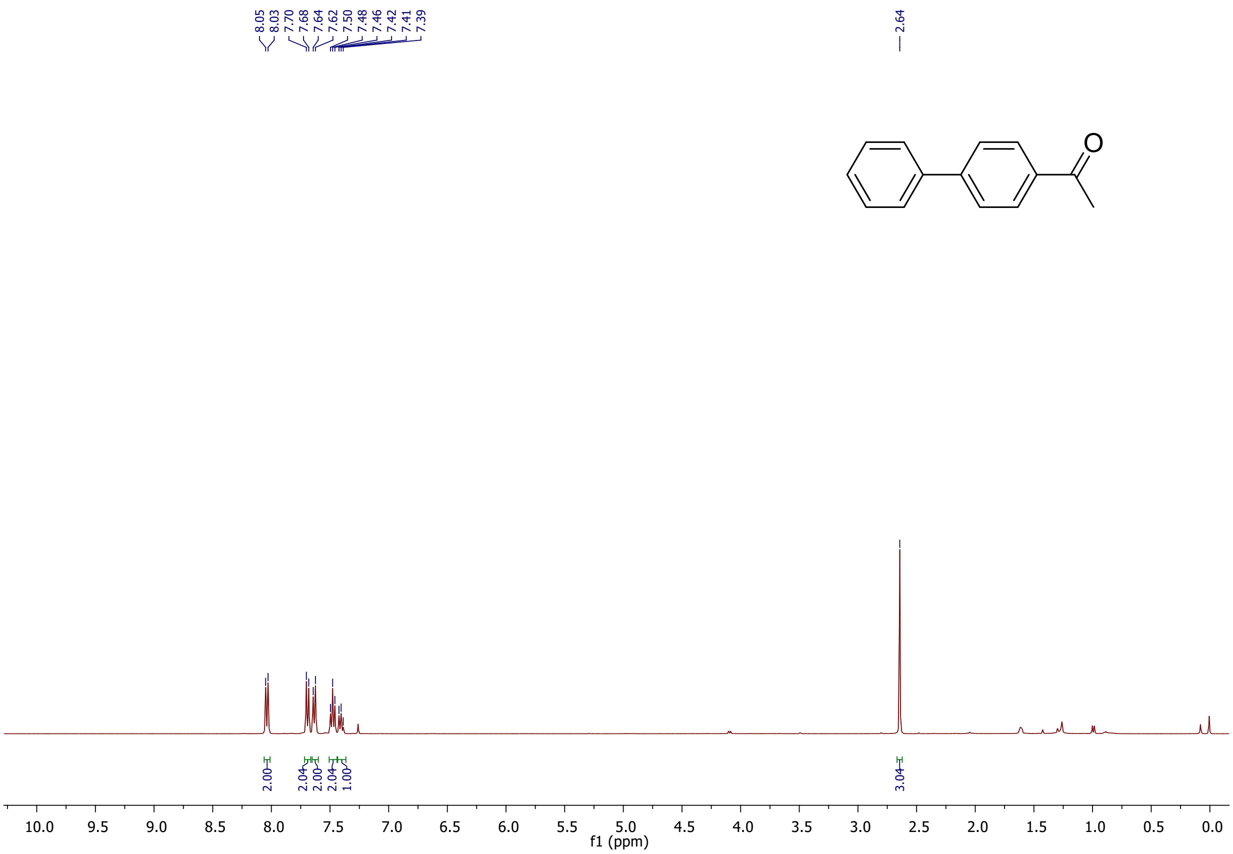
^{1}H NMR spectrum of **3l**



^{1}H NMR (400 MHz, $CDCl_3$)

