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De Novo Three-Component Synthesis of *meta*-Substituted Anilines

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Supporting Information

Table of Contents

1. GENERAL INFORMATION

^{1}H and ^{13}C NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) spectrometer at ambient temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; DMSO-d_6, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm). Coupling constants (*J*) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sept (septet), m (multiplet), dd (doublet of doublets) and br (broadened). High-resolution mass measurements were carried out using a BrukermicroTOF-QTM ESI-TOF (Electro Spray Ionization/Time of Flight) mass spectrometer. GC/MS analysis was performed on «Agilent 7890B» interfaced to HP-5MS capillarity column and «Agilent 5977A» mass selective detector. Chiral HPLC analysis was performed on «Hitachi Chromaster» equipped with cellulose-1 Phenomenex column and 5430 diode array detector. Melting points were determined with «Stuart SMP 30. Data sets for X-Ray diffraction were collected with a «New Xcalibur, Ruby» diffractometer. Column chromatography was performed on silica gel Macherey Nagel (40-63 μm). Pre-coated TLC sheets ALUGRAM SIL G/UV$_{254}$ were used for thin-layer analytical chromatography. All reagent-grade aromatic and aliphatic amines, as well as some acetylvinyl ketones and *N*-acylpyridiniums salts used in the study were purchased from the respective suppliers and used as received. All the reactions were carried out under ambient atmosphere using freshly distilled and dry solvents from solvent stills unless otherwise stated. Non-commercially available starting *N*-acylpyridiniums salts[1] and acetylvinyl ketones[2] were synthesized according to known procedures and were known compounds, which spectral data were in agreement with previously reported.

2. LIST OF THE STARTING MATERIALS USED IN THE PRESENT STUDY

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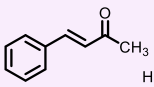
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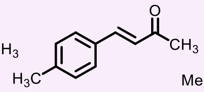
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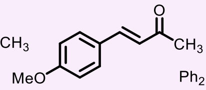
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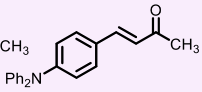
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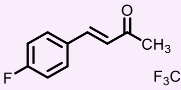
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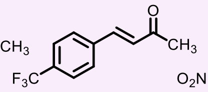
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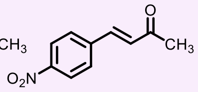
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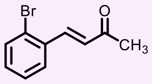
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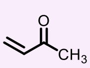
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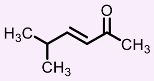
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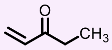
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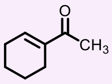
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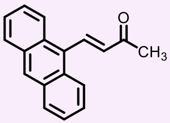
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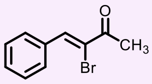
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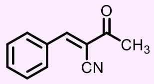
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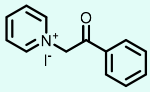
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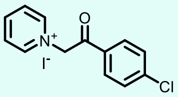
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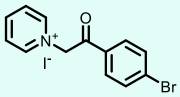
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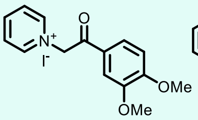
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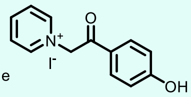
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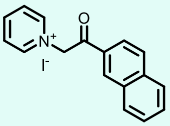
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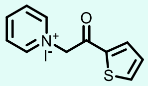
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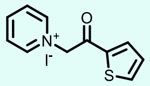
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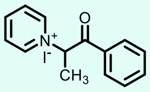
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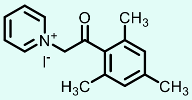
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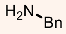
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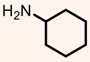
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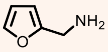
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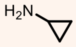
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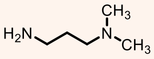
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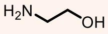
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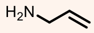
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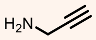
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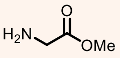
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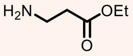
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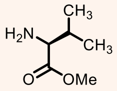
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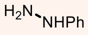
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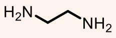
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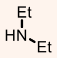
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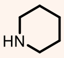
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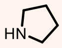
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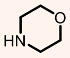
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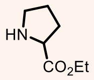
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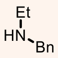
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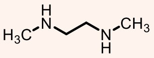
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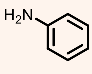
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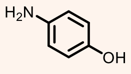
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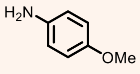
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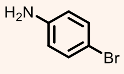
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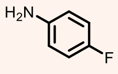
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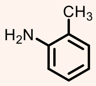
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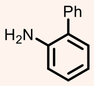
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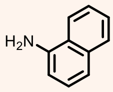
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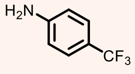
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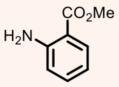
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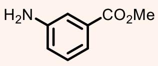
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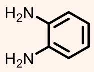
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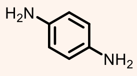
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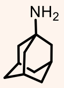
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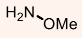
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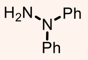
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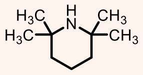
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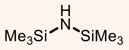
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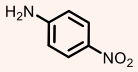
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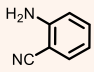
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3. SUMMARY OF THE OPTIMIZATION STUDIES

ANILINES FROM PRIMARY/SECONDARY AMINES

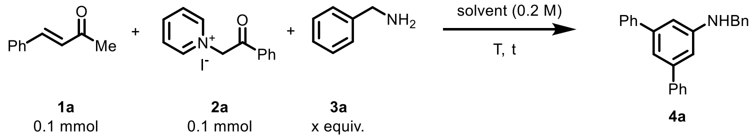
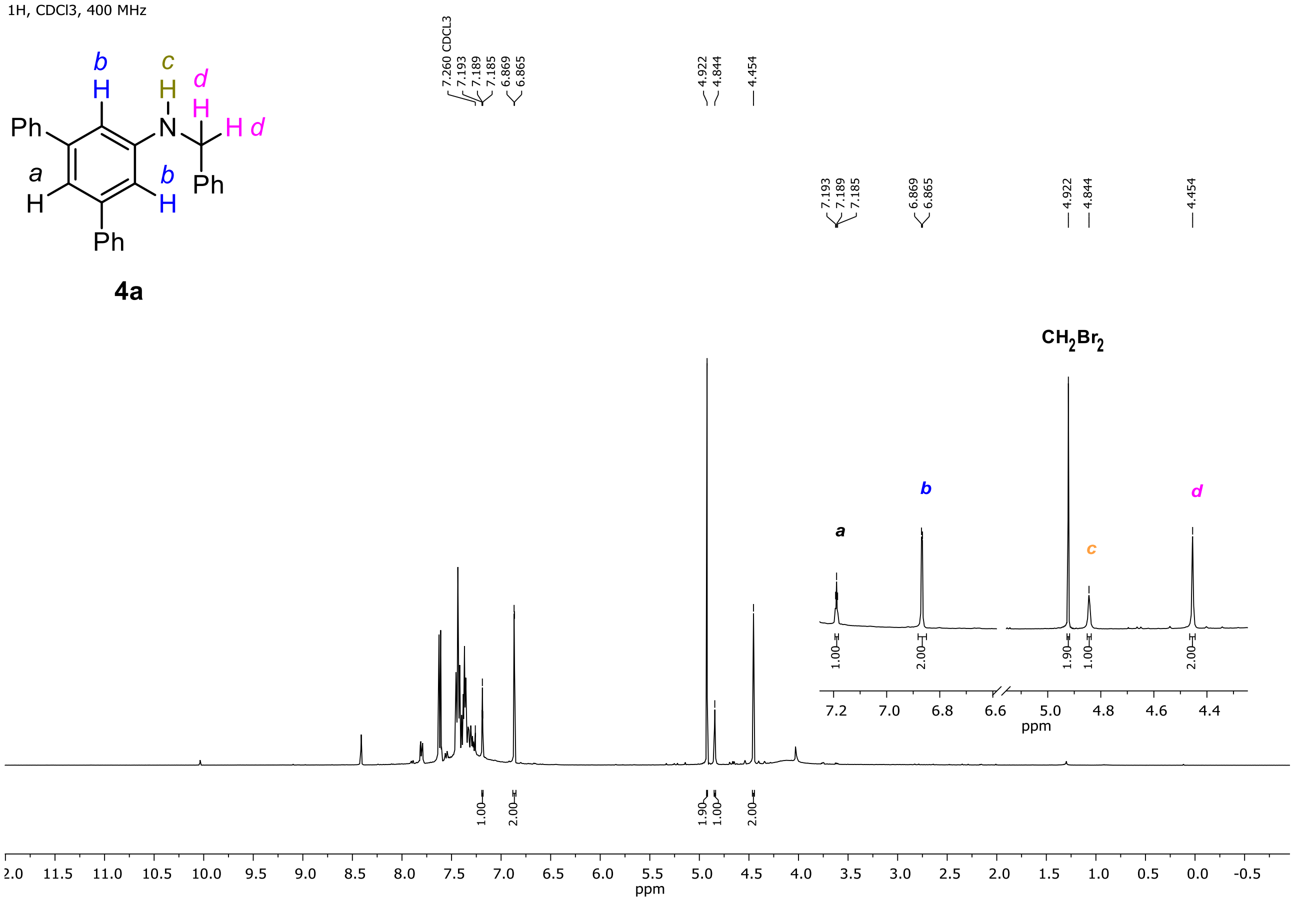


*Table S1.Optimization experiments for the synthesis of aniline **4a***

Entry	3a, equiv.	Solvent	T, °C	Time, h	Yield of 4a, %[a]
1	1	Dioxane	80	20	65 (15 **1a** remained)
2	1	EA	80	20	60
3	1	EtOH	80	20	35
4	1	ACN	80	20	55
5	1	PhMe	80	20	45
6	1	DCE	80	20	15
7	1	Dioxane	90	24	85
8	1	Dioxane	100	24	90
9	2	Dioxane	100	4	95

[a] The yield was determined by NMR ^{1}H with CH_2Br_2 as an internal standard

Example of the procedure for the optimization of reaction conditions for the synthesis of aniline 4a (Table S1, entry 9). 3 mL Weaton microreactor was charged with enone **1a** (14.6 mg, 0.1 mmol), pyridinium salt **2a** (32.5 mg, 0.1 mmol), amine **3a** (22 μL, 0.2 mmol, 2 equiv.), and dioxane (1 mL). The microreactor was capped with a Teflon pressure cap and placed into a pre-heated (100 °C) aluminum block, then the content was stirred at the same temperature for 4 h. Upon completion (TLC or GC control; **1a** and **4a** could be detected by either method), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with DCM, concentrated *in vacuo*, dissolved in $CDCl_3$ (0.6 mL). CH_2Br_2 (7 μL, 0.1 mmol, 1 equiv.) was added to the solution, and the resulting mixture was analyzed by ^{1}H NMR.



ANILINES FROM AROMATIC AMINES

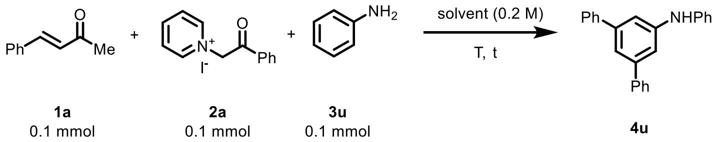
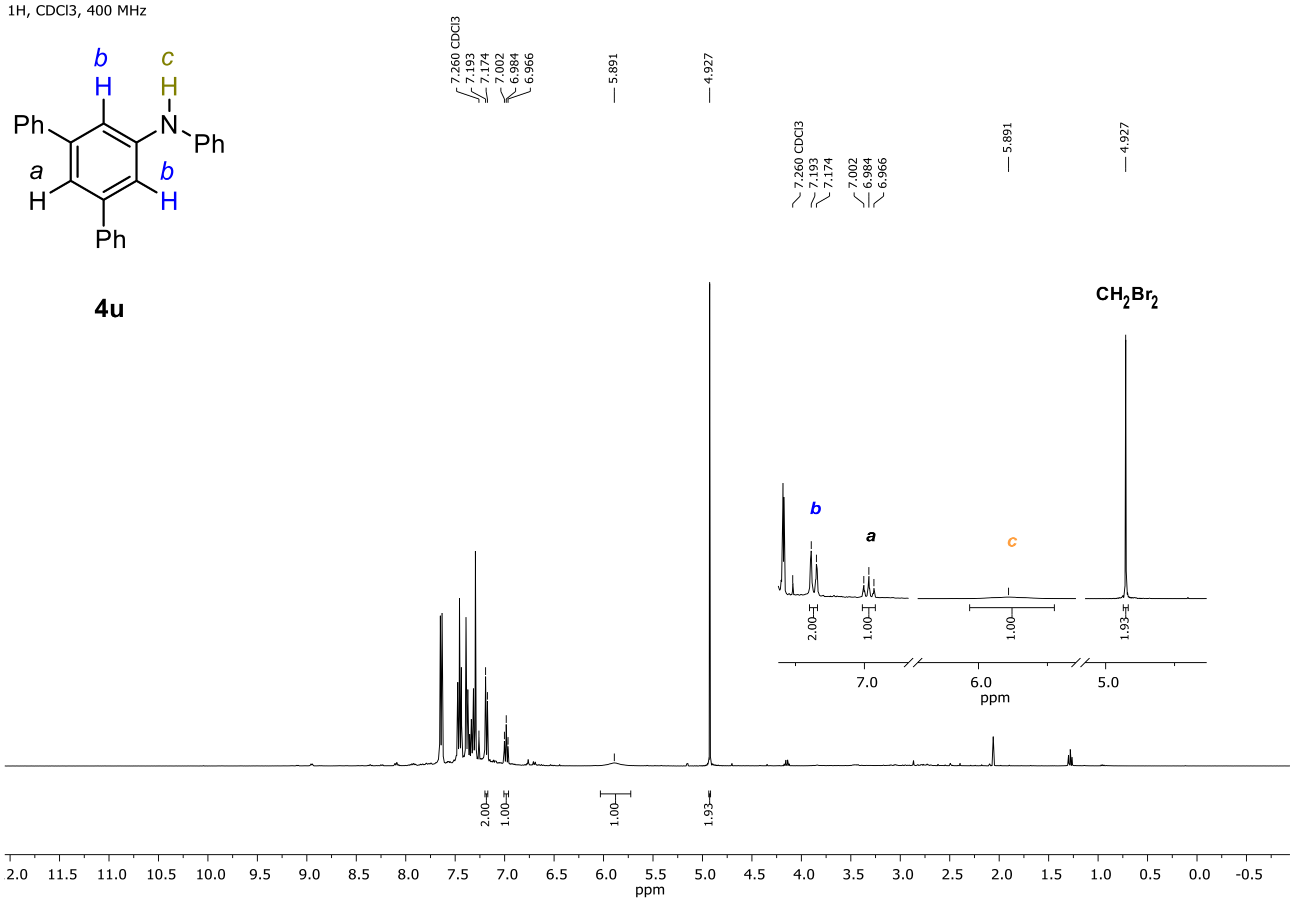


Table S2. *Optimization experiments for the synthesis of aniline **4u***

Entry	Solvent	T, °C	Yield of 4u, %[a]
1	Dioxane	100	52
2	Dioxane	90	51
3	Dioxane	80	43
4	EA	90	57
5	EtOH	90	38
6	DCE	90	24
7	PhMe	90	57
8	ACN	90	95

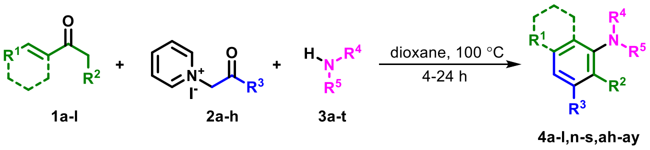
[a]The yield was determined by NMR ^{1}H with CH_2Br_2 as an internal standard

Example of the procedure for the optimization of reaction conditions for the synthesis of aniline 4u (Table S2, entry 8). 3 mL Weaton microreactor was charged with enone **1a** (14.6 mg, 0.1 mmol), pyridinium salt **2a** (32.5 mg, 0.1 mmol), amine **3u** (22 μL, 0.2 mmol, 2 equiv.), and acetonitrile (1 mL). The microreactor was capped with a Teflon pressure cap and placed into a pre-heated (90 °C) aluminum block, then the content was stirred at the same temperature for 24 h. Upon completion (TLC or GC control; **1a** and **4a** could be detected by either method), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with DCM, concentrated *in vacuo*, dissolved in $CDCl_3$ (0.6 mL). CH_2Br_2 (7 μL, 0.1 mmol, 1 equiv.) was added to the solution, and the resulting mixture was analyzed by ^{1}H NMR.



4. SYNTHESIS OF ANILINES 4

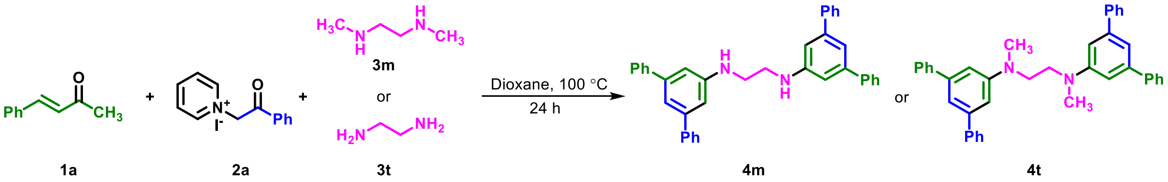
General synthetic procedure for the synthesis of anilines 4a-k,n-s,ah-ay



5 mL Weaton microreactor was charged with respective enone **1** (1 mmol), pyridinium salt **2** (1 mmol), amine **3** (2 mmol, 2 equiv.), and dioxane (4.8 mL). The microreactor was capped with a Teflon pressure cap and placed into a pre-heated (100 °C) aluminum block, then the content was stirred at the same temperature for 4-24 h. Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with DCM, concentrated *in vacuo*, dry-loaded on silica and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 9:1 to 7:1 to 5:1) to afford target compound **4**.

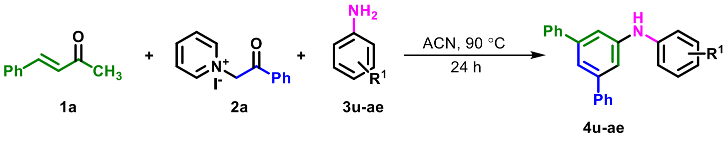
Compound **4e** could be isolated with high purity via acid-base extraction. Upon completion, the reaction mixture was poured into 5M HCl (15 mL) and washed with EA (2 × 10 mL). Aqueous phase was collected, treated with 5M NaOH to pH ~8-9, then extracted with EA (2 × 15 mL), washed with water (2 × 20 mL), brine (20 mL), dried over anhydrous Na_2SO_4, concentrated and dried *in vacuo* to afford the target aniline.

Synthetic procedure for the synthesis of anilines 4m,t



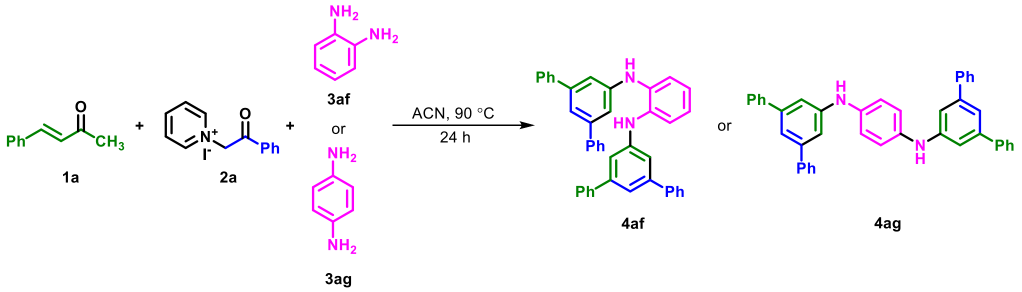
5 mL Weaton microreactor was charged with respective enone **1a** (145 mg, 1 mmol), pyridinium salt **2a** (325 mg, 1 mmol), amine **3m** or **3t** (0.5 mmol, 0.5 equiv.), and dioxane (4.8 mL). The microreactor was capped with a Teflon pressure cap and placed into a pre-heated (100 ºC) aluminum block, then the content was stirred at the same temperature for 24 h. Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with DCM, concentrated *in vacuo*, dry-loaded on silica and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 9:1 to 7:1 to 5:1) to afford target compound **4m** or **4t**.

General synthetic procedure for the synthesis of anilines 4u-ae



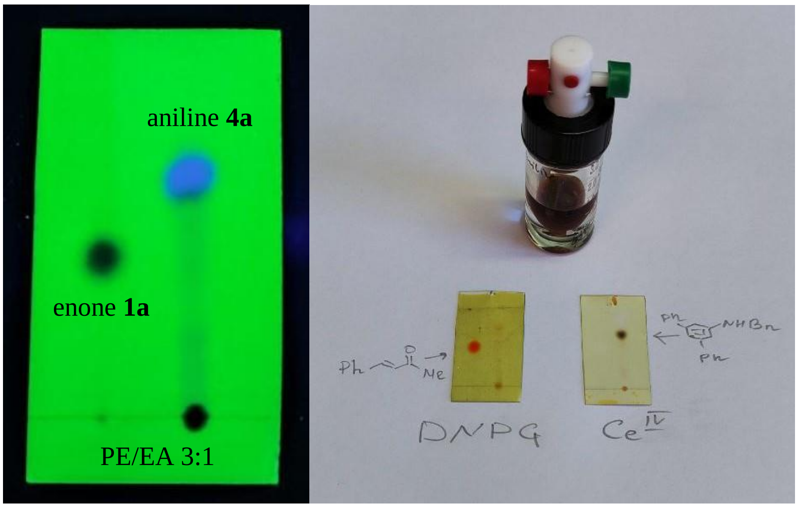
5 mL Weaton microreactor was charged with enone **1a** (145 mg, 1 mmol), pyridinium salt **2a** (325 mg, 1 mmol), amine **3** (1 mmol, 1 equiv.), and acetonitrile (4.8 mL). The microreactor was capped with a Teflon pressure cap and placed into a pre-heated (90 °C) aluminum block, then the content was stirred at the same temperature for 24 h. Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with DCM, concentrated *in vacuo*, dry-loaded on silica and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 9:1 to 7:1 to 5:1) to afford target compound **4**. *NOTE! The boiling point of acetonitrile is 82 °C; therefore, the content is pressurized when heated at 90 °C. Make sure that the temperature of the reaction vessel is below 70°C before opening.*

Synthetic procedure for the synthesis of anilines 4af,ag



5 mL Weaton microreactor was charged with enone **1a** (145 mg, 1 mmol), pyridinium salt **2a** (325 mg, 1 mmol), amine **3af** or **3ag** (0.5 mmol, 0.5 equiv.), and acetonitrile (4.8 mL). The microreactor was capped with a Teflon pressure cap and placed into a pre-heated (90 °C) aluminum block, then the content was stirred at the same temperature for 24 h. Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with DCM, concentrated *in vacuo*, dry-loaded on silica and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 9:1 to 7:1 to 5:1) to afford target compound **4af** or **4ag**. *NOTE! The boiling point of acetonitrile is 82 °C; therefore, the content is pressurized when heated at 90 °C. Make sure that the temperature of the reaction vessel is below 70 °C before opening.*

General note 1*. Reactions could be efficiently monitored by TLC: starting enones* ***1*** *are visualized with 2,4-DNPG solution with or without gentle heating, while anilines* ***4*** *usually are not stained. In the contrary, anilines* ***4*** *are well stained with* $Ce(SO_4)_2$ *solution without heating, but enones* ***1*** *are not. Both enones* ***1*** *and anilines* ***4*** *are detectable by UV (365 nm). Alternatively, enones* ***2*** *and anilines* ***4*** *could be detected by GC-MS. Conditions: injection = 0.5 µL (ca. 1 mg/mL) at 300 °C, split 10:1; carrier gas – helium (1 mL/min); oven: initial temperature = 100 °C (2 min hold time), then 300 °C (ramp rate 40 °C/min, 20 min hold time); ionization method – EI (70 eV).*



The staining solutions were prepared as follows:

2,4-DNPG: 3 g of 2,4-dinitrophenylhydrazine, 15 mL H_2SO_4 *conc., 20 mL* H_2O*, 50 mL EtOH;*
$Ce(SO_4)_2$*: 5 g* $Ce(SO_4)_2$*, 4 mL* H_2SO_4 *conc., 50 mL* H_2O*.*

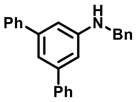
General note 2*. In the vast majority of cases, products* ***4*** *are the most unipolar reaction mixture components and could be separated quickly with rather unpolar eluents (petroleum ether/DCM 9:1 or even less polar).*

General note 3*. Melting points of crystalline compounds were measured upon solidification after column chromatography without recrystallization.*

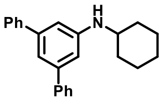
General note 4*. For the synthesis of anilines* ***4*** *from primary aliphatic amines* ***3a-m****, it is important to use no less than 2 equiv. of amine component. In some cases we observed the formation of tertiary anilines resulting from the competition between the starting amines* ***3*** *and desired aniline products* ***4*** *for the reaction with the remaining amounts of enone* ***2*** *and pyridinium salt* ***3****.*

General note 5. *We observed that some anilines obtained from primary aliphatic amines (especially, from benzylamine) could undergo oxidation to form imines when exposed to air at moderate-to-high temperature or during column chromatography. In order to achieve even higher yields, one might consider running reactions under inert atmosphere and performing column chromatography as quick as possible.*

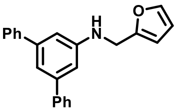
General note 6. *We have not detected any significant change in the yields of products **4** when we used solvents without prior drying.*



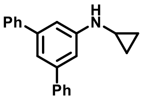
N-benzyl-[1,1':3',1''-terphenyl]-5'-amine (**4a**).
Pale yellow solid (315 mg, 94%) R_f = 0.59 (PE/EA 4:1). Mp = 119 – 121 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.75 – 7.73 (m, 4H), 7.56 – 7.52 (m, 6H), 7.50 – 7.40 (m, 4H), 7.44 – 7.39 (m, 1H), 7.33 (t, ^{4}J = 1.4 Hz, 1H), 6.96 (d, ^{4}J = 1.5 Hz, 2H), 4.51 (s, 2H), 4.24 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 149.0, 143.0 (2C), 141.8 (2C), 139.5, 128.78 (2C), 128.74 (4C), 127.7 (2C), 127.41, 127.38 (2C), 127.35 (4C), 116.2, 110.9 (2C), 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{25}H_{22}N^{\bullet+}$ 336.1747, found 336.1746.



N-cyclohexyl-[1,1':3',1''-terphenyl]-5'-amine (**4b**).
Pale yellow oil (298 mg, 91%). R_f = 0.58 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.86 – 7.84 (m, 4H), 7.65 – 7.61 (m, 4H), 7.55 – 7.51 (m, 2H), 7.36 (s, 1H), 6.99 (s, 2H), 3.81 (br s, 1H), 3.59 (tt, ^{3}J = 9.9; 3.8 Hz, 1H), 2.32 – 2.30 (m, 2H), 1.97 – 1.95 (m, 2H), 1.87 – 1.84 (m, 1H), 1.64 – 1.55 (m, 2H), 1.48 – 1.34 (m, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 148.1, 143.0 (2C), 142.0 (2C), 128.7 (4C), 127.31 (4C), 127.24 (2C), 115.5, 111.2 (2C), 51.8, 33.5 (2C), 26.0, 25.0 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{24}H_{25}N^{\bullet+}$ 328.2060, found 328.2059.

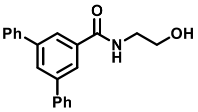


N-(furan-2-ylmethyl)-[1,1':3',1''-terphenyl]-5'-amine (**4c**).
Yellow oil (221 mg, 68%). R_f = 0.50 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.73 – 7.71 (m, 4H), 7.54 – 7.51 (m, 4H), 7.47 – 7.42 (m, 3H), 7.31 (s, 1H), 6.96 (s, 2H), 6.43 (s, 1H), 6.37 (s, 1H) 4.49 (s, 2H), 4.24 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 152.8, 148.4, 142.9 (2C), 142.0 (2C), 141.8, 128.7 (4C), 127.39 (2C), 127.34 (4C), 116.6, 111.2 (2C), 110.5, 107.2, 41.6 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{23}H_{20}NO^{\bullet+}$ 326.1539, found 326.1533.

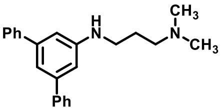


N-cyclopropyl-[1,1':3',1''-terphenyl]-5'-amine (**4d**).
Colourless oil (174 mg, 61%). R_f = 0.59 (PE/EA 3:1). **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ = 7.68 – 7.66 (m, 4H), 7.48 – 7.44 (m, 4H), 7.37 – 7.33 (m, 2H), 7.11 (t, ^{4}J = 1.7 Hz, 1H), 7.00 (d, ^{4}J = 1.3 Hz, 2H), 6.26 (s, 1H), 2.50 – 2.44 (m, 1H), 0.76 – 0.72 (m, 2H), 0.49 – 0.46 (m, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, DMSO-d$_6$): δ = 150.2, 141.5 (2C), 141.1 (2C), 128.6 (4C), 127.1 (2C), 126.6 (4C), 113.7, 110.0 (2C), 24.5, 6.8 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{21}H_{20}N^{\bullet+}$ 286.1590, found 286.1577.

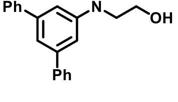
NOTE. *Compound **4d** is highly sensitive towards oxidants[3] (including oxygen in air) and unstable in acidic media (e.g. silica gel, CDCL$_3$). Column chromatography afforded compound **4d** with 35% yield along with its oxidation product – compound **SI4**. Compound **4d** could be isolated with reasonable degree of purity via neutral extraction: reaction mixture was poured into H$_2$O (50 mL), extracted with petroleum ether (3 × 50 mL), combined organic fraction was dried over Na$_2$SO$_4$, concentrated and dried in vacuo. The yield of the compound **4d** in the description refers to the yield obtained via neutral extraction.*



N-(2-hydroxyethyl)-[1,1':3',1''-terphenyl]-5'-carboxamide (**SI4**).
Colourless oil, yield and R_f were not determined. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ = 10.04 (s, 1H), 7.93 – 7.92 (m, 2H), 7.71 – 7.67 (m, 4H), 7.56 – 7.47 (m, 5H), 7.41 – 7.37 (m. 2H), 4.64 (t, ^{3}J = 5.5 Hz, 1H), 3.78 – 3.72 (m, 2H), 2.53 (t, ^{3}J = 6.5 Hz, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, DMSO-d$_6$): δ = 170.0, 141.3 (2C), 140.3, 140.1 (2C), 128.1 (4C), 127.5 (2C), 126.7 (4C), 119.8, 116.4 (2C), 57.4, 40.3 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{21}H_{20}NO_2^{\bullet+}$ 318.1489, found 318.1491.

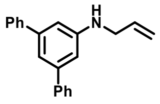


N^{1}-([1,1':3',1''-terphenyl]-5'-yl)-*N*^{3},*N*^{3}-dimethylpropane-1,3-diamine (**4e**).
Yellow oil (270 mg, 82%). R_f = 0.01 (EA). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.77 – 7.75 (m, 4H), 7.55 – 7.51 (m, 4H), 7.45 – 7.42 (m, 2H), 7.27 (s, 1H), 6.92 (s, 2H), 4.73 (br s, 1H), 3.38 (t, ^{3}J = 6.3 Hz, 2H), 2.52 (t, ^{3}J = 6.3 Hz, 2H), 2.36 (s, 6H), 1.91 (pent, ^{3}J = 6.3 Hz, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 149.4, 142.8 (2C), 141.9 (2C), 128.6 (4C), 127.21 (4C), 127.16 (2C), 115.5, 110.6 (2C), 58.1, 45.5 (2C), 43.1, 27.0 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{23}H_{27}N_2^{\bullet+}$ 331.2169, found 331.2177.

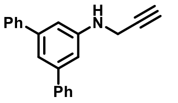


2-([1,1':3',1''-terphenyl]-5'-ylamino)ethan-1-ol (**4f**).
Yellow oil (246 mg, 85%). R_f = 0.14 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.65– 7.62 (m, 4H), 7.47 – 7.43 (m, 4H), 7.39 – 7.35 (m, 2H), 7.23 (t, ^{4}J = 1.5 Hz, 1H), 6.90 (d, ^{4}J = 1.3 Hz, 2H), 3.90 (t, ^{3}J = 5.2 Hz, 2H), 3.43 (t, ^{3}J = 5.2 Hz, 2H), 3.22 (br s, 2H) ppm.

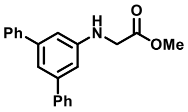
^{13}C {^{1}H} NMR (100 MHz, CDCl$_3$): δ = 148.5, 143.1 (2C), 141.7 (2C), 128.8 (4C), 127.5 (2C), 127.4 (4C), 116.9, 111.6 (2C), 61.3, 46.7 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{20}H_{20}NO^{\bullet+}$ 290.1539, found 290.1537.



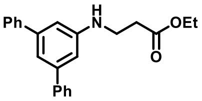
N-allyl-[1,1':3',1''-terphenyl]-5'-amine (**4g**).
Pale yellow oil (148 mg, 52%). R_f = 0.61 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.75 – 7.73 (m, 4H), 7.55 – 7.52 (m, 4H), 7.46 – 7.42 (m, 2H), 7.29 (t, ^{4}J = 1.6 Hz, 1H), 6.92 (d, ^{4}J = 1.3 Hz, 2H), 6.09 (ddt, ^{3}J = 5.3; 10.3; 17.2 Hz, 1H), 5.44 (dd, ^{4}J = 1.3; ^{3}J = 17.2 Hz, 1H), 5.31 (dd, ^{4}J = 1.2; ^{3}J = 10.3 Hz, 1H), 4.01 (br s, 1H), 3.96 (dt, ^{4}J = 1.2; ^{3}J = 5.3 Hz, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 148.9, 142.9 (2C), 141.9 (2C), 135.5. 128.7 (4C), 127.4 (6C), 116.4, 116.2, 111.1 (2C), 46.8 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{21}H_{20}N^{\bullet+}$ 286.1590, found 286.1593.



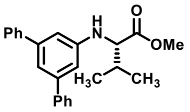
N-(prop-2-yn-1-yl)-[1,1':3',1''-terphenyl]-5'-amine (**4h**).
Colourless oil (79 mg, 28%). R_f = 0.59 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.65 – 7.63 (m, 4H), 7.46 – 7.43 (m, 4H), 7.37 -7.34 (m, 2H), 7.24 (t, ^{4}J = 1.4 Hz, 1H), 6.90 (d, ^{4}J = 1.4 Hz, 2H), 4.06 (d, ^{4}J = 2.1 Hz, 2H), 2.27 (t, ^{4}J = 2.1 Hz, 1H) ppm. The resonance of N-H has not been observed. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 147.8, 143.1 (2C), 141.8 (2C), 128.8 (4C), 127.52 (2C), 127.45 (4C), 117.3, 111.6 (2C), 81.0, 71.7, 34.0 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{21}H_{18}N^{\bullet+}$ 284.1434, found 284.1432.



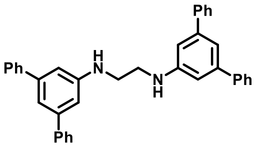
Methyl [1,1':3',1''-terphenyl]-5'-ylglycinate (**4i**).
Pale yellow oil (282 mg, 89%). R_f = 0.59 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.65 – 7.63 (m, 4H), 7.47 – 7.43 (m, 4H), 7.38 – 7.35 (m, 2H), 7.23 (t, ^{4}J = 1.3 Hz, 1H), 6.83 (d, ^{4}J = 1.3 Hz, 2H), 4.05 (s, 2H), 3.82 (s, 3H) ppm. The resonance of N-H has not been observed. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 171.6, 147.9, 143.2 (2C), 141.7 (2C), 128.8 (4C), 127.51 (2C), 127.41 (4C), 117.0, 111.1 (2C), 52.4, 46.0 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{21}H_{20}NO_2^{\bullet+}$ 318.1489, found 318.1487.



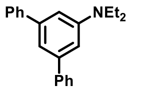
Ethyl 3-([1,1':3',1''-terphenyl]-5'-ylamino)propanoate (**4j**).
Pale yellow oil (301 mg, 87%). R_f = 0.50 (PE/EA 3:1).**^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.77 – 7.75 (m, 4H), 7.57 – 7.53 (m, 4H) 7.47 – 7.44 (m, 2H), 7.33 (s, 1H), 6.95 (s, 2H), 4.28 (q, ^{3}J = 6.7 Hz, 2H), 3.65 (t, ^{3}J = 6.2 Hz, 2H), 2.74 (t, ^{3}J = 6.2 Hz, 2H), 1.36 (t, ^{3}J = 6.7 Hz, 3H) ppm. The resonance of N-H has not been observed. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 172.2. 148.5, 142.9 (2C), 141.7 (2C), 128.6 (4C), 127.29 (2C), 127.23 (4C), 116.1, 110.9 (2C), 60.6, 39.6, 34.1, 14.2 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{23}H_{24}NO_2^{\bullet+}$ 346.1802, found 346.1804.



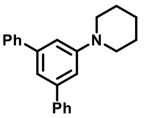
Methyl [1,1':3',1''-terphenyl]-5'-yl-*L*-valinate (**4k**).
Pale yellow oil (327 mg, 91%). R_f = 0.55 (PE/EA 4:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.76 – 7.74 (m, 4H), 7.56 – 7.52 (m, 4H), 7.47 – 7.43 (m, 2H), 7.34 (s, 1H), 7.00 (s, 2H), 4.51 (br s, 1H), 4.16 (br s, 1H), 3.83 (s, 3H), 2.36 – 2.24 (m, 1H), 1.22 (d, ^{3}J = 6.7 Hz, 3H), 1.19 (d, ^{3}J = 6.7 Hz, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 174.1, 148.2, 143.0 (2C), 141.7 (2C), 128.7 (4C), 127.35 (2C), 127.26 (4C), 116.7, 111.5 (2C), 62.7, 51.8, 31.7, 19.2, 18.8 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{24}H_{26}NO_2^{\bullet+}$ 360.1958, found 360.1948.



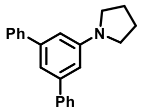
N^{1},*N*^{2}-di([1,1':3',1''-terphenyl]-5'-yl)ethane-1,2-diamine (**4m**).
White solid (356 mg, 69%). R_f = 0.52 (PE/EA 3:1). Mp = 224 – 226 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.62 – 7.60 (m, 8H), 7.44 – 7.41 (m, 8H), 7.36 – 7.33 (m, 4H), 7.19 (s, 2H), 6.87 (s, 4H), 4.12 (br s, 2H), 3.59 (s, 4H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 148.9 (2C), 143.3 (4C), 141.8 (4C), 128.8 (8C), 127.51 (4C), 127.43 (8C), 116.8 (2C), 111.2 (4C), 43.9 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{38}H_{33}N_2^{\bullet+}$ 517.2638, found 517.2640.



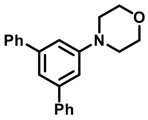
N,*N*-diethyl-[1,1':3',1''-terphenyl]-5'-amine (**4n**).
Off-white solid (268 mg, 89%). R_f = 0.70 (PE/EA 4:1). Mp = 68 – 69 °C (PE/DCM). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.83 - 7.81 (m, 4H), 7.61 – 7.57 (m, 4H) 7.51 – 7.47 (m, 2H), 7.27 (t, ^{4}J = 1.4 Hz, 1H), 7.06 (d, ^{4}J = 1.4 Hz, 2H), 3.61 (q, ^{3}J = 7.1 Hz, 4H), 1.40 (t, ^{3}J = 7.1 Hz, 6H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 148.6, 148.1 (2C), 142.6 (2C), 128.7 (4C), 127.5 (4C), 127.2 (2C), 114.4, 110.2 (2C), 44.7 (2C), 12.9 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{22}H_{24}N^{\bullet+}$ 302.1903, found 302.1893.



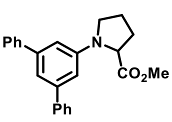
1-([1,1':3',1''-terphenyl]-5'-yl)piperidine (**4o**).[4]
Pale yellow oil, crystallizes as white solid (263 mg, 84%). R_f = 0.86 (PE/EA 3:1). Mp = 108 – 109 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.79 – 7.77 (m, 4H), 7.58 – 7.54 (m, 4H), 7.48 – 7.45 (m, 2H), 7.42 (br s, 1H), 7.29 (br s, 2H), 3.41 (t, ^{3}J = 5.5 Hz, 4H), 1.91 – 1.85 (m, 4H), 1.76 – 1.70 (m, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): 153.1, 142.7 (2C), 142.1 (2C), 128.7 (4C), 127.4 (4C), 127.3 (2C), 117.7, 114.7 (2C), 50.9 (2C), 26.0 (2C), 24.5 ppm.



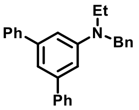
1-([1,1':3',1''-terphenyl]-5'-yl)pyrrolidine (**4p**).[5]
White solid (263 mg, 88%). R_f = 0.71 (PE/EA 3:1). Mp = 162 – 163 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.85 – 7.82 (m, 4H), 7.61 – 7.57 (m, 4H), 7.52 – 7.47 (m, 2H), 7.30 (t, ^4J = 1.4 Hz, 1H), 6.94 (d, ^4J = 1.4 Hz, 2H), 3.55 – 3.52 (m, 4H), 2.17 – 2.13 (m, 4H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): 148.7, 142.9 (2C), 142.5 (2C), 128.7 (4C), 127.5 (4C), 127.2 (2C), 114.3, 109.9 (2C), 47.9 (2C), 25.6 (2C) ppm.



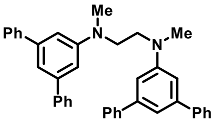
4-([1,1':3',1''-terphenyl]-5'-yl)morpholine (**4q**).[6]
Yellow oil, (259 mg, 82%). R_f = 0.51 (PE/EA 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76 – 7.74 (m, 4H), 7.60 – 7.53 (m, 4H), 7.48 – 7.44 (м, 3H), 7.23 (br s, 2H), 4.00 – 3.97 (m, 4H), 3.38 – 3.36 (m, 4H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): 152.1, 142.8 (2C), 141.8 (2C), 128.7 (4C), 127.4 (2C), 127.4 (4C), 118.4, 113.8 (2C), 66.9 (2C), 49.6 (2C) ppm.



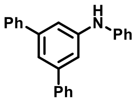
Methyl [1,1':3',1''-terphenyl]-5'-ylprolinate (**4r**).
Pale yellow oil (282 mg, 79%). R_f = 0.45 (PE/EA 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.77-7.74 (m, 4H), 7.56 – 7.52 (m, 4H), 7.46 – 7.42 (m, 2H), 7.30 (t, ^4J = 1.3 Hz, 1H), 6.88 (d, ^4J = 1.3 Hz, 2H), 4.50 (dd, ^3J = 8.2, 2.0 Hz, 1H), 3.83 (s, 3H), 3.81 – 3.77 (m, 1H), 3.60 – 3.55 (m, 1H), 2.41 – 2.11 (m, 4H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 174.8, 147.5, 142.9 (2C), 142.1 (2C), 128.7 (4C), 127.4 (4C), 127.3 (2C), 115.4, 110.1 (2C), 61.0, 52.1, 48.6, 30.9, 23.9 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{24}H_{24}NO_2^{\bullet+}$ 358.1802, found 358.1801.



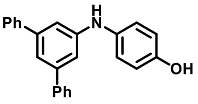
N-benzyl-*N*-ethyl-[1,1':3',1''-terphenyl]-5'-amine (**4s**).
Colourless oil, crystallizes as white solid (199 mg, 55%). R_f = 0.61 (PE/EA 3:1). Mp = 91 – 92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.82 – 7.80 (m, 4H), 7.63 – 7.55 (m, 4H), 7.53 – 7.50 (m, 6H), 7.48 – 7.42 (m, 1H), 7.38 (br s, 1H), 7.16 (br s, 2H), 4.82 (s, 2H), 3.77 (q, ^3J = 7.0 Hz, 2H), 1.48 (t, ^3J = 7.0 Hz, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 149.4, 143.0 (2C), 142.4 (2C), 139.3, 128.7 (6C), 127.5 (4C), 127.3 (2C), 126.98, 126.84 (2C), 115.0, 110.6 (2C), 54.3, 45.5, 12.4 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{27}H_{26}N^{\bullet+}$ 364.2060, found 364.2051.



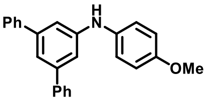
N^1,*N*^{2}-di([1,1':3',1''-terphenyl]-5'-yl)-*N*^{1},*N*^{2}-dimethylethane-1,2-diamine (**4t**).
Colourless oil (174 mg, 32%). R_f = 0.41 (PE/EA 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60-7.57 (m, 8H), 7.43 – 7.39 (m, 8H), 7.36 – 7.31 (m, 4H), 7.17 (t, ^4J = 1.2 Hz, 2H), 6.92 (d, ^4J = 1.2 Hz, 4H), 3.79 (s, 4H), 3.11 (s, 6H) ppm. **^{13}C {^{1}H} NMR** (400 MHz, $CDCl_3$): δ = 149.8 (2C), 143.1 (4C), 142.3 (4C), 128.8 (8C), 127.5 (8C), 127.3 (4C), 115.3 (2C), 110.1 (4C), 50.8 (2C), 39.2 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{40}H_{37}N_2^{\bullet+}$ 545.2951, found 545.2958.



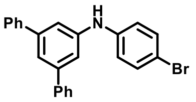
N-phenyl-[1,1':3',1''-terphenyl]-5'-amine (**4u**).
Yellow oil, crystallizes as off-white solid (260 mg, 81%). R_f = 0.53 (PE/EA 4:1). Mp = 68 – 69 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ =7.66 – 7.64 (m, 4H), 7.48 – 7.45 (m, 4H), 7.40– 7.36 (m, 3H), 7.35 – 7.29 (m, 4H), 7.20 – 7.18 (m, 2H), 7.02 – 6.98 (m, 1H), 5.84 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.3, 143.22 (2C), 143.18, 141.4 (2C), 129.6 (2C), 128.9 (4C), 127.6 (2C), 127.4 (4C), 121.5, 119.3, 118.5 (2C), 115.6 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{24}H_{20}N^{\bullet+}$ 322.1590, found 322.1581.



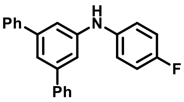
4-([1,1':3',1''-terphenyl]-5'-ylamino)phenol (**4v**).
Yellow semisolid (294 mg, 87%). R_f = 0.18 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 – 7.66 (m, 4H), 7.50 – 7.46 (m, 4H), 7.42 – 7.36 (m, 2H), 7.36 (t, ^4J = 1.5 Hz, 1H), 7.14 (d, ^4J = 1.2 Hz, 2H), 7.13 – 7.11 (m, 2H), 6.86 – 6.84 (m, 2H), 5.48 (br s, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 151.4, 146.2, 143.1 (2C), 141.5 (2C), 135.8, 128.8 (4C), 127.5 (2C), 127.3 (4C), 123.0 (2C), 118.0, 116.4 (2C), 113.5 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{24}H_{20}NO^{\bullet+}$ 338.1539, found 338.1535.



N-(4-methoxyphenyl)-[1,1':3',1''-terphenyl]-5'-amine (**4w**).
Pale yellow oil (260 mg, 74%). R_f = 0.51 (PE/EA 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.70 – 7.68 (m, 4H), 7.52– 7.48 (m, 4H), 7.44 -7.40 (m, 2H), 7.38 (t, ^4J = 1.5 Hz, 1H), 7.22 – 7.20 (m, 2H), 7.17 (d, ^4J = 1.2 Hz, 2H), 6.98 - 6.96 (m, 2H), 5.67 (br s, 1H), 3.86 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 155.7, 146.2, 143.1 (2C), 141.5 (2C), 135.7, 128.8 (4C), 127.5 (2C), 127.3 (4C), 122.8 (2C), 117.9, 114.9 (2C), 113.5 (2C), 55.6 ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{25}H_{21}NO^{\bullet+}$ 351.1618, found 351.1605.

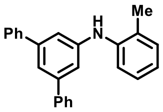


N-(4-bromophenyl)-[1,1':3',1''-terphenyl]-5'-amine (**4x**).
White solid (276 mg, 69%). R_f = 0.57 (PE/EA 3:1). Mp = 169 – 171 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 – 7.63 (m, 4H), 7.49 – 7.45 (m, 4H), 7.44 – 7.37 (m, 5H), 7.26 (s, 2H), 7.04 – 7.02 (m, 2H), 5.80 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 143.6, 143.3 (2C), 142.4, 141.2 (2C), 132.5 (2C), 128.9 (4C), 127.7 (2C), 127.3 (4C), 119.84, 119.74 (2C), 116.0 (2C), 113.3 ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{24}H_{18}{}^{79}BrN^{\bullet+}$ 399.0617, found 399.0605.



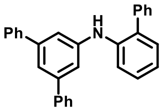
N-(4-fluorophenyl)-[1,1':3',1''-terphenyl]-5'-amine (**4y**).

Pale yellow oil, solidifies to off-white solid (248 mg, 73%). R_f = 0.64 (PE/EA 3:1). Mp = 132 – 134 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.78 – 7.76 (m, 4H), 7.61 – 7.57 (m, 4H), 7.53 - 7.49 (m, 3H), 7.29 (s, 2H), 7.24 – 7.20 (m, 2H), 7.16 – 7.12 (m, 2H), 5.75 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 158.3 (d, $^1J_{CF}$ = 241 Hz), 145.0, 143.1 (2C), 141.2 (2C), 138.9 (d, $^4J_{CF}$ = 2 Hz), 128.8 (4C), 127.6 (2C), 127.3 (4C), 121.2 (d, $^3J_{CF}$ = 8 Hz, 2C), 118.7, 116.1 (d, $^2J_{CF}$ = 22 Hz, 2C), 114.5 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{24}H_{18}FN^{\bullet+}$ 339.1418, found 339.1411.



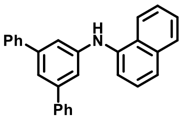
N-(*o*-tolyl)-[1,1':3',1''-terphenyl]-5'-amine (**4z**).

Colourless oil (228 mg, 68%) R_f = 0.66 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.78 – 7.76 (m, 4H), 7.59 – 7.55 (m, 4H), 7.52 – 7.47 (m, 4H), 7.38 (d, ^3J = 7.5 Hz, 1H), 7.33 (t, ^3J = 7.5 Hz, 1H), 7.29 (d, ^4J = 1.3 Hz, 2H), 7.13 (t, ^3J = 7.5 Hz, 1H), 5.63 (br s, 1H), 2.45 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 145.2, 143.1 (2C), 141.4 (2C), 141.1, 131.2, 129.1, 128.8 (4C), 127.5 (2C), 127.3 (4C), 127.0, 122.7, 119.9, 118.6, 114.9 (2C), 18.0 ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{25}H_{21}N^{\bullet+}$ 335.1669, found 335.1679.



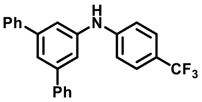
N-([1,1'-biphenyl]-2-yl)-[1,1':3',1''-terphenyl]-5'-amine (**4aa**).

Colourless oil (282 mg, 71%). R_f = 0.62 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.67 – 7.63 (m, 4H), 7.59 – 7.54 (m, 3H), 7.48 – 7.43 (m, 6H), 7.40 – 7.32 (m, 6H), 7.30 – 7.26 (m, 2H), 7.10 – 7.06 (m, 1H), 5.80 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 144.5, 143.1 (2C), 141.3 (2C), 140.1, 139.2, 132.1, 131.1, 129.4 (2C), 129.0 (2C), 128.8 (4C), 128.5, 127.60, 127.54 (2C), 127.3 (4C), 121.7, 119.2, 118.4, 115.7 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{30}H_{24}N^{\bullet+}$ 398.1903, found 398.1917.



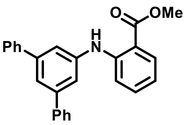
N-([1,1':3',1''-terphenyl]-5'-yl)naphthalen-1-amine (**4ab**).

Pale yellow oil (178 mg, 48%). R_f = 0.71 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.15 – 8.13 (m, 1H), 7.94 – 7.91 (m, 1H), 7.66 – 7.64 (m, 5H), 7.56 – 7.53 (m, 3H), 7.48 – 7.44 (m, 5H), 7.42 – 7.37 (m, 3H), 7.24 (d, ^4J = 1.5 Hz, 2H), 6.09 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 145.9, 143.2 (2C), 141.4 (2C), 138.8, 134.9, 128.84 (4C), 128.73, 128.2, 127.6 (2C), 127.4 (4C), 126.3, 126.2, 125.9, 123.5, 122.0, 118.8, 116.8, 115.1 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{28}H_{21}N^{\bullet+}$ 371.1669, found 371.1678.



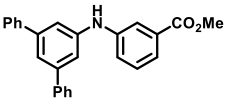
N-(4-(trifluoromethyl)phenyl)-[1,1':3',1''-terphenyl]-5'-amine (**4ac**).

Yellow oil (210 mg, 54%) R_f = 0.59 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.76 – 7.70 (m, 4H), 7.67 – 7.57 (m, 4H), 7.55 – 7.53 (m, 3H), 7.49 – 7.45 (m, 2H), 7.389 – 7.386 (m, 2H), 7.17 – 7.15 (m, 2H), 6.02 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 146.7, 143.3 (2C), 142.3, 140.8 (2C), 129.0 (4C), 127.8 (2C), 127.3 (4C), 126.9 (q, $^3J_{CF}$ = 4 Hz, 2C), 124.8 (q, $^1J_{CF}$ = 271 Hz), 122.1 (q, $^2J_{CF}$ = 33 Hz), 120.9, 120.8, 117.5 (2C), 115.9 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{25}H_{18}F_3N^{\bullet+}$ 389.1386, found 389.1380.



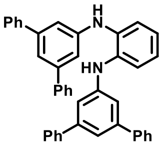
Methyl 2-([1,1':3',1''-terphenyl]-5'-ylamino)benzoate (**4ad**).

Colourless oil (91 mg, 24%) R_f = 0.49 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 9.63 (s, 1H), 8.01 (d, ^3J = 7.8 Hz, 1H), 7.67 – 7.65 (m, 4H), 7.55 (s, 1H), 7.47 -7.45 (m, 6H), 7.42 – 7.34 (m, 4H), 6.78 (t, ^3J =7.3 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 169.1, 148.0, 143.3 (2C), 141.9, 141.1 (2C), 134.4, 131.9, 128.9 (4C), 127.7 (2C), 127.4 (4C), 121.6, 120.1 (2C), 117.56, 114.6, 112.5, 51.9 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{26}H_{22}NO_2^{\bullet+}$ 380.1645, found 380.1635.



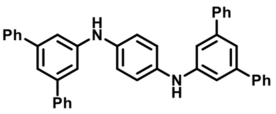
Methyl 3-([1,1':3',1''-terphenyl]-5'-ylamino)benzoate (**4ae**).

White solid (136 mg, 36%). R_f = 0.38 (PE/EA 4:1). Mp = 115 – 117 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.83 – 7.82 (m, 1H), 7.65 – 7.61 (m, 5H), 7.47 – 7.42 (m, 5H), 7.39 – 7.35 (m, 4H), 7.29 (d, ^4J = 1.5 Hz, 2H), 5.95 (s, 1H), 3.93 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 167.2, 143.67, 143.56, 143.4 (2C), 141.2 (2C), 131.7, 129.6, 128.9 (4C), 127.7 (2C), 127.4 (4C), 122.3, 122.0, 120.1, 119.0, 116.3 (2C), 52.2 ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{26}H_{21}NO_2^{\bullet+}$ 379.1567, found 379.1559.



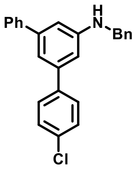
N^1,*N*^{2}-di([1,1':3',1''-terphenyl]-5'-yl)benzene-1,2-diamine (**4af**).

Pale yellow oil (192 mg, 34%). R_f = 0.76 (PE/EA 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.61 – 7.58 (m, 8H), 7.44 – 7.39 (m, 10 H), 7.37 – 7.32 (m, 6H), 7.18 (d, ^4J = 1.5 Hz, 4H), 7.08 – 7.06 (m, 2H), 5.87 (br s, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 144.5 (2C), 143.3 (4C), 141.4 (4C), 135.2 (2C), 128.9 (8C), 127.6 (4C), 127.4 (8C), 123.7 (2C), 121.4 (2C), 119.0 (2C), 114.9 (4C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{42}H_{33}N_2^{\bullet+}$ 565.2638, found 565.2630.

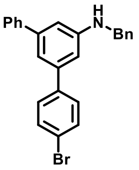


N^1,*N*^{4}-di([1,1':3',1''-terphenyl]-5'-yl)benzene-1,4-diamine (**4ag**).

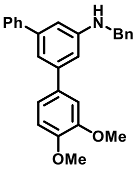
White solid (220 mg, 39%). R_f = 0.59 (PE/EA 3:1). Mp = 200 – 202 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.64 – 7.62 (m, 8H), 7.46 – 7.42 (m, 8H), 7.38 – 7.36 (m, 4H), 7.34 – 7.32 (m, 2H), 7.20 – 7.18 (m, 8H), 5.74 (br s, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 145.5 (2C), 143.2 (4C), 141.5 (4C), 137.6 (2C), 128.9 (8C), 127.6 (4C), 127.4 (8C), 121.5 (4C), 118.6 (2C), 114.4 (4C) ppm. **HRMS** (ESI/TOF) *m/z*: [M]$^{\bullet+}$ calcd for $C_{42}H_{32}N_2^{\bullet+}$ 564.2560, found 564.2563.



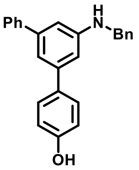
N-benzyl-4-chloro-[1,1':3',1''-terphenyl]-5'-amine (**4ah**).
Pale brown oil, (281 mg, 76%). R_f = 0.71 (PE/EA, 3:1). **^{1}H NMR**(400 MHz, CDCl$_3$): δ = 7.70 – 7.18 (m, 2H), 7.61 – 7.58 (m. 2H), 7.54 – 7.37 (m, 10H), 7.23 (br t, ^{4}J = 1.5 Hz, 1H), 6.94 (br t, ^{4}J = 1.5 Hz, 1H), 6.86 (br t, ^{4}J = 1.5 Hz, 1H), 4.48 (s, 2H), 4.41 (br s, 1H) ppm. **^{13}C {^{1}H} NMR**(100 MHz, CDCl$_3$): δ =148.9, 143.1, 141.7, 141.6, 140.2, 139.2, 133.4, 128.9 (2C), 128.79 (2C), 128.77 (2C), 128.5 (2C), 127.7 (2C), 127.48, 127.47, 127.3 (2C), 116.0, 111.3, 110.7, 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{25}H_{21}{}^{35}ClN^{\bullet+}$ 370.1357, found 370.1355.



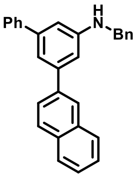
N-benzyl-4-bromo-[1,1':3',1''-terphenyl]-5'-amine (**4ai**).
Pale yellow oil, (306 mg, 74%). R_f = 0.68 (PE/EA, 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.48 – 7.45 (m, 2H), 7.42 – 7.39 (m, 2H), 7.33 – 7.30 (m, 4H), 7.29 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 7.21 – 7.17 (m, 1H), 6.99 (t, ^{4}J = 1.5 Hz, 1H), 6.73 (br t, ^{4}J = 2.0 Hz, 1H), 6.65 (br t, ^{4}J = 1.9 Hz, 1H), 4.29 (s, 2H), 4.06 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 149.1, 143.2, 141.8, 141.7, 140.8, 139.3, 131.9 (2C), 128.94 (2C), 128.85 (2C), 128.8 (2C), 127.7 (2C), 127.5 (2C), 127.4 (2C), 121.6, 115.9, 111.3, 110.6, 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{25}H_{21}{}^{79}BrN^{\bullet+}$ 414.0852, found 414.0857.



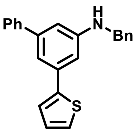
N-benzyl-3,4-dimethoxy-[1,1':3',1''-terphenyl]-5'-amine (**4aj**).
Brown oil, (264 mg, 67%). R_f = 0.64 (PE/EA, 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.63 – 7.61 (m, 2H), 7.46 – 7.42 (m, 4H), 7.40 – 7.29 (m, 4H), 7.17 (dd, ^{3}J = 8.3, ^{4}J = 2 Hz, 1H), 7.15 (br t, ^{4}J = 1.5 Hz, 1H), 7.11 (d, ^{4}J = 2 Hz, 1H), 6.94 (d, ^{3}J = 8.3 Hz, 1H), 6.84 (br t, ^{4}J = 2 Hz, 1H), 6.81 (br t, ^{4}J = 1.6 Hz, 1H), 4.46 (s, 2H), 4.18 (br s, 1H), 3.93 (s, 6H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 149.3, 149.0, 148.9, 143.1, 142.9, 142.0, 139.5, 135.0, 128.82 (2C), 128.76 (2C), 127.71 (2C), 127.44, 127.40 (3C), 119.6, 116.0, 111.8, 111.0, 110.8, 110.7, 56.2, 56.1, 48.7 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{27}H_{26}NO_2{}^{\bullet+}$ 396.1958, found 396.1958.



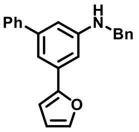
5'-(benzylamino)-[1,1':3',1''-terphenyl]-4-ol (**4ak**).
Pale yellow oil, (228 mg, 65%). R_f = 0.75 (PE/EA, 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.62 – 7.59 (m, 2H), 7.50 – 7.48 (m, 2H), 7.45 – 7.41 (m, 4H), 7.39 – 7.33 (m, 3H), 7.33 – 7.28 (m, 1H), 7.13 (br t, ^{4}J = 1.5 Hz, 1H), 6.90 – 6.88 (m, 2H), 6.83 (br t, ^{4}J = 2.2 Hz, 1H), 6.81 (br t, ^{4}J = 1.6 Hz, 1H),
4.58 (br s, 1H), 4.54 (br s, 1H), 4.44 (s, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 155.3, 149.0, 143.1, 142.6, 142.0, 139.5, 134.7, 128.9 (2C), 128.8 (2C), 128.6 (2C), 127.8 (2C), 127.50, 127.41 (3C), 116.0, 115.7 (2C), 110.7, 110.6, 48.8 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{25}H_{22}NO^{\bullet+}$ 352.1696, found 352.1683.



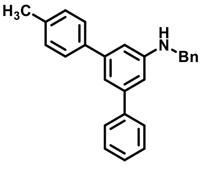
N-benzyl-5-(naphthalen-2-yl)-[1,1'-biphenyl]-3-amine (**4al**).
Pale brown oil, (266 mg, 69%). R_f = 0.64 (PE/EA, 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.16 (br s, 1H), 8.00 – 7.93 (m, 3H), 7.87 – 7.85 (m, 1H), 7.76 – 7.74 (m, 2H), 7.61 – 7.51 (m, 6H), 7.49 – 7.38 (m, 5H), 7.05 (br t, ^{4}J = 1.8 Hz, 1H), 6.97 (br t, ^{4}J = 1.7 Hz, 1H), 4.52 (s, 2H), 4.20 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 149.1, 143.1, 142.8, 141.8, 139.4, 139.2, 133.8, 132.8, 128.78 (2C), 128.76 (2C), 128.4, 128.3, 127.73, 127.70 (2C), 127.41 (2C), 127.38 (2C), 126.3, 125.93 (2C), 125.85, 116.4, 111.2, 111.0, 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{29}H_{24}N^{\bullet+}$ 386.1903, found 386.1893.



N-benzyl-5-(thiophen-2-yl)-[1,1'-biphenyl]-3-amine (**4am**).
Brown oil, (276 mg, 81%). R_f = 0.61 (PE/EA, 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.67 – 7.65 (m, 2H), 7.51 – 7.42 (m, 7H), 7.38 – 7.36 (m, 1H), 7.37 (dd, ^{4}J = 0.9, ^{3}J = 3.6 Hz, 1H), 7.31 (dd, ^{4}J = 0.9, ^{3}J = 5.1 Hz, 1H), 7.30 (br t, ^{4}J = 1.5 Hz, 1H), 7.13 (dd, ^{3}J = 3.6, 5.1 Hz, 1H), 6.94 (br t, ^{4}J = 1.8 Hz, 1H), 6.84 (br t, ^{4}J = 1.7 Hz, 1H), 4.46 (s, 2H), 4.20 (s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 149.0, 145.0, 143.2, 141.6, 139.3, 135.9, 128.79 (2C), 128.75(2C), 127.9, 127.7 (2C), 127.48, 127.45, 127.3 (2C), 124.7, 123.3, 115.0, 111.2, 109.7, 48.5 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{23}H_{20}NS^{\bullet+}$ 342.1311, found 342.1306.

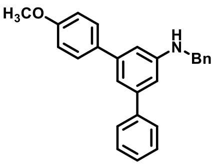


N-benzyl-5-(furan-2-yl)-[1,1'-biphenyl]-3-amine (**4an**).
Brown oil, (253 mg, 78%). R_f = 0.78 (PE/EA, 3:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.42 – 7.40 (m, 2H), 7.27 – 7.16 (m, 8H), 7.14 – 7.11 (m, 2H), 6.80 (br t, ^{4}J = 1.6 Hz, 1H), 6.58 (br t, ^{4}J = 1.6 Hz, 1H), 6.46 (d, ^{3}J = 3.3 Hz, 1H), 6.28 (dd, ^{3}J = 3.3, 1.8 Hz, 1H), 4.22 (s, 2H), 3.94 (s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 154.5, 148.9, 143.0, 142.0, 141.7, 139.4, 132.3, 128.8 (2C), 128.7 (2C), 127.7 (2C), 127.4 (2C), 127.3 (2C), 112.9, 111.7, 111.2, 107.4, 105.2, 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{23}H_{20}NO^{\bullet+}$ 326.1539, found 326.1541.

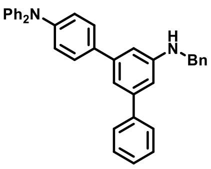


N-benzyl-4-methyl-[1,1':3',1''-terphenyl]-5'-amine (**4ao**).
Pale yellow oil (286 mg, 82%). R_f = 0.63 (PE/EA 4:1). **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.52 – 7.49 (m, 2H), 7.42 – 7.40 (m, 2H), 7.34 – 7.18 (m, 8H), 7.15 – 7.13 (m, 2H), 7.07 (t, ^{4}J = 1.4 Hz, 1H), 6.74 (t, ^{4}J = 1.6 Hz, 2H), 4.34 (s, 2H), 4.08 (br s, 1H), 2.30 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, CDCl$_3$): δ = 149.0, 143.05, 142.99, 142.0, 139.5, 139.0, 137.2, 129.5 (2C), 128.9 (2C), 128.8 (2C), 127.8 (2C), 127.5, 127.42 (2C), 127.39, 127.3 (2C), 116.2,

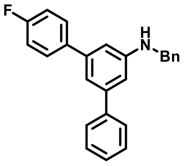
110.85, 110.74, 48.8, 21.2 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{26}H_{24}N^{\bullet+}$ 350.1903, found 350.1897.



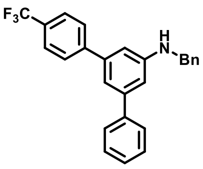
N-benzyl-4-methoxy-[1,1':3',1''-terphenyl]-5'-amine (**4ap**).
Pale yellow oil (288 mg, 79%). R_f = 0.55 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62 – 7.60 (m, 2H), 7.56 – 7.54 (m, 2H), 7.45 – 7.29 (m, 7H), 7.15 (br s, 1H), 6.99 – 6.97 (m, 2H), 6.82 (br s, 2H), 4.45 (s, 2H), 4.19 (br s, 1H), 3.86 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 159.4, 149.0, 143.1, 142.7, 142.0, 139.6, 134.4, 128.9 (2C), 128.8 (2C), 128.4 (2C), 127.8 (2C), 127.5, 127.41 (2C), 127.38, 116.0, 114.3 (2C), 110.6, 110.5, 55.5, 48.7 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{26}H_{24}NO^{\bullet+}$ 366.1852, found 366.1849.



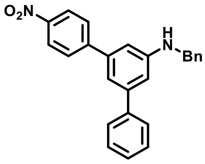
N$^{5'}$-benzyl-*N*^{4},*N*^{4}-diphenyl-[1,1':3',1''-terphenyl]-4,5'-diamine (**4aq**).
Pale yellow oil (296 mg, 59%). R_f = 0.53 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51 – 7.49 (m, 2H), 7.39 – 7.38 (m, 2H), 7.33 – 7.25 (m, 6H), 7.23 – 7.15 (m, 6H), 7.06 – 7.01 (m, 7H), 6.95 – 6.91 (m, 2H), 6.74 – 6.72 (m, 2H), 4.34 (s, 2H), 4.08 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 149.0, 147.9 (2C), 147.4, 143.0, 142.5, 141.9, 139.5, 135.9, 129.4 (4C), 128.9 (2C), 128.8 (2C), 128.0 (2C), 127.8 (2C), 127.5, 127.4 (3C), 124.6 (4C), 124.0 (2C), 123.0 (2C), 116.0, 110.7, 110.5, 48.7 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{37}H_{31}N_2^{\bullet+}$ 503.2482, found 503.2467.



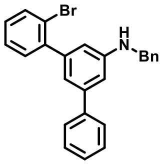
N-benzyl-4-fluoro-[1,1':3',1''-terphenyl]-5'-amine (**4ar**).
White solid (215 mg, 61%). Mp = 125 – 126 ºC. R_f = 0.62 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.49 – 7.45 (m, 2H), 7.43 – 7.39 (m, 2H), 7.31 – 7.15 (m, 8H), 6.99 – 6.95 (m, 3H), 6.70 (s, 1H), 6.64 (s, 1H), 4.28 (s, 2H), 4.04 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 162.6 (d, $^1J_{CF}$ = 246 Hz), 149.0, 143.2, 142.0, 141.8, 139.4, 138.0 (d, $^4J_{CF}$ = 3 Hz), 128.88 (d, $^3J_{CF}$ = 7 Hz, 2C), 128.85 (2C), 128.80 (2C), 127.7 (2C), 127.5, 127.48, 127.37 (2C), 116.1, 115.6 (d, $^2J_{CF}$ = 21 Hz, 2C), 110.94, 110.77, 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{25}H_{21}FN^{\bullet+}$ 534.1653, found 534.1648.



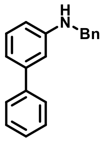
N-benzyl-4-(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-amine (**4as**).
Yellow oil (254 mg, 63%) R_f = 0.75 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 (s, 4H), 7.62 – 7.60 (m, 2H), 7.47 – 7.31 (m, 8H), 7.21 (t, ^4J = 1.5 Hz, 1H), 7.96 (t, ^4J = 1.8 Hz, 1H), 6.89 (t, ^4J = 1.8 Hz, 1H), 5.19 (br s, 1H), 4.47 (s, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 148.2, 145. 3, 143.4, 141.6, 141.4, 138.6, 129.6 (q, $^2J_{CF}$ = 32 Hz), 128.92 (2C), 128.89 (2C), 128.0 (2C), 127.73, 127.69, 127.65 (2C), 127.4 (2C), 125.8 (q, $^3J_{CF}$ = 4 Hz, 2C), 124.5 (q, $^1J_{CF}$ = 272 Hz), 116.9, 112.5, 111.6, 49.2 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{26}H_{21}F_3N^{\bullet+}$ 404.1621, found 404.1616.



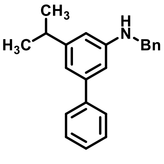
N-benzyl-4-nitro-[1,1':3',1''-terphenyl]-5'-amine (**4at**).
Red-orange oil (247 mg, 65%). R_f = 0.48 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.28 – 8.26 (m, 2H), 7.73 – 7.71 (m, 2H), 7.61 – 7.59 (m, 2H), 7.47 – 7.30 (m, 8H), 7.16 (s, 1H), 6.93 (s, 1H), 6.83 (s, 1H), 4.47 (s, 2H), 4.31 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 149.2, 148.3, 147.3, 143.6, 141.3, 140.6, 139.1, 128.93 (2C), 128.91 (2C), 128.0 (2C), 127.8, 127.68 (2C), 127.64, 127.4 (2C), 124.1 (2C), 116.2, 112.4, 110.8, 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{25}H_{21}N_2O_2^{\bullet+}$ 381.1598, found 381.1586.



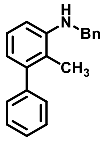
N-benzyl-2-bromo-[1,1':3',1''-terphenyl]-5'-amine (**4au**).
Pale yellow oil (248 mg, 60%). R_f = 0.46 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55 – 7.53 (d, ^3J = 8 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.31 – 7.13 (m, 10 H), 7.09 – 7.04 (m, 1H), 6.90 (s, 1H), 6.79 (s, 1H), 6.58 (s, 1H), 4.53 (br s, 1H), 4.30 (s, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 147.8, 143.0, 142.6, 142.1, 141.5, 139.0, 133.3, 131.4, 128.84 (2C), 128.78 (3C), 127.9 (2C), 127.55, 127.44, 127.42, 127.36 (2C), 122.7, 118.6, 113.4, 111.4, 48.9 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{25}H_{21}{}^{79}BrN^{\bullet+}$ 414.0852, found 414.0860.



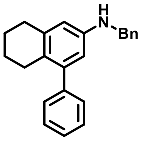
N-benzyl-[1,1'-biphenyl]-3-amine (**4av**).
Pale yellow oil (165 mg, 64%). R_f = 0.70 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60 – 7.57 (m, 2H), 7.45 – 7.41 (m, 4H), 7.40 – 7.30 (m, 4H), 7.27 (t, ^3J = 7.8 Hz, 1H), 6.99 (ddd, ^4J = 1.7; 1.6 Hz, ^3J = 7.6 Hz, 1H), 6.86 (t, ^4J = 2.0 Hz, 1H), 6.66 (ddd, ^4J = 2.4; 2.5 Hz, ^3J = 8.1 Hz, 1H), 4.42 (s, 2H), 4.12 (br s, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 148.7, 142.6, 141.9, 139.6, 129.8, 128.81 (2C), 129.73 (2C), 127.71 (2C), 127.43, 127.31 (2C), 127.27, 116.9, 112.0, 111.9, 48.6 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{19}H_{18}N^{\bullet+}$ 260.1434, found 260.1431.



N-benzyl-5-isopropyl-[1,1'-biphenyl]-3-amine (**4aw**).
Yellow oil (199 mg, 66%). R_f = 0.57 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.58 - 7.56 (m, 2H), 7.43 – 7.38 (m, 5H), 7.37 – 7.34 (m, 2H), 7.32 – 7.30 (m, 1H), 6.87 (t, ^4J = 1.5 Hz, 1H), 6.73 (t, ^4J = 2.0 Hz, 1H), 6.56 (t, ^4J = 1.7 Hz, 1H), 4.40 (s, 2H), 2.90 (hept, ^3J = 7 Hz, 1H), 1.29 (d, ^3J = 7 Hz, 6H), ppm. The resonance for N-H is has not been observed. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 150.7, 148.5, 142.6, 142.3, 139.5, 128.8 (2C), 128.7 (2C), 127.9 (2C), 127.5, 127.4 (2C), 127.2, 115.7, 110.8, 109.7, 49.0, 34.5, 24.1 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{\bullet+}$ calcd for $C_{22}H_{24}N^{\bullet+}$ 302.1903, found 302.1913.



N-benzyl-2-methyl-[1,1'-biphenyl]-3-amine (**4ax**).
Pale yellow oil (207 mg, 76%). R$_f$ = (PE/EA 4:1). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 7.48 – 7.33 (m, 10H), 7.21 – 7.17 (m, 1H), 6.76 – 6.71 (m, 2H), 4.47 (s, 2H), 4.02 (br s, 1H), 2.11 (s, 3H) ppm. ^{13}**C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 146.5, 142.90, 142.84, 139.7, 129.6 (2C), 128.8 (2C), 128.1 (2C), 127.7 (2C), 127.4, 126.7, 126.4, 119.5 (2C), 109.3, 48.8, 14.4 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{•+}$ calcd for $C_{20}H_{20}N^{•+}$ 274.1590, found 274.1584.



N-benzyl-4-phenyl-5,6,7,8-tetrahydronaphthalen-2-amine (**4ay**).
Pale yellow oil (225 mg, 72%). R$_f$ = 0.57 (PE/EA 4:1). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 7.60 – 7.57 (m, 2H), 7.48 – 7.39 (m, 6H), 7.36 – 7.32 (m, 2H), 6.82 (d, ^4J = 1.5 Hz, 1H), 6.76 (d, ^4J = 1.5 Hz, 1H), 4.48 (s, 2H), 3.96 (br s, 1H), 2.88 (t, ^3J = 6.2 Hz, 2H), 2.52 (t, ^3J = 6.2 Hz, 2H), 1.96 (tt, ^3J = 6.2; 6.0 Hz, 2H), 1.86 (tt, ^3J = 6.2; 6.0 Hz, 2H) ppm. ^{13}**C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 146.3 142.4, 139.7, 139.5, 138.1, 128.8 (2C), 128.6 (2C), 127.8 (2C), 127.4, 127.3 (2C), 126.9, 120.6, 117.6, 106.5, 48.7, 30.4, 23.9, 23.3, 22.9 ppm. **HRMS** (ESI/TOF) *m/z*: [M + H]$^{•+}$ calcd for $C_{23}H_{24}N^{•+}$ 314.1903, found 314.1896.

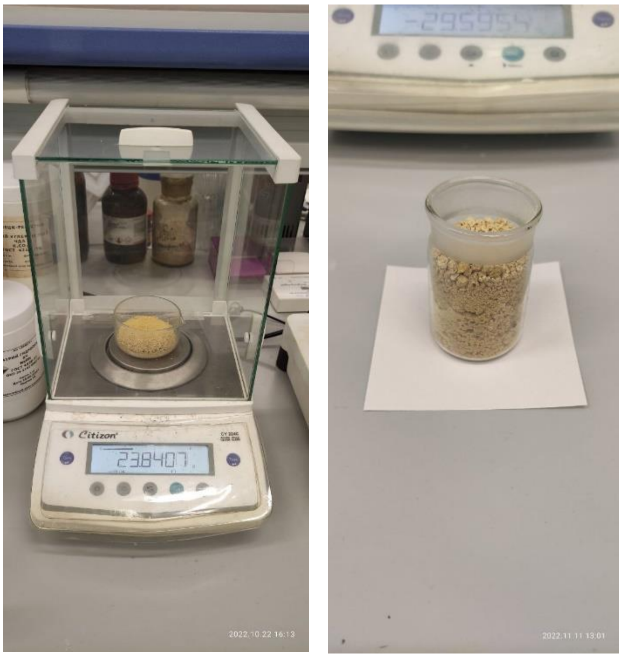
5. SCALE-UP EXPERIMENTS

10 mmol synthesis of aniline 4a

100 mL round-bottom flask was charged with benzylideneacetone (**1a**) (1.45 g, 10 mmol), *N-phenacyl*pyridinium iodide (**2a**) (3.25 g, 10 mmol), benzylamine (**3a**) (2.18 mL, 20 mmol, 2 equiv.), and dioxane (50 mL). The flask was equipped with a magnetic spinning bar, placed into a pre-heated (100 ℃) aluminum block, and the reaction mixture was refluxed with stirring up to full conversion of the starting enone **2a** (ca. 4-6 h). Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, concentrated *in vacuo*, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 5:1 to 3:1) to afford target compound **4a** with 88% yield (2.95 g) in a form of pale yellow oil that solidified upon standing.

100 mmol synthesis of aniline 4a

1000 mL round-bottom flask was charged with benzylideneacetone (**1a**) (14.5 g, 100 mmol), *N-phenacyl*pyridinium iodide (**2a**) (32.5 g, 100 mmol), benzylamine (**3a**) (21.8 mL, 200 mmol, 2 equiv.), and dioxane (500 mL). The flask was equipped with a magnetic spinning bar, placed into a pre-heated (100 ℃) heating mantle, and the reaction mixture was refluxed with stirring up to full conversion of the starting enone **2a** (ca. 24 h). Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, concentrated *in vacuo*, redissolved in DCM (ca 200 mL), washed with H_2O (2 × 100 mL), brine (2 × 50 mL), dried over anhydrous Na_2SO_4, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 5:1 to 3:1) to afford target compound **4a** with 71% yield (23.84 g) in a form of pale yellow oil that solidified upon standing.

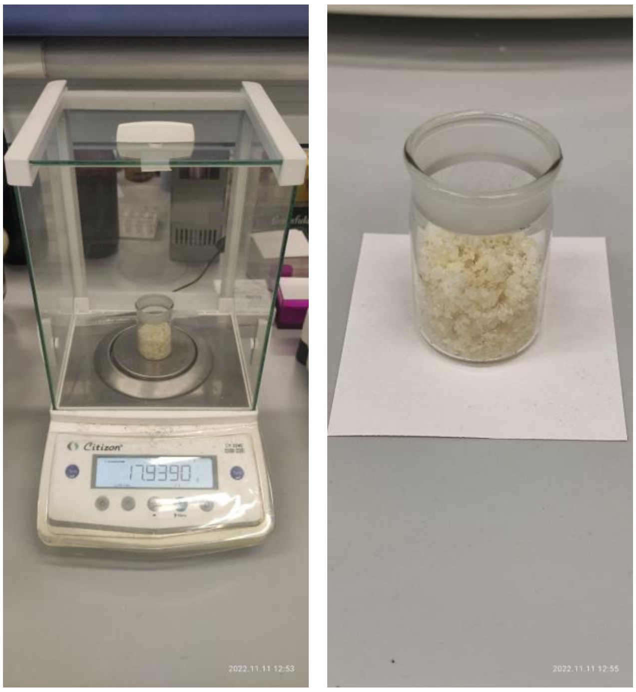


10 mmol synthesis of aniline 4n

100 mL round-bottom flask was charged with benzylideneacetone (**1a**) (1.45 g, 10 mmol), *N*-phenacylpyridinium iodide (**2a**) (3.25 g, 10 mmol), diethylamine (**3n**) (2.07 mL, 20 mmol, 2 equiv.), and dioxane (50 mL). The flask was equipped with a magnetic spinning bar, placed into a pre-heated (100 ℃) aluminum block, and the reaction mixture was refluxed with stirring up to full conversion of the starting enone **2a** (ca. 4-6 h). *NOTE! As the boiling point of diethylamine is ~56 °C, the cooling liquid in the condenser should be chosen accordingly.* Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, concentrated *in vacuo*, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 5:1 to 3:1) to afford target compound **4n** with 79% yield (2.37 g) in a form of pale yellow oil that solidified upon standing.

100 mmol synthesis of aniline 4n

1000 mL round-bottom flask was charged with benzylideneacetone (**1a**) (14.5 g, 100 mmol), *N-phenacyl*pyridinium iodide (**2a**) (32.5 g, 100 mmol), diethylamine (**3n**) (20.7 mL, 200 mmol, 2 equiv.), and dioxane (50 mL). The flask was equipped with a magnetic spinning bar, placed into a pre-heated (100 ℃) heating mantle, and the reaction mixture was refluxed with stirring up to full conversion of the starting enone **2a** (ca. 4-6 h). *NOTE! As the boiling point of diethylamine is ~56 °C, the cooling liquid in the* *condenser should be chosen accordingly.* Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, concentrated *in vacuo*, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 5:1 to 3:1) to afford target compound **4n** with 60% yield (17.93 g) in a form of pale yellow oil that solidified upon standing.

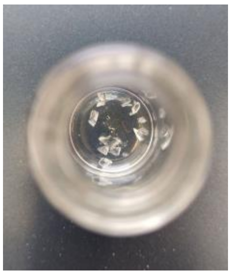


10 mmol synthesis of aniline 4u

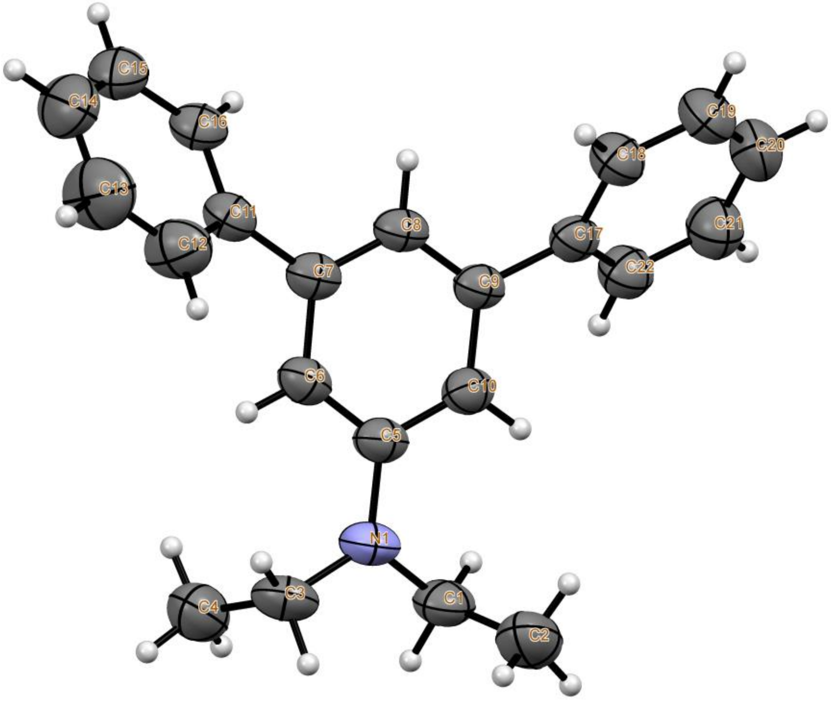
100 mL heavy wall pressure tube with internal thread was charged with benzylideneacetone (**1a**) (1.45 g, 10 mmol), *N*-phenacylpyridinium iodide (**2a**) (3.25 g, 10 mmol), aniline (**3u**) (0.91 mL, 20 mmol, 2 equiv.), and acetonitrile (50 mL). The flask was equipped with a magnetic spinning bar, sealed with PTFE bushing through O-ring, placed into a pre-heated (90 ℃) oil bath, and the reaction mixture was stirred up to full conversion of the starting enone **2a** (ca. 24 h). Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, concentrated *in vacuo*, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 3:1 to 2:1) to afford target compound **4u** with 63% yield (2.02 g) in a form of pale yellow oil that solidified upon standing. *NOTE! The boiling point of acetonitrile is 82 °C; therefore, the content is pressurized when heated at 90 ℃. Make sure that the temperature of the reaction tube is below 70°C before opening.*

6. SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS OF ANILINE 4n

A crystal of compound **4n** suitable for single crystal X-ray diffraction analysis was obtained via slow evaporation from acetonitrile at ambient temperature and atmosphere.



The X-ray diffraction data for compound **4n** (*CCDC 2235359*) was obtained on «New Xcalibur, Ruby» automated diffractometer with a CCD detector [MoKα radiation, 293(2) K, ω-scanning with a step of 1°] according to standard procedure.[7] A correction for absorption by the crystal was applied empirically using SCALE3 ABSPACK algorithm. The structure was solved by the direct method and refined against F2 by the fullmatrix least-squares method in anisotropic approximation for all non-hydrogen atoms. The positions of hydrogen atoms were refined according to the riding model in isotropic approximation with dependent thermal parameters. All calculations were performed using SHELX97 software package.[8] A detailed crystallographic data is attached as a separate CIF file.

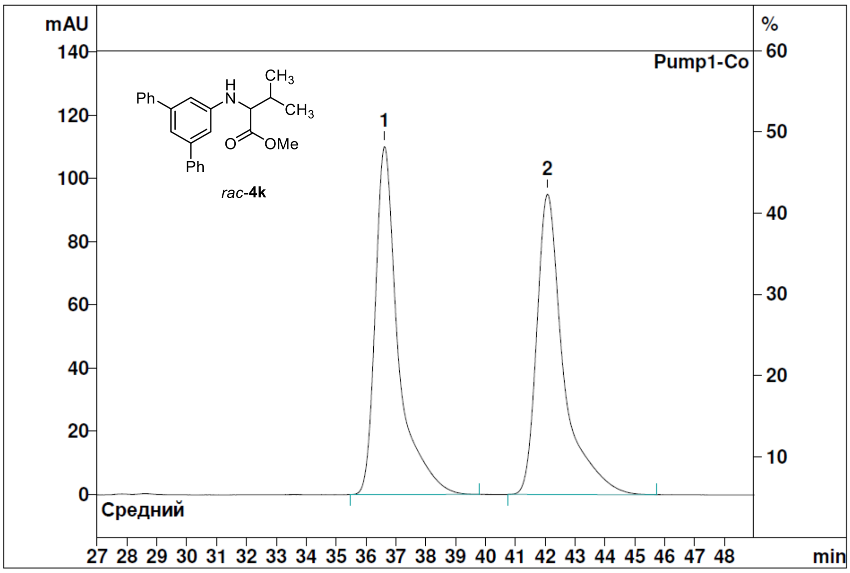


Structure of the molecule of *N*,*N*-diethyl-[1,1':3',1''-terphenyl]-5'-amine (**4n**) according to the X-ray diffraction data; non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

7. CHIRAL HPLC TRACES FOR ANILINE 4k

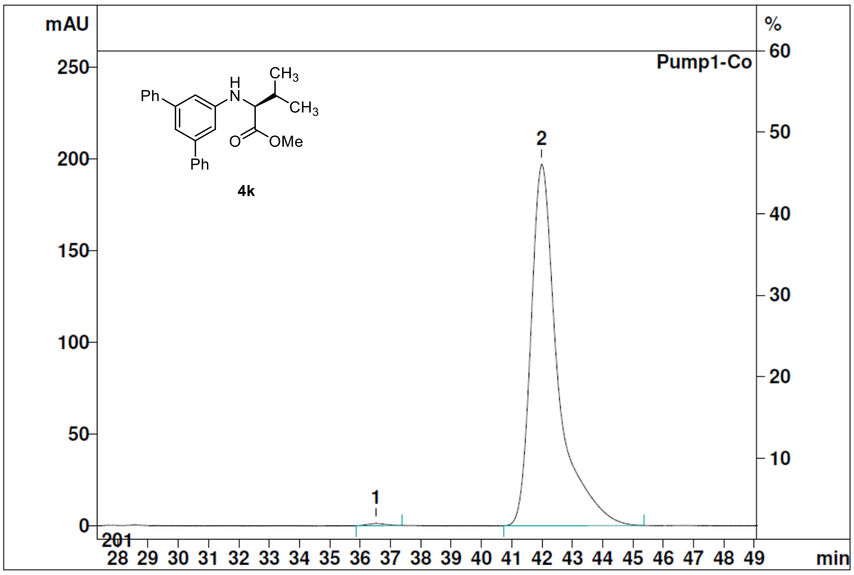
The sample of *rac*-**4k** was obtained analogously from *rac*-methyl valinate. Analysis was performed on «Hitachi Chromaster» equipped with Lux (5μm) cellulose-1 column (Phenomenex) and 5430 diode array detector (UV detection).

Conditions: isocratic elution water/acetonitrile 40:60, flow rate 0.75 mL/min at 35 °C.



```
Quantitation method:   Response normalization

Peak   Retention        Area      Area           Component
             min     mAU*sec         %
   1       36.62   20233.554     49.89
   2       42.07   20321.362     50.11
___________________________________________________________
   2       50.31   40554.916    100.00
```



```
Quantitation method:   Response normalization

Peak   Retention        Area      Area           Component
             min     mAU*sec         %
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   2       41.99   12178.091     99.60
___________________________________________________________
   2       50.00   12227.306    100.00
```
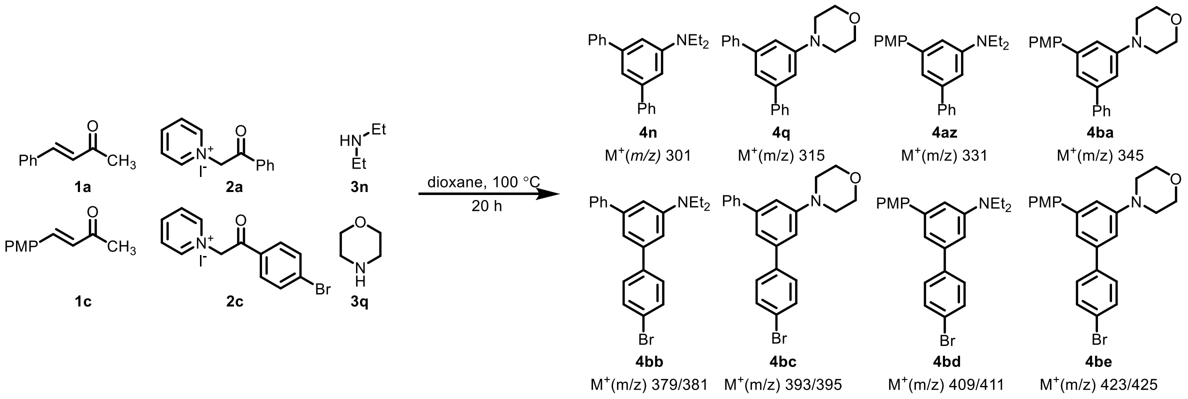
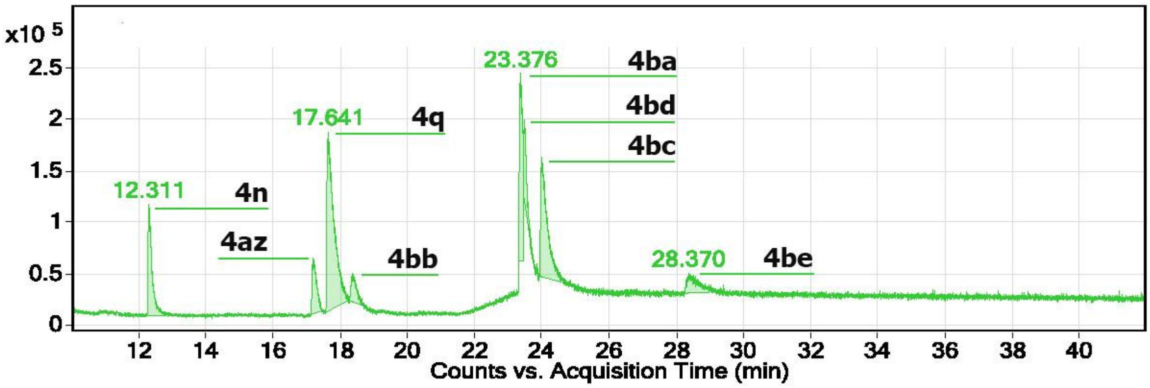

8. COMBINATORIAL EXPERIMENT

3 mL Weaton microreactor was charged with enone **1a** (29.2 mg, 0.2 mmol), enone **1c** (35.2 mg, 0.2 mmol), pyridinium salt **2a** (65.0 mg, 0.2 mmol), pyridinium salt **2c** (80.8 mg, 0.2 mmol), amine **3n** (20.7 μL, 0.2 mmol), amine **3q** (17.2 μL, 0.2 mmol) and dioxane (2 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (100 ℃) aluminum block, then the content was stirred at the same temperature for 20 h. Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with EA, concentrated *in vacuo* and redissolved in DCM (2 mL). 10 μL of the resulting solution was transferred into a 1.5 mL GC-vial, diluted with 1 mL of DCM and subjected to the GC-MS analysis.

Conditions: injection = 0.5 μL at 300 °C, split 10:1; carrier gas – helium (1 mL/min); oven: initial temperature = 100 °C (5 min hold time), then 250 °C (ramp rate 100 °C/min, 15 min hold time), then 300 °C (ramp rate 120 °C/min, 20 min hold time); ionization method – EI (70 eV).





*Note 1: **4q**&**4bb** intersected; **4ba**&**4bd** intersected – we have not been able to find a method in order to achieve better separation.*

Note 2: peaks with m/z = 28, 207 correspond to background.

Qualitative Analysis Report

Data Filename AM1882-3.D
Sample Type
Instrument Name 7890B-5977A
Acq Method Method_Anton_1-10_cut10gr100-250-300aniline41min.M
IRM Calibration Status Not Applicable
Comment

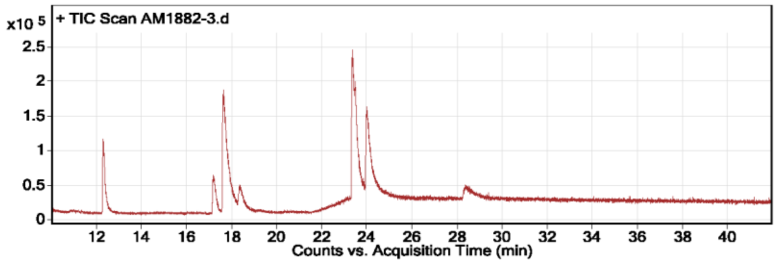
Sample Name AM1882-3
Position 15
User Name AM
Acquired Time 07/11/2022 14:10:41
DA Method default.m

Expected Barcode
Dual Inj Vol 0.5
TunePath D:\MassHunter\GCMS\1\5977 \
Acquisition Time #2 2022-11-07 09:10:41Z
RunCompletedFlag True

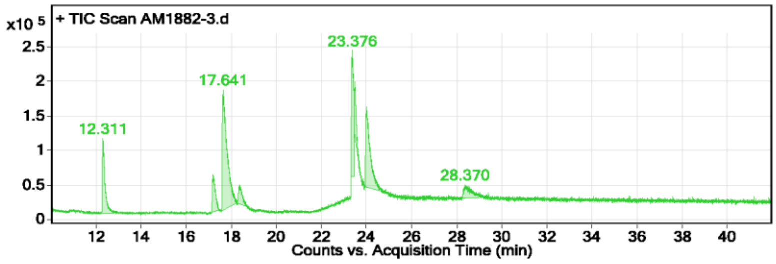
Sample Amount
TuneName ATUNE.U
MSFirmwareVersion 6.00.21
OperatorName AM
Acquisition SW Version MassHunter GC/MS Acquisition B.07.02.1938 08-Sep-2014 Copyright © 1989-2014 Agilent Technologies, Inc.

User Chromatograms

Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** Unspecified



Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** Unspecified

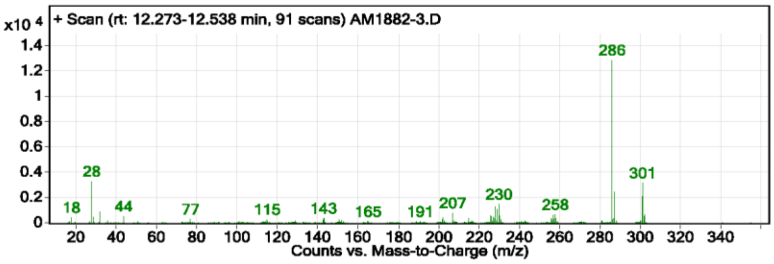


Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	12.262	12.311	12.815	107659.19	865060.98	34.49
2	17.135	17.199	17.463	53831.91	489228.25	19.5
3	17.578	17.641	18.232	173930.14	2508384.94	100
4	18.287	18.362	18.633	27992.78	288307.77	11.49
5	23.319	23.376	23.468	183518	1278534.54	50.97
6	23.468	23.479	23.667	77572.41	394712.11	15.74
7	23.941	23.994	24.571	116257.05	1562447.65	62.29
8	28.261	28.37	28.97	18924.77	407878.83	16.26

User Spectra

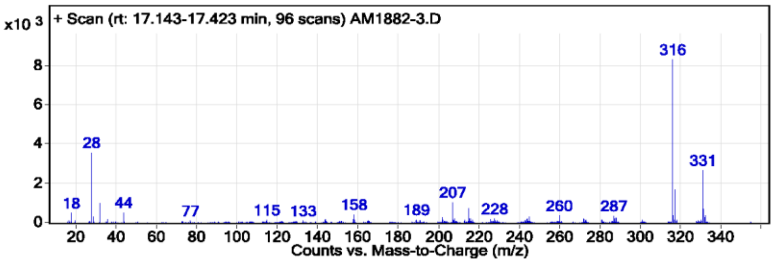
Spectrum Source	Collision Energy	Ionization Mode
Peak (1) in "+ TIC Scan"	0	Unspecified



Peak List

m/z	z	Abund
28		3272.65
32		876.41
207	1	772.33
228	1	1276.34
229		1064.9
230	1	1463.48
286	1	12841.27
287		2430.76
301	1	2086.27
301	1	3139.25

Spectrum Source	Collision Energy	Ionization Mode
Peak (2) in "+ TIC Scan"	0	Unspecified



Peak List

m/z	z	Abund
28		3552.01
32		984.48
44		497.59
207	1	519.73
207	1	1017.7
215	1	704.67
316	1	8282.95
317		1673.64
331	1	2644.6
331		668.03

Spectrum Source	Collision Energy	Ionization Mode
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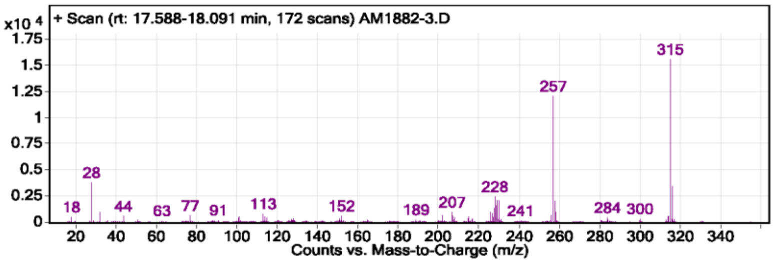

Peak List

m/z	z	Abund
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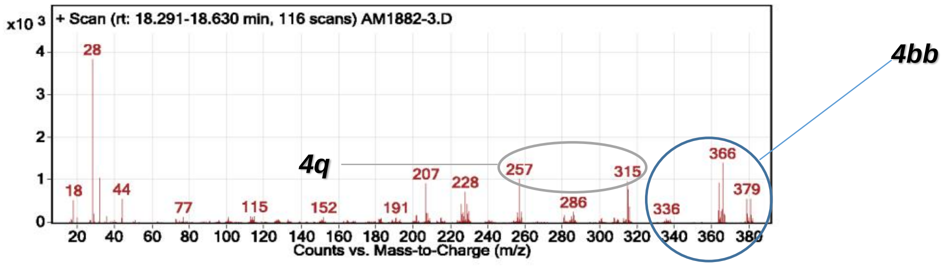
228		2426.95
229	1	1562.62
229	1	2047.42
230	1	2069.66
257		1733.88
257	1	12054.16
258	1	2004.3
315	1	15574.46
316		3427.04

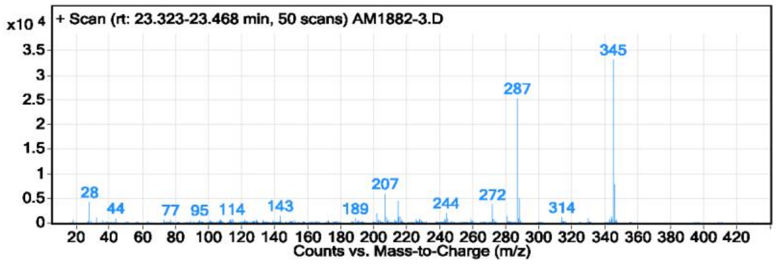
Spectrum Source	Collision Energy	Ionization Mode
Peak (4) in "+ TIC Scan"	0	Unspecified



Peak List

m/z	z	Abund
28		3826.34
32		1039.44
207	1	903.06
228		707.72
257	1	1011.87
315	1	959.04
315	1	770.88
364	1	918.78
364	1	792.33
366	1	1385.16

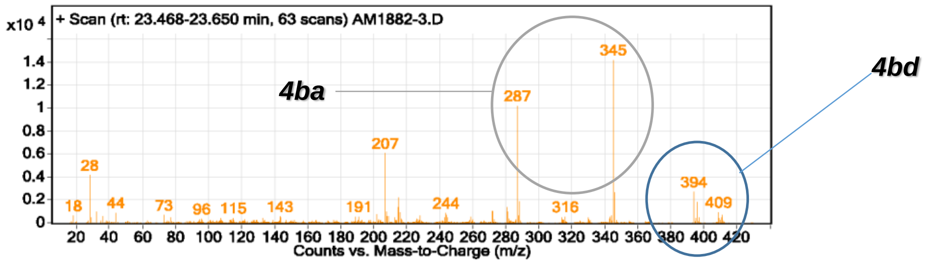
Spectrum Source	Collision Energy	Ionization Mode
Peak (5) in "+ TIC Scan"	0	Unspecified



Peak List

m/z	z	Abund
28		4174.32
202	1	1909.88
207	1	5891.76
215	1	4484.46
244		1956.68
272	1	3699.38
287	1	25278.2
288		4907.8
345	1	33141.28
346	1	7784.84

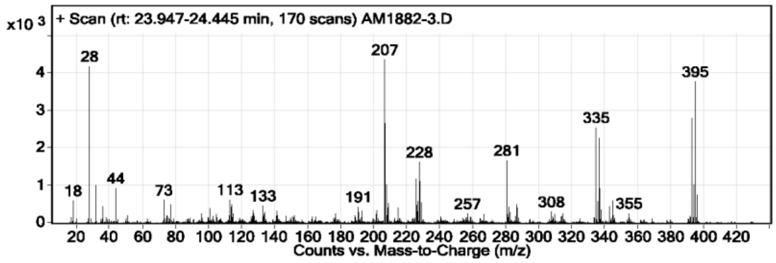
Spectrum Source	Collision Energy	Ionization Mode
Peak (6) in "+ TIC Scan"	0	Unspecified



Peak List

m/z	z	Abund
28		4130.67
207	1	6037.43
215		1363.86
215		2182.32
287	1	10176.54
288		1834.41
345	1	14172.22
346		2657.6
394	1	2675.52
396		1799.08

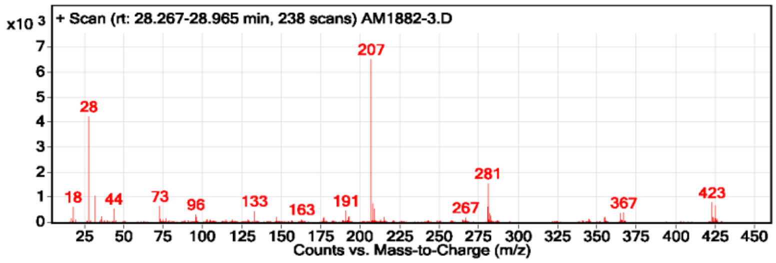
Spectrum Source	Collision Energy	Ionization Mode
Peak (7) in "+ TIC Scan"	0	Unspecified



Peak List

m/z	z	Abund
28		4172.31
207	1	4350.45
207		2649.82
228	1	1611.59
281	1	1657.1
335	1	2533.85
337	1	2251.81
393		1708.18
393	1	2783.35
395	1	3762.09

Spectrum Source	Collision Energy	Ionization Mode
Peak (8) in "+ TIC Scan"	0	Unspecified



Peak List

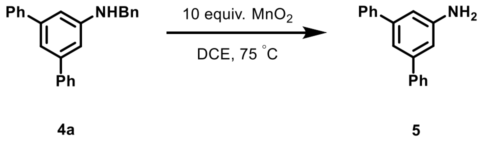
m/z	z	Abund
28		4216.85

32		1039.09
73		629.13
207		729.47
207	1	6505.15
208	1	727.63
208	1	729.35
281	1	1539.03
423	1	775.14
425	1	649.63

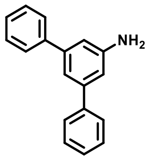
--- End Of Report ---

9. FURTHER TRANSFORMATIONS OF THE OBTAINED PRODUCTS

Synthesis of aniline 5

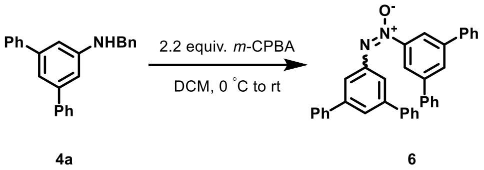


5 mL Weaton microreactor was charged with aniline **4a** (170 mg, 0.5 mmol), MnO_2 (400 mg, 5 mmol, 10 equiv.), and DCE (3.5 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (75 ℃) aluminum block, then the content was stirred at the same temperature for 3 days. Upon completion (TLC or GC control), the reaction mixture was cooled to ambient temperature, filtered through a pad of silica gel, washed with DCM, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 5:1 to 3:1) to afford target compound **5**. Aniline **5** could be recrystallized from $CHCl_3$/PE (off-white solid).

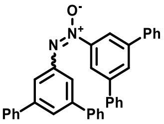


[1,1':3',1''-Terphenyl]-5'-amine (**5**).[9]
Colourless oil (110 mg, 90%). $R_f = 0.17$ (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55 – 7.53 (m, 4H), 7.37 – 7.34 (m, 4H), 7.37 – 7.26 (m, 2H), 7.20 (t, ^4J = 1.5 Hz, 1H), 6.87 (d, ^4J = 1.5 Hz, 2H), 4.40 (br s, 2H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 146.1, 143.1 (2C), 141.4 (2C), 128.8 (4C), 127.5 (2C), 127.3 (4C), 117.8, 113.6 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{•+}$ calcd for $C_{18}H_{19}N^{•+}$ 246.1277, found 246.1275.

Synthesis of azoxyarene 6

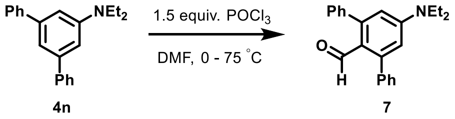


10 mL round-bottom flask was charged with aniline **4a** (136 mg, 0.4 mmol) and DCM (5 mL). The flask was equipped with a magnetic spinning bar and cooled to 0 ℃. To the resulting solution was added *m*-CPBA (70-77%, 205 mg, 0.88 mmol, 2.2 equiv.) portionwise upon stirring. The reaction mixture was allowed to reach an ambient temperature, after which is was stirred for 72 h. Upon completion (TLC control), the reaction mixture was poured into 5% NaOH (50 mL), extracted with DCM (2 × 20 mL), washed with H_2O (2 × 10 mL), brine (15 mL), dried over anhydrous Na_2SO_4, concentrated, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, 4:1) to afford target compound **6**.



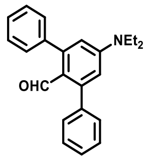
1,2-Di([1,1':3',1''-terphenyl]-5'-yl)diazene 1-oxide (**6**).
Yellow oil (162 mg, 81%). $R_f = 0.53$ (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.58 (d, ^4J = 1.5 Hz, 2H), 8.46 (d, ^4J = 1.5 Hz, 2H), 8.02 (t, ^4J = 1.5 Hz, 1H), 7.88 (t, ^4J = 1.5 Hz, 1H), 7.76 – 7.73 (m, 8H), 7.54 – 7.48 (m, 8H), 7.46 – 7.39 (m, 4H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 149.6, 145.1, 143.0 (2C), 142.5 (2C), 140.7 (2C), 140.0 (2C), 129.24, 129.20 (4C), 129.0 (4C), 128.3 (2C), 127.9 (2C), 127.5 (8C), 127.4, 123.3 (2C), 120.0 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{•+}$ calcd for $C_{36}H_{27}N_2O^{•+}$ 503.2118, found 503.2109.

Synthesis of aldehyde 7



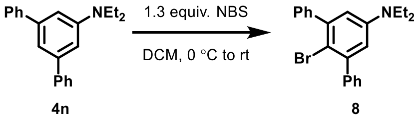
10 mL round-bottom flask was charged with dry DMF (5 mL), a spinning bar, and cooled to 0 ℃. $POCl_3$ (70 µL, 0.75 mmol, 1.5 equiv.) was added, and the resulting solution was stirred for 30 min at the same temperature. In 30 min, aniline **4n** (150 mg, 0.5 mmol) was added to the reaction mixture at 0 ℃ upon stirring. The reaction mixture was allowed to reach ambient temperature, after which the flask was placed into a pre-heated (75 ℃) aluminum block, then the content was stirred for 24 h. Upon completion (TLC control), the reaction mixture was poured into saturated solution of $NaHCO_3$ (50 mL), extracted with DCM (2 × 15 mL),

washed with H_2O (2 × 10 mL), brine (15 mL), dried over anhydrous Na_2SO_4, concentrated, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 9:1 to 4:1) to afford target compound **7**.

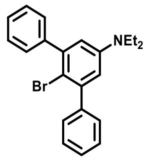


5'-(Diethylamino)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (**7**).
Pale yellow oil (138 mg, 84%). R_f = 0.53 (PE/EA 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 7.49 – 7.44 (m, 10H), 6.60 (s, 2H), 3.51 (q, ^3J = 7.1 Hz, 4H), 1.29 (t, ^3J = 7.1 Hz, 6H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 190.3, 149.6, 148.1 (2C), 141.5 (2C), 129.3 (4C), 127.9 (4C), 127.3 (2C), 120.4, 112.6 (2C), 44.5 (2C), 12.6 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{23}H_{24}NO^{\bullet+}$ 330.1852, found 330.1851.

Synthesis of bromoaniline 8

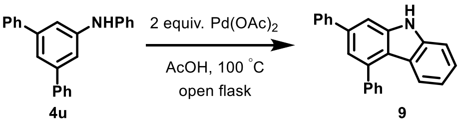


5 mL Weaton microreactor was charged with aniline **4n** (120 mg, 0.4 mmol) and DCM (3 mL). The resulting solution was cooled to 0 °C followed by addition of freshly recrystallized NBS (95 mg, 0.52 mmol, 1.3 equiv.) portionwise upon stirring. *NOTE! Exothermic reaction, precautions should be taken. Controlling the temperature at the initial phase of the reaction is important: we observed the formation of overbromination products when NBS was added at higher temperatures.* The reaction mixture was allowed to reach ambient temperature and stirred further for 24 h (TLC control), after which it was poured into H_2O (50 mL), extracted with DCM (2 × 15 mL), washed with H_2O (2 × 10 mL), brine (15 mL), dried over anhydrous Na_2SO_4, concentrated, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, gradient elution from 1:0 to 20:1) to afford target compound **8**.

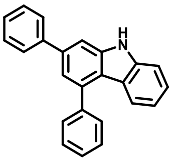


2'-Bromo-*N*,*N*-diethyl-[1,1':3',1''-terphenyl]-5'-amine (**8**).
Colourless oil (141 mg, 93%). R_f = 0.65 (PE/EA 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.36 – 7.28 (m, 10H), 6.52 (br s, 2H), 3.26 (q, ^3J = 7.0 Hz, 4H), 1.09 (t, ^3J = 7.0 Hz, 6H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 146.1, 144.6 (2C), 143.2 (2C), 129.7 (5C), 128.0 (4C), 127.4 (2C), 114.5 (2C), 44.9 (2C), 12.6 (2C) ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{22}H_{23}{}^{79}BrN^{\bullet+}$ 380.1008, found 380.1014.

Synthesis of carbazole 9



25 mL round-bottom flask was charged with a spinning bar, aniline **4u** (128 mg, 0.4 mmol), $Pd(OAc)_2$ (180 mg, 0.8 mmol, 2 equiv.) and acetic acid (7 mL). The flask was placed into a pre-heated (100 ℃) aluminum block, and the content was stirred for 5 h unsealed. Upon completion (TLC control), the reaction mixture was passed through a pad of silica gel, washed with DCM, concentrated, dry-loaded on silica gel and subjected to column chromatography (silica gel, eluent: petroleum ether/DCM, 2:1) to afford target compound **9**.



2,4-Diphenyl-9H-carbazole (**9**).
Pale yellow oil (99 mg, 78%). R_f = 0.37 (PE/EA 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 (br s, 1H), 7.61 – 7.56 (m, 4H), 7.45 – 7.42 (m, 2H), 7.41 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 7.27 (d, ^4J = 1.4 Hz, 1H), 7.42 – 7.21 (m, 3H), 6.89 (ddd, ^3J = 8.1; 5.6 Hz, ^4J = 2.6 Hz, 1H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 141.7, 141.4, 140.7, 140.4, 139.2, 138.1, 129.4 (2C), 128.9 (2C), 128.6 (2C), 127.76, 127.65 (2C), 127.3, 125.9, 123.0, 122.6, 121.0, 120.3, 119.4, 110.6, 108.1 ppm. **HRMS** (ESI/TOF) *m/z*: $[M + H]^{\bullet+}$ calcd for $C_{24}H_{18}N^{\bullet+}$ 320.1434, found 320.1434.

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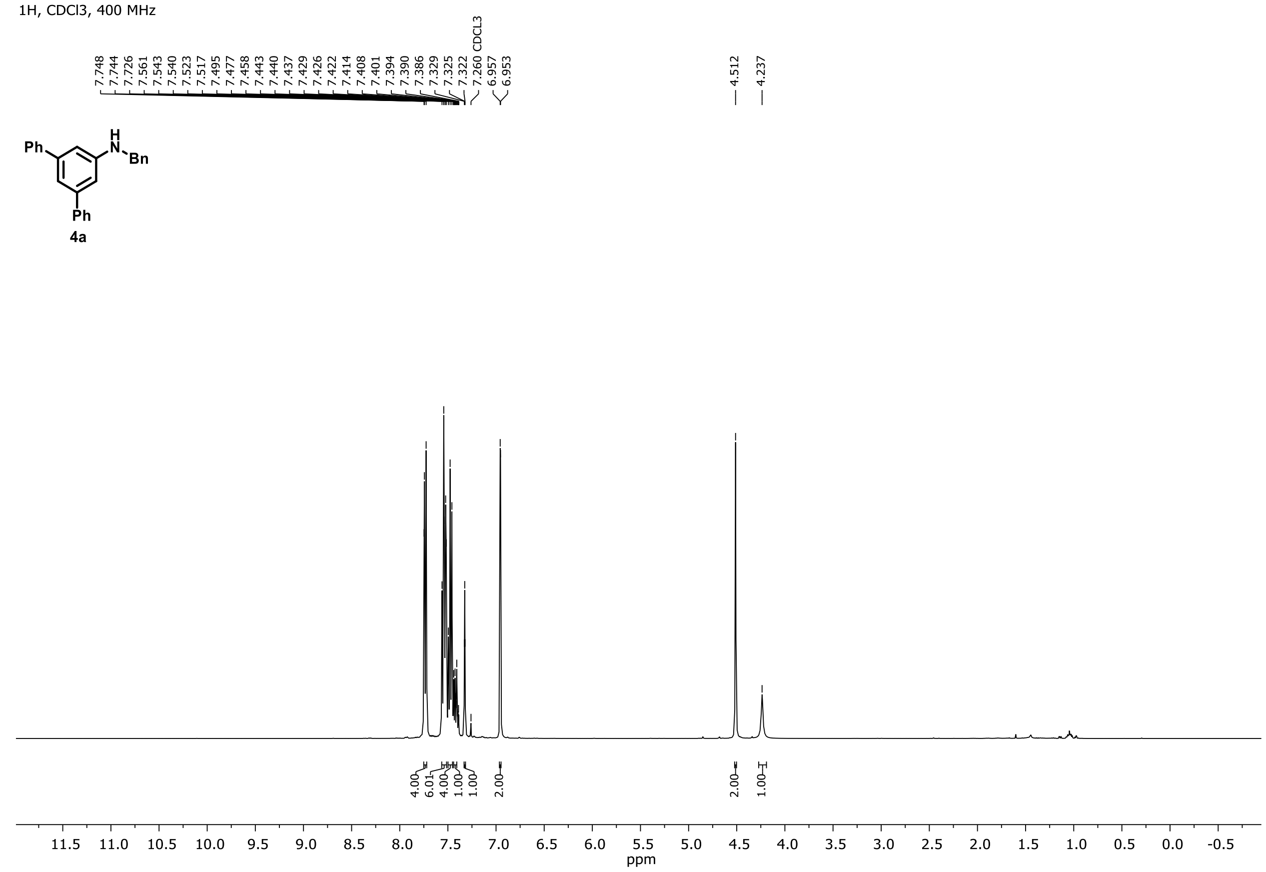
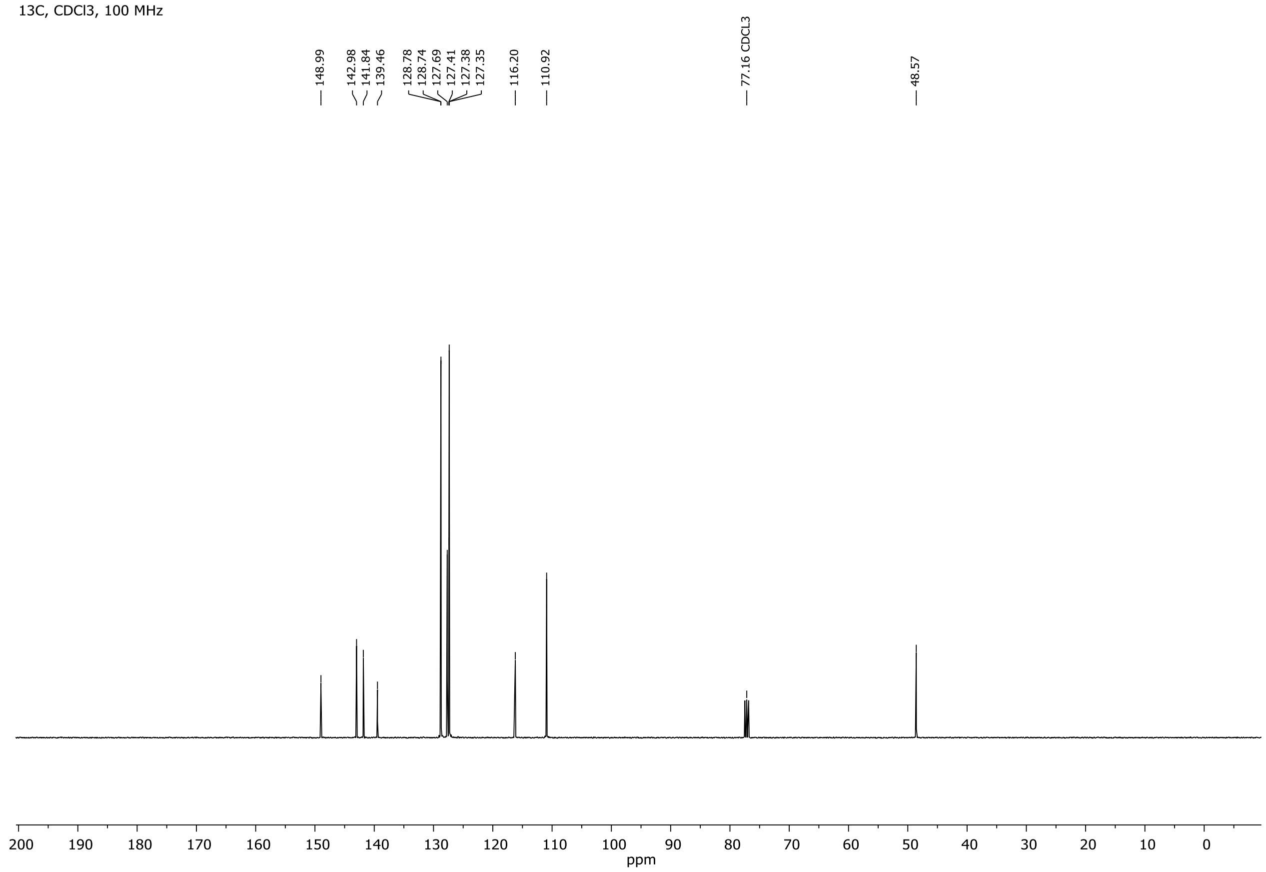
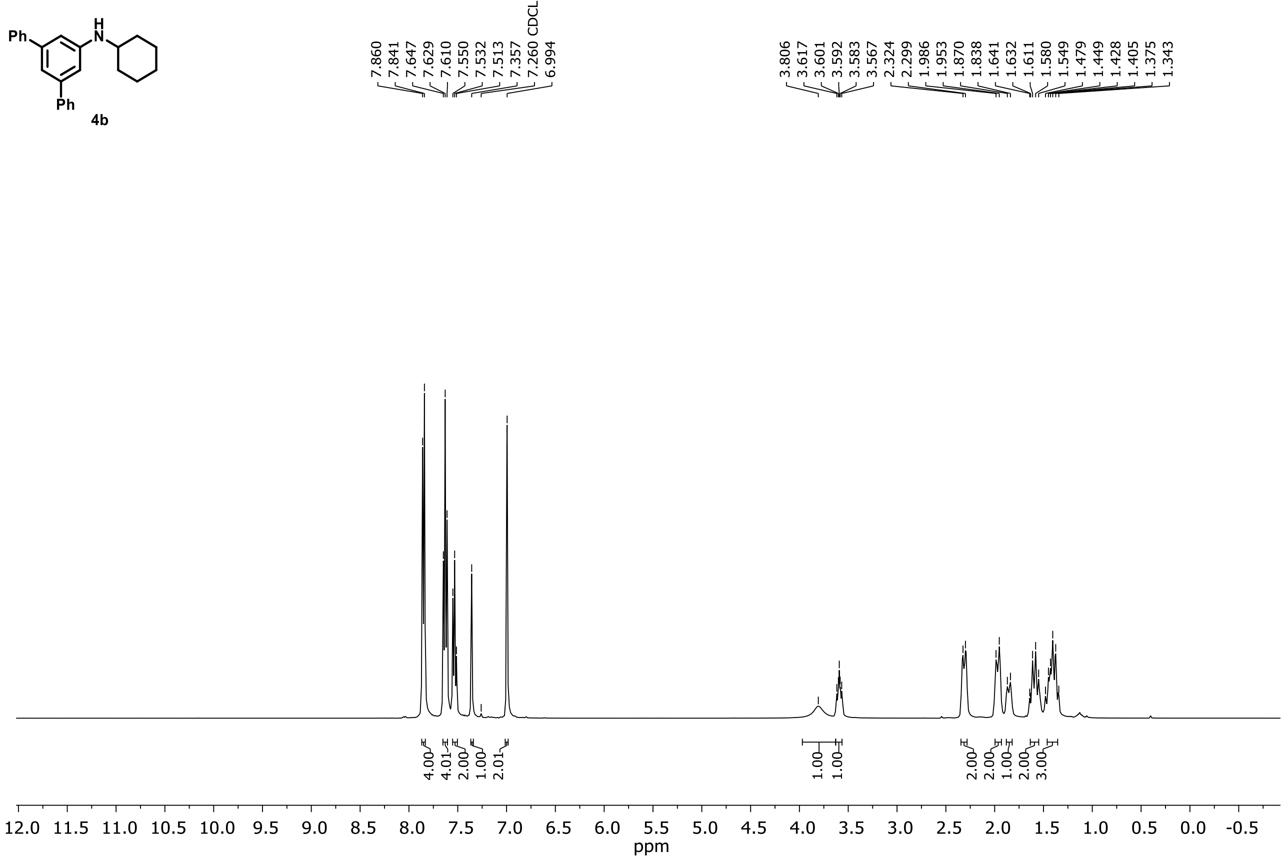
11. COPIES OF NMR SPECTRA

General note. *All spectra were recorded by taking samples from the combined fractions after column chromatography in order to estimate the overall degree of purity and homogeneity of the obtained compounds.*