This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
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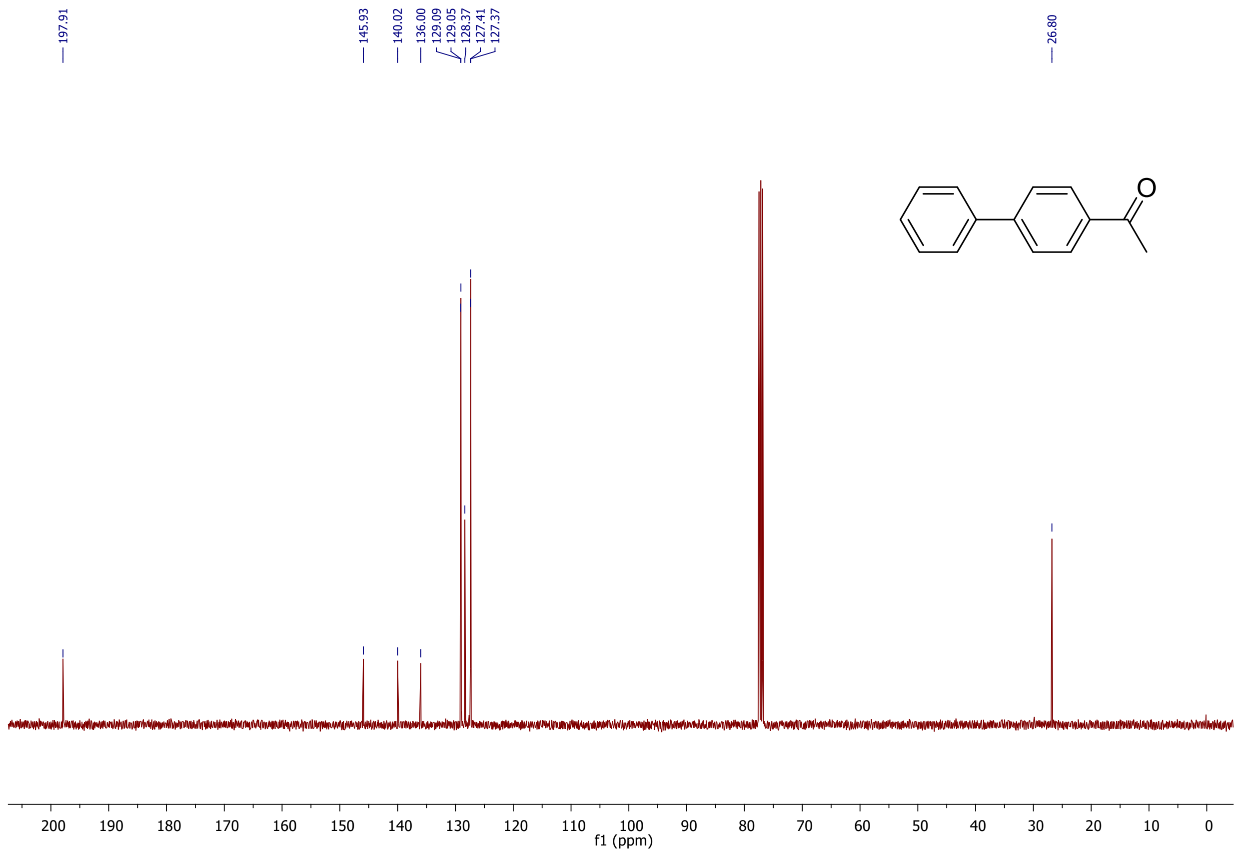
^{13}C NMR spectrum of **3l**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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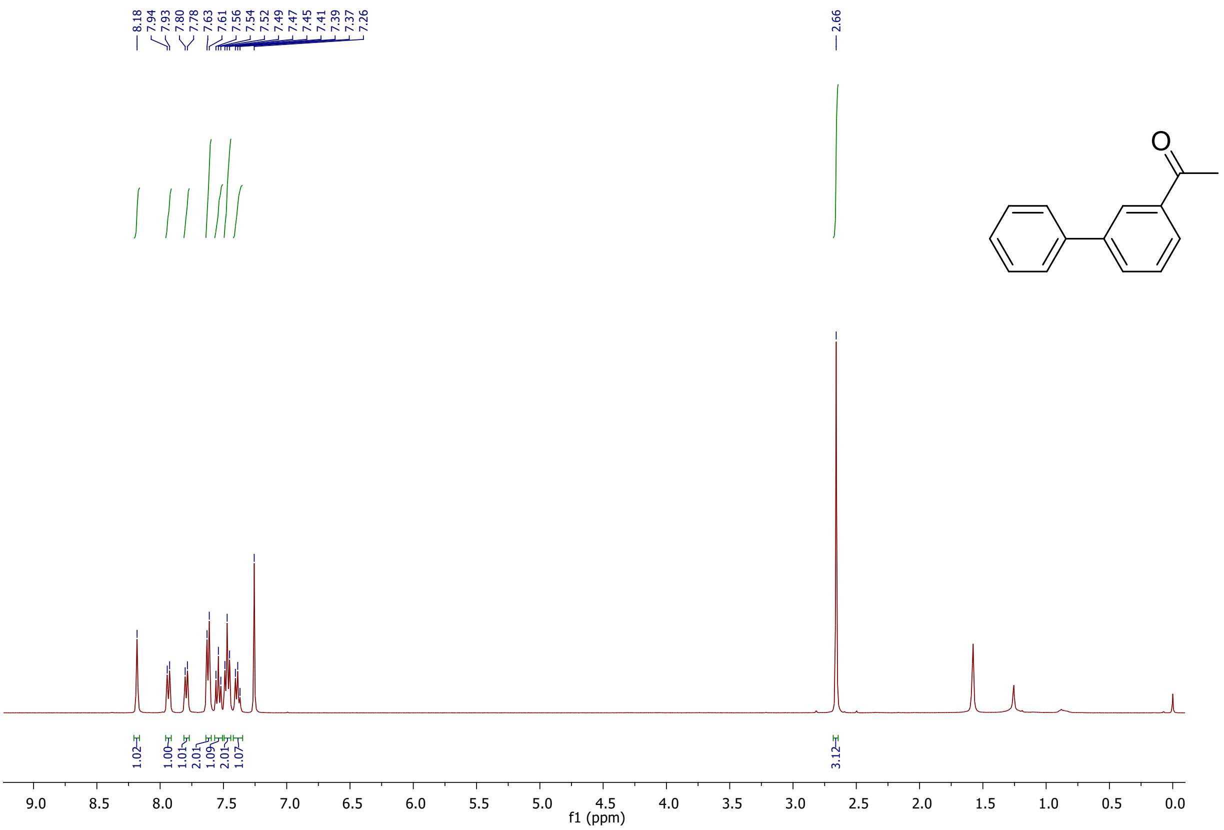
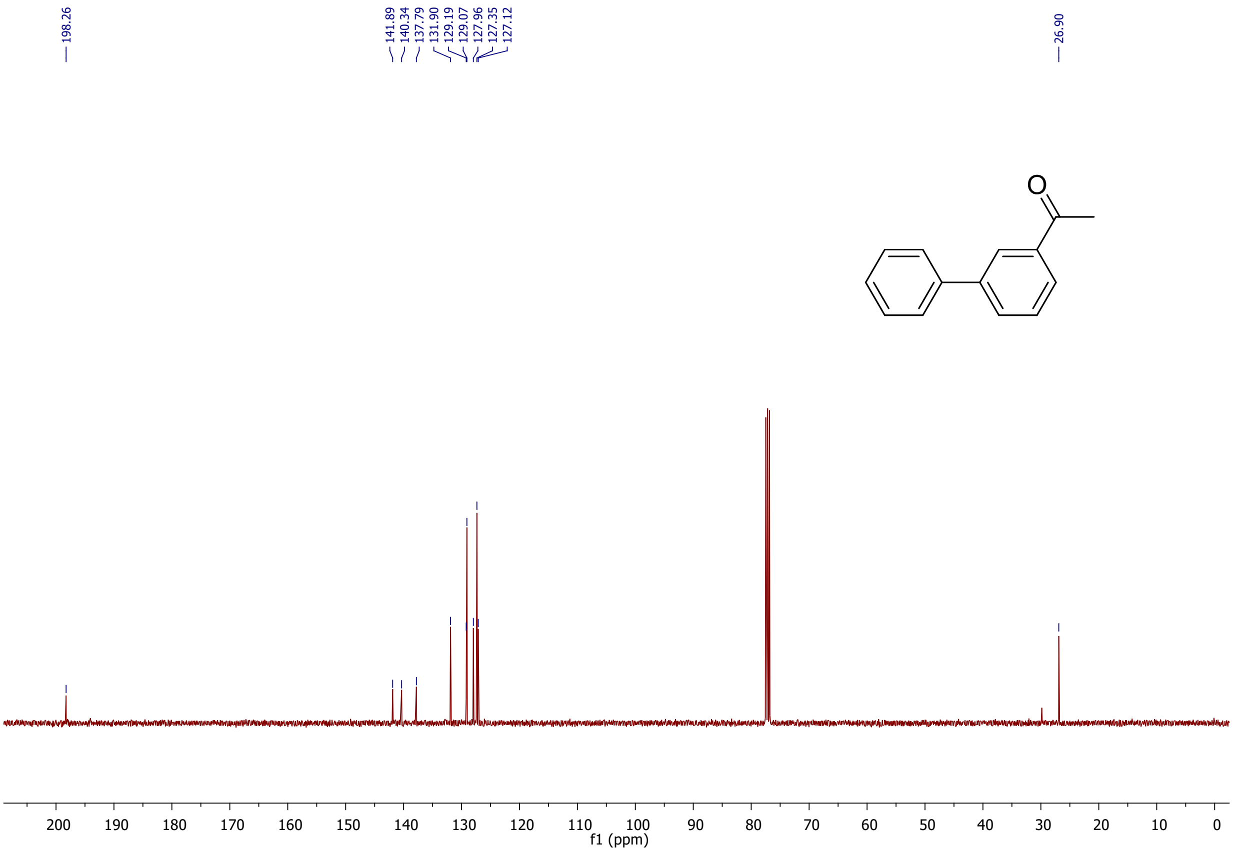
^{1}H NMR spectrum of **3m**