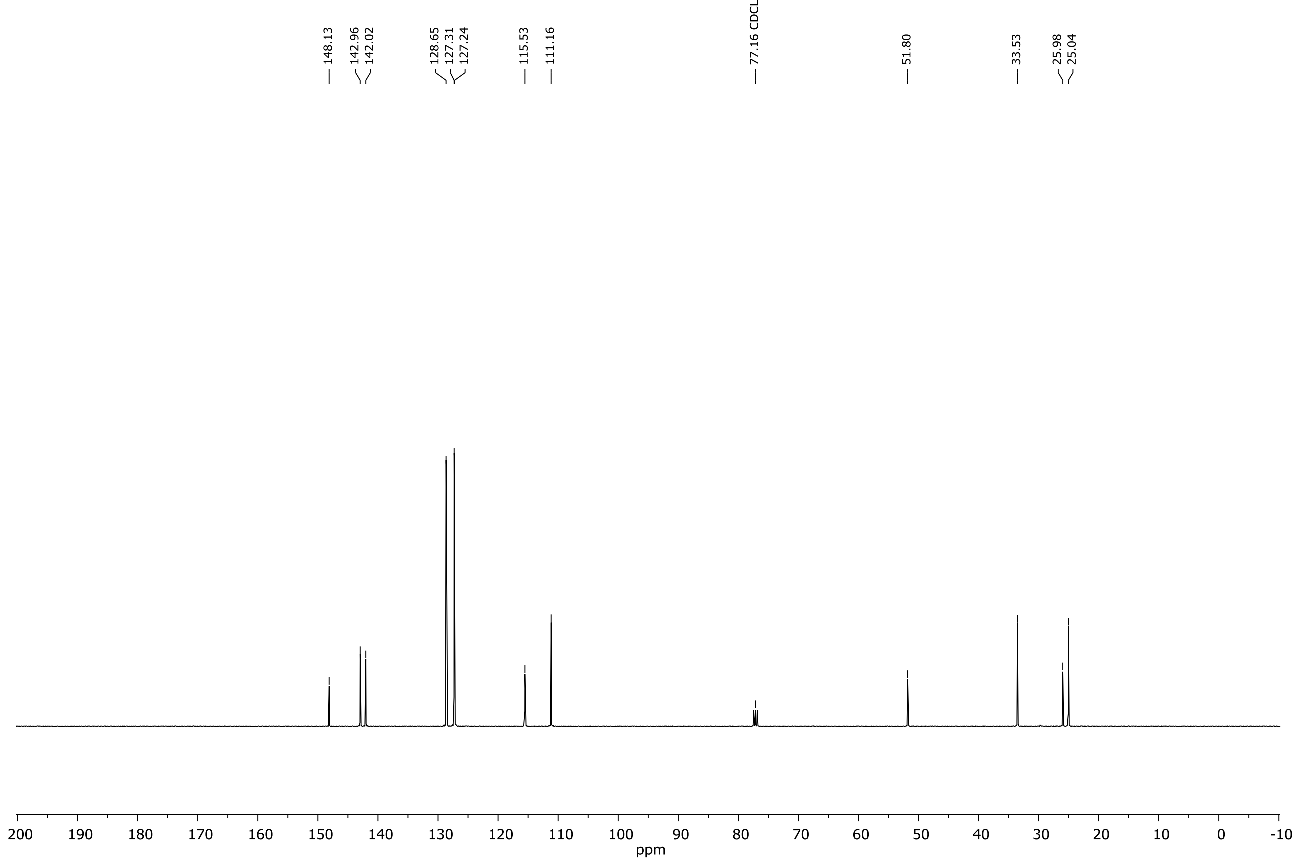




1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz



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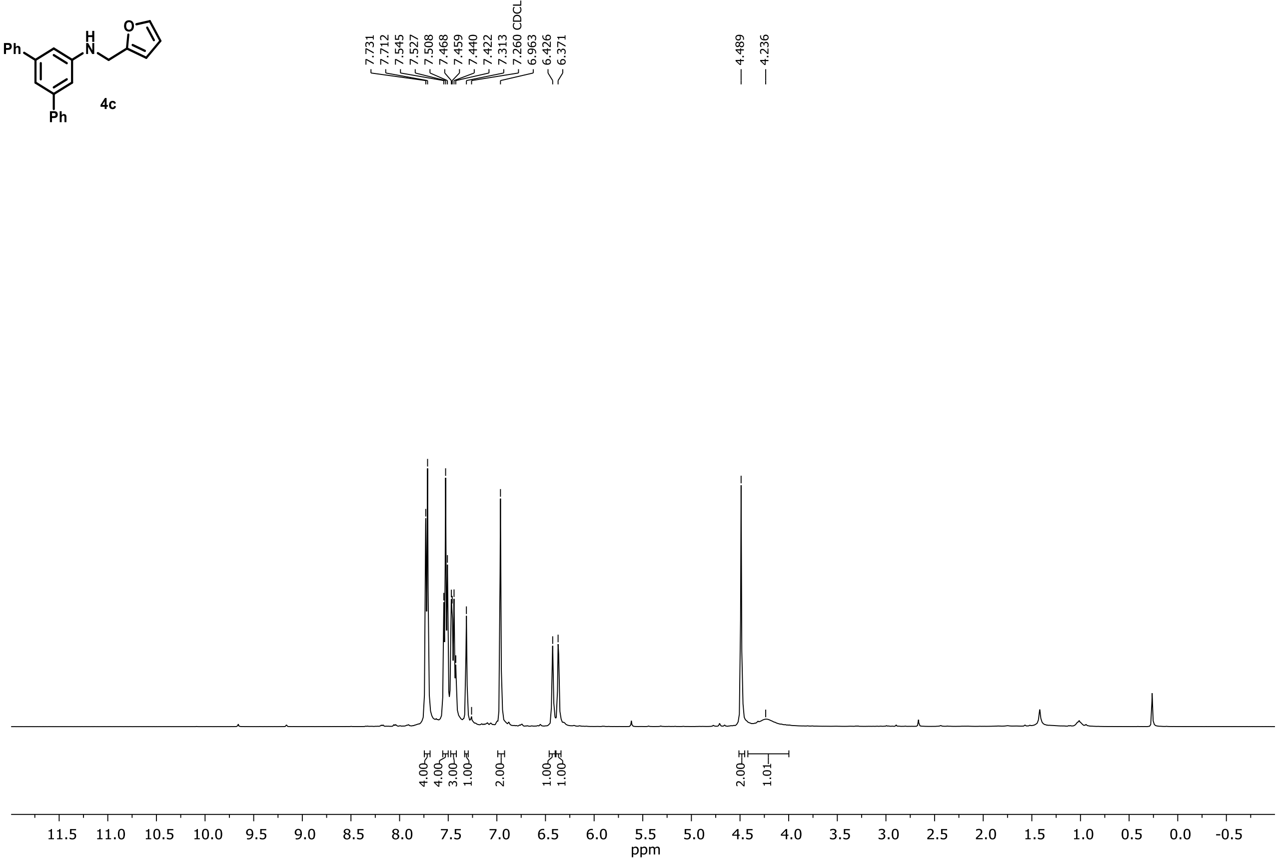
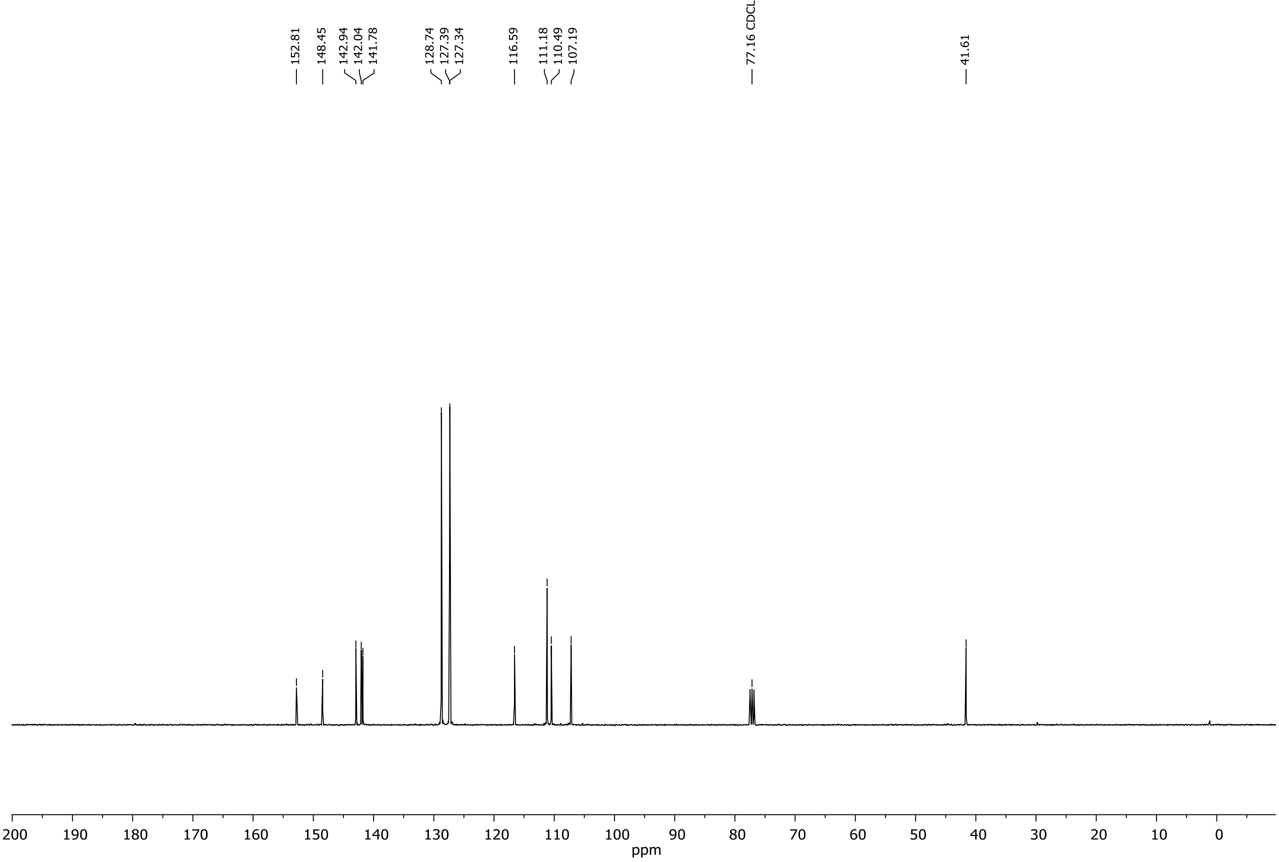
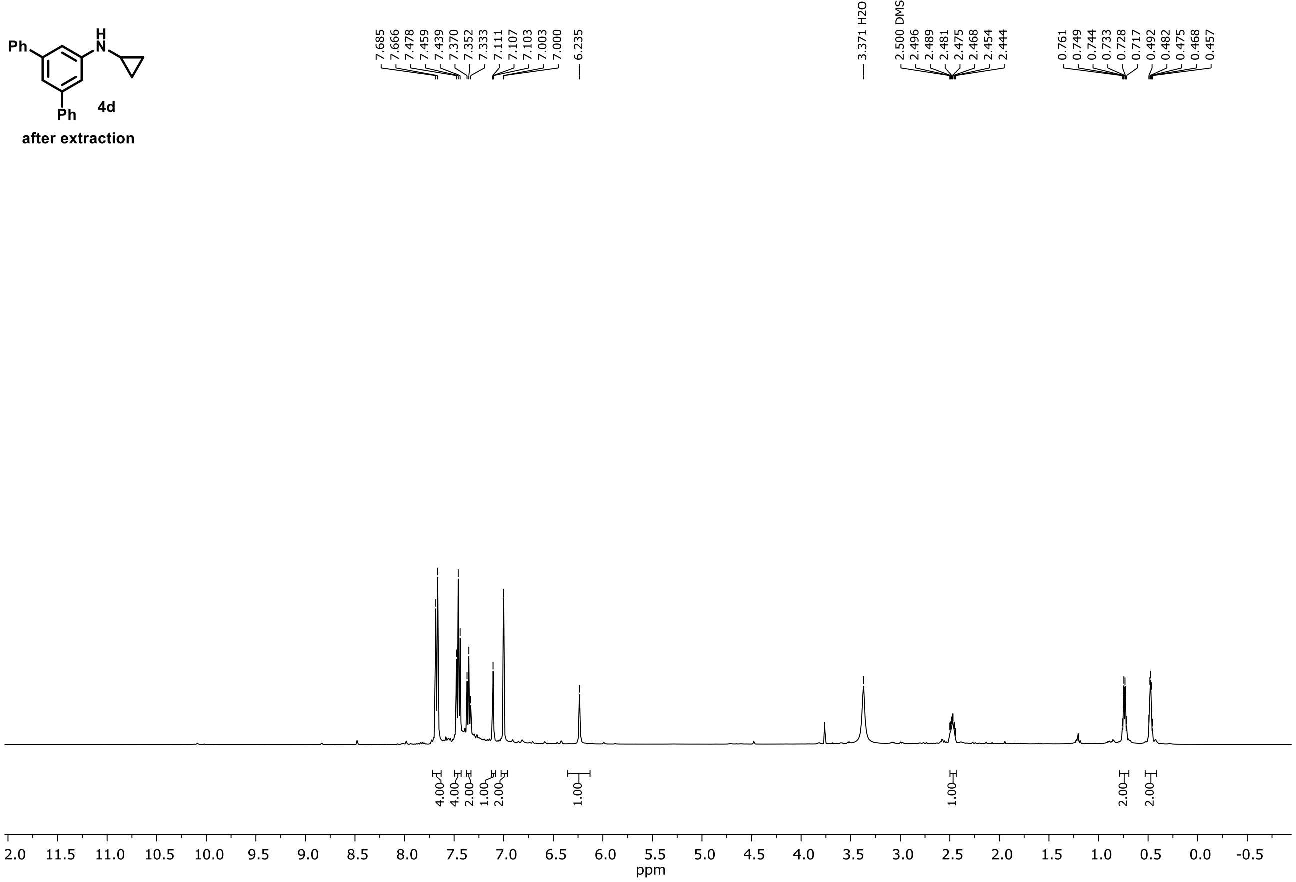


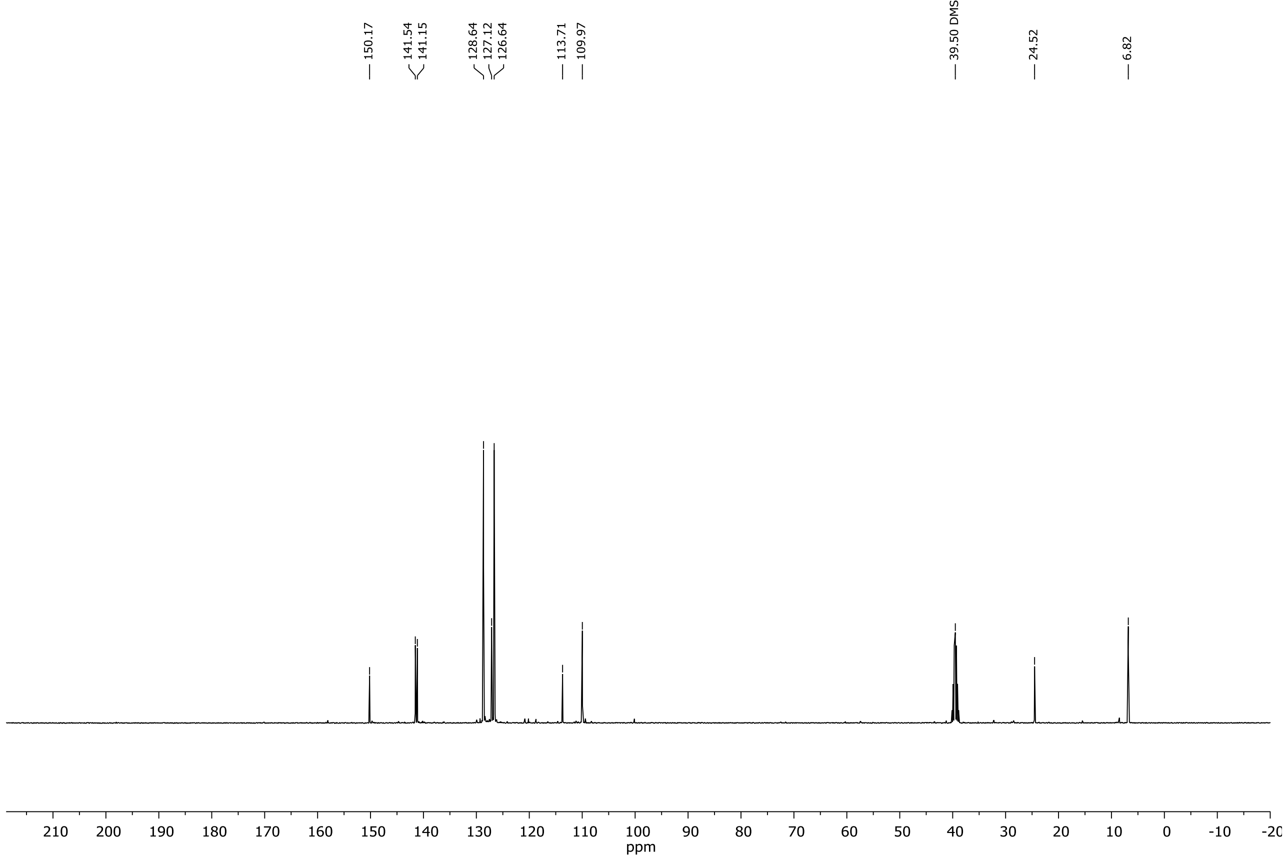
13C, CDCl3, 100 MHz



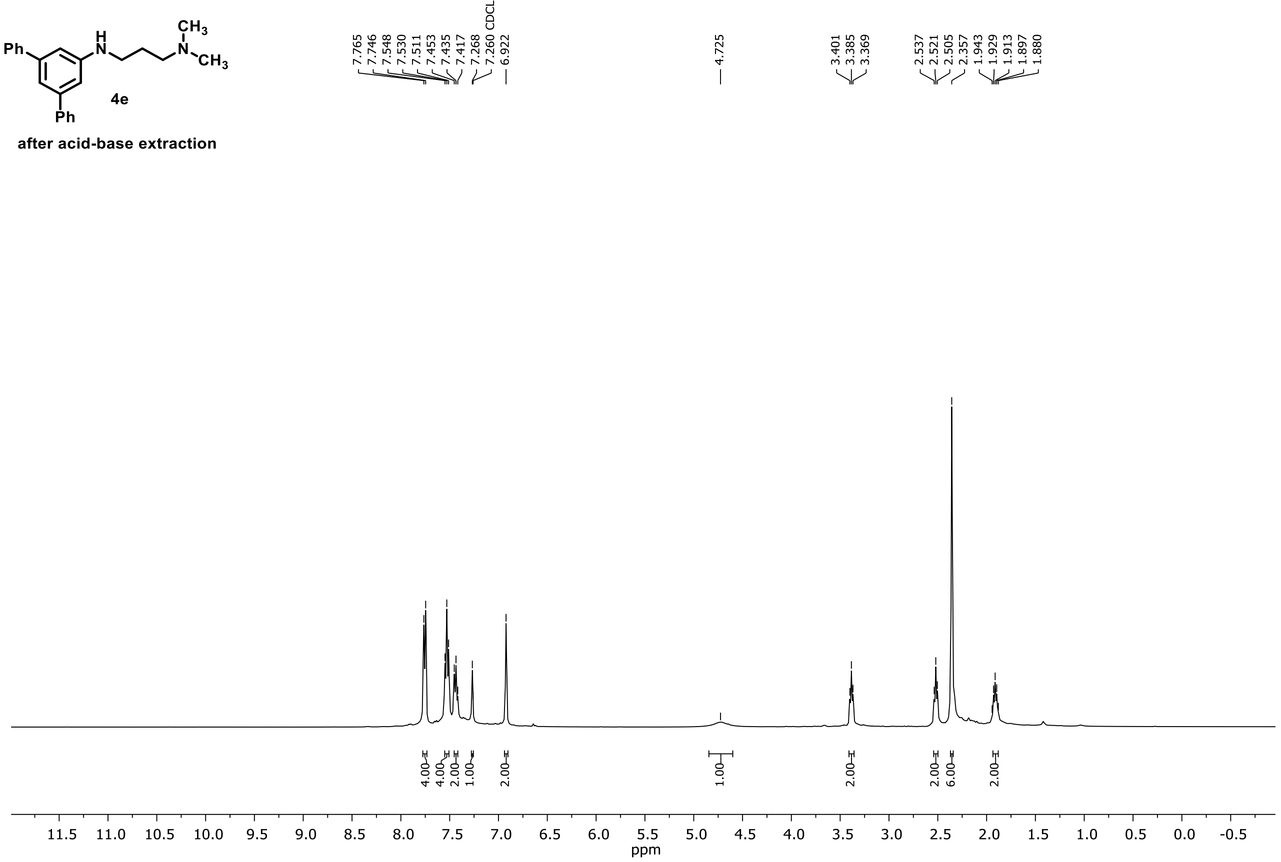
1H, DMSO-d6, 400 MHz



13C, DMSO-d6, 100 MHz

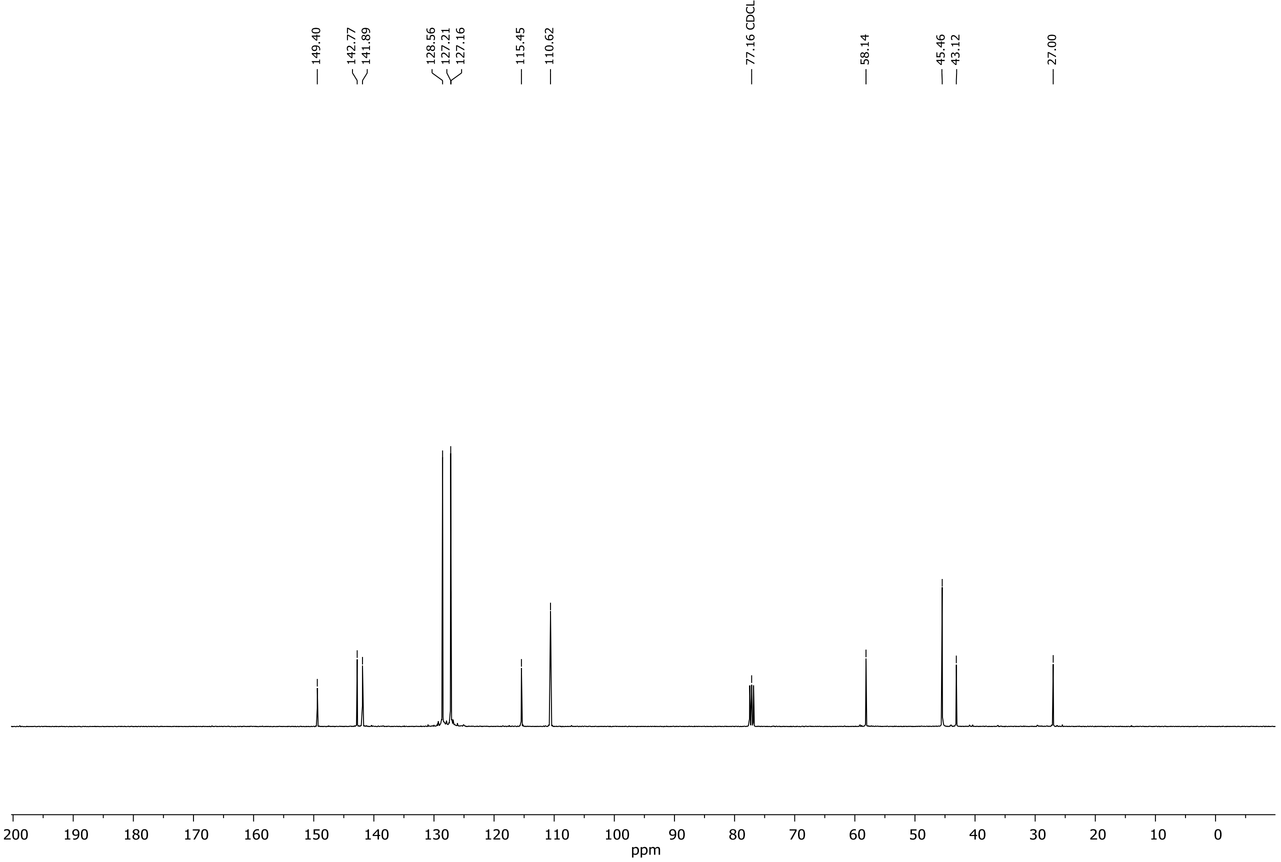


1H, CDCl3, 400 MHz

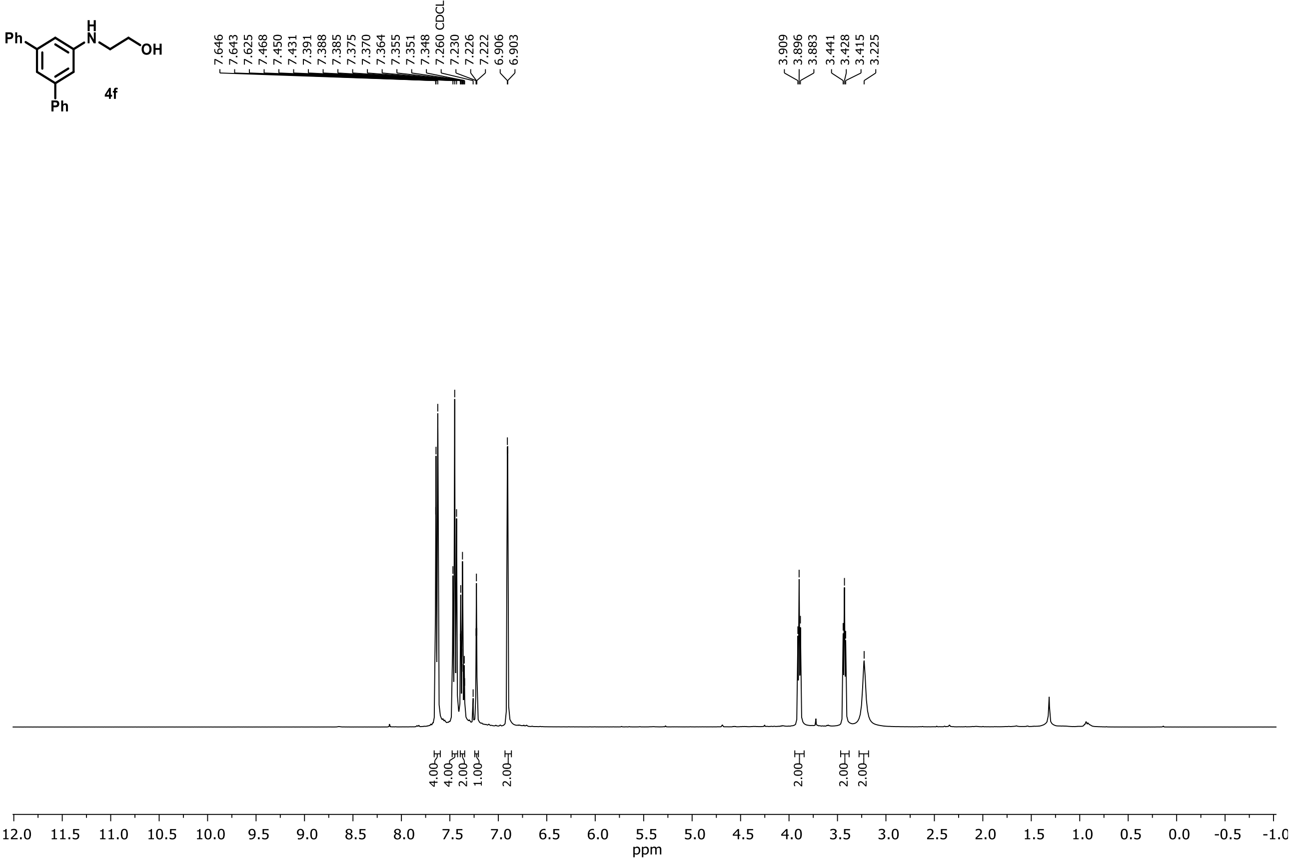

4e

after acid-base extraction

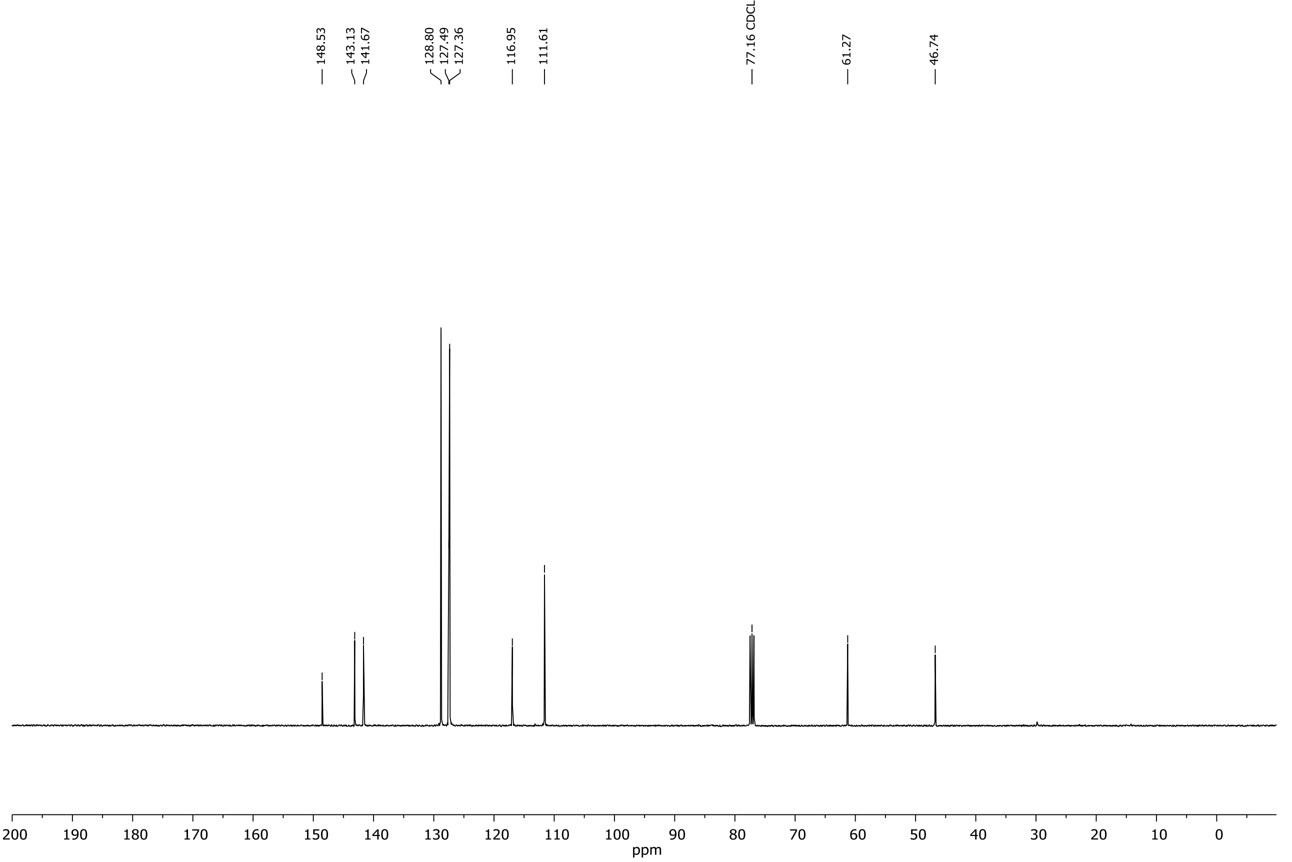
13C, CDCl3, 100 MHz



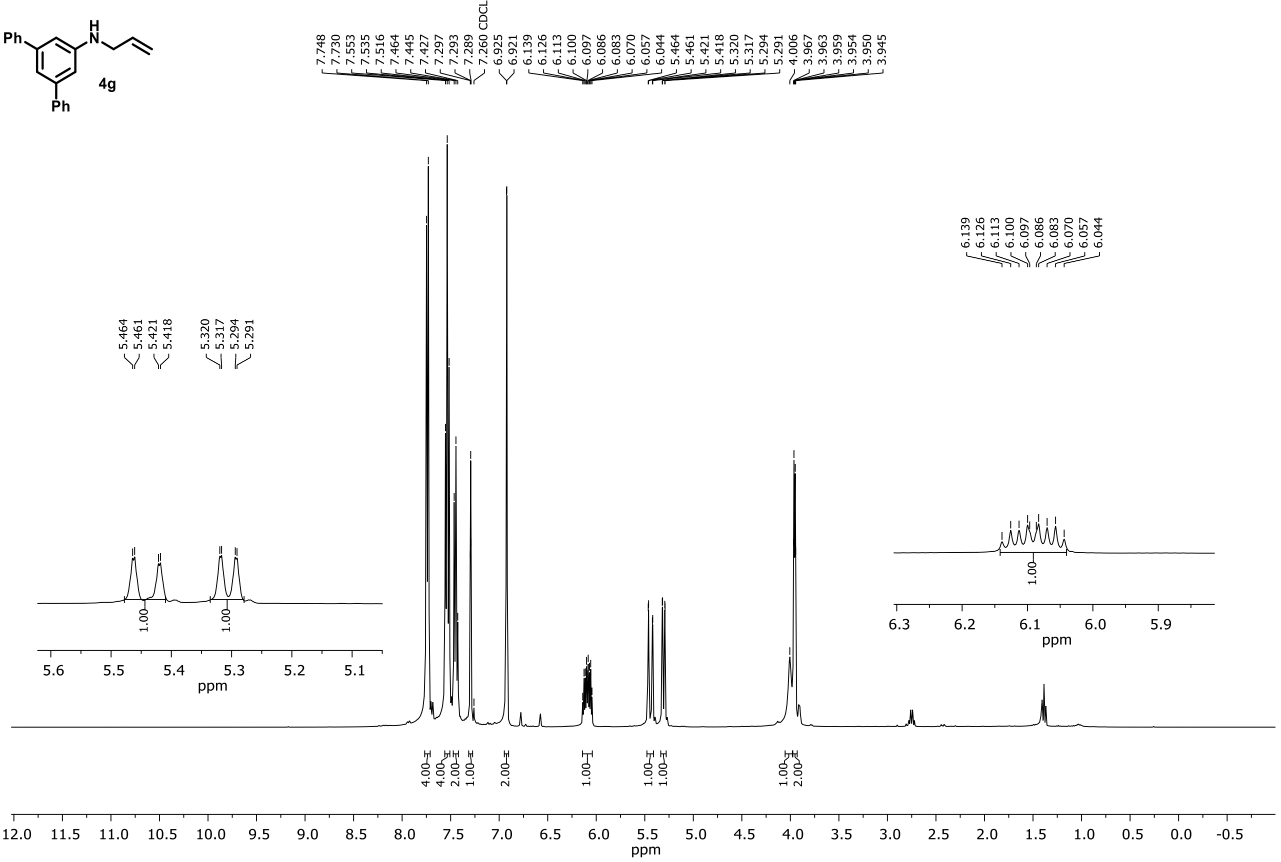
1H, CDCl3, 400 MHz



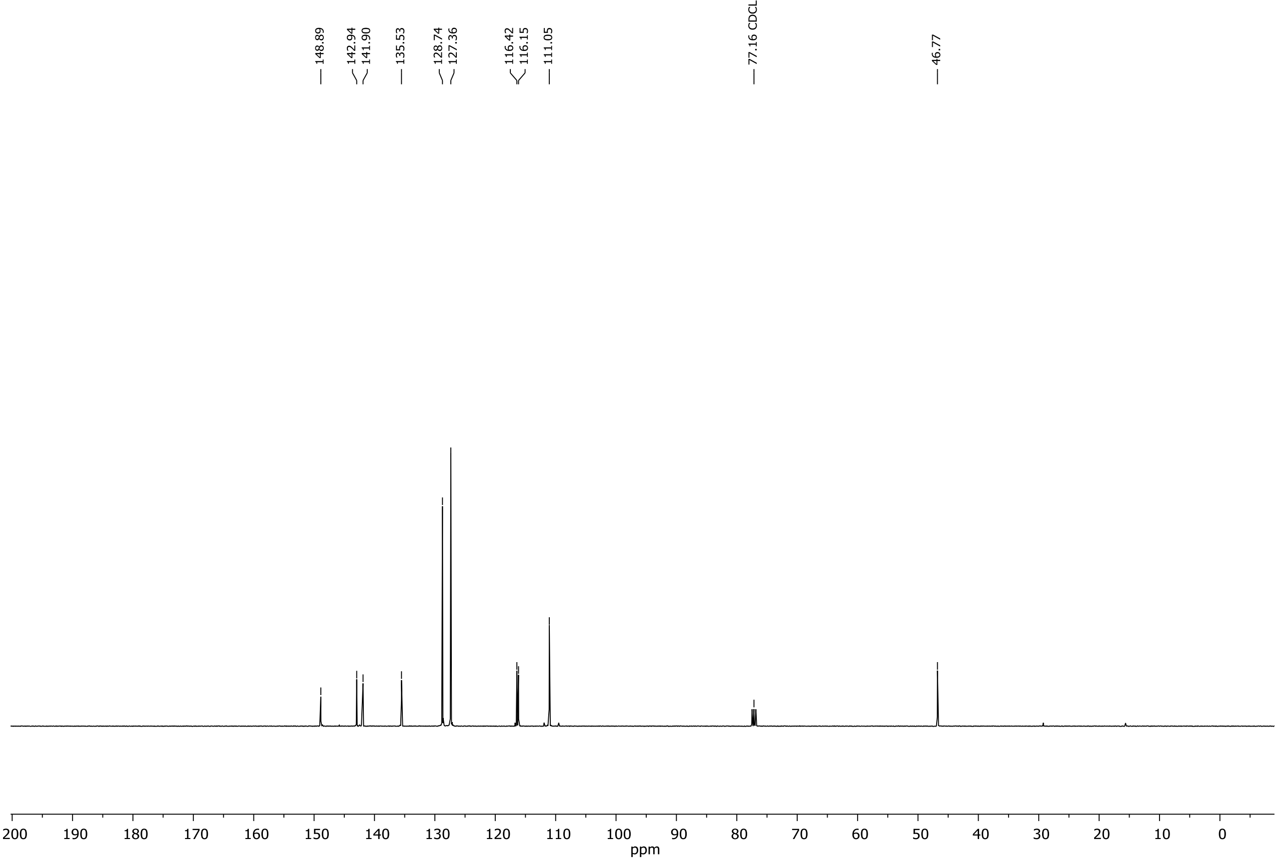
13C, CDCl3, 100 MHz



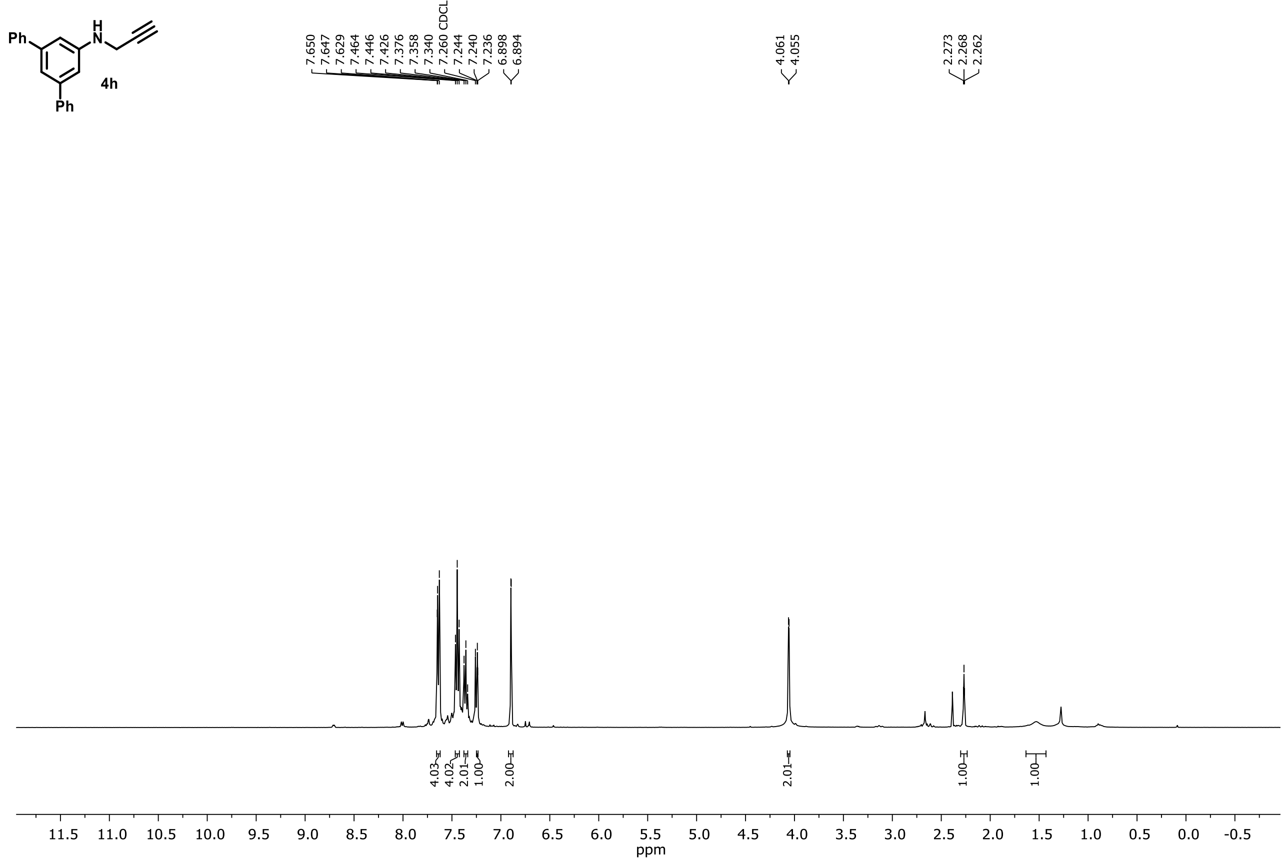
1H, CDCl3, 400 MHz



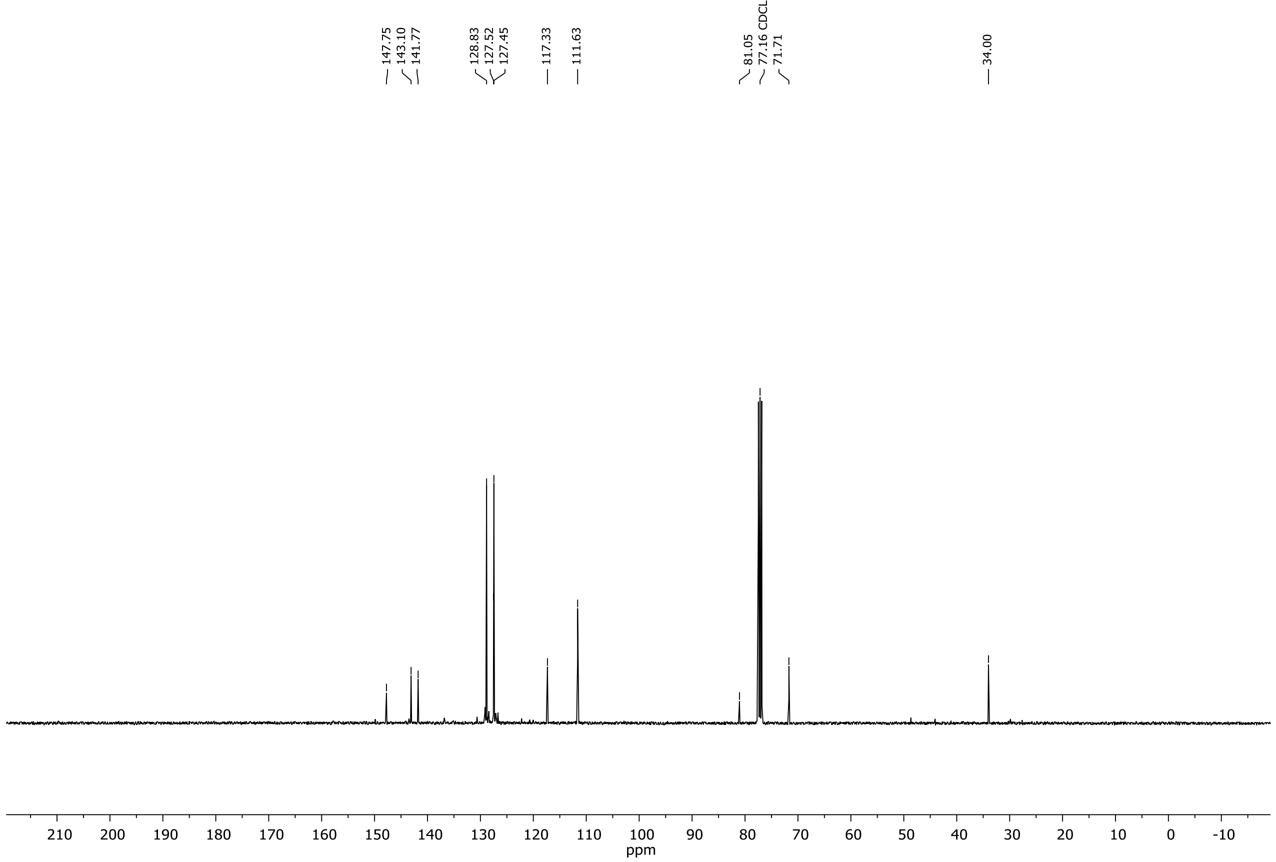
13C, CDCl3, 100 MHz



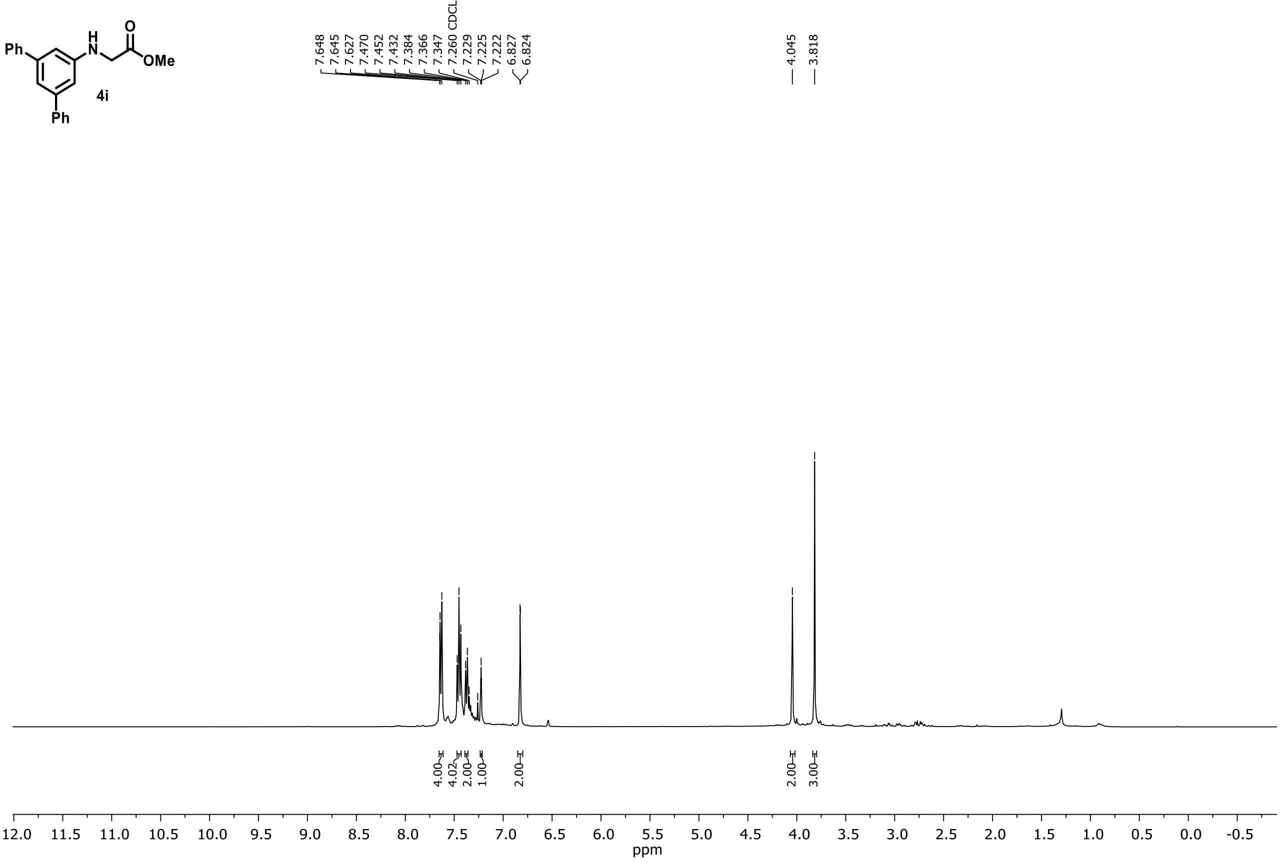
1H, CDCl3, 400 MHz



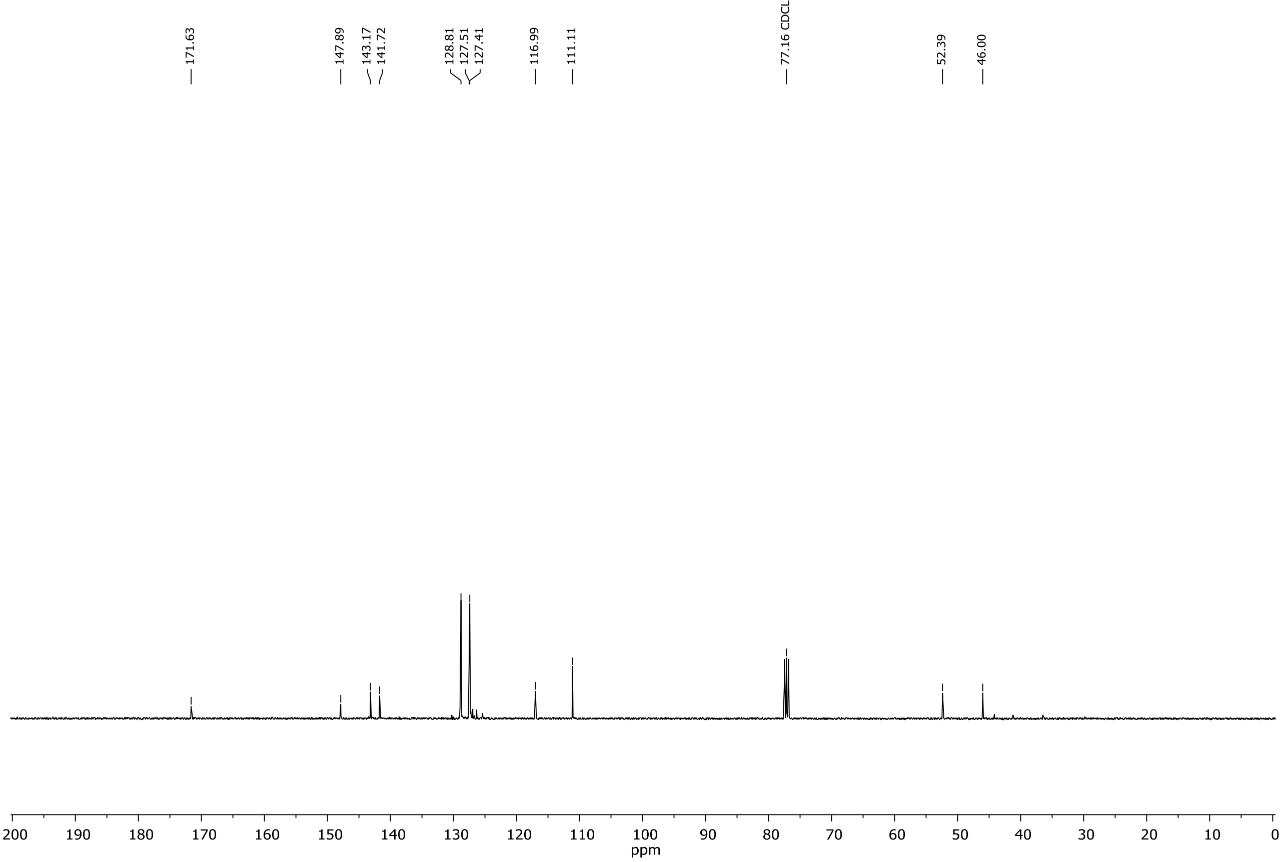
13C, CDCl3, 100 MHz



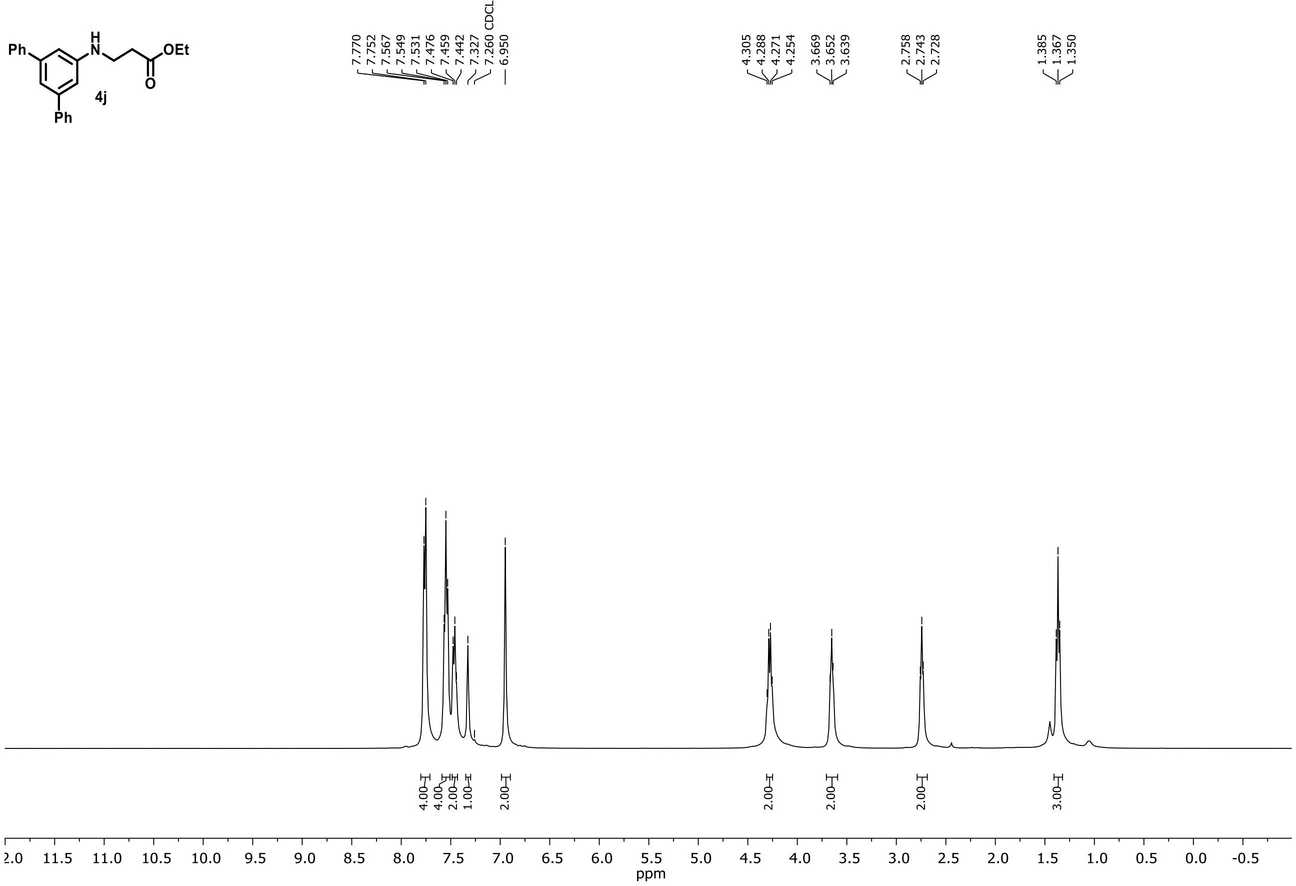
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

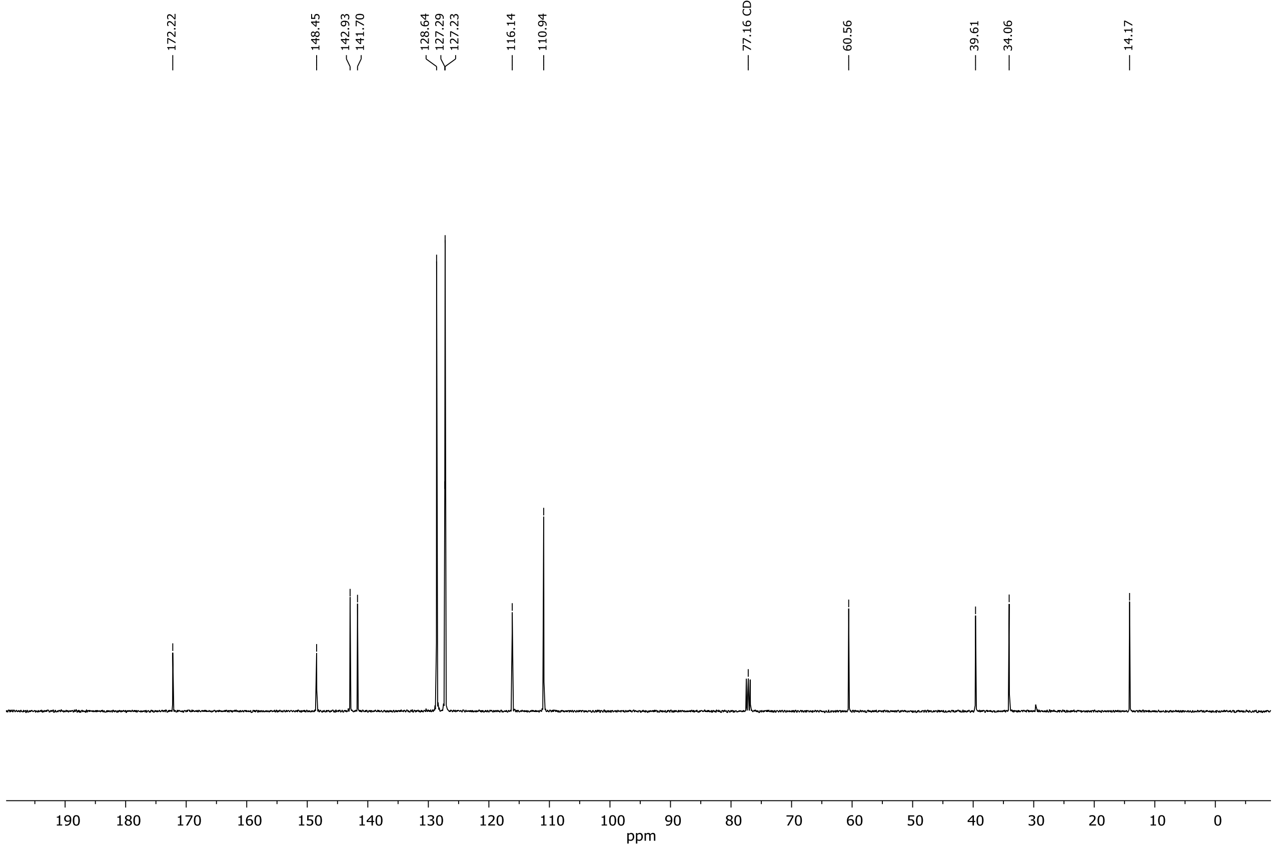


1H, CDCl3, 400 MHz

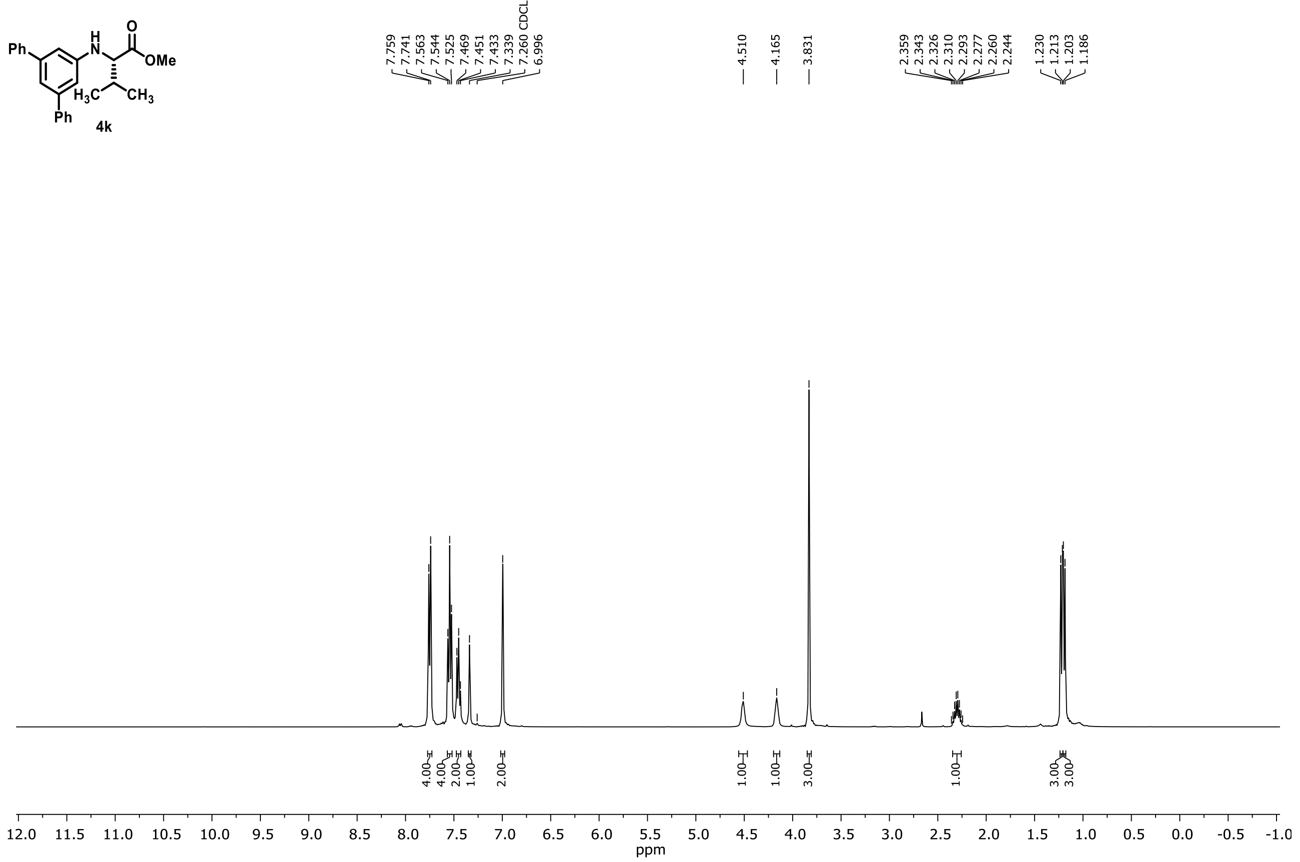


4j

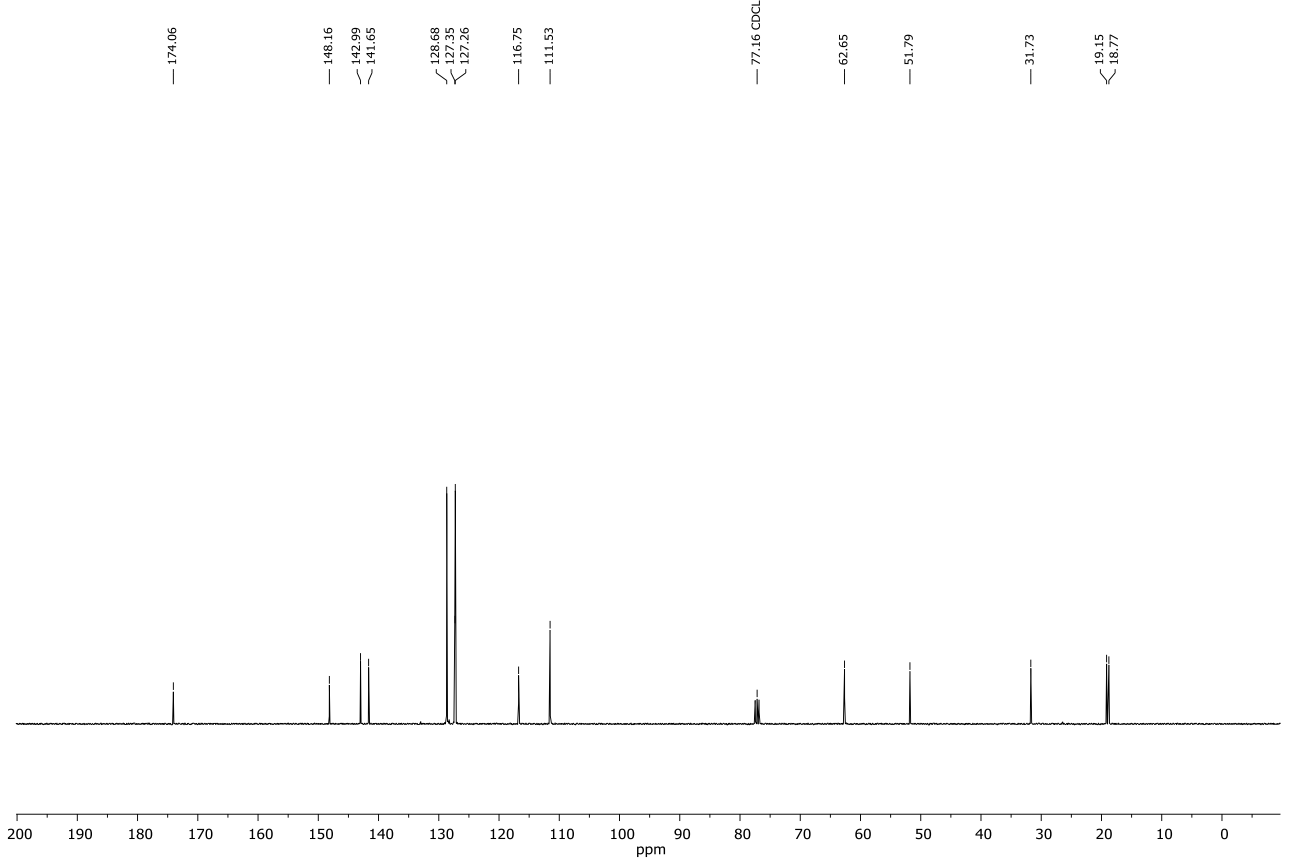
13C, CDCl3, 100 MHz



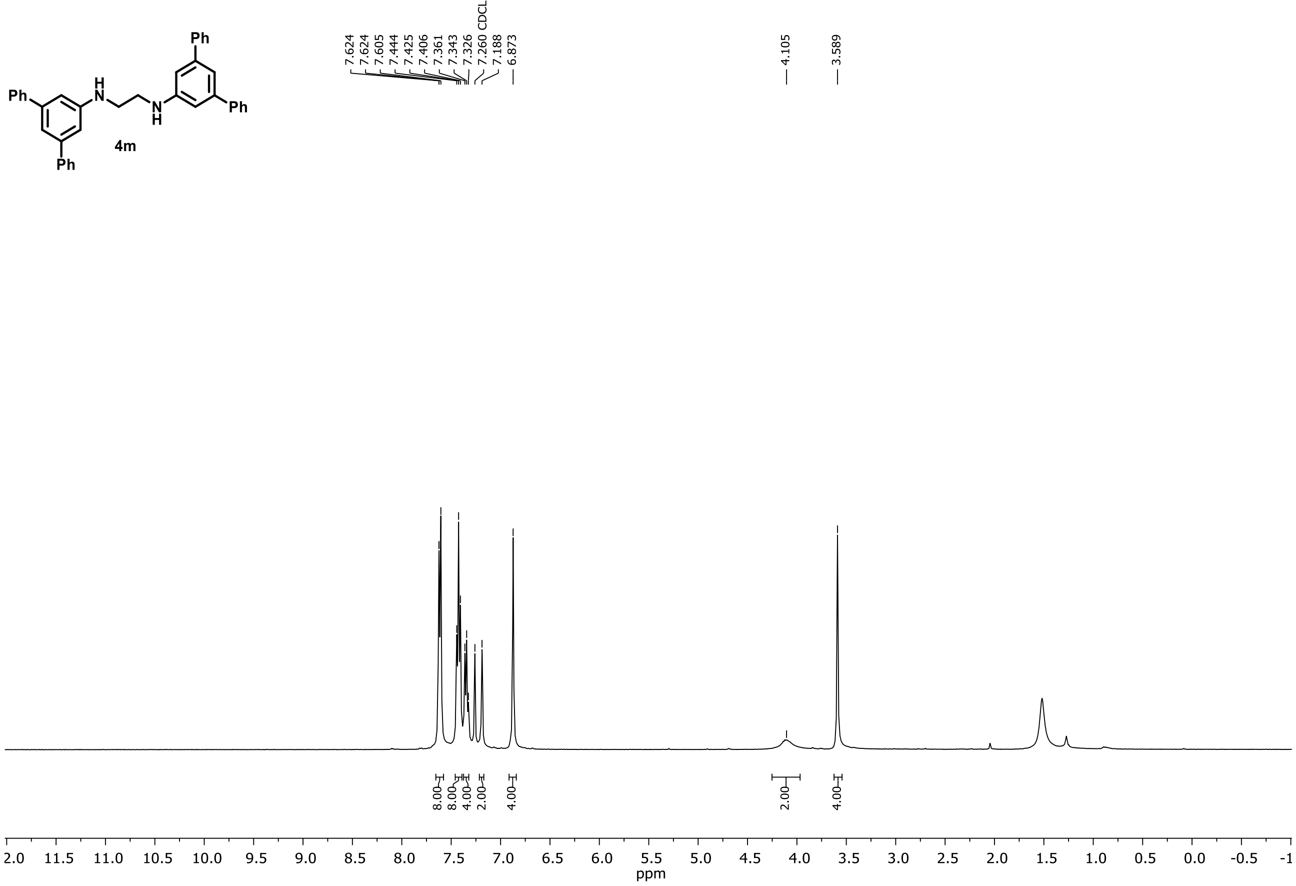
1H, CDCl3, 400 MHz



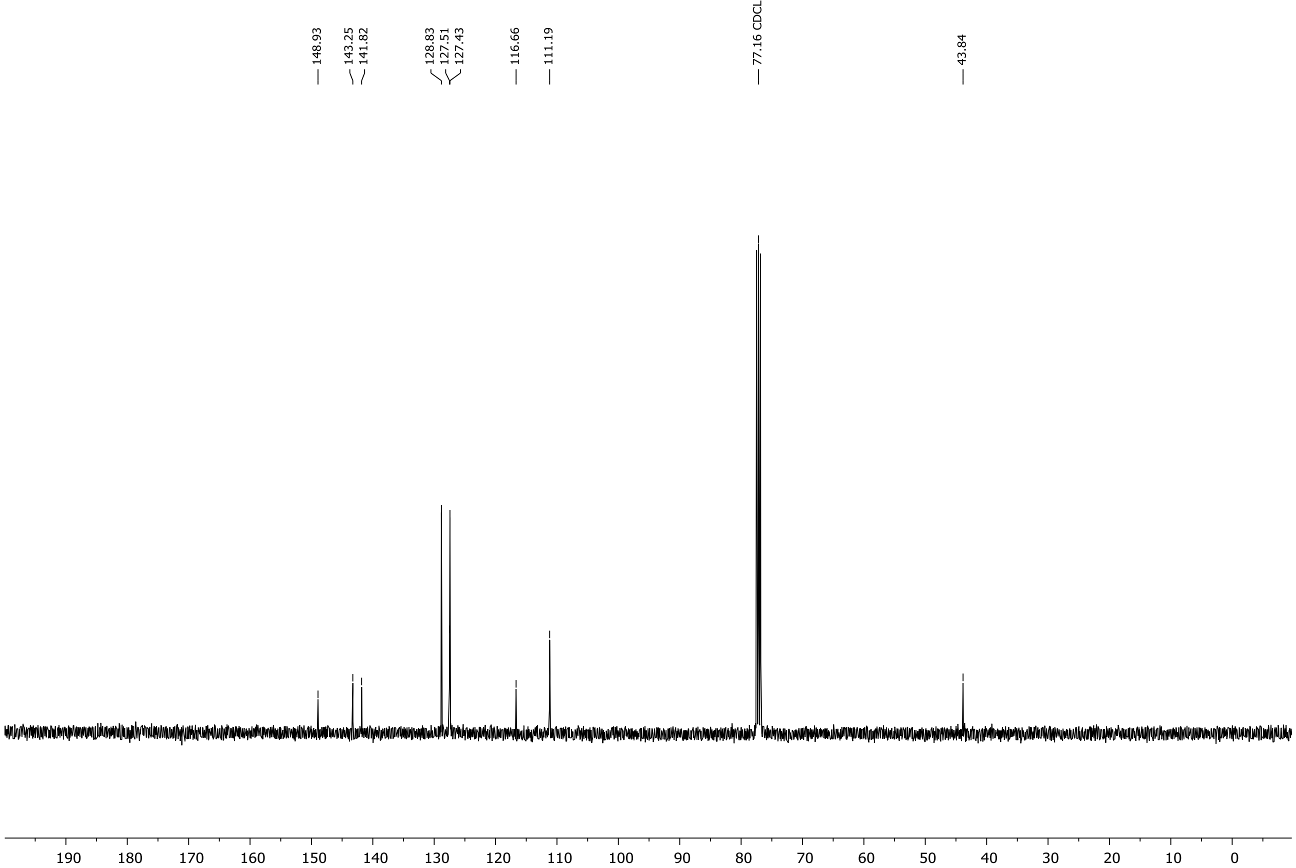
13C, CDCl3, 100 MHz

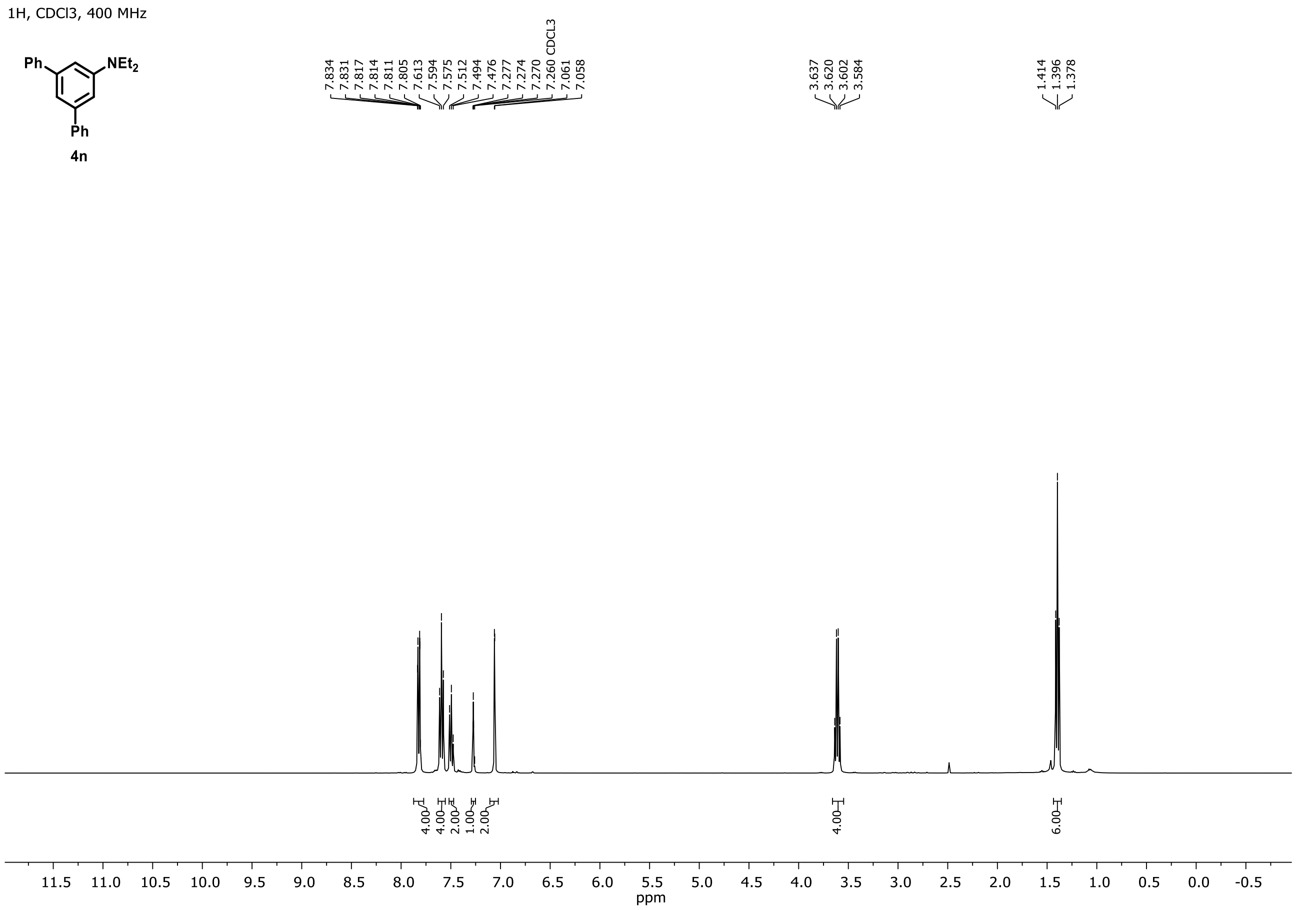


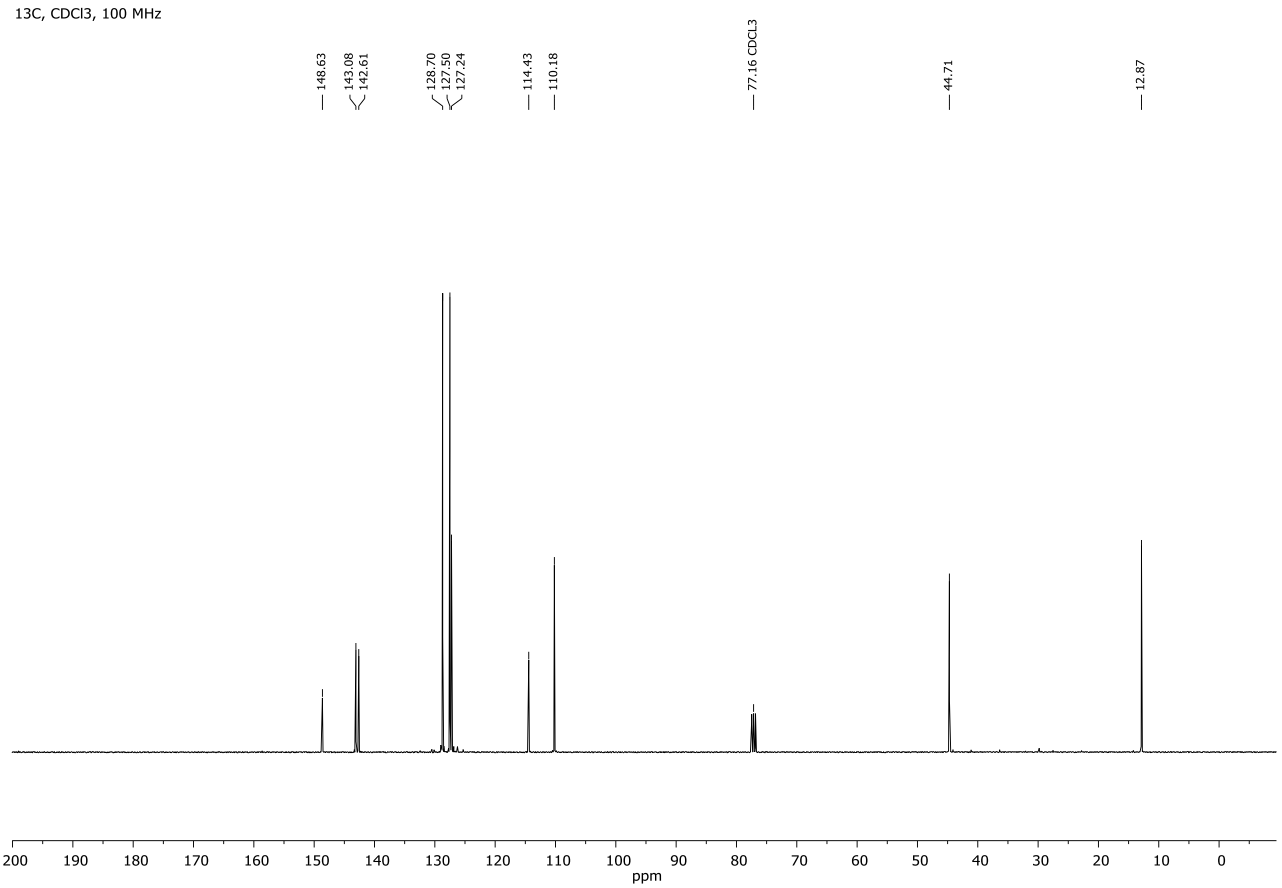
1H, CDCl3, 400 MHz



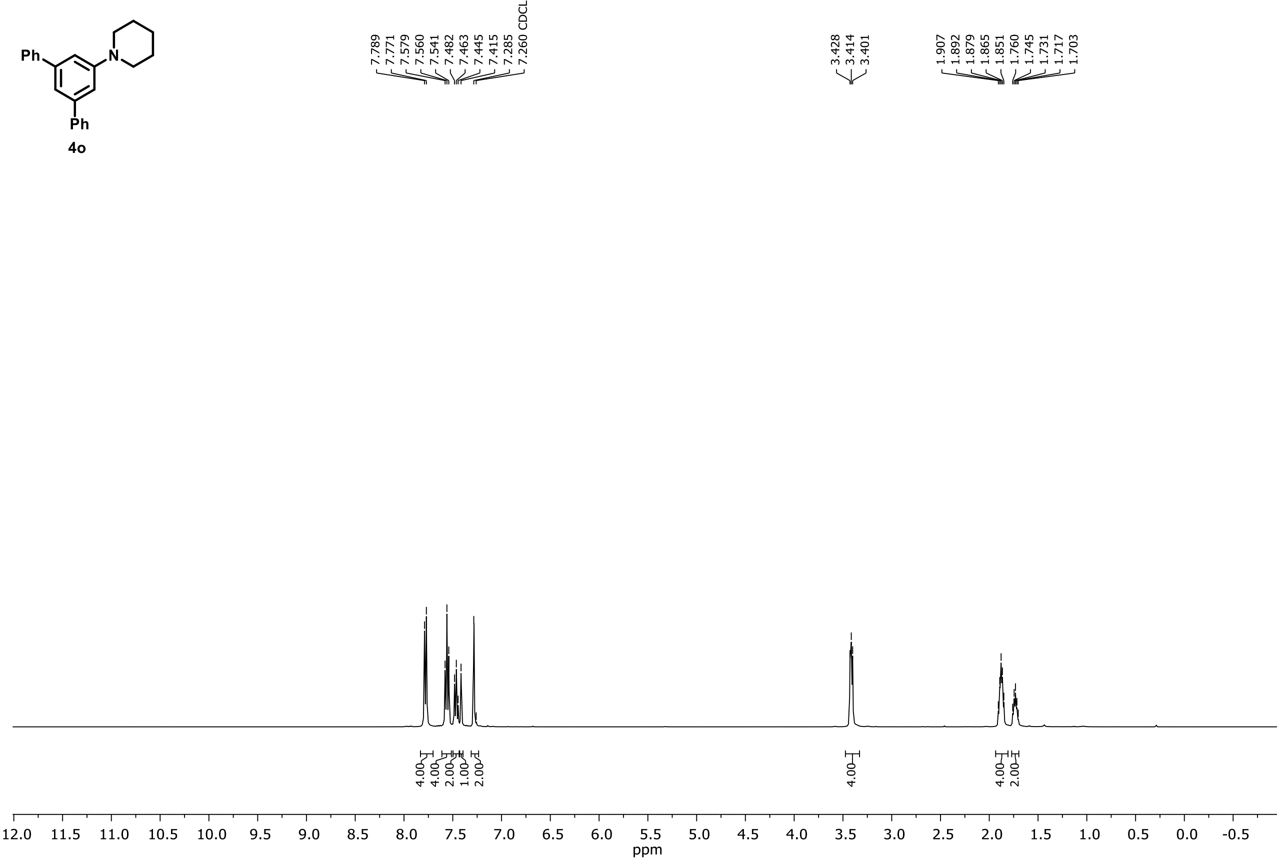
13C, CDCl3, 100 MHz



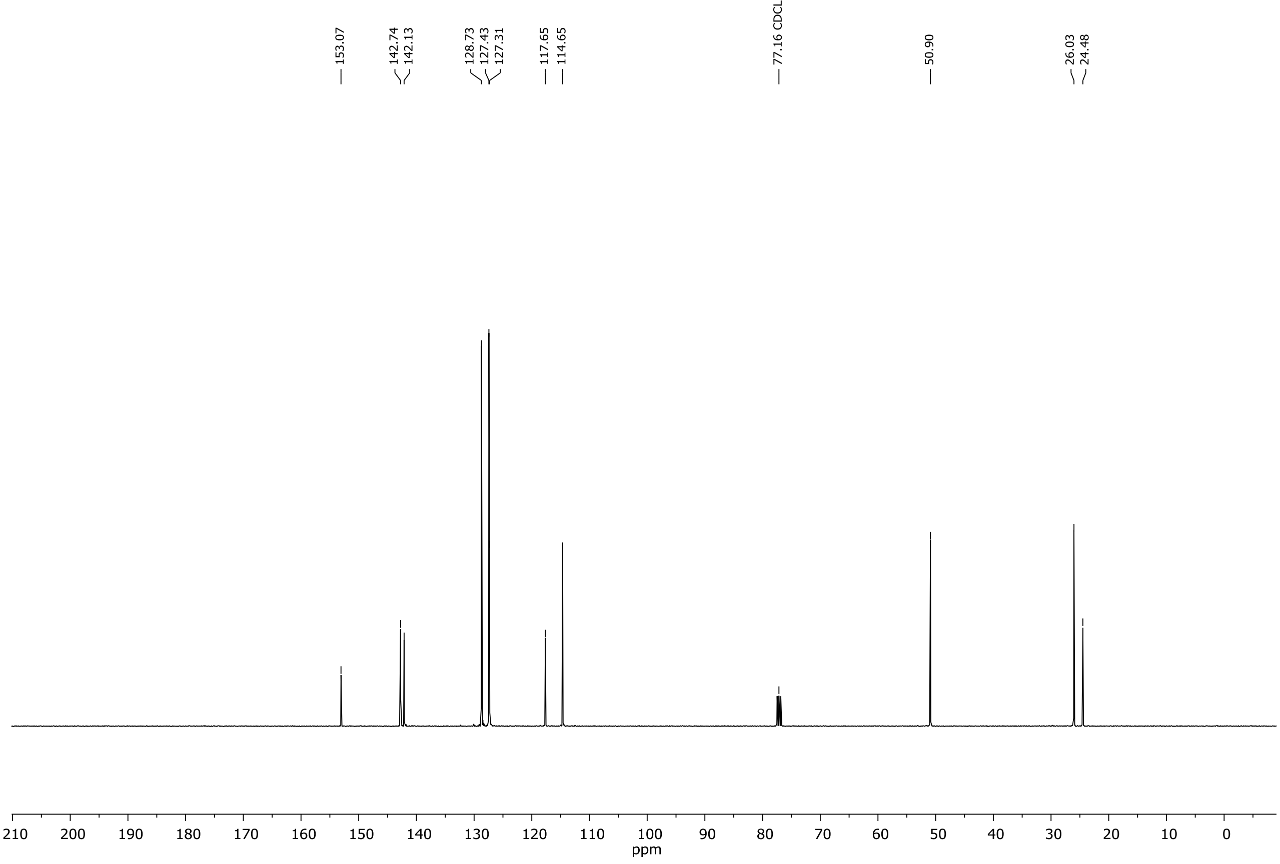

1H, CDCl3, 400 MHz
Ph
NEt2
Ph
4n
7.834
7.831
7.817
7.814
7.811
7.805
7.613
7.594
7.575
7.512
7.494
7.476
7.277
7.274
7.270
7.260 CDCL3
7.061
7.058
3.637
3.620
3.602
3.584
1.414
1.396
1.378
4.00
4.00
2.00
1.00
2.00
4.00
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


13C, CDCl3, 100 MHz
148.63
143.08
142.61
128.70
127.50
127.24
114.43
110.18
77.16 CDCL3
44.71
12.87
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

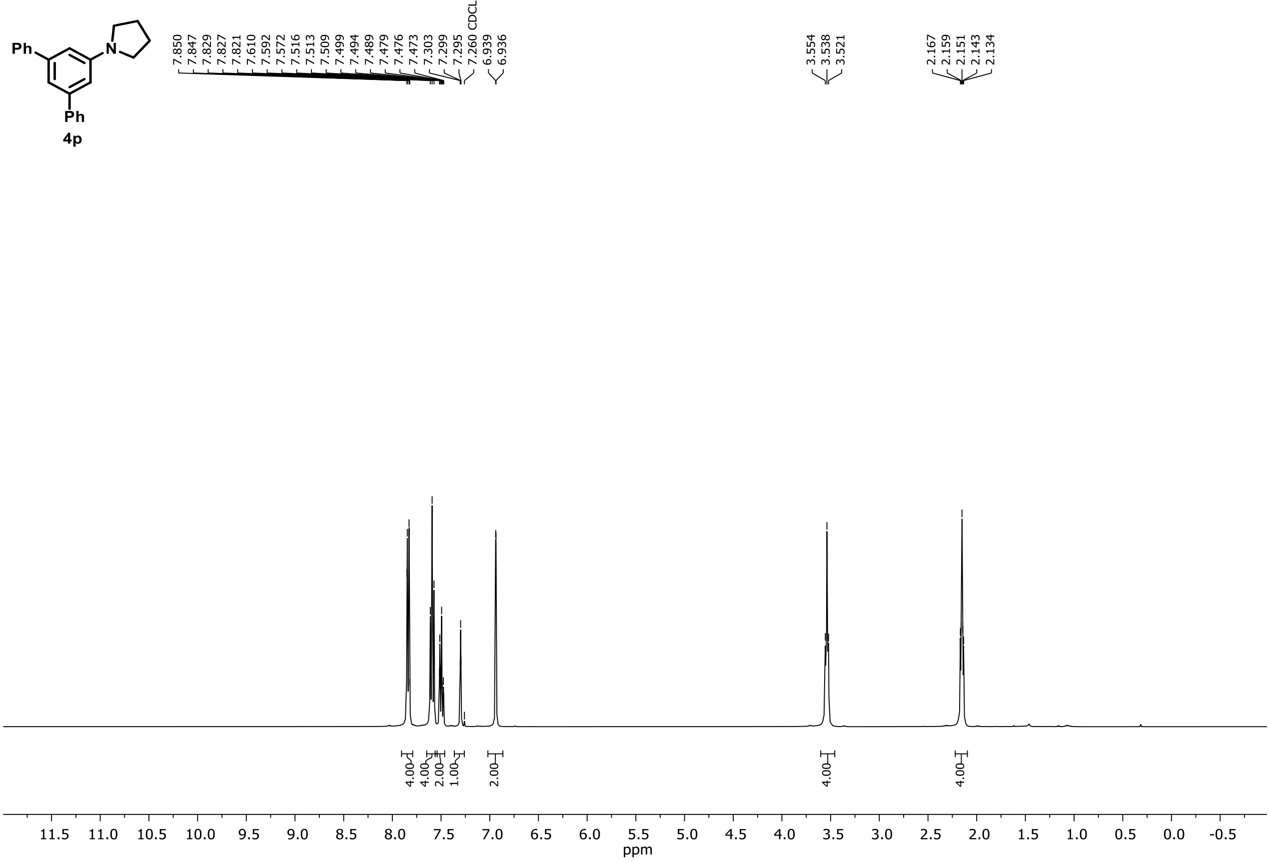
1H, CDCl3, 400 MHz



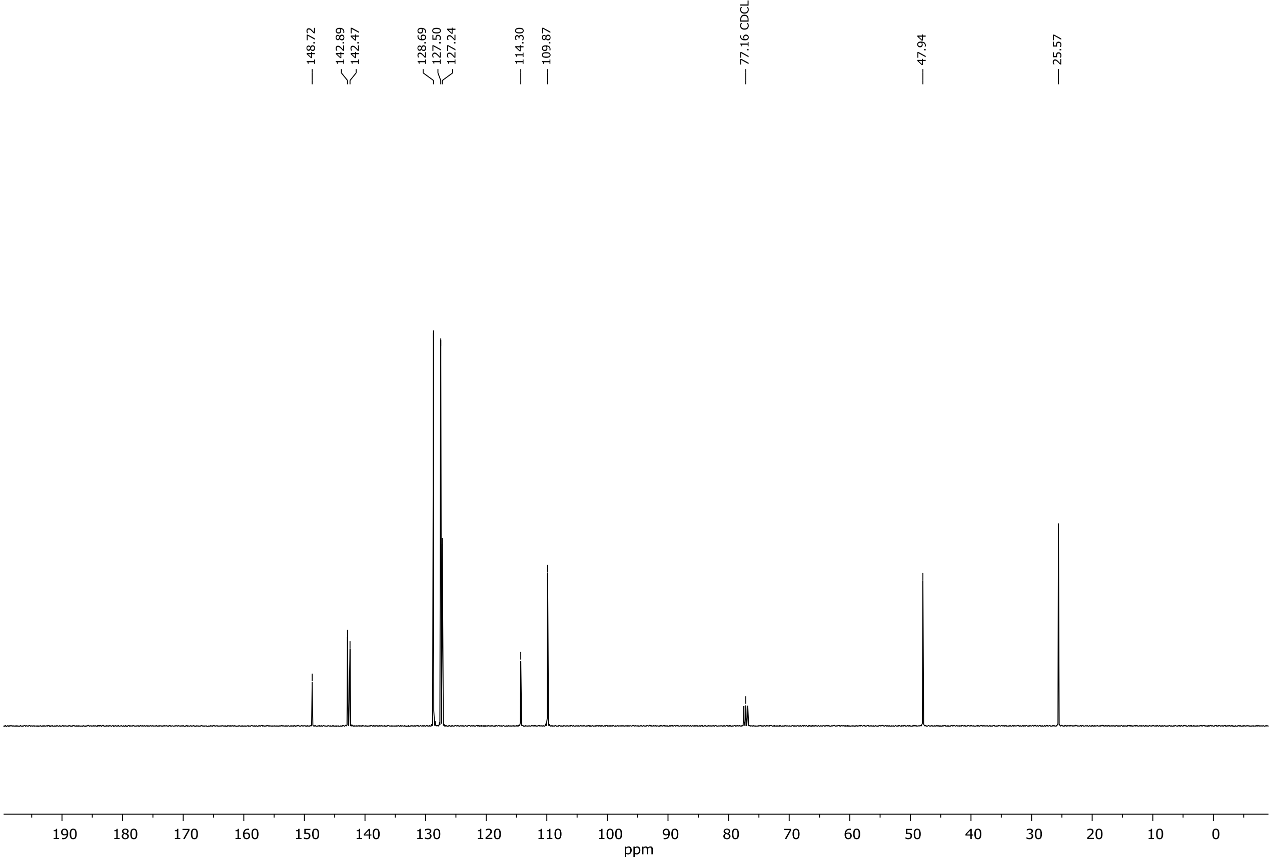
13C, CDCl3, 100 MHz



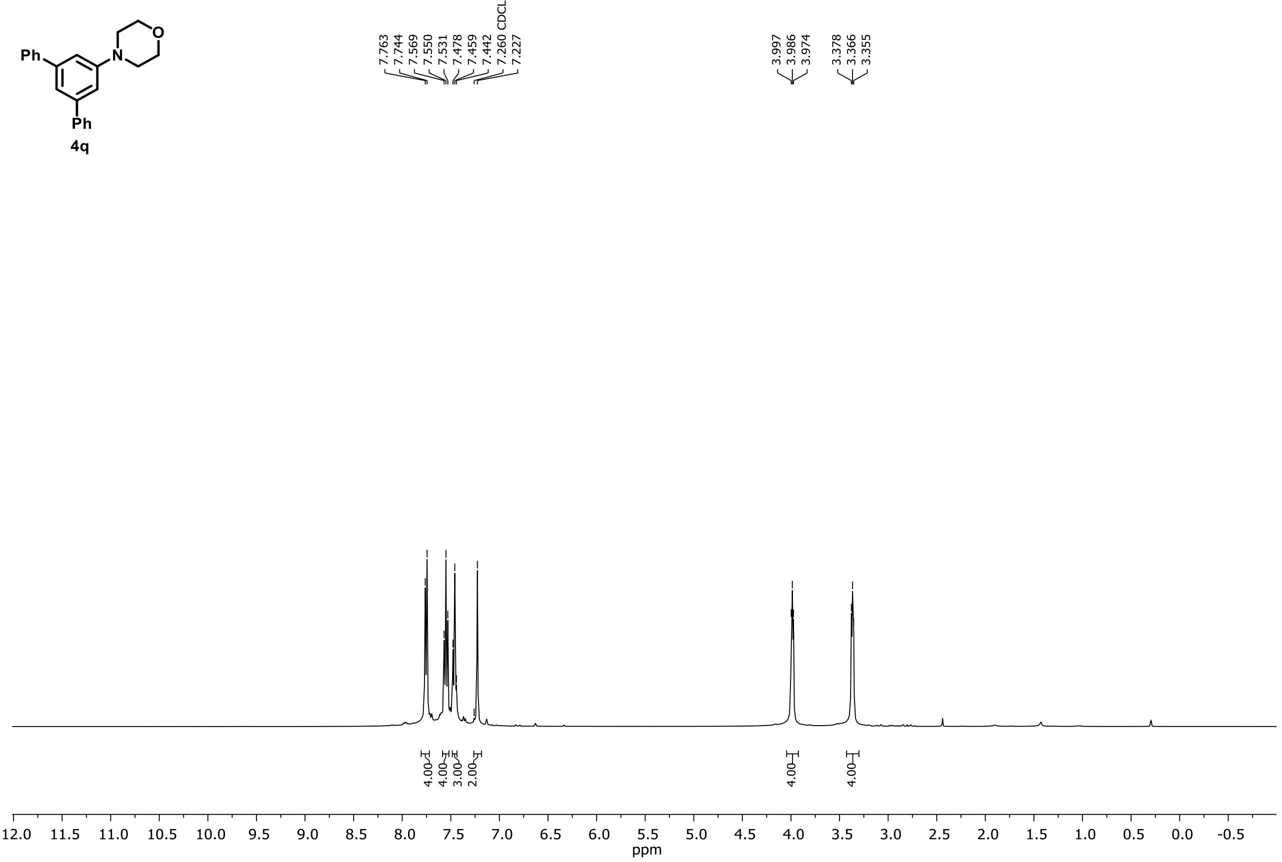
1H, CDCl3, 400 MHz



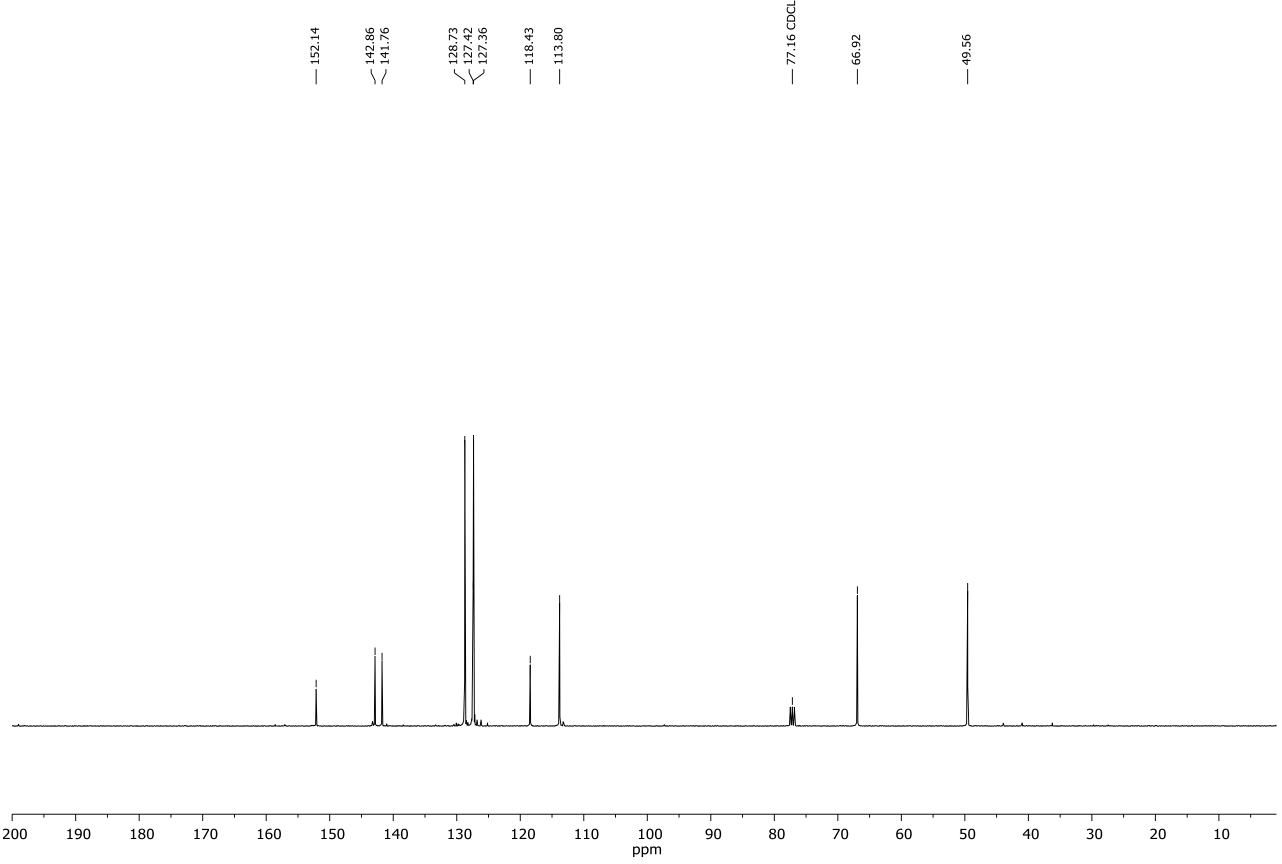
13C, CDCl3, 100 MHz



1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz



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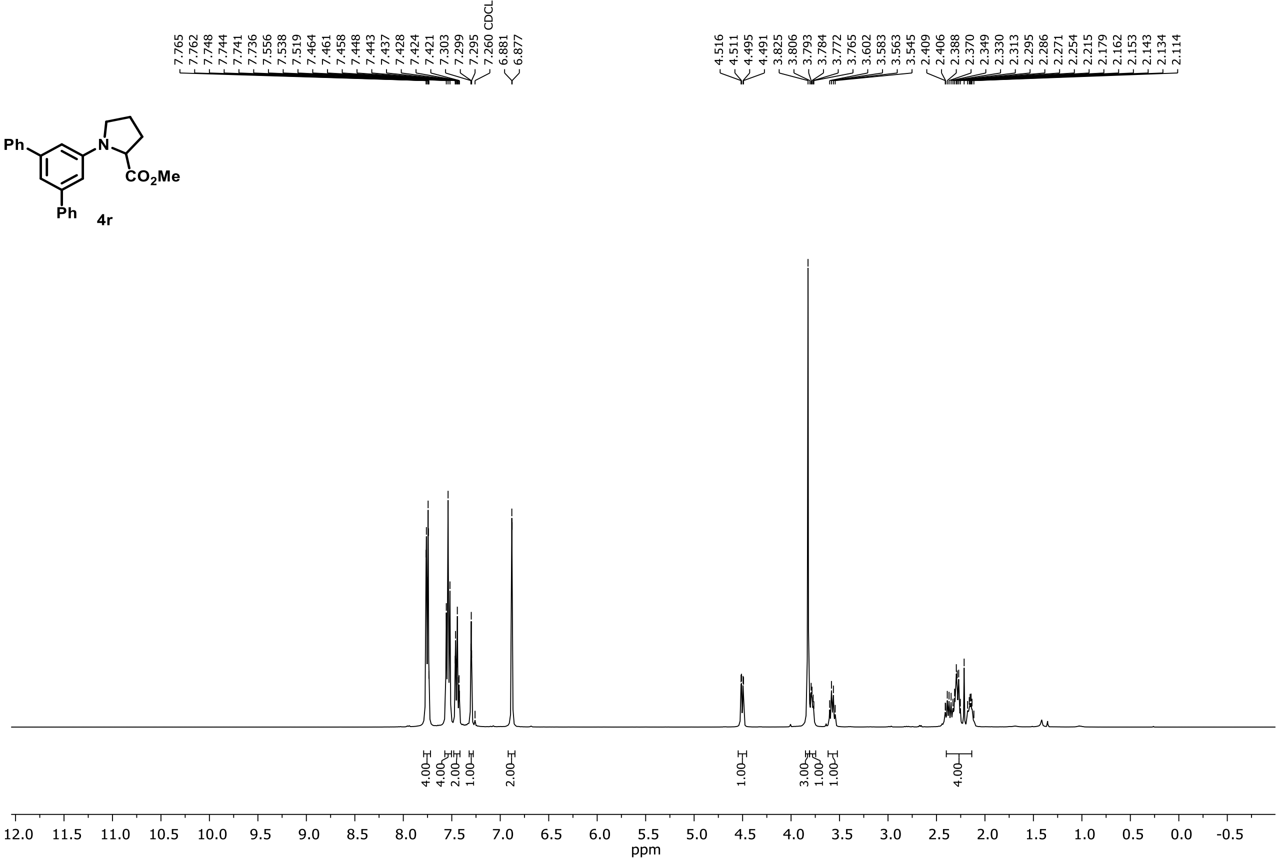
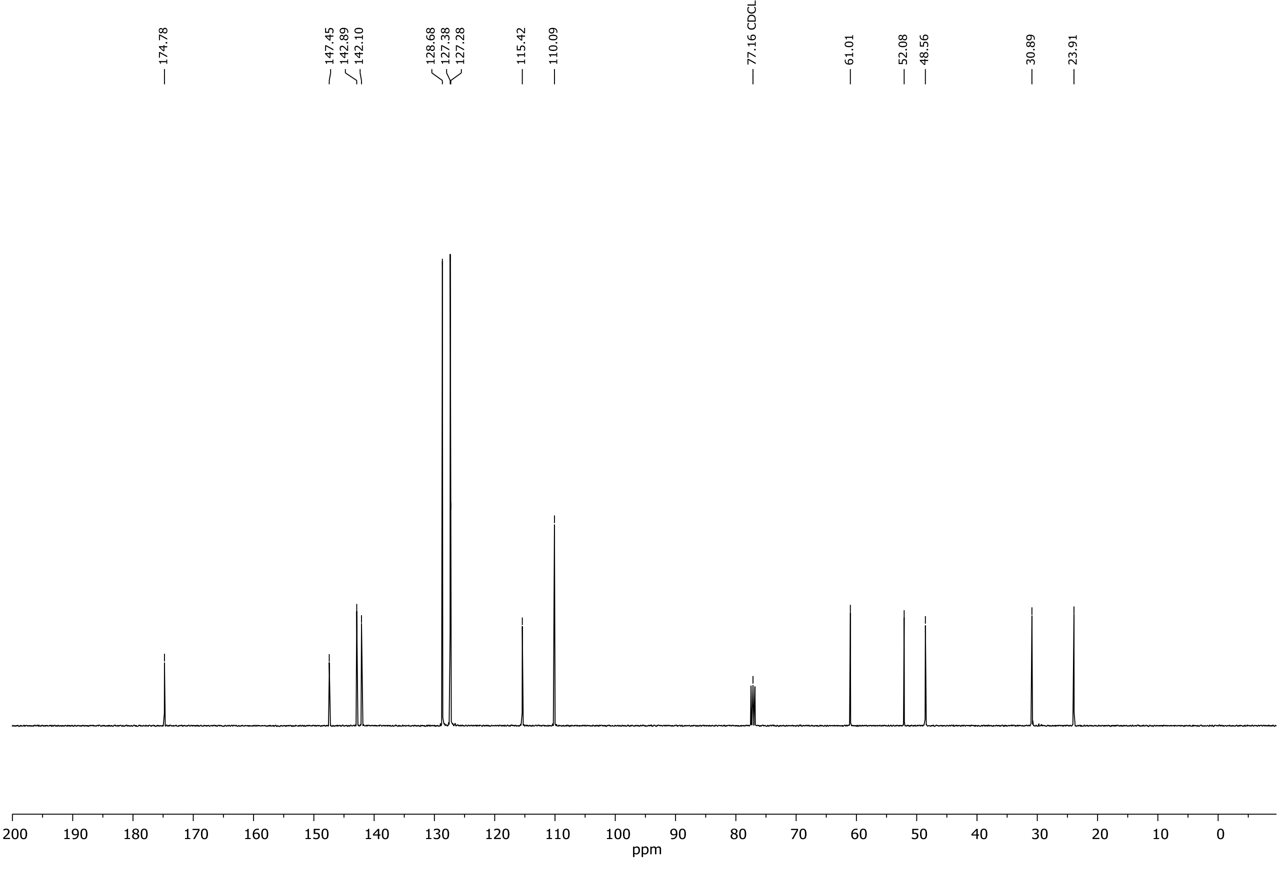
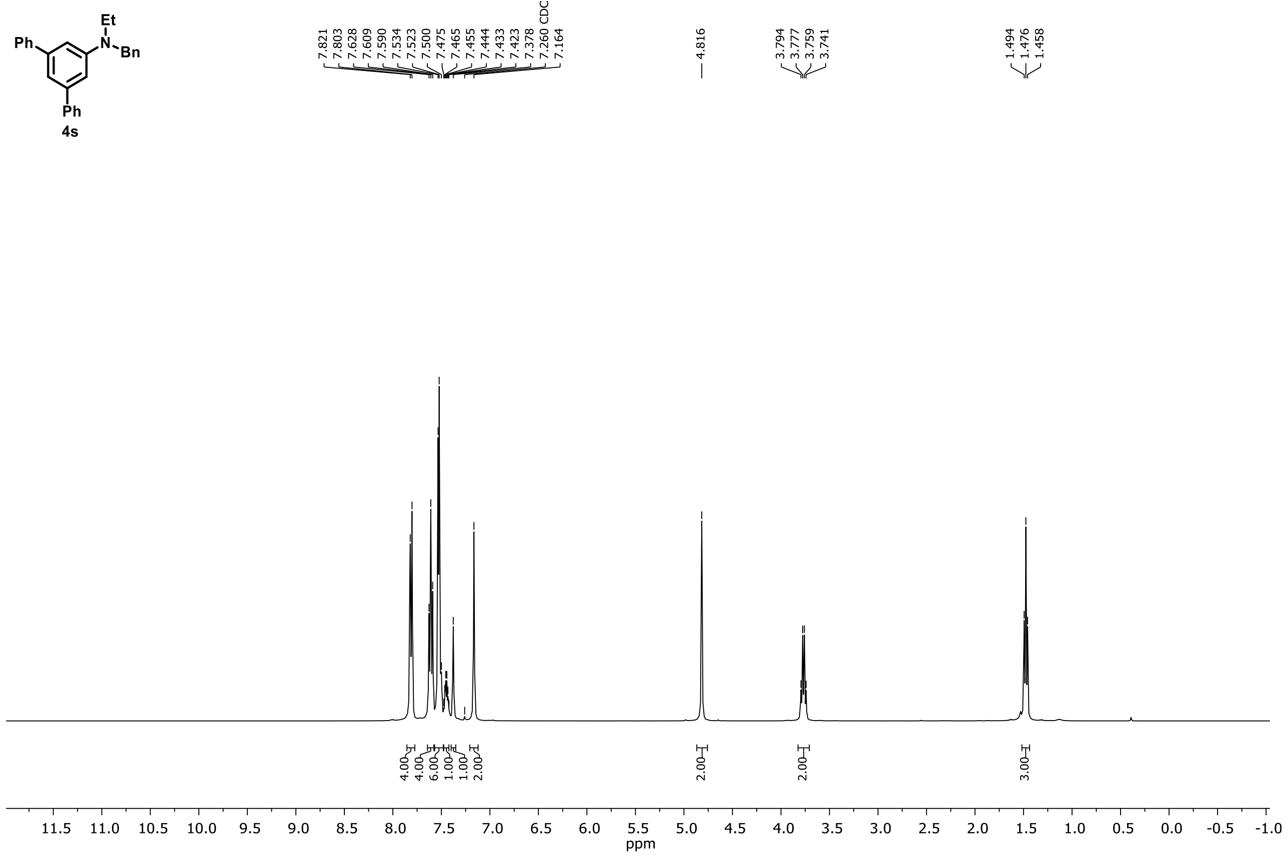


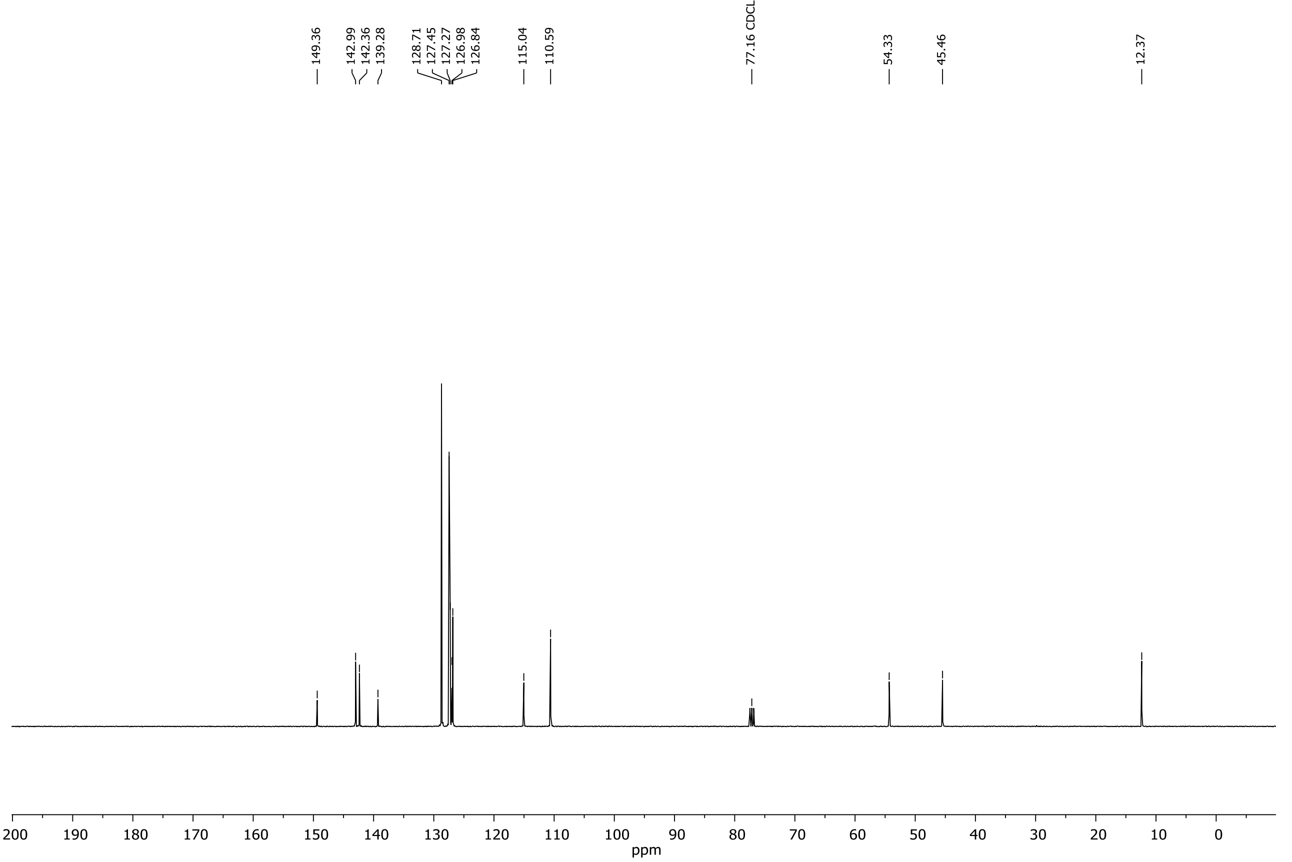
13C, CDCl3, 100 MHz



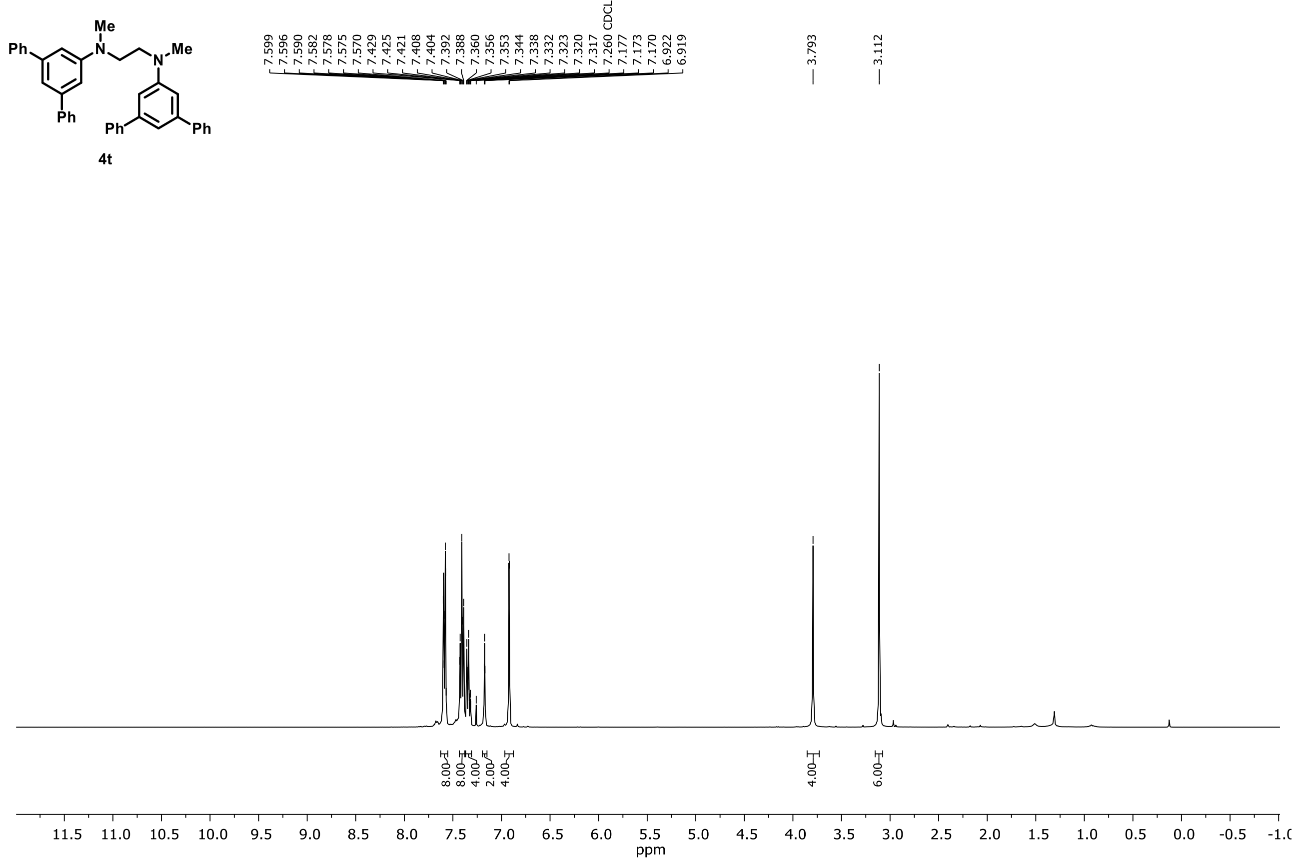
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