^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum of **3m**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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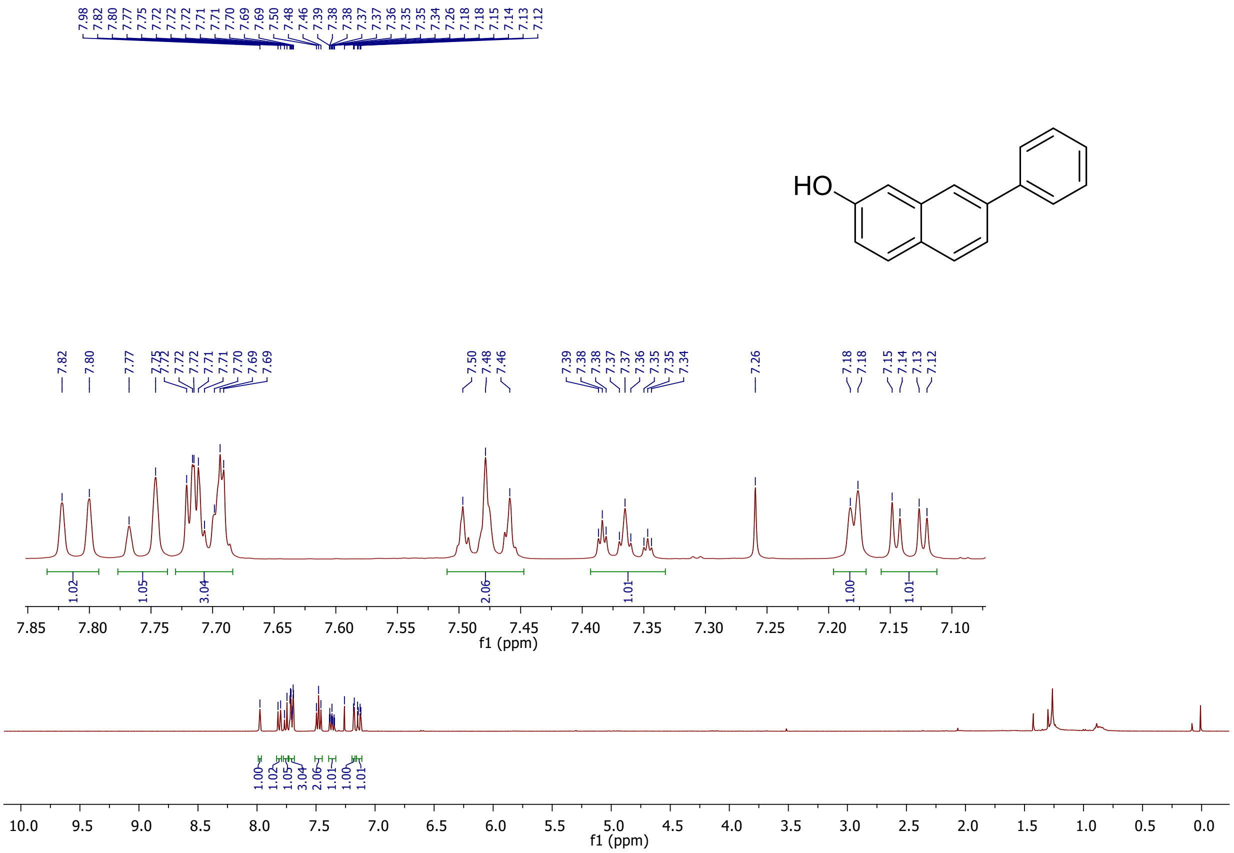
^{1}H NMR spectrum of **3n**



^{1}H NMR (400 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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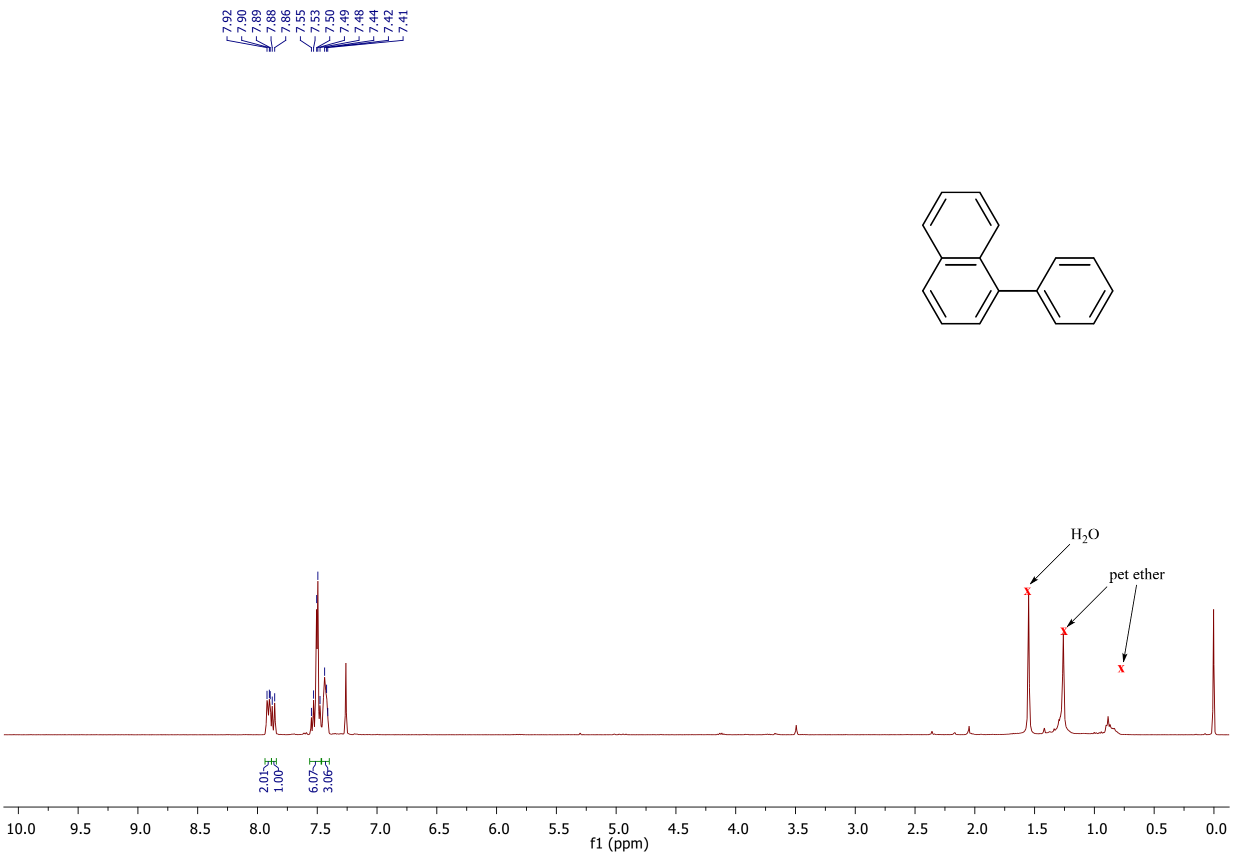
^{1}H NMR spectrum of **3o**



^{1}H NMR (400 MHz, $CDCl_3$)