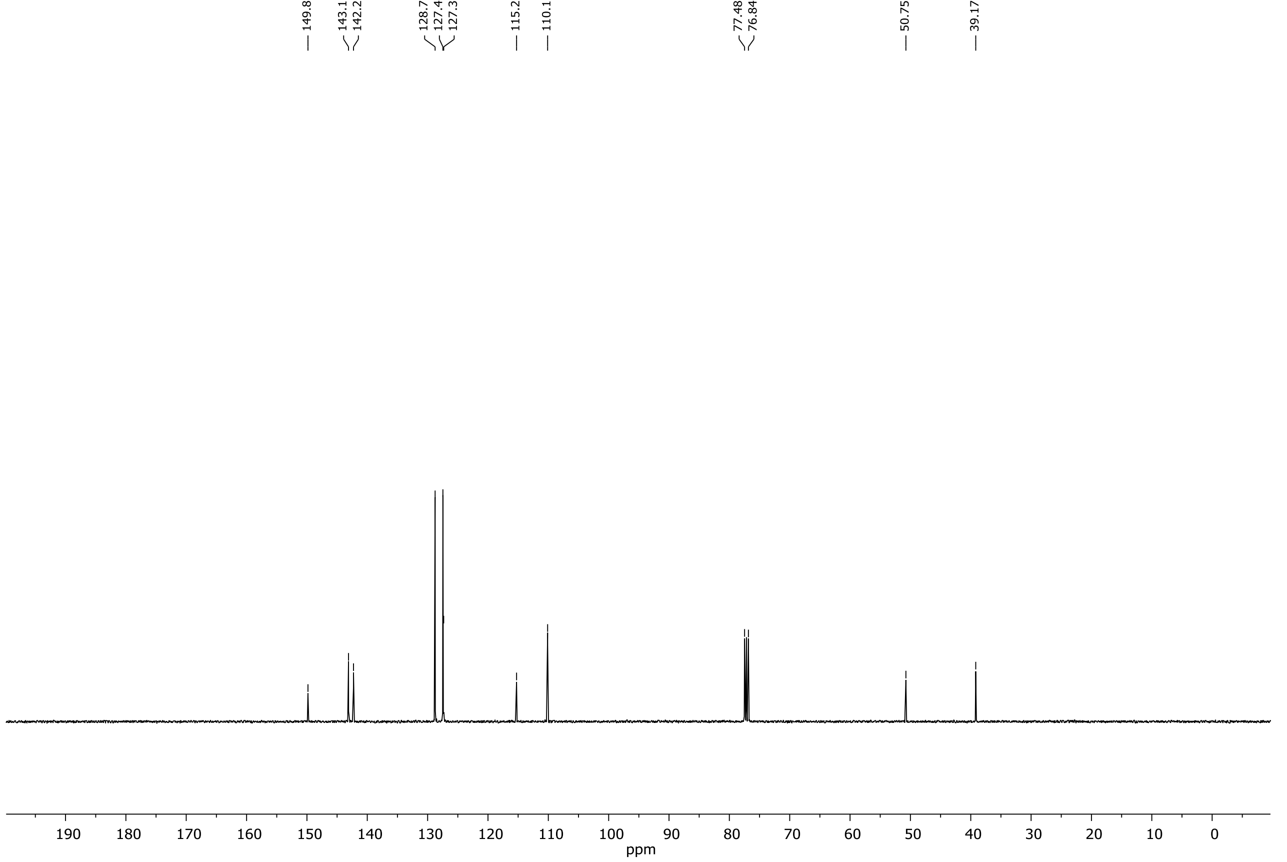


1H, CDCl3, 400 MHz

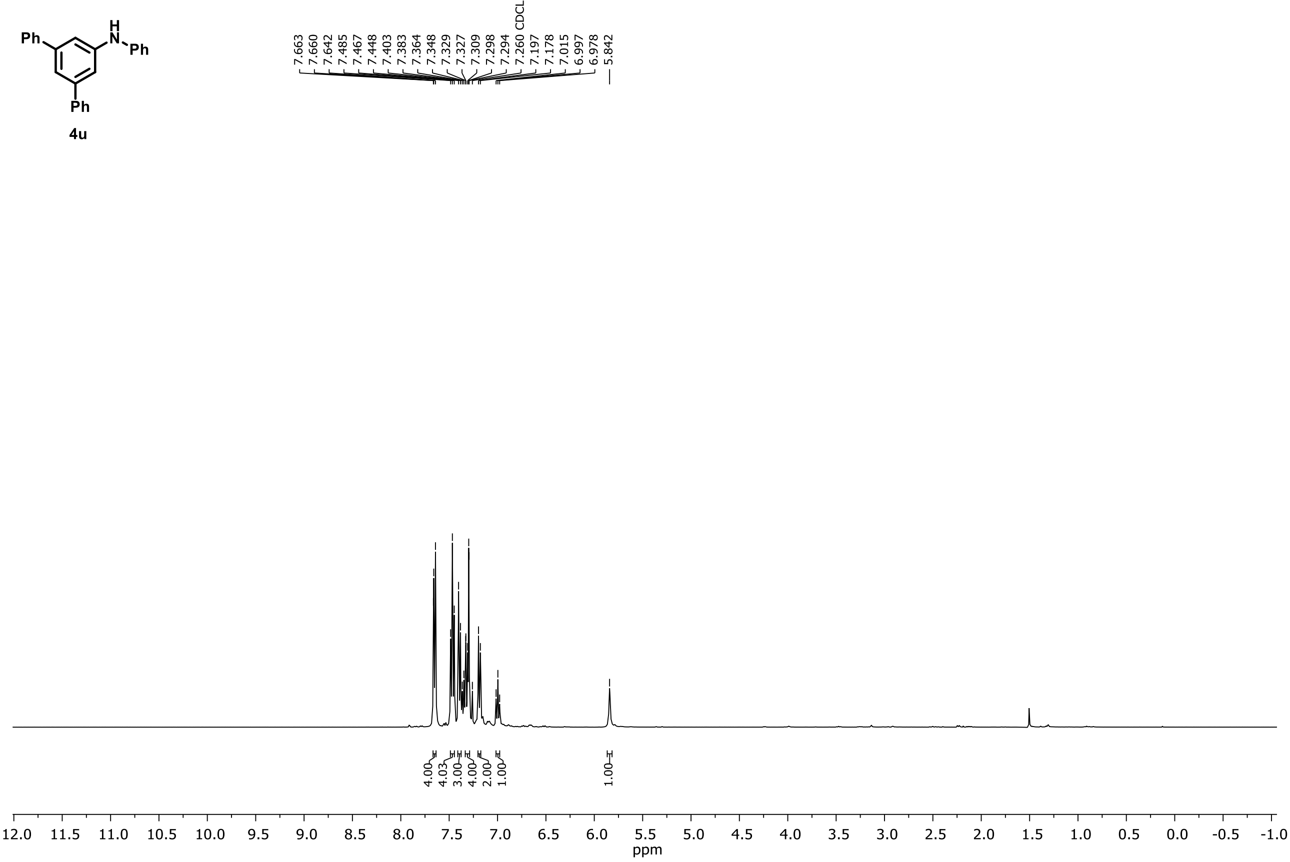


4t

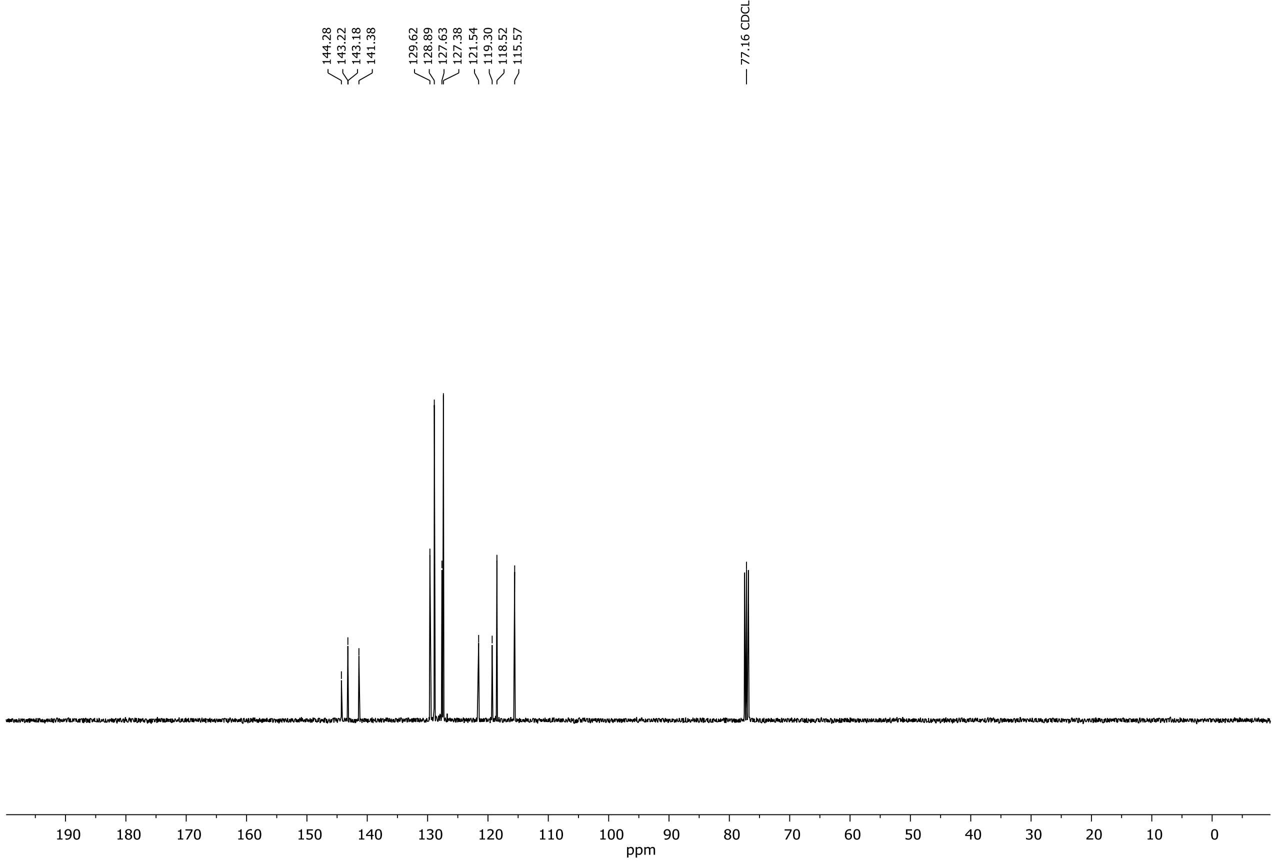
13C, CDCl3, 100 MHz



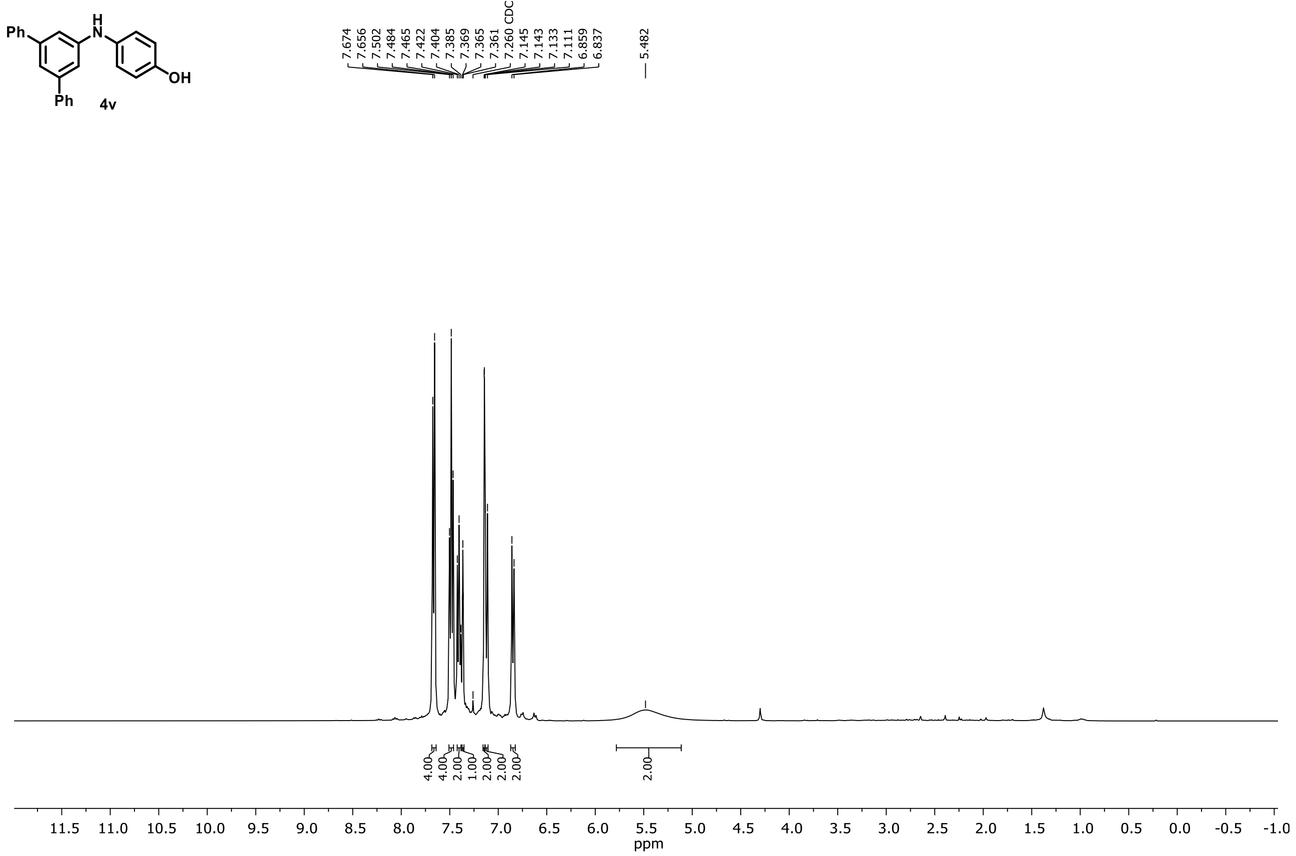
1H, CDCl3, 400 MHz



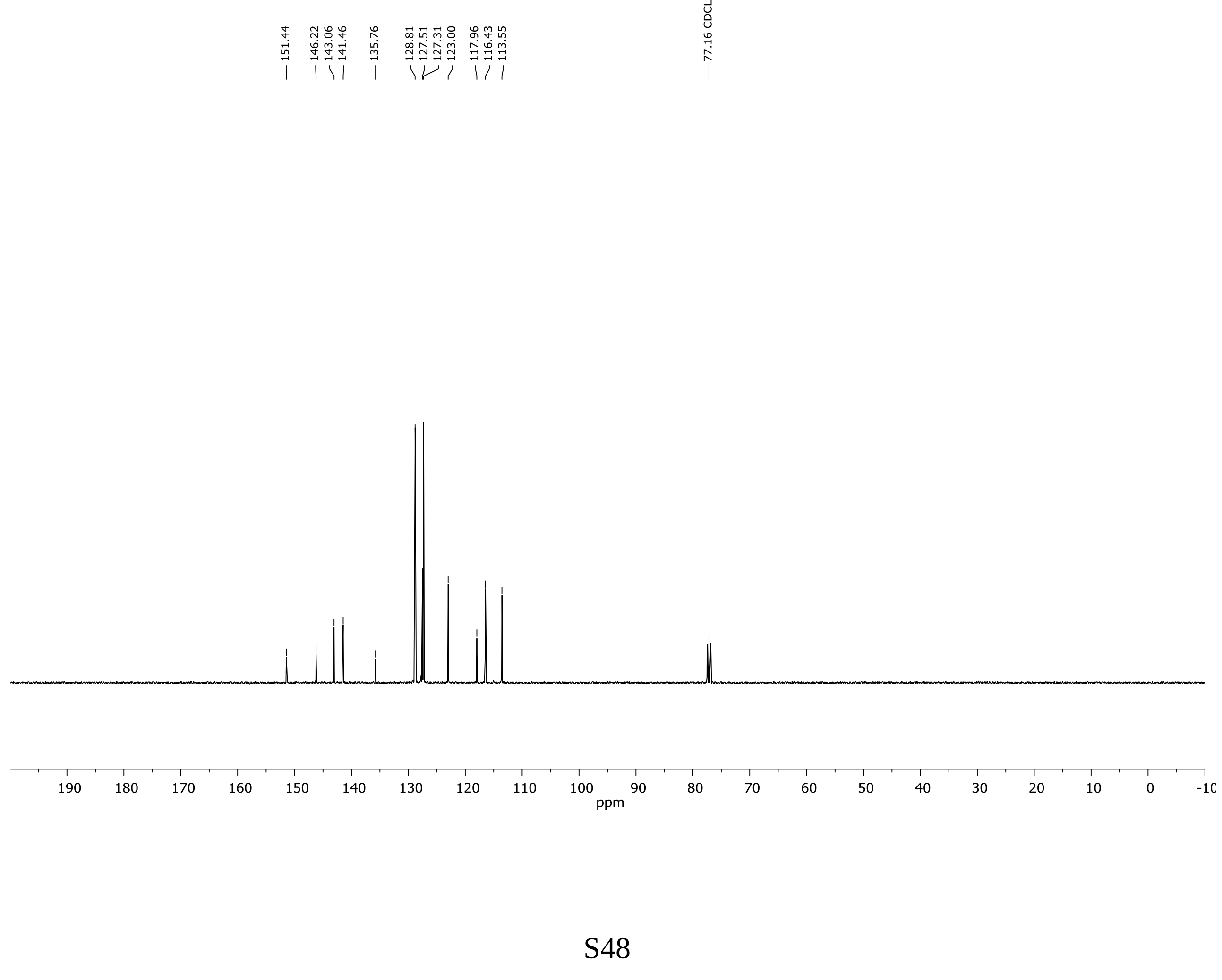
13C, CDCl3, 100 MHz



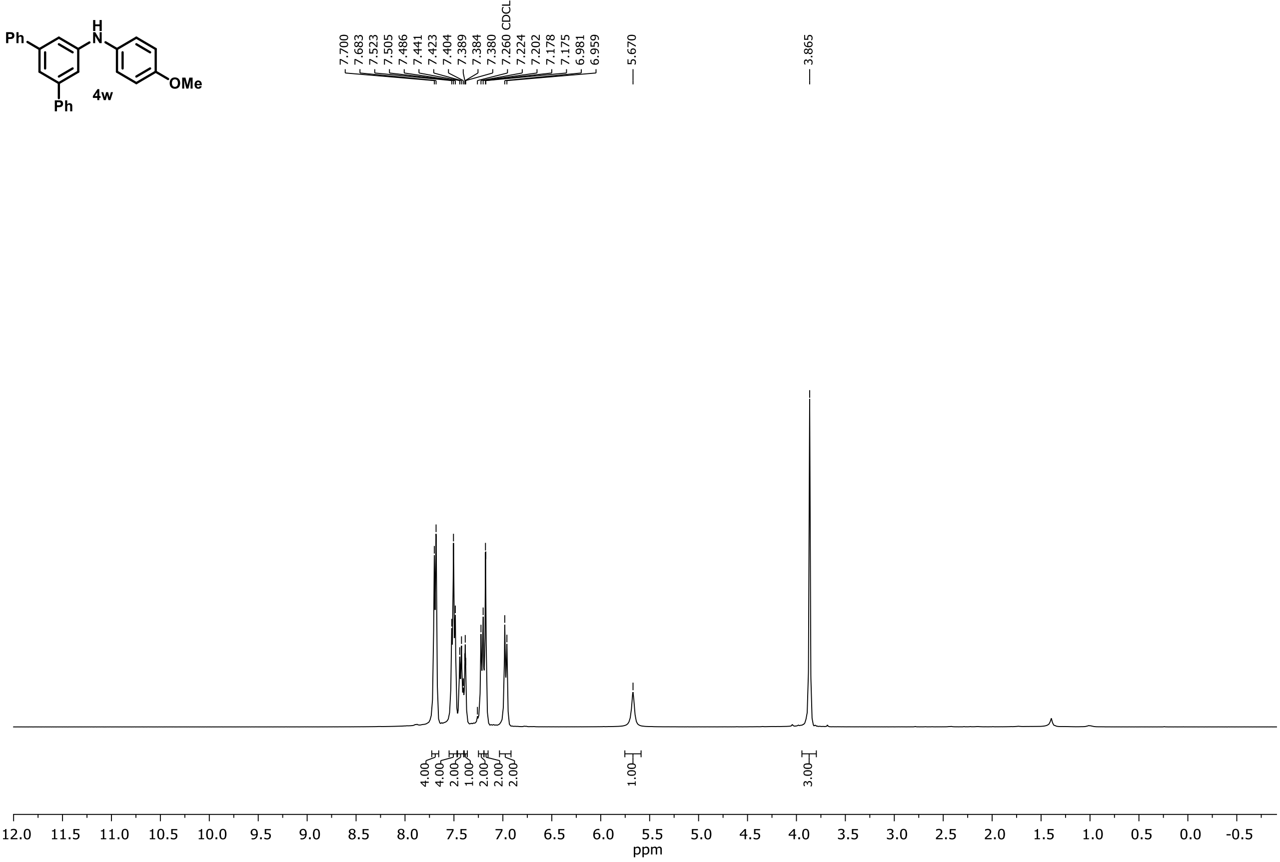
1H, CDCl3, 400 MHz



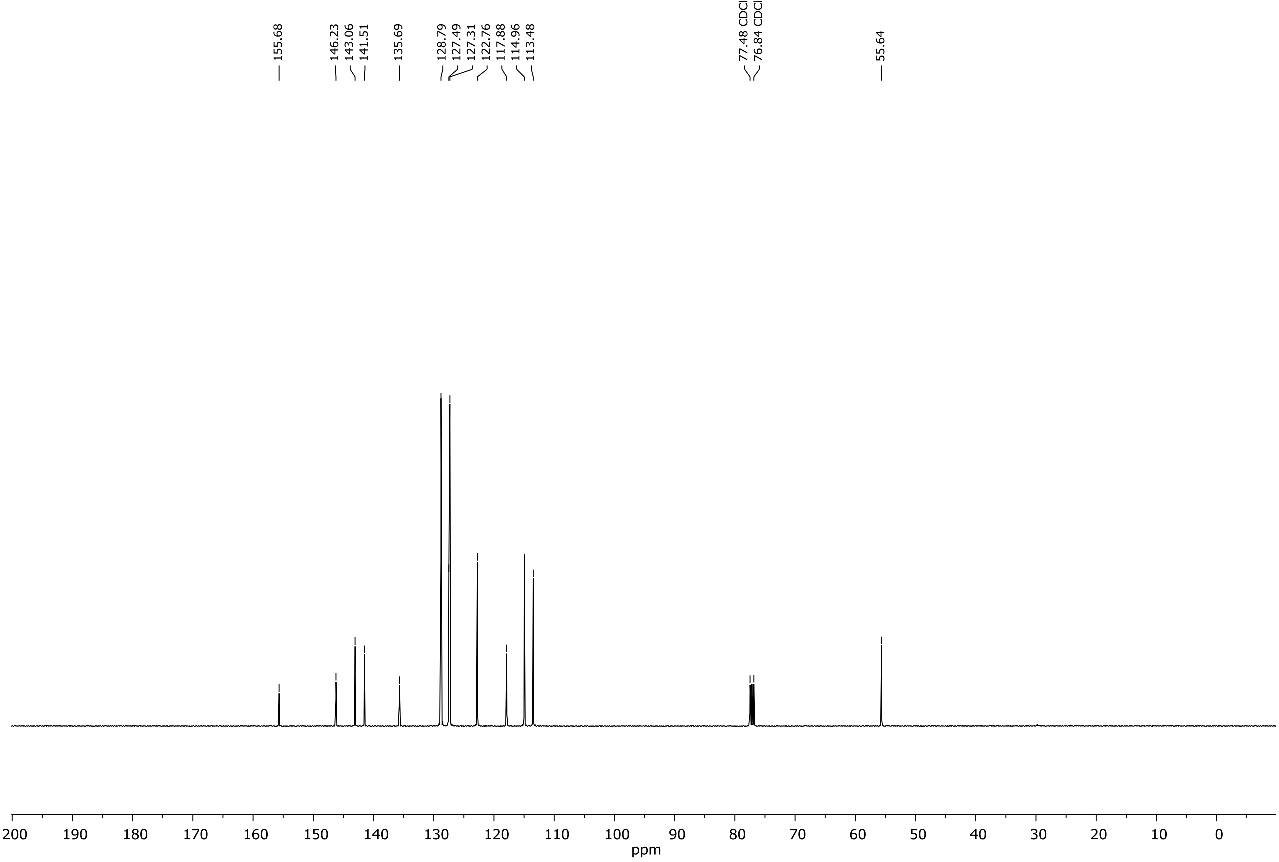
13C, CDCl3, 100 MHz



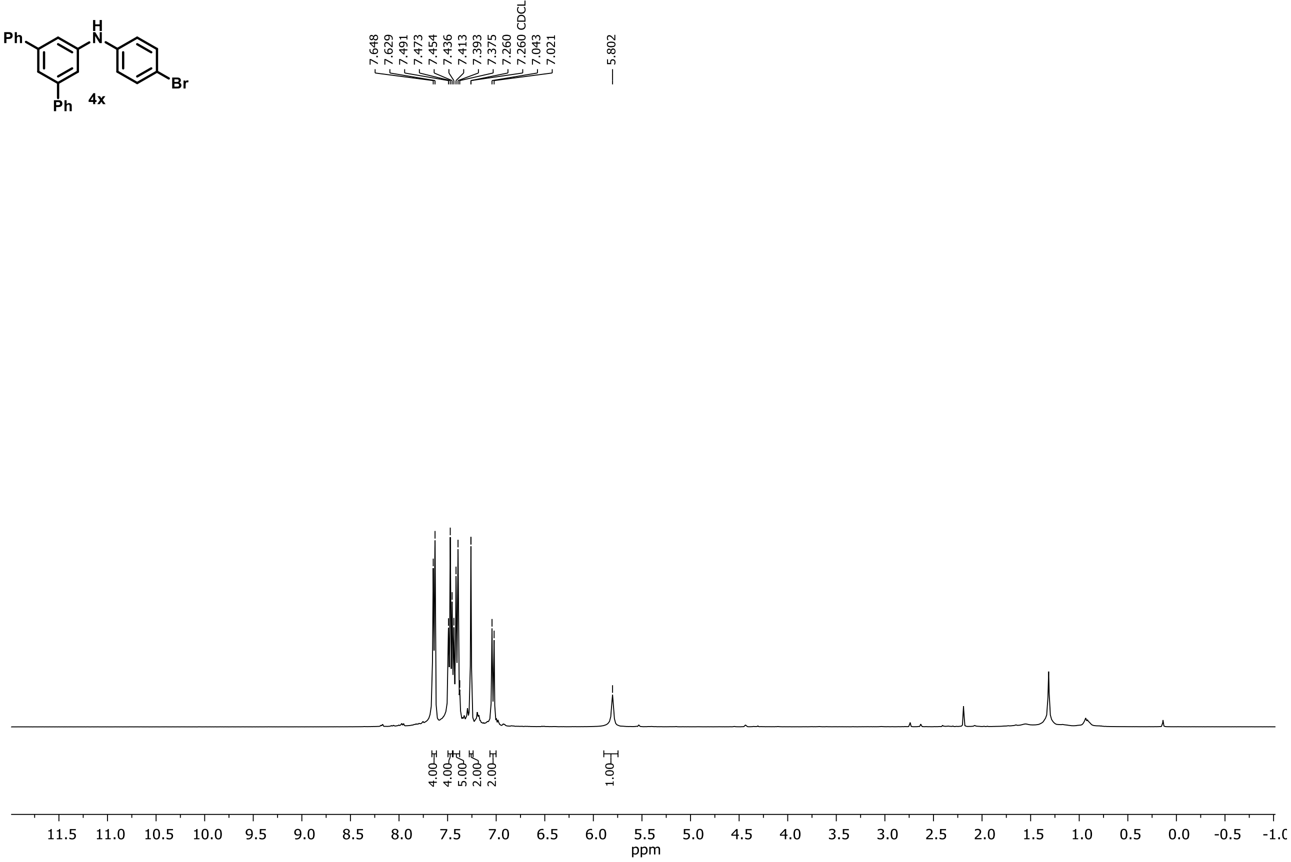
1H, CDCl3, 400 MHz



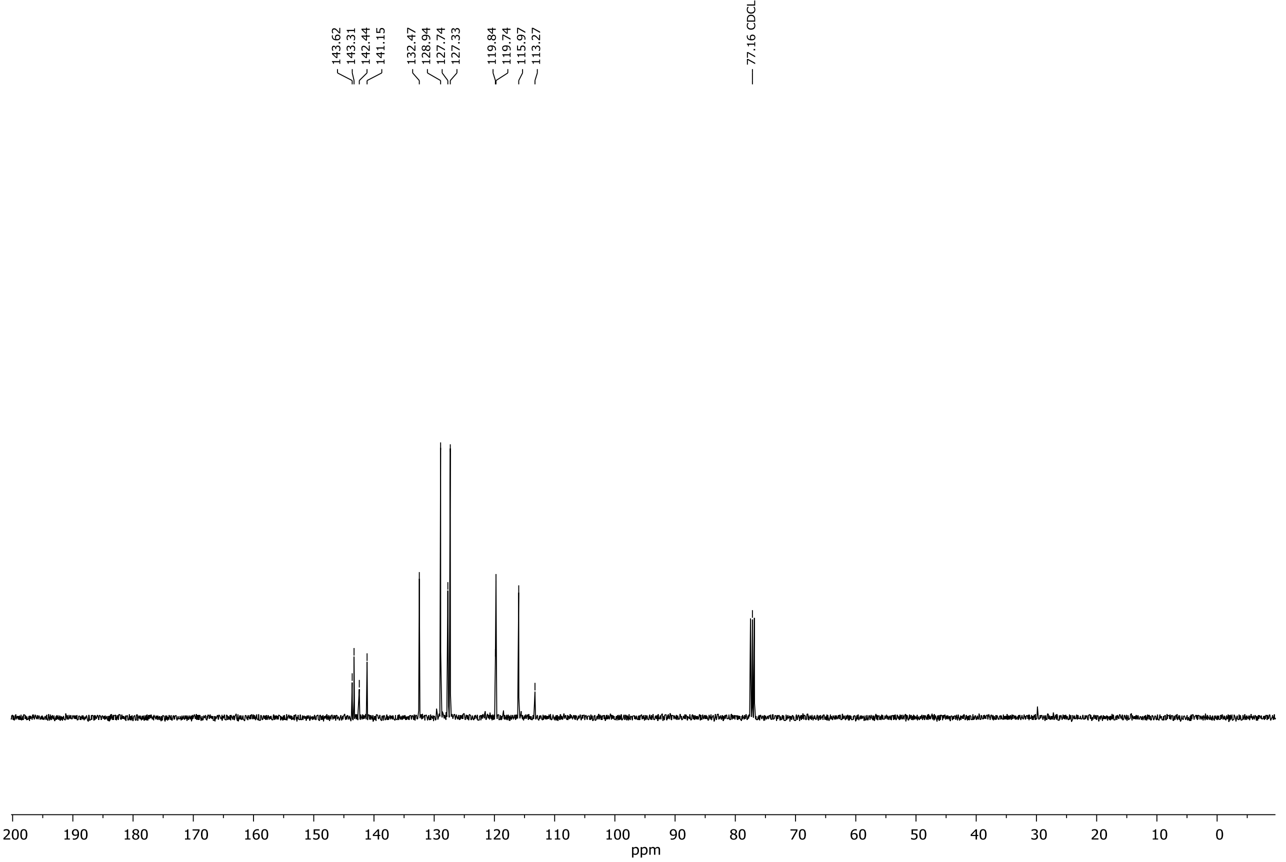
13C, CDCl3, 100 MHz



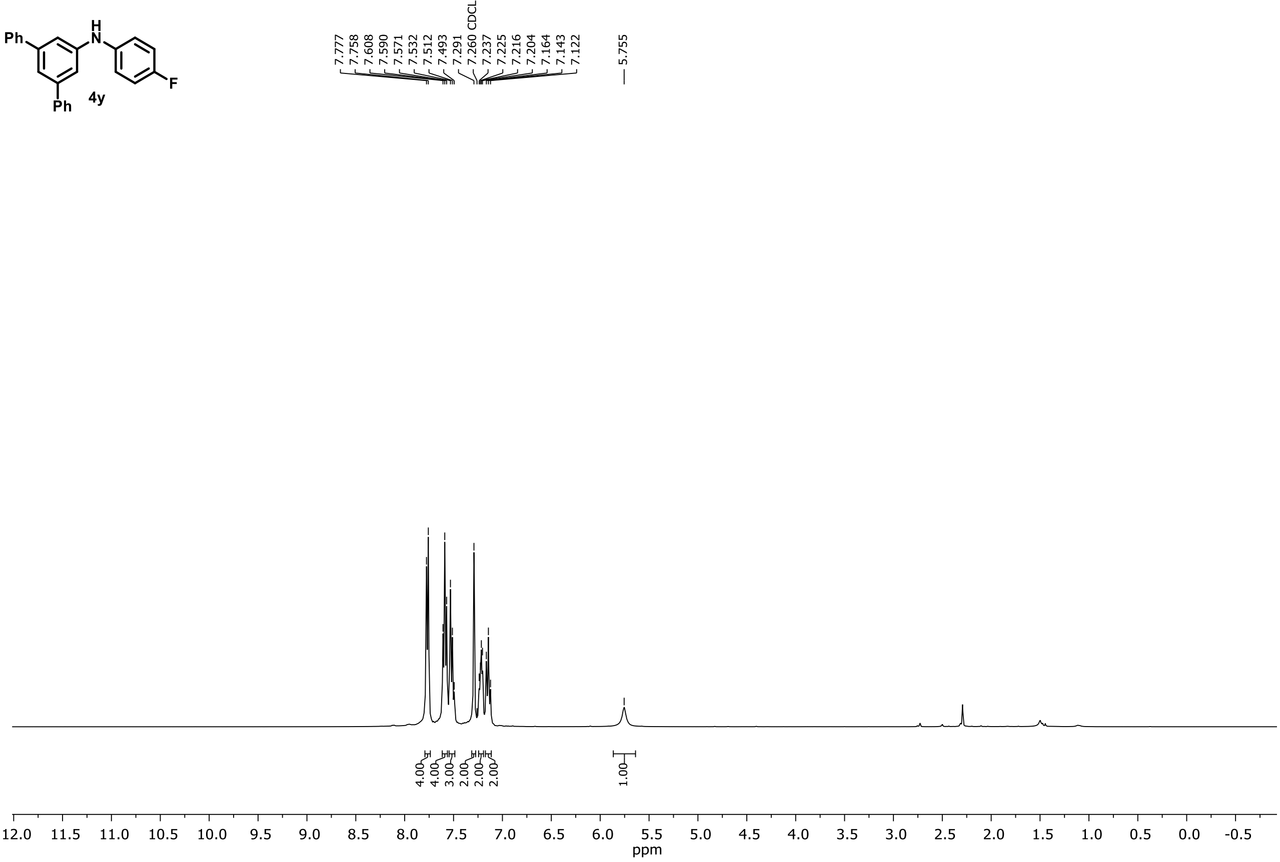
1H, CDCl3, 400 MHz


4x

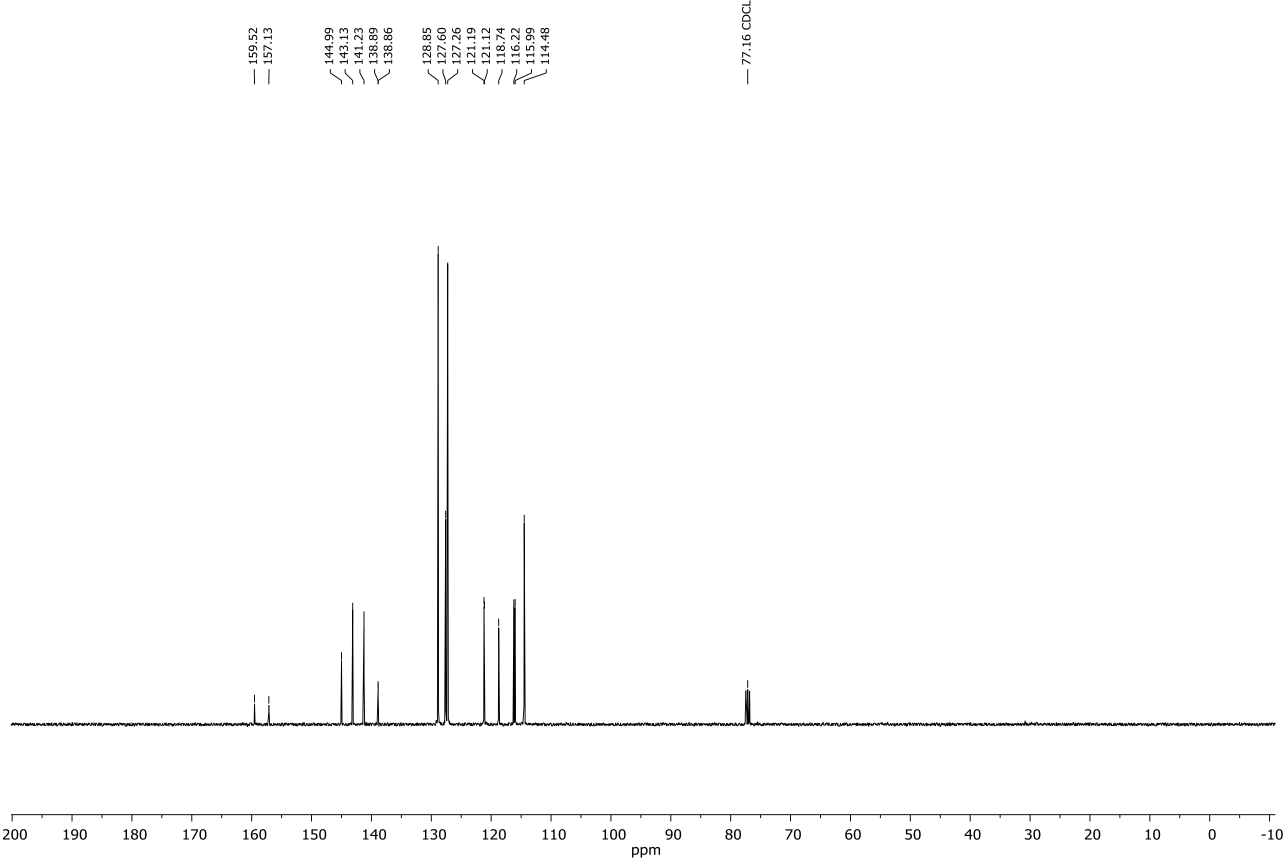
13C, CDCl3, 100 MHz



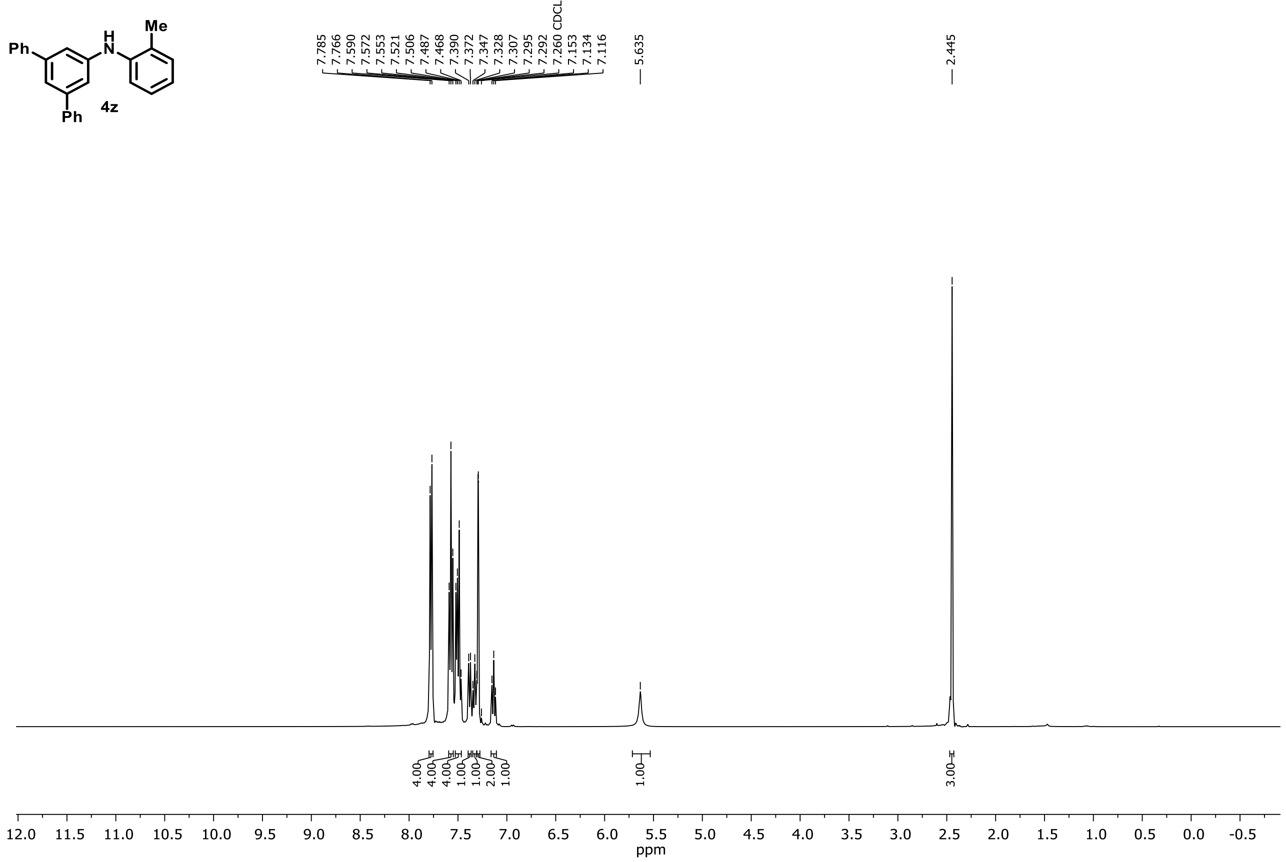
1H, CDCl3, 400 MHz



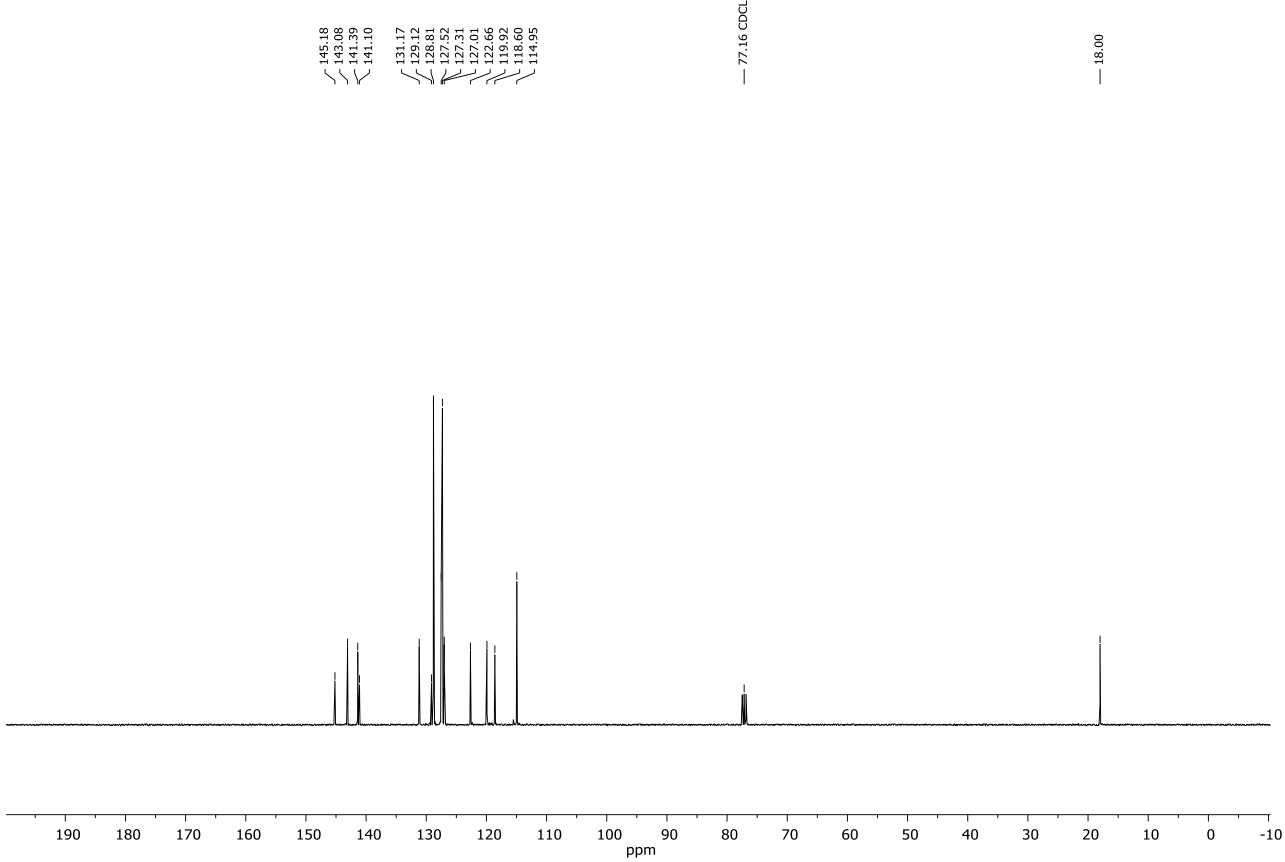
13C, CDCl3, 100 MHz



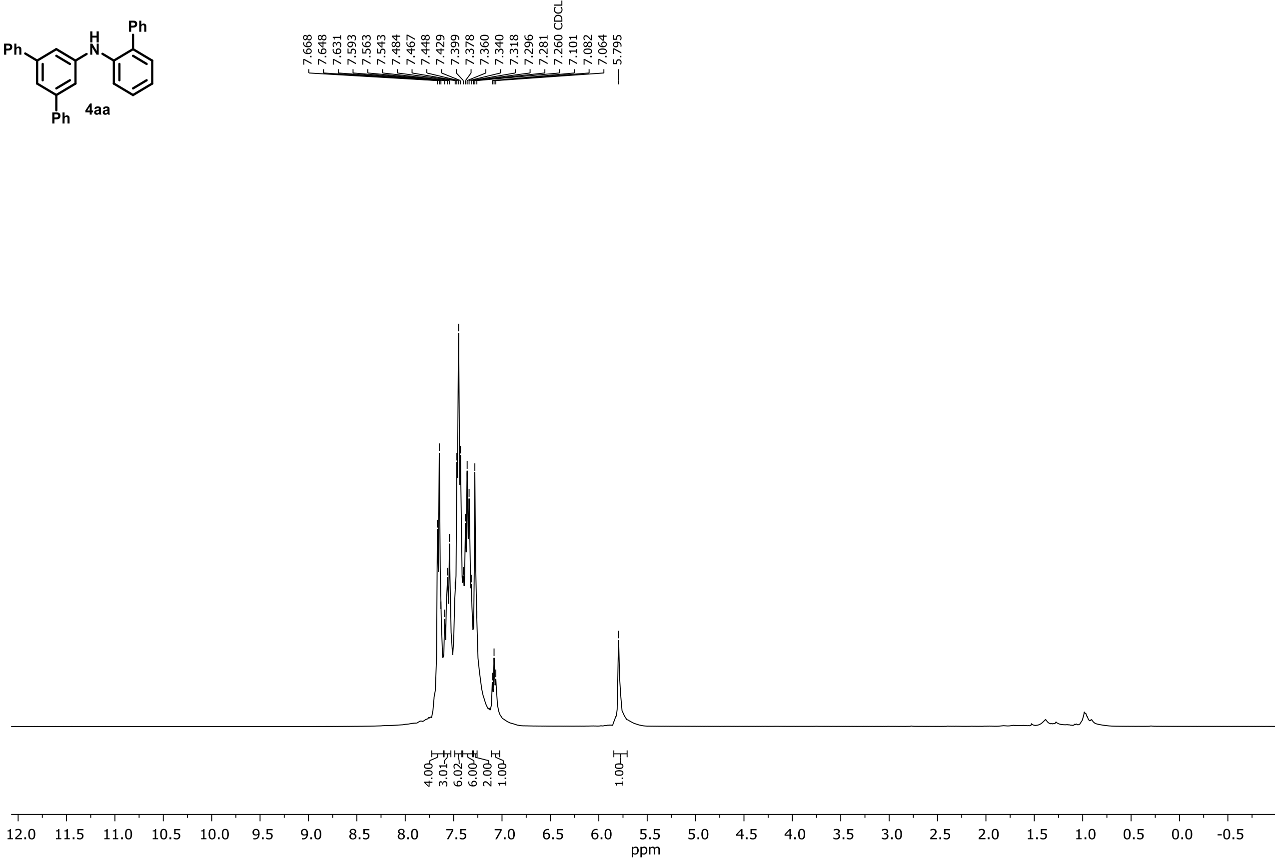
1H, CDCl3, 400 MHz



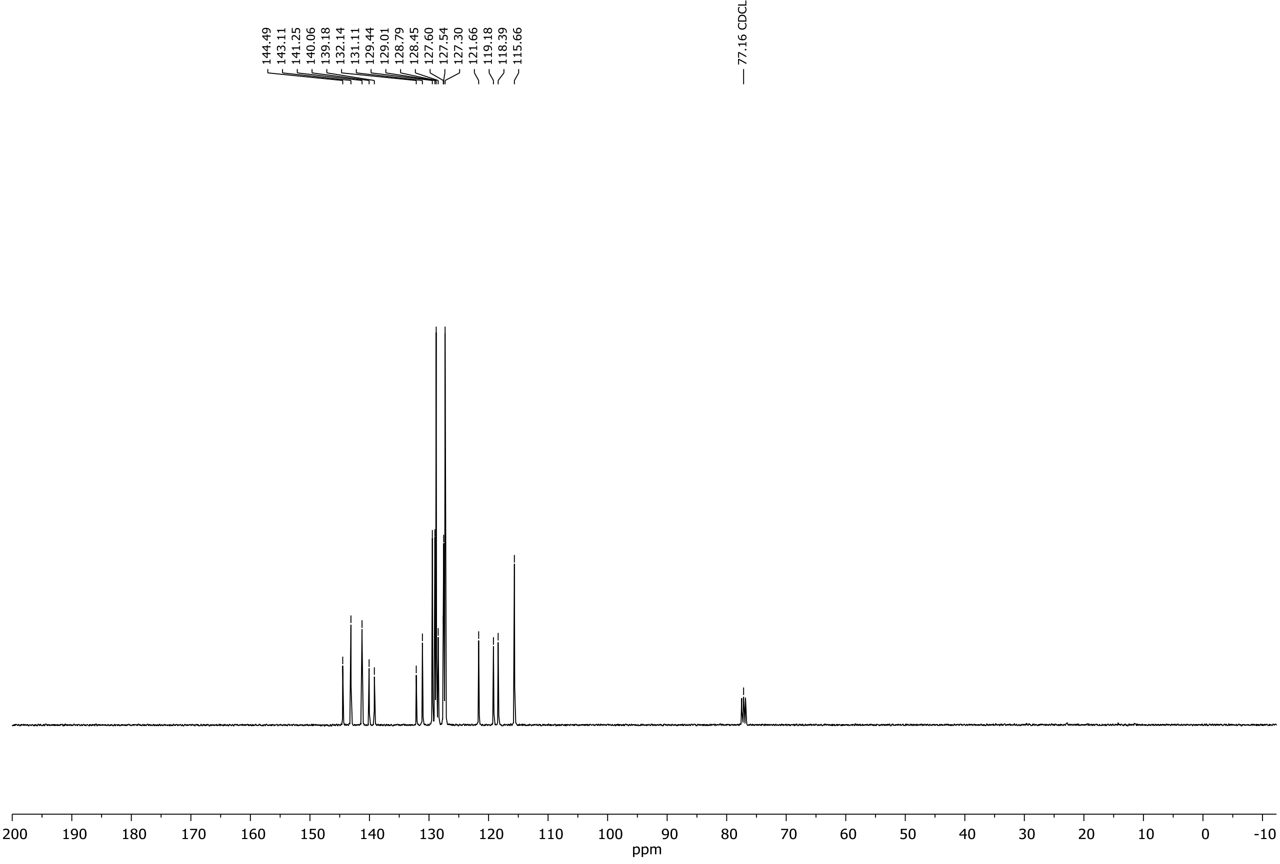
13C, CDCl3, 100 MHz



1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz



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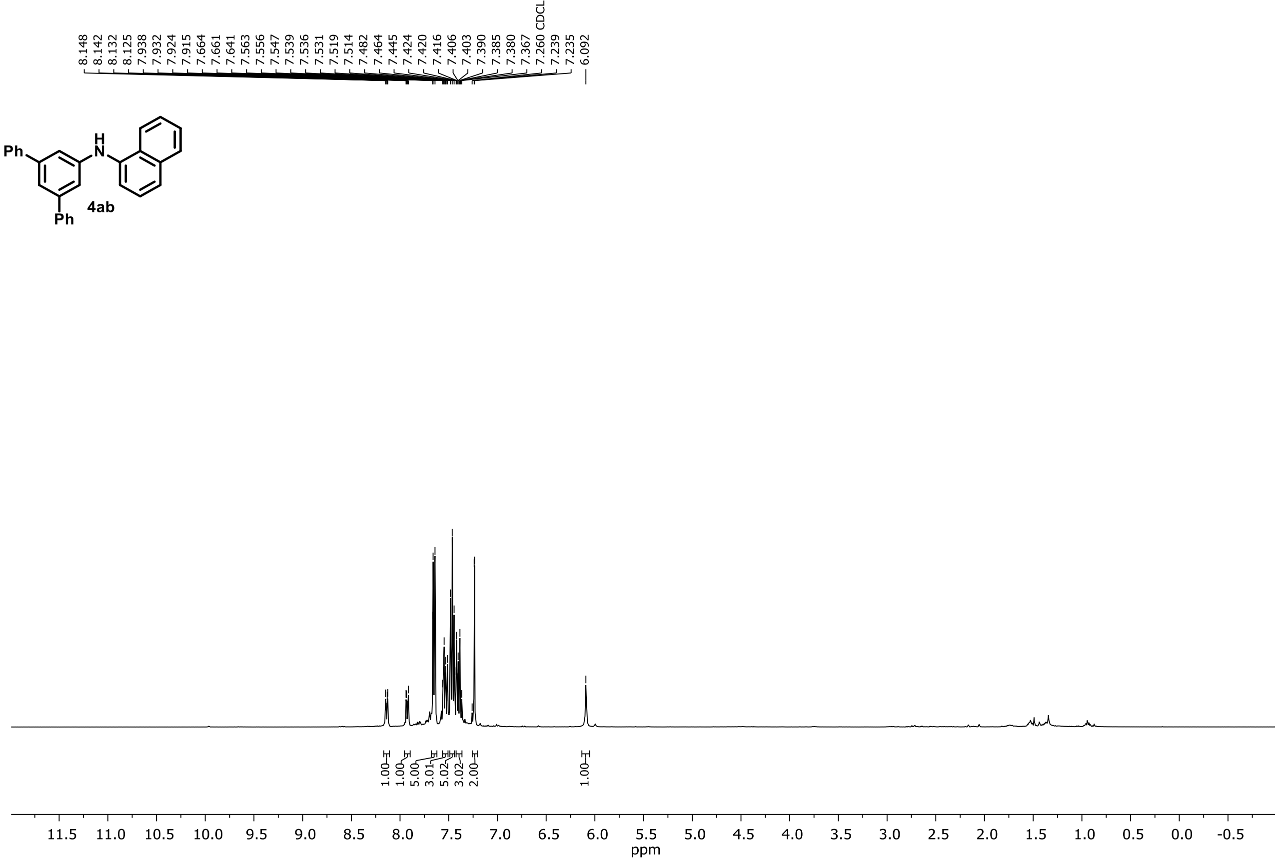
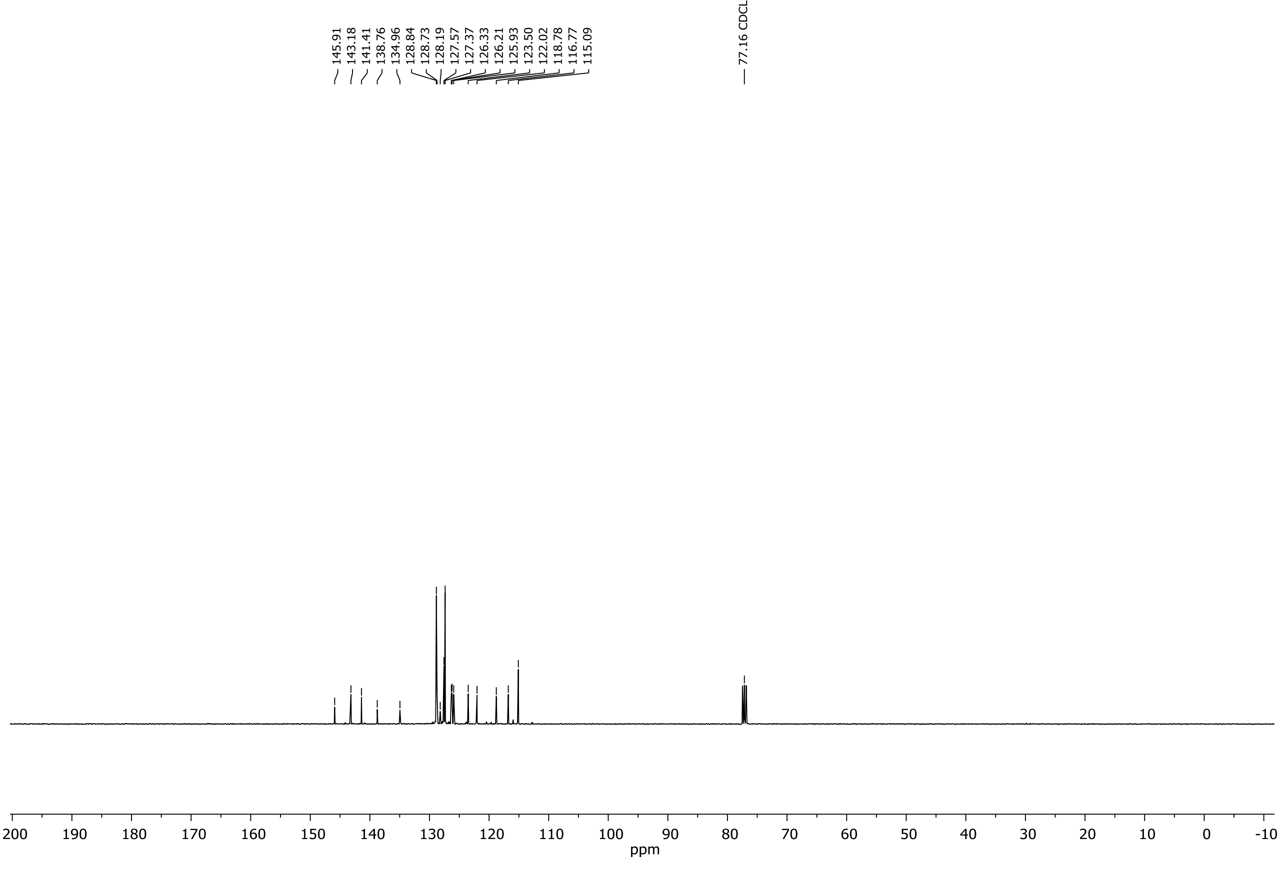
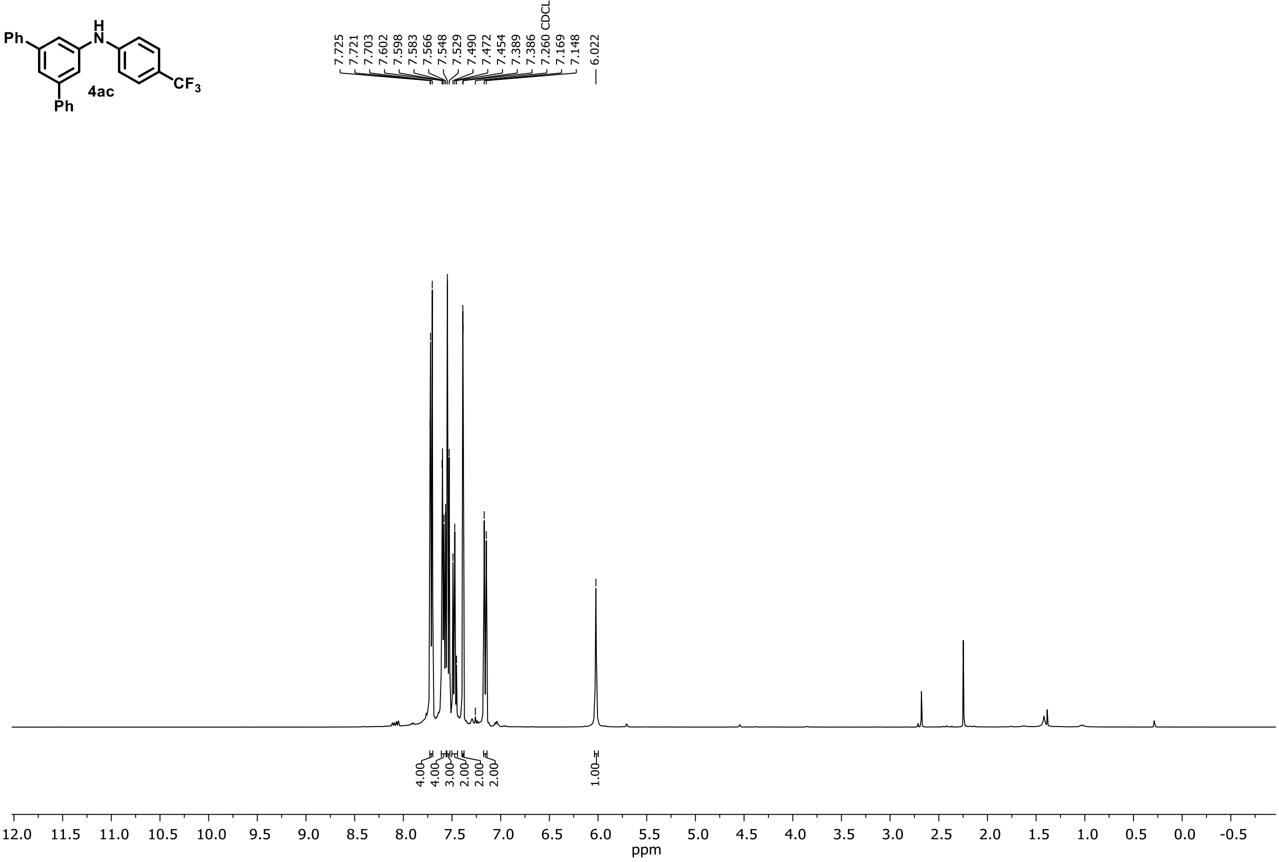


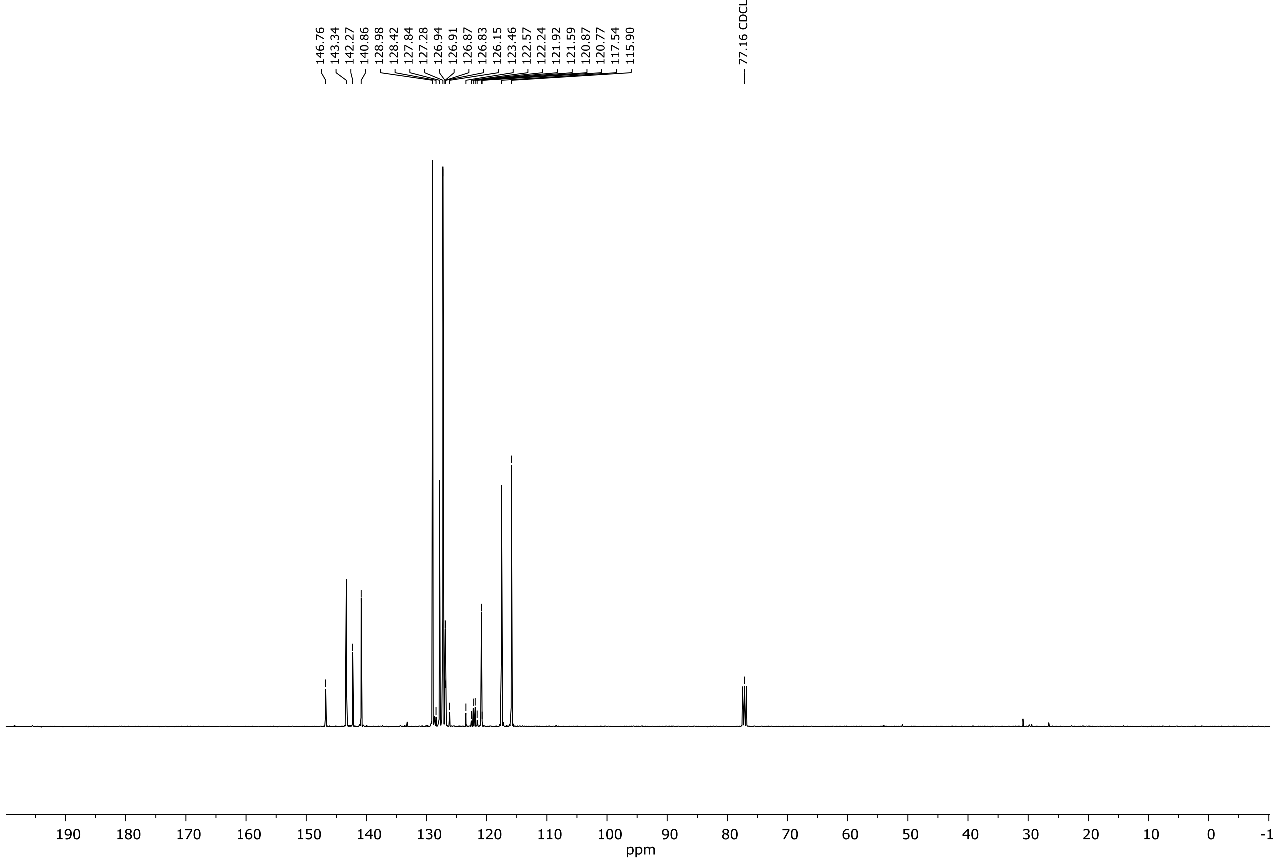
13C, CDCl3, 100 MHz



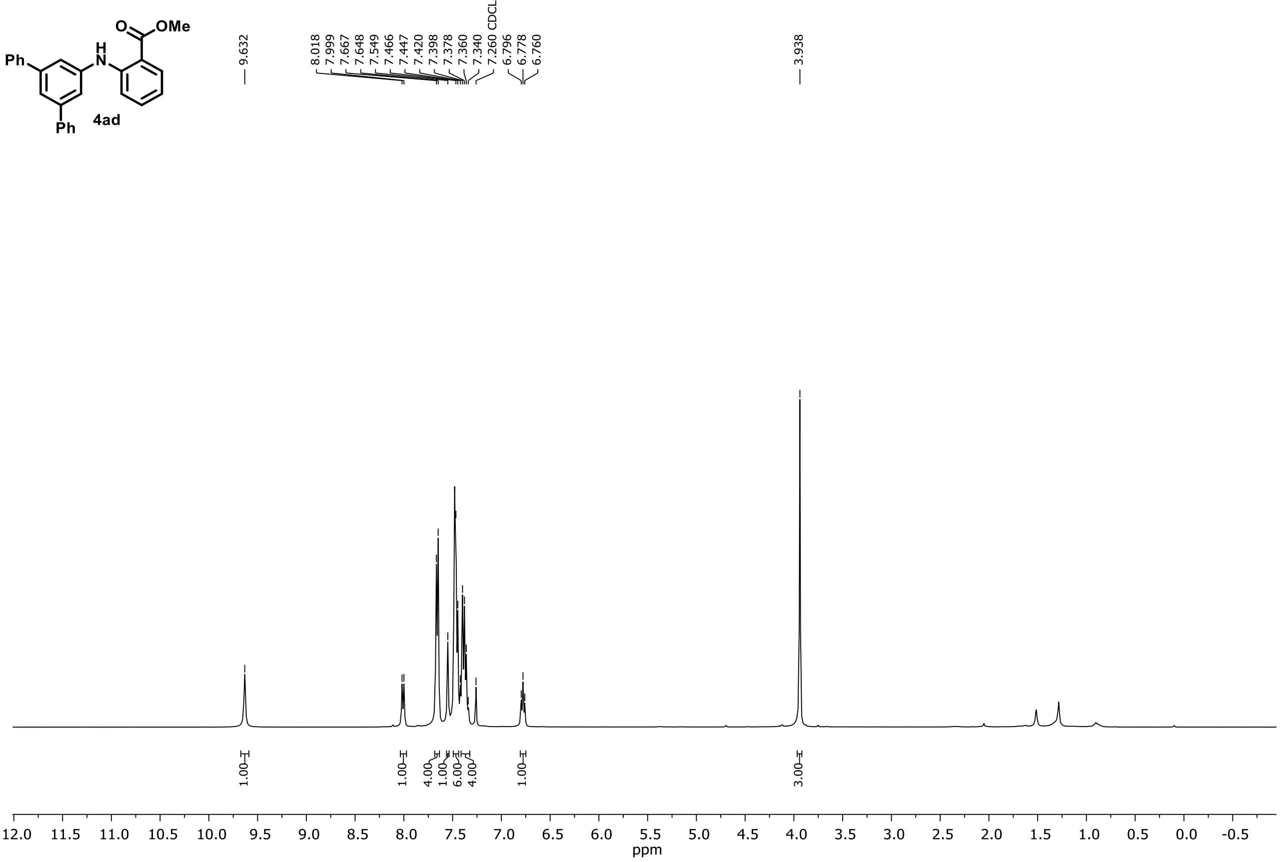
1H, CDCl3, 400 MHz



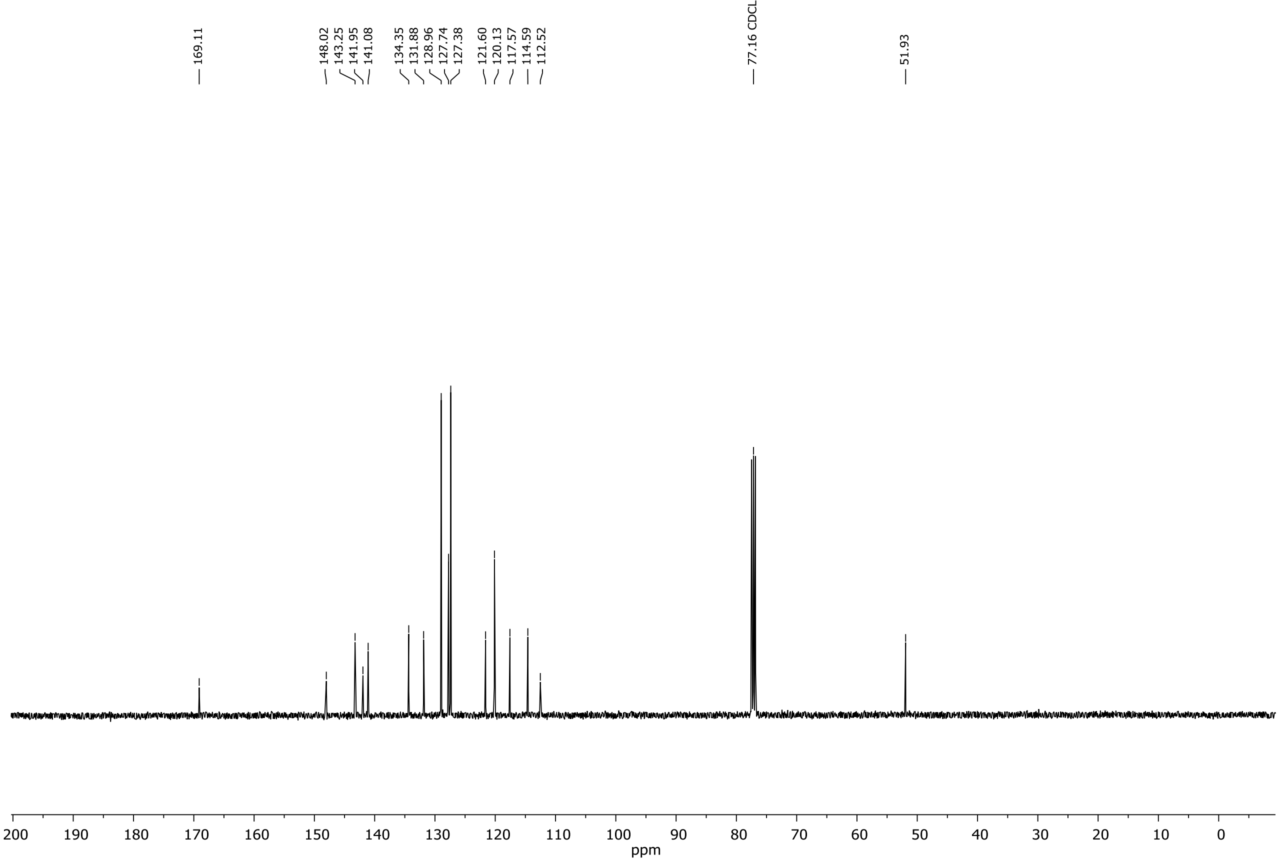
13C, CDCl3, 100 MHz



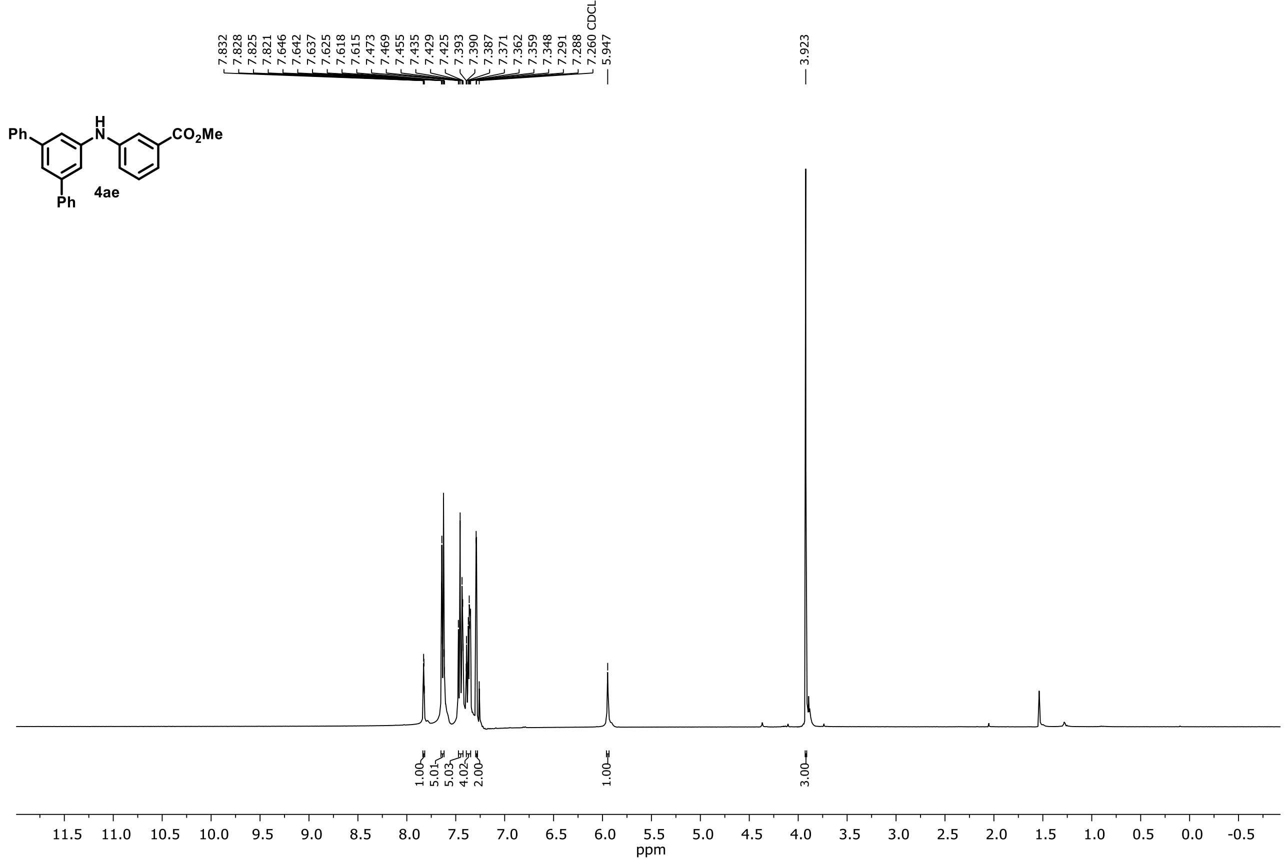
1H, CDCl3, 400 MHz



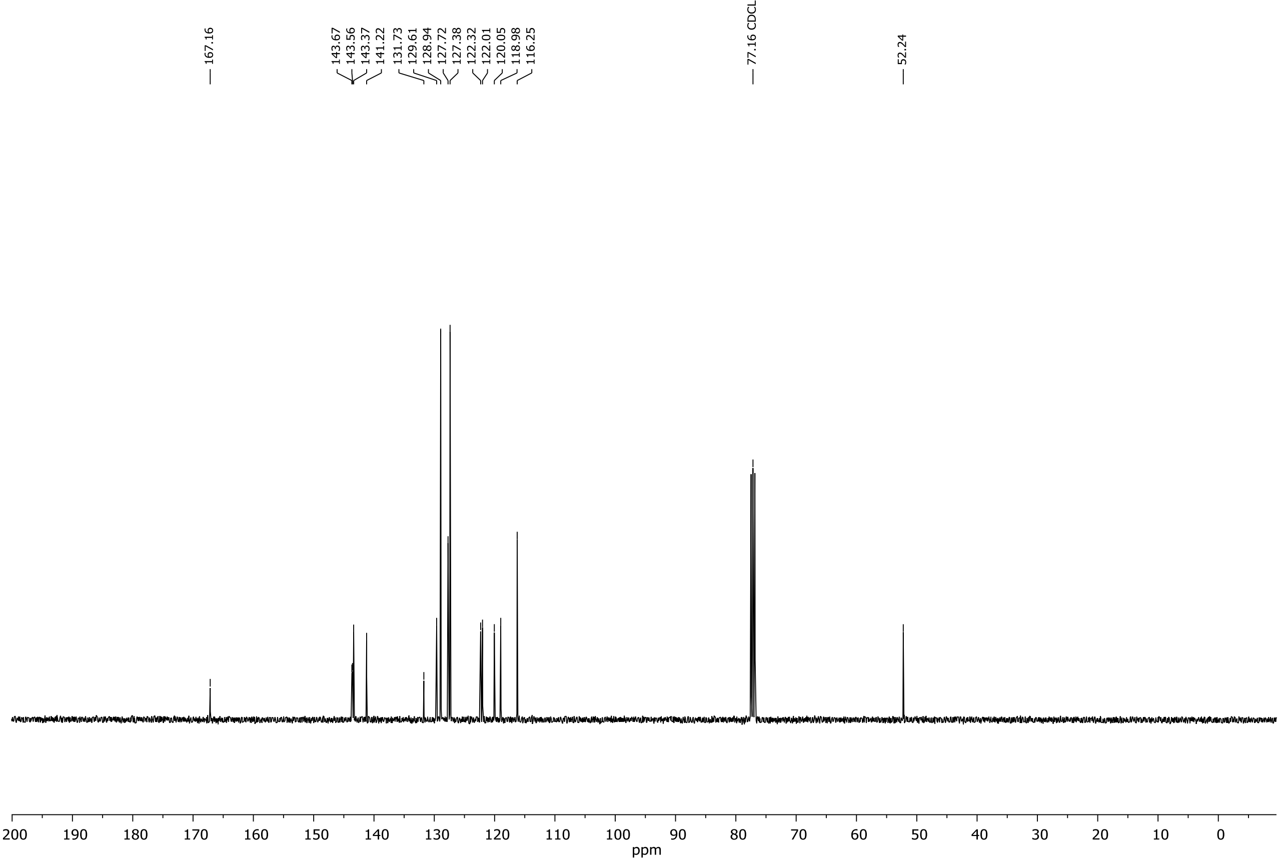
13C, CDCl3, 100 MHz



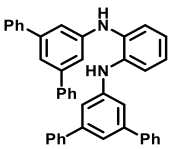
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz



1H, CDCl3, 400 MHz



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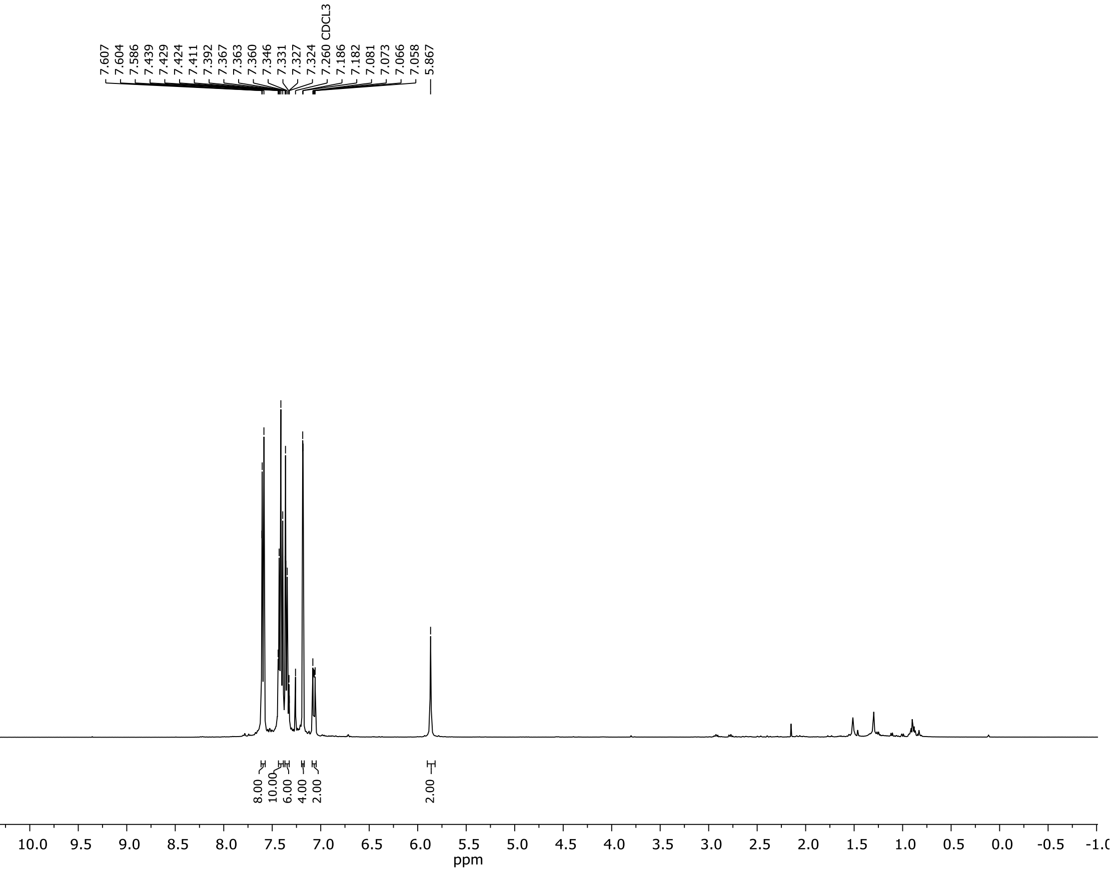
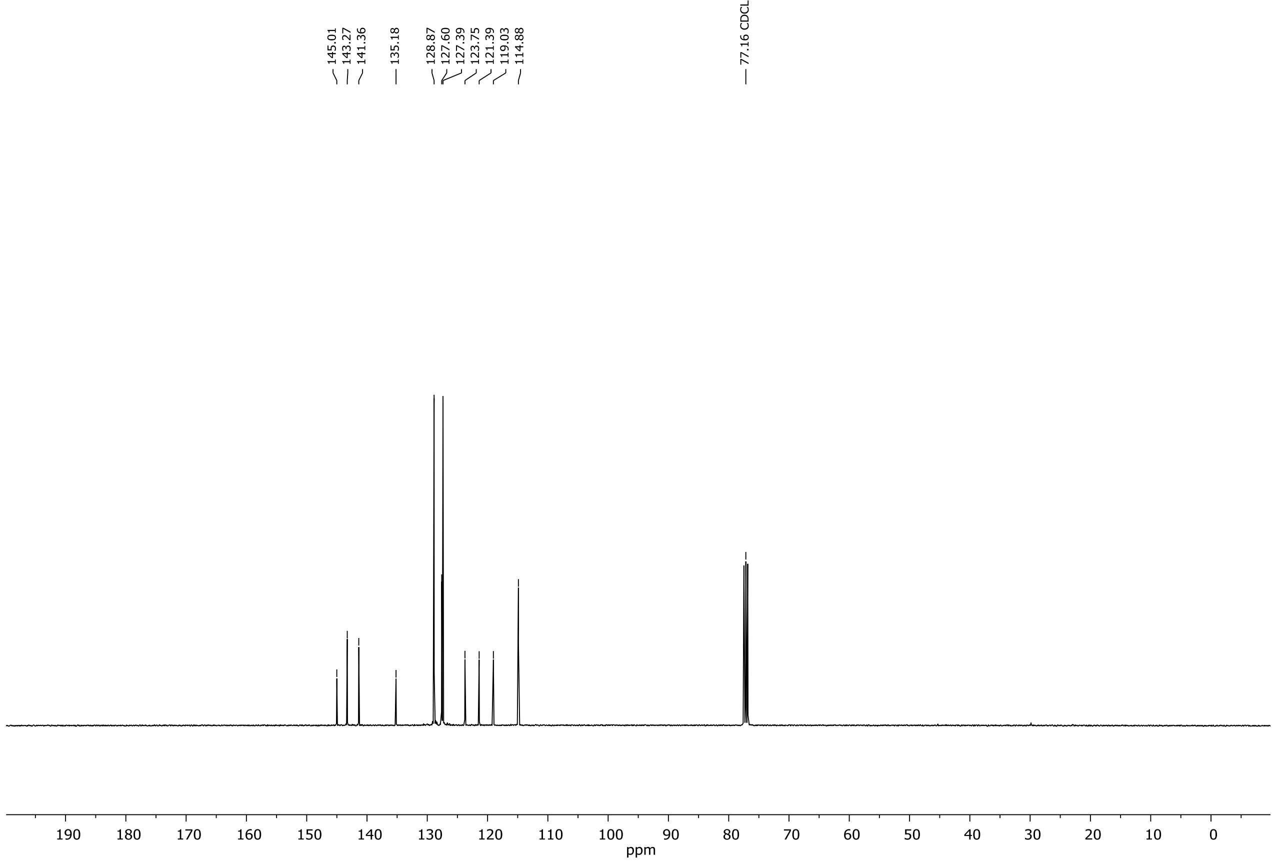
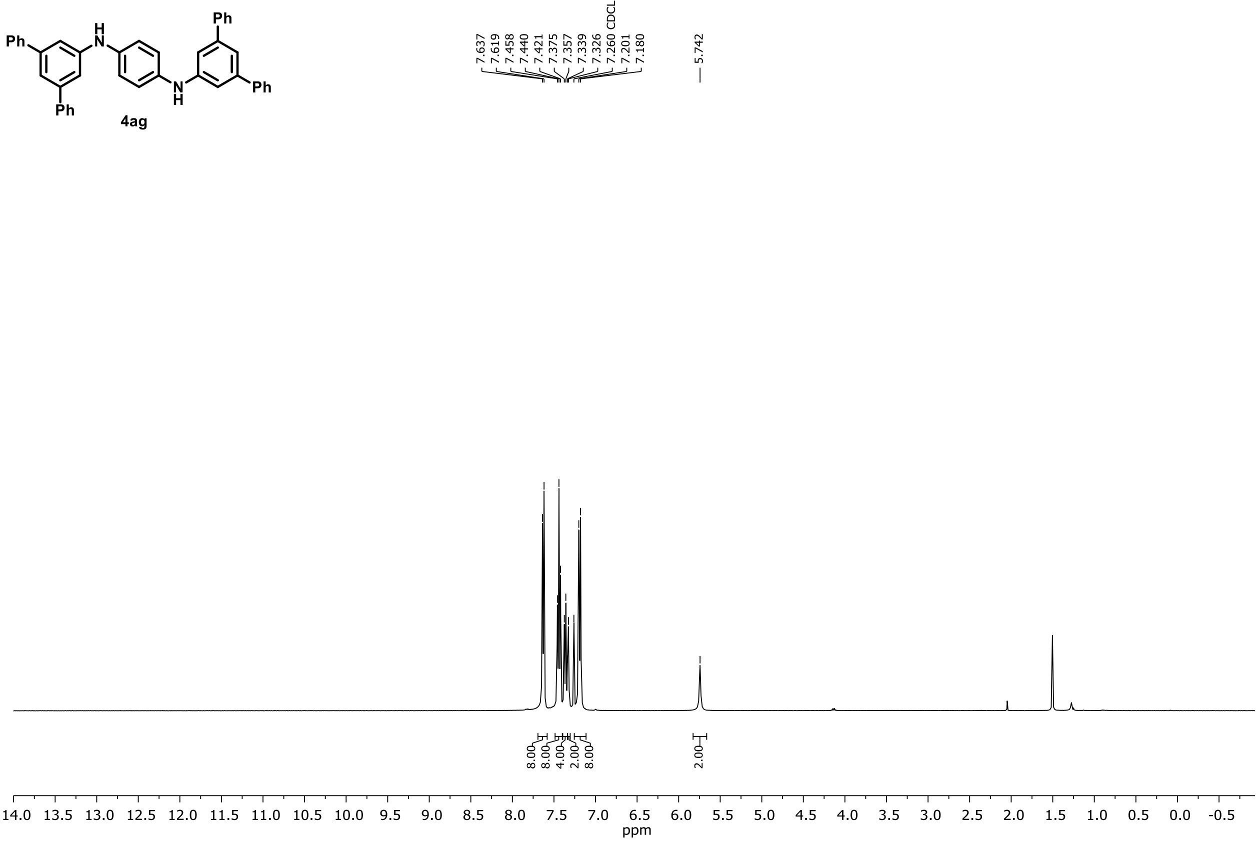


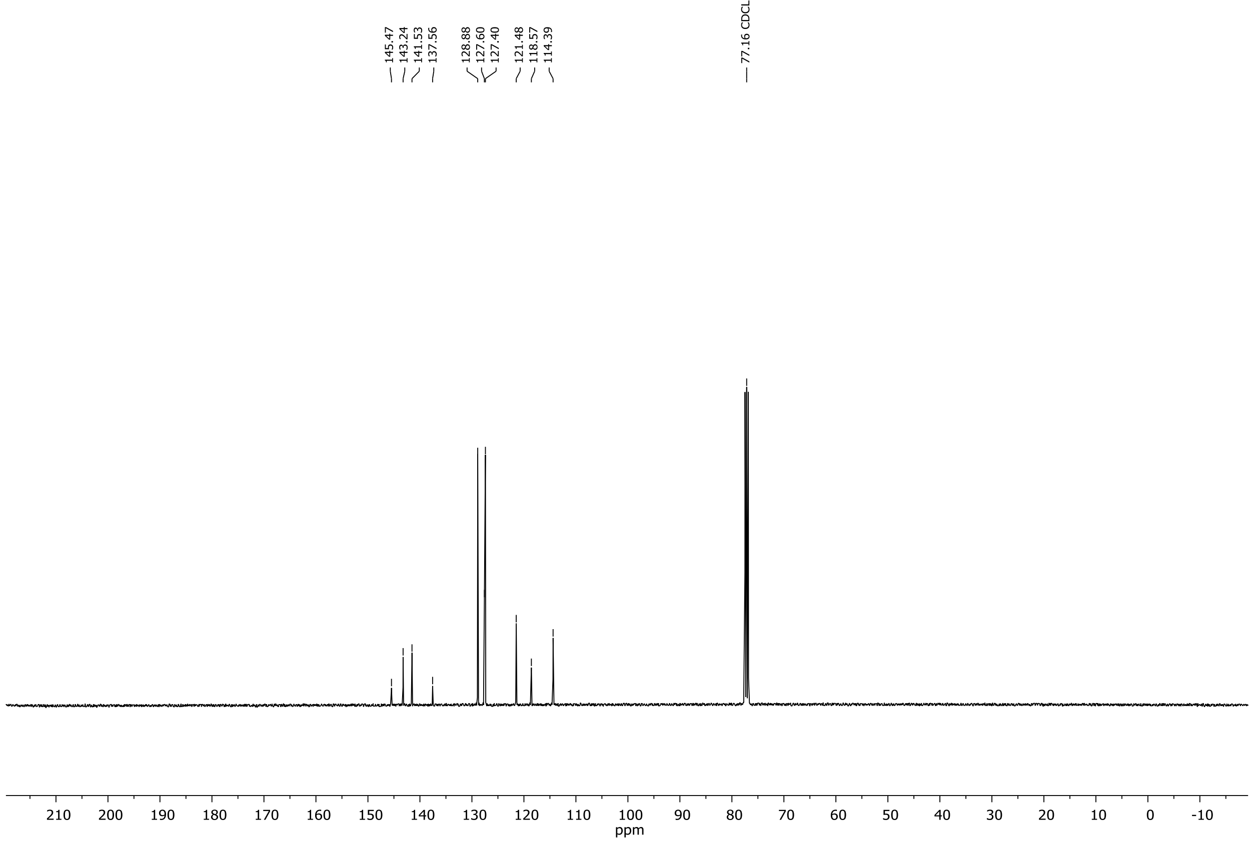
13C, CDCl3, 100 MHz



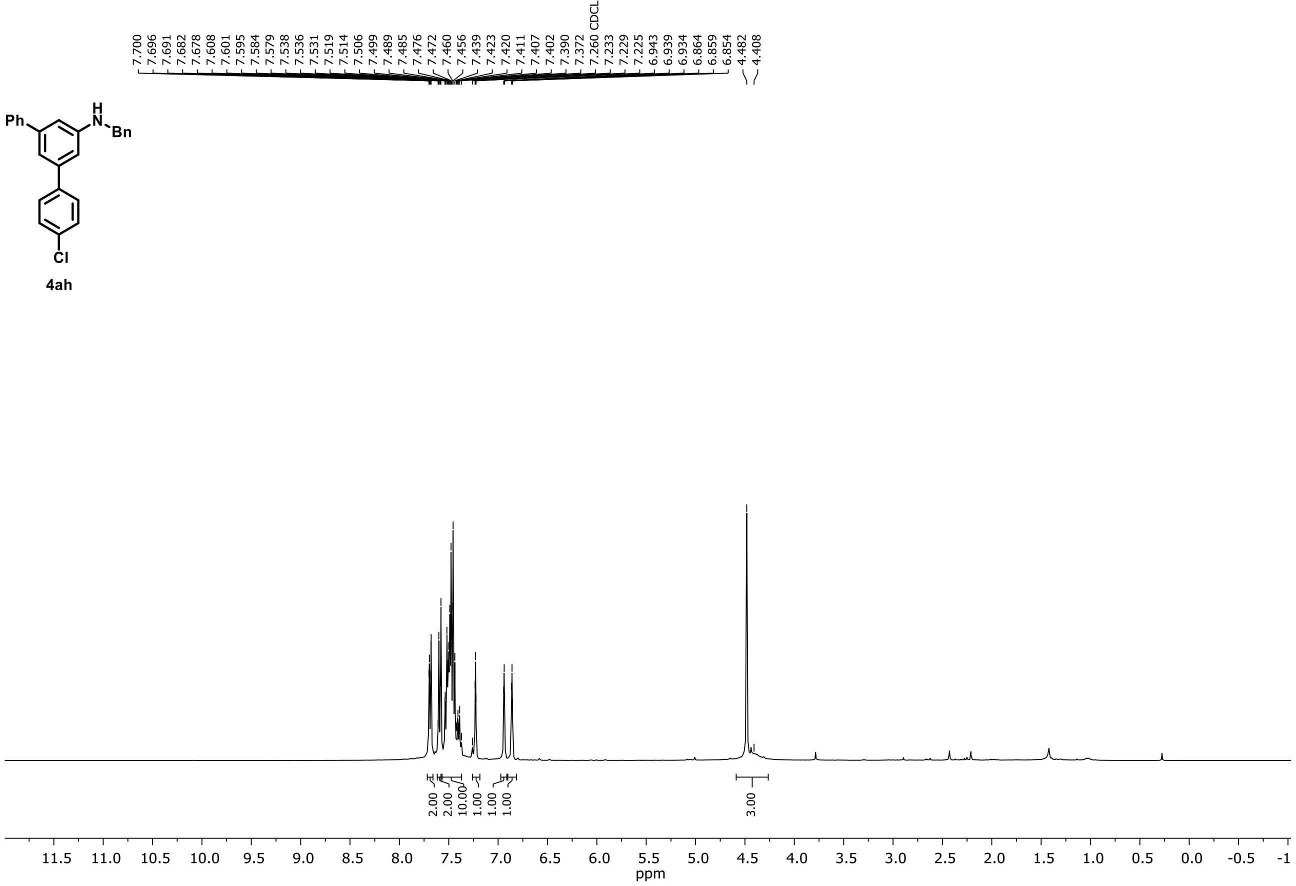
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

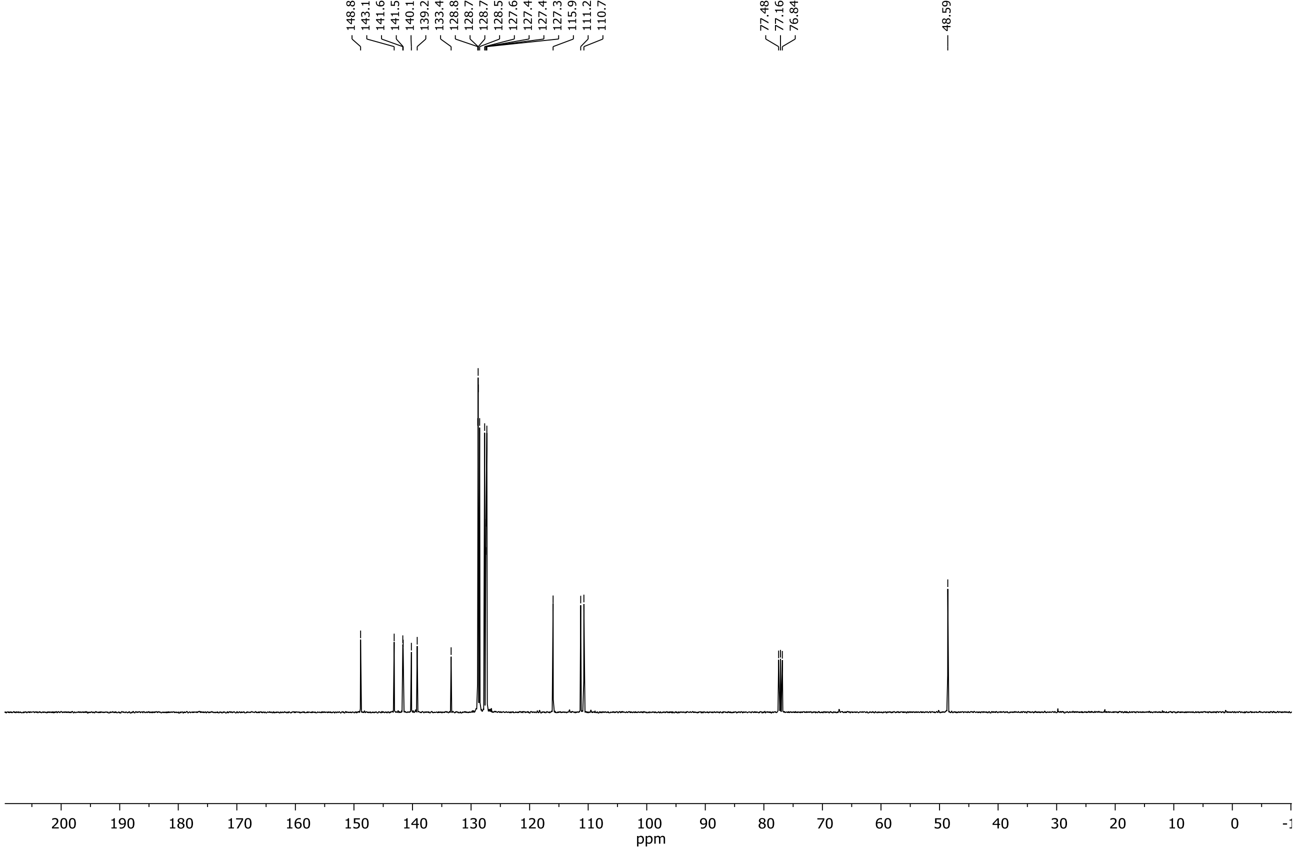


1H, CDCl3, 400 MHz

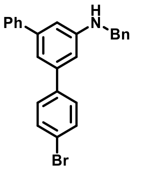


4ah

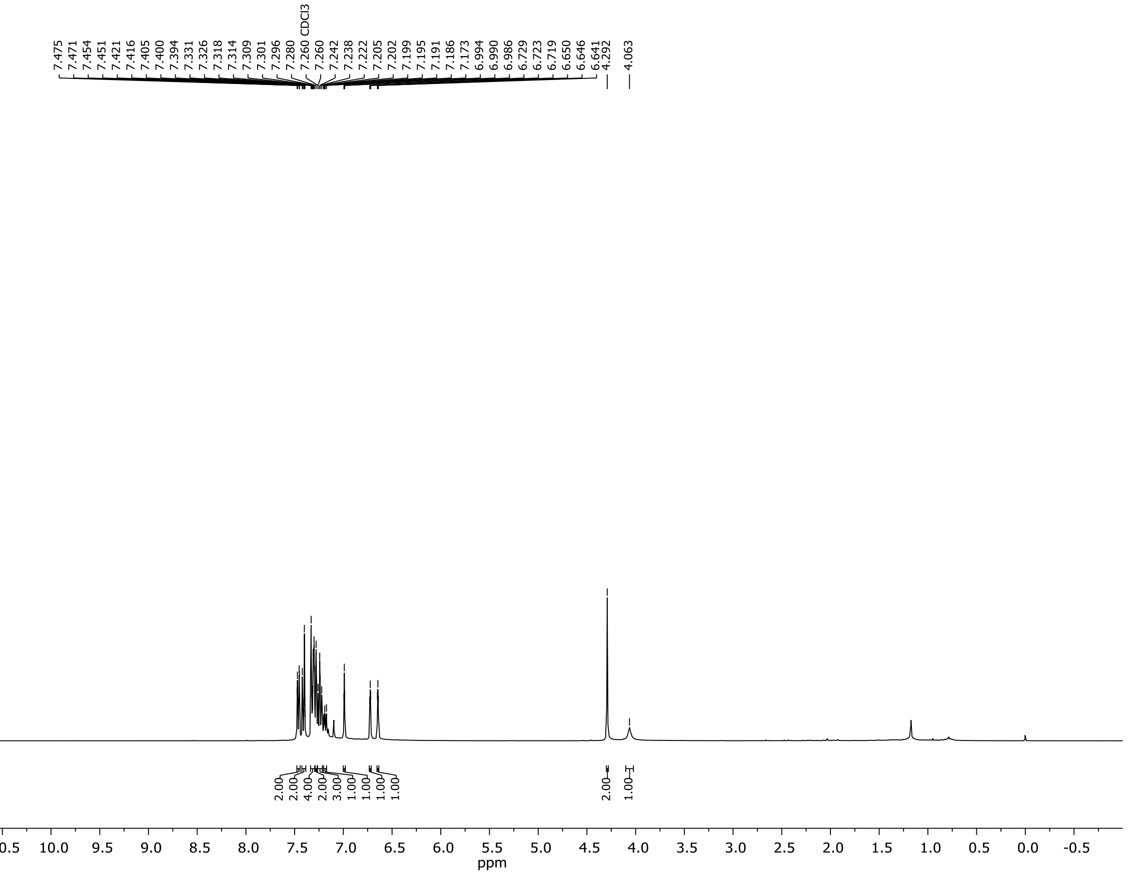
13C, CDCl3, 100 MHz



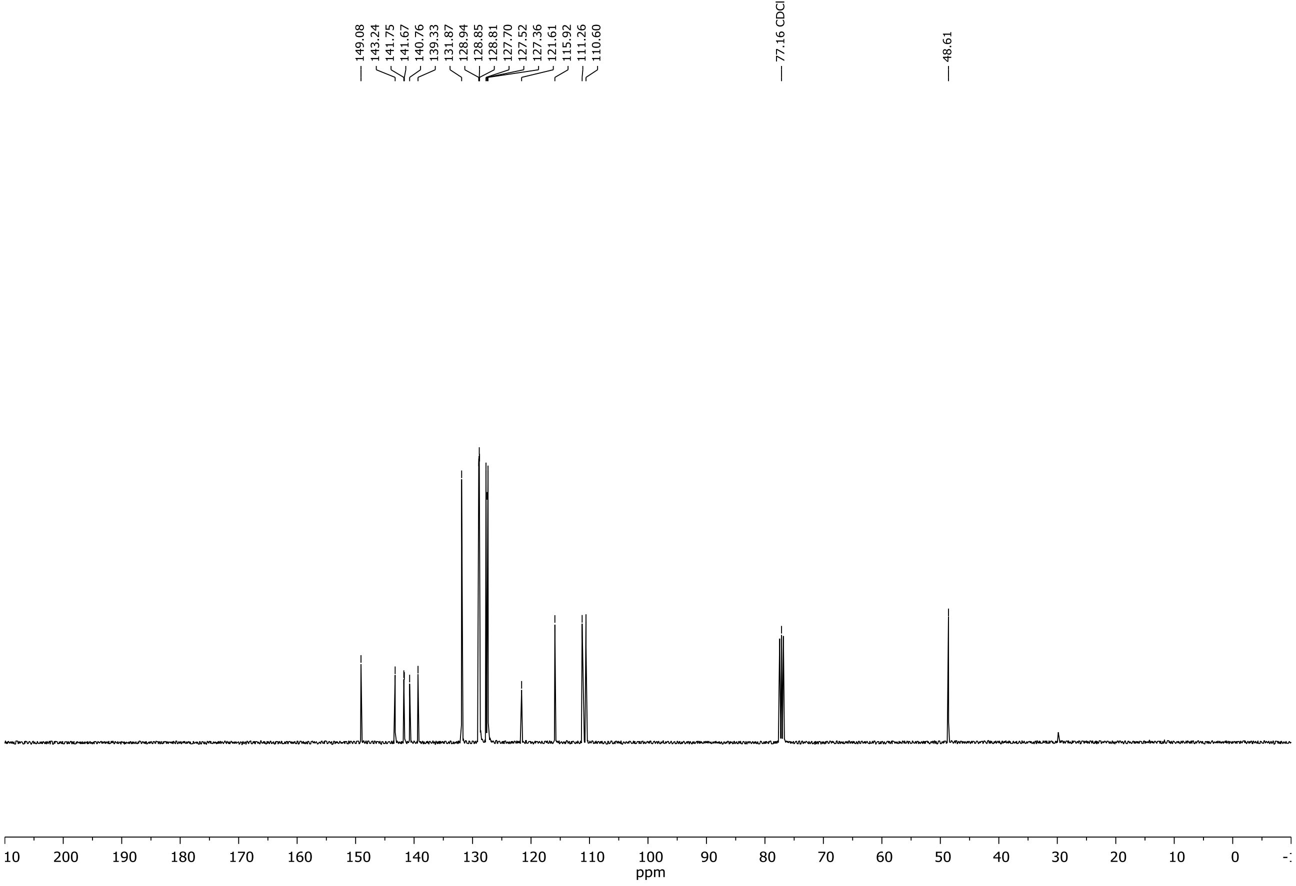
1H, CDCl3, 400 MHz



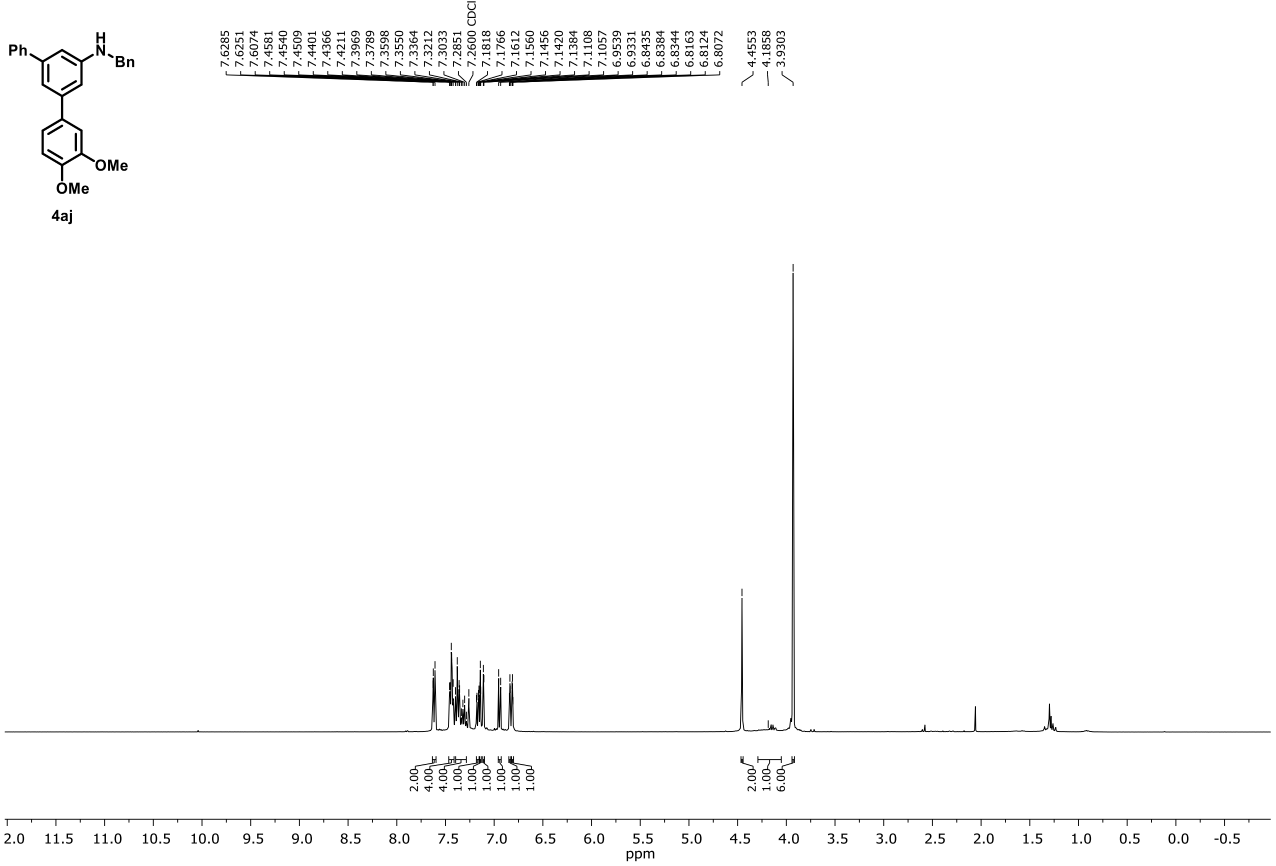
4ai



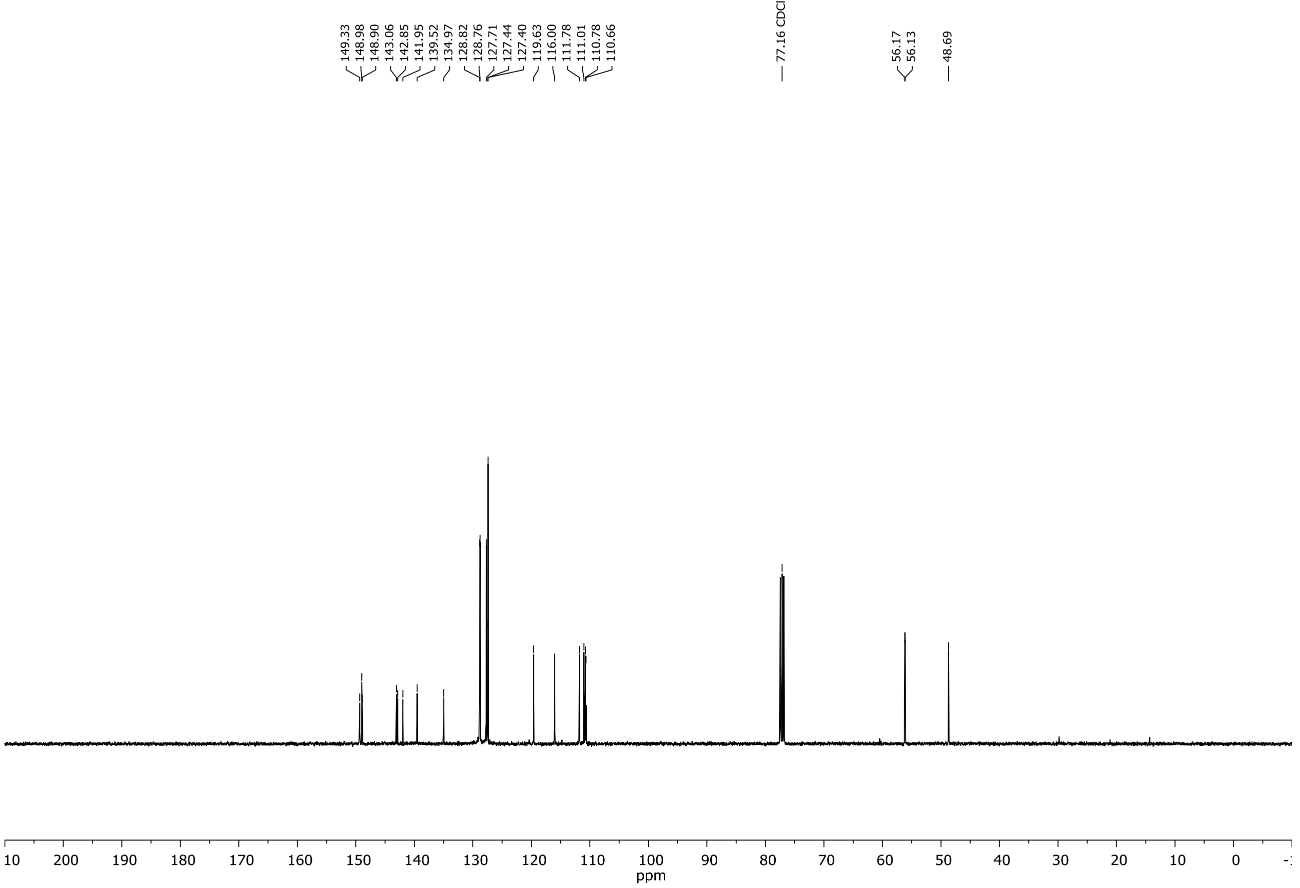
13C, CDCl3, 100 MHz



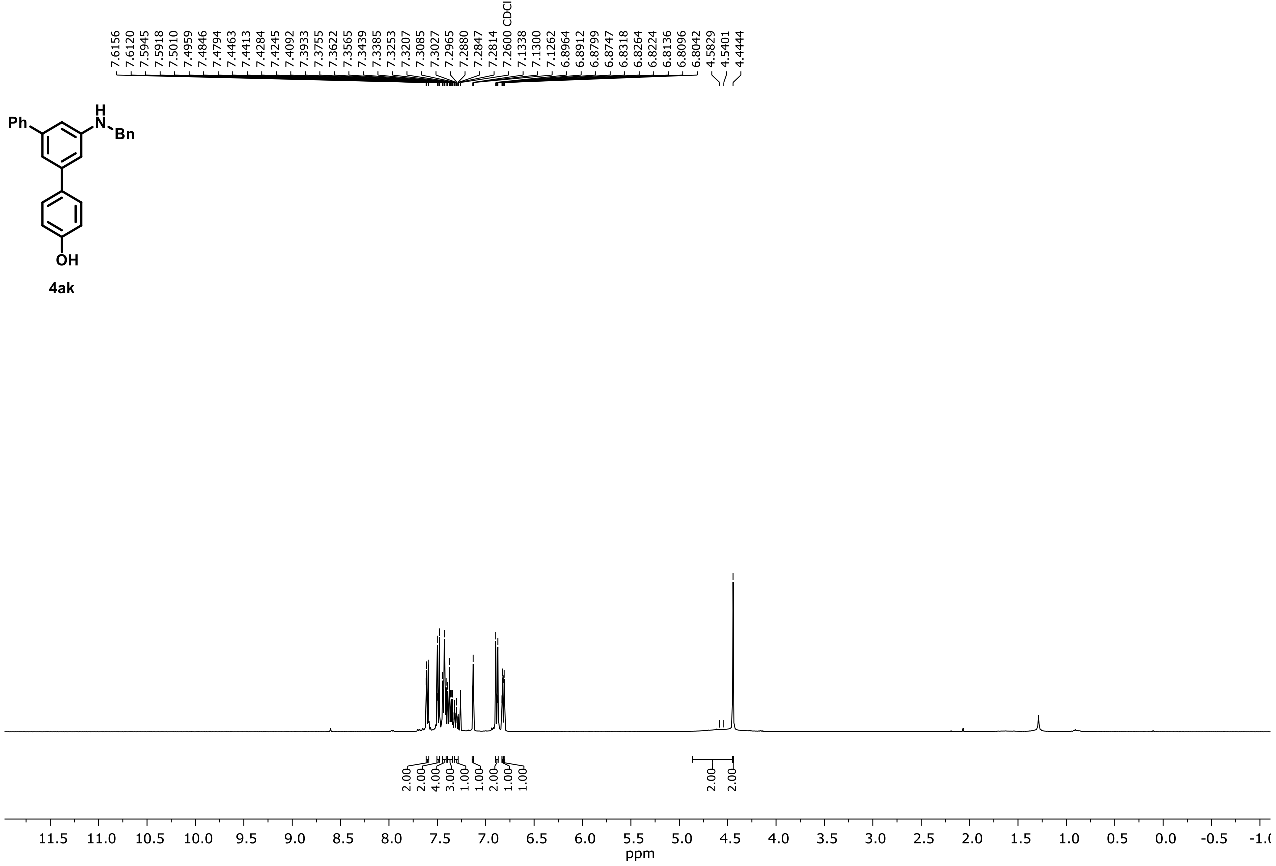
1H, CDCl3, 400 MHz



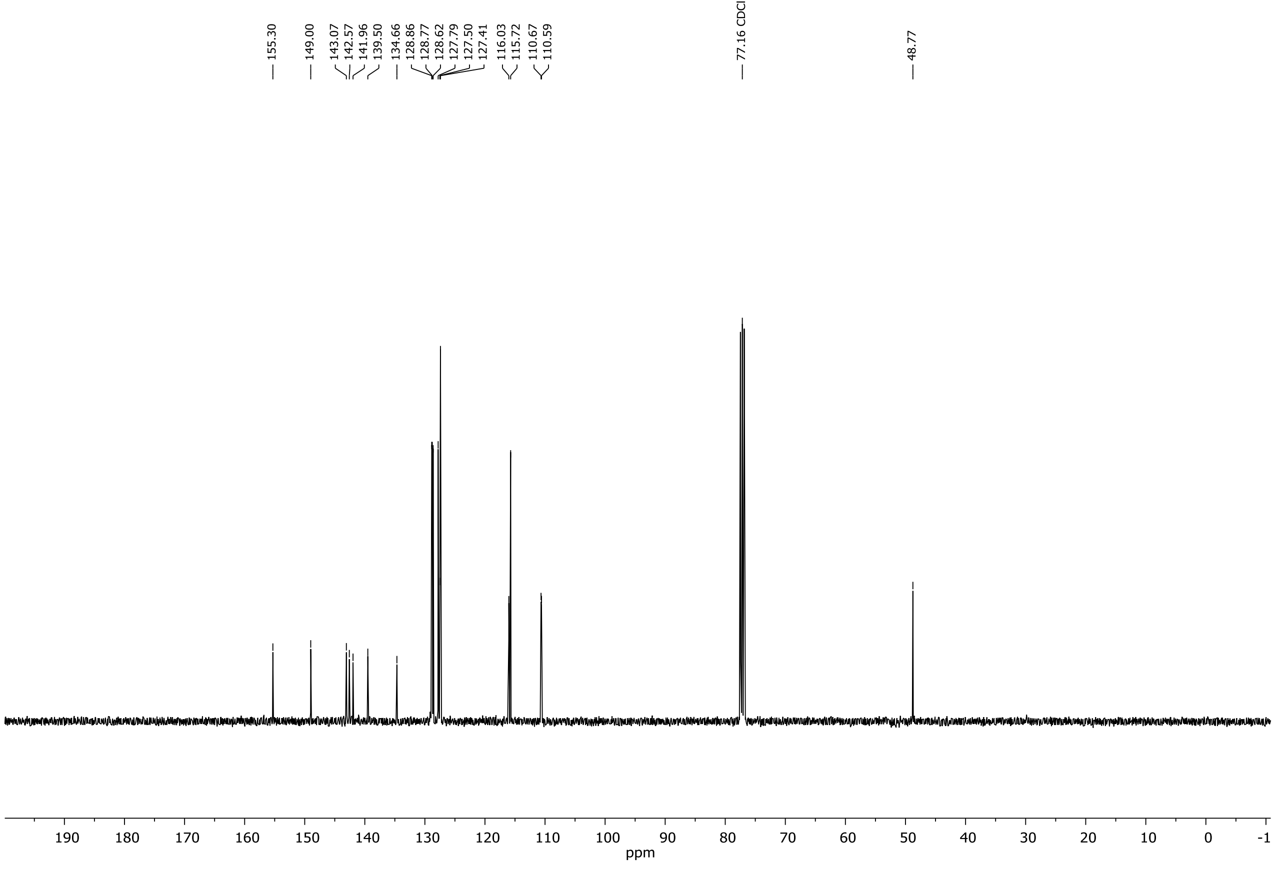
13C, CDCl3, 100 MHz



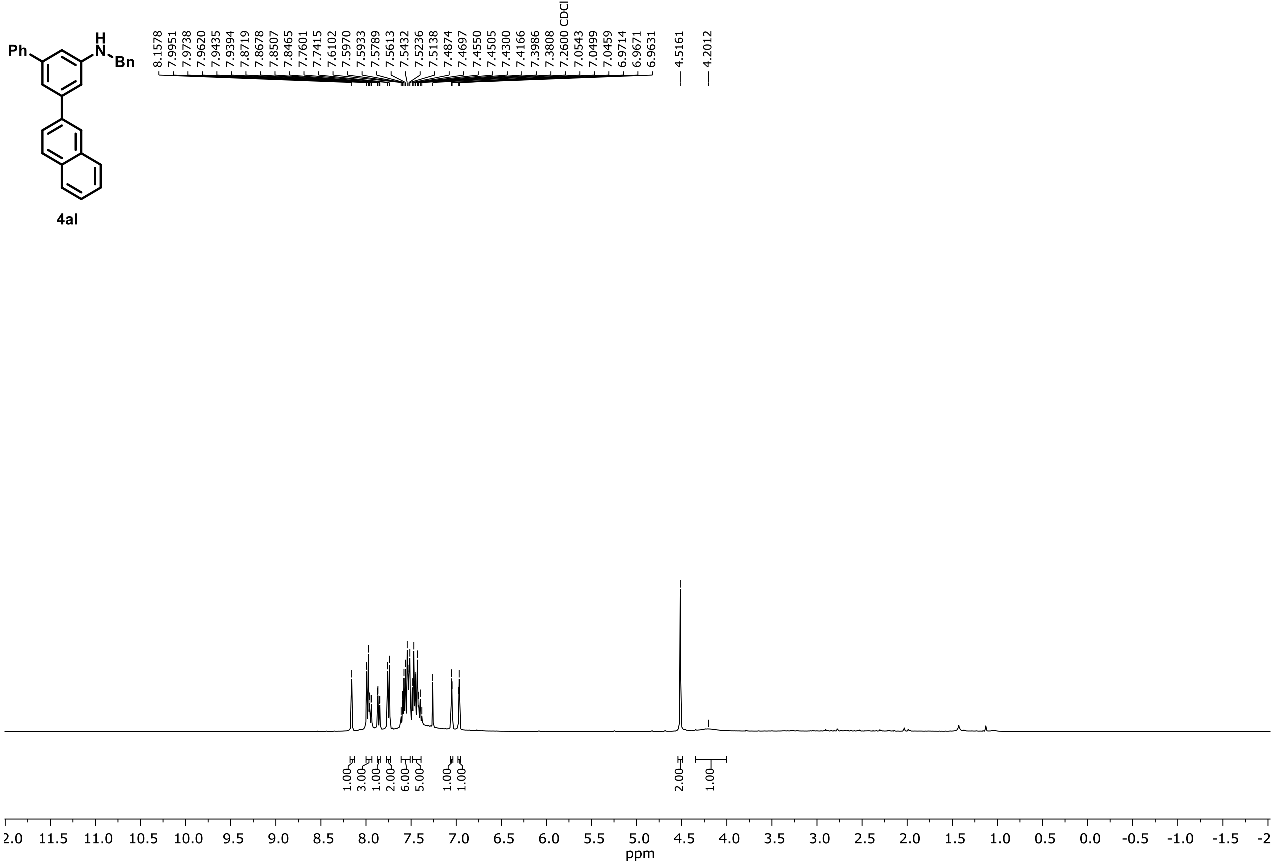
1H, CDCl3, 400 MHz



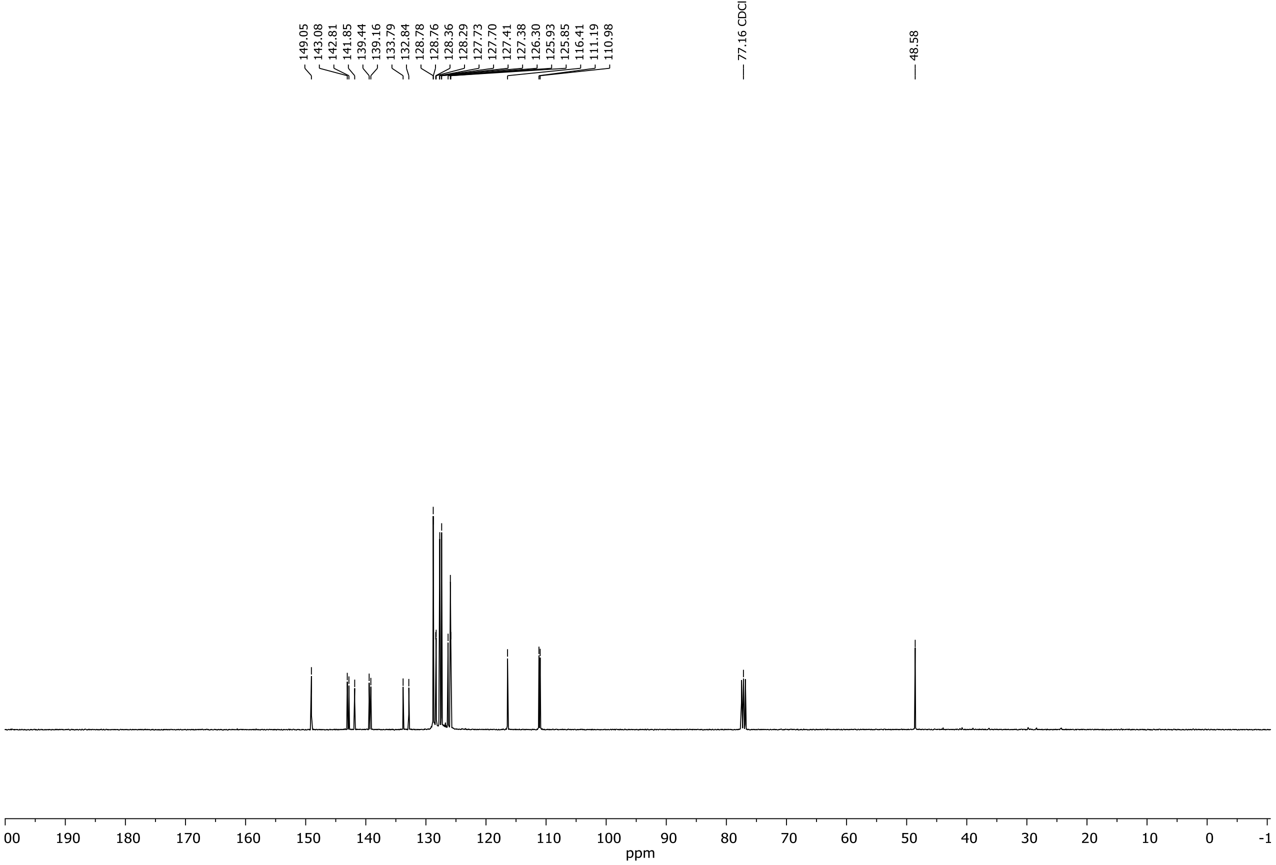
13C, CDCl3, 100 MHz



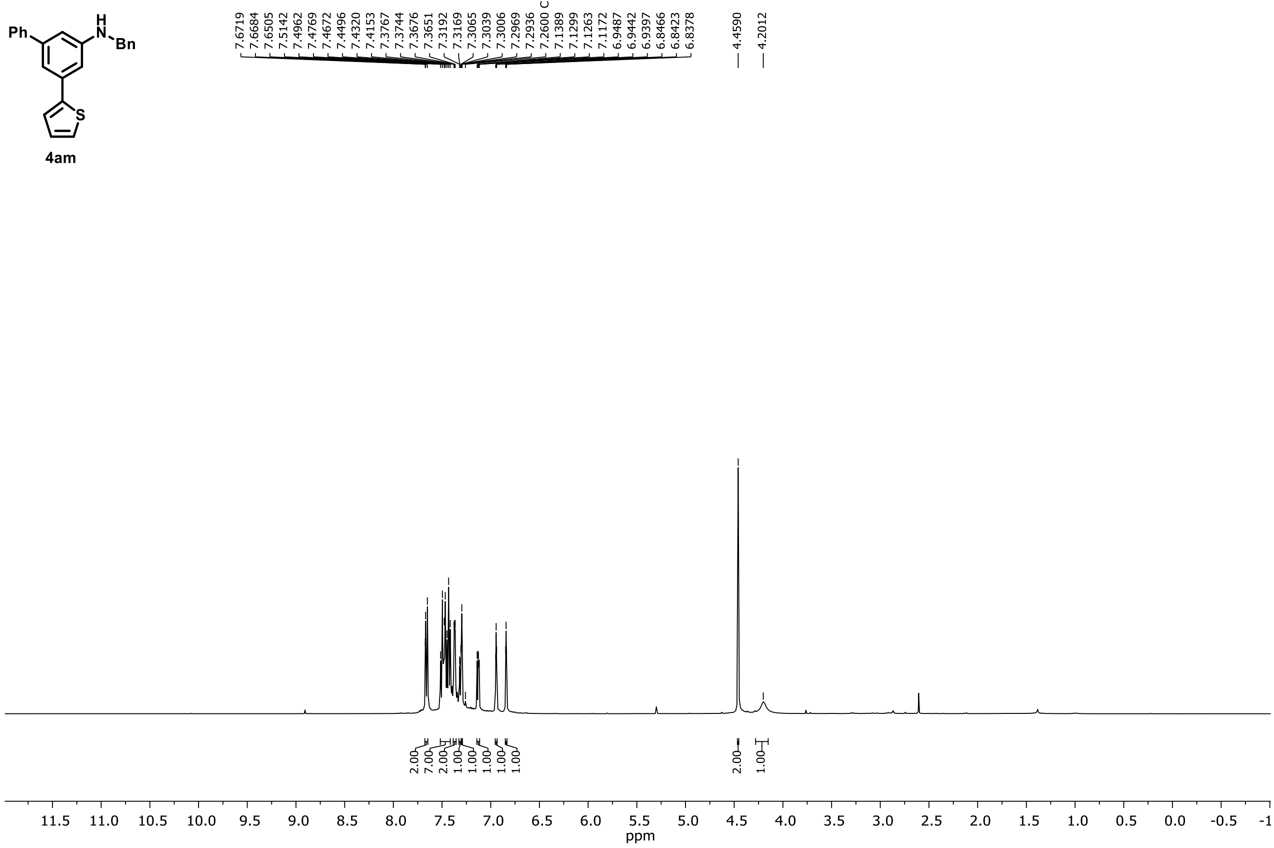
1H, CDCl3, 400 MHz



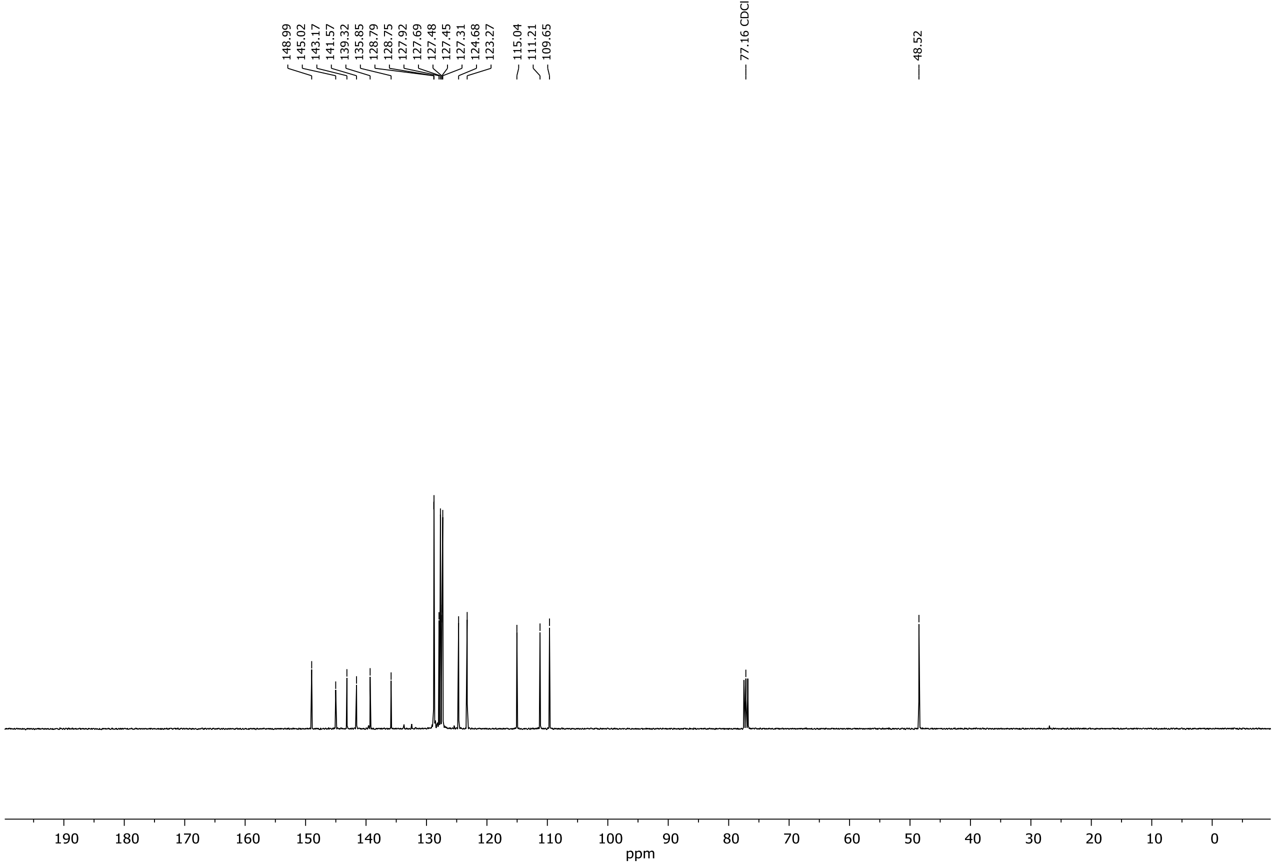
13C, CDCl3, 100 MHz



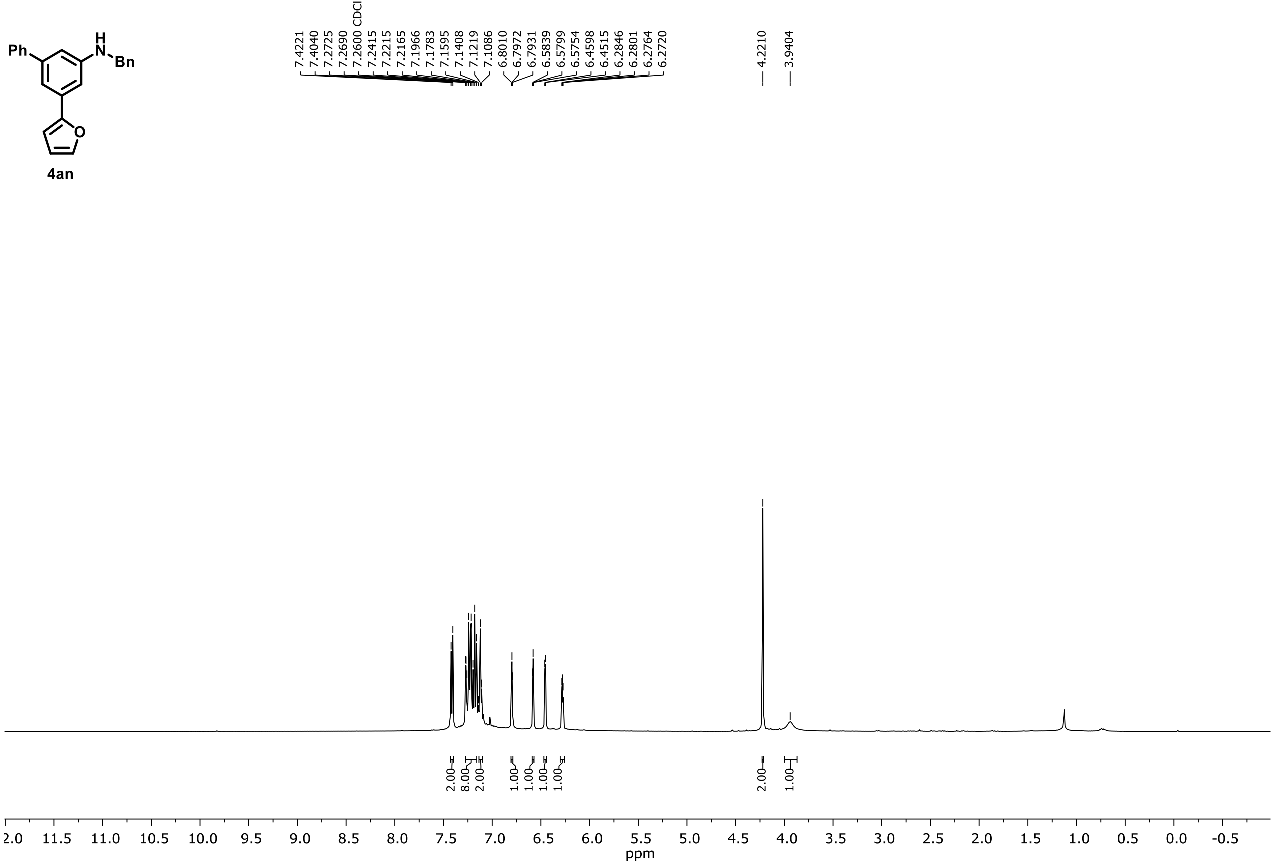
1H, CDCl3, 400 MHz



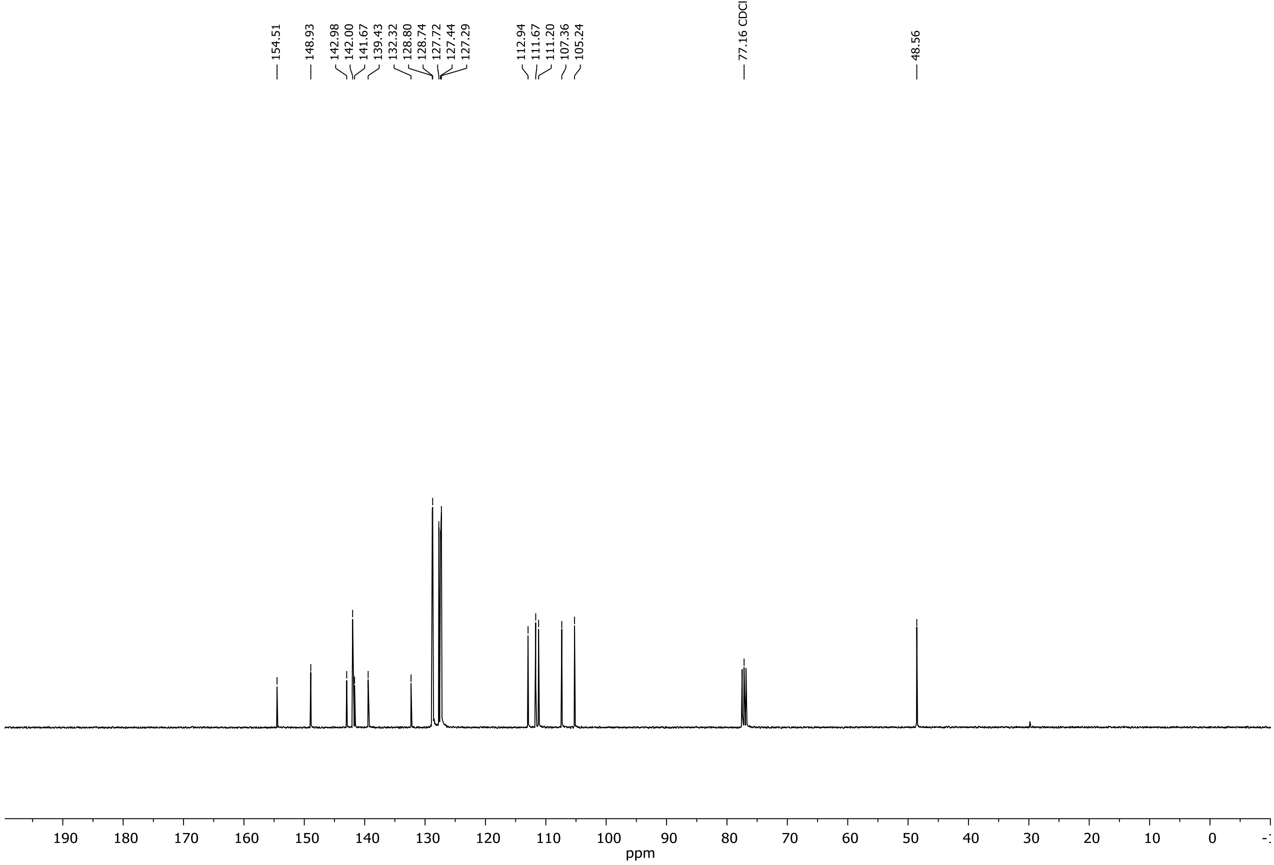
13C, CDCl3, 100 MHz



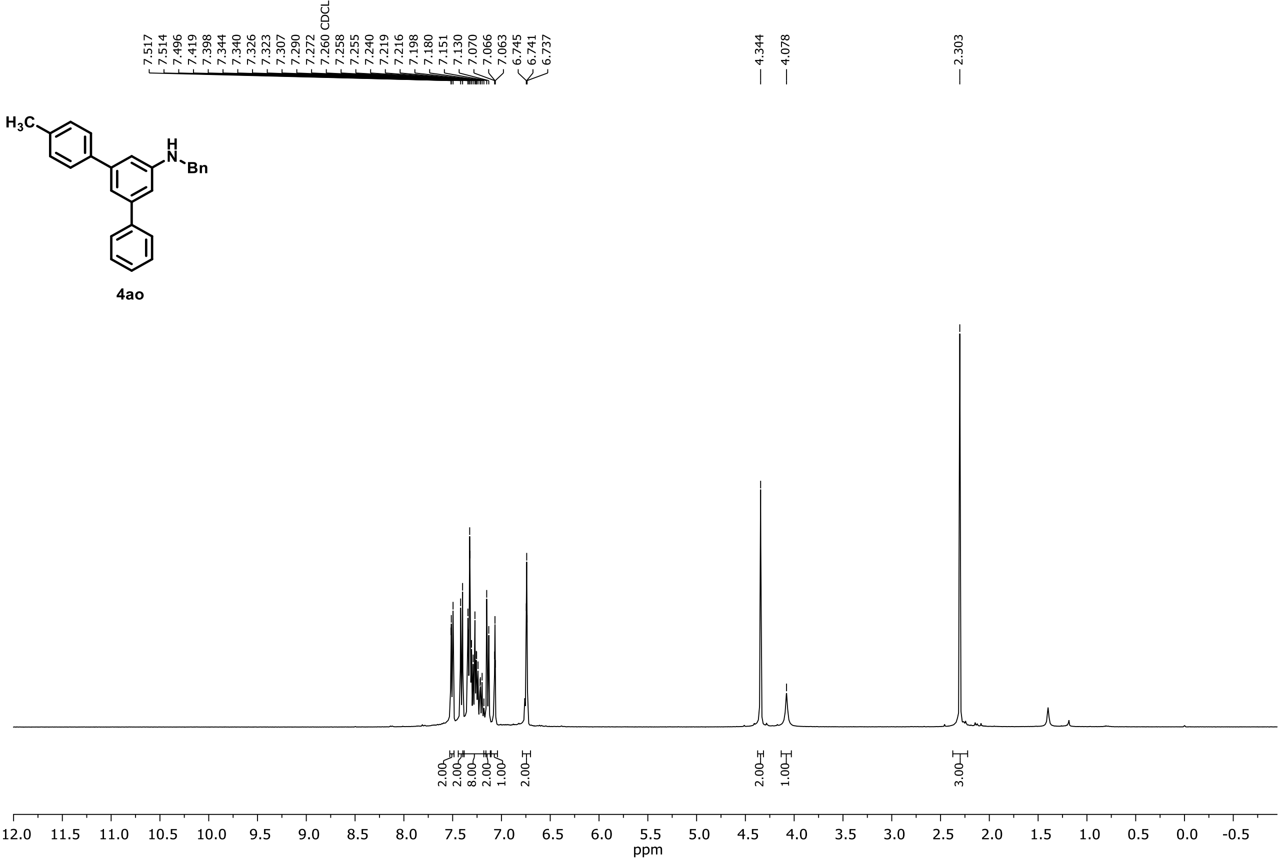
1H, CDCl3, 400 MHz



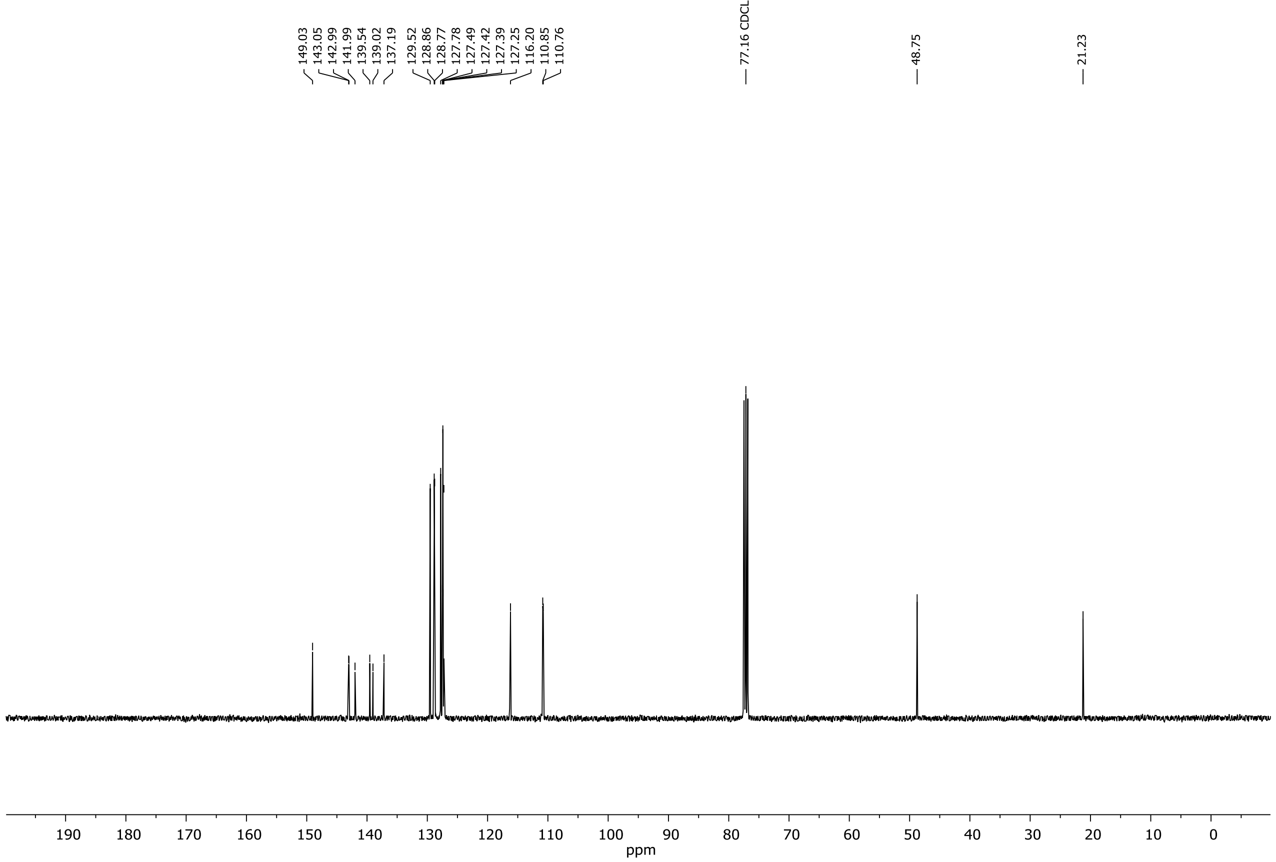
13C, CDCl3, 100 MHz



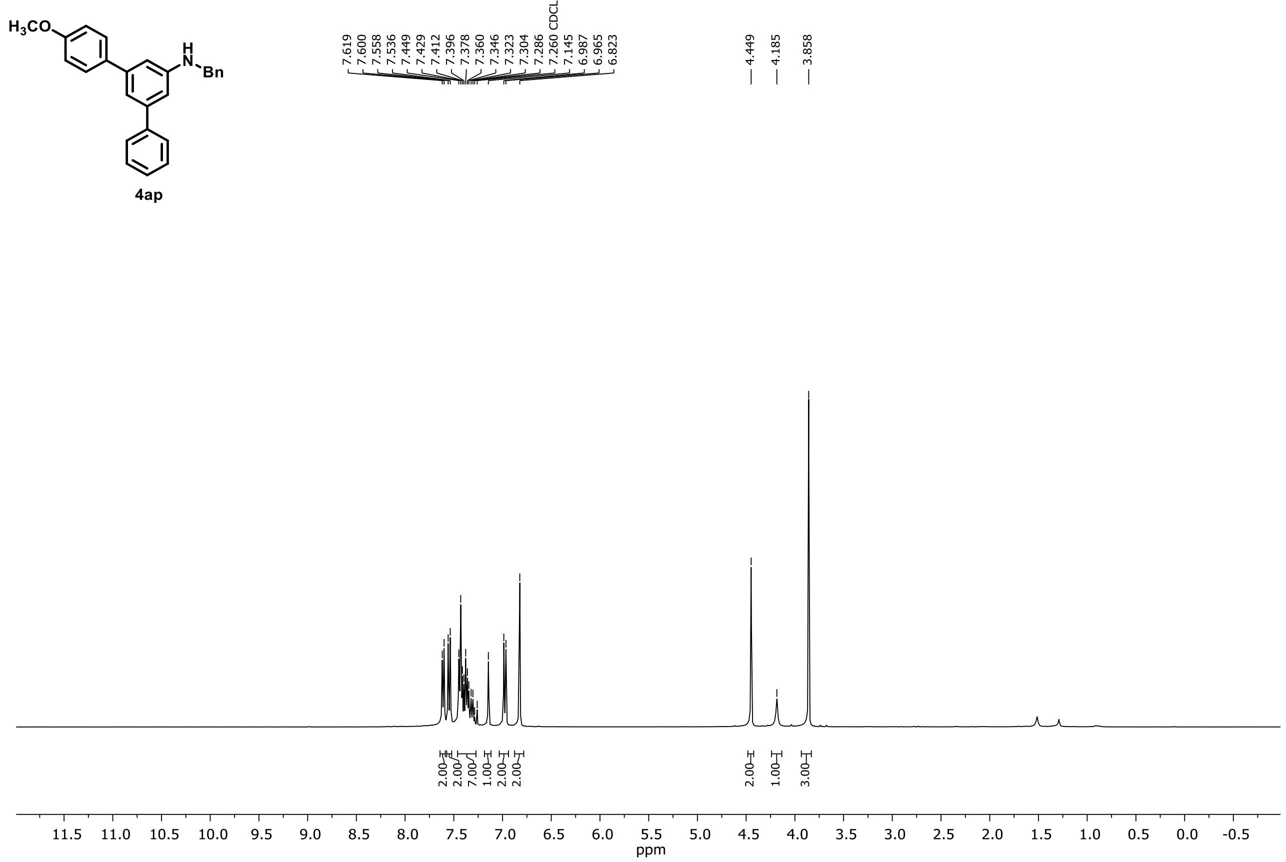
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