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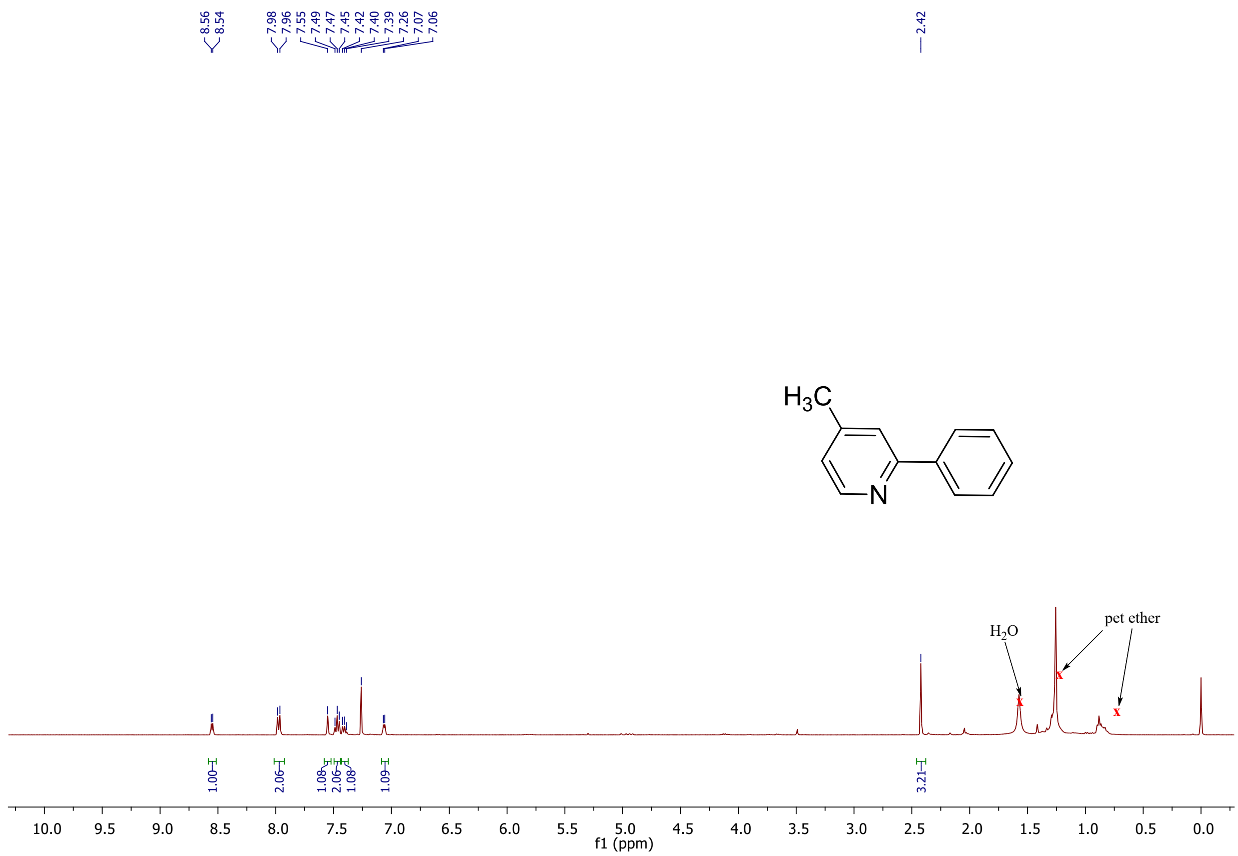
^{1}H NMR spectrum of **3p**



^{1}H NMR (400 MHz, $CDCl_3$)

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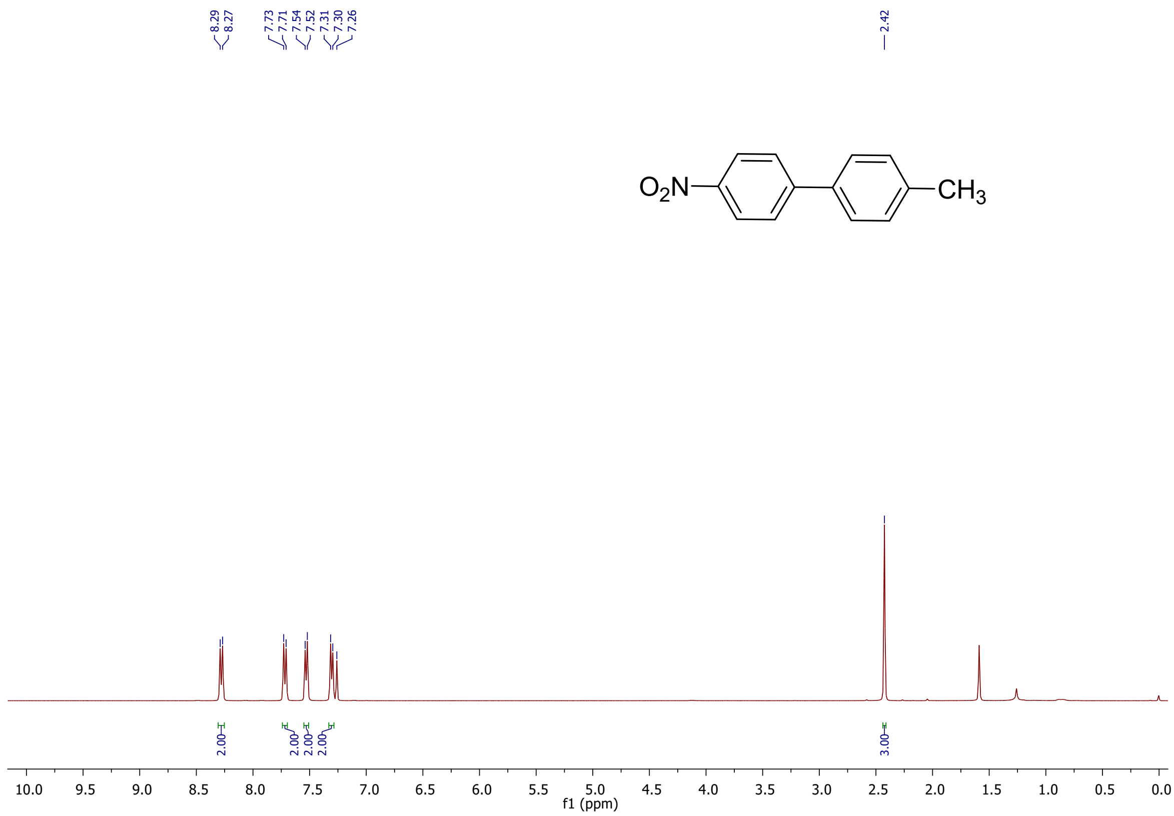
^{1}H NMR of **3q**



^{1}H NMR (400 MHz, $CDCl_3$)

This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
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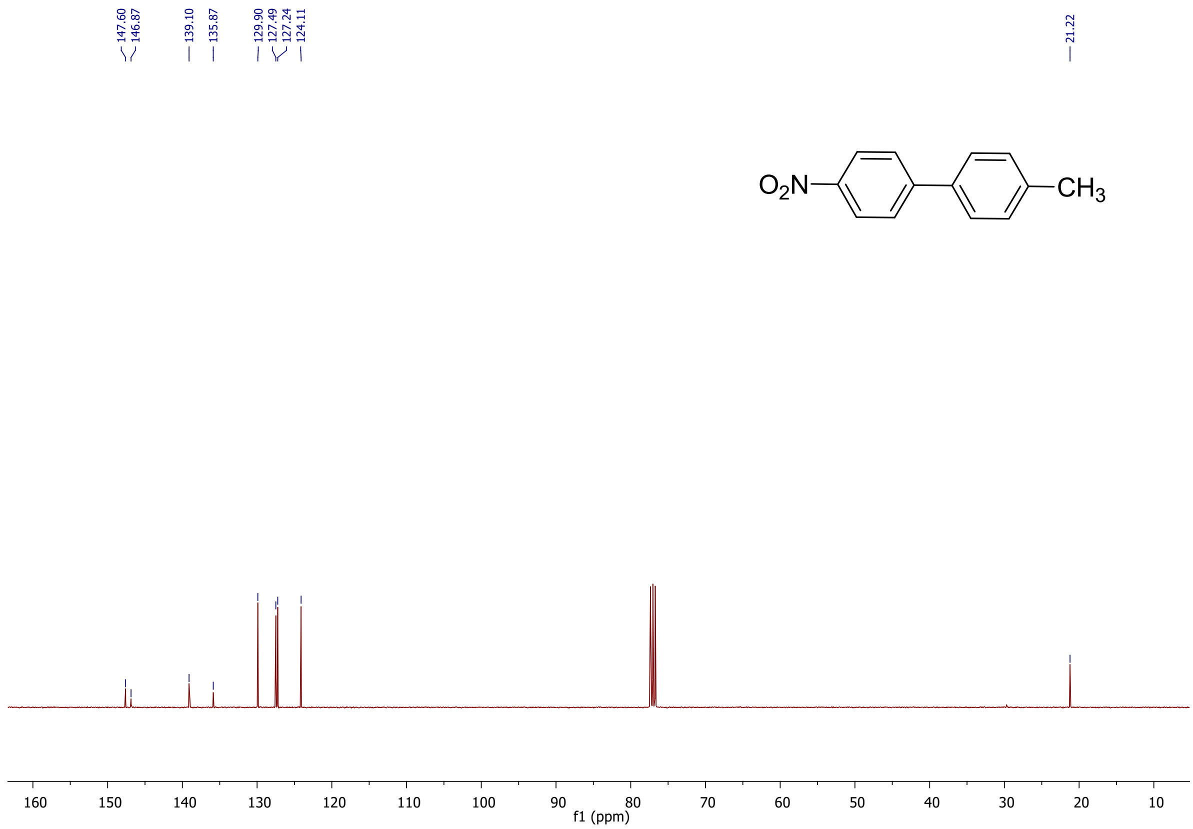
^{13}C NMR spectrum of **3q**



^{13}C NMR (100 MHz, $CDCl_3$)

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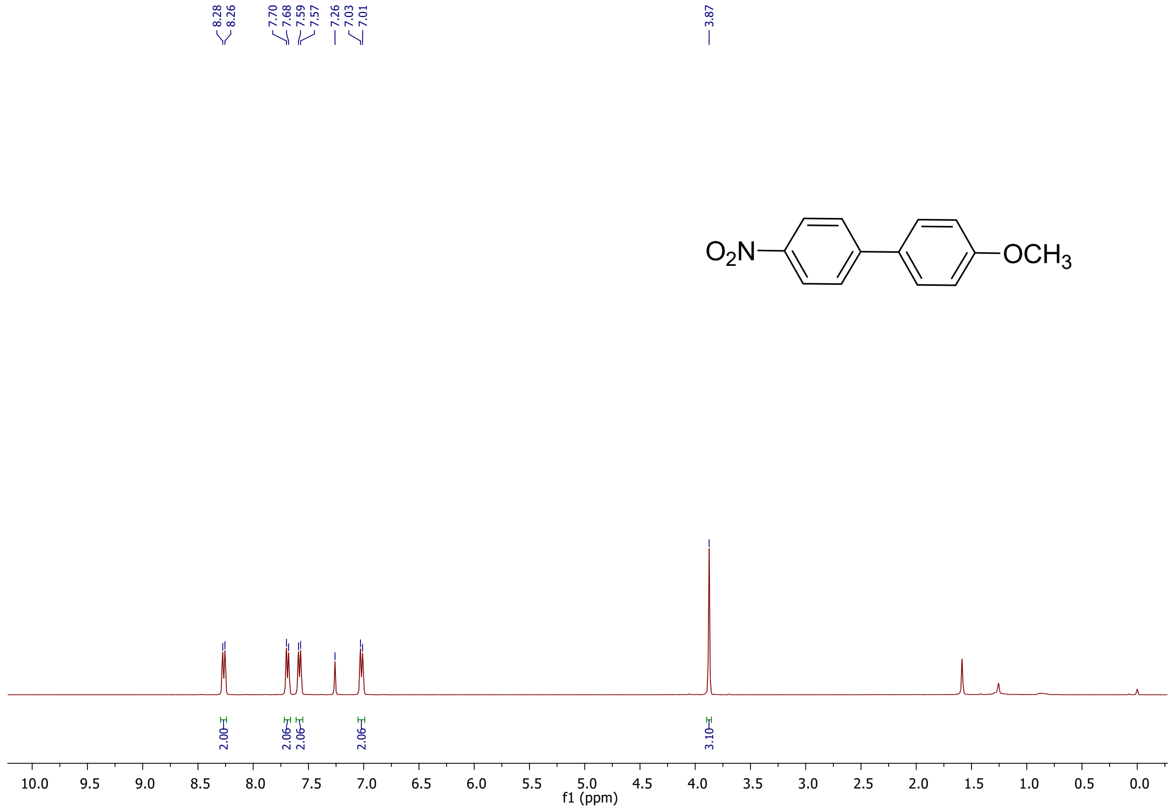
^{1}H NMR of **3r**



^{1}H NMR (400 MHz, $CDCl_3$)