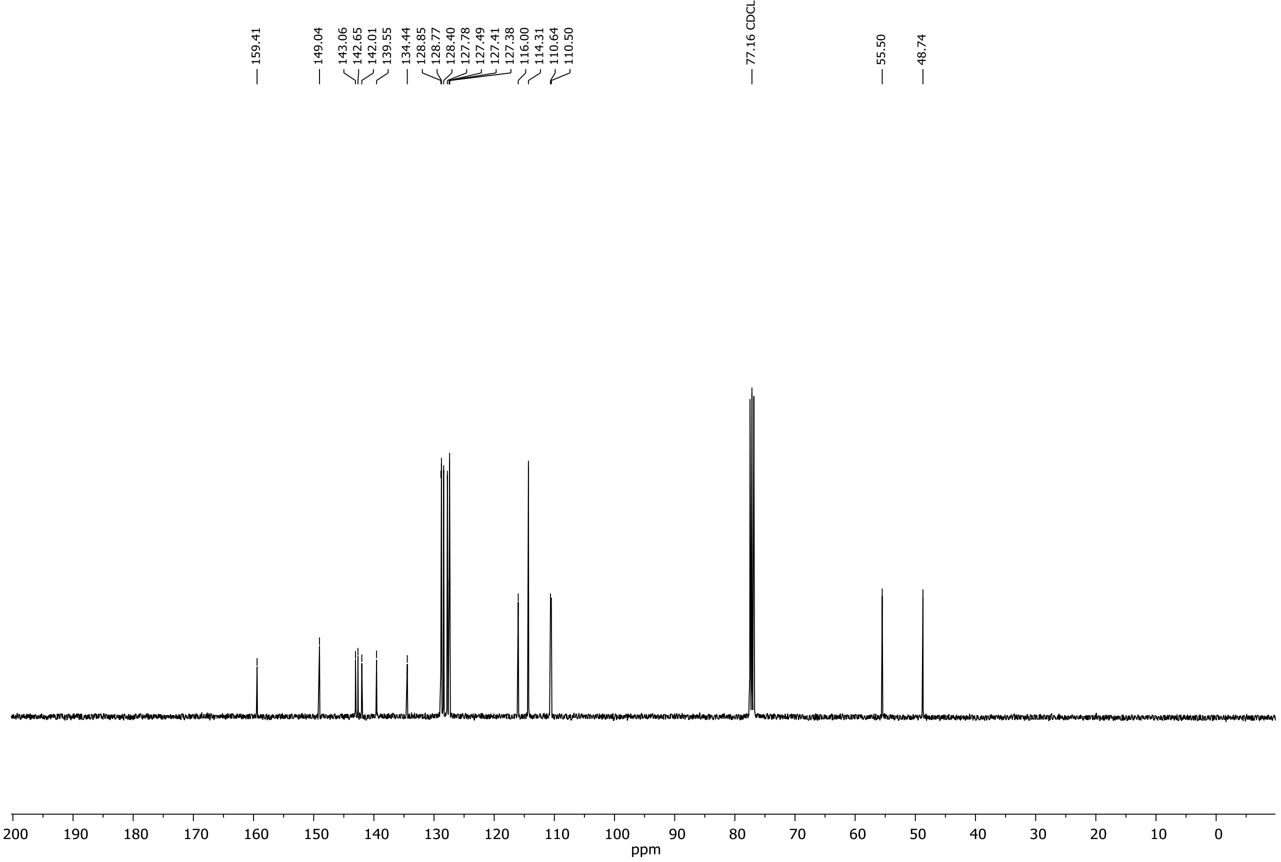


1H, CDCl3, 400 MHz

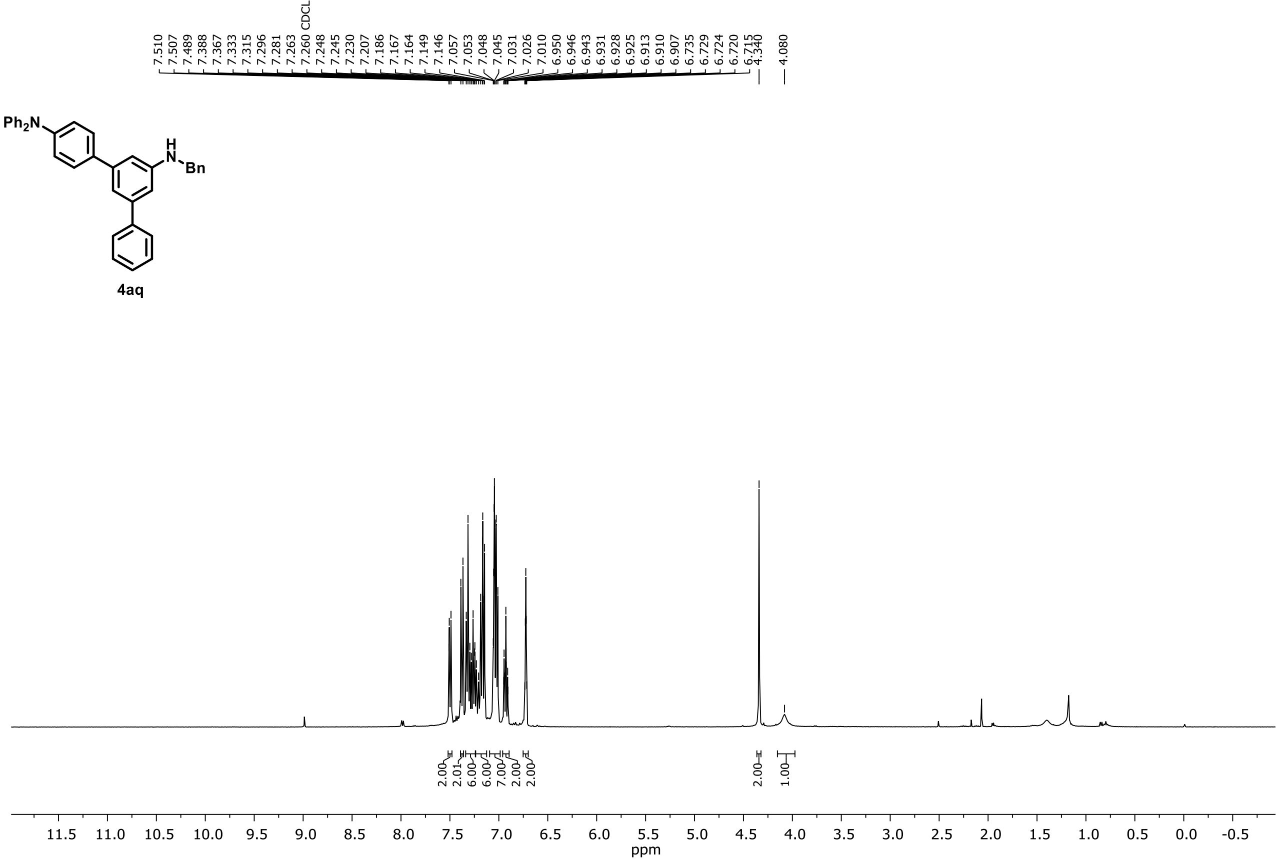


4ap

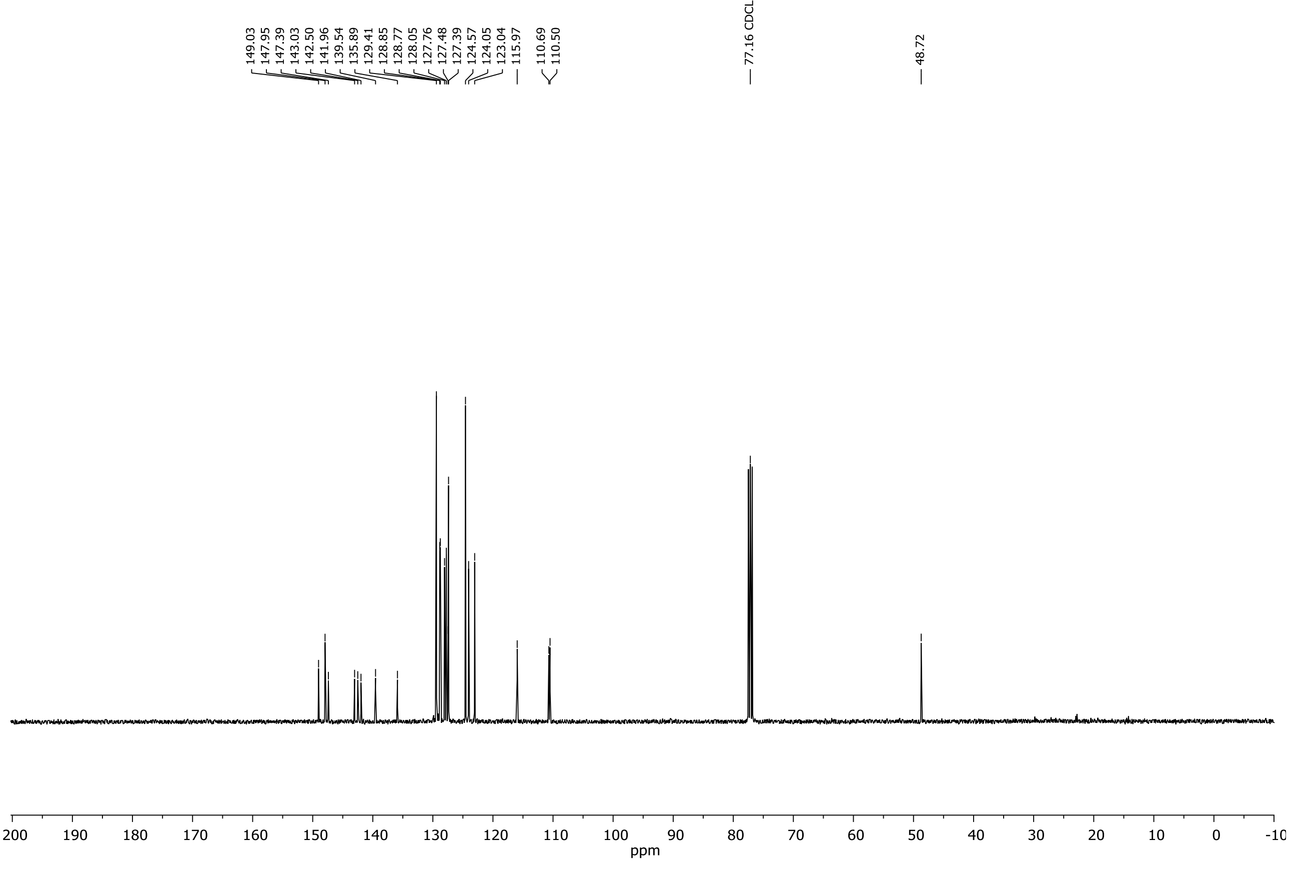
13C, CDCl3, 100 MHz



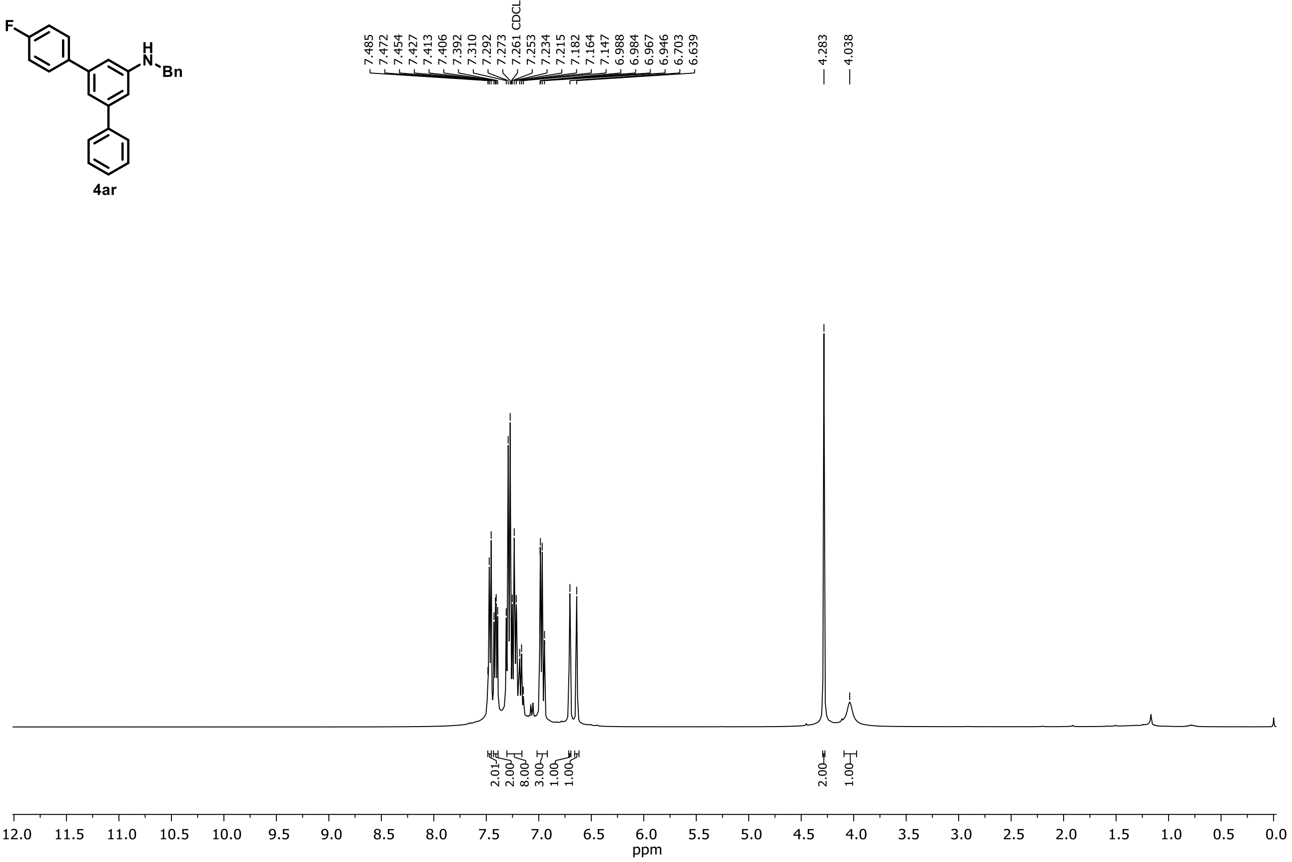
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

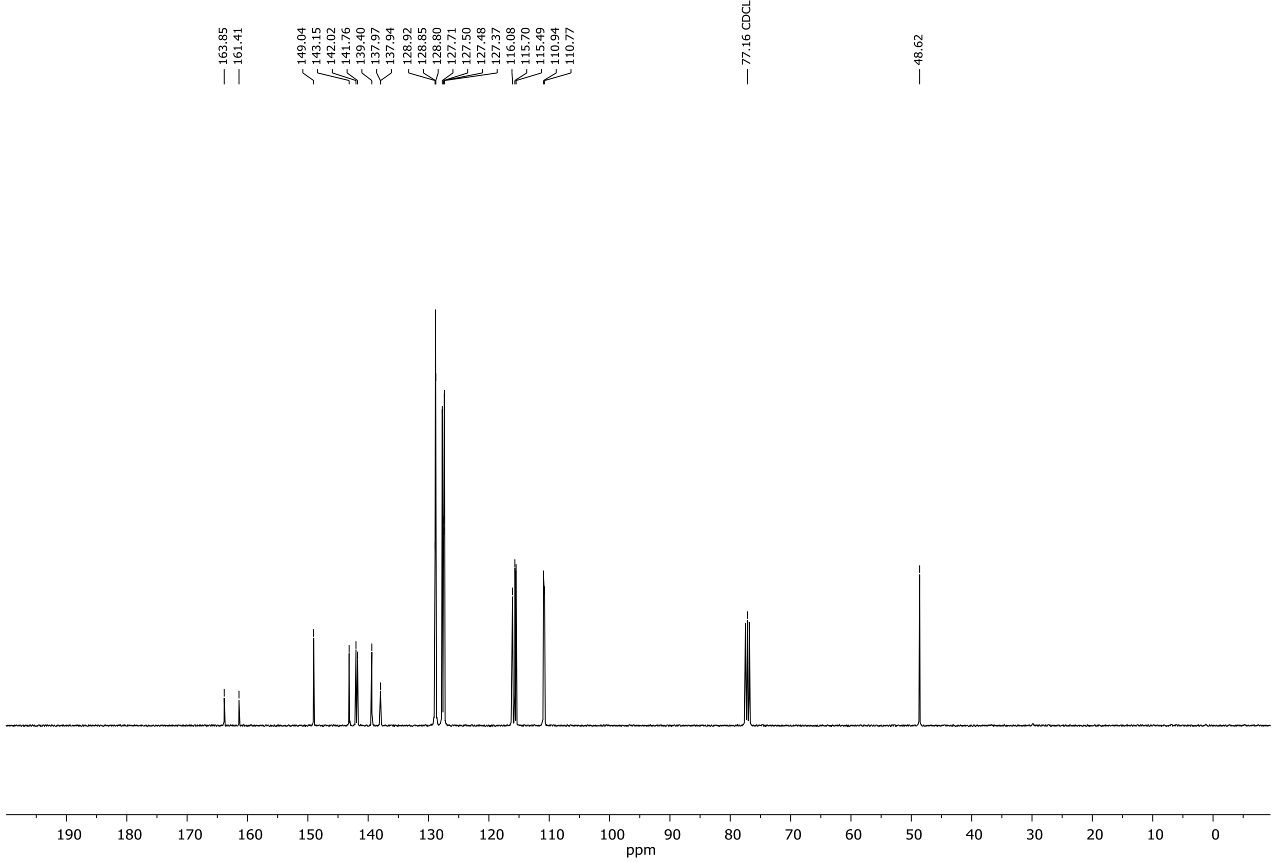


1H, CDCl3, 400 MHz

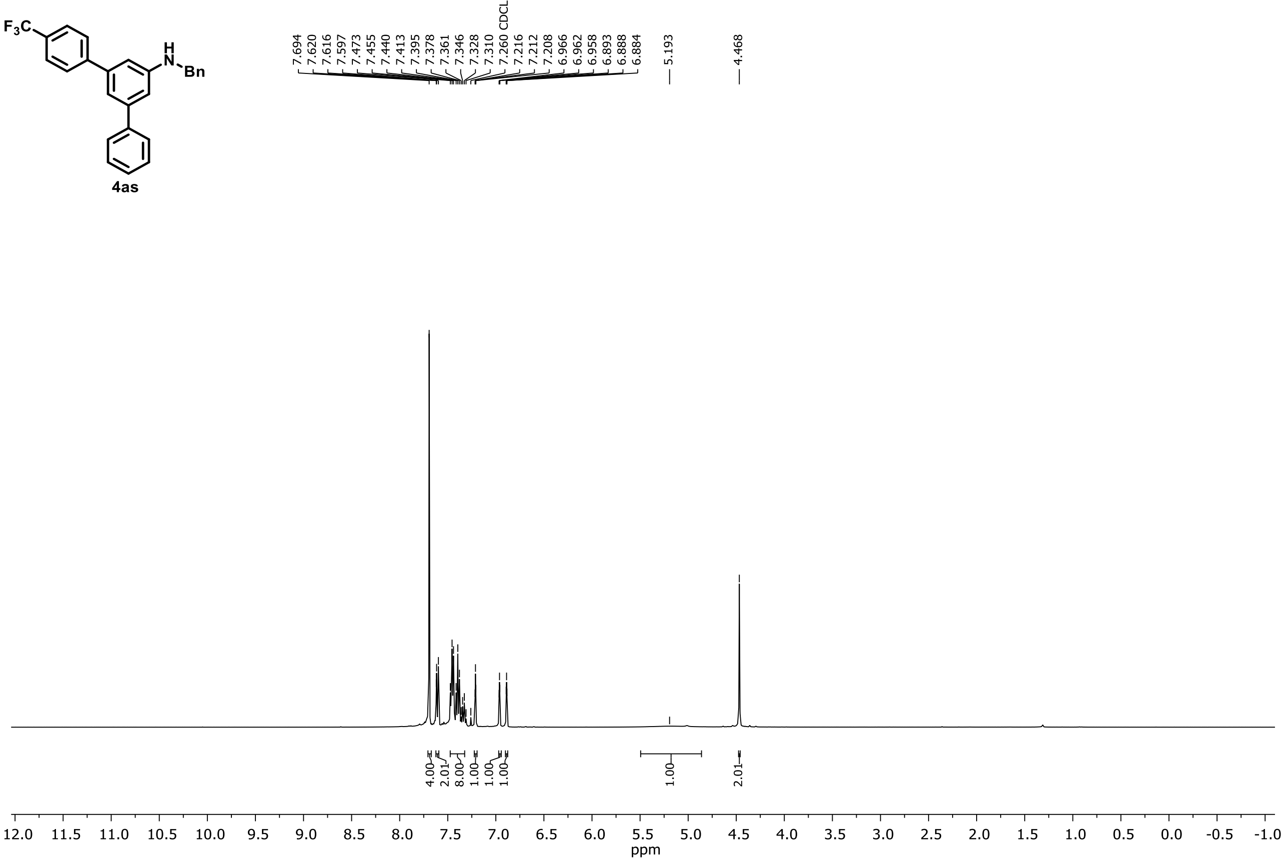


4ar

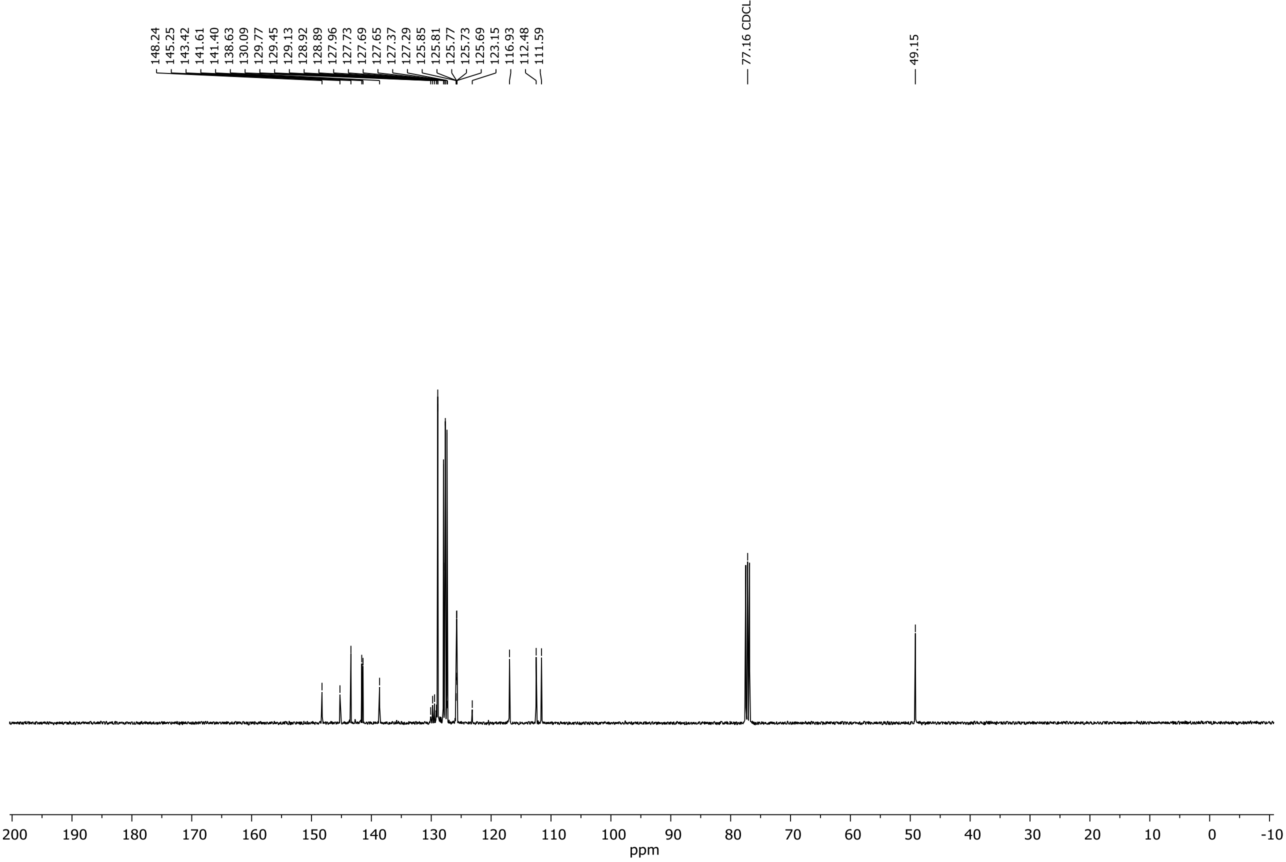
13C, CDCl3, 100 MHz



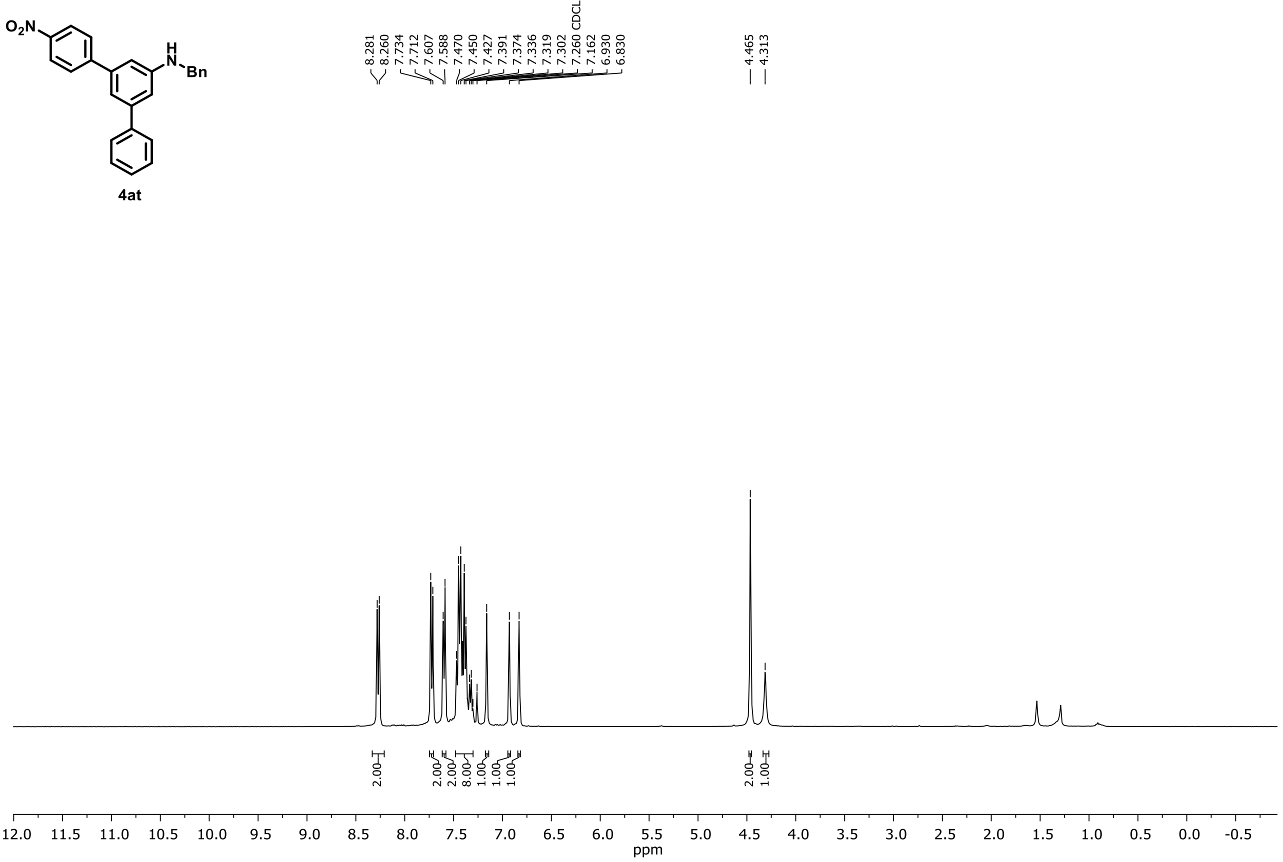
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

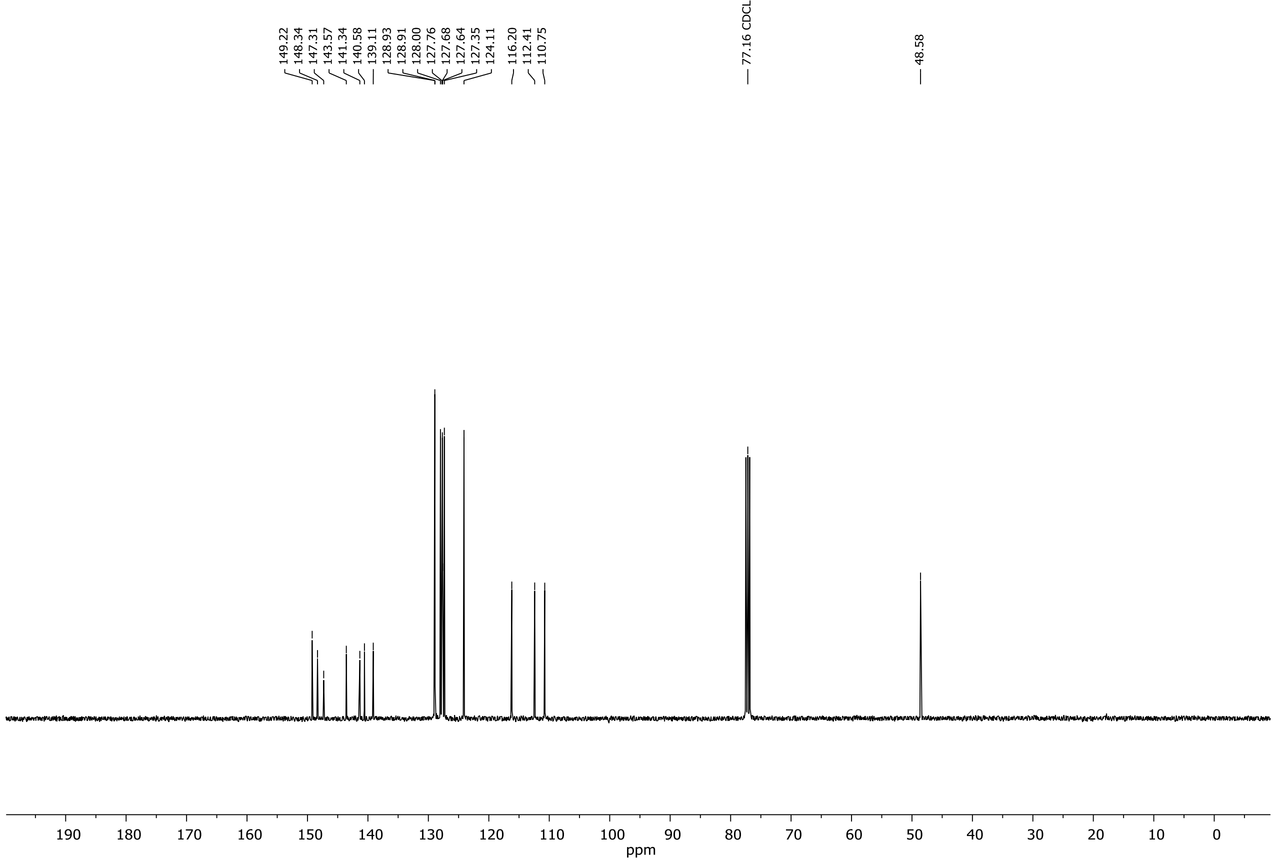


1H, CDCl3, 400 MHz

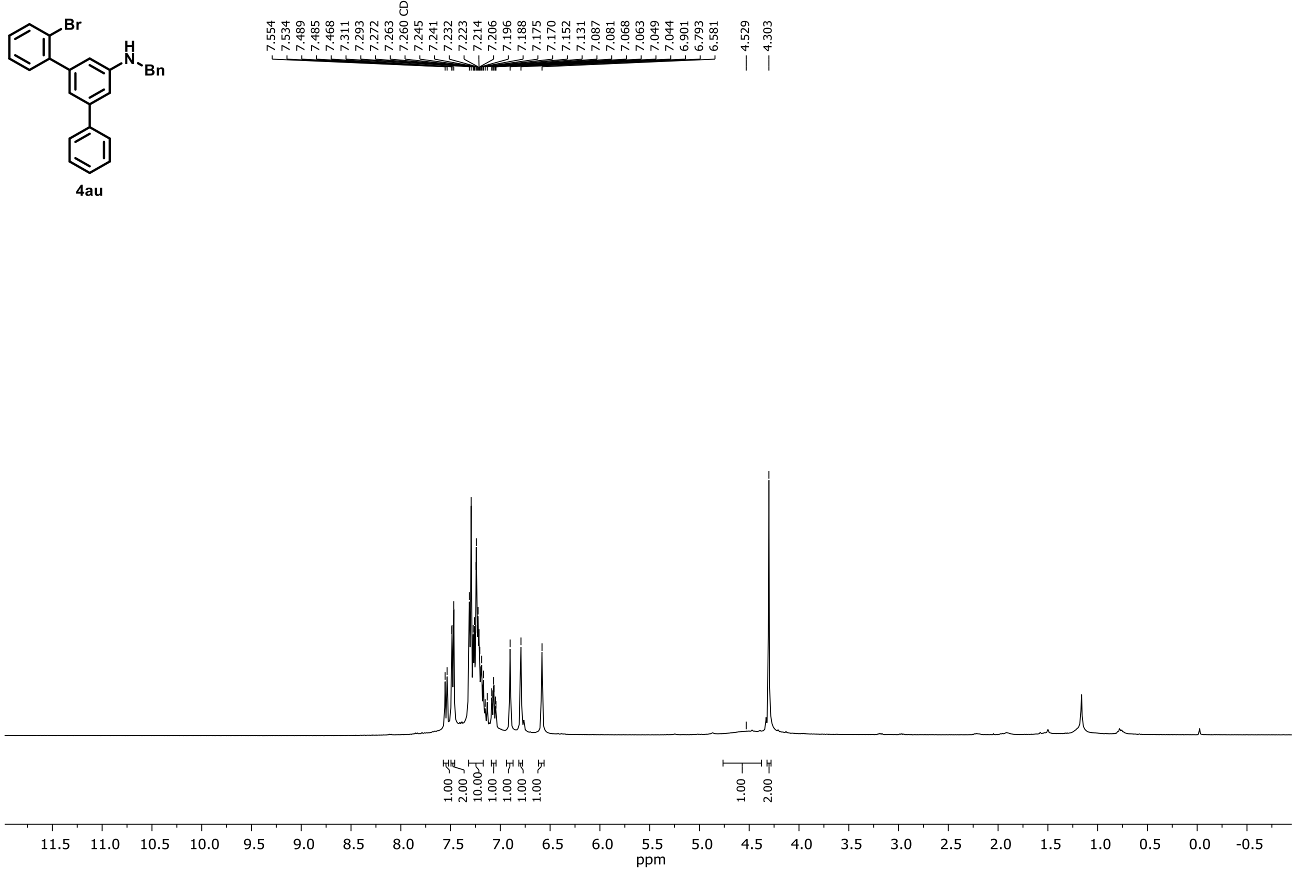


4at

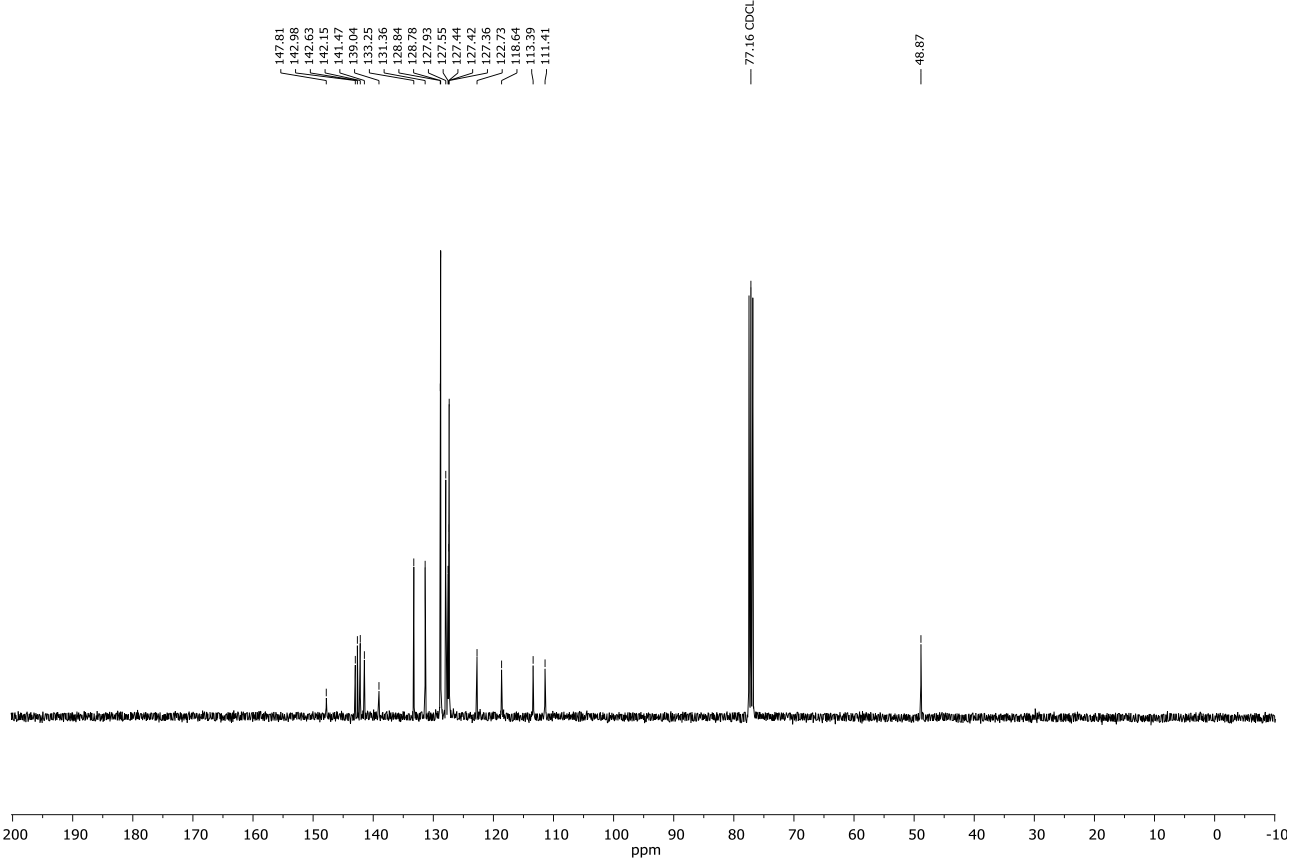
13C, CDCl3, 100 MHz



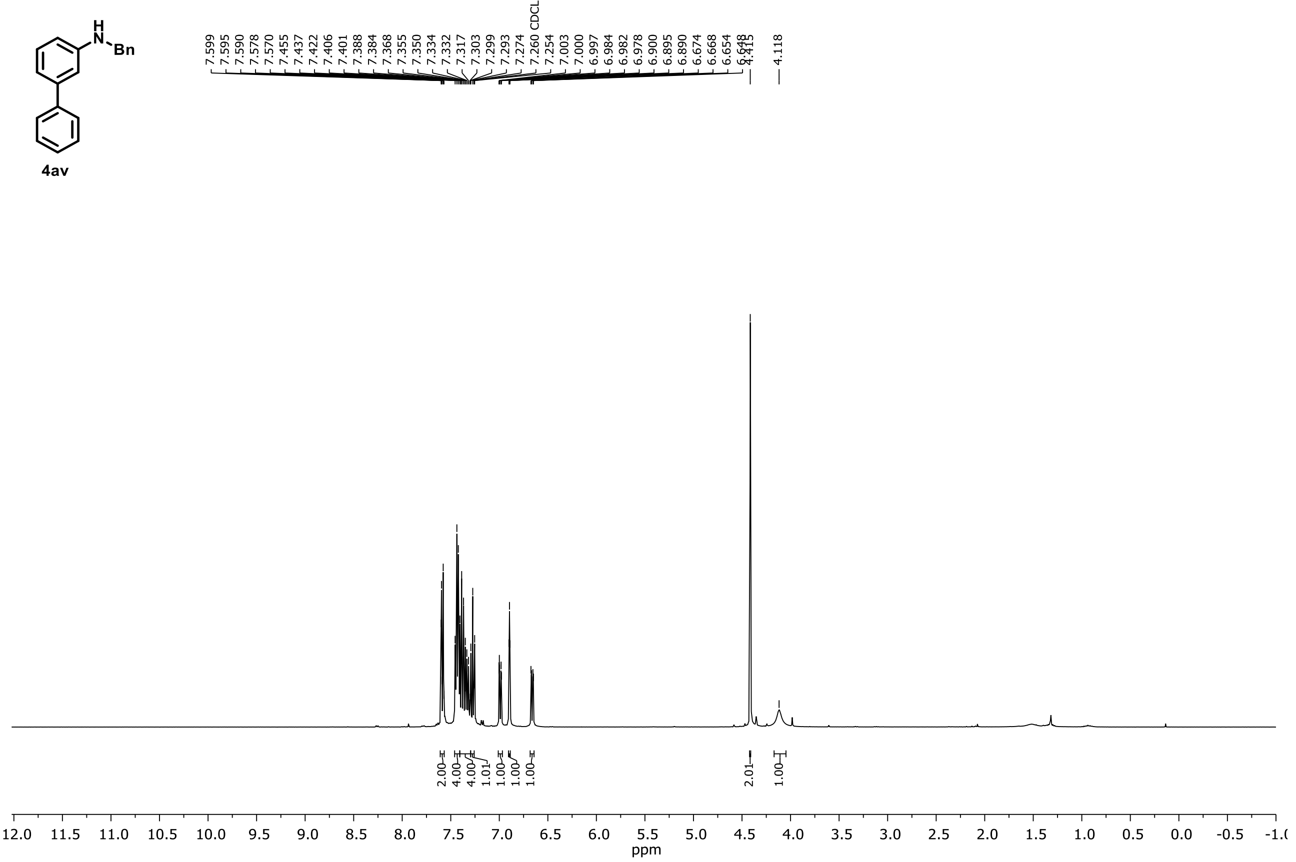
1H, CDCl3, 400 MHz



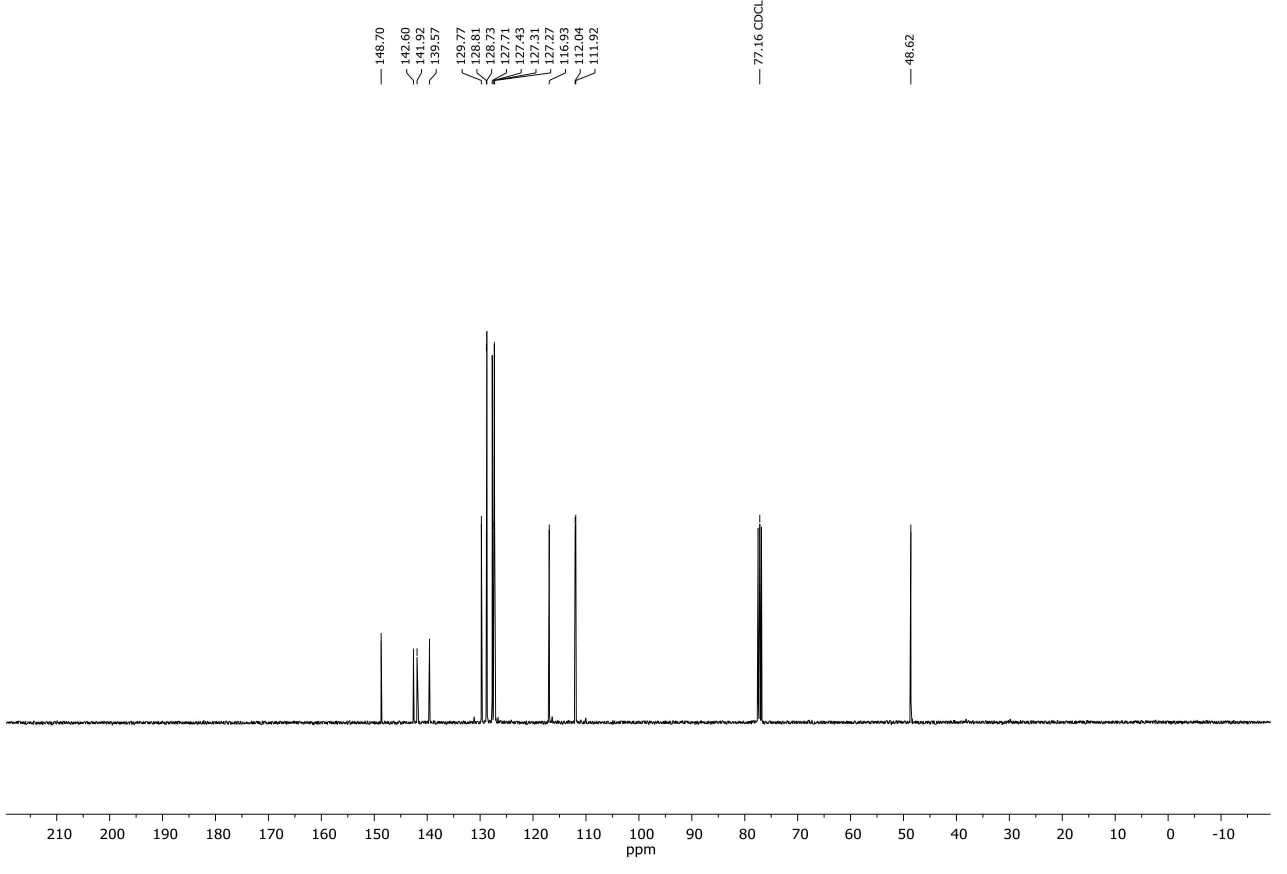
13C, CDCl3, 100 MHz



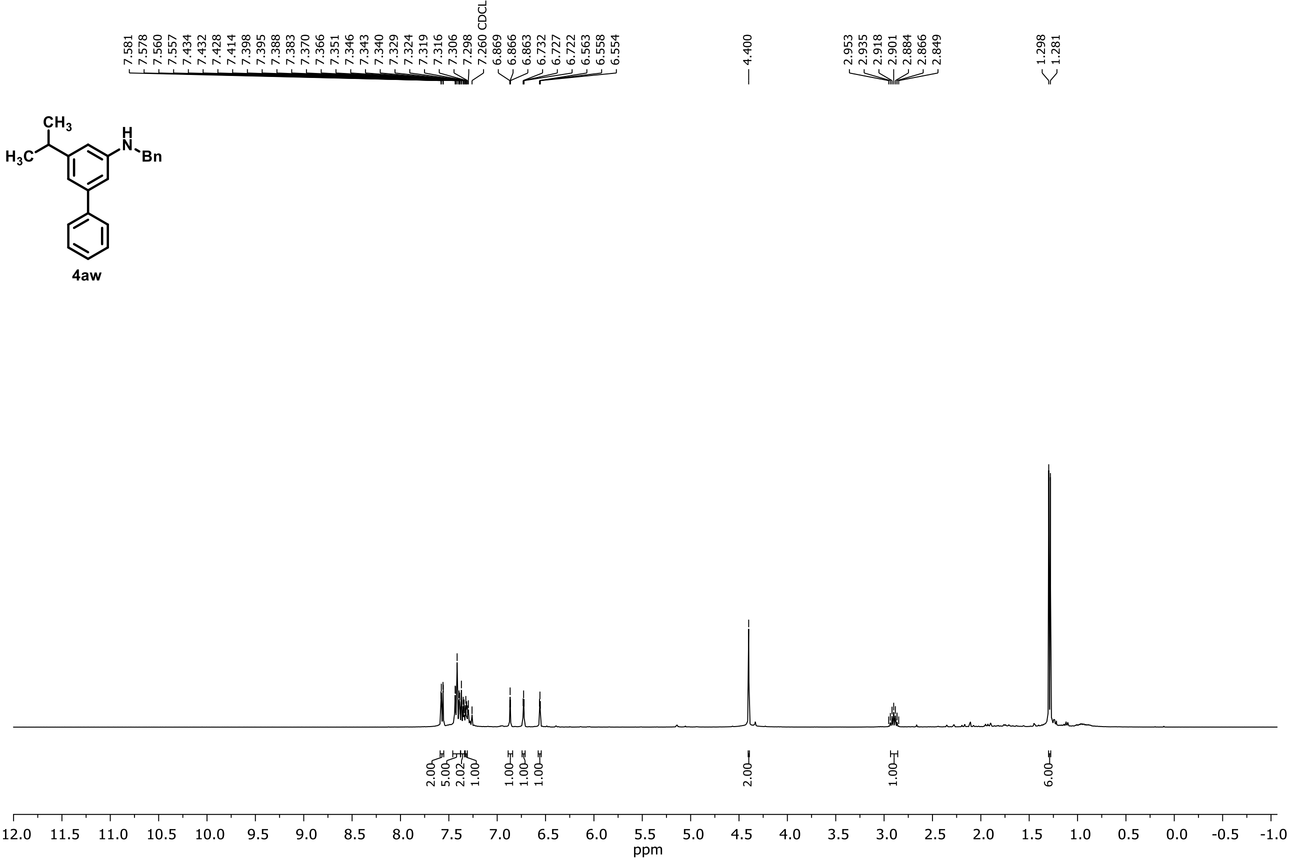
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

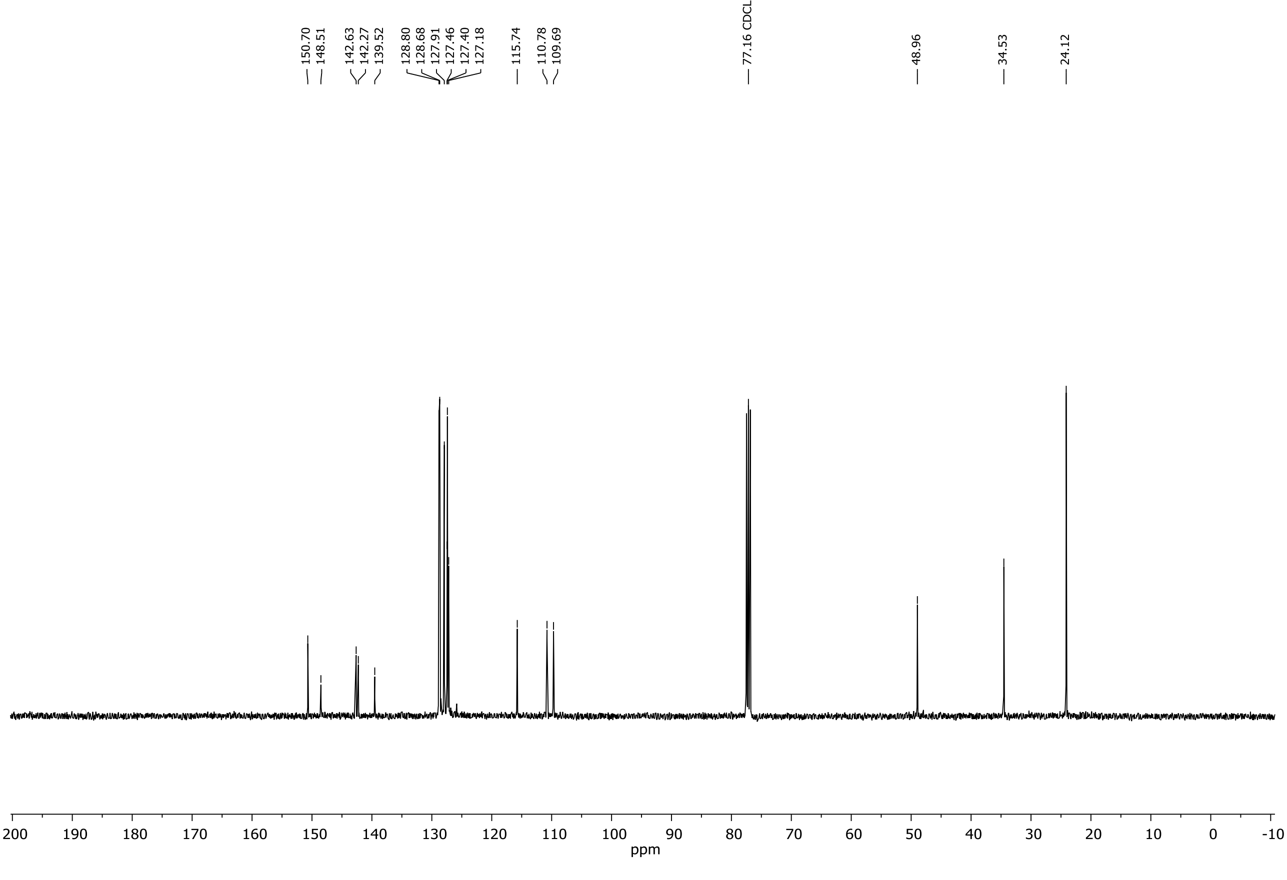


1H, CDCl3, 400 MHz

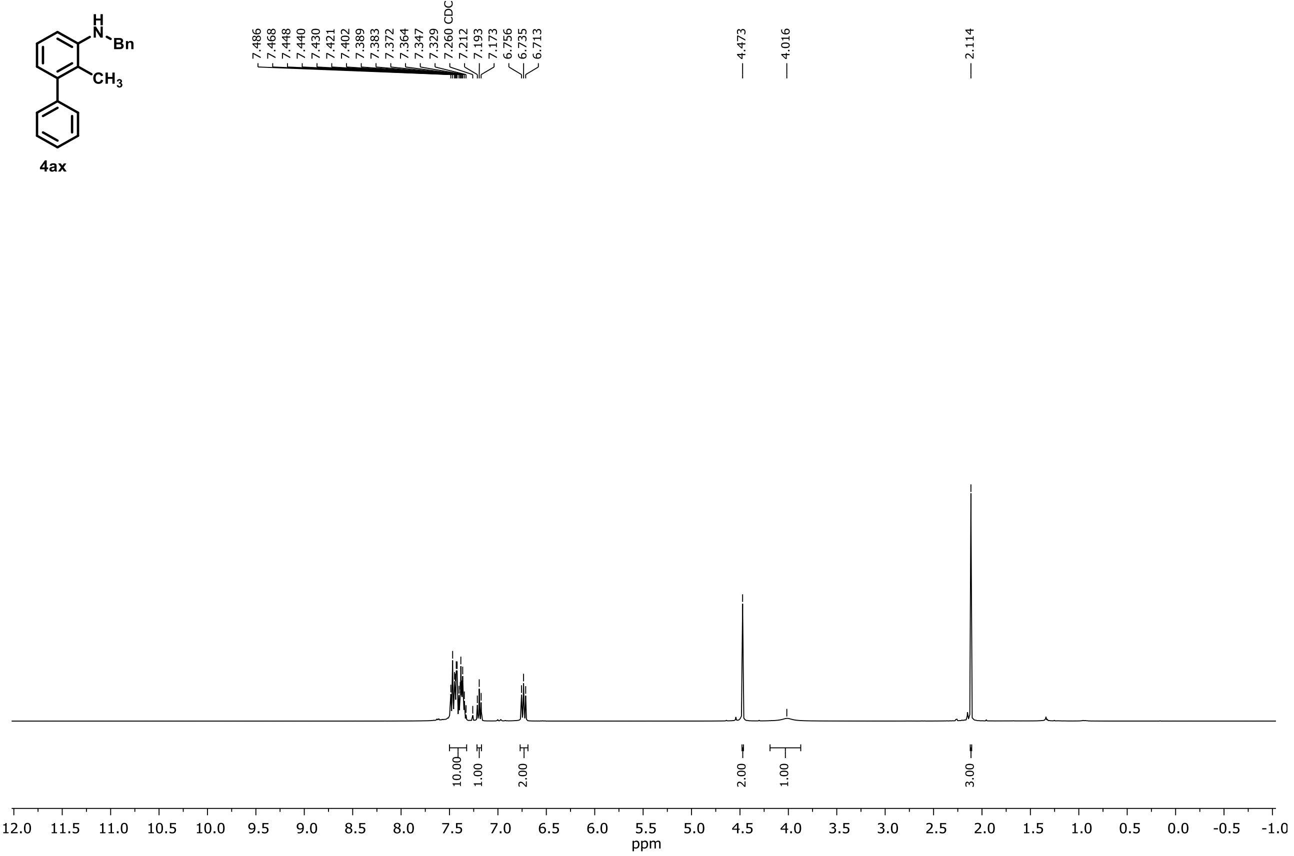


4aw

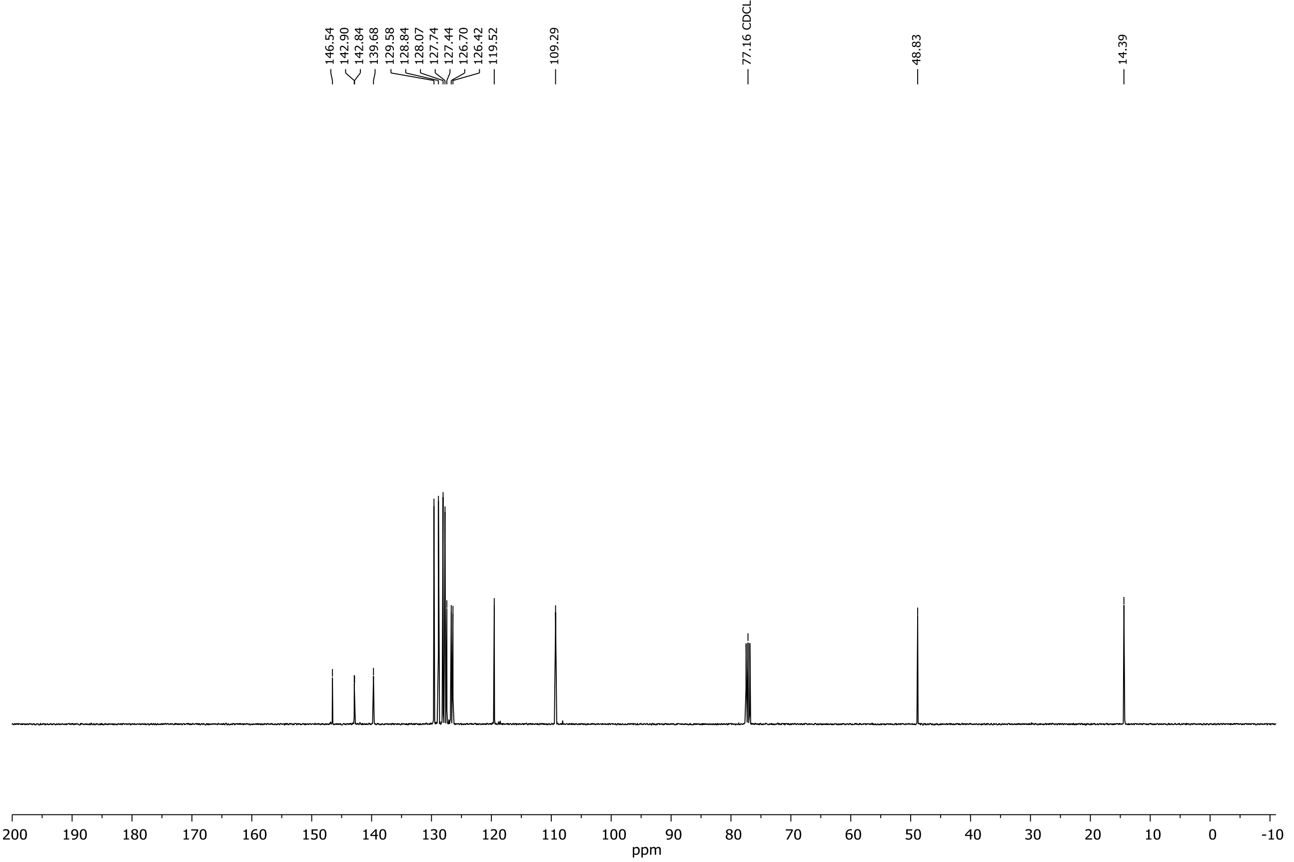
13C, CDCl3, 100 MHz



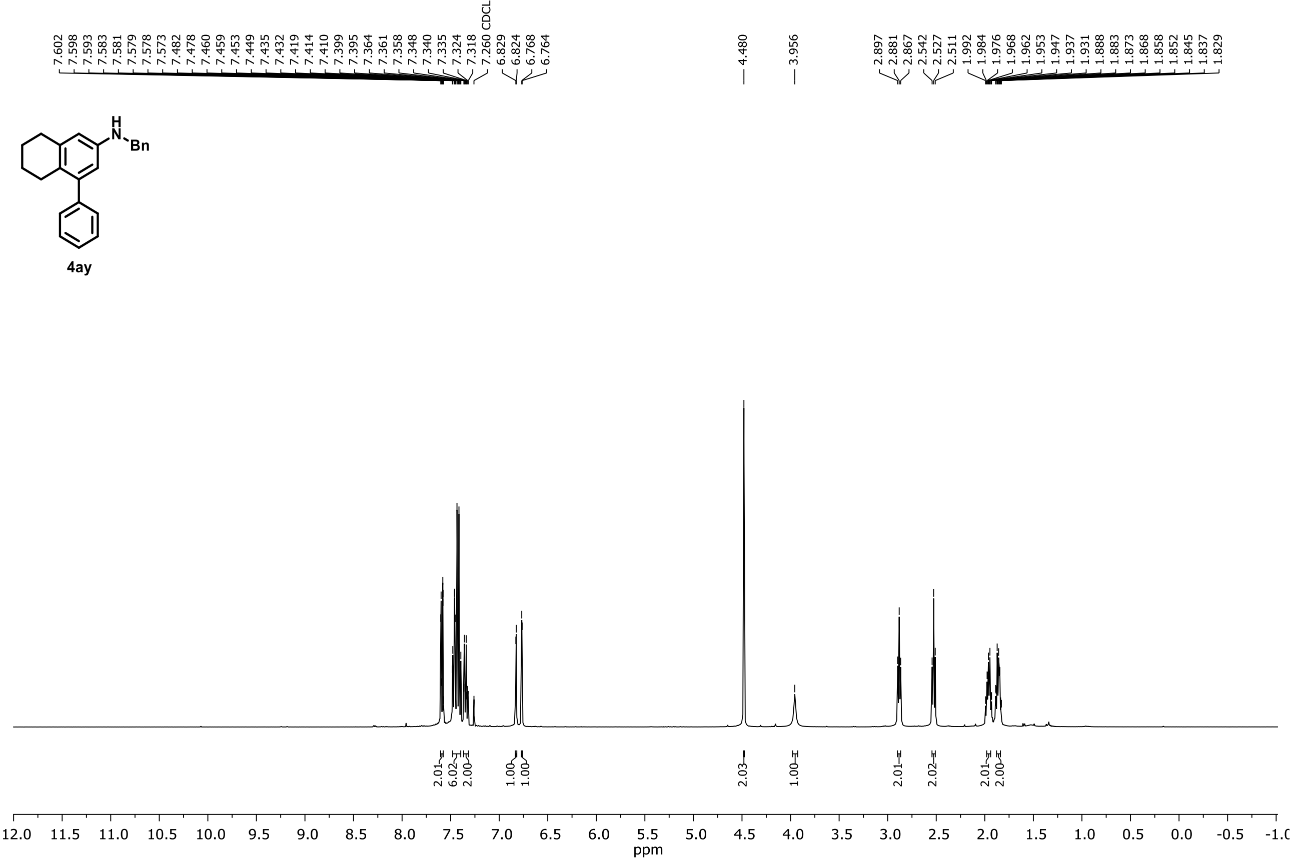
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