This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
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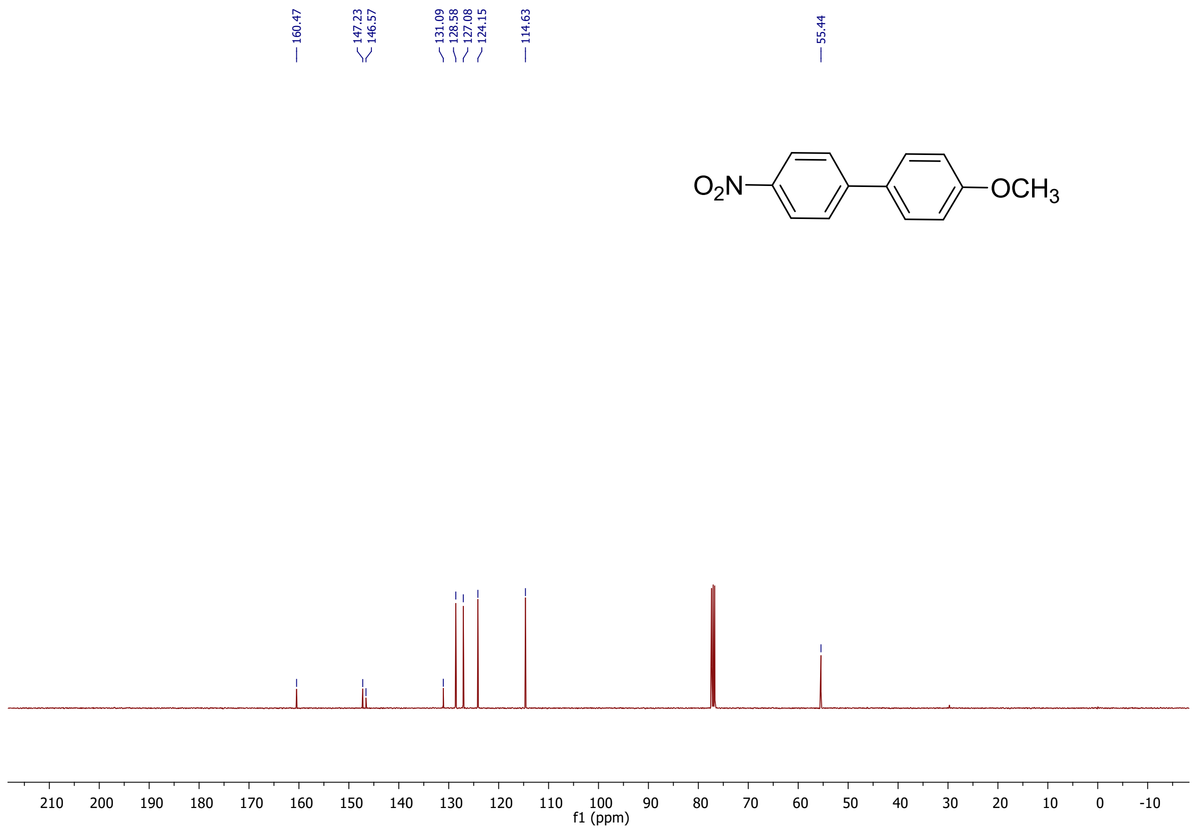
^{13}C NMR spectrum of **3r**



^{13}C NMR (100 MHz, $CDCl_3$)

This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
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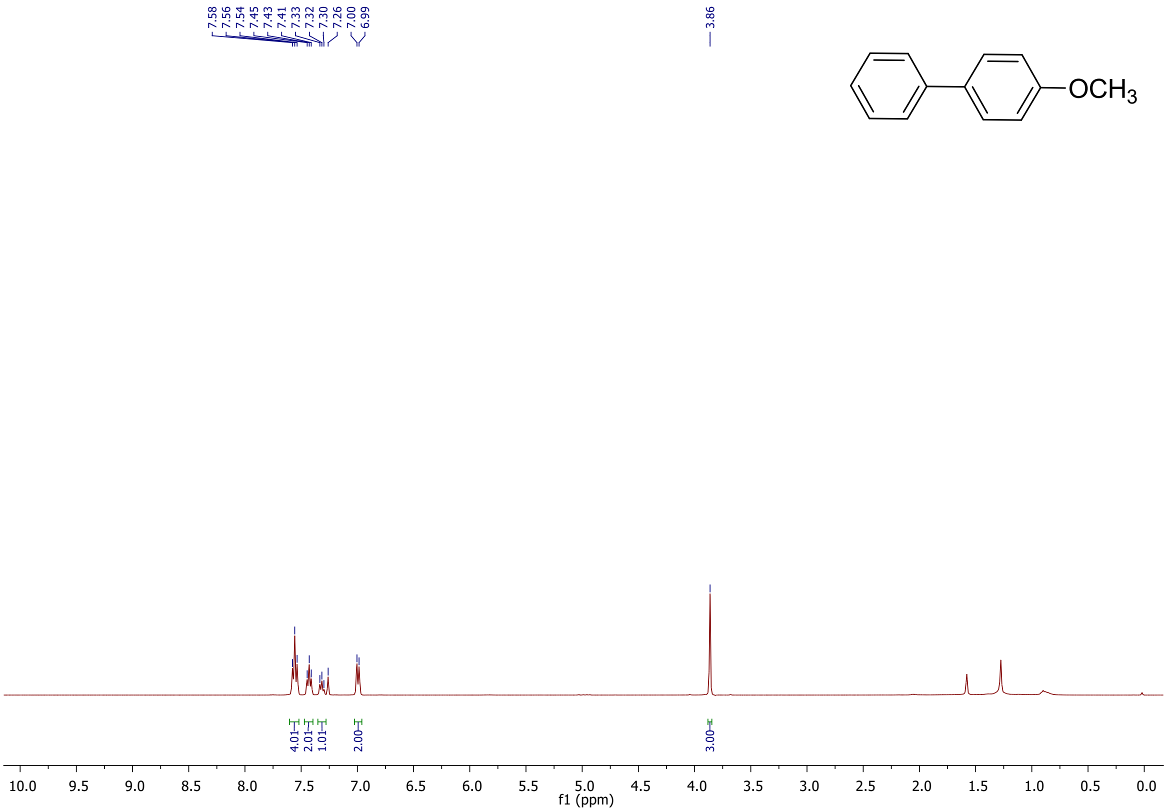
^{1}H NMR of **3u**



^{1}H NMR (400 MHz, $CDCl_3$)

This version of the ESI published 8th of July 2024 replaces
the original version published 5th of July 2024.
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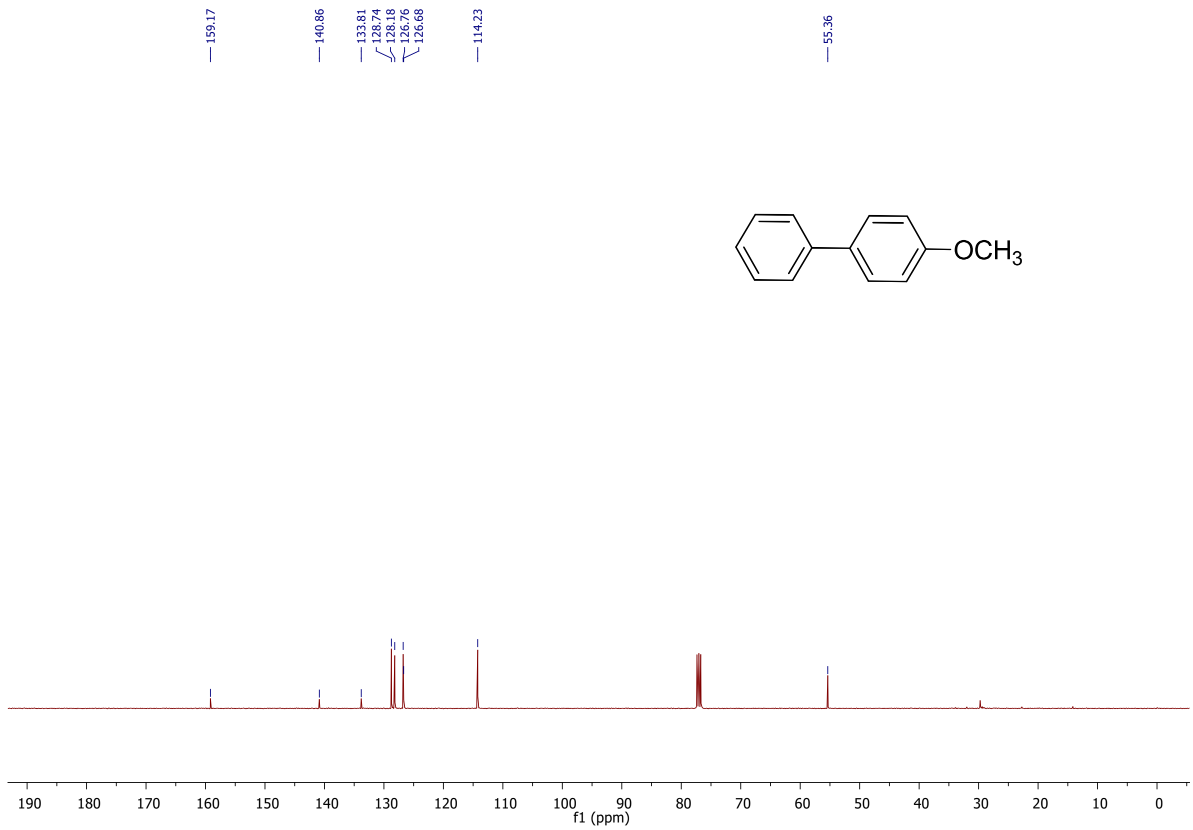
^{13}C NMR spectrum of **3u**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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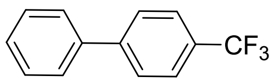
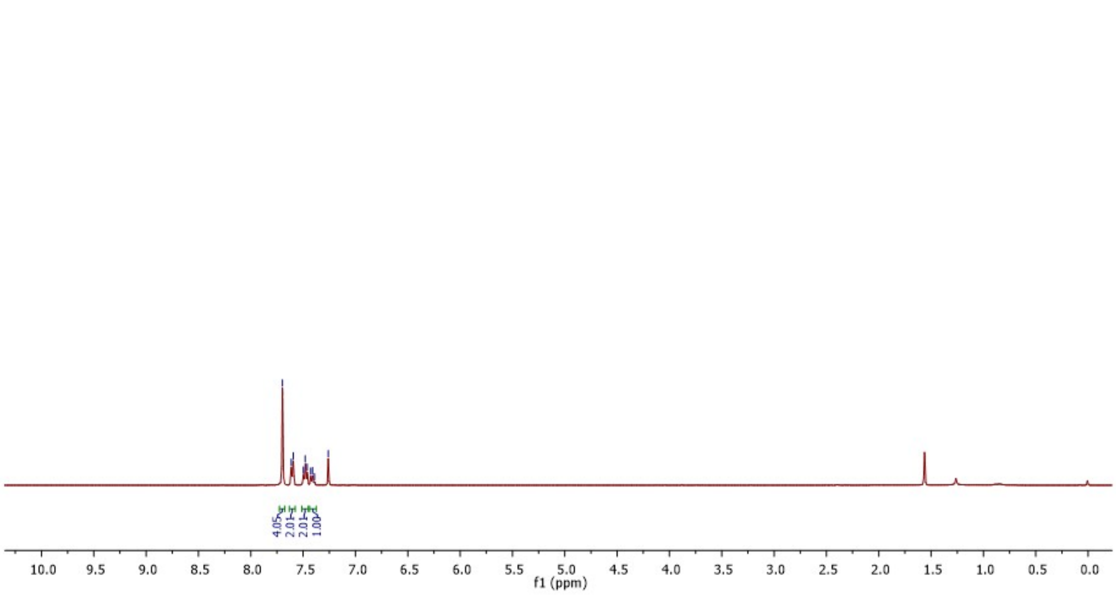
[1]H NMR of **3t**





[1]H NMR (400 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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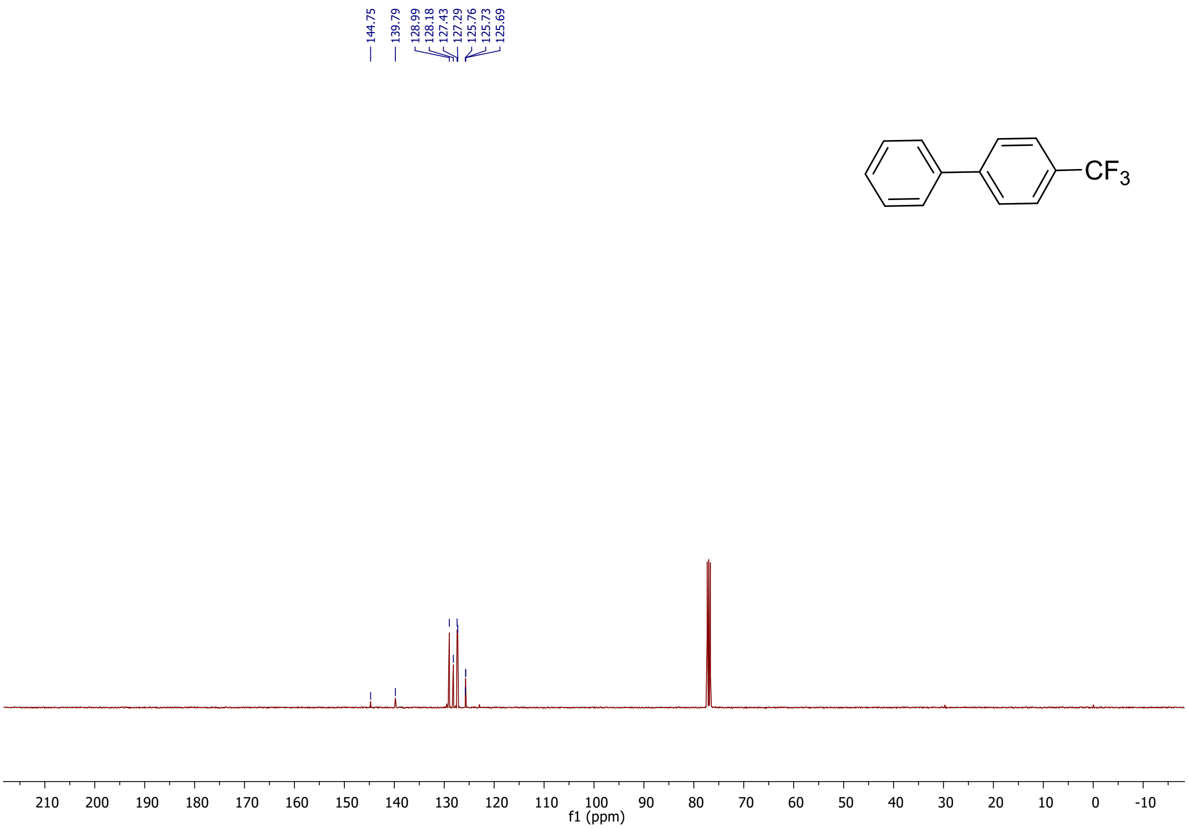
^{13}C NMR spectrum of **3t**