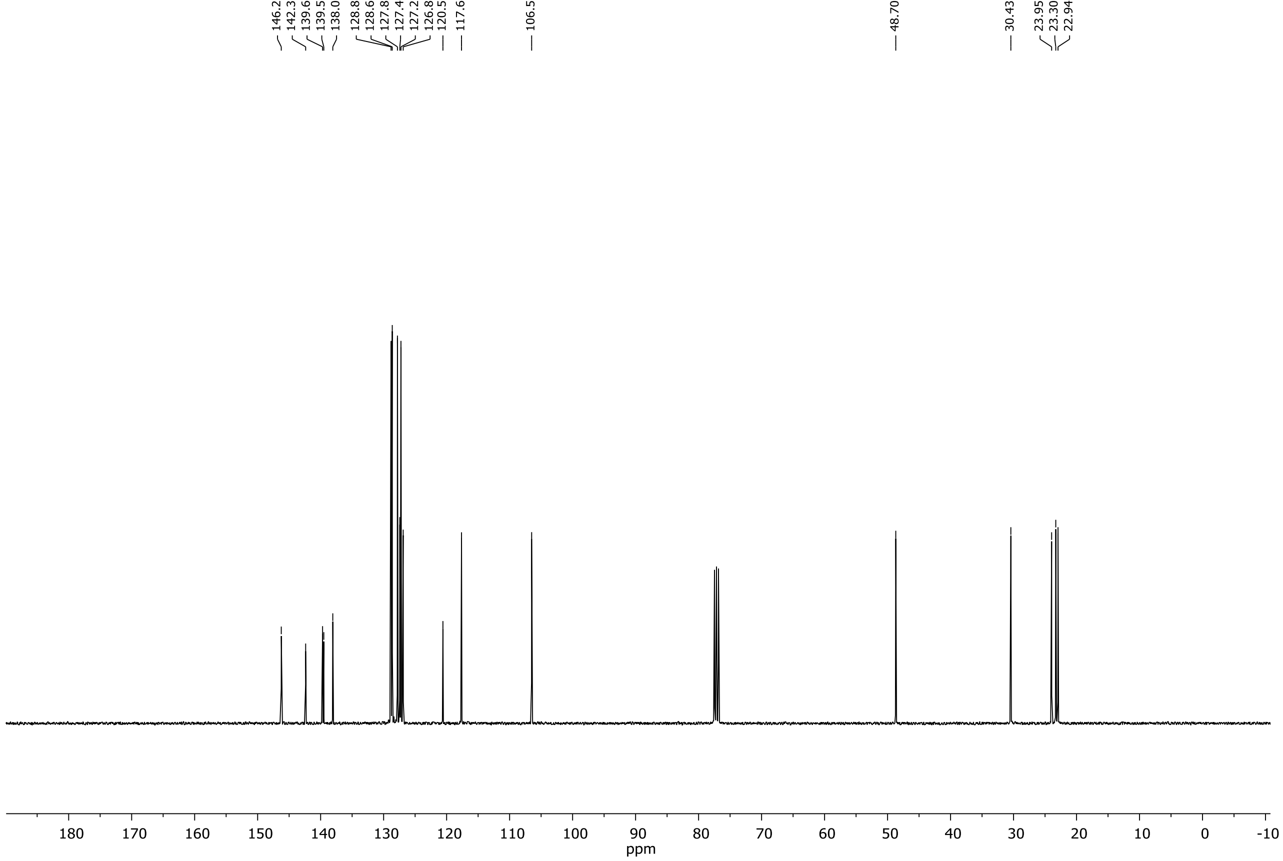


1H, CDCl3, 400 MHz

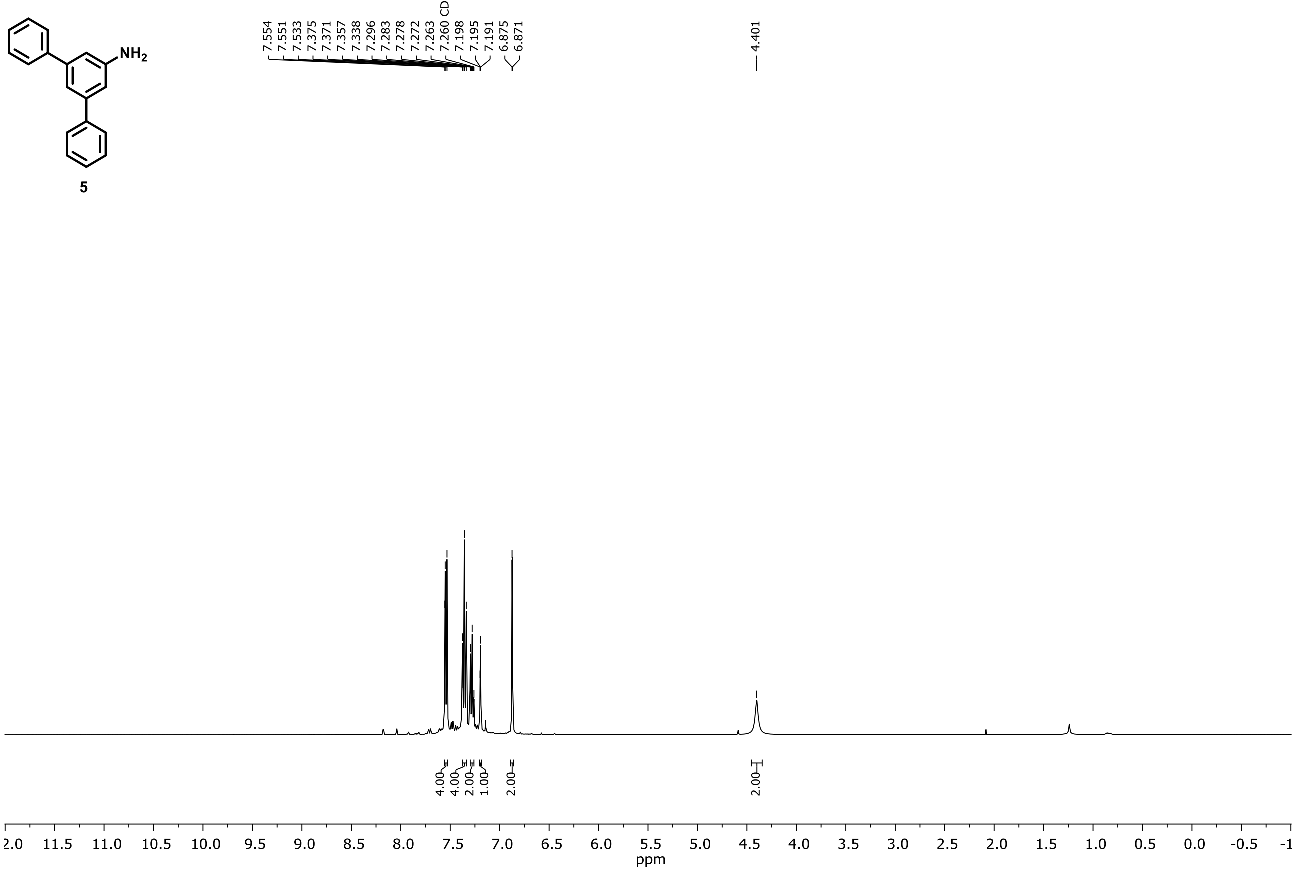


4ay

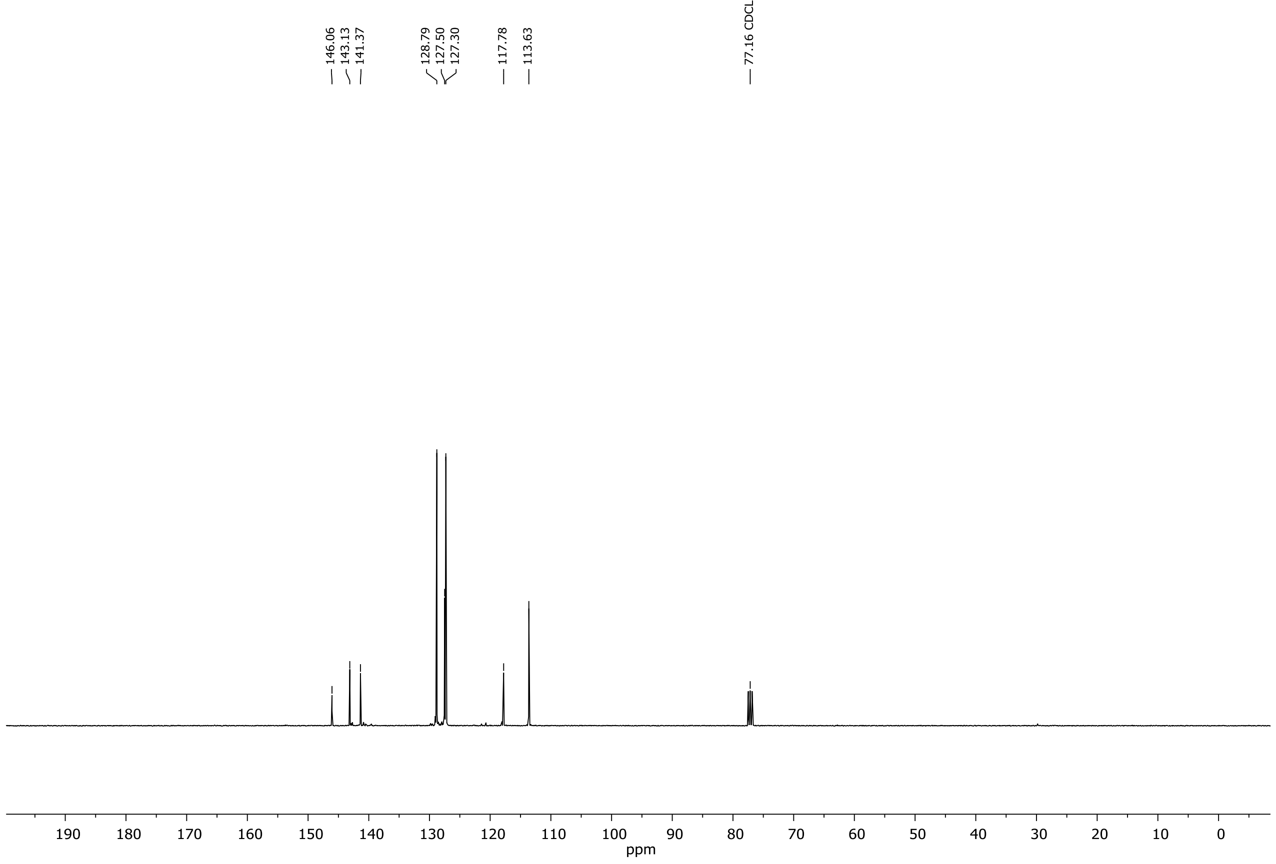
13C, CDCl3, 100 MHz



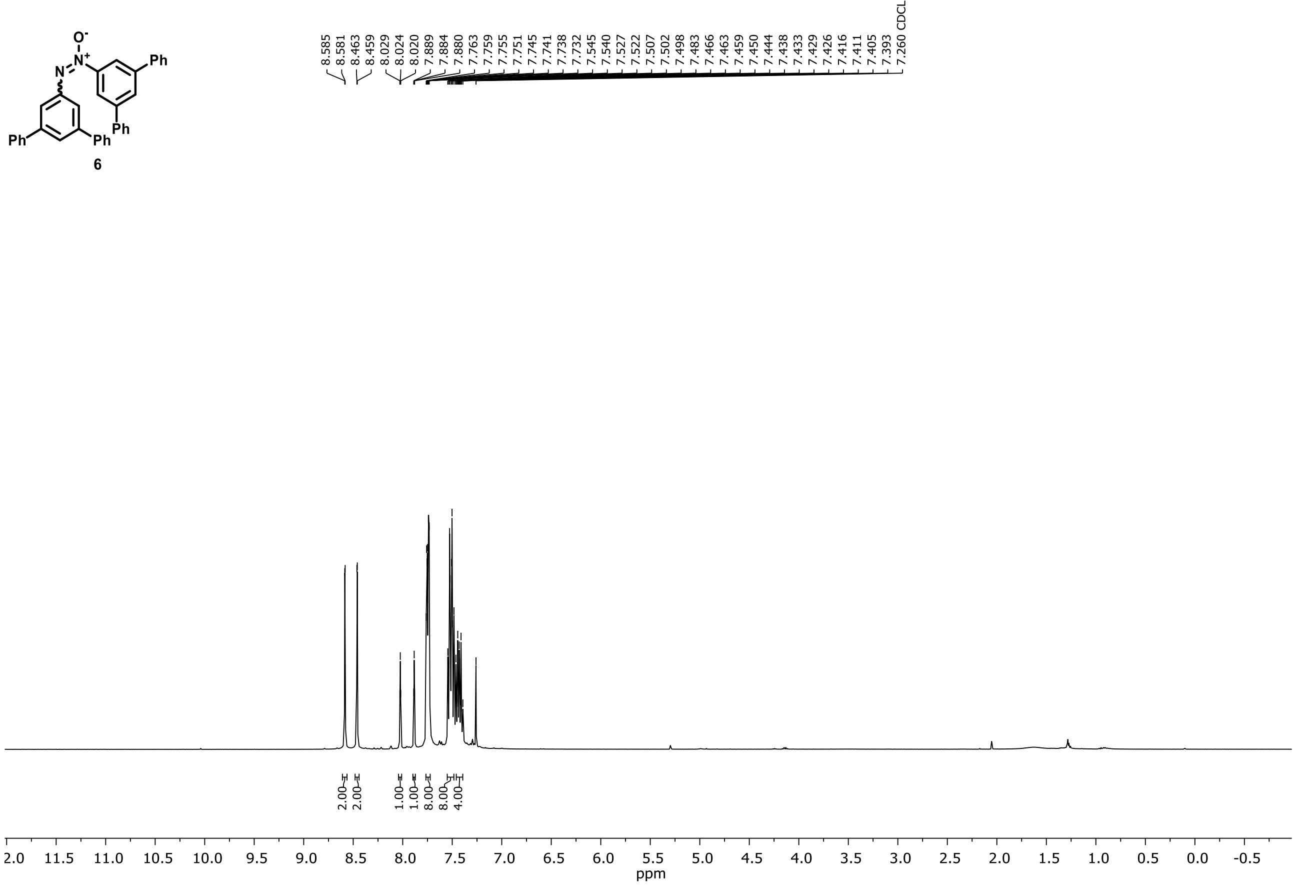
1H, CDCl3, 400 MHz



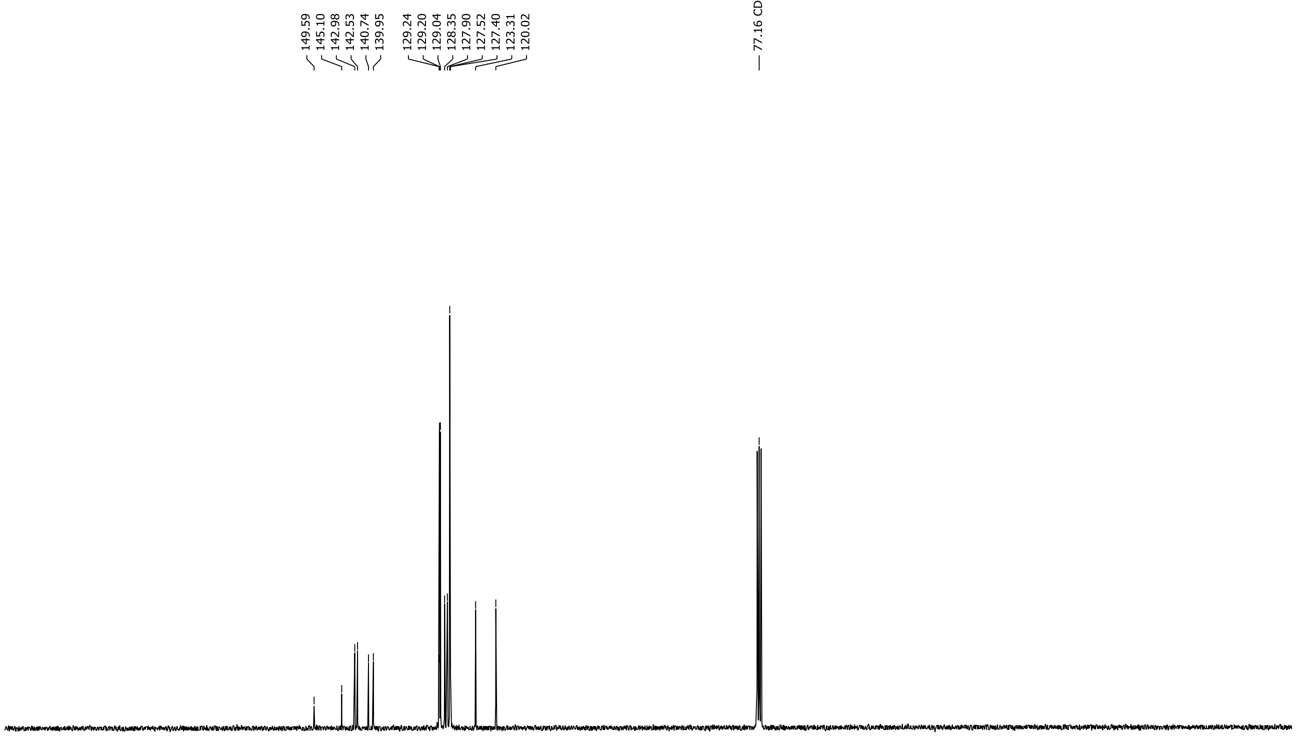
13C, CDCl3, 100 MHz



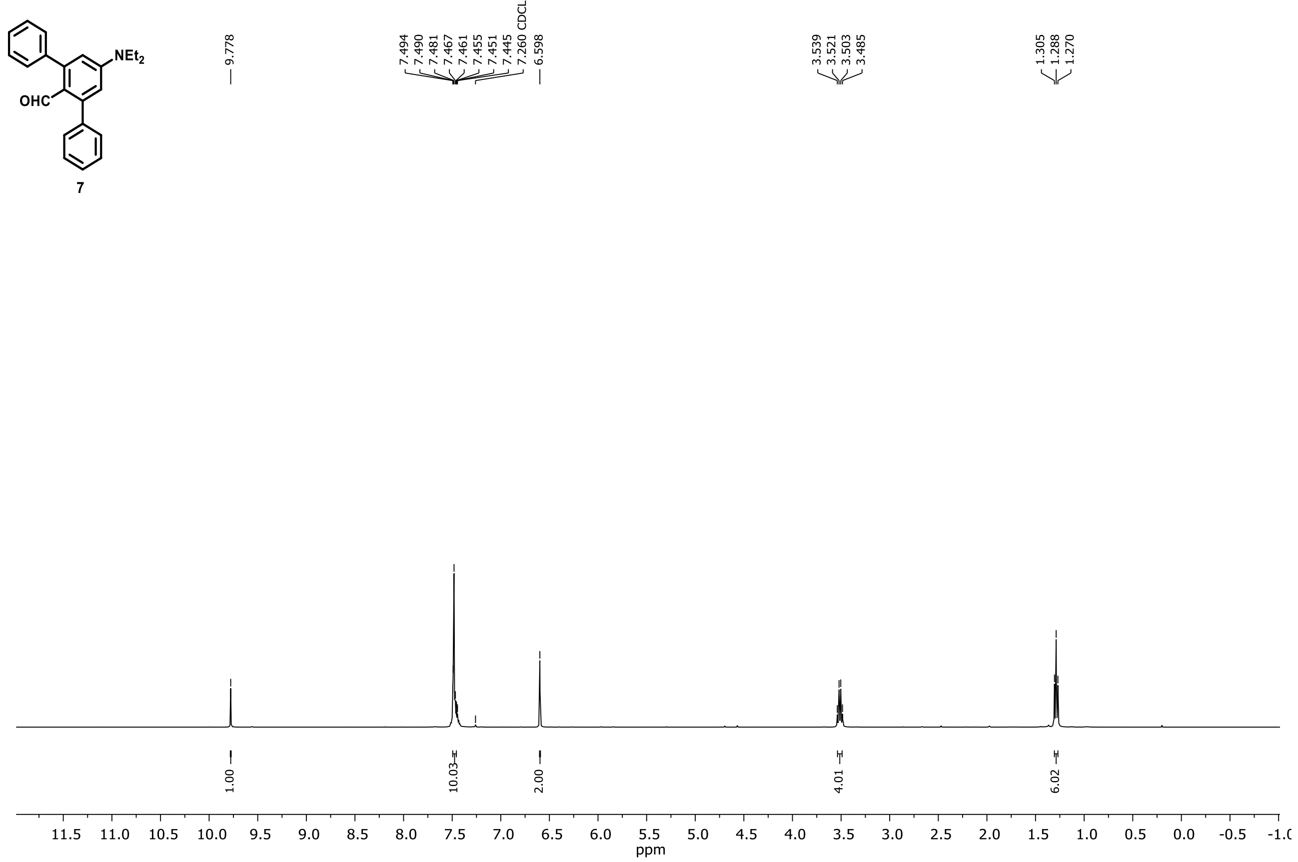
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

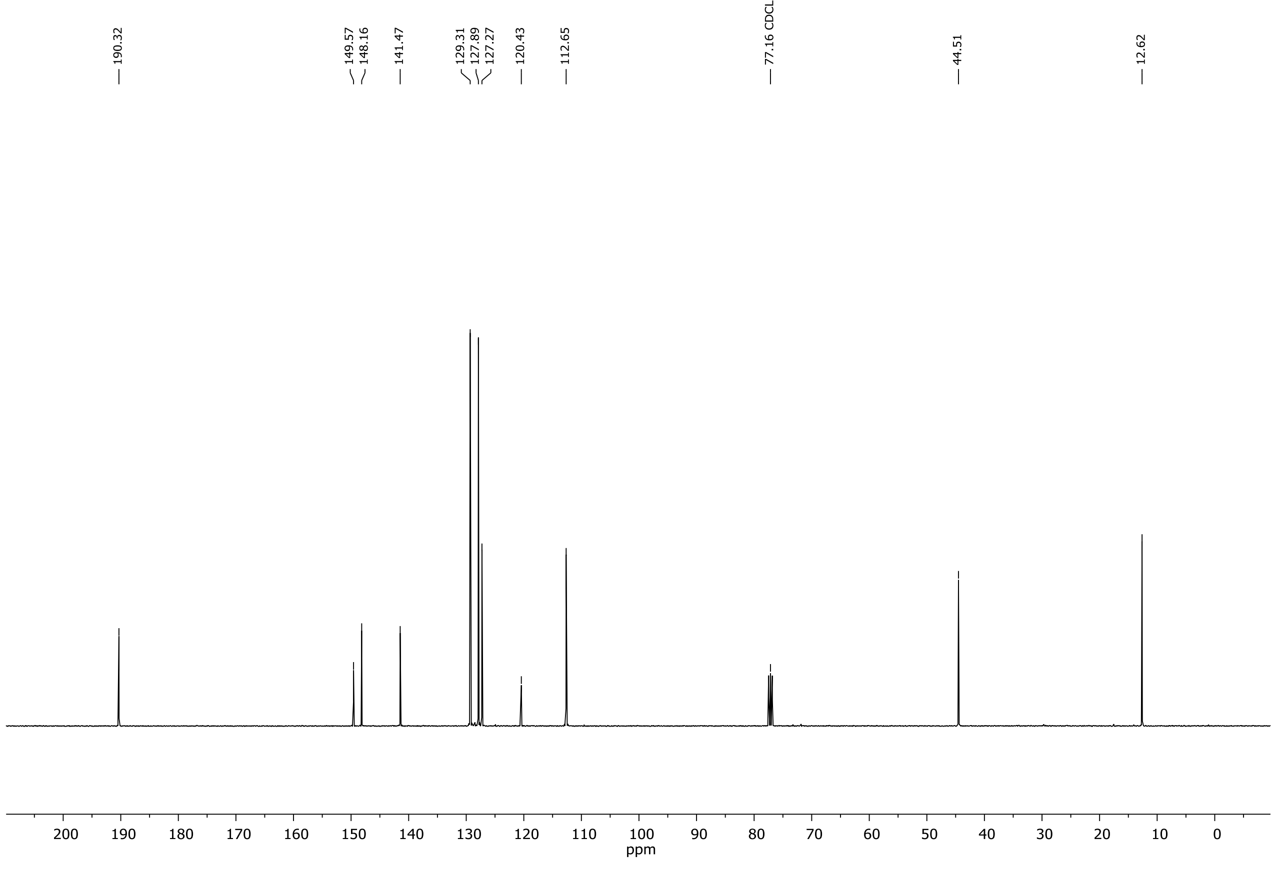


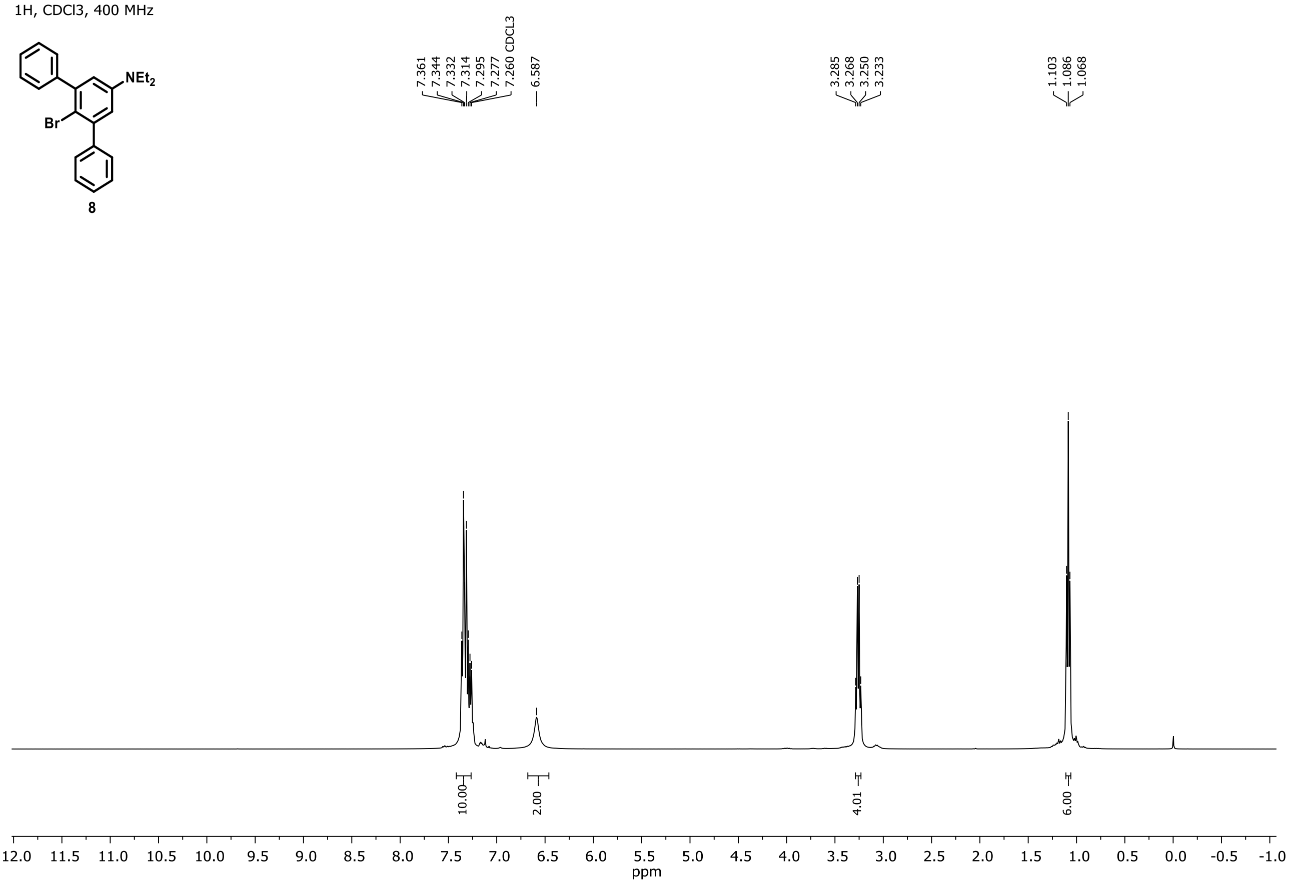
1H, CDCl3, 400 MHz

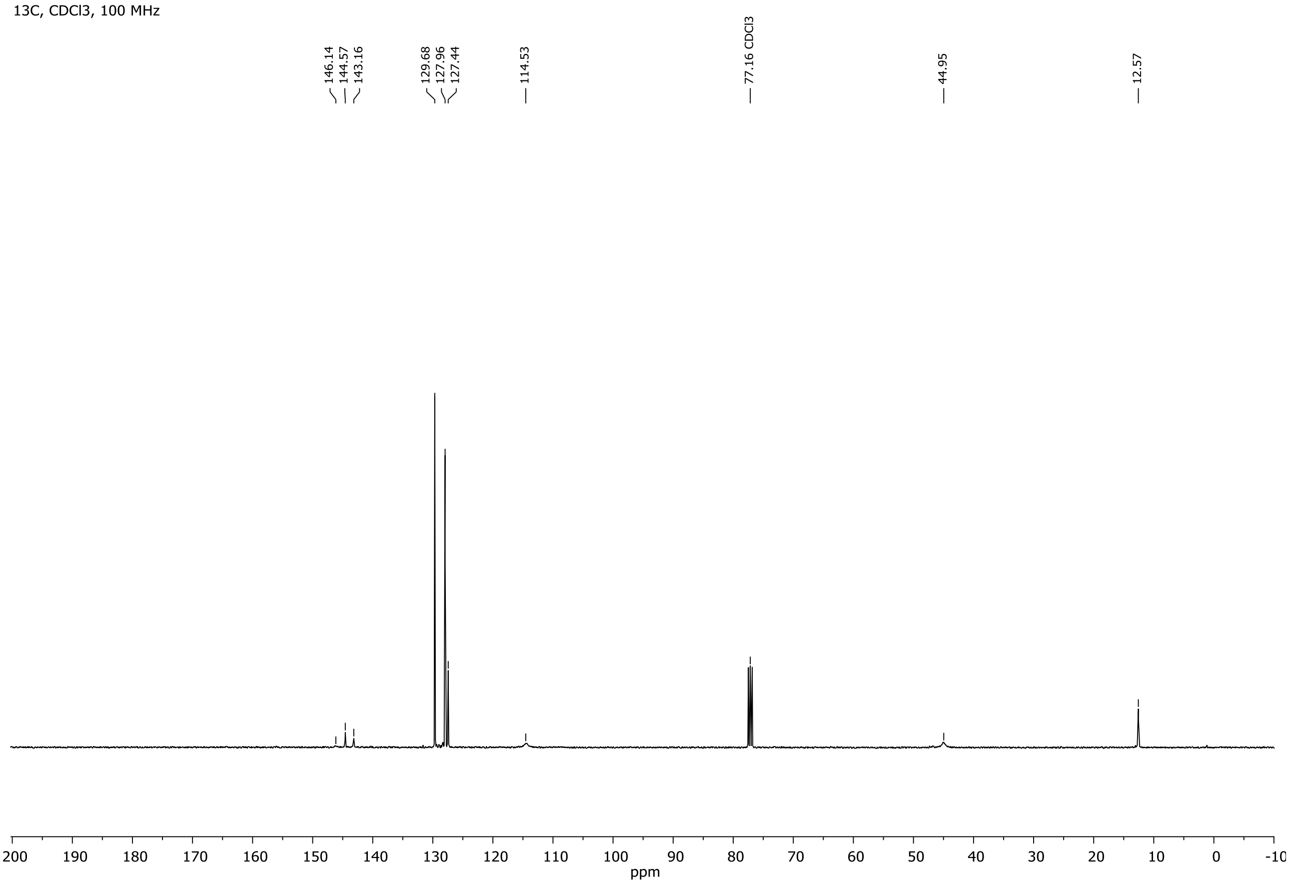


7

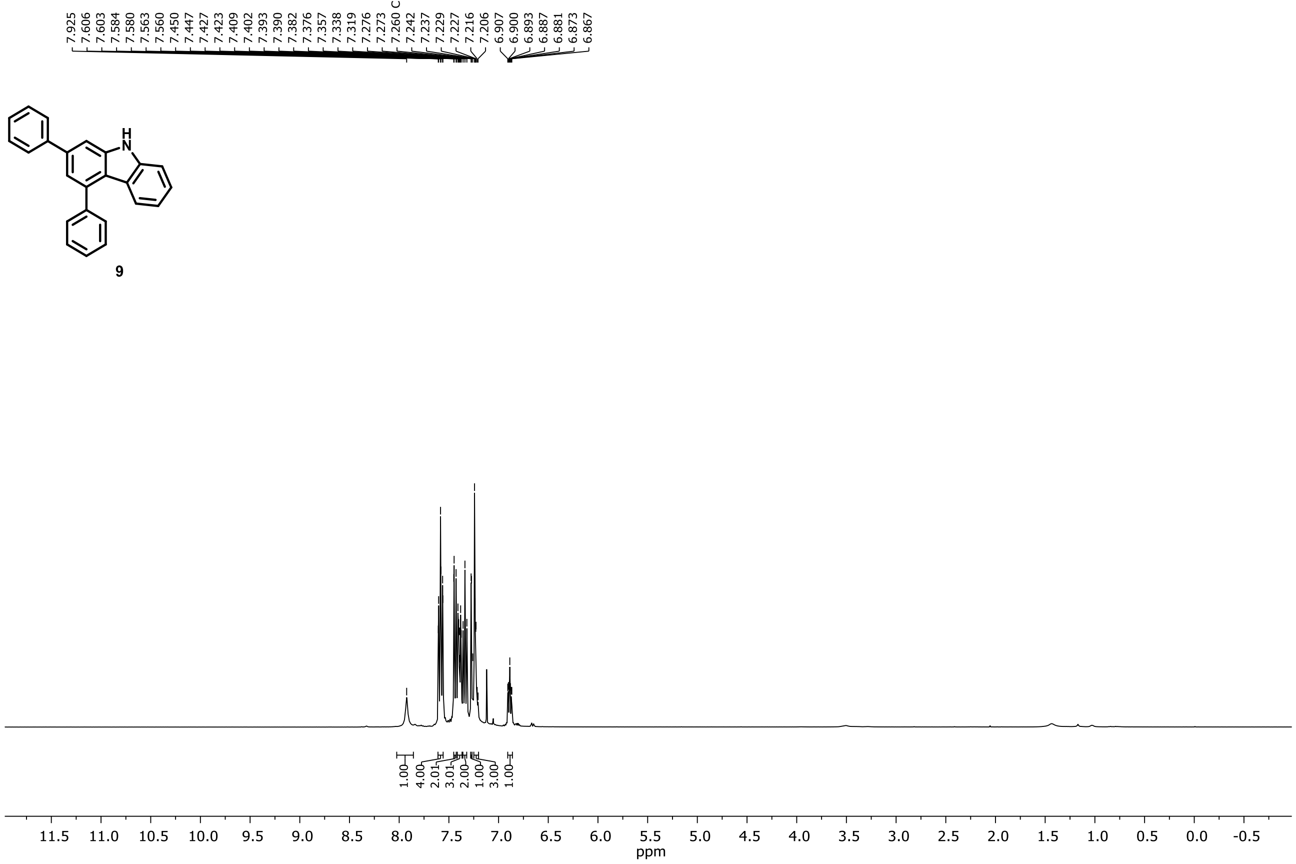
13C, CDCl3, 100 MHz




1H, CDCl3, 400 MHz
NEt$_2$
Br
8
7.361
7.344
7.332
7.314
7.295
7.277
7.260 CDCL3
6.587
3.285
3.268
3.250
3.233
1.103
1.086
1.068
10.00
2.00
4.01
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

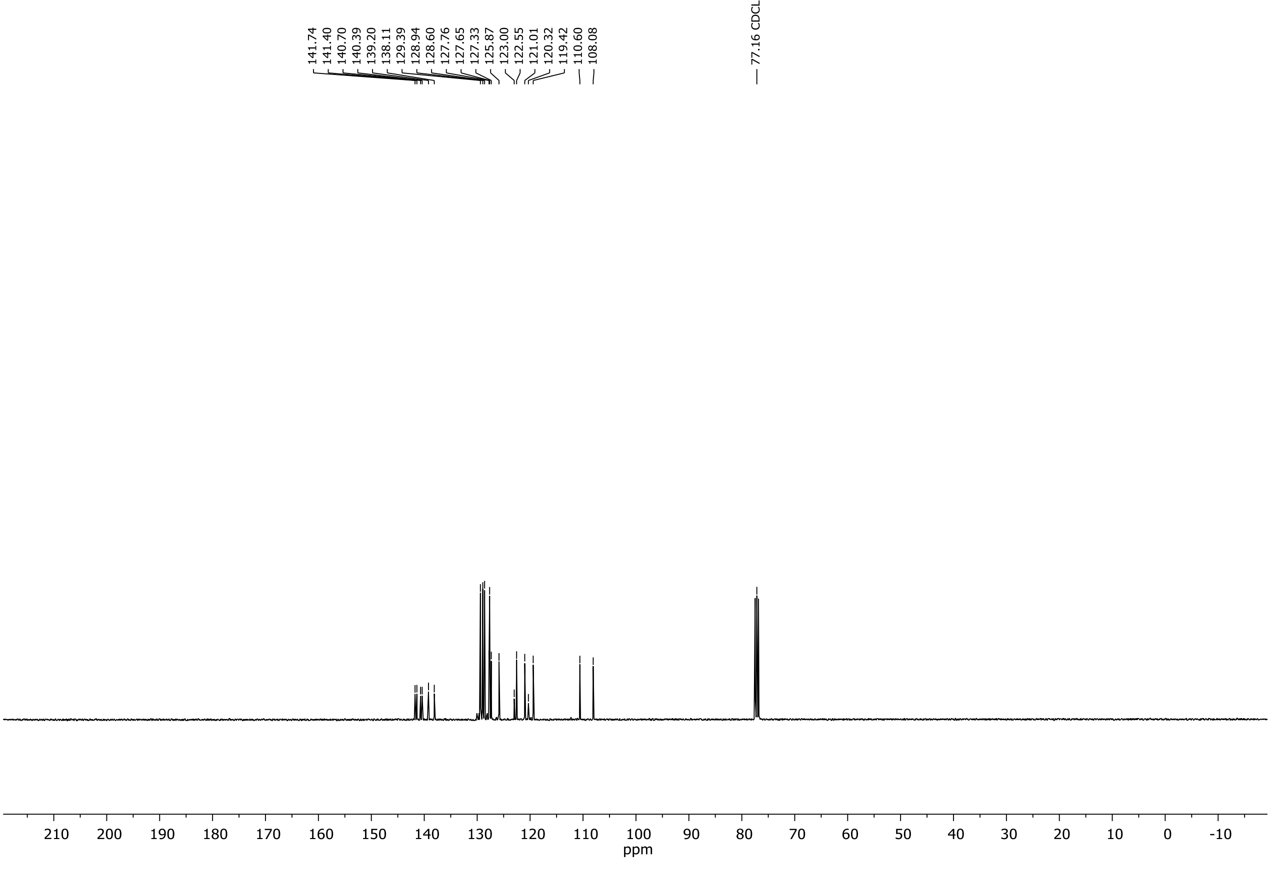

13C, CDCl3, 100 MHz
146.14
144.57
143.16
129.68
127.96
127.44
114.53
77.16 CDCl3
44.95
12.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

1H, CDCl3, 400 MHz

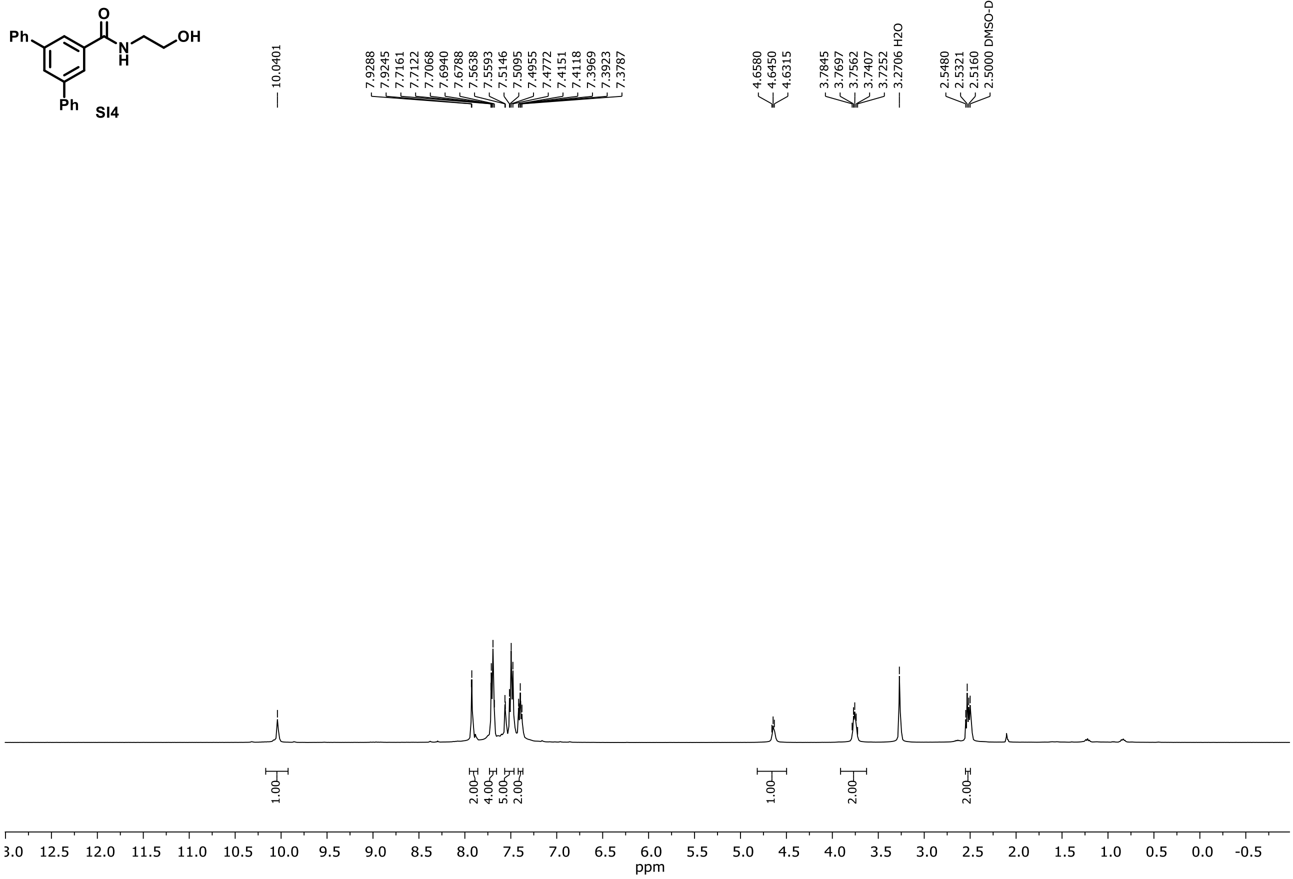


9

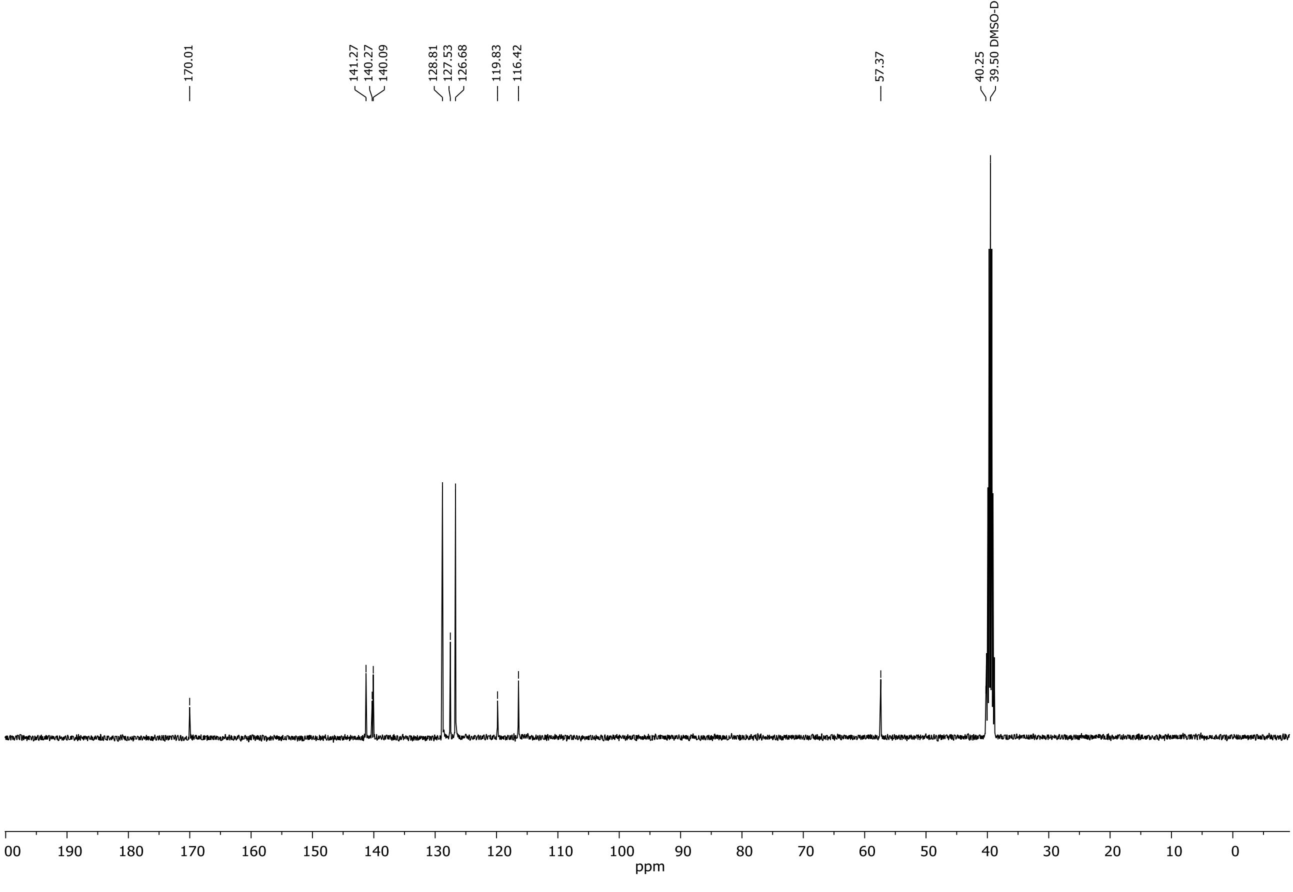
13C, CDCl3, 100 MHz

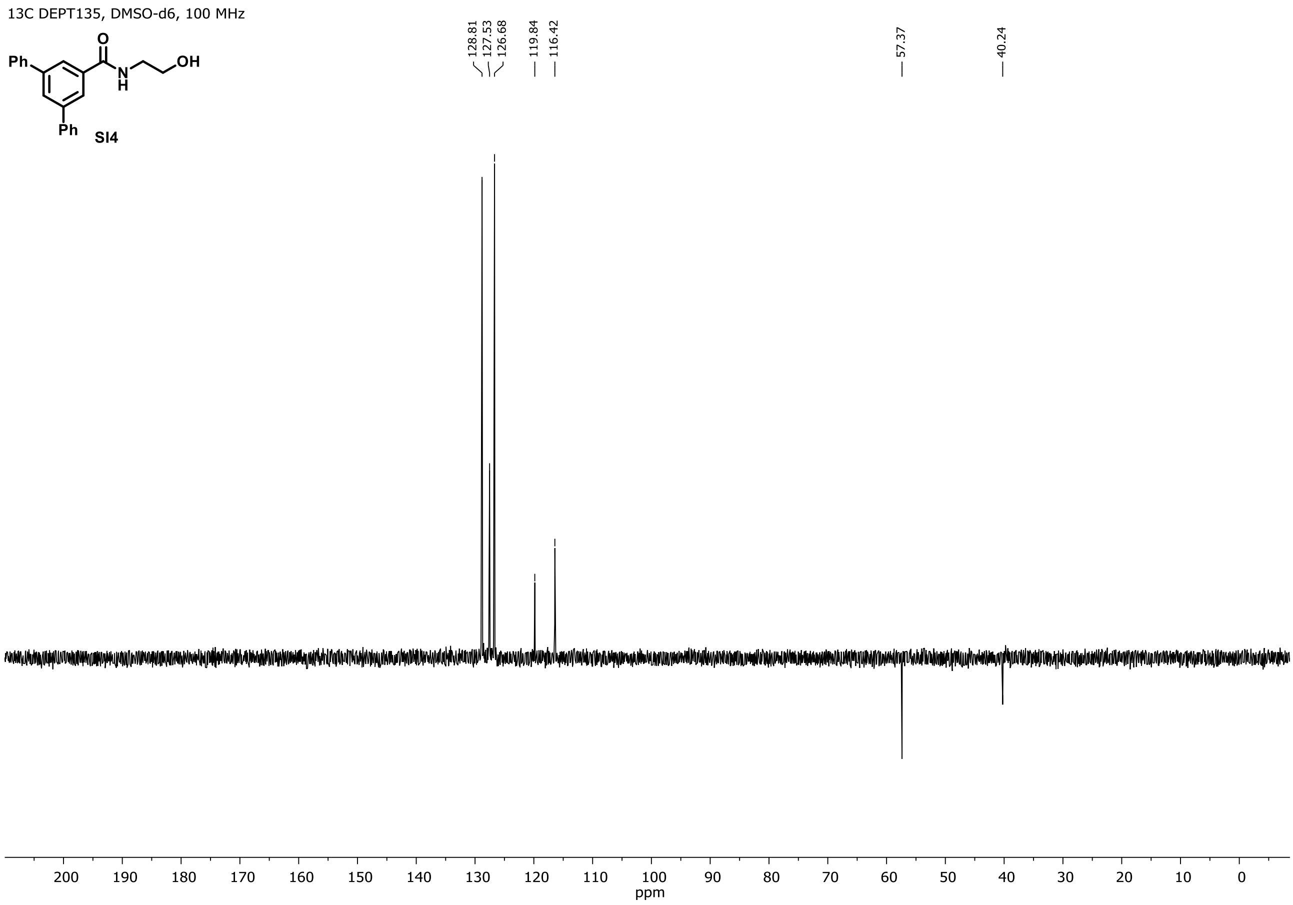


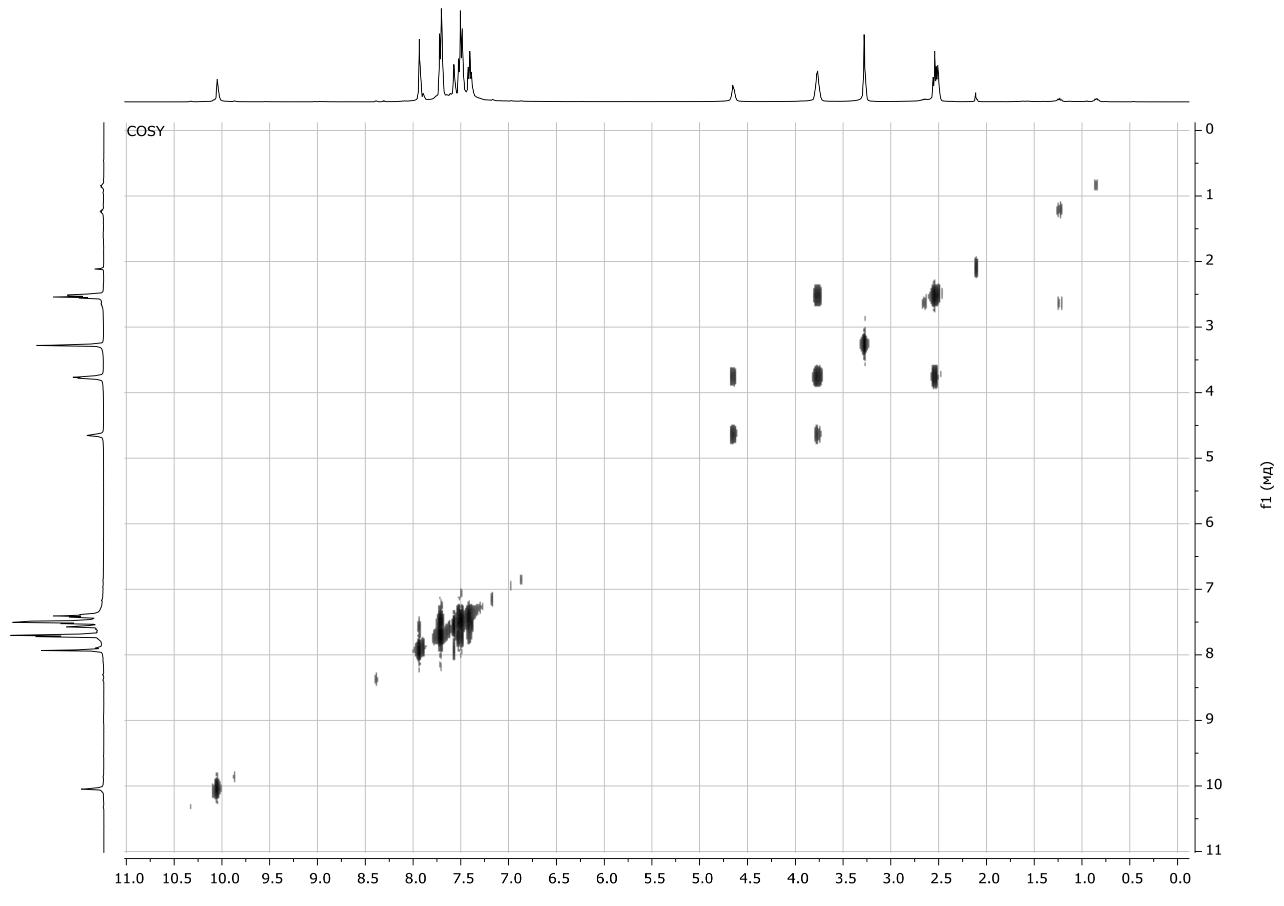
1H, DMSO-d6, 400 MHz

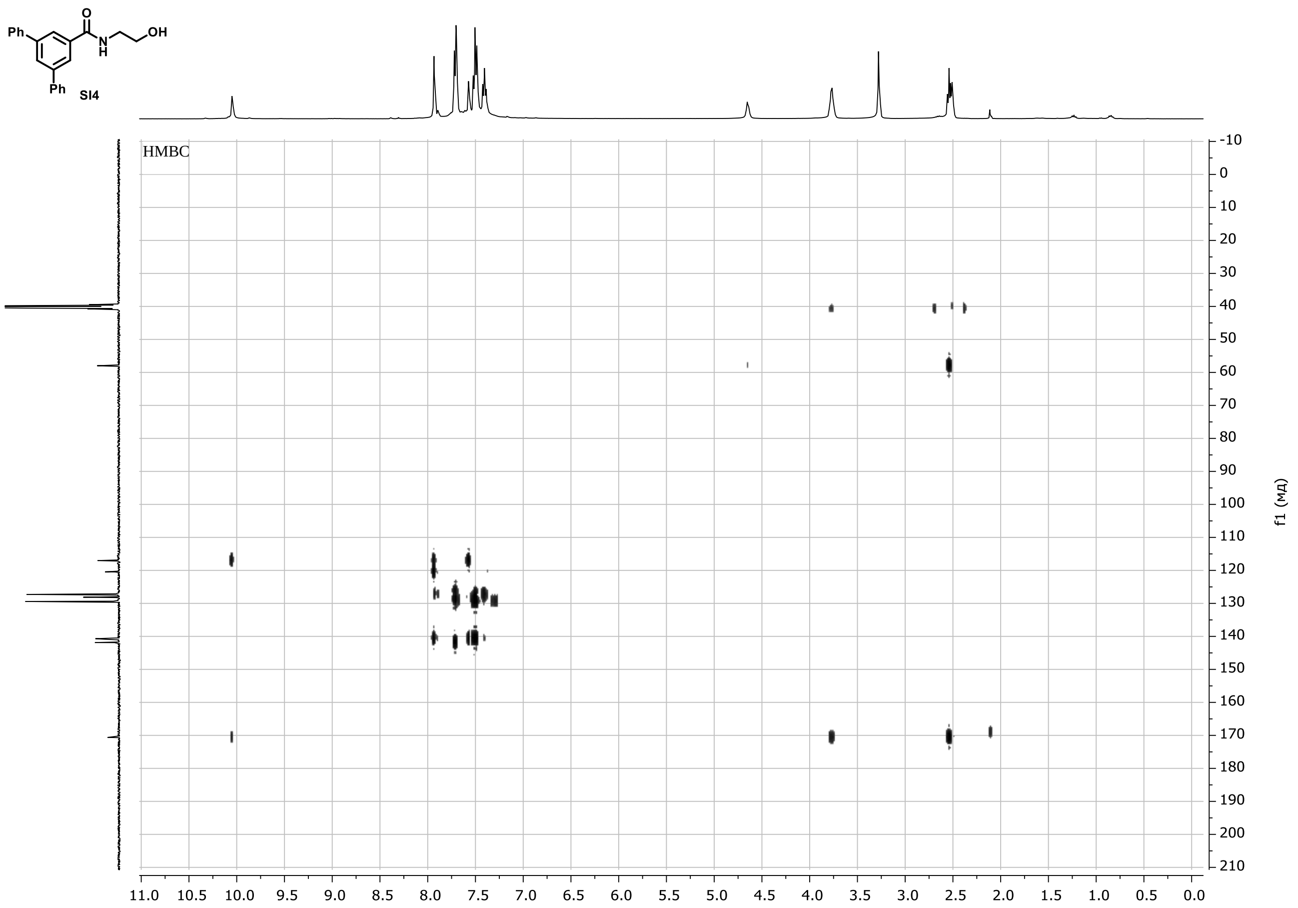


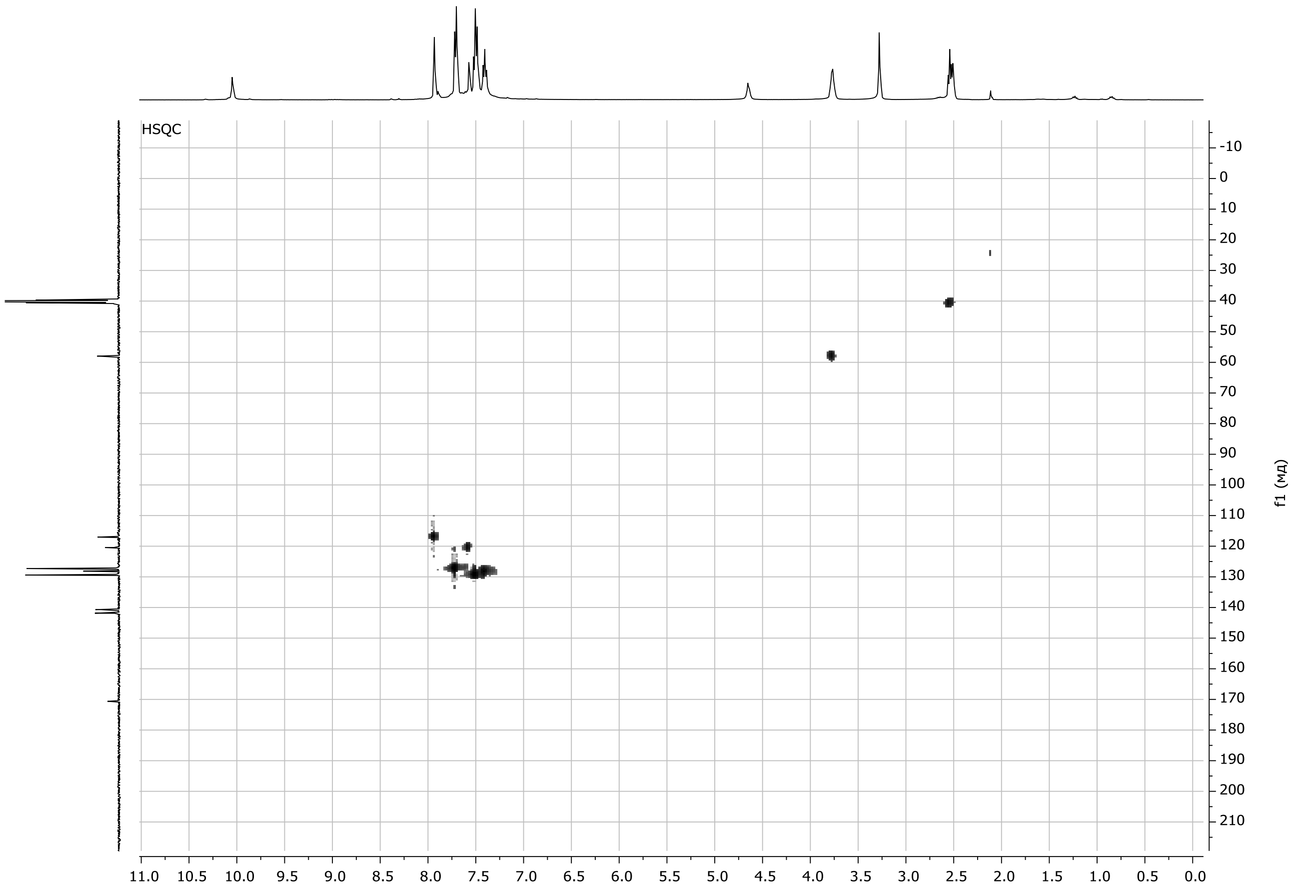
13C, DMSO-d6, 100 MHz




13C DEPT135, DMSO-d6, 100 MHz
Ph
O
N
H
OH
Ph
SI4
128.81
127.53
126.68
119.84
116.42
57.37
40.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


COSY
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8 9 10 11
f1 (мд)


SI4
Ph
O
N
H
OH
Ph
HMBC
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (мд)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


HSQC
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (мд)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0