^{13}C NMR (100 MHz, $CDCl_3$)

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the original version published 5th of July 2024.
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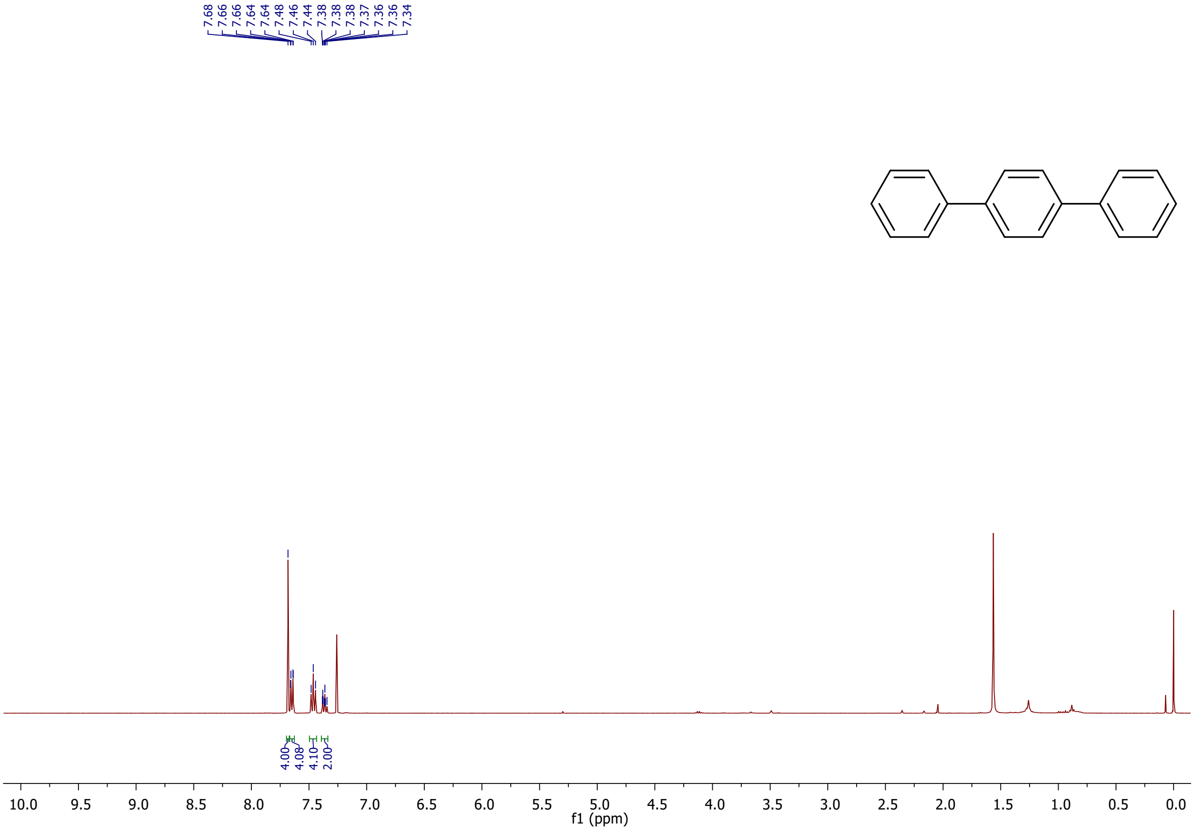
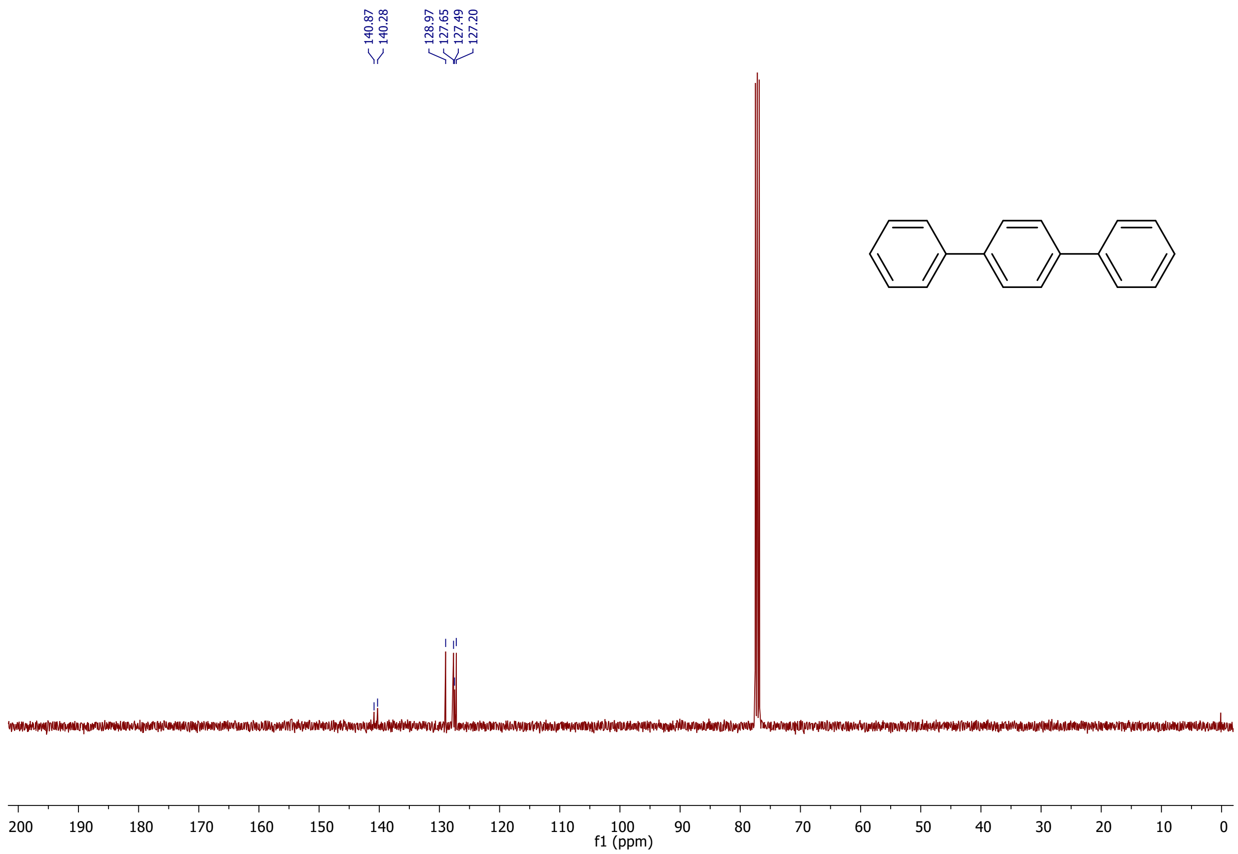
^{1}H NMR spectrum of **3v**



^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum of **3v**



^{13}C NMR (100 MHz, $CDCl_3$)

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